Supporting Information

Cobalt-Catalyzed Ligand-Controlled Regioselective Hydroboration/Cyclization of 1,6-Enynes

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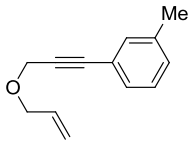
I. General information

Ether, tetrahydrofuran, 1,4-dioxane and toluene were distilled from sodium benzophenoneketyl prior to use. Pinacolborane (HBpin) was purchased from Tokyo Chemical Industry Co.. Sodium triethylborohydride solution 1.0 M in THF was purchased from Sigma-Aldrich Co.. The other commercially available chemicals were used as received. NMR spectra were recorded on a Bruker-400 instrument. ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$), ^{19}F NMR chemical shifts were referenced to the solvent resonance. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. High-resolution mass spectra (HRMS) were recorded on EI-TOF (electrospray ionization-time of flight).

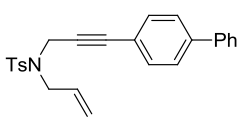
II. Synthesis of substrates and cobalt Complexes

Substrates **1a-d**,[1] **1e**,[2] **1f**,[3] **1h-i**,[3] **1j-l**,[1] **1n-o**,[1] **1q**,[3] **1r**,[4] **1s**,[5] **1t**,[6] **1u-v**[3] are known compounds and have been synthesized according to the previously reported methods.



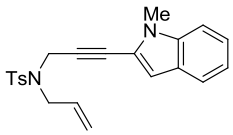
1g

1-(3-(allyloxy)prop-1-yn-1-yl)-3-methylbenzene **(1g):** To a solution of 3-(*m*-tolyl)prop-2-yn-1-ol (1.0 equiv), 3-bromoprop-1-ene (2 equiv), and NaH (1.5 equiv) in dry THF under nitrogen atmosphere stirred for overnight. The mixture was quenched by sat. NH_4Cl (aq).The resulting solution was extracted with ether (50 mL x 2). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under vacuum. The crude residue was purified by flash chromatography on silica gel (PE/EA = 50/1-30/1) to give **1g** (84%) as a yellow oil. IR (neat): 2925, 2854, 1603, 1581, 1485, 1458; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.26-7.32 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 5.93-6.04 (m, 1H), 5.34-5.42 (m, 1H), 5.24-5.20 (m, 1H), 4.41 (s, 2H), 4.17 (dt, *J* = 6.0, 1.2 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 137.9, 134.1, 132.3, 129.3, 128.8, 128.1, 122.4, 117.8, 86.4, 84.6, 70.6, 57.9, 21.1; HRMS (EI) calculated for $[C_{13}H_{14}O]^+$ requires *m/z* 186.1045, found *m/z* 186.1044.



1m

N-(3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)-N-allyl-4-methylbenzenesulfonamide (**1m**): To a solution of *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.04 equiv), 4-iodo-1,1'-biphenyl (1 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol%) and CuI (6 mol%) in dry toluene under nitrogen atmosphere was added NEt_3 (2 equiv) at room temperature and stirred for overnight. The solvent was removed under vacuo, and the crude residue was purified by flash chromatography on silica gel (PE/EA = 8/1) to give **1m** (39%) as a white solid, mp 60-61 ^{o}C; IR (neat): 2956, 2923, 2854, 1599, 1487, 1453; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.80-7.85 (m, 2H), 7.57-7.62 (m, 2H), 7.45-7.54 (m, 4H), 7.37-7,43 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.15-7.20 (m, 2H), 5.79-5.91 (m, 1H), 5.35-5.42 (m, 1H), 5.29-5.34 (m, 1H), 4.37 (s, 2H), 3.94 (d, *J* = 6.4 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.5, 141.1, 140.1, 135.9, 132.0, 131.9, 129.5, 128.9, 127.8, 127.7, 126.9, 126.7, 121.0, 119.9, 85.5, 82.3, 49.3, 36.7, 21.4; HRMS (EI) calculated for $[C_{25}H_{23}NO_2S]^+$ requires *m/z* 401.1450, found *m/z* 401.1450.



1p

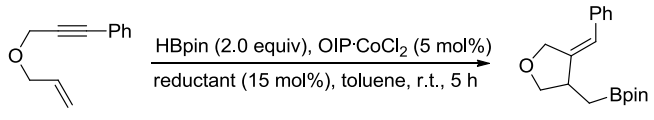
N-allyl-4-methyl-*N*-(3-(1-methyl-1*H*-indol-2-yl)prop-2-yn-1-yl)benzenesul

fonamide **(1p)**: To a solution of *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.04 equiv), 2-iodo-1-methyl-1*H*-indole (1 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol%) and CuI (6 mol%) in dry toluene under nitrogen atmosphere was added NEt_3 (2 equiv) at room temperature and stirred for overnight. The solvent was removed under vacuo, and the crude residue was purified by flash chromatography on silica gel (PE/EA = 8/1) to give **1p** as a yellow solid in 76% yield. IR (neat): 3057, 2923, 1644, 1598, 1462, 1428 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.28-7.22 (m, 4H), 7.13-7.07 (m, 1H), 6.47 (s, 1H), 5.87-5.75 (m, 1H), 5.37-5.31 (m, 1H), 5.31-5.26 (m, 1H), 4.40 (s, 2H), 3.92 (d, J = 6.4 Hz, 2H), 3.55 (s, 3H), 2.30 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.6, 136.9, 136.0, 132.0, 129.6, 127.7, 126.8, 123.2, 120.9, 120.8, 120.1, 120.0, 109.3, 107.7, 88.0, 77.5, 49.4, 36.9, 30.3, 21.4; HRMS (EI) calculated for $[C_{22}H_{22}N_2O_2S]^+$ requires *m/z* 378.1402, found *m/z* 378.1408.

Synthesis of Cobalt Complex

IP·$CoCl_2$: Prepared according to a previously reported procedure, A 100 mL Schlenk flask was charged with 1.0666 g (4.0 mmol) of (*E*)-2,6-diisopropyl-*N*-(pyridin-2-ylmethylene)aniline, 10 mL of THF and 0.4948 g (3.8 mmol) of $CoCl_2$ in argon atmosphere, then the mixture was stirred at room temperature for 5 h, then 10 mL of ether was injected to precipitate the complex. The resulting mixture was filtered under air, washed with ether and dried in vacuo to yield 0.4259 g (0.82 mmol, 86% yield). OIP·$CoCl_2$,[7] BIP·$CoCl_2$,[8] BOP·$CoCl_2$,[7] OP·$CoCl_2$ were synthesized by the previously reported literatures.

III. Optimization of Hydroboration/Cyclization of 1,6-Enynes



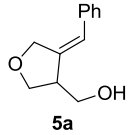
1a **2a**

Entry	Reductant	Yield of **2a** [a] (%)	Recovery
1	$NaBHs\text{-}Bu_3$	36	0
2	$LiBHEt_3$	65	0
3	MeLi	29	0
4	MeMgBr	6	49
5	$ZnEt_2$	32	0

[a]Yields determined by ^1H NMR analysis using $PhSiMe_3$ as an internal standard.

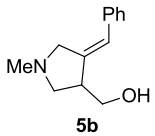
IV Hydroboration/cyclization of 1,6-enynes for alkenylboronates

General procedure A for OIP·$CoCl_2$ catalyzed hydroboration/cyclization cyclization followed by oxidation: To a 50 mL flame-dried Schlenk flask cooled under argon, OIP·$CoCl_2$ complex (0.05 mmol) and toluene (2 mL) were added and stirred for 5 min. Then $NaBHEt_3$ (0.15 mmol, 150 μl, 1 M in THF), HBpin (2 mmol) and enyne **1** (1 mmol) were added sequently. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched by ether (5 mL), and filtered through a plug of silica gel by ether. The filtrates were concentrated. The resulting residue was treated with NaOH (3 N, 3 mL) and H_2O_2 (30%, 3 mL) in ether (6 mL), and stirred for overnight at room temperature. The resulting suspension was added by water (20 mL) and ether (20 mL). The aquous layer was extracted with ether (10 mL * 2). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by column chromatography with silica gel to give **5**.



5a

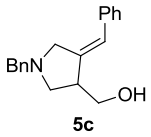
(*Z*)-(4-benzylidenetetrahydrofuran-3-yl)methanol (**5a**): According to general procedure A, the reaction with (3-(allyloxy)prop-1-yn-1-yl)benzene **1a** (0.1792 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0279 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1) as eluent afforded **5a** (0.1419 g, 72%) as a colorless oil; IR (neat): 3414, 2932, 2865, 1663, 1599, 1492, 1449; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.6 Hz, 2H), 7.20-7.26 (m, 1H), 7.14 (d, J = 7.2 Hz, 2H), 6.46 (d, J = 2.0 Hz, 1H), 4.64-4.72 (m, 1H), 4.55-4.62 (m, 1H), 3.98 (dd, J = 9.2, 6.4 Hz, 1H), 3.91 (dd, J = 8.8, 4.0 Hz, 1H), 3.72-3.78 (m, 2H), 3.00-3.10 (m, 1H), 1.74 (t, J = 5.6 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.6, 136.9, 128.6, 128.0, 126.9, 122.3, 70.14, 70.07, 64.2, 48.2; HRMS (EI) calculated for $[C_{12}H_{14}O_2]^+$ requires *m/z* 190.0994, found *m/z* 190.0997.



5b

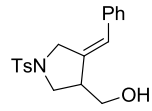
(*Z*)-(4-benzylidene-1-methylpyrrolidin-3-yl)methanol (**5b**) : According to general procedure A, the reaction with *N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine **1b** (0.1819 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0283 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using EtOAc/MeOH (8/1-7/1) as eluent afforded **5b** (0.1410 g, 71%) as a colorless oil; IR (neat): 3345, 2938, 2846, 2782, 1662, 1596, 1492, 1449; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30-7.36 (m, 2H), 7.18-7.24 (m, 3H), 6.37 (d, J = 1.6 Hz, 1H), 4.44 (br, 1H), 3.72-3.86

(m, 3H), 3.33 (dd, *J* = 14.4, 1.6 Hz, 1H), 2.95-3.02 (m, 1H), 2.89-3.95 (m, 1H), 2.74 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.9, 137.3, 128.4, 128.0, 126.6, 122.7, 66.2, 59.8, 58.7, 47.4, 42.0; HRMS (EI) calculated for $[C_{13}H_{17}NO]^+$ requires *m/z* 203.1310, found *m/z* 203.1314.



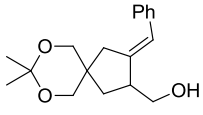
5c

(*Z*)-(1-benzyl-4-benzylidenepyrrolidin-3-yl)methanol (**5c**): According to general procedure A, the reaction with *N*-benzyl-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine **1c** (0.2643 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0297 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1) as eluent afforded **5c** (0.1388 g, 49%) as a yellow oil; IR (neat): 3355, 2923, 2874, 2793, 1663, 1599, 1494, 1450; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.29-7.34 (m, 4H), 7.21-7.28 (m, 3H), 7.13-7.19 (m, 3H), 6.35 (d, *J* = 1.6 Hz, 1H), 3.82 (dd, *J* = 6.0, 4.0 Hz, 1H), 3.71-3.76 (m, 2H), 3.69 (s, 2H), 3.32 (dd, *J* = 14.4, 2.8 Hz, 1H), 3.21 (br, 1H), 2.88-2.94 (m, 1H), 2.82 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.72 (dd, *J* = 8.8, 6.4 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 142.2, 138.1, 137.4, 128.5, 128.4, 128.3, 127.9, 127.1, 126.4, 122.5, 66.9, 60.1, 58.1, 56.9, 46.7; HRMS (EI) calculated for $[C_{19}H_{21}NO]^+$ requires *m/z* 279.1623, found *m/z* 279.1624.



5d

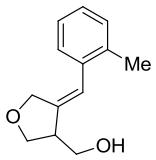
(*Z*)-(4-benzylidene-1-tosylpyrrolidin-3-yl)methanol[9] (**5d**): According to general procedure A, the reaction with *N*-allyl-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide **1d** (0.3522 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0279 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1) as eluent afforded **5d** (0.2900 g, 84%) as a white solid, Mp 127-128 ^{o}C; IR (neat): 3515, 2942, 2870, 1598, 1493, 1449; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.29-7.38 (m, 4H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.35 (d, *J* = 0.8 Hz, 1H), 4.17-4.24 (m, 1H), 4.01 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.57-3.67 (m, 2H), 3.38 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.28 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.94-3.03 (m, 1H), 2.41 (s, 3H), 2.07 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.9, 137.0, 136.2, 132.5, 129.8, 128.7, 128.2, 127.9, 127.4, 124.7, 64.0, 50.8, 49.4, 47.5, 21.6; HRMS (EI) calculated for $[C_{19}H_{21}NO_3S]^+$ requires *m/z* 343.1242, found *m/z* 343.1239.



5e

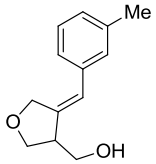
(*E*)-(3-benzylidene-8,8-dimethyl-7,9-dioxaspiro[*4.5*]decan-2-yl)methanol (**5e**):

According to general procedure A, the reaction with 5-allyl-2,2-dimethyl-5-(3-phenylprop-2-yn-1-yl)-1,3-dioxane **1e** (0.2782 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0283 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (3/1-2/1) as eluent afforded **5e** (0.2224 g, 75%) as a colorless oil; IR (neat): 3410, 2991, 2941, 2862, 1653, 1598, 1490, 1450; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.26-7.35 (m, 4H), 7.15-7.22 (m, 1H), 6.38 (d, J = 2.0 Hz, 1H), 3.66-3.76 (m, 4H), 3.59 (d, J = 11.6 Hz, 1H), 3.50 (d, J = 11.6 Hz, 1H), 2.84-2.92 (m, 1H), 2.80 (d, J = 16.8 Hz, 1H), 2.34-2.44 (m, 1H), 2.26-2.32 (m, 1H), 1.97 (dd, J = 13.2, 8.4 Hz, 1H), 1.35-1.45 (m, 7H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.7, 137.7, 128.3, 128.1, 126.3, 123.7, 97.9, 69.4, 67.7, 65.6, 45.9, 41.2, 39.0, 34.8, 24.3, 23.0; HRMS (EI) calculated for $[C_{18}H_{24}O_3]^+$ requires *m/z* 288.1725, found *m/z* 288.1728.



5f

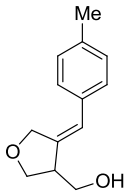
(*Z*)-(4-(2-methylbenzylidene)tetrahydrofuran-3-yl)methanol (**5f**): According to general procedure A, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-2-methylbenzene **1f** (0.1883 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0294 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1) as eluent afforded **5f** (0.0946 g, 46%) as a colorless oil; IR (neat): 3396, 2940, 2863, 1660, 1602, 1482, 1459; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.11-7.19 (m, 3H), 6.98-7.04 (m, 1H), 6.55 (d, J = 2.0 Hz, 1H), 4.50-4.57 (m, 1H), 4.44 (dd, J = 14.0, 2.0 Hz, 1H), 4.00 (dd, J = 8.8, 6.8 Hz, 1H), 3.91 (dd, J = 8.8, 4.0 Hz, 1H), 3.68-3.80 (m, 2H), 3.01-3.10 (m, 1H), 2.30 (s, 3H), 2.00 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.8, 135.9, 135.8, 130.1, 127.4, 127.2, 125.8, 120.4, 70.3, 69.8, 64.4, 47.6, 19.9; HRMS (EI) calculated for $[C_{13}H_{16}O_2]^+$ requires *m/z* 204.1150, found *m/z* 204.1147.



5g

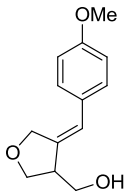
(*Z*)-(4-(3-methylbenzylidene)tetrahydrofuran-3-yl)methanol (**5g**): According to general procedure A, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-3-methylbenzene **1g** (0.1865 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0283 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (3/1-2/1) as eluent afforded **5g** (0.1236 g, 60%) as a colorless oil; IR (neat): 3402, 2938, 2863, 1661, 1603, 1485, 1457; ^{1}H

NMR: (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 7.6, 7.6 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.94 (s, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H), 4.62-4.68 (m, 1H), 4.55 (dd, J = 14.0, 2.0 Hz, 1H), 3.87-3.97 (m, 2H), 3.62-3.74 (m, 2H), 2.95-3.05 (m, 1H), 2.70 (br, 1H), 2.33 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.1, 138.0, 136.8, 128.7, 128.3, 127.6, 124.9, 122.3, 70.01, 69.97, 64.0, 48.1, 21.3; HRMS (EI) calculated for $[C_{13}H_{16}O_2]^+$ requires *m/z* 204.1150, found *m/z* 204.1155.



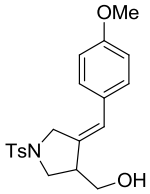
5h

(*Z*)-(4-(4-methylbenzylidene)tetrahydrofuran-3-yl)methanol (**5h**): According to general procedure A, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-4-methylbenzene **1h** (0.1883 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0291 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1) as eluent afforded **5h** (0.1069 g, 52%) as a colorless oil; IR (neat): 3413, 2939, 2864, 1656, 1611, 1513, 1454; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.39-6.43 (m, 1H), 4.62-4.69 (m, 1H), 4.56 (dd, J = 10.0, 1.2 Hz, 1H), 3.87-3.99 (m, 2H), 3.76-3.77 (m, 2H), 2.97-3.06 (m, 1H), 2.34 (s, 3H), 1.86 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 140.4, 136.7, 134.1, 129.2, 127.9, 122.1, 70.12, 70.05, 64.2, 48.2, 21.1; HRMS (EI) calculated for $[C_{13}H_{16}O_2]^+$ requires *m/z* 204.1150, found *m/z* 204.1155.



5i

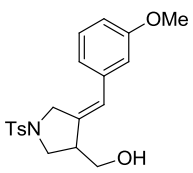
(*Z*)-(4-(4-methoxybenzylidene)tetrahydrofuran-3-yl)methanol (**5i**): According to general procedure A, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-4-methoxybenzene **1i** (0.2066 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0282 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1-1/1) as eluent afforded **5i** (0.0994 g, 44%) as a colorless oil; IR (neat): 3413, 2936, 2839, 1606, 1574, 1511, 1462; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.03-7.09 (m, 2H), 6.84-6.90 (m, 2H), 6.37 (d, J = 1.2 Hz, 1H), 4.64 (d, J = 14.0 Hz, 1H), 4.54 (d, J = 14.0 Hz, 1H), 3.87-3.98 (m, 2H), 3.80 (s, 3H), 3.65-3.75 (m, 2H), 2.95-3.05 (m, 1H), 2.39 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 158.4, 139.0, 129.8, 129.2, 121.6, 113.9, 70.0, 64.1, 55.2, 48.1, 24.7; HRMS (EI) calculated for $[C_{13}H_{16}O_3]^+$ requires *m/z* 220.1099, found *m/z* 220.1103.



5j

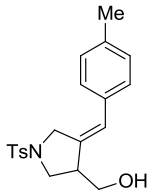
(*Z*)-(4-(4-methoxybenzylidene)-1-tosylpyrrolidin-3-yl)methanol (**5j**): According to

general procedure A, the reaction with *N*-allyl-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1j** (0.3594 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0293 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (1.5/1-1/1) as eluent afforded **5j** (0.2810 g, 74%) as a white solid, mp 121-122 ^oC; IR (neat): 3511, 2937, 2871, 2839, 1605, 1574, 1511, 1462; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.85-6.90 (m, 2H), 6.29 (d, J = 1.6 Hz, 1H), 4.15-4.23 (m, 1H), 3.99 (dd, J = 14.8, 2.4 Hz, 1H), 3.81 (s, 3H), 3.59-3.65 (m, 2H), 3.37 (dd, J = 9.6, 4.0 Hz, 1H), 3.26 (dd, J = 9.6, 6.8 Hz, 1H), 2.90-3.00 (m, 1H), 2.41 (s, 3H), 1.94 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 158.7, 143.8, 134.4, 132.5, 129.7, 129.4, 128.9, 127.8, 124.1, 114.0, 63.9, 55.3, 50.6, 49.3, 47.4, 21.5; HRMS (EI) calculated for $[C_{20}H_{23}NO_4S]^+$ requires m/z 373.1348, found m/z 373.1342.



5k

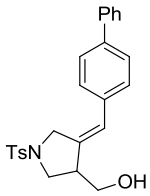
(*Z*)-(4-(3-methoxybenzylidene)-1-tosylpyrrolidin-3-yl)methanol (**5k**): According to general procedure A, the reaction with *N*-allyl-*N*-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1k** (0.3603 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0288 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1-1.5/1) as eluent afforded **5k** (0.2389 g, 63%) as a colorless oil; IR (neat): 3519, 2943, 2872, 1599, 1490, 1459, 1434; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.24-7.30 (m, 1H), 6.80 (dd, J = 8.4, 2.4 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.45-6.48 (m, 1H), 6.33 (d, J = 1.6 Hz, 1H), 4.16-4.24 (m, 1H), 4.01 (dd, J = 14.8, 2.4 Hz, 1H), 3.81 (s, 3H), 3.61-3.68 (m, 2H), 3.37 (dd, J = 9.6, 4.0 Hz, 1H), 3.28 (dd, J = 9.6, 6.8 Hz, 1H), 2.92-3.02 (m, 1H), 2.42 (s, 3H), 1.83 (t, J = 5.6 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.6, 143.8, 137.5, 137.3, 132.4, 129.8, 129.6, 127.8, 124.5, 120.5, 114.1, 112.6, 63.8, 55.2, 50.7, 49.3, 47.4, 21.5; HRMS (EI) calculated for $[C_{20}H_{23}NO_4S]^+$ requires m/z 373.1348, found m/z 373.1349.



5l

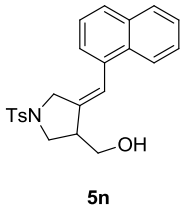
(*Z*)-(4-(4-methylbenzylidene)-1-tosylpyrrolidin-3-yl)methanol (**5l**): According to general procedure A, the reaction with *N*-allyl-4-methyl-*N*-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide **1l** (0.3458 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0287 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1-1/1) as

eluent afforded **5l** (0.2458 g, 67%) as a white solid, mp 117-118 ^{o}C; IR (neat): 3517, 2924, 2869, 1598, 1513, 1452; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.31 (d, J = 1.6 Hz, 1H), 4.16-4.24 (m, 1H), 4.00 (dd, J = 14.8, 2.4 Hz, 1H), 3.58-3.67 (m, 2H), 3.37 (dd, J = 9.6, 4.0 Hz, 1H), 3.26 (dd, J = 9.4, 6.8 Hz, 1H), 2.90-3.02 (m, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.04 (t, J = 5.2 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.8, 137.2, 135.8, 133.3, 132.5, 129.7, 129.3, 128.0, 127.8, 124.5, 63.9, 50.7, 49.3, 47.4, 21.5, 21.1; HRMS (EI) calculated for $[C_{20}H_{23}NO_3S]^+$ requires *m/z* 357.1399, found *m/z* 357.1401.



5m

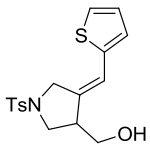
(*Z*)-(4-([1,1'-biphenyl]-4-ylmethylene)-1-tosylpyrrolidin-3-yl)methanol (**5m**): According to general procedure A, the reaction with *N*-(3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)-*N*-allyl-4-methylbenzenesulfonamide **1m** (0.3996 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0287 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1) as eluent afforded **5m** (0.2574 g, 62%) as a white foam; IR (neat): 3349, 2924, 2861, 1658, 1598, 1485, 1450; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 5.56-7.62 (m, 4H), 7.45 (dd, J = 7.6, 7.6 Hz, 2H), 7.30-7.40 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 0.9 Hz, 1H), 4.22-4.30 (m, 1H), 4.06 (dd, J = 14.8, 2.0 Hz, 1H), 3.62-3.70 (m, 2H), 3.40 (dd, J = 9.6, 4.0 Hz, 1H), 3.29 (dd, J = 9.6, 6.8 Hz, 1H), 2.96-3.06 (m, 1H), 2.41 (s, 3H), 1.99 (t, J = 5.2 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.8, 140.3, 140.0, 137.0, 135.1, 132.5, 129.8, 128.8, 128.6, 127.8, 127.5, 127.2, 126.9, 124.2, 63.9, 50.8, 49.3, 47.5, 21.5; HRMS (EI) calculated for $[C_{25}H_{25}NO_3S]^+$ requires *m/z* 419.1555, found *m/z* 419.1568.



5n

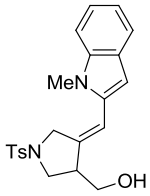
(*Z*)-(4-(naphthalen-1-ylmethylene)-1-tosylpyrrolidin-3-yl)methanol (**5n**): According to general procedure A, the reaction with *N*-allyl-4-methyl-*N*-(3-(naphthalen-1-yl)prop-2-yn-1-yl)benzenesulfonamide **1m** (0.3770 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0291 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1) as eluent afforded **5m** (0.1236 g, 31%) as a colorless oil; IR (neat): 3510, 2942, 2871, 1595, 1452; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.82-7.87 (m, 2H), 7.78 (d, J = 8.4 Hz, 1H), 7.60-7.66 (m, 2H), 7.40-7.52 (m, 3H), 7.19-7.27 (m, 3H), 6.93 (d, J = 2.0 Hz, 1H), 4.02-4.09 (m, 1H), 3.86 (dd, J =

14.8, 2.4 Hz, 1H), 3.68-3.81 (m, 2H), 3.34-3.44 (m, 2H), 3.05-3.15 (m, 1H), 2.38 (s, 3H), 2.10-2.25 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.7, 139.3, 133.5, 133.3, 132.5, 131.1, 129.7, 128.6, 128.0, 127.7, 126.1, 125.9, 125.6, 125.3, 124.1, 122.1, 64.0, 50.5, 49.8, 46.6, 21.5; HRMS (EI) calculated for $[C_{23}H_{23}NO_3S]^+$ requires *m/z* 393.1399, found *m/z* 393.1396.



5o

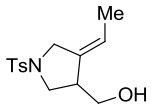
(*Z*)-(4-(thiophen-2-ylmethylene)-1-tosylpyrrolidin-3-yl)methanol (**5o**): According to general procedure A, the reaction with *N*-allyl-4-methyl-*N*-(3-(thiophen-2-yl)prop-2-yn-1-yl)benzenesulfonamide **1o** (0.3355 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0277 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2.5/1-1.5/1) as eluent afforded **5o** (0.2260 g, 64%) as a colorless oil; IR (neat): 3510, 2932, 2871, 1655, 1597, 1451, 1429; ^{1}H NMR: (400 MHz, $CDCl_3$) *δ* 7.75 (d, *J* = 8.0 Hz, 2H), 7.29-7.37 (m, 3H), 7.03 (dd, *J* = 5.2, 4.0 Hz, 1H), 6.90 (d, *J* = 4.0 Hz, 1H), 6.56 (d, *J* = 1.6 Hz, 1H), 4.11-4.19 (m, 1H), 3.98 (dd, *J* = 15.2, 2.0 Hz, 1H), 3.65 (dd, *J* = 6.4, 6.0 Hz, 2H), 3.40 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.29 (dd, *J* = 9.6, 6.8 Hz, 1H), 2.93-3.02 (m, 1H), 2.42 (s, 3H), 1.80 (t, *J* = 5.2 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) *δ* 143.9, 139.8, 135.1, 132.2, 129.8, 127.9, 127.4, 126.8, 126.0, 117.4, 63.7, 51.2, 49.9, 46.9, 21.5; HRMS (EI) calculated for $[C_{17}H_{19}NO_3S_2]^+$ requires *m/z* 349.0806, found *m/z* 349.0802.



5p

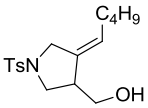
(*Z*)-(4-((1-methyl-1H-indol-2-yl)methylene)-1-tosylpyrrolidin-3-yl)methanol (**5p**): According to general procedure A, the reaction with *N*-allyl-4-methyl-*N*-(3-(1-methyl-1H-indol-2-yl)prop-2-yn-1-yl)benzenesulfonamide **1p** (0.3790 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0285 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc/DCM (2/1/0-2/1/1) as eluent afforded **5p** (0.2235 g, 56%) as a white solid, mp 155-156 ^{o}C; IR (neat): 3526, 2939, 2875, 1658, 1597, 1466, 1403; ^{1}H NMR: (400 MHz, $CDCl_3$) *δ* 7.76 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25-7.30 (m, 1H), 7.19-7.25 (m, 1H), 7.08-7.15 (m, 1H), 6.48 (d, *J* = 2.0 Hz, 1H), 6.33 (s, 1H), 4.19-4.25 (m, 1H), 4.03 (dd, *J* = 15.2, 2.4 Hz, 1H), 3.66-3.73 (m, 5H), 3.42 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.31 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.01-3.10 (m, 1H), 2.41 (s, 3H), 1.81 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) *δ* 143.8, 138.9, 137.1, 135.1, 132.5, 129.8, 127.9, 127.8, 122.3, 120.7, 120.0, 112.9, 109.1,

102.1, 63.9, 51.4, 49.6, 47.3, 29.6, 21.5; HRMS (EI) calculated for $[C_{22}H_{24}N_2O_3S]^+$ requires *m/z* 396.1508, found *m/z* 396.1517.



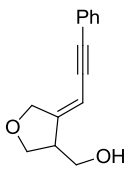
5q

(*Z*)-(4-ethylidene-1-tosylpyrrolidin-3-yl)methanol (**5q**): The reaction with *N*-allyl-*N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide **1q** (0.2593 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0287 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1-1/1) as eluent afforded **5q** (0.1374 g, 50%) as a colorless oil; IR (neat): 3526 (br), 2925, 2866, 1598, 1451; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69-7.75 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.32-5.42 (m, 1H), 3.78-3.87 (m, 1H), 3.69 (d, *J* = 14.0 Hz, 1H), 3.44-3.57 (m, 2H), 3.22-3.33 (m, 2H), 2.73-2.83 (m, 1H), 2.43 (s, 3H), 2.18 (t, *J* = 6.0 Hz, 1H), 1.55 (dq, *J* = 6.8, 1.6 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.7, 135.8, 132.2, 129.6, 127.8, 118.8, 63.7, 50.5, 49.5, 45.3, 21.5, 14.6; HRMS (EI) calculated for $[C_{14}H_{19}NO_3S]^+$ requires *m/z* 281.1086, found *m/z* 281.1089.



5r

(*Z*)-(4-pentylidene-1-tosylpyrrolidin-3-yl)methanol (**5r**): According to general procedure A, the reaction with *N*-allyl-*N*-(hept-2-yn-1-yl)-4-methylbenzenesulfonamide **1r** (0.3104 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0285 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (3/1-2/1) as eluent afforded **5r** (0.1628 g, 50%) as a colorless oil; IR (neat): 3532, 2955, 2926, 2861, 1597, 1460; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69-7.74 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.25-5.33 (m, 1H), 3.78-3.86 (m, 1H), 3.65-3.73 (m, 1H), 3.44-3.65 (m, 2H), 3.21-3.33 (m, 2H), 2.72-2.83 (m, 1H), 2.43 (s, 3H), 2.18-2.27 (m, 1H), 1.89 (q, *J* = 6.8 Hz, 2H), 1.20-1.35 (m, 4H), 0.84-0.90 (m, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.7, 134.8, 132.2, 129.6, 127.8, 124.8, 63.7, 50.4, 49.5, 45.3, 31.2, 29.1, 22.2, 21.4, 13.8; HRMS (EI) calculated for $[C_{17}H_{25}NO_3S]^+$ requires *m/z* 323.1555, found *m/z* 323.1555.



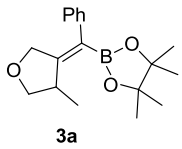
5s

(*Z*)-(4-(3-phenylprop-2-yn-1-ylidene)tetrahydrofuran-3-yl)methanol (**5s**): According to general procedure A, the reaction with (5-(allyloxy)penta-1,3-diyn-1-yl)benzene **1s** (0.2008 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), OIP·$CoCl_2$ (0.0292 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (2/1) as eluent afforded **5s** (0.0344 g, 16%) as a colorless oil; IR (neat): 3425, 2925, 2865, 1730, 1666, 1597, 1490, 1448; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.37-7.45 (m, 2H), 7.28-7.35 (m,

3H), 5.75 (q, *J* = 2.0 Hz, 1H), 4.59-4.67 (m, 1H), 4.54 (dd, *J* = 15.6, 2.0 Hz, 1H), 4.04 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.92 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.70 (d, *J* = 6.8 Hz, 2H), 2.95-3.07 (m, 1H), 1.63 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 154.8, 134.3, 131.3, 128.3, 128.3, 123.1, 101.3, 94.3, 85.6, 71.5, 63.7, 46.8; HRMS (EI) calculated for $[C_{14}H_{14}O_2]^+$ requires *m/z* 214.0994, found *m/z* 214.1003.

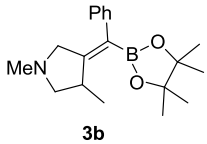
V. Hydroboration/cyclization of 1,6-enynes for alkylboronate

General procedure B for IP·$CoCl_2$ catalyzed hydroboration/cyclization cyclization: To a 50 mL flame-dried Schlenk flask cooled under argon, IP·$CoCl_2$ complex (0.25 mmol) and toluene (10 mL) were added and stirred for 5 min, Then $NaBHEt_3$ (0.75 mmol, 0.75 mL, 1 M in THF) , HBpin (10 mmol) and enyne **1** (5 mmol) were added sequently. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched by ether (15 mL), and filtered through a plug of silica gel by ether. The filtrates were concentrated and purified by column chromatography with silica gel to give **3**.



3a

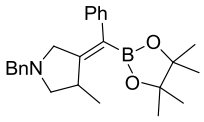
(*Z*)-4,4,5,5-tetramethyl-2-((4-methyldihydrofuran-3(2H)-ylidene)(phenyl)methyl)-1,3,2-dioxaborolane (**3a**): According to general procedure B, the reaction with (3-(allyloxy)prop-1-yn-1-yl)benzene **1a** (0.8665 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0981 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1-20/1) as eluent afforded **3a** (1.0131 g, 68%) as a colorless oil; IR (neat): 2977, 2933, 2868, 1726, 1677, 1634, 1599, 1452; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.25-7.31 (m, 2H), 7.15-7.21 (m, 1H), 7.06-7.11 (m, 2H), 4.47 (dd, *J* = 15.2, 1.6 Hz, 1H), 4.06 (d, *J* = 15.2 Hz, 1H), 3.89 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.70 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.35-3.45 (m, 1H), 1.22-1.30 (m, 15H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.8, 141.9, 128.1, 127.9, 126.0, 83.3, 75.3, 70.5, 38.6, 25.0, 24.5, 21.0; HRMS (EI) calculated for $[C_{18}H_{25}BO_3]^+$ requires *m/z* 300.1897, found *m/z* 300.1893.



3b

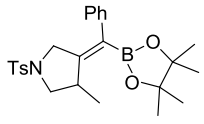
(*Z*)-1,3-dimethyl-4-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)pyrrolidine (**3b**): According to general procedure B, the reaction with *N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine **1b** (0.9289 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0994 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL,

0.75 mmol) in toluene (10 mL), using hexane/EtOAc (5/1-3/1-0/1) as eluent afforded **3b** (1.0575 g, 68%) as a yellow oil, IR (neat): 2977, 2935, 2772, 1631, 1453; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.23-7.30 (m, 2H), 7.15-7.20 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 3.46 (d, *J* = 15.2 Hz, 1H), 3.30-3.40 (m, 1H), 2.81 (d, *J* = 15.2 Hz, 1H), 2.64-2.71 (m, 1H), 2.52-2.59 (m, 1H), 2.28 (s, 3H), 1.20-1.34 (m, 15H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 142.8, 134.3, 130.0, 128.4, 127.8, 127.6, 125.7, 83.1, 64.0, 60.9, 42.6, 38.3, 24.9, 24.5, 22.0; HRMS (EI) calculated for $[C_{19}H_{28}BNO_2]^+$ requires *m/z* 313.2213, found *m/z* 313.2207.



3c

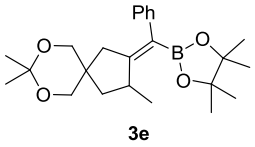
(*Z*)-1-benzyl-3-methyl-4-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)pyrrolidine (**3c**): According to general procedure B, the reaction with *N*-benzyl-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine **1c** (1.0851 g, 4.15 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0990 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (20/1) as eluent afforded **3c** (0.8280 g, 51%) as a white solid, mp 104-106 ^{o}C; IR (neat): 2975, 2927, 2869, 2784, 1631, 1492, 1451; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.20-7.29 (m, 7H), 7.12-7.17 (m, 1H), 7.07-7.11 (m, 2H), 3.48-3.58 (m, 2H), 3.44 (d, *J* = 15.2 Hz, 1H), 3.25-3.35 (m, 1H), 2.96 (d, *J* = 15.2 Hz, 1H), 2.66 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.43 (dd, *J* = 8.8, 3.2 Hz, 1H), 1.23-1.29 (m, 15H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 163.8, 142.8, 139.1, 128.5, 128.4, 128.1, 127.8, 126.7, 125.6, 83.1, 61.4, 60.4, 59.4, 37.9, 25.0, 24.5, 22.1; HRMS (EI) calculated for $[C_{25}H_{32}BNO_2]^+$ requires *m/z* 389.2526, found *m/z* 389.2529.



3d

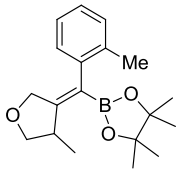
(*Z*)-3-methyl-4-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-1-tosylpyrrolidine (**3d**): According to general procedure B, the reaction with *N*-allyl-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide **1d** (1.6210 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0989 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (15/1) as eluent afforded **3d** (1.2304 g, 54%) as a white solid, mp 123-125 ^{o}C; IR (neat): 2978, 2929, 2868, 1633, 1598, 1491, 1450; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.25-7.30 (m, 4H), 7.17-7.23 (m, 1H), 6.95-7.00 (m, 2H), 4.08 (dd, *J* = 16.0, 1.2 Hz, 1H), 3.38-4.47 (m, 2H), 3.27 (dd, *J* = 9.2, 0.8 Hz, 1H), 3.11 (dd, *J* = 9.2, 2.0 Hz, 1H), 2.41 (s, 3H), 1.17-1.25 (m, 15H); ^{13}C NMR:

(100 MHz, $CDCl_3$) δ 157.7, 143.4, 141.1, 132.6, 129.5, 128.1, 127.9, 127.7, 126.3, 83.4, 54.6, 50.9, 37.8, 24.9, 24.4, 21.6, 21.5; HRMS (EI) calculated for $[C_{25}H_{32}BNO_4S]^+$ requires *m/z* 453.2145, found *m/z* 453.2151.



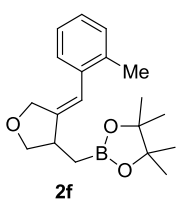
3e

(*E*)-4,4,5,5-tetramethyl-2-(phenyl(3,8,8-trimethyl-7,9-dioxaspiro[4.5]decan-2-ylidene)methyl)-1,3,2-dioxaborolane (**3e**): According to general procedure B, the reaction with 5-allyl-2,2-dimethyl-5-(3-phenylprop-2-yn-1-yl)-1,3-dioxane **1d** (0.2751 g, 1.0 mmol), HBpin (290 μL, 2.0 mmol), IP·$CoCl_2$ (0.0196 g, 0.05 mmol) and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (30/1-20/1) as eluent afforded **3e** (0.1444 g, 36%) as a colorless oil; IR (neat): 2985, 2940, 2859, 1730, 1620, 1488, 1453; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.23-7.30 (m, 2H), 7.12-7.18 (m, 1H), 7.05-7.10 (m, 2H), 3.62-3.72 (m, 2H), 3.46 (d, *J* = 11.2 Hz, 1H), 3.38 (d, *J* = 11.2 Hz, 1H), 3.23-3.34 (m, 1H), 2.22-2.33 (m, 2H), 2.09 (dd, *J* = 13.6, 8.8 Hz, 1H), 1.38 (s, 3H), 1.30 (s, 3H), 1.25 (s, 12H), 1.19-1.23 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 164.2, 142.9, 128.9, 127.7, 125.4, 97.6, 83.0, 70.1, 68.0, 40.6, 39.4, 36.6, 24.9, 24.4, 24.3, 24.0, 23.4; HRMS (EI) calculated for $[C_{24}H_{35}BO_4]^+$ requires *m/z* 398.2628, found *m/z* 398.2623.



3f

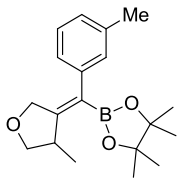
(*Z*)-4,4,5,5-tetramethyl-2-((4-methyldihydrofuran-3(2H)-ylidene)(p-tolyl)methyl)-1,3,2-dioxaborolane (**3f**): According to general procedure B, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-2-methylbenzene **1f** (0.9323 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0997 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1-20/1) as eluent afforded **3f** (0.4645 g, 30%) as a colorless oil; IR (neat): 2975, 2930, 2850, 1638, 1481, 1453; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.07-7.17 (m, 3H), 6.89-6.95 (m, 1H), 4.05-4.25 (m, 1H), 3.88 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.82 (d, *J* = 15.6 Hz, 1H), 3.74 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.37-3.49 (m, 1H), 2.15 (s, 3H), 1.27 (d, *J* = 7.2 Hz, 3H), 1.21-1.25 (m, 12H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 164.0, 141.6, 134.7, 129.8, 127.9, 126.2, 125.7, 83.1, 75.8, 70.9, 38.3, 24.9, 24.5, 21.0, 19.6; HRMS (EI) calculated for $[C_{19}H_{27}BO_3]^+$ requires *m/z* 314.2053, found *m/z* 314.2050.



2f

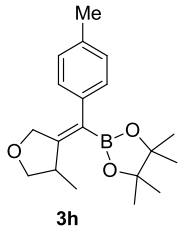
(*Z*)-4,4,5,5-tetramethyl-2-((4-(2-methylbenzylidene)tetrahydrofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2f**): as a colorless oil (0.2252 g, 14%); IR (neat): 2975,

2930, 2865, 1663, 1597, 1459; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.08-7.18 (m, 3H), 6.98-7.03 (m, 1H), 6.43 (q, J = 2.4 Hz, 1H), 4.55 (dd, J = 13.6, 1.6 Hz, 1H), 4.03-4.50 (m, 1H), 4.13 (dd, J = 8.0, 7.6 Hz, 1H), 3.42 (dd, J = 8.0, 8.0 Hz, 1H), 2.97-3.07 (m, 1H), 2.30 (s, 3H), 1.25 (s, 12H), 1.20-1.24 (m, 1H), 1.00-1.05 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 147.0, 136.4, 135.9, 130.0, 127.5, 126.7, 125.7, 118.0, 83.3, 74.4, 69.8, 40.6, 24.9, 24.7, 19.9; HRMS (EI) calculated for $[C_{19}H_{27}BO_3]^+$ requires *m/z* 314.2053, found *m/z* 314.2060.



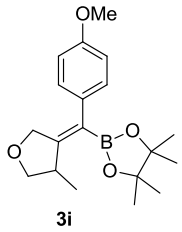
3g

(*Z*)-4,4,5,5-tetramethyl-2-((4-methyldihydrofuran-3(2H)-ylidene)(m-tolyl)methyl)-1,3,2-dioxaborolane (**3g**): According to general procedure B, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-3-methylbenzene **1g** (0.9343 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0981 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1-20/1) as eluent afforded **3g** (1.0309 g, 65%) as a white solid, mp 80-82 ^{o}C; IR (neat): 2975, 2929, 2862, 1634, 1602, 1481, 1453; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.14-7.21 (m, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.85-6.92 (m, 2H), 4.48 (d, J = 15.2 Hz, 1H), 4.07 (dd, J = 15.2, 2.8 Hz, 1H), 3.85-3.93 (m, 1H), 3.70 (d, J = 8.4 Hz, 1H), 3.35-3.45 (m, 1H), 2.32 (s, 3H), 1.22-1.32 (m, 15H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.5, 141.8, 137.3, 128.8, 127.8, 126.7, 125.1, 83.2, 75.3, 70.4, 38.6, 24.9, 24.5, 21.4, 20.9; HRMS (EI) calculated for $[C_{19}H_{27}BO_3]^+$ requires *m/z* 314.2053, found *m/z* 314.2059.



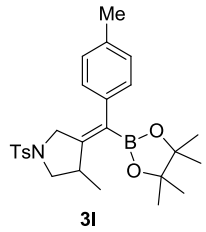
3h

(*Z*)-4,4,5,5-tetramethyl-2-((4-methyldihydrofuran-3(2H)-ylidene)(p-tolyl)methyl)-1,3,2-dioxaborolane (**3h**): According to general procedure B, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-4-methylbenzene **1h** (0.9293 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0994 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1-20/1) as eluent afforded **3h** (1.004 g, 64%) as a white solid, mp 91-92 ^{o}C; IR (neat): 2975, 2929, 2864, 1632, 1511, 1452; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 4.48 (dd, J = 15.2, 1.2 Hz, 1H), 4.07 (d, J = 15.2 Hz, 1H), 3.88 (dd, J = 8.4, 6.0 Hz, 1H), 3.69 (dd, J = 8.4, 2.0 Hz, 1H), 3.35-3.44 (m, 1H), 2.31 (s, 3H), 1.27 (s, 12H), 1.24 (d, J = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.4, 138.8, 135.4, 128.7, 128.0, 83.2, 75.2, 70.4, 38.6, 24.9, 24.5, 21.1, 20.9; HRMS (EI) calculated for $[C_{19}H_{27}BO_3]^+$ requires *m/z* 314.2053, found *m/z* 314.2060.



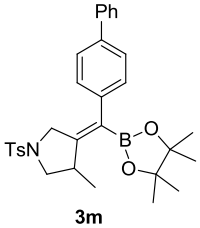
3i

(*Z*)-2-((4-methoxyphenyl)(4-methyldihydrofuran-3(2H)-ylidene)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**): According to general procedure B, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-4-methoxybenzene **1i** (1.0097 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.1003 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1-20/1) as eluent afforded **4i** (0.9825 g, 60%) as a colorless oil; IR (neat): 2976, 2934, 2839, 1605, 1510, 1458; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.02 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 4.49 (dd, J = 14.8, 1.2 Hz, 1H), 4.08 (dd, J = 14.8 Hz, 1H), 3.89 (dd, J = 8.4, 6.0 Hz, 1H), 3.79 (s, 3H), 3.69 (dd, J = 8.4, 2.0 Hz, 1H), 3.36,-3.42 (m, 1H), 1.28 (s, 12H), 1.24 (d, J = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.1, 157.7, 134.2, 129.2, 113.4, 83.3, 75.2, 70.5, 55.1, 38.6, 25.0, 24.5, 21.0; HRMS (EI) calculated for $[C_{19}H_{27}BO_4]^+$ requires *m/z* 330.2002, found *m/z* 330.2008.



3l

(*Z*)-3-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methylene)-1-tosylpyrrolidine (**3l**): According to general procedure B, the reaction with *N*-allyl-4-methyl-*N*-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide **1l** (1.6960 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0998 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (20/1) as eluent afforded **3l** (1.4650 g, 63%) as a white solid, mp 184-185 ^{o}C; IR (neat): 2978, 2927, 2868, 1632, 1599, 1511, 1452; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 4.08 (dd, J = 16.0, 1.2 Hz, 1H), 3.37-3.47 (m, 2H), 3.26 (dd, J = 9.2, 1.2 Hz, 1H), 3.10 (dd, J = 9.2, 6.4 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 1.21 (s, 12H), 1.18 (d, J = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 157.3, 143.4, 138.1, 135.7, 132.7, 129.5, 128.8, 127.8, 127.7, 83.4, 54.6, 50.9, 37.8, 24.8, 24.4, 21.6, 21.4, 21.1; HRMS (EI) calculated for $[C_{26}H_{34}BNO_4S]^+$ requires *m/z* 467.2302, found *m/z* 467.2293.

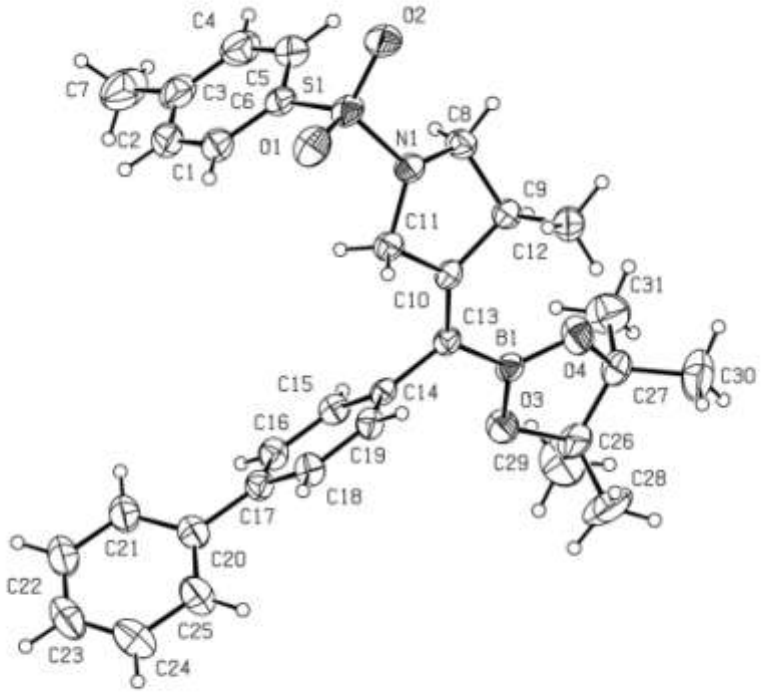


3m

(*Z*)-3-([1,1'-biphenyl]-4-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-4-methyl-1-tosylpyrrolidine (**3m**): According to general procedure B, the reaction with *N*-(3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)-*N*-allyl-4-methylbenzenesulfonamide **1m** (2.0013 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.1006 g,

0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (15/1-10/1) as eluent afforded **3m** (1.6603 g, 63%) as a white solid, mp 161-162 ^{o}C; IR (neat): 2978, 2930, 2868, 1631, 1599, 1485, 1450; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.60-7.65 (m, 4H), 7.50-7.56 (m, 2H), 7.41-7.48 (m, 2H), 7.30-7.37 (m, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.04-7.11 (m, 2H), 4.11-4.20 (m, 1H), 3.42-3.54 (m, 2H), 3.26-3.33 (m, 1H), 3.10-3.18 (m, 1H), 2.41 (s, 3H), 1.20-1.27 (m, 15H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 158.0, 143.5, 140.9, 140.2, 139.0, 132.7, 129.6, 128.7, 128.5, 127.8, 127.1, 127.0, 126.9, 83.5, 54.6, 51.0, 37.9, 24.9, 24.5, 21.6, 21.5; HRMS (EI) calculated for $[C_{31}H_{36}BNO_4S]^+$ requires *m/z* 529.2458, found *m/z* 529.2457.

X-ray diffraction of **3m** (CCDC 1499396)



Bond precision: C-C = 0.0043 A Wavelength=0.71073

Cell: a=10.9835(7) b=12.2187(8) c=13.4045(10)
alpha=62.987(7) beta=70.987(6) gamma=71.821(6)
Temperature: 280 K

	Calculated	Reported
Volume	1486.2(2)	1486.25(18)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C31 H36 B N O4 S	C31 H36 B N O4 S
Sum formula	C31 H36 B N O4 S	C31 H36 B N O4 S
Mr	529.48	529.48
Dx,g cm-3	1.183	1.183
Z	2	2
Mu (mm-1)	0.144	0.144
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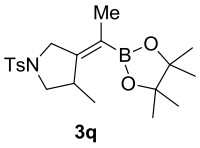
F000'	564.48	
h,k,lmax	13,14,16	13,14,16
Nref	5454	5434
Tmin,Tmax	0.936,0.949	0.959,1.000
Tmin'	0.936	

Correction method= # Reported T Limits: Tmin=0.959 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.350

R(reflections)= 0.0525(3603) wR2(reflections)= 0.1478(5434)

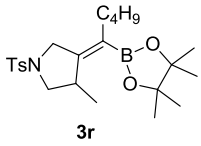
S = 1.025 Npar= 349



3q

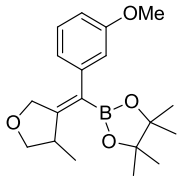
(*Z*)-3-methyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-1-tosylpyrrolidine (**3q**): According to general procedure B, the reaction with *N*-allyl-*N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide **1q** (1.3353 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0988 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (20/1) as eluent afforded **3q** (1.1069 g, 56%) as a white solid, mp 131-132 ^{o}C; IR (neat): 2978, 2929, 2867, 1650, 1598, 1452; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.06 (d, J = 14.8 Hz, 1H), 3.50 (d, J = 14.8 Hz, 1H), 3.24-3.32 (m, 2H), 2.97 (dd, J = 8.8, 6.4 Hz, 1H), 2.43 (s, 3H), 1.57 (s, 3H), 1.22 (d, J = 1.6 Hz, 12H), 1.11 (d, J = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 157.0, 143.5,

132.3, 129.5, 127.9, 83.1, 55.2, 50.9, 37.6, 24.9, 24.6, 21.6, 21.5, 16.9; HRMS (EI) calculated for $[C_{20}H_{30}BNO_4S]^+$ requires *m/z* 391.1989, found *m/z* 391.1994.



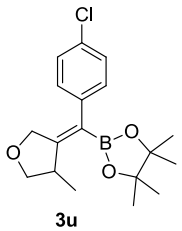
3r

(*Z*)-3-methyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentylidene)-1-tosylpyrrolidine (**3r**): According to general procedure B, the reaction with *N*-allyl-*N*-(hept-2-yn-1-yl)-4-methylbenzenesulfonamide **1r** (1.5087 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0991 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1-20/1) as eluent afforded **3r** (0.4060 g, 19%) as a white solid, mp 104-105 ^oC; IR (neat): 2973, 2927, 2866, 1645, 1597, 1454; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 4.10 (d, *J* = 15.6 Hz, 1H), 3.58 (d, *J* = 15.6 Hz, 1H), 3.21-3.30 (m, 2H), 2.96 (dd, *J* = 8.8, 6.0 Hz, 1H), 2.43 (s, 3H), 1.88-1.98 (m, 2H), 1.18-1.28 (m, 16H), 1.10 (d, *J* = 7.2 Hz, 3H), 0.82-0.90 (m, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 155.4, 143.5, 132.3, 129.5, 127.9, 83.0, 55.0, 50.2, 37.6, 31.8, 31.6, 24.8, 24.5, 22.6, 21.8, 21.5, 14.1; HRMS (EI) calculated for $[C_{23}H_{36}BNO_4S]^+$ requires *m/z* 433.2458, found *m/z* 433.2458.



3t

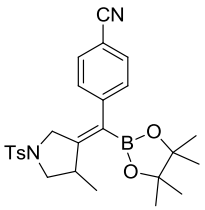
(*Z*)-2-((3-methoxyphenyl)(4-methyldihydrofuran-3(2H)-ylidene)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**): According to general procedure B, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-3-methoxybenzene **1t** (1.0088 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0985 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1-25/1) as eluent afforded **3t** (0.7894 g, 48%) as a colorless oil; IR (neat): 2975, 2933, 2840, 1663, 1598, 1579, 1483, 1460; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.74 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.63-6.65 (m, 1H), 4.49 (dd, *J* = 15.2, 1.2 Hz, 1H), 4.09 (d, *J* = 15.2 Hz, 1H), 3.89 (dd, *J* = 8.4, 5.2 Hz, 1H), 3.78 (s, 3H), 3.70 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.35-3.43 (m, 1H), 1.28 (s, 12H), 1.25 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.8, 159.1, 143.2, 128.9, 120.6, 113.8, 111.5, 83.3, 75.3, 70.4, 55.0, 38.6, 25.0, 24.5, 20.9; HRMS (EI) calculated for $[C_{19}H_{27}BO_4]^+$ requires *m/z* 330.2002, found *m/z* 330.2003.



3u

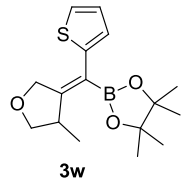
(*Z*)-2-((4-chlorophenyl)(4-methyldihydrofuran-3(2H)-ylidene)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3u**): According to general procedure B, the reaction with 1-(3-(allyloxy)prop-1-yn-1-yl)-4-chlorobenzene **1u** (1.0401 g, 5.0

mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0996 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1-20/1) as eluent afforded **3u** (0.6093 g, 36%) as a yellow oil; IR (neat): 2976, 2931, 2863, 1634, 1594, 1488, 1454; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.22-7.28 (m, 2H), 6.98-7.04 (m, 2H), 4.43 (dd, *J* = 15.2, 1.2 Hz, 1H), 4.03 (d, *J* = 15.2 Hz, 1H), 3.88 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.70 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.35-3.45 (m, 1H), 1.27 (s, 12H), 1.24 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 163.9, 140.3, 131.7, 129.5, 128.1, 83.4, 75.3, 70.4, 38.7, 25.0, 24.5, 20.9; HRMS (EI) calculated for $[C_{18}H_{24}BO_3Cl]^+$ requires *m/z* 334.1507, found *m/z* 334.1512.



3v

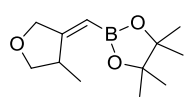
(*Z*)-4-((4-methyl-1-tosylpyrrolidin-3-ylidene)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzonitrile (**3v**): According to general procedure B, the reaction with 4-(3-(allyloxy)prop-1-yn-1-yl)benzonitrile **1v** (1.7523 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0992 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (8/1-5/1) as eluent afforded **3v** (0.6944 g, 29%) as a white solid, mp 173-174 ^{o}C; IR (neat): 2979, 2870, 2227, 1634, 1602, 1499, 1452; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56-7.63 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.07-7.12 (m, 2H), 4.00 (d, *J* = 16.0 Hz, 1H), 3.42-3.54 (m, 1H), 3.27-3.35 (m, 2H), 3.11 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.42 (s, 3H), 1.18-1.25 (m, 15H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.3, 146.4, 143.7, 132.4, 132.0, 129.6, 128.8, 127.7, 119.0, 110.1, 83.8, 54.5, 50.8, 38.0, 24.8, 24.4, 21.5, 21.5; HRMS (EI) calculated for $[C_{26}H_{31}BN_2O_4S]^+$ requires *m/z* 478.2098, found *m/z* 478.2092.



3w

(*Z*)-4,4,5,5-tetramethyl-2-((4-methyldihydrofuran-3(2H)-ylidene)(thiophen-2-yl)methyl)-1,3,2-dioxaborolane (**3w**): According to general procedure B, the reaction with 2-(3-(allyloxy)prop-1-yn-1-yl)thiophene **1w** (0.8924 g, 5.0 mmol), HBpin (1.45 mL, 10.0 mmol), IP·$CoCl_2$ (0.0997 g, 0.25 mmol) and $NaBHEt_3$ (0.75 mL, 0.75 mmol) in toluene (10 mL), using hexane/EtOAc (30/1) as eluent afforded **3w** (1.3098 g, 85%) as a colorless oil; IR (neat): 2976, 2932, 2865, 1621, 1514, 1451; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.98 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.93-6.96 (m, 1H), 4.73 (dd, *J* = 15.6, 1.6 Hz, 1H), 4.43 (d, *J* = 15.6 Hz, 1H), 3.87 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.73 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.31-3.39 (m, 1H), 1.34 (d, *J* = 1.6 Hz, 12H), 1.24 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.5, 143.4, 126.7, 126.0, 124.4, 83.7, 75.0, 71.3, 39.5, 25.0, 24.7,

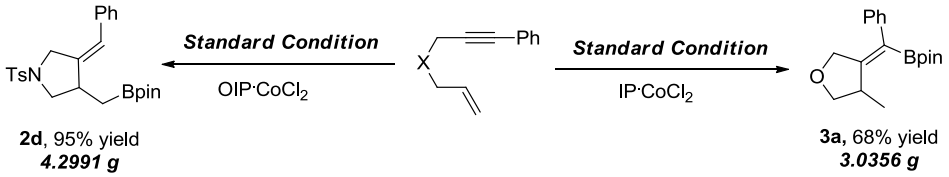
21.0; HRMS (EI) calculated for $[C_{16}H_{23}BO_3S]^+$ requires *m/z* 304.1461, found *m/z* 304.1459.



3x

(*E*)-4,4,5,5-tetramethyl-2-((4-methyldihydrofuran-3(2*H*)-ylidene)methyl)-1,3,2-dioxaborolane **(3x):** According to general procedure B, the reaction with *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **1x** (0.2477 g, 1.0 mmol), HBpin (290 uL, 2.0 mmol), IP·$CoCl_2$ (0.0196 g, 0.05 mmol) and $NaBHEt_3$ (150 uL, 0.15 mmol) in toluene (2 mL), using hexane/EtOAc (7/1) as eluent afforded **3x** (0.1552 g, 41%) as a colorless oil; IR (neat): 2978, 2929, 2870, 1657, 1598, 1454; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.18 (d, *J* = 1.6 Hz, 1H), 4.07-4.14 (m, 1H), 3.57 (dd, *J* = 15.2, 2.0 Hz, 1H), 3.19-3.28 (m, 2H), 3.09 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.42 (s, 3H), 1.22 (d, *J* = 1.2 Hz, 12H), 1.13 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.5, 143.5, 132.3, 129.6, 127.8, 83.0, 55.3, 53.4, 37.7, 24.8, 24.6, 21.5, 21.0; HRMS (EI) calculated for $[C_{19}H_{28}BNO_4S]^+$ requires *m/z* 377.11832, found *m/z* 377.1832.

VI. Gram scale reactions and further derivatizations

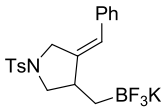


2d, 95% yield
4.2991 g

3a, 68% yield
3.0356 g

To a 50 mL flame-dried Schlenk flask cooled under argon, OIP·$CoCl_2$ complex (0.2853 g, 0.5 mmol) and toluene (20 mL) were added, and stirred for 5 min. Then $NaBHEt_3$ (1.5 mmol, 1.5 mL, 1 M in THF), HBpin (2.9 mL, 20 mmol) and **1d** (3.2597 g, 10 mmol) were added sequently. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched by ether (15 mL), and filtered through a plug of silica gel by ether. The filtrates were concentrated and purified by column chromatography with silica gel (PE/EA = 10/1-5/1) to give **2d** (4.2991 g, 95% yield) as colorless oil; IR (neat): 2978, 2925, 1598, 1451, 1372, 1345; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.30-7.39 (m, 4H), 7.22-7.27 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.26 (d, *J* = 2.0 Hz, 1H), 4.27 (dd, *J* = 14.8, 1.6 Hz, 1H), 3.98-4.06 (m, 1H), 3.66 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.95-3.5 (m, 1H), 2.82 (t, *J* = 8.8 Hz, 1H), 2.43 (s, 3H), 1.21 (d, *J* = 6.8 Hz, 12H), 1.12-1.18 (m, 1H), 0.96 (dd, *J* = 16.0, 8.0 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.5, 142.3, 136.6, 133.0, 129.7, 128.5, 128.0, 127.8, 126.8, 121.9, 83.4, 53.6, 50.8, 40.3, 24.8, 24.7, 21.5; HRMS (EI) calculated for $[C_{25}H_{32}BNO_4S]^+$ requires *m/z* 453.2145, found *m/z* 453.2140.

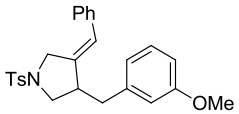
To a 50 mL flame-dried Schlenk flask cooled under argon, IP·$CoCl_2$ complex (0.2950 g, 0.75 mmol) and toluene (30 mL) were added, and stirred for 5 min. Then $NaBHEt_3$ (2.25 mmol, 2.25 mL, 1 M in THF), HBpin (4.35 mL, 30 mmol) and **1a** (2.5843 g, 15 mmol) were added sequently. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched by ether (15 mL), and filtered through a plug of silica gel by ether. The filtrates were concentrated and purified by column chromatography with silica gel (PE/EA = 30/1-20/1) to give **3a** (3.0356 g, 68% yield) as colorless oil.



6d

potassium (Z)-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)trifluoroborate (**6d**): The titled product was prepared according to a reported procedure with some modification.[10] Boronic ester **2d** (1.3650 g, 3.0 mmol) was dissloved in methanol (15 mL). To the solution was added KHF_2 (3 mL, 4.5 M saturated aqueous solution, 13.5 mmol, 2.25 equiv) dropwise. The reaction mixture stirred at 25 ℃ for 1.5 h. The solvent was then removed under vacuum and the solid residue was triturated with dry acetone (30 mL). The liquid phase was filtered, and the residual inorganic salts were washed with additional acetone (2×10 mL). The combined solution was concentrated in vacuo to give white solids. The solids was washed with ether (3×20 mL) to remove pinacol and dried under vacuum, affording the desired product **6d** as white solids (1.0652 g, 82%) as white solid; ^{1}H NMR: (400.1 MHz, DMSO) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.20-7.25 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 2.0 Hz, 1H), 4.20 (d, *J* = 14.8 Hz, 1H), 3.77 (d, *J* = 14.8 Hz, 1H), 3.57 (dd, *J* = 8.0, 7.6 Hz, 1H), 2.55-2.65 (m, 1H), 2.43-2.49 (m, 1H), 2.37 (s, 3H), 0.45-0.57 (m, 1H), -0.25- -0.10 (m, 1H); ^{13}C NMR: (100.6 MHz, DMSO) δ 145.9, 143.9, 137.4, 133.0, 130.3, 129.0, 128.4, 127.9, 126.9, 120.3, 54.5, 51.1, 42.6 (d, *J* = 1.8 Hz), 21.5; ^{19}F NMR: (376.5 MHz, DMSO) δ -136.15.

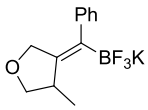
Representative procedure for cross-coupling of alkylboronates with aryl chlorides



7

(Z)-3-benzylidene-4-(3-methoxybenzyl)-1-tosylpyrrolidine (**7**): The titled product was prepared according to a reported procedure with some modification.[11] Under argon, $Pd(OAc)_2$ (0.0046 g, 0.02 mmol), Ruphos (0.0186 g, 0.04 mmol), 1-chloro-3-methoxybenzene (0.1381 g, 1 mmol), alkylboronic ester **3d** (0.4320 g, 1 mmol,1.0 equiv) and K_2CO_3 (0.4156 g, 3.0 mmol), and were added to a

Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon. Toluene (5 mL) and H_2O (0.5 mL) were added to the Schlenk tube by syringe. The resulting reaction mixture stirred vigorously at 80 ℃ for 24 h. The resulting suspension was partitioned between water (20 mL) and EtOAc (20 mL) and extracted with EtOAc (10 mL) in two times. The EtOAc extracts were washed with brine (50 mL), dried ($MgSO_4$), filtered and concentrated under vacuum. The resulting residue was purified by column chromatography with silica gel to give **7** (0.3461g, 80%) as a colorless oil; IR (neat): 2955, 2924, 2854, 1599, 1491, 1455; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.31-7.41 (m, 4H), 7.21-7.31 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.80 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.71-6.74 (m, 1H), 6.28 (d, *J* = 1.2 Hz, 1H), 4.21-4.27 (m, 1H), 4.13 (dd, *J* = 14.8, 2.4 Hz, 1H), 3.83 (s, 3H), 3.17-3.24 (m, 1H), 3.02-3.12 (m, 2H), 2.97 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.65 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.7, 143.7, 140.7, 139.8, 136.4, 132.8, 129.7, 129.6, 128.6, 128.1, 127.7, 127.1, 123.3, 121.2, 114.7, 111.8, 55.2, 51.5, 50.8, 46.5, 39.5, 21.5; HRMS (EI) calculated for $[C_{26}H_{27}NO_3S]^+$ requires *m/z* 433.1712, found *m/z* 433.1715.



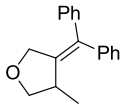
8a

Potassium (Z)-trifluoro((4-methyldihydrofuran-3(2H)-ylidene)(phenyl)methyl)borate (**8a**): The titled product was prepared according to a reported procedure with some modification.[10] Boronic ester **4a** (0.2976 g, 1.0 mmol) was dissloved in methanol (3 mL). To the solution was added KHF_2 (1 mL, 4.5 M saturated aqueous solution, 4.5 mmol, 2.25 equiv) dropwise. The reaction mixture stirred at 25 ℃ for 0.5 h. The solvent was then removed under vacuum and the solid residue was triturated with dry acetone (10 mL). The liquid phase was filtered, and the residual inorganic salts were washed with additional acetone (2×5 mL). The combined solution was concentrated in vacuo to give white solids. The solids was washed with ether (3×5 mL) to remove pinacol and dried under vacuum, affording the desired product **8a** as white solids (0.2375 g, 85%) as white solid. ^{1}H NMR: (400 MHz, DMSO) δ 7.09-7.15 (m, 2H), 6.94-7.01 (m, 3H), 4.08 (d, *J* = 12.8 Hz, 1H), 3.68 (d, *J* = 12.8 Hz, 1H), 3.62 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.47 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.02-3.17 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, DMSO) δ 148.4, 144.0, 128.1, 127.3, 124.1, 75.2, 69.6 (d, *J* = 1.4 Hz), 65.4, 40.6, 40.4, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 37.1, 37.1, 21.2 (q, *J* = 1.6 Hz), 15.7; ^{19}F NMR: (376.5 MHz,

DMSO) δ -148.35;

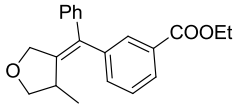
Tow-step, Suzuki cross-coupling of alkenylboronates with aryl bromide[12]:

General Procedure C: To a 50 mL flame-dried Schlenk flask cooled under argon, IP·$CoCl_2$ complex (0.05 mmol) and toluene (2 mL) were added, and stirred for 5 min. Then $NaBHEt_3$ (0.15 mmol, 150 μl, 1 M in THF), HBpin (2 mmol) and enyne **1** (174 μl, 1 mmol) were added sequently. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched by ether (5 mL), and filtered through a plug of silica gel by. The filtrates were concentrated. Under argon, $Pd(PPh_3)_4$ (0.05 mmol), aryl bromide (1.2 mmol), and K_2CO_3 (3.0 mmol), and were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon. Toluene (5 mL) were added to the Schlenk tube by syringe. The resulting reaction mixture stirred vigorously at 110 ℃ for 24 h. The reaction mixture was filtered through celite and washed with DCM (15×3 mL). The solution was combined and the volatiles were removed under vacuum. The residue was purified by column chromatography to afford the product **9**.



9aa

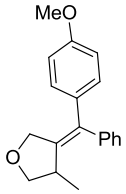
3-(Diphenylmethylene)-4-methyltetrahydrofuran (**9aa**): (According to general procedure C) colorless oil, 48% yield. IR (neat): 3056, 3024, 2965, 2929, 2845, 1599, 1492, 1445; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.18-7.36 (m, 8H), 7.07-7.11 (m, 2H), 4.61 (dd, *J* = 13.2, 1.6 Hz, 1H), 4.27 (d, *J* = 13.2 Hz, 1H), 4.06 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.52 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.10-3.19 (m, 1H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.4, 142.1, 141.8, 133.6, 129.1, 128.5, 128.3, 128.1, 126.8, 126.7, 75.5, 70.6, 37.3, 17.3; HRMS (EI) calculated for $[C_{18}H_{18}O]^+$ requires *m/z* 250.1358, found *m/z* 250.1356.



9ab

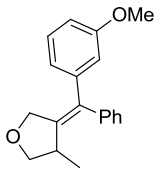
(*E*)-ethyl 3-((4-methyldihydrofuran-3(*2H*)-ylidene)(phenyl)methyl)benzoate (**9ab**): (According to general procedure C) colorless oil, 45% yield. IR (neat): 3059, 2979, 2880, 1716, 1600, 1581, 1445; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.93-7,99 (m, 2H), 7.38-7.43 (m, 2H), 7.25-7.32 (m, 2H), 7.19-7.25 (m, 1H), 7.05-7,11 (m, 2H), 4.62 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.32-4.42 (m, 2H), 4.28 (d, *J* = 14.0 Hz, 1H), 4.07 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.53 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.07-3.17 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.85 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 166.5, 144.4, 142.0, 141.5, 133.6, 132.7, 130.7, 130.1, 128.5, 128.4,

128.2, 128.0, 127.0, 75.4, 70.6, 61.0, 37.3, 17.3, 14.3; HRMS (EI) calculated for $[C_{21}H_{22}O_3]^+$ requires *m/z* 322.1569, found *m/z* 322.1565.



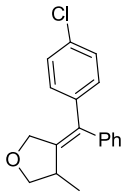
9ac

(*Z*)-3-((4-methoxyphenyl)(phenyl)methylene)-4-methyltetrahydrofuran (**9ac**): (According to general procedure C) colorless oil, 48% yield. IR (neat): 3055, 2962, 2837, 1606, 1574, 1510, 1438; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.29-7.35 (m, 2H), 7.19-7.26 (m, 3H), 6.97-7.03 (m, 2H), 6.77-6.84 (m, 2H), 4.61 (dd, *J* = 13.6, 2.0 Hz, 1H), 4.29 (d, *J* = 13.6 Hz, 1H), 4.04 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.76 (s, 3H), 3.50 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.07-3.17 (m, 1H), 0.83 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 158.3, 142.4, 142.0, 134.6, 133.0, 129.6, 129.1, 128.2, 126.6, 113.4, 75.4, 70.5, 55.1, 37.3, 17.2; HRMS (EI) calculated for $[C_{19}H_{20}O_2]^+$ requires *m/z* 280.1463, found *m/z* 280.1466.



9ad

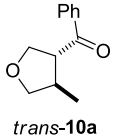
(*Z*)-3-((3-methoxyphenyl)(phenyl)methylene)-4-methyltetrahydrofuran (**9ad**): (According to general procedure C) colorless oil, 52% yield. IR (neat): 3056, 2963, 2837, 1598, 1580, 1487; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.28-7.35 (m, 2H), 7.21-7.26 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.73-6.78 (m, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.62-6.67 (m, 1H), 4.60 (dd, *J* = 13.2, 1.6 Hz, 1H), 4.28 (d, *J* = 13.2 Hz, 1H), 4.05 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.73 (s, 3H), 3.51 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.08-3.18 (m, 1H), 0.85 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.3, 143.5, 143.4, 141.6, 133.4, 129.03, 128.96, 128.2, 126.7, 121.0, 114.4, 112.0, 75.4, 70.6, 55.1, 37.3, 17.2; HRMS (EI) calculated for $[C_{19}H_{20}O_2]^+$ requires *m/z* 280.1463, found *m/z* 280.1460.



9ae

(*Z*)-3-((4-chlorophenyl)(phenyl)methylene)-4-methyltetrahydrofuran (**9ae**): (According to general procedure C) colorless oil, 47% yield. IR (neat): 3055, 3024, 2967, 2929, 2844, 1666, 1595, 1489; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30-7.36 (m, 2H), 7.22-7.28 (m, 3H), 7.18-7.22 (m, 2H), 6.99-7.04 (m, 2H), 4.58 (dd, *J* = 13.2, 1.6 Hz, 1H), 4.24 (d, *J* = 13.2 Hz, 1H), 4.06 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.51 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.09-3.19 (m, 1H), 0.84 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 144.2, 141.3, 140.5, 132.6, 132.4, 129.8, 129.0, 128.4, 128.3, 126.9, 75.4, 70.5, 37.4, 17.1; HRMS (EI) calculated for $[C_{18}H_{17}ClO]^+$ requires *m/z* 284.0968, found *m/z* 284.0967.

Oxidation of Alkenylboronate[13]

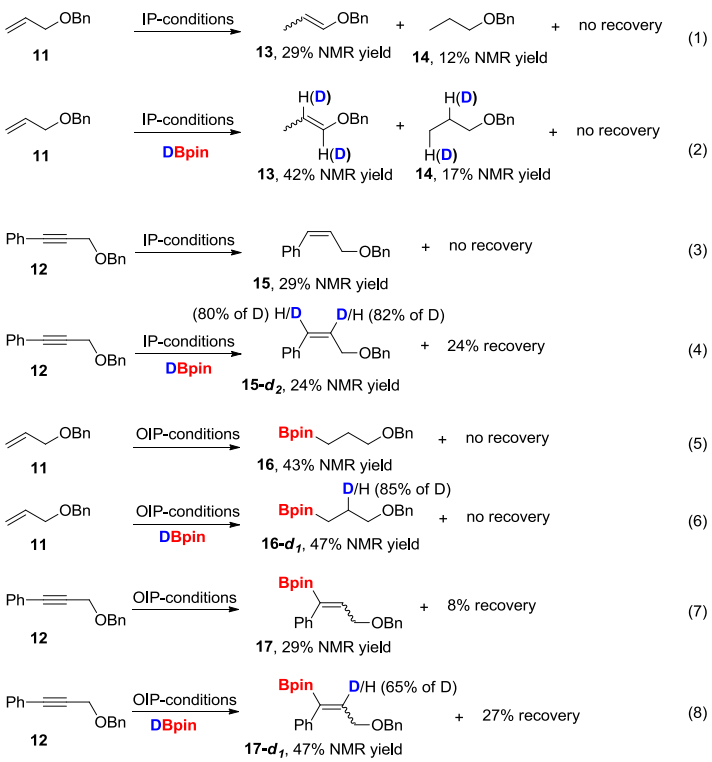


trans-**10a**

(*Trans*)-(4-methyltetrahydrofuran-3-yl)(phenyl)methanone (*trans*-**10a**): The

alkenylboronate **4a** (0.3007 g, 1 mmol) was treated with NaOH (3 N, 3 mL) and H_2O_2 (30%, 3 mL) in 6 mL, and stirred for overnight at room temperature. The resulting suspension was partitioned between water (20 mL) and (20 mL) and extracted with (10 mL) in two times. The ether extracts were washed with brine (50 mL), dried ($MgSO_4$), filtered and concentrated under vacuum. The resulting residue was purified by column chromatography with silica gel to give **10a** (0.1347g, 70%, *dr* 6:1) as a colorless oil. (*trans)*-**10a**, IR (neat): 2963, 2931, 2871, 1680, 1597, 1451; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.93-7.98 (m, 2H), 7.56-7.62 (m, 1H), 7.46-7.52 (m, 2H), 4.20 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.07 (dd, *J* = 7.2, 8.4 Hz, 1H), 3.95 (dd, *J* = 8.8, 7.2 Hz, 1H), 3.61-3.68 (m, 1H), 3.49 (dd, *J* = 8.4, 7.2 Hz, 1H), 2.71-2.83 (m, 1H), 1.14 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 199.4, 136.8, 133.3, 128.7, 128.3, 75.3, 70.8, 54.3, 37.7, 17.4; HRMS (EI) calculated for $[C_{12}H_{14}O_2]^+$ requires *m/z* 190.0994, found *m/z* 190.0994. (*cis*)-**10a**, ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.97-8.01 (m, 2H), 7.56-7.62 (m, 1H), 7.46-7.53 (m, 2H), 4.33 (dd, J = 8.0, 7.2 Hz, 1H), 4.03-4.16 (m, 3H), 3.57 (dd, *J* = 8.4, 5.2 Hz, 1H), 2.74-2.86 (m, 1H), 0.84 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 199.2, 137.5, 133.3, 128.8, 128.1, 75.6, 69.0, 49.8, 37.7, 14.2.

VII. Mechanistic Studies



According to general procedure B: ((allyloxy)methyl)benzene **11** was afford **13**[14] in 29% NMR

yield and **14**[15] in 12% NMR yield (eq 1); (3-(benzyloxy)prop-1-yn-1-yl)benzene **12** was afford **15**[16] in 29% NMR yield (eq 3).

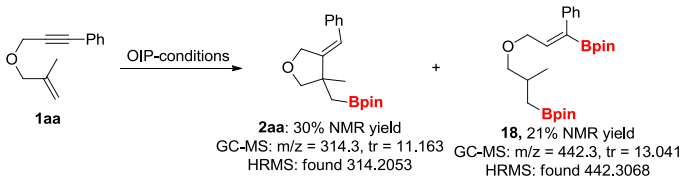
According to general procedure B (): ((allyloxy)methyl)benzene **11** with DBpin was afford **13**[17] in 42% NMR yield and **14**[18] in 17% NMR yield, however, it was difficult to identify the deuteration percentage (eq 2).; (3-(benzyloxy)prop-1-yn-1-yl)benzene **12** was afford **15**[19] in 24% NMR yield with around 80% deuteration (eq 4).

According to general procedure A: ((allyloxy)methyl)benzene **11** was afford **16** in 43% NMR yield (95% purity) (eq 5). IR (neat): 2963, 2931, 2899, 1580, 1452; ^{1}H NMR: (300.1 MHz, $CDCl_3$) δ 7.25-7.35 (m, 5H), 4.50 (s, 2H), 3.44 (t, J = 8.8 Hz, 2H), 1.68-1.80 (m, 2H), 1.22 (s, 12H), 0.83 (t, J = 10.4 Hz, 2H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 138.7, 128.2, 127.5, 127.3, 82.9, 72.6, 72.0, 24.7, 24.1; HRMS (EI) calculated for $[C_{16}H_{25}BO_3]^+$ requires *m/z* 276.1897, found *m/z* 276.1895.

According to general procedure A (with **DBpin)**: ((allyloxy)methyl)benzene **11** was afford **16** in **16**-d_1 in 47% NMR yield with 85% deuteration (eq 6).

The raction of (3-(benzyloxy)prop-1-yn-1-yl)benzene **12** was afford **17** in 29% NMR yield (71% purity, 29% undetermined isomers) (eq 7). IR (neat): 2963, 2931, 2871, 1680, 1451; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.26-7.32 (m, 8H), 7.10-7.15 (m, 2H), 6.75 (t, *J* = 6.0 Hz, 1H), 4.45 (s, 2H), 4.15 (d, *J* = 6.0 Hz, 2H), 1.27 (s, 12H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.3, 139.1, 138.2, 128.7, 128.3, 127.8, 127.7, 127.5, 126.4, 83.7, 72.5, 67.8, 24.7; HRMS (EI) calculated for $[C_{22}H_{27}BO_3]^+$ requires *m/z* 350.2053, found *m/z* 350.2045.

The raction of (3-(benzyloxy)prop-1-yn-1-yl)benzene **12** with DBpin was afford **17**-d_1 in 47% NMR yield with 65% deuteration (eq 8).



1aa

2aa: 30% NMR yield
GC-MS: m/z = 314.3, tr = 11.163
HRMS: found 314.2053

18, 21% NMR yield
GC-MS: m/z = 442.3, tr = 13.041
HRMS: found 442.3068

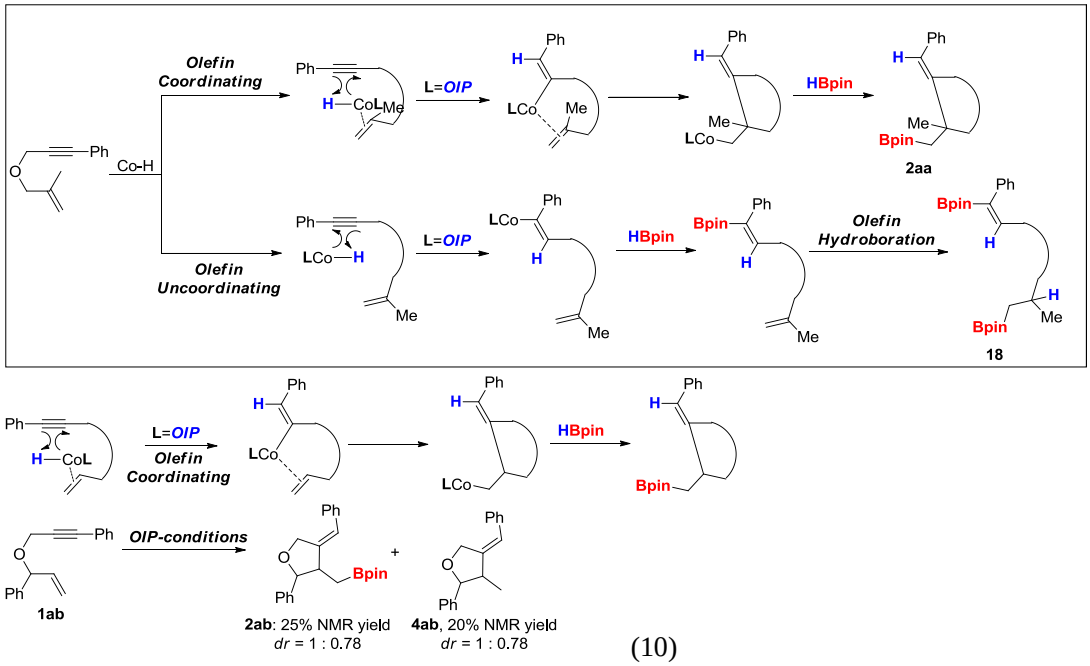
(9)

According to general procedure A: (3-((2-methylallyl)oxy)prop-1-yn-1-yl)benzene **1aa** was afford **2aa** in 30% NMR yield and **18** in 21% NMR yield (eq 9);

(Z)-2-((4-benzylidene-3-methyltetrahydrofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2aa**): colorless oil, m/z = 314.3; IR(neat): 2977, 2882, 1725, 1600, 1451; ^{1}H NMR: (400.1

MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.17-7.20 (m, 1H), 7.10-7.15 (m, 2H), 6.21-6.24 (m, 1H), 4.71 (d, *J* = 2.0 Hz, 2H), 3.80 (d, *J* = 8.0 Hz, 1H), 3.65 (d, *J* = 8.0 Hz, 1H), 1.28 (s, 3H), 1.18-1.23 (m, 14H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 151.3, 137.6, 128.4, 127.9, 126.2, 118.4, 83.0, 79.3, 70.5, 44.9, 26.4, 24.8, 24.8; HRMS (EI) calculated for $[C_{19}H_{27}O_3B]^+$ requires m/z 314.2053, found m/z 314.2060.

(*Z*)-4,4,5,5-tetramethyl-2-(2-methyl-3-((3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)propyl)-1,3,2-dioxaborolane (**18**): m/z = 442.3; HRMS (EI) calculated for $[C_{25}H_{40}O_5B_2]^+$ requires m/z 442.3062, found m/z 442.3068.



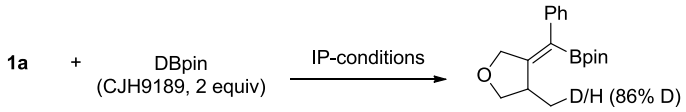
(10)

According to general procedure A: (3-((1-phenylallyl)oxy)prop-1-yn-1-yl)benzene **1ab** was afford **2ab** in 25% NMR yield and **4ab** in 20% NMR yield (eq 10); **2ab**: m/z = 376.3; **4ab**: m/z = 250.2.

5a-*d*, 61% yield

5a-*d*: To a 50 mL flame-dried Schlenk flask cooled under argon, OIP·$CoCl_2$ complex (0.0282 g, 0.05 mmol) and toluene (2 mL) were added, and stirred for 5 min. Then $NaBHEt_3$ (150 μl, 0.15 mmol), DBpin[20] (0.2543 g, 2 mmol) and **1a** (174 μl, 1 mmol) were added sequently. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched by ether (5 mL), and filtered through a plug of silica gel by ether. The filtrates were concentrated. The resulting reaction residue was treated with NaOH (3 N, 3 mL) and H_2O_2 (30%, 3 mL) in ether (6 mL), and stirred for

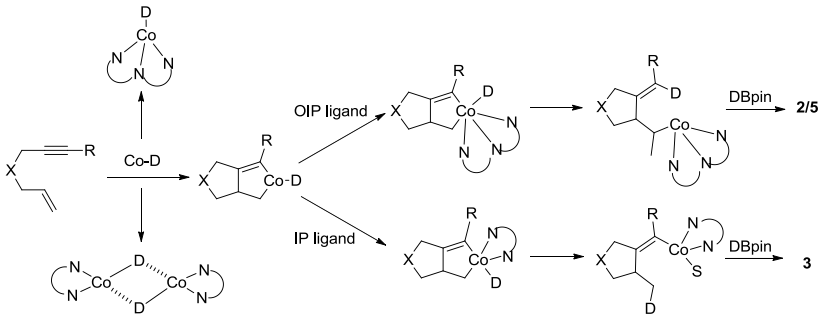
overnight at room temperature. The resulting suspension was partitioned between water (20 mL) and ether (20 mL) and extracted with ether (10 mL * 2). The ether extracts were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by column chromatography with silica gel to give **5a-*d*** as colorless oil (61%, purity 86%, 93% D). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 7.6, 7.6 Hz, 2H), 7.20-7.26 (m, 1H), 7.14 (d, J = 7.2 Hz, 2H), 6.46 (d, J = 2.0 Hz, 0.07 H), 4.64-4.72 (m, 1H), 4.55-4.62 (m, 1H), 3.98 (dd, J = 9.2, 6.4 Hz, 1H), 3.91 (dd, J = 8.8, 4.0 Hz, 1H), 3.72-3.78 (m, 2H), 3.00-3.10 (m, 1H), 1.74 (t, J = 5.6 Hz, 1H). ^{2}H NMR: (76.7 MHz, $CDCl_3$) δ 6.47.



3a-*d*, 71% yield

3a-*d*: To a 50 mL flame-dried Schlenk flask cooled under argon, IP·$CoCl_2$ complex (0.0198 g, 0.25 mmol) and toluene (2 mL) were added, and stirred for 5 min. Then $NaBHEt_3$ (150 μl, 0.15 mmol) , DBpin (0.2541 g, 2 mmol) and enyne **1** (174 μl, 1 mmol) were added sequently. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched by ether (5 mL), and filtered through a plug of silica gel by ether. The filtrates were concentrated and purified by column chromatography with silica gel to give **3a-*d*** (61%, 93% D) as colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.25-7.31 (m, 2H), 7.15-7.21 (m, 1H), 7.06-7.11 (m, 2H), 4.47 (dd, J = 15.2, 1.6 Hz, 1H), 4.06 (d, J = 15.2 Hz, 1H), 3.89 (dd, J = 8.4, 5.6 Hz, 1H), 3.70 (dd, J = 8.4, 2.0 Hz, 1H), 3.35-3.45 (m, 1H), 1.27 (s, 12 H), 1.23 (d, J = 7.2 Hz, 2.14H). ^{2}H NMR: (76.7 MHz, $CDCl_3$) δ 1.27.

The possible cyclometallation mechanism[21]



VIII. References

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[16] Kim, I. S.; Dong, G. R.; Jung, Y. H. *J. Org. Chem.* **2007**, *72*, 5424-5426.

[17] Wissam, D.; Alain; D. *Sci. China Chem.* **2010**, *53*, 1937-1945.

[18] Imada, Y.; Kitagawa, T.; Ohno, T.; Iida, H.; Naota, T. *Org. Lett.* **2010**, *12*, 32-35.

[19] Kim, I. S.; Dong, G. R.; Jung, Y. H. *J. Org. Chem.* **2007**, *72*, 5424-5426.

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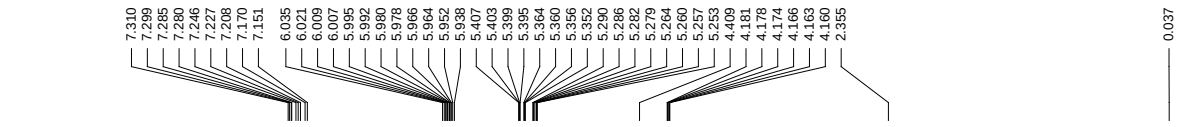
[21] We appreciated the suggestion about the possible cyclometallation mechanism from one of the reviewers.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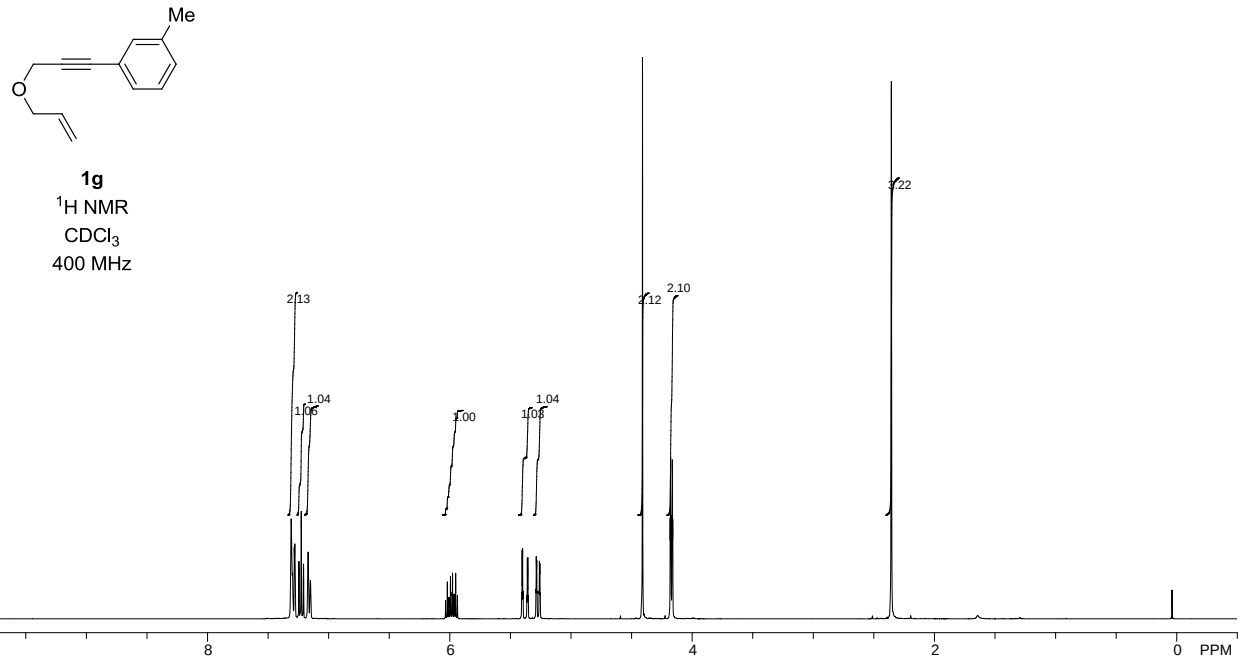
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3.22
8
6
4
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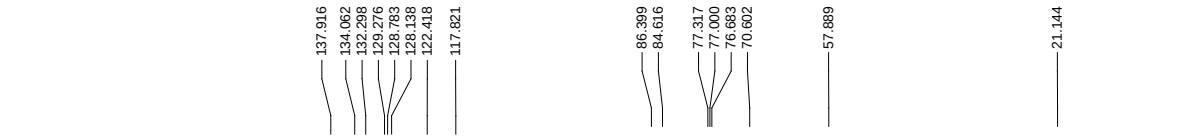
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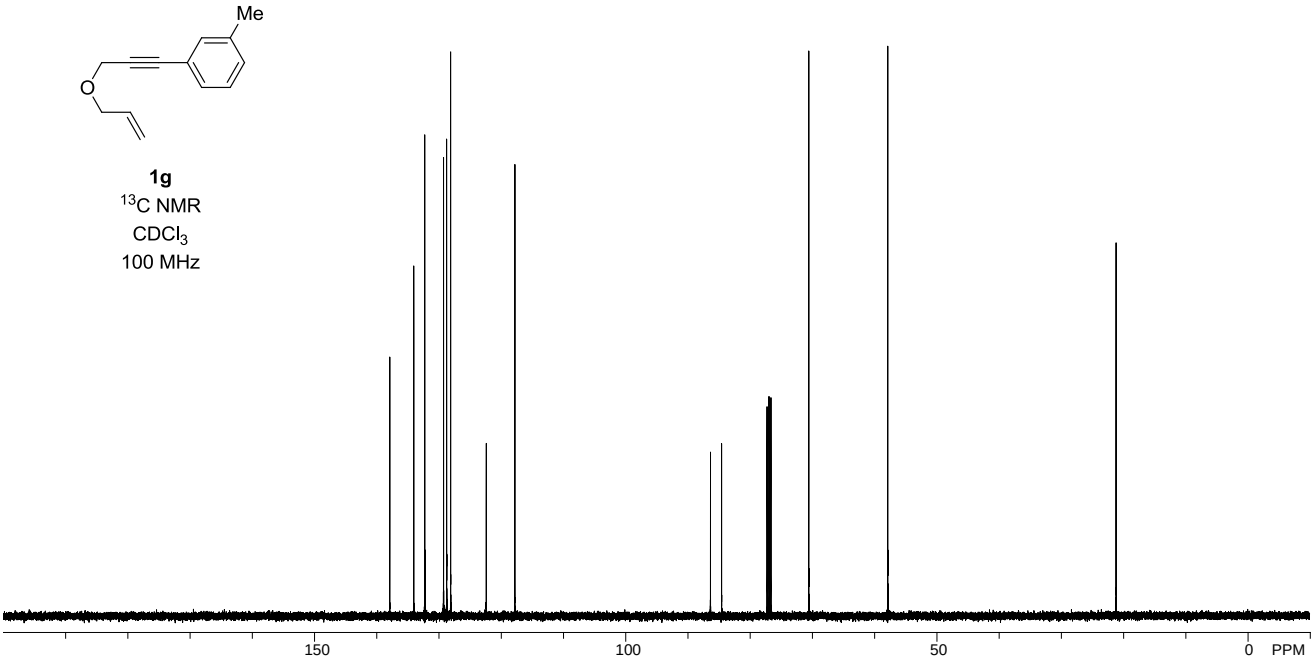
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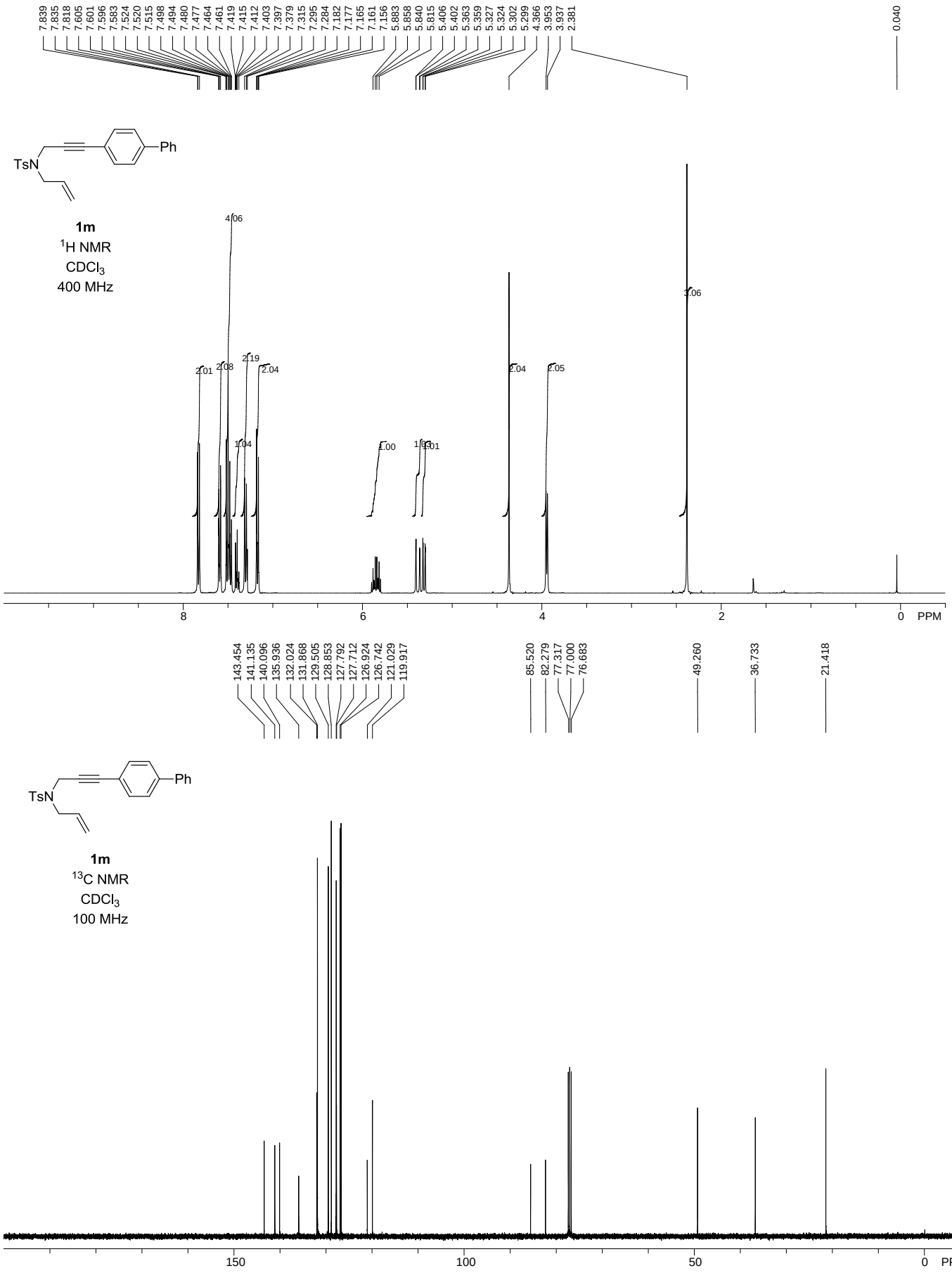
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7.464
7.461
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7.403
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7.295
7.284
7.182
7.177
7.165
7.161
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2.08
2.04
2.01
2.04
2.05
1.04
1.00
1.99
1.01
8
6
4
2
0
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126.742
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77.000
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50
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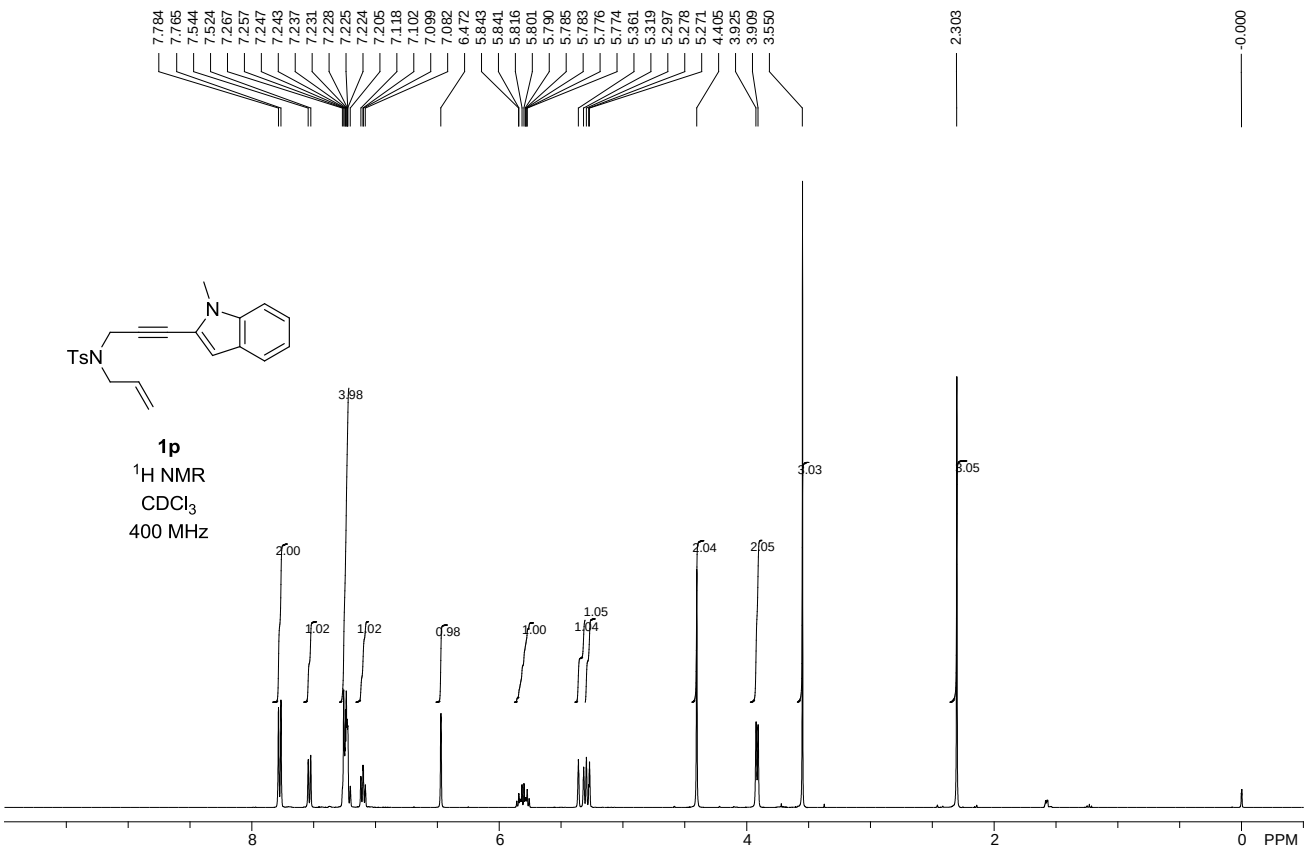
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3.98
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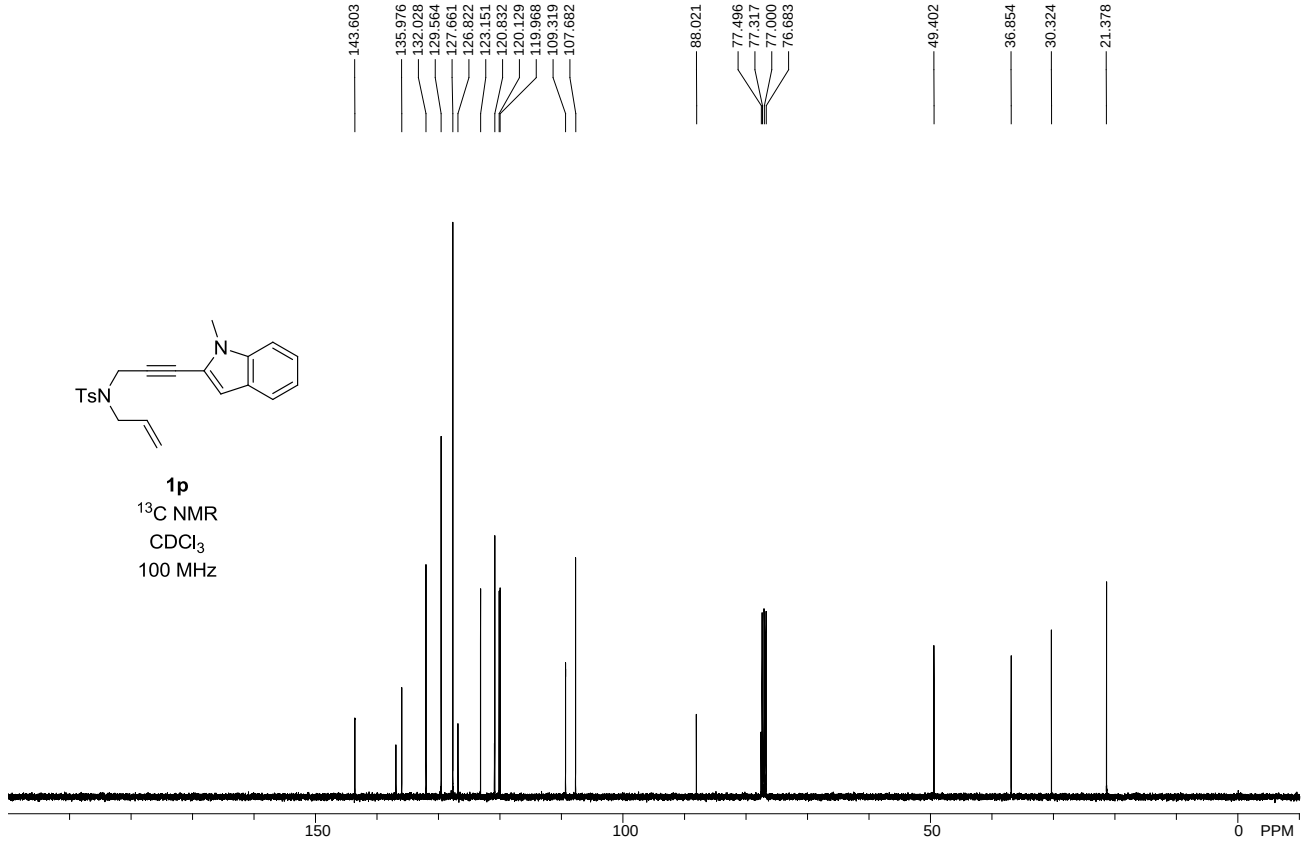
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77.496
77.317
77.000
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CDCl3
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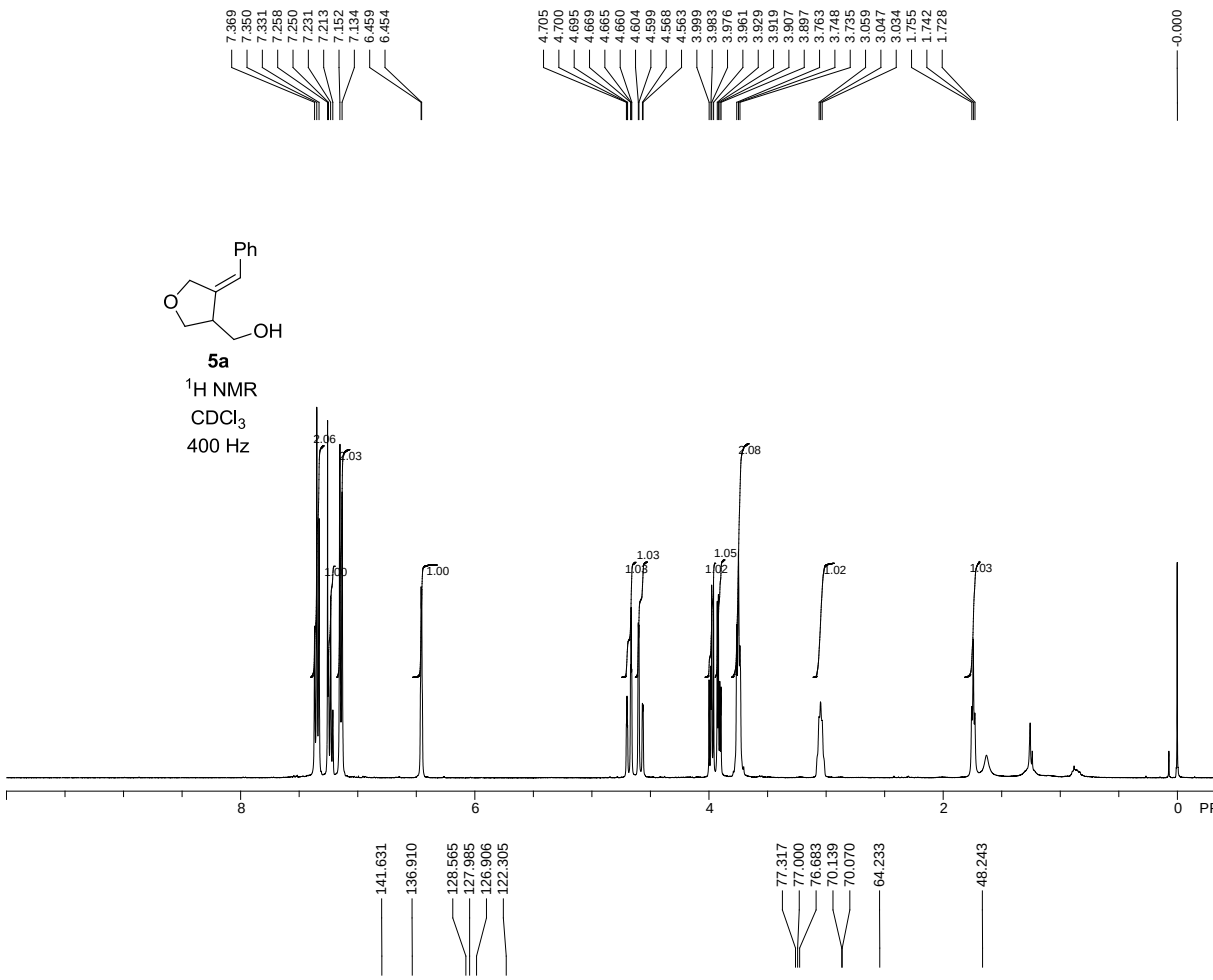
100
50
0
PPM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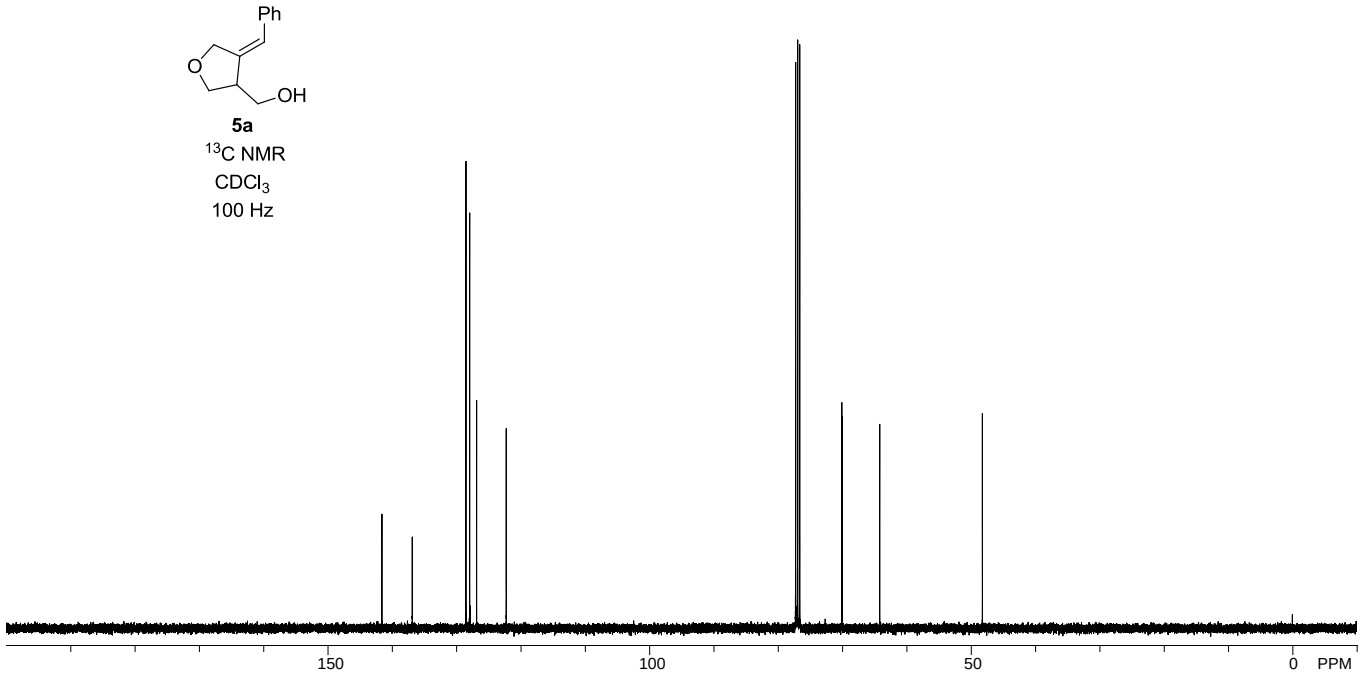
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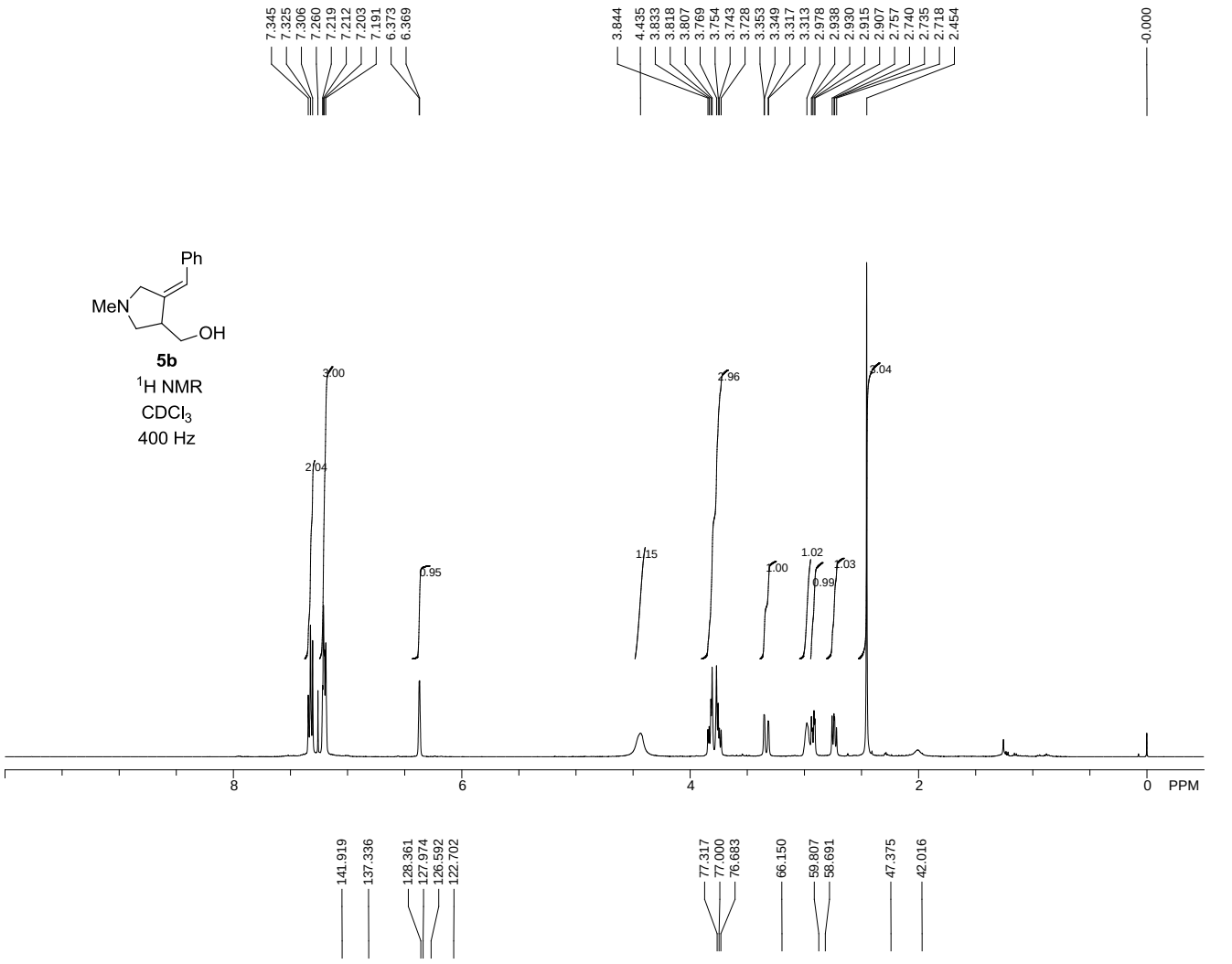
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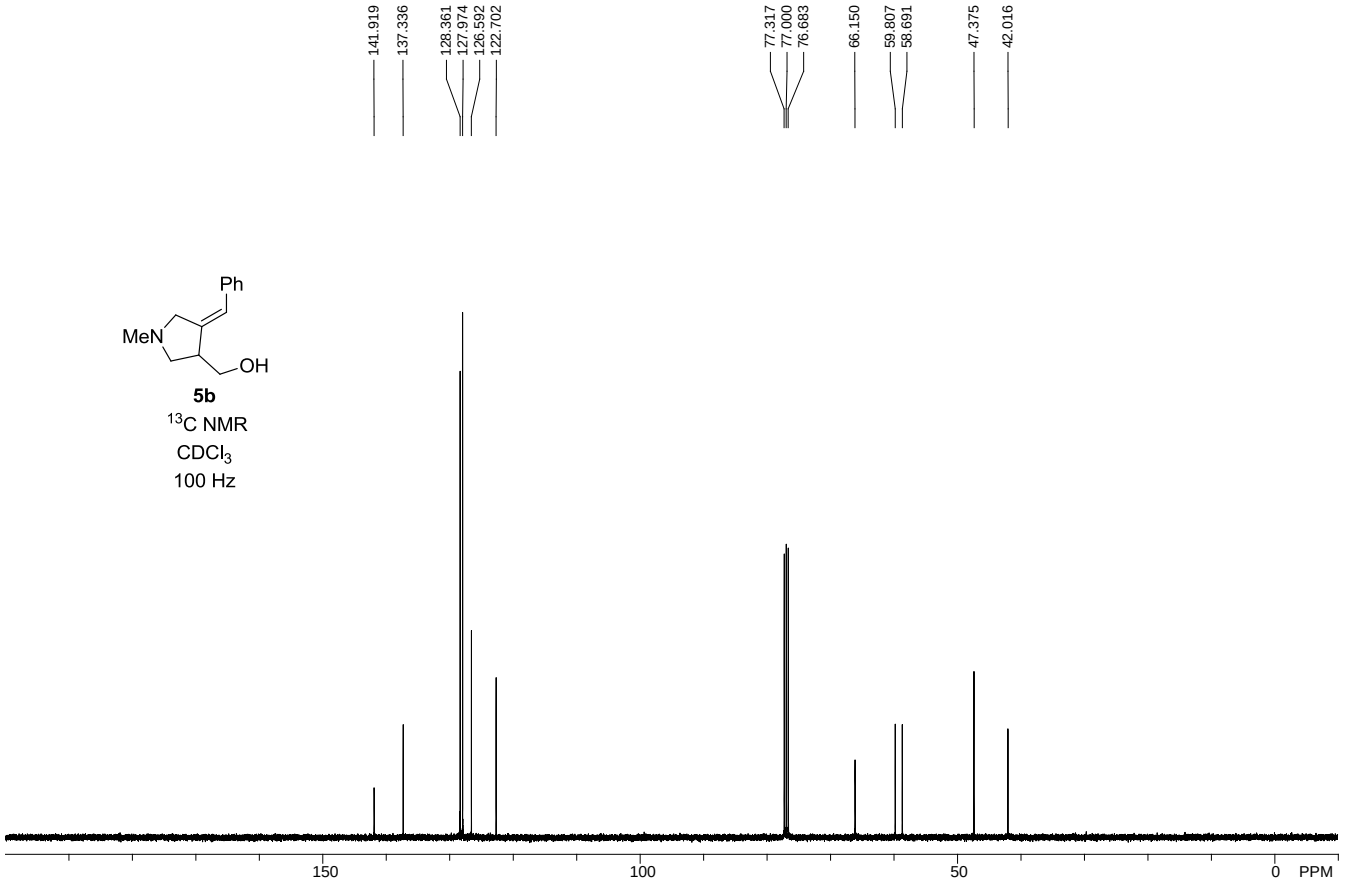
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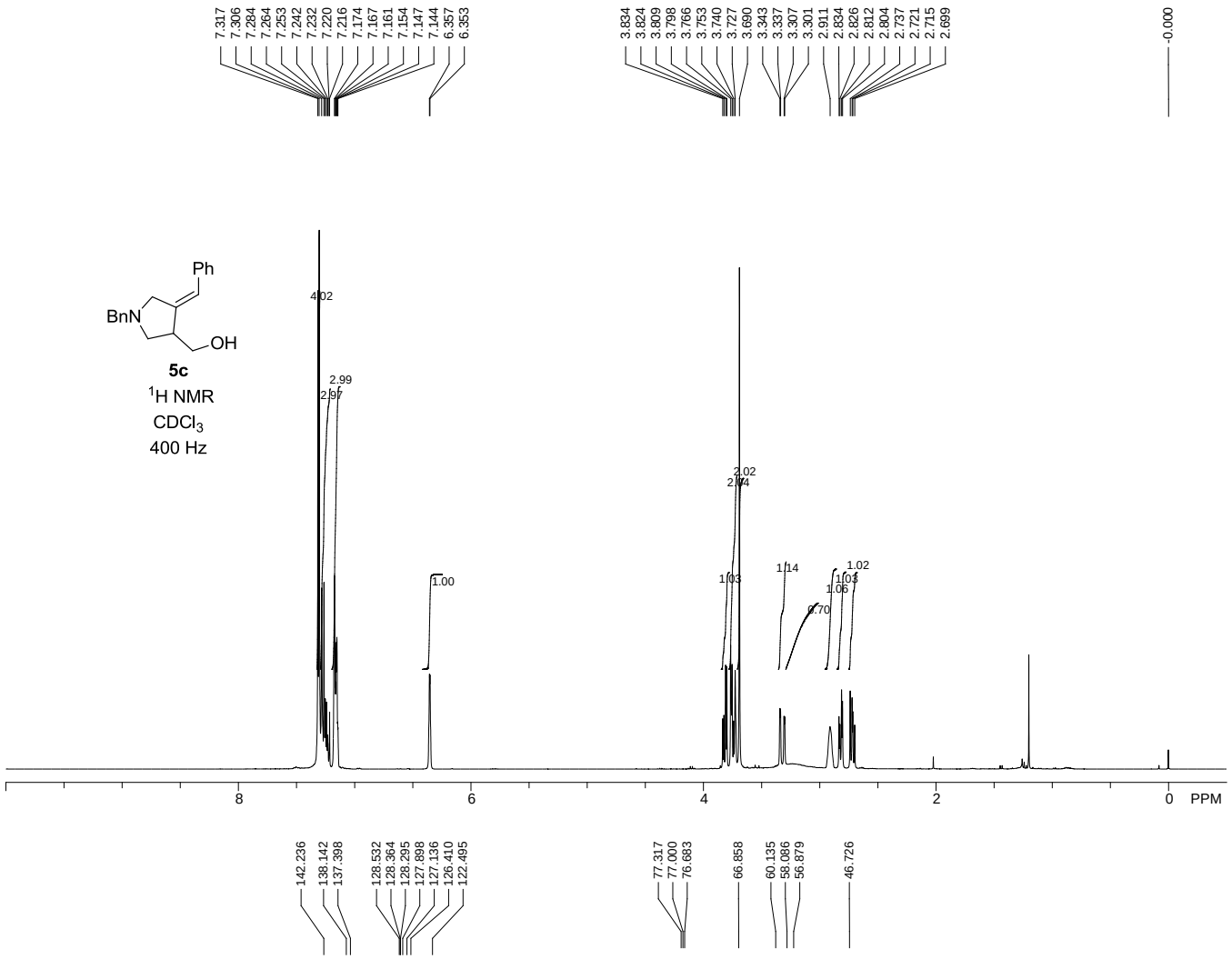
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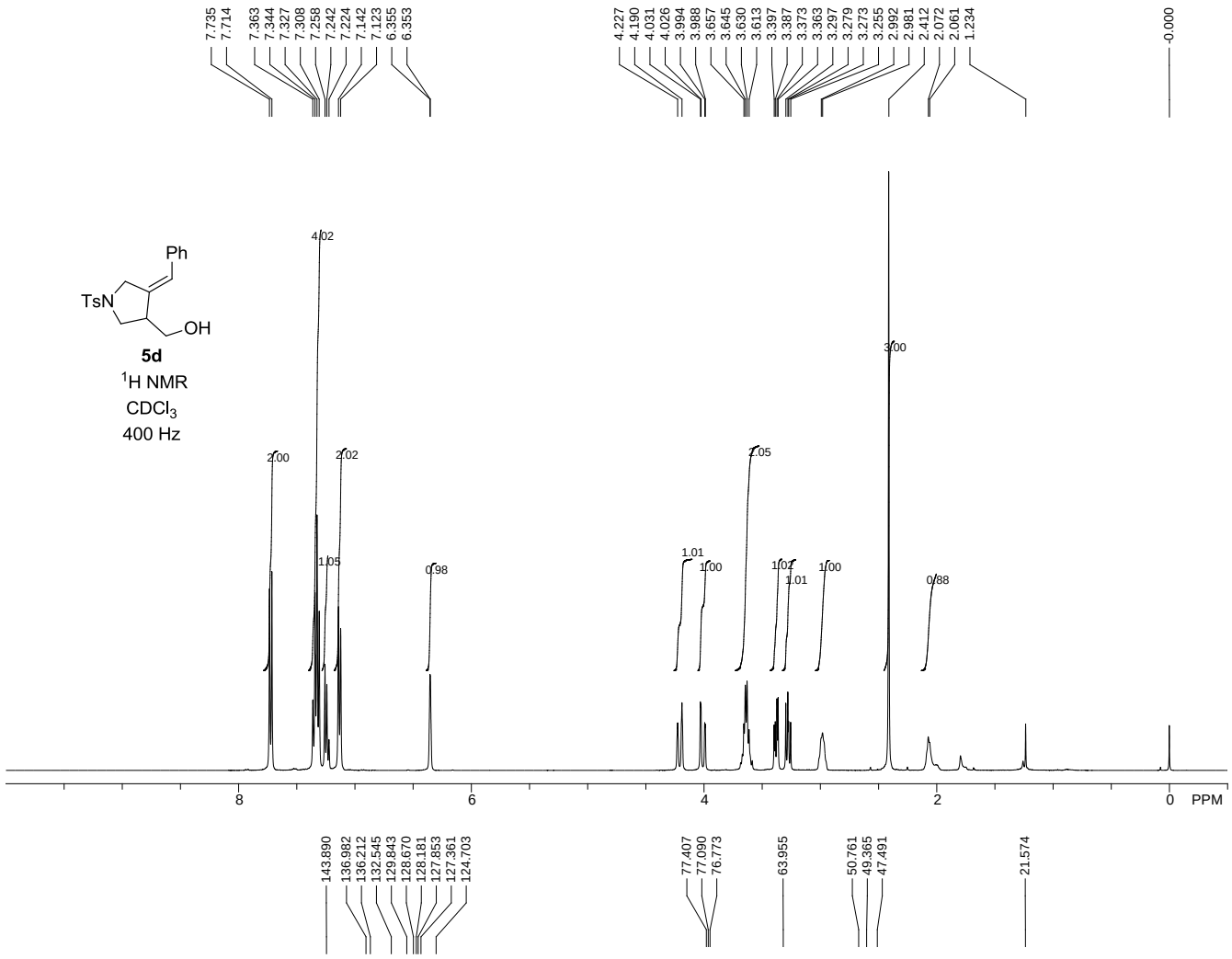
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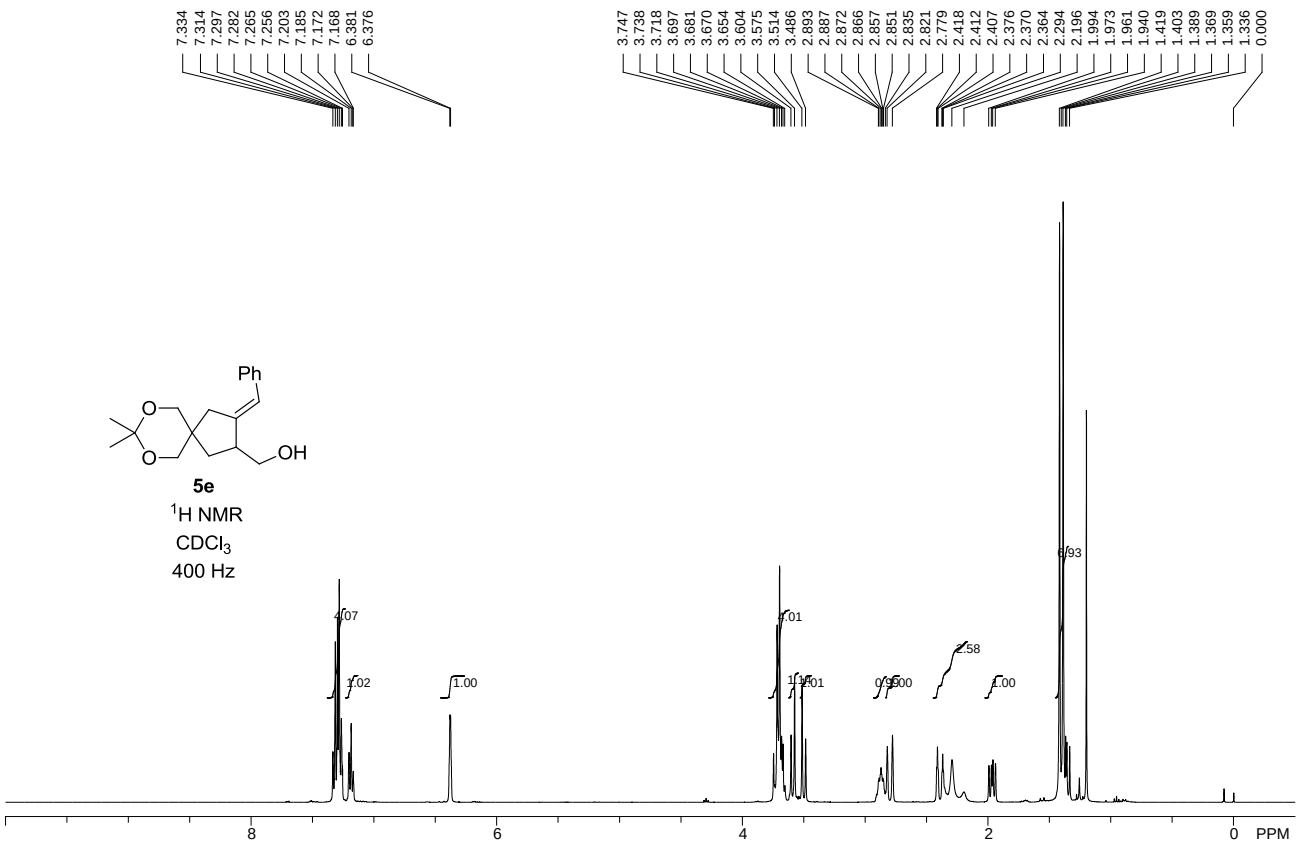
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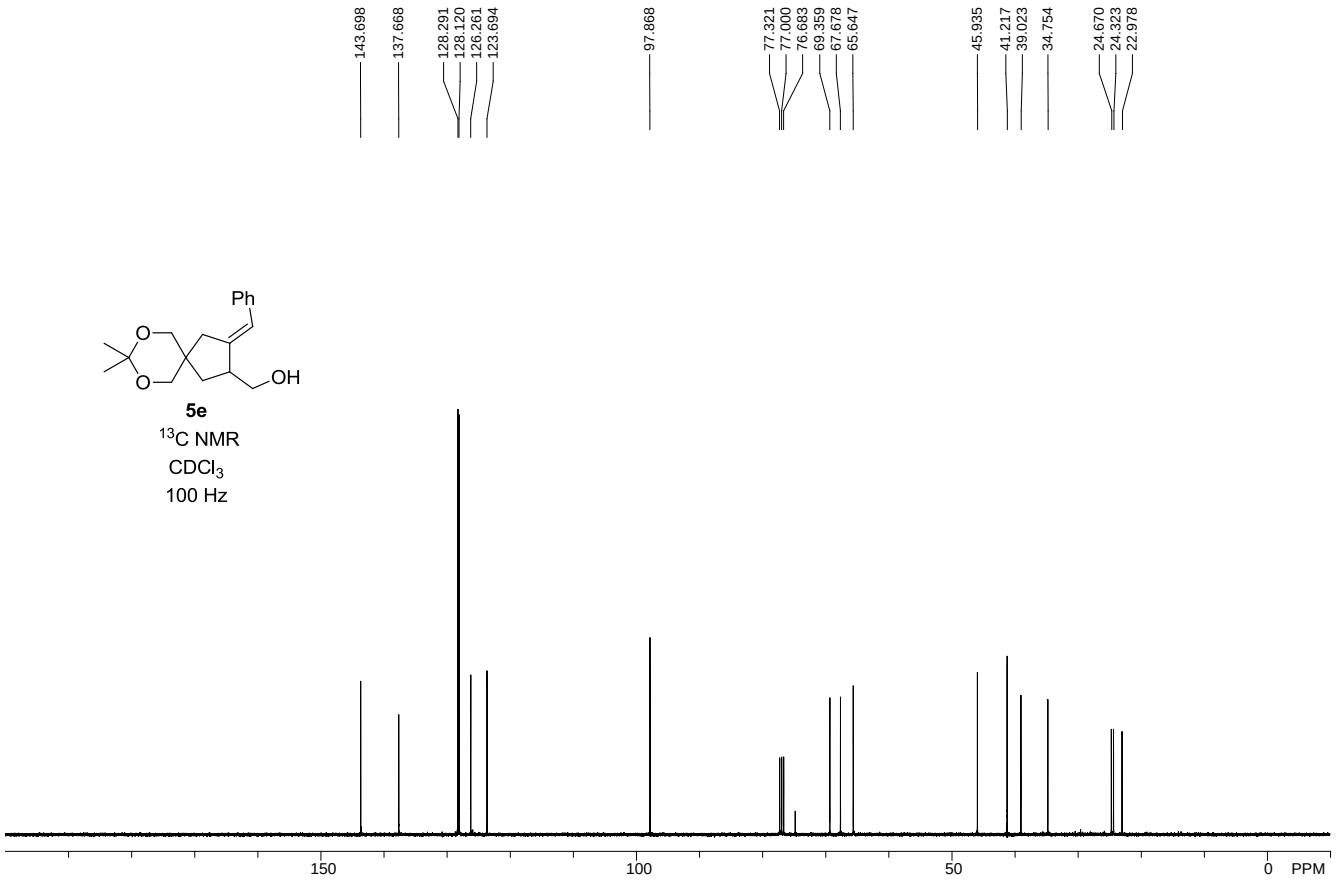
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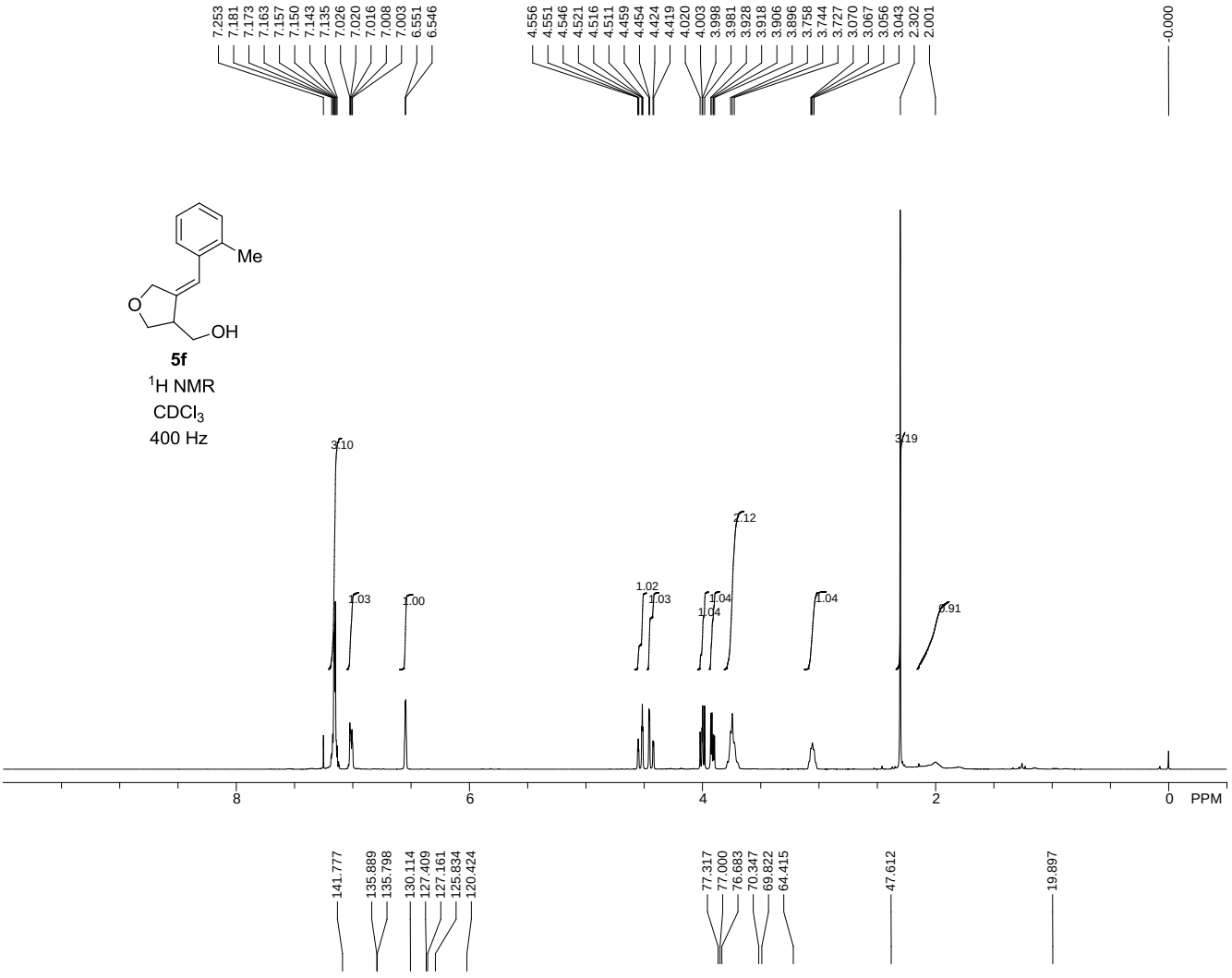
PPM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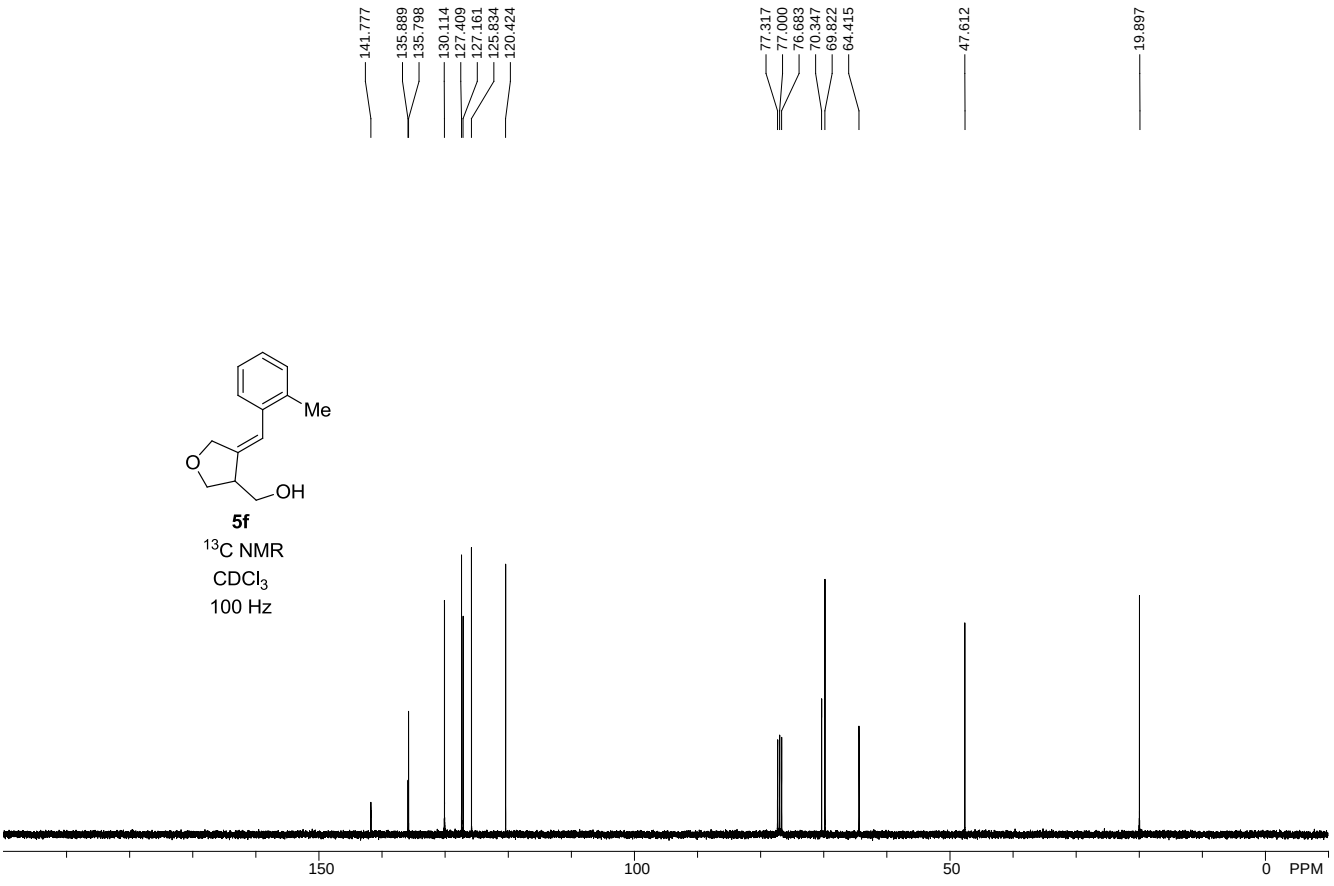
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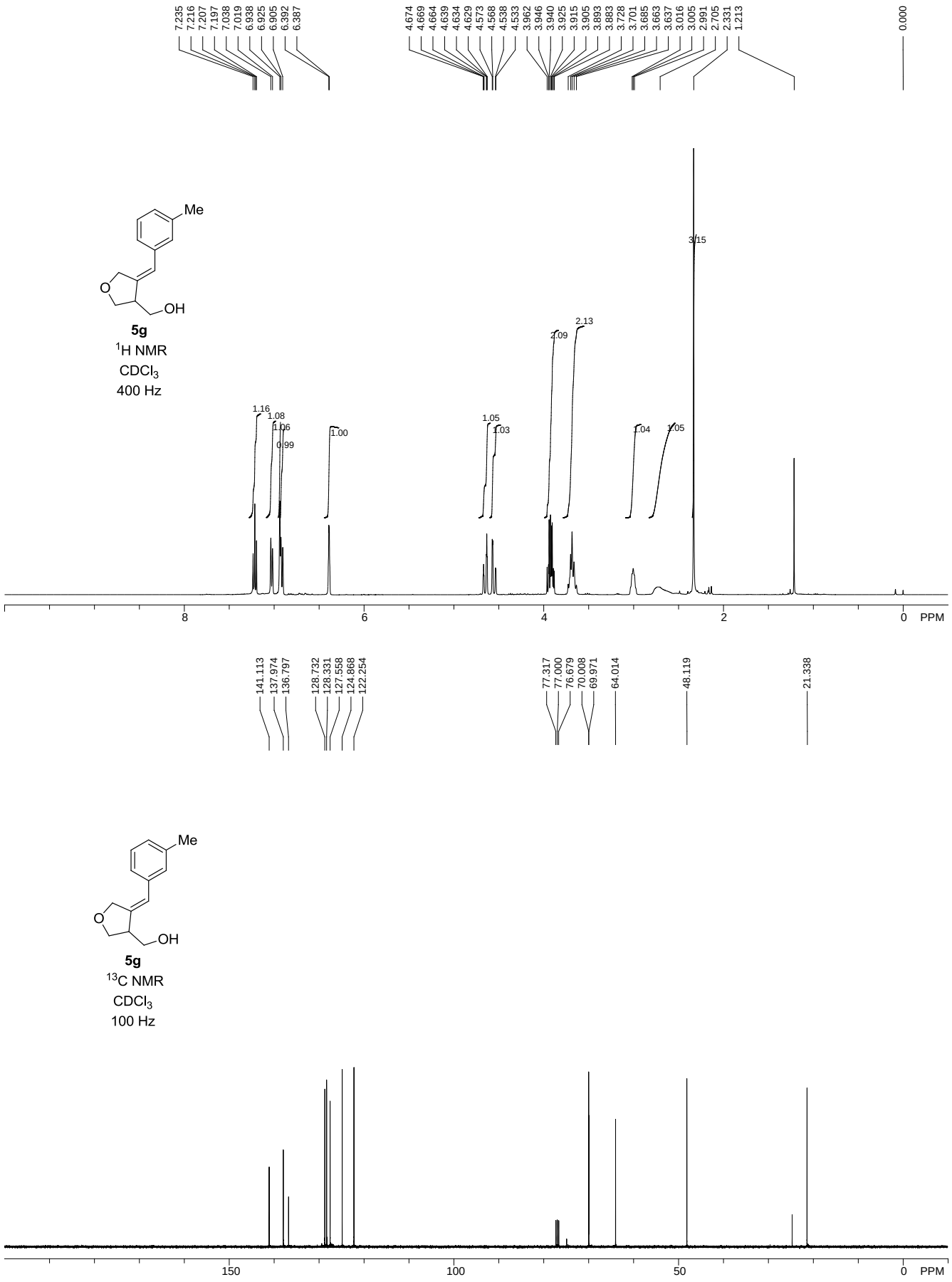
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O
OH
5g
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0.99
1.00
1.05
1.03
2.09
2.13
1.04
1.05
3.15
8
6
4
2
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128.732
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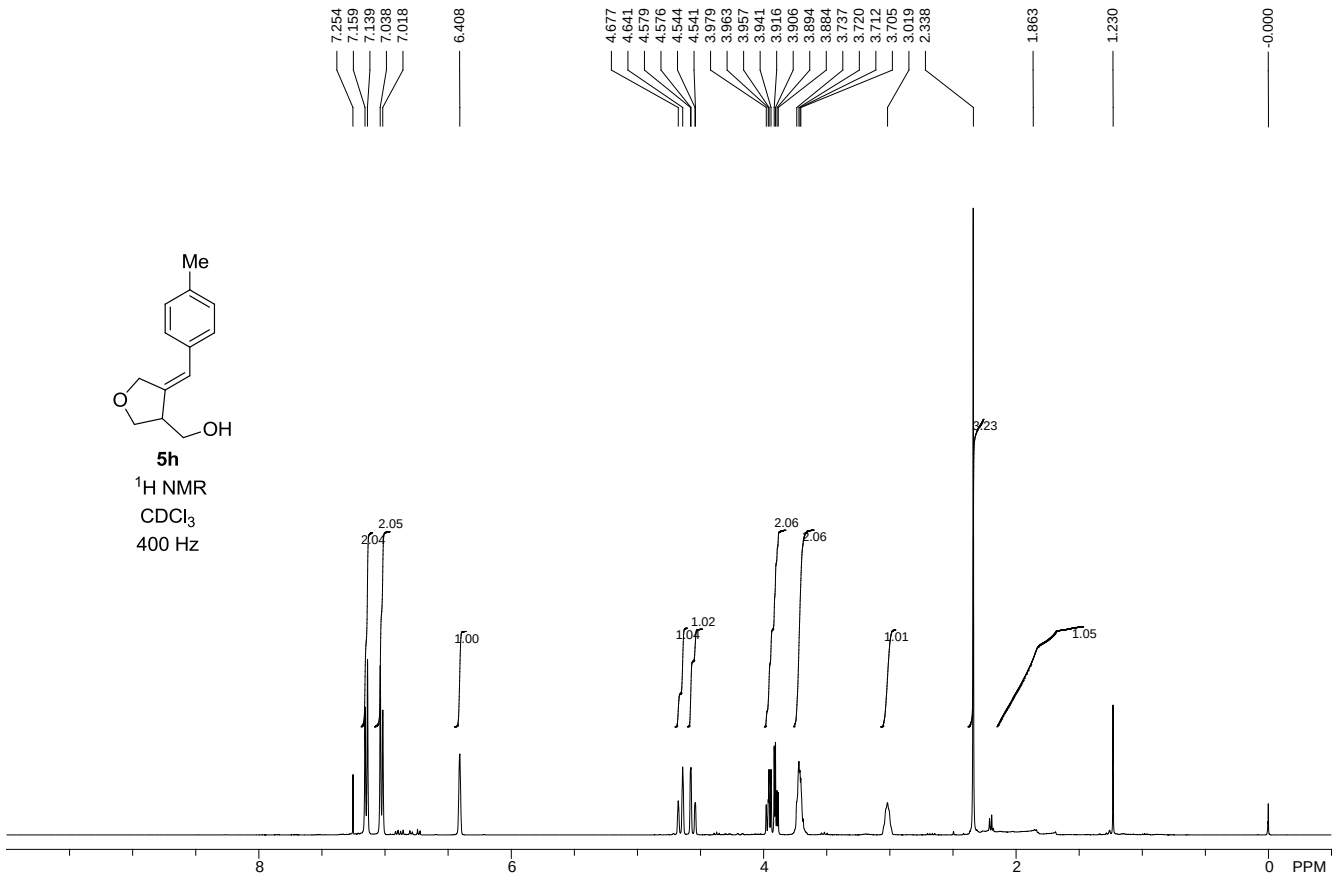
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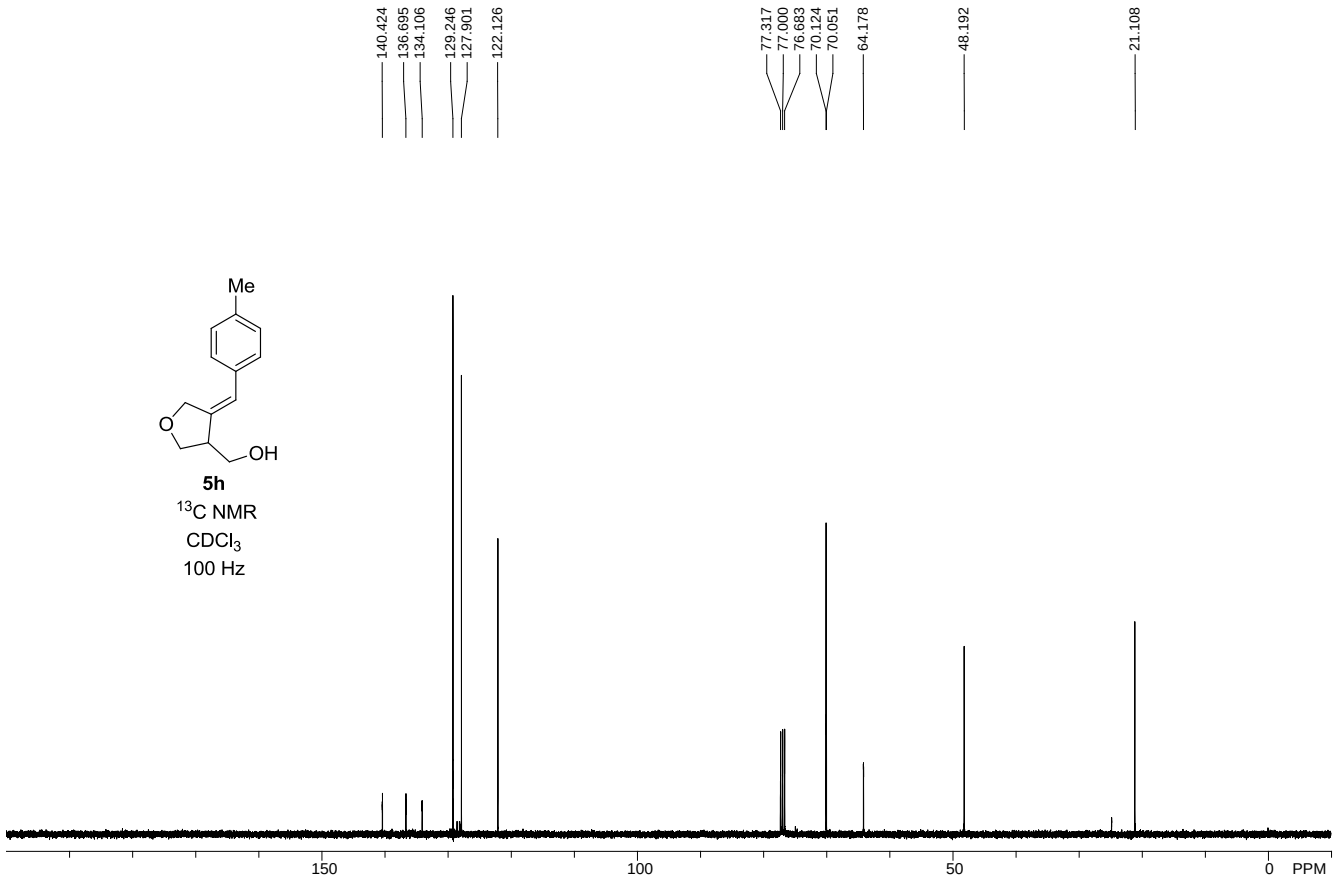
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OH
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CDCl3
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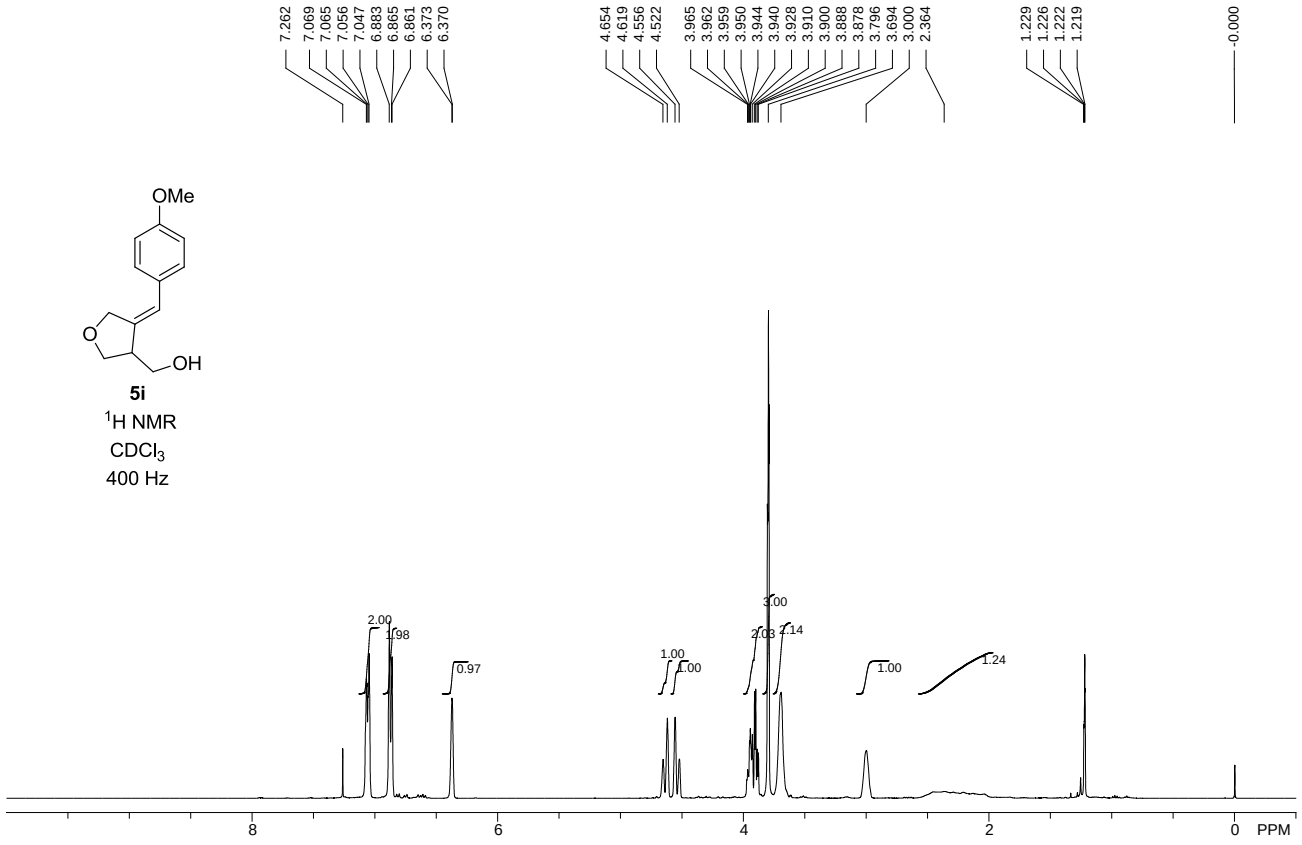
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4.522
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3.959
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3.944
3.940
3.928
3.910
3.900
3.888
3.878
3.796
3.694
3.000
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1.229
1.226
1.222
1.219
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OMe
O
OH
5i
1H NMR
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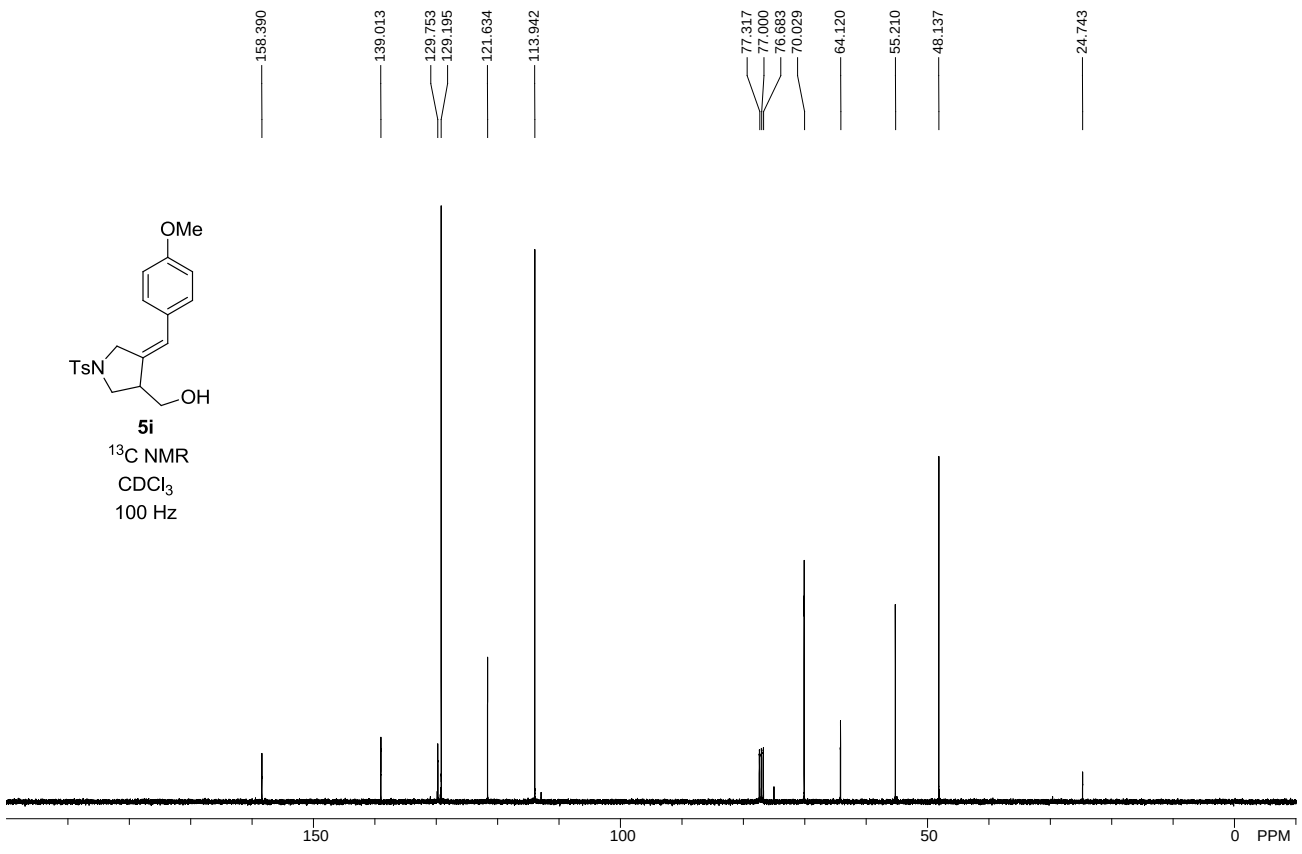
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OH
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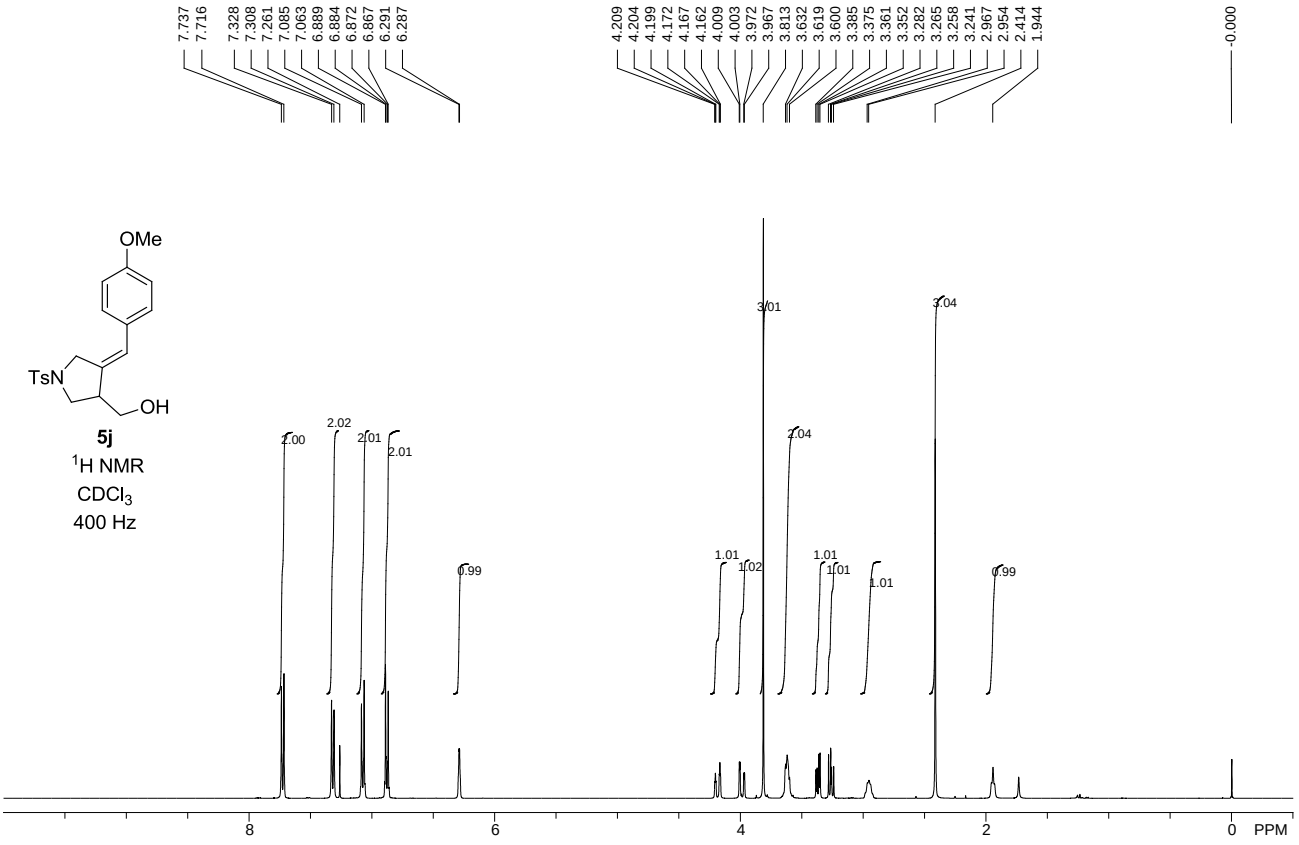
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3.813
3.632
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TsN
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2.01
0.99
3.01
2.04
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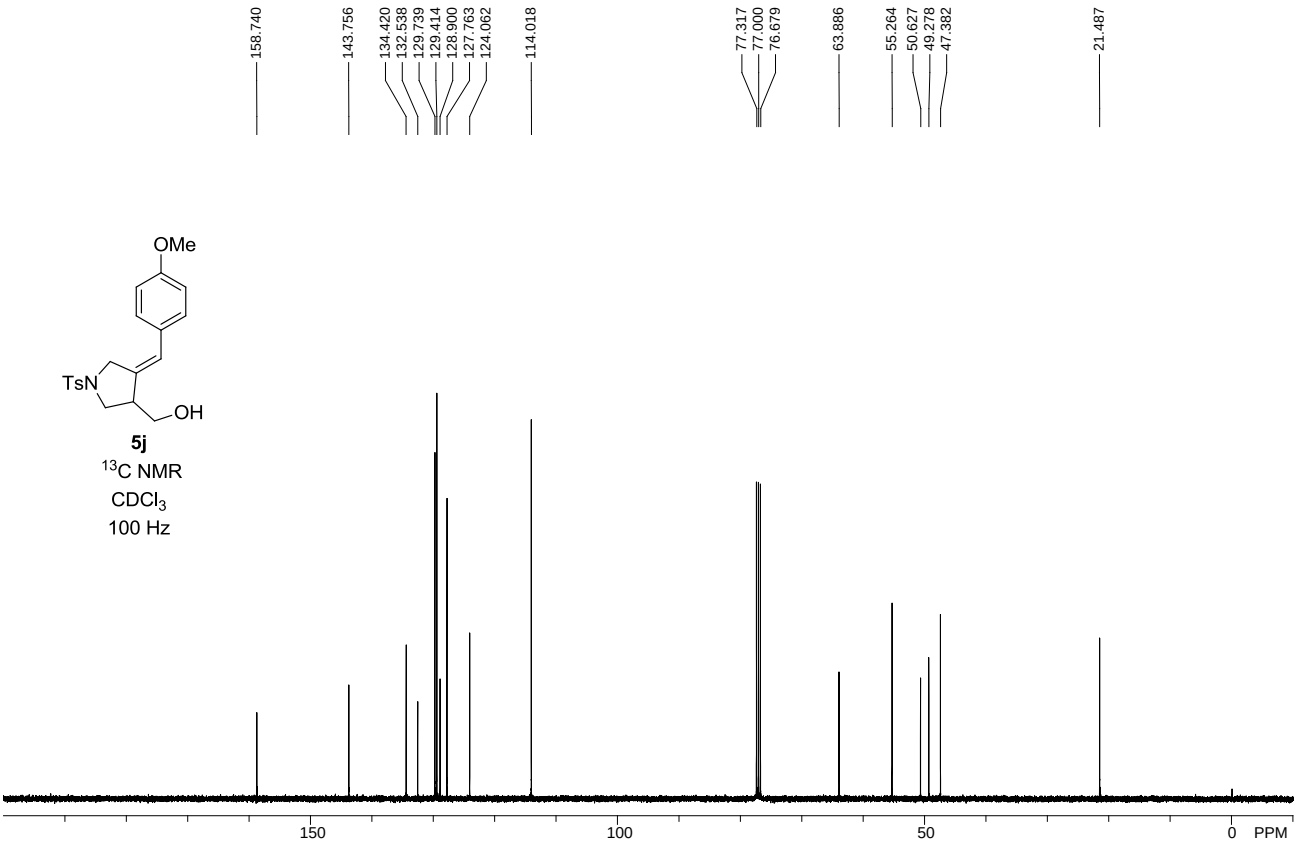
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13C NMR
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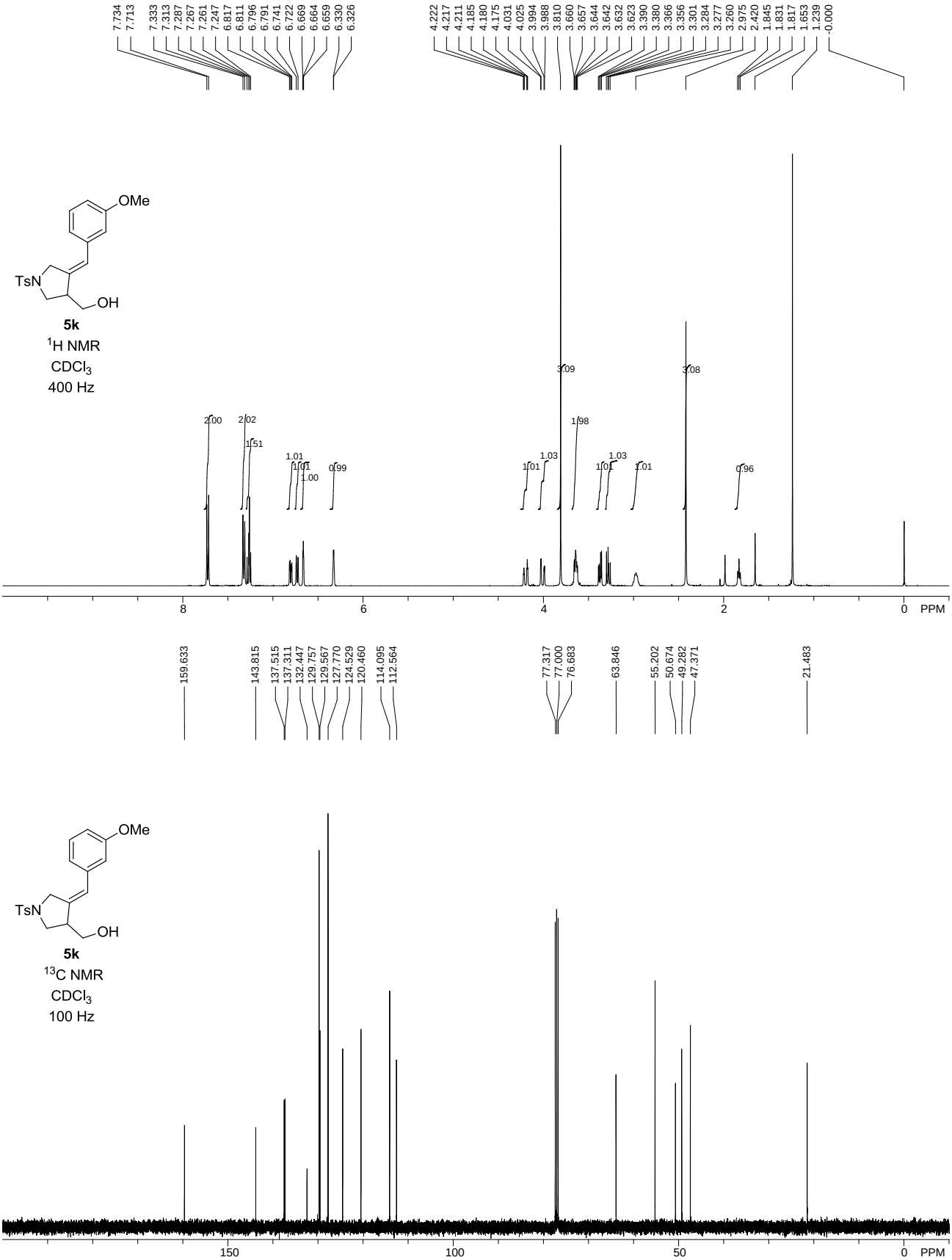
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6.722
6.669
6.664
6.659
6.330
6.326
4.222
4.217
4.211
4.185
4.180
4.175
4.031
4.025
3.994
3.988
3.810
3.660
3.657
3.644
3.642
3.632
3.623
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3.380
3.366
3.356
3.301
3.284
3.277
3.260
2.975
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1.845
1.831
1.817
1.653
1.239
-0.000
OMe
TsN
OH
5k
1H NMR
CDCl3
400 Hz
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2.02
1.51
1.01
1.01
1.00
0.99
1.01
1.03
3.09
1.98
1.01
1.03
1.01
3.08
1.01
0.96
8
6
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PPM
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50.674
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OH
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CDCl3
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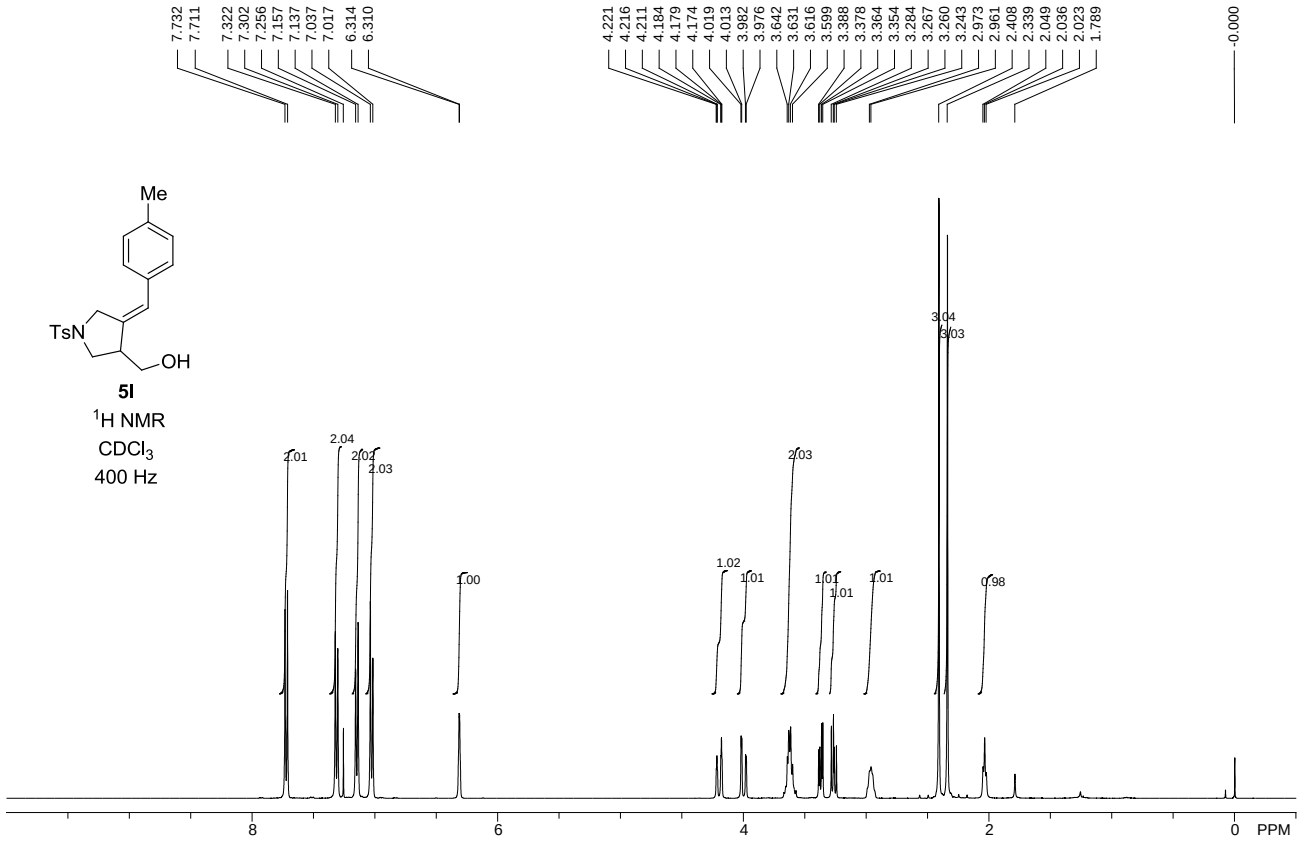
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6.310
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4.216
4.211
4.184
4.179
4.174
4.019
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3.982
3.976
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3.616
3.599
3.388
3.378
3.364
3.354
3.284
3.267
3.260
3.243
2.973
2.961
2.408
2.339
2.049
2.036
2.023
1.789
-0.000
Me
TsN
OH
5l
1H NMR
CDCl3
400 Hz
2.01
2.04
2.01
2.03
1.00
1.02
1.01
2.03
1.01
1.01
1.01
3.04
3.03
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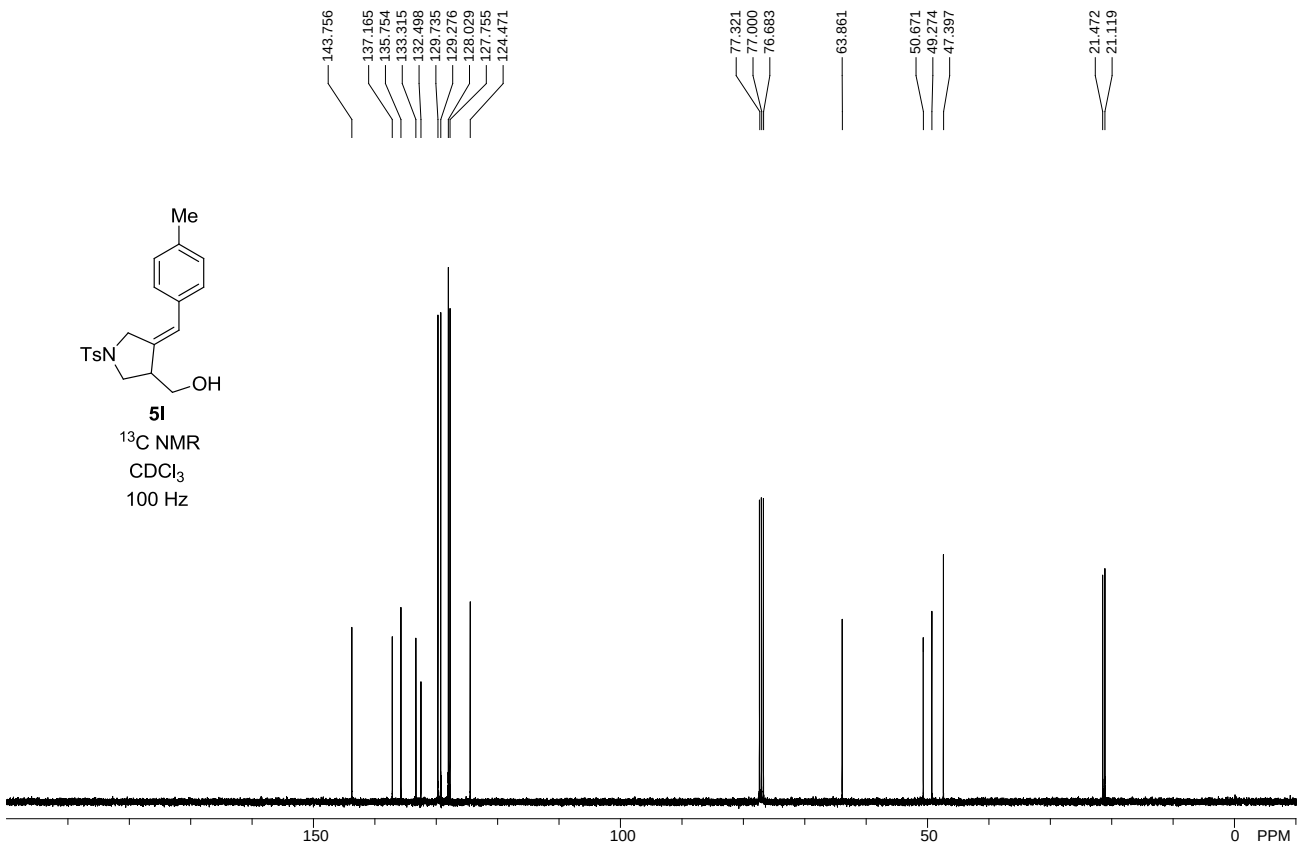
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77.000
76.683
63.861
50.671
49.274
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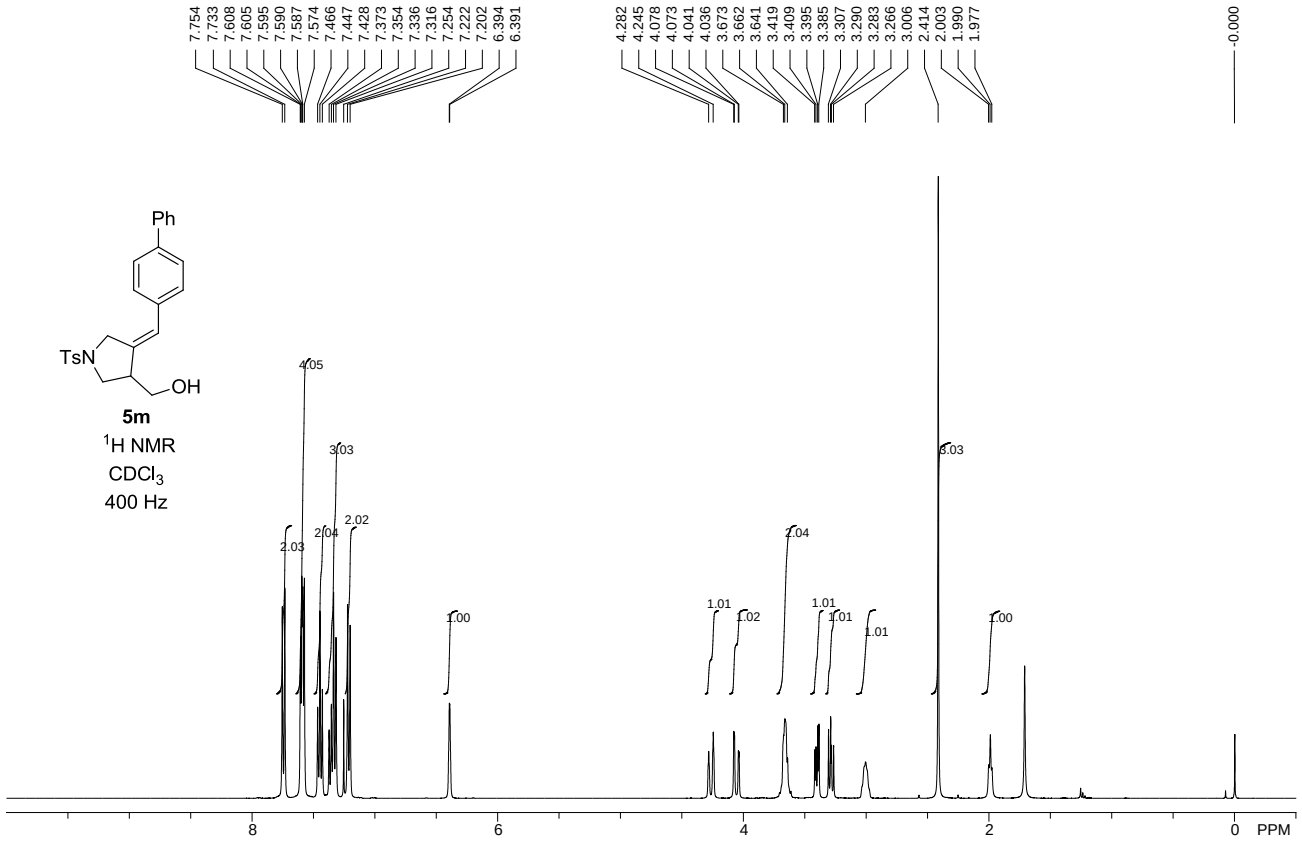
21.119
Me
TsN
OH
5l
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM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6.391
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4.245
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4.041
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3.307
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3.266
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2.414
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Ph
TsN
OH
5m
1H NMR
CDCl3
400 Hz
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3.03
2.03
2.04
2.02
1.00
1.01
1.02
2.04
1.01
1.01
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3.03
1.00
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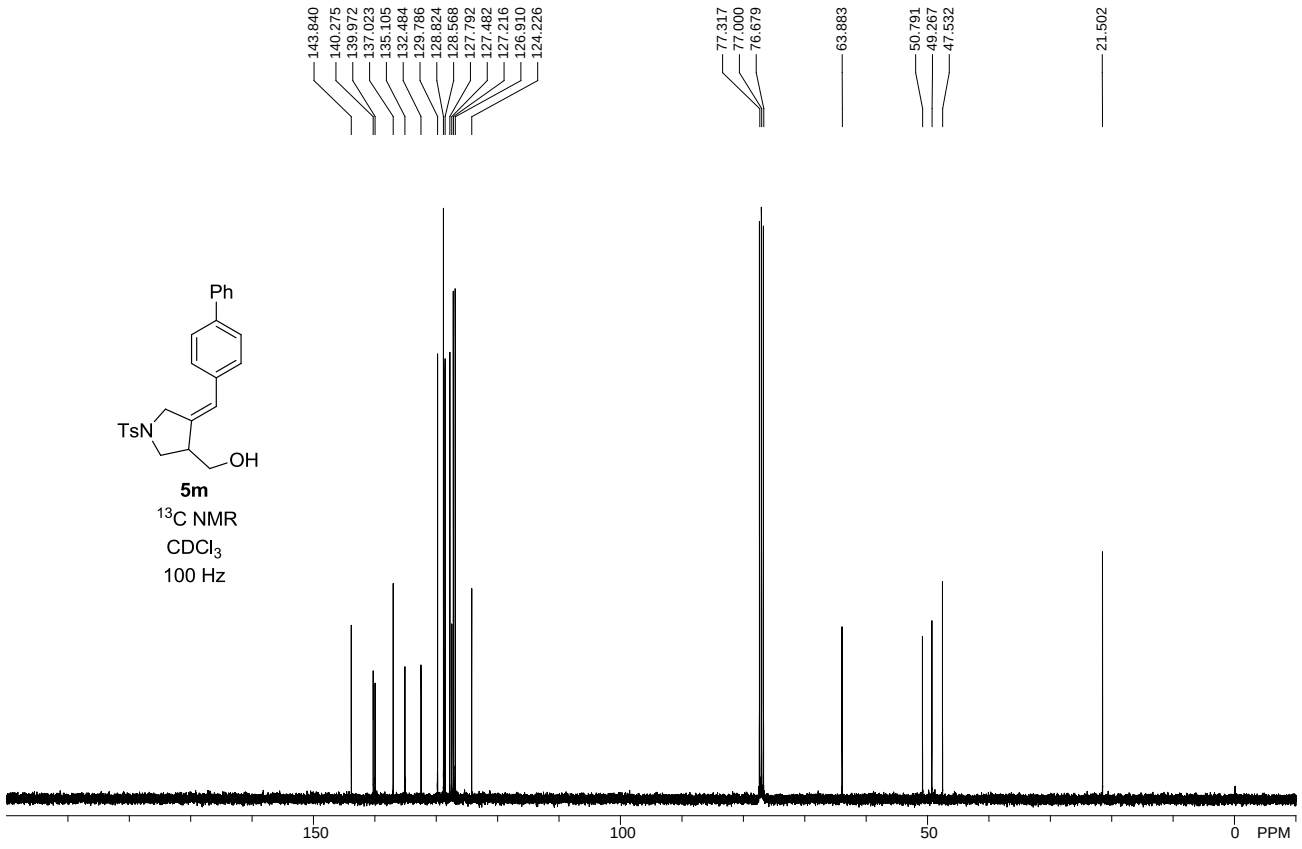
PPM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77.317
77.000
76.679
63.883
50.791
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Ph
TsN
OH
5m
13C NMR
CDCl3
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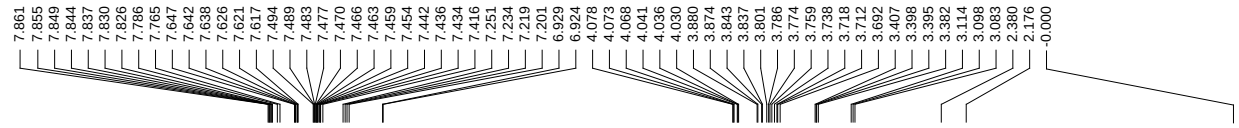
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7.621
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7.483
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7.219
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4.030
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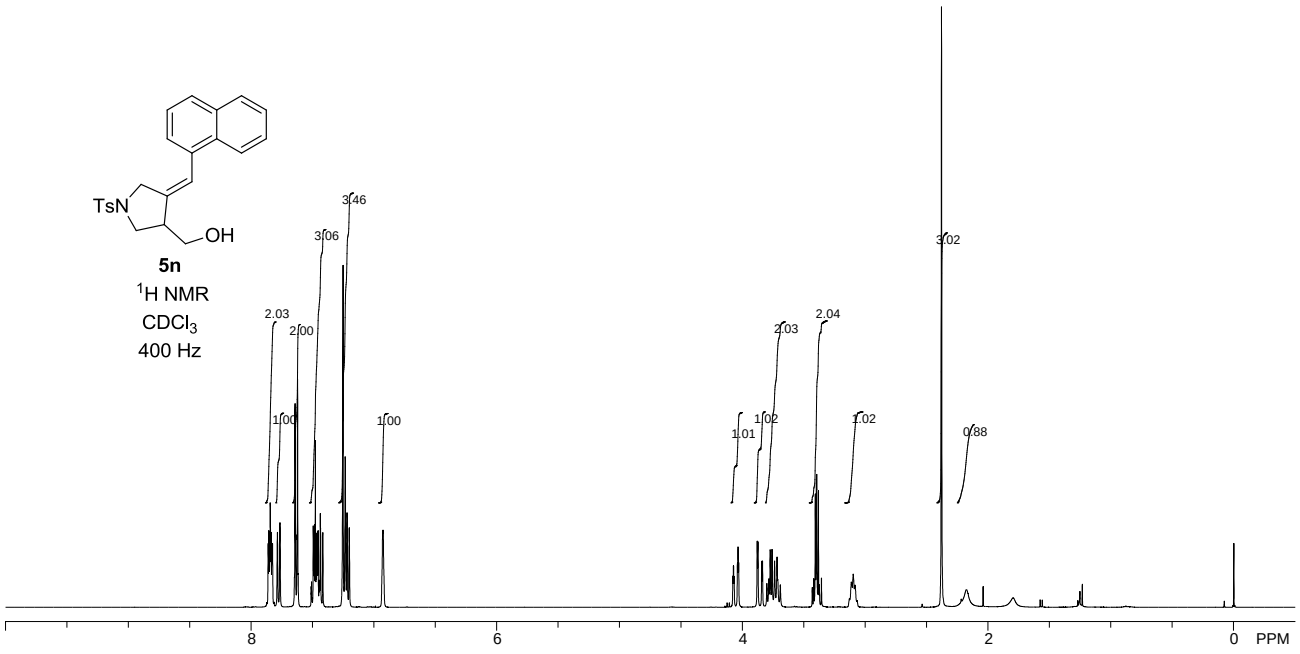
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5n
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CDCl3
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2.03
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3.02
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4
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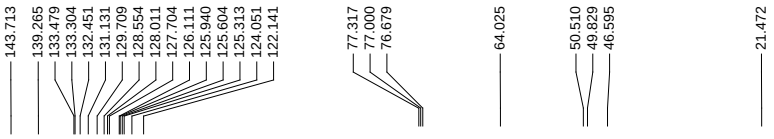
PPM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77.000
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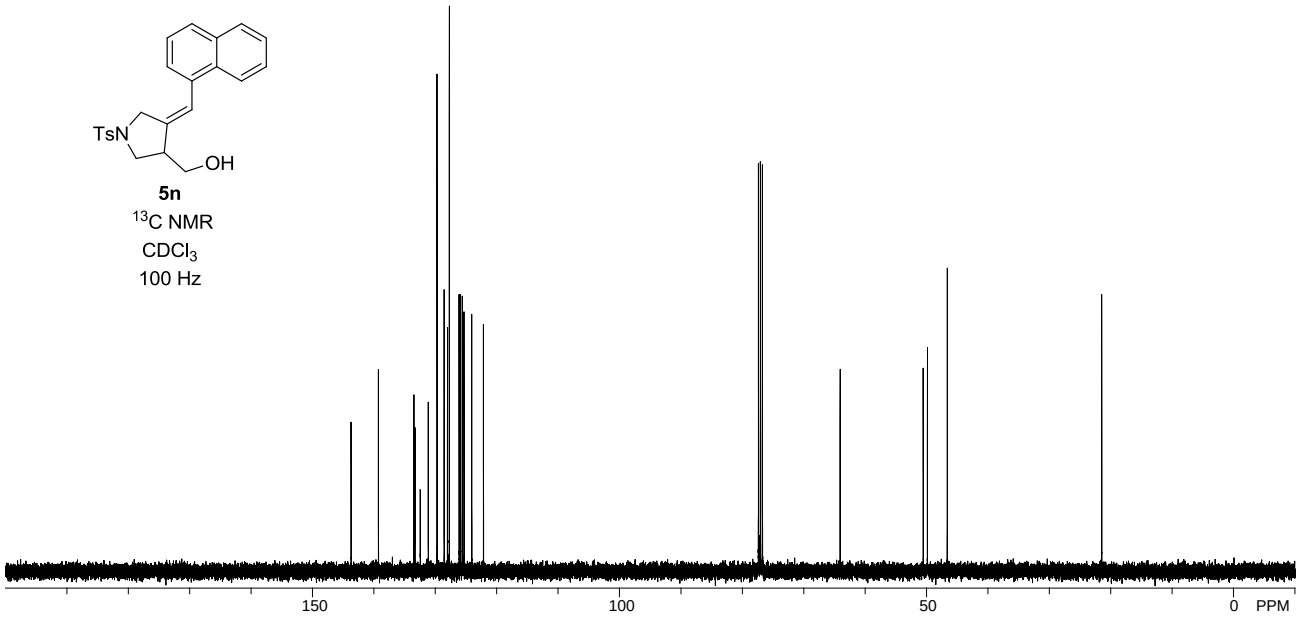
21.472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13C NMR
CDCl3
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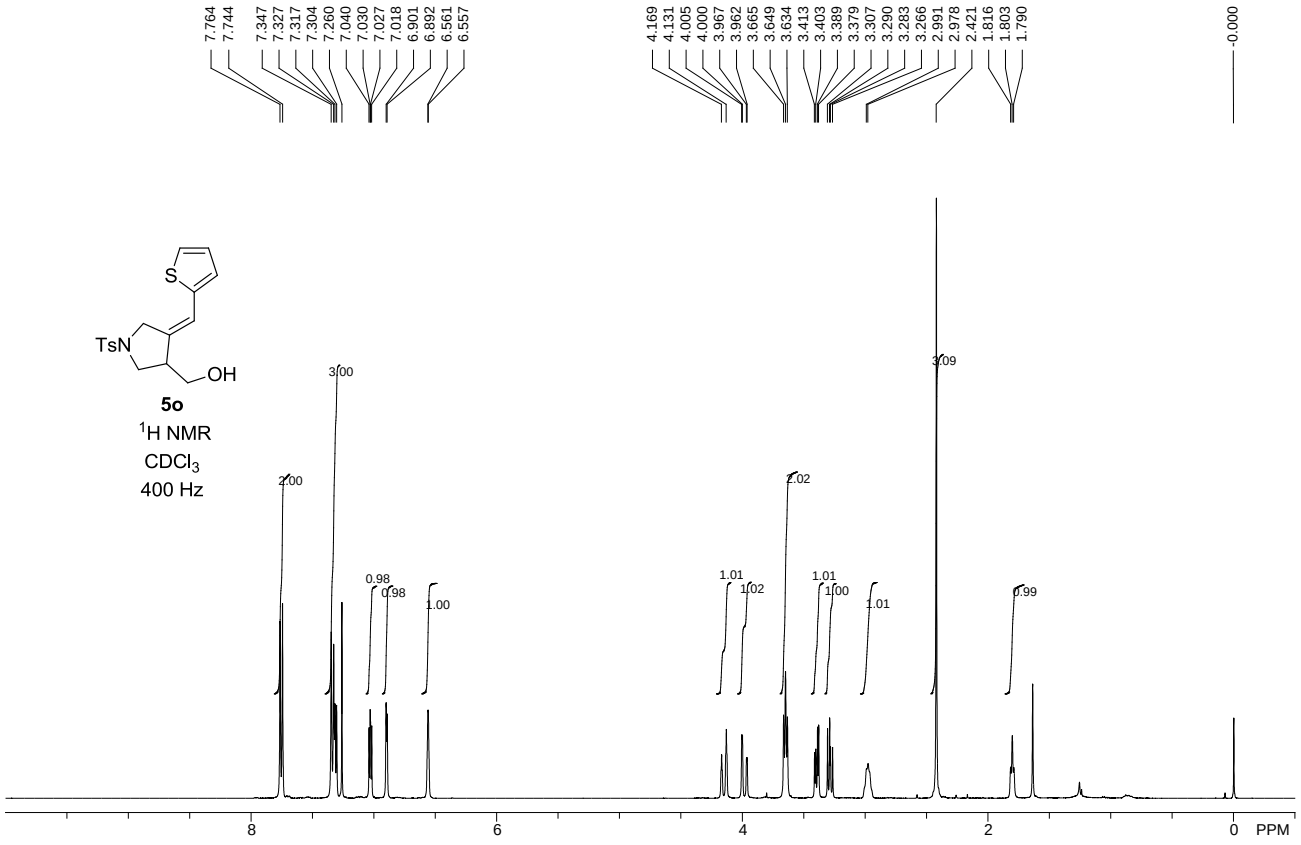
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6.557
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4.000
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3.634
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3.403
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3.379
3.307
3.290
3.283
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2.421
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1.803
1.790
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S
TsN
OH
5o
1H NMR
CDCl3
400 Hz
2.00
3.00
0.98
0.98
1.00
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1.02
2.02
1.01
1.00
1.01
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0.99
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6
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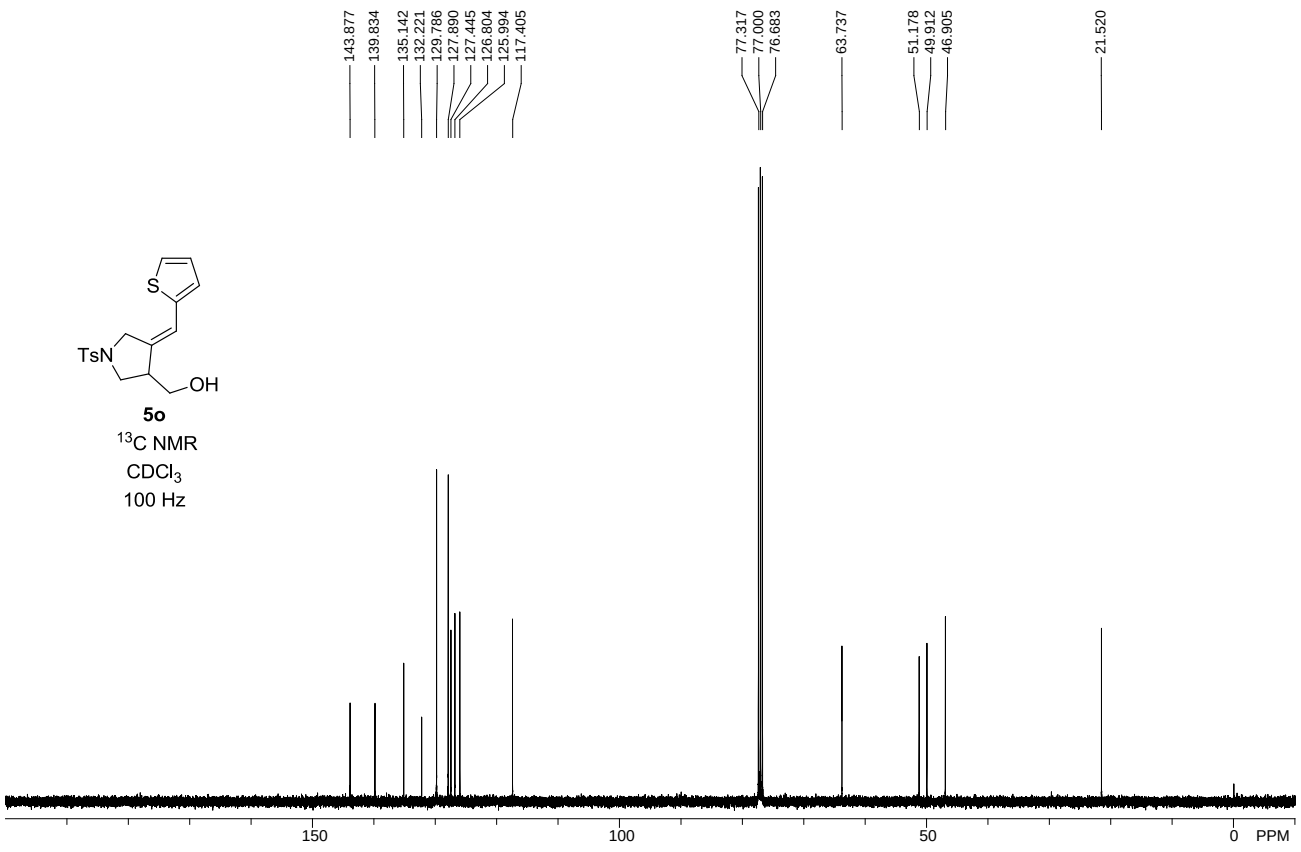
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76.683
63.737
51.178
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21.520
S
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OH
5o
13C NMR
CDCl3
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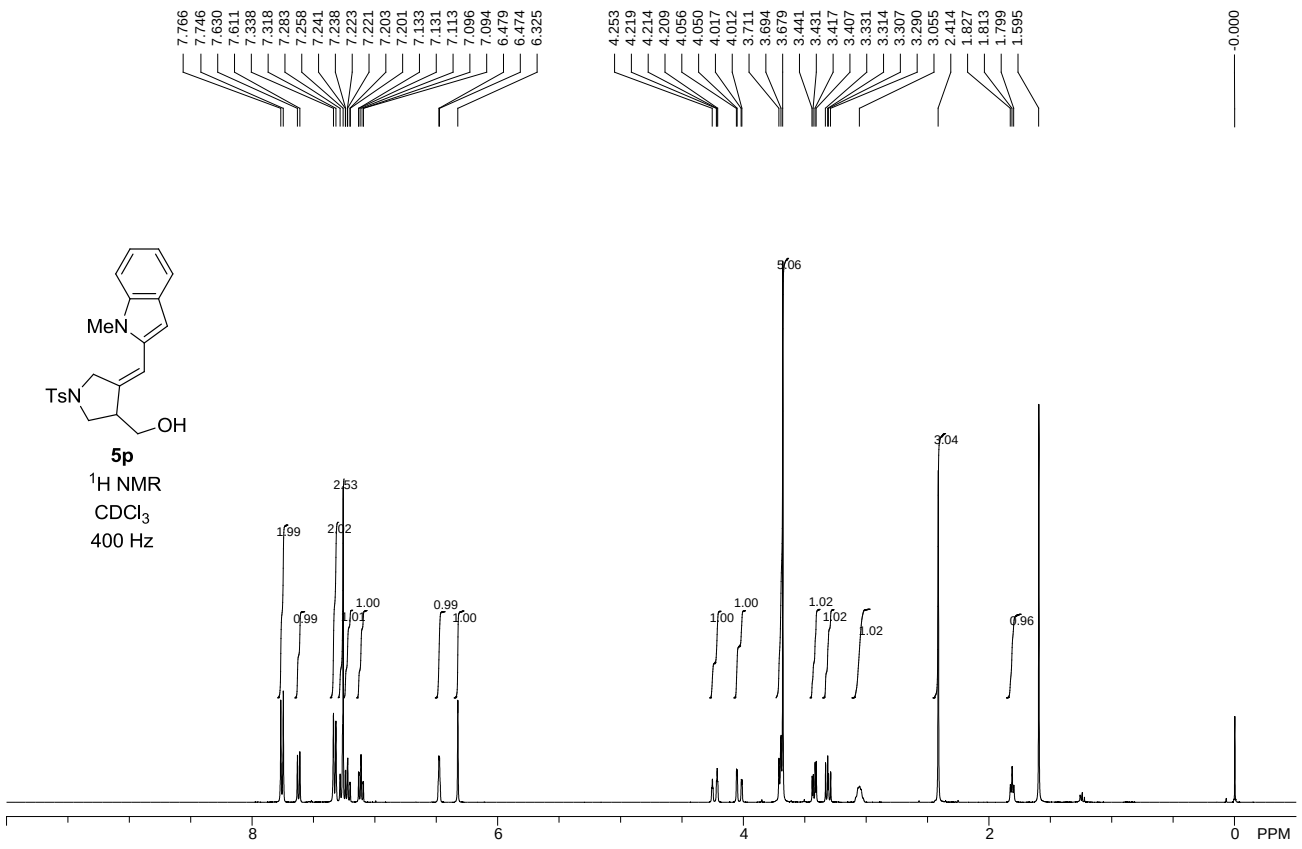
PPM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2.414
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1.813
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MeN
TsN
OH
5p
1H NMR
CDCl3
400 Hz
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3.04
2.53
2.02
1.99
1.02
1.00
1.00
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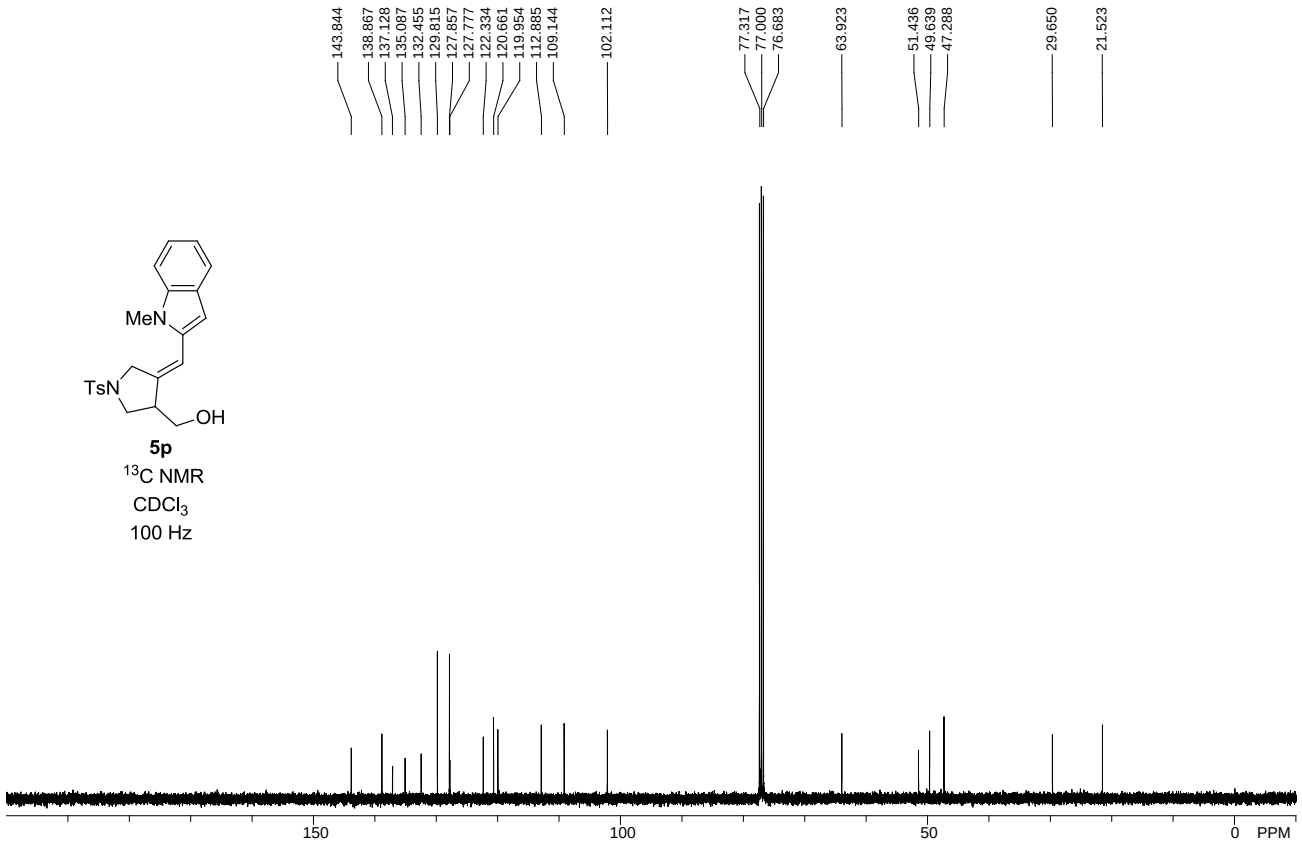
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102.112
77.317
77.000
76.683
63.923
51.436
49.639
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MeN
TsN
OH
5p
13C NMR
CDCl3
100 Hz
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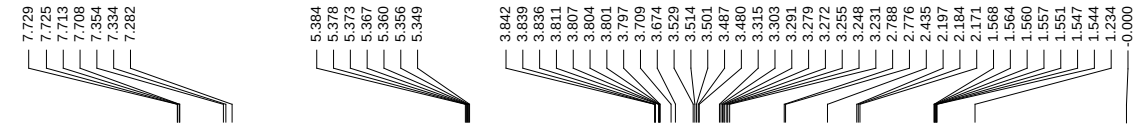
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3.807
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3.801
3.797
3.709
3.674
3.529
3.514
3.501
3.487
3.480
3.315
3.303
3.291
3.279
3.272
3.255
3.248
3.231
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2.776
2.435
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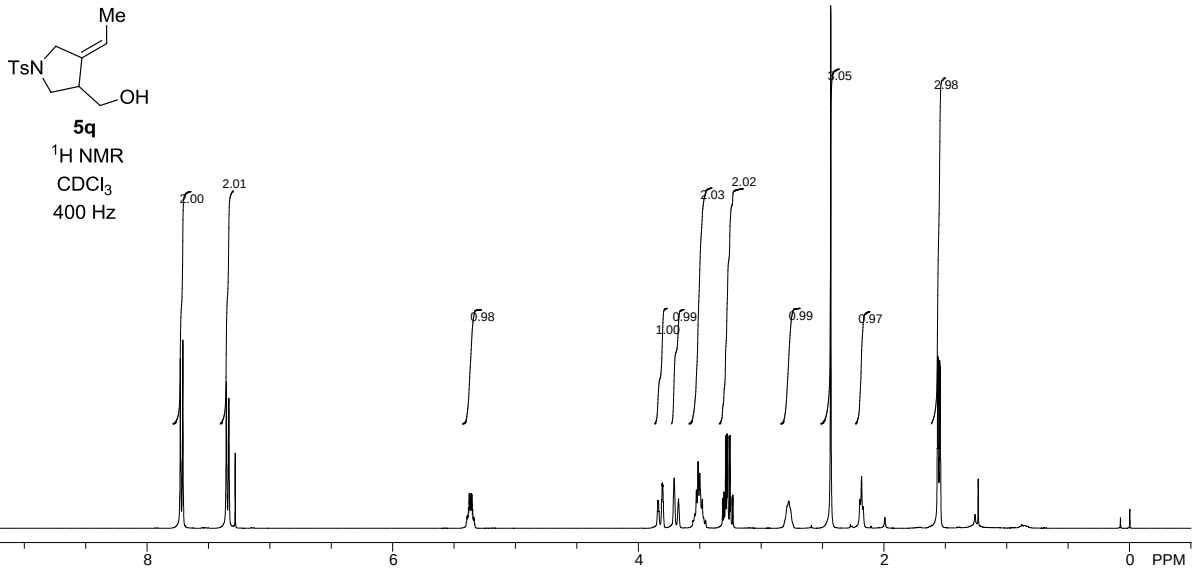
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TsN
OH
5q
1H NMR
CDCl3
400 Hz
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2.01
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6
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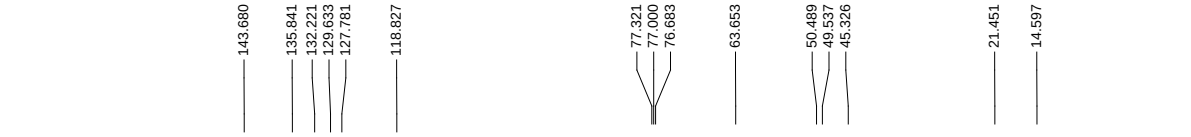
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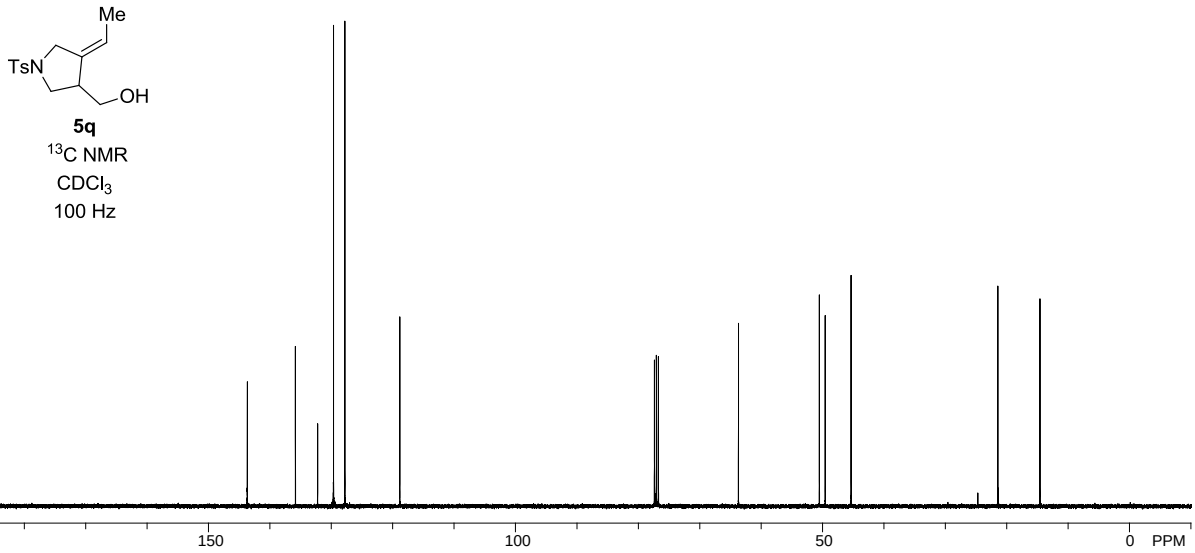
14.597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TsN
OH
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13C NMR
CDCl3
100 Hz
150
100
50
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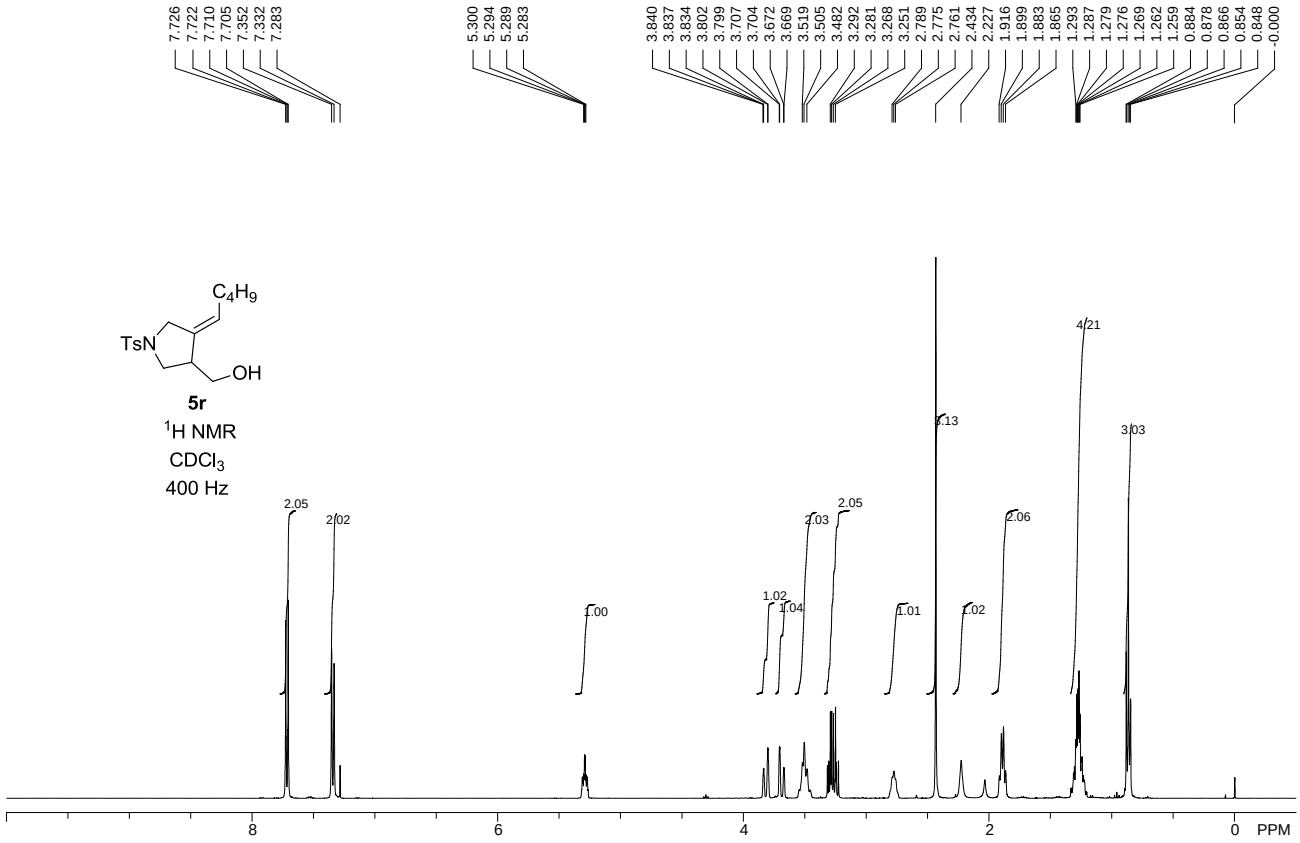
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TsN
OH
5r
1H NMR
CDCl3
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1.00
1.02
1.04
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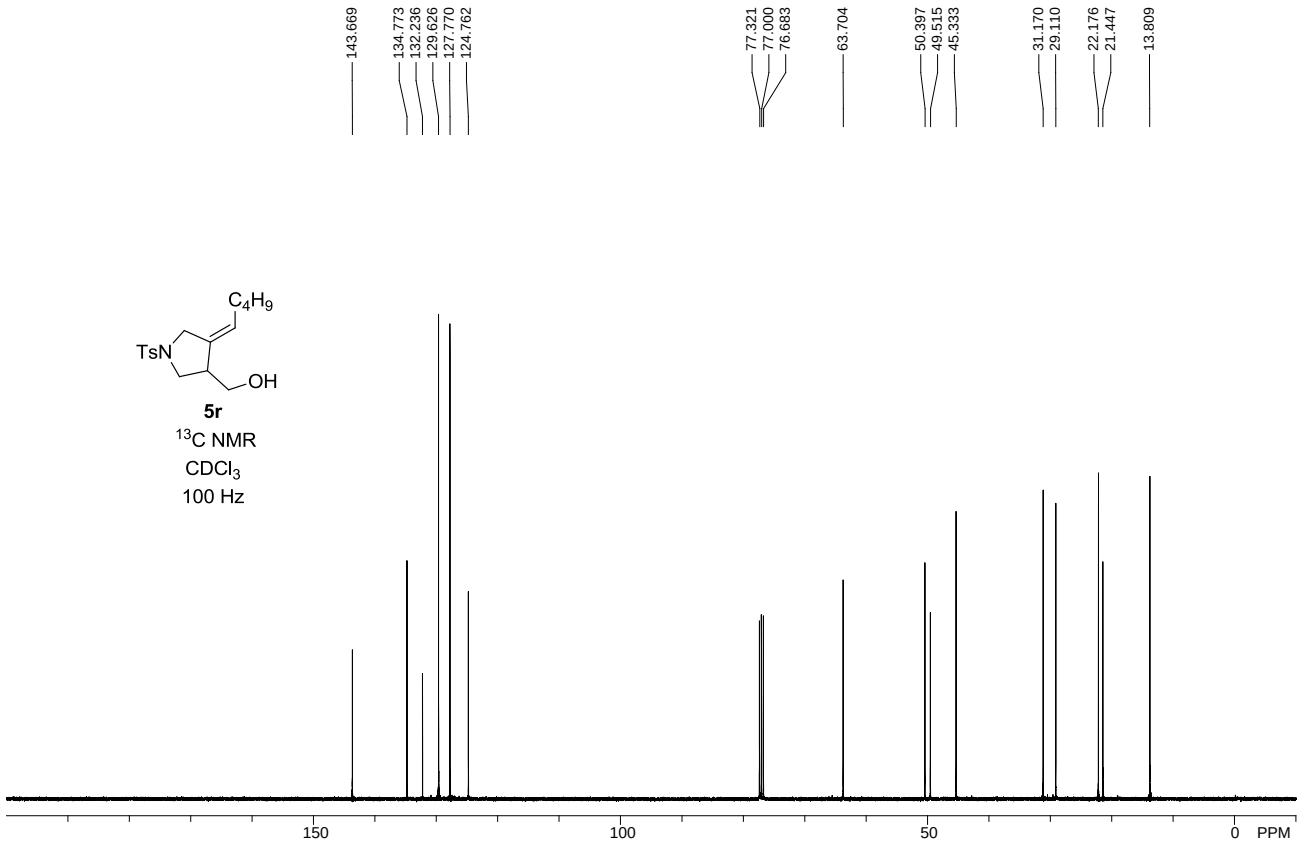
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29.110
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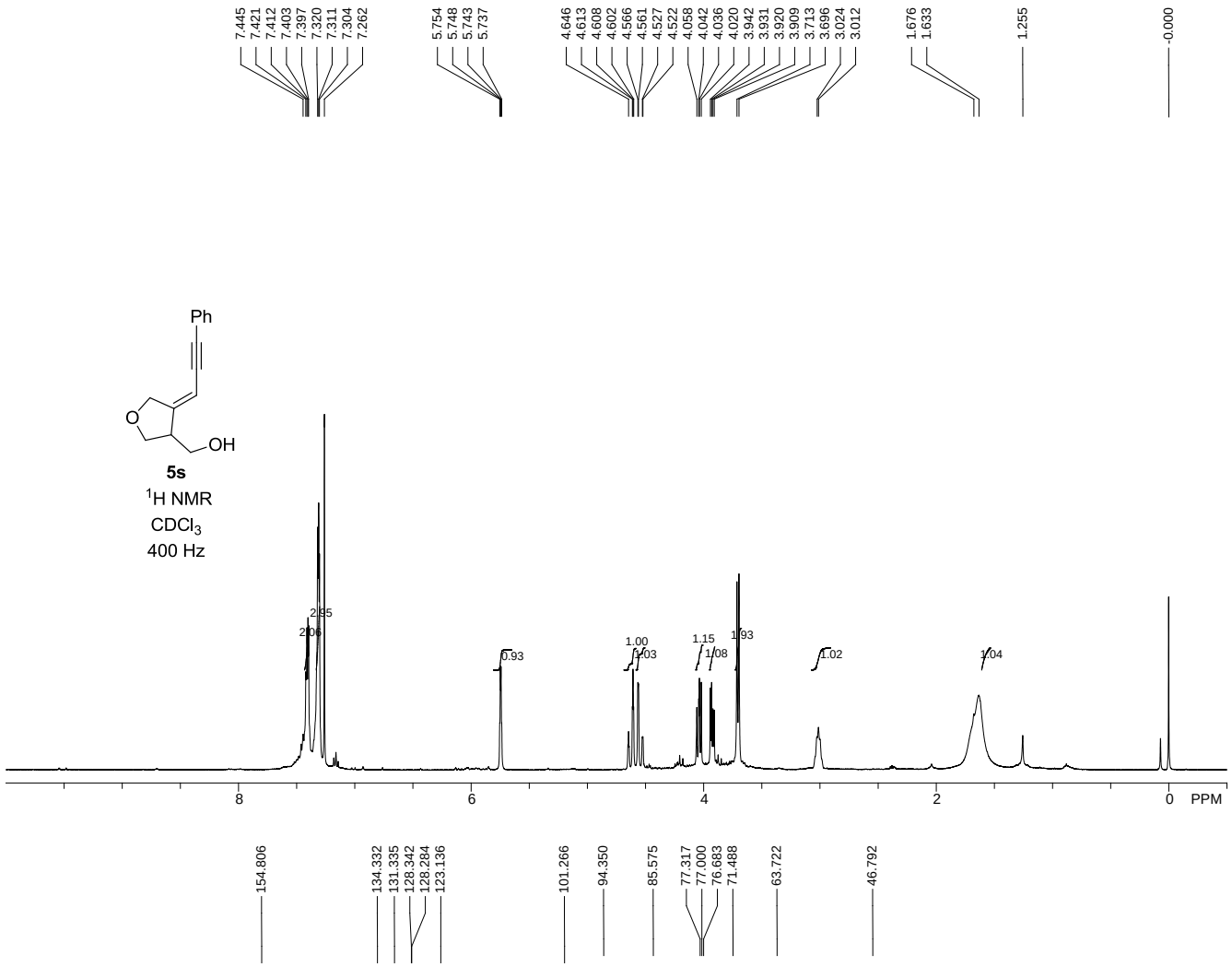
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4.613
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4.566
4.561
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3.931
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3.713
3.696
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3.012
1.676
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Ph
O
OH
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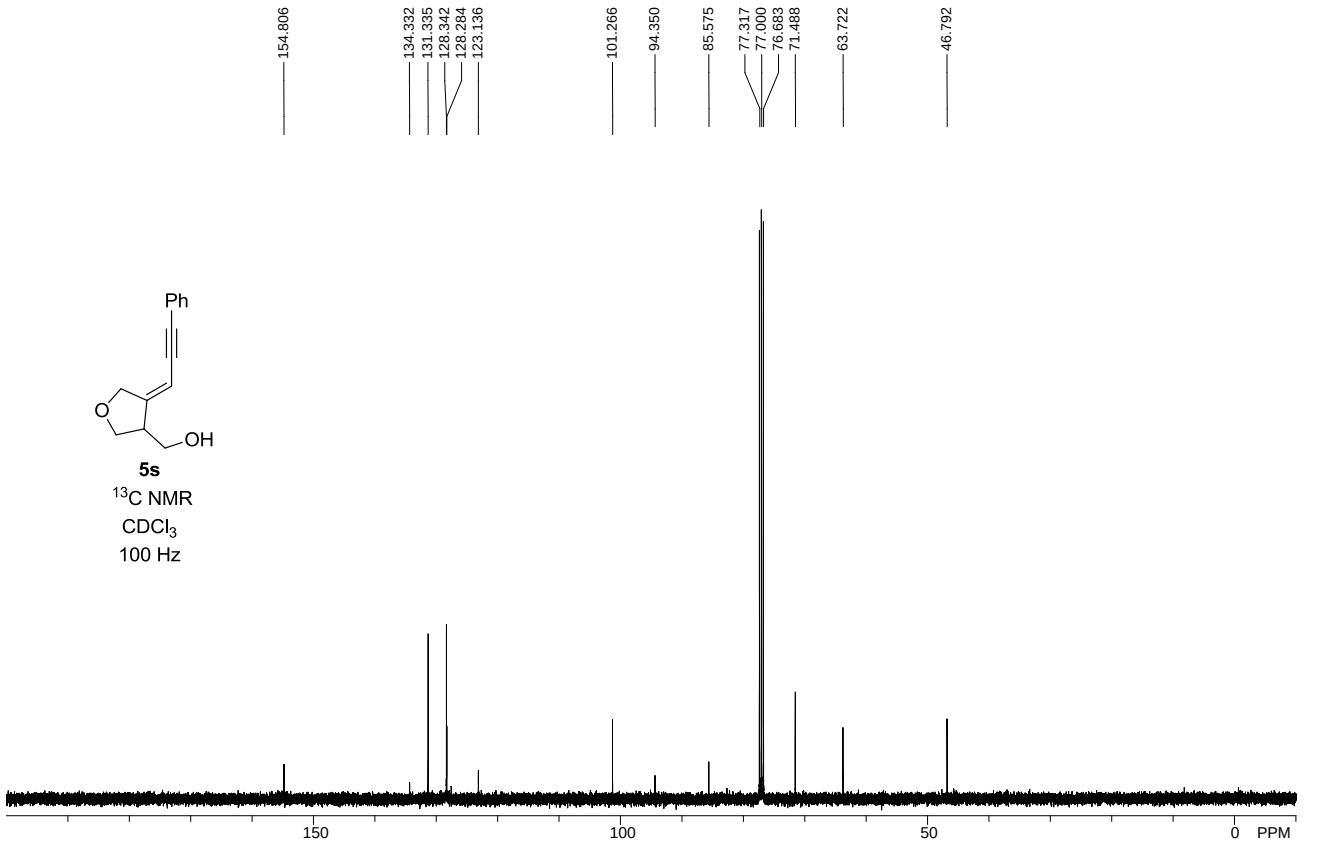
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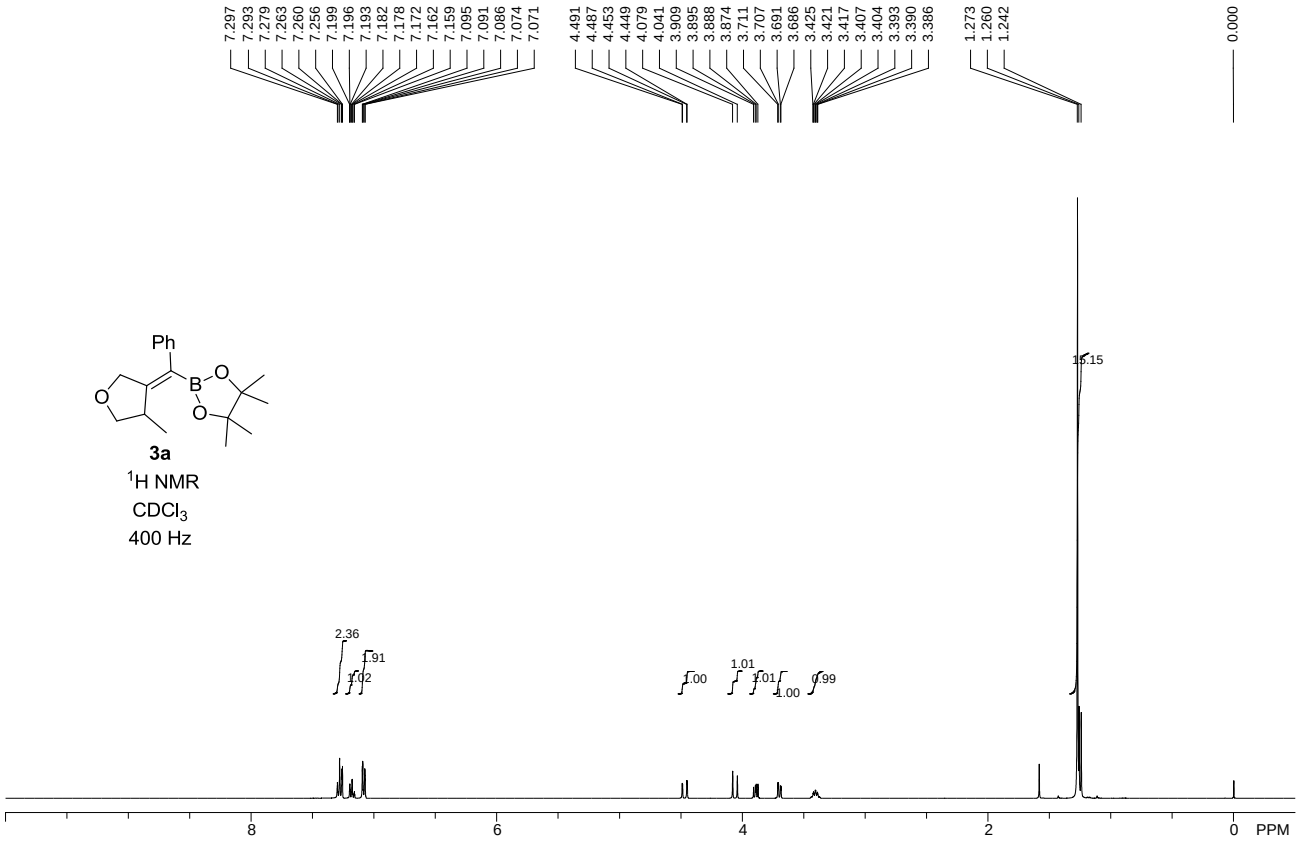
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7.162
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7.086
7.074
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4.453
4.449
4.079
4.041
3.909
3.895
3.888
3.874
3.711
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3.691
3.686
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3.421
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3.404
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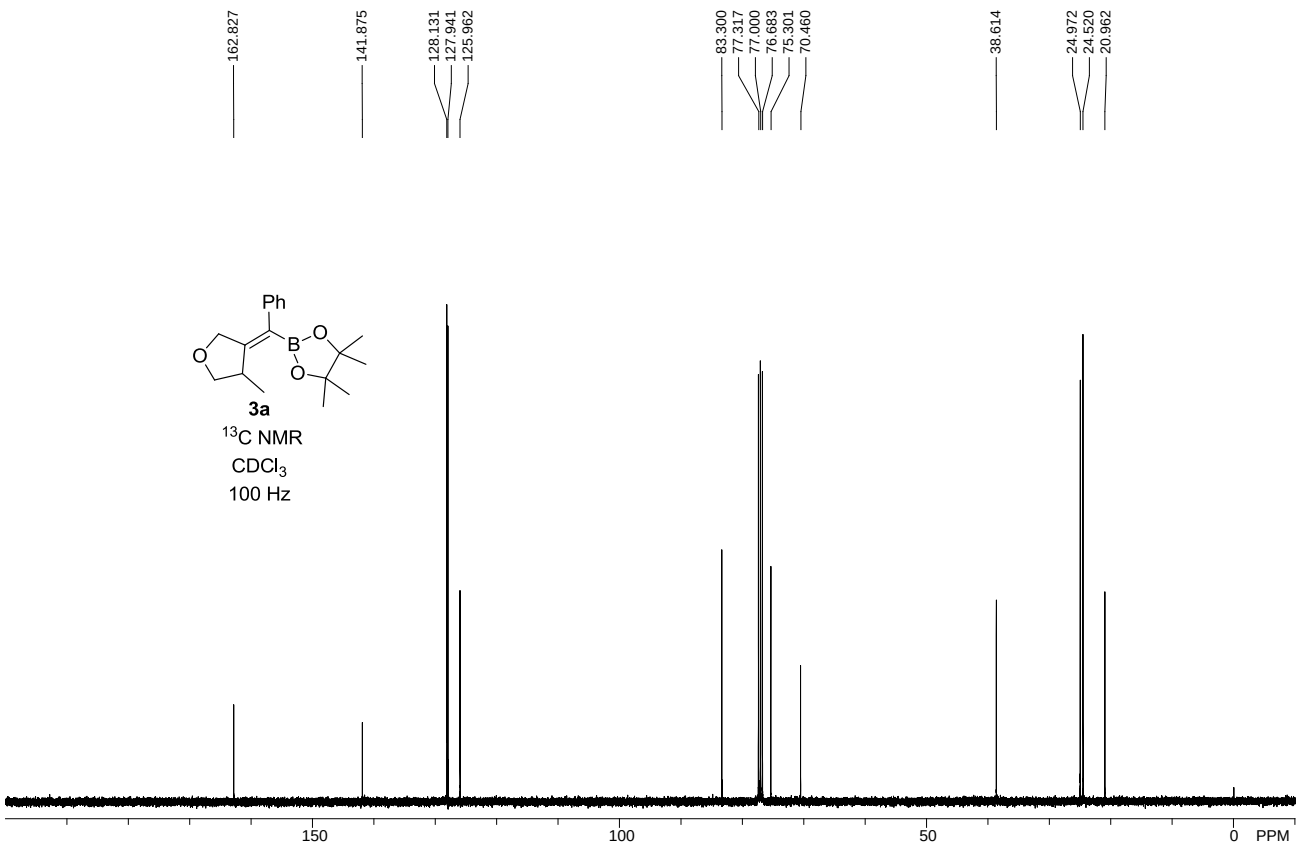
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24.972
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Ph
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B
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O
3a
13C NMR
CDCl3
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150
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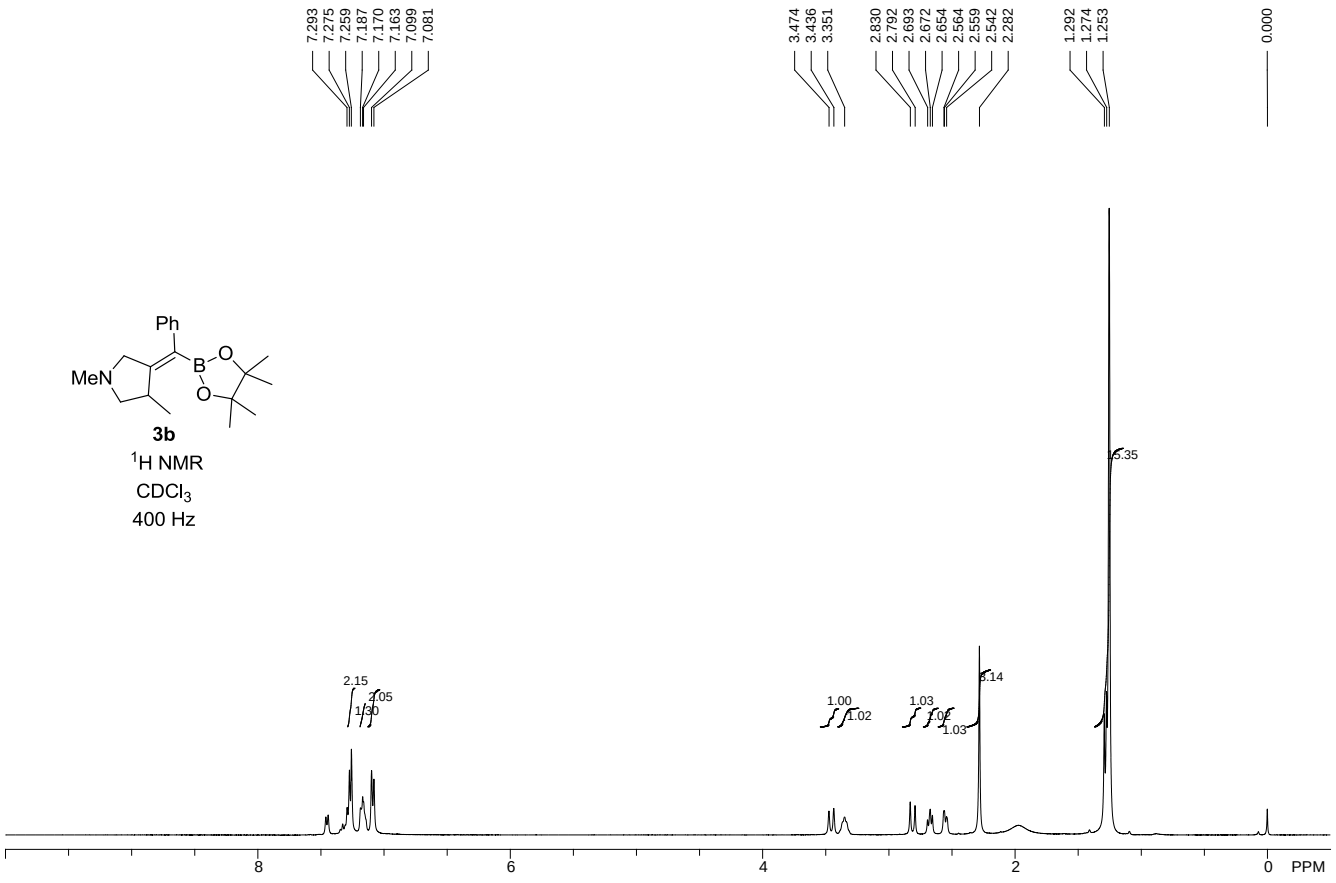
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2.830
2.792
2.693
2.672
2.654
2.564
2.559
2.542
2.282
1.292
1.274
1.253
0.000
Ph
MeN
B
O
O
3b
1H NMR
CDCl3
400 Hz
2.15
2.05
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1.02
1.03
1.02
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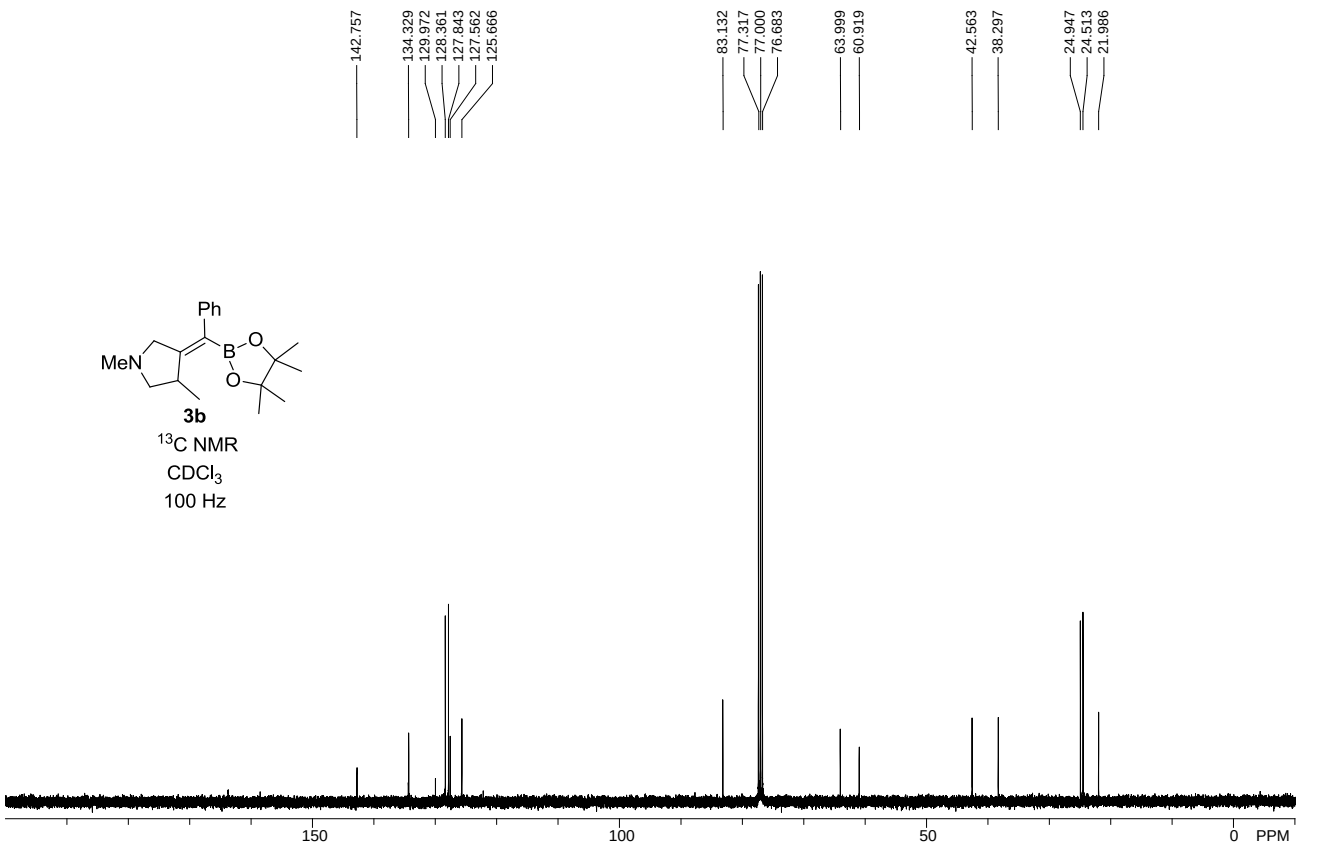
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60.919
42.563
38.297
24.947
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Ph
MeN
B
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O
3b
13C NMR
CDCl3
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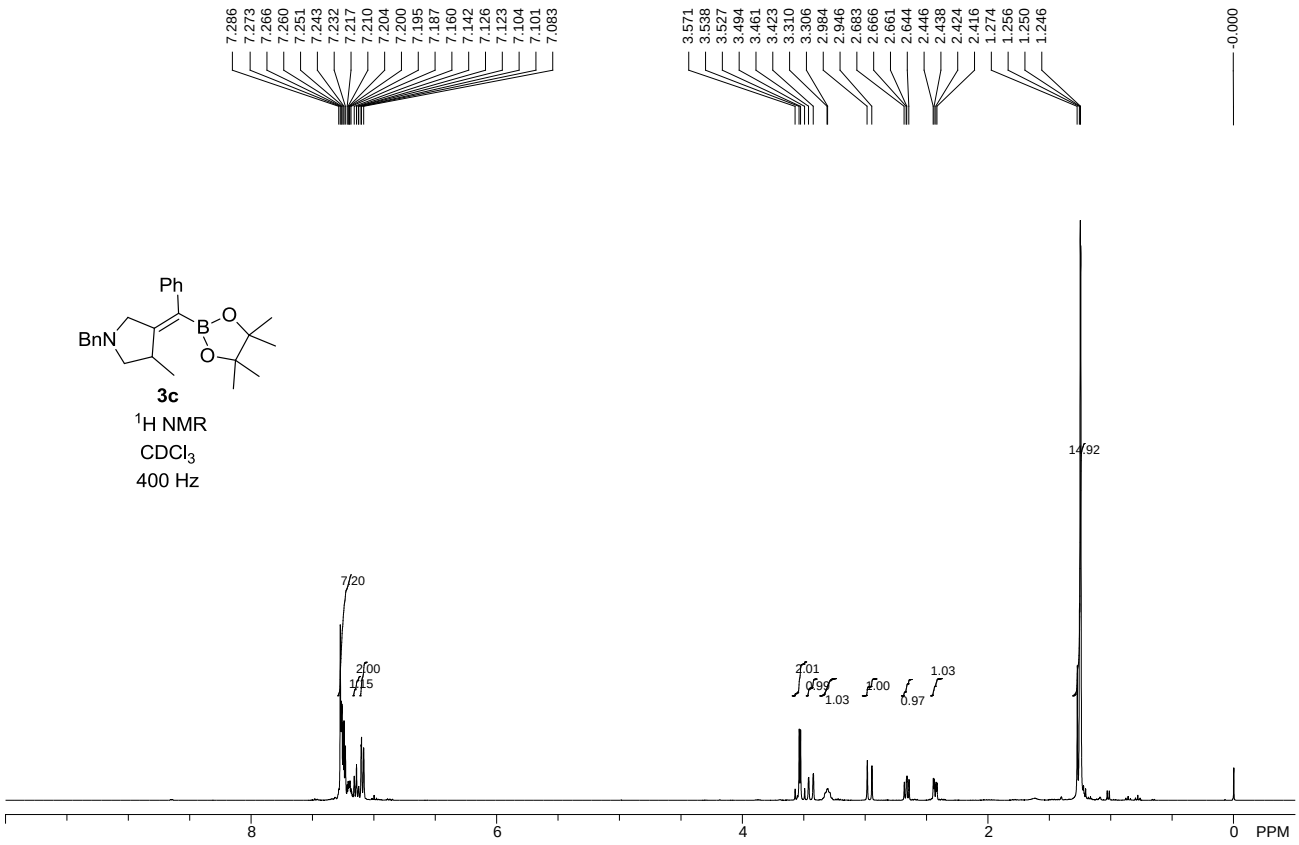
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7.160
7.142
7.126
7.123
7.104
7.101
7.083
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3.538
3.527
3.494
3.461
3.423
3.310
3.306
2.984
2.946
2.683
2.666
2.661
2.644
2.446
2.438
2.424
2.416
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1.250
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Ph
BnN
B
O
O
3c
1H NMR
CDCl3
400 Hz
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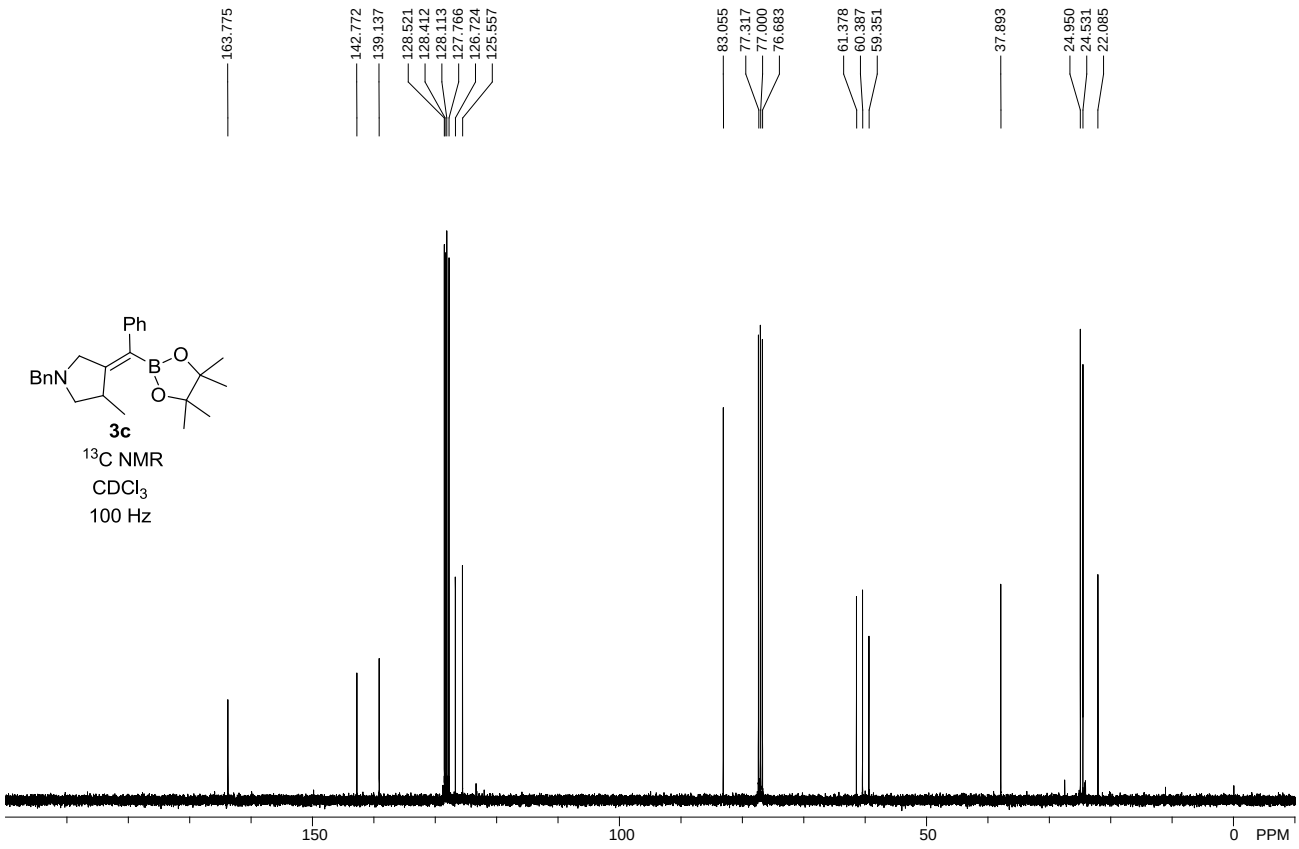
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3c
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CDCl3
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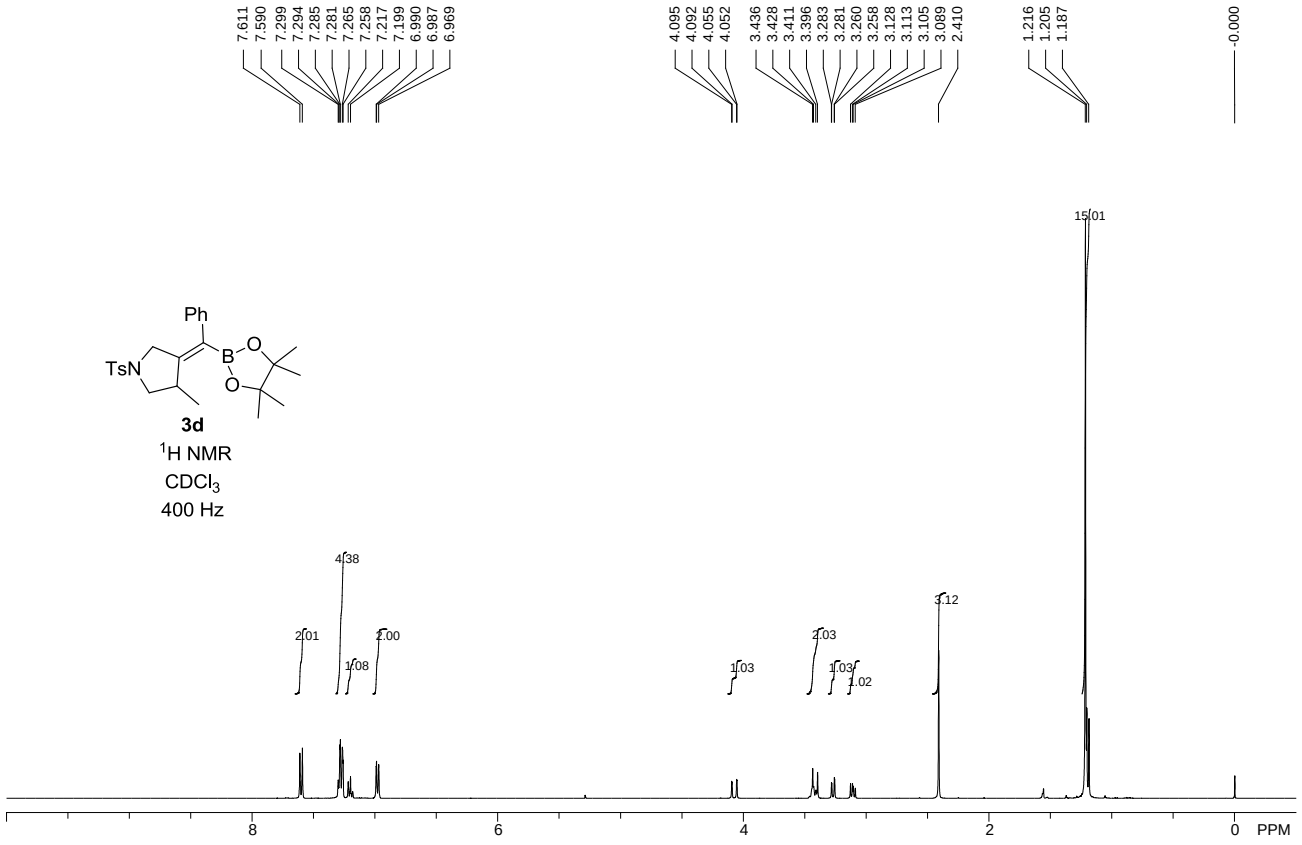
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4.055
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3.428
3.411
3.396
3.283
3.281
3.260
3.258
3.128
3.113
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1.187
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CDCl3
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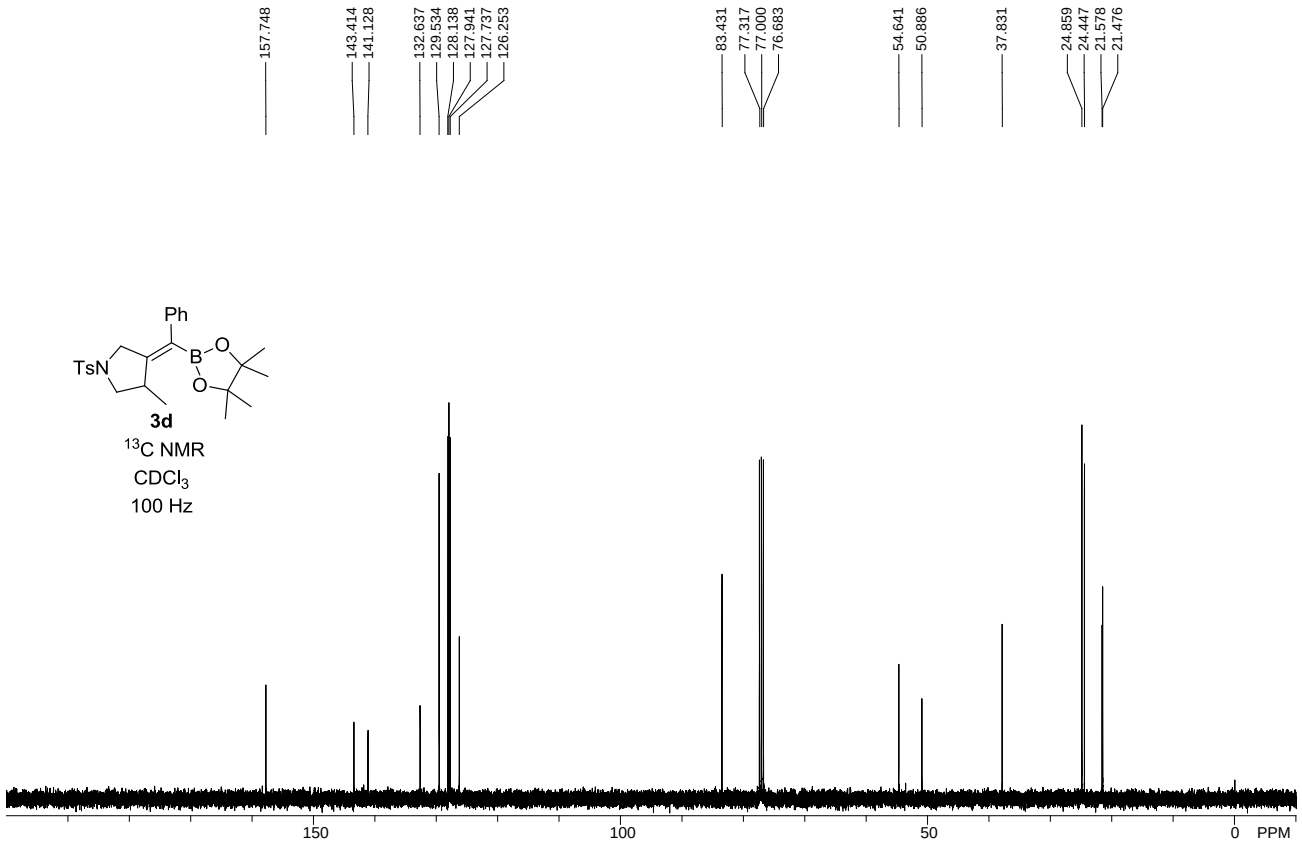
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76.683
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37.831
24.859
24.447
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CDCl3
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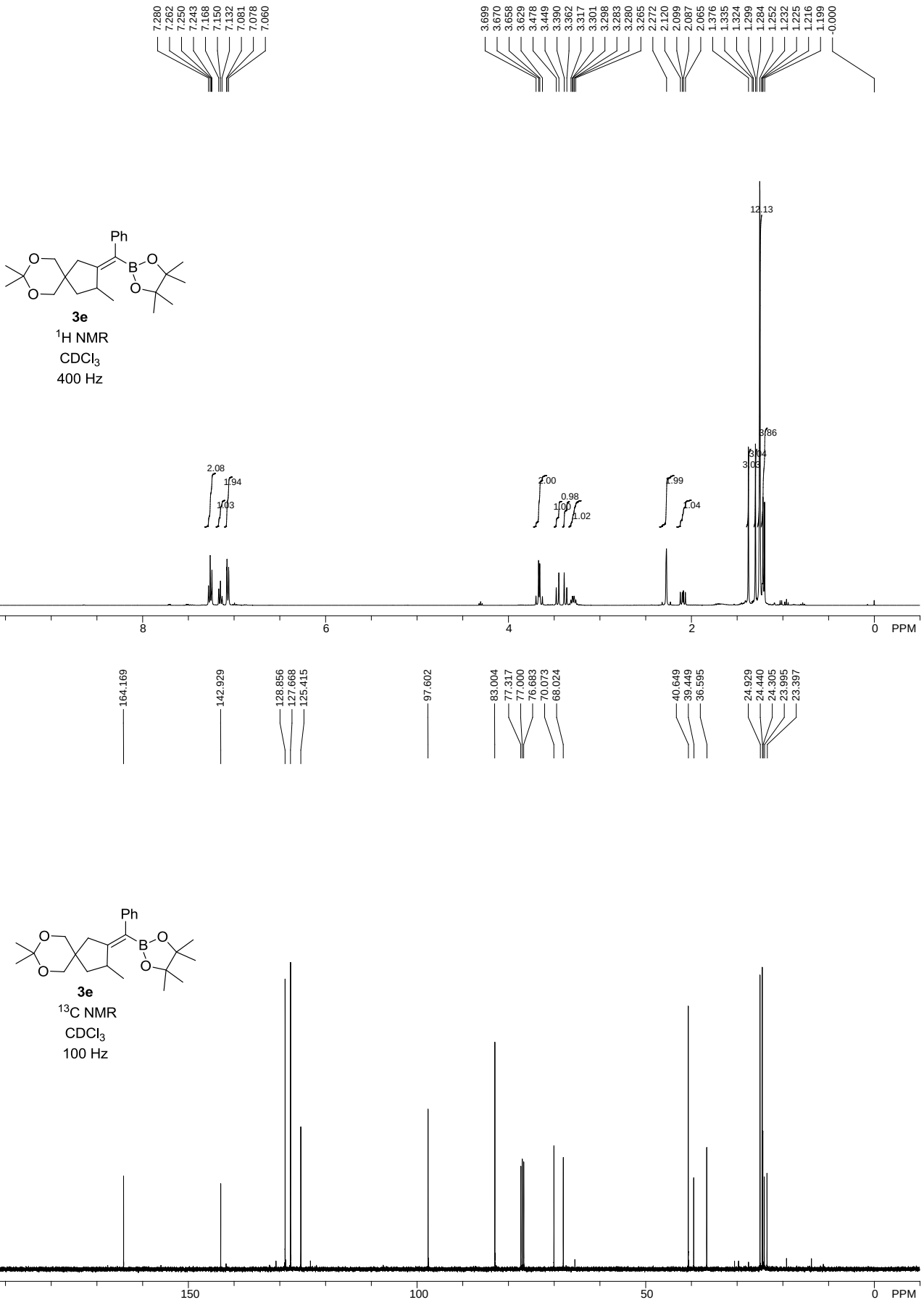
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3.478
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3.283
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O
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1.03
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1.00
1.02
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1.04
8
6
4
2
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24.440
24.305
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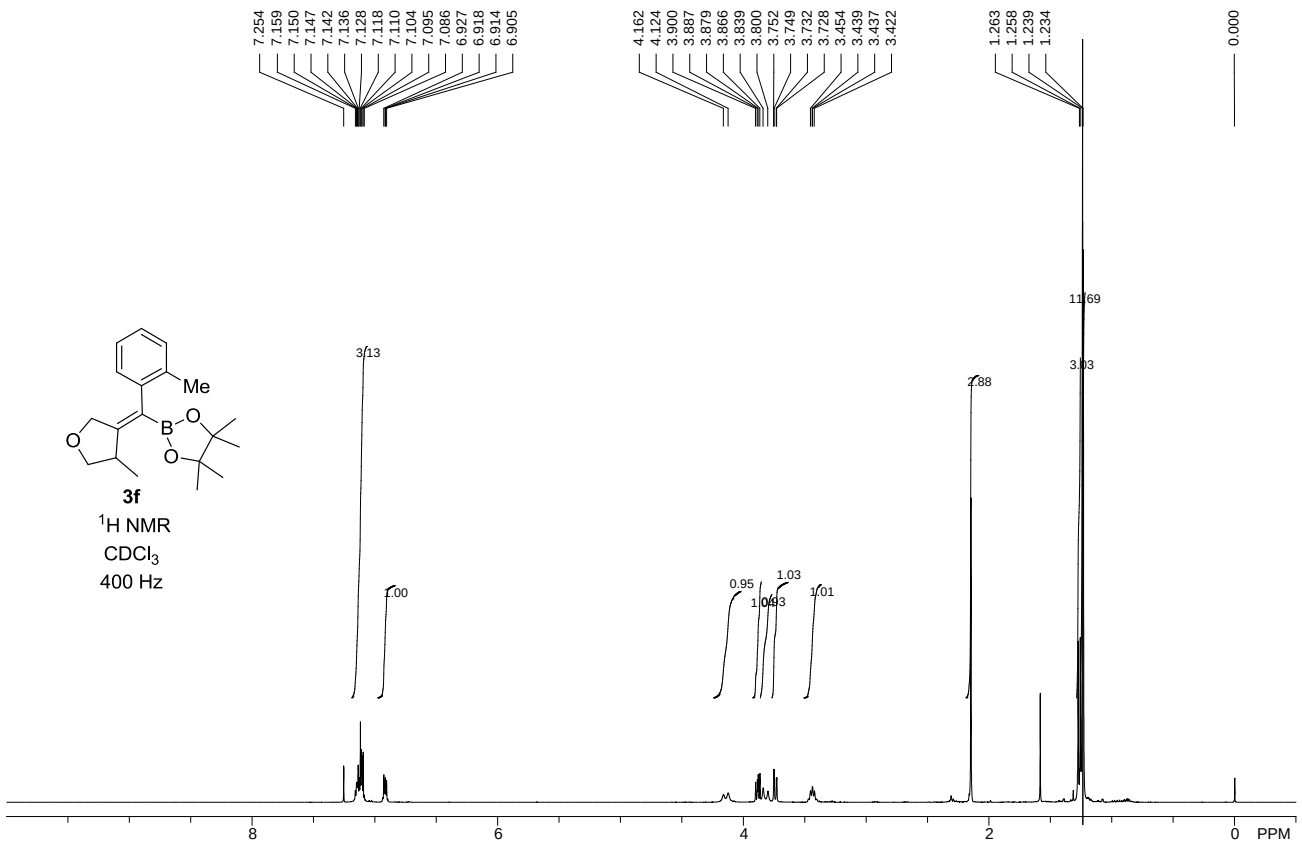
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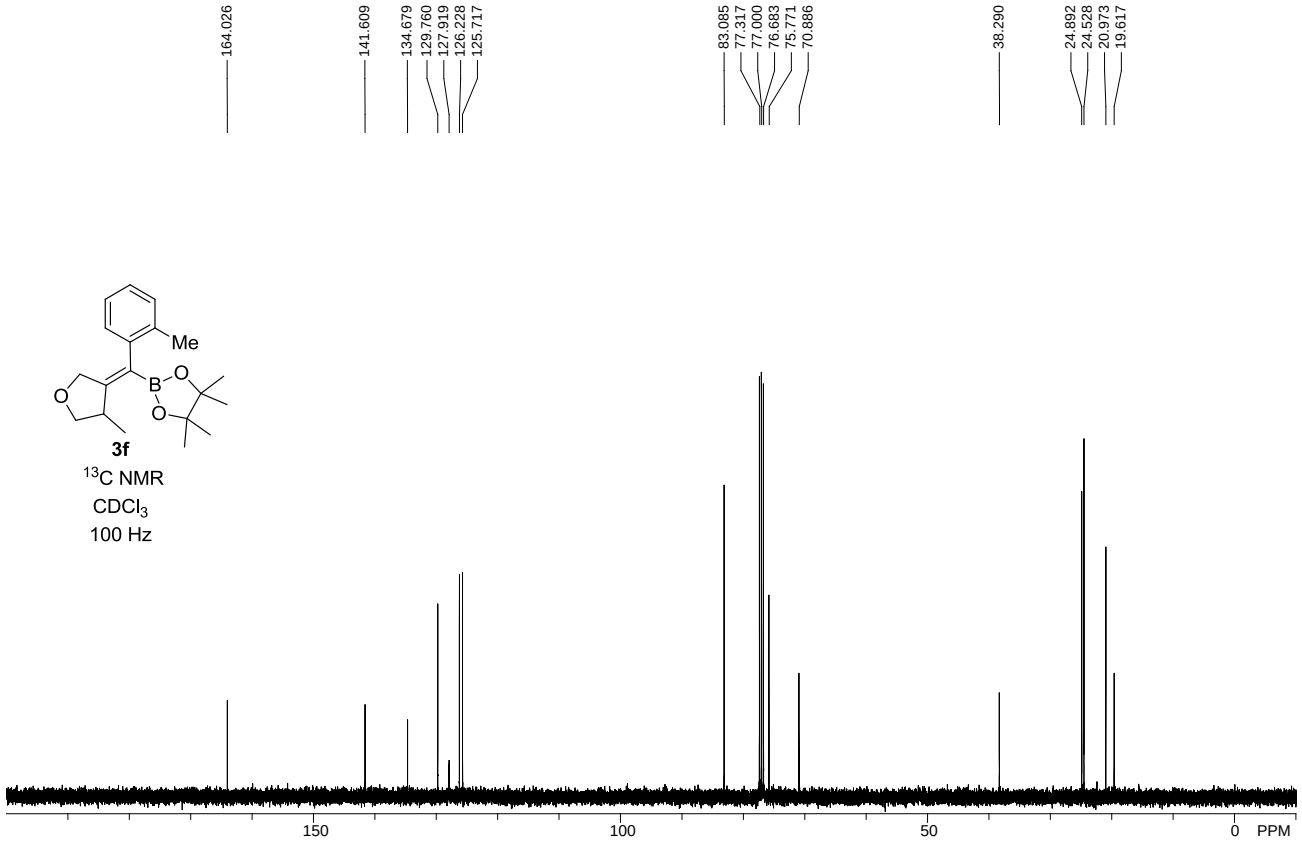
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24.892
24.528
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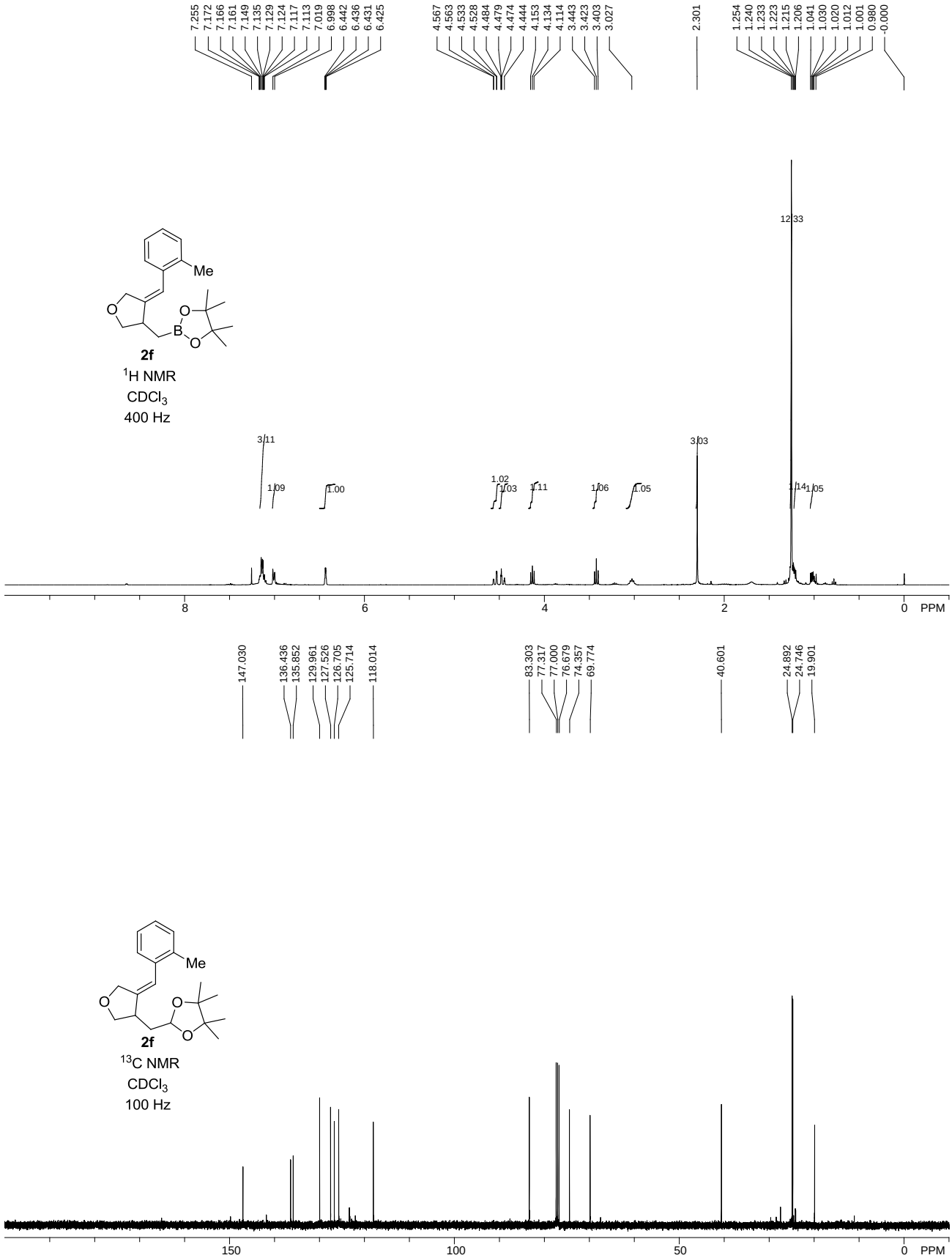
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77.000
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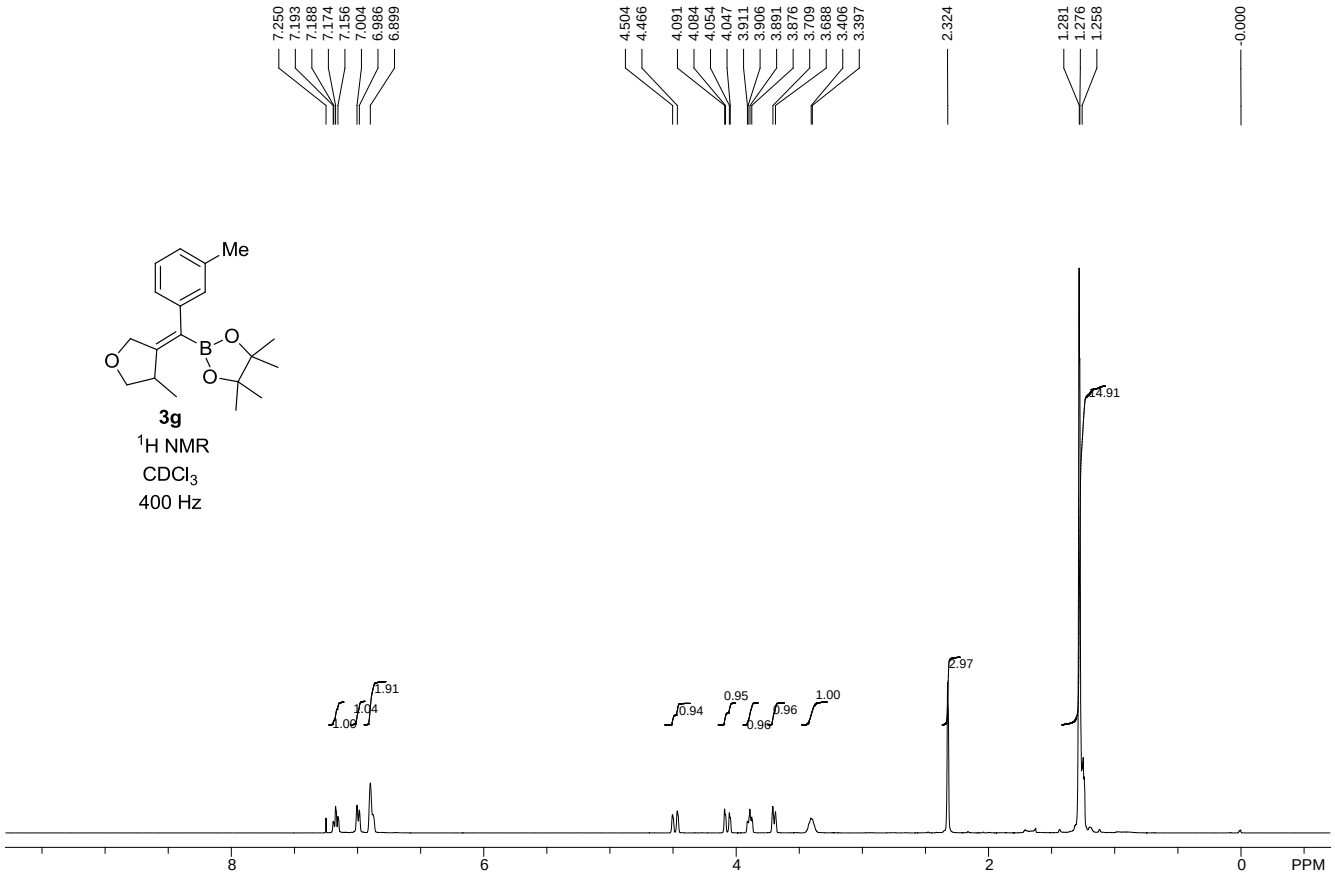
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1.276
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3g
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1.04
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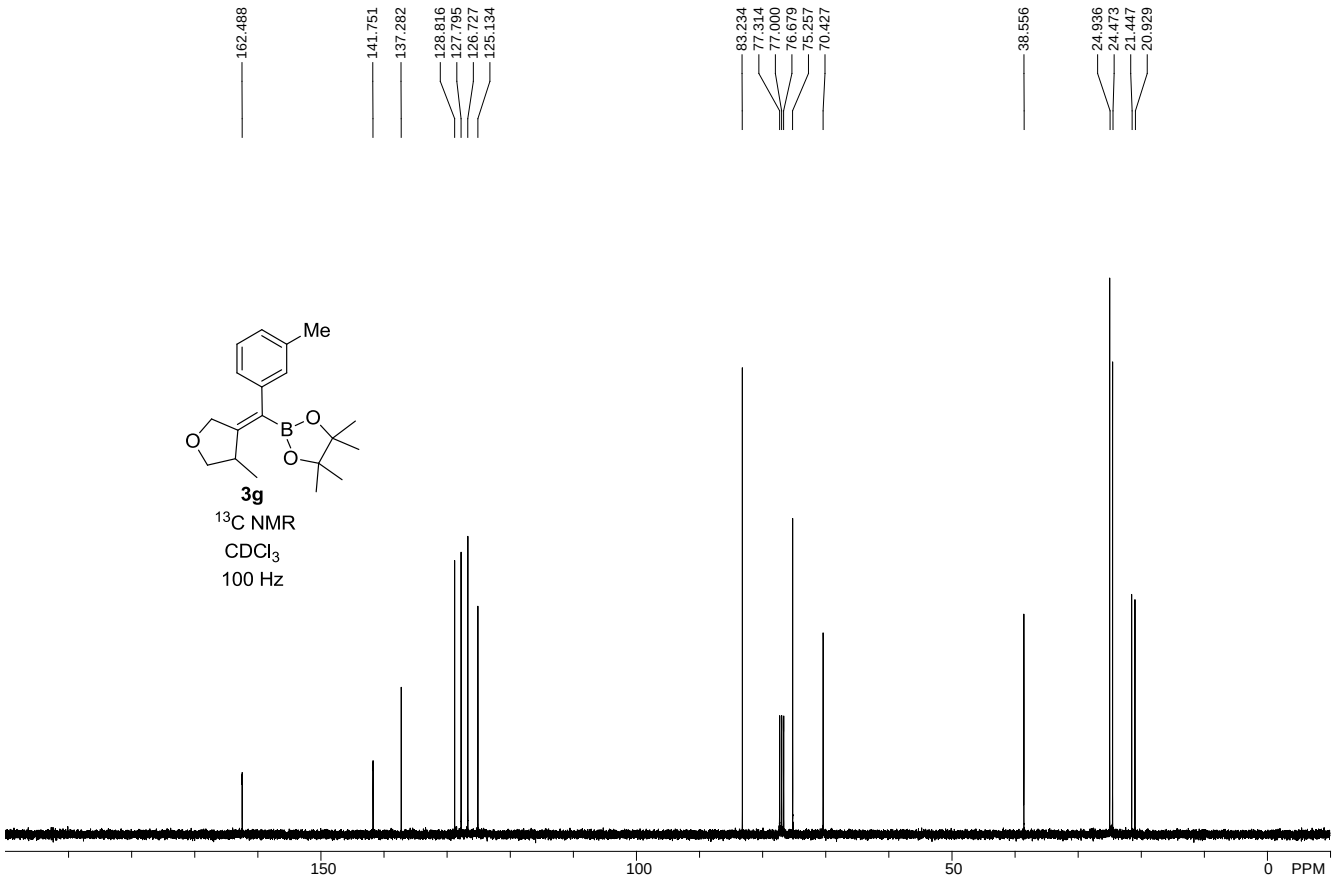
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38.556
24.936
24.473
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O
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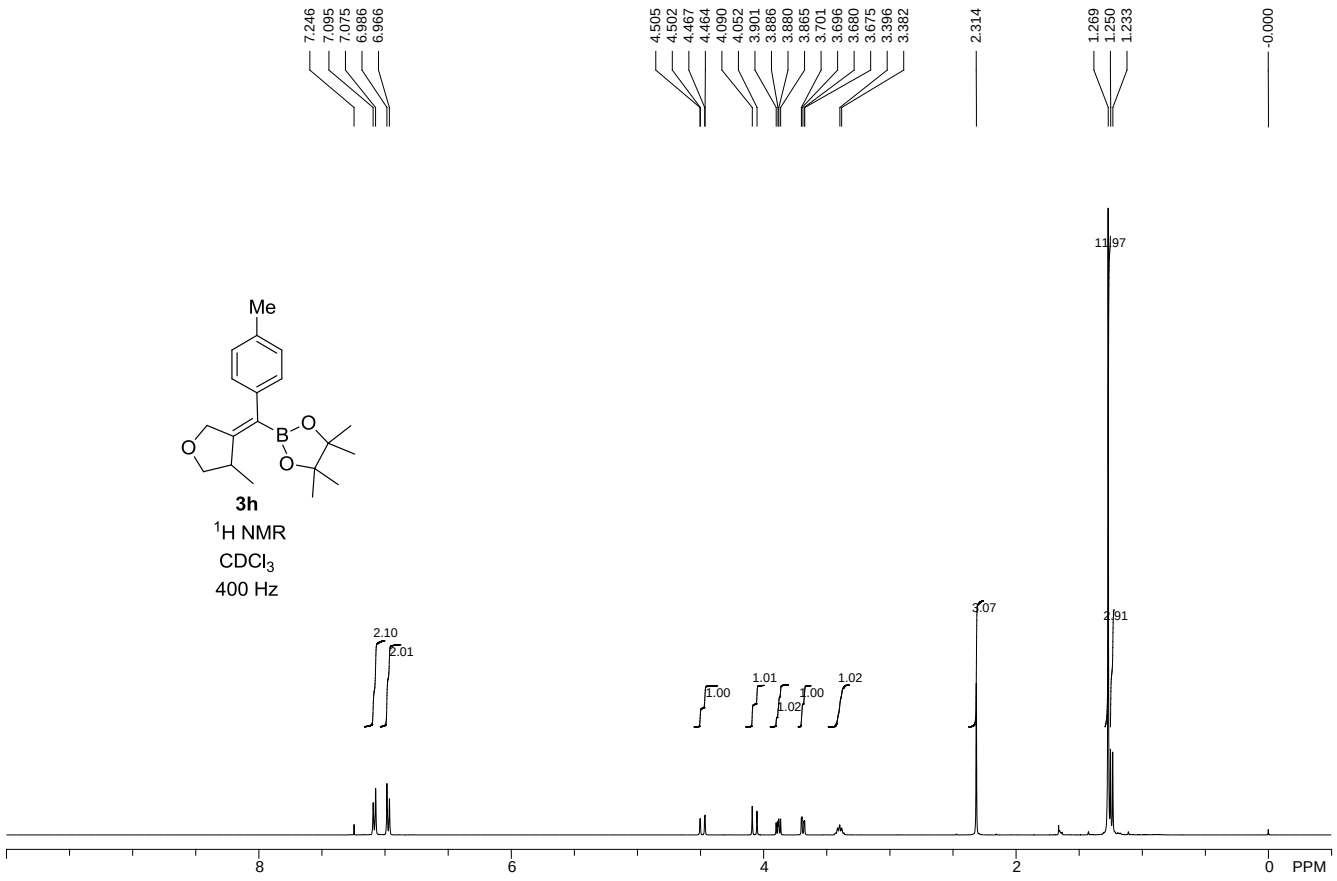
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3.675
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2.314
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1.233
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2.01
1.00
1.01
1.02
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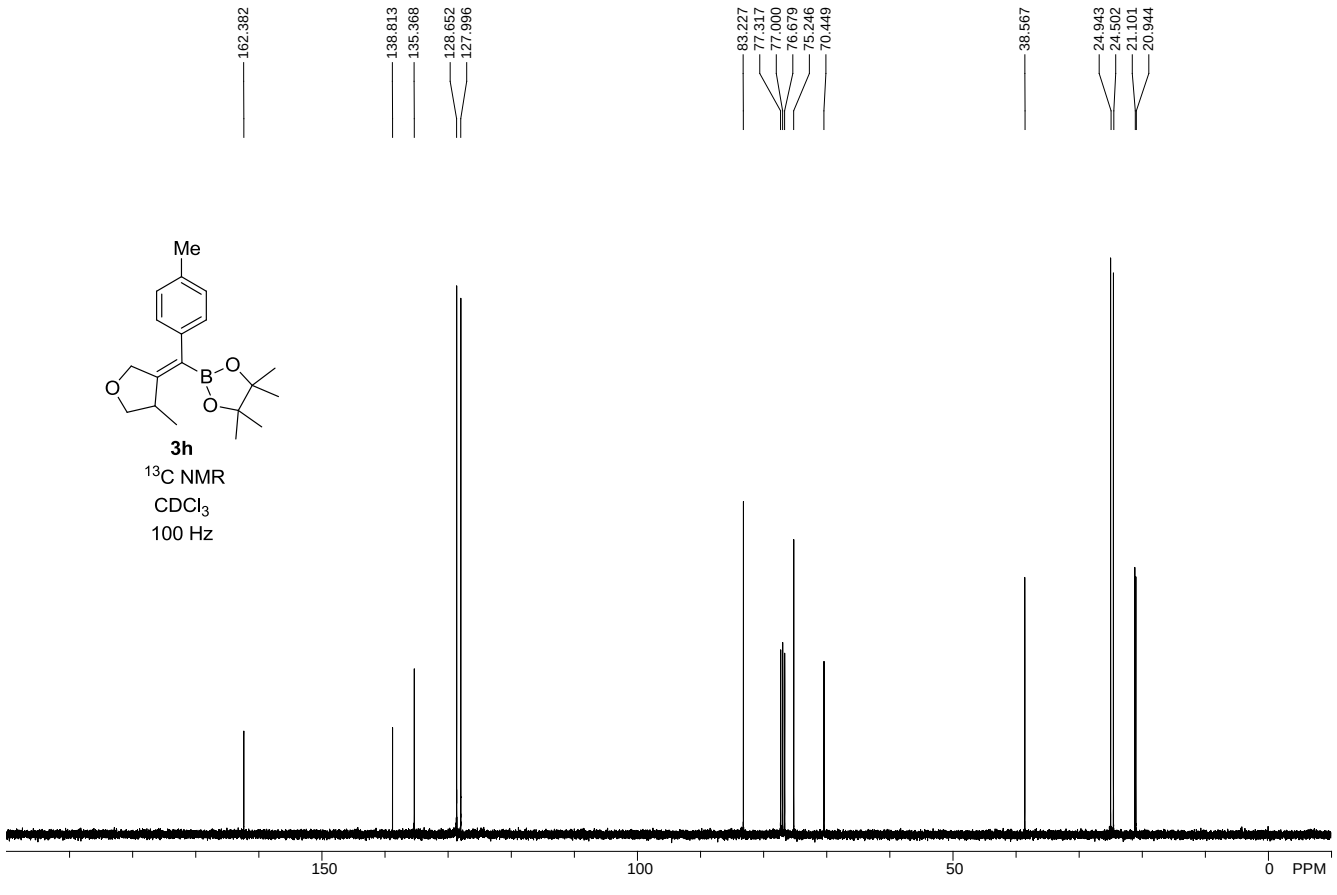
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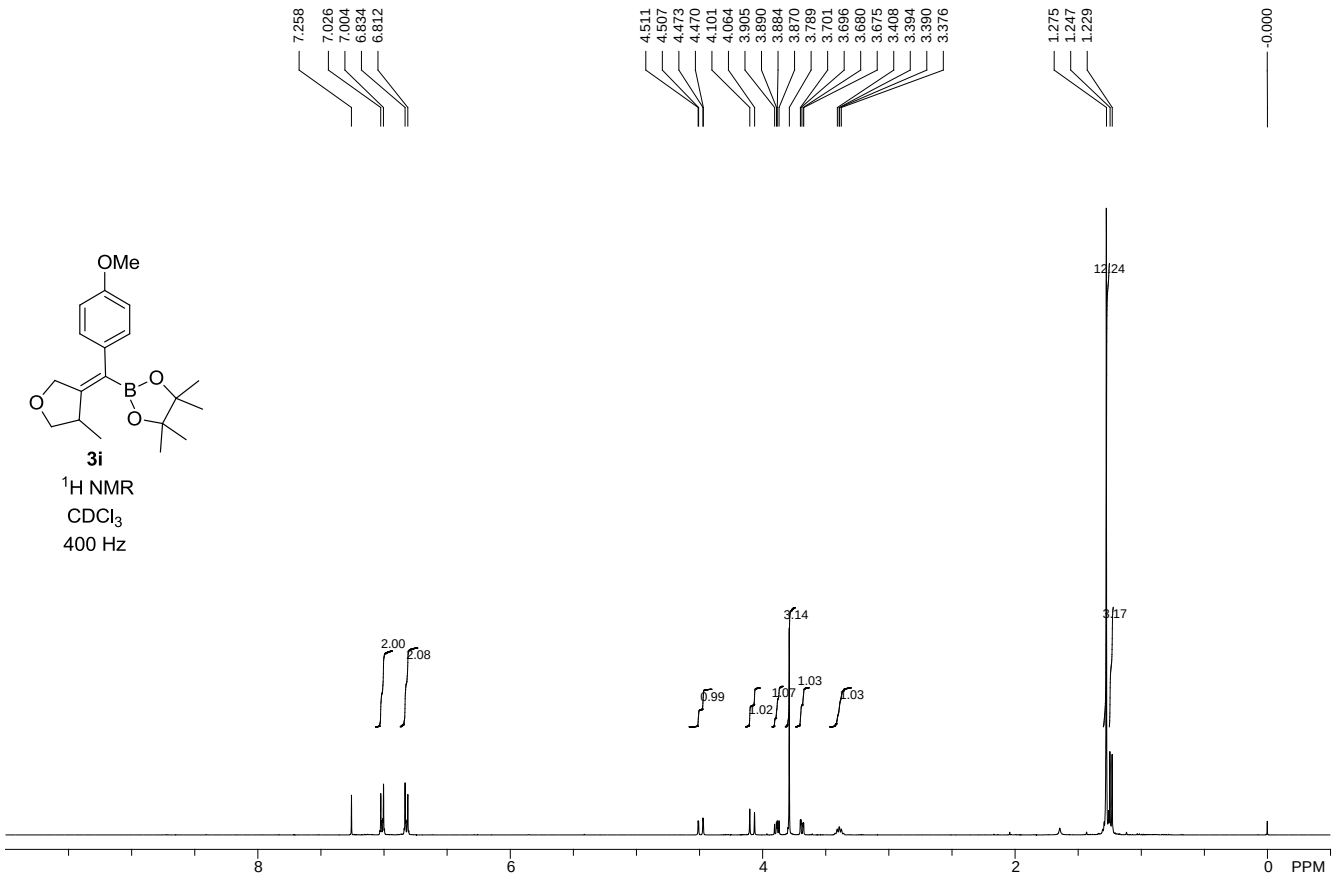
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3.884
3.870
3.789
3.701
3.696
3.680
3.675
3.408
3.394
3.390
3.376
1.275
1.247
1.229
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OMe
B
O
O
O
3i
1H NMR
CDCl3
400 Hz
12.24
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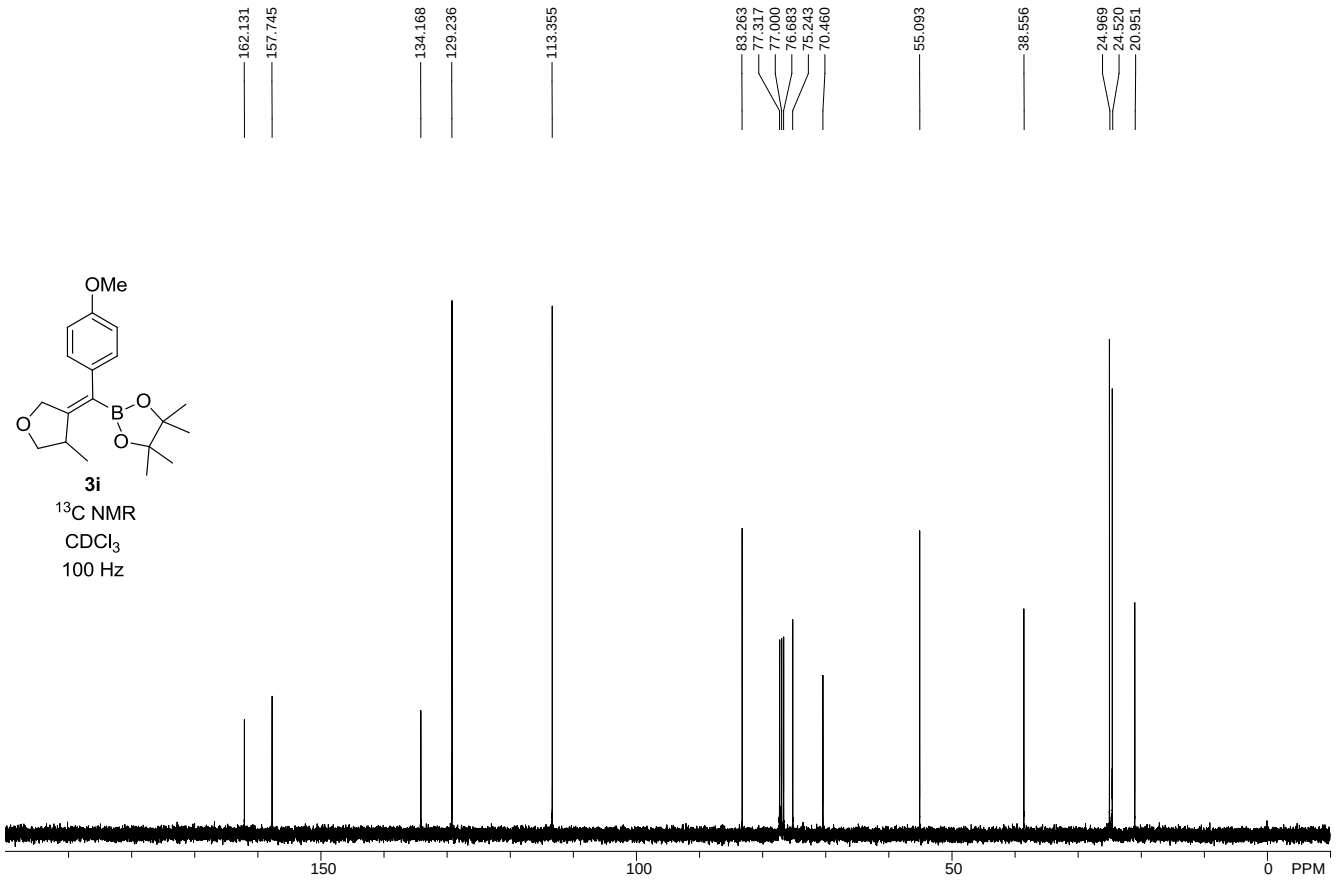
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70.460
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24.969
24.520
20.951
OMe
B
O
O
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3i
13C NMR
CDCl3
100 Hz
150
100
50
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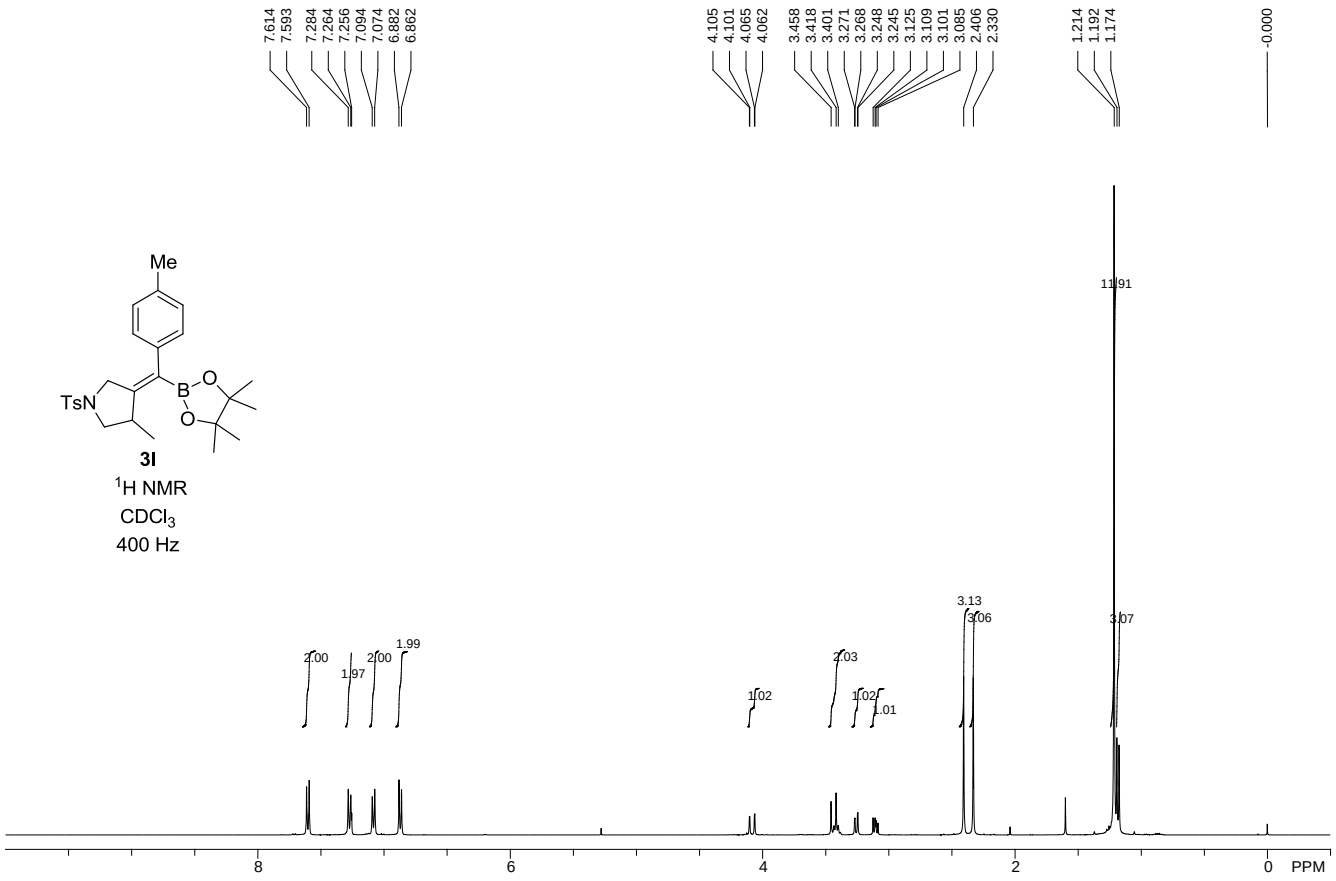
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6.882
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3.458
3.418
3.401
3.271
3.268
3.248
3.245
3.125
3.109
3.101
3.085
2.406
2.330
1.214
1.192
1.174
-0.000
Me
TsN
B
O
O
3I
1H NMR
CDCl3
400 Hz
11.91
3.13
3.06
3.07
2.00
1.97
2.00
1.99
1.02
2.03
1.02
1.01
8
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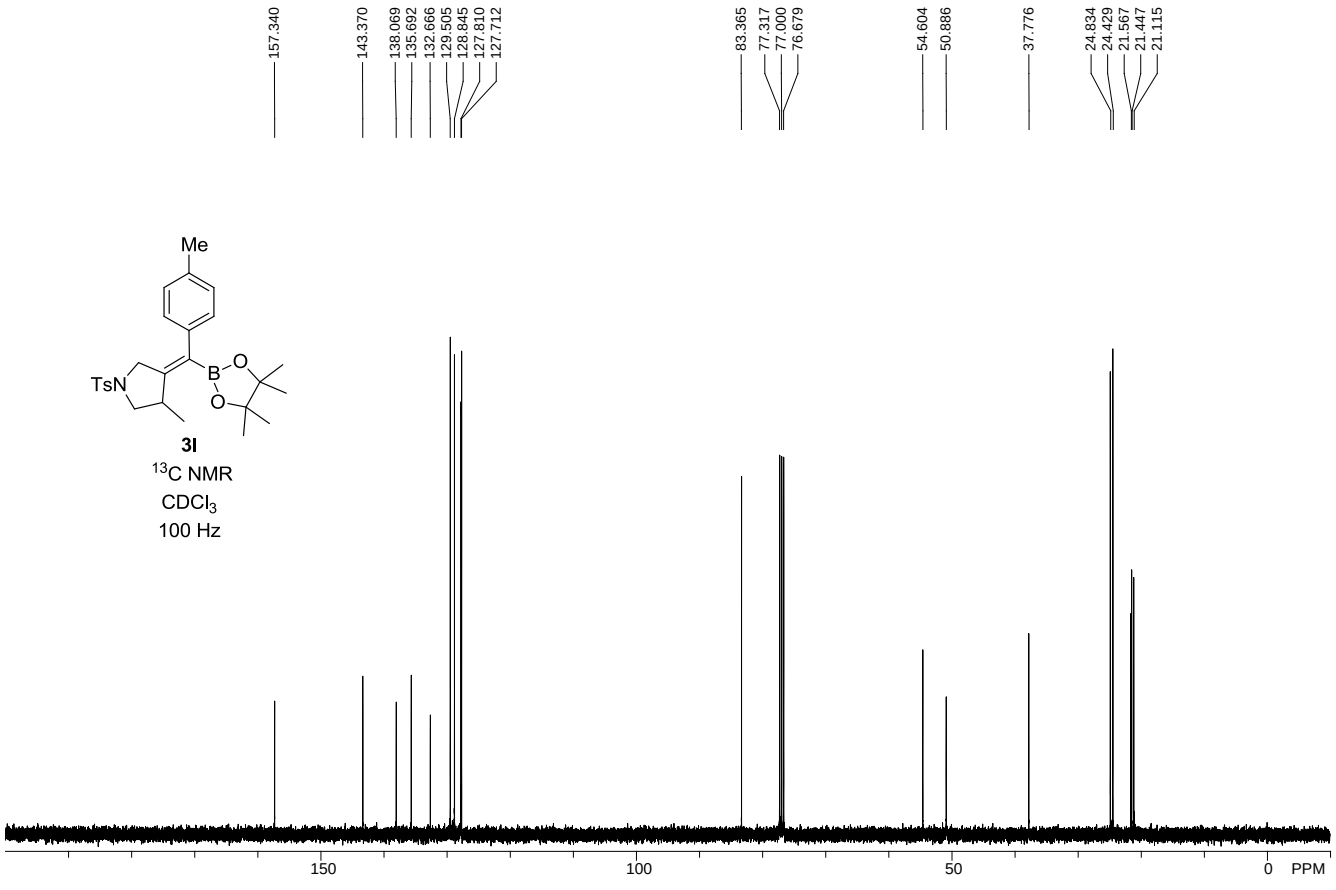
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127.810
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83.365
77.317
77.000
76.679
54.604
50.886
37.776
24.834
24.429
21.567
21.447
21.115
Me
TsN
B
O
O
3I
13C NMR
CDCl3
100 Hz
150
100
50
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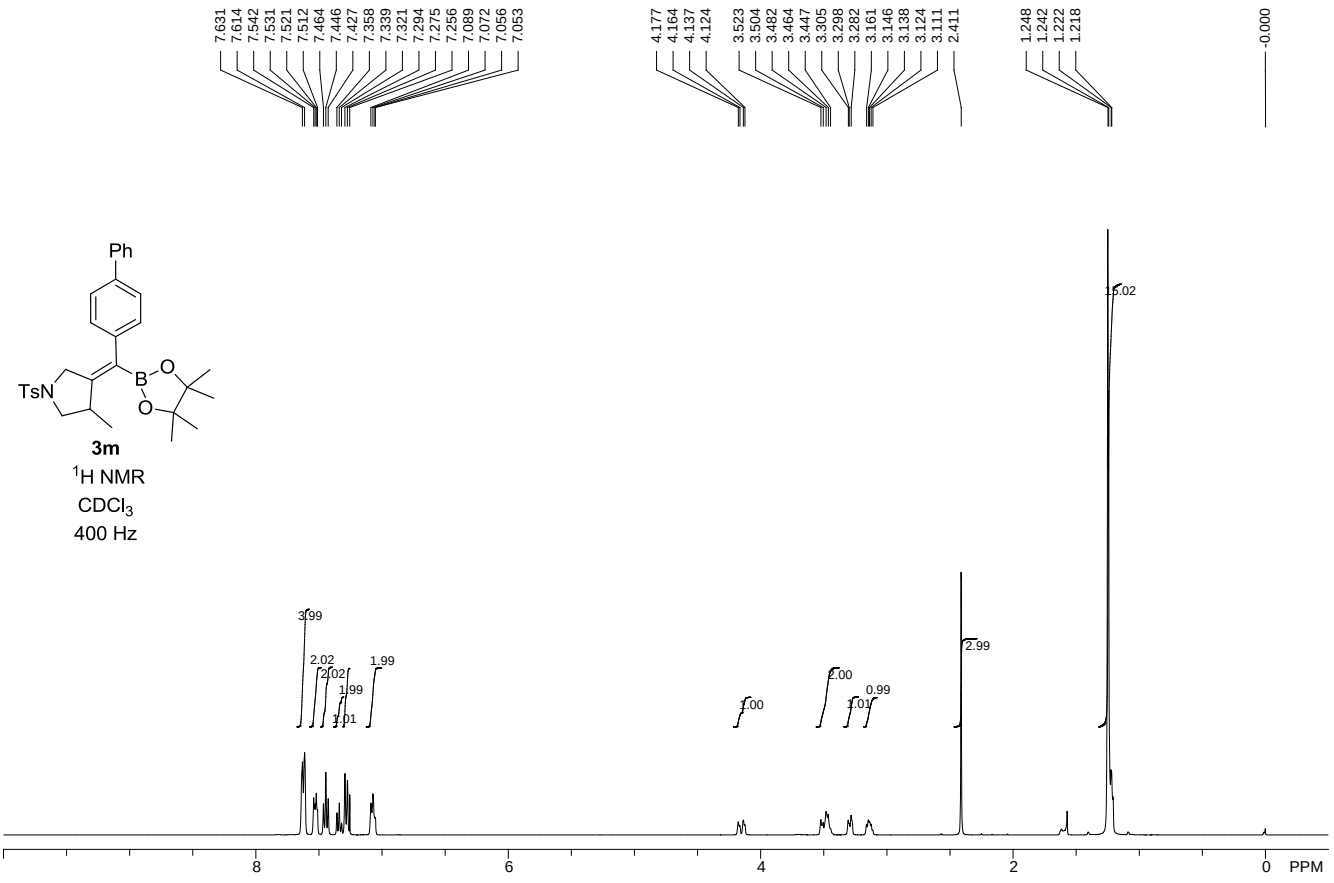
PPM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7.446
7.427
7.358
7.339
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7.294
7.275
7.256
7.089
7.072
7.056
7.053
4.177
4.164
4.137
4.124
3.523
3.504
3.482
3.464
3.447
3.305
3.298
3.282
3.161
3.146
3.138
3.124
3.111
2.411
1.248
1.242
1.222
1.218
-0.000
Ph
TsN
B
O
O
3m
1H NMR
CDCl3
400 Hz
3.99
2.02
2.02
1.99
1.99
1.01
1.00
2.00
1.01
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2.99
15.02
8
6
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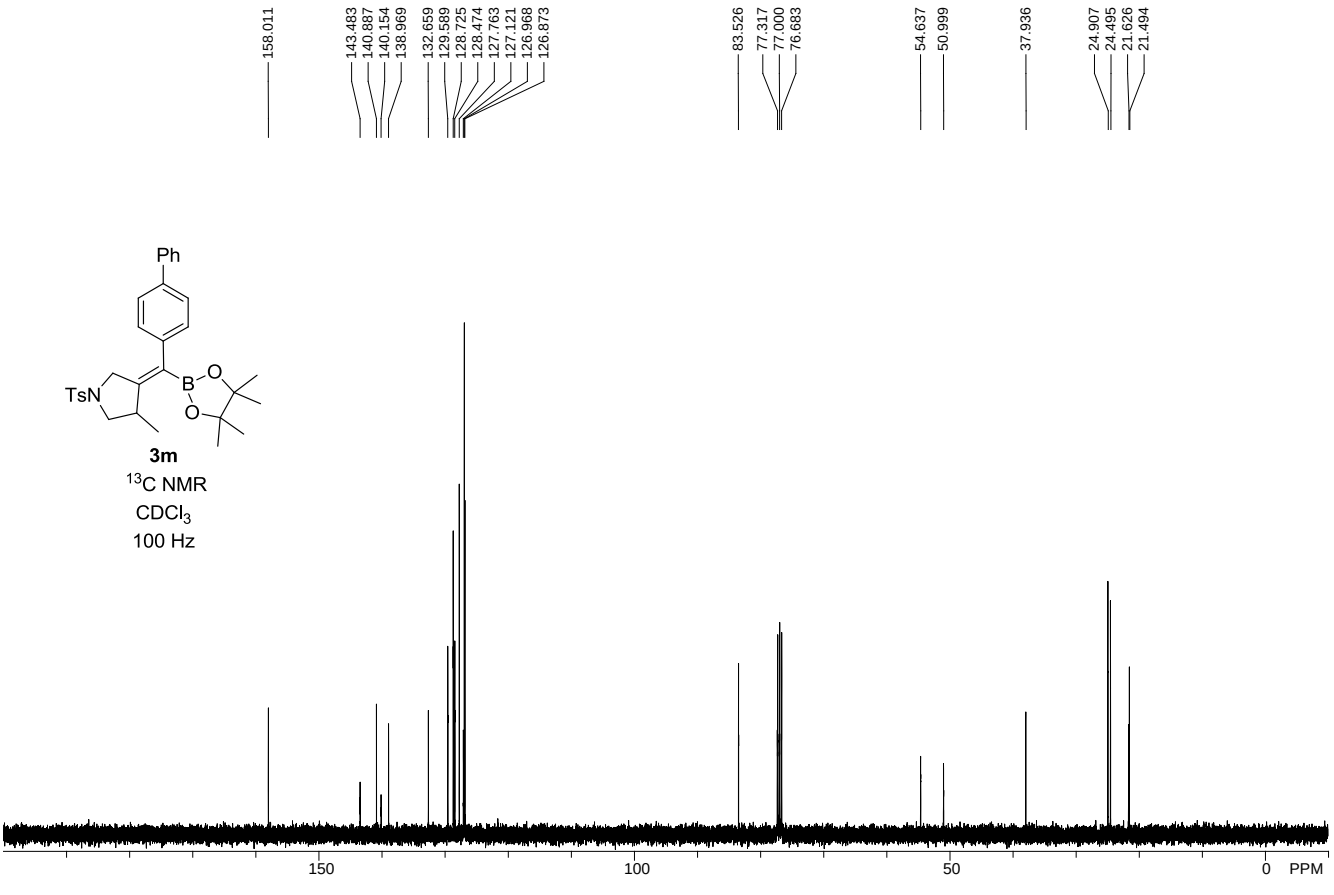
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127.763
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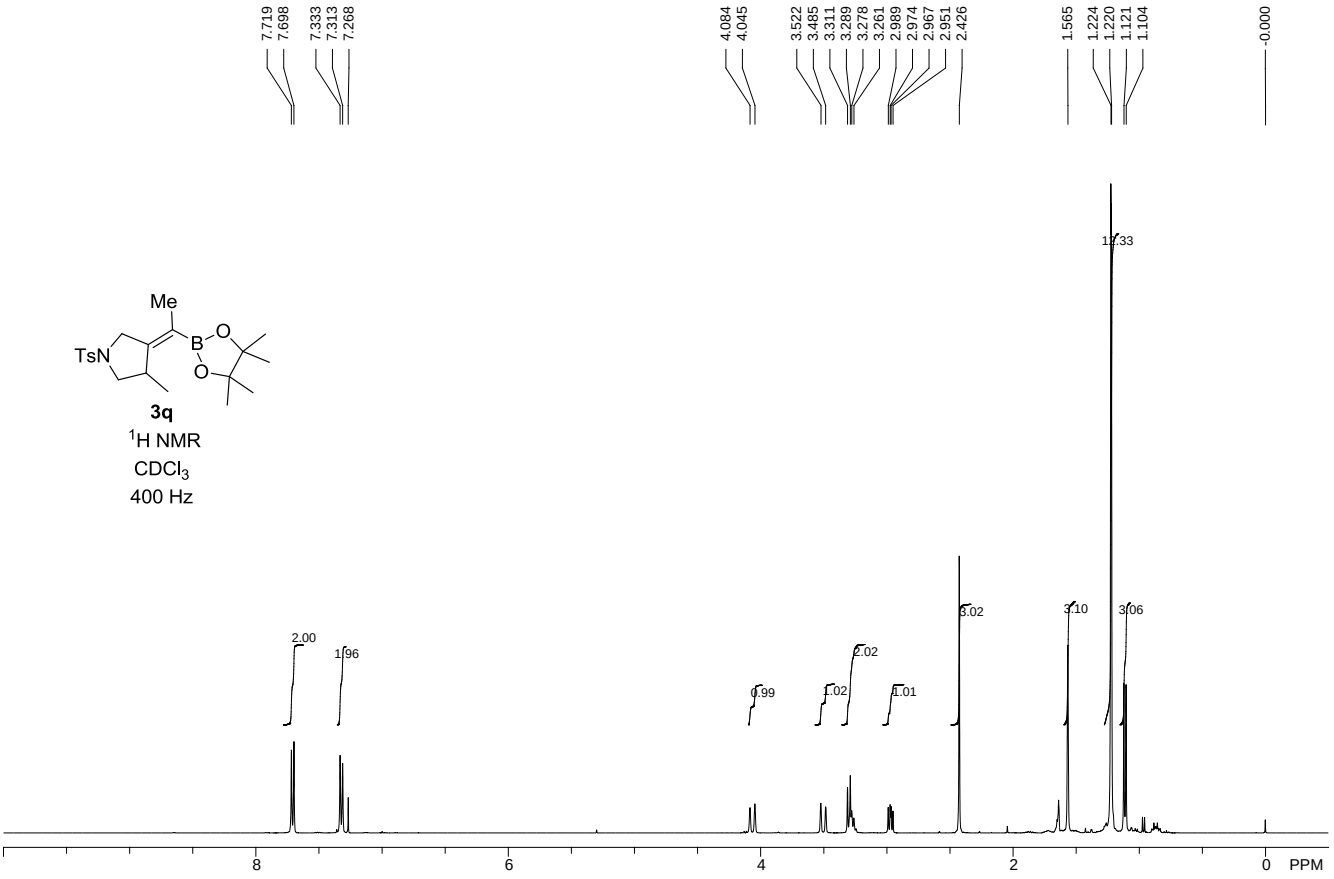
126.968
126.873
83.526
77.317
77.000
76.683
54.637
50.999
37.936
24.907
24.495
21.626
21.494
Ph
TsN
B
O
O
3m
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM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7.333
7.313
7.268
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4.045
3.522
3.485
3.311
3.289
3.278
3.261
2.989
2.974
2.967
2.951
2.426
1.565
1.224
1.220
1.121
1.104
-0.000
Me
TsN
B
O
O
3q
1H NMR
CDCl3
400 Hz
2.00
1.96
0.99
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2.02
1.01
3.02
3.10
3.06
12.33
8
6
4
2
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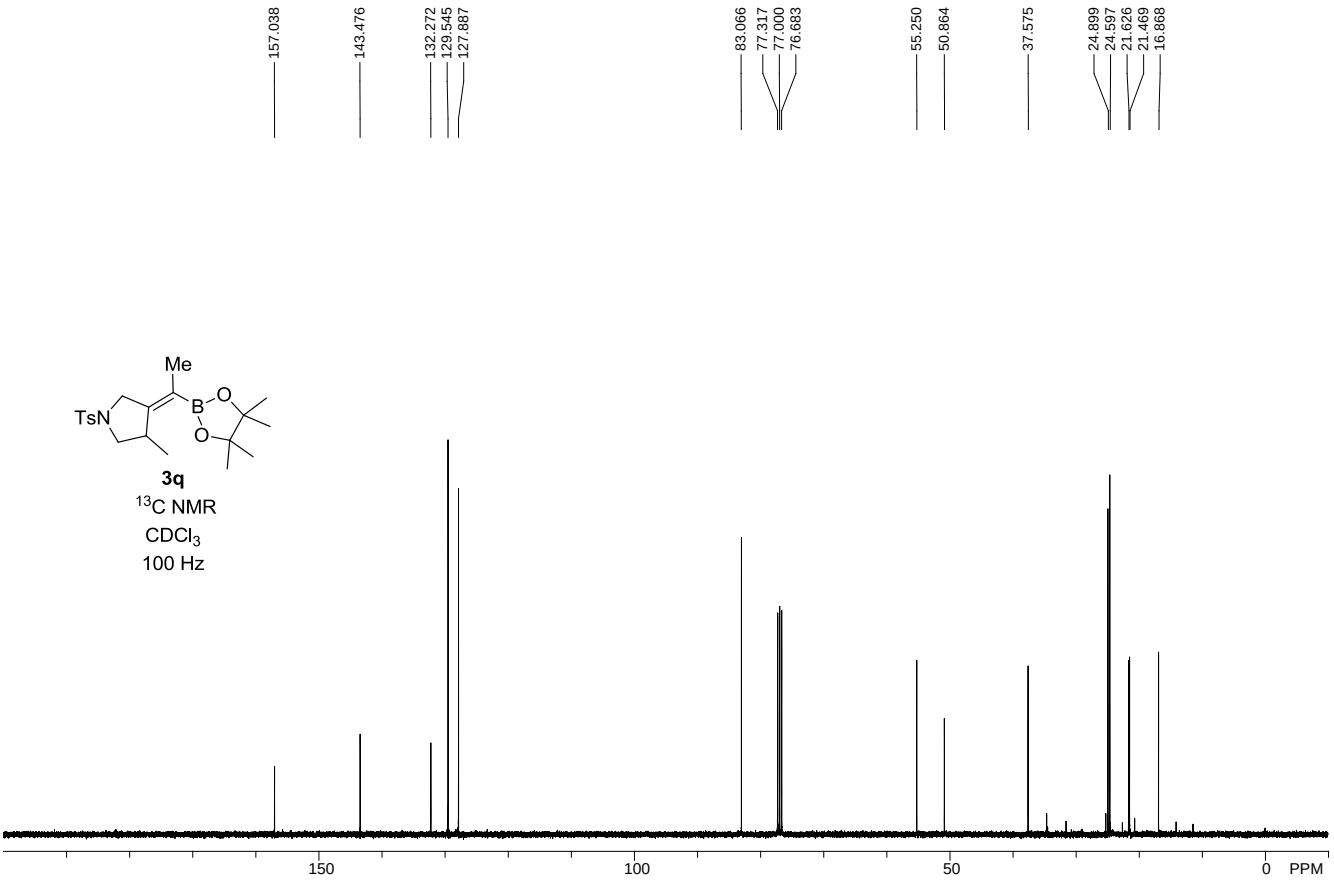
PPM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132.272
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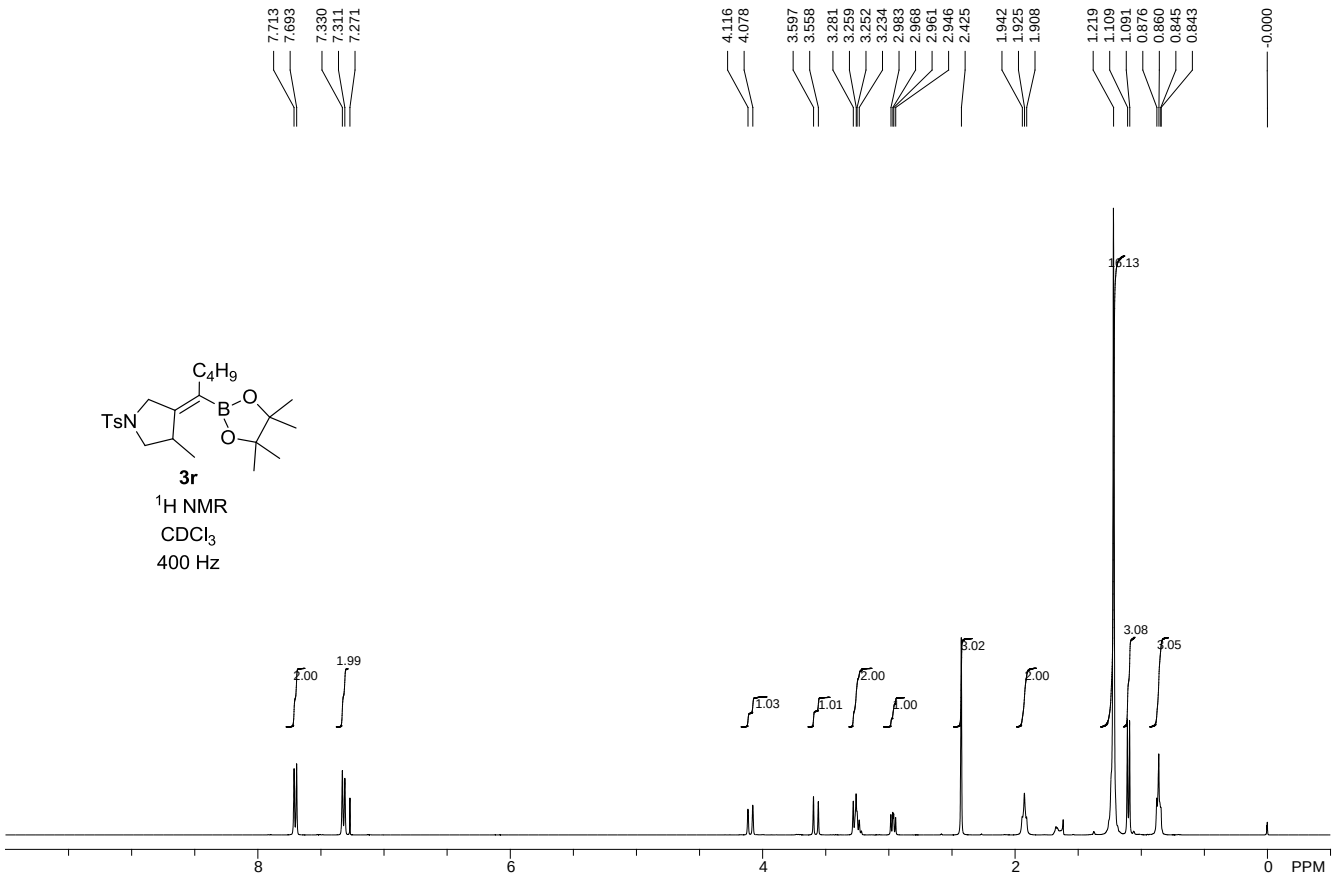
127.887
83.066
77.317
77.000
76.683
55.250
50.864
37.575
24.899
24.597
21.626
21.469
16.868
Me
TsN
B
O
O
3q
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM

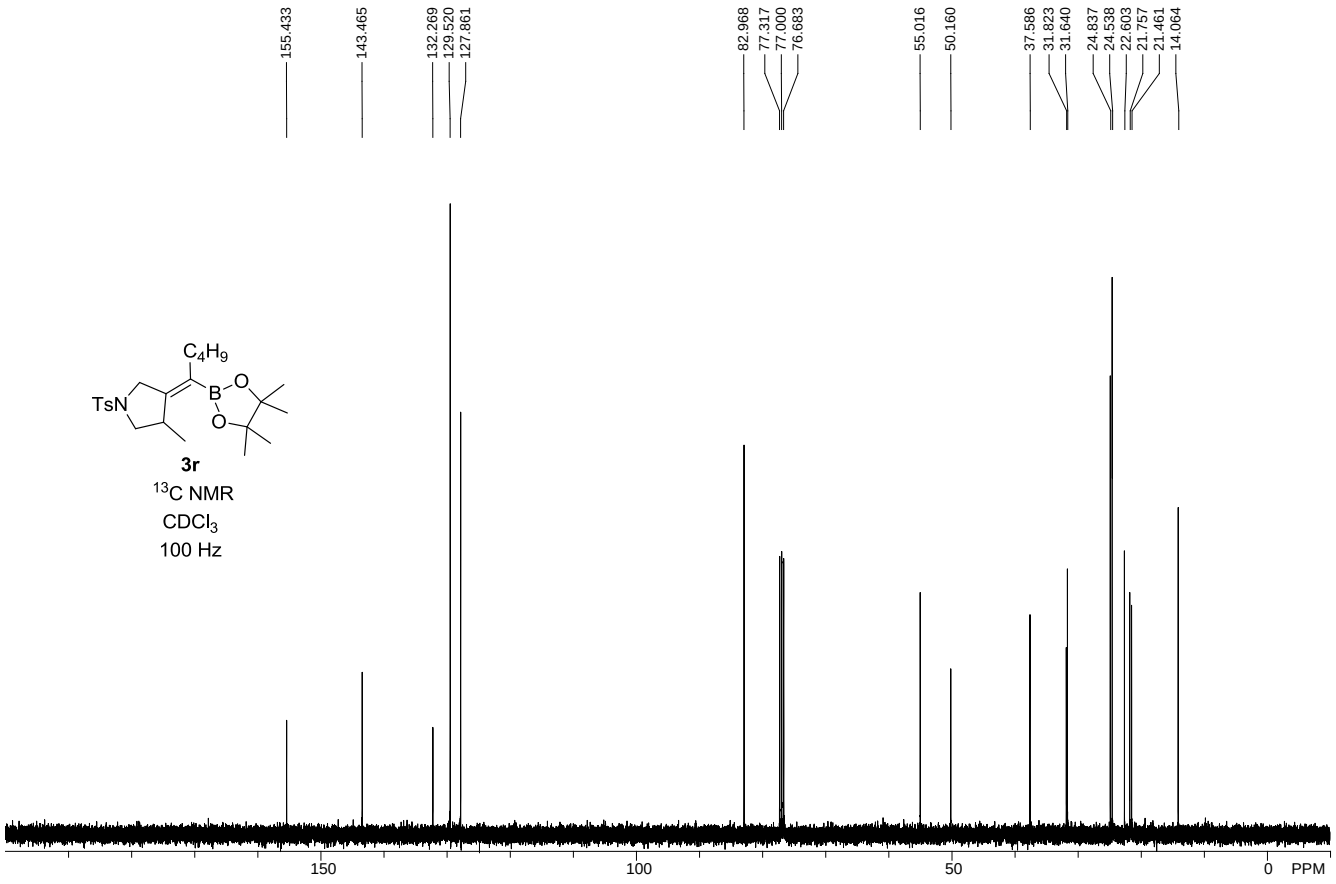


3r

^{1}H NMR

$CDCl_3$

400 Hz

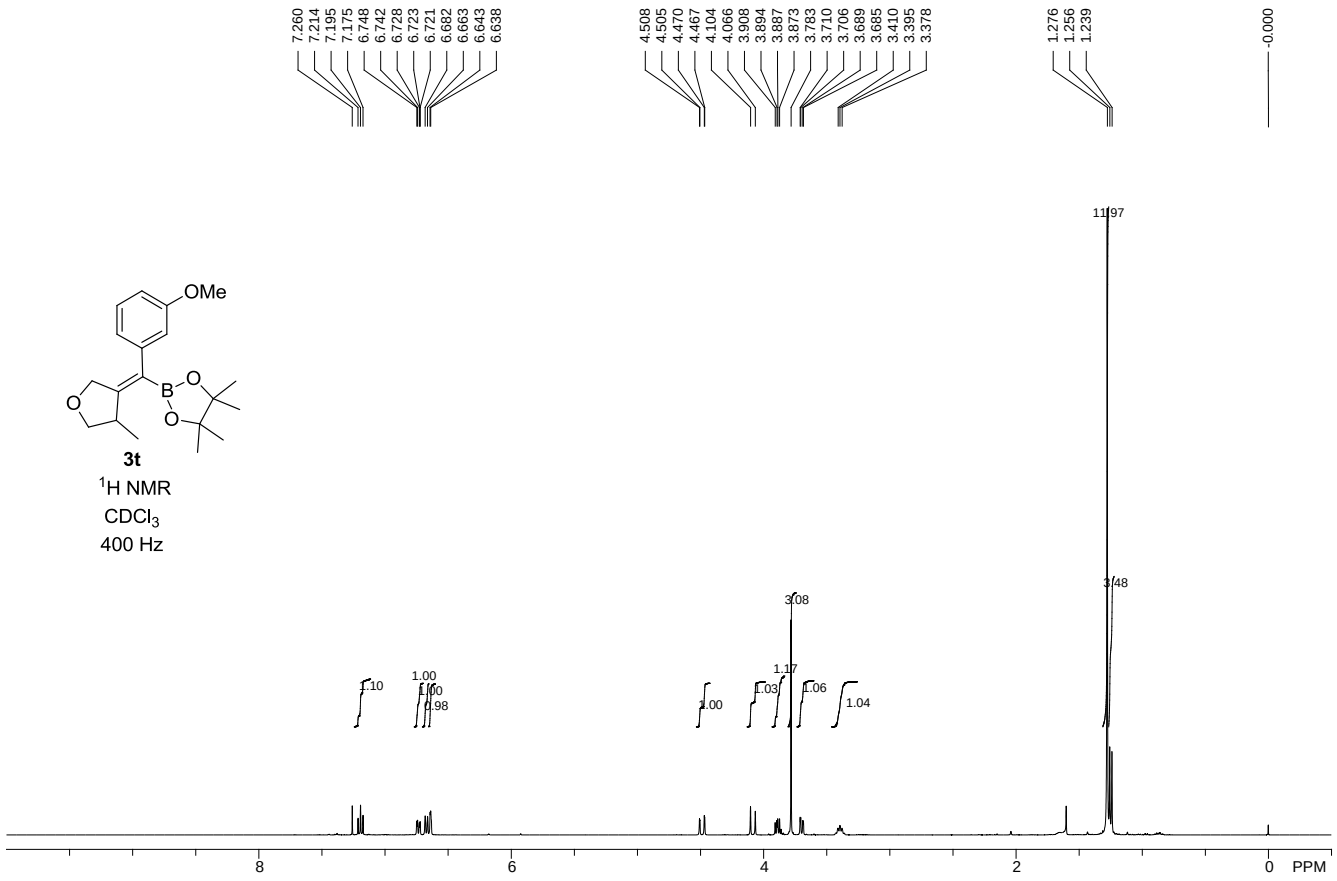


3r

^{13}C NMR

$CDCl_3$

100 Hz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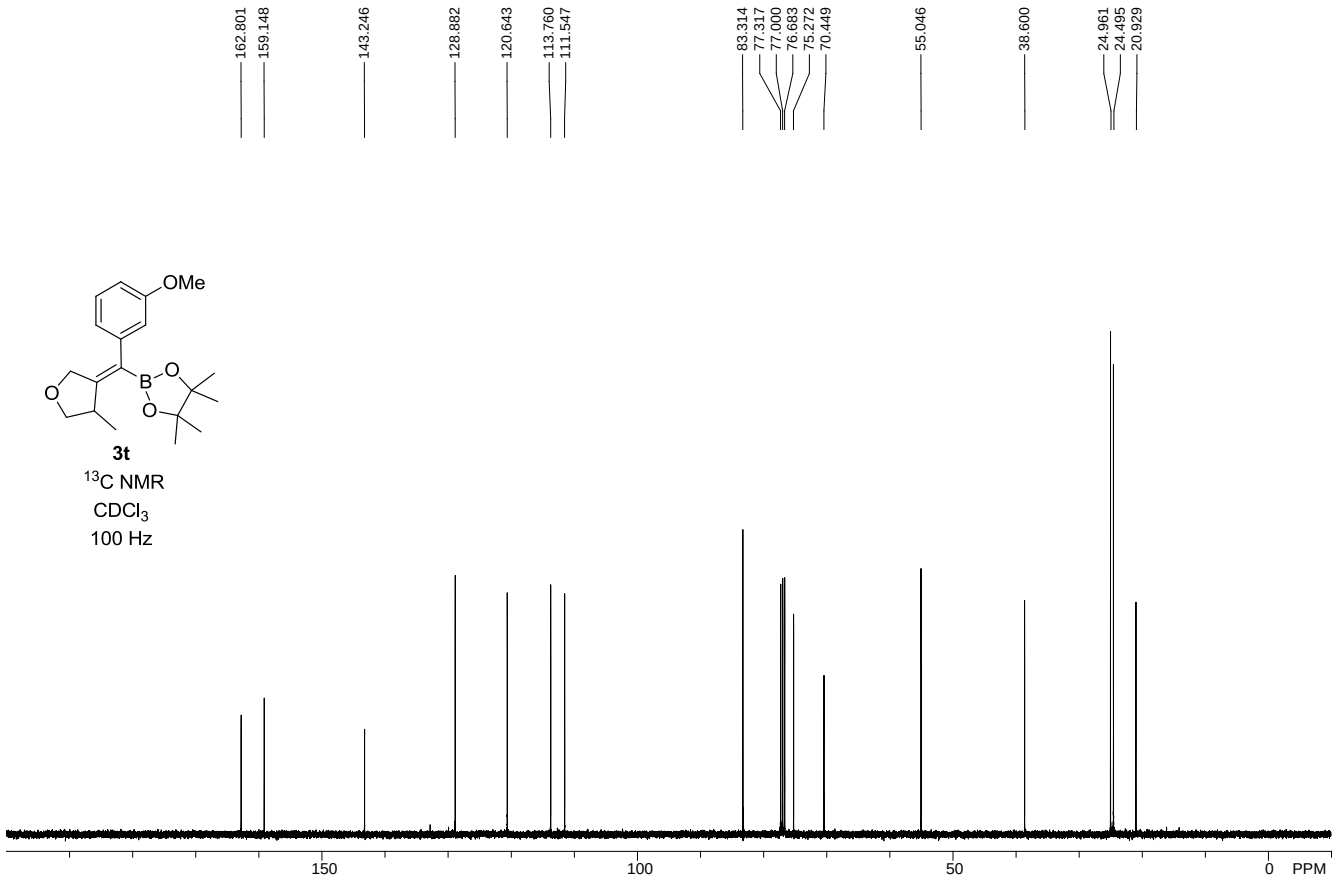
7.175
6.748
6.742
6.728
6.723
6.721
6.682
6.663
6.643
6.638
4.508
4.505
4.470
4.467
4.104
4.066
3.908
3.894
3.887
3.873
3.783
3.710
3.706
3.689
3.685
3.410
3.395
3.378
1.276
1.256
1.239
-0.000
OMe
O
B
O
O
3t
1H NMR
CDCl3
400 Hz
11.97
3.48
3.08
1.17
1.10
1.00
1.00
0.98
1.03
1.06
1.04
1.00
8
6
4
2
0
PPM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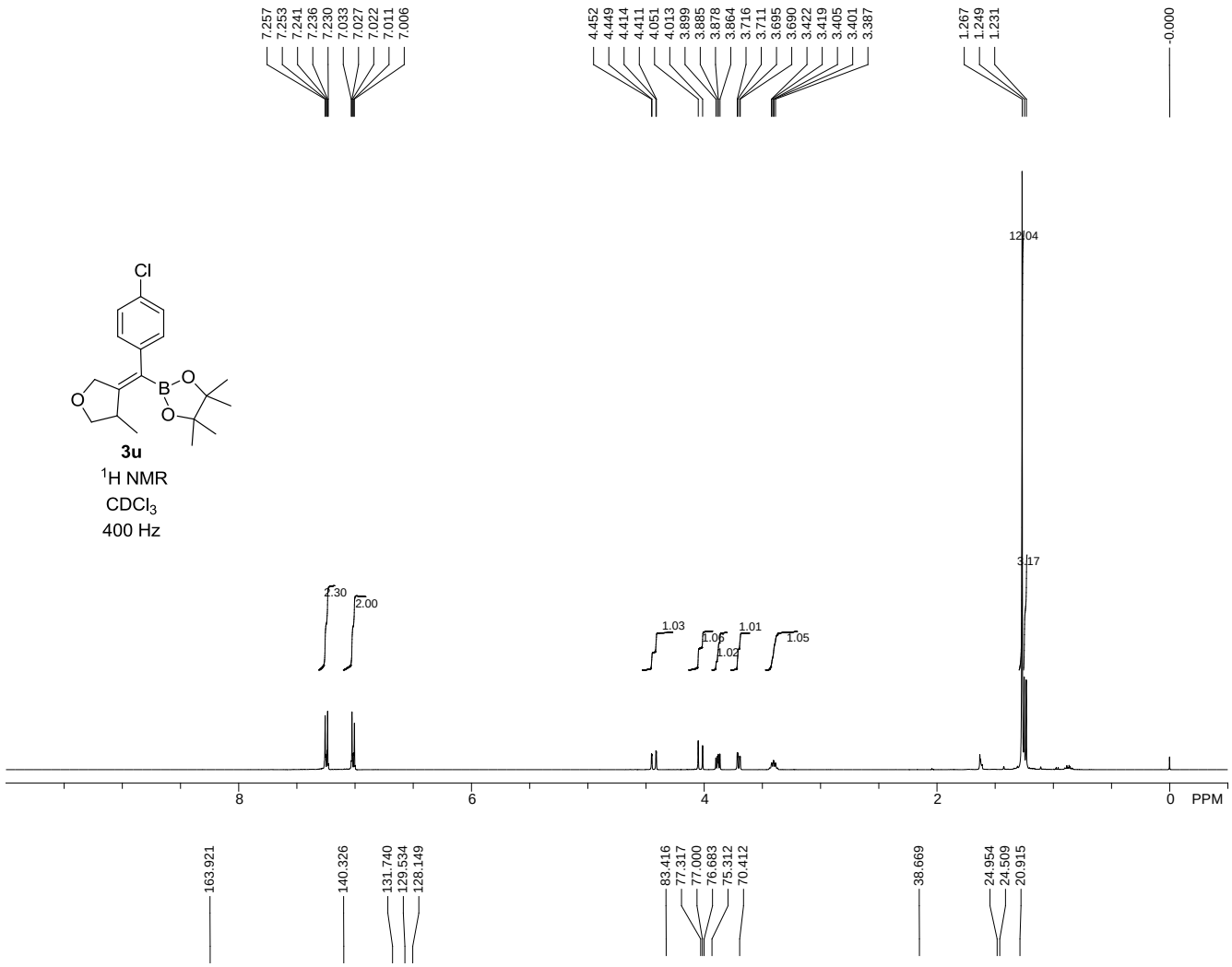
143.246
128.882
120.643
113.760
111.547
83.314
77.317
77.000
76.683
75.272
70.449
55.046
38.600
24.961
24.495
20.929
OMe
O
B
O
O
3t
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM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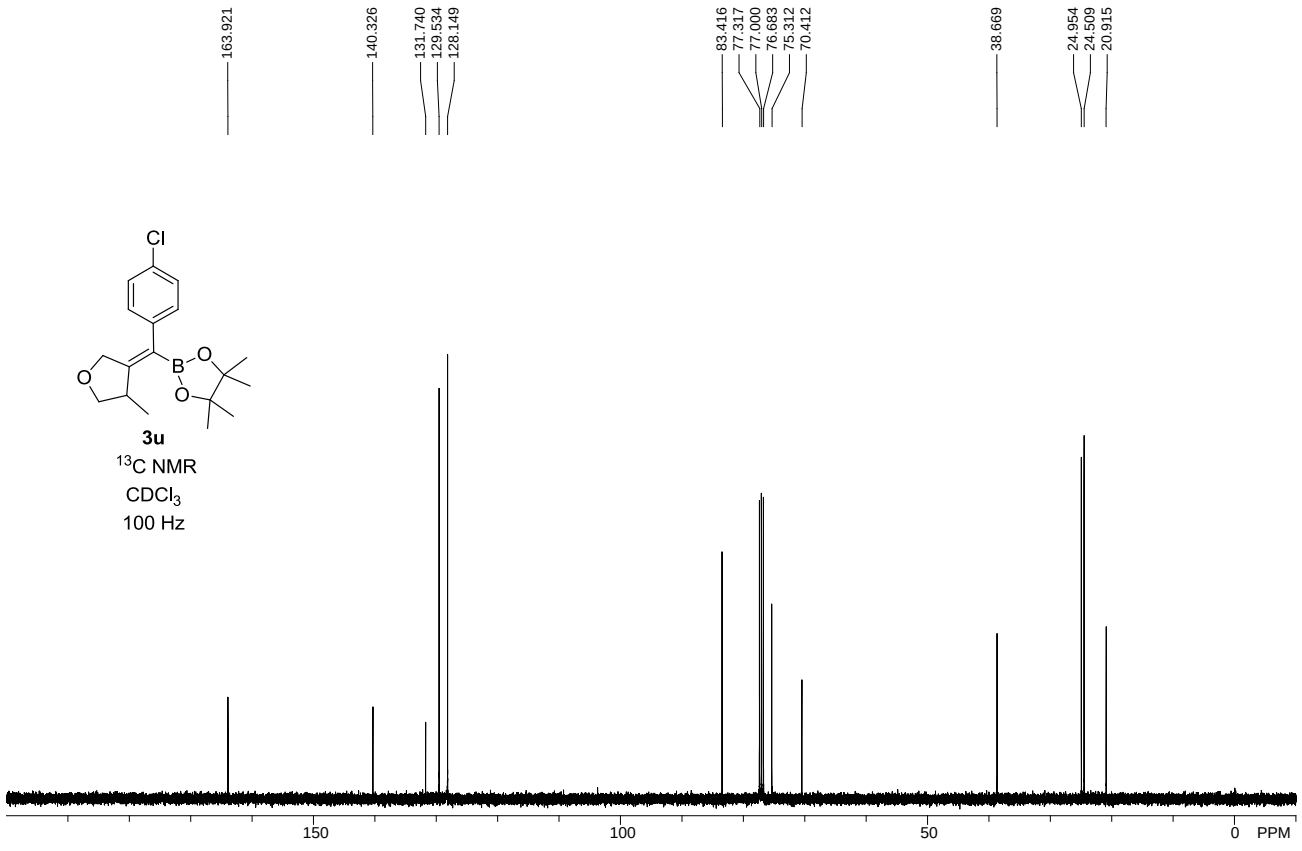
7.027
7.022
7.011
7.006
4.452
4.449
4.414
4.411
4.051
4.013
3.899
3.885
3.878
3.864
3.716
3.711
3.695
3.690
3.422
3.419
3.405
3.401
3.387
1.267
1.249
1.231
-0.000
12.04
3.17
2.30
2.00
1.03
1.06
1.02
1.01
1.05
Cl
O
B
O
O
3u
1H NMR
CDCl3
400 Hz
8
6
4
2
0
PPM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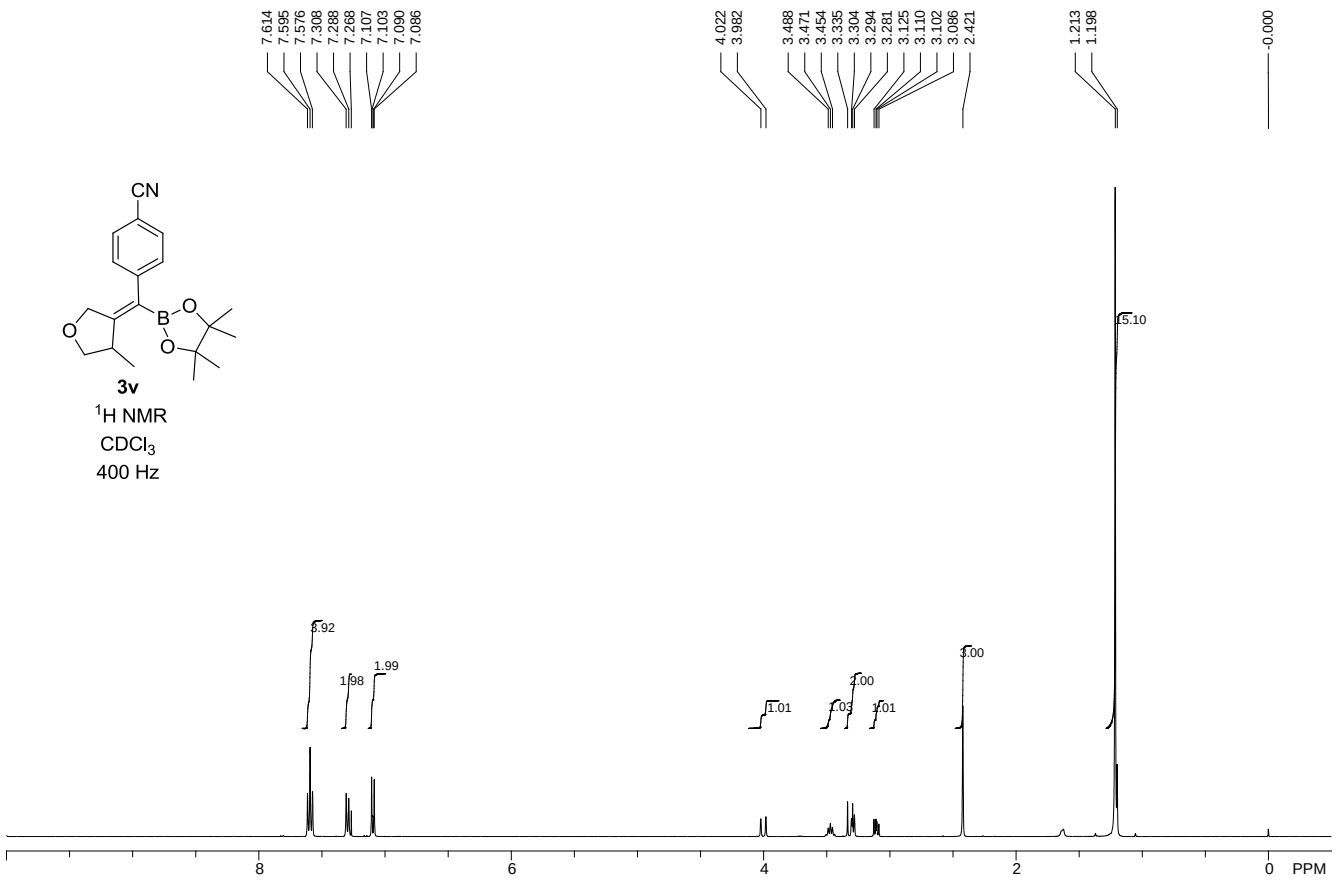
131.740
129.534
128.149
83.416
77.317
77.000
76.683
75.312
70.412
38.669
24.954
24.509
20.915
Cl
O
B
O
O
3u
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM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7.576
7.308
7.288
7.268
7.107
7.103
7.090
7.086
4.022
3.982
3.488
3.471
3.454
3.335
3.304
3.294
3.281
3.125
3.110
3.102
3.086
2.421
1.213
1.198
-0.000
CN
O
B
O
O
3v
1H NMR
CDCl3
400 Hz
15.10
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1.99
1.01
1.03
1.00
1.01
3.00
8
6
4
2
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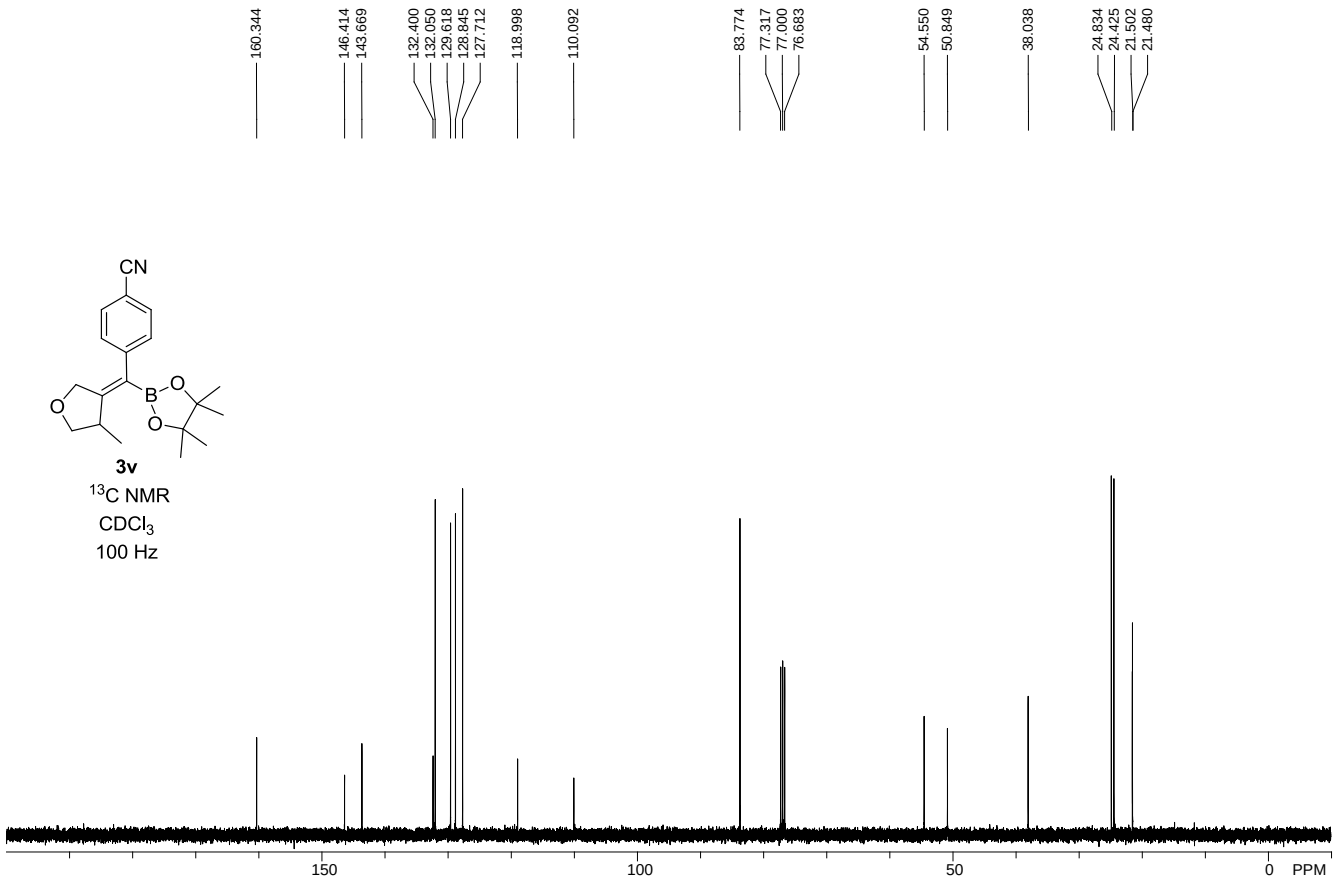
PPM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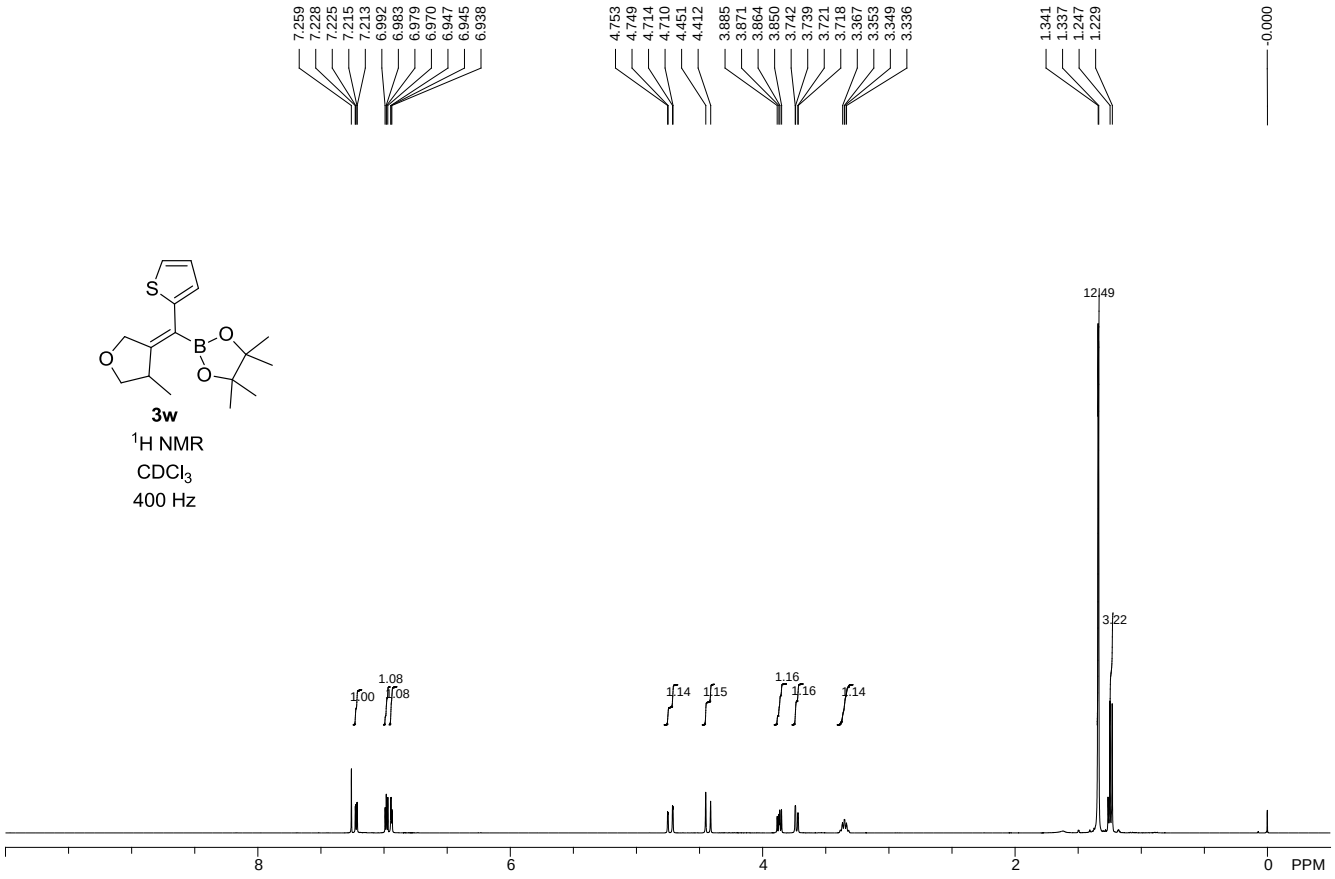
132.400
132.050
129.618
128.845
127.712
118.998
110.092
83.774
77.317
77.000
76.683
54.550
50.849
38.038
24.834
24.425
21.502
21.480
CN
O
B
O
O
3v
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM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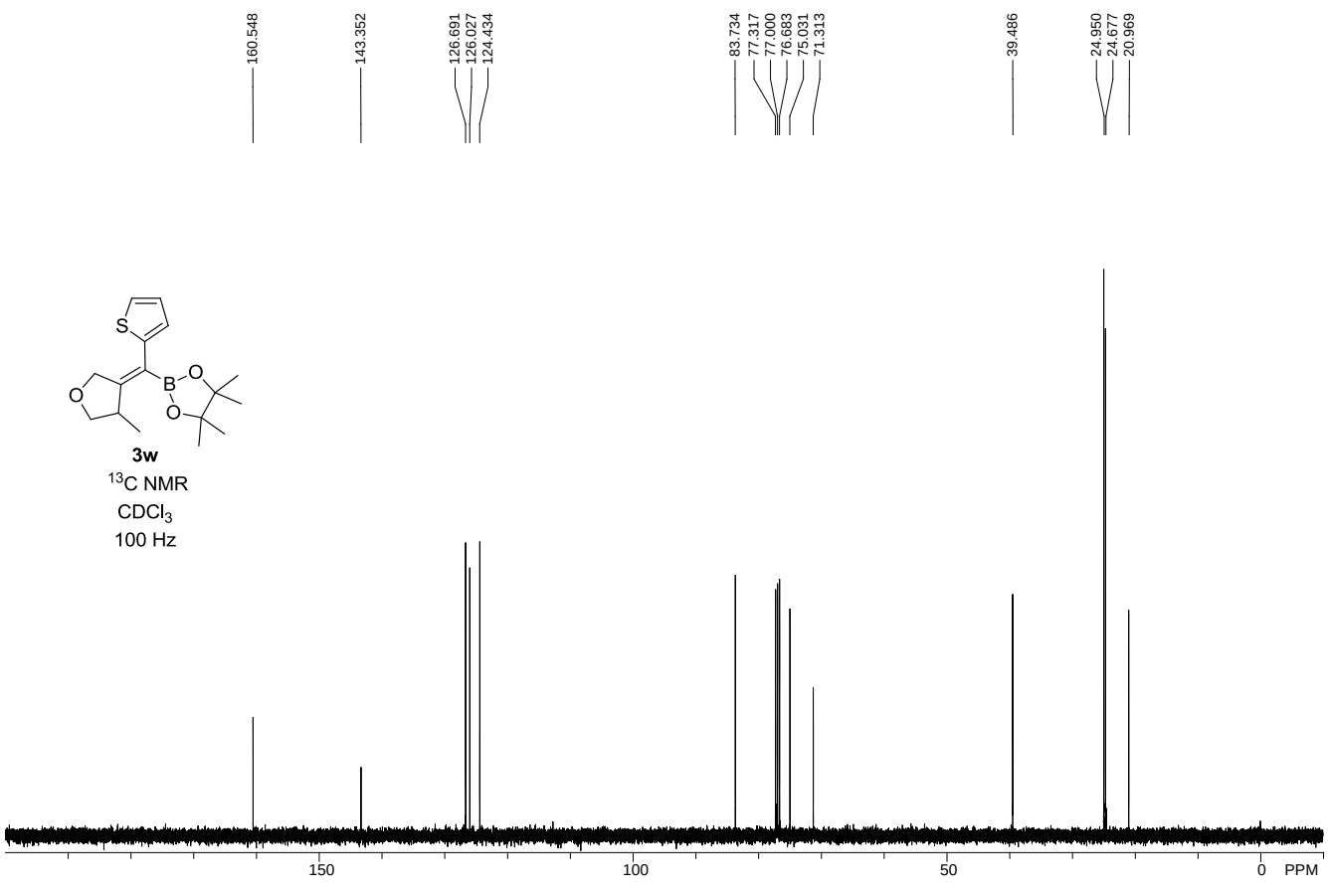
7.215
7.213
6.992
6.983
6.979
6.970
6.947
6.945
6.938
4.753
4.749
4.714
4.710
4.451
4.412
3.885
3.871
3.864
3.850
3.742
3.739
3.721
3.718
3.367
3.353
3.349
3.336
1.341
1.337
1.247
1.229
-0.000
3w
1H NMR
CDCl3
400 Hz
12.49
3.22
1.00
1.08
1.08
1.14
1.15
1.16
1.16
1.14
8
6
4
2
0
PPM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124.434
83.734
77.317
77.000
76.683
75.031
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24.677
20.969
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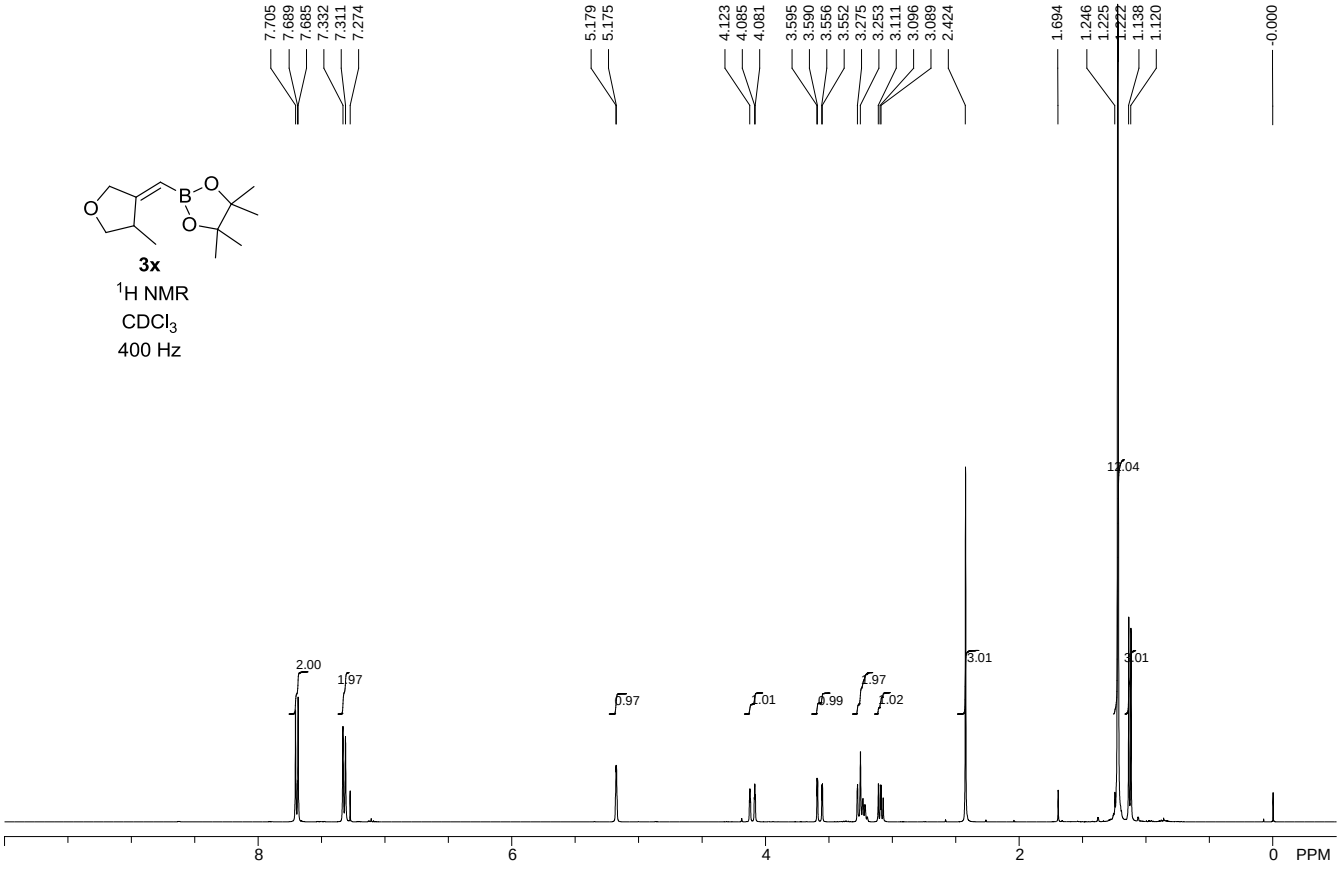
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM

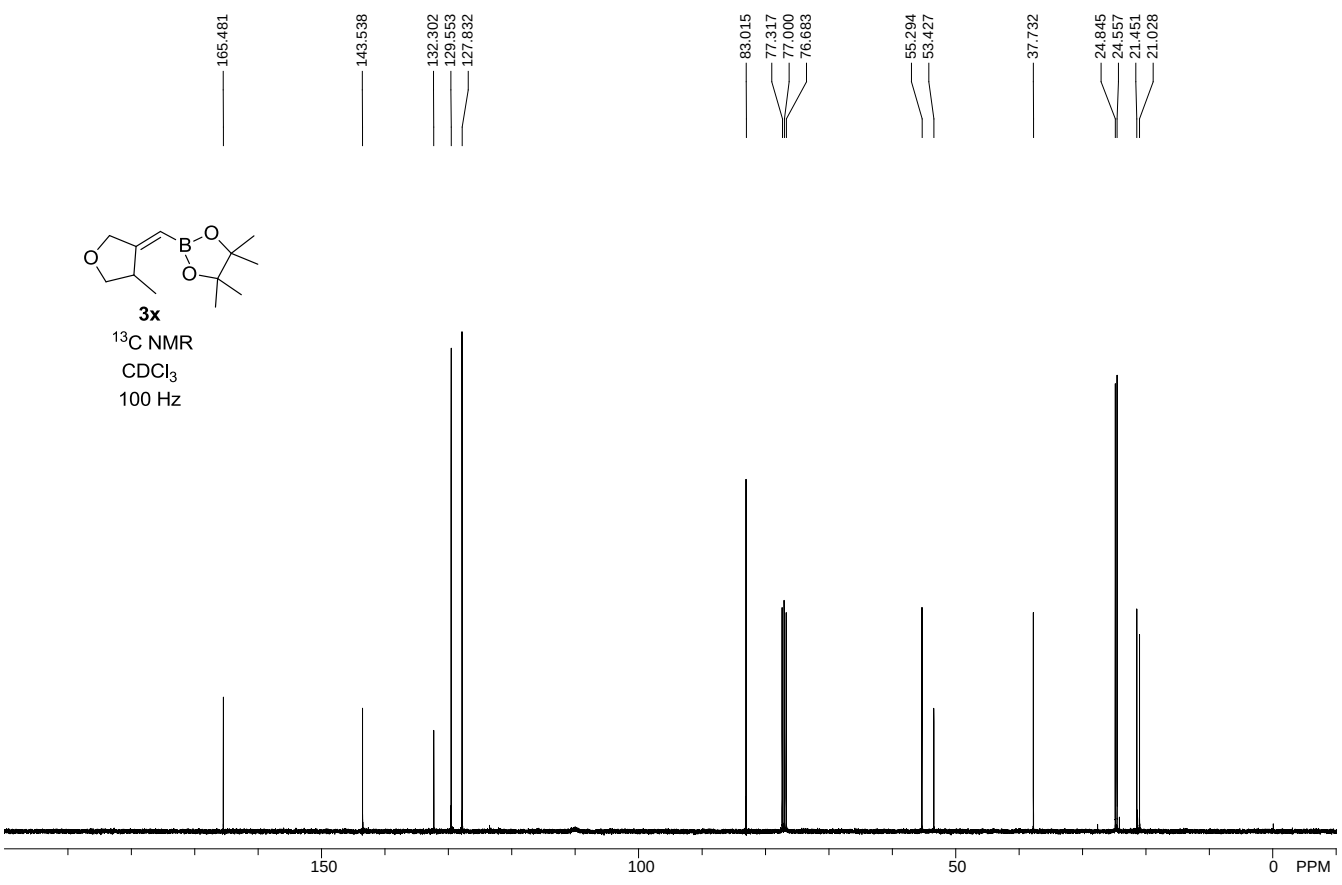


3x

^{1}H NMR

$CDCl_3$

400 Hz

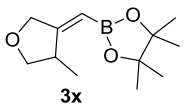


3x

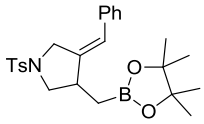
^{13}C NMR

$CDCl_3$

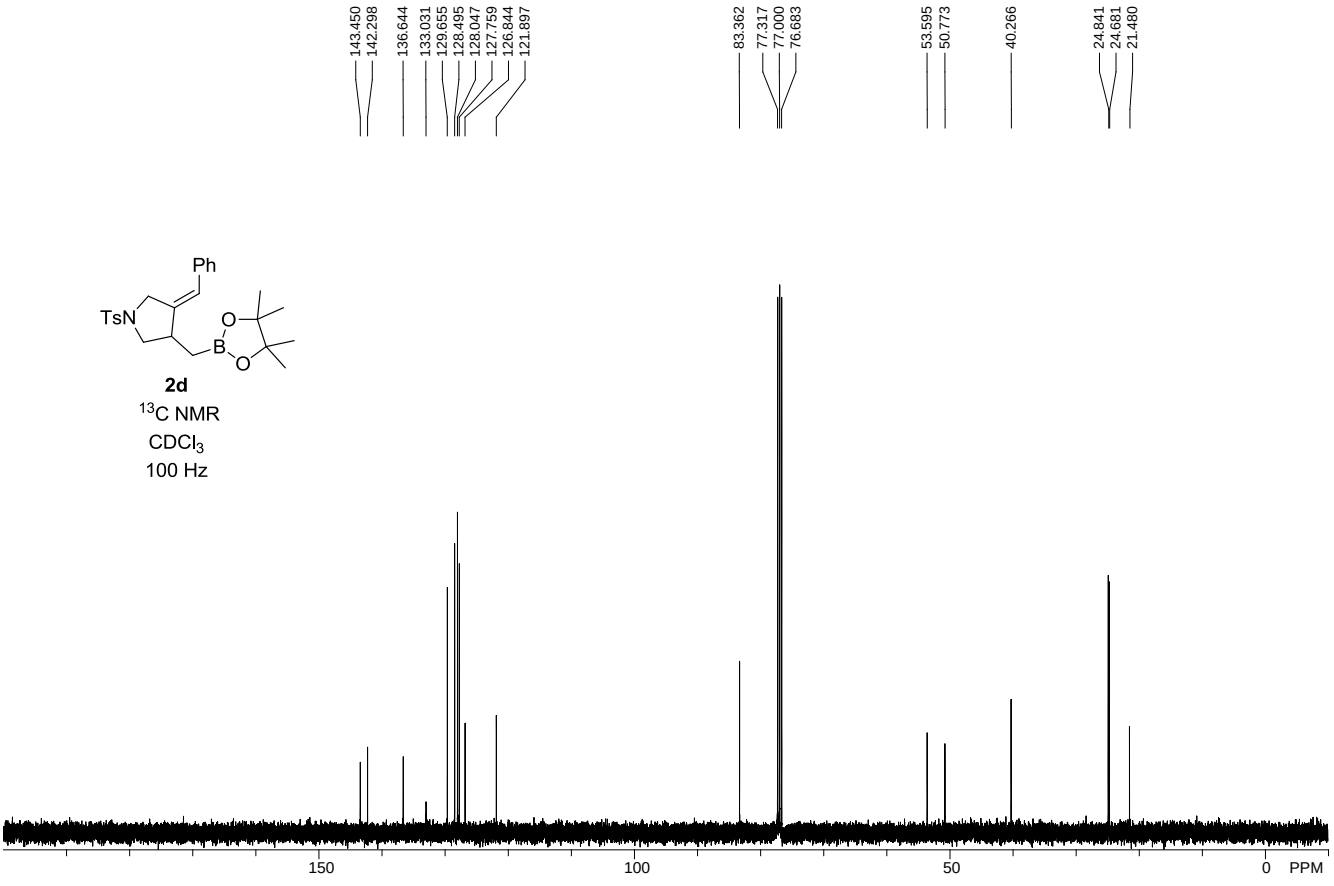
100 Hz



3x
NOE
$CDCl_3$
100 Hz



2d
^1H NMR
$CDCl_3$
400 Hz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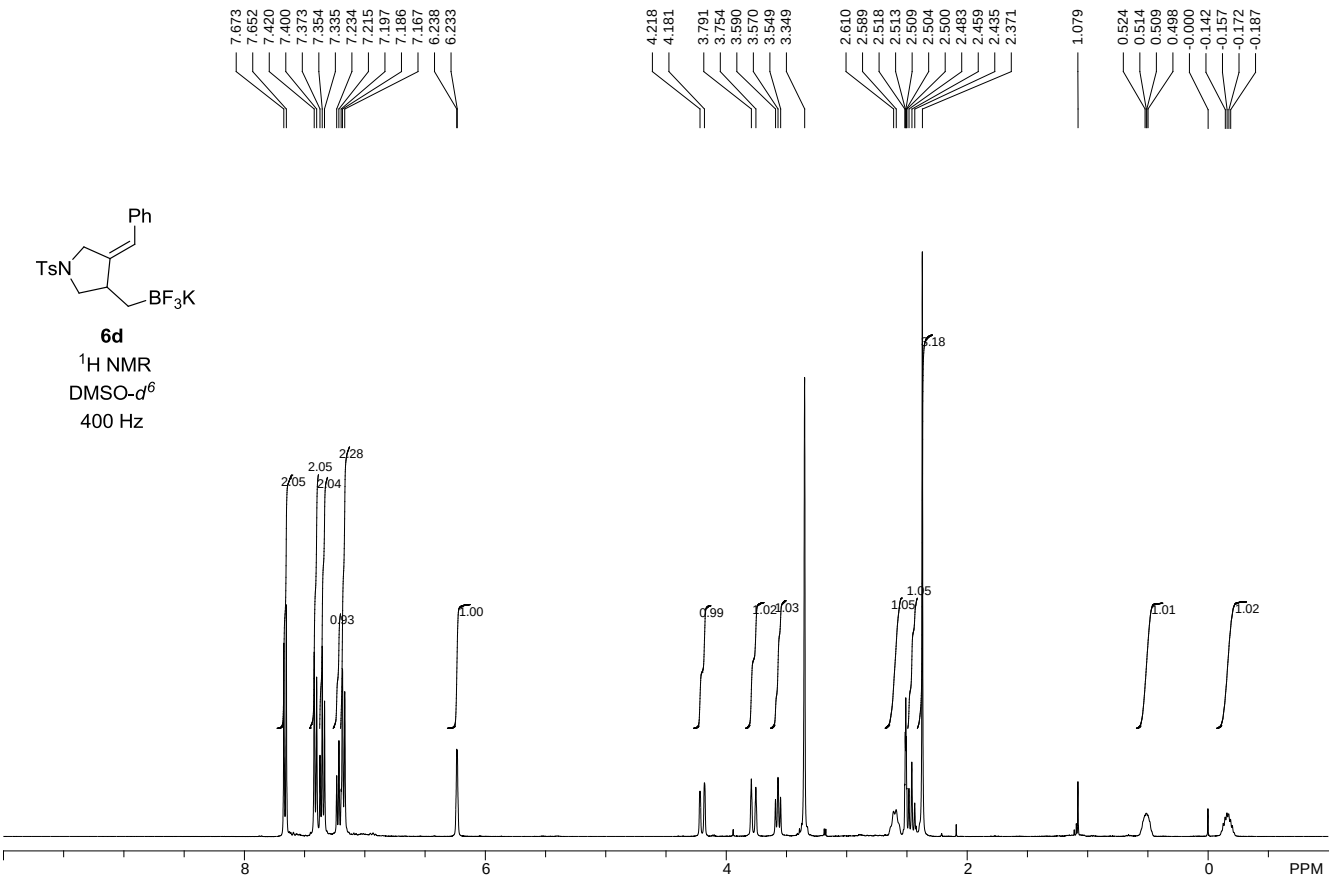
133.031
129.655
128.495
128.047
127.759
126.844
121.897
83.362
77.317
77.000
76.683
53.595
50.773
40.266
24.841
24.681
21.480
Ph
TsN
O
B
O
2d
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM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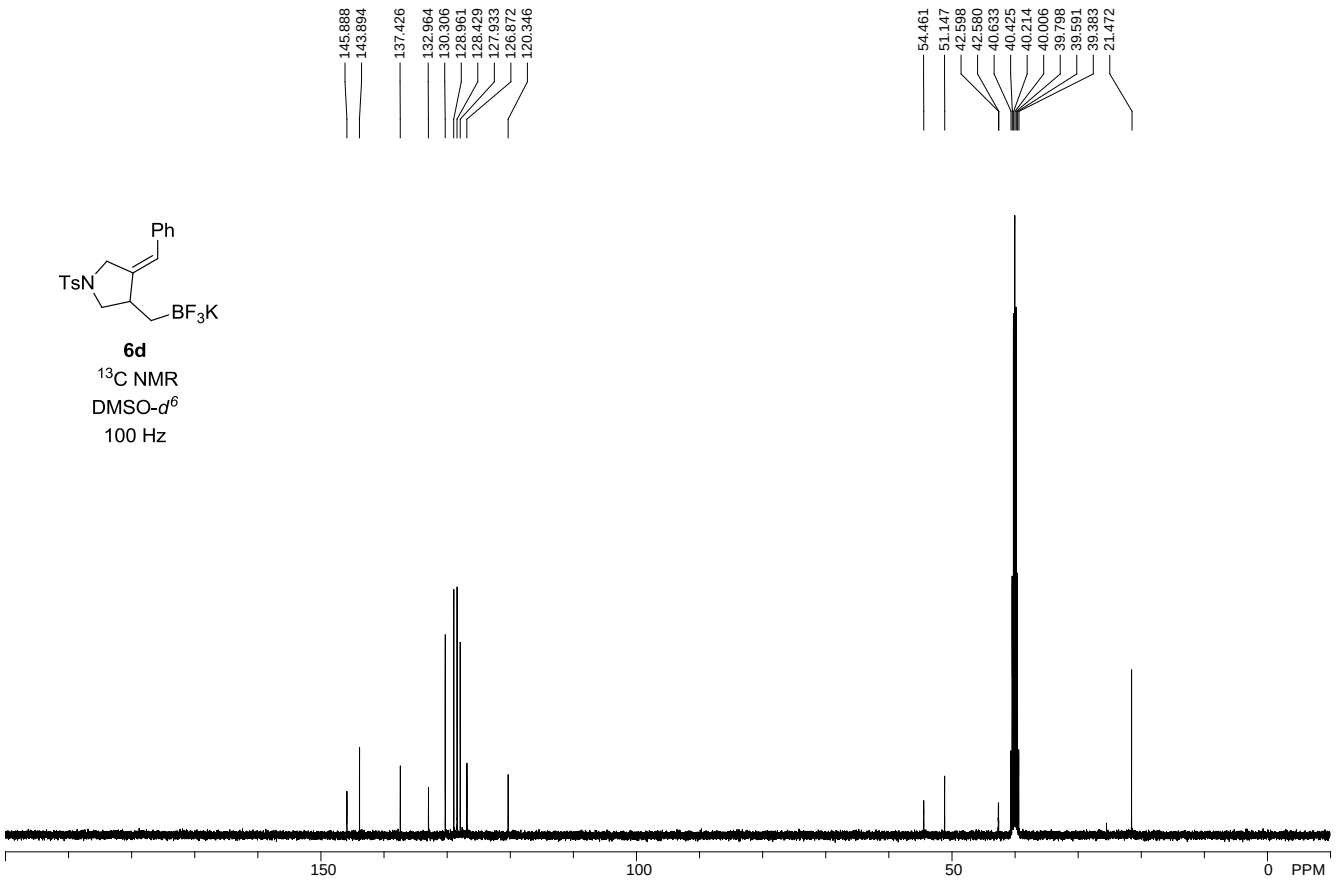
7.197
7.186
7.167
6.238
6.233
4.218
4.181
3.791
3.754
3.590
3.570
3.549
3.349
2.610
2.589
2.518
2.513
2.509
2.504
2.500
2.483
2.459
2.435
2.371
1.079
0.524
0.514
0.509
0.498
-0.000
-0.142
-0.157
-0.172
-0.187
Ph
TsN
BF3K
6d
1H NMR
DMSO-d6
400 Hz
2.05
2.05
2.04
2.28
0.93
1.00
0.99
1.02
1.03
3.18
1.05
1.05
1.01
1.02
8
6
4
2
0
PPM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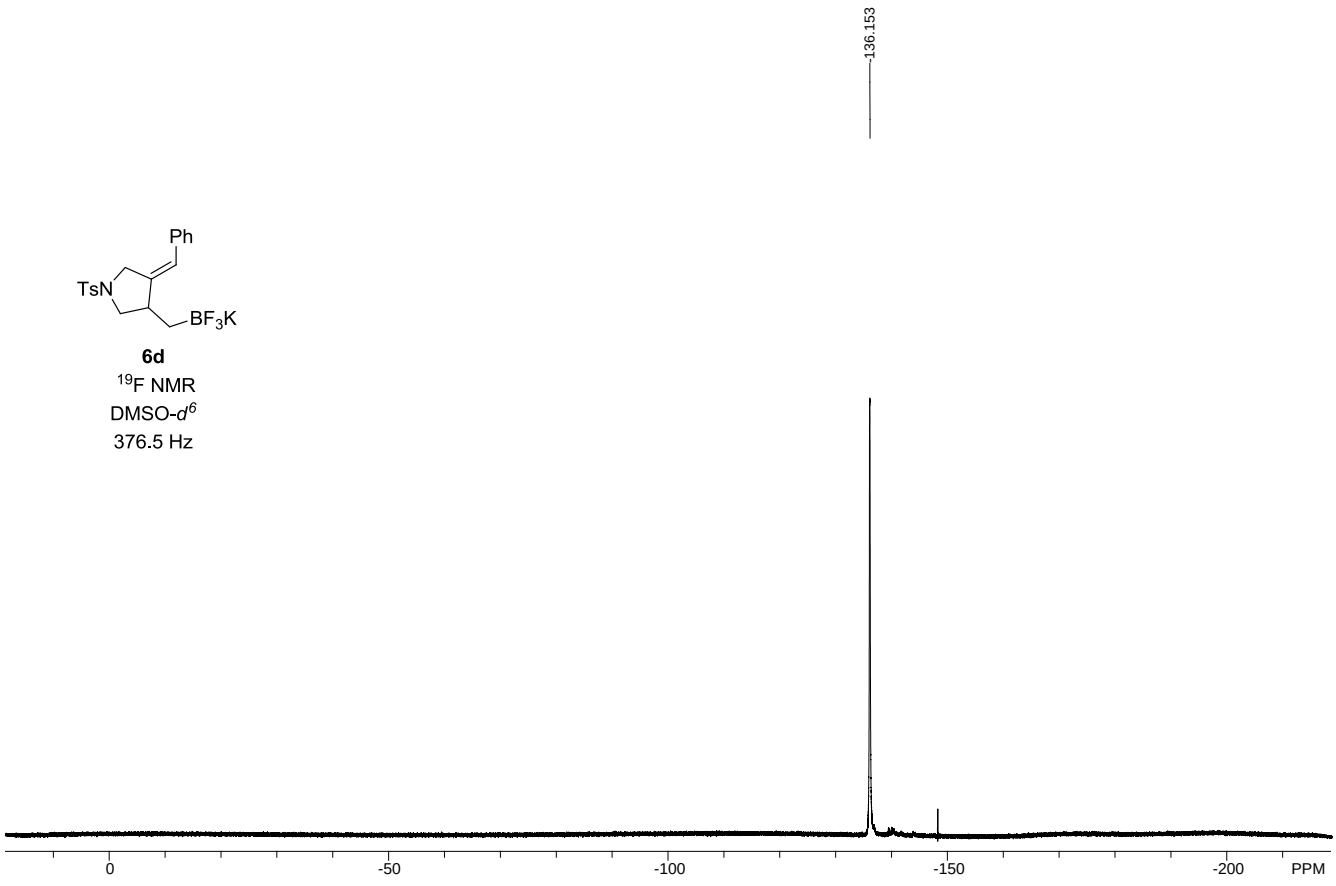
137.426
132.964
130.306
128.961
128.429
127.933
126.872
120.346
54.461
51.147
42.598
42.580
40.633
40.425
40.214
40.006
39.798
39.591
39.383
21.472
Ph
TsN
BF3K
6d
13C NMR
DMSO-d6
100 Hz
150
100
50
0
PPM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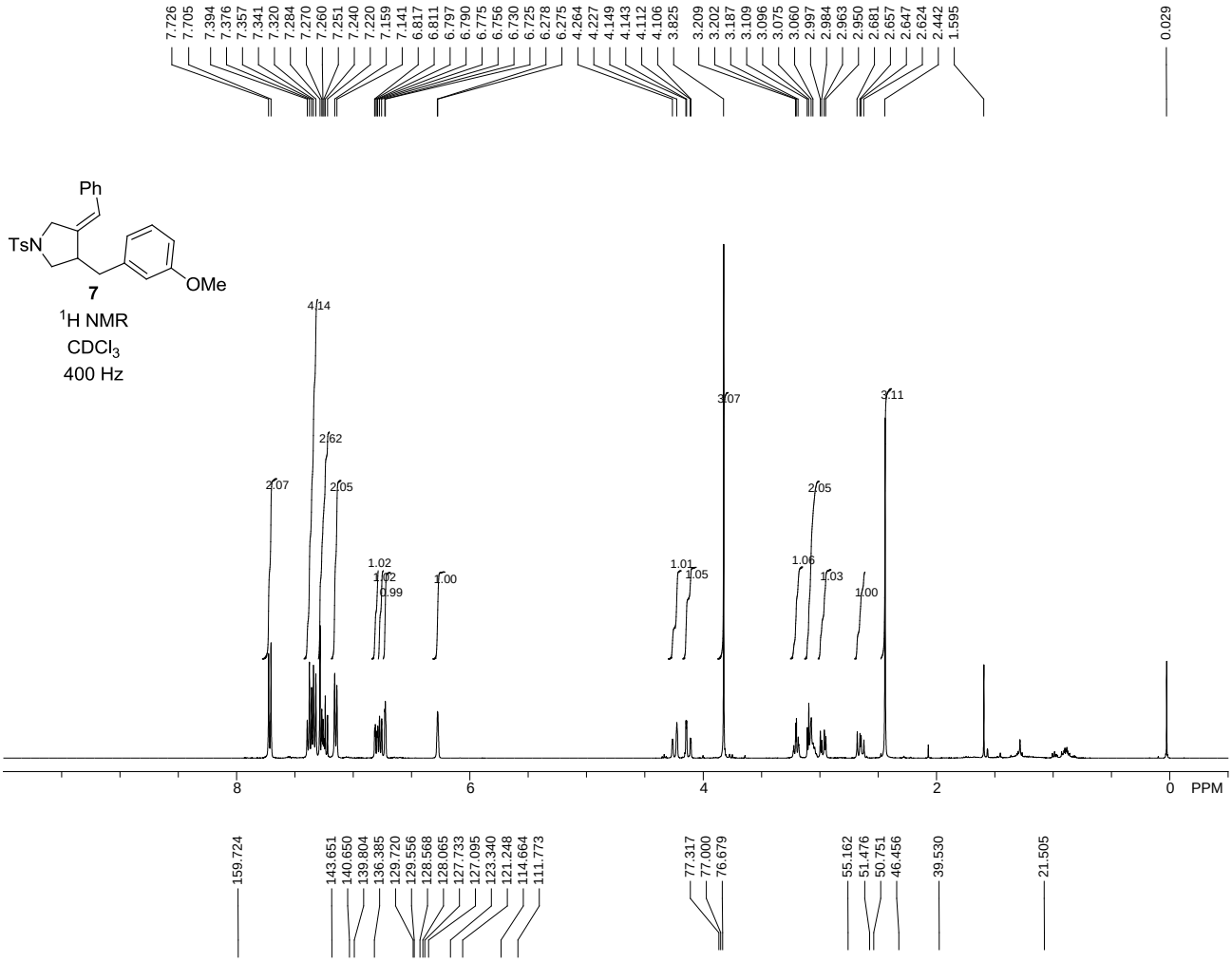
Ph
TsN
BF3K
6d
19F NMR
DMSO-d6
376.5 Hz
0
-50
-100
-150
-200
PPM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7.357
7.341
7.320
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7.260
7.251
7.240
7.220
7.159
7.141
6.817
6.811
6.797
6.790
6.775
6.756
6.730
6.725
6.278
6.275
4.264
4.227
4.149
4.143
4.112
4.106
3.825
3.209
3.202
3.187
3.109
3.096
3.075
3.060
2.997
2.984
2.963
2.950
2.681
2.657
2.647
2.624
2.442
1.595
0.029
Ph
TsN
OMe
7
1H NMR
CDCl3
400 Hz
4.14
3.07
3.11
2.62
2.07
2.05
2.05
1.02
1.02
0.99
1.00
1.01
1.05
1.06
1.03
1.00
8
6
4
2
0
PPM
159.724
143.651
140.650
139.804
136.385
129.720
129.556
128.568
128.065
127.733
127.095
123.340
121.248
114.664
111.773
77.317
77.000
76.679
55.162
51.476
50.751
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21.505
Ph
TsN
OMe
7
13C NMR
CDCl3
100 Hz
150
100
50
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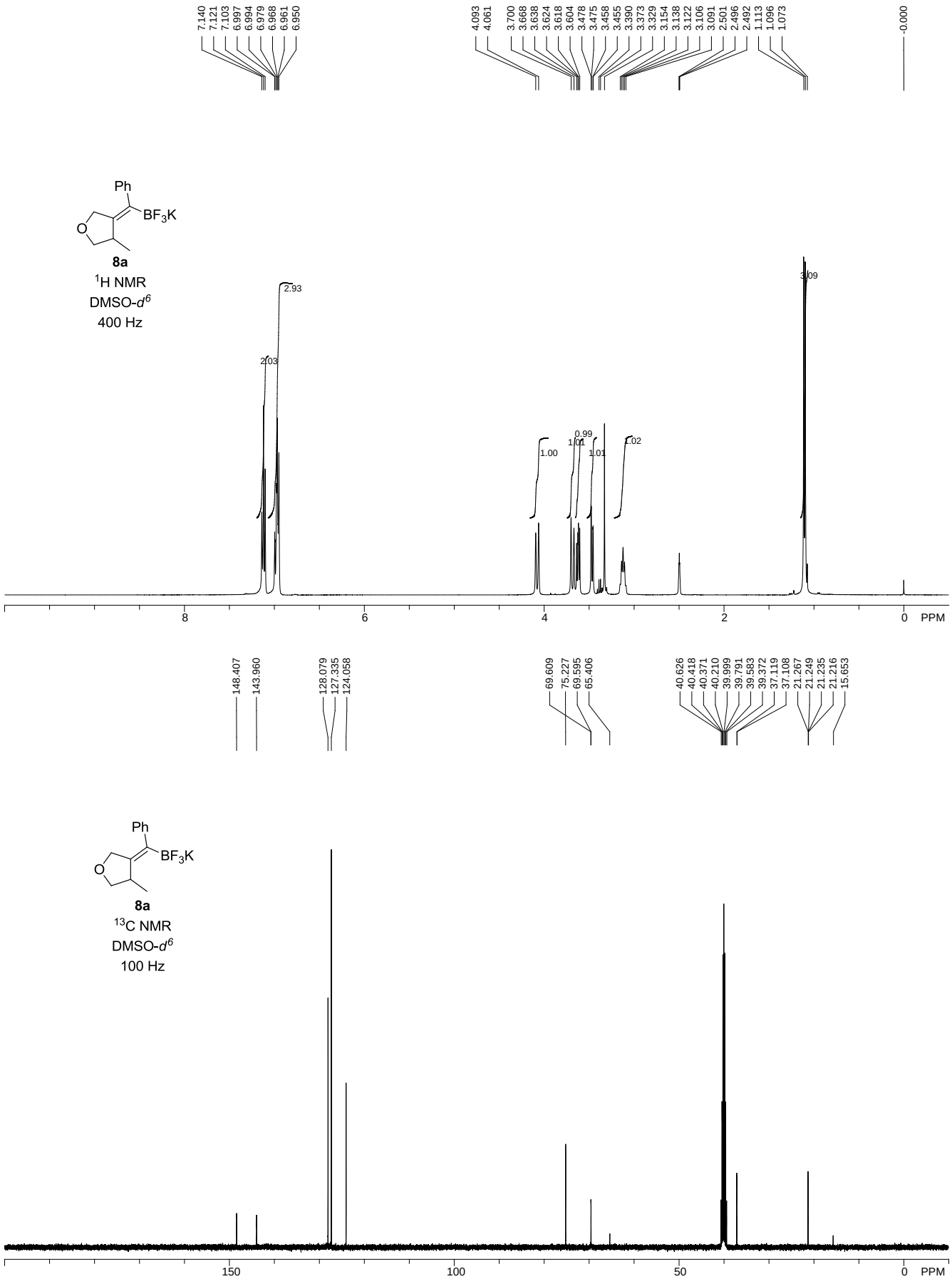
PPM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7.103
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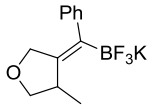
6.994
6.979
6.968
6.961
6.950
4.093
4.061
3.700
3.668
3.638
3.624
3.618
3.604
3.478
3.475
3.458
3.455
3.390
3.373
3.329
3.154
3.138
3.122
3.106
3.091
2.501
2.496
2.492
1.113
1.096
1.073
-0.000
Ph
BF3K
O
8a
1H NMR
DMSO-d6
400 Hz
2.93
2.03
1.00
0.99
1.01
1.01
1.02
3.09
8
6
4
2
0
PPM
148.407
143.960
128.079
127.335
124.058
69.609
75.227
69.595
65.406
40.626
40.418
40.371
40.210
39.999
39.791
39.583
39.372
37.119
37.108
21.267
21.249
21.235
21.216
15.653
Ph
BF3K
O
8a
13C NMR
DMSO-d6
100 Hz
150
100
50
0
PPM

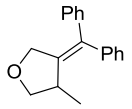


8a

^{19}F NMR

DMSO-*d*^{6}

376.5 Hz

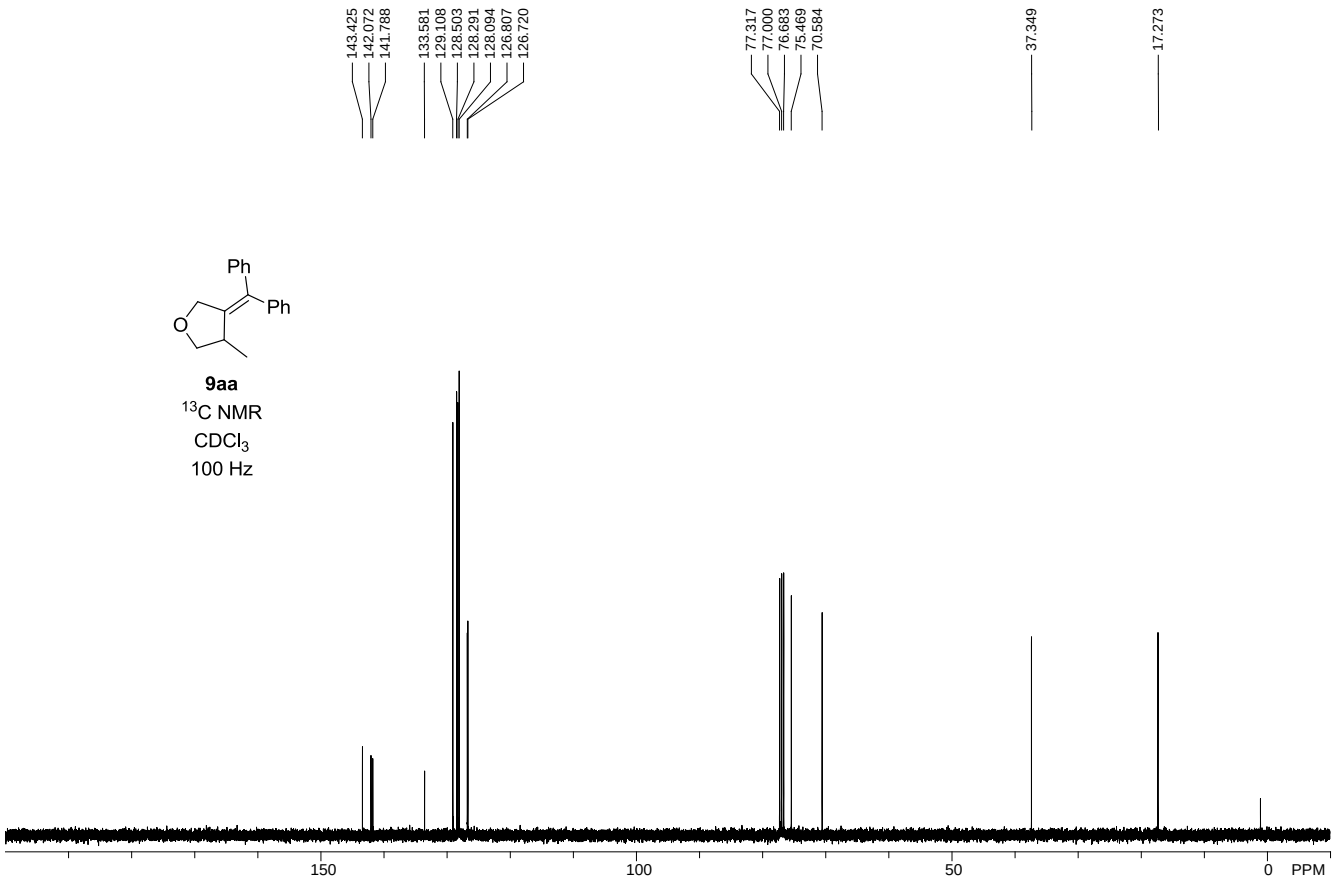


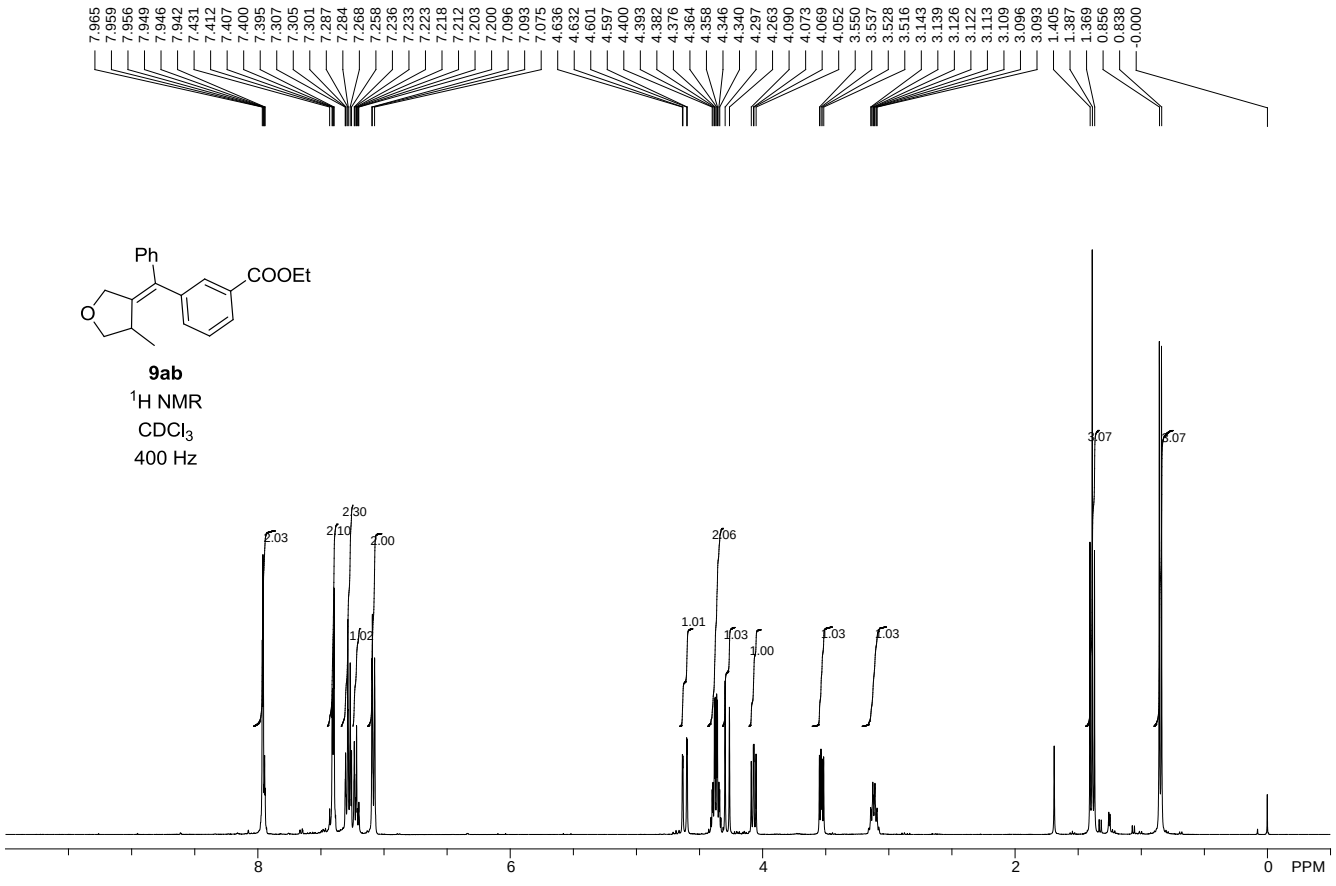
9aa

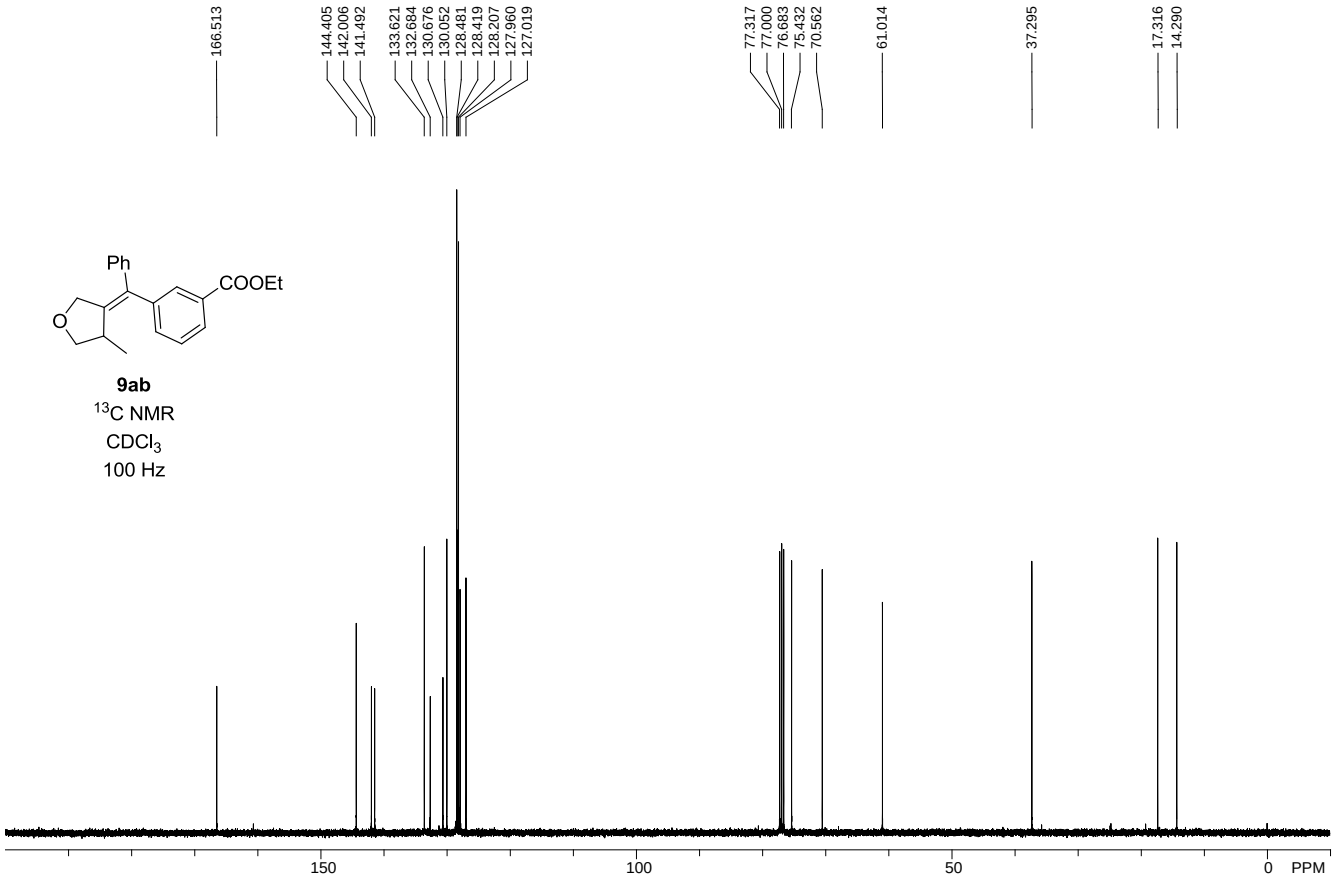
^{1}H NMR

$CDCl_3$

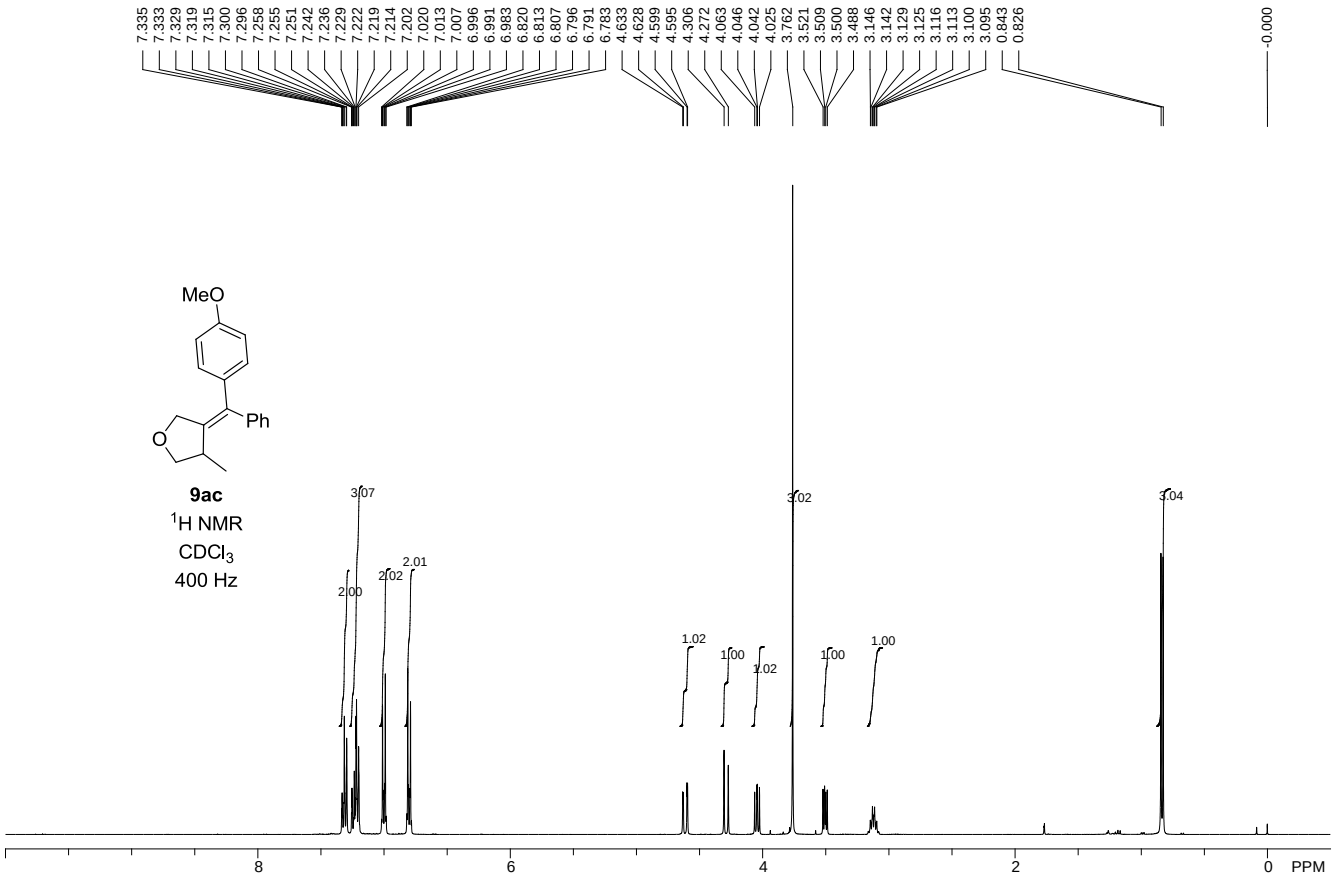
400 Hz


143.425
142.072
141.788
133.581
129.108
128.503
128.291
128.094
126.807
126.720
77.317
77.000
76.683
75.469
70.584
37.349
17.273
Ph
Ph
O
9aa
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM

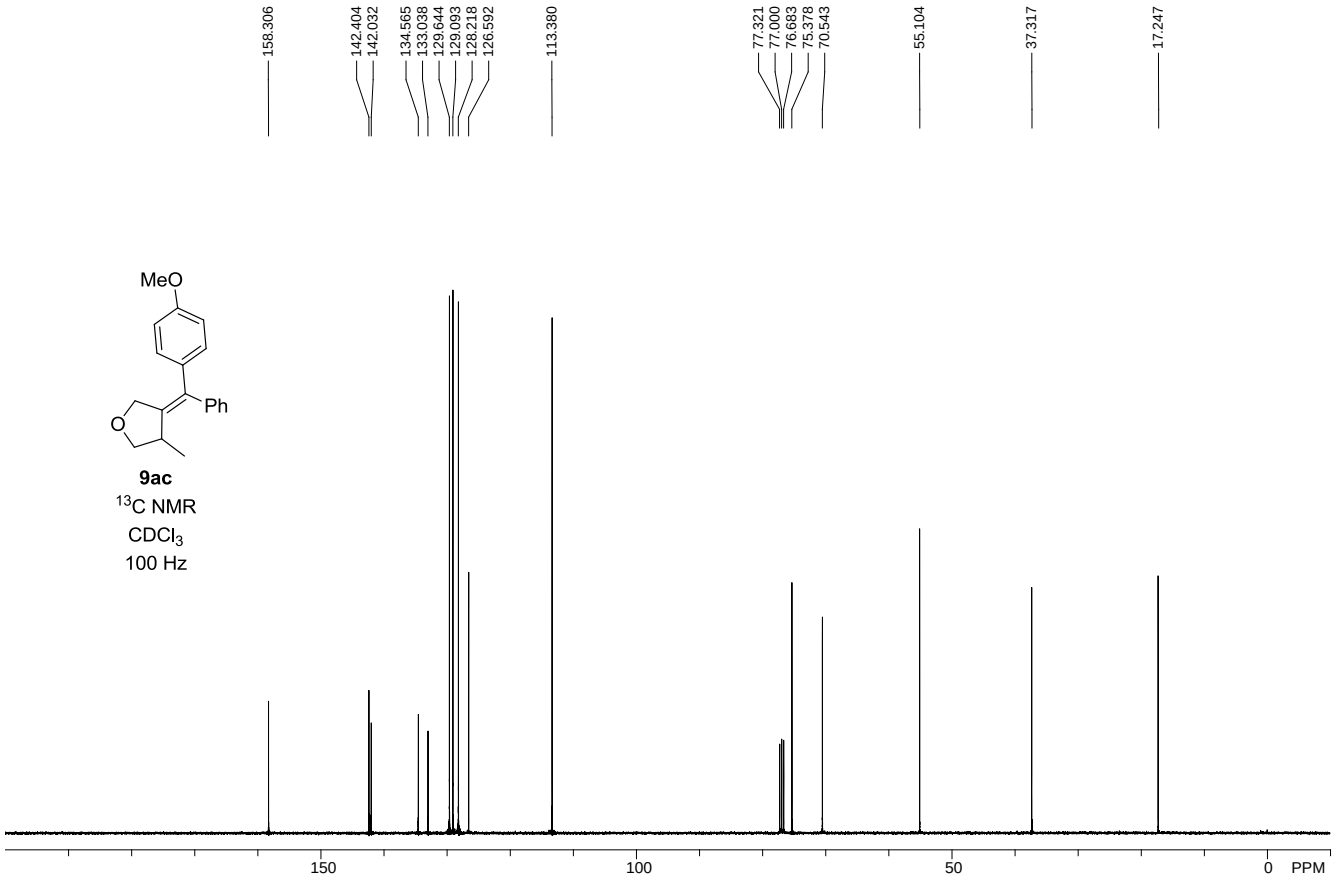

7.965
7.959
7.956
7.949
7.946
7.942
7.431
7.412
7.407
7.400
7.395
7.307
7.305
7.301
7.287
7.284
7.268
7.258
7.236
7.233
7.223
7.218
7.212
7.203
7.200
7.096
7.093
7.075
4.636
4.632
4.601
4.597
4.400
4.393
4.382
4.376
4.364
4.358
4.346
4.340
4.297
4.263
4.090
4.073
4.069
4.052
3.550
3.537
3.528
3.516
3.143
3.139
3.126
3.122
3.113
3.109
3.096
3.093
1.405
1.387
1.369
0.856
0.838
-0.000
Ph
COOEt
O
9ab
1H NMR
CDCl3
400 Hz
2.03
2.10
2.30
2.00
1.02
1.01
2.06
1.03
1.00
1.03
1.03
3.07
3.07
8
6
4
2
0
PPM

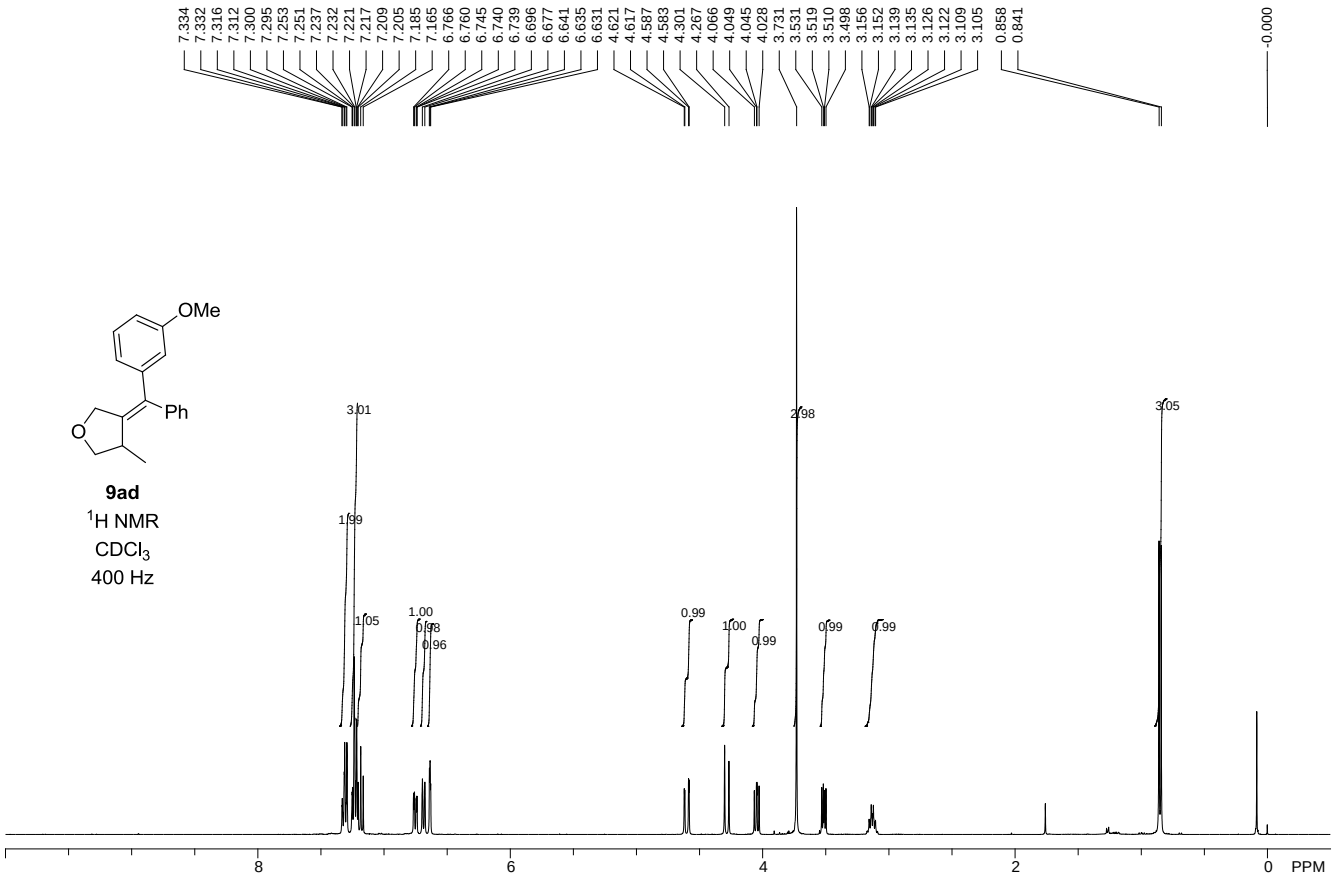


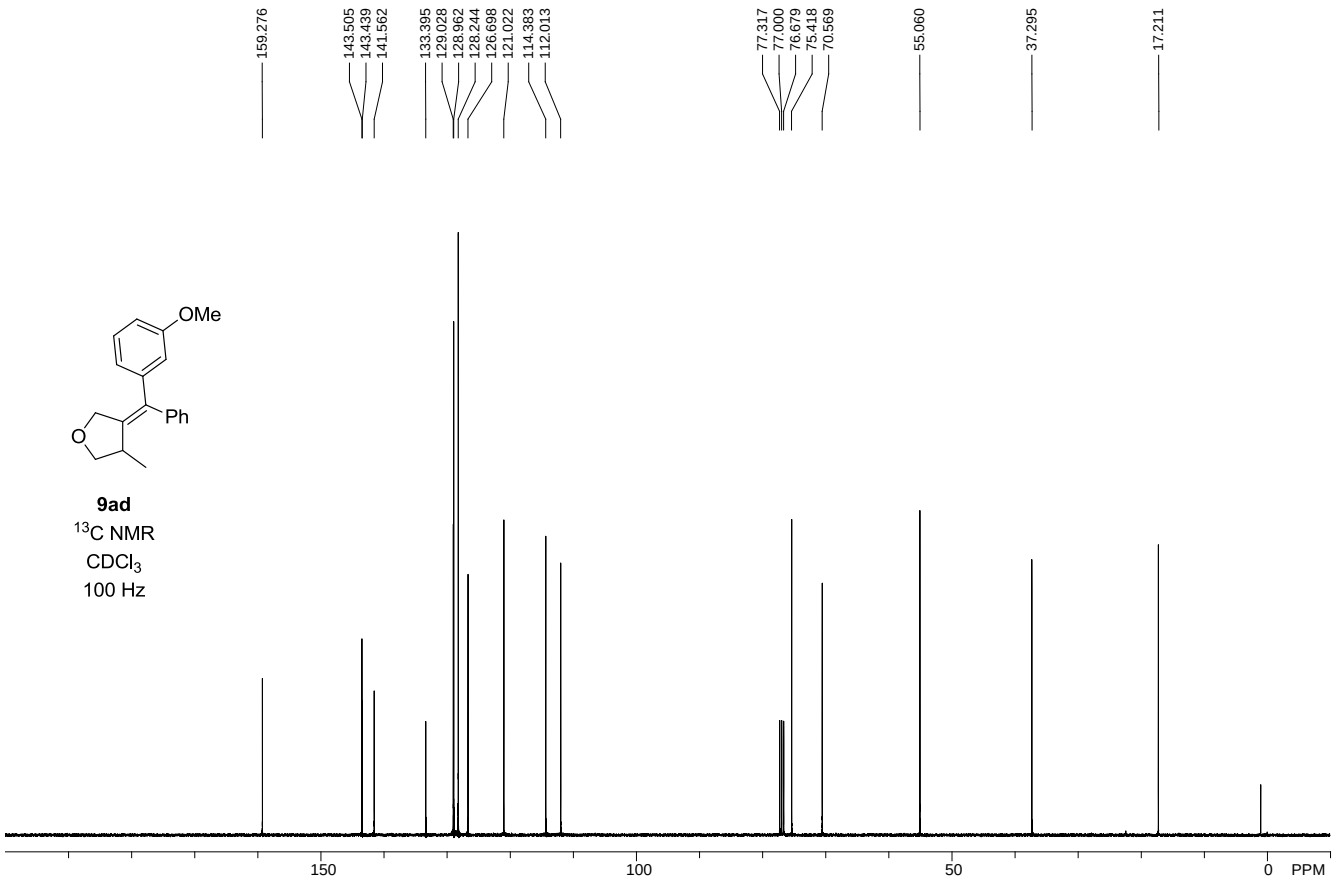
9ab
^{13}C NMR
$CDCl_3$
100 Hz

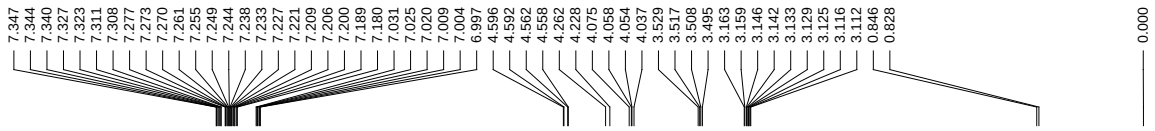


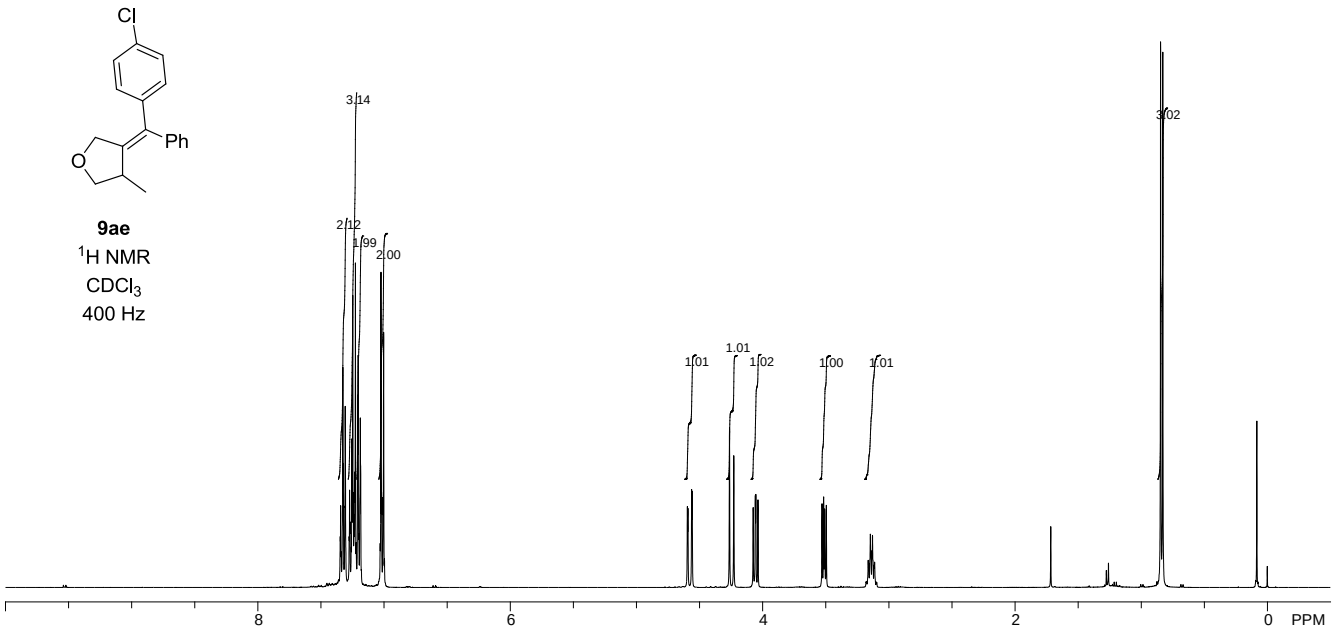
9ac
^{1}H NMR
$CDCl_3$
400 Hz

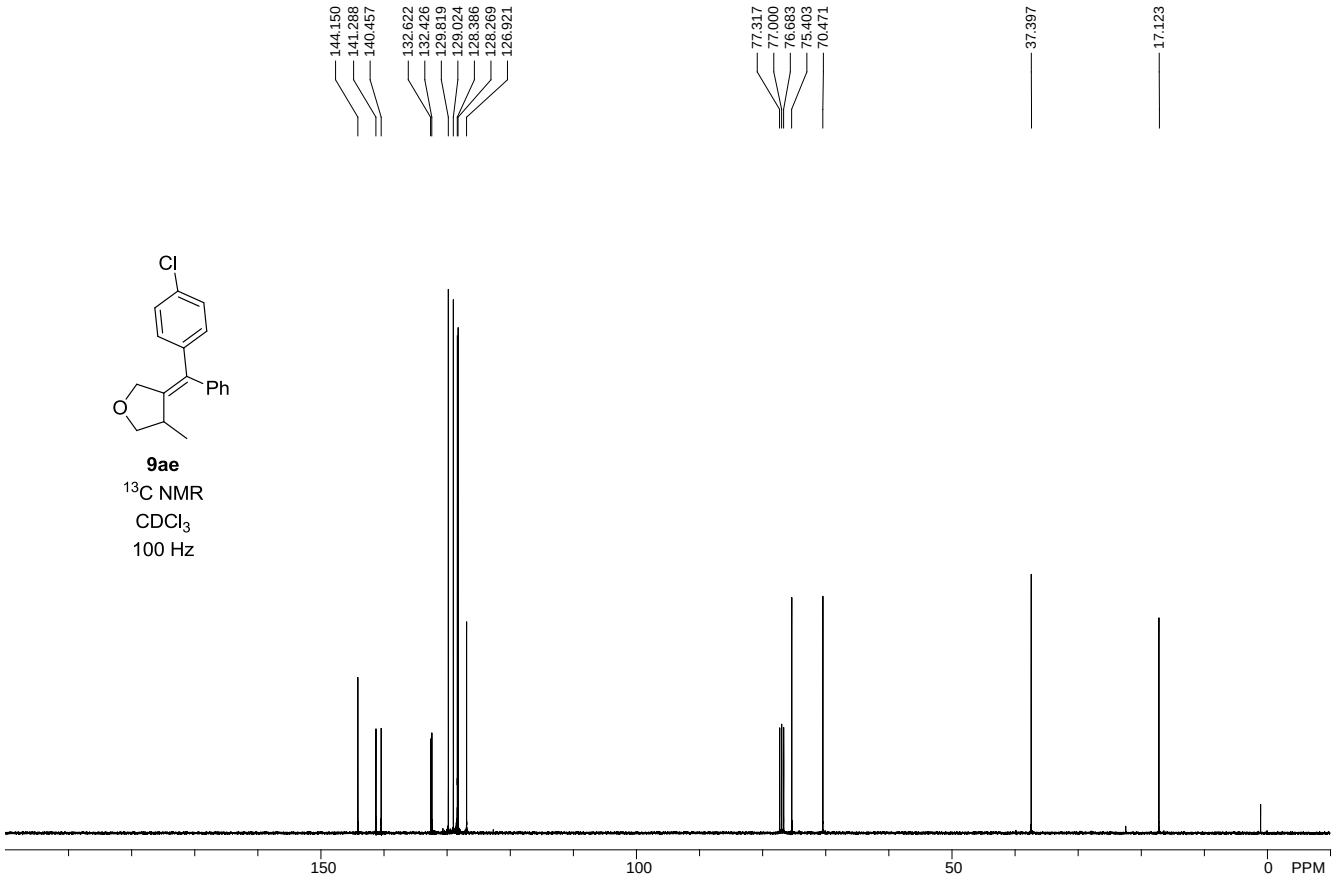

158.306
142.404
142.032
134.565
133.038
129.644
129.093
128.218
126.592
113.380
77.321
77.000
76.683
75.378
70.543
55.104
37.317
17.247
MeO
Ph
O
9ac
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM

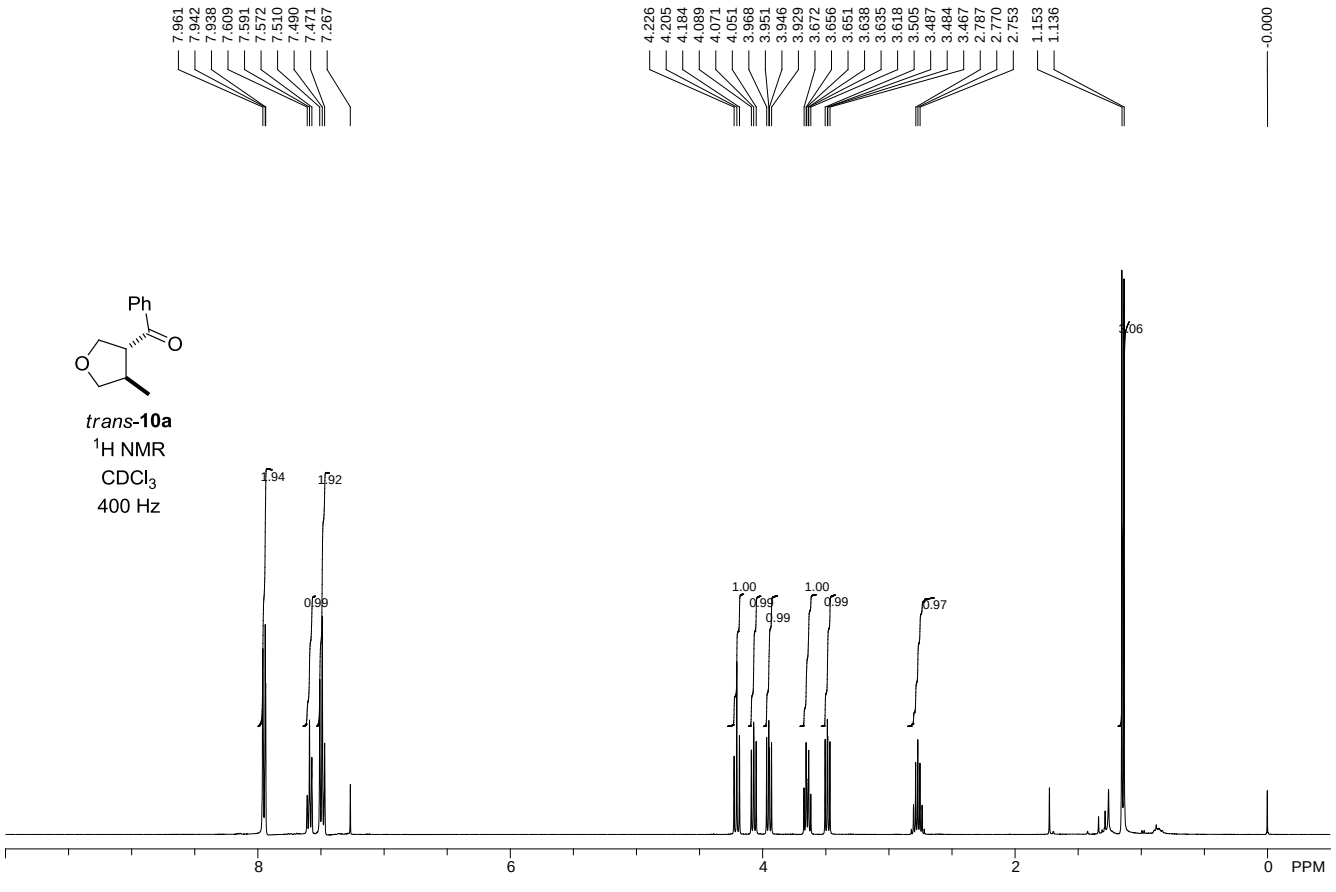

7.334
7.332
7.316
7.312
7.300
7.295
7.253
7.251
7.237
7.232
7.221
7.217
7.209
7.205
7.185
7.165
6.766
6.760
6.745
6.740
6.739
6.696
6.677
6.641
6.635
6.631
4.621
4.617
4.587
4.583
4.301
4.267
4.066
4.049
4.045
4.028
3.731
3.531
3.519
3.510
3.498
3.156
3.152
3.139
3.135
3.126
3.122
3.109
3.105
0.858
0.841
-0.000
OMe
Ph
O
9ad
1H NMR
CDCl3
400 Hz
3.01
1.99
1.05
1.00
0.98
0.96
0.99
1.00
0.99
2.98
0.99
0.99
3.05
8
6
4
2
0
PPM

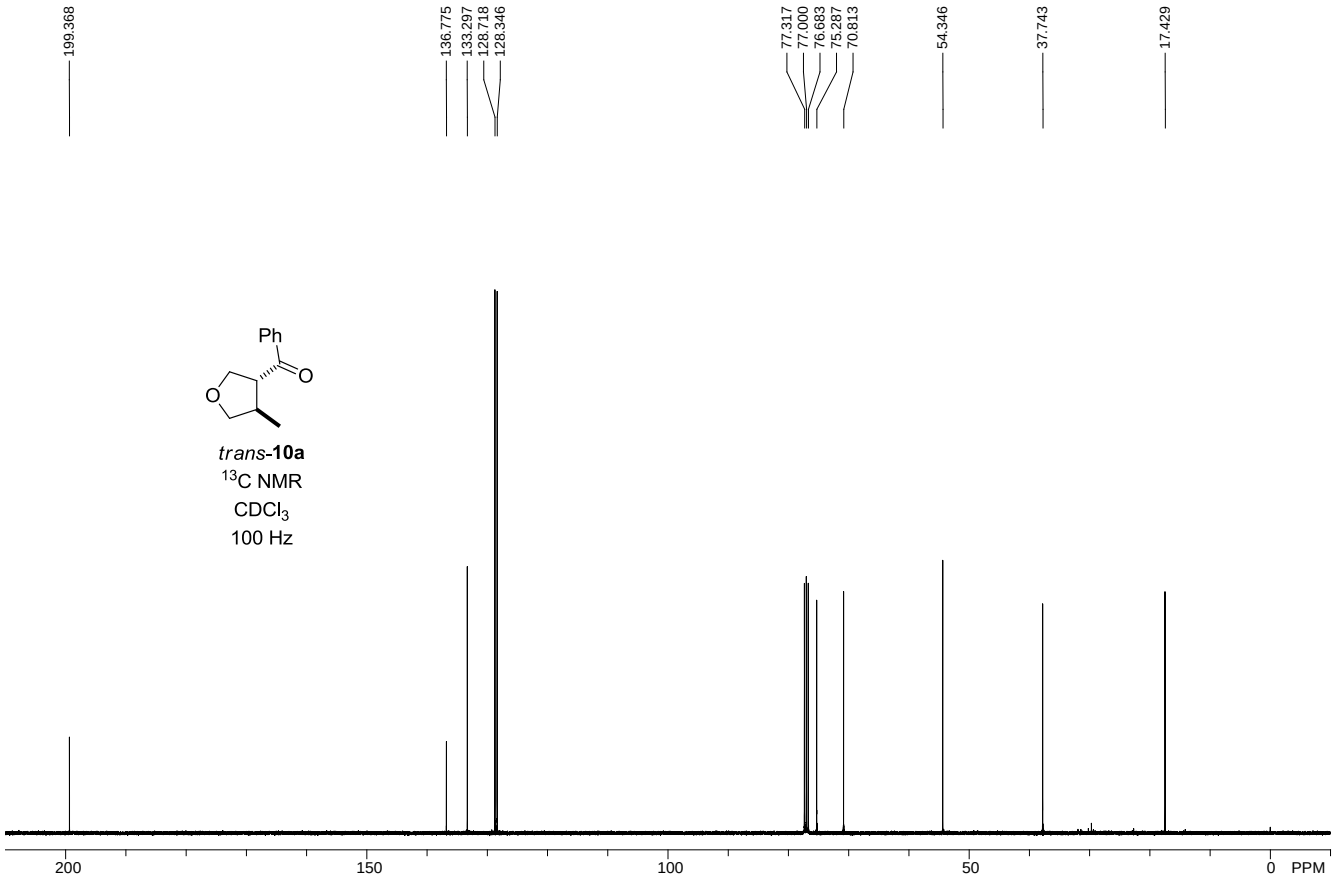

159.276
143.505
143.439
141.562
133.395
129.028
128.962
128.244
126.698
121.022
114.383
112.013
77.317
77.000
76.679
75.418
70.569
55.060
37.295
17.211
OMe
Ph
O
9ad
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM

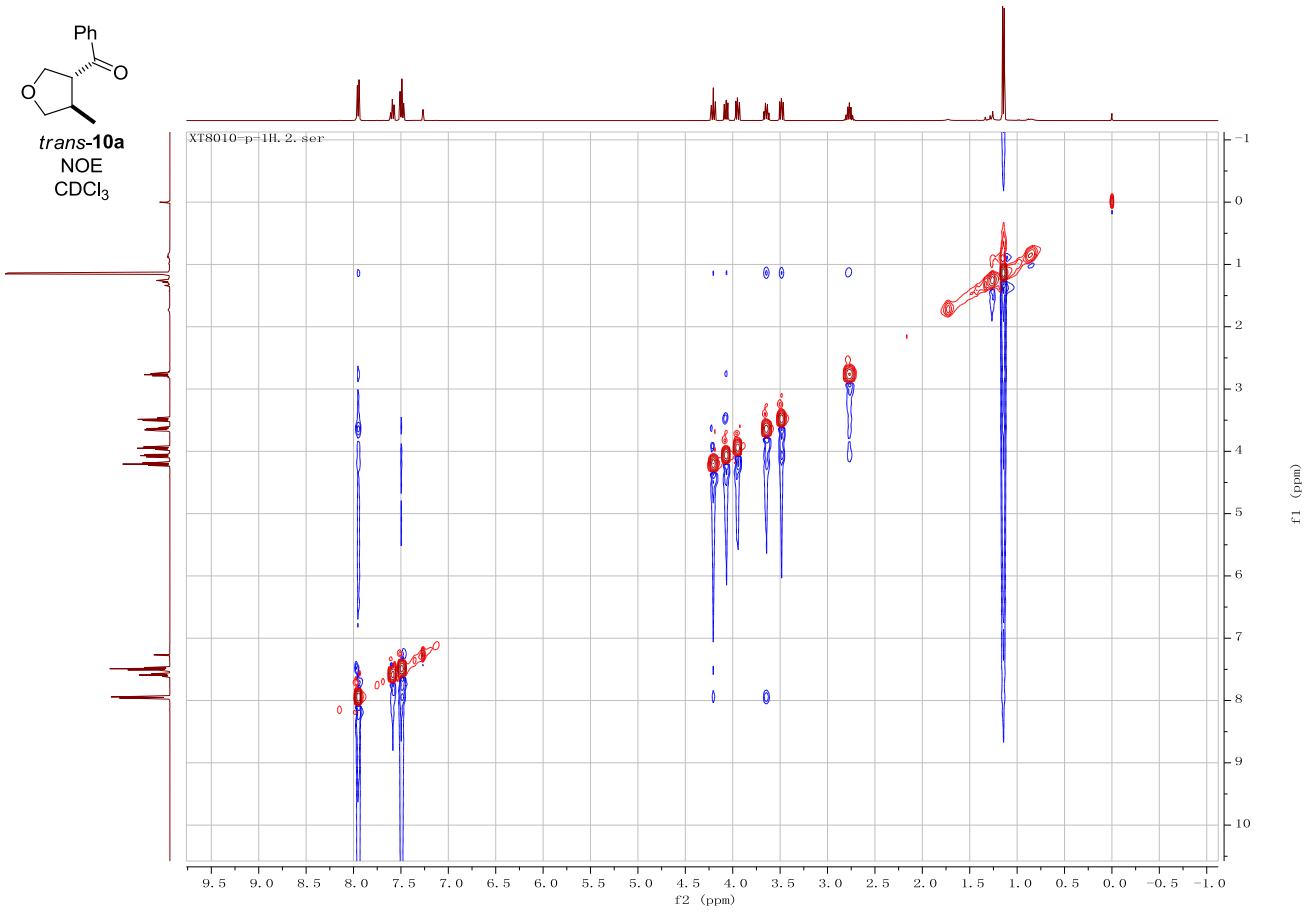

7.347
7.344
7.340
7.327
7.323
7.311
7.308
7.277
7.273
7.270
7.261
7.255
7.249
7.244
7.238
7.233
7.227
7.221
7.209
7.206
7.200
7.189
7.180
7.031
7.025
7.020
7.009
7.004
6.997
4.596
4.592
4.562
4.558
4.262
4.228
4.075
4.058
4.054
4.037
3.529
3.517
3.508
3.495
3.163
3.159
3.146
3.142
3.133
3.129
3.125
3.116
3.112
0.846
0.828
0.000

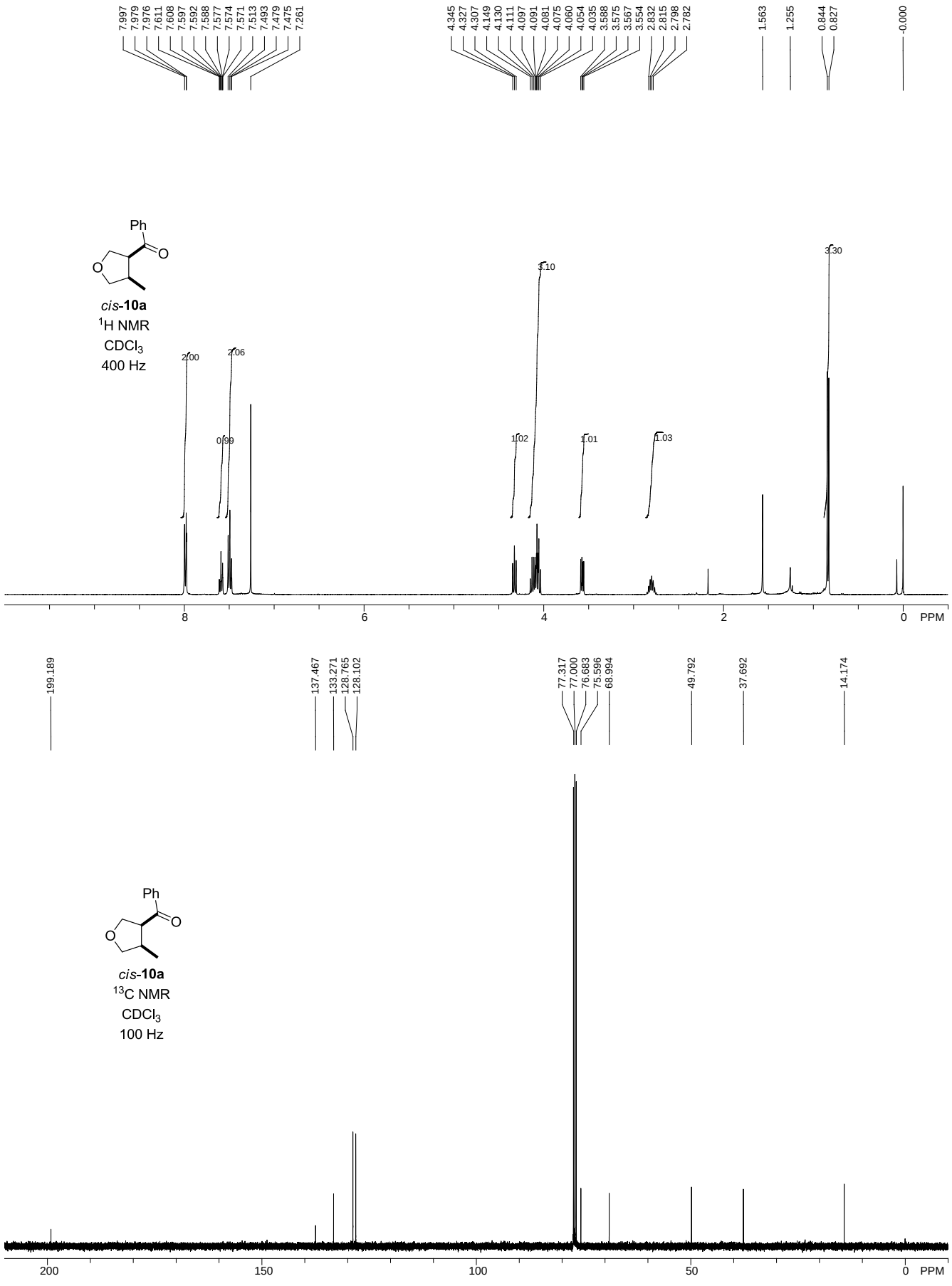

Cl
Ph
O
9ae
1H NMR
CDCl3
400 Hz
3.14
2.12
1.99
2.00
1.01
1.01
1.02
1.00
1.01
3.02
8
6
4
2
0
PPM

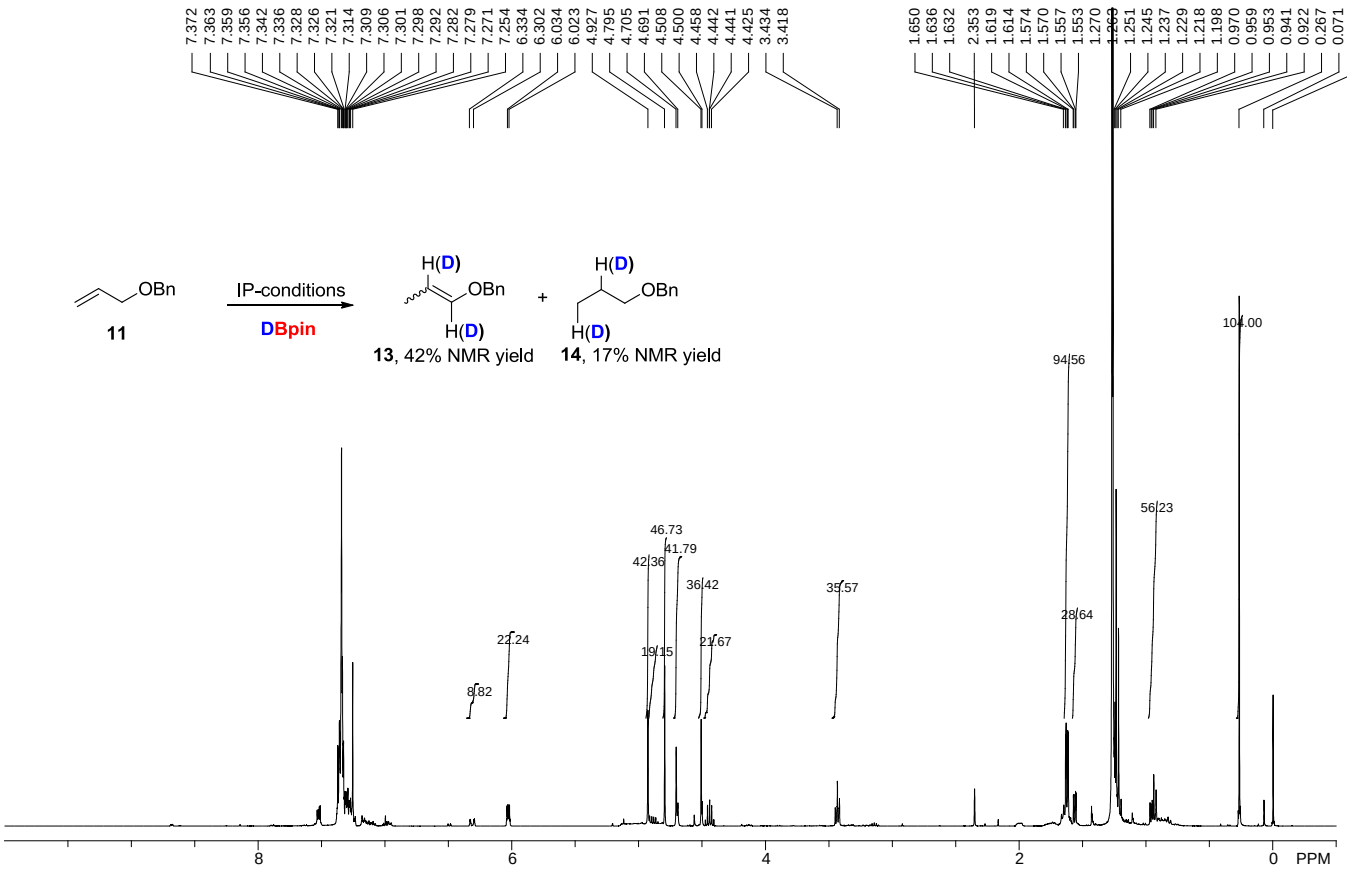

144.150
141.288
140.457
132.622
132.426
129.819
129.024
128.386
128.269
126.921
77.317
77.000
76.683
75.403
70.471
37.397
17.123
Cl
Ph
O
9ae
13C NMR
CDCl3
100 Hz
150
100
50
0
PPM

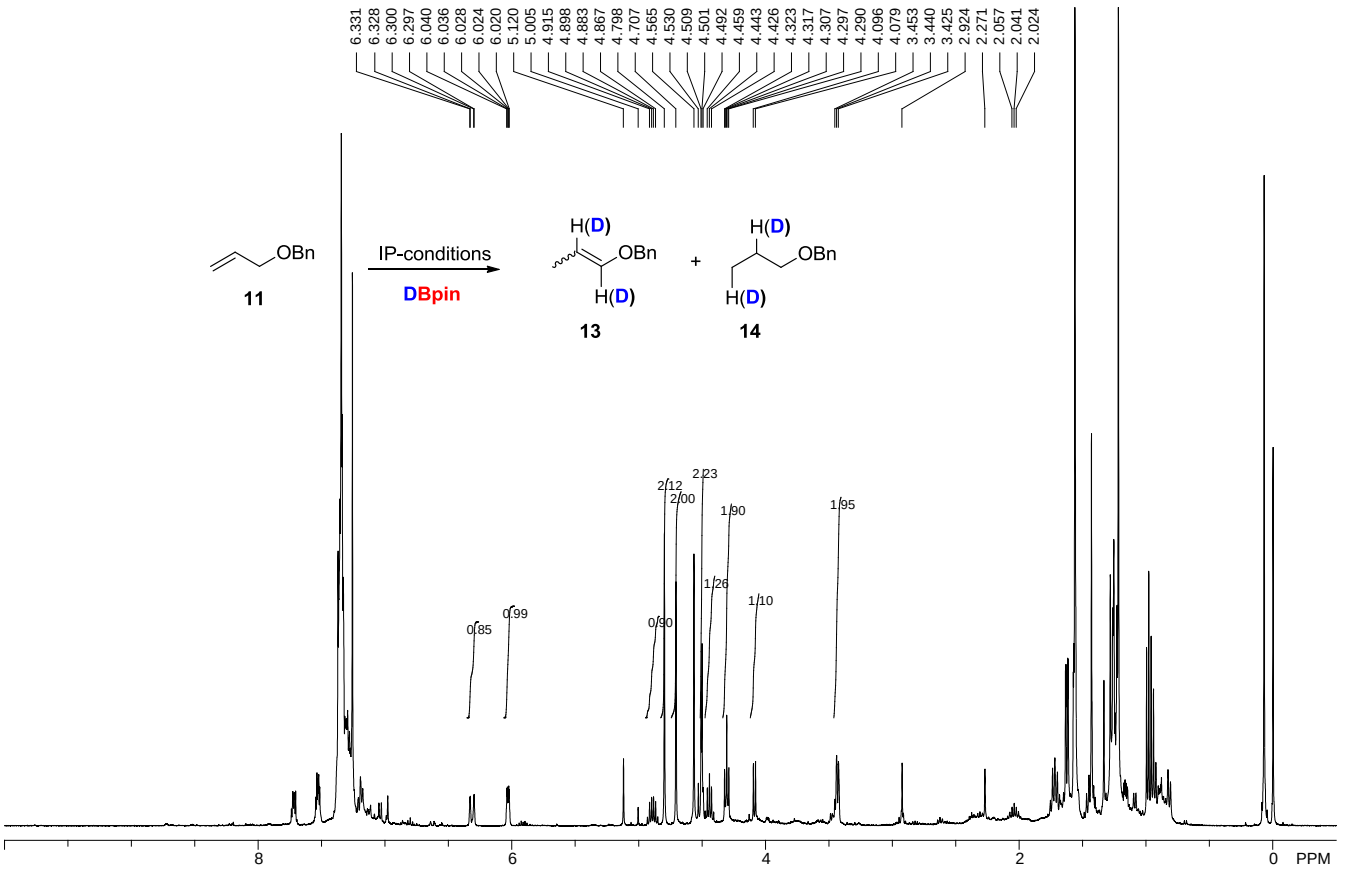

7.961
7.942
7.938
7.609
7.591
7.572
7.510
7.490
7.471
7.267
4.226
4.205
4.184
4.089
4.071
4.051
3.968
3.951
3.946
3.929
3.672
3.656
3.651
3.638
3.635
3.618
3.505
3.487
3.484
3.467
2.787
2.770
2.753
1.153
1.136
-0.000
Ph
O
O
trans-10a
1H NMR
CDCl3
400 Hz
1.94
1.92
0.99
1.00
0.99
0.99
1.00
0.99
0.97
3.06
8
6
4
2
0
PPM

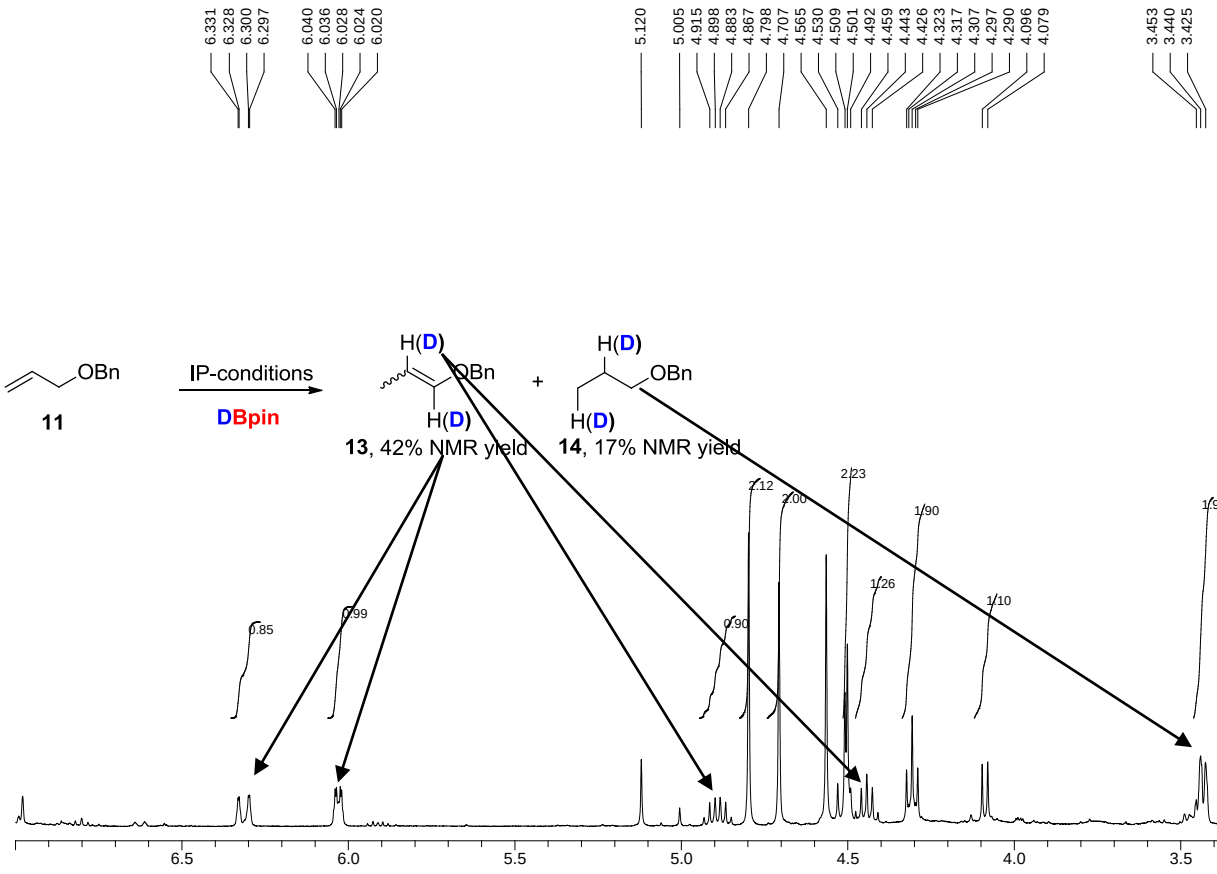

199.368
136.775
133.297
128.718
128.346
77.317
77.000
76.683
75.287
70.813
54.346
37.743
17.429
Ph
O
O
trans-10a
13C NMR
CDCl3
100 Hz
200
150
100
50
0 PPM

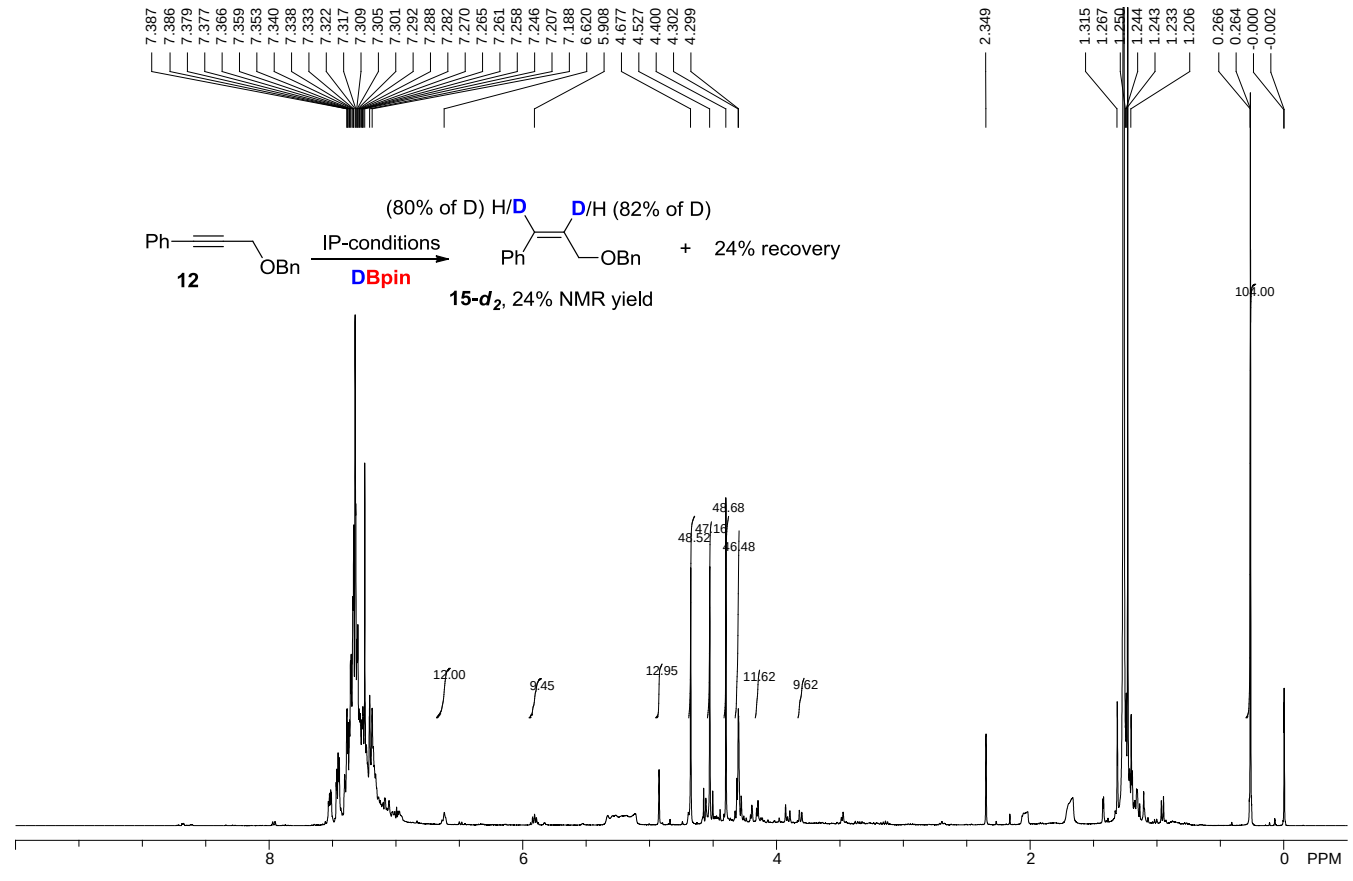

Ph
O
O
trans-10a
NOE
CDCl3
XT8010-p-1H. 2. ser
f2 (ppm)
f1 (ppm)

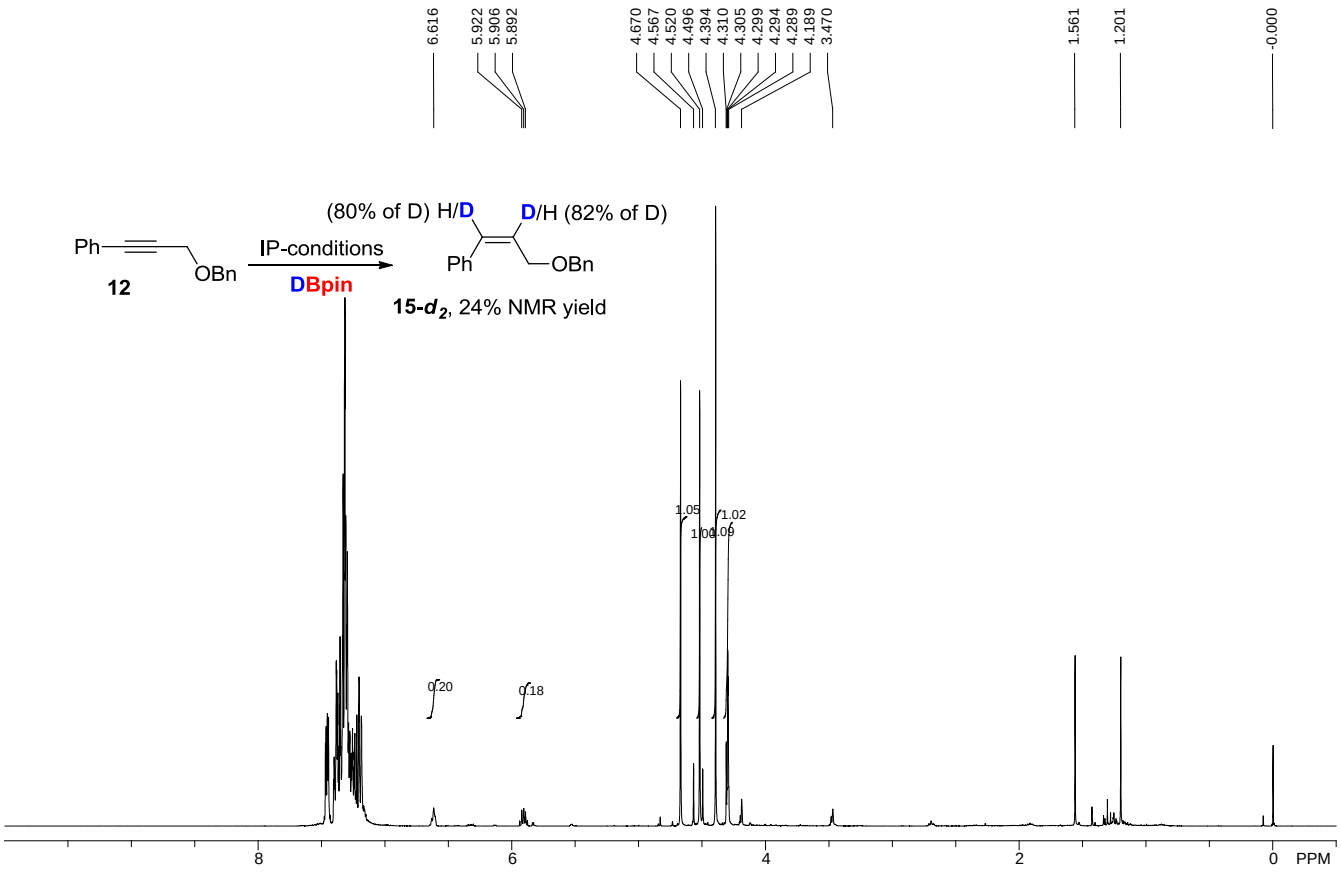

7.997
7.979
7.976
7.611
7.608
7.597
7.592
7.588
7.577
7.574
7.571
7.513
7.493
7.479
7.475
7.261
4.345
4.327
4.307
4.149
4.130
4.111
4.097
4.091
4.081
4.075
4.060
4.054
4.035
3.588
3.575
3.567
3.554
2.832
2.815
2.798
2.782
1.563
1.255
0.844
0.827
-0.000
Ph
O
O
cis-10a
1H NMR
CDCl3
400 Hz
2.00
2.06
0.99
3.10
1.02
1.01
1.03
3.30
8
6
4
2
0
PPM
199.189
137.467
133.271
128.765
128.102
77.317
77.000
76.683
75.596
68.994
49.792
37.692
14.174
Ph
O
O
cis-10a
13C NMR
CDCl3
100 Hz
200
150
100
50
0
PPM

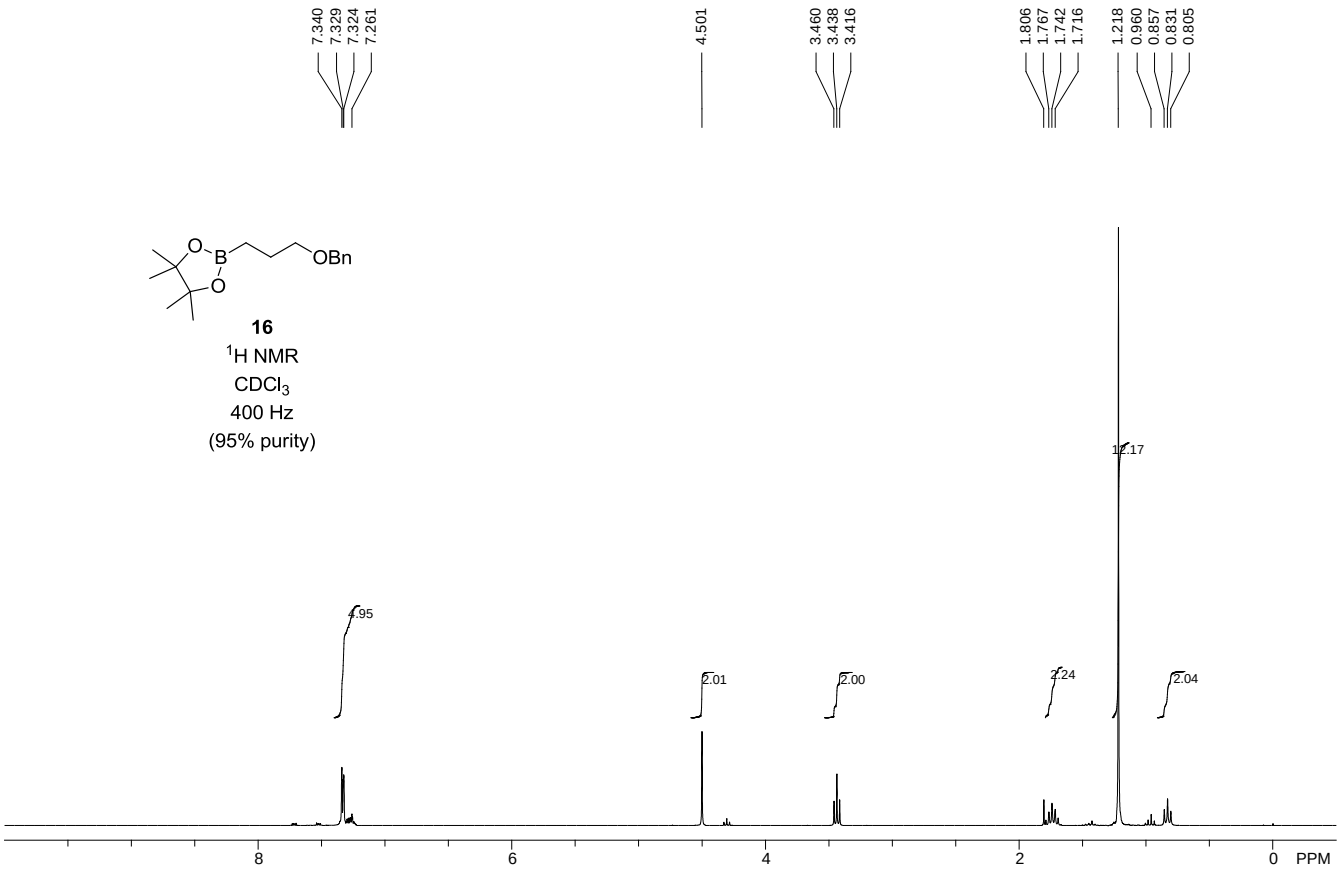

11
IP-conditions
DBpin
13, 42% NMR yield
14, 17% NMR yield
104.00
94.56
56.23
46.73
41.79
42.36
36.42
35.57
28.64
22.24
21.67
19.15
8.82
PPM

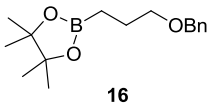

11
IP-conditions
DBpin
13
14
2.23
2.12
2.00
1.95
1.90
1.26
1.10
0.99
0.90
0.85
PPM


6.331
6.328
6.300
6.297
6.040
6.036
6.028
6.024
6.020
5.120
5.005
4.915
4.898
4.883
4.867
4.798
4.707
4.565
4.530
4.509
4.501
4.492
4.459
4.443
4.426
4.323
4.317
4.307
4.297
4.290
4.096
4.079
3.453
3.440
3.425
OBn
11
IP-conditions
DBpin
H(D)
OBn
H(D)
13, 42% NMR yield
+
H(D)
OBn
H(D)
14, 17% NMR yield
2.12
2.00
2.23
1.90
1.95
1.26
1.10
0.99
0.85
0.90
6.5
6.0
5.5
5.0
4.5
4.0
3.5
PPM


7.387
7.386
7.379
7.377
7.366
7.359
7.353
7.340
7.338
7.333
7.322
7.317
7.309
7.305
7.301
7.292
7.288
7.282
7.270
7.265
7.261
7.258
7.246
7.207
7.188
6.620
5.908
4.677
4.527
4.400
4.302
4.299
2.349
1.315
1.267
1.250
1.244
1.243
1.233
1.206
0.266
0.264
-0.000
-0.002
Ph
12
OBn
IP-conditions
DBpin
(80% of D) H/D
Ph
OBn
D/H (82% of D)
+
24% recovery
15-d2, 24% NMR yield
100.00
48.68
47.16
48.52
46.48
12.00
9.45
12.95
11.62
9.62
8
6
4
2
0
PPM


6.616
5.922
5.906
5.892
4.670
4.567
4.520
4.496
4.394
4.310
4.305
4.299
4.294
4.289
4.189
3.470
1.561
1.201
-0.000
(80% of D) H/D
D/H (82% of D)
Ph
OBn
12
IP-conditions
DBpin
15-d2, 24% NMR yield
1.05
1.04
1.02
1.09
0.20
0.18
8
6
4
2
0
PPM


7.340
7.329
7.324
7.261
4.501
3.460
3.438
3.416
1.806
1.767
1.742
1.716
1.218
0.960
0.857
0.831
0.805
O
B
OBn
O
16
1H NMR
CDCl3
400 Hz
(95% purity)
12.17
4.95
2.01
2.00
2.24
2.04
8
6
4
2
0
PPM



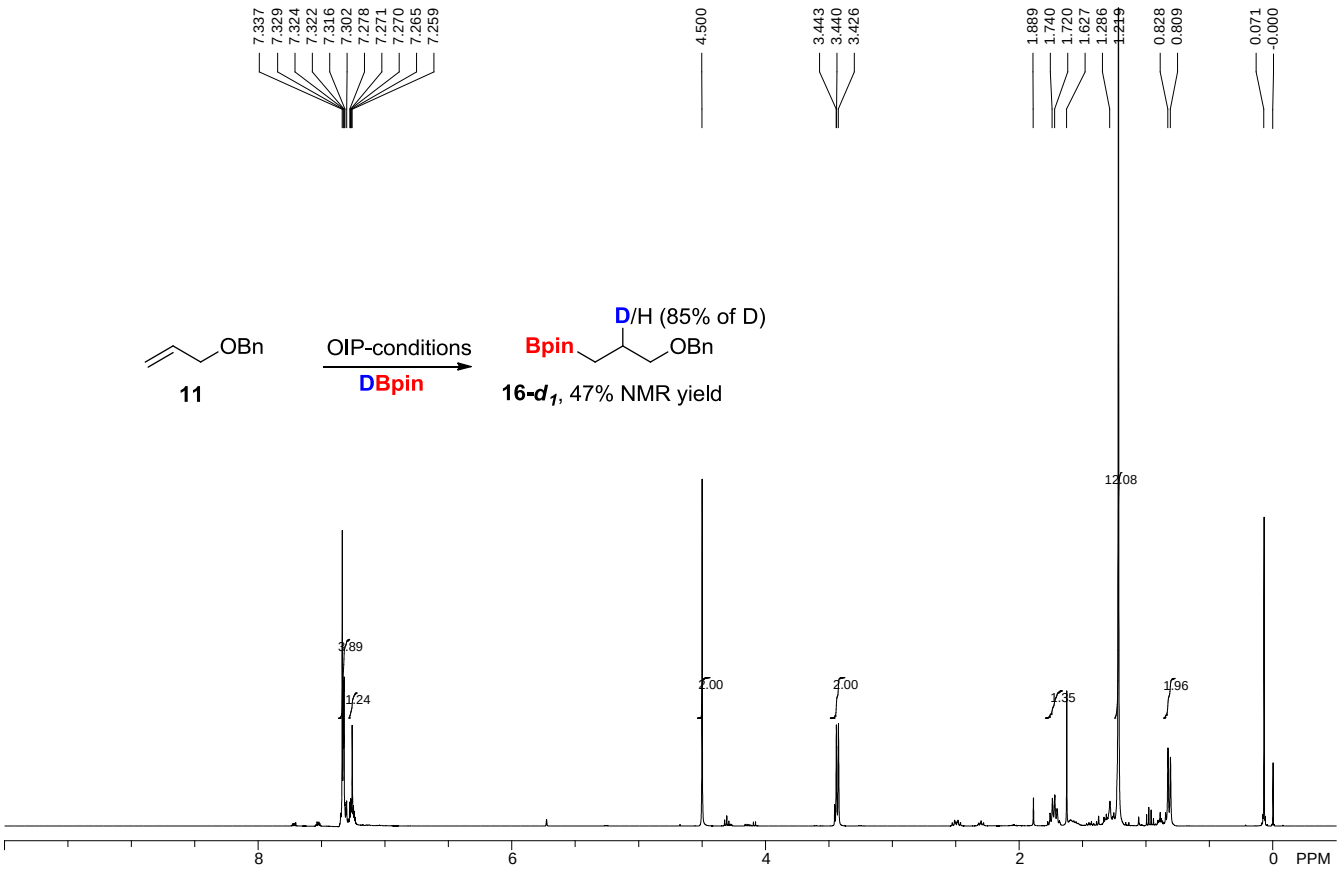
16

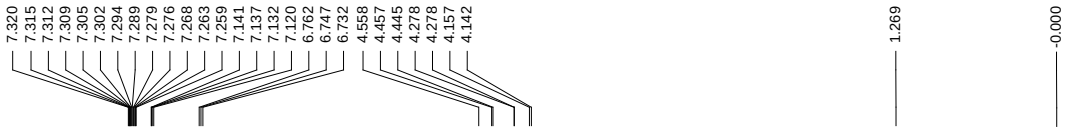
^{13}C NMR

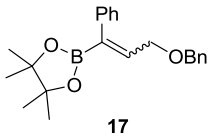
$CDCl_3$

100 Hz

(95% purity)







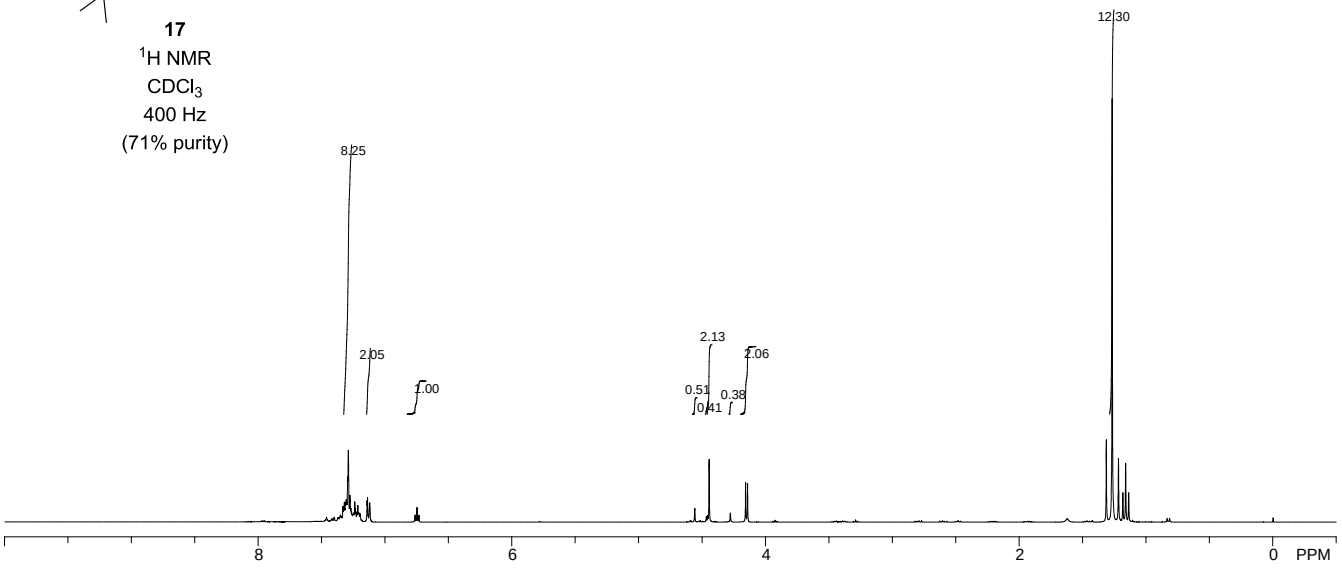
17

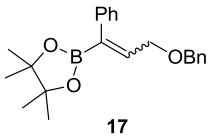
^{1}H NMR

$CDCl_3$

400 Hz

(71% purity)





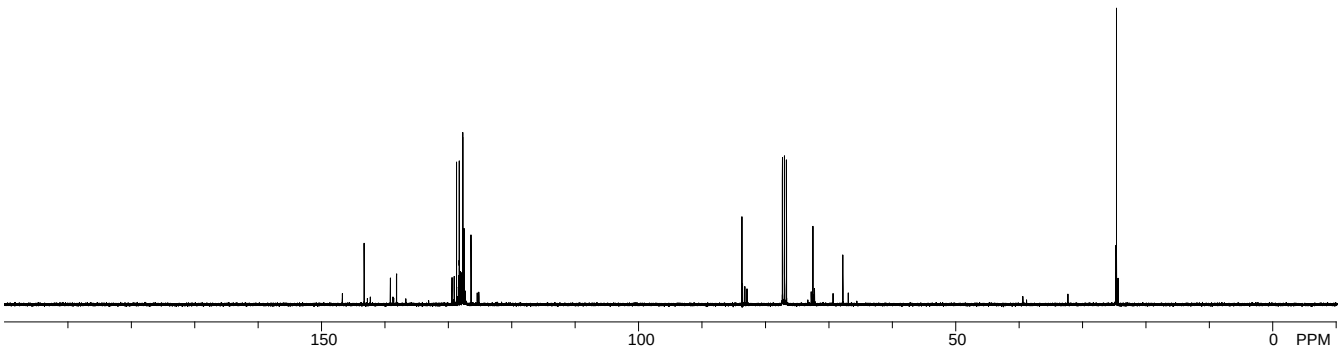
17

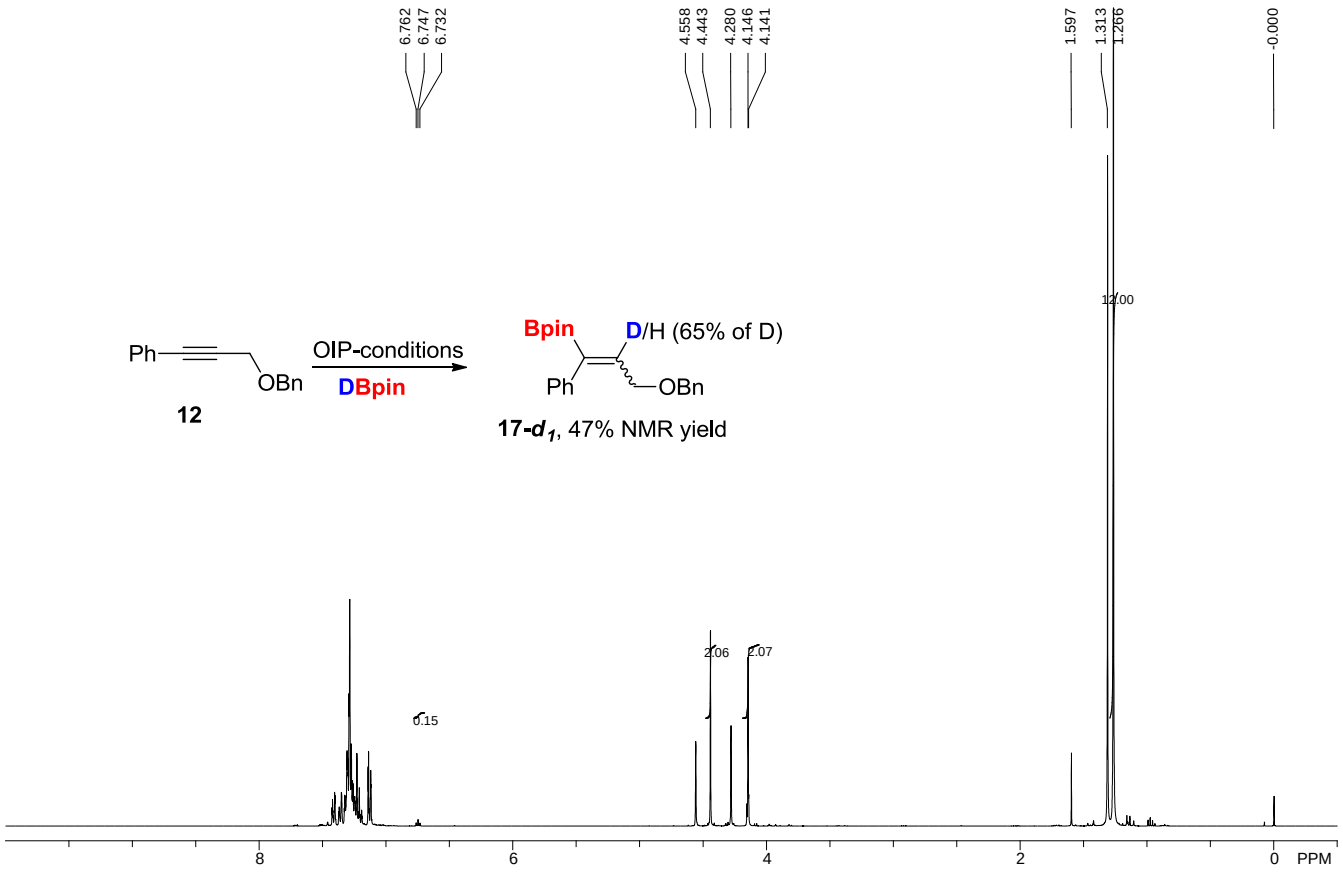
^{13}C NMR

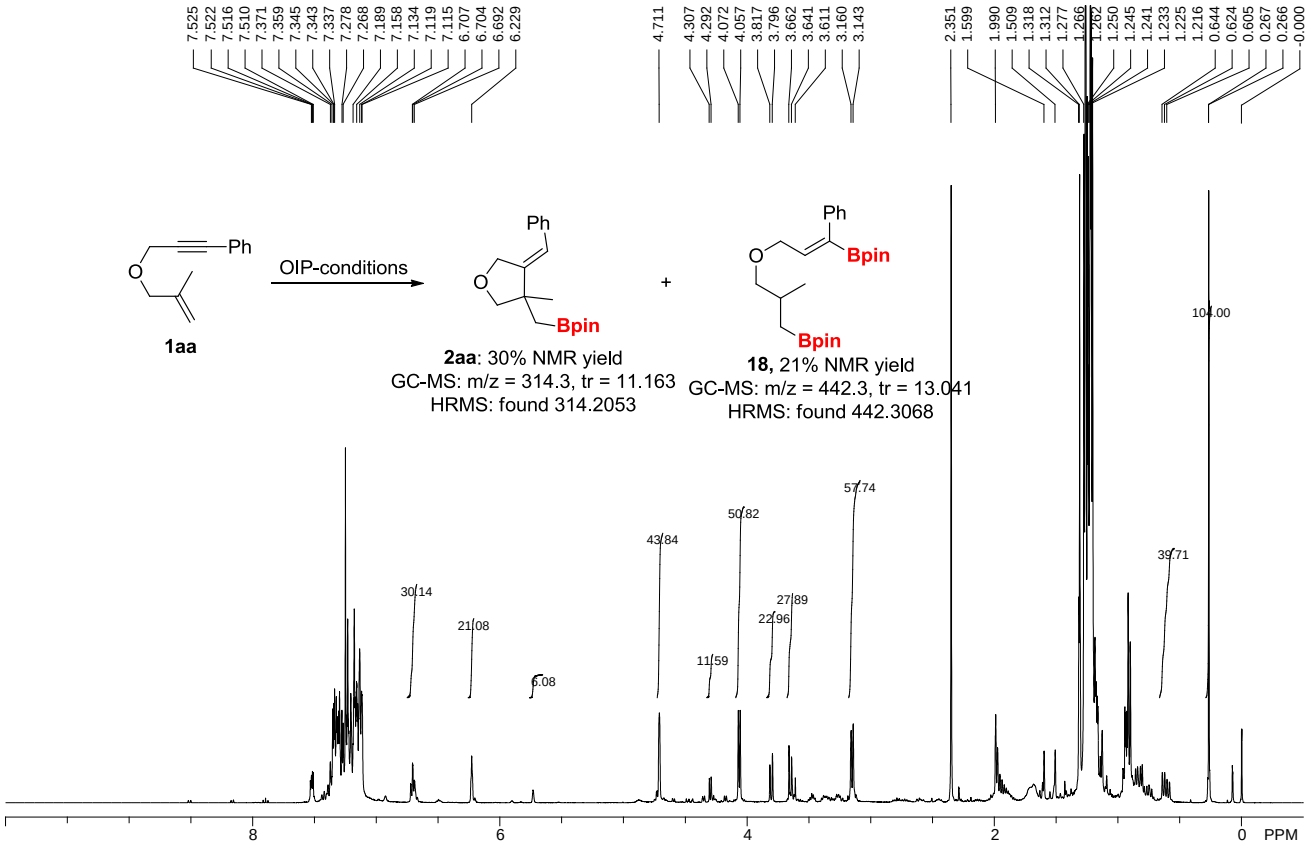
$CDCl_3$

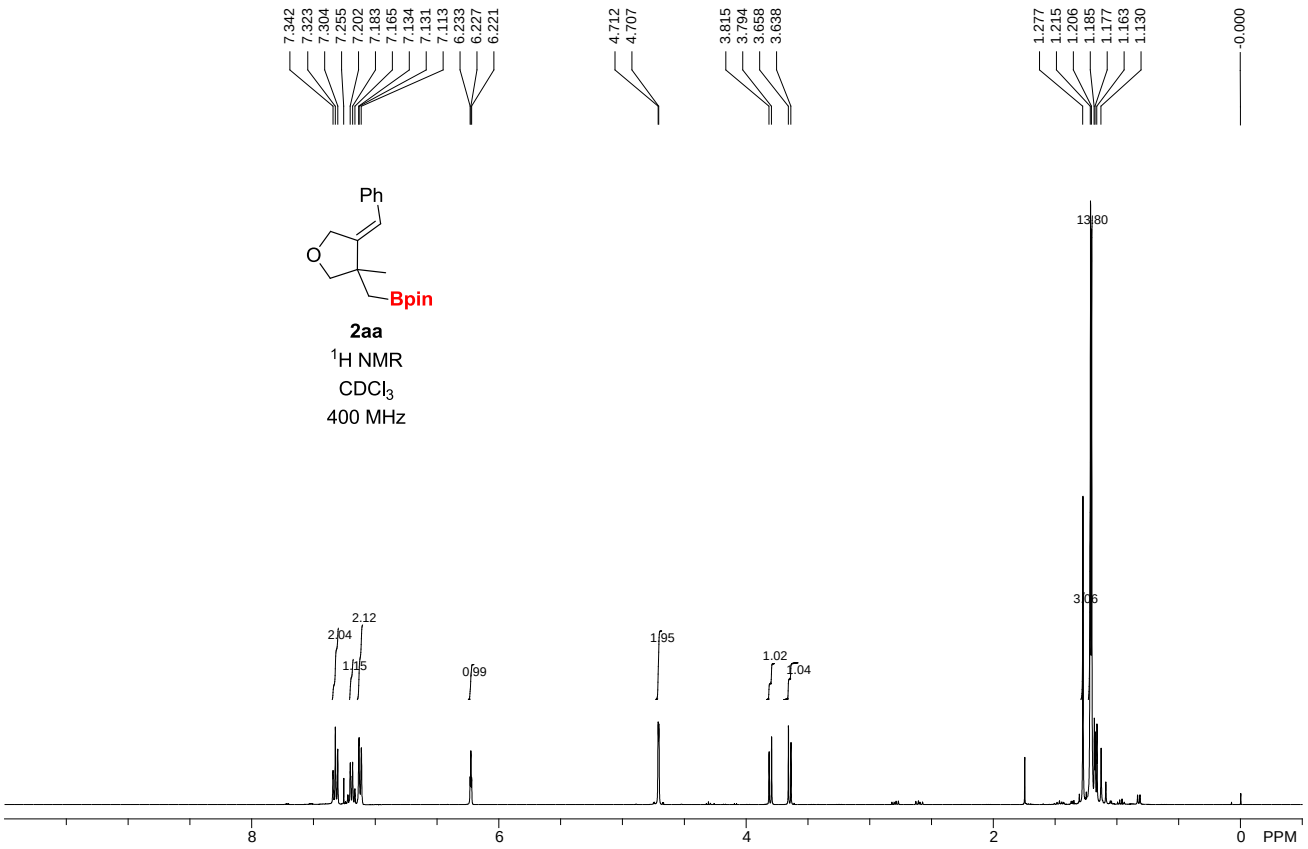
100 Hz

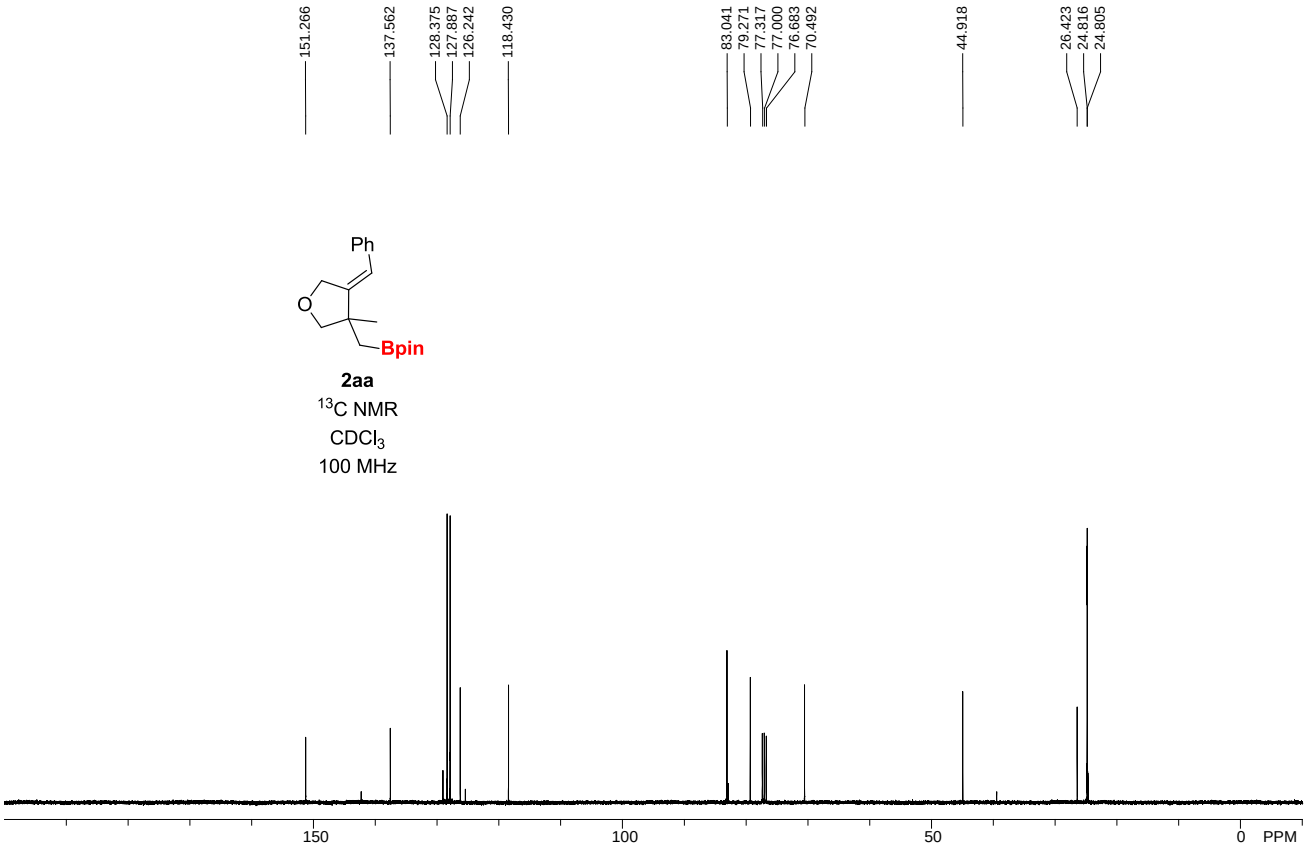
(71% purity)

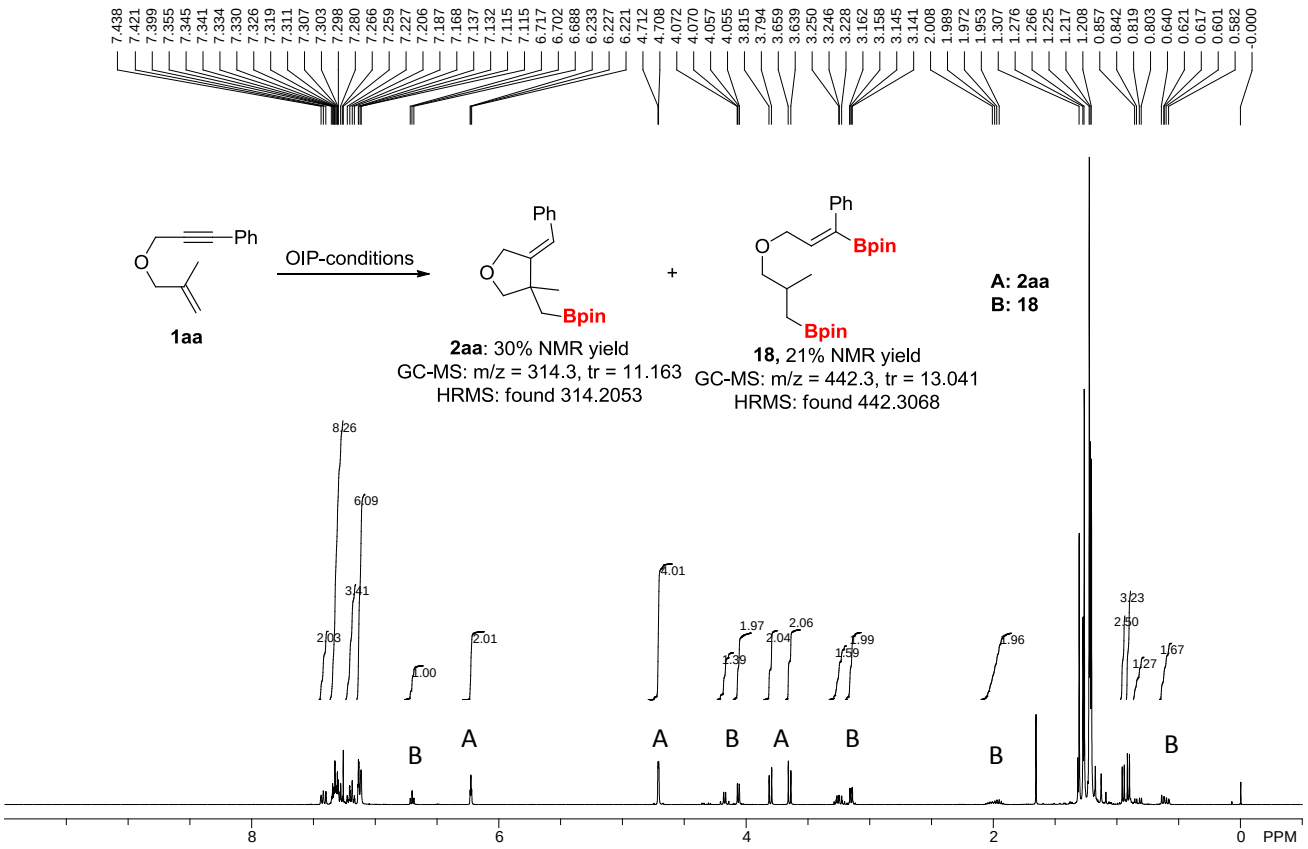


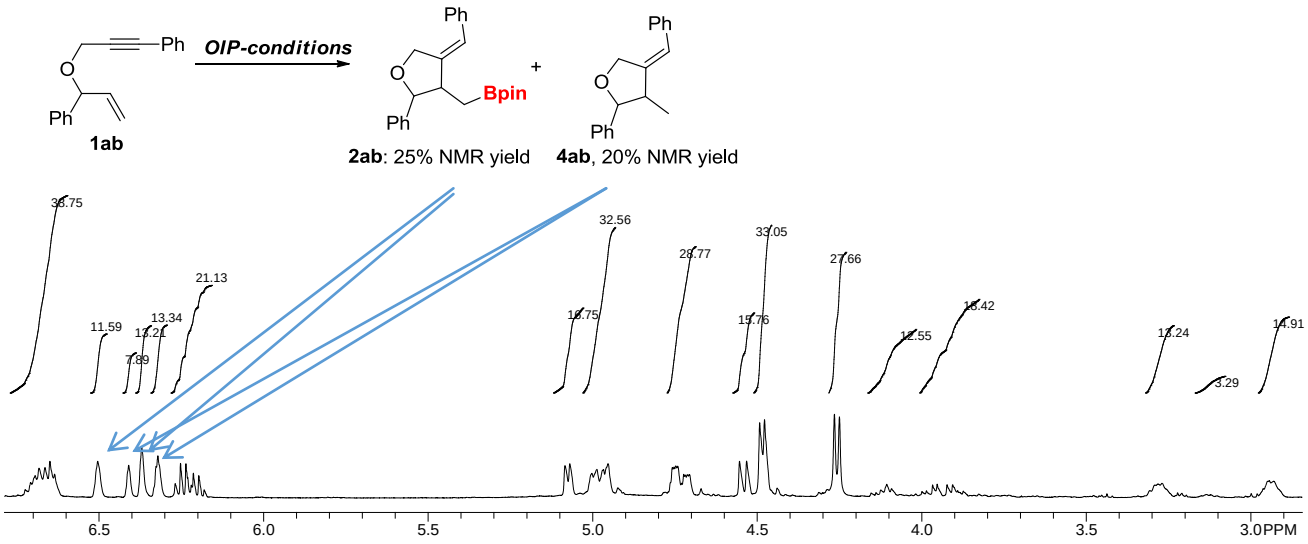

6.762
6.747
6.732
4.558
4.443
4.280
4.146
4.141
1.597
1.313
1.266
-0.000
12.00
Ph
OBn
12
OIP-conditions
DBpin
Bpin
D/H (65% of D)
Ph
OBn
17-d1, 47% NMR yield
2.06
2.07
0.15
8
6
4
2
0
PPM

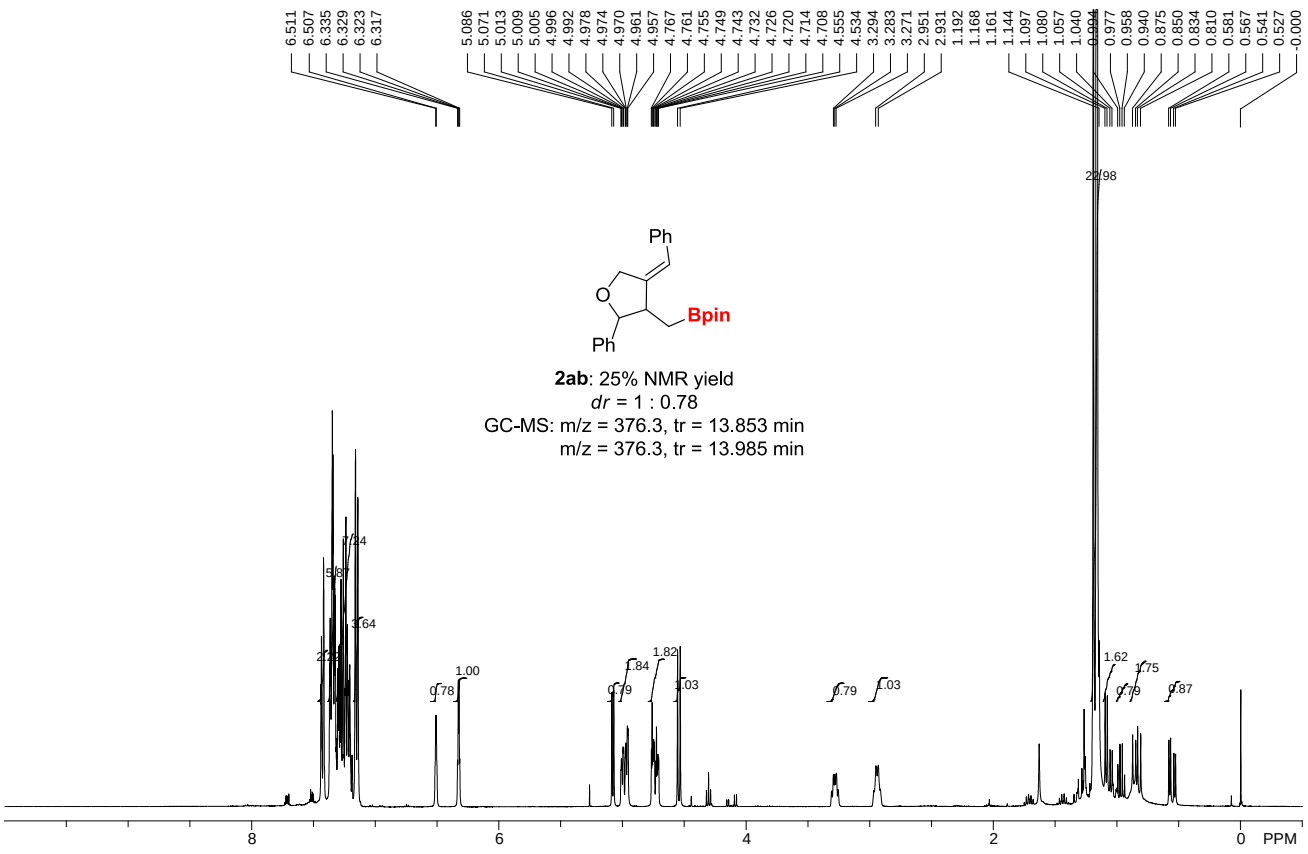

7.525
7.522
7.516
7.510
7.371
7.359
7.345
7.343
7.337
7.278
7.268
7.189
7.158
7.134
7.119
7.115
6.707
6.704
6.692
6.229
4.711
4.307
4.292
4.072
4.057
3.817
3.796
3.662
3.641
3.611
3.160
3.143
2.351
1.599
1.990
1.509
1.318
1.312
1.277
1.266
1.262
1.250
1.245
1.241
1.233
1.225
1.216
0.644
0.624
0.605
0.267
0.266
-0.000
Ph
O
1aa
OIP-conditions
Ph
O
Bpin
2aa: 30% NMR yield
GC-MS: m/z = 314.3, tr = 11.163
HRMS: found 314.2053
+
Ph
O
Bpin
Bpin
18, 21% NMR yield
GC-MS: m/z = 442.3, tr = 13.041
HRMS: found 442.3068
104.00
57.74
50.82
43.84
39.71
30.14
27.89
22.96
21.08
11.59
6.08
8
6
4
2
0
PPM


7.342
7.323
7.304
7.255
7.202
7.183
7.165
7.134
7.131
7.113
6.233
6.227
6.221
4.712
4.707
3.815
3.794
3.658
3.638
1.277
1.215
1.206
1.185
1.177
1.163
1.130
-0.000
Ph
O
Bpin
2aa
1H NMR
CDCl3
400 MHz
13.80
3.06
2.12
2.04
1.15
0.99
1.95
1.02
1.04
8
6
4
2
0
PPM

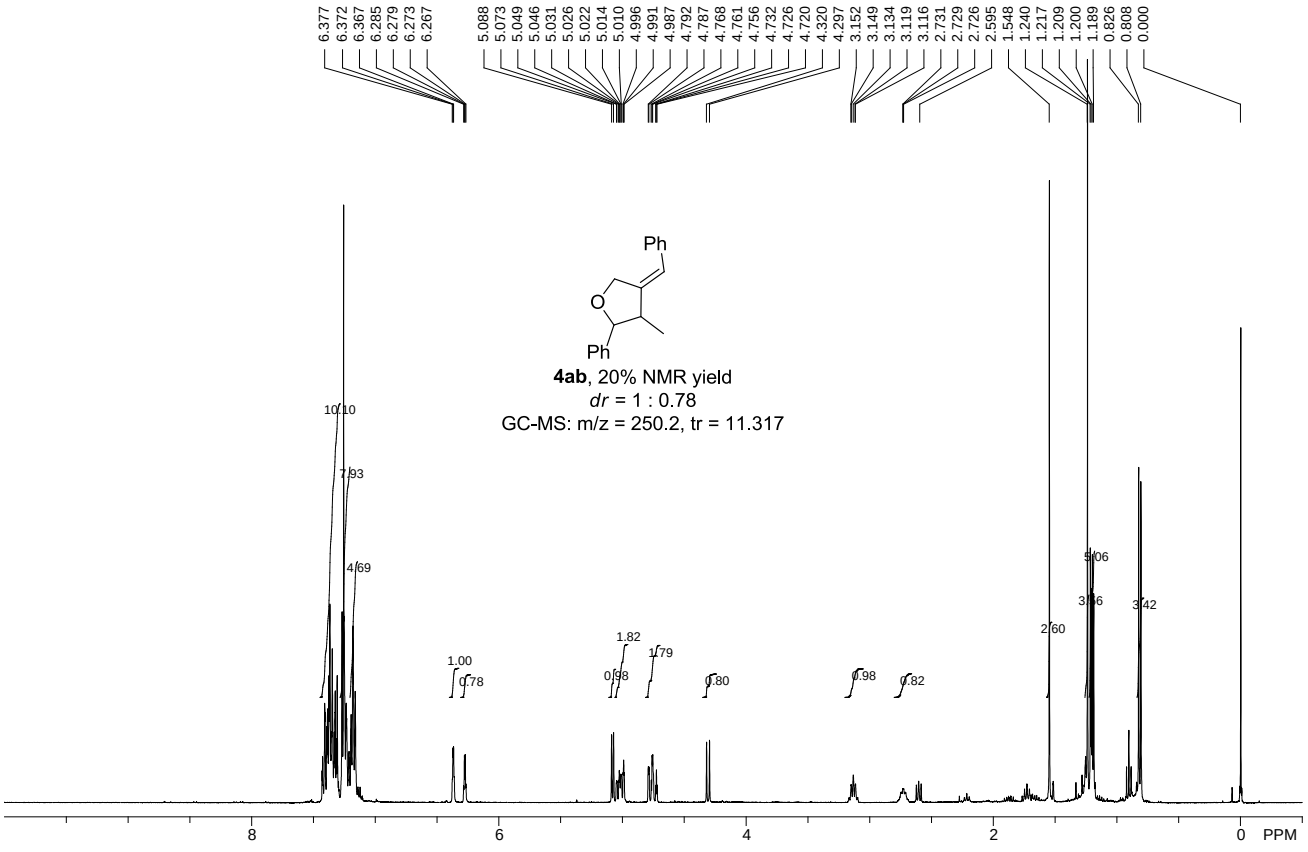

151.266
137.562
128.375
127.887
126.242
118.430
83.041
79.271
77.317
77.000
76.683
70.492
44.918
26.423
24.816
24.805
Ph
O
Bpin
2aa
13C NMR
CDCl3
100 MHz
150
100
50
0
PPM


OIP-conditions
1aa
2aa: 30% NMR yield
GC-MS: m/z = 314.3, tr = 11.163
HRMS: found 314.2053
18, 21% NMR yield
GC-MS: m/z = 442.3, tr = 13.041
HRMS: found 442.3068
A: 2aa
B: 18
PPM

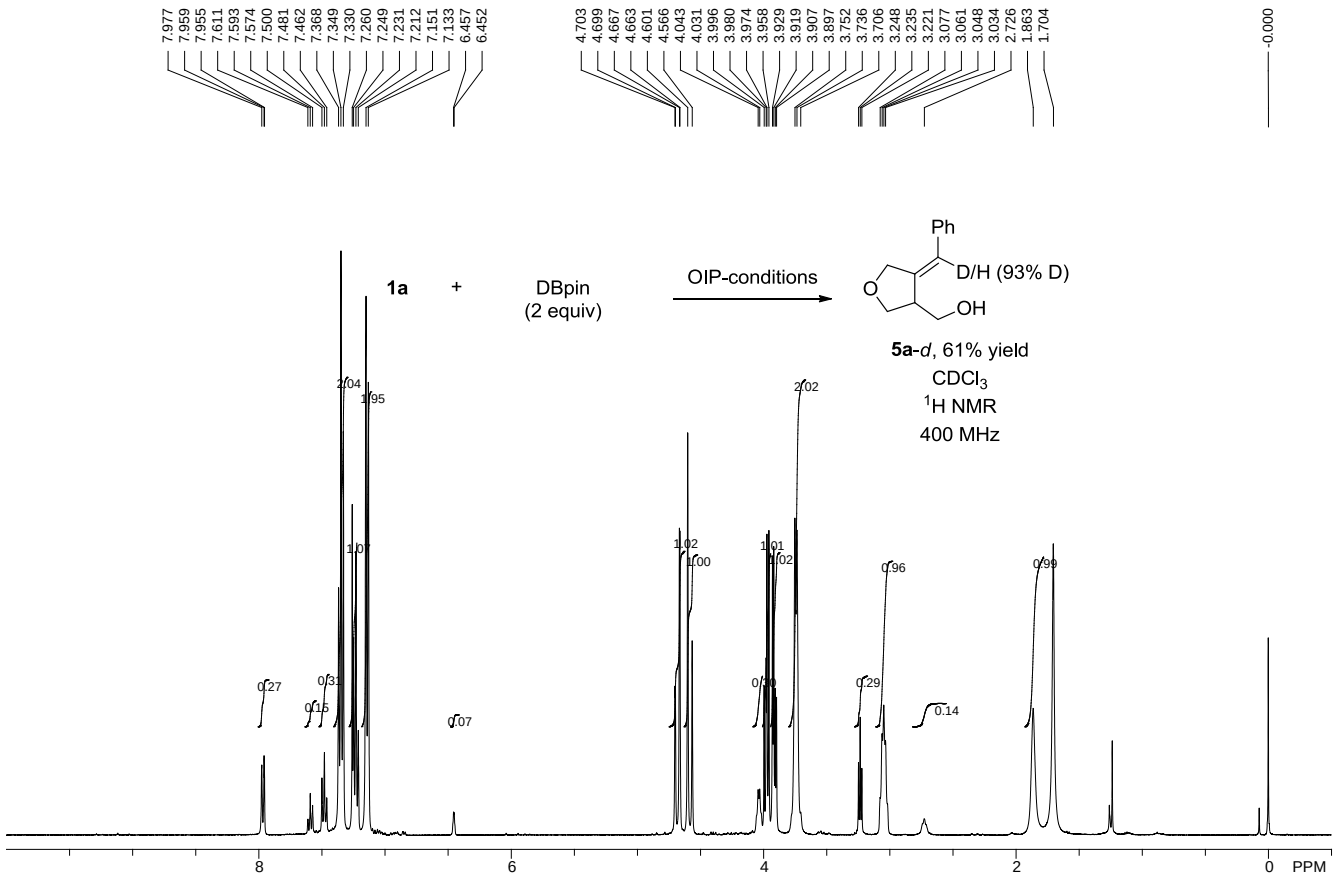

OIP-conditions
1ab
2ab: 25% NMR yield
4ab, 20% NMR yield
PPM

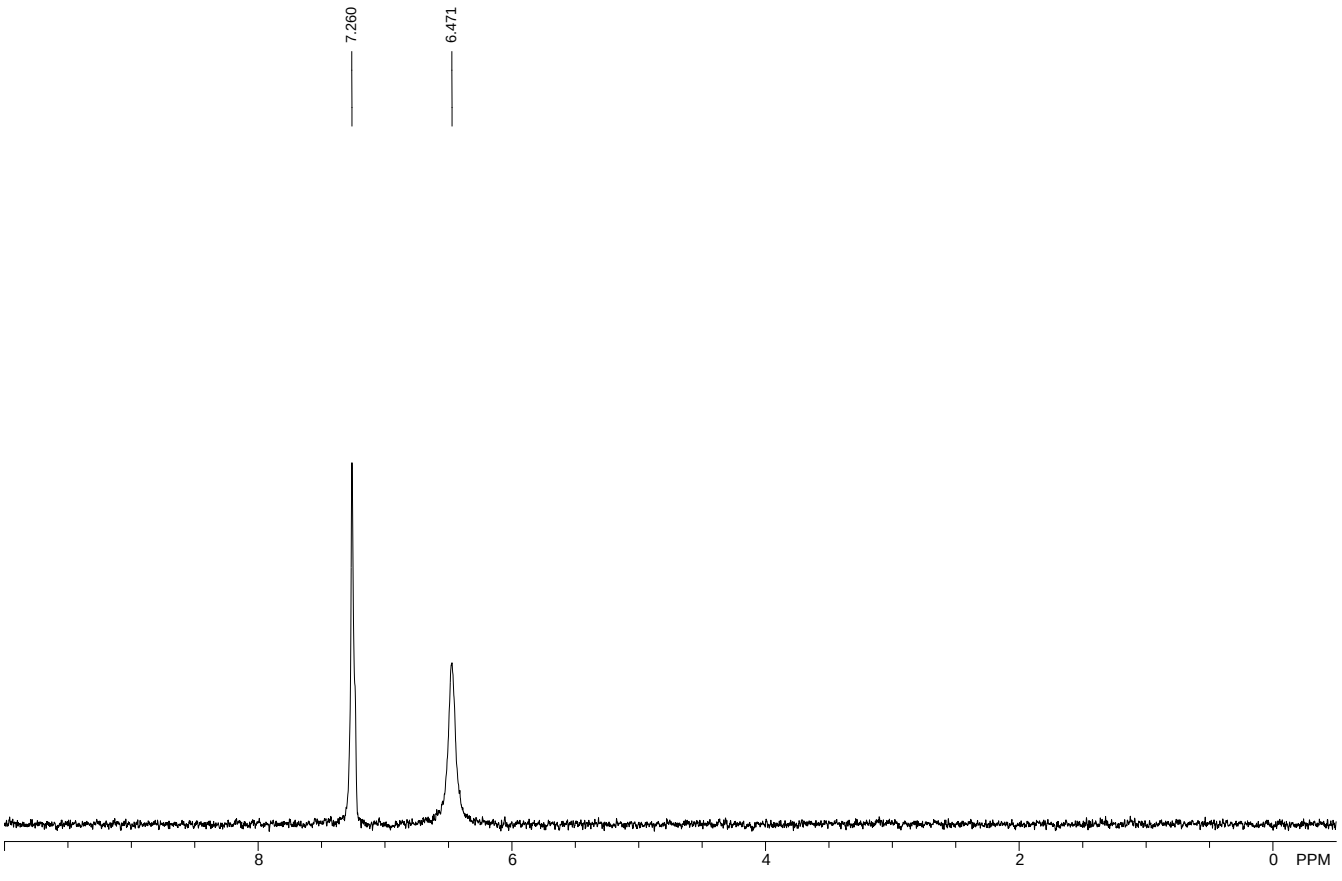


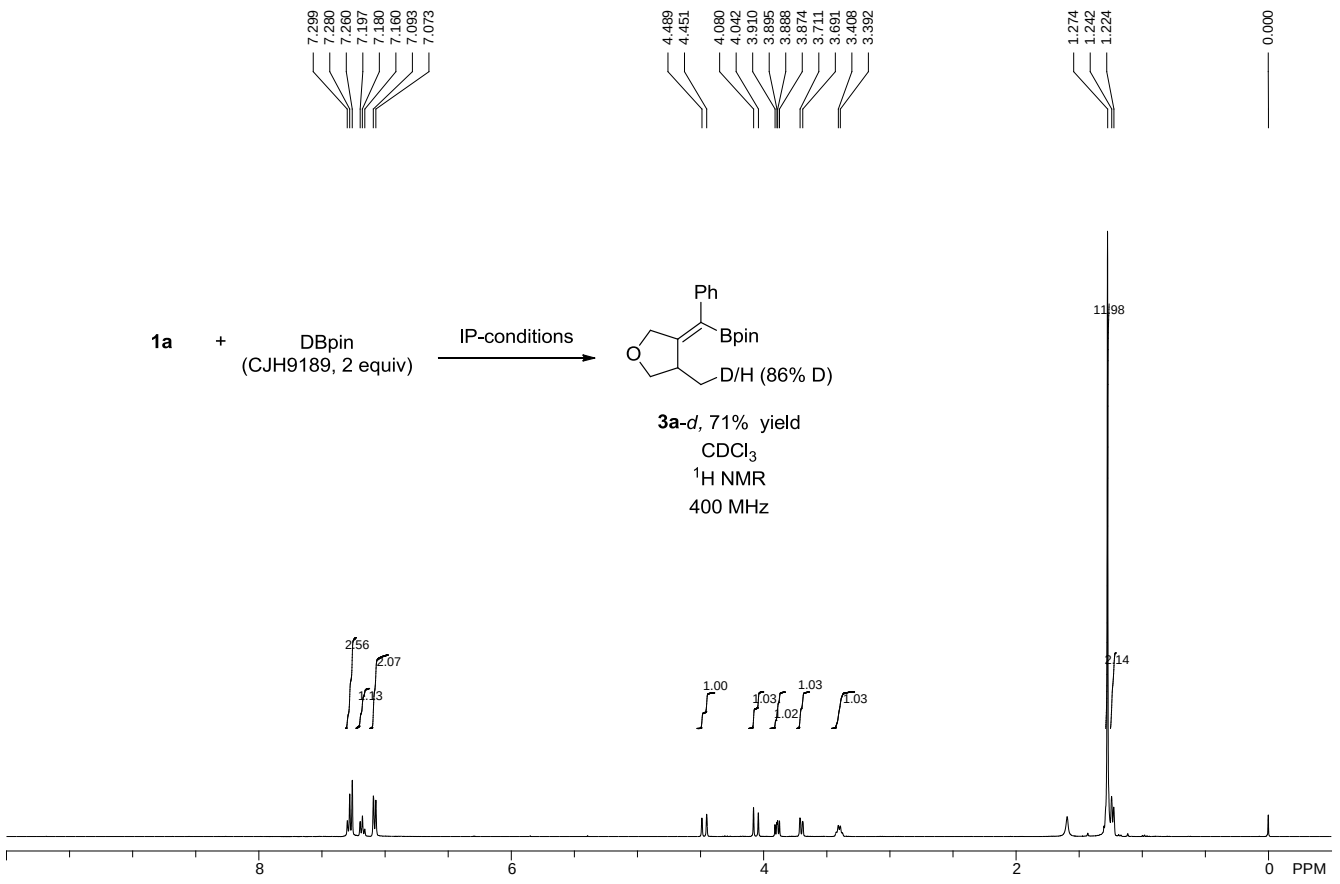
2ab: 25% NMR yield
dr = 1 : 0.78
GC-MS: m/z = 376.3, tr = 13.853 min
m/z = 376.3, tr = 13.985 min

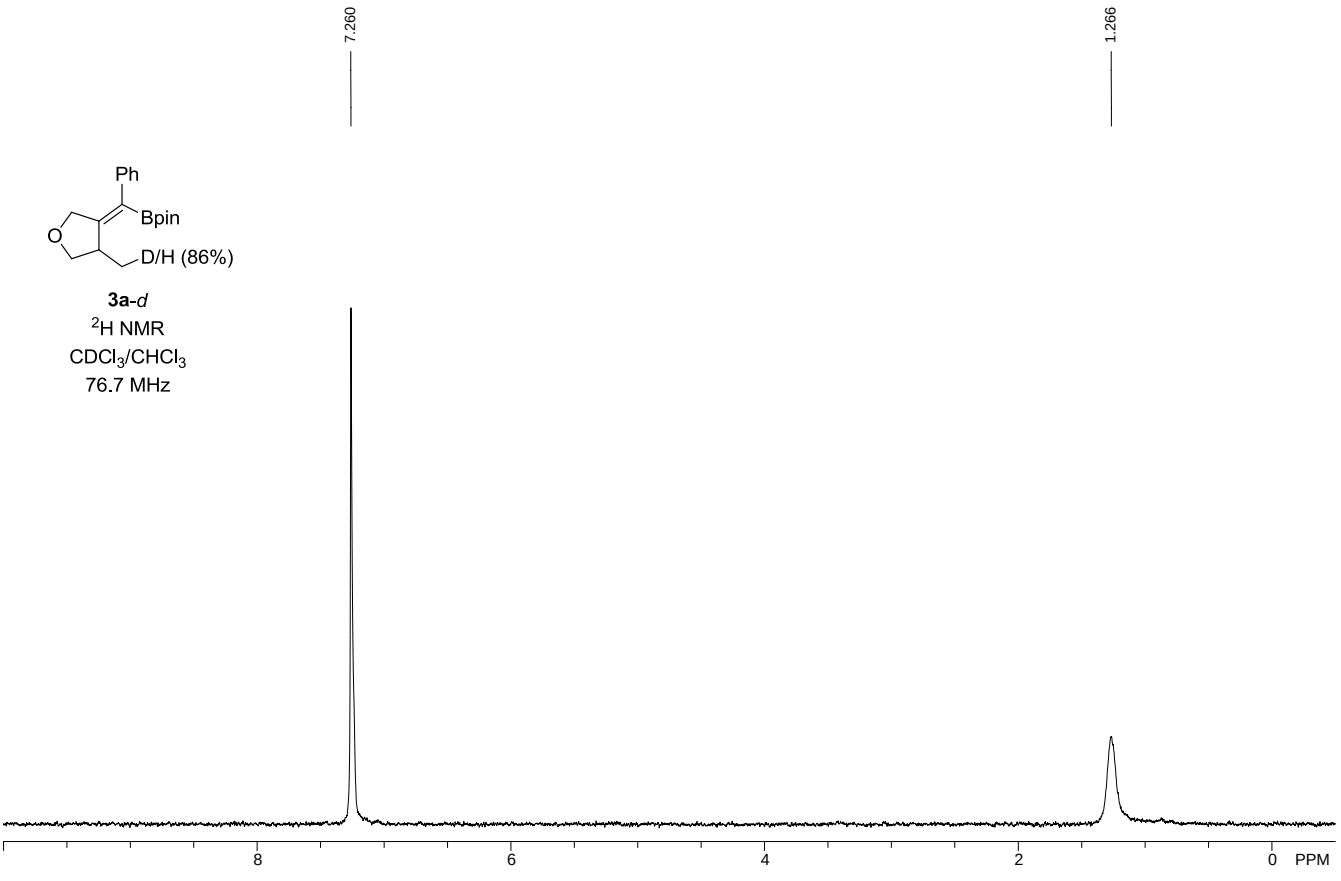


4ab, 20% NMR yield
dr = 1 : 0.78
GC-MS: m/z = 250.2, tr = 11.317


7.977
7.959
7.955
7.611
7.593
7.574
7.500
7.481
7.462
7.368
7.349
7.330
7.260
7.249
7.231
7.212
7.151
7.133
6.457
6.452
4.703
4.699
4.667
4.663
4.601
4.566
4.043
4.031
3.996
3.980
3.974
3.958
3.929
3.919
3.907
3.897
3.752
3.736
3.706
3.248
3.235
3.221
3.077
3.061
3.048
3.034
2.726
1.863
1.704
-0.000
1a
+
DBpin
(2 equiv)
OIP-conditions
Ph
D/H (93% D)
O
OH
5a-d, 61% yield
CDCl3
1H NMR
400 MHz
2.04
1.95
1.07
2.02
1.02
1.00
1.01
1.02
0.96
0.99
0.27
0.31
0.15
0.07
0.30
0.29
0.14
8
6
4
2
0
PPM


7.260
6.471
8
6
4
2
0
PPM


7.299
7.280
7.260
7.197
7.180
7.160
7.093
7.073
4.489
4.451
4.080
4.042
3.910
3.895
3.888
3.874
3.711
3.691
3.408
3.392
1.274
1.242
1.224
0.000
1a
+
DBpin
(CJH9189, 2 equiv)
IP-conditions
Ph
Bpin
O
D/H (86% D)
3a-d, 71% yield
CDCl3
1H NMR
400 MHz
11.98
2.56
2.07
1.13
1.00
1.03
1.02
1.03
1.03
2.14
8
6
4
2
0
PPM


7.260
1.266
Ph
Bpin
O
D/H (86%)
3a-d
2H NMR
CDCl3/CHCl3
76.7 MHz
8
6
4
2
0
PPM