General Reagent Information

All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry toluene was obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. 1-Bromo-2,4,6-tri-*tert*-butylbenzene, sodium *tert*-butoxide, lithium *tert*-butoxide and 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (SIPr·HBF_4) were purchased from Aldrich and used as received. $Pd_2(dba)_3$ was purchased from STREM and used as received. Flash chromatography was performed using a Biotage SP4 instrument with prepacked silica cartridges.

General Analytical Information

All compounds were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy, as well as, in most instances, elemental analysis. Copies of the ^1H and ^{13}C spectra can be found at the end of the supporting information. NMR spectra were recorded on a Bruker AMX 400 spectrometer and were calibrated using residual solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, ovrlp = overlapping. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer using KBr plates (thin film). Melting points (m. p.) were obtained on a Mel-Temp capillary melting point apparatus. Gas chromatographic analyses were performed on a Agilent 6890 gas chromatography with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.). Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

General Procedure for Ligand Evaluation (Table 1)

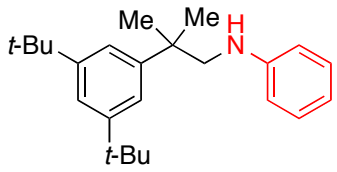
In a nitrogen-filled glovebox, to an oven-dried test tube containing a magnetic stir bar, was added 1-bromo-2,4,6-tri-*tert*-butylbenzene (0.5 mmol, 1.0 equiv), $Pd_2(dba)_3$ (5 mol %), ligand (20 mol %), NaO^tBu (0.75 mmol, 1.5 equiv), aniline (0.6 mmol, 1.2 equiv) and dioxane (5 mL). The test tube was sealed with a Teflon-lined septum, removed from the glovebox, and heated at 120 °C in a pre-heated oil bath for 40 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature. Dodecane

was then added as an internal standard. The mixture was filtered through a small plug of silica gel, eluted with diethyl ether and analyzed by GC.

General Procedure for Table 2 and Table 3

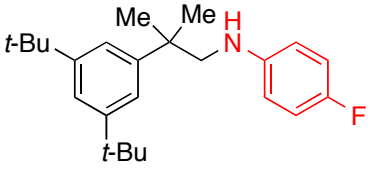
In a nitrogen-filled glovebox, to an oven-dried test tube containing a magnetic stir bar, was added aryl bromide (1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (46 mg, 5 mol %), SIPr·HBF_4 (53 mg, 11 mol %), NaO^tBu (144 mg, 1.5 mmol, 1.5 equiv), aryl amine (1.2 mmol, 1.2 equiv) and toluene (10 mL). The test tube was sealed with a Teflon-lined septum, removed from the glovebox, and heated at 110 °C in a pre-heated oil bath for 4 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature, filtered through a plug of silica gel and eluted with diethyl ether. The filtrate was concentrated in vacuo and the crude product was purified via the Biotage SP4 (silica-packed 25g or 50g snap cartridge).

Experimental Procedures for Examples Described in Table 2



***N*-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)aniline** (Table 2, **3a**)

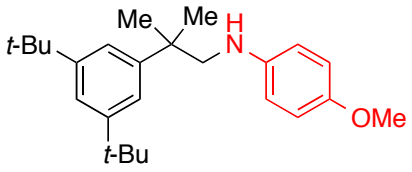
Following the general procedure, a mixture of 1-bromo-2,4,6-tri-*tert*-butylbenzene (326.8 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (46.5 mg, 5 mol %), SIPr·HBF_4 (54.5 mg, 11 mol %), NaO^tBu (145.0 mg, 1.5 mmol, 1.5 equiv), aniline (115.6 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (281.3 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (t, J = 1.7 Hz, 1H), 7.23 (d, J = 1.7 Hz, 2H), 7.11 (dd, J = 8.5, 7.3 Hz, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 8.5 Hz, 2H), 3.42 (br, 1H), 3.24 (s, 2H), 1.42 (s, 6H), 1.32 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7, 149.0, 145.8, 129.3, 120.3, 117.1, 112.9, 56.0, 39.4, 35.2, 31.7, 31.6, 27.6. IR (film, cm^{-1}): 3407, 2963, 1602, 1505, 1362, 1250, 874, 746, 715, 690. Anal. Calcd. for $C_{24}H_{35}N$: C, 85.40; H, 10.45. Found: C, 85.49; H, 10.57.



***N*-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-4-fluoroaniline** (Table 2, **3b**)

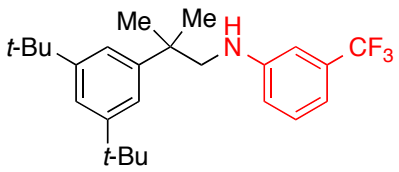
Following the general procedure, a mixture of 1-bromo-2,4,6-tri-*tert*-butylbenzene (326.2 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (46.4 mg, 5 mol %), SIPr·HBF_4 (54.2 mg, 11 mol %), NaO^tBu (146.7 mg, 1.5 mmol, 1.5 equiv), 4-fluoroaniline (137.8 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (299.1 mg, 84%). ^{1}H NMR (400 MHz,

$CDCl_3$) δ: 7.31 (t, J = 1.7 Hz, 1H), 7.25 (d, J = 1.7 Hz, 2H), 6.83 (t, J = 8.7 Hz, 2H), 6.45 (dd, J = 8.7, 4.4 Hz, 2H), 3.32 (br, 1H), 3.21 (s, 2H), 1.43 (s, 6H), 1.33 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.72 (d, J = 234.3 Hz), 150.7, 145.7, 145.4, 120.4, 120.3, 115.6 (d, J = 22.2 Hz), 113.7 (d, J = 7.3 Hz), 56.9, 39.4, 35.2, 31.7, 27.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -128.9. IR (film, cm^{-1}): 3388, 2963, 1596, 1511, 1477, 1362, 1249, 1222, 817, 715. Anal. Calcd. for $C_{24}H_{34}FN$: C, 81.08; H, 9.64. Found: C, 81.02; H, 9.51.



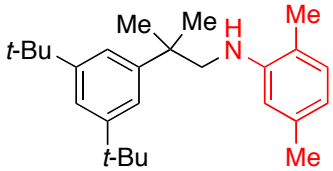
***N*-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-4-methoxyaniline** (Table 2, **3c**)

Following the general procedure, a mixture of 1-bromo-2,4,6-tri-*tert*-butylbenzene (326.3 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (47.1 mg, 5 mol %), SIPr·HBF_4 (51.8 mg, 11 mol %), NaO^{t}Bu (145.5 mg, 1.5 mmol, 1.5 equiv), *p*-anisidine (148.7 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (317.5 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (t, J = 1.7 Hz, 1H), 7.24 (d, J = 1.7 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 8.8, 2H), 3.74 (s, 3H), 3.22 (s, 2H), 3.21 (br, 1H), 1.44 (s, 6H), 1.34 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.0, 150.6, 145.9, 143.3, 120.3, 120.2, 115.0, 114.2, 57.3, 56.0, 39.4, 35.2, 31.7, 27.7. IR (film, cm^{-1}): 3405, 2962, 1596, 1513, 1477, 1362, 1247, 1235, 817, 715. Anal. Calcd. for $C_{25}H_{37}NO$: C, 81.69; H, 10.15. Found: C, 81.65; H, 10.11.



***N*-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-3-(trifluoromethyl)aniline** (Table 2, **3d**)

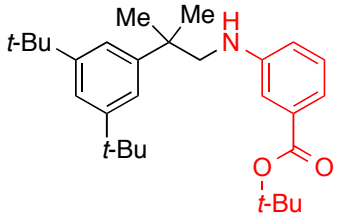
Following the general procedure, a mixture of 1-bromo-2,4,6-tri-*tert*-butylbenzene (325.6 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (47.6 mg, 5 mol %), SIPr·HBF_4 (53.9 mg, 11 mol %), NaO^{t}Bu (144.0 mg, 1.5 mmol, 1.5 equiv), 3-(trifluoromethyl)aniline (197.8 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (295.7 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (t, J = 1.7 Hz, 1H), 7.24 (d, J = 1.7 Hz, 2H), 7.19 (t, J = 7.9 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.70 (s, 1H), 6.64 (d, J = 8.2, 1H), 3.63 (t, J = 5.5 Hz, 1H), 3.29 (d, J = 5.5 Hz, 1H), 1.46 (s, 6H), 1.34 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.9, 149.1, 145.4, 131.8 (q, J = 31.6 Hz), 129.6, 124.5 (q, J = 272.3 Hz), 120.5, 120.3, 115.9, 113.4 (q, J = 3.9 Hz), 108.8 (q, J = 3.9 Hz), 55.9, 39.4, 35.2, 31.7, 27.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -63.1. IR (film, cm^{-1}): 3407, 2964, 2869, 1616, 1596, 1477, 1362, 1332, 1163, 1124, 1068, 781, 696. Anal. Calcd. for $C_{25}H_{34}F_3N$: C, 74.04; H, 8.45. Found: C, 74.36; H, 8.42.



***N*-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-2,5-dimethylaniline** (Table 2, **3e**)

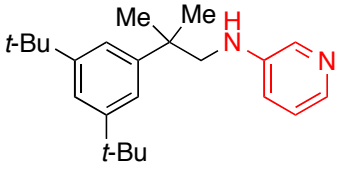
Following the general procedure, a mixture of 1-bromo-2,4,6-tri-*tert*-butylbenzene (326.2 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (47.2 mg, 5 mol %), SIPr·HBF_4 (55.0 mg, 11 mol %), NaO^{t}Bu (149.6 mg, 1.5 mmol, 1.5 equiv), 2,5-dimethylaniline (147.7 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (278.3 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (t, J = 1.7 Hz, 1H), 7.29 (d, J = 1.7 Hz, 2H), 6.87 (d, J = 7.2 Hz, 1H), 6.45 (d, J = 7.2, 1H), 6.43 (s, 1H), 3.24 (d, J = 5.2 Hz, 2H), 3.16 (t, J = 5.2 Hz, 1H), 2.30 (s,

3H), 1.83 (s, 3H), 1.51 (s, 6H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7, 146.7, 145.6, 136.8, 129.8, 120.4, 120.3, 119.0, 117.2, 110.8, 56.3, 39.1, 35.1, 31.7, 27.4, 21.7, 16.8. IR (film, cm^{-1}): 3398, 2963, 2867, 1616, 1584, 1522, 1459, 1362, 792, 716. Anal. Calcd. for $C_{26}H_{39}N$: C, 85.42; H, 10.75. Found: C, 85.50; H, 10.84.



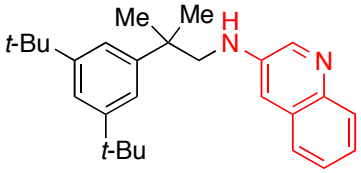
***tert*-Butyl 3-((2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)amino)benzoate** (Table 2, **3f**)

Following the general procedure, a mixture of 1-bromo-2,4,6-tri-*tert*-butylbenzene (326.9 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (47.5 mg, 5 mol %), SIPr·HBF_4 (52.5 mg, 11 mol %), NaO^{t}Bu (147.1 mg, 1.5 mmol, 1.5 equiv), *tert*-Butyl 3-aminobenzoate (233.1 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (334.2 mg, 76%). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.61 (d, J = 7.8 Hz, 1H), 7.52 (s, 1H), 7.43 (t, J = 1.7 Hz, 1H), 7.33 (d, J = 1.7 Hz, 2H), 6.99 (t, J = 7.8 Hz, 1H), 6.29 (d, J = 7.8, 1H), 3.37 (t, J = 5.8, 1H), 3.16 (d, J = 5.8, 2H), 1.48 (s, 9H), 1.31 (s, 18H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 150.8, 148.9, 145.6, 133.0, 129.0, 120.4, 120.3, 118.2, 116.8, 113.5, 80.8, 56.0, 39.4, 35.2, 31.7, 28.3, 27.6. IR (film, cm^{-1}): 3406, 2964, 1713, 1605, 1477, 1365, 1295, 1248, 1163, 1110, 753. Anal. Calcd. for $C_{29}H_{43}NO_2$: C, 79.59; H, 9.90. Found: C, 79.30; H, 10.00.



***N*-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)pyridin-3-amine** (Table 2, **3g**)

Following the general procedure, a mixture of 1-bromo-2,4,6-tri-*tert*-butylbenzene (325.9 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (47.2 mg, 5 mol %), SIPr·HBF_4 (52.2 mg, 11 mol %), NaO^tBu (147.0 mg, 1.5 mmol, 1.5 equiv), 3-aminopyridine (114.5 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-30% EtOAc/hexanes) to provide the title compound as a pale yellow oil (254.6 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J = 2.8 Hz, 1H), 7.89 (d, J = 4.6 Hz, 1H), 7.31 (t, J = 1.7 Hz, 1H), 7.23 (d, J = 1.7 Hz, 2H), 7.01 (dd, J = 8.3, 4.6 Hz, 1H), 6.75 (d, J = 8.3, 1H), 3.46 (t, J = 5.8, 1H), 3.26 (d, J = 5.8, 2H), 1.44 (s, 6H), 1.32 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.8, 145.3, 144.9, 138.5, 136.2, 123.7, 120.5, 120.2, 118.4, 55.6, 39.5, 35.1, 31.7, 27.5. IR (film, cm^{-1}): 3278, 2962, 2866, 1588, 1478, 1362, 1246, 790, 708. Anal. Calcd. for $C_{23}H_{34}N_2$: C, 81.60; H, 10.12. Found: C, 81.47; H, 10.02.

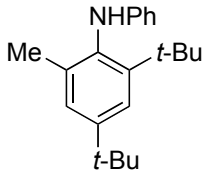


***N*-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)quinolin-3-amine** (Table 2, **3h**)

Following the general procedure, a mixture of 1-bromo-2,4,6-tri-*tert*-butylbenzene (326.2 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (48.2 mg, 5 mol %), SIPr·HBF_4 (53.6 mg, 11 mol %), NaO^tBu (145.4 mg, 1.5 mmol, 1.5 equiv), 3-aminoquinoline (176.5 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-30% EtOAc/hexanes) to provide the title compound as a yellow oil (327.6 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (d, J = 2.7 Hz, 1H), 7.92 (d, J = 7.2 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.40 (m, 1H), 7.34 (t, J = 1.6 Hz, 1H), 7.29 (d, J = 1.6 Hz, 2H), 6.94 (d, J = 2.7 Hz, 1H), 3.80 (t, J = 5.8, 1H), 3.37 (d, J = 5.8, 2H), 1.51 (s, 6H), 1.34 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.8, 145.3, 143.6, 142.2, 142.1, 129.7, 129.0, 126.9, 125.9, 124.8, 120.6, 120.2, 109.9, 55.7, 39.4, 35.1, 31.7, 27.6. IR (film, cm^{-1}): 3279, 2962, 2866, 1612,

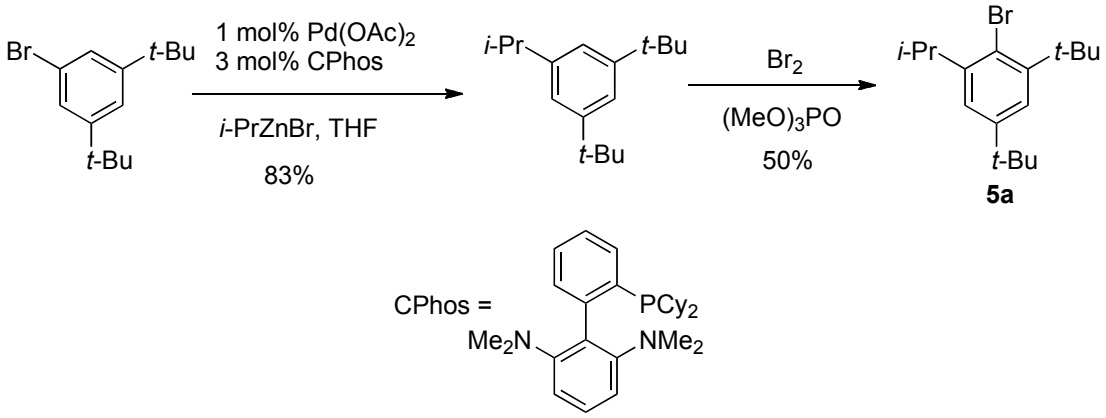
1476, 1391, 1362, 1222, 746, 714. Anal. Calcd. for $C_{27}H_{36}N_2$: C, 83.45; H, 9.34. Found: C, 83.19; H, 9.46.

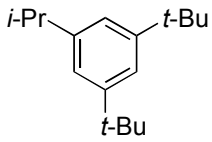
Experimental Procedures for Examples Described in Table 3



2,4-Di-*tert*-butyl-6-methyl-*N*-phenylaniline (Table 3, **4b**)

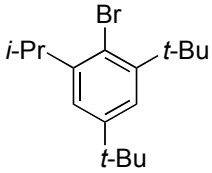
Following the general procedure, a mixture of 2-bromo-1,5-di-*tert*-butyl-3-methylbenzene[1] (285.9 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (49.7 mg, 5 mol %), SIPr·HBF_4 (57.8 mg, 12 mol %), NaO^{t}Bu (145.8 mg, 1.5 mmol, 1.5 equiv), aniline (115.9 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a off-white solid (280.5 mg, 94%), m.p. = 87 – 89 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, J = 2.2 Hz, 1H), 7.17 (ovrlp, 3H), 6.71 (t, J = 7.5 Hz, 1H), 6.44 (d, J = 7.5 Hz, 2H), 5.18 (br, 1H), 2.14 (s, 3H), 1.40 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 147.6, 147.5, 138.1, 135.5, 129.3, 126.3, 122.0, 117.5, 113.5, 35.8, 34.8, 31.6, 31.4, 19.6. IR (film, cm^{-1}): 3437, 2962, 2868, 1604, 1498, 1482, 1361, 1309, 875, 746, 693. Anal. Calcd. for $C_{21}H_{29}N$: C, 85.37; H, 9.89. Found: C, 85.16; H, 9.84.





1,3-Di-*tert*-butyl-5-isopropylbenzene[2]

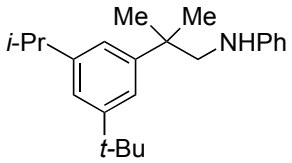
Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added 1-bromo-3,5-di-*tert*-butylbenzene (2.70 g, 10.0 mmol), $Pd(OAc)_2$ (28.3 mg, 1 mol %), CPhos (125.4 mg, 3 mol %) and THF (25 mL). The flask was sealed with a rubber septum and cooled to 0 ºC. A solution of 2-propylzinc bromide (0.5 M in THF, 25 mL, 12.5 mmol) was then added slowly via syringe. After addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was filtered through a thin pad of silica gel and eluted with diethyl ether. The filtrate was concentrated in vacuo and the crude product was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a colorless oil (1.93 g, 83%). Note: The product was a mixture of 1,3-Di-*tert*-butyl-5-isopropylbenzene and 1,3-di-*tert*-butyl-5-propylbenzene in a ratio of 15 : 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (t, J = 1.8 Hz, 1H), 7.14 (d, J = 1.8 Hz, 2H), 2.96 (septet, J = 6.9 Hz, 1H), 1.39 (s, 18H), 1.33 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.6, 148.0, 120.8, 120.0, 35.0, 34.8, 31.7, 24.4. IR (film, cm^{-1}): 2963, 2868, 1598, 1478, 1463, 1362, 1248, 1203, 897, 871, 714. Anal. Calcd. for $C_{17}H_{28}$: C, 87.86; H, 12.14. Found: C, 88.03; H, 12.19.



2-Bromo-1,5-di-*tert*-butyl-3-isopropylbenzene (Table 3, **5a**)

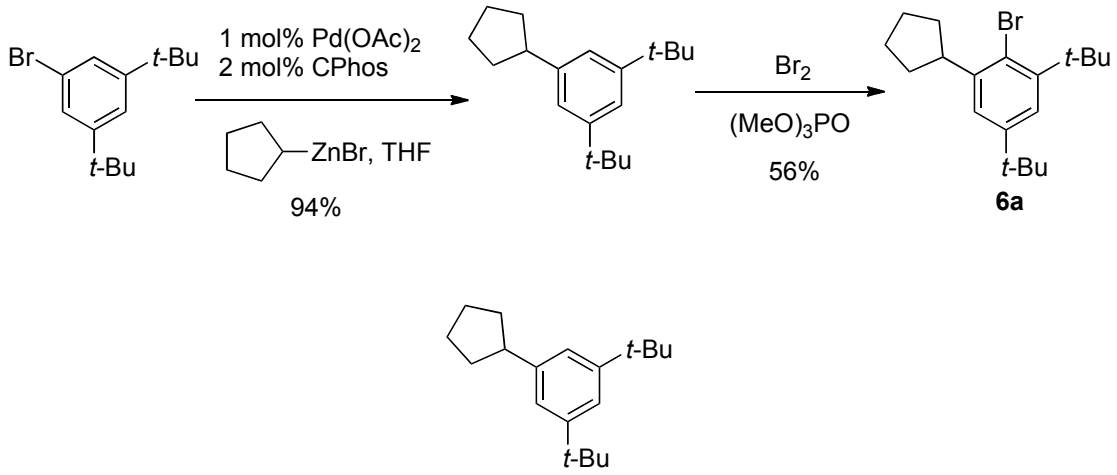
To an oven-dried test tube containing a magnetic stir bar, was added 1,3-di-*tert*-butyl-5-isopropylbenzene (1.04 g, 4.46 mmol) and trimethyl phosphate (5 mL). The test tube was sealed with a Teflon-lined septum and heated at 70 ºC in a pre-heated oil bath. A solution of Br_2 (2.16 g, 13.51 mmol) in trimethyl phosphate (2 mL) was then added slowly over a period of 2 h via syringe pump. After addition, the reaction mixture was stirred at 70 ºC

for 12 h. The reaction was then cooled to room temperature and an aqueous solution of saturated $NaHCO_3$ (60 mL) was added. The aqueous solution was extracted with hexanes (3 × 50 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified via the Biotage SP4 (silica-packed 50 g snap cartridge; hexanes) to provide the title compound as a white solid (689 mg, 50%), m.p. = 66 – 67 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (t, *J* = 2.5 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 3.63 (septet, *J* = 6.8 Hz, 1H), 1.56 (s, 9H), 1.32 (s, 9H), 1.25 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 148.5, 147.4, 123.3, 122.4, 121.7, 37.8, 35.0, 33.7, 31.5, 30.5, 23.5. IR (film, cm^{-1}): 2963, 2869, 1459, 1422, 1363, 1238, 1199, 1010, 877, 738.



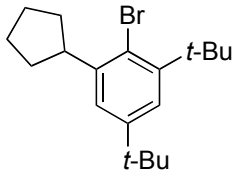
***N*-(2-(3-(*tert*-butyl)-5-isopropylphenyl)-2-methylpropyl)aniline** (Table 3, **5b**)

Following the general procedure, a mixture of **5a** (311.8 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (48.8 mg, 5 mol %), SIPr·HBF_4 (53.6 mg, 11 mol %), NaO^{t}Bu (146.0 mg, 1.5 mmol, 1.5 equiv), aniline (115.7 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (243.3 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (t, *J* = 1.7 Hz, 1H), 7.15 (ovrlp, 3H), 7.09 (t, *J* = 1.7 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 2H), 3.43 (t, *J* = 5.8 Hz, 1H), 3.28 (d, *J* = 5.8 Hz, 2H), 2.93 (septet, *J* = 6.9 Hz, 1H), 1.45 (s, 6H), 1.35 (s, 9H), 1.29 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.1, 149.0, 148.6, 146.2, 129.3, 121.5, 121.4, 120.7, 117.1, 112.9, 56.0, 39.3, 35.0, 34.7, 31.7, 27.6, 24.4. IR (film, cm^{-1}): 3411, 2961, 2868, 1602, 1505, 1465, 1362, 1255, 746, 690. Anal. Calcd. for $C_{23}H_{33}N$: C, 85.39; H, 10.28. Found: C, 85.12; H, 10.24.



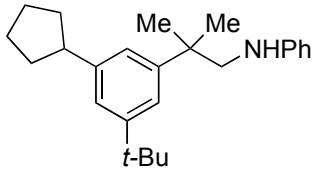
1,3-Di-*tert*-butyl-5-cyclopentylbenzene

Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added 1-bromo-3,5-di-*tert*-butylbenzene (2.70 g, 10.0 mmol), $Pd(OAc)_2$ (28.0 mg, 1 mol %), CPhos (95.1 mg, 2 mol %) and THF (25 mL). The flask was sealed with a rubber septum and cooled to 0 ºC. A solution of cyclopentylzinc bromide (0.5 M in THF, 25 mL, 12.5 mmol) was then added slowly via syringe. After addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was filtered through a thin pad of silica gel and eluted with diethyl ether. The filtrate was concentrated in vacuo and the crude product was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a colorless oil (2.43 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (t, J = 1.8 Hz, 1H), 7.11 (d, J = 1.8 Hz, 2H), 2.99 (m, 1H), 2.08 (m, 2H), 1.83 (m, 2H), 1.67 (ovrlp, 4H). 1.34 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 145.5, 121.5, 120.0, 46.8, 35.0, 34.9, 31.7, 25.7. IR (film, cm^{-1}): 3495, 2960, 2867, 1598, 1476, 1362, 1247, 1202, 870, 713. Anal. Calcd. for $C_{19}H_{30}$: C, 88.30; H, 11.70. Found: C, 88.20; H, 11.72.



2-Bromo-1,5-di-*tert*-butyl-3-cyclopentylbenzene (Table 3, **6a**)

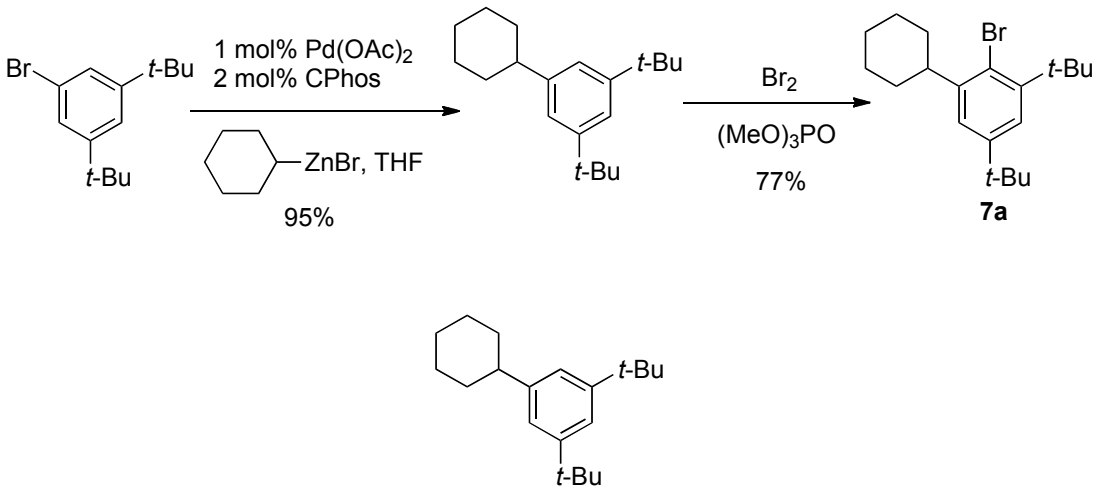
To an oven-dried test tube containing a magnetic stir bar, was added 1,3-di-*tert*-butyl-5-cyclopentylbenzene (1.18 g, 4.57 mmol) and trimethyl phosphate (5 mL). The test tube was sealed with a Teflon-lined septum and heated at 70 ºC in a pre-heated oil bath. A solution of Br_2 (2.35 g, 14.70 mmol) in trimethyl phosphate (2 mL) was then added slowly over a period of 2 h via syringe pump. After addition, the reaction mixture was stirred at 70 ºC for 12 h. The reaction mixture was then cooled to room temperature and an aqueous solution of saturated $NaHCO_3$ (60 mL) was added. The aqueous solution was extracted with hexanes (3 × 50 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified via the Biotage SP4 (silica-packed 50 g snap cartridge; hexanes) to provide the title compound as a white solid (872.3 mg, 56%), m.p. = 76 – 77 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (t, *J* = 2.5 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 3.65 (m, 1H), 2.11 (m, 2H), 1.83 (m, 2H), 1.72 (m, 2H), 1.57 (ovrlp, 11H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.3, 147.5, 146.4, 123.3, 123.1, 122.2, 46.0, 37.7, 35.0, 34.0, 31.5, 30.5, 25.6. IR (film, cm^{-1}): 2954, 2865, 1393, 1361, 1199, 1010, 875. Anal. Calcd. for $C_{19}H_{29}Br$: C, 67.65; H, 8.66. Found: C, 67.87; H, 8.61.



***N*-(2-(3-(*tert*-butyl)-5-cyclopentylphenyl)-2-methylpropyl)aniline** (Table 3, **6b**)

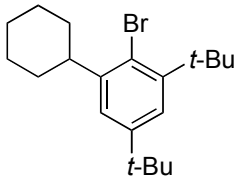
Following the general procedure, a mixture of **6a** (341.8 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (46.6 mg, 5 mol %), SIPr·HBF_4 (53.1 mg, 11 mol %), NaO^{t}Bu (148.0 mg, 1.5 mmol, 1.5 equiv), aniline (116.1 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (273.4 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (t, *J* = 1.7 Hz, 1H), 7.14 (ovrlp, 3H), 7.09 (t, *J* = 1.7 Hz, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 2H), 3.40 (t, *J* = 5.7 Hz, 1H), 3.25 (d, *J* = 5.7 Hz, 2H), 2.99 (m, 1H), 2.07 (m, 2H), 1.82

(m, 2H), 1.65 (ovrlp, 4H), 1.42 (s, 6H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.0, 149.0, 146.2, 146.1, 129.3, 122.2, 120.7, 117.1, 112.9, 55.9, 46.7, 39.2, 35.0, 34.9, 31.7, 27.6, 25.6. IR (film, cm^{-1}): 3411, 2958, 2867, 1601, 1505, 1362, 1320, 1255, 871, 746, 690. Anal. Calcd. for $C_{25}H_{35}N$: C, 85.90; H, 10.09. Found: C, 85.69; H, 10.11.



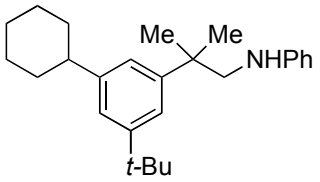
1,3-Di-*tert*-butyl-5-cyclohexylbenzene

Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added 1-bromo-3,5-di-*tert*-butylbenzene (2.68 g, 9.94 mmol), $Pd(OAc)_2$ (25.6 mg, 1 mol %), CPhos (94.1 mg, 2 mol %) and THF (25 mL). The flask was sealed with a rubber septum and cooled to 0 ºC. A solution of cyclohexylzinc bromide (0.5 M in THF, 25 mL, 12.5 mmol) was then added slowly via syringe. After addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was filtered through a thin pad of silica gel and eluted with diethyl ether. The filtrate was concentrated in vacuo and the crude product was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a white solid (2.58 g, 95%), m.p. = 116 – 117 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (t, J = 1.8 Hz, 1H), 7.07 (d, J = 1.8 Hz, 2H), 2.50 (m, 1H), 1.74 – 1.90 (ovrlp, 5H), 1.34 – 1.45 (ovrlp, 23H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 147.3, 121.2, 120.0, 45.3, 35.0, 34.8, 31.7, 27.2, 26.4. IR (film, cm^{-1}): 2962, 2849, 1597, 1477, 1445, 1361, 1247, 864, 713. Anal. Calcd. for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.34; H, 11.89.



2-Bromo-1,5-di-*tert*-butyl-3-cyclohexylbenzene (Table 3, **7a**)

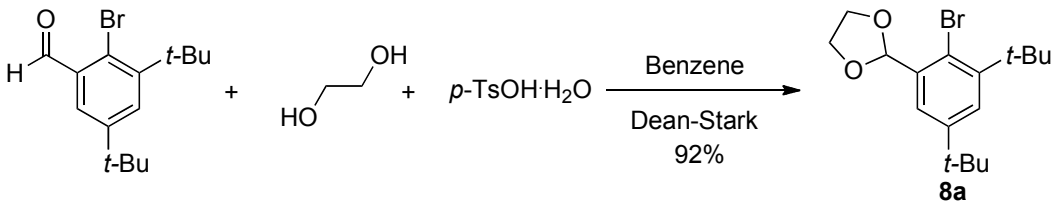
To an oven-dried test tube containing a magnetic stir bar, was added 1,3-di-*tert*-butyl-5-cyclohexylbenzene (1.22 g, 4.46 mmol) and trimethyl phosphate (5 mL). The test tube was sealed with a Teflon-lined septum and heated at 70 ºC in a pre-heated oil bath. A solution of Br_2 (2.17 g, 13.58 mmol) in trimethyl phosphate (2 mL) was then added slowly over a period of 2 h via syringe pump. After addition, the reaction mixture was stirred at 70 ºC for 12 h. The reaction mixture was then cooled to room temperature and an aqueous solution of saturated $NaHCO_3$ (60 mL) was added. The aqueous solution was extracted with hexanes (3 × 50 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified via the Biotage SP4 (silica-packed 50 g snap cartridge; hexanes) to provide the title compound as a white solid (1.21 g, 77%), m.p. = 62 – 65 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (t, *J* = 2.5 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 3.22 (m, 1H), 1.77 – 1.90 (ovrlp, 5H), 1.56 (s, 9H), 1.32 – 1.49 (ovrlp, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.3, 147.5, 147.4, 123.3, 122.6, 122.4, 44.4, 37.8, 35.0, 34.0, 31.5, 30.5, 27.2, 26.5. IR (film, cm^{-1}): 2927, 2852, 1589, 1563, 1448, 1394, 1363, 1236, 1011, 871. Anal. Calcd. for $C_{20}H_{31}Br$: C, 68.37; H, 8.89. Found: C, 68.61; H, 8.83.



***N*-(2-(3-(*tert*-butyl)-5-cyclohexylphenyl)-2-methylpropyl)aniline** (Table 3, **7b**)

Following the general procedure, a mixture of **7a** (352.8 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (48.2 mg, 5 mol %), SIPr·HBF_4 (53.2 mg, 11 mol %), NaO^{t}Bu (146.8 mg, 1.5 mmol, 1.5 equiv), aniline (116.1 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was

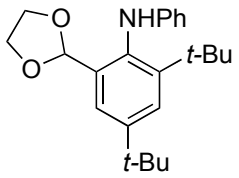
heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a pale yellow oil (296.4 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (t, *J* = 1.7 Hz, 1H), 7.12 (ovrlp, 3H), 7.05 (t, *J* = 1.7 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 2H), 3.40 (t, *J* = 5.7 Hz, 1H), 3.25 (d, *J* = 5.7 Hz, 2H), 2.50 (m, 1H), 1.74 – 1.90 (ovrlp, 5H), 1.42 (ovrlp, 10H), 1.32 (ovrlp, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.0, 149.0, 147.8, 146.2, 129.3, 121.9, 121.8, 120.7, 117.1, 112.9, 56.0, 45.3, 39.3, 35.0, 34.8, 31.7, 27.6, 27.1, 26.3. IR (film, cm^{-1}): 3407, 2925, 2851, 1602, 1505, 1448, 1362, 1255, 865, 746, 690. Anal. Calcd. for $C_{26}H_{37}N$: C, 85.89; H, 10.26. Found: C, 85.88; H, 10.24.



8a

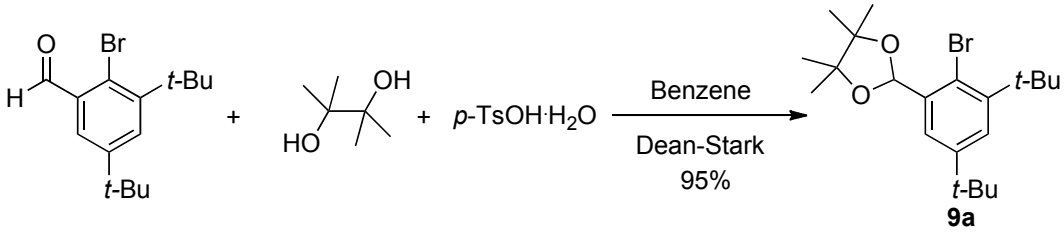
2-(2-Bromo-3,5-di-*tert*-butylphenyl)-1,3-dioxolane (Table 3, **8a**)

To a round bottom flask containing a magnetic stir bar, was added 2-bromo-3,5-di-*tert*-butylbenzaldehyde[3] (616 mg, 2.07 mmol), ethylene glycol (1322 mg, 21.30 mmol), *p*-TsOH·H_2O (4.2 mg, 0.02 mmol) and benzene (50 mL). The flask was fitted with a Dean-Stark trap and the reaction mixture was heated to reflux for 16 h. After cooling to room temperature, the reaction was concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 50 g snap cartridge; 0-20% EtOAc/hexanes) to provide the title compound as a colorless oil (653.4 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (s, 2H), 6.24 (s, 1H), 4.17 (m, 2H), 4.08 (m, 2H), 1.55 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 147.8, 137.6, 126.6, 122.6, 120.9, 103.8, 65.5, 37.6, 35.0, 31.4, 30.3. IR (film, cm^{-1}): 2962, 2875, 1477, 1430, 1396, 1364, 1177, 1097, 1016, 885. Anal. Calcd. for $C_{17}H_{25}BrO_2$: C, 59.83; H, 7.38. Found: C, 60.09; H, 7.40.



2,4-Di-*tert*-butyl-6-(1,3-dioxolan-2-yl)-*N*-phenylaniline (Table 3, **8b**)

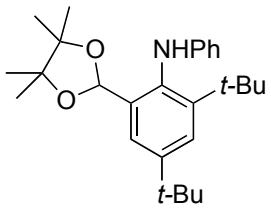
Following the general procedure, a mixture of **8a** (346.5 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (49.1 mg, 5 mol %), SIPr·HBF_4 (55.7 mg, 11 mol %), NaO^{t}Bu (148.2 mg, 1.5 mmol, 1.5 equiv), aniline (115.7 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a yellow oil (294.5 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, J = 2.4 Hz, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.13 (t, J = 7.5 Hz, 2H), 6.70 (t, J = 7.5 Hz, 1H), 6.46 (d, J = 7.5 Hz, 2H), 5.73 (s, 1H), 5.36 (s, 1H), 4.06 (m, 2H), 3.89 (m, 2H), 1.37 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 148.7, 148.5, 137.4, 135.9, 129.2, 125.7, 121.8, 117.8, 113.7, 101.1, 65.2, 36.1, 35.1, 31.6, 31.5. IR (film, cm^{-1}): 3381, 2962, 1600, 1498, 1393, 1362, 1308, 1090, 886, 748. Anal. Calcd. for $C_{23}H_{31}NO_2$: C, 78.15; H, 8.84. Found: C, 78.39; H, 8.87.



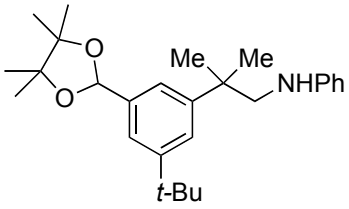
2-(2-Bromo-3,5-di-*tert*-butylphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (Table 3, **9a**)

To a round bottom flask containing a magnetic stir bar, was added 2-bromo-3,5-di-*tert*-butylbenzaldehyde[3] (929.5 mg, 3.13 mmol), pinacol (3702 mg, 31.33 mmol), *p*-TsOH·H_2O (5.4 mg, 0.03 mmol) and benzene (50 mL). The flask was fitted with a Dean-Stark trap and the reaction mixture was heated to reflux for 40 h. After cooling to room temperature, the reaction was concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 50 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a white solid (1183 mg, 95%), m.p. = 74 – 75 ºC. ^{1}H NMR

(400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 2.6 Hz, 1H), 7.46 (d, *J* = 2.6 Hz, 1H), 6.35 (s, 1H), 1.54 (s, 9H), 1.36 (s, 6H), 1.31 (ovrlp, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 147.5, 139.0, 126.0, 123.2, 121.2, 100.0, 82.8, 37.6, 35.0, 31.4, 30.4, 24.6, 22.4. IR (film, cm^{-1}): 2964, 1478, 1364, 1155, 1091, 1016, 961, 886, 730.



9b



9c

Following the general procedure, a mixture of **9a** (397.4 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (49.4 mg, 5 mol %), SIPr·HBF_4 (55.0 mg, 11 mol %), NaO^{t}Bu (148.6 mg, 1.5 mmol, 1.5 equiv), aniline (114.6 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap cartridge; 0-10% EtOAc/hexanes) to provide **9b** as a pale yellow oil (165.5 mg, 40%) and **9c** as a pale yellow oil (167.3mg, 41%).

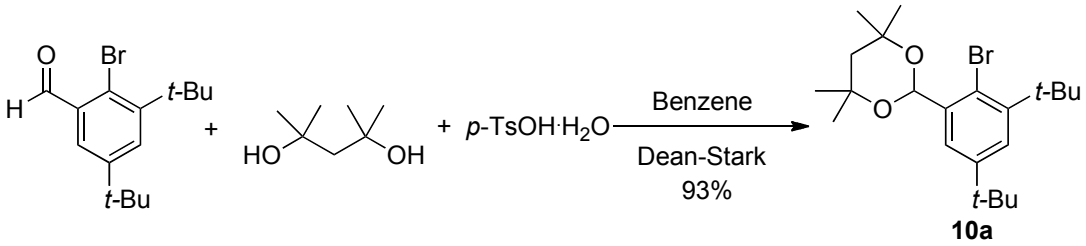
2,4-Di-*tert*-butyl-*N*-phenyl-6-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)aniline (Table 3, **9b**)

^1H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 7.5 Hz, 2H), 5.81 (s, 1H), 5.35 (br, 1H), 1.38 (s, 9H), 1.35 (s, 9H), 1.22 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.1, 148.7, 139.1, 136.1, 129.1, 124.9, 122.0, 117.7, 113.9, 97.2, 82.4, 36.1, 35.1, 31.6, 31.5, 24.4, 22.2. IR (film, cm^{-1}): 3380, 2964, 1600, 1496, 1389, 1363, 1156, 1084, 749, 693.

***N*-(2-(3-(*tert*-butyl)-5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl)-2-methylpropyl)aniline** (Table 3, **9c**)

^1H NMR (400 MHz, $CDCl_3$) δ: 7.40 (t, *J* = 1.6 Hz, 1H), 7.39 (t, *J* = 1.6 Hz, 1H), 7.35 (t, *J* = 1.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 2H), 5.97 (s, 1H), 3.34 (br, 1H), 3.28 (s, 2H), 1.42 (s, 6H), 1.34 (s, 6H), 1.32 (s, 9H), 1.31 (s,

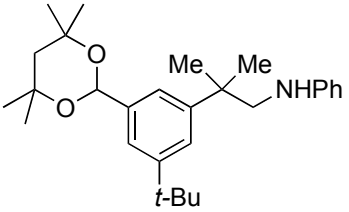
6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.4, 148.8, 146.4, 139.1, 129.3, 123.9, 121.8, 121.7, 117.2, 113.0, 100.8, 82.8, 55.9, 39.3, 35.1, 31.6, 27.6, 24.6, 22.4. IR (film, cm^{-1}): 3403, 2965, 1602, 1506, 1476, 1255, 1155, 1090, 746, 691. Anal. Calcd. for $C_{27}H_{39}NO_2$: C, 79.17; H, 9.60. Found: C, 78.96; H, 9.48.



10a

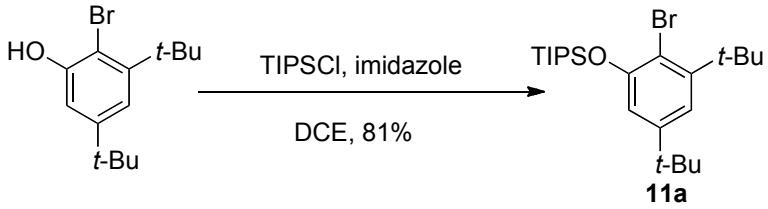
2-(2-Bromo-3,5-di-*tert*-butylphenyl)-4,4,6,6-tetramethyl-1,3-dioxane (Table 3, **10a**)

To a round bottom flask containing a magnetic stir bar, was added 2-bromo-3,5-di-*tert*-butylbenzaldehyde[3] (1008 mg, 3.39 mmol), 2,4-dimethyl-2,4-pentanediol (4493 mg, 33.99 mmol), *p*-TsOH·H_2O (5.6 mg, 0.03 mmol) and benzene (50 mL). The flask was fitted with a Dean-Stark trap and the reaction mixture was heated to reflux for 80 h. After cooling to room temperature, the reaction was concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 50 g snap cartridge; 0-10% EtOAc/hexanes) to provide the title compound as a white solid (1300 mg, 93%), m.p. = 97 – 98 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 2.6 Hz, 1H), 7.46 (d, J = 2.6 Hz, 1H), 6.38 (s, 1H), 1.77 (d, J = 13.7 Hz, 1H), 1.58 (d, J = 13.7 Hz, 1H), 1.53 (ovrlp, 15H), 1.34 (s, 6H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 147.1, 139.3, 126.4, 123.9, 120.8, 91.0, 72.5, 45.9, 37.6, 35.0, 33.6, 31.4, 30.4, 25.4. IR (film, cm^{-1}): 2966, 1478, 1380, 1364, 1241, 1199, 1175, 1082, 1014, 882. Anal. Calcd. for $C_{22}H_{35}BrO_2$: C, 64.23; H, 8.57. Found: C, 63.97; H, 8.72.



***N*-(2-(3-(*tert*-butyl)-5-(4,4,6,6-tetramethyl-1,3-dioxan-2-yl)phenyl)-2-methylpropyl)aniline** (Table 3, **10b**)

Following the general procedure, a mixture of **10a** (411.7mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (47.4 mg, 5 mol %), SIPr·HBF_4 (54.3 mg, 11 mol %), NaO^tBu (146.7 mg, 1.5 mmol, 1.5 equiv), aniline (117.3 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide **10b** as a pale yellow oil (297.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (t, *J* = 1.7 Hz, 1H), 7.37 (t, *J* = 1.7 Hz, 1H), 7.33 (t, *J* = 1.7 Hz, 1H), 7.14 (dd, *J* = 8.0, 7.3 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 5.85 (s, 1H), 3.41 (br, 1H), 3.29 (s, 2H), 1.78 (d, *J* = 13.7 Hz, 1H), 1.58 (d, *J* = 13.7 Hz, 1H), 1.49 (s, 6H), 1.41 (s, 6H), 1.34 (s, 6H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.3, 149.0, 146.3, 139.4, 129.3, 123.9, 121.9, 121.7, 117.0, 112.9, 91.2, 72.0, 55.7, 45.8, 39.3, 35.0, 33.6, 31.6, 27.8, 25.4. IR (film, cm^{-1}): 3397, 2968, 2869, 1602, 1506, 1383, 1363, 1198, 1082, 1015, 871, 746. Anal. Calcd. for $C_{28}H_{41}NO_2$: C, 79.39; H, 9.76. Found: C, 79.57; H, 9.79.

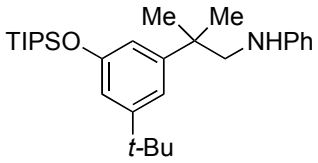


11a

(2-Bromo-3,5-di-*tert*-butylphenoxy)triisopropylsilane (Table 3, **11a**)

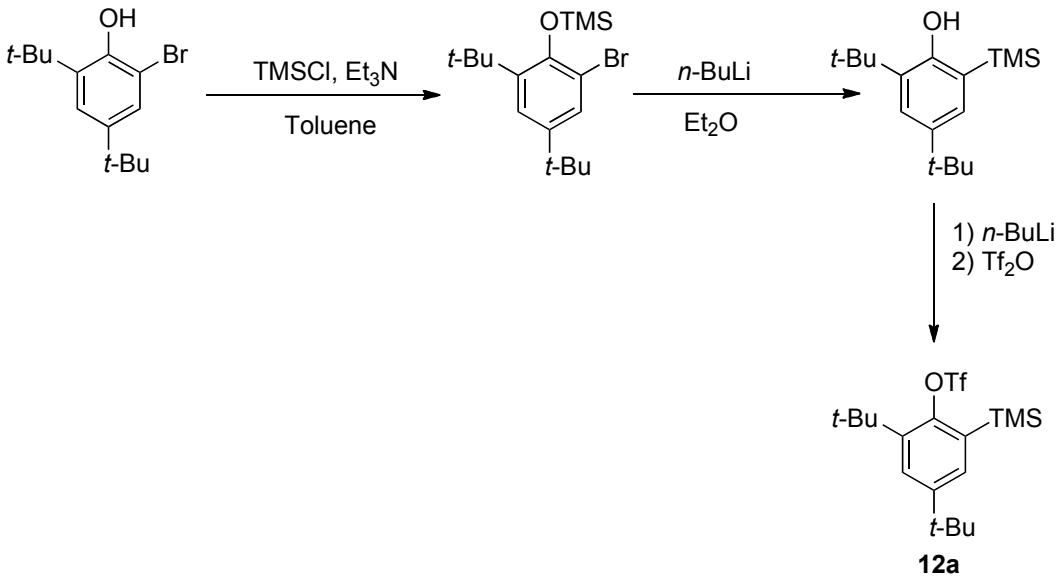
To a round bottom flask containing a magnetic stir bar, was added 2-bromo-3,5-di-*tert*-butylphenol[4] (3.03 g, 10.62 mmol), imidazole (1.44 g, 21.15 mmol), and 1,2-dichloroethane (50 mL). TIPSCl (3.04 g, 15.77 mmol) was then added. The reaction mixture was heated 80 ºC to 30 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and eluted with diethyl ether. The filtrate was concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; 0-5% EtOAc/hexanes) to provide the title compound as a colorless oil (3.78 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.04 (d, *J* = 2.3 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 1.53 (s, 9H), 1.33 (septet, *J* = 7.3 Hz, 3H), 1.28 (s, 9H), 1.14 (d, *J* =

7.3 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 150.0, 148.7, 117.3, 114.8, 113.1, 37.5, 34.8, 31.4, 30.2, 18.2, 13.3. IR (film, cm^{-1}): 2962, 2868, 1563, 1464, 1408, 1315, 1031, 1003, 882, 755, 684. Anal. Calcd. for $C_{23}H_{41}BrOSi$: C, 62.56; H, 9.36. Found: C, 62.64; H, 9.30.

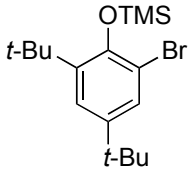


***N*-(2-(3-(*tert*-butyl)-5-((triisopropylsilyl)oxy)phenyl)-2-methylpropyl)aniline** (Table 3, **11b**)

Following the general procedure, a mixture of **11a** (442.9 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (46.2 mg, 5 mol %), SIPr·HBF_4 (53.6 mg, 11 mol %), NaO^{t}Bu (148.5 mg, 1.5 mmol, 1.5 equiv), aniline (116.0 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide **11b** as a pale yellow oil (363.5 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13 (dd, J = 8.0, 7.3 Hz, 2H), 6.98 (t, J = 1.7 Hz, 1H), 6.81 (t, J = 1.7 Hz, 1H), 6.75 (t, J = 1.7 Hz, 1H), 6.65 (t, J = 7.3 Hz, 1H), 6.15 (d, J = 8.0 Hz, 2H), 3.34 (br, 1H), 3.23 (s, 2H), 1.40 (s, 6H), 1.30 (s, 9H), 1.25 (septet, J = 7.4 Hz, 3H), 1.10 (d, J = 7.4 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.0, 152.7, 148.9, 147.5, 129.3, 117.1, 115.9, 115.3, 115.1, 112.9, 56.0, 39.1, 34.9, 31.5, 27.5, 18.1, 12.9. IR (film, cm^{-1}): 3401, 2962, 2867, 1597, 1505, 1429, 1318, 995, 882, 746, 689. Anal. Calcd. for $C_{29}H_{47}NOSi$: C, 76.76; H, 10.44. Found: C, 76.87; H, 10.38.

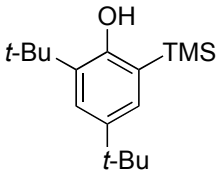


12a



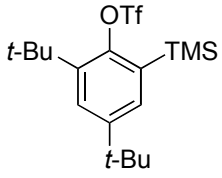
(2-Bromo-4,6-di-*tert*-butylphenoxy)trimethylsilane

To a round bottom flask containing a magnetic stir bar, was added 2-bromo-4,6-di-*tert*-butylphenol (11.49 g, 40.28 mmol), Et_3N (8.79 g, 86.87 mmol), and toluene (50 mL). TMSCl (6.85 g, 63.05 mmol) was then added. The reaction mixture was heated 50 ºC to 12 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and eluted with hexanes. The filtrate was concentrated in vacuo to provide the title compound as a yellow oil (13.94 g). Note: This product was directly used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J = 2.4 Hz, 1H), 7.25 (d, J = 2.4 Hz, 1H), 1.37 (s, 9H), 1.28 (s, 9H), 0.44 (s, 9H).



2,4-Di-*tert*-butyl-6-(trimethylsilyl)phenol

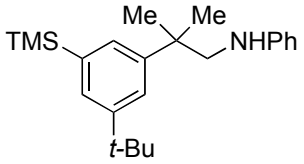
Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added (2-bromo-4,6-di-*tert*-butylphenoxy)trimethylsilane (12.50 g, 34.97 mmol), and diethyl ether (150 mL). The reaction mixture was cooled to -78 ºC, and then a solution of *n*-BuLi (2.5 M in hexanes, 20 mL, 50 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl (80 mL). The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a white solid (8.10 g, 81% in two steps), m.p. = 62 – 63 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 2.4 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 4.94 (s, 1H), 1.44 (s, 9H), 1.31 (s, 9H), 0.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.2, 142.5, 134.0, 129.7, 125.8, 125.3, 34.5, 34.4, 31.8, 30.4, -0.2. IR (film, cm^{-1}): 3636, 2955, 1581, 1428, 1361, 1243, 1112, 873, 836, 769. Anal. Calcd. for $C_{17}H_{30}OSi$: C, 73.31; H, 10.86. Found: C, 73.53; H, 10.99.



2,4-Di-*tert*-butyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (Table 3, **12a**)

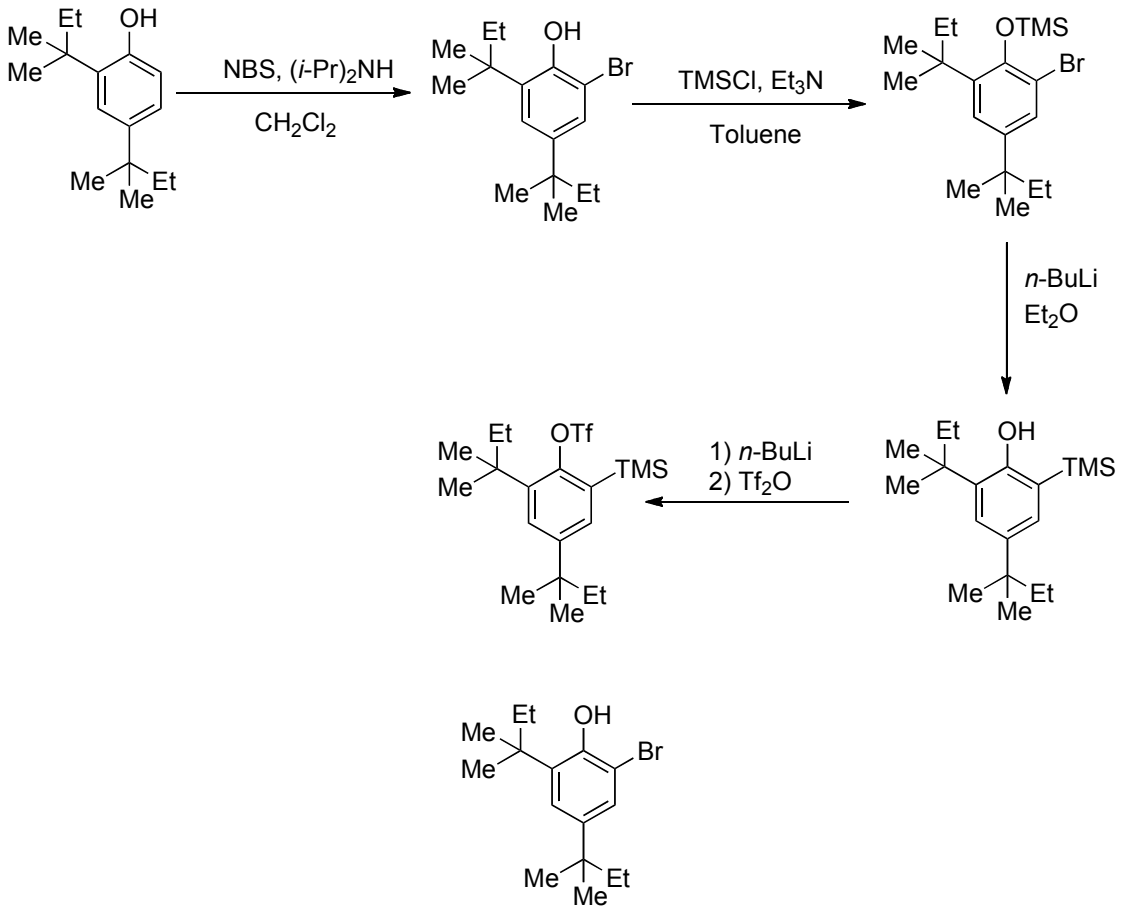
Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added 2,4-di-*tert*-butyl-6-(trimethylsilyl)phenol (2.90 g, 10.41 mmol), and diethyl ether (50 mL). The reaction mixture was cooled to -78 ºC, and then a solution of *n*-BuLi (2.5 M in hexanes, 6 mL, 15.0 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 30 min. The mixture was cooled back to -78 ºC, and triflic anhydride (6.05 g, 21.44 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 12h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (60 mL). The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a white solid

(3.63 g, 85%), m.p. = 60 – 62 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 2.6 Hz, 1H), 7.38 (d, *J* = 2.6 Hz, 1H), 1.43 (s, 9H), 1.33 (s, 9H), 0.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 145.8, 142.6, 135.6, 132.2, 129.0, 118.5 (q, *J* = 319.9 Hz), 36.5, 34.8, 32.1, 31.5, 1.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -72.8. IR (film, cm^{-1}): 2964, 2909, 1583, 1465, 1394, 1250, 1215, 1142, 1052, 851, 637. Anal. Calcd. for $C_{18}H_{29}F_3O_3SSi$: C, 52.66; H, 7.12. Found: C, 52.82; H, 7.14.



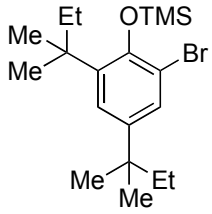
***N*-(2-(3-(*tert*-butyl)-5-(trimethylsilyl)phenyl)-2-methylpropyl)aniline** (Table 3, **12b**)

Following the general procedure, a mixture of **12a** (414.1 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (48.2 mg, 5 mol %), SIPr·HBF_4 (54.9 mg, 11 mol %), LiO^tBu (204.3 mg, 2.5 mmol, 2.5 equiv), aniline (115.4 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; 0-10% EtOAc/hexanes) to provide **12b** as a pale yellow oil (248.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (s, 2H), 7.37 (s, 1H), 7.15 (t, *J* = 7.5 Hz, 2H), 6.66 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 7.5 Hz, 2H), 3.42 (br, 1H), 3.29 (s, 2H), 1.45 (s, 6H), 1.35 (s, 9H), 0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.3, 149.0, 145.6, 140.0, 129.3, 128.1, 128.0, 123.9, 117.1, 112.9, 55.9, 39.3, 35.0, 31.6, 27.6, -0.78. IR (film, cm^{-1}): 3413, 2961, 2903, 1603, 1505, 1248, 1147, 877, 835, 747, 690. Anal. Calcd. for $C_{23}H_{35}NSi$: C, 78.12; H, 9.98. Found: C, 78.28; H, 9.93.



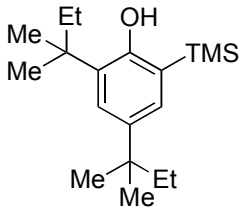
2-Bromo-4,6-di-*tert*-pentylphenol

To a round bottom flask containing a magnetic stir bar, was added 2,4-di-*tert*-pentylphenol (5.23 g, 22.31 mmol), $(i\text{-Pr})_2NH$ (452 mg, 4.47 mmol), and CH_2Cl_2 (150 mL). NBS (4.89 g, 27.47 mmol) was then added batchwise. After addition of NBS, the reaction was stirred at room temperature for 30 min. HCl (1 N, 100 mL) was charged. The organic layer was separated, washed with H_2O, brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a colorless oil (5.38 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, J = 2.3 Hz, 1H), 7.08 (d, J = 2.3 Hz, 1H), 5.58 (s, 1H), 1.83 (q, J = 7.5 Hz, 2H), 1.56 (q, J = 7.5 Hz, 2H), 1.33 (s, 6H), 1.21 (s, 6H), 0.65 (t, J = 7.5 Hz, 3H), 0.62 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 142.0, 135.1, 127.0, 125.9, 112.0, 39.3, 37.7, 37.1, 33.0, 28.6, 27.7, 9.59, 9.24. IR (film, cm^{-1}): 3510, 2962, 1569, 1472, 1362, 1305, 1178, 865, 779, 744, 704, 607. Anal. Calcd. for $C_{16}H_{25}BrO$: C, 61.34; H, 8.04. Found: C, 61.42; H, 8.02.



(2-Bromo-4,6-di-*tert*-pentylphenoxy)trimethylsilane

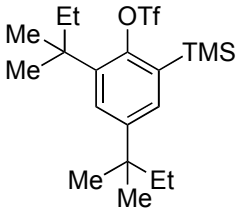
To a round bottom flask containing a magnetic stir bar, was added 2-bromo-4,6-di-*tert*-pentylphenol (3.90 g, 12.45 mmol), Et_3N (2.54 g, 25.10 mmol), and toluene (50 mL). TMSCl (2.07 g, 19.05 mmol) was then added. The reaction mixture was heated 50 ºC to 12 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and eluted with hexanes. The filtrate was concentrated in vacuo to provide the title compound as a yellow oil (4.78 g). Note: This product was directly used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, J = 2.5 Hz, 1H), 7.11 (d, J = 2.5 Hz, 1H), 1.77 (q, J = 7.5 Hz, 2H), 1.57 (q, J = 7.5 Hz, 2H), 1.33 (s, 6H), 1.23 (s, 6H), 0.67 (t, J = 7.5 Hz, 3H), 0.66 (t, J = 7.5 Hz, 3H), 0.42 (s, 9H).



2,4-Di-*tert*-pentyl-6-(trimethylsilyl)phenol

Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added (2-bromo-4,6-di-*tert*-pentylphenoxy)trimethylsilane (4.43 g, 11.49 mmol), and diethyl ether (50 mL). The reaction mixture was cooled to -78 ºC, and then a solution of *n*-BuLi (2.5 M in hexanes, 7.0 mL, 17.5 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl (80 mL). The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap

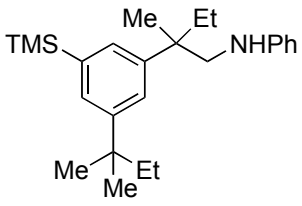
cartridge; hexanes) to provide the title compound as a colorless oil (3.21 g, 91% in two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (d, *J* = 2.4 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 4.90 (s, 1H), 1.83 (q, *J* = 7.5 Hz, 2H), 1.62 (q, *J* = 7.5 Hz, 2H), 1.41 (s, 6H), 1.28 (s, 6H), 0.73 (t, *J* = 7.5 Hz, 3H), 0.72 (t, *J* = 7.5 Hz, 3H), 0.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.1, 140.6, 131.9, 130.2, 127.6, 125.0, 38.1, 37.6, 37.2, 34.5, 28.7, 28.5, 9.61, 9.34, -0.13. IR (film, cm^{-1}): 3640, 3616, 2963, 1579, 1458, 1383, 1212, 1165, 1113, 864, 837, 770, 626. Anal. Calcd. for $C_{19}H_{34}OSi$: C, 74.44; H, 11.18. Found: C, 74.18; H, 10.95.



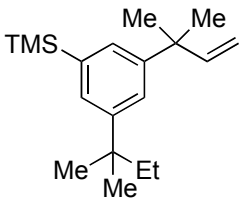
2,4-Di-*tert*-pentyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (Table 3, **13a**)

Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added 2,4-di-*tert*-pentyl-6-(trimethylsilyl)phenol (2.62 g, 8.55 mmol), and diethyl ether (30 mL). The reaction mixture was cooled to -78 ºC, and then a solution of *n*-BuLi (2.5 M in hexanes, 5.2 mL, 13.0 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 60 min. The mixture was cooled back to -78 ºC, and triflic anhydride (4.89 g, 17.33 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 12h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (60 mL). The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a colorless oil (3.21 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 2.6 Hz, 1H), 7.31 (d, *J* = 2.6 Hz, 1H), 1.76 (q, *J* = 7.5 Hz, 2H), 1.63 (q, *J* = 7.5 Hz, 2H), 1.40 (s, 6H), 1.28 (s, 6H), 0.69 (t, *J* = 7.5 Hz, 3H), 0.67 (t, *J* = 7.5 Hz, 3H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 146.4, 140.6, 135.3, 132.8, 130.3, 118.5 (q, *J* = 320 Hz), 40.0, 38.0,

37.1, 36.9, 29.6, 28.4, 9.29, 9.18, 1.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -72.9. IR (film, cm^{-1}): 2966, 1582, 1462, 1399, 1250, 1212, 1141, 1052, 845, 775, 638.



13b



13c

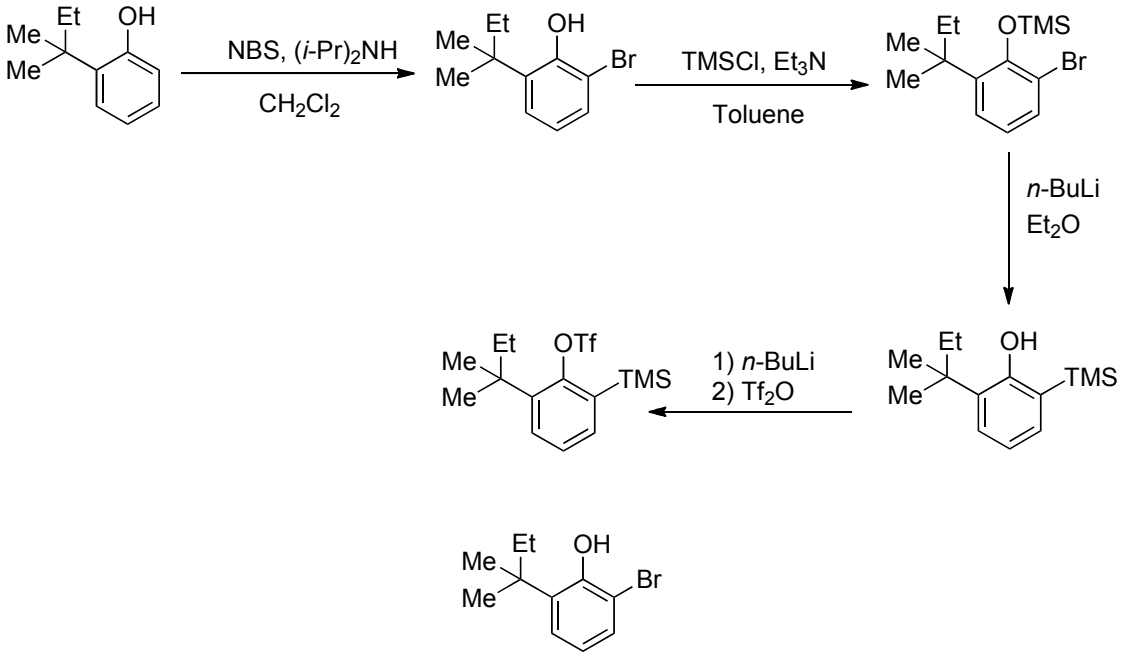
Following the general procedure, a mixture of **13a** (443.5 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (50.2 mg, 5 mol %), SIPr·HBF_4 (56.2 mg, 11 mol %), LiO^tBu (203.3 mg, 2.5 mmol, 2.5 equiv), aniline (119.5 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap cartridge; 0-10% EtOAc/hexanes) to provide **13b** as a pale yellow oil (142.4 mg, 37%) and **13c** as a colorless oil (102.5 mg, 35%).

***N*-(2-methyl-2-(3-(*tert*-pentyl)-5-(trimethylsilyl)phenyl)butyl)aniline** (Table 3, **13b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (s, 1H), 7.29 (ovrlp, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 2H), 3.39 (br, 1H), 3.32 (d, *J* = 11.6 Hz, 1H), 3.22 (d, *J* = 11.6 Hz, 1H), 1.92 (m, 1H), 1.67 (m, 1H), 1.63 (q, *J* = 7.4 Hz, 2H), 1.41 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 0.78 (t, *J* = 7.4 Hz, 3H), 0.68 (t, *J* = 7.4 Hz, 3H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 148.4, 143.6, 139.7, 129.3, 128.6, 125.1, 117.1, 112.9, 54.8, 42.6, 38.1, 37.2, 33.3, 28.6, 23.0, 9.31, 8.63, -0.77. IR (film, cm^{-1}): 3411, 2963, 1603, 1505, 1248, 1146, 872, 836, 747, 690. Anal. Calcd. for $C_{25}H_{39}NSi$: C, 78.67; H, 10.30. Found: C, 78.96; H, 10.42.

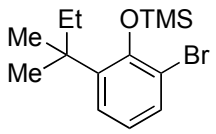
Trimethyl(3-(2-methylbut-3-en-2-yl)-5-(*tert*-pentyl)phenyl)silane (Table 3, **13c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (ovrlp, 3H), 6.06 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.07 (d, *J* = 17.4 Hz, 1H), 5.03 (d, *J* = 10.6 Hz, 1H), 1.64 (q, *J* = 7.4 Hz, 2H), 1.42 (s, 6H), 1.29 (s, 6H), 0.72 (t, *J* = 7.4 Hz, 3H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 148.3, 147.1, 139.2, 128.4, 127.9, 124.9, 110.5, 41.4, 38.1, 37.0, 28.5, 9.31, -0.76.



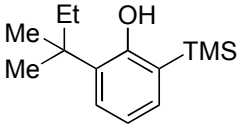
2-Bromo-6-(*tert*-pentyl)phenol

To a round bottom flask containing a magnetic stir bar, was added 2-(*tert*-pentyl)phenol (3.31 g, 20.15 mmol), (*i*-Pr)$_2$NH (403 mg, 3.99 mmol), and CH_2Cl_2 (150 mL). The mixture was heated to 40 °C. A solution of NBS (3.56 g, 20.0 mmol) in CH_2Cl_2 (150 mL) was then added dropwise over a period of 10 h through an addition funnel. After addition of NBS, the reaction was stirred at 40 °C for 10 h. The reaction mixture was cooled down to room temperature, and HCl (1 N, 100 mL) was added. The organic layer was separated, washed with H_2O, brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a colorless oil (4.52 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J = 7.9 Hz, 1H), 7.16 (d, J = 7.9 Hz, 1H), 6.74 (t, J = 7.9 Hz, 1H), 5.77 (s, 1H), 1.87 (q, J = 7.5 Hz, 2H), 1.35 (s, 6H), 0.64 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.4, 136.2, 129.8, 128.1, 121.0, 112.3, 39.2, 32.9, 27.7, 9.65. IR (film, cm^{-1}): 3503, 2964, 2876, 1594, 1433, 1334, 1243, 1184, 844, 770, 736, 563. Anal. Calcd. for $C_{11}H_{15}BrO$: C, 54.34; H, 6.22. Found: C, 54.08; H, 6.05.



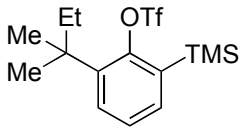
(2-Bromo-6-(*tert*-pentyl)phenoxy)trimethylsilane

To a round bottom flask containing a magnetic stir bar, was added 2-bromo-6-(*tert*-pentyl)phenol (2.45 g, 10.08 mmol), Et_3N (2.04 g, 20.16 mmol), and toluene (20 mL). TMSCl (1.66 g, 15.28 mmol) was then added. The reaction mixture was heated 50 ºC to 12 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and eluted with hexanes. The filtrate was concentrated in vacuo to provide the title compound as a yellow oil (3.13 g). Note: This product was directly used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, J = 7.9 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 6.76 (t, J = 7.9 Hz, 1H), 1.79 (q, J = 7.5 Hz, 2H), 1.33 (s, 6H), 0.68 (t, J = 7.5 Hz, 3H), 0.43 (s, 9H).



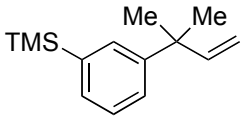
2-(*tert*-Pentyl)-6-(trimethylsilyl)phenol

Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added (2-bromo-6-(*tert*-pentyl)phenoxy)trimethylsilane (2.756 g, 8.74 mmol), and diethyl ether (50 mL). The reaction mixture was cooled to -78 ºC, and then a solution of *n*-BuLi (2.5 M in hexanes, 5.0 mL, 12.5 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl (50 mL). The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a colorless oil (1.95 g, 93% in two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (ovrlp, 2H), 6.87 (t, J = 7.5 Hz, 1H), 5.03 (s, 1H), 1.79 (q, J = 7.5 Hz, 2H), 1.36 (s, 6H), 0.68 (t, J = 7.5 Hz, 3H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5, 133.2, 132.8, 129.8, 126.1, 120.5, 37.9, 34.4, 28.5, 9.67, -0.31. IR (film, cm^{-1}): 3635, 3612, 2964, 2878, 1572, 1414, 1252, 1175, 1122, 861, 839, 758, 631.

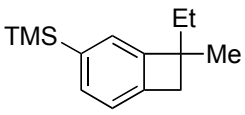


2-(*tert*-Pentyl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (14a)

Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added 2-(*tert*-pentyl)-6-(trimethylsilyl)phenol (1.94 g, 8.21 mmol), and diethyl ether (30 mL). The reaction mixture was cooled to -78 ºC, and then a solution of *n*-BuLi (2.5 M in hexanes, 5.0 mL, 12.5 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 60 min. The mixture was cooled back to -78 ºC, and triflic anhydride (4.73 g, 16.76 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 12h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (50 mL). The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via the Biotage SP4 (silica-packed 100 g snap cartridge; hexanes) to provide the title compound as a colorless oil (1.78 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 1.78 (q, J = 7.4 Hz, 2H), 1.41 (s, 6H), 0.69 (t, J = 7.4 Hz, 3H), 0.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.5, 142.0, 136.6, 135.2, 132.3, 127.6, 118.5 (q, J = 320 Hz), 39.9, 36.7, 29.6, 9.32, 1.14. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -72.7. IR (film, cm^{-1}): 2967, 1462, 1399, 1251, 1214, 1139, 1053, 868, 775, 654. Anal. Calcd. for $C_{15}H_{23}F_3O_3SSi$: C, 48.89; H, 6.29. Found: C, 49.13; H, 6.24.



14b



14c

Following the general procedure, a mixture of **14a** (369.3 mg, 1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (47.8 mg, 5 mol %), SIPr·HBF_4 (54.7 mg, 11 mol %), LiO^tBu (199.9 mg, 2.5 mmol, 2.5 equiv), aniline (115.6 mg, 1.2 mmol, 1.2 equiv) and toluene (10 mL) was

heated to 110 °C for 4 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap cartridge; hexanes) to provide a mixture of **14b** & **14c** as a colorless oil (177.6 mg, 81% combined yield %) in a ratio of 1:1.4 (^{1}H-NMR).

Trimethyl(3-(2-methylbut-3-en-2-yl)phenyl)silane (14b)

^{1}H NMR (600 MHz, C_6D_6) δ: 7.70 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 6.02 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.04 (d, *J* = 17.4 Hz, 1H), 5.01 (d, *J* = 10.6 Hz, 1H), 1.35 (s, 6H), 0.26 (s, 9H).

(8-Ethyl-8-methylbicyclo[4.2.0]octa-1,3,5-trien-3-yl)trimethylsilane (14c)

^{1}H NMR (600 MHz, C_6D_6) δ: 7.43 (d, *J* = 7.2 Hz, 1H), 7.33 (s, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 2.89 (d, *J* = 13.7 Hz, 1H), 2.77 (d, *J* = 13.7 Hz, 1H), 1.63 (q, *J* = 7.4 Hz, 2H), 1.32 (s, 3H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.25 (s, 9H).

References:

[1] M. Baudler, J. Simon, *Chem. Ber.* **1988**, *121*, 281.
[2] C. Han, S. L. Buchwald, *J. Am. Chem. Soc.* **2009**, *131*, 7532.
[3] J. Clayden, J. Senior, *Synlett* **2009**, 2769.
[4] H. Zhang, F. Y. Kwong, Y. Tian, K. S. Chan, *J. Org. Chem.* **1998**, *63*, 6886.

DFT Calculations of the Oxidative Addition Intermediates Described in Table 3

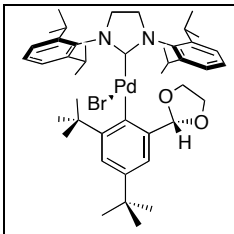
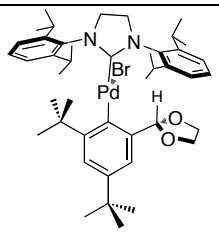
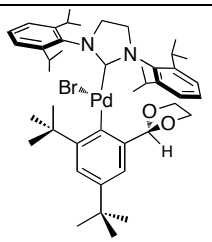
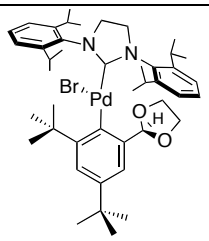
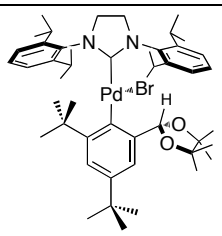
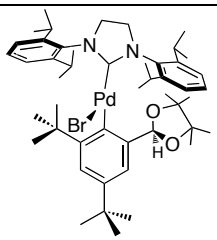
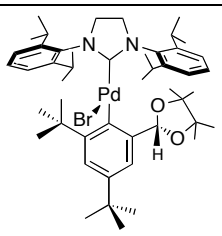
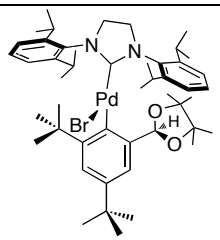
Computational Methods. All calculations were carried out with Gaussian03 suite of computational programs.[1] Ground state geometry optimizations were evaluated using B3LYP[2] density functional method. For C, H, O, N and Br atoms, the 6-31G(d) basis set was used; while LANL2DZ effective core potentials of Hay and Wadt[3] with double-ζ basis sets were used for Pd atom. Frequency calculations were performed on all optimized structures to verify that they have no negative imaginary frequency.

References:

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision E.01; Gaussian, Inc.: Wallingford CT, 2004.

[2] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[3] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

			
OA1a	OA1b	OA1c	OA1d
			
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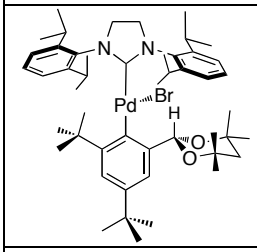
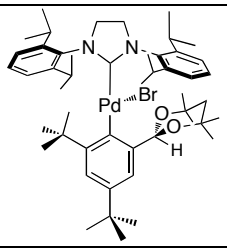
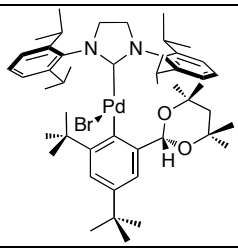
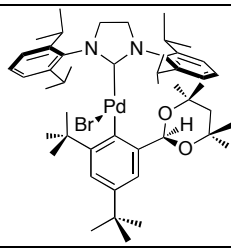
			
OA3a	OA3b	OA3c	OA3d

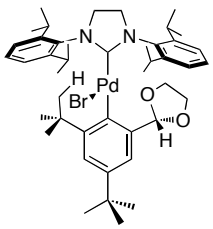
Table S1. **Relative Energies of the Oxidative Addition Intermediates**

	Relative Energy (kcal/mol)
OA1a	**0**
OA1b	1.3
OA1c	8.0
OA1d	0.0
OA2a	**0**
OA2b	15.1
OA2c	3.1
OA2d	6.1
OA3a	**0**
OA3b	n.d.*
OA3c	8.7
OA3d	n.d.*

*Attempts to evaluate OA3b and OA3d intermediates were not successful, where the output file suggested dissociation of the carbene ligand.

Table S1 shows the relative energies of the oxidative addition intermediates with respect to the each of the most stable structure (**OA1a**, **OA2a**, and **OA3a**). Attempts to evaluate the intermediates with the carbene ligand cis to the aromatic ring resulted in the trans conformations.

Cartersian Coordinates for all Calculated Complexes:



Complex OA1a

Pd 0.130349 -0.172274 -0.120345
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N -2.996251 -0.496431 0.019811
C 2.971180 -1.670818 -0.153402
N -2.415894 1.531308 0.588708
C 4.360349 -1.475265 0.019756
H 4.975921 -2.356994 0.149205
C 4.988342 -0.227468 0.025445
C 4.176318 0.886101 -0.229841
H 4.603450 1.879441 -0.340451
C 2.798898 0.731044 -0.358531
C -3.243347 -2.933098 0.264525
C -3.305310 -4.195846 -0.337442
H -3.493859 -5.068452 0.280397
C -3.127529 -4.356965 -1.707352
C -2.895815 -3.244181 -2.508229
H -2.774719 -3.375609 -3.579525
C -2.831223 -1.955703 -1.963000
C -2.988935 -1.814004 -0.564035
C -1.944155 0.346289 0.138132
C -4.294255 0.171440 0.272466
H -4.821093 0.324675 -0.678724
C -3.857522 1.485212 0.923745
H -3.984065 1.472423 2.012710
C -1.678577 2.757072 0.772375
C -1.028557 3.022256 2.000209
C -0.355306 4.245192 2.132280
H 0.158800 4.467300 3.062065
C -0.343129 5.184113 1.105779
C -1.025640 4.923077 -0.078059

H -1.029156 5.668572 -0.868168
C -1.709974 3.716781 -0.267507
H 0.187292 6.124150 1.233342
H -3.176108 -5.347908 -2.151142
C -1.094815 2.075752 3.194425
C -2.135178 2.581021 4.218323
C 0.268350 1.873509 3.880126
H -1.409783 1.092784 2.836079
H -3.127652 2.707666 3.769884
H -2.226470 1.871826 5.049554
H -1.838443 3.551486 4.635162
H 1.024875 1.534505 3.167633
H 0.625388 2.789687 4.366374
H 0.179240 1.102726 4.652735
C -2.492935 3.509050 -1.561510
C -1.612352 3.693403 -2.810907
C -3.720832 4.441160 -1.626056
H -2.855853 2.476747 -1.573886
H -0.717937 3.071260 -2.737939
H -2.168610 3.415808 -3.714564
H -1.290955 4.734539 -2.930547
H -4.381916 4.307978 -0.762046
H -3.414942 5.493723 -1.644418
H -4.304447 4.246489 -2.533980
C -3.491813 -2.817997 1.766724
C -2.641690 -3.805360 2.588218
C -4.987742 -3.021123 2.095607
H -3.192868 -1.812341 2.077839
H -1.578693 -3.668997 2.378429
H -2.801847 -3.627608 3.658333
H -2.914630 -4.847961 2.386289
H -5.639717 -2.340076 1.536275
H -5.305464 -4.042489 1.853037
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C -2.655547 -0.770131 -2.908839
C -3.942985 -0.520175 -3.722452
C -1.448732 -0.944300 -3.848989
H -2.461464 0.123469 -2.309560
H -4.808955 -0.361094 -3.069630
H -3.831134 0.365023 -4.360610
H -4.172692 -1.374057 -4.370822
H -0.531089 -1.123881 -3.279837
H -1.585047 -1.783884 -4.539948
H -1.310331 -0.041694 -4.456609
Br 0.007216 -1.309782 2.101987
C 6.501105 -0.045815 0.247795

C 7.224993 -1.379993 0.511461
C 7.137528 0.606582 -1.002911
C 6.728196 0.872890 1.472118
H 6.829123 -1.888542 1.397766
H 7.143432 -2.064985 -0.340395
H 8.291491 -1.193844 0.684114
H 6.696500 1.585348 -1.219911
H 8.214959 0.752433 -0.854119
H 6.999729 -0.026825 -1.887241
H 7.801063 1.028059 1.644050
H 6.265979 1.855738 1.331781
H 6.298229 0.428905 2.377243
C 2.493078 -3.139483 -0.305698
C 1.060081 -3.256451 -0.860322
C 3.406668 -3.875397 -1.322639
C 2.575674 -3.872846 1.053476
H 0.314120 -2.852712 -0.175688
H 0.963894 -2.735832 -1.821423
H 0.819536 -4.313737 -1.030198
H 4.441136 -3.971910 -0.979223
H 3.026411 -4.890611 -1.490186
H 3.421045 -3.356876 -2.289209
H 2.277884 -4.923786 0.939579
H 3.597274 -3.856388 1.451641
H 1.915063 -3.400789 1.784802
C 1.945027 1.927244 -0.744982
H 1.511928 2.483226 0.089446
C 2.558221 2.262075 -2.904718
C 1.376419 1.258565 -2.870007
H 2.407938 3.076992 -3.617638
H 3.502744 1.753098 -3.126805
H 0.587929 1.484295 -3.589251
H 1.713299 0.227130 -2.995476
O 2.583783 2.840953 -1.595758
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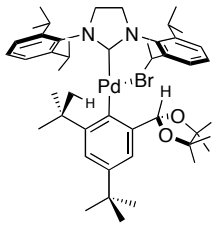

Complex OA2a

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C 1.620906 -2.747964 0.362916
N -2.342375 1.962752 -0.036935
C 2.862836 -3.402196 0.300158
H 2.896760 -4.459682 0.523450
C 4.049783 -2.753305 -0.050064
C 3.974000 -1.376500 -0.270324
H 4.862126 -0.809823 -0.524869
C 2.762747 -0.680505 -0.205382
C -4.146072 -1.830041 1.256105
C -4.531188 -3.173613 1.342043
H -4.814806 -3.587507 2.305808
C -4.581328 -3.980384 0.208739
C -4.263789 -3.448066 -1.037396
H -4.333945 -4.078820 -1.918354
C -3.861110 -2.113670 -1.181589
C -3.772302 -1.324119 -0.012122
C -2.185490 0.619807 0.013508
C -4.481134 1.064885 -0.360934
H -5.343176 0.880443 0.285299
C -3.764767 2.379307 -0.056251
H -4.035759 2.796909 0.922672
C -1.367785 2.986314 0.238225
C -0.930148 3.191784 1.567290
C -0.114838 4.299970 1.827947
H 0.234644 4.475134 2.841364
C 0.247775 5.183842 0.816945
C -0.185168 4.959883 -0.486661
H 0.107122 5.651188 -1.271759
C -0.997565 3.865280 -0.806622
H 0.869326 6.046263 1.043857
H -4.887189 -5.019924 0.294014
C -1.308086 2.270285 2.722717
C -2.073270 3.018719 3.832367
C -0.067462 1.554276 3.293372

H -1.975810 1.495533 2.336756
H -2.972614 3.509492 3.441843
H -2.381598 2.320223 4.619600
H -1.452055 3.790321 4.301356
H 0.511931 1.061857 2.504348
H 0.606116 2.263458 3.789499
H -0.367640 0.804369 4.035578
C -1.468706 3.689212 -2.248200
C -0.291275 3.633173 -3.239959
C -2.453280 4.806646 -2.655896
H -1.982779 2.725911 -2.318777
H 0.384923 2.811424 -2.992589
H -0.668748 3.464196 -4.255481
H   0.277336 4.570794 -3.251027
H -3.311093 4.877336 -1.976591
H -1.959533 5.785890 -2.655827
H -2.835906 4.627961 -3.667749
C -4.237871 -0.948972 2.501862
C -3.409983 -1.473960 3.689026
C -5.711988 -0.761008 2.921770
H -3.840161 0.037953 2.247487
H -2.347024 -1.534885 3.440483
H -3.519106 -0.802591 4.549191
H -3.739596 -2.469915 4.006855
H -6.321040 -0.365618 2.100802
H -6.159697 -1.712165 3.232607
H -5.784825 -0.065252 3.766232
C -3.623950 -1.544476 -2.578663
C -4.976025 -1.293852 -3.284207
C -2.731007 -2.432824 -3.462966
H -3.102843 -0.588779 -2.471620
H -5.642449 -0.656554 -2.691703
H -4.815236 -0.809463 -4.254547
H -5.504129 -2.238159 -3.464888
H -1.745661 -2.577400 -3.015327
H -3.183566 -3.413577 -3.652163
H -2.581474 -1.947693 -4.433997
Br -0.017548 -0.054319 -2.404261
C   5.397258 -3.486683 -0.186927
C   5.278648 -4.997419 0.091316
C   5.932815 -3.304777 -1.627432
C   6.417663 -2.894432 0.814043
H   4.937206 -5.199644 1.113293
H   4.585430 -5.485694 -0.603226
H   6.258407 -5.474511 -0.029028
H   6.074386 -2.248126 -1.876415

H 6.899493 -3.811208 -1.744940
H 5.234982 -3.727381 -2.359354
H 7.386612 -3.401437 0.720686
H 6.582751 -1.826152 0.639350
H 6.068818 -3.014688 1.846431
C 0.370104 -3.547449 0.777871
C -0.516939 -3.808837 -0.456864
C 0.705475 -4.912720 1.418928
C -0.412197 -2.756382 1.848169
H -0.796841 -2.870614 -0.942886
H 0.025779 -4.414919 -1.191604
H -1.434954 -4.340714 -0.178866
H 1.375903 -4.808091 2.279691
H -0.218676 -5.389507 1.766937
H 1.170513 -5.599010 0.703581
H -1.294044 -3.313188 2.184750
H 0.217437 -2.523900 2.713538
H -0.814327 -1.791950 1.460881
C 2.798845 0.835903 -0.339356
H 1.933574 1.192089 -0.904569
C 4.413258 2.489693 -0.317341
C 3.965845 2.224454 1.158790
O 4.003817 1.262886 -0.947438
O 2.750149 1.477893 0.953941
H -3.937537 3.145650 -0.813648
H -4.811566 1.002106 -1.403707
C 3.623419 3.479974 1.962230
H 3.295637 3.198106 2.968868
H 4.505364 4.123704 2.065716
H 2.820153 4.049493 1.492715
C 4.957856 1.361355 1.956143
H 4.471038 1.033667 2.880495
H 5.252295 0.468233 1.401101
H 5.859879 1.923702 2.224711
C 5.918928 2.632450 -0.533759
H 6.129213 2.764568 -1.600226
H 6.305078 3.509475 -0.001673
H 6.460157 1.748311 -0.188948
C 3.670691 3.663155 -0.977093
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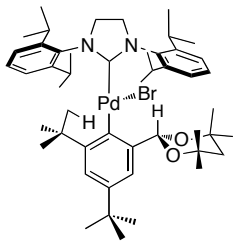
H 3.860498 3.636968 -2.055045
H 2.590670 3.598755 -0.817937



Complex OA3a

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C 1.535121 -2.717553 0.652164
N -2.577860 1.827121 -0.054980
C 2.726346 -3.454970 0.521494
H 2.693030 -4.515678 0.746177
C 3.938537 -2.880498 0.141521
C 3.939012 -1.493979 -0.029119
H 4.860477 -0.965936 -0.247885
C 2.774265 -0.727579 0.064409
C -4.369390 -2.156275 0.484880
C -4.624748 -3.530317 0.407449
H -5.154626 -4.021738 1.218961
C -4.218137 -4.275989 -0.695399
C -3.565853 -3.650464 -1.753242
H -3.274284 -4.235838 -2.619578
C -3.285072 -2.276913 -1.731597
C -3.667810 -1.546371 -0.583799
C -2.298157 0.502935 -0.104958
C -4.499125 0.809899 -0.911333
H -4.551338 0.860341 -2.006054
C -4.013046 2.116124 -0.291698
H -4.140374 2.975305 -0.950503
C -1.763474 2.882362 0.488518
C -1.505169 2.925801 1.878590
C -0.796614 4.023930 2.383182
H -0.582928 4.073489 3.447065
C -0.375102 5.056924 1.553454
C -0.657515 5.007503 0.191719
H -0.333287 5.821630 -0.449816
C -1.356065 3.932121 -0.369728
H 0.169100 5.901343 1.967888
H -4.422835 -5.342591 -0.736750
C -1.993463 1.863888 2.860393
C -3.006911 2.449607 3.865271

C -0.821651 1.185859 3.596491
H -2.511476 1.084588 2.295371
H -3.861889 2.907202 3.353854
H -3.387340 1.661703 4.526509
H -2.548213 3.219575 4.496169
H -0.093412 0.775800 2.887953
H -0.290747 1.892141 4.245465
H -1.188073 0.367641 4.228700
C -1.688290 3.965309 -1.860606
C -0.441866 4.156474 -2.744088
C -2.724710 5.068334 -2.169931
H -2.115039 2.994510 -2.130034
H 0.276980 3.352372 -2.574481
H -0.731615 4.138211 -3.801697
H 0.049705 5.118406 -2.555474
H -3.631753 4.977053 -1.560776
H -2.306038 6.063194 -1.976762
H -3.018761 5.031550 -3.225639
C -4.904165 -1.369645 1.681721
C -4.374370 -1.887010 3.032520
C -6.448006 -1.359005 1.684450
H -4.565245 -0.333882 1.585600
H -3.284211 -1.814312 3.089040
H -4.794631 -1.294753 3.854152
H -4.652758 -2.933009 3.204546
H -6.854582 -0.984145 0.738176
H -6.850259 -2.367349 1.836059
H -6.826547 -0.723843 2.494125
C -2.649021 -1.618830 -2.951567
C -3.705112 -1.421493 -4.061044
C -1.438234 -2.397264 -3.496380
H -2.274403 -0.635871 -2.656144
H -4.565756 -0.840289 -3.708888
H -3.264792 -0.892401 -4.914207
H -4.085364 -2.385151 -4.422092
H -0.680623 -2.546627 -2.721967
H -1.723874 -3.374802 -3.904057
H -0.968073 -1.825492 -4.303017
Br 0.309589 0.551287 -2.042707
C 5.237566 -3.685390 -0.039910
C 5.033364 -5.194651 0.192020
C 5.761087 -3.486854 -1.482412
C 6.304027 -3.184359 0.962898
H 4.702997 -5.410035 1.215044
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H 5.979472 -5.725475 0.033602

H 5.953875 -2.431437 -1.699930
H 6.697686 -4.039640 -1.631356
H 5.031123 -3.848412 -2.215866
H 7.242316 -3.739481 0.835127
H 6.521974 -2.120603 0.823869
H 5.964167 -3.322190 1.995987
C 0.338263 -3.463947 1.270134
C 0.731822 -3.972820 2.679156
C -0.873726 -2.535967 1.440327
C -0.102174 -4.660458 0.396319
H 1.573759 -4.670230 2.640592
H 1.022626 -3.137595 3.327242
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H -1.382674 -2.372604 0.481236
H -1.635256 -2.964840 2.100799
H -0.577797 -1.582482 1.941561
H -0.967766 -5.168413 0.840860
H -0.383733 -4.326363 -0.608162
H 0.700346 -5.397857 0.292732
C 3.002429 0.774844 0.034724
H 2.063855 1.327987 -0.056655
C 4.056782 2.439859 1.461250
C 4.313739 2.438274 -1.144221
C 4.880157 2.880553 0.226498
H 5.023806 3.968341 0.239650
H 5.873493 2.426534 0.325509
O 3.629511 1.076452 1.282104
O 3.860005 1.074610 -1.049812
C 4.972023 2.391579 2.690685
H 5.793892 1.688384 2.523680
H 5.392609 3.381884 2.902133
H 4.409714 2.056785 3.568994
C 2.853621 3.346962 1.769155
H 2.106406 3.351575 0.974448
H 2.359472 2.999880 2.682672
H 3.180127 4.382181 1.926905
C 5.449199 2.386749 -2.173485
H 5.898711 3.377739 -2.306883
H 6.227673 1.689914 -1.846675
H 5.066453 2.043953 -3.140403
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H 3.563242 4.377004 -1.791426
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H 2.313996 3.372027 -1.043718
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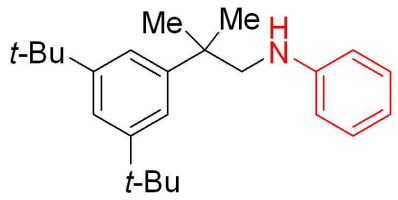

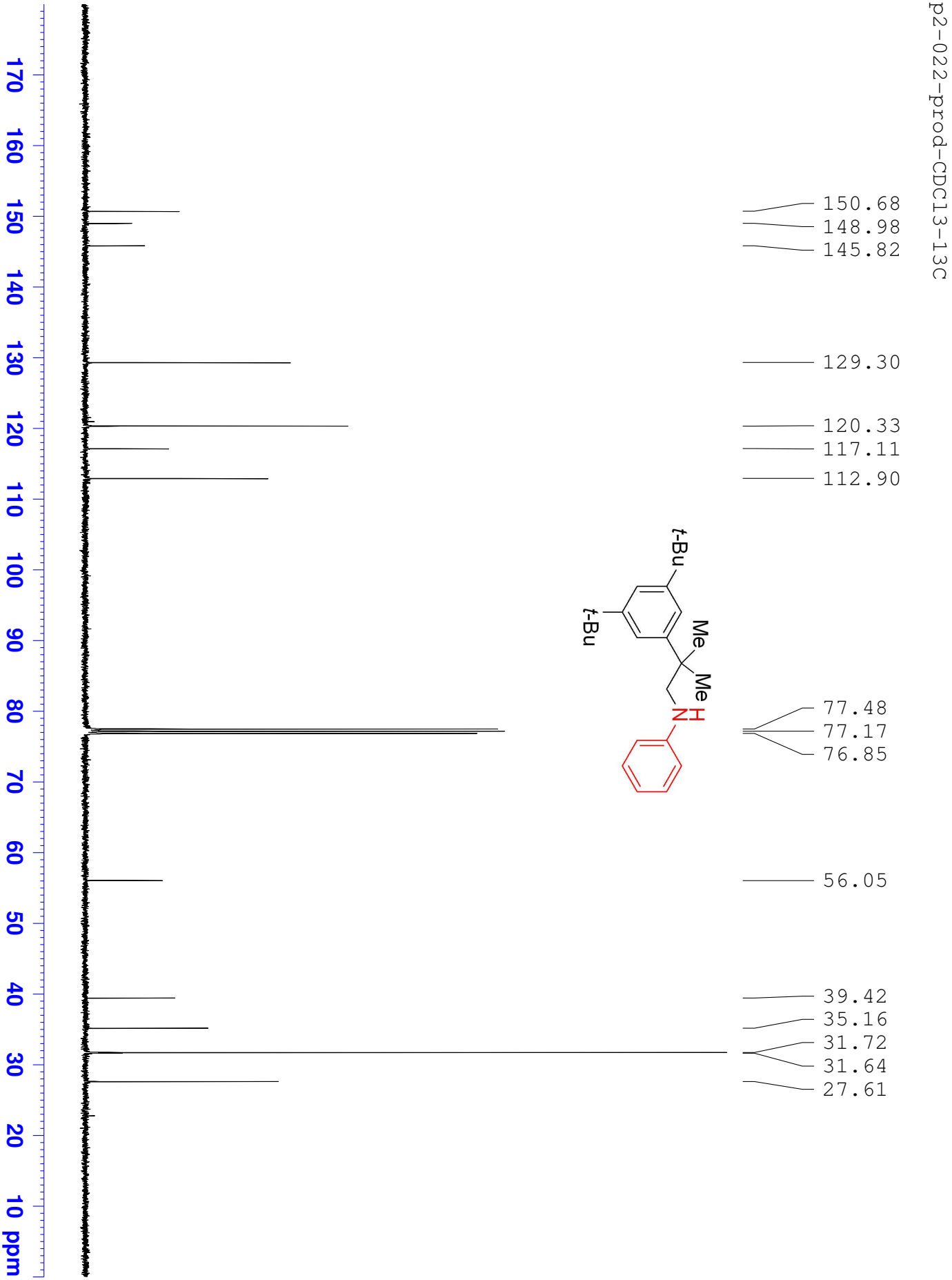
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56.05
39.42
35.16
31.72
31.64
27.61
t-Bu
t-Bu
Me
Me
N
H
170
160
150
140
130
120
110
100
90
80
70
60
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40
30
20
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ppm

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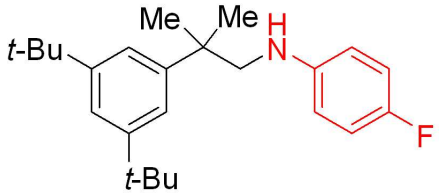

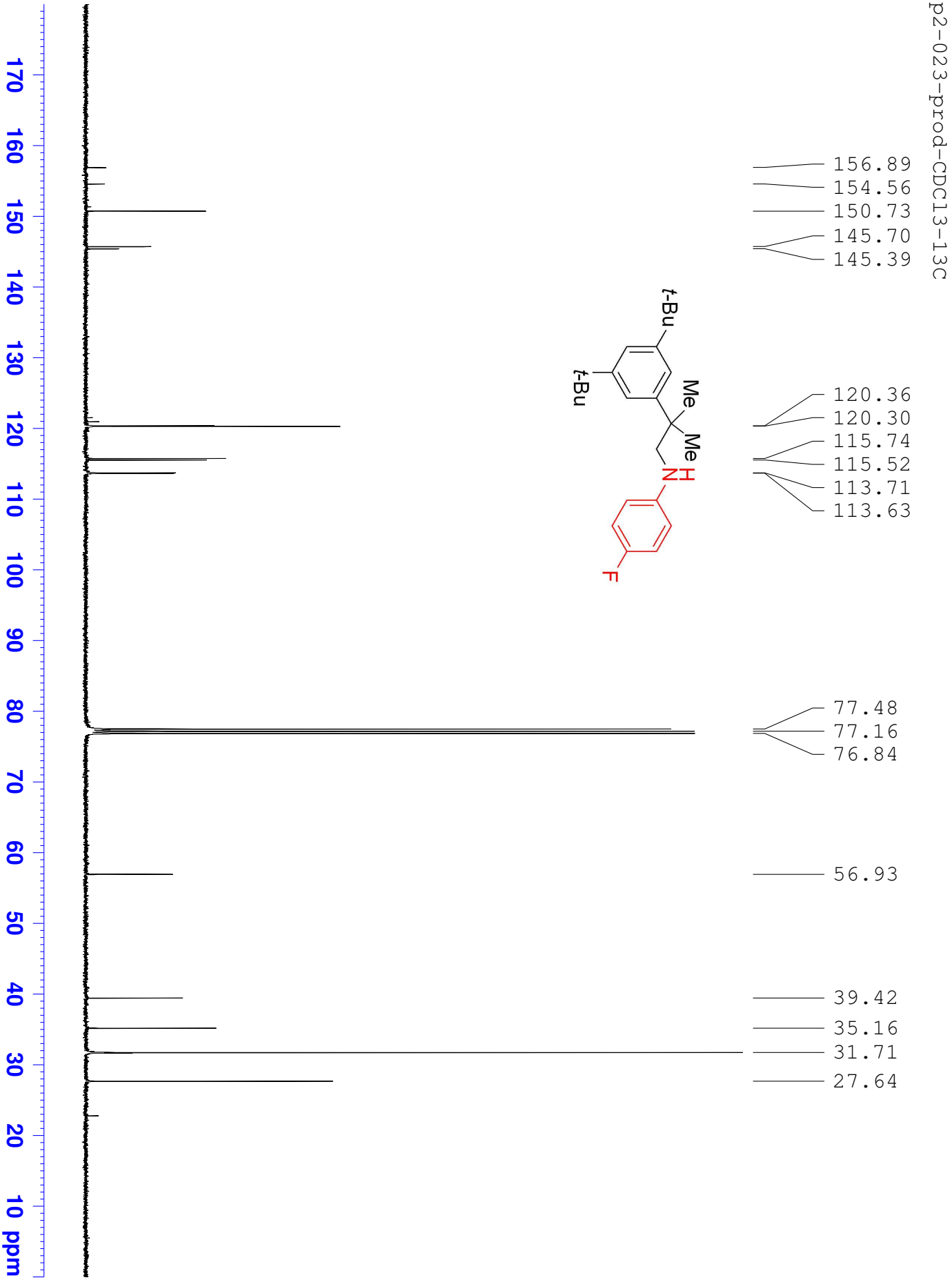
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113.63
77.48
77.16
76.84
56.93
39.42
35.16
31.71
27.64
t-Bu
t-Bu
Me
Me
H
N
F
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160
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60
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20
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ppm

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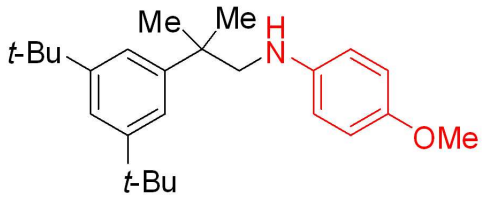

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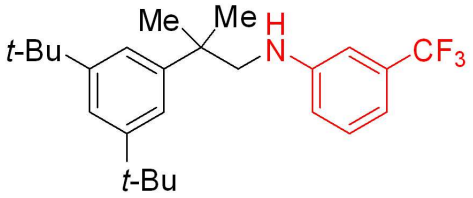
27.68
t-Bu
t-Bu
Me
Me
H
N
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

jp2-214-prod-CDCl3-1H



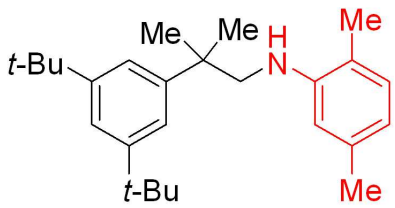
50

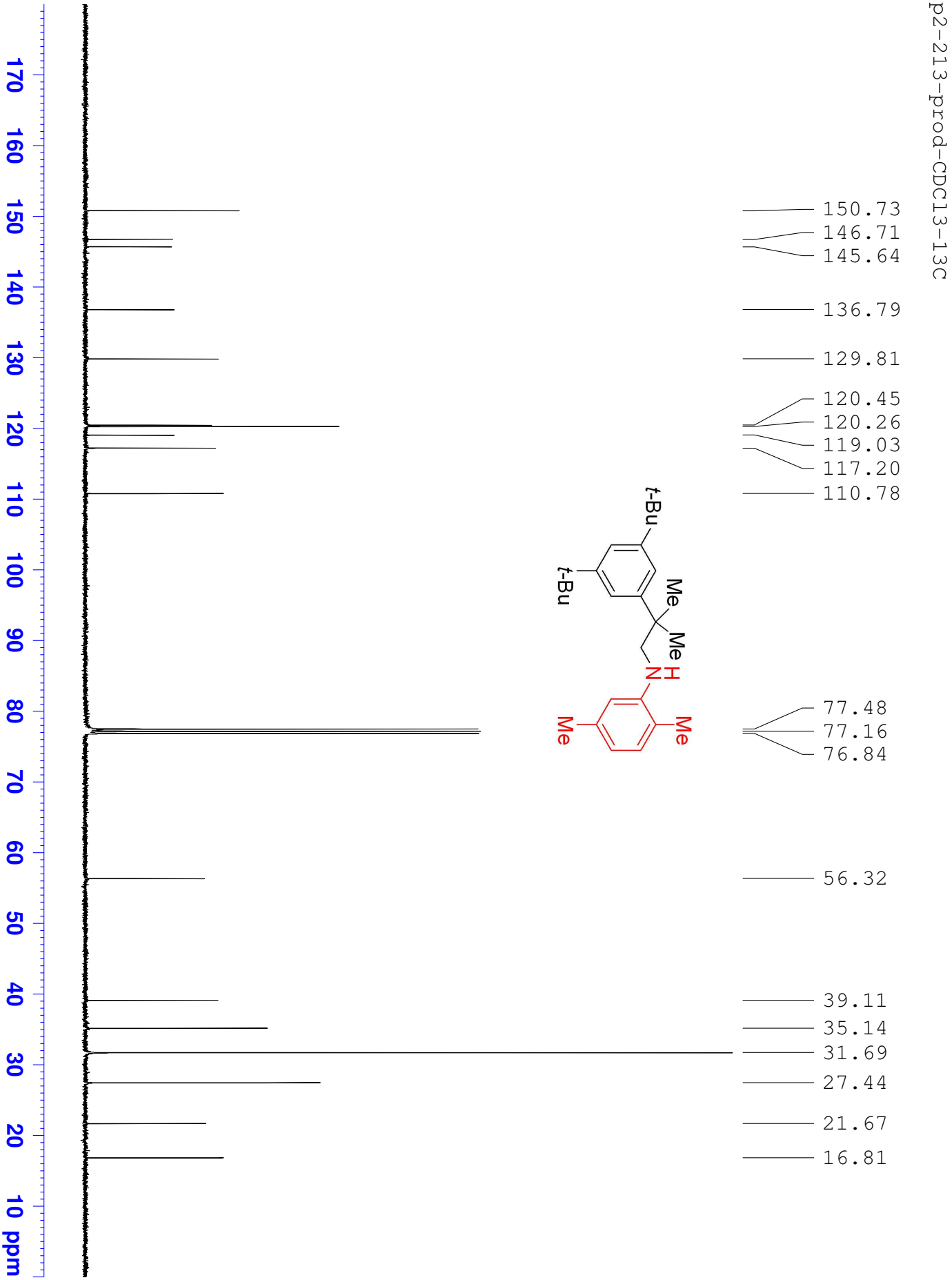
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.00 1.97 1.06 1.00 1.00 1.02 0.97 2.02 5.85 18.61

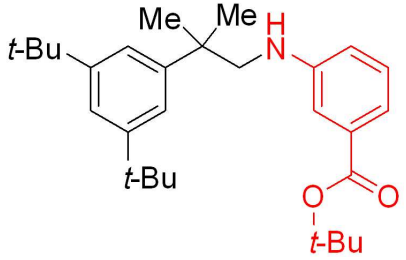
jp2-214-prod-CDCl3-13C

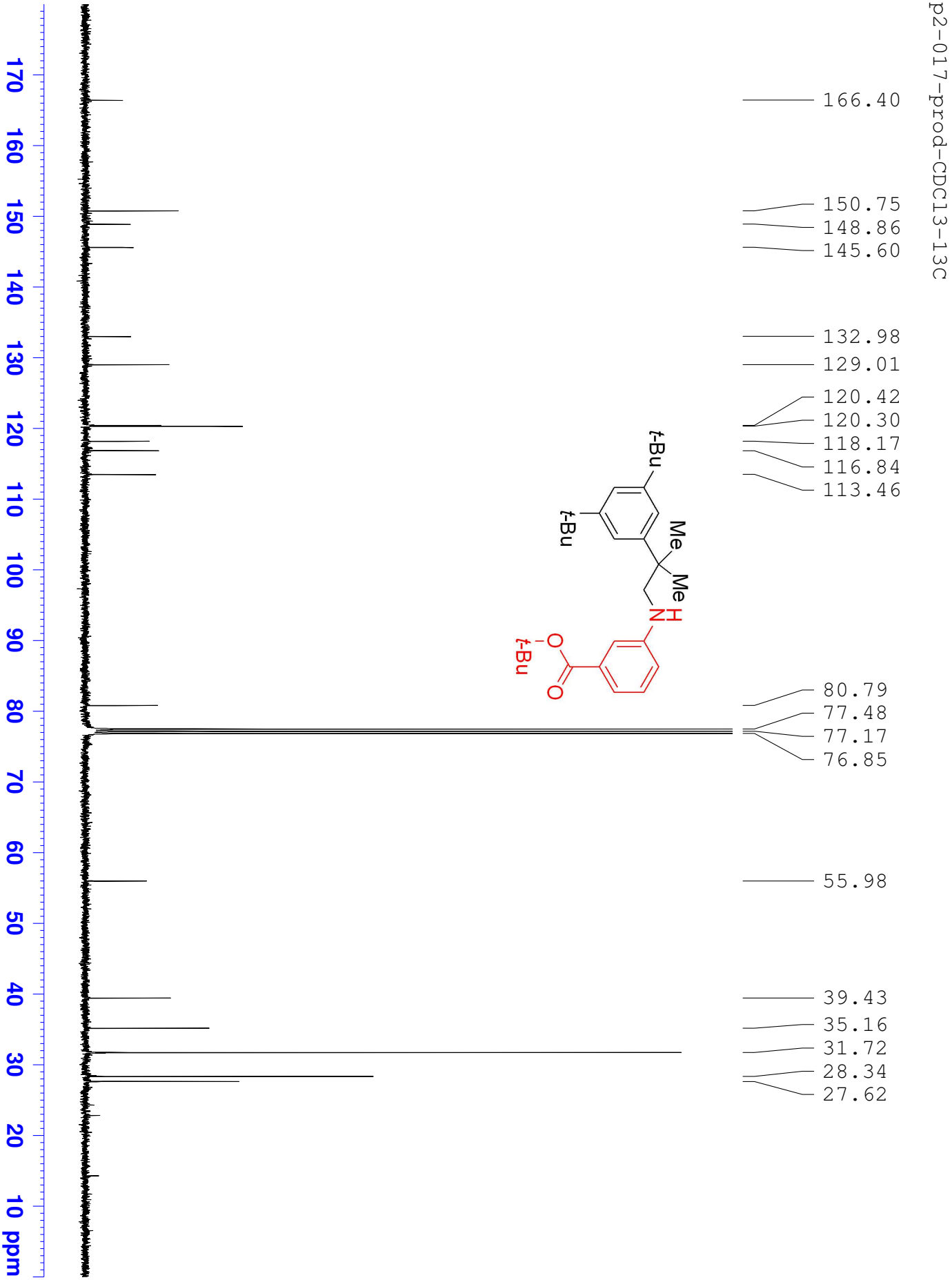
jp2-213-prod-CDCl3-1H-400



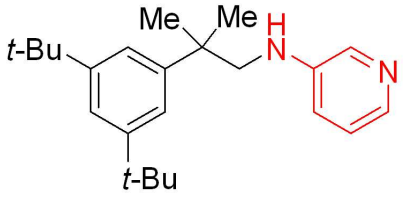

jp2-213-prod-CDC13-13C
150.73
146.71
145.64
136.79
129.81
120.45
120.26
119.03
117.20
110.78
77.48
77.16
76.84
56.32
39.11
35.14
31.69
27.44
21.67
16.81
t-Bu
t-Bu
Me
Me
N
H
Me
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

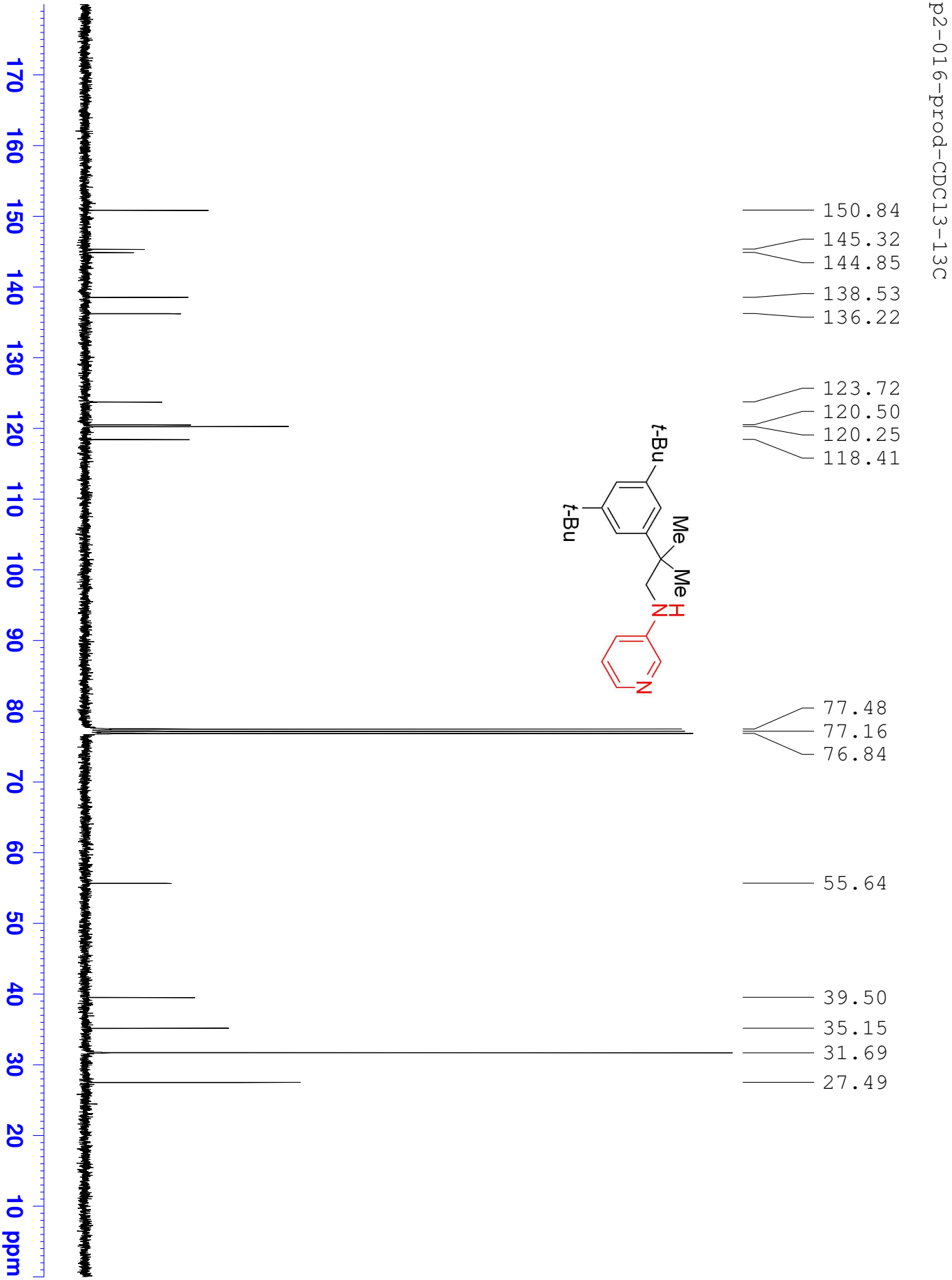
jp2-209-prod-C6D6-1H-400



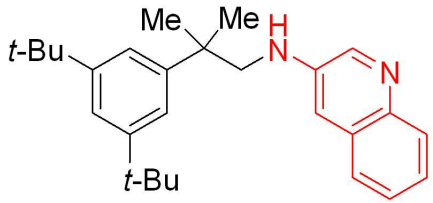

jp2-017-prod-CDC13-13C
166.40
150.75
148.86
145.60
132.98
129.01
120.42
120.30
118.17
116.84
113.46
80.79
77.48
77.17
76.85
55.98
39.43
35.16
31.72
28.34
27.62
t-Bu
t-Bu
Me
Me
H
N
O
O
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

jp2-016-prod-CDCl3-1H



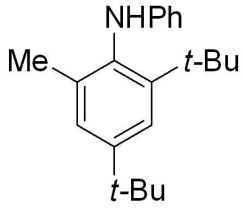

jp2-016-prod-CDC13-13C
150.84
145.32
144.85
138.53
136.22
123.72
120.50
120.25
118.41
77.48
77.16
76.84
55.64
39.50
35.15
31.69
27.49
t-Bu
t-Bu
Me
Me
H
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

jp2-215-prod-CDCl3-1H-400-2



jp2-215-prod-CDC13-13C-2
150.87
145.32
143.56
142.17
142.09
129.68
129.08
126.93
125.94
124.75
120.56
120.23
109.92
77.48
77.16
76.84
55.69
39.41
35.13
31.67
27.61
t-Bu
t-Bu
Me
Me
NH
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

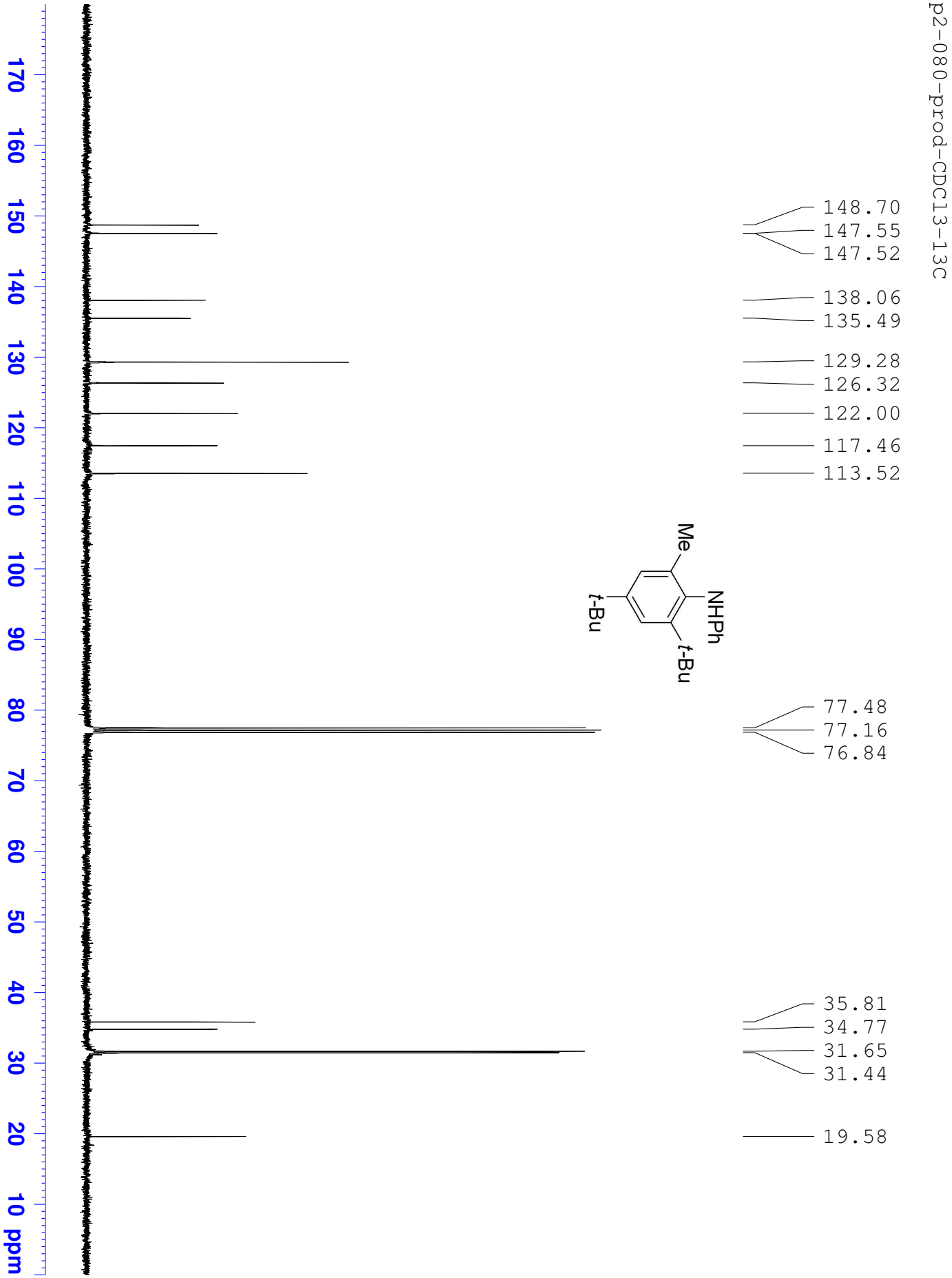
jp2-080-prod-CDCl3-1H-400



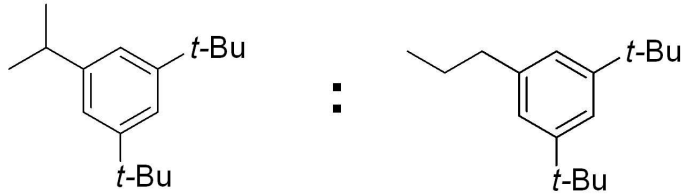
60

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.02 3.03 1.00 1.98 0.99 3.03 9.08 8.99


jp2-080-prod-CDC13-13C
148.70
147.55
147.52
138.06
135.49
129.28
126.32
122.00
117.46
113.52
77.48
77.16
76.84
35.81
34.77
31.65
31.44
19.58
Me
NHPh
t-Bu
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

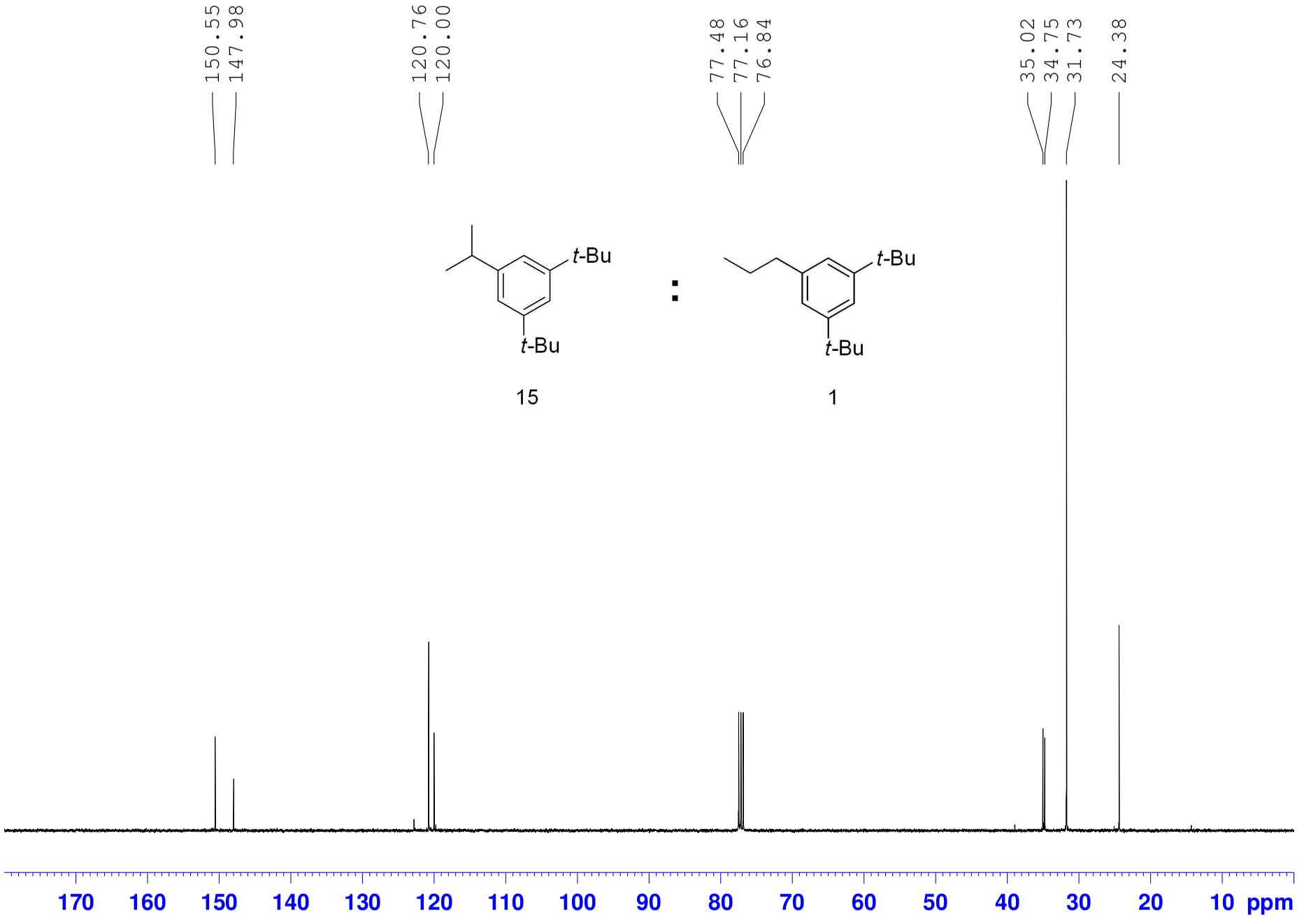
jp2-071-prod-CDCl3-1H-2



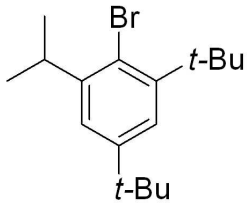
15 : 1

62

jp2-071-prod-CDCl3-13C-400-1

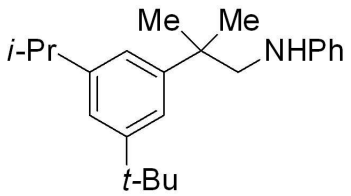


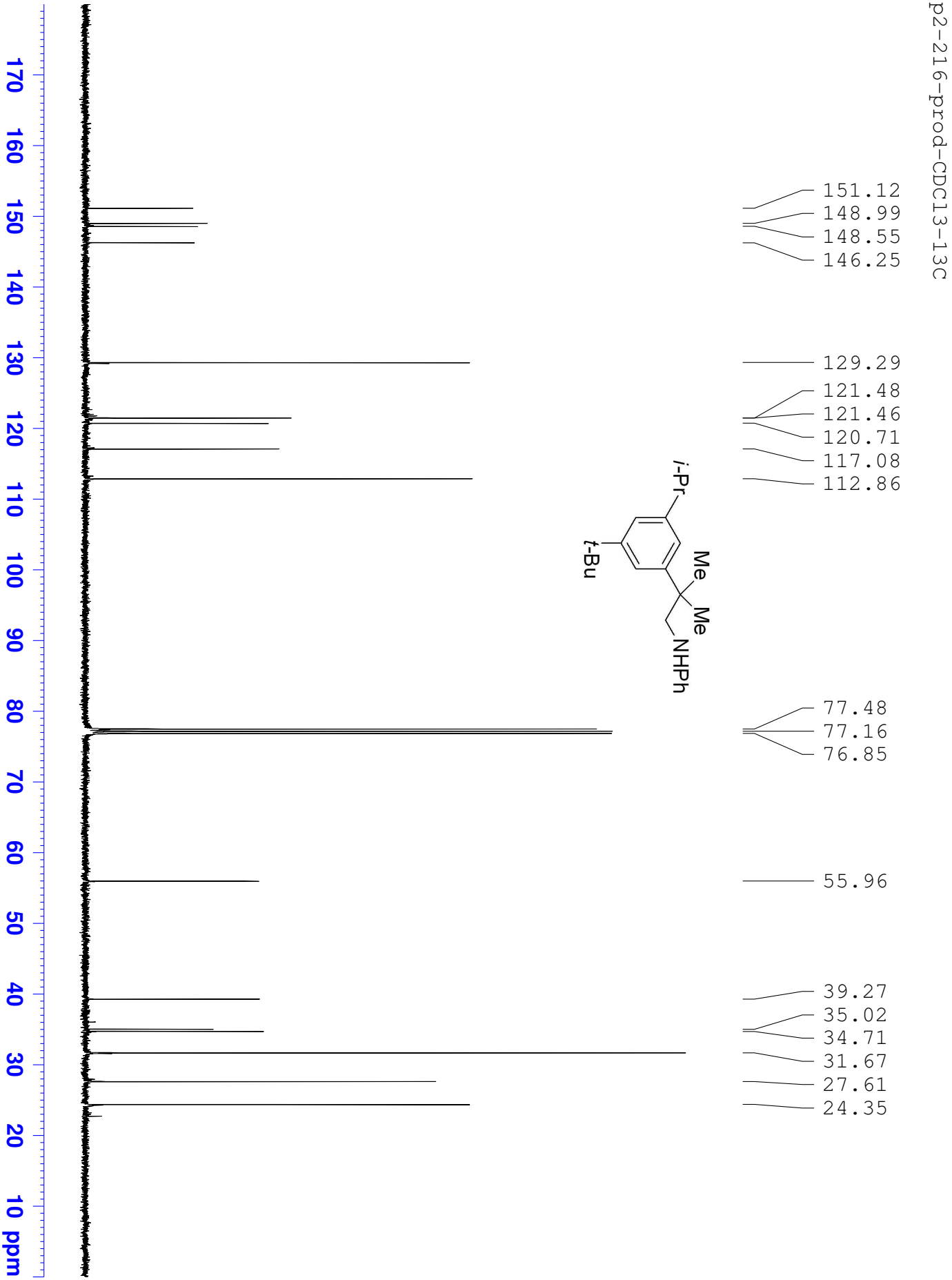
jp2-179-prod-CDCl3-1H



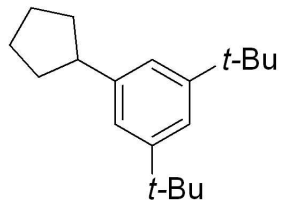
jp2-179-prod-CDC13-13C-2
149.44
148.45
147.44
123.34
122.35
121.72
77.48
77.17
76.85
37.77
35.00
33.72
31.51
30.52
23.51
Br
t-Bu
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

jp2-216-prod-CDCl3-1H-400



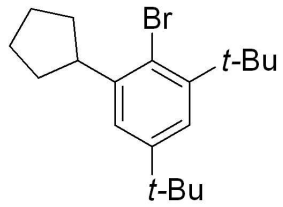

jp2-216-prod-CDC13-13C
151.12
148.99
148.55
146.25
129.29
121.48
121.46
120.71
117.08
112.86
77.48
77.16
76.85
55.96
39.27
35.02
34.71
31.67
27.61
24.35
i-Pr
t-Bu
Me
Me
NHPh
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

jp2-072-prod-CDCl3-1H

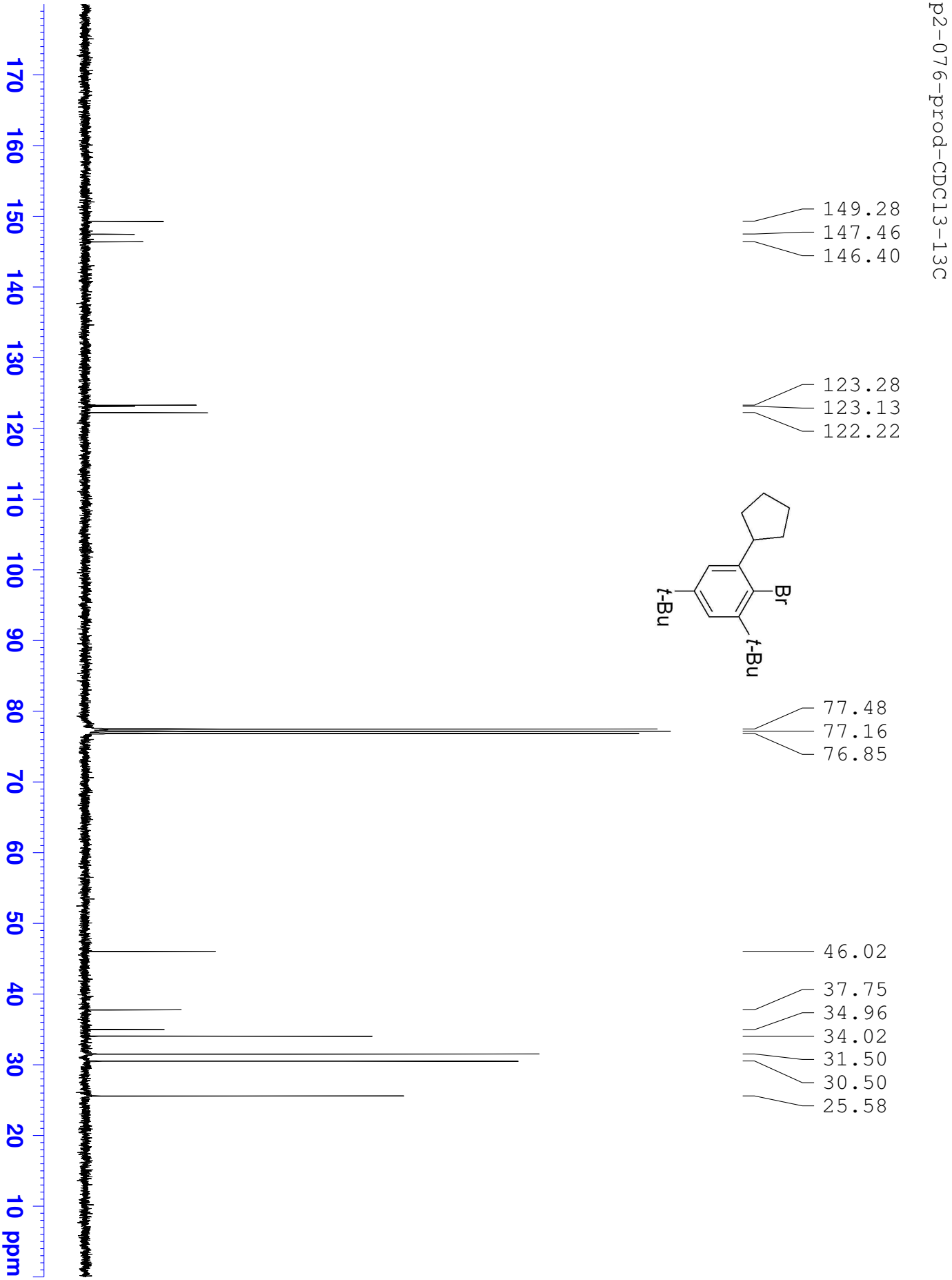


jp2-072-prod-CDC13-13C
150.49
145.52
121.47
119.99
77.48
77.16
76.84
46.78
34.98
34.95
31.70
25.67
t-Bu
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

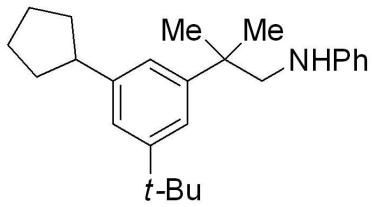
jp2-076-prod-CDCl3-1H-2



70


jp2-076-prod-CDC13-13C
149.28
147.46
146.40
123.28
123.13
122.22
Br
t-Bu
t-Bu
77.48
77.16
76.85
46.02
37.75
34.96
34.02
31.50
30.50
25.58
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

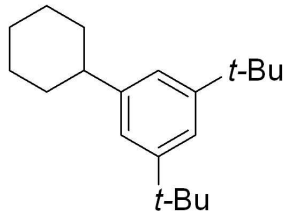
jp2-077-prod-CDCl3-1H



72

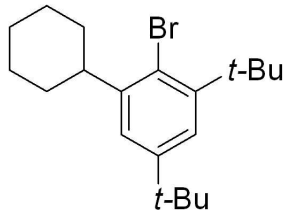
jp2-217-prod-CDC13-13C

jp2-067-prod-CDCl3-1H-2



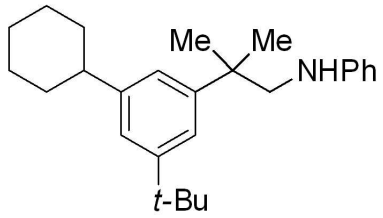
jp2-067-prod-CDC13-13C
150.48
147.26
121.18
120.01
77.48
77.16
76.85
45.32
35.01
34.80
31.72
27.21
26.41
t-Bu
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

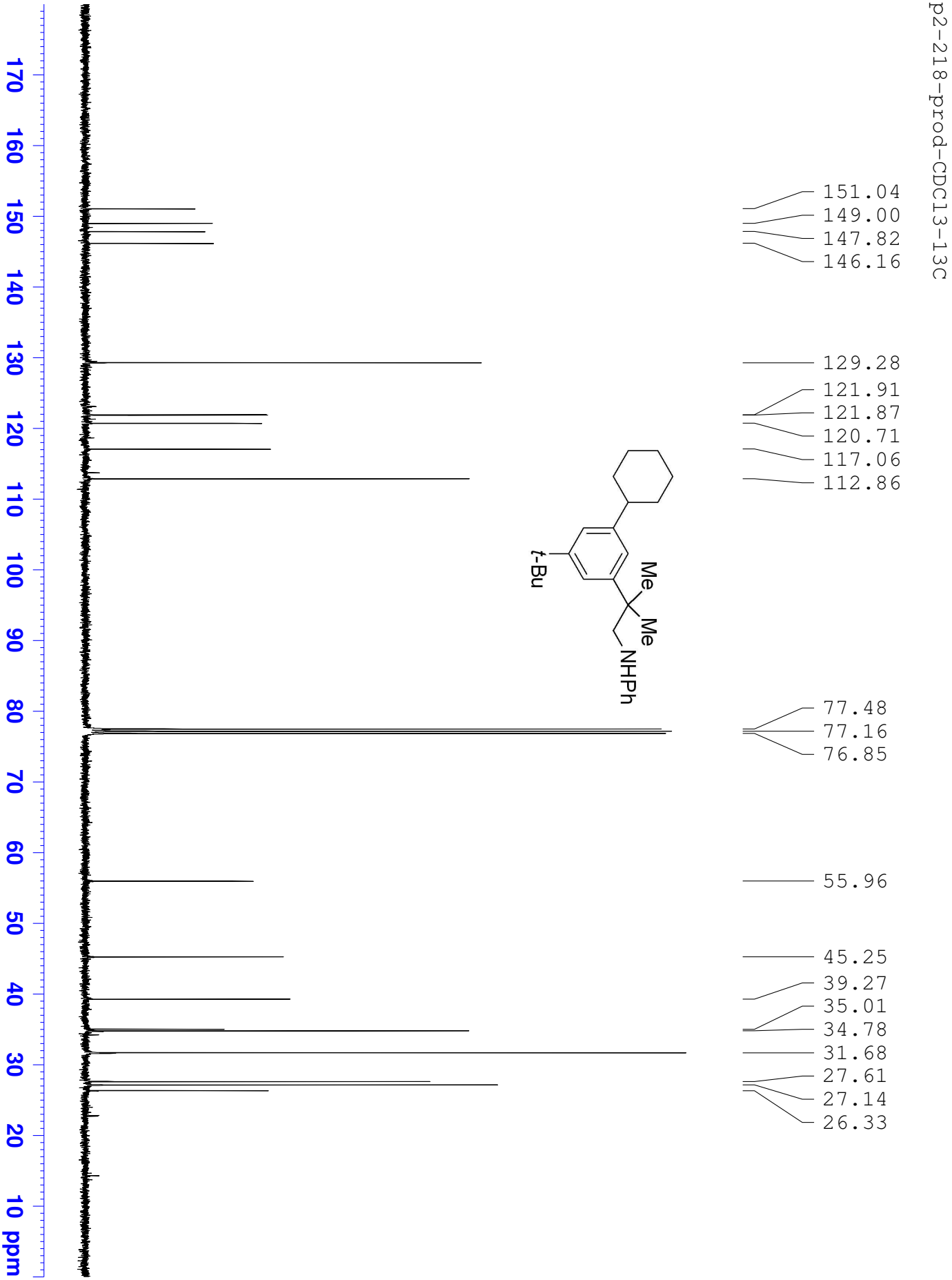
jp2-074-prod-CDCl3-1H-2



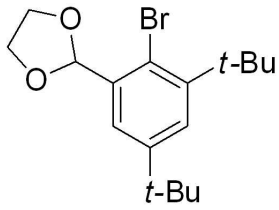
jp2-074-prod-CDC13-13C
149.32
147.45
147.39
123.29
122.56
122.45
77.48
77.16
76.84
44.40
37.78
34.98
33.97
31.52
30.52
27.21
26.50
Br
t-Bu
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

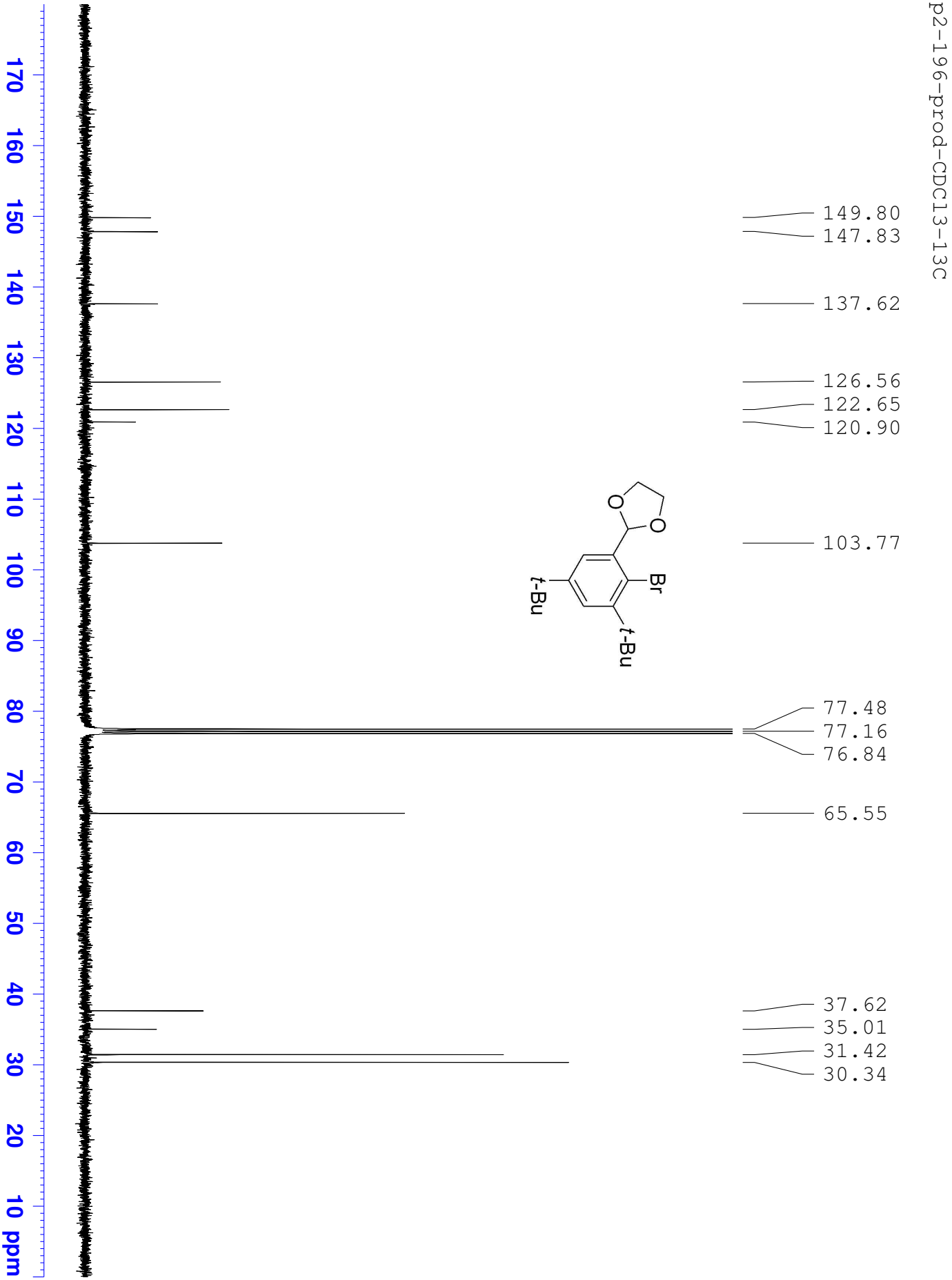
jp2-078-prod-CDCl3-1H



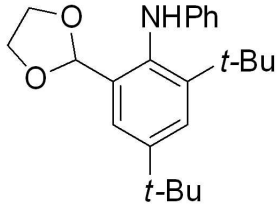

jp2-218-prod-CDC13-13C
151.04
149.00
147.82
146.16
129.28
121.91
121.87
120.71
117.06
112.86
77.48
77.16
76.85
55.96
45.25
39.27
35.01
34.78
31.68
27.61
27.14
26.33
t-Bu
Me
Me
NHPh
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

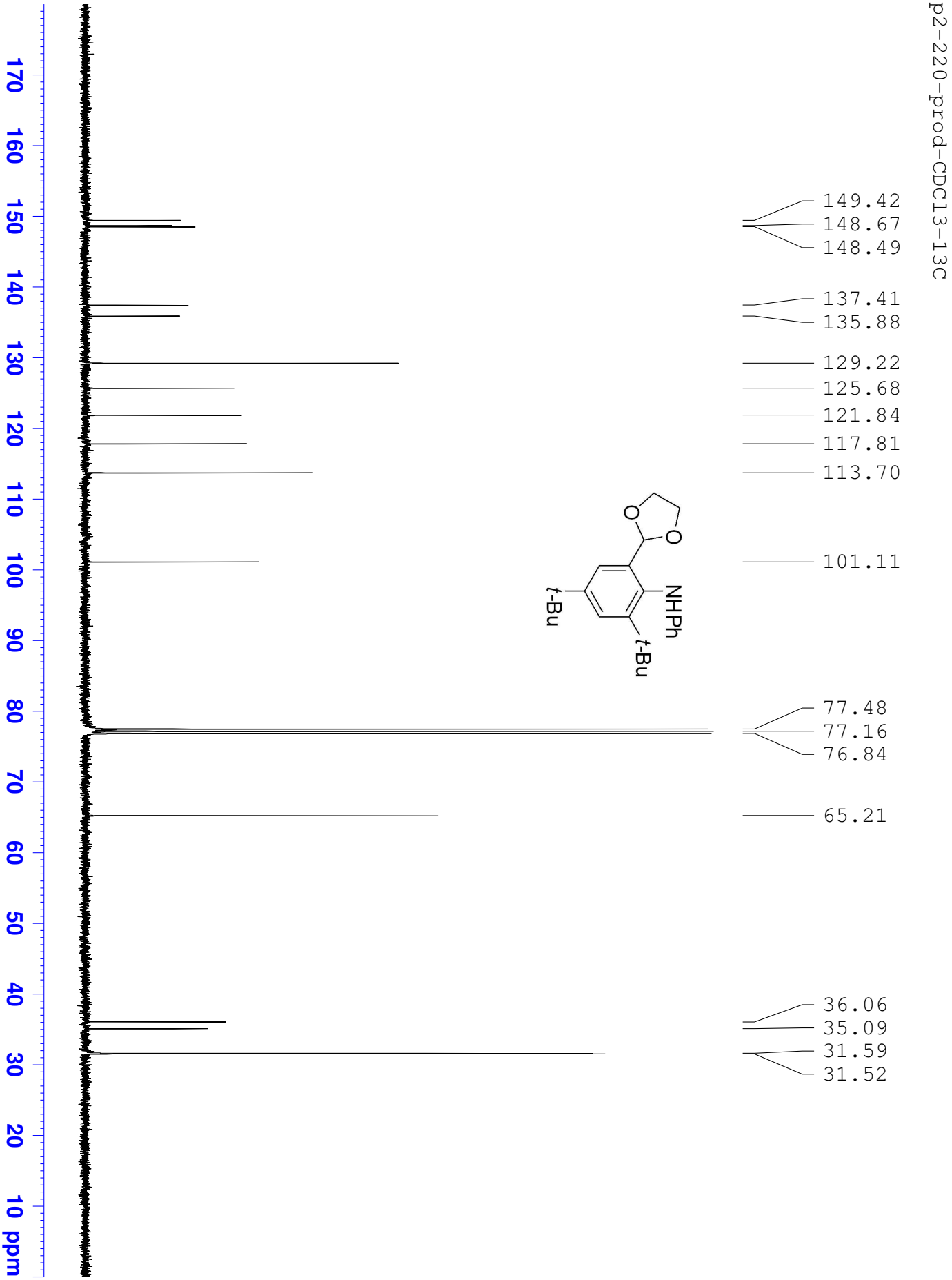
jp2-196-prod-CDCl3-1H-400-3



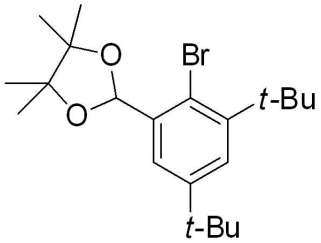

jp2-196-prod-CDC13-13C
149.80
147.83
137.62
126.56
122.65
120.90
103.77
77.48
77.16
76.84
65.55
37.62
35.01
31.42
30.34
Br
t-Bu
t-Bu
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

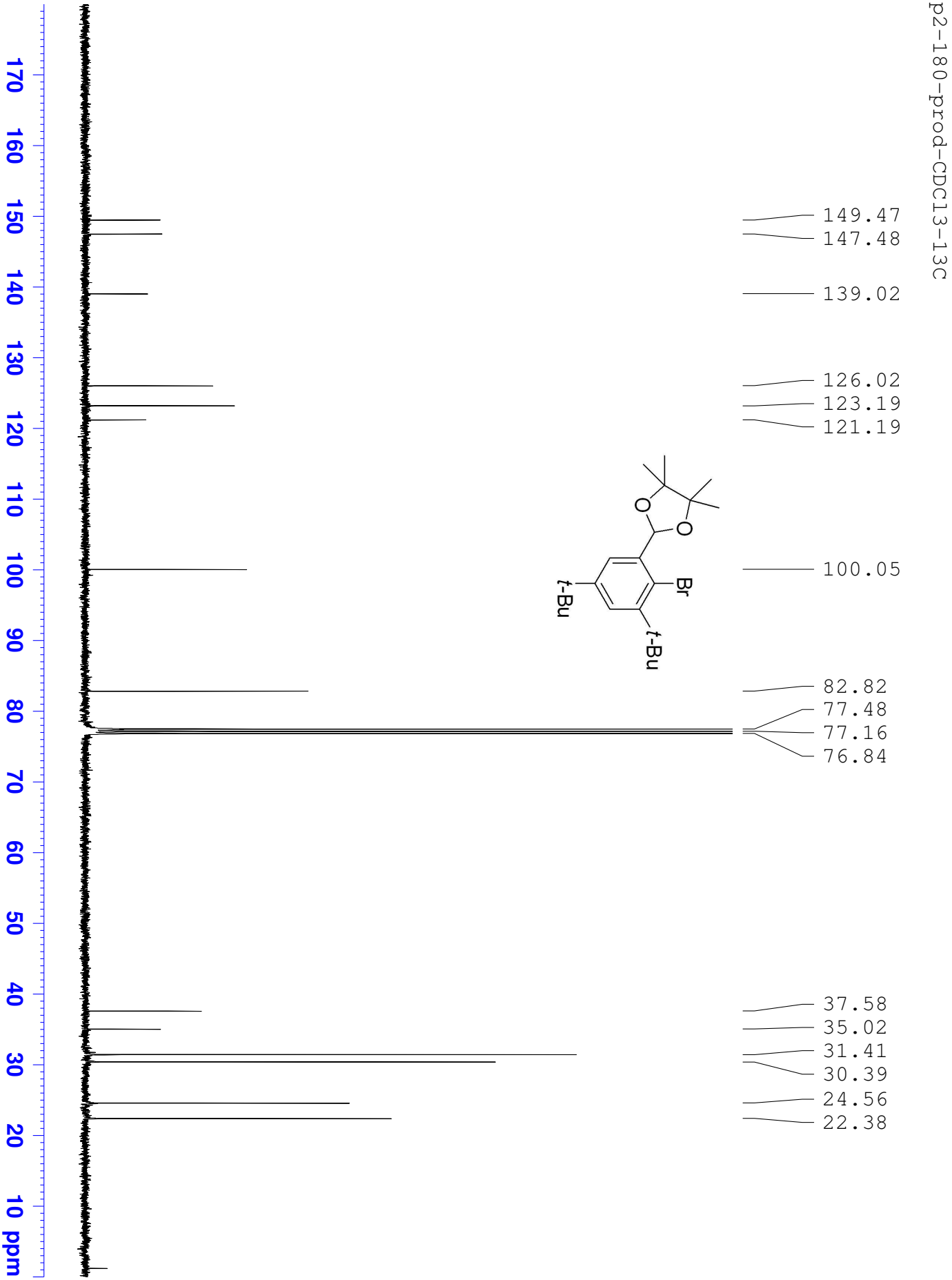
jp2-220-prod-CDCl3-1H-400



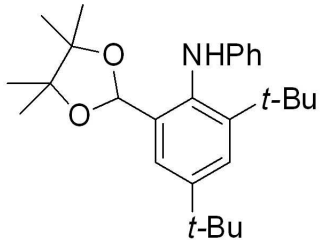

jp2-220-prod-CDC13-13C
149.42
148.67
148.49
137.41
135.88
129.22
125.68
121.84
117.81
113.70
101.11
77.48
77.16
76.84
65.21
36.06
35.09
31.59
31.52
O
O
NHPh
t-Bu
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

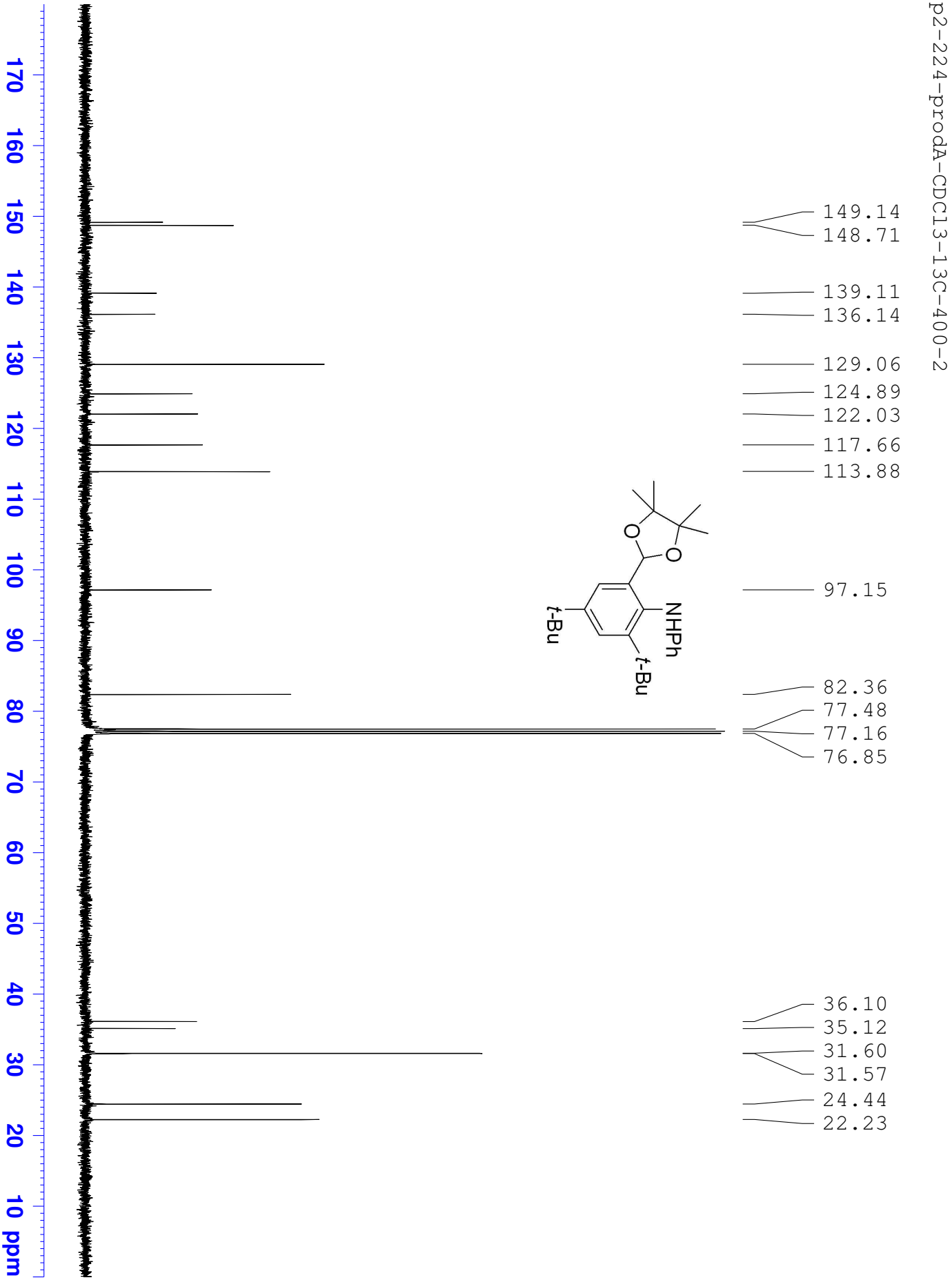
jp2-180-prod-CDCl3-1H-3



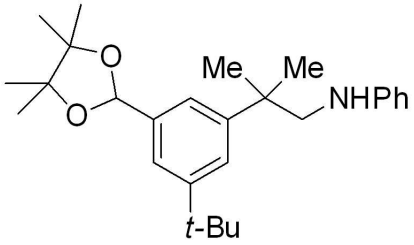

jp2-180-prod-CDC13-13C
149.47
147.48
139.02
126.02
123.19
121.19
100.05
82.82
77.48
77.16
76.84
37.58
35.02
31.41
30.39
24.56
22.38
Br
t-Bu
t-Bu
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

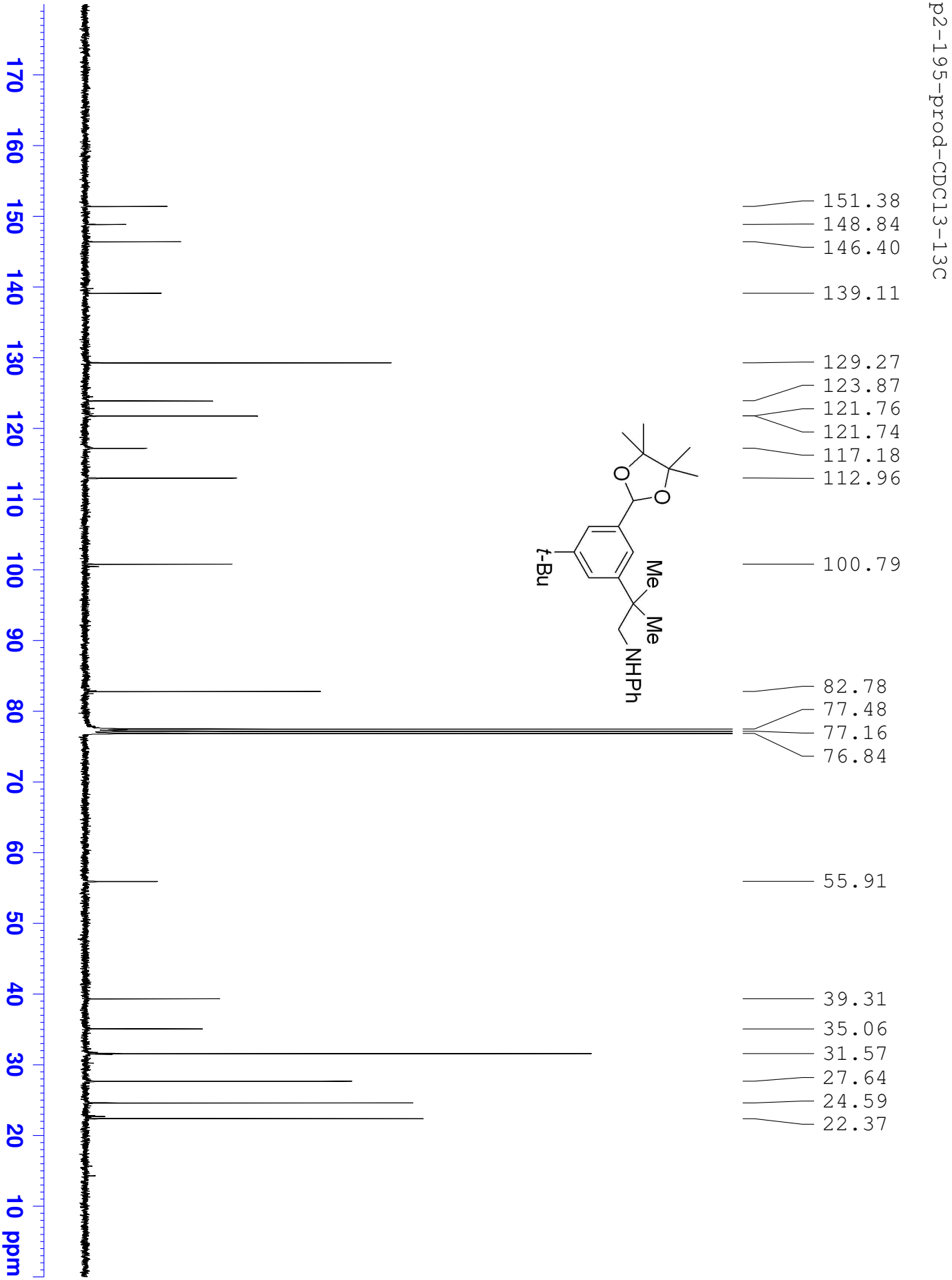
jp2-224-prodA-CDCl3-1H-400-2



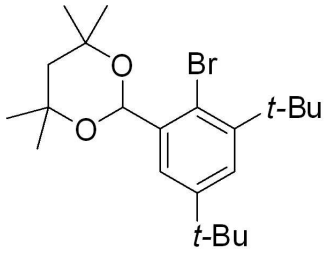

jp2-224-prodA-CDC13-13C-400-2
149.14
148.71
139.11
136.14
129.06
124.89
122.03
117.66
113.88
97.15
82.36
77.48
77.16
76.85
36.10
35.12
31.60
31.57
24.44
22.23
NHPh
t-Bu
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

jp2-224-prodB-CDCl3-1H



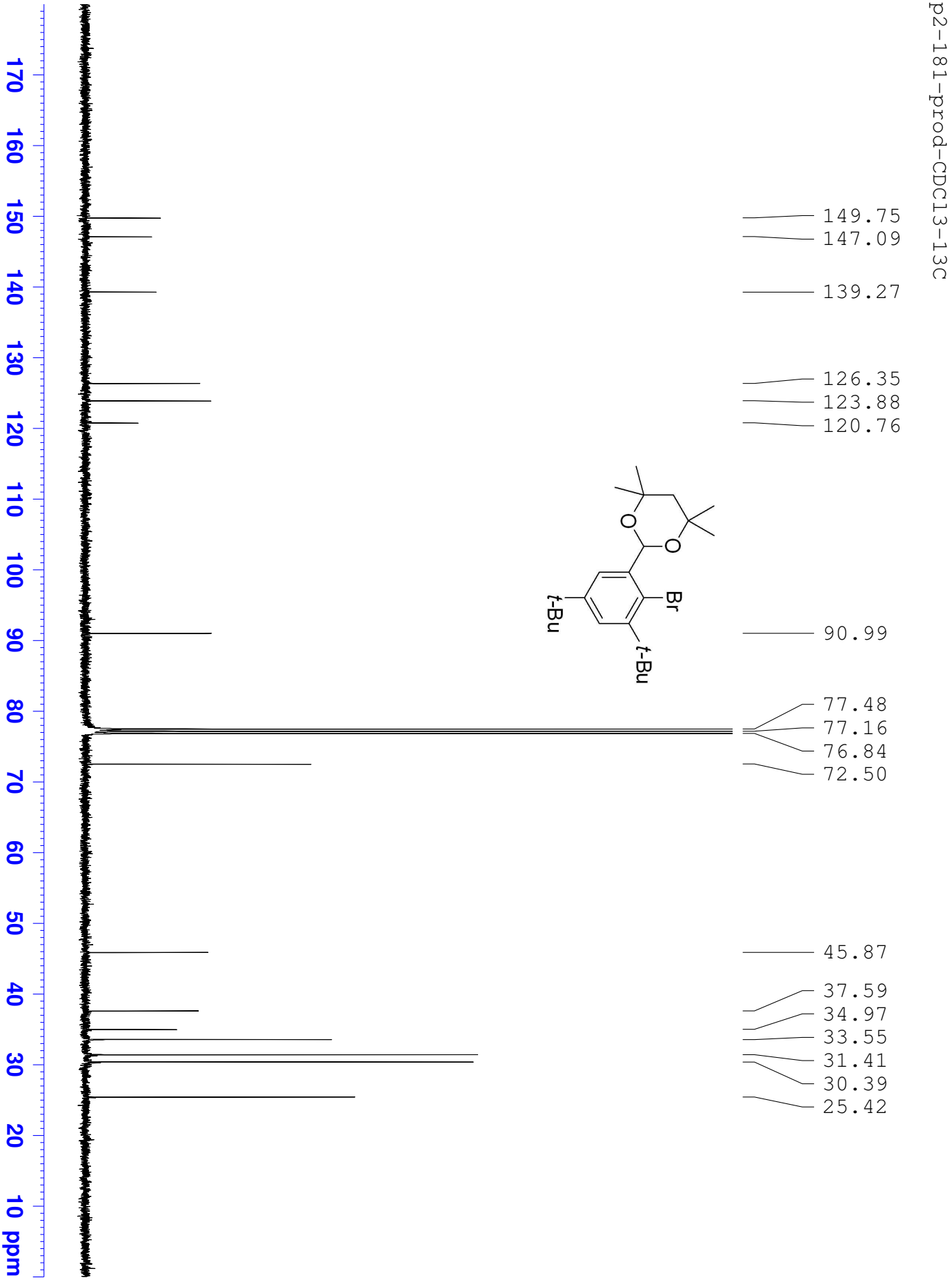

jp2-195-prod-CDC13-13C
151.38
148.84
146.40
139.11
129.27
123.87
121.76
121.74
117.18
112.96
100.79
82.78
77.48
77.16
76.84
55.91
39.31
35.06
31.57
27.64
24.59
22.37
t-Bu
Me
Me
NHPh
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

jp2-181-prod-CDCl3-1H-400

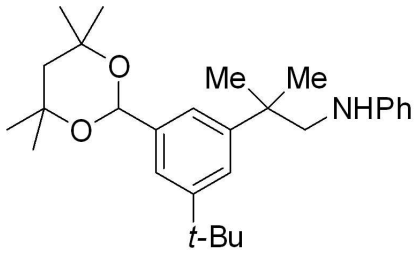


7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

1.00 1.04 1.02 1.09 1.58 15.73 6.62 9.57


jp2-181-prod-CDC13-13C
149.75
147.09
139.27
126.35
123.88
120.76
90.99
77.48
77.16
76.84
72.50
45.87
37.59
34.97
33.55
31.41
30.39
25.42
t-Bu
Br
t-Bu
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

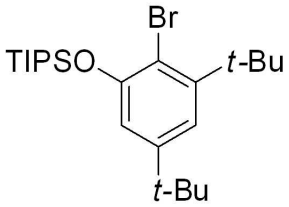
jp2-223-prod-CDCl3-1H



92

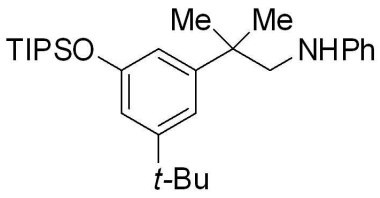
jp2-194-prod-CDCl3-13C

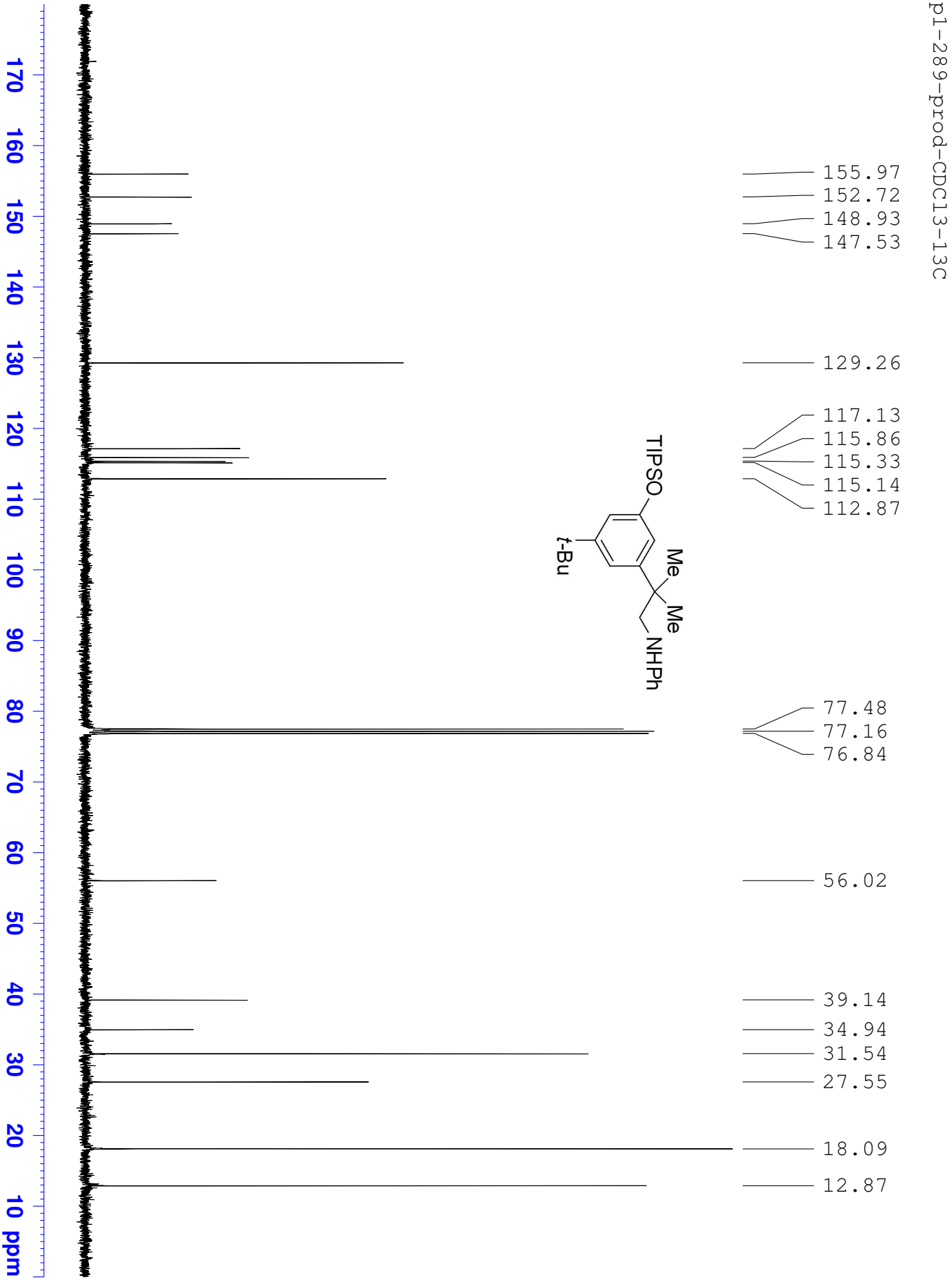
jp1-291-prod-CDCl3-1H



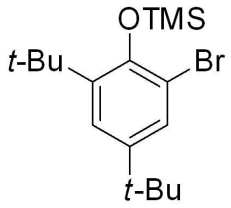
jp1-291-prod-CDC13-13C
153.28
150.05
148.71
117.30
114.82
113.10
77.48
77.16
76.85
37.50
34.84
31.41
30.19
18.25
13.29
TIPSO
Br
t-Bu
t-Bu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

jp1-289-prod-CDCl3-1H-2

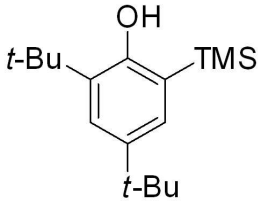


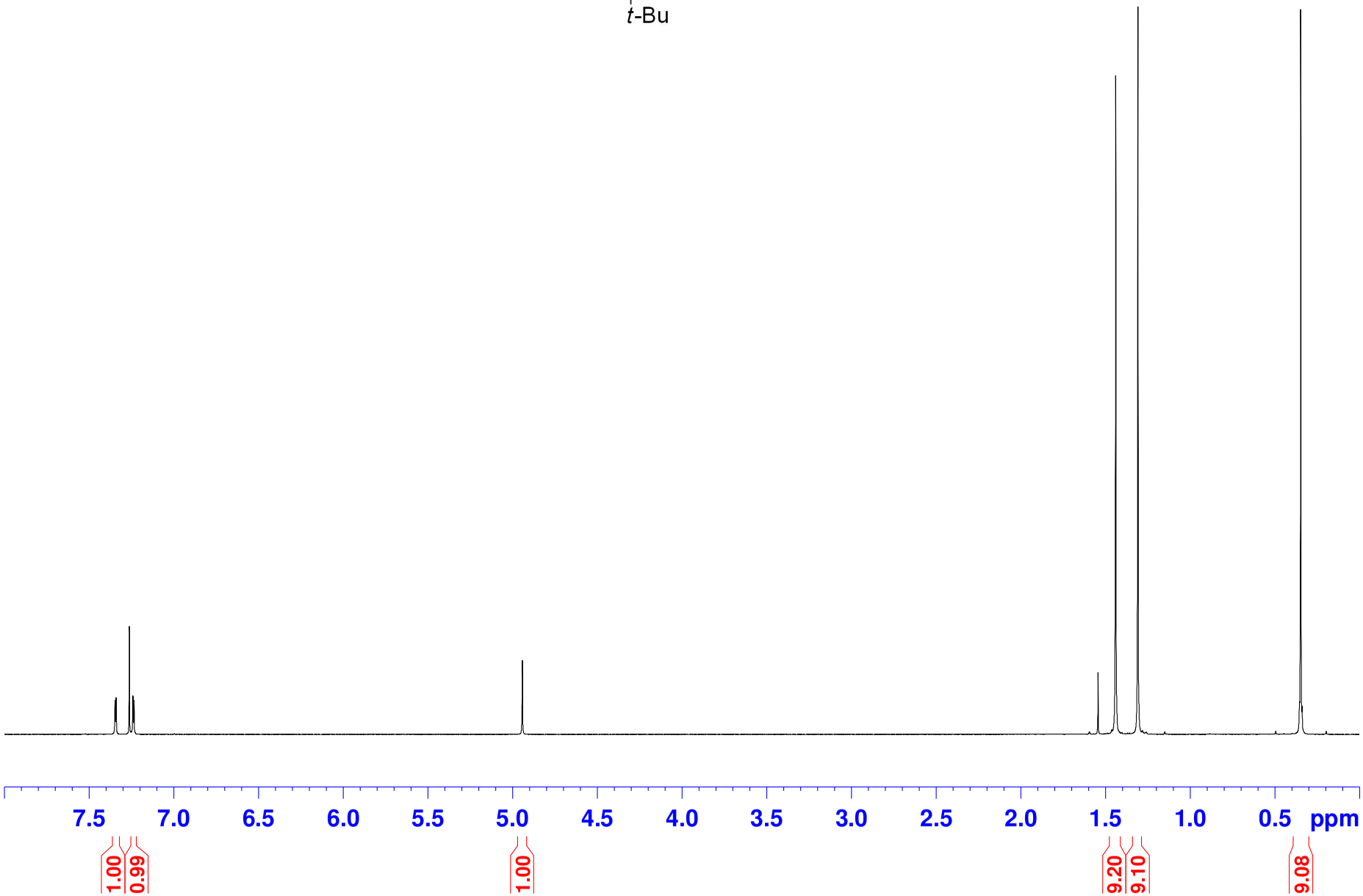

jp1-289-prod-CDC13-13C
155.97
152.72
148.93
147.53
129.26
117.13
115.86
115.33
115.14
112.87
77.48
77.16
76.84
56.02
39.14
34.94
31.54
27.55
18.09
12.87
TIPSO
t-Bu
Me
Me
NHPh
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

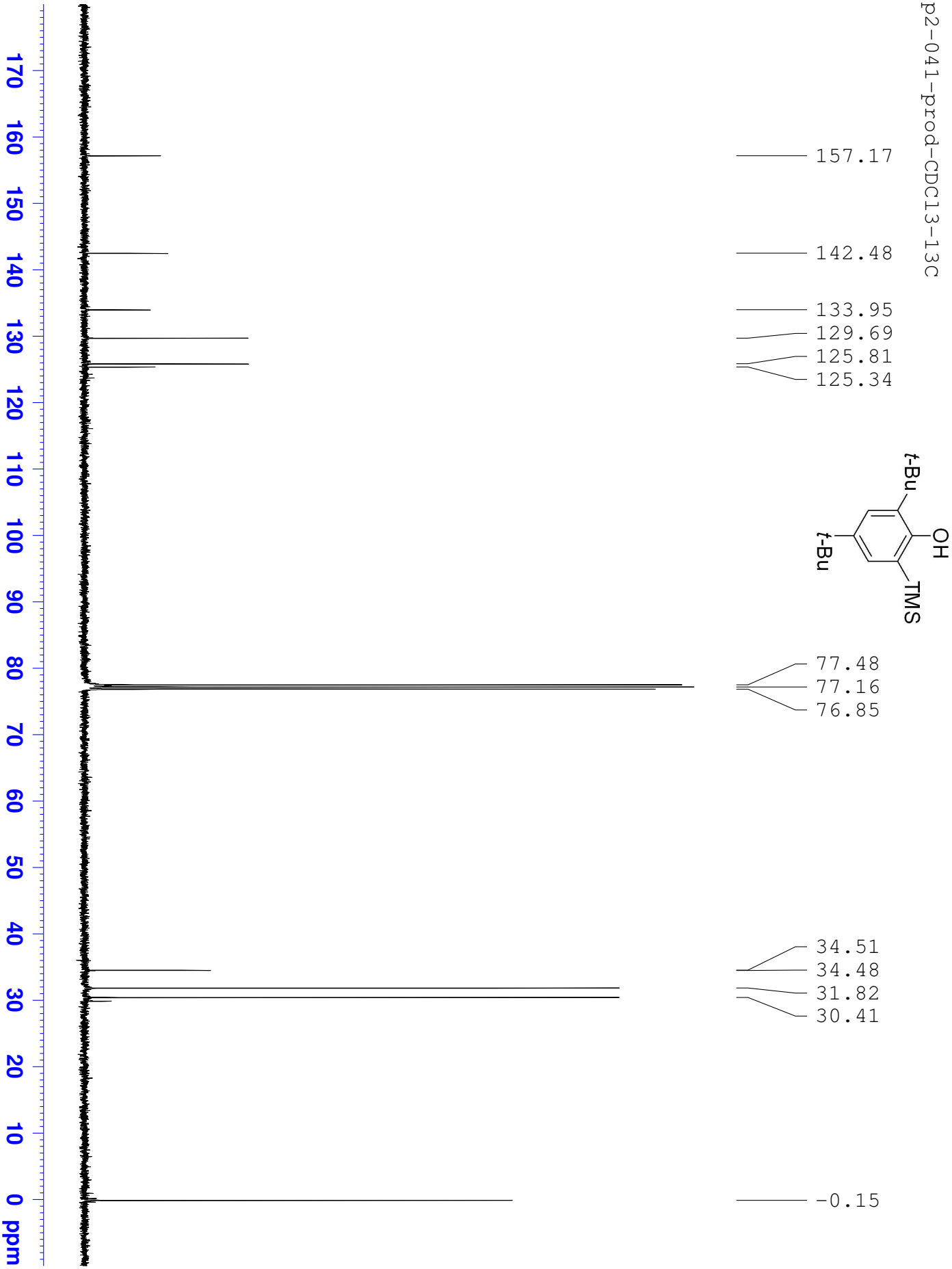
jp1-281-prod-CDCl3-1H



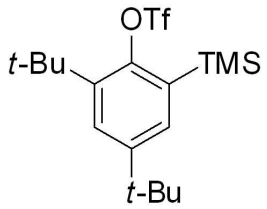
jp2-041-prod-CDCl3-1H






jp2-041-prod-CDC13-13C
157.17
142.48
133.95
129.69
125.81
125.34
77.48
77.16
76.85
34.51
34.48
31.82
30.41
-0.15
t-Bu
t-Bu
OH
TMS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

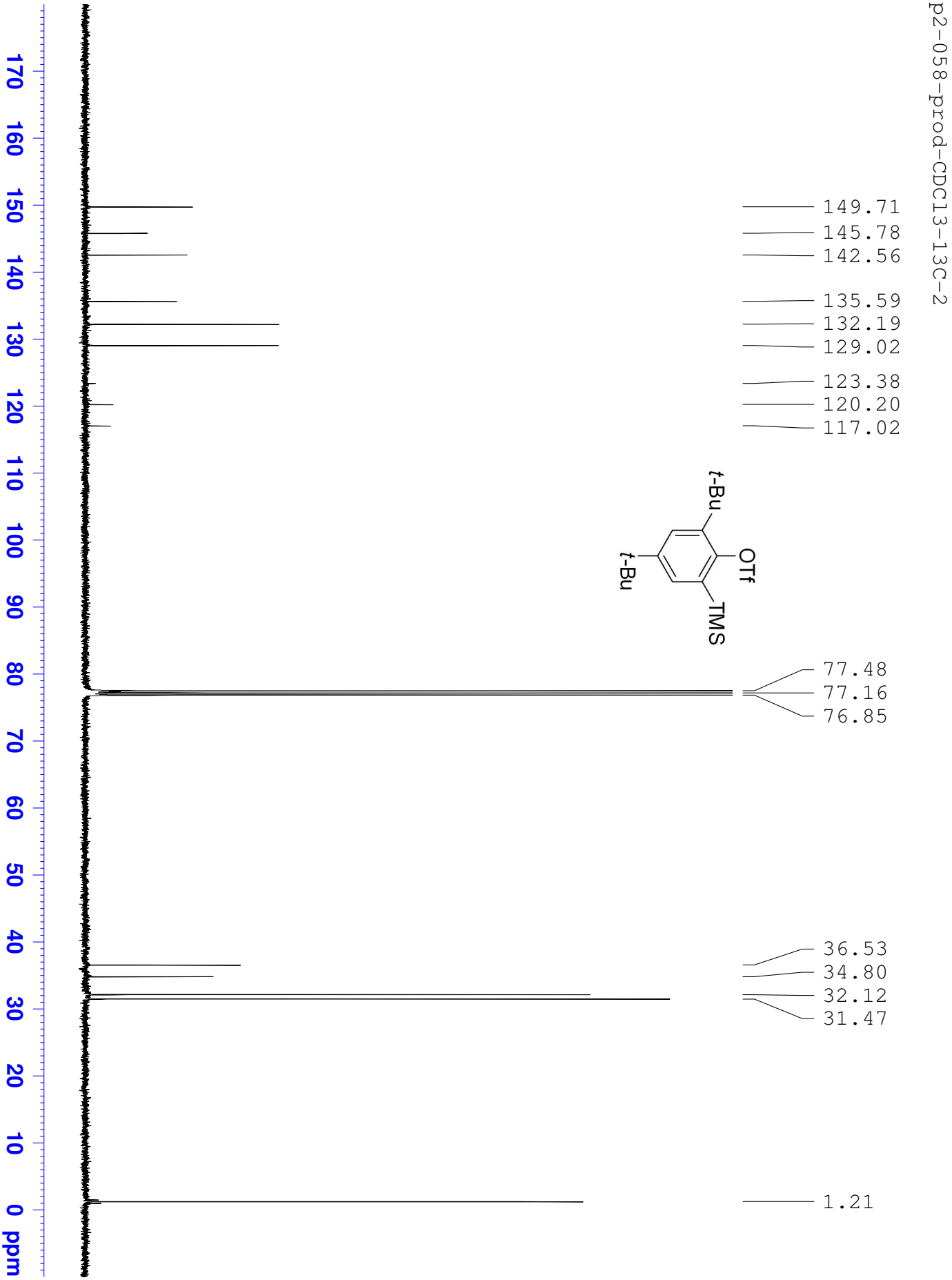
jp2-058-prod-CDCl3-1H-2



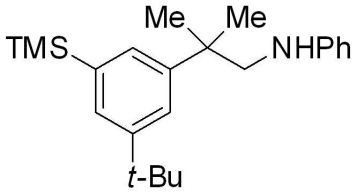
101

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.00 0.98 9.02 9.02 8.97


jp2-058-prod-CDC13-13C-2
149.71
145.78
142.56
135.59
132.19
129.02
123.38
120.20
117.02
77.48
77.16
76.85
36.53
34.80
32.12
31.47
1.21
t-Bu
t-Bu
OTf
TMS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

jp2-222-prod-CDCl3-1H



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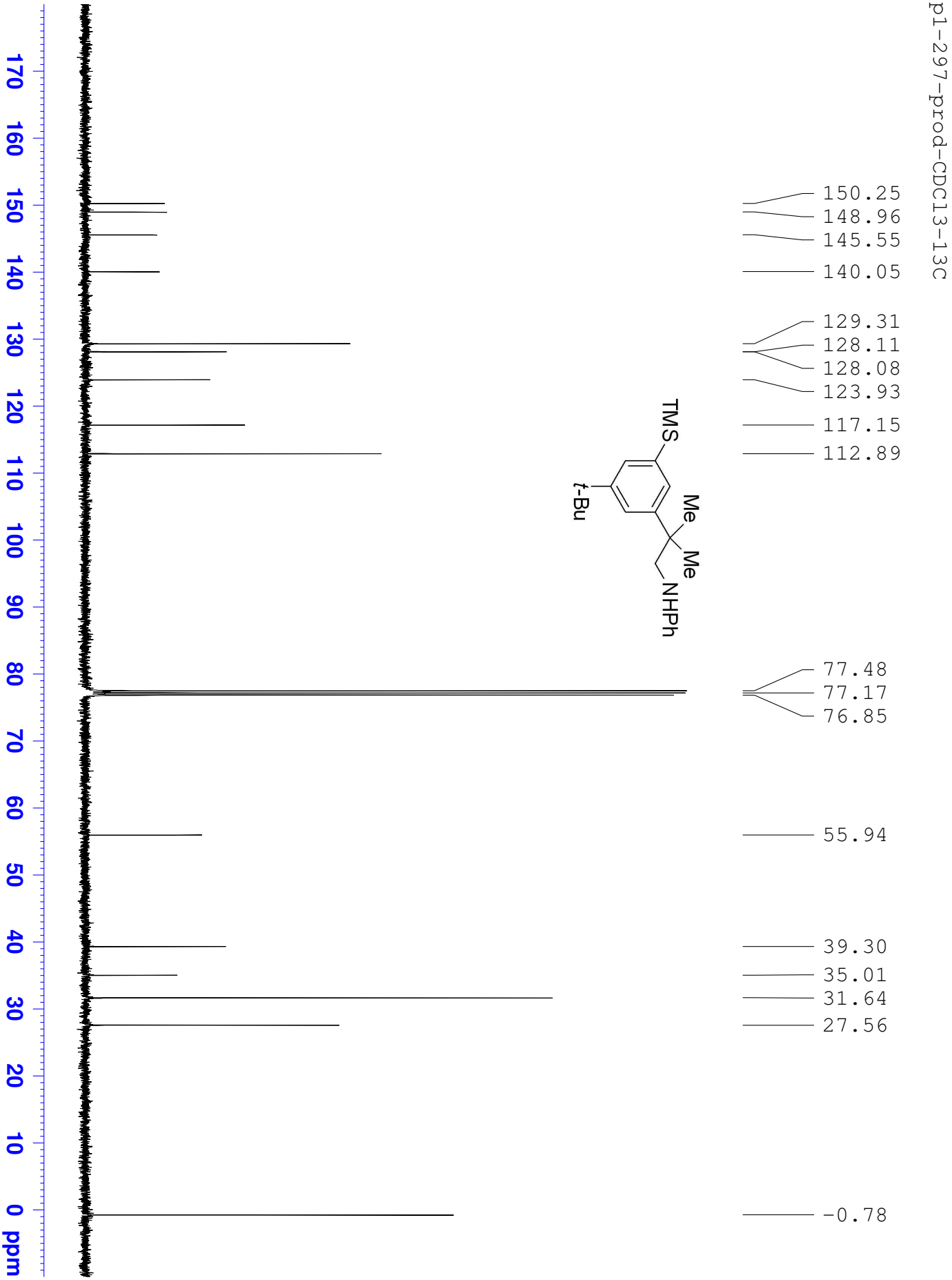
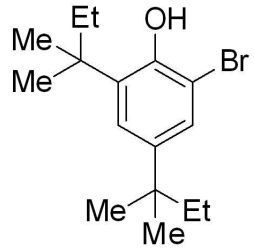
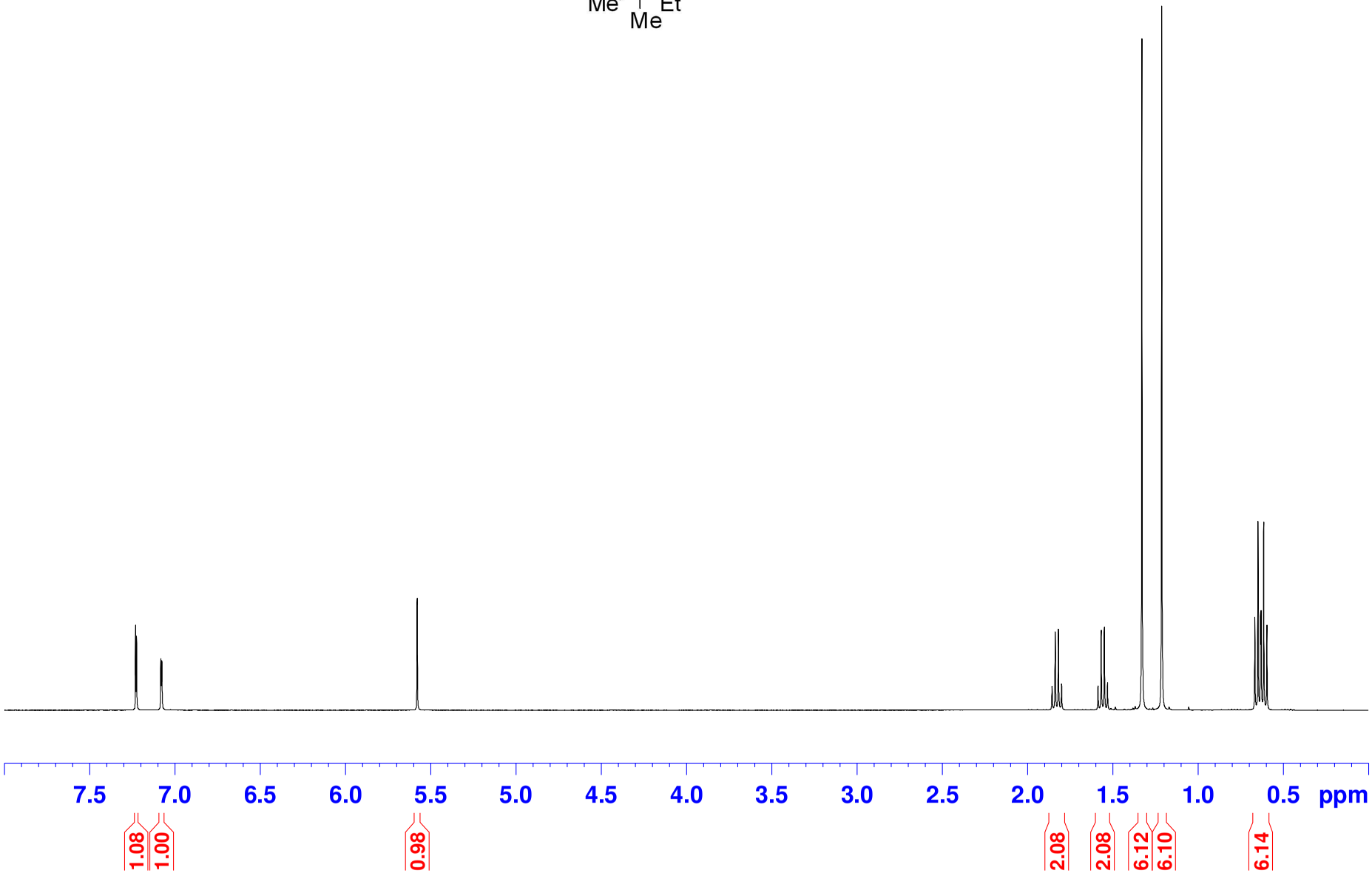
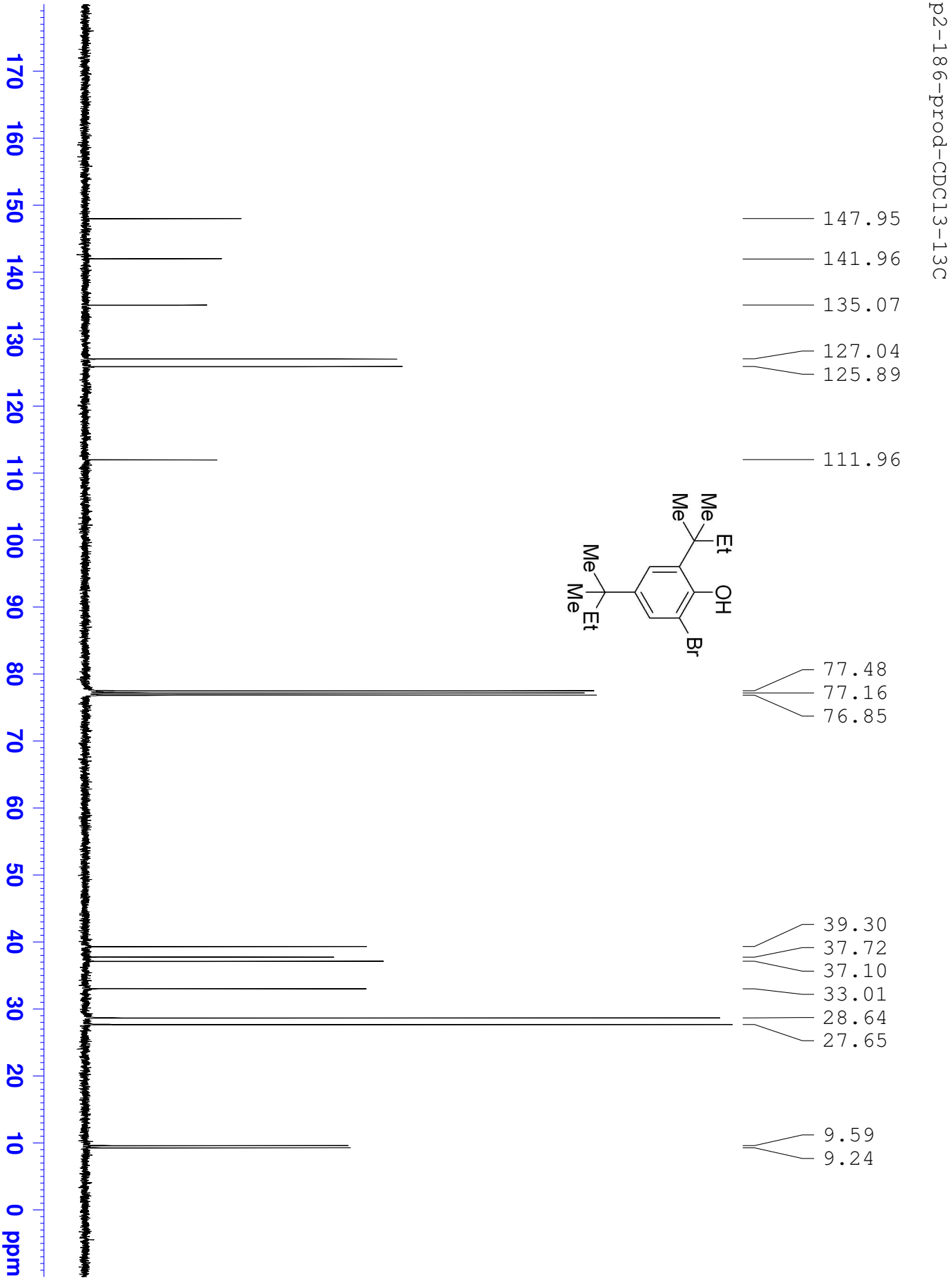

jp1-297-prod-CDC13-13C
150.25
148.96
145.55
140.05
129.31
128.11
128.08
123.93
117.15
112.89
77.48
77.17
76.85
55.94
39.30
35.01
31.64
27.56
-0.78
TMS
t-Bu
Me
Me
NHPh
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

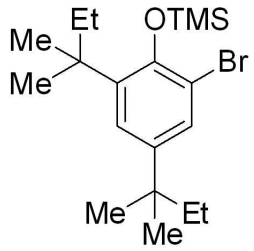
jp2-186-prod-CDCl3-1H






jp2-186-prod-CDC13-13C
147.95
141.96
135.07
127.04
125.89
111.96
77.48
77.16
76.85
39.30
37.72
37.10
33.01
28.64
27.65
9.59
9.24
Me
Me
Et
OH
Br
Me
Me
Et
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

jp2-189-prod-CDCl3-1H

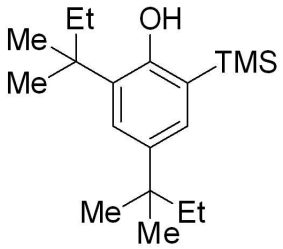


107

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.00 1.00 2.07 2.07 6.10 6.11 6.13 9.08

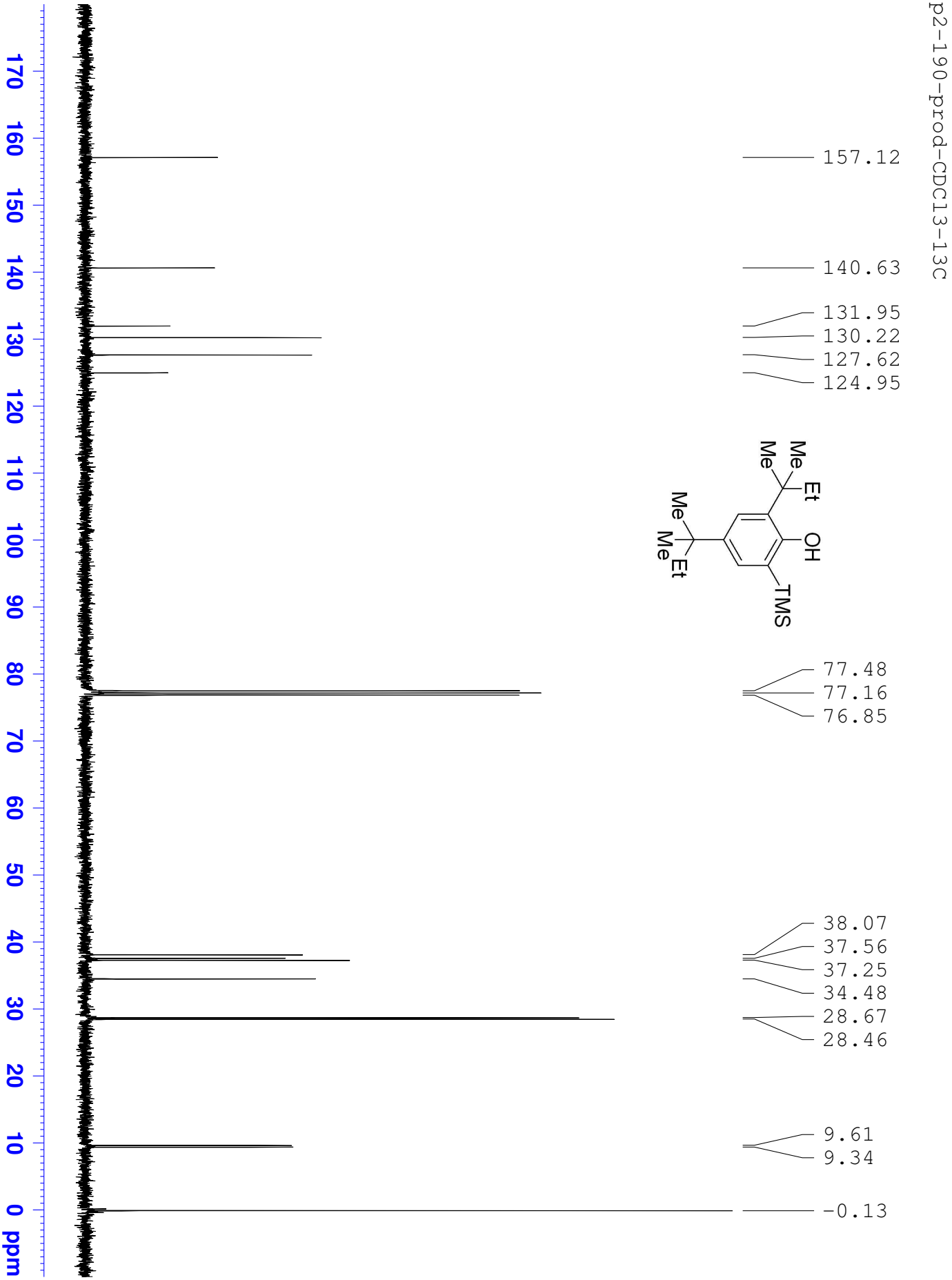
jp2-190-prod-CDCl3-1H-2



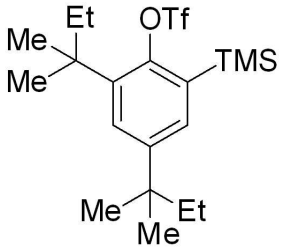
108

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.00 1.00 1.00 2.08 2.07 6.05 6.06 6.14 9.04


jp2-190-prod-CDC13-13C
157.12
140.63
131.95
130.22
127.62
124.95
77.48
77.16
76.85
38.07
37.56
37.25
34.48
28.67
28.46
9.61
9.34
-0.13
Me
Me
Et
Me
Me
Et
OH
TMS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

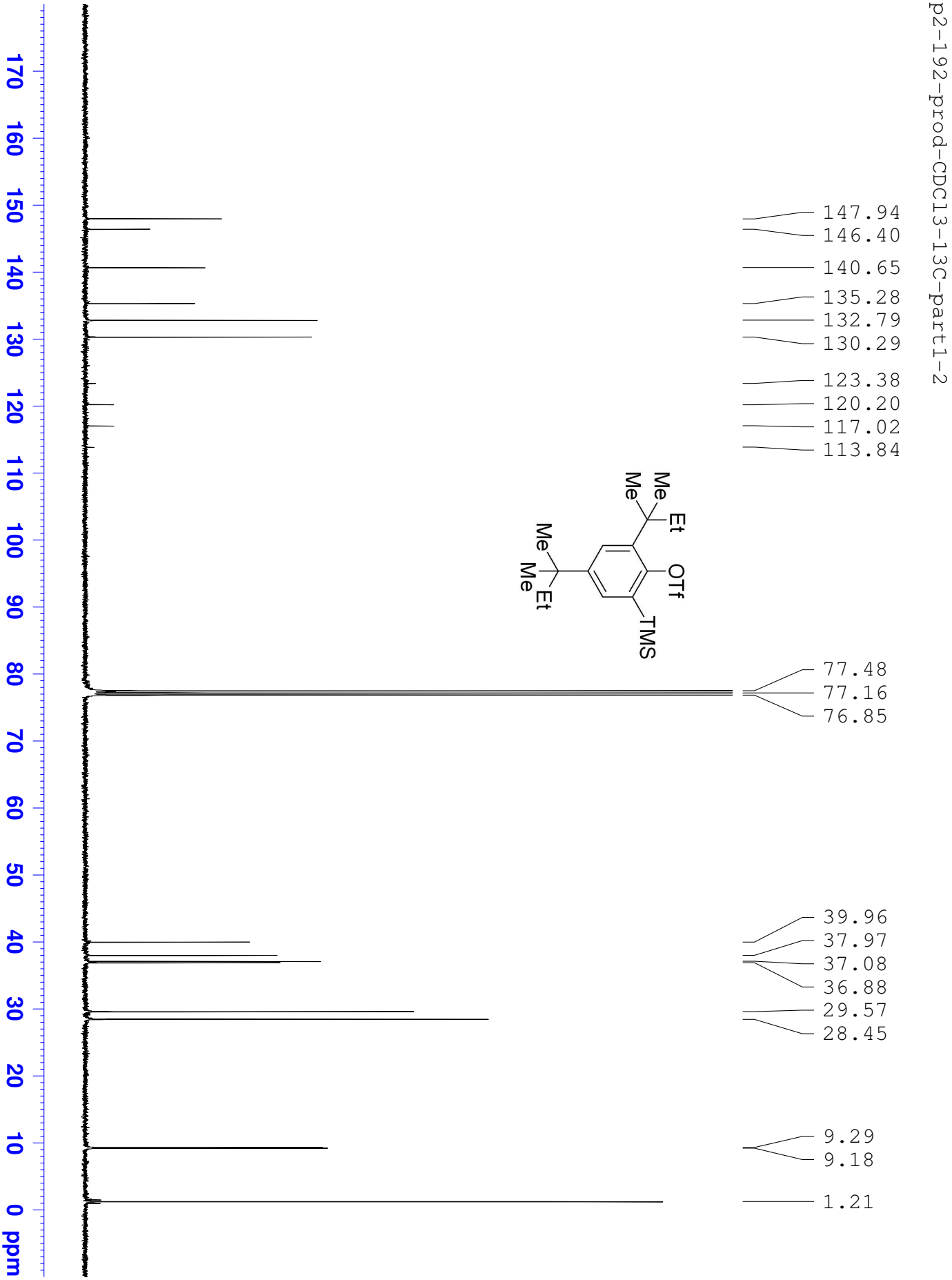
jp2-192-prod-CDCl3-1H-part1



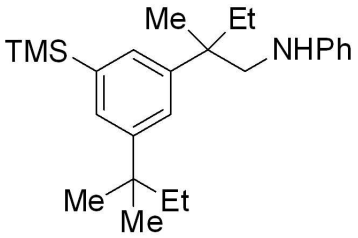
110

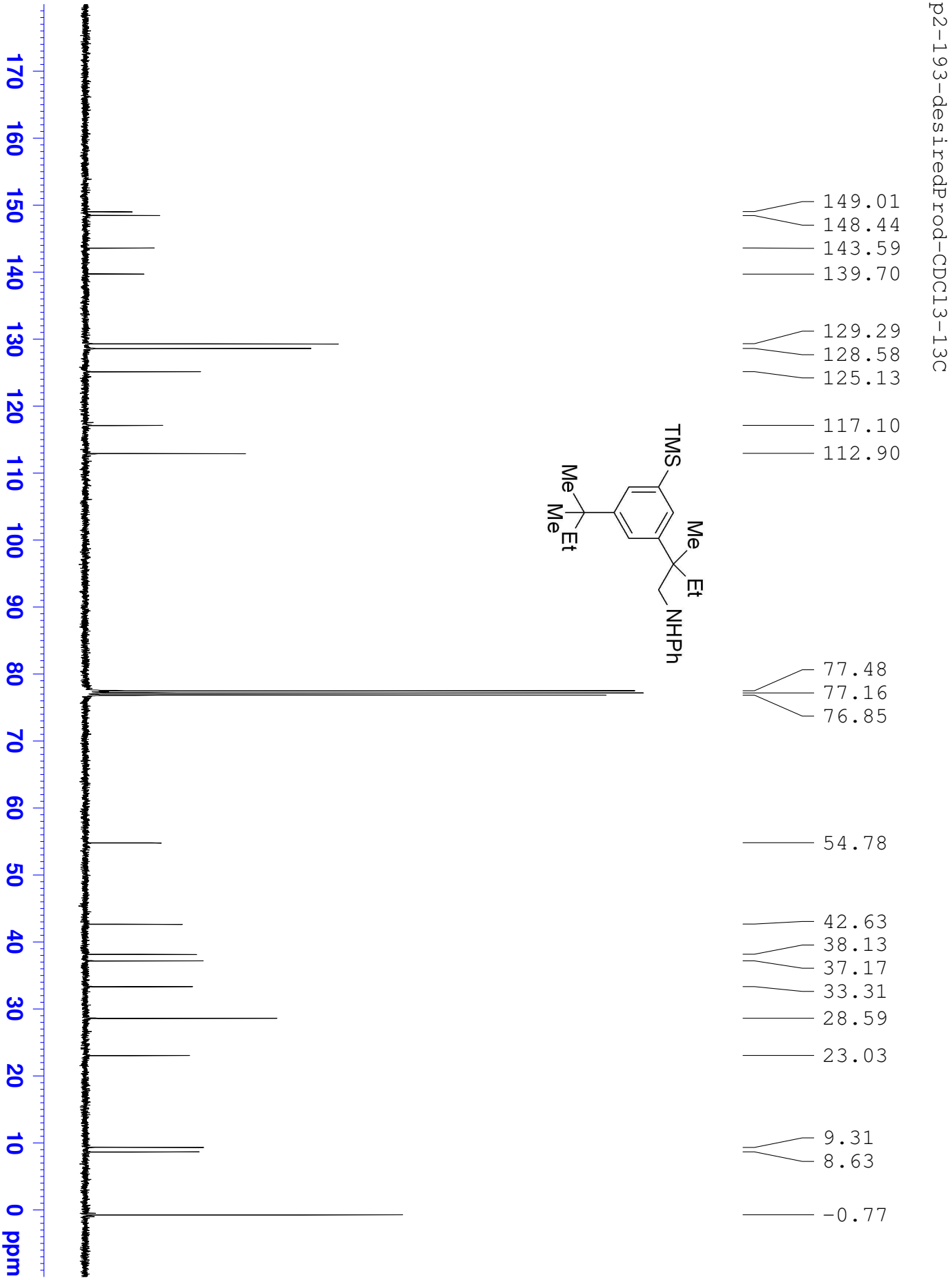
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.00 1.01 2.10 2.12 5.99 6.00 6.30 8.98

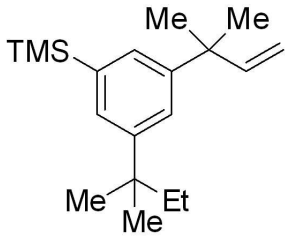

jp2-192-prod-CDC13-13C-part1-2
147.94
146.40
140.65
135.28
132.79
130.29
123.38
120.20
117.02
113.84
77.48
77.16
76.85
39.96
37.97
37.08
36.88
29.57
28.45
9.29
9.18
1.21
Me
Me
Et
OTf
TMS
Me
Me
Et
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

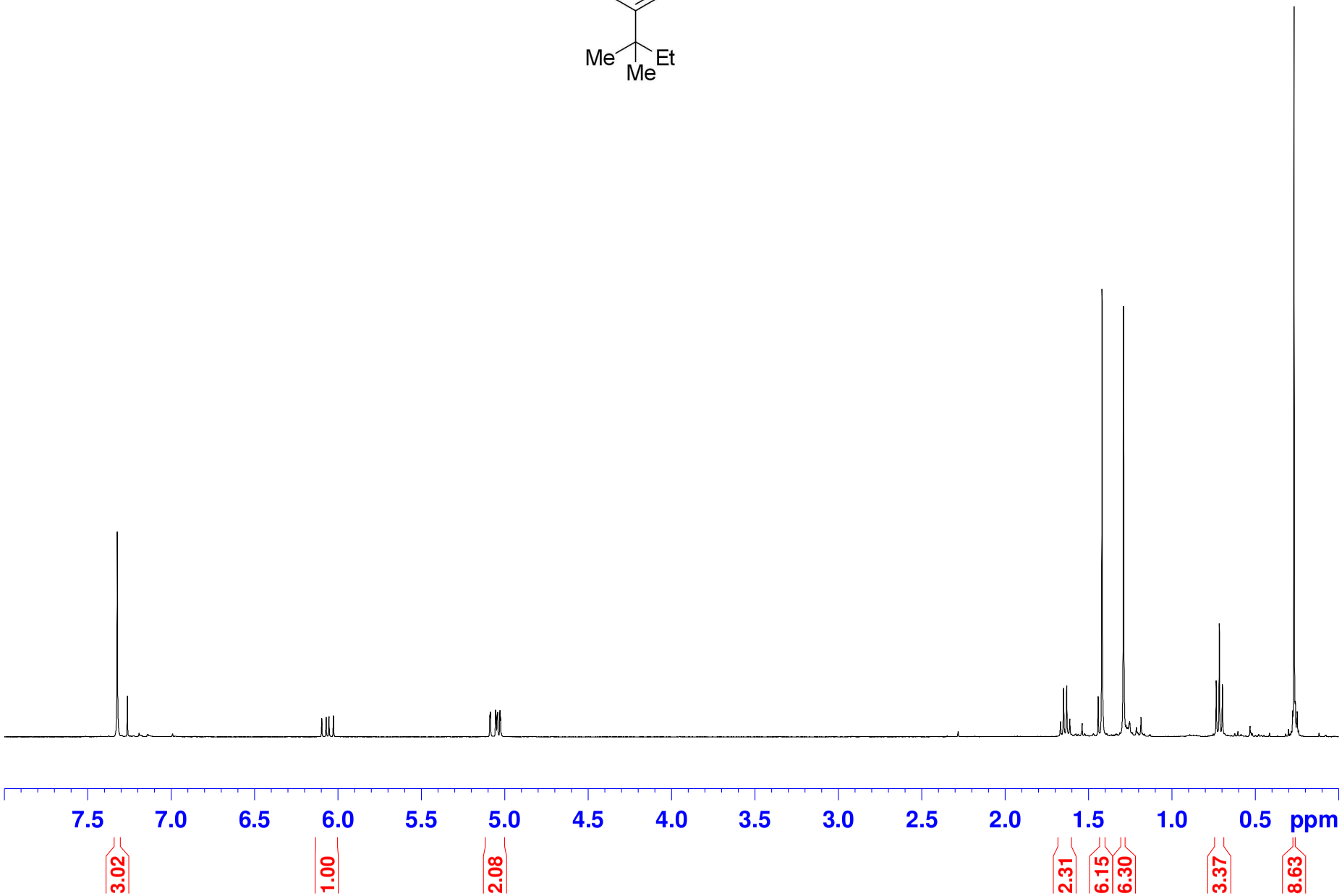
jp2-193-prod2-CDCl3-1H

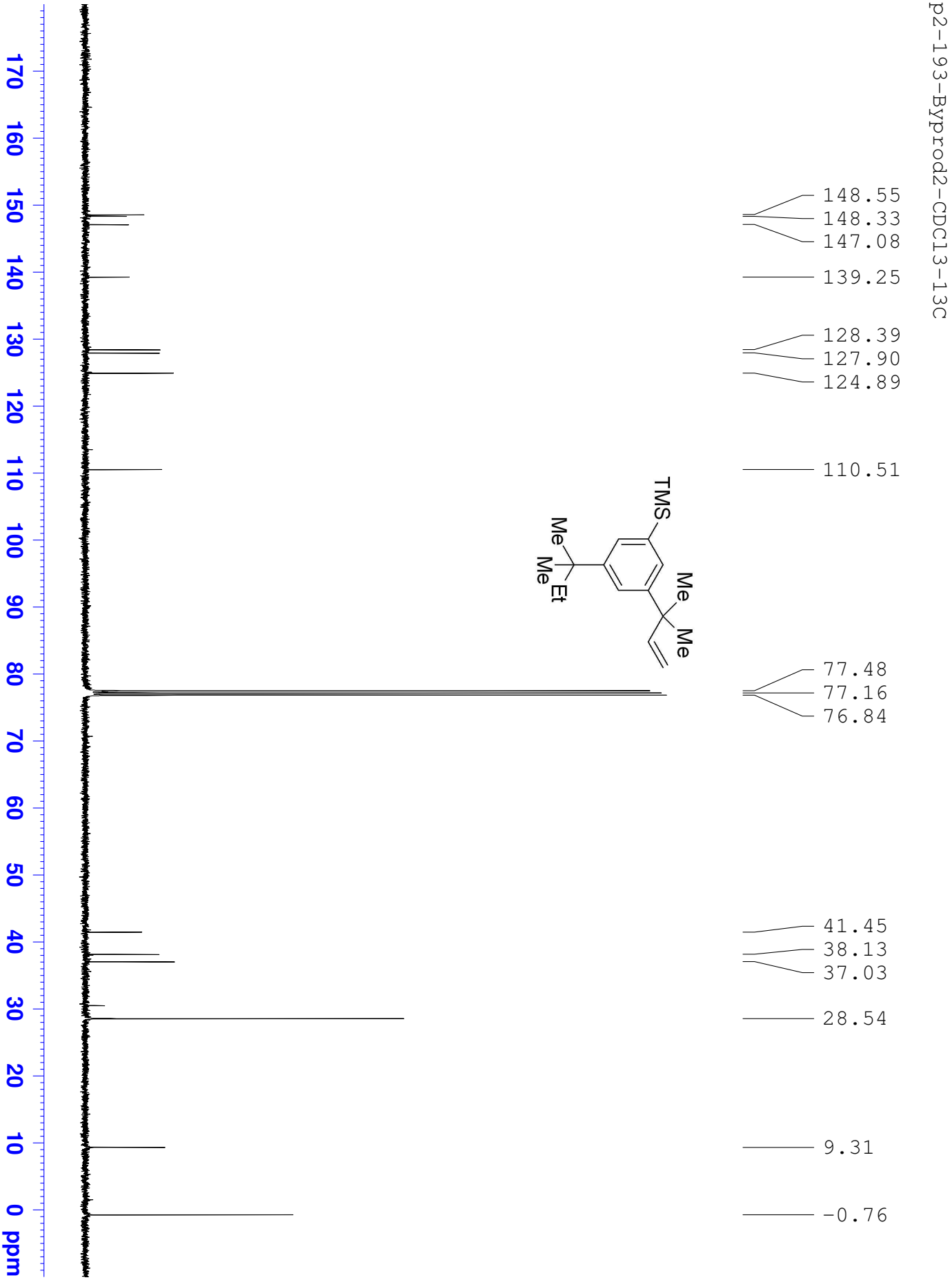



jp2-193-desiredProd-CDC13-13C
149.01
148.44
143.59
139.70
129.29
128.58
125.13
117.10
112.90
77.48
77.16
76.85
54.78
42.63
38.13
37.17
33.31
28.59
23.03
9.31
8.63
-0.77
TMS
Me
Et
NHPh
Me
Et
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

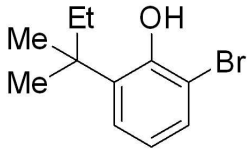
jp2-193-Byprod2-CDCl3-1H

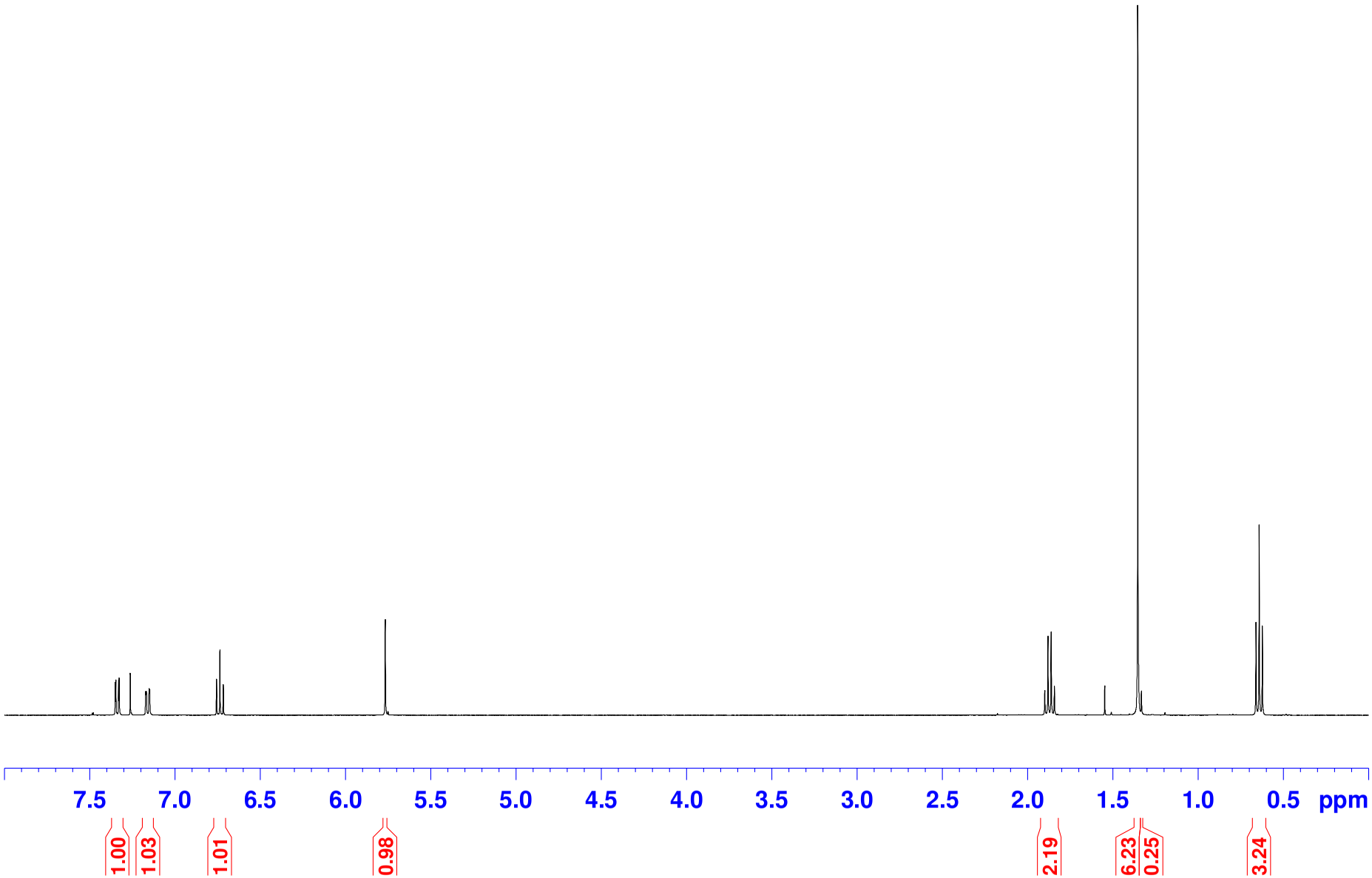


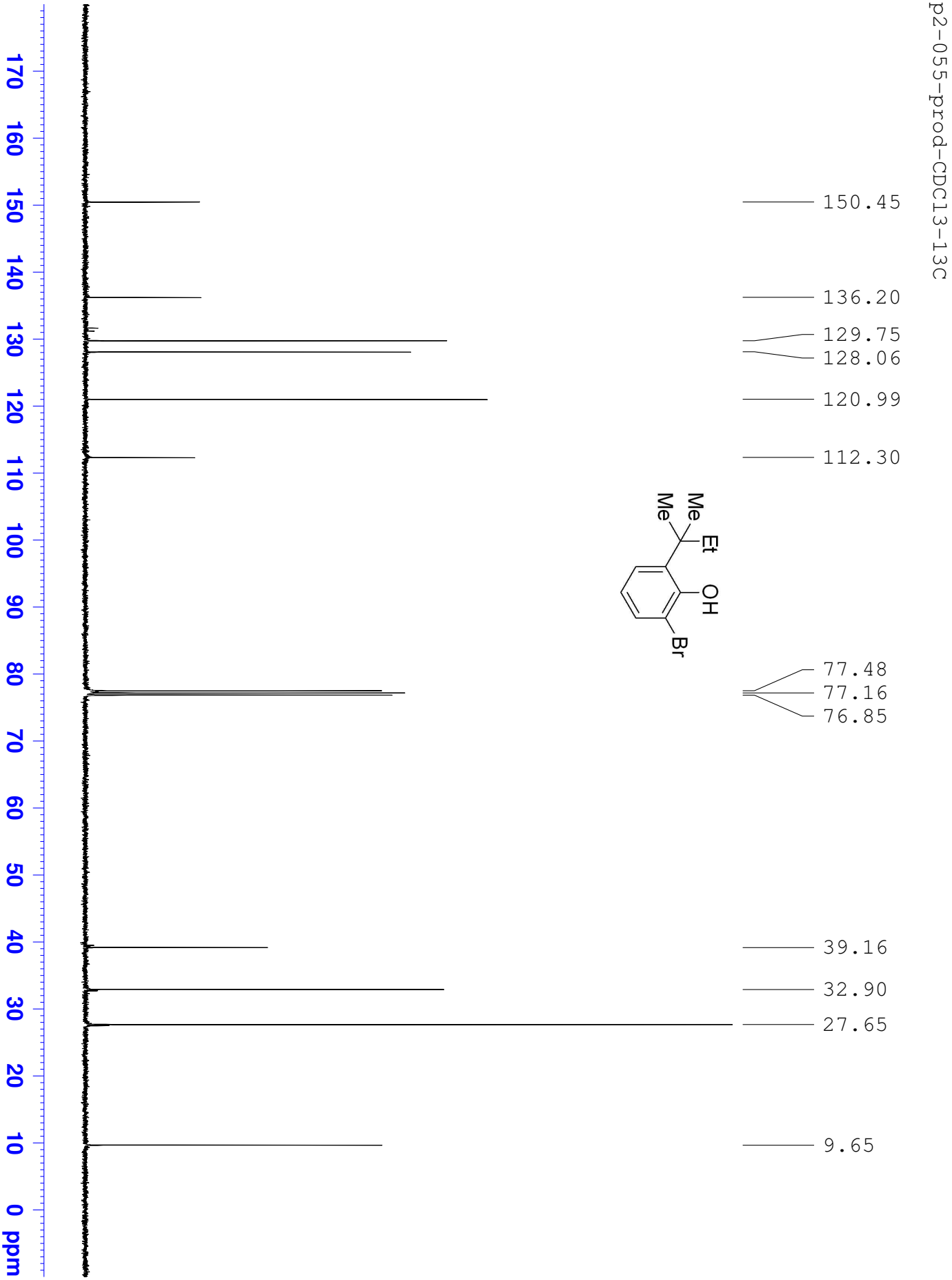



jp2-193-Byprod2-CDC13-13C
148.55
148.33
147.08
139.25
128.39
127.90
124.89
110.51
77.48
77.16
76.84
41.45
38.13
37.03
28.54
9.31
-0.76
TMS
Me
Me
Et
Me
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

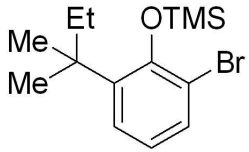
jp2-055-prod-CDCl3-1H






jp2-055-prod-CDC13-13C
150.45
136.20
129.75
128.06
120.99
112.30
77.48
77.16
76.85
39.16
32.90
27.65
9.65
Me
Me
Et
OH
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

jp2-059-prod-CDCl3-1H



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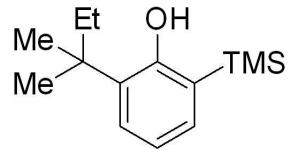
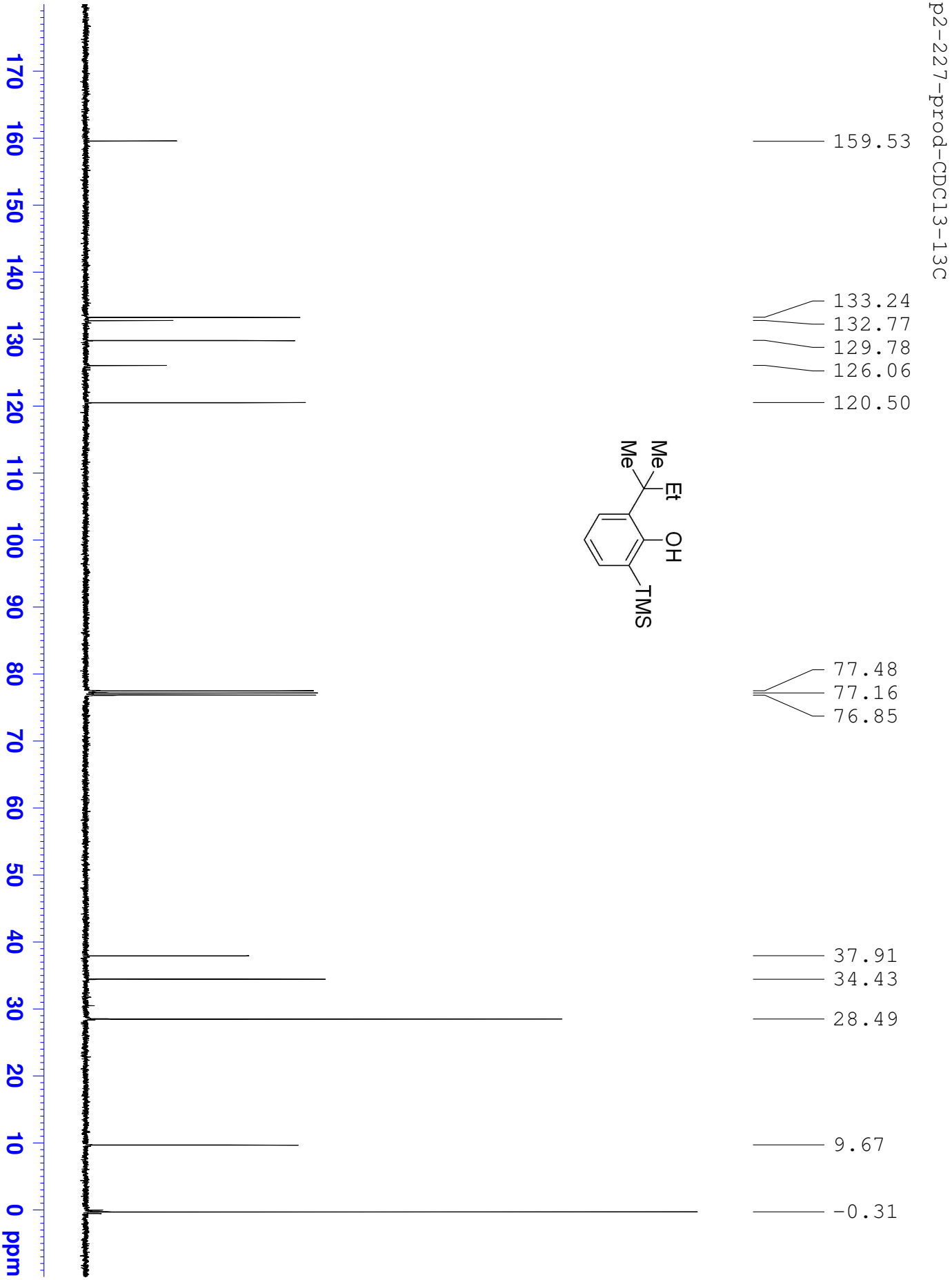
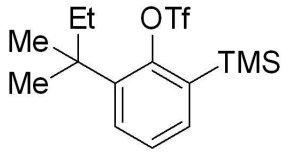
jp2-227-prod-CDCl3-1H-400




jp2-227-prod-CDC13-13C
159.53
133.24
132.77
129.78
126.06
120.50
77.48
77.16
76.85
37.91
34.43
28.49
9.67
-0.31
Me
Me
Et
OH
TMS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

jp2-061-prod-CDCl3-1H-3



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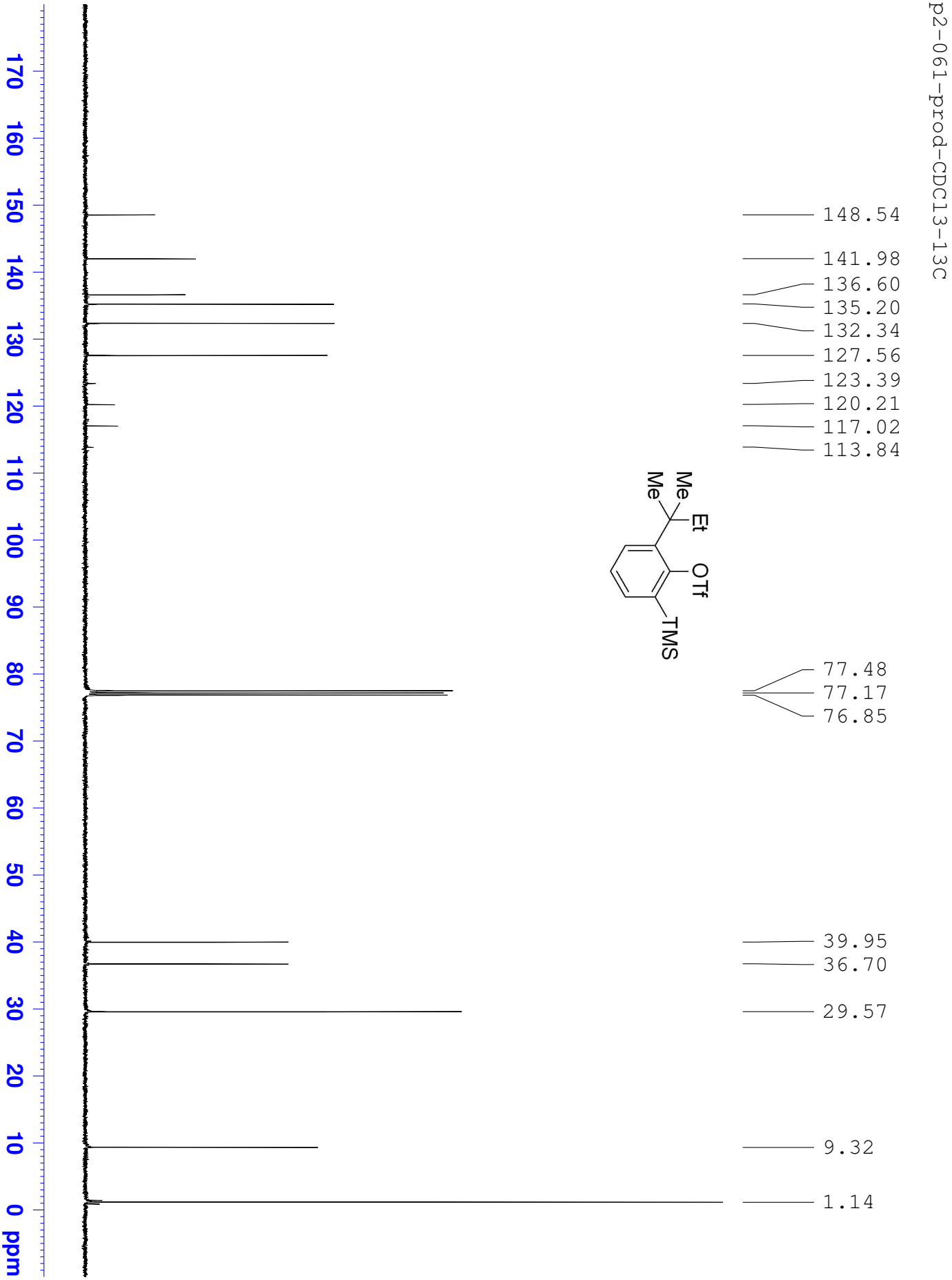
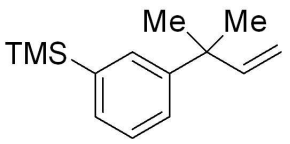
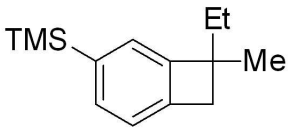

jp2-061-prod-CDC13-13C
148.54
141.98
136.60
135.20
132.34
127.56
123.39
120.21
117.02
113.84
77.48
77.17
76.85
39.95
36.70
29.57
9.32
1.14
Me
Me
Et
OTf
TMS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

jp2-065-prod-C6D6-1H-600



1.0

:



1.4

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