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Supporting Information

Cycloadditions of Oxacyclic Allenes and a Catalytic Asymmetric Entryway to Enantioenriched Cyclic Allenes

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Supporting Information – Table of Contents

Part I. Experimental Section.

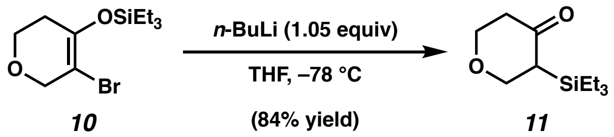
Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received unless otherwise specified. Cesium fluoride (CsF), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), and tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) were obtained from Strem Chemicals. (1,3)-diphenylisobenzofuran (**21**), *N*-*tert*-butyl-α-phenylnitrone (**SI-3**), chlorotrimethylsilane (TMSCl) were obtained from Alfa Aesar. *N*-(5-chloro-2-pyridyl)bis(trifluoromethanesulfonimide) (Comins' Reagent), *n*-butyllithium (*n*-BuLi), potassium bis(trimethylsilyl)amide (KHMDS), *N*-Boc pyrrole (**17**), *N*-phenylpyrrole (**15**), 2,5-dimethylfuran (**19**), dicyclopentadiene, dimethylphenylsilyl chloride ($PhMe_2SiCl$), and allyl chloroformate were obtained from Sigma Aldrich. Diisopropylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO) were obtained from Acros Organics. Indene (**43**) was purchased from Combi-Blocks. (**19**), TMSCl, and diisopropylamine were distilled over CaH_2 prior to use. Allyl chloroformate was dessicated with $CaCl_2$ and distilled prior to use. **17** was filtered over basic alumina prior to use. Dicyclopentadiene was cracked and cyclopentadiene (**23**) was stored at –80 °C prior to use. Reaction temperatures were controlled using an IKAmag temperature modulator and, unless stated otherwise, reactions were performed at room temperature (approximately 23 °C). Thin layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV light, anisaldehyde, and potassium permanganate staining. Silicycle Siliaflash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^{1}H-NMR and 2D-NOESY spectra were recorded on Bruker spectrometers (at 300, 400, 500, and 600 MHz) and are reported relative to the residual solvent signal. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C-NMR spectra were recorded on Bruker spectrometers (at 100 and 125 MHz) and are reported relative to the residual solvent signal. Data for ^{13}C-NMR spectra are reported in terms of chemical shift and, when necessary, multiplicity, and coupling constant (Hz). ^{19}F NMR spectra were recorded on Bruker spectrometers (at 376 MHz) and reported in terms of chemical shift (δ ppm). IR spectra were obtained on a Perkin-Elmer UATR Two FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Uncorrected melting points were measured using a Digimelt

MPA160 melting point apparatus. DART-MS spectra were collected on a Thermo Exactive Plus MSD (Thermo Scientific) equipped with an ID-CUBE ion source and a Vapur Interface (IonSense Inc.). Both the source and MSD were controlled by Excalibur software v. 3.0. The analyte was spotted onto OpenSpot sampling cards (IonSense Inc.) using $CDCl_3$ as the solvent. Ionization was accomplished using UHP He (Airgas Inc.) plasma with no additional ionization agents. The mass calibration was carried out using Pierce LTQ Velos ESI (+) and (–) Ion calibration solutions (Thermo Fisher Scientific). Determination of enantiopurity was carried out on a Mettler Toledo SFC (supercritical fluid chromatography) using a Daicel ChiralPak IC-3 column and a Daicel ChiralPak AD-3 column. Optical rotations were measured with a Rudolph Autopol III Automatic Polarimeter.

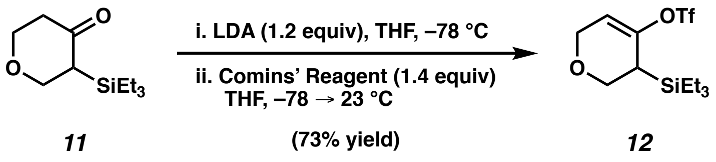
Nitrones **SI-2**,[1] **54**,[2] **SI-4**, **SI-5**,[3] **SI-6**,[4] **SI-7**,[4] **SI-8**,[3] azomethine imines **37**[5] and **39**,[6] nitrile oxide **41**,[7] imidazole carboxylate **SI-14**,[8] and (*S*)-$(CF_3)_3$-*t*-BuPHOX (**47**)[9] are all known compounds. ^{1}H-NMR spectral data matched those reported in the literature.

Experimental Procedures.

A. Synthesis of Silyl Triflate 12.



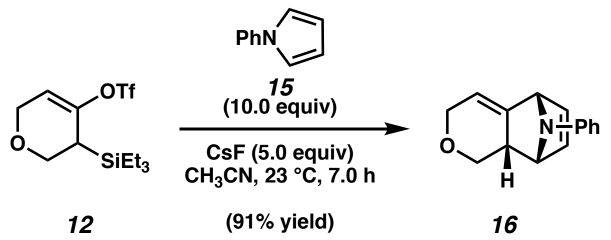
Silyl ketone 11. To a solution of known silyl enol ether **10**[10] (5.6 g, 19.1 mmol, 1.0 equiv) in THF (225 mL) at –78 °C was added *n*-BuLi (2.02 M in hexanes, 9.9 mL, 20.1 mmol, 1.05 equiv) dropwise over 18 min. The solution was stirred for 43 min at –78 °C, then the reaction was quenched with sat. aq. $NaHCO_3$ (80 mL) and allowed to warm to 23 °C. The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 80 mL). The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (19:1 hexanes:EtOAc) to afford silyl ketone **11** (3.4 g, 84% yield) as a colorless oil. Silyl ketone **11**: R_f 0.29 (9:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.20–4.09 (m, 2H), 3.92 (dd, *J* = 11.4, 4.6, 1H), 3.74 (ddd, *J* = 11.4, 10.9, 4.0, 1H), 2.47 (ddd, *J* = 15.6, 10.9, 6.8, 1H) , 2.38–2.31 (m, 2H), 0.97 (t, *J* = 7.7 9H), 0.68 (q, *J* = 7.7, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 207.7, 68.1, 67.2, 44.5, 42.0, 7.4, 3.2; IR (film): 2954, 2911, 2876, 1691, 1218 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{11}H_{23}O_2Si^+$, 215.14618; found, 215.14678.



Silyl triflate 12. To a solution of diisopropylamine (1.30 mL, 9.1 mmol, 1.30 equiv) in THF (8.0 mL) at –78 °C was added *n*-BuLi (2.02M in hexanes, 4.20 mL, 8.4 mmol, 1.20 equiv) dropwise over 7 min. The reaction was then stirred at –78 °C for 20 min and then allowed to warm to 23 °C. After stirring for 10 min at 23 °C, the reaction mixture was again cooled to –78 °C and a solution of silyl ketone **11** (1.5 g, 7.01 mmol, 1.0 equiv) in THF (8.0 mL) was added dropwise over 15 min and left to stir for 1.0 h at –78 °C. A solution of Comins' Reagent (3.86 g, 9.81 mmol, 1.4 equiv) in THF (8.2 mL) was then added dropwise over 20 min at –78 °C. The reaction was then stirred for 10 min at –78 °C before being warmed to 23 °C. After stirring for an additional 14 h, the reaction mixture was quenched by the addition of sat. aq. $NaHCO_3$ (30 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 30 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (4:1 hexanes:benzene) to give silyl triflate **12** (1.77 g, 73% yield) as a colorless oil. Silyl triflate **12**: R_f 0.55 (9:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.67–5.65 (m, 1H), 4.25 (qt, J = 16.1, 3.1, 2H), 3.96 (dd, J = 11.2, 4.7, 1H), 3.86 (dd, J = 11.2, 4.7, 1H), 2.14–2.10 (m, 1H), 0.98 (t, J = 8.2, 9H), 0.68 (q, J = 8.0, 6H); ^{13}C-NMR (125 MHz): δ 149.7, 118.7 (q, J = 318.3), 113.0, 66.7, 64.4, 28.5, 7.3, 2.9; ^{19}F-NMR (376 Hz, $CDCl_3$): –73.5; IR (film): 2957, 2880, 1681, 1418, 1245, 1207 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{12}H_{22}F_3O_4Si^+$, 347.09547; found, 347.09659

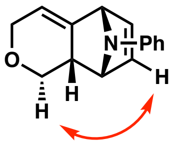
B. Diels–Alder Trapping Experiments.

Representative Procedure (Preparation of cycloadduct 16 is used as an example).



Cycloadduct 16. To a stirred solution of silyl triflate **12** (52.6 mg, 0.152 mmol, 1.0 equiv) and *N*-phenylpyrrole (**15**, 217 mg, 1.52 mmol, 10.0 equiv) in CH_3CN (1.52 mL) was added CsF (115.0 mg, 0.759 mmol, 5.0 equiv). The reaction vessel was sealed with a PTFE lined cap and allowed to stir at 23 °C for 7 h. The crude reaction mixture was then filtered by passage through a plug of silica gel (EtOAc eluent, 10 mL). Concentration under reduced pressure yielded the crude residue (3.8:1 dr, average of two experiments). Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) allowed for separation of the two diastereomers, which were obtained in a total yield of 91% (average of two experiments). The major diastereomer **16** was obtained as a light yellow amorphous solid. Cycloadduct **16**: R_f 0.15 (5:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.23–7.18 (m, 2H), 6.87–6.80 (m, 3H), 6.30 (dd, J = 5.6, 2.6, 1H), 5.97 (dd, J = 5.7, 2.1, 1H), 5.69–5.68 (m, 1H), 4.89 (br s, 1H), 4.71–4.70 (m, 1H), 4.25 (dt, J = 16.5, 2.1, 1H), 4.15 (dd, J = 9.4, 4.7, 1H), 3.96 (dt, J = 16.6, 3.0, 1H), 2.64–2.60 (m, 1H), 2.46 (t, J = 9.8, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.8, 137.6, 135.0, 129.2, 128.4, 120.7, 117.7, 117.3, 67.9, 65.4, 64.96, 64.95, 38.6; IR (film): 3060, 3005, 2920, 1496, 1315 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{15}H_{16}NO^+$, 226.12264; found, 226.12161.

The structure of **16** was verified by 2D-NOESY, as the following interaction was observed:



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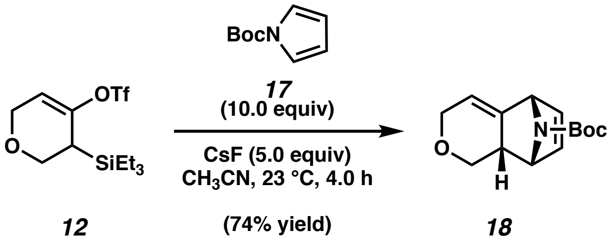
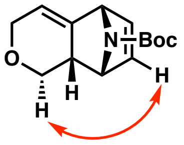
All reactions were monitored by TLC until starting material was consumed; the specific times are listed in the reaction scheme for each reaction. Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all of the results shown in Table 1. For all compounds in which the diastereomeric ratios were >20:1, the minor diastereomer was not observed in the ^{1}H-NMR spectrum of the crude reaction mixture.



Cycloadduct 18. Following concentration under reduced pressure, the crude residue was obtained (6.2:1 dr, average of two experiments). Purification by preparative thin layer chromatography (5:1 hexanes:Et_2O) allowed for separation of the two diastereomers, which provided a total yield of 74% (average of two experiments). Major diastereomer **18** was obtained as a clear oil. Cycloadduct **18**: R_f 0.28 (9:1 hexanes:EtOAc); ^{1}H-NMR (600 MHz, $CDCl_3$): δ 6.32 (br s, 1H), 5.99–5.95 (m, 1H), 5.61 (br s, 1H), 4.99–4.93 (m, 1H), 4.79–4.73 (m, 1H), 4.28 (dt, J = 16.6, 2.1, 1H), 4.14 (dd, J = 9.6, 4.8, 1H), 3.95 (dt, J = 16.6, 2.9, 1H), 2.65 (br s, 1H), 2.36 (t, J = 10.1, 1H), 1.43 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 155.1, 136.3, 135.5, 129.5, 128.3, 120.2, 117.0, 116.4, 80.6, 67.6, 65.0, 63.7, 63.0, 62.1, 61.6, 39.8, 39.3, 28.4; IR (film): 2978, 1738, 1599, 1319, 1160 cm^{-1}; HRMS–APCI (m/z) $[M + H]^+$ calcd for $C_{14}H_{20}NO_3^+$, 250.14377; found, 250.14536.

*Note: **18** was obtained as a mixture of rotamers. These data represent empirically observed chemical shifts from the ^{1}H-NMR and ^{13}C-NMR spectra.*

The structure of **18** was verified by 2D-NOESY, as the following interaction was observed:



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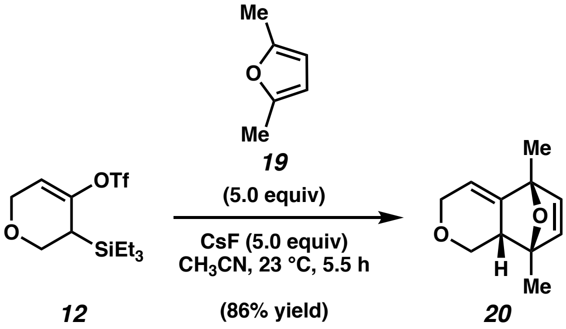
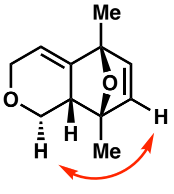


Cycloadduct 20. Following concentration under reduced pressure, the crude residue was obtained (9.2:1 dr, average of two experiments). Purification by flash chromatography (5:1 pentanes:Et_2O) allowed for separation of the two diastereomers, which afforded a total yield of 86% (average of two experiments). Major diastereomer **20** was obtained as a colorless oil. Cycloadduct **20**: R_f 0.27 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.13 (d, *J* = 5.4, 1H), 5.82 (d, *J* = 5.4, 1H), 5.48 (app q, *J* = 2.3, 1H), 4.28 (dt, *J* = 16.5, 2.1, 1H), 4.11 (dd, *J* = 9.3, 4.7, 1H), 3.94 (dt, *J* = 16.4, 2.9, 1H), 2.45–2.41 (m, 1H), 2.36–2.32 (m, 1H), 1.63 (s, 3H), 1.62 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 143.5, 139.9, 132.8, 113.7, 86.8, 86.6, 67.2, 64.6, 46.5, 18.2, 14.8; IR (film): 2973, 2929, 2851, 1382, 1308 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for $C_{11}H_{14}O_2^+$, 179.10666; found, 179.10719.

The structure of **20** was verified by 2D-NOESY, as the following interaction was observed:



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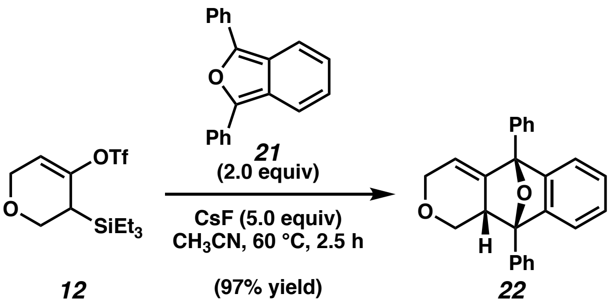
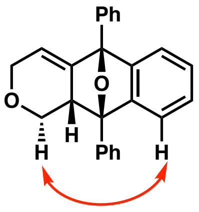
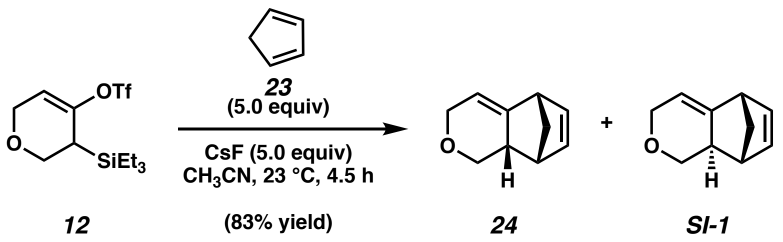


Cycloadduct 22. Following concentration under reduced pressure, the crude residue was obtained (2.0:1 dr, average of two experiments). Purification by preparative thin layer chromatography (9:1 hexanes:EtOAc) allowed for separation of the two diastereomers, which provided a total yield of 97% (average of two experiments). Major diastereomer **22** was obtained as a clear oil. Cycloadduct **22**: R_f 0.36 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.88–7.86 (m, 2H), 7.65–7.63 (m, 2H), 7.53–7.45 (m, 5H), 7.43–7.41 (m, 1H), 7.25–7.21 (m, 2H), 7.17–7.14 (m, 1H), 7.01–6.99 (m, 1H), 5.71 (app q, *J* = 2.5, 1H), 4.45 (dd, *J* = 9.8, 4.9, 1H), 4.34 (dt, *J* = 16.9, 2.5, 1H), 3.87 (ddd, *J* = 16.6, 3.6, 2.9, 1H), 3.43–3.39 (m, 1H), 2.40 (t, *J* = 10.2, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 148.1, 144.3, 142.5, 137.3, 134.1, 129.0, 128.72, 128.66, 128.6, 128.5, 127.6, 127.0, 126.4, 121.3, 118.6, 118.0, 90.2, 89.4, 67.0, 64.9, 46.3; IR (film): 3060, 2923, 1734, 1448, 734 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{25}H_{21}O_2^+$, 353.15361; found, 353.15563.

The structure of **22** was verified by 2D-NOESY, as the following interaction was observed:

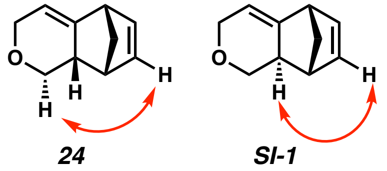


22



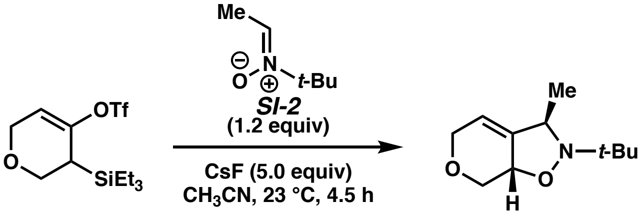
Cycloadducts 24 and SI-1. Following concentration under reduced pressure, the crude residue was obtained (1.6:1 dr, average of two experiments). Purification by flash chromatography (30:1 pentane:Et$_2$O), provided a total yield of 83% (average of two experiments) of **24** and **SI-1** as an inseparable mixture. **24** and **SI-1** (inseparable mixture) were obtained as a colorless oil. Cycloadducts **24** and **SI-1**: R$_f$ 0.62 (9:1 hexanes:EtOAc); ^{1}H-NMR (300 MHz, CDCl$_3$): δ 6.34 (dd, *J* = 5.7, 3.1, 1H, **SI-1**), 6.09–6.02 (m, 1H, **24**, 1H, **SI-1**), 5.77 (dd, *J* = 5.5, 2.9, 1H, **24**), 5.59–5.54 (m, 1H, **SI-1**), 5.48–5.44 (m, 1H, **24**), 4.29 (dt, *J* = 15.9, 2.0, 1H, **SI-1**), 4.26 (dt, *J* = 16.4, 2.2, 1H, **24**), 4.15–4.06 (m, 1H, **24**, 2H, **SI-1**), 3.97 (dt, *J* = 16.9, 2.9, 1H, **24**), 3.36 (br s, 1H, **SI-1**), 3.26 (br s, 1H, **24**), 2.99 (dd, *J* = 10.6, 9.6, 1H, **SI-1**), 2.95–2.90 (m, 1H, **24**), 2.70 (br s, 1H, **SI-1**), 2.54–2.45 (m, 1H, **24**), 2.41 (dd, *J* = 10.2, 8.7, 1H **24**), 2.02–1.92 (m, 1H, **SI-1**), 1.63 (dt, *J* = 8.2, 1.6, 1H, **24**), 1.59–1.54 (m, 1H, **SI-1**), 1.52–1.47 (m, 1H, **24**), 1.41–1.37 (m, 1H, **SI-1**); ^{13}C-NMR (125 MHz, CDCl$_3$): δ 142.6, 141.3, 138.7, 136.2, 132.8, 129.8, 114.9, 114.4, 69.0, 67.8, 65.2 (2C), 50.0, 49.1, 48.7, 47.4, 43.5, 41.9, 41.2, 40.9; IR (film): 3059, 2970, 2924, 2851, 1375 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for C$_{10}$H$_{13}$O$^+$, 149.09609; found, 149.09597.

The structures of **24** and **SI-1** were verified by 2D-NOESY, as the following interaction were observed:



C. (3+2) Trappings with Nitrones.

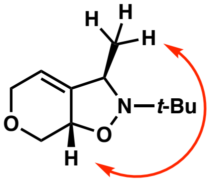
Representative Procedure (Preparation of isoxazolidine 27 is used as an example).



12 (85% yield) *27*

Isoxazolidine 27. To a stirred solution of silyl triflate **12** (52.2 mg, 0.151 mmol, 1.0 equiv) and nitrone **SI-2** (20.8 mg, 0.181 mmol, 1.2 equiv) in CH_3CN (1.51 mL) was added CsF (114 mg, 0.753 mmol, 5.0 equiv). The reaction vessel was sealed with a PTFE lined cap and allowed to stir at 23 °C for 4.5 h. The reaction mixture was filtered by passage through a plug of silica gel (EtOAc eluent, 10 mL). Concentration under reduced pressure yielded the crude residue (>20:1 dr, average of two experiments). Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) afforded isoxazolidine **27** as a clear, colorless oil (85% yield, average of two experiments). Isoxazolidine **27**: R_f 0.25 (9:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.46–5.45 (m, 1H), 4.38–4.34 (m, 1H), 4.27 (dd, J = 10.1, 5.9, 1H), 4.16 (dq, J = 16.3, 2.4, 1H), 4.07–4.01 (m, 1H), 3.74–3.70 (m, 1H), 3.11 (app t, J = 8.9, 1H), 1.29 (d, J = 6.4, 3H), 1.10 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.8, 114.1, 69.2, 66.5, 64.9, 58.8, 57.1, 25.9, 23.9; IR (film): 2971, 2929, 2865, 1361, 1129 cm^{-1}; HRMS–APCI (m/z) $[M + H]^+$ calcd for $C_{11}H_{20}NO_2^+$, 198.14886; found, 198.14936.

The structure of **27** was verified by 2D-NOESY, as the following interaction was observed:



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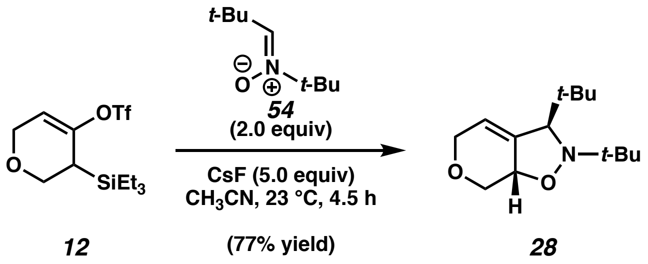
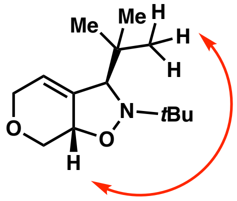
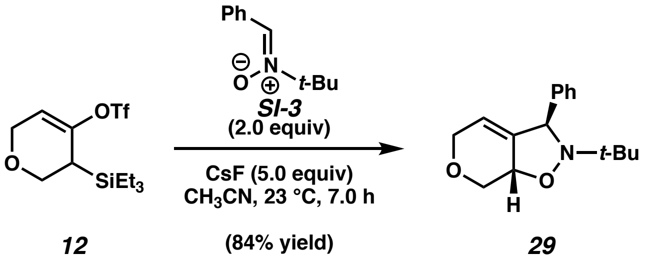


Isoxazolidine 28. Following concentration under reduced pressure, the crude residue was obtained (>20:1 dr, average of two experiments). Purification by flash chromatography (9:1 hexanes:EtOAc) afforded isoxazolidine **28** as a white powder in 77% yield (average of two experiments). Isoxazolidine **28**: Mp: 103–105 °C; R*f* 0.14 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.45 (s, 1H), 4.30–4.28 (m, 1H), 4.23–4.20 (m, 2H), 4.05–4.02 (m, 1H), 3.31 (s, 1H), 3.17 (t, *J* = 9.8, 1H), 1.03 (s, 9H), 0.95 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 141.7, 117.6, 71.5, 70.9, 66.9, 64.7, 59.9, 34.3, 27.1, 26.9; IR (film): 2955, 2836, 1595, 1417, 1205 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{14}H_{26}NO_2^+$, 240.19581; found, 240.19751.

The structure of **28** was verified by 2D-NOESY, as the following interaction was observed:



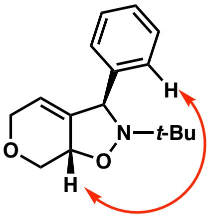
28



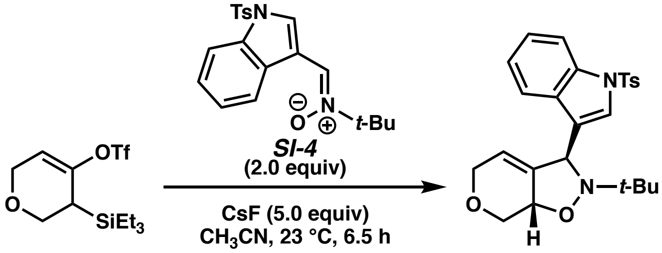
Isoxazolidine 29. Following concentration under reduced pressure, the crude residue was obtained (10.7:1 dr, average of two experiments). Purification by preparative thin layer chromatography (9:1 benzene:CH_3CN) allowed for separation of the two diastereomers, which provided a total yield of 84% (average of two experiments). Major diastereomer **29** was obtained as a white powder. Isoxazolidine **29**: Mp: 111–112 °C; R*f* 0.43 (9:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.49–7.47 (m, 2H), 7.33–7.30 (m, 2H), 7.25–7.22 (m, 1H), 5.44 (app quint,

J = 2.0, 1H), 4.62 (s, 1H), 4.50–4.46 (m, 1H), 4.31 (dd, J = 9.6, 5.6, 1H), 4.13–4.02 (m, 2H), 3.17 (app t, J = 9.4, 1H), 1.08 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 144.8, 143.8, 128.6, 127.3, 127.0, 115.5, 70.1, 66.3, 65.7, 65.0, 59.0, 26.2; IR (film): 2972, 2931, 2867, 1492, 1453 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for $C_{16}H_{22}NO_2^+$, 260.16451; found, 260.16520.

The structure of **29** was verified by 2D-NOESY, as the following interaction was observed:



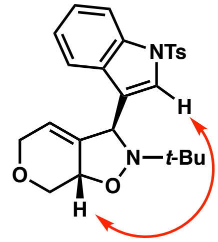
29



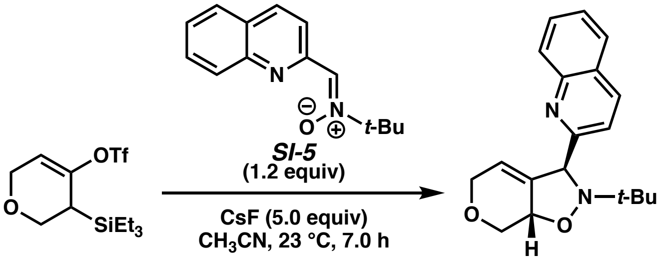
12 (77% yield) ***30***

Isoxazolidine 30. Following concentration under reduced pressure, the crude residue was obtained (>7.7:1 dr, average of two experiments). Purification by preparative thin layer chromatography (2:2:1 hexanes:benzene:Et_2O) allowed for separation of the two diastereomers, which provided a total yield of 77% (average of two experiments). Major diastereomer **30** was obtained as a white foam. Isoxazolidine **30**: R_f 0.27 (5:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.3, 1H), 7.75–7.70 (m, 4H), 7.33–7.29 (m, 1H), 7.25–7.21 (m, 1H), 7.21–7.16 (m, 2H), 5.55–5.52 (m, 1H), 4.87 (s, 1H), 4.51–4.45 (m, 1H), 4.30 (dd, J = 10.2, 5.6, 1H), 4.06–4.02 (m, 2H), 3.18 (app t, J = 9.0, 1H), 2.32 (s, 3H), 1.06 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.8, 142.9, 135.8, 135.3, 129.8, 129.0, 126.8, 125.0, 124.8, 124.0, 123.1, 120.3, 115.6, 114.0, 69.8, 66.1, 64.2, 58.8, 58.2, 25.8, 21.5; IR (film): 2971, 2931, 2868, 1445, 1363 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for $C_{25}H_{29}N_2O_4S^+$, 453.18425; found, 453.18223.

The structure of **30** was verified by 2D-NOESY, as the following interaction was observed:



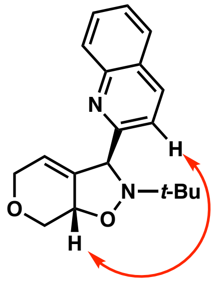
30



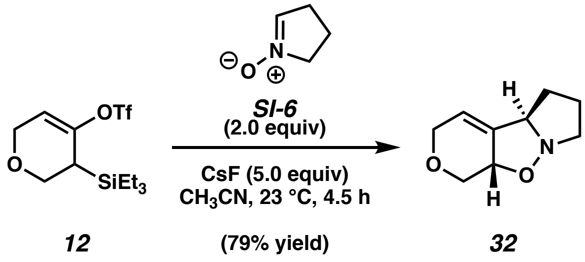
12 ***31***

Isoxazolidine 31. Following concentration under reduced pressure, the crude residue was obtained (2.8:1 dr, average of two experiments). Purification by preparative thin layer chromatography (2:2:1 hexanes:CH_2Cl_2:Et_2O) allowed for separation of the two diastereomers, which provided a total yield of 96% (average of two experiments). Major diastereomer **31** was obtained as a white powder. Isoxazolidine **31**: R$_f$ 0.33 (5:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.5, 1H), 8.06 (d, *J* = 7.8, 1H), 7.86 (d, *J* = 8.9, 1H), 7.80 (dd, *J* = 8.2, 1.3, 1H), 7.70 (ddd, *J* = 9.0, 7.8, 1.4, 1H), 7.51 (ddd, *J* = 9.0, 7.5, 1.2, 1H), 5.66 (app quint, *J* = 2.0, 1H), 5.02–5.01 (m, 1H), 4.60–4.56 (m, 1H), 4.35 (dd, *J* = 10.0, 5.5, 1H), 4.07 (app q, *J* = 2.6, 2H), 3.21 (dd, *J* = 10.2, 9.0, 1H), 1.10 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.0, 147.6, 143.3, 136.8, 129.6, 129.1, 127.82, 128.76, 126.3, 120.1, 117.2, 70.5, 68.5, 66.3, 65.1, 59.1, 26.0; IR (film): 3061, 2971, 2866, 1597, 1502 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for $C_{19}H_{23}N_2O_5^+$, 311.17540; found, 311.17394.

The structure of **31** was verified by 2D-NOESY, as the following interaction was observed:

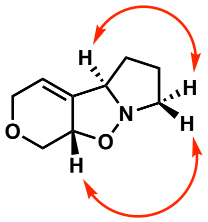


31

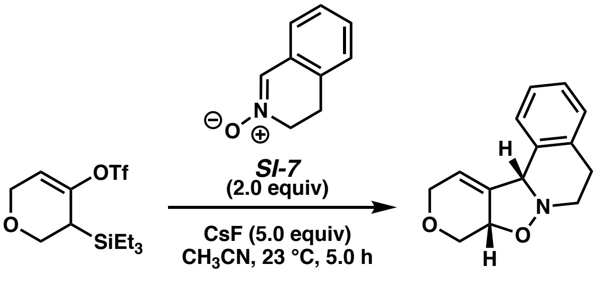


Isoxazolidine 32. Following concentration under reduced pressure, the crude residue was obtained (8.7:1 dr, average of two experiments). Purification by sequential preparative thin layer chromatography (99:1 $CHCl_3$:MeOH, eluted once, then 19:1 Et_2O:EtOAc, eluted twice) allowed for separation of the two diastereomers, which provided a total yield of 79% (average of two experiments). Major diastereomer **32** was obtained as a colorless oil. Isoxazolidine **32**: R_f 0.26 (19:1 Et_2O:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.62–5.57 (m, 1H), 4.45–4.39 (m, 1H), 4.23–4.15 (m, 3H), 4.09–4.03 (m, 1H), 3.29–3.19 (m, 2H), 3.09 (dd, J = 10.0, 9.6, 1H), 2.11–2.03 (m, 1H), 1.91–1.82 (m, 1H), 1.81–1.71 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 143.5, 116.2, 69.1, 66.9, 66.6, 64.7, 58.1, 32.2, 25.3; IR (film): 3032, 1695, 1414, 1229, 1109 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_9H_{14}NO_2^+$, 168.10191; found, 168.10434.

The structure of **32** was verified by 2D-NOESY, as the following interaction was observed:



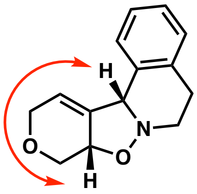
32



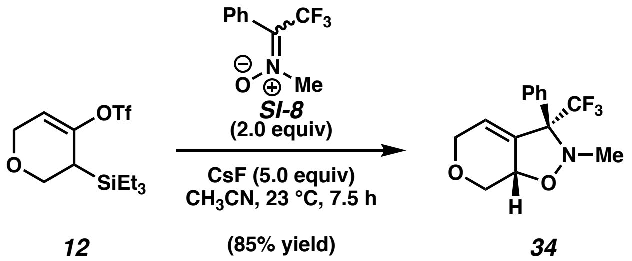
12 (94% yield) **33**

Isoxazolidine 33. Following concentration under reduced pressure, the crude residue was obtained (5.3:1 dr, average of two experiments). Purification by preparative thin layer chromatography (4:1 benzene:CH_3CN) allowed for separation of the two diastereomers, which provided a total yield of 94% (average of two experiments). Major diastereomer **33** was obtained as a colorless oil. Isoxazolidine **33**: R_f 0.53 (1:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29–7.19 (m, 2H), 7.18–7.13 (m, 2H), 5.34 (app quint, *J* = 2.2, 1H), 5.00 (br s, 1H), 4.54–4.46 (m, 1H), 4.35 (dd, *J* = 10.3, 5.5, 1H), 4.25 (dq, *J* = 16.9, 2.4, 1H), 3.99 (dq, *J* = 16.9, 2.6, 1H), 3.21 (ddd, *J* = 10.1, 4.5, 3.8, 1H), 3.07–2.98 (m, 2H), 2.84 (ddd, *J* = 11.7, 10.5, 3.0, 1H), 2.73 (dt, *J* = 16.2, 3.5, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.0, 134.4, 131.9, 128.6, 128.1, 127.2, 126.3, 119.3, 71.7, 68.9, 64.7, 64.4, 51.3, 28.9; IR (film): 3023, 2964, 2923, 1494, 1454 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{14}H_{16}NO_2^+$, 230.11756; found, 230.11828.

The structure of **33** was verified by 2D-NOESY, as the following interaction was observed:

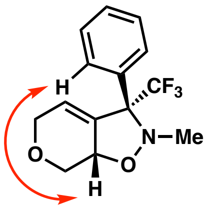


33



Isoxazolidine 34. In this reaction, nitrone **SI-8** was utilized as a mixture of double bond isomers (5:1 ratio, major isomer depicted). Following concentration under reduced pressure, the crude residue was obtained (5.5:1 dr, average of two experiments). Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) allowed for separation of the two diastereomers, which provided a total yield of 85% (average of two experiments). Major diastereomer **34** was obtained as a white solid. Isoxazolidine **34**: Mp: 67–68 °C; R_f 0.37 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.67–7.62 (m, 2H), 7.42–7.38 (m, 3H), 6.03–6.00 (m, 1H), 4.63–4.57 (m, 1H), 4.41 (dt, *J* = 17.3, 2.4, 1H), 4.32 (dd, *J* = 9.9, 5.4, 1H), 4.20 (dt, *J* = 17.3, 2.9, 1H), 3.25 (app t, *J* = 9.4, 1H), 2.62 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): 139.3, 133.0, 129.3, 128.74, 128.72, 128.6, 125.2 (q, *J* = 287), 122.8 (q, *J* = 1.6), 70.7, 66.1, 64.9, 41.4; IR (film): 2971, 2875, 1450, 1268, 1157 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{17}H_{21}F_3NO_2^+$, 286.10494; found, 286.10572.

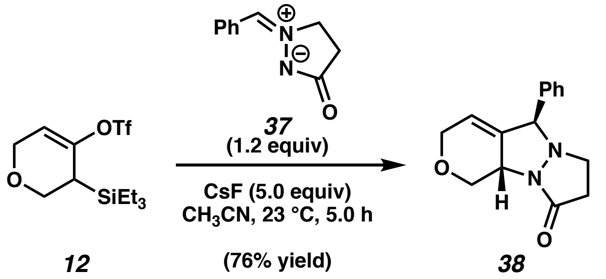
The structure of **34** was verified by 2D-NOESY, as the following interaction was observed:



34

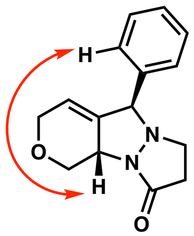
D. Additional (3+2) and (2+2) Trapping Experiments.

Representative Procedure (Preparation of pyrazolidine 38 is used as an example).

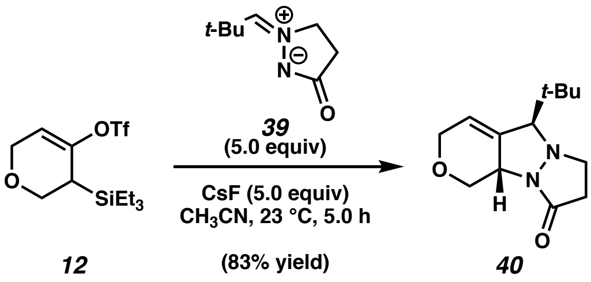


Pyrazolidine 38. To a stirred solution of silyl triflate **12** (51.3 mg, 0.148 mmol, 1.0 equiv) and azomethineimine **37** (31.0 mg, 0.178 mmol, 1.2 equiv) in CH_3CN (1.48 mL) was added CsF (112 mg, 0.740 mmol, 5.0 equiv). The reaction vessel was sealed with a PTFE lined cap and allowed to stir at 23 °C for 5 h. Then, the crude reaction mixture was filtered by passage through a plug of silica gel (EtOAc eluent, 10 mL). Concentration under reduced pressure yielded the crude residue (7.6:1 dr, average of two experiments). Purification by preparative thin layer chromatography (2:1 benzene:CH_3CN) allowed for separation of the two diastereomers, which were obtained in a total yield of 76% (average of two experiments). The major diastereomer **38** was obtained as a colorless oil. Pyrazolidine **38**: R_f 0.12 (1:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41–7.31 (m, 5H), 5.61–5.55 (m, 1H), 4.78 (dd, J = 10.2, 4.8, 1H), 4.31–4.22 (m, 3H), 4.20–4.11 (m, 1H), 3.54–3.44 (m, 2H), 3.05 (app q, J = 9.2, 1H), 2.70–2.55 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.9, 141.3, 138.5, 129.1, 128.5, 128.0, 119.7, 72.0, 65.1, 51.8, 49.7, 49.6, 34.7; IR (film): 3060, 2981, 2927, 1678, 1453 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{15}H_{17}N_2O_2^+$, 257.12845; found, 257.12933.

The structure of **38** was verified by 2D-NOESY, as the following interaction was observed:

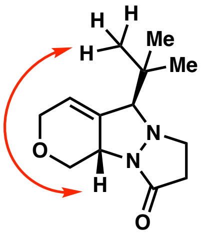


38

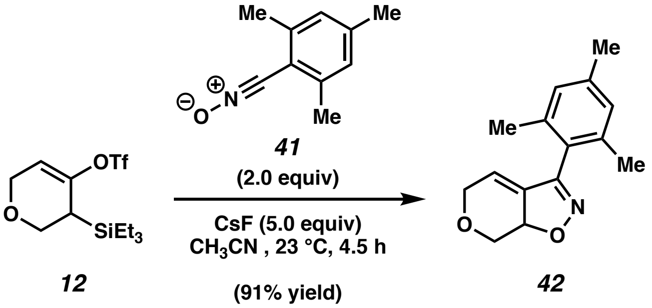


Pyrazolidine 40. Following concentration under reduced pressure, the crude residue was obtained (>20:1 dr, average of two experiments). Purification by preparative thin layer chromatography (2:1 benzene: CH_3CN) afforded Pyrazolidine **40** as a white powder in 83% yield (average of two experiments). Pyrazolidine **40**: Mp: 120–122 °C; R_f 0.15 (1:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.57 (app quint, *J* = 2.0, 1H), 4.88 (dd, *J* = 10.7, 5.4, 1H), 4.27 (dq, *J* = 16.8, 2.4, 1H), 4.14–4.06 (m, 1H), 3.93–3.85 (m, 1H), 3.67–3.58 (m, 1H), 3.42 (dd, *J* = 10.6, 9.8, 1H), 2.91–2.77 (m, 3H), 2.57–2.45 (m, 1H), 0.93 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.0, 138.0, 120.7, 78.9, 65.7, 65.2, 56.3, 51.1, 35.3, 35.2, 26.3; IR (film): 2955, 2868, 1679, 1445, 1421 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{21}N_2O_2^+$, 237.15975; found, 237.16054.

The structure of **40** was verified by 2D-NOESY, as the following interaction was observed:

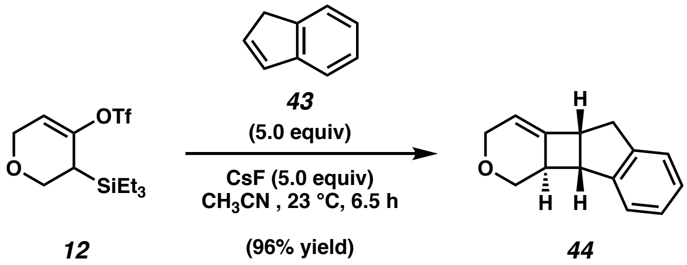


40



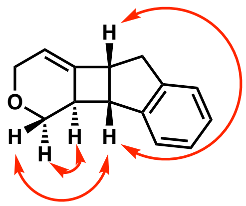
Isoxazoline 42. Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) afforded isoxazoline **42** as a clear, colorless oil (91% yield, average of two experiments).

Isoxazoline **42**: R_f 0.36 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.94–6.90 (m, 2H), 5.60–5.58 (m, 1H), 5.02–4.96 (m, 1H), 4.55 (dd, *J* = 9.6, 5.4, 1H), 4.36 (ddd, *J* = 18.4, 4.6, 2.4, 1H), 4.20 (ddd, *J* = 18.4, 5.0, 3.0, 1H), 3.35 (app t, *J* = 9.3, 1H), 2.31 (s, 3H), 2.20 (s, 3H), 2.18 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.7, 140.6, 139.2, 137.6, 137.3, 128.51, 128.48, 123.6, 120.1, 75.0, 66.0, 64.5, 21.2, 20.0, 19.7; IR (film) 2975, 2865, 1736, 1612, 1113 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{15}H_{17}NO_2^+$, 244.13321; found, 244.13475.



Cyclobutane 44. Following concentration under reduced pressure, the crude residue was obtained (5.2:1 dr, average of two experiments). Purification by successive preparative thin layer chromatography (20:5:1 hexanes:CH_2Cl_2:Et_2O, eluted twice) allowed for separation of the two diastereomers, which provided a total yield of 96% (average of two experiments). Major diastereomer **44** was obtained as a colorless oil. Cyclobutane **44**: R_f 0.48 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.30–7.23 (m, 1H), 7.21–7.12 (m, 3H), 5.47–5.42 (m, 1H), 4.32–4.26 (m, 1H), 4.19–4.10 (m, 2H), 3.83–3.75 (m, 1H), 3.63–3.59 (m, 1H), 3.34–3.25 (m, 2H), 3.21 (app t, *J* = 9.8, 1H), 3.07–3.00 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.0, 145.9, 141.4, 126.8, 126.7, 125.3, 123.5, 113.0, 66.9, 65.5, 50.1, 49.3, 48.8, 37.3; IR (film): 3067, 3041, 2939, 2844, 1480 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{14}H_{15}O^+$, 199.11174; found, 199.11236.

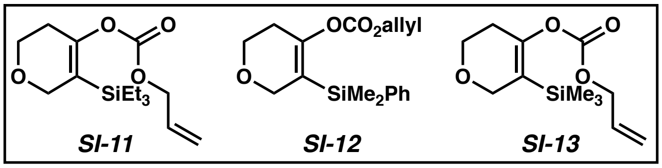
The structure of **44** was verified by 2D-NOESY, as the following interaction was observed:

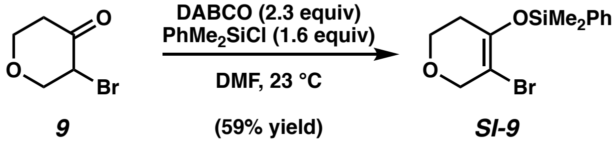


44

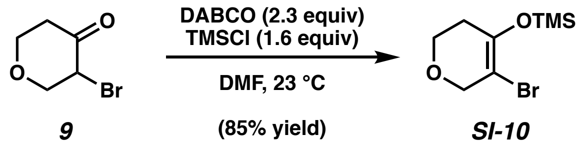
E. Synthesis of the Allylation Substrates.

In addition to **45**, enol carbonates **SI-11**, **SI-12**, and **SI-13** were prepared in order to determine the optimal substrate and conditions for the asymmetric allylic alkylation. The enol carbonates were then tested in the subsequent Pd-catalyzed allylic alkylation in Section F.

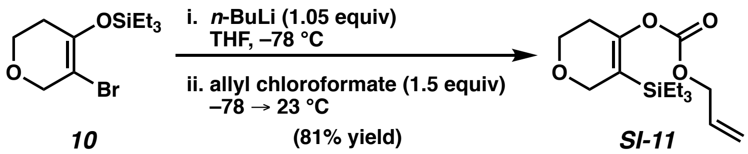




Silyl enol ether SI-9. To a stirred solution of known bromo ketone **9**[10] (300 mg, 1.68 mmol, 1.0 equiv) in DMF (1.52 mL) and $PhMe_2SiCl$ (0.45 mL, 2.68 mmol, 1.6 equiv) was added DABCO (432 mg, 3.85 mmol, 2.3 equiv). The reaction vessel was then purged with N_2 and sealed with a PTFE lined cap, before allowing it to stir at 23 °C. After 12 h, the mixture was cooled to –40 °C for 10 min before quenching the reaction with sat. $NaHCO_3$ (2.0 mL) and water (4.0 mL). The layers were then separated and the aqueous layer was then extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (2 x 10 mL) and brine (1 x 10 mL), before being dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The resultant crude oil was purified via flash chromatography (19:1 hexanes:EtOAc) to afford silyl enol ether **SI-9** as a colorless oil (308.5 mg, 59% yield). Silyl enol ether **SI-9**: R_f 0.48 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, C_6D_6): δ 7.59–7.53 (m, 2H), 7.20–7.14 (m, 3H), 4.10–4.07 (m, 2H), 3.27 (t, J = 5.5, 2H), 1.83–1.77 (m, 2H), 0.37 (s, 6H); ^{13}C-NMR (125 MHz, C_6D_6): δ 145.1, 137.5, 133.7, 130.3, 98.8, 69.8, 64.7, 32.9, –0.5; IR (film): 3071, 2964, 2828, 1675, 1428 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{18}BrO_2Si^+$, 313.02540; found, 313.02630.

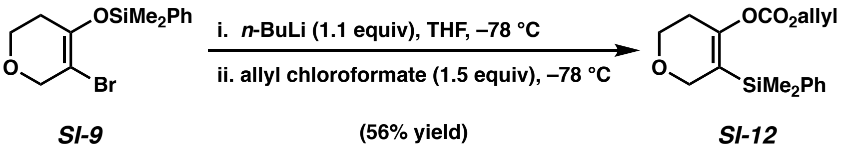


Silyl enol ether SI-10. To a stirred solution of known bromo ketone **9**[10] (100 mg, 0.559 mmol, 1.0 equiv) and TMSCl (0.11 mL, 0.894 mmol, 1.6 equiv) in DMF (0.51 mL) was added DABCO (144 mg, 1.28 mmol, 2.3 equiv). The reaction vessel was then purged with N_2 and sealed with a PTFE lined cap, before allowing it to stir at 23 °C. After 22 h, the mixture was cooled to –40 °C for 10 min and quenched with sat. aq. $NaHCO_3$ (0.5 mL) and deionized water (0.5 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 3 mL). The combined organic layers were washed with water (2 x 5 mL) and brine (1 x 5 mL), before being dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The resultant crude oil was purified via flash chromatography (19:1 hexanes:EtOAc) to afford silyl enol ether **SI-10** as a colorless oil (119.1 mg, 85% yield). Silyl enol ether **SI-10**: R_f 0.49 (9:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, C_6D_6): δ 4.10 (t, J = 2.3, 2H), 3.35 (t, J = 5.5, 2H), 1.86–1.81 (m, 2H), 0.10 (s, 9H); ^{13}C-NMR (100 MHz, C_6D_6): δ 144.7, 98.2, 69.4, 64.4, 32.6, 0.4; IR (film): 2968, 2861, 1675, 1265, 1252 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_8H_{15}BrO_2Si^+$, 253.00770; found, 253.00876.

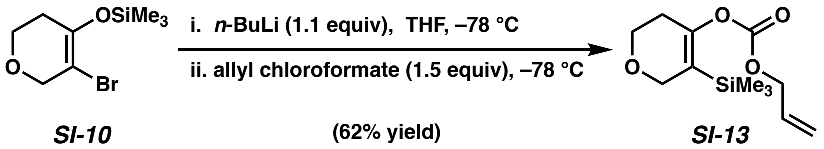


Enol carbonate SI-11. To a solution of known silyl enol ether **10**[10] (330 mg, 1.13 mmol, 1.00 equiv) in THF (13.2 mL) at –78 °C was added *n*-BuLi (2.24 M in hexanes, 0.527 mL, 1.18 mmol, 1.05 equiv) dropwise over 2.0 min. The solution was stirred for 34 min at –78 °C, before neat allyl chloroformate (0.180 mL, 1.69 mmol, 1.5 equiv) was then added dropwise over 1 min and the reaction was allowed to stir for 1.0 h at –78 °C, before warming to 23 °C. After stirring for 2.0 h, the reaction was quenched with water (10 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (19:1 hexanes:EtOAc) to afford enol carbonate **SI-11** (273.1 mg, 81% yield) as a colorless oil. Enol carbonate **SI-11**: R_f 0.58 (5:1 hexanes:EtOAc);

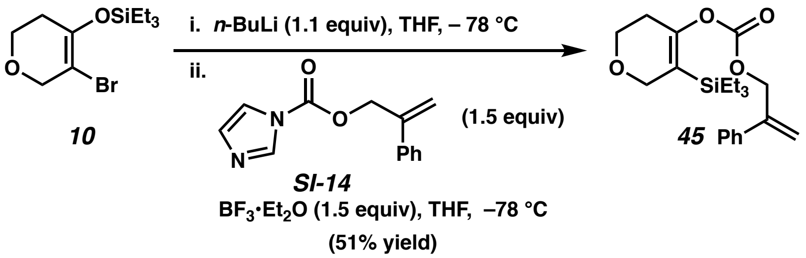
^{1}H-NMR (600 MHz, CDCl$_3$): δ 5.99–5.91 (m, 1H), 5.39 (dq, *J* = 17.2, 1.4, 1H), 5.30 (dq, *J* = 1.4, 1.3, 1H), 4.66 (dt, *J* = 5.9, 1.3, 2H), 4.22 (t, *J* = 2.6, 2H), 3.85 (t, *J* = 5.6 6H), 2.41 (s, *J* = 2.6, 2H), 0.93 (t, *J* = 8.0, 9H), 0.62 (q, *J* = 8.0, 6H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ 152.9, 151.7, 131.5, 120.1, 119.4, 68.8, 67.5, 64.3, 28.1, 7.4, 3.0; IR (film): 2954, 1754, 1657, 1228, 1161 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for $C_{15}H_{27}O_4Si^+$, 299.16731; found, 299.16694.



Enol carbonate SI-12. To a solution of silyl enol ether **SI-9** (150.0 mg, 0.479 mmol, 1.00 equiv) in THF (5.6 mL) at –78 °C was added *n*-BuLi (2.22 M in hexanes, 0.237 mL, 0.527 mmol, 1.1 equiv) dropwise over 1.0 min. The solution was stirred for 20 min at –78 °C, then neat allyl chloroformate (76.6 μL, 0.718 mmol, 1.5 equiv) was added dropwise over 1 min and the reaction was allowed to stir at –78 °C. After stirring for 4.0 h, the reaction was quenched with water (4.0 mL) at –78 °C. The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (15:1 hexanes:EtOAc) to afford enol carbonate **SI-12** (84.6 mg, 56% yield) as a colorless oil. Enol carbonate **SI-12**: R$_f$ 0.31 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, CD$_3$CN): δ 7.54–7.49 (m, 2H), 7.39–7.31 (m, 3H), 5.92–5.82 (m, 1H), 5.33–5.27 (m, 1H), 5.25–5.21 (m, 1H), 4.47–4.43 (m, 2H), 4.17–4.14 (m, 2H), 3.78–3.75 (m, 2H), 2.32–2.27 (m, 2H), 1.92 (app quint, *J* = 2.4, 2H), 0.34 (s, 6H); ^{13}C-NMR (125 MHz, CD$_3$CN): δ 153.4, 153.3, 138.2, 134.7, 132.8, 130.3, 128.8, 121.8, 119.3, 69.4, 67.6, 64.8, 28.7, –2.8; IR (film): 2958, 2855, 1755, 1428, 1253 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for $C_{17}H_{23}O_4Si^+$, 319.13601; found, 319.13757.



Enol carbonate SI-13. To a solution of silyl enol ether **SI-10** (60.0 mg, 0.239 mmol, 1.00 equiv) in THF (2.8 mL) at –78 °C was added *n*-BuLi (2.25 M in hexanes, 0.117 mL, 0.263 mmol, 1.1 equiv) dropwise over 2.0 min. The solution was stirred for 21 min at –78 °C, then neat allyl chloroformate (38.2 µL, 0.385 mmol, 1.5 equiv) was added dropwise over 1 min and the reaction was allowed to stir at –78 °C. After stirring for 3.0 h, the reaction was quenched with water (2.0 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (15:1 hexanes:EtOAc) to afford enol carbonate **SI-13** (37.7 mg, 62% yield) as a colorless oil. Enol carbonate **SI-13**: R_f 0.29 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, C_6D_6): δ 5.68–5.59 (m, 1H), 5.07 (dq, J = 17.2, 1.7, 1H), 4.91 (dq, J = 10.3, 1.2, 1H), 4.36 (dt, J = 5.8, 1.4, 2H), 4.13 (t, J = 2.6, 2H), 3.55 (t, J = 5.6, 2H), 2.26–2.21 (m, 2H), 0.06 (s, 9H); ^{13}C-NMR (125 MHz, C_6D_6): δ 153.3, 152.1, 131.9, 122.4, 118.7, 68.5, 67.0, 64.2, 28.3, –1.5; IR (film): 2956, 2856, 1755, 1252, 1231 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{12}H_{20}O_4Si^+$, 257.12036; found, 257.12173.

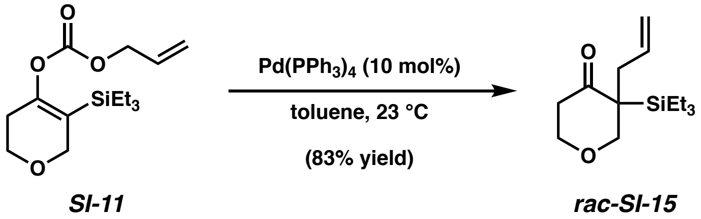


Enol carbonate 45. To a solution of silyl enol ether **10** (601.0 mg, 2.05 mmol, 1.00 equiv) in THF (24.1 mL) at –78 °C was added *n*-BuLi (2.19 M in hexanes, 1.03 mL, 2.25 mmol, 1.1 equiv) dropwise over 1.0 min. The solution was stirred for 45 min at –78 °C, then a solution of the known imidazole carboxylate[8] **SI-14** (702 mg, 3.07 mmol, 1.50 equiv) and $BF_3•Et_2O$ (390 µL, 2.25 mmol, 1.5 equiv) in THF (4.0 mL) that was prestirred for 35 min (at 23 °C) was added dropwise over 5 min and the reaction was allowed to stir at –78 °C. After stirring for 3.0 h the reaction was quenched with water (10.0 mL) at –78 °C. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (19:1 hexanes:EtOAc) to afford enol carbonate **45** (391 mg, 51% yield) as a colorless oil. Enol carbonate **45**: R_f 0.54 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47–7.43 (m, 2H), 7.38–7.29 (m, 3H), 5.60 (br s, 1H), 5.44 (q, J = 1.0, 1H), 5.10 (d, J = 0.9, 2H), 4.20 (t, J = 2.6, 2H), 3.82 (t, J = 5.5, 2H), 2.39–2.34 (m, 2H), 0.89 (t, J = 7.8, 9H), 0.57 (q, J = 7.6, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 152.9, 151.6, 142.1, 137.8, 128.7, 128.3, 126.2, 120.1, 116.4, 69.6, 67.5, 64.3, 28.1, 7.4, 3.0; IR (film): 2953, 1755, 1656, 1230, 1165 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{21}H_{31}O_4Si^+$, 375.19861; found, 357.20141.

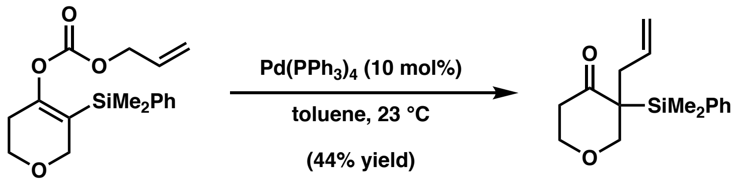
F. Pd-Catalyzed Decarboxylative Allylic Alkylation

i. Racemic Reactions Toward α-Silyl Substituted Ketones

Representative Procedure for Racemic Reactions (Preparation of silyl ketone SI-15 used as an example)

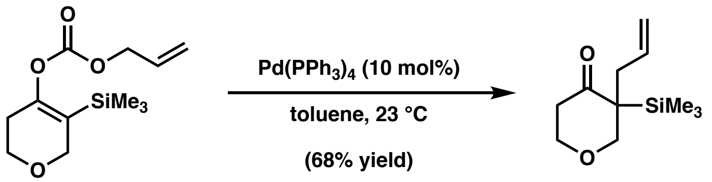


Silyl Ketone rac-SI-15. In a nitrogen-filled glovebox, an oven-dried 1-dram vial was equipped with a stir bar, enol carbonate **SI-11** (100 mg, 0.335 mmol, 1.0 equiv), and toluene (1.7 mL). Then $Pd(PPh_3)_4$ (38.7 mg, 0.034 mmol, 10 mol%) was added slowly in one portion, before sealing the vial with a PTFE-lined cap. The reaction was then allowed to stir for 20 h at 23 °C before the addition of hexanes (2 mL). After stirring for 2 min, the crude reaction mixture was filtered by passage through a plug of silica gel (Et_2O eluent), and concentrated under reduced pressure. The resulting crude oil was purified via flash chromatography (19:1 hexanes:EtOAc), to provide silyl ketone **rac-SI-15** as a colorless oil (70.5 mg, 83% yield). Silyl ketone **rac-SI-15**: R_f 0.58 (5:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.77–5.67 (m, 1H), 5.05–4.96 (m, 2H), 4.19–4.13 (m, 1H), 4.10 (dd, *J* = 11.8, 1.3, 1H), 3.76 (d, *J* = 11.7, 1H), 3.69 (ddd, *J* = 11.4, 11.4, 4.0, 1H), 2.99–2.93 (m, 1H), 2.55 (ddd, *J* = 16.6, 11.5. 7.7, 1H), 3.32 (ddd, *J* = 16.6, 4.0, 2.0, 1H), 1.92 (dd, *J* = 14.1, 8.8, 1H), 1.00 (t, *J* = 7.9, 9H), 0.80–0.66 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 208.7, 135.3, 117.6, 71.2, 67.0, 50.5, 41.3, 35.1, 7.8, 2.9; IR (film): 2956, 1682, 1211, 1187, 1005 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{14}H_{26}O_2Si^+$, 255.17748; found, 255.17914.



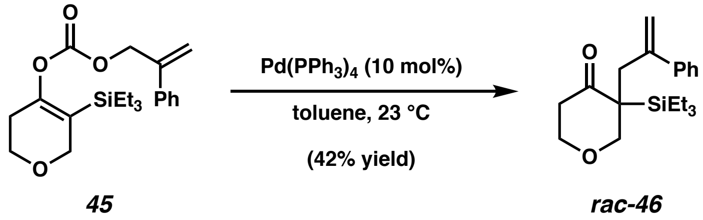
SI-12 ***rac-SI-16***

Silyl ketone rac-SI-16. Purification by preparative thin layer chromatography (9:1 hexanes:EtOAc) afforded silyl ketone **rac-SI-16** as a colorless oil (44% yield). Silyl ketone **rac-SI-16**: R*f* 0.14 (3:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.55–7.51 (m, 2H), 7.43–7.35 (m, 3H), 5.69–5.59 (m, 1H), 5.00–4.90 (m, 2H), 4.07 (dd, *J* = 11.8, 1.4, 1H), 4.05–4.00 (m, 1H), 3.70 (d, *J* = 11.7, 1H), 3.68–3.62 (m, 1H), 2.88 (ddt, *J* = 14.2, 5.5, 1.6, 1H), 2.22–2.18 (m, 2H), 1.88 (dd, *J* = 14.3, 8.7, 1H), 0.49 (s, 3H), 0.42 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 208.5, 135.1, 134.8, 134.7, 129.8, 127.9, 117.6, 71.2, 67.0, 50.4, 40.7, 34.7, –3.6, –4.8; IR (film): 3071, 2963, 2853, 1681, 1428 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for $C_{16}H_{23}O_2Si^+$, 275.14618; found, 275.14746.



SI-13 ***rac-SI-17***

Silyl ketone rac-SI-17. Purification by flash chromatography (15:1 hexanes:EtOAc) afforded silyl ketone **rac-SI-17** as a colorless oil (68% yield). Silyl ketone **rac-SI-17**: R*f* 0.26 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.77–5.67 (m, 1H), 5.05–4.96 (m, 2H), 4.19–4.13 (m, 1H), 4.07 (d, *J* = 11.8, 1H), 3.78 (d, *J* = 11.8, 1H), 3.70 (ddd, *J* = 11.6, 11.6, 3.9, 1H), 2.85 (dd, *J* = 14.2, 5.4, 1H), 2.54–2.45 (m, 1H), 2.36–2.29 (m, 1H), 1.89 (dd, *J* = 14.3, 8.8, 1H), 0.13 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 208.5, 135.0, 117.7, 71.1, 67.1, 50.1, 41.2, 34.5, –2.5; IR (film): 3076, 2925, 2853, 1682, 1251 cm^{-1}; HRMS–APCI (*m/z*) [M + H]$^+$ calcd for $C_{11}H_{21}O_2Si^+$, 213.13053; found, 213.13138.



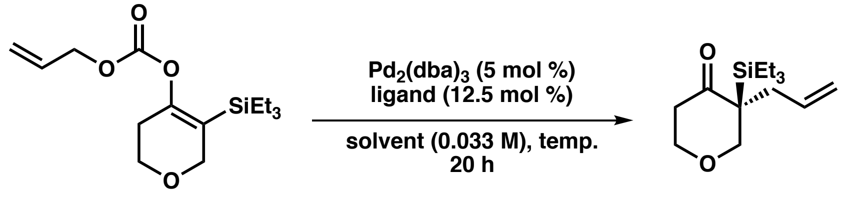
Silyl ketone rac-46. Purification by preparative thin layer chromatography (9:1 hexanes:EtOAc) afforded silyl ketone **rac-46** as a colorless oil (42% yield). Silyl ketone **rac-46**: R_f 0.34 (9:1 hexanes:EtOAc); ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.32–7.27 (m, 4H), 7.26–7.22 (m, 1H), 5.20 (d, *J* = 1.4, 1H), 5.07 (s, 1H), 3.98–3.92 (m, 2H), 3.74–3.69 (m, 2H), 3.41 (ddd, *J* = 11.1, 11.1, 4.9, 1H), 2.44 (d, *J* = 14.4, 1H), 2.36 (ddd, *J* = 17.6, 10.7, 8.2, 1H), 1.94 (ddd, *J* = 17.7, 4.8, 2.5, 1H), 1.02 (t, *J* = 7.9, 9H), 0.84–0.69 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 208.3, 147.0, 141.7, 128.1, 127.5, 127.4, 116.8, 70.3, 66.1, 50.7, 40.1, 35.7, 7.8, 2.8; IR (film): 2955, 2877, 1680, 1444, 1188 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{21}H_{31}O_4Si^+$, 331.20878; found, 331.20983.

ii. Additional Asymmetric Allylic Alkylation Optimization Reactions.

Representative Procedure for Optimization Reactions for Table 3, Table S1, Table S2, and Table S3.

In a nitrogen-filled glovebox, an oven-dried 1-dram vial was equipped with a stir bar, ligand (6.25 µmol, 12.5 mol %), $Pd_2(dba)_3$ (2.50 µmol, 5 mol %), and toluene (0.75 mL). The vial was then capped with a PTFE-lined cap and stirred at 23 °C for 30 min before cooling to the desired temperature. A solution of enol carbonate starting material (0.05 mmol, 1 equiv) in toluene (0.75 mL) was slowly added over 1 min to the catalyst mixture. The vial was sealed with a PTFE-lined cap and stirred at the desired temperature for 20 h. The crude reaction mixture was filtered through a silica plug, eluted with Et_2O, and concentrated under reduced pressure. 1,3,5-Trimethoxybenzene was used then added and used as an external standard in quantitative NMR analysis.

Table S1. Additional Optimization Experiments.



SI-11 ***SI-15***

entry	ligand	solvent	temp (°C)	% conversion[b]	% ee[c]
1	***L1***	toluene	23	>95	21
2	***L2***	toluene	23	>95	2
3	***L3***	toluene	23	>95	7
4	***L4***	toluene	23	>95	13
5	***L5***	toluene	23	>95	0
6	***47***	toluene	23	>95	62
7	***L7***	toluene	23	>95	53
8	***L8***	toluene	23	47	61
9	***L9***	toluene	23	>95	58
10	***47***	THF	23	>95	47
11	***47***	1,4-dioxane	23	>95	57
12	***47***	MTBE	23	>95	52
13	***47***	benzene	23	>95	60
14	***47***	2:1 hexanes:toluene	23	>95	61
15	***47***	toluene	0	>95	68
16	***47***	toluene	–10	>95	70

[a] Conditions: enol carbonate (0.05 mmol), $Pd_2(dba)_3$ (5 mol %), and ligand (12.5 mol %) for 20 h.
[b] Conversion determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as a standard.
[c] Determined by chiral SFC analysis of the isolated product.

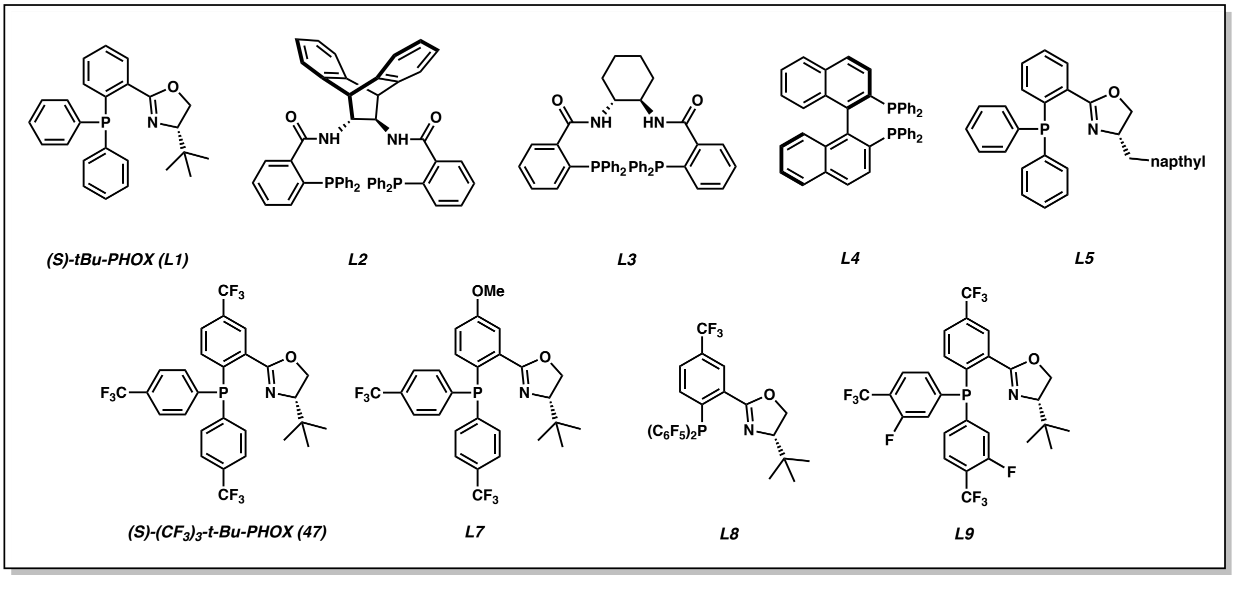
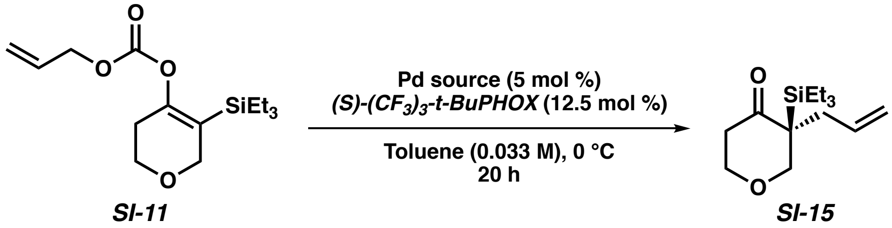


Table S2. Testing Alternative Palladium Sources.



entry	Pd source	% conversion[b]	% ee[c]
1	$Pd_2(dba)_3$	>95	68
2	$Pd(dmdba)_2$[d]	>95	68
3	$Pd_2(pmdba)_3$	>95	68
4	$[PdCl(allyl)]_2$	<10	–

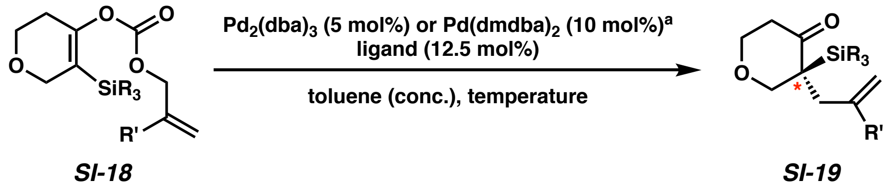
[a] Conditions: enol carbonate(0.05 mmol), Pd source (5 mol %), and ligand (12.5 mol %) for 20 h.

[b] Conversion determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an external standard.

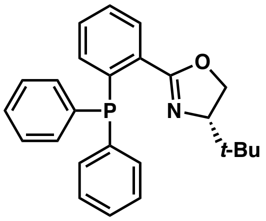
[c] Determined by chiral SFC analysis of isolated product.

[d] Used 10 mol% of Pd source.

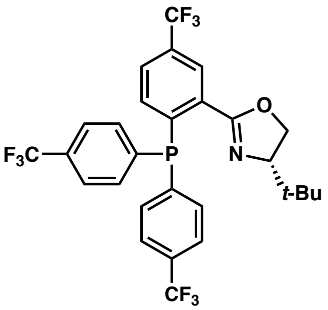
Table S3. Substrate, Temperature, and Concentration Optimization Experiments.



Entry	*Ligand*	*SiR$_3$*	*R'*	*temperature*	*conc. (M)*	*%ee*[b]	*yield*[c]
1	***L1***	SiEt$_3$	H	23 °C	0.033	25	51%
2	***47***	SiEt$_3$	H	23 °C	0.033	62	85%
3	***47***	SiMe$_2$Ph	H	23 °C	0.033	58	69%
4	***47***	SiMe$_3$	H	23 °C	0.033	70	88%
5	***47***	SiMe$_3$	H	–10 °C	0.005	75	85%
6	***47***	SiEt$_3$	H	–10 °C	0.005	74	95%
7	***47***	SiEt$_3$	Ph	–10 °C	0.005	81	75%



(S)-tBu-PHOX (L1)



(S)-(CF$_3$)$_3$-tBu-PHOX (47)

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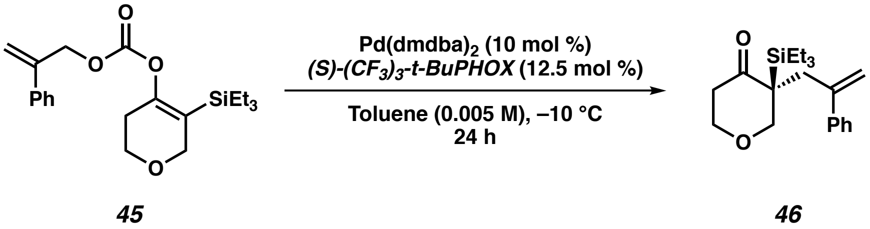
[a] Reactions perfomed at 23 °C utilized Pd$_2$(dba)$_3$, while reactions performed at –10 °C utilized Pd(dmdba)$_2$. Utilizing different palladium sources did not have an observable effect on enantioselectivity (see Table S2 for details) and was only utilized to aid purification.

[b] Enantiomeric excesses (ee's) were determined by SFC analysis using a chiral stationary phase (see SI for details).

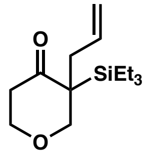
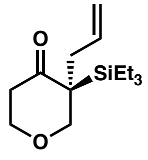
[c] Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an external standard.

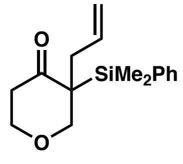
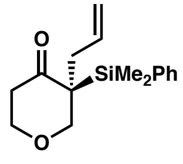
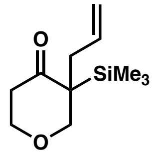
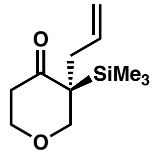
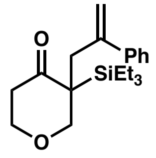
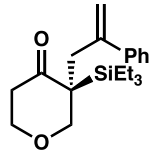
iii. Optimized Decarboxylative Allylic Alkylation Reactions.

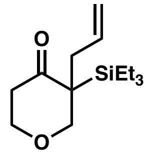
Representative Procedure for Pd-Catalyzed Decarboxylative Allylic Alkylation Reactions



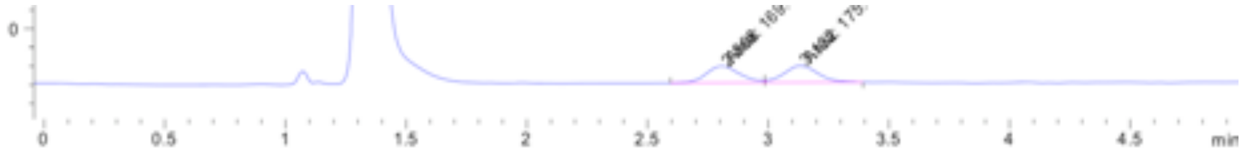
In a nitrogen-filled glovebox, an oven-dried scintillation vial was equipped with a stir bar, *(S)*-$(CF_3)_3$-*t*-BuPHOX ligand (3.70 mg, 6.25 µmol, 12.5 mol %), $Pd(dmdba)_2$ (4.08 mg, 5.00 µmol, 10 mol %), and toluene (0.75 mL). The vial was then sealed with a PTFE-lined cap and stirred at 23 °C. After 30 min, the catalyst mixture was diluted with 8.5 mL of toluene and cooled to –10 °C. A solution of enol carbonate starting material (0.05 mmol, 1 equiv) in toluene (0.75 mL) was added dropwise to the catalyst mixture. The vial was sealed with a PTFE-lined septum cap and stirred at –10 °C for 24 h. The crude reaction mixture was filtered through a silica plug (Et_2O eluent), concentrated under reduced pressure, and purified by flash chromatography to furnish the product. **Silyl ketones SI-15**, **SI-16**, **SI-17**, **and 46** spectral data matched those previously reported (same as pages S24–S26).

Compound	**Method Column/Temp.**	**Solvent**	**Method Flow Rate**	**Retention Times (min)**	**Enantiomeric Ratio (er)**
 ***rac-SI-15***	ChiralPak AD-3/40°C	3% isopropanol in CO_2	2.5 mL/min	2.81/3.13	49.1:50.9
 ***SI-15***	ChiralPak AD-3/40°C	3% isopropanol in CO_2	2.5 mL/min	2.80/3.12	87.0:13.0

 ***rac-SI-16***	ChiralPak IC-3/35°C	2% isopropanol in CO_2	3.5 mL/min	7.47/9.01	50.4/49.6
 ***SI-16***	ChiralPak IC-3/35°C	2% isopropanol in CO_2	3.5 mL/min	9.76/11.9	77.0/23.0
 ***rac-SI-17***	ChiralPak IC-3/40°C	1% isopropanol in CO_2	2.5 mL/min	7.05/7.91	49.2/50.8
 ***SI-17***	ChiralPak IC-3/40°C	1% isopropanol in CO_2	2.5 mL/min	6.67/7.67	87.7/12.3
 ***rac-46***	Chiralcel IC-3/40°C	2% isopropanol in CO_2	2.5 mL/min	4.37/4.93	50.8/49.2
 ***46***	Chiralcel IC-3/40°C	2% isopropanol in CO_2	2.5 mL/min	4.47/5.05	90.3/9.7

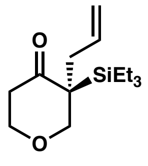


rac-SI-15

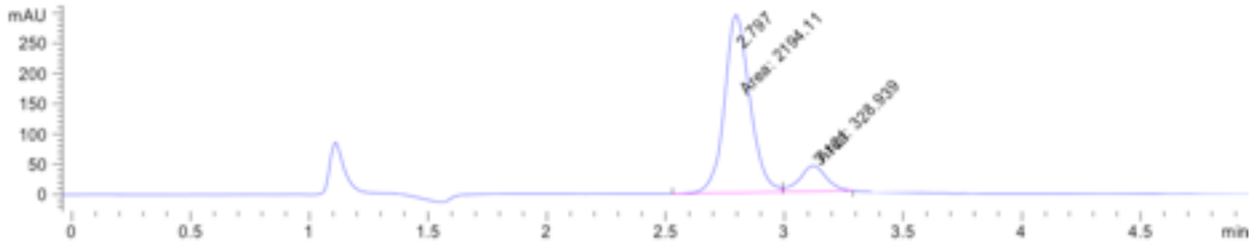


```
Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1    2.808 MF    0.1586  169.78801   17.84176  49.1226
  2    3.132 FM    0.1629  175.85304   17.98790  50.8774
```



SI-15



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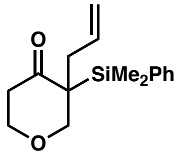
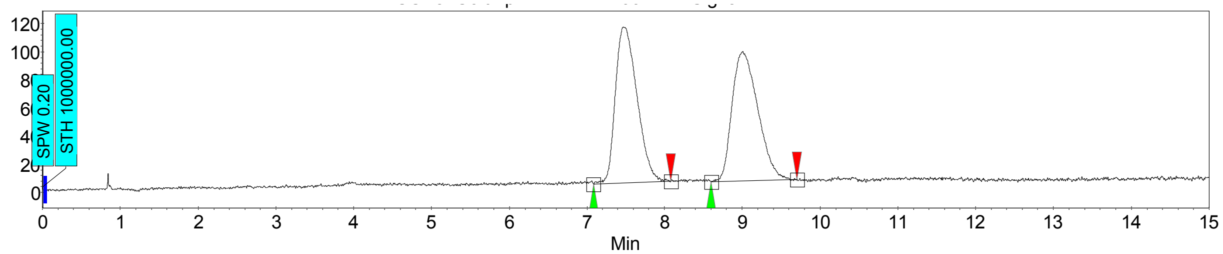
Signal 1: DAD1 A, Sig=210,8 Ref=360,100

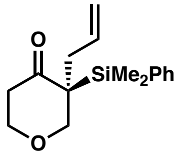
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1    2.797 MF    0.1241 2194.10840  294.65942  86.9626
  2    3.121 FM    0.1286  328.93912   42.63451  13.0374
```



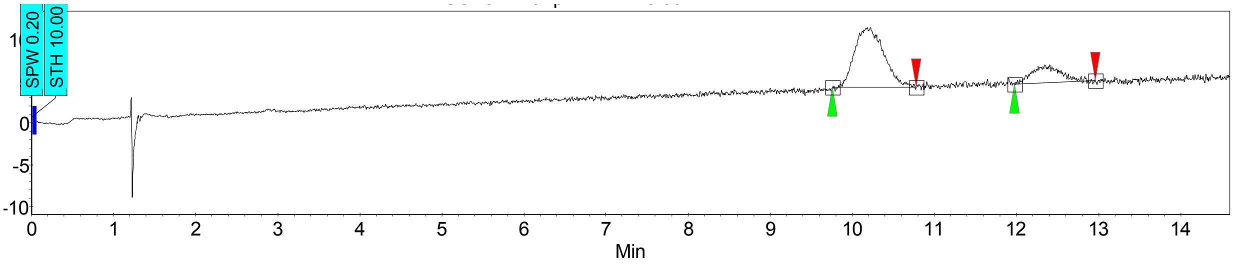
rac-SI-16



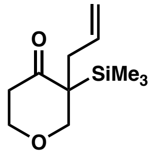
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.09	7.47	8.09	0.00	50.38	110.9	35.9	50.385
2	UNKNOWN	8.60	9.01	9.71	0.00	49.62	92.2	35.4	49.615
Total						100.00	203.1	71.3	100.000



SI-16



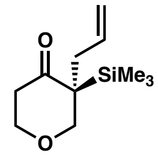
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	9.76	10.17	10.78	0.00	77.01	7.1	2.9	77.005
1	UNKNOWN	11.97	12.34	12.96	0.00	22.99	2.2	0.9	22.995
Total						100.00	9.3	3.8	100.000



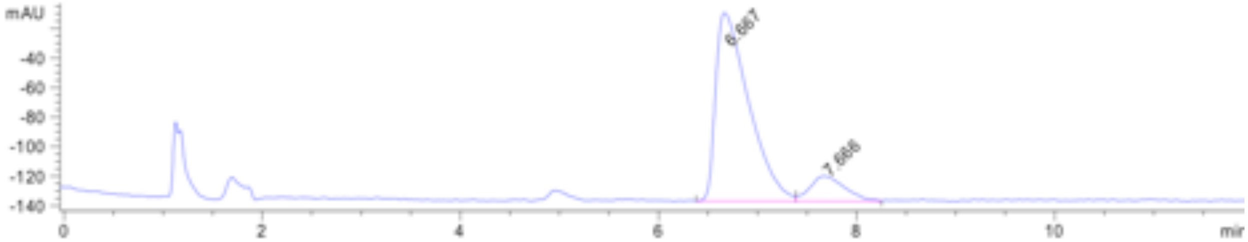
rac-SI-17

```
Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.050 VV    0.2814  576.97528   29.59732  49.1807
   2   7.909 VB    0.3027  596.19904   26.47661  50.8193
```

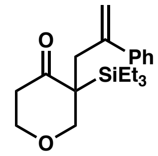


SI-17

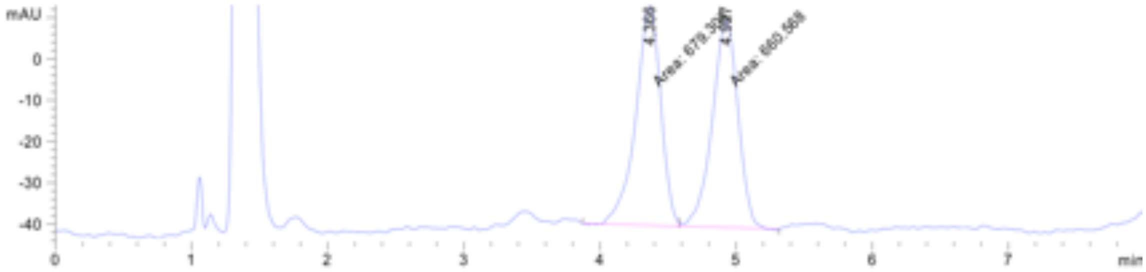


```
Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.667 BV    0.3324 2952.77930  127.38860  87.7272
   2   7.666 VV    0.2993  413.08606   17.01272  12.2728
```

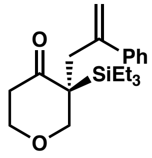


rac-46

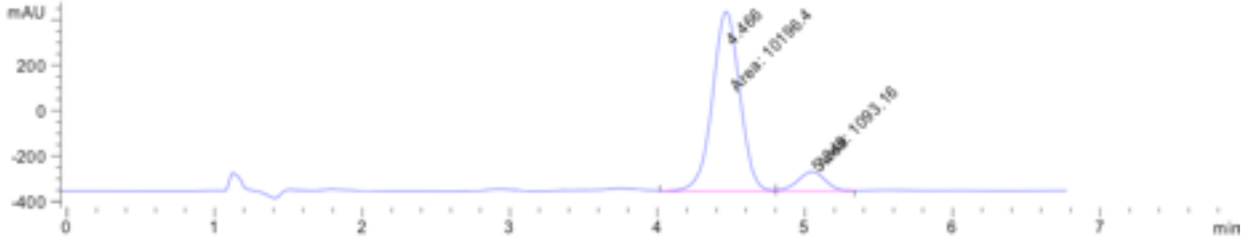


```
Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.366 MF    0.2166  696.71619   53.61436  50.7874
   2   4.927 FM    0.2232  675.11218   50.40852  49.2126
```



46

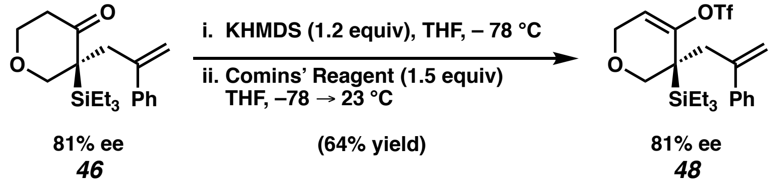


```
Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.466 MM    0.2144 1.01964e4   792.47705  90.3170
   2   5.049 MM    0.2135 1093.16394   85.33304   9.6830
```

G. Enantiospecific trappings

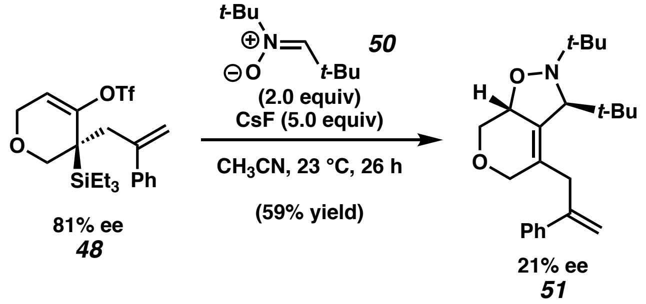
Preparation of Silyl Triflate 48



Silyl triflate 48. To a solution of KHMDS (7.31 mg, 0.0367 mmol, 1.20 equiv) in THF (0.1 mL) at –78 °C was added silyl ketone **46** (10.1 mg, 0.0306 mmol, 1.00 equiv) in THF (0.1 mL) dropwise over 1 min. The solution was stirred for 1 h at –78 °C, before a solution of Comins' Reagent (18.0 mg, 0.0458 mmol, 1.50 equiv) in THF (0.1 mL) was added dropwise over 30 sec. Following the addition, the cooling bath was removed and the reaction was allowed to stir at 23 °C. After stirring for 11 h, the reaction was quenched with sat. aq. $NaHCO_3$ (1.0 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 4 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by preparative thin layer chromatography (9:1 hexanes:EtOAc) to afford silyl triflate **48** as a colorless oil (15.0 mg, 64% yield, 81% ee). Silyl Triflate **48**: R_f 0.48 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36–7.22 (m, 5H), 5.49 (app t, *J* = 5.8, 1H), 5.23 (d, *J* = 1.1, 1H), 5.13 (s, 1H), 3.97 (d, *J* = 3.0, 2H), 3.72 (d, *J* =

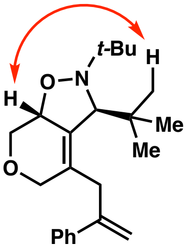
11.8, 1H), 3.54 (d, *J* = 11.8, 1H), 3.02 (d, *J* = 14.2, 1H), 2.68 (d, *J* = 14.2, 1H), 1.02 (t, *J* = 7.9, 9H), 0.72 (q, *J* = 7.9, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.3, 146.4, 143.4, 142.7, 128.2, 126.7, 118.4 (q, *J* = 320), 117.1, 110.7, 70.2, 64.2, 36.5, 36.3, 8.1, 2.6; ^{19}F-NMR (376 Hz, $CDCl_3$): –74.9; IR (film): 2955, 2878, 1739, 1366, 1216 cm^{-1}; $[\alpha]^{26.3}_{D}$ –4.00° (*c* = 1.00, CH_2Cl_2).

Representative Procedure (Preparation of cycloadduct 51 is used as an example).

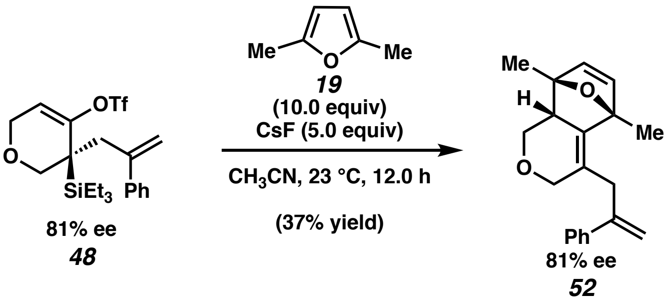


Isoxazolidine 51. To a stirred solution of silyl triflate **48** (14.2 mg, 0.031 mmol, 1.0 equiv) and nitrone **50** (9.7 mg, 0.0614 mmol, 2.0 equiv) in CH_3CN (0.30 mL) was added CsF (23.3 mg, 0.153 mmol, 5.0 equiv). The reaction vessel was sealed and allowed to stir at 23 °C for 26 h. The reaction mixture was filtered by passage through a plug of silica gel (EtOAc eluent, 15 mL). Concentration under reduced pressure yielded the crude residue (1.6:1 dr). Purification by preparative thin layer chromatography (1:1 hexanes:CH_2Cl_2) allowed for separation of the two diastereomers, which were obtained in a total yield of 59%. The major diastereomer **51** was obtained as a colorless oil (21% ee). Isoxazolidine **51**: R_f 0.12 (9:1 hexanes:EtOAc); ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.40–7.20 (m, 5H), 5.38 (d, *J* = 0.7, 1H), 5.30 (s, 1H), 5.13–5.11 (m, 1H), 4.40–4.34 (m, 1H), 4.23–4.17 (m, 2H), 3.82 (dd, *J* = 16.2, 2.9, 1H), 3.54 (s, 1H), 3.30 (s, 2H), 3.16 (app t, *J* = 9.6, 1H), 0.98 (s, 9H), 0.97 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 144.4, 141.5, 137.4, 128.5, 127.8, 126.1, 125.8, 115.0, 71.7, 67.7, 67.4, 67.2, 59.5, 53.4, 37.0, 36.0, 27.8, 26.9; IR (film): 2954, 1738, 1445, 1363, 1217, 1096 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{23}H_{33}NO_2^+$, 355.25058; found, 355.25071. $[\alpha]^{29.5}_{D}$ –4.00° (*c* = 1.00, CH_2Cl_2).

The structure of **51** was verified by 2D-NOESY, as the following interaction was observed:

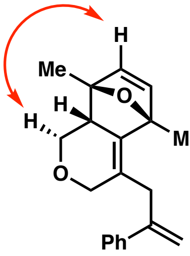


51

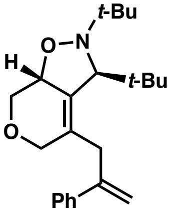
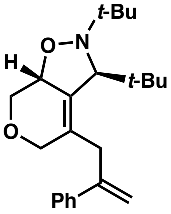
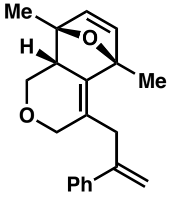
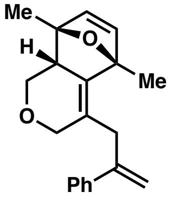


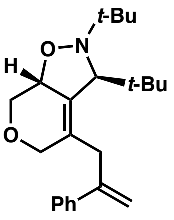
Cycloadduct 52. Following concentration under reduced pressure, the crude residue was obtained (>20:1 dr). Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) afforded cycloadduct **52** as a colorless oil in 37% yield (81% ee). Cycloadduct **52**: R_f 0.35 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.42–7.38 (m, 2H), 7.36–7.27 (m, 3H), 6.17 (d, *J* = 5.4, 1H), 5.85 (d, *J* = 5.4, 1H), 5.39–5.37 (m, 1H), 5.09–5.06 (m, 1H), 4.13–4.06 (m, 2H), 3.82 (dd, *J* = 10.1, 2.8, 1H), 3.30 (d, *J* = 16.7, 1H), 3.15 (d, *J* = 16.7, 1H), 2.51–2.46 (m, 1H), 2.40 (dd, *J* = 10.6, 9.3, 1H), 1.76 (s, 3H), 1.62 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 145.4, 141.3, 139.8, 138.6, 133.5, 128.4, 127.7, 125.9, 123.4, 113.7, 87.4, 85.7, 67.3, 67.2, 46.7, 34.2, 18.2, 17.5; IR (film): 2924, 2852, 1741, 1632, 1380 cm^{-1}; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{20}H_{23}O_2^+$, 295.16926; found, 295.17032. $[\alpha]^{28.6}_D$ +73.3° (*c* = 1.00, CH_2Cl_2).

The structure of **52** was verified by 2D-NOESY, as the following interaction was observed:

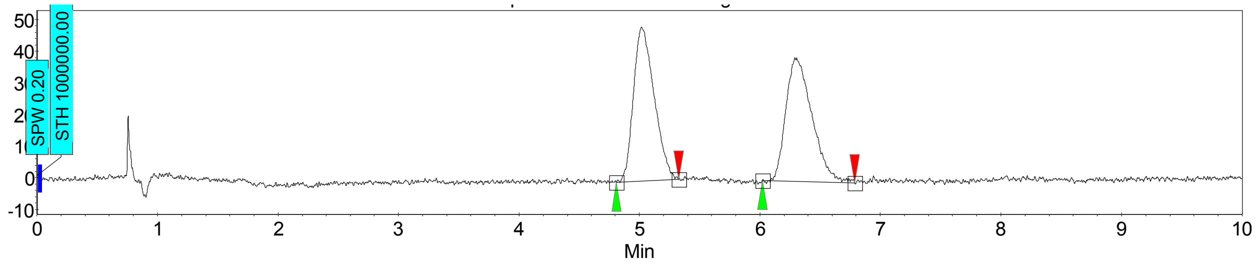


52

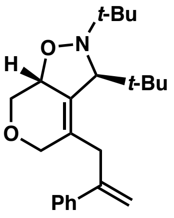
Compound	**Method** **Column/Temp.**	**Solvent**	**Method** **Flow Rate**	**Retention Times (min)**	**Enantiomeric Ratio (er)**
 ***rac-51***	ChiralPak IC-3/35°C	5% isopropanol in CO_2	3.5 mL/min	5.02/6.29	49.7/50.3
 ***51***	ChiralPak IC-3/35°C	5% isopropanol in CO_2	3.5 mL/min	5.29/6.55	39.2/60.8
 ***rac-52***	ChiralPak AD-3/35°C	5% isopropanol in CO_2	3.5 mL/min	5.41/6.80	49.9/50.1
 ***52***	ChiralPak AD-3/35°C	5% isopropanol in CO_2	3.5 mL/min	6.06/6.91	90.7/9.3



***rac*-51**



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.81	5.02	5.33	0.00	49.74	48.7	9.7	49.742
2	UNKNOWN	6.02	6.29	6.79	0.00	50.26	39.3	9.8	50.258
Total						100.00	88.0	19.6	100.000



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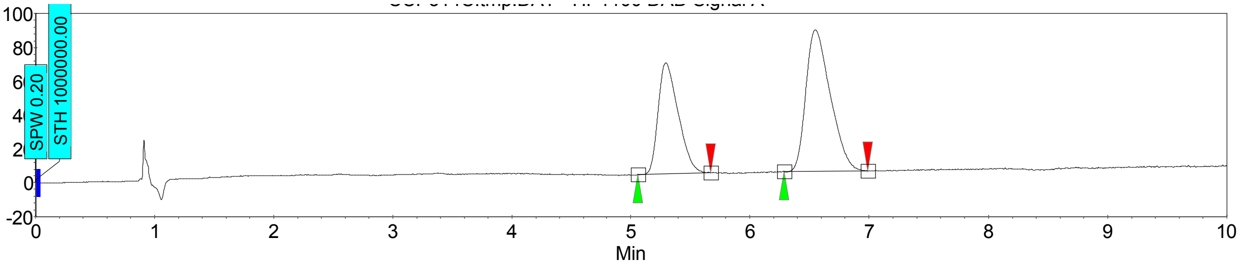
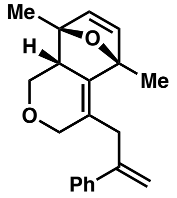
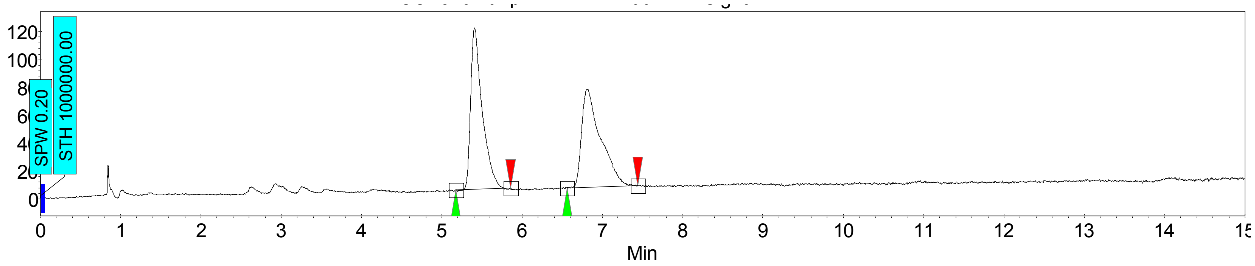


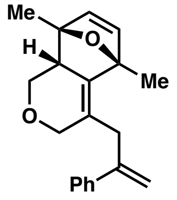
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.06	5.29	5.67	0.00	39.25	65.6	12.8	39.249
2	UNKNOWN	6.28	6.55	6.99	0.00	60.75	83.3	19.7	60.751
Total						100.00	148.9	32.5	100.000



rac-52



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.17	5.41	5.86	0.00	49.86	115.6	19.3	49.859
2	UNKNOWN	6.56	6.80	7.45	0.00	50.14	70.3	19.4	50.141
Total						100.00	185.9	38.7	100.000



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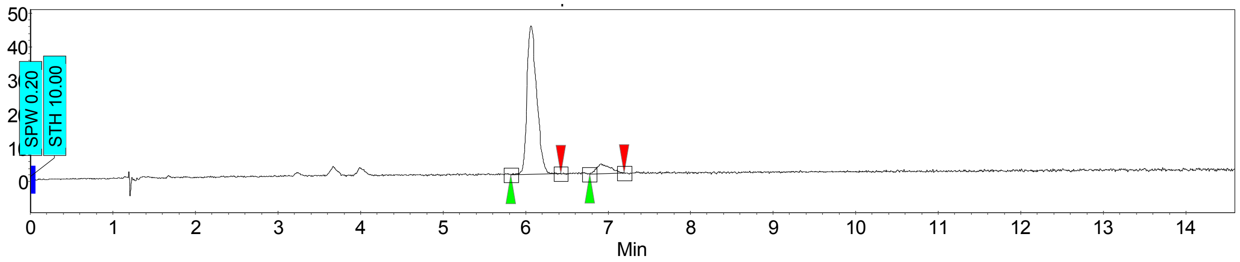

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.82	6.06	6.42	0.00	90.73	44.0	6.0	90.732
2	UNKNOWN	6.77	6.91	7.20	0.00	9.27	3.0	0.6	9.268
Total						100.00	47.0	6.6	100.000

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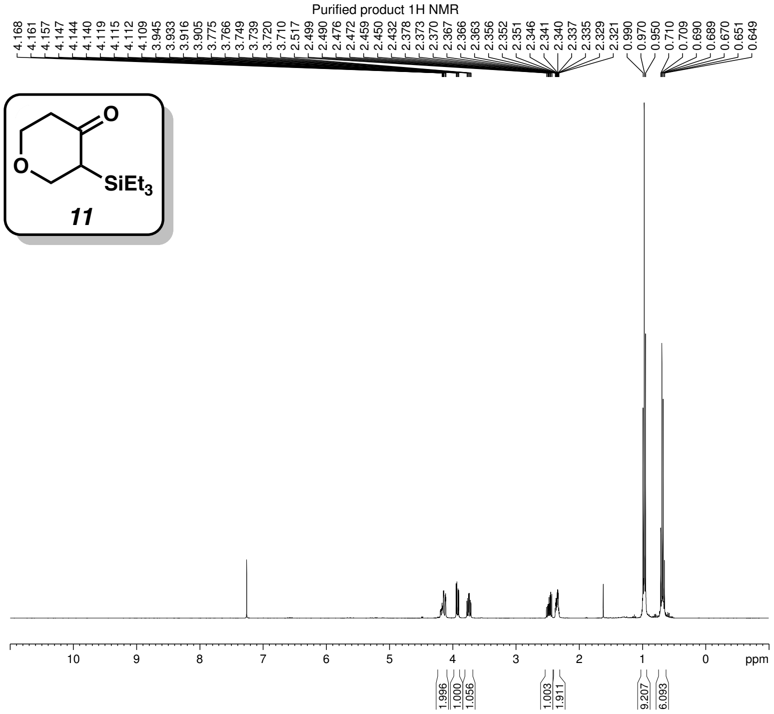
NMR Spectra:

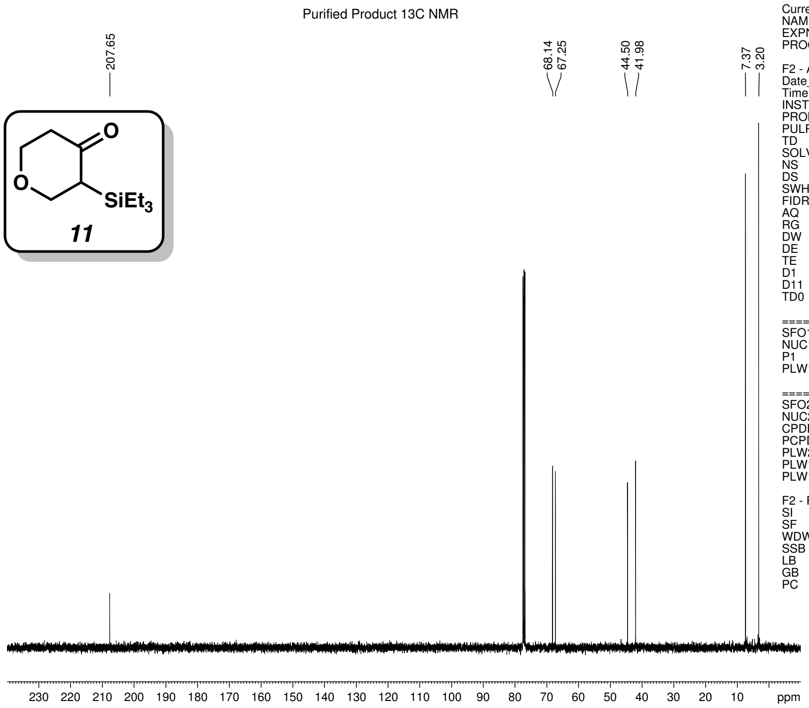


```
Current Data Parameters
NAME     MY-2018-020a-p-char
EXPNO              20
PROCNO              1

F2 - Acquisition Parameters
Date_         20180911
Time             20.07
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               52882
SOLVENT          CDCl3
NS                   8
DS                   0
SWH          8012.820 Hz
FIDRES       0.151523 Hz
AQ          3.2998369 sec
RG              155.85
DW              62.400 usec
DE               6.50 usec
TE              298.5 K
D1        2.00000000 sec
TD0                  1

======== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1                1H
P1               15.00 usec
PLW1       13.00000000 W

F2 - Processing parameters
SI               65536
SF         400.1300184 MHz
WDW                 EM
SSB    0
LB                0.30 Hz
GB     0
PC                1.00
```



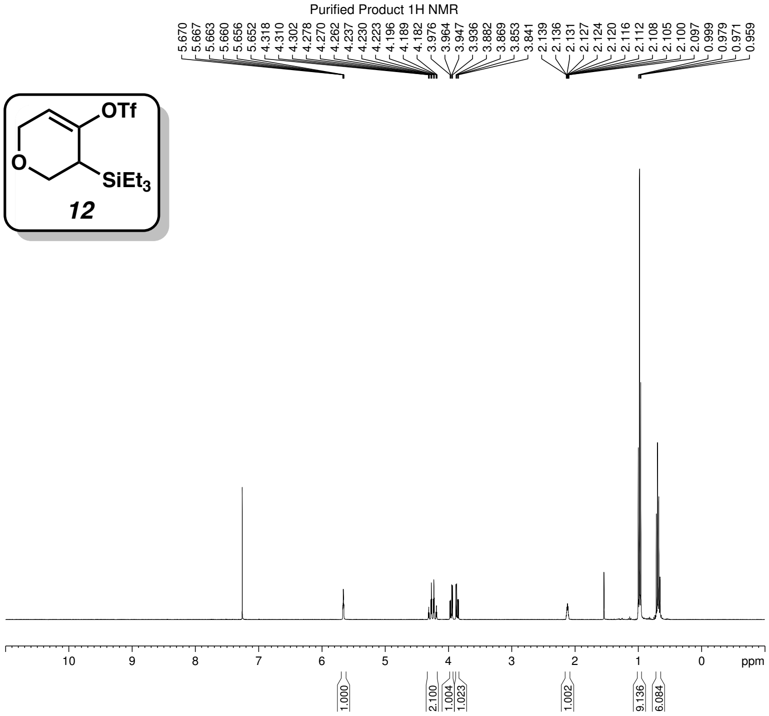
```
Current Data Parameters
NAME     MY-2018-020a-p-cha
EXPNO              21
PROCNO              1

F2 - Acquisition Parameters
Date_         20180911
Time             20.23
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 256
DS                   0
SWH         25252.525 Hz
FIDRES       0.385323 Hz
AQ          1.2976128 sec
RG              189.85
DW              19.800 usec
DE               6.50 usec
TE              299.4 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                  1

======== CHANNEL f1 =====
SFO1      100.6243395 MHz
NUC1               13C
P1               10.00 usec
PLW1       52.00000000 W

======== CHANNEL f2 =====
SFO2      400.1324008 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2       13.00000000 W
PLW12       0.36111000 W
PLW13       0.29249999 W

F2 - Processing parameters
SI               65536
SF         100.6127570 MHz
WDW                 EM
SSB    0
LB                1.00 Hz
GB     0
PC                1.40
```



Current Data Parameters

NAME	MY-2017-019a-p-char
EXPNO	30
PROCNO	1

F2 - Acquisition Parameters

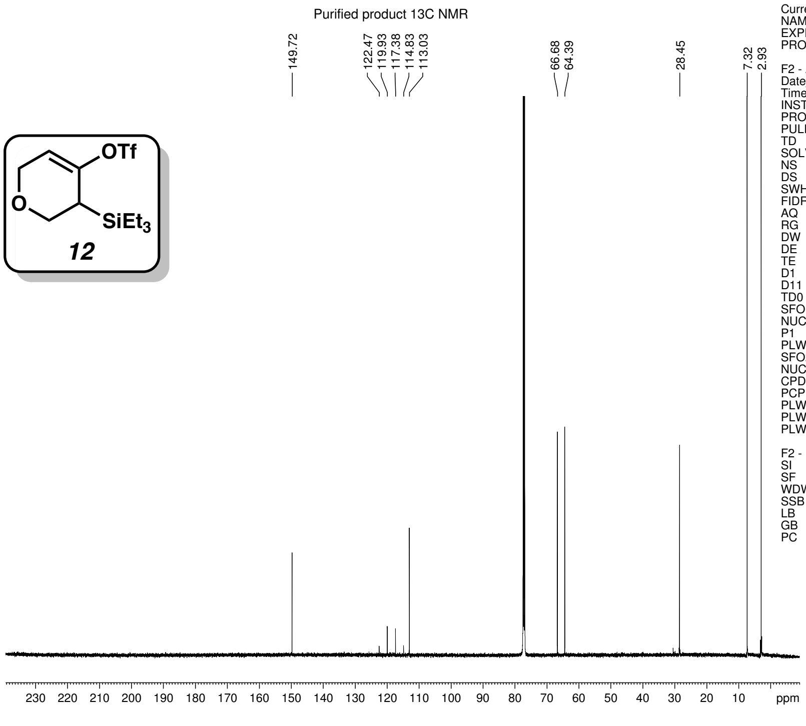
Date_	20180911
Time	20.27
INSTRUM	av400
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	52882
SOLVENT	CDCl3
NS	4
DS	0
SWH	8012.820 Hz
FIDRES	0.151523 Hz
AQ	3.2998369 sec
RG	155.85
DW	62.400 usec
DE	6.50 usec
TE	298.7 K
D1	2.00000000 sec
TD0	1

======== CHANNEL f1 ======

SFO1	400.1324008 MHz
NUC1	1H
P1	15.00 usec
PLW1	13.00000000 W

F2 - Processing parameters

SI	65536
SF	400.1300184 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



Current Data Parameters

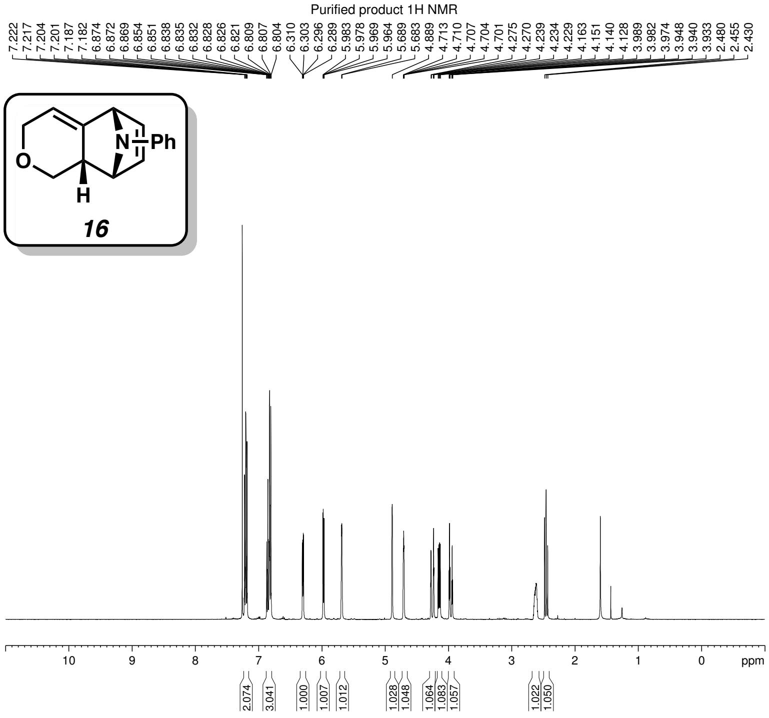
NAME	ST-char-2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20181019
Time	10.36 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	272
DS	2
SWH	31250.000 Hz
FIDRES	0.953674 Hz
AQ	1.0485760 sec
RG	204.54
DW	16.000 usec
DE	18.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.7722511 MHz
NUC1	13C
P1	9.63 usec
PLW1	23.00000000 W
SFO2	500.1330008 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	13.50000000 W
PLW12	0.21094000 W
PLW13	0.13500001 W

F2 - Processing parameters

SI	131072
SF	125.7577708 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

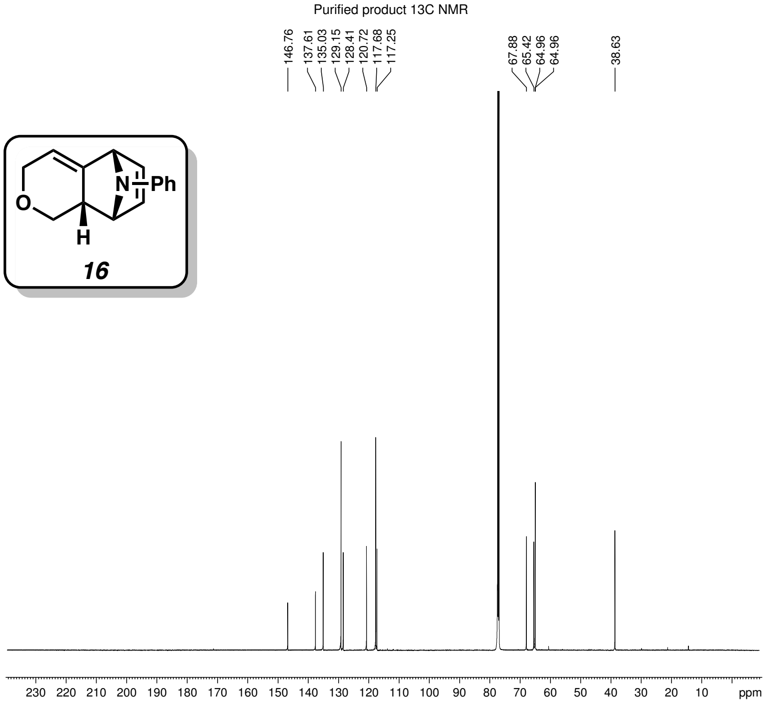


```
Current Data Parameters
NAME     MY-2018-036a-p-b2-cl
EXPNO              30
PROCNO              1

F2 - Acquisition Parameters
Date_         20180822
Time             22.17
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               52882
SOLVENT          CDCl3
NS                   8
DS                   0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ        3.2998369 sec
RG              155.85
DW          62.400 usec
DE            6.50 usec
TE             298.3 K
D1       2.00000000 sec
TD0                  1

======== CHANNEL f1 =====
SFO1    400.1324008 MHz
NUC1                1H
P1         15.00 usec
PLW1     13.00000000 W

F2 - Processing parameters
SI               65536
SF      400.1300184 MHz
WDW                 EM
SSB     0
LB             0.30 Hz
GB      0
PC                1.00
```

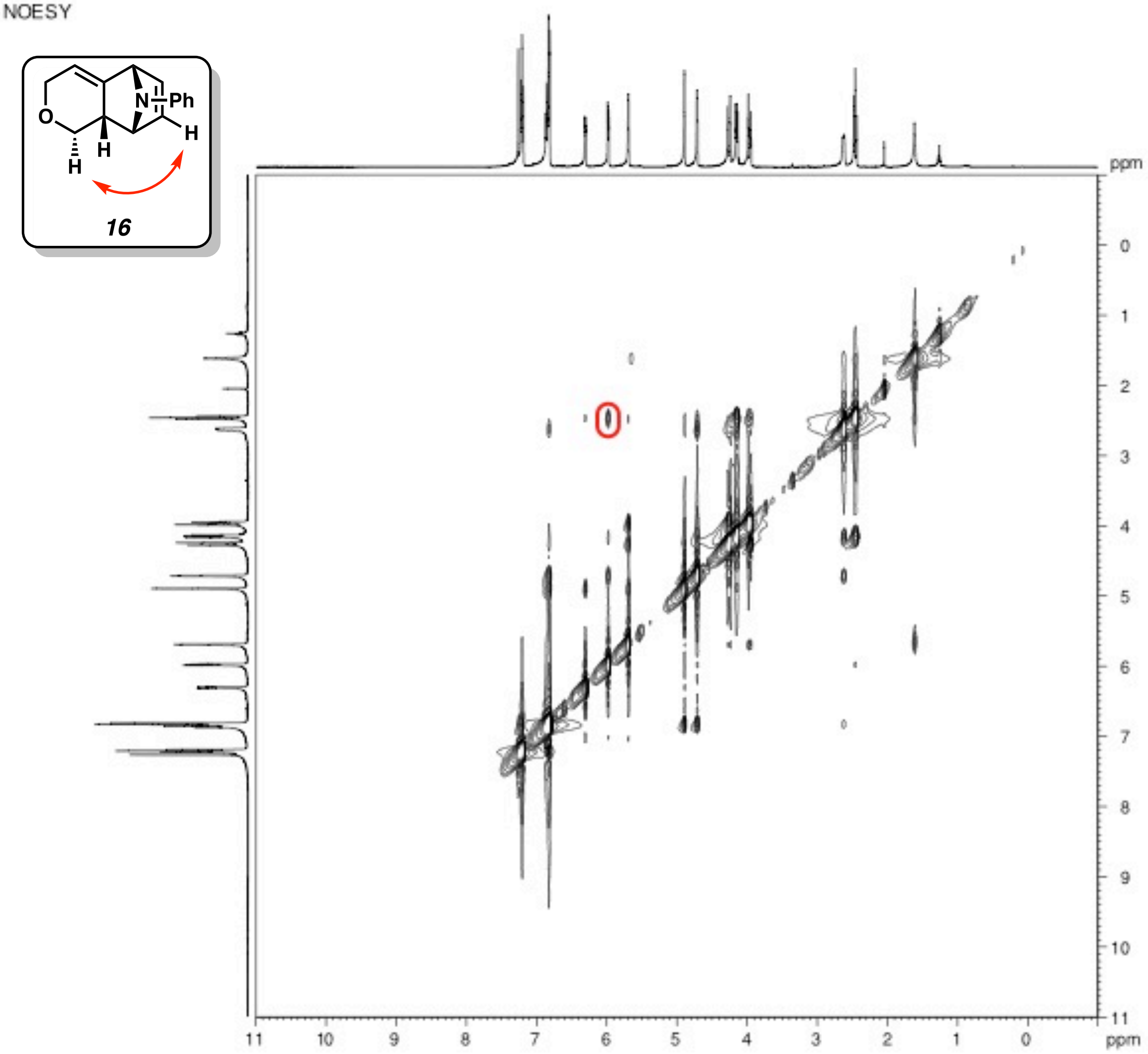


```
Current Data Parameters
NAME     MY-2017-016a-p-b2-
EXPNO               4
PROCNO              1

F2 - Acquisition Parameters
Date_         20171003
Time            2.42 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                2800
DS                   2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ        1.0485760 sec
RG              204.54
DW          16.000 usec
DE           18.00 usec
TE             298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                  1
SFO1    125.7722511 MHz
NUC1               13C
P1           9.63 usec
PLW1     23.00000000 W
SFO2    500.1330008 MHz
NUC2                1H
CPDPRG[2       waltz16
PCPD2        80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.13500001 W

F2 - Processing parameters
SI              131072
SF      125.7577727 MHz
WDW                 EM
SSB     0
LB             1.00 Hz
GB      0
PC                1.40
```

NOESY



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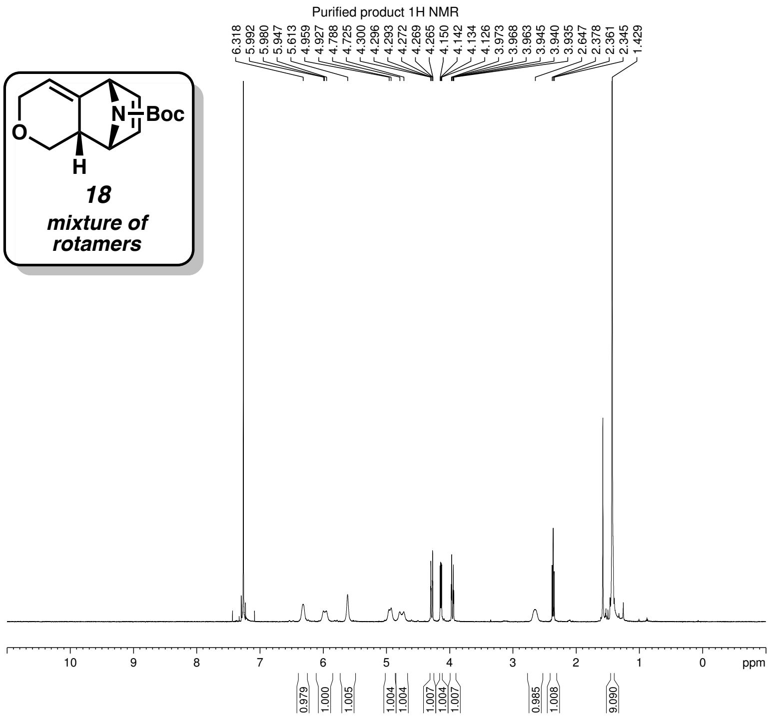
```
Current Data Parameters
NAME      MY-2017-016a-p-b2-2(
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20171002
Time           21.27 h
INSTRUM         av500
PROBHD   Z119248_0002 (
PULPROG      noesygpph
TD              2048
SOLVENT         CDCl3
NS                 8
DS                 8
SWH        10000.000 Hz
FIDRES      9.765625 Hz
AQ         0.1024000 sec
RG              7.89
DW            50.000 usec
DE            10.00 usec
TE             298.0 K
D0        0.00003727 sec
D1        2.00000000 sec
D8        0.75000000 sec
D16       0.00020000 sec
IN0       0.00010000 sec
TDav               1
SFO1     500.1330008 MHz
NUC1              1H
P1            10.00 usec
P2            20.00 usec
PLW1     13.50000000 W
GPNAM[1]      SINE.100
GPZ1          40.00 %
P16         1000.00 usec

F1 - Acquisition parameters
TD               256
SFO1         500.133 MHz
FIDRES     78.125000 Hz
SW            19.995 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI              2048
SF       500.1300146 MHz
WDW            QSINE
SSB                2
LB       0 Hz
GB       0
PC              1.40

F1 - Processing parameters
SI              2048
MC2       States-TPPI
SF       500.1300146 MHz
WDW            QSINE
SSB                2
LB       0 Hz
GB       0
```

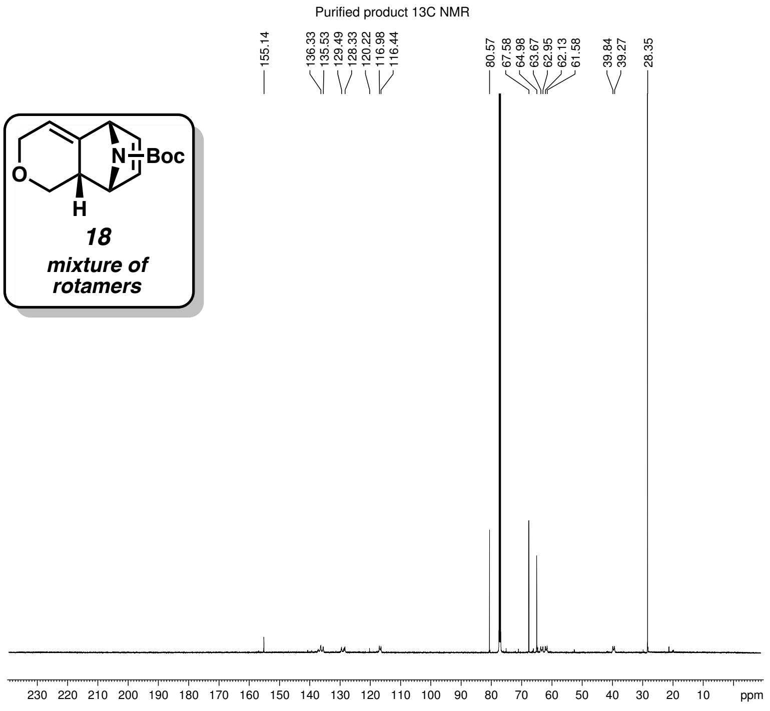

18
mixture of rotamers

```
Current Data Parameters
NAME      RRK-2018-030
EXPNO           103
PROCNO            1

F2 - Acquisition Parameters
Date_       20180925
Time          18.15
INSTRUM         av600
PROBHD   5 mm BB5
PULPROG          zg30
TD           65536
SOLVENT         CDCl3
NS               8
DS               0
SWH        12376.237 Hz
FIDRES      0.188846 Hz
AQ         2.6476543 sec
RG              256
DW            40.400 usec
DE             6.50 usec
TE            295.2 K
D1         2.00000000 sec
TD0               1

======== CHANNEL f1 =====
NUC1              1H
P1            16.50 usec
PL1           -1.00 dB
PL1W       31.62277603 W
SFO1       600.1336008 MHz

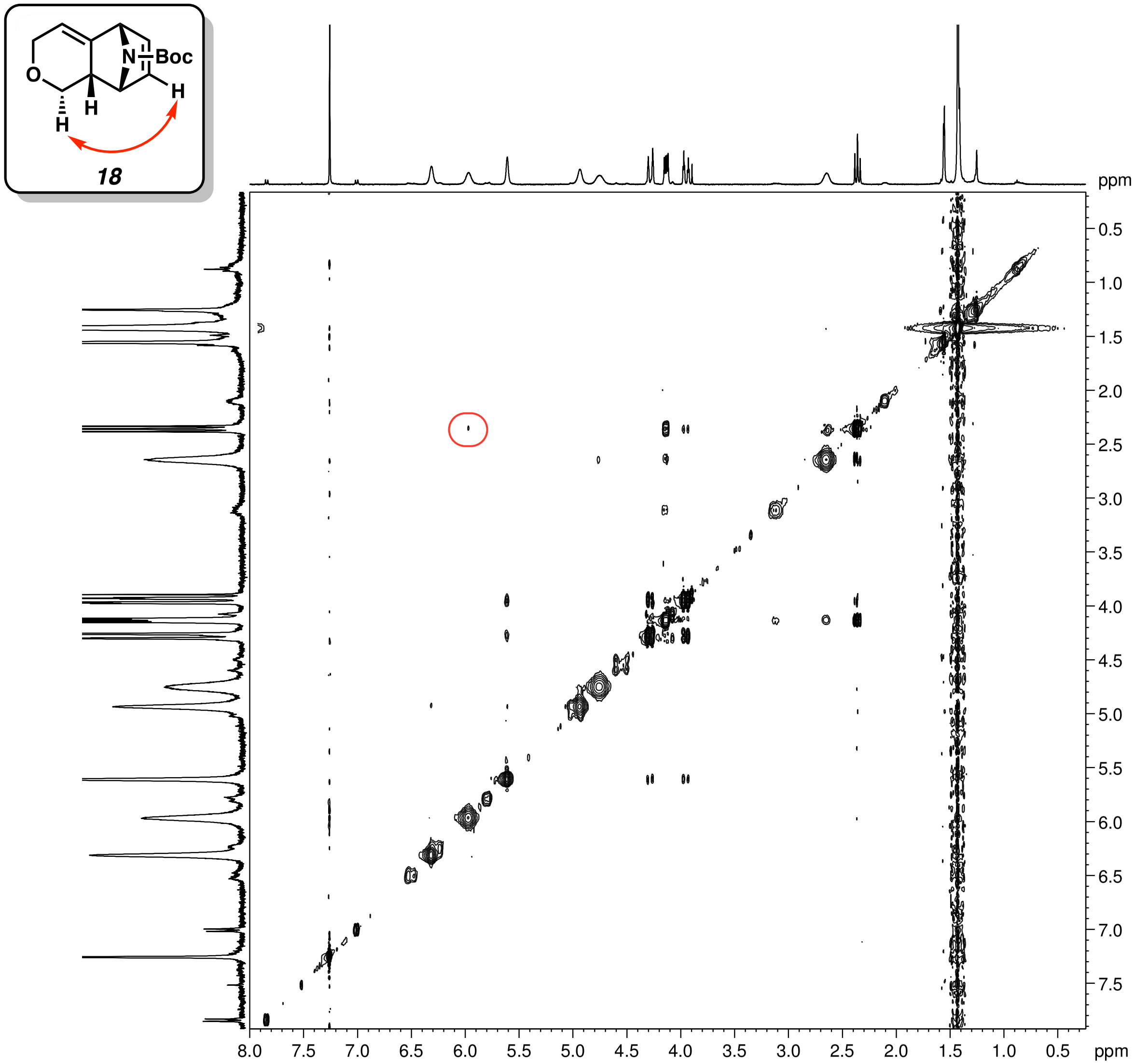
F2 - Processing parameters
SI            65536
SF         600.1300273 MHz
WDW              EM
SSB    0
LB            0.30 Hz
GB     0
PC            1.00
```


18
mixture of rotamers

```
Current Data Parameters
NAME      RRK-2018-157
EXPNO             4
PROCNO            1

F2 - Acquisition Parameters
Date_       20181025
Time          13.07 h
INSTRUM         av500
PROBHD   Z119248_0002 (
PULPROG        zgpg30
TD           65536
SOLVENT         CDCl3
NS              468
DS                2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ         1.0485760 sec
RG           204.54
DW            16.000 usec
DE            18.00 usec
TE            298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0               1
SFO1       125.7722511 MHz
NUC1             13C
P1            10.50 usec
PLW1       23.00000000 W
SFO2       500.1330008 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2         80.00 usec
PLW2       13.50000000 W
PLW12       0.21094000 W
PLW13       0.10610000 W

F2 - Processing parameters
SI           131072
SF         125.7577735 MHz
WDW              EM
SSB    0
LB            1.00 Hz
GB     0
PC            1.40
```



18

Current Data Parameters

NAME	RRK-2018-028
EXPNO	222
PROCNO	1

F2 - Acquisition Parameters

Date_	20180215
Time	15.57
INSTRUM	av400
PROBHD	5 mm PABBO BB/
PULPROG	noesygpphpp
TD	2048
SOLVENT	CDCl3
NS	2
DS	8
SWH	3105.590 Hz
FIDRES	1.516401 Hz
AQ	0.3297280 sec
RG	137.18
DW	161.000 usec
DE	6.50 usec
TE	298.4 K
D0	0.00014190 sec
D1	2.00000000 sec
D8	0.75000000 sec
D11	0.03000000 sec
D12	0.00002000 sec
D16	0.00020000 sec
IN0	0.00032200 sec

======== CHANNEL f1 ======

SFO1	400.1316362 MHz
NUC1	1H
P1	15.00 usec
P2	30.00 usec
P17	2500.00 usec
PLW1	13.00000000 W
PLW10	4.32690001 W

====== GRADIENT CHANNEL

GPNAM[1]	SMSQ10.100
GPZ1	40.00 %
P16	1000.00 usec

F1 - Acquisition parameters

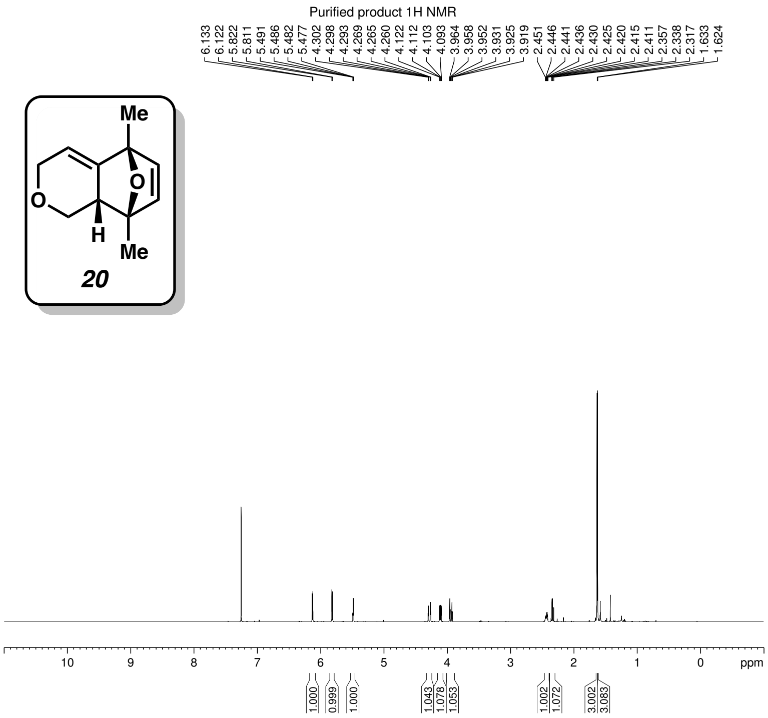
TD	256
SFO1	400.1316 MHz
FIDRES	24.262423 Hz
SW	7.761 ppm
FnMODE	States-TPPI

F2 - Processing parameters

SI	1024
SF	400.1300184 MHz
WDW	QSINE
SSB	2
LB	0 Hz
GB	0
PC	1.00

F1 - Processing parameters

SI	1024
MC2	States-TPPI
SF	400.1300184 MHz
WDW	QSINE
SSB	2
LB	0 Hz
GB	0



Current Data Parameters

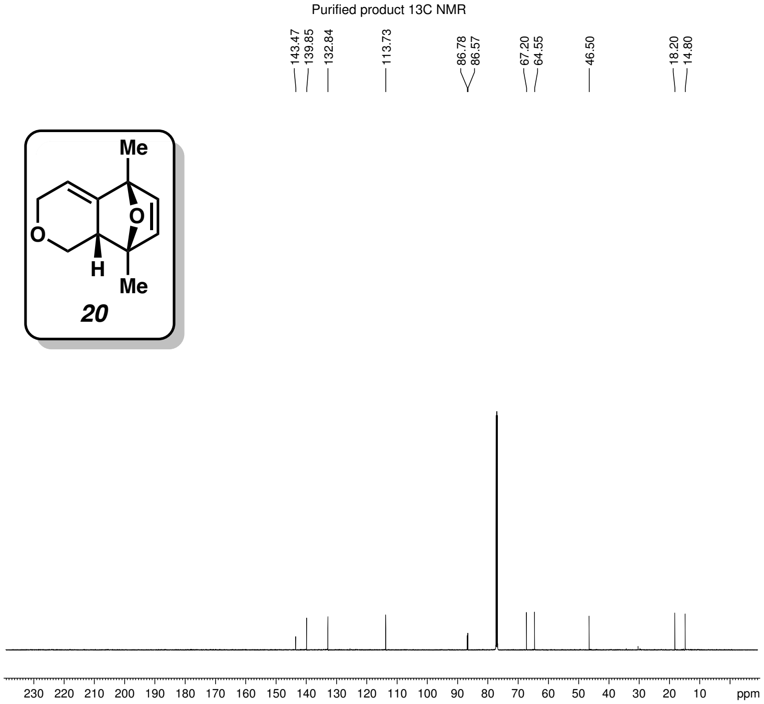
NAME	MY-2018-265a-p-b1-1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20181003
Time	13.52 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.305176 Hz
AQ	3.2767999 sec
RG	12.14
DW	50.000 usec
DE	10.00 usec
TE	298.0 K
D1	2.00000000 sec
TD0	1
SFO1	500.1330008 MHz
NUC1	1H
P1	10.00 usec
PLW1	13.50000000 W

F2 - Processing parameters

SI	65536
SF	500.1300146 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



Current Data Parameters

NAME	MY-2018-265a-p-b1-
EXPNO	2
PROCNO	1

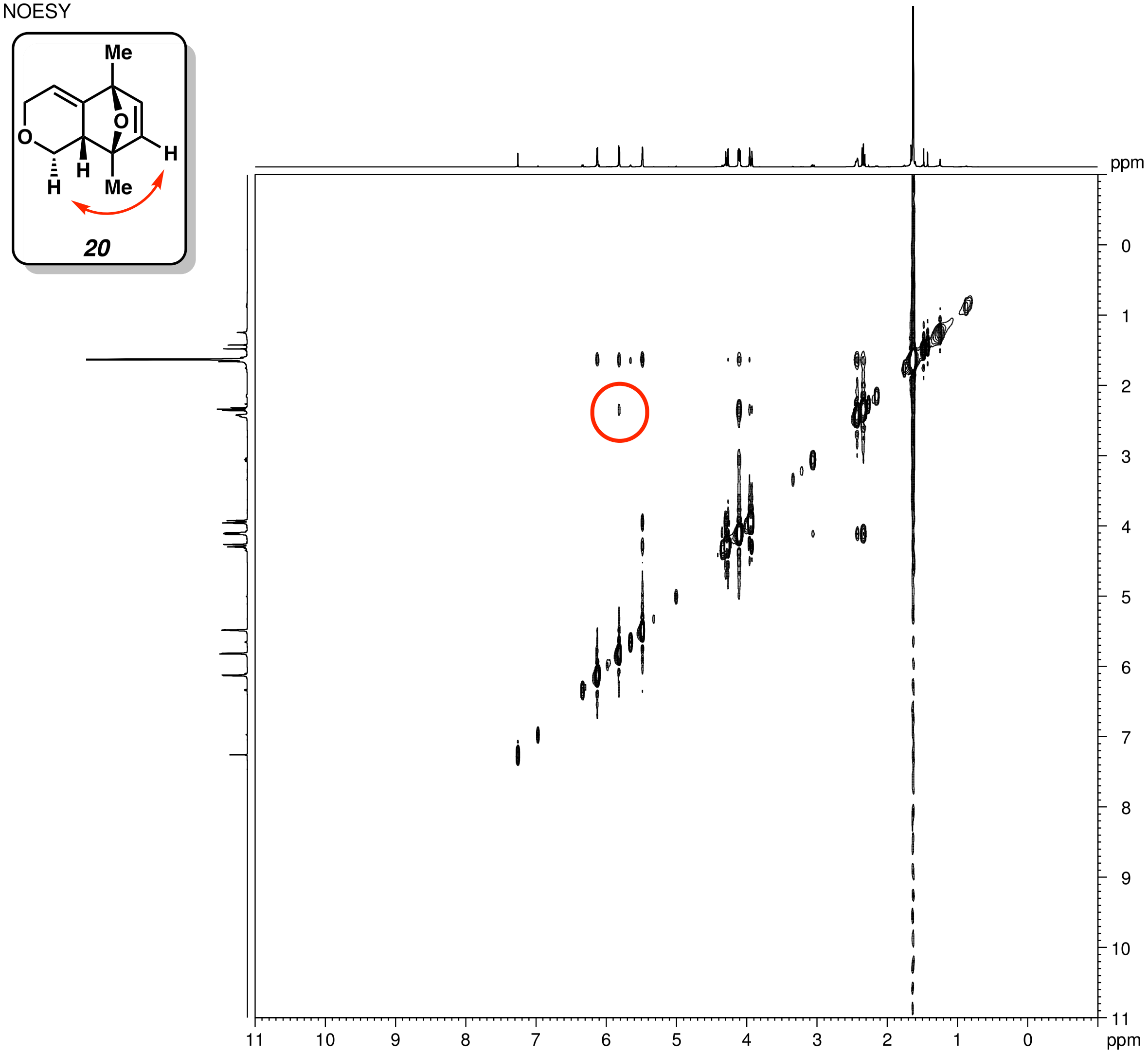
F2 - Acquisition Parameters

Date_	20181003
Time	13.59 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	64
DS	2
SWH	31250.000 Hz
FIDRES	0.953674 Hz
AQ	1.0485760 sec
RG	204.54
DW	16.000 usec
DE	18.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.7722511 MHz
NUC1	13C
P1	9.63 usec
PLW1	23.00000000 W
SFO2	500.1330008 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	13.50000000 W
PLW12	0.21094000 W
PLW13	0.13500001 W

F2 - Processing parameters

SI	131072
SF	125.7577892 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

NOESY



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Current Data Parameters

NAME	MY-2018-034a-p-b1-N
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20180202
Time	11.32 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	noesygpph
TD	2048
SOLVENT	CDCl3
NS	2
DS	8
SWH	10000.000 Hz
FIDRES	9.765625 Hz
AQ	0.1024000 sec
RG	19.06
DW	50.000 usec
DE	10.00 usec
TE	298.0 K
D0	0.00003727 sec
D1	2.00000000 sec
D8	0.75000000 sec
D16	0.00020000 sec
IN0	0.00010000 sec
TDav	1
SFO1	500.1330008 MHz
NUC1	1H
P1	10.00 usec
P2	20.00 usec
PLW1	13.50000000 W
GPNAM[1]	SINE.100
GPZ1	40.00 %
P16	1000.00 usec

F1 - Acquisition parameters

TD	256
SFO1	500.133 MHz
FIDRES	78.125000 Hz
SW	19.995 ppm
FnMODE	States-TPPI

F2 - Processing parameters

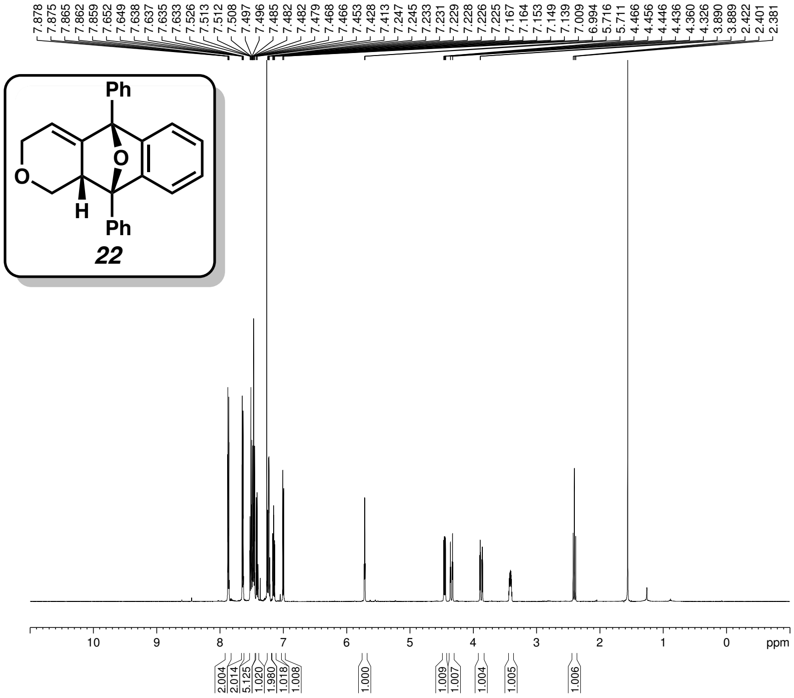
SI	2048
SF	500.1300146 MHz
WDW	QSINE
SSB	2
LB	0 Hz
GB	0
PC	1.40

F1 - Processing parameters

SI	2048
MC2	States-TPPI
SF	500.1300146 MHz
WDW	QSINE
SSB	2
LB	0 Hz
GB	0

22

Purified product 1H NMR



Current Data Parameters
NAME RRK-2018-033
EXPNO 500
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181003
Time 11.01 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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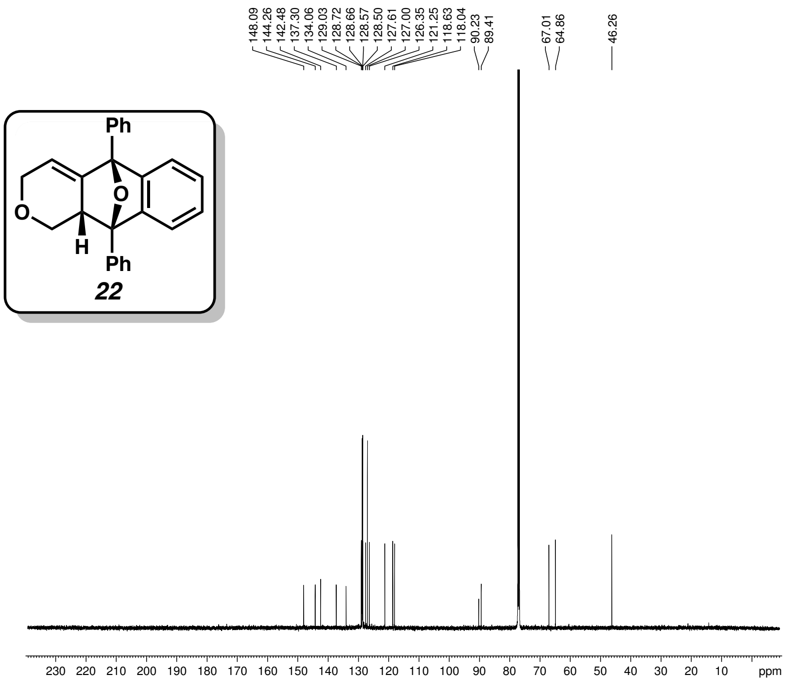
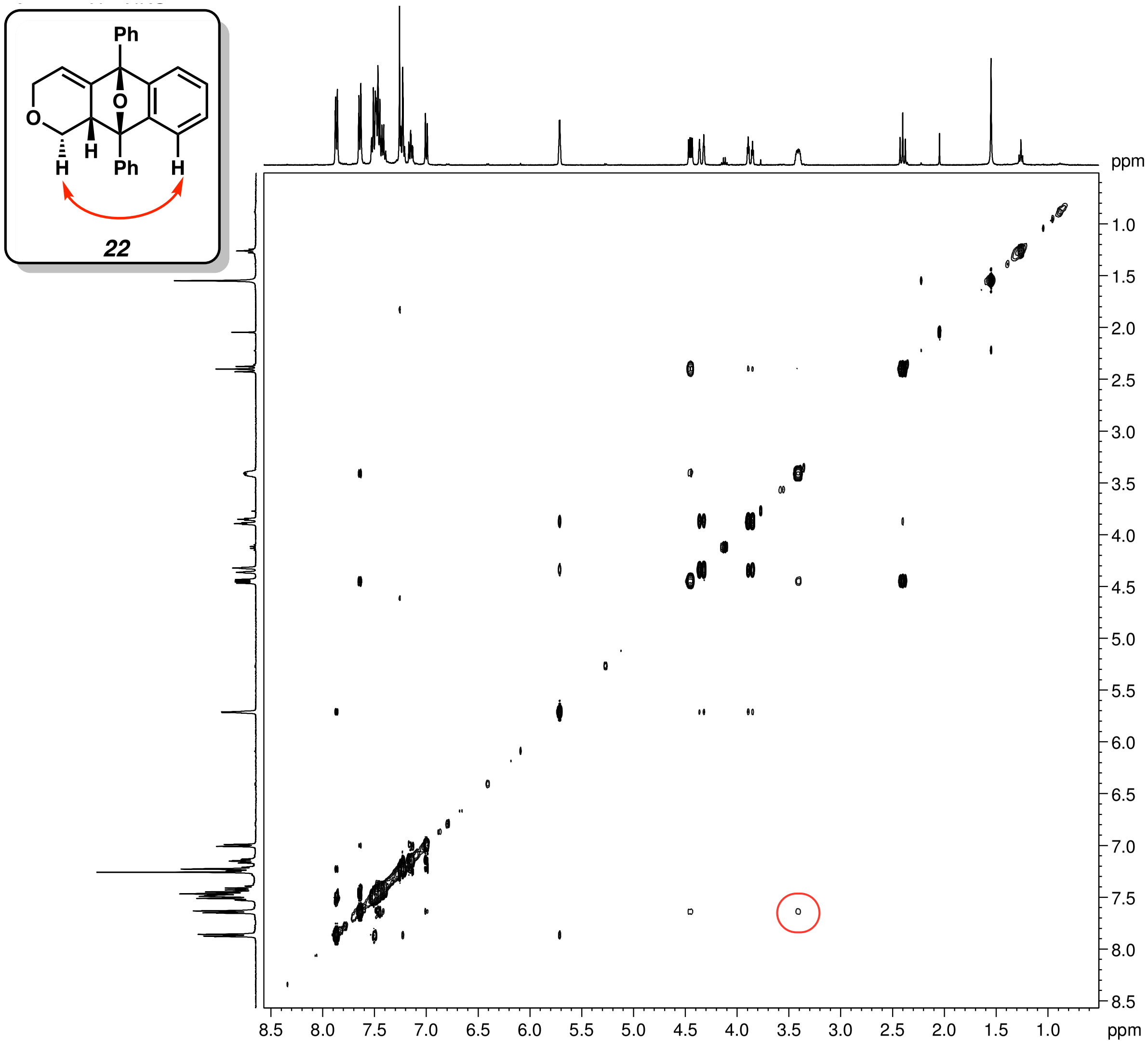
Purified product 13C NMR



Current Data Parameters
NAME RRK-2018-021 2D
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180204
Time 11.25 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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```
Current Data Parameters
NAME       RRK-2018-021
EXPNO              52
PROCNO              1

F2 - Acquisition Parameters
Date_        20180204
Time            11.52
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG    noesygpphpp
TD              2048
SOLVENT         CDCl3
NS                 2
DS                 8
SWH         3225.806 Hz
FIDRES      1.575101 Hz
AQ         0.3174400 sec
RG            137.18
DW           155.000 usec
DE             6.50 usec
TE            298.1 K
D0        0.00013590 sec
D1        2.00000000 sec
D8        0.75000000 sec
D11       0.03000000 sec
D12       0.00002000 sec
D16       0.00020000 sec
IN0       0.00031000 sec

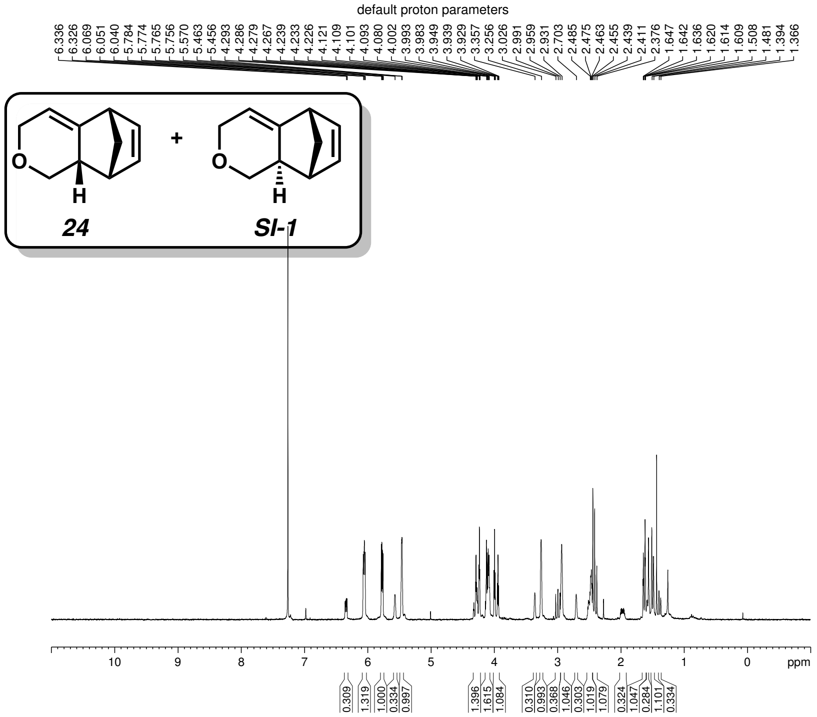
======== CHANNEL f1 ======
SFO1      400.1318344 MHz
NUC1               1H
P1              15.00 usec
P2              30.00 usec
P17           2500.00 usec
PLW1      13.00000000 W
PLW10      4.32690001 W

====== GRADIENT CHANNEL
GPNAM[1]     SMSQ10.100
GPZ1            40.00 %
P16           1000.00 usec

F1 - Acquisition parameters
TD                256
SFO1        400.1318 MHz
FIDRES     25.201612 Hz
SW             8.062 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI               1024
SF        400.1300184 MHz
WDW             QSINE
SSB                2
LB       0 Hz
GB       0
PC              1.00

F1 - Processing parameters
SI               1024
MC2         States-TPPI
SF        400.1300184 MHz
WDW             QSINE
SSB                2
LB       0 Hz
GB       0
```

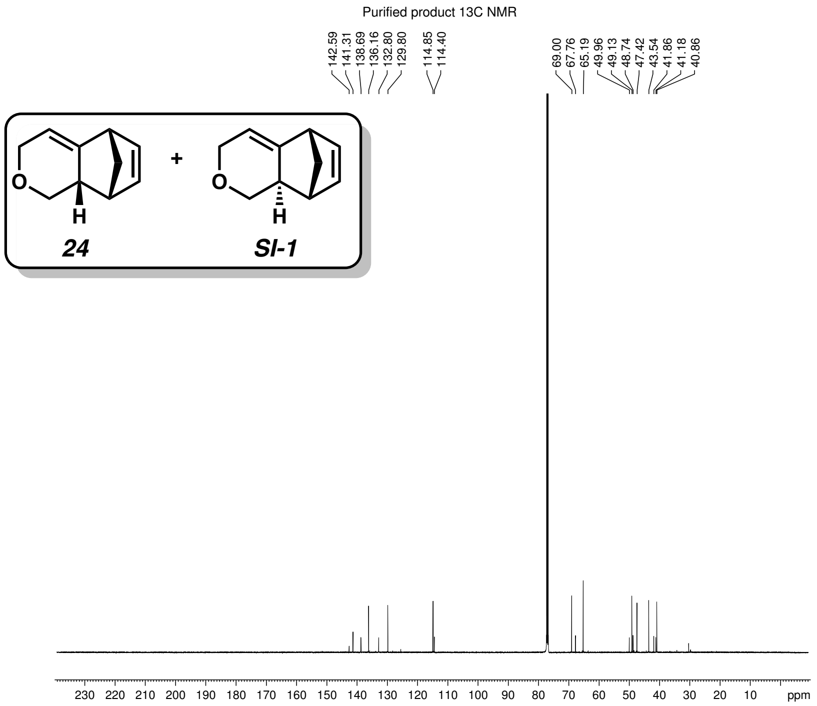


```
Current Data Parameters
NAME     MY-2018-272a-p-b2-1
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20181016
Time            15.34
INSTRUM         av300
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  8
DS                  0
SWH          5995.204 Hz
FIDRES       0.091480 Hz
AQ          5.4657025 sec
RG              812.7
DW             83.400 usec
DE               6.00 usec
TE              298.8 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 =====
NUC1               1H
P1              16.00 usec
PL1      0 dB
PL1W       9.31909847 W
SFO1     300.1318008 MHz

F2 - Processing parameters
SI              65536
SF        300.1300123 MHz
WDW                EM
SSB    0
LB               0.30 Hz
GB     0
PC               1.40
```

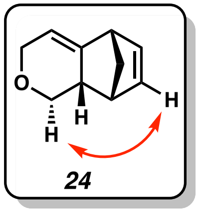


```
Current Data Parameters
NAME     MY-2018-272a-p-che
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20181028
Time          11.42 h
INSTRUM         av500
PROBHD   Z119248_0002 (
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                160
DS                  2
SWH         31250.000 Hz
FIDRES       0.953674 Hz
AQ          1.0485760 sec
RG             204.54
DW             16.000 usec
DE              18.00 usec
TE              298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec
PLW1      23.00000000 W
SFO2      500.1330008 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.13500001 W

F2 - Processing parameters
SI             131072
SF        125.7577892 MHz
WDW                EM
SSB    0
LB               1.00 Hz
GB     0
PC               1.40
```

NOESY



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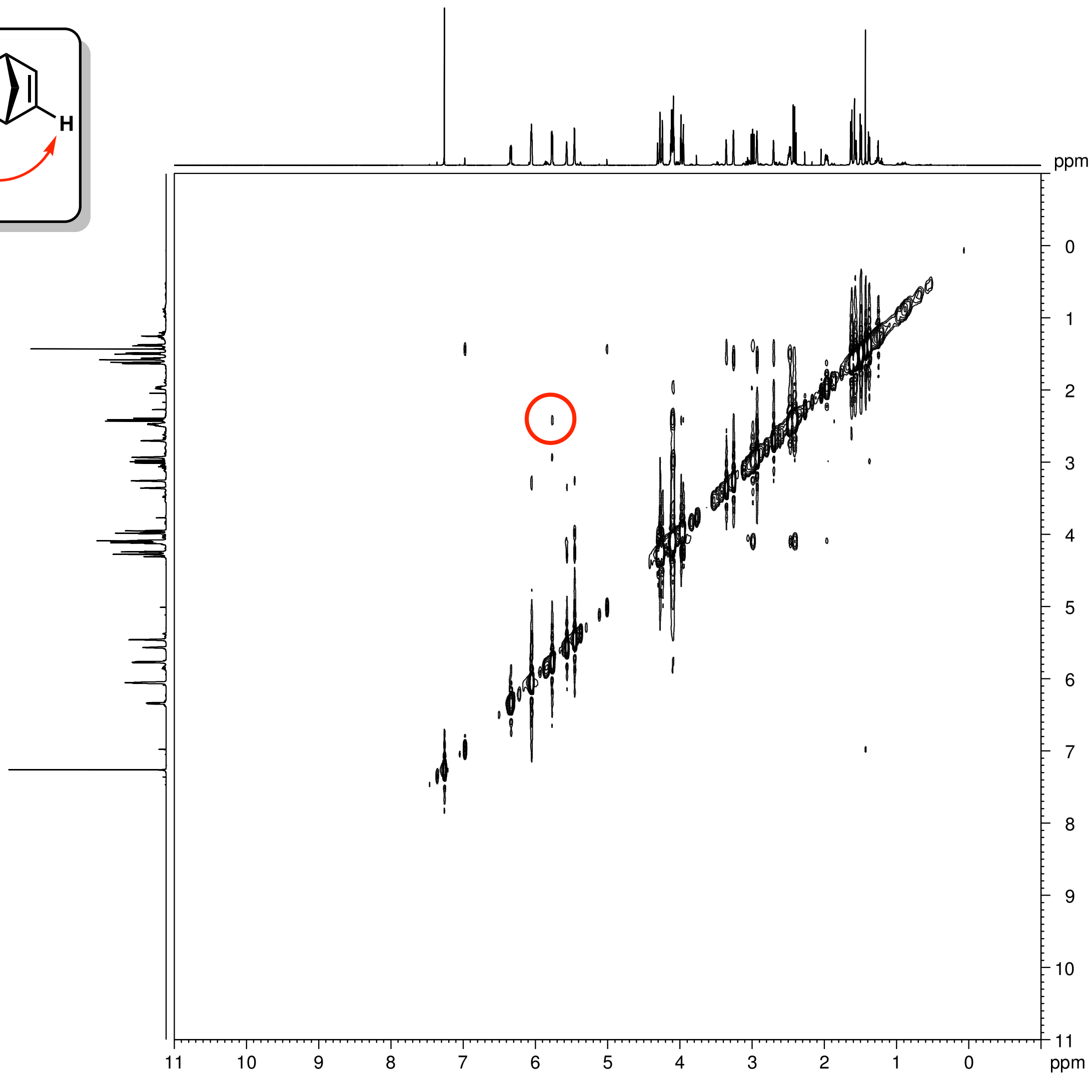


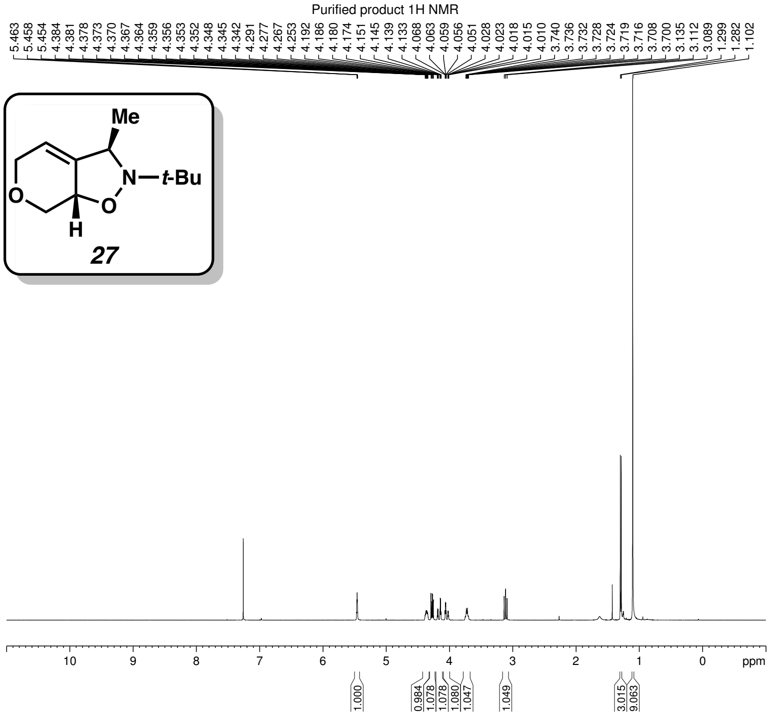
```
Current Data Parameters
NAME      MY-2018-030a-p-ba-nc
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_          20180207
Time             15.59 h
INSTRUM           av500
PROBHD   Z119248_0002 (
PULPROG        noesygpph
TD               2048
SOLVENT          CDCl3
NS                  2
DS                  8
SWH        10000.000 Hz
FIDRES      9.765625 Hz
AQ         0.1024000 sec
RG              12.14
DW             50.000 usec
DE             10.00 usec
TE              298.0 K
D0         0.00003727 sec
D1         2.00000000 sec
D8         0.75000000 sec
D16        0.00020000 sec
IN0        0.00010000 sec
TDav                1
SFO1     500.1330008 MHz
NUC1               1H
P1             10.00 usec
P2             20.00 usec
PLW1      13.50000000 W
GPNAM[1]      SINE.100
GPZ1           40.00 %
P16          1000.00 usec

F1 - Acquisition parameters
TD                256
SFO1          500.133 MHz
FIDRES      78.125000 Hz
SW             19.995 ppm
FnMODE     States-TPPI

F2 - Processing parameters
SI               2048
SF        500.1300146 MHz
WDW             QSINE
SSB                 2
LB        0 Hz
GB        0
PC               1.40

F1 - Processing parameters
SI               2048
MC2        States-TPPI
SF        500.1300146 MHz
WDW             QSINE
SSB                 2
LB        0 Hz
GB        0
```

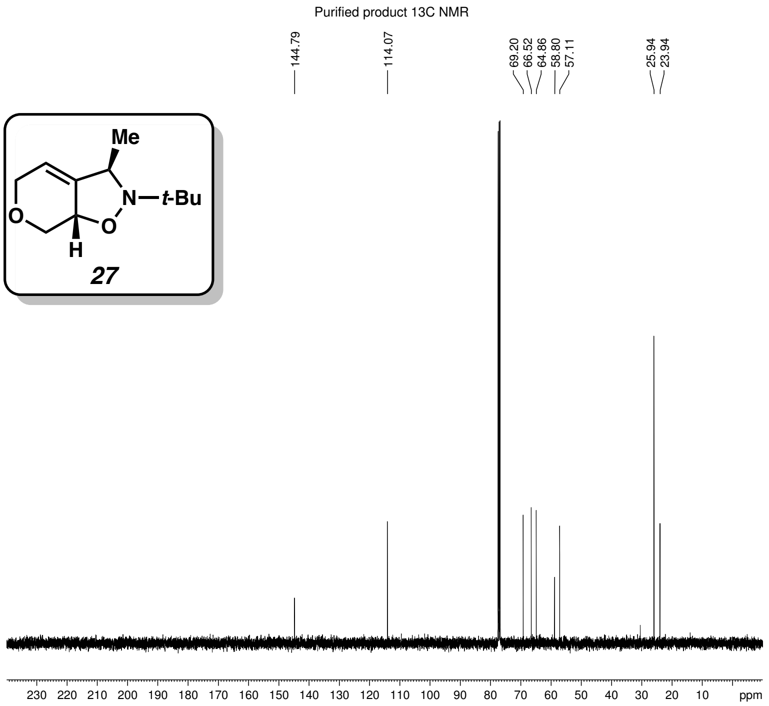


```
Current Data Parameters
NAME     MY-2018-013a-p-char
EXPNO              50
PROCNO              1

F2 - Acquisition Parameters
Date_         20180916
Time             17.58
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               52882
SOLVENT          CDCl3
NS                   8
DS                   0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ         3.2998369 sec
RG              155.85
DW            62.400 usec
DE             6.50 usec
TE             298.3 K
D1       2.00000000 sec
TD0                  1

======== CHANNEL f1 =====
SFO1     400.1324008 MHz
NUC1                1H
P1             15.00 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI               65536
SF       400.1300184 MHz
WDW                 EM
SSB     0
LB             0.30 Hz
GB      0
PC                1.00
```



```
Current Data Parameters
NAME     MY-2018-013a-p-cha
EXPNO              51
PROCNO              1

F2 - Acquisition Parameters
Date_         20180916
Time             18.13
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 256
DS                   0
SWH        25252.525 Hz
FIDRES      0.385323 Hz
AQ         1.2976128 sec
RG              189.85
DW            19.800 usec
DE             6.50 usec
TE             299.1 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                  1

======== CHANNEL f1 =====
SFO1     100.6243395 MHz
NUC1               13C
P1             10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 =====
SFO2     400.1324008 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2          90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W
PLW13      0.29249999 W

F2 - Processing parameters
SI               65536
SF       100.6127557 MHz
WDW                 EM
SSB     0
LB             1.00 Hz
GB      0
PC                1.40
```

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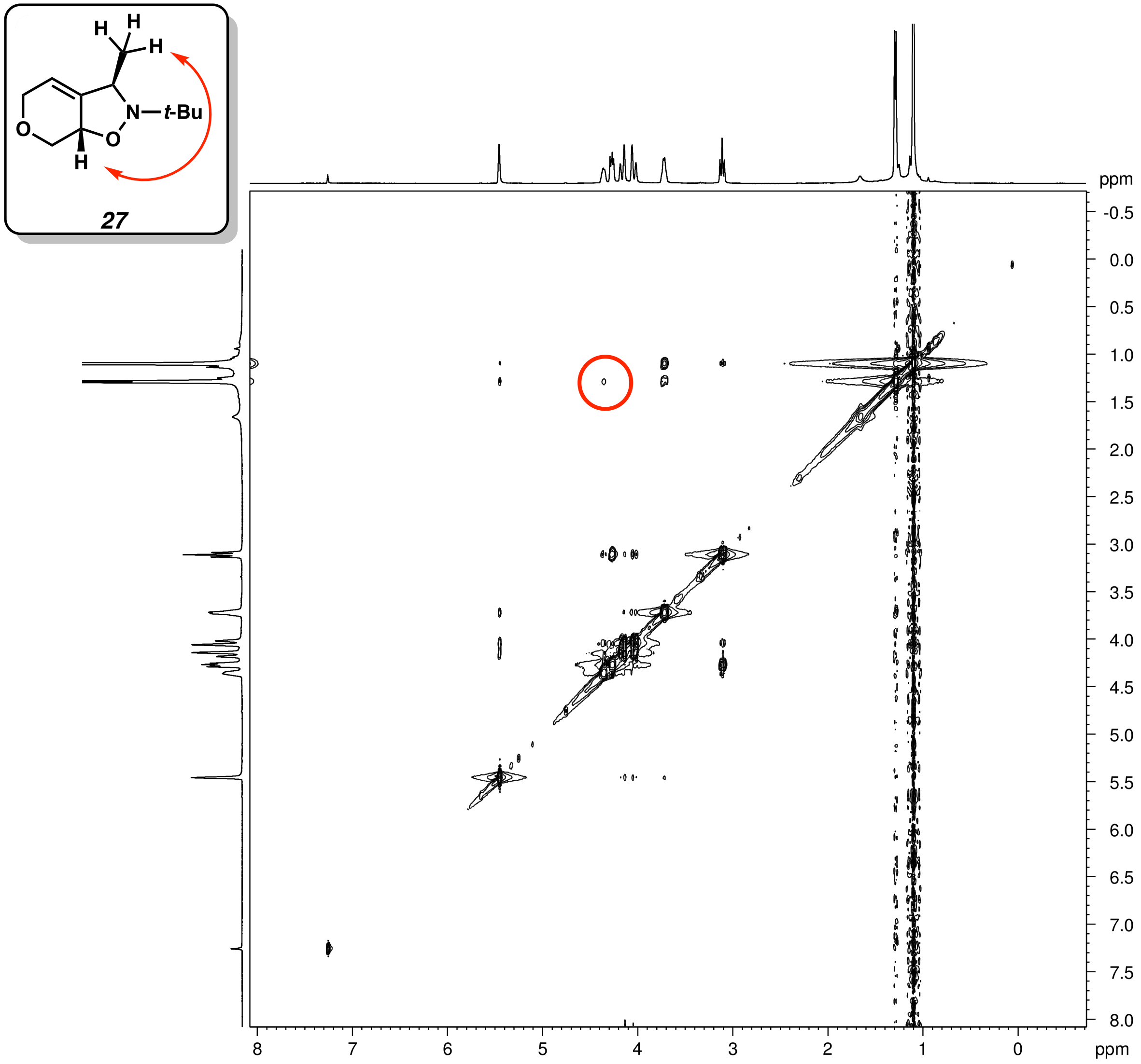

```
Current Data Parameters
NAME     MY-2018-010a-p-b2-nc
EXPNO              12
PROCNO              1

F2 - Acquisition Parameters
Date_         20180111
Time             16.20
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG     noesygpphpp
TD              2048
SOLVENT          CDCl3
NS                 2
DS                 8
SWH          3521.127 Hz
FIDRES       1.719300 Hz
AQ          0.2908160 sec
RG             73.86
DW           142.000 usec
DE             6.50 usec
TE            298.3 K
D0        0.00012290 sec
D1        2.00000000 sec
D8        0.75000000 sec
D11       0.03000000 sec
D12       0.00002000 sec
D16       0.00020000 sec
IN0       0.00028400 sec

======== CHANNEL f1 ======
SFO1      400.1314921 MHz
NUC1               1H
P1              15.00 usec
P2              30.00 usec
P17           2500.00 usec
PLW1      13.00000000 W
PLW10      4.32690001 W

====== GRADIENT CHANNEL
GPNAM[1]     SMSQ10.100
GPZ1            40.00 %
P16           1000.00 usec

F1 - Acquisition parameters
TD                256
SFO1         400.1315 MHz
FIDRES      27.508802 Hz
SW              8.800 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI               1024
SF        400.1300184 MHz
WDW             QSINE
SSB                2
LB       0 Hz
GB       0
PC               1.00

F1 - Processing parameters
SI               1024
MC2         States-TPPI
SF        400.1300184 MHz
WDW             QSINE
SSB                2
LB       0 Hz
GB       0
```

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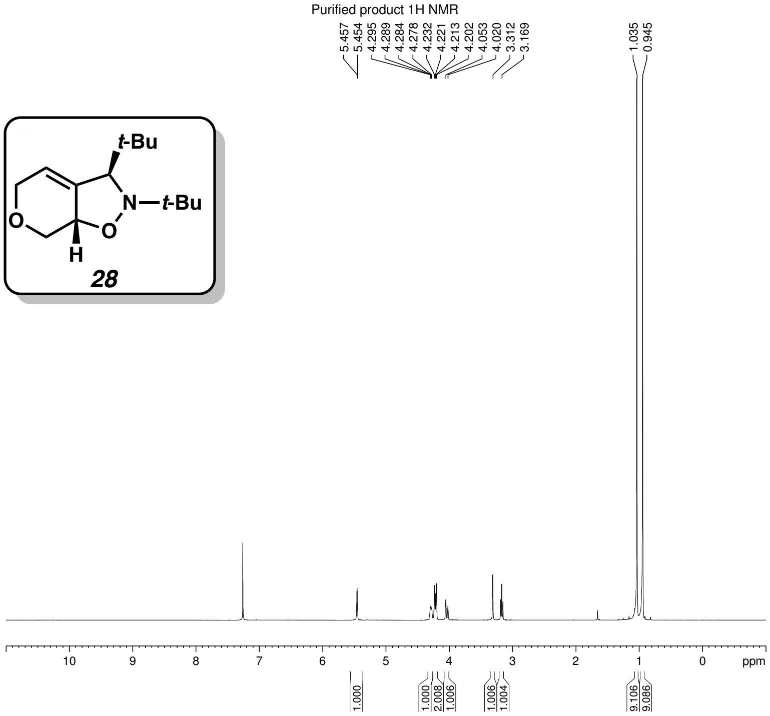

```
Current Data Parameters
NAME       RRK-2018-015
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20180124
Time             17.05
INSTRUM         drx500
PROBHD   5 mm bb-Z Z800
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   0
SWH       10000.000 Hz
FIDRES     0.152588 Hz
AQ       3.2767999 sec
RG                  64
DW          50.000 usec
DE           6.00 usec
TE             297.1 K
D1      2.00000000 sec
TD0                  1

======== CHANNEL f1 =====
NUC1                1H
P1          13.30 usec
PL1     0 dB
SFO1    500.3330020 MHz

F2 - Processing parameters
SI               32768
SF      500.3300220 MHz
WDW                 EM
SSB     0
LB             0.30 Hz
GB      0
PC                1.00
```

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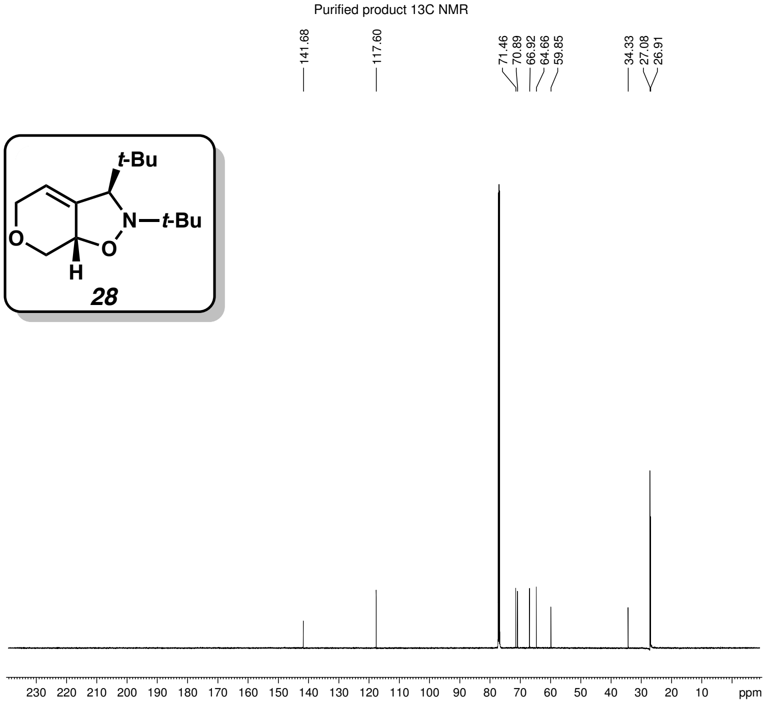
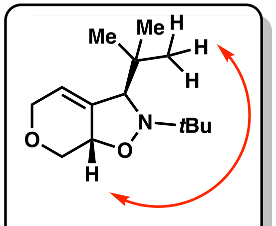


```
Current Data Parameters
NAME       RRK-2018-013
EXPNO              6
PROCNO             1

F2 - Acquisition Parameters
Date_         20180123
Time            18.46 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG        zgpg30
TD               65536
SOLVENT          CDCl3
NS                 100
DS                   2
SWH       31250.000 Hz
FIDRES     0.953674 Hz
AQ       1.0485760 sec
RG              204.54
DW          16.000 usec
DE           18.00 usec
TE             298.0 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0                  1
SFO1    125.7722511 MHz
NUC1               13C
P1          10.50 usec
PLW1    23.00000000 W
SFO2    500.1330008 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2       80.00 usec
PLW2    13.50000000 W
PLW12    0.21094000 W
PLW13    0.10610000 W

F2 - Processing parameters
SI              131072
SF      125.7577892 MHz
WDW                 EM
SSB     0
LB             1.00 Hz
GB      0
PC                1.40
```



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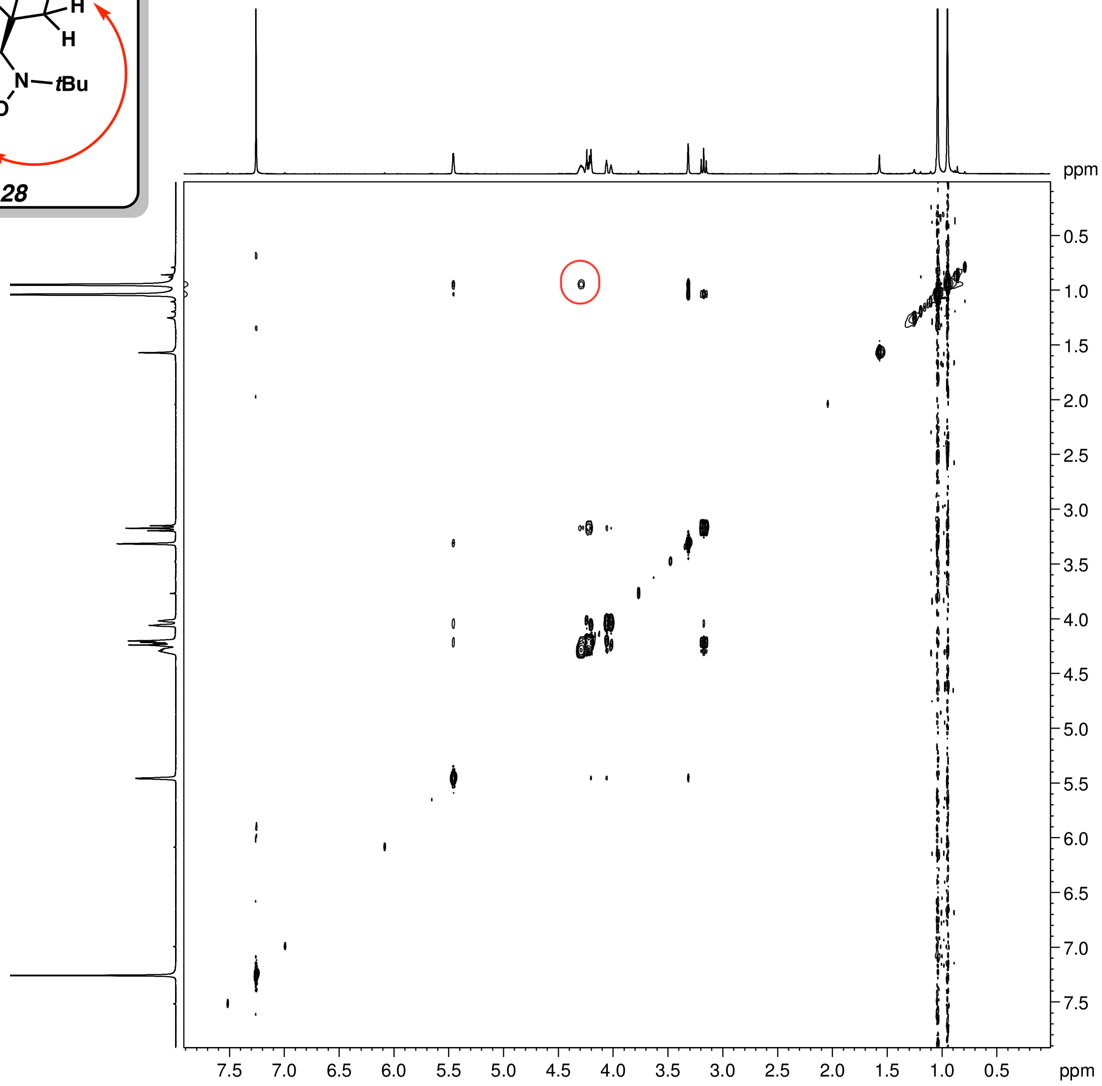


```
Current Data Parameters
NAME        RRK-2018-013
EXPNO              162
PROCNO               1

F2 - Acquisition Parameters
Date_          20180123
Time              12.43
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG     noesygpphpp
TD                 2048
SOLVENT           CDCl3
NS                    2
DS                    8
SWH          3164.557 Hz
FIDRES       1.545194 Hz
AQ         0.3235840 sec
RG               107.83
DW           158.000 usec
DE              6.50 usec
TE              298.1 K
D0       0.00013890 sec
D1       2.00000000 sec
D8       0.75000000 sec
D11      0.03000000 sec
D12      0.00002000 sec
D16      0.00020000 sec
IN0      0.00031600 sec

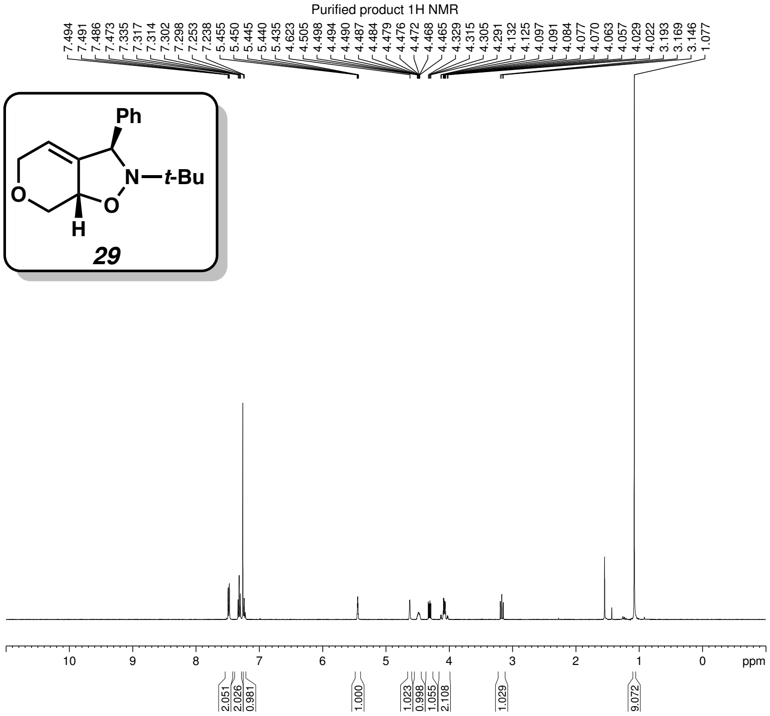
======== CHANNEL f1 ======
SFO1      400.1316045 MHz
NUC1                  1H
P1              15.00 usec
P2              30.00 usec
P17           2500.00 usec
PLW1       13.00000000 W
PLW10       4.32690001 W

====== GRADIENT CHANNEL
GPNAM[1]     SMSQ10.100
GPZ1            40.00 %
P16           1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1        400.1316 MHz
FIDRES     24.723101 Hz
SW            7.909 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                 1024
SF       400.1300184 MHz
WDW               QSINE
SSB                   2
LB       0 Hz
GB       0
PC                 1.00

F1 - Processing parameters
SI                 1024
MC2         States-TPPI
SF       400.1300184 MHz
WDW               QSINE
SSB                   2
LB       0 Hz
GB       0
```

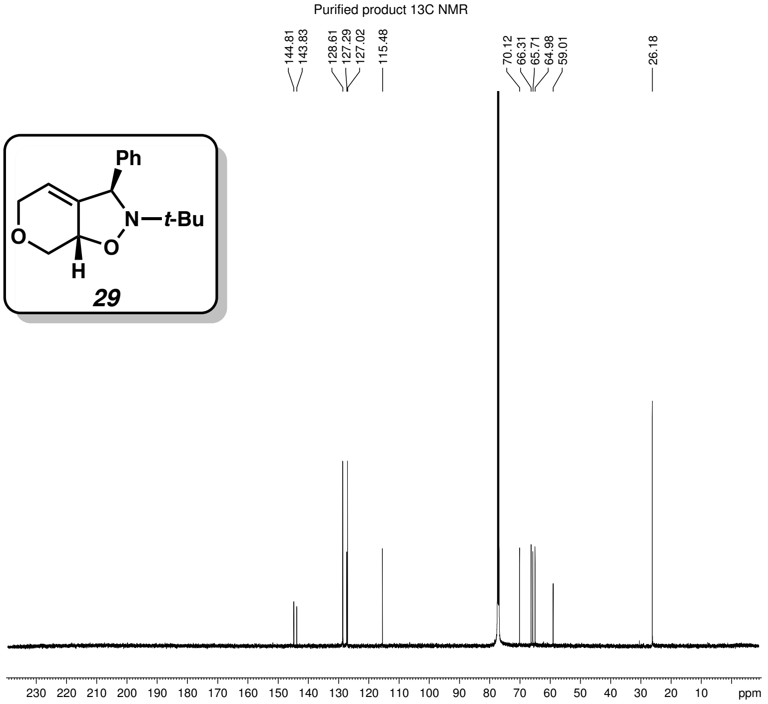


```
Current Data Parameters
NAME     MY-2018-001a-p-char
EXPNO              40
PROCNO              1

F2 - Acquisition Parameters
Date_          20180916
Time              17.37
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                52882
SOLVENT           CDCl3
NS                    4
DS                    0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ        3.2998369 sec
RG               189.85
DW           62.400 usec
DE             6.50 usec
TE              298.2 K
D1       2.00000000 sec
TD0                   1

======== CHANNEL f1 =====
SFO1     400.1324008 MHz
NUC1                 1H
P1          15.00 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI                65536
SF       400.1300177 MHz
WDW                  EM
SSB      0
LB              0.30 Hz
GB       0
PC                 1.00
```

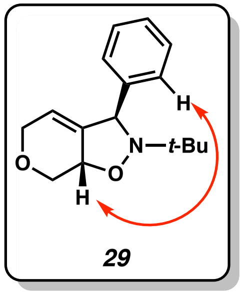


```
Current Data Parameters
NAME     MY-2018-001-13c
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_          20181023
Time            13.59 h
INSTRUM           av500
PROBHD   Z119248_0002 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  160
DS                    2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ        1.0485760 sec
RG               204.54
DW           16.000 usec
DE            18.00 usec
TE              298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                   1
SFO1     125.7722511 MHz
NUC1                13C
P1          10.50 usec
PLW1      23.00000000 W
SFO2     500.1330008 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2        80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.10610000 W

F2 - Processing parameters
SI               131072
SF       125.7577721 MHz
WDW                  EM
SSB      0
LB              1.00 Hz
GB       0
PC                 1.40
```

NOESY



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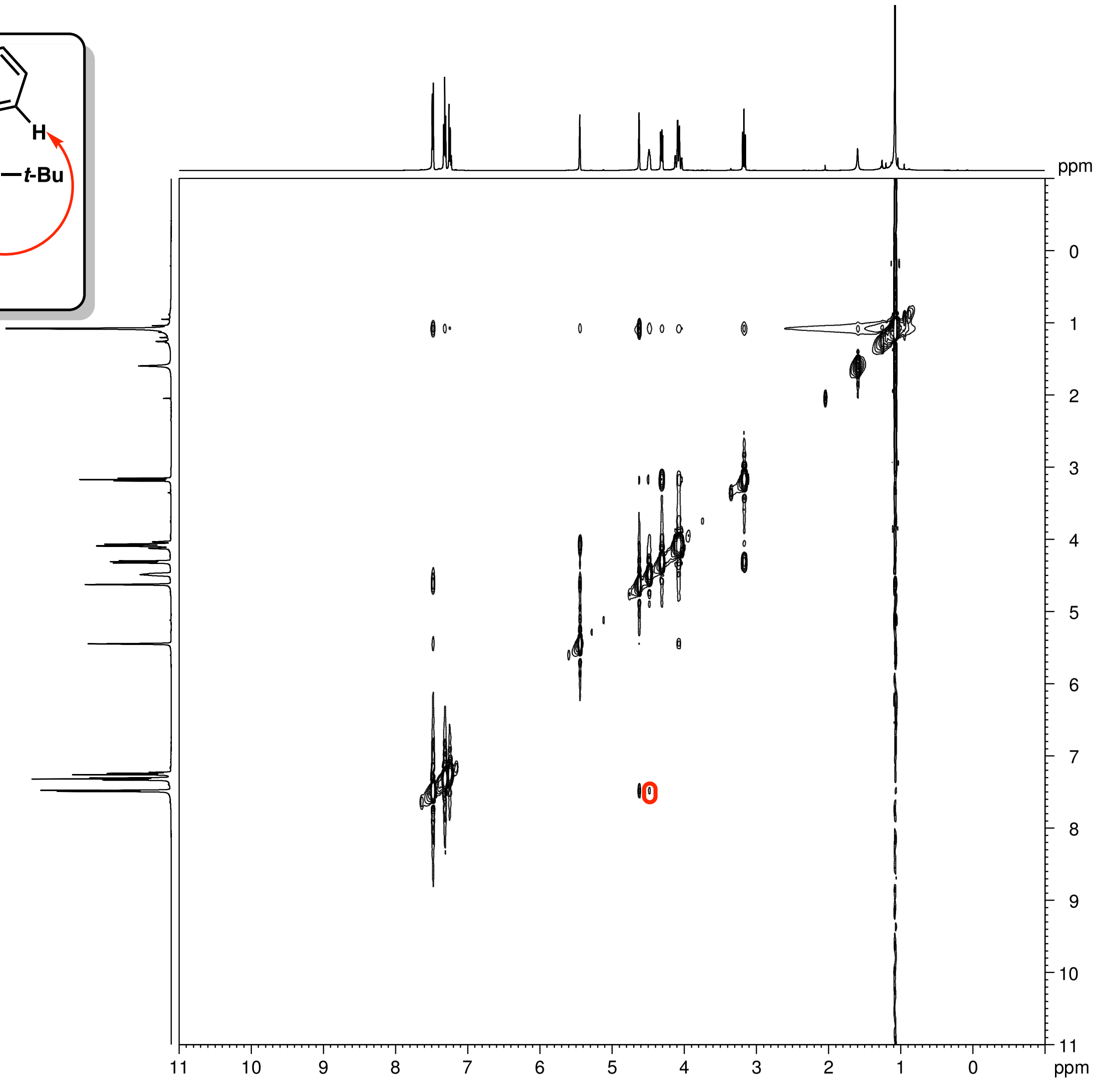


Current Data Parameters

NAME	MY-2017-017a-p-b1-N
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20171003
Time	18.35 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	noesygpph
TD	2048
SOLVENT	CDCl3
NS	2
DS	8
SWH	10000.000 Hz
FIDRES	9.765625 Hz
AQ	0.1024000 sec
RG	12.14
DW	50.000 usec
DE	10.00 usec
TE	298.0 K
D0	0.00003727 sec
D1	2.00000000 sec
D8	0.75000000 sec
D16	0.00020000 sec
IN0	0.00010000 sec
TDav	1
SFO1	500.1330008 MHz
NUC1	1H
P1	10.00 usec
P2	20.00 usec
PLW1	13.50000000 W
GPNAM[1]	SINE.100
GPZ1	40.00 %
P16	1000.00 usec

F1 - Acquisition parameters

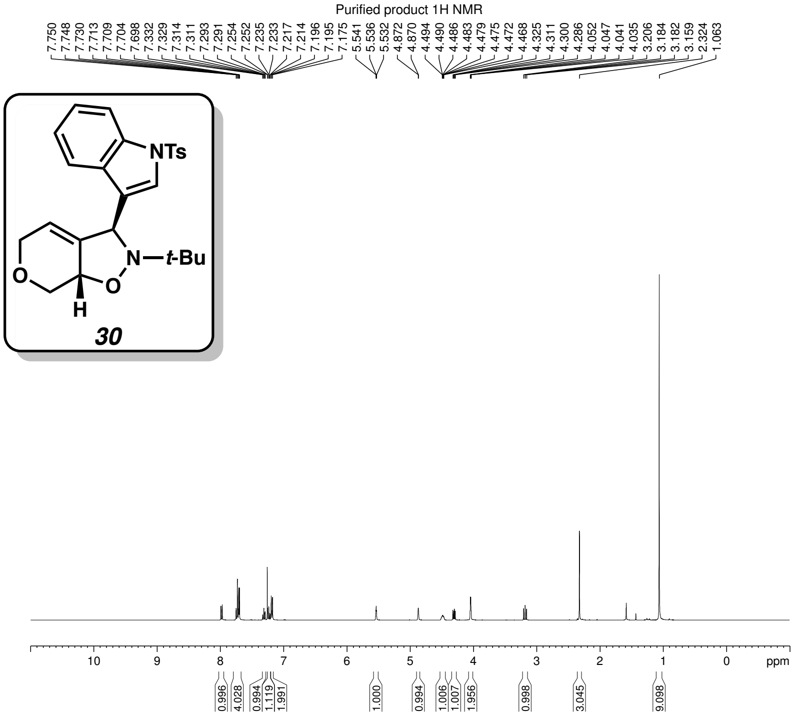
TD	256
SFO1	500.133 MHz
FIDRES	78.125000 Hz
SW	19.995 ppm
FnMODE	States-TPPI

F2 - Processing parameters

SI	2048
SF	500.1300146 MHz
WDW	QSINE
SSB	2
LB	0 Hz
GB	0
PC	1.40

F1 - Processing parameters

SI	2048
MC2	States-TPPI
SF	500.1300146 MHz
WDW	QSINE
SSB	2
LB	0 Hz
GB	0

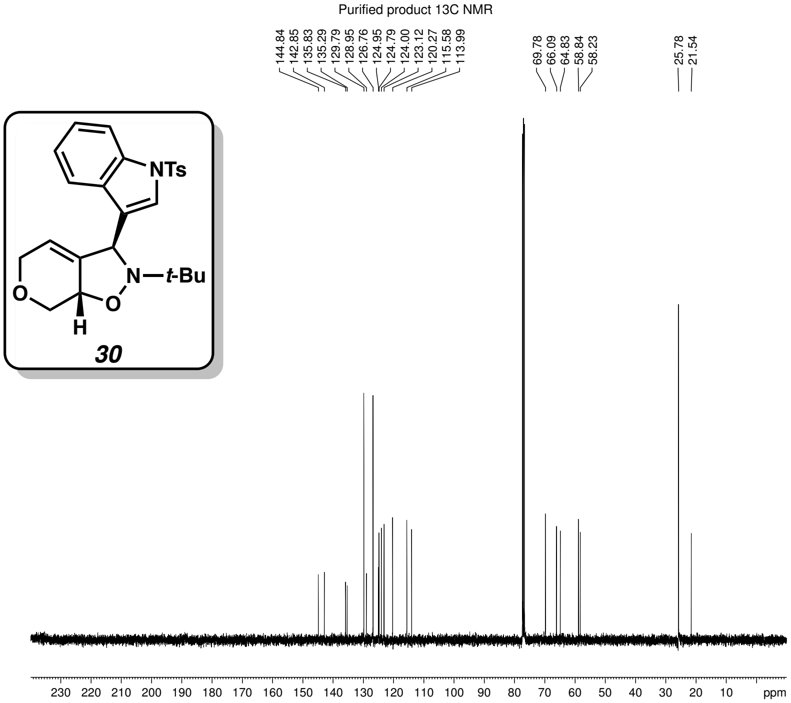


```
Current Data Parameters
NAME     MY-2017-073a-p-char
EXPNO              20
PROCNO              1

F2 - Acquisition Parameters
Date_        20180822
Time            10.52
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              52882
SOLVENT         CDCl3
NS                  4
DS                  0
SWH          8012.820 Hz
FIDRES       0.151523 Hz
AQ          3.2998369 sec
RG             155.85
DW             62.400 usec
DE               6.50 usec
TE              298.6 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1               1H
P1              15.00 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI              65536
SF        400.1300184 MHz
WDW                EM
SSB     0
LB               0.30 Hz
GB      0
PC               1.00
```



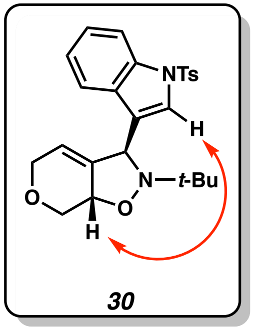
```
Current Data Parameters
NAME     MY-2017-073a-p-cha
EXPNO              21
PROCNO              1

F2 - Acquisition Parameters
Date_        20180822
Time            11.07
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                256
DS                  0
SWH         25252.525 Hz
FIDRES       0.385323 Hz
AQ          1.2976128 sec
RG             189.85
DW             19.800 usec
DE               6.50 usec
TE              299.4 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

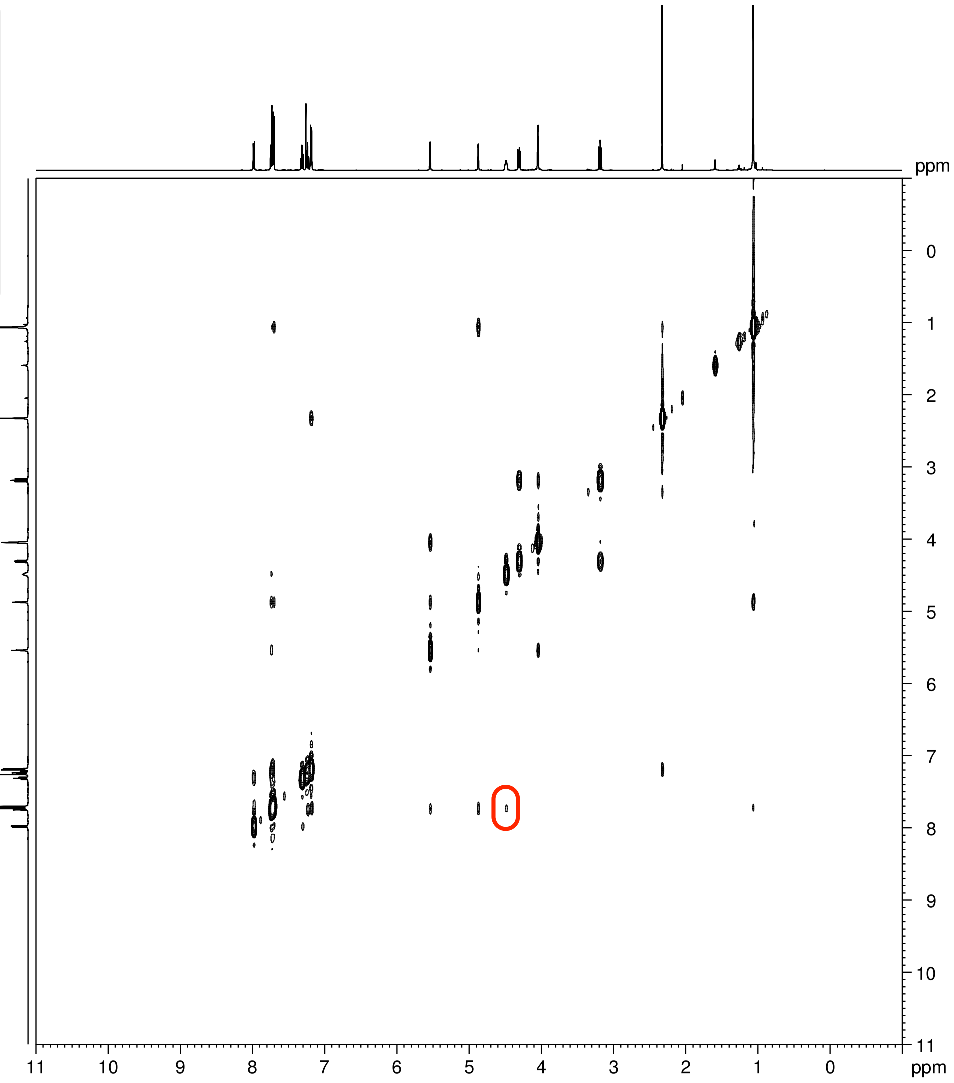
======== CHANNEL f1 =====
SFO1      100.6243395 MHz
NUC1              13C
P1              10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 =====
SFO2      400.1324008 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W
PLW13      0.29249999 W

F2 - Processing parameters
SI              65536
SF        100.6127701 MHz
WDW                EM
SSB     0
LB               1.00 Hz
GB      0
PC               1.40
```



30



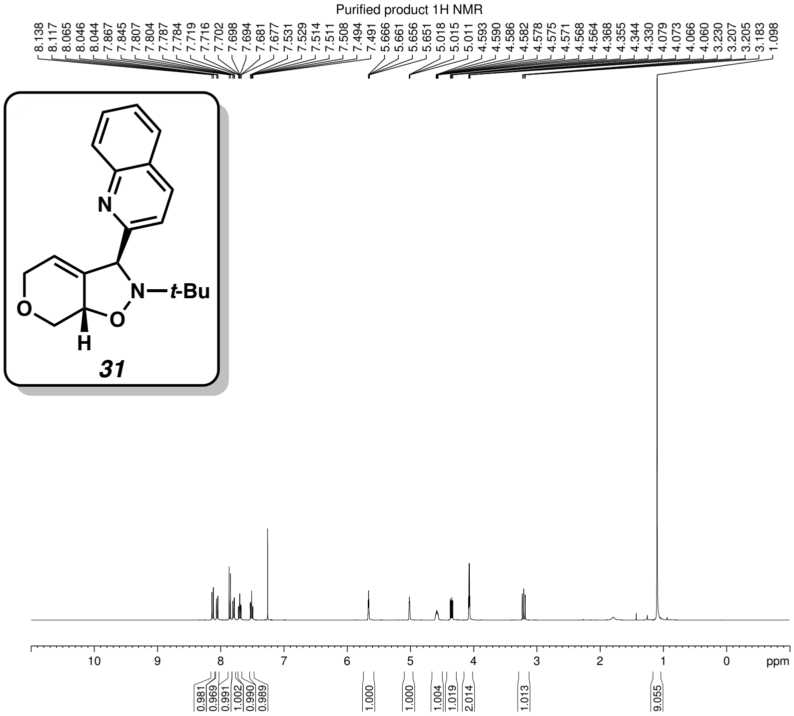
```
Current Data Parameters
NAME      MY-2017-021a-p-b1-nc
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_          20171005
Time             18.05 h
INSTRUM           av500
PROBHD   Z119248_0002 (
PULPROG       noesygpph
TD               2048
SOLVENT           CDCl3
NS                  2
DS                  8
SWH         10000.000 Hz
FIDRES       9.765625 Hz
AQ         0.1024000 sec
RG              12.14
DW             50.000 usec
DE              10.00 usec
TE              298.0 K
D0         0.00003727 sec
D1         2.00000000 sec
D8         0.75000000 sec
D16        0.00020000 sec
IN0        0.00010000 sec
TDav                1
SFO1     500.1330008 MHz
NUC1               1H
P1              10.00 usec
P2              20.00 usec
PLW1      13.50000000 W
GPNAM[1]     SINE.100
GPZ1           40.00 %
P16          1000.00 usec

F1 - Acquisition parameters
TD                256
SFO1          500.133 MHz
FIDRES      78.125000 Hz
SW             19.995 ppm
FnMODE     States-TPPI

F2 - Processing parameters
SI               2048
SF        500.1300146 MHz
WDW             QSINE
SSB                 2
LB           0 Hz
GB           0
PC               1.40

F1 - Processing parameters
SI               2048
MC2        States-TPPI
SF        500.1300146 MHz
WDW             QSINE
SSB                 2
LB           0 Hz
GB           0
```

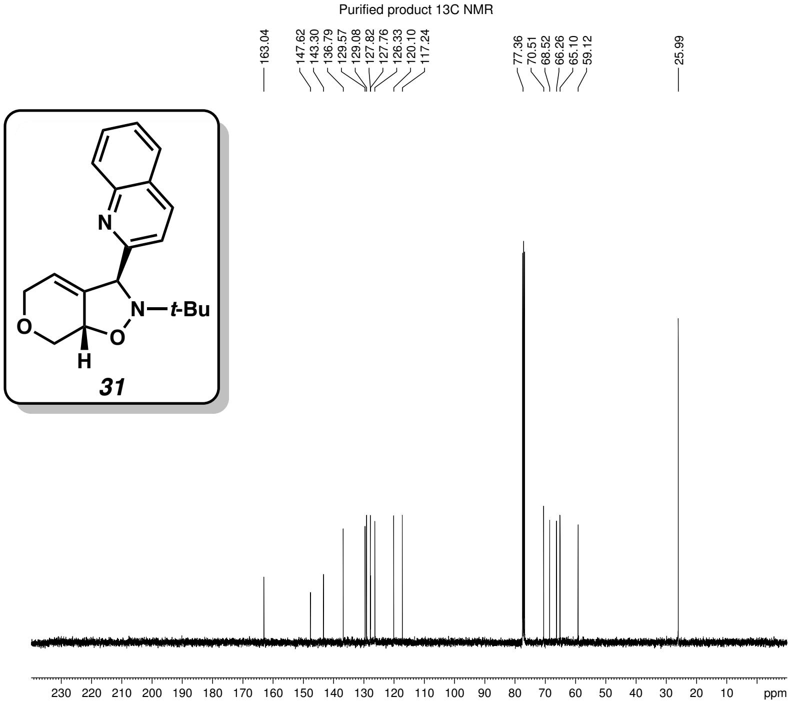


Current Data Parameters
NAME MY-2018-009a-p-char
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180822
Time 10.31
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300184 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



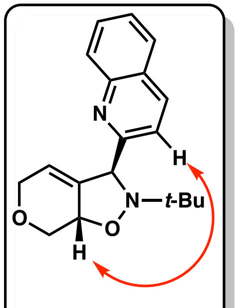
Current Data Parameters
NAME MY-2018-009a-p-cha
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180822
Time 10.47
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 189.85
DW 19.800 usec
DE 6.50 usec
TE 299.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =====
SFO1 100.6243395 MHz
NUC1 13C
P1 10.00 usec
PLW1 52.00000000 W

======== CHANNEL f2 =====
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W
PLW13 0.29249999 W

F2 - Processing parameters
SI 65536
SF 100.6127574 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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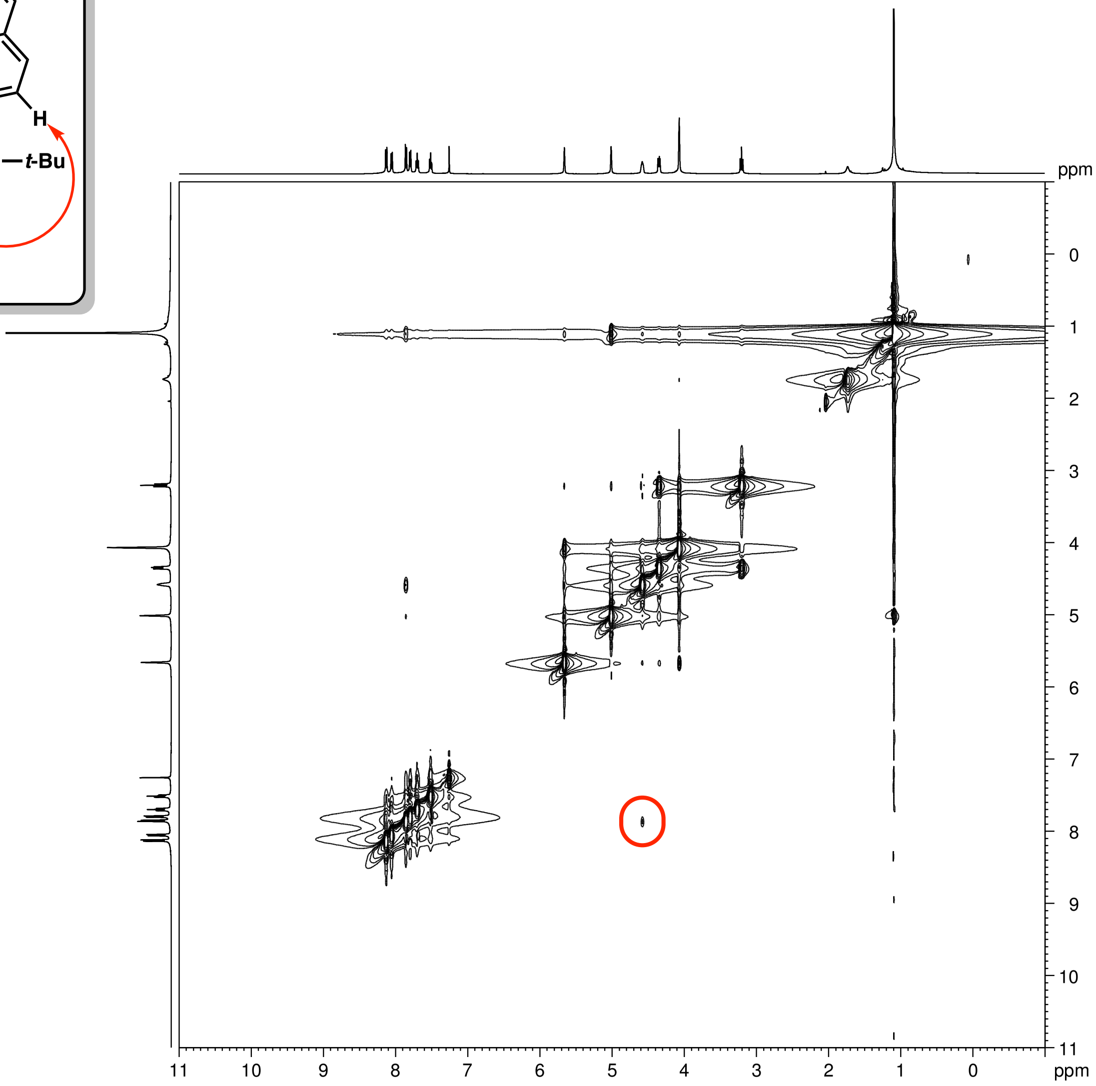


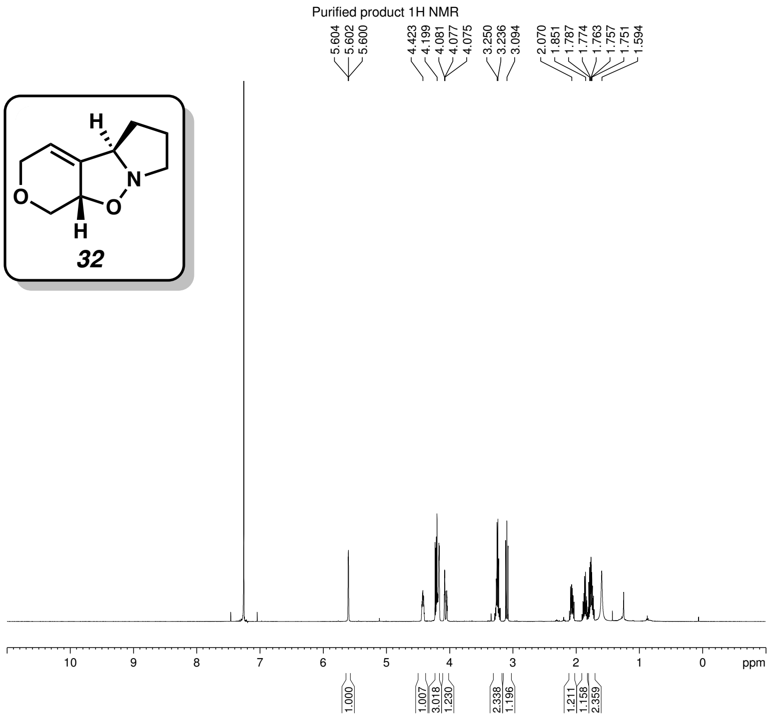
```
Current Data Parameters
NAME     MY-2018-004a-p-b2-2c
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20180107
Time            20.25 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG       noesygpph
TD             2048
SOLVENT           CDCl3
NS                10
DS                 8
SWH         10000.000 Hz
FIDRES       9.765625 Hz
AQ          0.1024000 sec
RG              12.14
DW             50.000 usec
DE             10.00 usec
TE              298.0 K
D0        0.00003727 sec
D1        2.00000000 sec
D8        0.75000000 sec
D16       0.00020000 sec
IN0       0.00010000 sec
TDav               1
SFO1      500.1330008 MHz
NUC1              1H
P1             10.00 usec
P2             20.00 usec
PLW1       13.50000000 W
GPNAM[1]        SINE.100
GPZ1            40.00 %
P16          1000.00 usec

F1 - Acquisition parameters
TD               256
SFO1          500.133 MHz
FIDRES      78.125000 Hz
SW             19.995 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI              2048
SF        500.1300135 MHz
WDW             QSINE
SSB                2
LB       0 Hz
GB       0
PC              1.40

F1 - Processing parameters
SI              2048
MC2         States-TPPI
SF        500.1300135 MHz
WDW             QSINE
SSB                2
LB       0 Hz
GB       0
```



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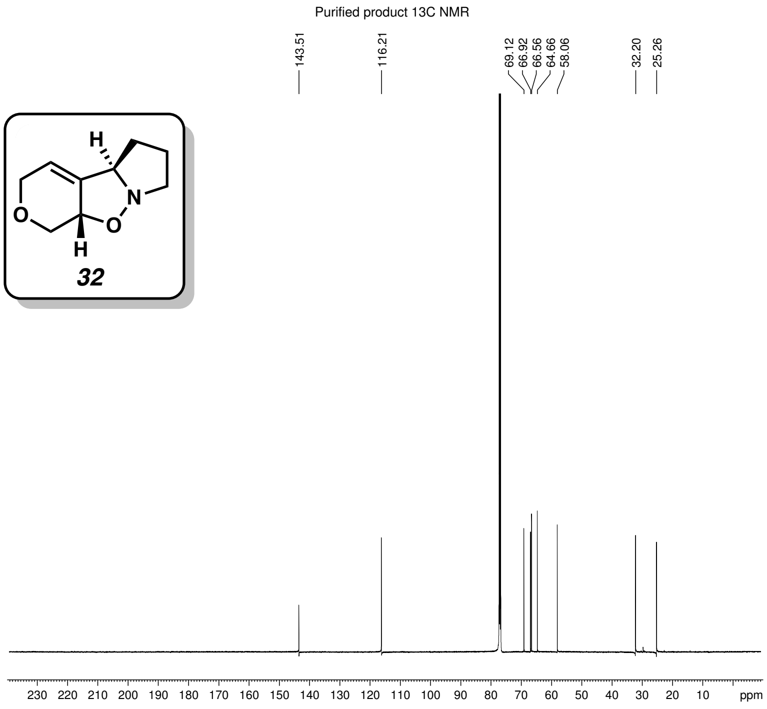
Current Data Parameters
NAME RRK-2018-005 2D
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180109
Time 19.40 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



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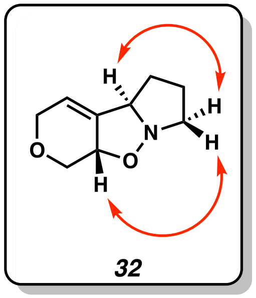
Current Data Parameters
NAME RRK-2018-005 2D
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180110
Time 0.57 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3000
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

NOSEY



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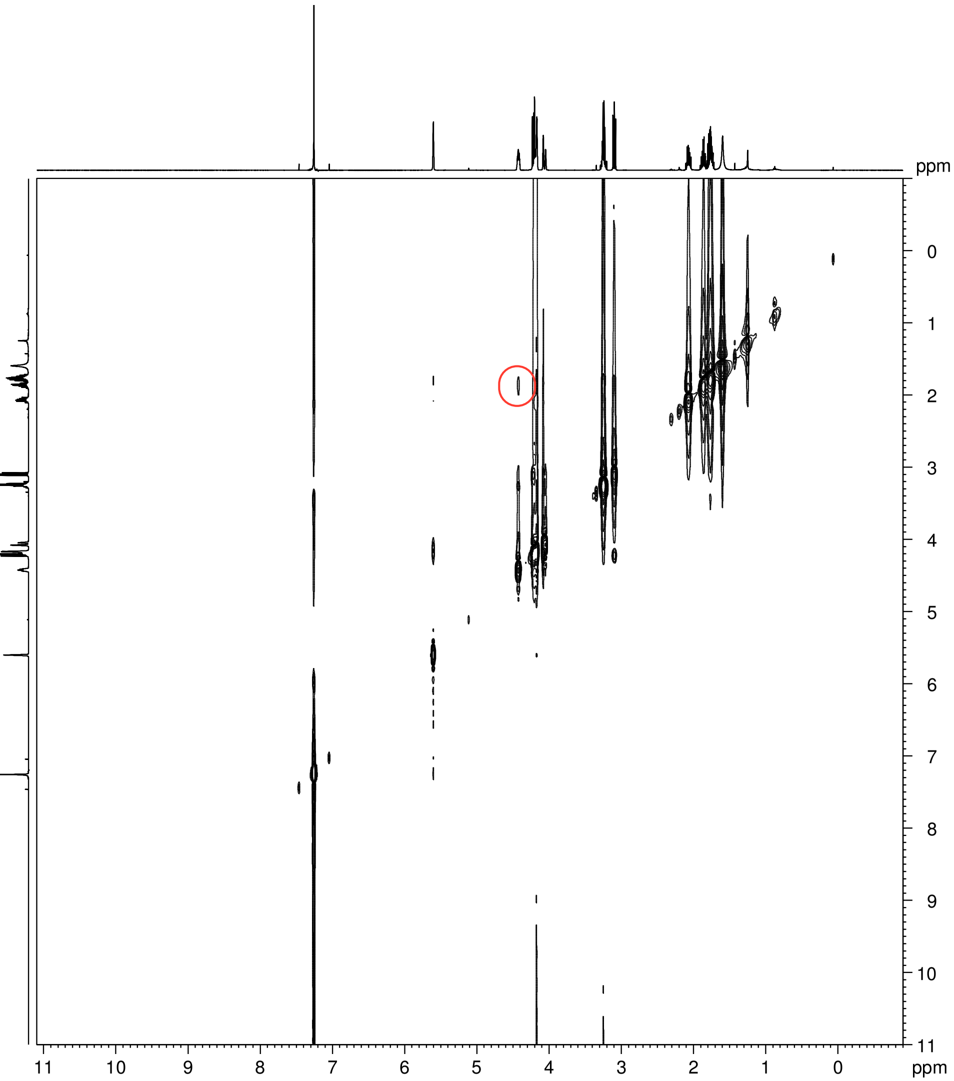


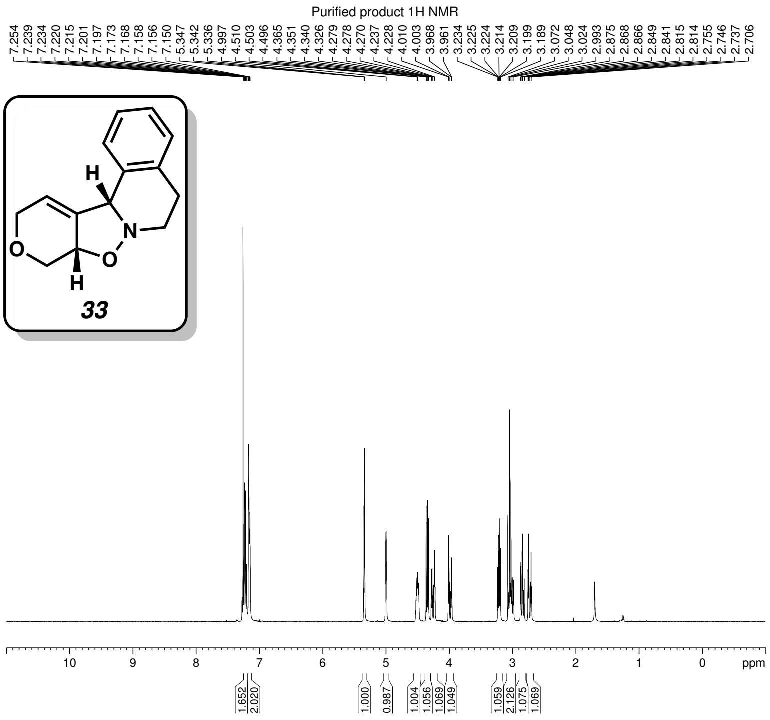
```
Current Data Parameters
NAME     RRK-2018-005 2D
EXPNO              4
PROCNO             1

F2 - Acquisition Parameters
Date_        20180109
Time           19.55 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG      noesygpph
TD             2048
SOLVENT          CDCl3
NS                 6
DS                 8
SWH         10000.000 Hz
FIDRES       9.765625 Hz
AQ          0.1024000 sec
RG             12.14
DW            50.000 usec
DE             10.00 usec
TE             298.0 K
D0        0.00003727 sec
D1        2.00000000 sec
D8        0.75000000 sec
D16       0.00020000 sec
IN0       0.00010000 sec
TDav               1
SFO1      500.1330008 MHz
NUC1              1H
P1             10.00 usec
P2             20.00 usec
PLW1     13.50000000 W
GPNAM[1]     SINE.100
GPZ1           40.00 %
P16          1000.00 usec

F1 - Acquisition parameters
TD              256
SFO1         500.133 MHz
FIDRES    78.125000 Hz
SW           19.995 ppm
FnMODE     States-TPPI

F2 - Processing parameters
SI             2048
SF        500.1300146 MHz
WDW            QSINE
SSB               2
LB        0 Hz
GB        0
PC             1.40

F1 - Processing parameters
SI             2048
MC2       States-TPPI
SF        500.1300146 MHz
WDW            QSINE
SSB               2
LB        0 Hz
GB        0
```

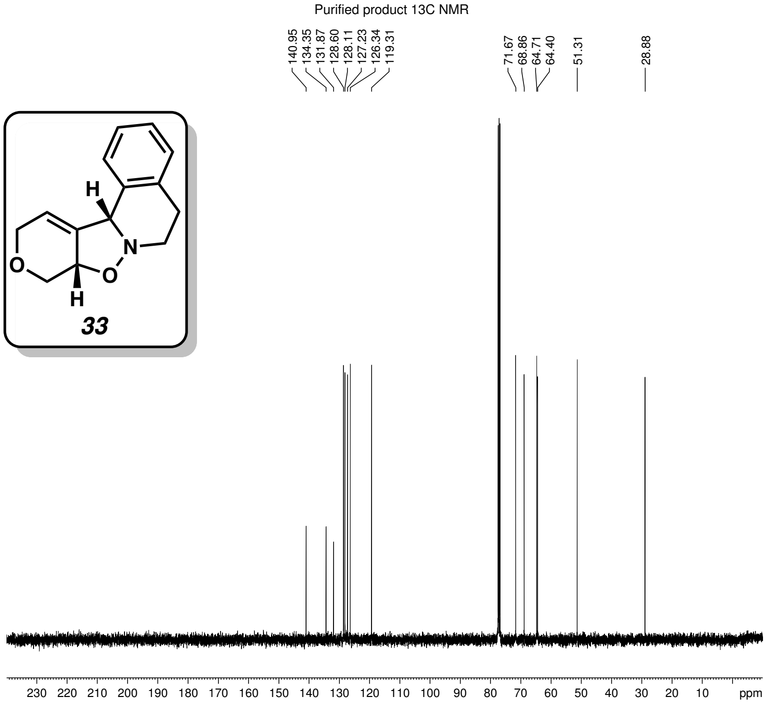


```
Current Data Parameters
NAME     MY-2017-065a-p-char
EXPNO              30
PROCNO              1

F2 - Acquisition Parameters
Date_        20180826
Time            20.33
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              52882
SOLVENT         CDCl3
NS                  8
DS                  0
SWH          8012.820 Hz
FIDRES       0.151523 Hz
AQ          3.2998369 sec
RG             155.85
DW             62.400 usec
DE               6.50 usec
TE              298.6 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1               1H
P1              15.00 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI              65536
SF        400.1300184 MHz
WDW                EM
SSB    0
LB               0.30 Hz
GB     0
PC               1.00
```



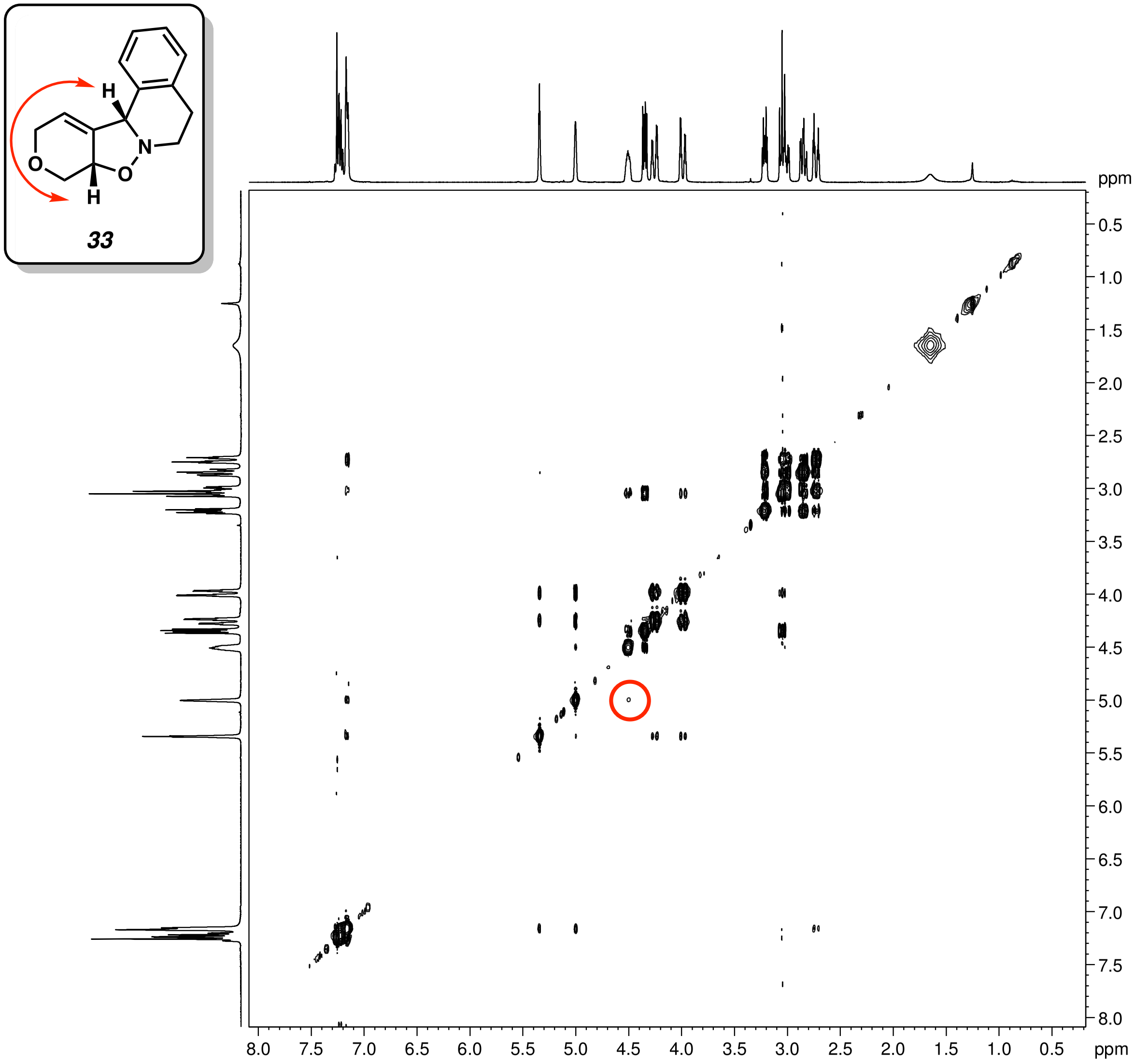
```
Current Data Parameters
NAME     MY-2017-065a-p-cha
EXPNO              31
PROCNO              1

F2 - Acquisition Parameters
Date_        20180826
Time            20.49
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                256
DS                  0
SWH         25252.525 Hz
FIDRES       0.385323 Hz
AQ          1.2976128 sec
RG             189.85
DW             19.800 usec
DE               6.50 usec
TE              299.3 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 =====
SFO1      100.6243395 MHz
NUC1              13C
P1              10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 =====
SFO2      400.1324008 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W
PLW13      0.29249999 W

F2 - Processing parameters
SI              65536
SF        100.6127580 MHz
WDW                EM
SSB    0
LB               1.00 Hz
GB     0
PC               1.40
```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```
Current Data Parameters
NAME     MY-2017-047a-p-b2-2-
EXPNO              12
PROCNO              1

F2 - Acquisition Parameters
Date_        20171026
Time            17.39
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG    noesygpphpp
TD              2048
SOLVENT         CDCl3
NS                 2
DS                 8
SWH         3164.557 Hz
FIDRES      1.545194 Hz
AQ        0.3235840 sec
RG            122.31
DW           158.000 usec
DE             6.50 usec
TE             298.4 K
D0        0.00013890 sec
D1        2.00000000 sec
D8        0.75000000 sec
D11       0.03000000 sec
D12       0.00002000 sec
D16       0.00020000 sec
IN0       0.00031600 sec

======== CHANNEL f1 ======
SFO1      400.1316732 MHz
NUC1               1H
P1             15.00 usec
P2             30.00 usec
P17          2500.00 usec
PLW1     13.00000000 W
PLW10     4.32690001 W

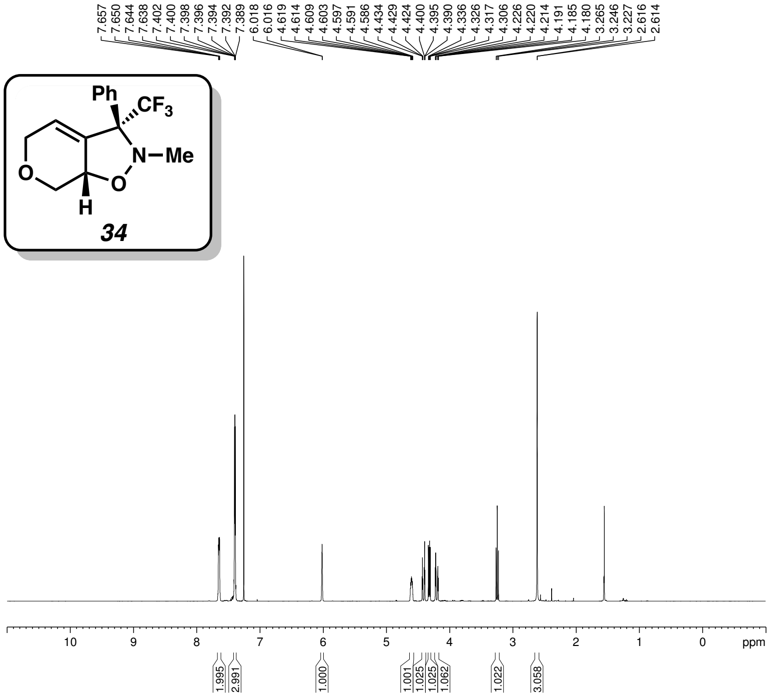
====== GRADIENT CHANNEL
GPNAM[1]     SMSQ10.100
GPZ1            40.00 %
P16          1000.00 usec

F1 - Acquisition parameters
TD                256
SFO1        400.1317 MHz
FIDRES     24.723101 Hz
SW             7.909 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI               1024
SF        400.1300184 MHz
WDW             QSINE
SSB                 2
LB        0 Hz
GB        0
PC               1.00

F1 - Processing parameters
SI               1024
MC2        States-TPPI
SF        400.1300184 MHz
WDW             QSINE
SSB                 2
LB        0 Hz
GB        0
```

Purified product 1H NMR

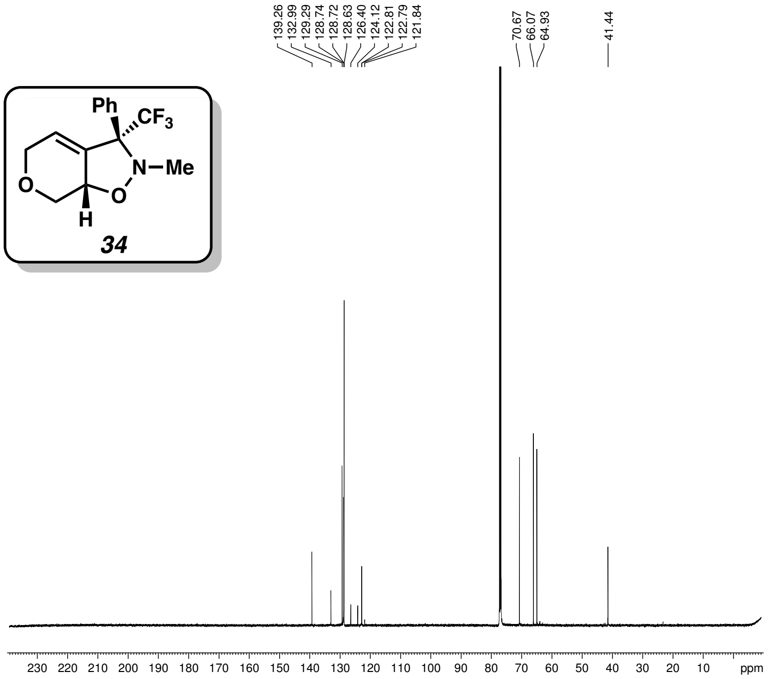


Current Data Parameters
NAME MY-2017-069a-p-char
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180923
Time 18.53 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

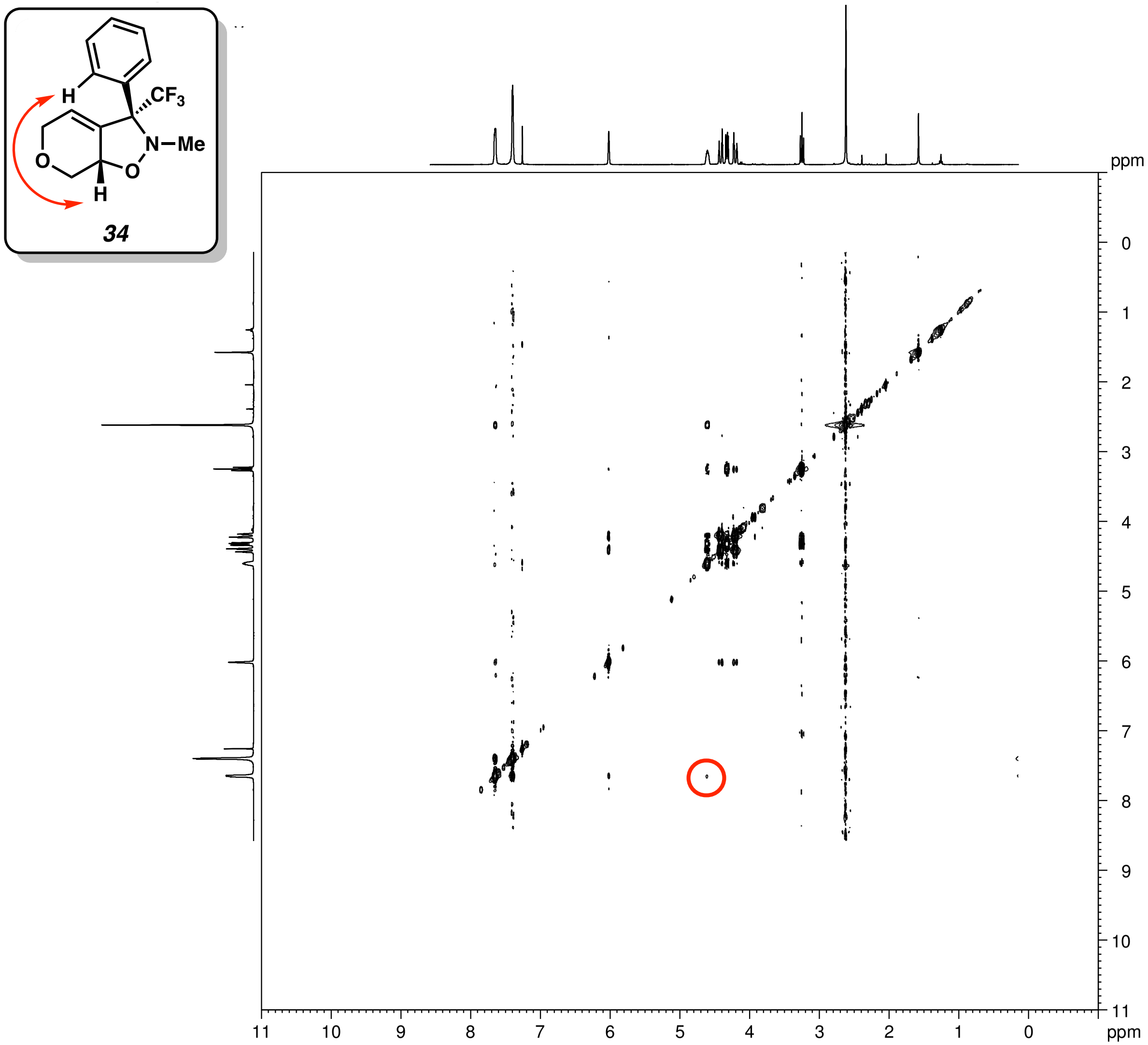
Purified product 13C NMR



Current Data Parameters
NAME MY-2017-069a-p-cha
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180923
Time 19.10 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 264
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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```
Current Data Parameters
NAME       MY-2017-059a-p-b2-N
EXPNO              12
PROCNO              1

F2 - Acquisition Parameters
Date_        20171031
Time            17.20
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG    noesygpphpp
TD              2048
SOLVENT         CDCl3
NS                 2
DS                 8
SWH         3378.378 Hz
FIDRES      1.649599 Hz
AQ        0.3031040 sec
RG              94.6
DW           148.000 usec
DE             6.50 usec
TE             298.1 K
D0        0.00012890 sec
D1        2.00000000 sec
D8        0.75000000 sec
D11       0.03000000 sec
D12       0.00002000 sec
D16       0.00020000 sec
IN0       0.00029600 sec

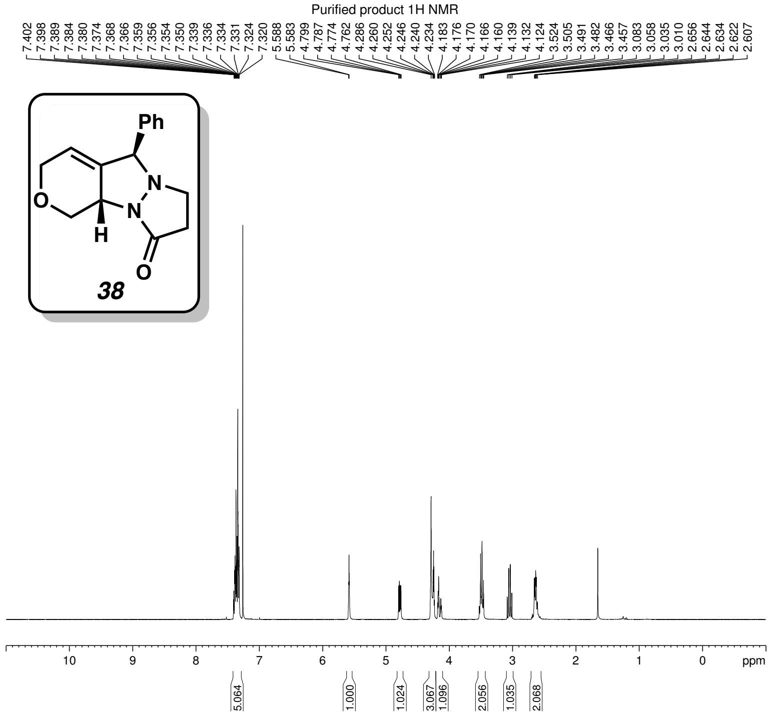
======== CHANNEL f1 ======
SFO1      400.1317619 MHz
NUC1              1H
P1             15.00 usec
P2             30.00 usec
P17          2500.00 usec
PLW1      13.00000000 W
PLW10      4.32690001 W

====== GRADIENT CHANNEL
GPNAM[1]     SMSQ10.100
GPZ1           40.00 %
P16          1000.00 usec

F1 - Acquisition parameters
TD               256
SFO1       400.1318 MHz
FIDRES    26.393581 Hz
SW            8.443 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI              1024
SF        400.1300184 MHz
WDW            QSINE
SSB               2
LB        0 Hz
GB        0
PC              1.00

F1 - Processing parameters
SI              1024
MC2       States-TPPI
SF        400.1300184 MHz
WDW            QSINE
SSB               2
LB        0 Hz
GB        0
```

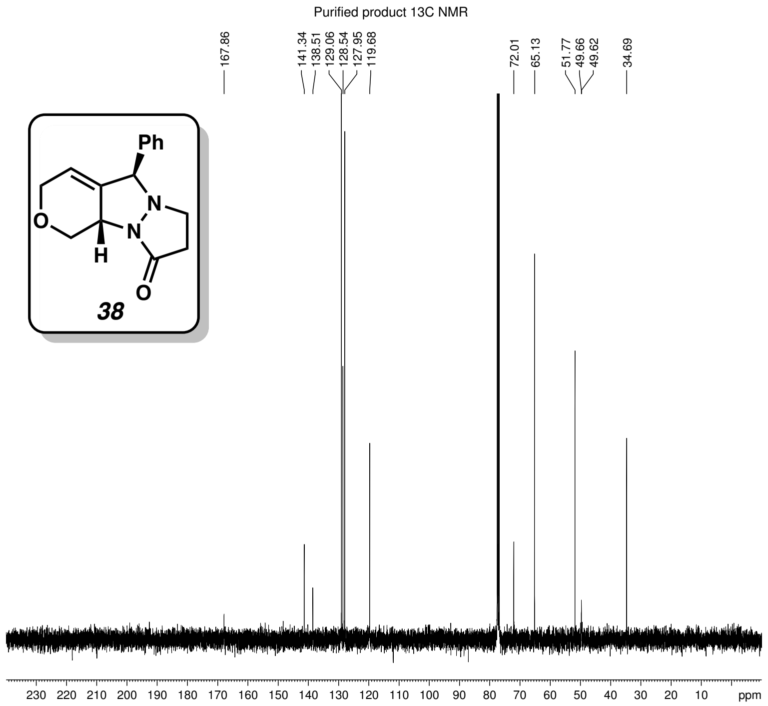


```
Current Data Parameters
NAME      MY-2017-086a-p-char
EXPNO               10
PROCNO               1

F2 - Acquisition Parameters
Date_        20180827
Time            10.49
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              52882
SOLVENT         CDCl3
NS                  8
DS                  0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ         3.2998369 sec
RG             155.85
DW             62.400 usec
DE               6.50 usec
TE              298.5 K
D1        2.00000000 sec
TD0                 1

======== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1                1H
P1              15.00 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI              65536
SF        400.1300177 MHz
WDW                EM
SSB     0
LB               0.30 Hz
GB      0
PC               1.00
```



```
Current Data Parameters
NAME      MY-2017-086a-p-cha
EXPNO               11
PROCNO               1

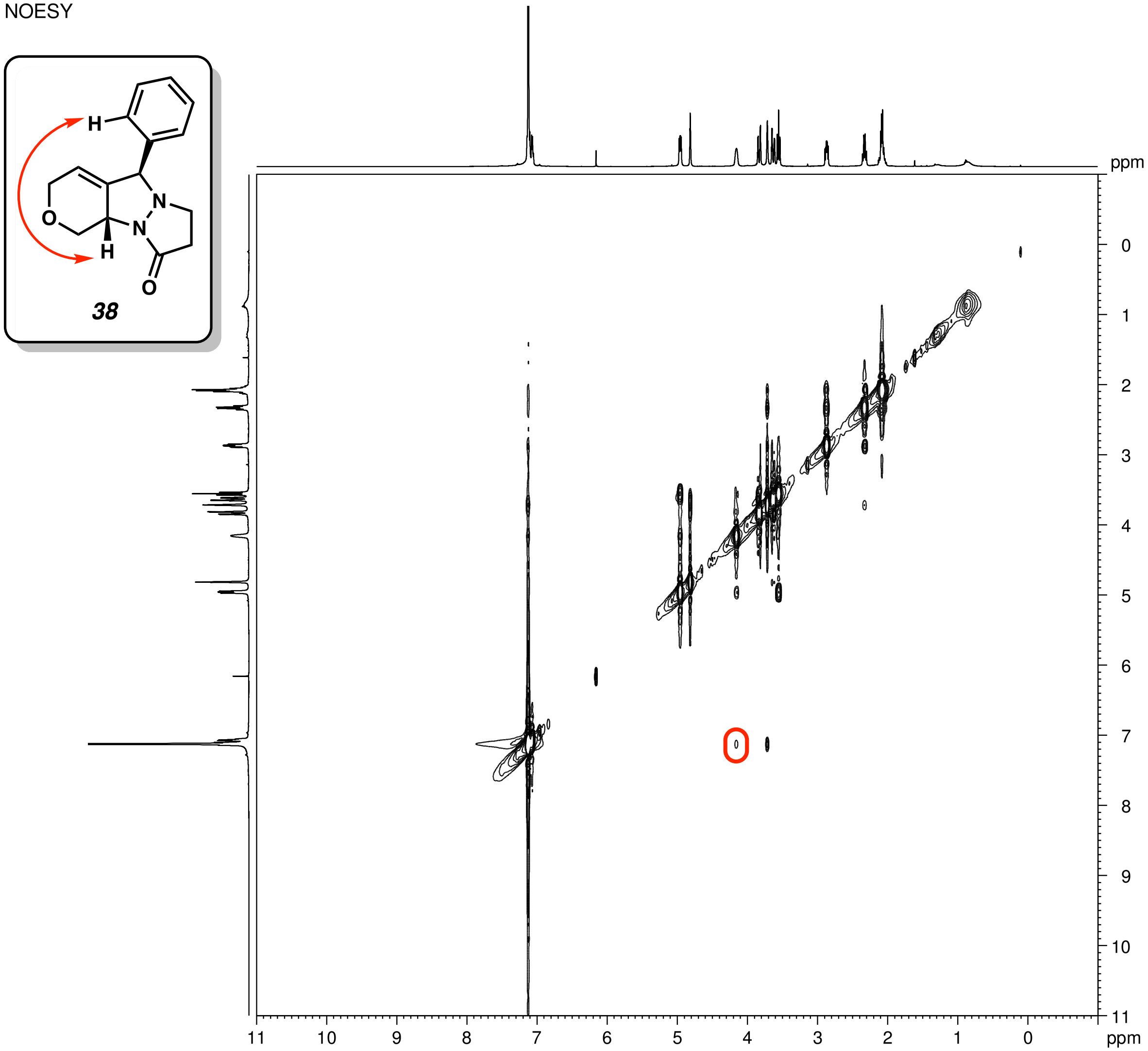
F2 - Acquisition Parameters
Date_        20180827
Time            11.05
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                256
DS                  0
SWH        25252.525 Hz
FIDRES      0.385323 Hz
AQ         1.2976128 sec
RG             189.85
DW             19.800 usec
DE               6.50 usec
TE              299.2 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                 1

======== CHANNEL f1 =====
SFO1      100.6243395 MHz
NUC1               13C
P1              10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 =====
SFO2      400.1324008 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2           90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W
PLW13      0.29249999 W

F2 - Processing parameters
SI              65536
SF        100.6127572 MHz
WDW                EM
SSB     0
LB               1.00 Hz
GB      0
PC               1.40
```

NOESY



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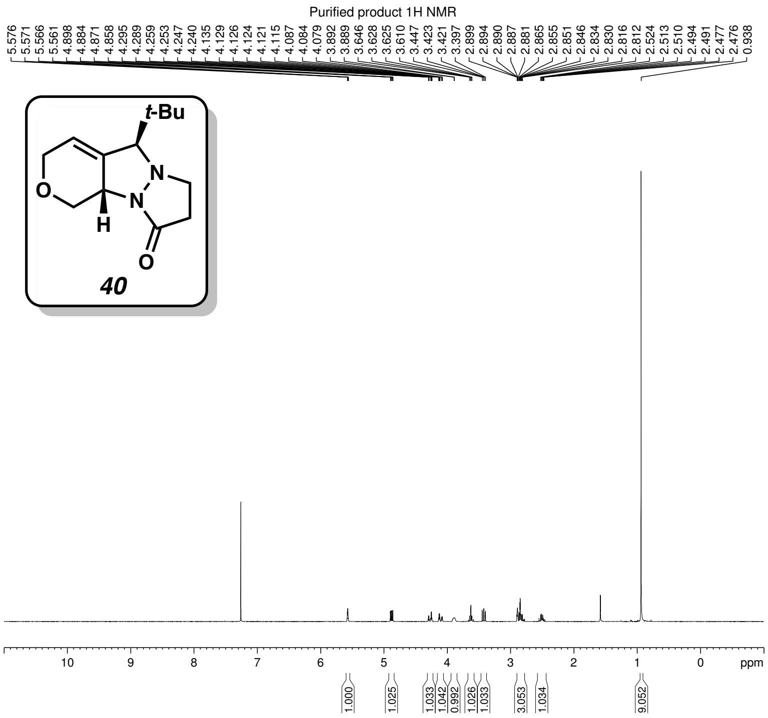
```
Current Data Parameters
NAME      MY-2017-018a-p-b2-2-
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20171004
Time           21.25 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG      noesygpph
TD             2048
SOLVENT          C6D6
NS                 8
DS                 8
SWH       10000.000 Hz
FIDRES     9.765625 Hz
AQ        0.1024000 sec
RG             12.14
DW            50.000 usec
DE             10.00 usec
TE             298.0 K
D0       0.00003727 sec
D1       2.00000000 sec
D8       0.75000000 sec
D16      0.00020000 sec
IN0      0.00010000 sec
TDav               1
SFO1     500.1330008 MHz
NUC1              1H
P1             10.00 usec
P2             20.00 usec
PLW1     13.50000000 W
GPNAM[1]      SINE.100
GPZ1           40.00 %
P16          1000.00 usec

F1 - Acquisition parameters
TD              256
SFO1         500.133 MHz
FIDRES    78.125000 Hz
SW            19.995 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI              2048
SF        500.1300146 MHz
WDW             QSINE
SSB                2
LB      0 Hz
GB      0
PC              1.40

F1 - Processing parameters
SI              2048
MC2        States-TPPI
SF        500.1300146 MHz
WDW             QSINE
SSB                2
LB      0 Hz
GB      0
```

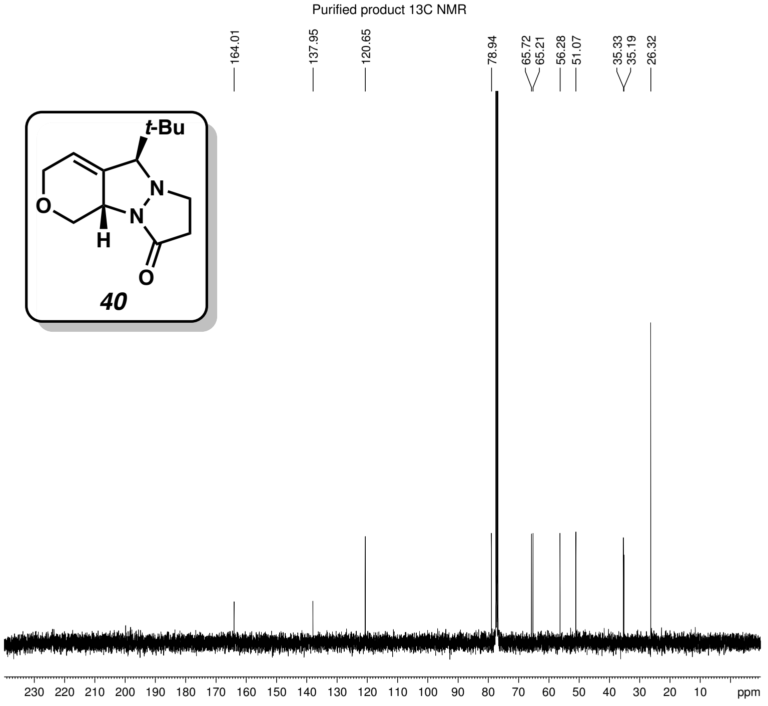


Current Data Parameters
NAME MY-2018-055a-p-char
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180916
Time 11.18
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300177 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME MY-2018-055a-p-cha
EXPNO 11
PROCNO 1

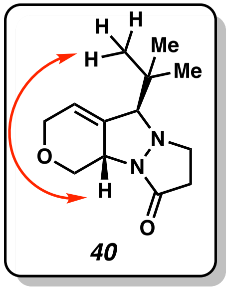
F2 - Acquisition Parameters
Date_ 20180916
Time 11.48
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 189.85
DW 19.800 usec
DE 6.50 usec
TE 299.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =====
SFO1 100.6243395 MHz
NUC1 13C
P1 10.00 usec
PLW1 52.00000000 W

======== CHANNEL f2 =====
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W
PLW13 0.29249999 W

F2 - Processing parameters
SI 65536
SF 100.6127557 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

NOESY



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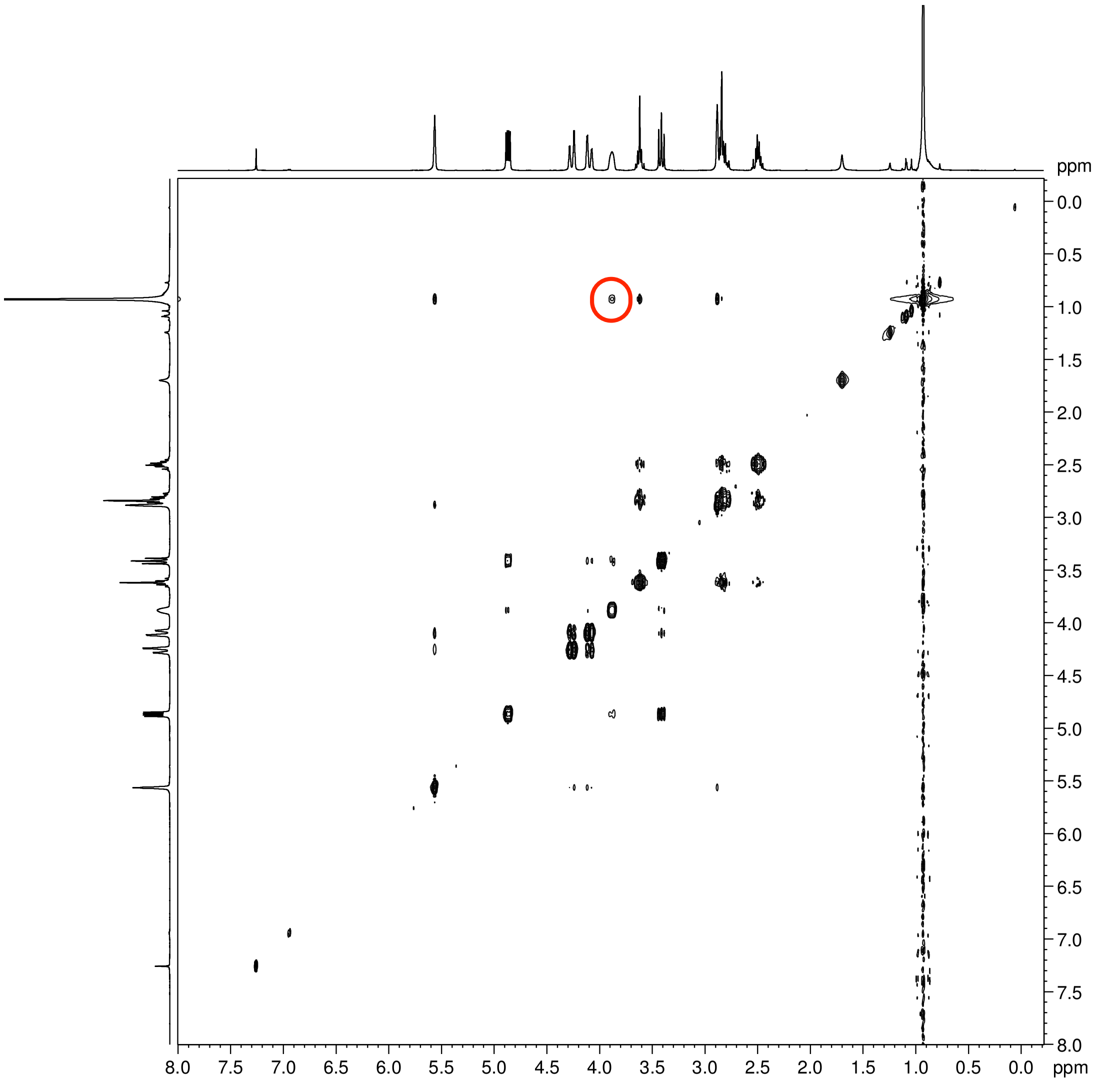


```
Current Data Parameters
NAME      MY-2018-052a-p-b1-2
EXPNO              12
PROCNO              1

F2 - Acquisition Parameters
Date_          20180214
Time              21.53
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG      noesygpphpp
TD                2048
SOLVENT           CDCl3
NS                    2
DS                    8
SWH           3289.474 Hz
FIDRES        1.606188 Hz
AQ           0.3112960 sec
RG                73.86
DW              152.000 usec
DE                 6.50 usec
TE                298.3 K
D0         0.00013290 sec
D1         2.00000000 sec
D8         0.75000000 sec
D11        0.03000000 sec
D12        0.00002000 sec
D16        0.00020000 sec
IN0        0.00030400 sec

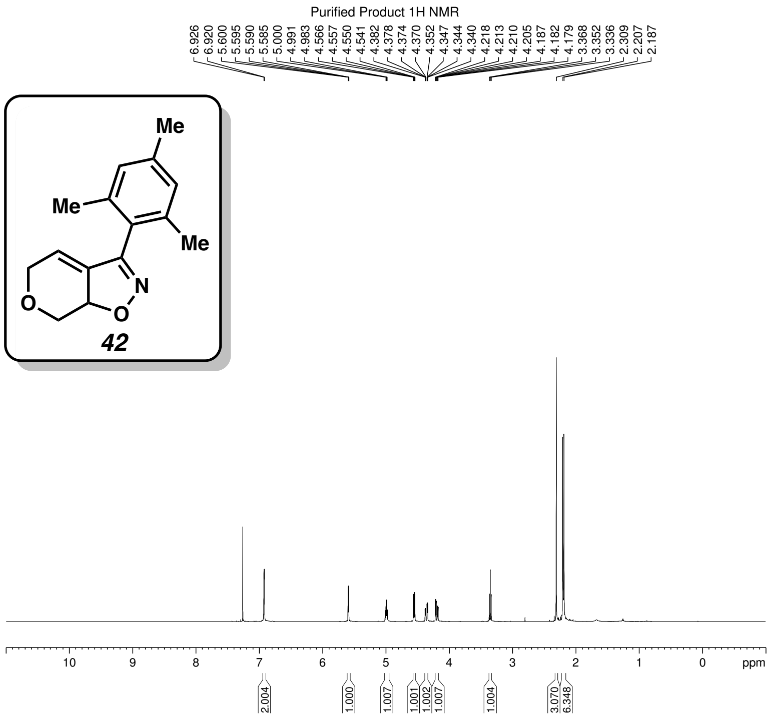
======== CHANNEL f1 ======
SFO1        400.1315761 MHz
NUC1                 1H
P1                15.00 usec
P2                30.00 usec
P17             2500.00 usec
PLW1        13.00000000 W
PLW10        4.32690001 W

====== GRADIENT CHANNEL
GPNAM[1]      SMSQ10.100
GPZ1              40.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1          400.1316 MHz
FIDRES       25.699013 Hz
SW               8.221 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                  1024
SF        400.1300184 MHz
WDW               QSINE
SSB                   2
LB         0 Hz
GB         0
PC                 1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF        400.1300184 MHz
WDW               QSINE
SSB                   2
LB         0 Hz
GB         0
```

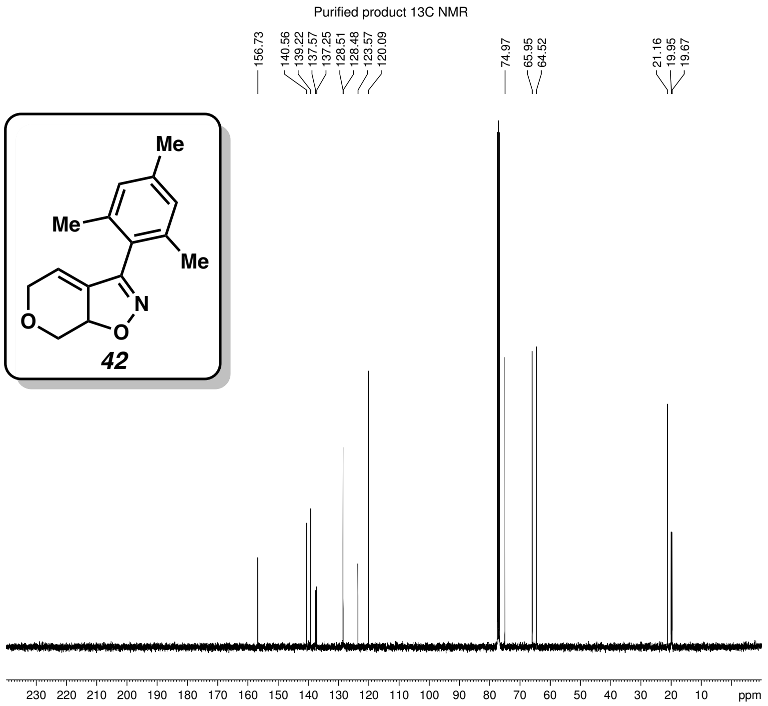


```
Current Data Parameters
NAME       RRK-2018-002
EXPNO              4
PROCNO             1

F2 - Acquisition Parameters
Date_         20180918
Time             17.25
INSTRUM          av600
PROBHD   5 mm BB5
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   0
SWH       12376.237 Hz
FIDRES     0.188846 Hz
AQ        2.6476543 sec
RG                 114
DW          40.400 usec
DE           6.50 usec
TE             294.2 K
D1      2.00000000 sec
TD0                  1

======== CHANNEL f1 =====
NUC1                1H
P1          16.50 usec
PL1           -1.00 dB
PL1W     31.62277603 W
SFO1    600.1336008 MHz

F2 - Processing parameters
SI               65536
SF      600.1300284 MHz
WDW                 EM
SSB     0
LB             0.30 Hz
GB      0
PC                1.00
```



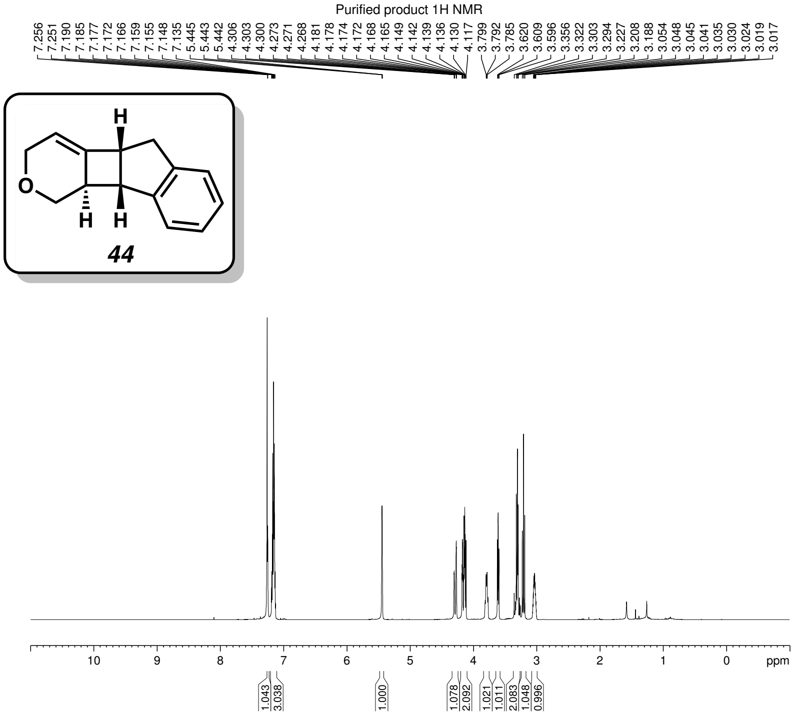
```
Current Data Parameters
NAME       RRK-2018-002
EXPNO             30
PROCNO             1

F2 - Acquisition Parameters
Date_         20180918
Time             18.36
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 512
DS                   0
SWH       25252.525 Hz
FIDRES     0.385323 Hz
AQ        1.2976128 sec
RG              189.85
DW          19.800 usec
DE           6.50 usec
TE             299.3 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0                  1

======== CHANNEL f1 =====
SFO1    100.6243395 MHz
NUC1               13C
P1          10.00 usec
PLW1     52.00000000 W

======== CHANNEL f2 =====
SFO2    400.1324008 MHz
NUC2                1H
CPDPRG[2       waltz16
PCPD2       90.00 usec
PLW2     13.00000000 W
PLW12     0.36111000 W
PLW13     0.29249999 W

F2 - Processing parameters
SI               65536
SF      100.6127701 MHz
WDW                 EM
SSB     0
LB             1.00 Hz
GB      0
PC                1.40
```



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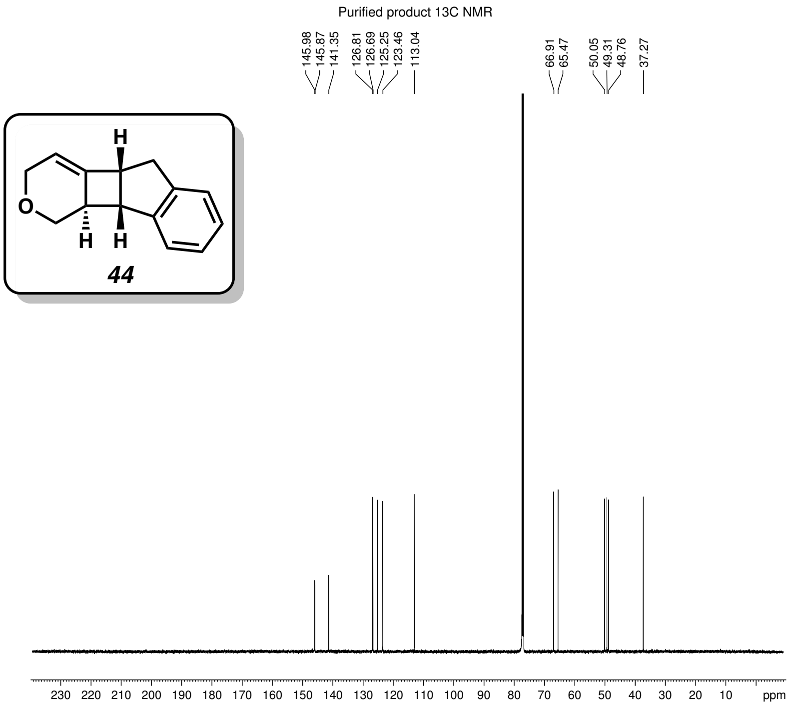
```
Current Data Parameters
NAME     MY-2018-261a-p-char
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20181015
Time             13.11 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                  8
DS                  0
SWH          10000.000 Hz
FIDRES        0.305176 Hz
AQ           3.2767999 sec
RG              12.14
DW              50.000 usec
DE              10.00 usec
TE              298.0 K
D1         2.00000000 sec
TD0                 1
SFO1       500.1330008 MHz
NUC1               1H
P1              10.00 usec
PLW1       13.50000000 W

F2 - Processing parameters
SI              65536
SF         500.1300126 MHz
WDW                EM
SSB    0
LB               0.30 Hz
GB     0
PC               1.00
```



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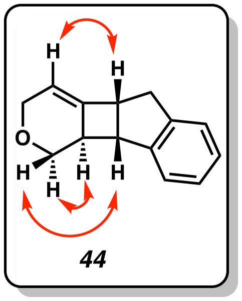
```
Current Data Parameters
NAME     MY-2018-261a-p-cha
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20181015
Time             13.16 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG          zgpg30
TD              65536
SOLVENT          CDCl3
NS                 48
DS                  2
SWH          31250.000 Hz
FIDRES        0.953674 Hz
AQ           1.0485760 sec
RG             204.54
DW              16.000 usec
DE              18.00 usec
TE              298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1
SFO1       125.7722511 MHz
NUC1              13C
P1               9.63 usec
PLW1       23.00000000 W
SFO2       500.1330008 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           80.00 usec
PLW2       13.50000000 W
PLW12       0.21094000 W
PLW13       0.13500001 W

F2 - Processing parameters
SI             131072
SF         125.7577736 MHz
WDW                EM
SSB    0
LB               1.00 Hz
GB     0
PC               1.40
```

NOESY



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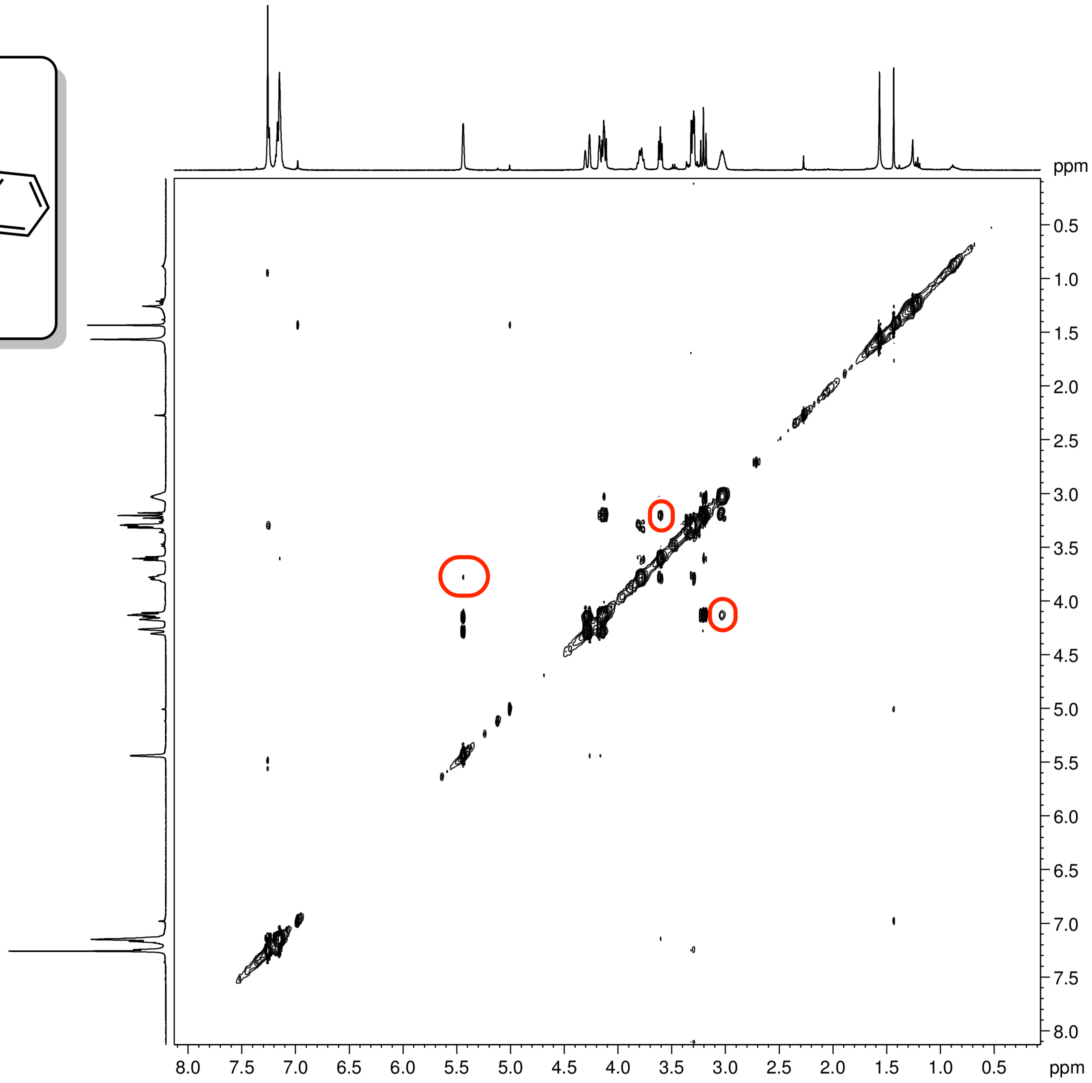


```
Current Data Parameters
NAME     MY-2018-239a-rp2-b1-
EXPNO              42
PROCNO              1

F2 - Acquisition Parameters
Date_         20180821
Time            19.13
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG      noesygpphpp
TD               2048
SOLVENT          CDCl3
NS                  2
DS                  8
SWH          3225.806 Hz
FIDRES       1.575101 Hz
AQ          0.3174400 sec
RG             137.18
DW            155.000 usec
DE              6.50 usec
TE             298.8 K
D0        0.00013590 sec
D1        2.00000000 sec
D8        0.75000000 sec
D11       0.03000000 sec
D12       0.00002000 sec
D16       0.00020000 sec
IN0       0.00031000 sec

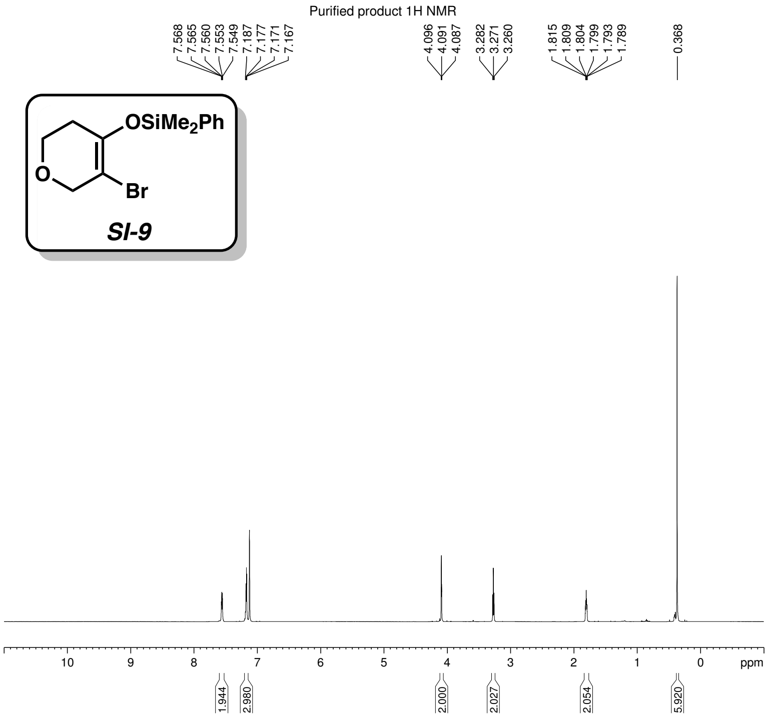
======== CHANNEL f1 ======
SFO1       400.1316585 MHz
NUC1                1H
P1               15.00 usec
P2               30.00 usec
P17            2500.00 usec
PLW1       13.00000000 W
PLW10       4.32690001 W

====== GRADIENT CHANNEL
GPNAM[1]     SMSQ10.100
GPZ1            40.00 %
P16           1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1         400.1317 MHz
FIDRES      25.201612 Hz
SW             8.062 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                 1024
SF          400.1300184 MHz
WDW               QSINE
SSB                  2
LB          0 Hz
GB          0
PC                1.00

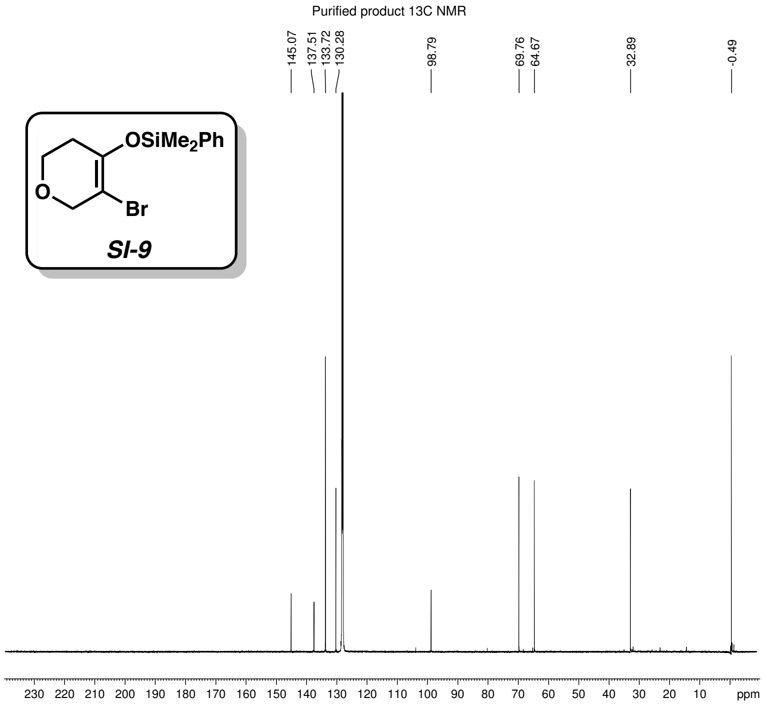
F1 - Processing parameters
SI                 1024
MC2          States-TPPI
SF          400.1300184 MHz
WDW               QSINE
SSB                  2
LB          0 Hz
GB          0
```


Purified product 1H NMR

```
Current Data Parameters
NAME     MY-2018-230a-rp
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20180924
Time          11.03 h
INSTRUM         av500
PROBHD   Z119248_0002 (
PULPROG          zg30
TD             65536
SOLVENT          C6D6
NS                 8
DS                 0
SWH        10000.000 Hz
FIDRES      0.305176 Hz
AQ         3.2767999 sec
RG             12.14
DW            50.000 usec
DE             10.00 usec
TE             298.0 K
D1        2.00000000 sec
TD0                1
SFO1     500.1330008 MHz
NUC1              1H
P1             10.00 usec
PLW1     13.50000000 W

F2 - Processing parameters
SI             65536
SF       500.1300146 MHz
WDW               EM
SSB    0
LB              0.30 Hz
GB     0
PC              1.00
```


Purified product 13C NMR

```
Current Data Parameters
NAME     MY-2018-230a-rp
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20180924
Time          11.14 h
INSTRUM         av500
PROBHD   Z119248_0002 (
PULPROG        zgpg30
TD             65536
SOLVENT          C6D6
NS               176
DS                 2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ         1.0485760 sec
RG            204.54
DW            16.000 usec
DE             18.00 usec
TE             298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1
SFO1     125.7722511 MHz
NUC1             13C
P1              9.63 usec
PLW1     23.00000000 W
SFO2     500.1330008 MHz
NUC2              1H
CPDPRG[2      waltz16
PCPD2          80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.13500001 W

F2 - Processing parameters
SI            131072
SF       125.7577426 MHz
WDW               EM
SSB    0
LB              1.00 Hz
GB     0
PC              1.40
```

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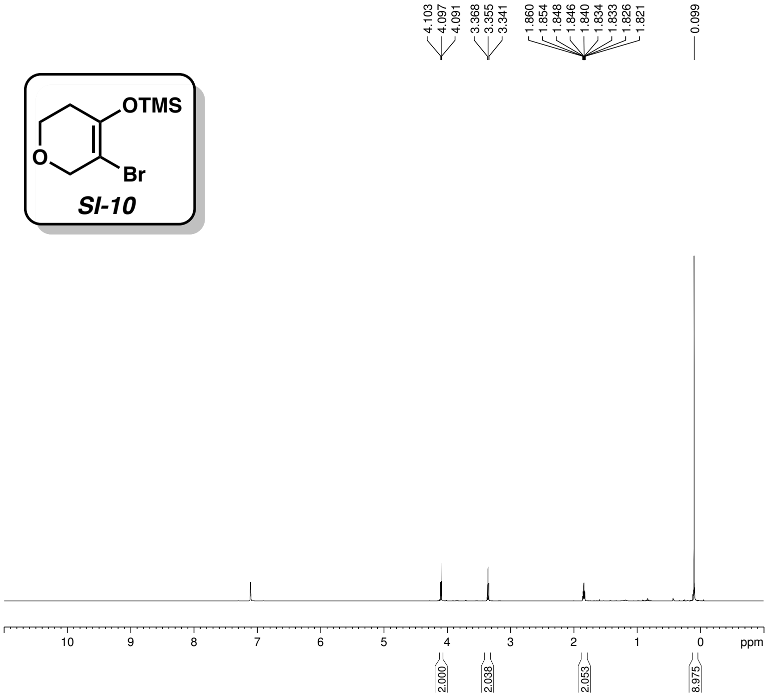
Purified product 1H NMR



```
Current Data Parameters
NAME     MY-2018-257a-p-char
EXPNO              20
PROCNO              1

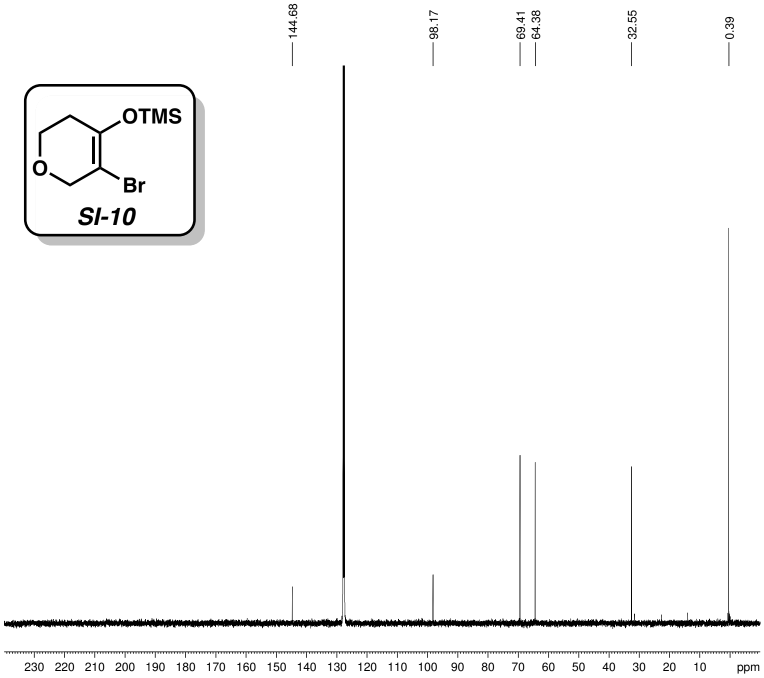
F2 - Acquisition Parameters
Date_         20180912
Time             19.25
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               52882
SOLVENT           C6D6
NS                   4
DS                   0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ        3.2998369 sec
RG              155.85
DW          62.400 usec
DE            6.50 usec
TE             298.6 K
D1       2.00000000 sec
TD0                  1

======== CHANNEL f1 =====
SFO1     400.1324008 MHz
NUC1                1H
P1             15.00 usec
PLW1     13.00000000 W

F2 - Processing parameters
SI               65536
SF       400.1300184 MHz
WDW                 EM
SSB     0
LB             0.30 Hz
GB      0
PC                1.00
```

SI-10

Purified product 13C NMR



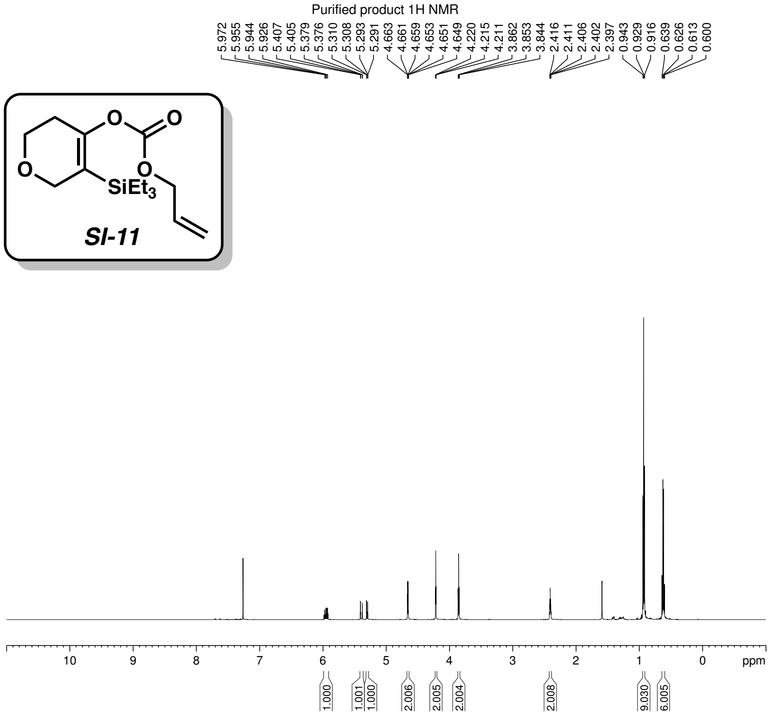
```
Current Data Parameters
NAME     MY-2018-257a-p-cha
EXPNO              21
PROCNO              1

F2 - Acquisition Parameters
Date_         20180912
Time             19.42
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT           C6D6
NS                 256
DS                   0
SWH        25252.525 Hz
FIDRES      0.385323 Hz
AQ        1.2976128 sec
RG              189.85
DW          19.800 usec
DE            6.50 usec
TE             299.4 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                  1

======== CHANNEL f1 =====
SFO1     100.6243395 MHz
NUC1               13C
P1             10.00 usec
PLW1     52.00000000 W

======== CHANNEL f2 =====
SFO2     400.1324008 MHz
NUC2                1H
CPDPRG[2       waltz16
PCPD2          90.00 usec
PLW2     13.00000000 W
PLW12     0.36111000 W
PLW13     0.29249999 W

F2 - Processing parameters
SI               65536
SF       100.6127701 MHz
WDW                 EM
SSB     0
LB             1.00 Hz
GB      0
PC                1.40
```

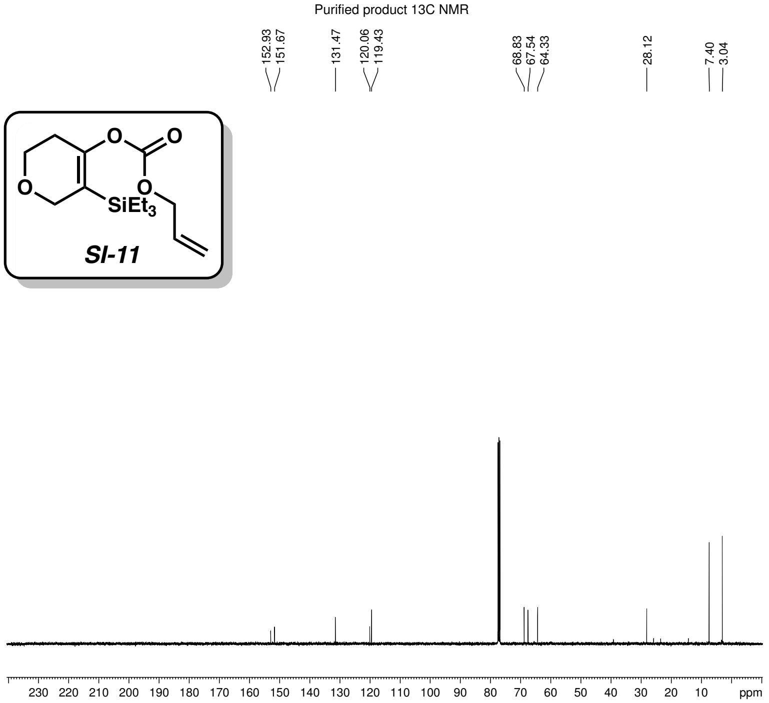


```
Current Data Parameters
NAME      RRK-2018-156
EXPNO              8
PROCNO             1

F2 - Acquisition Parameters
Date_       20181023
Time           14.24
INSTRUM        av600
PROBHD   5 mm BB5
PULPROG         zg30
TD             65536
SOLVENT        CDCl3
NS                16
DS                 0
SWH       12376.237 Hz
FIDRES     0.188846 Hz
AQ        2.6476543 sec
RG               256
DW            40.400 usec
DE             6.50 usec
TE             294.5 K
D1        2.00000000 sec
TD0                1

======== CHANNEL f1 =====
NUC1              1H
P1             16.50 usec
PL1            -1.00 dB
PL1W     31.62277603 W
SFO1    600.1336008 MHz

F2 - Processing parameters
SI             65536
SF       600.1300273 MHz
WDW               EM
SSB    0
LB              0.30 Hz
GB     0
PC              1.00
```



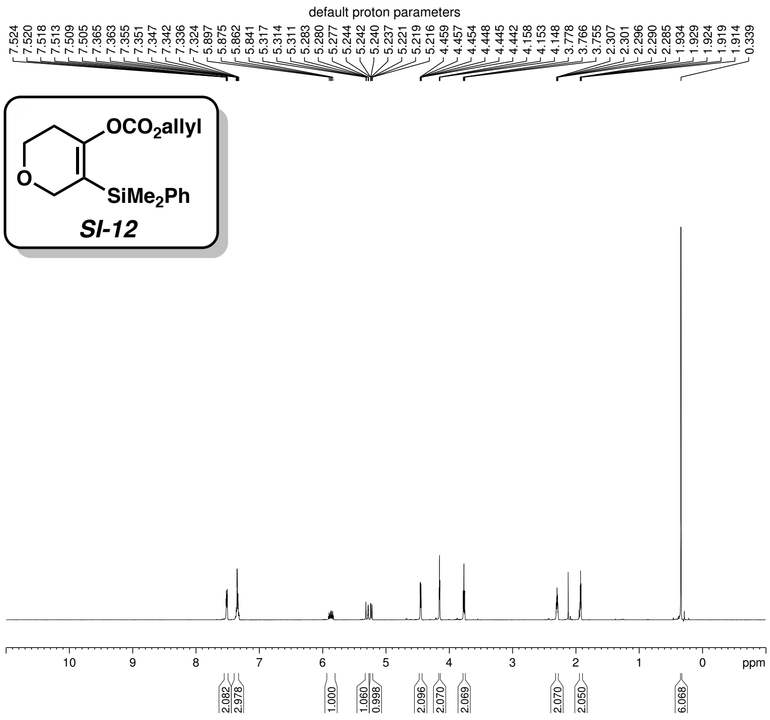
```
Current Data Parameters
NAME      RRK-2018-156
EXPNO             20
PROCNO             1

F2 - Acquisition Parameters
Date_       20181023
Time           15.30
INSTRUM        av400
PROBHD   5 mm PABBO BB/
PULPROG       zgpg30
TD             65536
SOLVENT        CDCl3
NS               512
DS                 0
SWH       25252.525 Hz
FIDRES     0.385323 Hz
AQ        1.2976128 sec
RG            189.85
DW            19.800 usec
DE             6.50 usec
TE             299.5 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

======== CHANNEL f1 =====
SFO1    100.6243395 MHz
NUC1             13C
P1             10.00 usec
PLW1     52.00000000 W

======== CHANNEL f2 =====
SFO2    400.1324008 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2          90.00 usec
PLW2     13.00000000 W
PLW12     0.36111000 W
PLW13     0.29249999 W

F2 - Processing parameters
SI             65536
SF       100.6127561 MHz
WDW               EM
SSB    0
LB              1.00 Hz
GB     0
PC              1.40
```

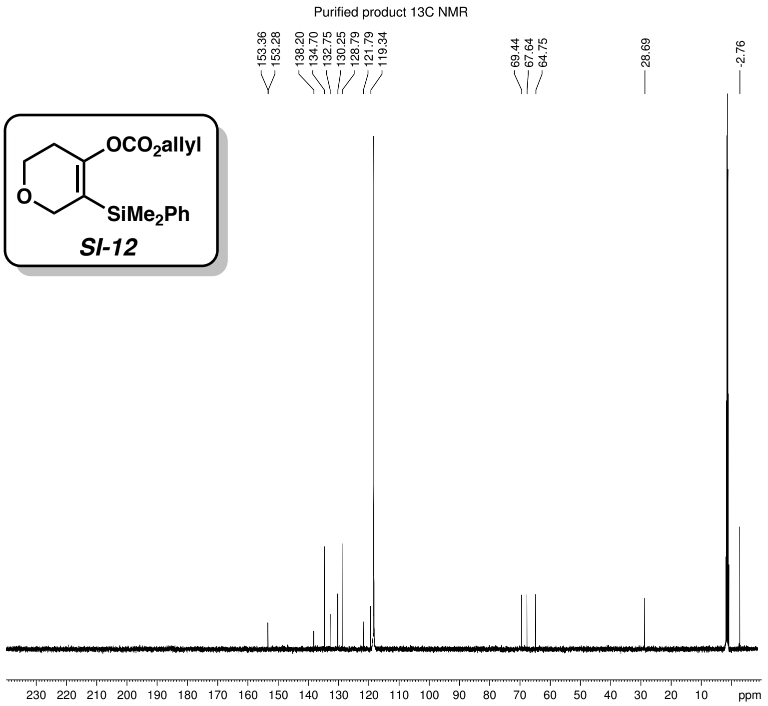


```
Current Data Parameters
NAME     MY-2018-263a-rp-ME
EXPNO              3
PROCNO             1

F2 - Acquisition Parameters
Date_        20180927
Time            18.11
INSTRUM        drx500
PROBHD   5 mm bb-Z Z800
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  8
DS                  0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ         3.2767999 sec
RG              161.3
DW             50.000 usec
DE               6.00 usec
TE              296.9 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 ====
NUC1               1H
P1              13.30 usec
PL1     0 dB
SFO1       500.3330020 MHz

F2 - Processing parameters
SI              32768
SF        500.3300220 MHz
WDW                EM
SSB      0
LB               0.30 Hz
GB       0
PC               1.00
```



```
Current Data Parameters
NAME     MY-2018-263a-rp-ME
EXPNO              2
PROCNO             1

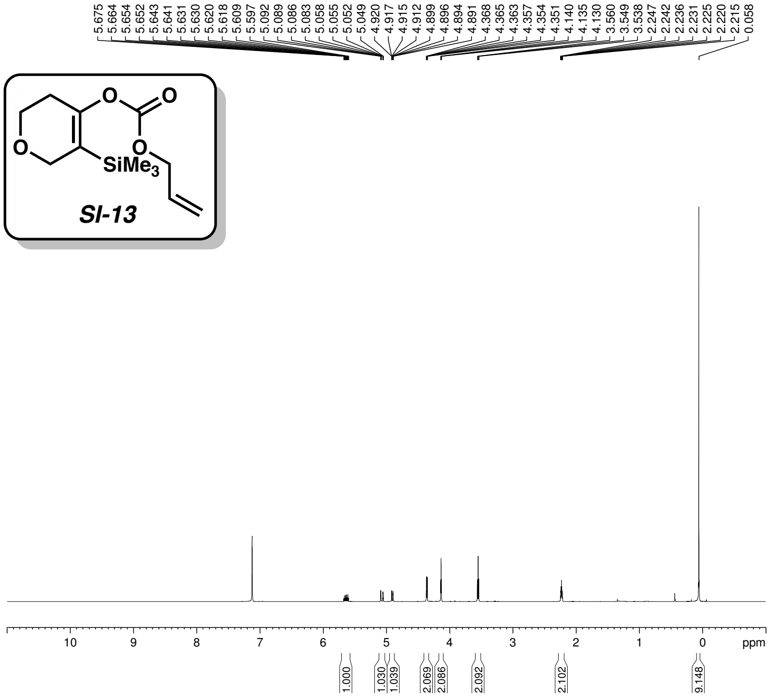
F2 - Acquisition Parameters
Date_        20180927
Time            18.01
INSTRUM        drx500
PROBHD   5 mm bb-Z Z800
PULPROG        zgdc30
TD              65536
SOLVENT         CDCl3
NS                128
DS                  0
SWH        32679.738 Hz
FIDRES      0.498653 Hz
AQ         1.0027008 sec
RG               4096
DW             15.300 usec
DE               6.00 usec
TE              297.2 K
D1         2.00000000 sec
d11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ====
NUC1              13C
P1               6.20 usec
PL1     0 dB
SFO1       125.8231939 MHz

======== CHANNEL f2 ====
CPDPRG[2       waltz16
NUC2               1H
PCPD2          100.00 usec
PL2            120.00 dB
PL12            16.10 dB
SFO2       500.3320013 MHz

F2 - Processing parameters
SI              65536
SF        125.8079550 MHz
WDW                EM
SSB      0
LB               1.00 Hz
GB       0
PC               1.40
```

Purified product 1H NMR



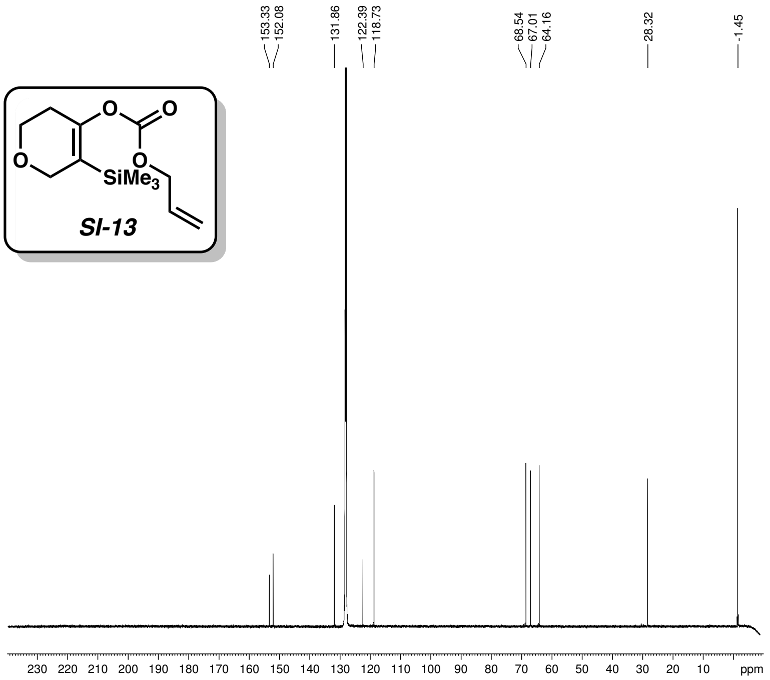
SI-13

Current Data Parameters
NAME MY-2018-267a-p-char
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181002
Time 16.06 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product 13C NMR

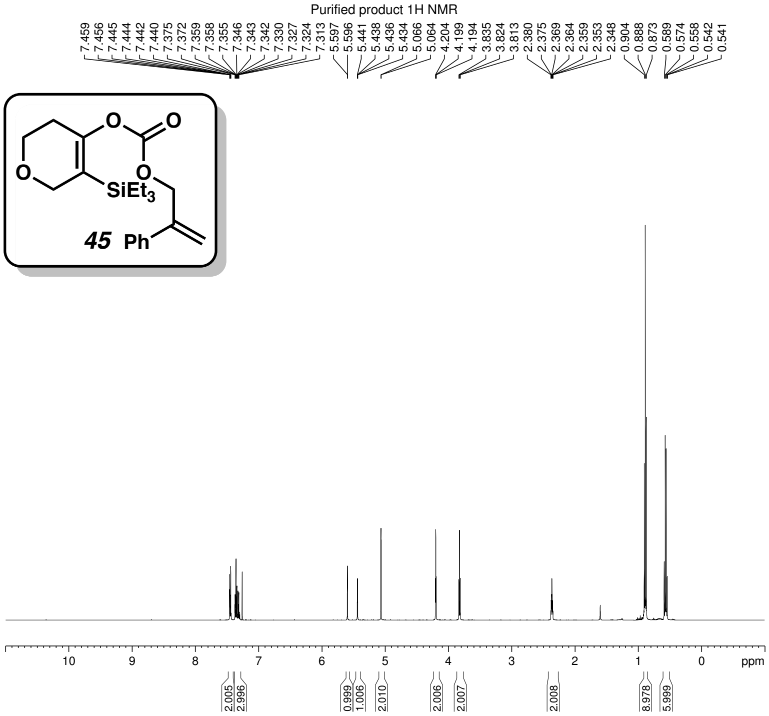


SI-13

Current Data Parameters
NAME MY-2018-267a-p-cha
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181002
Time 16.16 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 161
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W

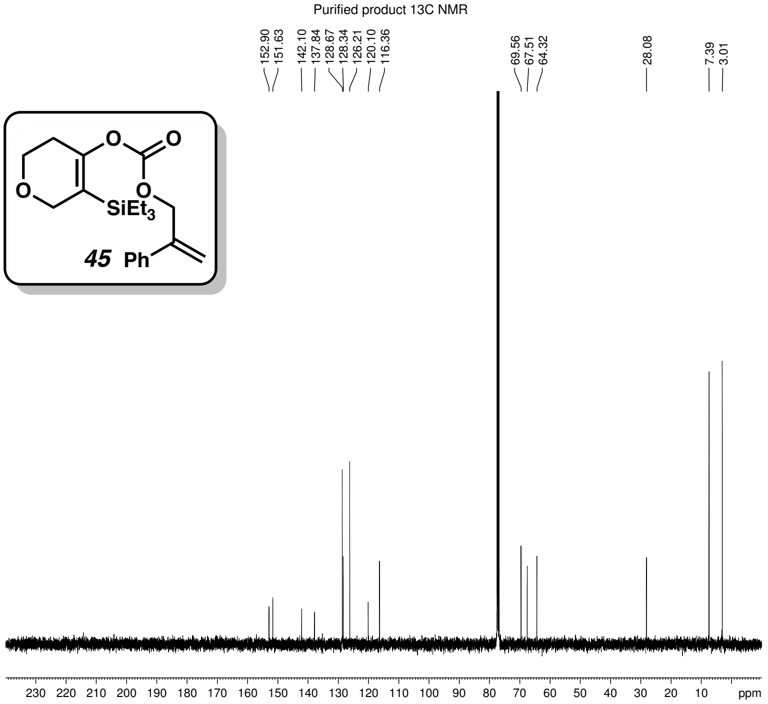
F2 - Processing parameters
SI 131072
SF 125.7577425 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
NAME RRK-2018-142
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180928
Time 11.32 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



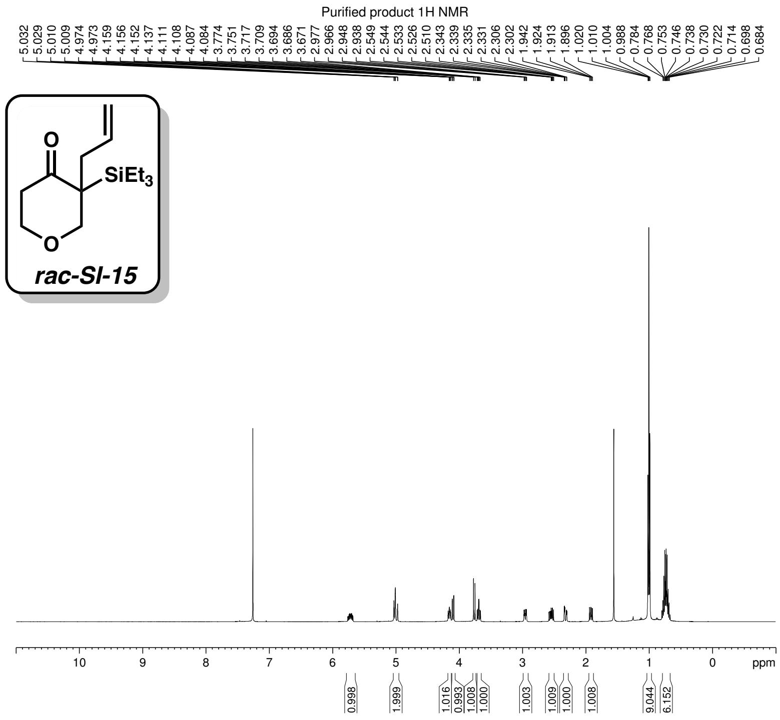
Current Data Parameters
NAME RRK-2018-142
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180911
Time 13.59
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 189.85
DW 19.800 usec
DE 6.50 usec
TE 299.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ====
SFO1 100.6243395 MHz
NUC1 13C
P1 10.00 usec
PLW1 52.00000000 W

======== CHANNEL f2 ====
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W
PLW13 0.29249999 W

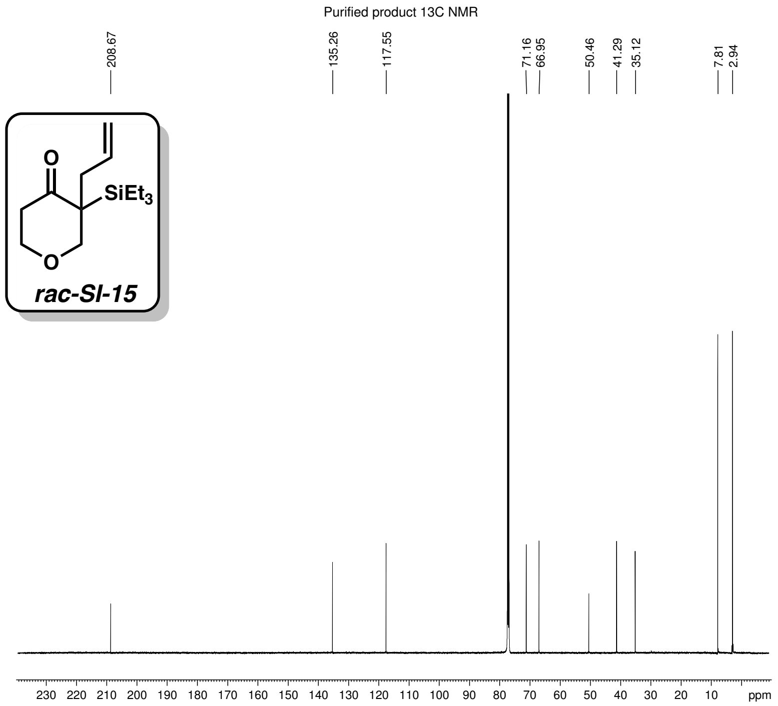
F2 - Processing parameters
SI 65536
SF 100.6127560 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
NAME MY-2018-087
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180930
Time 17.14 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 21.37
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

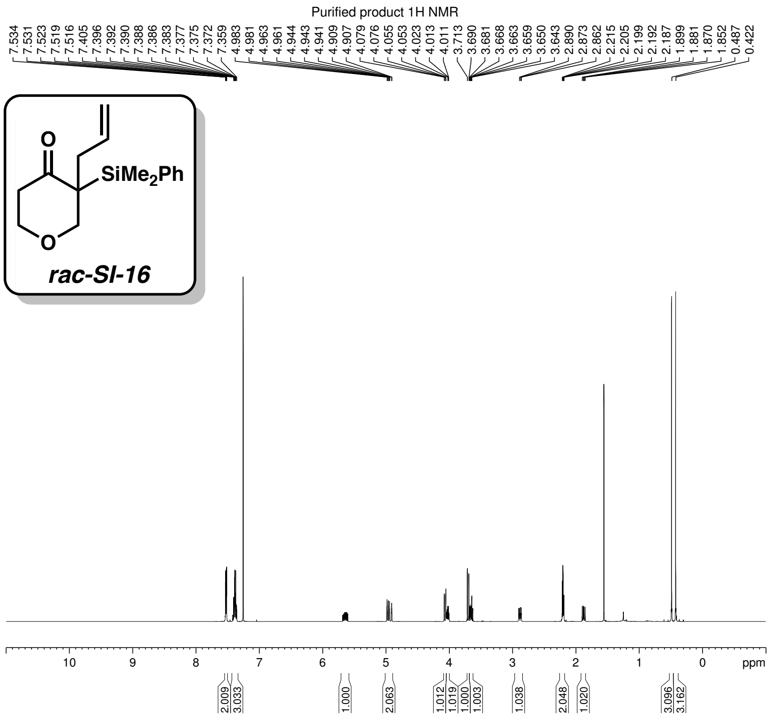
F2 - Processing parameters
SI 65536
SF 500.1300125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME MY-2018-087
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181001
Time 10.02 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 960
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

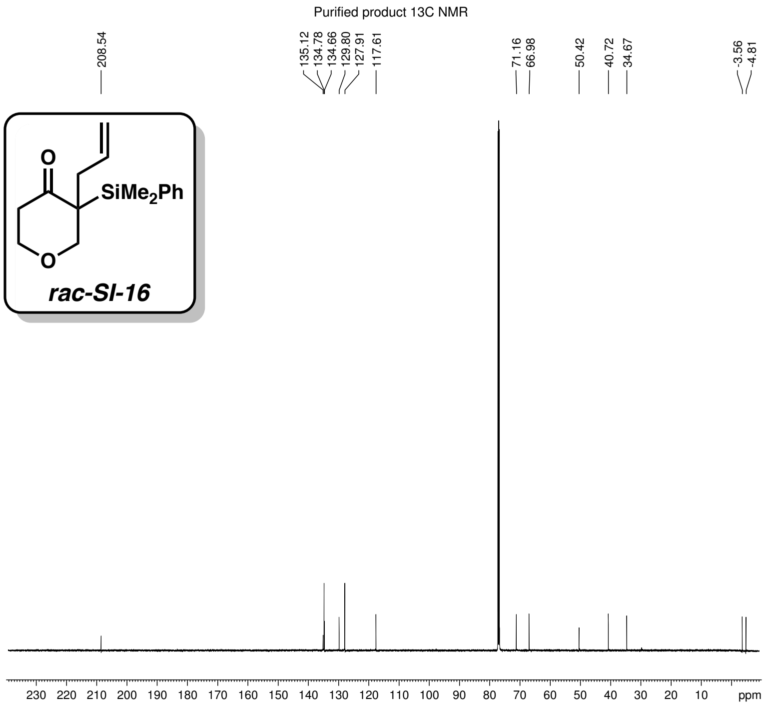
F2 - Processing parameters
SI 131072
SF 125.7577761 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
NAME MY-2018-264a-rp2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181001
Time 11.33 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

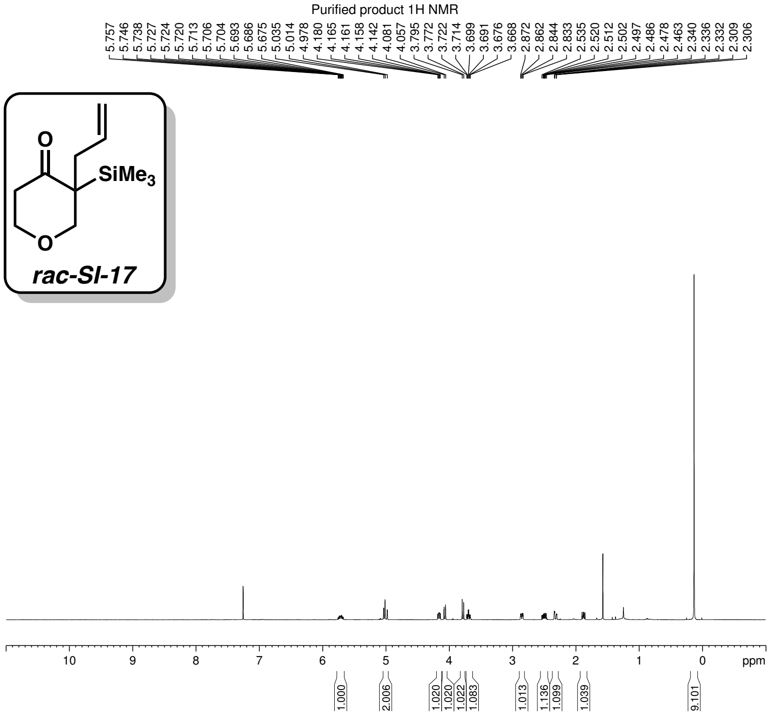


Current Data Parameters
NAME MY-2018-264a-rp2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181001
Time 11.38 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product 1H NMR



Current Data Parameters

NAME	MY-2018-269a-rp
EXPNO	1
PROCNO	1

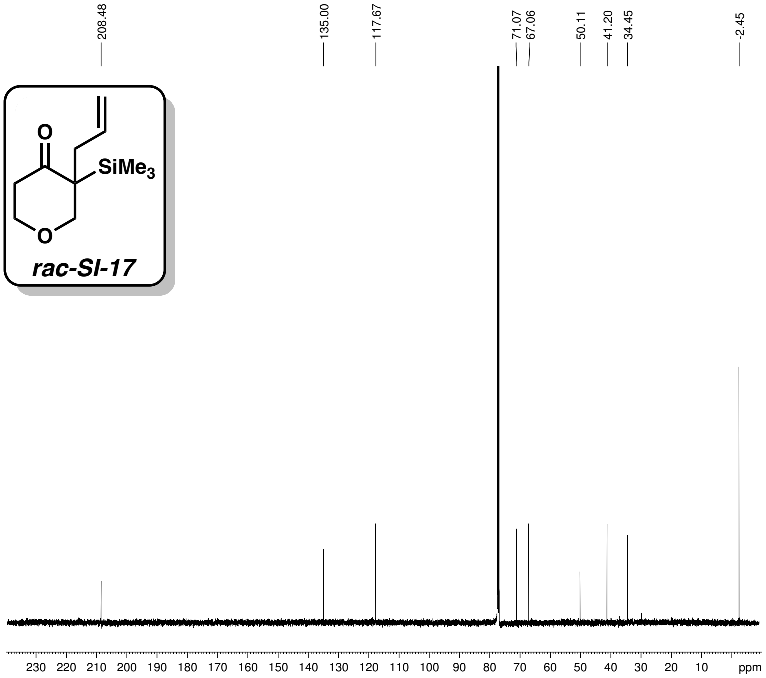
F2 - Acquisition Parameters

Date_	20181009
Time	15.41 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.305176 Hz
AQ	3.2767999 sec
RG	12.14
DW	50.000 usec
DE	10.00 usec
TE	298.0 K
D1	2.00000000 sec
TD0	1
SFO1	500.1330008 MHz
NUC1	1H
P1	10.00 usec
PLW1	13.50000000 W

F2 - Processing parameters

SI	65536
SF	500.1300146 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Purified product 13C NMR



Current Data Parameters

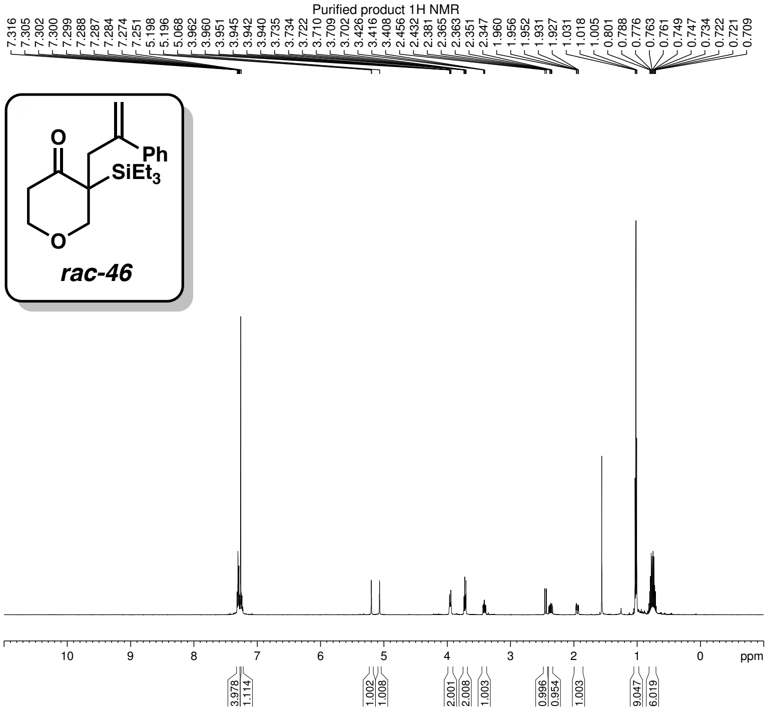
NAME	MY-2018-269a-rp
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20181009
Time	15.47 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	31250.000 Hz
FIDRES	0.953674 Hz
AQ	1.0485760 sec
RG	204.54
DW	16.000 usec
DE	18.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.7722511 MHz
NUC1	13C
P1	9.63 usec
PLW1	23.00000000 W
SFO2	500.1330008 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	13.50000000 W
PLW12	0.21094000 W
PLW13	0.13500001 W

F2 - Processing parameters

SI	131072
SF	125.7577754 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

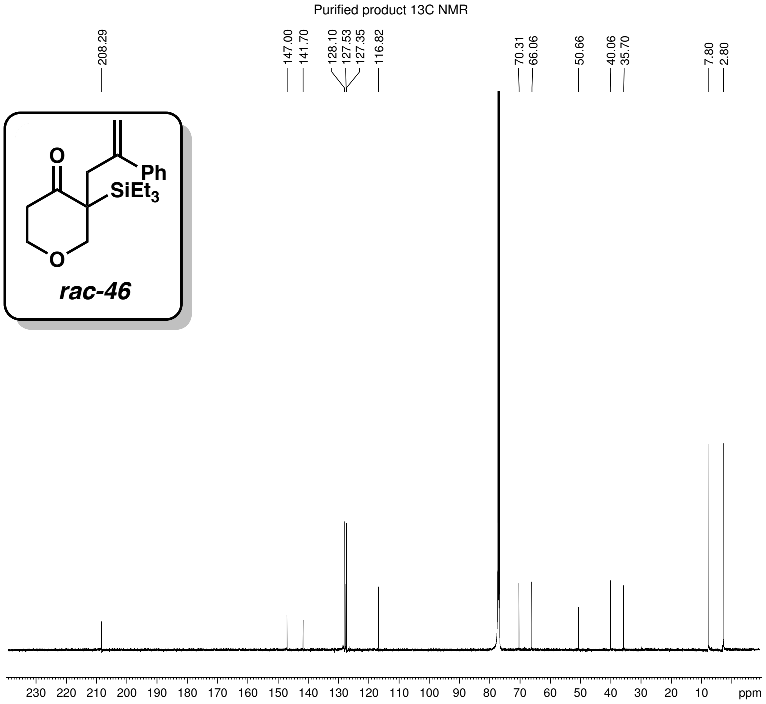


```
Current Data Parameters
NAME        MY-2018-167
EXPNO              1
PROCNO              1

F2 - Acquisition Parameters
Date_         20181016
Time              18.26
INSTRUM          av600
PROBHD   5 mm BB5
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   0
SWH           12376.237 Hz
FIDRES          0.188846 Hz
AQ            2.6476543 sec
RG                 256
DW               40.400 usec
DE                6.50 usec
TE               294.5 K
D1          2.00000000 sec
TD0                  1

======== CHANNEL f1 =====
NUC1                1H
P1               16.50 usec
PL1              -1.00 dB
PL1W       31.62277603 W
SFO1       600.1336008 MHz

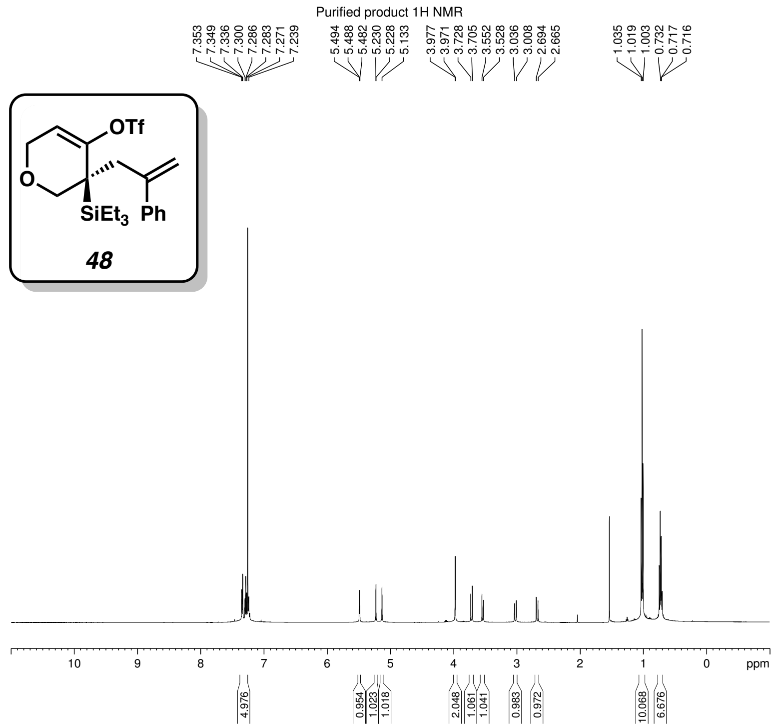
F2 - Processing parameters
SI              65536
SF          600.1300285 MHz
WDW                EM
SSB      0
LB               0.30 Hz
GB       0
PC                1.00
```



```
Current Data Parameters
NAME        MY-2018-167
EXPNO             21
PROCNO              1

F2 - Acquisition Parameters
Date_         20181017
Time              9.28 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 768
DS                   2
SWH          31250.000 Hz
FIDRES          0.953674 Hz
AQ            1.0485760 sec
RG                14.67
DW               16.000 usec
DE               18.00 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1
SFO1       125.7722511 MHz
NUC1               13C
P1               10.50 usec
PLW1       23.00000000 W
SFO2       500.1330008 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2       13.50000000 W
PLW12       0.21094000 W
PLW13       0.10610000 W

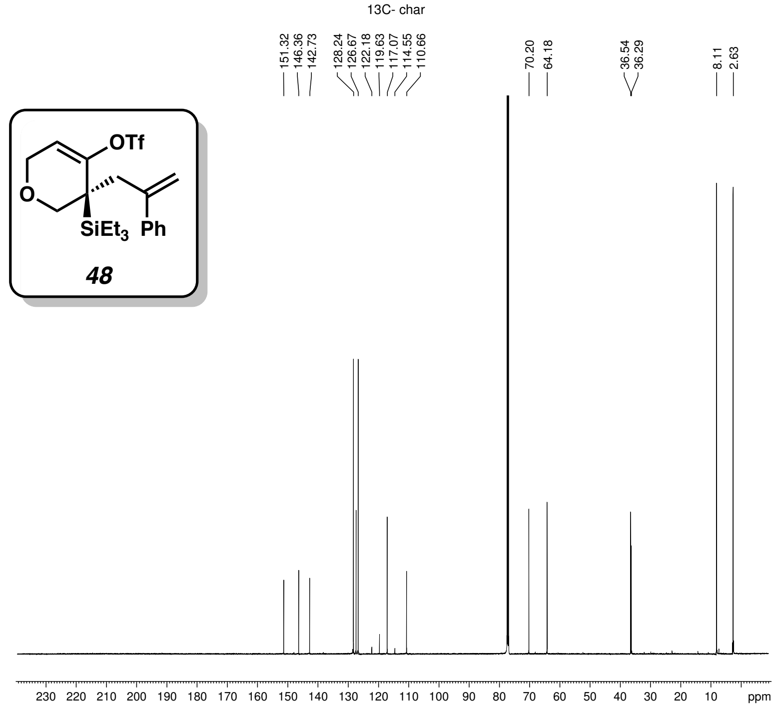
F2 - Processing parameters
SI             131072
SF          125.7577892 MHz
WDW                EM
SSB      0
LB               1.00 Hz
GB       0
PC                1.40
```



```
Current Data Parameters
NAME      RRK-2018-144
EXPNO            3
PROCNO           1

F2 - Acquisition Parameters
Date_       20180916
Time          14.06 h
INSTRUM        av500
PROBHD   Z119248_0002 (
PULPROG          zg30
TD             65536
SOLVENT         CDCl3
NS                 8
DS                 0
SWH        10000.000 Hz
FIDRES      0.305176 Hz
AQ         3.2767999 sec
RG             12.14
DW            50.000 usec
DE            10.00 usec
TE             298.0 K
D1        2.00000000 sec
TD0                1
SFO1     500.1330008 MHz
NUC1              1H
P1             10.00 usec
PLW1     13.50000000 W

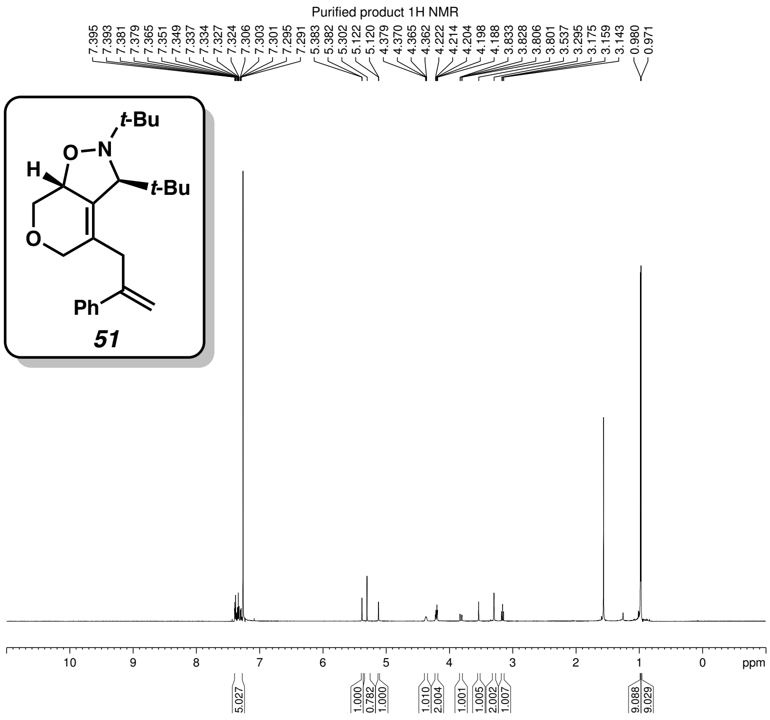
F2 - Processing parameters
SI             65536
SF       500.1300146 MHz
WDW               EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```



```
Current Data Parameters
NAME      RRK-2018-144
EXPNO         1001
PROCNO           1

F2 - Acquisition Parameters
Date_       20181023
Time          18.32 h
INSTRUM        av500
PROBHD   Z119248_0002 (
PULPROG        zgpg30
TD             65536
SOLVENT         CDCl3
NS               372
DS                 2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ         1.0485760 sec
RG            204.54
DW            16.000 usec
DE            18.00 usec
TE             298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1
SFO1     125.7722511 MHz
NUC1             13C
P1             10.50 usec
PLW1     23.00000000 W
SFO2     500.1330008 MHz
NUC2              1H
CPDPRG[2      waltz16
PCPD2          80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.10610000 W

F2 - Processing parameters
SI            131072
SF       125.7577721 MHz
WDW               EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```

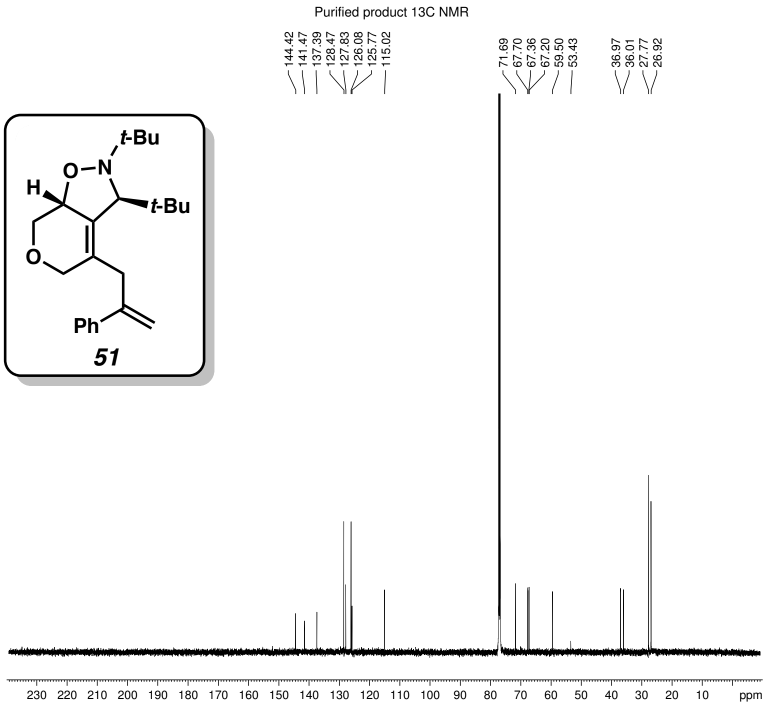


```
Current Data Parameters
NAME      RRK-2018-150
EXPNO              3
PROCNO             1

F2 - Acquisition Parameters
Date_       20181010
Time           12.39
INSTRUM        av600
PROBHD   5 mm BB5
PULPROG         zg30
TD            65536
SOLVENT        CDCl3
NS                32
DS                 0
SWH        12376.237 Hz
FIDRES      0.188846 Hz
AQ         2.6476543 sec
RG             322.5
DW            40.400 usec
DE              6.50 usec
TE             294.4 K
D1        2.00000000 sec
TD0                1

======== CHANNEL f1 =====
NUC1              1H
P1             16.50 usec
PL1            -1.00 dB
PL1W     31.62277603 W
SFO1     600.1336008 MHz

F2 - Processing parameters
SI             65536
SF       600.1300273 MHz
WDW               EM
SSB    0
LB              0.30 Hz
GB     0
PC              1.00
```

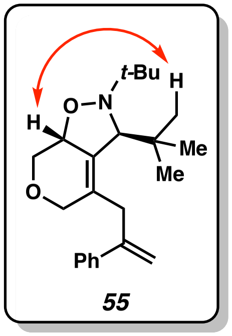


```
Current Data Parameters
NAME      RRK-2018-150
EXPNO             11
PROCNO             1

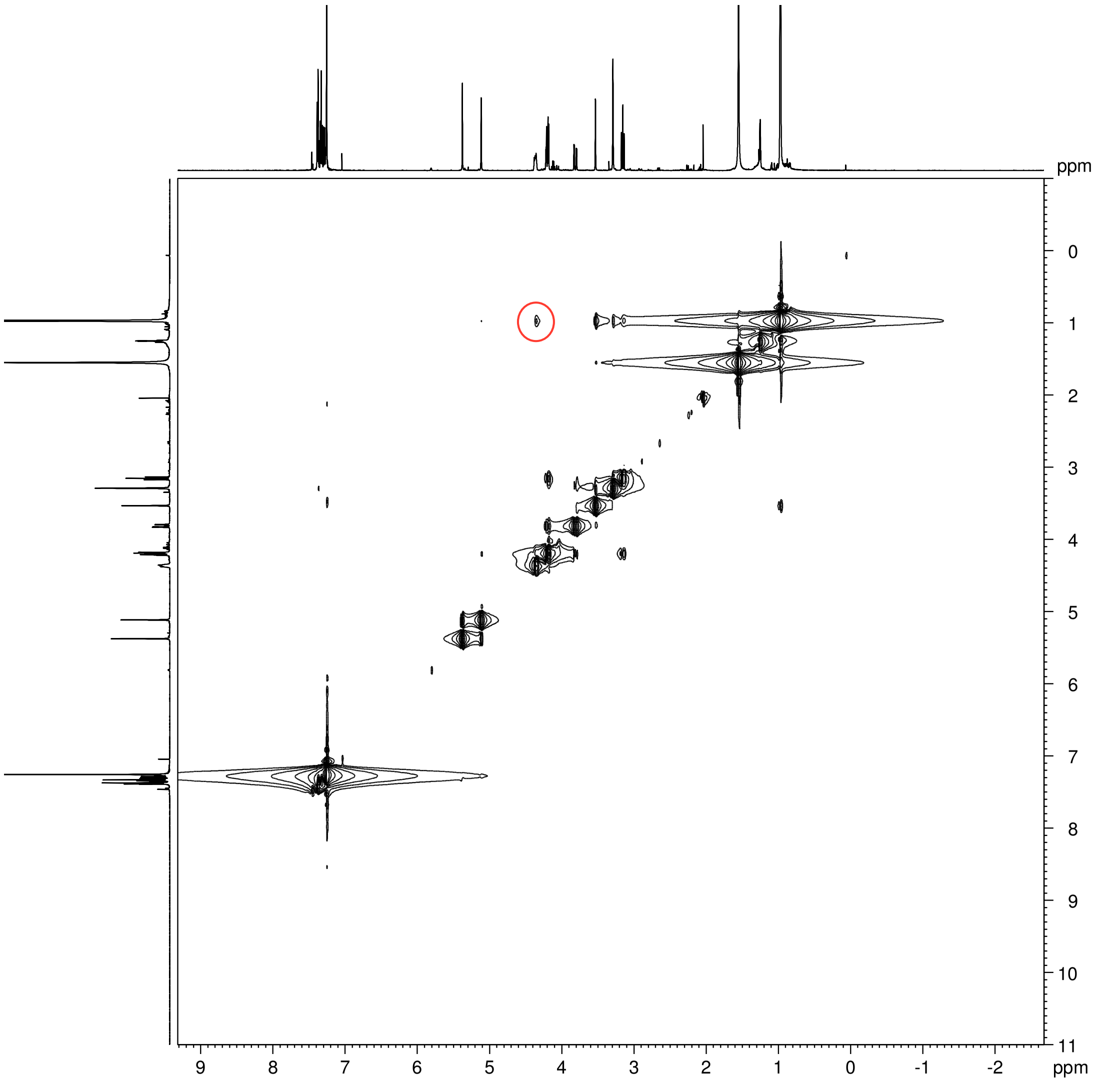
F2 - Acquisition Parameters
Date_       20181010
Time          17.35 h
INSTRUM        av500
PROBHD   Z119248_0002 (
PULPROG       zgpg30
TD            65536
SOLVENT        CDCl3
NS               240
DS                 2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ         1.0485760 sec
RG             12.14
DW            16.000 usec
DE             18.00 usec
TE             298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1
SFO1     125.7722511 MHz
NUC1             13C
P1             10.50 usec
PLW1     23.00000000 W
SFO2     500.1330008 MHz
NUC2              1H
CPDPRG[2     waltz16
PCPD2          80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.10610000 W

F2 - Processing parameters
SI            131072
SF       125.7577892 MHz
WDW               EM
SSB    0
LB              1.00 Hz
GB     0
PC              1.40
```

NOESY



55



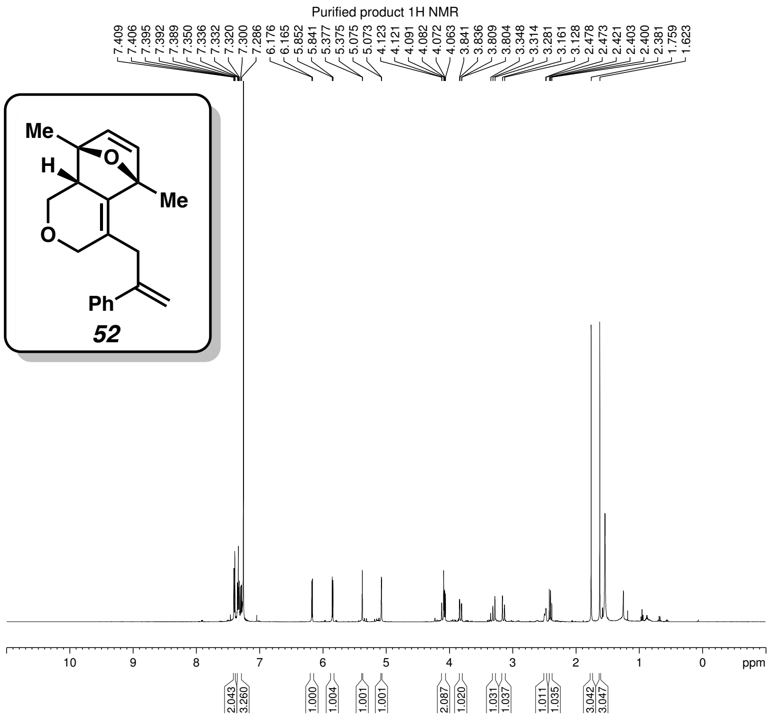
```
Current Data Parameters
NAME     RRK-2018-138 2D
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20180917
Time            20.25 h
INSTRUM           av500
PROBHD   Z119248_0002 (
PULPROG       noesygpph
TD             2048
SOLVENT           CDCl3
NS                 10
DS                  8
SWH         10000.000 Hz
FIDRES       9.765625 Hz
AQ          0.1024000 sec
RG               12.14
DW              50.000 usec
DE               10.00 usec
TE               298.0 K
D0          0.00003727 sec
D1          2.00000000 sec
D8          0.75000000 sec
D16         0.00020000 sec
IN0         0.00010000 sec
TDav                1
SFO1       500.1330008 MHz
NUC1               1H
P1               10.00 usec
P2               20.00 usec
PLW1       13.50000000 W
GPNAM[1]       SINE.100
GPZ1             40.00 %
P16            1000.00 usec

F1 - Acquisition parameters
TD              256
SFO1          500.133 MHz
FIDRES      78.125000 Hz
SW             19.995 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI             2048
SF         500.1300146 MHz
WDW              QSINE
SSB                2
LB       0 Hz
GB       0
PC              1.40

F1 - Processing parameters
SI             2048
MC2         States-TPPI
SF         500.1300146 MHz
WDW              QSINE
SSB                2
LB       0 Hz
GB       0
```



Current Data Parameters

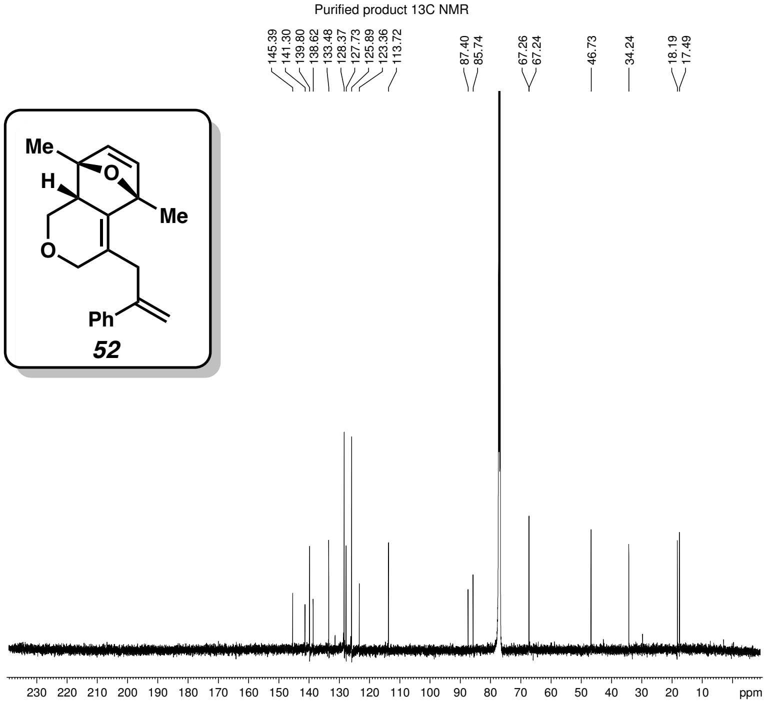
NAME	RRK-2018-154
EXPNO	1001
PROCNO	1

F2 - Acquisition Parameters

Date_	20181019
Time	9.26 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	64
DS	0
SWH	10000.000 Hz
FIDRES	0.305176 Hz
AQ	3.2767999 sec
RG	21.37
DW	50.000 usec
DE	10.00 usec
TE	298.0 K
D1	2.00000000 sec
TD0	1
SFO1	500.1330008 MHz
NUC1	1H
P1	10.00 usec
PLW1	13.50000000 W

F2 - Processing parameters

SI	65536
SF	500.1300146 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



Current Data Parameters

NAME	RRK-2018-154
EXPNO	1002
PROCNO	1

F2 - Acquisition Parameters

Date_	20181019
Time	10.14 h
INSTRUM	av500
PROBHD	Z119248_0002 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	831
DS	2
SWH	31250.000 Hz
FIDRES	0.953674 Hz
AQ	1.0485760 sec
RG	12.14
DW	16.000 usec
DE	18.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.7722511 MHz
NUC1	13C
P1	10.50 usec
PLW1	23.00000000 W
SFO2	500.1330008 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	13.50000000 W
PLW12	0.21094000 W
PLW13	0.10610000 W

F2 - Processing parameters

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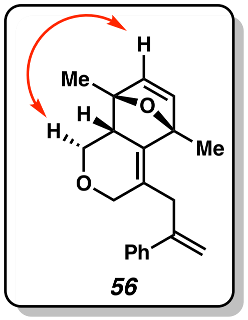
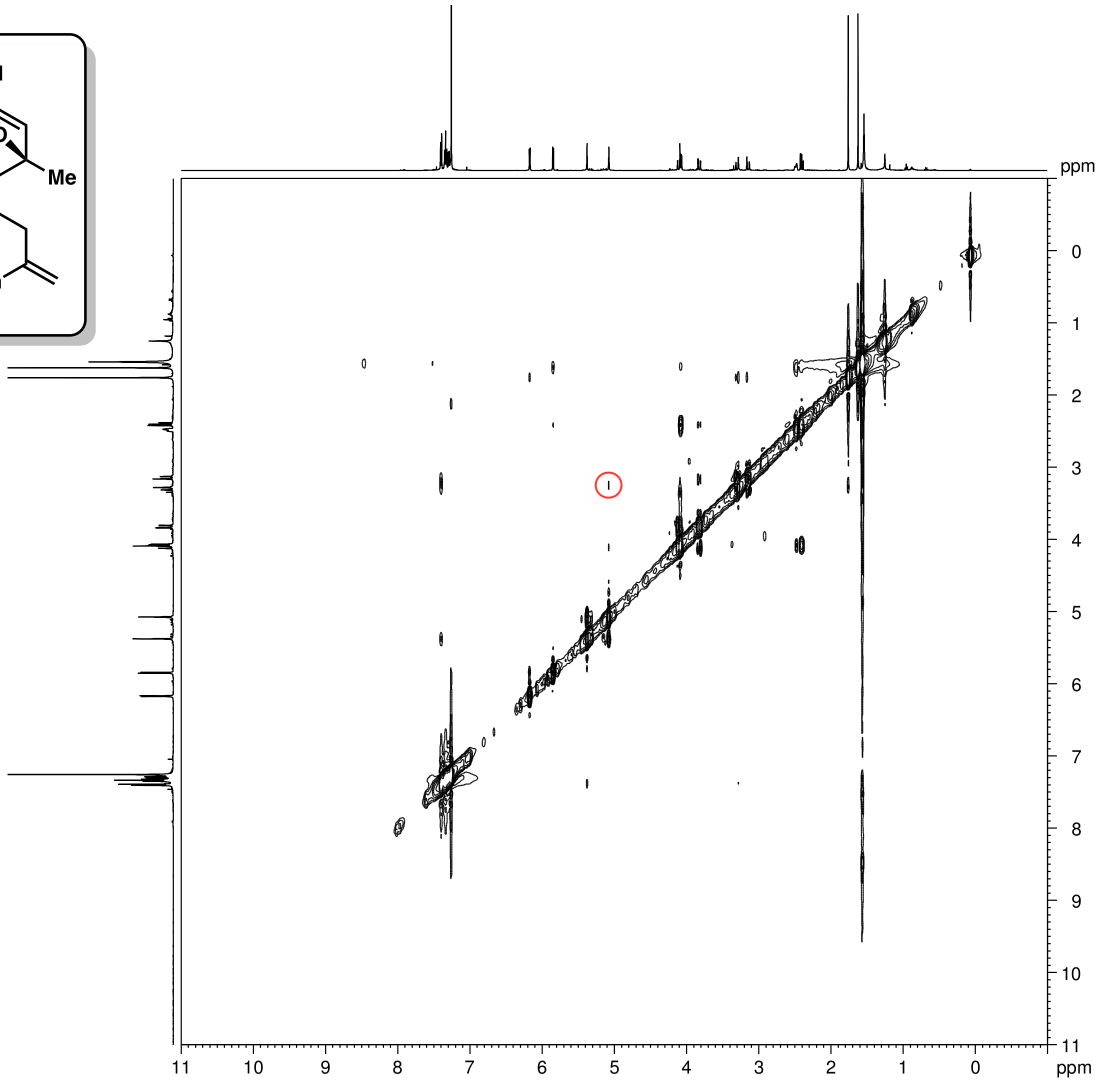
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

NOESY



56



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EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
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Time             21.22 h
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PROBHD   Z119248_0002 (
PULPROG      noesygpph
TD            2048
SOLVENT          CDCl3
NS               10
DS               8
SWH         10000.000 Hz
FIDRES        9.765625 Hz
AQ          0.1024000 sec
RG               7.89
DW             50.000 usec
DE             10.00 usec
TE             298.0 K
D0         0.00003727 sec
D1         2.00000000 sec
D8         0.75000000 sec
D16        0.00020000 sec
IN0        0.00010000 sec
TDav             1
SFO1       500.1330008 MHz
NUC1             1H
P1             10.00 usec
P2             20.00 usec
PLW1       13.50000000 W
GPNAM[1]      SINE.100
GPZ1           40.00 %
P16          1000.00 usec

F1 - Acquisition parameters
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SFO1         500.133 MHz
FIDRES      78.125000 Hz
SW            19.995 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI            2048
SF         500.1300135 MHz
WDW              QSINE
SSB              2
LB       0 Hz
GB       0
PC               1.40

F1 - Processing parameters
SI            2048
MC2        States-TPPI
SF         500.1300135 MHz
WDW              QSINE
SSB              2
LB       0 Hz
GB       0
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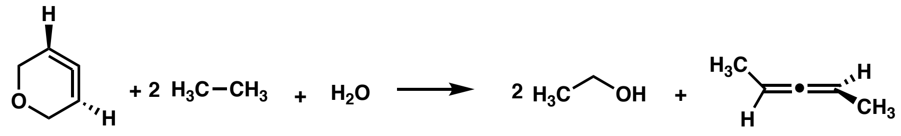
Part II: Computational Methods
Computational Details

All calculations were carried out with the Gaussian 09 package. Geometry optimizations were performed with ωB97XD and 6-31G(d) basis set. Frequency analysis was conducted at the same level of theory to verify the stationary points to be minima or saddle points. Free energy corrections were calculated with and without Truhlar's quasiharmonic oscillator approximation.[11] Single-point energies and solvent effects in acetonitrile were computed with the 6-311+G(d,p) basis set and SMD solvation model.[12] Computed structures are illustrated with CYLview.[13]

A. Complete Citation of Gaussian 09

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Rev. D.01*; Gaussian, Inc., Wallingford, CT, **2010**.

B. Strain Energy in 3,4-Oxacyclohexadiene



8 –269.0456 Hartrees

SI-20 –79.7262 Hartrees

SI-21 –76.3654 Hartrees

SI-22 –154.9039 Hartrees

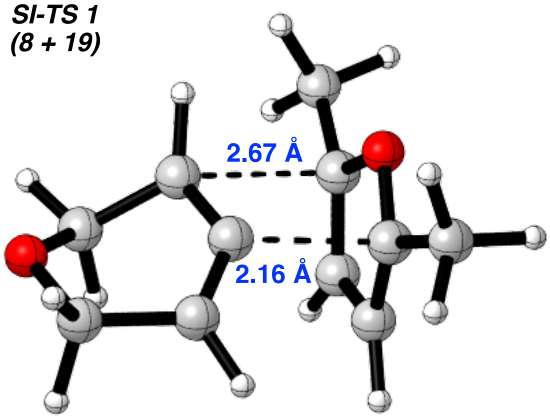
SI-23 –195.1050 Hartrees

Δ(E+ZPVE) = –31.0 kcal/mol

A homodesmotic equation at the ωB97XD/6-31G(d)+ZPVE level of theory was used to estimate strain in 3,4-oxacyclohexadiene **8**. Molecular strain in 3,4-oxacyclohexadiene **8** was calculated relative to penta-2,3-diene (**SI-15**).

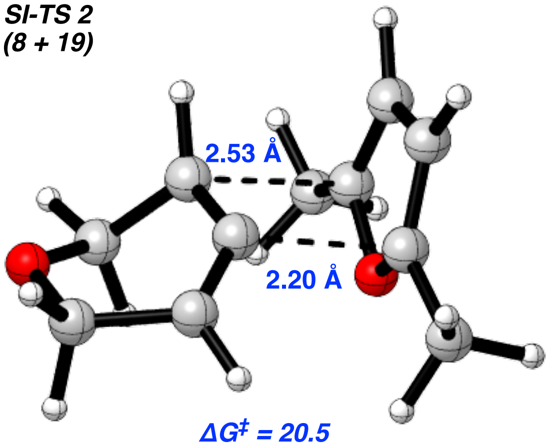
C. Geometries of Diastereomeric Transition States

SI-TS 1
(8 + 19)



ΔG‡ = 18.1

SI-TS 2
(8 + 19)



ΔG‡ = 20.5

Transition states geometries for concerted cycloaddition of 3,4-oxacyclohexadiene 8 with dimethylfuran (SI-16) at the ωB97XD/6-31G(d) level of theory. SI-TS 1 leads to endo product (major diastereomer) while SI-TS 2 leads to exo product (minor diastereomer). Endo and exo refer to the position of dimethylfuran (SI-16) relative to the additional π bond in 3,4-oxacyclohexadiene 8. $\Delta G^{\ddagger}$ values are provided (ωB97XD/6-311+G(d,p)/SMD(MeCN)//ωB97XD/6-31G(d)). The reaction occurs with a notable preference for formation of endo product ($\Delta\Delta G^{\ddagger}$ = 2.4 kcal/mol).

D. Energies and Cartesian Coordinates for Optimized Structures

8

C	-1.24674000	-0.57333100	-0.16257500
C	-1.12327600	0.91341500	0.18876500
C	0.08600700	1.36248600	-0.07564900
C	1.24937000	0.76182500	-0.23306100
C	1.11910400	-0.61060800	0.41350800
H	-1.86684900	1.38110200	0.82463900
H	-1.84708100	-1.01059600	0.64995900
H	-1.74890600	-0.77716500	-1.11281700
H	1.99450900	0.97944500	-0.99017200
H	1.96652800	-1.26520500	0.20070900

H	0.96600200	-0.54212500	1.49727300
O	0.00362700	-1.23602200	-0.23194000

Electronic energy (ωB97XD/6-311+G(d,p)/SMD(MeCN)) = -269.226878421 Hartrees
Zero-point correction = 0.098770 Hartrees
Thermal correction to enthalpy = 0.104786 Hartrees
Thermal correction to Gibbs free energy = 0.070625 Hartrees
Quasiharmonic free energy correction = 0.070625 Hartrees

SI-20

C	0.00000	0.00000	0.76352
H	-0.51001	0.88390	1.16085
H	-0.51048	-0.88363	1.16085
C	0.00000	0.00000	-0.76352
H	0.51001	0.88390	-1.16085
H	0.51048	-0.88363	-1.16085
H	-1.02049	-0.00027	-1.16085
H	1.02049	-0.00027	1.16085

Zero-point correction = 0.075745 Hartrees
Thermal correction to enthalpy = 0.080183 Hartrees
Thermal correction to Gibbs free energy = 0.054300 Hartrees
Sum of electronic and zero-point energies = -79.726239 Hartrees
Sum of electronic and thermal free energies = -79.747684 Hartrees

SI-21

O	0.00000000	0.00000000	0.11835300
H	0.00000000	-0.75982300	-0.47341300
H	0.00000000	0.75982300	-0.47341300

Zero-point correction = 0.021663 Hartrees
Thermal correction to enthalpy = 0.025442 Hartrees
Thermal correction to Gibbs free energy = 0.004014 Hartrees
Sum of electronic and zero-point energies = -76.365400 Hartrees
Sum of electronic and thermal free energies = -76.383049 Hartrees

SI-22

C	1.21220100	-0.23804600	-0.02145400
H	1.27565200	-0.96134700	0.80086000
H	1.27171200	-0.78838200	-0.96517700
H	2.07963300	0.42696600	0.05161300
C	-0.08746000	0.55385200	0.04686200
H	-0.13308800	1.12497000	0.98764200
H	-0.13020500	1.27850500	-0.77122400
O	-1.23362900	-0.26044600	-0.10945000

H	-1.24312300	-0.89198300	0.61943800

Zero-point correction = 0.081357 Hartrees
Thermal correction to enthalpy = 0.086504 Hartrees
Thermal correction to Gibbs free energy = 0.056044 Hartrees
Sum of electronic and zero-point energies = -154.903918 Hartrees
Sum of electronic and thermal free energies = -154.929231 Hartrees

SI-23

C	-1.24593	0.42500	-0.39103
H	-1.53233	1.11346	-1.18552
C	0.00103	0.42443	0.00316
C	1.24770	0.41219	0.39710
H	1.54455	1.07911	1.20724
C	2.32360	-0.46493	-0.19107
C	-2.32704	-0.46771	0.18235
H	1.92918	-1.08347	-1.00123
H	3.14621	0.14154	-0.58765
H	2.74684	-1.12632	0.57413
H	-2.09267	-1.52653	0.03124
H	-2.45039	-0.30527	1.25798
H	-3.28755	-0.26641	-0.29927

Zero-point correction = 0.114035 Hartrees
Thermal correction to enthalpy = 0.120870 Hartrees
Thermal correction to Gibbs free energy = 0.084996 Hartrees
Sum of electronic and zero-point energies = -195.105045 Hartrees
Sum of electronic and thermal free energies = -195.134084 Hartrees

19 (dimethylfuran)

C	-1.10062400	-0.00470800	0.00004100
C	-0.71706500	1.29740800	-0.00025200
C	0.71706700	1.29740700	0.00006000
C	1.10062300	-0.00471000	0.00005200
O	-0.00000100	-0.80721700	-0.00020300
H	-1.37548700	2.15469400	-0.00042000
H	1.37549200	2.15469100	0.00014700
C	2.42341600	-0.68444500	0.00015600
H	2.54622400	-1.31905700	0.88483900
H	2.54636800	-1.31906000	-0.88450600
H	3.22063300	0.06276700	0.00022400
C	-2.42341600	-0.68444400	0.00010500
H	-3.22063500	0.06276600	-0.00005000
H	-2.54625500	-1.31920100	-0.88446900
H	-2.54633500	-1.31891500	0.88487600

Electronic energy (ωB97XD/6-311+G(d,p)/SMD(MeCN)) = -308.653185 Hartrees

Zero-point correction = 0.127026 Hartrees
Thermal correction to enthalpy = 0.135217 Hartrees
Thermal correction to Gibbs free energy = 0.094751 Hartrees
Quasiharmonic free energy correction = 0.095992 Hartrees

SI-TS 1 (Endo TS)

C	-3.09697200	0.53986500	0.08949300
C	-1.72490200	1.19375000	0.16339200
C	-0.73978900	0.47238900	-0.35074300
C	-0.72115400	-0.84428800	-0.64485900
C	-1.82221600	-1.51330600	0.13848900
C	1.26139500	1.20505200	-0.02795700
C	1.83661800	-0.89929500	0.10820000
C	1.24115600	0.86703000	1.32807100
C	1.56843800	-0.48951000	1.40092100
O	1.83315000	0.17071900	-0.71773600
H	-3.56915800	0.71581500	1.07102100
H	-3.74945400	0.97662800	-0.67491100
H	-1.99004000	-2.55380600	-0.14818000
H	-1.62636700	-1.46235800	1.21941500
H	0.91250500	1.51476100	2.12839500
H	1.55397900	-1.13047700	2.27124300
H	-0.38847700	-1.24903100	-1.59519300
H	-1.59926300	2.08697200	0.77041400
O	-3.05573100	-0.84722300	-0.17652800
C	2.36268600	-2.17793600	-0.44282200
C	1.30390200	2.54298400	-0.69062900
H	3.44754900	-2.12521100	-0.59328000
H	2.15096500	-2.99456400	0.25125200
H	1.89920300	-2.40941000	-1.40529700
H	2.30831900	2.97814400	-0.64227400
H	1.00628600	2.46175800	-1.73838300
H	0.60963000	3.22240700	-0.18943600

Electronic energy (ωB97XD/6-311+G(d,p)/SMD(MeCN)) = -577.874242 Hartrees
Zero-point correction = 0.227431 Hartrees
Thermal correction to enthalpy = 0.240808 Hartrees
Thermal correction to Gibbs free energy = 0.188687 Hartrees
Quasiharmonic free energy correction = 0.189677 Hartrees

SI-TS 2 (Exo TS)

C	1.69391300	1.30305400	-0.03890400
C	3.06127400	0.62432200	-0.06184600
C	1.76074100	-1.40882000	-0.18107600

C	0.71350700	-0.77499800	0.69939200
C	0.71501400	0.55747900	0.44412900
C	-1.91718400	0.80237900	1.16055900
C	-1.34207800	1.16635600	-0.06112500
C	-1.66289200	-0.98957100	-0.14049000
C	-2.09782500	-0.57607500	1.11331500
O	-1.42199300	0.09598800	-0.90790000
H	3.49701300	0.84836400	-1.04985300
H	3.74982300	1.00641200	0.70036000
H	1.51457900	-1.28143500	-1.24511200
H	1.92870700	-2.46775000	0.02777800
H	-2.06169900	1.46437000	2.00284000
H	-2.41623500	-1.23272100	1.91112800
H	0.52789900	-1.19348700	1.68285300
O	3.01143800	-0.77500900	0.12792000
H	1.58138800	2.24346900	-0.57139500
C	-1.21761600	2.50721200	-0.70306000
H	-2.18574500	2.86027200	-1.07503400
H	-0.84111000	3.23114900	0.02429100
H	-0.52180600	2.46445900	-1.54419100
C	-1.74103500	-2.30600600	-0.83144500
H	-1.68160300	-3.11271900	-0.09696800
H	-2.68372300	-2.41089500	-1.38191400
H	-0.91796400	-2.41931400	-1.54164000

Electronic energy (ωB97XD/6-311+G(d,p)/SMD(MeCN)) = -577.871663 Hartrees
Zero-point correction = 0.228067 Hartrees
Thermal correction to enthalpy = 0.241220 Hartrees
Thermal correction to Gibbs free energy = 0.189701 Hartrees
Quasiharmonic free energy correction = 0.190847 Hartrees

References

[11] R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. B* **2011**, *115*, 14556.
[12] A. V. Marenich, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
[13] C. Y. Legault, CYLView, 1.0b; Université de Sherbrooke: Quebec, Montreal, Canada, http://www.cylview.org (2009).