Supporting Information for

"A Facile and Modular Synthesis of Phosphinooxazoline (PHOX) Ligands"

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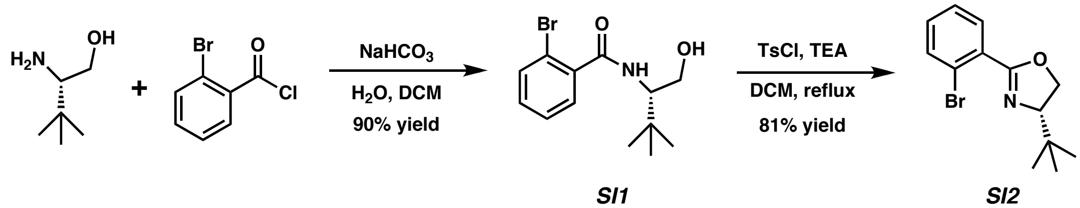
Materials and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Diphenylphosphine, di-*p*-tolylphosphine, dicyclohexylphosphine, and diisobutylphosphine were purchased from Strem Chemicals, Inc. and were used as received. Copper (I) iodide, *N,N′*-dimethylethylenediamine, cesium carbonate, 2-bromobenzoyl chloride, tetrafluoroboric acid solution and molecular sieves 4Å were purchased from Sigma-Aldrich Chemical Company and used as received. Bis-(4-(trifluoromethyl)phenyl)phosphine was prepared by the known method.[1] (*S*)-Leucinol and (*S*)-tryptophanol were purchased from Sigma-Aldrich Chemical Company and Chem-Impex International, Inc., respectively. The other starting chiral amino alcohols were prepared by the reduction of the corresponding amino acids,[2] which were purchased from Chem-Impex International, Inc. 2-Bromo-5-methoxybenzoyl chloride and 2-bromo-5-(trifluoromethyl)-benzoyl chloride were prepared from the corresponding benzoic acid derivatives.[3] Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, anisaldehyde, CAM, or $KMnO_4$ staining. ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm. ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz, 75 MHz, 121 MHz and 282 MHz, respectively). ^1H NMR spectra are reported relative to Me_4Si (δ 0.0 ppm) or residual $CHCl_3$ (δ 7.26 ppm) or CHD_2CN (δ 1.94 ppm). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept. = septet, m = multiplet, comp. m = complex multiplet, app. = apparent, bs = broad singlet. ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.0 ppm) and CD_3CN (δ 1.39 ppm), respectively. ^{19}F NMR spectra were reported relative to $CFCl_3$ (δ 0.0 ppm). ^{31}P NMR spectra were reported relative to external H_3PO_4 (δ 0.0 ppm). FTIR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the Caltech Mass Spectral Facility.

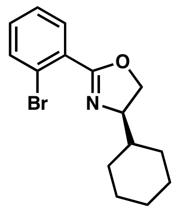
General Procedure for the Synthesis of Aryl Bromide Precursors



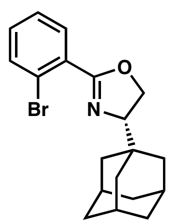
(*S*)-2-Bromo-*N*-(1-hydroxy-3,3-dimethylbutan-2-yl)benzamide (SI1). To a solution of (*S*)-*t*-leucinol (3.57 g, 30.5 mmol, 1.0 equiv) in DCM (100 mL) was added a solution of Na_2CO_3 (9.70 g, 91.5 mmol, 3.0 equiv) in water (75.0 mL). To the vigorously stirred biphasic mixture was added 2-bromobenzoyl chloride (4.58 mL, 35.1 mmol, 1.15 equiv) in a dropwise manner. After 12 h at ambient temperature, the layers were separated, and the aqueous layer was extracted with DCM (2 x 50 mL). The combined organics were treated with KOH (15 mL of a 1 M methanolic solution) for 15 min, neutralized with 3 M HCl, and water (50 mL) was added. The layers were separated, and the aqueous layer extracted with DCM (2 x 50 mL). The combined organics were dried (Na_2SO_4), evaporated, and the residue chromatographed (25 to 35% acetone in hexanes on SiO_2) to give amide **SI1** (8.19 g, 89.5% yield): mp 50.0-51.0 °C from acetone/hexanes; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.54 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.34 (app. dt, *J* = 7.4, 1.1 Hz, 1H), 7.26 (app. dt, *J* = 7.7, 1.8 Hz, 1H), 6.24 (bd, *J* = 8.1 Hz, 1H), 4.05 (m, 1H), 3.93 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.66 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.68 (bs, 1H), 1.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 137.9, 133.3, 131.2, 129.7, 127.6, 119.0, 62.9, 60.2, 33.8, 27.1; FTIR (Neat Film NaCl) 3245, 3070, 2963, 1640, 1557 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{13}H_{19}NO_2Br$ $[M+H]^+$: 300.0599, found 300.0590; $[\alpha]_D^{29}$ +20.2 (*c* 2.38, methanol, >99 % ee).

(*S*)-2-(2-Bromophenyl)-4-*tert*-butyl-4,5-dihydrooxazole[4] (SI2). A solution of amide **SI1** (8.10 g, 27.0 mmol, 1.0 equiv), *p*-toluenesulfonyl chloride (6.69 g, 35.1 mmol, 1.3 equiv), triethylamine (18.7 mL, 135.0 mmol, 5.0 equiv) in DCM (200 mL) in a round bottom flask equipped with a reflux condenser was heated at 55 °C for 22 h. At which time, water (28 mL) was added and heating continued at 75 °C for 2 h. The reaction mixture was cooled, the layers separated, and the aqueous layer extracted with DCM (2 x 25 mL). The combined organics were dried (Na_2SO_4), evaporated, and the residue chromatographed (5% EtOAc in hexanes on SiO_2) to give phenyloxazoline **SI2** (6.19 g, 81.2% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (app. dt, *J* = 8.7, 1.7 Hz, 2H), 7.33 (app. dt, *J* = 7.7, 1.5 Hz, 1H), 7.26 (m, 1H), 4.38 (dd, *J* = 10.5, 8.9 Hz, 1H), 4.25 (app. t, *J* = 8.3 Hz, 1H), 4.10 (dd, *J* = 10.2, 8.1 Hz, 1H), 1.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 133.6, 131.4, 131.2, 130.2, 127.0, 121.8, 76.6, 69.0, 34.0, 25.9; FTIR (Neat Film NaCl) 2956, 1661, 1478, 1354, 1099, 1022, 963 cm^{-1}; HRMS (FAB Pos.) *m/z* calc'd for $C_{13}H_{17}NOBr$ $[M+H]^+$: 282.0493, found 282.0488; $[\alpha]_D^{29}$ -48.3 (c 3.77, hexane, >99 % ee).

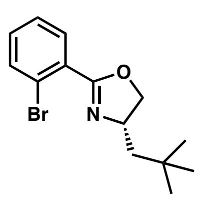
The following aryl bromides were synthesized from the corresponding chiral amino alcohols and 2-bromobenzoyl chlorides by the same manner as described above.



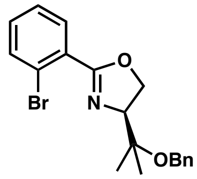
(*R*)-2-(2-Bromophenyl)-4-cyclohexyl-4,5-dihydrooxazole. White powder; mp 132-134 ºC; R_f = 0.50 (hexanes/EtOAc, 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.33 (td, *J* = 7.4, 1.4 Hz, 1H), 7.27 (td, *J* = 7.7, 2.2 Hz, 1H), 5.44 (m, 1H), 4.17 (m, 2H), 1.97 (d, *J* = 12.7 Hz, 1H), 1.73 (m, 4H), 1.58 (m, 1H), 1.17 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 133.9, 131.6, 131.5, 127.2, 121.9, 72.3, 70.7, 42.8, 29.6, 29.0, 26.7, 26.3; FTIR (Neat Film NaCl) 2924, 1640, 1537, 1468, 1328, 1057, 1026 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{18}NOBr$ [M$^+$]: 307.0572, found 307.0581; $[\alpha]_D^{25}$ = +14.5 (*c* 0.125, $CHCl_3$).



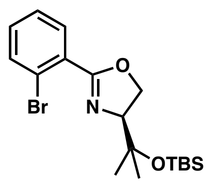
(*S*)-4-(1-Adamantyl)-2-(2-bromophenyl)-4,5-dihydrooxazole. White wax; R_f = 0.43 (hexanes/Et_2O, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.60 (m, 2H), 7.36-7.23 (m, 2H), 4.39-4.26 (m, 2H), 3.94 (m, 1H), 2.01 (m, 3H), 1.80-1.63 (m, 10H), 1.58-1.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 133.7, 131.4, 131.3, 130.3, 127.0, 121.8, 76.8, 67.5, 38.6, 37.1, 35.7, 28.2; FTIR (Neat Film NaCl) 2902, 2848, 1659, 1591, 1478, 1449, 1346, 1308, 1246, 1095, 1022, 960, 764, 731 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{19}H_{23}BrNO$ [M+H]$^+$: 360.0963, found 360.0958; $[\alpha]_D^{26}$ = -80.8 (*c* 1.12, $CHCl_3$).



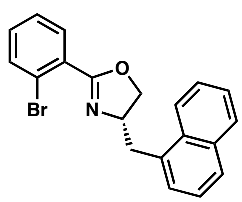
(*S*)-2-(2-Bromophenyl)-4-neopentyl-4,5-dihydrooxazole. Colorless oil; R_f = 0.48 (hexanes/Et_2O, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.32 (td, *J* = 7.8, 1.5 Hz, 1H), 7.26 (td, *J* = 7.8, 1.5 Hz, 1H), 4.57 (dd, *J* = 9.3, 8.1 Hz, 1H), 4.35 (m, 1H), 3.99 (t, *J* = 8.1 Hz, 1H), 1.92 (dd, *J* = 13.8, 4.8 Hz, 1H), 1.47 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 133.7, 131.5, 131.3, 130.0, 127.0, 121.8, 74.5, 64.5, 50.5, 30.3, 30.0; FTIR (Neat Film NaCl) 2955, 1654, 1592, 1475, 1431, 1356, 1244, 1093, 1026, 966, 765, 730 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{14}H_{19}BrNO$ [M+H]$^+$: 296.0650, found 296.0660; $[\alpha]^{26}_D$ = -47.7 (*c* 1.04, $CHCl_3$).



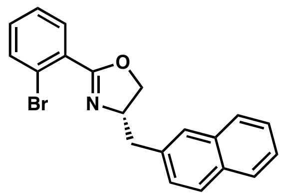
(*S*)-4-(2-(Benzyloxy)propan-2-yl)-2-(2-bromophenyl)-4,5-dihydrooxazole. White solid; mp 54-56 ºC; R_f = 0.26 (hexanes/Et_2O, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.62 (m, 2H), 7.37-7.24 (m, 7H), 4.65-4.39 (m, 5H), 1.49 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 139.4, 133.7, 131.6, 131.3, 130.0, 128.3, 127.2, 127.14, 127.07, 121.8, 77.0, 75.1, 69.2, 64.0, 24.0, 20.1; FTIR (Neat Film NaCl) 3064, 3031, 2975, 2906, 1654, 1590, 1474, 1454, 1435, 1386, 1354, 1244, 1155, 1100, 1064, 1027, 960, 735 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{19}H_{21}BrNO_2$ $[M+H]^+$: 374.0756, found 374.0748; $[\alpha]^{26}_D$ = +18.1 (*c* 1.04, $CHCl_3$).



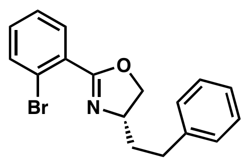
(*S*)-2-(2-Bromophenyl)-4-(2-(*tert*-butyldimethylsilyloxy)propan-2-yl)-4,5-dihydrooxazole. Colorless oil; R_f = 0.52 (hexanes/Et_2O, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.62 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.32 (td, *J* = 7.5, 1.2 Hz, 1H), 7.26 (td, *J* = 7.5, 2.1 Hz, 1H), 4.52 (dd, *J* = 8.4, 7.2 Hz, 1H), 4.39 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.22 (dd, *J* = 10.2, 7.2 Hz, 1H), 1.39 (s, 3H), 1.29 (s, 3H), 0.84 (s, 9H), 0.114 (s, 3H), 0.111 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 133.8, 131.5, 131.3, 130.0, 127.0, 121.8, 77.0, 74.8, 69.3, 28.8, 25.7, 24.7, 18.0, -2.1, -2.2; FTIR (Neat Film NaCl) 2956, 2929, 2856, 1656, 1591, 1472, 1435, 1381, 1355, 1253, 1187, 1162, 1101, 1053, 835, 773 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{18}H_{29}BrNO_2Si$ $[M+H]^+$: 398.1151, found 398.1150; $[\alpha]^{26}_D$ = +37.4 (*c* 1.01, $CHCl_3$).



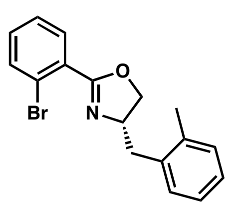
(*S*)-2-(2-Bromophenyl)-4-(naphthalen-1-ylmethyl)-4,5-dihydrooxazole. Colorless oil; R_f = 0.44 (hexanes/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.88 (m, 1H), 7.78 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.70-7.64 (m, 2H), 7.60-7.26 (m, 6H), 4.84 (m, 1H), 4.36-4.23 (m, 2H), 3.84 (dd, *J* = 14.1, 4.8 Hz, 1H), 3.12 (dd, *J* = 14.1, 9.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 134.0, 133.80, 133.76, 132.0, 131.6, 131.3, 129.9, 128,8, 127.5, 127.1, 127.0, 126.1, 125.7, 125.4, 123.8, 121.8, 72.2, 67.2, 38.9; FTIR (Neat Film NaCl) 3057, 1653, 1590, 1476, 1430, 1355, 1087, 1024, 960, 780, 729 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{20}H_{17}BrNO$ [M+H]$^+$: 366.0493, found 366.0471; $[\alpha]^{26}_{D}$ = -10.4 (*c* 1.08, $CHCl_3$).



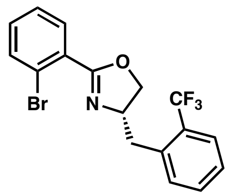
(*S*)-2-(2-Bromophenyl)-4-(naphthalen-2-ylmethyl)-4,5-dihydrooxazole. Colorless oil; R_f = 0.37 (hexanes/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84-7.78 (m, 3H), 7.73 (br s, 1H), 7.68-7.63 (m, 2H), 7.51-7.41 (m, 3H), 7.37-7.28 (m, 2H), 4.75 (m, 1H), 4.39 (dd, *J* = 9.3, 8.4 Hz, 1H), 4.24 (dd, *J* = 8.4, 7.5 Hz, 1H), 3.42 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.99 (dd, *J* = 13.8, 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 135.2, 133.8, 133.5, 132.3, 131.6, 131.2, 129.8, 128.2, 127.74, 127.70, 127.6, 127.5, 127.0, 126.0, 125.5, 121.8, 71.9, 68.1, 41.7; FTIR (Neat Film NaCl) 3054, 2896, 1650, 1590, 1508, 1477, 1431, 1356, 1244, 1097, 1024, 962, 818, 756, 729 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{20}H_{17}BrNO$ [M+H]$^+$: 366.0493, found 366.0484; $[\alpha]^{26}_{D}$ = +2.0 (*c* 0.92, $CHCl_3$).



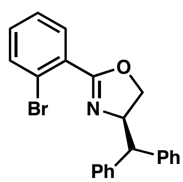
(*S*)-2-(2-Bromophenyl)-4-phenethyl-4,5-dihydrooxazole. Colorless oil; R_f = 0.43 (hexanes/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.62 (m, 2H), 7.38-7.17 (m, 7H), 4.50 (dd, *J* = 9.3, 8.1 Hz, 1H), 4.36 (m, 1H), 4.08 (t, *J* = 8.1 Hz, 1H), 2.94-2.74 (m, 2H), 2.09 (m, 1H), 1.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 141.6, 133.7, 131.5, 131.2, 130.0, 128.43, 128.40, 127.1, 125.9, 121.8, 72.6, 66.5, 37.6, 32.2; FTIR (Neat Film NaCl) 2924, 1653, 1590, 1476, 1430, 1355, 1096, 1024, 962, 764, 730, 700 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{17}H_{17}BrNO$ [M+H]$^+$: 330.0493, found 330.0480; $[\alpha]^{24}_{D}$ = -70.7 (c 1.14, $CHCl_3$).



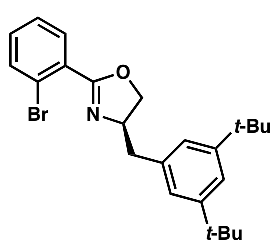
(*S*)-2-(2-Bromophenyl)-4-(2-methylbenzyl)-4,5-dihydrooxazole. White solid; mp 53-55 ºC; R_f = 0.43 (hexanes/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.65 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 (td, *J* = 7.5, 2.1 Hz, 1H), 7.25-7.14 (m, 4H), 4.66 (m, 1H), 4.41 (t, *J* = 8.7 Hz, 1H), 4.21 (dd, *J* = 8.7, 7.5 Hz, 1H), 3.29 (dd, *J* = 14.1, 5.4 Hz, 1H), 2.79 (dd, *J* = 14.1, 9.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 136.4, 136.1, 133.7, 131.5, 131.2, 130.4, 129.8, 129.5, 127.0, 126.6, 126.0, 121.7, 72.1, 66.9, 38.9, 19.7; FTIR (Neat Film NaCl) 2954, 1653, 1590, 1476, 1436, 1355, 1244, 1097, 1025, 962, 765, 730 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{17}H_{17}BrNO$ $[M+H]^+$: 330.0493, found 330.0501; $[\alpha]^{24}_D$ = -18.7 (*c* 1.03, $CHCl_3$).



(*S*)-2-(2-Bromophenyl)-4-(2-(trifluoromethyl)benzyl)-4,5-dihydrooxazole. Colorless oil; R_f = 0.52 (hexanes/EtOAc, 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.72-7.63 (m, 3H), 7.59 (m, 1H), 7.51 (m, 1H), 7.39-7.26 (m, 3H), 4.68 (m, 1H), 4.50 (t, *J* = 8.4 Hz, 1H), 4.15 (t, *J* = 8.4 Hz, 1H), 3.27 (dd, *J* = 14.7, 7.2 Hz, 1H), 3.12 (ddd, *J* = 14.7, 6.3, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 136.6 (q, J_{CF} = 1 Hz), 133.7, 132.1, 131.8, 131.7, 131.2, 129.7, 128.8 (q, J_{CF} = 29 Hz), 127.1, 126.6, 126.0 (q, J_{CF} = 6 Hz), 124.5 (q, J_{CF} = 272 Hz), 121.8, 72.1, 67.5, 38.1 (q, J_{CF} = 1 Hz); FTIR (Neat Film NaCl) 3068, 2897, 1653, 1591, 1478, 1457, 1432, 1357, 1314, 1161, 1117, 1061, 1040, 964, 766, 730, 654 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{17}H_{14}BrF_3NO$ $[M+H]^+$: 384.0211, found 384.0216; $[\alpha]^{25}_D$ = -72.7 (*c* 0.85, $CHCl_3$).

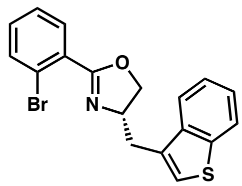


(*R*)-4-Benzhydryl-2-(2-bromophenyl)-4,5-dihydrooxazole. White solid; mp 73-74 ºC; R_f = 0.52 (hexanes/EtOAc, 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.62-7.55 (m, 2H), 7.39-7.15 (m, 12H), 5.18 (m, 1H), 4.49 (t, *J* = 6.0 Hz, 1H), 4.22-4.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 142.0, 141.8, 133.6, 131.5, 131.3, 129.9, 128.70, 128.67, 128.4, 127.0, 126.8, 126.5, 121.9, 71.5, 70.5, 56.7; FTIR (Neat Film NaCl) 3026, 1654, 1559, 1540, 1496, 1474, 1450, 1356, 1097, 1024, 963, 701 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{22}H_{19}BrNO$ $[M+H]^+$: 392.0650, found 392.0641; $[\alpha]^{25}_D$ = +49.9 (*c* 0.68, $CHCl_3$).

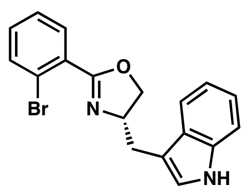


(*R*)-2-(2-Bromophenyl)-4-(3,5-di-*tert*-butylbenzyl)-4,5-dihydrooxazole. Colorless oil; R_f = 0.57 (hexanes/EtOAc, 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.5, 2.1

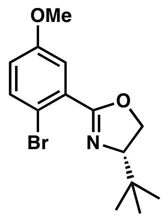
Hz, 1H), 7.65 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.38-7.28 (m, 3H), 7.10 (d, *J* = 1.8 Hz, 2H), 4.64 (m, 1H), 4.39 (t, *J* = 8.4 Hz, 1H), 4.22 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.27 (dd, *J* = 13.5, 4.8 Hz, 1H), 2.77 (dd, *J* = 13.5, 9.0 Hz, 1H), 1.34 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 150.8, 136.8, 133.8, 131.5, 131.3, 129.7, 127.0, 123.4, 121.8, 120.5, 72.0, 68.4, 42.1, 34.7, 31.4; FTIR (Neat Film NaCl) 2963, 1654, 1598, 1476, 1362, 1247, 1098, 1023, 964 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{24}H_{31}BrNO$ [M+H]$^+$: 428.1589, found 428.1597; $[\alpha]^{25}_D$ = -3.8 (*c* 1.04, $CHCl_3$).



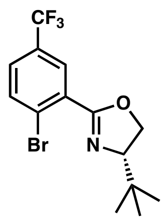
(*S*)-4-(Benzo[*b*]thiophen-3-ylmethyl)-2-(2-bromophenyl)-4,5-dihydrooxazole. Pale yellow oil; R_f = 0.45 (hexanes/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.84 (m, 2H), 7.67-7.63 (m, 2H), 7.45-7.26 (m, 5H), 4.81 (m, 1H), 4.44 (dd, *J* = 9.3, 8.7 Hz, 1H), 4.22 (dd, *J* = 8.7, 7.2 Hz, 1H), 3.46 (ddd, *J* = 14.7, 4.8, 1.2 Hz, 1H), 3.06 (ddd, *J* = 14.7, 8.4, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 140.4, 138.9, 133.8, 132.3, 131.7, 131.3, 129.7, 127.1, 124.3, 124.0, 123.1, 122.9, 121.8, 121.7, 72.3, 66.5, 34.4; FTIR (Neat Film NaCl) 3067, 2895, 1653, 1590, 1476, 1427, 1357, 1314, 1287, 1250, 1095, 1022, 961, 758, 728 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{18}H_{15}BrNOS$ [M+H]$^+$: 372.0058, found 372.0064; $[\alpha]^{25}_D$ = -1.3 (*c* 0.62, $CHCl_3$).



(*S*)-4-((1*H*-Indol-3-yl)methyl)-2-(2-bromophenyl)-4,5-dihydrooxazole. Pale yellow powder; mp 143-145 ºC; R_f = 0.17 (hexanes/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 7.72-7.62 (m, 3H), 7.38-7.06 (m, 6H), 4.77 (m, 1H), 4.39 (dd, *J* = 9.3, 8.7 Hz, 1H), 4.22 (dd, *J* = 8.7, 7.5 Hz, 1H), 3.39 (ddd, *J* = 14.7, 5.1, 1.2 Hz, 1H), 2.97 (dd, *J* = 14.7, 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 136.2, 133.7, 131.6, 131.3, 129.9, 127.6, 127.1, 122.5, 122.1, 121.8, 119.4, 118.8, 111.8, 111.1, 72.4, 67.3, 31.2; FTIR (Neat Film NaCl) 3413, 3217, 3057, 2923, 1652, 1590, 1477, 1456, 1433, 1358, 1243, 1099, 1025, 957, 743 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{18}H_{16}BrN_2O$ [M+H]$^+$: 355.0446, found 355.0448; $[\alpha]^{25}_D$ = -1.0 (*c* 0.62, $CHCl_3$).

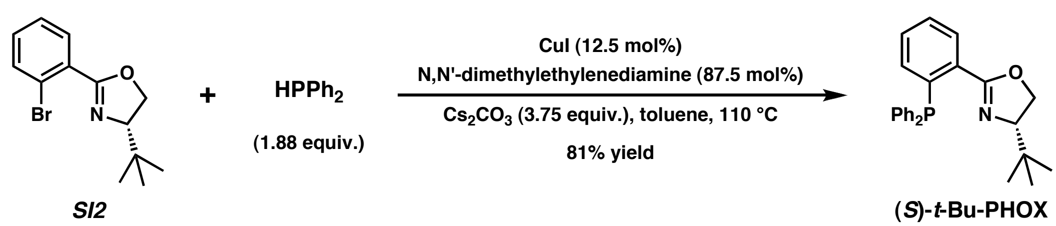


(*S*)-2-(2-Bromo-5-methoxyphenyl)-4-*tert*-butyl-4,5-dihydrooxazole. White powder; mp 41-43 °C; R_f = 0.52 (hexanes/Et_2O, 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 9.0 Hz, 1H), 7.19 (d, *J* = 3.0 Hz, 1H), 6.84 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.38 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.26 (t, *J* = 8.3 Hz, 1H), 4.10 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.81 (s, 3H), 1.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 158.5, 134.4, 130.7, 117.9, 116.1, 112.1, 76.6, 69.0, 55.6, 34.0, 25.9; FTIR (Neat Film NaCl) 2957, 1662, 1594, 1571, 1476, 1410, 1364, 1336, 1290, 1224, 1181, 1102, 1040, 1016, 969, 816 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{18}BrNO_2$ [M^+]: 311.0521, found 311.0536; $[\alpha]^{24}_D$ = -64.4 (*c* 1.08, $CHCl_3$).



(*S*)-2-(2-Bromo-5-(trifluoromethyl)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole. White powder; mp 32-33 °C; R_f = 0.42 (hexanes/Et_2O, 9/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.42 (dd, *J* = 10.2, 9.0 Hz, 1H), 4.29 (t, *J* = 8.3 Hz, 1H), 4.14 (dd, *J* = 10.2, 8.1 Hz, 1H), 1.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 134.5, 130.9, 129.8 (q, J_{CF} = 33 Hz), 128.2 (q, J_{CF} = 4 Hz), 127.9 (q, J_{CF} = 4 Hz), 125.9 (q, J_{CF} = 1 Hz), 123.4 (q, J_{CF} = 271 Hz), 76.9, 69.2, 34.0, 25.9; FTIR (Neat Film NaCl) 2959, 1662, 1607, 1479, 1341, 1325, 1298, 1262, 1242, 1174, 1134, 1082, 1028, 966, 912, 830 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{15}BrF_3NO$ [M^+]: 349.0289, found 349.0299; $[\alpha]^{25}_D$ = -64.7 (*c* 1.26, $CHCl_3$).

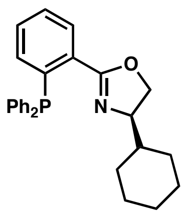
General Procedure for the Copper Catalyzed Synthesis of PHOX Ligands



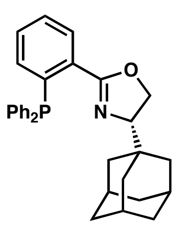
(*S*)-4-*tert*-Butyl-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole (*S*)-*t*-Bu-PHOX). A mixture of copper(I) iodide (338.3 mg, 1.77 mmol, 0.125 equiv), diphenylphosphine (4.64 mL, 26.7 mmol, 1.88 equiv), *N,N*'-dimethylethylenediamine

(1.32 mL, 12.4 mmol, 0.875 equiv) in toluene (60 mL) was stirred for 20 min at ambient temperature. At which point, phenyloxazoline **SI2** (4.00 g, 14.2 mmol, 1.00 equiv), cesium carbonate (17.4 g, 53.3 mmol, 3.75 equiv), and toluene (60 mL) were added, the flask sealed and heated to 110 °C with stirring. After 6 h, the reaction mixture was allowed to cool to ambient temperature, filtered, and the filter cake was washed with DCM (2 x 50 mL). Evaporation of the solvent and chromatography (3 to 7 % Et_2O in hexanes on SiO_2) afforded the known[5] **(*S*)-*t*-Bu-PHOX** (4.48 g, 81 % yield).

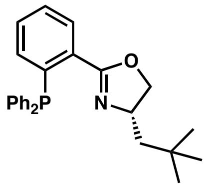
The following PHOX derivatives were synthesized from the corresponding aryl bromides and diarylphosphines by the procedure described above.



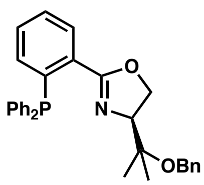
(*R*)-4-Cyclohexyl-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole. White solid; mp 122-124 ºC; R_f = 0.57 (hexanes/EtOAc, 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (ddd, *J* = 7.7, 4.1, 1.7 Hz, 1H), 7.27 (m, 13H), 6.82 (ddd, *J* = 7.7, 4.1, 1.1 Hz, 1H), 4.12 (ddd, *J* = 14.6, 9.1, 1.4 Hz, 1H), 3.85 (t, *J* = 8.3 Hz, 1H), 3.81 (t, *J* = 8.5 Hz, 1H), 1.60 (m, 4H), 1.28 (d, *J* = 13.5 Hz, 1H), 1.05 (m, 4H), 0.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7 (d, J_{CP} = 3 Hz), 138.0-139.0 (6 lines), 134.5 (d, J_{CP} = 21 Hz), 133.8, 133.7 (d, J_{CP} = 20 Hz), 131.8 (d, J_{CP} = 19 Hz), 130.4, 129.8 (d, J_{CP} = 3 Hz), 128.6-128.0 (7 lines), 71.2, 70.1, 42.7, 29.4, 29.0, 26.4, 26.1, 26.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ -4.21; FTIR (Neat Film NaCl) 3053, 2923, 2852, 1651, 1478, 1434, 1356, 1089, 1044, 964, 908 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{27}H_{28}NOP$ [M$^+$]: 413.1909, found 413.1923; $[\alpha]^{25}_D$ = +47.9 (*c* 0.175, $CHCl_3$).



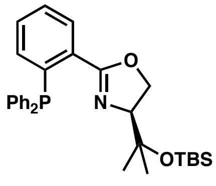
(*S*)-4-(1-Adamantyl)-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole. White solid; mp 163-164 ºC; R_f = 0.59 (hexanes/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (m, 1H), 7.40-7.20 (m, 12H), 6.85 (m, 1H), 4.11 (t, *J* = 9.0 Hz, 1H), 4.03 (t, *J* = 9.0 Hz, 1H), 3.73 (t, *J* = 9.0 Hz, 1H), 1.85 (m, 3H), 1.68-1.46 (m, 6H), 1.44-1.34 (m, 3H), 1.24-1.14 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4 (d, J_{CP} = 3 Hz), 138.8-138.3 (6 lines), 134.4 (d, J_{CP} = 21 Hz), 134.1, 133.4 (d, J_{CP} = 20 Hz), 132.0 (d, J_{CP} = 20 Hz), 130.3, 129.7 (d, J_{CP} = 3 Hz), 128.5-128.0 (7 lines), 76.8, 66.8, 38.2, 37.0, 35.3, 28.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ -5.67; FTIR (Neat Film NaCl) 3053, 2902, 2848, 1651, 1586, 1477, 1434, 1346, 1248, 1089, 1044, 1026, 963, 744, 696 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{31}H_{33}NOP$ [M+H]$^+$: 466.2300, found 466.2309; $[\alpha]^{27}_D$ = -31.8 (*c* 0.48, $CHCl_3$).



(*S*)-2-(2-(Diphenylphosphino)phenyl)-4-neopentyl-4,5-dihydrooxazole. White solid; mp 83-86 ºC; R_f = 0.52 (hexanes/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 7.8, 3.6, 1.5 Hz, 1H), 7.38-7.23 (m, 12H), 6.84 (ddd, *J* = 7.8, 4.5, 1.5 Hz, 1H), 4.25 (dd, *J* = 9.3, 8.1 Hz, 1H), 4.03 (m, 1H), 3.58 (t, *J* = 8.1 Hz, 1H), 1.52 (dd, *J* = 14.1, 4.5 Hz, 1H), 0.93 (dd, *J* = 14.1, 8.1 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0 (d, J_{CP} = 3 Hz), 138.7 (d, J_{CP} = 25 Hz), 137.9 (d, J_{CP} = 12 Hz), 137.8 (d, J_{CP} = 10 Hz), 134.3 (d, J_{CP} = 21 Hz), 133.9 (d, J_{CP} = 21 Hz), 133.5 (d, J_{CP} = 2 Hz), 131.8 (d, J_{CP} = 18 Hz), 130.3, 129.8 (d, J_{CP} = 3 Hz), 128.6-128.3 (6 lines), 127.9, 73.9, 64.0, 49.7, 30.0, 29.8; ^{31}P NMR (121 MHz, $CDCl_3$) δ -3.95; FTIR (Neat Film NaCl) 3054, 2955, 1652, 1586, 1476, 1434, 1355, 1248, 1089, 1035, 968, 742, 697 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{26}H_{29}NOP$ [M+H]$^+$: 402.1987, found 402.2002; $[\alpha]^{26}_D$ = -6.9 (*c* 1.03, $CHCl_3$).

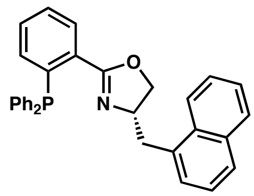


(*S*)-4-(2-(Benzyloxy)propan-2-yl)-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole. Colorless viscous oil; R_f = 0.45 (hexanes/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (ddd, *J* = 7.5, 3.6, 1.2 Hz, 1H), 7.41-7.19 (m, 17H), 6.88 (ddd, *J* = 7.5, 4.2, 0.9 Hz, 1H), 4.43-4.23 (m, 4H), 4.15 (dd, *J* = 9.6, 7.8 Hz, 1H), 1.21 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (d, J_{CP} = 3 Hz), 139.5, 139.1-138.3 (5 lines), 134.4 (d, J_{CP} = 21 Hz), 134.2, 133.5 (d, J_{CP} = 20 Hz), 131.6 (d, J_{CP} = 19 Hz), 130.5, 129.9 (d, J_{CP} = 3 Hz), 128.6-128.1 (6 lines), 127.14, 127.12, 76.9, 74.9, 68.5, 63.9, 23.9, 19.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ -5.51; FTIR (Neat Film NaCl) 3067, 2973, 2905, 1649, 1586, 1478, 1434, 1352, 1248, 1155, 1091, 1065, 1027, 964, 743, 697 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{31}H_{31}NO_2P$ [M+H]$_+$: 480.2092, found 480.2078; $[\alpha]^{26}_D$ = -2.0 (*c* 1.03, $CHCl_3$).

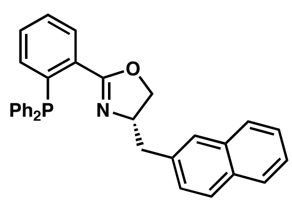


(*S*)-4-(2-(*tert*-Butyldimethylsilyloxy)propan-2-yl)-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole. White solid; mp 104-106 ºC; R_f = 0.62 (hexanes/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (ddd, *J* = 7.5, 3.6, 1.2 Hz, 1H), 7.40-7.20 (m, 12H), 6.88

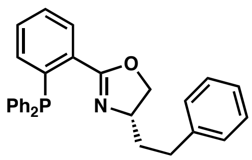
(ddd, *J* = 7.5, 3.9, 0.9 Hz, 1H), 4.32 (dd, *J* = 7.5, 6.6 Hz, 1H), 4.09 (dd, *J* = 10.2, 7.5 Hz, 1H), 4.02 (dd, *J* = 10.2, 6.6 Hz, 1H), 1.15 (s, 3H), 0.86 (s, 3H), 0.78 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 139.0-138.3 (6 lines), 134.3 (d, J_{CP} = 21 Hz), 134.2, 133.5 (d, J_{CP} = 20 Hz), 131.9 (d, J_{CP} = 19 Hz), 130.4, 129.8 (d, J_{CP} = 3 Hz), 128.5-128.0 (5 lines), 76.8, 74.9, 68.7, 28.7, 25.7, 23.9, 17.9, -2.2, -2.3; ^{31}P NMR (121 MHz, $CDCl_3$) δ -5.99; FTIR (Neat Film NaCl) 3054, 2955, 2929, 2856, 1652, 1586, 1472, 1434, 1353, 1251, 1162, 1091, 1058, 835, 774, 743, 696 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{30}H_{39}NO_2PSi$ $[M+H]^+$: 504.2488, found 504.2469; $[\alpha]^{26}_D$ = +19.8 (*c* 1.16, $CHCl_3$).



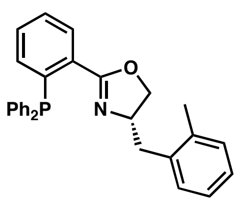
(*S*)-2-(2-(Diphenylphosphino)phenyl)-4-(naphthalen-1-ylmethyl)-4,5-dihydrooxazole. White amorphous solid; R_f = 0.29 (hexanes/Et_2O, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (m, 1H), 7.91 (m, 1H), 7.85 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.56-7.45 (m, 2H), 7.42-7.28 (m, 13H), 7.16 (m, 1H), 6.87 (m, 1H), 4.55 (m, 1H), 3.97 (t, *J* = 8.4 Hz, 1H), 3.86 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.44 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.39 (dd, *J* = 14.4, 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1 (d, J_{CP} = 3 Hz), 138.9 (d, J_{CP} = 25 Hz), 137.84 (d, J_{CP} = 10 Hz), 137.79 (d, J_{CP} = 12 Hz), 134.5 (d, J_{CP} = 21 Hz), 134.0, 133.82 (d, J_{CP} = 21 Hz), 133.80, 133.5 (d, J_{CP} = 3 Hz), 131.9, 131.3 (d, J_{CP} =17 Hz), 130.6, 130.0 (d, J_{CP} =3 Hz), 128.8-128.4 (6 lines), 127.9, 127.2, 126.6, 126.0, 125.6, 125.4, 123.8, 71.7, 66.7, 38.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ -3.59; FTIR (Neat Film NaCl) 3052, 2962, 1651, 1585, 1511, 1476, 1434, 1354, 1216, 1089, 1037, 963, 745, 697 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{32}H_{27}NOP$ $[M+H]^+$: 472.1830, found 472.1835; $[\alpha]^{24}_D$ = +29.7 (*c* 0.50, $CHCl_3$).



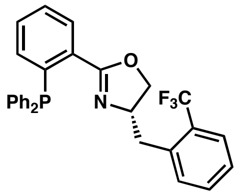
(*S*)-2-(2-(Diphenylphosphino)phenyl)-4-(naphthalen-2-ylmethyl)-4,5-dihydrooxazole. White amorphous solid; R_f = 0.24 (hexanes/Et_2O, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (m, 1H), 7.82-7.72 (m, 3H), 7.53 (br s, 1H), 7.49-7.27 (m, 14H), 7.23 (m, 1H), 6.88 (m, 1H), 4.46 (m, 1H), 4.05 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.83 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.08 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.30 (dd, *J* = 14.1, 9.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0 (d, J_{CP} = 3 Hz), 138.9 (d, J_{CP} = 25 Hz), 137.0-137.7 (3 lines), 135.6, 134.4 (d, J_{CP} = 21 Hz), 133.8 (d, J_{CP} = 21 Hz), 133.5 (d, J_{CP} = 2 Hz), 133.4, 132.1, 131.4 (d, J_{CP} = 18 Hz), 130.5, 129.9 (d, J_{CP} = 3 Hz), 128.7-127.4 (12 lines), 125.9, 125.4, 71.4, 67.7, 41.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ -4.05; FTIR (Neat Film NaCl) 3052, 1651, 1508, 1476, 1434, 1354, 1217, 1090, 1027, 964, 817, 743, 697 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{32}H_{27}NOP$ $[M+H]^+$: 472.1830, found 472.1845; $[\alpha]^{25}_D$ = +42.7 (*c* 0.50, $CHCl_3$).



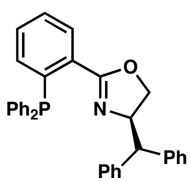
(*S*)-2-(2-(Diphenylphosphino)phenyl)-4-phenethyl-4,5-dihydrooxazole. Colorless viscous oil; R_f = 0.38 (hexanes/Et_2O, 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (ddd, *J* = 7.5, 3.6, 1.5 Hz, 1H), 7.40-7.14 (m, 15H), 7.11-7.07 (m, 2H), 6.87 (ddd, *J* = 7.5, 4.2, 1.5 Hz, 1H), 4.22 (dd, *J* = 9.6, 8.1 Hz, 1H), 4.08 (m, 1H), 3.71 (t, *J* = 8.1 Hz, 1H), 2.66-2.45 (m, 2H), 1.72-1.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0 (d, J_{CP} = 2 Hz), 141.8, 138.7 (d, J_{CP} = 25 Hz), 138.1 (d, J_{CP} = 12Hz), 138.0 (d, J_{CP} = 10 Hz), 134.2 (d, J_{CP} = 21 Hz), 133.73 (d, J_{CP} = 1 Hz), 133.69 (d, J_{CP} = 20 Hz), 131.7 (d, J_{CP} = 19 Hz), 130.4, 129.7 (d, J_{CP} = 3 Hz), 128.5-128.1 (6 lines), 127.9,125.6, 72.0, 66.3, 37.2, 32.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ -4.55; FTIR (Neat Film NaCl) 3055, 2926, 1652, 1602, 1585, 1495, 1476, 1454, 1434, 1355, 1308, 1251, 1217, 1134, 1090, 1036, 968, 743, 696 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{29}H_{27}NOP$ $[M+H]^+$: 436.1830, found 436.1817; $[\alpha]^{25}_D$ = -56.9 (*c* 0.50, $CHCl_3$).



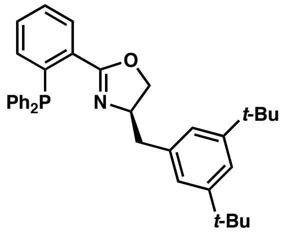
(*S*)-2-(2-(Diphenylphosphino)phenyl)-4-(2-methylbenzyl)-4,5-dihydrooxazole. Colorless viscous oil; R_f = 0.33 (hexanes/Et_2O, 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (m, 1H), 7.40-7.26 (m, 12H), 7.14-7.06 (m, 3H), 7.00-6.95 (m, 1H), 6.86 (m, 1H), 4.35 (m, 1H), 4.06 (t, *J* = 8.4 Hz, 1H), 3.79 (dd, *J* = 8.4, 7.5 Hz, 1H), 2.91 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.26 (s, 3H), 2.10 (dd, *J* = 14.1, 9.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (d, J_{CP} = 3 Hz), 138.9 (d, J_{CP} = 25 Hz), 137.9-137.7 (3 lines), 136.4, 134.4 (d, J_{CP} = 21 Hz), 133.8 (d, J_{CP} = 21 Hz), 133.5 (d, J_{CP} = 3Hz), 131.4 (d, J_{CP} = 18 Hz), 130.5, 130.3, 129.9 (d, J_{CP} = 3 Hz), 129.2, 128.7-128.3 (5 lines), 127.9, 126.4, 125.9, 71.6, 66.4, 38.4, 19.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ -3.77; FTIR (Neat Film NaCl) 3052, 1649, 1477, 1434, 1354, 1090, 1027, 964, 741, 697 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{29}H_{27}NOP$ $[M+H]^+$: 436.1830, found 436.1798; $[\alpha]^{25}_D$ = +33.0 (*c* 0.26, $CHCl_3$).



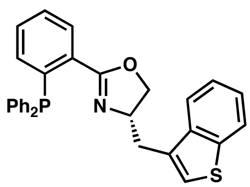
(*S*)-2-(2-(Diphenylphosphino)phenyl)-4-(2-(trifluoromethyl)benzyl)-4,5-dihydrooxazole. Colorless viscous oil; R_f = 0.48 (hexanes/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (ddd, *J* = 7.5, 3.6, 1.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.45-7.27 (m, 15H), 6.88 (ddd, *J* = 7.5, 3.9, 1.2 Hz, 1H), 4.39 (m, 1H), 4.19 (dd, *J* = 9.3, 8.4 Hz, 1H), 3.79 (t, *J* = 8.4 Hz, 1H), 2.89 (dd, *J* = 14.7, 7.2 Hz, 1H), 2.64 (ddd, *J* = 14.7, 6.3, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (d, J_{CP} = 3 Hz), 138.9 (d, J_{CP} = 25 Hz), 137.9 (d, J_{CP} = 12Hz), 137.8 (d, J_{CP} = 10Hz), 137.0, 134.3 (d, J_{CP} = 21 Hz), 133.72 (d, J_{CP} = 20 Hz), 133.66 (d, J_{CP} = 2 Hz), 131.8, 131.7, 131.5 (d, J_{CP} = 19 Hz), 130.6, 129.9 (d, J_{CP} = 3 Hz), 128.7-128.3 (6 lines), 128.0, 126.3, 125.8 (q, J_{CF} = 6 Hz), 124.5 (q, J_{CF} = 273 Hz), 71.6, 67.3, 37.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ -4.64; ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.76; FTIR (Neat Film NaCl) 3067, 1648, 1608, 1584, 1477, 1434, 1356, 1313, 1161, 1117, 1038, 742, 696 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{29}H_{24}F_3NOP$ $[M+H]^+$: 490.1548, found 490.1528; $[\alpha]^{26}_D$ = -39.1 (*c* 0.75, $CHCl_3$).



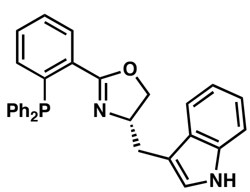
(*R*)-4-Benzhydryl-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole. White amorphous solid; R_f = 0.45 (hexanes/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 1H), 7.38-7.13 (m, 22H), 6.88 (m, 1H), 4.92 (q, *J* = 9.0 Hz, 1H), 4.13 (dd, *J* = 9.3, 9.0 Hz, 1H), 3.79 (t, *J* = 9.0 Hz, 1H), 3.72 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 142.2, 142.1, 138.8 (d, J_{CP} = 25 Hz), 138.0-137.7 (3 lines), 134.1 (d, J_{CP} = 21 Hz), 133.9 (d, J_{CP} = 21 Hz), 133.7 (d, J_{CP} = 2 Hz), 131.7 (d, J_{CP} = 19 Hz), 130.5, 130.0 (d, J_{CP} = 3 Hz), 128.7-128.2 (9 lines), 128.0, 126.5, 126.2, 71.1, 70.1, 56.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ -5.22; FTIR (Neat Film NaCl) 3056, 3026, 2895, 1649, 1598, 1584, 1494, 1477, 1451, 1434, 1356, 1091, 1029, 909, 741 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{34}H_{29}NOP$ $[M+H]^+$: 498.1987, found 498.1963; $[\alpha]^{24}_D$ = +10.4 (*c* 1.00, $CHCl_3$).



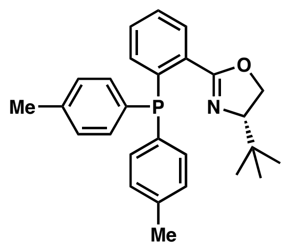
(*R*)-4-(3,5-Di-*tert*-butylbenzyl)-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole. Colorless viscous oil; R_f = 0.52 (hexanes/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (m, 1H), 7.40-7.28 (m, 13H), 6.92 (d, *J* = 1.8 Hz, 2H), 6.86 (m, 1H), 4.33 (m, 1H), 4.00 (t, *J* = 8.7 Hz, 1H), 3.78 (dd, *J* = 8.7, 7.5 Hz, 1H), 2.95 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.01 (dd, *J* = 13.8, 10.2 Hz, 1H), 1.30 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9 (d, J_{CP} = 3 Hz), 150.8, 138.9 (d, J_{CP} = 25 Hz), 137.9 (d, J_{CP} = 12 Hz), 137.8 (d, J_{CP} = 10 Hz), 137.2, 134.4 (d, J_{CP} = 21 Hz), 134.0 (d, J_{CP} = 21 Hz), 133.4 (d, J_{CP} = 3 Hz), 131.5 (d, J_{CP} = 17 Hz), 130.5, 130.0 (d, J_{CP} = 3 Hz), 128.8-128.4 (6 lines), 127.9, 123.3, 120.3, 71.6, 68.1, 41.6, 34.7, 31.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ -3.60; FTIR (Neat Film NaCl) 2963, 1649, 1598, 1477, 1434, 1361, 1248, 1090, 1027, 965, 742, 696 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{36}H_{41}NOP$ [M+H]$^+$: 534.2926, found 534.2905; $[\alpha]^{25}_D$ = -49.3 (*c* 0.36, $CHCl_3$).



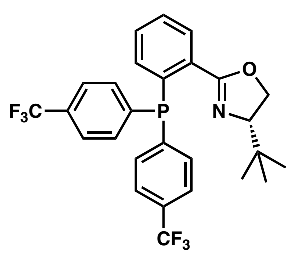
(*S*)-4-(Benzo[*b*]thiophen-3-ylmethyl)-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole. White amorphous solid; R_f = 0.38 (hexanes/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (m, 1H), 7.85 (m, 1H), 7.69 (m, 1H), 7.42-7.28 (m, 14H), 7.01 (s, 1H), 6.88 (m, 1H), 4.54 (m, 1H), 4.14 (t, *J* = 8.4 Hz, 1H), 3.83 (dd, *J* = 8.4, 7.5 Hz, 1H), 3.03 (ddd, *J* = 14.7, 5.4, 1.2 Hz, 1H), 2.40 (dd, *J* = 14.7, 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (d, J_{CP} = 3 Hz), 140.2, 139.0-138.7 (3 lines), 137.9-137.8 (3 lines), 134.4 (d, J_{CP} = 21 Hz), 133.7 (d, J_{CP} = 21 Hz), 133.6 (d, J_{CP} = 2 Hz), 132.6, 131.3 (d, J_{CP} = 18 Hz), 130.5, 129.9 (d, J_{CP} = 2 Hz), 128.7-128.3 (6 lines), 127.9, 124.2, 123.8, 122.7, 122.6, 121.5, 71.7, 66.0, 33.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ -4.21; FTIR (Neat Film NaCl) 3054, 2963, 1651, 1585, 1476, 1434, 1356, 1252, 1216, 1090, 1026, 965, 749, 697 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{30}H_{25}NOPS$ [M+H]$^+$: 478.1394, found 478.1416; $[\alpha]^{26}_D$ = +30.1 (*c* 1.00, $CHCl_3$).



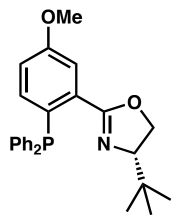
(*S*)-4-((1*H*-Indol-3-yl)methyl)-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole.[6]



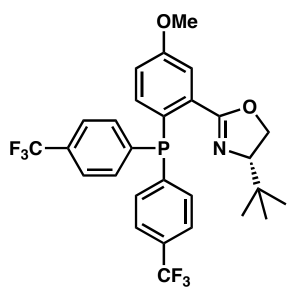
(*S*)-4-*tert*-Butyl-2-(2-(di-*p*-tolylphosphino)phenyl)-4,5-dihydrooxazole. Colorless viscous oil; R_f = 0.39 (hexanes/EtOAc, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (ddd, *J* = 7.5, 3.6, 1.5 Hz, 1H), 7.33 (m, 1H), 7.26 (m, 1H), 7.23-7.05 (m, 8H), 6.89 (ddd, *J* = 7.5, 4.2, 1.5 Hz, 1H), 4.06 (dd, *J* = 10.2, 8.4 Hz, 1H), 3.98 (t, *J* = 8.3 Hz, 1H), 3.85 (dd, *J* = 10.2, 7.8 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 0.75 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0 (d, J_{CP} = 3 Hz), 139.3 (d, J_{CP} = 25 Hz), 138.4, 138.1, 135.0-134.7 (4 lines), 134.3 (d, J_{CP} = 21 Hz), 133.9, 133.6 (d, J_{CP} = 20 Hz), 131.9 (d, J_{CP} = 20 Hz), 130.2, 129.9 (d, J_{CP} = 3 Hz), 129.2 (d, J_{CP} = 7 Hz), 129.0 (d, J_{CP} = 7 Hz), 127.8, 76.5, 68.3, 33.6, 25.7, 21.3, 21.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ -6.98; FTIR (Neat Film NaCl) 2953, 1653, 1496, 1476, 1394, 1353, 1306, 1248, 1185, 1134, 1089, 1024, 967, 805, 743 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{27}H_{30}NOP$ [M$^+$]: 415.2065, found 415.2065; $[\alpha]^{25}_D$ = -58.8 (*c* 2.23, $CHCl_3$).



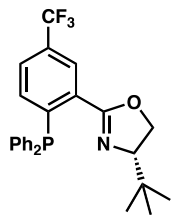
(*S*)-2-(2-(Bis(4-(trifluoromethyl)phenyl)phosphino)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole. White amorphous powder; R_f = 0.44 (hexanes/EtOAc, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (ddd, *J* = 7.5, 3.9, 1.2 Hz, 1H), 7.62-7.50 (m, 4H), 7.44 (m, 1H), 7.40-7.28 (m, 5H), 6.82 (ddd, *J* = 7.5, 3.9, 0.9 Hz, 1H), 4.20 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.06 (t, *J* = 8.4 Hz, 1H), 3.93 (dd, *J* = 10.2, 8.4 Hz, 1H), 0.69 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8 (d, J_{CP} = 3 Hz), 143.4-143.2 (m), 136.7 (d, J_{CP} = 24 Hz), 134.4 (d, J_{CP} = 21 Hz), 134.2, 133.7 (d, J_{CP} = 20 Hz), 132.0 (d, J_{CP} = 20 Hz), 130.74, 130.65 (q, J_{CF} = 32 Hz), 130.5 (q, J_{CF} = 32 Hz), 129.9 (d, J_{CP} = 3 Hz), 128.9, 125.3-124.9 (m), 124.1 (q, J_{CF} = 271 Hz,), 77.0, 68.4, 33.6, 25.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ -7.29; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.23, -63.28; FTIR (Neat Film NaCl) 2958, 1653, 1606, 1480, 1396, 1324, 1166, 1128, 1106, 1061, 1017, 831, 700 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{27}H_{24}NOPF_6$ [M$^+$]: 523.1500, found 523.1494; $[\alpha]^{25}_D$ = -21.1 (*c* 2.26, $CHCl_3$).



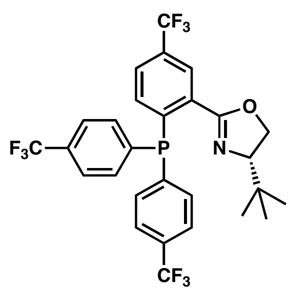
(*S*)-4-*tert*-Butyl-2-(2-(diphenylphosphino)-5-methoxyphenyl)-4,5-dihydrooxazole. White amorphous powder; R_f = 0.61 (hexanes/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, *J* = 2.9 Hz, 1H), 7.34-7.18 (m, 10H), 6.84 (ddd, *J* = 8.7, 2.4, 0.6 Hz, 1H), 6.78 (ddd, *J* = 8.7, 3.3, 0.6 Hz, 1H), 4.13 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.03 (t, *J* = 8.1 Hz, 1H), 3.92 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.82 (s, 3H), 0.73 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (d, J_{CP} = 3 Hz), 159.4, 139.0 (d, J_{CP} = 13 Hz), 138.7 (d, J_{CP} = 10 Hz), 135.8, 134.1 (d, J_{CP} = 20 Hz), 133.41 (d, J_{CP} = 33 Hz), 133.36 (d, J_{CP} = 20 Hz), 129.3 (d, J_{CP} = 22 Hz), 128.3-128.0 (6 lines), 116.5, 114.9 (d, J_{CP} = 4 Hz), 76.7, 68.3, 55.3, 33.6, 25.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ -10.12; FTIR (Neat Film NaCl) 3069, 2956, 2903, 1654, 1594, 1561, 1479, 1434, 1354, 1336, 1297, 1224, 1181, 1093, 1050, 1022, 973, 744, 697 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{26}H_{28}NO_2P$ [M^+]: 417.1858, found 417.1844; $[\alpha]^{25}_D$ = -48.8 (*c* 2.11, $CHCl_3$).



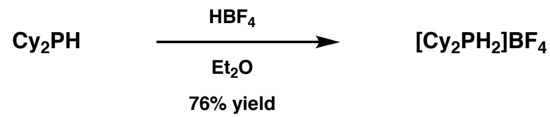
(*S*)-2-(2-(Bis(4-(trifluoromethyl)phenyl)phosphino)-5-methoxyphenyl)-4-*tert*-butyl-4,5-dihydrooxazole. White amorphous powder; R_f = 0.43 (hexanes/EtOAc, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.50 (m, 5H), 7.40-7.26 (m, 4H), 6.89 (dd, *J* = 8.4, 3.0 Hz, 1H), 6.74 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.23 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.08 (t, *J* = 8.4 Hz, 1H), 3.96 (dd, *J* = 10.2, 8.4 Hz, 1H), 3.85 (s, 3H), 0.69 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (d, J_{CP} = 3 Hz), 160.0, 143.9-143.6 (3 lines), 135.9, 134.2 (d, J_{CP} = 21 Hz), 133.6 (d, J_{CP} = 21 Hz), 130.5 (q, J_{CF} = 32 Hz), 130.3 (q, J_{CF} = 32 Hz), 127.1 (d, J_{CP} = 21 Hz), 125.2-124.8 (7 lines), 124.1 (q, J_{CF} = 270 Hz), 116.7, 115.1 (d, J_{CP} = 4 Hz), 77.0 (d, J_{CP} = 1 Hz), 68.4, 55.4, 33.6, 25.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ -13.06; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.20, -63.24; FTIR (Neat Film NaCl) 2959, 2870, 1652, 1595, 1563, 1485, 1396, 1322, 1226, 1166, 1127, 1106, 1061, 1017, 973, 909, 832, 735, 700 cm^{-1}; HRMS (FAB, Pos) *m/z* calc'd for $C_{28}H_{27}F_6NO_2P$ $[M+H]^+$: 554.1683, found 554.1659; $[\alpha]^{24}_D$ = -24.5 (*c* 2.61, $CHCl_3$).



(*S*)-4-*tert*-Butyl-2-(2-(diphenylphosphino)-5-(trifluoromethyl)phenyl)-4,5-dihydrooxazole. White powder; mp 98-100 ºC; R_f = 0.45 (hexanes/EtOAc, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (m, 1H), 7.51 (dd, J = 8.1, 1.8 Hz, 1H), 7.38-7.18 (m, 10H), 6.99 (dd, J = 8.1, 3.3 Hz, 1H), 4.12 (dd, J = 10.2, 8.4 Hz, 1H), 4.03 (t, J = 8.4 Hz, 1H), 3.90 (dd, J = 10.2, 8.4 Hz, 1H), 0.72 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4 (d, J_{CP} = 3 Hz), 144.2 (d, J_{CP} = 30 Hz), 137.7 (d, J_{CP} = 12 Hz), 137.3 (d, J_{CP} = 9 Hz), 134.6, 134.3 (d, J_{CP} = 21 Hz), 133.6 (d, J_{CP} = 20 Hz), 132.2 (d, J_{CP} = 19 Hz), 130.1 (q, J_{CF} = 33 Hz), 128.9-128.4 (6 lines), 126.6-126.3 (m), 123.7 (q, J_{CF} = 271 Hz), 77.0 (d, J_{CP} = 1 Hz), 68.4, 33.6, 25.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ -6.55 (J_{PF} = 2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.36; FTIR (Neat Film NaCl) 3071, 2957, 1655, 1478, 1434, 1407, 1357, 1343, 1326, 1302, 1262, 1244, 1174, 1131, 1080, 969, 744, 696 cm^{-1}; HRMS (EI) m/z calc'd for $C_{26}H_{25}NOPF_3$ [M^+]: 455.1626, found 455.1646; $[\alpha]^{25}_D$ = -36.3 (c 2.39, $CHCl_3$).



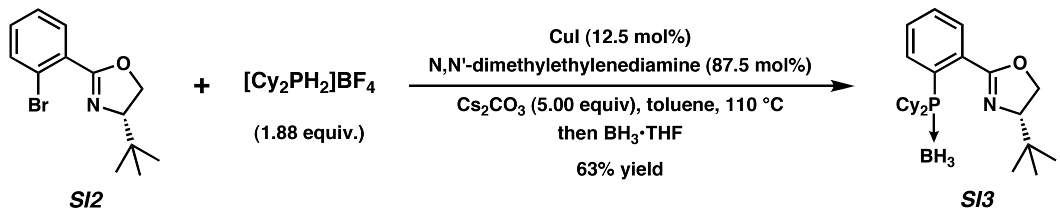
(*S*)-2-(2-(Bis(4-(trifluoromethyl)phenyl)phosphino)-5-(trifluoromethyl)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole. White amorphous powder; R_f = 0.63 (hexanes/EtOAc, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (m, 1H), 7.64-7.54 (m, 5H), 7.39-7.27 (m, 4H), 6.95 (dd, J = 7.8, 3.0 Hz, 1H), 4.25 (dd, J = 10.2, 8.7 Hz, 1H), 4.09 (t, J = 8.7 Hz, 1H), 3.95 (dd, J = 10.2, 8.7 Hz, 1H), 0.69 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7 (d, J_{CP} = 4 Hz), 142.6-141.7 (6 lines), 134.7-133.6 (5 lines), 132.4 (d, J_{CP} = 20 Hz), 131.1 (q, J_{CF} = 32 Hz), 130.9 (q, J_{CF} = 32 Hz), 127.0 (q, J_{CF} = 3 Hz), 126.7-126.4 (6 lines), 125.6-125.1 (8 lines), 123.9 (q, J_{CF} = 271 Hz), 123.5 (q, J_{CF} = 271 Hz), 77.3 (d, J_{CP} = 1 Hz), 68.6, 33.5, 25.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ -6.57; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.33, -63.39, -63.53; FTIR (Neat Film NaCl) 2960, 1657, 1606, 1479, 1397, 1324, 1169, 1129, 1107, 1082, 1061, 1017, 832, 700 cm^{-1}; HRMS (FAB, Pos) m/z calc'd for $C_{28}H_{24}F_9NOP$ [$M+H$]$^+$: 592.1452, found 592.1480; $[\alpha]^{24}_D$ = -16.0 (c 2.56, $CHCl_3$).



[Cy_2PH_2]BF_4.[7] To a cooled (0 ºC) solution of Cy_2PH (0.700 mL, 3.46 mmol, 1.00 equiv) in Et_2O (10 mL) was added HBF_4 (54 wt% in Et_2O, 0.386 mL, 5.19 mmol, 1.50 equiv) in a dropwise fashion over 1 min. During the addition, a white precipitate was formed. After this, the ice-bath was removed and the reaction mixture was stirred for 15 min at ambient temperature. The resulting precipitate was collected by filtration, washed with dry Et_2O (2 x 10 mL) and dried under vacuum to afford [Cy_2PH_2]BF_4 (755 mg, 2.63 mmol, 76% yield) as a white powder; mp 275 ºC (dec.); ^1H NMR (300 MHz, $CDCl_3$) δ 5.89 (dm, J_{HP} = 482 Hz, 2H), 2.65 (m, 2H), 2.09 (m, 4H), 1.87 (m, 4H), 1.76 (m, 2H), 1.68-1.20 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.9 (d, J_{CP} = 3.4 Hz), 25.8 (d, J_{CP} = 42 Hz), 25.7 (d, J_{CP} = 14 Hz), 24.8 (d, J_{CP} = 1.4 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ -0.37; FTIR (KBr) 2932, 2858, 2231, 1452, 1061 cm^{-1}.

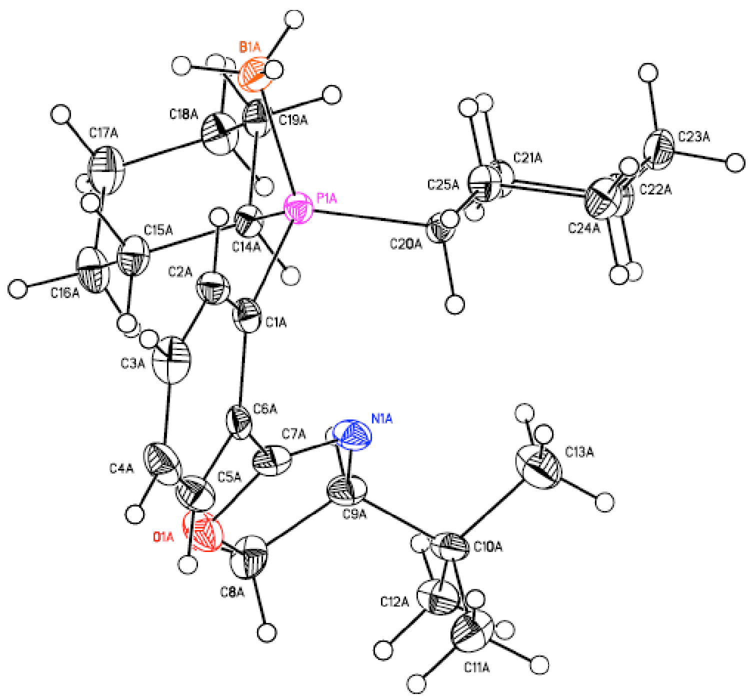
[*i*-Bu_2PH_2]BF_4. Prepared in an analogous manner to the previous entry. White powder; mp 280 ºC (dec.); ^1H NMR (300 MHz, CD_3CN) δ 5.98 (dm, J_{HP} = 496 Hz, 2H), 2.30-2.15 (m, 4H), 2.07 (m, 2H), 1.07 (dd, J_{HH} = 6.6 Hz, J_{HP} = 1.5 Hz, 12H); ^{13}C NMR (75 MHz, CD_3CN) δ 25.8 (d, J_{CP} = 4.8 Hz), 23.5 (d, J_{CP} = 46 Hz), 23.2 (d, J_{CP} = 11 Hz); ^{31}P NMR (121 MHz, CD_3CN) δ -27.4; FTIR (KBr) 2965, 1471, 1393, 1084 cm^{-1}.

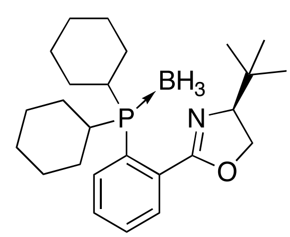
General Procedure for the Copper Catalyzed Synthesis of PHOX Ligands Utilizing a Dialkylphosphonium Salt



(*S*)-4-*tert*-Butyl-2-(2-(dicyclohexylphosphino)phenyl)-4,5-dihydrooxazole, borane complex (SI3). A flame-dried 50 mL Schlenk tube containing stir bar was evacuated and refilled with dry nitrogen and then charged with [Cy_2PH_2]BF_4 (538 mg, 1.88 mmol, 1.88 equiv), anhydrous toluene (4.0 mL) followed by Cs_2CO_3 (1630 mg, 5.00 mmol, 5.00 equiv). After 10 min of stirring, CuI (23.8 mg, 0.125 mmol, 0.125 eq.) and *N,N'*-dimethylethylenediamine (93 μL, 0.875 mmol, 0.875 eq.) were added to the mixture and the resulting suspension was stirred for 10 min. To this was added **SI2** (282 mg, 1.00 mmol, 1.0 eq.) and toluene (4.0 mL) and the Schlenk tube was sealed and the reaction mixture was stirred at 110ºC until the complete consumption of the aryl bromide (27 h). The resulting reaction mixture was allowed to cool to 0 ºC, BH_3-THF complex (1.0 M in THF, 3.0 mL, 3.00 mmol, 3.00 eq.) was slowly add to this mixture. After 2 h stirring at ambient temperature, the reaction was quenched by the addition of 20 mL of water and extracted with ether (20 mL x 2). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residual crude oil was purified by flash SiO_2 column (hexanes/EtOAc, 40/1) to afford 259 mg (63% yield) of desired borane complex **SI3** as a white solid; mp 143-145 ºC; R_f = 0.52 (hexanes/Et_2O, 5/1); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (m, 1H), 7.78 (m, 1H), 7.54-7.46 (m, 2H), 4.41 (dd, J = 9.9, 8.1 Hz, 1H), 4.21 (dd, J = 9.9, 8.1 Hz, 1H), 4.10 (t, J = 9.9 Hz, 1H), 2.83 (m, 1H), 2.57 (m, 1H), 1.98-1.74 (m, 4H), 1.74-1.55 (m, 6H), 1.32-1.10 (m, 10H), 1.02 (s, 9H), 1.00-0.00 (br., 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1 (d, J_{CP} = 2 Hz), 138.2 (d, J_{CP} = 15 Hz), 132.0, 130.7-130.2 (6 lines), 127.3 (d, J_{CP} =43 Hz), 77.3, 68.6, 33.7, 33.6 (d, J_{CP} = 32 Hz), 33.5 (d, J_{CP} = 32 Hz), 28.64, 28.55, 27.84, 27.78, 27.3 (d, J_{CP} = 6 Hz), 27.1 (d, J_{CP} = 6 Hz), 27.0, 26.9, 26.2, 25.78, 25.76; ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.22 (br d); FTIR (Neat Film NaCl) 2930, 2852, 2363, 2344, 1653, 1477, 1448, 1364, 1332, 1305, 1246, 1100, 1063, 1037, 962, 760 cm^{-1}; HRMS (EI) m/z calc'd for $C_{25}H_{40}BNOP$ $[M-H]^+$: 412.2941, found 412.2971; $[\alpha]^{24}_D$ = -5.6 (c 1.71, $CHCl_3$).

The phosphine-borane complex **SI3** was recrystallized from hexanes to provide crystals suitable for X-ray analysis.





SI3

Figure 1. ORTEP drawing of **SI3**

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 292036.

Table 1. Crystal data and structure refinement for SI3 (CCDC 292036).

Empirical formula	$C_{25}H_{41}BNOP$	
Formula weight	413.37	
Crystallization Solvent	Hexanes	
Crystal Habit	Blade	
Crystal size	0.33 x 0.30 x 0.12 mm^3	
Crystal color	Colorless	

Data Collection

Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 20368 reflections used in lattice determination	2.13 to 27.97°	
Unit cell dimensions	a = 10.5651(5) Å	α= 88.9530(10)°
	b = 19.0701(10) Å	β= 87.6200(10)°
	c = 24.3655(12) Å	γ = 85.2710(10)°
Volume	4887.6(4) $Å^3$	
Z	8	
Crystal system	Triclinic	
Space group	P1	
Density (calculated)	1.124 Mg/m^3	
F(000)	1808	
Data collection program	Bruker SMART v5.630	
θ range for data collection	1.67 to 28.47°	
Completeness to θ = 28.47°	90.0 %	
Index ranges	$-13 \leq h \leq 14$, $-24 \leq k \leq 25$, $-31 \leq l \leq 31$	
Data collection scan type	ω scans at 5 ϕ settings	
Data reduction program	Bruker SAINT v6.45A	
Reflections collected	72958	
Independent reflections	43112 [R_{int}= 0.0534]	
Absorption coefficient	0.128 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9848 and 0.9590	

Table 1 (cont.)

Structure solution and Refinement

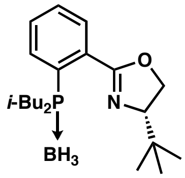
Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	43112 / 3 / 2121
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.001
Final R indices [I>2σ(I), 26848 reflections]	R1 = 0.0512, *w*R2 = 0.0789
R indices (all data)	R1 = 0.0963, *w*R2 = 0.0881
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	-0.04(5)
Largest diff. peak and hole	0.424 and -0.360 e.$Å^{-3}$

Special Refinement Details

This crystal has eight molecules in the unit cell, each of them distinct with respect to the torsion angles within the (4-*tert*-butyl-1,3-oxazolin-2-yl)phenyl ligand. These conformational difference are propagated to the cyclohexyl ligands as well. An interesting feature in this figure is the fan-like positions of the eight oxygen atoms relative the more-or-less centralized position of the eight nitrogen atoms.

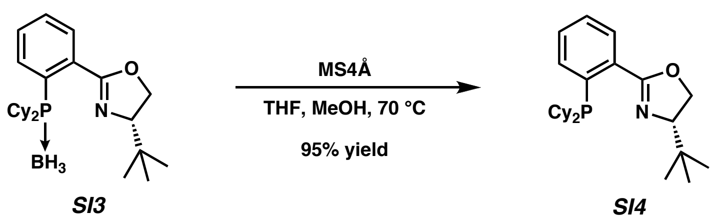
Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.



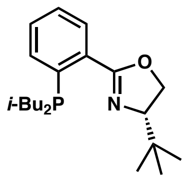
(*S*)-4-*tert*-Butyl-2-(2-(diisobutylphosphino)phenyl)-4,5-dihydrooxazole, borane complex. Prepared in an analogous manner to the previous entry. White powder; R_f = 0.46 (hexanes/Et_2O, 5/1); mp 44-46 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (m, 1H), 7.85 (m, 1H), 7.57-7.48 (m, 2H), 4.39 (dd, *J* = 9.6, 8.4 Hz, 1H), 4.21 (dd, *J* = 9.6, 8.4 Hz, 1H), 4.10 (t, *J* = 9.6 Hz, 1H), 2.59 (m, 1H), 2.26 (m, 1H), 2.08-1.70 (m, 4H), 2.00-0.00 (br, 3H), 1.00 (s, 9H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.71 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (d, J_{CP} = 2 Hz), 137.8 (d, J_{CP} = 18 Hz), 132.0, 130.95 (d, J_{CP} = 3 Hz), 130.90, 130.6 (d, J_{CP} = 13 Hz), 128.7 (d, J_{CP} = 41 Hz), 77.2, 68.5, 35.4 (d, J_{CP} = 35 Hz), 34.5 (d, J_{CP} = 35 Hz), 33.9, 26.1, 24.9 (d, J_{CP} = 7 Hz), 24.8 (d, J_{CP} = 6 Hz), 24.6, 24.3 (d, J_{CP} = 7 Hz), 24.1 (d, J_{CP} = 7 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 18.77 (br d); FTIR (Neat film, NaCl) 2957, 2870, 2381, 1661, 1588, 1568, 1466, 1366, 1335, 1247, 1103, 1064, 1038, 1025, 963, 819, 773, 735 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{21}H_{36}BNOP$ $[M-H]^+$: 360.2628, found 360.2623; $[\alpha]^{25}_D$ = +8.9 (*c* 1.00, $CHCl_3$).

General Procedure for the Deprotection of PHOX-Borane Complexes.[8]



(*S*)-4-*tert*-Butyl-2-(2-(dicyclohexylphosphino)phenyl)-4,5-dihydrooxazole (SI4).[9] Molecular sieves 4Å (MS4Å) were heated to 180 ºC under vacuum for 24 h prior to use. A Schlenk tube equipped with a stir bar was flame-dried under vacuum and backfilled with dry nitrogen. The Schlenk tube was charged with the phosphine-borane complex **SI3** (40.0 mg, 0.0968 mmol), MS4Å (160 mg), THF (2 mL) and MeOH (1 mL). The mixture was stirred at 70 ºC for 72 h. After cooling, the resulting mixture was filtered through a plug of Celite under nitrogen and concentrated in vacuo. The resulting residue was dissolved in ether, passed through a plug of silica gel under nitrogen and concentrated in vacuo to afford desired phosphine **SI4** (36.8 mg, 0.0921 mmol, 95% yield) as a colorless oil, without further purification; R_f = 0.33 (hexanes/Et_2O, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (m, 1H), 7.52 (m, 1H), 7.42-7.28 (m, 2H), 4.37 (dd, *J* = 10.2, 8.1 Hz, 1H), 4.21 (t, *J* = 8.1 Hz, 1H), 4.08 (dd, *J* = 10.2, 8.1 Hz, 1H), 1.96-1.46 (m, 12H), 1.34-1.04 (m, 10H), 0.98 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (d, J_{CP} = 2 Hz), 136.8 (d, J_{CP} = 29 Hz), 136.7 (d, J_{CP} = 26 Hz), 132.6 (d, J_{CP} = 3 Hz), 129.7 (d, J_{CP} = 7 Hz), 129.1, 128.2, 76.6, 68.7, 34.7 (d, J_{CP} = 14 Hz), 34.4(d, J_{CP} = 14 Hz), 34.0, 30.2-29.8 (6 lines), 27.3-27.1 (6 lines), 26.40, 26.37, 26.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ -4.92; FTIR (Neat film, NaCl) 2925, 2850, 1658, 1478, 1446, 1351, 1240, 1091, 1024, 966 cm^{-1};

HRMS (FAB, Pos.) *m/z* calc'd for $C_{25}H_{39}NOP$ $[M+H]^+$: 400.2769, found 400.2754; $[\alpha]^{24}_D$ = -34.5 (*c* 0.50, $CHCl_3$).



(*S*)-4-*tert*-Butyl-2-(2-(diisobutylphosphino)phenyl)-4,5-dihydrooxazole. Prepared in an analogous manner to the previous entry. Colorless oil; R_f = 0.37 (hexanes/Et_2O, 5/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65-7.53 (m, 2H), 7.42 (m, 1H), 7.33 (m, 1H), 4.39 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.24 (t, *J* = 8.4 Hz, 1H), 4.09 (dd, *J* = 10.2, 8.4 Hz, 1H), 1.85-1.40 (m, 6H), 1.00 (s, 9H), 0.96 (dd, J_{HH} = 6.6 Hz, J_{HP} = 2.4 Hz, 6H), 0.92 (dd, J_{HH} = 6.3 Hz, J_{HP} = 3.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (d, J_{CP} = 1 Hz), 140.5 (d, J_{CP} = 25 Hz), 135.5 (d, J_{CP} = 30 Hz), 130.6 (d, J_{CP} = 3 Hz), 129.9, 129.3 (d, J_{CP} = 6 Hz), 128.2, 76.7, 68.7, 40.1 (d, J_{CP} = 14 Hz), 39.9 (d, J_{CP} = 14 Hz), 33.9, 26.32 (d, J_{CP} = 13 Hz), 26.27 (d, J_{CP} = 13 Hz), 26.1, 24.51 (d, J_{CP} = 9 Hz), 24.46 (d, J_{CP} = 8 Hz), 24.14 (d, J_{CP} = 9 Hz), 24.06 (d, J_{CP} = 9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ -38.92 ; FTIR (Neat film, NaCl) 2953, 2868, 1660, 1464, 1364, 1351, 1335, 1243, 1093, 1048, 967 cm^{-1}; HRMS (FAB, Pos.) *m/z* calc'd for $C_{21}H_{35}NOP$ $[M+H]^+$: 348.2456, found 348.2445; $[\alpha]^{24}_D$ = -40.7 (*c* 0.52, $CHCl_3$).

References:

1. Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, S.; Varsolona, R.; Wei, X.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277-4280.

2. McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. *J. Org. Chem.* **1993**, *58*, 3568-3571.

3. 2-Bromo-5-methoxybenzoic acid was purchased from Sigma-Aldrich Chemical Company. 2-Bromo-5-(tri-fluoromethyl)benzoic acid was synthesized by the known method, see: Mongin, F.; Desponds, O.; Schlosser, M. *Tetrahedron Lett.* **1996**, *37*, 2767-2770.

4. Zhou, Q. L.; Pfaltz, A. *Tetrahedron Lett.* **1993**, *34*, 7725-7728.

5. Koch, G.; Lloyd-Jones, G. C.; Loiseleur, O.; Pfaltz, A.; Prétôt, R.; Schaffner, S.; Schnider, P.; Matt, P. *Recl. Trav. Chim. Pays-Bas.* **1995**, *114*, 206-210.

6. Peer, M.; de Jong, J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahedron* **1996**, *52*, 7547-7583.

7. The preparation of [*t*-Bu_2PH_2]BF_4 has been reported, see: Stefanescu, D. M.; Yuen, H. F.; Glueck, D. S.; Golen, J. A.; Zakharov, L. N.; Incarvito, C. D.; Rheingold, A. L. *Inorg. Chem.* **2003**, *42*, 8891-8901.

8. Schröder, M.; Nozaki, K.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2004,** *77*, 1931-1932.

9. This compound was obtained with a small amount (5-10%) of the corresponding phosphine oxide, see: Blackmond, D. G., Lightfoot, A., Pfaltz, A., Rosner, T., Schnider, P., Zimmermann, N. *Chirality* **2000**, *12*, 442-449.

[1]H NMR spectra of Aryl Bromides

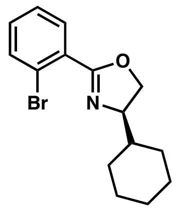
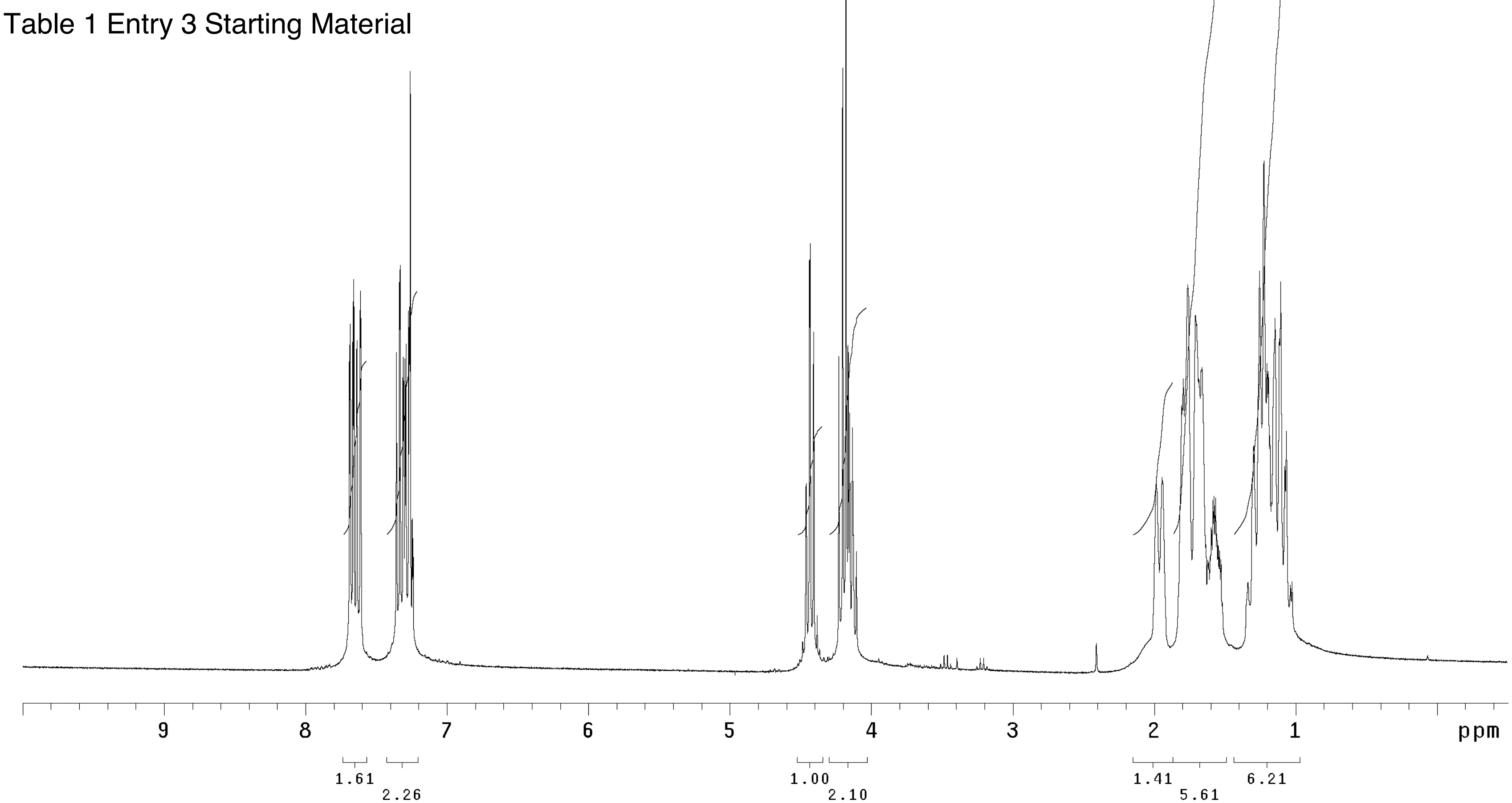
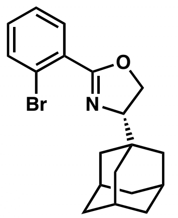


Table 1 Entry 3 Starting Material





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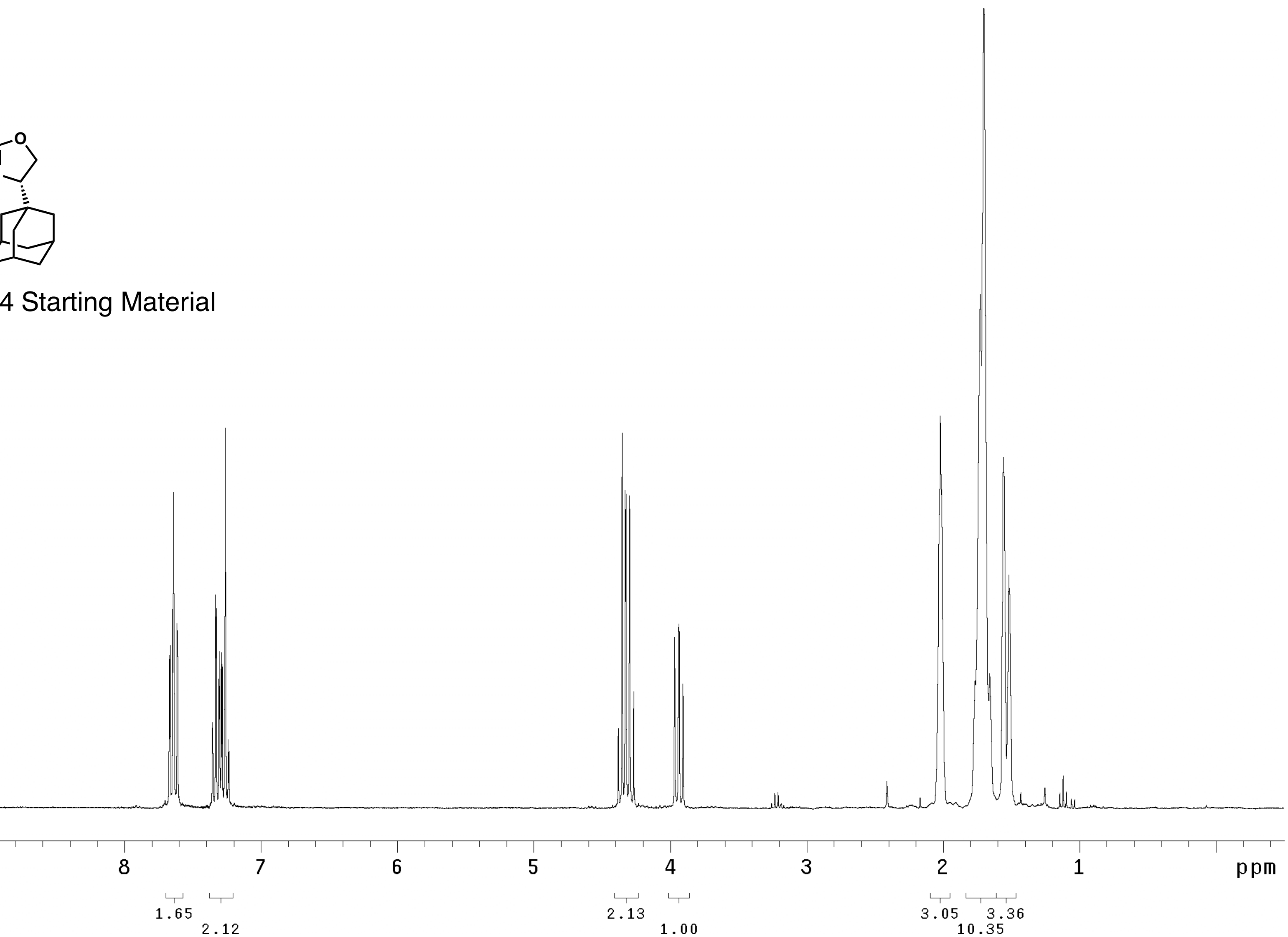


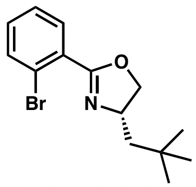
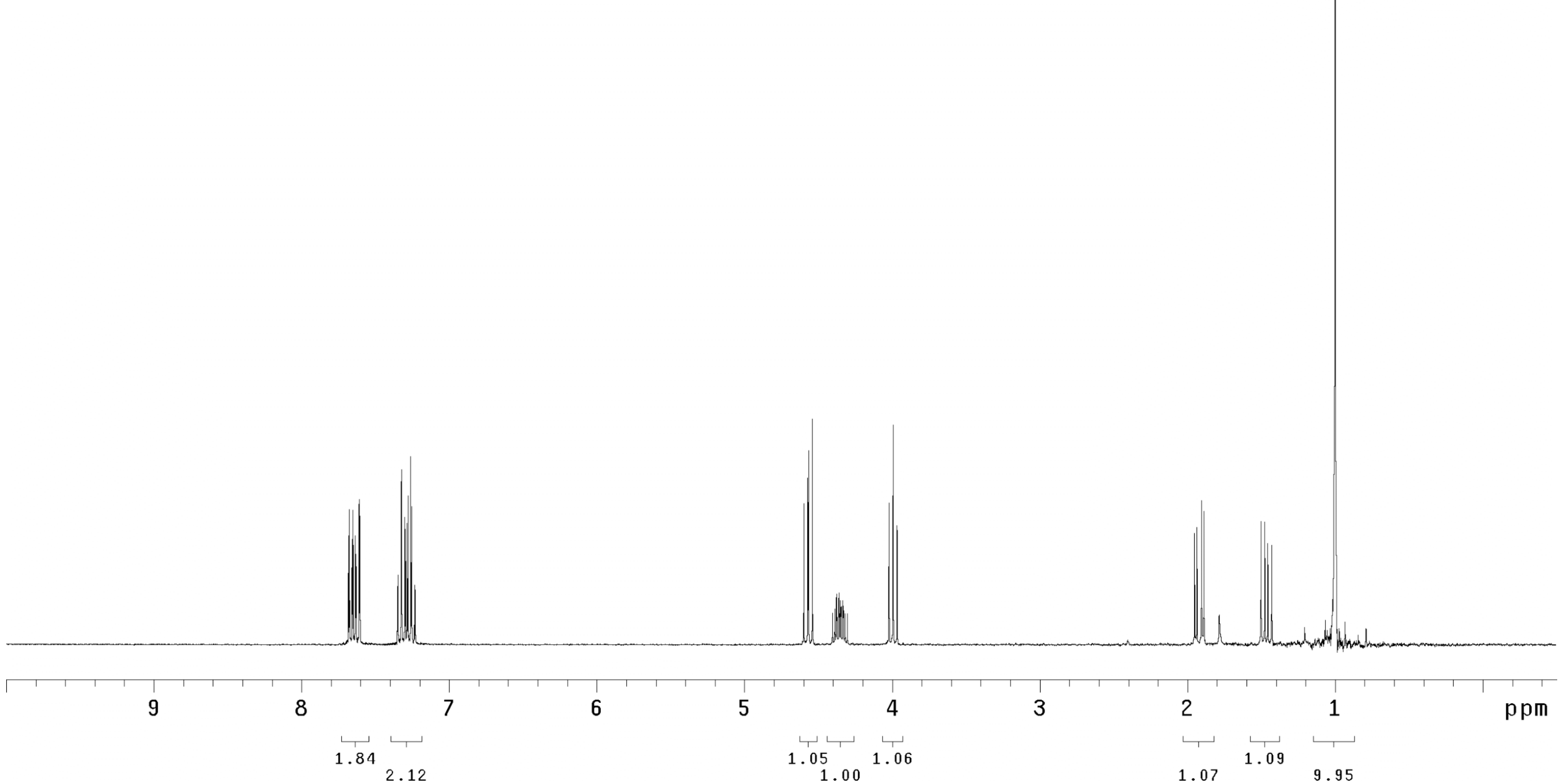
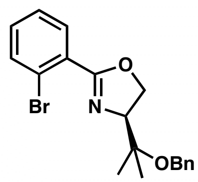


Table 1 Entry 5 Starting Material





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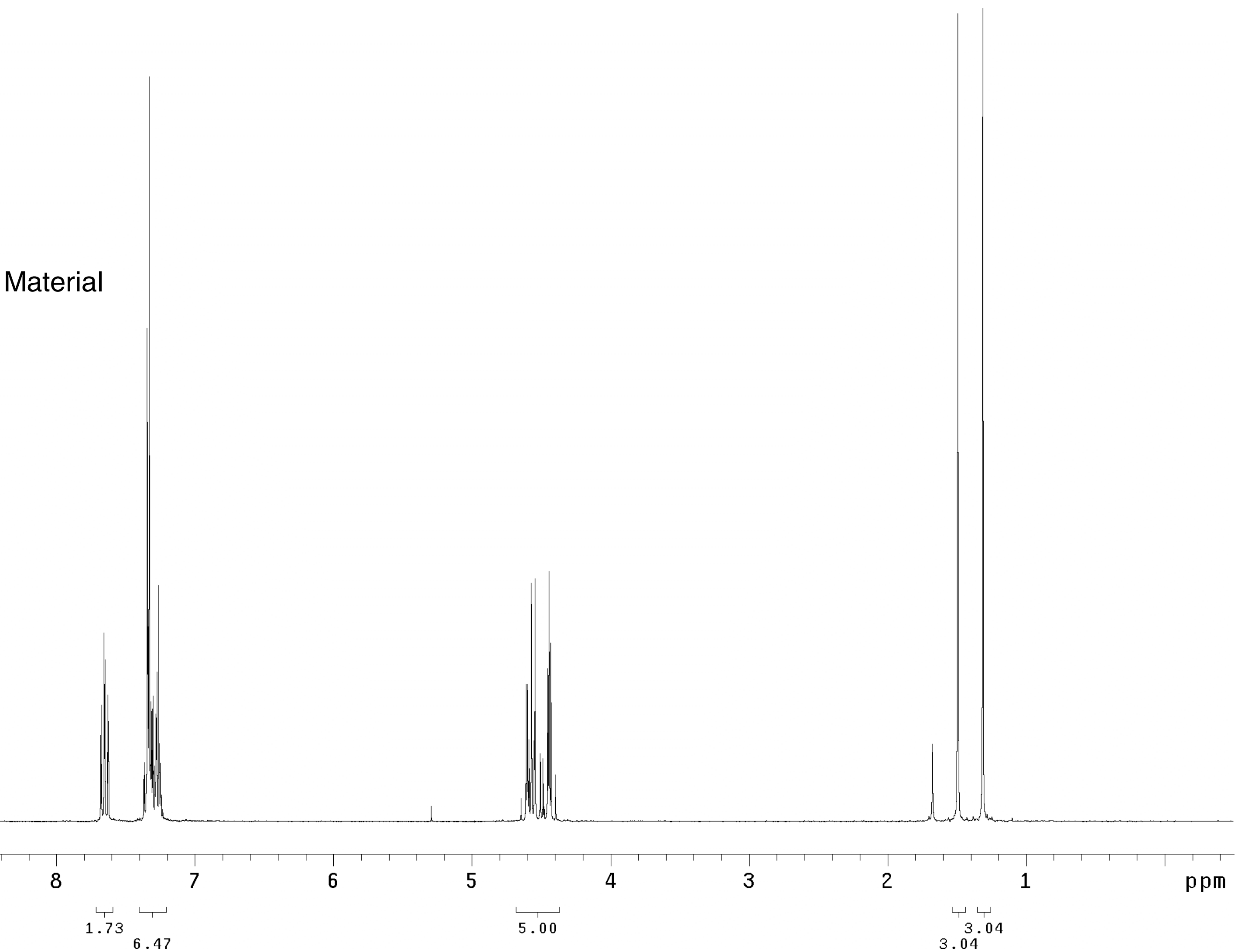

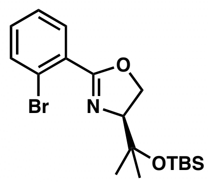

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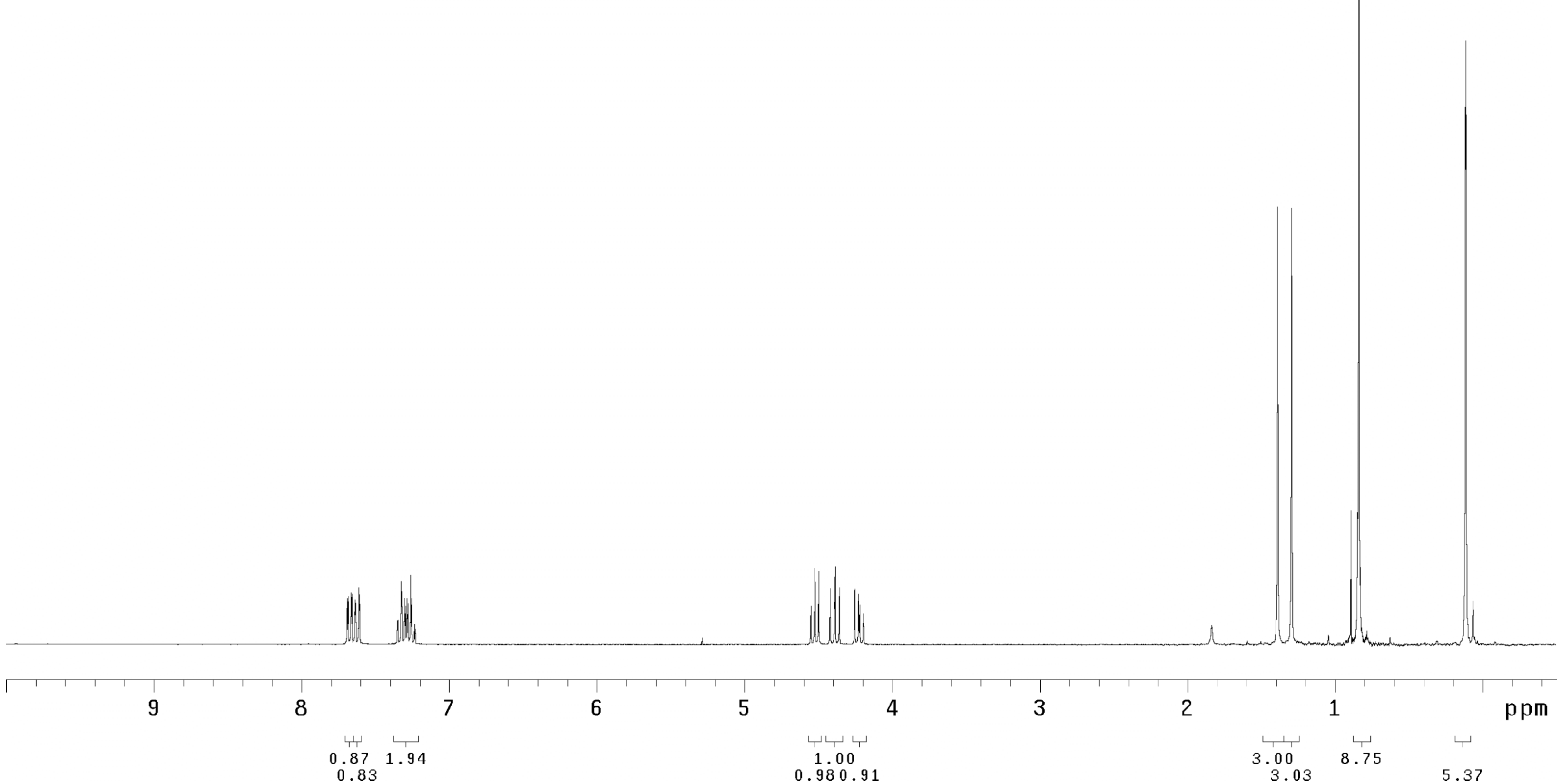

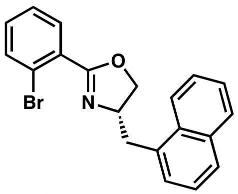

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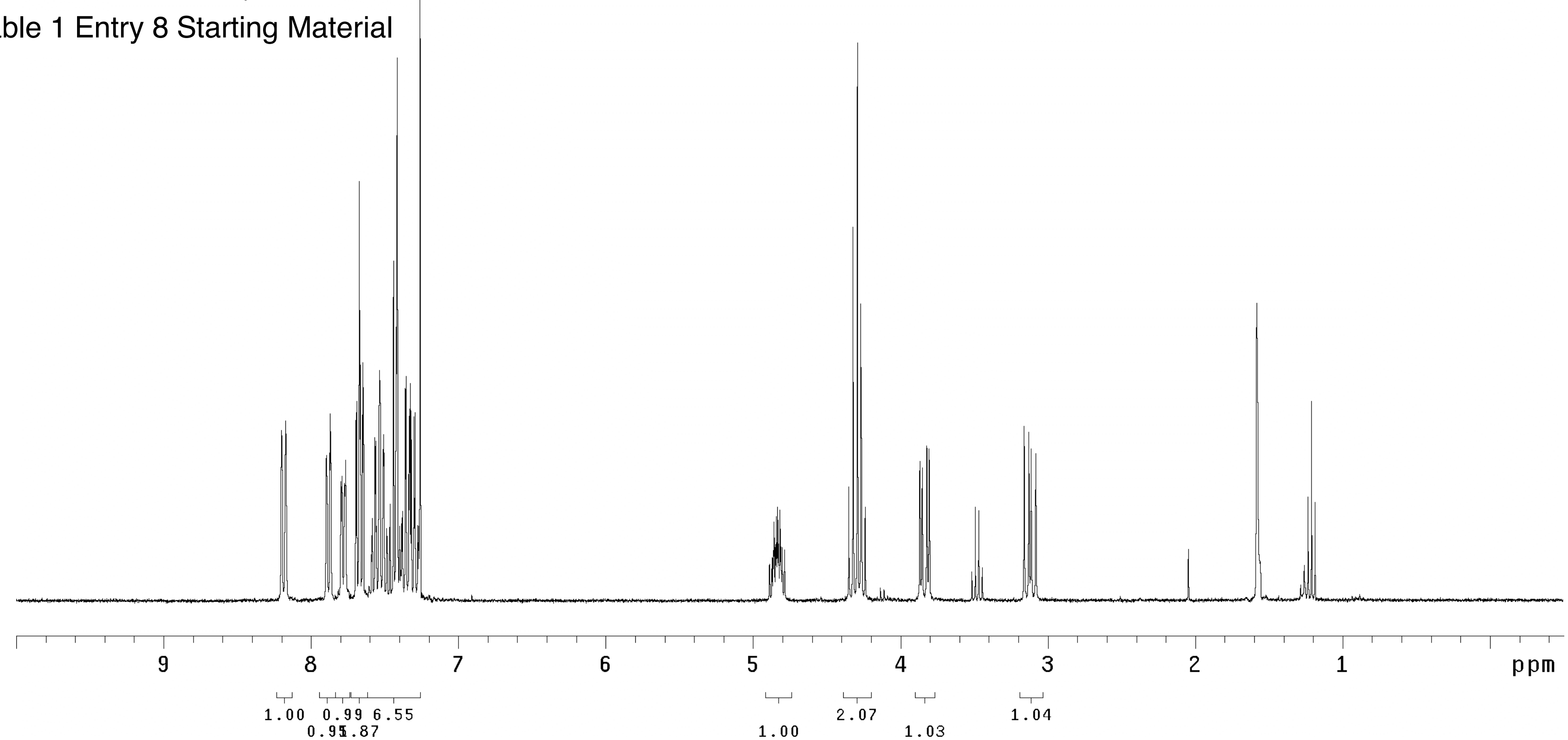

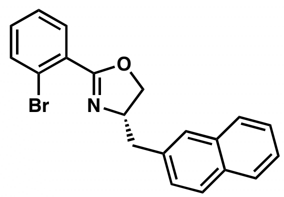

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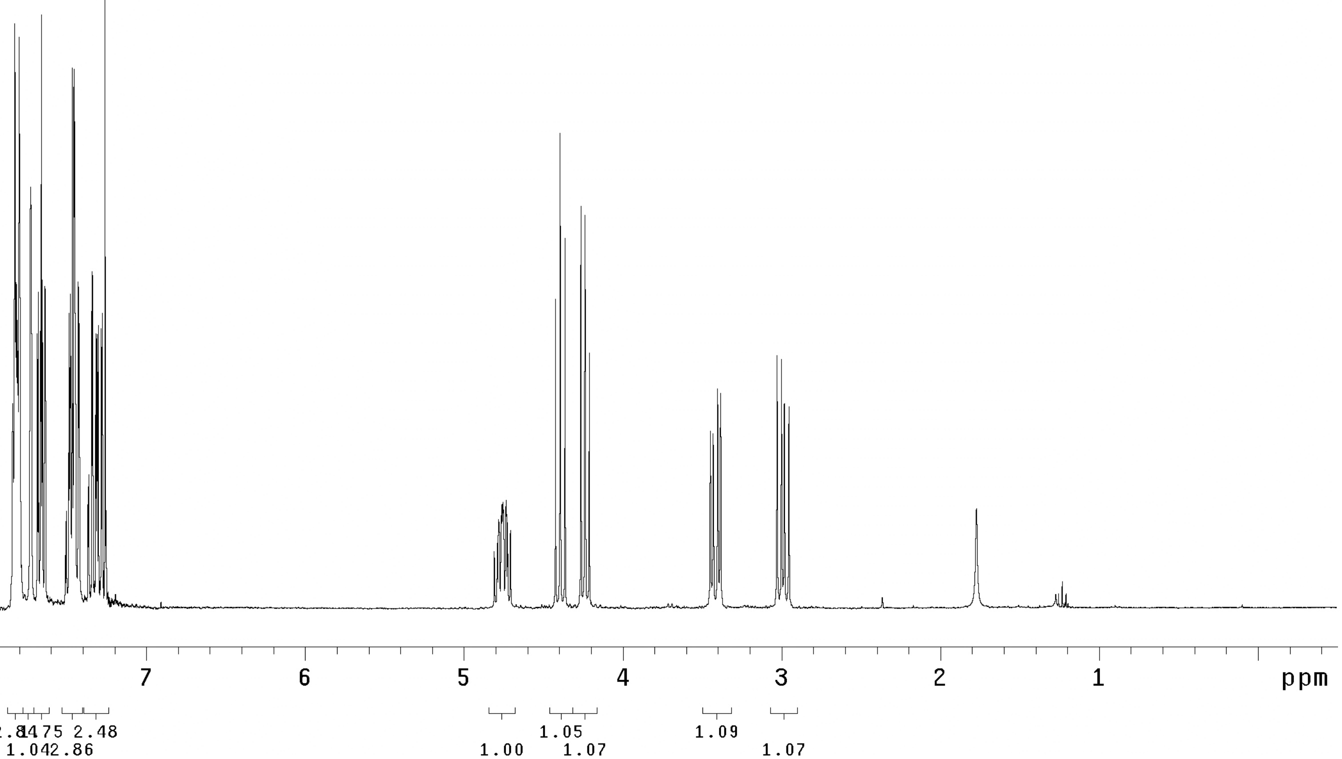

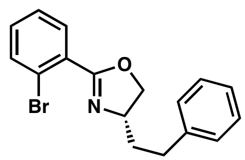

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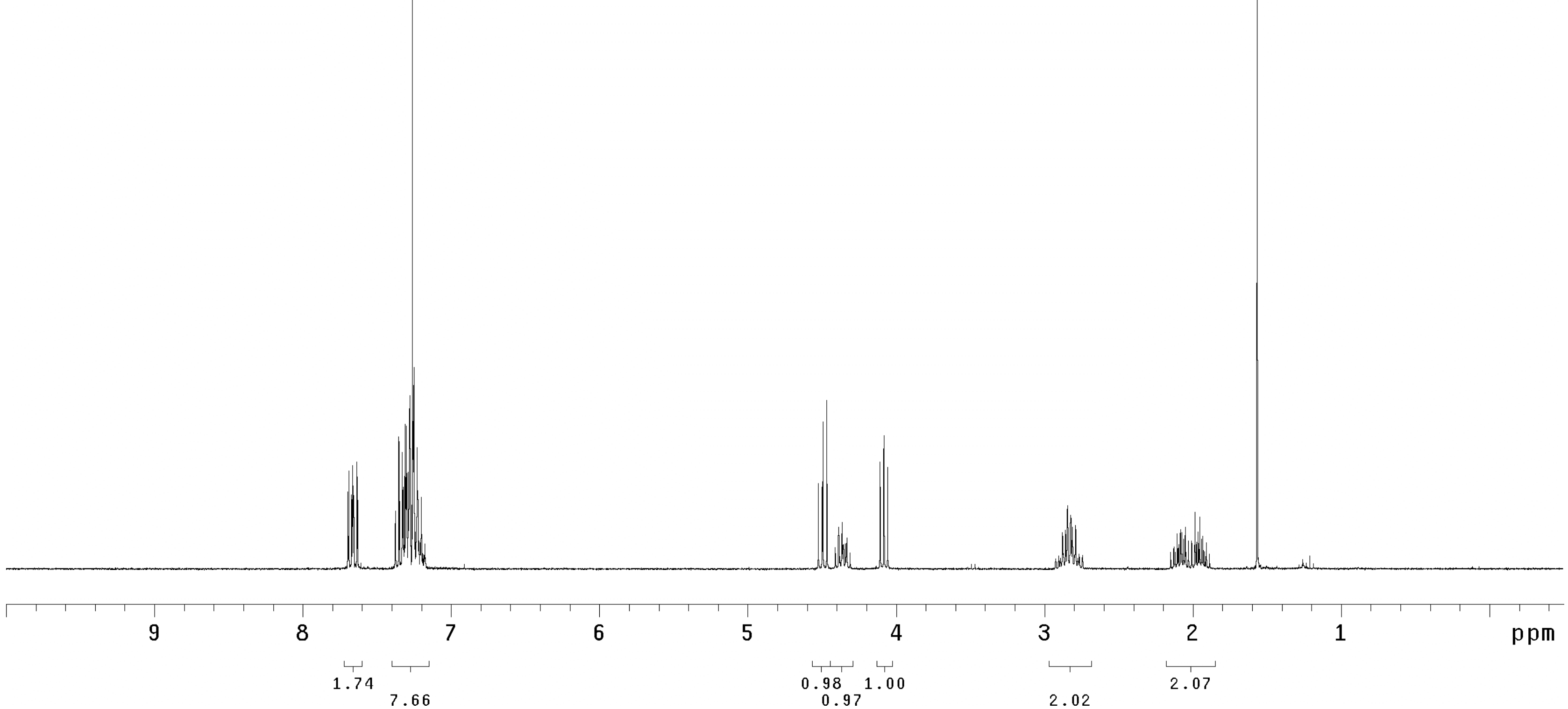

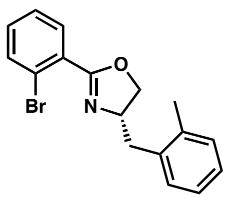

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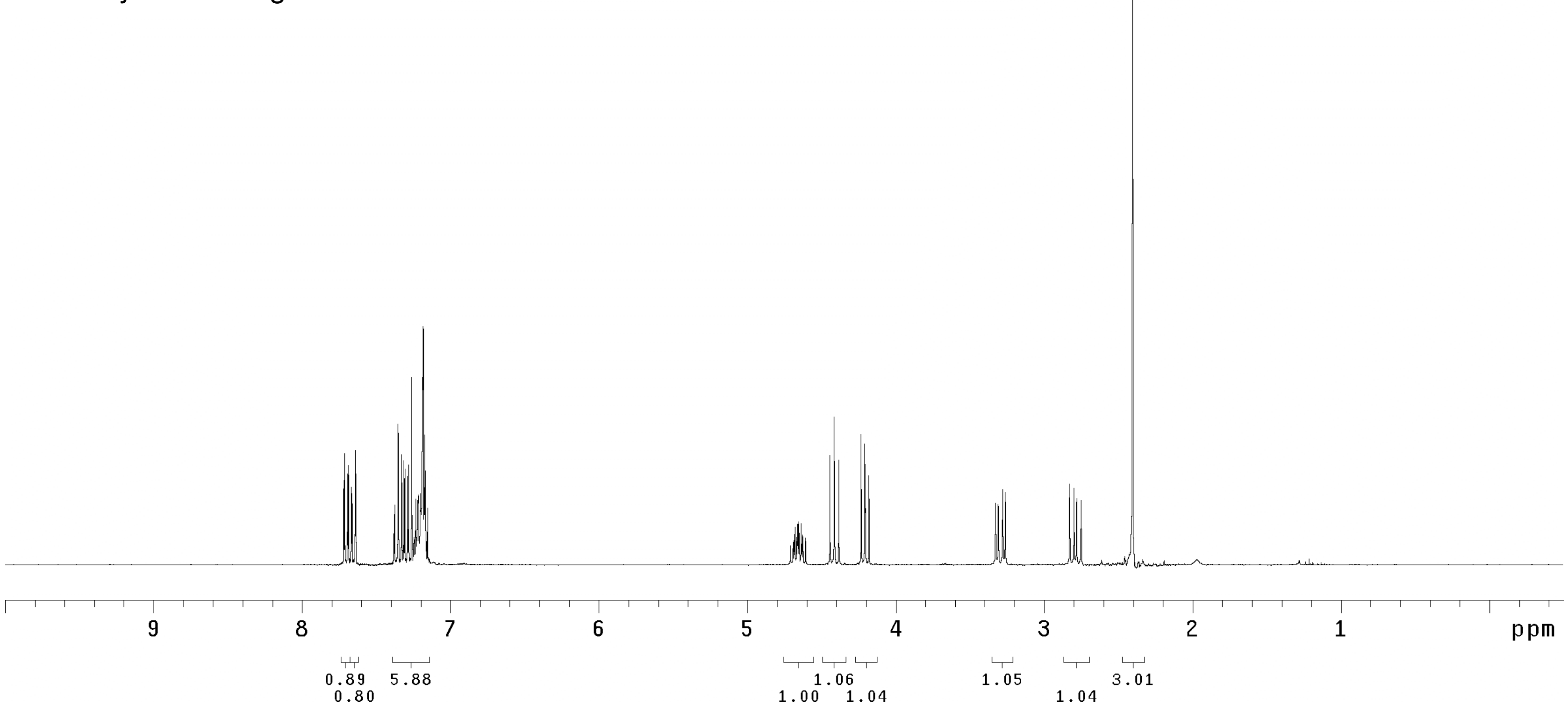

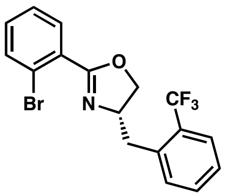

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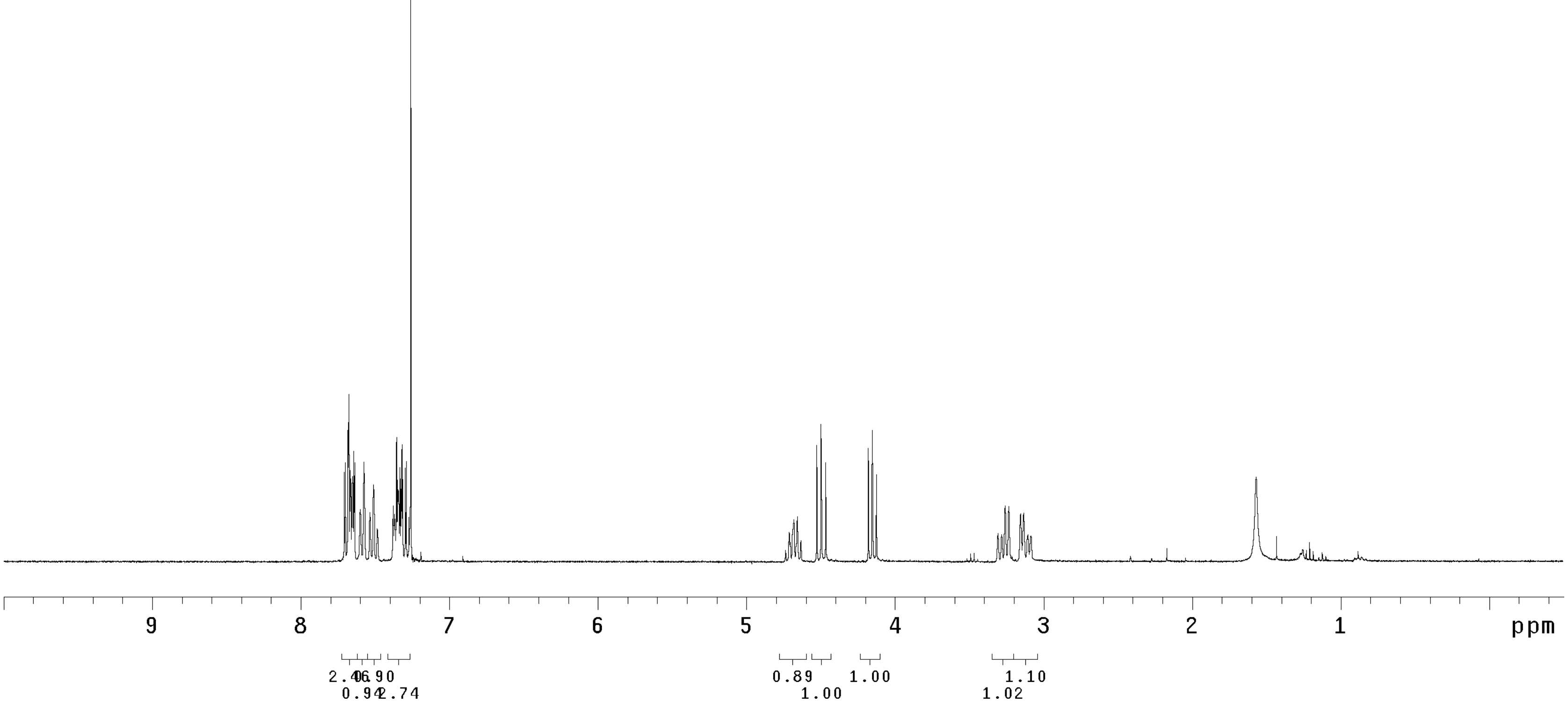

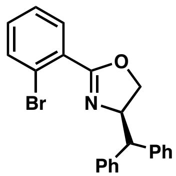

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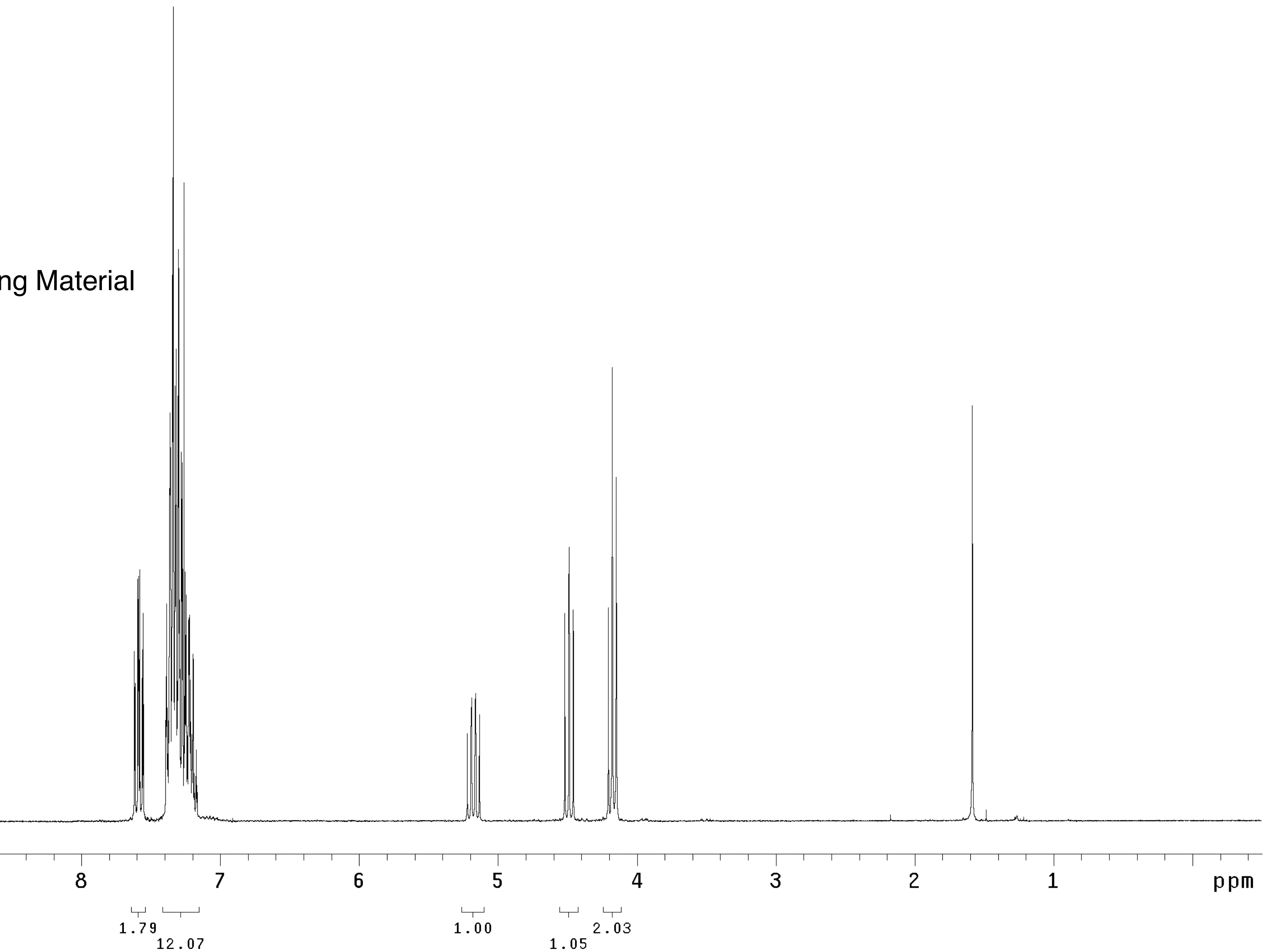

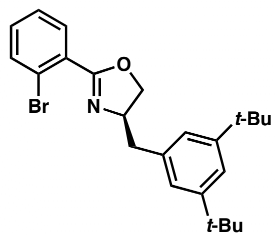

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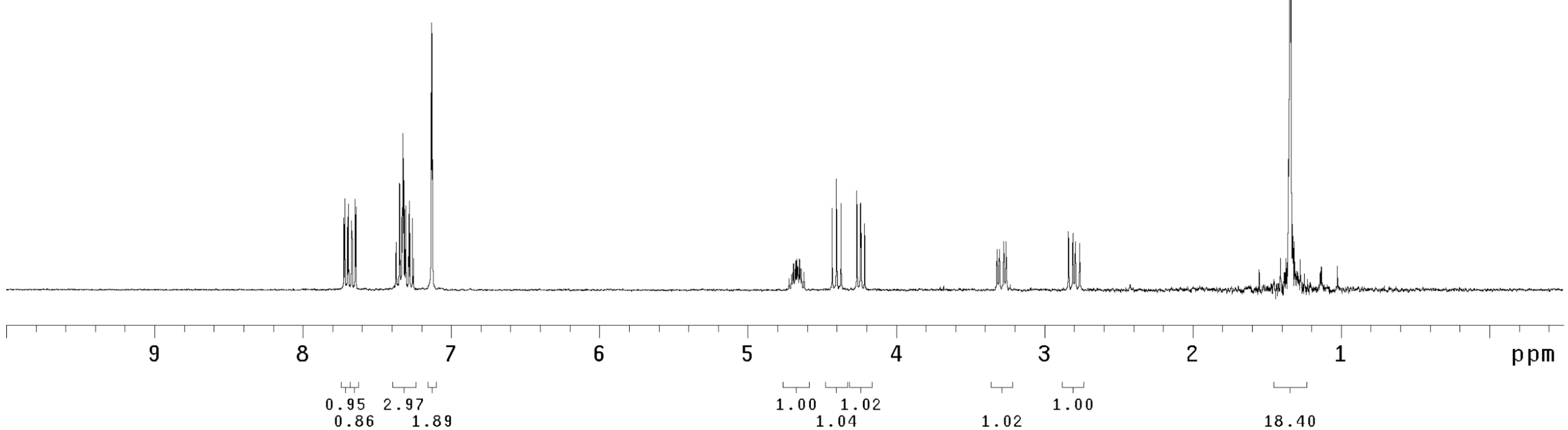

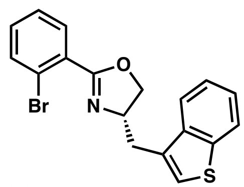

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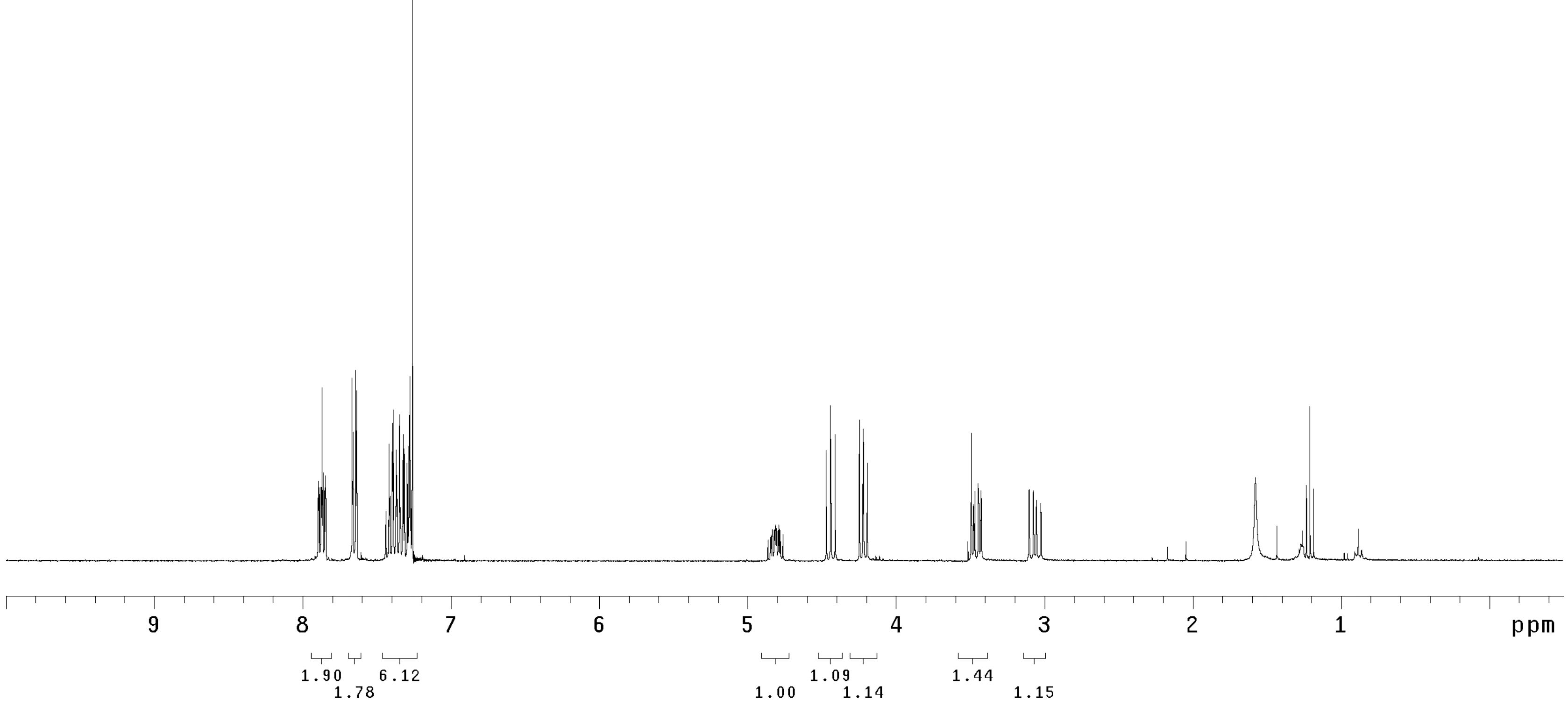

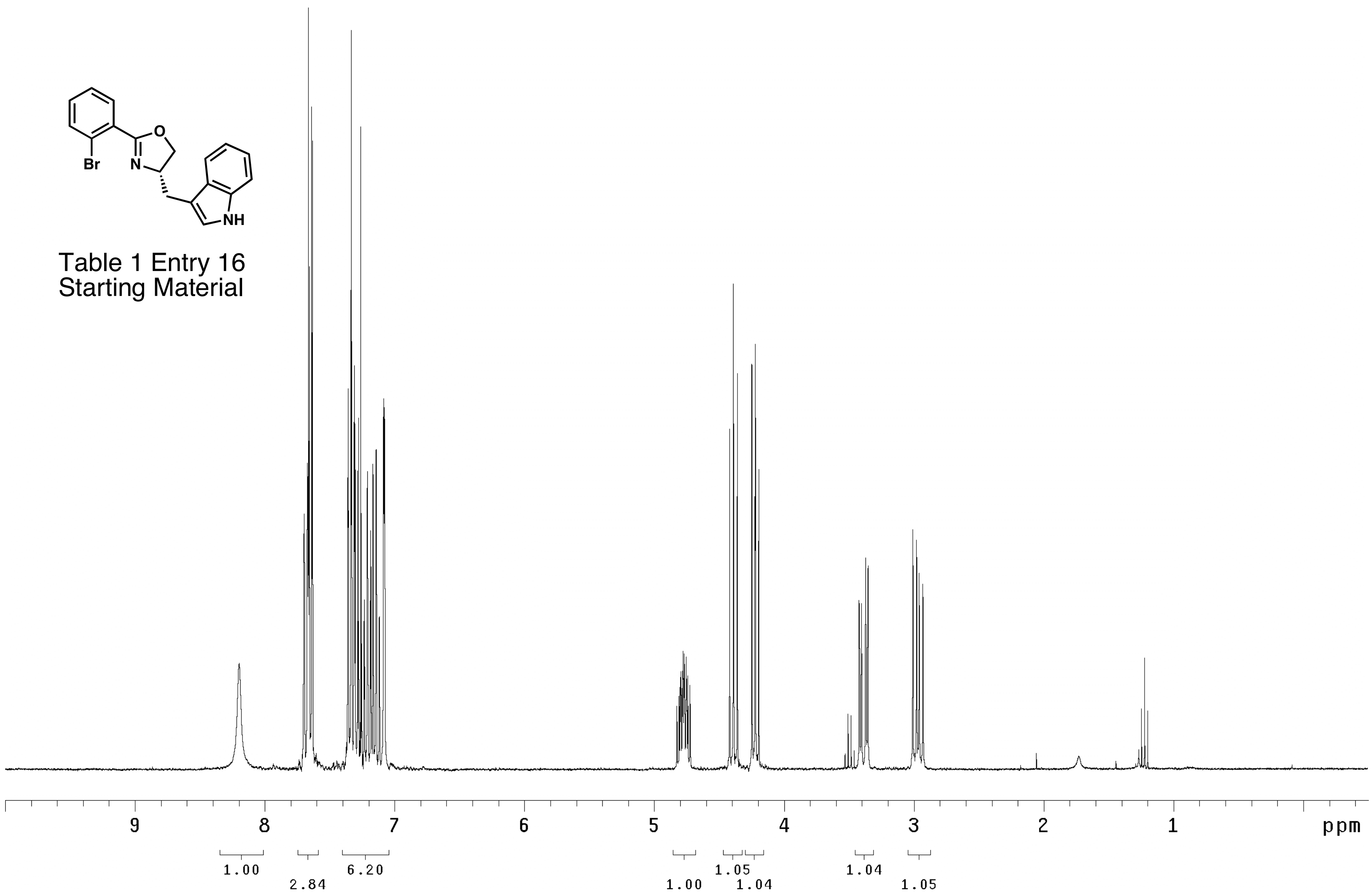
Br
N
O
NH
Table 1 Entry 16
Starting Material
9
8
7
6
5
4
3
2
1
ppm
1.00
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1.04
1.04
1.05

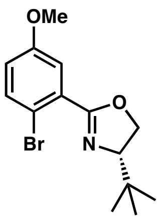
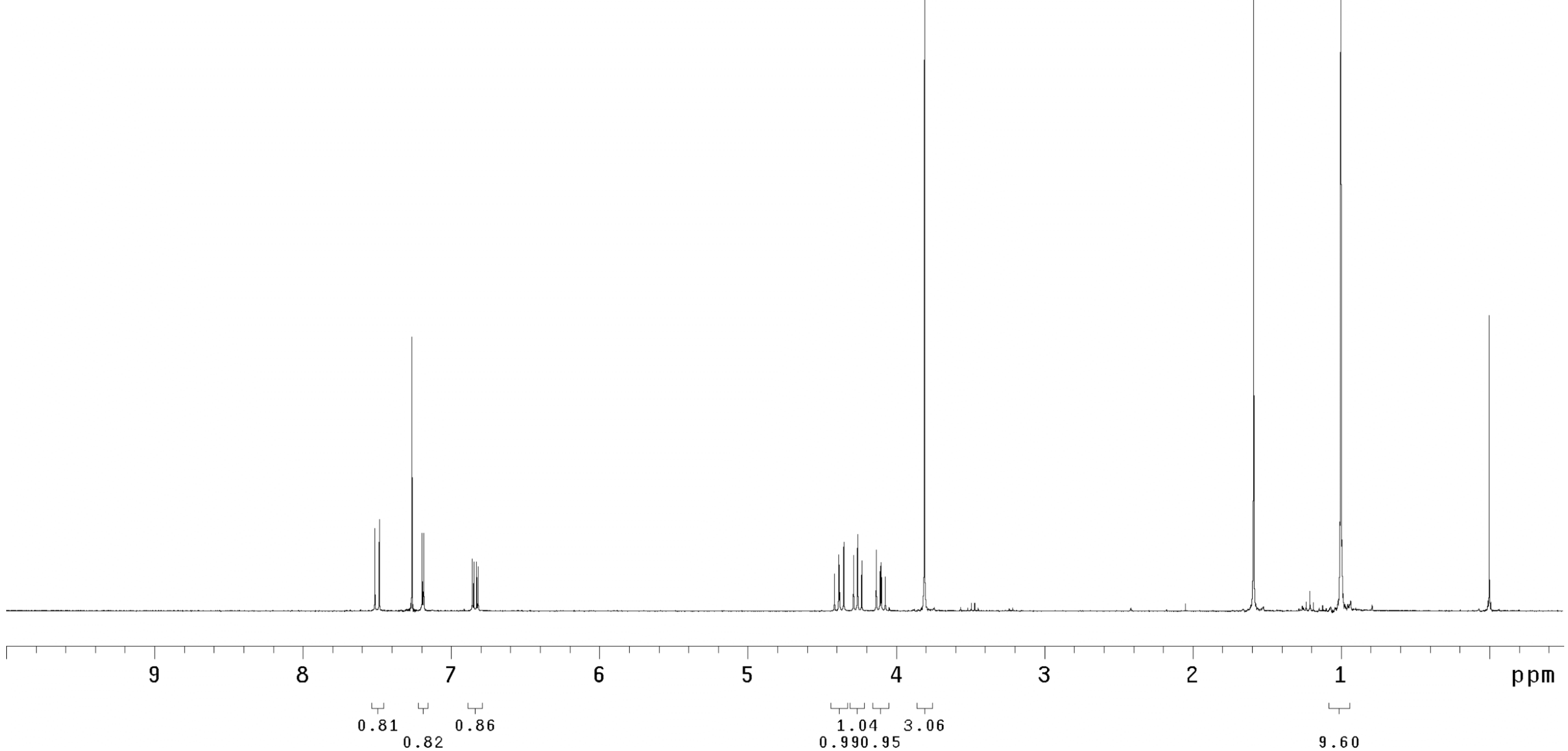


Table 2 Entry 5 and 6 Aryl Bromide



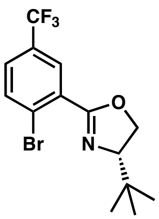
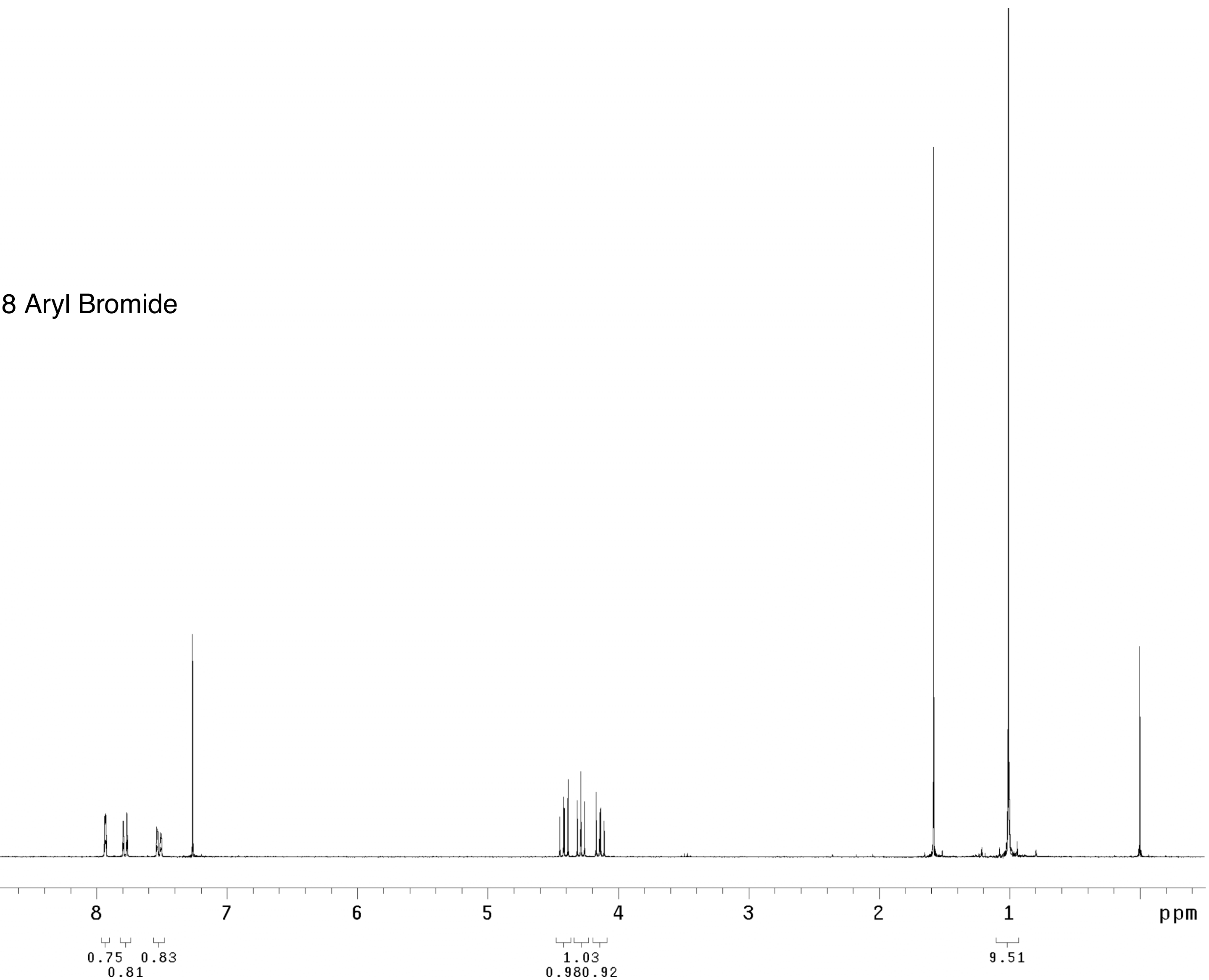
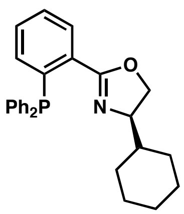


Table 2 Entry 7 and 8 Aryl Bromide



^{1}H and ^{31}P NMR Spectra of PHOX Derivatives
^{1}H NMR



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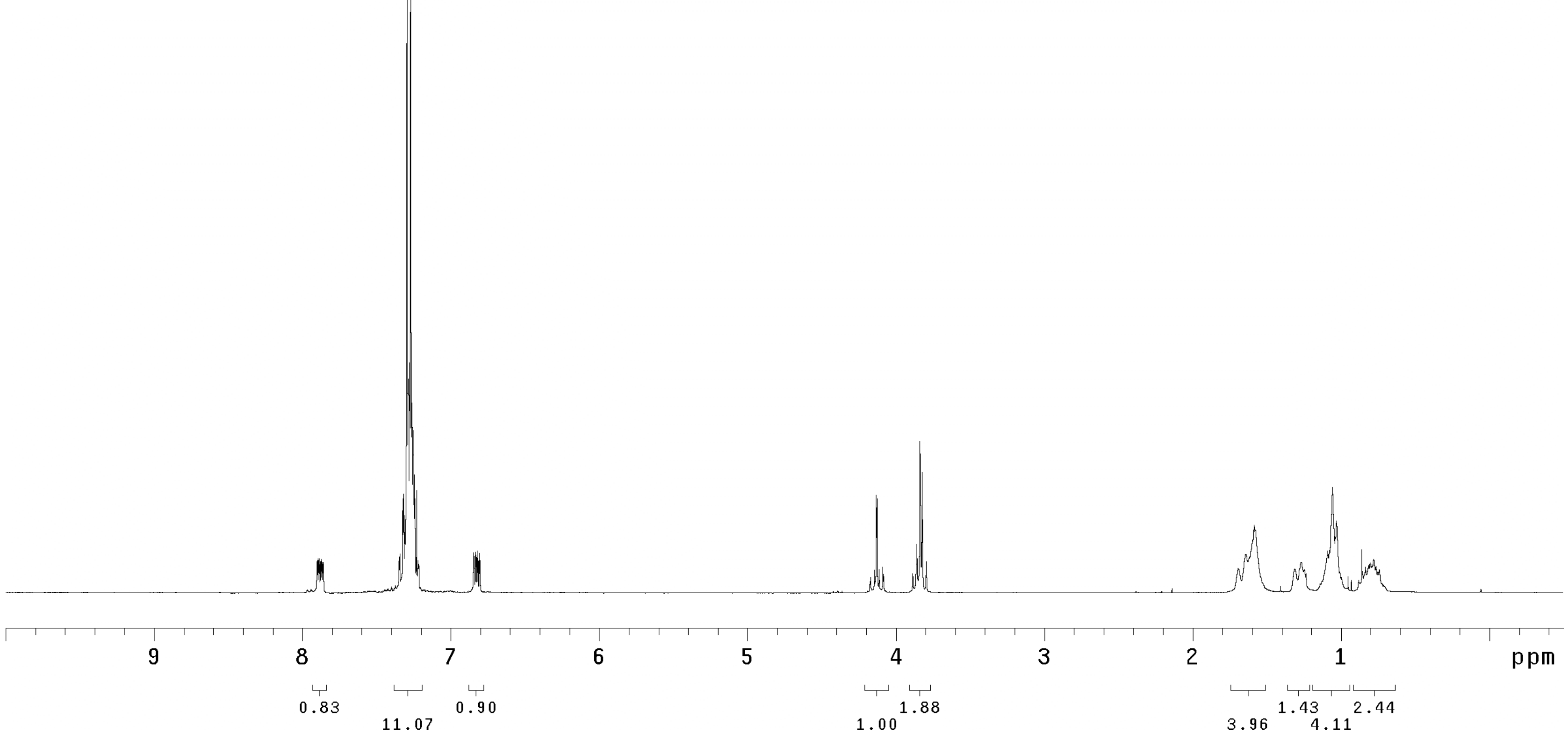


^{31}P NMR

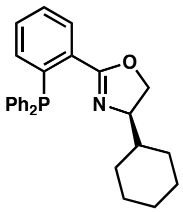
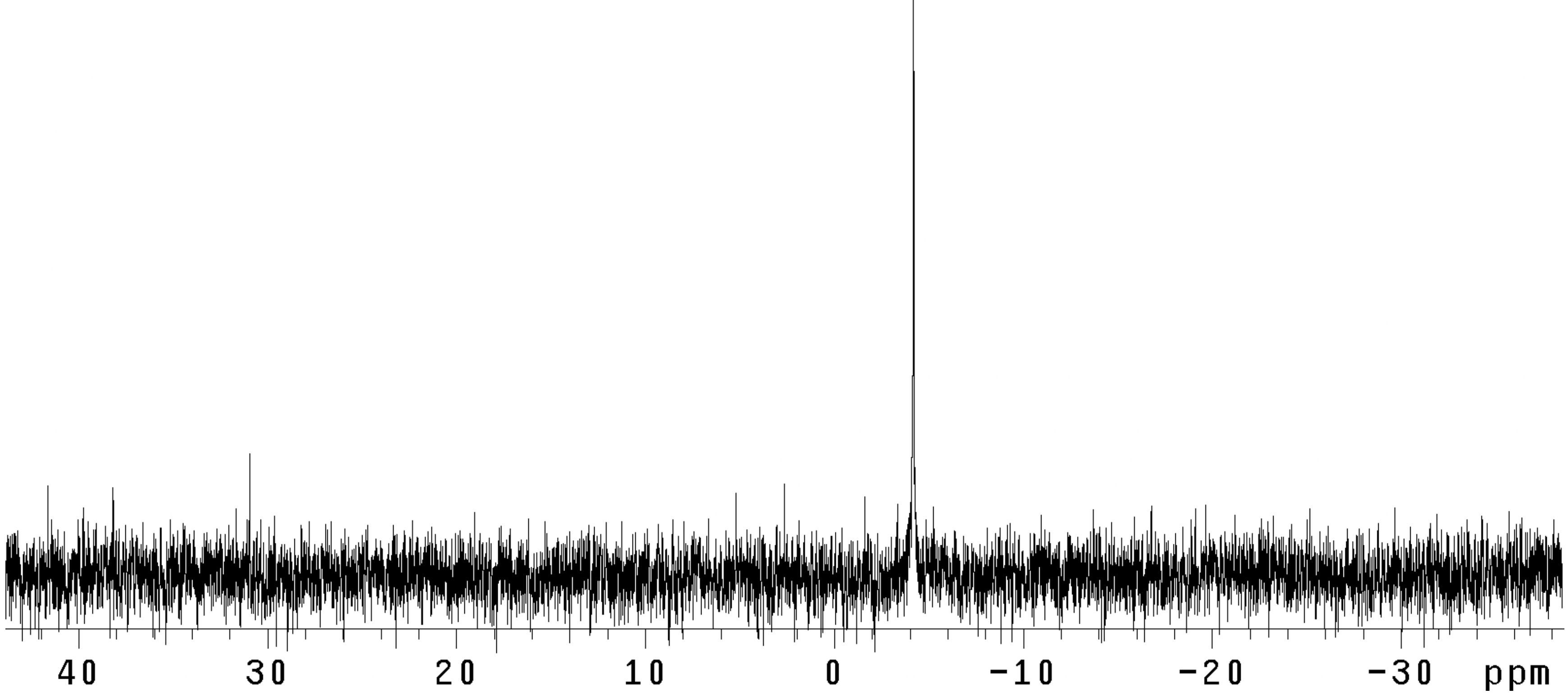
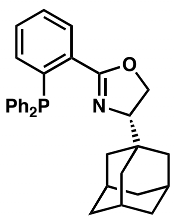


Table 1 Entry 3 Product



^{1}H NMR



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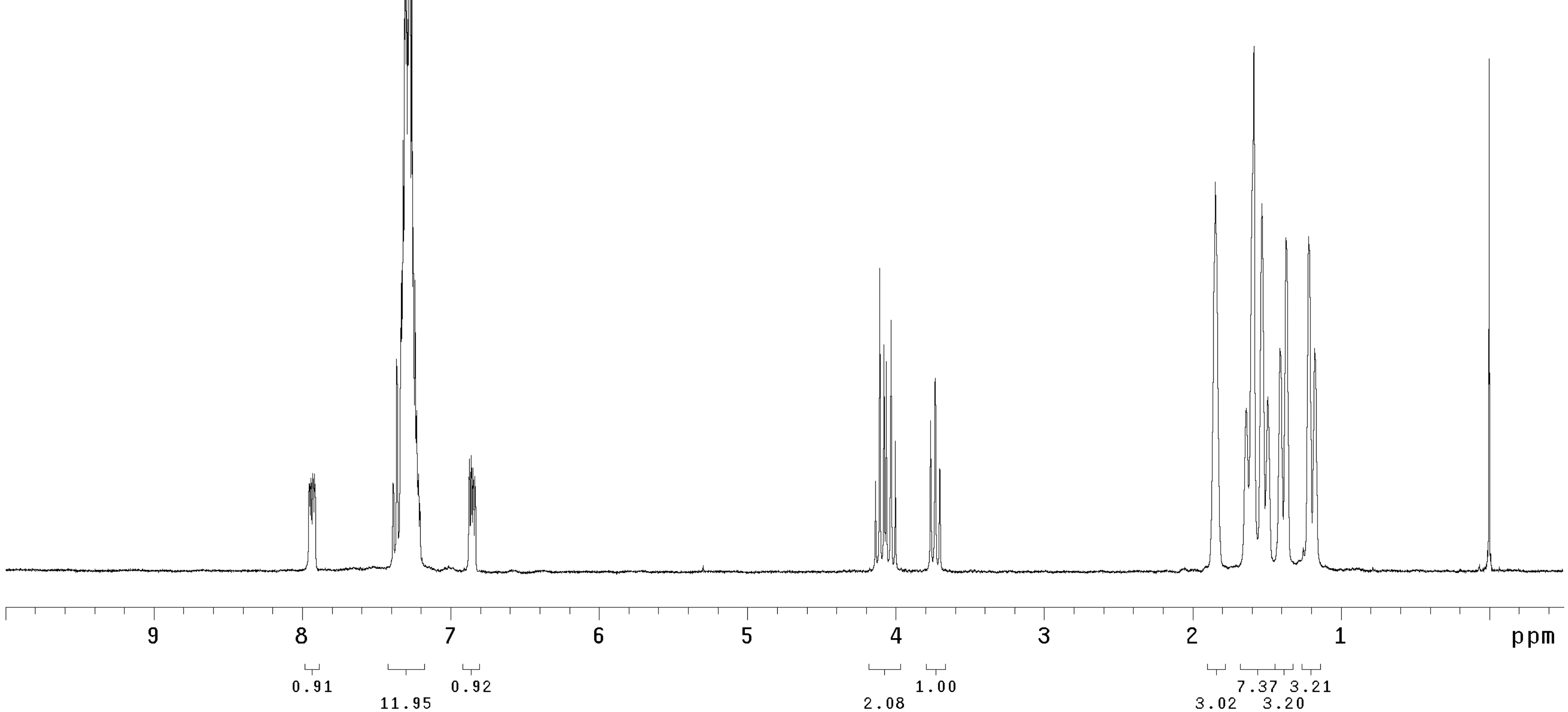
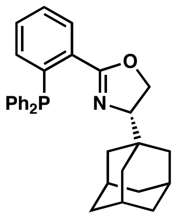


^{31}P NMR



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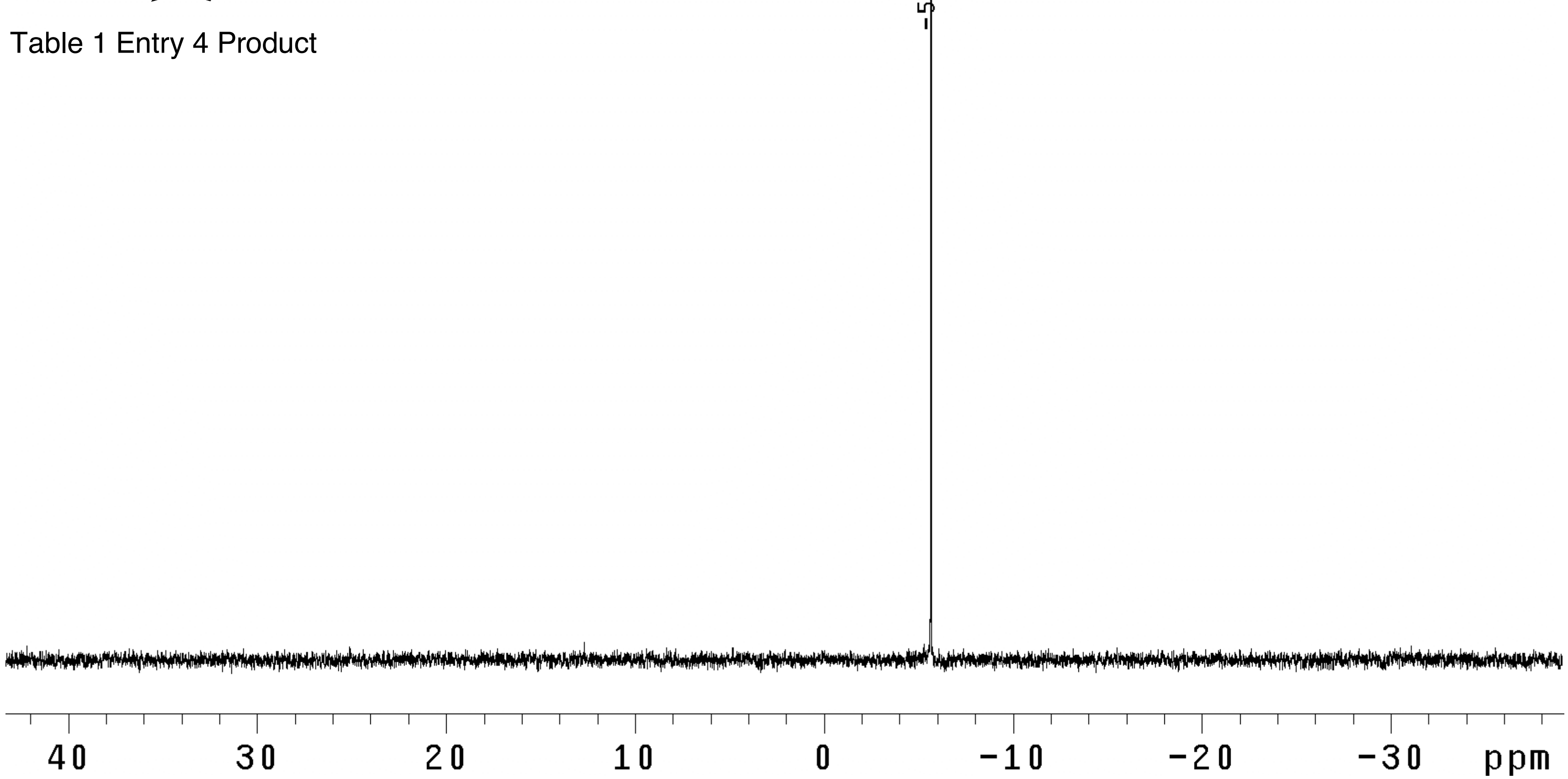
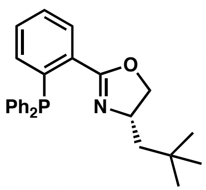


^{1}H NMR



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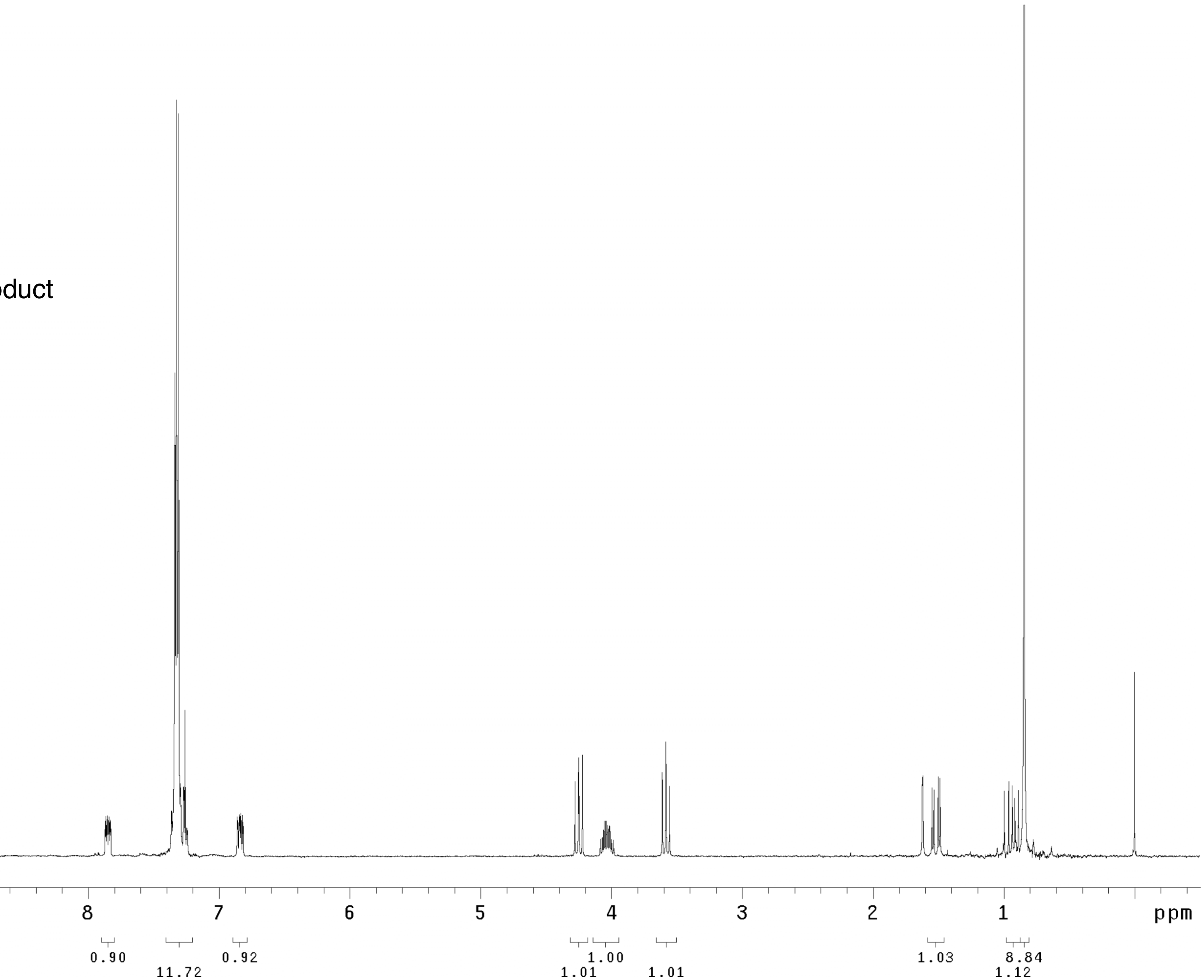
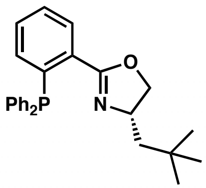


^{31}P NMR



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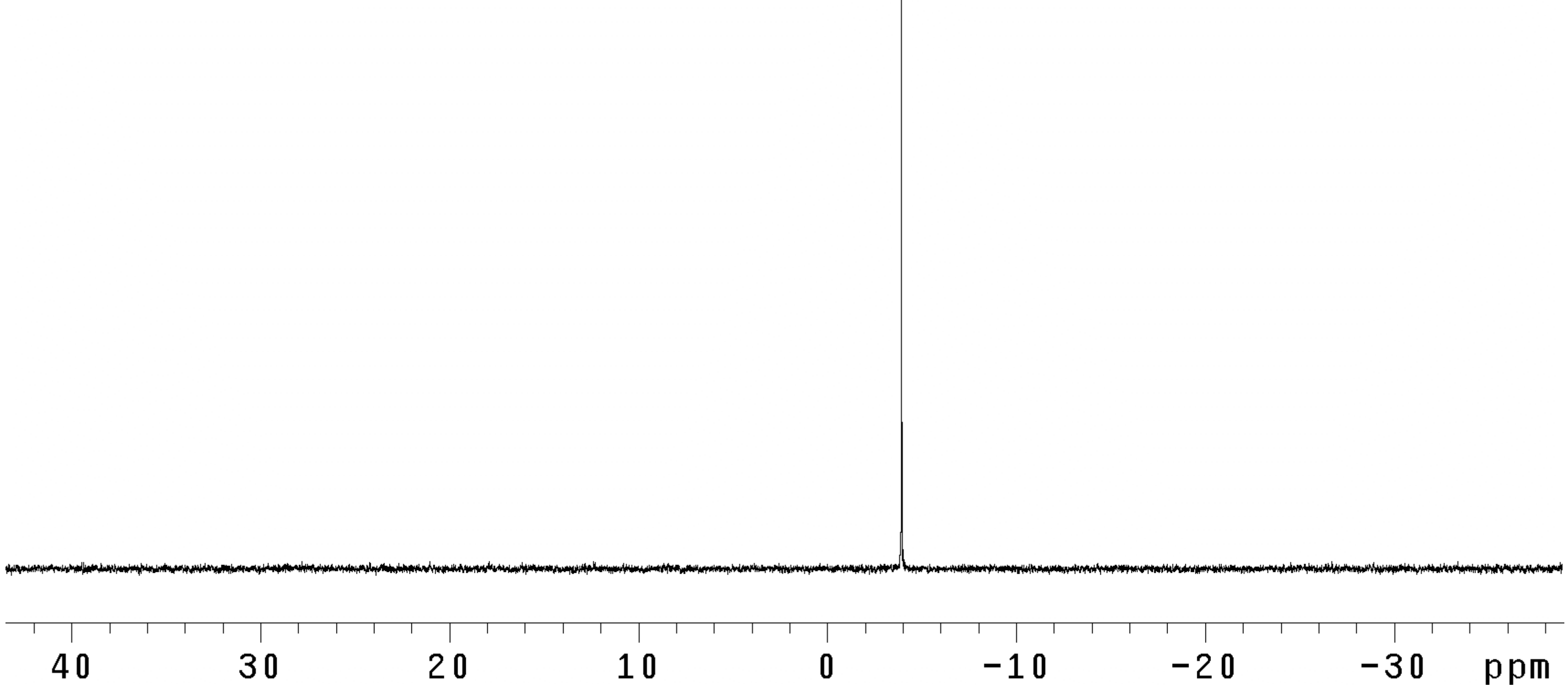


^{1}H NMR

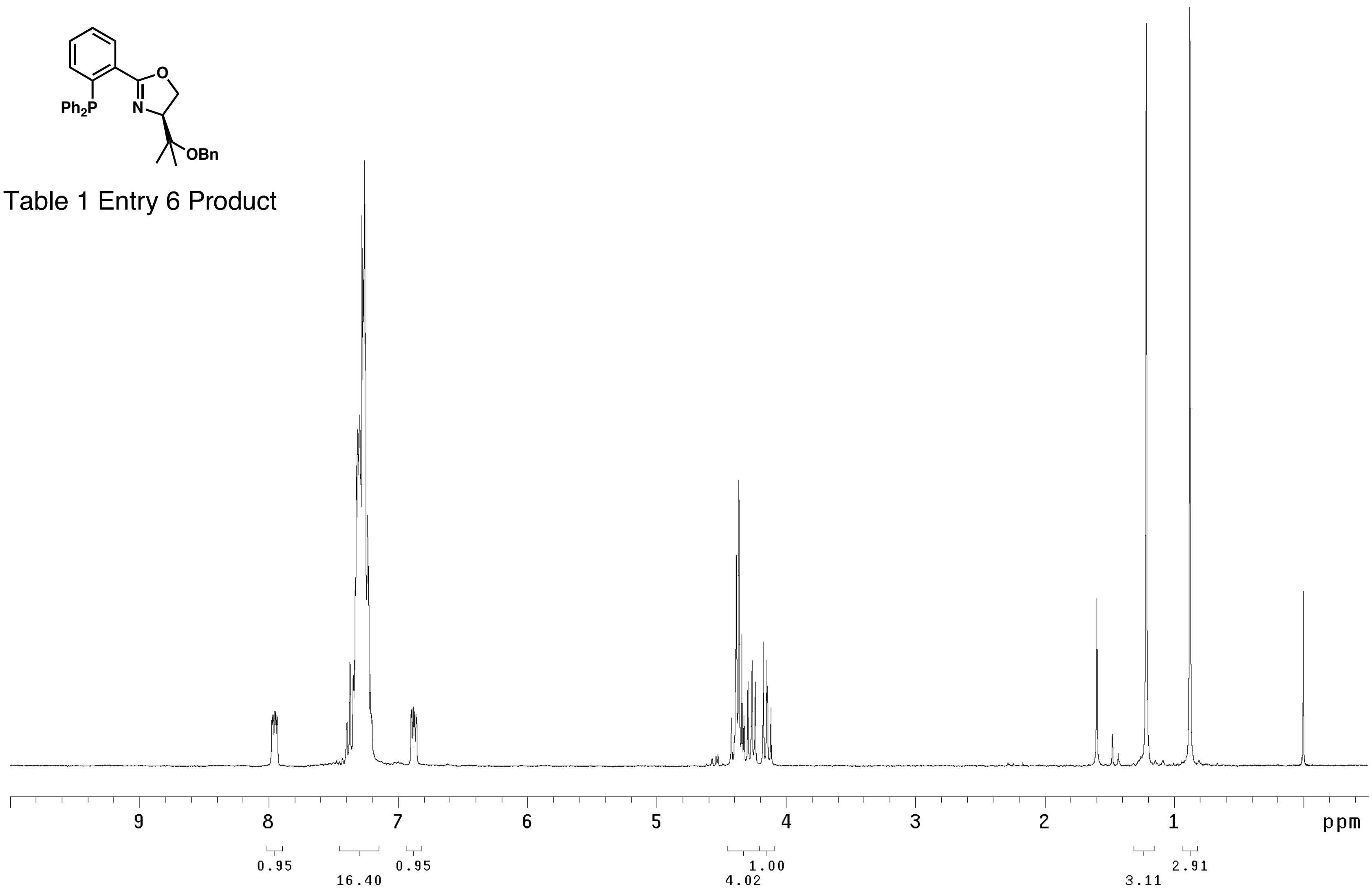
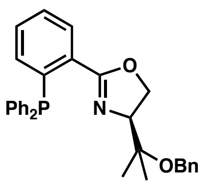


Table 1 Entry 6 Product

^{31}P NMR



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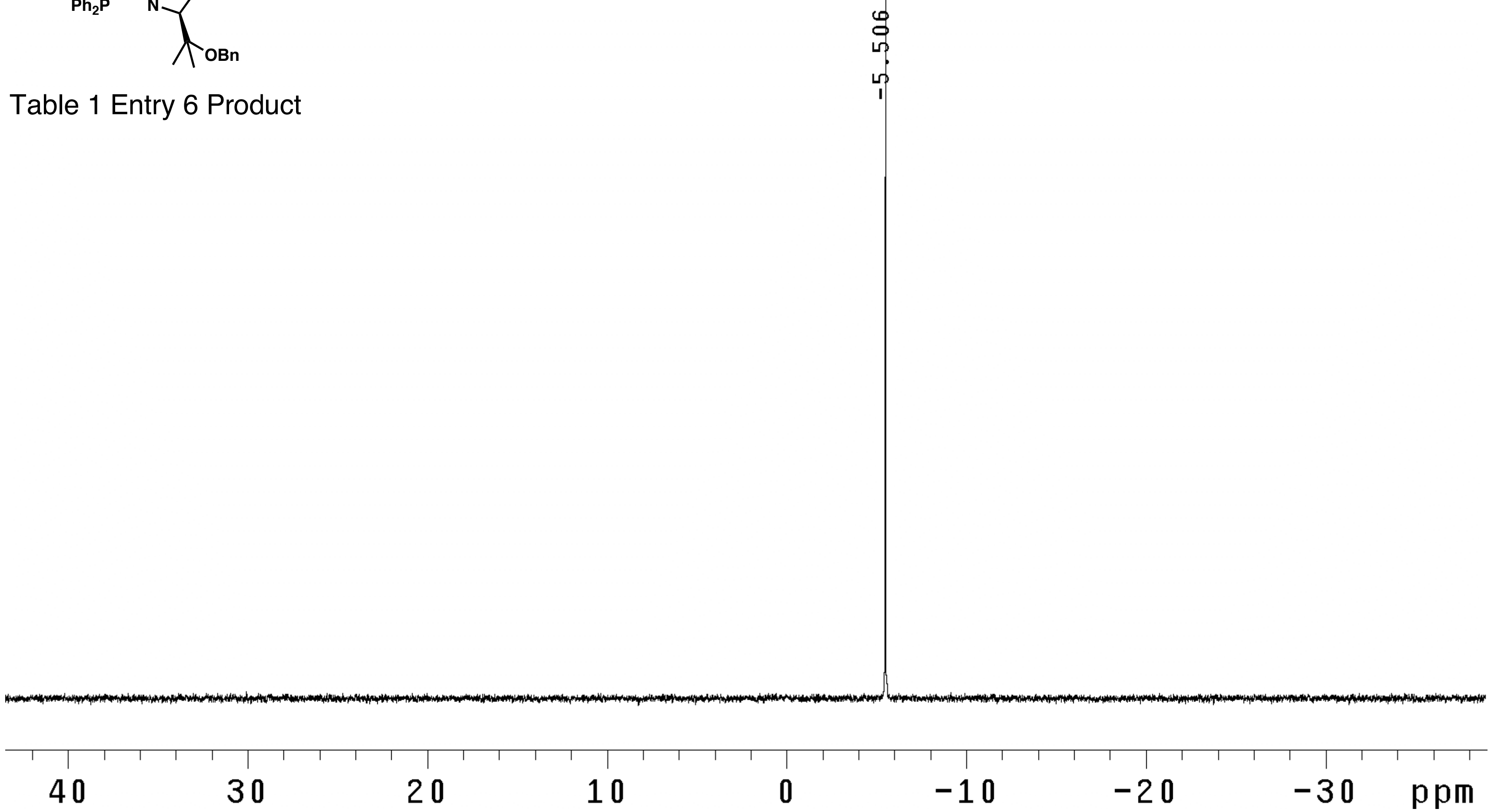
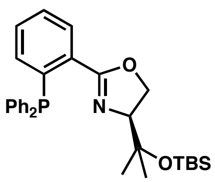


^{1}H NMR



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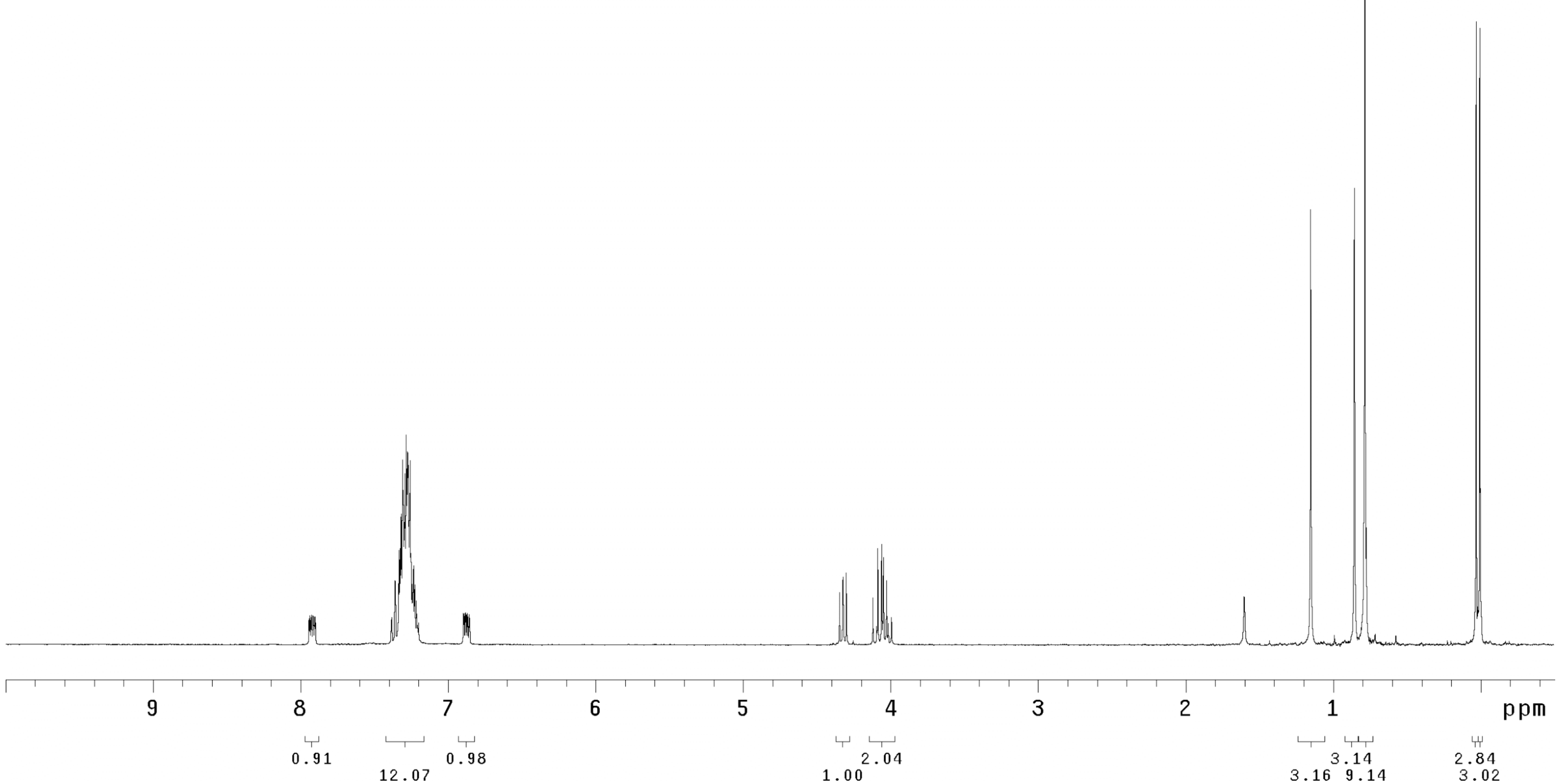
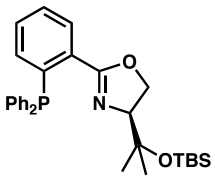


^{31}P NMR



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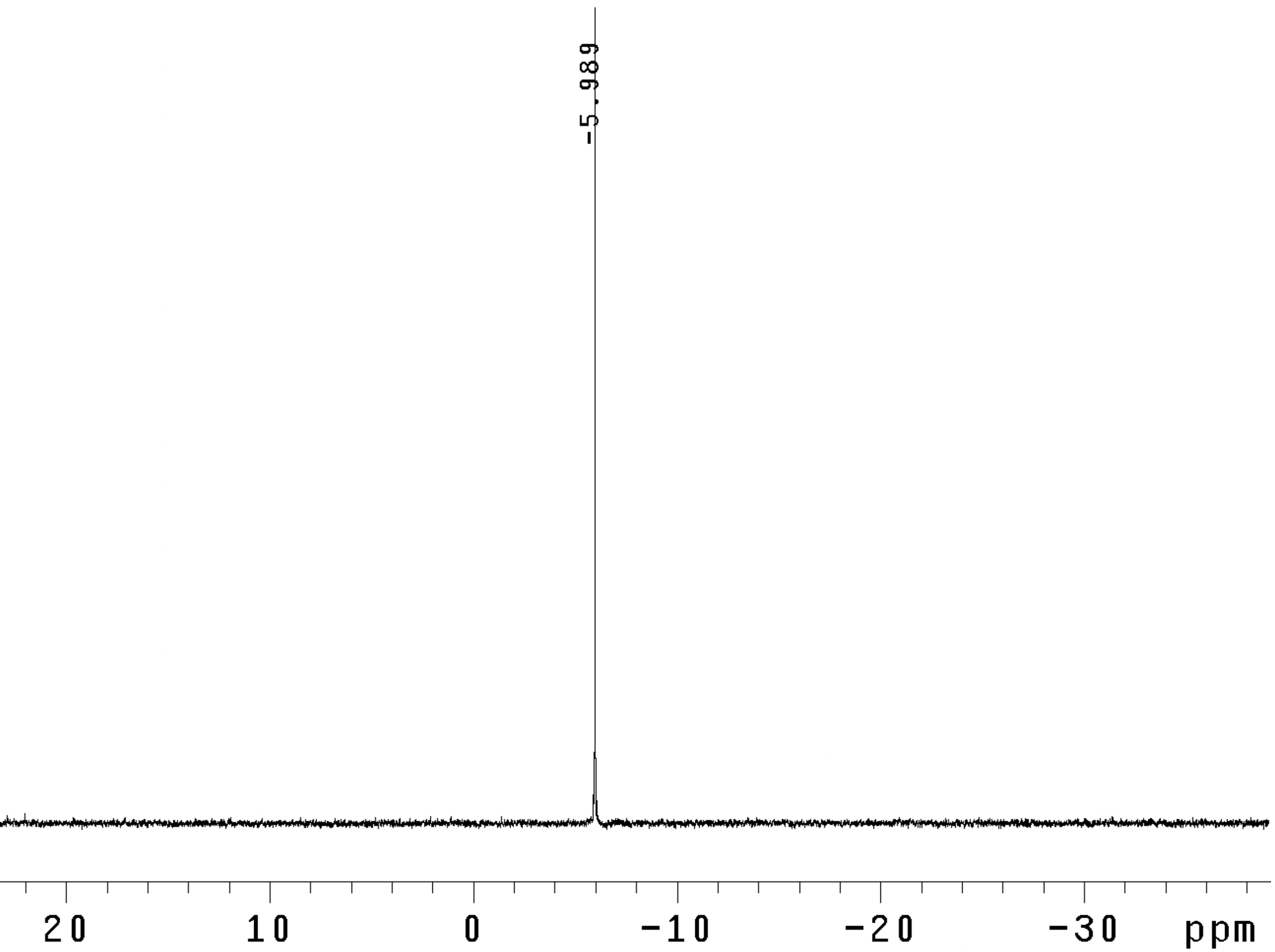


^{1}H NMR

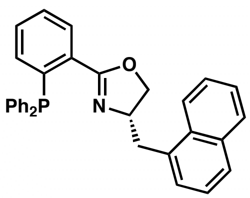
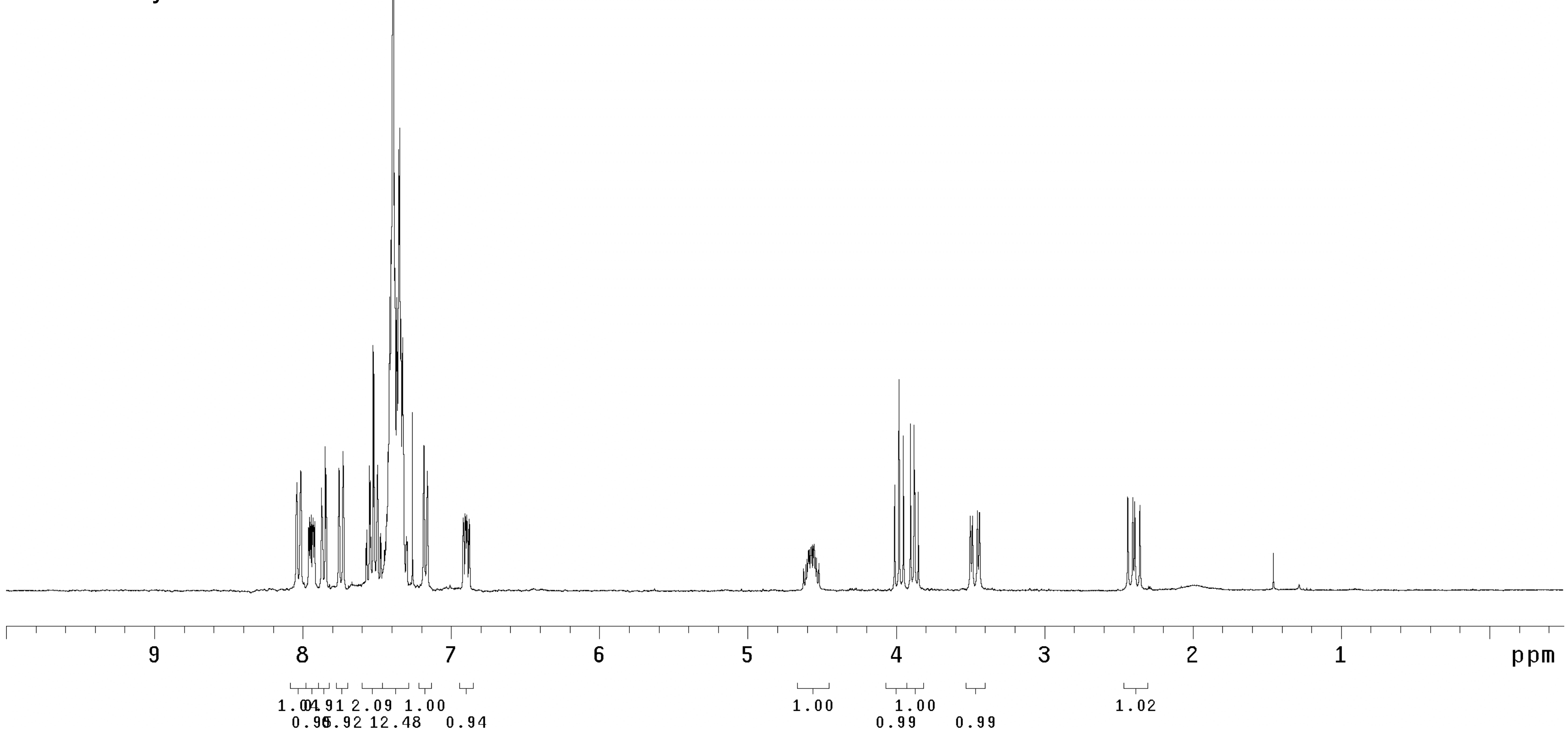
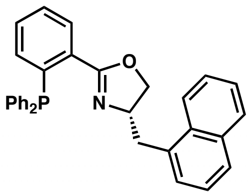


Table 1 Entry 8 Product



^{31}P NMR



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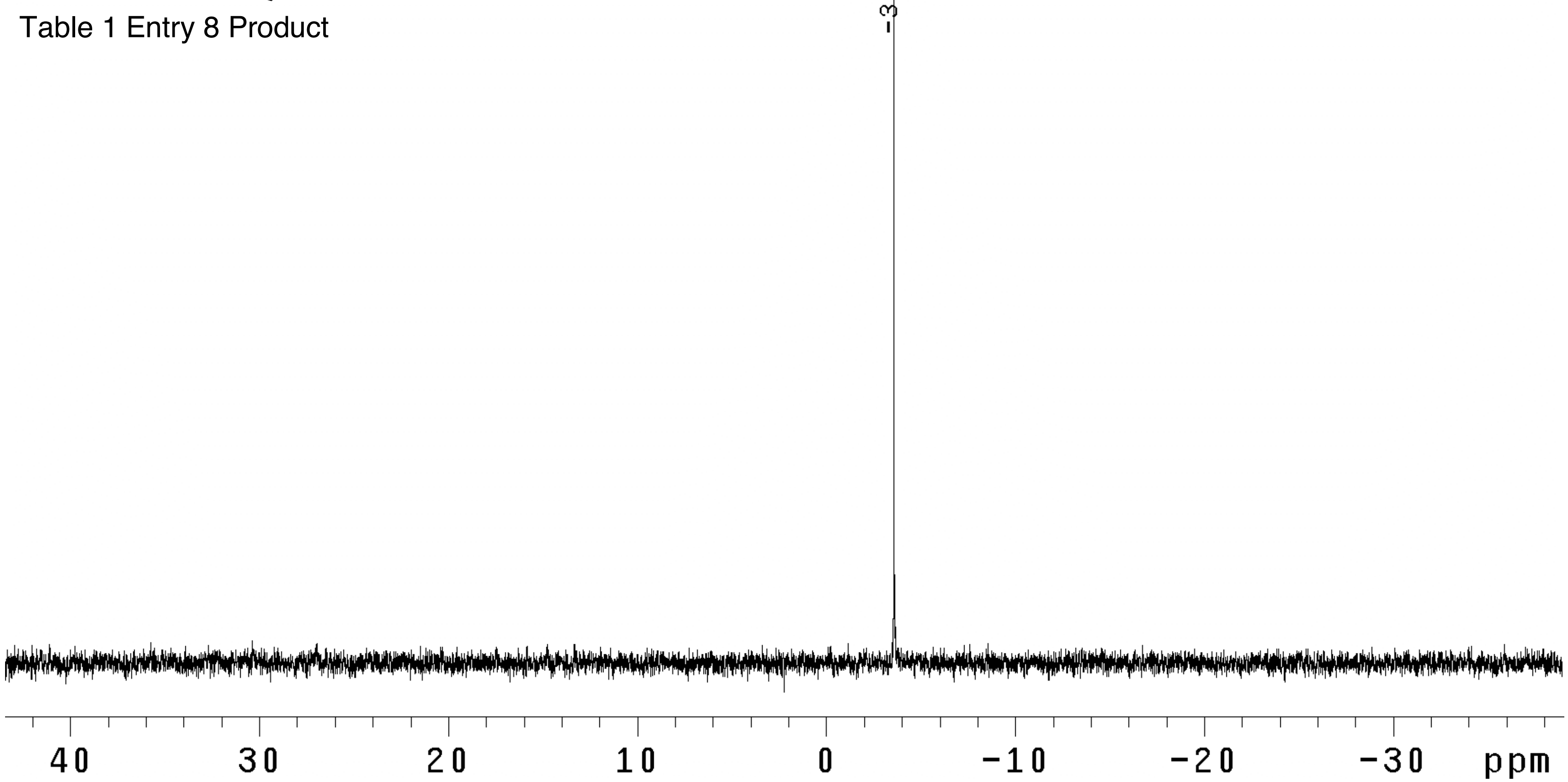

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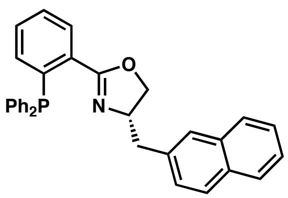

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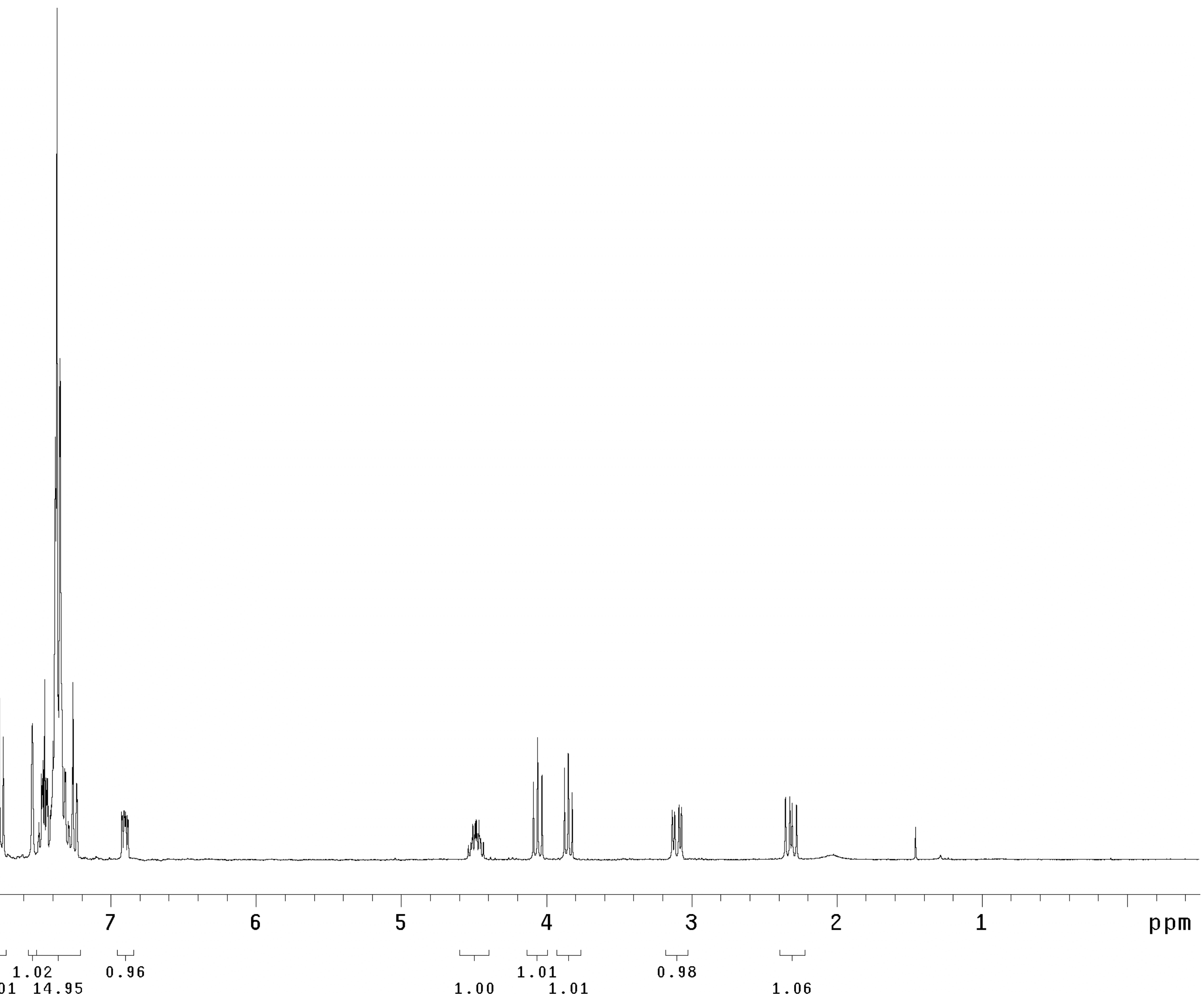
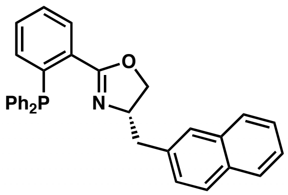


^{31}P NMR



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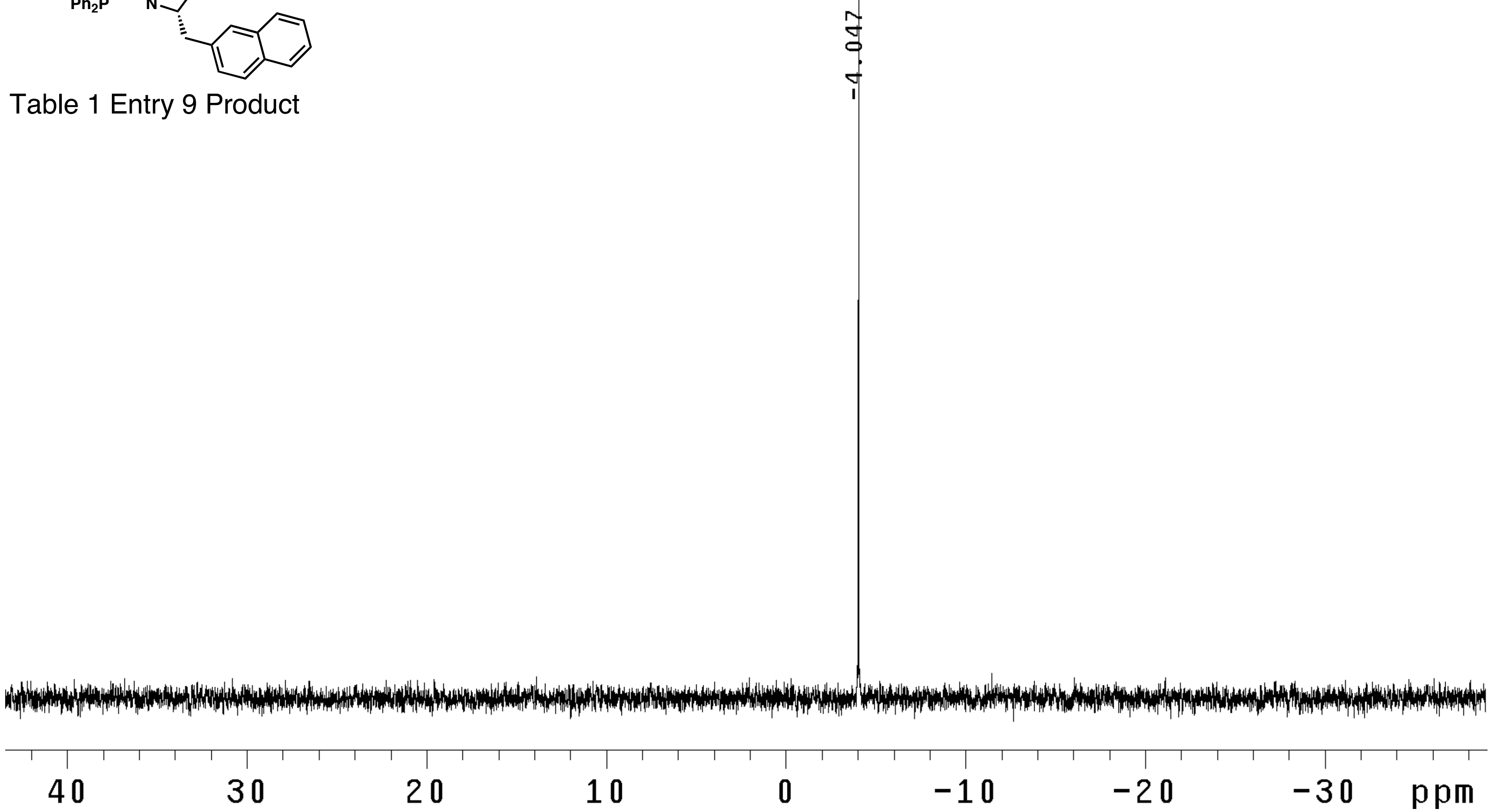
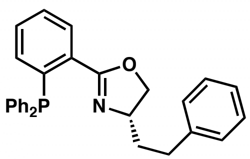


[1]H NMR



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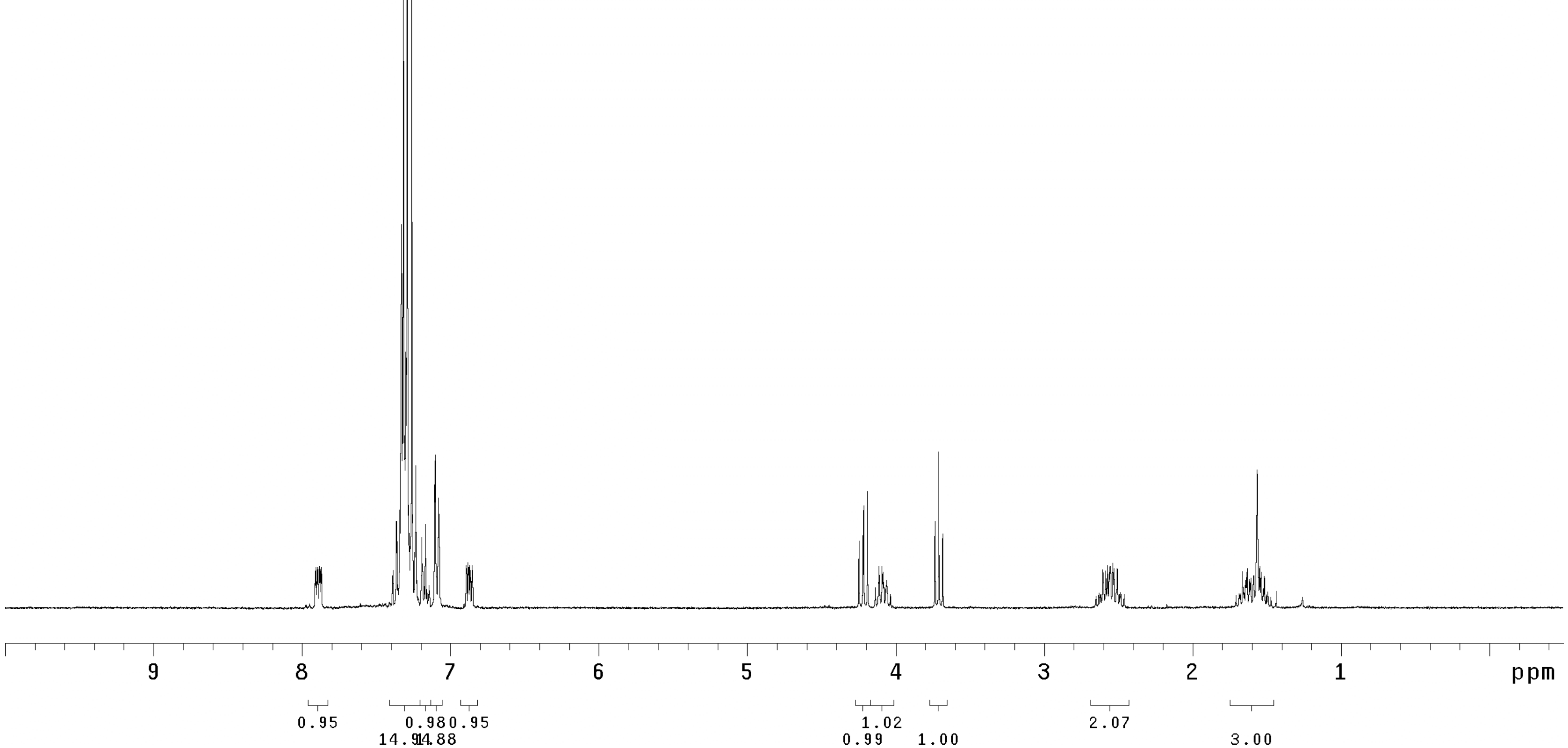
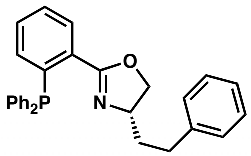


^{31}P NMR



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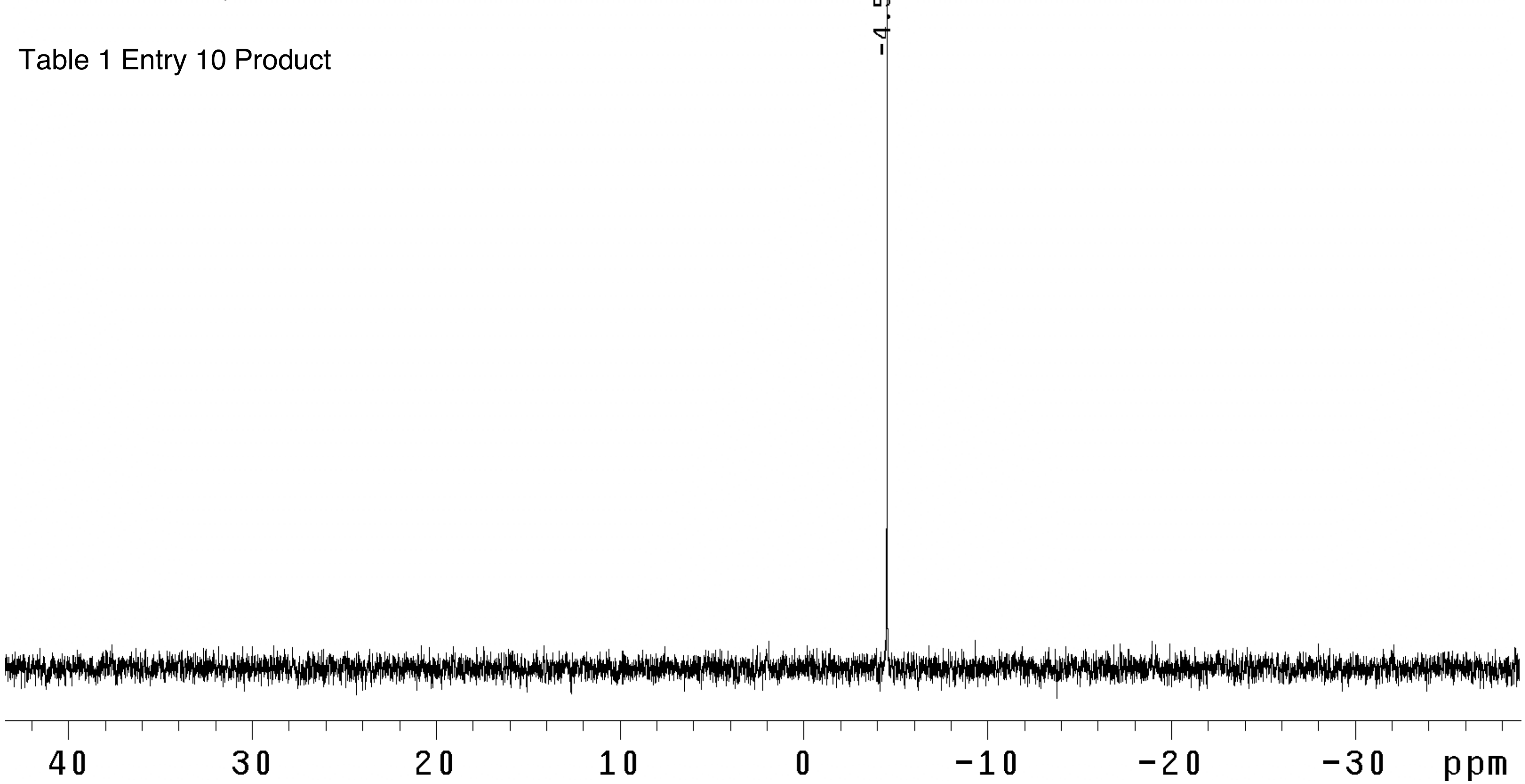
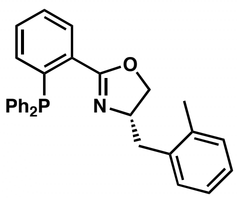


^{1}H NMR



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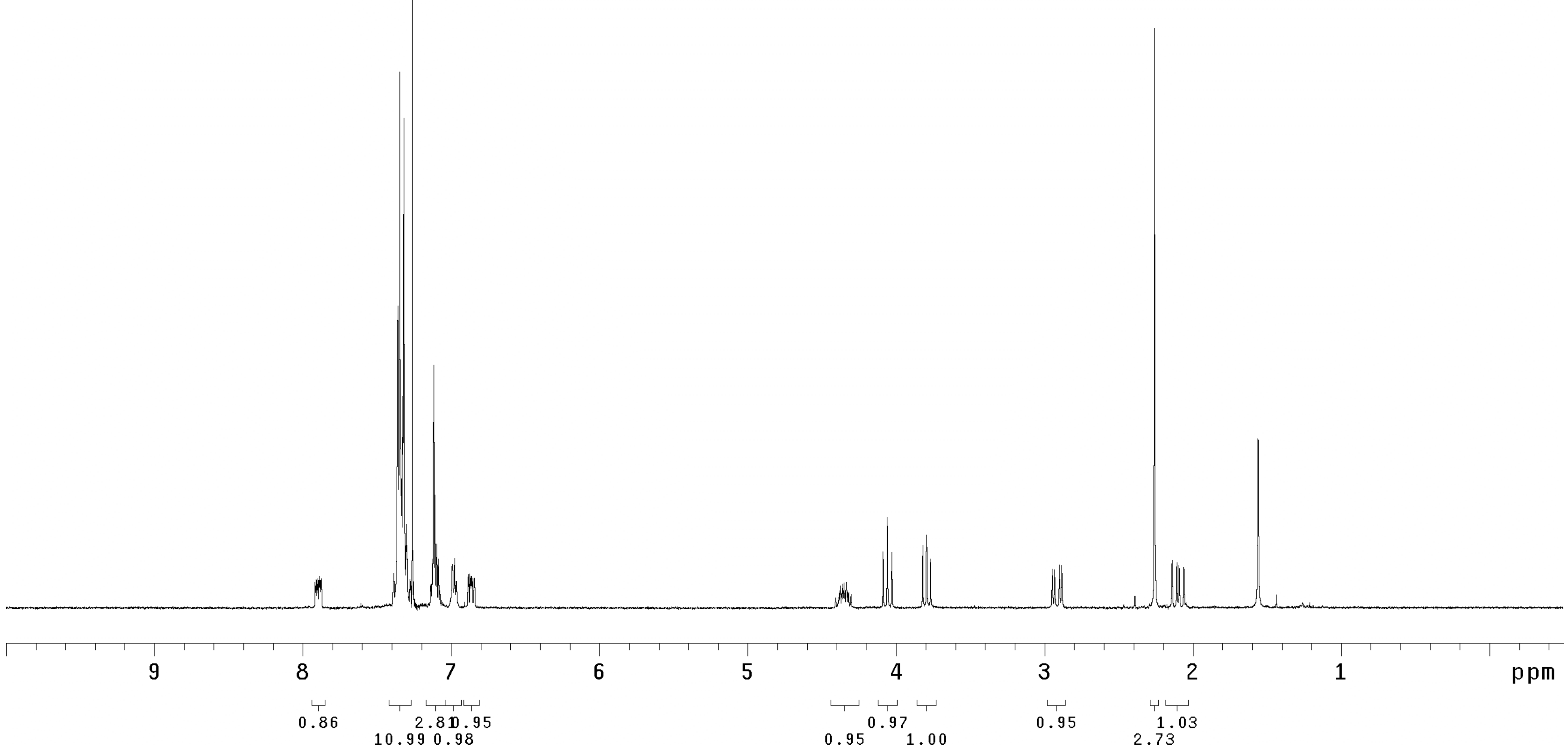
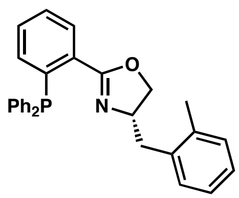


^{31}P NMR



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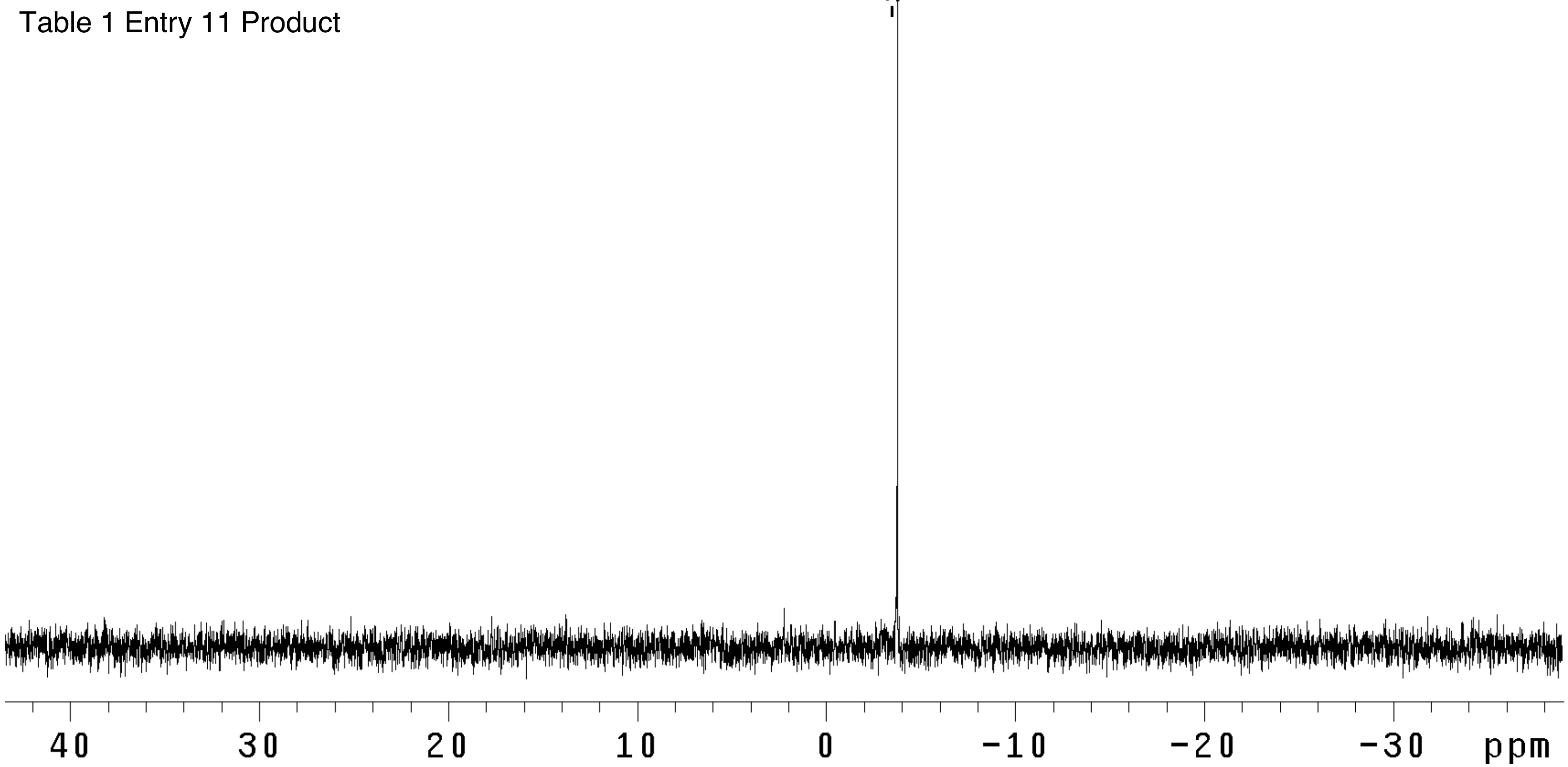
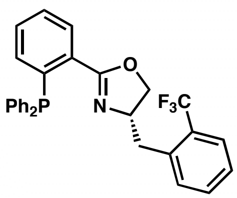


^{1}H NMR



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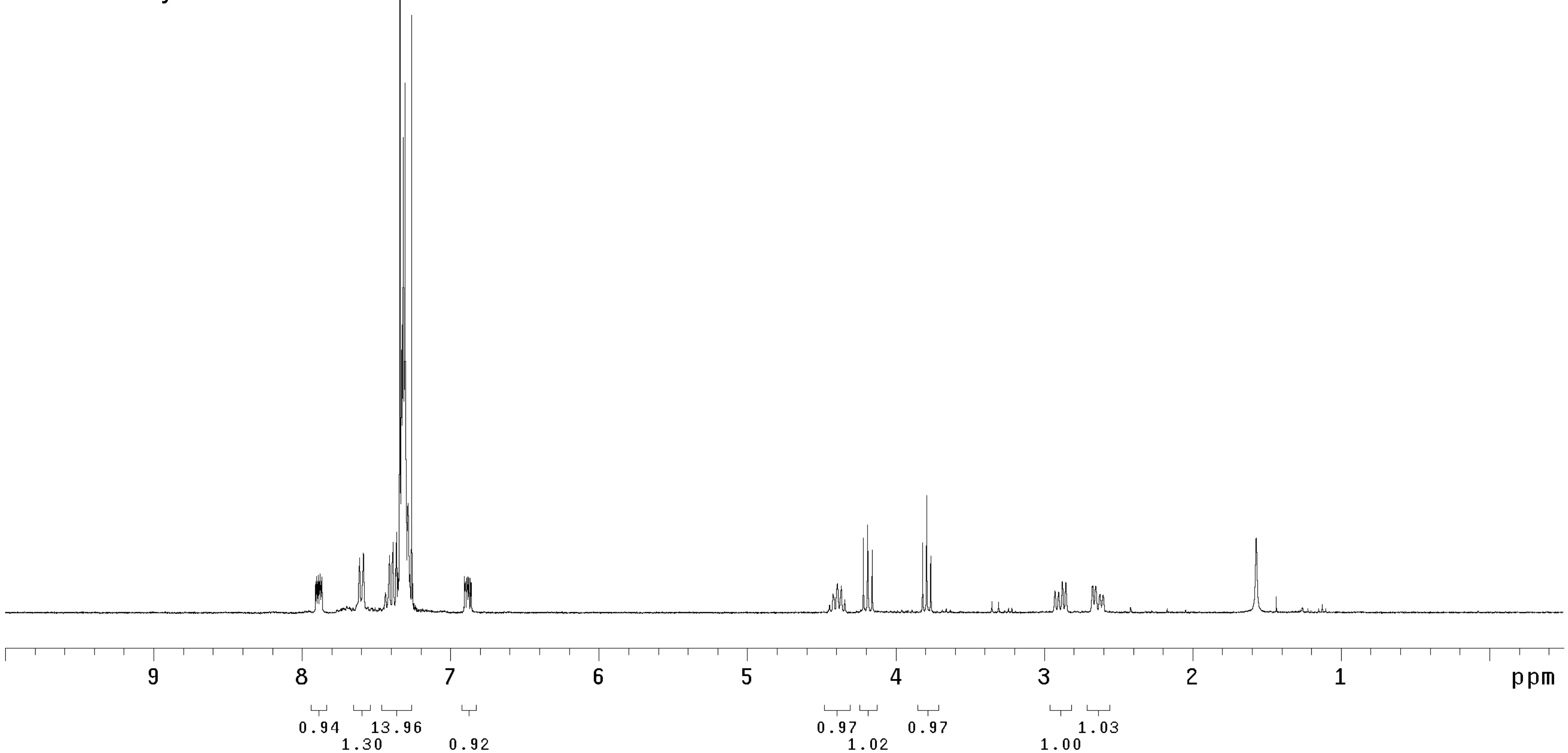

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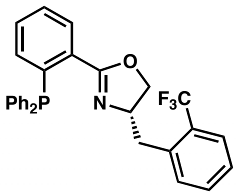

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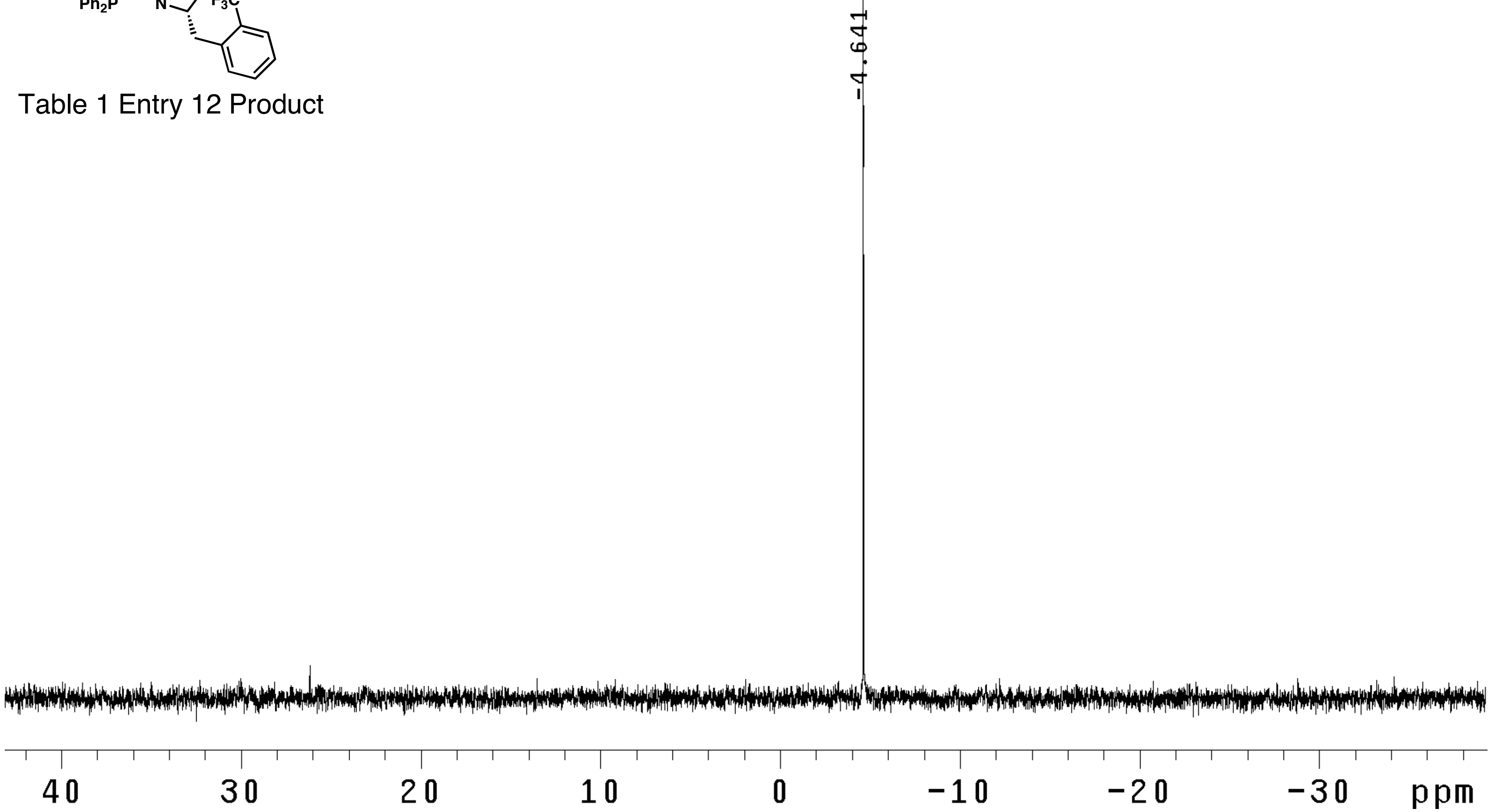
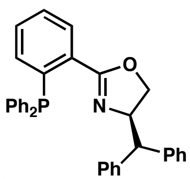


^{1}H NMR



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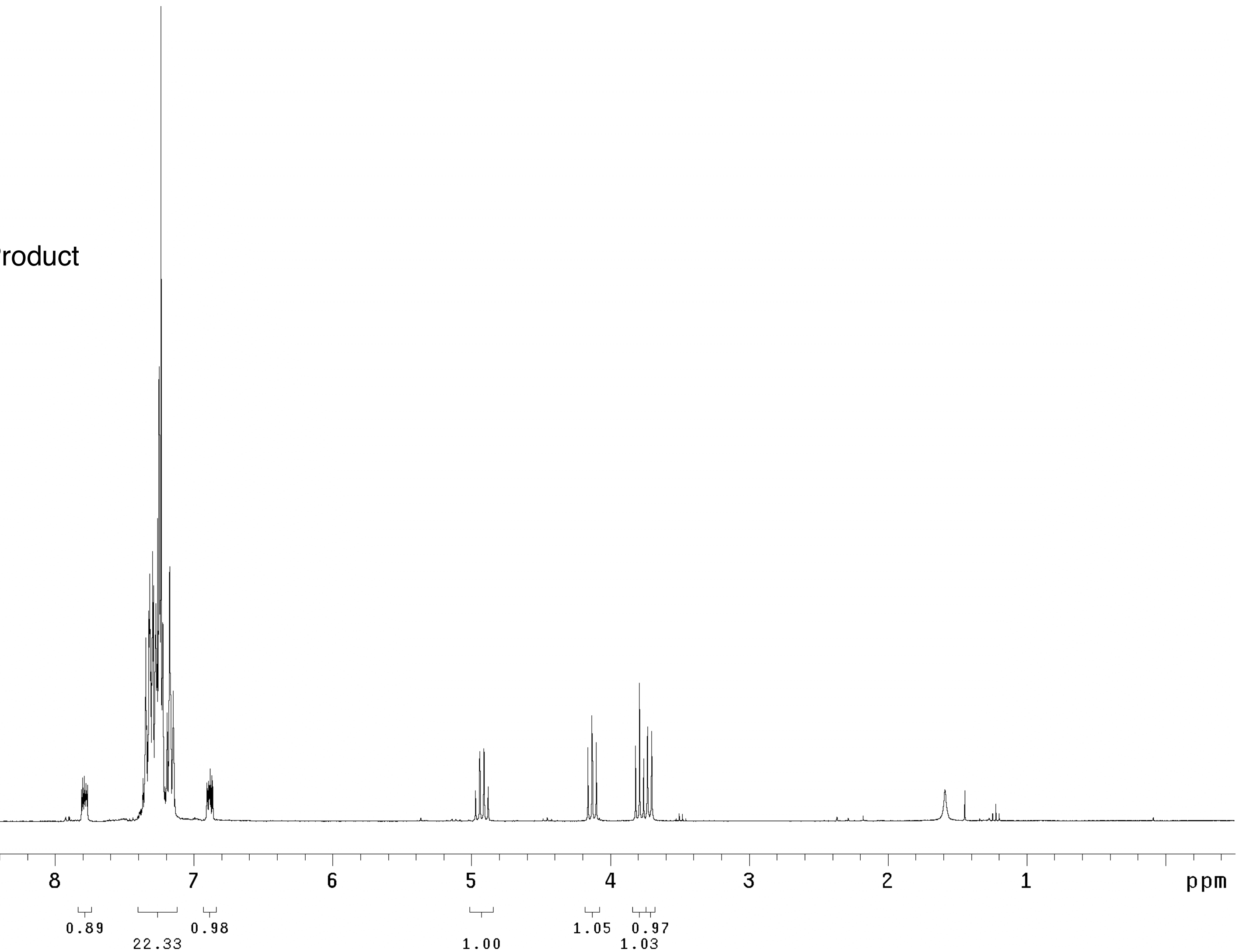
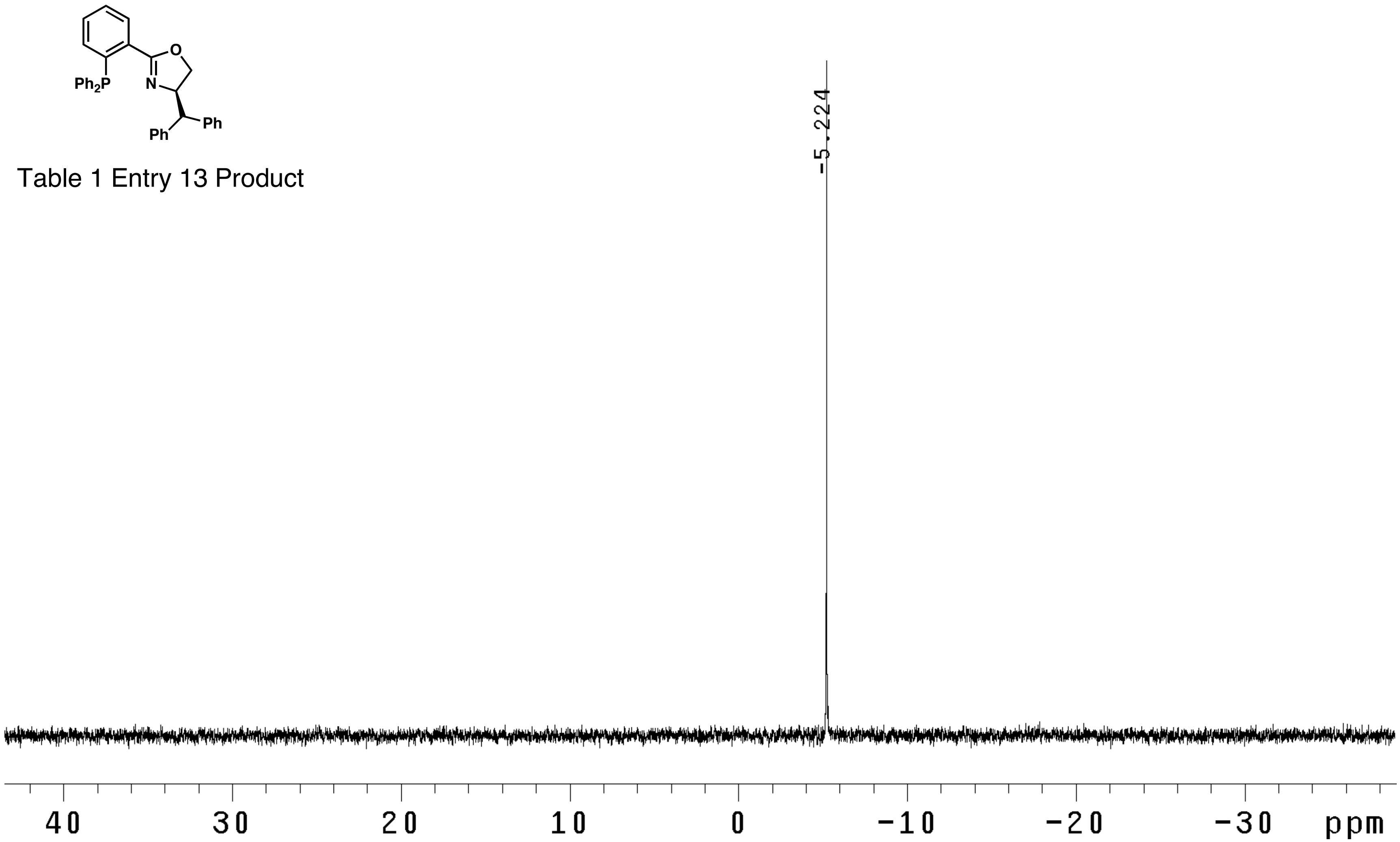


^{31}P NMR


Ph2P
N
O
Ph
Ph
Table 1 Entry 13 Product
-5.224
40
30
20
10
0
-10
-20
-30
ppm

^{1}H NMR

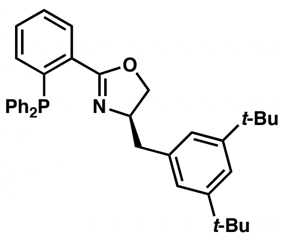
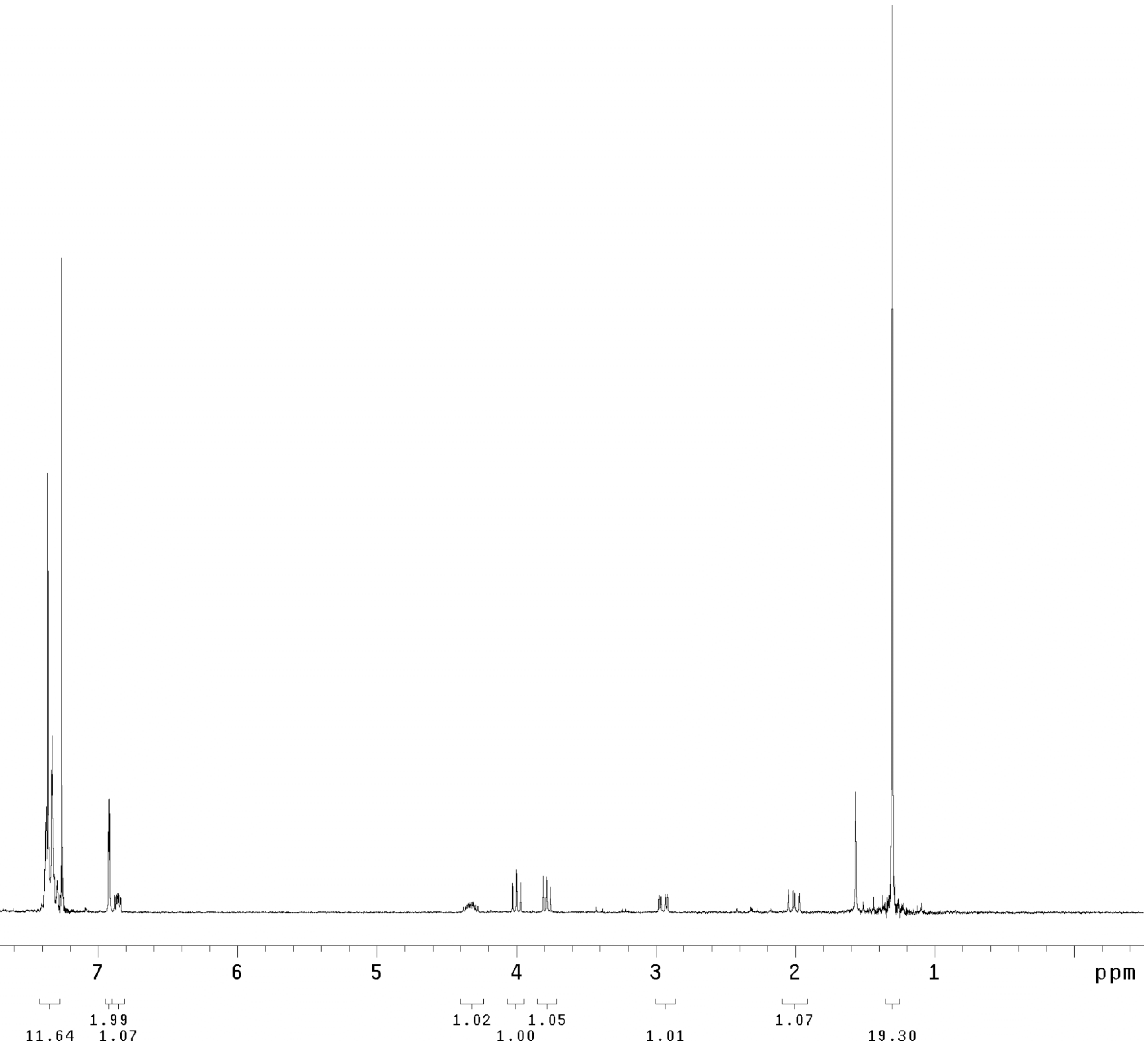


Table 1 Entry 14 Product



^{31}P NMR

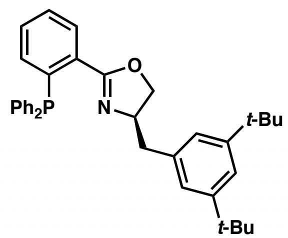
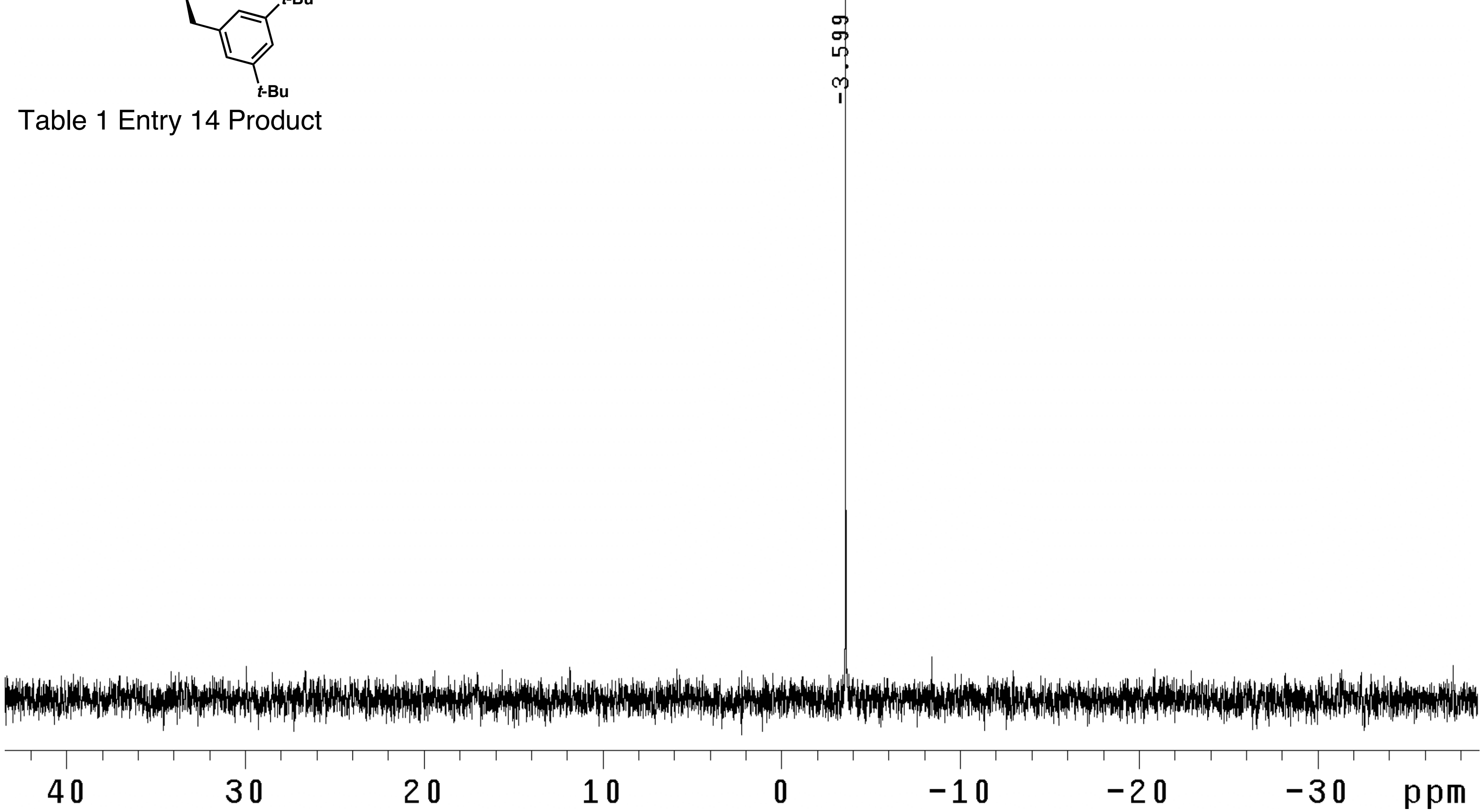
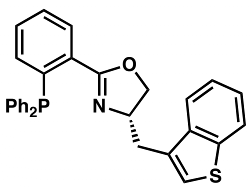


Table 1 Entry 14 Product



^{1}H NMR



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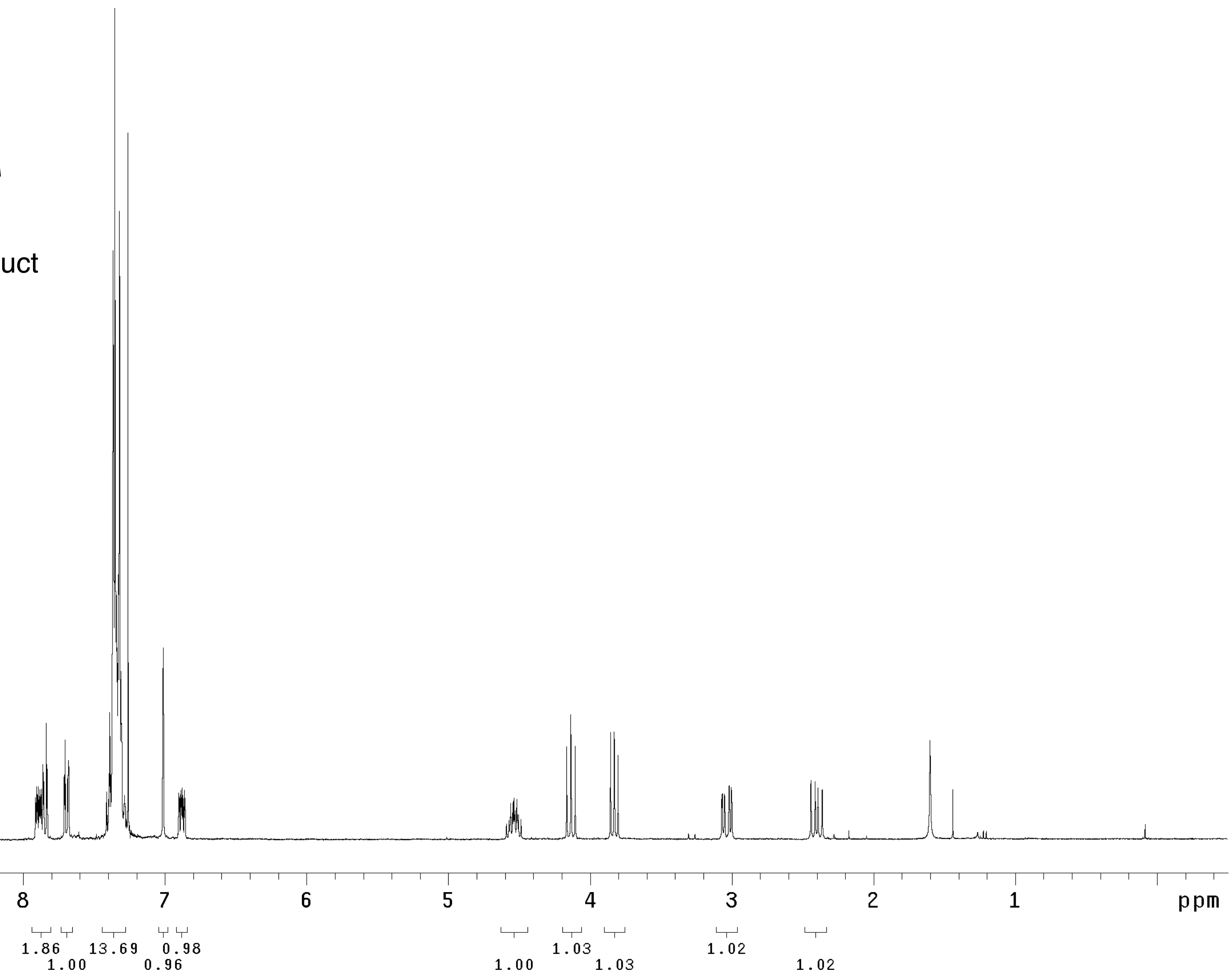


[31]P NMR

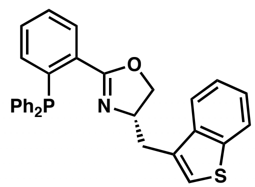
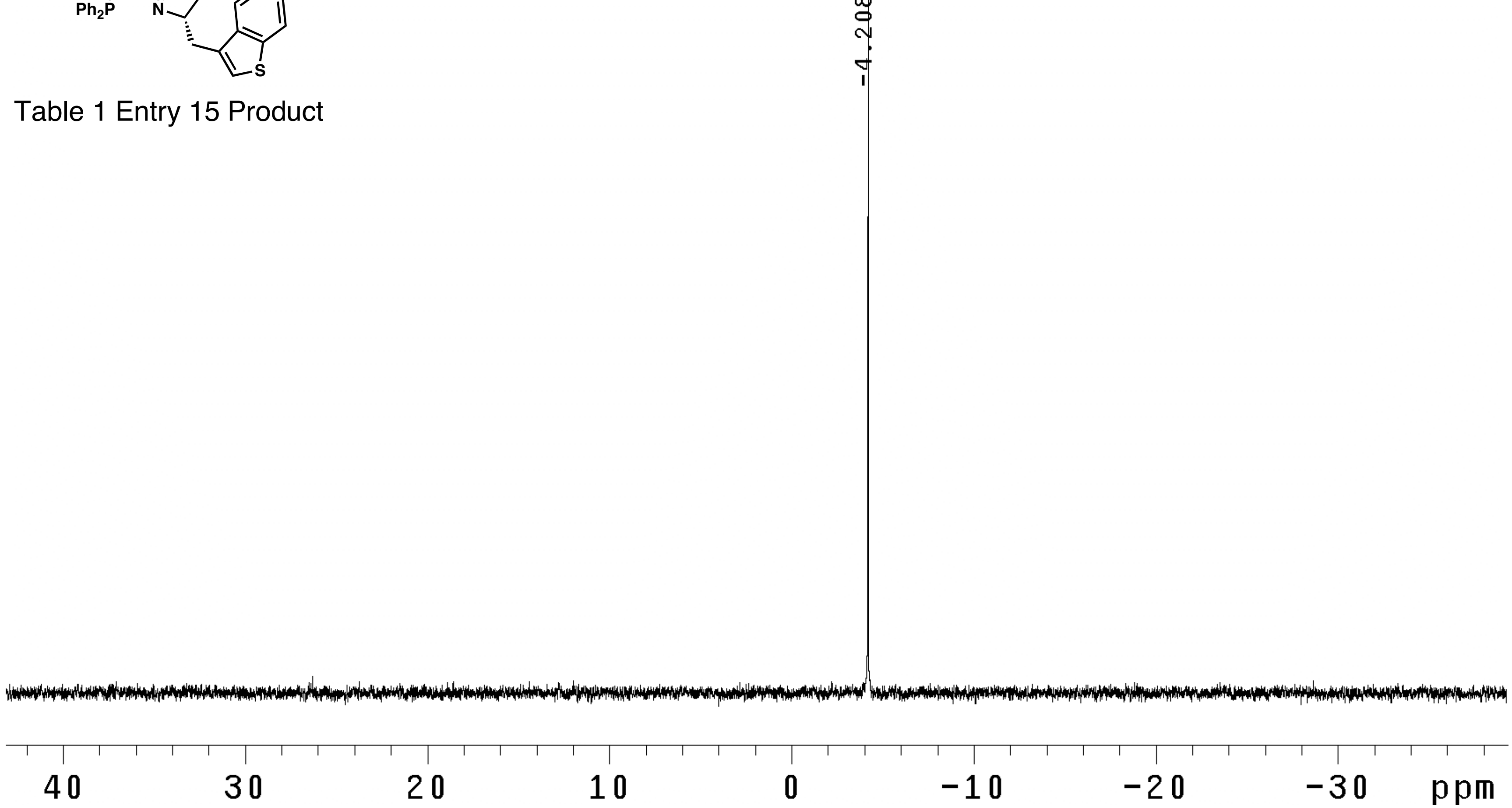


Table 1 Entry 15 Product



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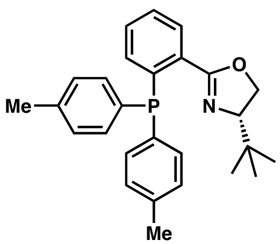

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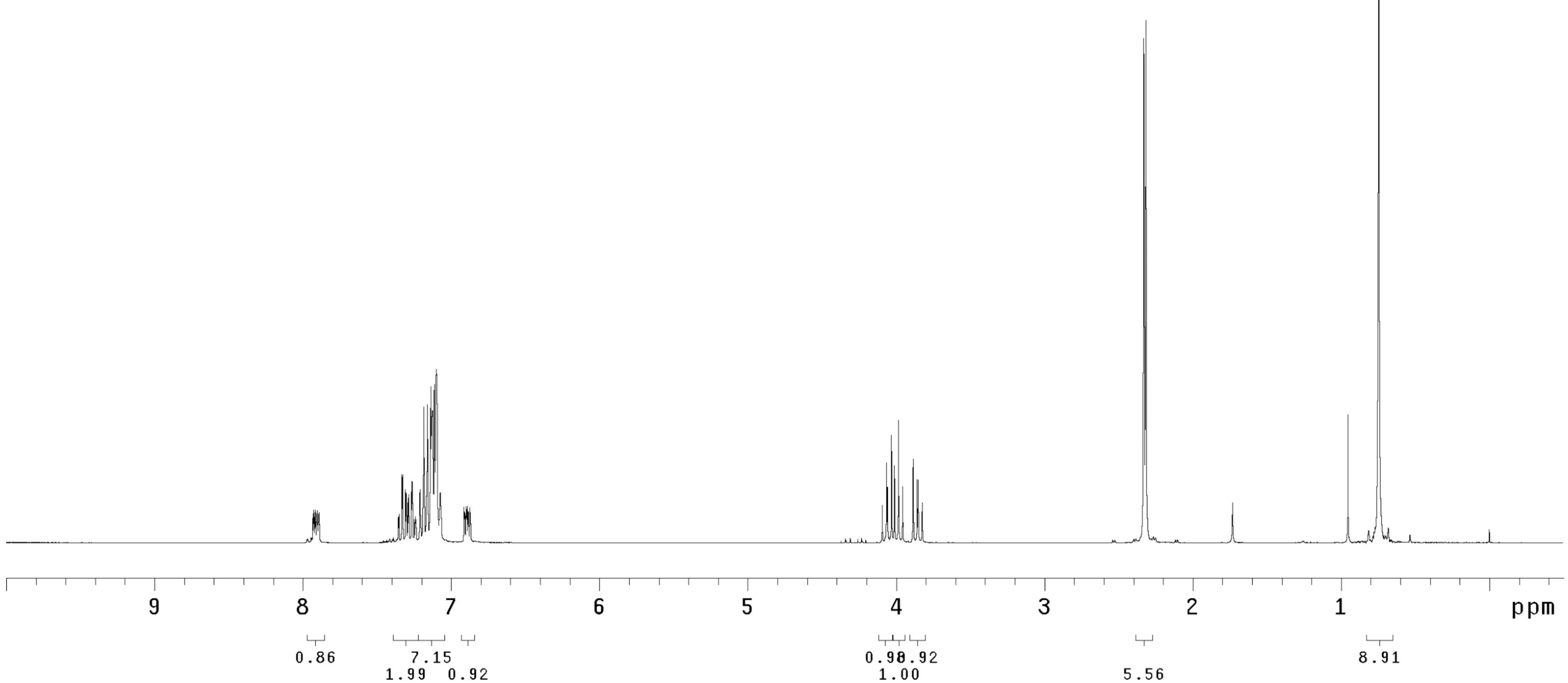

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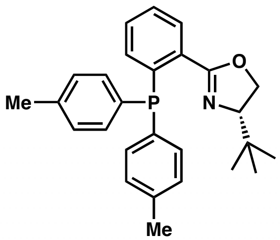

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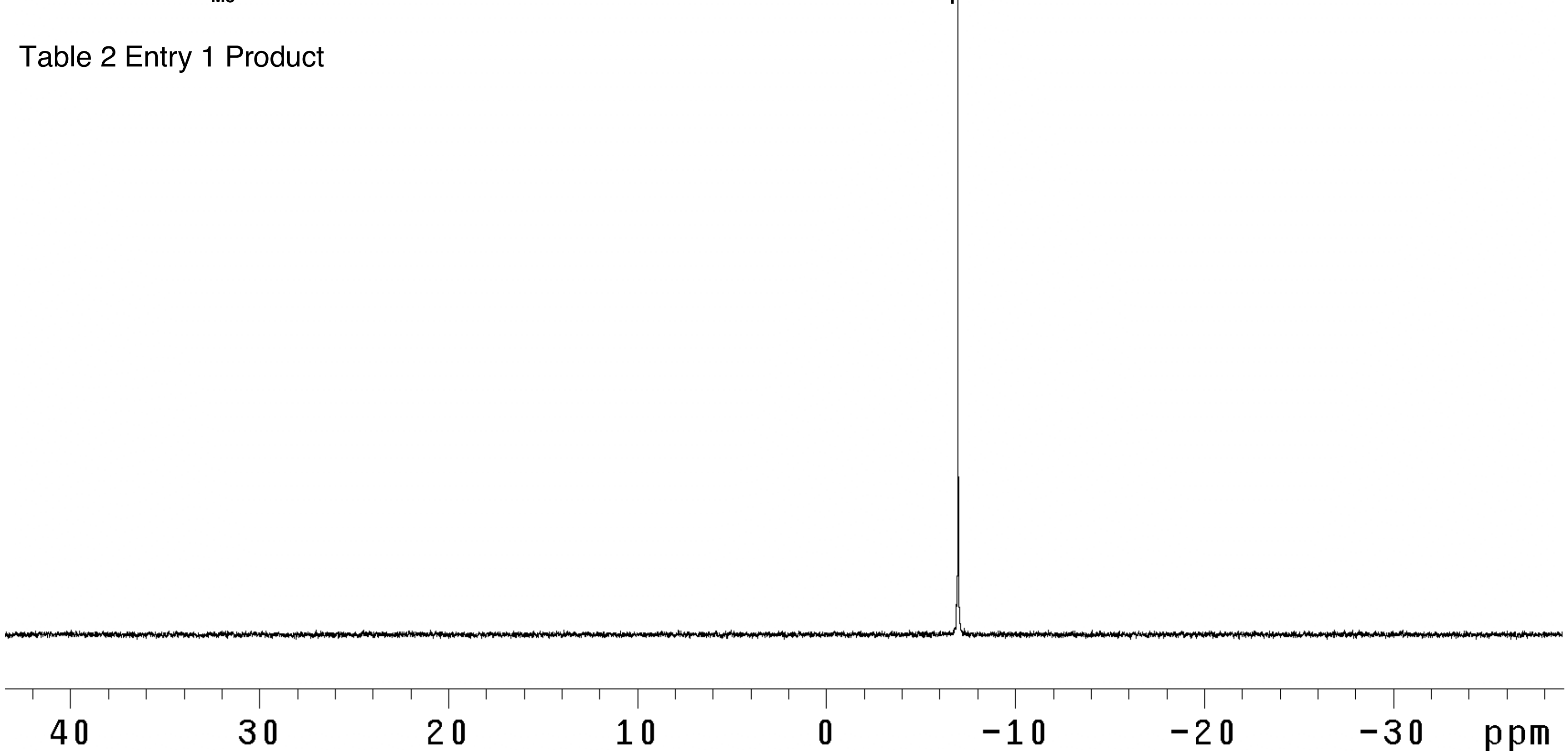

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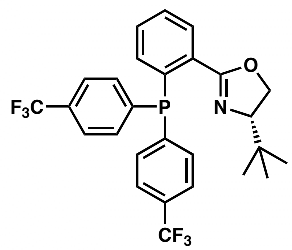

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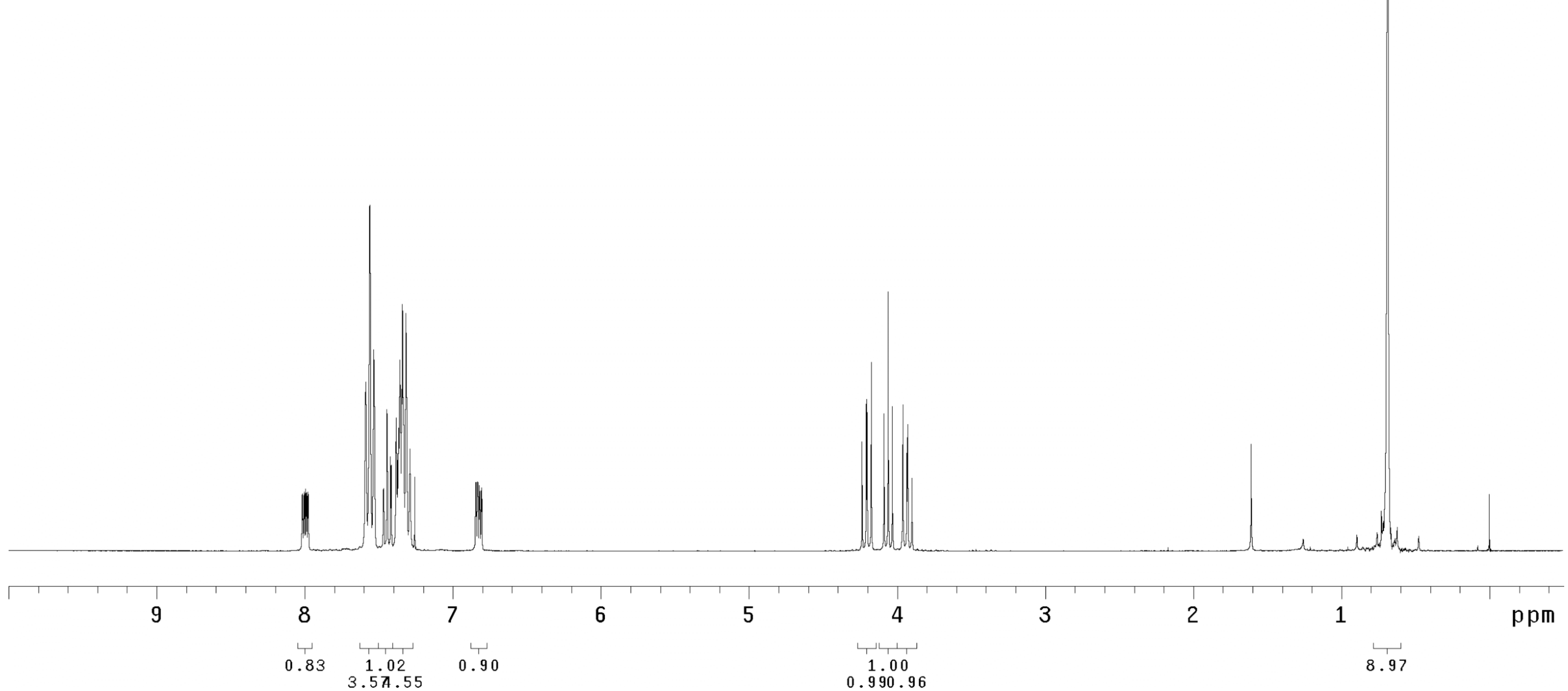

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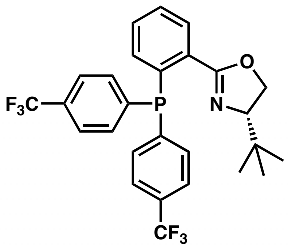

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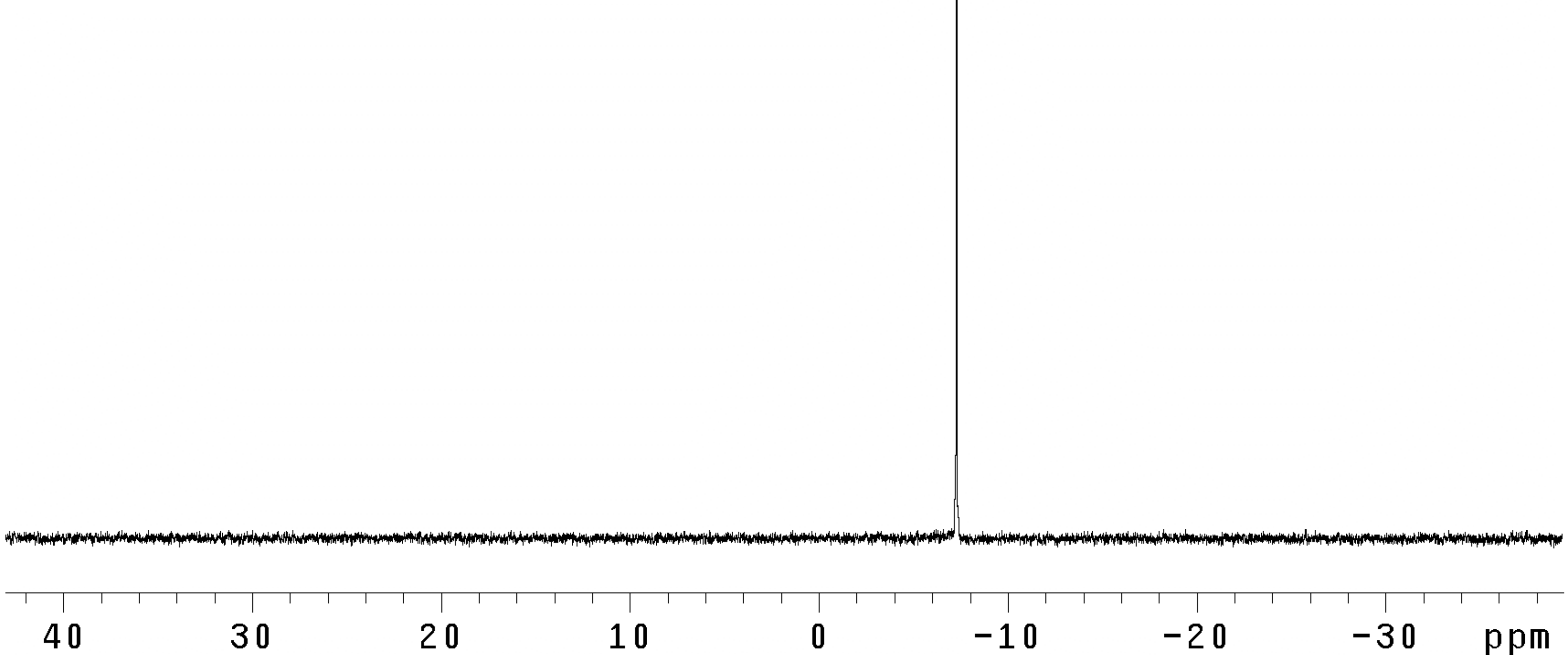
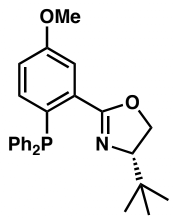


^{1}H NMR



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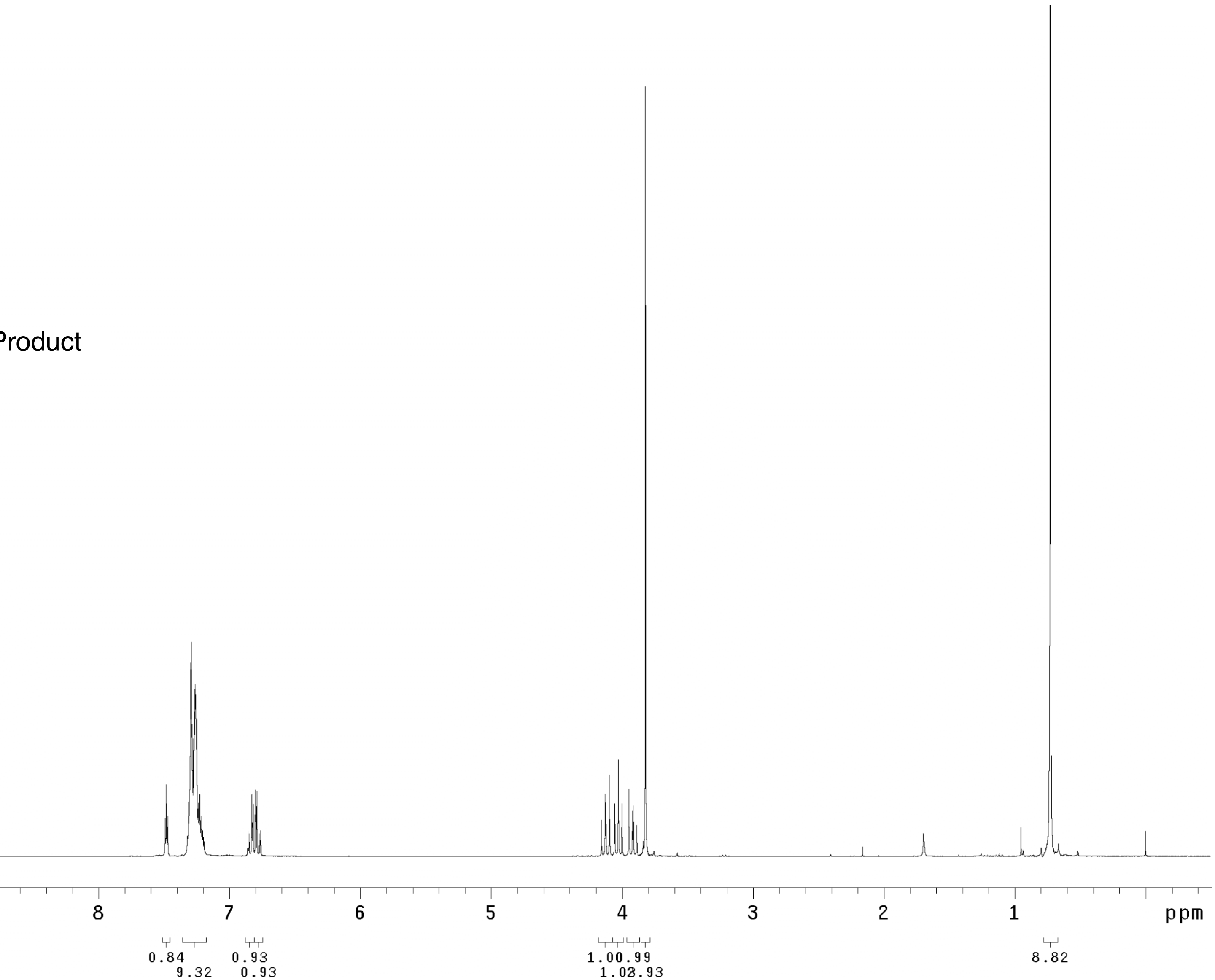
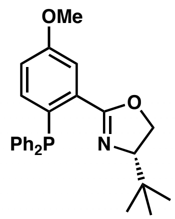


^{31}P NMR



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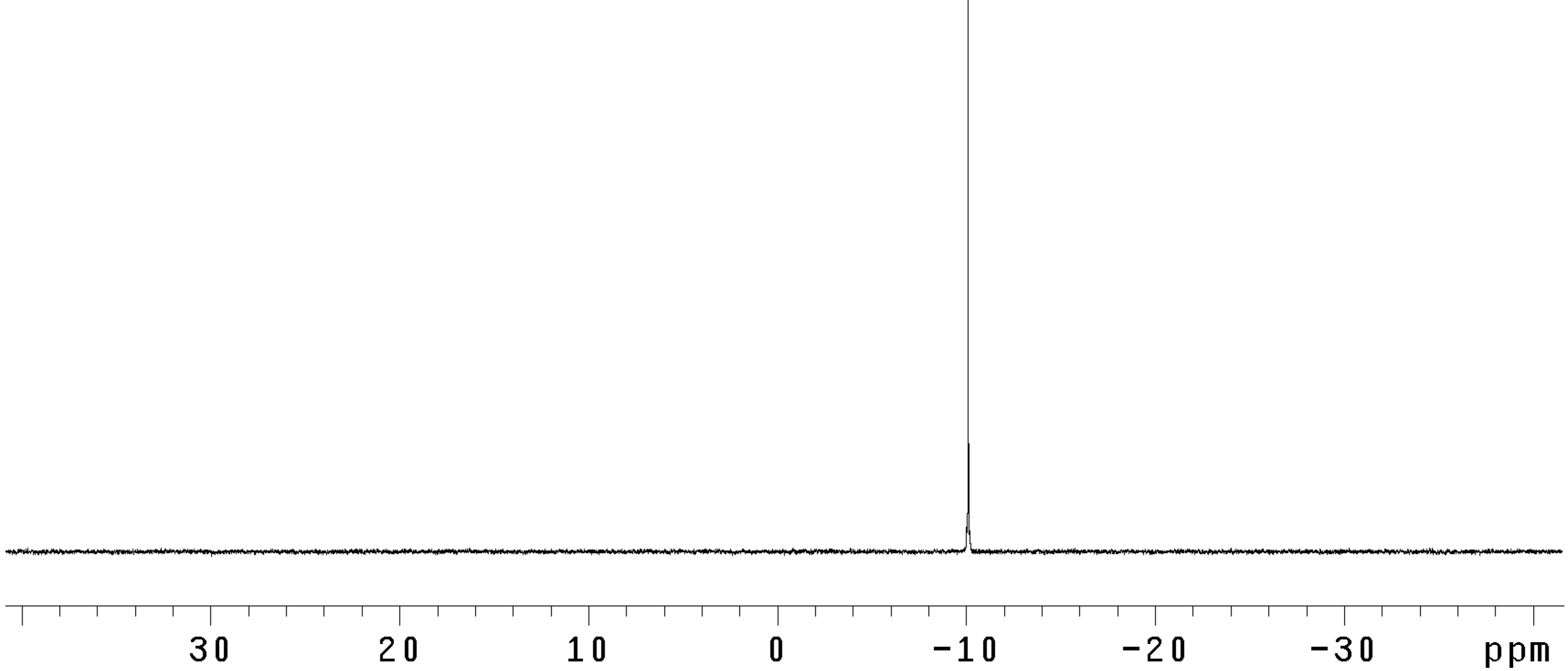
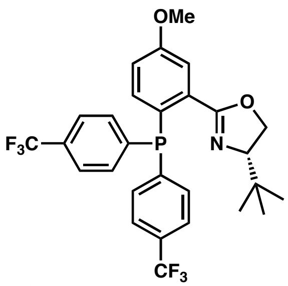


[1]H NMR



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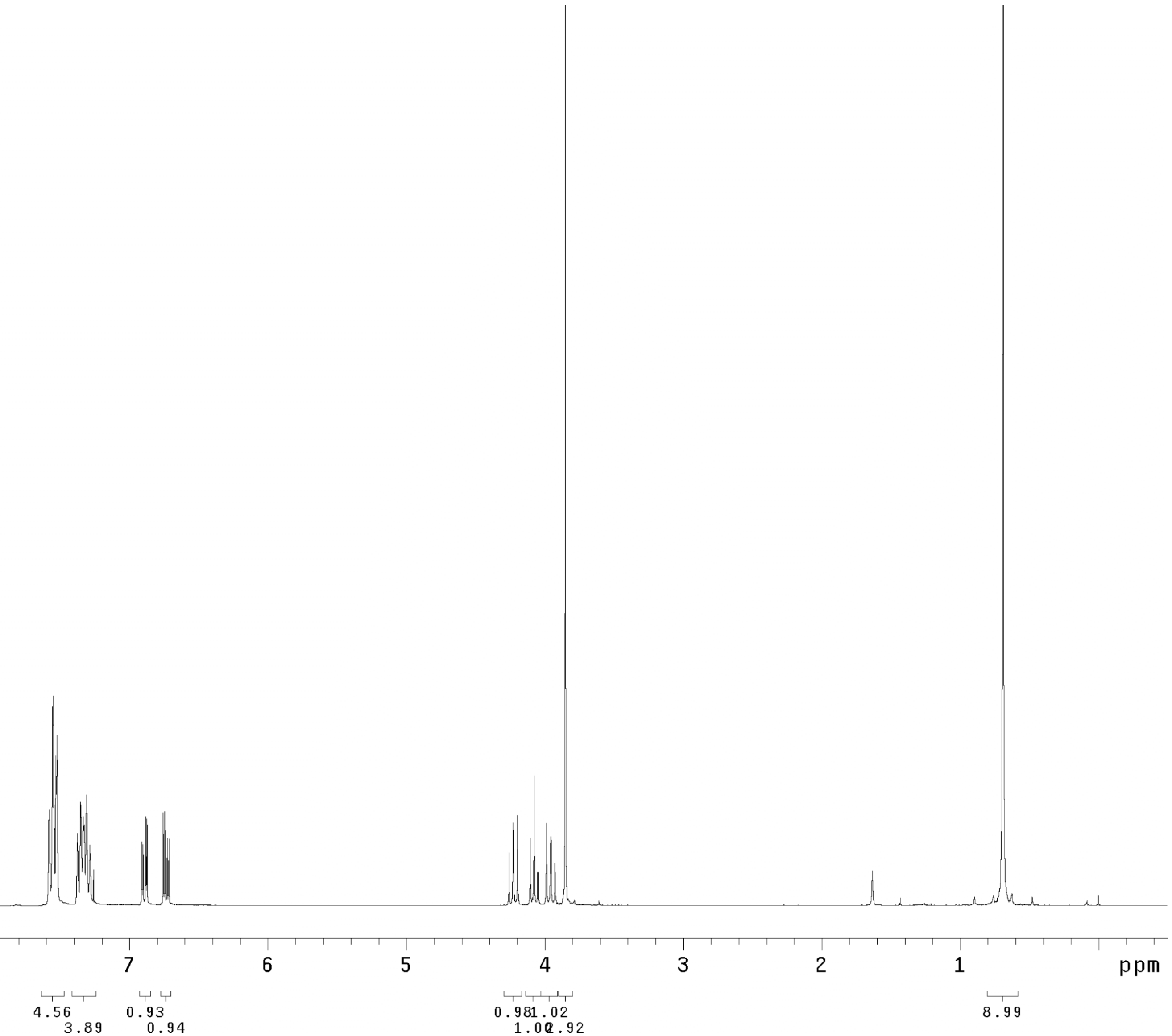

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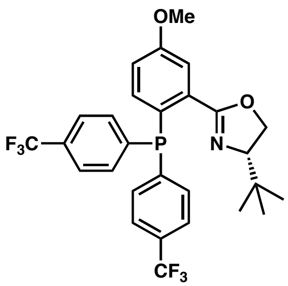

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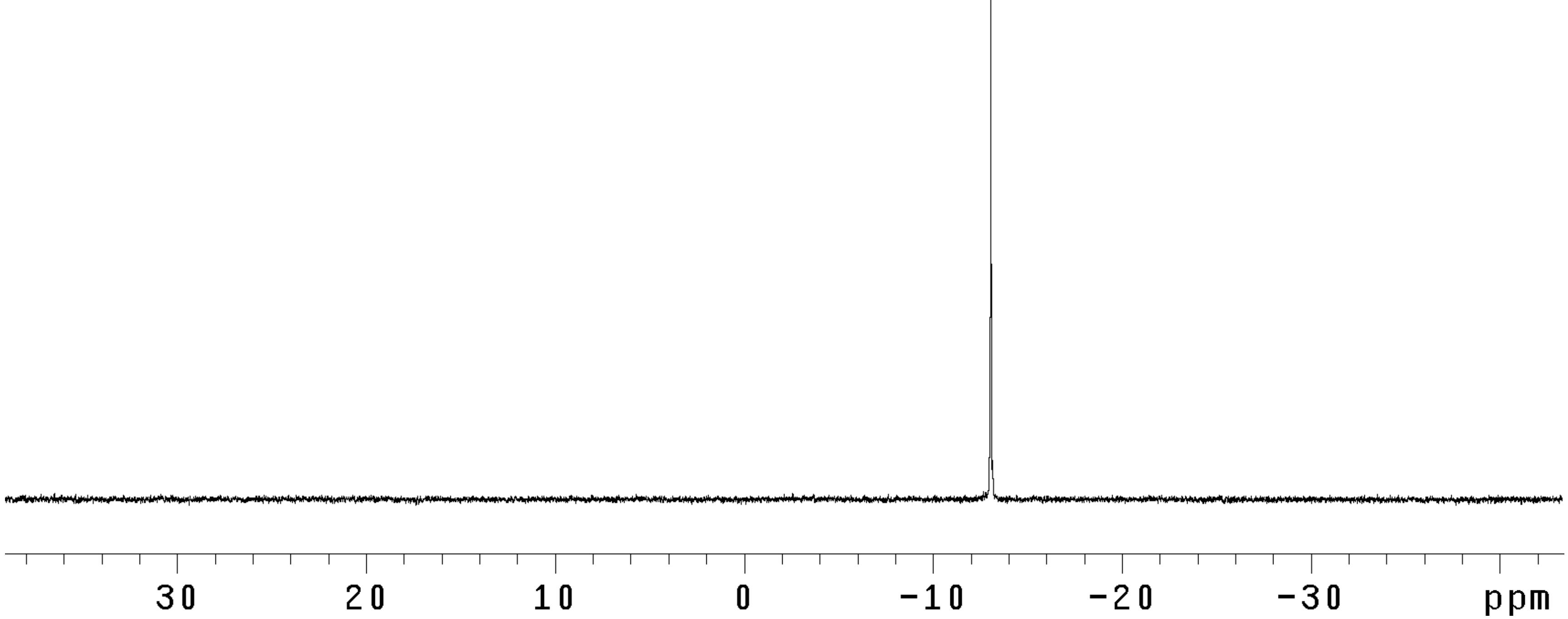
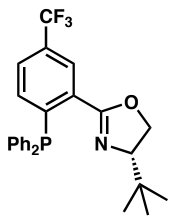


^{1}H NMR



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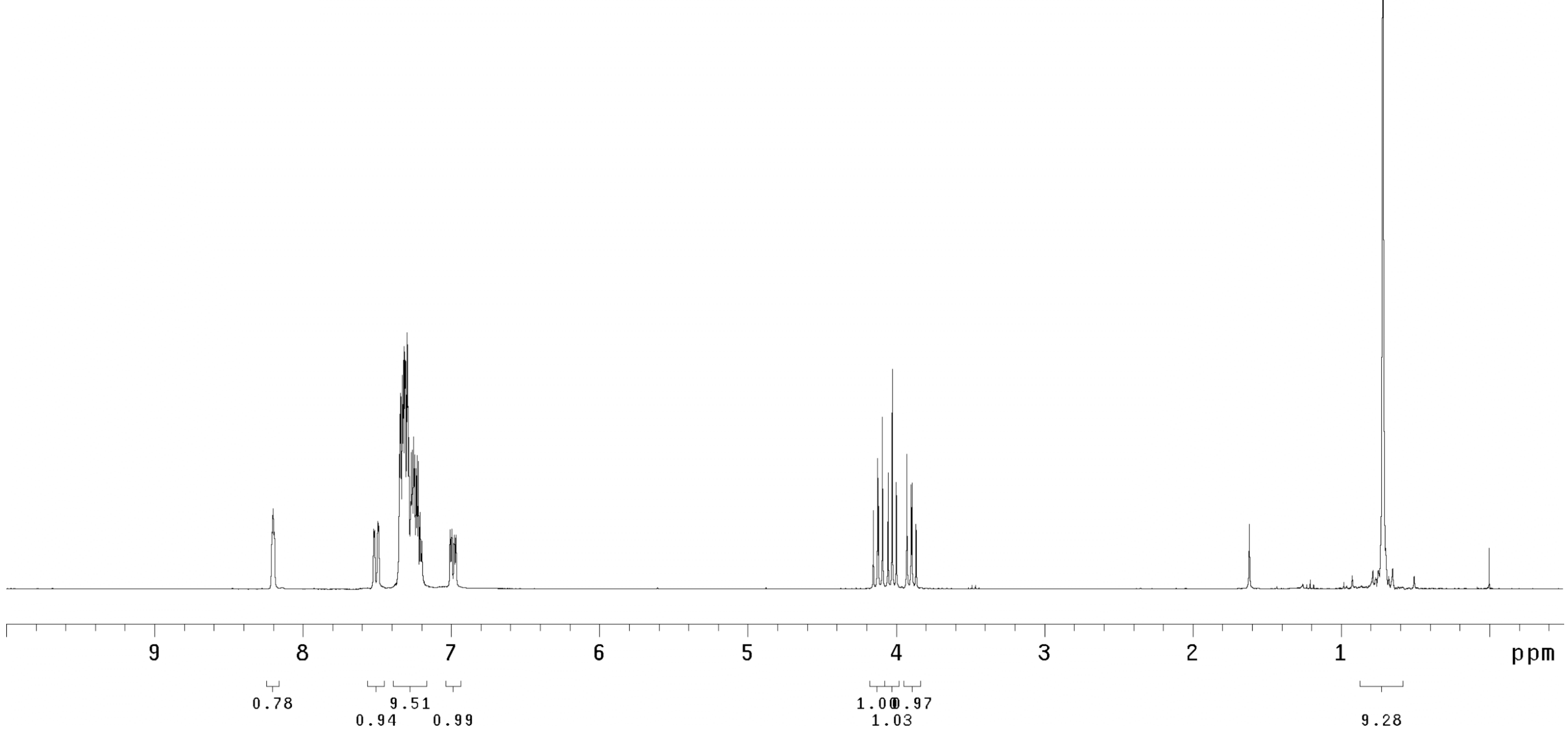
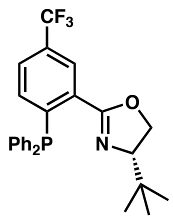


^{31}P NMR



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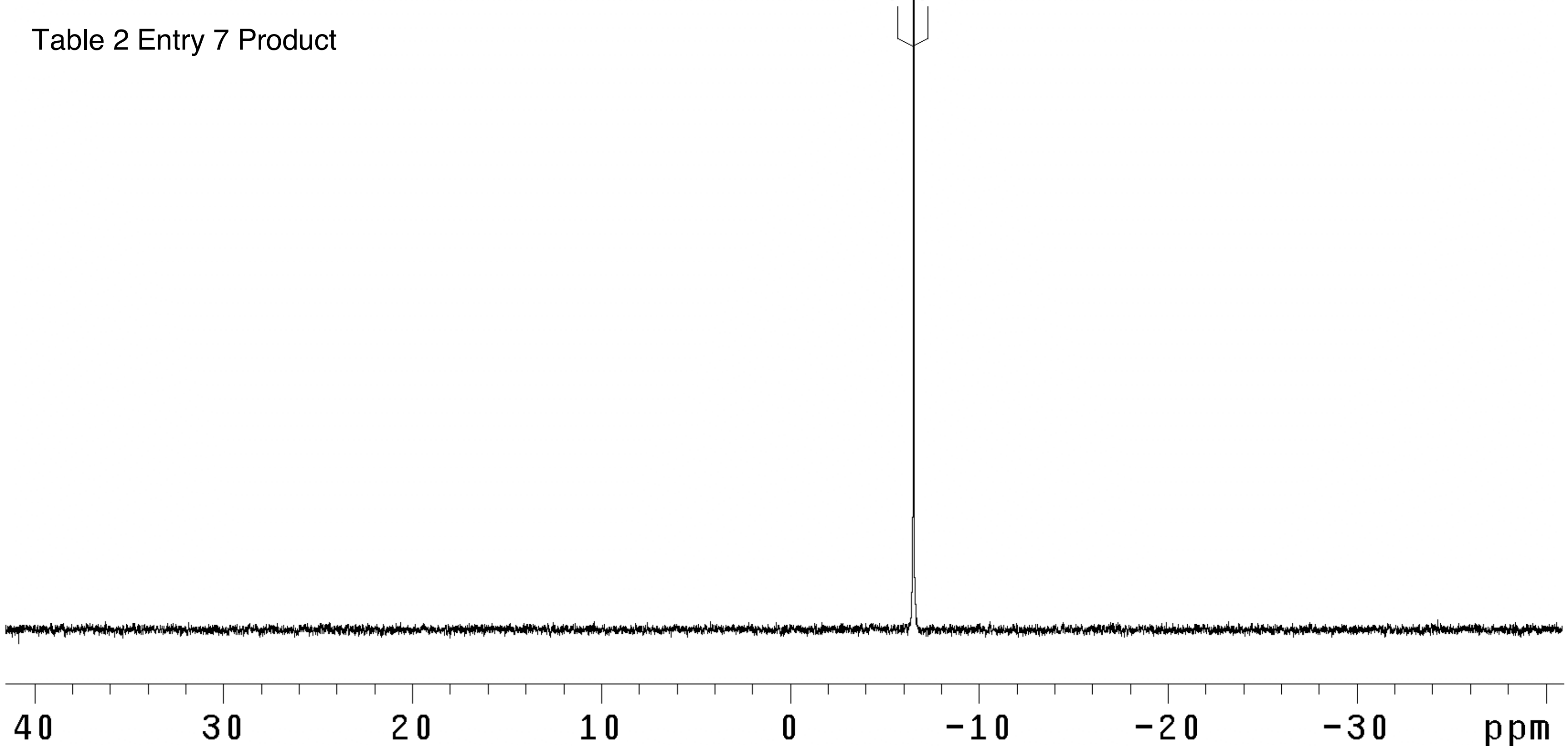

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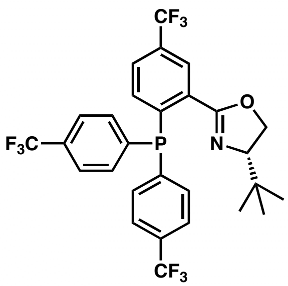

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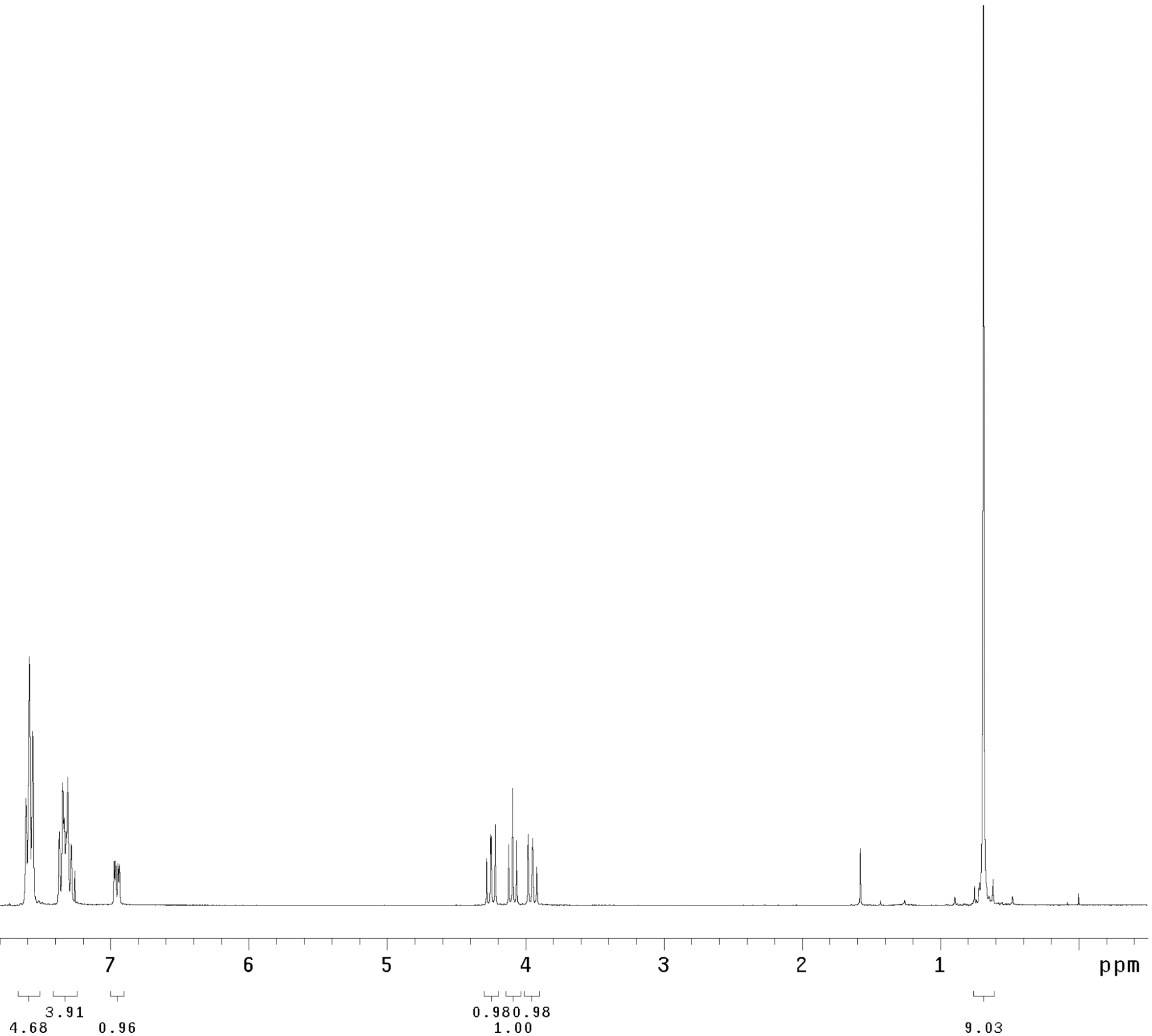


^{31}P NMR

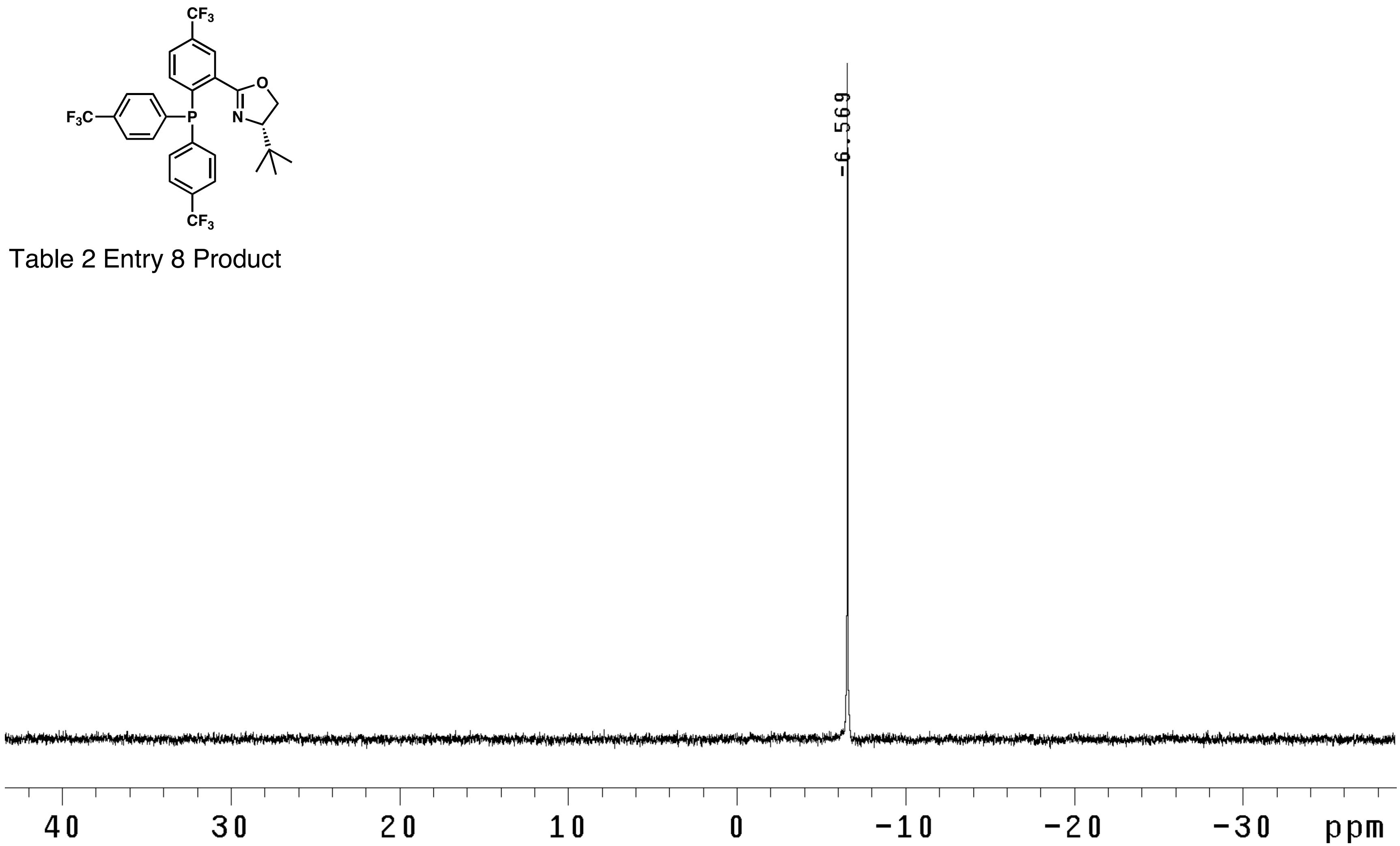


Table 2 Entry 8 Product

^{1}H NMR

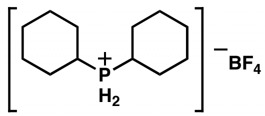
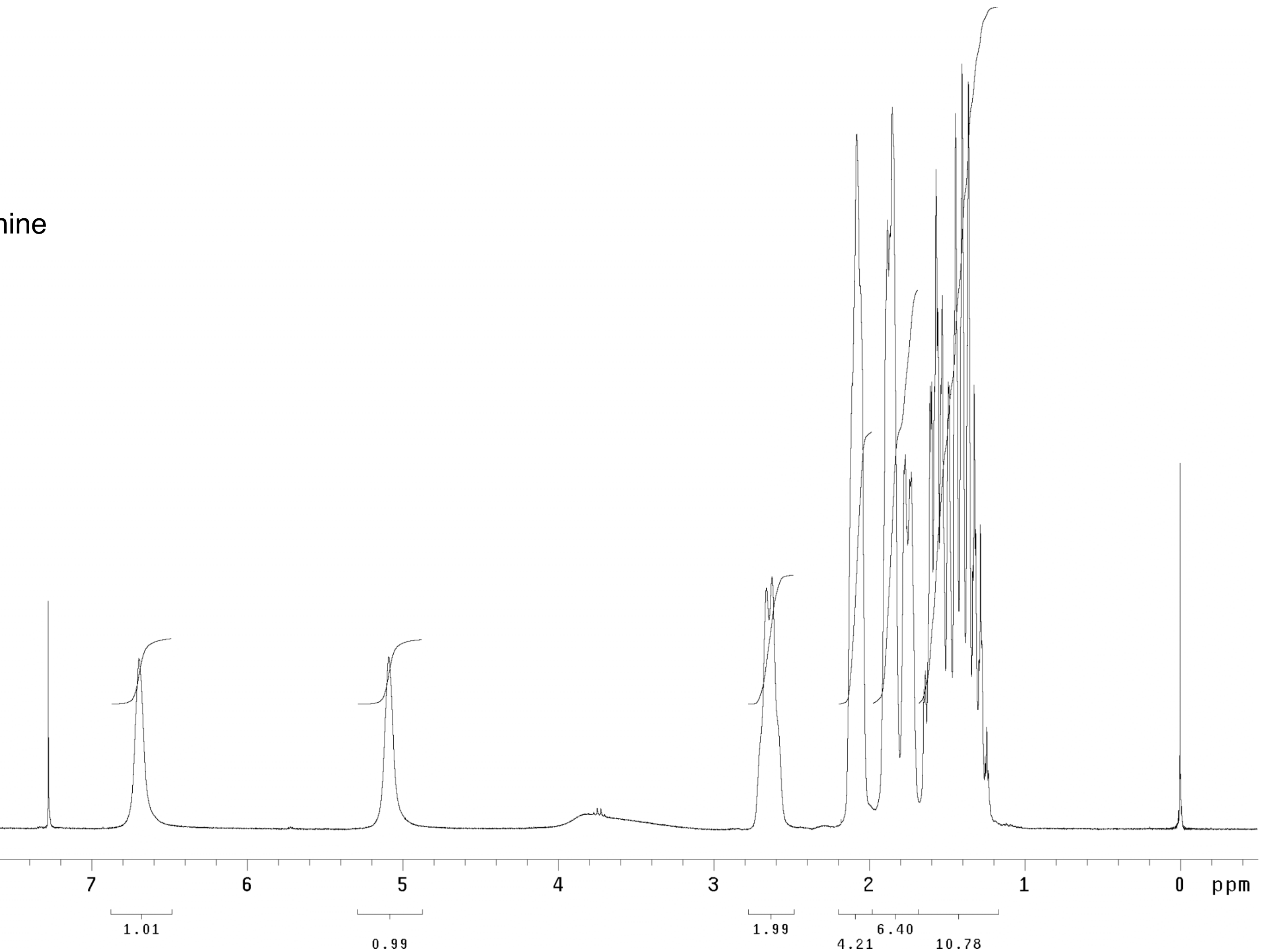


Table 2 Entry 3 Phosphine



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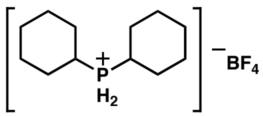
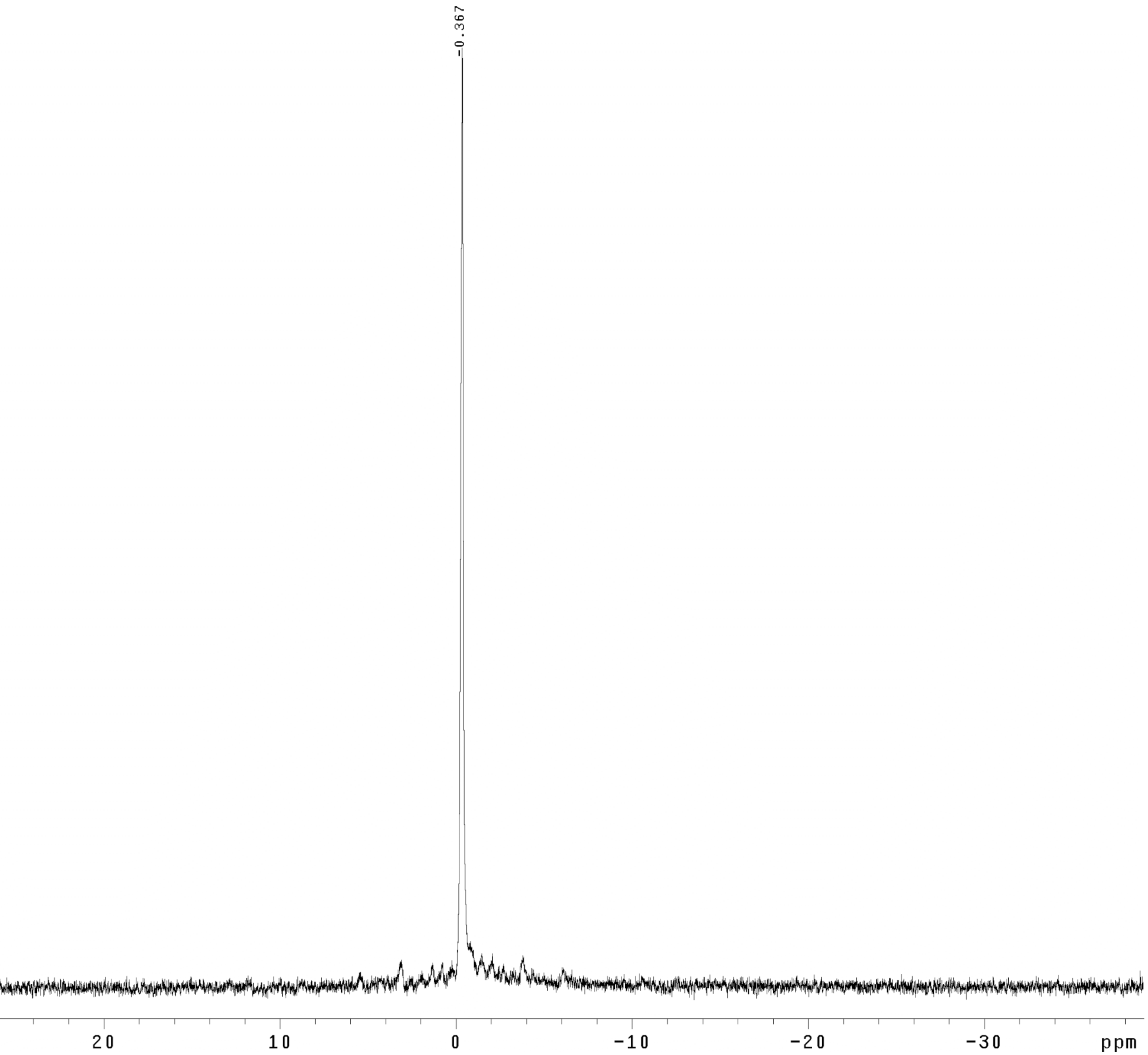


Table 2 Entry 3 Phosphine



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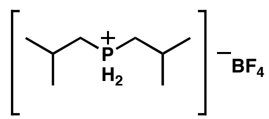
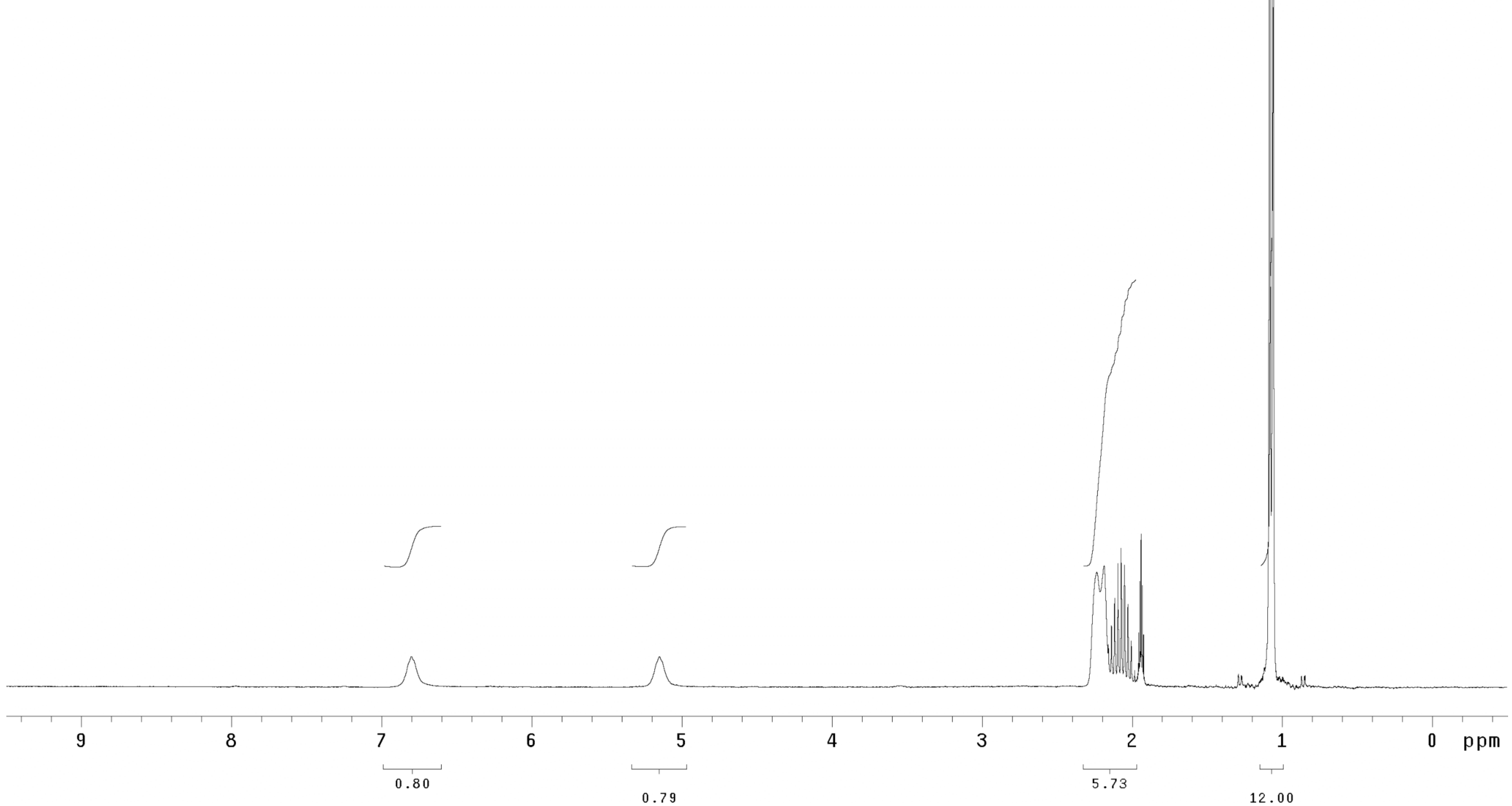


Table 2 Entry 4 Phosphine



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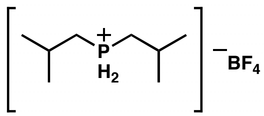

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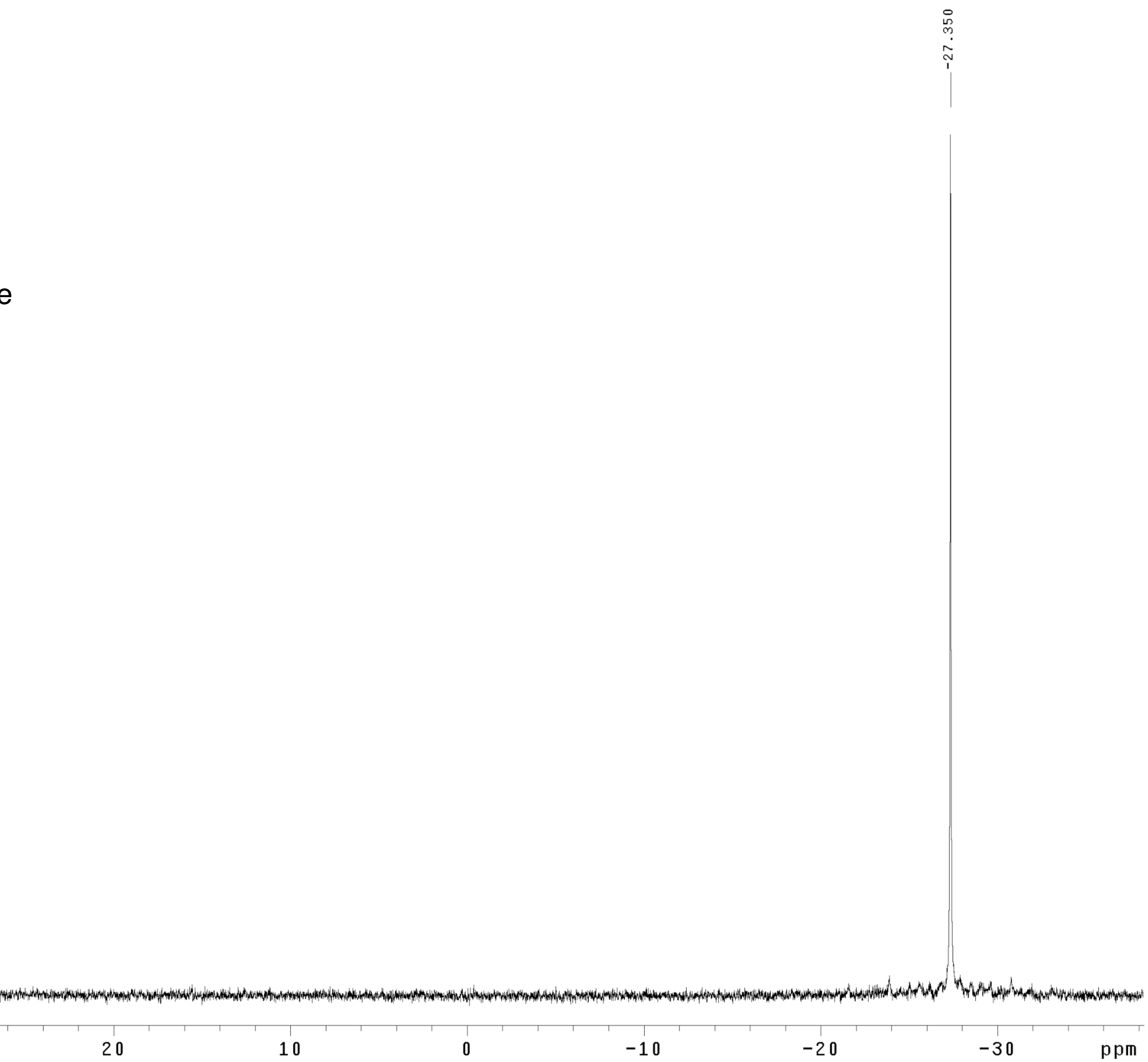

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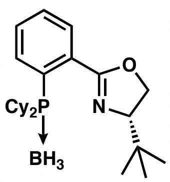

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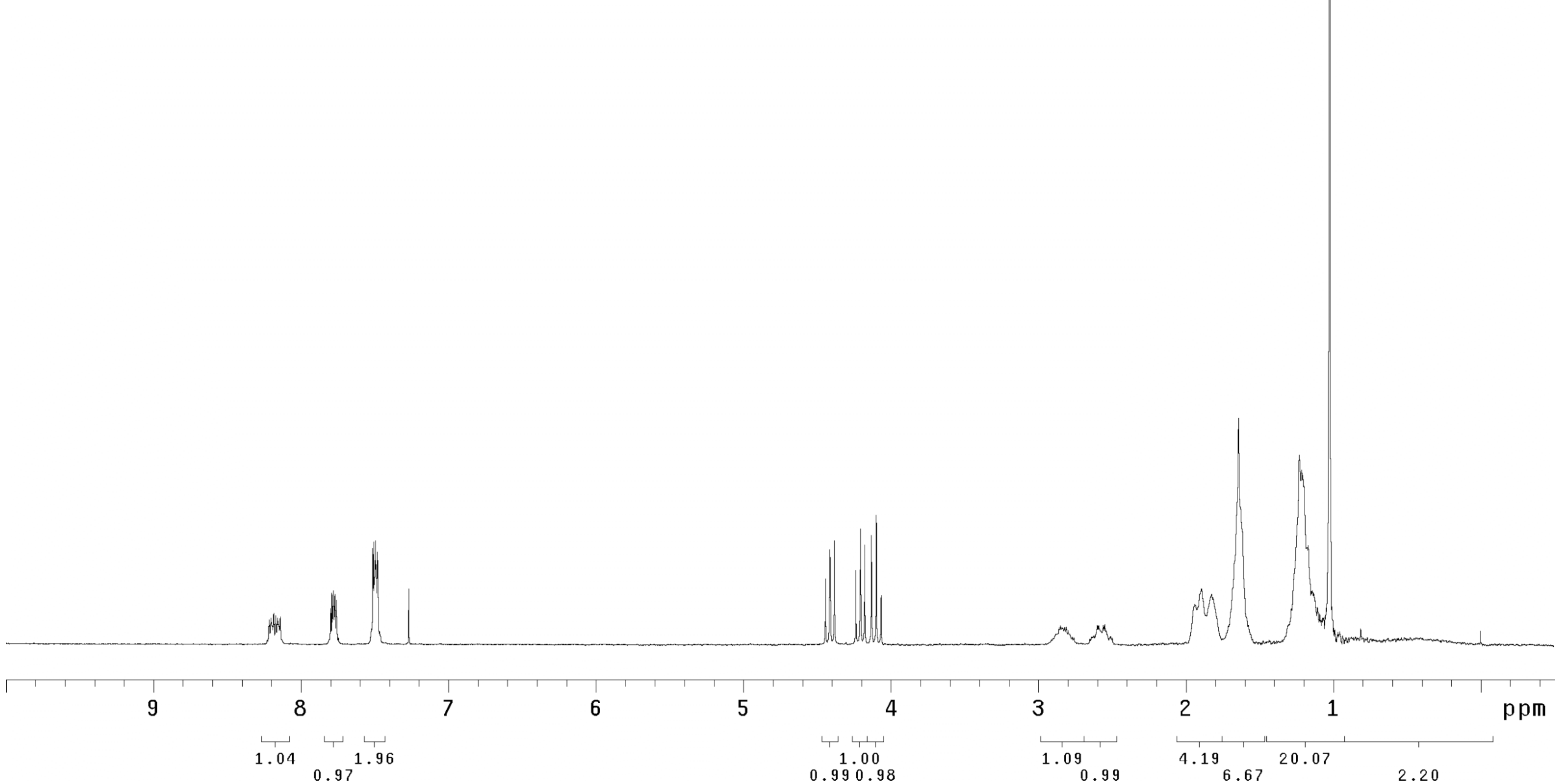
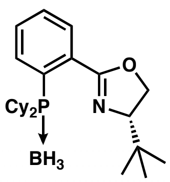


^{31}P NMR



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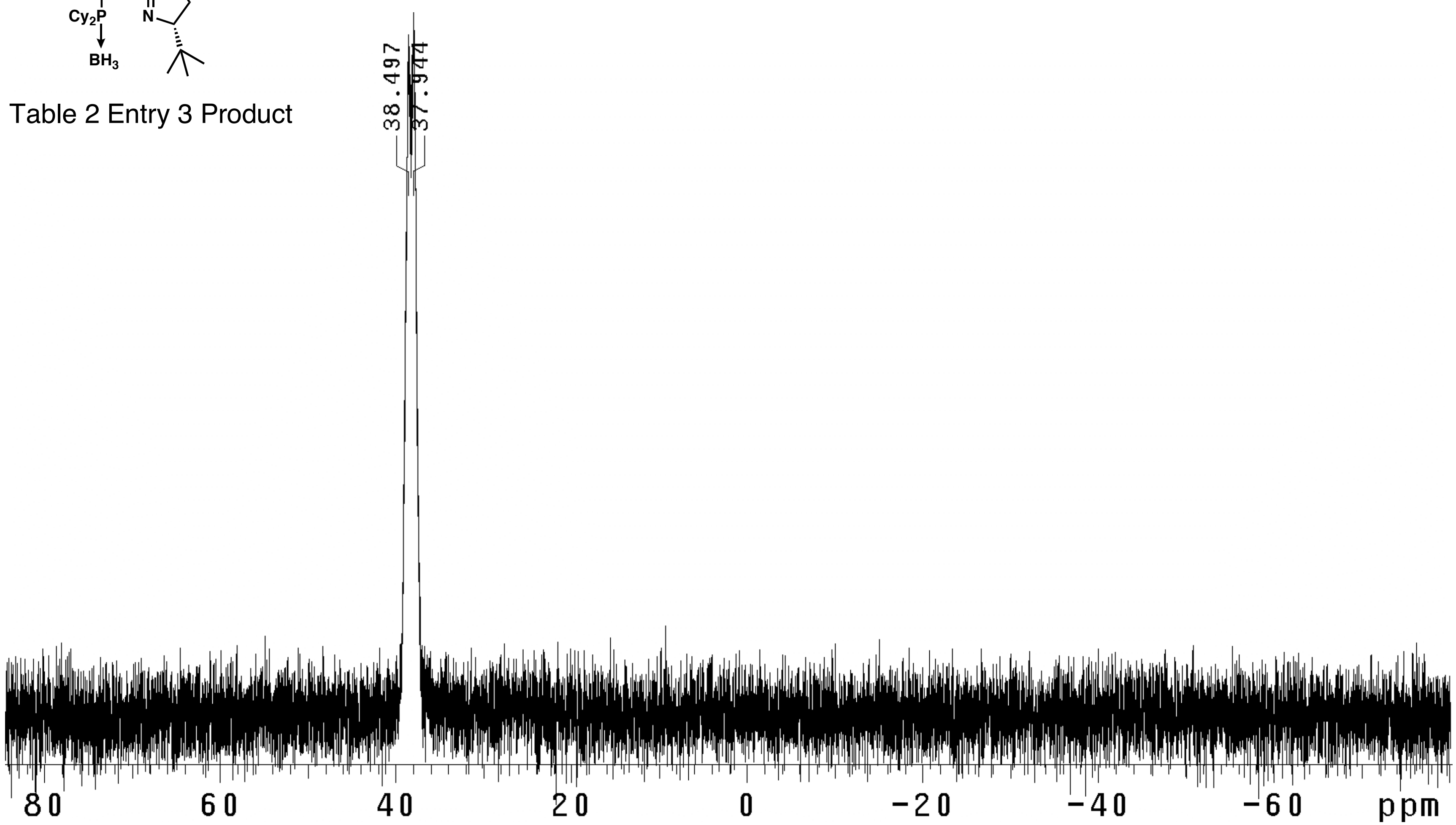

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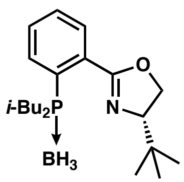

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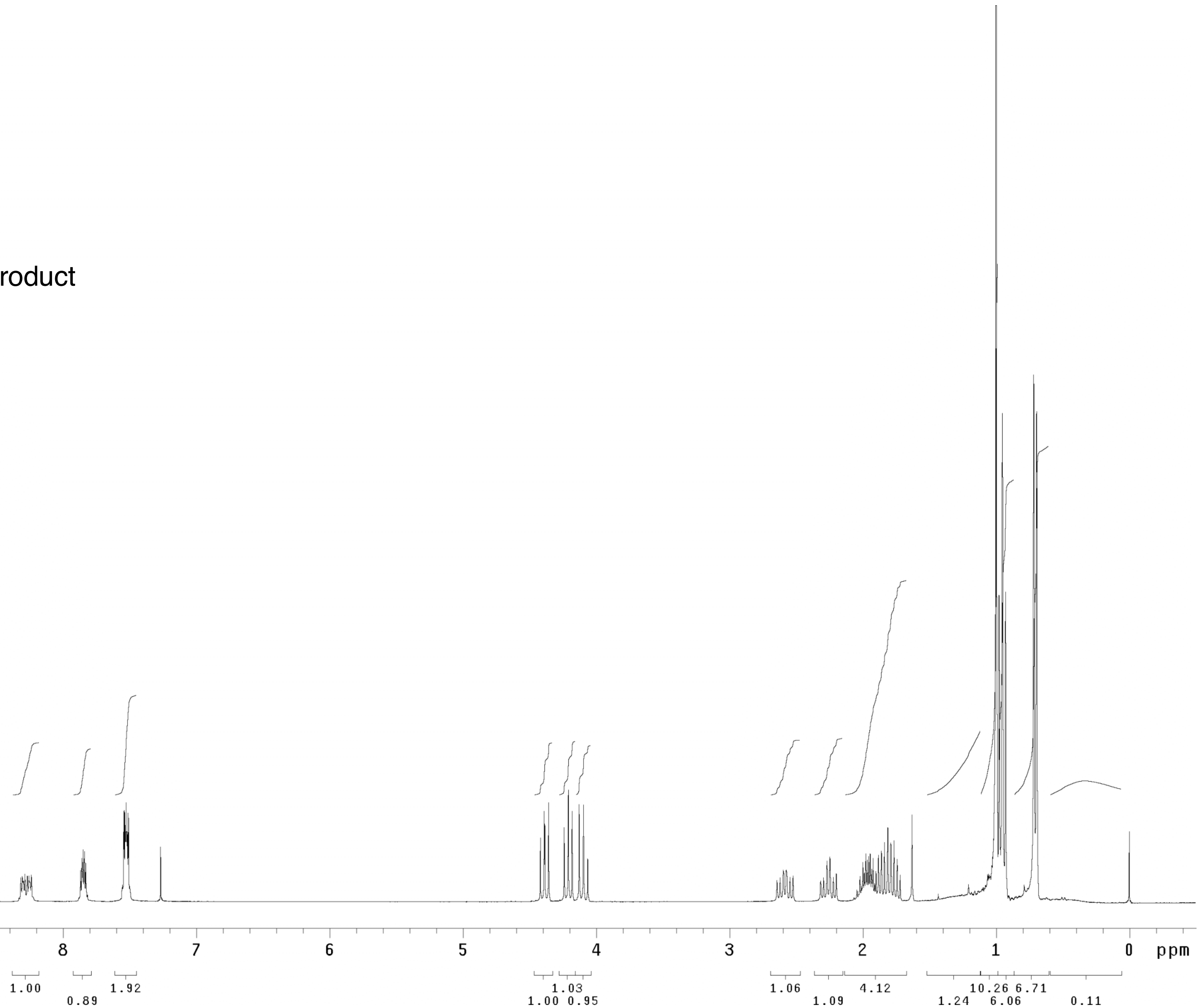

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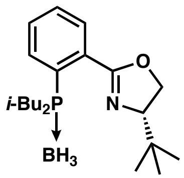

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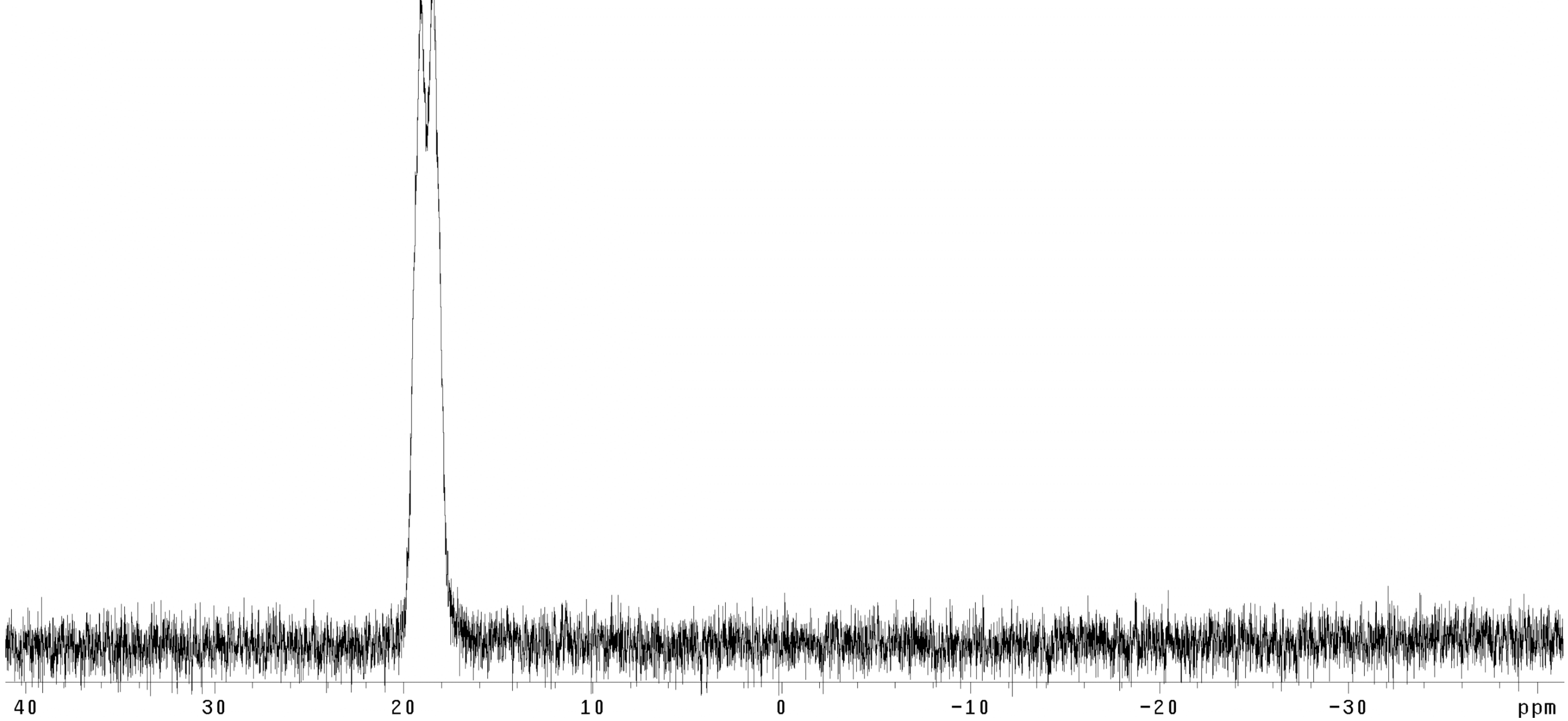

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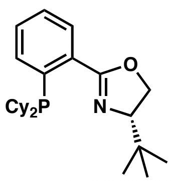
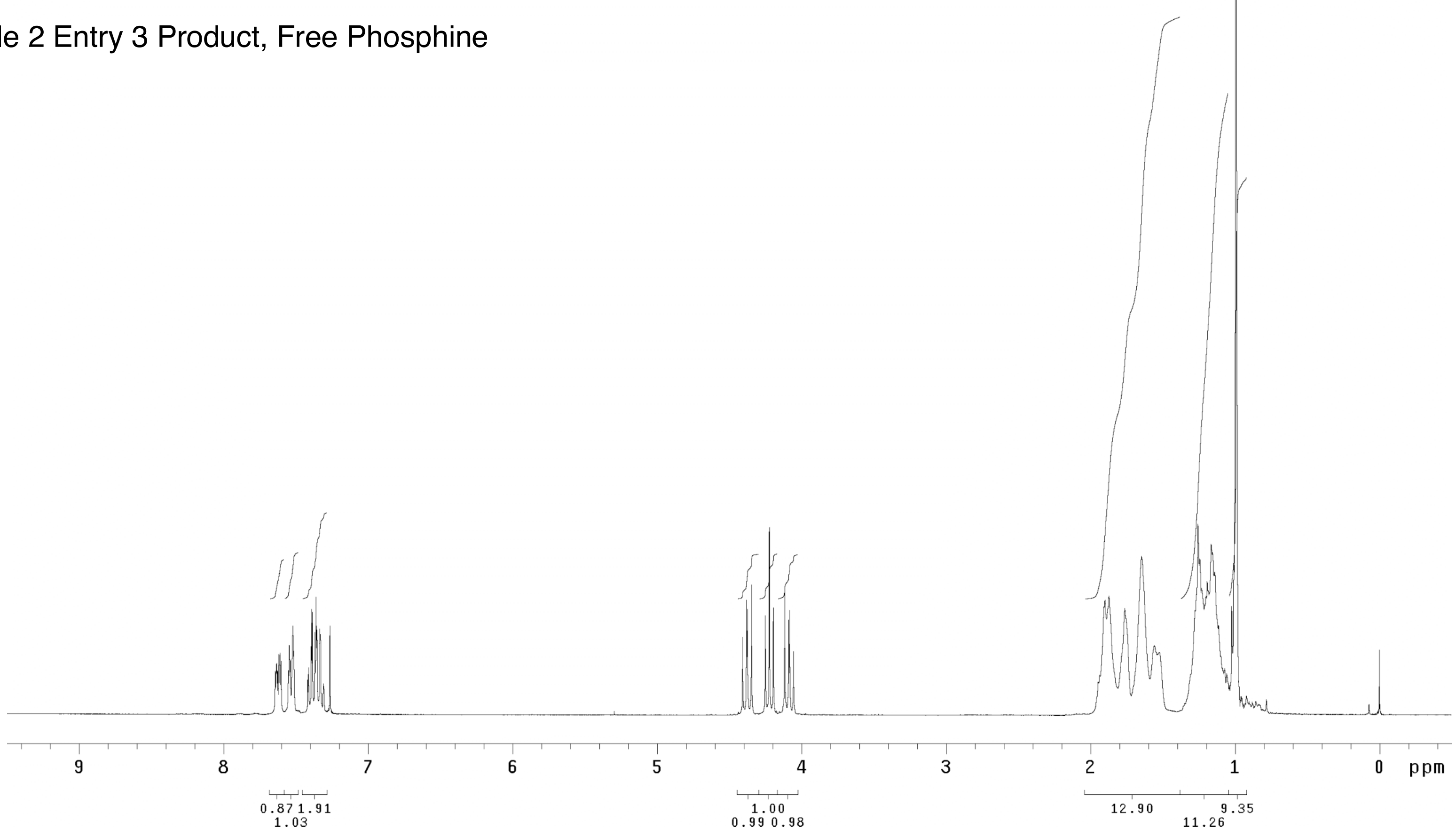


Table 2 Entry 3 Product, Free Phosphine



^{31}P NMR

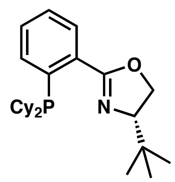
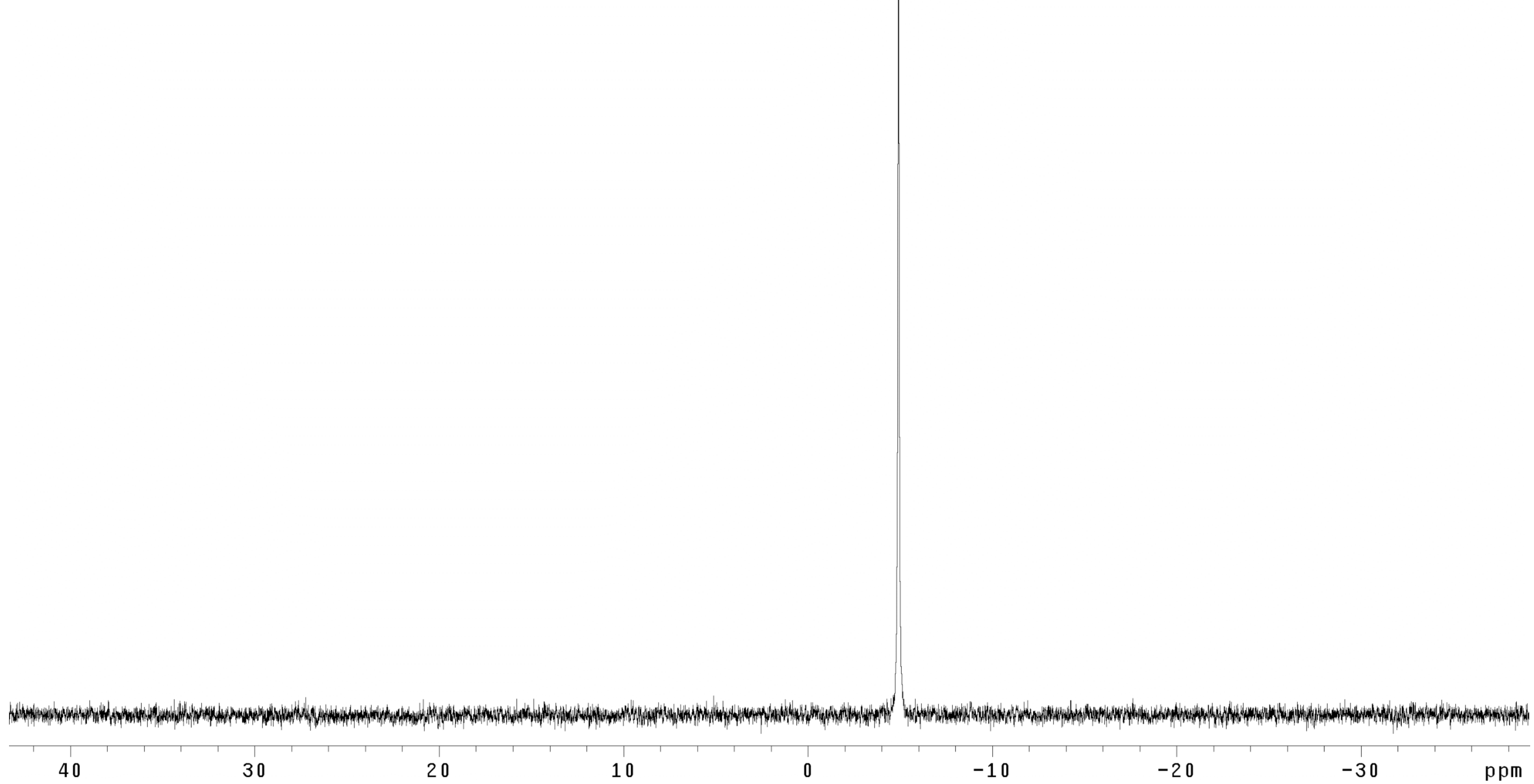
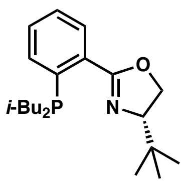


Table 2 Entry 3 Product, Free Phosphine



^{1}H NMR



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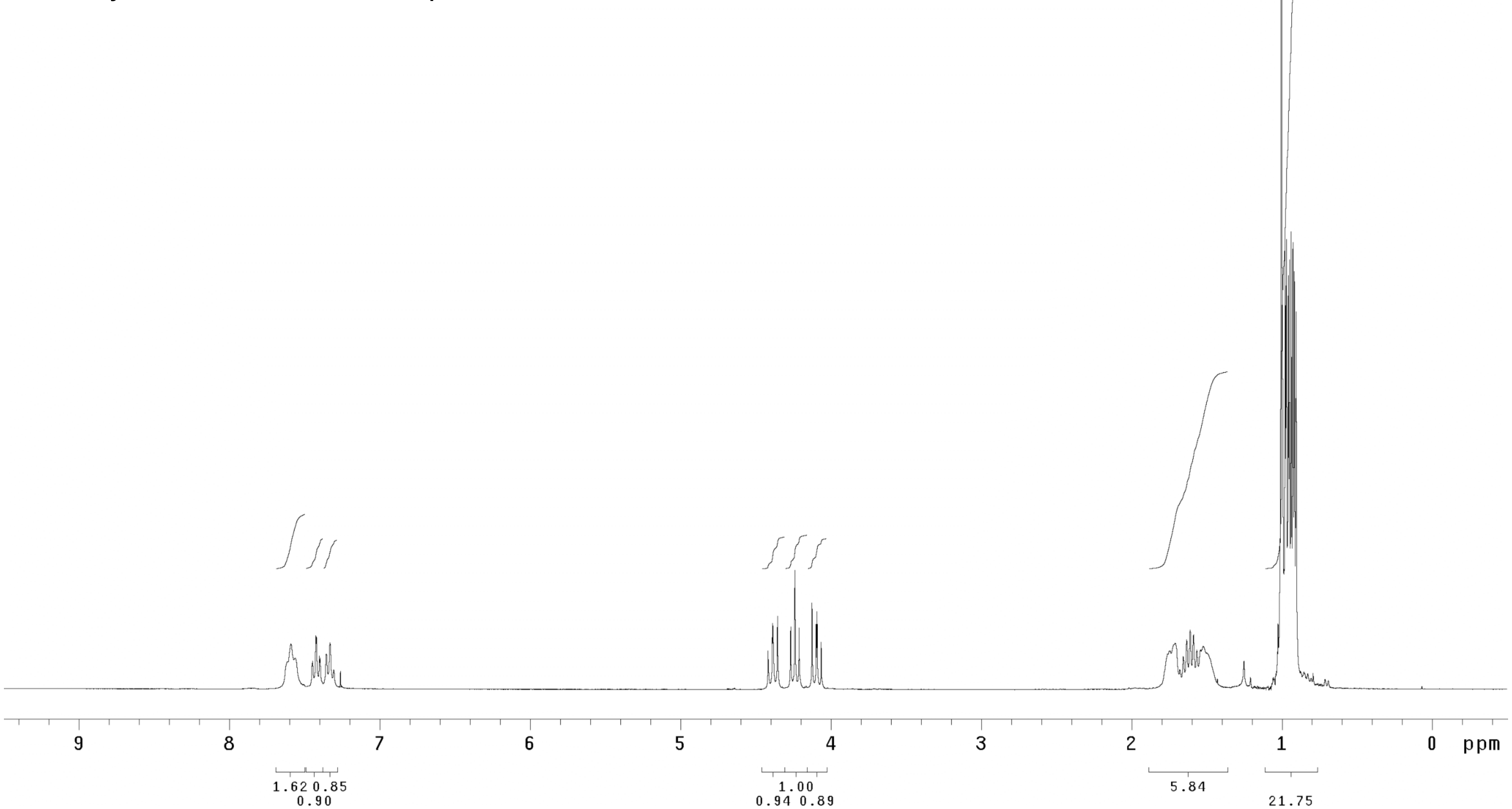

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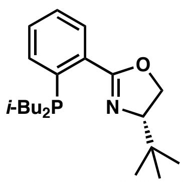

Table 2 Entry 4 Product, Free Phosphine