Supporting Information

Catalyst-Controlled Selective Functionalization of Unactivated C–H Bonds in the Presence of Electronically Activated C–H Bonds

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1. General Considerations

All solvents were purified and dried by a *Glass Contour Solvent System* unless otherwise stated. The dichloromethane used for the C–H Functionalization was dried and degassed at reflux over activated 4 Å molecular sieves for 1 hours under argon, then stored with activated 4 Å molecular sieves under argon atmosphere and was used directly.

^{1}H and ^{13}C NMR spectra were recorded at 600 MHz (^{13}C at 150 MHz) on Bruker-600 spectrometer or Varian IVONA-600 spectrometer, or 500 MHz (^{13}C at 126 MHz) on Varian INOVA-500 spectrometer, or 300 MHz (^{19}F at 282 MHz) on Varian Mercury-300. Unless otherwise stated, NMR spectra were run in solutions of deuterated chloroform ($CDCl_3$) with residual chloroform taken as an internal standard (7.26 ppm for ^{1}H, and 77.16 ppm for ^{13}C), and were reported in parts per million (ppm). Abbreviations for signal multiplicity are as follow: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (*J* values) were calculated directly from the spectra.

IR spectra were collected on a Nicolet iS10 FT-IR spectrometer.

Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic (TLC) analysis was performed with aluminum-sheet silica gel plates, visualizing with UV light and/or staining with aqueous $KMnO_4$ stain.

Melting points (mp) were measured in open capillary tubes with a Mel-Temp Electrothermal melting points apparatus and are uncorrected.

Optical rotations were measured on Jasco P-2000 polarimeters.

Analytical enantioselective chromatographs were measured on either Varian Prostar instrument or Agilent-1100 series instrument, and used isopropanol/hexane as gradient. Chiral HPLC conditions were determined by obtaining separation of the racemic products using Rh_2(*R/S*-*o*-ClTPCP)$_4$ as catalyst for C2 insertion products and Rh_2(*R/S*-DOSP)$_4$ as catalyst for benzylic insertion products.

2. Acquisition and Preparation of Compounds

The substrates and reagents were purchased from the following suppliers and used without further purification (unless otherwise stated):

Sigma-Aldrich: *N*-bromosuccinimide; 4-*n*-Pentylbenzoic acid; *n*-Pentylmagnesium bromide solution (2.0 M in diethyl ether); Ni(dppp)Cl_2; 3-Bromothiophene; Di-*tert*-butylpyrocarbonate; Hexanal; Methyl (triphenylphosphoranylidene)acetate; Diisobutylaluminum hydride (DIBAl-H); 4-*tert*-Butyliodobenzene; 1-Iodo-4-nitrobenzene; Triphenylphosphine; 4-Pentylphenol; 4-Methoxyphenylmagnesium bromide solution (0.5 M in THF); *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine; Pyridine.

Alfa-Aesar: Acetyl chloride; 1-Bromo-4-*n*-pentylbenzene; 1-Iodo-4-*n*-pentylbenzene; *n*-Pentylbenzene; 1-Bromo-4-*n*-decylbenzene; Acetic anhydride; Cobalt (II) chloride.

Acros Organic: Silver carbonate.

TCI America: 1-Bromo-4-*n*-butylbenzene.

Oakwood Chemical: 4-Dimethylaminopyridine; 3-Bromofuran; 1-Bromopentane.

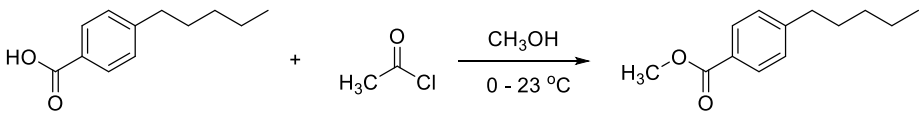
Oxchem: 4-*n*-Pentylacetophenone.

Fisher Scientific: Triethylamine.

Strem: $Pd(PPh_3)_4$; $Rh_2(OAc)_4$.

The following substrates were prepared by procedures adapted from literatures:

2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate[1]; 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate[2]; 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate[2]; 2,2,2-Trichloroethyl 2-diazoacetate[3]; 2,2,2-Trifluoroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate[4]; 2,2,2-Trifluoroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate[4]; 2,2,2-Trifluoroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate[4]; Rh_2(*S*-2-ClTPCP)$_4$[5]; Rh_2(*S*-2-Cl-4-BrTPCP)$_4$[6]; Rh_2(*S*-2-Cl-5-BrTPCP)$_4$[6].



Methyl 4-pentylbenzoate:

A dry 50-mL round-bottom flask was charged with 4-*n*-pentylbenzoic acid (961.3 mg, 5 mmol, 1.0 equiv.). After the flask was flushed with argon gas (3 times), 10 mL of anhydrous methanol was added via syringes slowly. Then, the reaction mixture was cooled to 0 °C via ice bath. The acetylchloride (0.43 mL, 6 mmol, 1.2 equiv.) was then added into the solution dropwise at 0 °C. The reaction mixture was warmed to room temperature (23 °C) and stirred overnight. The reacted solution was poured into a separation funnel containing ethyl ether and saturated NH_4Cl. The NH_4Cl layer was then extracted twice with diethyl ether. The combined organic layer was concentrated under reduced pressure and purified by flash column chromatography (pentane/diethyl ether = 20/1) to afford the colorless oil in 92% yield (949.0 mg).

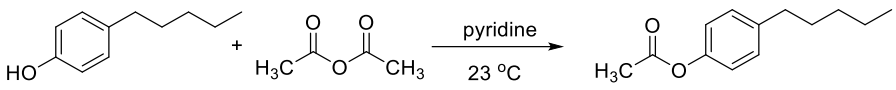
Rf = 0.63 (pentane/diethyl ether = 19/1);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.70 – 2.62 (m, 2H), 1.63 (p, *J* = 7.6 Hz, 2H), 1.39 – 1.27 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 148.7, 129.8, 128.6, 127.7, 52.1, 36.1, 31.6, 31.0, 22.7, 14.2;

IR (neat) 2930, 2858, 1720, 1273, 1107, 762, 703 cm^{-1};

HRMS (+p APCI) calcd for $C_{13}H_{19}O_2$ $(M+H)^+$ 207.1380 found 207.13791.



4-Pentylphenyl acetate:

The synthesis is adapted from literature[7]: A dry 10-mL round-bottom flask was charged with 4-*n*-pentylphenol (1.64 g, 10 mmol, 1.0 equiv.). After the flask was flushed with argon gas (3 times), acetic anhydride (1.42 ml, 15 mmol, 1.5 equiv.) and pyridine (0.5 ml, 6 mmol,0.6 equiv.) were added. Then, the reaction mixture was stirred at room temperature (23 ^{o}C) until the full consumption of 4-*n*-pentylphenol (35 mins by TLC monitoring). The resulting solution was poured into an Erlenmeyer flask with 80 mL of DI H_2O and stirred vigorously for 30 mins. The mixture was then extracted with ethyl acetate (50 mL X 3) and the combined organic layer was washed sequentially with aqueous HCl (1 M), saturated aqueous $NaHCO_3$, DI H_2O and brine. The collected solution was dried over Na_2SO_4 and concentrated under reduced pressure to afford the pure product as colorless oil in 94% yield (1.94 g).

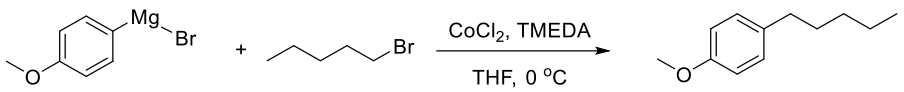
Rf = 0.64 (pentane/diethyl ether = 4/1);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 2.63 – 2.54 (m, 2H), 2.28 (s, 3H), 1.65 – 1.56 (m, 2H), 1.39 – 1.25 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 148.7, 140.6, 129.4, 121.3, 35.5, 31.6, 31.3, 22.7, 21.3, 14.2;

IR (neat) 2956, 2929, 2858, 1761, 1507, 1368, 1213, 1191, 1165, 910 cm^{-1};

HRMS (+p NSI) calcd for $C_{13}H_{19}O_2$ $(M+H)^+$ 207.1380 found 207.13796.



1-Methoxy-4-pentylbenzene:

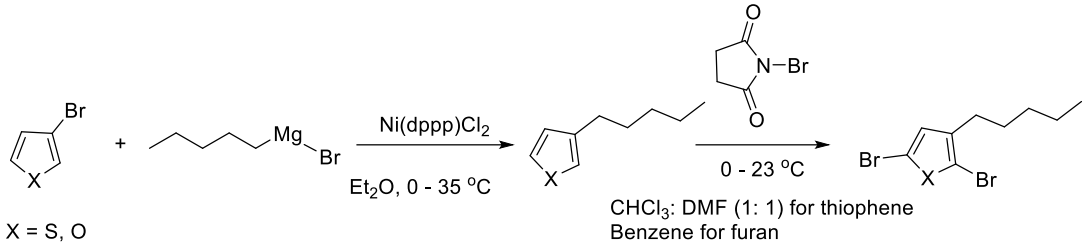
The synthesis is adapted from literature[8]: A dry 10-mL round-bottom flask was charged with 2-bromopentane (2.49 mL, 20 mmol, 1.0 equiv.), $CoCl_2$ (130 mg, 1 mmol, 5 mol%) and TMEDA (0.14 mL, 1 mmol, 5 mol%). After the flask was flushed with argon gas (3 times), 10 mL of anhydrous THF was added and the solution was cooled to 0 °C via ice bath. 4-Methoxyphenylmagnesium bromide (0.5 M in THF, 44 ml, 22 mmol, 1.1 equiv.) was added to the reaction mixture slowly over 50 mins. Then, the reaction mixture was stirred at 0 °C for another 30 mins. The resulting solution was quenched with 20 mL of aqueous HCl (1 M) and extracted with diethyl ether (50 mL X 3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The product was purified by distillation under reduced pressure (Kugelrogr, 92 °C at 0.7 mbar) to afford the pure product as colorless oil in 90% yield (3.21 g).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.58 – 2.48 (m, 2H), 1.62 – 1.54 (m, 2H), 1.38 – 1.26 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 135.1, 129.2, 113.6, 55.2, 35.0, 31.5, 31.4, 22.6, 14.0;

IR (neat) 2955, 2927, 2855, 1612, 1510, 1464, 1243, 1175, 1038, 828, 807 cm^{-1};

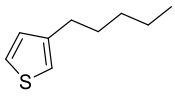
HRMS (+p NSI) calcd for $C_{12}H_{19}O$ $(M+H)^+$ 179.1430 found 179.14306.



The synthesis for 2,5-dibromo-3-n-pentylthiophene and 2,5-dibromo-3-n-pentylfuran is adapted from literature[9,10]: (reactions were done in dark and products were used immediately)

A 250-mL flame-dried round-bottom flask was charged with $Ni(dppp)Cl_2$ (81 mg, 0.15 mmol, 0.5 mol%) and 3-bromothiophene (or 3-bromofuran, 30 mmol, 1.0 equiv.). After the flask was flushed with argon, 30 mL of distilled diethyl ether was added to dissolve the mixture. Then, the mixture was cooled to 0 °C via ice bath, followed by the addition of n-pentylmagnesium bromide solution (2.0 M in diethyl ether, 60 mL, 4.0 equiv.) slowly by syringe pump. After the addition, the mixture was heated to reflux (35 °C) for overnight. The resulted solution was quenched by adding DI H_2O dropwise at 0 °C until no bubble generate and extracted by hexane (3x100 mL). After dried over Na_2SO_4, the crude product was concentrated under reduced pressure and purified by flash column chromatography (hexane) to provide colorless oil of 3-n-pentylthiophene in 63% yield (or 3-n-pentylfuran in 58% yield).

The product from last step was dissolved in 60 mL of corresponding anhydrous solvents in a 100 mL flame-dried 3-neck round-bottom flask under argon. Then, N-bromosuccinimide (2.2 equiv.) was added slowly at 0 °C and the resulted mixture was stirred overnight at room temperature (23 °C). The reacted solution was quenched by DI H_2O and $Na_2S_2O_3$, followed by the extraction by hexane (3x50 mL). After dried over Na_2SO_4, the crude product was concentrated under reduced pressure and purified by flash column chromatography (hexane) to provide colorless oil of 2,5-dibromo-3-n-pentylthiophene in 75% yield (or 2,5-dibromo-3-n-pentylfuran in 60% yield).



3-*n*-Pentylthiophene:

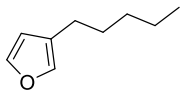
Rf = 0.72 (hexane);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 4.9, 2.9 Hz, 1H), 6.94 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.92 (dq, *J* = 3.1, 1.0 Hz, 1H), 2.65 – 2.59 (m, 2H), 1.62 (p, *J* = 7.6 Hz, 2H), 1.38 – 1.28 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 128.4, 125.2, 119.9, 31.7, 30.4, 22.7, 14.2;

IR (neat) 2956, 2926, 2857, 1458, 860, 834, 771, 681 cm^{-1};

HRMS (+p APCI) calcd for $C_9H_{15}S$ $(M+H)^+$ 155.0889 found 155.08890.



3-*n*-Pentylfuran:

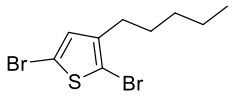
Rf = 0.67 (hexane);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.20 (s, 1H), 6.26 (s, 1H), 2.40 (t, *J* = 7.7 Hz, 2H), 1.56 (q, *J* = 7.0 Hz, 2H), 1.37 – 1.28 (m, 4H), 0.90 (t, *J* = 6.5 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 138.9, 125.5, 111.2, 31.7, 29.9, 24.9, 22.6, 14.2;

IR (neat) 2957, 2928, 2859, 1759, 1465, 1341, 1065, 945 cm^{-1};

HRMS (+p APCI) calcd for $C_9H_{15}O$ $(M+H)^+$ 139.1117 found 139.11178.



2,5-Dibromo-3-*n*-pentylthiophene:

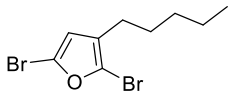
Rf = 0.85 (hexane);

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (s, 1H), 2.53 – 2.48 (m, 2H), 1.58 – 1.51 (m, 2H), 1.37 – 1.26 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 131.1, 110.4, 108.1, 31.4, 29.6, 29.4, 22.6, 14.1;

IR (neat) 2955, 2926, 2857, 1541, 1465, 1418, 1004, 824 cm^{-1};

HRMS (-p NSI) calcd for $C_9H_{11}Br_2S$ $(M-H)^-$ 308.8954 found 308.89390.



2,5-Dibromo-3-*n*-pentylfuran:

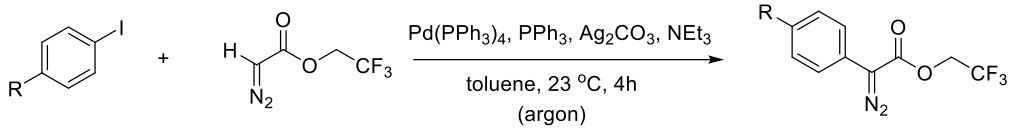
Rf = 0.71 (hexane);

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.23 (s, 1H), 2.34 – 2.27 (m, 2H), 1.50 (p, *J* = 7.5 Hz, 2H), 1.37 – 1.25 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H);

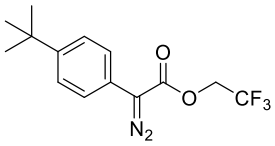
^{13}C NMR (151 MHz, $CDCl_3$) δ 127.5, 121.3, 119.7, 114.9, 31.3, 29.0, 25.3, 22.5, 14.1;

IR (neat) 2956, 2929, 2858, 1592, 1493, 1466, 1135, 1105, 1077, 930, 804 cm^{-1};

HRMS (+p NSI) calcd for $C_9H_{12}Br_2O$ $(M)^+$ 293.9249 found 293.92442.



The synthesis is adapted from literatures[11]: A 50-mL round-bottom flask was charged with aryl iodide (10 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (577.8 mg, 0.5 mmol, 5 mol%), PPh_3 (262.3 mg, 1 mmol, 10 mol%) and Ag_2CO_3 (1.38 g, 5 mmol, 0.5 equiv.). After the flask was flushed with argon, 40 mL of toluene was added, followed by the addition of NEt_3 (1.8 mL, 13 mmol, 1.3 equiv.) and 2,2,2-trifluoroethyl 2-diazoacetate (2.18 g, 13 mmol, 1.3 equiv.). The resulted mixture was stirred at room temperature (23 °C) for 4 h and then, filtered through a short silica plug (3.5 cm *diameter*, 5 cm *height*), eluting with ethyl acetate (20 mL). The crude product was concentrated and purified by column chromatography (pentane/diethyl ether = 9/1) to afford 2,2,2-trifluoroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate as yellow oil in 62% yield (or 2,2,2-trifluoroethyl 2-diazo-2-(4-nitrophenyl)acetate as yellow solid in 65% yield).



2,2,2-Trifluoroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate:

Rf = 0.71 (pentane/diethyl ether = 9/1);

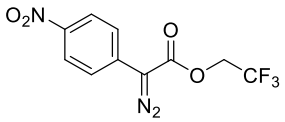
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 4.65 (q, *J* = 8.4 Hz, 2H), 1.32 (s, 9H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 149.9, 126.3, 124.3, 123.1 (q, *J* = 277.5 Hz); 121.3, 60.4 (q, *J* = 36.9 Hz), 34.7, 31.4 (The resonance resulting from the diazo carbon was not observed);

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.9 (t, *J* = 8.3 Hz);

IR (neat) 2966, 2091, 1716, 1410, 1352, 1280, 1244, 1167, 1145, 1111, 1073, 975, 835 cm^{-1};

HRMS (+p NSI) calcd for $C_{14}H_{15}F_3N_2O_2$ $(M)^+$ 300.1080 found 300.10851.



2,2,2-Trifluoroethyl 2-diazo-2-(4-nitrophenyl)acetate:

Rf = 0.18 (pentane/diethyl ether = 9/1);

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.2 Hz, 2H), 7.65 (d, *J* = 9.2 Hz, 2H), 4.69 (q, *J* = 8.2 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0, 145.7, 132.8, 124.6, 123.5, 122.8 (q, *J* = 277.5 Hz), 60.8 (q, *J* = 37.2 Hz) (The resonance resulting from the diazo carbon was not observed);

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.9 (t, *J* = 8.3 Hz);

IR (neat) 3116, 2100, 1716, 1593, 1514, 1335, 1279, 1236, 1140, 1068, 973, 850, 750 cm^{-1};

HRMS (+p NSI) calcd for $C_{10}H_7F_3N_3O_4$ $(M+H)^+$ 290.0383 found 290.03883.

3. C-H Functionalization Reactions

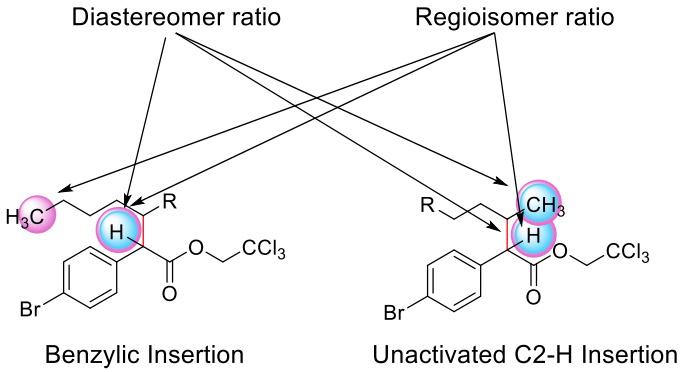
3.1. General Procedure for C–H Functionalization Reactions

A 16-mL reaction vial (21x70mm) with screw cap (open top with PTFE faced silicone septum) was charged with Rh_2L_4 (0.003 mmol, 1 mol%) and corresponding substrate (0.6 mmol, 2.0 equiv.). The reaction vessel was then evacuated and back filled with argon (3 times), followed by the addition of dry degassed CH_2Cl_2 (3 mL) and the solution was heated to 40 °C (b.p. of CH_2Cl_2) for 10 min. Desired donor/acceptor diazo compounds (0.3 mmol, 1.0 equiv.) was weighed in a 20-mL scintillation vial and dissolved in 6 mL of dry degassed CH_2Cl_2 under argon atmosphere. Then, under reflux condition and argon atmosphere, the diazo solution was added to the reaction vessel dropwise via syringe pump over 3 h. The reaction mixture was stirred at 40 °C for another 30 min, and concentrated under vacuum for crude ^{1}H NMR. Finally, the crude product was purified by flash column chromatography to afford the product (mixture of regioisomers and diastereomers) as colorless oil (gradient elution from pentane to 8% diethyl ether/pentane).

3.2. Regioisomer and Diastereomer Ratios Determination

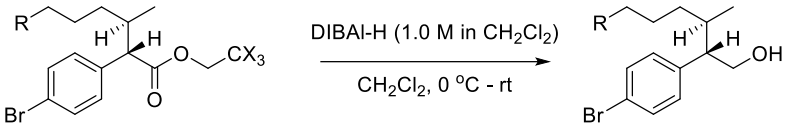
The crude ^{1}H NMR in general procedure was utilized for regioisomer and diastereomer ratios determination, and it was obtained using Bruker-600 MHz spectrometer with an ID probe, and the acquisition was done with 16 times of scans and 1 seconds of relaxation time.

The crude ^{1}H NMR spectra data was analyzed with MestReNova 11.0 (MestRelab Research S.L.). Before integration, spectra were processed through a Segments Smoother baseline correction manually. The ratios were measured by integration of the peaks corresponding to the hydrogens indicated below (Section 4).



3.3. Enantiomer Ratio Determination

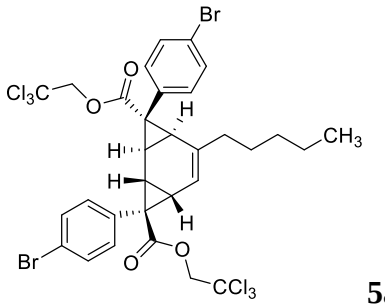
Most of the enantiomer ratios of these C–H insertion products were obtained by separation on our available chiral HPLC columns directly. However, for some C–H functionalization reactions, their regioisomers and diastereomers are inseparable by flash column chromatography, which cause additional difficulty for enantiomers separation on our available chiral HPLC columns. Hence, for better separation, some of them were reduced to alcohols, without influence on the chiral centers (confirmed by **4d**, 92% ee before reduction and 91% ee after reduction-spectra at page S-207 to S209), and used for enantiomeric excess (ee) determination of corresponding C–H functionalization products (for C–H functionalization products **3b-d, 4b-d, 6a**, **7b**, **21** and **29**)



A flask with solution of corresponding ester (0.2 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was flushed with argon and cooled to 0 °C via ice bath. Under argon atmosphere, a solution of 1 M diisobutylaluminum hydride (DIBAl-H) in CH_2Cl_2 (0.4 mL, 0.4 mmol, 2.0 equiv.) was added dropwise into the flask at 0 °C, and the mixture was stirred for 4 h at room temperature (23 °C). The reaction was quenched by adding 2 mL of 2 M aqueous HCl solution dropwise. The resulted solution was extracted by diethyl ether (3x3 mL) and dried over Na_2SO_4. The crude product was concentrated and confirmed by ^{1}H NMR, then the crude alcohol product was used for HPLC directly.

3.4. Characterization Data of C–H Functionalization Products

The C–H functionalization products of *n*-pentylbenzene, catalyzed by Rh_2(*S*-DOSP)$_4$, were used for characterization. For all other C–H functionalization products, the characterization of C2 insertion products was obtained from reaction catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$, while the characterization of benzylic insertion products was obtained from reaction catalyzed by Rh_2(*S*-TCPTAD)$_4$.



5a

Bis(2,2,2-trichloroethyl) (1*S*,2*R*,3*S*,4*R*,7*S*,8*R*)-3,8-bis(4-bromophenyl)-5-pentyltricyclo[5.1.0.0^{2,4}]oct-5-ene-3,8-dicarboxylate

This compound was obtained according to general procedure from C–H functionalization reaction between *n*-pentylbenzene (89.0 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (111.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-DOSP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford white solid in 65% yield.

m.p. 48-49 ^{o}C

Rf = 0.58 (pentane/diethyl ether = 4/1);

[α]$^{20}_{D}$: -44.8° (c = 1.03, $CHCl_3$, 34% ee);

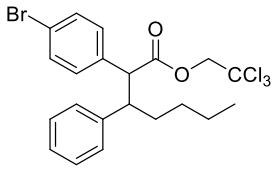
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.6, 2.8 Hz, 4H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 5.16 (d, *J* = 4.9 Hz, 1H), 4.66 – 4.62 (m, 3H), 4.59 (d, *J* = 11.9 Hz, 1H), 2.69 (dd, *J* = 9.4, 1.2 Hz, 1H), 2.63 (dd, *J* = 9.4, 1.2 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.86 – 1.79 (m, 1H), 1.73 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.67 (d, *J* = 9.3 Hz, 1H), 1.27 – 1.20 (m, 2H), 1.09 (m, 1H), 1.03 (p, *J* = 7.0 Hz, 2H), 1.00 – 0.94 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 167.9, 135.9, 134.8, 133.8, 132.0, 131.5, 131.2, 131.1, 129.2, 121.8, 121.6, 117.6, 94.8, 74.4, 74.3, 39.0, 38.8, 37.0, 31.5, 30.8, 28.3, 27.8, 27.4, 26.6, 22.5, 13.9;

IR (neat) 2928, 2856, 1731, 1489, 1208, 1151, 1072, 1011, 827, 770. 716 cm^{-1};

HRMS (+p APCI) calcd for $C_{31}H_{28}O_4Br_2Cl_6$ $(M)^+$ 831.8480 found 831.84812;

HPLC (ADH column, 1% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}, 30 min, UV 230 nm) retention times of 10.43 min (major) and 21.53 min (minor) 34% ee with Rh_2(*S*-DOSP)$_4$. (Stereocenters assigned according to literature.[12])



3a

2,2,2-Trichloroethyl 2-(4-bromophenyl)-3-phenylheptanoate

This compound was obtained according to general procedure from C–H functionalization reaction between *n*-pentylbenzene (89.0 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (111.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-DOSP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 24% yield.

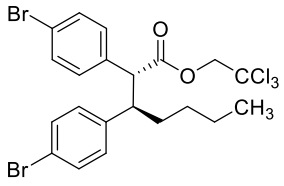
Rf = 0.72 (pentane/diethyl ether = 4/1);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.08 – 7.05 (m, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 7.0 Hz, 2H), 4.82 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 3.86 (d, *J* = 11.4 Hz, 1H), 3.32 (td, *J* = 11.2, 3.4 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.76 – 1.69 (m, 1H), 1.31 – 1.26 (m, 1H), 1.23 – 1.16 (m, 1H), 1.16 – 1.09 (m, 1H), 1.09 – 1.00 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 140.8, 135.7, 131.4, 130.5, 128.4, 128.4, 126.6, 121.4, 94.9, 74.5, 58.1, 49.3, 34.8, 29.6, 22.7, 14.0;

IR (neat) 3028, 2955, 2930, 2858, 1750, 1488, 1135, 1074, 1035, 764, 723, 700 cm^{-1};

HRMS (+p APCI) calcd for $C_{21}H_{23}O_2{}^{81}BrCl_3$ $(M+H)^+$ 492.9921 found 492.99088.



3b

2,2,2-Trichloroethyl (2*R*,3*R*)-2,3-bis(4-bromophenyl)heptanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (111.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-TCPTAD)$_4$ (6.4 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 78% yield.

Rf = 0.63 (pentane/diethyl ether = 19/1);

[α]$^{20}_{D}$: -55.3° (c = 1.08, $CHCl_3$, 93% ee);

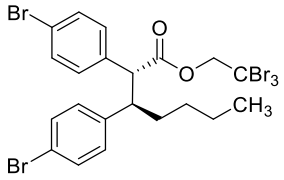
^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.33 (t, *J* = 8.7 Hz, 4H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.96 (d, *J* = 12.2 Hz, 1H), 4.90 (d, *J* = 12.3 Hz, 1H), 4.11 (d, *J* = 11.5 Hz, 1H), 3.46 (td, *J* = 11.3, 3.3 Hz, 1H), 1.92 – 1.85 (m, 1H), 1.81 – 1.72 (m, 1H), 1.35 – 1.30 (m, 1H), 1.26 – 1.17 (m, 1H), 1.17 – 1.09 (m, 1H), 1.08 – 1.00 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 172.2, 141.7, 137.3, 132.3, 132.1, 131.9, 131.7, 121.8, 120.6, 96.2, 74.9, 57.9, 49.3, 35.5, 30.5, 23.2, 14.3;

IR (neat) 2955, 2930. 2859, 1750, 1488, 1136, 1074, 1101, 825, 760, 731 cm^{-1};

HRMS (+p APCI) calcd for $C_{21}H_{22}O_2Br_2Cl_3$ $(M+H)^+$ 568.9047 found 568.90484;

HPLC (the ester product was reduced to 2,3-bis(4-bromophenyl)heptan-1-ol for better separation) (ODH column, 5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 19.57 min (minor) and 24.69 min (major) 93% ee with Rh_2(*S*-TCPTAD)$_4$.



3c

2,2,2-Tribromoethyl (2*R*,3*R*)-2,3-bis(4-bromophenyl)heptanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (151.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-TCPTAD)$_4$ (6.4 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 75% yield.

Rf = 0.63 (pentane/diethyl ether = 19/1);

[α]$^{20}_{D}$: -42.1° (c = 1.00, $CHCl_3$, 90% ee);

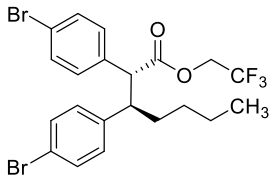
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (s, 2H), 7.26 (s, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.97 (d, *J* = 12.3 Hz, 1H), 4.90 (d, *J* = 12.3 Hz, 1H), 3.83 (d, *J* = 11.4 Hz, 1H), 3.34 (td, *J* = 11.3, 3.3 Hz, 1H), 1.89 – 1.82 (m, 1H), 1.73 – 1.65 (m, 1H), 1.30 – 1.24 (m, 1H), 1.23 – 1.16 (m, 1H), 1.15 – 1.07 (m, 1H), 1.06 – 0.99 (m, 1H), 0.80 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 140.0, 135.4, 131.6, 131.6, 130.5, 130.1, 121.7, 120.4, 58.0, 48.7, 35.1, 34.8, 29.5, 22.6, 14.1;

IR (neat) 2930, 2857, 1746, 1488, 1134, 1074, 1011, 822, 736 cm^{-1};

HRMS (+p APCI) calcd for $C_{21}H_{22}O_2{}^{79}Br_4{}^{81}Br$ $(M+H)^+$ 702.7511 found 702.75130;

HPLC (the ester product was reduced to 2,3-bis(4-bromophenyl)heptan-1-ol for better separation) (ODH column, 5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 19.16 min (minor) and 24.14 min (major) 90% ee with Rh_2(*S*-TCPTAD)$_4$.



3d

2,2,2-Trifluoroethyl (2*R*,3*R*)-2,3-bis(4-bromophenyl)heptanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-TCPTAD)$_4$ (6.4 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 80% yield.

Rf = 0.63 (pentane/diethyl ether = 19/1);

[α]^{20}D: -59.4° (c = 1.02, $CHCl_3$, 85% ee);

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.28 – 7.24 (m, 4H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.61 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.38 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.76 (d, *J* = 11.3 Hz, 1H), 3.25 (td, *J* = 11.1, 3.6 Hz, 1H), 1.77 – 1.59 (m, 2H), 1.30 – 1.24 (m, 1H), 1.23 – 1.16 (m, 1H), 1.11 – 1.05 (m, 1H), 1.05 – 1.01 (m, 1H), 0.80 (t, *J* = 7.3 Hz, 3H);

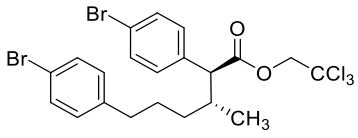
^{13}C NMR (151 MHz, CDCl$_3$) δ 171.7, 139.8, 135.2, 131.7, 131.6, 130.3, 130.0, 122.9 (q, *J* = 277.4 Hz), 121.8, 120.5, 60.70 (*q*, J = 36.6 Hz), 57.5, 49.0, 34.4, 29.4, 22.5, 13.9;

^{19}F NMR (282 MHz, CDCl$_3$) δ -73.6 (t, *J* = 8.4 Hz);

IR (neat) 2958, 2932, 2860, 1754, 1488, 1407, 1280, 1169, 1138, 1074, 1101, 738 cm^{-1};

HRMS (+p APCI) calcd for $C_{21}H_{22}O_2Br_2F_3$ $(M+H)^+$ 520.9933 found 520.99340;

HPLC (the ester product was reduced to 2,3-bis(4-bromophenyl)heptan-1-ol for better separation) (ODH column, 5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 19.34 min (minor) and 24.28 min (major) 85% ee with Rh_2(*S*-TCPTAD)$_4$.



4b

2,2,2-Trichloroethyl (2*S*,3*R*)-2,6-bis(4-bromophenyl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (111.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 87% yield. The pure major diastereomer of C2 insertion product was obtained from prep HPLC (Ascentis® C18 column, 90–95% acetonitrile in H_2O with 0.1% trifluoroacetic acid).

Rf = 0.60 (pentane/diethyl ether = 19/1);

[α]$^{20}_D$: +19.8° (c = 0.95, $CHCl_3$, 89% ee);

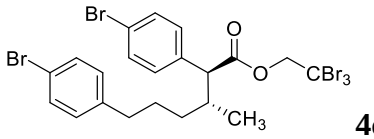
^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 4.90 (d, *J* = 12.3 Hz, 1H), 4.81 (d, *J* = 12.2 Hz, 1H), 3.53 (d, *J* = 10.5 Hz, 1H), 2.54 – 2.47 (m, 1H), 2.44 – 2.37 (m, 1H), 2.33 – 2.23 (m, 1H), 1.71 – 1.61 (m, 1H), 1.56 – 1.47 (m, 1H), 1.27 – 1.20 (m, 1H), 1.07 (d, *J* = 6.5 Hz, 3H), 1.05 – 0.98 (m, 1H);

^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 172.3, 142.6, 137.8, 132.6, 132.1, 131.8, 131.5, 122.0, 119.9, 96.2, 74.7, 58.4, 36.9, 35.6, 33.4, 28.6, 18.2.;

IR (neat) 2933, 2858, 1749, 1488, 1130, 1073, 1011, 827, 761, 719 cm^{-1};

HRMS (+p NSI) calcd for $C_{21}H_{22}O_2Br_2Cl_3$ $(M+H)^+$ 568.9047 found 568.90475;

HPLC (the ester product was reduced to 2,6-bis(4-bromophenyl)-3-methylhexan-1-ol for better separation) (OJH column, 5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 180 min, UV 230 nm) retention times of 99.82 min (minor) and 146.59 min (major) (89% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$).



4c

2,2,2-Tribromoethyl (2*S*,3*R*)-2,6-bis(4-bromophenyl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (151.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 84% yield.

Rf = 0.39 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: +2.9° (c = 0.83, $CHCl_3$, 84% ee);

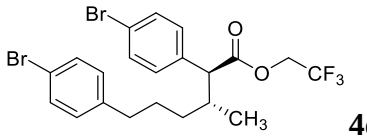
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 4.91 (d, *J* = 12.3 Hz, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 3.38 (d, *J* = 10.7 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.38 – 2.31 (m, 1H), 2.31 – 2.24 (m, 1H), 1.64 – 1.56 (m, 1H), 1.51 – 1.40 (m, 1H), 1.24 – 1.17 (m, 1H), 1.08 (d, *J* = 6.5 Hz, 3H), 1.01 – 0.91 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 141.2, 136.2, 131.9, 131.4, 130.6, 130.2, 121.8, 119.6, 58.2, 36.0, 35.3, 35.2, 32.8, 28.0, 18.1;

IR (neat) 2936, 2858, 1746, 1488, 1128, 1073, 1011, 825, 737 cm^{-1};

HRMS (+p NSI) calcd for $C_{21}H_{22}O_2Br_5$ $(M+H)^+$ 700.7531 found 700.75407;

HPLC (the ester product was reduced to 2,6-bis(4-bromophenyl)-3-methylhexan-1-ol for better separation) (OJH column, 5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 180 min, UV 230 nm) retention times of 109.22 min (minor) and 160.76 min (major) 84% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



4d

2,2,2-Trifluoroethyl (2*S*,3*R*)-2,6-bis(4-bromophenyl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 86% yield.

Rf = 0.55 (pentane/diethyl ether = 19/1);

[α]^{20}D: +29.6° (c = 1.00, $CHCl_3$, 91% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 4.54 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.32 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.32 (d, *J* = 10.6 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.37 – 2.30 (m, 1H), 2.25 – 2.15 (m, 1H), 1.62 – 1.55 (m, 1H), 1.48 – 1.39 (m, 1H), 1.20 – 1.13 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.97 – 0.90 (m, 1H);

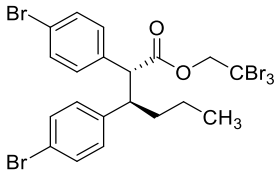
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 141.2, 136.0, 132.0, 131.4, 130.3, 130.2, 123.0 (q, *J* = 277.3 Hz), 121.9, 119.6, 60.5 (q, *J* = 36.6 Hz), 57.6, 36.4, 35.2, 32.7, 28.0, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.3 Hz);

IR (neat) 2937, 2860, 1754, 1488, 1281, 1168, 1134, 1074, 1011, 819 cm^{-1};

HRMS (+p NSI) calcd for $C_{21}H_{22}O_2Br_2F_3$ $(M+H)^+$ 520.9933 found 520.99285;

HPLC (the ester product was reduced to 2,6-bis(4-bromophenyl)-3-methylhexan-1-ol for better separation) (OJH column, 5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 180 min, UV 230 nm) retention times of 96.81 min (minor) and 140.95 min (major) 91% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



6a

2,2,2-Tribromoethyl (2*R*,3*R*)-2,3-bis(4-bromophenyl)hexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-butylbenzene (127.9 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (151.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-TCPTAD)$_4$ (6.4 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 82% yield.

Rf = 0.49 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: -44.2° (c = 1.06, $CHCl_3$, 94% ee);

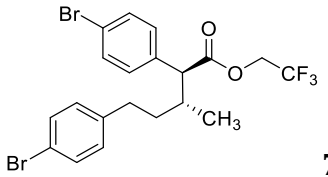
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 2.5 Hz, 2H), 7.26 (d, *J* = 2.6 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.96 (d, *J* = 12.3 Hz, 1H), 4.92 (d, *J* = 12.2 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H), 3.37 (td, *J* = 11.3, 3.4 Hz, 1H), 1.86 – 1.79 (m, 1H), 1.73 – 1.66 (m, 1H), 1.17 – 1.06 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 139.9, 135.3, 131.6, 131.5, 130.5, 130.1, 121.7, 120.4, 77.4, 58.0, 48.5, 37.2, 35.1, 20.6, 14.0;

IR (neat) 2956, 2870, 1744, 1487, 1133, 1073, 1010, 820, 731 cm^{-1};

HRMS (+p APCI) calcd for $C_{20}H_{20}O_2{}^{79}Br_4{}^{81}Br$ $(M+H)^+$ 688.7354 found 688.73522;

HPLC (the ester product was reduced to 2,5-bis(4-bromophenyl)-3-methylpentan-1-ol for better separation) (ODH column, 6% *i*-propanol in hexane, 0.25 mL min^{-1}, 1 mg mL^{-1}, 70 min, UV 230 nm) retention times of 31.63 min (minor) and 39.48 min (major) 94% ee with Rh_2(*S*-TCPTAD)$_4$.



7b

2,2,2-Trifluoroethyl (2*S*,3*R*)-2,5-bis(4-bromophenyl)-3-methylpentanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-butylbenzene (127.9 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 90% yield.

Rf = 0.44 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: +16.8° (c = 1.09, $CHCl_3$, 92% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 7.9 Hz, 2H), 4.47 (dq, *J* = 12.3, 8.4 Hz, 1H), 4.24 (dq, *J* = 12.0, 8.3 Hz, 1H), 3.30 (d, *J* = 10.5 Hz, 1H), 2.56 – 2.49 (m, 1H), 2.35 –2.27 (m, 1H), 2.17 – 2.08 (m, 1H), 1.42 – 1.35 (m, 1H), 1.17 – 1.10 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H);

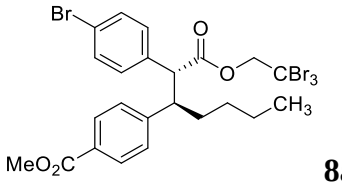
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 140.7, 135.8, 132.0, 131.5, 130.3, 130.2, 122.9 (q, *J* = 277.3 Hz), 122.0, 119.7, 60.5 (q, *J* = 36.6 Hz)., 57.6, 35.8, 35.0, 32.2, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.5 Hz);

IR (neat) 2932, 1749, 1488, 1130, 1072, 1011, 826, 801, 760, 717 cm^{-1};

HRMS (+p NSI) calcd for $C_{20}H_{20}O_2Br_2F_3$ $(M+H)^+$ 506.9777 found 506.97899;

HPLC (the ester product was reduced to 2,5-bis(4-bromophenyl)-3-methylpentan-1-ol for better separation) (ODH column, 6% *i*-propanol in hexane, 0.25 mL min^{-1}, 1 mg mL^{-1}, 70 min, UV 230 nm) retention times of 43.05 min (major) and 50.56 min (minor) 92% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



8a

Methyl 4-((2*R*,3*R*)-2-(4-bromophenyl)-1-oxo-1-(2,2,2-tribromoethoxy)heptan-3-yl)benzoate

This compound was obtained according to general procedure from C–H functionalization reaction between methyl 4-pentylbenzoate (123.8 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (151.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-TCPTAD)$_4$ (6.4 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 42% yield.

Rf = 0.56 (pentane/diethyl ether = 19/1);

[α]$^{20}_{D}$: -46.0° (c = 0.27, $CHCl_3$, 92% ee);

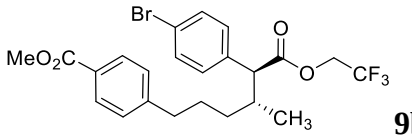
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.06 (dd, *J* = 8.4, 4.5 Hz, 4H), 4.98 (d, *J* = 12.2 Hz, 1H), 4.91 (d, *J* = 12.2 Hz, 1H), 3.89 (d, *J* = 11.5 Hz, 1H), 3.86 (s, 3H), 3.44 (td, *J* = 11.2, 3.3 Hz, 1H), 1.93 – 1.87 (m, 1H), 1.78 – 1.71 (m, 1H), 1.32 – 1.26 (m, 1H), 1.23 – 1.17 (m, 1H), 1.16 – 1.06 (m, 1H), 1.05 – 0.95 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 167.0, 146.6, 135.3, 131.6, 130.5, 129.8, 128.7, 128.5, 121.7, 57.9, 52.2, 49.3, 35.1, 34.8, 29.9, 29.6, 22.6, 14.0;

IR (neat) 2953, 2929, 2857, 1747, 1720, 1281, 1137, 1111, 761 cm^{-1};

HRMS (+p APCI) calcd for $C_{23}H_{25}O_4Br_4$ $(M+H)^+$ 680.8481 found 680.84717;

HPLC (ADH column, 5% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 16.69 min (minor) and 39.38 min (major) 92% ee with Rh_2(*S*-TCPTAD)$_4$.



9b

Methyl 4-((4*R*,5*S*)-5-(4-bromophenyl)-4-methyl-6-oxo-6-(2,2,2-trifluoroethoxy)hexyl)benzoate

This compound was obtained according to general procedure from C–H functionalization reaction between methyl 4-pentylbenzoate (123.8 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 2 – 6% diethyl ether in pentane) to afford colorless oil in 90% yield.

Rf = 0.18 (pentane/diethyl ether = 19/1);

[α]$^{20}_{D}$: +23.6° (c = 1.00, $CHCl_3$, 94% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.54 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.32 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.90 (s, 3H), 3.32 (d, *J* = 10.6 Hz, 1H), 2.59 – 2.52 (m, 1H), 2.47 – 2.40 (m, 1H), 2.26 – 2.15 (m, 1H), 1.66 – 1.58 (m, 1H), 1.53 – 1.42 (m, 1H), 1.22 – 1.15 (m 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.98 – 0.91 (m, 1H);

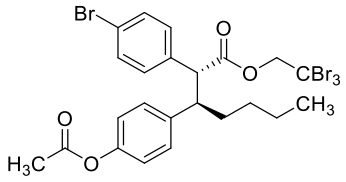
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 167.2, 147.8, 136.0, 132.0, 130.3, 129.8, 128.4, 127.9, 123.0 (q, *J* = 277.3 Hz), 121.9, 60.5 (q, *J* = 36.6 Hz), 57.6, 52.1, 36.4, 35.8, 32.8, 27.8, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2937, 1753, 1719, 1489, 1436, 1277, 1167, 1132, 1109, 1011, 978, 762 cm^{-1};

HRMS (+p NSI) calcd for $C_{23}H_{25}O_4BrF_3$ $(M+H)^+$ 501.0883 found 501.08848;

HPLC (ODH column, 0.5% *i*-propanol in hexane, 1.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 25.16 min (minor) and 27.00 min (major) 94% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



10a

2,2,2-Tribromoethyl (2*R*,3*R*)-3-(4-acetoxyphenyl)-2-(4-bromophenyl)heptanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 4-pentylphenyl acetate (123.8 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (151.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-TCPTAD)$_4$ (6.4 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 5% diethyl ether in pentane) to afford colorless oil in 83% yield.

Rf = 0.16 (pentane/diethyl ether = 19/1);

[α]$^{20}_D$: -46.1° (c = 0.96, $CHCl_3$, 94% ee);

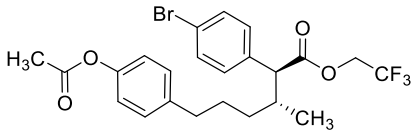
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.97 (d, *J* = 12.2 Hz, 1H), 4.90 (d, *J* = 12.2 Hz, 1H), 3.84 (d, *J* = 11.3 Hz, 1H), 3.36 (td, *J* = 11.2, 3.3 Hz, 1H), 2.24 (s, 3H), 1.90 – 1.81 (m, 1H), 1.77 – 1.67 (m, 1H), 1.32 – 1.24 (m, 1H), 1.24 – 1.18 (m, 1H), 1.16 – 1.02 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 169.2, 149.1, 138.2, 135.4, 131.4, 130.4, 129.1, 121.4, 121.2, 58.1, 48.6, 35.0, 34.7, 29.4, 22.5, 21.2, 13.9;

IR (neat) 2930, 2858, 1747, 1506, 1488, 1368, 1202, 1134, 1011, 911, 733, 632 cm^{-1};

HRMS (-p APCI) calcd for $C_{23}H_{23}O_4Br_4$ $(M-H)^-$ 678.8335 found 678.83411;

HPLC (ADH column, 1% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 90 min, UV 230 nm) retention times of 45.26 min (minor) and 62.57 min (major) 94% ee with Rh_2(*S*-TCPTAD)$_4$.



11b

2,2,2-Trifluoroethyl (2*S*,3*R*)-6-(4-acetoxyphenyl)-2-(4-bromophenyl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 4-pentylphenyl acetate (123.8 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 5% diethyl ether in pentane) to afford colorless oil in 90% yield.

Rf = 0.16 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: +19.4° (c = 1.01, $CHCl_3$, 94% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.54 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.32 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.33 (d, *J* = 10.5 Hz, 1H), 2.48 (ddd, *J* = 14.7, 9.3, 5.9 Hz, 1H), 2.37 (ddd, *J* = 13.9, 9.3, 6.5 Hz, 1H), 2.28 (s, 3H), 2.25 – 2.14 (m, 1H), 1.65 – 1.56 (m, 1H), 1.49 – 1.39 (m, 1H), 1.23 – 1.15 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.99 – 0.90 (m, 1H).;

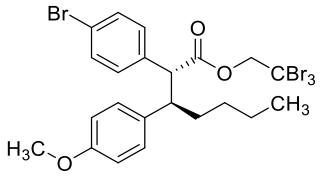
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 169.6, 148.7, 139.7, 135.9, 131.8, 130.2, 129.1, 122.8 (q, *J* = 277.4 Hz), 121.7, 121.2, 60.3 (q, *J* = 36.7 Hz)., 57.5, 36.3, 35.1, 32.7, 28.0, 21.1, 17.6;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2937, 2861, 1755, 1507, 1489, 1217, 1195, 1166. 1134, 1011, 979 cm^{-1};

HRMS (-p APCI) calcd for $C_{23}H_{23}O_4BrF_3$ $(M-H)^-$ 499.0737 found 499.07424;

HPLC (ADH column, 1% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 34.22 min (minor) and 36.44 min (major) 94% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



12a

2,2,2-Tribromoethyl (2*R*,3*R*)-2-(4-bromophenyl)-3-(4-methoxyphenyl)heptanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-methoxy-4-pentylbenzene (107.0 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (151.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-TCPTAD)$_4$ (6.4 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 3% diethyl ether in pentane) to afford colorless oil in 91% yield.

Rf = 0.51 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: -47.9° (c = 0.93, $CHCl_3$, 87% ee);

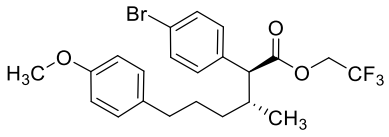
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 4.97 (d, *J* = 12.2 Hz, 1H), 4.90 (d, *J* = 12.3 Hz, 1H), 3.83 (d, *J* = 11.3 Hz, 1H), 3.72 (s, 3H), 3.30 (td, *J* = 11.2, 3.4 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.74 – 1.65 (m, 1H), 1.31 – 1.23 (m, 1H), 1.24 – 1.16 (m, 1H), 1.16 – 1.03 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 157.9, 135.7, 132.7, 131.3, 130.5, 129.1, 121.2, 113.6, 58.3, 55.1, 48.3, 35.1, 34.8, 29.5, 22.5, 13.9;

IR (neat) 2954, 2930, 2857, 1745, 1611, 1512, 1488, 1247, 1133, 1114, 1074, 1037, 828, 732, 717, 632 cm^{-1};

HRMS (+p NSI) calcd for $C_{22}H_{25}O_3Br_3{}^{81}Br$ $(M+H)^+$ 654.8511 found 654.85226;

HPLC (ADH column, 1% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 18.41 min (minor) and 32.61 min (major) 87% ee with Rh_2(*S*-TCPTAD)$_4$.



13b

2,2,2-Trifluoroethyl (2*S*,3*R*)-2-(4-bromophenyl)-6-(4-methoxyphenyl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-methoxy-4-pentylbenzene (107.0 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 3% diethyl ether in pentane) to afford colorless oil in 39% yield (mixture of minor diastereomer of benzylic and C2 (**13b**) insertion product) and 15% yield of major diastereomer of benzylic insertion product. The pure major diastereomer of C2 insertion product was obtained from prep HPLC (Ascentis® C18 column, 85% acetonitrile in H_2O with 0.1% trifluoroacetic acid).

Rf = 0.29 (pentane/diethyl ether = 19/1);

[α]$^{20}_{D}$: +26.0° (c = 1.02, $CHCl_3$, 93% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 4.53 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.32 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.78 (s, 3H), 3.32 (d, *J* = 10.5 Hz, 1H), 2.45 (ddd, *J* = 14.5, 9.1, 5.9 Hz, 1H), 2.32 (ddd, *J* = 13.8, 9.1, 6.7 Hz, 1H), 2.27 – 2.16 (m, 1H), 1.61 – 1.52 (m, 2H), 1.48 – 1.38 (m, 1H), 1.22 – 1.14 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.98 – 0.90 (m, 1H);

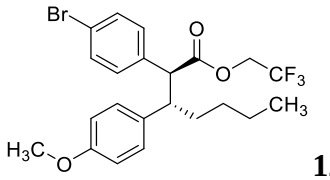
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 157.7, 136.0, 134.2, 131.8, 130.2, 129.1, 122.8 (q, *J* = 277.5 Hz), 121.6, 113.7, 60.3 (q, *J* = 36.6 Hz), 57.5, 55.3, 36.3, 34.7, 32.6, 28.2, 17.6;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2936, 2858, 1754, 1513, 1281, 1246, 1173, 1134, 1038, 1012, 979, 821 cm^{-1};

HRMS (+p APCI) calcd for $C_{22}H_{25}O_4BrF_3$ $(M+H)^+$ 473.0934 found 473.09428;

HPLC (R,R-Whelk column, 0.5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 41.67 min (minor) and 49.72 min (major) 93% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



12b

2,2,2-Trifluoroethyl (2*S*,3*S*)-2-(4-bromophenyl)-3-(4-methoxyphenyl)heptanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-methoxy-4-pentylbenzene (107.0 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 3% diethyl ether in pentane) to afford colorless oil in 39% yield (mixture of C2 and minor diastereomer of benzylic insertion product) and 15% yield of major diastereomer of benzylic insertion product (**12b**).

Rf = 0.51 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: +69.8° (c = 0.79, $CHCl_3$, 82% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 4.60 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.38 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.76 (d, *J* = 11.2 Hz, 1H), 3.71 (s, 3H), 3.21 (td, *J* = 10.7, 4.4 Hz, 1H), 1.72 – 1.60 (m, 2H), 1.32 – 1.27 (m, 1H), 1.23 – 1.16 (m, 1H), 1.13 – 0.99 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H);

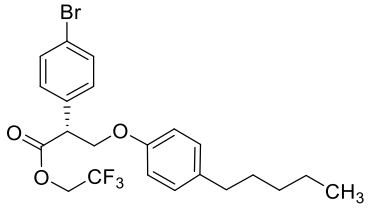
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 158.0, 135.5, 132.5, 131.4, 130.2, 129.1, 122.9 (q, *J* = 277.1 Hz), 121.3, 113.6, 60.5 (q, *J* = 36.6 Hz), 57.8, 55.1, 48.6, 34.4, 29.4, 22.4, 13.8;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.6 (t, *J* = 8.4 Hz);

IR (neat) 2957, 2932, 2859, 1753, 1512, 1489, 1281, 1174, 1137, 1037, 1012, 828 cm^{-1};

HRMS (-p APCI) calcd for $C_{22}H_{23}O_4BrF_3$ $(M-H)^-$ 471.0788 found 471.07924;

HPLC (R,R-Whelk column, 0.5% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}, 40 min, UV 230 nm) retention times of 18.64 min (major) and 20.20 min (minor) 82% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



2,2,2-Trifluoroethyl (*R*)-2-(4-bromophenyl)-3-(4-pentylphenoxy)propanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-methoxy-4-pentylbenzene (107.0 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 3% diethyl ether in pentane) to afford colorless oil in 36% yield.

Rf = 0.59 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: +21.3° (c = 0.98, $CHCl_3$, 84% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 3H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.60 – 4.53 (m, 1H), 4.52 – 4.45 (m, 2H), 4.20 – 4.09 (m, 2H), 2.56 – 2.49 (m, 2H), 1.60 – 1.54 (m, 2H), 1.34 – 1.26 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H);

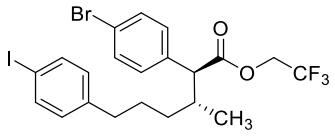
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 156.1, 136.0, 133.2, 132.1, 129.9, 129.3, 122.7 (q, *J* = 277.4 Hz), 122.4, 114.6, 69.0, 60.7 (q, *J* = 36.9 Hz), 50.7, 35.0, 31.4, 31.4, 22.5, 14.0;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2967, 2929, 1760, 1511, 1490, 1282, 1242, 1169, 1149, 1012, 824 cm^{-1};

HRMS (-p APCI) calcd for $C_{22}H_{23}O_4BrF_3$ $(M-H)^-$ 471.0788 found 471.07916;

HPLC (OD column, 0.5% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}, 45 min, UV 230 nm) retention times of 20.13 min (major) and 24.92 min (minor) 84% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



14

2,2,2-Trifluoroethyl (2*S*,3*R*)-2-(4-bromophenyl)-6-(4-iodophenyl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-iodo-4-pentylbenzene (164.5 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 88% yield.

Rf = 0.35 (pentane/diethyl ether = 19/1);

[α]^{20}D: +23.2° (c = 1.05, $CHCl_3$, 89% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 4.54 (dq, *J* = 12.6, 8.4 Hz, 1H), 4.32 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.32 (d, *J* = 10.6 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.36 – 2.28 (m, 1H), 2.25 – 2.15 (m, 1H), 1.48 – 1.38 (m, 1H), 1.48 – 1.38 (m, 1H), 1.20 – 1.13 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.97 – 0.89 (m, 1H);

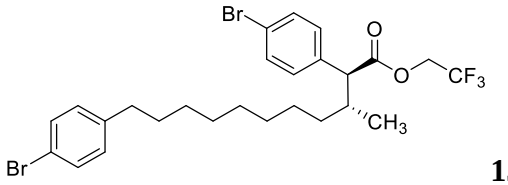
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 141.9, 137.4, 136.0, 132.0, 130.5, 130.3, 123.0 (q, *J* = 277.3 Hz), 121.9, 90.9, 60.5 (q, *J* = 36.6 Hz), 57.6, 36.4, 35.3, 32.7, 28.0, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2937, 2860, 1754, 1487, 1280, 1168, 1134, 1008, 879, 820, 734 cm^{-1};

HRMS (+p NSI) calcd for $C_{21}H_{22}O_2Br_2F_3I$ $(M+H)^+$ 568.9794 found 568.97916;

HPLC (ADH column, 0.5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 21.39 min (minor) and 22.93 min (major) 89% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



15

2,2,2-Trifluoroethyl (2*S*,3*R*)-2,11-bis(4-bromophenyl)-3-methylundecanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-decylbenzene (178.4 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 1% diethyl ether in pentane) to afford colorless oil in 92% yield.

Rf = 0.63 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: +17.9° (c = 1.00, $CHCl_3$, 94% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.54 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.33 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.33 (d, *J* = 10.5 Hz, 1H), 2.53 (t, *J* = 7.7 Hz, 2H), 2.22 – 2.12 (m, 1H), 1.58 – 1.50 (m, 2H), 1.32 – 1.18 (m, 5H), 1.19 – 1.08 (m, 5H), 1.07 – 1.02 (m, 1H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.83 (m, 1H);

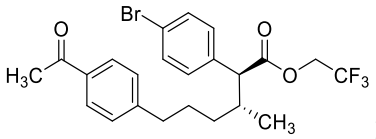
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 141.9, 136.3, 131.9, 131.4, 130.4, 130.3, 123.0 (q, *J* = 277.3 Hz), 121.8, 119.4, 60.5 (q, *J* = 36.6 Hz), 57.8, 36.5, 35.5, 33.3, 31.4, 29.6, 29.5, 29.5, 29.3, 26.3, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.5 Hz);

IR (neat) 2929, 2855, 1755, 1488, 1281, 1169, 1132, 1074, 1102, 979, 912, 761, 737 cm^{-1};

HRMS (-p NSI) calcd for $C_{26}H_{31}O_2Br_2F_3Cl$ $(M+Cl)^-$ 625.0337 found 625.03609;

HPLC (ADH column, 0.3% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 33.36 min (minor) and 46.06 min (major) 94% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



16

2,2,2-Trifluoroethyl (2*S*,3*R*)-6-(4-acetylphenyl)-2-(4-bromophenyl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-(4-pentylphenyl)ethan-1-one (114.2 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 2 – 10% diethyl ether in pentane) to afford colorless oil in 35% yield.

Rf = 0.04 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: -5.9° (c = 1.23, $CHCl_3$, 93% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 4.54 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.32 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.32 (d, *J* = 10.6 Hz, 1H), 2.62 – 2.53 (m, 4H), 2.48 – 2.41 (m, 1H), 2.25 – 2.18 (m, 1H), 1.66 – 1.58 (m, 1H), 1.53 – 1.44 (m, 1H), 1.22 – 1.15 (m, 1H), 1.02 (d, *J* = 6.5 Hz, 3H), 0.99 – 0.92 (m, 1H);

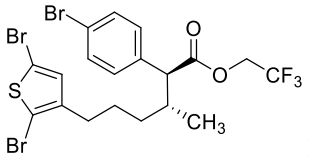
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.0, 172.0, 148.0, 136.0, 135.2, 132.0, 130.3, 128.6, 128.6, 123.0 (q, *J* = 277.4 Hz), 121.9, 60.5 (q, *J* = 36.6 Hz), 57.6, 36.4, 35.8, 32.8, 27.8, 26.7, 17.8;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2935, 2860, 1752, 1681, 1268, 1165, 1132, 1074, 1011, 978, 818 cm^{-1};

HRMS (+p NSI) calcd for $C_{23}H_{25}O_3BrF_3$ $(M+H)^+$ 485.0934 found 485.09463;

HPLC (ADH column, 1% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 210 nm) retention times of 33.13 min (major) and 37.95 min (minor) 93% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



17

2,2,2-Trifluoroethyl (2*S*,3*R*)-2-(4-bromophenyl)-6-(2,5-dibromothiophen-3-yl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 2,5-dibromo-3-pentylthiophene (187.2 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 78% yield.

Rf = 0.38 (pentane/diethyl ether = 19/1);

[α]$^{20}_{D}$: +21.6° (c = 1.08, $CHCl_3$, 84% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.62 (s, 1H), 4.55 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.33 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.33 (d, *J* = 10.6 Hz, 1H), 2.42 – 2.36 (m, 1H), 2.35 – 2.29 (m, 1H), 2.25 – 2.17 (m, 1H), 1.57 – 1.52 (m, 1H), 1.44 – 1.34 (m, 1H), 1.19 – 1.12 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.97 – 0.90 (m, 1H);

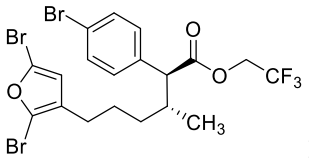
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 142.3, 135.9, 132.0, 130.8, 130.3, 122.95 (q, *J* = 277.3 Hz), 122.0, 110.7, 108.3, 60.5 (q, *J* = 36.6 Hz), 57.6, 36.3, 32.5, 29.3, 26.2, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2938, 2862, 1754, 1489, 1281, 1168, 1133, 1011, 979, 820 cm^{-1};

HRMS (+p NSI) calcd for $C_{19}H_{19}SO_2Br_3F_3$ $(M+H)^+$ 604.8602 found 604.86132;

HPLC (R,R-Whelk column, 0.1% *i*-propanol in hexane, 0.6 mL min^{-1}, 1 mg mL^{-1}, 90 min, UV 230 nm) retention times of 54.10 min (minor) and 68.83 min (major) 84% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



18

2,2,2-Trichloroethyl (2*S*,3*R*)-2-(4-bromophenyl)-6-(2,5-dibromofuran-3-yl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 2,5-dibromo-3-pentylfuran (161.4 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (96.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 83% yield.

Rf = 0.38 (pentane/diethyl ether = 19/1);

[α]$^{20}_{D}$: +16.0° (c = 1.00, $CHCl_3$, 86% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.06 (s, 1H), 4.55 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.32 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.32 (d, *J* = 10.6 Hz, 1H), 2.24 – 2.16 (m, 2H), 2.15 – 2.09 (m, 1H), 1.53 – 1.45 (m, 1H), 1.41 – 1.31 (m, 1H), 1.18 – 1.11 (m, 1H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.96 – 0.88 (m, 1H);

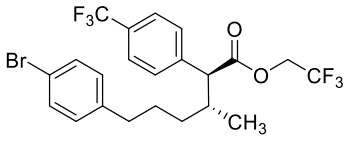
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 135.9, 132.0, 130.3, 126.8, 123.0 (q, *J* = 277.3 Hz), 122.0, 121.6, 119.8, 114.6, 60.5 (q, *J* = 36.7 Hz), 57.6, 36.2, 32.5, 25.8, 25.1, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2937, 2859, 1735, 1489, 1280, 1166, 1130, 1075, 1011, 979, 929, 818 cm^{-1};

HRMS (+p NSI) calcd for $C_{19}H_{19}O_3Br_3F_3$ $(M+H)^+$ 588.8831 found 588.88462;

HPLC (R,R-Whelk column, 0.3% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 90 min, UV 230 nm) retention times of 37.50 min (minor) and 45.33 min (major) 86% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



19

2,2,2-Trifluoroethyl (2*S*,3*R*)-6-(4-bromophenyl)-3-methyl-2-(4-(trifluoromethyl)phenyl)hexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (93.7 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 76% yield.

Rf = 0.64 (pentane/diethyl ether = 9/1);

[α]^{20}D: +25.3° (c = 1.04, $CHCl_3$, 93% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 4.55 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.33 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.43 (d, *J* = 10.5 Hz, 1H), 2.49 – 2.43 (m, 1H), 2.37 – 2.30 (m, 1H), 2.29 – 2.19 (m, 1H), 1.64 – 1.55 (m, 1H), 1.49 – 1.41 (m, 1H), 1.19 – 1.12 (m, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.99 – 0.91 (m, 1H).;

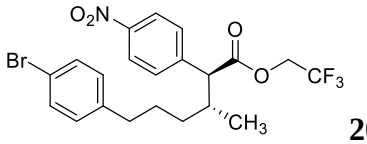
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 141.1, 141.0, 131.4, 130.1, 129.1, 125.8 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.0 Hz), 122.9 (q, *J* = 277.4 Hz), 119.6, 60.9, 60.7, 60.4, 60.2, 58.0, 36.5, 35.1, 32.7, 28.0, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.6, -73.7 (t, *J* = 8.8 Hz);

IR (neat) 2970, 2937, 2862, 1755, 1325, 1165, 1128, 1069, 1019, 834 cm^{-1};

HRMS (+p APCI) calcd for $C_{22}H_{22}O_2BrF_6$ $(M+H)^+$ 511.0702 found 511.07004;

HPLC (ODH column, 0.5% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 30 min, UV 230 nm) retention times of 14.03 min (major) and 15.63 min (minor) 93% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



20

2,2,2-Trifluoroethyl (2*S*,3*R*)-6-(4-bromophenyl)-3-methyl-2-(4-nitrophenyl)hexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-diazo-2-(4-nitrophenyl)acetate (86.8 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 4 – 6% diethyl ether in pentane) to afford colorless oil in 67% yield.

Rf = 0.53 (pentane/diethyl ether = 6/1);

[α]^{20}D: +25.0° (c = 1.02, $CHCl_3$, 83% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 4.55 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.36 (dq, *J* = 12.7, 8.3 Hz, 1H), 3.50 (d, *J* = 10.4 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.38 – 2.32 (m, 1H), 2.31 – 2.22 (m, 1H), 1.65 – 1.56 (m, 1H), 1.51 – 1.42 (m, 1H), 1.18 – 1.09 (m, 1H), 1.04 (d, *J* = 6.5 Hz, 1H), 1.00 – 0.93 (m, 1H);

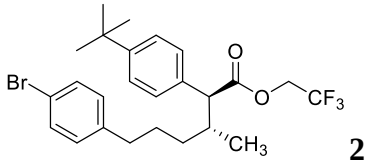
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 147.7, 144.3, 140.9, 131.5, 130.1, 129.6, 124.0, 122.8 (q, *J* = 277.3 Hz), 119.7, 60.7 (q, *J* = 36.9 Hz), 57.9, 36.8, 35.1, 32.8, 28.0, 17.6;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2937, 2860, 1754, 1523, 1347, 1276, 1167, 1136, 979, 840 cm^{-1};

HRMS (+p APCI) calcd for $C_{21}H_{22}O_4NBrF_3$ $(M+H)^+$ 488.0679 found 488.06776;

HPLC (ADH column, 1% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 32.57 min (minor) and 36.81 min (major) 83% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



21

2,2,2-Trifluoroethyl (2*S*,3*R*)-6-(4-bromophenyl)-2-(4-(*tert*-butyl)phenyl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (83.9 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 0 – 2% diethyl ether in pentane) to afford colorless oil in 76% yield.

Rf = 0.32 (pentane/diethyl ether = 19/1);

$[\alpha]^{20}_D$: +20.4° (c = 1.11, $CHCl_3$, 81% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.3, 6.3 Hz, 4H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.56 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.28 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.33 (d, *J* = 10.6 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.39 – 2.31 (m, 1H), 2.27 – 2.17 (m, 1H), 1.62 – 1.55 (m, 1H), 1.48 – 1.40 (m, 1H), 1.32 (s, 9H), 1.21 – 1.17 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.97 – 0.90 (m, 1H);

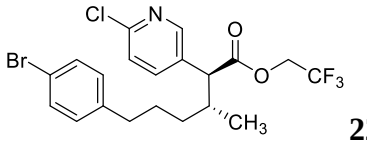
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 150.7, 141.4, 133.8, 131.4, 130.2, 128.3, 125.7, 123.1 (q, *J* = 277.2 Hz), 119.5, 60.4 (q, *J* = 36.5 Hz), 57.8, 36.2, 35.1, 34.7, 32.8, 31.5, 28.0, 17.8;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.4 Hz);

IR (neat) 2965, 2866, 1755, 1488, 1281, 1168, 1132, 979, 912, 738 cm^{-1};

HRMS (+p NSI) calcd for $C_{25}H_{31}O_2BrF_3$ $(M+H)^+$ 499.1454 found 499.14681;

HPLC (the ester product was reduced to 6-(4-bromophenyl)-2-(4-(tert-butyl)phenyl)-3-methylhexan-1-ol for better separation) (ADH column, 2% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}, 30 min, UV 230 nm) retention times of 11.08 min (minor) and 11.86 min (major) 81% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



22

2,2,2-Trifluoroethyl (2*S*,3*R*)-6-(4-bromophenyl)-2-(6-chloropyridin-3-yl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (90.1 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 3 – 6% diethyl ether in pentane) to afford colorless oil in 84% yield.

Rf = 0.15 (pentane/diethyl ether = 9/1);

[α]^{20}D: +13.7° (c = 0.94, $CHCl_3$, 84% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.6 Hz, 1H), 7.57 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 2H), 4.49 (dq, *J* = 12.7, 8.3 Hz, 1H), 4.29 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.33 (d, *J* = 10.2 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.34 – 2.25 (m, 1H), 2.16 – 2.06 (m, 1H), 1.59 – 1.49 (m, 1H), 1.44 – 1.32 (m, 1H), 1.13 – 1.05 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.93 – 0.85 (m, 1H);

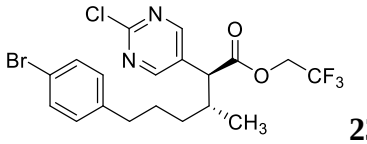
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 151.2, 150.0, 140.9, 138.5, 131.7, 131.5, 130.1, 124.6, 122.8 (q, *J* = 277.3 Hz), 119.7, 60.7 (q, *J* = 36.8 Hz), 54.7, 36.7, 35.1, 32.7, 28.0, 17.6;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.3 Hz);

IR (neat) 2934, 2860, 1754, 1460, 1278, 1168, 1139, 1106, 979, 832, 741 cm^{-1};

HRMS (+p NSI) calcd for $C_{20}H_{21}O_2NBrClF_3$ $(M+H)^+$ 478.0391 found 478.04067;

HPLC (ADH column, 1% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}, 60 min, UV 230 nm) retention times of 32.57 min (minor) and 36.81 min (major) 84% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.



23

2,2,2-Trifluoroethyl (2*S*,3*R*)-6-(4-bromophenyl)-2-(2-chloropyrimidin-5-yl)-3-methylhexanoate

This compound was obtained according to general procedure from C–H functionalization reaction between 1-bromo-4-pentylbenzene (136.3 mg, 0.6 mmol, 2.0 equiv.) and 2,2,2-trifluoroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate (84.2 mg, 0.3 mmol, 1.0 equiv.), catalyzed by Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (5.7 mg, 0.003 mmol, 1.0 mol%). The product was purified by flash column chromatography on silica gel (gradient elution: 5 – 8% diethyl ether in pentane) to afford colorless oil in 83% yield.

Rf = 0.38 (pentane/diethyl ether = 3/1);

[α]^{20}D: +17.5° (c = 1.00, $CHCl_3$, 83% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (s, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 4.59 (dq, *J* = 12.7, 8.3 Hz, 1H), 4.40 (dq, *J* = 12.7, 8.3 Hz, 1H), 3.44 (d, *J* = 9.5 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.43 – 2.34 (m, 1H), 2.26 – 2.17 (m, 1H), 1.67 – 1.58 (m, 1H), 1.53 – 1.44 (m, 1H), 1.24 – 1.17 (m, 1H), 1.08 – 0.94 (m, 4H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 161.1, 159.6, 140.7, 131.6, 130.1, 129.2, 122.7 (q, *J* = 277.3 Hz), 119.9, 61.0 (q, *J* = 36.9 Hz), 52.6, 37.0, 35.2, 32.9, 28.2, 17.4;

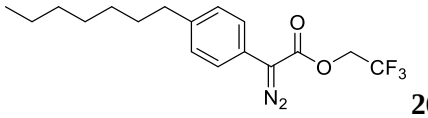
^{19}F NMR (282 MHz, $CDCl_3$) δ -73.6 (t, *J* = 8.3 Hz);

IR (neat) 2934, 2861, 1754, 1547, 1398, 1279, 1159, 1011 cm^{-1};

HRMS (+p APCI) calcd for $C_{19}H_{20}O_2N_2BrClF_3$ $(M+H)^+$ 479.0343 found 479.03463;

HPLC (ADH column, 2% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}, 30 min, UV 230 nm) retention times of 14.48 min (minor) and 19.58 min (major) 83% ee with Rh_2(*S*-2-Cl-5-BrTPCP)$_4$.

4. Experimental Data for Macrocyclization



26

2,2,2-Trifluoroethyl 2-diazo-2-(4-heptylphenyl)acetate

The procedure is adapted from literatures[11]: A 250-ml round-bottom flask with stir bar was flame dried under vacuum. Once cool enough all solids were added first: PPh_3 (1.65 mmol, 0.1 equiv.), $Pd(PPh_3)_4$ (0.825 mmol, 0.05 equiv.) and Ag_2CO_3 (8.25 mmol, 0.5 equiv.). After solids added, the reaction vessel was purged with argon three times. Next the liquids were added: toluene (66 ml), Et_3N (21.5 mmol, 1.3 equiv.), aryl iodide (16.5 mmol, 1 equiv.), and finally the 2,2,2-trifluoroethyl 2-diazoacetate (21.5 mmol, 1.3 equiv.) was added last. The resulted mixture was stirred at room temperature (23 °C) for 5 h and then, filtered through a short silica plug (3.5 cm *diameter*, 5 cm *height*), eluting with ethyl acetate until elutes clear. The crude product was concentrated and purified by column chromatography (5% ether in pentane) to afford **26** as a yellow oil in 85% yield.

Rf = 0.71 (pentane/diethyl ether = 9/1);

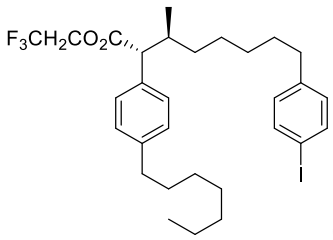
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.65 (q, *J* = 8.4 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.36 – 1.22 (m, 8H), 0.87 (t, *J* = 6.6 Hz 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 141.5, 129.1, 124.3, 122.9 (q, *J* = 277.6 Hz), 121.3, 60.3 (q, *J* = 36.9 Hz), 35.4, 31.7, 31.2, 29.1, 29.1, 22.6, 13.9 (The resonance resulting from the diazo carbon was not observed);

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.9 (t, *J* = 8.4 Hz);

IR (neat) 2957, 2927, 2856, 2089, 1715, 1515, 1456, 1410, 1350, 1280, 1242, 1167, 1137, 1074, 1020, 974, 923, 839, 810, 733, 653 cm^{-1};

HRMS (+p NSI) calcd for $C_{17}H_{22}F_3N_2O_2$ $(M+H)^+$ 343.1628 found 343.08576.



(-)-**27**

2,2,2-Trifluoroethyl (2*R*,3*S*)-2-(4-heptylphenyl)-8-(4-iodophenyl)-3-methyloctanoate

The procedure is adjusted from the general procedure for C–H functionalization reactions: A 50-ml flame-dried round-bottom flask with condenser was charged with 4 Å MS and Rh_2(*R*-2-Cl-5-BrTPCP)$_4$ (0.02 mmol, 1.0 mol%) and then, purged three times with argon. 1-n-Heptyl-4-iodobenzene (6.29 mmol, 3.0 equiv.) and distilled CH_2Cl_2 (8 ml) were added next, then the mixture was heated to 40 °C and refluxed for at least 15 min before addition of the diazo compounds. Next, **26** (2.09 mmol, 1.0 equiv.) was purged under argon in a 20-mL scintillation vial, then diluted with distilled CH_2Cl_2 (8 ml). Then, under reflux conditions and argon atmosphere, the diazo solution was added to the reaction vessel dropwise via syringe pump over 3 h. The reaction mixture was stirred at 40 °C for another 30 min, and concentrated under vacuum for crude ^{1}H NMR. The crude product was purified by flash column chromatography (3% ether in pentane) to afford (-)-**27** as an opaque oil in 62% yield.

Note: Solvent must be carefully dried (distilled over CaH_2 and stored on activated 4 Å MS).

Rf = 0.71 (pentane/diethyl ether = 19/1);

[α]$^{20}_D$: -18.6° (c = 1.00, $CHCl_3$, 91% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J*= 8.0 Hz 2H), 6.86 (d, *J*= 8.1 Hz, 2H), 4.55 (dq, *J* = 8.5, 4.1 Hz, 1H), 4.29 (dq, *J* = 8.5, 4.2 Hz, 1H), 3.32 (d, *J* = 10.9 Hz, 1H), 2.57 (t, *J*= 7.6 Hz, 2H), 2.45 (t, *J* = 7.7 Hz, 2H), 2.23 – 2.16 (m, 1H), 1.63 – 1.56 (m, 2H), 1.51 – 1.41 (m 2H), 1.34 – 1.23 (m, 10H), 1.22 – 1.09 (m, 4H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H);

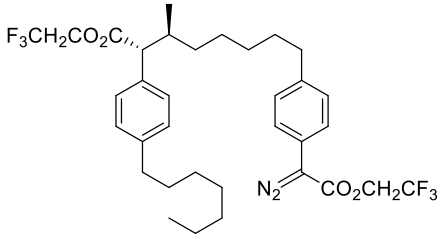
^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 142.3, 137.2, 134.1, 130.5, 128.6, 128.4, 123.0 (q, *J* = 277.2 Hz), 90.5, 60.2 (q, *J* = 36.5 Hz), 57.9, 36.2, 35.6, 35.3, 33.1, 31.8, 31.3, 31.0, 29.3, 29.2, 29.0, 26.0, 22.7, 17.7, 14.1;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.5 Hz);

IR (neat) 2927,2855,1753,1484,1464,1400,1278,1165,1128,1061,1006,979,824,793,737cm^{-1};

HRMS (+p NSI) calcd for $C_{30}H_{41}O_2IF_3$ $(M+H)^+$ 617.2098 found 617.20986;

HPLC (R,R-Whelk column, 0 % *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}, 30 min, UV 210 nm) retention times of 14.9 min (major) and 17.6 min (minor) 91% ee with Rh_2(*R*-2-Cl-5-BrTPCP)$_4$.



(-)-**28**

2,2,2-Trifluoroethyl (2*R*,3*S*)-8-(4-(1-diazo-2-oxo-2-(2,2,2-trifluoroethoxy)ethyl)phenyl)-2-(4-heptylphenyl)-3-methyloctanoate

The procedure is adapted from literatures[11]: A 50-ml round-bottom flask with stir bar was flame dried under vacuum. Once cool enough all solids were added first: PPh_3 (0.129 mmol, 0.1 equiv.), $Pd(PPh_3)_4$ (0.065 mmol, 0.05 equiv.) and Ag_2CO_3 (0.645 mmol, 0.5 equiv.). After solids added, the reaction vessel was purged with argon three times. Next the liquids were added: toluene (5.2 ml), Et_3N (1.67 mmol, 1.3 equiv.), aryl iodide (**27**, 1.29 mmol, 1 equiv.), and finally the 2,2,2-trifluoroethyl 2-diazoacetate (1.67 mmol, 1.3 equiv.) was added last. The resulted mixture was stirred at room temperature (23 °C) for 5 h and then, filtered through a short silica plug (3.5 cm *diameter*, 5 cm *height*), eluting with ethyl acetate until elutes clear. The crude product was concentrated and purified by column chromatography (2% ether in pentane) to afford product (-)-**28** as a yellow oil in 81% yield.

Rf = 0.45 (pentane/diethyl ether = 9/1);

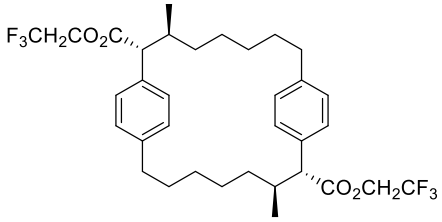
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.64 (q, *J* = 8.4 Hz, 2H), 4.55 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.29 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.32 (d, *J* = 10.5 Hz, 1H), 2.57 (t, *J*= 7.6 Hz, 2H), 2.51 (t, *J* = 7.7 Hz, 2H), 2.23 – 2.15 (m, 1H), 1.62 – 1.56 (m, 2H), 1.52 – 1.44 (m, 2H), 1.35 – 1.24 (m, 10H), 1.22 – 1.11 (m, 4H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 142.3, 141.3, 134.1, 129.2, 128.6, 128.4, 124.2, 123.0 (q, *J*= 277.7 Hz), 122.9 (q, *J*= 277.7 Hz), 121.3, 60.3 (q, *J*= 36.9 Hz), 60.2 (q, *J*= 36.6 Hz), 57.9, 36.2, 35.6, 35.3, 33.1, 31.8, 31.3, 31.1, 29.3, 29.2, 29.1, 26.0, 22.7, 17.7, 14.1;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.5 Hz), -73.9 (t, *J* = 8.3 Hz);

IR (neat) 2928, 2856, 2090, 1753, 1717, 1514, 1456, 1409, 1350, 1279, 1242, 1165, 1135, 1074, 976, 923, 839, 733 cm^{-1};

HRMS (+p NSI) calcd for $C_{34}H_{41}O_4N_2F_6$ $(M-H)^-$ 655.2976 found 655.29807;



(-)-**29**

Bis(2,2,2-trifluoroethyl) (2*R*,3*S*,10*R*,11*S*)-3,11-dimethyl-1,9(1,4)-dibenzenacyclohexadecaphane-2,10-dicarboxylate

The procedure is adjusted from the general procedure for C–H functionalization reactions: A 100-ml flame-dried round-bottom flask with condenser were charged with 4 Å MS and Rh_2(*R*-2-Cl-5-BrTPCP)$_4$ (0.01 mmol, 1.0 mol%), then purged three times under argon. Distilled CH_2Cl_2 (10.5 ml) was added using oven dried syringes, then the mixture was heated to 40 ^oC and refluxed for at least 15 min before addition of the diazo compounds. Next, (-)-**28** (1.04 mmol, 1.0 equiv.) was purged under argon in a 20-mL scintillation vial, then diluted with distilled CH_2Cl_2 (10.5 ml). Then, under reflux conditions and argon atmosphere, the diazo solution was added to the reaction vessel dropwise via syringe pump over 3 h. The reaction mixture was stirred at 40 ^oC for another 30 min, and concentrated under vacuum for crude ^1H NMR. The crude product was purified by flash column chromatography (3% ether in pentane) to afford the product (-)-**29** as a white solid in 68% yield.

Note: Solvent must be carefully dried (distilled over CaH_2 and stored on activated 4 Å MS).

m.p. 141-143 ^oC

Rf = 0.45 (pentane/diethyl ether = 9/1);

$[\alpha]^{20}_D$: -11.0 ° (c = 1.00, $CHCl_3$, 5.6:1 d.r., >99% ee);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.0 Hz, 4H), 7.01 (d, *J* = 8.1 Hz, 4H), 4.55 (dq, *J* = 12.7, 8.5 Hz, 2H), 4.27 (dq, *J* = 12.7, 8.4 Hz, 2H), 3.21 (d, *J* = 11.4 Hz, 2H), 2.58 (dt, *J* = 13.1, 6.4 Hz, 2H), 2.42 (dt, *J* = 13.6, 7.6 Hz, 2H), 2.19 – 2.09 (m, 2H), 1.48 – 1.27 (m, 6H), 1.12 – 0.96 (m, 10H), 0.96 – 0.85 (m, 4H), 0.80 – 0.68 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 141.8, 134.4, 128.8, 128.2, 122.95 (q, *J* = 277.3 Hz), 60.21 (q, *J* = 36.5 Hz), 58.3, 36.4, 35.5, 32.7, 30.8, 28.3, 26.0, 17.7;

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (t, *J* = 8.5 Hz);

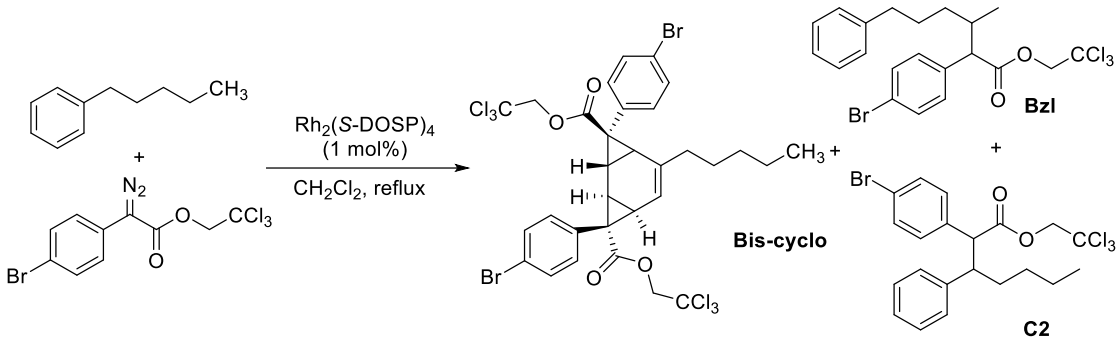
IR (neat) 2929, 2856, 1748, 1403, 1385, 1347, 1303, 1275, 1225, 1160, 1123, 1052, 981, 909, 838, 822, 740, 661 cm^{-1};

HRMS (+p NSI) calcd for $C_{30}H_{42}O_2IF_3$ $(M)^+$ 628.2987 found 628.29995;

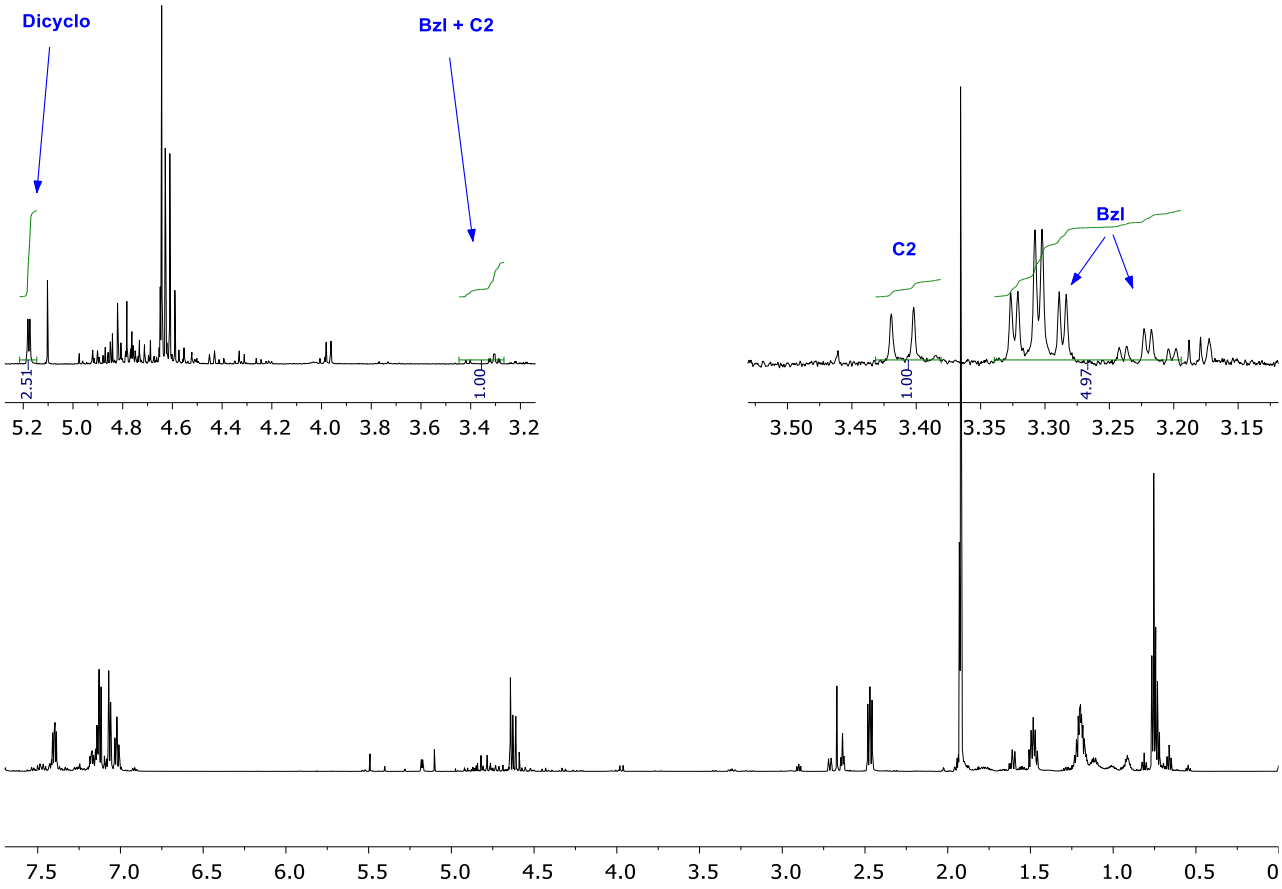
HPLC [for better separation, the ester product was reduced to ((2*R*,3*S*,10*R*,11*S*)-3,11-dimethyl-1,9(1,4)-dibenzenacyclohexadecaphane-2,10-diyl)dimethanol, and the pure major diastereomer of the alcohol derivative was obtained via prep HPLC (Ascentis® C18 column, 80% acetonitrile in H_2O with 0.1% trifluoroacetic acid)]

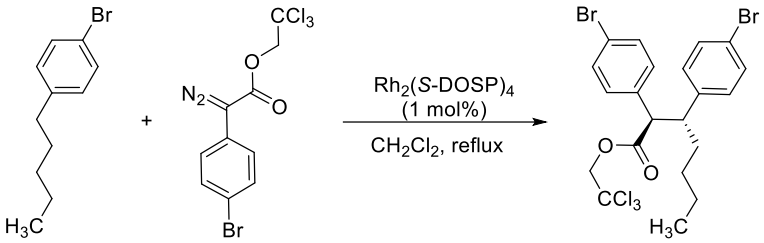
(ADH column, 10 % *i*-propanol in hexane, 1.0 mL min^{-1}, 1 mg mL^{-1}, 80 min, UV 210 nm) retention times of 28.69 min (major) and 60.71 min (minor) >99% ee with Rh_2(*R*-2-Cl-5-BrTPCP)$_4$.

5. Crude ^{1}H-NMR Spectra for *r.r.* and *d.r.* Determination

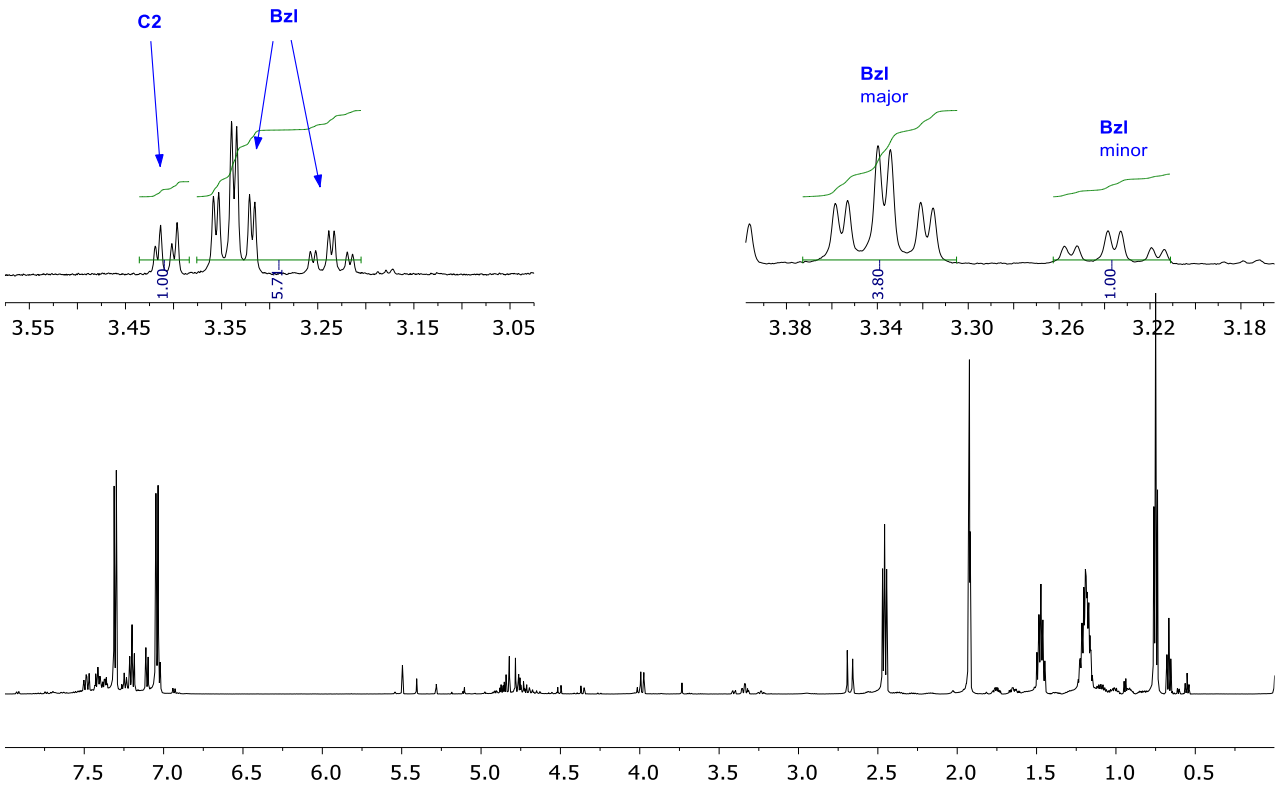


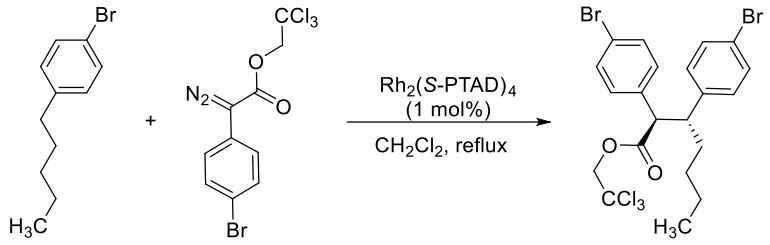
(Acetone-*d6*)



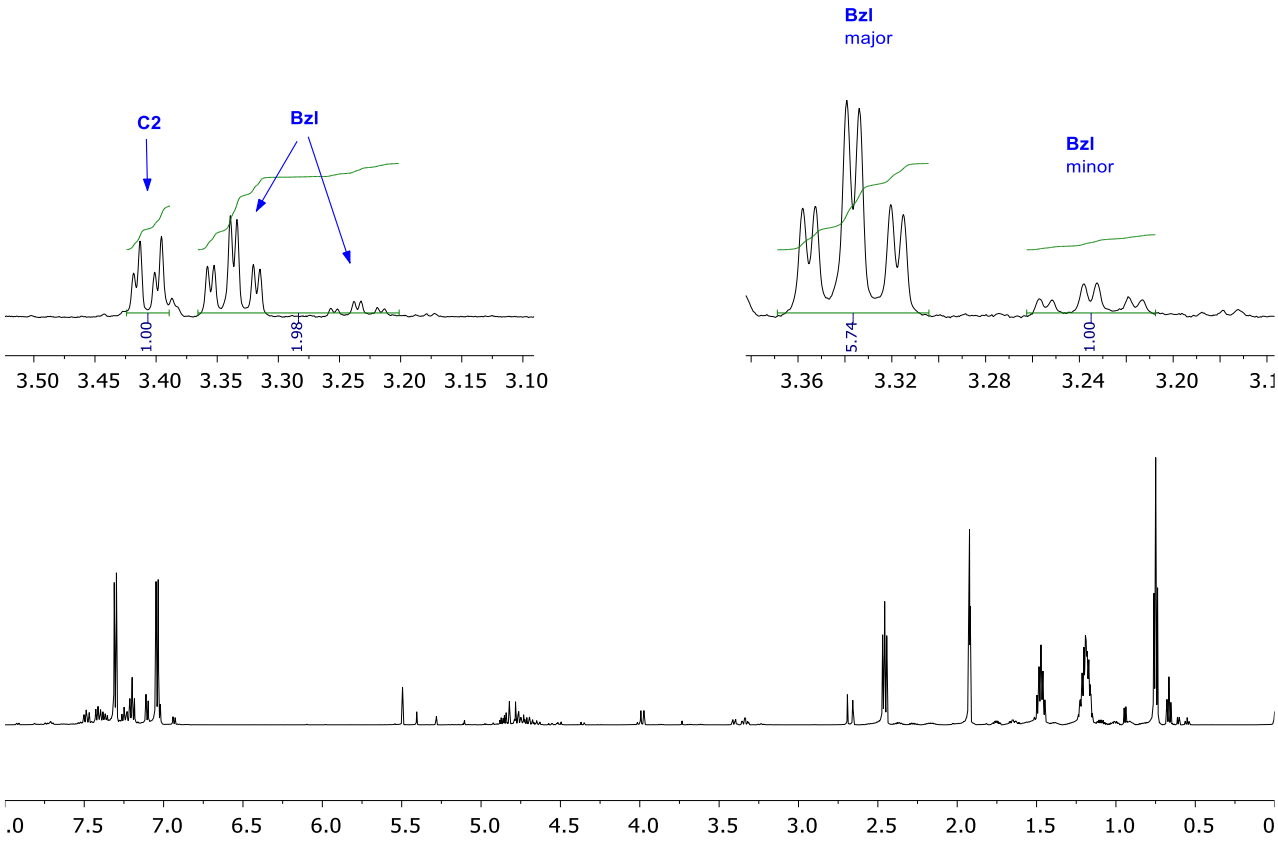

Br
CCl3
O
N2
O
Br
+
Rh2(S-DOSP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
O
O
CCl3
H3C
H3C

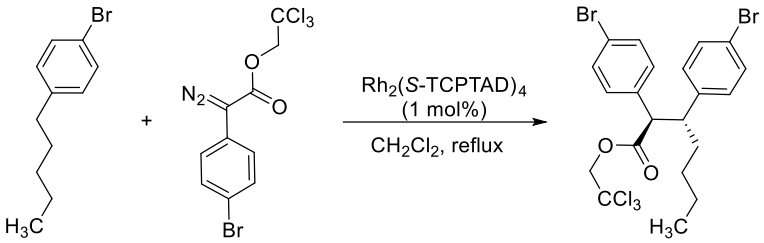
(Acetone-*d6*)


C2
Bzl
Bzl
major
Bzl
minor
1.00
5.71
3.80
1.00
3.55
3.45
3.35
3.25
3.15
3.05
3.38
3.34
3.30
3.26
3.22
3.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

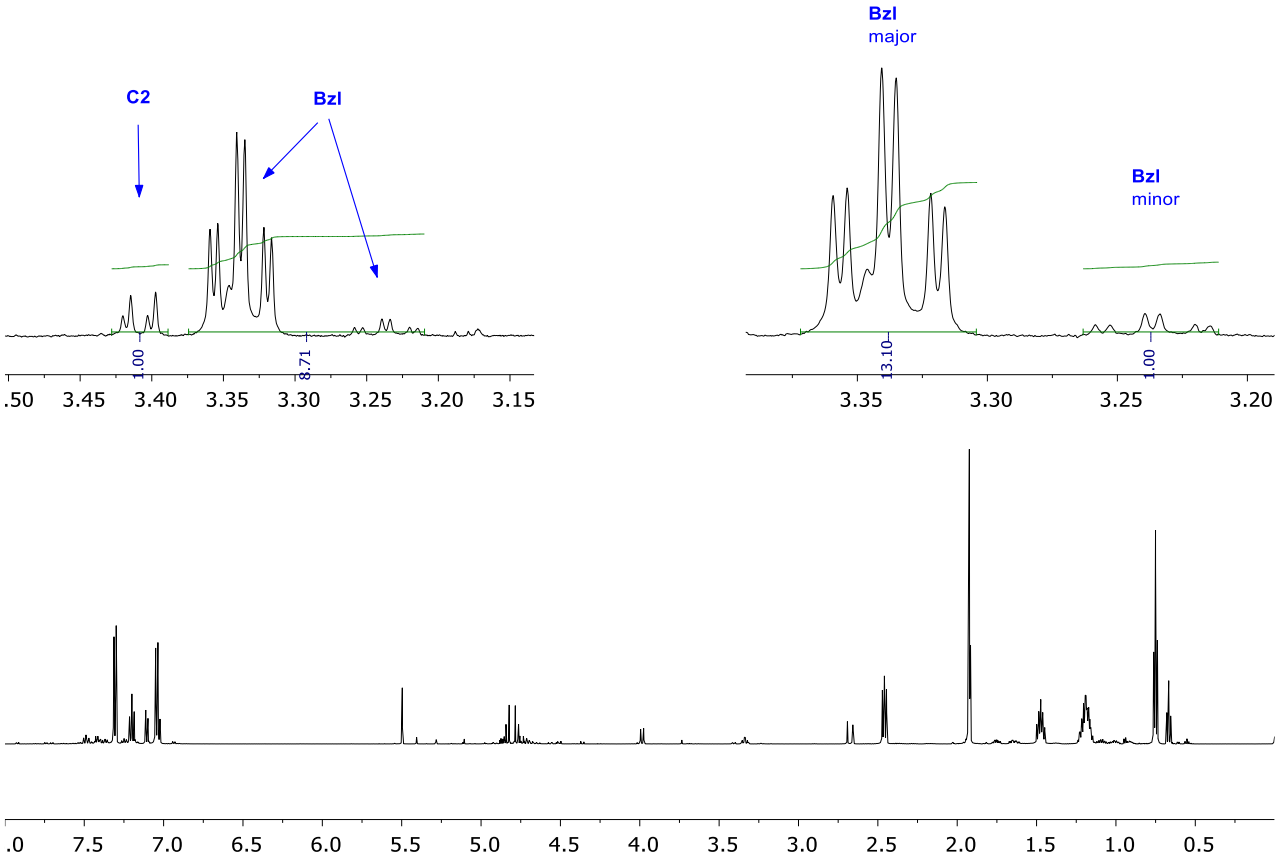

Br
CCl3
O
N2
O
Br
+
Rh2(S-PTAD)4
(1 mol%)
CH2Cl2, reflux
Br
Br
O
O
CCl3
H3C
H3C

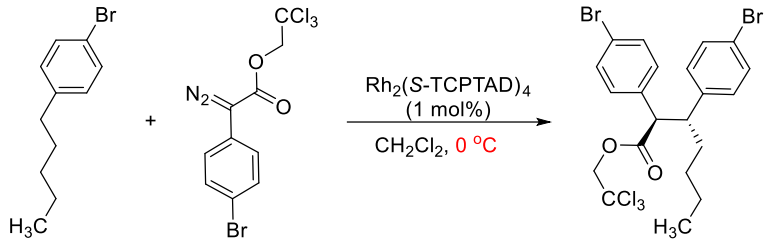
(Acetone-*d6*)


C2
Bzl
1.00
1.98
3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10
Bzl
major
Bzl
minor
5.74
1.00
3.36 3.32 3.28 3.24 3.20
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

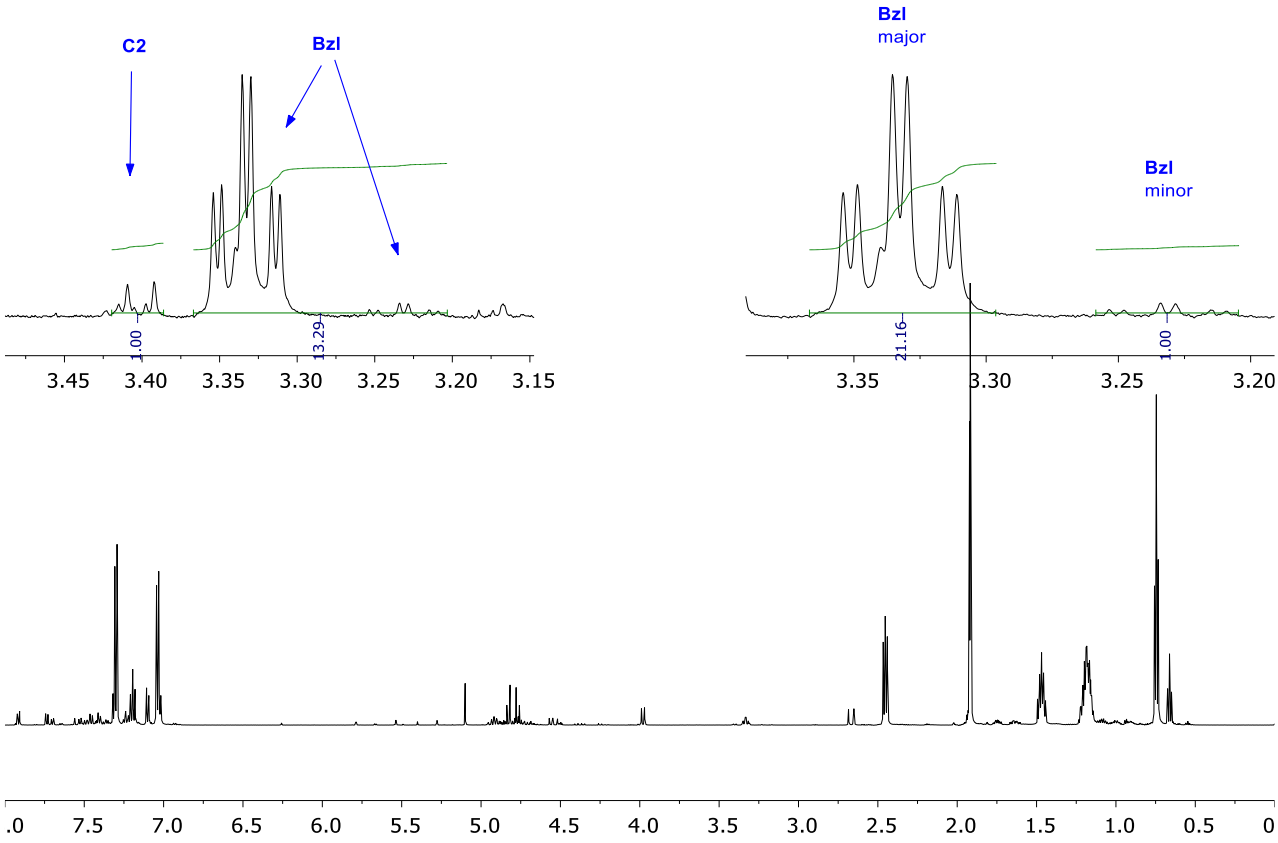

Br
CCl3
O
N2
O
Br
+
Rh2(S-TCPTAD)4
(1 mol%)
CH2Cl2, reflux
Br
Br
O
O
CCl3
H3C
H3C

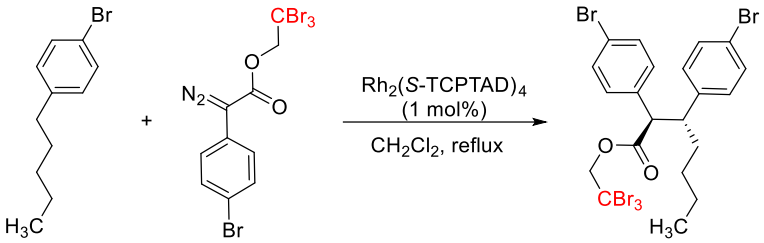
(Acetone-*d6*)


C2
Bzl
Bzl
major
Bzl
minor
1.00
8.71
13.10
1.00
.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15
3.35 3.30 3.25 3.20
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

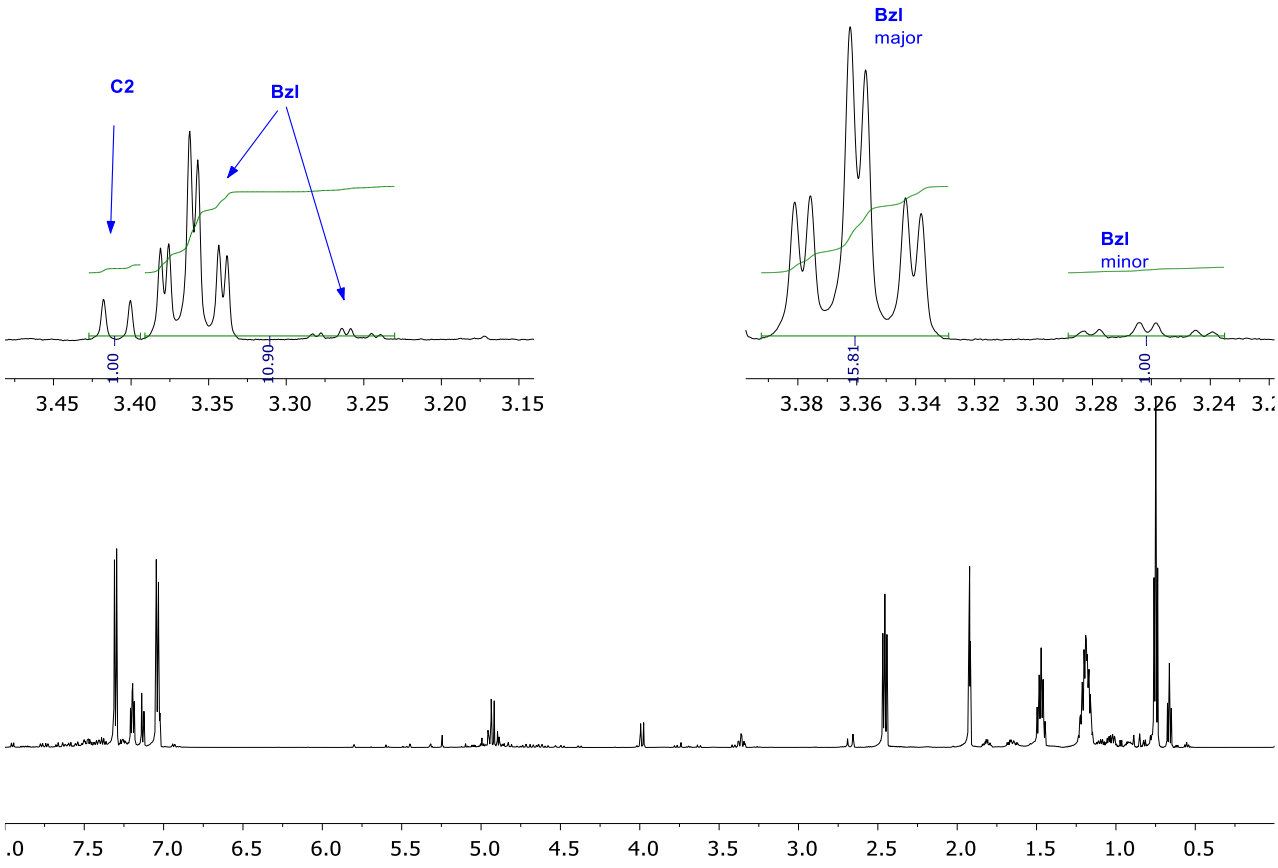

Br
CCl3
O
N2
O
Br
H3C
Rh2(S-TCPTAD)4
(1 mol%)
CH2Cl2, 0 °C
Br
Br
O
O
CCl3
H3C

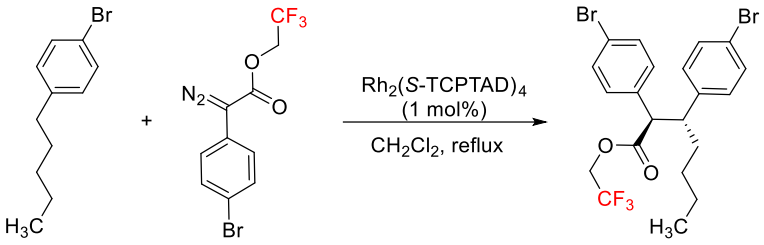
(Acetone-*d6*)


C2
Bzl
Bzl
major
Bzl
minor
1.00
13.29
21.16
1.00
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.35
3.30
3.25
3.20
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

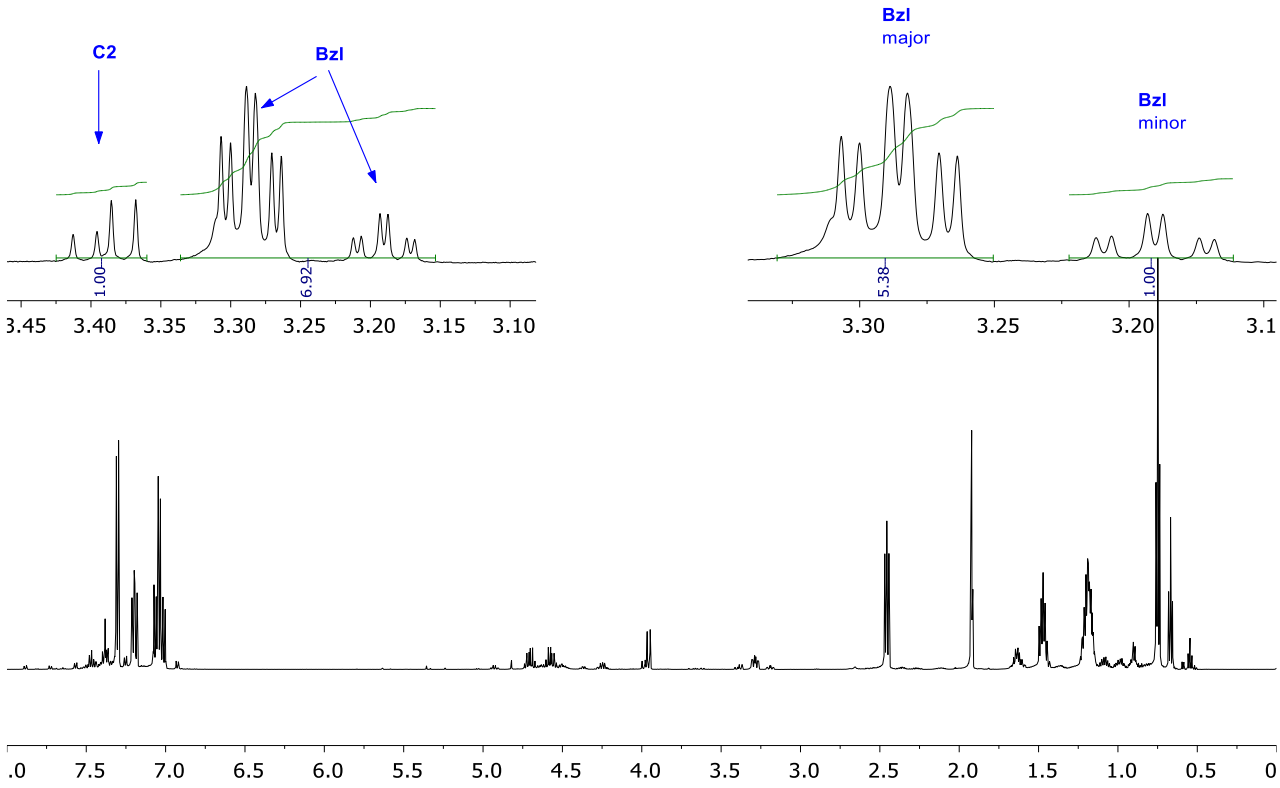

Br
CBr3
O
N2
O
Br
H3C
+
Rh2(S-TCPTAD)4
(1 mol%)
CH2Cl2, reflux
Br
Br
O
O
CBr3
H3C

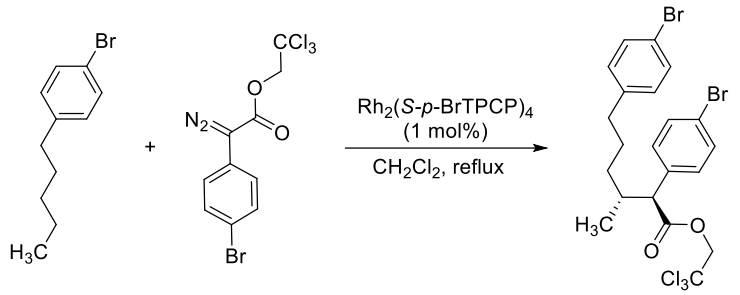
(Acetone-*d6*)


C2
Bzl
Bzl
major
Bzl
minor
1.00
10.90
15.81
1.00
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.38
3.36
3.34
3.32
3.30
3.28
3.26
3.24
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

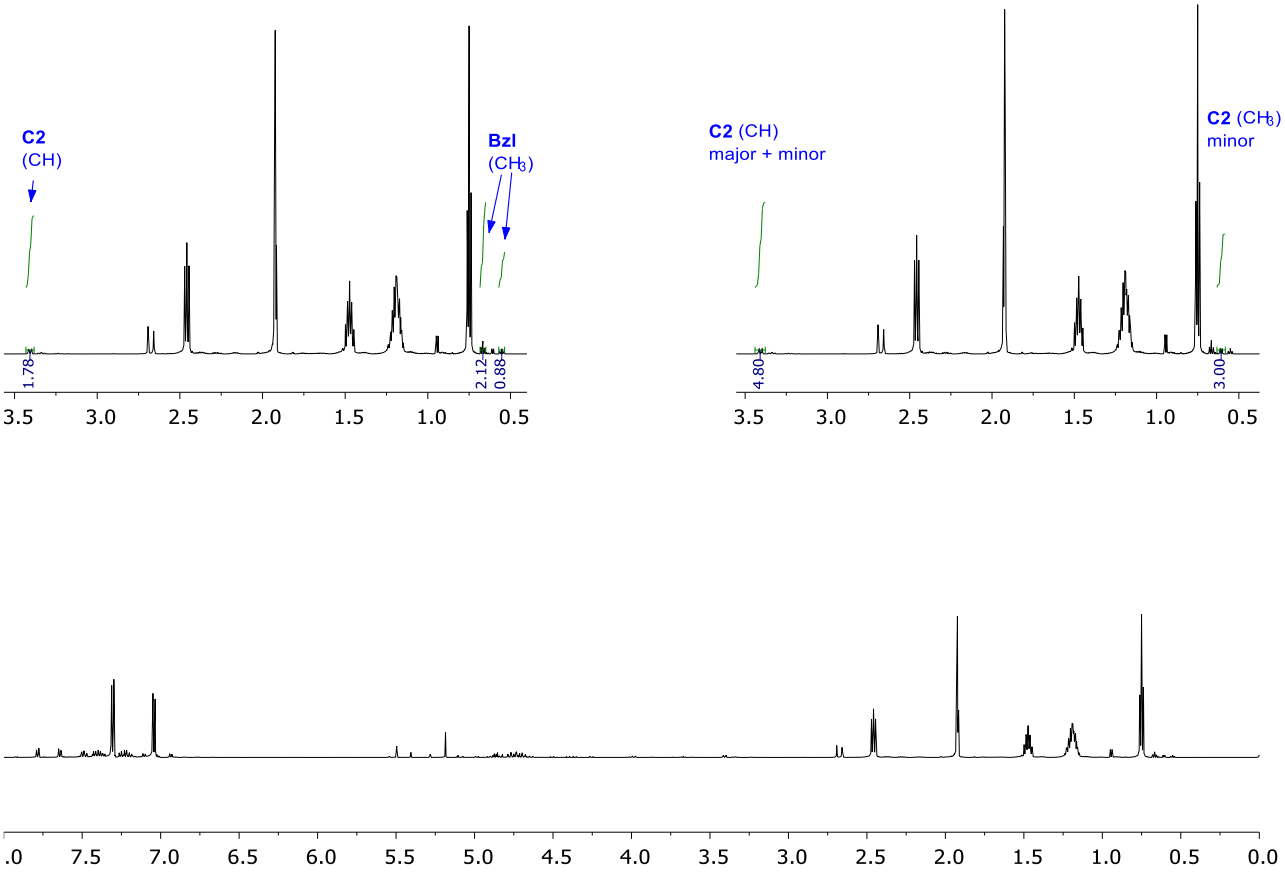

Br
CF3
O
N2
O
Br
H3C
Rh2(S-TCPTAD)4
(1 mol%)
CH2Cl2, reflux
Br
Br
O
O
CF3
H3C

(Acetone-*d6*)

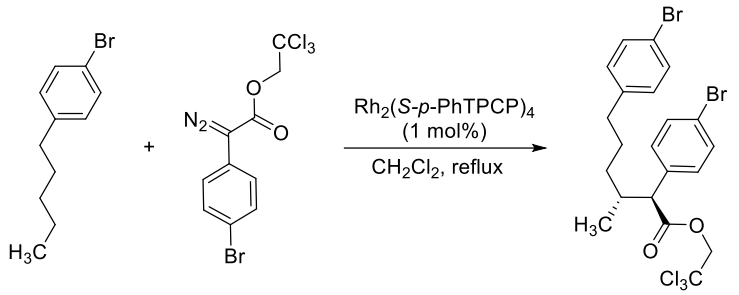

C2
Bzl
Bzl
major
Bzl
minor
1.00
6.92
5.38
1.00
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.10
3.30
3.25
3.20
3.1
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0


Br
CCl3
O
N2
O
Br
H3C
Rh2(S-p-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
H3C
O
O
Cl3C

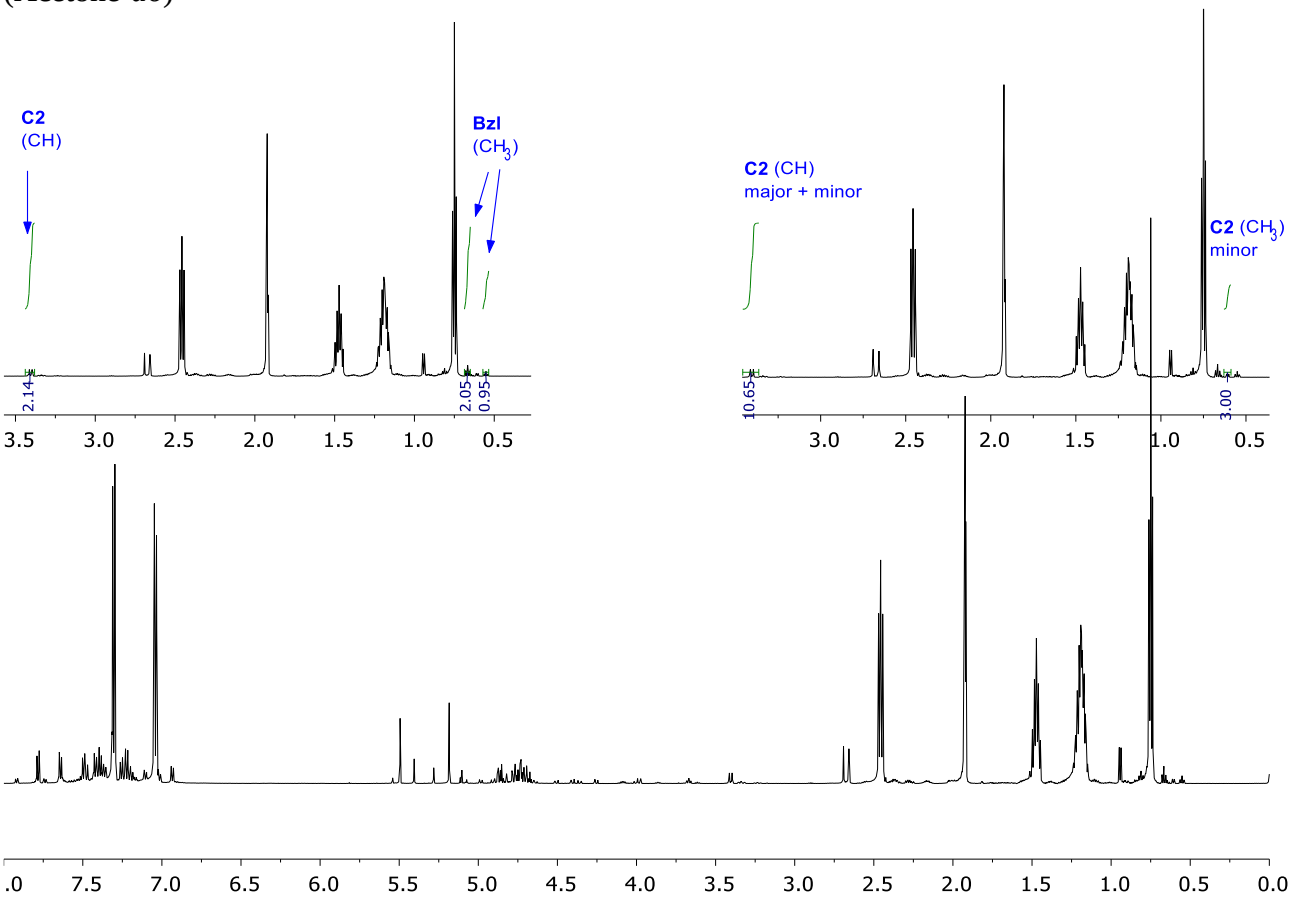
(Acetone-*d6*)

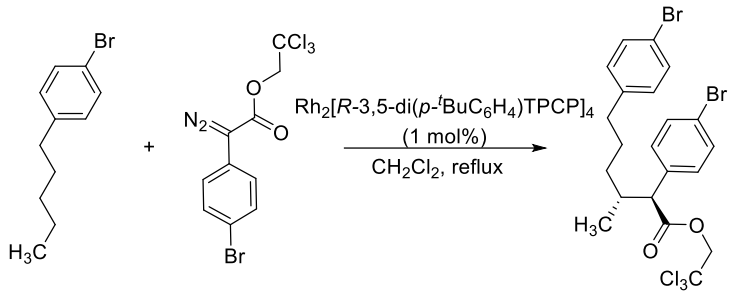

C2
(CH)
Bzl
(CH3)
1.78
2.12
0.88
3.5
3.0
2.5
2.0
1.5
1.0
0.5
C2 (CH)
major + minor
C2 (CH3)
minor
4.80
3.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5

.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

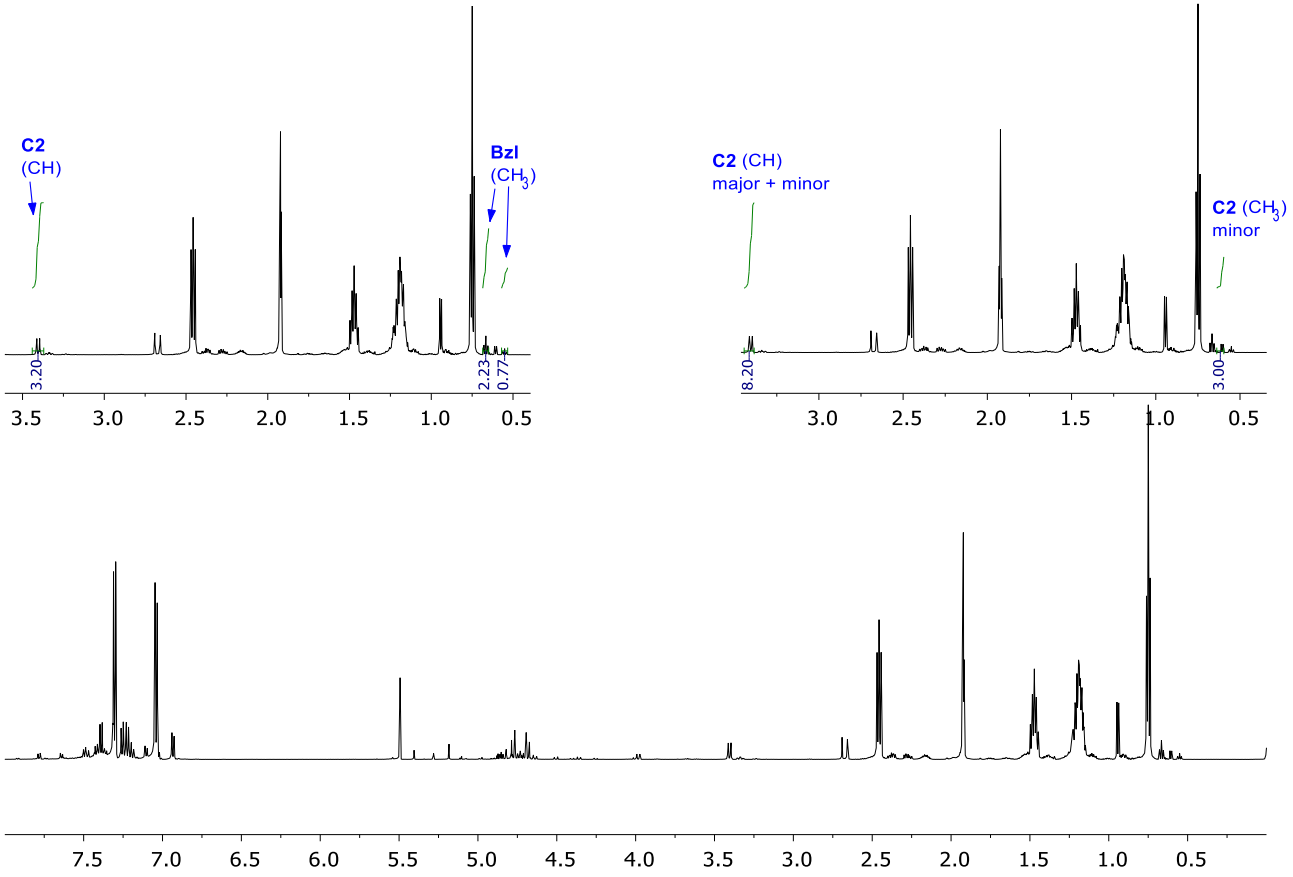

Br
CCl3
O
N2
O
Br
H3C
Rh2(S-p-PhTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
H3C
O
O
Cl3C

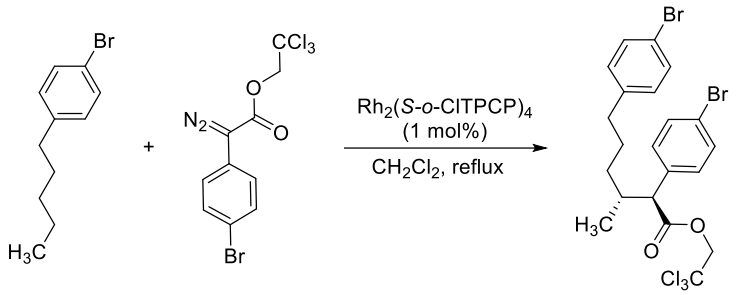
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
C2 (CH)
major + minor
C2 (CH3)
minor
2.14
2.05
0.95
10.65
3.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

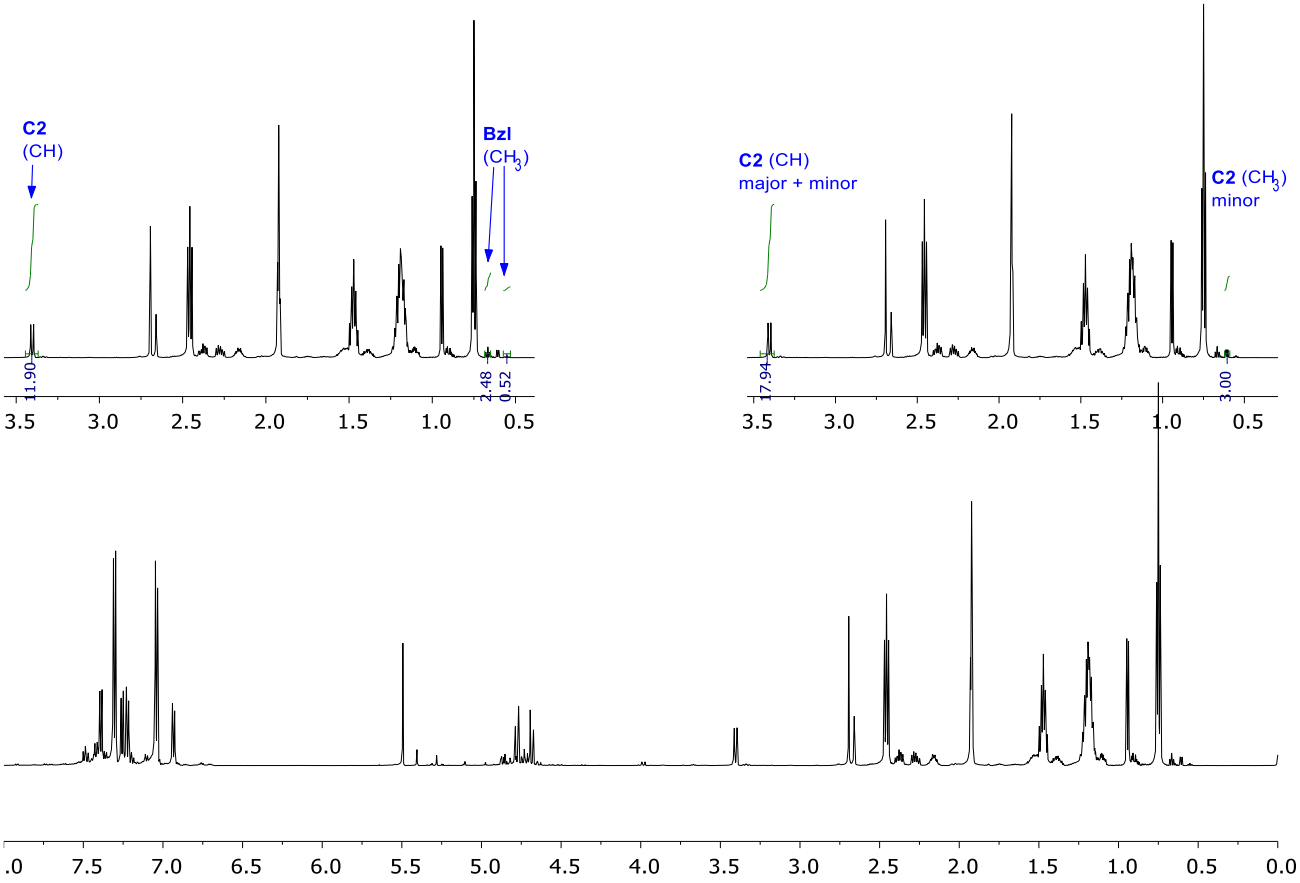

Br
CCl3
O
N2
O
Br
H3C
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
(1 mol%)
CH2Cl2, reflux
Br
Br
H3C
O
O
Cl3C

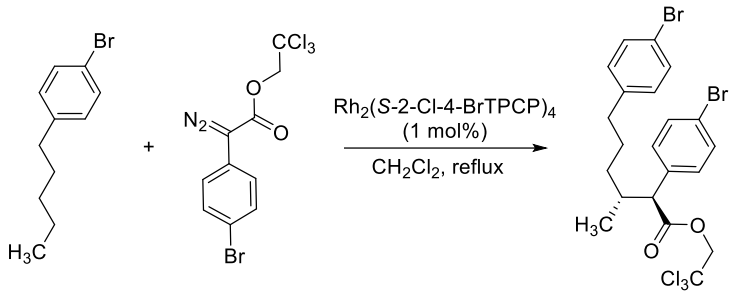
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
3.20
2.23
0.77
3.5
3.0
2.5
2.0
1.5
1.0
0.5
C2 (CH)
major + minor
C2 (CH3)
minor
8.20
3.00
3.0
2.5
2.0
1.5
1.0
0.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

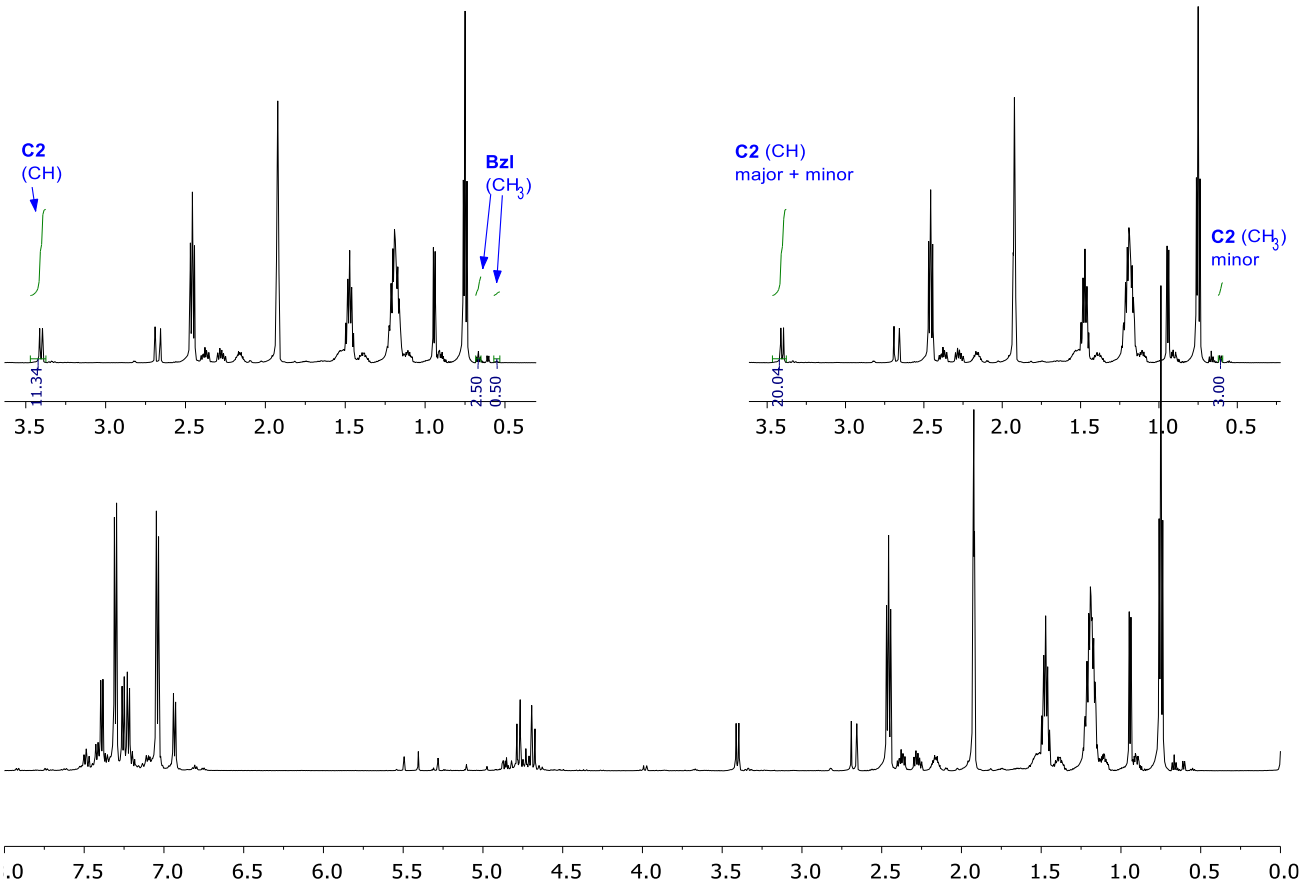

Br
CCl3
O
N2
O
Br
H3C
Rh2(S-o-ClTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
H3C
O
O
Cl3C

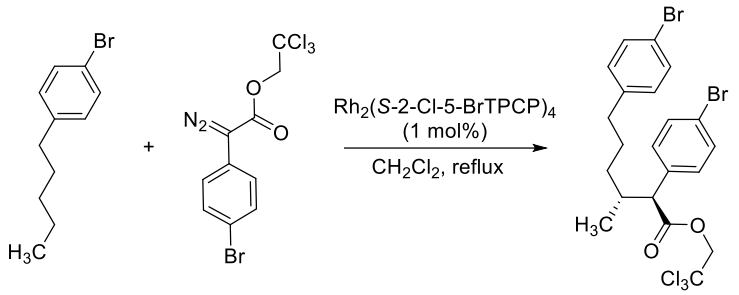
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
11.90
2.48
0.52
3.5
3.0
2.5
2.0
1.5
1.0
0.5
C2 (CH)
major + minor
C2 (CH3)
minor
17.94
3.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

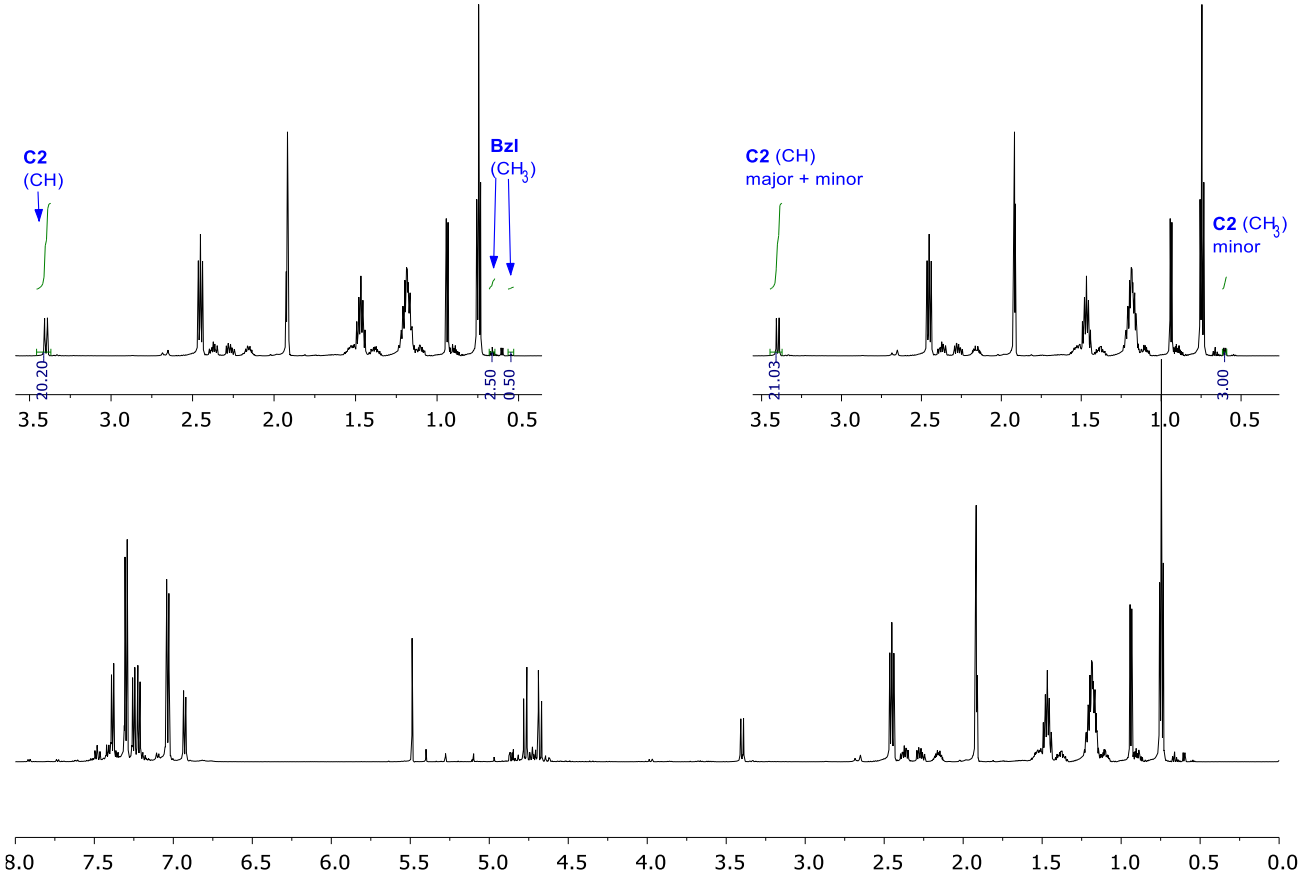

Br
CCl3
O
N2
O
Br
H3C
Rh2(S-2-Cl-4-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
H3C
O
O
Cl3C

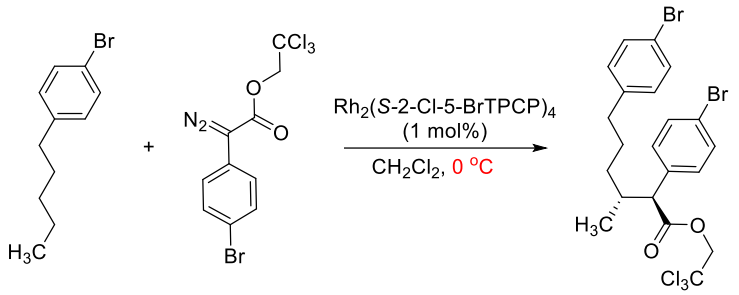
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
C2 (CH)
major + minor
C2 (CH3)
minor
11.34
2.50
0.50
20.04
3.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

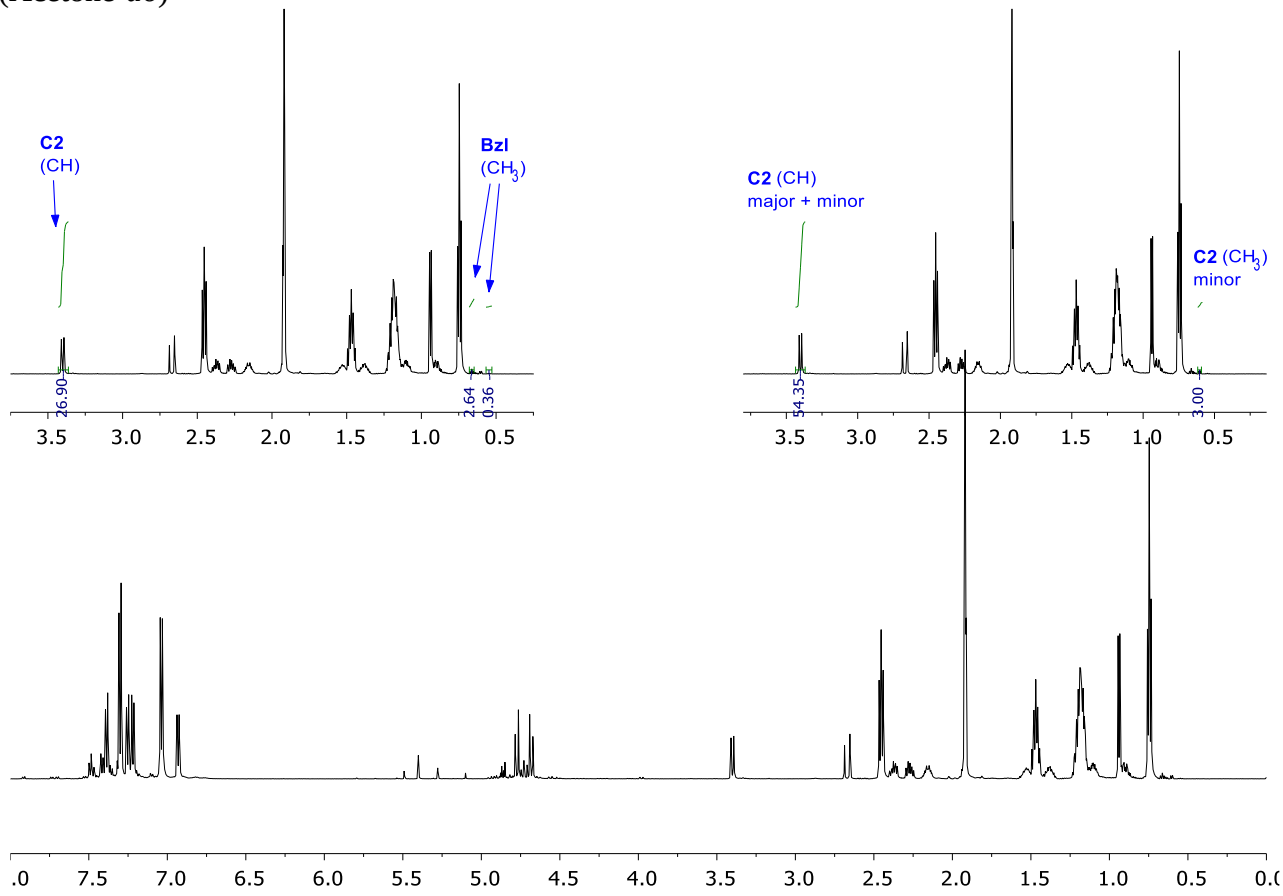

Br
CCl3
O
N2
O
Br
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
H3C
O
O
Cl3C

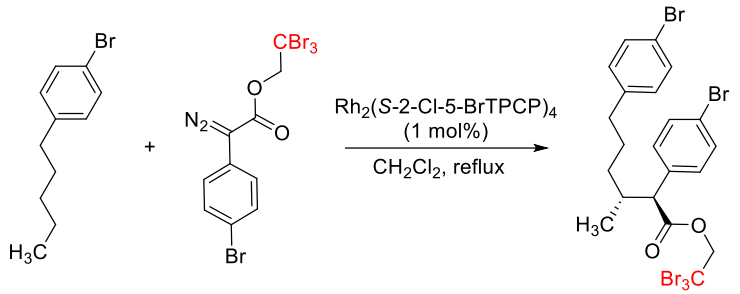
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
C2 (CH)
major + minor
C2 (CH3)
minor
20.20
2.50
0.50
21.03
3.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

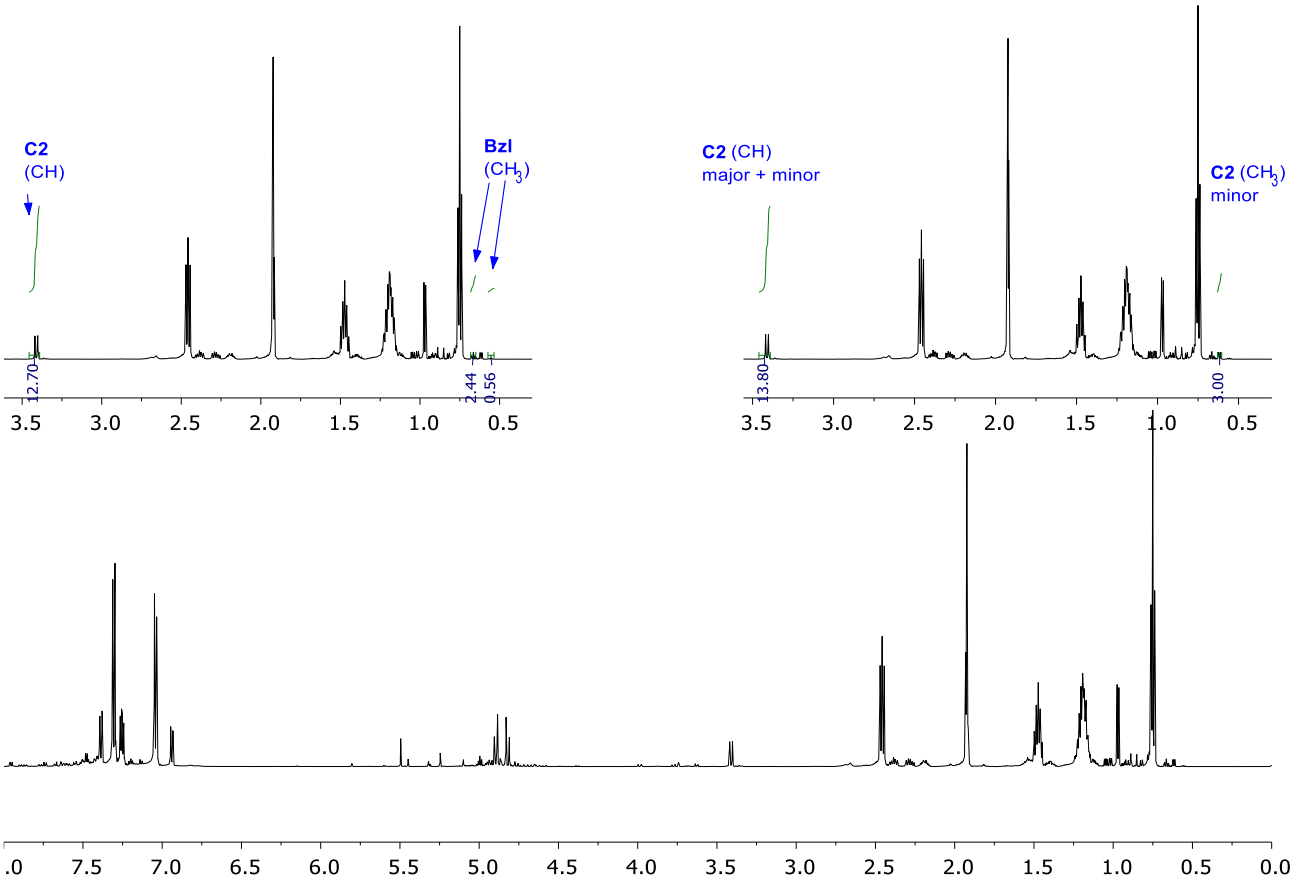

Br
CCl3
O
N2
O
Br
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, 0 °C
Br
Br
H3C
O
O
Cl3C

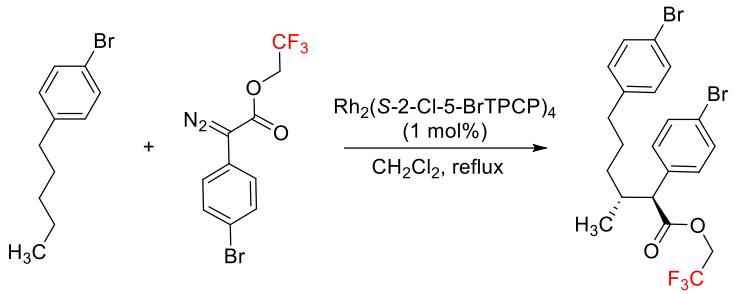
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
C2 (CH)
major + minor
C2 (CH3)
minor
26.90
2.64
0.36
54.35
3.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0

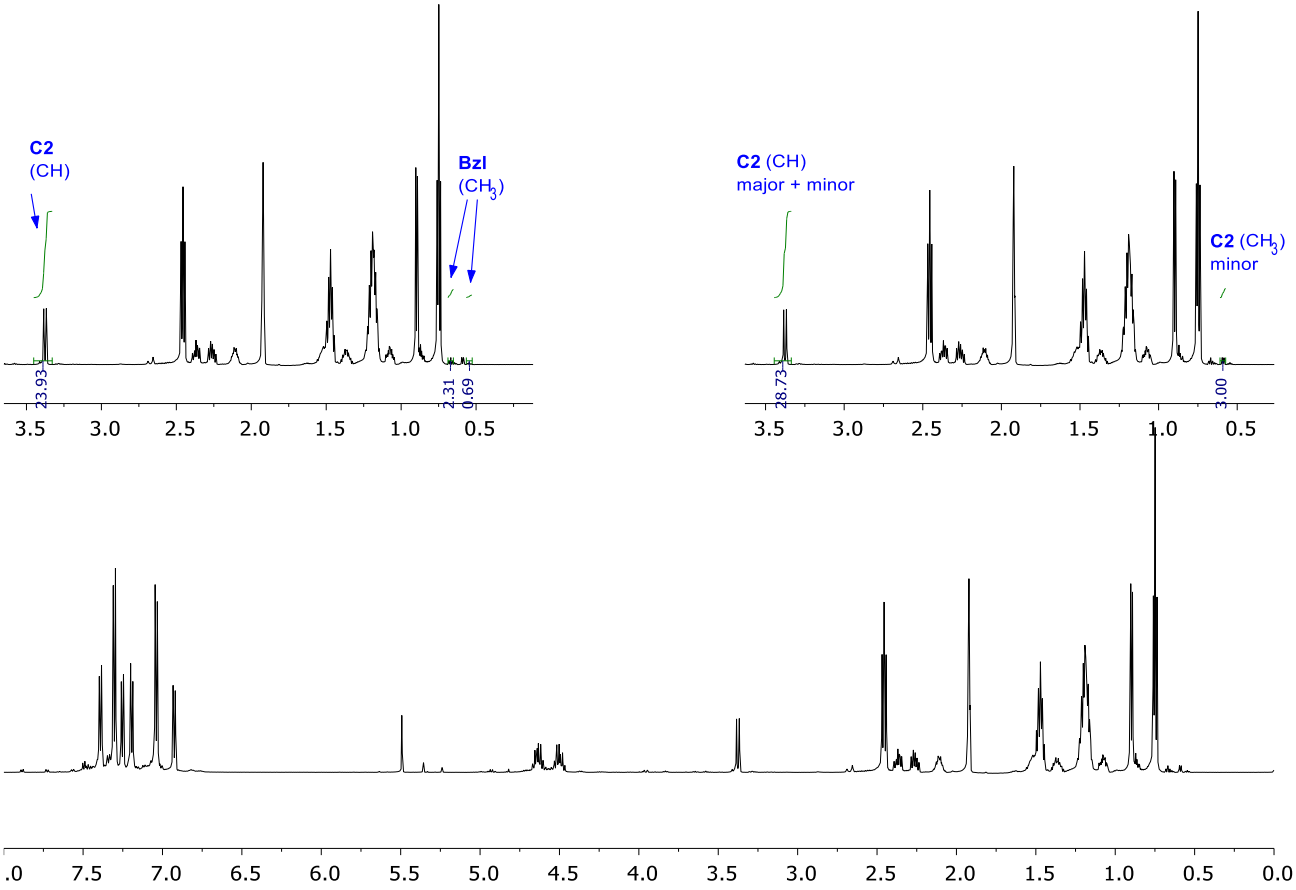

Br
CBr3
O
N2
O
Br
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
H3C
O
O
Br3C

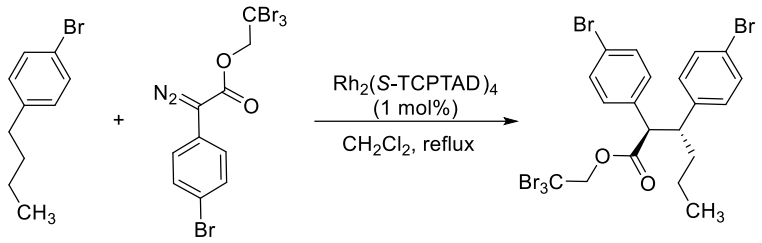
(Acetone-*d6*)


C2
(CH)
BzI
(CH3)
12.70
2.44
0.56
C2 (CH)
major + minor
C2 (CH3)
minor
13.80
3.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

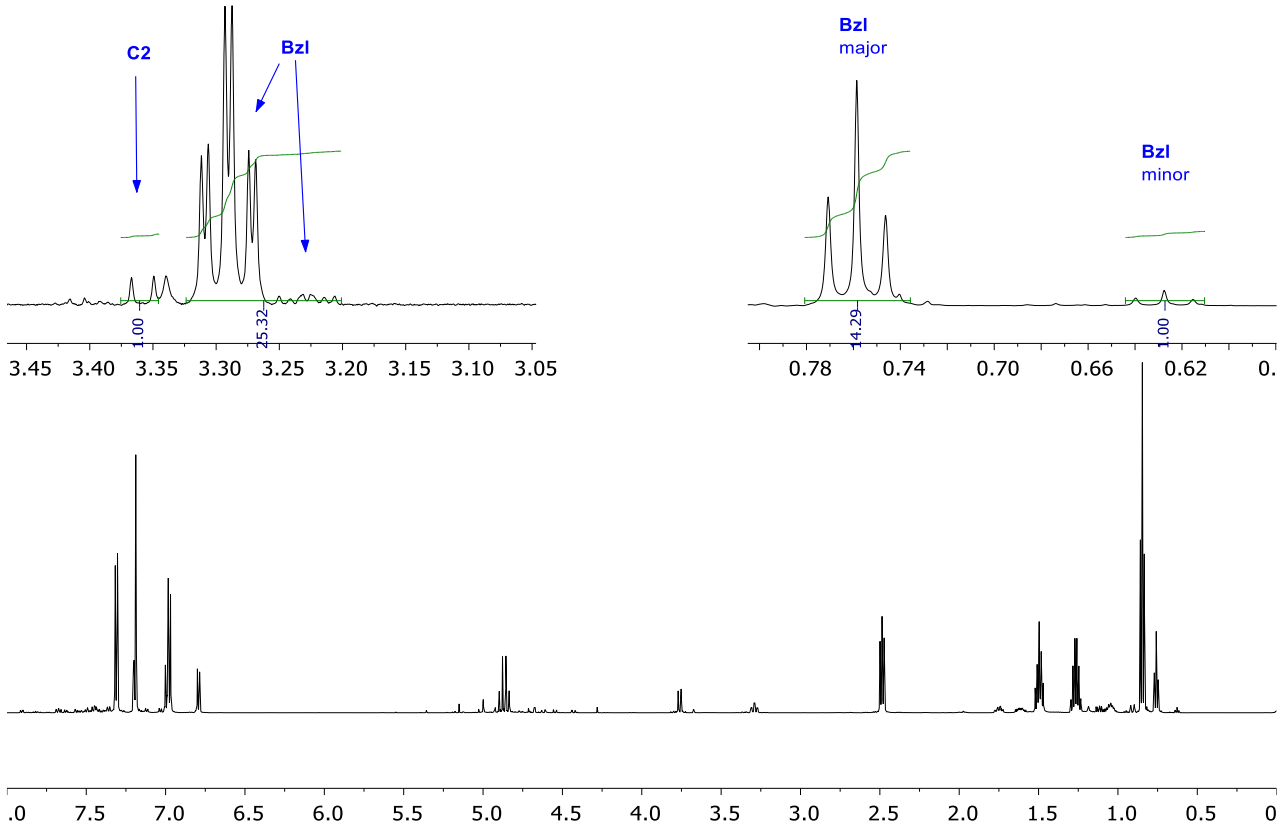

Br
CF3
O
N2
O
Br
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
H3C
O
O
F3C

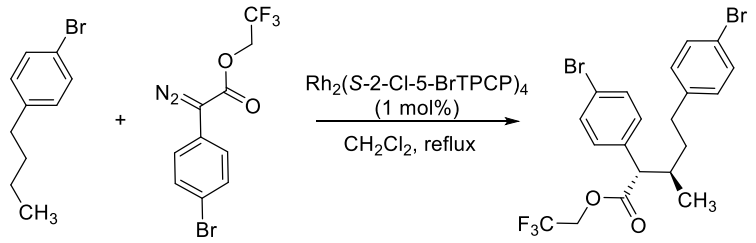
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
C2 (CH)
major + minor
C2 (CH3)
minor
23.93
2.31
0.69
28.73
3.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

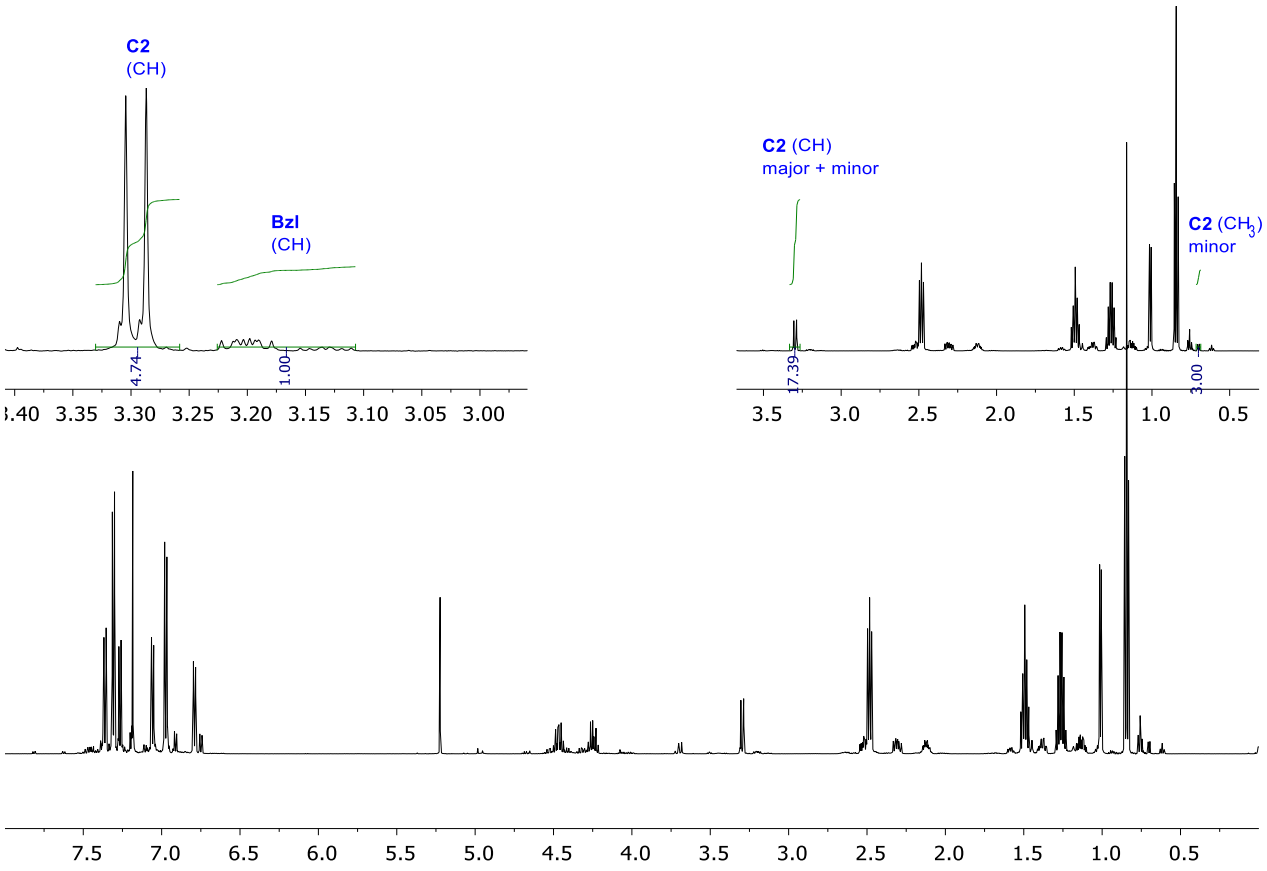


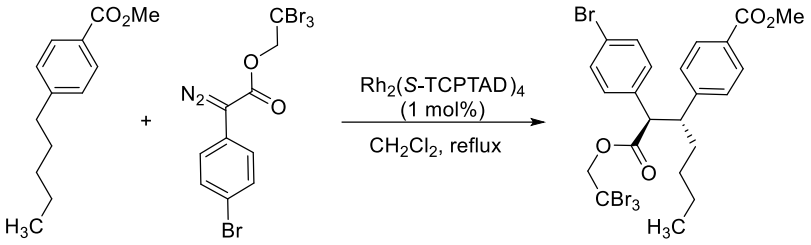
(Chloroform-*d*)



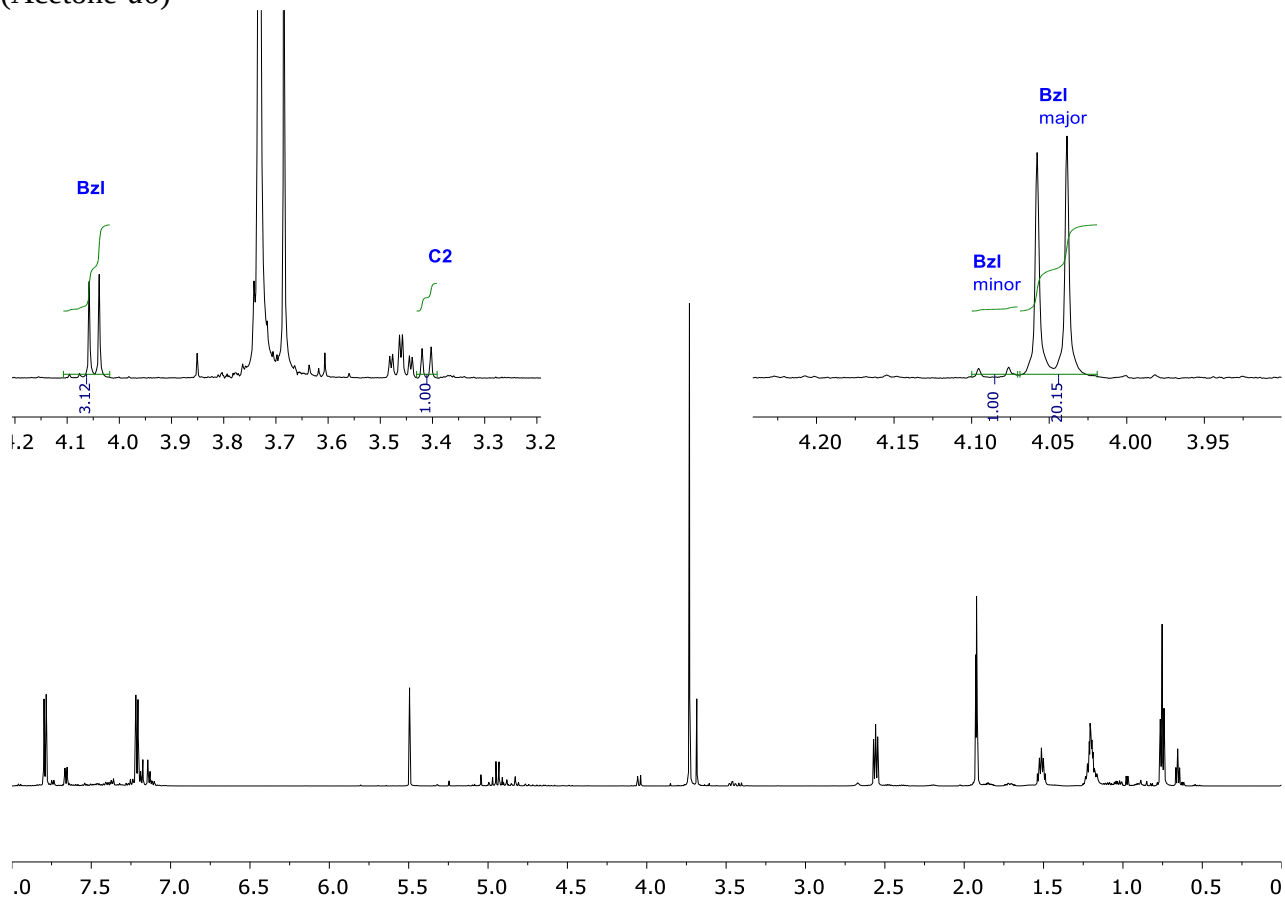


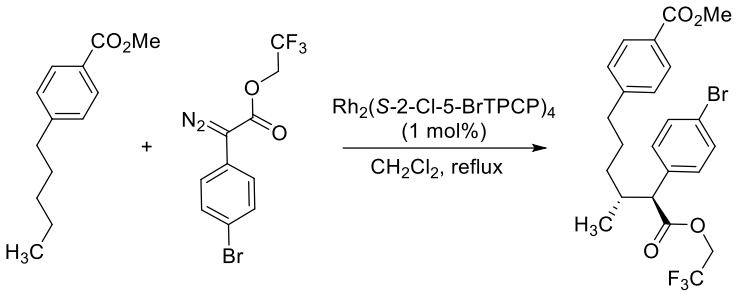
(Chloroform-*d*)



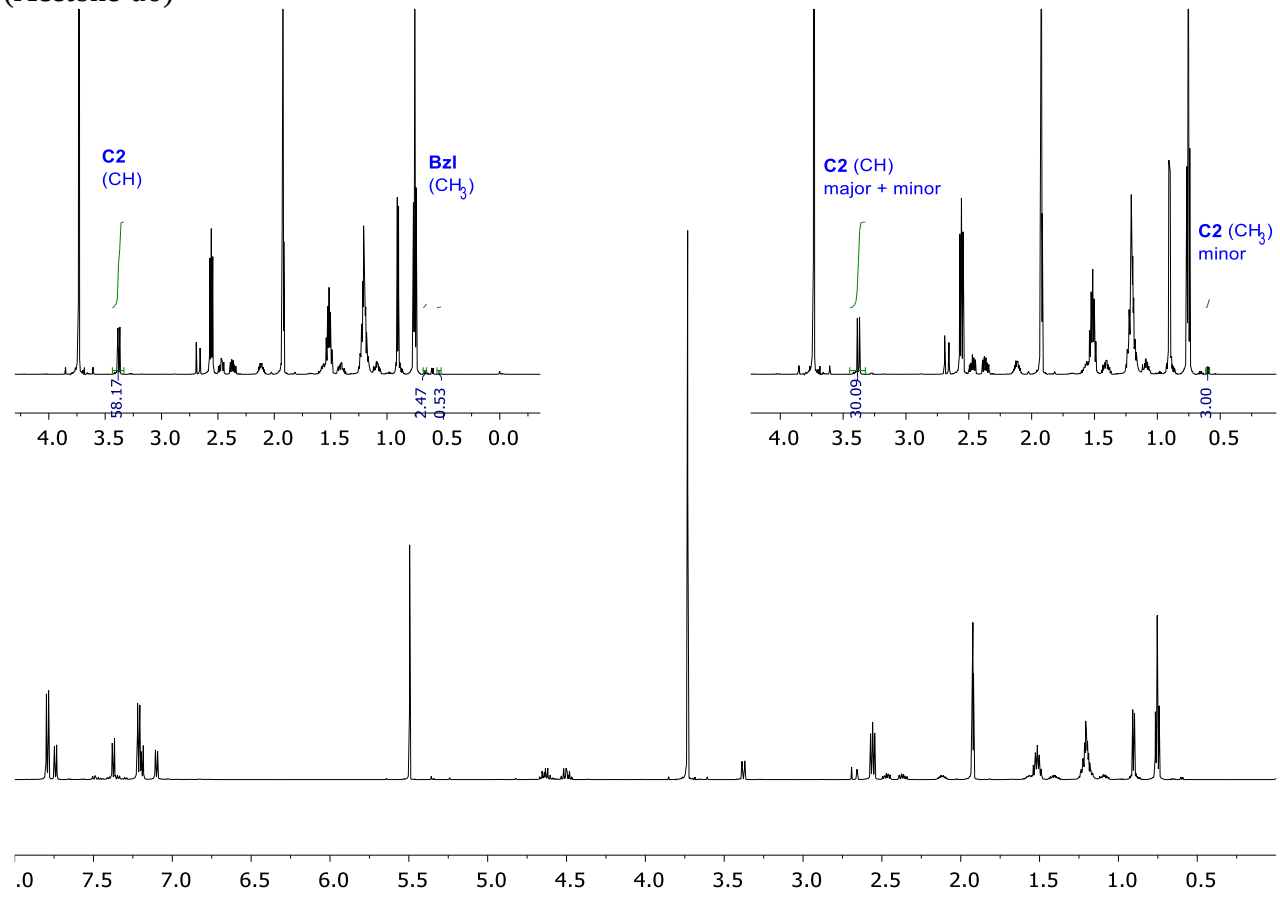

CO2Me
CBr3
N2
O
O
Br
H3C
Rh2(S-TCPTAD)4
(1 mol%)
CH2Cl2, reflux
Br
CO2Me
O
O
CBr3
H3C

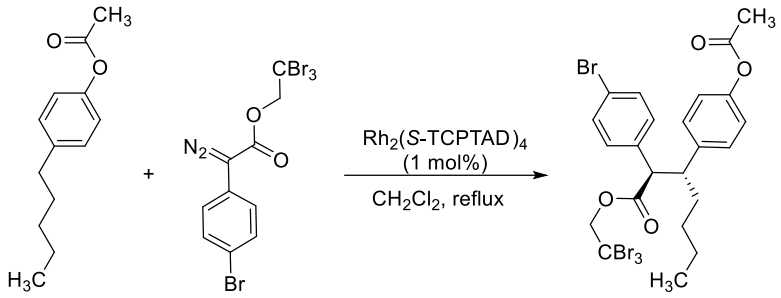
(Acetone-*d6*)


Bzl
C2
3.12
1.00
Bzl
major
Bzl
minor
1.00
20.15
4.20
4.15
4.10
4.05
4.00
3.95
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

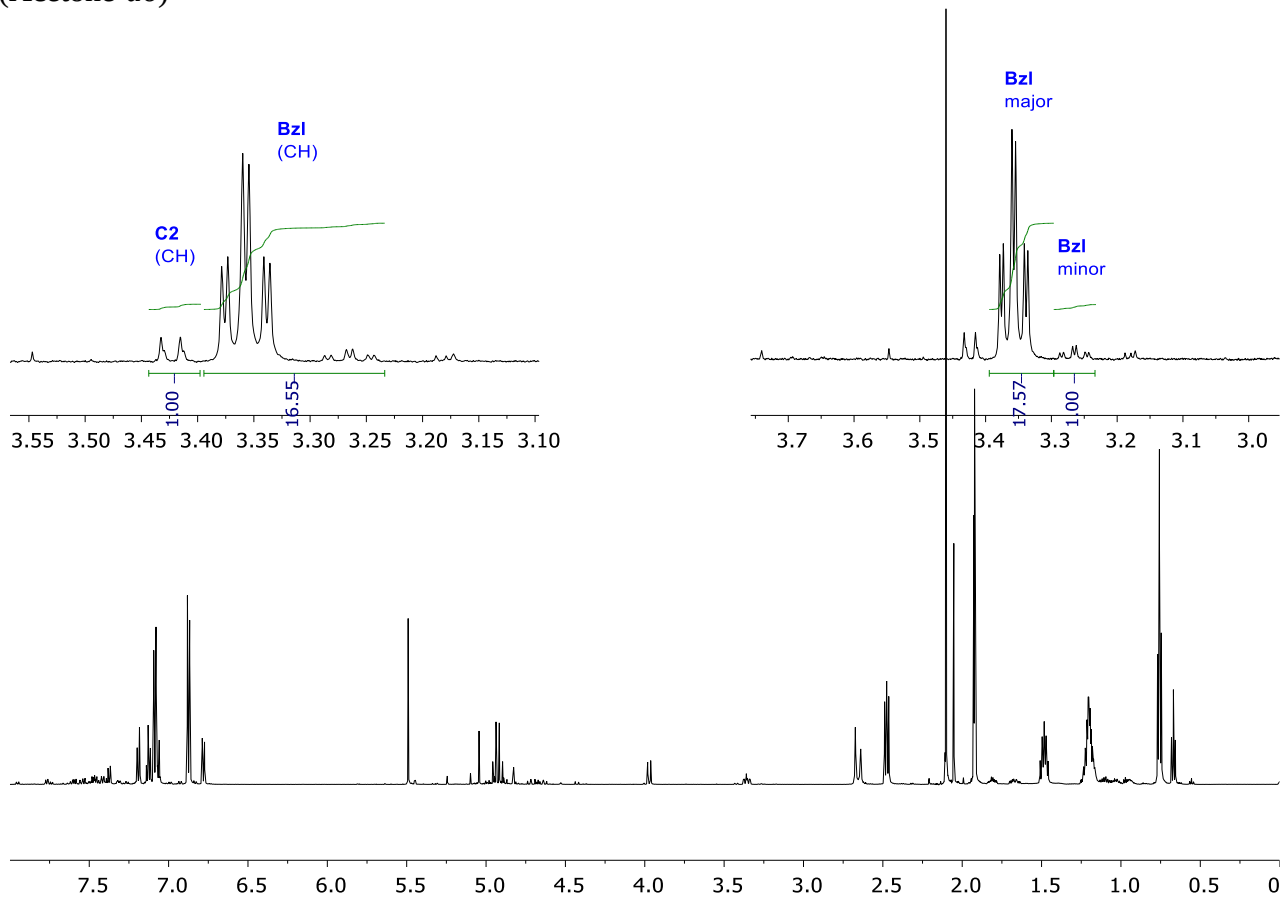

CO2Me
CF3
O
N2
O
H3C
Br
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
CO2Me
Br
H3C
O
O
F3C

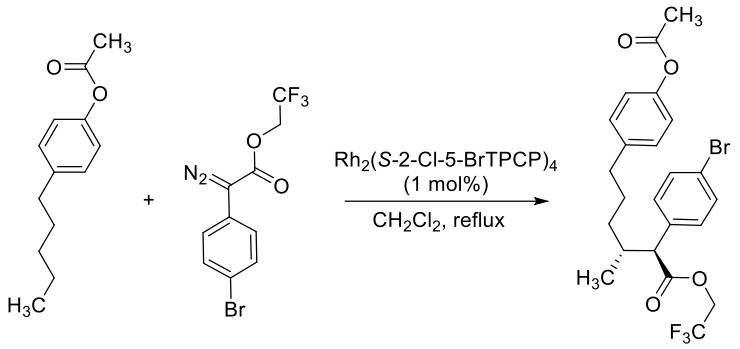
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
58.17
2.47
0.53
C2 (CH)
major + minor
C2 (CH3)
minor
30.09
3.00

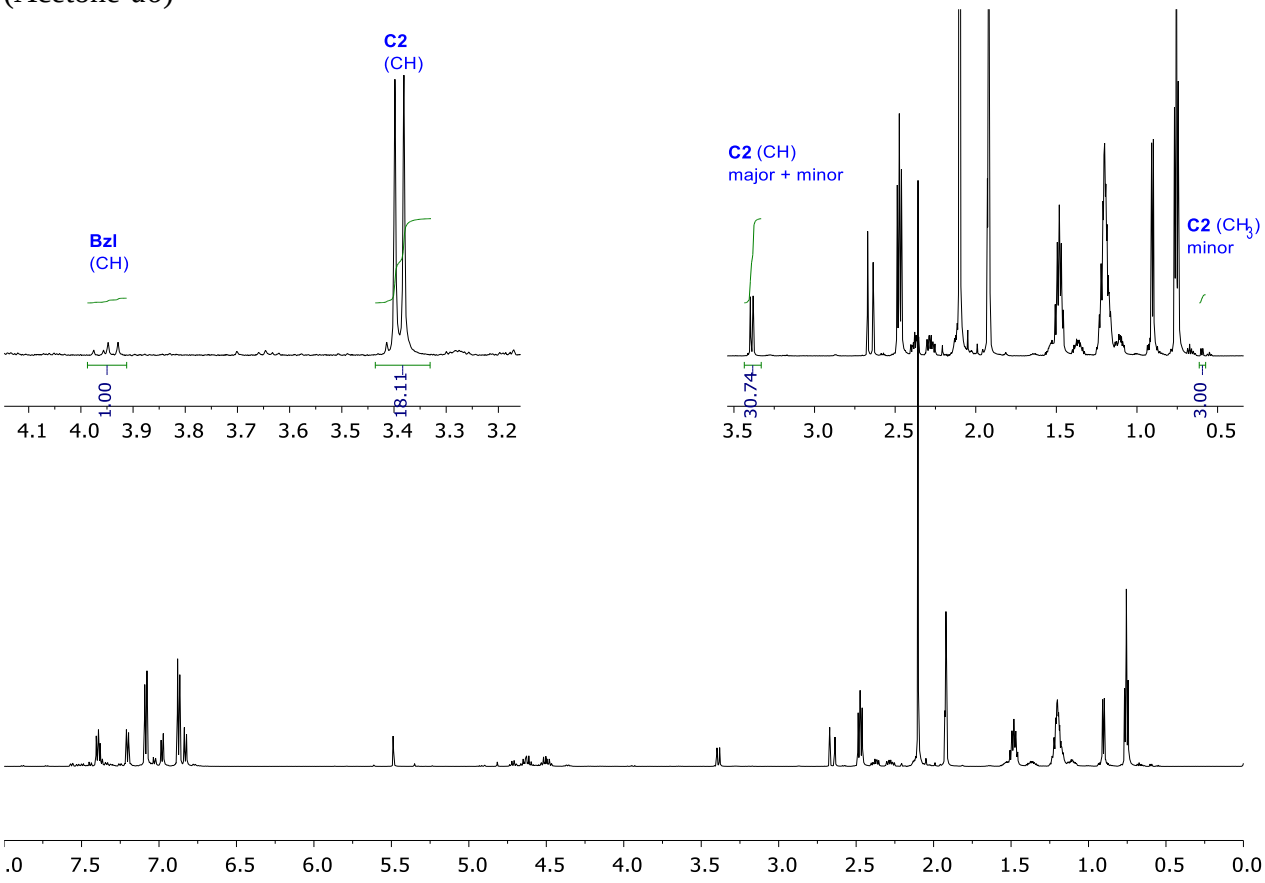

CH3
O
O
H3C
CBr3
O
N2
O
Br
Rh2(S-TCPTAD)4
(1 mol%)
CH2Cl2, reflux
Br
CH3
O
O
O
O
CBr3
H3C

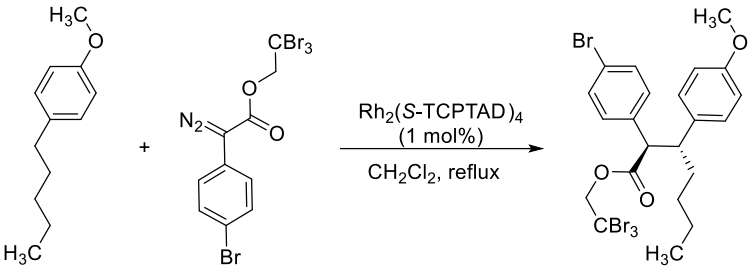
(Acetone-*d6*)


Bzl
(CH)
C2
(CH)
1.00
16.55
Bzl
major
Bzl
minor
17.57
1.00
3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

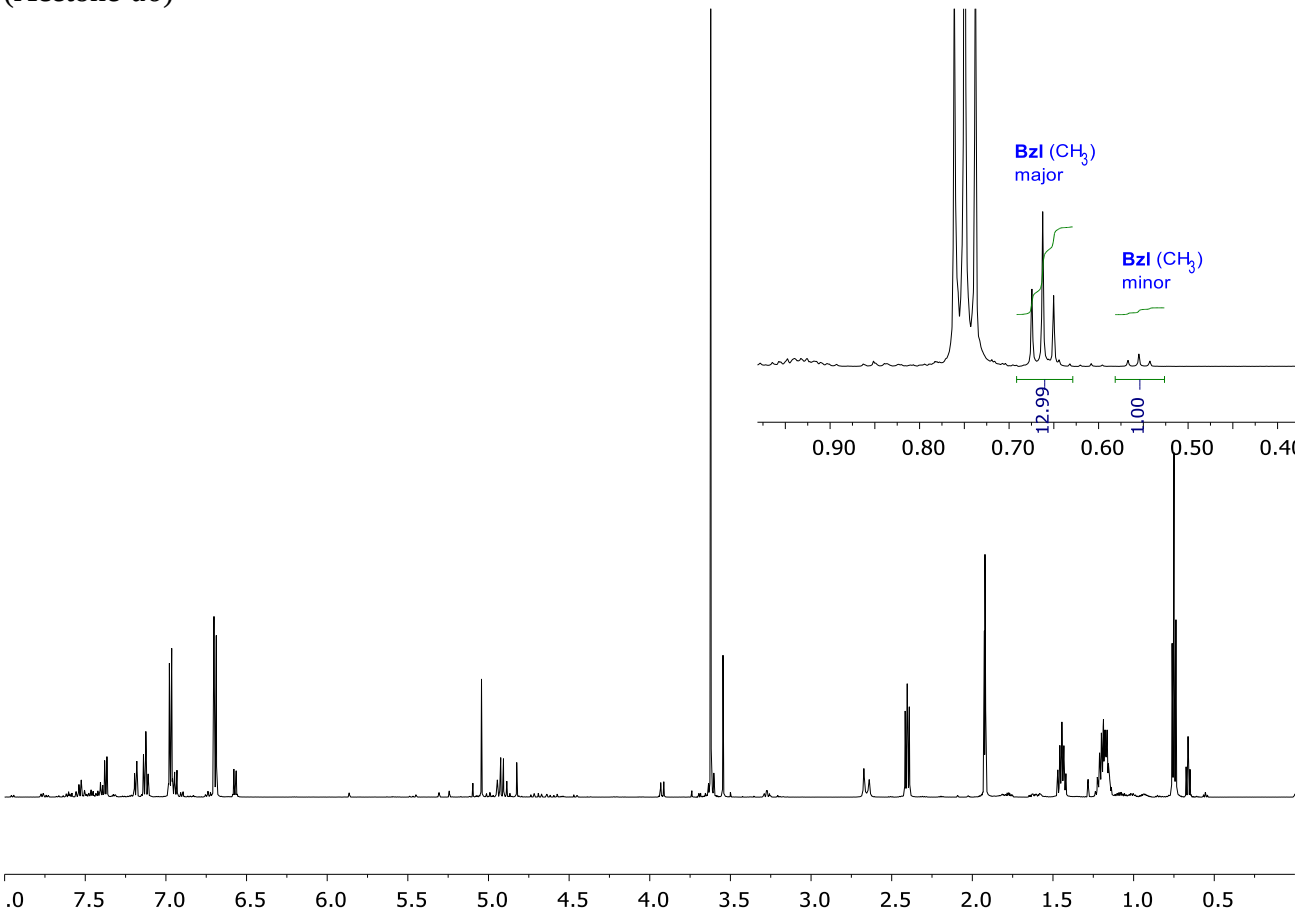

CH3
O
O
H3C
CF3
O
N2
O
Br
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
CH3
O
O
Br
H3C
O
O
F3C

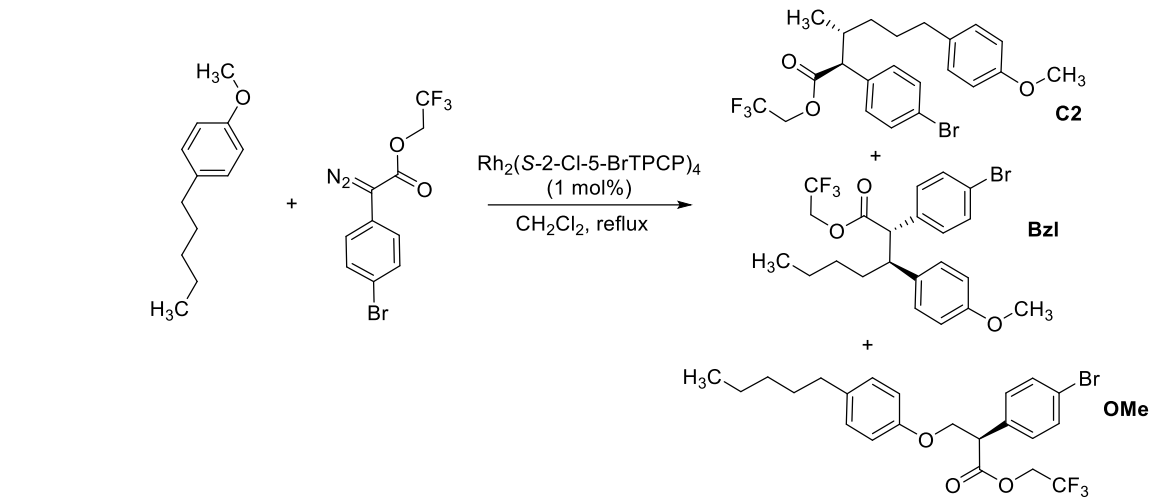
(Acetone-*d6*)


C2
(CH)
Bzl
(CH)
C2 (CH)
major + minor
C2 (CH3)
minor
1.00
18.11
30.74
3.00
4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2
3.5 3.0 2.5 2.0 1.5 1.0 0.5
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

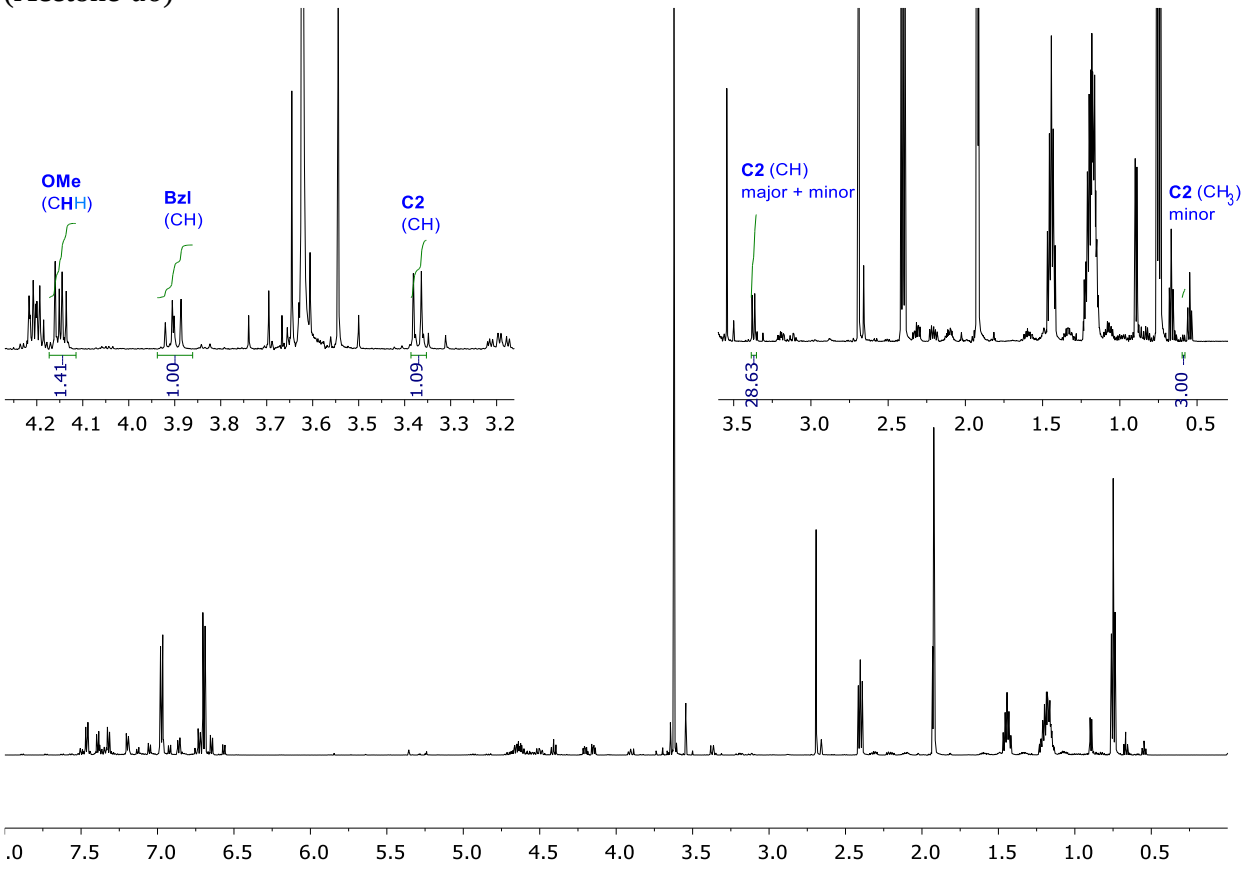

H3C
O
H3C
+
N2
CBr3
O
O
Br
Rh2(S-TCPTAD)4
(1 mol%)
CH2Cl2, reflux
Br
H3C
O
O
O
CBr3
H3C

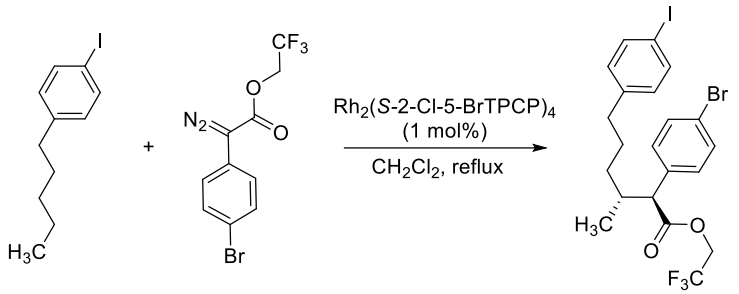
(Acetone-*d6*)


Bzl (CH3)
major
Bzl (CH3)
minor
12.99
1.00
0.90
0.80
0.70
0.60
0.50
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

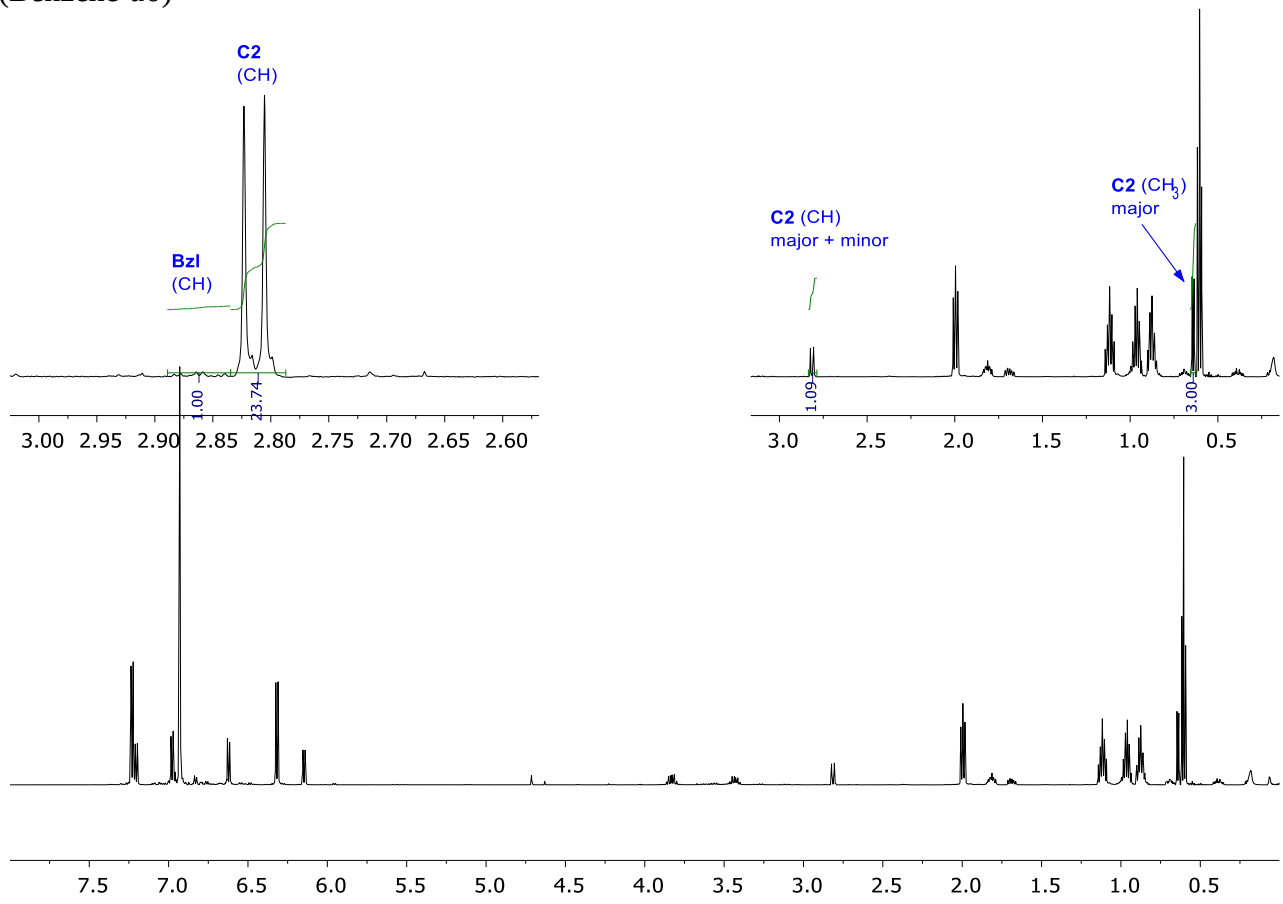

Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
C2
BzI
OMe

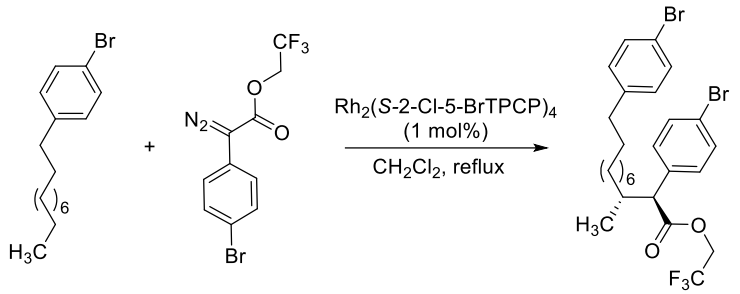
(Acetone-*d6*)


OMe
(CHH)
BzI
(CH)
C2
(CH)
C2 (CH)
major + minor
C2 (CH3)
minor
1.41
1.00
1.09
28.63
3.00

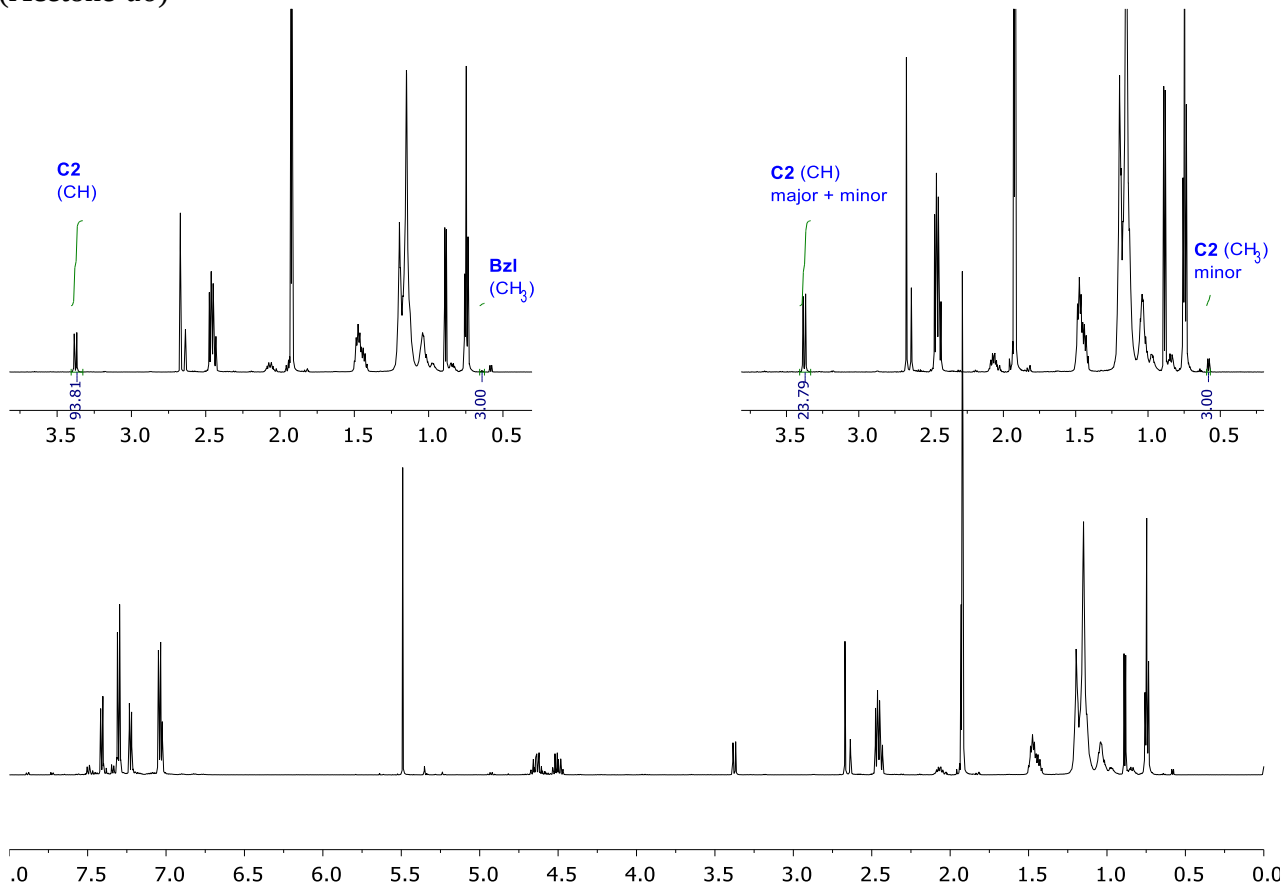

I
H3C
+
CF3
O
N2
O
Br
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
I
Br
H3C
O
O
F3C

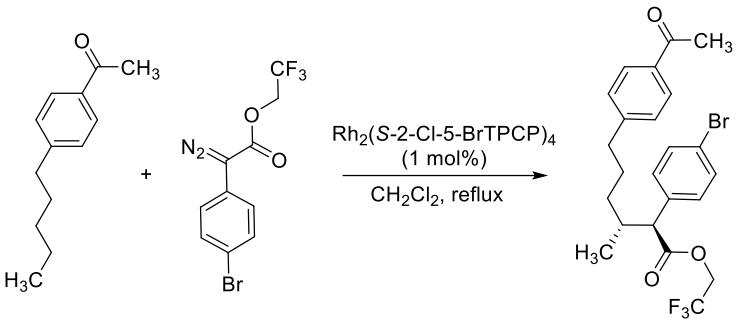
(Benzene-*d6*)


C2
(CH)
Bzl
(CH)
1.00
23.74
3.00 2.95 2.90 2.85 2.80 2.75 2.70 2.65 2.60
C2 (CH)
major + minor
C2 (CH3)
major
1.09
3.00
3.0 2.5 2.0 1.5 1.0 0.5
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

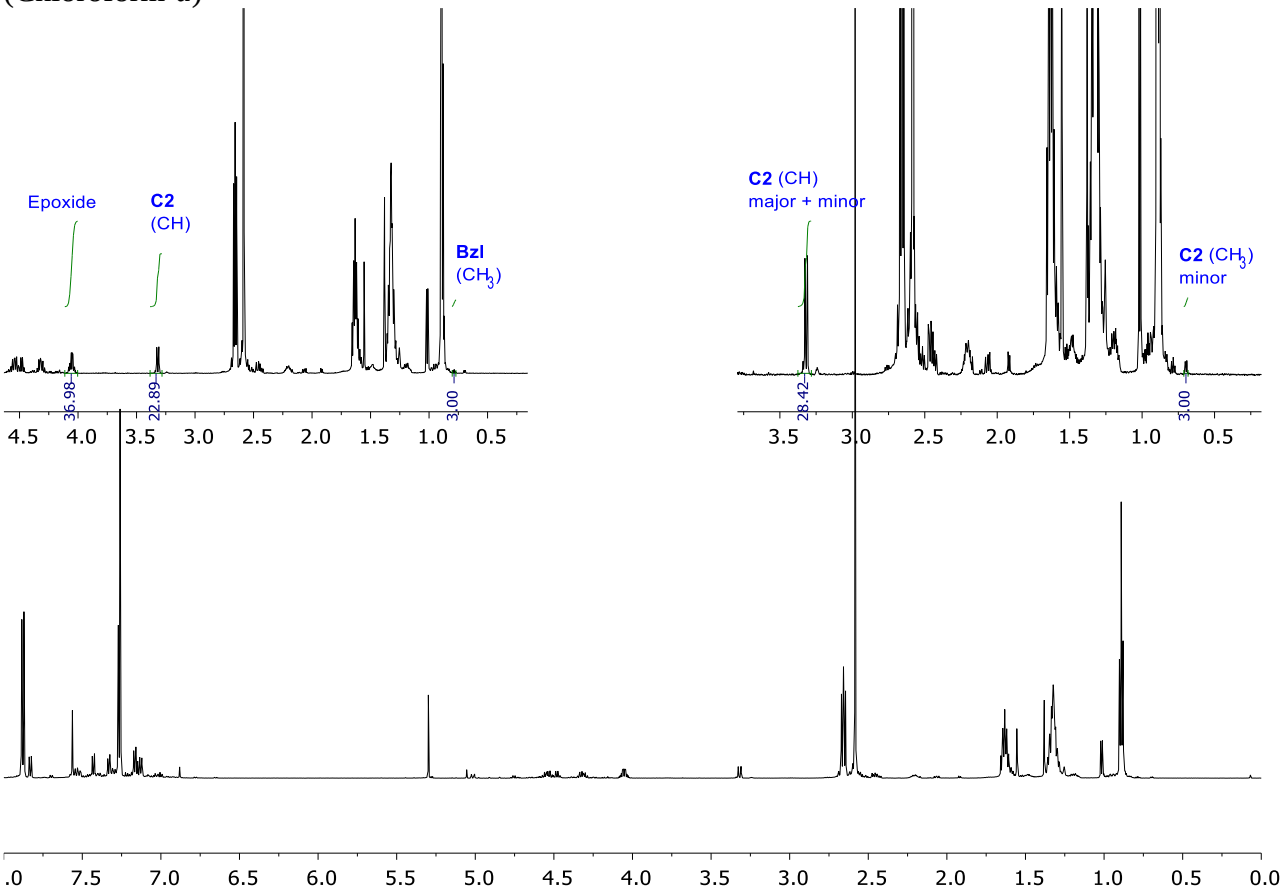

Br
CF3
O
N2
O
Br
6
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Br
6
H3C
O
O
F3C

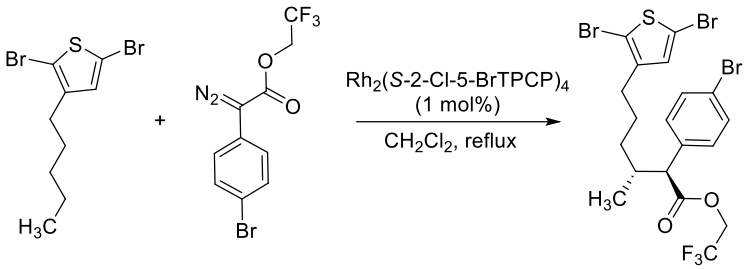
(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
93.81
3.00
C2 (CH)
major + minor
C2 (CH3)
minor
23.79
3.00

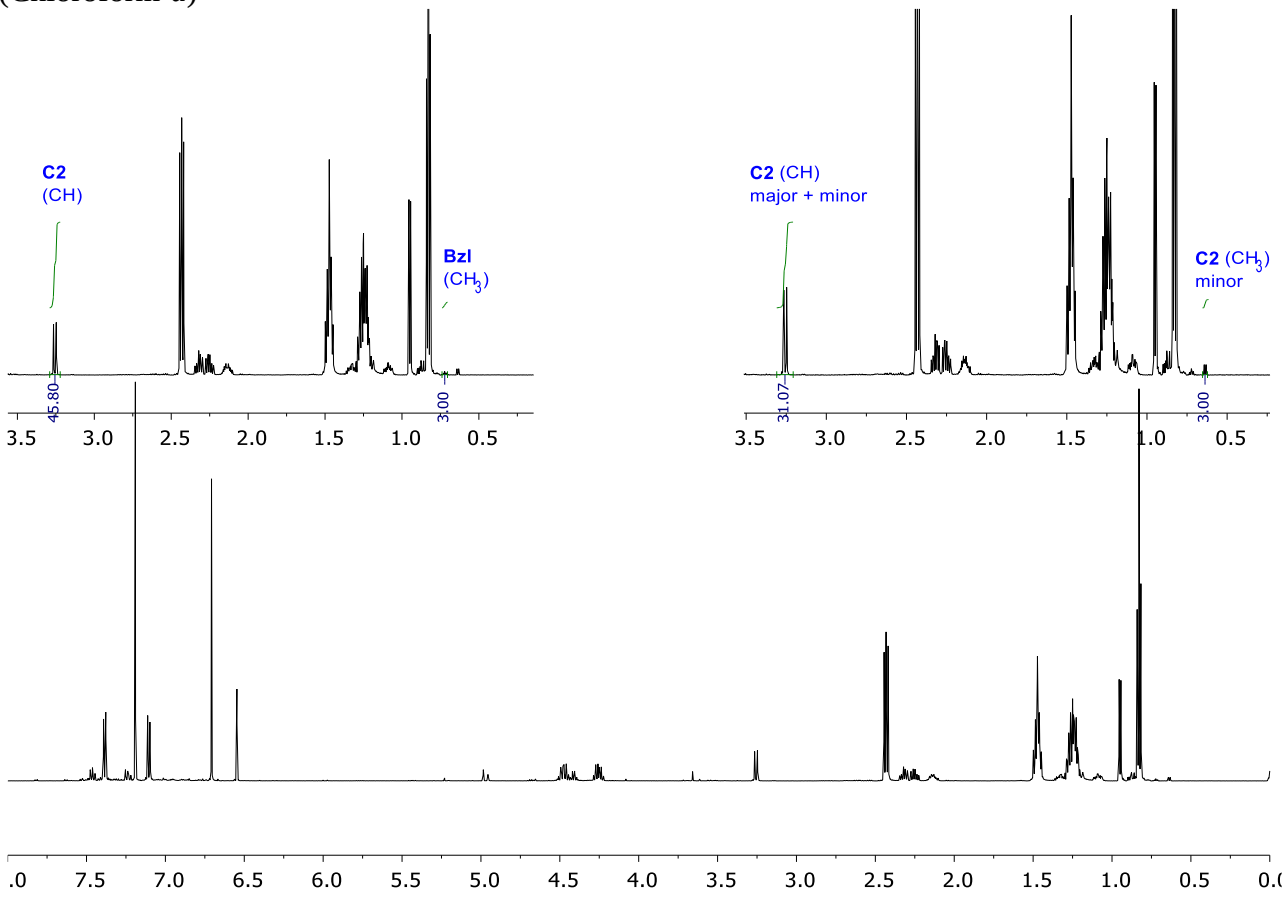


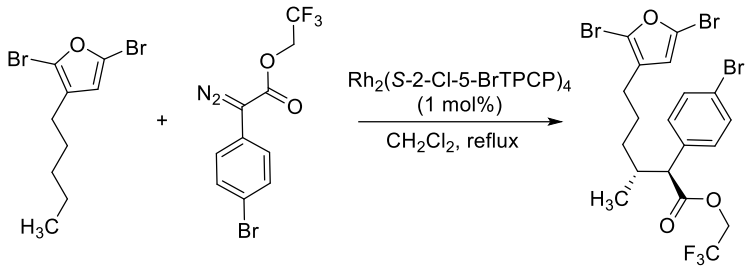
(Chloroform-*d*)



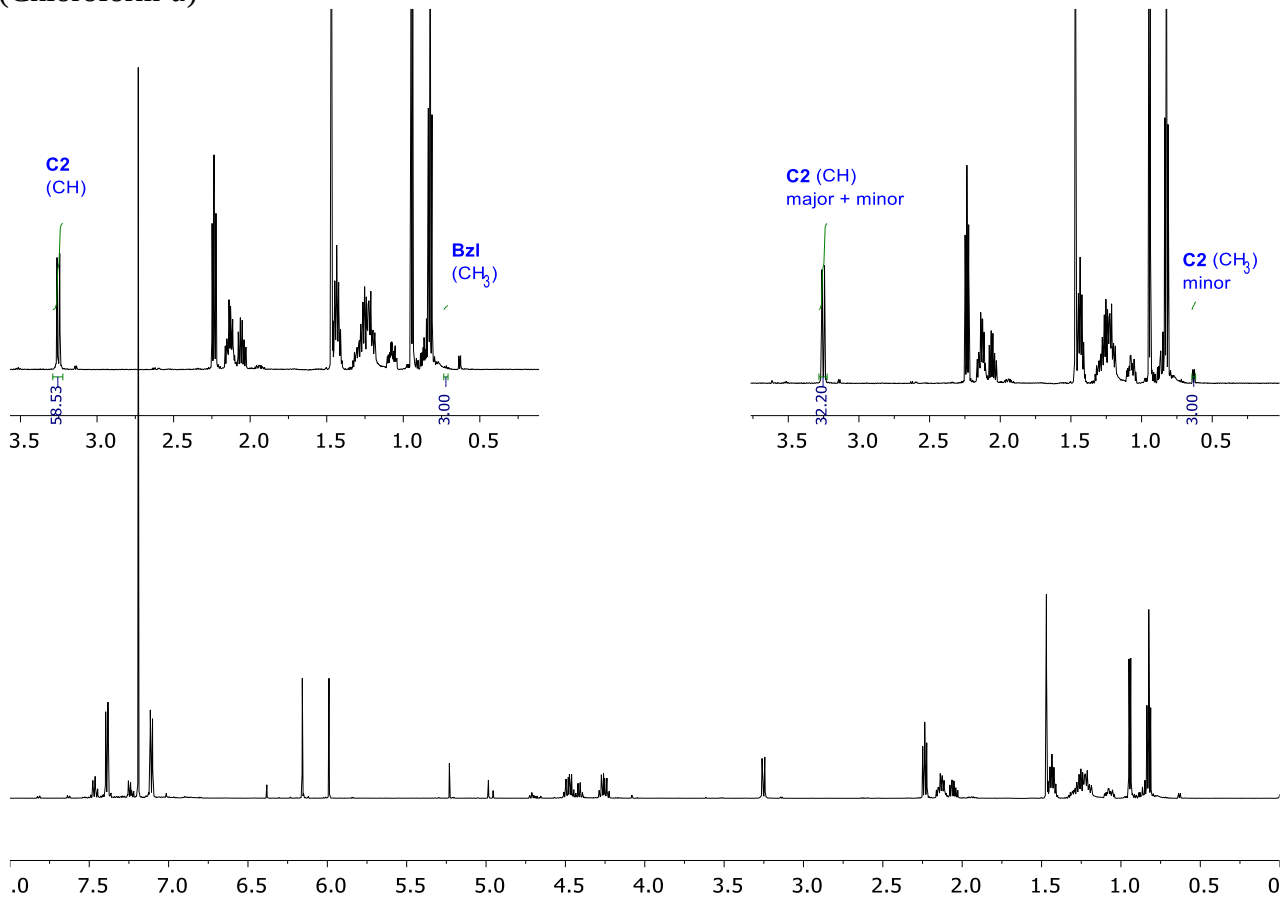


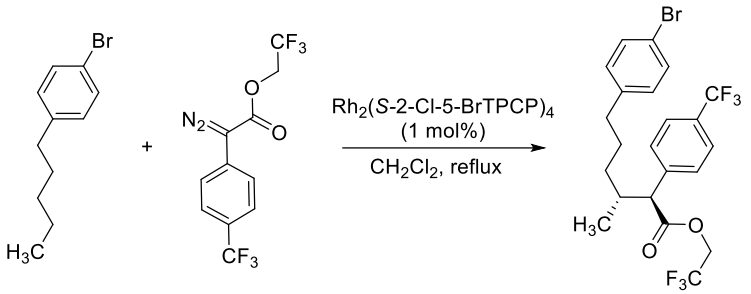
(Chloroform-*d*)



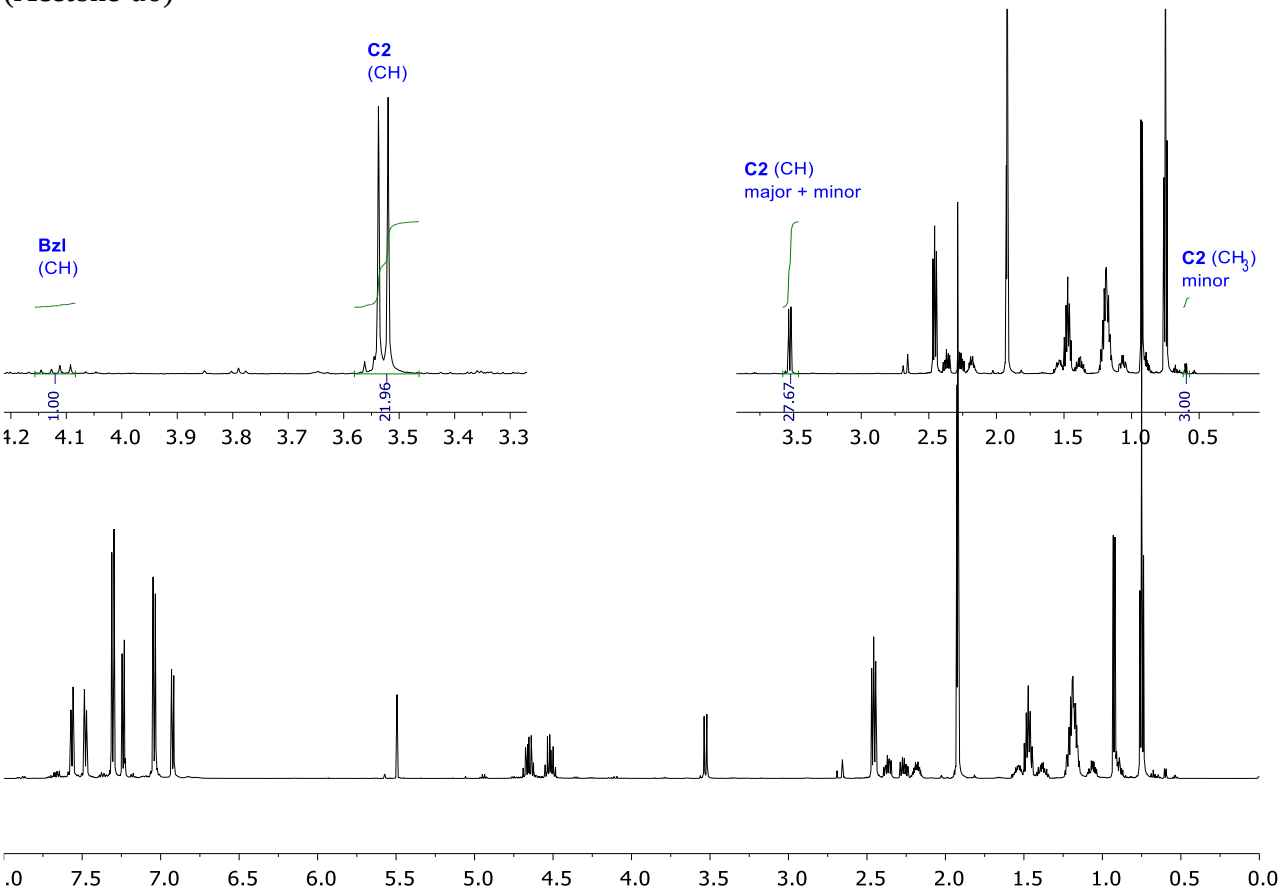


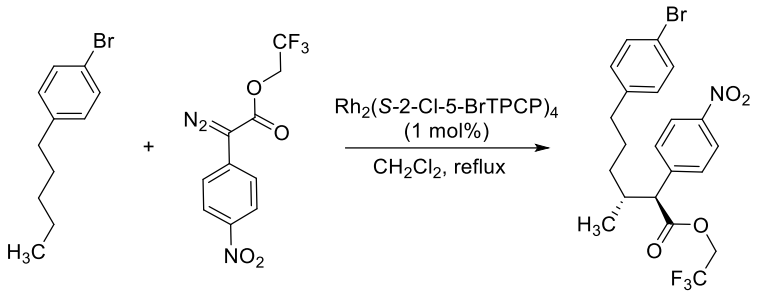
(Chloroform-*d*)



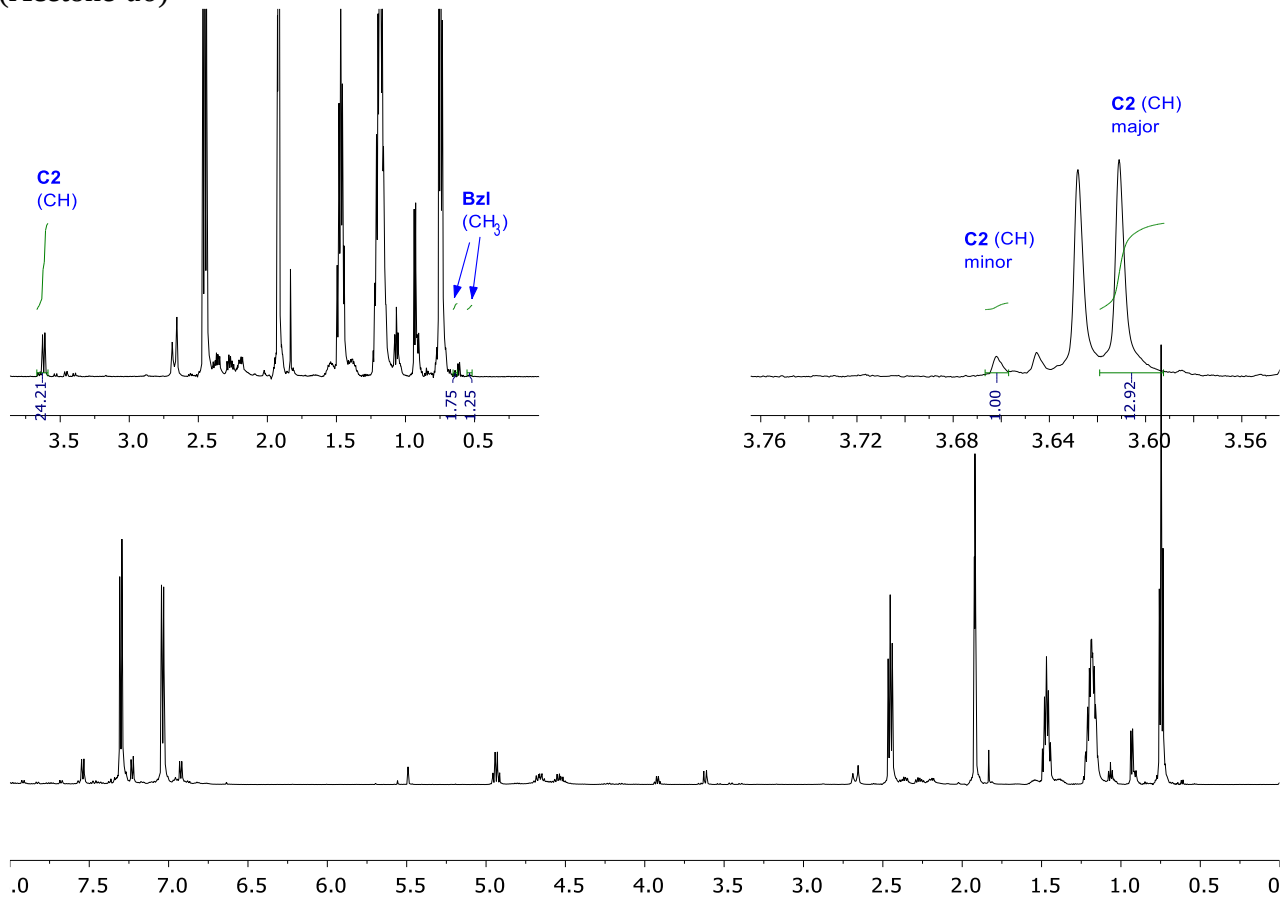

Br
CF3
O
N2
O
H3C
CF3
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
CF3
H3C
O
O
F3C

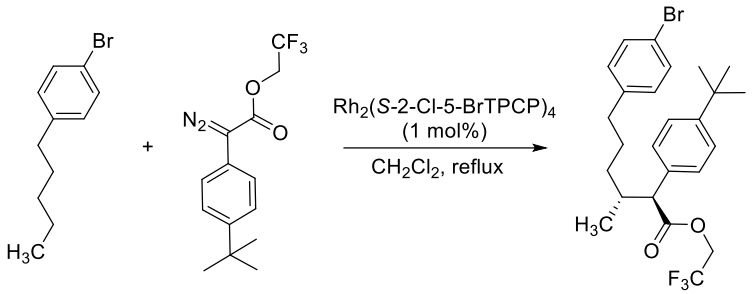
(Acetone-*d6*)


C2
(CH)
Bzl
(CH)
C2 (CH)
major + minor
C2 (CH3)
minor
1.00
21.96
27.67
3.00
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.5
3.0
2.5
2.0
1.5
1.0
0.5
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

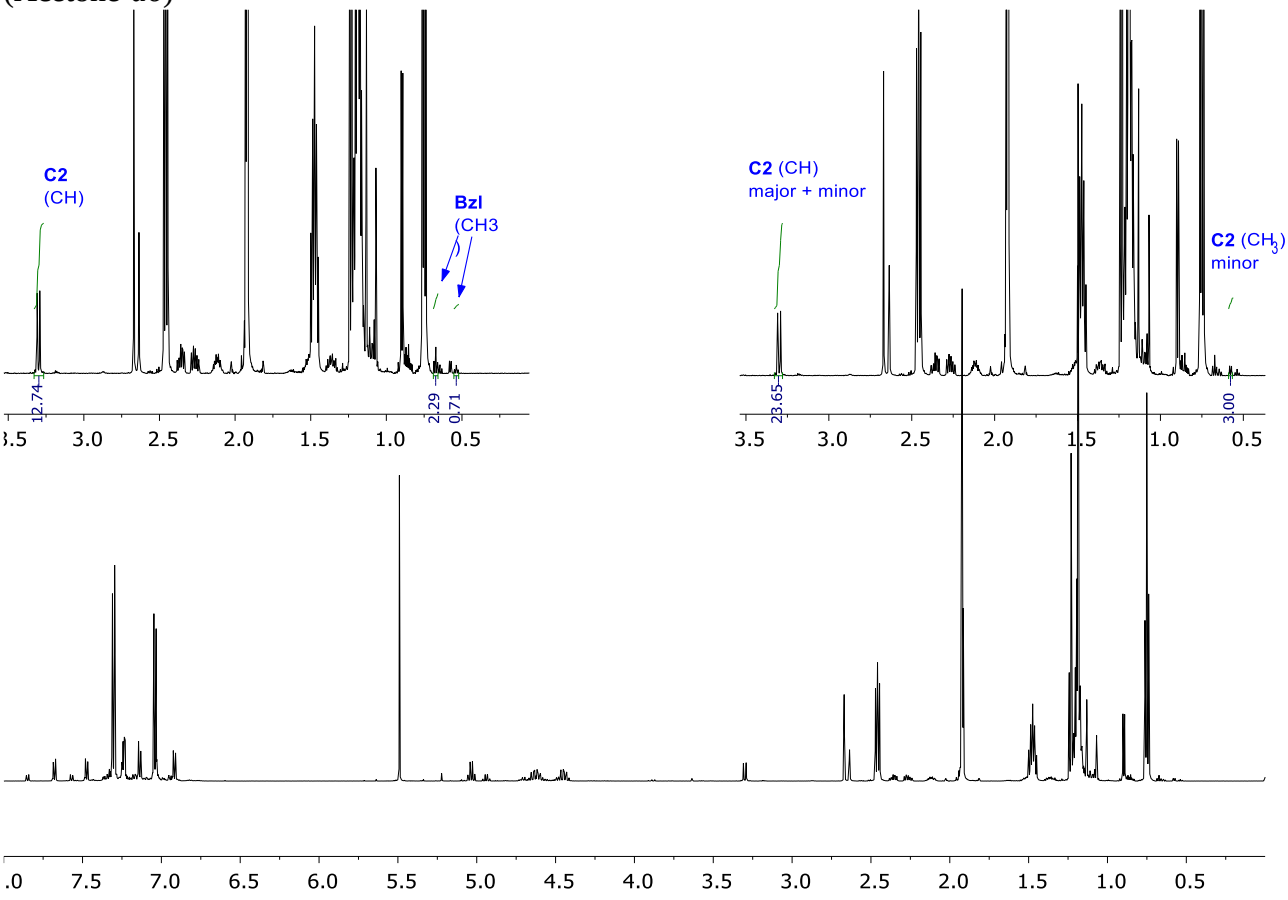

Br
CF3
O
N2
O
NO2
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
NO2
H3C
O
O
F3C

(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
C2 (CH)
major
C2 (CH)
minor
24.21
1.75
1.25
1.00
12.92
3.5
3.0
2.5
2.0
1.5
1.0
0.5
3.76
3.72
3.68
3.64
3.60
3.56
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0


Br
CF3
O
N2
O
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
H3C
O
O
F3C

(Acetone-*d6*)


C2
(CH)
Bzl
(CH3
C2 (CH)
major + minor
C2 (CH3)
minor
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2.29
0.71
23.65
3.00
3.5
3.0
2.5
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1.5
1.0
0.5
7.5
7.0
6.5
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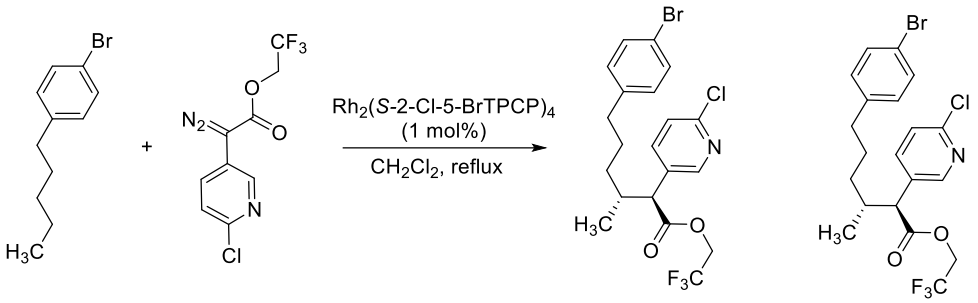
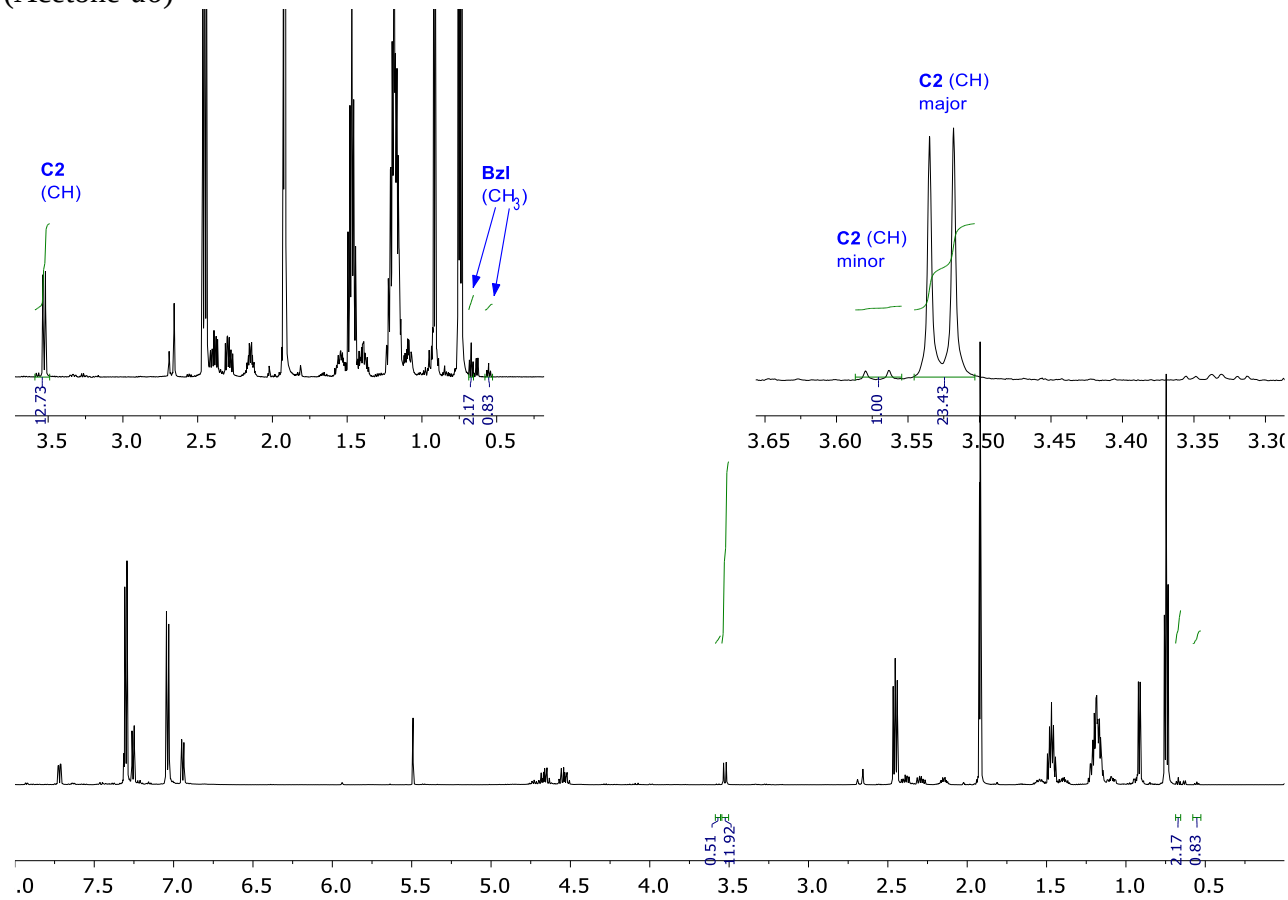
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


Br
CF3
O
N2
O
N
Cl
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Cl
N
H3C
O
O
F3C
Br
Cl
N
H3C
O
O
F3C

(Acetone-*d6*)


C2
(CH)
Bzl
(CH3)
C2 (CH)
major
C2 (CH)
minor
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2.17
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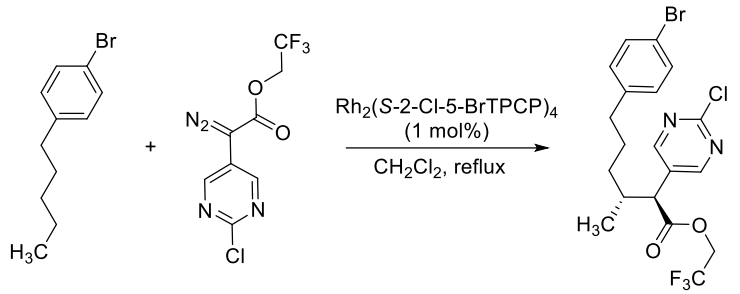
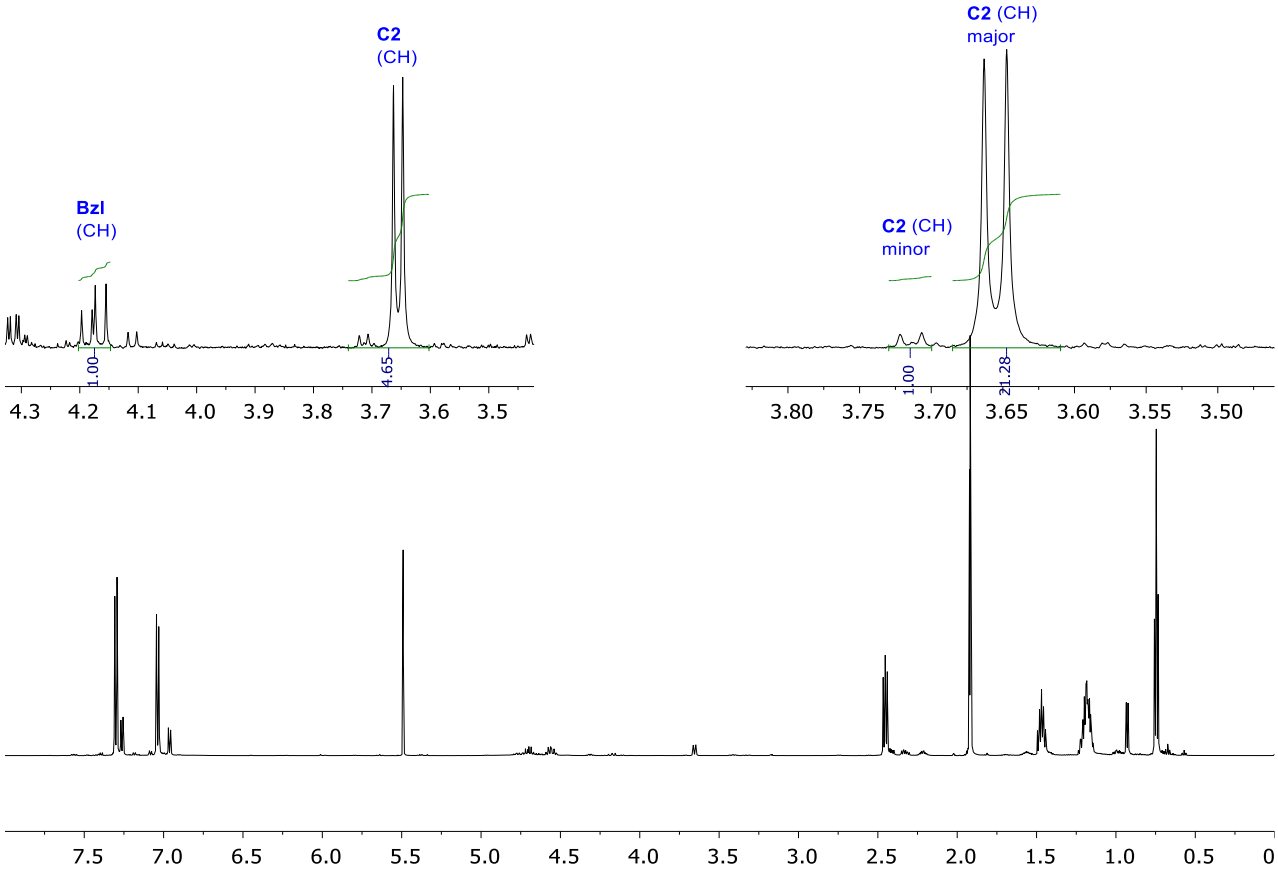
1.00
23.43
0.51
11.92
2.17
0.83


Br
CF3
O
N2
O
N
N
Cl
H3C
Rh2(S-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux
Br
Cl
N
N
H3C
O
O
F3C

(Acetone-*d6*)


C2
(CH)
Bzl
(CH)
C2 (CH)
major
C2 (CH)
minor
1.00
4.65
1.00
21.28
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.80
3.75
3.70
3.65
3.60
3.55
3.50
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
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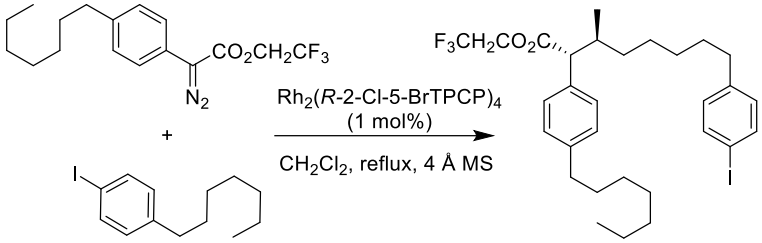
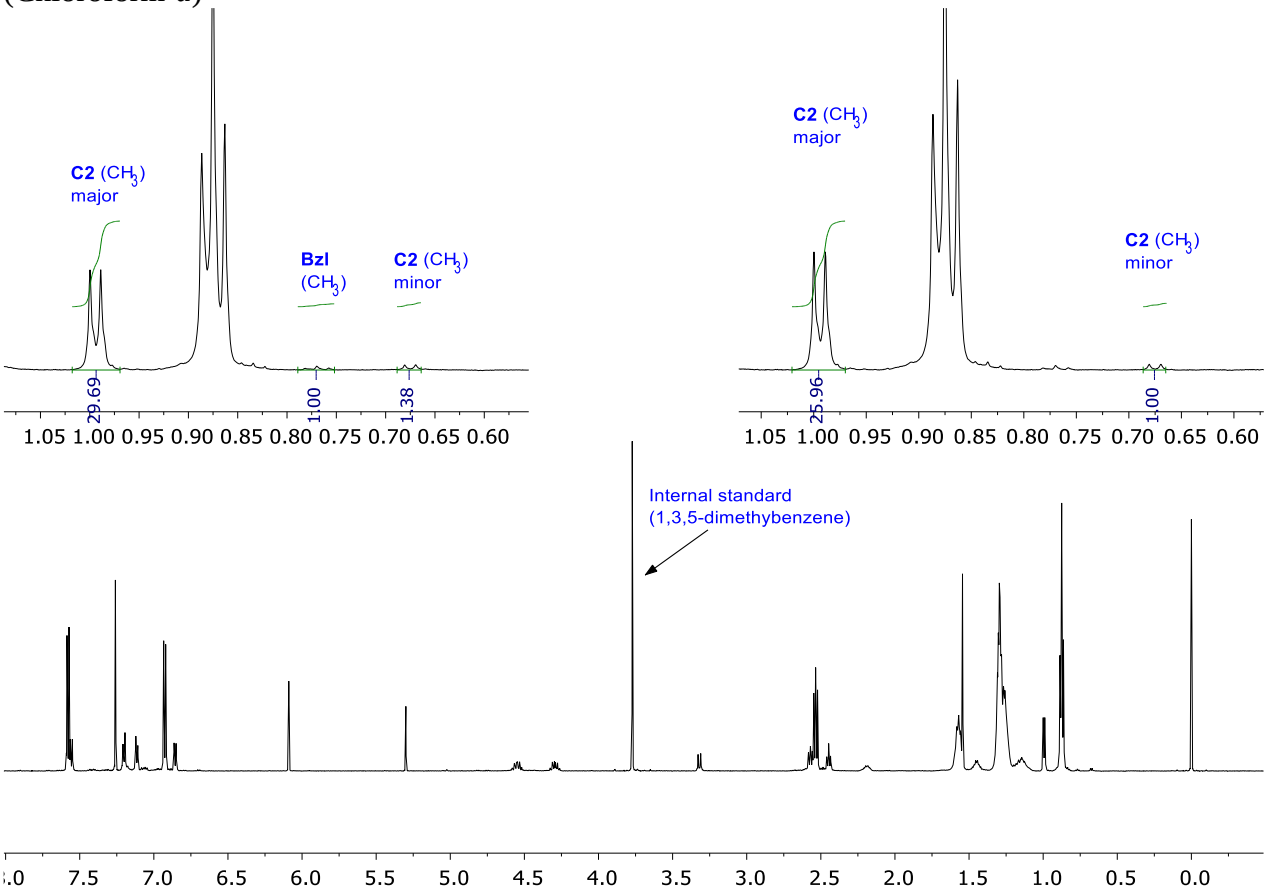
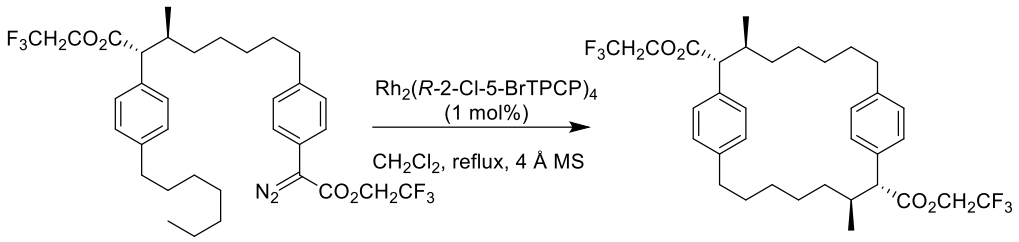
2.0
1.5
1.0
0.5
0

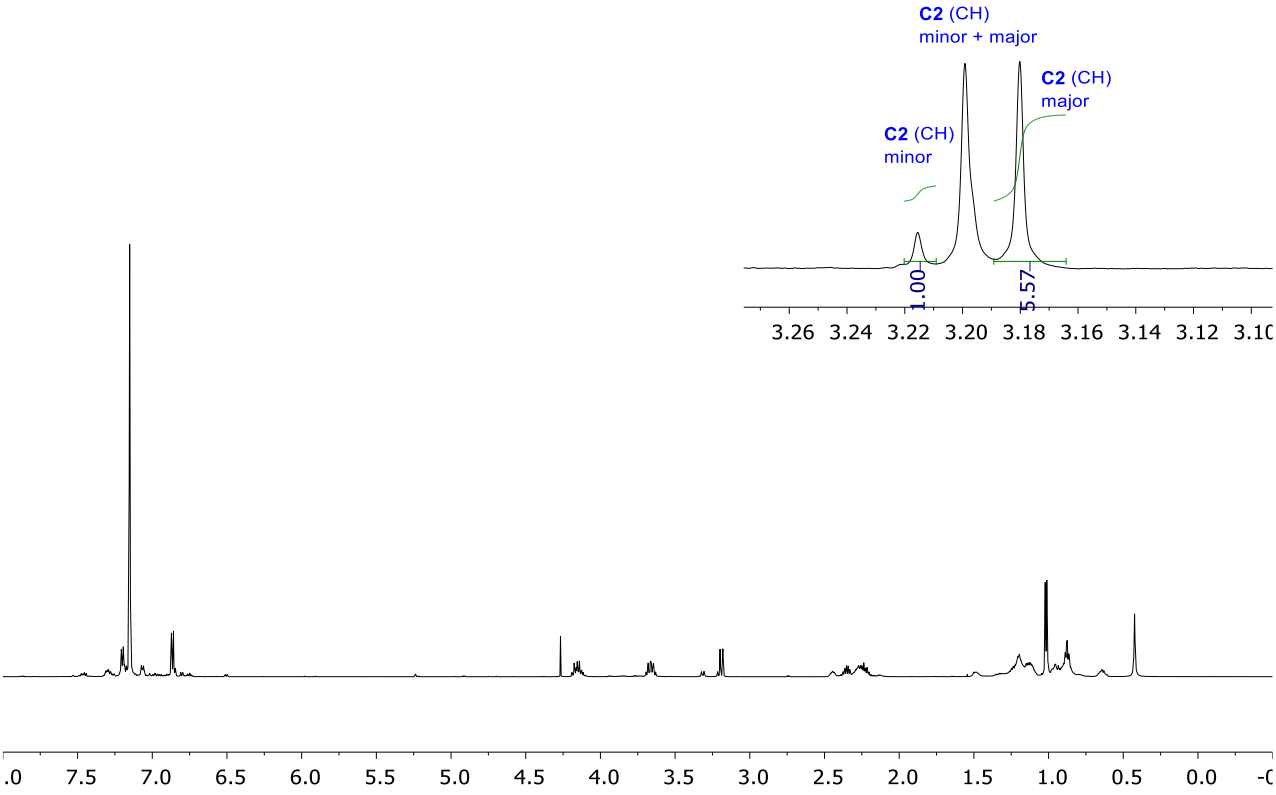


(Chloroform-*d*)

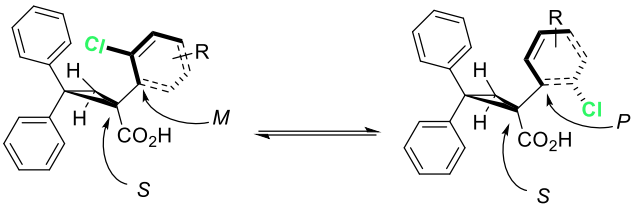



F3CH2CO2C
Rh2(R-2-Cl-5-BrTPCP)4
(1 mol%)
CH2Cl2, reflux, 4 Å MS
N2
CO2CH2CF3
F3CH2CO2C
CO2CH2CF3

(Benzene-*d6*)


C2 (CH)
minor + major
C2 (CH)
major
C2 (CH)
minor
1.00
5.57
3.26 3.24 3.22 3.20 3.18 3.16 3.14 3.12 3.10
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

6. VT-NMR for Rotational Barrier Estimation of Three Ligands



The Variable-temperature ^{1}H NMR was used for estimation of the rotational barriers of three ligands, and it was obtained using Varian INOVA-600 MHz spectrometer and analyzed using MestRenova 11.0.4.

Solvent: $CDCl_3$ (with TMS as reference at 0 ppm)

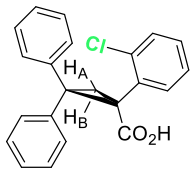
Number of scans: 64

Temperature measurement: Temperature of the probe.

Spectra were taken after the samples spin for 15 mins under that temperature.

Spectra:

(a) *S*-*o*-ClTPCP



31

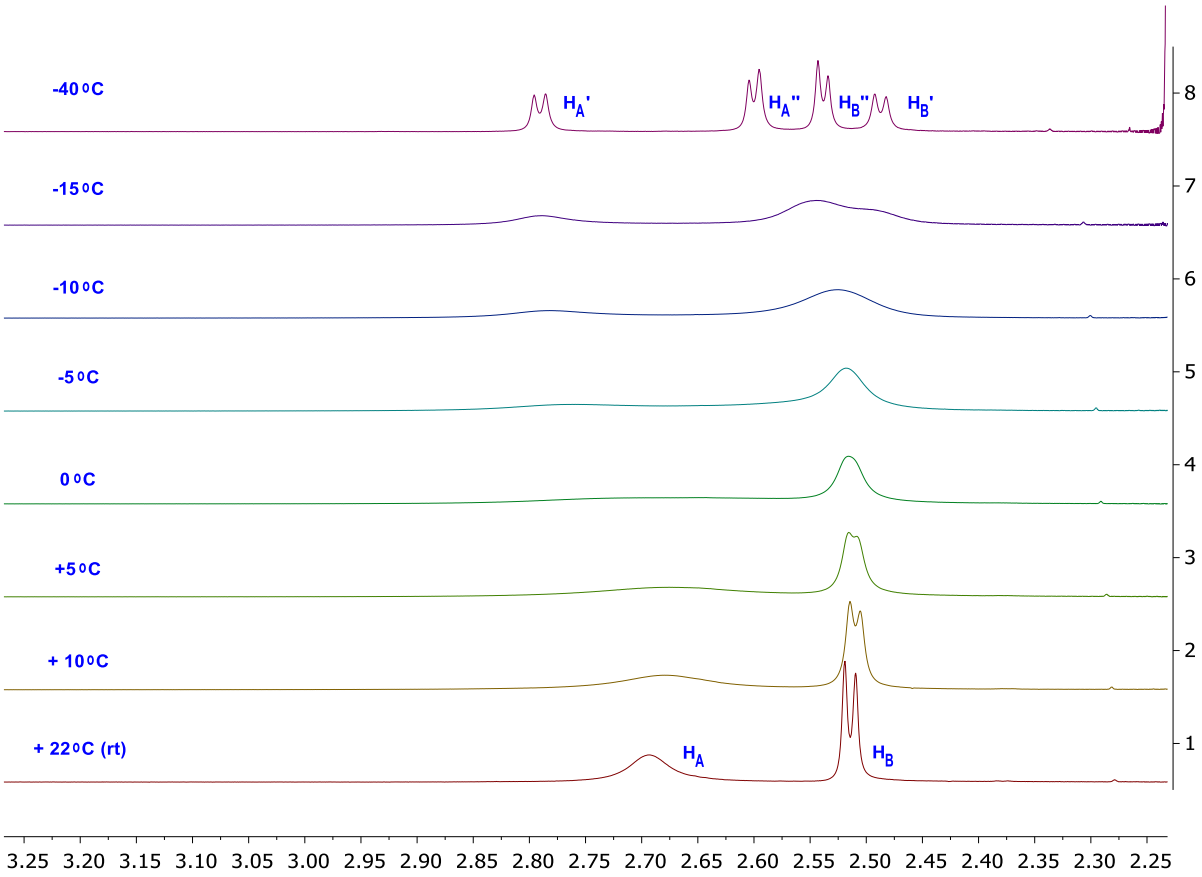
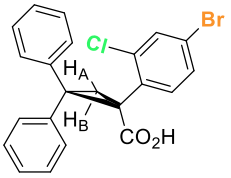


Figure S6.1. ^{1}H-NMR spectra of ligand *S*-*o*-ClTPCP (range δ 3.25-2.25 ppm, -40 ºC-+22ºC).

(b) *S*-2-Cl-4-BrTPCP



32

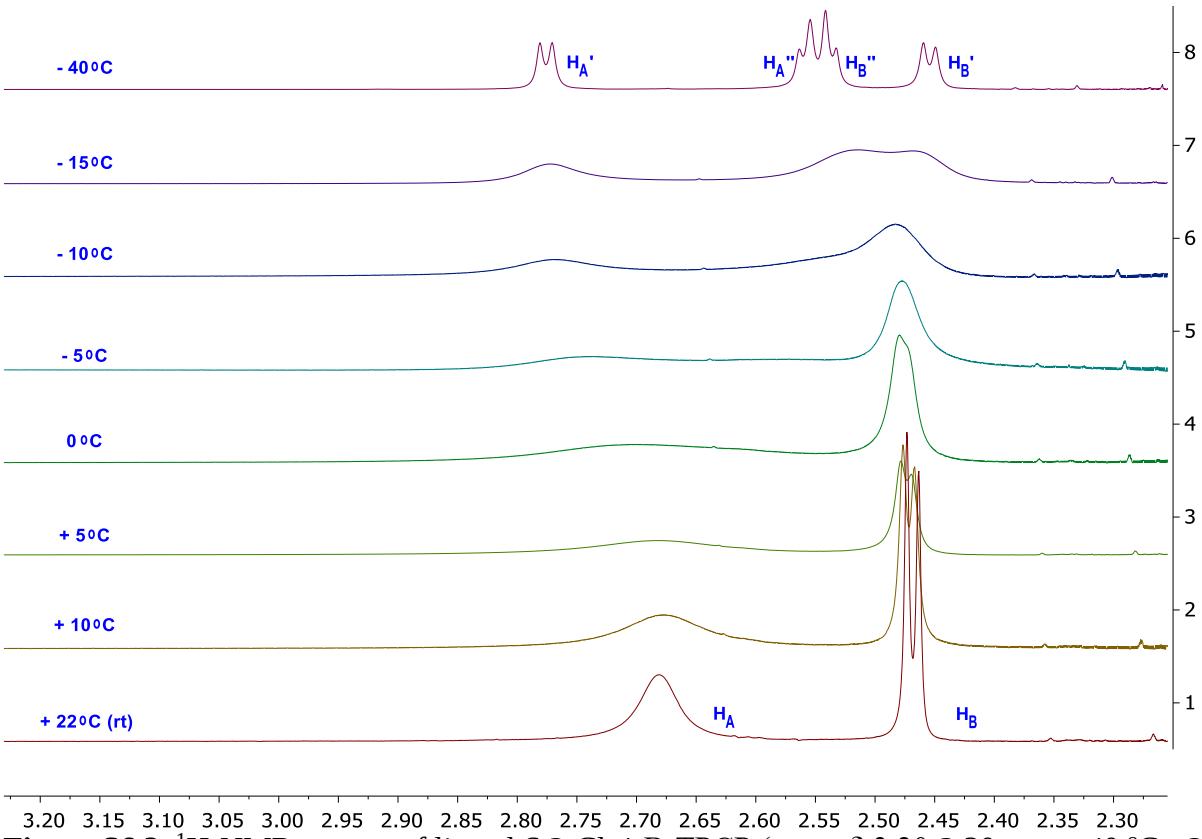
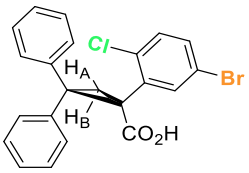


Figure S6.2. ^{1}H-NMR spectra of ligand *S*-2-Cl-4-BrTPCP (range δ 3.20-2.30 ppm, -40 ºC-+22ºC).

(c) *S*-2-Cl-5-BrTPCP



30

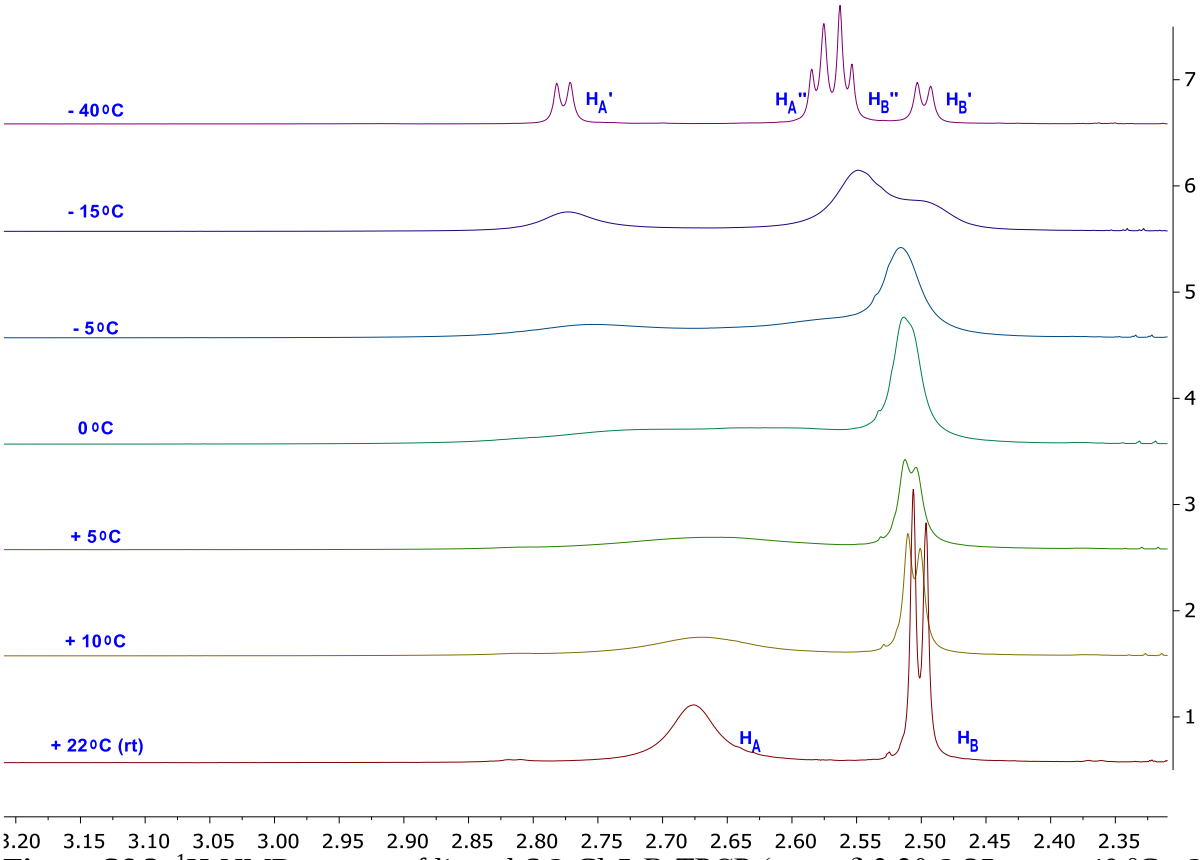


Figure S6.3. ^{1}H-NMR spectra of ligand *S*-2-Cl-5-BrTPCP (range δ 3.20-2.35 ppm, -40 ºC-+22ºC).

Calculations:

The proton H_A and H_B is a AB coupling system, so the crude estimations of rate constants, *k*, at coalescence were obtained using approximate formula.[13]

$$k = \frac{\pi\sqrt{\Delta\upsilon^2 + 6\bar{J}^2}}{\sqrt{2}}$$

Table S6.1. Parameters from VT-NMR spectra and calculated *k* values.

Ligands	$\Delta\upsilon(H_A)$, Hz	$\bar{J}$ (H_A), Hz	T_c (H_A), K	*k* (H_A), s^{-1}	$\Delta\upsilon(H_B)$, Hz	$\bar{J}$ (H_B), Hz	T_c (H_A), K	*k* (H_B), s^{-1}
31	113.91	5.85	273.15	255.05	29.98	5.85	263.15	67.85
32	131.90	5.90	278.15	294.76	53.96	5.90	263.15	120.58
30	119.91	6.00	278.15	268.37	35.97	5.95	268.15	81.00

Eyring plots, ln(*k*/T) vs 1/T, were then plotted using two data points (H_A and H_B at coalescence) for each ligand.

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{R}\cdot\frac{1}{T} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

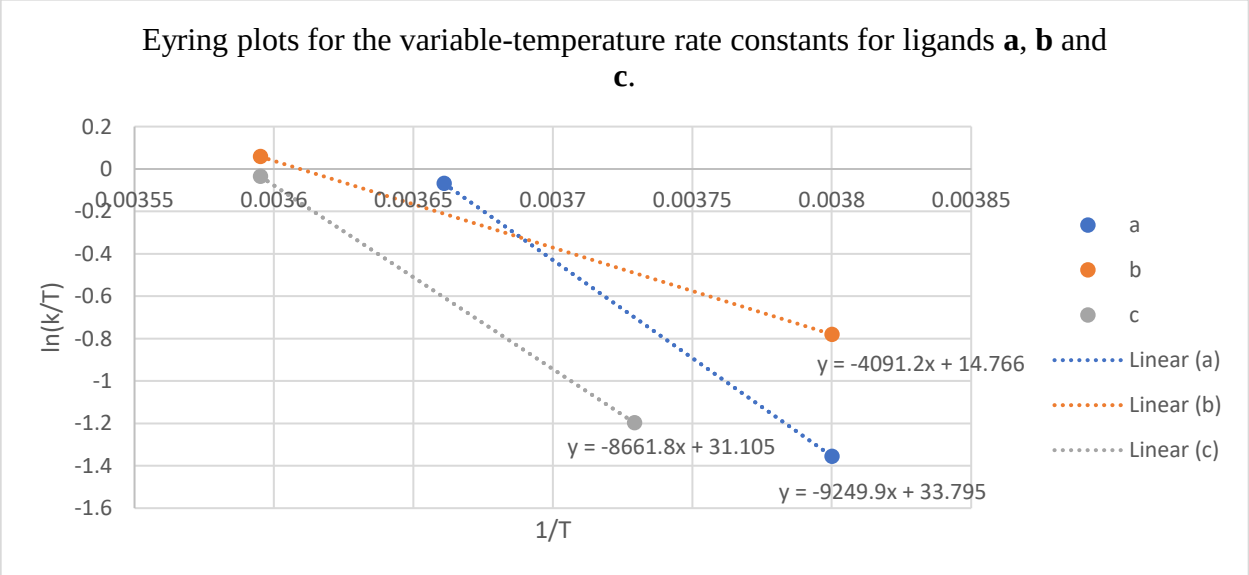


Figure S6.4. Eyring plots, ln(*k*/T) vs 1/T, of three ligands.

Table S6.2. Calculated energies of three ligands.

Ligand	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, kcal/mol·K	$\Delta G^{\ddagger}$ (at 273.15K), kcal/mol
31	18.38	0.02	12.94
32	8.13	-0.02	13.01
30	17.21	0.01	13.23

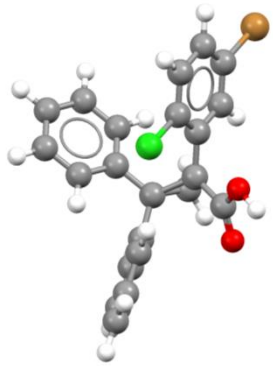
7. Calculation

7.1. Computational Details

Geometry optimizations and frequency calculations were conducted with the Gaussian 09[14] program. We employed the B3LYP[15] with D3BJ[16] function theory with basis set 6-31G(d) + Lanl2dz for Rh, which uses Hay-Wadt effective core potential for Rh.[17] For each minimum, the frequency analysis was conducted to calculate enthalpy and entropy corrections to their electronic energies under 1 atm and 298.15 K. The model for solvent effects is the conductor-like polarizable continuum model (CPCM), and chloroform was used for free ligand structural analysis, while dichloromethane was used as solvent for catalysts conformational analysis.[18] Images were generated with Mercury.

7.2. Computational Studies of Carboxylic Acid Ligand

30a



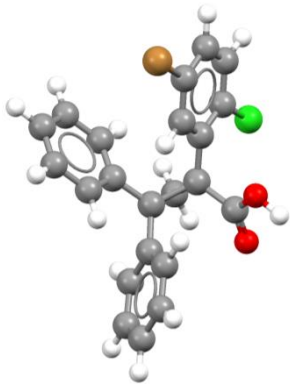
E_{tot}	*H* (Ethalpy)	*G* (Gibbs Free Energy)
-4030.13987549 a. u.	-4029.796431 a. u.	-4029.873700 a. u.

Cl	-4.61878700	1.55914000	-1.74560200
O	-0.10277200	2.47157800	-2.10060100
C	-1.18289100	2.53409100	-1.54691400
C	-3.27764200	3.74598500	-0.75019800
C	-1.67294700	4.82191800	-2.49586400
H	-2.04188200	5.79131800	-2.18461600
H	-0.61449500	4.78412800	-2.72452100
C	-2.21699400	3.59225200	-1.79897500

C	-4.57791300	5.45683600	-2.94660400
H	-4.02841600	6.03169600	-2.21214000
C	-2.56312500	3.92374600	-3.29724200
C	-1.22605600	3.75876700	-5.40588200
H	-1.11761700	4.83872300	-5.36534500
C	-3.98128600	4.36276400	-3.59241700
C	-3.15503400	4.77931800	0.18662800
H	-2.29504300	5.43622800	0.13807600
C	-2.06126900	1.71186600	-4.44498800
H	-2.59906500	1.19604000	-3.65711200
C	-5.37134800	3.10611600	0.33002300
H	-6.23000000	2.44656100	0.37502700
C	-5.24311200	4.14934800	1.24389800
C	-4.39695000	2.90649100	-0.64632800
C	-1.92166500	3.10277600	-4.38481600
C	-0.67558900	3.03967100	-6.46712100
H	-0.13629700	3.56252800	-7.25127000
C	-4.74898600	3.66293600	-4.53584100
H	-4.31493200	2.81942500	-5.05768400
C	-4.12443900	4.97370300	1.16443700
C	-0.81659100	1.65140500	-6.51869600
H	-0.38708000	1.08935000	-7.34236700
C	-6.64795600	5.11320600	-4.15280100
H	-7.67309000	5.40026600	-4.36572300
C	-6.06455300	4.03160100	-4.81282900
H	-6.63291500	3.46843800	-5.54697100
C	-1.51046000	0.98958700	-5.50361500
H	-1.62215100	-0.09007800	-5.53418200
C	-5.89489200	5.82495400	-3.21877000

H	-6.32865900	6.67350600	-2.69841700
Br	-3.91706000	6.40245000	2.41520200
H	-5.99987300	4.31047200	2.00190000
O	-1.56708300	1.64585600	-0.60825800
H	-0.83872300	1.00881400	-0.51208100

30b

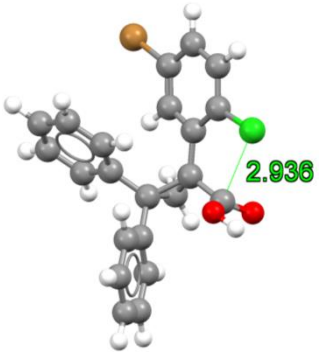


E_{tot}	*H* (Ethalpy)	*G* (Gibbs Free Energy)
-4030.13990705 a. u.	-4029.796490 a. u.	-4029.875449 a. u.

Cl	-1.60438800	5.76508000	0.53881800
O	0.07982400	3.04863100	-1.99900700
C	-1.04712500	2.94666800	-1.55853500
C	-3.22360300	3.98142300	-0.77729400
C	-1.79705100	5.09969600	-2.66267600
H	-2.26750800	6.04145400	-2.41250400
H	-0.74541900	5.16645900	-2.91579500
C	-2.17877800	3.89035000	-1.84655600
C	-4.74403600	5.39943300	-3.17200400
H	-4.22511100	6.15362100	-2.59314000
C	-2.59482100	4.03690700	-3.35551100
C	-1.27442500	3.77086900	-5.47054800
H	-1.28129500	4.85316000	-5.56031900

C	-4.05868700	4.27347700	-3.65237600
C	-4.38475800	3.20142600	-0.85015800
H	-4.52511900	2.53893300	-1.69311400
C	-1.87419700	1.77728700	-4.25361100
H	-2.33916300	1.30406100	-3.39364100
C	-4.05539900	4.91684100	1.32161300
H	-3.90933600	5.57970700	2.16636400
C	-5.21851700	4.15862200	1.21699200
C	-3.07361500	4.81986100	0.33542300
C	-1.88432200	3.17287800	-4.36307600
C	-0.66053700	2.98996900	-6.45005500
H	-0.18735100	3.46748200	-7.30273600
C	-4.78646300	3.32729600	-4.39076900
H	-4.28252300	2.45380700	-4.78622500
C	-5.36453400	3.30126000	0.12833700
C	-0.65231600	1.59834800	-6.33269500
H	-0.17252000	0.98980000	-7.09305100
C	-6.82287100	4.60781600	-4.12537100
H	-7.88658600	4.73401800	-4.30120200
C	-6.15255100	3.48949700	-4.62089000
H	-6.69098300	2.73749000	-5.18970500
C	-1.26025100	0.99343700	-5.23089500
H	-1.25492000	-0.08758200	-5.12996900
C	-6.10845600	5.56475200	-3.40355700
H	-6.61273200	6.44408600	-3.01463500
Br	-6.95349200	2.25315800	-0.03814200
H	-5.99119600	4.23299900	1.97244400
O	-1.42279100	1.93356300	-0.74889000
H	-0.63879700	1.37232300	-0.62193700

TS_I

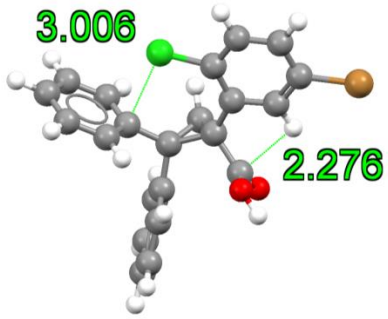


E_{tot}	*H* (Ethalpy)	*G* (Gibbs Free Energy)
-4030.12126100 a. u.	-4029.778863 a. u.	-4029.853344 a. u.
One imaginary frequency		

Cl	-2.32508400	1.65513300	0.72790000
O	0.01167400	3.32199300	-1.08185400
C	-1.02019900	2.92060000	-1.57806600
C	-3.28318300	3.86706000	-0.69776700
C	-1.91152800	5.05223900	-2.56247300
H	-2.42810700	5.96708400	-2.30024200
H	-0.86100800	5.19882100	-2.78182500
C	-2.24649900	3.78866400	-1.79544200
C	-4.50039200	5.32547500	-4.34050800
H	-3.74606500	6.04989200	-4.63374100
C	-2.65961700	3.97618800	-3.29523000
C	-0.82829100	3.73879900	-5.03706900
H	-0.45546500	4.71934400	-4.76266800
C	-4.11481100	4.18908400	-3.62112600

C	-4.23268900	4.90782800	-0.76049200
H	-4.19222700	5.62678800	-1.56270100
C	-2.41700900	1.94805500	-4.78496800
H	-3.28312400	1.52148000	-4.29217100
C	-4.45779700	3.12696200	1.33093300
H	-4.51718700	2.42309300	2.15250500
C	-5.39758000	4.14203600	1.21898800
C	-3.42618700	2.98872100	0.39632100
C	-1.94005500	3.20365300	-4.37921800
C	-0.19392000	3.03176400	-6.06262700
H	0.66685400	3.46755300	-6.56084800
C	-5.09145100	3.25806000	-3.24679400
H	-4.80477800	2.38765800	-2.66535400
C	-5.26245400	5.03048800	0.15798900
C	-0.66804500	1.77959400	-6.44769000
H	-0.17678600	1.22843400	-7.24371000
C	-6.80834300	4.60471400	-4.29012200
H	-7.85153000	4.76947200	-4.54135900
C	-6.42996800	3.46385700	-3.57894500
H	-7.17826000	2.73955100	-3.27218500
C	-1.78699700	1.24097300	-5.80415700
H	-2.16792400	0.26740800	-6.09788000
C	-5.83956900	5.53483800	-4.67201300
H	-6.12584300	6.42430400	-5.22497600
Br	-6.52951200	6.44262700	-0.06382400
H	-6.20158900	4.23716500	1.93804800
O	-1.17039800	1.67151200	-2.04698900
H	-0.33975600	1.19733600	-1.87005100

TS_II



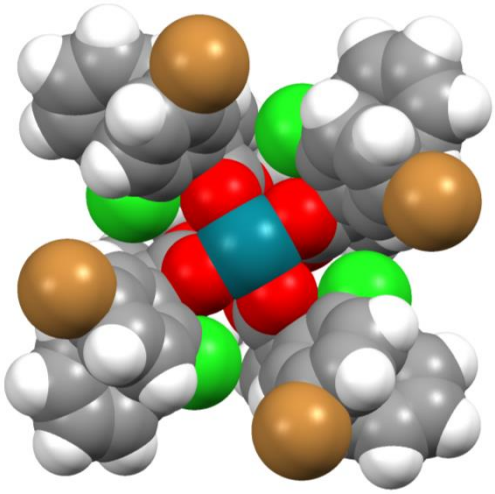
E_{tot}	*H* (Ethalpy)	*G* (Gibbs Free Energy)
-4030.11049102 a. u.	-4029.768435 a. u.	-4029.841825 a. u.
One imaginary frequency		

Cl	-5.84775200	4.77548300	-1.45729300
O	-0.40345000	2.70467500	-1.77839800
C	-1.60033600	2.53103000	-1.68558700
C	-3.48090900	3.65743300	-0.48895900
C	-2.17090800	4.90484300	-2.38432500
H	-2.70299400	5.79160400	-2.05676600
H	-1.09841700	5.01920000	-2.49809600
C	-2.66301500	3.60983700	-1.77158600
C	-4.40770000	5.67686200	-4.34290600
H	-3.65696300	6.42626300	-4.11380100
C	-2.90938200	3.96229800	-3.28351500
C	-1.13265200	3.87070400	-5.06512500
H	-0.96681900	4.92910200	-4.89017300

C	-4.20717700	4.35447500	-3.93782300
C	-2.74709400	3.26552700	0.65545000
H	-1.71383200	2.96338300	0.54743900
C	-2.29156900	1.82399300	-4.53704800
H	-3.01029800	1.27589900	-3.93912700
C	-5.32934500	4.11498100	1.05916400
H	-6.34545700	4.46636400	1.19395200
C	-4.59731200	3.68339400	2.15476200
C	-4.78571200	4.11634400	-0.23222300
C	-2.07487900	3.18567400	-4.28991000
C	-0.41078500	3.20876400	-6.05817900
H	0.31833600	3.75528100	-6.64872400
C	-5.16916800	3.39100800	-4.26772700
H	-5.02333800	2.36002000	-3.96479200
C	-3.28833300	3.27043800	1.93066800
C	-0.62403300	1.84873400	-6.29067400
H	-0.06022500	1.33088100	-7.06048800
C	-6.53655000	5.08285400	-5.32490700
H	-7.44187800	5.36526500	-5.85347500
C	-6.32823800	3.75251200	-4.94804000
H	-7.07355200	2.99793700	-5.18090500
C	-1.56689500	1.15909900	-5.52619800
H	-1.73992800	0.10104100	-5.69838000
C	-5.56915700	6.04240500	-5.02603100
H	-5.71530200	7.07616900	-5.32466000
Br	-2.20979100	2.70806000	3.40336800
H	-5.02873800	3.68306800	3.14803600
O	-2.14847400	1.31254300	-1.49793400
H	-1.41567900	0.67375200	-1.46546400

7.3. Computational Studies of Different Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ Conformers

Conformer I



E_{tot}	*H* (Ethalpy)	*G* (Gibbs Free Energy)
-16337.34716560 a. u.	-16336.006713 a. u.	-16336.245950 a. u.

Rh	2.66026000	9.21018200	17.86071800
Rh	0.91879700	10.51609100	16.86590600
Br	8.49697900	13.31119800	20.64918300
Cl	2.30758700	11.93773600	21.69788100
O	1.97424400	12.19078000	17.47664300
O	3.32884600	10.92485100	18.77200300
C	2.83988200	12.03929700	18.39482000
C	3.37035400	13.25717100	19.08854300
C	2.48829800	14.54372500	19.26891500
C	4.36342700	12.94321300	20.16754500
C	3.98339800	12.36841300	21.39073500
C	4.91260700	12.10060000	22.39272800
H	4.58598600	11.66523100	23.33026600
C	6.26161600	12.38843300	22.18755000
H	6.98930100	12.18450200	22.96382100
C	6.65118700	12.93177200	20.96722300

C	5.72173600	13.20602300	19.96860900
H	6.04989400	13.62386200	19.02469300
C	3.56720700	14.49577600	18.23282500
H	4.47876700	15.06592000	18.36435500
H	3.23823900	14.41250300	17.20362100
C	1.06378100	14.57832900	18.77999700
C	0.66052500	15.65241900	17.97767300
H	1.38652600	16.41358000	17.70423000
C	-0.65527900	15.74394800	17.51859400
H	-0.95076000	16.58009900	16.89104300
C	-1.58295600	14.75579800	17.85773300
H	-2.60497400	14.81554400	17.49395300
C	-1.18980600	13.68773800	18.66779700
H	-1.89863000	12.90773800	18.92364000
C	0.12207400	13.60813500	19.13285400
H	0.42781000	12.76289200	19.73523000
C	2.71671100	15.31171700	20.55323900
C	1.71919300	15.31515600	21.54011800
H	0.78566700	14.79646700	21.35656400
C	1.90901700	15.97527000	22.75319600
H	1.12124100	15.95716400	23.50096800
C	3.10188600	16.65512700	23.00578600
H	3.25193000	17.16952200	23.95051700
C	4.09659000	16.67246900	22.02759500
H	5.02746700	17.20405100	22.20299200
C	3.90348500	16.01057500	20.81455700
H	4.69615200	16.04422800	20.07704100
Br	1.47052100	7.60190400	25.33260800
Cl	-0.70824400	6.37490200	19.41390600

O	-0.03655300	10.45329600	18.69862400
O	1.38891600	8.86389500	19.44261200
C	0.30894100	9.53639500	19.50803900
C	-0.59860000	9.22037400	20.65795600
C	-2.14985900	9.44789900	20.56039800
C	-0.12441700	8.07375800	21.49978500
C	-0.15162800	6.74773400	21.03863000
C	0.27129200	5.68622600	21.83421800
H	0.23003300	4.67320500	21.45037000
C	0.74922900	5.92817300	23.12165500
H	1.07634500	5.10669800	23.74760700
C	0.80253600	7.24121800	23.57893700
C	0.37632900	8.30151300	22.78462600
H	0.43437200	9.31519400	23.16171600
C	-1.28419800	10.40104800	21.32254300
H	-1.31550500	10.42794100	22.40483600
H	-1.10906700	11.36471000	20.85850900
C	-2.78471200	9.95076900	19.28969500
C	-3.65959300	11.04090000	19.36680700
H	-3.83912800	11.51227300	20.32958900
C	-4.28834700	11.53206500	18.22038900
H	-4.95920600	12.38324600	18.29611600
C	-4.04446200	10.93626000	16.98042200
H	-4.52141800	11.32255300	16.08390000
C	-3.18296800	9.83925800	16.89848600
H	-2.97491600	9.37699000	15.93930100
C	-2.56978000	9.34526700	18.04891800
H	-1.88049500	8.51528100	17.97432500
C	-2.99675900	8.44241400	21.31050700

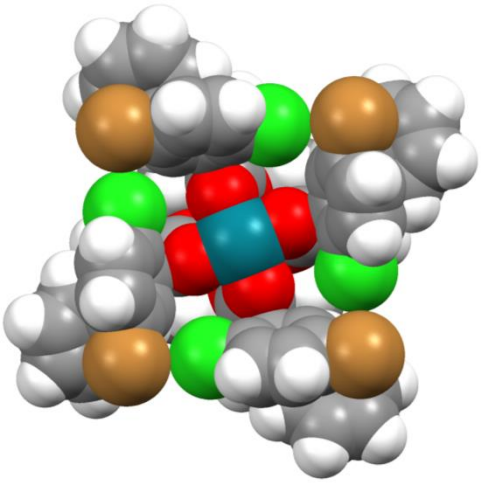
C	-3.72178100	7.48143000	20.58962800
H	-3.69258500	7.49362500	19.50648400
C	-4.47903800	6.51143900	21.24416000
H	-5.02556400	5.77568500	20.66102500
C	-4.53576400	6.48553000	22.63906200
H	-5.12502700	5.73041400	23.15110600
C	-3.83278100	7.44527500	23.36790800
H	-3.87341600	7.44606400	24.45336800
C	-3.07432300	8.41414500	22.70944000
H	-2.54169200	9.14631900	23.30458200
Br	1.41473000	1.67049900	17.77299800
Cl	2.77559900	6.61897600	13.90625700
O	0.01878500	8.72843500	16.34559100
O	1.88293300	7.57244400	16.89649200
C	0.74094300	7.68237300	16.34254800
C	0.21817000	6.45118100	15.66668700
C	-0.74727400	6.54503600	14.43190900
C	1.17396800	5.29644000	15.71235300
C	2.34732300	5.26567200	14.94211500
C	3.22059900	4.18179100	14.98278200
H	4.11407800	4.18452100	14.36888200
C	2.94724400	3.09702300	15.81543400
H	3.62163400	2.24971900	15.85019700
C	1.80055100	3.13123700	16.60294800
C	0.92431300	4.21130800	16.55708400
H	0.04243100	4.21771300	17.18586500
C	-1.27278800	6.19049500	15.78726100
H	-1.59670100	5.17947200	16.00178800
H	-1.84406100	6.95861700	16.29502400

C	-1.14526500	7.88309100	13.86523300
C	-2.50532200	8.14342300	13.65940800
H	-3.23882300	7.39074600	13.93637500
C	-2.92339900	9.36034900	13.11642600
H	-3.98297700	9.54960000	12.96890100
C	-1.98042000	10.33358000	12.77642000
H	-2.30068600	11.28712200	12.36582400
C	-0.62098900	10.07536500	12.96830800
H	0.11714500	10.83154200	12.72338100
C	-0.20885500	8.85329000	13.49796000
H	0.84379600	8.67141300	13.67153900
C	-0.57377300	5.46129100	13.38942000
C	-0.04199900	5.79240100	12.13381200
H	0.20674200	6.82415300	11.91517500
C	0.17193600	4.81576600	11.16234900
H	0.58918300	5.10046600	10.20060300
C	-0.14690400	3.48176700	11.42255900
H	0.02006700	2.71925700	10.66735500
C	-0.68929300	3.14022500	12.66185200
H	-0.95192600	2.10881700	12.87889300
C	-0.90281400	4.12032500	13.63171500
H	-1.32629700	3.82020200	14.58261100
Br	8.39365600	7.42819600	12.97723800
Cl	5.64445300	12.32313100	16.10199800
O	2.01561000	10.46069400	15.11149700
O	3.81413200	9.64834200	16.21413100
C	3.25500900	10.19661900	15.20925300
C	4.15049700	10.52511700	14.05317000
C	3.82211400	11.71526700	13.08127600

C	5.59779900	10.23082500	14.31295400
C	6.36664800	10.99522300	15.20546900
C	7.71506200	10.72766800	15.42651000
H	8.28151700	11.34142200	16.11767800
C	8.33360500	9.67020000	14.76037500
H	9.38363700	9.45901600	14.92394800
C	7.57452700	8.89297600	13.89100100
C	6.22703200	9.16147900	13.66948800
H	5.65628300	8.53629500	12.99373300
C	3.57749000	10.29860200	12.66568600
H	4.21072800	9.82686600	11.92435100
H	2.54244500	9.97874400	12.63463600
C	2.61752900	12.59175700	13.30702400
C	1.74494300	12.81860100	12.23612700
H	1.94110800	12.34152900	11.27939600
C	0.62403400	13.63732200	12.39209300
H	-0.04709400	13.79808800	11.55301600
C	0.36297700	14.23629400	13.62709300
H	-0.51428000	14.86408900	13.75671200
C	1.23712300	14.02443200	14.69631900
H	1.03672000	14.47064400	15.66459800
C	2.36189600	13.21794800	14.52956700
H	3.01659800	13.03213000	15.37003200
C	5.02648800	12.45567000	12.54055300
C	5.30814300	13.74678800	13.01257300
H	4.64106100	14.20929000	13.73032200
C	6.43246200	14.44385500	12.57366000
H	6.62945100	15.43966800	12.96047200
C	7.29950300	13.86721400	11.64347900

H	8.17665900	14.40832100	11.30082100
C	7.02223800	12.59091100	11.15291200
H	7.68027900	12.13116200	10.42113400
C	5.89620800	11.89531800	11.59516800
H	5.70845600	10.90692000	11.19301500

Conformer Ia



E_{tot}	H (Ethalpy)	G (Gibbs Free Energy)
-16337.34181470 a. u.	-16336.001605 a. u.	-16336.240746 a. u.

Rh	2.56167700	9.28402100	17.81659000
Rh	0.82569900	10.58530300	16.82566700
Br	4.40628700	12.26966600	24.21712600
Cl	6.16261600	12.76830800	18.05478400
O	1.87867300	12.25577900	17.46361300
O	3.11830400	10.97036300	18.85201500
C	2.70600200	12.09630900	18.41509600
C	3.28150000	13.30569800	19.08772600
C	2.39565700	14.58465100	19.32194600
C	4.33105500	12.95094200	20.09817700
C	5.66300100	12.70578400	19.74115400
C	6.62478400	12.35838600	20.69028700

H	7.64872800	12.18006200	20.38199800
C	6.26437000	12.23364600	22.03039800
H	7.00652800	11.97199000	22.77526100
C	4.93373500	12.44207800	22.38817200
C	3.97717900	12.78600300	21.44240900
H	2.95085700	12.94919300	21.74224200
C	3.44209100	14.56239100	18.25471500
H	4.36298700	15.11778400	18.38197900
H	3.09518500	14.50080800	17.23066100
C	0.95880900	14.58419300	18.86960700
C	0.50993900	15.63345600	18.05879100
H	1.20824600	16.41165600	17.76236000
C	-0.81451500	15.67728800	17.61939300
H	-1.14585800	16.49364400	16.98385200
C	-1.70551000	14.66660800	17.98942500
H	-2.73394100	14.68761800	17.63987600
C	-1.26806600	13.62535000	18.81108200
H	-1.94979100	12.82681500	19.08220200
C	0.05319000	13.59257000	19.25543600
H	0.39418400	12.76486900	19.86733900
C	2.63842500	15.34798800	20.60467100
C	1.66366500	15.32893000	21.61469400
H	0.72557300	14.81309700	21.44260400
C	1.88668100	15.95386000	22.84092400
H	1.11983700	15.91414500	23.60918700
C	3.08659300	16.62624700	23.08013400
H	3.26328400	17.11191200	24.03524400
C	4.05441700	16.67166800	22.07608600
H	4.99005700	17.19766700	22.24254500

C	3.83134900	16.03999900	20.85235700
H	4.60897400	16.08138900	20.09884600
Br	-0.54084100	4.08905500	21.98593800
Cl	1.57134400	10.12274700	22.64626700
O	-0.12595500	10.49380200	18.66581100
O	1.22895700	8.80160500	19.31015500
C	0.20300300	9.54751000	19.44794000
C	-0.64913900	9.27228800	20.65005800
C	-2.21218700	9.42941500	20.57083700
C	-0.06676200	8.21330500	21.53703800
C	0.92551800	8.49373000	22.48510000
C	1.46827000	7.49689800	23.29627900
H	2.23134900	7.74792900	24.02425000
C	1.03260500	6.18010000	23.16312900
H	1.44182800	5.40069900	23.79488600
C	0.07093000	5.88739700	22.19824500
C	-0.46615400	6.87990700	21.38920200
H	-1.21460700	6.63077300	20.64937800
C	-1.37508100	10.44920200	21.27321800
H	-1.37514400	10.50354000	22.35473300
H	-1.24586300	11.40338700	20.77766000
C	-2.85000200	9.84277000	19.27044700
C	-3.74143100	10.92211400	19.27209800
H	-3.94066800	11.44559400	20.20347400
C	-4.35889300	11.33675600	18.09059200
H	-5.04217100	12.18118900	18.10602800
C	-4.08825200	10.67190800	16.89175900
H	-4.55427000	10.99896400	15.96644500
C	-3.21194500	9.58423800	16.88627100

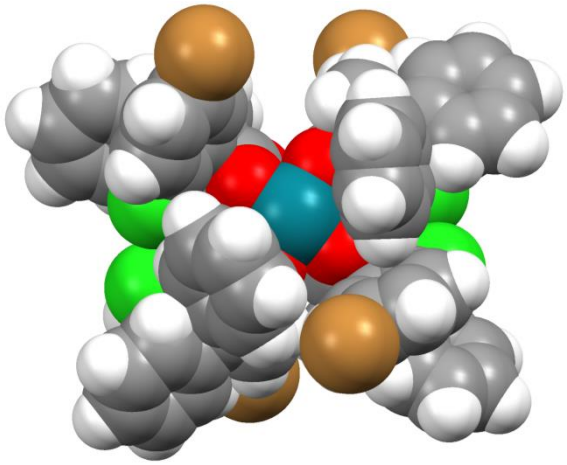
H	-2.97855700	9.08096700	15.95454900
C	-2.60827700	9.16681900	18.07186500
H	-1.90529200	8.34141700	18.05621700
C	-3.03565000	8.44590900	21.37215900
C	-3.78243600	7.46413500	20.70184300
H	-3.80091600	7.45403400	19.61771100
C	-4.49306900	6.49434900	21.40759800
H	-5.05341000	5.73953800	20.86341900
C	-4.48447500	6.49264600	22.80378500
H	-5.03562600	5.73714500	23.35582900
C	-3.76356800	7.47609500	23.48196800
H	-3.75303500	7.49445100	24.56794700
C	-3.04857200	8.44197400	22.77313800
H	-2.48964400	9.18460900	23.33041400
Br	4.16386200	3.70447600	13.37321200
Cl	0.17299000	4.91942600	18.26243500
O	-0.05288900	8.78641000	16.28135800
O	1.88103300	7.69295700	16.70757300
C	0.69893600	7.76266300	16.23193700
C	0.18148200	6.50895900	15.59334300
C	-0.74808100	6.58183800	14.32674600
C	1.14011800	5.36353400	15.72749200
C	1.20578000	4.57167100	16.88073400
C	2.11444200	3.51943100	16.99728300
H	2.13654000	2.92181900	17.90149100
C	2.99611500	3.24498400	15.95386400
H	3.69976900	2.42476600	16.03258400
C	2.96006800	4.05008100	14.81700300
C	2.05655000	5.09817700	14.70314100

H	2.04050600	5.70697800	13.80944500
C	-1.31082200	6.24969200	15.67089400
H	-1.61911400	5.23674200	15.89774400
H	-1.90093300	7.01644300	16.15753300
C	-1.10409900	7.92573300	13.74771400
C	-2.45362000	8.23009400	13.53413800
H	-3.21210800	7.50028500	13.80469500
C	-2.82888600	9.46154000	12.99398500
H	-3.88073600	9.68636100	12.84165600
C	-1.85216700	10.40356300	12.66116300
H	-2.13831400	11.36910300	12.25360000
C	-0.50296700	10.10014600	12.85732900
H	0.25699000	10.83726600	12.62208800
C	-0.13355100	8.86400100	13.38663300
H	0.91393200	8.64599300	13.56450700
C	-0.56752100	5.49263200	13.29288000
C	-0.01564300	5.81162200	12.04210600
H	0.22286600	6.84351500	11.81007700
C	0.24357200	4.82033000	11.09651000
H	0.68172900	5.09393400	10.14097900
C	-0.05745300	3.48591000	11.37489000
H	0.14571100	2.71198500	10.64068200
C	-0.62734900	3.15851700	12.60569800
H	-0.87543500	2.12636900	12.83574500
C	-0.87988300	4.15144400	13.55248600
H	-1.30823700	3.86092600	14.50465200
Br	9.02954300	11.91176400	15.58130600
Cl	4.72972400	7.52699500	13.68643900
O	1.95049700	10.54585900	15.08295000

O	3.76309000	9.86224300	16.25123600
C	3.19390200	10.30969900	15.20035100
C	4.09162900	10.54480400	14.02353800
C	3.83373800	11.75683000	13.05591800
C	5.50036700	10.09923300	14.27843800
C	5.89842900	8.76371400	14.13578700
C	7.20869700	8.35771200	14.38936600
H	7.48644500	7.31728000	14.26437000
C	8.15472600	9.28974900	14.81115800
H	9.17633000	8.98441000	15.00367400
C	7.75776700	10.61332400	14.98990600
C	6.45275500	11.01596800	14.73873500
H	6.16750200	12.04938100	14.88003400
C	3.49281700	10.36182900	12.64202000
H	4.10409500	9.84466500	11.91305500
H	2.44236400	10.10104900	12.61055100
C	2.68560000	12.69230800	13.33083400
C	1.77966200	12.96620100	12.29927700
H	1.91434600	12.48847400	11.33237800
C	0.70416400	13.83158300	12.50803200
H	0.00478300	14.02817100	11.70032500
C	0.52518400	14.43350700	13.75625900
H	-0.31760100	15.09701200	13.92896300
C	1.43440000	14.17660700	14.78489800
H	1.28715200	14.62265900	15.76226600
C	2.51299700	13.32013300	14.56710200
H	3.19614500	13.09867300	15.37957800
C	5.05520400	12.43879500	12.48118700
C	5.40484400	13.72163300	12.93184200

H	4.76703800	14.22898800	13.64720900
C	6.56550300	14.34968900	12.48288100
H	6.81858500	15.33758400	12.85684700
C	7.39747700	13.71355900	11.55936500
H	8.30319900	14.20002900	11.20964400
C	7.04874000	12.44829300	11.08607500
H	7.67960600	11.94362800	10.36002600
C	5.88952300	11.81936000	11.54174500
H	5.65207100	10.83239200	11.16219300

Conformer Ib



E_{tot}	*H* (Ethalpy)	*G* (Gibbs Free Energy)
-16337.33486180 a. u.	-16335.996640 a. u.	-16336.228805 a. u.

Rh	3.01956800	9.55144300	17.73788400
Rh	1.27360900	10.85385100	16.76238900
Br	8.80926700	13.64195900	20.42041700
Cl	2.64474200	12.47832400	21.78420700
O	2.29479400	12.51670000	17.42045200
O	3.55667800	11.23976800	18.79798300
C	3.11449100	12.36186500	18.37983500

C	3.62652400	13.59307200	19.06302400
C	2.68240100	14.84190100	19.22201800
C	4.65216000	13.32663800	20.12329900
C	4.31471000	12.82804900	21.39008400
C	5.28061200	12.58674700	22.36445200
H	4.98480200	12.21240300	23.33803400
C	6.62487700	12.83053500	22.08689600
H	7.38176700	12.64812100	22.84030700
C	6.97189700	13.30883300	20.82663100
C	6.00573200	13.55430900	19.85534900
H	6.29834700	13.92783100	18.88118500
C	3.76516900	14.82591400	18.18849800
H	4.64784300	15.44005200	18.32110700
H	3.44961500	14.70567100	17.15861700
C	1.26027300	14.77180700	18.72483500
C	0.81810100	15.75572000	17.83308400
H	1.51090800	16.52683800	17.50677800
C	-0.49309700	15.74743300	17.35421100
H	-0.81966800	16.51736600	16.66070700
C	-1.37920100	14.74783000	17.76433800
H	-2.39900600	14.73341200	17.38969900
C	-0.94640500	13.76657200	18.65933300
H	-1.61933200	12.97658500	18.97226100
C	0.36158100	13.78469200	19.14303800
H	0.69195400	13.00136800	19.81368200
C	2.86612400	15.65955300	20.48259500
C	1.81913900	15.74451500	21.41324500
H	0.88101400	15.24366500	21.20669400
C	1.96648200	16.45671600	22.60250500

H	1.13908300	16.50008000	23.30511000
C	3.16701500	17.10822700	22.88965500
H	3.28439600	17.66287900	23.81606500
C	4.21317600	17.04294100	21.96882000
H	5.15265900	17.54944700	22.17078600
C	4.06181200	16.33065300	20.77879300
H	4.89661800	16.30167800	20.08930500
Br	-5.20471000	9.92611400	17.76034900
Cl	-0.70283600	11.49245300	22.06325000
O	0.24898100	10.61889400	18.55967000
O	1.65717200	8.95802700	19.16226300
C	0.55731400	9.58876300	19.24476200
C	-0.51628500	9.03073100	20.13774600
C	-0.15856300	8.10841200	21.35325200
C	-1.76287200	9.86442800	20.12740300
C	-1.94911200	10.99077200	20.93727600
C	-3.10457100	11.76806300	20.85493900
H	-3.22251800	12.62864800	21.50336000
C	-4.09212600	11.45395100	19.92293300
H	-4.98461100	12.06302800	19.84419200
C	-3.89994200	10.35416400	19.08933400
C	-2.76366200	9.56221700	19.19691700
H	-2.63758500	8.70724000	18.54509000
C	-0.65418900	7.51601100	20.07120800
H	-1.65430300	7.10066800	20.02606700
H	0.07693500	7.00865400	19.45473500
C	1.29960300	7.89198600	21.66935300
C	1.85803600	6.61697800	21.53928300
H	1.23760100	5.78662700	21.21406500

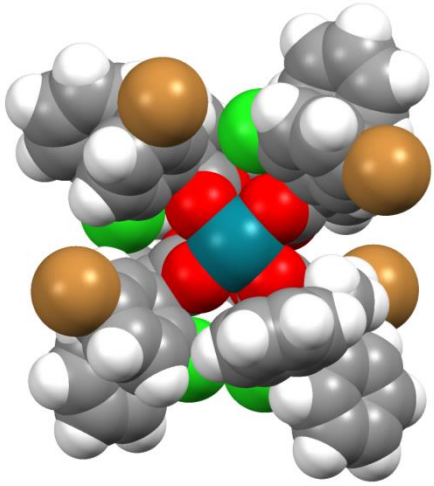
C	3.21429500	6.40639200	21.79512100
H	3.63447000	5.41231800	21.67097900
C	4.02511300	7.47164800	22.19582400
H	5.08162200	7.31078700	22.39092800
C	3.46747900	8.74491200	22.34803600
H	4.08809400	9.58303800	22.65254800
C	2.11325700	8.94878400	22.08911000
H	1.68894200	9.94092900	22.17837300
C	-1.08929600	8.14915600	22.54680800
C	-0.57631200	8.36898200	23.83415700
H	0.49051900	8.49386200	23.97185700
C	-1.41601200	8.43134400	24.94619200
H	-0.98647100	8.60504000	25.92877000
C	-2.79425600	8.27296300	24.80014900
H	-3.44981500	8.32387100	25.66454700
C	-3.31890200	8.04176800	23.52792200
H	-4.38837300	7.90817900	23.39255800
C	-2.47691800	7.97560800	22.41837000
H	-2.92508200	7.79650200	21.44891900
Br	2.40490600	3.11871600	19.42663700
Cl	2.02836300	5.78575800	13.59764600
O	0.37976400	9.08136900	16.23918400
O	2.28655800	7.93771600	16.64576100
C	1.05920100	8.00955100	16.30773000
C	0.34280000	6.70958700	16.07126000
C	-0.95669000	6.65852000	15.19484300
C	1.24226600	5.51866200	16.21132400
C	2.04368900	5.02341800	15.17612400
C	2.90239000	3.94111000	15.37002200

H	3.50130300	3.57367600	14.54463100
C	3.00876700	3.35091100	16.62820000
H	3.68485700	2.51941000	16.78735900
C	2.24199300	3.86121500	17.67366700
C	1.36188700	4.91634300	17.46885000
H	0.76867700	5.29192100	18.29279600
C	-1.04751600	6.64763700	16.68845100
H	-1.33417100	5.73662500	17.20076800
H	-1.38611400	7.56074700	17.16090000
C	-1.39499800	7.92744300	14.50757800
C	-2.60476700	8.53017700	14.86515300
H	-3.22576500	8.07993000	15.63440900
C	-3.00781200	9.72462800	14.26493800
H	-3.94154100	10.18862600	14.56971200
C	-2.20662500	10.32340600	13.28914400
H	-2.51615600	11.25517900	12.82418600
C	-1.00566200	9.71429800	12.91259100
H	-0.37008900	10.17310500	12.16045000
C	-0.60776500	8.52332800	13.51730200
H	0.33777600	8.07020300	13.24713000
C	-1.22879400	5.37675600	14.43664500
C	-1.49285600	5.41575600	13.05911400
H	-1.51461900	6.36838000	12.54458500
C	-1.72847300	4.24727900	12.33488500
H	-1.92818000	4.31232600	11.26903900
C	-1.70795100	3.00600700	12.97115600
H	-1.88881600	2.09492600	12.40835000
C	-1.45841900	2.95130600	14.34305800
H	-1.44575900	1.99584900	14.85966100

C	-1.22726100	4.12135000	15.06570700
H	-1.03612800	4.03500500	16.12818700
Br	3.42448200	15.28392400	11.13724300
Cl	2.70150200	8.99760800	12.22511700
O	2.41160600	10.90989700	15.03688500
O	4.22133900	10.21585000	16.20477800
C	3.65348600	10.63569800	15.14784900
C	4.51097000	10.85213600	13.93773200
C	5.72391200	9.88760900	13.66731000
C	3.78227200	11.45511900	12.77527100
C	2.94131700	10.70870400	11.93775300
C	2.26746600	11.29217900	10.86685800
H	1.63603800	10.68374900	10.22925700
C	2.40882400	12.65610500	10.61585100
H	1.88935300	13.11695300	9.78418800
C	3.22612100	13.40980800	11.45369700
C	3.90519800	12.82457800	12.51812400
H	4.53690100	13.42929500	13.15817400
C	5.94565900	11.26557300	14.21014900
H	6.37820500	12.02903800	13.57444900
H	6.22215400	11.33735500	15.25559800
C	5.97802400	8.73516400	14.60625500
C	7.24731800	8.61250900	15.18293300
H	8.00671800	9.35725900	14.95992200
C	7.53999500	7.55381800	16.04445400
H	8.52956900	7.47428500	16.48582000
C	6.55937100	6.60321900	16.33960000
H	6.78011800	5.78088100	17.01457100
C	5.29281600	6.71529900	15.76116100

H	4.51922200	5.99296800	15.99477700
C	5.00806800	7.76929500	14.89316000
H	4.01386200	7.86056200	14.47360300
C	6.04867600	9.59874300	12.21740300
C	6.01128700	8.27693900	11.74698800
H	5.76340400	7.47488400	12.43163800
C	6.28083200	7.97726500	10.41245400
H	6.24067400	6.94423600	10.07865400
C	6.59845200	8.99490000	9.51171200
H	6.80834500	8.76379700	8.47142800
C	6.64746500	10.31333500	9.96577800
H	6.89818000	11.11897100	9.28163200
C	6.37974700	10.60979100	11.30236500
H	6.42537100	11.64581300	11.61522600

Conformer Ic



E_{tot}	*H* (Ethalpy)	*G* (Gibbs Free Energy)
-16337.33943450 a. u.	-16336.000316 a. u.	-16336.239250 a. u.

Rh	2.68190900	9.01763600	17.70992400
Rh	0.98351000	10.37700700	16.72366300
Br	8.39202600	13.17836700	21.03033800
Cl	2.14906500	11.73714600	21.50034000
O	2.11476000	12.00786900	17.30160800
O	3.35579100	10.70801700	18.67451300
C	2.92321400	11.83680500	18.26903200
C	3.43712500	13.04638600	18.98555400
C	2.56642000	14.35540100	19.05999800
C	4.32977400	12.74040500	20.15089900
C	3.84423900	12.16915300	21.33860500
C	4.67771700	11.91343400	22.42445800
H	4.26804400	11.47789200	23.32872300
C	6.03625900	12.21687300	22.34714700
H	6.68965000	12.02493600	23.18980100
C	6.53167000	12.76412500	21.16776500
C	5.69787800	13.02111100	20.08357600
H	6.11055500	13.44440300	19.17623800
C	3.72364100	14.25987500	18.11847400
H	4.63267600	14.81691900	18.30850500
H	3.48108600	14.14561100	17.06789300
C	1.18557700	14.38932900	18.45772400
C	0.88694100	15.37563200	17.51101600
H	1.65720900	16.08412600	17.21830200
C	-0.38320700	15.44733500	16.93480100
H	-0.59871100	16.21690900	16.19875900
C	-1.37020700	14.52869600	17.30177700
H	-2.35771000	14.57560600	16.85088200
C	-1.08091300	13.54576400	18.25162400

H	-1.83321000	12.81656300	18.53090700
C	0.18606600	13.48565900	18.82891600
H	0.42009000	12.69492700	19.52913700
C	2.70959200	15.14901400	20.34109200
C	1.67053600	15.13378600	21.28417300
H	0.76127700	14.58554900	21.06919200
C	1.78833200	15.81306300	22.49570500
H	0.97027000	15.77893700	23.20964600
C	2.94795000	16.53267600	22.79021200
H	3.04165100	17.06176800	23.73408400
C	3.98193100	16.57096700	21.85451800
H	4.88711400	17.13448800	22.06180900
C	3.86116500	15.88897800	20.64301300
H	4.68156000	15.94215800	19.93734300
Br	1.89462800	7.54263000	25.08408200
Cl	-0.93702100	6.34752500	19.44608900
O	0.04663100	10.34869500	18.56936200
O	1.38078200	8.66125400	19.26487300
C	0.35980100	9.41696800	19.37382900
C	-0.50679800	9.18361200	20.57632700
C	-2.04442700	9.49468000	20.56003400
C	-0.04386200	8.03214300	21.41771500
C	-0.19756200	6.70209400	20.99835000
C	0.24015500	5.63128400	21.77243900
H	0.10727600	4.61560300	21.41689000
C	0.85813500	5.87124600	22.99967400
H	1.20056800	5.04472700	23.61072400
C	1.03228600	7.18788700	23.41601800
C	0.59324500	8.25711100	22.64047600

H	0.75186900	9.27319500	22.97989800
C	-1.08591100	10.41496100	21.24929700
H	-1.05470900	10.46700100	22.33104400
H	-0.89157600	11.35748200	20.75125200
C	-2.72643600	10.01137600	19.31942400
C	-3.58926400	11.10657000	19.44846100
H	-3.71586000	11.57143300	20.42268900
C	-4.27487900	11.60827800	18.34028000
H	-4.93597500	12.46244800	18.45629900
C	-4.09806000	11.02055100	17.08521100
H	-4.61941500	11.41560300	16.21782800
C	-3.24688400	9.92084700	16.95113500
H	-3.09227800	9.46357400	15.97914500
C	-2.57740800	9.41481400	18.06491600
H	-1.90117700	8.57919600	17.94912600
C	-2.90546800	8.56004400	21.38225200
C	-3.77589500	7.67553500	20.72730000
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H	-2.21074800	9.19604500	23.33082900
Br	1.08658400	1.95003400	18.64843200
Cl	2.29998500	5.82157800	13.67224800
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O	1.86217700	7.40920300	16.70356100
C	0.67682100	7.53947300	16.25176100
C	0.01765000	6.29730200	15.72264100
C	-0.99821300	6.38066000	14.52925700
C	0.86143200	5.06692500	15.87825000
C	1.92236100	4.76108000	15.01466800
C	2.71225200	3.62743100	15.19648000
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C	2.46887700	2.77419500	16.27235900
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C	1.42884800	3.08043700	17.14536000
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H	-2.16245800	11.09604800	12.16711600
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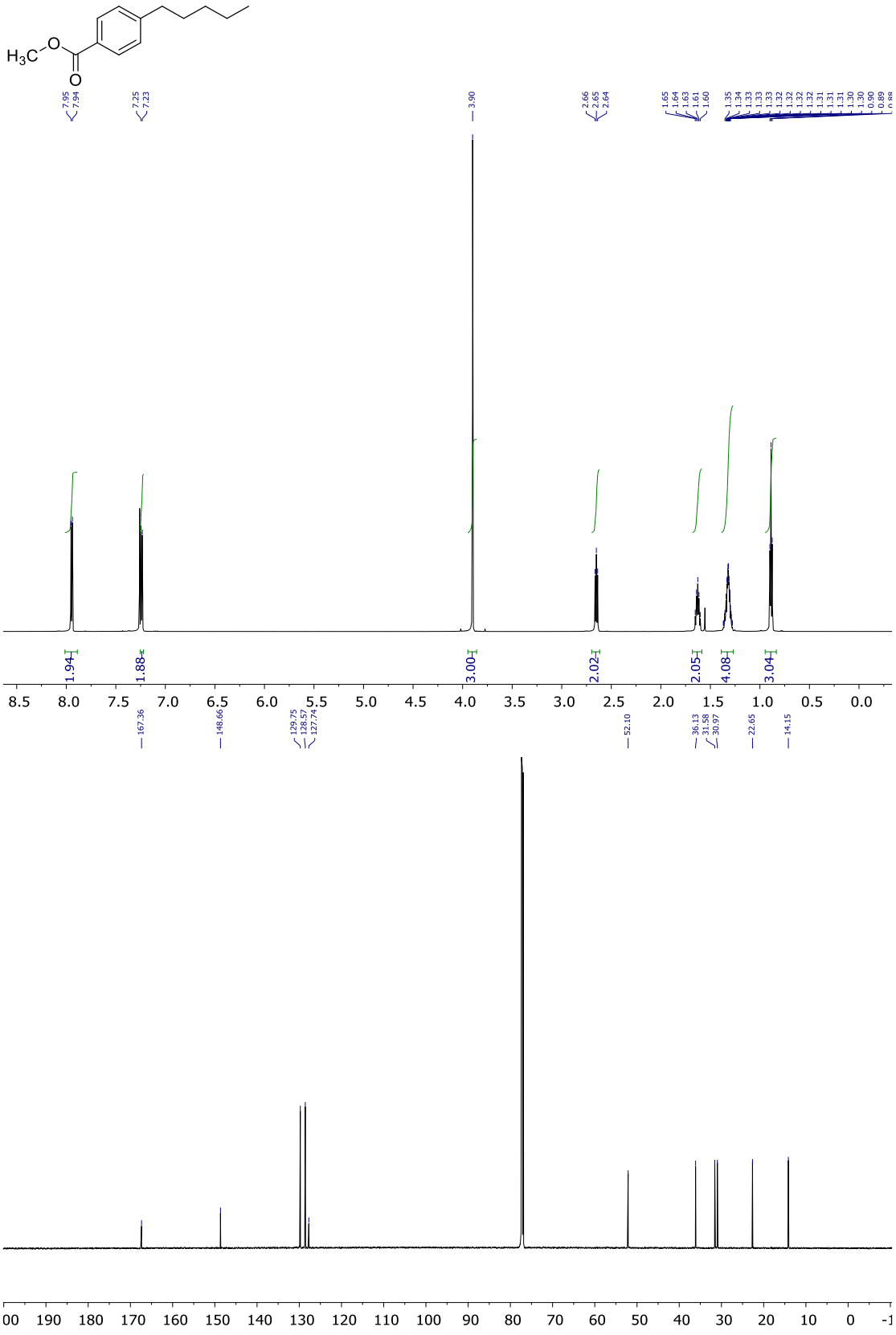
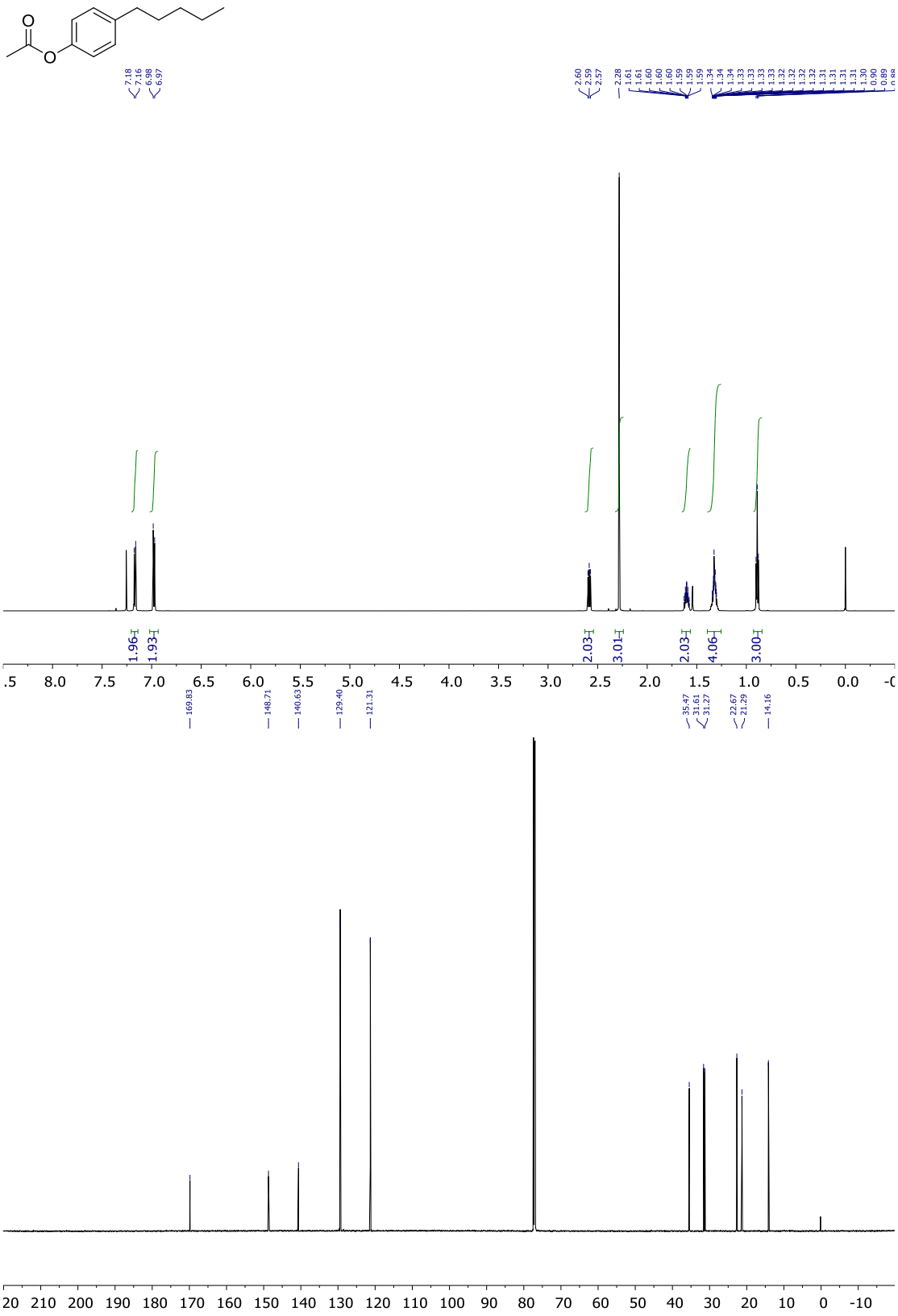
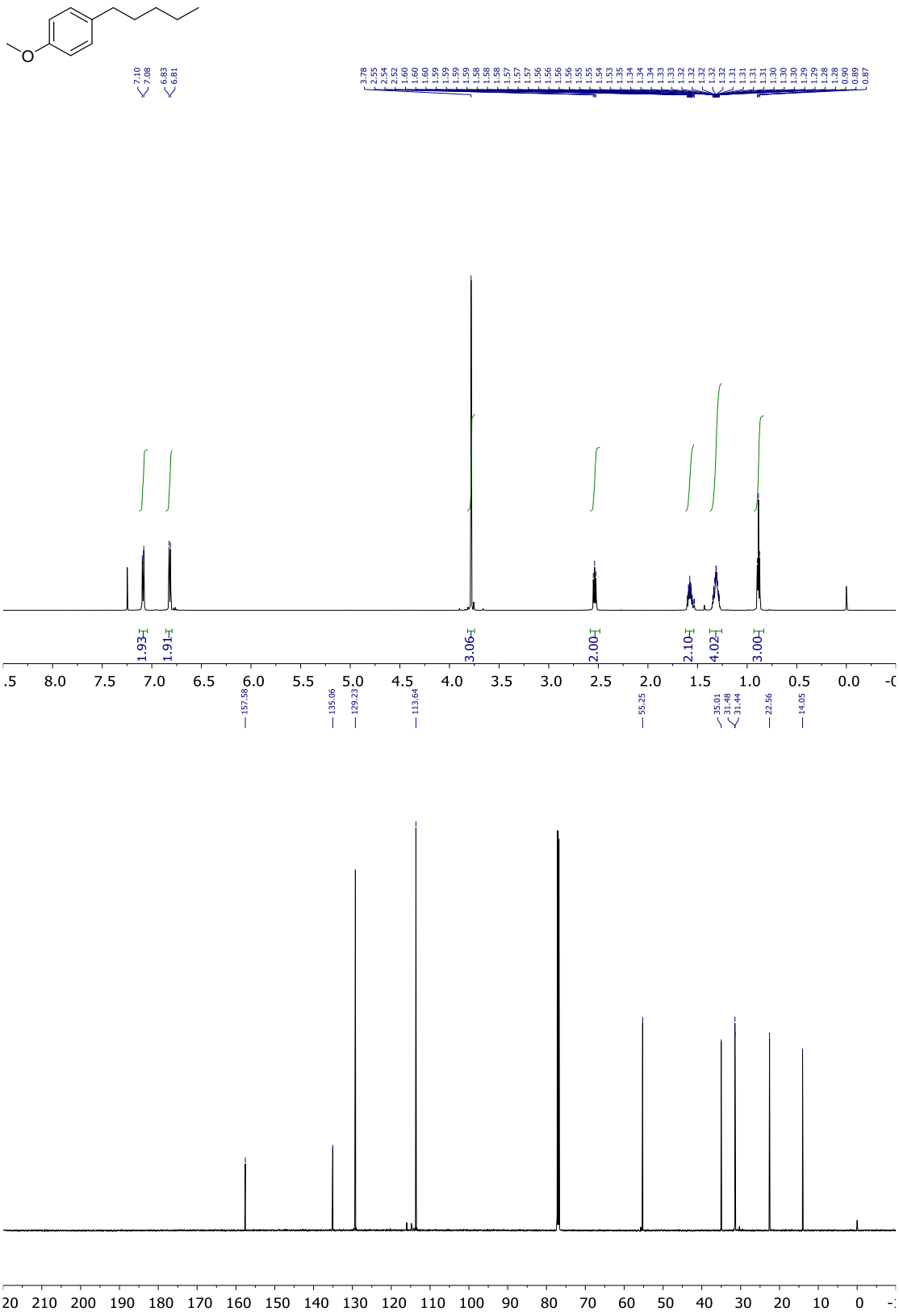
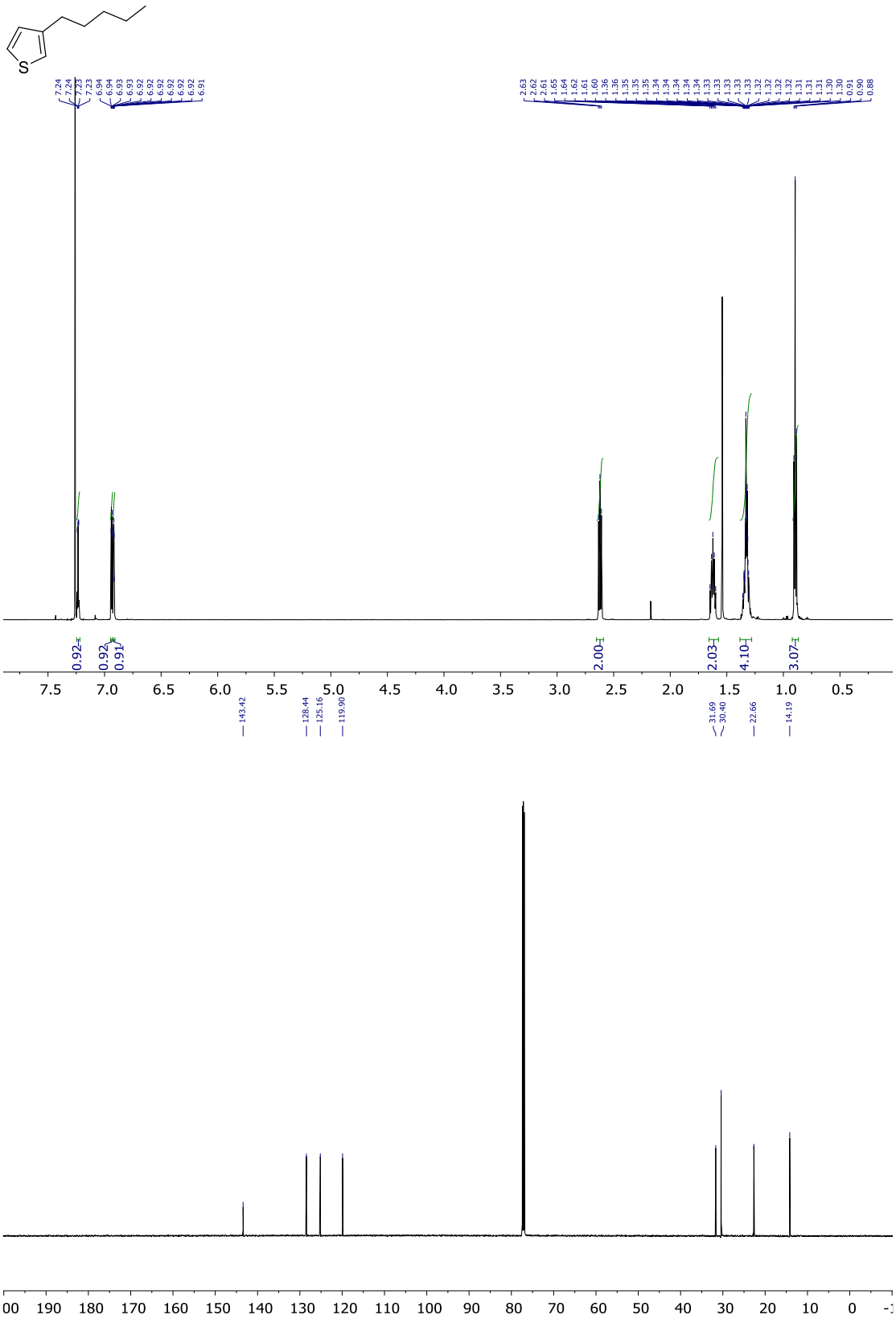
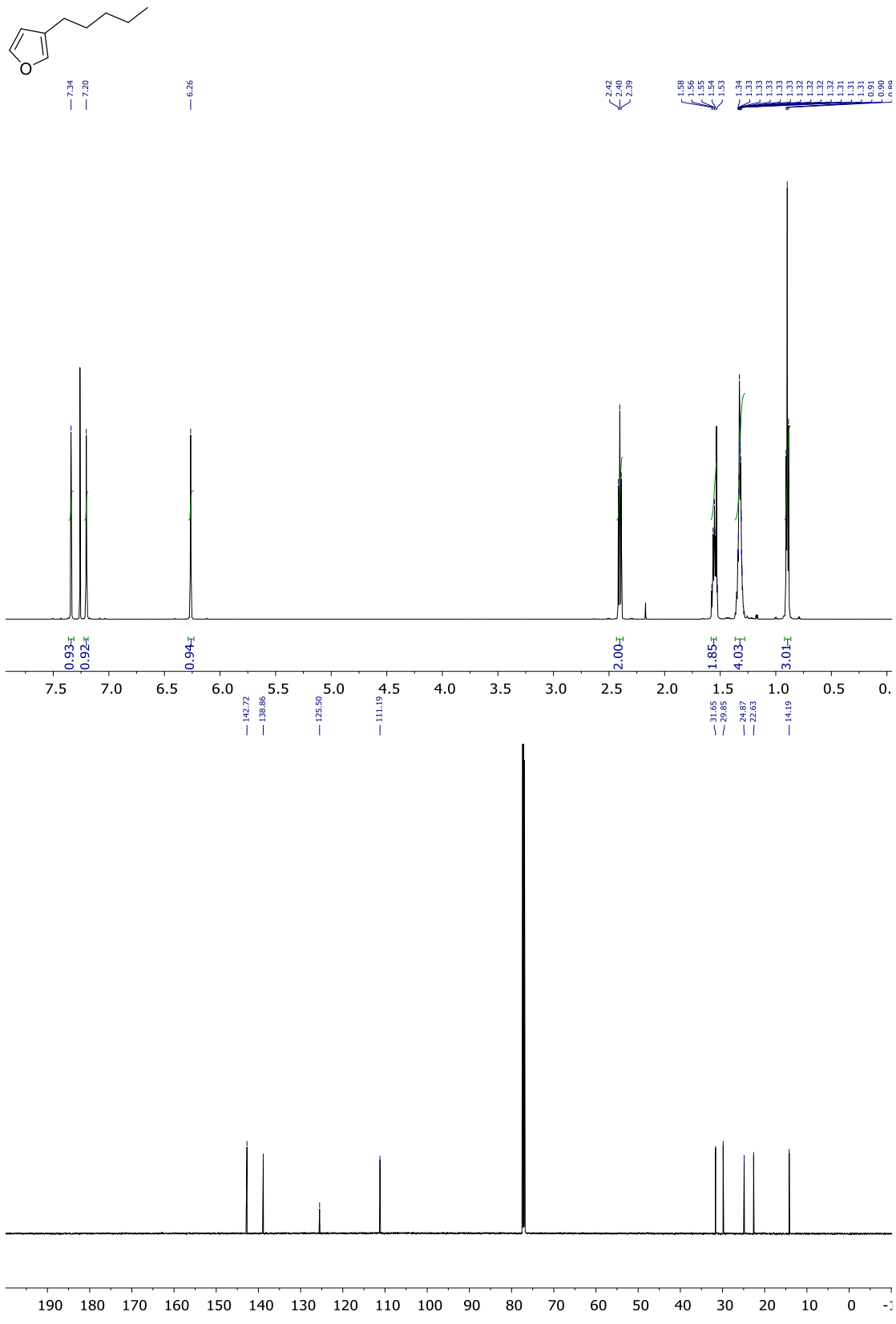
9. NMR Spectra for Characterizations







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1.33
1.33
1.33
1.33
1.32
1.32
1.32
1.31
1.31
1.31
1.31
0.91
0.90
0.93
0.92
0.94
2.00
1.85
4.03
3.01
7.5
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6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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138.86
125.50
111.19
31.65
29.85
24.87
22.63
14.19
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30
20
10
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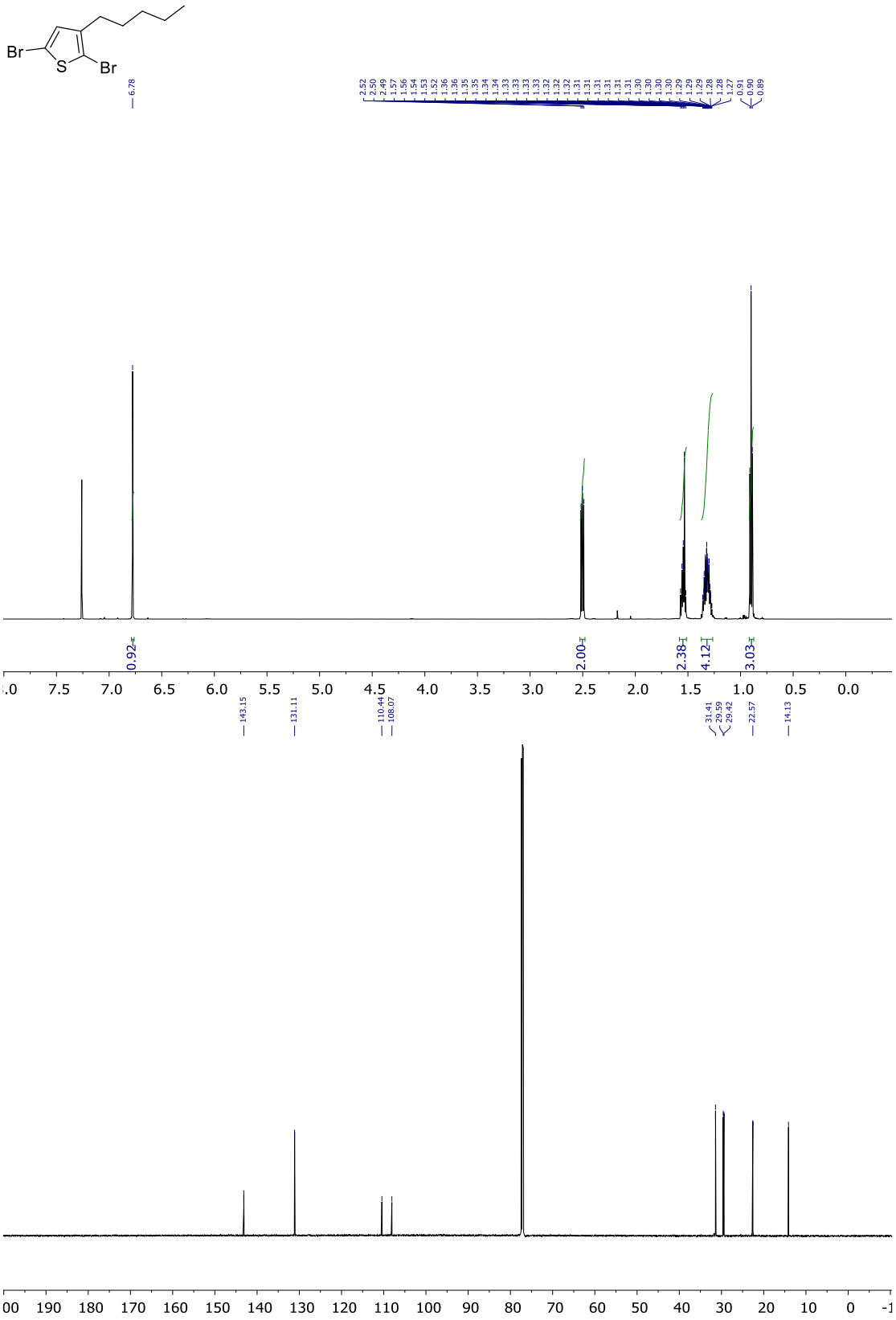
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1.31
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1.30
1.30
1.30
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0.89
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4.12
3.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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131.11
110.44
108.07
31.41
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29.42
22.57
14.13
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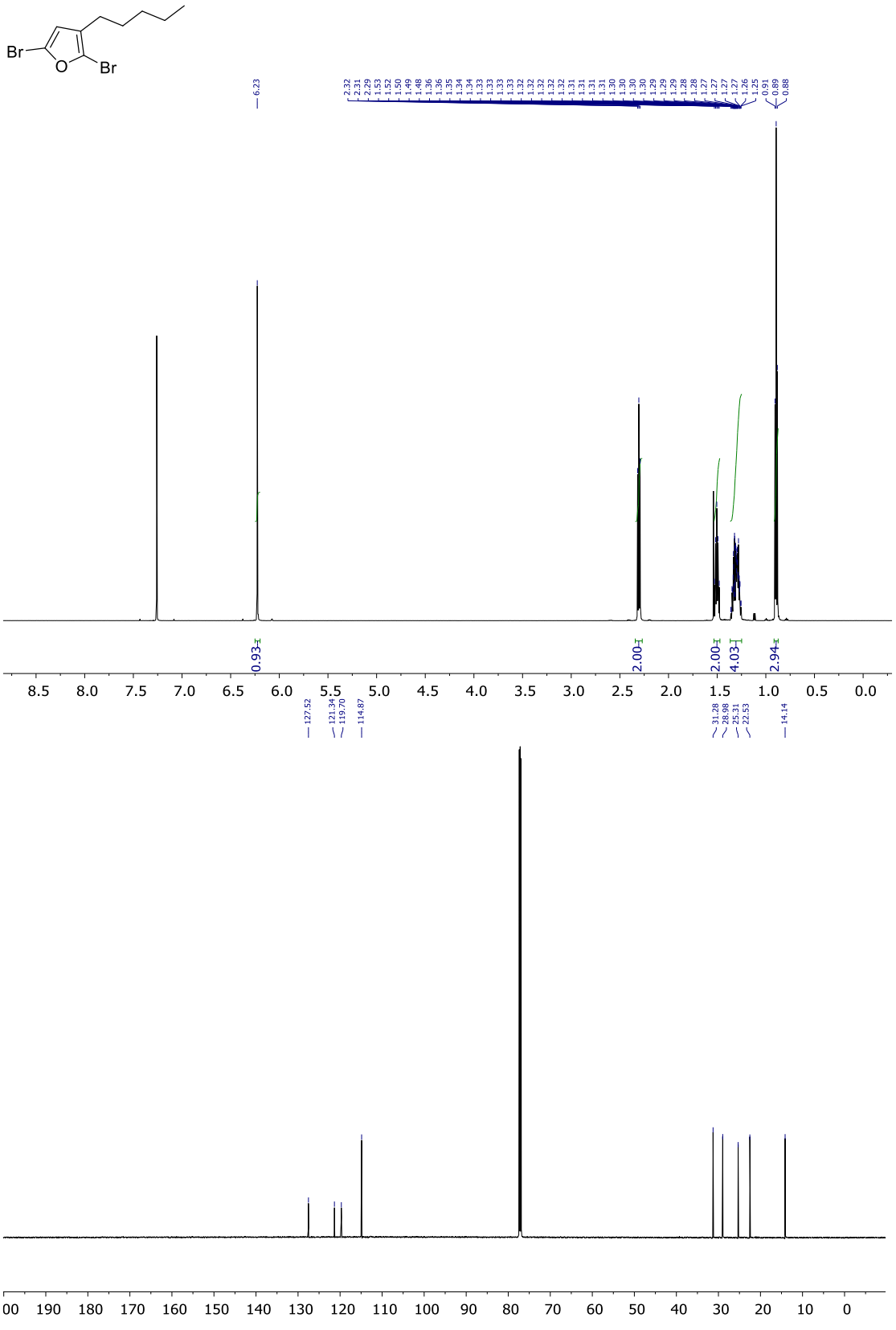
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Br
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127.52
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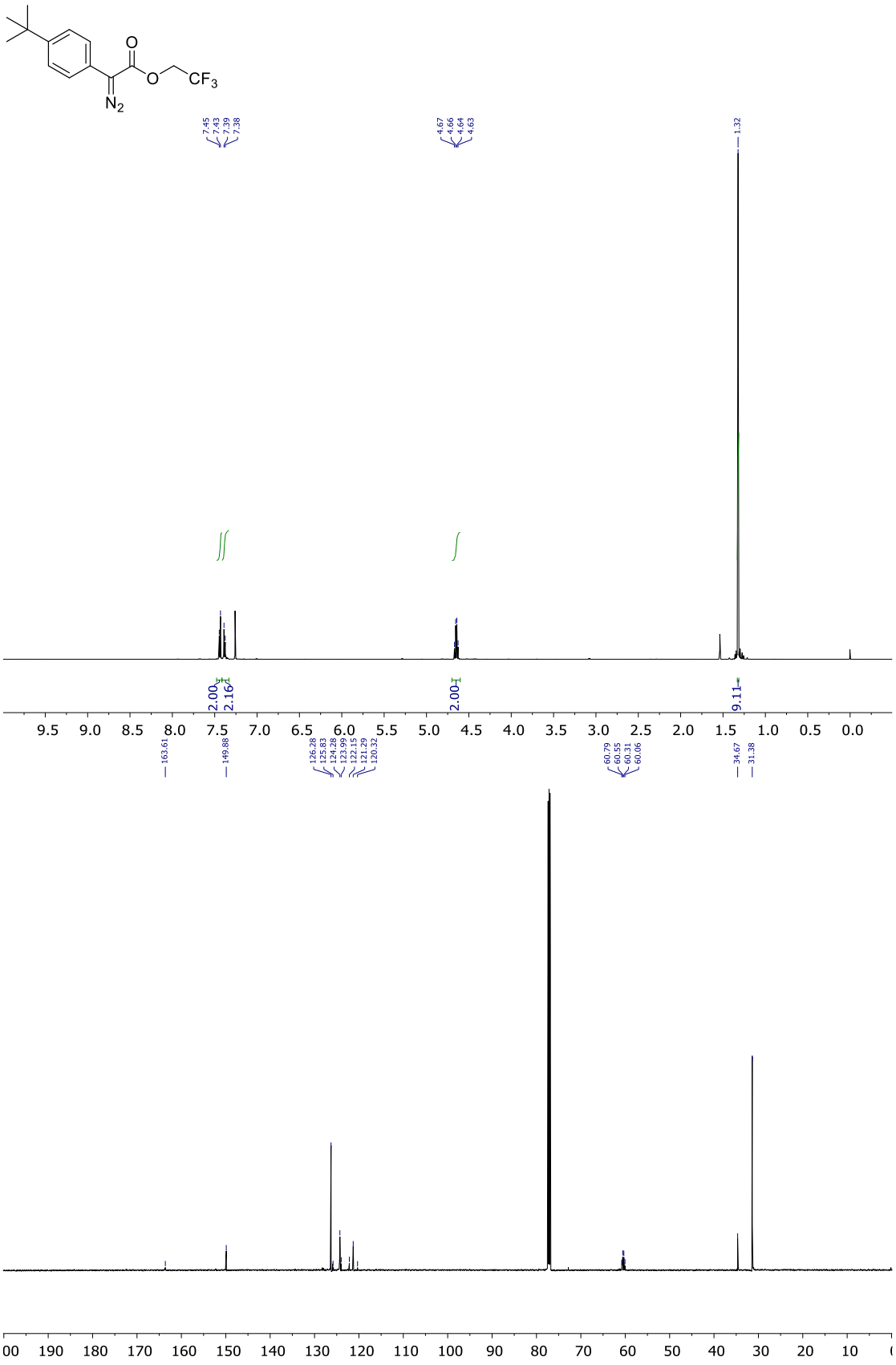
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9.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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149.88
126.28
125.83
124.28
123.99
122.15
121.29
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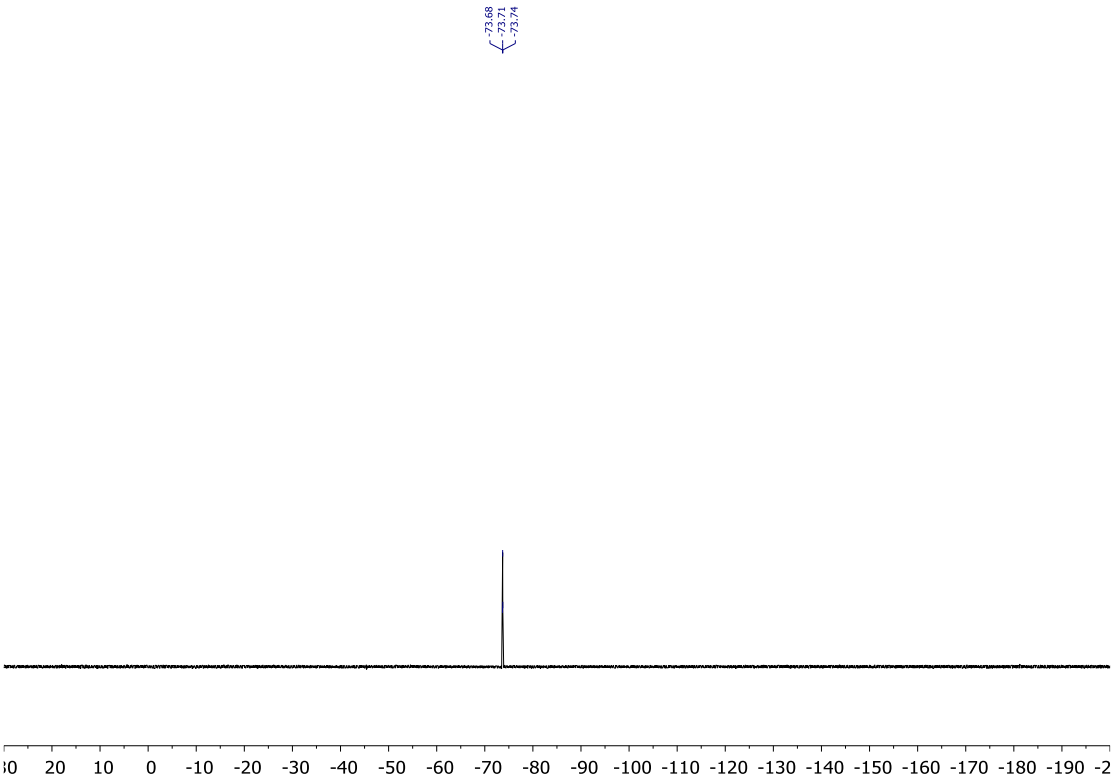
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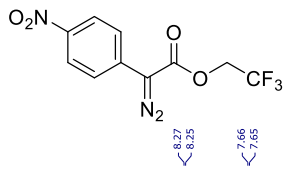
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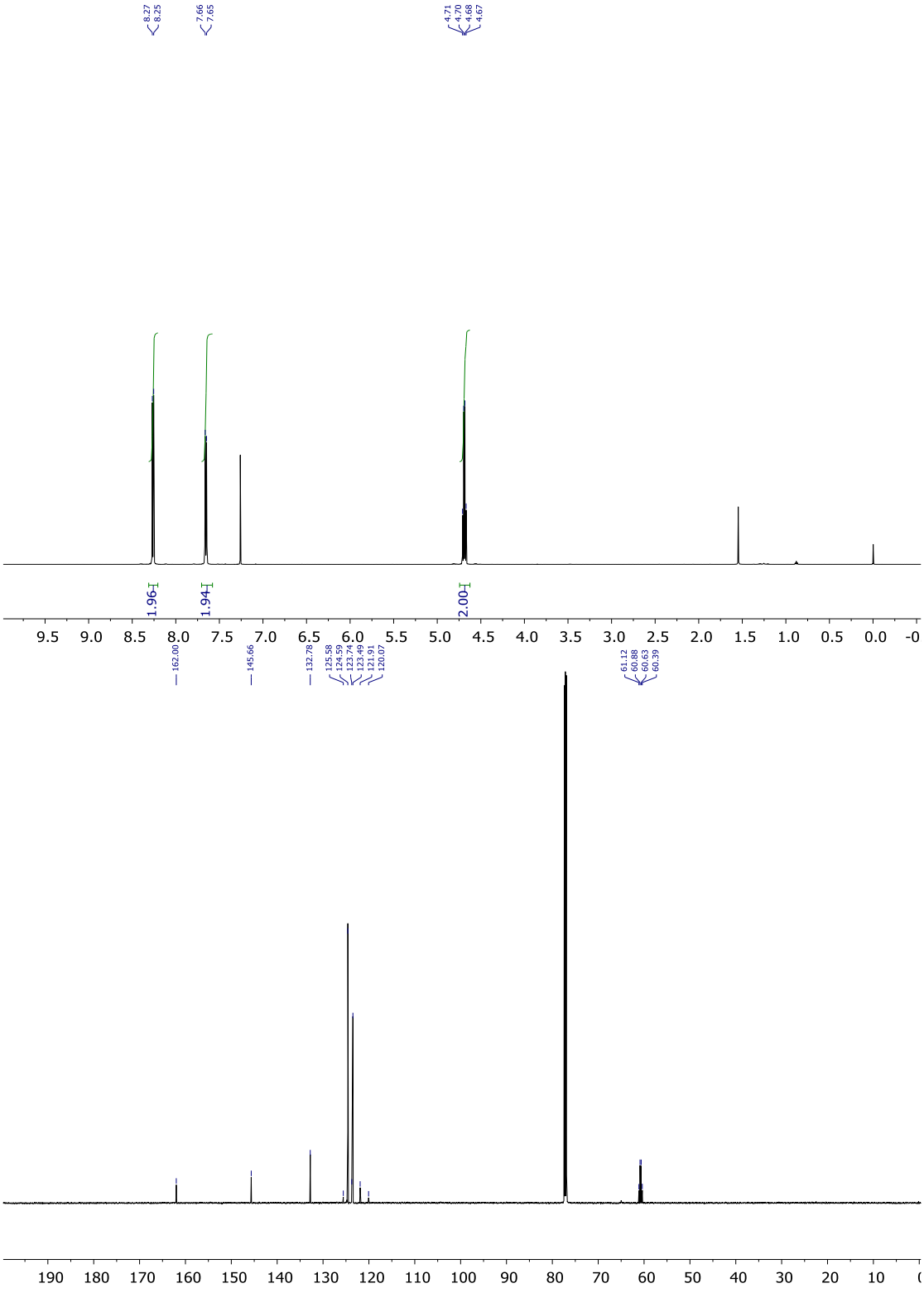
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4.70
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4.67
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1.94
2.00
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125.58
124.59
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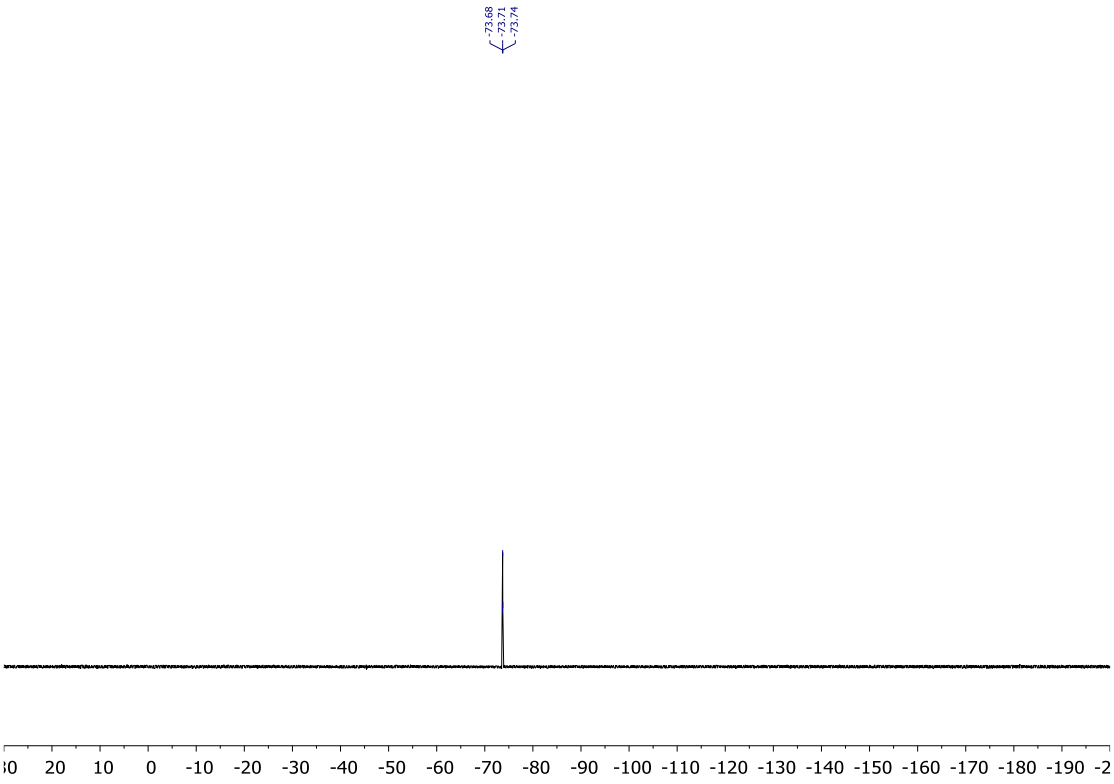
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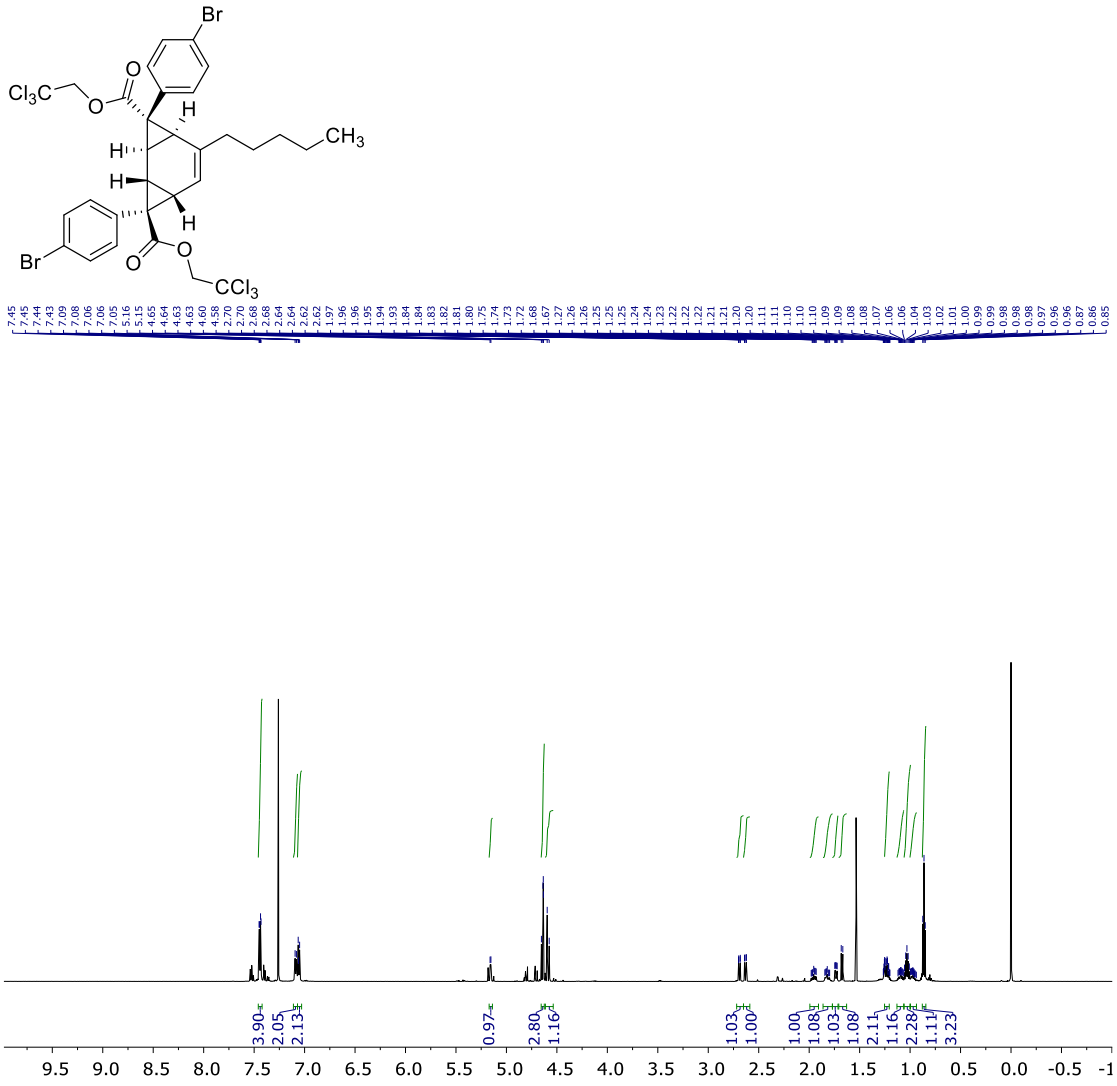
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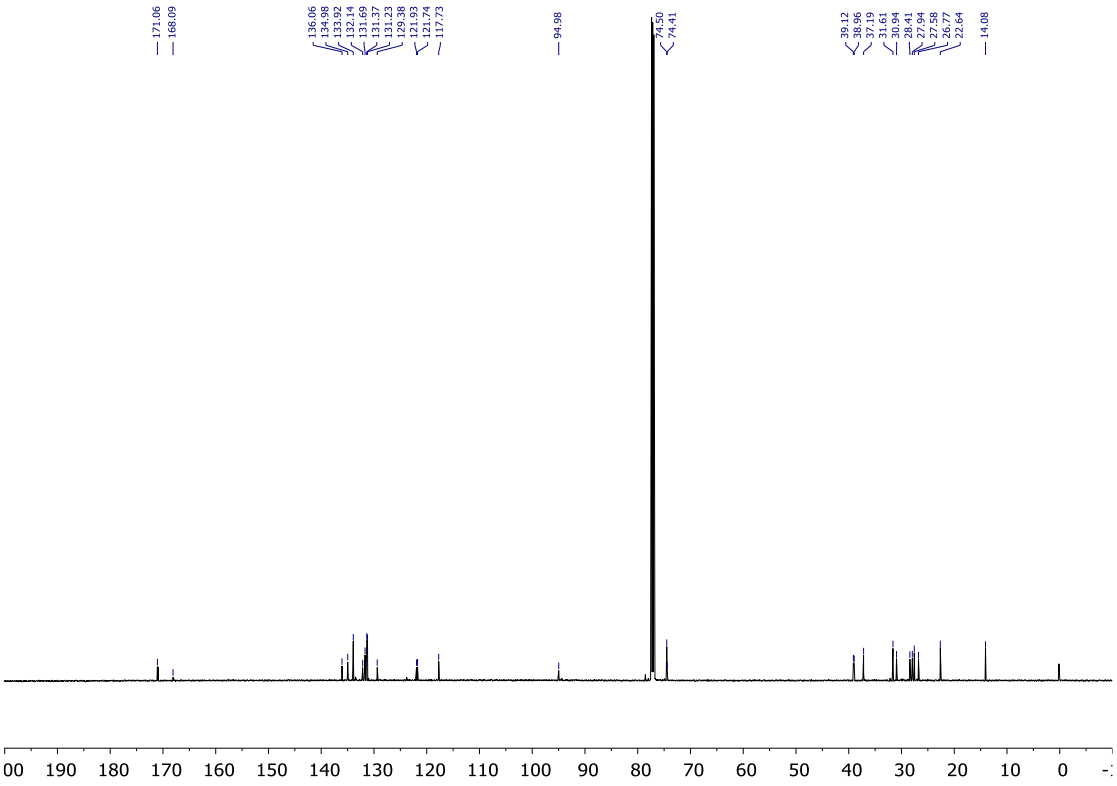
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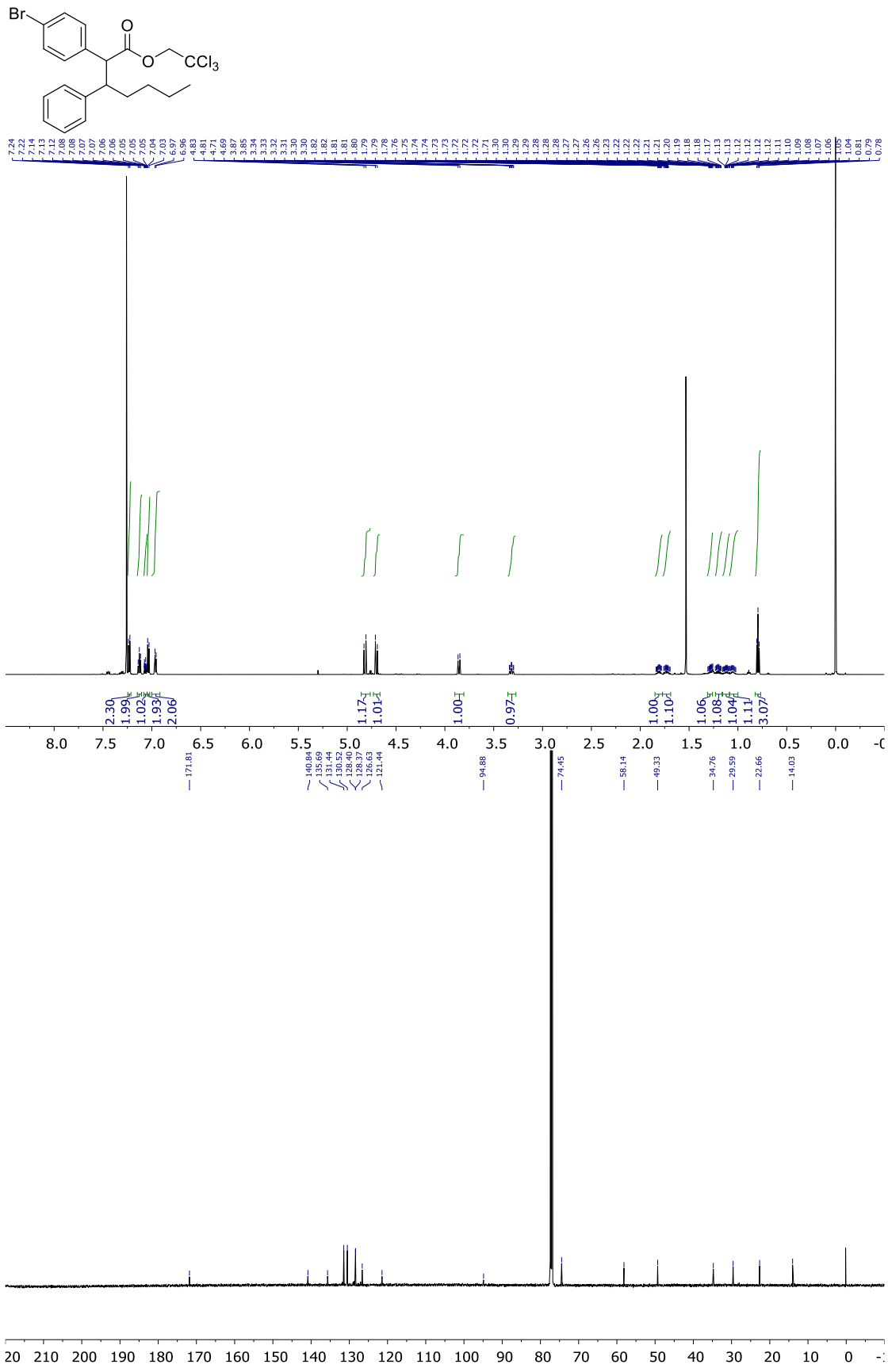
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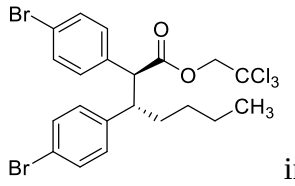
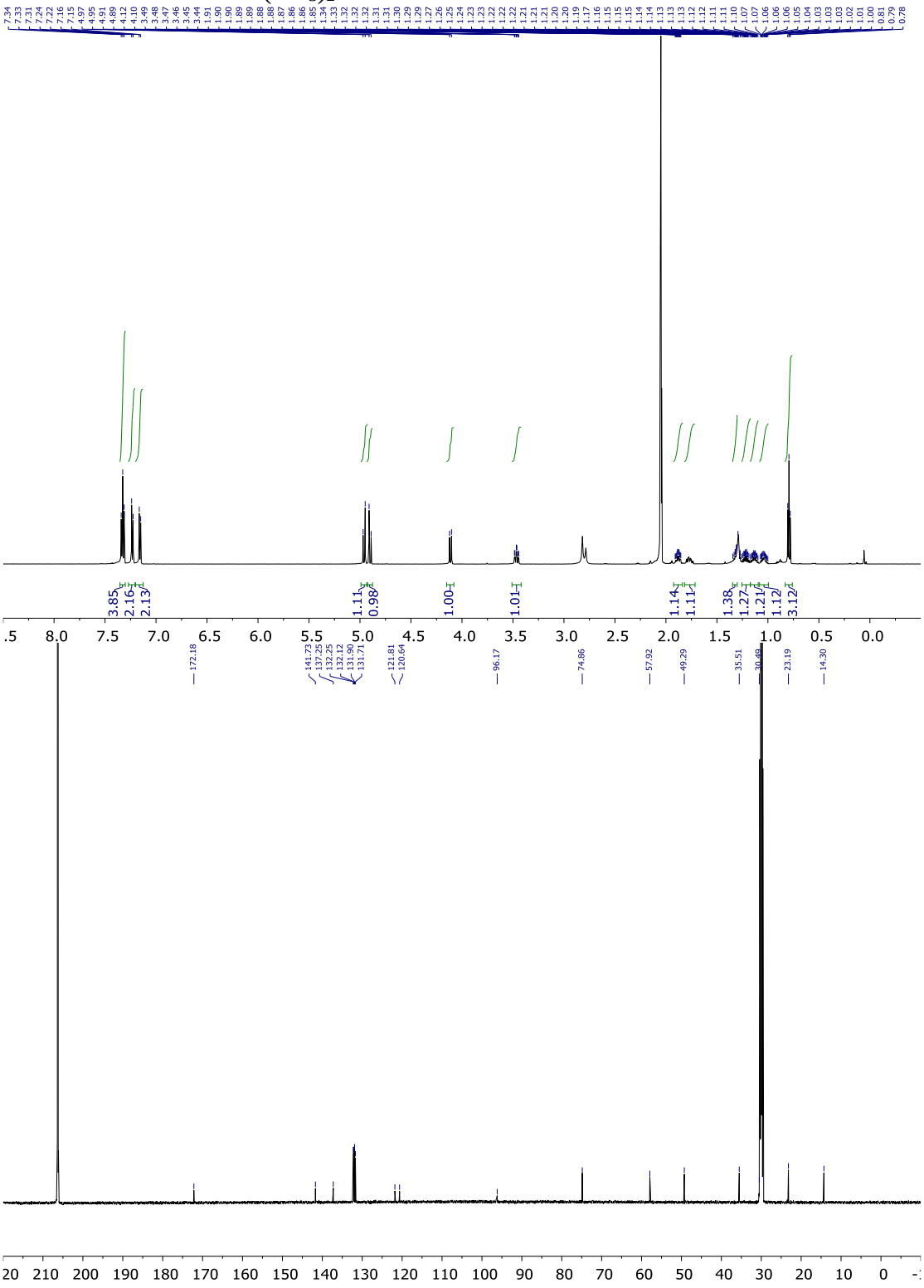
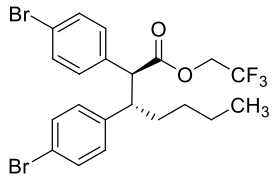


in $(CD_3)_2CO$

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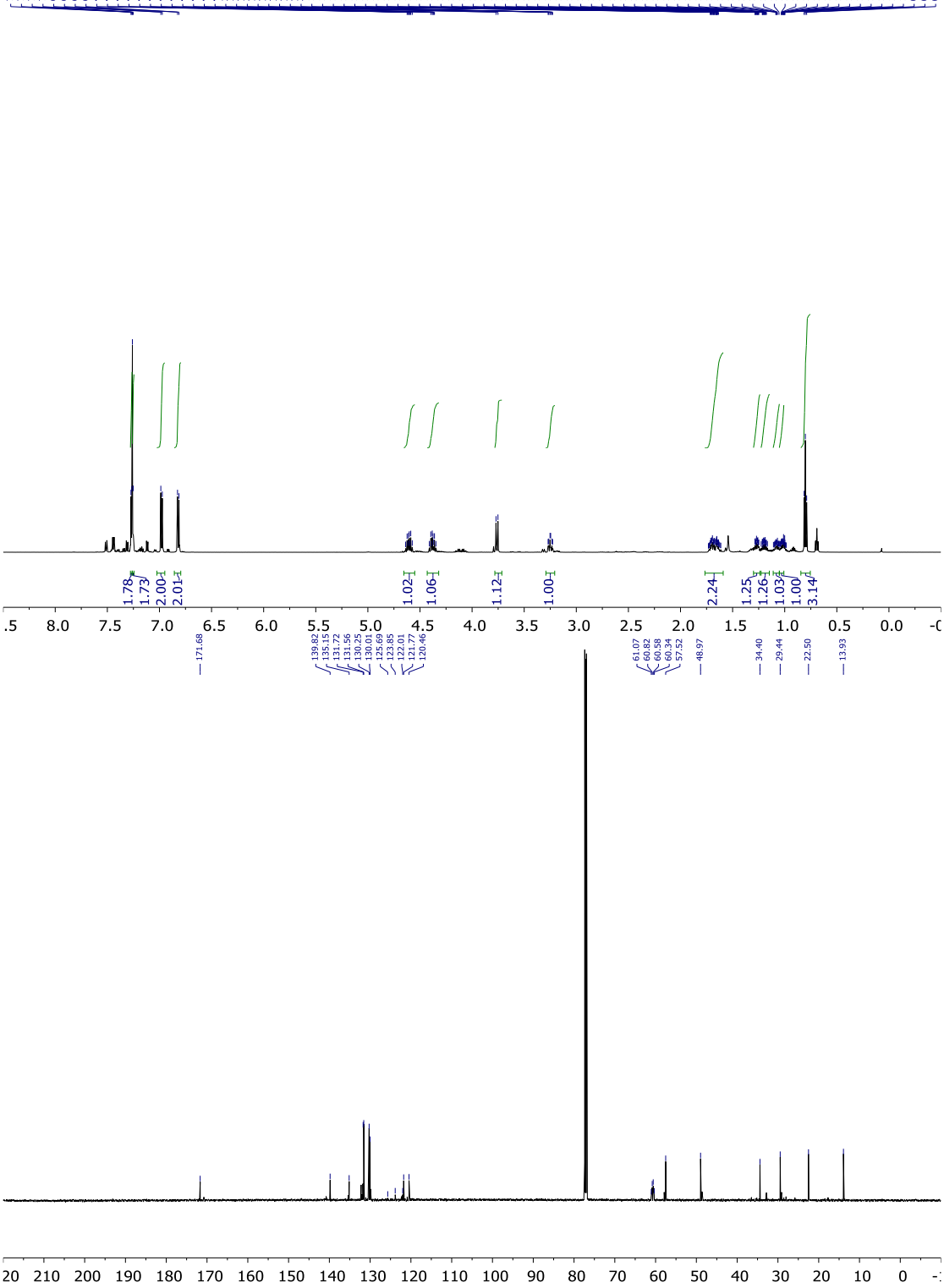
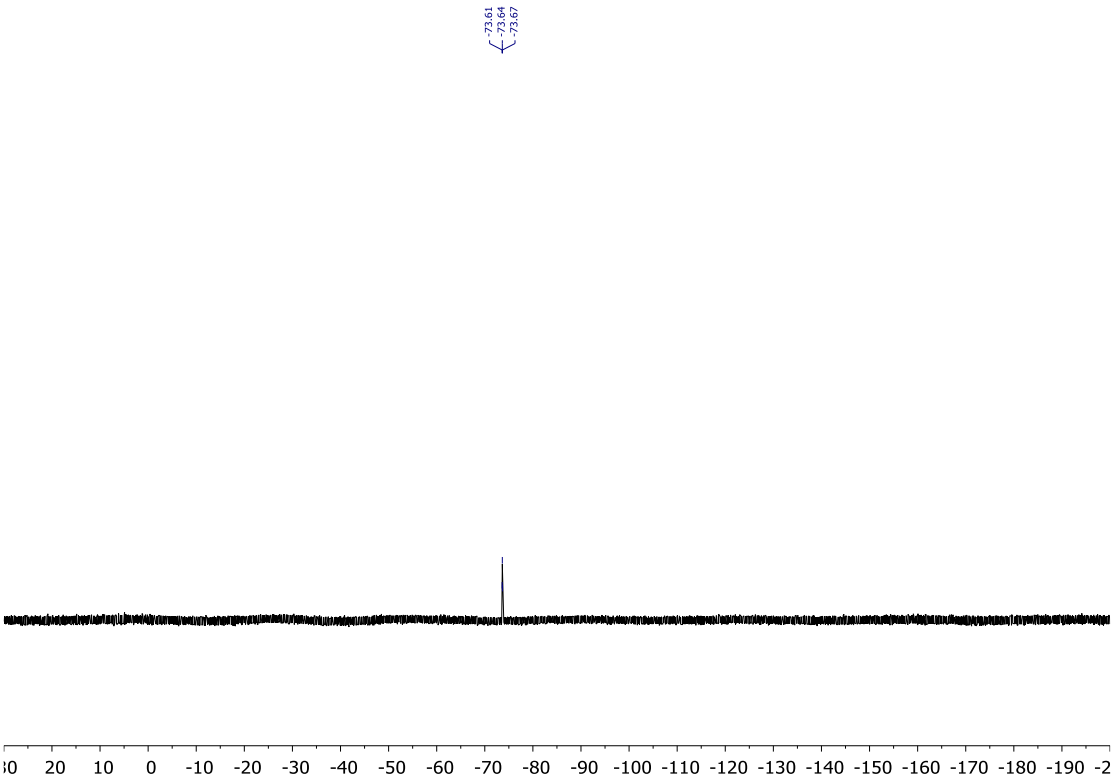
O
O
CF3
CH3
Br

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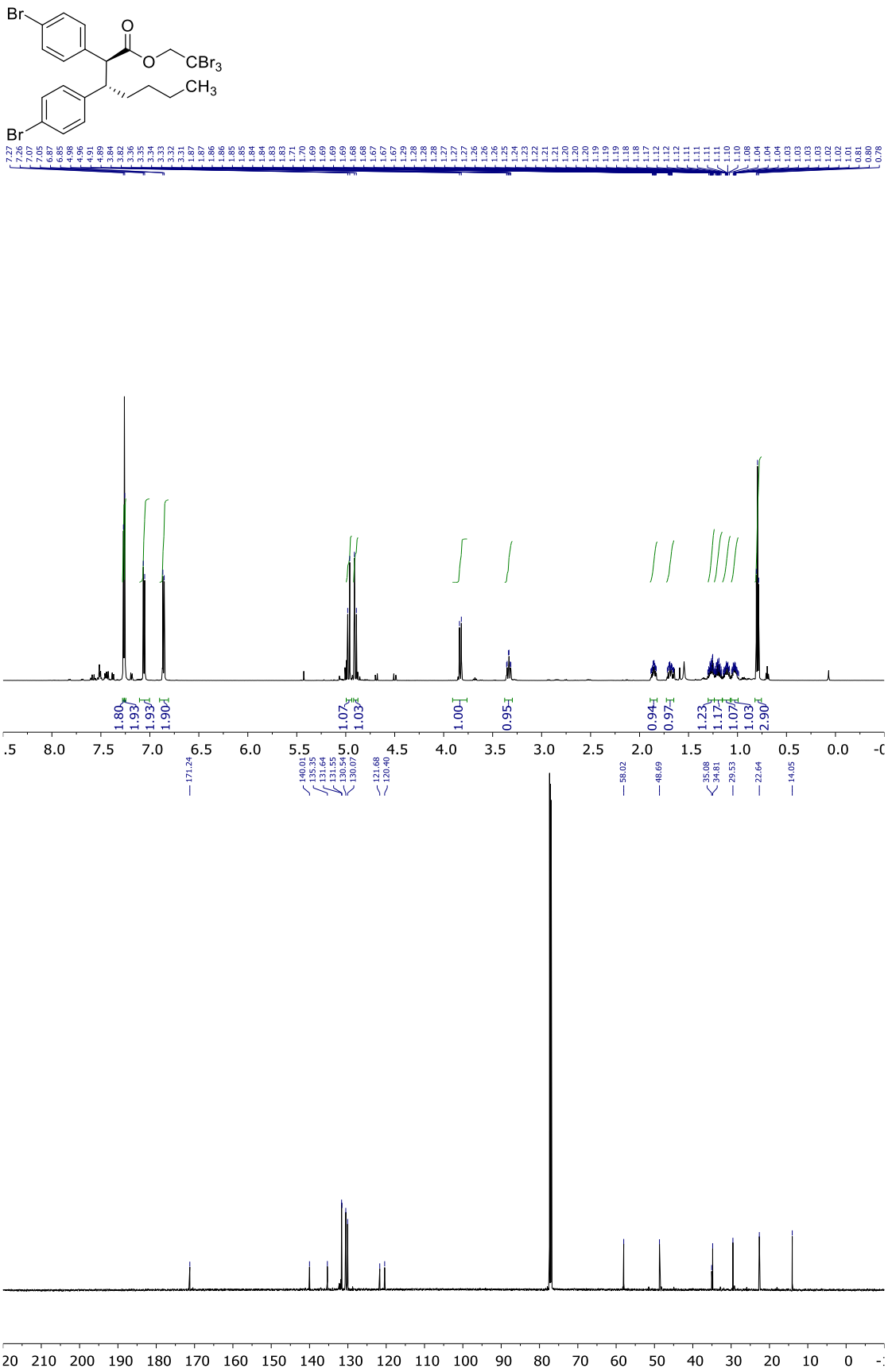
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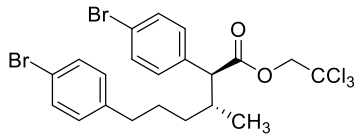
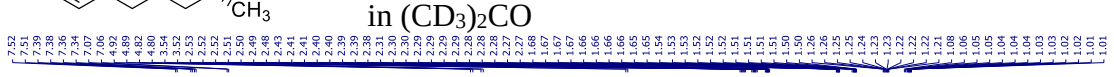
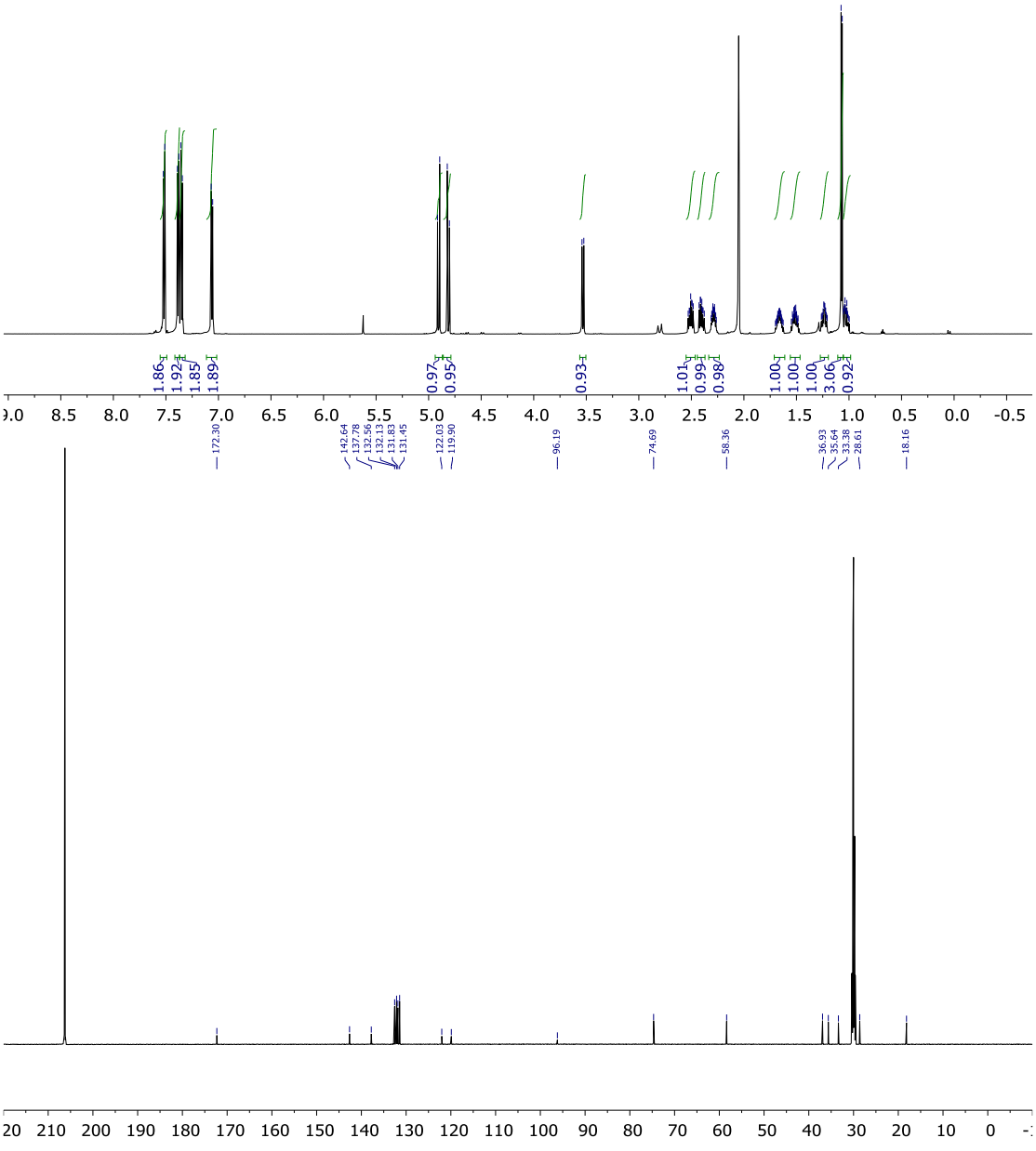
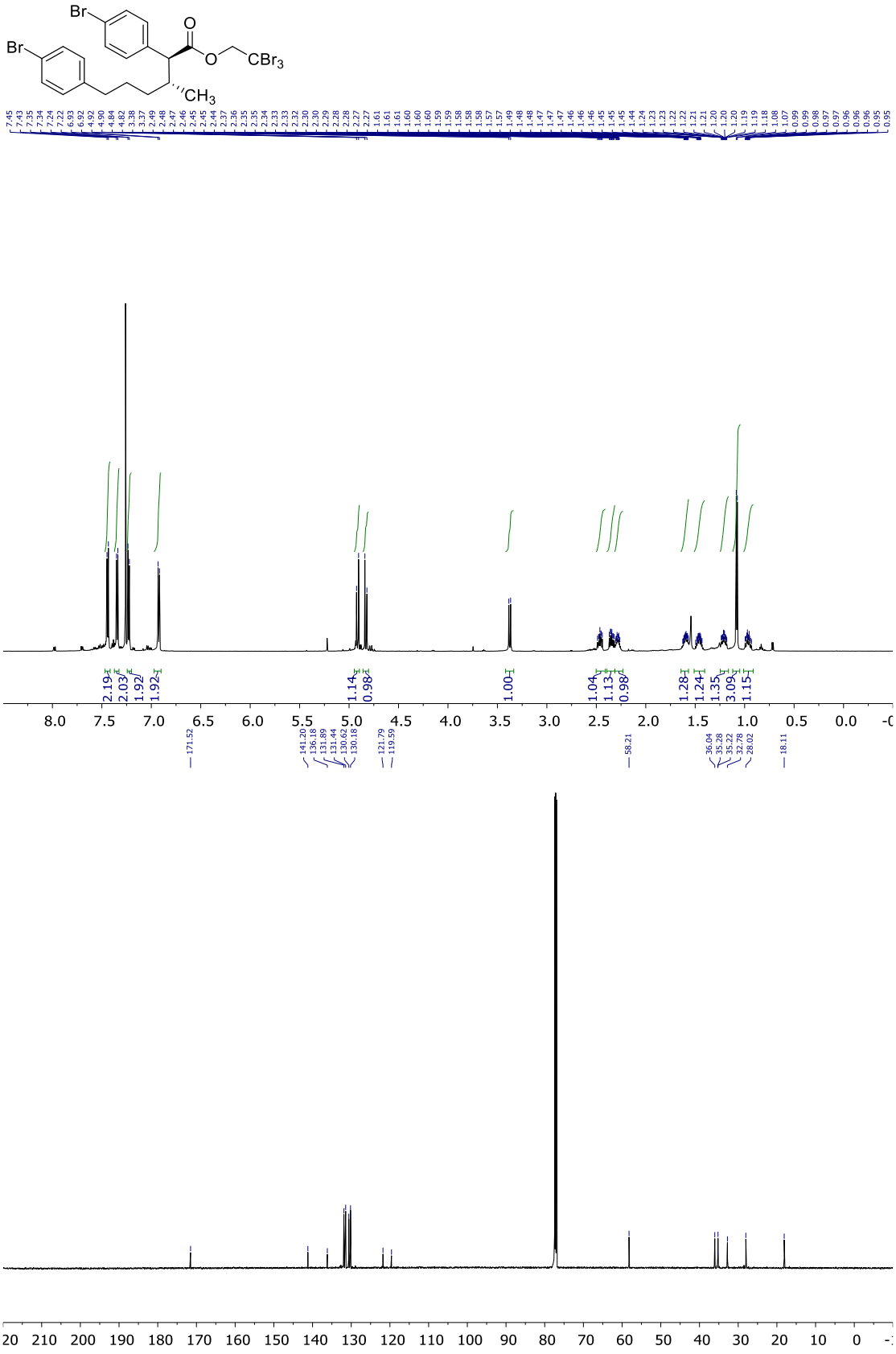
O
O
CBr3
CH3
Br



in $(CD_3)_2CO$



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O
CBr3
CH3
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1.92
1.14
0.98
1.00
1.04
1.13
0.98
1.28
1.24
1.35
3.09
1.15
171.52
141.20
136.18
131.89
131.44
130.62
130.18
121.79
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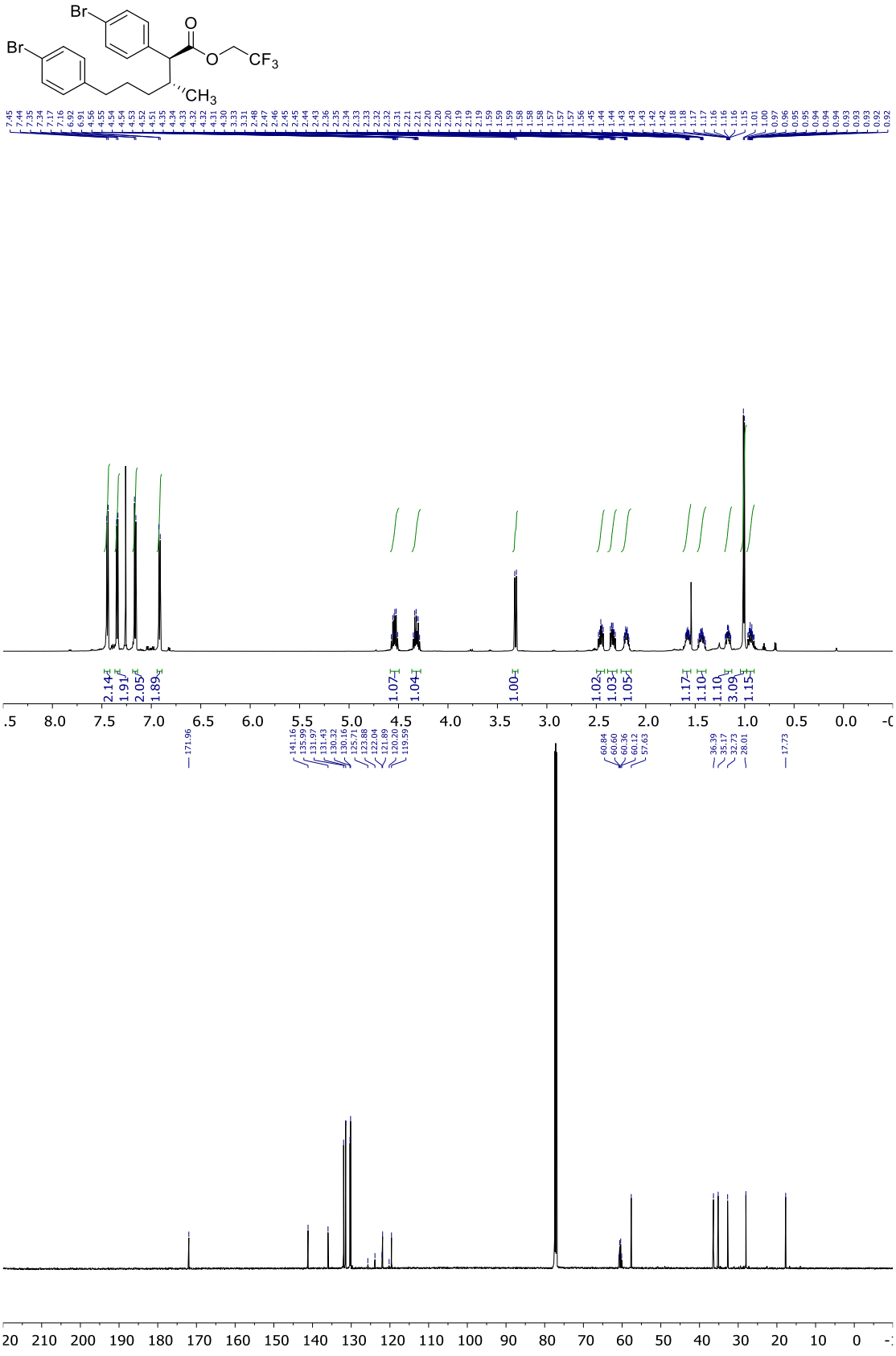
35.28
35.22
32.78
28.02
18.11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Br
O
O
CF3
CH3
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1.89
1.07
1.04
1.00
1.02
1.03
1.05
1.17
1.10
3.09
1.15
171.96
141.16
135.99
131.97
131.43
130.32
130.16
125.71
123.88
122.04
121.89
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57.63
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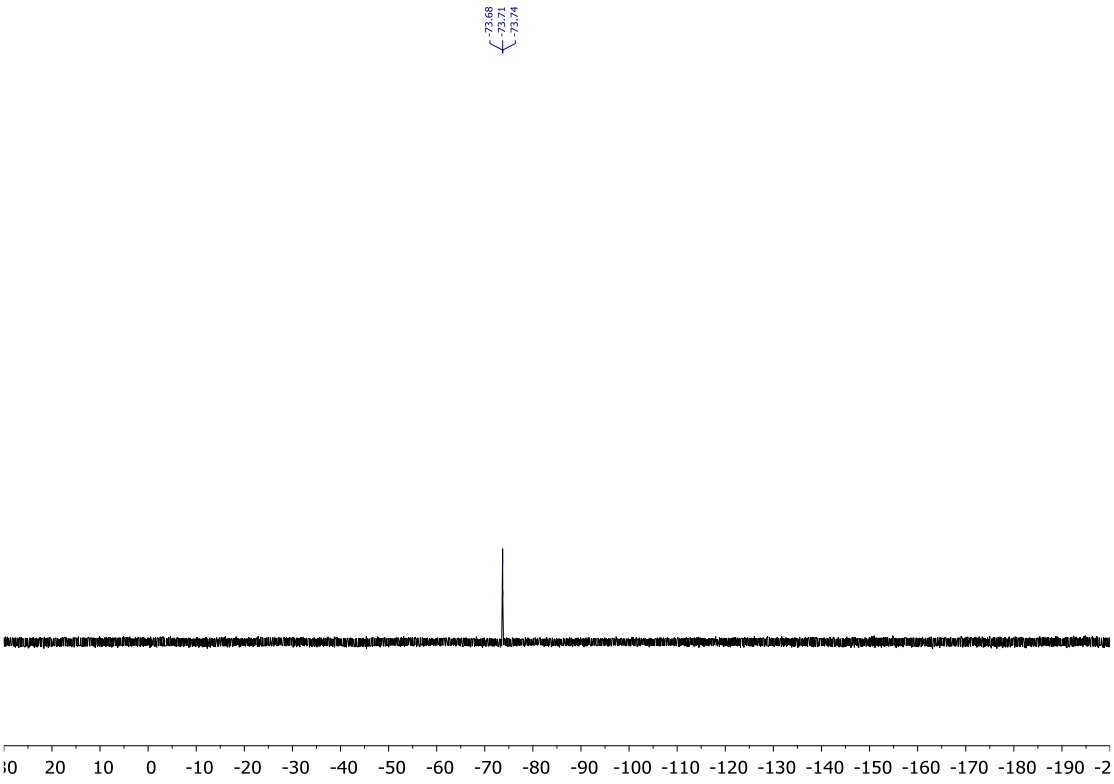
28.01
17.73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-73.74
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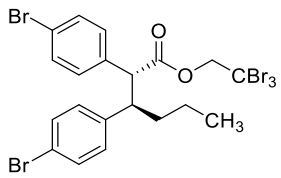
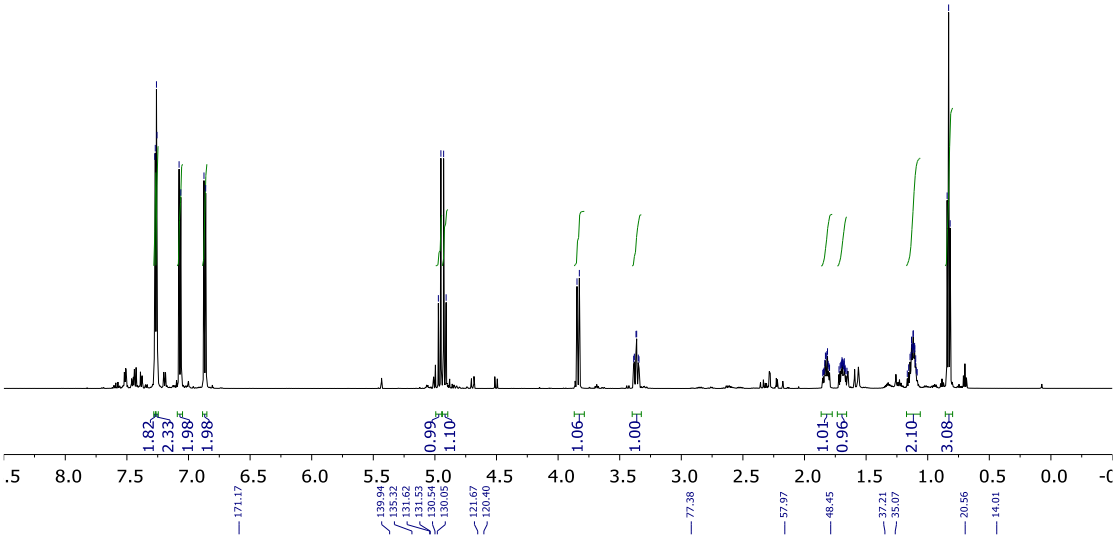

Br
O
O
CBr3
CH3
Br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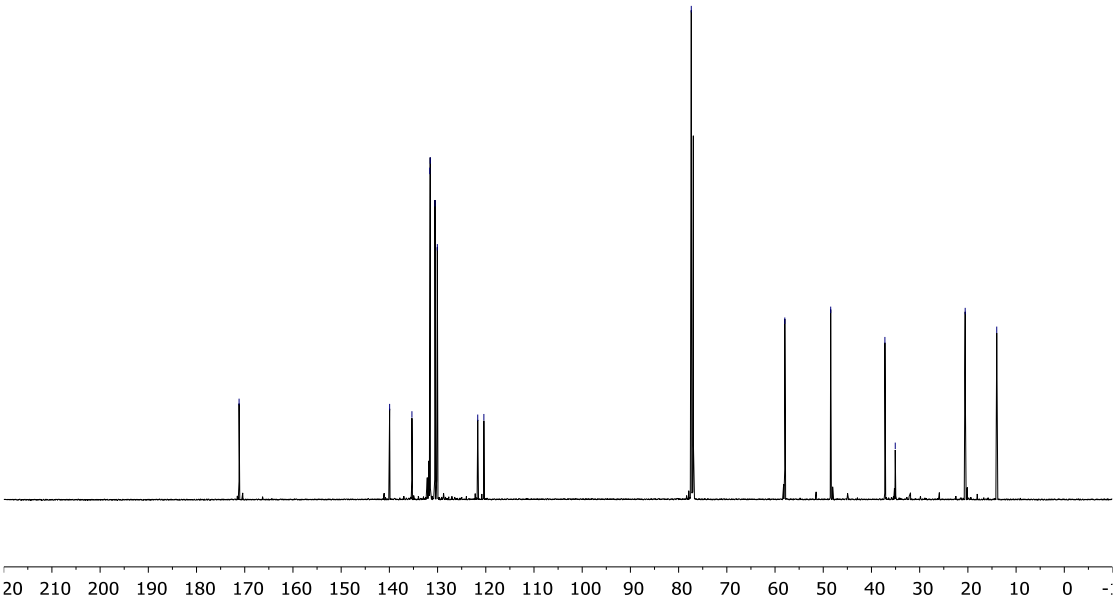
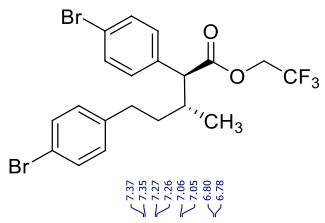
1.00
1.01
0.96
2.10
3.08

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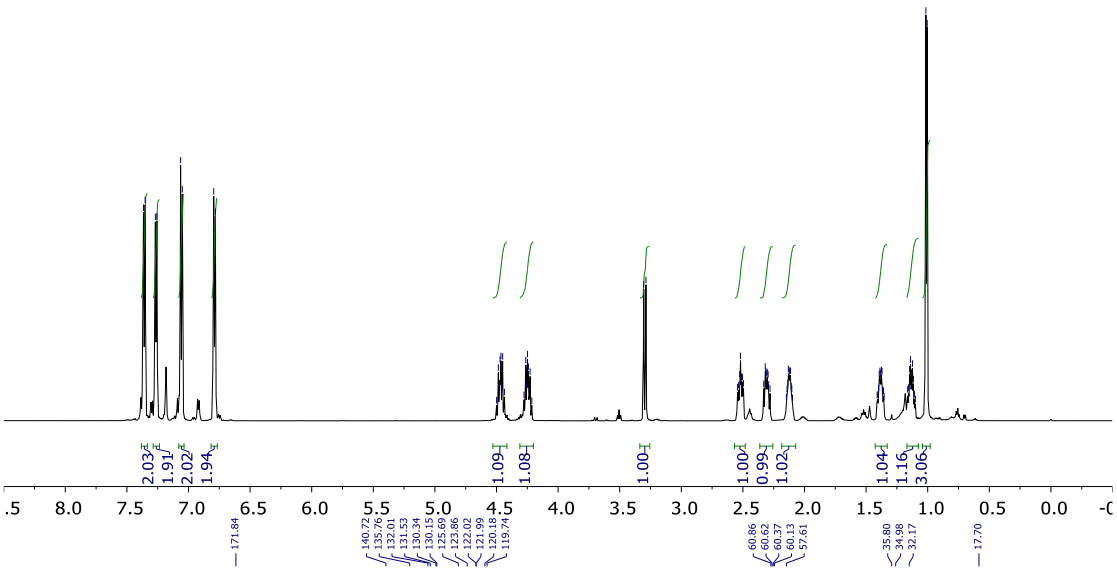
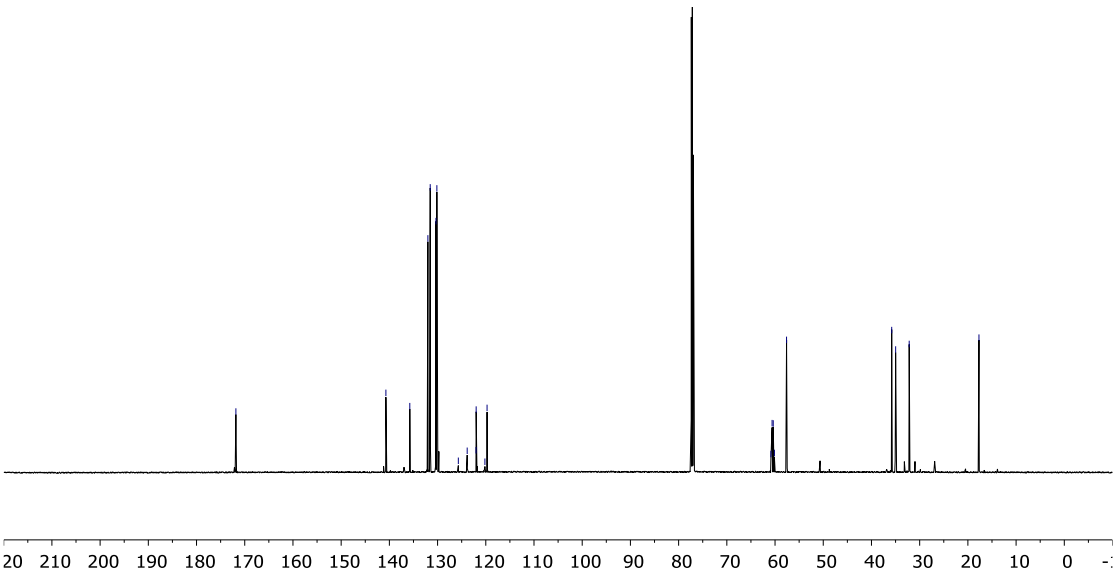
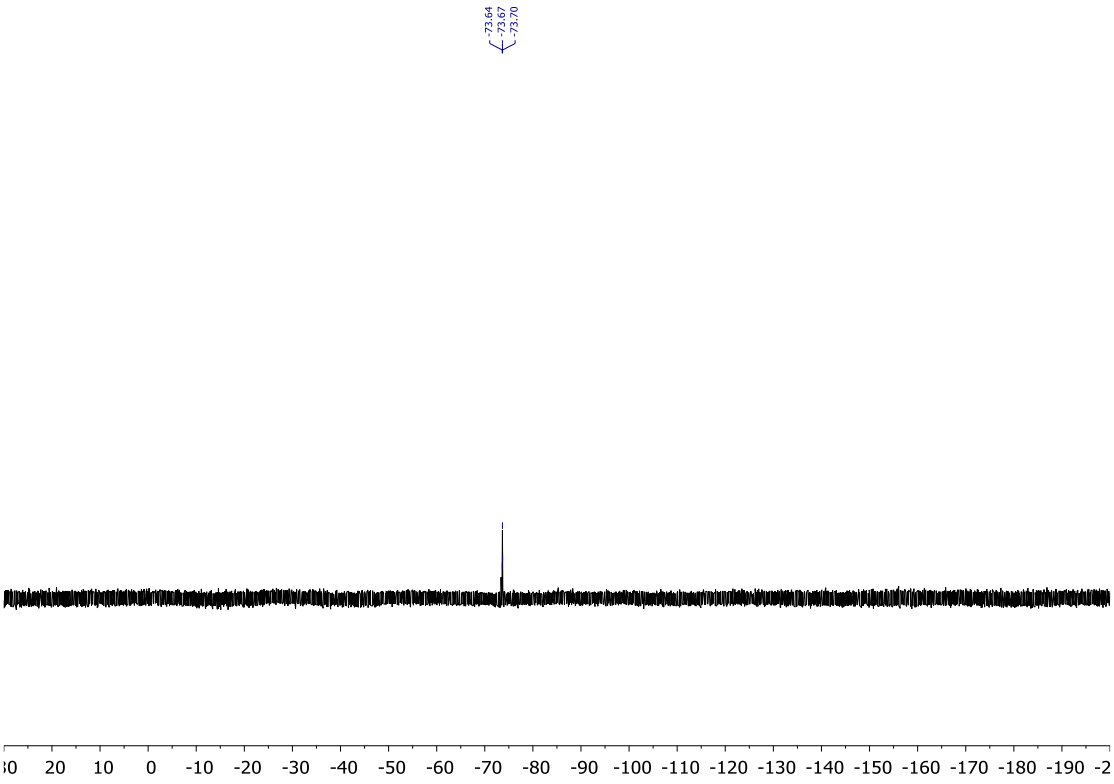
O
CF3
CH3
Br



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-73.70
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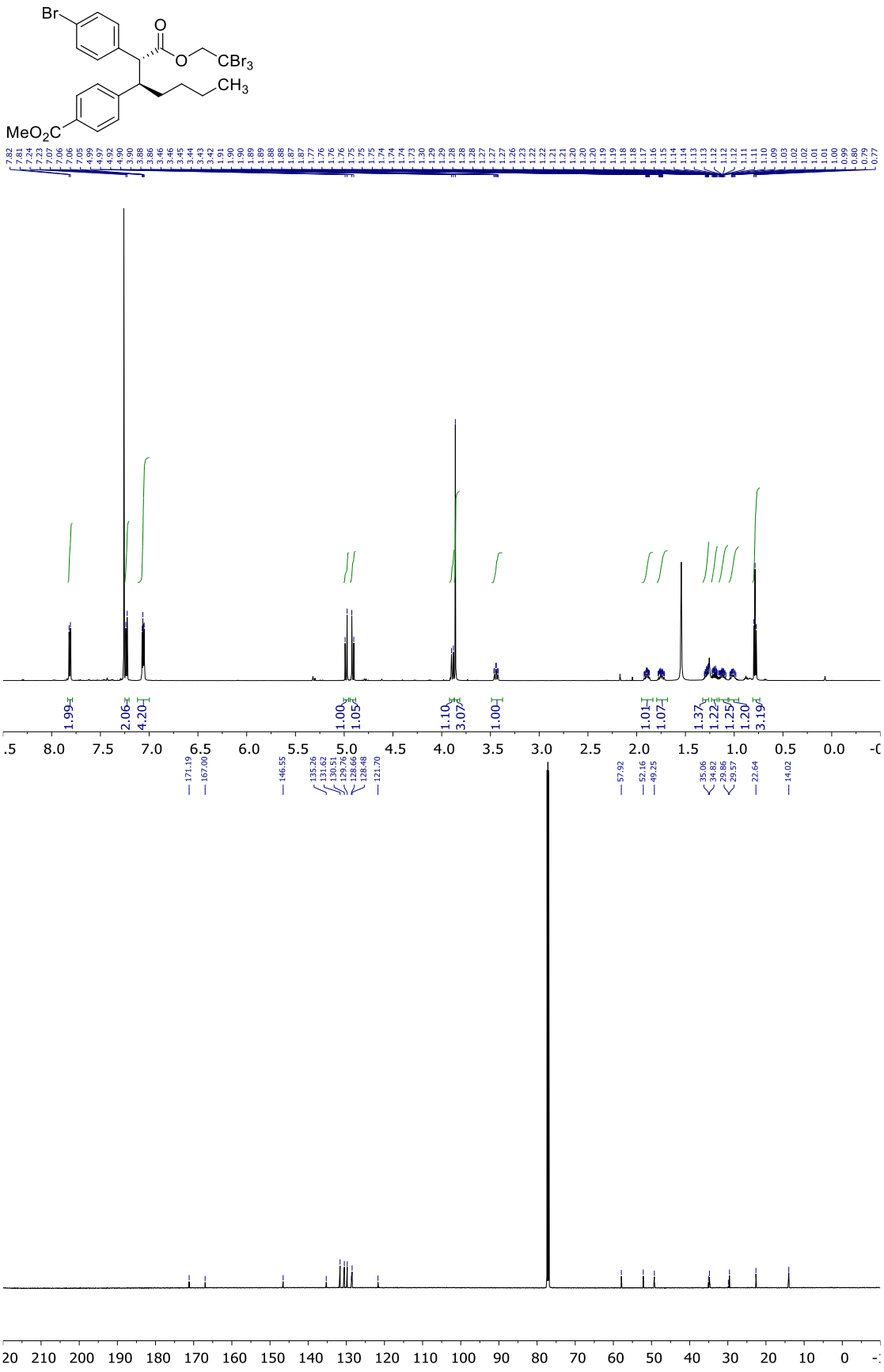
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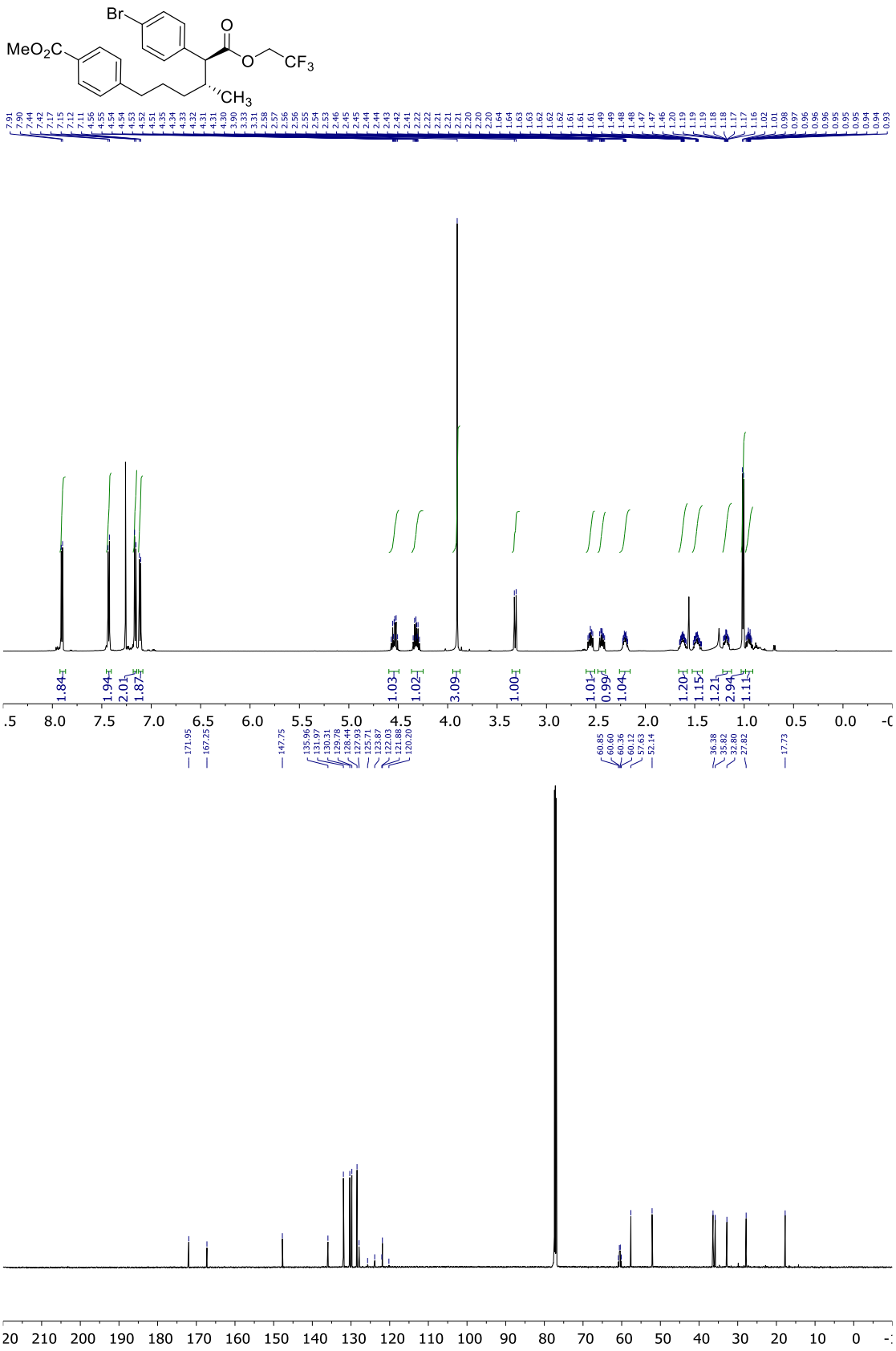
O
CBr3
CH3
MeO2C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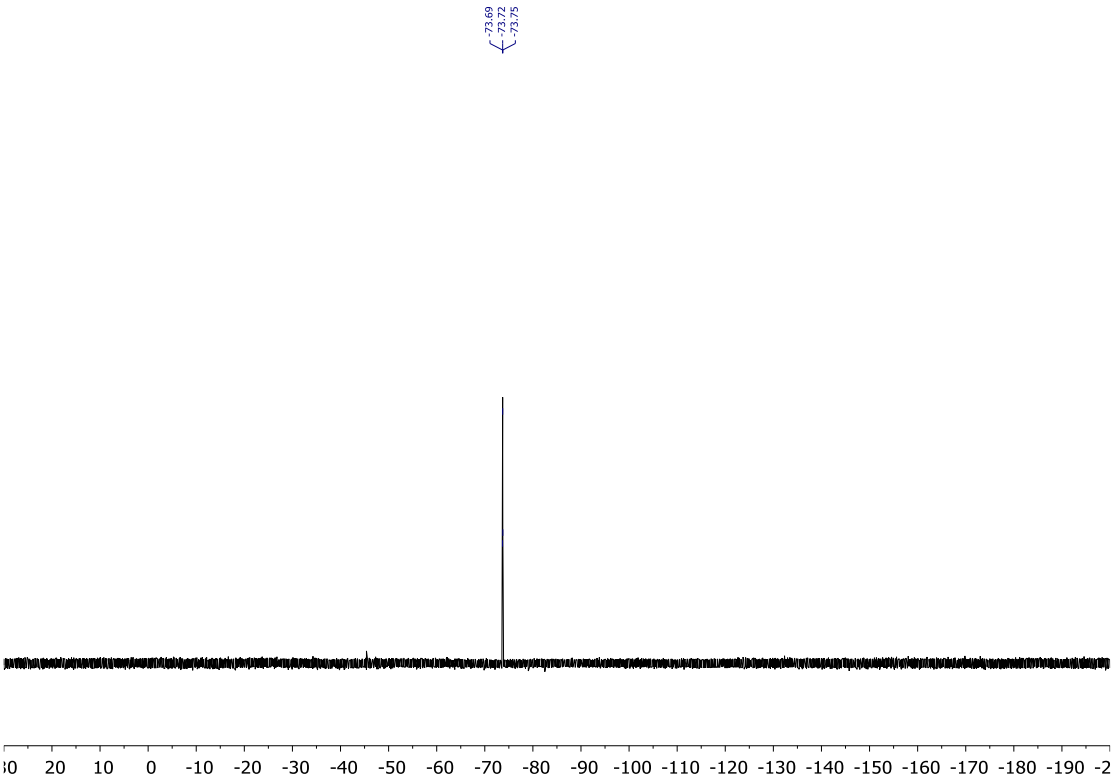
O
MeO2C
O
CF3
CH3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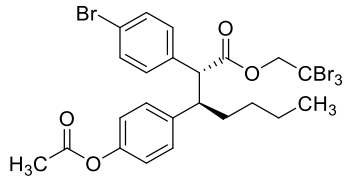
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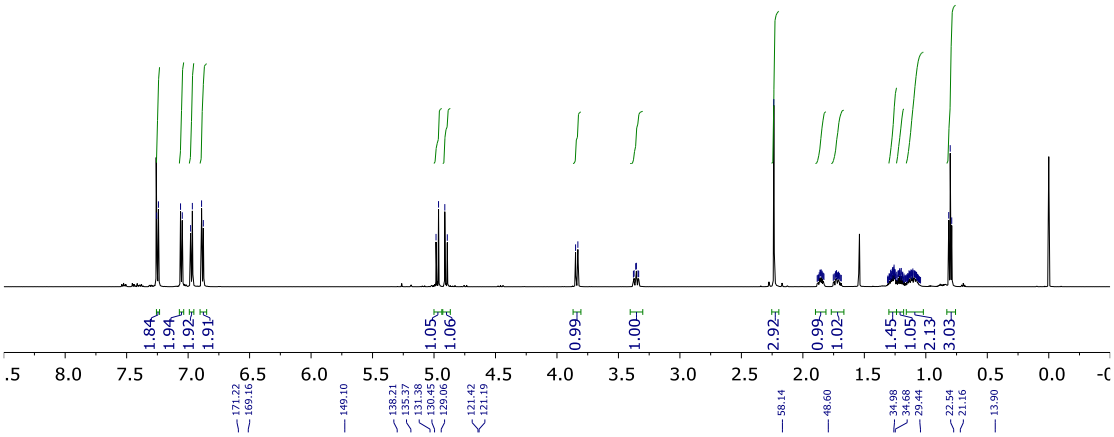
CBr3
CH3
O
H3C
O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1.91
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1.06
0.99
1.00
2.92
0.99
1.02
1.45
1.05
2.13
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
171.22
169.16
149.10
138.21
135.37
131.38
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121.19
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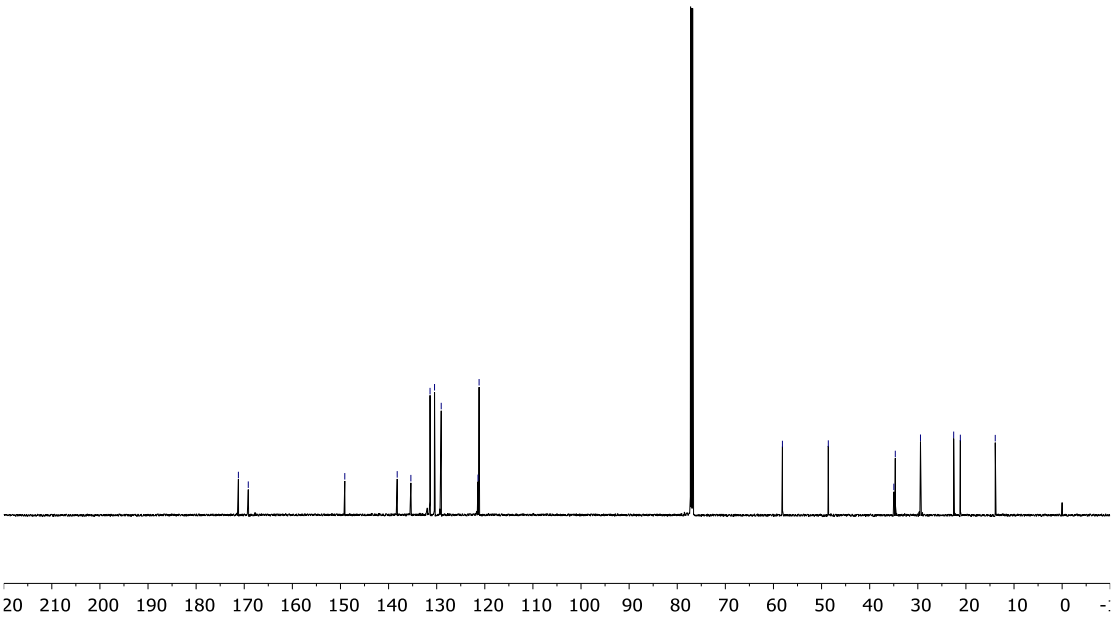
21.16
13.90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90
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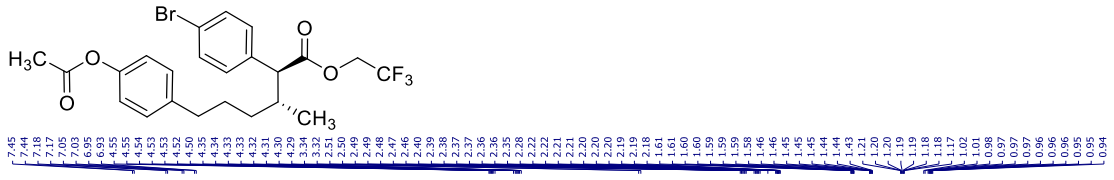
10
0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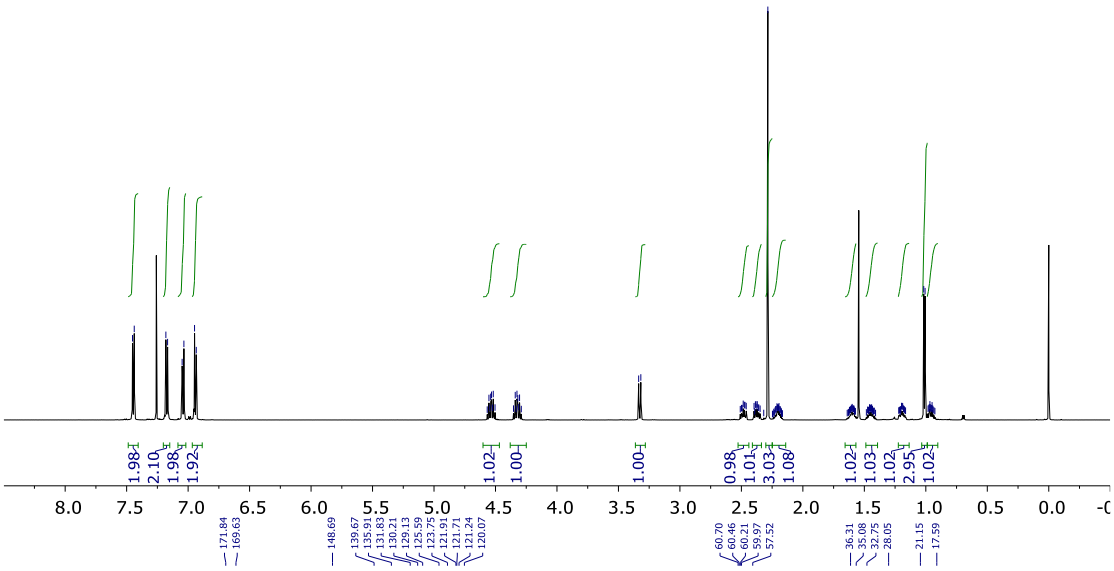
O
O
O
CF3
CH3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1.00
0.98
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3.03
1.08
1.02
1.03
1.02
2.95
1.02
8.0
7.5
7.0
6.5
6.0
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2.0
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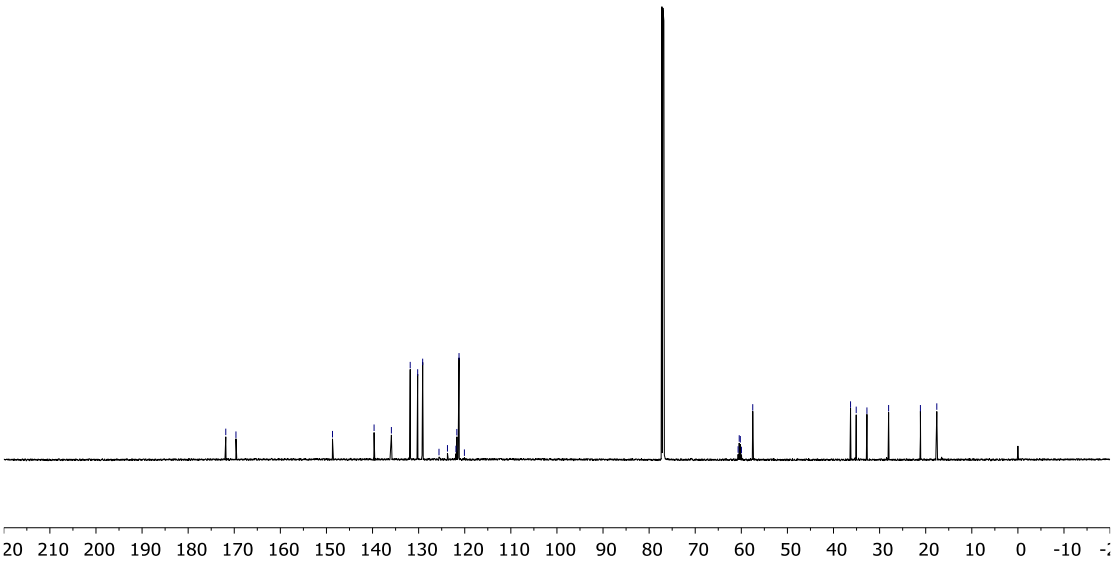
20
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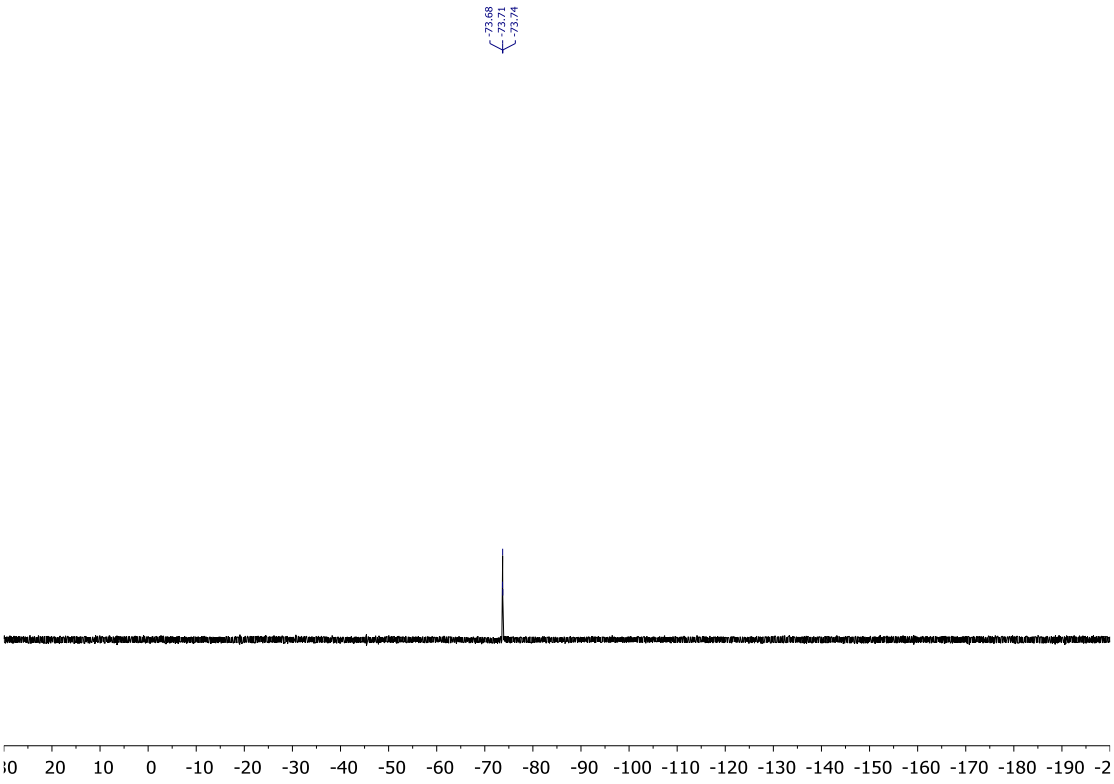
-10


-73.68
-73.71
-73.74
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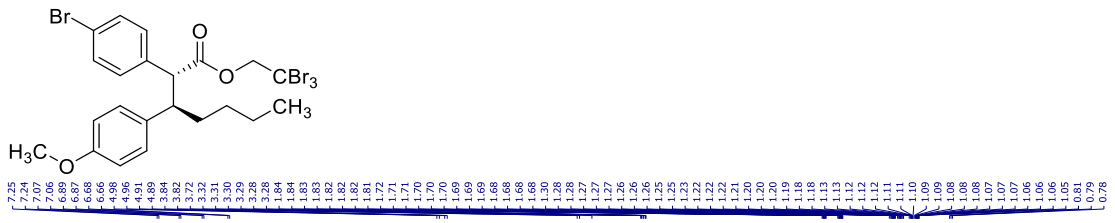
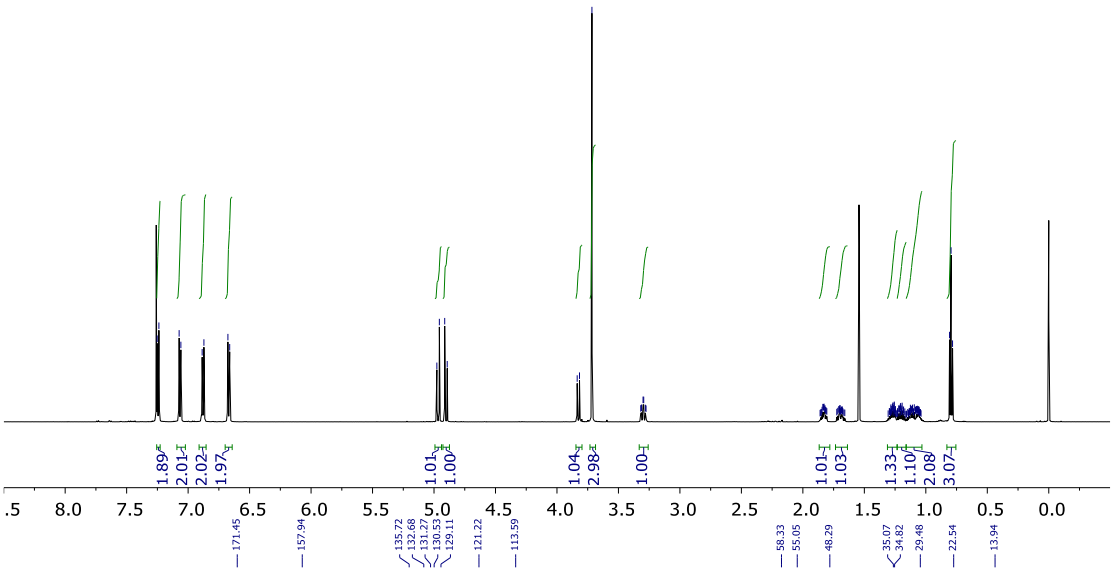

Br
O
O
CBr3
CH3
H3C
O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6.5
6.0
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3.0
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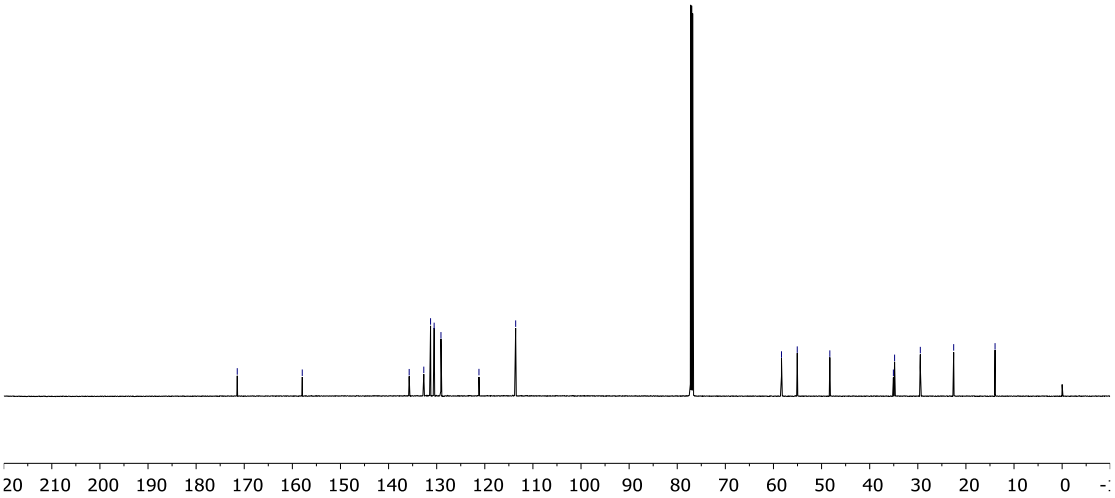
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10
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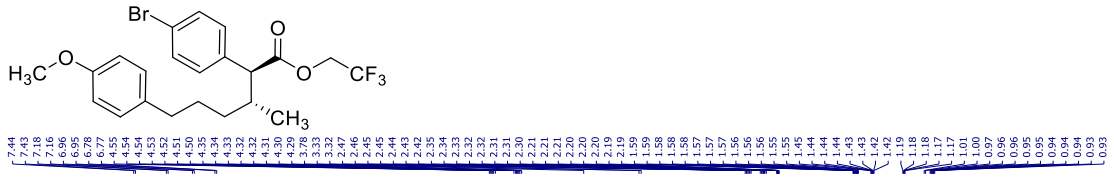
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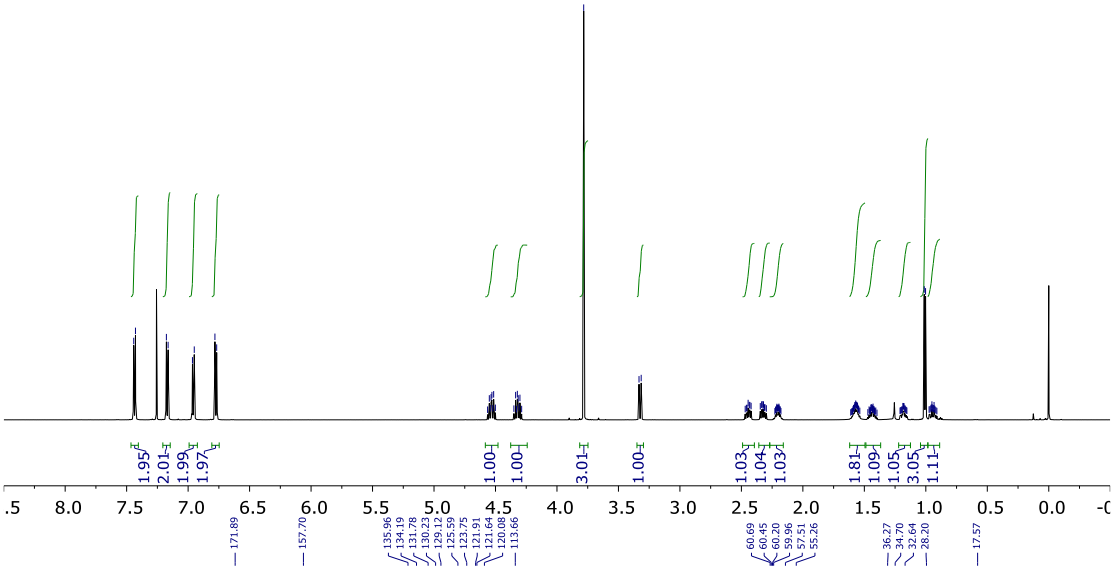
O
O
O
H_3C
CF_3
CH_3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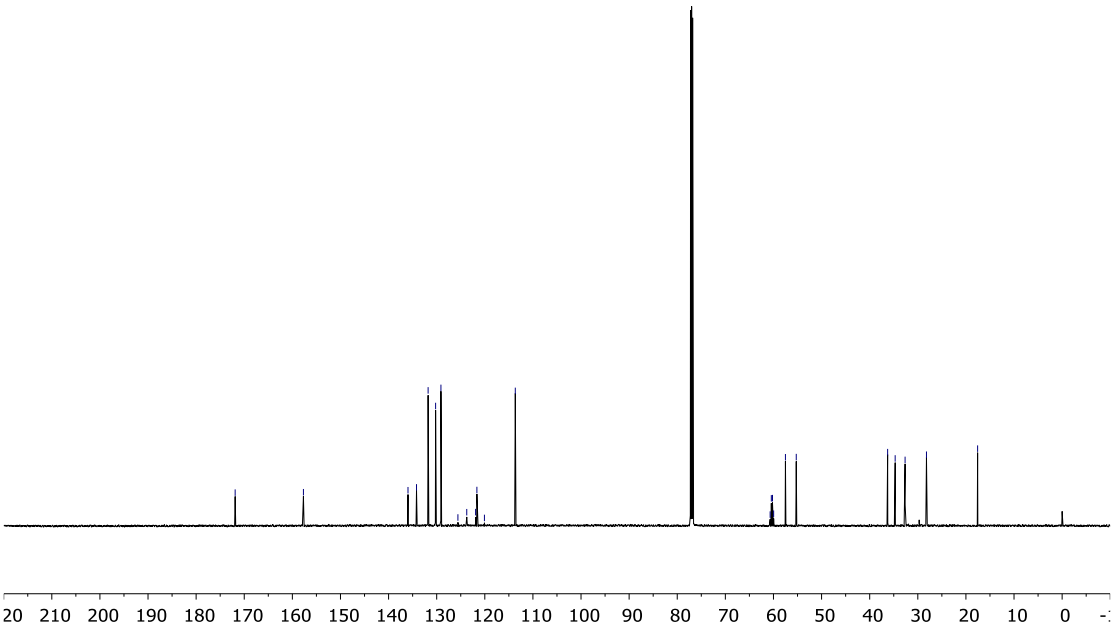
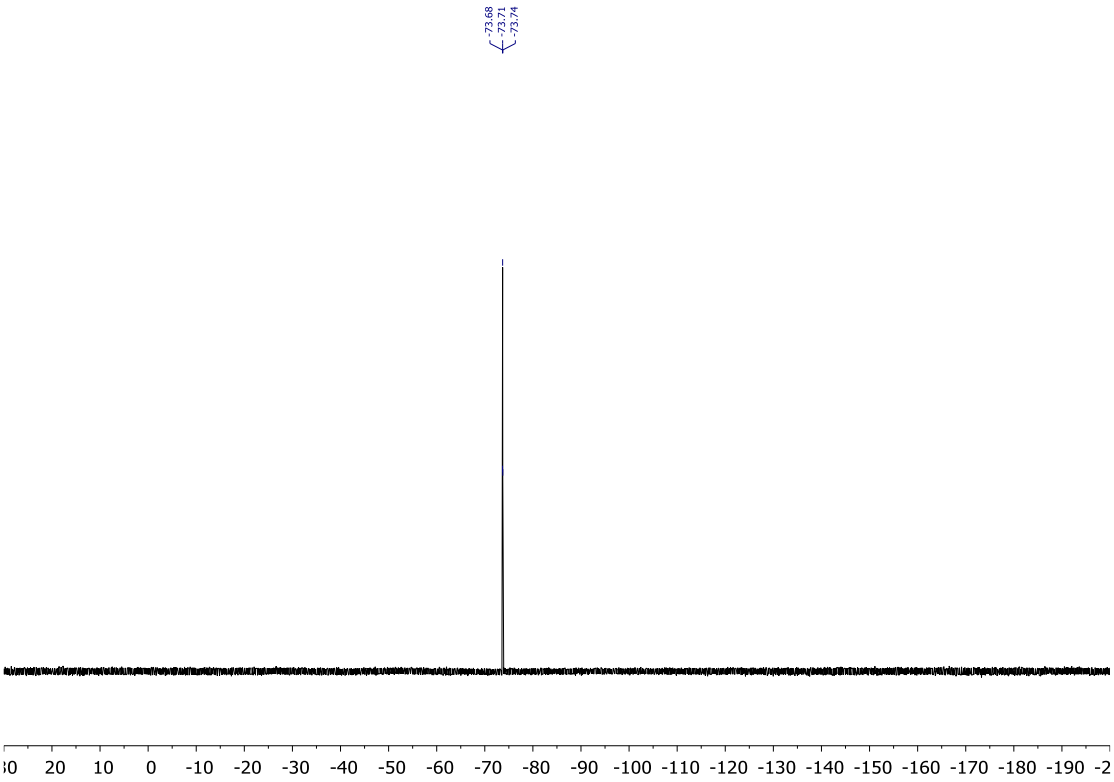
3.05
1.11

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-73.71
-73.74
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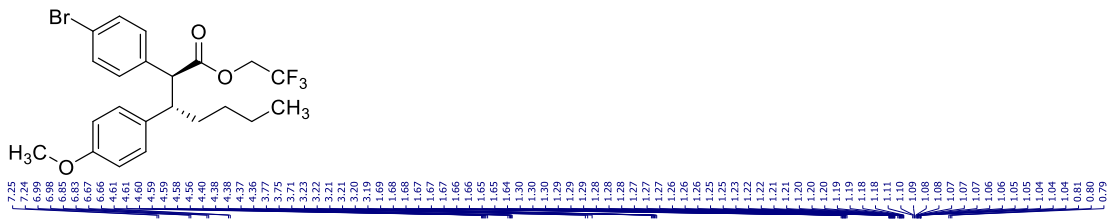
Br
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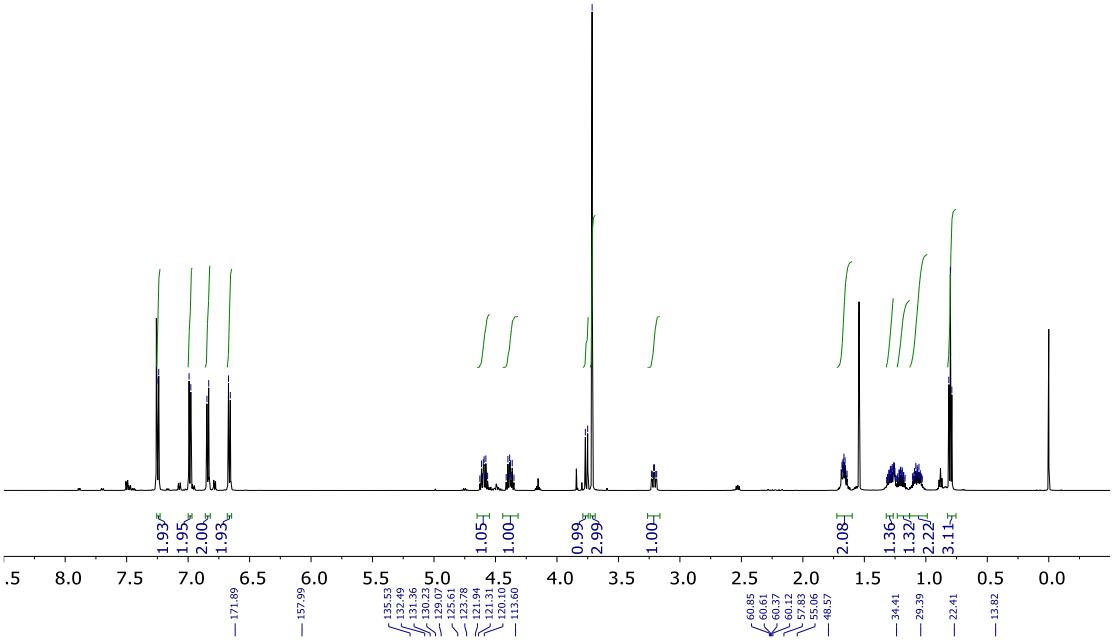
O
CF3
CH3
H3C
O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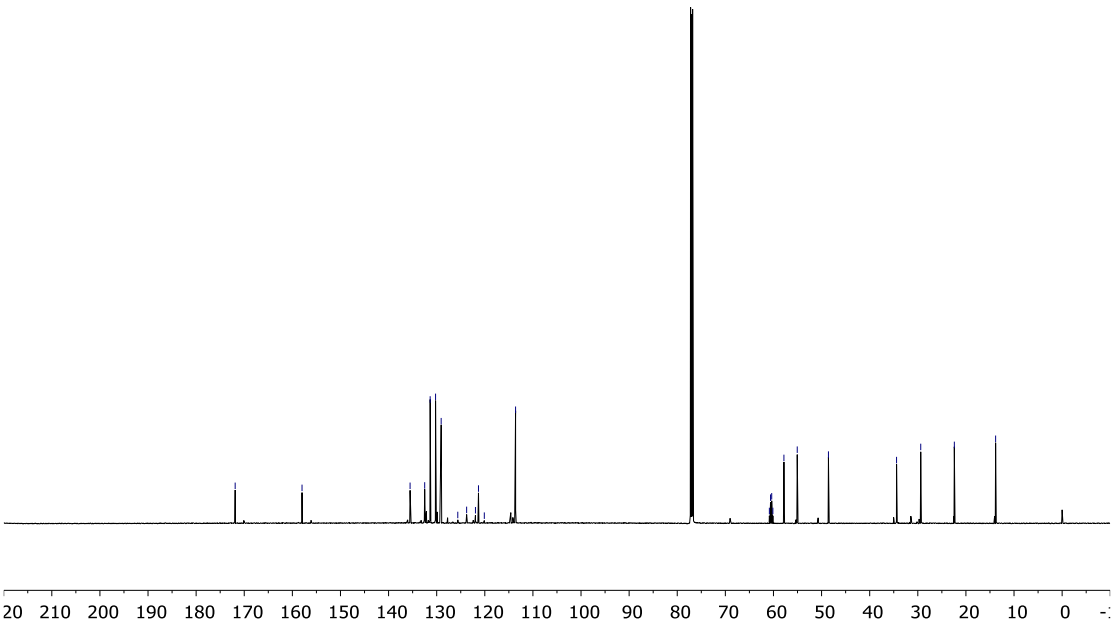
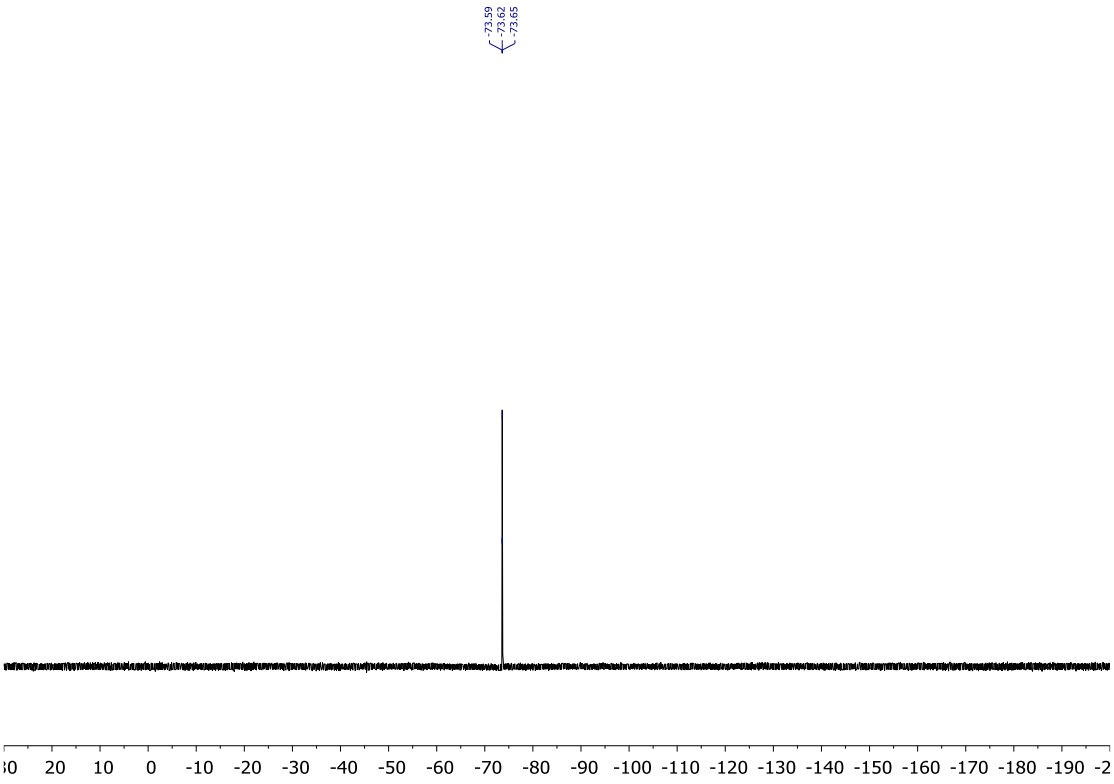
2.22
3.11

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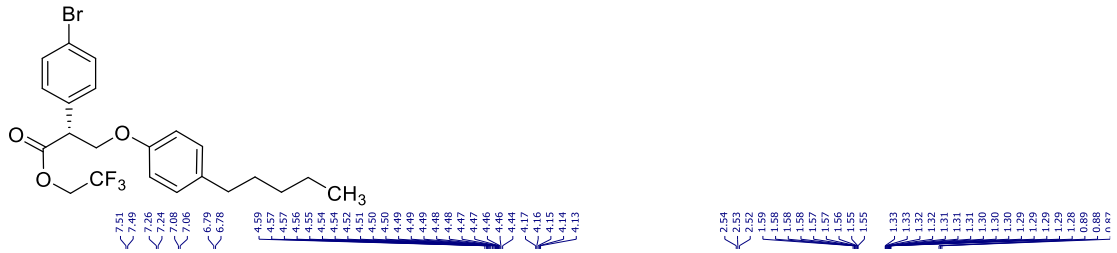
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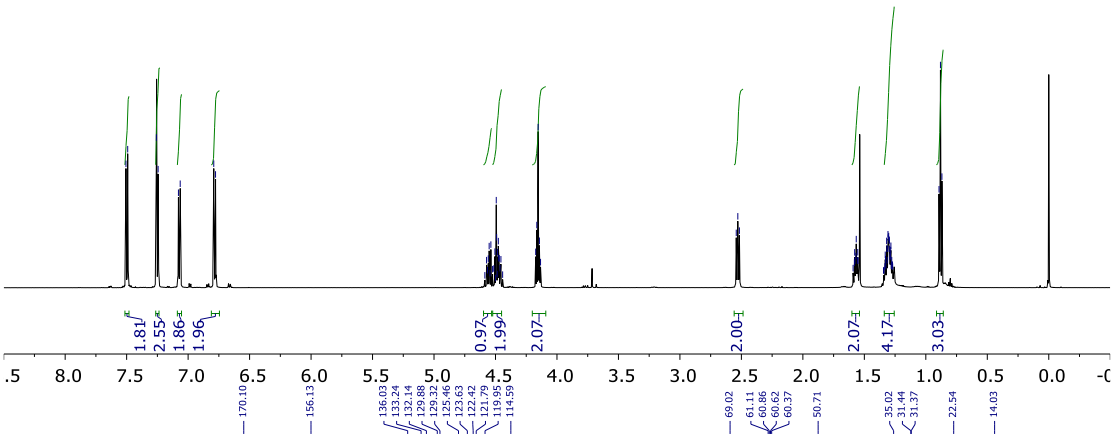
CF3
CH3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2.07
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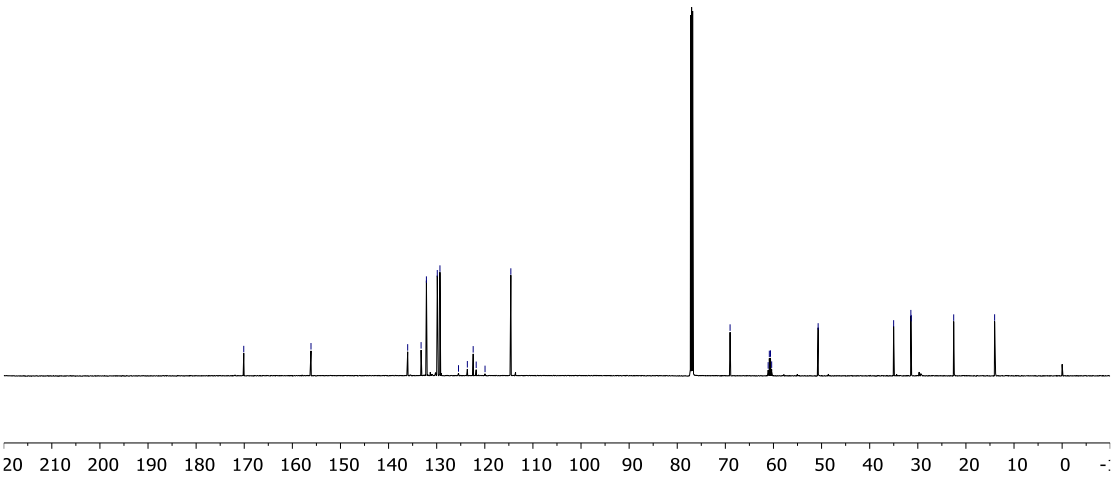

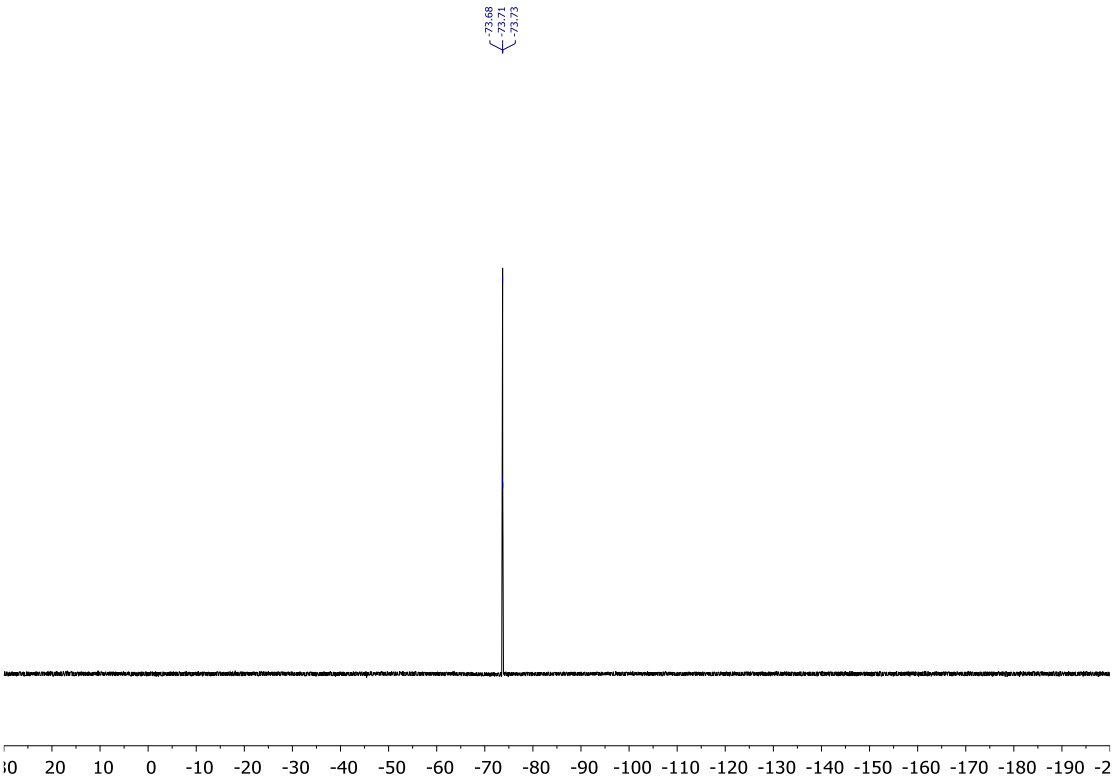
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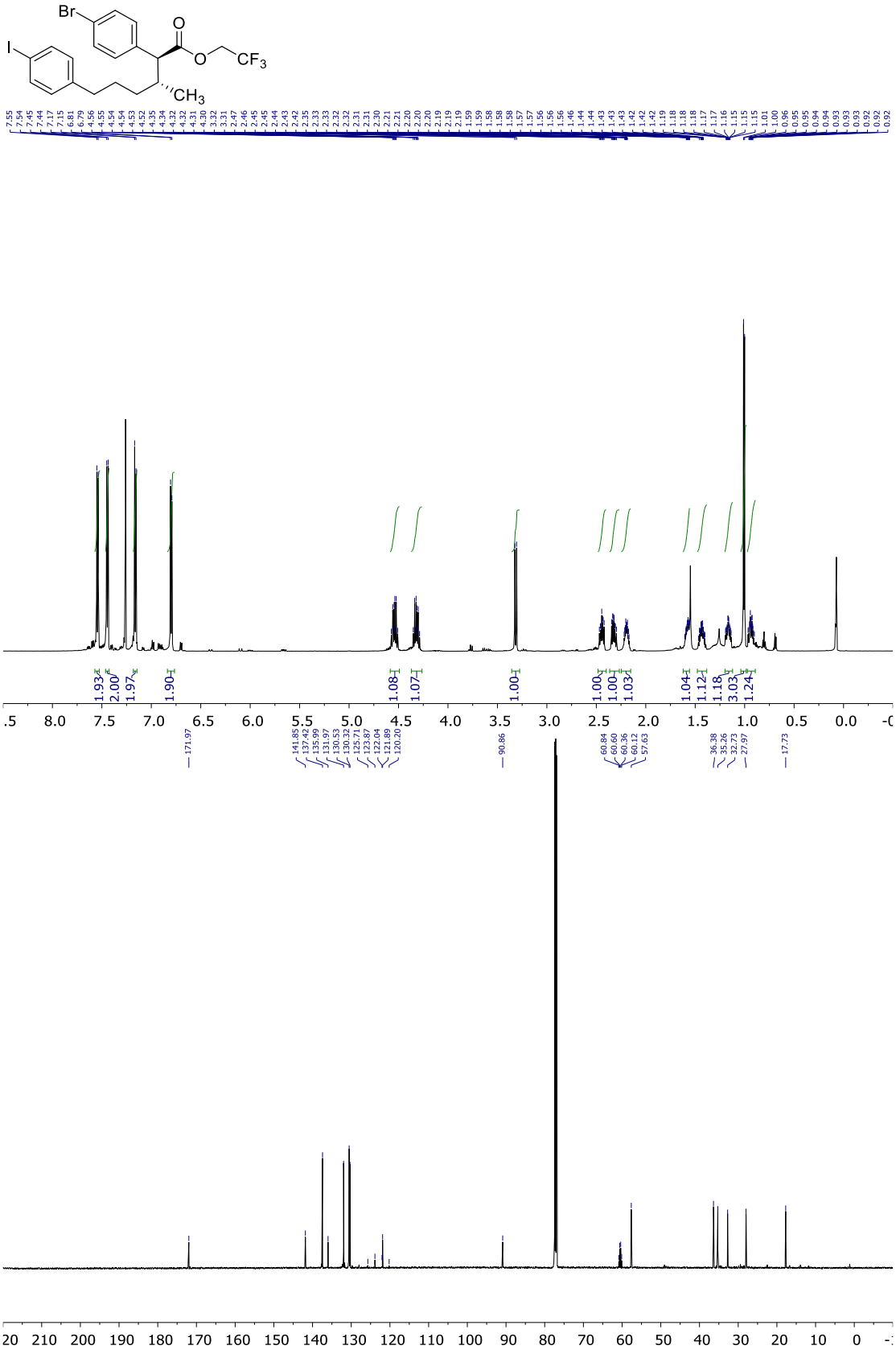
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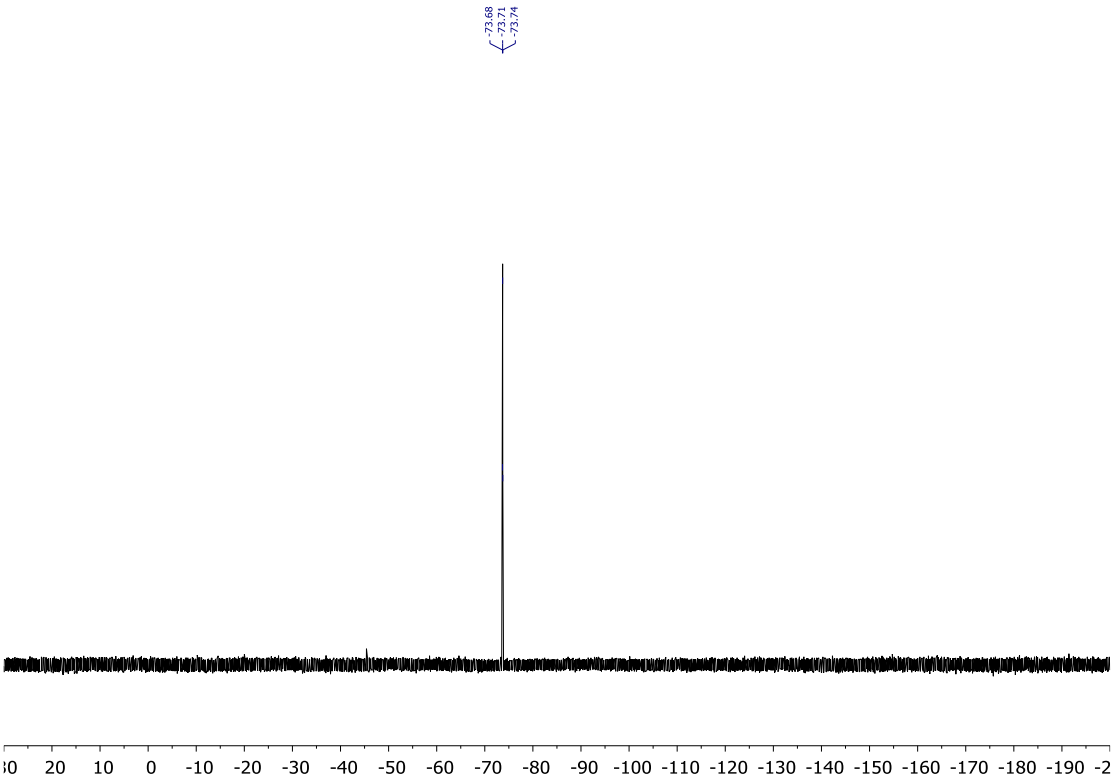
CF3
CH3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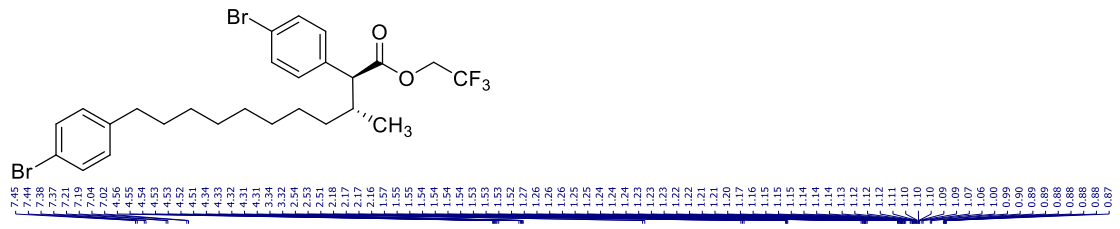
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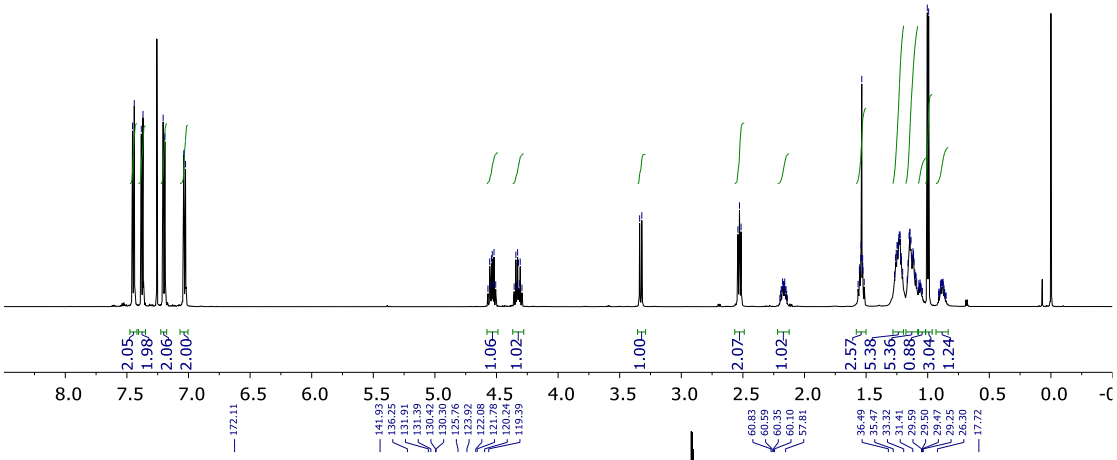
Br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2.06
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1.06
1.02
1.00
2.07
1.02
2.57
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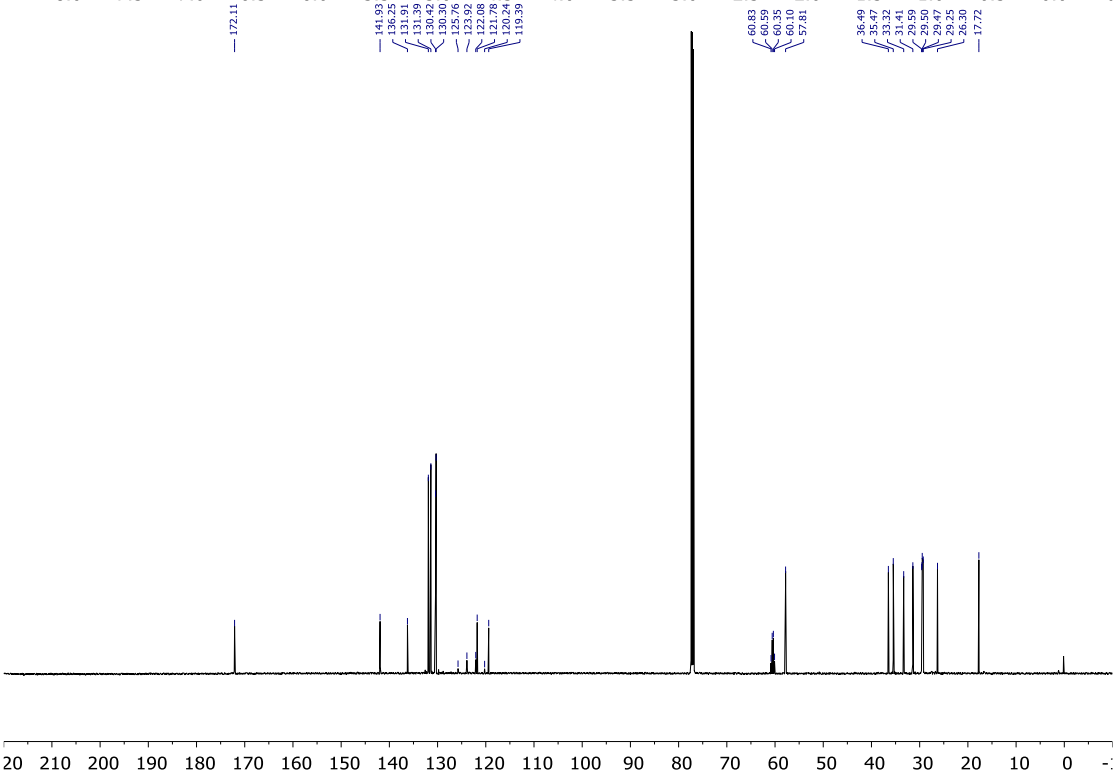
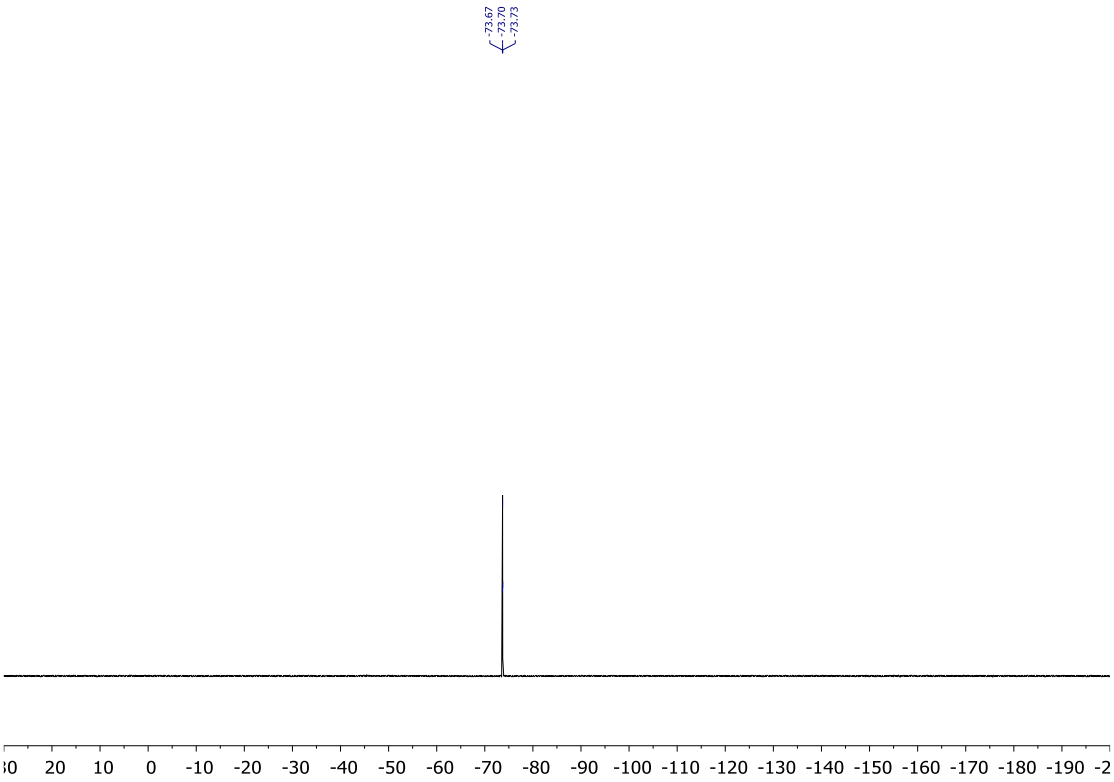
5.36
0.88
3.04
1.24

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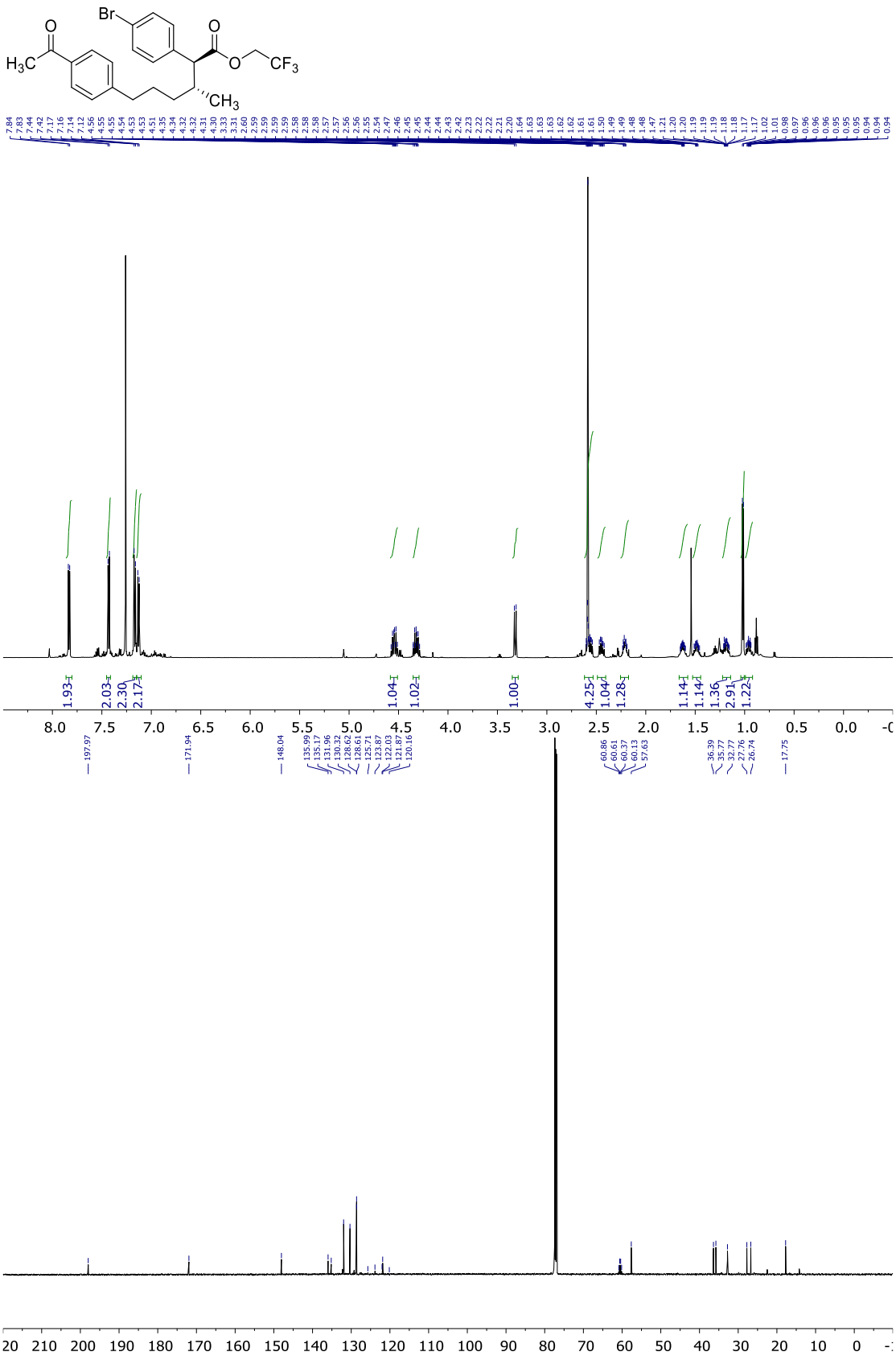
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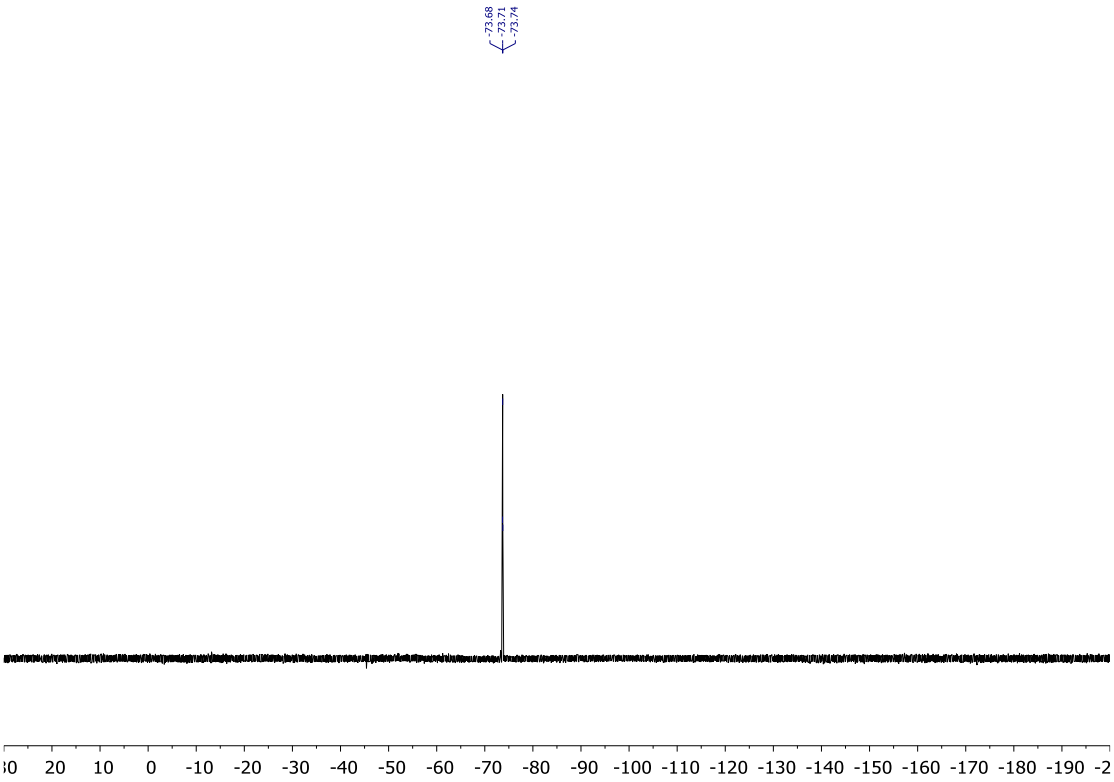
H3C
O
CF3
CH3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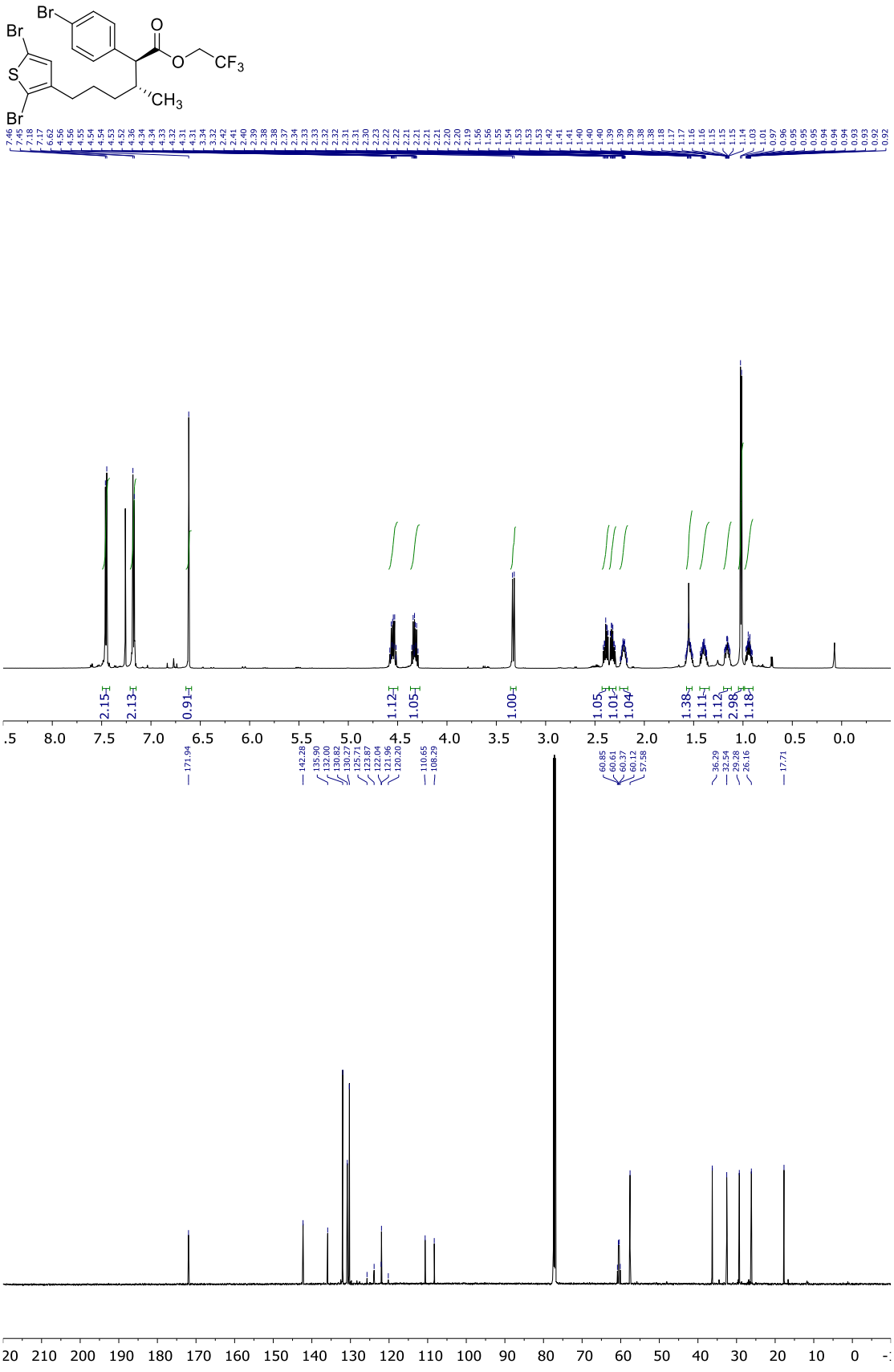
Br
Br
S
Br
O
O
CF3
CH3
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0.91
1.12
1.05
1.00
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1.01
1.04
1.38
1.11
1.12
2.98
1.18
171.94
142.28
135.90
132.00
130.82
130.27
125.71
123.87
122.04
121.96
120.20
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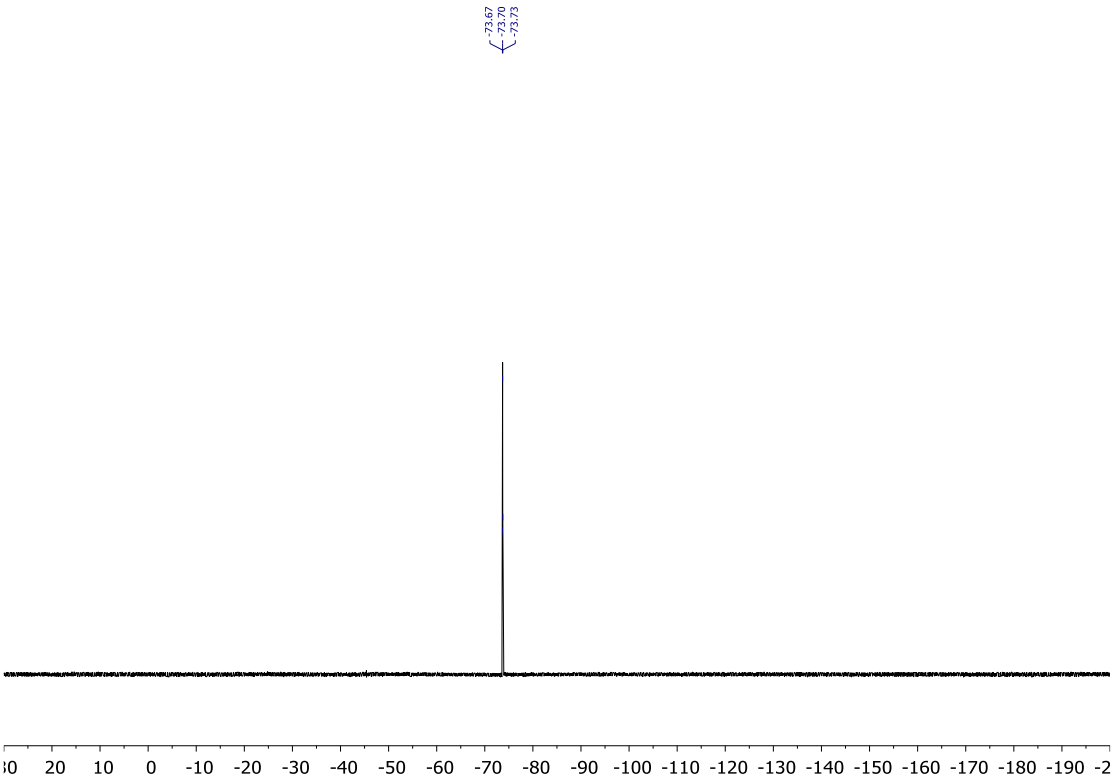
60.12
57.58
36.29
32.54
29.28
26.16
17.71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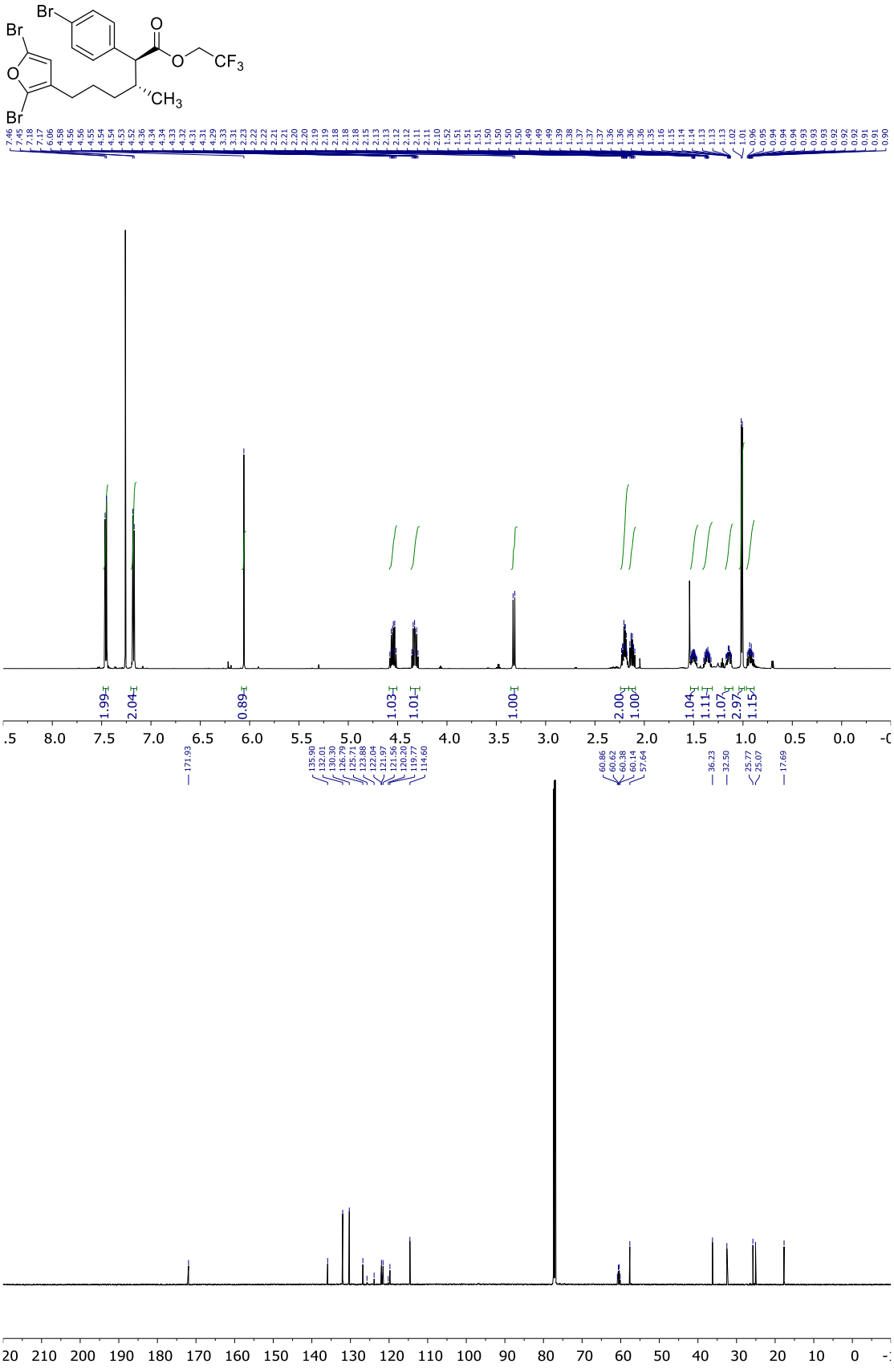
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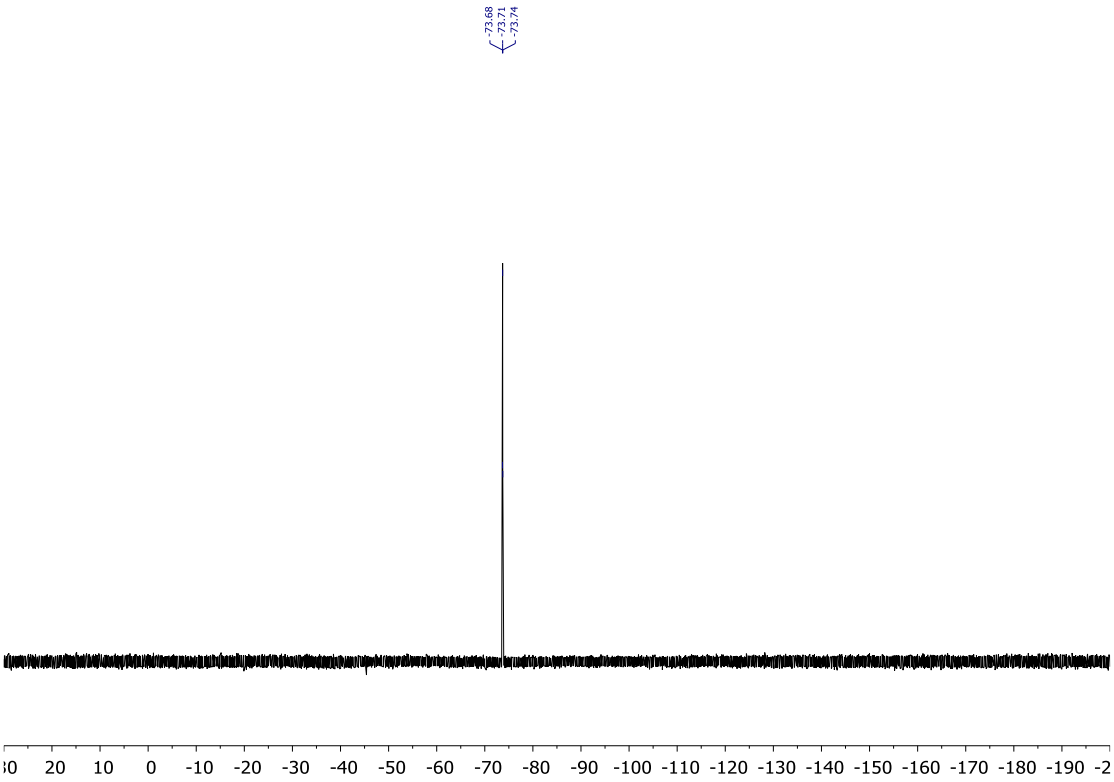
Br
O
O
O
CF3
CH3
Br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-73.71
-73.74
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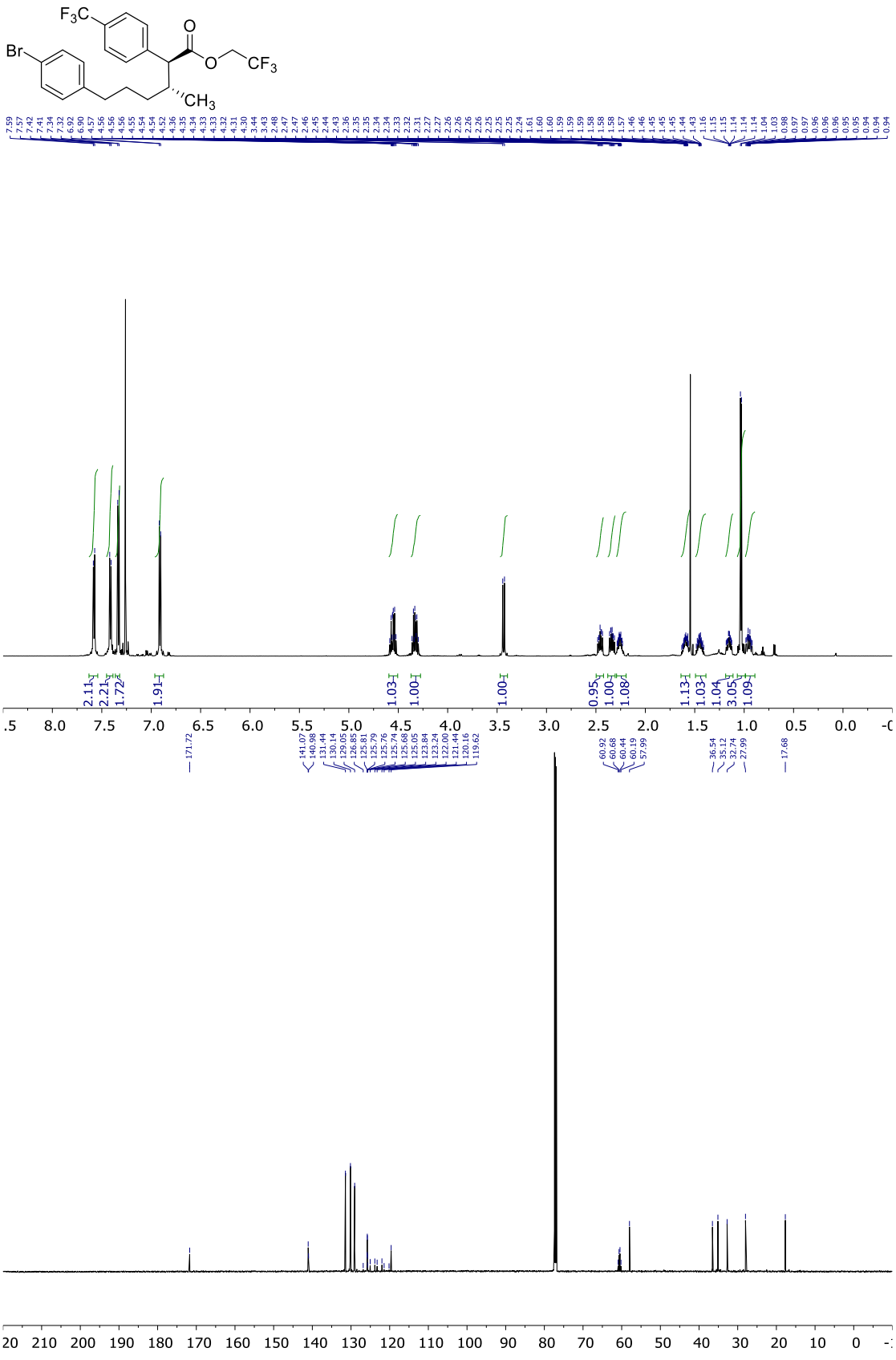
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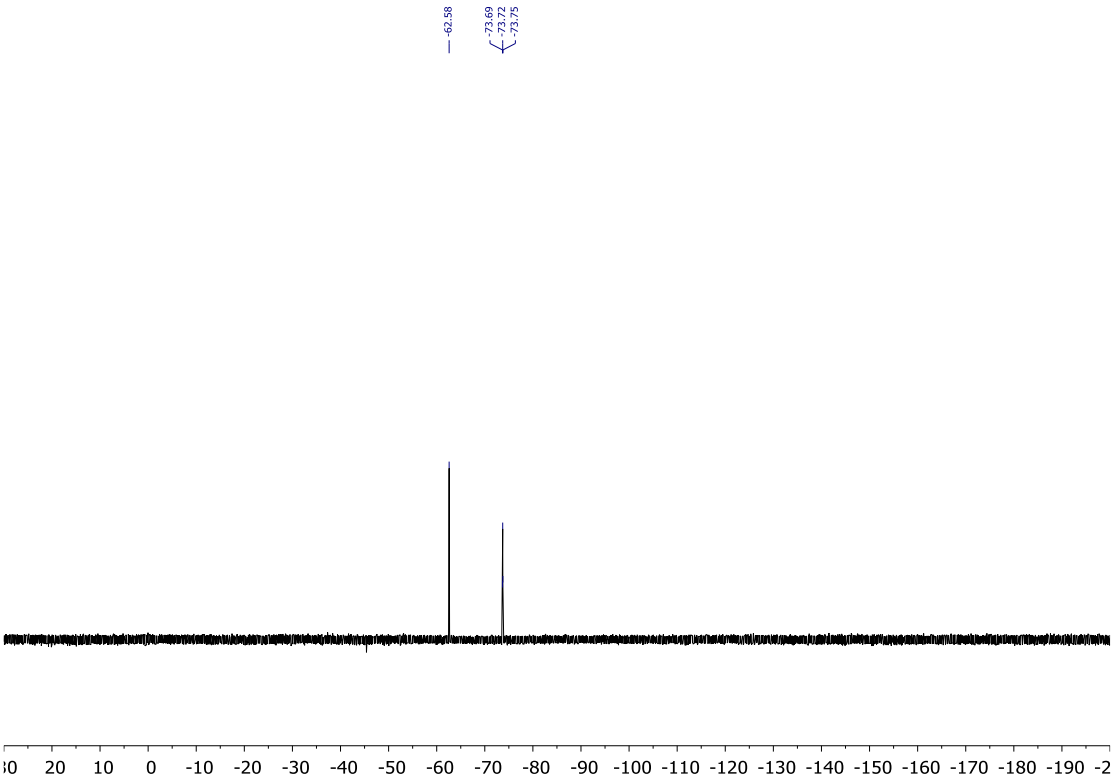
O
Br
O
CF3
CH3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-73.72
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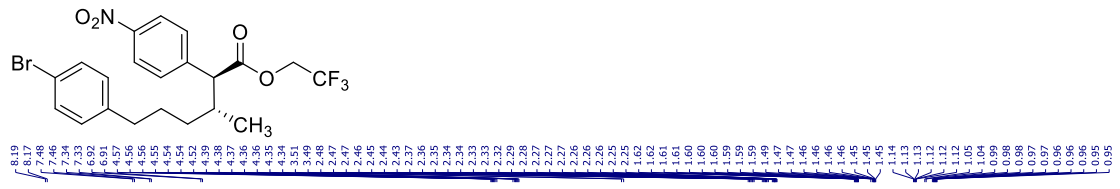
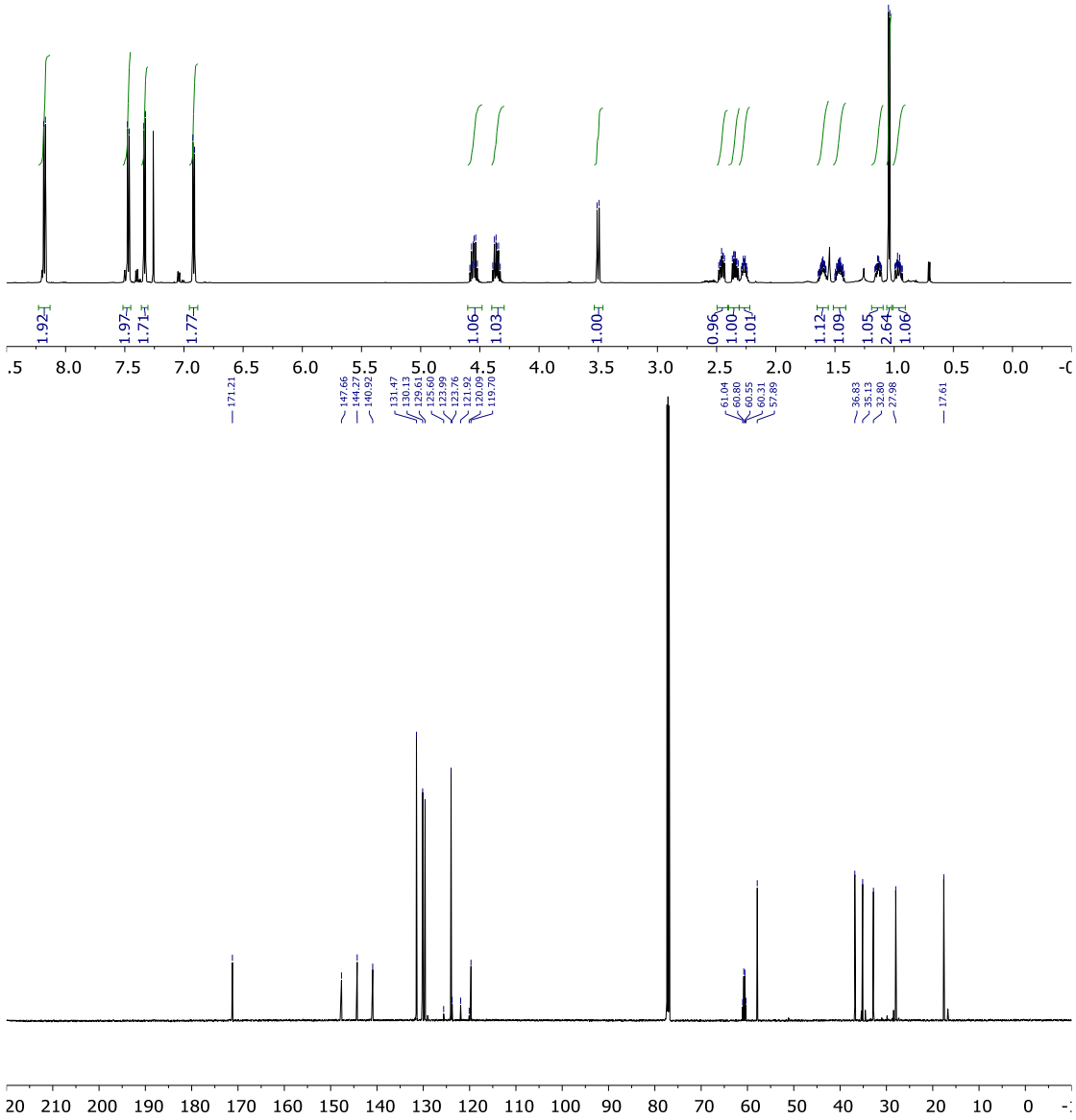

O2N
Br
O
O
CF3
CH3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1.97
1.71
1.77
1.06
1.03
1.00
0.96
1.00
1.01
1.12
1.09
1.05
2.64
1.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
171.21
147.66
144.27
140.92
131.47
130.13
129.61
125.60
123.99
123.76
121.92
120.09
119.70
61.04
60.80
60.55
60.31
57.89
36.83
35.13
32.80
27.98
17.61
210
200
190
180
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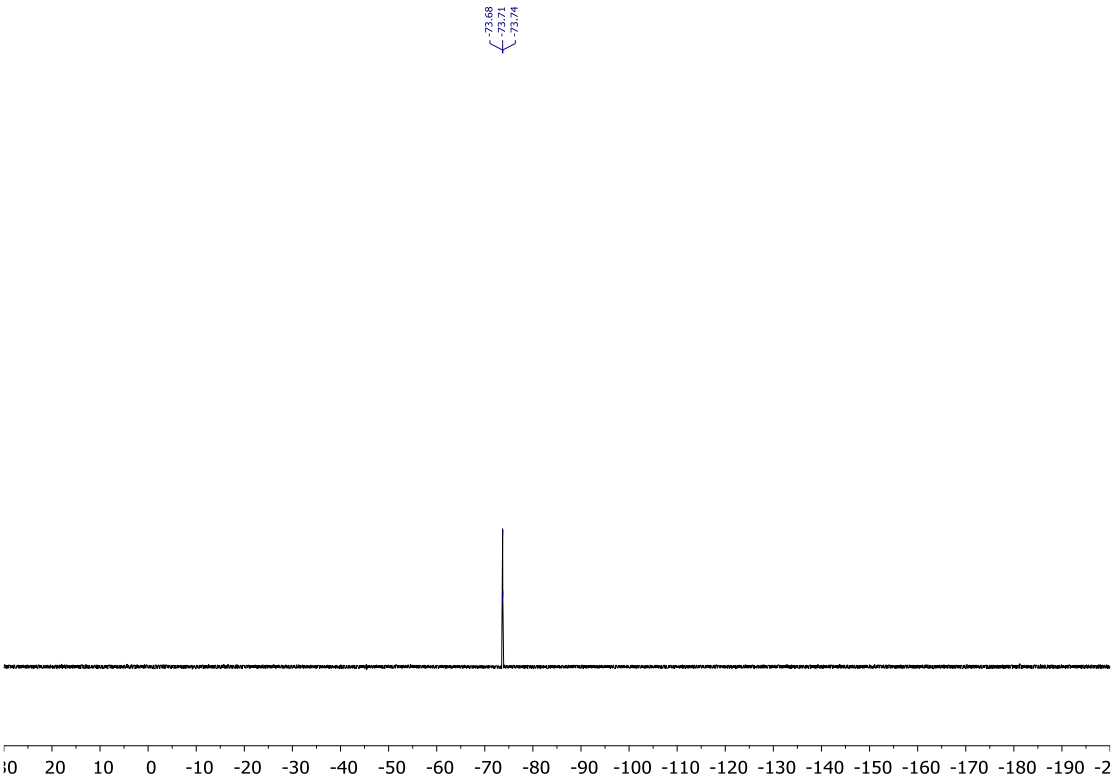
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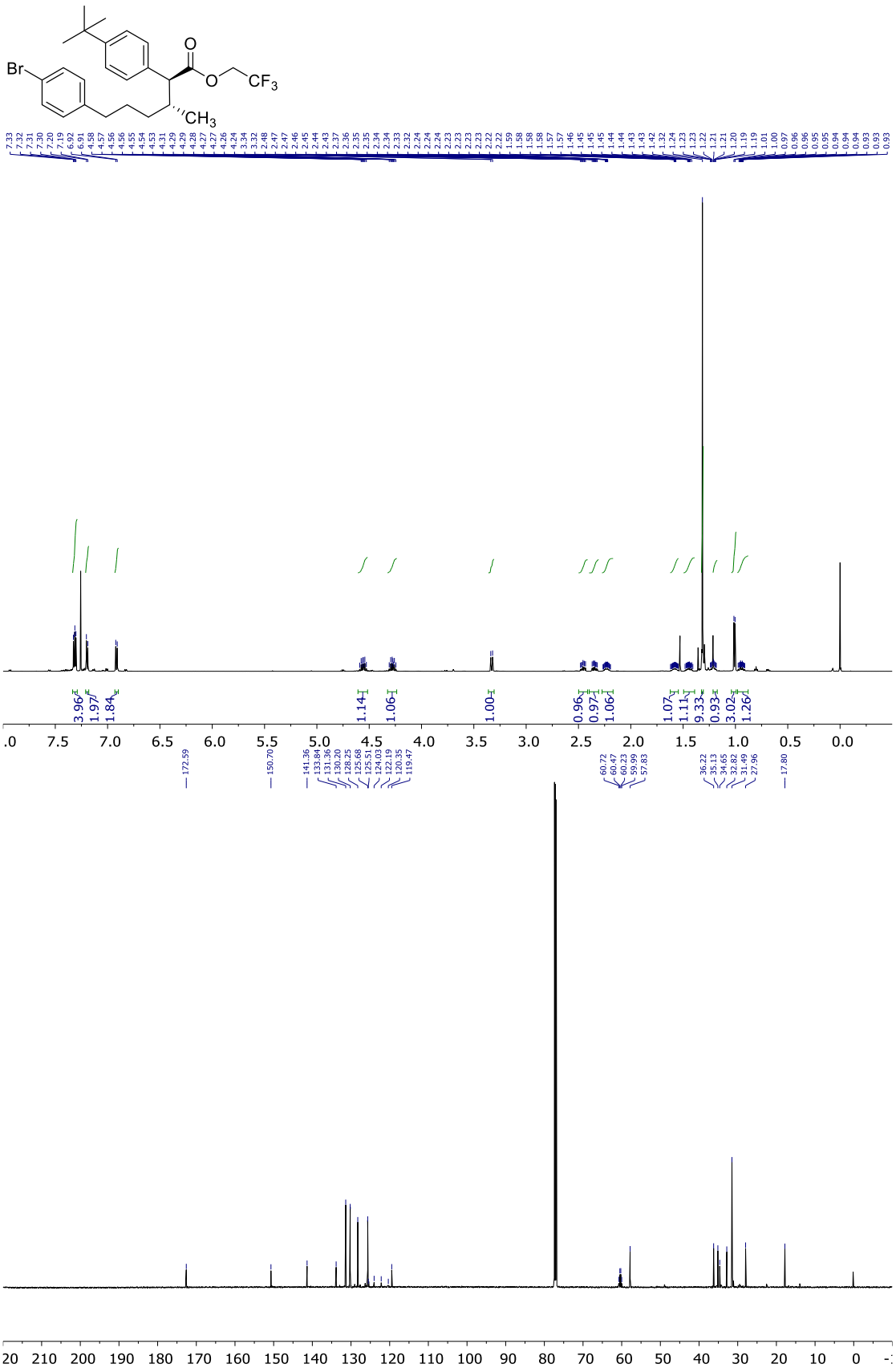
Br
O
O
CF3
CH3
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1.84
1.14
1.06
1.00
0.96
0.97
1.06
1.07
1.11
9.33
0.93
3.02
1.26
172.59
150.70
141.36
133.84
131.36
130.20
128.25
125.68
125.51
124.03
122.19
120.35
119.47
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60.23
59.99
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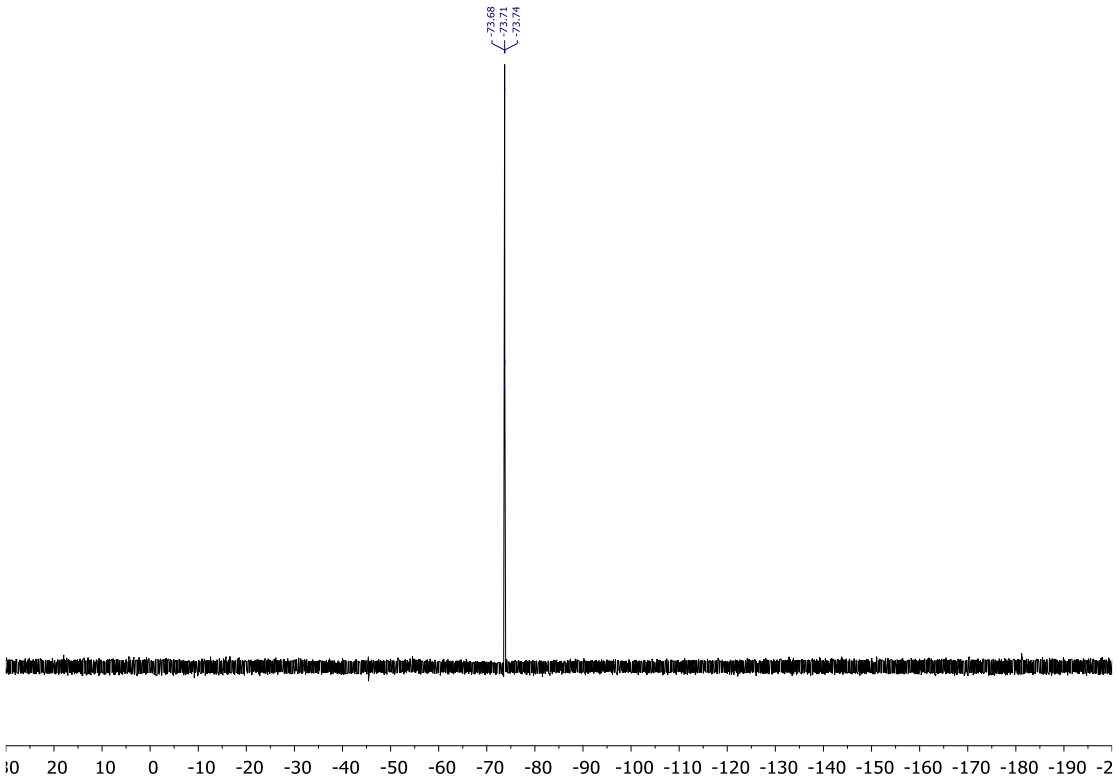
36.22
35.13
34.65
32.82
31.49
27.96
17.80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-73.71
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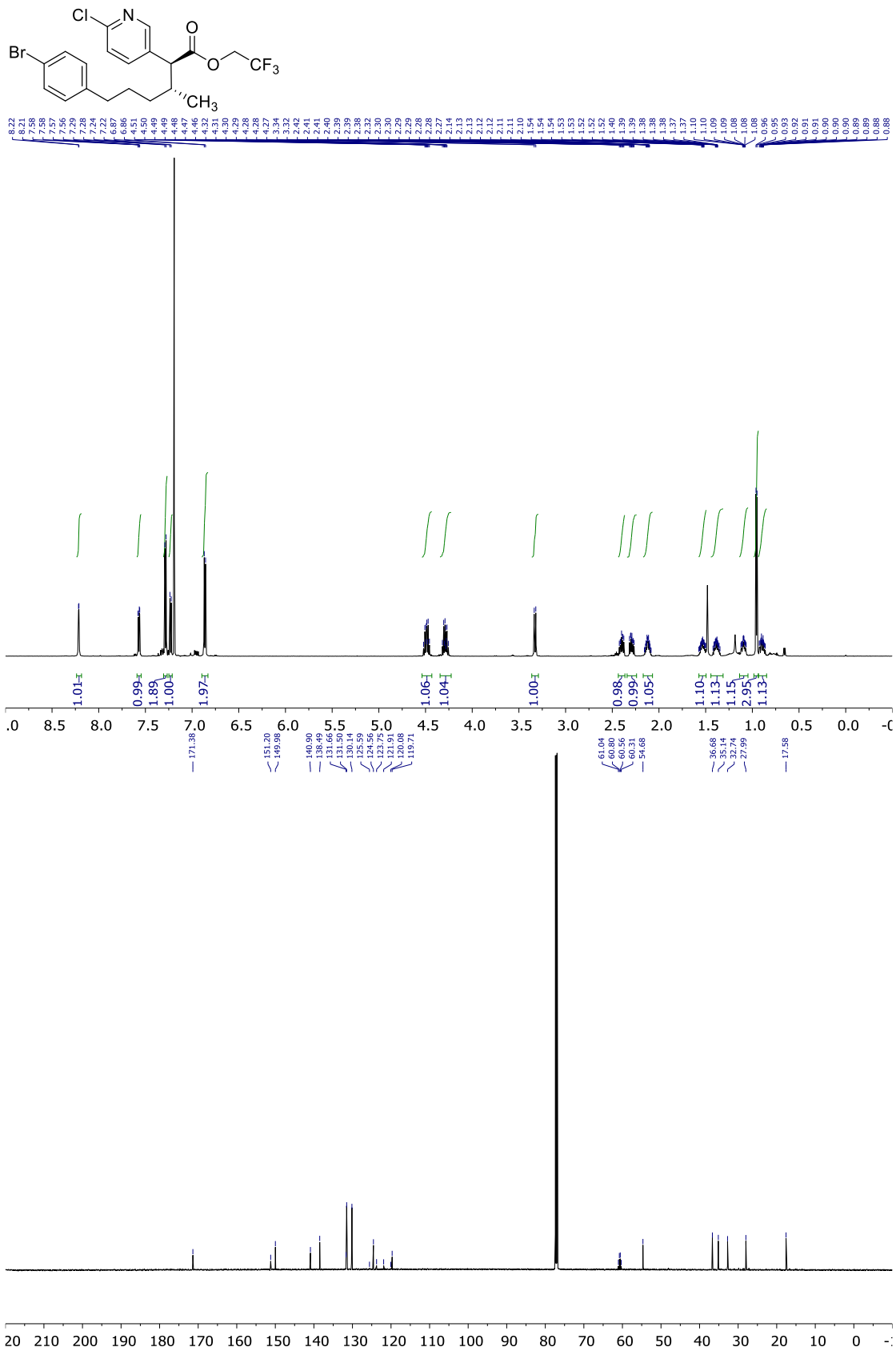
Cl
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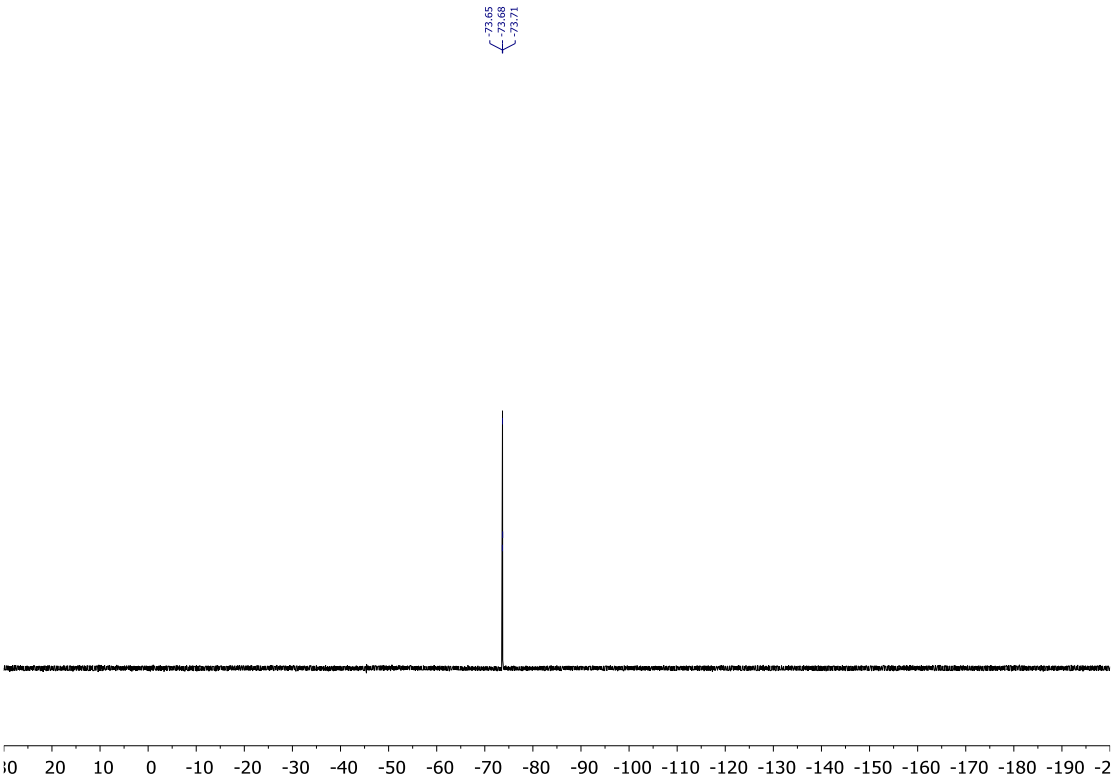
O
Br
O
CF3
CH3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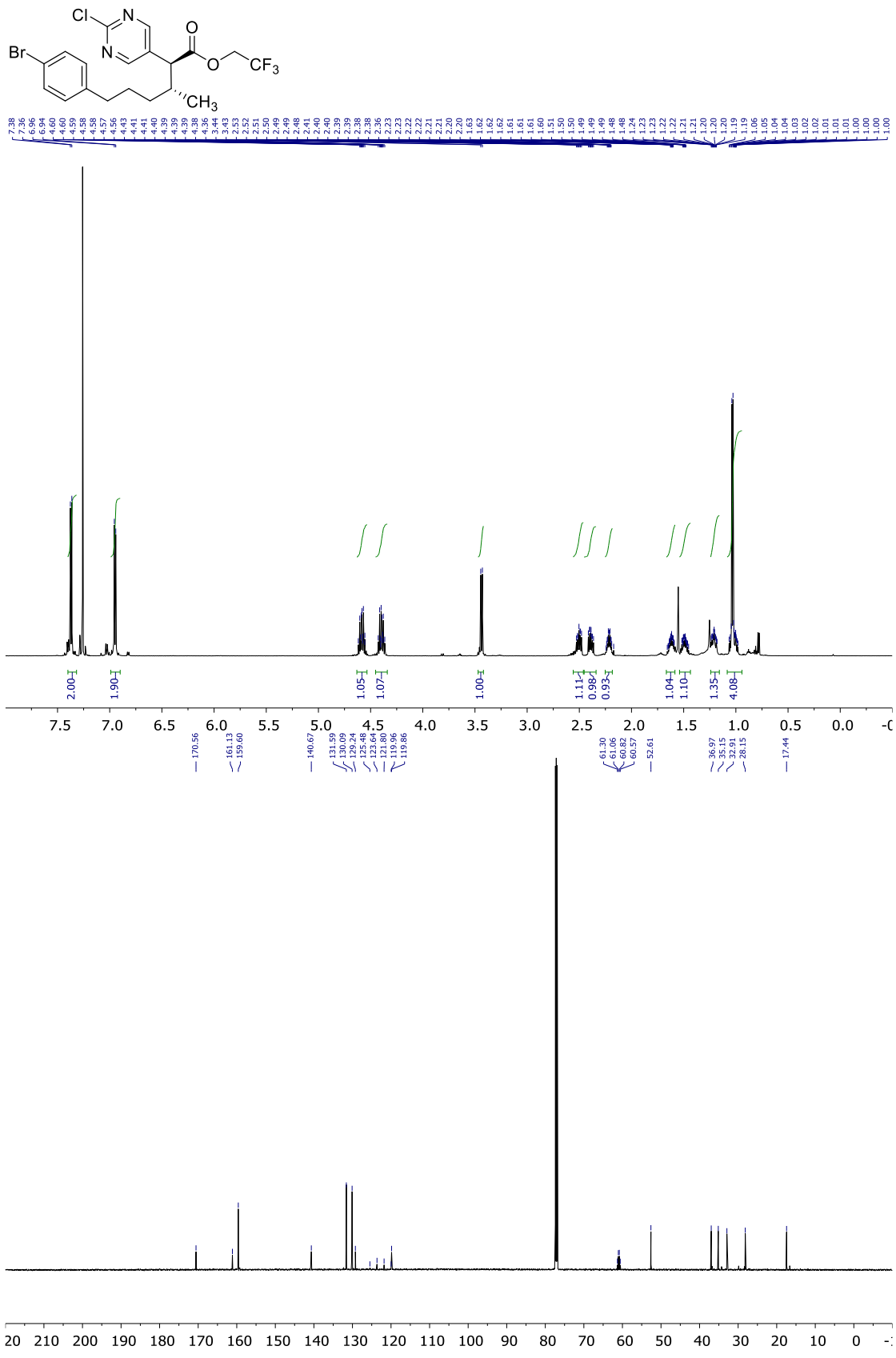
Cl
N
N
O
O
CF3
Br
CH3
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1.07
1.00
1.11
0.98
0.93
1.04
1.10
1.35
4.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
170.56
161.13
159.60
140.67
131.59
130.09
129.24
125.48
123.64
121.60
119.96
119.86
61.30
61.06
60.82
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20
210
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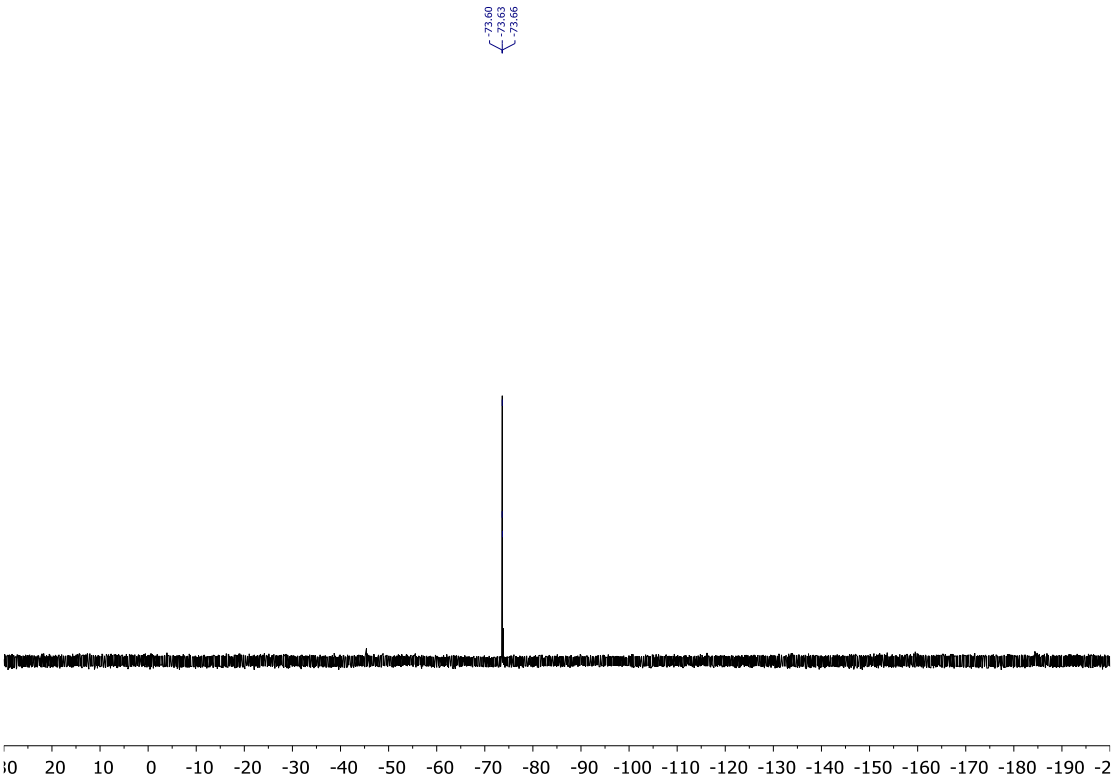
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-73.63
-73.66
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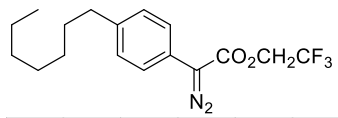
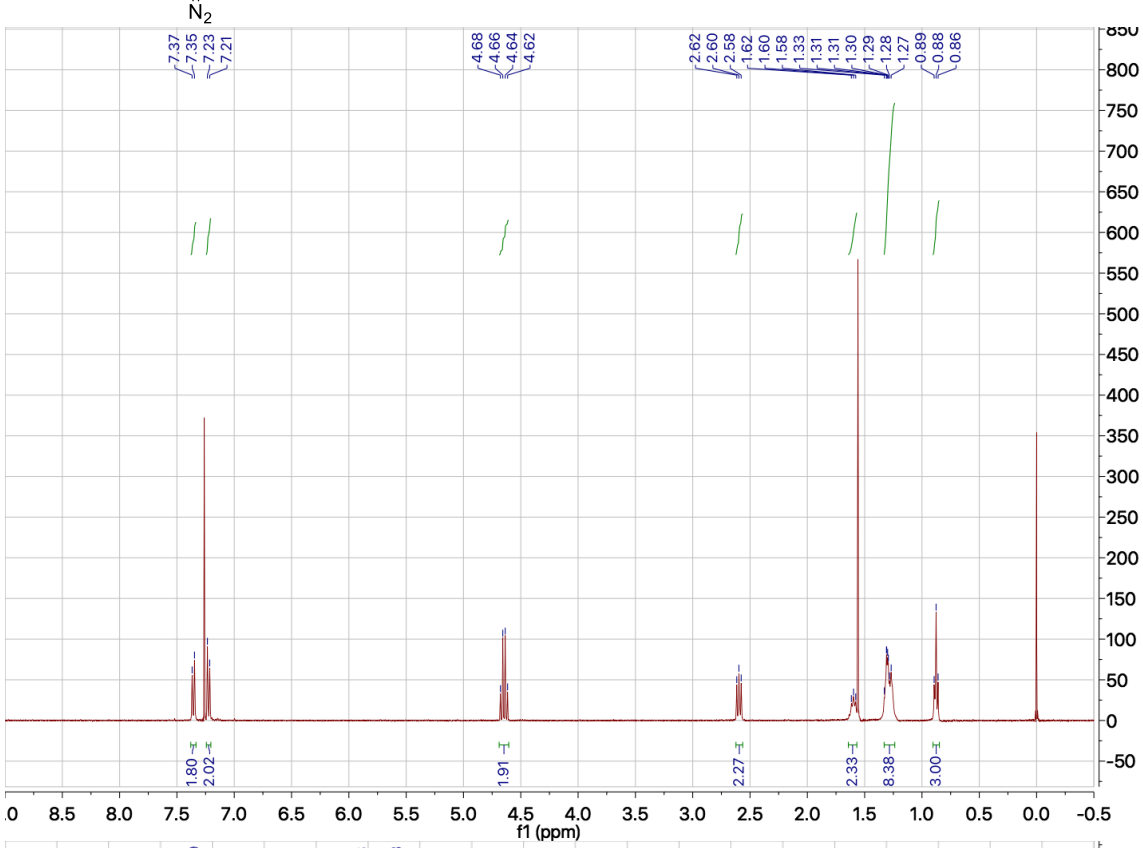
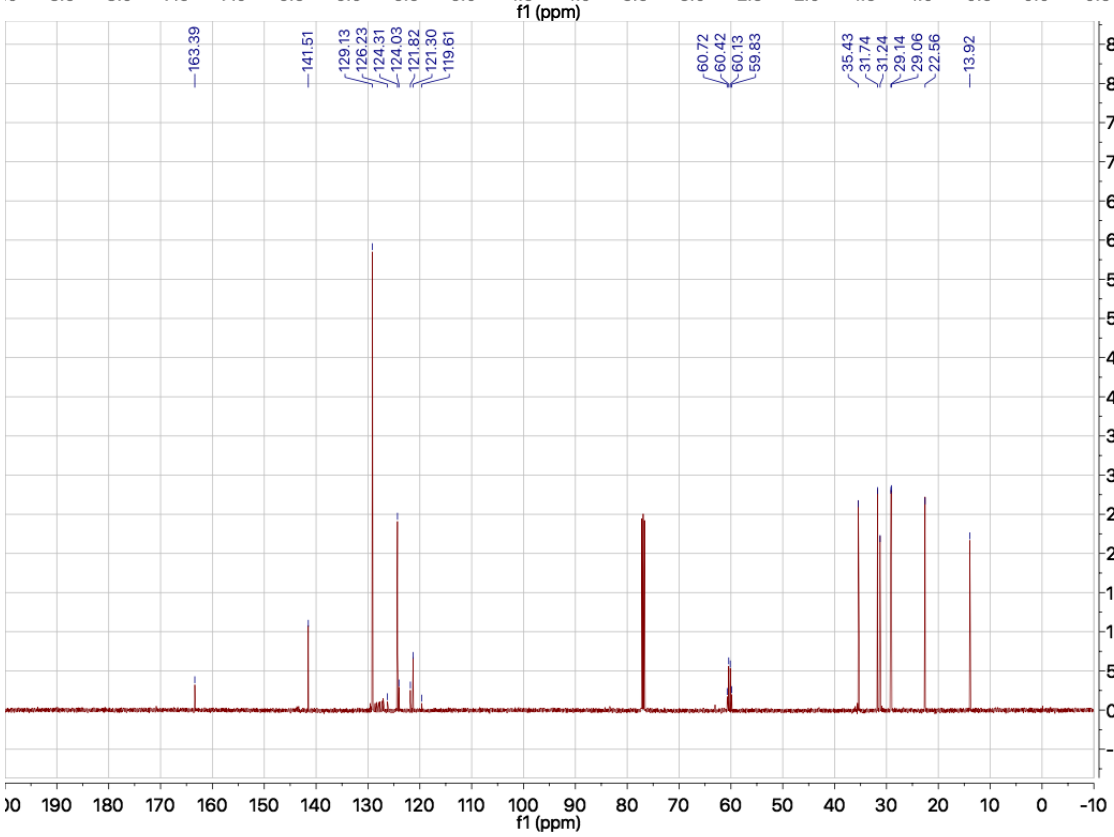

CO2CH2CF3
N2


7.37
7.35
7.23
7.21
4.68
4.66
4.64
4.62
2.62
2.60
2.58
1.62
1.60
1.58
1.33
1.31
1.31
1.30
1.29
1.28
1.27
0.89
0.88
0.86
1.80
2.02
1.91
2.27
2.33
8.38
3.00
f1 (ppm)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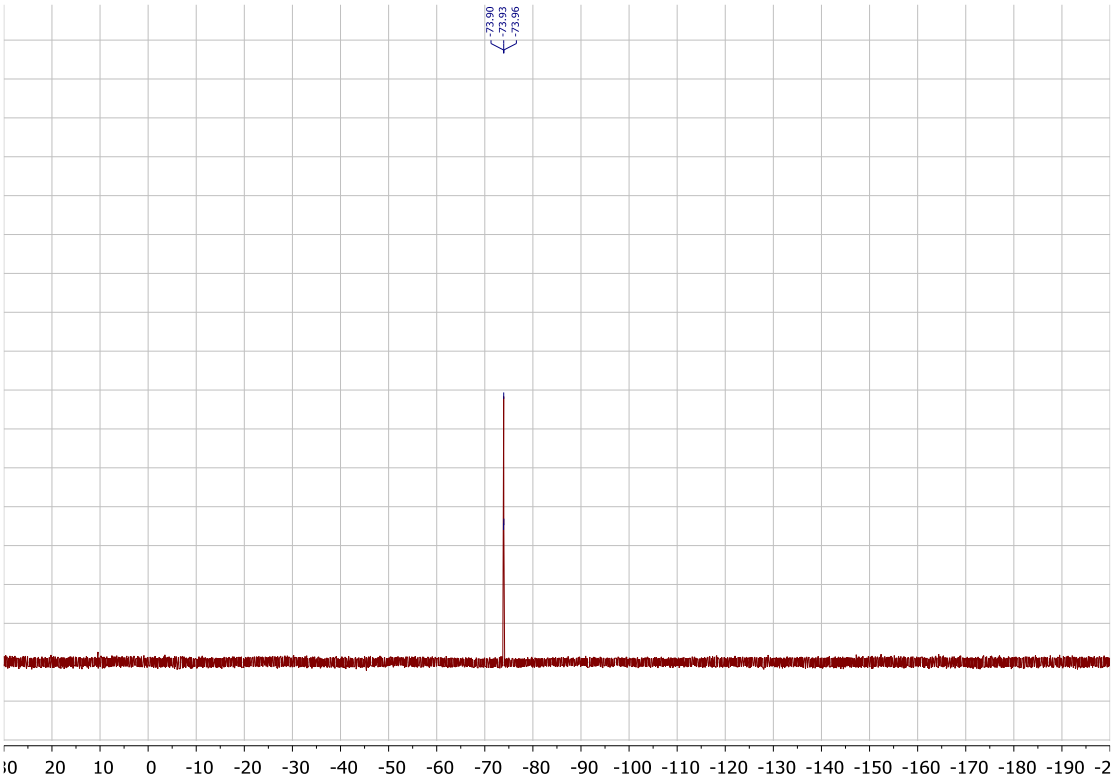
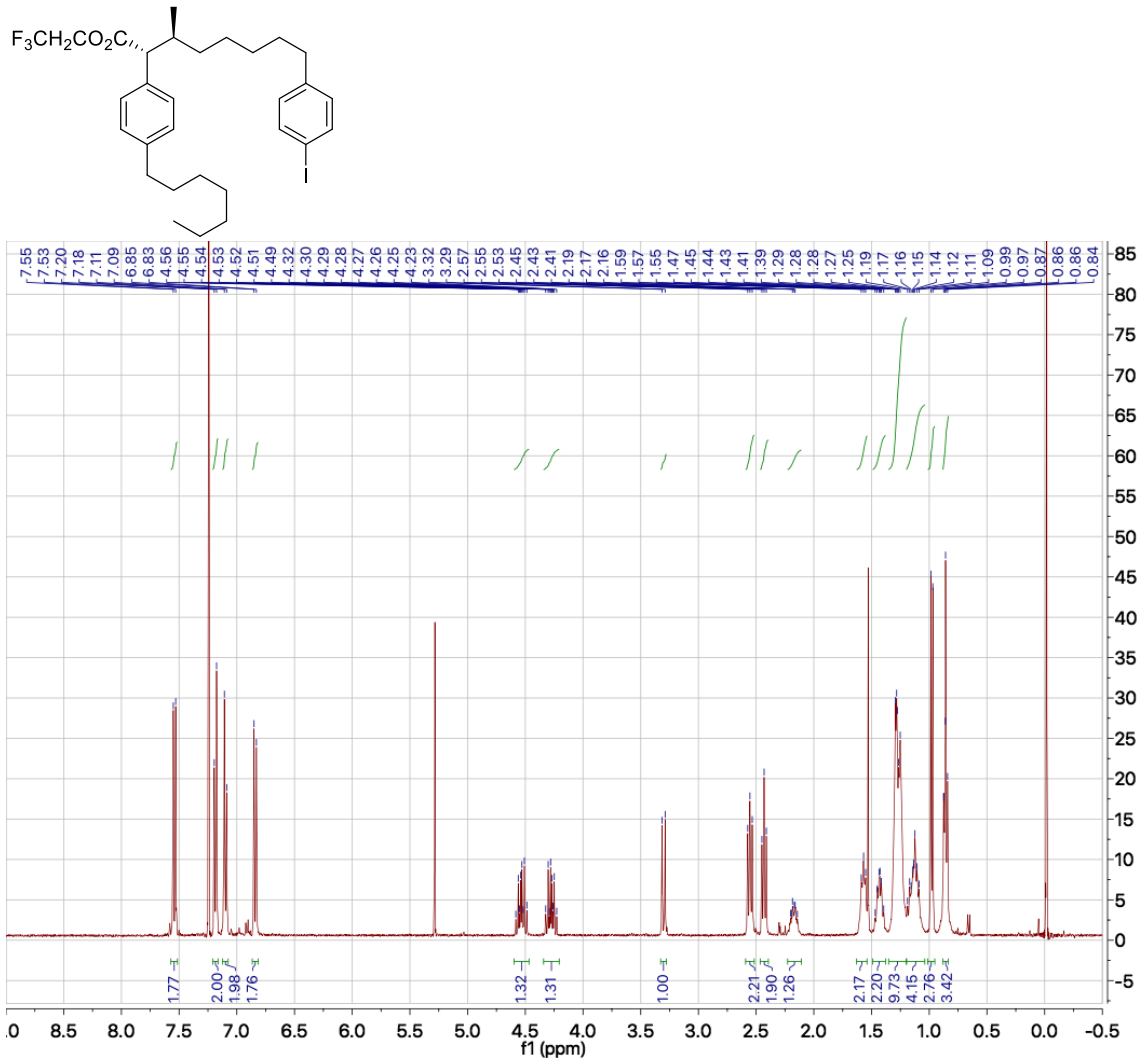
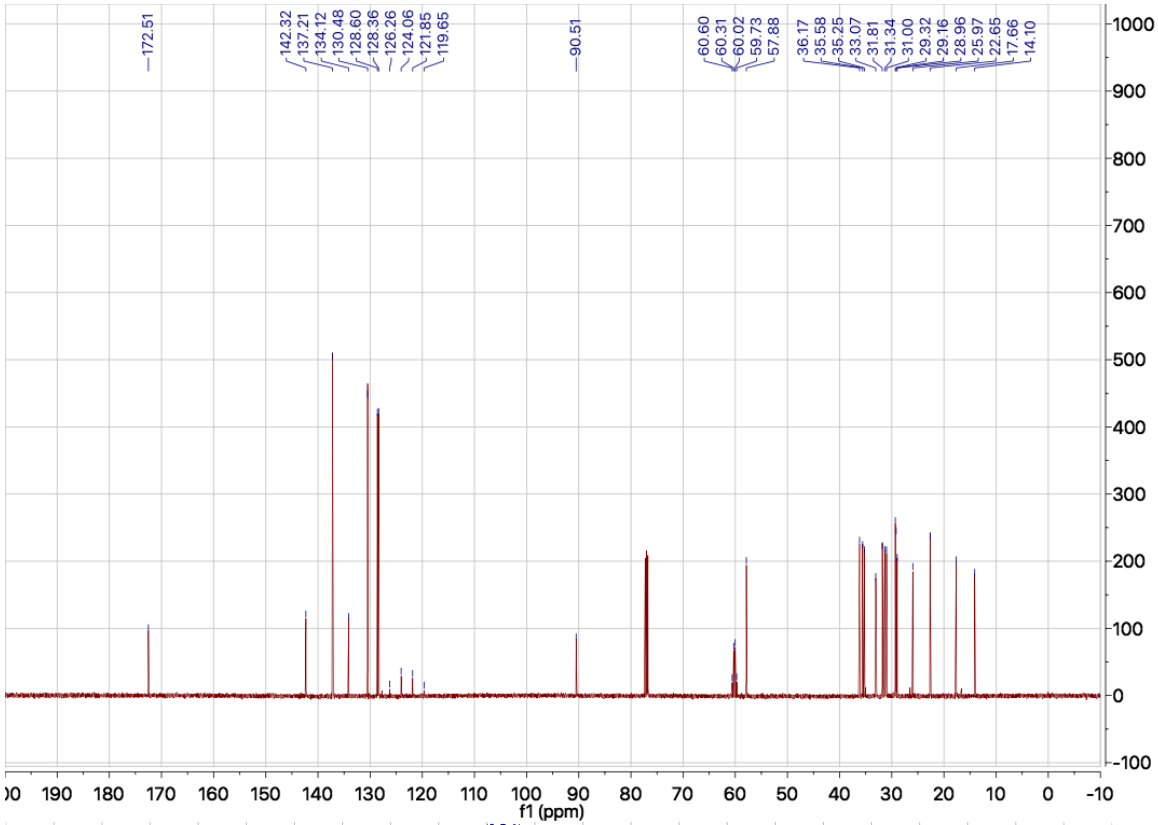
141.51
129.13
126.23
124.31
124.03
121.82
121.30
119.61
60.72
60.42
60.13
59.83
35.43
31.74
31.24
29.14
29.06
22.56
13.92
f1 (ppm)


-73.90
-73.93
-73.96
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2


F3CH2CO2C
I
f1 (ppm)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142.32
137.21
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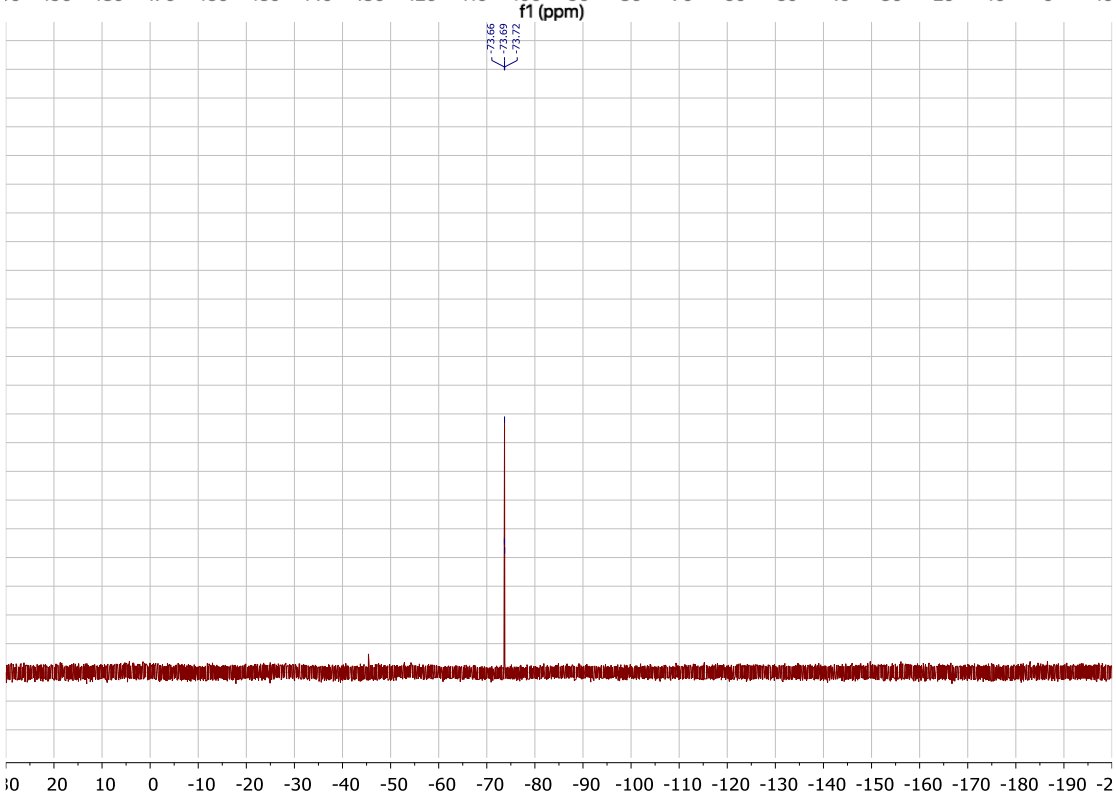
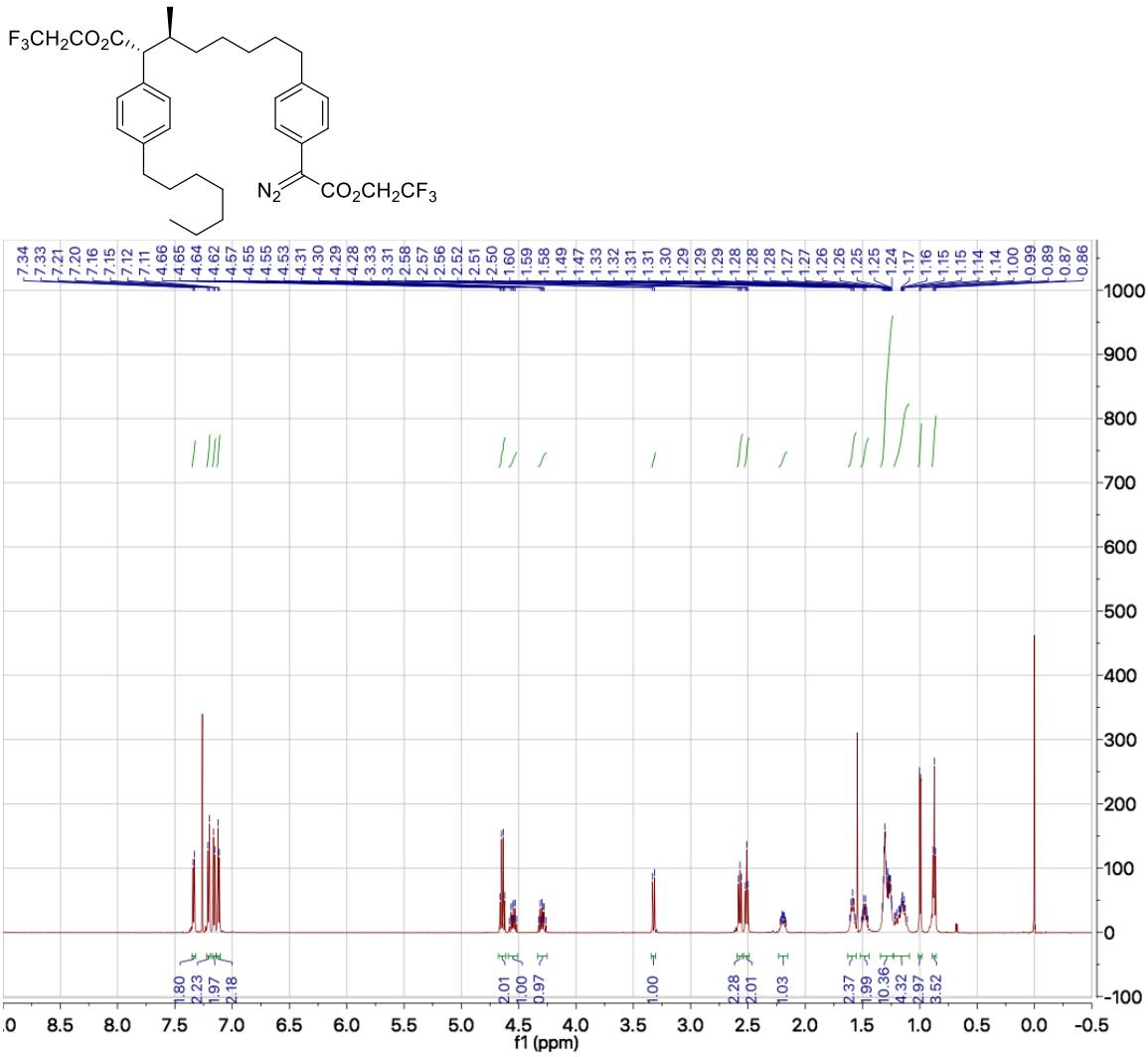
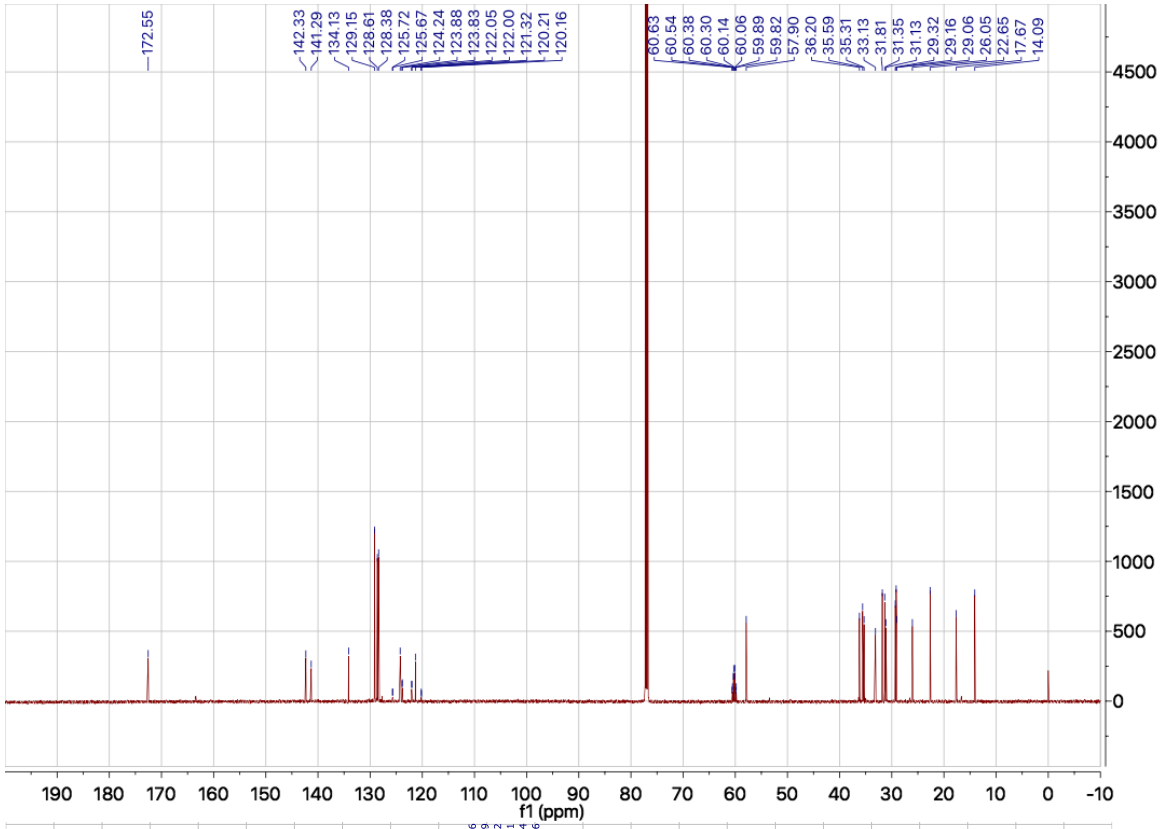
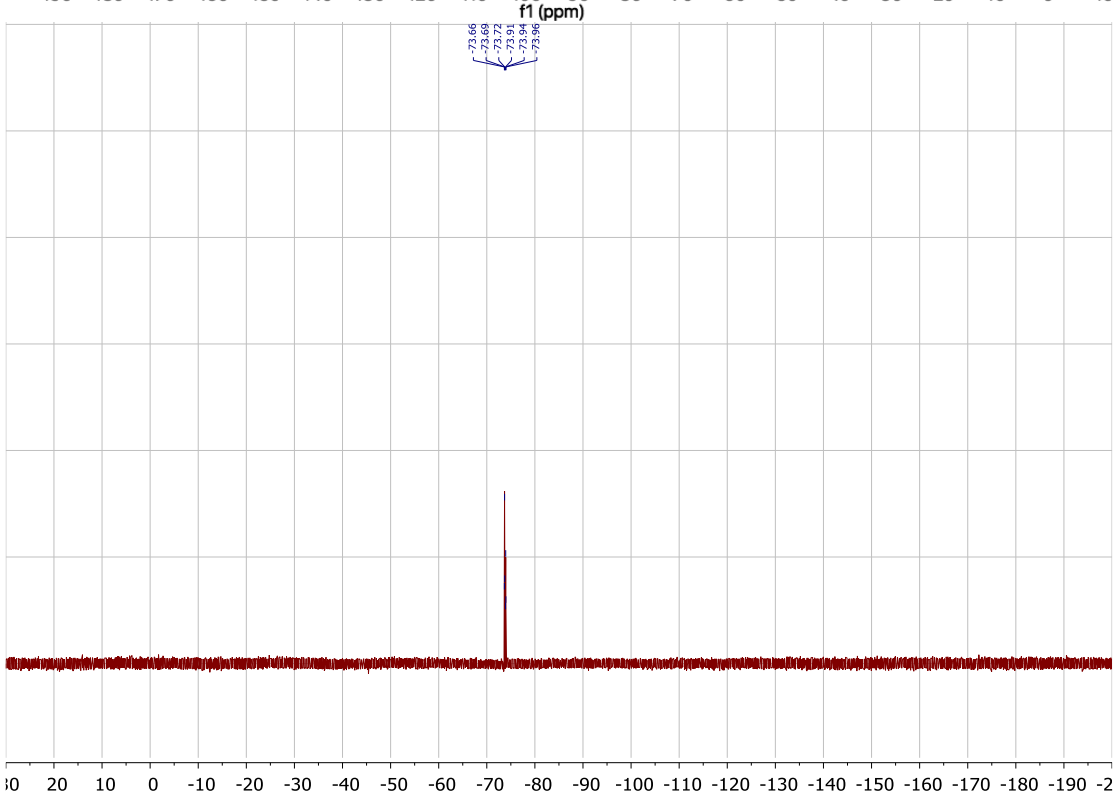
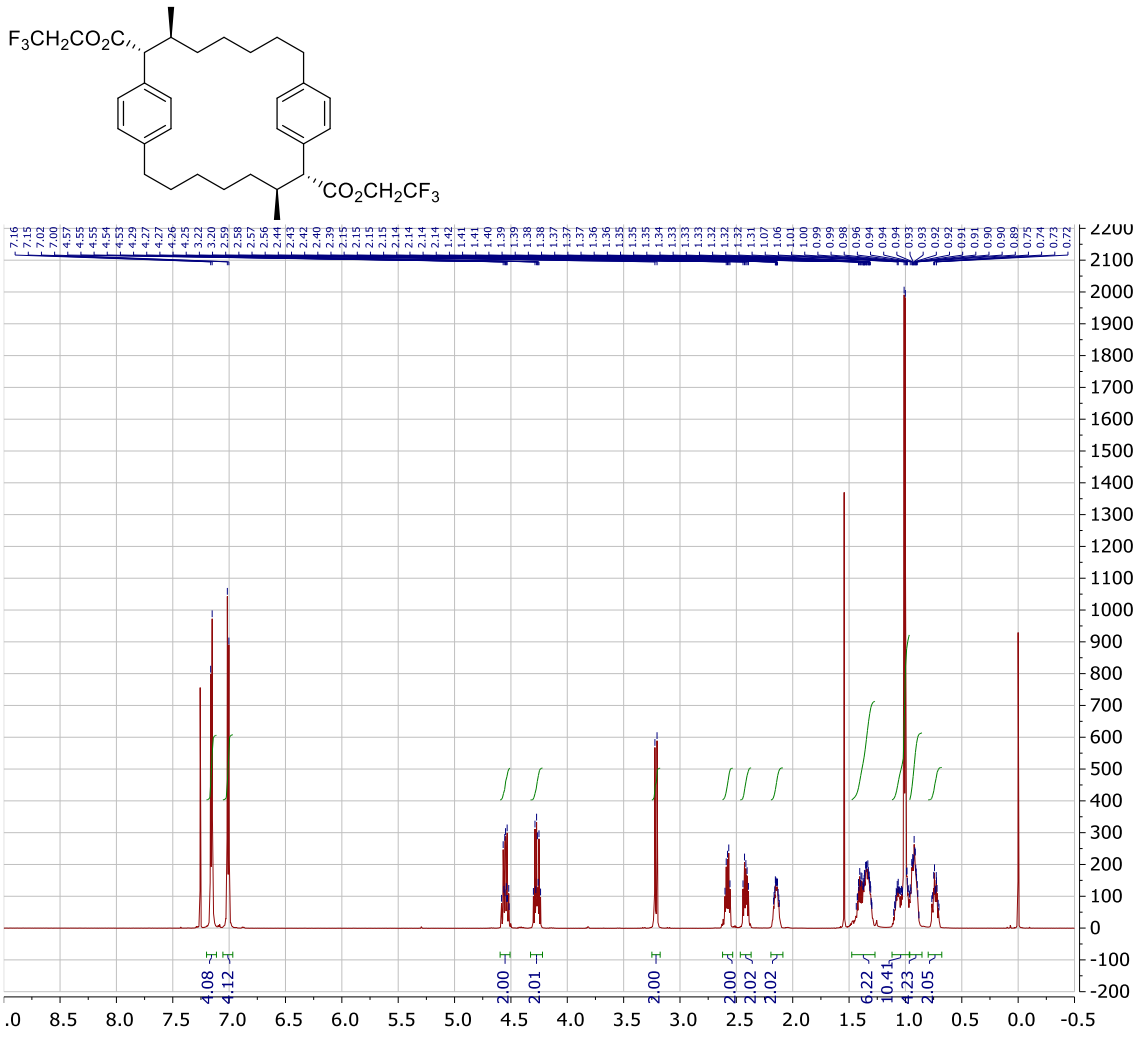
128.60
128.36
126.26
124.06
121.85
119.65
90.51
60.60
60.31
60.02
59.73
57.88
36.17
35.58
35.25
33.07
31.81
31.34
31.00
29.32
29.16
28.96
25.97
22.65
17.66
14.10
f1 (ppm)

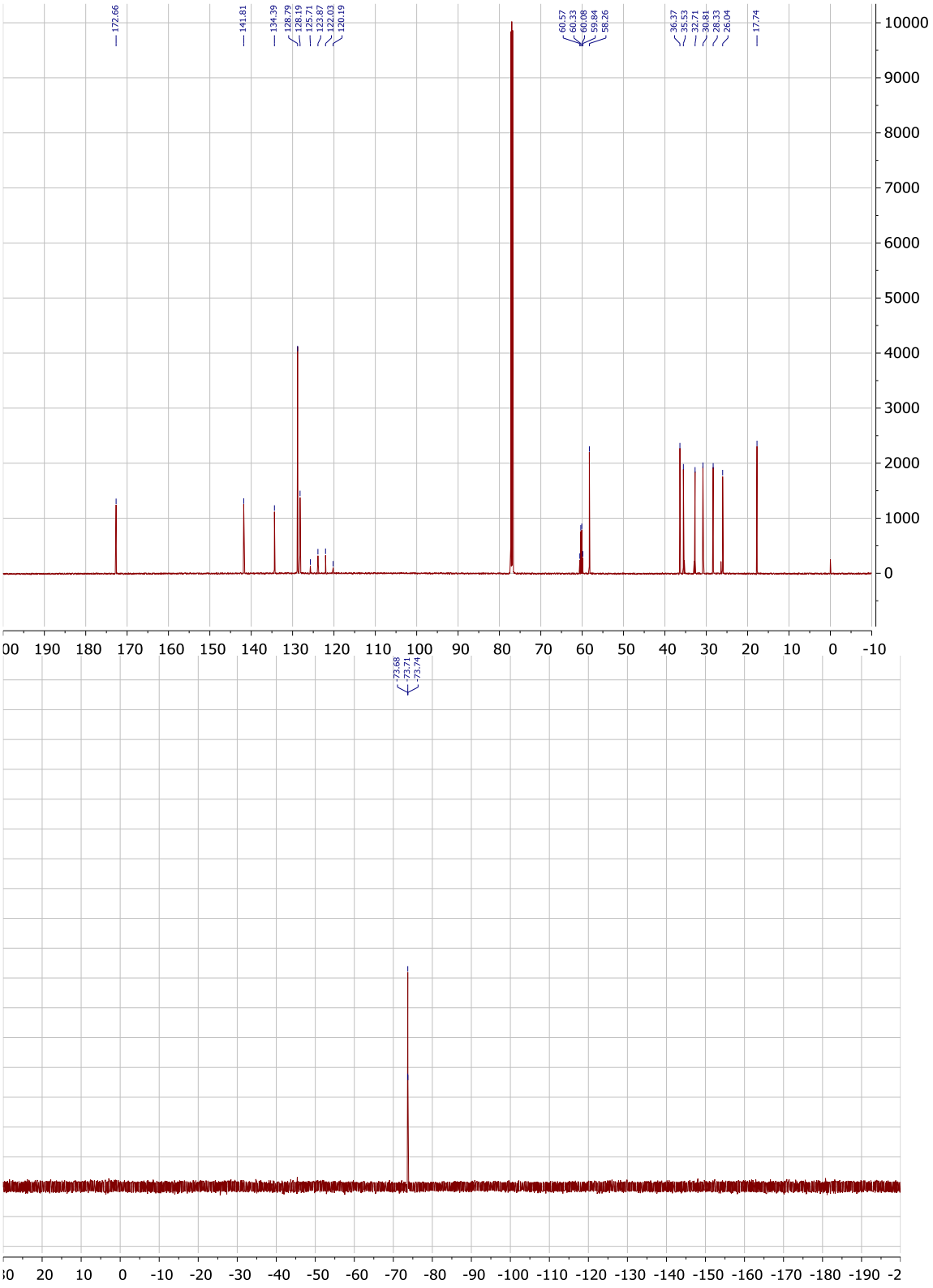

73.66
73.69
73.72


F3CH2CO2C
N2
CO2CH2CF3
f1 (ppm)

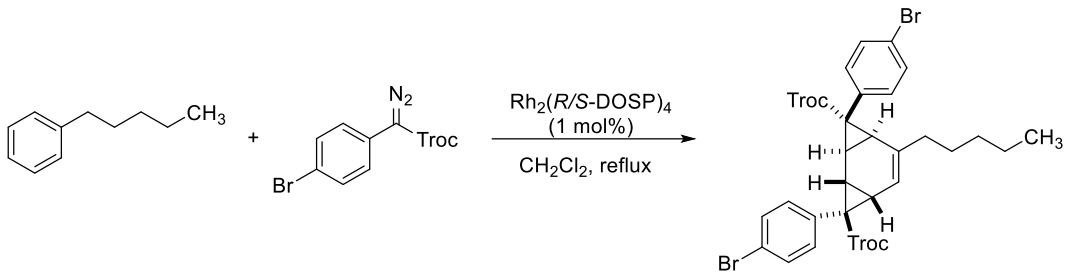

172.55
142.33
141.29
134.13
129.15
128.61
128.38
125.72
125.67
124.24
123.88
123.83
122.05
122.00
121.32
120.21
120.16
60.83
60.54
60.38
60.30
60.14
60.06
59.89
59.82
57.90
36.20
35.59
35.31
33.13
31.81
31.35
31.13
29.32
29.16
29.06
26.05
22.65
17.67
14.09
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

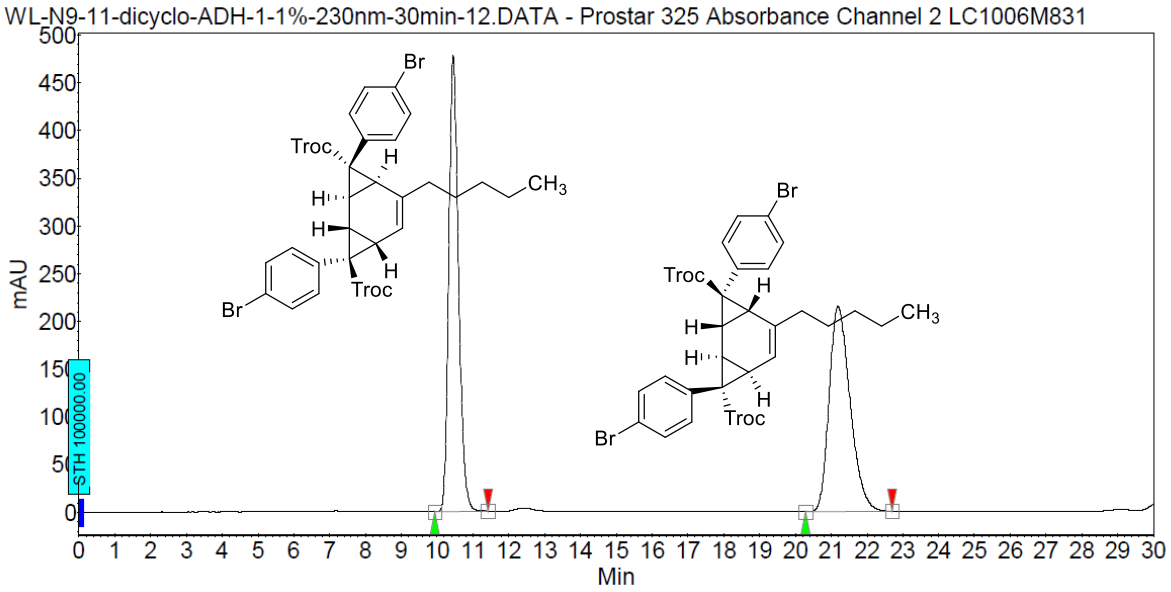

-73.66
-73.69
-73.72
-73.91
-73.94
-73.96
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2


F3CH2CO2C
CO2CH2CF3


172.66
141.81
134.39
128.79
128.19
125.71
123.87
122.03
120.19
60.57
60.33
60.08
59.84
58.26
36.37
35.53
32.71
30.81
28.33
26.04
17.74
73.68
73.71
73.74

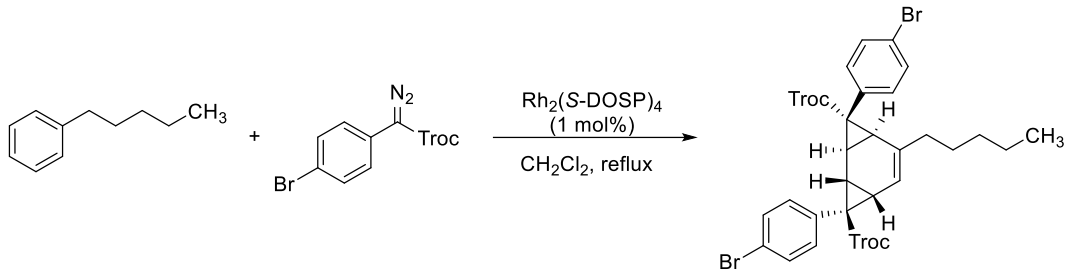
10. HPLC Spectra for Enantioselectivity Determination

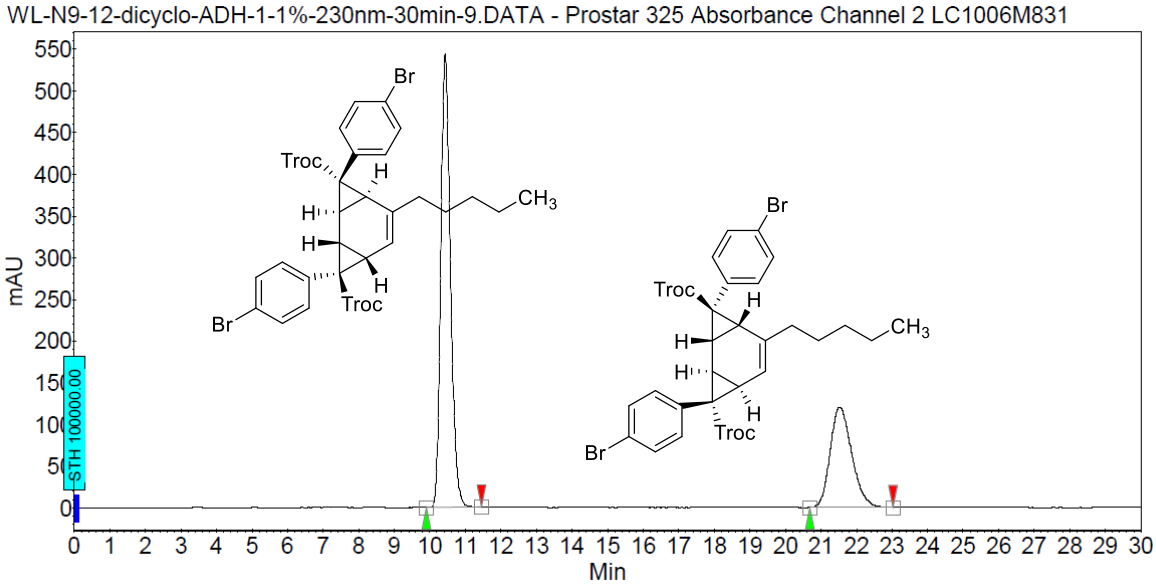




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.44	50.71	477.8	150.4	50.712
2	UNKNOWN	21.19	49.29	214.9	146.2	49.288
Total			100.00	692.7	296.7	100.000

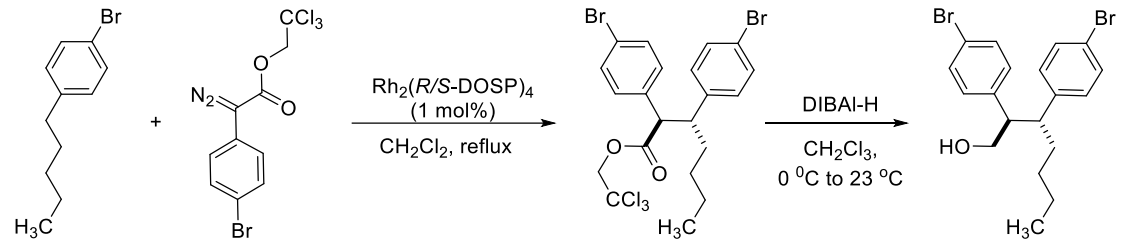


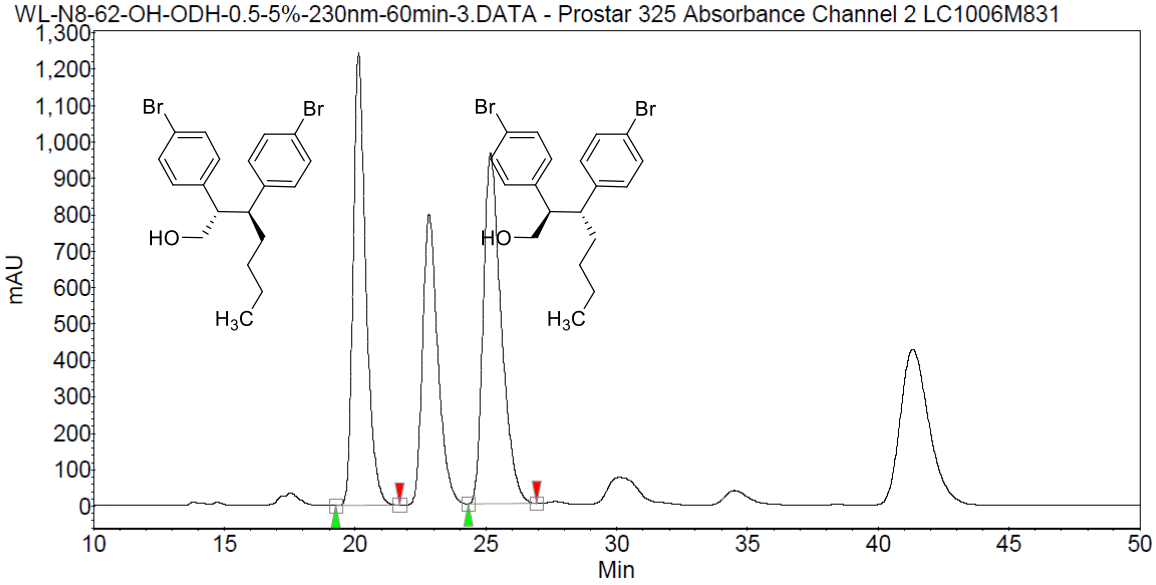


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.43	66.76	543.4	170.7	66.765
2	UNKNOWN	21.53	33.24	120.8	85.0	33.235
Total			100.00	664.2	255.7	100.000

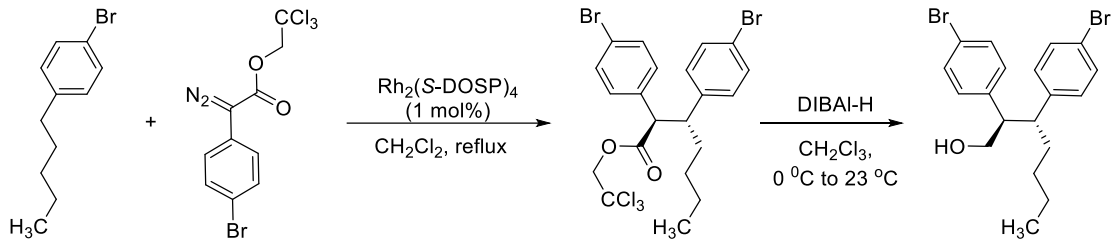
→ 34% ee

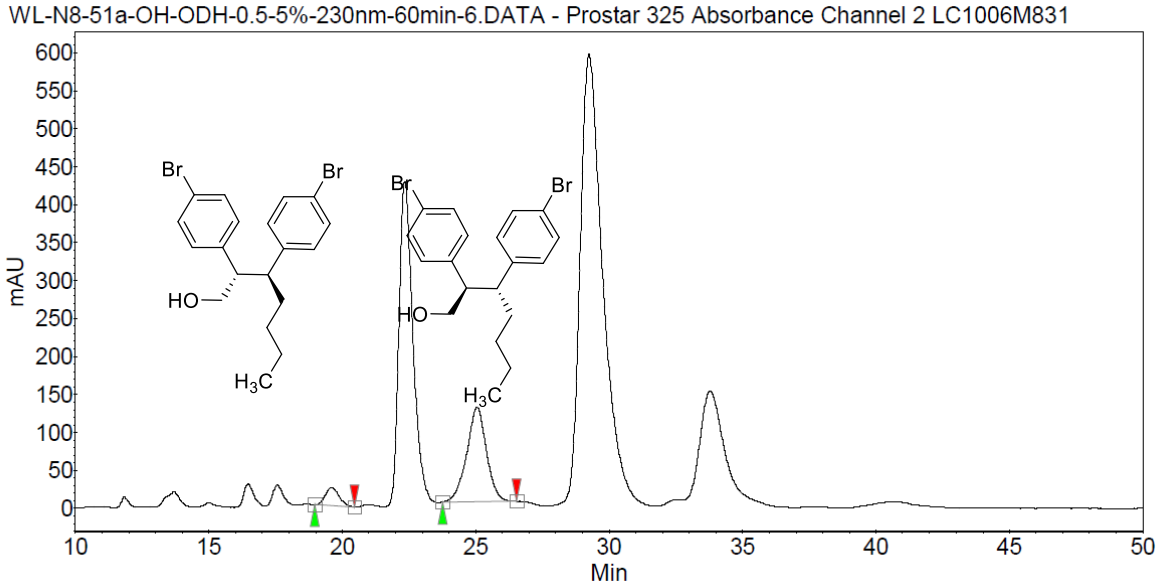




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.13	47.56	1242.5	699.2	47.563
2	UNKNOWN	25.17	52.44	963.2	770.9	52.437
Total			100.00	2205.7	1470.1	100.000

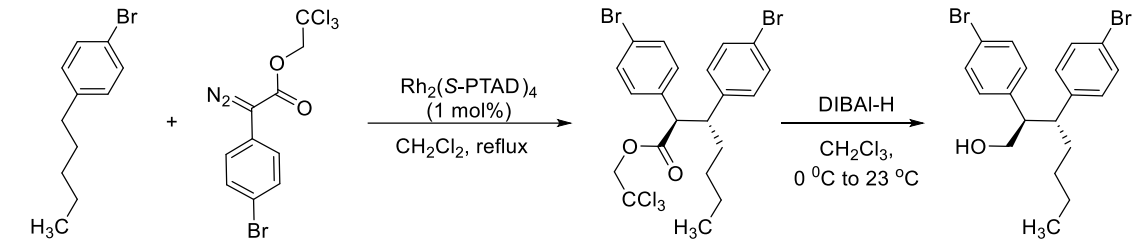


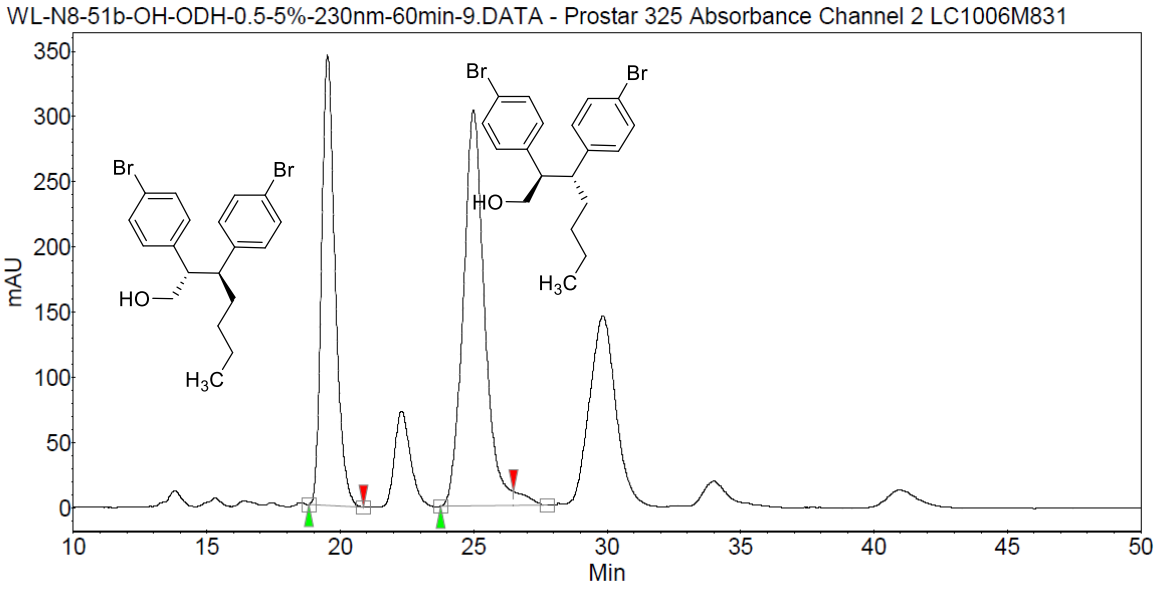


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.60	11.63	23.9	14.0	11.625
2	UNKNOWN	25.04	88.37	124.7	106.6	88.375
Total			100.00	148.6	120.6	100.000

→ 77% ee

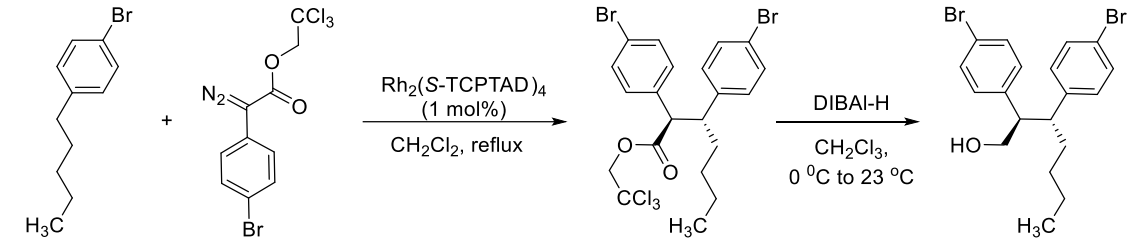


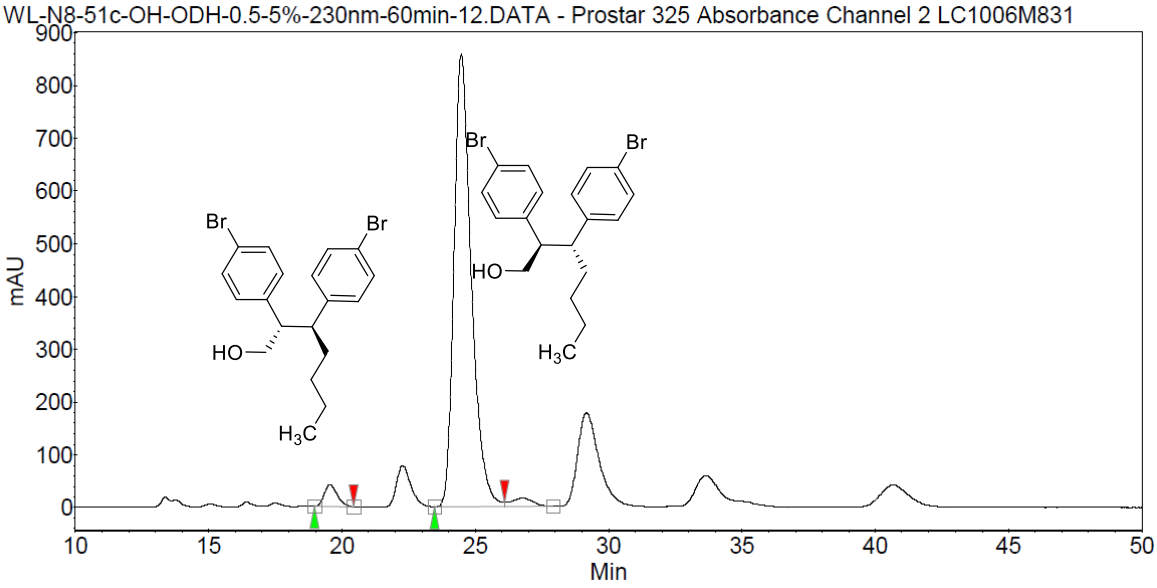


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.52	42.12	345.2	203.0	42.121
2	UNKNOWN	24.99	57.88	303.8	279.0	57.879
Total			100.00	649.0	482.0	100.000

→ 16% ee

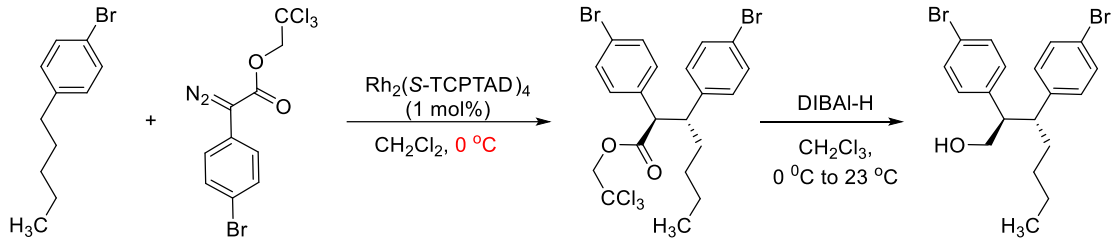


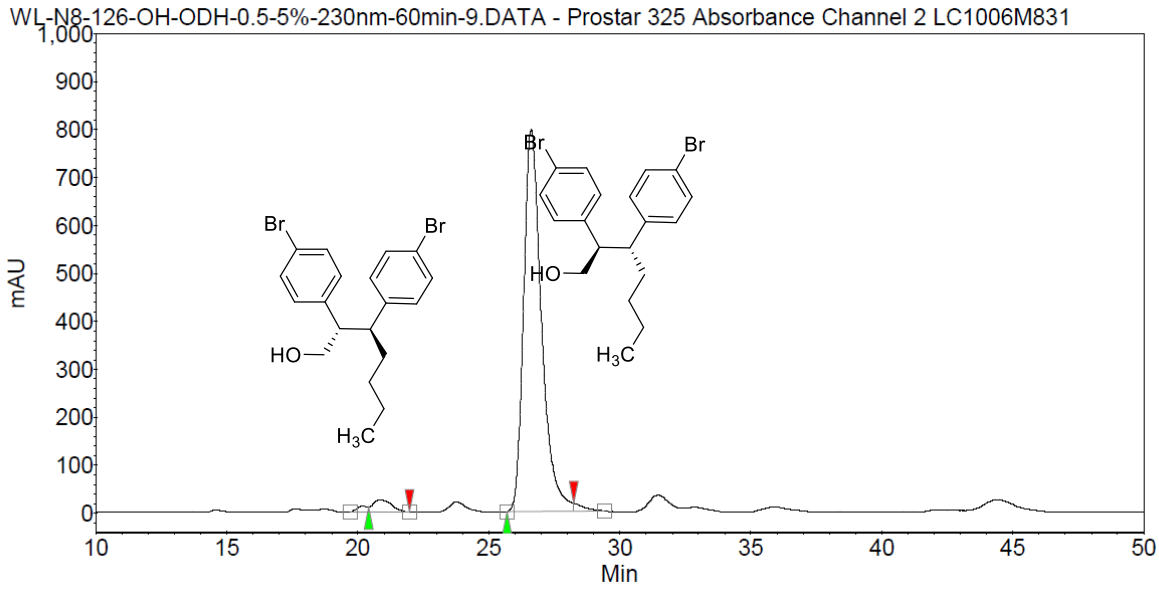


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.54	3.52	41.6	23.6	3.522
2	UNKNOWN	24.47	96.48	857.4	646.1	96.478
Total			100.00	899.0	669.7	100.000

→ 93% ee

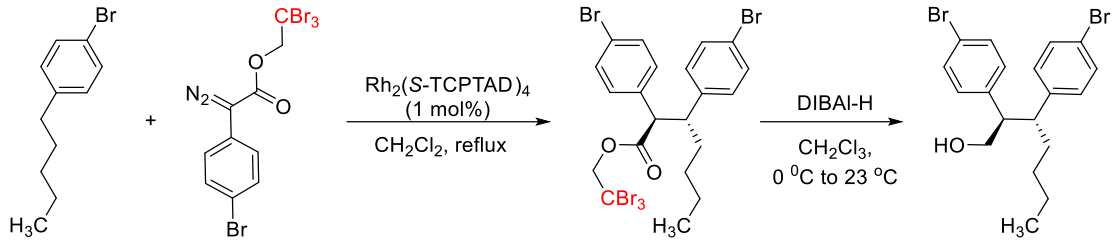


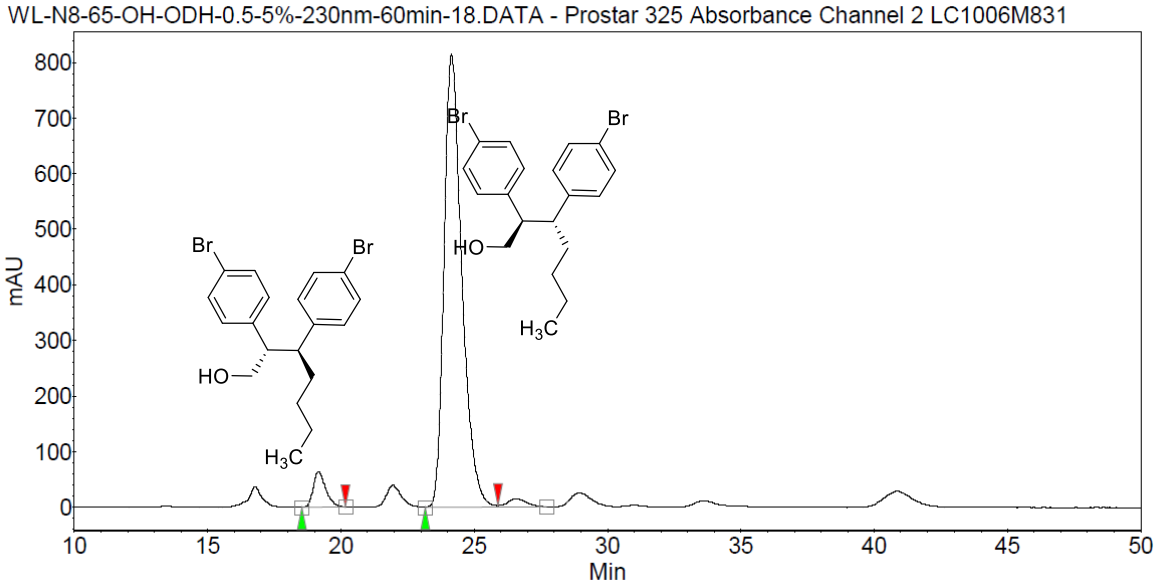


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	20.84	3.16	25.1	20.5	3.158
1	UNKNOWN	26.62	96.84	796.2	628.3	96.842
Total			100.00	821.3	648.8	100.000

→ 94% ee

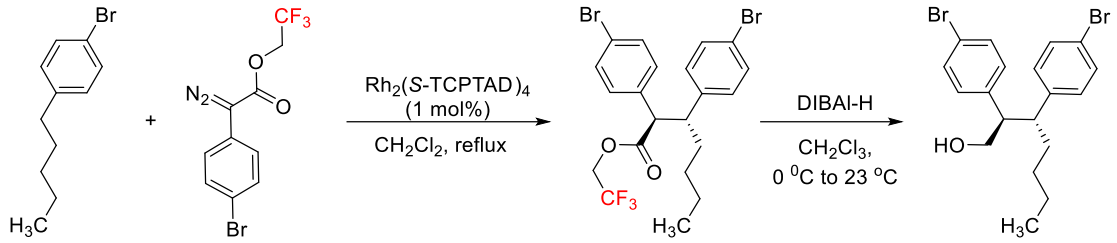


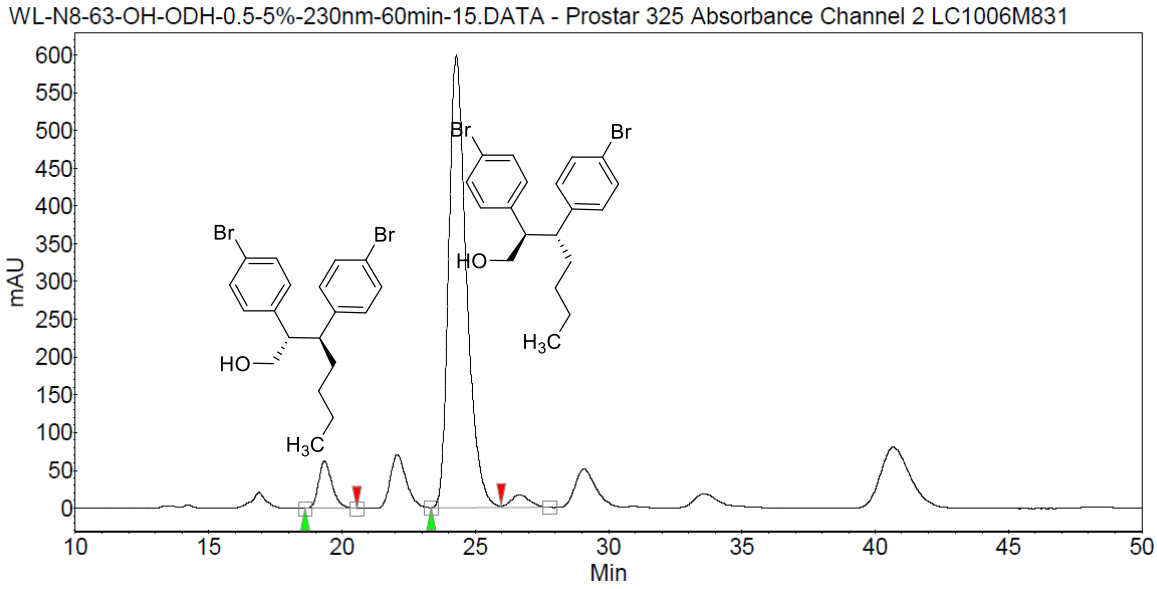


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.16	5.18	63.3	34.4	5.177
2	UNKNOWN	24.14	94.82	813.9	630.8	94.823
Total			100.00	877.1	665.2	100.000

→ 90% ee

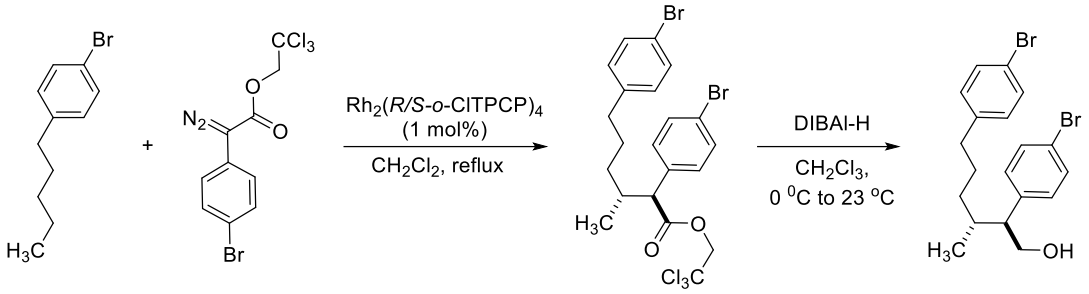


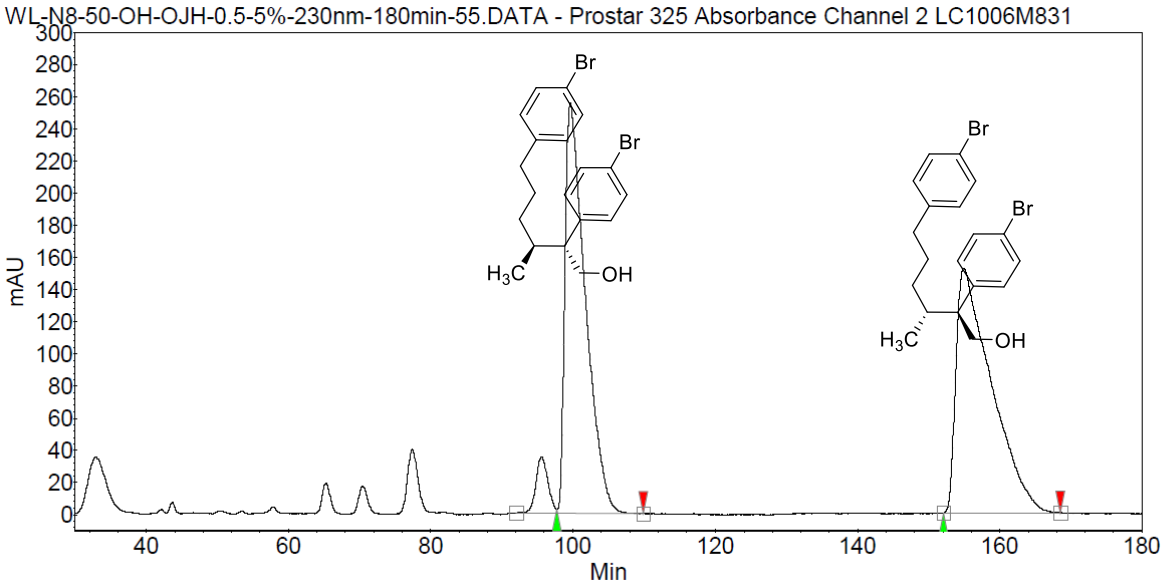


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.34	7.29	62.3	36.4	7.289
2	UNKNOWN	24.28	92.71	598.8	463.6	92.711
Total			100.00	661.1	500.0	100.000

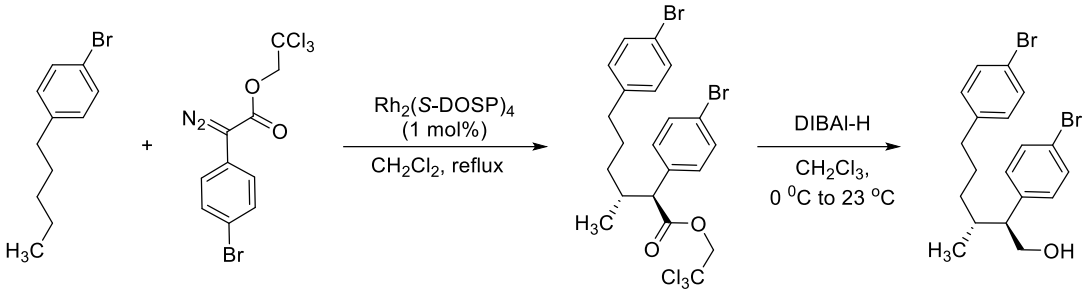
→ 85% ee

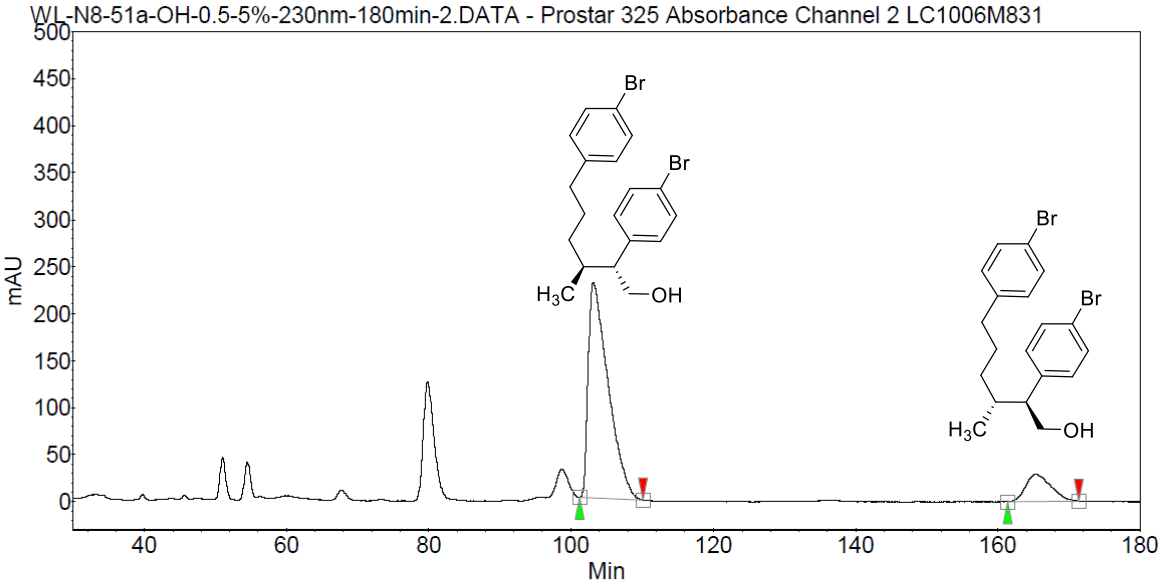




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	99.60	49.15	255.7	847.5	49.147
2	UNKNOWN	154.95	50.85	152.1	877.0	50.853
Total			100.00	407.8	1724.5	100.000

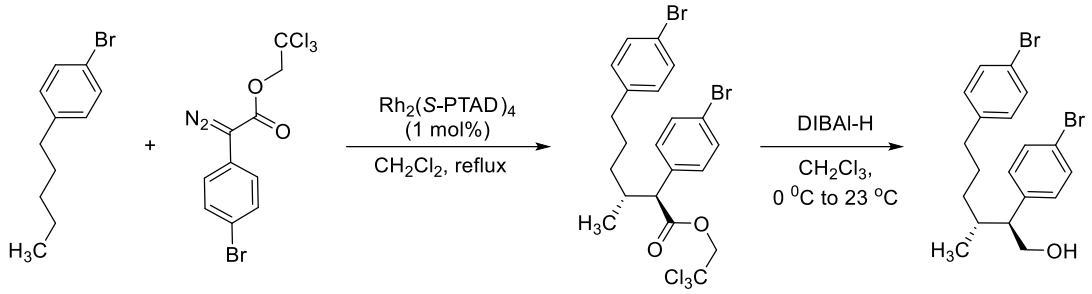


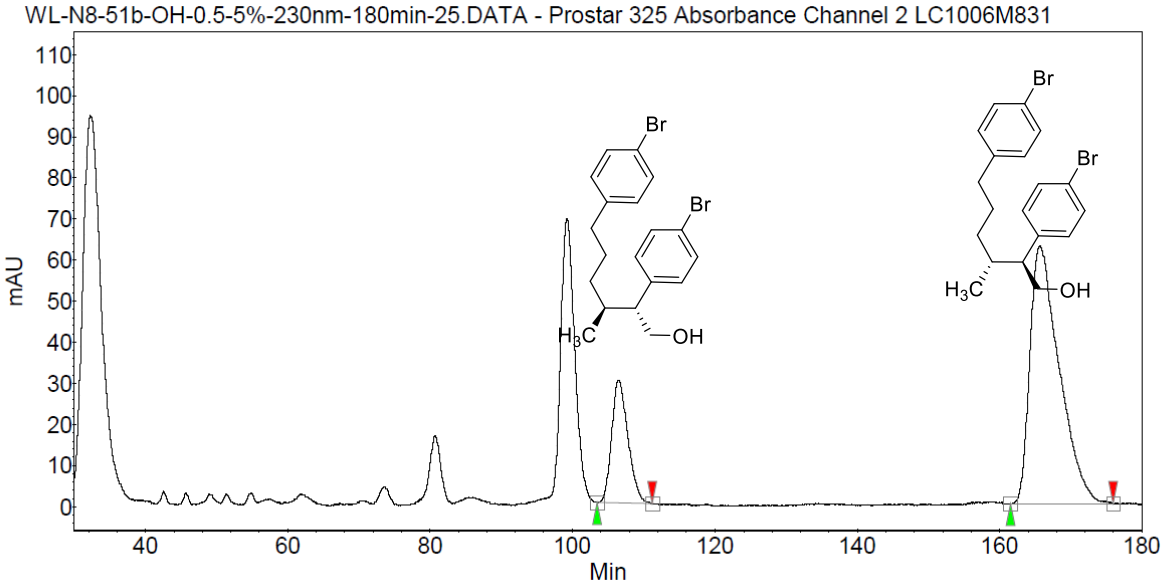


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	103.13	86.32	230.0	746.3	86.318
2	UNKNOWN	165.31	13.68	29.2	118.3	13.682
Total			100.00	259.2	864.6	100.000

→ -73% ee

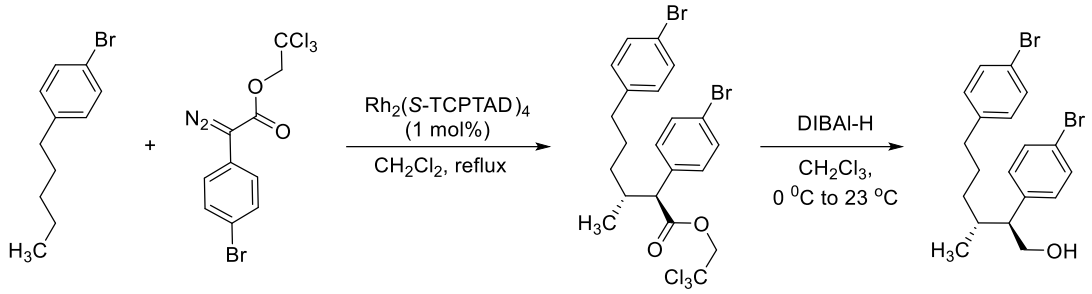


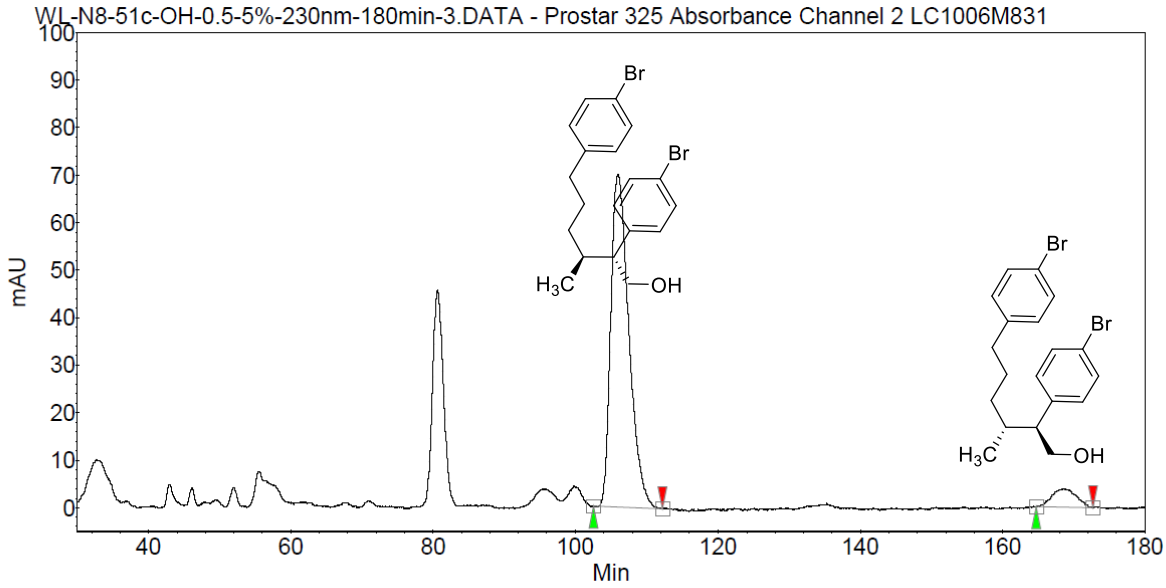


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	106.52	20.88	29.8	78.9	20.885
2	UNKNOWN	165.70	79.12	62.8	299.0	79.115
Total			100.00	92.6	378.0	100.000

→ 58% ee

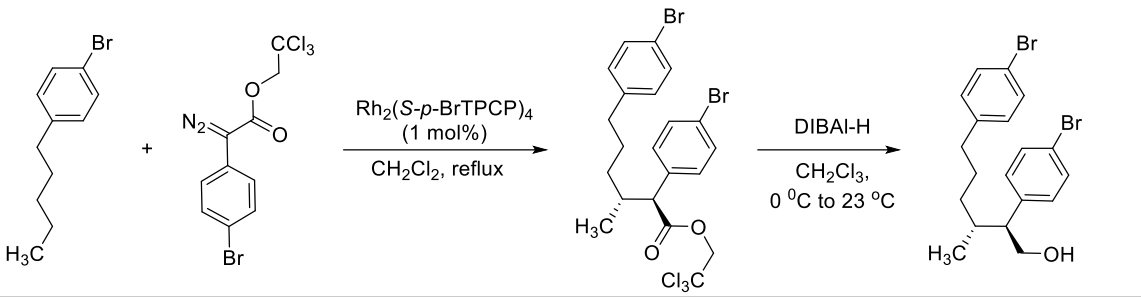


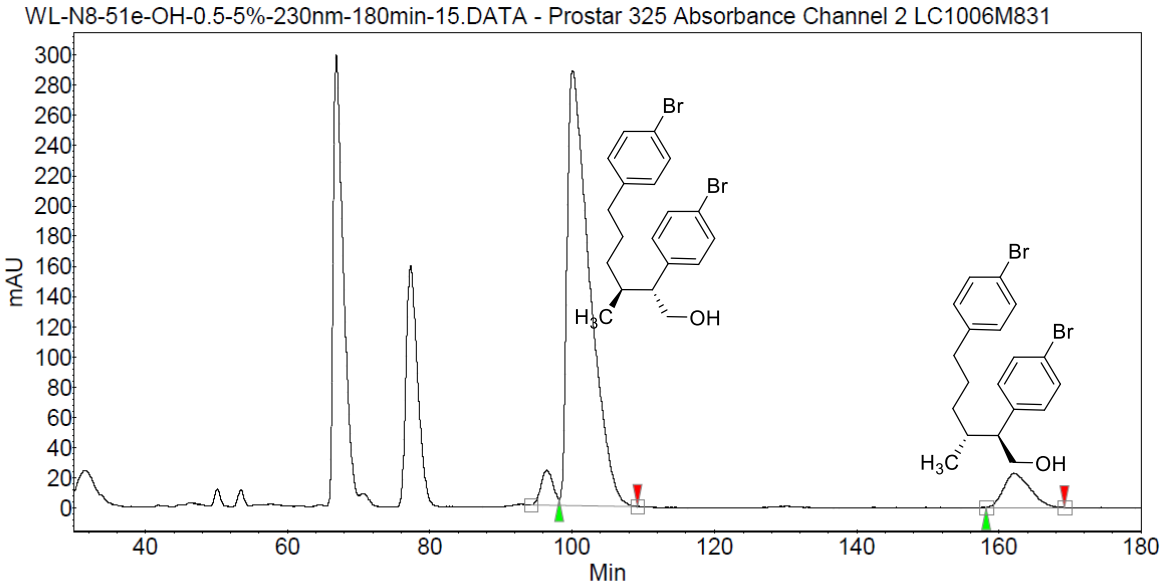


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	105.96	93.19	70.1	205.8	93.189
2	UNKNOWN	168.58	6.81	3.9	15.0	6.811
Total			100.00	73.9	220.9	100.000

→ -86% ee

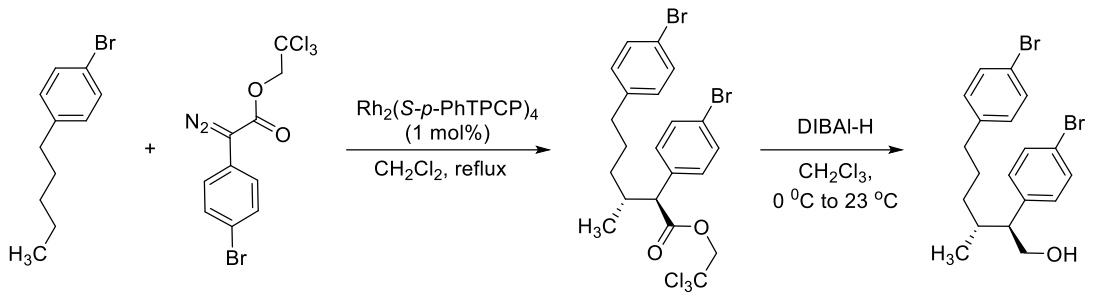


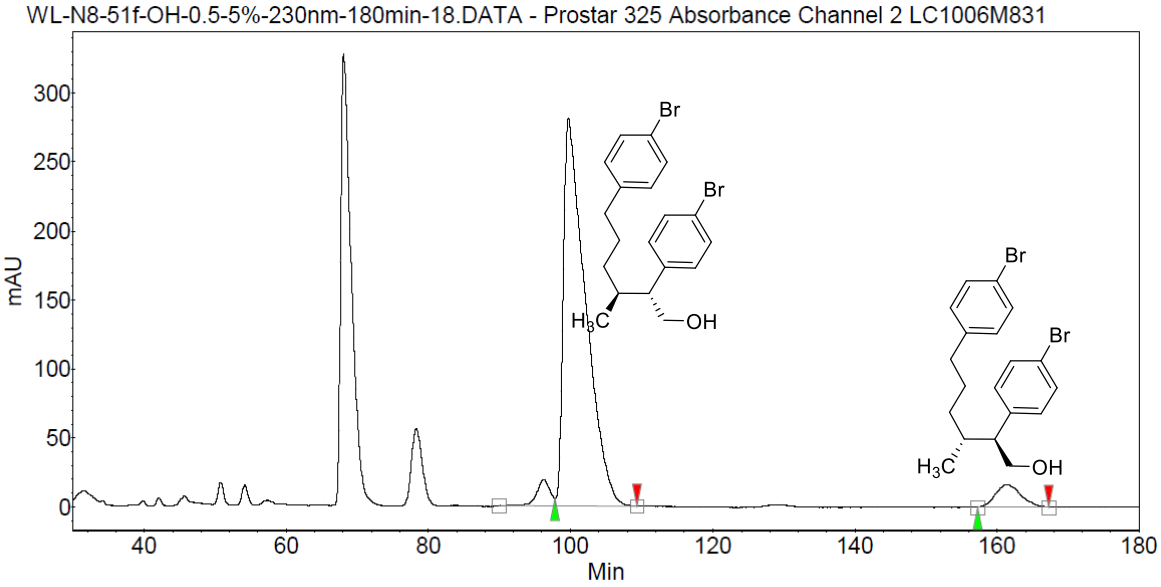


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	100.08	91.55	287.6	1055.5	91.547
1	UNKNOWN	162.12	8.45	22.7	97.5	8.453
Total			100.00	310.3	1153.0	100.000

→ -83% ee

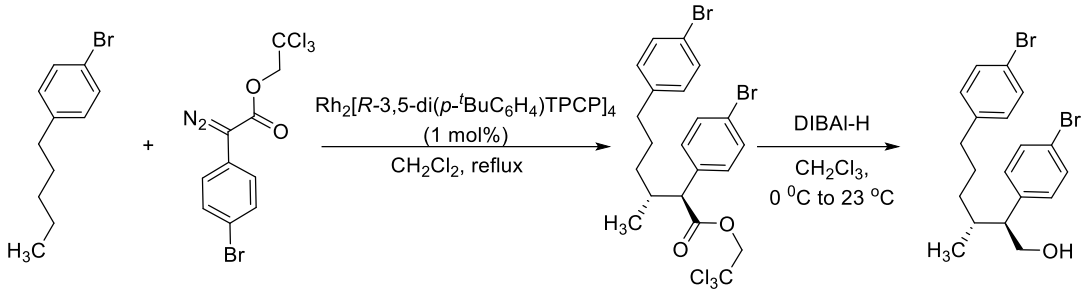


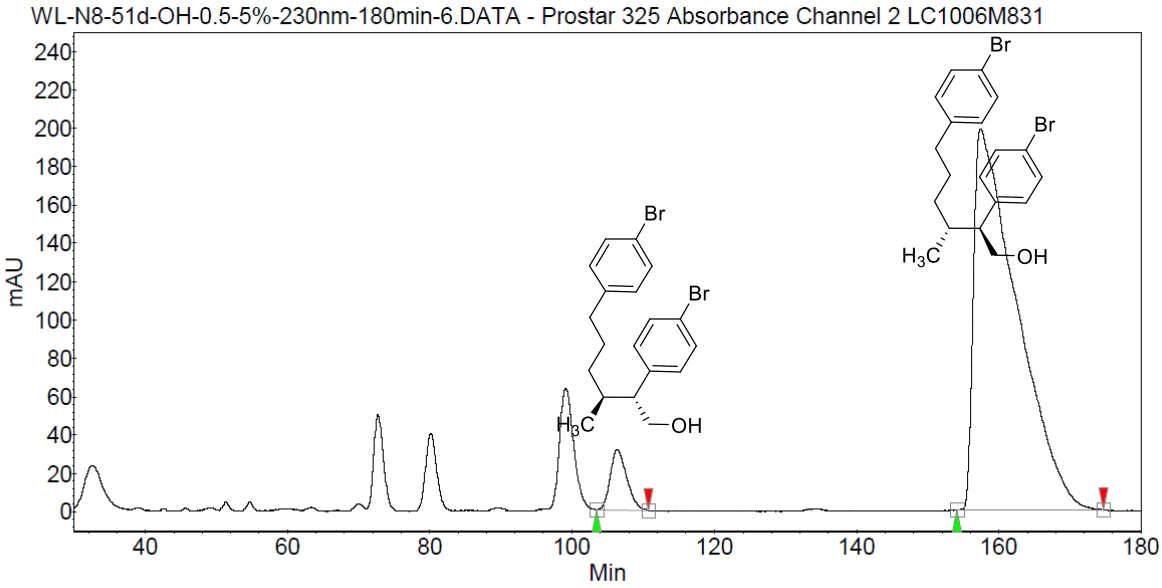


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	99.69	93.77	281.3	1016.0	93.768
2	UNKNOWN	161.51	6.23	15.9	67.5	6.232
Total			100.00	297.2	1083.6	100.000

→ -88% ee

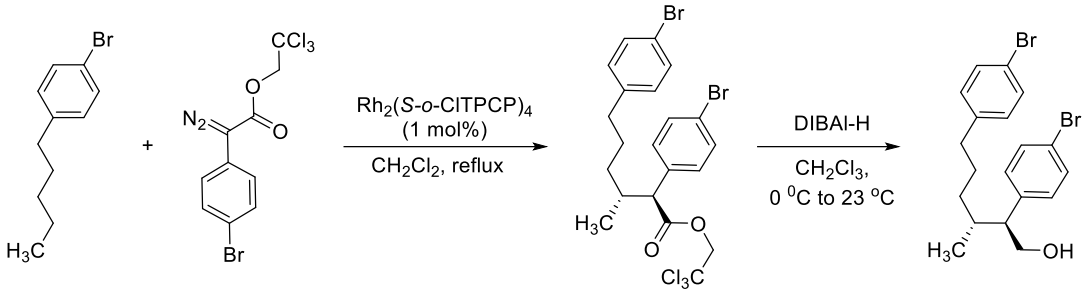


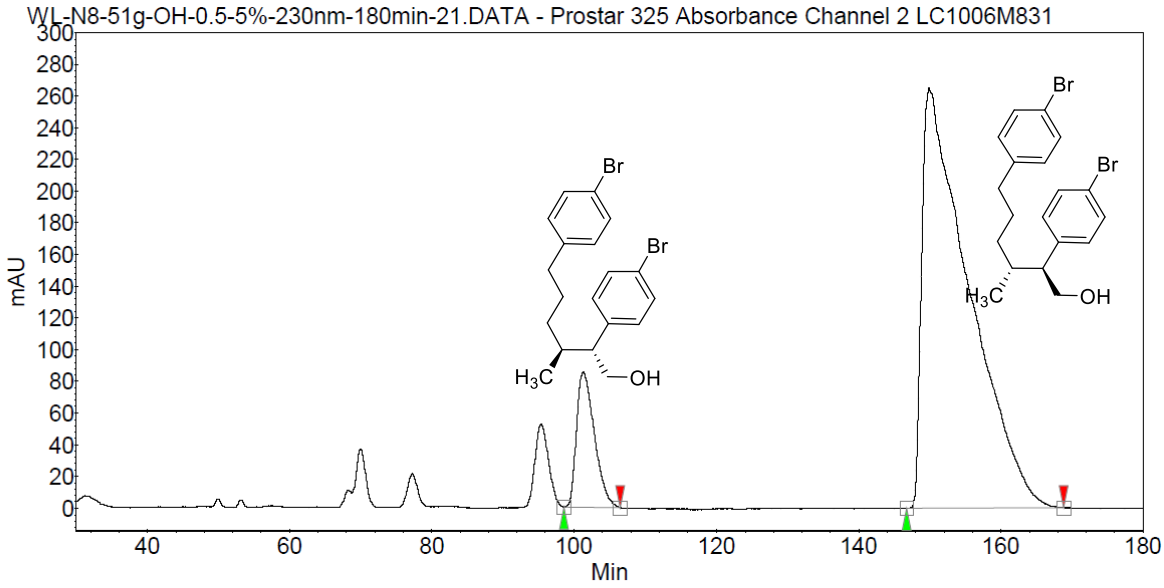


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	106.25	5.68	31.6	84.3	5.680
2	UNKNOWN	157.42	94.32	198.9	1399.0	94.320
Total			100.00	230.6	1483.3	100.000

→ 89% ee

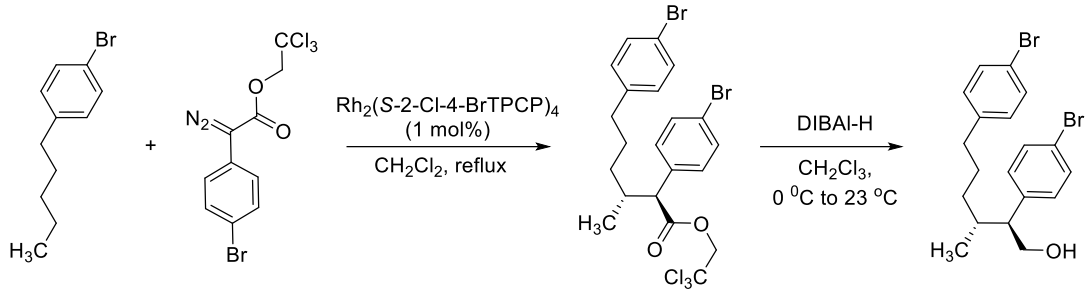


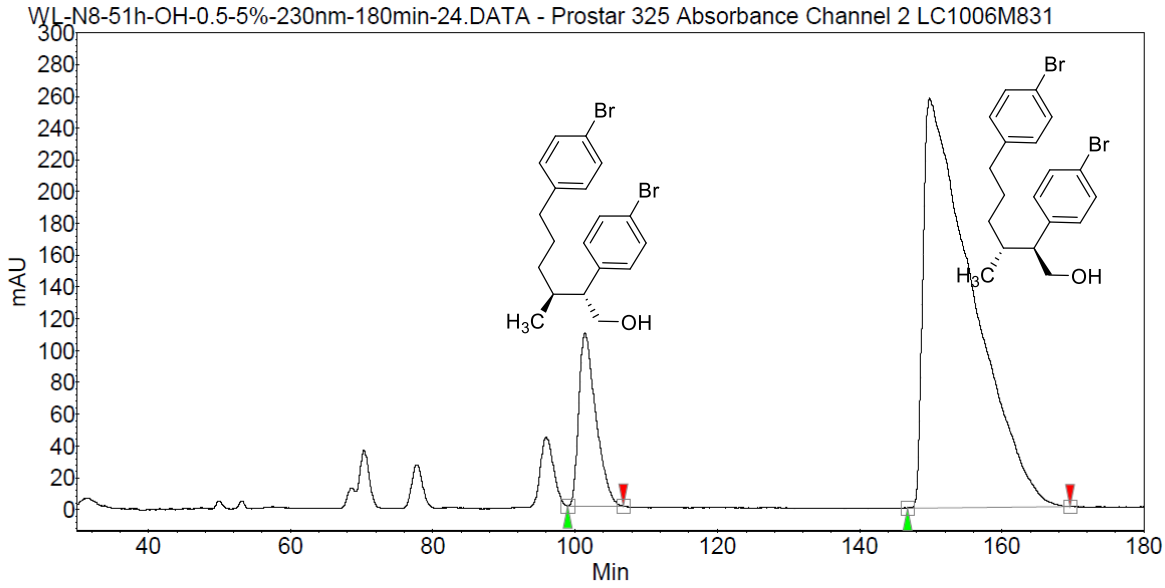


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	101.30	10.93	85.3	248.7	10.925
2	UNKNOWN	149.91	89.07	265.0	2027.6	89.075
Total			100.00	350.3	2276.2	100.000

→ 78% ee

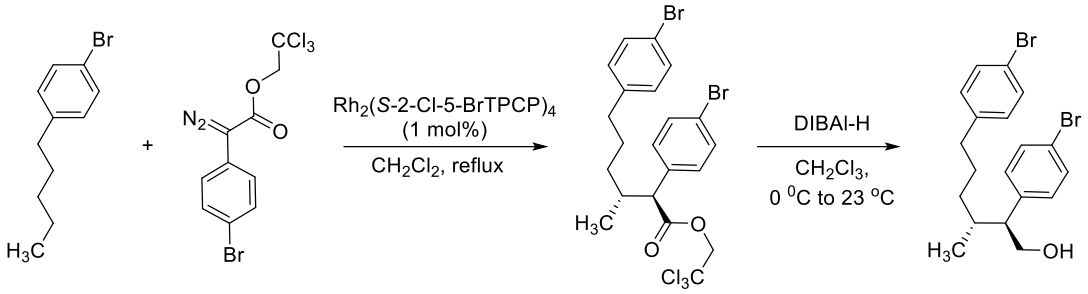


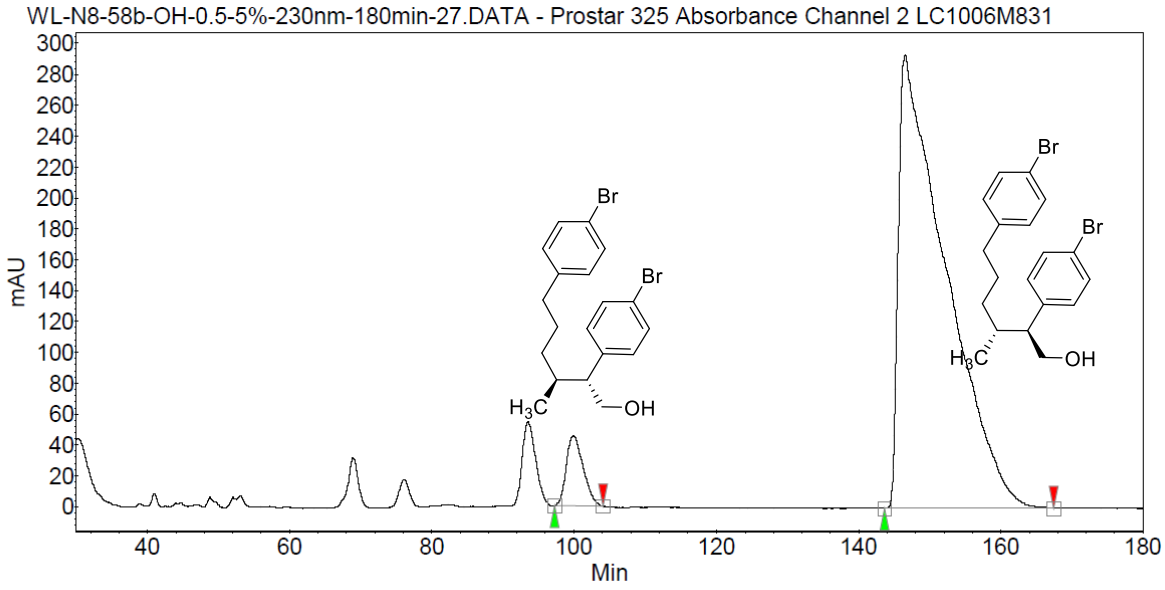


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	101.40	12.81	108.7	302.9	12.811
2	UNKNOWN	149.86	87.19	257.6	2061.7	87.189
Total			100.00	366.3	2364.7	100.000

→ 74% ee

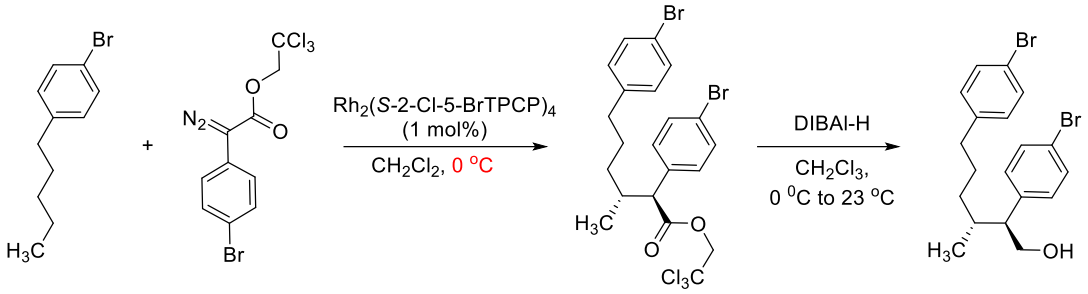


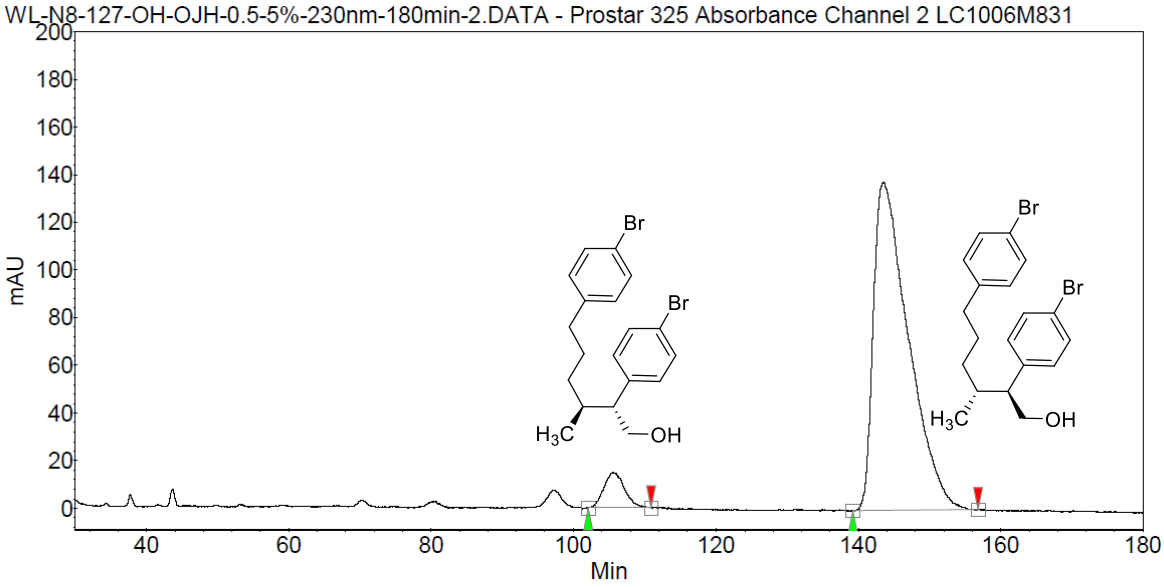


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	99.82	5.25	45.5	124.8	5.252
2	UNKNOWN	146.59	94.75	293.2	2251.4	94.748
Total			100.00	338.7	2376.2	100.000

→ 89% ee

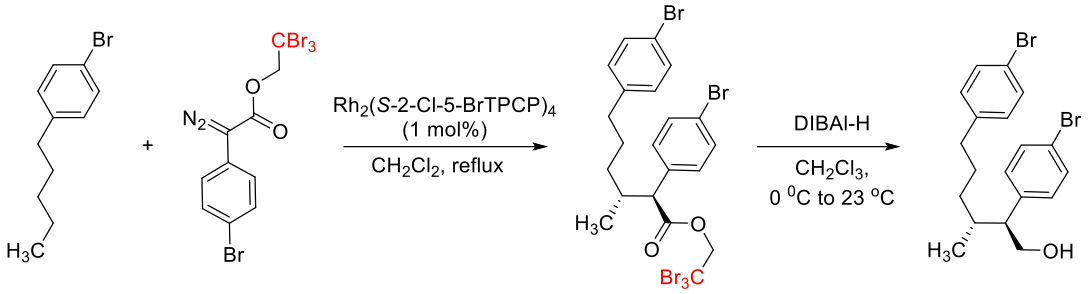


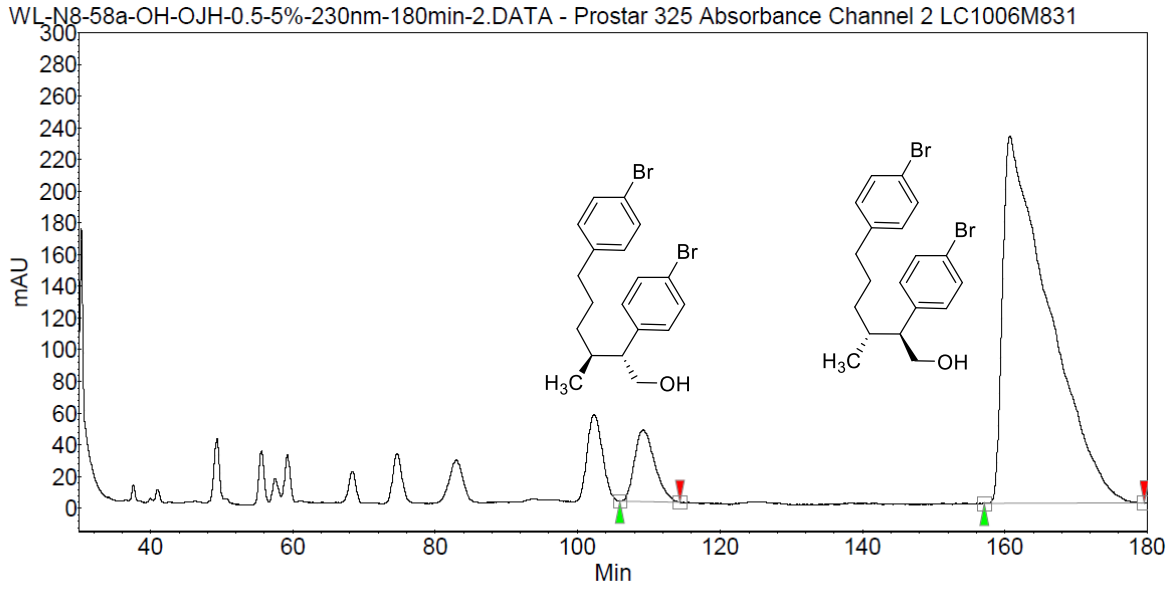


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	105.48	5.95	14.7	49.5	5.954
2	UNKNOWN	143.52	94.05	137.7	782.6	94.046
Total			100.00	152.4	832.2	100.000

→ 88% ee

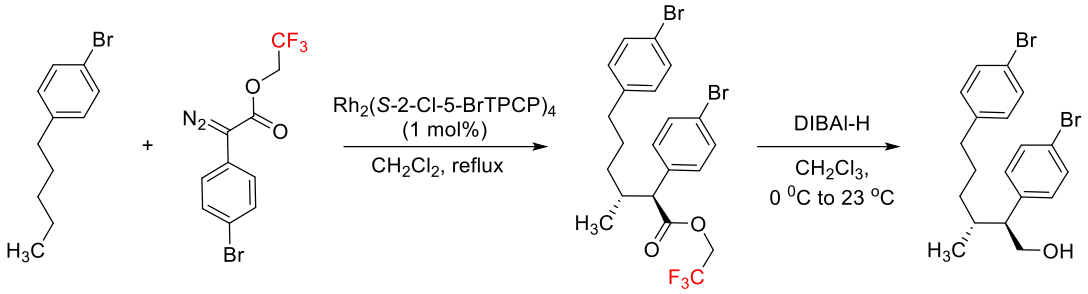


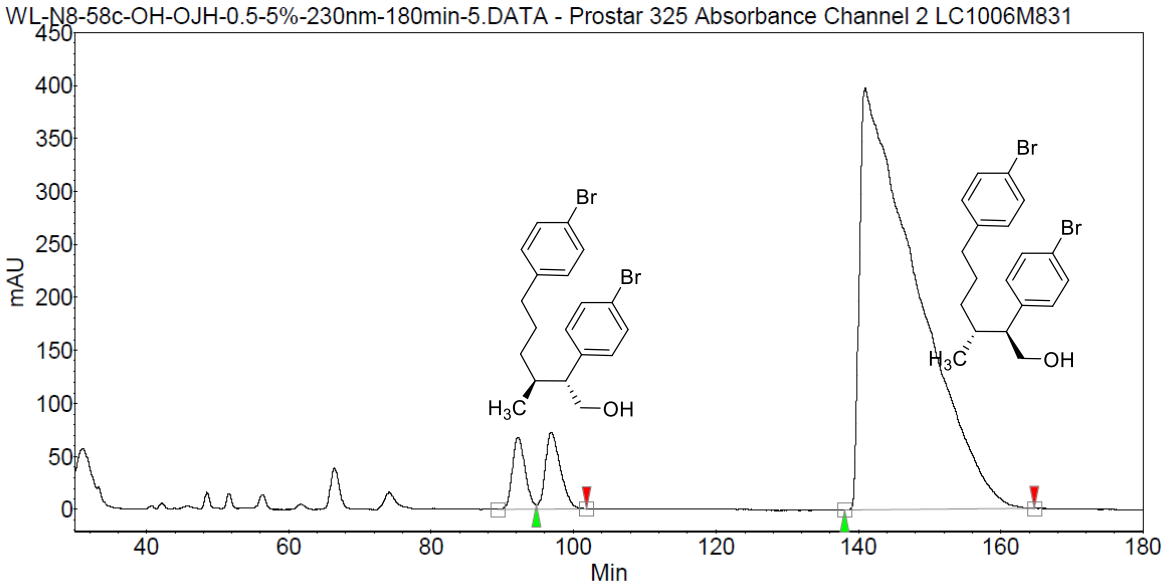


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	109.22	7.86	45.1	148.6	7.859
2	UNKNOWN	160.76	92.14	231.9	1742.6	92.141
Total			100.00	277.0	1891.3	100.000

→ 84% ee

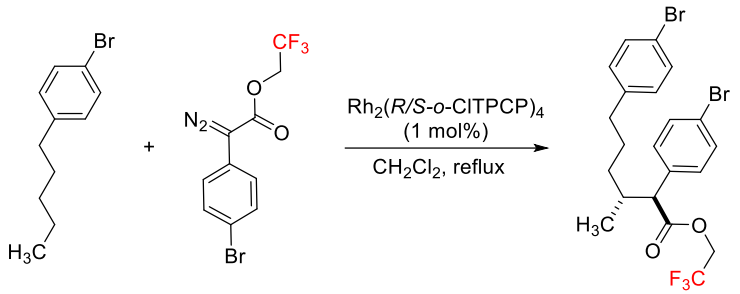


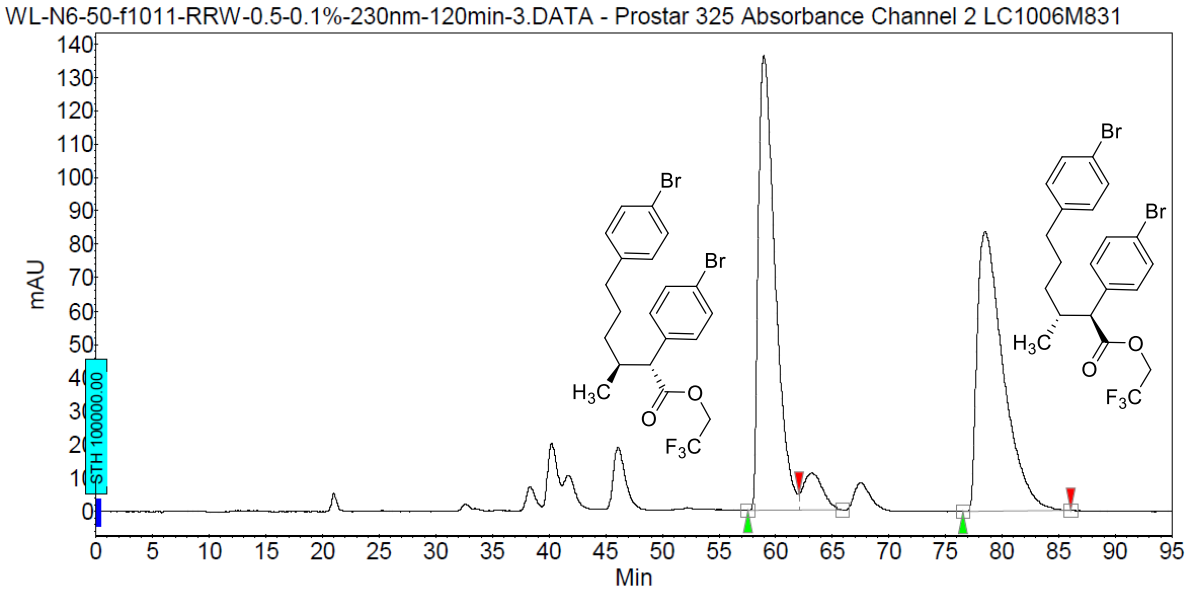


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	96.81	4.59	72.4	177.8	4.585
1	UNKNOWN	140.95	95.41	398.4	3699.3	95.415
Total			100.00	470.9	3877.1	100.000

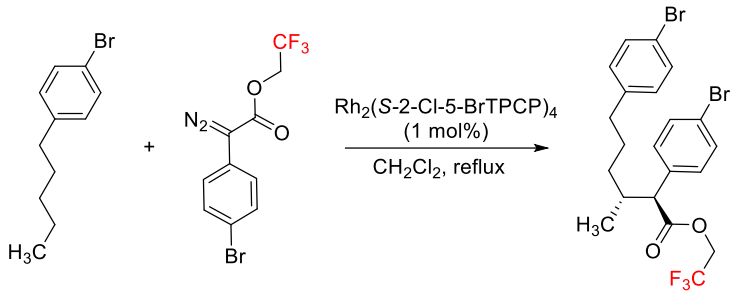
→ 91% ee

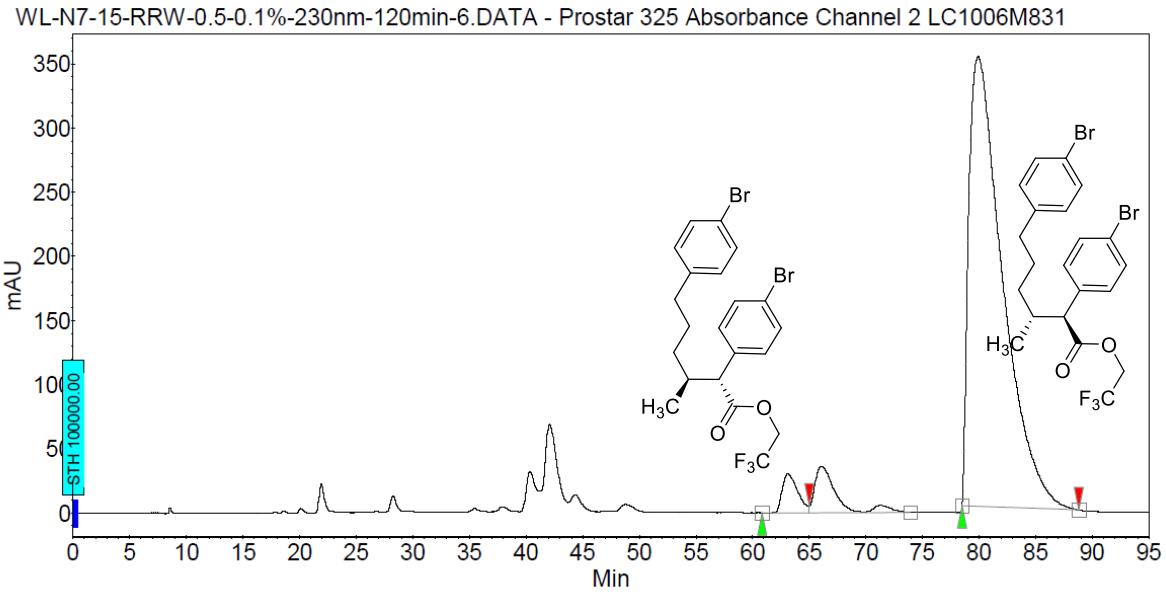




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	58.98	51.09	136.0	235.0	51.089
2	UNKNOWN	78.49	48.91	83.8	225.0	48.911
Total			100.00	219.8	460.1	100.000

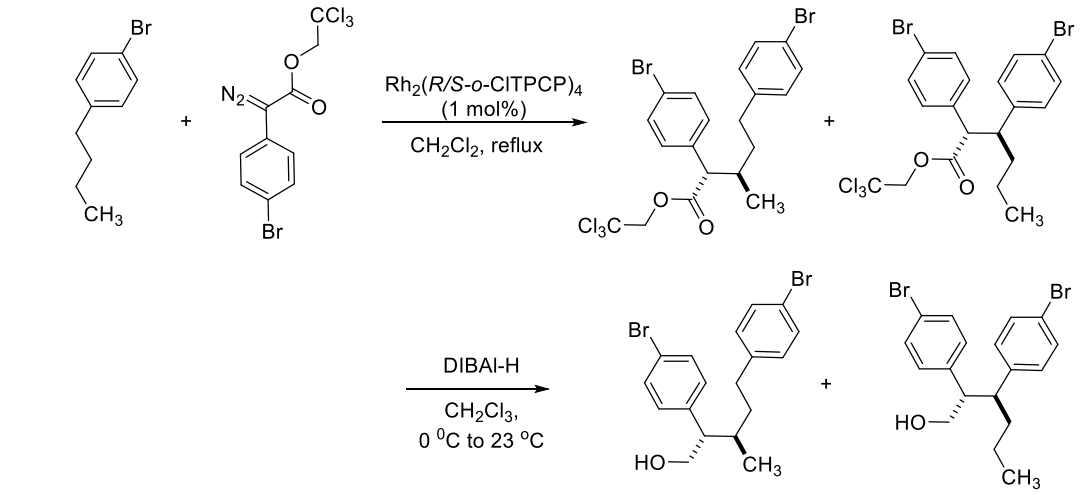


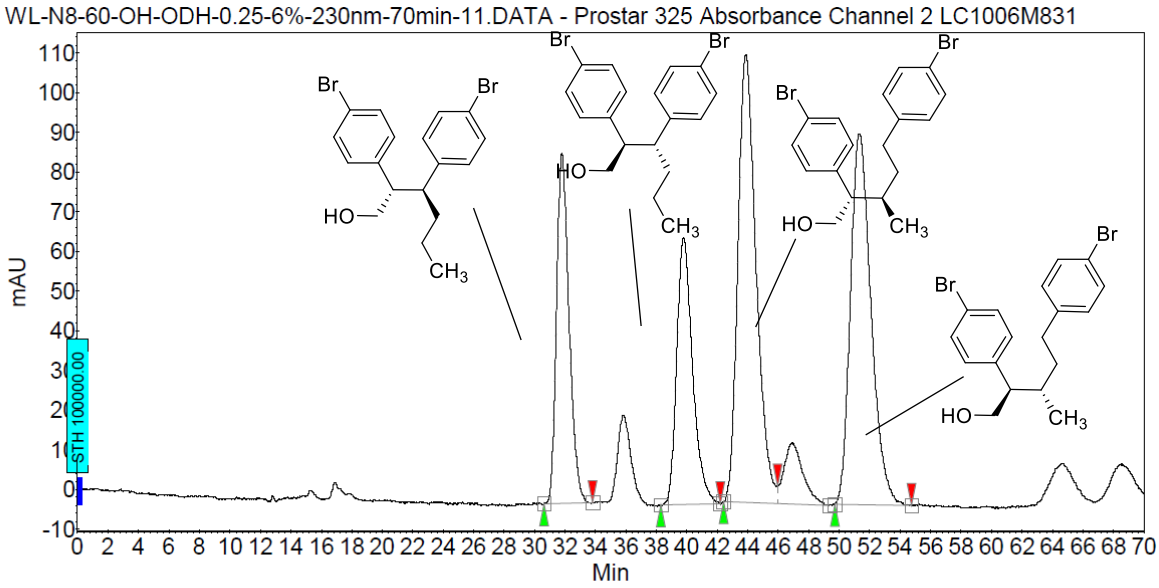


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	63.14	3.81	30.1	48.1	3.809
2	UNKNOWN	79.94	96.19	350.5	1214.8	96.191
Total			100.00	380.6	1262.9	100.000

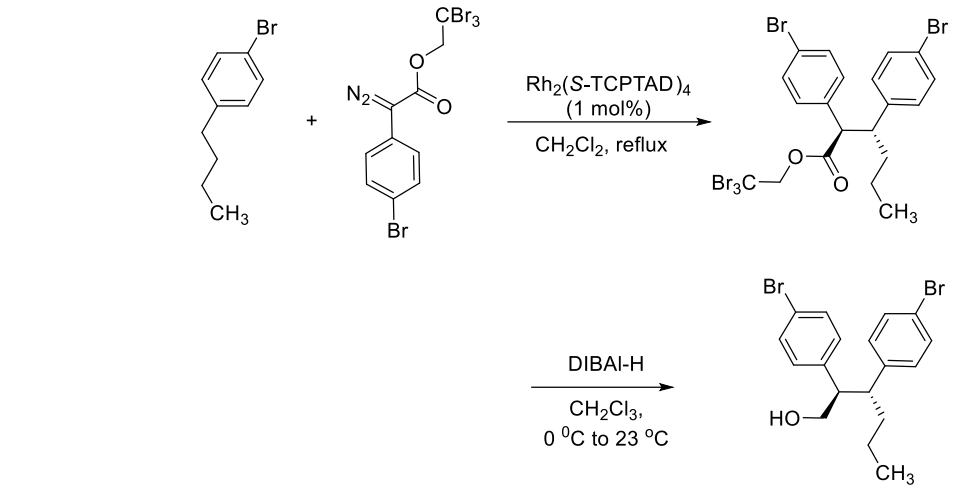
→ 92% ee

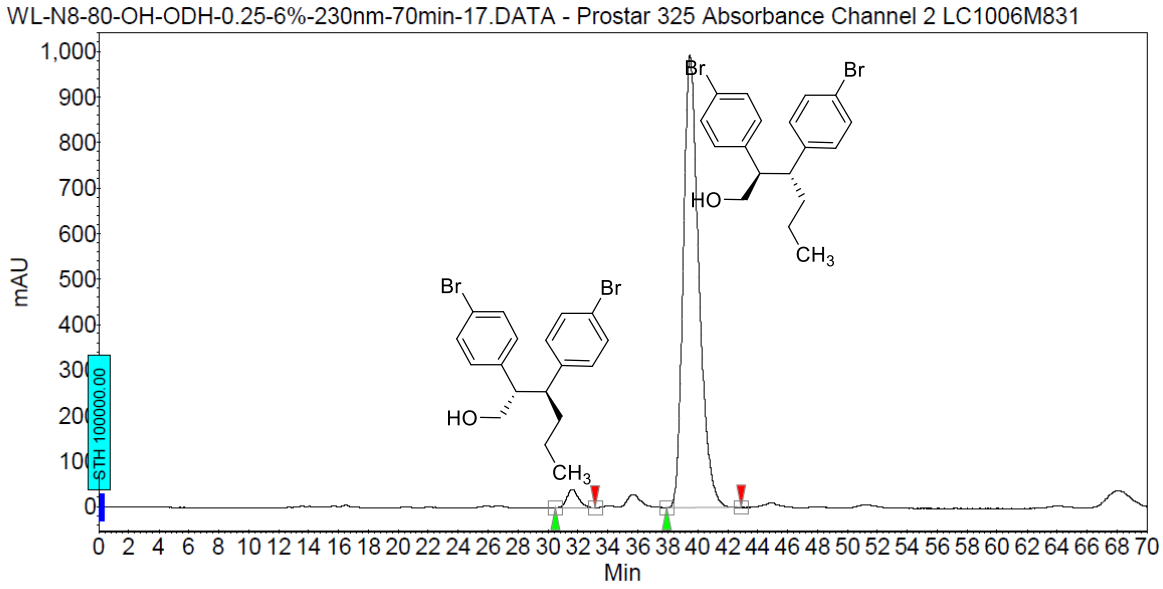




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	31.80	17.99	88.4	84.2	17.994
2	UNKNOWN	39.78	17.34	67.3	81.2	17.343
3	UNKNOWN	43.87	33.35	112.7	156.1	33.351
4	UNKNOWN	51.33	31.31	93.5	146.6	31.313
Total			100.00	362.0	468.1	100.000

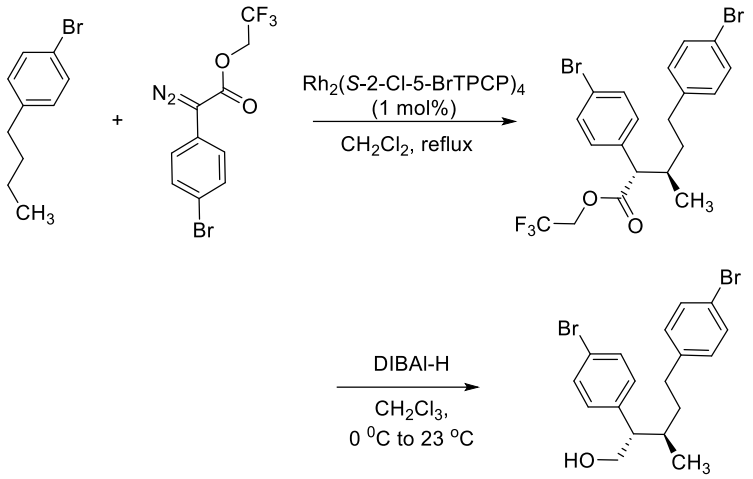


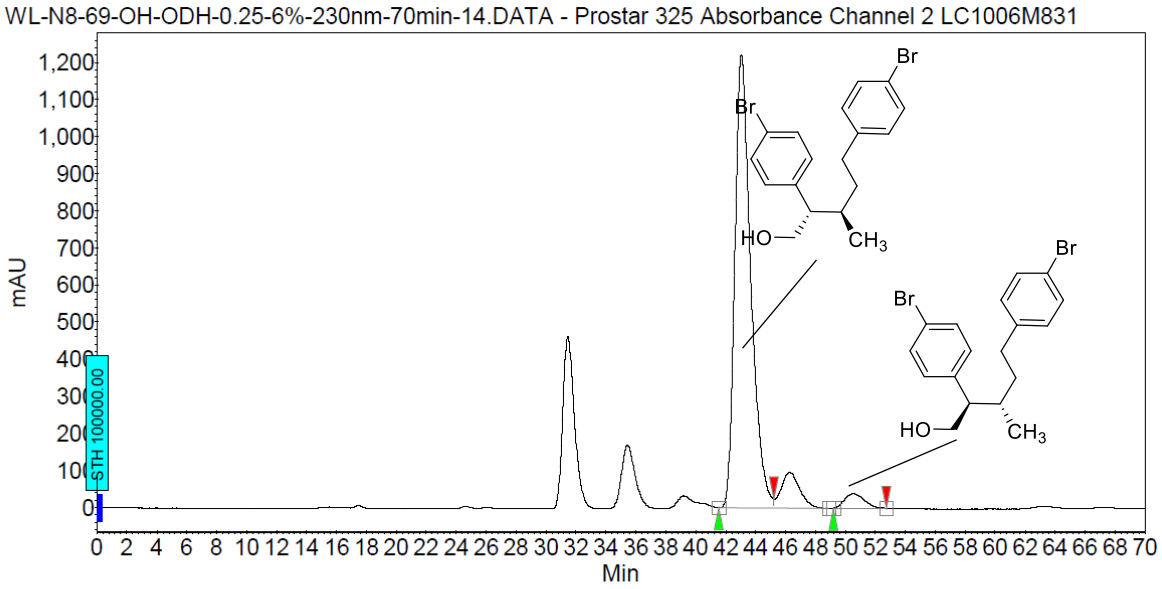


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	31.63	3.01	40.6	37.2	3.005
2	UNKNOWN	39.48	96.99	993.8	1201.6	96.995
Total			100.00	1034.5	1238.8	100.000

→ 94% ee

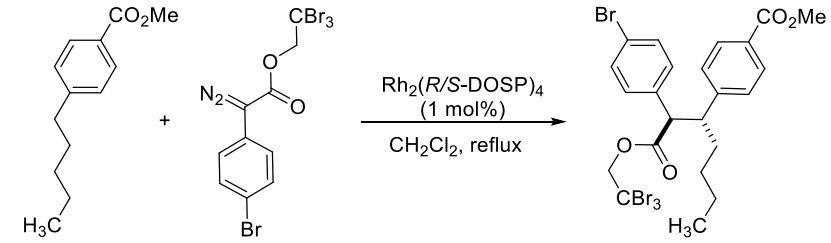


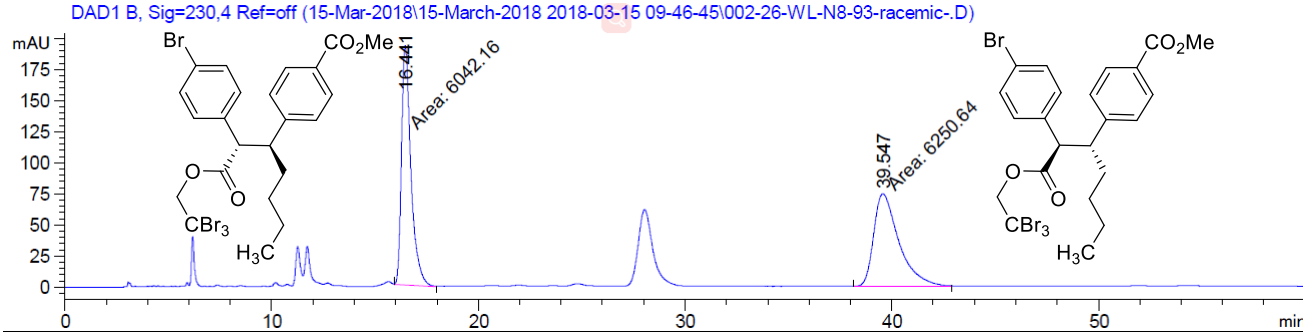


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	43.05	96.22	1220.8	1508.7	96.218
2	UNKNOWN	50.56	3.78	39.6	59.3	3.782
Total			100.00	1260.3	1568.0	100.000

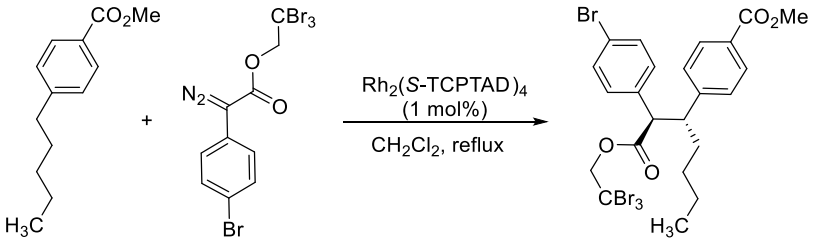
→ 92% ee

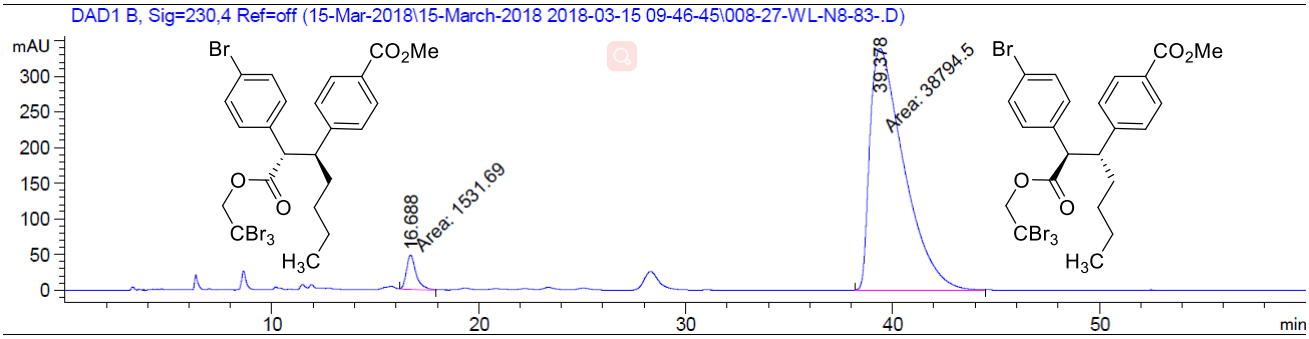




Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.441	MM	0.5242	6042.15674	192.09094	49.1520
2	39.547	MM	1.4064	6250.64160	74.07205	50.8480
Totals :				1.22928e4	266.16299	

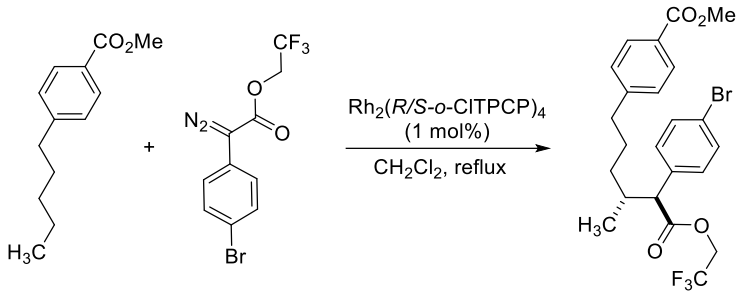


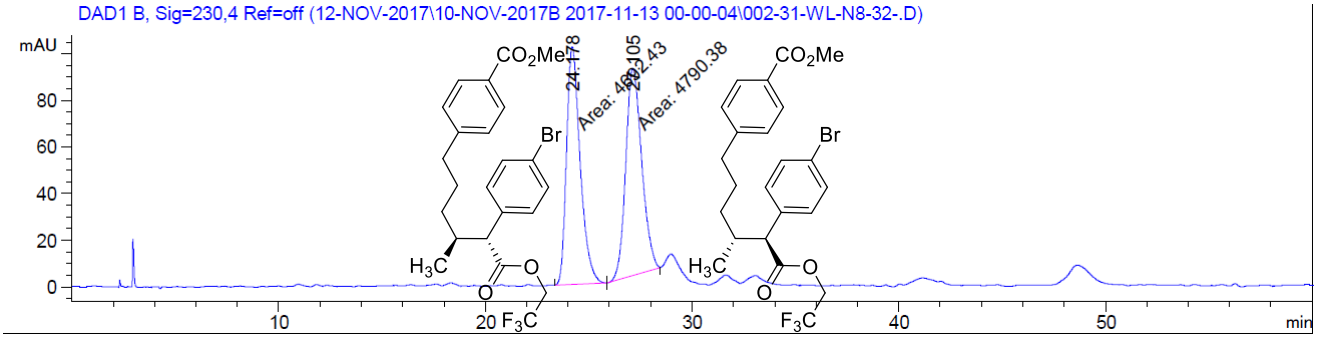


Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.688	MM	0.5329	1531.69250	47.90316	3.7983
2	39.378	MM	1.9084	3.87945e4	338.79602	96.2017
Totals :				4.03262e4	386.69918	

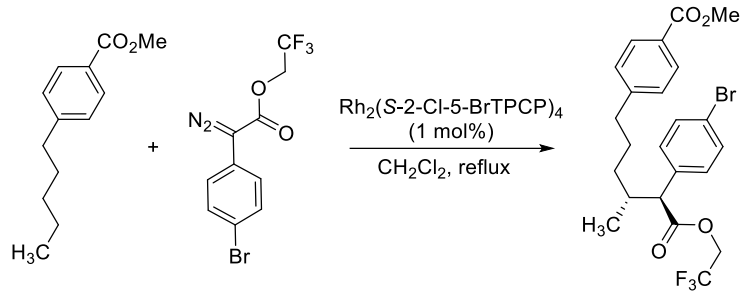
→ 92% ee

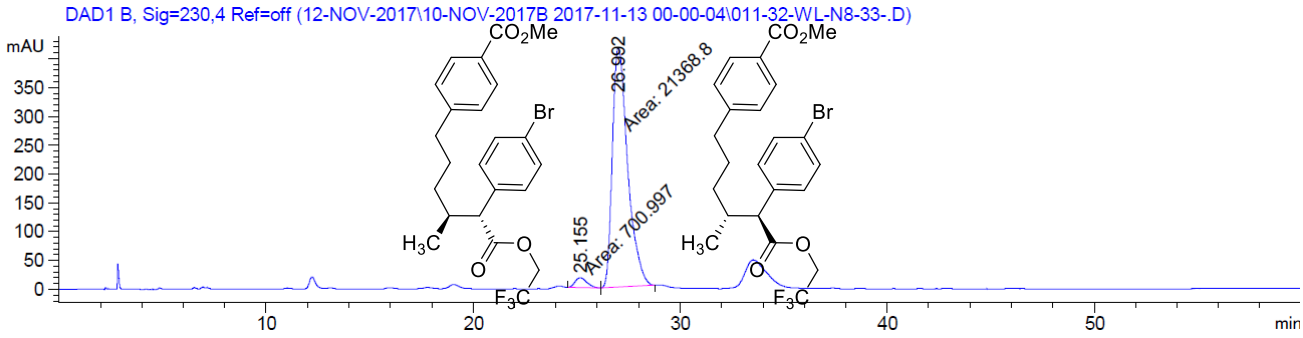




Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.178	MM	0.7662	4692.42627	102.07519	49.4835
2	27.105	MM	0.8980	4790.37549	88.91049	50.5165
Totals :				9482.80176	190.98568	

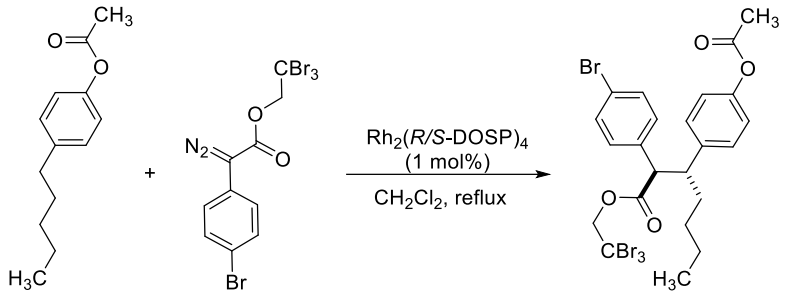


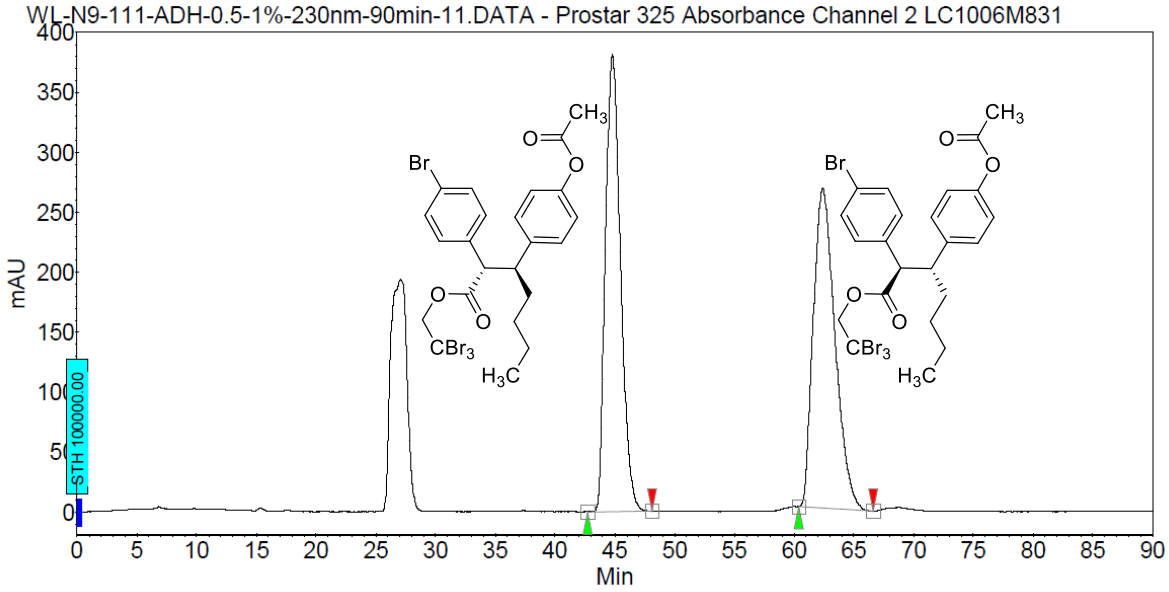


Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.155	MM	0.6661	700.99719	17.53858	3.1763
2	26.992	MM	0.8580	2.13688e4	415.07993	96.8237
Totals :				2.20698e4	432.61850	

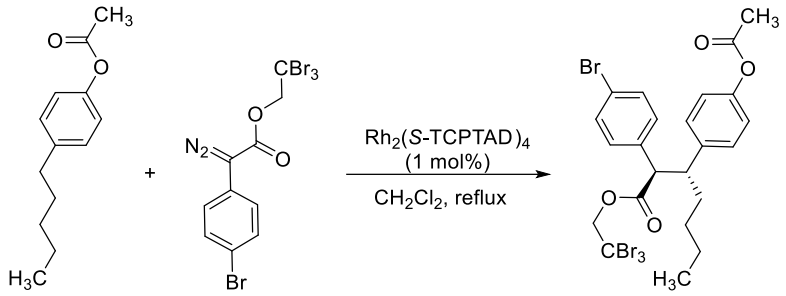
→ 94% ee

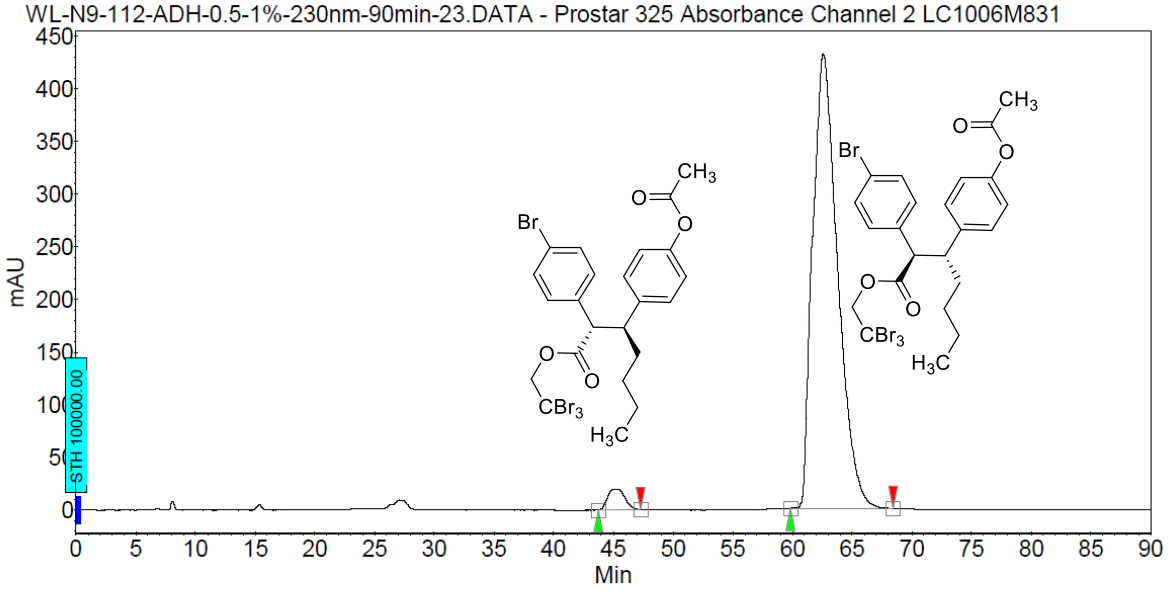




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	44.80	49.85	381.3	559.1	49.852
2	UNKNOWN	62.39	50.15	267.2	562.4	50.148
Total			100.00	648.4	1121.5	100.000

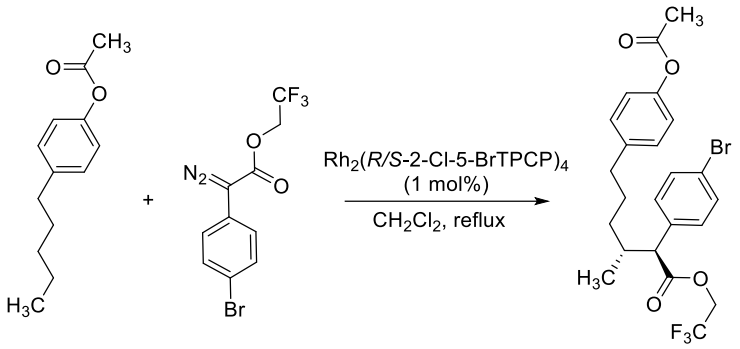


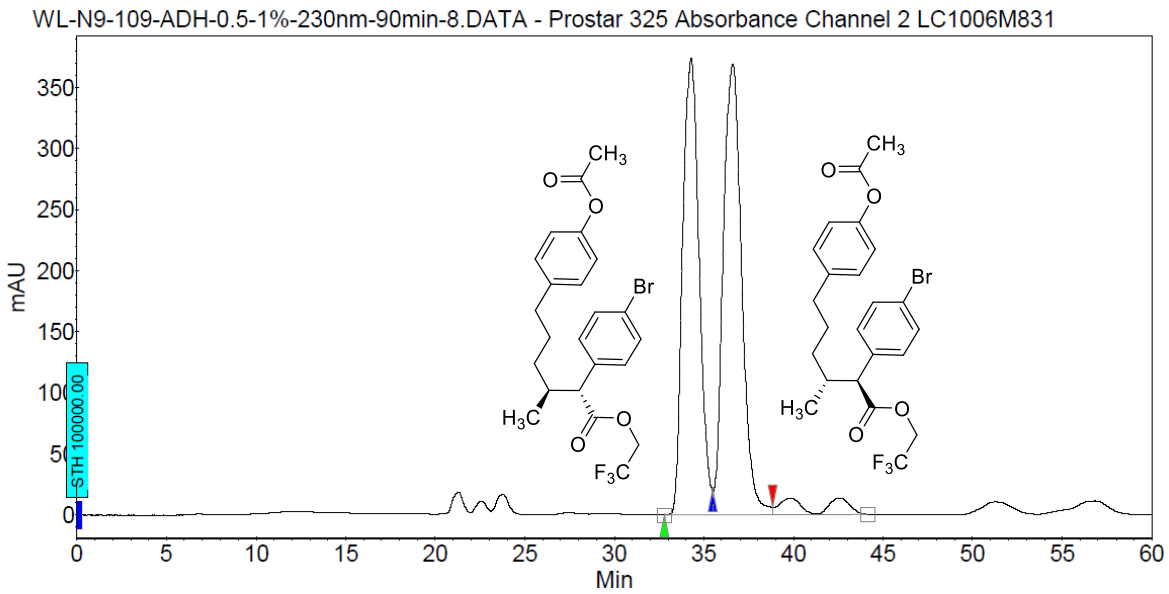


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	45.26	3.06	20.1	33.0	3.062
2	UNKNOWN	62.57	96.94	431.1	1044.6	96.938
Total			100.00	451.2	1077.6	100.000

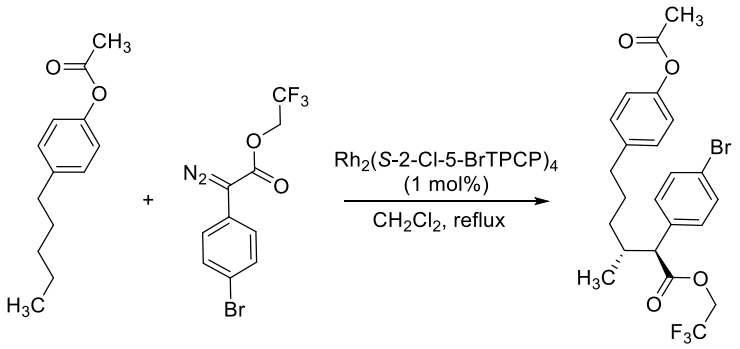
→ 94% ee

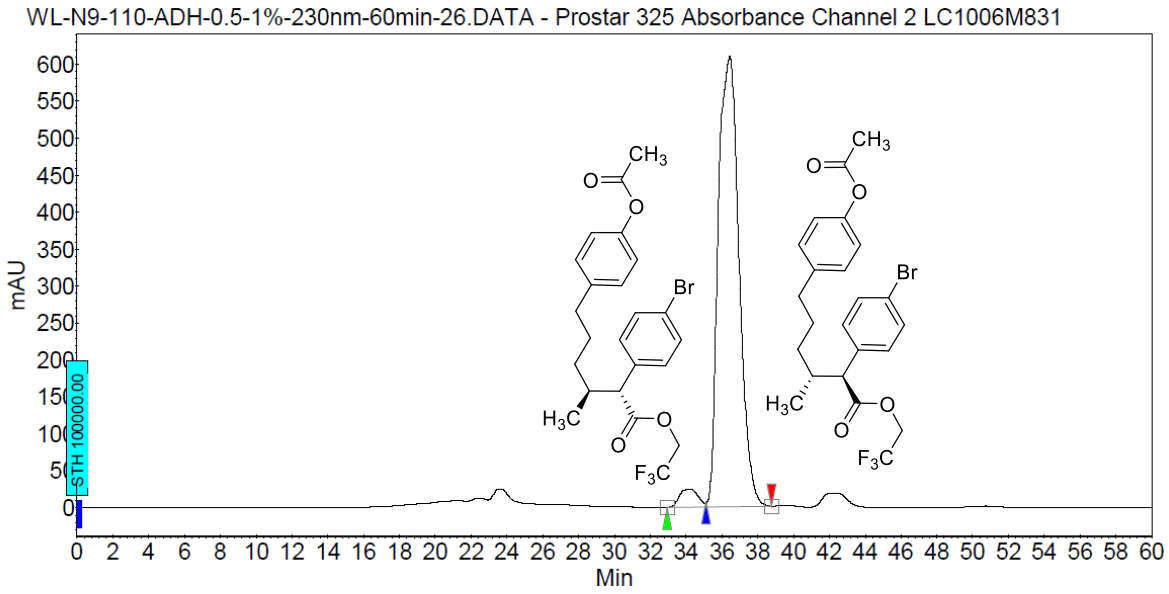




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	34.28	47.35	373.5	398.0	47.354
2	UNKNOWN	36.60	52.65	368.7	442.5	52.646
Total			100.00	742.2	840.6	100.000

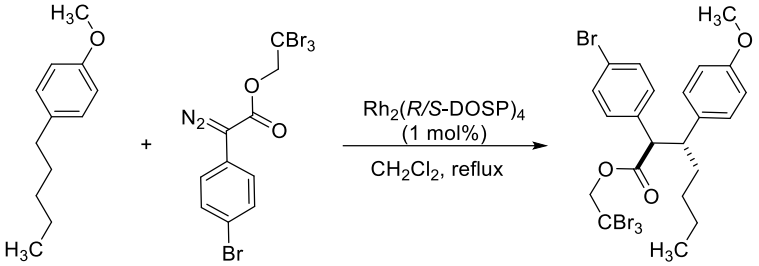




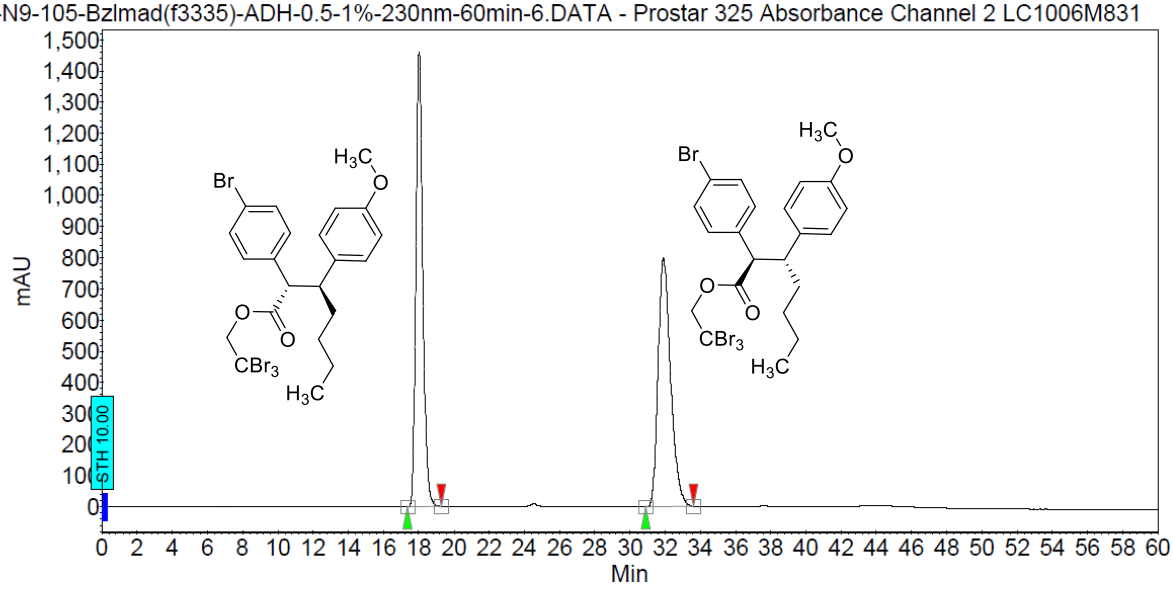
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	34.22	3.40	23.8	28.7	3.400
2	UNKNOWN	36.44	96.60	608.3	815.8	96.600
Total			100.00	632.1	844.5	100.000

→ 93% ee

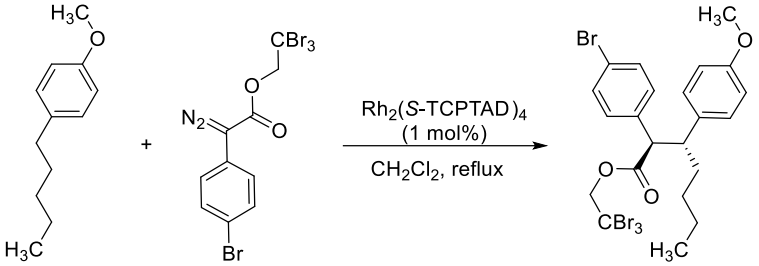


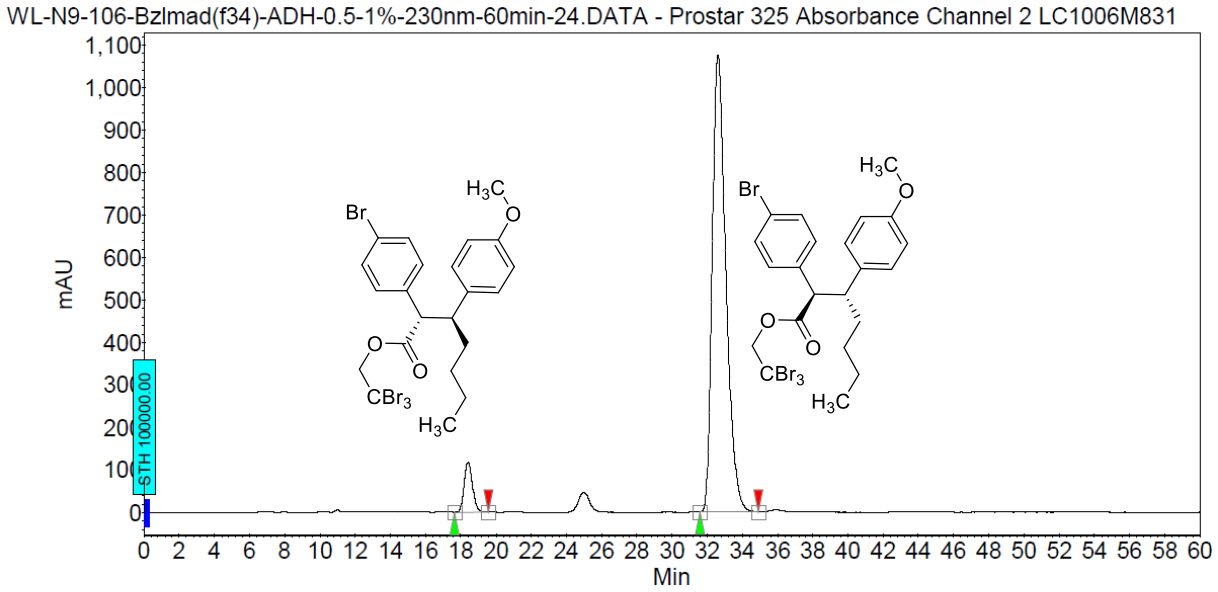
WL-N9-105-Bzlmad(f3335)-ADH-0.5-1%-230nm-60min-6.DATA - Prostar 325 Absorbance Channel 2 LC1006M831



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.02	50.12	1457.0	660.7	50.116
2	UNKNOWN	31.91	49.88	798.2	657.7	49.884
Total			100.00	2255.1	1318.4	100.000

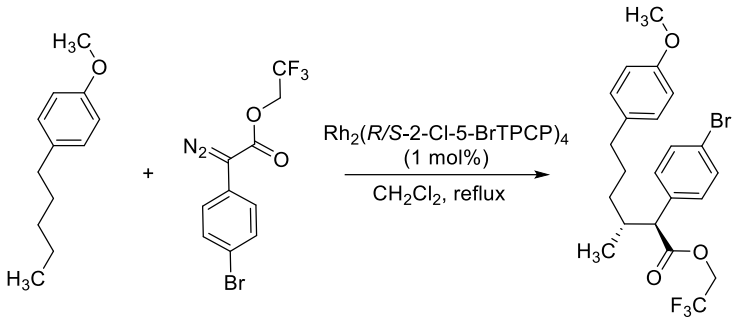




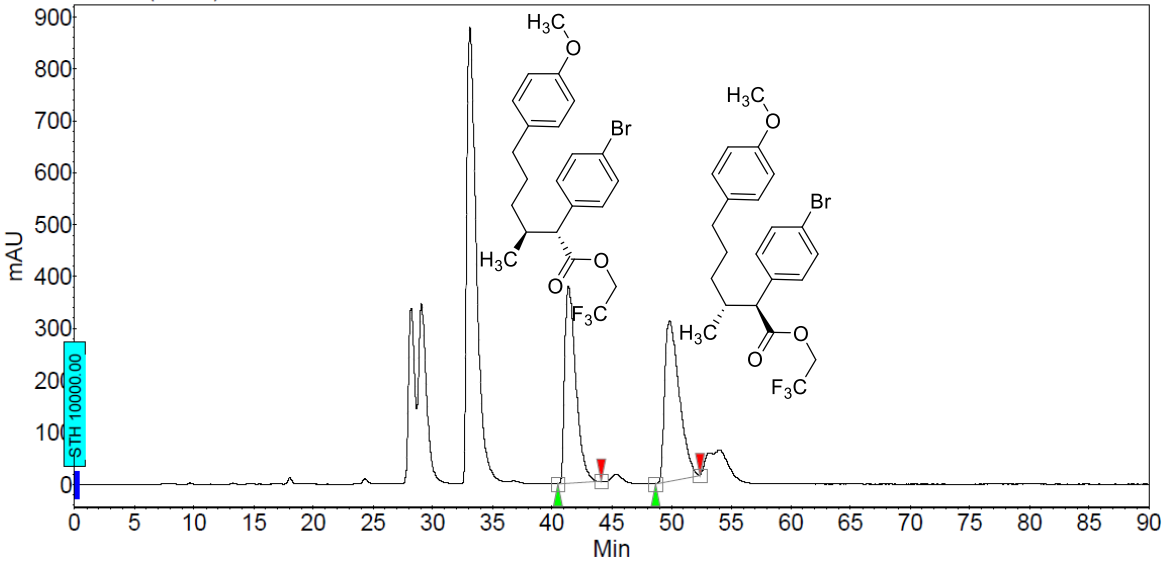
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.41	6.35	117.7	65.5	6.353
2	UNKNOWN	32.61	93.65	1074.1	965.1	93.647
Total			100.00	1191.8	1030.5	100.000

→ 87% ee

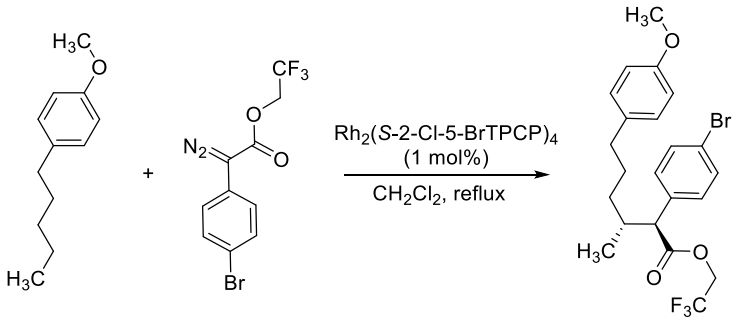


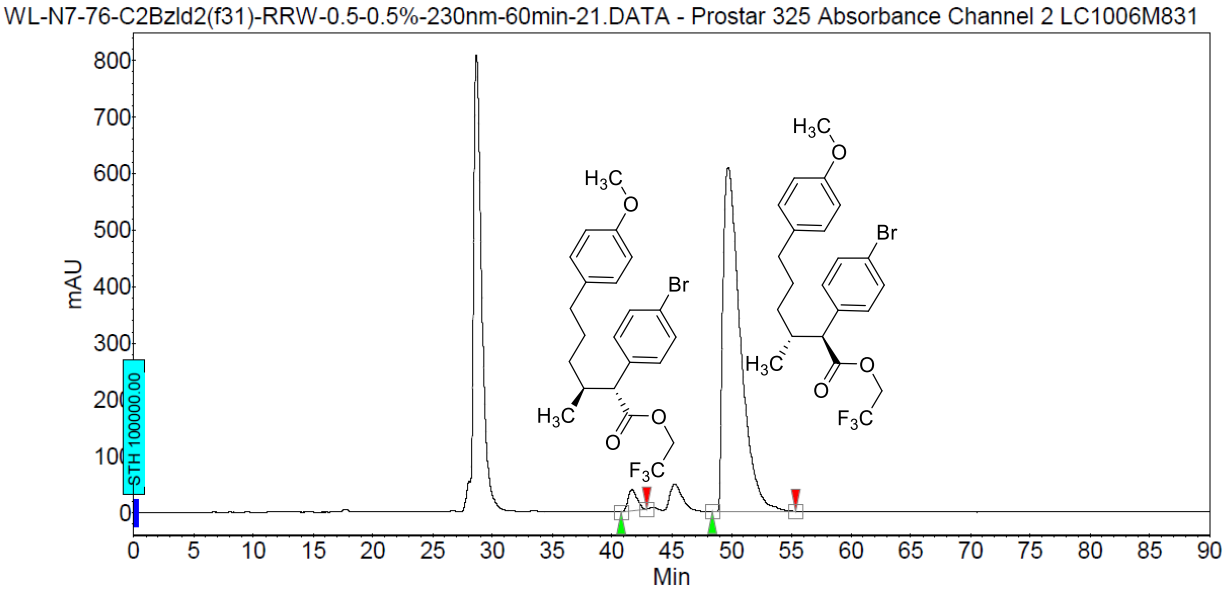
WL-N9-103-C2Bzld2(f4145)-RRW-0.5-0.5%-230nm-60min-3.DATA - Prostar 325 Absorbance Channel 2 LC1006M831



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	41.37	48.59	380.3	412.1	48.587
2	UNKNOWN	49.83	51.41	308.5	436.1	51.413
Total			100.00	688.8	848.2	100.000

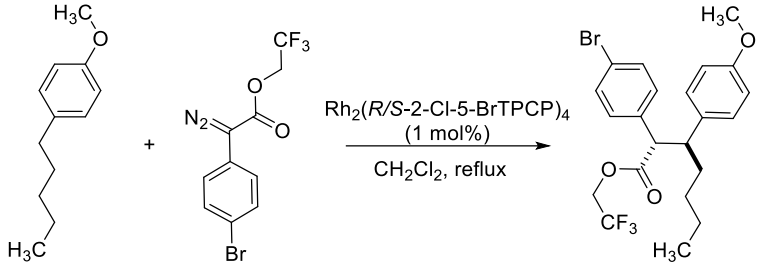


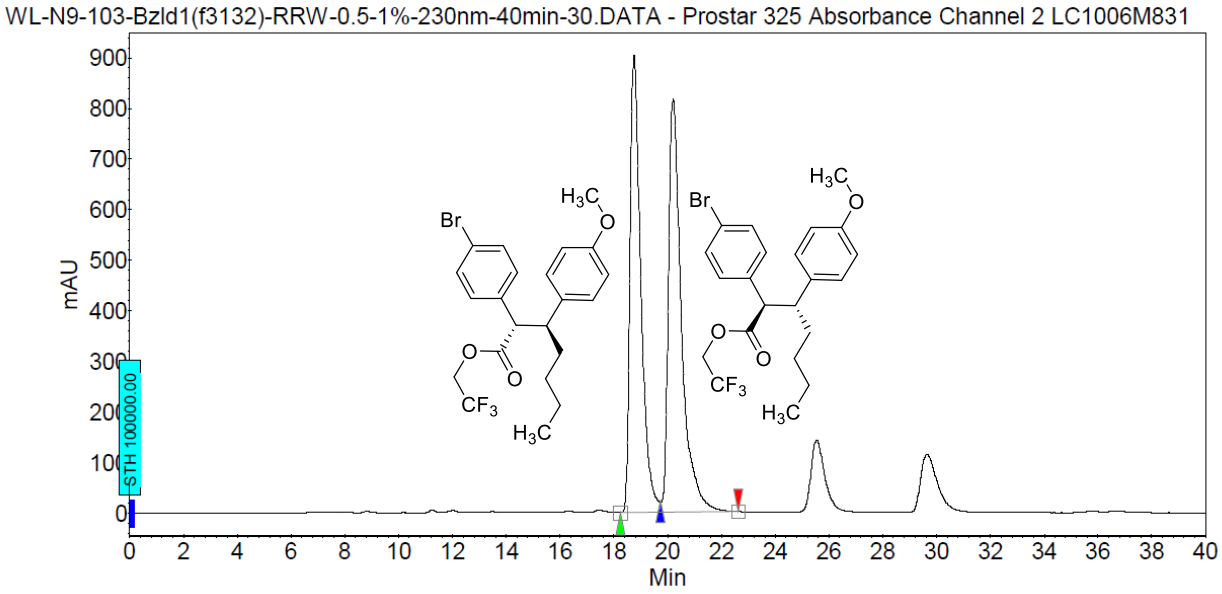


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	41.67	3.10	37.8	33.0	3.099
2	UNKNOWN	49.72	96.90	609.4	1032.2	96.901
Total			100.00	647.2	1065.2	100.000

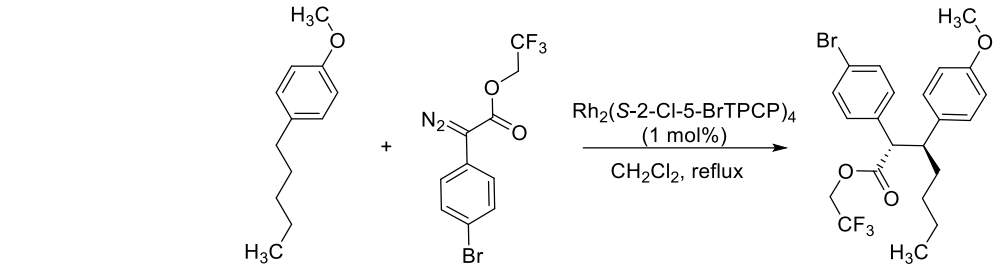
→ 94% ee

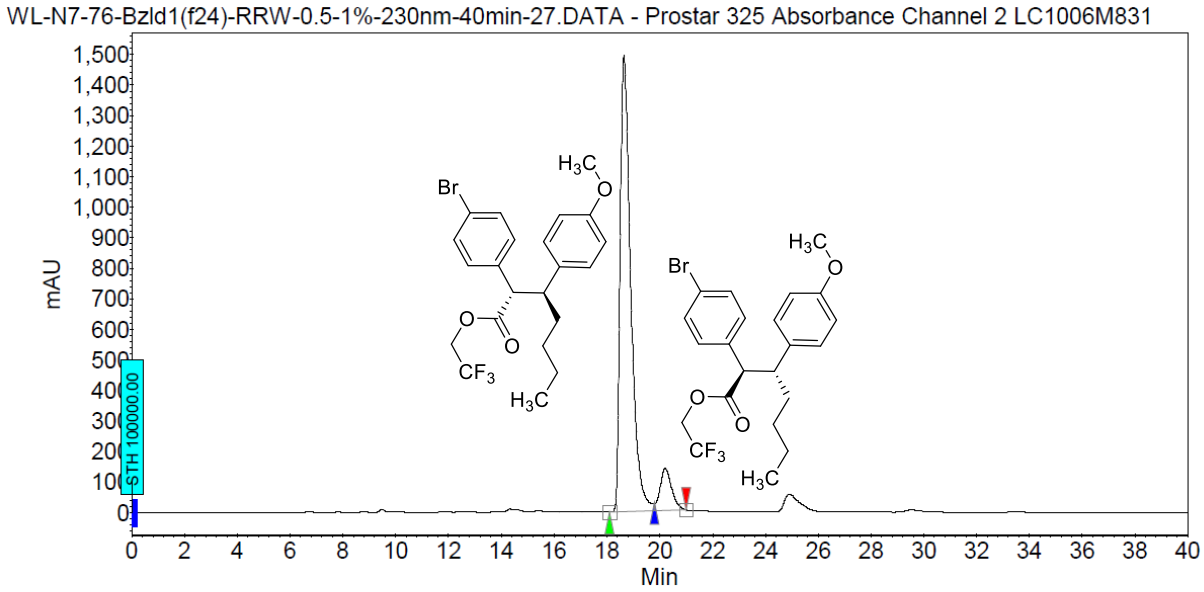




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.75	47.92	902.9	424.1	47.919
2	UNKNOWN	20.20	52.08	817.4	460.9	52.081
Total			100.00	1720.3	885.0	100.000

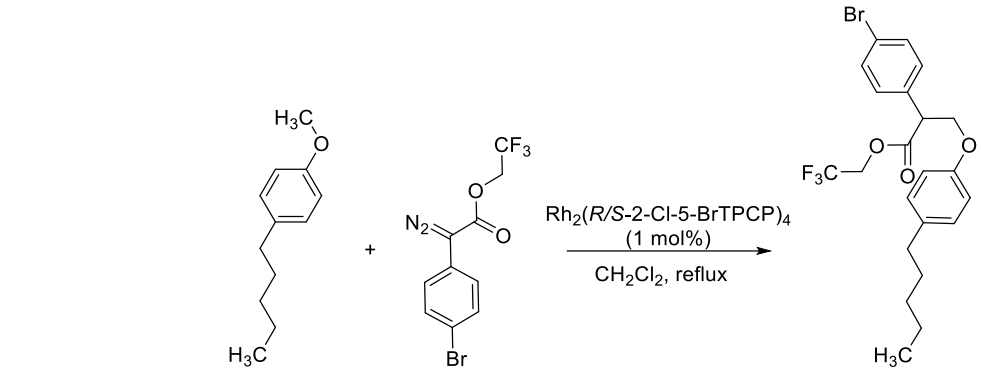


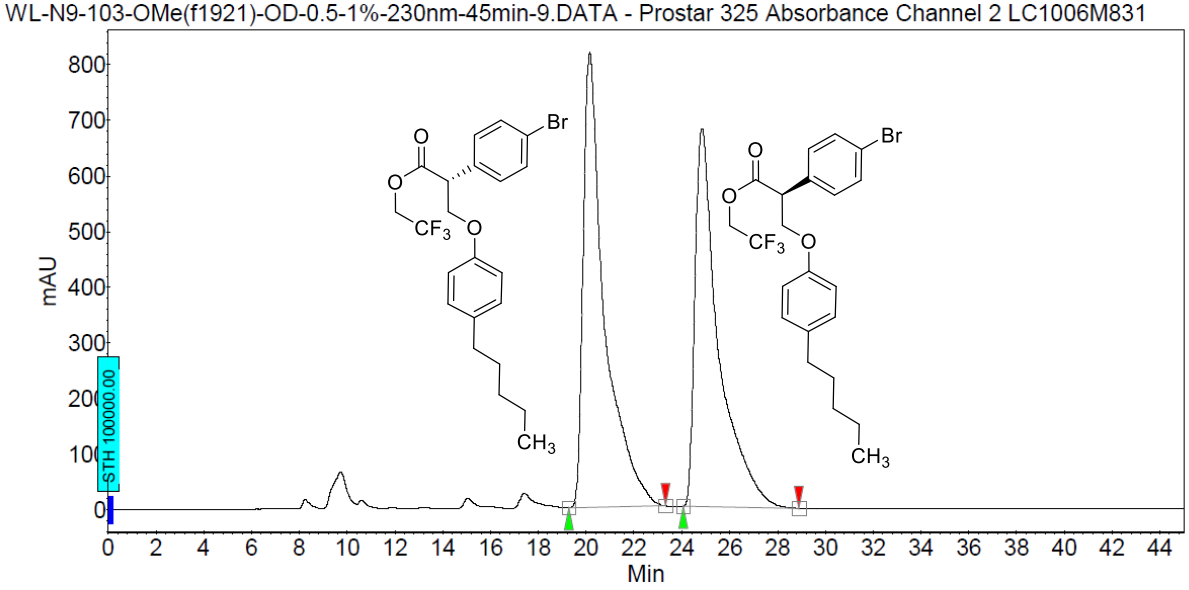


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.64	90.82	1492.7	694.3	90.819
2	UNKNOWN	20.20	9.18	138.2	70.2	9.181
Total			100.00	1630.9	764.5	100.000

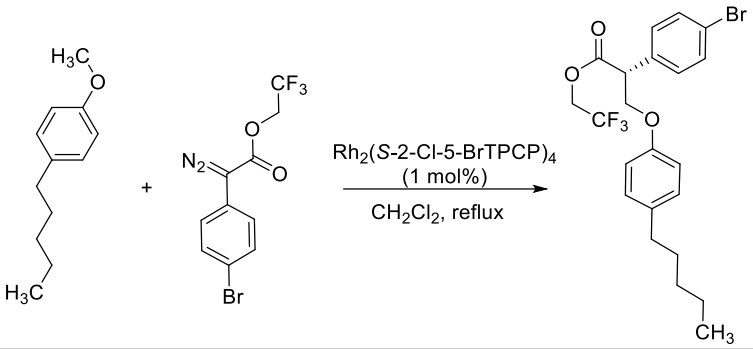
→ 82% ee

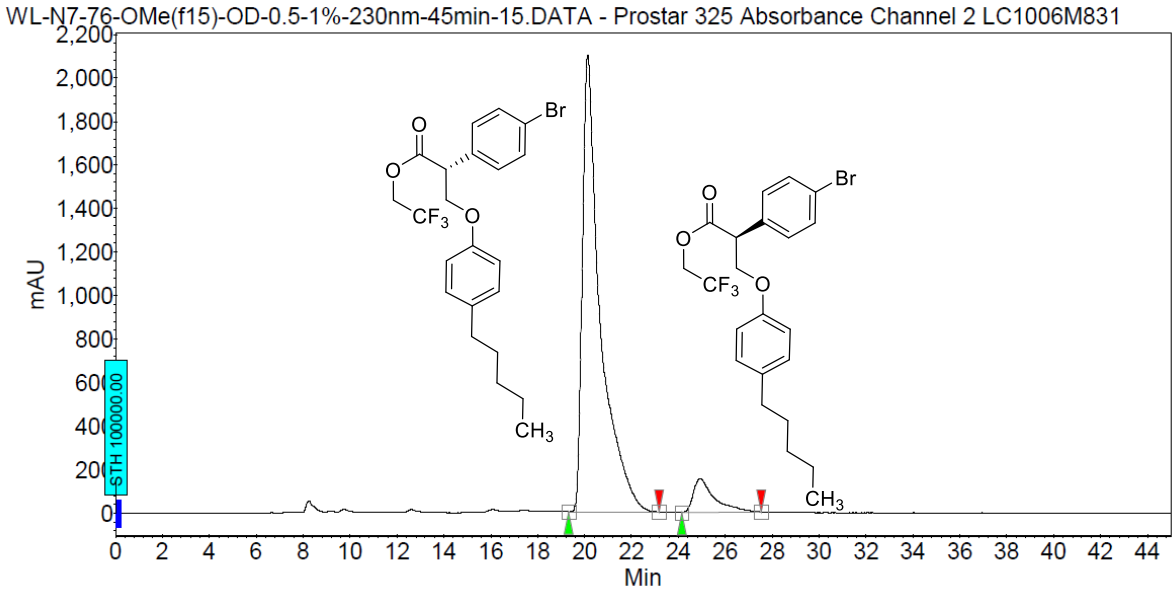




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.14	52.09	818.4	847.6	52.087
2	UNKNOWN	24.84	47.91	680.9	779.7	47.913
Total			100.00	1499.4	1627.3	100.000

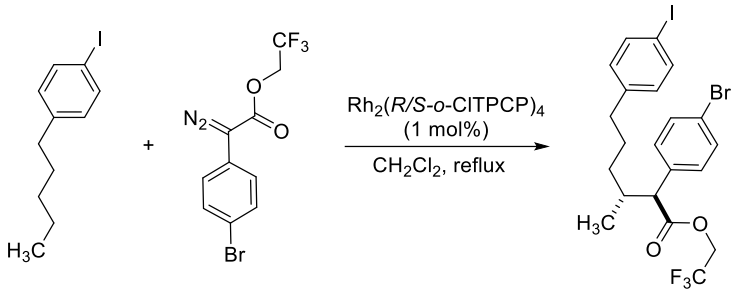


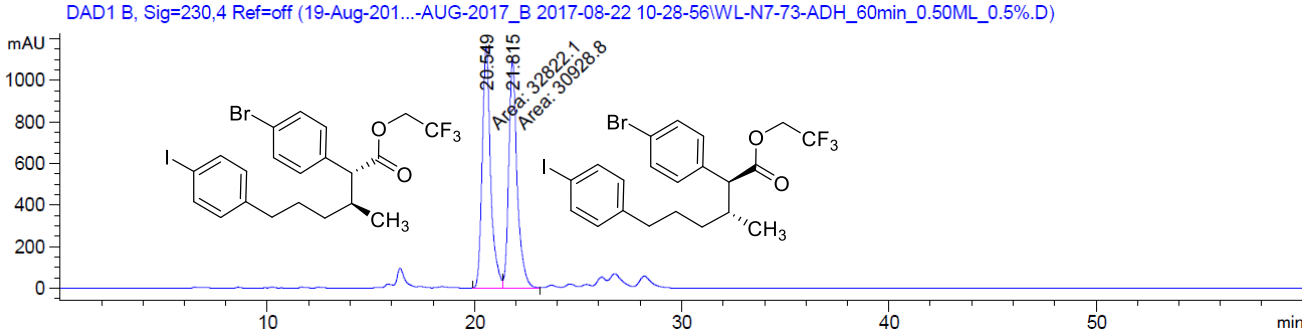


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.13	92.00	2097.0	1852.8	91.996
2	UNKNOWN	24.92	8.00	153.7	161.2	8.004
Total			100.00	2250.6	2014.0	100.000

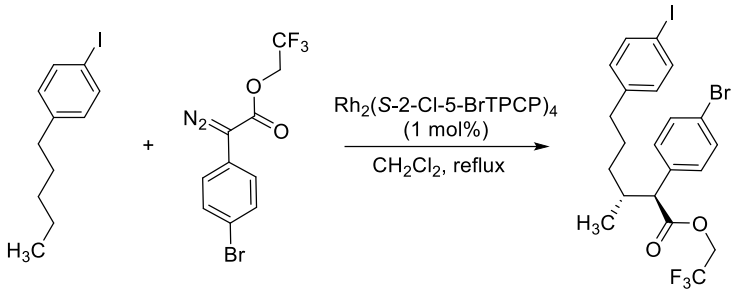
→ 84% ee

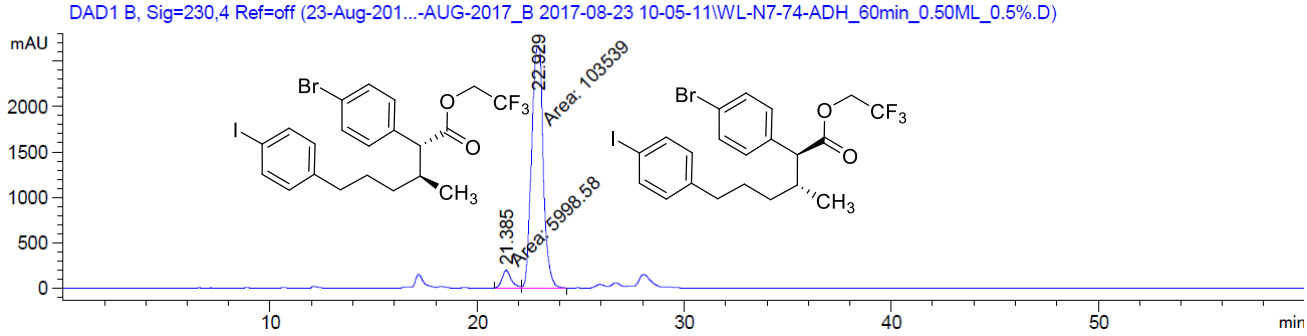




Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.549	MF	0.4695	3.28221e4	1165.09302	51.4849
2	21.815	FM	0.4685	3.09288e4	1100.34082	48.5151
Totals :				6.37509e4	2265.43384	



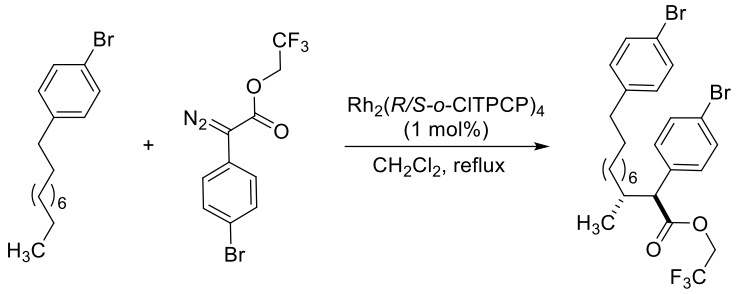


Signal 2: DAD1 B, Sig=230,4 Ref=off

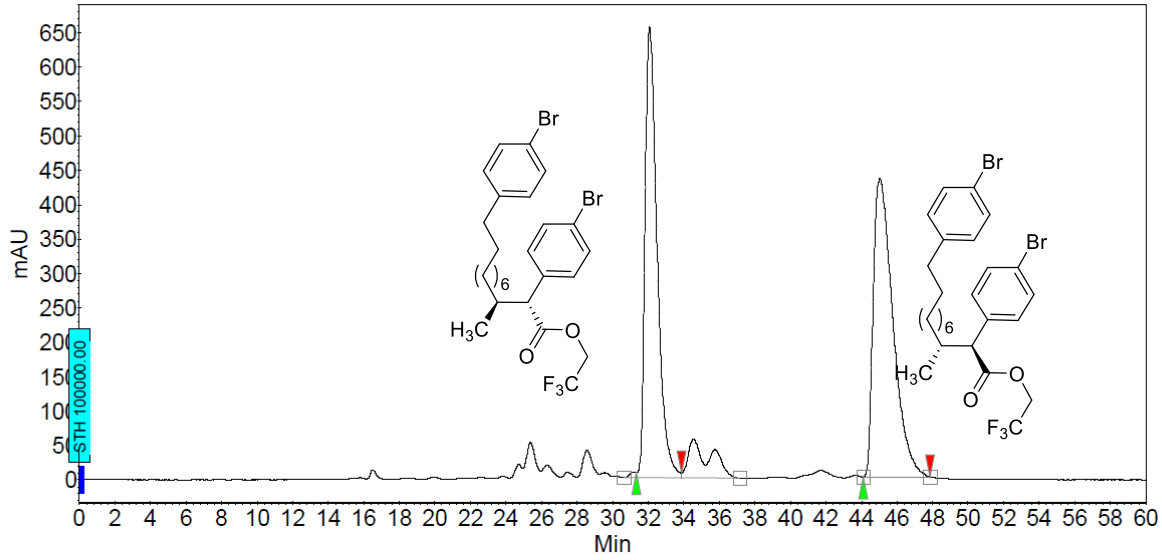
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.385	MF	0.5092	5998.58057	196.34985	5.4763
2	22.929	FM	0.6475	1.03539e5	2664.92432	94.5237

Totals : 1.09537e5 2861.27417

→ 89% ee

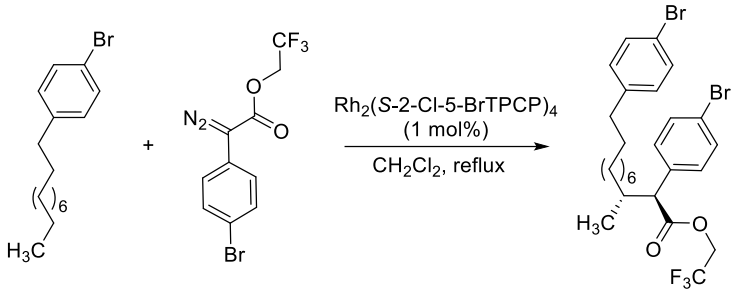


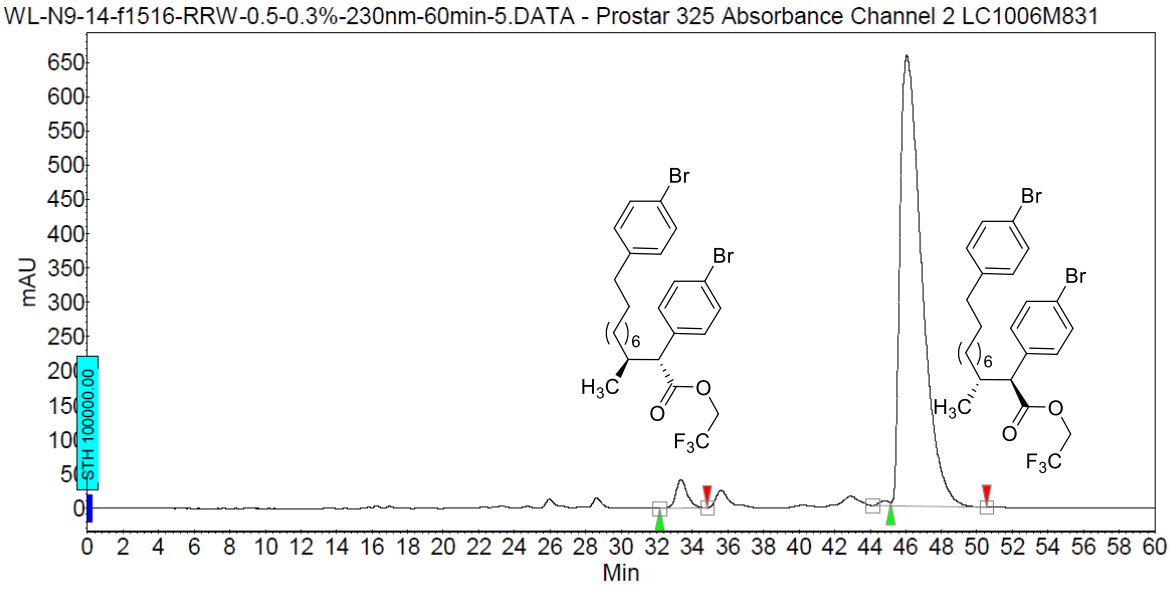
WL-N9-13-f1516-RRW-0.5-0.3%-230nm-60min-5.DATA - Prostar 325 Absorbance Channel 2 LC1006M831



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	32.08	48.10	655.0	516.5	48.096
2	UNKNOWN	45.03	51.90	434.1	557.4	51.904
Total			100.00	1089.0	1074.0	100.000

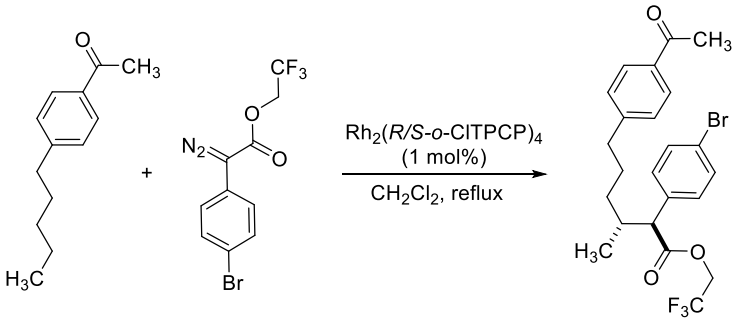


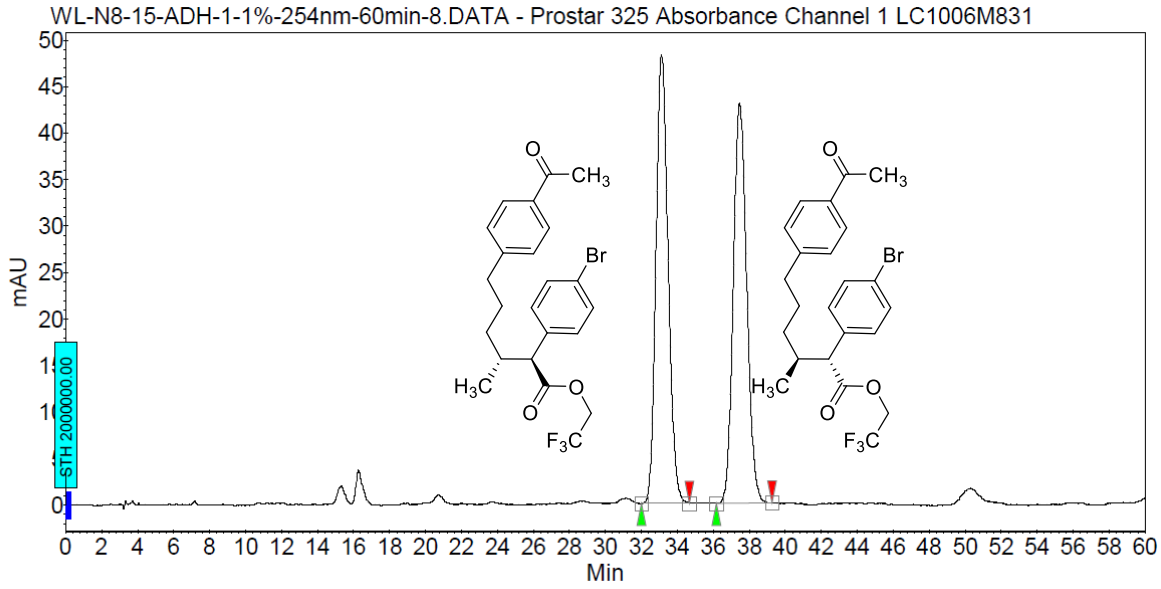


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	33.36	3.18	41.4	30.6	3.176
2	UNKNOWN	46.06	96.82	657.2	932.0	96.824
Total			100.00	698.5	962.6	100.000

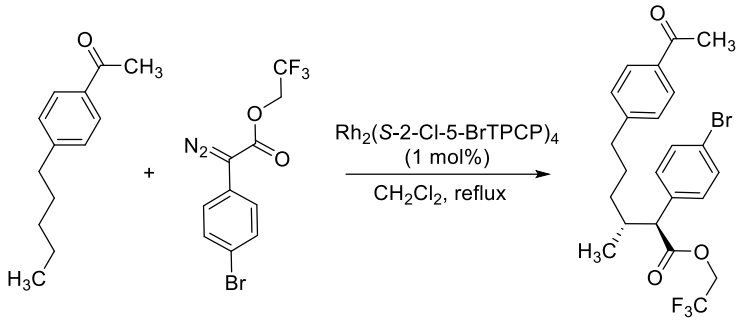
→ 94% ee

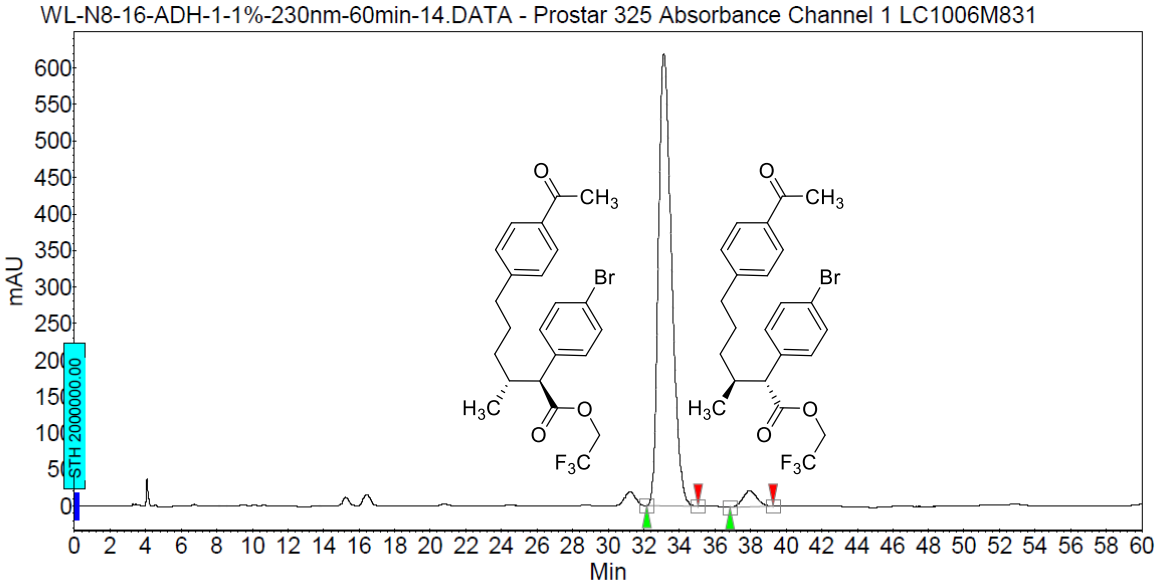




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	33.12	50.42	48.2	37.9	50.417
2	UNKNOWN	37.46	49.58	43.0	37.2	49.583
Total			100.00	91.2	75.1	100.000

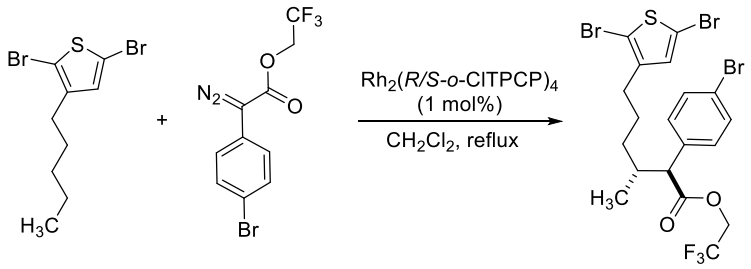


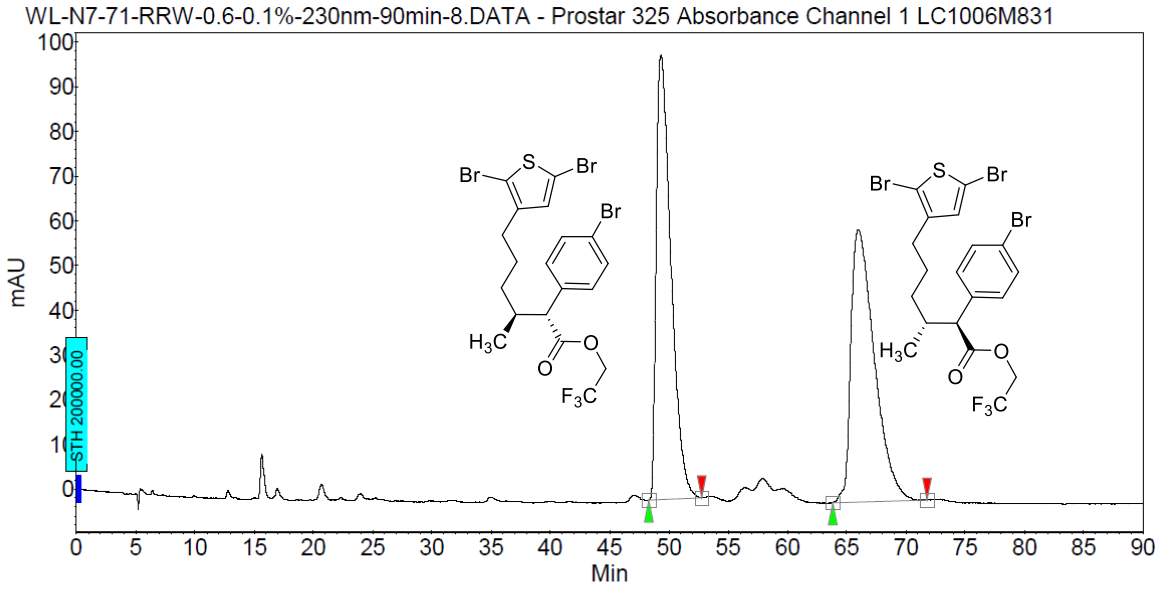


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	33.13	96.37	618.8	530.6	96.371
2	UNKNOWN	37.95	3.63	21.7	20.0	3.629
Total			100.00	640.4	550.6	100.000

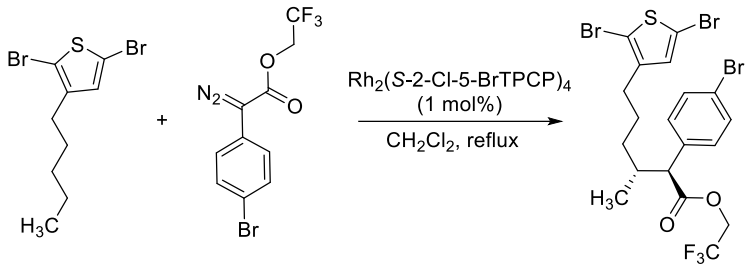
→ 93% ee

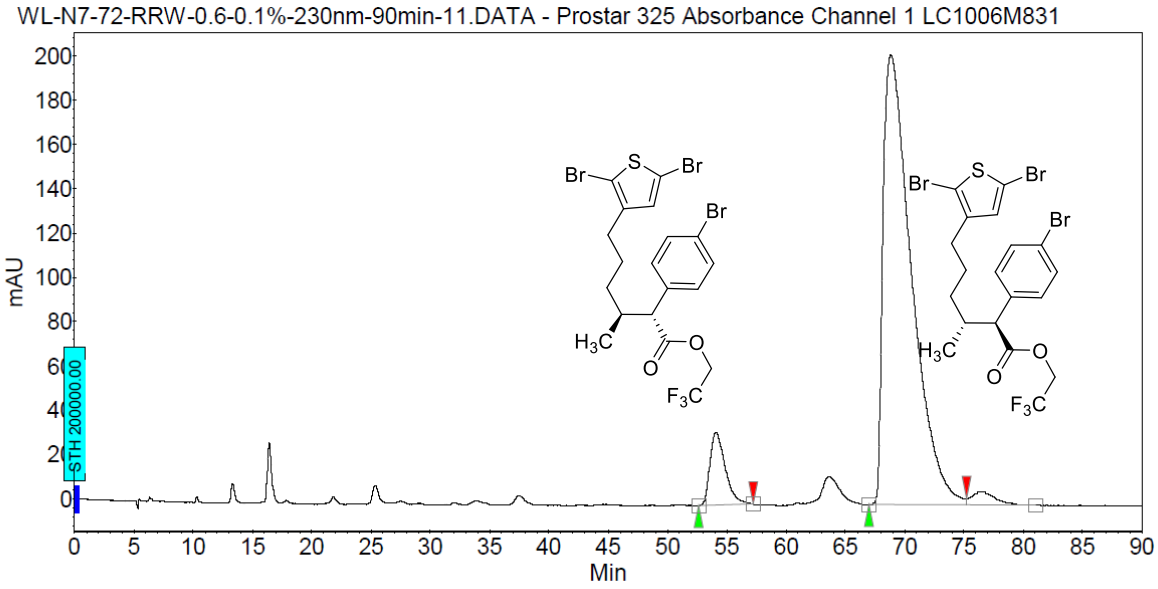




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	49.33	50.58	99.5	143.4	50.577
2	UNKNOWN	65.99	49.42	60.9	140.1	49.423
Total			100.00	160.3	283.5	100.000

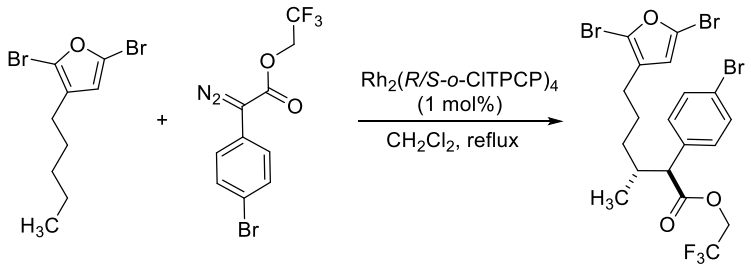


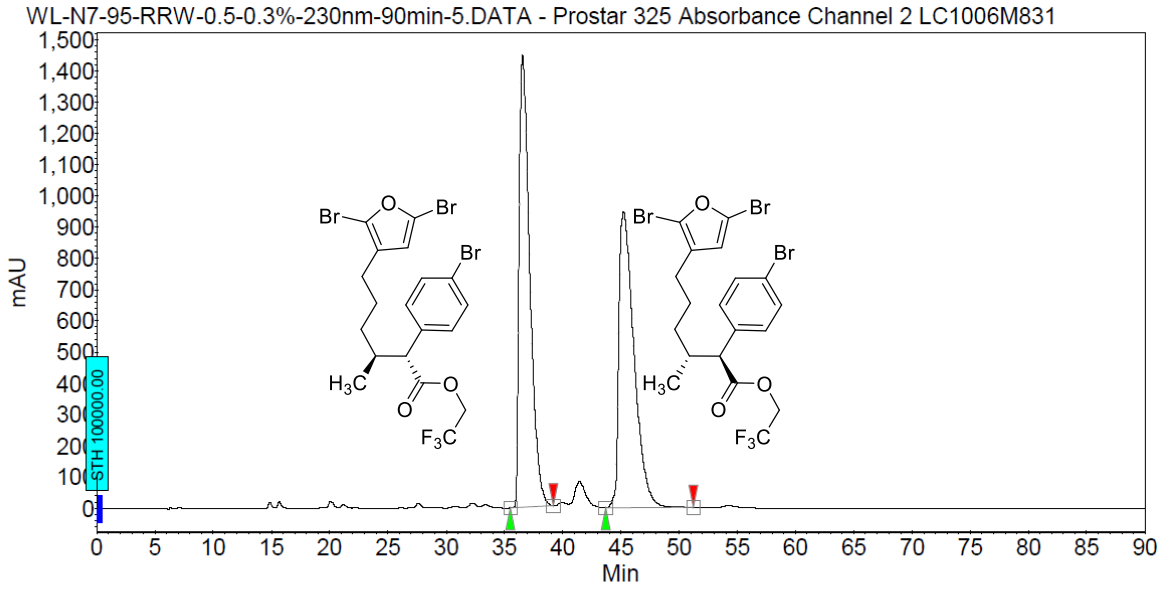


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	54.10	7.99	32.7	49.1	7.990
2	UNKNOWN	68.83	92.01	203.0	565.3	92.010
Total			100.00	235.7	614.4	100.000

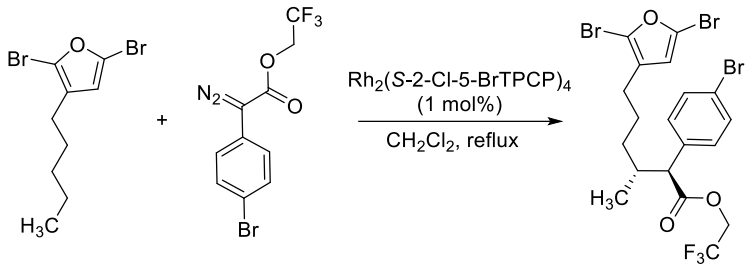
→ 84% ee

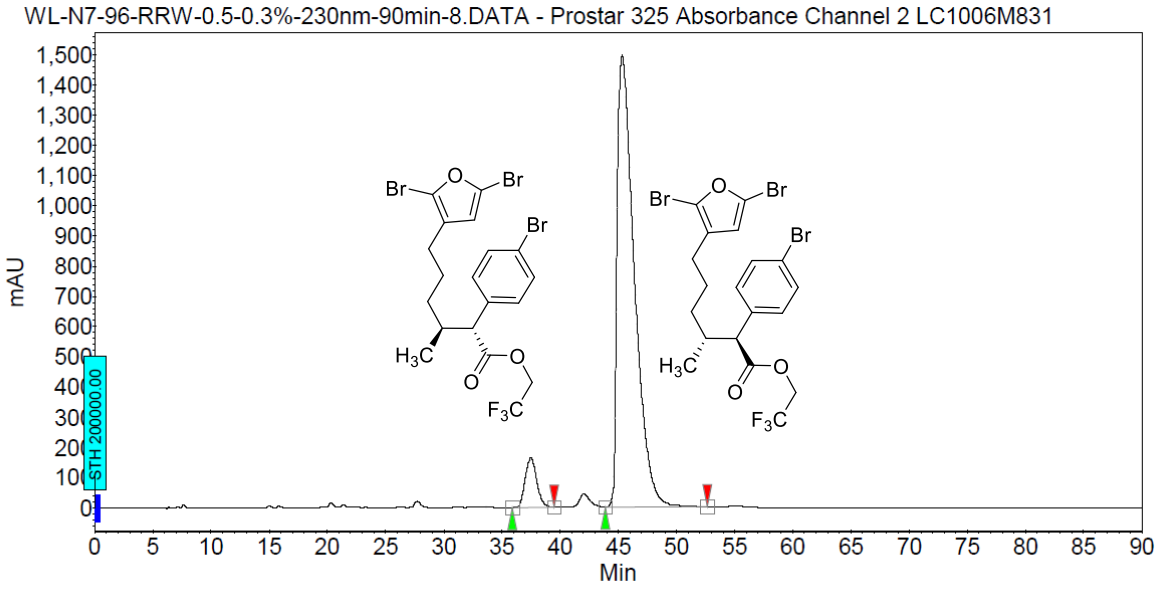




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	36.56	51.56	1446.9	1527.1	51.562
2	UNKNOWN	45.22	48.44	947.8	1434.5	48.438
Total			100.00	2394.8	2961.6	100.000

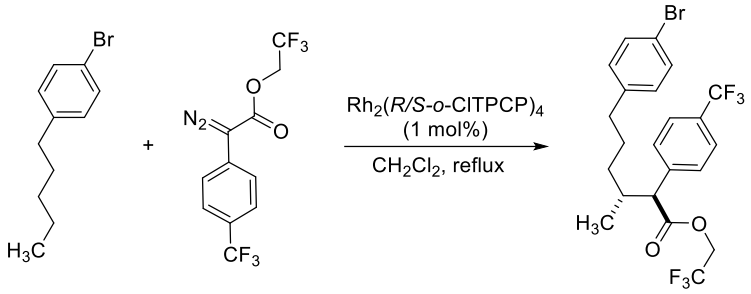


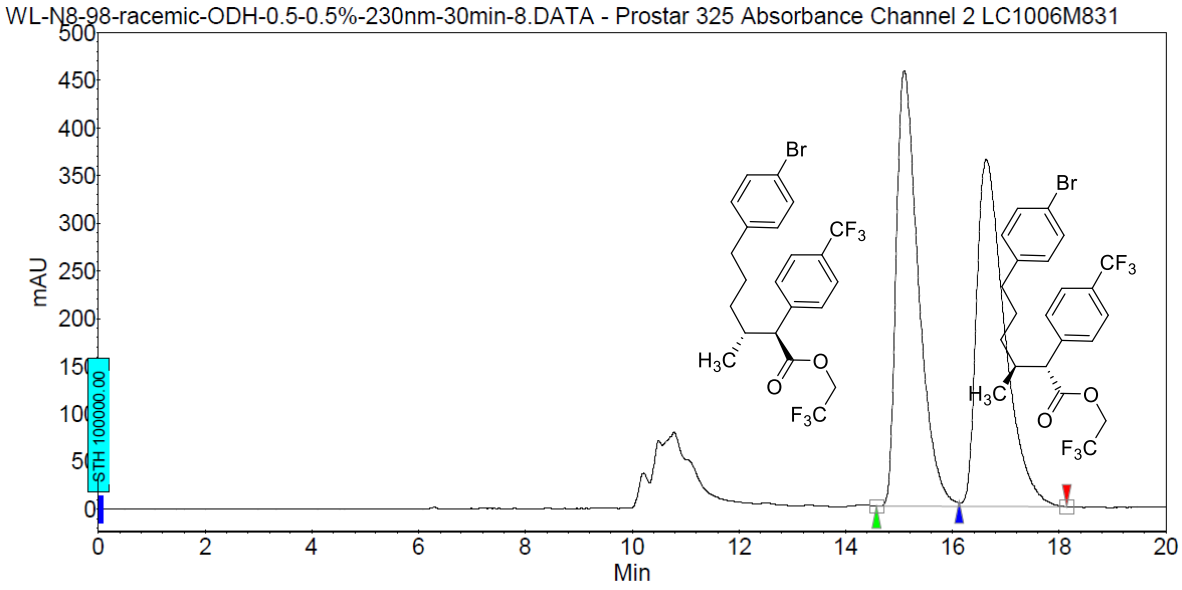


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	37.50	6.85	164.9	188.9	6.845
2	UNKNOWN	45.32	93.15	1495.3	2570.8	93.155
Total			100.00	1660.2	2759.7	100.000

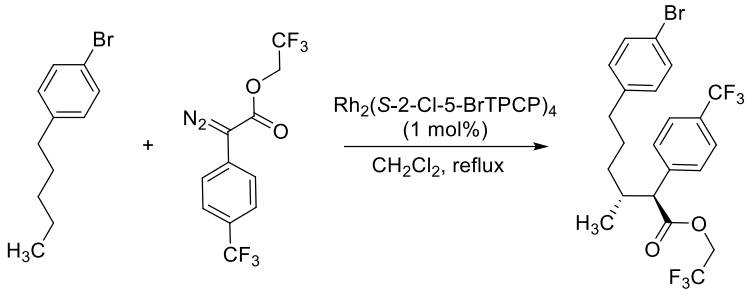
→ 86% ee

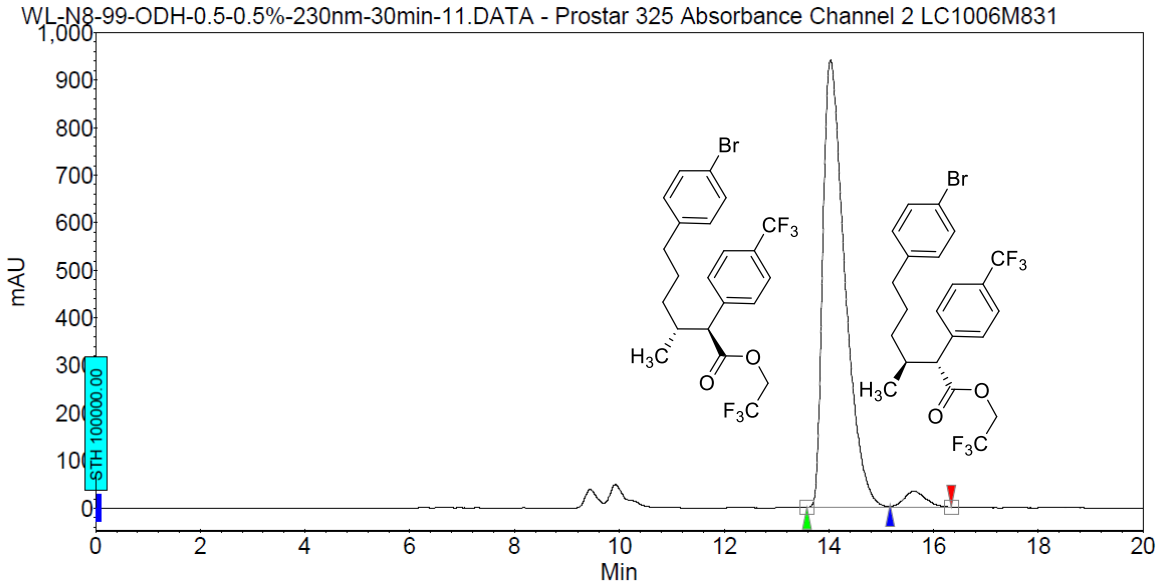




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.10	49.88	456.5	221.2	49.879
2	UNKNOWN	16.63	50.12	364.0	222.2	50.121
Total			100.00	820.5	443.4	100.000

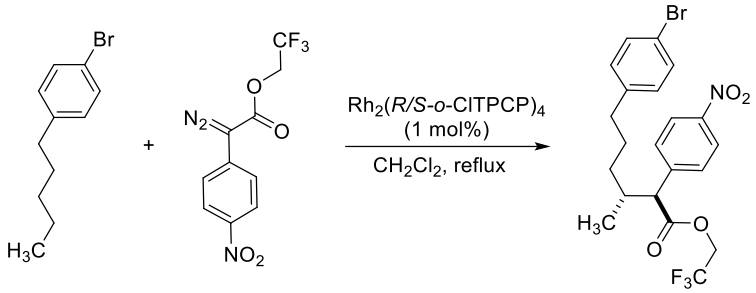


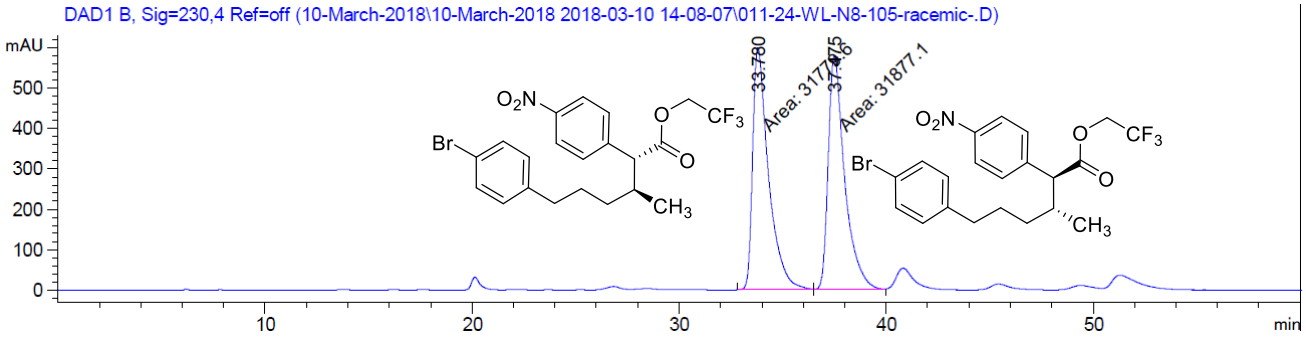


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.03	96.64	940.4	457.3	96.636
2	UNKNOWN	15.63	3.36	33.2	15.9	3.364
Total			100.00	973.6	473.2	100.000

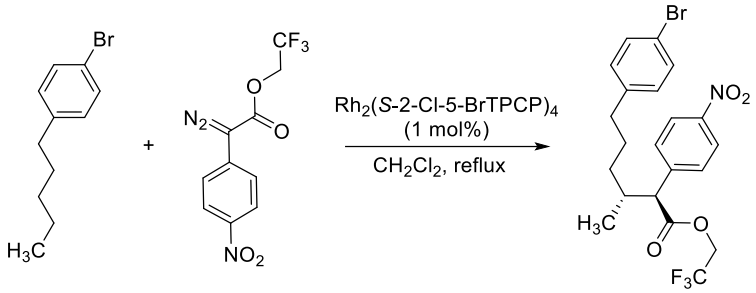
→ 93% ee

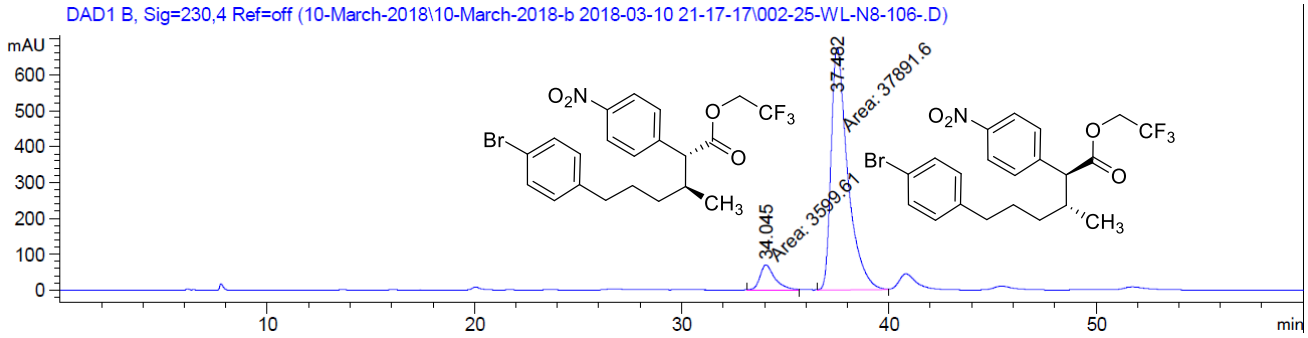




Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.780	MM	0.8854	3.17796e4	598.21277	49.9234
2	37.475	MM	0.9196	3.18771e4	577.73047	50.0766
Totals :				6.36567e4	1175.94324	

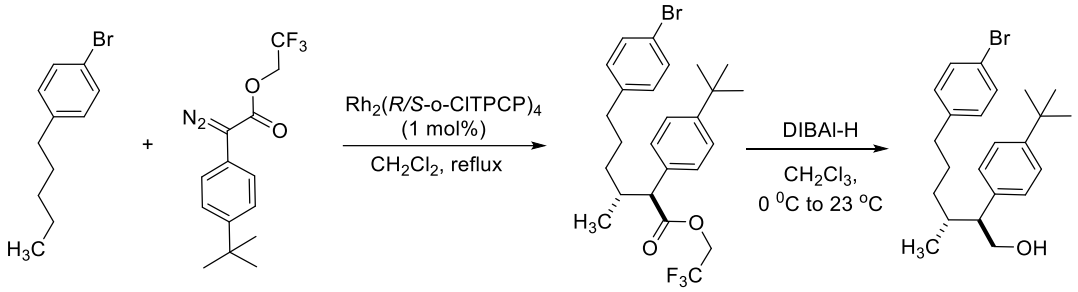


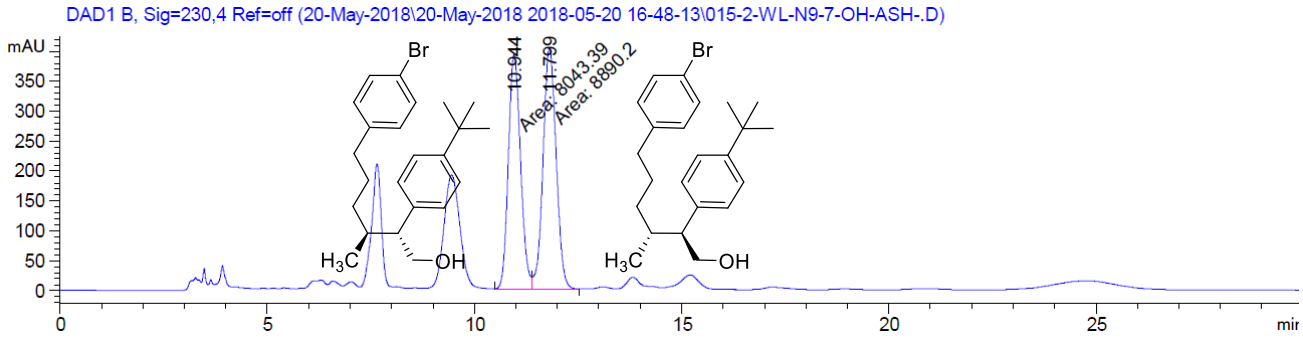


Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.045	MM	0.8502	3599.61426	70.55995	8.6756
2	37.482	MM	0.9355	3.78916e4	675.06329	91.3244
Totals :				4.14912e4	745.62325	

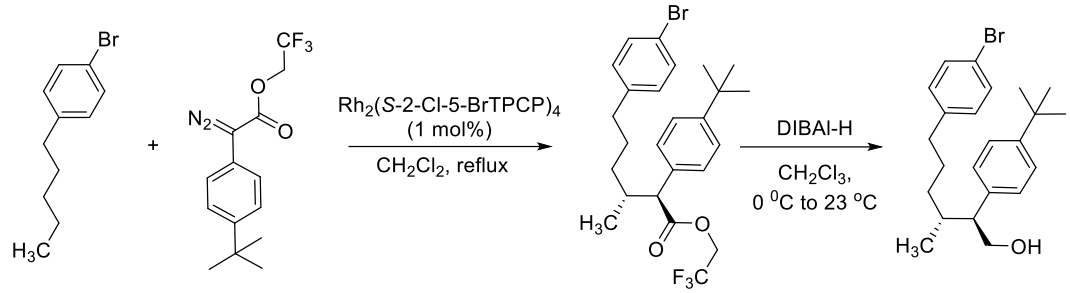
→ 83% ee

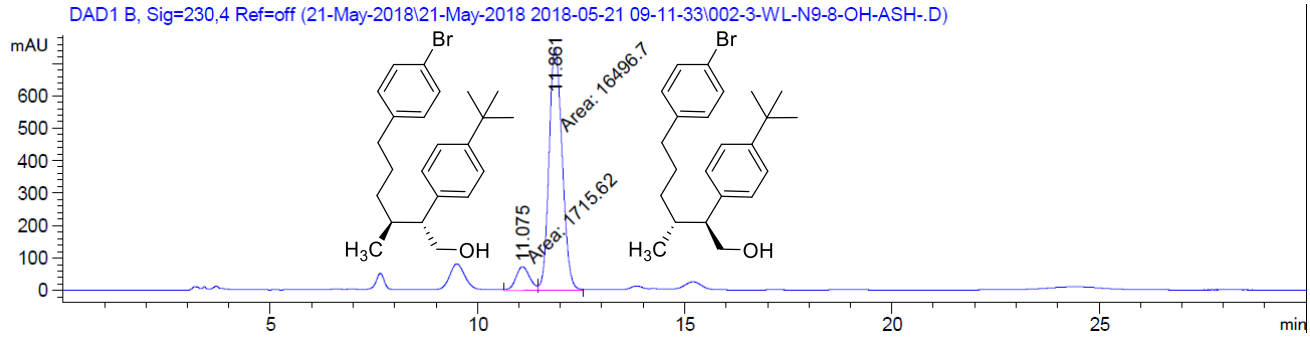




Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.944	MF	0.3415	8043.38867	392.54388	47.4996
2	11.799	FM	0.3673	8890.20117	403.36566	52.5004
Totals :				1.69336e4	795.90955	

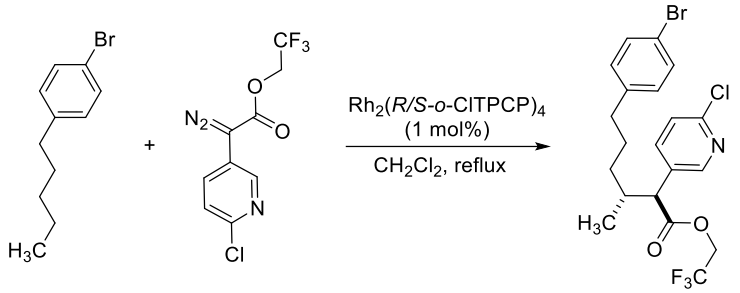


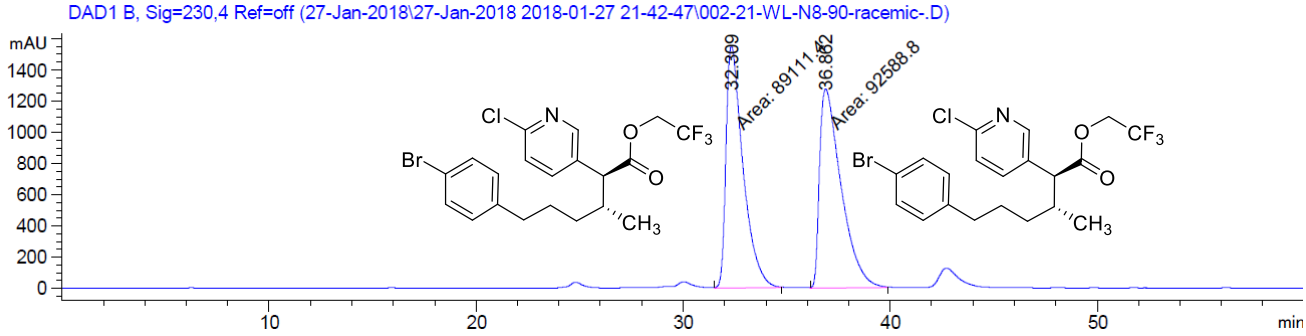


Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.075	MF	0.3897	1715.62219	73.37231	9.4201
2	11.861	FM	0.3671	1.64967e4	748.97400	90.5799
Totals :				1.82123e4	822.34631	

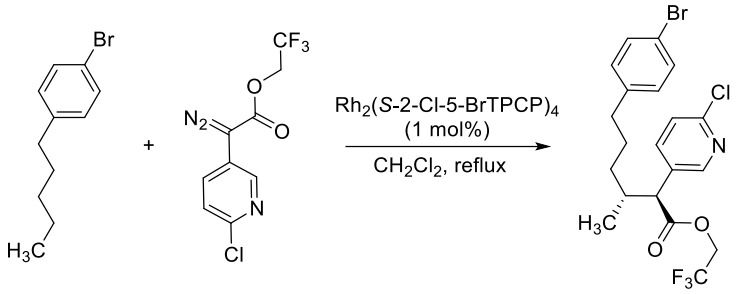
→ 81% ee

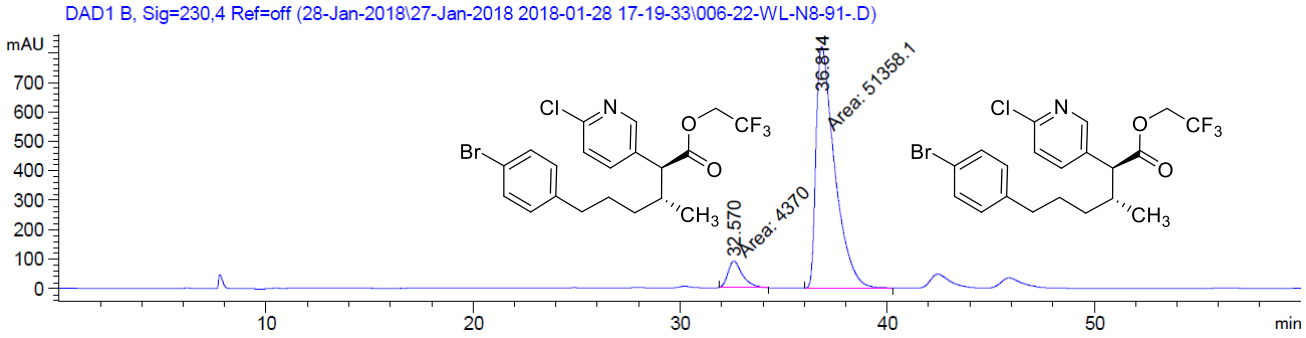




Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.309	MM	0.9548	8.91114e4	1555.56042	49.0431
2	36.862	MM	1.2062	9.25888e4	1279.33923	50.9569
Totals :				1.81700e5	2834.89966	

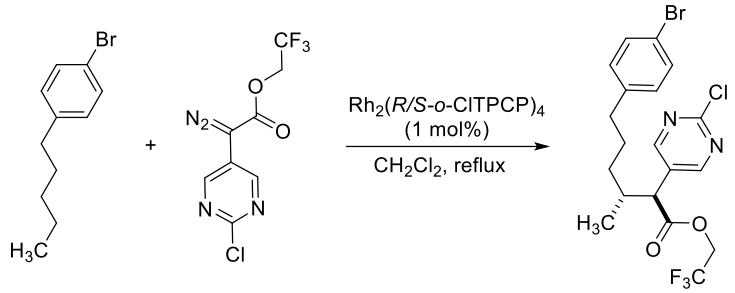


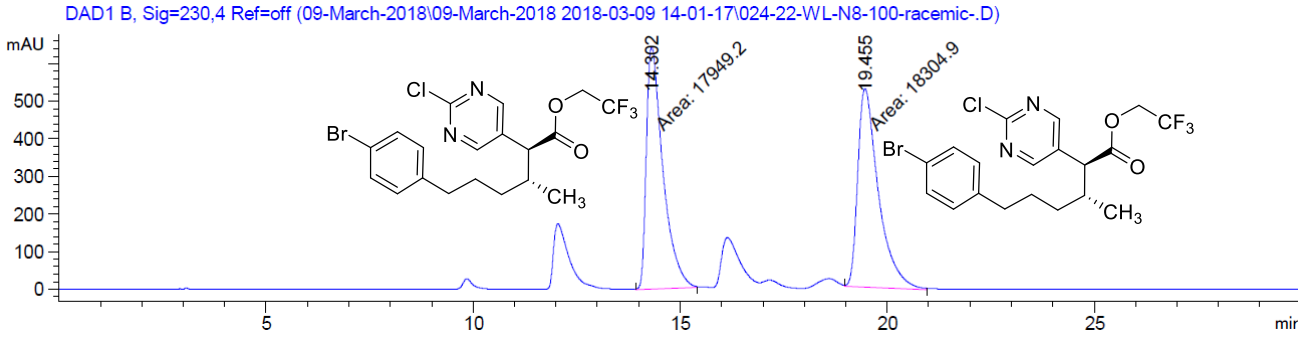


Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.570	MM	0.8084	4369.99707	90.09435	7.8416
2	36.814	MM	1.0451	5.13581e4	819.05475	92.1584
Totals :				5.57281e4	909.14910	

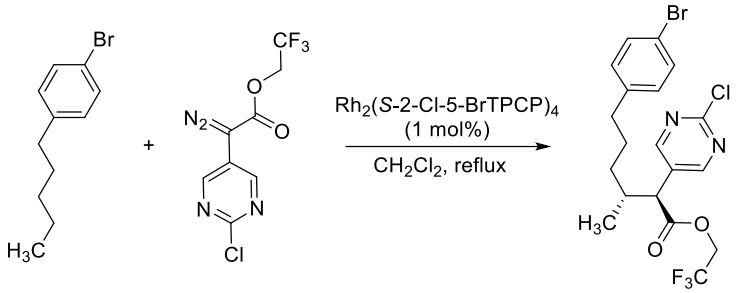
→ 84% ee

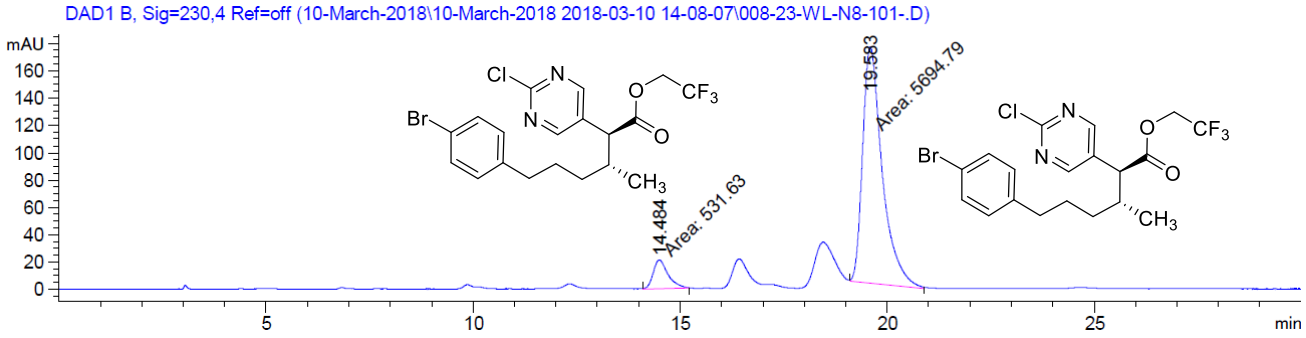




Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.302	MM	0.4637	1.79492e4	645.10413	49.5094
2	19.455	MM	0.5778	1.83049e4	528.02850	50.4906
Totals :				3.62542e4	1173.13263	

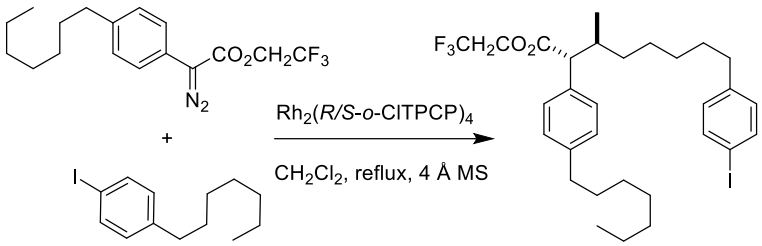


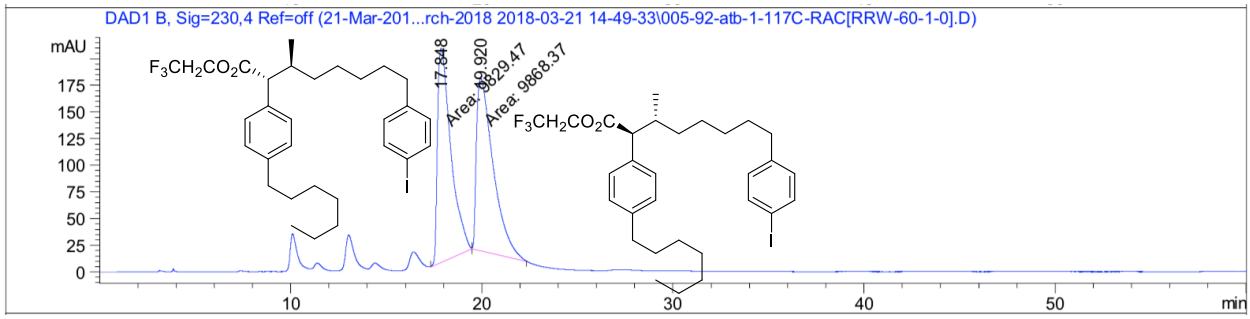


Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.484	MM	0.4185	531.63000	21.17127	8.5383
2	19.583	MM	0.5480	5694.78564	173.19611	91.4617
Totals :				6226.41565	194.36737	

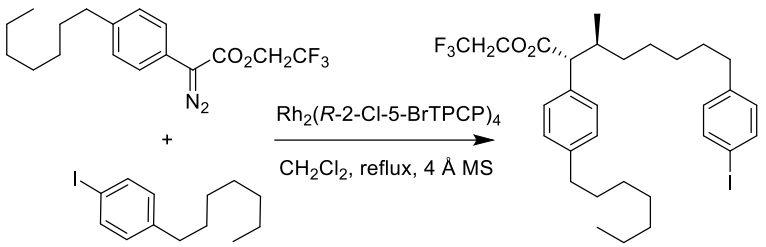
→ 83% ee

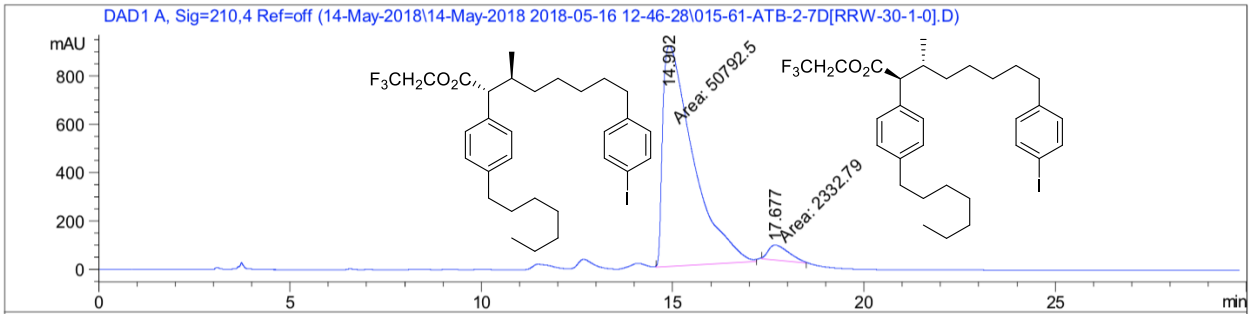




Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.848	MM	0.5750	9829.47168	200.90695	49.9013
2	19.920	MM	1.0183	9868.37109	161.51624	50.0987
Totals :				1.96978e4	362.42319	

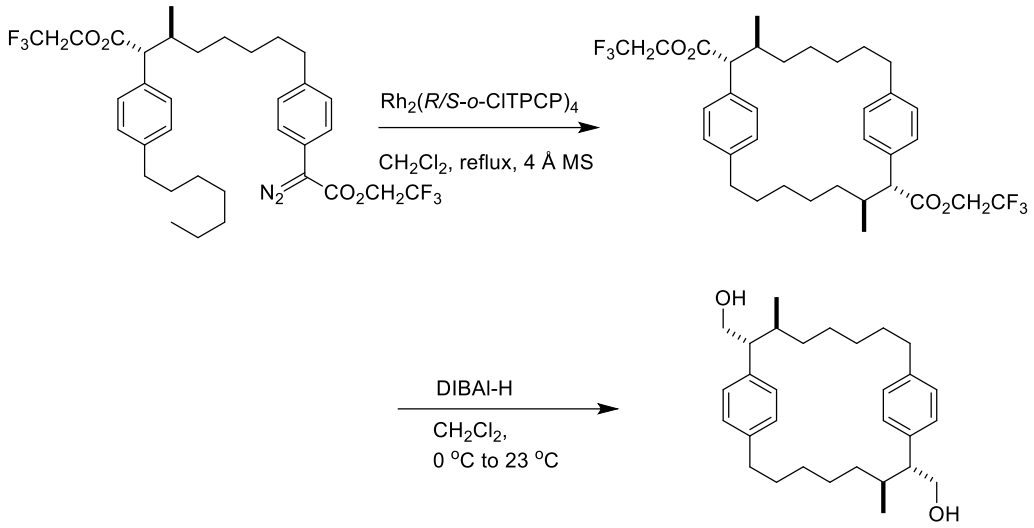


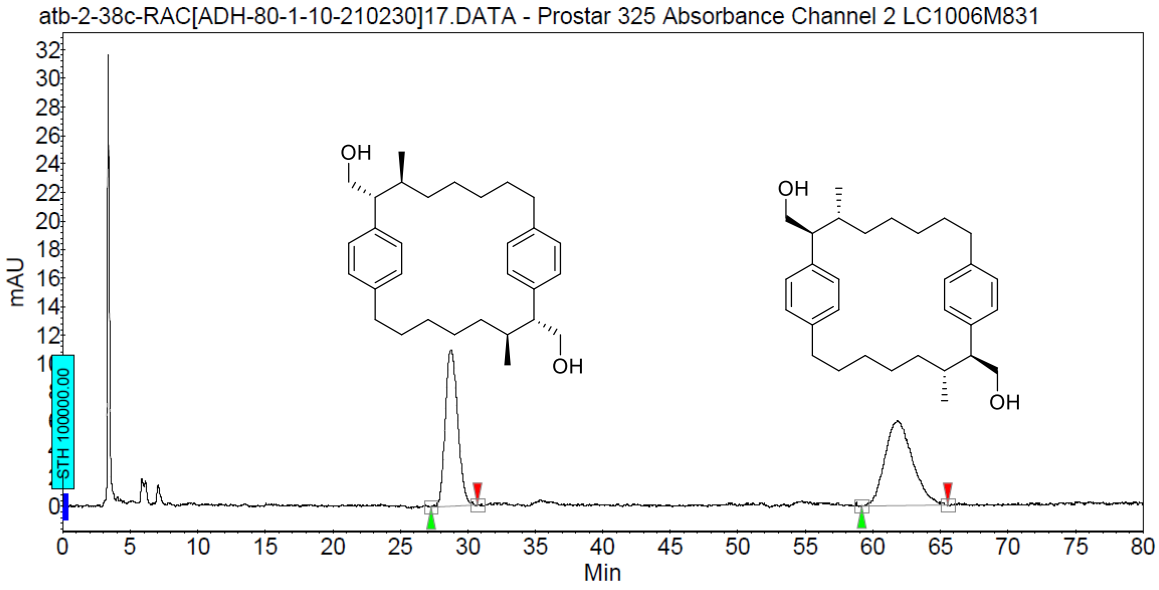


Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.902	MM	0.9260	5.07925e4	914.16620	95.6089
2	17.677	MM	0.6274	2332.78857	61.97265	4.3911
Totals :				5.31253e4	976.13885	

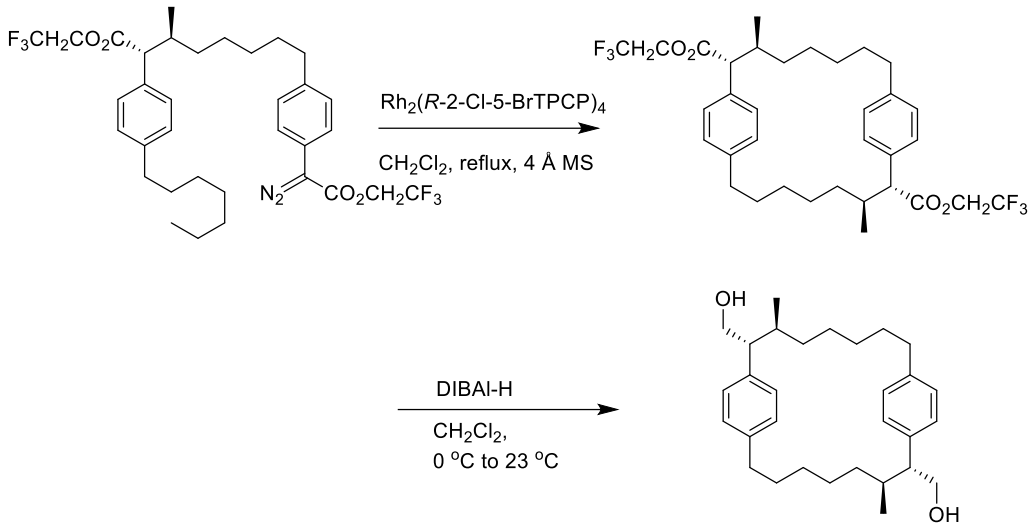
→ 91% ee

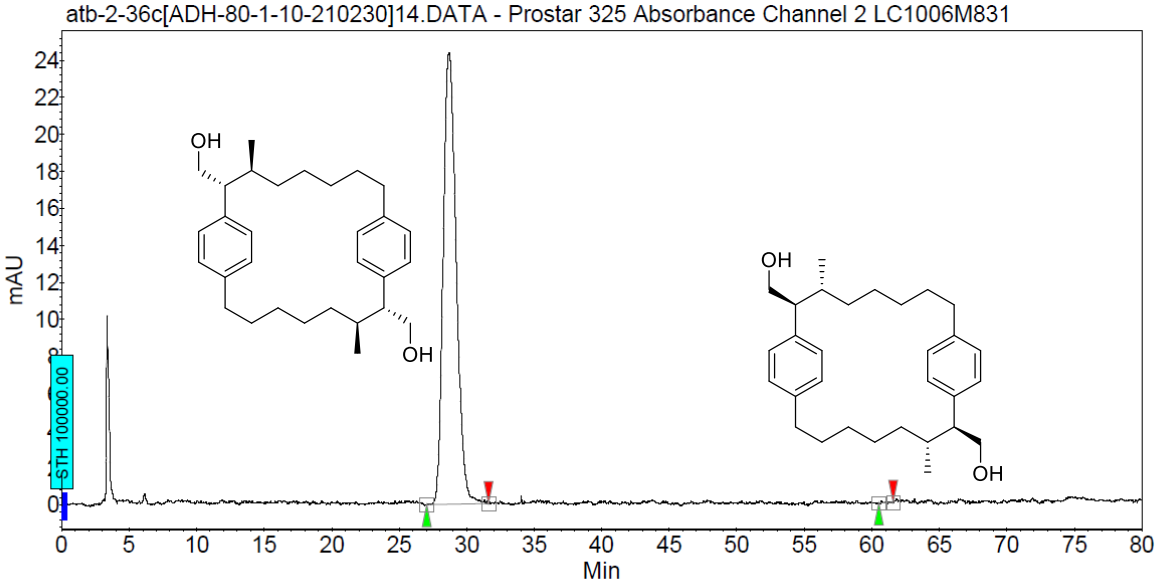




Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	28.74	45.33	11.0	11.7	45.329
2	UNKNOWN	61.84	54.67	6.0	14.1	54.671
Total			100.00	16.9	25.8	100.000





Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	28.69	99.92	24.3	27.2	99.923
2	UNKNOWN	60.71	0.08	0.1	0.0	0.077
Total			100.00	24.4	27.2	100.000

→ >99% ee

11. X-Ray Crystallographic Data of Ligands

11.1. *S*-2-Cl-5-BrTPCP Ligand (30)

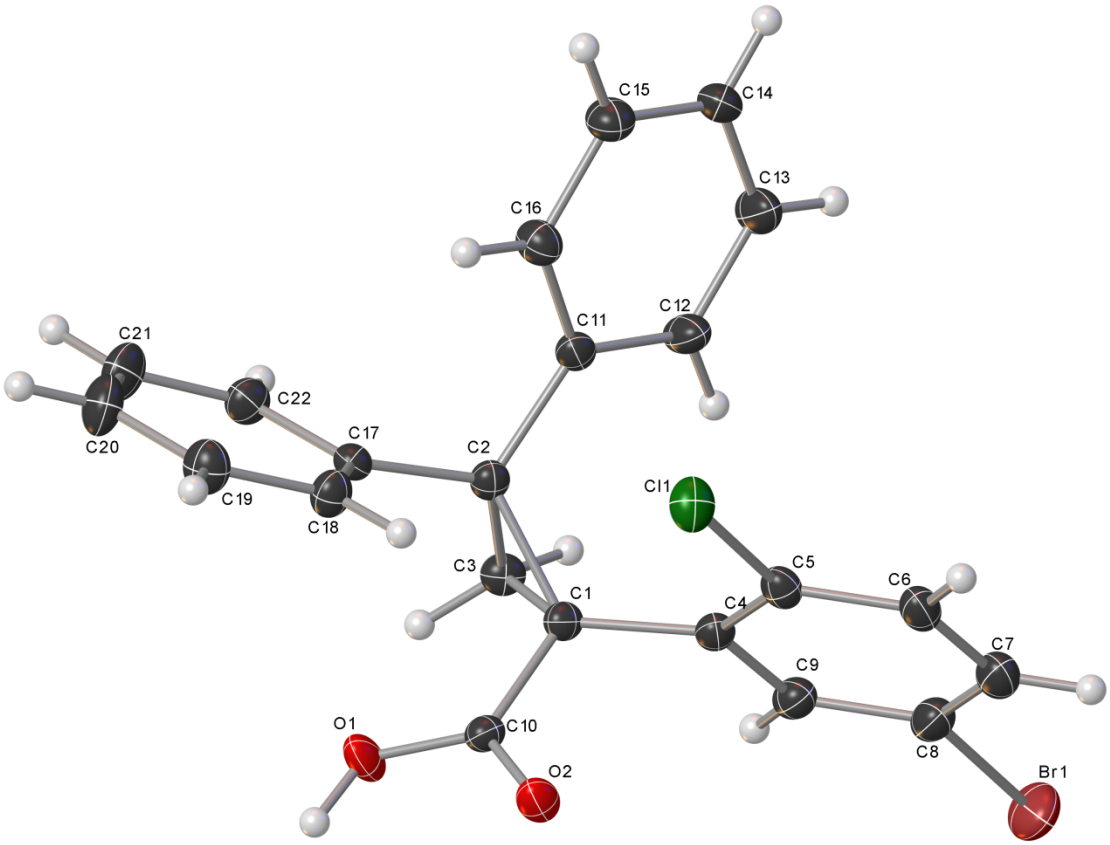


Table S11.1.1. Crystal data and structure refinement for WL-S2Cl5Br-ligand.

Identification code	WL-S2Cl5Br-ligand
Empirical formula	$C_{22}H_{16}BrClO_2$
Formula weight	427.71
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.91980(10)
b/Å	14.41860(10)
c/Å	29.7333(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3824.03(6)
Z	8
ρ_{calc}g/cm^3	1.486
μ/mm^{-1}	4.317
F(000)	1728.0
Crystal size/mm^3	0.21 × 0.168 × 0.094
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	6.814 to 155.826
Index ranges	$-8 \leq h \leq 11$, $-17 \leq k \leq 16$, $-35 \leq l \leq 37$
Reflections collected	23741
Independent reflections	7890 [R_{int} = 0.0333, R_{sigma} = 0.0319]
Data/restraints/parameters	7890/308/528
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0242, wR_2 = 0.0618
Final R indexes [all data]	R_1 = 0.0253, wR_2 = 0.0621
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.39
Flack parameter	-0.010(5)

Table S11.1.2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for WL-S2Cl5Br-ligand. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C11	3547(3)	5496.6(16)	7003.4(8)	17.0(4)
C1	5253(2)	4585.3(16)	6423.6(8)	16.0(4)
C16	2915(3)	5305.3(17)	7422.7(9)	21.5(5)
C2	3707(3)	4723.8(16)	6661.5(8)	16.2(4)
C15	2664(3)	6007.2(18)	7735.5(9)	24.0(5)
C3	3913(3)	4996.6(17)	6176.8(8)	18.2(5)
C14	3048(3)	6912.9(19)	7635.1(10)	25.1(5)
C13	3703(3)	7108.3(19)	7224.3(11)	29.7(6)
C12	3946(3)	6408.1(18)	6910.1(10)	24.4(5)
C10	5648(3)	3620.4(16)	6280.5(8)	16.1(4)
C17	2796(3)	3878.4(16)	6774.6(8)	16.3(4)
C18	3404(3)	3129.3(17)	7009.2(9)	20.6(5)
C19	2517(3)	2385.5(18)	7138.1(10)	25.7(5)
C20	997(3)	2389(2)	7041.5(11)	29.1(6)
C21	374(3)	3133(2)	6812.6(10)	28.4(6)
C22	1274(3)	3869.5(18)	6676.5(9)	21.4(5)
O1	4665(2)	3187.9(11)	6043.1(7)	23.8(4)
O2	6888(2)	3284.4(11)	6383.8(7)	20.9(4)
C1'	6977(3)	175.5(16)	5815.8(8)	17.0(4)
C2'	7088(3)	71.1(16)	5290.3(8)	17.3(4)
C3'	5828(3)	-360.7(16)	5550.2(9)	19.7(5)
C10'	6529(3)	1134.6(16)	5961.5(8)	16.6(5)
C17'	6741(3)	901.0(17)	4998.2(8)	19.5(5)
C18'	7633(3)	1694.7(18)	5007.1(9)	23.9(5)
C19'	7331(4)	2429.2(19)	4716.3(10)	31.6(6)
C20'	6155(4)	2369(2)	4415.0(11)	35.3(7)

C21'	5261(4)	1590(2)	4406.2(10)	34.5(7)
C22'	5556(3)	855.6(19)	4697.3(9)	25.7(5)
O1'	5258.5(19)	1442.6(8)	5884.6(7)	22.8(4)
O2'	7577(2)	1600.7(12)	6161.5(6)	22.2(4)
Br1_1	9360.8(4)	6964.9(2)	5835.5(2)	36.85(10)
Cl1_1	6634.0(7)	4428.1(4)	7390.4(2)	23.08(13)
C4_1	6605(2)	5159.1(15)	6544.4(7)	16.8(4)
C5_1	7331(2)	5116.1(15)	6958.8(7)	18.1(4)
C6_1	8642(3)	5604.3(16)	7045.0(8)	22.2(4)
C7_1	9268(3)	6163.9(17)	6713.6(8)	25.0(4)
C8_1	8553(3)	6212.3(16)	6301.2(8)	23.8(4)
C9_1	7246(3)	5726.5(16)	6215.8(8)	20.5(4)
Br1_2	12597.1(5)	146.7(10)	6382.7(2)	37.2(2)
Cl1_2	5892.7(16)	-1347.8(19)	6506.2(7)	34.8(3)
C4_2	8084(3)	-276(3)	6128.0(16)	17.7(5)
C5_2	7722(3)	-949(3)	6446.7(15)	21.4(5)
C6_2	8779(3)	-1314(4)	6740.8(15)	26.1(5)
C7_2	10252(3)	-1000(3)	6729.7(14)	27.3(5)
C8_2	10614(3)	-320(2)	6420.6(10)	23.3(6)
C9_2	9564(3)	42(2)	6126.7(11)	18.9(8)
Br1_3	12597(4)	-240(5)	6369.7(13)	37.2(2)
Cl1_3	5701(9)	-1381(14)	6441(6)	34.8(3)
C4_3	8037(9)	-365(19)	6109(10)	17.7(5)
C5_3	7556(12)	-1010(20)	6425(9)	21.4(5)
C6_3	8509(12)	-1360(20)	6754(9)	26.1(5)
C7_3	10025(10)	-1130(20)	6749(8)	27.3(5)
C8_3	10540(7)	-569(16)	6406(6)	23.3(6)
C9_3	9565(9)	-150(20)	6104(8)	18.9(8)
C11_4	8325(8)	-514(7)	5096(7)	19.5(6)
C12_4	8028(8)	-1413(7)	4943(4)	20.1(9)
C13_4	9157(10)	-1964(5)	4762(3)	23.2(9)
C14_4	10622(9)	-1639(6)	4762(3)	22.6(8)
C15_4	10936(7)	-748(7)	4902(3)	21.9(8)
C16_4	9790(8)	-175(6)	5058(4)	20.1(8)
C11_5	8222(6)	-592(5)	5098(5)	19.5(6)
C12_5	7720(6)	-1403(5)	4888(3)	20.1(9)
C13_5	8716(8)	-2022(4)	4689(2)	23.2(9)
C14_5	10240(8)	-1830(4)	4696(2)	22.6(8)
C15_5	10762(6)	-1027(5)	4894(2)	21.9(8)
C16_5	9762(6)	-400(4)	5088(3)	20.1(8)

Table S11.1.3. Anisotropic Displacement Parameters ($Å^2×10^3$) for WL-S2Cl5Br-ligand. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	14.2(10)	16.9(10)	19.7(12)	-1.5(9)	-0.4(9)	1.8(9)
C1	14.5(10)	18.2(11)	15.3(10)	-0.9(8)	-1.4(8)	0.5(8)
C16	27.0(13)	17.6(11)	19.9(12)	0.8(9)	0.9(10)	-0.4(9)
C2	14.7(10)	15.8(10)	18.0(11)	0.3(9)	-0.7(8)	1.2(8)
C15	27.0(13)	25.5(12)	19.5(12)	-1.3(10)	3.4(10)	-1.1(11)
C3	18.4(10)	18.9(11)	17.4(11)	1.7(9)	-1.6(9)	2.9(9)
C14	23.8(12)	23.1(12)	28.5(13)	-9.9(11)	6.0(10)	-1.7(10)
C13	32.6(14)	17.7(11)	38.7(16)	-5.6(11)	12.2(12)	-5.3(11)
C12	26.7(13)	19.7(11)	26.8(14)	-1.7(10)	11.1(11)	-2.1(10)
C10	14.1(10)	18.5(10)	15.7(10)	-0.5(8)	1.4(9)	0.5(9)
C17	16.8(11)	16.6(10)	15.7(10)	-3.1(8)	0.6(9)	-0.6(9)
C18	16.2(11)	20.3(11)	25.1(12)	1.8(10)	-1.8(10)	-0.3(9)
C19	26.9(13)	20.0(11)	30.2(14)	4.0(10)	-1.9(12)	-1.3(10)
C20	23.8(14)	29.0(13)	34.5(15)	5.0(11)	-1.7(11)	-9.6(11)
C21	17.2(12)	34.6(14)	33.3(15)	1.7(12)	-4.8(11)	-4.5(11)
C22	17.9(12)	23.2(12)	23.2(13)	-0.2(10)	-2.5(10)	1.5(10)
O1	20.8(9)	22.4(9)	28.2(10)	-10.6(7)	-7.0(7)	1.1(7)
O2	17.1(8)	19.3(8)	26.4(9)	-3.9(7)	-3.3(7)	3.3(6)
C1'	17.0(10)	16.9(10)	17.0(11)	-0.7(9)	1.9(9)	-1.4(8)
C2'	17.5(11)	17.8(10)	16.5(11)	-2.5(9)	-1.5(9)	0.1(9)
C3'	18.8(11)	18.5(11)	21.8(12)	-2.1(9)	1.8(10)	-2.0(9)
C10'	18.2(11)	17.9(11)	13.7(10)	0.6(8)	2.7(9)	-2.6(9)
C17'	21.1(12)	22.1(11)	15.4(11)	-3.7(9)	2.1(10)	3.3(9)
C18'	25.2(13)	25.3(12)	21.3(12)	0.5(10)	4.5(11)	-1.8(10)
C19'	41.8(17)	23.3(13)	29.8(14)	3.1(11)	12.5(13)	2.2(12)
C20'	45.8(18)	33.6(15)	26.7(15)	8.3(12)	10.8(13)	20.0(13)
C21'	35.0(16)	43.4(16)	25.1(14)	0.2(12)	-3.5(12)	16.8(13)
C22'	24.1(12)	29.8(13)	23.1(13)	-4.2(10)	-1.3(11)	5.4(11)
O1'	18.1(8)	21.8(8)	28.7(10)	-4.3(7)	1.4(7)	2.9(7)
O2'	22.9(9)	17.7(8)	25.9(9)	-4.1(7)	-3.3(8)	0.0(7)
Br1_1	38.92(17)	34.89(16)	36.75(17)	3.10(13)	14.12(14)	-14.05(13)
Cl1_1	25.5(3)	24.0(3)	19.7(3)	5.3(2)	-5.9(2)	-3.3(2)
C4_1	14.8(8)	16.3(9)	19.3(8)	-1.4(6)	0.9(6)	1.1(7)
C5_1	19.3(8)	14.3(8)	20.8(8)	-1.3(7)	-1.9(6)	1.7(7)
C6_1	19.9(8)	19.1(9)	27.5(10)	-5.4(7)	-1.4(7)	-0.2(7)
C7_1	23.2(10)	20.0(10)	31.7(9)	-4.5(7)	1.9(7)	-1.2(8)
C8_1	20.2(8)	22.1(10)	29.2(9)	-1.9(8)	5.5(7)	-1.8(7)
C9_1	20.2(8)	18.8(9)	22.4(9)	0.3(7)	3.6(7)	-0.2(7)
Br1_2	19.10(14)	56.6(6)	35.83(18)	-4.0(2)	-4.60(12)	-1.8(2)
Cl1_2	27.4(5)	41.5(4)	35.4(9)	16.7(6)	1.5(4)	-9.5(5)
C4_2	19.3(6)	16.3(10)	17.5(9)	-2.9(8)	1.4(5)	1.7(6)
C5_2	23.6(7)	19.0(9)	21.7(8)	0.5(7)	2.8(6)	1.2(6)
C6_2	27.9(8)	25.9(12)	24.5(10)	1.3(8)	0.6(9)	5.8(9)
C7_2	27.6(8)	30.3(14)	24.1(10)	-0.4(9)	-0.2(8)	5.4(9)

C8_2	22.8(8)	26.3(15)	20.7(9)	-4.3(10)	-0.7(7)	5.9(7)
C9_2	19.3(6)	17.9(17)	19.4(11)	-4.1(12)	1.0(6)	1.3(7)
Br1_3	19.10(14)	56.6(6)	35.83(18)	-4.0(2)	-4.60(12)	-1.8(2)
Cl1_3	27.4(5)	41.5(4)	35.4(9)	16.7(6)	1.5(4)	-9.5(5)
C4_3	19.3(6)	16.3(10)	17.5(9)	-2.9(8)	1.4(5)	1.7(6)
C5_3	23.6(7)	19.0(9)	21.7(8)	0.5(7)	2.8(6)	1.2(6)
C6_3	27.9(8)	25.9(12)	24.5(10)	1.3(8)	0.6(9)	5.8(9)
C7_3	27.6(8)	30.3(14)	24.1(10)	-0.4(9)	-0.2(8)	5.4(9)
C8_3	22.8(8)	26.3(15)	20.7(9)	-4.3(10)	-0.7(7)	5.9(7)
C9_3	19.3(6)	17.9(17)	19.4(11)	-4.1(12)	1.0(6)	1.3(7)
C11_4	21.5(8)	19.6(9)	17.4(9)	2.0(8)	0.7(7)	1.2(8)
C12_4	21.8(12)	18.5(8)	20(2)	2.7(11)	-3.2(15)	2.9(11)
C13_4	22.4(15)	18.7(10)	29(2)	-0.3(11)	-0.7(16)	1.6(13)
C14_4	22.4(14)	20.6(15)	24.8(18)	2.2(11)	-1.4(15)	1.3(12)
C15_4	21.4(11)	21.7(18)	22.6(13)	1.6(16)	2.2(11)	-0.2(12)
C16_4	21.6(8)	21.7(16)	17.0(16)	2.4(18)	0.5(7)	0.6(10)
C11_5	21.5(8)	19.6(9)	17.4(9)	2.0(8)	0.7(7)	1.2(8)
C12_5	21.8(12)	18.5(8)	20(2)	2.7(11)	-3.2(15)	2.9(11)
C13_5	22.4(15)	18.7(10)	29(2)	-0.3(11)	-0.7(16)	1.6(13)
C14_5	22.4(14)	20.6(15)	24.8(18)	2.2(11)	-1.4(15)	1.3(12)
C15_5	21.4(11)	21.7(18)	22.6(13)	1.6(16)	2.2(11)	-0.2(12)
C16_5	21.6(8)	21.7(16)	17.0(16)	2.4(18)	0.5(7)	0.6(10)

Table S11.1.4. Bond Lengths for WL-S2Cl5Br-ligand.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C11	C16	1.396(4)	C21'	C22'	1.393(4)
C11	C2	1.515(3)	Br1_1	C8_1	1.901(2)
C11	C12	1.390(3)	Cl1_1	C5_1	1.737(2)
C1	C2	1.563(3)	C4_1	C5_1	1.393(3)
C1	C3	1.523(3)	C4_1	C9_1	1.397(3)
C1	C10	1.497(3)	C5_1	C6_1	1.388(3)
C1	C4_1	1.506(3)	C6_1	C7_1	1.390(3)
C16	C15	1.393(4)	C7_1	C8_1	1.384(3)
C2	C3	1.505(3)	C8_1	C9_1	1.383(3)
C2	C17	1.503(3)	Br1_2	C8_2	1.895(2)
C15	C14	1.383(4)	Cl1_2	C5_2	1.739(2)
C14	C13	1.383(4)	C4_2	C5_2	1.394(3)
C13	C12	1.392(4)	C4_2	C9_2	1.397(3)
C10	O1	1.287(3)	C5_2	C6_2	1.390(3)
C10	O2	1.247(3)	C6_2	C7_2	1.390(3)
C17	C18	1.396(3)	C7_2	C8_2	1.382(3)
C17	C22	1.389(4)	C8_2	C9_2	1.384(3)
C18	C19	1.387(4)	Br1_3	C8_3	1.898(3)

C19	C20	1.386(4)	Cl1_3	C5_3	1.738(3)
C20	C21	1.387(4)	C4_3	C5_3	1.394(3)
C21	C22	1.390(4)	C4_3	C9_3	1.397(3)
C1'	C2'	1.573(3)	C5_3	C6_3	1.390(3)
C1'	C3'	1.507(3)	C6_3	C7_3	1.391(4)
C1'	C10'	1.504(3)	C7_3	C8_3	1.383(4)
C1'	C4_2	1.503(3)	C8_3	C9_3	1.385(3)
C1'	C4_3	1.503(3)	C11_4	C12_4	1.398(4)
C2'	C3'	1.499(3)	C11_4	C16_4	1.400(4)
C2'	C17'	1.511(3)	C12_4	C13_4	1.392(5)
C2'	C11_4	1.505(4)	C13_4	C14_4	1.388(6)
C2'	C11_5	1.505(3)	C14_4	C15_4	1.380(6)
C10'	O1'	1.238(3)	C15_4	C16_4	1.393(5)
C10'	O2'	1.296(3)	C11_5	C12_5	1.399(4)
C17'	C18'	1.394(4)	C11_5	C16_5	1.401(4)
C17'	C22'	1.387(4)	C12_5	C13_5	1.391(4)
C18'	C19'	1.394(4)	C13_5	C14_5	1.387(6)
C19'	C20'	1.382(5)	C14_5	C15_5	1.380(6)
C20'	C21'	1.378(5)	C15_5	C16_5	1.394(5)

Table S11.1.5. Bond Angles for WL-S2Cl5Br-ligand.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	C11	C2	119.5(2)	C19'	C18'	C17'	120.1(3)
C12	C11	C16	117.9(2)	C20'	C19'	C18'	120.0(3)
C12	C11	C2	122.5(2)	C21'	C20'	C19'	120.2(3)
C3	C1	C2	58.37(15)	C20'	C21'	C22'	119.9(3)
C10	C1	C2	117.0(2)	C17'	C22'	C21'	120.6(3)
C10	C1	C3	114.2(2)	C5_1	C4_1	C1	123.97(19)
C10	C1	C4_1	112.99(19)	C5_1	C4_1	C9_1	117.01(19)
C4_1	C1	C2	121.91(19)	C9_1	C4_1	C1	118.87(19)
C4_1	C1	C3	122.0(2)	C4_1	C5_1	Cl1_1	120.80(16)
C15	C16	C11	121.2(2)	C6_1	C5_1	Cl1_1	117.05(16)
C11	C2	C1	118.7(2)	C6_1	C5_1	C4_1	122.15(19)
C3	C2	C11	117.5(2)	C5_1	C6_1	C7_1	120.1(2)
C3	C2	C1	59.49(15)	C8_1	C7_1	C6_1	118.2(2)
C17	C2	C11	113.3(2)	C7_1	C8_1	Br1_1	119.97(17)
C17	C2	C1	118.34(19)	C9_1	C8_1	Br1_1	118.35(18)
C17	C2	C3	119.5(2)	C9_1	C8_1	C7_1	121.7(2)
C14	C15	C16	120.2(2)	C8_1	C9_1	C4_1	120.9(2)
C2	C3	C1	62.14(16)	C5_2	C4_2	C1'	124.6(2)
C15	C14	C13	119.2(2)	C5_2	C4_2	C9_2	116.7(2)
C14	C13	C12	120.7(3)	C9_2	C4_2	C1'	118.5(2)
C11	C12	C13	120.8(3)	C4_2	C5_2	Cl1_2	121.13(18)

O1	C10	C1	116.5(2)	C6_2	C5_2	Cl1_2	116.56(18)
O2	C10	C1	120.0(2)	C6_2	C5_2	C4_2	122.3(2)
O2	C10	O1	123.5(2)	C7_2	C6_2	C5_2	120.2(2)
C18	C17	C2	122.0(2)	C8_2	C7_2	C6_2	117.9(2)
C22	C17	C2	119.3(2)	C7_2	C8_2	Br1_2	120.64(18)
C22	C17	C18	118.5(2)	C7_2	C8_2	C9_2	121.9(2)
C19	C18	C17	121.0(2)	C9_2	C8_2	Br1_2	117.43(19)
C20	C19	C18	119.9(3)	C8_2	C9_2	C4_2	121.0(2)
C19	C20	C21	119.7(3)	C5_3	C4_3	C1'	123.0(7)
C20	C21	C22	120.2(3)	C5_3	C4_3	C9_3	116.9(3)
C17	C22	C21	120.7(2)	C9_3	C4_3	C1'	119.7(5)
C3'	C1'	C2'	58.21(16)	C4_3	C5_3	Cl1_3	121.0(3)
C10'	C1'	C2'	113.0(2)	C6_3	C5_3	Cl1_3	117.0(3)
C10'	C1'	C3'	116.2(2)	C6_3	C5_3	C4_3	121.9(4)
C10'	C1'	C4_2	113.2(3)	C5_3	C6_3	C7_3	120.1(4)
C4_2	C1'	C2'	122.1(3)	C8_3	C7_3	C6_3	118.0(3)
C4_2	C1'	C3'	123.3(2)	C7_3	C8_3	Br1_3	120.6(3)
C4_3	C1'	C2'	119.1(15)	C7_3	C8_3	C9_3	121.5(4)
C4_3	C1'	C3'	117.8(11)	C9_3	C8_3	Br1_3	117.6(3)
C4_3	C1'	C10'	118.5(15)	C8_3	C9_3	C4_3	120.9(3)
C3'	C2'	C1'	58.72(15)	C12_4	C11_4	C2'	120.4(5)
C3'	C2'	C17'	118.2(2)	C12_4	C11_4	C16_4	118.3(3)
C3'	C2'	C11_4	121.0(6)	C16_4	C11_4	C2'	121.3(5)
C3'	C2'	C11_5	115.9(4)	C13_4	C12_4	C11_4	121.2(4)
C17'	C2'	C1'	118.9(2)	C14_4	C13_4	C12_4	119.2(4)
C11_4	C2'	C1'	118.8(8)	C15_4	C14_4	C13_4	120.4(4)
C11_4	C2'	C17'	111.9(8)	C14_4	C15_4	C16_4	120.2(4)
C11_5	C2'	C1'	118.7(6)	C15_4	C16_4	C11_4	120.4(4)
C11_5	C2'	C17'	115.0(6)	C12_5	C11_5	C2'	119.0(4)
C2'	C3'	C1'	63.07(16)	C12_5	C11_5	C16_5	118.0(3)
O1'	C10'	C1'	121.3(2)	C16_5	C11_5	C2'	122.8(4)
O1'	C10'	O2'	124.0(2)	C13_5	C12_5	C11_5	121.4(3)
O2'	C10'	C1'	114.7(2)	C14_5	C13_5	C12_5	119.5(4)
C18'	C17'	C2'	121.5(2)	C15_5	C14_5	C13_5	120.3(3)
C22'	C17'	C2'	119.3(2)	C14_5	C15_5	C16_5	120.3(4)
C22'	C17'	C18'	119.1(3)	C15_5	C16_5	C11_5	120.5(3)

Table S11.1.6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for WL-S2Cl5Br-ligand.

Atom	*x*	*y*	*z*	U(eq)
H16	2656.53	4698.17	7494.43	26
H15	2236.63	5866.44	8012.5	29
H3A	3960(40)	5668(11)	6098(11)	21(4)

H3B	3460(30)	4586(18)	5944(8)	21(4)
H1	4917.2	2548.6	5994.8	32
H14	2869.02	7384.93	7841.35	30
H13	3984.5	7713.73	7157.18	36
H12	4380.31	6552.33	6634.47	29
H18	4419.2	3129.03	7080.33	25
H19	2941.62	1885.3	7288.97	31
H20	397.29	1893.78	7129.77	35
H21	-647.02	3140.27	6750.06	34
H22	851.33	4360.8	6518.33	26
H3'A	5870(40)	-1040(11)	5611(11)	21(4)
H3'B	4800(20)	-90(20)	5528(11)	21(4)
H18'	8430.53	1734.11	5207.57	29
H19'	7921.44	2960.5	4724.88	38
H20'	5967.55	2855.13	4217.59	42
H21'	4461.03	1554.88	4206.17	41
H22'	4952.17	329.85	4689.78	31
H2'	7223.53	2211.63	6226.42	27
H6_1	9102.13	5556.9	7324.7	27
H7_1	10142.49	6496.52	6767.68	30
H9_1	6788.21	5778.38	5935.95	25
H6_2	8500.81	-1770.43	6945.59	31
H7_2	10971	-1239.86	6924.16	33
H9_2	9846.73	503	5925.24	23
H6_3	8133.58	-1744.12	6978.71	31
H7_3	10672.72	-1354.92	6968.79	33
H9_3	9933.25	269.12	5895.55	23
H12_4	7058.07	-1646.5	4963.05	24
H13_4	8933.64	-2543.8	4642.02	28
H14_4	11395.58	-2023.54	4666.45	27
H15_4	11916.56	-528.81	4893.46	26
H16_4	9998.76	435.31	5136.53	24
H12_5	6698.54	-1531.14	4881.68	24
H13_5	8362.87	-2559.82	4553.35	28
H14_5	10911.83	-2244.17	4566.16	27
H15_5	11784.8	-902.73	4897.52	26
H16_5	10119.72	149.32	5211.14	24

Table S11.1.8. Atomic Occupancy for WL-S2Cl5Br-ligand.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
Br1_2	0.867(4)	Cl1_2	0.867(4)	C4_2	0.867(4)
C5_2	0.867(4)	C6_2	0.867(4)	H6_2	0.867(4)
C7_2	0.867(4)	H7_2	0.867(4)	C8_2	0.867(4)

C9_2	0.867(4)	H9_2	0.867(4)	Br1_3	0.133(4)		
Cl1_3	0.133(4)	C4_3	0.133(4)	C5_3	0.133(4)		
C6_3	0.133(4)	H6_3	0.133(4)	C7_3	0.133(4)		
H7_3	0.133(4)	C8_3	0.133(4)	C9_3	0.133(4)		
H9_3	0.133(4)	C11_4	0.410(11)	C12_4	0.410(11)		
H12_4	0.410(11)	C13_4	0.410(11)	H13_4	0.410(11)		
C14_4	0.410(11)	H14_4	0.410(11)	C15_4	0.410(11)		
H15_4	0.410(11)	C16_4	0.410(11)	H16_4	0.410(11)		
C11_5	0.590(11)	C12_5	0.590(11)	H12_5	0.590(11)		
C13_5	0.590(11)	H13_5	0.590(11)	C14_5	0.590(11)		
H14_5	0.590(11)	C15_5	0.590(11)	H15_5	0.590(11)		
C16_5	0.590(11)	H16_5	0.590(11)				

Experimental

Single crystals of $C_{22}H_{16}BrClO_2$ **[WL-S2Cl5Br-ligand]** were **[slow evaporation of 2% EtOAc in hexane]**. A suitable crystal was selected and **[The crystal was mounted on a loop with paratone oil]** on a **XtaLAB Synergy, Dualflex, HyPix** diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [WL-S2Cl5Br-ligand]

Crystal Data for $C_{22}H_{16}BrClO_2$ (M =427.71 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.91980(10) Å, b = 14.41860(10) Å, c = 29.7333(2) Å, V = 3824.03(6) Å^3, Z = 8, T = 100(2) K, μ(CuKα) = 4.317 mm^{-1}, *Dcalc* = 1.486 g/cm^3, 23741 reflections measured (6.814° ≤ 2Θ ≤ 155.826°), 7890 unique (R_{int} = 0.0333, R_{sigma} = 0.0319) which were used in all calculations. The final R_1 was 0.0242 (I > 2σ(I)) and wR_2 was 0.0621 (all data).

Refinement model description

Number of restraints - 308, number of constraints - unknown.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All O(H) groups
 At 1.5 times of:
  All H(H) groups
2. Restrained distances
 O1-H1
 0.955 with sigma of 0.002
 H1-O1'
 1.655 with sigma of 0.001
 C3'-H3'B ≈ C3'-H3'A
 with sigma of 0.002
 C3-H3A ≈ C3'-H3'B
 with sigma of 0.002
 C4_2-C1' ≈ C4_3-C1'
 with sigma of 0.001
 C3-H3A ≈ C3-H3B
 with sigma of 0.001
 C2'-C11_5 ≈ C2'-C11_4
 with sigma of 0.001
3. Uiso/Uaniso restraints and constraints

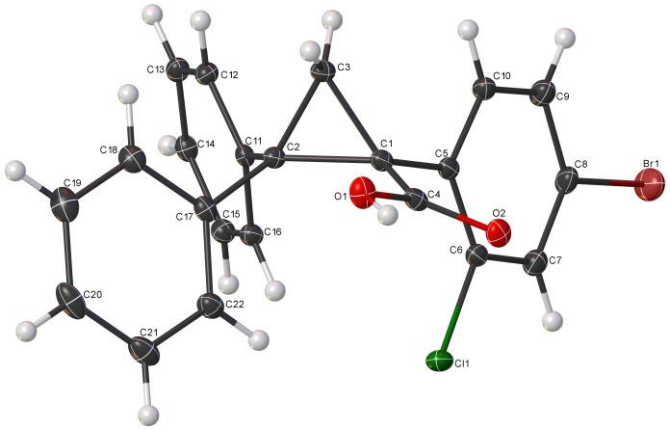
Uanis(C4_3) ≈ Ueq: with sigma of 0.001 and sigma for terminal atoms of 0.002
Uanis(C5_3) ≈ Ueq: with sigma of 0.001 and sigma for terminal atoms of 0.002
Uanis(C11_4) ≈ Ueq: with sigma of 0.001 and sigma for terminal atoms of

0.002
Uiso(H3'B) = Uiso(H3'A)
Uanis(C11_4) = Uanis(C11_5)
Uanis(C16_4) = Uanis(C16_5)
Uanis(C15_4) = Uanis(C15_5)
Uanis(C14_4) = Uanis(C14_5)
Uanis(C13_4) = Uanis(C13_5)
Uanis(C12_4) = Uanis(C12_5)
Uanis(C5_2) = Uanis(C5_3)
Uanis(C4_2) = Uanis(C4_3)
Uanis(C9_2) = Uanis(C9_3)
Uanis(C8_2) = Uanis(C8_3)
Uanis(C7_2) = Uanis(C7_3)
Uanis(C6_2) = Uanis(C6_3)
Uiso(H3A) = Uiso(H3B)
Uiso(H3B) = Uiso(H3'B)
Uanis(Br1_2) = Uanis(Br1_3)
Uanis(Cl1_3) = Uanis(Cl1_2)
4. Rigid body (RIGU) restrains
Br1_1, Cl1_1, C4_1, C5_1, C6_1, C7_1, C8_1, C9_1
Br1_2, Cl1_2, C4_2, C5_2, C6_2, C7_2, C8_2, C9_2
Br1_3, Cl1_3, C4_3, C5_3, C6_3, C7_3, C8_3, C9_3
with sigma for 1-2 distances of 0.0002 and sigma for 1-3 distances of 0.0004
C11_4, C12_4, C13_4, C14_4, C15_4, C16_4
C11_5, C12_5, C13_5, C14_5, C15_5, C16_5
with sigma for 1-2 distances of 0.0002 and sigma for 1-3 distances of 0.0004
5. Same fragment restrains
{Br1_2, Cl1_2, C4_2, C5_2, C6_2, C7_2, C8_2, C9_2}
{Br1_3, Cl1_3, C4_3, C5_3, C6_3, C7_3, C8_3, C9_3}
as
{Br1_1, Cl1_1, C4_1, C5_1, C6_1, C7_1, C8_1, C9_1} sigma for 1-2: 0.002 1-3:
0.004
{C11_5, C12_5, C13_5, C14_5, C15_5, C16_5}
as
{C11_4, C12_4, C13_4, C14_4, C15_4, C16_4} sigma for 1-2: 0.002 1-3: 0.004
6. Others
Sof(Br1)=Sof(Cl1)=Sof(C4)=Sof(C5)=Sof(C6)=Sof(H6)=Sof(C7)=Sof(H7)=Sof(C8)=
Sof(C9)=Sof(H9)=1-FVAR(1)
Sof(Br1)=Sof(Cl1)=Sof(C4)=Sof(C5)=Sof(C6)=Sof(H6)=Sof(C7)=Sof(H7)=Sof(C8)=
Sof(C9)=Sof(H9)=FVAR(1)
Sof(C11)=Sof(C12)=Sof(H12)=Sof(C13)=Sof(H13)=Sof(C14)=Sof(H14)=Sof(C15)=
Sof(H15)=Sof(C16)=Sof(H16)=1-FVAR(2)
Sof(C11)=Sof(C12)=Sof(H12)=Sof(C13)=Sof(H13)=Sof(C14)=Sof(H14)=Sof(C15)=
Sof(H15)=Sof(C16)=Sof(H16)=FVAR(2)
Fixed X: H1(0.49172)
Fixed Y: H1(0.25486)
Fixed Z: H1(0.59948)
7.a Aromatic/amide H refined with riding coordinates:
C16(H16), C15(H15), C14(H14), C13(H13), C12(H12), C18(H18), C19(H19),
C20(H20), C21(H21), C22(H22), C18'(H18'), C19'(H19'), C20'(H20'), C21'(H21'),
C22'(H22'), C6(H6), C7(H7), C9(H9), C6(H6), C7(H7), C9(H9), C6(H6), C7(H7),
C9(H9), C12(H12), C13(H13), C14(H14), C15(H15), C16(H16), C12(H12), C13(H13),
C14(H14), C15(H15), C16(H16)
7.b Idealised tetrahedral OH refined as rotating group:
O2'(H2')

This report has been created with Olex2, compiled on 2018.04.26 svn.r3501 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

11.2. *S*-2-Cl-4-BrTPCP Ligand (32)

Crystal Data and Experimental



Experimental. Single colourless block-shaped crystals of **WL-C22H16BrClO2_iso1** were chosen from the sample as supplied. A suitable crystal 0.38×0.29×0.21 mm^3 was selected and mounted on a loop with paratone oil on an XtaLAB Synergy, Dualflex, HyPix diffractometer.The crystal was kept at a steady T = 105(7) K during data collection.The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program usingthe Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface.The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{22}H_{16}BrClO_2$, M_r = 427.71, monoclinic, $P2_1/c$ (No. 14), a = 10.2116(3) Å, b = 17.9533(5) Å, c = 10.9656(4) Å, = 110.432(4)°, = = 90°, V = 1883.88(11) $Å^3$, T = 105(7) K, Z = 4, Z' = 1, (MoK) = 2.337 mm^{-1}, 23622 reflections measured, 5515 unique (R_{int} = 0.0377) which were used in all calculations. The final wR_2 was 0.1239 (all data) and R_1 was 0.0487 (I > 2σ(I)).

Compound	**WL-C22H16BrClO2_iso1**
Formula	$C_{22}H_{16}BrClO_2$
$D_{calc.}$/ g cm^{-3}	1.508
/mm^{-1}	2.337
Formula Weight	427.71
Colour	colourless
Shape	block
Size/mm^3	0.38×0.29×0.21
T/K	105(7)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	10.2116(3)
b/Å	17.9533(5)
c/Å	10.9656(4)
/°	90
/°	110.432(4)
/°	90
V/$Å^3$	1883.88(11)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK
$_{min}$/°	2.128
$_{max}$/°	30.033
Measured Refl.	23622
Independent Refl.	5515
Reflections with I > 2σ(I)	4624
R_{int}	0.0377
Parameters	243
Restraints	74
Largest Peak	1.867
Deepest Hole	-1.241
GooF	1.034
wR_2 (all data)	0.1239
wR_2	0.1189
R_1 (all data)	0.0596
R_1	0.0487

Structure Quality Indicators

Reflections:	d min (Mo) 0.71	I/σ 32.9	Rint 3.77%	complete 100% (IUCr) 100%
Refinement:	Shift -0.004	Max Peak 1.9	Min Peak -1.2	GooF 1.034

A colourless block-shaped crystal with dimensions 0.38×0.29×0.21 mm^3 was mounted on a loop with paratone oil. Data were collected using an XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 105(7) K.

Data were measured using scans of 0.5° per frame for 13.8 s using MoK radiation. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.20a, 2015). The maximum resolution that was achieved was = 30.033°.

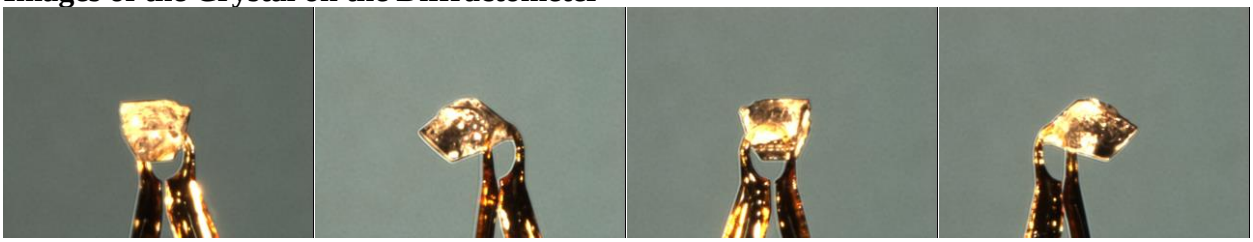
The diffraction pattern was indexed using **CrysAlisPro** (Rigaku, V1.171.39.20a, 2015) and the unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.39.46, 2018) on 13197 reflections, 56% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.39.46, 2018). The final completeness is 100.00 % out to 30.033° in . A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed using CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018). An empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK was also applied. The absorption coefficient of this material is 2.337 mm^{-1} at this wavelength (= 0.71073Å) and the minimum and maximum transmissions are 0.424 and 1.00.

The structure was solved and the space group $P2_1/c$ (# 14) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

Images of the Crystal on the Diffractometer



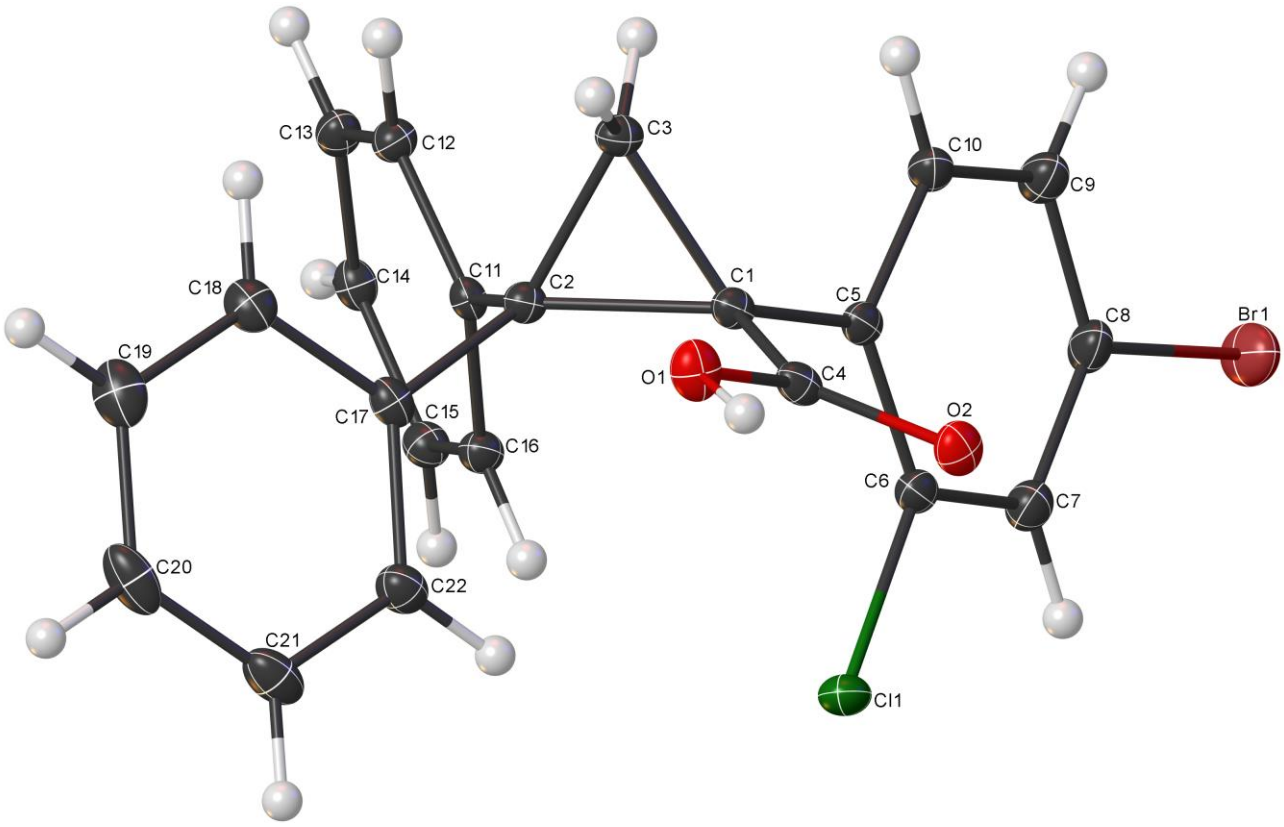
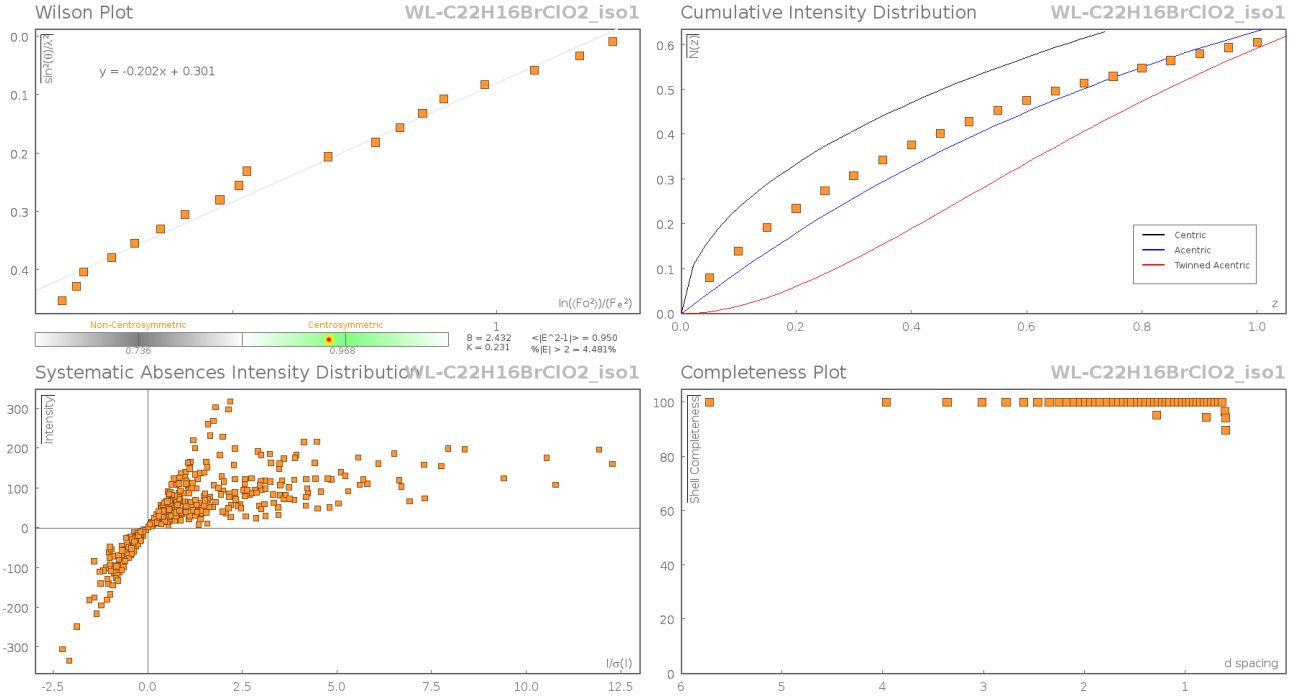
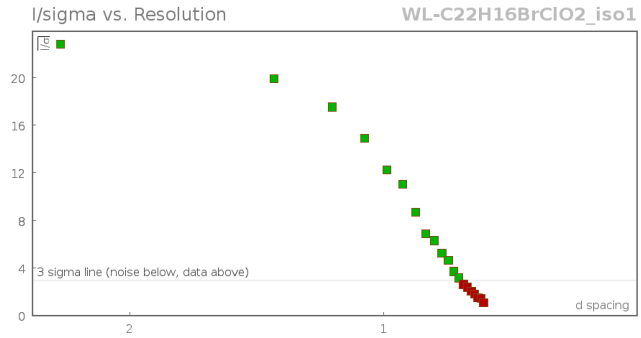


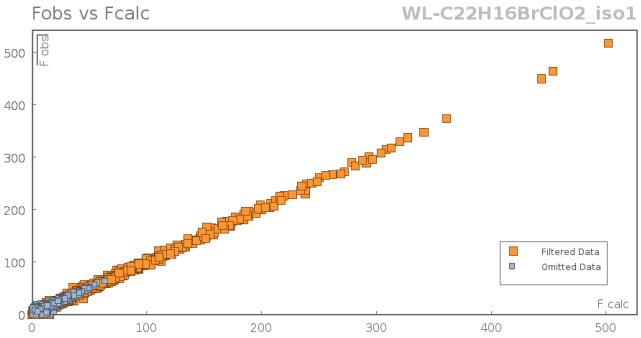
Figure S11.2.1:

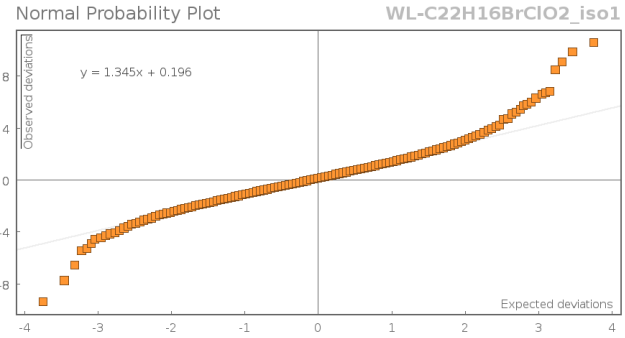
Data Plots: Diffraction Data





Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	24028	Unique reflections	5515
Completeness	1.0	Mean I/	20.74
hkl_{max} collected	(17, 29, 18)	hkl_{min} collected	(-17, -29, -18)
hkl_{max} used	(13, 25, 15)	hkl_{min} used	(-14, 0, 0)
Lim d_{max} collected	20.0	Lim d_{min} collected	0.71
d_{max} used	10.28	d_{min} used	0.71
Friedel pairs	8381	Friedel pairs merged	1
Inconsistent equivalents	25	R_{int}	0.0377
R_{sigma}	0.0304	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(17223, 6154, 1145, 168, 59, 5)	Maximum multiplicity	12
Removed systematic absences	406	Filtered off (Shel/OMIT)	9935

Table S11.2.1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **WL-C22H16BrClO2_iso1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Br1B	8641.7(9)	5402.9(8)	2731(3)	39.4(3)
Cl1	3600.0(6)	5124.8(3)	3483.6(6)	24.71(13)
O1	386.2(18)	4092.1(10)	454.4(18)	27.5(4)
O2	1765.9(18)	5080.6(10)	609.8(17)	25.0(3)
C11	4109(2)	2890.0(12)	3029(2)	16.2(4)
C2	2751(2)	3187.1(12)	2069(2)	17.2(4)
C14	6593(2)	2299.4(13)	4780(2)	20.4(4)
C5	4219(2)	4296.6(12)	1652(2)	18.7(3)
C12	4675(2)	2235.4(12)	2743(2)	19.7(4)
C17	1513(2)	3039.1(13)	2479(2)	19.8(4)
C4	1578(2)	4396.9(13)	778(2)	19.6(3)
C16	4788(2)	3236.1(12)	4224(2)	20.0(4)
C1	2839(2)	3910.4(12)	1317(2)	17.8(4)
C15	6027(2)	2945.5(13)	5091(2)	21.1(4)

Atom	x	y	z	U_{eq}
C13	5910(2)	1941.4(13)	3612(2)	21.7(4)
C6	4666(2)	4836.0(12)	2633(2)	20.8(3)
C10	5138(2)	4119.6(13)	1014(2)	22.2(4)
C3	2618(2)	3140.5(12)	671(2)	20.2(4)
C18	773(2)	2382.5(15)	2086(2)	25.0(5)
C22	1125(3)	3525.6(14)	3282(2)	25.5(5)
C9	6449(3)	4437.4(14)	1339(3)	27.1(4)
C7	5981(3)	5166.7(14)	2992(2)	25.3(4)
C19	-343(3)	2209.4(17)	2490(3)	31.8(6)
C21	-2(3)	3358.4(17)	3667(3)	31.3(5)
C8	6866(3)	4954.5(13)	2338(3)	26.8(4)
C20	-731(3)	2701.1(18)	3277(3)	33.1(6)
Br1A	8705.0(19)	5337(2)	3068(5)	39.4(3)

Table S11.2.2: Anisotropic Displacement Parameters ($\times 10^4$) **WL-C22H16BrClO2_iso1**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1B	33.94(18)	38.5(3)	51.8(8)	-10.0(4)	22.8(3)	-16.79(16)
Cl1	29.4(3)	23.1(3)	24.2(3)	-3.9(2)	12.7(2)	2.2(2)
O1	20.7(6)	29.3(8)	30.3(9)	8.2(7)	6.2(5)	4.4(5)
O2	24.1(8)	23.7(6)	26.4(8)	6.5(5)	8.0(7)	5.9(4)
C11	15.9(9)	17.8(9)	15.7(9)	2.9(7)	6.3(7)	-0.3(7)
C2	17.0(9)	17.9(9)	16.2(9)	0.7(7)	5.1(7)	2.0(7)
C14	15.8(9)	24.1(10)	21.0(10)	4.7(8)	6.0(8)	0.2(8)
C5	21.8(7)	16.1(7)	19.2(7)	3.7(6)	8.4(6)	4.7(5)
C12	20.7(10)	18.5(10)	19.2(10)	-0.5(8)	6.2(8)	0.3(7)
C17	15.4(9)	25.5(11)	17.6(9)	5.0(8)	4.6(8)	2.0(8)
C4	20.2(6)	23.1(6)	16.1(8)	4.2(5)	7.2(5)	6.4(4)
C16	21.7(10)	19.9(10)	19.4(10)	0.2(8)	8.4(8)	1.6(8)
C1	18.6(7)	18.7(8)	16.4(9)	1.8(7)	6.2(6)	3.6(6)
C15	20.6(10)	23.8(10)	18.1(10)	-0.2(8)	5.7(8)	-1.3(8)
C13	22.2(10)	19.3(10)	25.3(11)	1.7(8)	10.5(9)	2.6(8)
C6	25.5(6)	17.2(7)	21.6(7)	1.7(6)	10.4(6)	3.0(5)
C10	24.9(7)	19.2(8)	26.1(8)	-0.6(6)	13.3(6)	1.0(5)
C3	21.8(10)	20.8(10)	17.5(9)	-1.1(8)	6.3(8)	2.0(8)
C18	19.8(10)	31.7(12)	20.6(10)	0.1(9)	3.4(8)	-2.5(9)
C22	25.1(11)	27.8(12)	25.8(11)	1.5(9)	11.7(9)	3.3(9)
C9	25.9(7)	22.6(8)	36.6(9)	-2.4(7)	15.9(7)	-0.8(6)
C7	27.2(7)	20.8(8)	28.8(9)	0.0(7)	10.9(6)	-0.3(6)
C19	19.6(11)	41.6(15)	28.9(12)	5.3(11)	1.8(9)	-6.8(10)
C21	26.4(12)	43.3(15)	28.5(12)	6.9(11)	14.9(10)	9.9(10)
C8	28.5(7)	19.5(8)	36.1(9)	-0.8(7)	15.9(6)	-4.0(6)
C20	16.0(10)	55.0(17)	29.5(13)	14.4(12)	9.3(9)	2.9(10)
Br1A	33.94(18)	38.5(3)	51.8(8)	-10.0(4)	22.8(3)	-16.79(16)

Table S11.2.3: Bond Lengths in Å for **WL-C22H16BrClO2_iso1**.

Atom	Atom	Length/Å
Br1B	C8	1.891(3)
Cl1	C6	1.741(2)
O1	C4	1.267(3)
O2	C4	1.266(3)
C11	C2	1.515(3)
C11	C12	1.393(3)
C11	C16	1.396(3)
C2	C17	1.506(3)
C2	C1	1.558(3)
C2	C3	1.493(3)
C14	C15	1.390(3)
C14	C13	1.385(3)
C5	C1	1.496(3)
C5	C6	1.401(3)
C5	C10	1.389(3)
C12	C13	1.392(3)

Atom	Atom	Length/Å
C17	C18	1.385(3)
C17	C22	1.392(3)
C4	C1	1.496(3)
C16	C15	1.392(3)
C1	C3	1.533(3)
C6	C7	1.393(3)
C10	C9	1.382(3)

Atom	Atom	Length/Å
C18	C19	1.394(4)
C22	C21	1.391(3)
C9	C8	1.385(4)
C7	C8	1.389(3)
C19	C20	1.385(4)
C21	C20	1.381(4)
C8	Br1A	1.895(3)

Table S11.2.4: Bond Angles in ° for **WL-C22H16BrClO2_iso1**.

Atom	Atom	Atom	Angle/°
C12	C11	C2	119.46(19)
C12	C11	C16	118.5(2)
C16	C11	C2	121.96(19)
C11	C2	C1	116.96(18)
C17	C2	C11	113.01(17)
C17	C2	C1	120.98(18)
C3	C2	C11	115.26(18)
C3	C2	C17	120.74(18)
C3	C2	C1	60.28(14)
C13	C14	C15	119.7(2)
C6	C5	C1	122.4(2)
C10	C5	C1	121.0(2)
C10	C5	C6	116.6(2)
C13	C12	C11	120.9(2)
C18	C17	C2	118.7(2)
C18	C17	C22	119.1(2)
C22	C17	C2	122.1(2)
O1	C4	C1	118.0(2)
O2	C4	O1	123.9(2)
O2	C4	C1	118.1(2)
C15	C16	C11	120.6(2)
C5	C1	C2	118.66(17)
C5	C1	C3	120.37(18)

Atom	Atom	Atom	Angle/°
C4	C1	C2	119.66(18)
C4	C1	C5	115.67(18)
C4	C1	C3	112.08(18)
C3	C1	C2	57.77(14)
C14	C15	C16	120.2(2)
C14	C13	C12	120.1(2)
C5	C6	Cl1	121.34(18)
C7	C6	Cl1	116.29(18)
C7	C6	C5	122.4(2)
C9	C10	C5	122.7(2)
C2	C3	C1	61.95(14)
C17	C18	C19	120.6(2)
C21	C22	C17	120.3(2)
C10	C9	C8	118.9(2)
C8	C7	C6	118.3(2)
C20	C19	C18	119.9(3)
C20	C21	C22	120.3(3)
C9	C8	Br1B	118.1(2)
C9	C8	C7	121.1(2)
C9	C8	Br1A	124.2(2)
C7	C8	Br1B	120.7(2)
C7	C8	Br1A	114.2(2)
C21	C20	C19	119.8(2)

Table S11.2.5: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **WL-C22H16BrClO2_iso1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H14	7427.34	2108.54	5354.86	24
H12	4222.19	1991.4	1960.08	24
H16	4408.95	3664.82	4442.57	24
H15	6477.16	3183.96	5879.17	25
H13	6276.21	1504.04	3407.8	26
H10	4861.05	3773.17	341.58	27
H3A	1701.42	3030.5	40.56	24
H3B	3391.19	2924.93	472.64	24
H18	1023.38	2054.26	1548.88	30
H22	1622.71	3964.68	3561.67	31
H9	7040.9	4306.22	893.42	32
H7	6259.14	5520.33	3653.06	30
H19	-826.08	1764.21	2231.94	38
H21	-266.43	3690.58	4189.46	38

Atom	x	y	z	U_{eq}
H20	-1480.56	2588.94	3541.18	40
H1	-440(40)	4410(30)	40(70)	160(30)

Table S11.2.6: Hydrogen Bond information for **WL-C22H16BrClO2_iso1**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	O2[1]	0.995(2)	1.576(3)	2.570(2)	179(7)

[1]-x,1-y,-z

Table S11.2.7: Atomic Occupancies for all atoms that are not fully occupied in **WL-C22H16BrClO2_iso1**.

Atom	Occupancy
Br1B	0.751(9)
Br1A	0.249(9)

Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2015).

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2018).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

```
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# PLATON/CHECK-( 70414) versus check.def version of 310314   for Entry: wl-c22h1
# Data: WL-C22H16BrClO2_iso1.cif - Type: CIF     Bond Precision   C-C = 0.0033 A
# Refl: WL-C22H16BrClO2_iso1.fcf - Type: LIST4                    Temp = 105 K
#                                      X-Ray        Nref/Npar =  22.7
# Cell  10.2116(3)  17.9533(5)  10.9656(4)          90   110.432(4)          90
# Wavelength 0.71073    Volume Reported   1883.88(11)   Calculated   1883.87(11)
# SpaceGroup from Symmetry P 21/c     Hall: -P 2ybc              monoclinic
#               Reported P 1 21/c 1       -P 2ybc              monoclinic
# MoietyFormula C22 H16 Br Cl O2
#      Reported C22 H16 Br Cl O2
#    SumFormula C22 H16 Br Cl O2
#      Reported C22 H16 Br Cl O2
# Mr        =    427.70[Calc],    427.71[Rep]
# Dx,gcm-3  =     1.508[Calc],     1.508[Rep]
# Z         =         4[Calc],         4[Rep]
# Mu (mm-1) =     2.337[Calc],     2.337[Rep]
# F000      =     864.0[Calc],     864.0[Rep]  or F000' =    863.77[Calc]
# Reported   T Limits: Tmin=0.424             Tmax=1.000  AbsCorr=GAUSSIAN
# Calculated T Limits: Tmin=0.453 Tmin'=0.410  Tmax=0.611
# Reported   Hmax= 14, Kmax= 25, Lmax= 15, Nref=   5515        , Th(max)= 30.033
# Obs in FCF Hmax= 14, Kmax= 25, Lmax= 15, Nref=   5515[  5515], Th(max)= 30.033
# Calculated Hmax= 14, Kmax= 25, Lmax= 15, Nref=   5517        , Ratio  =  1.000
# Reported   Rho(min) = -1.24, Rho(max) =  1.87 e/Ang**3 (From CIF)
# Calculated Rho(min) = -1.20, Rho(max) =  1.73 e/Ang**3 (From CIF+FCF data)
# w=1/[sigma**2(Fo**2)+(0.0522P)**2+  3.1505P], P=(Fo**2+2*Fc**2)/3
# R= 0.0487(  4624), wR2= 0.1239(  5515), S = 1.034      (From CIF+FCF data)
# R= 0.0487(  4624), wR2= 0.1239(  5515), S = 1.034      (From FCF data only)
# R= 0.0487(  4624), wR2= 0.1239(  5515), S = 1.034, Npar=  243
#==============================================================================
For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
#==============================================================================

#==============================================================================
>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
#==============================================================================
Format: alert-number_ALERT_alert-type_alert-level text

222_ALERT_3_C Large Non-Solvent    H    Uiso(max)/Uiso(min) ..        6.7 Ratio
761_ALERT_1_C CIF Contains no X-H Bonds .....................      Please Check
762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles .........     Please Check
906_ALERT_3_C Large K value in the Analysis of Variance .....       2.535 Check
971_ALERT_2_C Check Calcd Residual Density  0.78A From    Br1B       1.73 eA-3
#==============================================================================
002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          5 Note
003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         13 Why ?
008_ALERT_5_G No _iucr_refine_reflections_details   in the CIF     Please Do !
301_ALERT_3_G Main Residue  Disorder ..... Percentage =          4 Note
760_ALERT_1_G CIF Contains no Torsion Angles .................          ? Info
793_ALERT_4_G The Model has Chirality at C1      .............          R Verify
795_ALERT_4_G C-Atom in CIF Coordinate List out of Sequence ..         C2 Note
802_ALERT_4_G CIF Input Record(s) with more than 80 Characters          ! Info
860_ALERT_3_G Number of Least-Squares Restraints .............         74 Note
#==============================================================================

ALERT_Level and ALERT_Type Summary
==================================
5 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight
9 ALERT_Level_G = General Info/Check that it is not Something Unexpected

3 ALERT_Type_1 CIF Construction/Syntax Error, Inconsistent or Missing Data.
3 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
4 ALERT_Type_3 Indicator that the Structure Quality may be Low.
```

3 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.
1 ALERT_Type_5 Informative Message, Check.
#==

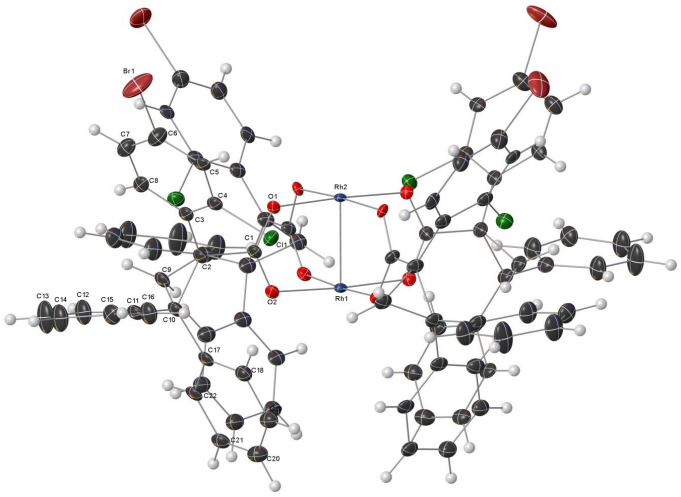
1 Missing Experimental Info Issue(s) (Out of 54 Tests) -   98 % Satisfied
0 Experimental Data Related Issue(s) (Out of 28 Tests) - 100 % Satisfied
7 Structural Model   Related Issue(s) (Out of 117 Tests) -   94 % Satisfied
6 Unresolved or to be Checked Issue(s) (Out of 223 Tests) -   97 % Satisfied

#==

12. X-Ray Crystallographic Data for Rh_2(*S*-2-Cl-4-BrTPCP)$_4$ and Rh_2(*S*-2-Cl-5-BrTPCP)$_4$

12.1. Rh_2(*S*-2-Cl-4-BrTPCP)$_4$

Crystal Data and Experimental



Experimental. Single bluish green needle-shaped crystals of **WL-N2-137-27** were recrystallised from a mixture of ethyl acetate and hexane by slow evaporation. A suitable crystal 0.59×0.07×0.03 mm^3 was selected and mounted on a mylar loop with paratone oil on an Bruker D8 diffractometer with APEX2 detector.The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{88}H_{64}Br_4Cl_4O_{10}Rh_2$, M_r = 1948.61, tetragonal, $P42_12$ (No. 90), a = 20.4695(6) Å, b = 20.4695(6) Å, c = 19.2209(8) Å, = = = 90°, V = 8053.5(6) Å^3, T = 100(2) K, Z = 4, Z' = 0.5, (MoK) = 2.586 mm^{-1}, 40044 reflections measured, 6882 unique (R_{int} = 0.1306) which were used in all calculations. The final wR_2 was 0.1273 (all data) and R_1 was 0.0611 (I > 2σ(I)).

Compound	**WL-N2-137-27**
Formula	$C_{88}H_{64}Br_4Cl_4O_{10}Rh_2$
$D_{calc.}$/ g cm^{-3}	1.607
/mm^{-1}	2.586
Formula Weight	1948.61
Colour	bluish green
Shape	needle
Size/mm^3	0.59×0.07×0.03
T/K	100(2)
Crystal System	tetragonal
Flack Parameter	0.015(11)
Hooft Parameter	0.021(8)
Space Group	$P42_12$
a/Å	20.4695(6)
b/Å	20.4695(6)
c/Å	19.2209(8)
/°	90
/°	90
/°	90
V/Å^3	8053.5(6)
Z	4
Z'	0.5
Wavelength/Å	0.710730
Radiation type	MoK
$_{min}$/°	1.761
$_{max}$/°	24.712
Measured Refl.	40044
Independent Refl.	6882
Reflections with I > 2σ(I)	4969
R_{int}	0.1306
Parameters	481
Restraints	478
Largest Peak	1.526
Deepest Hole	-0.531
GooF	1.027
wR_2 (all data)	0.1273
wR_2	0.1166
R_1 (all data)	0.0938
R_1	0.0611

Structure Quality Indicators

Reflections: d min (Mo) 0.85 | I/σ 11.1 | Rint 13.06% | complete 100% (IUCr) 100%

Refinement: Shift 0.001 | Max Peak 1.5 | Min Peak -0.5 | GooF 1.027 | Flack .015(11)

A bluish green needle-shaped crystal with dimensions 0.59×0.07×0.03 mm^3 was mounted on a mylar loop with paratone oil. Data were collected using an Bruker D8 diffractometer with APEX2 detector equipped with an Oxford Cryosystems low-temperature device operating at T = 100(2) K.

Data were measured using scans of 0.5° per frame for 120.0 s using MoK radiation. The total number of runs and images was based on the strategy calculation from the program APEX2 (Bruker, V2 v2014.1-1). The maximum resolution that was achieved was = 24.712°.

The diffraction pattern was indexed using APEX2 (Bruker, V2 v2014.1-1) and the unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.39.43c, 2018) on 14776 reflections, 37% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.39.43c, 2018). The final completeness is 99.90 % out to 24.712° in . A multi-scan absorption correction was performed using CrysAlisPro 1.171.39.43c (Rigaku Oxford Diffraction, 2018). A spherical absorption correction using equivalent radius of 0.11 mm and absorption coefficient 2.586 mm^{-1} was used. An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient of this material is 2.586 mm^{-1} at this wavelength (= 0.71073Å) and the minimum and maximum transmissions are 0.65 and 0.66.

The structure was solved and the space group $P42_12$ (# 90) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Images of the Crystal on the Diffractometer

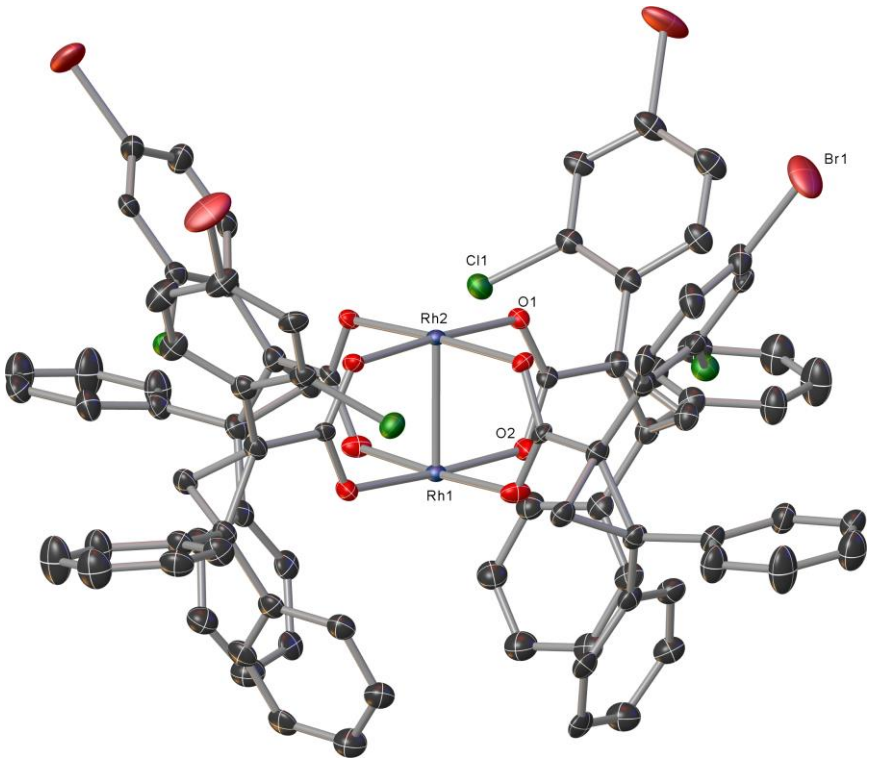


Figure S12.1.2:

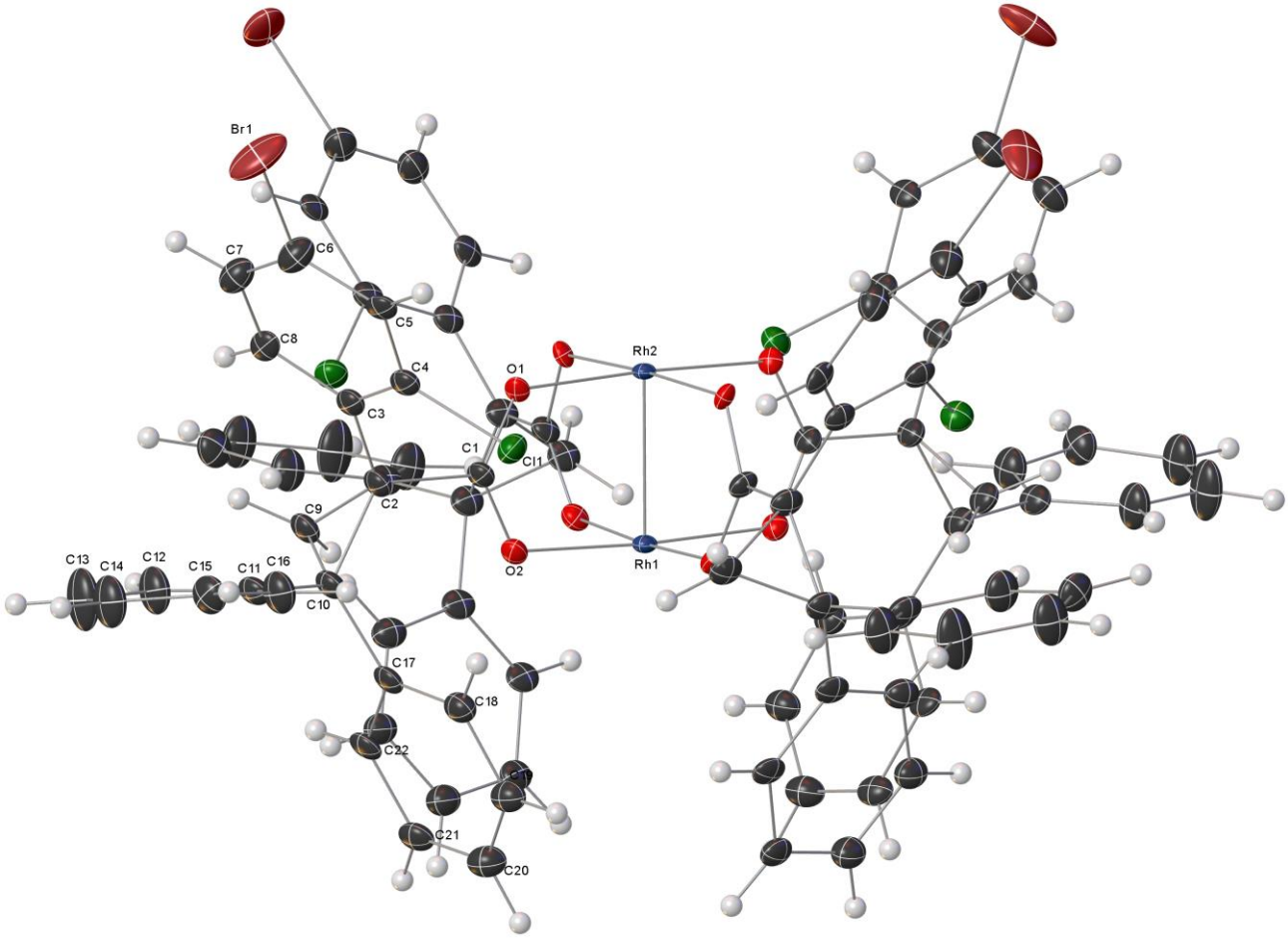
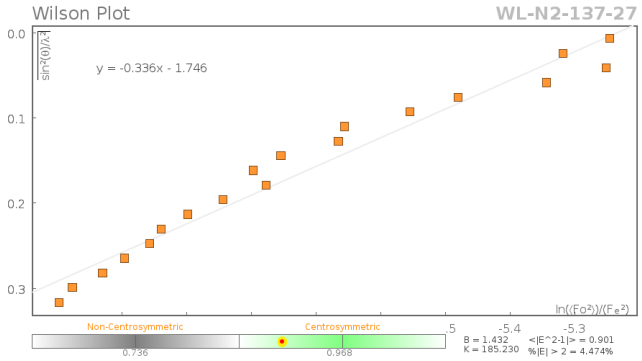
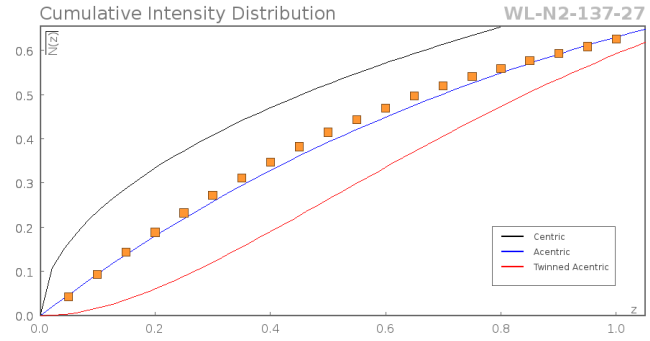
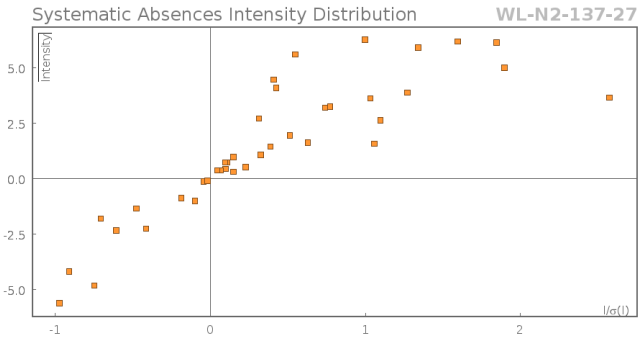


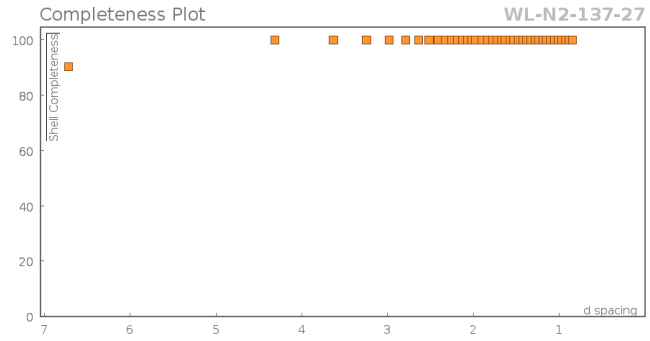
Figure S12.1.2:

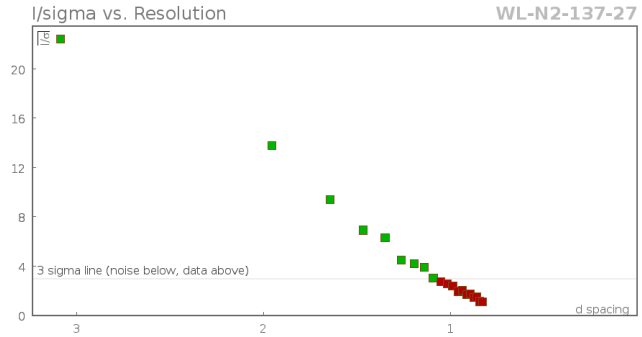
Data Plots: Diffraction Data



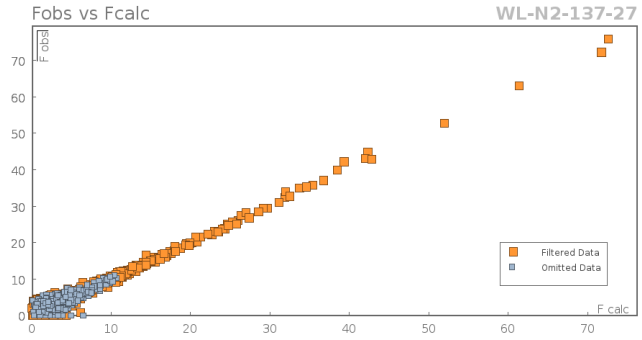


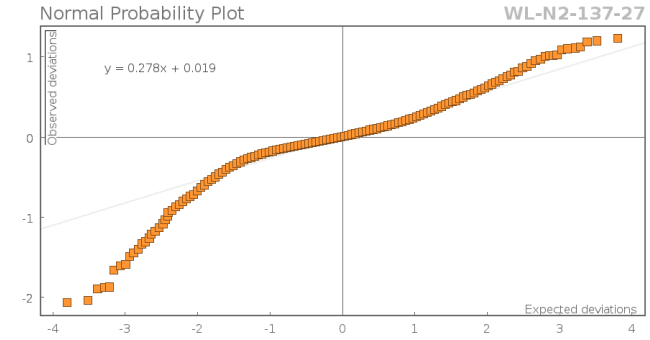






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	40088	Unique reflections	6882
Completeness	1.0	Mean I/	11.75
hkl_{max} collected	(24, 23, 23)	hkl_{min} collected	(-24, -22, -23)
hkl_{max} used	(17, 24, 22)	hkl_{min} used	(-16, 0, 0)
Lim d_{max} collected	20.0	Lim d_{min} collected	0.85
d_{max} used	11.56	d_{min} used	0.85

Friedel pairs	14791	Friedel pairs merged	0
Inconsistent equivalents	1	R_{int}	0.1306
R_{sigma}	0.0899	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	5
Multiplicity	(37582, 2497, 59)	Maximum multiplicity	15
Removed systematic absences	39	Filtered off (Shel/OMIT)	2665

Table S12.1.8: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **WL-N2-137-27**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Rh1	5000	10000	859.6(8)	10.3(4)
Rh2	5000	10000	2096.3(8)	9.3(4)
Rh3	10000	5000	2974.9(9)	10.7(4)
Rh4	10000	5000	4205.3(9)	11.6(4)
Br1_1	6535.6(7)	6761.6(8)	4102.1(8)	46.4(4)
Cl1_1	6672.9(13)	8491.4(13)	1925.3(13)	19.0(6)
O1_1	5229(3)	9030(3)	2067(3)	11.7(14)
O2_1	5151(3)	9031(3)	894(3)	14.4(15)
C1_1	5262(5)	8760(4)	1480(4)	15.0(13)
C2_1	5309(4)	8019(4)	1476(4)	17.4(9)
C3_1	5585(4)	7735(4)	2119(4)	16.5(11)
C4_1	6207(4)	7903(5)	2357(4)	16.9(19)
C5_1	6492(5)	7640(5)	2961(5)	16.4(18)
C6_1	6142(5)	7163(5)	3307(5)	25(2)
C7_1	5556(4)	6949(5)	3073(5)	23(2)
C8_1	5277(5)	7243(4)	2502(5)	17.6(19)
C9_1	4766(4)	7697(4)	1080(4)	18.8(10)
C10_1	5428(4)	7645(4)	792(4)	18.6(9)
C11_1	5777(4)	6986(4)	850(4)	19.6(12)
C12_1	5416(5)	6413(4)	829(7)	29(3)
C13_1	5717(5)	5805(5)	854(8)	41(4)
C14_1	6377(5)	5763(5)	955(7)	34(3)
C15_1	6748(5)	6335(4)	1030(6)	25(2)
C16_1	6439(4)	6931(4)	956(6)	27(3)
C17_1	5610(5)	7985(4)	120(4)	18.4(12)
C18_1	6201(5)	8281(5)	5(5)	21(2)
C19_1	6363(5)	8561(5)	-623(4)	22(2)
C20_1	5922(5)	8561(5)	-1163(5)	25(2)
C21_1	5315(4)	8279(5)	-1072(5)	21(2)
C22_1	5161(4)	7978(5)	-431(4)	18.9(19)
Br1_2	6603.6(8)	3735.8(9)	951.5(8)	67.3(6)
Cl1_2	7673.9(16)	5274.2(14)	3006.1(17)	34.8(8)
O1_2	9092(3)	4554(3)	3026(3)	13.1(14)
O2_2	9223(3)	4385(3)	4179(3)	11.2(14)
C1_2	8920(4)	4318(5)	3603(4)	17.1(15)
C2_2	8251(4)	4003(4)	3635(4)	19.3(9)
C3_2	7910(4)	3962(4)	2956(4)	20.8(11)
C4_2	7582(5)	4490(4)	2663(5)	22(2)
C5_2	7188(6)	4442(5)	2065(6)	37(3)
C6_2	7138(6)	3832(5)	1761(5)	32(3)
C7_2	7468(5)	3307(5)	2008(5)	30(2)
C8_2	7841(5)	3371(5)	2597(5)	28(2)
C9_2	8192(4)	3436(4)	4129(4)	19.4(10)
C10_2	7837(4)	4038(4)	4302(4)	19.1(9)
C11_2	7099(4)	4090(4)	4193(5)	18.9(12)
C12_2	6730(4)	3549(5)	4013(7)	30(3)
C13_2	6063(5)	3599(5)	3891(9)	50(4)

Atom	x	y	z	U_{eq}
C14_2	5751(5)	4185(5)	3974(8)	42(3)
C15_2	6108(5)	4737(5)	4180(8)	42(4)
C16_2	6768(4)	4667(5)	4306(6)	26(2)
C17_2	8036(4)	4406(5)	4953(4)	19.0(12)
C18_2	8202(5)	5054(5)	4972(5)	21(2)
C19_2	8369(6)	5366(5)	5581(5)	24(2)
C20_2	8387(6)	5028(5)	6198(4)	28(2)
C21_2	8224(5)	4373(5)	6209(4)	22(2)
C22_2	8054(5)	4056(5)	5582(4)	17(2)

Table S12.1.9: Anisotropic Displacement Parameters ($\times 10^4$) **WL-N2-137-27**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	12.2(6)	12.2(6)	6.4(9)	0	0	0
Rh2	11.3(6)	11.3(6)	5.1(8)	0	0	0
Rh3	11.2(6)	11.2(6)	9.8(9)	0	0	0
Rh4	12.8(6)	12.8(6)	9.1(9)	0	0	0
Br1_1	38.0(9)	61.3(10)	39.8(9)	35.4(8)	0.7(7)	11.0(8)
Cl1_1	20.7(14)	18.5(14)	17.7(13)	3.3(12)	1.2(12)	-2.5(12)
O1_1	10(4)	11(2)	13.7(18)	-2.4(16)	3(2)	2(2)
O2_1	16(4)	13(2)	14.1(18)	-2.5(15)	3(2)	1(2)
C1_1	19(4)	12.4(16)	13.9(18)	-3.0(12)	3.4(19)	3.0(14)
C2_1	24(2)	12.2(16)	15.8(15)	-3.8(12)	1.5(15)	2.8(13)
C3_1	22.1(19)	12(2)	15.5(16)	-3.4(16)	3.4(16)	4.3(16)
C4_1	22(2)	14(3)	15(3)	-3(3)	3.6(18)	4(2)
C5_1	21(2)	15(3)	14(2)	-3(3)	6(2)	7(2)
C6_1	23(2)	25(4)	26(3)	8(3)	3(2)	3(3)
C7_1	22(3)	22(4)	26(3)	6(3)	4(2)	4(3)
C8_1	20(2)	12(3)	20(3)	-1(3)	6(2)	7(2)
C9_1	24.8(18)	14(2)	18(2)	-5.9(18)	0.8(14)	3.2(14)
C10_1	25.1(19)	14.2(16)	16.5(15)	-5.2(13)	0.7(15)	4.0(14)
C11_1	27(2)	14.9(16)	17(3)	-4.2(16)	3(2)	5.3(15)
C12_1	28(2)	14.5(17)	45(8)	-1(2)	-3(3)	5.2(16)
C13_1	31(3)	15.1(17)	78(11)	-2(3)	-7(4)	6.4(18)
C14_1	30(3)	17(2)	54(9)	-1(3)	-3(4)	6.8(19)
C15_1	28(3)	17(2)	31(7)	-2(3)	3(3)	6.7(18)
C16_1	27(2)	16(2)	36(7)	-3(3)	0(2)	5.7(16)
C17_1	27(2)	13(3)	15.8(16)	-6.2(18)	1.0(15)	4.5(18)
C18_1	27(2)	18(5)	18(2)	-2(3)	-0.2(19)	3(3)
C19_1	26(3)	20(5)	19(2)	0(3)	0.8(19)	6(3)
C20_1	27(3)	27(5)	19(3)	1(3)	0(2)	5(3)
C21_1	26(3)	19(5)	16.8(19)	-4(3)	2(2)	8(3)
C22_1	26(3)	15(5)	15.5(18)	-7(2)	1.2(19)	6(3)
Br1_2	66.0(12)	103.3(15)	32.5(9)	17.7(9)	-30.5(9)	-54.7(11)
Cl1_2	43(2)	27.2(17)	33.9(18)	9.6(14)	-9.4(17)	-3.7(13)
O1_2	13(3)	13(3)	13.1(19)	-2(2)	1.8(17)	-2(2)
O2_2	10(3)	11(4)	12.9(18)	-2(2)	3.9(17)	3(2)
C1_2	15.7(18)	22(4)	14.1(19)	1.0(19)	1.3(14)	-5(2)
C2_2	15.9(16)	26(2)	16.3(14)	3.7(14)	0.6(13)	-6.6(14)
C3_2	16(2)	30(2)	16.2(15)	5.1(15)	0.4(17)	-9.5(15)
C4_2	14(4)	32(2)	21(3)	8.4(17)	-1(3)	-10.3(17)
C5_2	40(5)	36(3)	34(3)	7(2)	-20(4)	-11(2)
C6_2	35(5)	36(3)	25(3)	10(2)	-7(4)	-17(2)
C7_2	37(5)	35(3)	17(3)	6(2)	-5(3)	-16(2)
C8_2	36(5)	32(2)	17(3)	3.3(19)	-4(3)	-11(2)
C9_2	16(2)	25.3(19)	16.5(19)	3.7(15)	1.1(17)	-6.3(15)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10_2	15.3(17)	26(2)	16.3(15)	4.2(15)	0.5(13)	-5.9(14)
C11_2	15.3(17)	27(2)	15(3)	8(2)	0.1(15)	-6.7(14)
C12_2	16(2)	28(2)	46(8)	2(3)	-5(3)	-6.0(17)
C13_2	18(2)	33(3)	98(11)	-9(5)	-15(3)	-4.3(18)
C14_2	16(2)	32(3)	79(10)	-4(5)	-12(3)	-5.1(19)
C15_2	16(2)	32(3)	79(10)	-5(4)	-11(3)	-4.8(19)
C16_2	14(2)	28(2)	36(7)	3(3)	-3(3)	-6.2(17)
C17_2	14(3)	26(2)	16.6(15)	3.5(15)	0.0(16)	-4(2)
C18_2	18(6)	26(2)	18(2)	2.8(17)	0(2)	-5(2)
C19_2	26(7)	28(3)	19(2)	2.4(18)	-2(3)	-6(3)
C20_2	35(6)	30(3)	19(2)	3(2)	-2(3)	-6(3)
C21_2	19(6)	29(3)	16.9(16)	3(2)	0(2)	-2(3)
C22_2	9(5)	27(2)	16.2(16)	3.7(18)	2(2)	-1(3)

Table S12.1.10: Bond Lengths in Å for **WL-N2-137-27**.

Atom	Atom	Length/Å
Rh1	Rh2	2.377(2)
Rh1	O2_1[1]	2.008(6)
Rh1	O2_1	2.008(6)
Rh1	O2_1[2]	2.008(6)
Rh1	O2_1[3]	2.008(6)
Rh2	O1_1	2.041(6)
Rh2	O1_1[3]	2.041(6)
Rh2	O1_1[2]	2.041(6)
Rh2	O1_1[1]	2.041(6)
Rh3	Rh4	2.365(2)
Rh3	O1_2[4]	2.072(6)
Rh3	O1_2[5]	2.072(6)
Rh3	O1_2[6]	2.072(6)
Rh3	O1_2	2.072(6)
Rh4	O2_2[5]	2.029(6)
Rh4	O2_2	2.029(6)
Rh4	O2_2[6]	2.029(6)
Rh4	O2_2[4]	2.029(6)
Br1_1	C6_1	1.912(8)
Cl1_1	C4_1	1.746(8)
O1_1	C1_1	1.258(8)
O2_1	C1_1	1.276(8)
C1_1	C2_1	1.520(10)
C2_1	C3_1	1.479(11)
C2_1	C9_1	1.501(10)
C2_1	C10_1	1.540(10)
C3_1	C4_1	1.395(11)
C3_1	C8_1	1.399(11)
C4_1	C5_1	1.407(11)
C5_1	C6_1	1.382(12)
C6_1	C7_1	1.355(12)
C7_1	C8_1	1.374(11)
C9_1	C10_1	1.468(11)
C10_1	C11_1	1.531(10)
C10_1	C17_1	1.513(11)
C11_1	C12_1	1.387(11)
C11_1	C16_1	1.374(11)
C12_1	C13_1	1.389(11)
C13_1	C14_1	1.368(12)
C14_1	C15_1	1.403(11)
C15_1	C16_1	1.382(11)
C17_1	C18_1	1.372(12)
C17_1	C22_1	1.403(10)
C18_1	C19_1	1.377(11)
C19_1	C20_1	1.375(11)
C20_1	C21_1	1.382(11)
C21_1	C22_1	1.413(11)
Br1_2	C6_2	1.912(8)
Cl1_2	C4_2	1.745(8)
O1_2	C1_2	1.260(8)
O2_2	C1_2	1.276(8)
C1_2	C2_2	1.515(10)
C2_2	C3_2	1.483(11)
C2_2	C9_2	1.504(10)
C2_2	C10_2	1.538(10)
C3_2	C4_2	1.392(11)
C3_2	C8_2	1.400(11)
C4_2	C5_2	1.407(11)
C5_2	C6_2	1.382(12)
C6_2	C7_2	1.356(12)
C7_2	C8_2	1.373(11)
C9_2	C10_2	1.468(11)
C10_2	C11_2	1.529(10)
C10_2	C17_2	1.516(11)
C11_2	C12_2	1.385(11)
C11_2	C16_2	1.378(11)
C12_2	C13_2	1.389(11)
C13_2	C14_2	1.368(12)
C14_2	C15_2	1.403(11)
C15_2	C16_2	1.381(11)
C17_2	C18_2	1.370(12)
C17_2	C22_2	1.405(10)
C18_2	C19_2	1.377(11)
C19_2	C20_2	1.374(11)
C20_2	C21_2	1.382(11)
C21_2	C22_2	1.412(11)

[1]-1/2+y,3/2-x,+z; [2]3/2-y,1/2+x,+z; [3]1-x,2-y,+z; [4]3/2-y,-1/2+x,+z; [5]2-x,1-y,+z; [6]1/2+y,3/2-x,+z

Table S12.1.11: Bond Angles in ° for **WL-N2-137-27**.

Atom	Atom	Atom	Angle/°
O2_1	Rh1	Rh2	88.13(17)
O2_1[1]	Rh1	Rh2	88.13(17)
O2_1[2]	Rh1	Rh2	88.13(17)
O2_1[3]	Rh1	Rh2	88.13(17)
O2_1[2]	Rh1	O2_1[3]	89.939(12)
O2_1	Rh1	O2_1[3]	176.3(3)
O2_1	Rh1	O2_1[1]	89.940(12)
O2_1[1]	Rh1	O2_1[3]	89.939(12)
O2_1	Rh1	O2_1[2]	89.938(12)
O2_1[2]	Rh1	O2_1[1]	176.3(3)
O1_1[1]	Rh2	Rh1	88.43(17)
O1_1[3]	Rh2	Rh1	88.43(17)
O1_1	Rh2	Rh1	88.42(17)
O1_1[2]	Rh2	Rh1	88.43(17)
O1_1[2]	Rh2	O1_1[3]	89.957(10)
O1_1	Rh2	O1_1[3]	176.8(3)
O1_1[1]	Rh2	O1_1[2]	176.9(3)
O1_1	Rh2	O1_1[1]	89.955(10)
O1_1	Rh2	O1_1[2]	89.959(11)
O1_1[1]	Rh2	O1_1[3]	89.957(10)
O1_2[4]	Rh3	Rh4	87.30(17)
O1_2[5]	Rh3	Rh4	87.30(17)
O1_2	Rh3	Rh4	87.30(17)
O1_2[6]	Rh3	Rh4	87.30(17)
O1_2[5]	Rh3	O1_2[6]	89.873(17)
O1_2[5]	Rh3	O1_2[4]	89.873(16)
O1_2[4]	Rh3	O1_2[6]	174.6(3)
O1_2[5]	Rh3	O1_2	174.6(3)
O1_2[6]	Rh3	O1_2	89.872(17)
O1_2[4]	Rh3	O1_2	89.874(17)
O2_2[5]	Rh4	Rh3	88.56(16)
O2_2[6]	Rh4	Rh3	88.56(16)
O2_2[4]	Rh4	Rh3	88.56(16)
O2_2	Rh4	Rh3	88.56(16)
O2_2[4]	Rh4	O2_2	89.966(9)
O2_2[4]	Rh4	O2_2[6]	177.1(3)
O2_2[5]	Rh4	O2_2	177.1(3)
O2_2[6]	Rh4	O2_2	89.962(9)
O2_2[5]	Rh4	O2_2[4]	89.964(9)
O2_2[5]	Rh4	O2_2[6]	89.964(9)
C1_1	O1_1	Rh2	117.6(5)
C1_1	O2_1	Rh1	119.0(5)
O1_1	C1_1	O2_1	126.3(7)
O1_1	C1_1	C2_1	116.5(7)
O2_1	C1_1	C2_1	116.1(7)
C1_1	C2_1	C10_1	120.7(7)
C3_1	C2_1	C1_1	114.4(7)
C3_1	C2_1	C9_1	122.3(7)
C3_1	C2_1	C10_1	117.2(7)
C9_1	C2_1	C1_1	113.3(7)
C9_1	C2_1	C10_1	57.7(5)
C4_1	C3_1	C2_1	121.7(7)
C4_1	C3_1	C8_1	114.6(7)
C8_1	C3_1	C2_1	123.5(7)
C3_1	C4_1	Cl1_1	120.8(6)
C3_1	C4_1	C5_1	123.7(8)
C5_1	C4_1	Cl1_1	115.4(7)
C6_1	C5_1	C4_1	116.9(8)
C5_1	C6_1	Br1_1	118.0(7)
C7_1	C6_1	Br1_1	120.0(7)
C7_1	C6_1	C5_1	121.8(8)
C6_1	C7_1	C8_1	119.5(8)
C7_1	C8_1	C3_1	123.2(8)
C10_1	C9_1	C2_1	62.5(5)
C9_1	C10_1	C2_1	59.8(5)
C9_1	C10_1	C11_1	117.8(7)
C9_1	C10_1	C17_1	121.0(7)
C11_1	C10_1	C2_1	116.7(6)
C17_1	C10_1	C2_1	122.6(7)
C17_1	C10_1	C11_1	110.6(6)
C12_1	C11_1	C10_1	119.6(8)
C16_1	C11_1	C10_1	122.9(7)
C16_1	C11_1	C12_1	117.5(7)
C11_1	C12_1	C13_1	121.3(8)
C14_1	C13_1	C12_1	120.0(9)
C13_1	C14_1	C15_1	119.7(9)
C16_1	C15_1	C14_1	118.6(9)
C11_1	C16_1	C15_1	122.6(8)
C18_1	C17_1	C10_1	124.0(7)
C18_1	C17_1	C22_1	117.4(8)
C22_1	C17_1	C10_1	118.6(8)
C17_1	C18_1	C19_1	122.5(8)
C20_1	C19_1	C18_1	120.3(8)
C19_1	C20_1	C21_1	119.6(8)
C20_1	C21_1	C22_1	119.6(8)
C17_1	C22_1	C21_1	120.5(8)
C1_2	O1_2	Rh3	117.4(5)
C1_2	O2_2	Rh4	118.0(5)
O1_2	C1_2	O2_2	125.9(7)
O1_2	C1_2	C2_2	116.9(7)
O2_2	C1_2	C2_2	116.6(7)
C1_2	C2_2	C10_2	120.9(7)
C3_2	C2_2	C1_2	114.4(7)
C3_2	C2_2	C9_2	118.3(7)

Atom	Atom	Atom	Angle/°
C3_2	C2_2	C10_2	118.5(6)
C9_2	C2_2	C1_2	115.3(7)
C9_2	C2_2	C10_2	57.7(5)
C4_2	C3_2	C2_2	122.6(7)
C4_2	C3_2	C8_2	115.0(7)
C8_2	C3_2	C2_2	122.1(7)
C3_2	C4_2	Cl1_2	120.6(6)
C3_2	C4_2	C5_2	123.5(8)
C5_2	C4_2	Cl1_2	115.8(7)
C6_2	C5_2	C4_2	116.8(8)
C5_2	C6_2	Br1_2	118.7(7)
C7_2	C6_2	Br1_2	119.2(7)
C7_2	C6_2	C5_2	122.1(8)
C6_2	C7_2	C8_2	119.4(8)
C7_2	C8_2	C3_2	123.1(8)
C10_2	C9_2	C2_2	62.3(5)
C9_2	C10_2	C2_2	60.0(5)
C9_2	C10_2	C11_2	121.1(7)
C9_2	C10_2	C17_2	118.1(7)
C11_2	C10_2	C2_2	115.7(6)
C17_2	C10_2	C2_2	124.2(7)
C17_2	C10_2	C11_2	110.1(6)
C12_2	C11_2	C10_2	121.1(8)
C16_2	C11_2	C10_2	121.6(7)
C16_2	C11_2	C12_2	117.2(7)
C11_2	C12_2	C13_2	121.3(8)
C14_2	C13_2	C12_2	120.3(9)
C13_2	C14_2	C15_2	119.7(9)
C16_2	C15_2	C14_2	118.4(9)
C11_2	C16_2	C15_2	122.9(8)
C18_2	C17_2	C10_2	124.8(7)
C18_2	C17_2	C22_2	117.6(7)
C22_2	C17_2	C10_2	117.7(8)
C17_2	C18_2	C19_2	122.3(8)
C20_2	C19_2	C18_2	120.5(8)
C19_2	C20_2	C21_2	119.7(8)
C20_2	C21_2	C22_2	119.4(7)
C17_2	C22_2	C21_2	120.5(8)

[1]-1/2+y,3/2-x,+z; [2]3/2-y,1/2+x,+z; [3]1-x,2-y,+z; [4]1/2+y,3/2-x,+z; [5]2-x,1-y,+z; [6]3/2-y,-1/2+x,+z

Table S12.1.12: Torsion Angles in ° for **WL-N2-137-27**.

Atom	Atom	Atom	Atom	Angle/°
Rh1	O2_1	C1_1	O1_1	7.1(13)
Rh1	O2_1	C1_1	C2_1	174.5(5)
Rh2	O1_1	C1_1	O2_1	-1.8(13)
Rh2	O1_1	C1_1	C2_1	-169.1(6)
Rh3	O1_2	C1_2	O2_2	7.7(13)
Rh3	O1_2	C1_2	C2_2	179.1(6)
Rh4	O2_2	C1_2	O1_2	6.7(13)
Rh4	O2_2	C1_2	C2_2	-164.7(6)
Br1_1	C6_1	C7_1	C8_1	179.8(8)
Cl1_1	C4_1	C5_1	C6_1	-178.7(8)
O1_1	C1_1	C2_1	C3_1	-24.7(11)
O1_1	C1_1	C2_1	C9_1	121.7(9)
O1_1	C1_1	C2_1	C10_1	-173.2(8)
O2_1	C1_1	C2_1	C3_1	166.6(8)
O2_1	C1_1	C2_1	C9_1	-47.0(10)
O2_1	C1_1	C2_1	C10_1	18.1(11)
C1_1	C2_1	C3_1	C4_1	-58.3(11)
C1_1	C2_1	C3_1	C8_1	127.2(9)
C1_1	C2_1	C9_1	C10_1	112.7(8)
C1_1	C2_1	C10_1	C9_1	-99.7(8)
C1_1	C2_1	C10_1	C11_1	152.2(7)
C1_1	C2_1	C10_1	C17_1	10.0(12)
C2_1	C3_1	C4_1	Cl1_1	3.3(13)
C2_1	C3_1	C4_1	C5_1	-179.3(9)
C2_1	C3_1	C8_1	C7_1	175.4(9)
C2_1	C9_1	C10_1	C11_1	106.3(8)
C2_1	C9_1	C10_1	C17_1	-112.1(8)
C2_1	C10_1	C11_1	C12_1	100.4(11)
C2_1	C10_1	C11_1	C16_1	-76.6(12)
C2_1	C10_1	C17_1	C18_1	69.7(12)
C2_1	C10_1	C17_1	C22_1	-112.9(9)

Atom	Atom	Atom	Atom	Angle/°
C3_1	C2_1	C9_1	C10_1	-103.9(8)
C3_1	C2_1	C10_1	C9_1	112.7(8)
C3_1	C2_1	C10_1	C11_1	4.5(11)
C3_1	C2_1	C10_1	C17_1	-137.7(8)
C3_1	C4_1	C5_1	C6_1	3.7(16)
C4_1	C3_1	C8_1	C7_1	0.7(15)
C4_1	C5_1	C6_1	Br1_1	176.8(8)
C4_1	C5_1	C6_1	C7_1	0.9(17)
C5_1	C6_1	C7_1	C8_1	-4.5(18)
C6_1	C7_1	C8_1	C3_1	3.7(17)
C8_1	C3_1	C4_1	Cl1_1	178.2(7)
C8_1	C3_1	C4_1	C5_1	-4.4(15)
C9_1	C2_1	C3_1	C4_1	158.6(9)
C9_1	C2_1	C3_1	C8_1	-15.8(13)
C9_1	C2_1	C10_1	C11_1	-108.2(8)
C9_1	C2_1	C10_1	C17_1	109.6(9)
C9_1	C10_1	C11_1	C12_1	32.1(12)
C9_1	C10_1	C11_1	C16_1	-144.8(10)
C9_1	C10_1	C17_1	C18_1	141.5(10)
C9_1	C10_1	C17_1	C22_1	-41.1(11)
C10_1	C2_1	C3_1	C4_1	91.3(10)
C10_1	C2_1	C3_1	C8_1	-83.1(11)
C10_1	C11_1	C12_1	C13_1	177.6(11)
C10_1	C11_1	C16_1	C15_1	177.9(10)
C10_1	C17_1	C18_1	C19_1	177.1(9)
C10_1	C17_1	C22_1	C21_1	-178.8(9)
C11_1	C10_1	C17_1	C18_1	-74.5(11)
C11_1	C10_1	C17_1	C22_1	102.9(9)
C11_1	C12_1	C13_1	C14_1	5(2)
C12_1	C11_1	C16_1	C15_1	0.9(18)
C12_1	C13_1	C14_1	C15_1	0(2)
C13_1	C14_1	C15_1	C16_1	-4(2)
C14_1	C15_1	C16_1	C11_1	3.7(19)
C16_1	C11_1	C12_1	C13_1	-5.3(19)
C17_1	C10_1	C11_1	C12_1	-113.1(10)
C17_1	C10_1	C11_1	C16_1	69.9(11)
C17_1	C18_1	C19_1	C20_1	1.0(17)
C18_1	C17_1	C22_1	C21_1	-1.2(15)
C18_1	C19_1	C20_1	C21_1	0.1(17)
C19_1	C20_1	C21_1	C22_1	-1.7(17)
C20_1	C21_1	C22_1	C17_1	2.3(16)
C22_1	C17_1	C18_1	C19_1	-0.4(15)
Br1_2	C6_2	C7_2	C8_2	-178.6(9)
Cl1_2	C4_2	C5_2	C6_2	176.4(10)
O1_2	C1_2	C2_2	C3_2	5.4(11)
O1_2	C1_2	C2_2	C9_2	147.5(8)
O1_2	C1_2	C2_2	C10_2	-146.4(9)
O2_2	C1_2	C2_2	C3_2	177.6(8)
O2_2	C1_2	C2_2	C9_2	-40.3(11)
O2_2	C1_2	C2_2	C10_2	25.8(12)
C1_2	C2_2	C3_2	C4_2	-80.0(11)
C1_2	C2_2	C3_2	C8_2	106.6(10)
C1_2	C2_2	C9_2	C10_2	111.9(8)
C1_2	C2_2	C10_2	C9_2	-102.2(8)
C1_2	C2_2	C10_2	C11_2	145.2(8)
C1_2	C2_2	C10_2	C17_2	3.1(12)
C2_2	C3_2	C4_2	Cl1_2	11.5(13)
C2_2	C3_2	C4_2	C5_2	-171.8(10)

Atom	Atom	Atom	Atom	Angle/°
C2_2	C3_2	C8_2	C7_2	172.7(10)
C2_2	C9_2	C10_2	C11_2	103.7(8)
C2_2	C9_2	C10_2	C17_2	-115.3(8)
C2_2	C10_2	C11_2	C12_2	77.4(11)
C2_2	C10_2	C11_2	C16_2	-106.2(11)
C2_2	C10_2	C17_2	C18_2	55.0(13)
C2_2	C10_2	C17_2	C22_2	-124.8(10)
C3_2	C2_2	C9_2	C10_2	-107.5(8)
C3_2	C2_2	C10_2	C9_2	107.1(8)
C3_2	C2_2	C10_2	C11_2	-5.5(11)
C3_2	C2_2	C10_2	C17_2	-147.5(8)
C3_2	C4_2	C5_2	C6_2	-0.4(19)
C4_2	C3_2	C8_2	C7_2	-1.2(16)
C4_2	C5_2	C6_2	Br1_2	179.5(9)
C4_2	C5_2	C6_2	C7_2	-2(2)
C5_2	C6_2	C7_2	C8_2	3(2)
C6_2	C7_2	C8_2	C3_2	-1.4(19)
C8_2	C3_2	C4_2	Cl1_2	-174.6(8)
C8_2	C3_2	C4_2	C5_2	2.1(16)
C9_2	C2_2	C3_2	C4_2	139.0(9)
C9_2	C2_2	C3_2	C8_2	-34.4(12)
C9_2	C2_2	C10_2	C11_2	-112.6(8)
C9_2	C2_2	C10_2	C17_2	105.3(9)
C9_2	C10_2	C11_2	C12_2	8.3(13)
C9_2	C10_2	C11_2	C16_2	-175.2(9)
C9_2	C10_2	C17_2	C18_2	126.1(10)
C9_2	C10_2	C17_2	C22_2	-53.7(11)
C10_2	C2_2	C3_2	C4_2	72.5(11)
C10_2	C2_2	C3_2	C8_2	-100.9(11)
C10_2	C11_2	C12_2	C13_2	-177.8(12)
C10_2	C11_2	C16_2	C15_2	176.8(11)
C10_2	C17_2	C18_2	C19_2	178.8(10)
C10_2	C17_2	C22_2	C21_2	-178.9(9)
C11_2	C10_2	C17_2	C18_2	-88.9(11)
C11_2	C10_2	C17_2	C22_2	91.3(10)
C11_2	C12_2	C13_2	C14_2	-3(2)
C12_2	C11_2	C16_2	C15_2	-6.6(18)
C12_2	C13_2	C14_2	C15_2	0(3)
C13_2	C14_2	C15_2	C16_2	-1(2)
C14_2	C15_2	C16_2	C11_2	4(2)
C16_2	C11_2	C12_2	C13_2	5.6(18)
C17_2	C10_2	C11_2	C12_2	-135.5(10)
C17_2	C10_2	C11_2	C16_2	41.0(12)
C17_2	C18_2	C19_2	C20_2	1.3(18)
C18_2	C17_2	C22_2	C21_2	1.3(15)
C18_2	C19_2	C20_2	C21_2	-1.2(18)
C19_2	C20_2	C21_2	C22_2	1.2(18)
C20_2	C21_2	C22_2	C17_2	-1.3(17)
C22_2	C17_2	C18_2	C19_2	-1.3(15)

Table S12.1.13: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **WL-N2-137-27**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5_1	6906.54	7783.6	3123.16	20

Atom	x	y	z	U_{eq}
H7_1	5338.6	6599.51	3301.22	28
H8_1	4853.91	7104.78	2361.6	21
H9A_1	4570.88	7297.42	1283.47	23
H9B_1	4452.25	7983.28	834.09	23
H12_1	4953.44	6437.05	796.01	35
H13_1	5463.84	5419.44	800.53	49
H14_1	6583.37	5347.21	973.62	40
H15_1	7202.26	6312.58	1129.43	30
H16_1	6693.91	7318.23	979.22	32
H18_1	6511.52	8293.8	372.23	25
H19_1	6780.32	8755.55	-684.1	26
H20_1	6034.62	8753.46	-1596.79	30
H21_1	5003.26	8286.75	-1437.64	25
H22_1	4749.7	7770.07	-372.72	23
H5_2	6967.47	4811.27	1879.36	44
H7_2	7441.75	2898.82	1774.28	36
H8_2	8062.15	2996.52	2769.8	34
H9A_2	7931.41	3055.25	3974.19	23
H9B_2	8578.65	3325.27	4414.41	23
H12_2	6937.29	3135.25	3971.91	36
H13_2	5822.65	3224.91	3748.75	60
H14_2	5294.14	4217.55	3892.66	51
H15_2	5900.18	5149.35	4232.1	51
H16_2	7005.09	5032.09	4477.17	32
H18_2	8202.68	5296.11	4550.2	25
H19_2	8472.13	5818.4	5574.59	29
H20_2	8510.07	5243.36	6615.77	34
H21_2	8227.19	4136.73	6634.61	26
H22_2	7950.72	3604.07	5584.88	21

Table S12.1.14: Hydrogen Bond information for **WL-N2-137-27**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
C46	H46	O3[1]	0.95	2.71	3.223(14)	114.4

[1]1/2+y,3/2-x,+z

Table S12.1.15: Solvent masking (Olex2) information for **WL-N2-137-27**.

No	x	y	z	V	e	Content
1	-0.951	-0.966	-0.862	2648.4	0.0	?
2	0.135	0.865	0.000	1.1	0.0	?
3	0.140	0.700	0.896	0.2	0.0	?
4	0.200	0.360	0.896	0.2	0.0	?
5	0.300	0.860	0.104	0.2	0.0	?
6	0.365	0.365	0.000	1.1	0.0	?
7	0.360	0.200	0.104	0.2	0.0	?
8	0.635	0.635	0.000	1.1	0.0	?
9	0.640	0.800	0.104	0.2	0.0	?
10	0.700	0.140	0.104	0.2	0.0	?
11	0.800	0.640	0.896	0.2	0.0	?
12	0.865	0.135	0.000	1.1	0.0	?
13	0.860	0.300	0.896	0.2	0.0	?

Citations

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#==============================================================================
# PLATON/CHECK-( 70414) versus check.def version of 310314   for Entry: wl-n2-13
# Data: WL-N2-137-27.cif - Type: CIF            Bond Precision   C-C = 0.0128 A
# Refl: WL-N2-137-27.fcf - Type: LIST4                          Temp = 100 K
#                                    X-Ray       Nref/Npar =   8.1
# Cell  20.4695(6)  20.4695(6)  19.2209(8)          90          90          90
# Wavelength 0.71073    Volume Reported     8053.5(6)   Calculated     8053.6(6)
# SpaceGroup from Symmetry P 4 21 2   Hall: P 4ab 2ab           tetragonal
#               Reported P 4 21 2        P 4ab 2ab           tetragonal
# MoietyFormula C88 H60 Br4 Cl4 O8 Rh2
#      Reported C88 H60 Br4 Cl4 O8 Rh2
#    SumFormula C88 H60 Br4 Cl4 O8 Rh2
#      Reported C88 H64 Br4 Cl4 O10 Rh2
# Mr       =   1912.58[Calc],   1948.61[Rep]
# Dx,gcm-3 =     1.577[Calc],     1.607[Rep]
# Z        =         4[Calc],         4[Rep]
# Mu (mm-1) =     2.583[Calc],     2.586[Rep]
# F000     =    3800.0[Calc],    3880.0[Rep]  or F000' =   3790.19[Calc]
# Reported   T Limits: Tmin=0.652             Tmax=0.660  AbsCorr=MULTI-SCAN
# Calculated T Limits: Tmin=0.795 Tmin'=0.217  Tmax=0.921
# Reported   Hmax= 24, Kmax= 22, Lmax= 22, Nref=   6882       , Th(max)= 24.712
# Obs in FCF Hmax= 17, Kmax= 24, Lmax= 22, Nref=   6882[  3911], Th(max)= 24.712
# Calculated Hmax= 24, Kmax= 24, Lmax= 22, Nref=   6886[  3915], Ratio=1.76/1.00
# PLATON/Squeeze:      2654.4 Ang**3, Total El.Count =     0.0 e-
# Reported   Rho(min) = -0.53, Rho(max) =  1.53 e/Ang**3 (From CIF)
# w=1/[sigma**2(Fo**2)+(0.0559P)**2+ 12.6996P], P=(Fo**2+2*Fc**2)/3
# R= 0.0611(  4969), wR2= 0.1274(  6882), S = 1.028      (From FCF data only)
# R= 0.0611(  4969), wR2= 0.1273(  6882), S = 1.027, Npar=  481, Flack 0.015(11)
# Number Bijvoet Pairs = 2971 (100%)     ( 1655 Selected for:  Parsons  0.021(9)
# P2(tr) 1.000, P3(tr) 1.000, P3(tw) 0.000,  Student-T Nu 99.53, Hooft  0.015(9)
#==============================================================================
For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
#==============================================================================

#==============================================================================
>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
#==============================================================================
Format: alert-number_ALERT_alert-type_alert-level text

041_ALERT_1_C Calc. and Reported SumFormula    Strings  Differ     Please Check
068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)...     Please Check
090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) .....       8.13 Note
094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.87 Why ?
213_ALERT_2_C Atom Br1_2          has ADP max/min Ratio .....        3.7 prolat
250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....       2.2 Note
342_ALERT_3_C Low Bond Precision on  C-C Bonds .............     0.0128 Ang.
973_ALERT_2_C Check Calcd Positive Residual Density on     Rh2       1.03 eA-3
#==============================================================================
002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         52 Note
003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         52 Why ?
008_ALERT_5_G No _iucr_refine_reflections_details   in the CIF     Please Do !
044_ALERT_1_G Calculated and Reported Density Dx  Differ by ..     0.0296 Check
083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.      12.70 Why ?
605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of .        121 A**3
720_ALERT_4_G Number of Unusual/Non-Standard Labels .....         82 Note
791_ALERT_4_G The Model has Chirality at C2_1    .............          S Verify
791_ALERT_4_G The Model has Chirality at C2_2    .............          S Verify
802_ALERT_4_G CIF Input Record(s) with more than 80 Characters          ! Info
860_ALERT_3_G Number of Least-Squares Restraints .............        478 Note
869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed          ! Info
909_ALERT_3_G Percentage of Observed Data at Theta(Max) still          50 %
910_ALERT_3_G Missing # of FCF Reflections Below Th(Min) .....          3 Why ?
951_ALERT_5_G Reported and Calculated Kmax Values Differ by ..          2
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ALERT_Level and ALERT_Type Summary
==================================
8 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight
15 ALERT_Level_G = General Info/Check that it is not Something Unexpected

3 ALERT_Type_1 CIF Construction/Syntax Error, Inconsistent or Missing Data.
7 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
5 ALERT_Type_3 Indicator that the Structure Quality may be Low.
6 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.
2 ALERT_Type_5 Informative Message, Check.
#==

1 Missing Experimental Info Issue(s) (Out of 54 Tests) -   98 % Satisfied
1 Experimental Data Related Issue(s) (Out of 28 Tests) -   96 % Satisfied
9 Structural Model   Related Issue(s) (Out of 117 Tests) -   92 % Satisfied
12 Unresolved or to be Checked Issue(s) (Out of 223 Tests) -   95 % Satisfied

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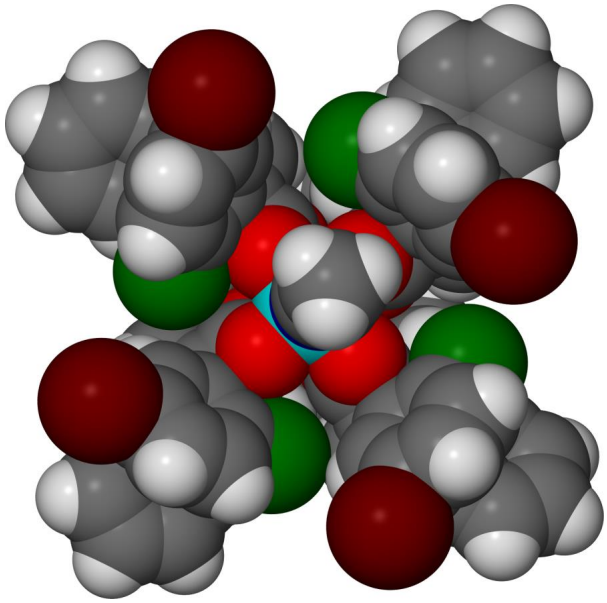
12.2. Rh_2(*S*-2-Cl-5-BrTPCP)$_4$

Crystal Data and Experimental



Experimental. Single green needle-shaped crystals of **WL-2ClBr** were chosen from the sample as supplied. A suitable crystal 0.34×0.11×0.08 mm^3 was selected and mounted on a loop with paratone oil on an XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100.3(5) K during the data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{182}H_{131}Br_8Cl_8N_3O_{17}Rh_4$, M_r = 3966.41, monoclinic, $P2_1$ (No. 4), a = 21.4690(3) Å, b = 17.1974(3) Å, c = 29.1637(4) Å, = 106.965(2)°, = = 90°, V = 10299.0(3) Å^3, T = 100.3(5) K, Z = 2, Z' = 1, (CuK) = 5.741 mm^{-1}, 121262 reflections measured, 36989 unique (R_{int} = 0.0704) which were used in all calculations. The final wR_2 was 0.2353 (all data) and R_1 was 0.0813 (I > 2σ(I)).

Compound	**WL-2ClBr**
Formula	$C_{182}H_{131}Br_8Cl_8N_3O_{17}Rh_4$
$D_{calc.}$/ g cm^{-3}	1.279
/mm^{-1}	5.741
Formula Weight	3966.41
Colour	green
Shape	needle
Size/mm^3	0.34×0.11×0.08
T/K	100.3(5)
Crystal System	monoclinic
Flack Parameter	0.066(12)
Hooft Parameter	0.047(3)
Space Group	$P2_1$
a/Å	21.4690(3)
b/Å	17.1974(3)
c/Å	29.1637(4)
/°	90
/°	106.965(2)
/°	90
V/Å^3	10299.0(3)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK
$_{min}$/°	2.152
$_{max}$/°	68.249
Measured Refl.	121262
Independent Refl.	36989
Reflections with I > 2σ(I)	30571
R_{int}	0.0704
Parameters	2131
Restraints	4101
Largest Peak	2.315
Deepest Hole	-2.101
GooF	1.079
wR_2 (all data)	0.2353
wR_2	0.2229
R_1 (all data)	0.0935
R_1	0.0813

Structure Quality Indicators

Reflections:	d min (Cu) 0.83	I/σ 15.6	Rint 7.04%	complete 99% (IUCr) 98%
Refinement:	Shift 0.010	Max Peak 2.3	Min Peak -2.1	GooF 1.079

A green needle-shaped crystal with dimensions 0.34×0.11×0.08 mm^3 was mounted on a loop with paratone oil. Data were collected using an XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100.3(5) K.

Data were measured using scans of 0.5° per frame for 3.0/7.2 s using CuK radiation. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.33a, 2017). The maximum resolution that was achieved was = 68.249°.

The diffraction pattern was indexed using **CrysAlisPro** (Rigaku, V1.171.39.33a, 2017) and the unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.39.33a, 2017) on 49303 reflections, 41% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.39.33a, 2017). The final completeness is 99.60 % out to 68.249° in . A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed using CrysAlisPro 1.171.39.33a (Rigaku Oxford Diffraction, 2017). An empirical absorption correction using spherical harmonics as implemented by SCALE3 ABSPACK was also performed. The absorption coefficient of this material is 5.741 mm^{-1} at this wavelength (= 1.54184Å) and the minimum and maximum transmissions are 0.028 and 0.486.

The structure was solved and the space group $P2_1$ (# 4) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: Refined as a 2-component inversion twin.

The Flack parameter was refined to 0.066(12). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.047(3). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

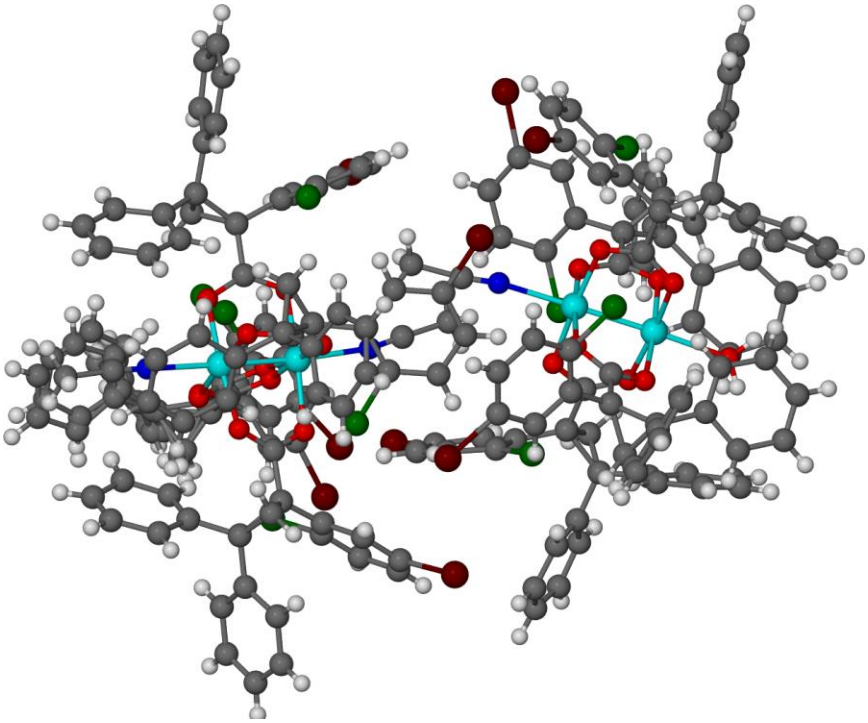


Figure S12.2.3:

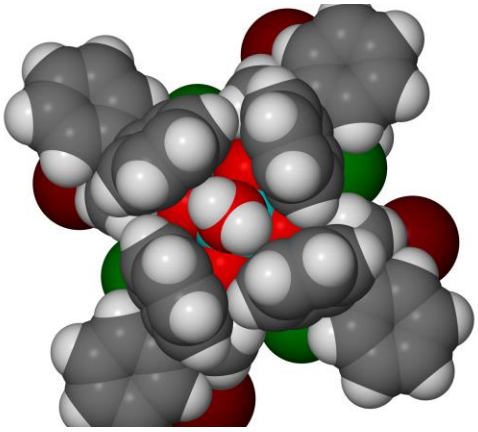


Figure S12.2.4:

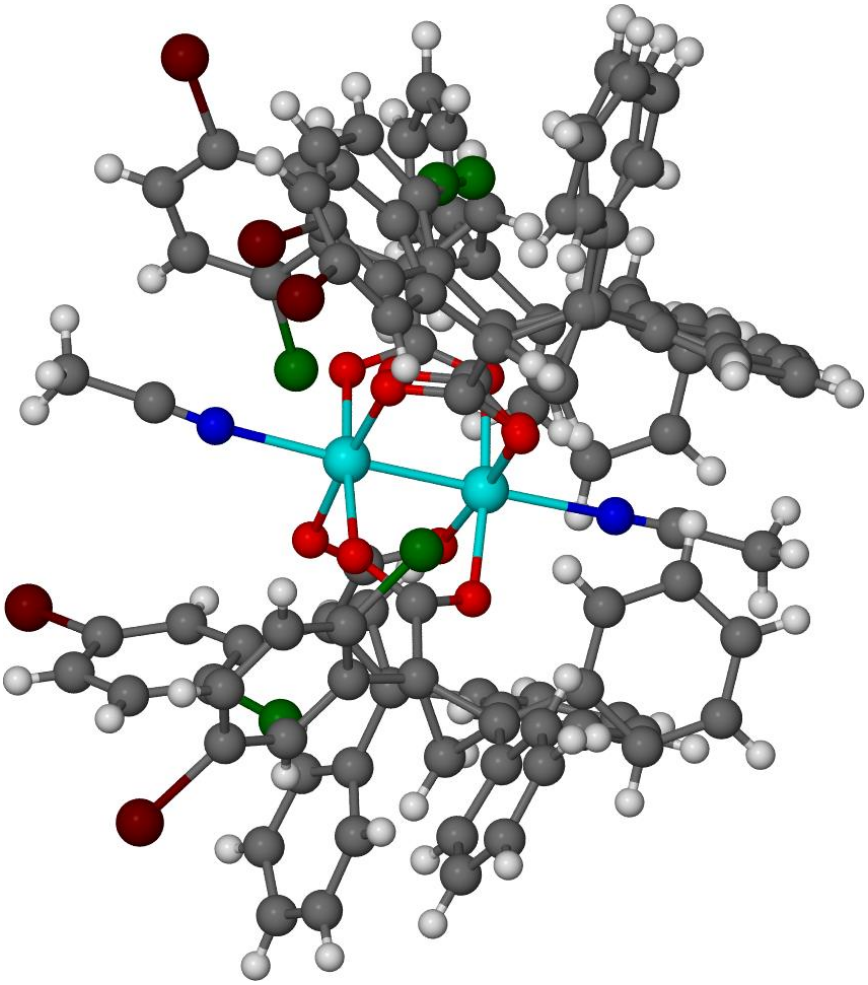


Figure S12.2.3:

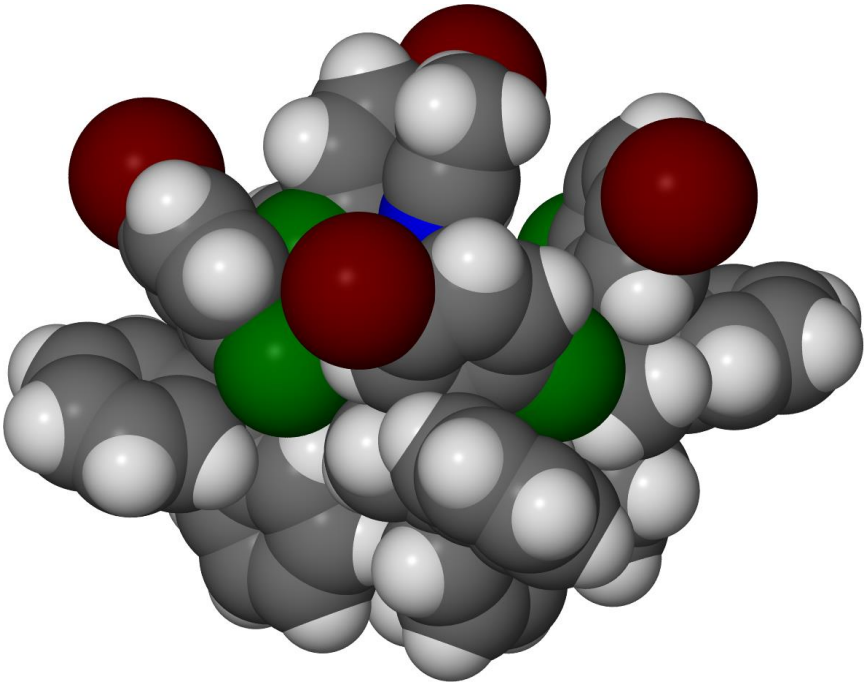


Figure S12.2.4:

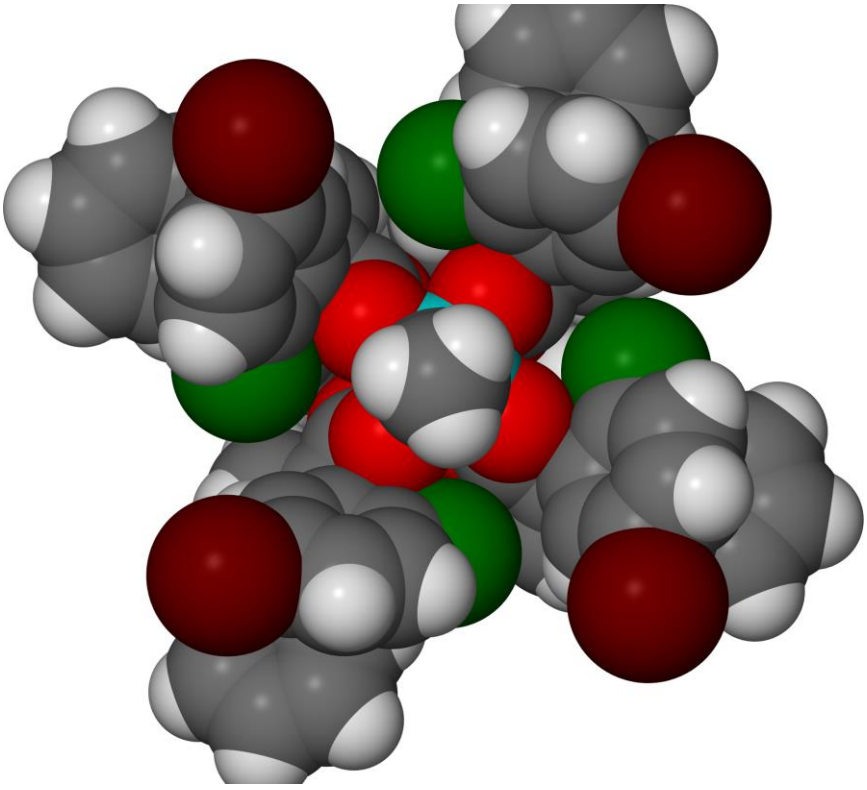


Figure S12.2.5:

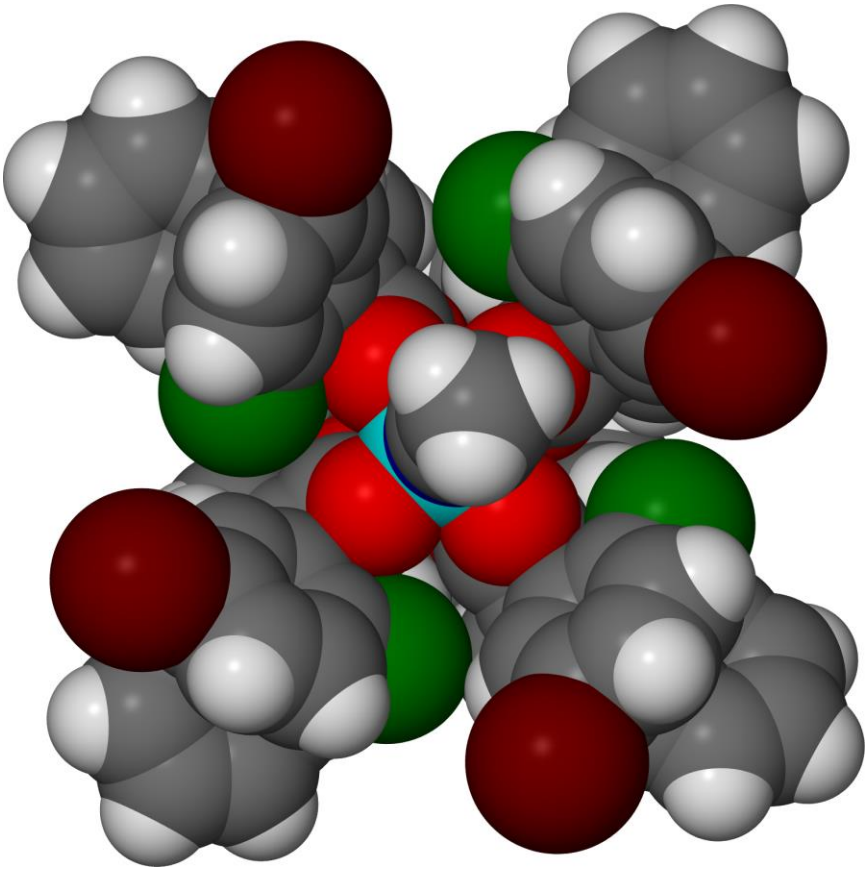
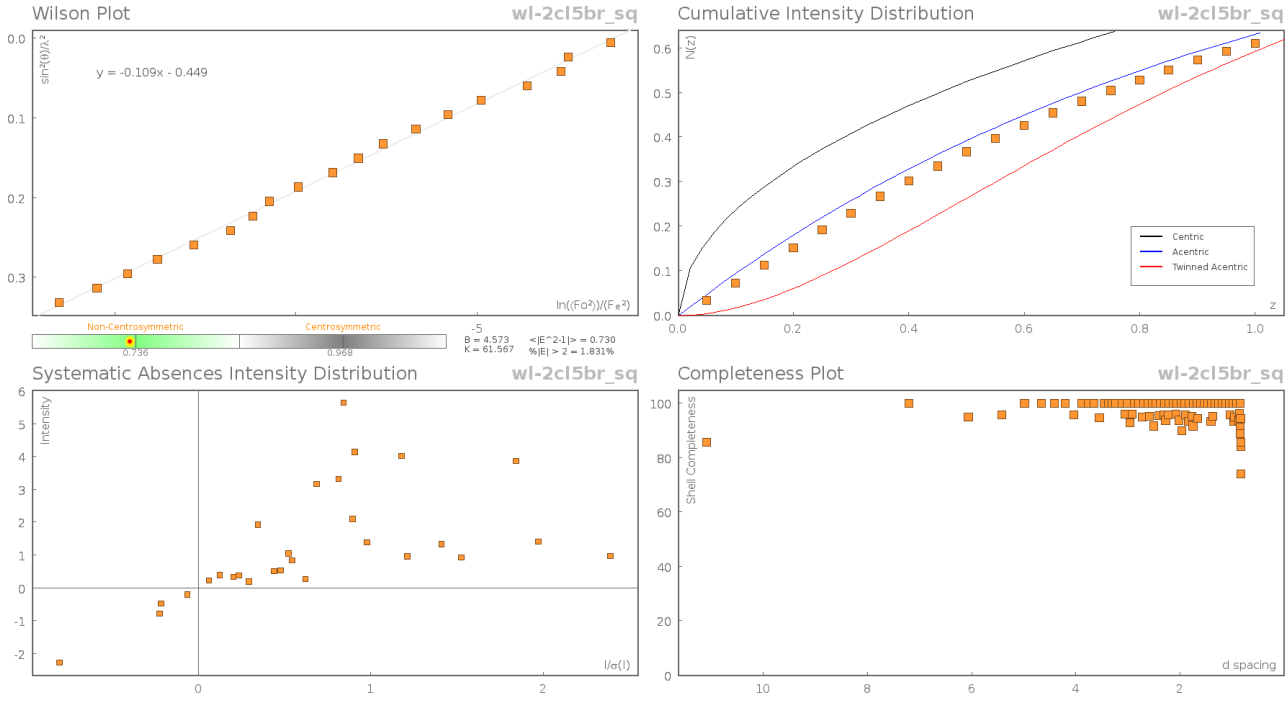
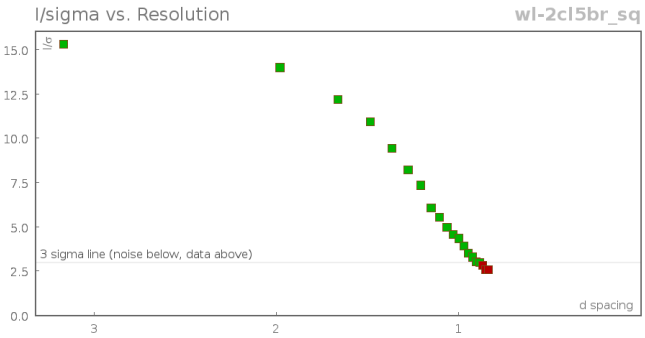


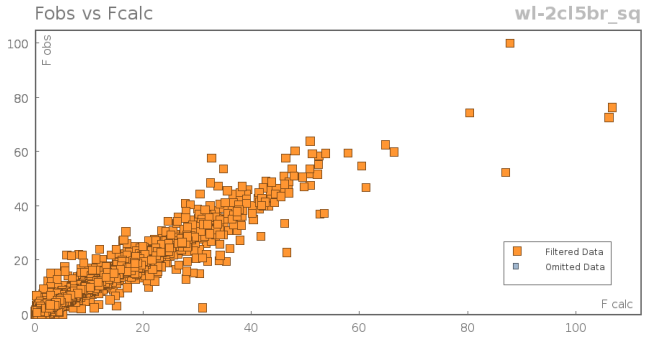
Figure S12.2.6:

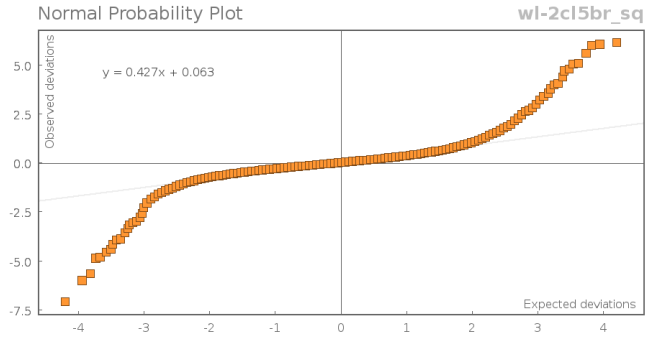
Data Plots: Diffraction Data





Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	121291	Unique reflections	36989
Completeness	0.98	Mean I/	10.9
hkl_{max} collected	(25, 20, 35)	hkl_{min} collected	(-24, -20, -34)
hkl_{max} used	(24, 20, 35)	hkl_{min} used	(-25, -20, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	20.53	d_{min} used	0.83
Friedel pairs	17130	Friedel pairs merged	0
Inconsistent equivalents	81	R_{int}	0.0704
R_{sigma}	0.064	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(19710, 16351, 9388, 4202, 1923, 1046, 607, 307, 120, 22, 1)	Maximum multiplicity	11
Removed systematic absences	29	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer

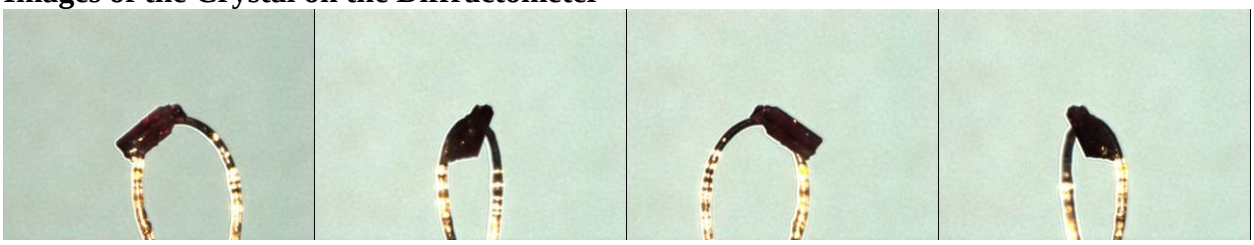


Table S12.2.16: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **WL-2ClBr**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Rh3	3819.6(5)	5342.6(9)	6409.1(3)	48.0(2)
Rh4	2877.8(5)	6113.9(9)	6064.4(4)	51.4(2)
O4	1997(6)	6889(8)	5752(5)	86(4)
Rh1	7456.2(5)	5161.4(10)	8208.2(3)	56.6(3)

Atom	x	y	z	U_{eq}
Rh2	8218.9(5)	4500.0(10)	8843.4(3)	58.5(3)
N1_9	8939(6)	3871(10)	9432(5)	84(4)
C23_9	9296(8)	3563(13)	9715(6)	102(7)
C24_9	9743(10)	3193(17)	10128(8)	123(10)
N1_10	6743(6)	5711(8)	7573(4)	66(3)
C23_10	6427(9)	5916(11)	7232(6)	86(4)
C24_10	5974(13)	6139(15)	6777(7)	125(9)
Br1_3	4923.9(9)	7484(2)	9084.7(8)	110.4(9)
Cl1_3	7939.8(13)	7437(2)	9214.5(15)	76.1(10)
O1_3	7781(4)	4999(4)	9299(2)	57(2)
O2_3	7237(4)	5846(5)	8727.7(17)	58(2)
C1_3	7456(3)	5613(4)	9159(2)	56(2)
C2_3	7232(3)	6064(3)	9527(2)	63(2)
C3_3	7626(3)	6083(4)	10066(2)	65(2)
C4_3	6839(3)	6770(3)	9319(3)	69(3)
C5_3	7117(3)	7426(4)	9188(5)	68(3)
C6_3	6757(4)	8115(5)	9023(6)	85(4)
C7_3	6117(4)	8138(5)	9007(6)	87(4)
C8_3	5830(3)	7496(5)	9140(5)	79(3)
C9_3	6181(3)	6818(5)	9299(5)	71(3)
C10_3	7049(3)	5577(4)	9891(2)	65(3)
C11_3	8301(3)	5709(5)	10246(2)	67(3)
C12_3	8433(5)	5297(9)	10680(4)	84(4)
C13_3	9050(5)	4959(9)	10865(4)	91(4)
C14_3	9513(4)	5052(9)	10635(4)	88(4)
C15_3	9362(5)	5408(11)	10200(5)	109(7)
C16_3	8771(4)	5784(8)	10017(4)	72(4)
C17_3	7587(3)	6811(4)	10342(3)	63(3)
C18_3	8073(5)	7358(7)	10444(6)	90(5)
C19_3	8044(6)	8031(7)	10698(6)	89(5)
C20_3	7505(6)	8171(8)	10843(7)	105(7)
C21_3	6987(6)	7690(8)	10716(7)	109(7)
C22_3	7019(5)	7010(7)	10465(6)	85(5)
Br1_5	6881.4(8)	7903.3(14)	7678.3(8)	84.2(5)
Cl1_5	4129.3(13)	6613(2)	7749.8(12)	63.0(8)
O1_5	3426(3)	7065(4)	6340(3)	57(2)
O2_5	4256(3)	6307(3)	6764(3)	55(2)
C1_5	3945(3)	6945(3)	6676(2)	55(2)
C2_5	4303(3)	7655(3)	6930(2)	58(2)
C3_5	3942(3)	8423(3)	6970(2)	65(2)
C4_5	4896(3)	7450(4)	7331(2)	55(2)
C5_5	4871(3)	6960(6)	7702(3)	61(3)
C6_5	5440(3)	6680(6)	8046(3)	63(3)
C7_5	6028(3)	6977(7)	8046(4)	72(3)
C8_5	6065(3)	7489(8)	7693(4)	73(4)
C9_5	5512(3)	7719(7)	7333(3)	67(3)
C10_5	4299(3)	8333(4)	6610(2)	67(3)
C11_5	3197(3)	8462(4)	6804(3)	70(3)
C12_5	2914(4)	8965(9)	6421(5)	86(4)
C13_5	2234(4)	9030(12)	6264(7)	117(8)
C14_5	1859(4)	8603(10)	6474(6)	110(6)
C15_5	2140(4)	8093(11)	6831(7)	106(6)
C16_5	2810(4)	8030(10)	7007(6)	92(5)
C17_5	4220(4)	8929(4)	7402(3)	74(3)
C18_5	4235(8)	8697(6)	7855(3)	84(4)
C19_5	4507(9)	9150(7)	8257(3)	101(5)
C20_5	4741(10)	9871(8)	8201(4)	122(7)
C21_5	4682(12)	10159(7)	7760(4)	128(8)

Atom	x	y	z	U_{eq}
C22_5	4432(11)	9693(6)	7359(4)	113(7)
Br1_6	4165.1(8)	4290.3(16)	9056.8(5)	85.0(6)
Cl1_6	2390.4(16)	3674(2)	6919.4(9)	62.6(8)
O1_6	2657(4)	6036(4)	6688(2)	53(2)
O2_6	3405(3)	5083(5)	6950(3)	51.4(19)
C1_6	2918(3)	5489(4)	6969(2)	52(3)
C2_6	2640(3)	5309(3)	7377.8(19)	55(2)
C3_6	1923(3)	5486(4)	7354(2)	61(2)
C4_6	2965(3)	4625(3)	7671.1(19)	50(2)
C5_6	2864(5)	3869(3)	7504(2)	54(2)
C6_6	3139(6)	3218(4)	7792(3)	63(3)
C7_6	3512(6)	3343(4)	8252(3)	67(3)
C8_6	3617(5)	4088(4)	8427(2)	61(3)
C9_6	3327(4)	4725(4)	8151(2)	53(2)
C10_6	2457(3)	6003(4)	7618(2)	62(2)
C11_6	1435(3)	5788(5)	6894(2)	64(3)
C12_6	1025(7)	6395(9)	6950(3)	93(6)
C13_6	561(8)	6682(10)	6541(4)	119(8)
C14_6	479(8)	6338(11)	6107(4)	116(8)
C15_6	881(7)	5752(10)	6059(3)	95(6)
C16_6	1361(5)	5470(7)	6451(2)	66(3)
C17_6	1599(3)	4950(5)	7622(2)	61(3)
C18_6	1188(6)	4366(7)	7395(3)	72(3)
C19_6	907(7)	3848(7)	7640(4)	82(4)
C20_6	1008(6)	3944(7)	8121(4)	76(4)
C21_6	1422(5)	4492(7)	8366(3)	72(3)
C22_6	1734(5)	4984(7)	8124(3)	65(3)
Br1_7	3271.6(13)	1027.9(14)	6392.8(12)	129.9(11)
Cl1_7	3331(3)	3856(2)	4995.1(17)	105.6(17)
O1_7	2389(3)	5089(3)	5844(3)	57(2)
O2_7	3340(3)	4423(4)	6031(3)	55.1(19)
C1_7	2724(3)	4478(4)	5862(3)	52(2)
C2_7	2377(3)	3762(3)	5611(2)	70(2)
C3_7	1748(3)	3810(4)	5183(2)	90(3)
C4_7	2833(3)	3093(3)	5628(2)	73(3)
C5_7	3272(6)	3077(5)	5363(4)	86(4)
C6_7	3680(6)	2428(5)	5363(5)	99(4)
C7_7	3659(7)	1812(5)	5653(5)	102(5)
C8_7	3272(7)	1847(6)	5954(5)	98(5)
C9_7	2863(6)	2478(5)	5948(4)	78(3)
C10_7	1719(3)	3620(4)	5670(3)	75(3)
C11_7	1473(3)	4590(4)	4962(3)	86(3)
C12_7	805(4)	4711(7)	4894(8)	109(6)
C13_7	531(5)	5422(7)	4700(7)	109(6)
C14_7	912(6)	5989(7)	4599(7)	116(6)
C15_7	1551(6)	5850(7)	4647(7)	113(6)
C16_7	1842(4)	5158(5)	4839(5)	92(4)
C17_7	1643(4)	3187(4)	4805(3)	96(3)
C18_7	1814(10)	3295(7)	4392(4)	122(3)
C19_7	1755(10)	2713(8)	4053(5)	121(3)
C20_7	1459(11)	2031(8)	4107(5)	131(5)
C21_7	1307(12)	1878(7)	4515(5)	133(5)
C22_7	1421(9)	2438(5)	4875(4)	111(4)
Br1_8	5826(2)	4561.9(18)	4562.8(15)	178.7(13)
Cl1_8	4949.9(18)	7183(2)	5790.6(13)	76.4(10)
O1_8	3160(3)	6147(6)	5453(2)	58(2)
O2_8	4153(3)	5657(5)	5842(2)	54(2)
C1_8	3741(3)	5964(5)	5483(2)	55(3)

Atom	x	y	z	U_{eq}
C2_8	3982(3)	6139(3)	5056(2)	62(2)
C3_8	3665(3)	6772(4)	4681(2)	60(2)
C4_8	4697(3)	5985(4)	5153(2)	79(2)
C5_8	5167(3)	6454(7)	5450(5)	83(2)
C6_8	5844(3)	6329(8)	5529(5)	87(3)
C7_8	6036(3)	5767(8)	5269(5)	91(3)
C8_8	5578(3)	5308(7)	4959(5)	90(3)
C9_8	4914(3)	5419(7)	4890(5)	85(2)
C10_8	3518(3)	5940(4)	4580(2)	65(3)
C11_8	3128(3)	7305(4)	4749(3)	64(3)
C12_8	2560(4)	7356(8)	4360(4)	79(4)
C13_8	2062(5)	7857(9)	4398(5)	96(5)
C14_8	2133(5)	8286(8)	4802(5)	88(4)
C15_8	2697(5)	8252(8)	5167(5)	86(4)
C16_8	3189(5)	7744(7)	5152(3)	68(3)
C17_8	4102(4)	7199(4)	4446(2)	54(2)
C18_8	4370(5)	7907(5)	4611(3)	57(3)
C19_8	4777(6)	8305(6)	4401(4)	68(3)
C20_8	4897(6)	8005(7)	4002(4)	69(3)
C21_8	4650(6)	7310(7)	3825(4)	72(3)
C22_8	4238(6)	6911(6)	4034(3)	65(3)
Br1_12	8344(4)	9472(3)	7955(3)	143.5(16)
Cl1_12	9279(5)	6059(4)	7617(3)	89.4(19)
O1_12	8811(10)	5469(10)	8898(6)	61.1(12)
O2_12	8136(6)	5989(10)	8221(5)	56(3)
C1_12	8649(4)	5985(5)	8576(4)	61.4(11)
C2_12	9133(4)	6629(4)	8587(3)	63.1(8)
C3_12	9874(4)	6533(4)	8832(3)	62.6(8)
C4_12	8918(4)	7161(4)	8161(3)	64.2(10)
C5_12	8990(12)	6972(6)	7718(4)	69(3)
C6_12	8848(18)	7503(8)	7329(5)	87(3)
C7_12	8653(16)	8237(7)	7399(4)	78(3)
C8_12	8600(14)	8448(6)	7841(4)	82(6)
C9_12	8695(11)	7911(6)	8212(4)	68(4)
C10_12	9457(5)	6956(5)	9072(3)	62.4(9)
C11_12	10168(5)	5753(4)	9042(3)	62.3(9)
C12_12	10583(12)	5772(6)	9514(5)	60(5)
C13_12	10856(12)	5070(7)	9726(6)	65(6)
C14_12	10675(13)	4384(6)	9493(6)	68(5)
C15_12	10248(12)	4375(5)	9045(6)	63(3)
C16_12	10020(11)	5059(5)	8805(5)	58(4)
C17_12	10332(4)	6971(5)	8622(5)	62.3(11)
C18_12	10848(7)	6614(7)	8520(8)	63.4(14)
C19_12	11241(10)	6995(8)	8292(10)	75(3)
C20_12	11164(12)	7776(9)	8211(12)	93(4)
C21_12	10686(9)	8168(7)	8325(9)	69(2)
C22_12	10270(9)	7776(6)	8533(9)	63.4(18)
Br1_1	7881.2(12)	5147.3(16)	5873.2(8)	103.0(7)
Cl1_1	7126.6(16)	2748(3)	7286.8(13)	79.9(12)
O1_1	8600(4)	4046(6)	8330.8(17)	68(3)
O2_1	7709(3)	4452(6)	7749(2)	61(2)
C1_1	8245(3)	4086(5)	7901(2)	66(4)
C2_1	8451(3)	3617(3)	7530.7(19)	54(3)
C3_1	8851(3)	2856(4)	7659(2)	60(3)
C4_1	7988(3)	3701(4)	7035(2)	54(3)
C5_1	7380(4)	3357(6)	6897(3)	55(3)
C6_1	6925(4)	3488(6)	6442(3)	56(3)
C7_1	7073(4)	4017(7)	6142(3)	70(4)

Atom	x	y	z	U_{eq}
C8_1	7655(4)	4410(7)	6285(3)	69(4)
C9_1	8124(4)	4234(6)	6715(3)	60(3)
C10_1	9168(3)	3596(4)	7599(2)	66(4)
C11_1	9009(3)	2498(5)	8161(2)	80(6)
C12_1	9665(4)	2309(9)	8381(3)	72(4)
C13_1	9831(5)	1961(11)	8836(4)	90(6)
C14_1	9366(6)	1821(14)	9057(5)	118(10)
C15_1	8742(6)	2058(13)	8853(4)	119(10)
C16_1	8562(5)	2418(11)	8410(4)	88(6)
C17_1	8739(4)	2235(4)	7280(3)	65(4)
C18_1	8372(7)	1586(6)	7293(4)	74(5)
C19_1	8270(8)	1006(7)	6951(5)	91(6)
C20_1	8588(8)	1039(6)	6609(4)	88(6)
C21_1	8964(10)	1655(8)	6582(6)	123(10)
C22_1	9042(7)	2258(6)	6912(4)	77(5)
Br1_4	8222(3)	9019(3)	7503(2)	143.5(16)
Cl1_4	9498(5)	5644(3)	7692(2)	89.4(19)
O1_4	8822(9)	5462(10)	8918(4)	61.1(12)
O2_4	8224(5)	5823(9)	8174(4)	56(3)
C1_4	8729(4)	5849(5)	8535(3)	61.4(11)
C2_4	9200(3)	6503(4)	8534(2)	63.1(8)
C3_4	9920(3)	6488(4)	8851(3)	62.6(8)
C4_4	9049(4)	6910(4)	8059(2)	64.5(10)
C5_4	9166(11)	6575(6)	7661(3)	69(3)
C6_4	9062(14)	6978(8)	7221(4)	87(3)
C7_4	8803(13)	7708(8)	7181(4)	87(3)
C8_4	8616(11)	8019(7)	7555(4)	78(3)
C9_4	8749(10)	7640(7)	7995(3)	64(4)
C10_4	9424(4)	6950(4)	8991(3)	62.4(9)
C11_4	10211(4)	5771(4)	9147(3)	62.3(9)
C12_4	10625(11)	5911(6)	9611(4)	66(5)
C13_4	10966(10)	5281(7)	9872(5)	64(5)
C14_4	10855(9)	4546(7)	9695(5)	59(4)
C15_4	10458(10)	4422(6)	9244(5)	63(3)
C16_4	10107(8)	5026(4)	8976(5)	54(3)
C17_4	10416(4)	6890(5)	8661(4)	62.3(11)
C18_4	10807(7)	6483(6)	8448(7)	63.4(14)
C19_4	11245(10)	6845(8)	8251(9)	82(3)
C20_4	11244(9)	7637(8)	8219(9)	70(3)
C21_4	10821(9)	8065(7)	8376(8)	69(2)
C22_4	10429(8)	7705(5)	8619(7)	63.4(18)
Br1_2	4316.8(7)	2706.9(14)	7064.4(6)	78.6(5)
Cl1_2	5909.2(14)	4638(2)	8897.4(9)	57.6(8)
O1_2	7557(2)	3594(5)	8744(3)	65(3)
O2_2	6781(3)	4360(4)	8260(3)	59(2)
C1_2	6977(3)	3748(4)	8503(3)	61(4)
C2_2	6455(3)	3173(3)	8528(2)	60(4)
C3_2	6533(3)	2626(4)	8965(2)	66(4)
C4_2	5782(3)	3444(4)	8261(2)	64(4)
C5_2	5511(4)	4113(5)	8384(3)	54(3)
C6_2	4909(3)	4419(5)	8097(3)	48(3)
C7_2	4564(4)	4009(5)	7705(3)	56(3)
C8_2	4807(4)	3321(6)	7589(4)	66(4)
C9_2	5404(4)	3028(6)	7866(4)	70(5)
C10_2	6636(3)	2338(4)	8515(2)	67(4)
C11_2	7120(3)	2689(4)	9412(2)	65(4)
C12_2	7435(5)	1989(5)	9591(4)	85(6)
C13_2	7924(7)	2003(7)	10032(4)	95(7)

Atom	x	y	z	U_{eq}
C14_2	8111(7)	2687(7)	10265(4)	103(8)
C15_2	7815(7)	3363(6)	10079(5)	89(6)
C16_2	7312(6)	3371(5)	9656(4)	81(5)
C17_2	5926(3)	2410(5)	9094(3)	89(4)
C18_2	5738(5)	2807(7)	9440(4)	87(4)
C19_2	5184(5)	2613(9)	9566(5)	90(4)
C20_2	4774(6)	2058(10)	9309(5)	107(5)
C21_2	4882(5)	1739(10)	8916(5)	104(4)
C22_2	5470(6)	1878(11)	8818(6)	145(8)
N1_11	4754(6)	4696(8)	6715(4)	67(3)
C23_11	5242(7)	4476(10)	6880(7)	87(4)
C24_11	5860(8)	4089(14)	7090(7)	102(6)

Table S12.2.17: Anisotropic Displacement Parameters ($\times 10^4$) **WL-2ClBr**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh3	57.0(5)	46.7(5)	43.7(5)	9.8(4)	19.9(4)	12.9(4)
Rh4	57.1(6)	48.6(5)	49.3(5)	11.1(4)	16.7(4)	12.3(4)
O4	63(7)	77(8)	115(10)	22(8)	19(7)	25(6)
Rh1	43.9(5)	85.3(8)	36.4(4)	-1.8(4)	5.1(4)	11.7(5)
Rh2	39.9(5)	90.6(8)	40.0(5)	3.7(5)	4.0(4)	7.3(5)
N1_9	62(7)	124(12)	59(7)	17(7)	9(5)	10(7)
C23_9	62(8)	148(18)	86(11)	46(12)	6(7)	3(10)
C24_9	83(12)	170(20)	101(13)	60(15)	5(10)	20(14)
N1_10	62(6)	71(7)	69(5)	-8(5)	25(4)	2(5)
C23_10	88(5)	85(5)	80(5)	2(3)	18(3)	1(3)
C24_10	161(18)	92(15)	91(9)	9(11)	-13(11)	-9(15)
Br1_3	64.4(11)	184(3)	87.4(13)	-23.9(15)	28.4(10)	28.2(13)
Cl1_3	67(2)	88(3)	75(2)	-3(2)	23.4(18)	-6(2)
O1_3	44(4)	84(5)	39(4)	1(3)	7(3)	-3(3)
O2_3	57(5)	69(6)	41(3)	-5(3)	5(3)	1(4)
C1_3	39(5)	82(6)	42(3)	-2(3)	3(3)	-6(4)
C2_3	56(5)	82(5)	52(3)	-7(4)	16(3)	-8(4)
C3_3	61(4)	88(6)	49(4)	-3(4)	19(3)	-18(4)
C4_3	64(5)	89(6)	55(6)	-6(5)	16(5)	0(4)
C5_3	71(6)	82(6)	53(7)	-11(5)	21(6)	2(4)
C6_3	89(7)	82(7)	85(11)	-9(7)	24(7)	9(6)
C7_3	91(7)	83(8)	88(12)	-20(7)	28(8)	13(6)
C8_3	80(7)	93(8)	64(8)	-17(6)	19(7)	13(5)
C9_3	66(5)	92(7)	58(8)	-11(6)	22(5)	4(5)
C10_3	57(5)	82(6)	56(6)	-8(4)	18(5)	-12(5)
C11_3	60(4)	90(8)	45(5)	-13(5)	7(3)	-20(4)
C12_3	85(7)	107(11)	48(6)	-3(6)	1(5)	-24(7)
C13_3	89(7)	102(13)	63(8)	-5(7)	-8(5)	-22(7)
C14_3	84(7)	75(11)	88(8)	-4(7)	-2(6)	-18(7)
C15_3	54(6)	151(18)	116(11)	41(11)	15(7)	-3(8)
C16_3	54(5)	105(11)	50(6)	-11(6)	6(5)	-14(5)
C17_3	62(6)	86(6)	43(5)	0(4)	19(5)	-20(4)
C18_3	74(7)	102(8)	103(13)	-32(8)	42(8)	-34(7)
C19_3	72(7)	104(9)	93(12)	-31(9)	28(8)	-28(7)
C20_3	78(8)	132(13)	112(15)	-63(12)	38(9)	-41(8)
C21_3	78(8)	136(11)	123(16)	-74(12)	43(9)	-42(8)
C22_3	72(6)	116(10)	76(10)	-41(8)	33(7)	-35(6)
Br1_5	67.6(10)	85.3(13)	98.5(14)	-9.5(10)	22.5(9)	-13.4(9)
Cl1_5	63.9(19)	72(2)	56.8(18)	2.4(16)	23.9(15)	6.4(17)
O1_5	60(4)	50(5)	60(4)	15(4)	20(3)	13(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2_5	61(5)	53(4)	51(5)	5(3)	16(4)	14(3)
C1_5	59(4)	54(4)	55(5)	8(3)	21(3)	13(3)
C2_5	62(4)	54(4)	63(5)	5(3)	29(3)	9(3)
C3_5	66(4)	53(4)	82(5)	3(4)	30(4)	8(4)
C4_5	65(4)	46(6)	58(5)	-4(4)	24(3)	4(4)
C5_5	72(5)	59(7)	56(6)	-1(5)	24(4)	4(5)
C6_5	75(5)	61(8)	57(6)	-1(5)	24(5)	11(5)
C7_5	76(5)	72(8)	68(7)	-8(6)	22(5)	2(6)
C8_5	67(5)	76(9)	79(7)	-1(6)	25(5)	1(6)
C9_5	67(4)	70(9)	67(7)	-6(6)	26(4)	-3(5)
C10_5	73(7)	56(5)	80(6)	14(5)	32(6)	14(5)
C11_5	66(4)	51(7)	98(8)	-5(5)	29(4)	13(4)
C12_5	82(6)	63(9)	104(10)	1(7)	14(7)	13(7)
C13_5	82(6)	120(16)	139(17)	26(13)	17(8)	24(9)
C14_5	85(8)	93(13)	151(15)	8(11)	35(9)	30(9)
C15_5	65(5)	90(13)	164(16)	16(11)	33(8)	11(7)
C16_5	65(5)	81(11)	131(13)	11(9)	31(7)	3(6)
C17_5	71(8)	63(6)	96(5)	-11(5)	35(5)	-4(6)
C18_5	87(10)	83(9)	89(6)	-16(5)	37(6)	10(7)
C19_5	102(13)	103(10)	101(7)	-31(7)	35(8)	7(9)
C20_5	115(15)	107(10)	154(12)	-48(10)	53(12)	-9(10)
C21_5	143(19)	81(10)	171(13)	-39(8)	62(12)	-37(11)
C22_5	134(17)	71(7)	149(12)	-21(6)	63(12)	-29(8)
Br1_6	63.2(9)	142.3(18)	49.7(8)	19.9(10)	16.9(7)	19.9(10)
Cl1_6	59.1(18)	62(2)	64(2)	2.9(16)	15.0(15)	-0.6(16)
O1_6	52(5)	59(5)	49(4)	8(3)	16(4)	11(4)
O2_6	50(4)	57(5)	49(4)	9(4)	18(3)	11(3)
C1_6	47(5)	61(6)	48(5)	8(4)	13(4)	12(4)
C2_6	49(4)	69(5)	47(4)	8(4)	15(3)	12(4)
C3_6	53(4)	74(6)	60(4)	8(4)	22(3)	20(3)
C4_6	37(4)	70(4)	49(4)	10(3)	21(3)	9(4)
C5_6	41(5)	68(4)	58(5)	10(3)	25(4)	10(4)
C6_6	48(6)	72(5)	73(6)	19(4)	24(5)	9(5)
C7_6	52(6)	82(5)	71(5)	23(5)	23(4)	19(5)
C8_6	50(6)	85(6)	56(5)	22(4)	24(4)	14(5)
C9_6	42(5)	78(6)	46(4)	14(4)	24(3)	11(4)
C10_6	54(5)	75(5)	61(6)	8(5)	23(4)	19(4)
C11_6	56(5)	70(7)	68(4)	15(4)	19(4)	20(5)
C12_6	71(9)	100(11)	99(8)	0(8)	11(7)	43(8)
C13_6	88(12)	152(18)	109(8)	19(9)	15(8)	71(12)
C14_6	93(13)	141(16)	101(8)	25(10)	10(9)	56(11)
C15_6	72(9)	124(13)	77(6)	16(7)	5(6)	31(9)
C16_6	49(6)	82(9)	66(4)	12(5)	17(4)	9(6)
C17_6	40(5)	82(6)	63(5)	16(4)	16(4)	23(4)
C18_6	55(6)	97(7)	64(6)	14(5)	17(5)	7(5)
C19_6	60(8)	102(9)	86(6)	23(6)	25(6)	6(6)
C20_6	53(7)	96(9)	87(6)	29(6)	31(6)	10(6)
C21_6	47(6)	94(8)	81(6)	25(5)	30(5)	19(5)
C22_6	49(6)	85(8)	64(4)	12(5)	20(4)	10(5)
Br1_7	107.5(17)	57.3(12)	188(3)	17.7(15)	-14.3(17)	7.2(11)
Cl1_7	133(4)	121(4)	78(3)	-18(3)	54(3)	-6(3)
O1_7	62(5)	58(4)	51(5)	11(4)	17(4)	12(4)
O2_7	67(3)	55(5)	47(4)	4(4)	23(3)	14(3)
C1_7	67(4)	53(4)	43(5)	16(3)	25(3)	12(3)
C2_7	74(4)	62(4)	73(6)	3(4)	22(3)	7(3)
C3_7	72(6)	96(3)	94(3)	15(3)	11(3)	2(4)
C4_7	73(6)	64(5)	74(8)	-17(4)	9(5)	5(5)
C5_7	86(9)	88(8)	81(9)	-38(6)	21(7)	-1(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6_7	86(10)	86(8)	119(13)	-49(7)	21(8)	-2(7)
C7_7	70(10)	87(9)	135(13)	-38(8)	9(8)	-1(7)
C8_7	78(10)	72(8)	128(13)	-13(7)	8(8)	19(7)
C9_7	74(9)	58(6)	90(9)	-12(5)	6(6)	7(5)
C10_7	70(5)	50(7)	102(5)	17(5)	20(6)	8(4)
C11_7	93(7)	94(5)	57(7)	5(5)	1(6)	4(5)
C12_7	99(7)	114(11)	104(15)	36(11)	15(9)	20(7)
C13_7	115(10)	117(12)	84(12)	34(10)	14(10)	27(7)
C14_7	128(10)	133(13)	74(12)	52(12)	9(10)	20(9)
C15_7	124(9)	122(10)	80(13)	41(10)	7(10)	9(9)
C16_7	100(8)	106(8)	48(8)	15(7)	-13(7)	-7(6)
C17_7	59(6)	109(3)	105(2)	3(2)	1(3)	12(3)
C18_7	123(3)	121(3)	122(3)	-2.4(11)	34.1(14)	-0.2(12)
C19_7	121(3)	120(3)	120(3)	-1.2(12)	34.6(15)	0.4(12)
C20_7	140(11)	124(3)	131(4)	-6(3)	45(5)	-8(5)
C21_7	151(12)	119(4)	133(4)	-12(3)	48(6)	-20(6)
C22_7	94(10)	111(3)	123(4)	-3(2)	22(5)	2(5)
Br1_8	266(3)	108.4(17)	240(2)	69.1(16)	196(2)	91.3(17)
Cl1_8	71.4(18)	90(2)	65.9(18)	13.0(16)	17.4(15)	-0.8(17)
O1_8	68(4)	55(5)	49(5)	13(4)	14(3)	10(4)
O2_8	65(4)	57(5)	44(4)	10(3)	23(3)	17(4)
C1_8	72(4)	45(7)	48(4)	11(4)	16(3)	12(4)
C2_8	81(3)	58(6)	47(4)	12(4)	18(3)	5(3)
C3_8	75(5)	57(4)	46(5)	10(3)	14(4)	1(3)
C4_8	79(2)	79(3)	78(3)	2.6(14)	23.3(14)	1.4(13)
C5_8	83(3)	83(3)	82(3)	1.0(14)	24.3(14)	-0.1(13)
C6_8	86(3)	88(3)	87(3)	1.5(14)	25.4(15)	0.2(14)
C7_8	91(3)	91(3)	91(3)	0.7(14)	27.6(15)	1.3(13)
C8_8	90(3)	90(3)	91(3)	0.6(14)	27.7(15)	1.8(14)
C9_8	86(3)	84(3)	84(3)	-0.4(14)	26.2(15)	1.6(14)
C10_8	90(6)	57(4)	46(4)	13(4)	18(4)	-2(5)
C11_8	66(5)	58(6)	68(5)	18(4)	18(4)	0(4)
C12_8	74(6)	72(9)	81(6)	24(6)	8(5)	3(6)
C13_8	73(7)	87(10)	120(10)	32(8)	17(7)	11(7)
C14_8	70(7)	78(10)	121(9)	39(7)	33(7)	18(7)
C15_8	73(7)	78(9)	113(9)	15(7)	34(6)	20(6)
C16_8	63(6)	69(7)	75(6)	12(5)	22(5)	11(5)
C17_8	60(6)	56(5)	40(5)	11(3)	4(4)	4(4)
C18_8	57(6)	57(5)	49(6)	7(4)	6(5)	4(4)
C19_8	62(7)	77(7)	60(6)	6(5)	9(5)	-9(6)
C20_8	59(8)	85(7)	60(6)	9(5)	12(5)	-4(6)
C21_8	72(8)	86(8)	58(7)	6(5)	18(6)	-5(6)
C22_8	70(7)	72(7)	50(5)	1(5)	14(5)	-3(6)
Br1_12	148(3)	139(3)	146(3)	26(2)	47(3)	12(2)
Cl1_12	98(4)	96(4)	68(3)	9.3(18)	15(3)	2(3)
O1_12	55(2)	70(2)	56(2)	9.0(18)	13.5(15)	3.8(18)
O2_12	51(2)	65(4)	53(3)	5(3)	17(2)	8(3)
C1_12	54.7(17)	70.6(18)	56.9(19)	9.7(14)	13.3(14)	3.5(16)
C2_12	55.7(15)	71.9(16)	58.8(14)	10.9(11)	12.2(12)	2.3(12)
C3_12	55.5(15)	70.8(15)	58.7(15)	10.4(12)	12.4(11)	2.4(12)
C4_12	56(2)	73.0(18)	58.9(14)	11.5(13)	10.5(14)	0.2(15)
C5_12	73(8)	73(2)	60.5(16)	12.5(15)	16(3)	2(3)
C6_12	119(8)	79(2)	65.2(17)	17.8(16)	29(3)	17(3)
C7_12	93(7)	77(2)	60.2(19)	14.5(17)	18(3)	10(3)
C8_12	107(17)	77(2)	61(2)	16(2)	21(5)	13(5)
C9_12	66(12)	75(2)	58(2)	12.5(19)	10(4)	5(4)
C10_12	55.0(17)	70.7(16)	58.7(14)	11.1(13)	12.3(12)	2.5(13)
C11_12	55.8(19)	70.8(15)	57.6(17)	9.9(12)	12.5(13)	2.6(13)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12_12	50(10)	71(2)	57(3)	9.9(17)	15(4)	2(3)
C13_12	61(10)	72(2)	58(4)	8.8(18)	10(5)	4(3)
C14_12	66(10)	72(2)	59(4)	8.7(18)	8(5)	5(3)
C15_12	58(5)	71.0(15)	57(3)	9.4(16)	12(3)	3.3(17)
C16_12	48(9)	70.9(15)	57(3)	10.0(15)	15(4)	2.0(18)
C17_12	56.0(16)	69.7(16)	59(2)	9.3(16)	13.0(15)	2.4(13)
C18_12	58(2)	69.7(17)	61(3)	9.5(19)	15(2)	2.7(16)
C19_12	73(5)	71(2)	89(8)	16(3)	36(6)	8(3)
C20_12	94(5)	73(2)	133(10)	24(3)	66(7)	13(3)
C21_12	66(3)	69.8(18)	75(5)	12(2)	26(3)	4.6(17)
C22_12	57(3)	69.8(16)	61(5)	9.6(17)	15(3)	2.7(14)
Br1_1	115.0(16)	97.3(16)	88.0(13)	39.5(12)	16.2(11)	-18.1(13)
Cl1_1	49.3(18)	115(3)	73(2)	34(2)	14.8(17)	0(2)
O1_1	44(5)	113(9)	42(5)	18(5)	7(4)	22(5)
O2_1	45(5)	92(7)	40(4)	1(5)	5(4)	19(5)
C1_1	47(7)	88(11)	63(9)	-2(8)	16(7)	12(7)
C2_1	50(7)	59(8)	61(8)	11(6)	28(6)	11(6)
C3_1	45(7)	68(9)	72(9)	0(7)	25(6)	2(6)
C4_1	49(7)	60(8)	56(7)	0(6)	21(6)	8(6)
C5_1	61(8)	52(8)	52(7)	5(6)	18(6)	7(6)
C6_1	63(8)	57(8)	49(7)	-3(6)	18(6)	-6(6)
C7_1	84(11)	65(10)	57(8)	-7(7)	13(8)	11(8)
C8_1	78(10)	57(9)	67(9)	12(7)	12(8)	2(8)
C9_1	70(9)	48(8)	59(8)	8(6)	14(7)	-1(7)
C10_1	64(9)	90(12)	51(8)	4(7)	26(7)	9(8)
C11_1	40(7)	139(17)	61(9)	32(10)	16(6)	15(9)
C12_1	60(9)	68(10)	83(11)	13(9)	16(8)	16(8)
C13_1	65(10)	114(16)	81(12)	19(11)	4(9)	48(11)
C14_1	98(14)	190(30)	73(12)	51(14)	40(11)	88(17)
C15_1	123(17)	170(20)	82(13)	62(15)	50(13)	92(18)
C16_1	81(11)	122(16)	72(11)	34(11)	38(9)	40(11)
C17_1	71(9)	63(9)	68(9)	10(7)	30(8)	27(8)
C18_1	61(9)	111(14)	58(9)	-6(9)	28(7)	-29(9)
C19_1	83(12)	75(12)	115(16)	10(11)	29(11)	-26(10)
C20_1	121(16)	58(10)	70(11)	1(8)	3(10)	-3(10)
C21_1	240(30)	72(13)	77(13)	-20(10)	85(17)	-11(16)
C22_1	97(12)	71(11)	63(9)	-6(8)	22(9)	2(9)
Br1_4	148(3)	139(3)	146(3)	26(2)	47(3)	12(2)
Cl1_4	98(4)	96(4)	68(3)	9.3(18)	15(3)	2(3)
O1_4	55(2)	70(2)	56(2)	9.0(18)	13.5(15)	3.8(18)
O2_4	51(2)	65(4)	53(3)	5(3)	17(2)	8(3)
C1_4	54.7(17)	70.6(18)	56.9(19)	9.7(14)	13.3(14)	3.5(16)
C2_4	55.7(15)	71.9(16)	58.8(14)	10.9(11)	12.2(12)	2.3(12)
C3_4	55.5(15)	70.8(15)	58.7(15)	10.4(12)	12.4(11)	2.4(12)
C4_4	58(2)	72.4(19)	58.8(14)	11.1(13)	10.5(13)	-0.9(16)
C5_4	73(8)	73(2)	60.5(16)	12.5(15)	16(3)	2(3)
C6_4	119(8)	79(2)	65.2(17)	17.8(16)	29(3)	17(3)
C7_4	119(8)	79(2)	65.2(17)	17.8(16)	29(3)	17(3)
C8_4	93(7)	77(2)	60.2(19)	14.5(17)	18(3)	10(3)
C9_4	58(9)	73(3)	58(2)	11(2)	9(3)	-1(5)
C10_4	55.0(17)	70.7(16)	58.7(14)	11.1(13)	12.3(12)	2.5(13)
C11_4	55.8(19)	70.8(15)	57.6(17)	9.9(12)	12.5(13)	2.6(13)
C12_4	62(9)	71.6(19)	59(3)	8.8(17)	9(4)	4(3)
C13_4	59(8)	71(2)	58(3)	9.0(19)	11(5)	4(3)
C14_4	51(7)	71(2)	56(3)	9.7(19)	15(4)	2(3)
C15_4	58(5)	71.0(15)	57(3)	9.4(16)	12(3)	3.3(17)
C16_4	43(6)	70.5(15)	53(3)	11.1(14)	20(3)	0.5(16)
C17_4	56.0(16)	69.7(16)	59(2)	9.3(16)	13.0(15)	2.4(13)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C18_4	58(2)	69.7(17)	61(3)	9.5(19)	15(2)	2.7(16)
C19_4	83(5)	69.7(18)	107(8)	12(3)	49(6)	5(2)
C20_4	66(5)	69.6(18)	78(8)	11(3)	27(6)	4(2)
C21_4	66(3)	69.8(18)	75(5)	12(2)	26(3)	4.6(17)
C22_4	57(3)	69.8(16)	61(5)	9.6(17)	15(3)	2.7(14)
Br1_2	46.2(8)	118.9(15)	63.3(9)	-28.9(10)	4.4(7)	0.3(8)
Cl1_2	54.8(17)	72(2)	45.0(15)	-5.2(14)	13.1(13)	3.6(15)
O1_2	46(5)	93(8)	53(5)	-2(5)	10(4)	17(5)
O2_2	48(5)	78(7)	44(4)	-16(5)	2(4)	16(5)
C1_2	32(6)	87(11)	58(8)	-23(8)	5(5)	20(7)
C2_2	38(6)	80(10)	57(8)	-9(7)	6(6)	20(6)
C3_2	67(9)	61(9)	72(10)	-7(7)	21(8)	8(7)
C4_2	39(7)	86(11)	58(8)	-19(8)	0(6)	16(7)
C5_2	54(7)	69(9)	47(7)	-8(6)	27(6)	9(6)
C6_2	30(5)	76(9)	39(6)	2(6)	9(4)	1(6)
C7_2	37(6)	89(11)	44(7)	1(7)	15(5)	7(6)
C8_2	41(7)	93(12)	69(9)	-23(8)	22(6)	4(7)
C9_2	46(7)	88(12)	61(9)	-28(8)	-8(6)	22(7)
C10_2	37(6)	84(11)	73(10)	-17(8)	3(6)	8(7)
C11_2	24(5)	98(12)	67(9)	16(8)	4(5)	8(7)
C12_2	45(8)	104(14)	109(14)	38(12)	29(9)	18(9)
C13_2	66(11)	123(18)	96(14)	65(14)	21(10)	16(11)
C14_2	57(10)	150(20)	85(13)	58(15)	3(9)	-21(12)
C15_2	73(11)	92(13)	69(10)	9(9)	-31(9)	-19(10)
C16_2	66(10)	80(12)	83(12)	2(10)	0(9)	-1(9)
C17_2	87(4)	79(7)	102(7)	9(6)	31(4)	16(4)
C18_2	75(5)	88(6)	98(7)	10(6)	24(5)	22(5)
C19_2	74(5)	97(7)	96(5)	10(5)	21(5)	19(5)
C20_2	92(6)	120(9)	109(6)	-5(7)	31(5)	-1(6)
C21_2	100(4)	107(5)	108(4)	-1(3)	34(3)	-3(3)
C22_2	126(6)	170(14)	159(10)	-60(11)	71(7)	-42(8)
N1_11	80(4)	67(7)	61(6)	5(5)	33(3)	-8(3)
C23_11	85(4)	90(5)	88(5)	1(3)	26(3)	2(3)
C24_11	99(6)	126(15)	75(10)	-18(10)	17(6)	25(8)

Table S12.2.18: Bond Lengths in Å for **WL-2ClBr**.

Atom	Atom	Length/Å
Rh3	Rh4	2.3816(13)
Rh3	O2_5	2.032(6)
Rh3	O2_6	2.075(5)
Rh3	O2_7	2.029(6)
Rh3	O2_8	2.055(6)
Rh3	N1_11	2.239(12)
Rh4	O4	2.276(11)
Rh4	O1_5	2.038(6)
Rh4	O1_6	2.013(5)
Rh4	O1_7	2.057(6)
Rh4	O1_8	2.043(6)
Rh1	Rh2	2.3740(14)
Rh1	N1_10	2.240(12)
Rh1	O2_3	2.078(6)
Rh1	O2_12	2.032(7)
Rh1	O2_1	2.000(6)
Rh1	O2_4	2.030(7)
Rh1	O2_2	2.037(6)
Rh2	N1_9	2.227(12)
Rh2	O1_3	2.028(5)
Rh2	O1_12	2.073(6)
Rh2	O1_1	2.056(6)
Rh2	O1_4	2.073(6)
Rh2	O1_2	2.071(7)
N1_9	C23_9	1.086(12)
C23_9	C24_9	1.450(16)
N1_10	C23_10	1.086(12)
C23_10	C24_10	1.450(16)
Br1_3	C8_3	1.904(6)
Cl1_3	C5_3	1.745(6)
O1_3	C1_3	1.266(6)
O2_3	C1_3	1.271(6)
C1_3	C2_3	1.514(6)
C2_3	C3_3	1.552(6)
C2_3	C4_3	1.501(7)
C2_3	C10_3	1.492(7)
C3_3	C10_3	1.478(7)
C3_3	C11_3	1.530(7)
C3_3	C17_3	1.505(7)

Atom	Atom	Length/Å
C4_3	C5_3	1.383(7)
C4_3	C9_3	1.398(7)
C5_3	C6_3	1.419(7)
C6_3	C7_3	1.363(8)
C7_3	C8_3	1.374(9)
C8_3	C9_3	1.393(8)
C11_3	C12_3	1.405(8)
C11_3	C16_3	1.370(8)
C12_3	C13_3	1.402(9)
C13_3	C14_3	1.361(10)
C14_3	C15_3	1.360(10)
C15_3	C16_3	1.383(8)
C17_3	C18_3	1.372(8)
C17_3	C22_3	1.408(8)
C18_3	C19_3	1.385(8)
C19_3	C20_3	1.365(9)
C20_3	C21_3	1.349(9)
C21_3	C22_3	1.392(9)
Br1_5	C8_5	1.904(6)
Cl1_5	C5_5	1.745(6)
O1_5	C1_5	1.267(6)
O2_5	C1_5	1.271(6)
C1_5	C2_5	1.516(7)
C2_5	C3_5	1.553(6)
C2_5	C4_5	1.500(7)
C2_5	C10_5	1.492(7)
C3_5	C10_5	1.478(7)
C3_5	C11_5	1.530(7)
C3_5	C17_5	1.505(7)
C4_5	C5_5	1.383(7)
C4_5	C9_5	1.399(7)
C5_5	C6_5	1.419(7)
C6_5	C7_5	1.363(8)
C7_5	C8_5	1.374(9)
C8_5	C9_5	1.393(8)
C11_5	C12_5	1.404(8)
C11_5	C16_5	1.370(8)
C12_5	C13_5	1.402(9)
C13_5	C14_5	1.360(10)
C14_5	C15_5	1.360(10)
C15_5	C16_5	1.383(8)
C17_5	C18_5	1.372(8)
C17_5	C22_5	1.409(8)
C18_5	C19_5	1.385(8)
C19_5	C20_5	1.365(9)
C20_5	C21_5	1.349(9)
C21_5	C22_5	1.392(9)
Br1_6	C8_6	1.903(6)
Cl1_6	C5_6	1.745(6)
O1_6	C1_6	1.265(6)
O2_6	C1_6	1.271(6)
C1_6	C2_6	1.513(6)
C2_6	C3_6	1.552(6)
C2_6	C4_6	1.502(7)
C2_6	C10_6	1.493(7)
C3_6	C10_6	1.478(7)
C3_6	C11_6	1.531(7)
C3_6	C17_6	1.505(7)

Atom	Atom	Length/Å
C4_6	C5_6	1.382(7)
C4_6	C9_6	1.398(7)
C5_6	C6_6	1.419(7)
C6_6	C7_6	1.363(8)
C7_6	C8_6	1.374(9)
C8_6	C9_6	1.393(8)
C11_6	C12_6	1.405(8)
C11_6	C16_6	1.370(8)
C12_6	C13_6	1.402(9)
C13_6	C14_6	1.361(10)
C14_6	C15_6	1.360(10)
C15_6	C16_6	1.383(8)
C17_6	C18_6	1.372(8)
C17_6	C22_6	1.408(8)
C18_6	C19_6	1.385(8)
C19_6	C20_6	1.365(9)
C20_6	C21_6	1.349(9)
C21_6	C22_6	1.392(9)
Br1_7	C8_7	1.903(6)
Cl1_7	C5_7	1.744(6)
O1_7	C1_7	1.266(6)
O2_7	C1_7	1.272(6)
C1_7	C2_7	1.513(7)
C2_7	C3_7	1.551(6)
C2_7	C4_7	1.501(7)
C2_7	C10_7	1.493(7)
C3_7	C10_7	1.478(7)
C3_7	C11_7	1.531(7)
C3_7	C17_7	1.505(7)
C4_7	C5_7	1.382(7)
C4_7	C9_7	1.399(7)
C5_7	C6_7	1.419(7)
C6_7	C7_7	1.363(8)
C7_7	C8_7	1.374(9)
C8_7	C9_7	1.393(8)
C11_7	C12_7	1.405(8)
C11_7	C16_7	1.369(8)
C12_7	C13_7	1.402(9)
C13_7	C14_7	1.361(10)
C14_7	C15_7	1.360(10)
C15_7	C16_7	1.383(8)
C17_7	C18_7	1.373(8)
C17_7	C22_7	1.408(8)
C18_7	C19_7	1.385(8)
C19_7	C20_7	1.365(9)
C20_7	C21_7	1.349(9)
C21_7	C22_7	1.393(9)
Br1_8	C8_8	1.904(6)
Cl1_8	C5_8	1.745(6)
O1_8	C1_8	1.265(6)
O2_8	C1_8	1.271(6)
C1_8	C2_8	1.513(6)
C2_8	C3_8	1.552(6)
C2_8	C4_8	1.502(7)
C2_8	C10_8	1.492(7)
C3_8	C10_8	1.477(7)
C3_8	C11_8	1.531(7)
C3_8	C17_8	1.505(7)

Atom	Atom	Length/Å
C4_8	C5_8	1.383(7)
C4_8	C9_8	1.399(7)
C5_8	C6_8	1.419(7)
C6_8	C7_8	1.363(8)
C7_8	C8_8	1.374(9)
C8_8	C9_8	1.393(8)
C11_8	C12_8	1.405(8)
C11_8	C16_8	1.369(8)
C12_8	C13_8	1.402(9)
C13_8	C14_8	1.360(10)
C14_8	C15_8	1.360(10)
C15_8	C16_8	1.383(8)
C17_8	C18_8	1.372(8)
C17_8	C22_8	1.408(8)
C18_8	C19_8	1.384(8)
C19_8	C20_8	1.365(9)
C20_8	C21_8	1.349(9)
C21_8	C22_8	1.392(9)
Br1_12	C8_12	1.904(6)
Cl1_12	C5_12	1.745(6)
O1_12	C1_12	1.266(6)
O2_12	C1_12	1.271(6)
C1_12	C2_12	1.513(7)
C2_12	C3_12	1.551(6)
C2_12	C4_12	1.502(7)
C2_12	C10_12	1.493(7)
C3_12	C10_12	1.478(7)
C3_12	C11_12	1.531(7)
C3_12	C17_12	1.505(7)
C4_12	C5_12	1.382(7)
C4_12	C9_12	1.399(7)
C5_12	C6_12	1.419(7)
C6_12	C7_12	1.363(8)
C7_12	C8_12	1.374(9)
C8_12	C9_12	1.393(8)
C11_12	C12_12	1.405(8)
C11_12	C16_12	1.370(8)
C12_12	C13_12	1.402(9)
C13_12	C14_12	1.361(10)
C14_12	C15_12	1.360(10)
C15_12	C16_12	1.383(8)
C17_12	C18_12	1.372(8)
C17_12	C22_12	1.408(8)
C18_12	C19_12	1.385(9)
C19_12	C20_12	1.365(9)
C20_12	C21_12	1.349(9)
C21_12	C22_12	1.392(9)
Br1_1	C8_1	1.904(6)
Cl1_1	C5_1	1.745(6)
O1_1	C1_1	1.266(6)
O2_1	C1_1	1.271(6)
C1_1	C2_1	1.514(7)
C2_1	C3_1	1.551(6)
C2_1	C4_1	1.502(7)
C2_1	C10_1	1.494(7)
C3_1	C10_1	1.478(7)
C3_1	C11_1	1.531(7)
C3_1	C17_1	1.505(7)

Atom	Atom	Length/Å
C4_1	C5_1	1.382(7)
C4_1	C9_1	1.400(7)
C5_1	C6_1	1.419(7)
C6_1	C7_1	1.363(8)
C7_1	C8_1	1.374(9)
C8_1	C9_1	1.393(8)
C11_1	C12_1	1.405(8)
C11_1	C16_1	1.370(8)
C12_1	C13_1	1.403(9)
C13_1	C14_1	1.361(10)
C14_1	C15_1	1.360(10)
C15_1	C16_1	1.383(8)
C17_1	C18_1	1.372(8)
C17_1	C22_1	1.408(8)
C18_1	C19_1	1.385(8)
C19_1	C20_1	1.365(9)
C20_1	C21_1	1.349(9)
C21_1	C22_1	1.392(9)
Br1_4	C8_4	1.904(6)
Cl1_4	C5_4	1.745(6)
O1_4	C1_4	1.266(6)
O2_4	C1_4	1.272(6)
C1_4	C2_4	1.514(7)
C2_4	C3_4	1.552(6)
C2_4	C4_4	1.501(7)
C2_4	C10_4	1.492(7)
C3_4	C10_4	1.478(7)
C3_4	C11_4	1.530(7)
C3_4	C17_4	1.506(7)
C4_4	C5_4	1.383(7)
C4_4	C9_4	1.398(7)
C5_4	C6_4	1.419(7)
C6_4	C7_4	1.363(8)
C7_4	C8_4	1.374(9)
C8_4	C9_4	1.393(8)
C11_4	C12_4	1.405(8)
C11_4	C16_4	1.370(8)
C12_4	C13_4	1.403(9)
C13_4	C14_4	1.361(10)
C14_4	C15_4	1.360(10)
C15_4	C16_4	1.383(8)
C17_4	C18_4	1.373(8)
C17_4	C22_4	1.409(8)
C18_4	C19_4	1.385(8)
C19_4	C20_4	1.365(9)
C20_4	C21_4	1.349(9)
C21_4	C22_4	1.392(9)
Br1_2	C8_2	1.904(6)
Cl1_2	C5_2	1.745(6)
O1_2	C1_2	1.266(6)
O2_2	C1_2	1.271(6)
C1_2	C2_2	1.514(7)
C2_2	C3_2	1.552(6)
C2_2	C4_2	1.501(7)
C2_2	C10_2	1.493(7)
C3_2	C10_2	1.477(7)
C3_2	C11_2	1.531(7)
C3_2	C17_2	1.505(7)

Atom	Atom	Length/Å
C4_2	C5_2	1.382(7)
C4_2	C9_2	1.399(7)
C5_2	C6_2	1.419(7)
C6_2	C7_2	1.363(8)
C7_2	C8_2	1.374(9)
C8_2	C9_2	1.393(8)
C11_2	C12_2	1.405(8)
C11_2	C16_2	1.370(8)
C12_2	C13_2	1.402(9)
C13_2	C14_2	1.360(10)
C14_2	C15_2	1.360(10)
C15_2	C16_2	1.383(8)
C17_2	C18_2	1.373(8)
C17_2	C22_2	1.409(8)
C18_2	C19_2	1.385(8)
C19_2	C20_2	1.365(9)
C20_2	C21_2	1.349(9)
C21_2	C22_2	1.393(9)
N1_11	C23_11	1.086(12)
C23_11	C24_11	1.450(16)

Table S12.2.19: Bond Angles in ° for **WL-2ClBr**.

Atom	Atom	Atom	Angle/°
O2_5	Rh3	Rh4	88.21(16)
O2_5	Rh3	O2_6	91.4(4)
O2_5	Rh3	O2_8	88.7(4)
O2_5	Rh3	N1_11	88.7(4)
O2_6	Rh3	Rh4	86.62(15)
O2_6	Rh3	N1_11	97.1(3)
O2_7	Rh3	Rh4	88.33(17)
O2_7	Rh3	O2_5	176.5(3)
O2_7	Rh3	O2_6	89.0(4)
O2_7	Rh3	O2_8	90.5(4)
O2_7	Rh3	N1_11	94.8(4)
O2_8	Rh3	Rh4	88.04(16)
O2_8	Rh3	O2_6	174.7(2)
O2_8	Rh3	N1_11	88.2(3)
N1_11	Rh3	Rh4	175.2(3)
O4	Rh4	Rh3	177.9(4)
O1_5	Rh4	Rh3	87.67(17)
O1_5	Rh4	O4	90.3(4)
O1_5	Rh4	O1_7	174.0(3)
O1_5	Rh4	O1_8	92.2(4)
O1_6	Rh4	Rh3	88.63(16)
O1_6	Rh4	O4	90.8(4)
O1_6	Rh4	O1_5	87.6(4)
O1_6	Rh4	O1_7	89.6(4)
O1_6	Rh4	O1_8	175.9(3)
O1_7	Rh4	Rh3	87.00(17)
O1_7	Rh4	O4	95.0(4)
O1_8	Rh4	Rh3	87.28(17)
O1_8	Rh4	O4	93.3(4)
O1_8	Rh4	O1_7	90.3(4)
N1_10	Rh1	Rh2	175.7(3)
O2_3	Rh1	Rh2	87.35(16)
O2_3	Rh1	N1_10	96.8(4)
O2_12	Rh1	Rh2	89.6(3)
O2_12	Rh1	N1_10	91.9(4)
O2_12	Rh1	O2_3	84.5(7)
O2_12	Rh1	O2_2	174.6(6)
O2_1	Rh1	Rh2	88.28(18)
O2_1	Rh1	N1_10	87.5(4)
O2_1	Rh1	O2_3	175.6(3)
O2_1	Rh1	O2_12	96.1(8)
O2_1	Rh1	O2_4	85.7(6)
O2_1	Rh1	O2_2	88.6(4)
O2_4	Rh1	Rh2	85.5(3)
O2_4	Rh1	N1_10	95.2(4)
O2_4	Rh1	O2_3	94.5(6)
O2_4	Rh1	O2_2	171.4(5)
O2_2	Rh1	Rh2	87.83(17)
O2_2	Rh1	N1_10	91.0(4)
O2_2	Rh1	O2_3	90.7(4)
N1_9	Rh2	Rh1	179.2(4)
O1_3	Rh2	Rh1	87.85(17)
O1_3	Rh2	N1_9	92.9(4)
O1_3	Rh2	O1_12	90.1(9)
O1_3	Rh2	O1_1	174.7(3)
O1_3	Rh2	O1_4	89.3(8)
O1_3	Rh2	O1_2	88.8(4)
O1_12	Rh2	Rh1	86.7(3)
O1_12	Rh2	N1_9	93.4(6)
O1_1	Rh2	Rh1	86.84(17)
O1_1	Rh2	N1_9	92.4(4)
O1_1	Rh2	O1_12	89.8(9)
O1_1	Rh2	O1_4	90.6(8)
O1_1	Rh2	O1_2	90.8(4)
O1_4	Rh2	Rh1	88.1(4)
O1_4	Rh2	N1_9	92.0(6)
O1_2	Rh2	Rh1	87.82(17)
O1_2	Rh2	N1_9	92.1(5)
O1_2	Rh2	O1_12	174.5(5)
O1_2	Rh2	O1_4	175.6(6)
C23_9	N1_9	Rh2	178.9(15)
N1_9	C23_9	C24_9	174(2)
C23_10	N1_10	Rh1	171.2(15)
N1_10	C23_10	C24_10	176(2)
C1_3	O1_3	Rh2	117.2(4)
C1_3	O2_3	Rh1	116.4(4)
O1_3	C1_3	O2_3	126.3(5)
O1_3	C1_3	C2_3	117.2(4)
O2_3	C1_3	C2_3	116.0(4)
C1_3	C2_3	C3_3	122.4(4)
C4_3	C2_3	C1_3	112.7(4)
C4_3	C2_3	C3_3	117.9(4)
C10_3	C2_3	C1_3	115.0(4)

Atom	Atom	Atom	Angle/°
C10_3	C2_3	C3_3	58.0(3)
C10_3	C2_3	C4_3	120.6(4)
C10_3	C3_3	C2_3	58.9(3)
C10_3	C3_3	C11_3	119.0(5)
C10_3	C3_3	C17_3	120.1(5)
C11_3	C3_3	C2_3	121.4(4)
C17_3	C3_3	C2_3	117.4(4)
C17_3	C3_3	C11_3	111.2(4)
C5_3	C4_3	C2_3	122.3(5)
C5_3	C4_3	C9_3	116.9(5)
C9_3	C4_3	C2_3	120.4(5)
C4_3	C5_3	Cl1_3	120.7(4)
C4_3	C5_3	C6_3	122.6(5)
C6_3	C5_3	Cl1_3	116.8(4)
C7_3	C6_3	C5_3	118.7(6)
C6_3	C7_3	C8_3	119.9(5)
C7_3	C8_3	Br1_3	121.1(4)
C7_3	C8_3	C9_3	121.5(6)
C9_3	C8_3	Br1_3	117.4(5)
C8_3	C9_3	C4_3	120.4(6)
C3_3	C10_3	C2_3	63.0(3)
C12_3	C11_3	C3_3	116.4(5)
C16_3	C11_3	C3_3	123.5(5)
C16_3	C11_3	C12_3	120.1(5)
C13_3	C12_3	C11_3	118.5(6)
C14_3	C13_3	C12_3	120.3(6)
C15_3	C14_3	C13_3	120.1(6)
C14_3	C15_3	C16_3	120.9(7)
C11_3	C16_3	C15_3	119.4(6)
C18_3	C17_3	C3_3	121.8(5)
C18_3	C17_3	C22_3	116.0(5)
C22_3	C17_3	C3_3	121.8(5)
C17_3	C18_3	C19_3	122.5(6)
C20_3	C19_3	C18_3	119.3(6)
C21_3	C20_3	C19_3	120.7(6)
C20_3	C21_3	C22_3	119.8(6)
C21_3	C22_3	C17_3	121.2(6)
C1_5	O1_5	Rh4	116.7(4)
C1_5	O2_5	Rh3	117.7(4)
O1_5	C1_5	O2_5	126.1(5)
O1_5	C1_5	C2_5	116.9(4)
O2_5	C1_5	C2_5	115.8(4)
C1_5	C2_5	C3_5	121.9(4)
C4_5	C2_5	C1_5	112.7(4)
C4_5	C2_5	C3_5	118.1(4)
C10_5	C2_5	C1_5	114.5(4)
C10_5	C2_5	C3_5	58.0(3)
C10_5	C2_5	C4_5	121.4(4)
C10_5	C3_5	C2_5	58.9(3)
C10_5	C3_5	C11_5	119.5(5)
C10_5	C3_5	C17_5	119.6(5)
C11_5	C3_5	C2_5	120.8(4)
C17_5	C3_5	C2_5	118.0(4)
C17_5	C3_5	C11_5	111.2(4)
C5_5	C4_5	C2_5	122.4(5)
C5_5	C4_5	C9_5	116.7(5)
C9_5	C4_5	C2_5	120.8(5)
C4_5	C5_5	Cl1_5	121.0(4)
C4_5	C5_5	C6_5	122.5(5)
C6_5	C5_5	Cl1_5	116.4(4)
C7_5	C6_5	C5_5	118.6(6)
C6_5	C7_5	C8_5	119.7(5)
C7_5	C8_5	Br1_5	120.7(4)
C7_5	C8_5	C9_5	121.5(6)
C9_5	C8_5	Br1_5	117.7(5)
C8_5	C9_5	C4_5	120.5(6)
C3_5	C10_5	C2_5	63.1(3)
C12_5	C11_5	C3_5	116.6(5)
C16_5	C11_5	C3_5	123.3(5)
C16_5	C11_5	C12_5	120.1(5)
C13_5	C12_5	C11_5	118.4(6)
C14_5	C13_5	C12_5	120.4(6)
C15_5	C14_5	C13_5	120.3(6)
C14_5	C15_5	C16_5	121.0(7)
C11_5	C16_5	C15_5	119.6(6)
C18_5	C17_5	C3_5	122.1(5)
C18_5	C17_5	C22_5	116.1(5)
C22_5	C17_5	C3_5	121.6(5)
C17_5	C18_5	C19_5	122.5(6)
C20_5	C19_5	C18_5	119.3(6)
C21_5	C20_5	C19_5	120.8(6)
C20_5	C21_5	C22_5	119.8(6)
C21_5	C22_5	C17_5	121.1(6)
C1_6	O1_6	Rh4	117.3(4)
C1_6	O2_6	Rh3	117.0(4)
O1_6	C1_6	O2_6	126.5(5)
O1_6	C1_6	C2_6	117.4(4)
O2_6	C1_6	C2_6	116.0(4)
C1_6	C2_6	C3_6	122.6(4)
C4_6	C2_6	C1_6	112.6(4)
C4_6	C2_6	C3_6	118.0(4)
C10_6	C2_6	C1_6	115.1(4)
C10_6	C2_6	C3_6	58.0(3)
C10_6	C2_6	C4_6	120.1(4)
C10_6	C3_6	C2_6	59.0(3)
C10_6	C3_6	C11_6	118.8(5)
C10_6	C3_6	C17_6	120.3(5)
C11_6	C3_6	C2_6	121.6(4)
C17_6	C3_6	C2_6	117.4(4)
C17_6	C3_6	C11_6	111.1(4)
C5_6	C4_6	C2_6	122.5(5)
C5_6	C4_6	C9_6	116.9(5)
C9_6	C4_6	C2_6	120.2(5)
C4_6	C5_6	Cl1_6	120.8(4)
C4_6	C5_6	C6_6	122.5(5)
C6_6	C5_6	Cl1_6	116.7(4)
C7_6	C6_6	C5_6	118.7(6)
C6_6	C7_6	C8_6	119.8(5)
C7_6	C8_6	Br1_6	121.1(4)
C7_6	C8_6	C9_6	121.4(6)
C9_6	C8_6	Br1_6	117.4(5)
C8_6	C9_6	C4_6	120.3(6)
C3_6	C10_6	C2_6	63.0(3)
C12_6	C11_6	C3_6	116.3(5)
C16_6	C11_6	C3_6	123.5(5)
C16_6	C11_6	C12_6	120.1(5)

Atom	Atom	Atom	Angle/°
C13_6	C12_6	C11_6	118.4(6)
C14_6	C13_6	C12_6	120.3(6)
C15_6	C14_6	C13_6	120.3(6)
C14_6	C15_6	C16_6	121.1(7)
C11_6	C16_6	C15_6	119.6(6)
C18_6	C17_6	C3_6	121.8(5)
C18_6	C17_6	C22_6	116.1(5)
C22_6	C17_6	C3_6	121.9(5)
C17_6	C18_6	C19_6	122.5(6)
C20_6	C19_6	C18_6	119.3(6)
C21_6	C20_6	C19_6	120.7(6)
C20_6	C21_6	C22_6	119.8(6)
C21_6	C22_6	C17_6	121.2(6)
C1_7	O1_7	Rh4	117.7(4)
C1_7	O2_7	Rh3	117.3(4)
O1_7	C1_7	O2_7	126.3(5)
O1_7	C1_7	C2_7	117.5(4)
O2_7	C1_7	C2_7	115.8(4)
C1_7	C2_7	C3_7	122.4(4)
C4_7	C2_7	C1_7	112.6(4)
C4_7	C2_7	C3_7	118.2(4)
C10_7	C2_7	C1_7	115.2(4)
C10_7	C2_7	C3_7	58.0(3)
C10_7	C2_7	C4_7	120.0(4)
C10_7	C3_7	C2_7	59.0(3)
C10_7	C3_7	C11_7	118.6(5)
C10_7	C3_7	C17_7	120.5(5)
C11_7	C3_7	C2_7	121.6(4)
C17_7	C3_7	C2_7	117.4(4)
C17_7	C3_7	C11_7	111.1(4)
C5_7	C4_7	C2_7	122.7(5)
C5_7	C4_7	C9_7	116.8(5)
C9_7	C4_7	C2_7	120.3(5)
C4_7	C5_7	Cl1_7	120.9(4)
C4_7	C5_7	C6_7	122.5(5)
C6_7	C5_7	Cl1_7	116.6(4)
C7_7	C6_7	C5_7	118.6(6)
C6_7	C7_7	C8_7	119.8(6)
C7_7	C8_7	Br1_7	121.1(4)
C7_7	C8_7	C9_7	121.5(6)
C9_7	C8_7	Br1_7	117.5(5)
C8_7	C9_7	C4_7	120.2(6)
C3_7	C10_7	C2_7	63.0(3)
C12_7	C11_7	C3_7	116.2(5)
C16_7	C11_7	C3_7	123.6(5)
C16_7	C11_7	C12_7	120.2(5)
C13_7	C12_7	C11_7	118.5(6)
C14_7	C13_7	C12_7	120.3(6)
C15_7	C14_7	C13_7	120.3(6)
C14_7	C15_7	C16_7	121.0(7)
C11_7	C16_7	C15_7	119.5(6)
C18_7	C17_7	C3_7	121.7(5)
C18_7	C17_7	C22_7	116.0(5)
C22_7	C17_7	C3_7	122.0(5)
C17_7	C18_7	C19_7	122.5(6)
C20_7	C19_7	C18_7	119.2(6)
C21_7	C20_7	C19_7	120.6(6)
C20_7	C21_7	C22_7	119.7(6)
C21_7	C22_7	C17_7	121.1(6)
C1_8	O1_8	Rh4	118.0(4)
C1_8	O2_8	Rh3	116.8(4)
O1_8	C1_8	O2_8	126.5(5)
O1_8	C1_8	C2_8	117.4(4)
O2_8	C1_8	C2_8	116.1(4)
C1_8	C2_8	C3_8	122.3(4)
C4_8	C2_8	C1_8	112.7(4)
C4_8	C2_8	C3_8	118.1(4)
C10_8	C2_8	C1_8	115.2(4)
C10_8	C2_8	C3_8	58.0(3)
C10_8	C2_8	C4_8	120.2(4)
C10_8	C3_8	C2_8	59.0(3)
C10_8	C3_8	C11_8	118.7(5)
C10_8	C3_8	C17_8	120.5(5)
C11_8	C3_8	C2_8	121.5(4)
C17_8	C3_8	C2_8	117.4(4)
C17_8	C3_8	C11_8	111.1(4)
C5_8	C4_8	C2_8	122.3(5)
C5_8	C4_8	C9_8	116.8(5)
C9_8	C4_8	C2_8	120.3(5)
C4_8	C5_8	Cl1_8	120.6(4)
C4_8	C5_8	C6_8	122.5(5)
C6_8	C5_8	Cl1_8	116.7(4)
C7_8	C6_8	C5_8	118.7(6)
C6_8	C7_8	C8_8	119.8(5)
C7_8	C8_8	Br1_8	120.9(4)
C7_8	C8_8	C9_8	121.4(6)
C9_8	C8_8	Br1_8	117.4(5)
C8_8	C9_8	C4_8	120.4(6)
C3_8	C10_8	C2_8	63.0(3)
C12_8	C11_8	C3_8	116.3(5)
C16_8	C11_8	C3_8	123.5(5)
C16_8	C11_8	C12_8	120.1(5)
C13_8	C12_8	C11_8	118.5(6)
C14_8	C13_8	C12_8	120.4(6)
C15_8	C14_8	C13_8	120.3(6)
C14_8	C15_8	C16_8	121.1(7)
C11_8	C16_8	C15_8	119.5(6)
C18_8	C17_8	C3_8	121.8(5)
C18_8	C17_8	C22_8	116.1(5)
C22_8	C17_8	C3_8	122.0(5)
C17_8	C18_8	C19_8	122.6(6)
C20_8	C19_8	C18_8	119.3(6)
C21_8	C20_8	C19_8	120.8(6)
C20_8	C21_8	C22_8	119.8(6)
C21_8	C22_8	C17_8	121.2(6)
C1_12	O1_12	Rh2	118.5(5)
C1_12	O2_12	Rh1	117.2(5)
O1_12	C1_12	O2_12	126.4(5)
O1_12	C1_12	C2_12	117.4(4)
O2_12	C1_12	C2_12	116.0(4)
C1_12	C2_12	C3_12	122.5(4)
C4_12	C2_12	C1_12	112.6(4)
C4_12	C2_12	C3_12	118.3(4)
C10_12	C2_12	C1_12	115.0(4)
C10_12	C2_12	C3_12	58.1(3)
C10_12	C2_12	C4_12	120.0(4)

Atom	Atom	Atom	Angle/°
C10_12	C3_12	C2_12	59.0(3)
C10_12	C3_12	C11_12	118.5(5)
C10_12	C3_12	C17_12	120.2(5)
C11_12	C3_12	C2_12	121.7(4)
C17_12	C3_12	C2_12	117.5(4)
C17_12	C3_12	C11_12	111.1(4)
C5_12	C4_12	C2_12	122.5(5)
C5_12	C4_12	C9_12	116.8(5)
C9_12	C4_12	C2_12	120.3(5)
C4_12	C5_12	Cl1_12	120.8(4)
C4_12	C5_12	C6_12	122.6(5)
C6_12	C5_12	Cl1_12	116.6(4)
C7_12	C6_12	C5_12	118.7(6)
C6_12	C7_12	C8_12	119.8(5)
C7_12	C8_12	Br1_12	121.0(4)
C7_12	C8_12	C9_12	121.4(6)
C9_12	C8_12	Br1_12	117.5(5)
C8_12	C9_12	C4_12	120.3(6)
C3_12	C10_12	C2_12	62.9(3)
C12_12	C11_12	C3_12	116.2(5)
C16_12	C11_12	C3_12	123.6(5)
C16_12	C11_12	C12_12	120.0(5)
C13_12	C12_12	C11_12	118.4(6)
C14_12	C13_12	C12_12	120.3(6)
C15_12	C14_12	C13_12	120.2(6)
C14_12	C15_12	C16_12	121.0(7)
C11_12	C16_12	C15_12	119.4(6)
C18_12	C17_12	C3_12	121.9(5)
C18_12	C17_12	C22_12	116.1(5)
C22_12	C17_12	C3_12	122.0(5)
C17_12	C18_12	C19_12	122.4(6)
C20_12	C19_12	C18_12	119.3(6)
C21_12	C20_12	C19_12	120.8(6)
C20_12	C21_12	C22_12	119.8(6)
C21_12	C22_12	C17_12	121.2(6)
C1_1	O1_1	Rh2	116.5(4)
C1_1	O2_1	Rh1	117.6(4)
O1_1	C1_1	O2_1	126.5(5)
O1_1	C1_1	C2_1	117.4(4)
O2_1	C1_1	C2_1	116.0(4)
C1_1	C2_1	C3_1	122.4(4)
C4_1	C2_1	C1_1	112.7(4)
C4_1	C2_1	C3_1	118.6(4)
C10_1	C2_1	C1_1	114.9(4)
C10_1	C2_1	C3_1	58.0(3)
C10_1	C2_1	C4_1	119.8(4)
C10_1	C3_1	C2_1	59.1(3)
C10_1	C3_1	C11_1	118.6(5)
C10_1	C3_1	C17_1	120.4(5)
C11_1	C3_1	C2_1	121.5(4)
C17_1	C3_1	C2_1	117.6(4)
C17_1	C3_1	C11_1	111.1(4)
C5_1	C4_1	C2_1	122.8(5)
C5_1	C4_1	C9_1	116.7(5)
C9_1	C4_1	C2_1	119.9(5)
C4_1	C5_1	Cl1_1	121.0(4)
C4_1	C5_1	C6_1	122.6(5)
C6_1	C5_1	Cl1_1	116.4(4)

Atom	Atom	Atom	Angle/°
C7_1	C6_1	C5_1	118.7(6)
C6_1	C7_1	C8_1	119.7(5)
C7_1	C8_1	Br1_1	120.9(4)
C7_1	C8_1	C9_1	121.4(6)
C9_1	C8_1	Br1_1	117.5(5)
C8_1	C9_1	C4_1	120.5(6)
C3_1	C10_1	C2_1	62.9(3)
C12_1	C11_1	C3_1	116.3(5)
C16_1	C11_1	C3_1	123.5(5)
C16_1	C11_1	C12_1	120.0(5)
C13_1	C12_1	C11_1	118.4(6)
C14_1	C13_1	C12_1	120.3(6)
C15_1	C14_1	C13_1	120.3(6)
C14_1	C15_1	C16_1	121.0(7)
C11_1	C16_1	C15_1	119.4(6)
C18_1	C17_1	C3_1	121.7(5)
C18_1	C17_1	C22_1	116.1(5)
C22_1	C17_1	C3_1	122.0(5)
C17_1	C18_1	C19_1	122.5(6)
C20_1	C19_1	C18_1	119.3(6)
C21_1	C20_1	C19_1	120.8(6)
C20_1	C21_1	C22_1	119.8(6)
C21_1	C22_1	C17_1	121.2(6)
C1_4	O1_4	Rh2	113.1(5)
C1_4	O2_4	Rh1	119.1(5)
O1_4	C1_4	O2_4	126.2(5)
O1_4	C1_4	C2_4	117.2(4)
O2_4	C1_4	C2_4	115.6(4)
C1_4	C2_4	C3_4	122.5(4)
C4_4	C2_4	C1_4	112.6(4)
C4_4	C2_4	C3_4	117.9(4)
C10_4	C2_4	C1_4	115.0(4)
C10_4	C2_4	C3_4	58.0(3)
C10_4	C2_4	C4_4	120.7(4)
C10_4	C3_4	C2_4	58.9(3)
C10_4	C3_4	C11_4	119.1(5)
C10_4	C3_4	C17_4	120.0(5)
C11_4	C3_4	C2_4	121.4(4)
C17_4	C3_4	C2_4	117.4(4)
C17_4	C3_4	C11_4	111.2(4)
C5_4	C4_4	C2_4	122.4(5)
C5_4	C4_4	C9_4	116.9(5)
C9_4	C4_4	C2_4	120.6(5)
C4_4	C5_4	Cl1_4	120.7(4)
C4_4	C5_4	C6_4	122.4(5)
C6_4	C5_4	Cl1_4	116.7(4)
C7_4	C6_4	C5_4	118.6(6)
C6_4	C7_4	C8_4	119.8(6)
C7_4	C8_4	Br1_4	121.0(4)
C7_4	C8_4	C9_4	121.4(6)
C9_4	C8_4	Br1_4	117.5(5)
C8_4	C9_4	C4_4	120.3(6)
C3_4	C10_4	C2_4	63.0(3)
C12_4	C11_4	C3_4	116.4(5)
C16_4	C11_4	C3_4	123.5(5)
C16_4	C11_4	C12_4	120.1(5)
C13_4	C12_4	C11_4	118.4(6)
C14_4	C13_4	C12_4	120.3(6)

Atom	Atom	Atom	Angle/°
C15_4	C14_4	C13_4	120.2(6)
C14_4	C15_4	C16_4	121.0(7)
C11_4	C16_4	C15_4	119.5(6)
C18_4	C17_4	C3_4	121.7(5)
C18_4	C17_4	C22_4	115.9(5)
C22_4	C17_4	C3_4	121.6(5)
C17_4	C18_4	C19_4	122.5(6)
C20_4	C19_4	C18_4	119.3(6)
C21_4	C20_4	C19_4	120.7(6)
C20_4	C21_4	C22_4	119.7(6)
C21_4	C22_4	C17_4	121.2(6)
C1_2	O1_2	Rh2	116.4(4)
C1_2	O2_2	Rh1	118.3(4)
O1_2	C1_2	O2_2	126.5(5)
O1_2	C1_2	C2_2	117.3(4)
O2_2	C1_2	C2_2	116.0(4)
C1_2	C2_2	C3_2	122.1(4)
C4_2	C2_2	C1_2	112.7(4)
C4_2	C2_2	C3_2	118.2(4)
C10_2	C2_2	C1_2	115.1(4)
C10_2	C2_2	C3_2	58.0(3)
C10_2	C2_2	C4_2	120.3(4)
C10_2	C3_2	C2_2	59.0(3)
C10_2	C3_2	C11_2	118.8(5)
C10_2	C3_2	C17_2	120.3(5)
C11_2	C3_2	C2_2	121.4(4)
C17_2	C3_2	C2_2	117.4(4)
C17_2	C3_2	C11_2	111.1(4)
C5_2	C4_2	C2_2	122.6(5)
C5_2	C4_2	C9_2	116.9(5)
C9_2	C4_2	C2_2	120.5(5)
C4_2	C5_2	Cl1_2	120.9(4)
C4_2	C5_2	C6_2	122.4(5)
C6_2	C5_2	Cl1_2	116.7(4)
C7_2	C6_2	C5_2	118.7(6)
C6_2	C7_2	C8_2	119.9(5)
C7_2	C8_2	Br1_2	120.9(4)
C7_2	C8_2	C9_2	121.3(6)
C9_2	C8_2	Br1_2	117.6(5)
C8_2	C9_2	C4_2	120.4(6)
C3_2	C10_2	C2_2	63.0(3)
C12_2	C11_2	C3_2	116.3(5)
C16_2	C11_2	C3_2	123.5(5)
C16_2	C11_2	C12_2	120.1(5)
C13_2	C12_2	C11_2	118.5(6)
C14_2	C13_2	C12_2	120.4(6)
C15_2	C14_2	C13_2	120.3(6)
C14_2	C15_2	C16_2	121.1(7)
C11_2	C16_2	C15_2	119.6(6)
C18_2	C17_2	C3_2	121.6(5)
C18_2	C17_2	C22_2	115.9(5)
C22_2	C17_2	C3_2	121.7(5)
C17_2	C18_2	C19_2	122.4(6)
C20_2	C19_2	C18_2	119.2(6)
C21_2	C20_2	C19_2	120.6(6)
C20_2	C21_2	C22_2	119.6(6)
C21_2	C22_2	C17_2	121.0(6)
C23_11	N1_11	Rh3	170.6(14)
N1_11	C23_11	C24_11	173.1(18)

Table S12.2.20: Torsion Angles in ° for **WL-2ClBr**.

Atom	Atom	Atom	Atom	Angle/°
Rh3	O2_5	C1_5	O1_5	-10.4(12)
Rh3	O2_5	C1_5	C2_5	-177.1(5)
Rh3	O2_6	C1_6	O1_6	0.3(13)
Rh3	O2_6	C1_6	C2_6	-177.8(5)
Rh3	O2_7	C1_7	O1_7	11.0(12)
Rh3	O2_7	C1_7	C2_7	-176.0(5)
Rh3	O2_8	C1_8	O1_8	5.6(14)
Rh3	O2_8	C1_8	C2_8	-175.7(5)
Rh4	O1_5	C1_5	O2_5	21.9(12)
Rh4	O1_5	C1_5	C2_5	-171.5(5)
Rh4	O1_6	C1_6	O2_6	15.9(14)
Rh4	O1_6	C1_6	C2_6	-166.0(5)
Rh4	O1_7	C1_7	O2_7	4.6(12)
Rh4	O1_7	C1_7	C2_7	-168.2(5)
Rh4	O1_8	C1_8	O2_8	10.3(14)
Rh4	O1_8	C1_8	C2_8	-168.4(5)
Rh1	O2_3	C1_3	O1_3	-1.7(13)
Rh1	O2_3	C1_3	C2_3	-173.4(5)
Rh1	O2_12	C1_12	O1_12	8(3)
Rh1	O2_12	C1_12	C2_12	-177.4(9)
Rh1	O2_1	C1_1	O1_1	9.6(16)
Rh1	O2_1	C1_1	C2_1	-174.3(5)

Atom	Atom	Atom	Atom	Angle/°
Rh1	O2_4	C1_4	O1_4	4(2)
Rh1	O2_4	C1_4	C2_4	-164.6(8)
Rh1	O2_2	C1_2	O1_2	4.1(13)
Rh1	O2_2	C1_2	C2_2	-180.0(5)
Rh2	O1_3	C1_3	O2_3	19.1(12)
Rh2	O1_3	C1_3	C2_3	-169.3(5)
Rh2	O1_12	C1_12	O2_12	3(3)
Rh2	O1_12	C1_12	C2_12	-171.9(11)
Rh2	O1_1	C1_1	O2_1	8.3(16)
Rh2	O1_1	C1_1	C2_1	-167.8(5)
Rh2	O1_4	C1_4	O2_4	19(2)
Rh2	O1_4	C1_4	C2_4	-172.5(9)
Rh2	O1_2	C1_2	O2_2	11.0(13)
Rh2	O1_2	C1_2	C2_2	-164.9(5)
Br1_3	C8_3	C9_3	C4_3	175.9(9)
Cl1_3	C5_3	C6_3	C7_3	-178.5(14)
O1_3	C1_3	C2_3	C3_3	31.4(9)
O1_3	C1_3	C2_3	C4_3	-178.6(7)
O1_3	C1_3	C2_3	C10_3	-35.3(8)
O2_3	C1_3	C2_3	C3_3	-156.2(7)
O2_3	C1_3	C2_3	C4_3	-6.2(9)
O2_3	C1_3	C2_3	C10_3	137.2(7)
C1_3	C2_3	C3_3	C10_3	-101.1(5)
C1_3	C2_3	C3_3	C11_3	6.0(7)
C1_3	C2_3	C3_3	C17_3	148.6(5)
C1_3	C2_3	C4_3	C5_3	-72.3(9)
C1_3	C2_3	C4_3	C9_3	114.7(9)
C1_3	C2_3	C10_3	C3_3	114.0(5)
C2_3	C3_3	C11_3	C12_3	-138.9(10)
C2_3	C3_3	C11_3	C16_3	43.6(11)
C2_3	C3_3	C17_3	C18_3	-101.2(12)
C2_3	C3_3	C17_3	C22_3	71.7(11)
C2_3	C4_3	C5_3	Cl1_3	5.1(14)
C2_3	C4_3	C5_3	C6_3	-175.4(12)
C2_3	C4_3	C9_3	C8_3	175.0(10)
C3_3	C2_3	C4_3	C5_3	79.2(9)
C3_3	C2_3	C4_3	C9_3	-93.8(9)
C3_3	C11_3	C12_3	C13_3	-178.5(12)
C3_3	C11_3	C16_3	C15_3	-178.3(12)
C3_3	C17_3	C18_3	C19_3	180.0(14)
C3_3	C17_3	C22_3	C21_3	-179.2(15)
C4_3	C2_3	C3_3	C10_3	110.3(5)
C4_3	C2_3	C3_3	C11_3	-142.5(5)
C4_3	C2_3	C3_3	C17_3	0.0(7)
C4_3	C2_3	C10_3	C3_3	-105.8(5)
C4_3	C5_3	C6_3	C7_3	2(2)
C5_3	C4_3	C9_3	C8_3	1.6(18)
C5_3	C6_3	C7_3	C8_3	-1(3)
C6_3	C7_3	C8_3	Br1_3	-176.0(14)
C6_3	C7_3	C8_3	C9_3	1(3)
C7_3	C8_3	C9_3	C4_3	-1(2)
C9_3	C4_3	C5_3	Cl1_3	178.4(10)
C9_3	C4_3	C5_3	C6_3	-2.2(19)
C10_3	C2_3	C3_3	C11_3	107.2(6)
C10_3	C2_3	C3_3	C17_3	-110.3(5)
C10_3	C2_3	C4_3	C5_3	146.6(9)
C10_3	C2_3	C4_3	C9_3	-26.4(10)
C10_3	C3_3	C11_3	C12_3	-69.6(10)

Atom	Atom	Atom	Atom	Angle/°
C10_3	C3_3	C11_3	C16_3	112.9(10)
C10_3	C3_3	C17_3	C18_3	-169.5(11)
C10_3	C3_3	C17_3	C22_3	3.4(11)
C11_3	C3_3	C10_3	C2_3	-111.2(5)
C11_3	C3_3	C17_3	C18_3	44.9(12)
C11_3	C3_3	C17_3	C22_3	-142.2(10)
C11_3	C12_3	C13_3	C14_3	2(2)
C12_3	C11_3	C16_3	C15_3	4.2(19)
C12_3	C13_3	C14_3	C15_3	-6(2)
C13_3	C14_3	C15_3	C16_3	10(2)
C14_3	C15_3	C16_3	C11_3	-9(2)
C16_3	C11_3	C12_3	C13_3	-1(2)
C17_3	C3_3	C10_3	C2_3	105.8(5)
C17_3	C3_3	C11_3	C12_3	76.5(10)
C17_3	C3_3	C11_3	C16_3	-101.0(10)
C17_3	C18_3	C19_3	C20_3	-2(3)
C18_3	C17_3	C22_3	C21_3	-6(2)
C18_3	C19_3	C20_3	C21_3	-4(3)
C19_3	C20_3	C21_3	C22_3	5(3)
C20_3	C21_3	C22_3	C17_3	0(3)
C22_3	C17_3	C18_3	C19_3	7(2)
Br1_5	C8_5	C9_5	C4_5	-178.4(10)
Cl1_5	C5_5	C6_5	C7_5	-175.2(11)
O1_5	C1_5	C2_5	C3_5	28.4(8)
O1_5	C1_5	C2_5	C4_5	177.9(7)
O1_5	C1_5	C2_5	C10_5	-37.9(8)
O2_5	C1_5	C2_5	C3_5	-163.6(7)
O2_5	C1_5	C2_5	C4_5	-14.1(8)
O2_5	C1_5	C2_5	C10_5	130.1(7)
C1_5	C2_5	C3_5	C10_5	-100.8(5)
C1_5	C2_5	C3_5	C11_5	7.2(7)
C1_5	C2_5	C3_5	C17_5	149.8(5)
C1_5	C2_5	C4_5	C5_5	-55.2(9)
C1_5	C2_5	C4_5	C9_5	121.5(9)
C1_5	C2_5	C10_5	C3_5	113.6(5)
C2_5	C3_5	C11_5	C12_5	-116.6(10)
C2_5	C3_5	C11_5	C16_5	62.4(13)
C2_5	C3_5	C17_5	C18_5	-66.7(11)
C2_5	C3_5	C17_5	C22_5	118.5(13)
C2_5	C4_5	C5_5	Cl1_5	-5.4(13)
C2_5	C4_5	C5_5	C6_5	171.2(10)
C2_5	C4_5	C9_5	C8_5	-176.2(11)
C3_5	C2_5	C4_5	C5_5	95.6(9)
C3_5	C2_5	C4_5	C9_5	-87.7(10)
C3_5	C11_5	C12_5	C13_5	-178.8(16)
C3_5	C11_5	C16_5	C15_5	-179.2(15)
C3_5	C17_5	C18_5	C19_5	178.1(13)
C3_5	C17_5	C22_5	C21_5	179.2(17)
C4_5	C2_5	C3_5	C10_5	111.2(5)
C4_5	C2_5	C3_5	C11_5	-140.7(5)
C4_5	C2_5	C3_5	C17_5	1.8(7)
C4_5	C2_5	C10_5	C3_5	-105.6(5)
C4_5	C5_5	C6_5	C7_5	8.1(19)
C5_5	C4_5	C9_5	C8_5	0.7(18)
C5_5	C6_5	C7_5	C8_5	-5(2)
C6_5	C7_5	C8_5	Br1_5	-179.2(11)
C6_5	C7_5	C8_5	C9_5	1(2)
C7_5	C8_5	C9_5	C4_5	2(2)

Atom	Atom	Atom	Atom	Angle/°
C9_5	C4_5	C5_5	Cl1_5	177.8(10)
C9_5	C4_5	C5_5	C6_5	-5.7(16)
C10_5	C2_5	C3_5	C11_5	108.0(6)
C10_5	C2_5	C3_5	C17_5	-109.4(5)
C10_5	C2_5	C4_5	C5_5	163.4(8)
C10_5	C2_5	C4_5	C9_5	-19.8(10)
C10_5	C3_5	C11_5	C12_5	-47.2(11)
C10_5	C3_5	C11_5	C16_5	131.7(12)
C10_5	C3_5	C17_5	C18_5	-134.9(10)
C10_5	C3_5	C17_5	C22_5	50.2(13)
C11_5	C3_5	C10_5	C2_5	-110.3(5)
C11_5	C3_5	C17_5	C18_5	79.3(11)
C11_5	C3_5	C17_5	C22_5	-95.5(13)
C11_5	C12_5	C13_5	C14_5	-1(3)
C12_5	C11_5	C16_5	C15_5	0(3)
C12_5	C13_5	C14_5	C15_5	-2(4)
C13_5	C14_5	C15_5	C16_5	4(3)
C14_5	C15_5	C16_5	C11_5	-3(3)
C16_5	C11_5	C12_5	C13_5	2(2)
C17_5	C3_5	C10_5	C2_5	106.8(5)
C17_5	C3_5	C11_5	C12_5	98.6(10)
C17_5	C3_5	C11_5	C16_5	-82.4(13)
C17_5	C18_5	C19_5	C20_5	3(3)
C18_5	C17_5	C22_5	C21_5	4(3)
C18_5	C19_5	C20_5	C21_5	3(3)
C19_5	C20_5	C21_5	C22_5	-6(4)
C20_5	C21_5	C22_5	C17_5	2(4)
C22_5	C17_5	C18_5	C19_5	-7(2)
Br1_6	C8_6	C9_6	C4_6	174.4(7)
Cl1_6	C5_6	C6_6	C7_6	-179.9(10)
O1_6	C1_6	C2_6	C3_6	26.6(10)
O1_6	C1_6	C2_6	C4_6	177.0(7)
O1_6	C1_6	C2_6	C10_6	-40.2(9)
O2_6	C1_6	C2_6	C3_6	-155.2(8)
O2_6	C1_6	C2_6	C4_6	-4.7(9)
O2_6	C1_6	C2_6	C10_6	138.0(8)
C1_6	C2_6	C3_6	C10_6	-101.2(5)
C1_6	C2_6	C3_6	C11_6	5.6(8)
C1_6	C2_6	C3_6	C17_6	148.2(5)
C1_6	C2_6	C4_6	C5_6	-72.5(8)
C1_6	C2_6	C4_6	C9_6	115.0(7)
C1_6	C2_6	C10_6	C3_6	114.1(5)
C2_6	C3_6	C11_6	C12_6	-136.7(11)
C2_6	C3_6	C11_6	C16_6	47.1(11)
C2_6	C3_6	C17_6	C18_6	-99.6(10)
C2_6	C3_6	C17_6	C22_6	75.9(9)
C2_6	C4_6	C5_6	Cl1_6	4.6(12)
C2_6	C4_6	C5_6	C6_6	-176.0(9)
C2_6	C4_6	C9_6	C8_6	178.5(8)
C3_6	C2_6	C4_6	C5_6	79.5(8)
C3_6	C2_6	C4_6	C9_6	-93.0(8)
C3_6	C11_6	C12_6	C13_6	-178.8(15)
C3_6	C11_6	C16_6	C15_6	176.2(13)
C3_6	C17_6	C18_6	C19_6	177.4(11)
C3_6	C17_6	C22_6	C21_6	178.8(10)
C4_6	C2_6	C3_6	C10_6	109.8(5)
C4_6	C2_6	C3_6	C11_6	-143.4(5)
C4_6	C2_6	C3_6	C17_6	-0.8(7)

Atom	Atom	Atom	Atom	Angle/°
C4_6	C2_6	C10_6	C3_6	-106.1(5)
C4_6	C5_6	C6_6	C7_6	0.7(19)
C5_6	C4_6	C9_6	C8_6	5.6(14)
C5_6	C6_6	C7_6	C8_6	0(2)
C6_6	C7_6	C8_6	Br1_6	-177.2(10)
C6_6	C7_6	C8_6	C9_6	3(2)
C7_6	C8_6	C9_6	C4_6	-5.5(17)
C9_6	C4_6	C5_6	Cl1_6	177.3(7)
C9_6	C4_6	C5_6	C6_6	-3.3(15)
C10_6	C2_6	C3_6	C11_6	106.8(6)
C10_6	C2_6	C3_6	C17_6	-110.5(5)
C10_6	C2_6	C4_6	C5_6	146.8(8)
C10_6	C2_6	C4_6	C9_6	-25.6(8)
C10_6	C3_6	C11_6	C12_6	-67.3(12)
C10_6	C3_6	C11_6	C16_6	116.4(10)
C10_6	C3_6	C17_6	C18_6	-167.9(9)
C10_6	C3_6	C17_6	C22_6	7.6(10)
C11_6	C3_6	C10_6	C2_6	-111.5(5)
C11_6	C3_6	C17_6	C18_6	46.8(10)
C11_6	C3_6	C17_6	C22_6	-137.7(8)
C11_6	C12_6	C13_6	C14_6	5(3)
C12_6	C11_6	C16_6	C15_6	0(2)
C12_6	C13_6	C14_6	C15_6	-5(3)
C13_6	C14_6	C15_6	C16_6	3(3)
C14_6	C15_6	C16_6	C11_6	0(3)
C16_6	C11_6	C12_6	C13_6	-2(2)
C17_6	C3_6	C10_6	C2_6	105.7(5)
C17_6	C3_6	C11_6	C12_6	78.6(12)
C17_6	C3_6	C11_6	C16_6	-97.6(10)
C17_6	C18_6	C19_6	C20_6	4(2)
C18_6	C17_6	C22_6	C21_6	-5.4(17)
C18_6	C19_6	C20_6	C21_6	-6(2)
C19_6	C20_6	C21_6	C22_6	2(2)
C20_6	C21_6	C22_6	C17_6	4(2)
C22_6	C17_6	C18_6	C19_6	1.6(18)
Br1_7	C8_7	C9_7	C4_7	-178.9(10)
Cl1_7	C5_7	C6_7	C7_7	178.6(13)
O1_7	C1_7	C2_7	C3_7	25.5(9)
O1_7	C1_7	C2_7	C4_7	176.1(7)
O1_7	C1_7	C2_7	C10_7	-41.3(9)
O2_7	C1_7	C2_7	C3_7	-148.1(7)
O2_7	C1_7	C2_7	C4_7	2.5(8)
O2_7	C1_7	C2_7	C10_7	145.1(7)
C1_7	C2_7	C3_7	C10_7	-101.4(5)
C1_7	C2_7	C3_7	C11_7	5.2(7)
C1_7	C2_7	C3_7	C17_7	147.8(5)
C1_7	C2_7	C4_7	C5_7	-71.9(10)
C1_7	C2_7	C4_7	C9_7	102.9(9)
C1_7	C2_7	C10_7	C3_7	113.9(5)
C2_7	C3_7	C11_7	C12_7	-131.2(13)
C2_7	C3_7	C11_7	C16_7	47.8(12)
C2_7	C3_7	C17_7	C18_7	-96.0(13)
C2_7	C3_7	C17_7	C22_7	78.0(12)
C2_7	C4_7	C5_7	Cl1_7	1.1(15)
C2_7	C4_7	C5_7	C6_7	-177.0(11)
C2_7	C4_7	C9_7	C8_7	178.2(11)
C3_7	C2_7	C4_7	C5_7	80.1(10)
C3_7	C2_7	C4_7	C9_7	-105.1(9)

Atom	Atom	Atom	Atom	Angle/°
C3_7	C11_7	C12_7	C13_7	179.0(16)
C3_7	C11_7	C16_7	C15_7	-179.2(13)
C3_7	C17_7	C18_7	C19_7	176.3(15)
C3_7	C17_7	C22_7	C21_7	178.0(15)
C4_7	C2_7	C3_7	C10_7	109.5(5)
C4_7	C2_7	C3_7	C11_7	-143.9(5)
C4_7	C2_7	C3_7	C17_7	-1.3(7)
C4_7	C2_7	C10_7	C3_7	-106.5(5)
C4_7	C5_7	C6_7	C7_7	-3(2)
C5_7	C4_7	C9_7	C8_7	-6.6(18)
C5_7	C6_7	C7_7	C8_7	-3(2)
C6_7	C7_7	C8_7	Br1_7	-176.1(14)
C6_7	C7_7	C8_7	C9_7	4(3)
C7_7	C8_7	C9_7	C4_7	1(2)
C9_7	C4_7	C5_7	Cl1_7	-173.9(10)
C9_7	C4_7	C5_7	C6_7	8.0(18)
C10_7	C2_7	C3_7	C11_7	106.6(6)
C10_7	C2_7	C3_7	C17_7	-110.8(5)
C10_7	C2_7	C4_7	C5_7	147.5(9)
C10_7	C2_7	C4_7	C9_7	-37.7(10)
C10_7	C3_7	C11_7	C12_7	-61.9(13)
C10_7	C3_7	C11_7	C16_7	117.1(11)
C10_7	C3_7	C17_7	C18_7	-164.4(12)
C10_7	C3_7	C17_7	C22_7	9.6(12)
C11_7	C3_7	C10_7	C2_7	-111.6(5)
C11_7	C3_7	C17_7	C18_7	50.3(13)
C11_7	C3_7	C17_7	C22_7	-135.7(11)
C11_7	C12_7	C13_7	C14_7	-3(3)
C12_7	C11_7	C16_7	C15_7	0(2)
C12_7	C13_7	C14_7	C15_7	5(3)
C13_7	C14_7	C15_7	C16_7	-6(3)
C14_7	C15_7	C16_7	C11_7	3(3)
C16_7	C11_7	C12_7	C13_7	0(3)
C17_7	C3_7	C10_7	C2_7	105.6(5)
C17_7	C3_7	C11_7	C12_7	84.2(13)
C17_7	C3_7	C11_7	C16_7	-96.8(11)
C17_7	C18_7	C19_7	C20_7	7(3)
C18_7	C17_7	C22_7	C21_7	-8(2)
C18_7	C19_7	C20_7	C21_7	-9(3)
C19_7	C20_7	C21_7	C22_7	4(3)
C20_7	C21_7	C22_7	C17_7	5(3)
C22_7	C17_7	C18_7	C19_7	2(3)
Br1_8	C8_8	C9_8	C4_8	-176.9(11)
Cl1_8	C5_8	C6_8	C7_8	-179.6(14)
O1_8	C1_8	C2_8	C3_8	23.0(10)
O1_8	C1_8	C2_8	C4_8	173.2(8)
O1_8	C1_8	C2_8	C10_8	-43.7(9)
O2_8	C1_8	C2_8	C3_8	-155.8(8)
O2_8	C1_8	C2_8	C4_8	-5.6(9)
O2_8	C1_8	C2_8	C10_8	137.4(8)
C1_8	C2_8	C3_8	C10_8	-101.5(5)
C1_8	C2_8	C3_8	C11_8	5.4(7)
C1_8	C2_8	C3_8	C17_8	147.8(5)
C1_8	C2_8	C4_8	C5_8	-71.6(10)
C1_8	C2_8	C4_8	C9_8	117.4(10)
C1_8	C2_8	C10_8	C3_8	113.8(5)
C2_8	C3_8	C11_8	C12_8	-128.8(10)
C2_8	C3_8	C11_8	C16_8	54.0(11)

Atom	Atom	Atom	Atom	Angle/°
C2_8	C3_8	C17_8	C18_8	-96.2(9)
C2_8	C3_8	C17_8	C22_8	86.4(9)
C2_8	C4_8	C5_8	Cl1_8	8.3(15)
C2_8	C4_8	C5_8	C6_8	-177.5(12)
C2_8	C4_8	C9_8	C8_8	176.1(12)
C3_8	C2_8	C4_8	C5_8	80.0(10)
C3_8	C2_8	C4_8	C9_8	-91.0(10)
C3_8	C11_8	C12_8	C13_8	-177.8(12)
C3_8	C11_8	C16_8	C15_8	175.3(11)
C3_8	C17_8	C18_8	C19_8	179.5(10)
C3_8	C17_8	C22_8	C21_8	-179.3(11)
C4_8	C2_8	C3_8	C10_8	109.8(5)
C4_8	C2_8	C3_8	C11_8	-143.3(5)
C4_8	C2_8	C3_8	C17_8	-0.9(7)
C4_8	C2_8	C10_8	C3_8	-106.2(5)
C4_8	C5_8	C6_8	C7_8	6(2)
C5_8	C4_8	C9_8	C8_8	4.7(19)
C5_8	C6_8	C7_8	C8_8	-4(3)
C6_8	C7_8	C8_8	Br1_8	176.2(14)
C6_8	C7_8	C8_8	C9_8	2(3)
C7_8	C8_8	C9_8	C4_8	-3(2)
C9_8	C4_8	C5_8	Cl1_8	179.5(11)
C9_8	C4_8	C5_8	C6_8	-6.3(19)
C10_8	C2_8	C3_8	C11_8	106.8(6)
C10_8	C2_8	C3_8	C17_8	-110.8(5)
C10_8	C2_8	C4_8	C5_8	147.4(9)
C10_8	C2_8	C4_8	C9_8	-23.5(11)
C10_8	C3_8	C11_8	C12_8	-59.5(10)
C10_8	C3_8	C11_8	C16_8	123.3(10)
C10_8	C3_8	C17_8	C18_8	-164.6(8)
C10_8	C3_8	C17_8	C22_8	18.1(10)
C11_8	C3_8	C10_8	C2_8	-111.4(5)
C11_8	C3_8	C17_8	C18_8	49.9(9)
C11_8	C3_8	C17_8	C22_8	-127.5(9)
C11_8	C12_8	C13_8	C14_8	0(3)
C12_8	C11_8	C16_8	C15_8	-1.8(19)
C12_8	C13_8	C14_8	C15_8	2(3)
C13_8	C14_8	C15_8	C16_8	-5(3)
C14_8	C15_8	C16_8	C11_8	5(2)
C16_8	C11_8	C12_8	C13_8	0(2)
C17_8	C3_8	C10_8	C2_8	105.6(5)
C17_8	C3_8	C11_8	C12_8	86.8(10)
C17_8	C3_8	C11_8	C16_8	-90.5(10)
C17_8	C18_8	C19_8	C20_8	3(2)
C18_8	C17_8	C22_8	C21_8	3.2(17)
C18_8	C19_8	C20_8	C21_8	-3(2)
C19_8	C20_8	C21_8	C22_8	4(2)
C20_8	C21_8	C22_8	C17_8	-4(2)
C22_8	C17_8	C18_8	C19_8	-3.0(17)
Br1_12	C8_12	C9_12	C4_12	-176.5(17)
Cl1_12	C5_12	C6_12	C7_12	-177(3)
O1_12	C1_12	C2_12	C3_12	23.5(19)
O1_12	C1_12	C2_12	C4_12	174.3(18)
O1_12	C1_12	C2_12	C10_12	-43.3(19)
O2_12	C1_12	C2_12	C3_12	-151.9(15)
O2_12	C1_12	C2_12	C4_12	-1.1(15)
O2_12	C1_12	C2_12	C10_12	141.4(15)
C1_12	C2_12	C3_12	C10_12	-101.2(5)

Atom	Atom	Atom	Atom	Angle/°
C1_12	C2_12	C3_12	C11_12	5.3(8)
C1_12	C2_12	C3_12	C17_12	148.3(5)
C1_12	C2_12	C4_12	C5_12	-80.0(15)
C1_12	C2_12	C4_12	C9_12	106.7(12)
C1_12	C2_12	C10_12	C3_12	114.0(5)
C2_12	C3_12	C11_12	C12_12	-130.0(16)
C2_12	C3_12	C11_12	C16_12	46.7(16)
C2_12	C3_12	C17_12	C18_12	-130.4(14)
C2_12	C3_12	C17_12	C22_12	51.9(16)
C2_12	C4_12	C5_12	Cl1_12	5(2)
C2_12	C4_12	C5_12	C6_12	-174(2)
C2_12	C4_12	C9_12	C8_12	169.2(17)
C3_12	C2_12	C4_12	C5_12	72.2(15)
C3_12	C2_12	C4_12	C9_12	-101.1(13)
C3_12	C11_12	C12_12	C13_12	179.0(19)
C3_12	C11_12	C16_12	C15_12	-172.2(16)
C3_12	C17_12	C18_12	C19_12	174.7(17)
C3_12	C17_12	C22_12	C21_12	-178.1(19)
C4_12	C2_12	C3_12	C10_12	109.5(5)
C4_12	C2_12	C3_12	C11_12	-144.0(5)
C4_12	C2_12	C3_12	C17_12	-0.9(7)
C4_12	C2_12	C10_12	C3_12	-106.5(5)
C4_12	C5_12	C6_12	C7_12	2(5)
C5_12	C4_12	C9_12	C8_12	-5(3)
C5_12	C6_12	C7_12	C8_12	0(5)
C6_12	C7_12	C8_12	Br1_12	179(3)
C6_12	C7_12	C8_12	C9_12	-5(4)
C7_12	C8_12	C9_12	C4_12	7(3)
C9_12	C4_12	C5_12	Cl1_12	178.8(17)
C9_12	C4_12	C5_12	C6_12	0(3)
C10_12	C2_12	C3_12	C11_12	106.5(6)
C10_12	C2_12	C3_12	C17_12	-110.4(5)
C10_12	C2_12	C4_12	C5_12	139.7(15)
C10_12	C2_12	C4_12	C9_12	-33.7(13)
C10_12	C3_12	C11_12	C12_12	-60.6(17)
C10_12	C3_12	C11_12	C16_12	116.1(15)
C10_12	C3_12	C17_12	C18_12	161.3(14)
C10_12	C3_12	C17_12	C22_12	-16.5(16)
C11_12	C3_12	C10_12	C2_12	-111.8(5)
C11_12	C3_12	C17_12	C18_12	16.4(15)
C11_12	C3_12	C17_12	C22_12	-161.4(15)
C11_12	C12_12	C13_12	C14_12	-6(4)
C12_12	C11_12	C16_12	C15_12	4(3)
C12_12	C13_12	C14_12	C15_12	3(4)
C13_12	C14_12	C15_12	C16_12	4(4)
C14_12	C15_12	C16_12	C11_12	-8(3)
C16_12	C11_12	C12_12	C13_12	2(3)
C17_12	C3_12	C10_12	C2_12	105.9(5)
C17_12	C3_12	C11_12	C12_12	84.9(16)
C17_12	C3_12	C11_12	C16_12	-98.4(15)
C17_12	C18_12	C19_12	C20_12	8(3)
C18_12	C17_12	C22_12	C21_12	4(3)
C18_12	C19_12	C20_12	C21_12	-4(4)
C19_12	C20_12	C21_12	C22_12	1(5)
C20_12	C21_12	C22_12	C17_12	-1(4)
C22_12	C17_12	C18_12	C19_12	-7(3)
Br1_1	C8_1	C9_1	C4_1	179.5(9)
Cl1_1	C5_1	C6_1	C7_1	173.8(11)

Atom	Atom	Atom	Atom	Angle/°
O1_1	C1_1	C2_1	C3_1	27.8(10)
O1_1	C1_1	C2_1	C4_1	179.2(8)
O1_1	C1_1	C2_1	C10_1	-38.8(10)
O2_1	C1_1	C2_1	C3_1	-148.7(8)
O2_1	C1_1	C2_1	C4_1	2.8(10)
O2_1	C1_1	C2_1	C10_1	144.7(8)
C1_1	C2_1	C3_1	C10_1	-101.1(5)
C1_1	C2_1	C3_1	C11_1	5.6(7)
C1_1	C2_1	C3_1	C17_1	148.3(5)
C1_1	C2_1	C4_1	C5_1	-73.5(9)
C1_1	C2_1	C4_1	C9_1	96.9(8)
C1_1	C2_1	C10_1	C3_1	113.9(5)
C2_1	C3_1	C11_1	C12_1	-129.4(10)
C2_1	C3_1	C11_1	C16_1	45.0(13)
C2_1	C3_1	C17_1	C18_1	-102.8(10)
C2_1	C3_1	C17_1	C22_1	81.9(10)
C2_1	C4_1	C5_1	Cl1_1	-3.8(13)
C2_1	C4_1	C5_1	C6_1	174.9(9)
C2_1	C4_1	C9_1	C8_1	-169.7(10)
C3_1	C2_1	C4_1	C5_1	79.1(9)
C3_1	C2_1	C4_1	C9_1	-110.5(8)
C3_1	C11_1	C12_1	C13_1	-178.4(13)
C3_1	C11_1	C16_1	C15_1	177.3(15)
C3_1	C17_1	C18_1	C19_1	-179.3(12)
C3_1	C17_1	C22_1	C21_1	176.0(15)
C4_1	C2_1	C3_1	C10_1	109.1(5)
C4_1	C2_1	C3_1	C11_1	-144.3(5)
C4_1	C2_1	C3_1	C17_1	-1.5(7)
C4_1	C2_1	C10_1	C3_1	-107.0(5)
C4_1	C5_1	C6_1	C7_1	-4.9(19)
C5_1	C4_1	C9_1	C8_1	1.3(16)
C5_1	C6_1	C7_1	C8_1	0(2)
C6_1	C7_1	C8_1	Br1_1	179.6(11)
C6_1	C7_1	C8_1	C9_1	6(2)
C7_1	C8_1	C9_1	C4_1	-6(2)
C9_1	C4_1	C5_1	Cl1_1	-174.5(9)
C9_1	C4_1	C5_1	C6_1	4.1(15)
C10_1	C2_1	C3_1	C11_1	106.6(6)
C10_1	C2_1	C3_1	C17_1	-110.6(5)
C10_1	C2_1	C4_1	C5_1	146.6(8)
C10_1	C2_1	C4_1	C9_1	-43.0(9)
C10_1	C3_1	C11_1	C12_1	-60.1(10)
C10_1	C3_1	C11_1	C16_1	114.4(12)
C10_1	C3_1	C17_1	C18_1	-171.3(10)
C10_1	C3_1	C17_1	C22_1	13.4(11)
C11_1	C3_1	C10_1	C2_1	-111.5(5)
C11_1	C3_1	C17_1	C18_1	43.6(11)
C11_1	C3_1	C17_1	C22_1	-131.7(10)
C11_1	C12_1	C13_1	C14_1	-1(3)
C12_1	C11_1	C16_1	C15_1	-8(2)
C12_1	C13_1	C14_1	C15_1	-4(3)
C13_1	C14_1	C15_1	C16_1	2(4)
C14_1	C15_1	C16_1	C11_1	4(3)
C16_1	C11_1	C12_1	C13_1	7(2)
C17_1	C3_1	C10_1	C2_1	105.9(5)
C17_1	C3_1	C11_1	C12_1	85.7(10)
C17_1	C3_1	C11_1	C16_1	-99.9(12)
C17_1	C18_1	C19_1	C20_1	6(2)

Atom	Atom	Atom	Atom	Angle/°
C18_1	C17_1	C22_1	C21_1	0(2)
C18_1	C19_1	C20_1	C21_1	-5(3)
C19_1	C20_1	C21_1	C22_1	1(3)
C20_1	C21_1	C22_1	C17_1	1(3)
C22_1	C17_1	C18_1	C19_1	-4(2)
Br1_4	C8_4	C9_4	C4_4	-178.8(15)
Cl1_4	C5_4	C6_4	C7_4	180(2)
O1_4	C1_4	C2_4	C3_4	29.2(15)
O1_4	C1_4	C2_4	C4_4	179.0(14)
O1_4	C1_4	C2_4	C10_4	-37.5(15)
O2_4	C1_4	C2_4	C3_4	-161.2(12)
O2_4	C1_4	C2_4	C4_4	-11.3(12)
O2_4	C1_4	C2_4	C10_4	132.1(12)
C1_4	C2_4	C3_4	C10_4	-101.1(5)
C1_4	C2_4	C3_4	C11_4	6.1(8)
C1_4	C2_4	C3_4	C17_4	148.7(5)
C1_4	C2_4	C4_4	C5_4	-73.0(13)
C1_4	C2_4	C4_4	C9_4	103.8(13)
C1_4	C2_4	C10_4	C3_4	114.0(5)
C2_4	C3_4	C11_4	C12_4	-139.3(14)
C2_4	C3_4	C11_4	C16_4	43.4(14)
C2_4	C3_4	C17_4	C18_4	-99.9(12)
C2_4	C3_4	C17_4	C22_4	69.3(12)
C2_4	C4_4	C5_4	Cl1_4	0(2)
C2_4	C4_4	C5_4	C6_4	-176.0(18)
C2_4	C4_4	C9_4	C8_4	179.3(16)
C3_4	C2_4	C4_4	C5_4	78.4(13)
C3_4	C2_4	C4_4	C9_4	-104.9(13)
C3_4	C11_4	C12_4	C13_4	-172.1(17)
C3_4	C11_4	C16_4	C15_4	171.3(14)
C3_4	C17_4	C18_4	C19_4	176.9(16)
C3_4	C17_4	C22_4	C21_4	-170.0(14)
C4_4	C2_4	C3_4	C10_4	110.5(5)
C4_4	C2_4	C3_4	C11_4	-142.2(5)
C4_4	C2_4	C3_4	C17_4	0.3(7)
C4_4	C2_4	C10_4	C3_4	-105.7(5)
C4_4	C5_4	C6_4	C7_4	-4(4)
C5_4	C4_4	C9_4	C8_4	-4(3)
C5_4	C6_4	C7_4	C8_4	-4(4)
C6_4	C7_4	C8_4	Br1_4	-178(2)
C6_4	C7_4	C8_4	C9_4	7(4)
C7_4	C8_4	C9_4	C4_4	-3(3)
C9_4	C4_4	C5_4	Cl1_4	-176.5(16)
C9_4	C4_4	C5_4	C6_4	7(3)
C10_4	C2_4	C3_4	C11_4	107.3(6)
C10_4	C2_4	C3_4	C17_4	-110.2(5)
C10_4	C2_4	C4_4	C5_4	145.9(13)
C10_4	C2_4	C4_4	C9_4	-37.3(14)
C10_4	C3_4	C11_4	C12_4	-69.9(15)
C10_4	C3_4	C11_4	C16_4	112.7(13)
C10_4	C3_4	C17_4	C18_4	-168.1(11)
C10_4	C3_4	C17_4	C22_4	1.2(12)
C11_4	C3_4	C10_4	C2_4	-111.2(5)
C11_4	C3_4	C17_4	C18_4	46.2(12)
C11_4	C3_4	C17_4	C22_4	-144.5(11)
C11_4	C12_4	C13_4	C14_4	-5(3)
C12_4	C11_4	C16_4	C15_4	-6(2)
C12_4	C13_4	C14_4	C15_4	6(3)

Atom	Atom	Atom	Atom	Angle/°
C13_4	C14_4	C15_4	C16_4	-7(3)
C14_4	C15_4	C16_4	C11_4	7(3)
C16_4	C11_4	C12_4	C13_4	5(3)
C17_4	C3_4	C10_4	C2_4	105.8(5)
C17_4	C3_4	C11_4	C12_4	76.1(15)
C17_4	C3_4	C11_4	C16_4	-101.2(13)
C17_4	C18_4	C19_4	C20_4	-7(3)
C18_4	C17_4	C22_4	C21_4	0(2)
C18_4	C19_4	C20_4	C21_4	0(4)
C19_4	C20_4	C21_4	C22_4	7(3)
C20_4	C21_4	C22_4	C17_4	-7(3)
C22_4	C17_4	C18_4	C19_4	7(2)
Br1_2	C8_2	C9_2	C4_2	-178.8(10)
Cl1_2	C5_2	C6_2	C7_2	-176.8(9)
O1_2	C1_2	C2_2	C3_2	25.3(9)
O1_2	C1_2	C2_2	C4_2	175.4(8)
O1_2	C1_2	C2_2	C10_2	-41.4(9)
O2_2	C1_2	C2_2	C3_2	-151.0(7)
O2_2	C1_2	C2_2	C4_2	-0.9(9)
O2_2	C1_2	C2_2	C10_2	142.3(7)
C1_2	C2_2	C3_2	C10_2	-101.4(5)
C1_2	C2_2	C3_2	C11_2	5.5(7)
C1_2	C2_2	C3_2	C17_2	148.0(5)
C1_2	C2_2	C4_2	C5_2	-62.0(9)
C1_2	C2_2	C4_2	C9_2	116.7(10)
C1_2	C2_2	C10_2	C3_2	113.6(5)
C2_2	C3_2	C11_2	C12_2	-132.6(9)
C2_2	C3_2	C11_2	C16_2	52.1(12)
C2_2	C3_2	C17_2	C18_2	-95.6(10)
C2_2	C3_2	C17_2	C22_2	74.0(13)
C2_2	C4_2	C5_2	Cl1_2	-6.3(13)
C2_2	C4_2	C5_2	C6_2	172.1(9)
C2_2	C4_2	C9_2	C8_2	-173.5(11)
C3_2	C2_2	C4_2	C5_2	89.4(9)
C3_2	C2_2	C4_2	C9_2	-91.8(10)
C3_2	C11_2	C12_2	C13_2	-172.4(11)
C3_2	C11_2	C16_2	C15_2	174.8(14)
C3_2	C17_2	C18_2	C19_2	-179.5(11)
C3_2	C17_2	C22_2	C21_2	-174.0(15)
C4_2	C2_2	C3_2	C10_2	109.9(5)
C4_2	C2_2	C3_2	C11_2	-143.1(5)
C4_2	C2_2	C3_2	C17_2	-0.7(7)
C4_2	C2_2	C10_2	C3_2	-106.2(5)
C4_2	C5_2	C6_2	C7_2	4.8(17)
C5_2	C4_2	C9_2	C8_2	5.4(19)
C5_2	C6_2	C7_2	C8_2	-1.3(18)
C6_2	C7_2	C8_2	Br1_2	176.6(10)
C6_2	C7_2	C8_2	C9_2	0(2)
C7_2	C8_2	C9_2	C4_2	-2(2)
C9_2	C4_2	C5_2	Cl1_2	174.9(10)
C9_2	C4_2	C5_2	C6_2	-6.7(16)
C10_2	C2_2	C3_2	C11_2	106.9(6)
C10_2	C2_2	C3_2	C17_2	-110.6(5)
C10_2	C2_2	C4_2	C5_2	156.9(8)
C10_2	C2_2	C4_2	C9_2	-24.3(11)
C10_2	C3_2	C11_2	C12_2	-63.3(10)
C10_2	C3_2	C11_2	C16_2	121.4(11)
C10_2	C3_2	C17_2	C18_2	-163.9(9)

Atom	Atom	Atom	Atom	Angle/°
C10_2	C3_2	C17_2	C22_2	5.6(13)
C11_2	C3_2	C10_2	C2_2	-111.3(5)
C11_2	C3_2	C17_2	C18_2	50.5(10)
C11_2	C3_2	C17_2	C22_2	-139.9(13)
C11_2	C12_2	C13_2	C14_2	-4(2)
C12_2	C11_2	C16_2	C15_2	0(2)
C12_2	C13_2	C14_2	C15_2	1(3)
C13_2	C14_2	C15_2	C16_2	1(3)
C14_2	C15_2	C16_2	C11_2	-2(3)
C16_2	C11_2	C12_2	C13_2	3.1(19)
C17_2	C3_2	C10_2	C2_2	105.7(5)
C17_2	C3_2	C11_2	C12_2	82.8(9)
C17_2	C3_2	C11_2	C16_2	-92.5(11)
C17_2	C18_2	C19_2	C20_2	-7(2)
C18_2	C17_2	C22_2	C21_2	-4(2)
C18_2	C19_2	C20_2	C21_2	-4(3)
C19_2	C20_2	C21_2	C22_2	11(2)
C20_2	C21_2	C22_2	C17_2	-6(3)
C22_2	C17_2	C18_2	C19_2	10.3(19)

Table S12.2.21: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **WL-2ClBr**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H4A	2007.75	7396.24	5699.83	130
H4B	1585.34	6730.96	5662.1	130
H24A_9	10014.35	2833.01	10023.06	185
H24B_9	9500	2919.29	10306.53	185
H24C_9	10009.78	3581.55	10328.84	185
H24A_10	6152.6	6003.51	6521.46	188
H24B_10	5901.23	6689.85	6773.77	188
H24C_10	5568.82	5870.92	6733.52	188
H6_3	6954.75	8541.6	8927.86	103
H7_3	5874.38	8587.28	8906.3	104
H9_3	5977.05	6394.5	9391.54	85
H10A_3	6659.66	5720.99	9975.41	78
H10B_3	7123.78	5021.16	9885.32	78
H12_3	8118.83	5249.7	10840.08	101
H13_3	9143.21	4670.64	11146.66	109
H14_3	9934.04	4871.6	10776.1	106
H15_3	9658.44	5397.68	10023.13	131
H16_3	8695.02	6084.53	9741.3	86
H18_3	8436.54	7274.01	10338.2	107
H19_3	8387.04	8383.35	10767.86	106
H20_3	7495.34	8603.67	11032.71	126
H21_3	6609.37	7812.26	10795.66	131
H22_3	6659.97	6681.45	10376.85	102
H6_5	5411.55	6301.39	8266.54	76
H7_5	6403.64	6834.02	8283.91	87

Atom	x	y	z	U_{eq}
H9_5	5551.87	8053.85	7093.22	80
H10A_5	4701.95	8621.3	6661.53	81
H10B_5	4043.5	8287	6276.6	81
H12_5	3172.14	9247.83	6273.91	103
H13_5	2036.85	9366.21	6013.66	140
H14_5	1408.97	8660.49	6374.29	132
H15_5	1878.05	7782.22	6959.12	128
H16_5	2996.79	7695.34	7260.12	110
H18_5	4055.86	8218.4	7894.51	101
H19_5	4530.9	8963.97	8560.66	121
H20_5	4942.9	10166.67	8470.4	147
H21_5	4807.52	10667.84	7725.17	154
H22_5	4405.18	9888.79	7056.24	136
H6_6	3066.03	2716.75	7668.68	76
H7_6	3694.83	2924.22	8446.2	81
H9_6	3375.36	5219.06	8285.99	63
H10A_6	2571.85	5998.3	7964.89	75
H10B_6	2489.31	6508.82	7479.05	75
H12_6	1060.56	6601.48	7251.53	112
H13_6	308.07	7109.9	6566.01	143
H14_6	146.8	6503.43	5842.62	139
H15_6	832.4	5537.11	5758.23	114
H16_6	1631	5068.1	6413.35	79
H18_6	1095.65	4315.05	7064.66	86
H19_6	651.32	3440	7478.13	98
H20_6	789.09	3627.04	8281.2	92
H21_6	1497.59	4542.38	8694.85	86
H22_6	2038.15	5340.75	8296.91	78
H6_7	3955.64	2421.86	5169.77	119
H7_7	3906.05	1370.3	5647.62	123
H9_7	2608.88	2490.85	6157.15	93
H10A_7	1610.19	3090.19	5730.45	90
H10B_7	1545.47	4013.39	5837.75	90
H12_7	550.18	4328.64	4976.72	130
H13_7	86.09	5505.64	4640.44	131
H14_7	734.39	6474.24	4495.64	140
H15_7	1797.24	6224.9	4549.15	136
H16_7	2284.19	5079.68	4885.28	110
H18_7	1975.77	3776.42	4336.46	146
H19_7	1915.71	2786.39	3792.45	145
H20_7	1360.16	1668.75	3859.36	157
H21_7	1127.94	1400.25	4556.3	159
H22_7	1349.01	2315.97	5165.9	133
H6_8	6149.64	6623.37	5752.63	104
H7_8	6476.01	5695.58	5301.23	109
H9_8	4613.32	5115.99	4668.1	101
H10A_8	3695.5	5692.36	4346.46	78
H10B_8	3088.34	5758.8	4574.95	78
H12_8	2514.89	7063.36	4084.02	94
H13_8	1681.23	7897.37	4144.83	115
H14_8	1794.61	8603.35	4828.49	106
H15_8	2751.64	8576.59	5430.9	104
H16_8	3559.66	7700.41	5412.82	82
H18_8	4275.11	8128.35	4873.68	68
H19_8	4967.01	8772.49	4531.34	82
H20_8	5151.38	8283.96	3850.47	83
H21_8	4754.2	7097.53	3563.21	86
H22_8	4049.8	6446.55	3898.93	77

Atom	x	y	z	U_{eq}
H6_12	8886.76	7353.34	7032.44	104
H7_12	8556.74	8593.6	7148.46	94
H9_12	8610.35	8051.48	8495.92	81
H10A_12	9506.55	7516.6	9098.97	75
H10B_12	9367.75	6707.08	9344.33	75
H12_12	10674.78	6237.5	9682.29	71
H13_12	11162.57	5074.72	10026.12	78
H14_12	10843.65	3919.29	9640.97	81
H15_12	10106	3900.89	8897.5	76
H16_12	9769.97	5048.1	8485.87	70
H18_12	10936.58	6096.96	8608.39	76
H19_12	11554.77	6722.68	8194.17	90
H20_12	11444.12	8040.73	8074.61	111
H21_12	10635.32	8699.15	8265.53	83
H22_12	9944.45	8051.34	8614.71	76
H6_1	6532.14	3218.57	6349.95	67
H7_1	6781.8	4111.09	5841.39	85
H9_1	8530.34	4472.21	6788.86	72
H10A_1	9314.27	3652.89	7316.33	79
H10B_1	9447.93	3839.67	7885.56	79
H12_1	9981.75	2411.79	8229.06	86
H13_1	10261.89	1824.9	8986.37	108
H14_1	9474.85	1561.46	9349.73	141
H15_1	8432.02	1976.09	9013.62	143
H16_1	8140.01	2605.37	8281.75	106
H18_1	8185.69	1534.96	7542.23	89
H19_1	7986.45	597.45	6953.17	109
H20_1	8545.37	631.33	6391.95	106
H21_1	9170.91	1677.33	6342.68	148
H22_1	9298.23	2683.6	6889.47	92
H6_4	9167.56	6749.48	6964.15	104
H7_4	8752.01	7993.67	6901.88	104
H9_4	8637.39	7874	8247.77	77
H10A_4	9446.6	7510.98	8968.21	75
H10B_4	9286.61	6764.67	9260.56	75
H12_4	10670.88	6408.44	9740.7	79
H13_4	11269.99	5366.14	10168.76	77
H14_4	11051.99	4125.75	9883	71
H15_4	10422.09	3924.9	9113.42	76
H16_4	9802.89	4926.69	8681.34	65
H18_4	10777.01	5943.34	8435.57	76
H19_4	11536.79	6551.88	8141.26	98
H20_4	11537.24	7883.49	8087.36	84
H21_4	10790.36	8598.62	8321.71	83
H22_4	10172.5	8008.35	8755.83	76
H6_2	4753.12	4890.57	8174.45	58
H7_2	4164.88	4194.73	7515.73	67
H9_2	5551.15	2552.4	7786.75	84
H10A_2	6310.75	1989.35	8319.24	81
H10B_2	7079.76	2221.69	8518.39	81
H12_2	7322.72	1527.77	9420.64	102
H13_2	8121.85	1541.14	10164.75	114
H14_2	8442.02	2692.21	10553.97	123
H15_2	7953.76	3828.32	10239.08	107
H16_2	7105	3834.99	9537.78	97
H18_2	5991.08	3221.4	9594.75	105
H19_2	5092.08	2857.19	9823.73	107
H20_2	4416.96	1898.75	9404.1	128

Atom	x	y	z	U_{eq}
H21_2	4566.67	1427.2	8712.31	125
H22_2	5561.69	1616.83	8566.42	174
H24A_11	6191	4331.77	6977.93	153
H24B_11	5823.24	3550.89	6998.24	153
H24C_11	5975.26	4127.95	7433.02	153

Table S12.2.22: Atomic Occupancies for all atoms that are not fully occupied in **WL-2ClBr**.

Atom	Occupancy
Br1_12	0.460(4)
Cl1_12	0.460(4)
O1_12	0.460(4)
O2_12	0.460(4)
C1_12	0.460(4)
C2_12	0.460(4)
C3_12	0.460(4)
C4_12	0.460(4)
C5_12	0.460(4)
C6_12	0.460(4)
H6_12	0.460(4)
C7_12	0.460(4)
H7_12	0.460(4)
C8_12	0.460(4)
C9_12	0.460(4)
H9_12	0.460(4)
C10_12	0.460(4)
H10A_12	0.460(4)
H10B_12	0.460(4)
C11_12	0.460(4)
C12_12	0.460(4)
H12_12	0.460(4)
C13_12	0.460(4)
H13_12	0.460(4)
C14_12	0.460(4)
H14_12	0.460(4)
C15_12	0.460(4)
H15_12	0.460(4)
C16_12	0.460(4)
H16_12	0.460(4)
C17_12	0.460(4)
C18_12	0.460(4)
H18_12	0.460(4)
C19_12	0.460(4)
H19_12	0.460(4)
C20_12	0.460(4)
H20_12	0.460(4)
C21_12	0.460(4)
H21_12	0.460(4)
C22_12	0.460(4)
H22_12	0.460(4)
Br1_4	0.540(4)
Cl1_4	0.540(4)
O1_4	0.540(4)
O2_4	0.540(4)
C1_4	0.540(4)
C2_4	0.540(4)
C3_4	0.540(4)
C4_4	0.540(4)
C5_4	0.540(4)
C6_4	0.540(4)
H6_4	0.540(4)
C7_4	0.540(4)
H7_4	0.540(4)
C8_4	0.540(4)
C9_4	0.540(4)
H9_4	0.540(4)
C10_4	0.540(4)
H10A_4	0.540(4)
H10B_4	0.540(4)
C11_4	0.540(4)
C12_4	0.540(4)
H12_4	0.540(4)
C13_4	0.540(4)
H13_4	0.540(4)
C14_4	0.540(4)
H14_4	0.540(4)
C15_4	0.540(4)
H15_4	0.540(4)
C16_4	0.540(4)
H16_4	0.540(4)
C17_4	0.540(4)
C18_4	0.540(4)
H18_4	0.540(4)
C19_4	0.540(4)
H19_4	0.540(4)
C20_4	0.540(4)
H20_4	0.540(4)
C21_4	0.540(4)
H21_4	0.540(4)
C22_4	0.540(4)
H22_4	0.540(4)

Table S12.2.23: Solvent masking (PLATON/SQUEEZE) information for **WL-2ClBr**.

No	x	y	z	V	e	Content
1	0.426	0.021	-0.073	3377	586	
2	0.520	0.082	0.136	6	0	
3	0.571	0.485	0.605	11	1	
4	0.480	0.582	0.864	7	0	
5	0.429	0.985	0.395	11	1	

Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2017).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

```
#==============================================================================
# PLATON/CHECK-( 70414) versus check.def version of 310314   for Entry: wl-2cl5b
# Data: WL-2ClBr.cif - Type: CIF            Bond Precision   C-C = 0.0137 A
# Refl: WL-2ClBr.fcf - Type: LIST4                    Temp = 100 K
#                                    X-Ray        Nref/Npar =   9.1
# Cell  21.4690(3)  17.1974(3)  29.1637(4)          90   106.965(2)          90
# Wavelength 1.54184    Volume Reported    10299.0(3)   Calculated    10299.0(3)
# SpaceGroup from Symmetry P 21       Hall: P 2yb              monoclinic
#              Reported P 1 21 1        P 2yb              monoclinic
# MoietyFormula C92 H66 Br4 Cl4 N2 O8 Rh2, C90 H65 Br4 Cl4 N O9 Rh2
#     Reported C90 H65 Br4 Cl4 N O9 Rh2, C92 H66 Br4 Cl4 N2 O8 Rh2
#    SumFormula C182 H131 Br8 Cl8 N3 O17 Rh4
#     Reported C182 H131 Br8 Cl8 N3 O17 Rh4
# Mr       =   3966.35[Calc],   3966.41[Rep]
# Dx,gcm-3 =     1.279[Calc],     1.279[Rep]
# Z        =         2[Calc],         2[Rep]
# Mu (mm-1) =     5.741[Calc],     5.741[Rep]
# F000     =    3952.0[Calc],    3952.0[Rep]  or F000' =   3956.25[Calc]
# Reported   T Limits: Tmin=0.028             Tmax=0.486  AbsCorr=GAUSSIAN
# Calculated T Limits: Tmin=0.485 Tmin'=0.132  Tmax=0.617
# Reported   Hmax= 25, Kmax= 20, Lmax= 35, Nref=  36989        , Th(max)= 68.249
# Obs in FCF Hmax= 25, Kmax= 20, Lmax= 35, Nref=  36989[ 19450], Th(max)= 68.248
# Calculated Hmax= 25, Kmax= 20, Lmax= 35, Nref=  37739[ 19552], Ratio=1.89/0.98
# PLATON/Squeeze:      3412.0 Ang**3, Total El.Count =   588.0 e-
# Reported   Rho(min) = -2.10, Rho(max) =  2.32 e/Ang**3 (From CIF)
# w=1/[sigma**2(Fo**2)+(0.1417P)**2+ 19.4469P], P=(Fo**2+2*Fc**2)/3
# R= 0.0813( 30574), wR2= 0.2354( 36989), S = 1.079      (From FCF data only)
# R= 0.0813( 30571), wR2= 0.2353( 36989), S = 1.079, Npar= 2131, Flack 0.066(12)
# Number Bijvoet Pairs =17539 ( 96%)     (12333 Selected for:  Parsons  0.074(3)
# P2(tr) 1.000, P3(tr) 1.000, P3(tw) 0.000,  Student-T Nu  7.58, Hooft  0.050(1)
#==============================================================================
For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
#==============================================================================

#==============================================================================
>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
#==============================================================================
Format: alert-number_ALERT_alert-type_alert-level text

420_ALERT_2_B D-H Without Acceptor       O4     -   H4A    ...     Please Check
420_ALERT_2_B D-H Without Acceptor       O4     -   H4B    ...     Please Check
#==============================================================================
090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) .....       9.13 Note
234_ALERT_4_C Large Hirshfeld Difference C6_1   --  C7_1    ..       0.17 Ang.
234_ALERT_4_C Large Hirshfeld Difference C3_2   --  C11_2   ..       0.17 Ang.
241_ALERT_2_C High      Ueq as Compared to Neighbors for .....      C15_3 Check
241_ALERT_2_C High      Ueq as Compared to Neighbors for .....      C15_1 Check
241_ALERT_2_C High      Ueq as Compared to Neighbors for .....      C21_1 Check
241_ALERT_2_C High      Ueq as Compared to Neighbors for .....      C22_2 Check
241_ALERT_2_C High      Ueq as Compared to Neighbors for .....      C13_5 Check
242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....      C16_3 Check
242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....      C17_3 Check
242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....      C20_1 Check
242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....      C22_1 Check
242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....      C21_2 Check
242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....       C8_8 Check
342_ALERT_3_C Low Bond Precision on  C-C Bonds .....      0.0137 Ang.
411_ALERT_2_C Short Inter H...H Contact  H19_7  ..  H7_4    ..       2.14 Ang.
911_ALERT_3_C Missing # FCF Refl Between THmin &amp;amp; STh/L=  0.600        83 Why ?
#==============================================================================
002_ALERT_2_G Number of Distance or Angle Restraints on AtSite       245 Note
003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...       197 Why ?
007_ALERT_5_G Number of Unrefined Donor-H Atoms .....          2 Why ?
```

008_ALERT_5_G No _iucr_refine_reflections_details in the CIF Please Do !
033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero 0.066
042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.14 Why ?
083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 19.45 Why ?
230_ALERT_2_G Hirshfeld Test Diff for Br1_4 -- C8_4 .. 11.8 su
232_ALERT_2_G Hirshfeld Test Diff (M-X) Rh1 -- N1_10 .. 5.8 su
232_ALERT_2_G Hirshfeld Test Diff (M-X) Rh2 -- O1_4 .. 6.5 su
232_ALERT_2_G Hirshfeld Test Diff (M-X) Rh2 -- O1_12 .. 6.5 su
232_ALERT_2_G Hirshfeld Test Diff (M-X) Rh3 -- N1_11 .. 6.8 su
301_ALERT_3_G Main Residue Disorder ..... Percentage = 12 Note
606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure ! Info
720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 387 Note
791_ALERT_4_G The Model has Chirality at C2_3 ..... S Verify
791_ALERT_4_G The Model has Chirality at C2_5 ..... S Verify
791_ALERT_4_G The Model has Chirality at C2_6 ..... S Verify
791_ALERT_4_G The Model has Chirality at C2_7 ..... S Verify
791_ALERT_4_G The Model has Chirality at C2_8 ..... S Verify
791_ALERT_4_G The Model has Chirality at C2_1 ..... S Verify
791_ALERT_4_G The Model has Chirality at C2_4 ..... S Verify
791_ALERT_4_G The Model has Chirality at C2_2 ..... S Verify
791_ALERT_4_G The Model has Chirality at C2_12 ..... S Verify
802_ALERT_4_G CIF Input Record(s) with more than 80 Characters ! Info
860_ALERT_3_G Number of Least-Squares Restraints ..... 4101 Note
869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed ! Info
910_ALERT_3_G Missing # of FCF Reflections Below Th(Min) ..... 1 Why ?
912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 18 Note
#==========

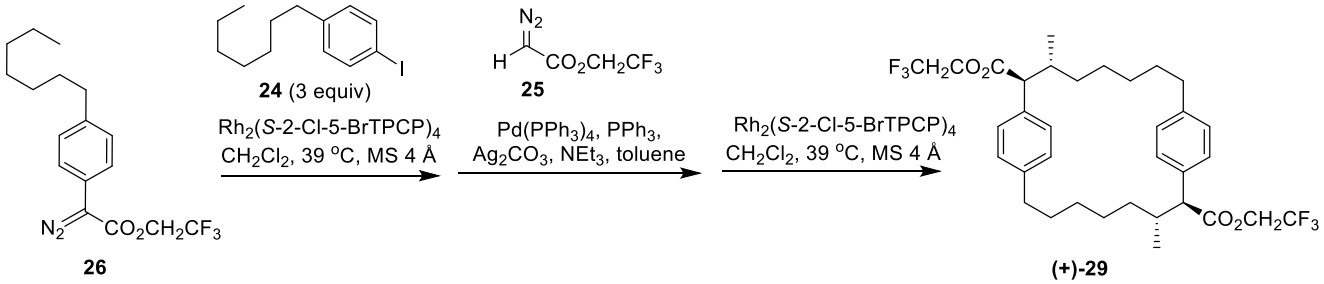
ALERT_Level and ALERT_Type Summary
==========
2 ALERT_Level_B = A Potentially Serious Problem - Consider Carefully
17 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight
30 ALERT_Level_G = General Info/Check that it is not Something Unexpected

1 ALERT_Type_1 CIF Construction/Syntax Error, Inconsistent or Missing Data.
23 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
6 ALERT_Type_3 Indicator that the Structure Quality may be Low.
17 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.
2 ALERT_Type_5 Informative Message, Check.
#==========

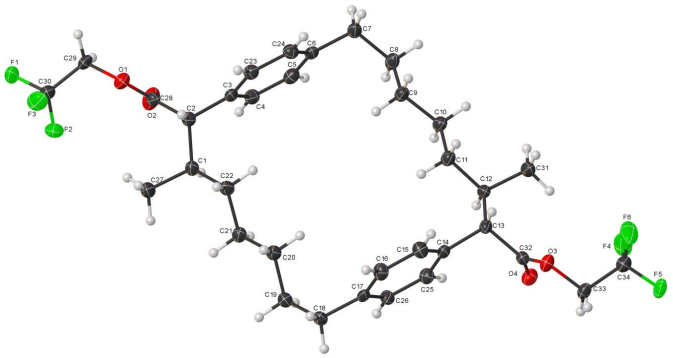
1 Missing Experimental Info Issue(s) (Out of 54 Tests) - 98 % Satisfied
0 Experimental Data Related Issue(s) (Out of 28 Tests) - 100 % Satisfied
25 Structural Model Related Issue(s) (Out of 117 Tests) - 79 % Satisfied
22 Unresolved or to be Checked Issue(s) (Out of 223 Tests) - 90 % Satisfied

#==========

13. X-Ray Crystallographic Data for (+)-29



Crystal Data and Experimental



Experimental. Single colorless needle-shaped crystals of **Aaron-macrocycle** were recrystallized from hexane by slow evaporation. A suitable crystal 0.57×0.06×0.04 mm^3 was selected and mounted on a loopon a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100(2) K during data collection.The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program usingthe Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015)using Least Squares minimisation.

Crystal Data. $C_{34}H_{42}F_6O_4$, M_r = 628.67, monoclinic, $P2$ (No. 3), a = 25.1525(4) Å, b = 5.53398(4) Å, c = 27.2474(4) Å, = 117.4652(19)°, = = 90°, V = 3365.19(9) $Å^3$, T = 100(2) K, Z = 4, Z' = 2, (CuK) = 0.866 mm^{-1}, 42058 reflections measured, 10947 unique (R_{int} = 0.0510) which were used in all calculations. The final wR_2 was 0.0885 (all data) and R_1 was 0.0363 (I > 2σ(I)).

Compound	**Aaron-macrocycle**
Formula	$C_{34}H_{42}F_6O_4$
$D_{calc.}$/ g cm^{-3}	1.241
/mm^{-1}	0.866
Formula Weight	628.67
Colour	colourless
Shape	needle
Size/mm^3	0.57×0.06×0.04
T/K	100(2)
Crystal System	monoclinic
Flack Parameter	-0.02(6)
Hooft Parameter	-0.00(5)
Space Group	$P2$
a/Å	25.1525(4)
b/Å	5.53398(4)
c/Å	27.2474(4)
/°	90
/°	117.4652(19)
/°	90
V/$Å^3$	3365.19(9)
Z	4
Z'	2
Wavelength/Å	1.54184
Radiation type	CuK
$_{min}$/°	1.980
$_{max}$/°	73.814
Measured Refl.	42058
Independent Refl.	10947
Reflections with I > 2σ(I)	9975
R_{int}	0.0510
Parameters	797
Restraints	1
Largest Peak	0.323
Deepest Hole	-0.205
GooF	0.985
wR_2 (all data)	0.0885
wR_2	0.0853
R_1 (all data)	0.0412
R_1	0.0363

Structure Quality Indicators

Reflections: d min (Cu) 0.80 | I/σ 23.6 | Rint 5.10%

Refinement: Shift -0.008 | Max Peak 0.3 | Min Peak -0.2 | GooF 0.985 | Flack -.02(6)

A colourless needle-shaped crystal with dimensions 0.57×0.06×0.04 mm^3 was mounted on a loop. Data were collected using an XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100(2) K.

Data were measured using scans with a narrow frame width of 0.5° per frame for 3.5/3.7/10.0 s using CuK radiation. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.43c, 2018). The maximum resolution that was achieved was = 73.814°.

The diffraction pattern was indexed using **CrysAlisPro** (Rigaku, V1.171.39.43c, 2018) and the unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.39.43c, 2018) on 24772 reflections, 59% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.39.43c, 2018). The final completeness is 98.70 % out to 73.814° in . A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was applied using CrysAlisPro 1.171.39.43c (Rigaku Oxford Diffraction, 2018). An empirical absorption correction using spherical harmonics as implemented by SCALE3 ABSPACK algorithm was applied. The absorption coefficient of this material is 0.866 mm^{-1} at this wavelength (= 1.54184Å) and the minimum and maximum transmissions are 0.487 and 1.000.

The structure was solved and the space group *P*2 (# 3) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL-2014** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.Hydrogen atom positions were calculated geometrically and refined using the riding model.

The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

The Flack parameter was refined to -0.02(6). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.00(5). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

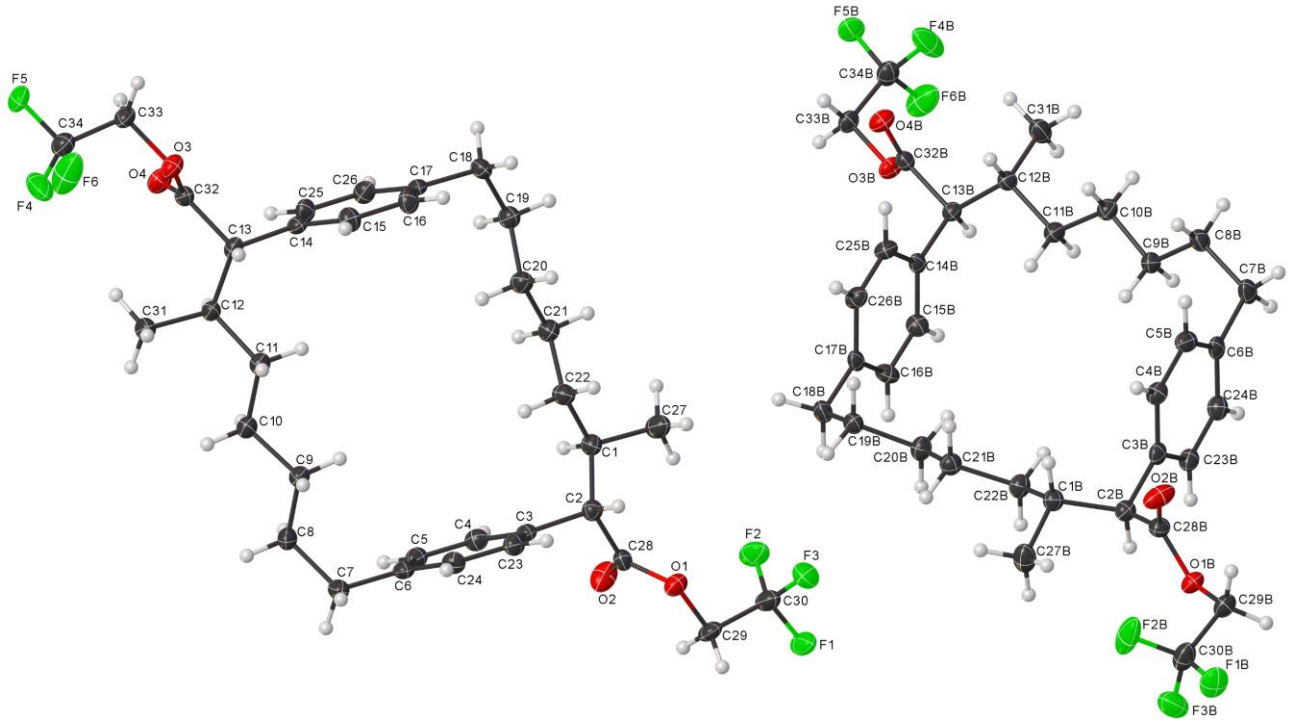


Figure S13.5: The asymmetric unit contains two molecules of the compound.

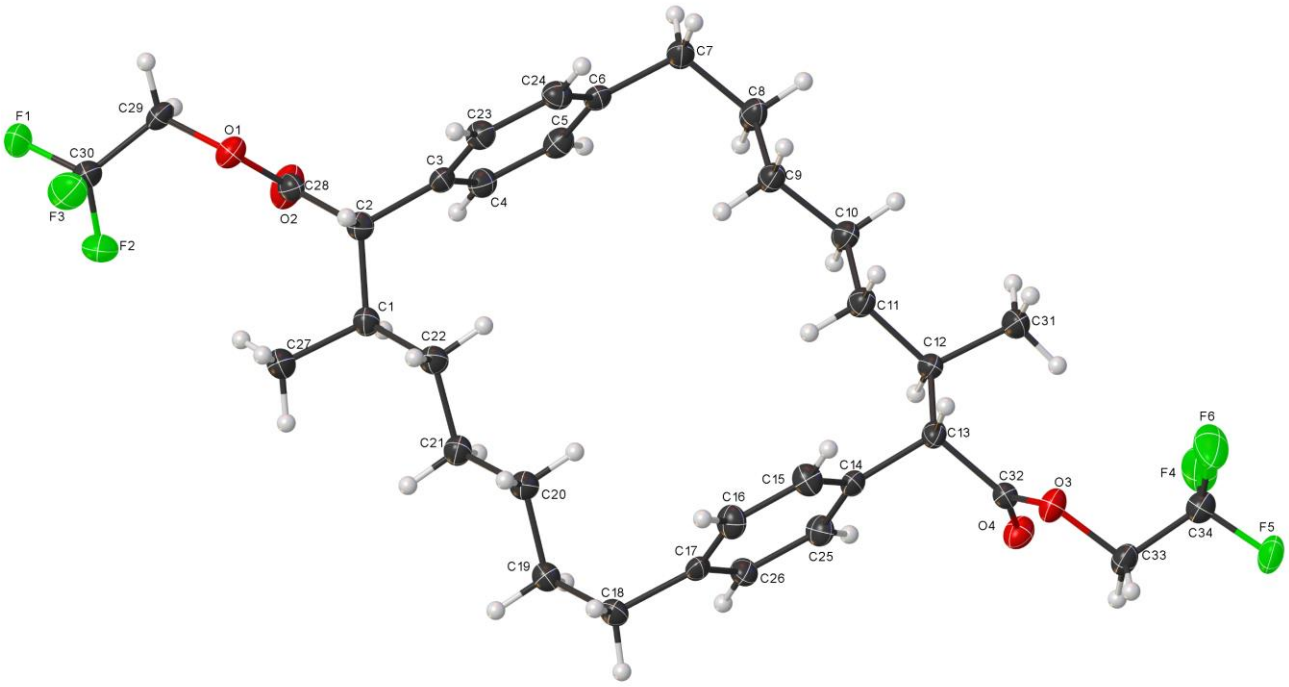


Figure S13.6:

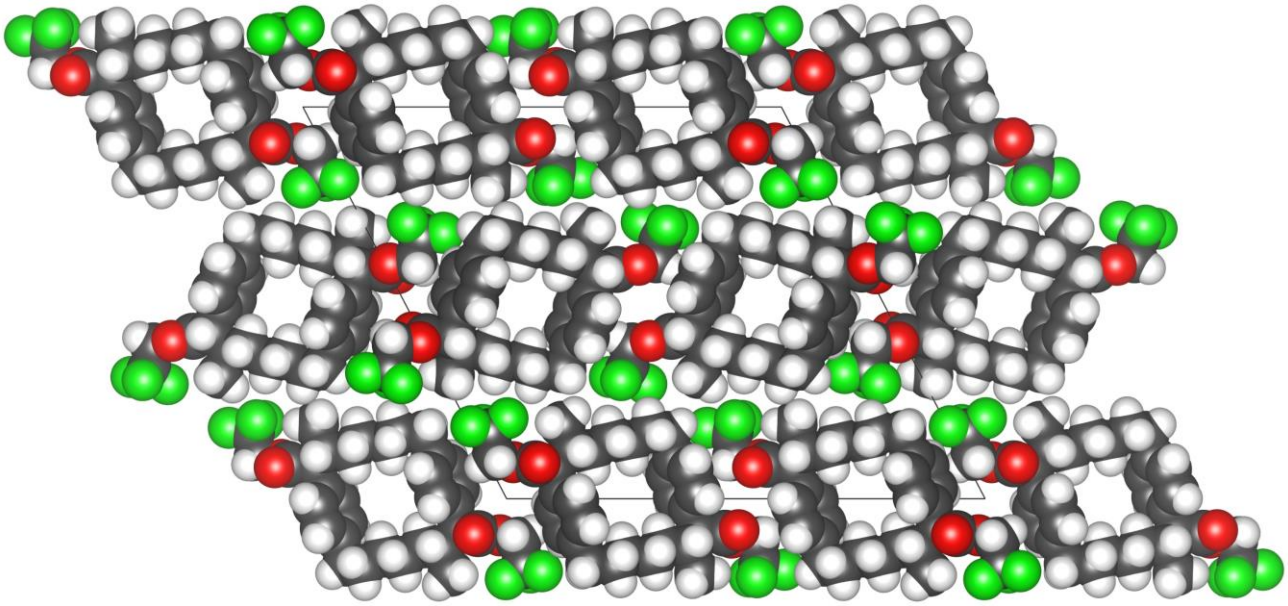


Figure S13.7:

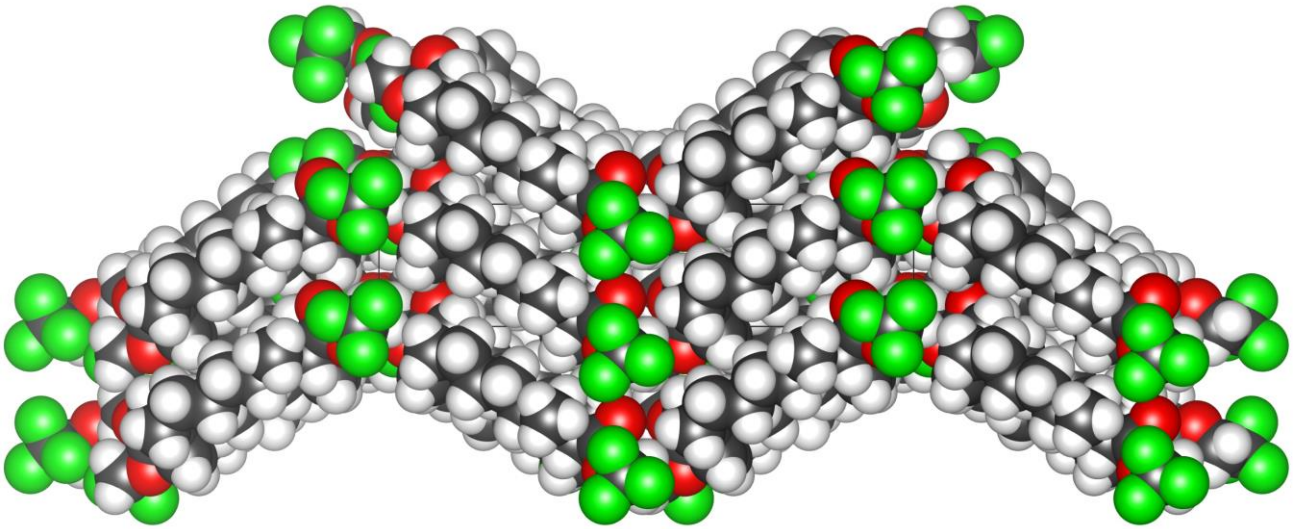
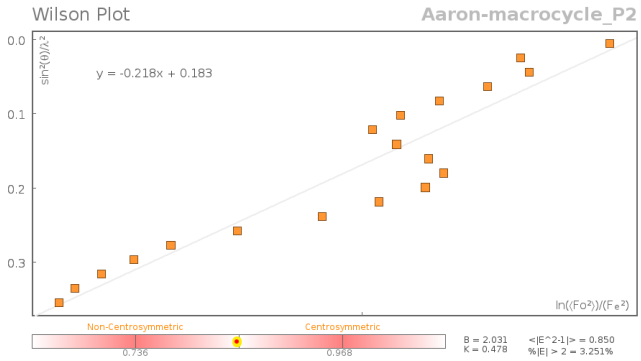
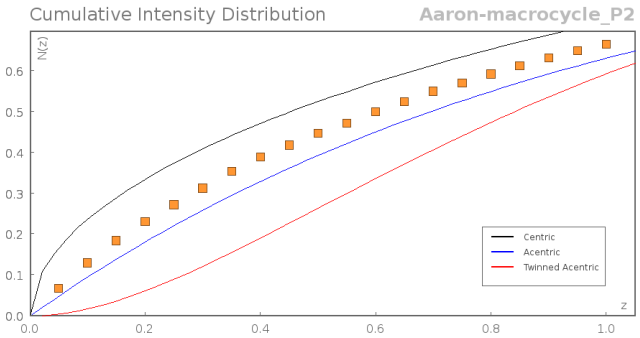
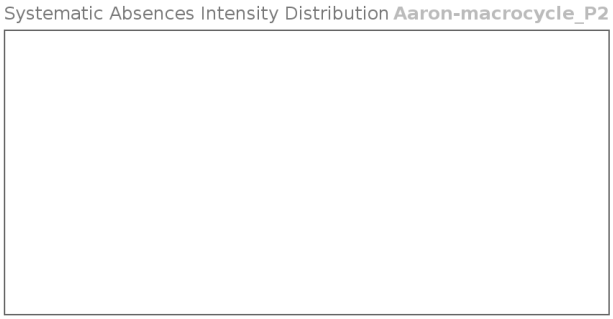


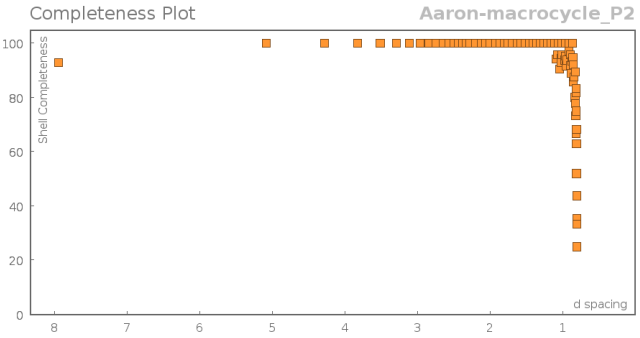
Figure S13.8:

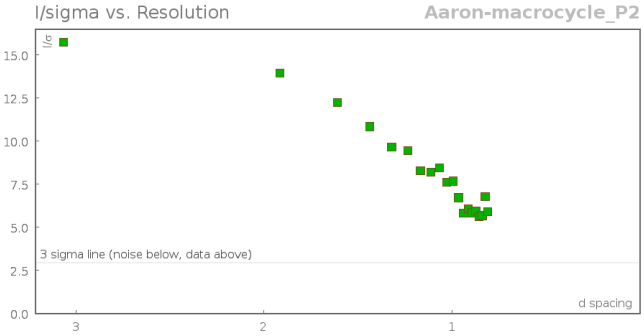
Data Plots: Diffraction Data



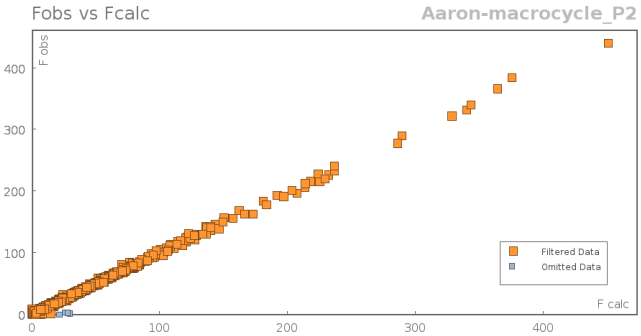


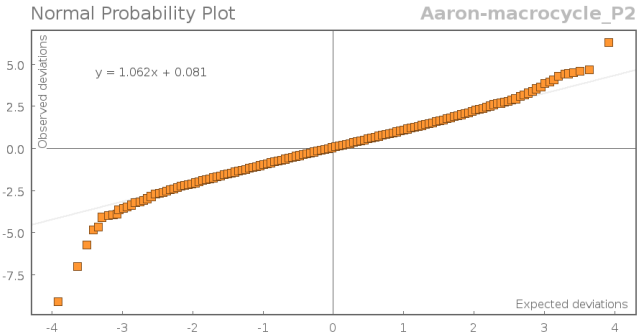






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	42062	Unique reflections	10947
Completeness	0.804	Mean I/	16.19
hkl_{max} collected	(30, 6, 33)	hkl_{min} collected	(-30, -6, -33)
hkl_{max} used	(27, 6, 33)	hkl_{min} used	(-30, -6, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	22.32	d_{min} used	0.8
Friedel pairs	5250	Friedel pairs merged	0
Inconsistent equivalents	10	R_{int}	0.051

R_{sigma}	0.0423	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	4
Multiplicity	(6310, 4911, 3058, 1507, 1006, 519, 204, 88, 40, 7, 2)	Maximum multiplicity	18
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer

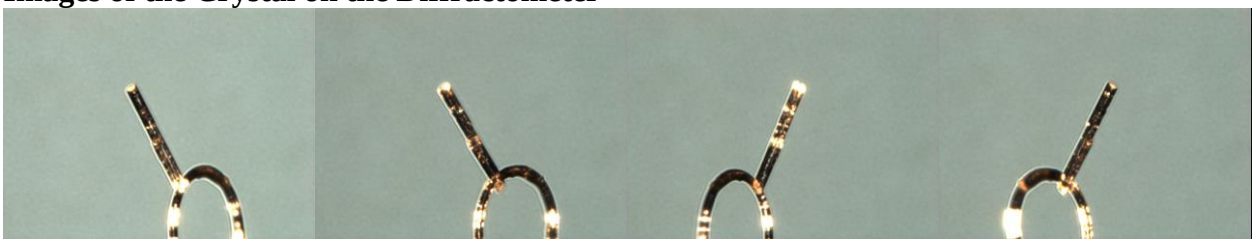


Table S13.24: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Aaron-macrocycle_P2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
F1	3107.8(7)	-1535(3)	3482.8(6)	40.3(4)
F2	2927.5(7)	-699(4)	4163.9(7)	43.1(5)
F3	3029.6(8)	2168(3)	3682.3(7)	44.3(5)
F4	6931.1(8)	10422(4)	11116.2(8)	54.0(5)
F5	6790.1(7)	13309(3)	11567.5(6)	34.1(4)
F6	7051.5(9)	14083(5)	10937.5(8)	63.2(7)
O1	4027.6(8)	1790(3)	4704.1(7)	24.9(4)
O2	4161.9(10)	-1186(3)	5309.5(8)	34.6(5)
O3	6006.0(8)	12270(3)	10110.3(7)	24.8(4)
O4	5755.0(8)	8401(3)	10163.3(7)	26.6(4)
C1	3780.7(11)	2906(5)	5830.5(10)	22.6(5)
C2	4251.8(11)	2953(5)	5616.8(10)	21.2(5)
C3	4891.6(11)	2815(5)	6079.4(10)	19.9(5)
C4	5096.8(12)	917(5)	6458.4(10)	23.7(6)
C5	5675.7(12)	905(5)	6887.6(10)	24.0(6)
C6	6074.6(11)	2778(5)	6953.4(10)	21.4(5)
C7	6704.0(11)	2795(5)	7419.2(10)	27.1(6)
C8	6739.8(12)	2951(5)	7994.2(10)	27.6(6)
C9	6465.4(12)	5221(5)	8095.4(10)	23.7(6)
C10	6516.9(12)	5313(5)	8675.3(10)	24.1(5)
C11	6212.8(12)	7497(5)	8772.7(10)	24.6(6)
C12	6209.5(11)	7575(5)	9334.4(9)	21.0(5)
C13	5839.4(11)	9758(5)	9353.0(10)	20.3(5)
C14	5191.4(11)	9689(5)	8912.1(10)	20.0(5)
C15	4964.7(12)	11456(5)	8505.7(11)	25.0(6)
C16	4377.1(12)	11353(5)	8087.6(11)	26.2(6)
C17	3996.1(11)	9483(5)	8059.1(10)	20.1(5)
C18	3362.9(11)	9314(5)	7599.5(10)	23.9(6)
C19	3252.2(12)	7142(5)	7217.6(11)	25.3(6)
C20	3625.5(12)	7131(5)	6911.5(11)	26.0(6)
C21	3517.0(12)	4965(5)	6538.5(11)	25.0(6)

Atom	x	y	z	U_{eq}
C22	3874.2(12)	5034(5)	6215.9(11)	24.8(6)
C23	5287.2(11)	4679(5)	6142.9(10)	22.6(5)
C24	5865.8(12)	4667(5)	6573.4(10)	23.7(5)
C25	4809.6(11)	7819(5)	8889.4(10)	23.6(5)
C26	4225.4(11)	7726(5)	8470.6(10)	23.9(5)
C27	3147.2(12)	2864(6)	5349.5(11)	35.0(7)
C28	4147.1(11)	936(5)	5211.2(10)	21.4(5)
C29	3900.7(12)	18(5)	4278.4(10)	26.0(6)
C30	3240.7(12)	-13(6)	3906.9(11)	32.9(7)
C31	6844.6(11)	7687(6)	9811.7(10)	31.4(6)
C32	5860.6(11)	9970(5)	9917.2(10)	20.3(5)
C33	6063.6(11)	12761(5)	10649.8(10)	24.3(5)
C34	6708.7(12)	12639(5)	11063.1(11)	29.0(6)
F1B	1848.2(8)	11712(3)	49.8(7)	39.7(4)
F2B	2053.5(8)	10844(4)	890.5(7)	53.2(6)
F3B	1882.0(8)	7990(3)	307.4(7)	43.7(4)
F4B	-2001.3(8)	-248(4)	4376.9(8)	50.5(5)
F5B	-1810.7(7)	-2763(3)	5035.6(6)	32.3(4)
F6B	-1985.5(8)	-4054(4)	4231.7(8)	51.2(5)
O1B	934.2(8)	8649(3)	534.8(7)	23.6(4)
O2B	917.9(10)	11669(3)	1080.3(8)	33.4(5)
O3B	-990.6(8)	-1732(3)	4282.2(7)	22.4(4)
O4B	-804.5(8)	2223(3)	4505.0(7)	26.6(4)
C1B	1271.4(11)	7679(5)	1922.1(10)	21.6(5)
C2B	793.8(11)	7555(5)	1304.6(10)	20.6(5)
C3B	155.1(11)	7692(5)	1223.3(9)	20.3(5)
C4B	-47.0(12)	9629(5)	1421.8(10)	22.4(5)
C5B	-630.8(12)	9684(5)	1349.5(10)	24.4(6)
C6B	-1030.0(11)	7828(5)	1080.7(9)	22.0(5)
C7B	-1664.2(11)	7860(5)	1009.2(10)	26.5(6)
C8B	-1693.1(11)	7697(5)	1557.4(10)	24.2(5)
C9B	-1433.2(11)	5398(5)	1880.1(10)	22.5(5)
C10B	-1508.1(12)	5231(5)	2401.0(10)	22.6(5)
C11B	-1201.5(12)	3046(5)	2755.0(10)	24.1(5)
C12B	-1242.2(11)	2857(5)	3298.8(10)	20.4(5)
C13B	-849.3(11)	741(5)	3648.3(9)	18.1(5)
C14B	-199.2(11)	914(4)	3765.3(9)	17.7(5)
C15B	47.6(12)	-830(5)	3567.6(10)	22.8(5)
C16B	638.0(12)	-664(5)	3658.9(11)	24.7(6)
C17B	1001.5(11)	1259(4)	3953.6(10)	19.3(5)
C18B	1643.5(11)	1494(5)	4061.0(10)	23.3(5)
C19B	1755.6(11)	3697(5)	3779.4(10)	21.7(5)
C20B	1415.4(12)	3584(5)	3151.1(10)	23.7(5)
C21B	1548.4(12)	5680(5)	2863.7(10)	23.4(5)
C22B	1177.7(12)	5569(5)	2236.1(10)	23.1(5)
C23B	-247.0(11)	5842(5)	950.0(10)	22.5(5)
C24B	-828.8(12)	5903(5)	881.9(10)	24.0(6)
C25B	163.1(11)	2841(5)	4062.7(10)	23.3(5)
C26B	749.2(11)	3003(5)	4151.5(10)	23.4(5)
C27B	1901.1(12)	7665(6)	1970.6(11)	33.0(6)
C28B	890.5(12)	9560(5)	978.9(10)	21.7(5)
C29B	1057.3(12)	10354(5)	202.4(10)	25.5(6)
C30B	1713.3(13)	10234(6)	369.5(11)	33.1(7)
C31B	-1887.4(12)	2491(6)	3189.4(11)	31.1(6)
C32B	-879.9(11)	590(4)	4189.4(10)	19.0(5)
C33B	-1060.2(11)	-2166(5)	4766.7(10)	21.9(5)
C34B	-1714.1(12)	-2286(5)	4600.9(10)	27.8(6)

Table S13.25: Anisotropic Displacement Parameters ($\times 10^4$) **Aaron-macrocycle_P2**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	28.1(9)	59.4(12)	28.7(8)	-19.7(8)	9.1(7)	0.2(8)
F2	27.6(9)	68.3(13)	39.7(10)	-10.2(9)	21.0(8)	-6.9(9)
F3	40.1(11)	53.9(12)	37.5(10)	7.1(9)	16.6(8)	20.2(9)
F4	39.0(11)	61.0(13)	43.9(11)	-12.8(10)	3.6(9)	25.4(10)
F5	36.5(9)	41.8(10)	18.0(7)	-5.3(7)	7.4(7)	3.0(8)
F6	46.0(12)	105.8(19)	36.2(10)	-6.7(11)	17.7(10)	-38.8(12)
O1	32.9(11)	22.1(9)	22.0(9)	0.3(7)	14.5(8)	0.7(8)
O2	54.7(14)	16.9(10)	29.3(10)	-1.3(8)	16.8(10)	-1.8(9)
O3	33.2(11)	21.3(9)	19.2(9)	-2.1(7)	11.6(8)	-1.9(8)
O4	34.1(11)	25.2(10)	23.5(9)	0.3(8)	15.9(8)	-5.2(8)
C1	21.1(13)	24.2(13)	20.9(12)	-2.6(11)	8.2(11)	-0.1(11)
C2	21.6(13)	20.5(12)	20.7(12)	0.1(10)	9.2(11)	0.2(11)
C3	20.2(13)	22.0(12)	18.5(11)	-4.1(10)	9.9(10)	1.0(11)
C4	24.9(15)	22.7(13)	24.7(13)	-3.7(11)	12.3(12)	-3.6(11)
C5	31.0(15)	20.8(13)	21.8(12)	3.5(10)	13.6(12)	5.5(11)
C6	21.6(13)	24.1(13)	20.5(12)	-3.5(11)	11.4(11)	2.4(11)
C7	22.3(14)	34.1(15)	22.5(13)	-4.3(12)	8.3(11)	6.3(12)
C8	27.9(15)	32.6(15)	18.6(12)	1.8(11)	7.7(11)	8.8(12)
C9	25.7(14)	25.8(14)	19.4(12)	0.3(11)	10.1(11)	4.1(12)
C10	24.2(14)	29.1(14)	19.3(12)	1.2(11)	10.3(11)	1.7(11)
C11	25.9(14)	27.7(14)	19.9(12)	1.0(11)	10.4(11)	3.5(12)
C12	18.4(12)	27.5(13)	17.2(11)	0.0(10)	8.2(10)	1.2(11)
C13	20.8(13)	23.6(13)	16.1(12)	-0.3(10)	8.3(11)	-3.1(11)
C14	20.1(13)	22.8(13)	17.2(12)	-4.3(10)	8.7(11)	0.5(10)
C15	24.9(15)	21.2(13)	26.5(13)	2.5(11)	9.7(12)	0.3(11)
C16	27.6(15)	24.3(14)	22.7(13)	4.1(11)	8.1(12)	3.2(12)
C17	19.4(13)	24.8(13)	16.8(12)	-3.9(10)	9.0(11)	4.0(11)
C18	18.1(13)	28.1(14)	24.0(13)	-1.3(11)	8.4(11)	3.3(11)
C19	21.0(14)	29.5(15)	23.8(13)	-2.2(11)	9.2(11)	-0.6(11)
C20	22.9(14)	30.3(15)	25.1(13)	-3.4(11)	11.4(12)	-0.9(11)
C21	24.1(14)	27.7(14)	21.8(13)	-2.1(11)	9.4(12)	1.0(11)
C22	22.0(14)	26.5(14)	25.8(13)	-3.4(11)	11.0(12)	0.3(11)
C23	24.9(14)	21.1(12)	22.3(13)	2.5(10)	11.4(12)	2.2(11)
C24	23.1(14)	22.8(13)	26.5(13)	-0.6(11)	12.6(12)	-1.8(11)
C25	25.1(14)	24.7(13)	19.3(12)	5.2(11)	8.9(11)	2.4(11)
C26	20.0(13)	29.3(14)	22.6(12)	-2.0(11)	10.0(11)	-5.5(12)
C27	22.9(14)	52.3(19)	28.1(14)	-11.8(14)	10.4(12)	-3.4(14)
C28	18.8(13)	23.8(14)	19.3(12)	2.4(10)	7.0(11)	2.7(10)
C29	28.5(15)	32.3(15)	20.6(13)	-7.7(11)	14.2(12)	-1.8(12)
C30	24.8(15)	49.4(19)	26.5(14)	-9.8(13)	13.6(13)	-0.6(14)
C31	21.5(14)	48.2(18)	22.0(13)	-2.5(13)	7.7(12)	5.9(13)
C32	16.9(13)	23.8(13)	18.8(12)	-1.7(10)	7.0(11)	-0.3(11)
C33	28.6(14)	25.0(13)	18.5(12)	-2.4(11)	10.2(11)	2.8(12)
C34	29.8(15)	34.0(15)	23.7(13)	-3.8(12)	12.7(12)	-1.1(13)
F1B	38.2(10)	52.4(11)	34.2(9)	6.0(8)	21.7(8)	-8.8(8)
F2B	37.3(11)	92.0(16)	23.4(8)	-7.7(10)	8.3(8)	-25.9(11)
F3B	38.2(10)	50.4(11)	49.1(10)	11.1(9)	25.6(9)	12.8(9)
F4B	39.5(11)	60.0(12)	61.5(12)	34.4(10)	31.4(10)	23.2(9)
F5B	33.3(9)	40.6(10)	31.5(8)	7.2(7)	22.1(7)	1.0(7)
F6B	40.4(11)	73.9(14)	41.0(10)	-22.3(10)	20.3(9)	-26.3(10)
O1B	30.8(10)	23.9(9)	19.2(8)	-2.0(7)	14.1(8)	-1.5(8)
O2B	60.9(14)	17.3(9)	35.3(11)	-0.6(8)	33.5(11)	-0.6(9)
O3B	32.1(10)	18.1(9)	21.2(9)	1.5(7)	15.9(8)	-1.6(8)
O4B	35.2(11)	24.0(10)	24.3(9)	-5.2(8)	16.8(9)	-3.6(8)
C1B	22.4(13)	20.6(12)	21.2(12)	1.5(10)	9.5(11)	0.0(11)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2B	23.0(13)	18.3(12)	20.8(12)	0.7(10)	10.3(11)	0.1(11)
C3B	24.2(13)	19.8(12)	15.0(11)	5.0(10)	7.4(10)	3.0(11)
C4B	27.5(15)	18.8(13)	20.4(12)	-1.6(10)	10.5(12)	-2.2(11)
C5B	30.8(15)	22.1(13)	23.1(13)	3.8(11)	14.6(12)	5.9(11)
C6B	22.8(13)	25.5(13)	15.1(11)	8.0(10)	6.7(10)	4.3(11)
C7B	22.2(13)	34.2(15)	21.2(12)	9.7(12)	8.4(11)	4.6(12)
C8B	21.1(13)	27.8(14)	22.9(12)	4.8(11)	9.5(11)	4.1(11)
C9B	22.6(14)	25.2(13)	19.1(12)	2.6(11)	9.0(11)	4.1(11)
C10B	24.5(14)	22.3(13)	19.8(12)	-0.9(10)	9.3(11)	1.4(11)
C11B	26.1(14)	26.8(14)	20.6(12)	1.0(11)	11.7(11)	4.4(11)
C12B	20.5(13)	21.6(12)	19.6(12)	2.4(10)	9.7(10)	3.7(11)
C13B	19.2(13)	18.2(12)	16.9(11)	-1.8(10)	8.5(10)	-1.4(10)
C14B	17.3(13)	19.8(12)	15.4(11)	4.7(10)	7.1(10)	1.9(10)
C15B	23.7(14)	18.3(13)	25.2(13)	-1.8(10)	10.2(12)	-0.7(10)
C16B	23.2(14)	22.7(13)	30.8(14)	1.0(11)	14.8(12)	5.8(11)
C17B	16.8(13)	23.6(13)	16.6(11)	7.1(10)	7.0(11)	3.6(10)
C18B	18.4(14)	28.9(14)	20.9(12)	4.7(11)	7.6(11)	3.6(11)
C19B	18.4(13)	24.7(13)	20.9(12)	0.6(10)	8.2(11)	0.8(11)
C20B	25.2(14)	24.0(13)	20.4(12)	1.3(11)	9.0(11)	-2.7(11)
C21B	23.8(14)	24.0(13)	22.9(13)	1.3(11)	11.3(11)	-0.4(11)
C22B	25.2(14)	21.7(13)	21.0(12)	1.2(11)	9.6(12)	-2.2(11)
C23B	26.9(15)	19.1(12)	19.3(12)	-0.2(10)	8.8(11)	2.3(11)
C24B	24.3(15)	22.2(13)	21.4(13)	0.1(11)	7.1(12)	-2.4(11)
C25B	26.9(14)	24.9(13)	22.3(12)	-3.2(11)	15.0(11)	0.0(12)
C26B	22.4(13)	26.8(13)	21.3(12)	-5.6(11)	10.4(11)	-5.9(11)
C27B	23.8(15)	45.9(18)	27.8(14)	6.3(14)	10.4(12)	-4.1(14)
C28B	24.0(14)	20.3(13)	21.7(13)	-0.2(10)	11.3(11)	3.1(11)
C29B	31.3(16)	28.1(14)	19.4(12)	1.3(11)	13.8(12)	-1.2(12)
C30B	31.0(16)	45.9(18)	22.1(14)	1.6(13)	11.9(13)	-6.7(14)
C31B	23.8(14)	42.4(17)	28.2(14)	9.0(13)	12.9(12)	6.4(13)
C32B	16.8(13)	20.0(12)	19.6(12)	2.1(10)	7.9(10)	1.2(10)
C33B	26.8(14)	23.0(13)	17.8(12)	3.4(10)	11.7(11)	-0.3(11)
C34B	27.1(14)	34.8(15)	23.0(13)	3.9(12)	12.7(12)	-1.9(13)

Table S13.26: Bond Lengths in Å for **Aaron-macrocycle_P2**.

Atom	Atom	Length/Å
F1	C30	1.342(3)
F2	C30	1.328(3)
F3	C30	1.347(4)
F4	C34	1.328(3)
F5	C34	1.345(3)
F6	C34	1.331(3)
O1	C28	1.356(3)
O1	C29	1.438(3)
O2	C28	1.201(3)
O3	C32	1.361(3)
O3	C33	1.435(3)
O4	C32	1.199(3)
C1	C2	1.543(3)
C1	C22	1.522(4)
C1	C27	1.527(4)
C2	C3	1.521(3)
C2	C28	1.506(3)
C3	C4	1.394(4)
C3	C23	1.388(4)
C4	C5	1.385(4)
C5	C6	1.395(4)
C6	C7	1.505(4)
C6	C24	1.393(4)
C7	C8	1.530(3)
C8	C9	1.518(4)
C9	C10	1.525(3)
C10	C11	1.517(4)
C11	C12	1.535(3)
C12	C13	1.540(3)
C12	C31	1.527(3)
C13	C14	1.515(3)
C13	C32	1.518(3)
C14	C15	1.388(4)
C14	C25	1.393(4)
C15	C16	1.390(4)
C16	C17	1.388(4)
C17	C18	1.508(4)
C17	C26	1.392(4)
C18	C19	1.529(4)
C19	C20	1.516(3)
C20	C21	1.513(4)

Atom	Atom	Length/Å
C21	C22	1.520(3)
C23	C24	1.385(4)
C25	C26	1.385(4)
C29	C30	1.494(4)
C33	C34	1.490(4)
F1B	C30B	1.347(3)
F2B	C30B	1.319(3)
F3B	C30B	1.348(4)
F4B	C34B	1.326(3)
F5B	C34B	1.341(3)
F6B	C34B	1.342(3)
O1B	C28B	1.361(3)
O1B	C29B	1.437(3)
O2B	C28B	1.194(3)
O3B	C32B	1.363(3)
O3B	C33B	1.430(3)
O4B	C32B	1.201(3)
C1B	C2B	1.554(3)
C1B	C22B	1.528(3)
C1B	C27B	1.527(3)
C2B	C3B	1.519(3)
C2B	C28B	1.509(3)
C3B	C4B	1.398(3)
C3B	C23B	1.390(4)
C4B	C5B	1.389(3)
C5B	C6B	1.386(4)
C6B	C7B	1.515(3)
C6B	C24B	1.392(4)
C7B	C8B	1.531(3)
C8B	C9B	1.513(4)
C9B	C10B	1.518(3)
C10B	C11B	1.517(4)
C11B	C12B	1.535(3)
C12B	C13B	1.545(3)
C12B	C31B	1.522(3)
C13B	C14B	1.518(3)
C13B	C32B	1.514(3)
C14B	C15B	1.384(3)
C14B	C25B	1.394(4)
C15B	C16B	1.391(3)
C16B	C17B	1.391(4)
C17B	C18B	1.508(3)
C17B	C26B	1.393(3)
C18B	C19B	1.534(3)
C19B	C20B	1.522(3)
C20B	C21B	1.520(3)
C21B	C22B	1.525(3)
C23B	C24B	1.388(4)
C25B	C26B	1.382(3)
C29B	C30B	1.497(4)
C33B	C34B	1.493(3)

Table S13.27: Bond Angles in ° for **Aaron-macrocycle_P2**.

Atom	Atom	Atom	Angle/°
C28	O1	C29	116.5(2)
C32	O3	C33	117.09(19)
C22	C1	C2	110.3(2)
C22	C1	C27	111.9(2)
C27	C1	C2	110.8(2)
C3	C2	C1	112.92(19)
C28	C2	C1	111.1(2)
C28	C2	C3	109.3(2)
C4	C3	C2	122.7(2)
C23	C3	C2	119.3(2)
C23	C3	C4	117.9(2)
C5	C4	C3	121.0(2)
C4	C5	C6	121.2(2)
C5	C6	C7	121.8(2)
C24	C6	C5	117.4(2)
C24	C6	C7	120.8(2)
C6	C7	C8	114.0(2)
C9	C8	C7	114.6(2)
C8	C9	C10	112.8(2)
C11	C10	C9	113.5(2)
C10	C11	C12	115.6(2)
C11	C12	C13	109.6(2)
C31	C12	C11	111.5(2)
C31	C12	C13	110.5(2)
C14	C13	C12	113.5(2)
C14	C13	C32	109.11(19)
C32	C13	C12	110.7(2)
C15	C14	C13	120.7(2)
C15	C14	C25	117.8(2)
C25	C14	C13	121.4(2)
C16	C15	C14	121.0(2)
C15	C16	C17	121.5(2)
C16	C17	C18	122.0(2)
C26	C17	C16	117.2(2)
C26	C17	C18	120.8(2)
C17	C18	C19	113.9(2)
C20	C19	C18	114.4(2)
C21	C20	C19	114.0(2)
C20	C21	C22	113.4(2)
C21	C22	C1	115.8(2)
C24	C23	C3	121.0(2)
C23	C24	C6	121.5(2)
C26	C25	C14	120.8(2)
C25	C26	C17	121.7(2)
O1	C28	C2	111.8(2)
O2	C28	O1	122.5(2)
O2	C28	C2	125.7(2)
O1	C29	C30	108.6(2)
F1	C30	F3	106.4(2)
F1	C30	C29	110.4(2)
F2	C30	F1	107.6(2)
F2	C30	F3	106.9(2)
F2	C30	C29	112.9(2)

Atom	Atom	Atom	Angle/°
F3	C30	C29	112.3(3)
O3	C32	C13	110.0(2)
O4	C32	O3	123.4(2)
O4	C32	C13	126.7(2)
O3	C33	C34	109.0(2)
F4	C34	F5	106.6(2)
F4	C34	F6	107.0(2)
F4	C34	C33	112.4(2)
F5	C34	C33	111.1(2)
F6	C34	F5	106.6(2)
F6	C34	C33	112.8(2)
C28B	O1B	C29B	116.5(2)
C32B	O3B	C33B	116.90(19)
C22B	C1B	C2B	109.3(2)
C27B	C1B	C2B	110.27(19)
C27B	C1B	C22B	111.7(2)
C3B	C2B	C1B	113.15(18)
C28B	C2B	C1B	110.5(2)
C28B	C2B	C3B	108.9(2)
C4B	C3B	C2B	122.1(2)
C23B	C3B	C2B	120.1(2)
C23B	C3B	C4B	117.9(2)
C5B	C4B	C3B	120.8(2)
C6B	C5B	C4B	121.3(2)
C5B	C6B	C7B	121.5(2)
C5B	C6B	C24B	117.9(2)
C24B	C6B	C7B	120.6(2)
C6B	C7B	C8B	113.2(2)
C9B	C8B	C7B	114.5(2)
C8B	C9B	C10B	112.8(2)
C11B	C10B	C9B	113.4(2)
C10B	C11B	C12B	115.3(2)
C11B	C12B	C13B	109.76(19)
C31B	C12B	C11B	111.1(2)
C31B	C12B	C13B	109.9(2)
C14B	C13B	C12B	113.73(19)
C32B	C13B	C12B	109.69(19)
C32B	C13B	C14B	109.43(19)
C15B	C14B	C13B	120.5(2)
C15B	C14B	C25B	118.0(2)
C25B	C14B	C13B	121.5(2)
C14B	C15B	C16B	121.2(2)
C15B	C16B	C17B	121.1(2)
C16B	C17B	C18B	122.5(2)
C16B	C17B	C26B	117.2(2)
C26B	C17B	C18B	120.2(2)
C17B	C18B	C19B	113.5(2)
C20B	C19B	C18B	113.1(2)
C21B	C20B	C19B	113.9(2)
C20B	C21B	C22B	112.4(2)
C21B	C22B	C1B	115.1(2)
C3B	C23B	C24B	121.0(2)
C23B	C24B	C6B	121.1(2)
C26B	C25B	C14B	120.7(2)
C25B	C26B	C17B	121.8(2)
O1B	C28B	C2B	110.6(2)
O2B	C28B	O1B	123.2(2)
O2B	C28B	C2B	126.2(2)
O1B	C29B	C30B	107.9(2)
F1B	C30B	C29B	110.3(2)
F2B	C30B	F1B	108.0(2)
F2B	C30B	F3B	106.6(3)
F2B	C30B	C29B	113.1(2)
F3B	C30B	F1B	106.9(2)
F3B	C30B	C29B	111.6(2)
O3B	C32B	C13B	109.8(2)
O4B	C32B	O3B	123.7(2)
O4B	C32B	C13B	126.4(2)
O3B	C33B	C34B	108.36(19)
F4B	C34B	F5B	107.0(2)
F4B	C34B	F6B	107.1(2)
F4B	C34B	C33B	113.1(2)
F5B	C34B	F6B	106.4(2)
F5B	C34B	C33B	111.4(2)
F6B	C34B	C33B	111.6(2)

Table S13.28: Torsion Angles in ° for **Aaron-macrocycle_P2**.

Atom	Atom	Atom	Atom	Angle/°
O1	C29	C30	F1	176.0(2)
O1	C29	C30	F2	-63.5(3)
O1	C29	C30	F3	57.5(3)
O3	C33	C34	F4	-66.4(3)
O3	C33	C34	F5	174.3(2)
O3	C33	C34	F6	54.6(3)
C1	C2	C3	C4	57.5(3)
C1	C2	C3	C23	-120.4(2)
C1	C2	C28	O1	118.2(2)
C1	C2	C28	O2	-61.6(3)
C2	C1	C22	C21	-169.3(2)
C2	C3	C4	C5	-177.3(2)
C2	C3	C23	C24	177.3(2)
C3	C2	C28	O1	-116.5(2)

Atom	Atom	Atom	Atom	Angle/°
C3	C2	C28	O2	63.7(3)
C3	C4	C5	C6	-0.5(4)
C3	C23	C24	C6	0.8(4)
C4	C3	C23	C24	-0.7(3)
C4	C5	C6	C7	179.7(2)
C4	C5	C6	C24	0.5(3)
C5	C6	C7	C8	-63.9(3)
C5	C6	C24	C23	-0.7(3)
C6	C7	C8	C9	-61.2(3)
C7	C6	C24	C23	-179.9(2)
C7	C8	C9	C10	-179.4(2)
C8	C9	C10	C11	-176.6(2)
C9	C10	C11	C12	175.5(2)
C10	C11	C12	C13	-175.0(2)
C10	C11	C12	C31	62.3(3)
C11	C12	C13	C14	60.4(3)
C11	C12	C13	C32	-176.5(2)
C12	C13	C14	C15	-116.8(3)
C12	C13	C14	C25	61.1(3)
C12	C13	C32	O3	130.1(2)
C12	C13	C32	O4	-51.4(3)
C13	C14	C15	C16	177.5(2)
C13	C14	C25	C26	-177.3(2)
C14	C13	C32	O3	-104.2(2)
C14	C13	C32	O4	74.3(3)
C14	C15	C16	C17	-0.2(4)
C14	C25	C26	C17	-0.2(4)
C15	C14	C25	C26	0.6(4)
C15	C16	C17	C18	-178.4(2)
C15	C16	C17	C26	0.7(4)
C16	C17	C18	C19	113.9(3)
C16	C17	C26	C25	-0.5(3)
C17	C18	C19	C20	-61.7(3)
C18	C17	C26	C25	178.6(2)
C18	C19	C20	C21	179.5(2)
C19	C20	C21	C22	177.5(2)
C20	C21	C22	C1	-179.7(2)
C22	C1	C2	C3	59.7(3)
C22	C1	C2	C28	-177.0(2)
C23	C3	C4	C5	0.6(3)
C24	C6	C7	C8	115.2(3)
C25	C14	C15	C16	-0.4(4)
C26	C17	C18	C19	-65.1(3)
C27	C1	C2	C3	-175.9(2)
C27	C1	C2	C28	-52.6(3)
C27	C1	C22	C21	66.9(3)
C28	O1	C29	C30	103.6(3)
C28	C2	C3	C4	-66.7(3)
C28	C2	C3	C23	115.4(2)
C29	O1	C28	O2	1.7(4)
C29	O1	C28	C2	-178.0(2)
C31	C12	C13	C14	-176.4(2)
C31	C12	C13	C32	-53.2(3)
C32	O3	C33	C34	97.2(3)
C32	C13	C14	C15	119.2(2)
C32	C13	C14	C25	-62.9(3)
C33	O3	C32	O4	3.4(4)
C33	O3	C32	C13	-178.11(19)

Atom	Atom	Atom	Atom	Angle/°
O1B	C29B	C30B	F1B	176.8(2)
O1B	C29B	C30B	F2B	-62.1(3)
O1B	C29B	C30B	F3B	58.1(3)
O3B	C33B	C34B	F4B	-61.4(3)
O3B	C33B	C34B	F5B	178.1(2)
O3B	C33B	C34B	F6B	59.4(3)
C1B	C2B	C3B	C4B	57.0(3)
C1B	C2B	C3B	C23B	-122.2(2)
C1B	C2B	C28B	O1B	126.1(2)
C1B	C2B	C28B	O2B	-55.0(4)
C2B	C1B	C22B	C21B	-170.6(2)
C2B	C3B	C4B	C5B	-178.9(2)
C2B	C3B	C23B	C24B	178.6(2)
C3B	C2B	C28B	O1B	-109.0(2)
C3B	C2B	C28B	O2B	69.9(3)
C3B	C4B	C5B	C6B	0.1(4)
C3B	C23B	C24B	C6B	0.5(4)
C4B	C3B	C23B	C24B	-0.7(4)
C4B	C5B	C6B	C7B	179.0(2)
C4B	C5B	C6B	C24B	-0.3(3)
C5B	C6B	C7B	C8B	-65.2(3)
C5B	C6B	C24B	C23B	0.0(3)
C6B	C7B	C8B	C9B	-61.8(3)
C7B	C6B	C24B	C23B	-179.3(2)
C7B	C8B	C9B	C10B	-176.1(2)
C8B	C9B	C10B	C11B	-174.9(2)
C9B	C10B	C11B	C12B	177.5(2)
C10B	C11B	C12B	C13B	-173.2(2)
C10B	C11B	C12B	C31B	65.1(3)
C11B	C12B	C13B	C14B	55.9(3)
C11B	C12B	C13B	C32B	178.8(2)
C12B	C13B	C14B	C15B	-117.0(2)
C12B	C13B	C14B	C25B	61.6(3)
C12B	C13B	C32B	O3B	131.5(2)
C12B	C13B	C32B	O4B	-50.3(3)
C13B	C14B	C15B	C16B	178.3(2)
C13B	C14B	C25B	C26B	-178.1(2)
C14B	C13B	C32B	O3B	-103.0(2)
C14B	C13B	C32B	O4B	75.1(3)
C14B	C15B	C16B	C17B	0.2(4)
C14B	C25B	C26B	C17B	-0.5(4)
C15B	C14B	C25B	C26B	0.6(4)
C15B	C16B	C17B	C18B	179.9(2)
C15B	C16B	C17B	C26B	-0.1(4)
C16B	C17B	C18B	C19B	115.1(3)
C16B	C17B	C26B	C25B	0.2(4)
C17B	C18B	C19B	C20B	-63.6(3)
C18B	C17B	C26B	C25B	-179.7(2)
C18B	C19B	C20B	C21B	-176.7(2)
C19B	C20B	C21B	C22B	-177.3(2)
C20B	C21B	C22B	C1B	177.7(2)
C22B	C1B	C2B	C3B	59.8(3)
C22B	C1B	C2B	C28B	-177.7(2)
C23B	C3B	C4B	C5B	0.4(3)
C24B	C6B	C7B	C8B	114.1(3)
C25B	C14B	C15B	C16B	-0.4(4)
C26B	C17B	C18B	C19B	-64.9(3)
C27B	C1B	C2B	C3B	-177.0(2)

Atom	Atom	Atom	Atom	Angle/°
C27B	C1B	C2B	C28B	-54.6(3)
C27B	C1B	C22B	C21B	67.1(3)
C28B	O1B	C29B	C30B	99.4(3)
C28B	C2B	C3B	C4B	-66.3(3)
C28B	C2B	C3B	C23B	114.5(2)
C29B	O1B	C28B	O2B	4.0(4)
C29B	O1B	C28B	C2B	-177.0(2)
C31B	C12B	C13B	C14B	178.4(2)
C31B	C12B	C13B	C32B	-58.7(3)
C32B	O3B	C33B	C34B	99.1(2)
C32B	C13B	C14B	C15B	119.9(2)
C32B	C13B	C14B	C25B	-61.4(3)
C33B	O3B	C32B	O4B	4.5(3)
C33B	O3B	C32B	C13B	-177.24(19)

Table S13.29: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Aaron-macrocycle_P2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H1	3838.87	1417.26	6044.01	27
H2	4207.62	4485.31	5421.4	25
H4	4840.99	-360.14	6422.28	28
H5	5801.05	-375.76	7136.72	29
H7A	6916.88	4159.71	7370.2	33
H7B	6906.2	1334.9	7398.66	33
H8A	6538.59	1555.85	8047.23	33
H8B	7157.54	2870.15	8269.03	33
H9A	6045.69	5298.2	7825.73	28
H9B	6663.7	6623.82	8041.48	28
H10A	6340.63	3858.89	8736.64	29
H10B	6937.65	5329.69	8943.77	29
H11A	5801.39	7546.94	8483.22	30
H11B	6410.9	8941.41	8737.19	30
H12	6017.59	6097.78	9373.73	25
H13	6022.18	11219.04	9293.16	24
H15	5209.75	12729.35	8513.21	30
H16	4236.17	12564.47	7821	31
H18A	3269.88	10780.41	7380.3	29
H18B	3091.16	9221.46	7761.05	29
H19A	3335.86	5676.06	7435.97	30
H19B	2831.8	7113.21	6948.5	30
H20A	3539.25	8588.14	6690.01	31
H20B	4046.03	7171.75	7180.08	31
H21A	3093.65	4881.95	6279.45	30
H21B	3620.75	3509.13	6761.73	30
H22A	4296.5	5121.09	6477.84	30
H22B	3772.08	6505.72	5998.13	30
H23	5162.07	5955.91	5892.69	27
H24	6120.38	5949.12	6609.47	28
H25	4948.78	6619.38	9158.69	28
H26	3979.76	6457.4	8463.97	29
H27A	3082.42	4291.05	5128.85	52
H27B	2861.64	2813.75	5491.26	52
H27C	3099.11	1459.46	5125.95	52
H29A	4033.67	-1564.23	4443.05	31
H29B	4111.57	420.45	4067.88	31
H31A	7042.46	9106.84	9774.92	47
H31B	7063.15	6277.03	9804.09	47
H31C	6827.48	7745.84	10156.27	47
H33A	5836.99	11583.49	10740.57	29
H33B	5905.86	14354.71	10655.57	29
H1B	1216.17	9191.66	2079.88	26
H2B	842	6011.03	1153.47	25
H4B	212.4	10895.87	1604.28	27
H5B	-756.36	10992.28	1484.09	29
H7BA	-1884.57	6514.62	775.82	32
H7BB	-1859.37	9339.1	821.4	32
H8BA	-1479.64	9064.2	1786.17	29

Atom	x	y	z	U_{eq}
H8BB	-2108.59	7825.21	1481.74	29
H9BA	-1009.95	5319.97	1980.83	27
H9BB	-1627.82	4021.27	1645.32	27
H10C	-1346.11	6682.04	2619.1	27
H10D	-1932.21	5164.79	2297.27	27
H11C	-781.77	3079.64	2841.42	29
H11D	-1376.03	1600.41	2538.96	29
H12B	-1091.09	4361.57	3506.93	24
H13B	-1015.29	-759.67	3443.49	22
H15B	-185.46	-2136.09	3370.18	27
H16B	792.41	-1858.43	3520.68	30
H18C	1755.56	43.85	3930.99	28
H18D	1899.36	1608.16	4456.72	28
H19C	1637.8	5146.66	3904.52	26
H19D	2181.16	3813.56	3892.11	26
H20C	1515.18	2084.57	3028.49	28
H20D	989.07	3560.12	3038.74	28
H21C	1970.68	5661.14	2959.15	28
H21D	1465.5	7188.06	2996.65	28
H22C	757.11	5506.24	2145.69	28
H22D	1272.99	4079.35	2106.12	28
H23B	-124.41	4542.27	810.61	27
H24B	-1088.59	4636.94	700.23	29
H25B	8.95	4029.39	4202.81	28
H26B	981.32	4312.22	4348.7	28
H27D	1963.79	6182.78	1821.78	50
H27E	2191.46	7799.8	2352.75	50
H27F	1943.79	9005.6	1767.83	50
H29C	949.16	11971.7	260.87	31
H29D	825.95	9956.17	-186.45	31
H31D	-2039.34	1012.82	2988.64	47
H31E	-2127.92	3820.41	2975.5	47
H31F	-1901.78	2409.07	3534.97	47
H33C	-874.84	-872.72	5031.91	26
H33D	-868.03	-3675.15	4937.83	26

Citations

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O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

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#===============================================================================
# PLATON/CHECK-( 70414) versus check.def version of 310314   for Entry: aaron-ma
# Data: Aaron-macrocycle_P2.cif - Type: CIF      Bond Precision   C-C = 0.0040 A
# Refl: Aaron-macrocycle_P2.fcf - Type: LIST4                    Temp = 100 K
#                                    X-Ray        Nref/Npar =   9.2
# Cell  25.1525(4)  5.53398(4)  27.2474(4)          90 117.4652(19)         90
# Wavelength 1.54184    Volume Reported    3365.19(9)   Calculated   3365.19(10)
# SpaceGroup from Symmetry P 2        Hall: P 2y                monoclinic
#               Reported P 1 2 1          P 2y                monoclinic
# MoietyFormula C34 H42 F6 O4
#      Reported C34 H42 F6 O4
#    SumFormula C34 H42 F6 O4
#      Reported C34 H42 F6 O4
# Mr       =    628.68[Calc],    628.67[Rep]
# Dx,gcm-3  =     1.241[Calc],     1.241[Rep]
# Z        =         4[Calc],         4[Rep]
# Mu (mm-1) =      0.866[Calc],      0.866[Rep]
# F000     =    1328.0[Calc],    1328.0[Rep]  or F000' =   1332.85[Calc]
# Reported   T Limits: Tmin=0.487             Tmax=1.000  AbsCorr=GAUSSIAN
# Calculated T Limits: Tmin=0.940 Tmin'=0.611  Tmax=0.968
# Reported   Hmax= 30, Kmax=  6, Lmax= 33, Nref=  10947        , Th(max)= 73.814
# Obs in FCF Hmax= 30, Kmax=  6, Lmax= 33, Nref=  10947[  7307], Th(max)= 73.814
# Calculated Hmax= 31, Kmax=  6, Lmax= 33, Nref=  13617[  7546], Ratio=1.45/0.80
# Reported   Rho(min) = -0.20, Rho(max) =  0.32 e/Ang**3 (From CIF)
# Calculated Rho(min) = -0.19, Rho(max) =  0.31 e/Ang**3 (From CIF+FCF data)
# w=1/[sigma**2(Fo**2)+(0.0388P)**2+  1.0793P], P=(Fo**2+2*Fc**2)/3
# R= 0.0363(  9975), wR2= 0.0885( 10947), S = 0.985      (From CIF+FCF data)
# R= 0.0363(  9975), wR2= 0.0885( 10947), S = 0.985      (From FCF data only)
# R= 0.0363(  9975), wR2= 0.0885( 10947), S = 0.985, Npar=  797, Flack  -0.02(6)
#===============================================================================
For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
#===============================================================================

#===============================================================================
>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
#===============================================================================
Format: alert-number_ALERT_alert-type_alert-level text

230_ALERT_2_C Hirshfeld Test Diff for    F3     --  C30     ..        6.0 su
761_ALERT_1_C CIF Contains no X-H Bonds .....      Please Check
762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles .....      Please Check
911_ALERT_3_C Missing # FCF Refl Between THmin &amp;amp; STh/L=  0.600         84 Why ?
915_ALERT_3_C Low Friedel Pair Coverage .....         60 %
#===============================================================================
008_ALERT_5_G No _iucr_refine_reflections_details   in the CIF     Please Do !
142_ALERT_4_G su on b - Axis Small or Missing .....    0.00004 Ang.
242_ALERT_2_G Low       Ueq as Compared to Neighbors for .....        C30 Check
242_ALERT_2_G Low       Ueq as Compared to Neighbors for .....        C34 Check
242_ALERT_2_G Low       Ueq as Compared to Neighbors for .....       C30B Check
242_ALERT_2_G Low       Ueq as Compared to Neighbors for .....       C34B Check
720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          6 Note
791_ALERT_4_G The Model has Chirality at C1      .....          R Verify
791_ALERT_4_G The Model has Chirality at C1B     .....          R Verify
791_ALERT_4_G The Model has Chirality at C2      .....          S Verify
791_ALERT_4_G The Model has Chirality at C2B     .....          S Verify
791_ALERT_4_G The Model has Chirality at C12     .....          R Verify
791_ALERT_4_G The Model has Chirality at C12B    .....          R Verify
791_ALERT_4_G The Model has Chirality at C13     .....          S Verify
791_ALERT_4_G The Model has Chirality at C13B    .....          S Verify
```

802_ALERT_4_G CIF Input Record(s) with more than 80 Characters ! Info
910_ALERT_3_G Missing # of FCF Reflections Below Th(Min) ..... 1 Why ?
912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 147 Note
#==========

ALERT_Level and ALERT_Type Summary
==========
5 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight
18 ALERT_Level_G = General Info/Check that it is not Something Unexpected

2 ALERT_Type_1 CIF Construction/Syntax Error, Inconsistent or Missing Data.
5 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
3 ALERT_Type_3 Indicator that the Structure Quality may be Low.
12 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.
1 ALERT_Type_5 Informative Message, Check.
#==========

2 Missing Experimental Info Issue(s) (Out of 54 Tests) - 96 % Satisfied
0 Experimental Data Related Issue(s) (Out of 28 Tests) - 100 % Satisfied
5 Structural Model Related Issue(s) (Out of 117 Tests) - 96 % Satisfied
16 Unresolved or to be Checked Issue(s) (Out of 223 Tests) - 93 % Satisfied

#==========