Electronic Supporting Information

For

Synthesis of Enantioenriched 2-Alkyl Piperidine Derivatives through Asymmetric Reduction of Pyridinium Salts

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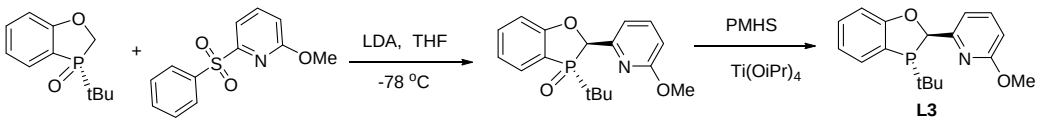
I. General Information

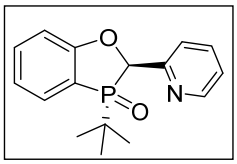
All reactions for the preparation of substrates and catalysts were performed in standard, dry glassware under an inert atmosphere of nitrogen or argon unless otherwise described. All starting materials and reagents were purchased from commercial sources and used as received unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded using 400 or 500 MHz spectrometers. Chemical shifts (δ) are given in ppm, and coupling constants (*J*) are given in Hz. The 7.26 resonance of residual $CHCl_3$ (or 0 ppm of TMS) for proton spectra and the 77.23 ppm resonance of $CDCl_3$ for carbon spectra were used as internal references. Flash chromatography was performed on a Combi-Flash automated system with silica columns. High resolution mass spectrometric data were obtained on an Agilent 6210 time-of-flight HPLC/MS spectrometer (ESI-TOF).

General procedure for the synthesis of ligands:



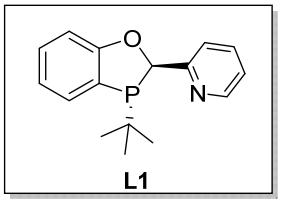
A 250 mL 3-neck round bottom flask equipped with a magnetic stir bar was charged with 3-(tert-butyl)-2H-benzo[d][1,3]oxaphosphole 3-oxide (2.0 g, 9.514 mmol), 2-methoxy-6-(phenylsulfonyl)pyridine (2.38 g, 9.514 mmol) and THF (20 mL). The mixture was cooled down to -78 ^{o}C with a dry ice/acetone bath. LDA (14.27 mL, 2 M in THF/ethyl benzene, 28.54 mmol) was added slowly and the internal temperature was kept under –60 ^{o}C. After 2 h, a sample was taken and completed conversion was indicated from LC-MS. The mixture was quenched with methanol (5 mL) and sat Na_2CO_3 solution (10 mL) was added; the mixture was further warmed to 50 °C and stir for 2 h for epimerization to the *trans*-diastereomer. The crude mixture was concentrated under reduced pressure, worked up with DCM (50 mLx2) and dried over Na_2SO_4 and purified using column chromatography with 80% EtOAc/hexanes to get the desired (2R,3S)-3-(tert-butyl)-2-(6-methoxypyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-oxide as a white solid, 2.45 g (7.72 mmol), 81% yield; mp 158.0−160.0 °C; $[\alpha]_D^{20}$ = + 208.8 (c 1.0, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (m, 3H), 7.04 (m, 3H), 6.63 (m, 1H), 5.60 (s, 1H), 3.88 (s, 3H), 1.37 (d, J = 7.8 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9 (d, $J_{C–P}$ = 17.5 Hz), 163.5 (d, $J_{C–P}$ = 1.7 Hz), 151.6 (d, $J_{C–P}$ = 4.5 Hz), 139.2 (d, $J_{C–P}$ = 2.0 Hz), 135.0 (d, $J_{C–P}$ = 1.8 Hz), 129.9 (d, $J_{C–P}$ = 6.1 Hz), 122.3 (d, $J_{C–P}$ = 8.8 Hz), 113.5 (d, $J_{C–P}$ = 90.0 Hz), 113.6 (d, $J_{C–P}$ = 5.6 Hz), 113.4 (d, $J_{C–P}$ = 3.3 Hz), 110.1 (d, $J_{C–P}$ = 2.3 Hz), 77.4, 53.3, 34.6 (d, $J_{C–P}$ = 70.5 Hz), 24.2; ^{31}P NMR (202 MHz, $CDCl_3$): δ 60.1; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{17}H_{21}NO_3P]^+$ 318.1254, found 318.1248.

An oven dried 100 mL Schlenk flask equipped with a magnetic stir bar was charged with phosphine oxide (500 mg, 1.331 mmol) and THF (10 mL) and the solution was thoroughly degassed by vacuum *purge-and-refill* with argon. The mixture was then added polymethylhydrosiloxane (1.50 g). To this solution at rt added titanium tetraisopropoxide (756 mg, 2.66 mmol). Reaction mixture was stirred at 60 °C for 14 h under argon atmosphere. The reaction was quenched with degassed 30% aqueous NaOH (10 mL) over 10 min. The resulting mixture was stirred at 60 °C for 1 h. Then the mixture was cooled to room temperature and the layers were separated under argon. The aqueous layer was further washed twice with degassed MTBE. The combined organic layers was dried over $MgSO_4$, loaded on to a short plug of basic alumina, and eluted with MTBE. The free phosphine 2-((2R,3R)-3-(tert-butyl)-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)-6-methoxypyridine **L3** was obtained as a white solid after dryness, 250 mg (0.83 mmol), 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (m, *2*H), 7.33 (m, 1H), 7.06 (m, 1H), 6.96 (m, 1H), 6.77 (m, 1H), 6.54 (m, 1H), 5.91 (s, 1H), 3.8 (s, 3H), 1.08 (d, J = 7.8 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, 163.8 (d, $J_{C–P}$ = 1.8 Hz), 158.7 (d, $J_{C–P}$ = 14.3 Hz), 139.2 (d, $J_{C–P}$ = 1.2 Hz), 131.6 (d, $J_{C–P}$ = 20.0 Hz), 131.2, 125.7, 122.2 (d, $J_{C–P}$ = 17.0 Hz), 121.4 (d, $J_{C–P}$ = 6.2 Hz), 111.4 (d, $J_{C–P}$ = 6.1 Hz), 111.0 (d, $J_{C–P}$ = 0.5 Hz), 109.1 (d, $J_{C–P}$ = 2.5 Hz), 85.1 (d, $J_{C–P}$ = 27.5 Hz), 53.3, 31.0 (d, $J_{C–P}$ = 21.7 Hz), 26.6 (d, $J_{C–P}$ = 14.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 17.6; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{17}H_{21}NO_2P]^+$ 302.1304, found 302.1295.



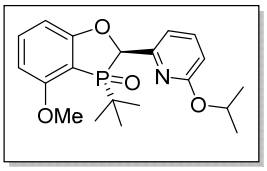
(2R,3S)-3-(tert-butyl)-2-(pyridin-2-yl)-2H-benzo[d][1,3] oxaphosphole 3-oxide: white solid, 2.077 g (7.23 mmol), 76% yield; mp 164.0-166.0 °C; $[\alpha]_D^{20}$ = + 87.4 (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61 (d, J = 5.0 Hz, 1H), 7.67 (qd, J = 7.0, 1.4 Hz, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.21

(m, 1H), 7.12 (m, 2H), 5.74 (d, J = 1.8 Hz, 1H), 1.37 (d, J = 5.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9 (d, J_{C-P} = 17.5 Hz), 154.3 (d, J_{C-P} = 4.0 Hz), 149.3 (d, J_{C-P} = 1.5 Hz),136.7 (d, J_{C-P} = 1.8 Hz), 135.1 (d, J_{C-P} = 1.9 Hz), 130.0 (d, J_{C-P} = 6.1 Hz), 122.9 (d, J_{C-P} = 2.0 Hz), 122.5 (d, J_{C-P} = 9.0 Hz), 121.4 (d, J_{C-P} = 2.6 Hz), 113.8 (d, J_{C-P} = 90.9 Hz), 113.7 (d, J_{C-P} = 5.6 Hz), 77.7 (d, J_{C-P} = 53.9 Hz), 33.9 (d, J_{C-P} = 71.7 Hz), 24.1; ^{31}P NMR (202 MHz, $CDCl_3$): δ 60.5; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{16}H_{19}NO_2P]^+$ is 288.1075, found 288.1148.



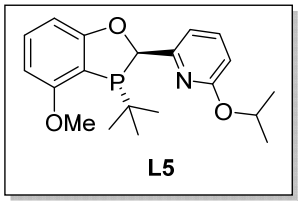
L1

2-((2R,3R)-3-(tert-butyl)-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)pyridine, L1: white solid, 282 mg (1.04 mmol), 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 4.80 Hz, 1H), 7.59 (td, J = 7.6, 1.5 Hz, 1H), 7.44 (ddd, J = 7.5, 3.6, 1.4 Hz, 1H), 7.36 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.11 (m, 2H), 7.00 (tdd, J = 7.4, 2.4, 1.0 Hz, 1H), 6.05 (s, 1H), 1.10 (d, J = 12.5 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 161.1 (d, J_{C-P} = 14.7 Hz), 149.4, 136.8, 131.7 (d, J_{C-P} = 20.0 Hz), 131.3, 121.9 (d, J_{C-P} = 2.4 Hz), 121.8 (d, J_{C-P} = 17.2 Hz), 121.5 (d, J_{C-P} = 6.2 Hz), 119.3 (d, J_{C-P} = 3.2 Hz), 110.9, 85.2 (d, J_{C-P} = 29.1 Hz), 31.1 (d, J_{C-P} = 20.2 Hz), 26.5 (d, J_{C-P} = 14.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 60.5; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{16}H_{19}NOP]^+$ is 272.1199, found 272.1204.



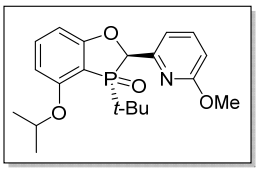
(2R,3S)-3-(tert-butyl)-2-(6-isopropoxypyridin-2-yl)-4-methoxy-2H-benzo[d][1,3] oxaphosphole 3-oxide: white solid, 2.32 g (6.18 mmol), 65% yield; mp 102.0-104.0 °C; $[\alpha]_D^{20}$ = + 153.0 (c 1.0, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (t, J = 7.9 Hz, 1H), 7.43 (t, J = 8.2 Hz, 1H), 6.92 (dd, J = 7.4, 1.2 Hz, 1H), 6.68 (dd, J = 8.2, 3.0 Hz, 1H), 6.57 (d, J = 8.2 Hz, 1H), 6.51 (dd, J = 8.2, 4.1 Hz, 1H), 5.51 (d, J = 2.1 Hz, 1H), 5.24 (Septet, J = 6.2 Hz, 1H), 3.86 (s, 3H), 1.39 (d, J = 16.5 Hz, 9H), 1.34 (d, J = 6.2 Hz, 3H), 1.32 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6 (d, J_{C-P} = 15.4

Hz), 162.8 (d, J_{C-P} = 1.6 Hz), 161.7 (d, J_{C-P} = 1.8 Hz),151.6 (d, J_{C-P} = 4.4 Hz), 139.1 (d, J_{C-P} = 1.9 Hz), 136.5 (d, J_{C-P} = 1.1 Hz), 113.6 (d, J_{C-P} = 3.0 Hz), 110.6 (d, J_{C-P} = 2.2 Hz), 106.0 (d, J_{C-P} = 5.4 Hz), 103.5 (d, J_{C-P} = 5.6 Hz), 102.0 (d, J_{C-P} = 89.4 Hz), 78.4 (d, J_{C-P} = 54.5 Hz), 68.1, 55.6, 34.3 (d, J_{C-P} = 73.8 Hz), 25.0 (d, J_{C-P} = 0.9 Hz), 22.05, 22.01; ^{31}P NMR (202 MHz, $CDCl_3$): δ 60.5; HRMS (ESI) $[M+H]^+$ m/z calcd for $[C_{20}H_{27}NO_4P]^+$ is 376.1599, found 376.1674.



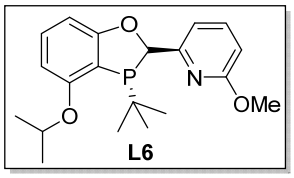
L5

2-((2R,3R)-3-(tert-butyl)-4-methoxy-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)-6-isopropoxypyridine, L5, white solid, 368 mg (1.02 mmol), 77% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 6.39 (m, 2H), 5.86 (s, 1H), 5.14 (septet, *J* = 6.2 Hz, 1H), 3.72 (s, 3H), 1.25 (t, *J* = 6.0 Hz, 6H), 1.06 (d, *J* = 12.4 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 162.8 (d, J_{C-P} = 1.9 Hz), 162.1 (d, J_{C-P} = 11.9 Hz), 158.5 (d, J_{C-P} = 14.6 Hz), 139.1 (d, J_{C-P} = 1.3 Hz), 132.3, 110.6 (d, J_{C-P} = 3.8 Hz), 109.4 (d, J_{C-P} = 2.6 Hz), 104.1, 103.0 (d, J_{C-P} = 1.8 Hz), 85.6 (d, J_{C-P} = 27.1 Hz), 68.3, 55.3, 32.2 (d, J_{C-P} = 22.3 Hz), 27.2 (d, J_{C-P} = 14.1 Hz), 22.0, 21.9; ^{31}P NMR (202 MHz, $CDCl_3$): δ 14.1; HRMS (ESI) $[M+H]^+$ *m/z* calcd for $[C_{20}H_{27}NO_3P]^+$ is 360.1650, found 360.1723.



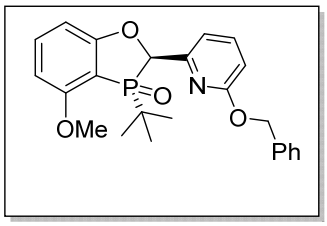
(2R,3S)-3-(tert-butyl)-2-(6-isopropoxypyridin-2-yl)-4-methoxy-2H-benzo[d][1,3] oxaphosphole 3-oxide White solid, 2.35 g (6.28 mmol), 66% yield; m.p: 101.0-103.0 °C; $[\alpha]_D^{20}$ = + 19.0 (c 0.05, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 8.2 Hz, 1H), 6.98 (dd, *J* = 7.9, 2.8 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 6.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 5.54 (d, *J* = 2.4 Hz, 1H), 5.24 (Septet, *J* = 6.1 Hz, 1H), 3.89 (s, 3H), 1.41 (d, *J* = 16.5 Hz, 9H), 1.39 (d, *J* = 6.0 Hz, 3H), 1.36 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9 (d, J_{C-P} = 15.1 Hz), 163.6 (d, J_{C-P} = 1.6 Hz), 160.2 (d, J_{C-P} = 1.8 Hz),152.1 (d, J_{C-P} = 4.4 Hz), 139.3 (d, J_{C-P} = 2.0

Hz), 136.5 (d, J_{C-P} = 1.1 Hz), 114.1 (d, J_{C-P}= 3.0 Hz), 110.0 (d, J_{C-P} = 2.1 Hz), 105.6 (d, J_{C-P} = 5.4 Hz), 105.4 (d, J_{C-P} = 5.6 Hz), 103.9 (d, J_{C-P} = 89.6 Hz), 78.4 (d, J_{C-P} = 53.8 Hz), 71.2, 53.6, 34.2 (d, J_{C-P} = 72.8 Hz), 25.5 (d, J_{C-P} = 0.9 Hz), 22.1(d, J_{C-P} = 5.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 61.3; HRMS (ESI) $[M+H]^+$ m/z calcd for $[C_{20}H_{27}NO_4P]^+$ is 376.1672, found 376.1669.



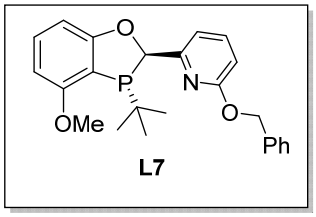
L6

2-((2R,3R)-3-(tert-butyl)-4-isopropoxy-2,3-dihydrobenzo[d][1,3] oxaphosphol-2-yl)-6-methoxypyridine L6: White solid, 373 mg (1.04 mmol), 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.74 (m, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 6.51 (d, *J* = 8.2 Hz, 1H), 6.44 (dd, *J* = 8.2, 3.6 Hz, 1H), 5.90 (s, 1H), 4.57 (Septet, *J* = 6.0 Hz, 1H), 3.88 (s, 3H), 1.31 (d, *J* = 6.0 Hz, 3H), 1.28 (d, *J* = 6.0 Hz, 3H), 1.14 (d, *J* = 12.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 163.7 (d, J_{C-P} = 1.7 Hz), 160.6 (d, J_{C-P} = 11.4 Hz),159.1 (d, J_{C-P} = 14.1 Hz), 139.1 (d, J_{C-P} = 1.1 Hz), 132.3, 125.7, 111.2 (d, J_{C-P} = 3.6 Hz), 108.9 (d, J_{C-P} = 2.6 Hz), 105.0 (d, J_{C-P} = 1.8 Hz), 103.6, 85.7 (d, J_{C-P} = 25.9 Hz), 69.9, 53.0, 32.56 (d, J_{C-P} = 22.2 Hz), 30.5, 27.4 (d, J_{C-P} = 13.5 Hz), 22.1 (d, J_{C-P} = 16.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 15.6; HRMS (ESI) $[M+H]^+$ m/z calcd for $[C_{20}H_{27}NO_3P]^+$ is 360.1650, found 360.1695.



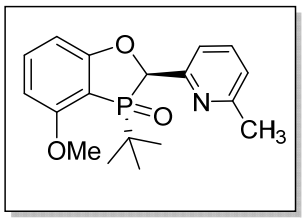
(2R,3S)-2-(6-(benzyloxy)pyridin-2-yl)-3-(tert-butyl)-4-methoxy-2H-benzo[d][1,3]oxaphosphole 3-oxide: white solid, 3.22 g (7.61 mmol), 80% yield; mp 148.0-150.0 °C; $[\alpha]_D^{20}$ = + 191.2 (c 1.0, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (t, *J* = 7.7 Hz, 1H), 7.44 (m, 3H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.31 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.68 (m, 2H), 6.51(dd, *J* = 8.2, 4.1 Hz, 1H), 5.54 (d, *J* = 2.7 Hz, 1H), 5.36 (d, *J* = 12.1 Hz, 1H), 5.28 (d, *J* = 12.1 Hz, 1H), 3.87 (s, 3H), 1.38 (d, *J* = 16.6 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7 (d, J_{C-P} = 11.9

Hz), 163.1, 161.7, 151.8 (d, J_{C-P} = 4.1 Hz),139.4 (d, J_{C-P} = 1.6 Hz), 137.6, 136.7, 128.4 (d, J_{C-P} = 36.1 Hz), 127.9, 114.5 (d, J_{C-P} = 2.6 Hz), 110.5 (d, J_{C-P} = 1.6 Hz), 106.2 (d, J_{C-P} = 5.0 Hz), 103.7 (d, J_{C-P} = 5.3 Hz), 78.4 (d, J_{C-P} = 58.4 Hz), 67.8, 55.7, 34.1(d, J_{C-P} = 74.0 Hz), 25.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 61.6; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{24}H_{27}NO_4P]^+$ is 424.1599, found 424.1686.



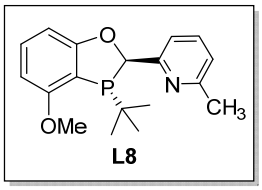
L7

2-(benzyloxy)-6-((2R,3R)-3-(tert-butyl)-4-methoxy-2,3-dihydro benzo[d][1,3]oxa phosphol-2-yl)pyridine, L7: white solid, 477 mg (1.17 mmol), 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.38 (m, 7H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.42 (dd, *J* = 8.0, 3.4 Hz, 1H), 5.85 (s, 1H), 5.27 (s, 2H), 1.07 (d, *J* = 12.4 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 163.0 (d, J_{C-P} = 1.8 Hz), 162.2 (d, J_{C-P} = 11.9 Hz), 158.6 (d, J_{C-P} = 14.6 Hz), 139.1, 137.6, 132.4, 128.4 (d, J_{C-P} = 5.4 Hz), 127.7, 111.5 (d, J_{C-P} = 3.8 Hz), 109.3 (d, J_{C-P} = 2.6 Hz), 104.2, 103.1 (d, J_{C-P} = 2.0 Hz), 85.7 (d, J_{C-P} = 27.2 Hz), 67.4, 55.4, 32.4 (d, J_{C-P} = 22.4 Hz), 27.2 (d, J_{C-P} = 11.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 13.7; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{24}H_{27}NO_3P]^+$ is 408.1650, found 408.1716.



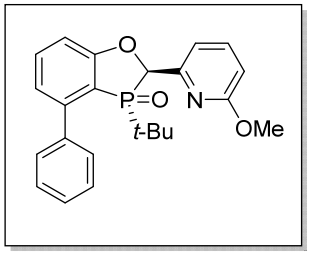
(2R,3S)-3-(tert-butyl)-4-methoxy-2-(6-methylpyridin-2-yl)-2H-benzo [d][1,3]oxaphosphole 3-oxide, white solid, 2.62 g (7.9 mmol), 83% yield; mp 142.0-144.0 °C; $[\alpha]_D^{20}$ = + 126.7 (c 1.0, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.67 (dd, *J* = 8.3, 3.0 Hz, 1H), 6.52 (dd, *J* = 8.2, 4.2 Hz, 1H), 5.62 (d, *J* = 3.4 Hz, 1H), 3.88 (s, 3H), 2.53 (s, 3H), 1.39 (d, *J* = 16.6 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, J_{C-P} = 15.0 Hz), 161.5 (d, J_{C-P} = 1.8 Hz), 157.8, 153.5 (J_{C-P} = 3.4 Hz), 136.8 (d, J_{C-P} = 1.8 Hz), 136.5, 122.6 (d, J_{C-P} = 1.8 Hz), 119.3 (d, J_{C-P} = 2.4

Hz), 106.1 (d, $J_{C–P}$ = 5.1 Hz), 103.4 (d, $J_{C–P}$ = 5.6 Hz), 102.5, 79.4 (d, $J_{C–P}$ = 54.2 Hz), 55.5, 34.2 (d, $J_{C–P}$ = 74.0 Hz), 25.2, 24.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.3; HRMS (ESI) $[M + H]^+$ *m*/*z* calcd for $[C_{18}H_{23}NO_3P]^+$ 332.1410, found 332.1395.



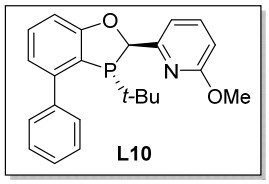
L8

2-((2R,3R)-3-(tert-butyl)-4-methoxy-2,3-dihydrobenzo[d][1,3] oxaphosphol-2-yl)-6-methylpyridine, white solid, 398 mg (1.26 mmol), 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 6.8 Hz, 2H), 6.92 (t, *J* = 6.8 Hz, 2H), 7.72 (dd, *J* = 8.1, 0.7 Hz, 1H), 6.50 (ddd, *J* = 8.2, 3.7, 0.5 Hz, 1H), 5.99 (d, *J* = 0.6 Hz, 1H), 3.79 (s, 3H), 2.52 (s, 3H), 1.13 (d, *J* = 12.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 162.2 (d, $J_{C–P}$ = 11.8 Hz), 160.5 (d, $J_{C–P}$ = 15.0 Hz), 158.1 (d, $J_{C–P}$ = 1.8 Hz), 136.6 ($J_{C–P}$ = 1.1 Hz), 132.4, 121.4 (d, $J_{C–P}$ = 2.5 Hz), 116.1 (d, $J_{C–P}$ = 4.2 Hz), 109.5 (d, $J_{C–P}$ = 17.5 Hz), 104.1, 103.1 (d, $J_{C–P}$ = 1.9 Hz), 86.4 (d, $J_{C–P}$ = 27.7 Hz), 55.3, 32.5 (d, $J_{C–P}$ = 22.1 Hz), 27.3 (d, $J_{C–P}$ = 14.1 Hz), 24.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ 12.6; HRMS (ESI) $[M + H]^+$ *m*/*z* calcd for $[C_{18}H_{23}NO_2P]^+$ 316.1461, found 316.1449.

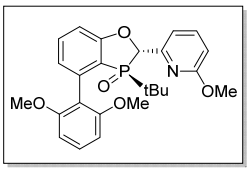


(2R,3S)-3-(tert-butyl)-2-(6-methoxypyridin-2-yl)-4-phenyl-2H-benzo [d][1,3]oxaphosphole 3-oxide White solid, 1.57 g (3.99 mmol), 42% yield; m.p: 138.0-140.0 °C; $[\alpha]_D^{20}$ = + 2.22 (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.3 Hz, 1H), 7.57 (m, 2H), 7.37 (m, 3H), 7.08 (m, 2H), 7.03 (d, *J* = 7.1 Hz,1H), 6.65 (d, *J* = 8.3 Hz, 1H), 5.59 (s, 1H), 3.02 (s, 3H), 0.90 (d, *J* = 16.3 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7 (d, $J_{C–P}$ = 18.2 Hz), 163.7 (d, $J_{C–P}$ = 1.3 Hz),152.4 (d, $J_{C–P}$ = 4.4 Hz), 147.2 (d, $J_{C–P}$ = 5.5 Hz), 140.8 (d, $J_{C–P}$ = 2.0 Hz), 135.0 (d, $J_{C–P}$ = 1.7 Hz), 130.1, 128.6, 128.5, 124.0 (d, $J_{C–P}$ = 8.1 Hz), 113.4 (d, $J_{C–P}$ = 3.2 Hz),112.5 (d, $J_{C–P}$ = 85.8 Hz), 112.5 (d, $J_{C–P}$ = 5.3 Hz), 110.1(d, $J_{C–P}$ = 2.3 Hz),77.0 (d, $J_{C–P}$ =

56.0 Hz), 53.5, 34.6 (d, J_{C-P} = 70.3 Hz), 24.5; ^{31}P NMR (202 MHz, $CDCl_3$): δ 62.2; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{23}H_{25}NO_3P]^+$ is 394.1494, found 394.1467.

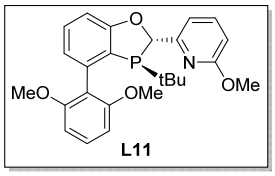


2-((2R,3R)-3-(tert-butyl)-4-phenyl-2,3-dihydro benzo [d] [1,3] oxaphosphol-2-yl)-6-methoxypyridine, L10: White solid, 447 mg (1.18 mmol), 89% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.35 (m, 1H), 7.35 (m, 2H), 7.28 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.01(dd, *J* = 7.3, 3.5 Hz, 1H), 6.83 (d, *J* = 7.4 Hz, 1H) , 6.58 (d, *J* = 8.2 Hz, 1H), 5.88 (s, 1H), 3.88 (s, 3H), 0.78 (d, *J* = 8.2 Hz, 9H);^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9, 163.9 (d, J_{C-P} = 2.0 Hz), 158.9 (d, J_{C-P} = 14.7 Hz),146.5 (d, J_{C-P} = 12.5 Hz), 142.6, 139.3 (d, J_{C-P} = 1.3 Hz), 131.6, 129.3 (d, J_{C-P} = 4.9 Hz), 128.6, 127.6, 122.5 (d, J_{C-P} = 2.7 Hz), 121.1(d, J_{C-P} = 22.5 Hz), 111.5 (d, J_{C-P} = 3.8 Hz), 110.0, 109.2 (d, J_{C-P} = 2.5 Hz), 85.2 (d, J_{C-P} = 27.4 Hz), 77.4, 53.3, 32.8 (d, J_{C-P} = 23.0 Hz), 26.9 (d, J_{C-P} = 13.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 15.7; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{23}H_{25}NO_2P]^+$ is 378.1545, found 378.1533.

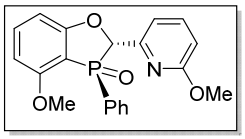


(2S,3R)-3-(tert-butyl)-4-(2,6-dimethoxyphenyl)-2-(6-methoxypyridinyl)-2H-benzo[d][1,3]oxaphosphole 3-oxide: white solid, 2.2 g (4.85 mmol), 51% yield; mp 196.0-198.0 °C; $[\alpha]_D^{20}$ = - 63.1 (c 1.0, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (m, 1H), 7.27 (m, 1H), 7.01 (m, 3H), 6.63(d, *J* = 8.2 Hz,1H), 6.58 (t, *J* = 7.5 Hz, 2H), 5.50 (s, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 3.57 (m, 3H), 0.98 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4 (d, J_{C-P} = 17.9 Hz), 163.5 (d, J_{C-P} = 1.4 Hz), 159.0, 157.5, 152.5 (d, J_{C-P} = 3.9 Hz), 139.0 (d, J_{C-P} = 1.9 Hz), 139.0, 134.3 (d, J_{C-P} = 1.8 Hz), 130.0, 125.5 (d, J_{C-P} = 8.3 Hz), 117.6 (d, J_{C-P} = 1.8 Hz), 114.4 (d, J_{C-P} = 89.0 Hz), 114.29 (d, J_{C-P} = 3.0 Hz), 112.3 (d, J_{C-P} = 5.5 Hz), 111.0 (d, J_{C-P} = 2.1 Hz), 104.8, 103.1, 77.6 (d, J_{C-P} = 55.1 Hz), 56.2, 55.4, 53.4, 34.2

(d, J_{C-P} = 72.9 Hz), 24.2 (d, J_{C-P} = 0.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 59.8; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{25}H_{29}NO_5P]^+$ is 454.1778, found 454.1776.

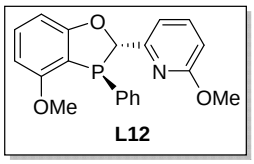


2-((2S,3S)-3-(tert-butyl)-4-(2,6-dimethoxyphenyl)-2,3-dihydro benzo[d][1,3]oxaphosphol-2-yl)-6-methoxypyridine, L11: white solid, 407.6 mg (0.93 mmol), 70% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.14 (m, 1H), 6.94 (m, 1H), 6.81 (m, 1H), 6.70 (m, 1H), 6.45 (m, 3H), 5.77 (s, 1H), 3.79 (s, 3H), 3.65 (s, 3H), 3.23 (m, 3H), 0.78 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 163.5 (d, J_{C-P} = 1.7 Hz), 159.2, 157.5 (d, J_{C-P} = 76.1 Hz),139.0 (d, J_{C-P} = 1.3 Hz), 130.8 (d, J_{C-P} = 1.9 Hz), 129.2, 124.3(d, J_{C-P} = 3.8 Hz), 116.7 (d, J_{C-P} = 4.1 Hz), 109.4 (d, J_{C-P} = 0.5 Hz), 108.6 (d, J_{C-P} = 2.5 Hz), 104.6, 103.7, 85.8 (d, J_{C-P} = 29.1 Hz), 55.6 (d, J_{C-P} = 2.3 Hz), 55.6 (d, J_{C-P} = 5.5 Hz), 53.3, 31.9 (d, J_{C-P} = 20.9 Hz), 26.8 (d, J_{C-P} = 14.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 18.6; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{25}H_{29}NO_4P]^+$ is 438.1829, found 438.1861.



(2S,3R)-4-methoxy-2-(6-methoxypyridin-2-yl)-3-phenyl-2H-benzo[d] [1,3]oxaphosphole 3-oxide: White solid, 1.92 g (5.23 mmol), 55% yield; m.p: 226.0-228.0 °C; $[\alpha]_D^{20}$ = + 14.9 (c 0.05, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, *J* = 8.4 Hz, 1H), 7.31 (m, 4H), 7.15 (dt, *J* = 7.2, 3.0 Hz, 2H), 6.82 (dd, *J* = 8.4, 3.5 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.52 (dd, *J* = 8.1, 4.6 Hz, 1H), 6.28 (d, *J* = 8.3 Hz, 1H), 5.90 (d, *J* = 14.1 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.2 (d, J_{C-P} = 17.6 Hz), 163.3 (d, J_{C-P} = 2.2 Hz), 162.1 (d, J_{C-P} = 1.1 Hz),152.5 (d, J_{C-P} = 1.2 Hz), 138.8 (d, J_{C-P} = 2.2 Hz), 137.7 (d, J_{C-P} = 0.7 Hz), 132.0 (d, J_{C-P} = 3.0 Hz), 131.8 (d, J_{C-P} = 10.5 Hz), 128.7 (d, J_{C-P} = 111.8 Hz), 127.8 (d, J_{C-P} = 13.4 Hz), 11.7 (d, J_{C-P} = 4.2 Hz), 109.5 (d, J_{C-P} = 2.8 Hz), 106.3 (d, *J* = 5.7 Hz), 103.9 (d, *J* = 5.2 Hz), 103.3 (d, *J* = 102.5 Hz), 84.4 (d, *J* = 66.9 Hz), 56.0, 53.4; ^{31}P

NMR (202 MHz, $CDCl_3$): δ 45.6; HRMS (ESI) $[M+H]^+$ m/z calcd for $[C_{20}H_{19}NO_4P]^+$ is 368.1046, found 368.1051.

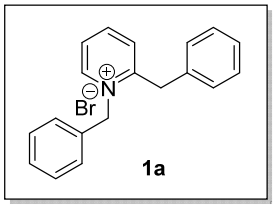


L12

2-methoxy-6-((2S,3S)-4-methoxy-3-phenyl-2,3-dihydrobenzo[d][1,3] oxaphosphol-2-yl)pyridine, L12: White solid, 201 mg (0.57 mmol), 43% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.01 (m, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 6.68 (m, 3H), 6.47 (dd, *J* = 8.0, 3.7 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 2H), 6.26 (dt, *J* = 8.3 Hz, 1H), 6.05 (d, *J* = 27.5 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.1, 163.0, 161.9 (d, J_{C-P} = 11.4 Hz),154.3 (d, J_{C-P} = 3.6 Hz), 138.6, 133.3, 133.1 (d, J_{C-P} = 19.6 Hz), 129.1, 127.8 (d, J_{C-P} = 6.5 Hz),112.8 (d, J_{C-P} = 2.1 Hz), 108.3 (d, J_{C-P} = 1.8 Hz), 105.0, 103.7 (d, J_{C-P} = 1.8 Hz), 88.9 (d, J_{C-P} = 27.0 Hz), 56.0, 53.5; ^{31}P NMR (202 MHz, $CDCl_3$): δ -20.7; HRMS (ESI) $[M+H]^+$ *m/z* calcd for $[C_{20}H_{19}NO_3P]^+$ is 352.1097, found 352.1102.

General procedure for the syntheses of pyridinium salts:

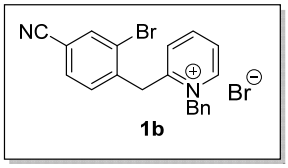
A 100 mL 3-neck round bottom flask equipped with a magnetic stir bar was charged with 2-benzylpyridine (2.0 g, 11.81 mmol) and toluene (5 mL). To this solution added benzyl bromide (2.01 g, 11.81 mmol) in one portion, and the resulting mixture was heated at reflux for 14 h. The solvent was evaporated under reduced pressure and recrystallized using DCM (5 mL)/methyl tertiary butyl ether (15 mL) to yield the desired product.



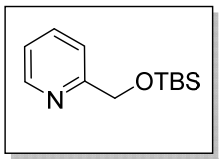
1a

1,2-dibenzylpyridinium bromide, 1a, White solid (2.86 g, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.59 (d, *J* = 6.1 Hz, 1H), 8.39 (t, *J* = 7.6 Hz, 1H), 7.95 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.35 (m, 8H), 7.13 (m, 2H), 6.29 (s, 2H), 4.63 (s, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ 157.9, 147.0, 145.6, 133.3,

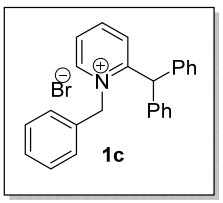
132.0, 129.7, 129.6, 129.57, 129.53, 128.3, 128.2, 126.2, 61.4, 39.0. HRMS (ESI) $[M]^+$ *m*/*z* calcd for $[C_{19}H_{18}N]^+$ is 260.1436, found 260.1434.



1-benzyl-2-(2-bromo-4-cyanobenzyl)pyridinium bromide, 1b, Synthesized according to the literature procedures:[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (d, *J* = 5.9 Hz, 1H), 8.28(d, *J* = 8.0 Hz, 1H), 7.97 (t, *J* = 6.6 Hz, 1H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.60 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.37-7.30 (m, 5H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.49 (s, 3H), 5.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 147.8, 145.4, 139.0, 136.3, 134.0, 132.2, 131.5, 129.8, 129.7, 128.3, 127.9, 126.3, 125.8, 116.8, 114.2, 62.3, 39.8.

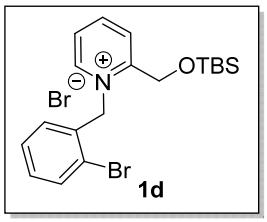


2-(((tert-butyldimethylsilyl)oxy)methyl)pyridine: To a solution of pyridin-2-ylmethanol (4.00 g, 36.35 mmol) and imidazole (6.18 g, 90.31 mmol) in DCM (15 mL) at rt was added tert-butylchlorodimethylsilane (6.07 g, 40.31 mmol). The reaction mixture was stirred for 2 h at room temperature. The mixture was extracted with DCM, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford 2-(((tert-butyldimethylsilyl)oxy)methyl)pyridine (7.45 g, 91%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (d, *J* = 4.9 Hz, 1H), 7.66 (m, 1H), 7.48 (m, 1H), 7.10 (m, 1H), 4.81 (s, 2H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.5, 148.8, 136.8, 121.9, 120.1, 66.2, 26.0, 18.5; HRMS (ESI) [M+1] *m*/*z* calcd for $[C_{12}H_{22}NOSi]^+$ is 224.1392, found 224.1470.

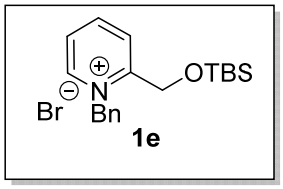


2-benzhydryl-1-benzylpyridinium bromide, 1c, white solid, 3.39 g, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.00 (d, *J* = 6.4 Hz, 1H), 8.32 (t, *J* =

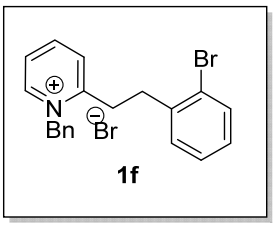
8.2 Hz, 1H), 8.03 (t, *J* = 7.0 Hz, 1H), 7.46-7.41 (m, 4H), 7.40-7.36 (m, 6H),7.19 (m, 2H), 6.97 (m, 2H), 6.21 (s, 2H), 6.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.9, 148.7, 144.9, 137.3, 132.3, 130.9, 130.0, 129.99, 129.9, 129.3, 128.9, 128.2, 126.2, 61.5, 53.0; HRMS (ESI) $[M]^+$ *m/z* calcd for $[C_{55}H_{22}N]^+$ is 336.1747, found 336.1753.



1-(2-bromobenzyl)-2-(((tert-butyldimethylsilyl)oxy)methyl) pyridinium bromide, 1d: To a solution of 2-(((tert-butyldimethylsilyl) oxy)methyl)pyridine (3.00 g, 13.42 mmol) in toluene (3 mL) was added 2-bromo benzyl bromide (3.69 g, 14.76 mmol) in one portion, and the resulting mixture was heated at reflux for 12 h. The solvent was evaporated under reduced pressure and recrystallized using DCM (10 mL)/methyl tertiary butyl ether (40 mL) to get the desired product as white crystalline solid, 5.142 g (81 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (d, *J* = 6.1 Hz, 1H), 8.55 (t, *J* = 7.7 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.00 (t, *J* = 6.8 Hz, 1H), 7.61 (m, 2H), 7.38 (m, 1H), 7.30(m, 1H), 6.24 (s, 2H), 5.17 (s, 2H), 0.88 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 146.0, 145.6, 133.7, 132.5, 131.9, 130.7, 129.1, 125.7, 126.5, 124.5, 61.5, 60.1, 25.8, 18.3, -5.1; HRMS (ESI) $[M]^+$ m/z calcd for $[C_{19}H_{27}BrNOSi]$+ is 392.1040, found 392.1040.

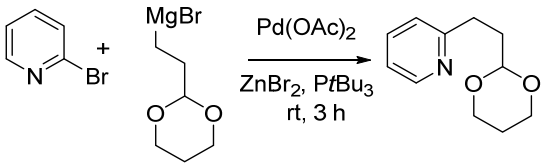


1-benzyl-2-(((tert-butyldimethylsilyl)oxy)methyl)pyridinium bromide, 1e, white solid, 3.73 g, 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.82 (d, *J* = 6.4 Hz, 1H), 8.47 (t, *J* = 7.7 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.02 (t, *J* = 7.7 Hz, 1H), 7.37-7.30 (m, 5H), 6.31 (s, 2H), 5.17 (s, 2H), 4.92 (s, 2H), 0.87 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 147.3, 145.5, 131.9, 129.8, 129.7, 128.4, 126.7, 126.1, 61.5, 61.3, 25.9, 18.3, -5.1; HRMS (ESI) $[M]^+$ m/z calcd for $[C_{19}H_{28}NOSi]^+$ is 314.1935, found 314.1944.



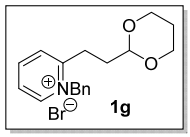
1-benzyl-2-(2-bromophenethyl)pyridinium bromide, 1f: Synthesized according to the literature procedure:[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (d, *J* = 5.9 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 8.43 (t, *J* = 7.8 Hz, 1H), 7.98 (t, *J* = 7.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.36-7.31 (m, 3H), 7.26-7.22 (m, 2H), 7.20-7.16 (m, 2H), 7.11-7.05 (m, 1H), 6.24 (s, 2H), 3.45 (t, *J* = 7.9 Hz, 2H), 3.07 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6 147.5 145.7, 137.4, 133.1, 132.6, 131.1, 129.8, 129.7, 129.6, 129.2, 128.3, 127.9, 126.5, 124.3, 61.5, 34.9, 34.2.

Synthesis of 2-(2-(1,3-dioxan-2-yl)ethyl)pyridine:[2]

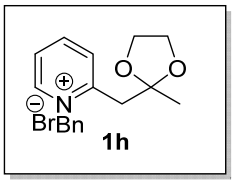


A 250 mL 3-neck round bottom flask equipped with a magnetic stir bar was charged 2-bromopyridine (2.00 g, 12.65 mmol), tri-tertbutylphosphine (0.14 mmol, 41 mg) and degassed THF (15 mL) under N_2 atmosphere. To this suspension added $Pd(OAc)_2$ (141 mg, 0.63 mmol, 0.05 equiv) and zinc bromide (854 mg, 3.79 mmol). After 5 min (2-(1,3-dioxolan-2-yl)ethyl) magnesium bromide (0.50 M in THF, 30.3 mL, 15.18 mmol, 1.2 equiv) was added slowly over 30 min while maintaining the temperature at 20-25 °C. The reaction mixture was stirred at room temperature for an additional 2 h and monitored by UPLC. Upon completion, the reaction was cooled to 0 °C, and water (20 mL) was added slowly while maintaining the temperature below 15 °C. Ethyl acetate (30 mL) was added, and the aqueous layer was extracted with ethyl acetate (2 x 30 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The crude mixture was purified by chromatography with 60% ethyl acetate/

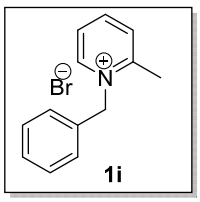
hexanes, the product was obtained as colorless liquid, 1.86 g, 76 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, *J* = 4.9 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 6.2 Hz, 1H), 4.44 (t, *J* = 5.0 Hz, 1H), 3.99 (dd, *J* = 11.2, 5.0 Hz, 2H), 3.63 (m, 2H), 2.79 (t, *J* = 7.9 Hz, 1H), 1.95 (m, 3H), 1.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4, 149.1, 136.2, 122.7, 1209, 101.4, 66.7, 34.7, 32.4, 25.7; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{11}H_{15}NO_2]^+$ is 194.1103, found 194.1185.



2-(2-(1,3-dioxan-2-yl)ethyl)pyridine 1g: light brown solid, 2.16 g (76.5%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.61 (d, *J* = 6.2 Hz, 1H), 8.42 (d, *J* = 7.5 Hz, 1H), 7.94 (t, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.35-7.29 (m, 3H), 7.23 (m, 2H), 6.19 (s, 1H), 4.63 (m,1H), 4.00 (m, 2H), 3.70 (m, 2H), 3.24 (t, *J* = 7.3 Hz, 1H), 2.11 (m, 2H), 2.02-1.92 (m, 3H), 1.30 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ159.2, 147.4, 145.5, 132.9, 129.7, 129.5, 129.4, 127.9, 126.3, 99.6, 66.9, 61.1, 33.6, 27.0, 25.6; HRMS (ESI) $[M]^+$ *m*/*z* calcd for $[C_{18}H_{22}NO_2]^+$ is 284.1645, found 284.1648.

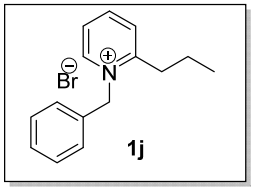


1-benzyl-2-((2-methyl-1,3-dioxolan-2-yl)methyl)pyridinium bromide, 1h: light brown solid, 2.73 g, 66%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (d, *J* = 6.3 Hz, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.06 (t, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.42-7.37(m, 3H), 7.23 (m, 2H), 6.19 (s, 2H), 3.90 (m, 2H), 3.58 (m, 2H), 3.53 (s, 2H), 1.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 148.3, 144.3, 132.0, 130.1, 129.9, 129.7, 129.0, 128.0, 127.1, 108.5, 65.3, 62.1, 42.3, 25.7; HRMS (ESI) $[M]^+$ m/z calcd for $[C_{17}H_{20}NO_2]$+ is 270.1489, found 270.1508.

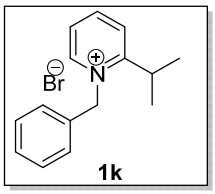


1-benzyl-2-methylpyridinium bromide, 1i: white crystalline solid, 2.24 g, 72%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.48 (d, *J*= 6.3 Hz, 1H), 8.41 (t, *J* = 7.6 Hz, 1H), 7.94 (m, 1H), 7.32-7.27 (m, 3H), 7.25 (m, 1H), 6.15 (s, 2H), 2.86 (s,

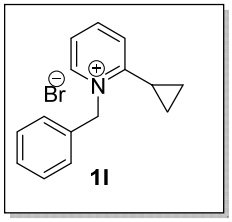
3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.4, 146.3, 145.8, 132.0, 130.6, 129.0, 126.0, 61.4, 21.2. HRMS (ESI) $[M]^+$ *m*/*z* calcd for $[C_{13}H_{44}N]^+$ is 184.1121, found 184.1129.



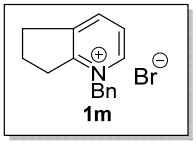
1-benzyl-2-propylpyridinium bromide, 1j: white crystalline solid (3.66 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (d, *J* = 6.5 Hz, 1H), 8.49 (t, *J* = 8.0 Hz, 1H), 7.91 (m, 2H), 7.28 (m, 3H), 7.19 (m, 2H) , 6.18 (s, 2H), 3.06 (m, 1H), 1.60 (m, 2H), 0.90, (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$):δ 158.8, 147.1, 145.9, 132.6, 129.5, 129.5, 129.32, 129.30, 128.9, 127.6, 125.9, 61.1, 34. 5, 21.5, 13.64, 13.62. HRMS (ESI) $[M]^+$ *m*/*z* calcd for $[C_{15}H_{18}N]^+$ is 212.1434, found 212.1442.



1-benzyl-2-isopropylpyridinium bromide, 1k: light brown solid, 2.0 g, 58%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.96 (d, *J* = 5.9 Hz, 1H), 8.42 (*t*, *J* = 7.8 Hz, 1H), 7.97 (m, 1H), 7.40 (m, 3H), 7.23 (m, 2H), 6.39 (s, 1H), 3.63 (m, 1H), 1.32 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.6, 147.4, 146.1, 133.1, 129.5, 129.2, 127.2, 126.4, 126.0, 61.4, 30.6, 22.6. HRMS (ESI) $[M]^+$ *m*/*z* calcd for $[C_{15}H_{18}N]^+$ is 212.1434, found 212.1429.

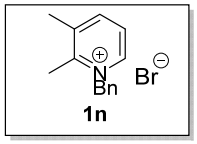


1-benzyl-2-cyclopropylpyridinium bromide, 1l: white crystalline solid, 2.05 g, 60%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (d, *J* = 6.3 Hz, 1H), 8.48 (t, *J* = 7.6 Hz, 1H), 7.89 (t, *J* = 6.7 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.32-7.24 (m, 5H), 6.34 (s, 2H), 2.44-2.38 (m, 1H), 1.33-1.27 (m, 2H), 1.07 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 147.0, 146.4, 132.6, 129.4, 127.8, 126.0, 61.2, 14.3, 10.7; HRMS (ESI) $[M]^+$ *m*/*z* calcd for $[C_{15}H_{16}N]^+$ is 210.1277, found 210.1273.



1-benzyl-6,7-dihydro-5H-cyclopenta[b]pyridinium bromide, 1m: Light gray solid, 2.95 g, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41 (d, *J* = 6.0

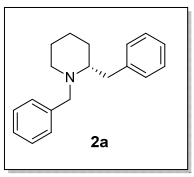
Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.0 Hz, 1H),7.44-7.41 (m, 2H), 7.39-7.35 (m, 3H), 6.19 (s, 2H), 3.50 (t, *J* = 7.9 Hz, 2H), 3.15 (t, *J* = 7.8 Hz, 2H), 2.33 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.8, 146.7, 143.3, 140.8, 132.1, 129.74, 129.7, 129.1, 126.0, 62.4, 32.9, 31.2, 22.7; HRMS (ESI) $[M]^+$ *m*/*z* calcd for $[C_{15}H_{16}N]^+$ is 210.1277, found 210.1280.



White crystalline solid, 2.76 g, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.49 (d, *J* = 6.2 Hz, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 6.8 Hz, 1H), 7.30-7.26 (m, 3H), 7.25-7.23 (m, 2H), 6.24 (s, 2H), 2.75 (s, 3H), 2.45 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 146.1, 144.9, 139.01, 132.3, 129.5, 129.2, 127.9, 125.2, 62.4, 20.3, 18.0;

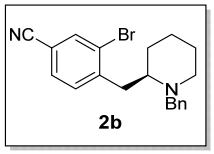
General procedure for the asymmetric hydrogenation of pyridinium salts:

A high pressure steel autoclave (HEL 100 mL) hydrogenation reactor was taken into the glove box. Catalyst solution was prepared in a vial with $[Ir(COD)Cl]_2$ (1 mol%) and ligand (*S*,*S*)-MeO-BoQPhos (3 mol%), and stir for 15 min in THF (5 mL) (or use the 2 mol% of catalyst **3**), followed by addition of I_2. Pyridinium salt (0.5 g) was added to the reactor and THF (15 ml). The catalyst solution was then transferred to the reactor before taking out of the glove box. The mixture was purged with N_2 and H_2 and stirred at the desired pressure and temperature for 5–24 h. Upon completion, the reactor was vented and the samples were collected. Percentage conversions and enantiomeric ratios were determined by chiral HPLC and SFC and the products were purified by silica gel (100% hexanes to 30% EtOAc/hexanes).

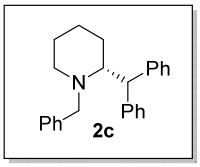


1,2-dibenzylpiperidine 2a:[3] 370.5 mg (1.39 mmol), 95% yield, 90:10 er, colorless liquid; $[\alpha]_D^{20}$ = + 2.0 (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (m, 2H), 7.31 (m, 2H), 7.25 (m, 2H), 7.24 (m, 1H), 7.15 (m, 3H), 4.05 (d, *J* = 13.5 Hz, 1H), 3.49 (d, *J* = 13.5 Hz, 1H), 3.16 (d, *J* = 9.9 Hz, 1H), 2.71 (m, 1H), 2.68-2.58 (m,

2H), 2.22 (m, 1H), 1.63 (m, 1H), 1.51 (m, 3H), 1.29 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.5, 139.8, 129.4, 128.9, 128.3, 128.2, 126.8, 125.8, 61.8, 58.6, 50.9, 36.5, 29.4, 25.4, 22.5; Enantiomeric ratio was determined by HPLC: OJ-3R column (150 x 4.6 mm), A: MeCN; B: 0.1%AcOH, pH = 7.0 adjusted with NH_4OH in water; A/B = 60/40 flow rate 1.3 mL/min. HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{19}H_{24}N]^+$ is 266.1903, found 266.1916.

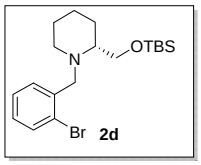


4-((1-benzylpiperidin-2-yl)methyl)-3-bromobenzonitrile, **2b:** 382 mg (1.035 mmol), 92% yield, 93:7 er, light yellow solid; m.p 56.0-58.0 °C; $[\alpha]_D^{20}$ = - 2.8 (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (m, 1H), 7.48 (m, 1H), 7.33-7.21 (m, 6H), 4.00 (d, *J* = 13.7 Hz, 1H), 3.56 (d, *J* = 13.7 Hz, 1H), 3.30 (d, *J* = 9.0 Hz, 1H), 2.89 (m, 2H), 2.78 (m, 1H), 2.32 (m, 1H), 1.68 (m, 1H), 1.59-149 (m, 3H), 1.41-1.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.3, 139.9, 136.2, 132.4, 130.7, 128.7, 128.4, 127.0, 125.3, 117.6, 111.6, 59.6, 58.7, 50.1, 36.4, 28.8, 25.1, 22.1; Enantiomeric ratio was determined by HPLC: Lux Amylose-2, (250 x 4.6 mm), particle size 3um, A: Heptane; B: ethanol denatured (5% IPA and 5% MeOH), A/B = 35/65 flow rate 1.3 mL/min. HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{20}H_{22}BrN_2]^+$ is 369.0968 found 369.0961.

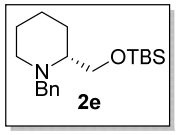


2-benzhydryl-1-benzylpiperidine, 2c: 377mg (1.10 mmol), 92% yield, 84:16 er, white solid; m.p 102.0-104.0 °C; $[\alpha]_D^{20}$ = + 21.6 (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31(m, 4H), 7.27-7.21 (m, 4H), 7.19-7.11 (m, 5H), 6.82 (m, 2H), 4.31 (d, *J* = 11.3 Hz, 1H), 3.71 (m, 2H), 3.52 (m, 1H), 2.86 (m, 1H), 2.47 (m, 1H), 1.78 (m, 1H), 1.56-1.33 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 143.7, 140.6, 128.9, 129.9, 128.7, 128.6, 128.2, 128.0, 126.6, 126.3, 126.0, 62.5, 53.9, 47.3, 23.1, 23.0, 19.8; Enantiomeric ratio was determined by SFC: Chiralpak OD-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 97/3, v/v,

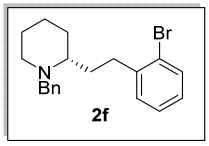
flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{55}H_{28}N]^+$ is 342.2143, found 342.2217.



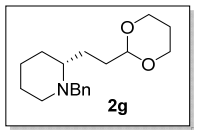
1-benzyl-2-(((tert-butyldimethylsilyl)oxy)methyl)piperidine, **2d:** 379 mg (0.95 mmol), 90% yield, 82:18 er, colorless liquid; $[\alpha]_D^{20}$ = + 24.3 (c 1.0, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.26 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 4.13 (d, *J* = 15.5 Hz, 1H), 3.83 (dd, *J* = 10.2, 5.2 Hz, 1H), 3.54 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.48 (d, *J* = 15.4 Hz, 1H), 2.74 (m, 1H), 2.51 (m, 1H), 2.17 (m, 1H), 1.77 (m, 1H), 1.67 (m, 1H), 1.57-1.31 (m, 4H), 0.88 (m, 9H). 0.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 132.6, 130.5, 127.9, 127.2, 124.2, 65.7, 63.3, 58.5, 52.4, 29.2, 26.1, 25.8, 23.4, 18.4; Enantiomeric ratio was determined by SFC: Chiralpak IC-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 99/1, v/v, flow rate 3.0 mL/min. HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{19}H_{33}BrNOSi]^+$ is 398.1437,found 398.1507.



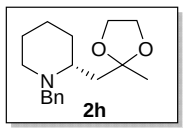
1-benzyl-2-(((tert-butyldimethylsilyl)oxy)methyl)piperidine, 2e: 376 mg (1.18 mmol), 93% yield, 84:16 er, colorless liquid; $[\alpha]_D^{20}$ = + 19.8 (c 1.0, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.21 (m, 4H), 7.19-7.14 (m, 1H), 4.07 (d, *J* = 13.7 Hz, 1H), 3.86 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.52 (dd, *J* = 10.2, 5.7 Hz, 1H), 3.25 (d, *J* = 13.7 Hz, 1H), 2.69 (m, 1H), 2.35 (m, 1H), 1.97 (m, 1H), 1.73 (m, 1H), 1.63 (m, 1H), 1.49-1.19 (m, 4H), 0.85 (m, 9H), 0.004 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 129.0, 128.2, 126.7, 65.9, 63.2, 59.3, 29.3, 26.1, 25.7, 23.7, 18.5; Enantiomeric ratio was determined by SFC: Chiralpak IC-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 93/7, v/v, flow rate 3.0 mL/min. HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{19}H_{34}NOSi]^+$ is 320.2421 found 320.2404.



1-benzyl-2-(2-bromophenethyl)piperidine, 2f: 368 mg(1.027 mmol), 89% yield, 88:12 er, colorless liquid; $[\alpha]_D^{20}$ = + 29.3 (c 1.0, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (m, 1H), 7.44 (m, 2H), 7.38 (m, 2H), 7.31 (m, 3H), 7.11 (m, 1H), 4.13 (d, *J* = 14.0 Hz, 1H), 3.37 (d, *J* = 14.0 Hz, 1H), 2.97-2.91 (m, 1H), 2.88-2.81 (m, 2H), 2.52 (m, 1H), 2.16 (m,1H), 1.97 (m, 2H), 1.82 (m, 2H), 1.68 (m, 1H), 1.58 (m, 2H), 1.45 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 140.0, 132.9, 130.5, 129.2, 129.0, 128.5, 128.3, 128.2, 127.64, 127.6, 126.8, 124.5, 60.3, 57.7, 51.5, 32.4, 32.1, 30.1, 27.1, 25.2, 23.6; Enantiomeric ratio was determined by SFC: Chiralpak OZ-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 77/23, v/v, flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{20}H_{25}BrN]^+$ is 358.1167 found 358.1165.

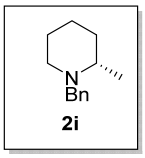


2-(2-(1,3-dioxan-2-yl)ethyl)-1-benzylpiperidine, 2g, 333.7 mg (1.15 mmol), 84% yield, 88:12 er, colorless liquid; $[\alpha]_D^{20}$ = + 59.2 (c 0.05, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.26 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 4.13 (d, *J* = 15.5 Hz, 1H), 3.83 (dd, *J* = 10.2, 5.2 Hz, 1H), 3.54 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.48 (d, *J* = 15.4 Hz, 1H), 2.74 (m, 1H), 2.51 (m, 1H), 2.17 (m, 1H), 1.77 (m, 1H), 1.67 (m, 1H), 1.57-1.31 (m, 4H), 0.88 (m, 9H). 0.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 132.6, 130.5, 127.9, 127.2, 124.2, 65.7, 63.3, 58.5, 52.4, 29.2, 26.1, 25.8, 23.4, 18.4; Enantiomeric ratio was determined by SFC: Chiralpak IC-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 97/3, v/v, flow rate 3.0 mL/min. HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{18}H_{28}NO_2]^+$ is 290.2115, found 290.2124.

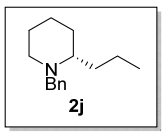


1-benzyl-2-((2-methyl-1,3-dioxolan-2-yl)methyl)piperidine, 2h: 271 mg (0.98 mmol), 69% yield, 83.5:16.5 er, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.34 (m, 2H), 7.28 (m, 2H), 7.20 (m, 1H), 3.97-3.87 (m, 4H), 3.81 (d, *J* = 13.9 Hz, 1H), 3.35 (d, *J* = 13.9 Hz, 1H), 2.69 (m, 1H), 2.59 (m, 1H), 2.21 (m, 1H), 2.04 (m, 1H), 1.89-1.69 (m, 2H), 1.61-1.38 (m, 5H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 128.9, 128.2, 126.7, 110.3, 64.8, 64.5, 58.6, 56.3, 50.1, 38.6, 32.0, 25.2, 24.6, 22.2; Enantiomeric ratio was determined by SFC: Chiralpak IC-3, 4.6 mm x 150 mm, particle size: 3 µm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 99/1, v/v, flow rate 3.0 mL/min. HRMS (ESI) $[M+H]^+$ *m/z* calcd for $[C_{17}H_{26}NO_2]^+$ is 276.1885, found 276.1970.

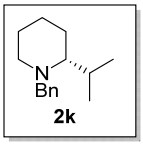


1-benzyl-2-methylpiperidine, 2i[3]: 315 mg (1.66 mmol), 88% yield, 82:18 er, colorless liquid; $[\alpha]_D^{20}$ = + 66.4 (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.30 (m, 4H), 7.24 (m, 1H), 4.02 (d, *J* = 13.6 Hz, 1H), 3.21 (d, *J* = 13.6 Hz, 1H), 2.78-2.72 (m, 1H), 2.33 (m, 1H), 1.97 (m, 1H), 1.66 (m, 2H), 1.51-1.44 (m, 2H), 1.42-1.26 (m, 2H), 1.19 (d, *J* = 13.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.7, 129.3, 128.2, 126.7, 58.7, 56.6, 52.4, 34.9, 26.2, 24.2, 19.7; Enantiomeric ratio was determined by SFC: Chiralpak IC-3, 4.6 mm x 150 mm, particle size: 3 µm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 99/1, v/v, flow rate 3.0 mL/min. HRMS (ESI) $[M+H]^+$ *m/z* calcd for $[C_{13}H_{20}N]^+$ is 190.1587 found 190.1590.

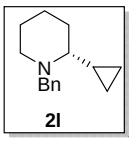


1-benzyl-2-cyclopropylpiperidine, 2j: 335 mg (1.54 mmol), 90% yield, 88:12 er, colorless liquid; $[\alpha]_D^{20}$ = + 57.0 (c 0.05, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.19 (m, 4H), 7.16 (m, 1H), 3.89 (d, *J* = 13.2 Hz, 1H), 3.16 (d, *J* = 13.2 Hz, 1H), 2.66 (m, 1H), 2.22 (t, *J* = 8.1 Hz, 1H), 1.96 (m, 1H), 1.61-1.50 (m, 2H), 1.47-1.30 (m, 5H), 1.28-1.17 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 129.1, 128.3, 126.8, 60.8, 57.6, 51.8, 34.2, 30.4, 25.3, 23.8, 19.0, 14.8; Enantiomeric ratio was determined by GC-MS: Chiral Dex B-PH, 30 m, 0.25 mm, 0.12 um, oven temp: hold 110 °C for 80 min, split ratio:

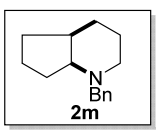
100:1, flow rate 1.0 mL/min. HRMS (ESI) $[M+H]^+$ *m/z* calcd for $[C_{15}H_{24}N]^+$ is 218.1903, found 218.1922.



1-benzyl-2-isopropylpiperidine, 2k: 346 mg (1.59 mmol), 93% yield, 91:9 er, colorless liquid; $[\alpha]_D^{20}$ = + 71.6 (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (d, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.54 (s, 1H),3.57 (m, 1H), 3.35 (m, 1H), 3.02 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.71 (m, 1H), 2.60 (dd, *J* = 15.6, 9.7 Hz, 1H), 1.86 (m, 2H), 1.72 (m, 1H), 1.61-1.36 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.5, 129.0, 128.2, 126.7, 66.7, 567, 52.8, 27.7, 29.9, 24.8, 23.7, 20.4, 16.2; Enantiomeric ratio was determined by SFC: Chiralpak OZ-3, 4.6 mm x 150 mm, Particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 70/30, v/v, flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ *m/z* calcd for $[C_{15}H_{24}N]^+$ is 218.1903, found 218.1906.

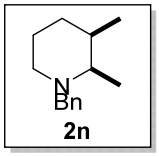


1-benzyl-2-cyclopropylpiperidine, 2l: 304 mg (1.41 mmol), 82% yield, 92:8 er, colorless liquid; $[\alpha]_D^{20}$ = + 49.6 (c 0.05, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 2H), 7.29 (m, 2H), 7.21 (m, 1H), 4.65 (d, *J* = 13.2 Hz, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.76 (m, 1H), 1.81 (m, 1H), 1.63-1.37 (m, 3H), 1.31-1.19 (m, 1H), 0.89-0.75 (m, 1H), 0.68-0.62 (m, 1H), 0.50-0.43 (m, 1H), 0.32-0.26 (m, 1H), 0.07-0.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 129.1, 128.2, 126.6, 68.4, 59.2, 52.7, 32.8, 25.9, 24.6, 15.4, 8.0, 1.6; Enantiomeric ratio was determined by SFC: Chiralpak OZ-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 70/30, v/v, flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ *m/z* calcd for $[C_{15}H_{22}N]^+$ is 216.1747, found 216.1749.



***cis*-1-Benzyloctahydro-1H-cyclopenta[b]pyridine, 2m:** 319 mg (1.48 mmol), 86% yield, 81:19 er, colorless liquid; $[\alpha]_D^{20}$ = + 41.6 (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.27 (m, 4H), 7.23 (m, 1H), 3.77 (d, *J* = 13.5 Hz, 1H), 3.29 (d, *J* = 13.5

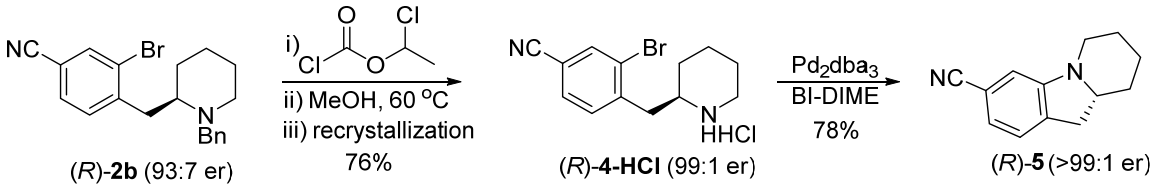
Hz, 1H), 2.79 (m, 1H), 2.56 (m, 1H), 2.14 (m, 1H), 1.98 (m, 1H), 1.87 (m, 2H), 1.65-1.49 (m, 6H), 1.46-1.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0, 129.0, 128.2, 126.7, 64.1, 59.8, 49.9, 39.2, 28.3, 26.0, 23.2, 21.7; Enantiomeric ratio was determined by SFC: Chiralpak IC-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 95/5, v/v, flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{15}H_{22}N]^+$ is 216.1674, found 216.1747.



2n

***cis*-1-Benzyl-2,3-dimethylpiperidine, 2n**: 299.7 mg (1.47 mmol), 82% yield, 78:22 er, colorless liquid,. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 2H), 7.31 (m, 2H), 7.23 (m, 1H), 3.66 (d, *J* = 7.7 Hz, 1H), 3.54 (d, *J* = 7.7 Hz, 1H), 2.78 (m, 1H), 2.47 (m, 1H), 2.34 (m, 1H), 1.91 (m, 1H), 1.56 (m, 2H), 1.46 (m, 1H), 1.29 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.5, 128.7, 128.2, 126.7, 59.3, 57.9, 46.8, 35.1, 28.1, 25.9, 18.1, 6.7; Enantiomeric ratio was determined by SFC: Lux Cellulose-4, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 40 ºC, A: CO_2, B: Methanol with 0.2% of isobutylamine, isocratic: A/B: 95/5, v/v, flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ m/z calcd for $[C_{14}H_{22}N]^+$ is 204.1747 found 204.1755.

Synthesis of 6,7,8,9,9a,10-hexahydropyrido[1,2-a]indole-3-carbonitrile (*R*)-5



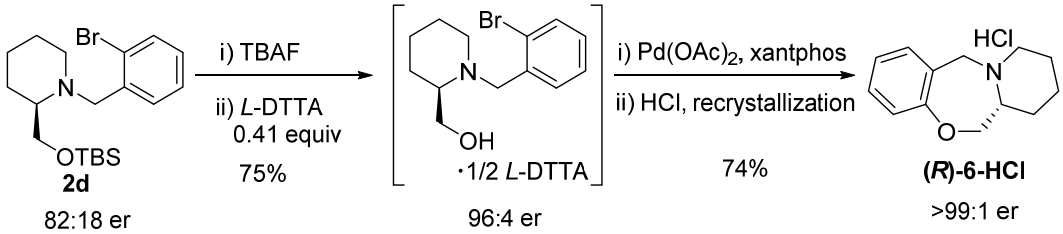
To a 100 mL 2-necked round-bottom flask was added **2b** (1.5 g, 4.06 mmol) and dry toluene (5 mL) and dry acetonitrile (5 mL). The mixture was heated to 60 °C, a clear solution was obtained. To this solution added N,N-diisopropylethylamine (104 mg, 0.812 mmol) followed by 1-

chloroethylchloroformate (0.75 g, 5.28 mmol) slowly over 5 min. Reaction was kept at this temperature for 2 h and monitored by LC-MS, complete conv to the amide intermediate was observed. The solvent mixture was concentrated on rotavap to remove the solvent. Then MeOH (10 mL) was added and the resulting reaction mixture was heated to 50 °C for 90 min, complete conversion to the deprotected amine **4** was observed. The mixture was cooled to rt to observe the formation of the HCl salt of **4**. The slurry was concentrated to remove MeOH. Then toluene (20 mL) was added to the crude and stir and filtered. The resulting solid was dissolved in EtOAc (10 mL) at 60 °C, and then MTBE (20 mL) was added slowly to observe formation of brown crystals. The mixture was cooled down to rt over 1 h. The crystals were filtered and washed with EtOAc/MTBE(1:3). Light brown crystalline **4-HCl** was obtained after dryness, 0.97 g, 76% yield, 99:1 er; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 1.5 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.5 Hz, 1H),7.34 (d, *J* = 7.9 Hz, 1H), 3.71 (m, 1H), 3.52 (m, 1H), 3.33 (m, 2H), 2.90 (m, 1H), 2.00 (m, 1H), 1.85 (m, 1H), 1.68 (m, 1H), 1.53 (m, 1H), 1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 136.7, 132.1, 130.9, 125.4, 117.5, 112.0, 56.3, 47.3, 43.4, 33.0, 26.4, 24.8; Enantiomeric ratio was determined by SFC: Chiralpak OZ-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 88/12, v/v, flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{13}H_{16}BrN_2]^+$ is 279.0419 found 279.0491.

A 20 mL Easymax vial equipped with a magnetic stir bar was charged with amine **4-HCl** (300 mg, 1.075 mmol), *rac*-BIDIME (5 mol%), $Pd_2(dba)_3$ (2.5 mol%) and sodium *t*-butoxide (309 mg, 3.22 mmol) in 5 mL of degassed toluene. Reaction was kept at 110 °C under argon for 14 h. The crude mixture was filtered through a pad of celite and the filtrate was concentrated. The crude mixture was extracted with DCM (20 mL) and washed with sat $NaHCO_3$ (5 mL). The organic

layer was concentrated and purified using 30% EtOAc/hexanes to get (*R*)-**5** as reddish brown oil, 147 mg, 78% yield, 99.2:0.8 er; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (d, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.54 (s, 1H), 3.57 (m, 1H), 3.35 (m, 1H), 3.02 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.71 (m, 1H), 2.60 (dd, *J* = 15.6, 9.7 Hz, 1H), 1.86 (m, 2H), 1.72 (m, 1H), 1.61-1.36 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 135.4, 125.0, 122.5, 120.2, 110.9, 108.0, 44.9, 35.7, 30.8, 24.4, 24.2; Enantiomeric excess was determined by SFC: Chiralpak OZ-3, 4.6 mm x 150 mm, particle size: 3 μm, temperature: 30 ºC, A: CO_2, B: Ethanol with 0.2% of isobutylamine, isocratic: A/B: 95/5, v/v, flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{13}H_{15}N_2]^+$ is 199.1157 found 199.1237.

Synthesis of (*R*)-6,6a,7,8,9,10-hexahydro-12H-benzo[f]pyrido[2,1-c][1,4]oxazepine (*R*)-6



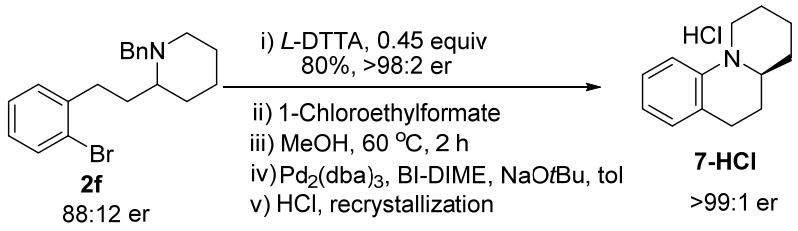
To a 100 mL round bottom flask was added **2d** (1.0 g, 2.5 mmol) and THF (10 mL), and cooled down to 0 ^{o}C with an ice bath. To this solution was added TBAF (1.343 mL 1.0 M in THF, 1.34 mmol), and the reaction mixture was stirred at 0 °C for 2 h. LC-MS indicates the disappearance of SM and formation of the alcohol. The mixture was concentrated and passed through a short silica pad and eluted with 50% EtOAc/hexane. The eluent was concentrated to obtain the alcohol as colorless liquid after concentration. The liquid was dissolved in EtOAc (6 mL) in a 50 mL round bottom flask and the solution was heated to 60 °C. To this solution added di-*p*-toluoyl-L-tartaric acid (*L*-DTTA) (398 mg, 0.41 equiv) in EtOAc (5 mL) added slowly and kept the solution at 60 °C for 1 h and cooled down to rt over 1 h and stirred for 14 h. The resulting solid

was filtered and washed with 10% IPA/heptane and dried. The piperidine 1/2 *L*-DBTA salt was collected as a white solid, 898 mg, 96:4 er (from NMR analysis). The solid was transferred to a 100 mL round bottom flask. 10% NaOH (10 mL) and toluene (25 mL) were added. The mixture was stirred at room temperature for 5 h. Organic layer was extracted and dried and concentrated to oily liquid and was used directly for the next step.

The liquid was dissolved in 1,4-dioxane (5 mL) and transferred to a 20 mL Easymax vial equipped with a magnetic stir bar and cesium carbonate (1.23 g, 2 equiv). The mixture was sparged with argon for 5 min. Then $Pd_2(dba)_3$ (43 mg, 2.5 mol%) and xantphos (54.5 mg, 5 mol%) were added to the vial. The mixture was heated to 110 °C and stirred at this temperature for 14 h to observe complete conversion. The reaction was cooled down and the crude was filtered through a short pad of celite and the filtrate was concentrated. The crude mixture was extracted with DCM (20 mL) and washed with sat $NaHCO_3$ (5 mL). The organic layer was dried and dissolved in 2 mL of THF. To this solution was added 1.0 M HCl (470 uL of 4.0 M in dioxane). The salt was filtered after stirring at rt for 3 h. The salt was then dissolved in EtOAc at 60 °C and hexane was added slowly to observe the formation of the crystalline compound. The slurry was cooled down and filtered and washed with EtOAc/hexanes (1:4) to get a light brown crystalline product (*R*)-**6**-HCl, 334 mg, 74% yield, 99.0:1.0 er; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (m, 2H), 6.98 (m, 2H), 4.13 (d, *J* = 12.1 Hz, 1H), 3.78 (d, *J* = 13.6 Hz, 1H), 3.59 (m, 1H), 3.48 (d, *J* = 13.6 Hz, 1H), 2.97 (m, 1H), 2.51 (t, *J* = 9.5 Hz, 1H), 2.31 (m, 1H), 1.72-1.60 (m, 4H), 1.37-1.15 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.3, 132.0, 130.9, 128.7, 123.7, 120.1, 65.9, 62.1, 56.4, 28.4, 26.2, 23.4; Enantiomeric ratio was determined by SFC: Chiralpak OZ-3, 4.6 mm x 150 mm, particle size: 3 µm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2%

of isobutylamine, isocratic: A/B: 97/3, v/v, flow rate 3.0 mL/min; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{13}H_{17}NO]^+$ is 204.1310 found 204.1379.

Synthesis of 2,3,4,4a,5,6-hexahydro-1H-pyrido[1,2-a]quinolone (*R*)-7



To a 100 mL round bottom flask was added **2f** (1.0 g, 2.78 mmol) and EtOAc (10 mL). The solution was heated to 60 °C. To this solution was added di-*p*-toluoyl-*L*-tartaric acid (*L*-DTTA) (858 mg 42.9 mg, 1.24 mmol, 0.45 equiv) in EtOAc (10 mL) slowly and the solution was kept at 60 °C for 1 h and then cool down to rt over 1 h and stirred for 14 h to observe formation of white solid. The solid was washed with 10% IPA/heptane and dried to yield the white solid of benzyl protected amine·1/2 *L*-DTTA salt, 1.23 g (2.233 mmol, 98:2 er). The resulting salt was added to a 100 mL round bottom flask and followed by toluene (25 mL) and saturated NaOH (10 mL). The mixture was stirred at rt for 5 h. The organic layer was extracted and dried to obtain colorless liquid, which was directly used for the next step.

The liquid was added to a 100 mL round bottom flask, followed by dry toluene (2.5 mL). To this solution was added dry acetonitrile (2.5 mL). The mixture was heated to 60 °C, a clear solution was obtained. To this solution was added N,N-Diisopropylethylamine (61 mg, 0.445 mmol) followed by 1-chloroethyl chloro formate (414 mg, 2.90 mmol) added slowly over 5 min. Reaction was kept at this temperature for 2 h and monitored by LC-MS, complete conversion to the amide was observed. The solvent mixture was concentrated and MeOH (15 mL) was added. The mixture was heated to 50 °C for 1 h to observe 100% conversion to the deprotected amine.

The solution was cooled to rt and concentrate. Toluene (35 mL) was added to crude mixture, brown solid was obtained. The slurry was cooled to rt and filtered and dried to give the crude amine HCl salt 585 mg (1.92 mmol). The salt was added to a 50 mL round bottom flask under argon, followed by 10 ml of degassed toluene. Then $Pd_2(dba)_3$ (44.0 mg, 2.5 mol%) and *rac*-BIDIME (31.5 mg, 5 mol%), and sodium *t*-butoxide (553 mg, 3 equiv) were added. Reaction was heated to 110 °C and stirred at this temperature for 14 h. Complete cyclization was resulted. The crude mixture was filtered through celite pad and the filtrate was concentrated. The crude mixture was washed with water (20 mL) and extracted with DCM (20 mL). The organic layer was dried and dissolved in THF (8 mL). To this solution was added HCl (480 uL 4.0 M in dioxane) slowly at rt and stir for 3 h. The salt was then filtered and dissolved in EtOAc (10 mL) at 60 °C. To the solution was added hexane to observe the formation of crystalline product. The slurry was cooled down to rt over 1 h, filtered and dried to yield reddish brown solid of **(*R*)-7**, 272 mg, total yield 52% yield starting from **2f**, 99.2:0.8 er; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (br s, 1H), 7.28-7.34 (m, 2H), 7.22-7.24 (m, 1H), 3.87 (m, 1H), 3.56 (m, 1H), 3.32 (m, 1H), 3.00-3.03 (m, 2H), 2.46-2.74 (m, 3H), 1.65-2.05 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 130.4, 129.2, 127.9, 124.1, 55.9, 54.5, 27.3, 25.2, 22.9, 20.3, 17.1; Enantiomeric excess was determined by SFC: Chiralpak OD-3, 4.6 mm x 150 mm, particle size: 3 µm, temperature: 30 ºC, A: CO_2, B: ethanol with 0.2% of isobutylamine, isocratic: A/B: 95/5, v/v, flow rate 3.0 mL/min. HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{13}H_{18}N]^+$ is 188.1361 found 188.1429.

References:

1. J. N. Desrosiers, X. Wei, O. Gutierrez, J. Savoie, B. Qu, X. Zeng, H. Lee, N. Grinberg, N. Haddad, N. K. Yee, F. Roschangar, J. J. Song, M. C. Kozlowski, C. H. Senanayake, *Chem. Sci.* **2016**, *7*, 5581.
2. C. Shu, K. Sidhu, L. Zhang, X-J. Wang, D. Krishnamurthy, C.H. Senanayake, *J. Org. Chem*. **2010**, *75*, 6677.
3. M. Chang, Y. Huang, S. Liu, Y. Chen, S. W. Krska, I. W. Davies, X. Zhang, *Angew. Chem., Int. Ed*. **2014**, *53*, 12761.

Table 1. Crystal data and structure refinement for complex 3.

Identification code	IrCl(MeO-BoQPhos)(COD)
Empirical formula	$C_{26}H_{34}ClIrNO_3P$
Formula weight	667.16
Temperature/K	99.59
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.8573(4)
b/Å	14.3398(6)
c/Å	16.3961(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2552.73(18)
Z	4
ρ_{calc}g/cm^3	1.736
μ/mm^{-1}	11.903
F(000)	1320.0
Crystal size/mm^3	0.06 × 0.04 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.19 to 132.934
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 16$, $-19 \leq l \leq 19$
Reflections collected	12048
Independent reflections	3958 [R_{int} = 0.0451, R_{sigma} = 0.0514]
Data/restraints/parameters	3958/324/303
Goodness-of-fit on F^2	0.976
Final R indexes [I>=2σ (I)]	R_1 = 0.0252, wR_2 = 0.0512
Final R indexes [all data]	R_1 = 0.0273, wR_2 = 0.0519
Largest diff. peak/hole / e Å^{-3}	0.55/-0.52
Flack parameter	0.002(9)

Table 2. Crystal data and structure refinement for 7-HCl.

Identification code	**7**-HCl
Empirical formula	$C_{13}H_{18}ClN$
Formula weight	223.73
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_1$
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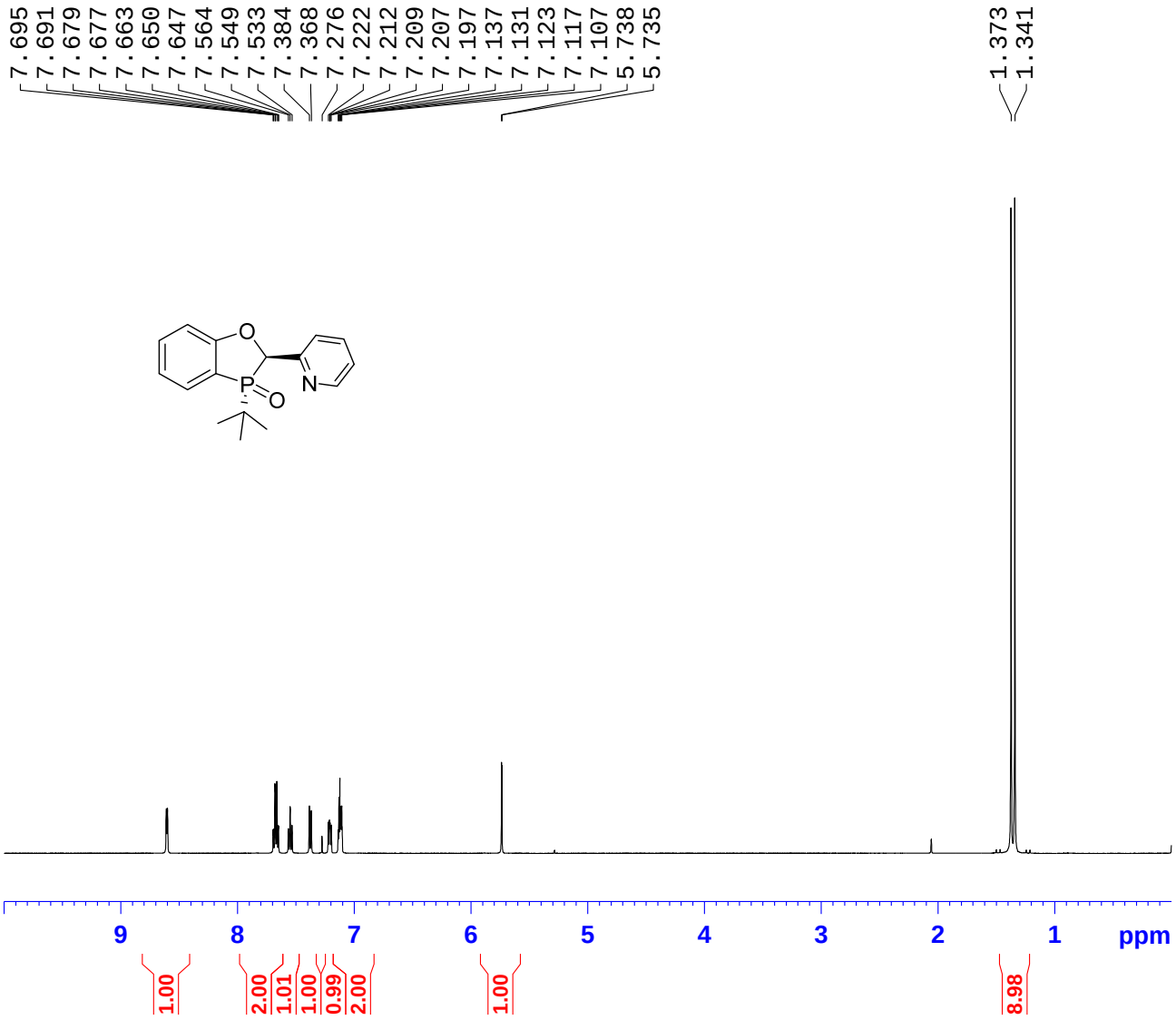
b/Å	7.0058(5)
c/Å	9.7900(6)
α/°	90
β/°	108.318(4)
γ/°	90
Volume/Å^3	582.32(7)
Z	2
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	2.608
F(000)	240.0
Crystal size/mm^3	0.12 × 0.06 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.516 to 132.892
Index ranges	$-10 \leq h \leq 10$, $-7 \leq k \leq 7$, $-11 \leq l \leq 11$
Reflections collected	2759
Independent reflections	1678 [R_{int} = 0.0216, R_{sigma} = 0.0421]
Data/restraints/parameters	1678/1/136
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0299, wR_2 = 0.0713
Final R indexes [all data]	R_1 = 0.0315, wR_2 = 0.0723
Largest diff. peak/hole / e Å^{-3}	0.21/-0.25
Flack parameter	0.074(15)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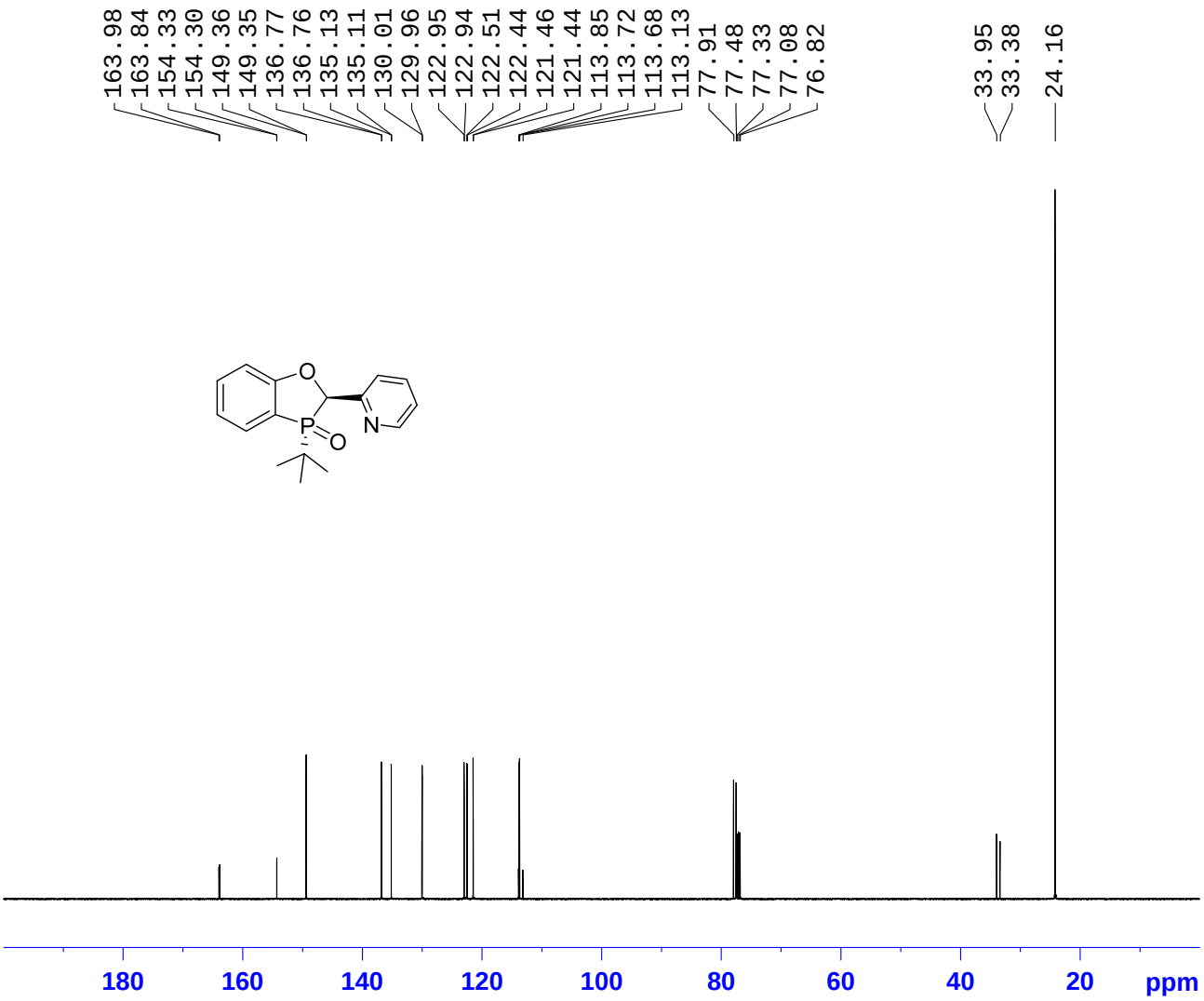
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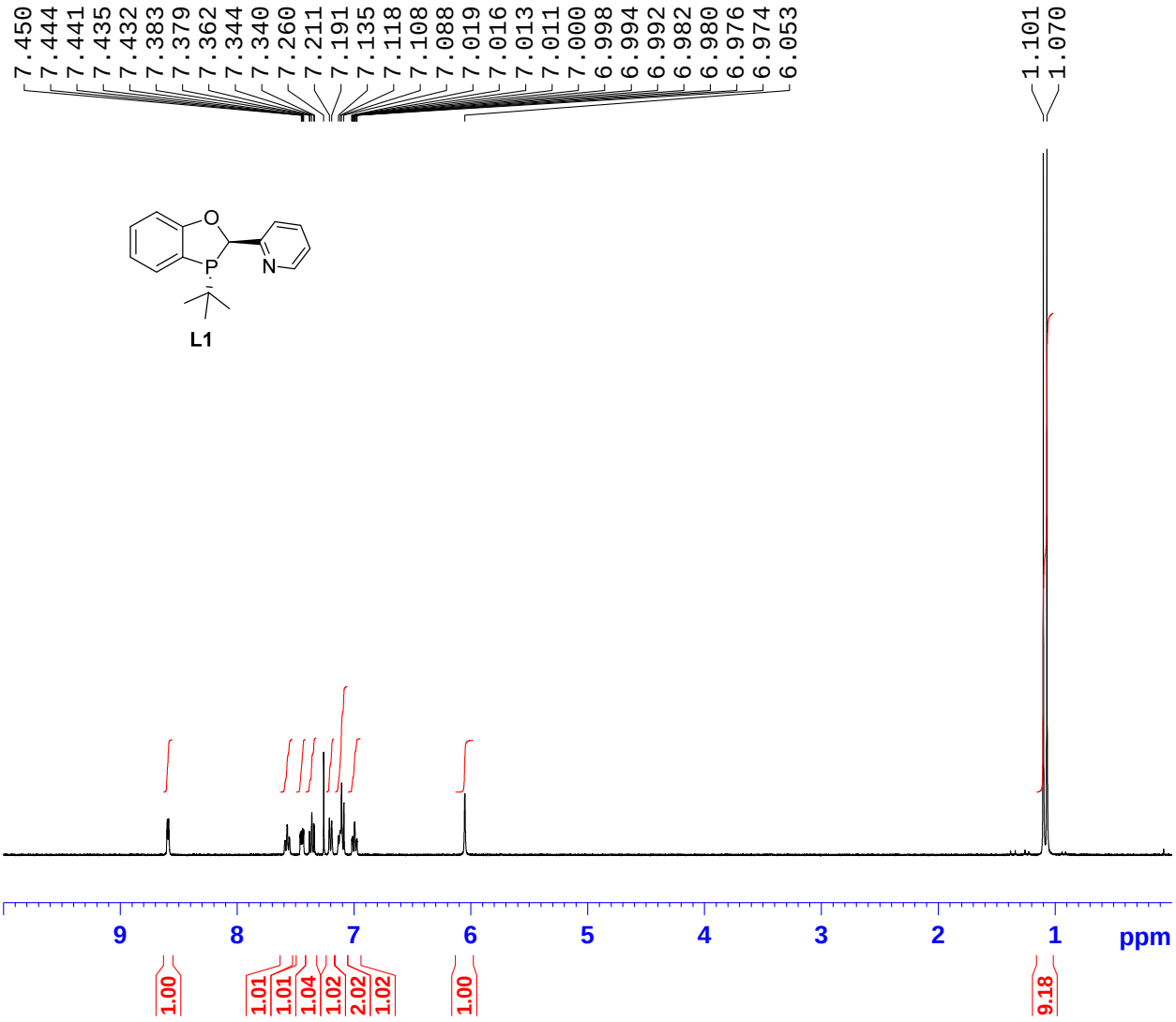
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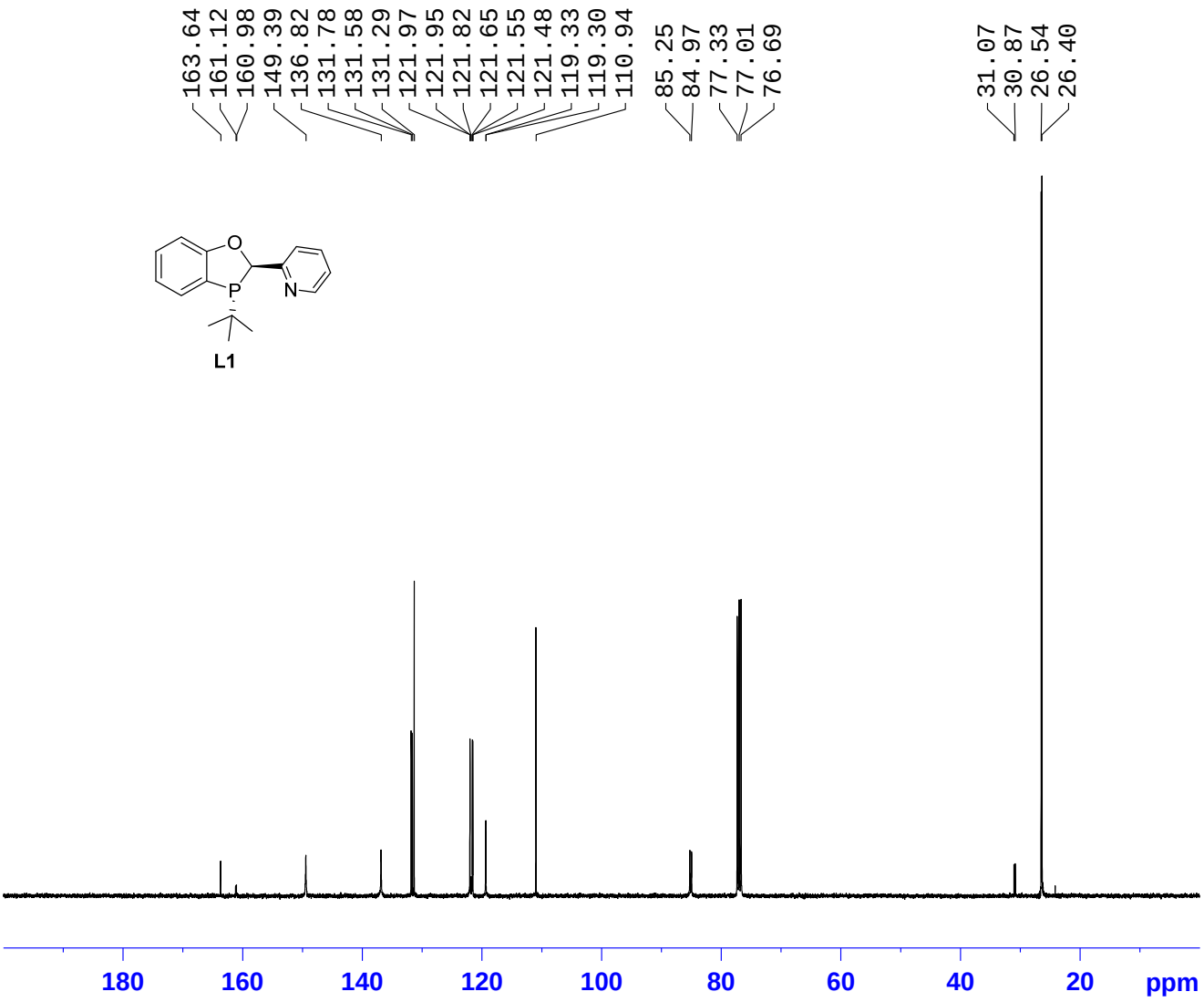
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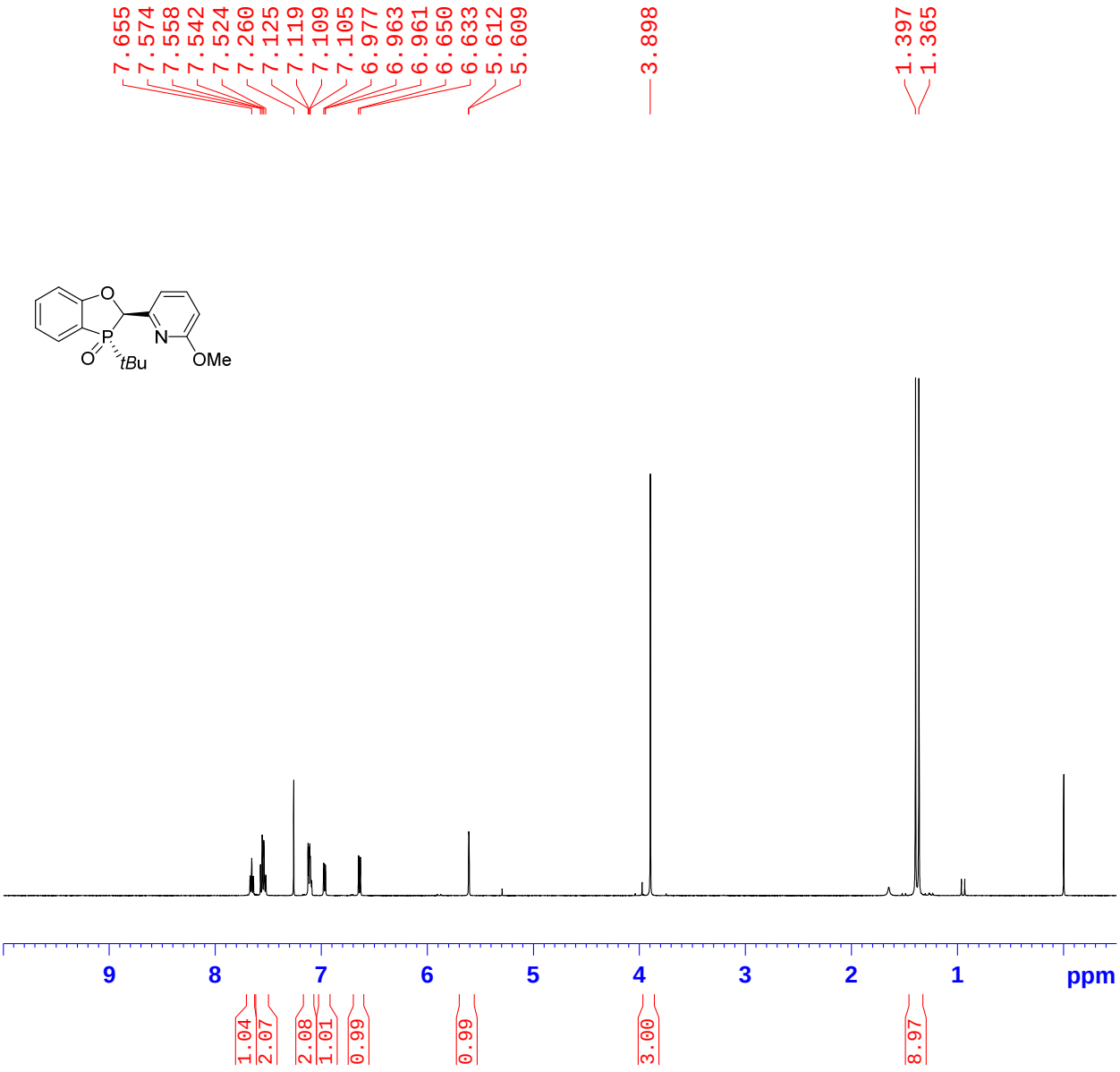
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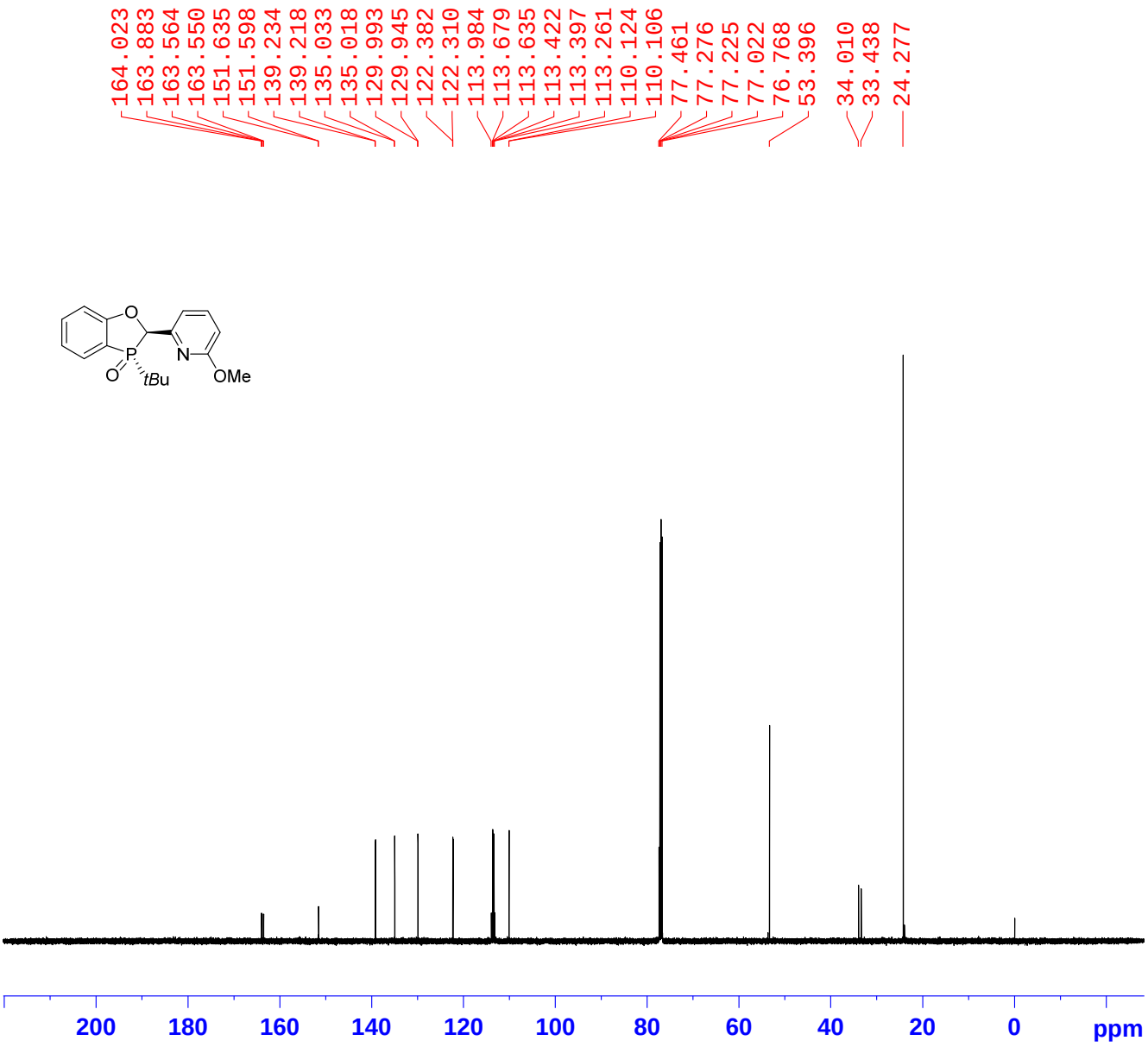
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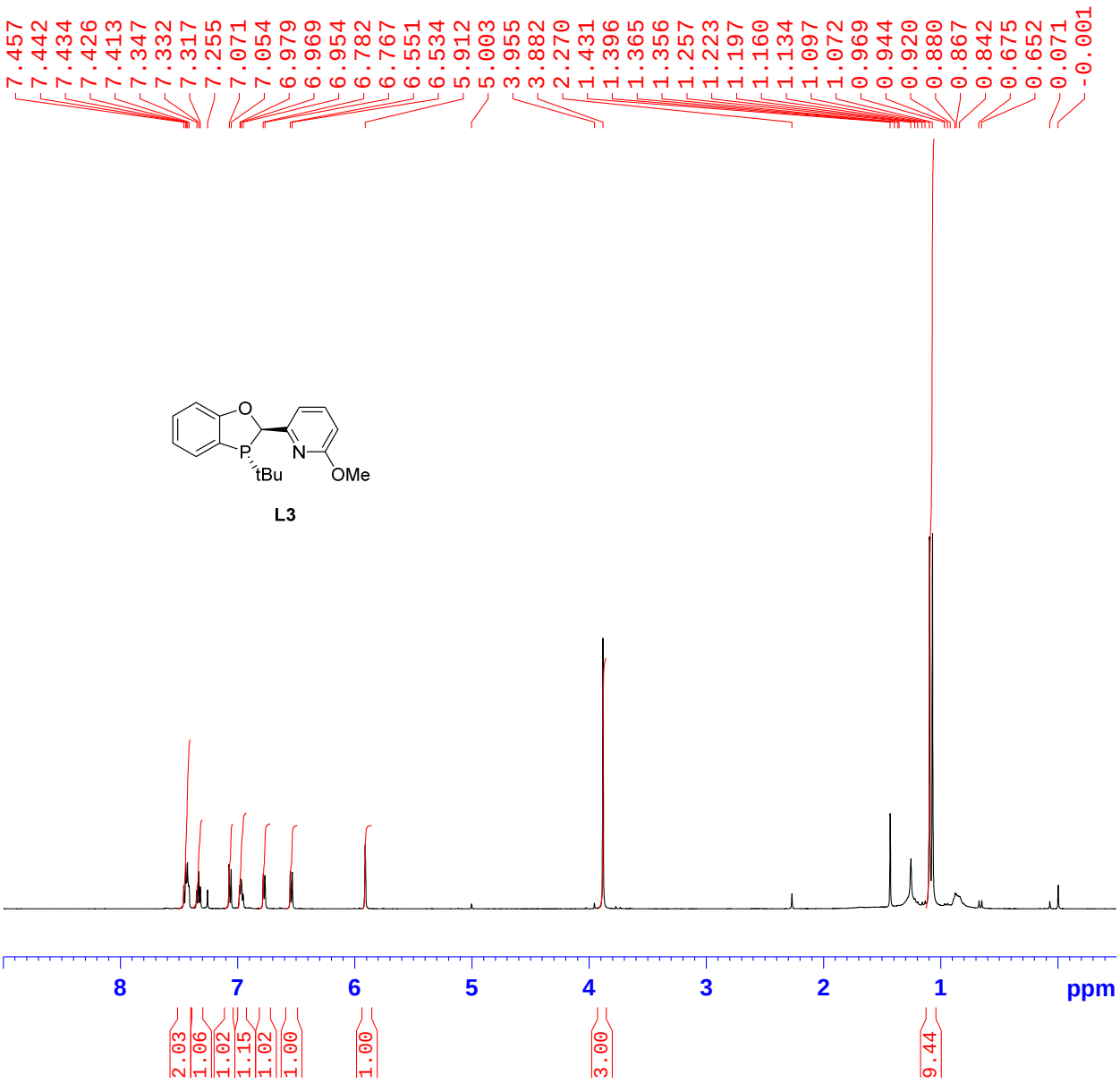
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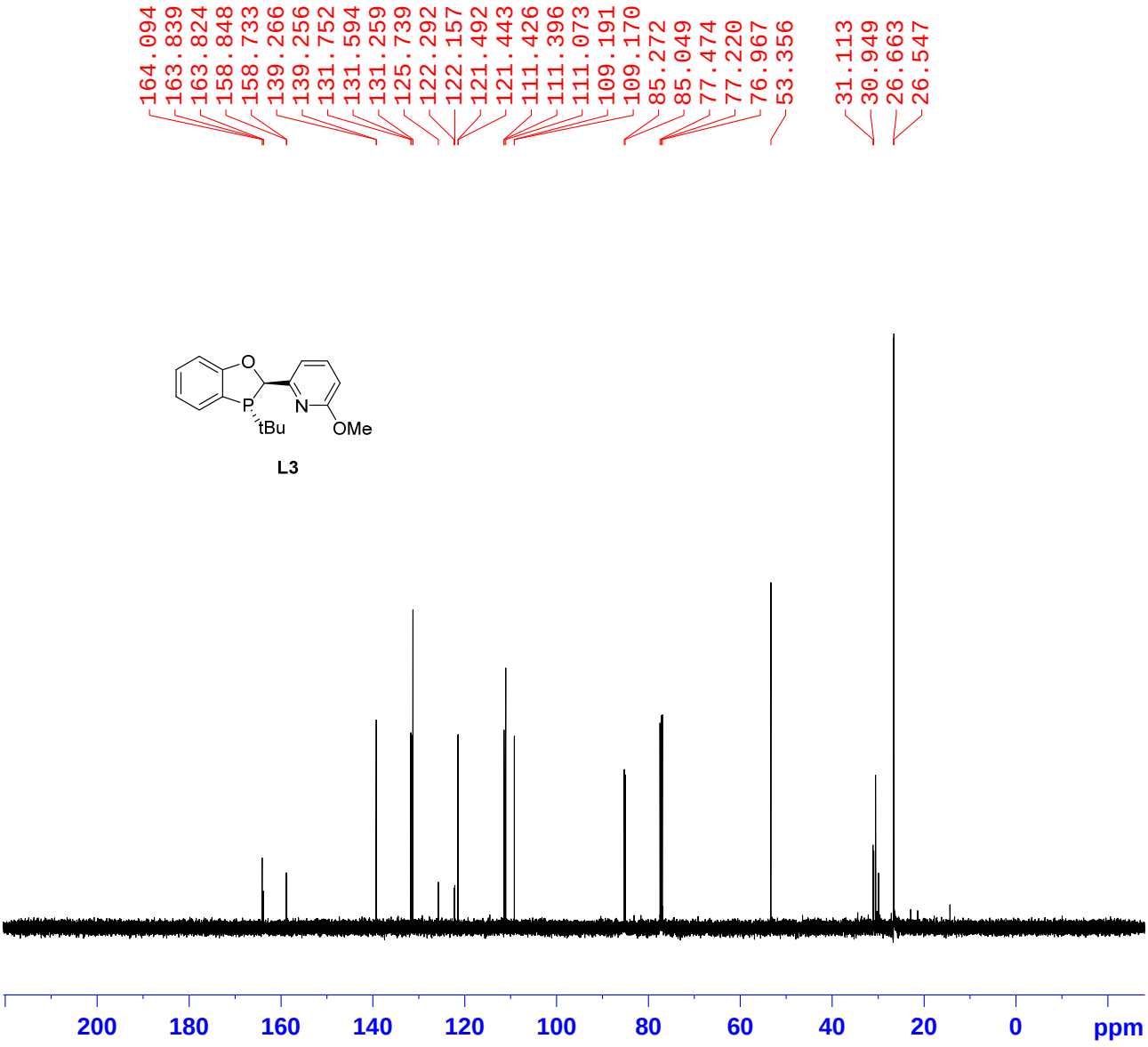
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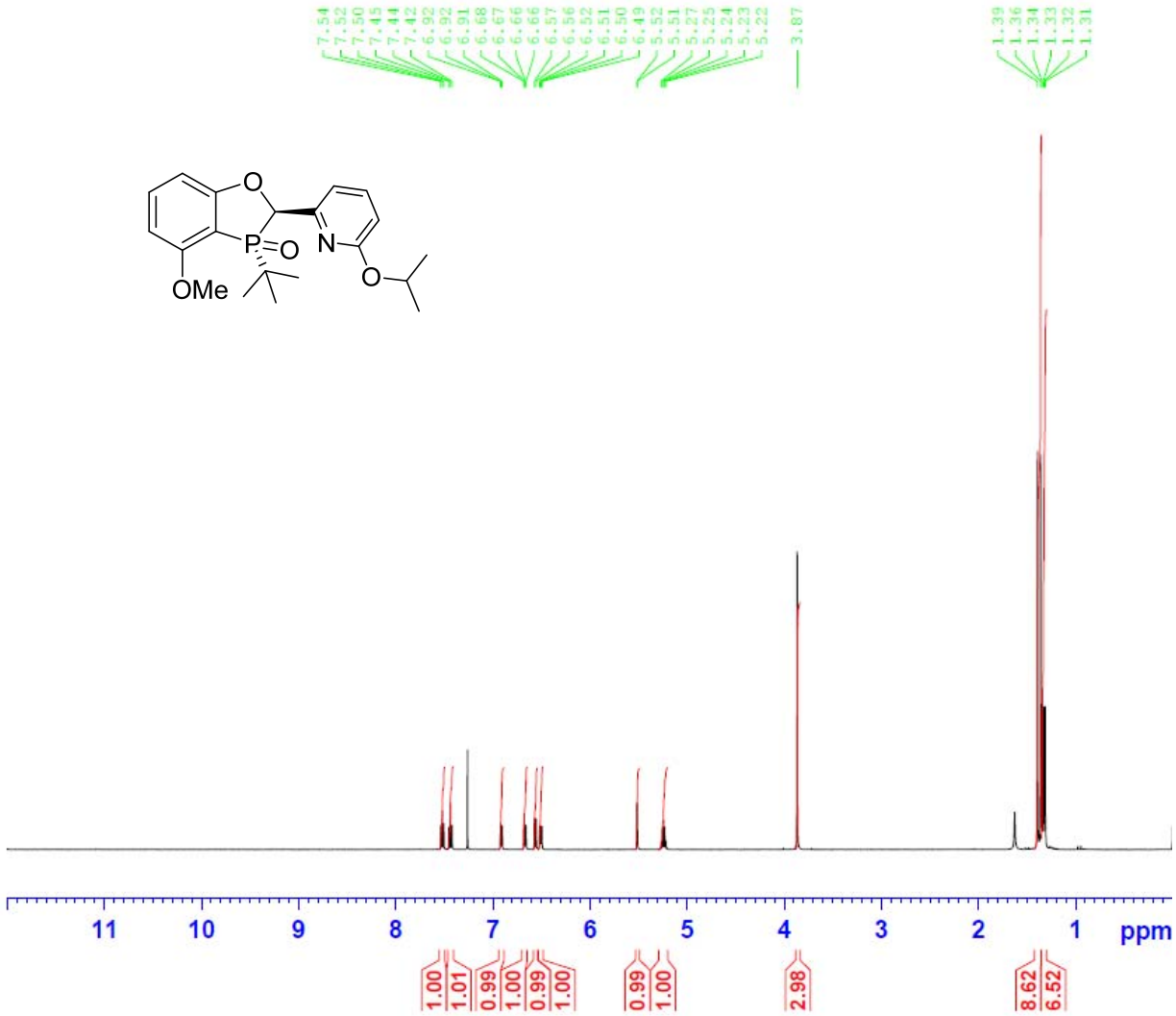
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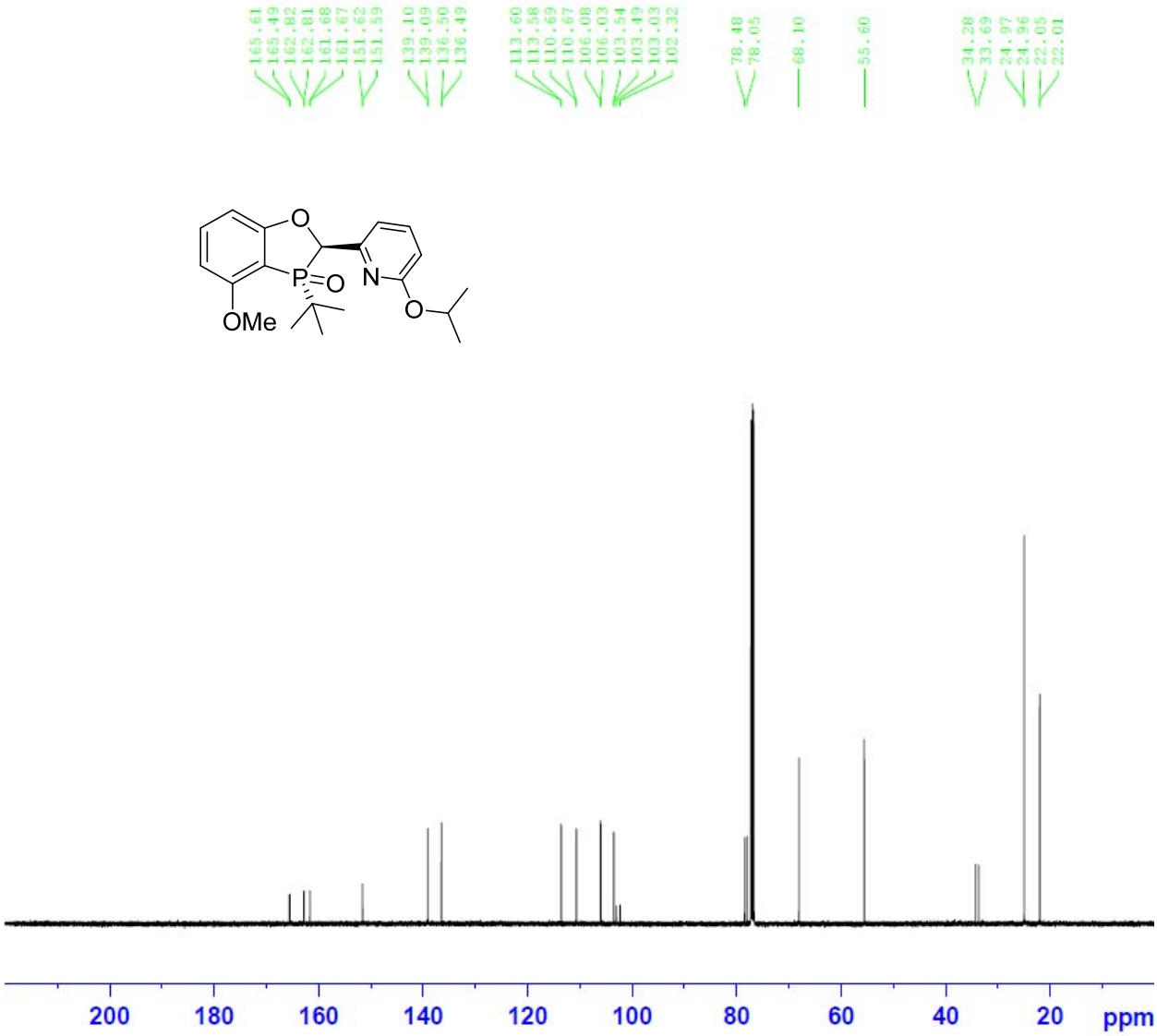
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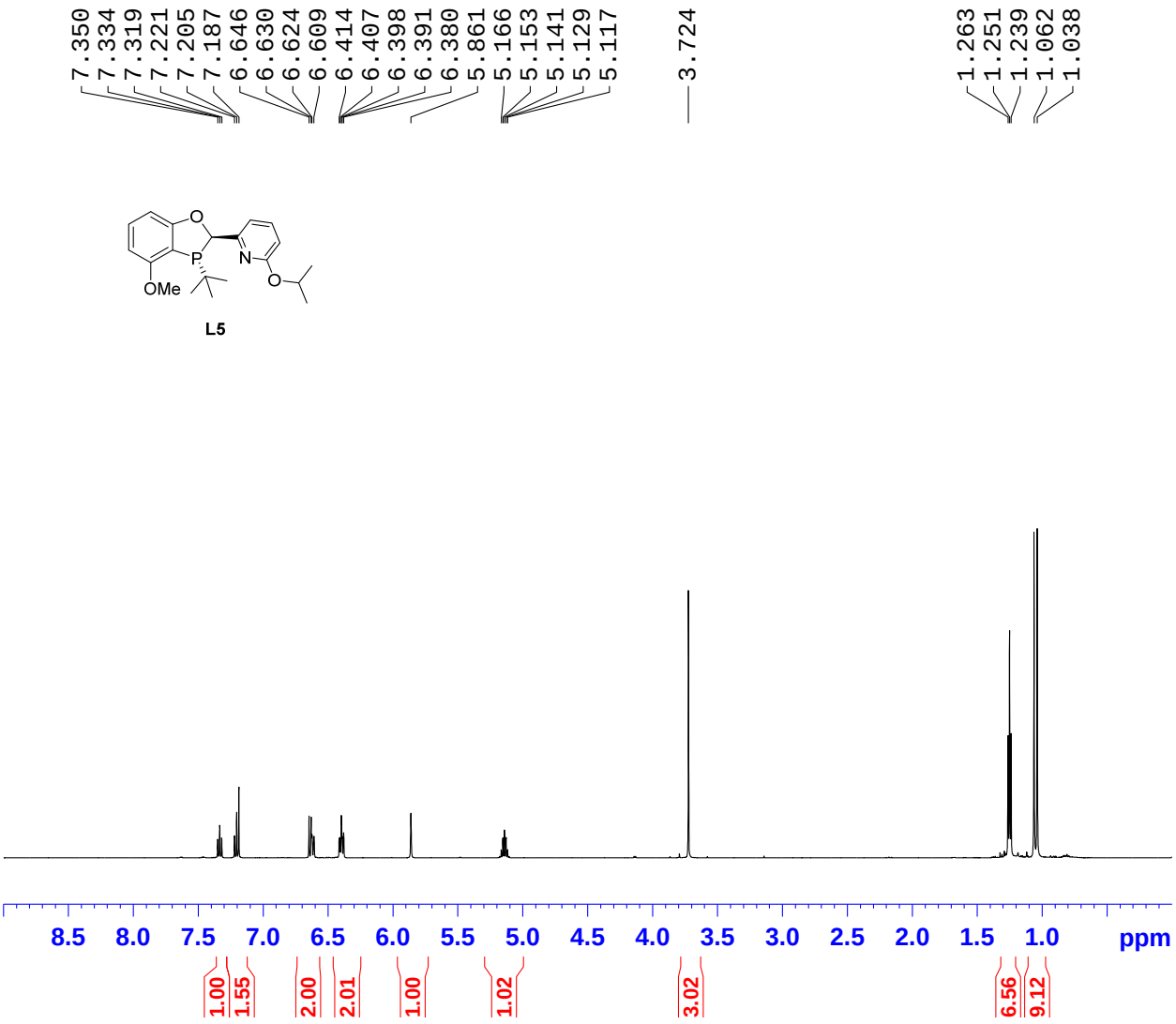
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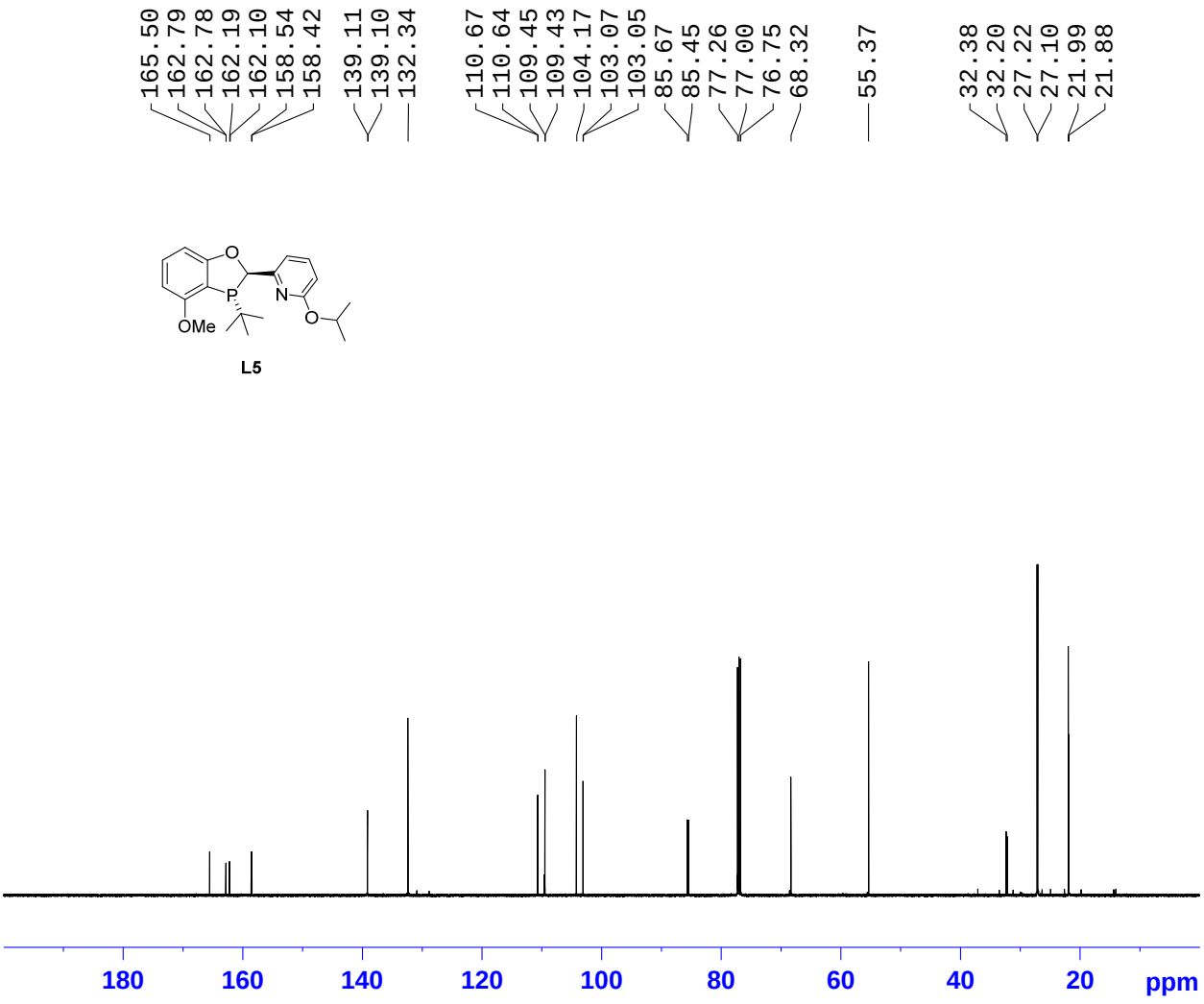
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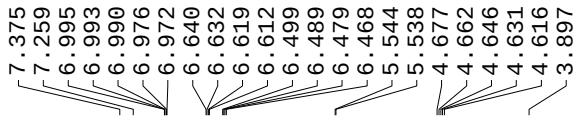
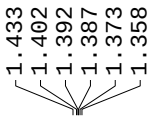
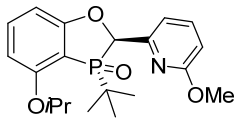
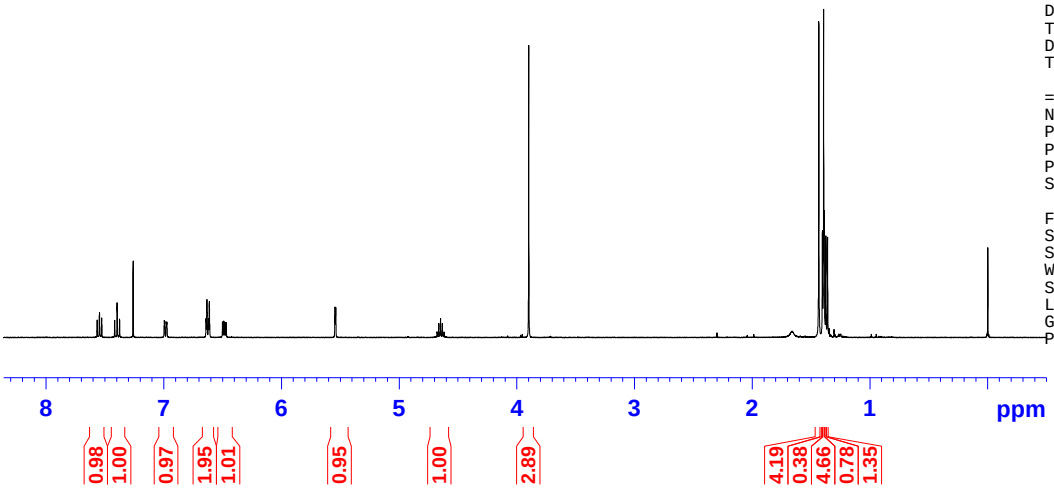
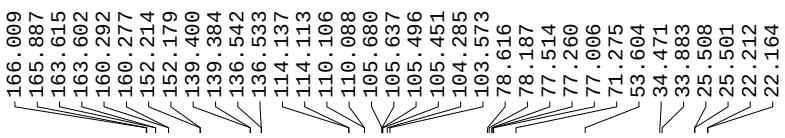


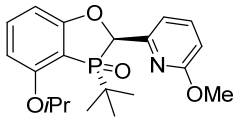




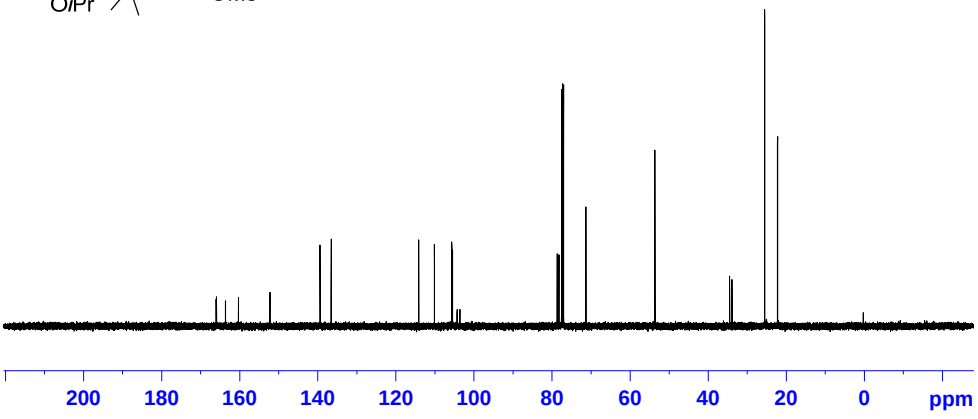

```
Current Data Parameters
NAME          10854-031
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150921
Time               9.41
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    4
SWH            5896.227 Hz
FIDRES        0.179939 Hz
AQ            2.7787263 sec
RG                  724
DW               84.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1       0 dB
PL1W        10.49968529 W
SFO1        400.1327209 MHz

F2 - Processing parameters
SI                65536
SF          400.1300101 MHz
WDW                  EM
SSB       0
LB                0.05 Hz
GB        0
PC                1.00
```

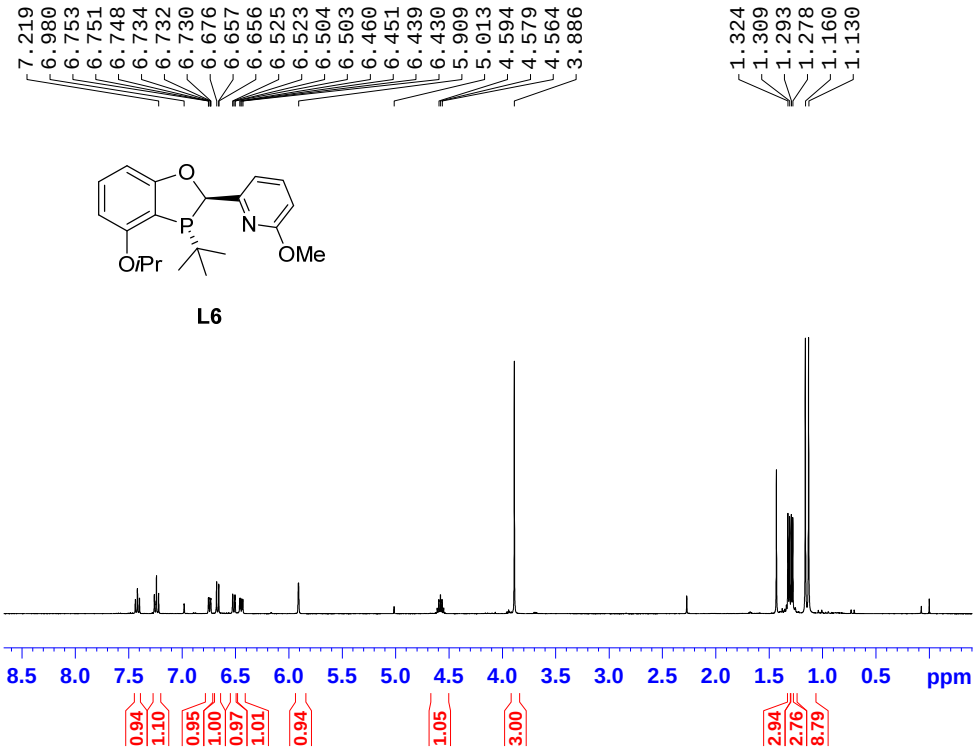




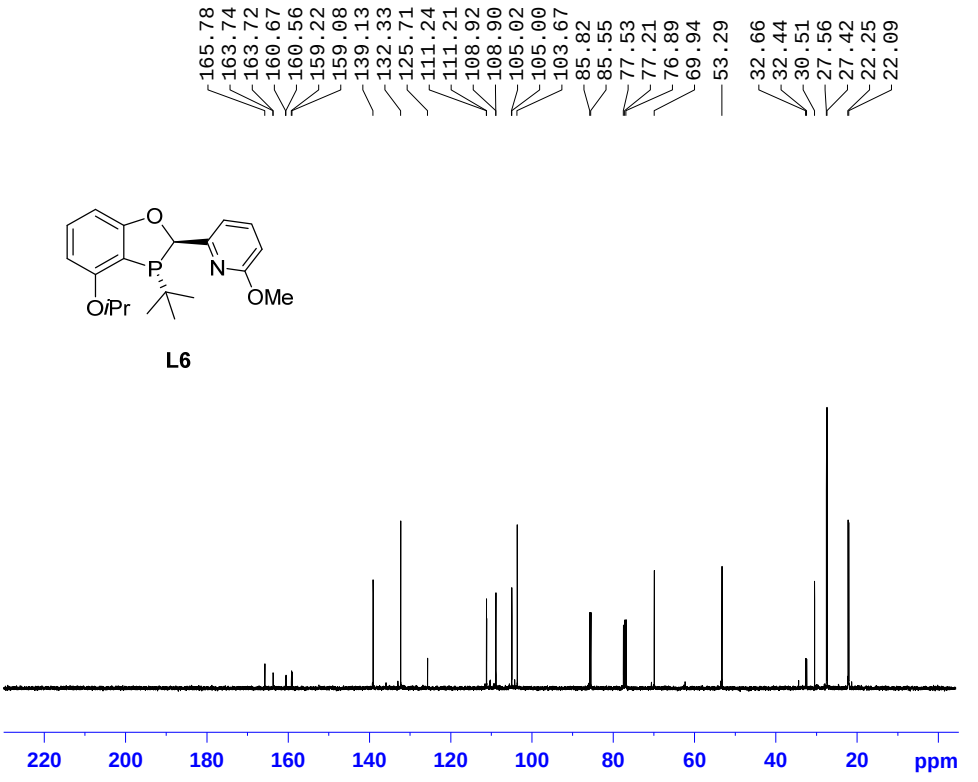



```
Current Data Parameters
NAME          10854-042
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20160526
Time              17.21
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg
TD               262144
SOLVENT           CDCl3
NS                  300
DS                    0
SWH           31250.000 Hz
FIDRES         0.119209 Hz
AQ            4.1943040 sec
RG                 2050
DW               16.000 usec
DE                6.50 usec
TE                299.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         125.7698617 MHz
NUC1                 13C
P1                9.75 usec
PLW1       126.00000000 W

======== CHANNEL f2 ========
SFO2         500.1325007 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         18.39999962 W
PLW12         0.41056001 W
PLW13         0.20651001 W

F2 - Processing parameters
SI               131072
SF          125.7577596 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.40
```

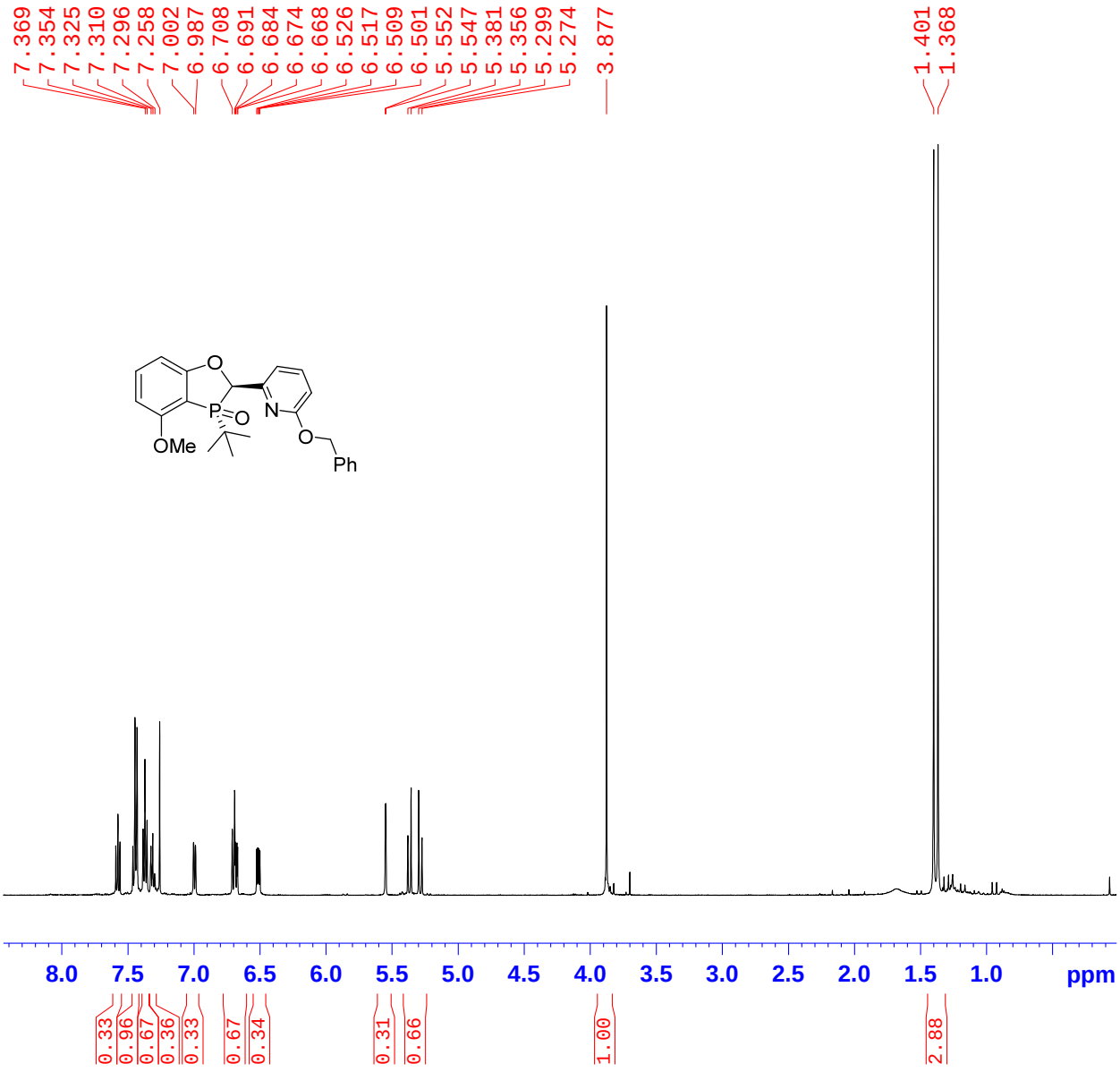


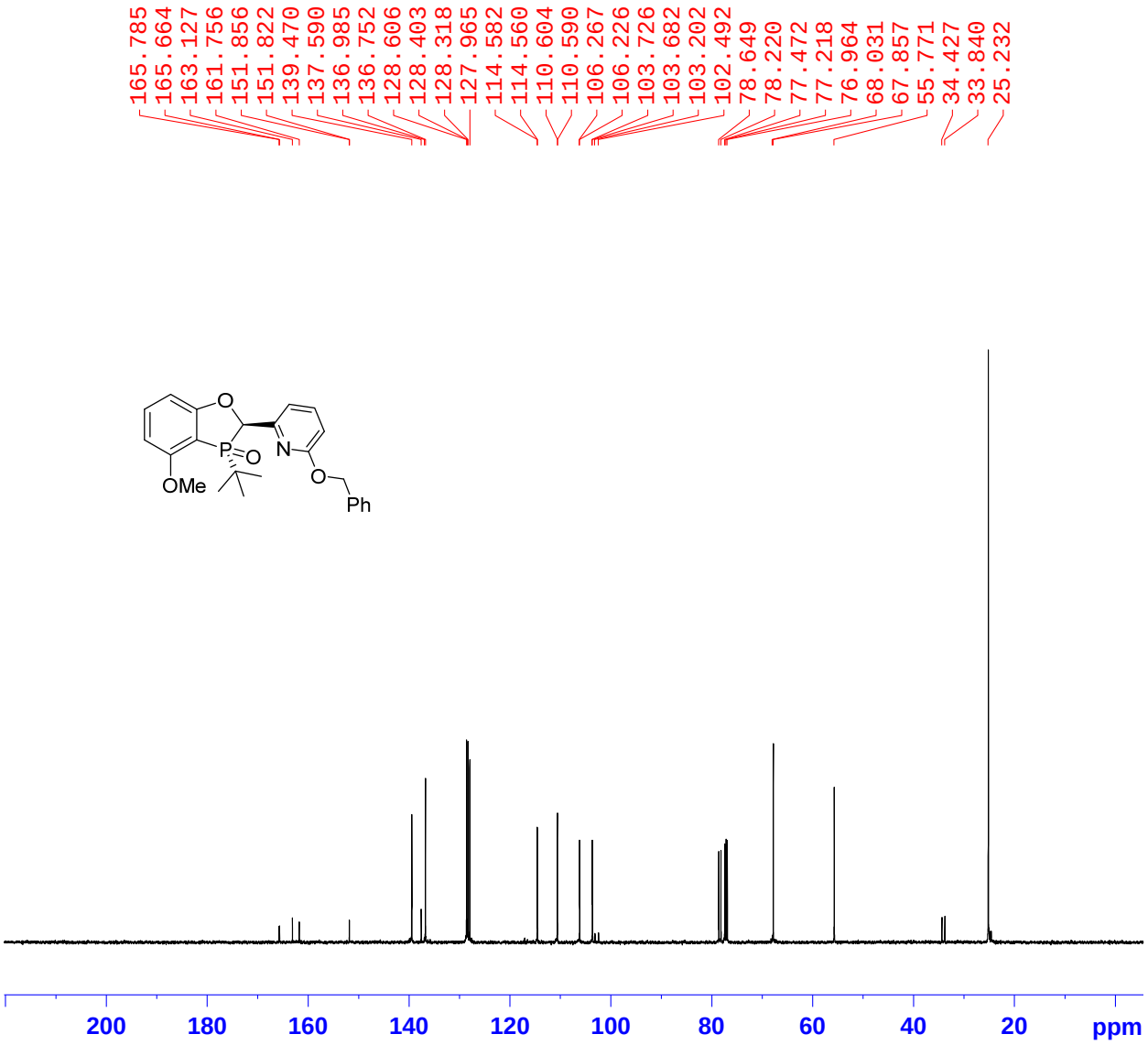


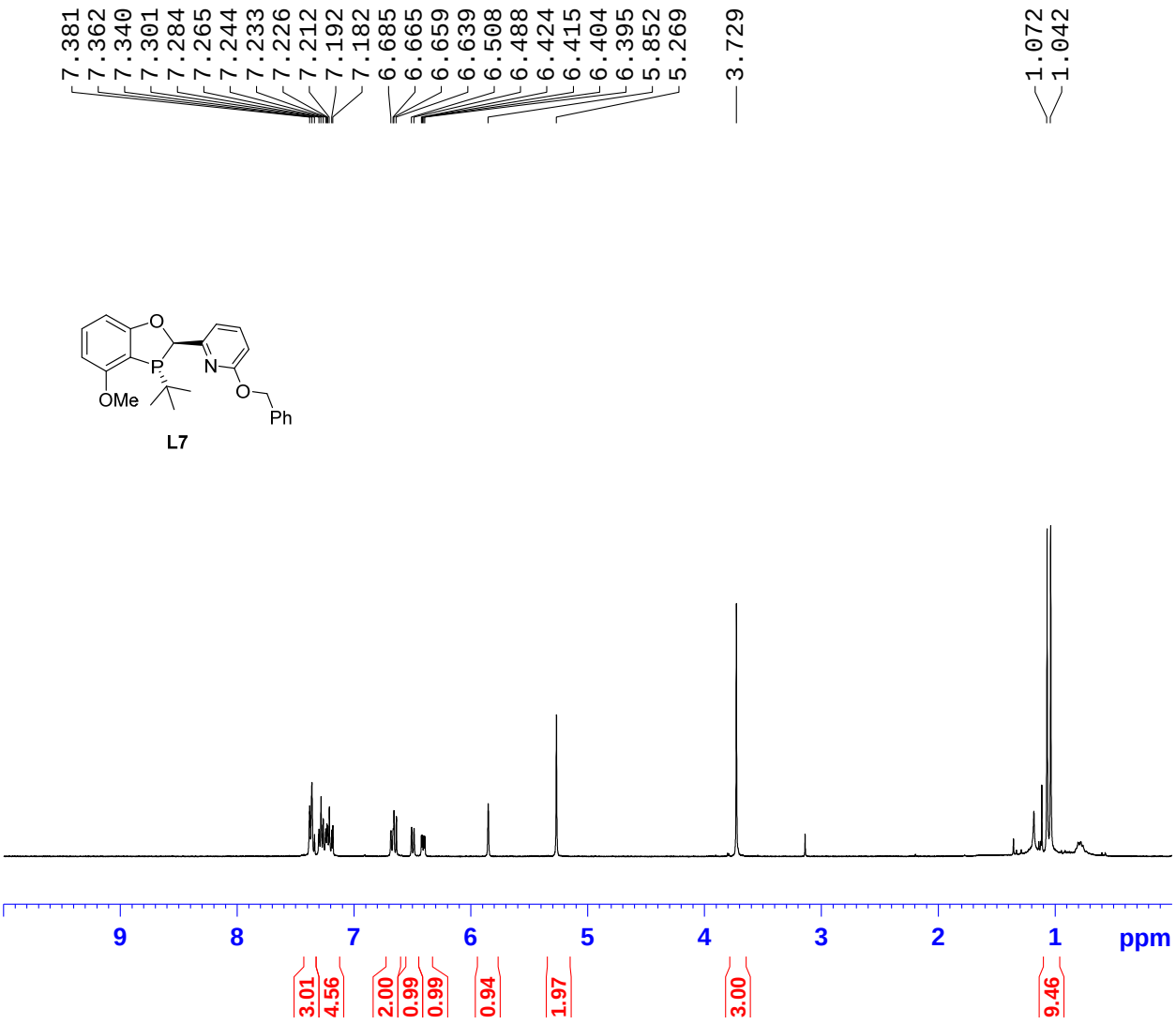

```
Current Data Parameters
NAME          10854-033
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_           20150924
Time               10.26
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg10
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     4
SWH             5896.227 Hz
FIDRES          0.179939 Hz
AQ             2.7787263 sec
RG                   287
DW                84.800 usec
DE                 6.50 usec
TE                295.7 K
D1             2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1       0 dB
PL1W        10.49968529 W
SFO1        400.1327209 MHz

F2 - Processing parameters
SI                65536
SF           400.1300116 MHz
WDW                  EM
SSB       0
LB                0.05 Hz
GB        0
PC                1.00
```

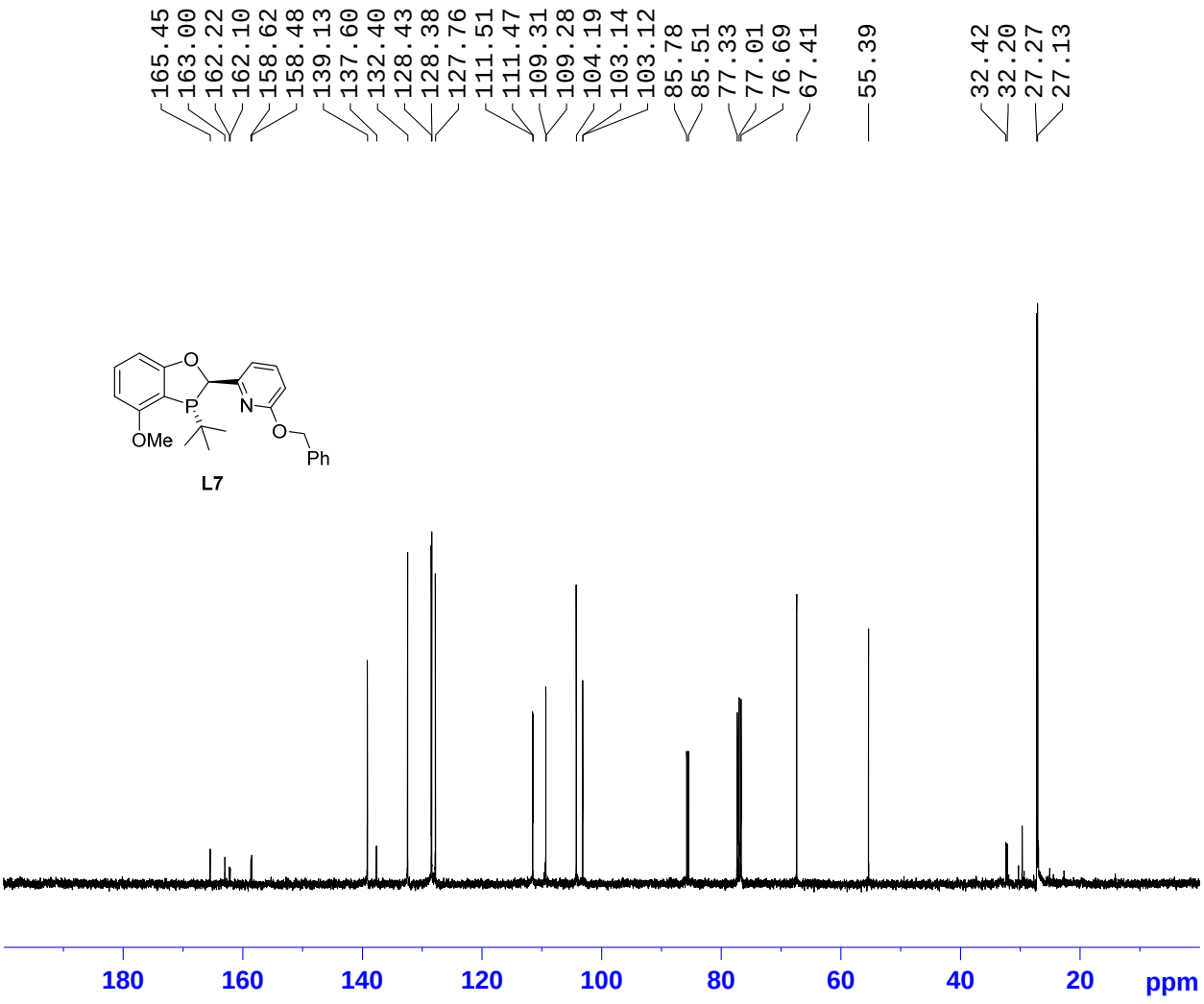


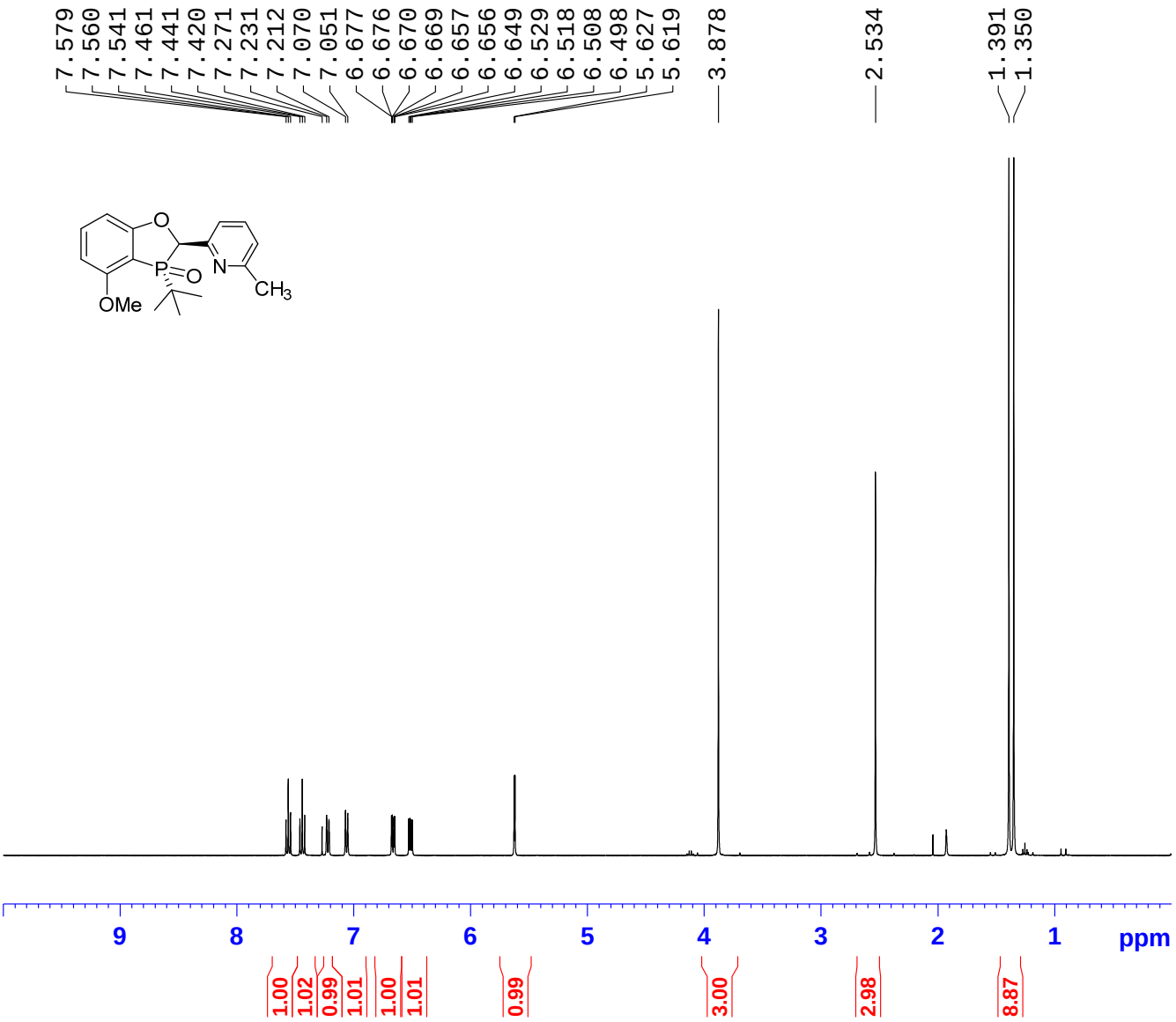

```
Current Data Parameters
NAME          10854-033
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_           20150924
Time               11.00
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ             0.6815744 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                296.4 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   1
SFO1         100.6243395 MHz
NUC1                 13C
P1                10.10 usec
PLW1        -1.00000000 W
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        -1.00000000 W
PLW12       -1.00000000 W
PLW13       -1.00000000 W

F2 - Processing parameters
SI                65536
SF           100.6127510 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

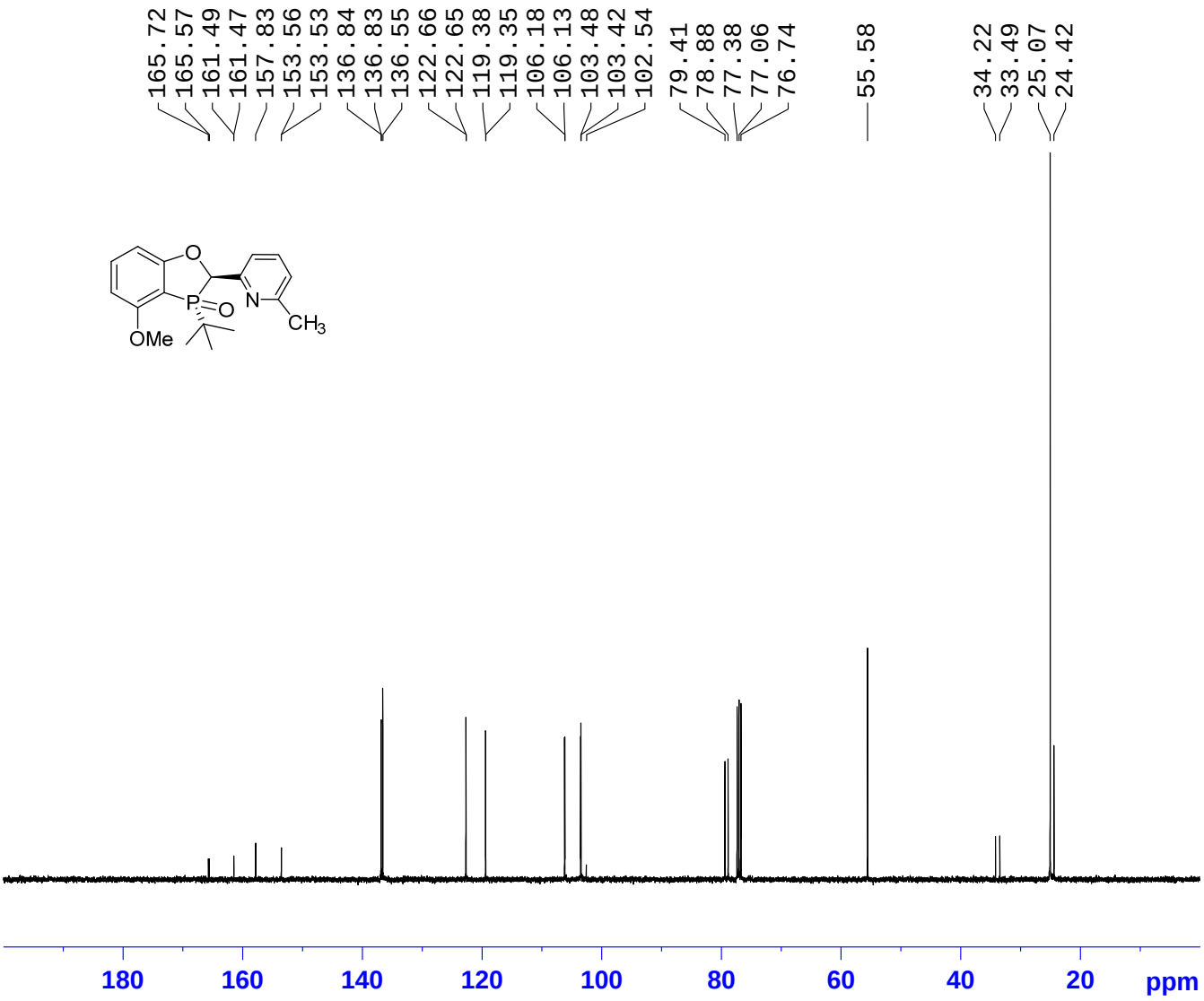

7.369
7.354
7.325
7.310
7.296
7.258
7.002
6.987
6.708
6.691
6.684
6.674
6.668
6.526
6.517
6.509
6.501
5.552
5.547
5.381
5.356
5.299
5.274
3.877
1.401
1.368
O
P
O
N
O
OMe
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.33
0.96
0.67
0.36
0.33
0.67
0.34
0.31
0.66
1.00
2.88

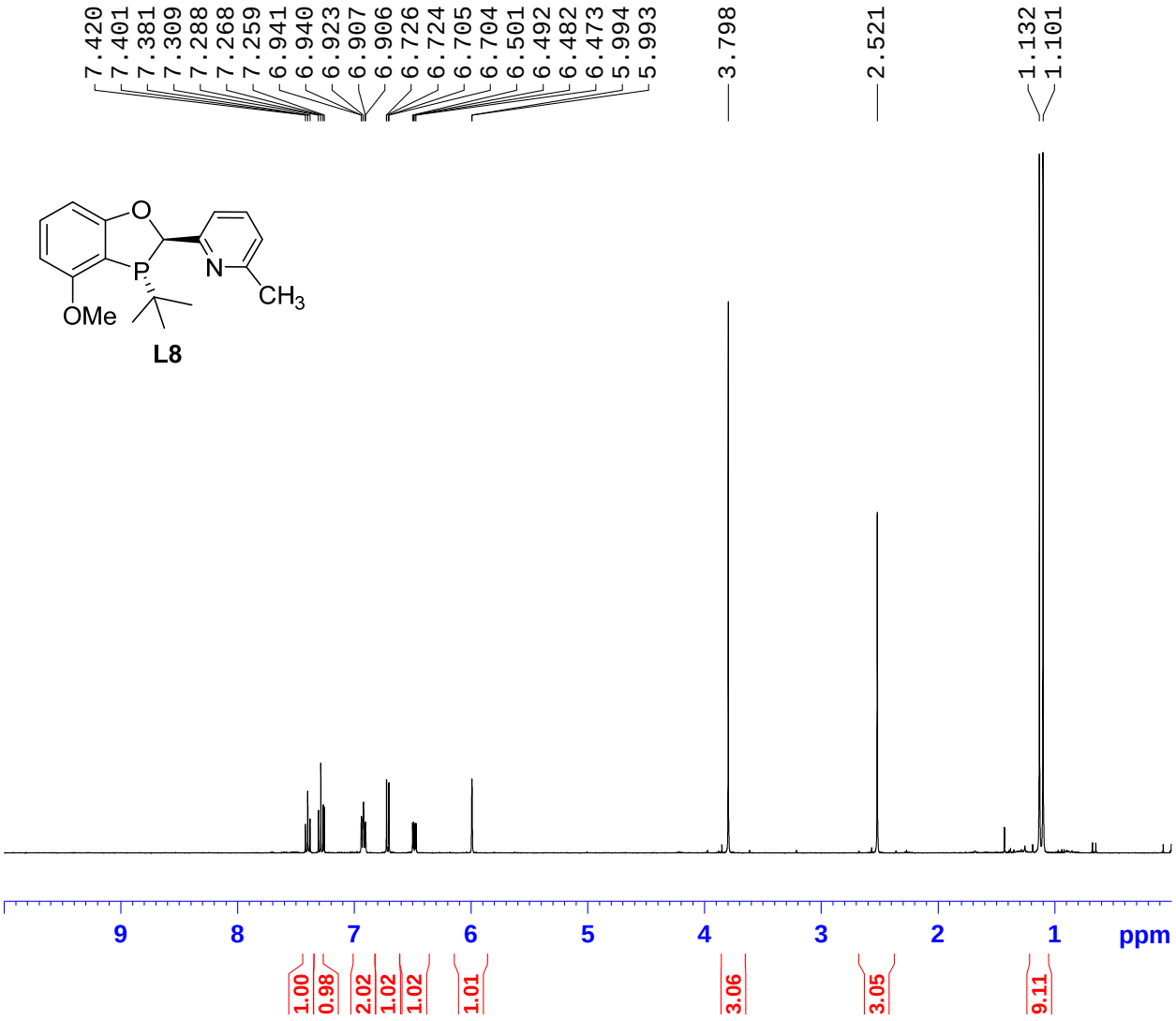

165.785
165.664
163.127
161.756
151.856
151.822
139.470
137.590
136.985
136.752
128.606
128.403
128.318
127.965
114.582
114.560
110.604
110.590
106.267
106.226
103.726
103.682
103.202
102.492
78.649
78.220
77.472
77.218
76.964
68.031
67.857
55.771
34.427
33.840
25.232
O
P
O
N
O
OMe
Ph
200
180
160
140
120
100
80
60
40
20
ppm

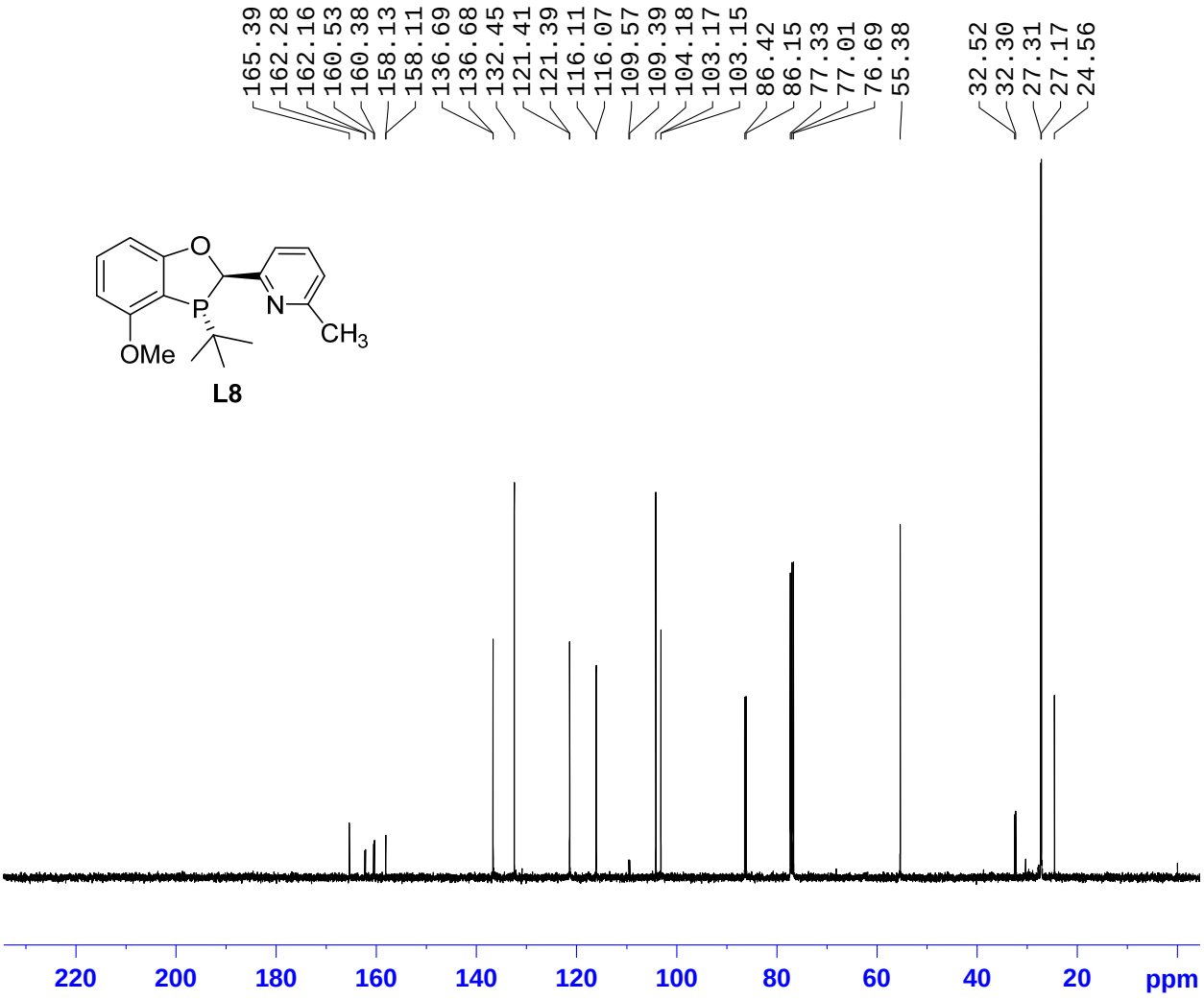

7.381
7.362
7.340
7.301
7.284
7.265
7.244
7.233
7.226
7.212
7.192
7.182
6.685
6.665
6.659
6.639
6.508
6.488
6.424
6.415
6.404
6.395
5.852
5.269
3.729
1.072
1.042
O
P
N
O
OMe
Ph
L7
9
8
7
6
5
4
3
2
1
ppm
3.01
4.56
2.00
0.99
0.99
0.94
1.97
3.00
9.46


165.45
163.00
162.22
162.10
158.62
158.48
139.13
137.60
132.40
128.43
128.38
127.76
111.51
111.47
109.31
109.28
104.19
103.14
103.12
85.78
85.51
77.33
77.01
76.69
67.41
55.39
32.42
32.20
27.27
27.13
O
P
N
O
OMe
Ph
L7
180
160
140
120
100
80
60
40
20
ppm

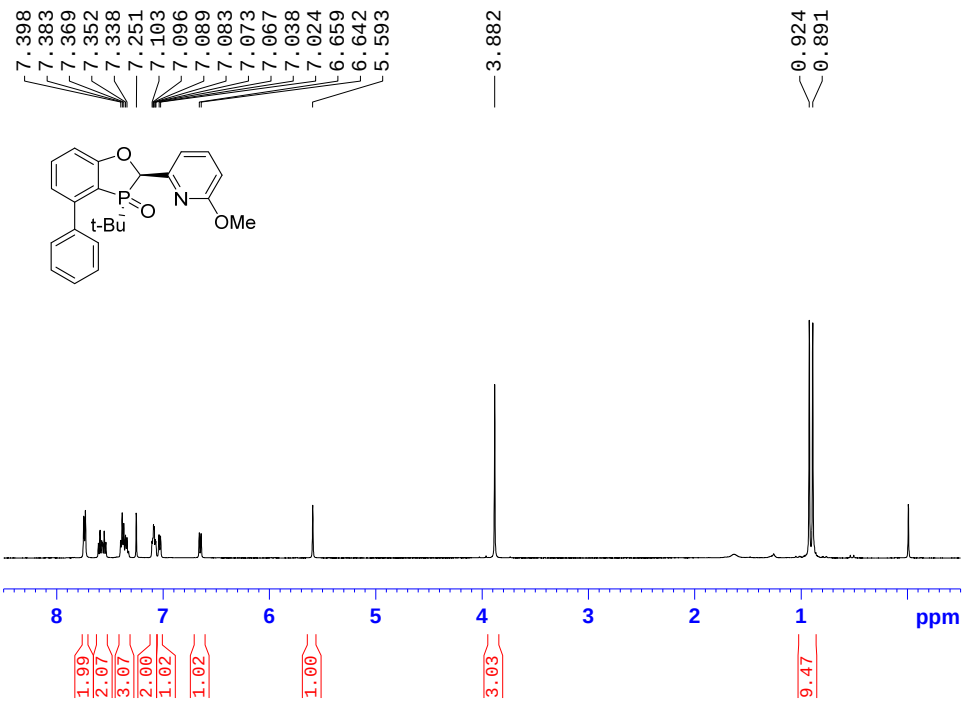

7.579
7.560
7.541
7.461
7.441
7.420
7.271
7.231
7.212
7.070
7.051
6.677
6.676
6.670
6.669
6.657
6.656
6.649
6.529
6.518
6.508
6.498
5.627
5.619
3.878
2.534
1.391
1.350
O
P
O
N
CH3
OMe
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
0.99
1.01
1.00
1.01
0.99
3.00
2.98
8.87


165.72
165.57
161.49
161.47
157.83
153.56
153.53
136.84
136.83
136.55
122.66
122.65
119.38
119.35
106.18
106.13
103.48
103.42
102.54
79.41
78.88
77.38
77.06
76.74
55.58
34.22
33.49
25.07
24.42
O
P
O
N
CH3
OMe
180
160
140
120
100
80
60
40
20
ppm

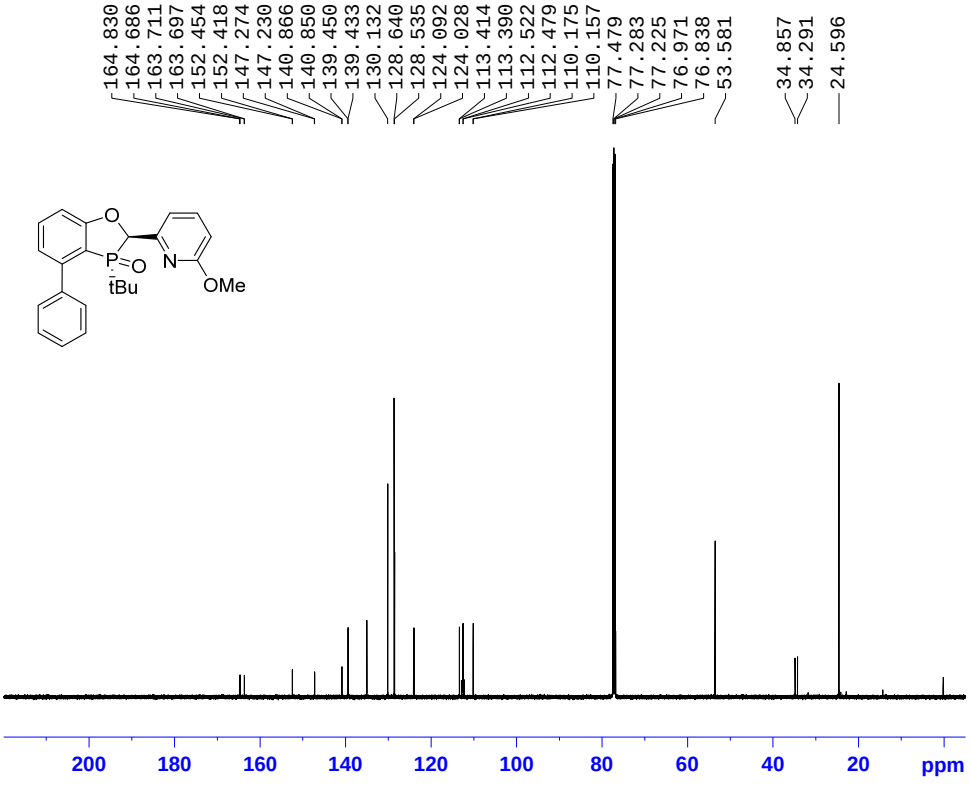

7.420
7.401
7.381
7.309
7.288
7.268
7.259
6.941
6.940
6.923
6.907
6.906
6.726
6.724
6.705
6.704
6.501
6.492
6.482
6.473
5.994
5.993
3.798
2.521
1.132
1.101
O
P
N
CH3
OMe
L8
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
2.02
1.02
1.02
1.01
3.06
3.05
9.11


165.39
162.28
162.16
160.53
160.38
158.13
158.11
136.69
136.68
132.45
121.41
121.39
116.11
116.07
109.57
109.39
104.18
103.17
103.15
86.42
86.15
77.33
77.01
76.69
55.38
32.52
32.30
27.31
27.17
24.56
O
P
N
CH3
OMe
220
200
180
160
140
120
100
80
60
40
20
ppm

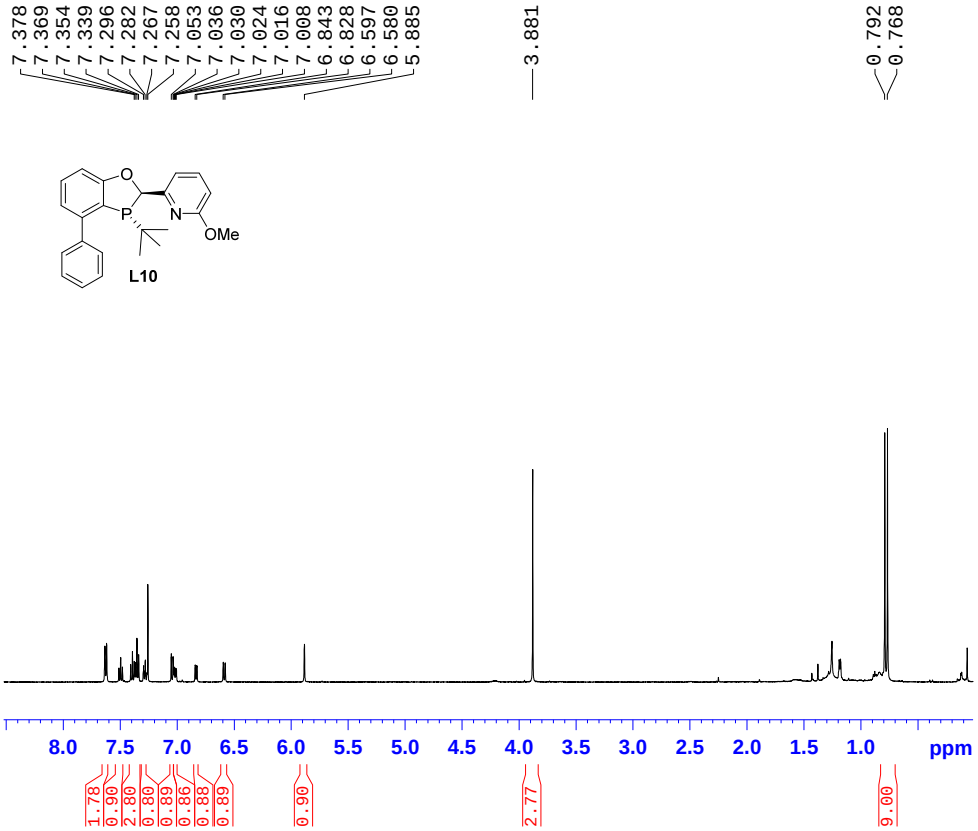
L8



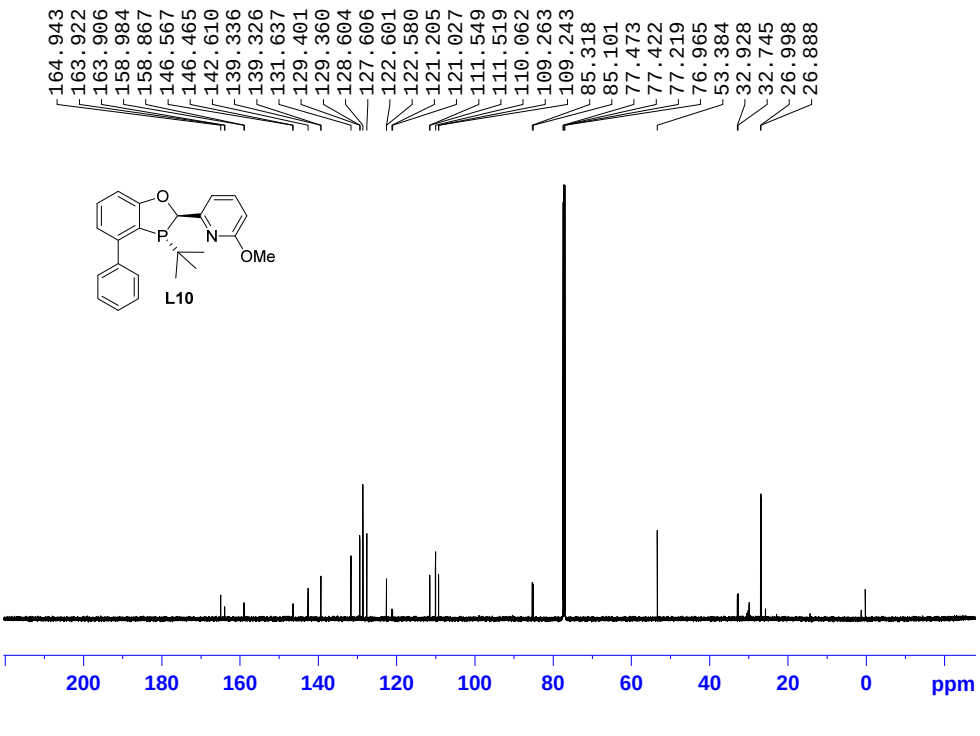

```
Current Data Parameters
NAME          10854-063
EXPNO                 8
PROCNO                1

F2 - Acquisition Parameters
Date_          20151019
Time              14.56
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         q_zg10
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    0
SWH            9014.423 Hz
FIDRES         0.275098 Hz
AQ             1.8175317 sec
RG                  512
DW               55.467 usec
DE                6.50 usec
TE                299.0 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                11.95 usec
PL1                2.10 dB
PL1W        18.43091774 W
SFO1        500.1334009 MHz

F2 - Processing parameters
SI                16384
SF          500.1300172 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



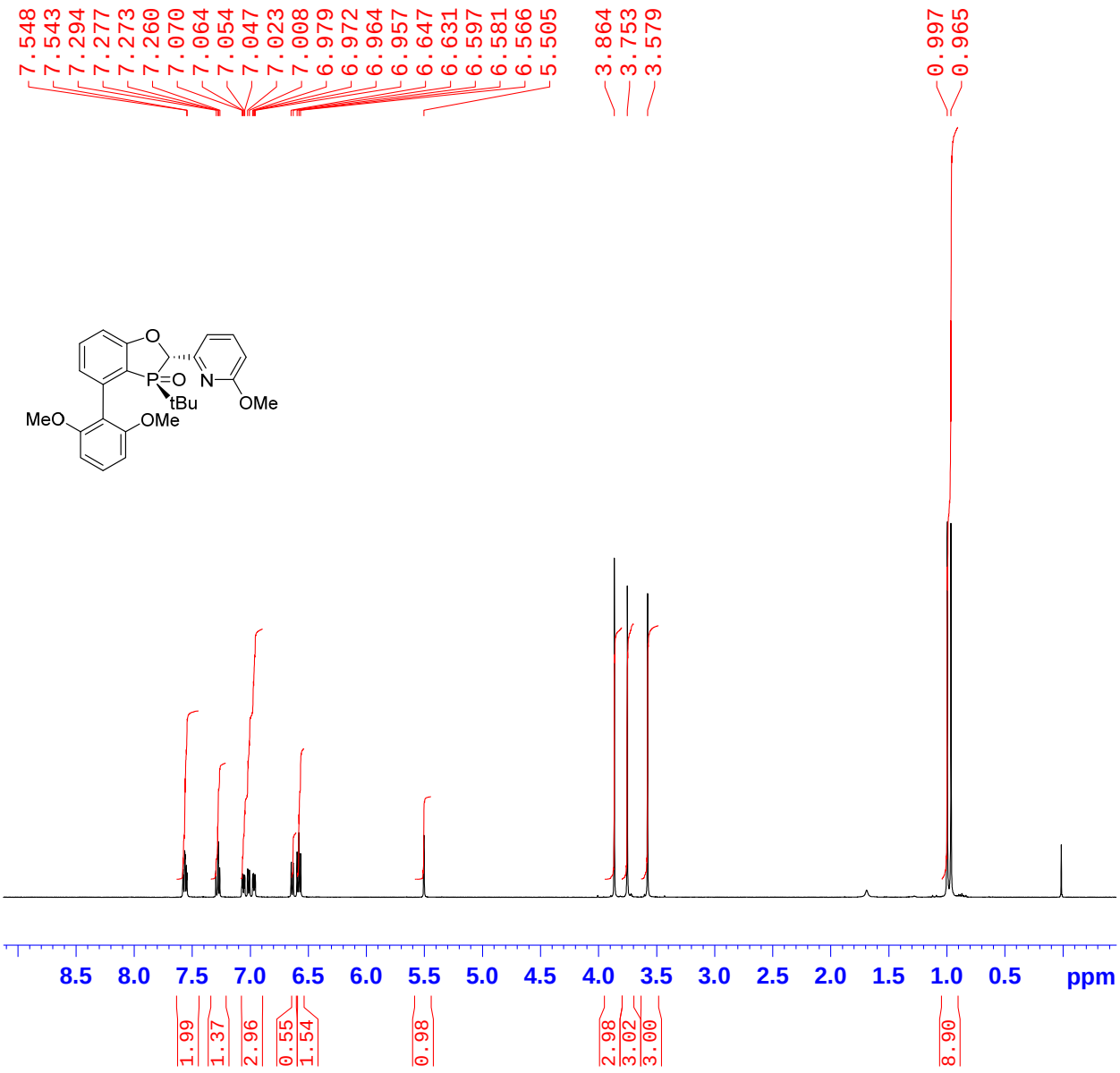

```
Current Data Parameters
NAME          10854-063
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20151020
Time              0.10
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg
TD              262144
SOLVENT           CDCl3
NS                3500
DS                   0
SWH           31250.000 Hz
FIDRES         0.119209 Hz
AQ             4.1943040 sec
RG                2050
DW              16.000 usec
DE                6.50 usec
TE                299.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                   1
SFO1        125.7698617 MHz
NUC1                 13C
P1                9.75 usec
PLW1        -1.00000000 W
SFO2        500.1325007 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        -1.00000000 W
PLW12       -1.00000000 W
PLW13       -1.00000000 W

F2 - Processing parameters
SI               131072
SF          125.7577627 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.40
```




```
Current Data Parameters
NAME          10854-065
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160526
Time              22.05
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7500.000 Hz
FIDRES         0.228882 Hz
AQ           2.1845334 sec
RG                  575
DW               66.667 usec
DE                6.50 usec
TE                299.0 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.1325007 MHz
NUC1                  1H
P1                11.75 usec
PLW1        18.39999962 W

F2 - Processing parameters
SI                16384
SF          500.1300119 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```




```
Current Data Parameters
NAME          10854-065
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20160527
Time               6.55
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg
TD               262144
SOLVENT           CDCl3
NS                 6000
DS                    0
SWH           31250.000 Hz
FIDRES         0.119209 Hz
AQ            4.1943040 sec
RG                 2050
DW               16.000 usec
DE                6.50 usec
TE                299.0 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7698617 MHz
NUC1                 13C
P1                9.75 usec
PLW1       126.00000000 W

======== CHANNEL f2 ========
SFO2        500.1325007 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        18.39999962 W
PLW12        0.41056001 W
PLW13        0.20651001 W

F2 - Processing parameters
SI               131072
SF          125.7577610 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.40
```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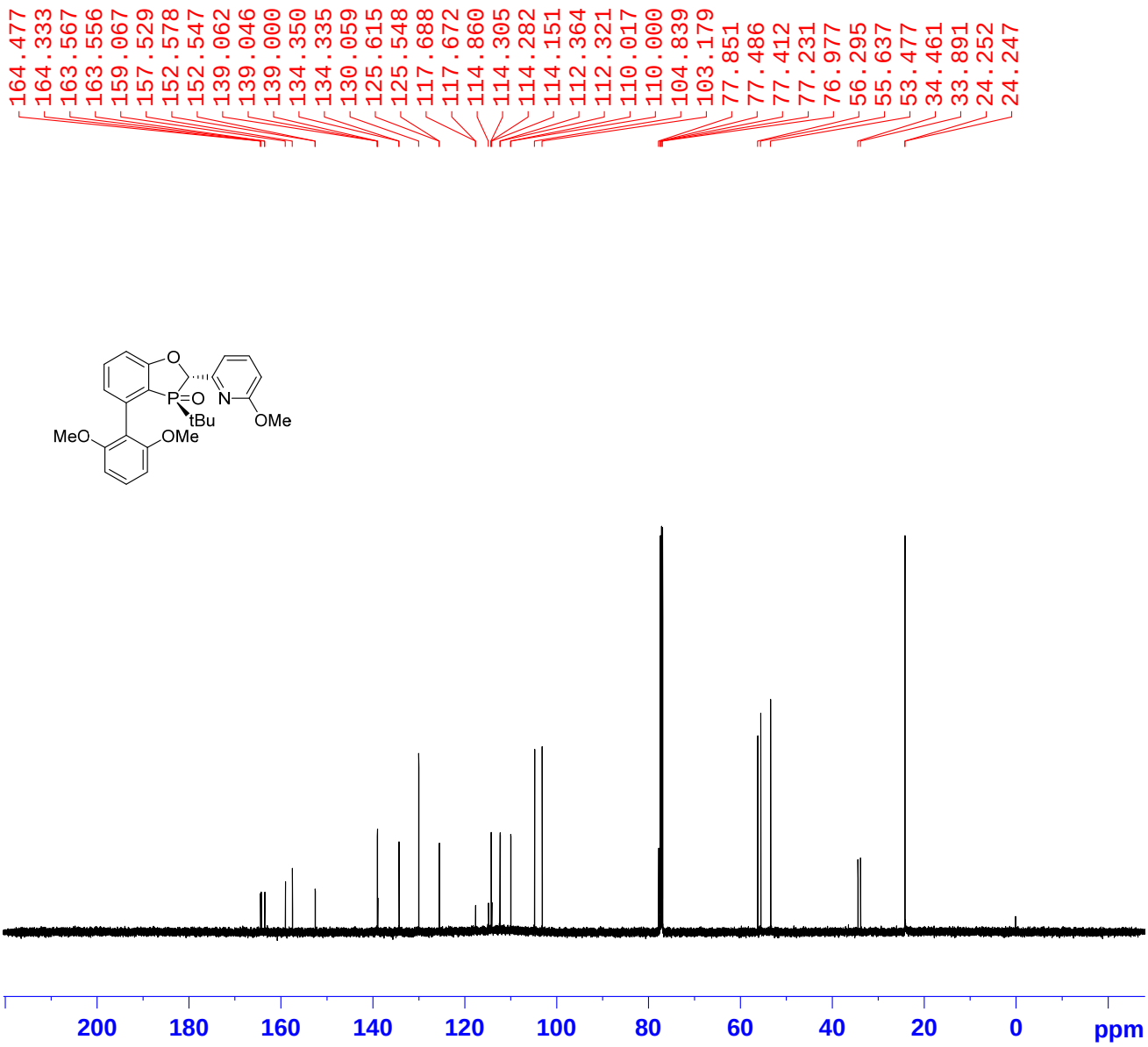
7.543
7.294
7.277
7.273
7.260
7.070
7.064
7.054
7.047
7.023
7.008
6.979
6.972
6.964
6.957
6.647
6.631
6.597
6.581
6.566
5.505
3.864
3.753
3.579
0.997
0.965
O
P=O
tBu
N
OMe
MeO
OMe
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.99
1.37
2.96
0.55
1.54
0.98
2.98
3.02
3.00
8.90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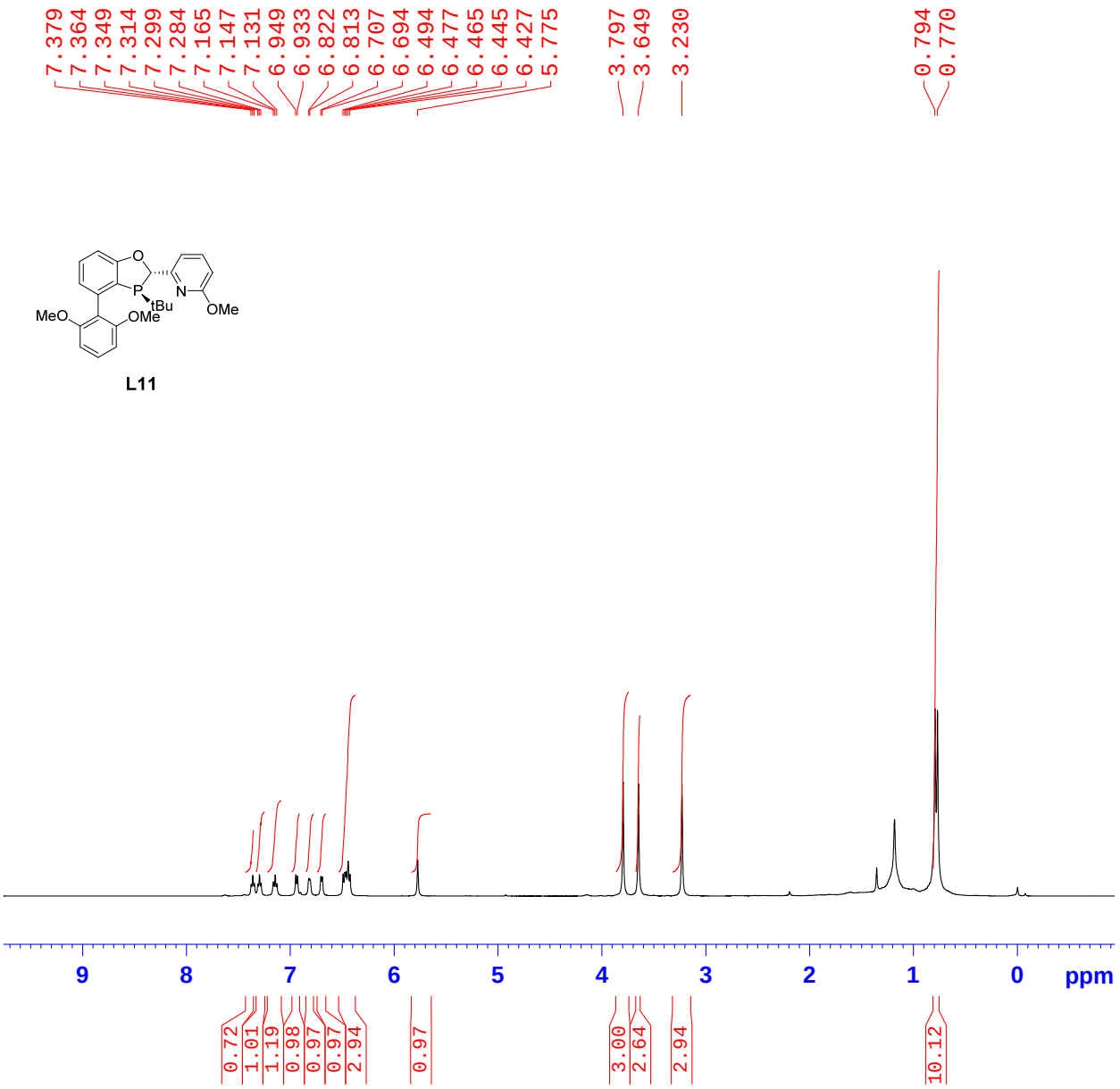
164.333
163.567
163.556
159.067
157.529
152.578
152.547
139.062
139.046
139.000
134.350
134.335
130.059
125.615
125.548
117.688
117.672
114.860
114.305
114.282
114.151
112.364
112.321
110.017
110.000
104.839
103.179
77.851
77.486
77.412
77.231
76.977
56.295
55.637
53.477
34.461
33.891
24.252
24.247
O
P=O
tBu
N
OMe
MeO
OMe
200
180
160
140
120
100
80
60
40
20
0
ppm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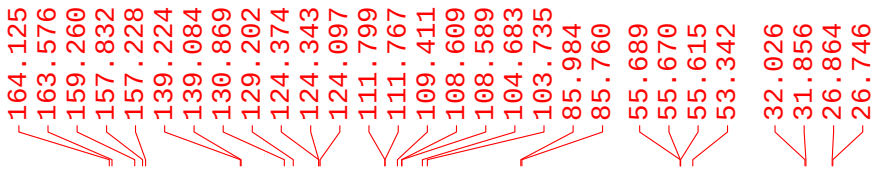
7.364
7.349
7.314
7.299
7.284
7.165
7.147
7.131
6.949
6.933
6.822
6.813
6.707
6.694
6.494
6.477
6.465
6.445
6.427
5.775
3.797
3.649
3.230
0.794
0.770
O
P
tBu
N
MeO
OMe
OMe
L11
9
8
7
6
5
4
3
2
1
0
ppm
0.72
1.01
1.19
0.98
0.97
0.97
2.94
0.97
3.00
2.64
2.94
10.12


164.125
163.576
159.260
157.832
157.228
139.224
139.084
130.869
129.202
124.374
124.343
124.097
111.799
111.767
109.411
108.609
108.589
104.683
103.735
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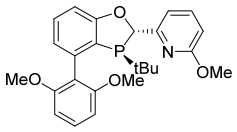
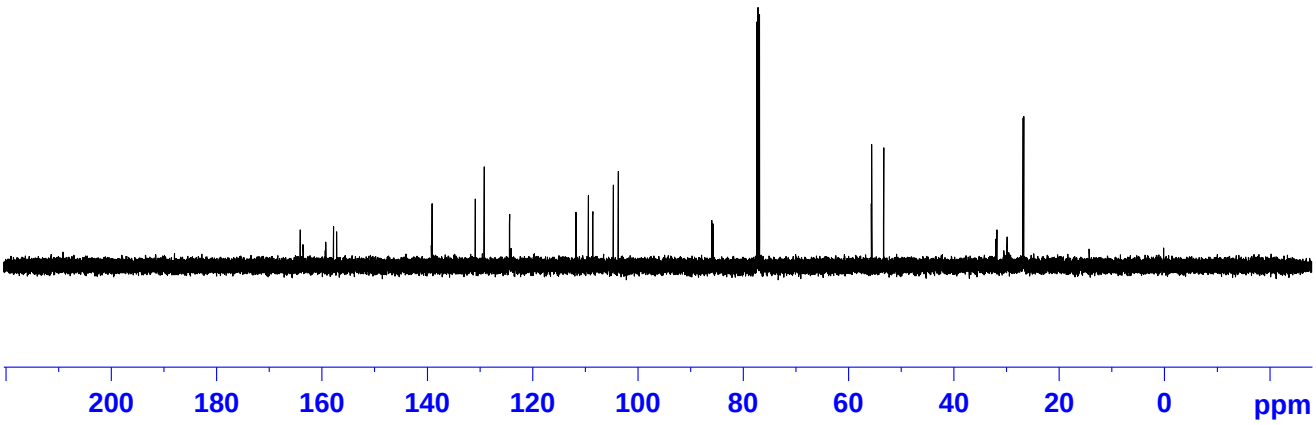
85.760
55.689
55.670
55.615
53.342
32.026
31.856
26.864
26.746


O
P
N
tBu
MeO
OMe
OMe

L11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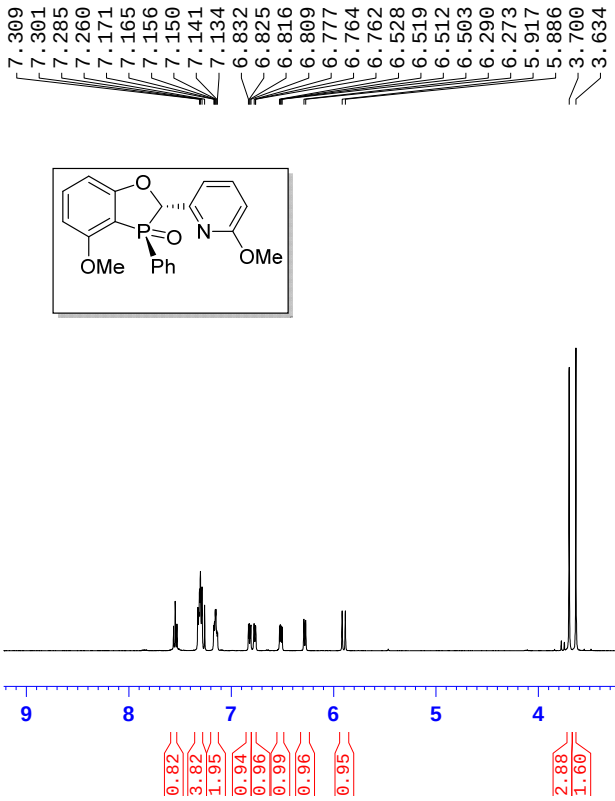
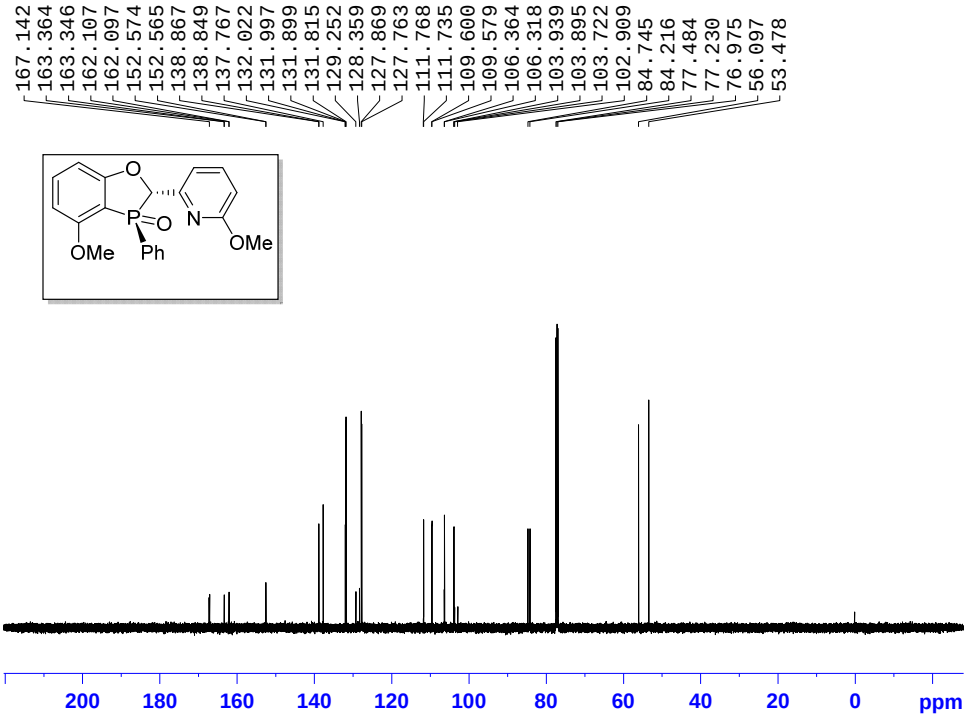
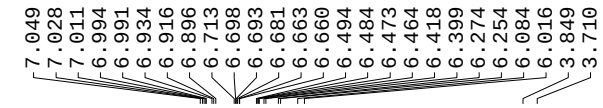
180
160
140
120
100
80
60
40
20
0
ppm

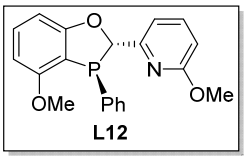


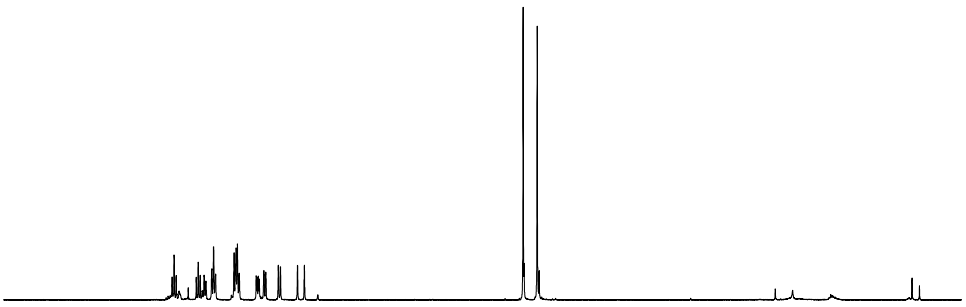

```
Current Data Parameters
NAME          10889-181
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160606
Time              10.43
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7500.000 Hz
FIDRES         0.228882 Hz
AQ             2.1845334 sec
RG                  362
DW               66.667 usec
DE                6.50 usec
TE                299.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.1325007 MHz
NUC1                1H
P1                11.75 usec
PLW1        18.39999962 W

F2 - Processing parameters
SI                16384
SF          500.1300112 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

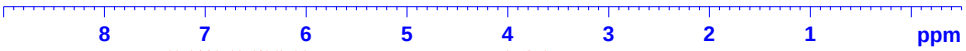


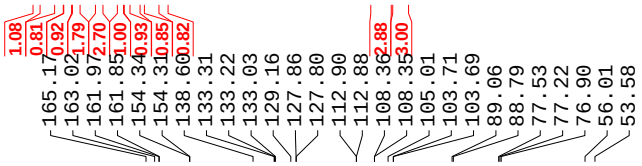

```
Current Data Parameters
NAME          10889-181
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20160606
Time              11.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg
TD                262144
SOLVENT           CDCl3
NS                  200
DS                    0
SWH           31250.000 Hz
FIDRES         0.119209 Hz
AQ             4.1943040 sec
RG                 2050
DW               16.000 usec
DE                6.50 usec
TE                299.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7698617 MHz
NUC1                13C
P1                 9.75 usec
PLW1       126.00000000 W

======== CHANNEL f2 ========
SFO2        500.1325007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        18.39999962 W
PLW12        0.41056001 W
PLW13        0.20651001 W

F2 - Processing parameters
SI                131072
SF          125.7577638 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.40
```

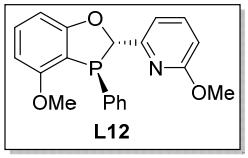


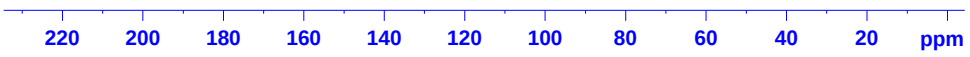






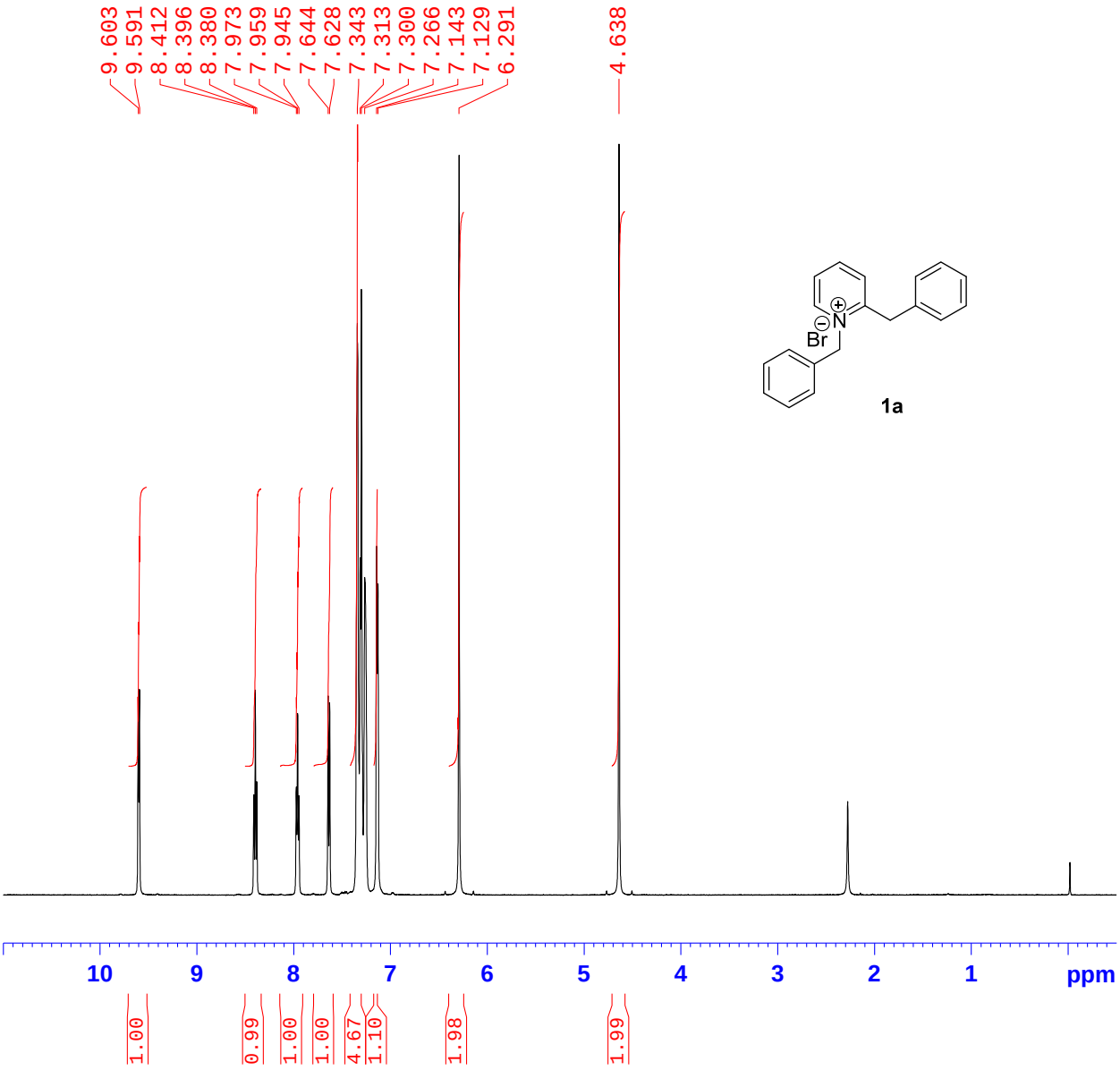







```
Current Data Parameters
NAME          10889-186
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20160527
Time              11.17
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT           CDCl3
NS                    4
DS                    4
SWH            5896.227 Hz
FIDRES         0.179939 Hz
AQ           2.7787263 sec
RG                  456
DW               84.800 usec
DE                6.50 usec
TE               298.0 K
D1          2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1327209 MHz
NUC1                1H
P1                15.00 usec
PLW1        10.50000000 W

F2 - Processing parameters
SI                65536
SF          400.1300462 MHz
WDW                  EM
SSB      0
LB                0.05 Hz
GB       0
PC                1.00
```

```
Current Data Parameters
NAME          10889-186
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_           20160527
Time              11.54
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg
TD                32768
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ           0.6815744 sec
RG                  912
DW               20.800 usec
DE                6.50 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6243395 MHz
NUC1                13C
P1                10.90 usec
PLW1        43.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        10.50000000 W
PLW12        0.29166999 W
PLW13        0.14670999 W

F2 - Processing parameters
SI                65536
SF          100.6127503 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```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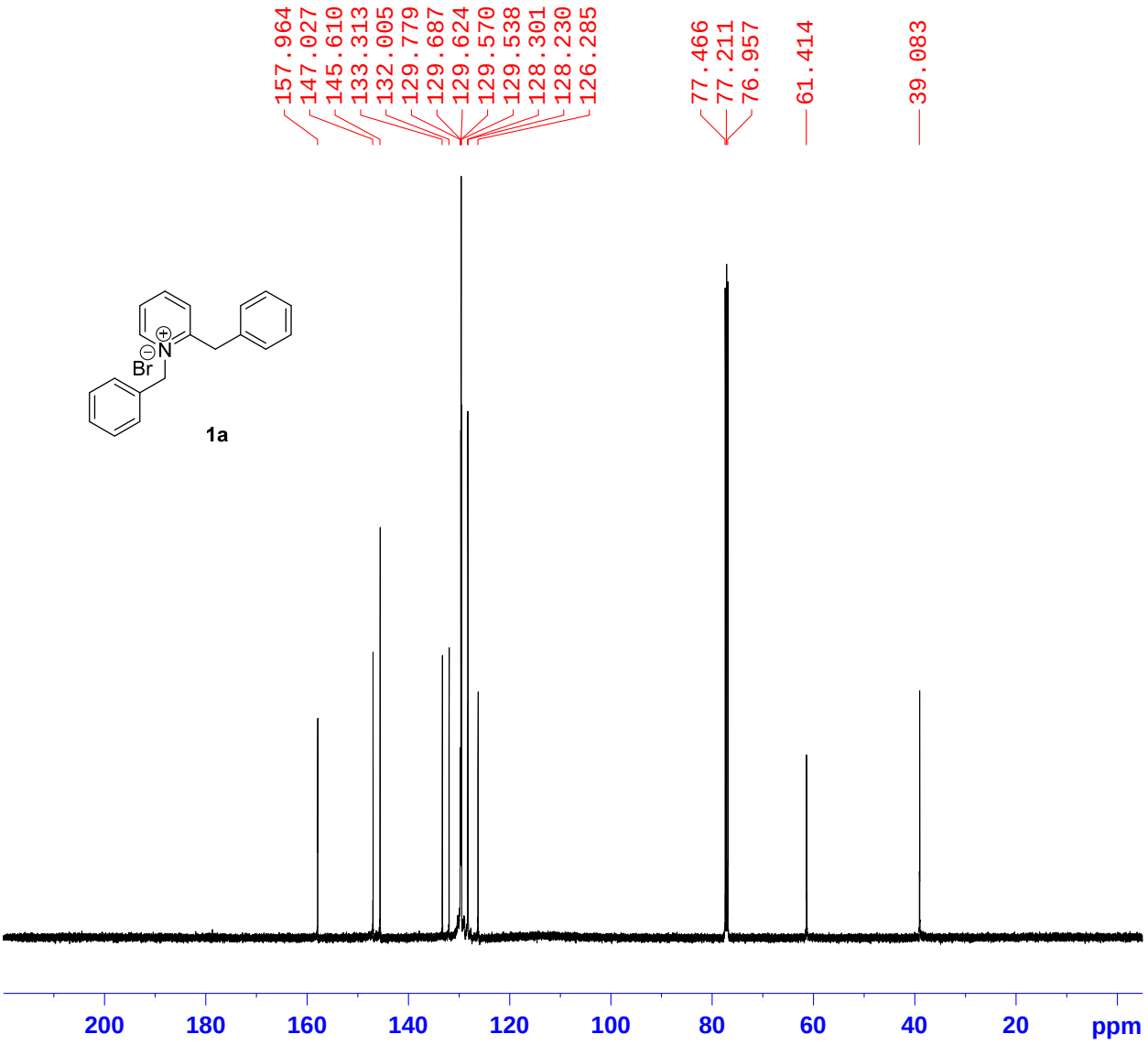
9.591
8.412
8.396
8.380
7.973
7.959
7.945
7.644
7.628
7.343
7.313
7.300
7.266
7.143
7.129
6.291
4.638
Br
1a
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.99
1.00
1.00
4.67
1.10
1.98
1.99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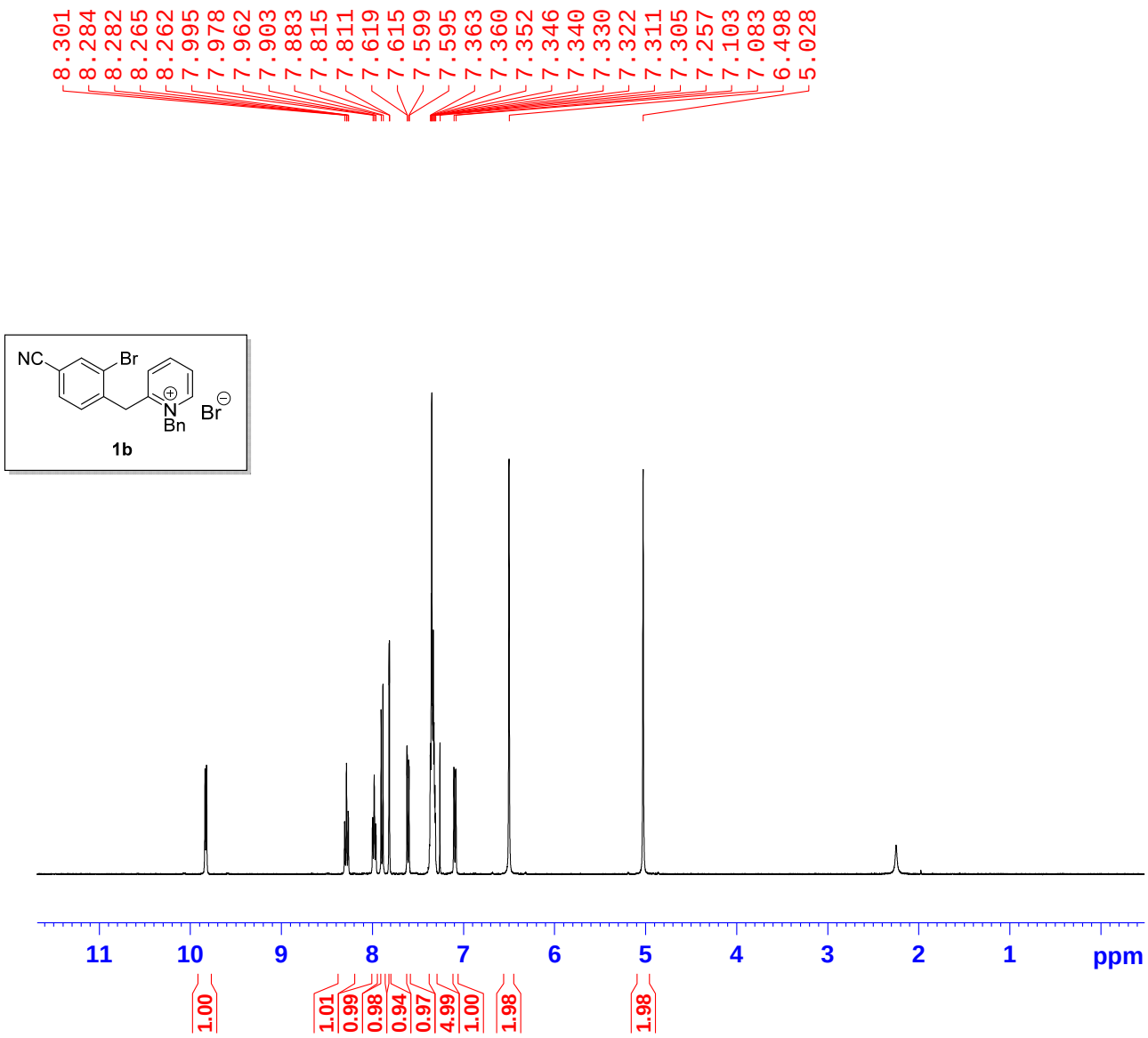
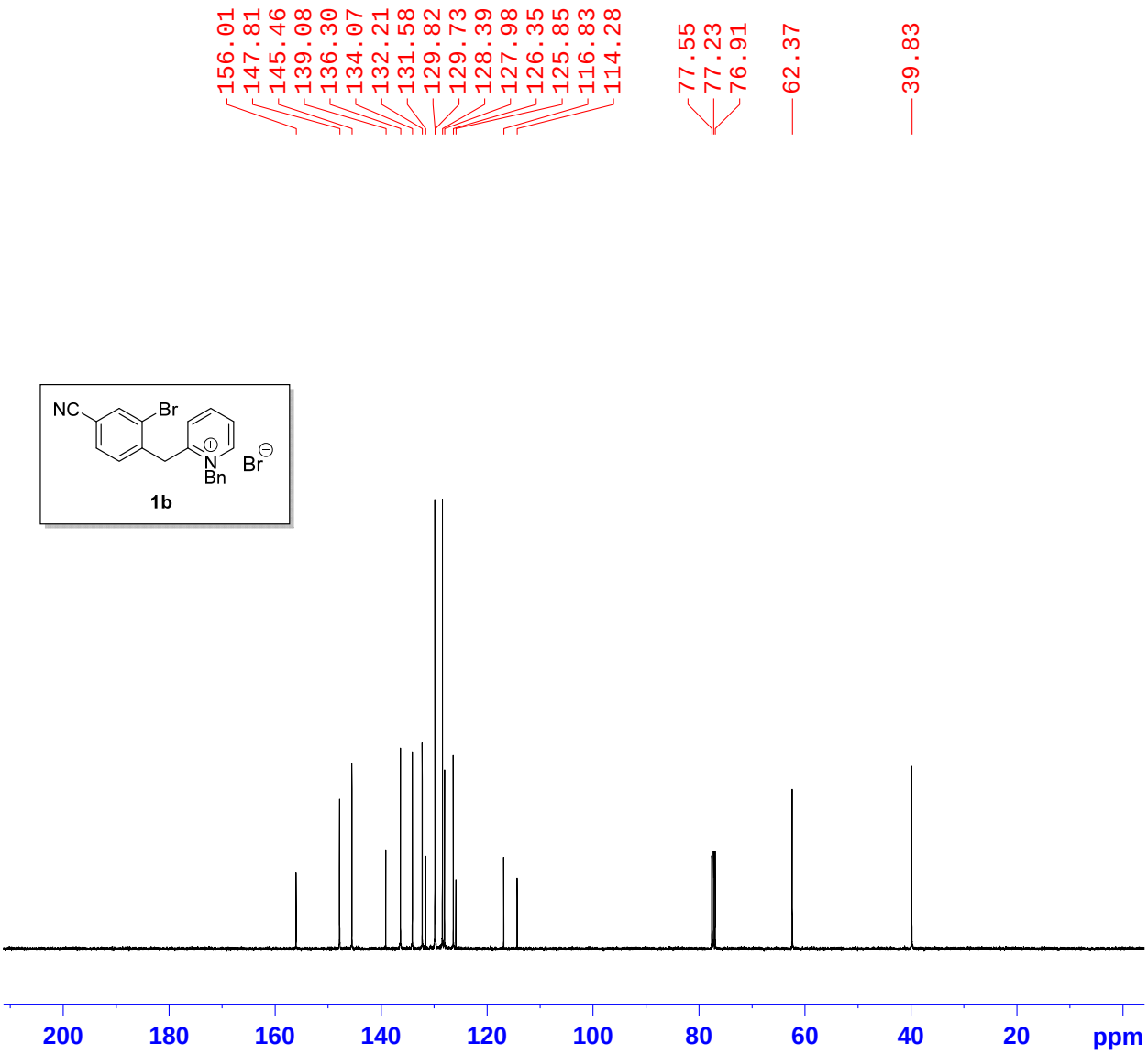
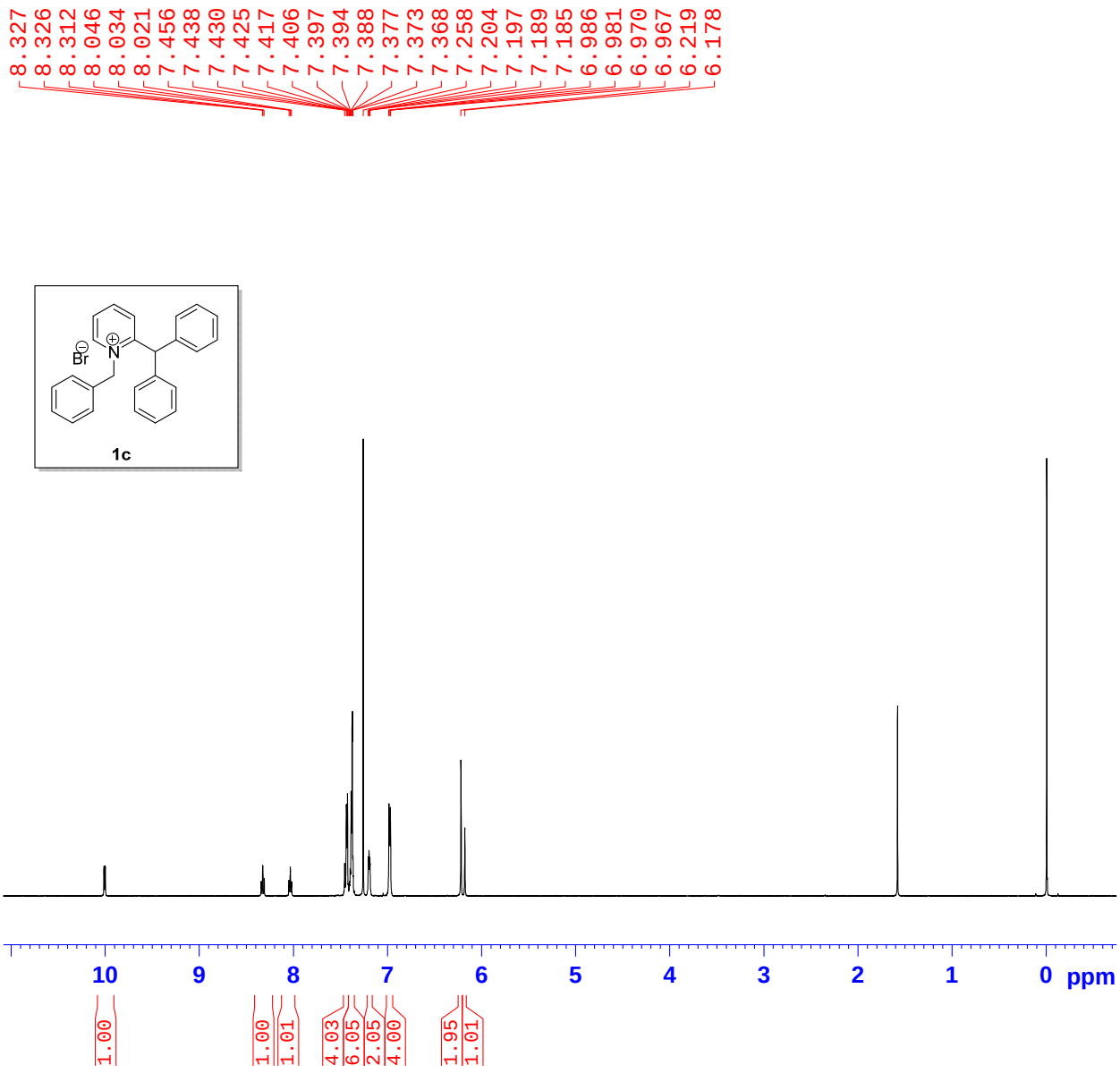
145.610
133.313
132.005
129.779
129.687
129.624
129.570
129.538
128.301
128.230
126.285
77.466
77.211
76.957
61.414
39.083
Br
1a
200
180
160
140
120
100
80
60
40
20
ppm


8.301
8.284
8.282
8.265
8.262
7.995
7.978
7.962
7.903
7.883
7.815
7.811
7.619
7.615
7.599
7.595
7.363
7.360
7.352
7.346
7.340
7.330
7.322
7.311
7.305
7.257
7.103
7.083
6.498
5.028
NC
Br
N
Bn
Br
1b
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
0.99
0.98
0.94
0.97
4.99
1.00
1.98
1.98


156.01
147.81
145.46
139.08
136.30
134.07
132.21
131.58
129.82
129.73
128.39
127.98
126.35
125.85
116.83
114.28
77.55
77.23
76.91
62.37
39.83
NC
Br
N
Bn
Br
1b
200
180
160
140
120
100
80
60
40
20
ppm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8.312
8.046
8.034
8.021
7.456
7.438
7.430
7.425
7.417
7.406
7.397
7.394
7.388
7.377
7.373
7.368
7.258
7.204
7.197
7.189
7.185
6.986
6.981
6.970
6.967
6.219
6.178
Br
N
1c
10
9
8
7
6
5
4
3
2
1
0
ppm
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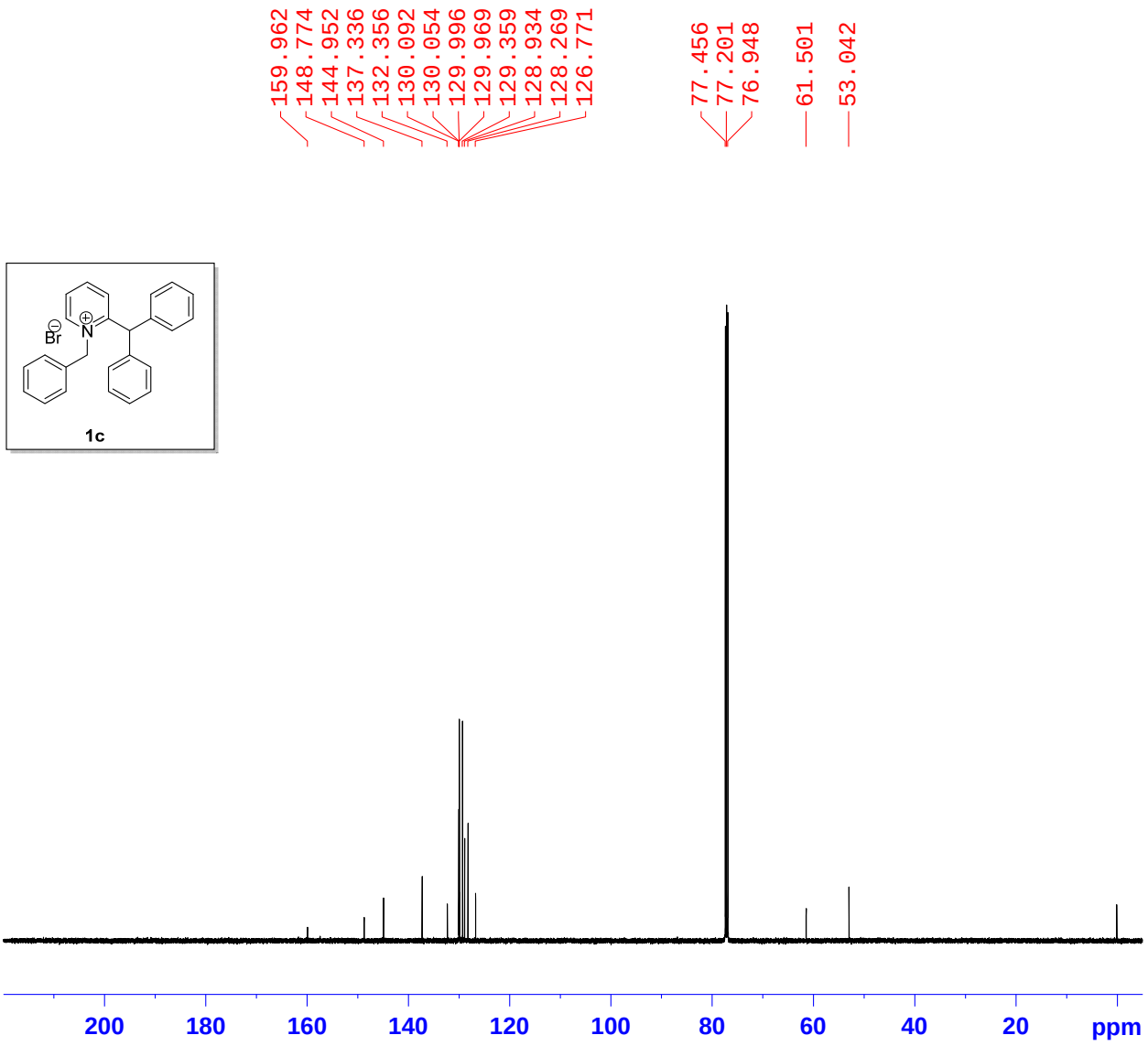
1.00
1.01
4.03
6.05
2.05
4.00
1.95
1.01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130.054
129.996
129.969
129.359
128.934
128.269
126.771
77.456
77.201
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61.501
53.042
Br
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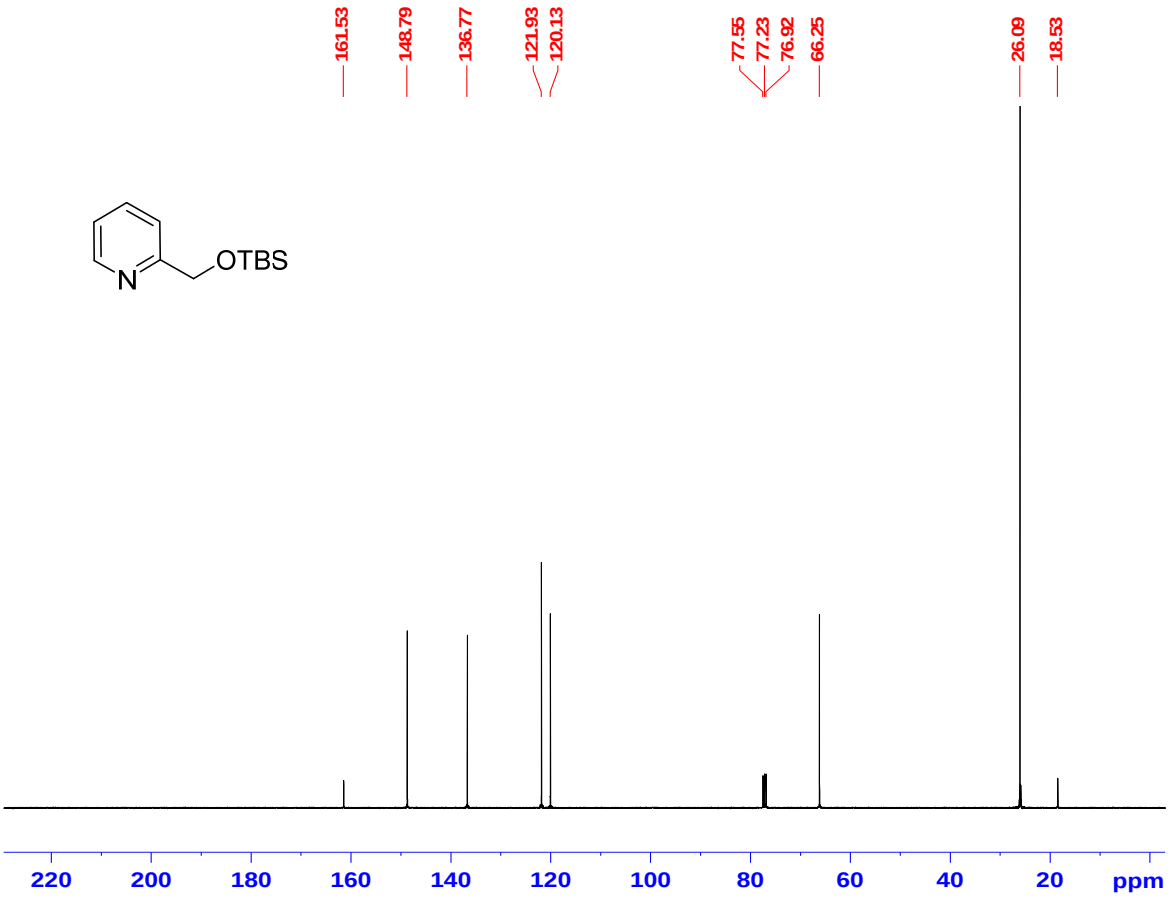
1c
200
180
160
140
120
100
80
60
40
20
ppm


161.53
148.79
136.77
121.93
120.13
77.55
77.23
76.92
66.25
26.09
18.53
OTBS
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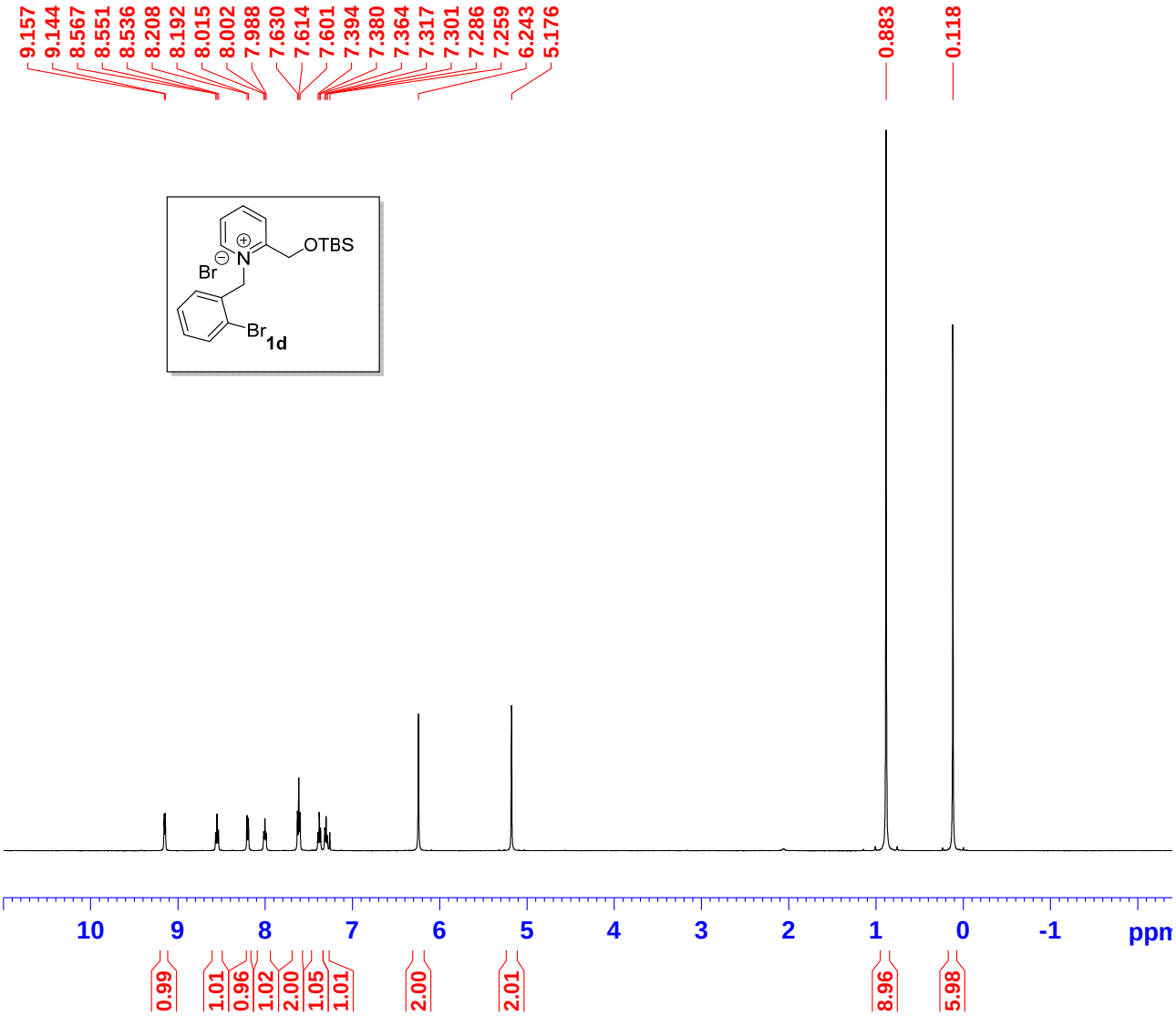
200
180
160
140
120
100
80
60
40
20
ppm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9.144
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8.551
8.536
8.208
8.192
8.015
8.002
7.988
7.630
7.614
7.601
7.394
7.380
7.364
7.317
7.301
7.286
7.259
6.243
5.176
0.883
0.118
OTBS
Br
N
Br
1d
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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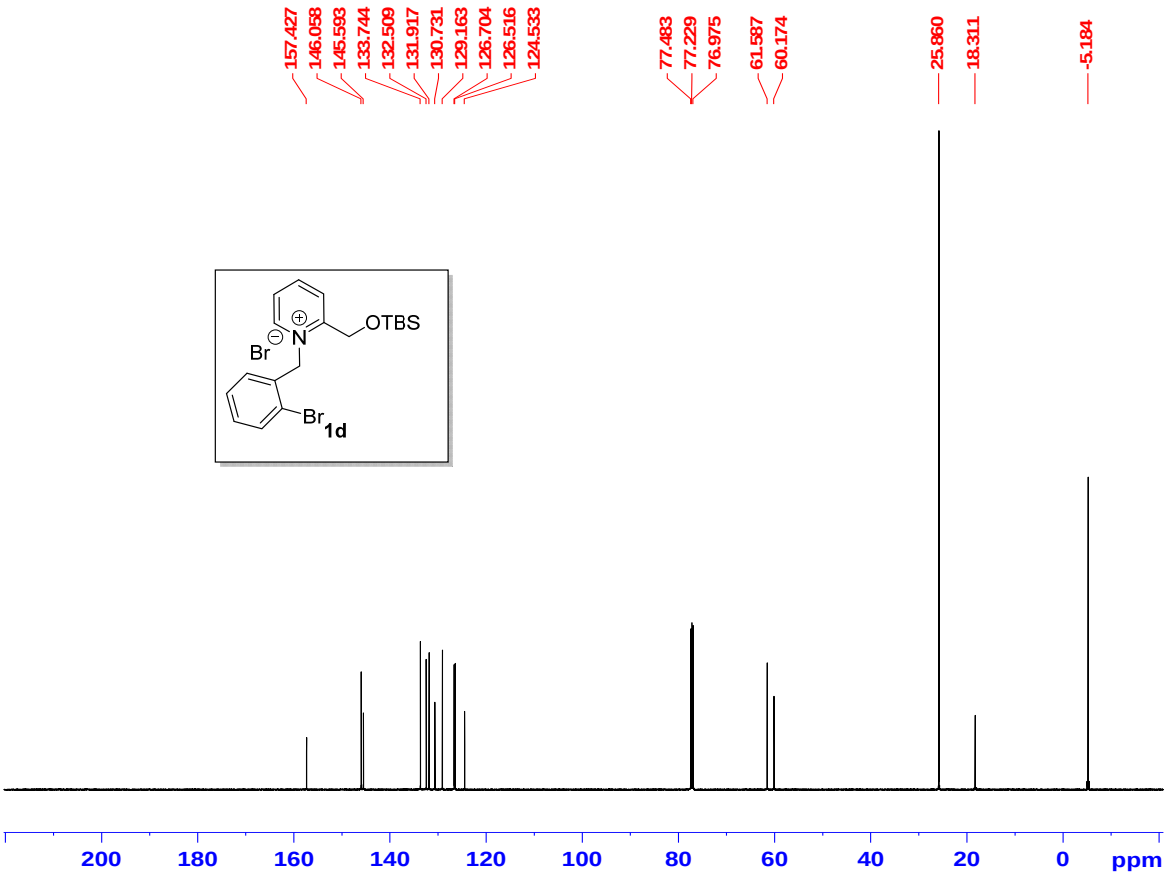
1.01
0.96
1.02
2.00
1.05
1.01
2.00
2.01
8.96
5.98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131.917
130.731
129.163
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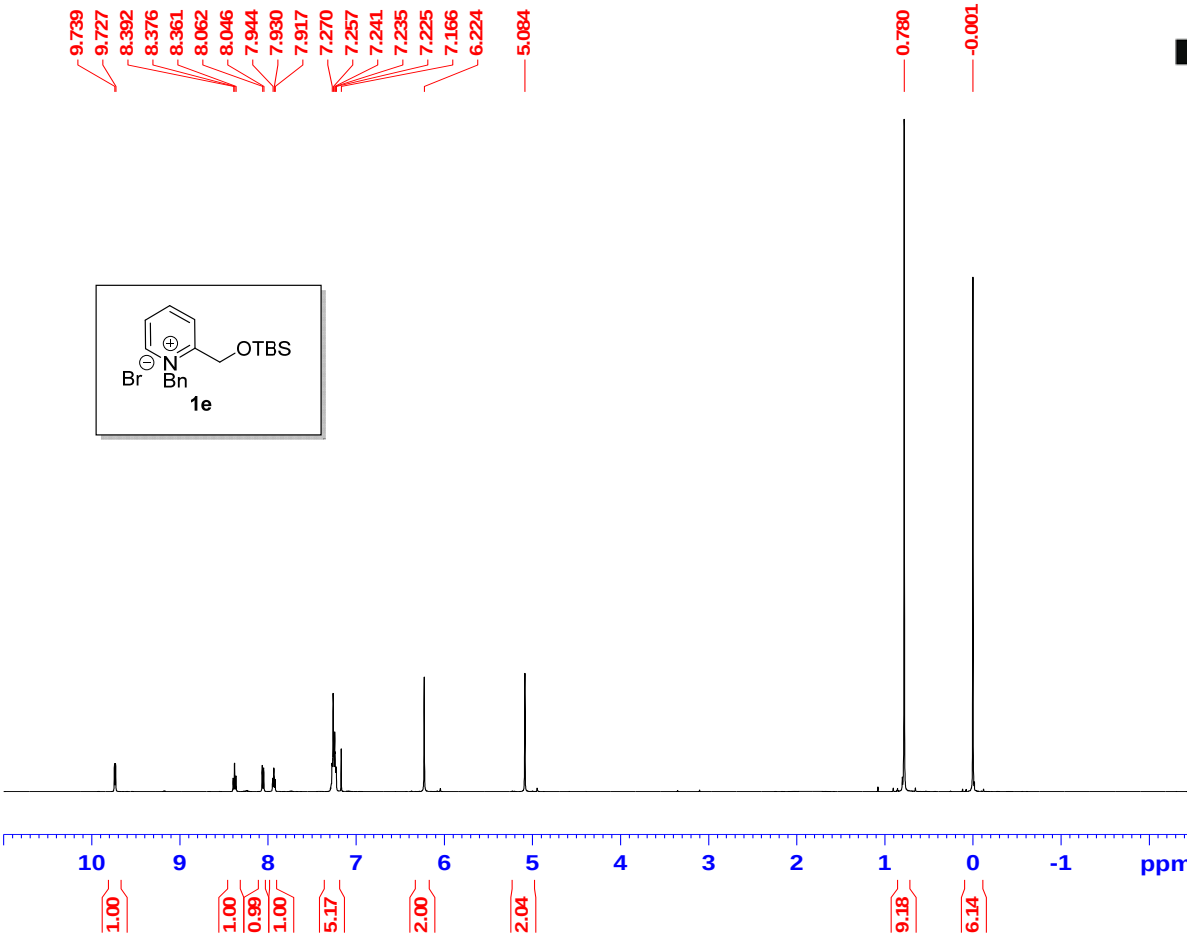
126.516
124.533
77.483
77.229
76.975
61.587
60.174
25.860
18.311
-5.184
OTBS
Br
N
Br
1d
200
180
160
140
120
100
80
60
40
20
0
ppm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8.376
8.361
8.062
8.046
7.944
7.930
7.917
7.270
7.257
7.241
7.235
7.225
7.166
6.224
5.084
0.780
-0.001
OTBS
Br
N
Bn
1e
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.00
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1.00
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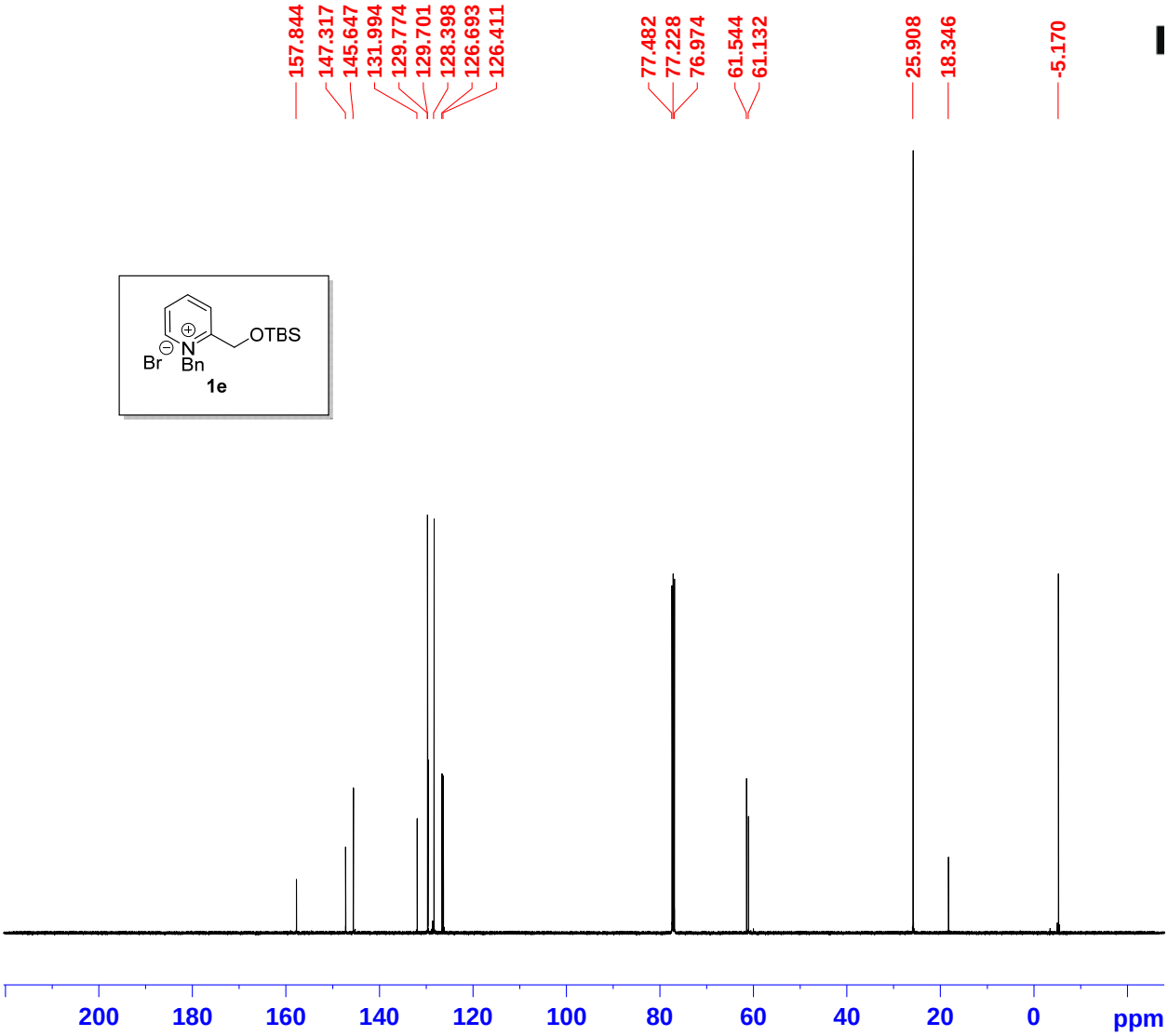
2.00
2.04
9.18
6.14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128.398
126.693
126.411
77.482
77.228
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61.544
61.132
25.908
18.346
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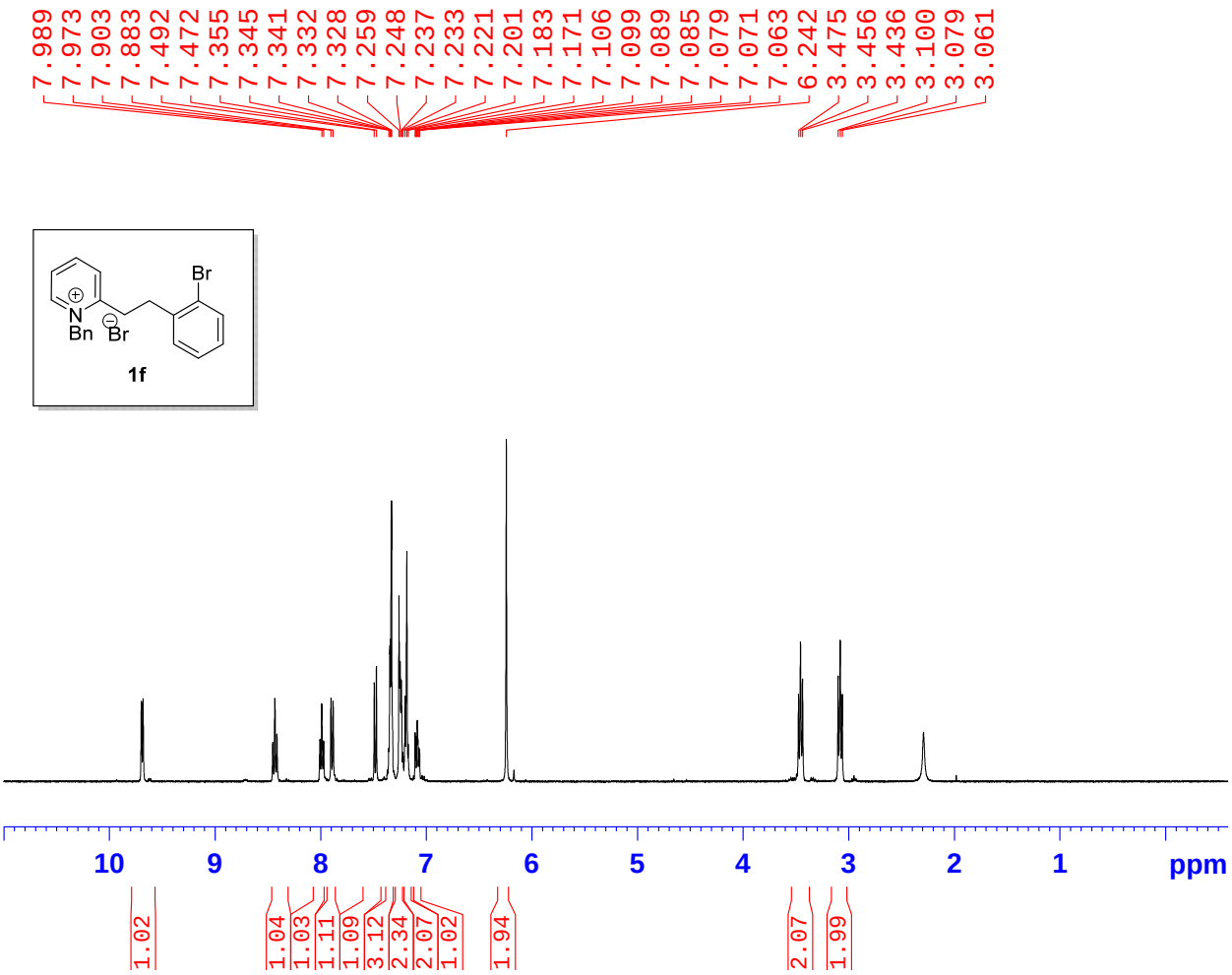
OTBS
Br
N
Bn
1e
200
180
160
140
120
100
80
60
40
20
0
ppm


7.989
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7.903
7.883
7.492
7.472
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7.345
7.341
7.332
7.328
7.259
7.248
7.237
7.233
7.221
7.201
7.183
7.171
7.106
7.099
7.089
7.085
7.079
7.071
7.063
6.242
3.475
3.456
3.436
3.100
3.079
3.061
Br
N
Bn
Br
1f
10
9
8
7
6
5
4
3
2
1
ppm
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1.03
1.11
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2.07
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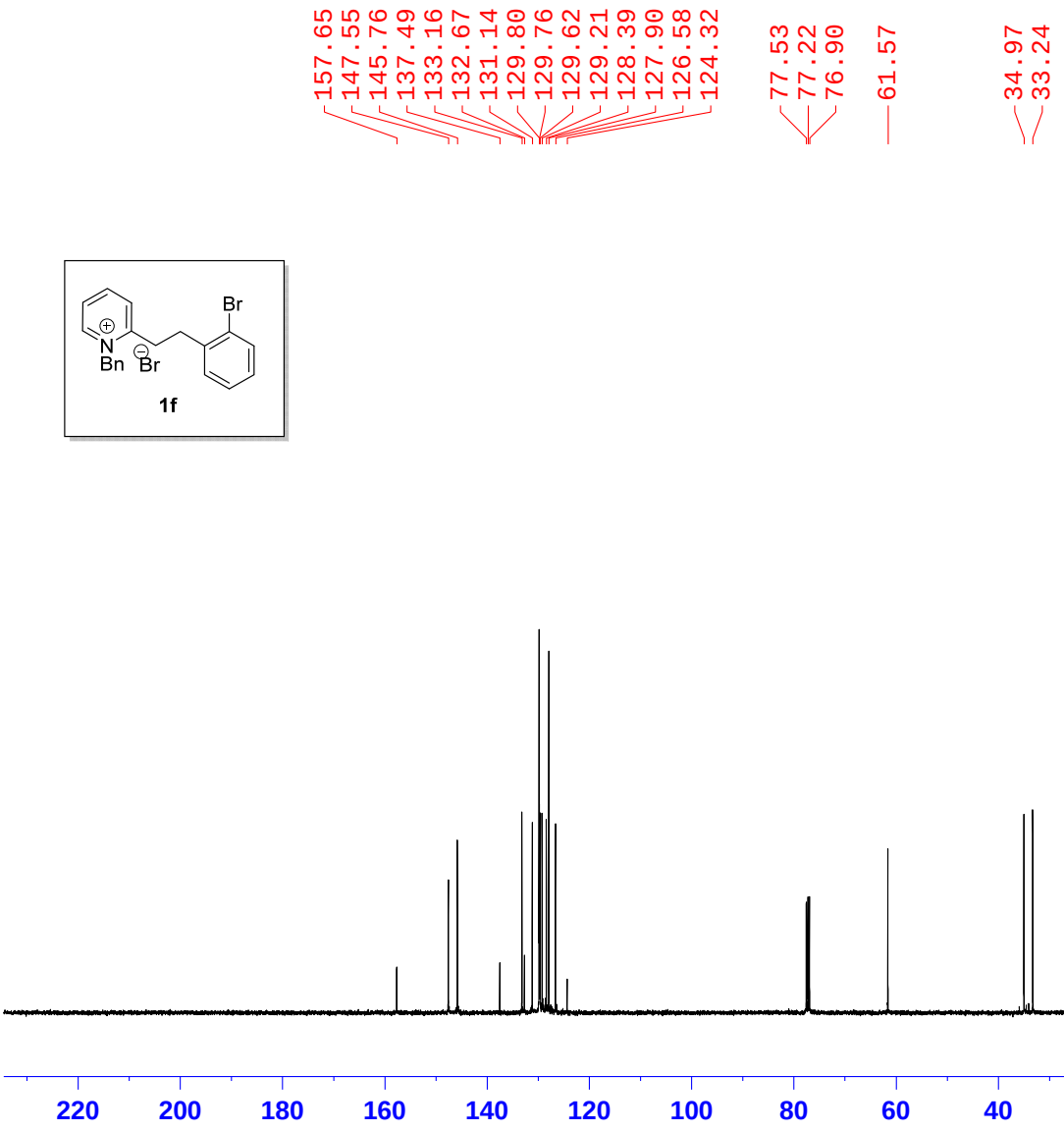
2.07
1.99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129.62
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128.39
127.90
126.58
124.32
77.53
77.22
76.90
61.57
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33.24
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Bn
Br
1f
220
200
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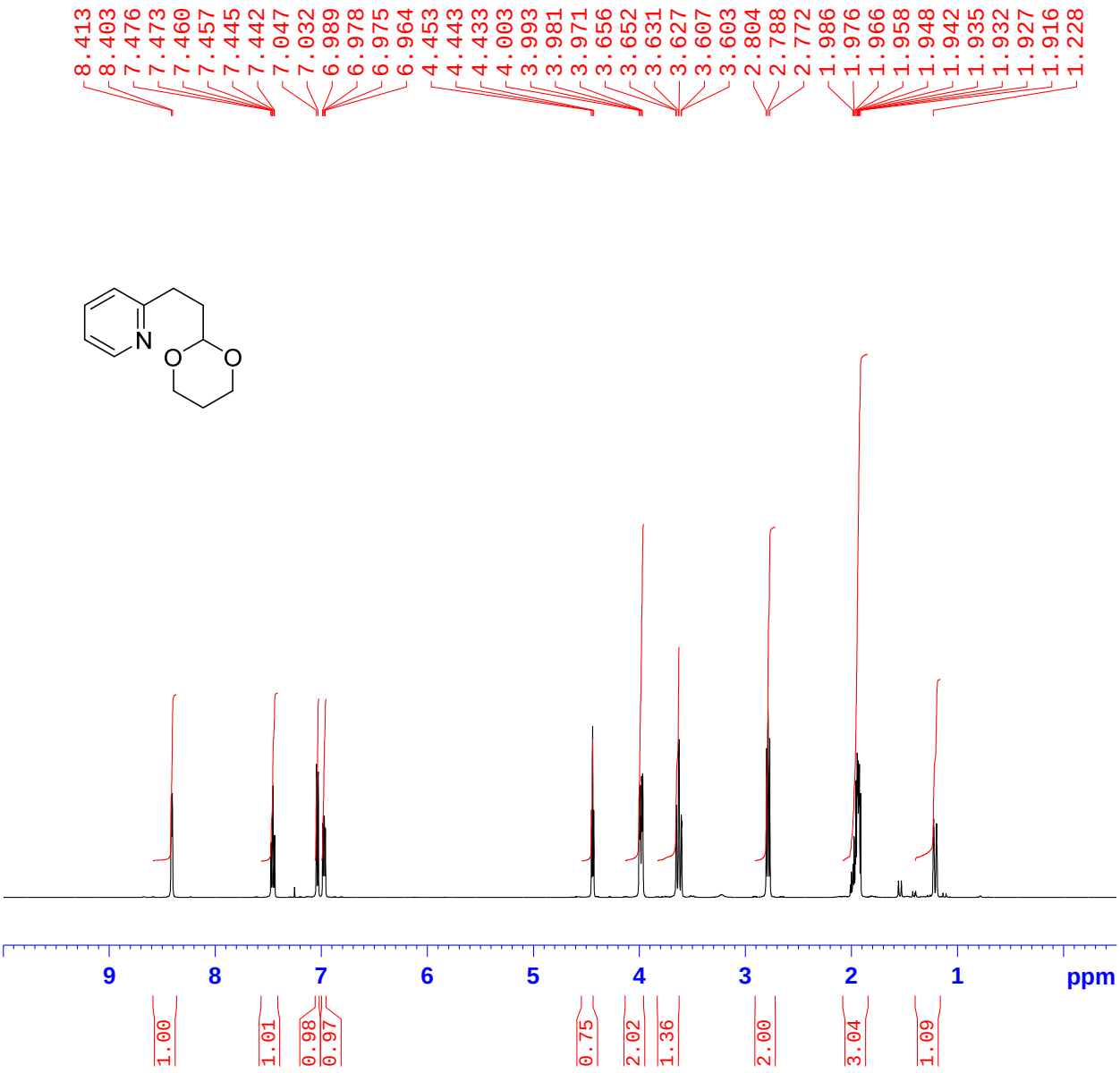
140
120
100
80
60
40
20
ppm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7.442
7.047
7.032
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6.975
6.964
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4.443
4.433
4.003
3.993
3.981
3.971
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3.652
3.631
3.627
3.607
3.603
2.804
2.788
2.772
1.986
1.976
1.966
1.958
1.948
1.942
1.935
1.932
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1.916
1.228
N
O
O
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
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0.97
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2.02
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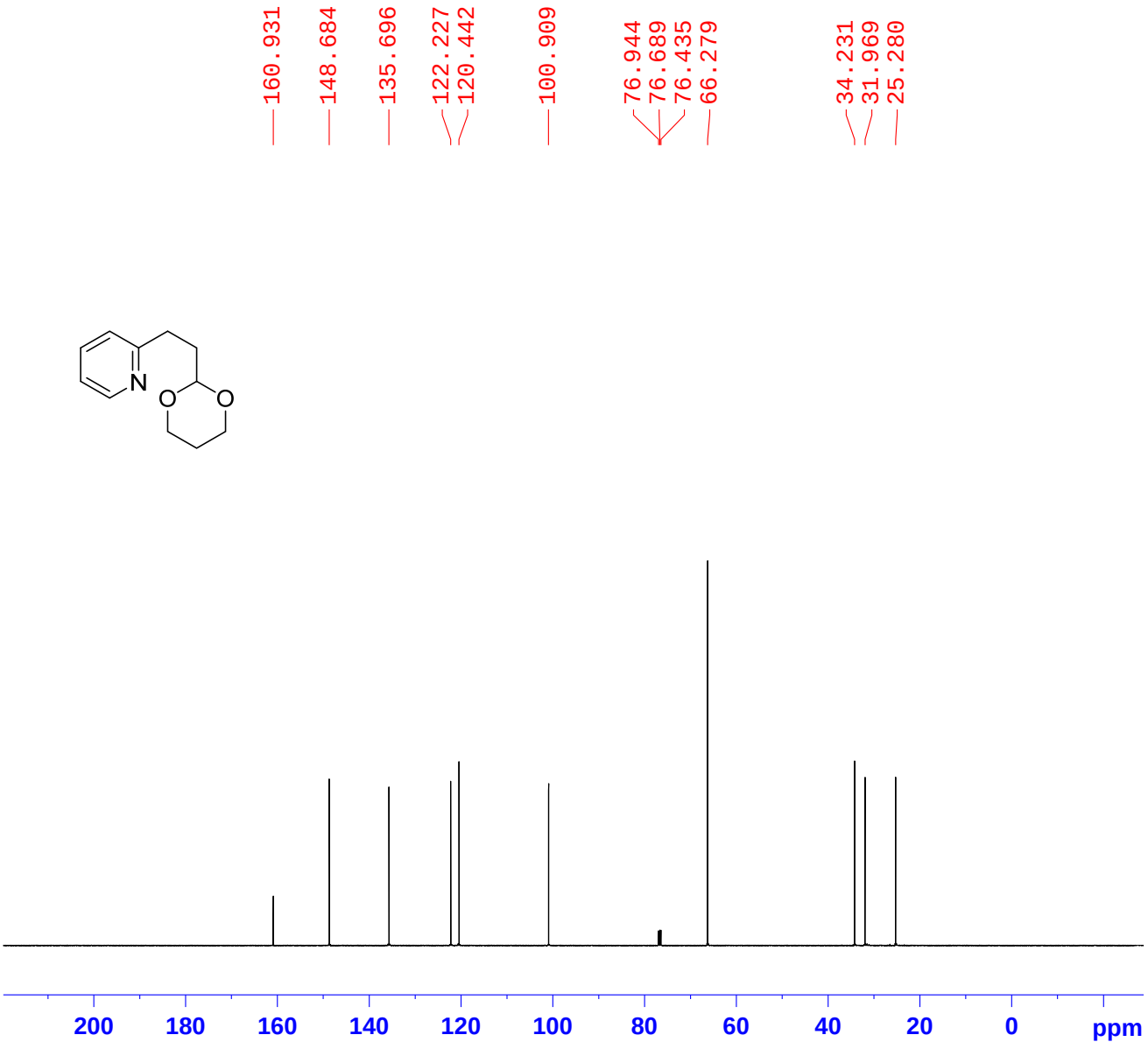
2.00
3.04
1.09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135.696
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76.689
76.435
66.279
34.231
31.969
25.280
N
O
O
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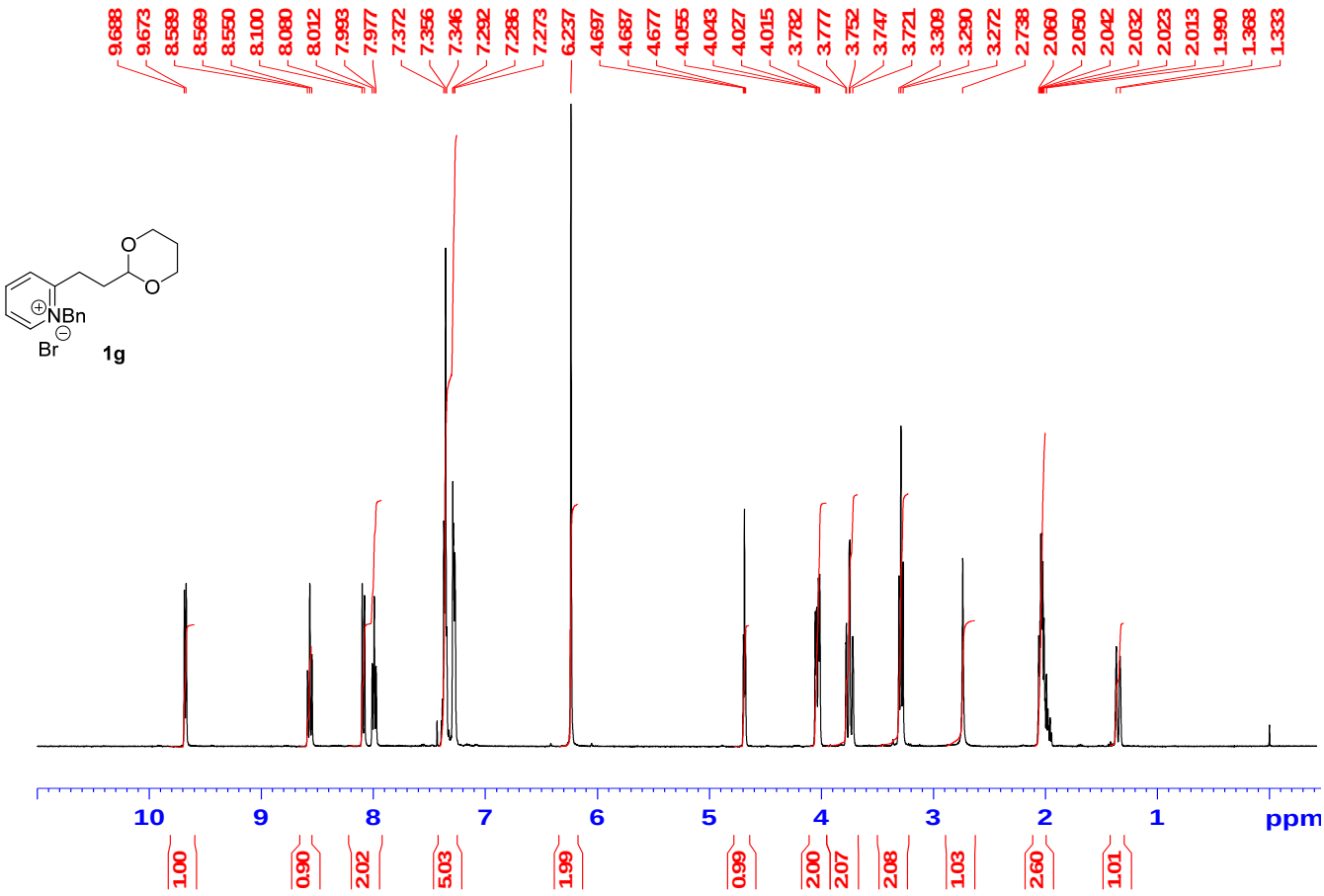
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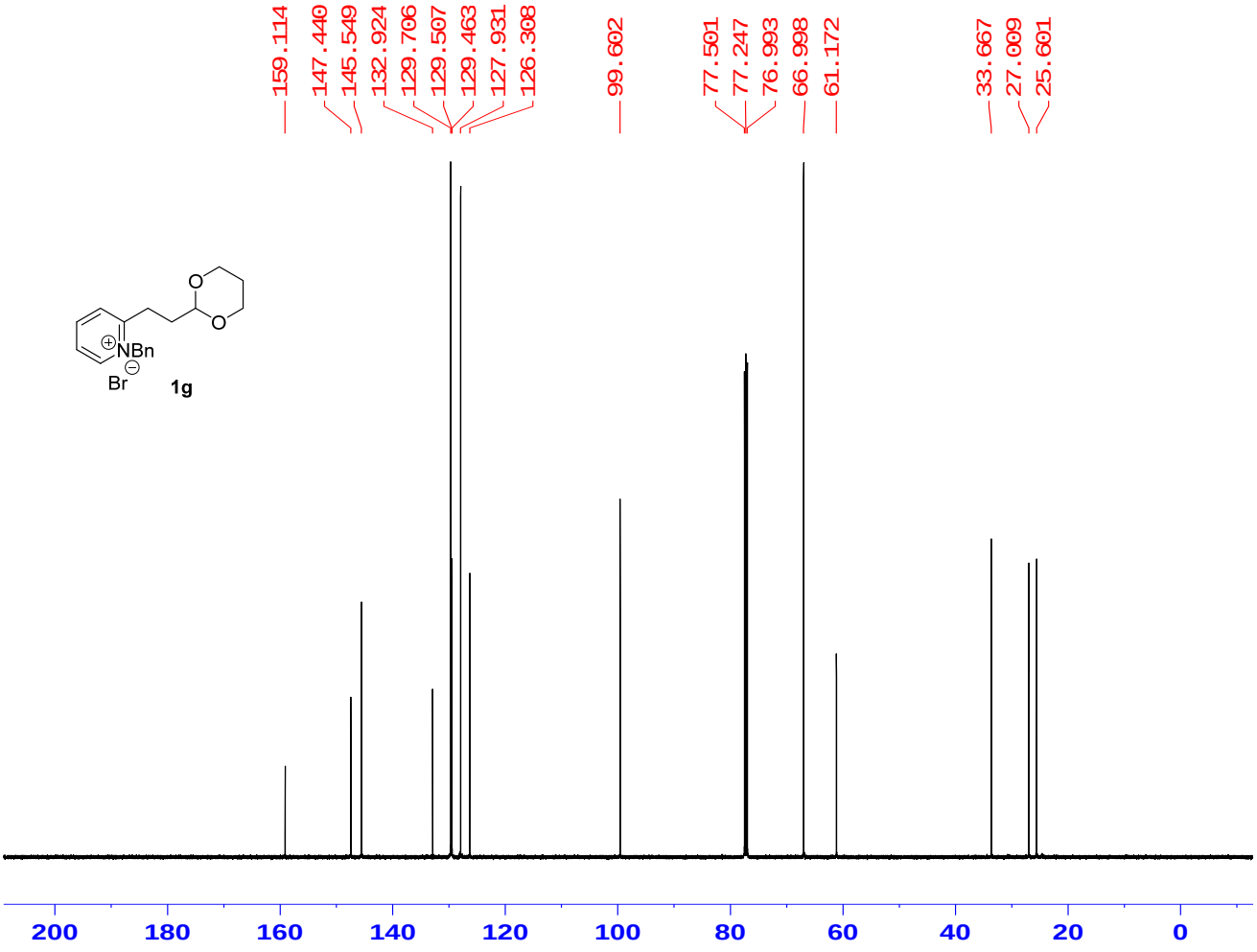
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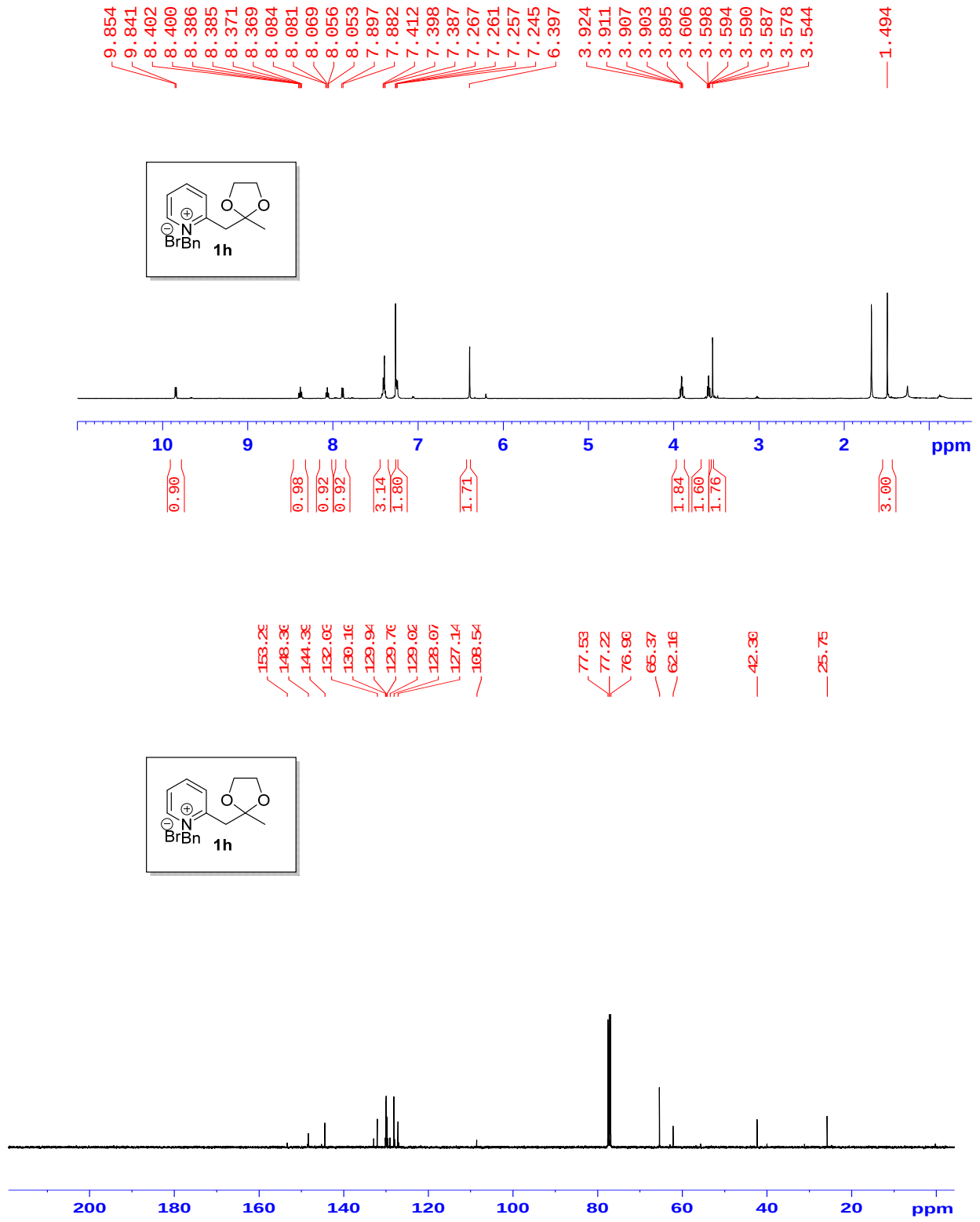
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7
6
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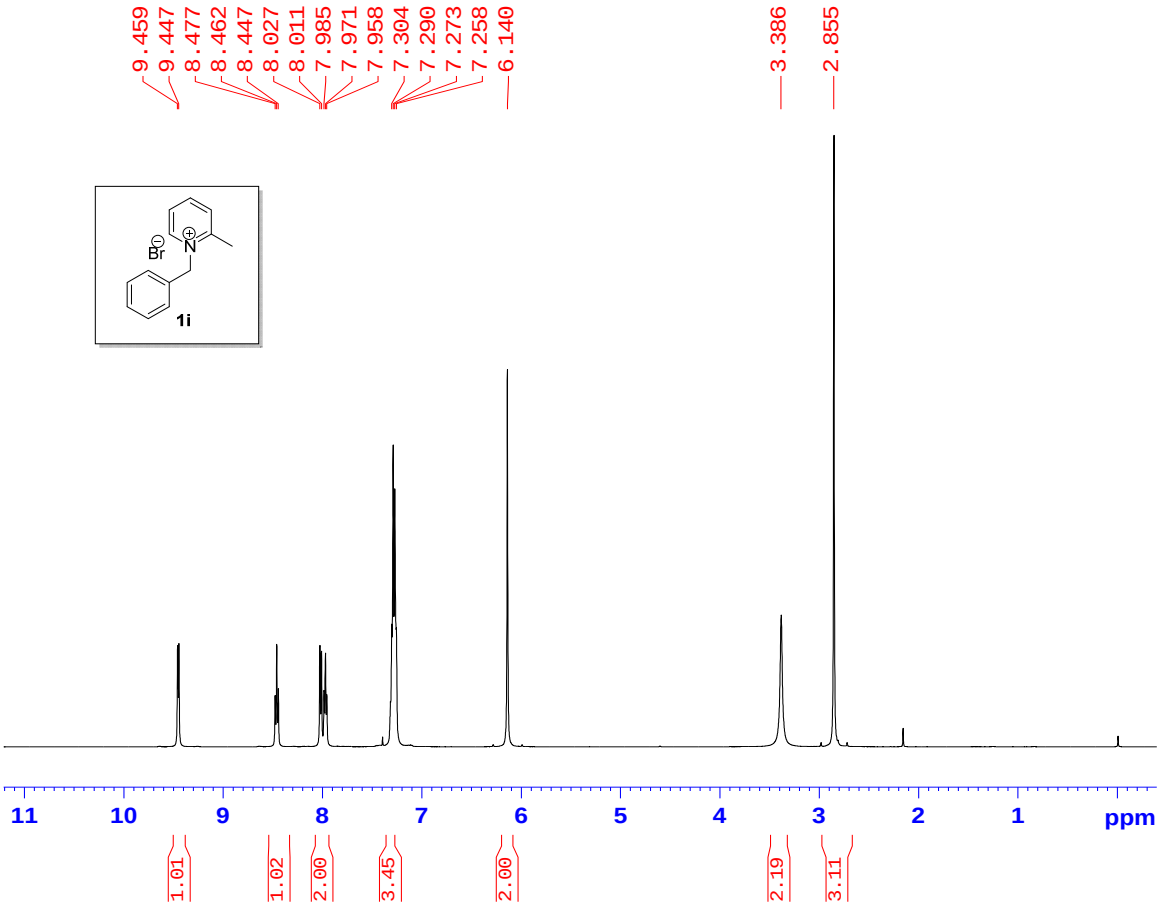
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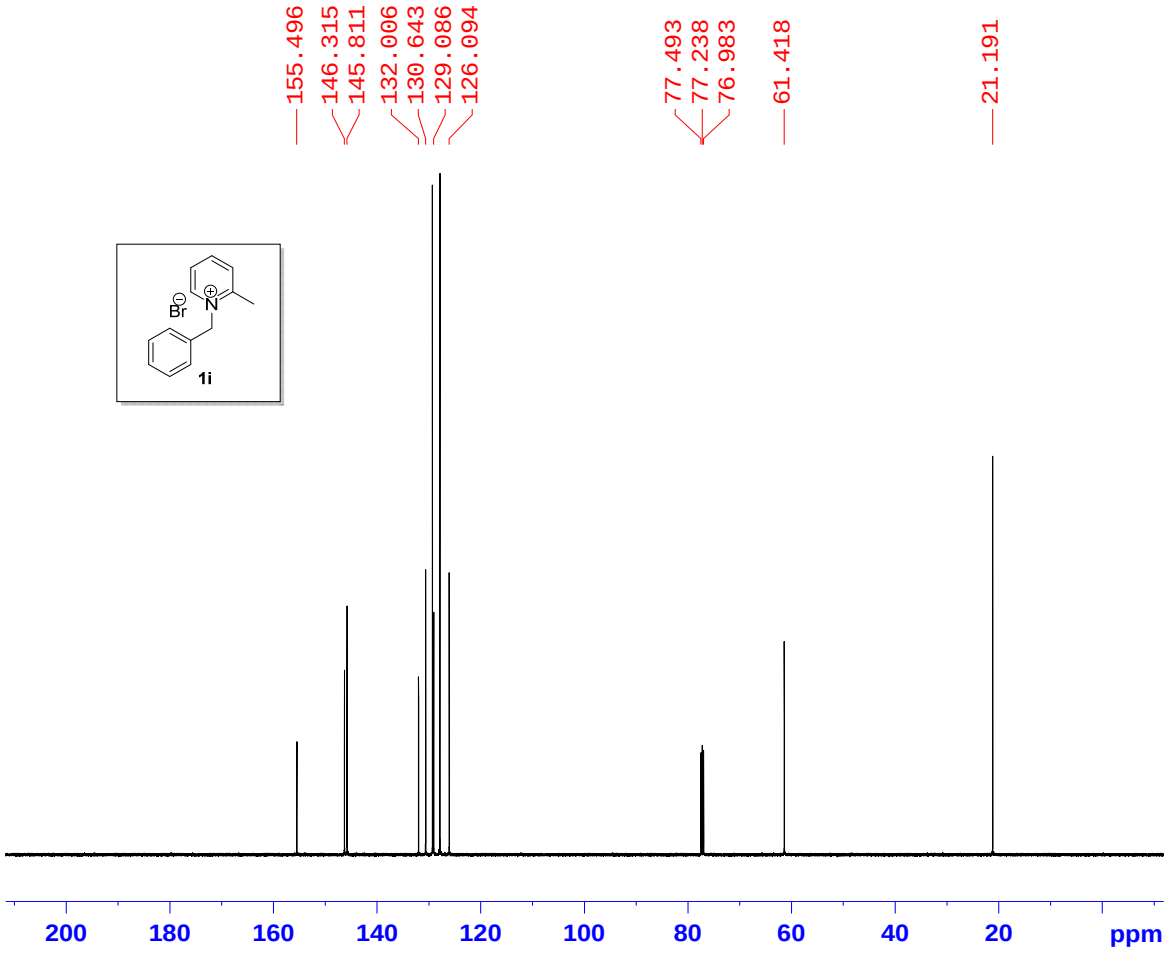
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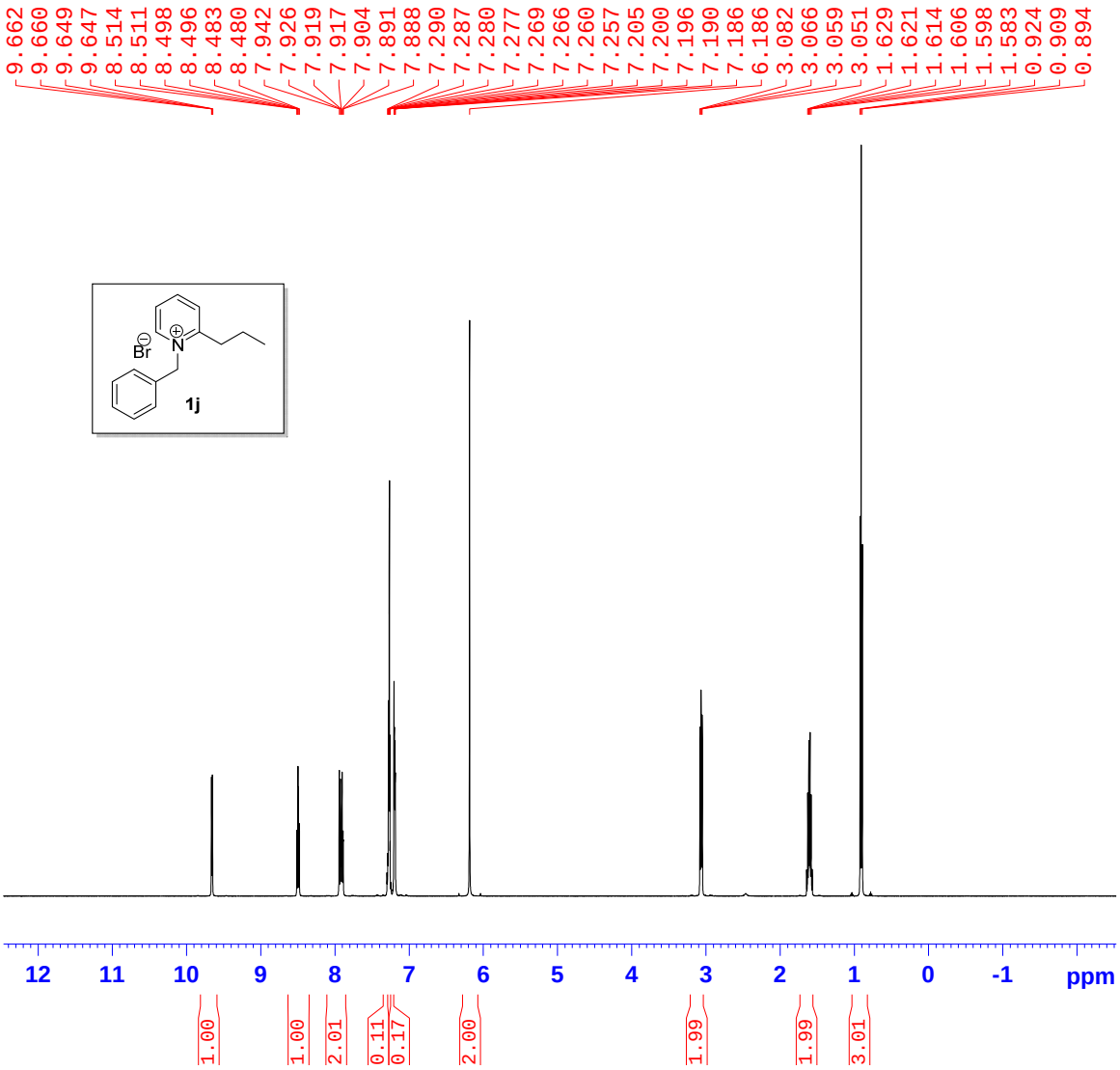
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10
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8
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5
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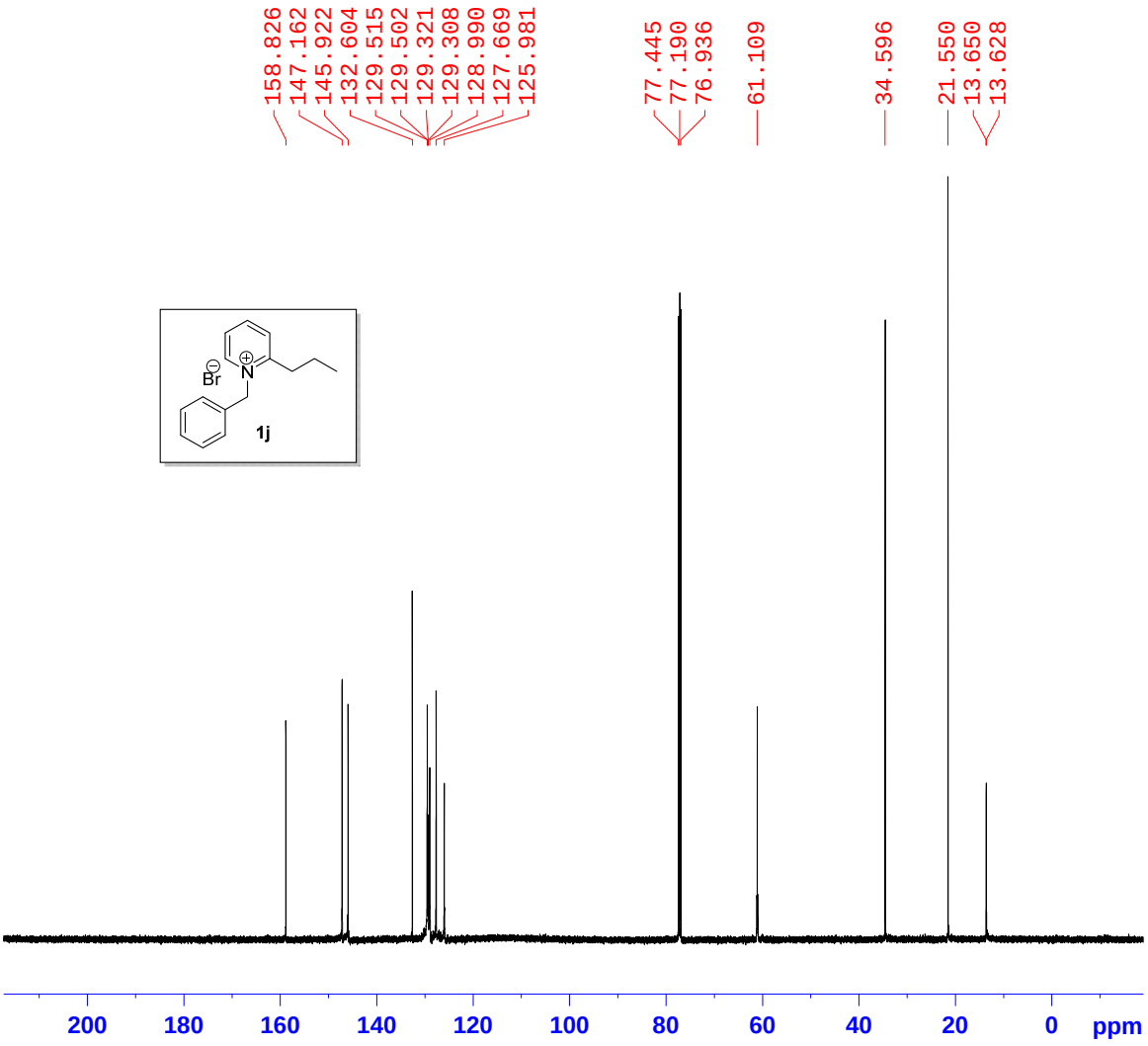
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34.596
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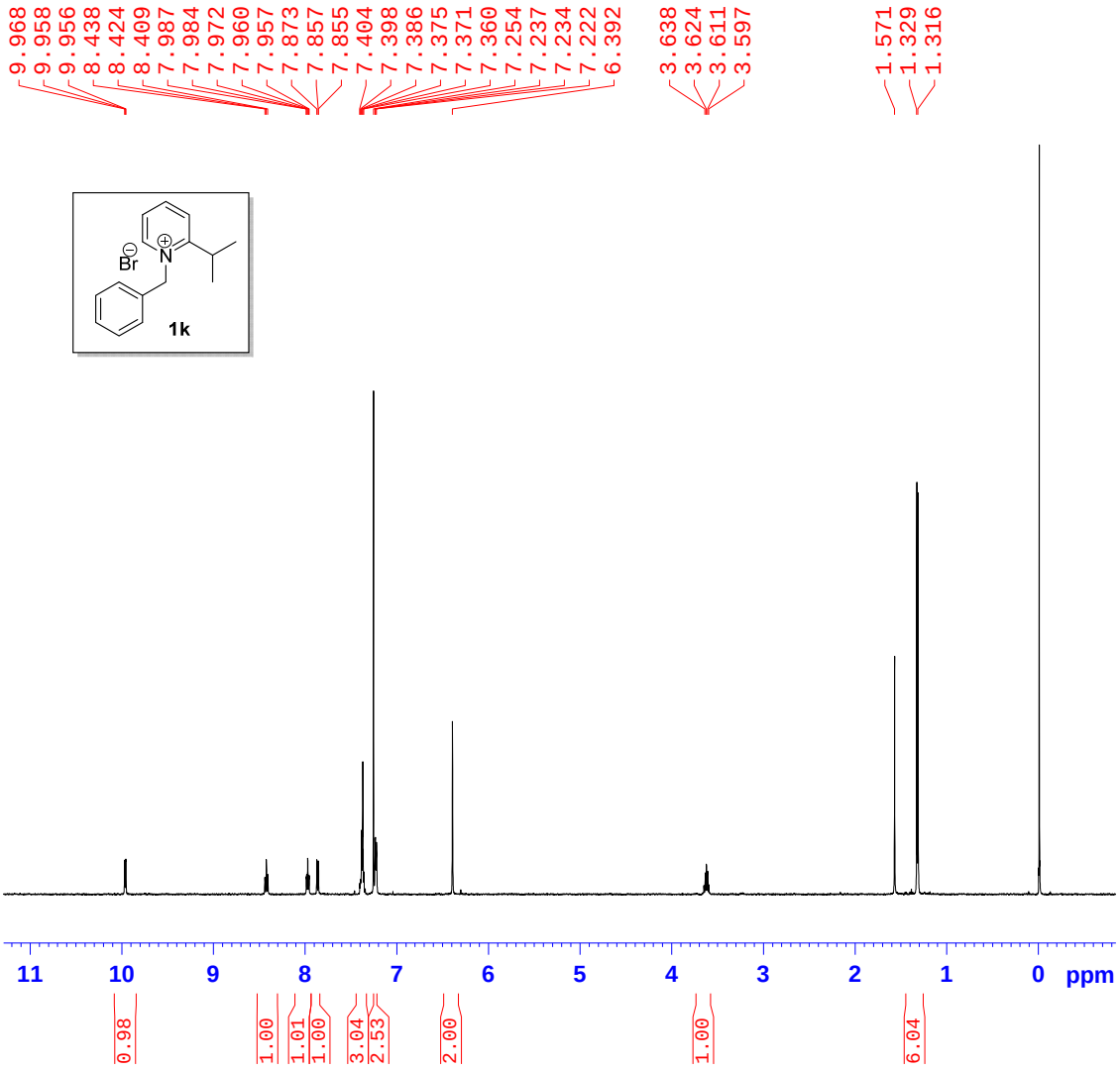
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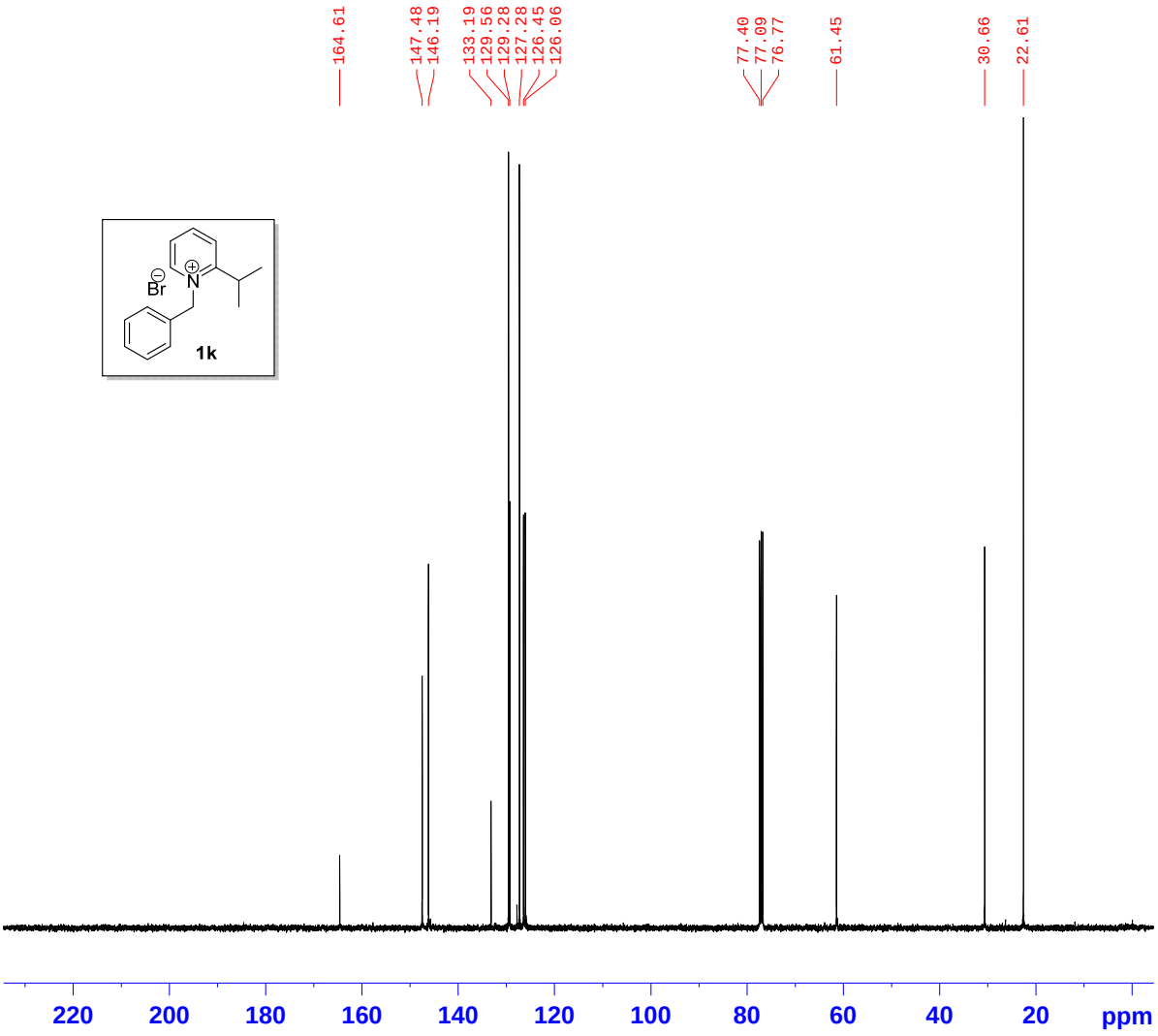
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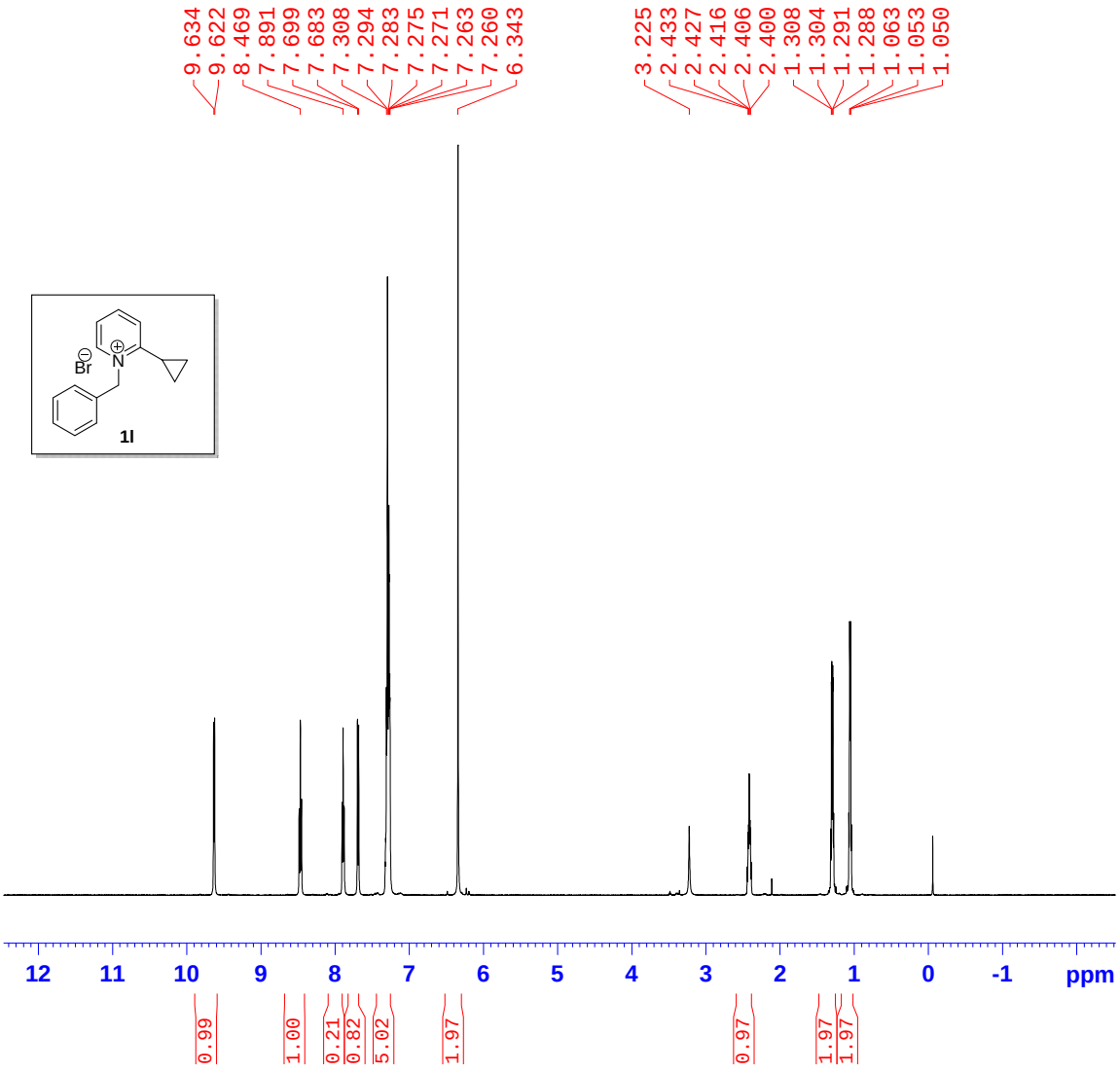
ppm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2.427
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2.400
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Br
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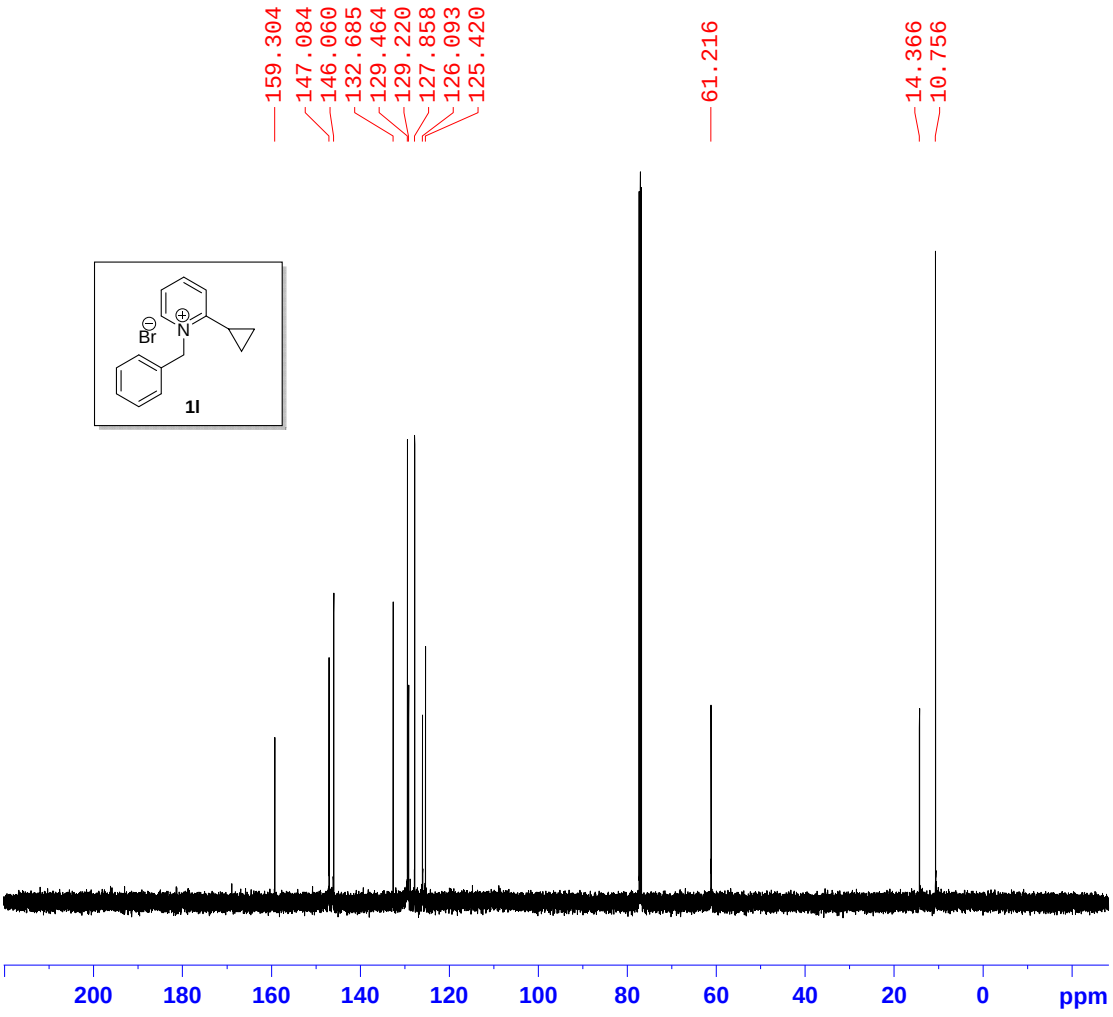
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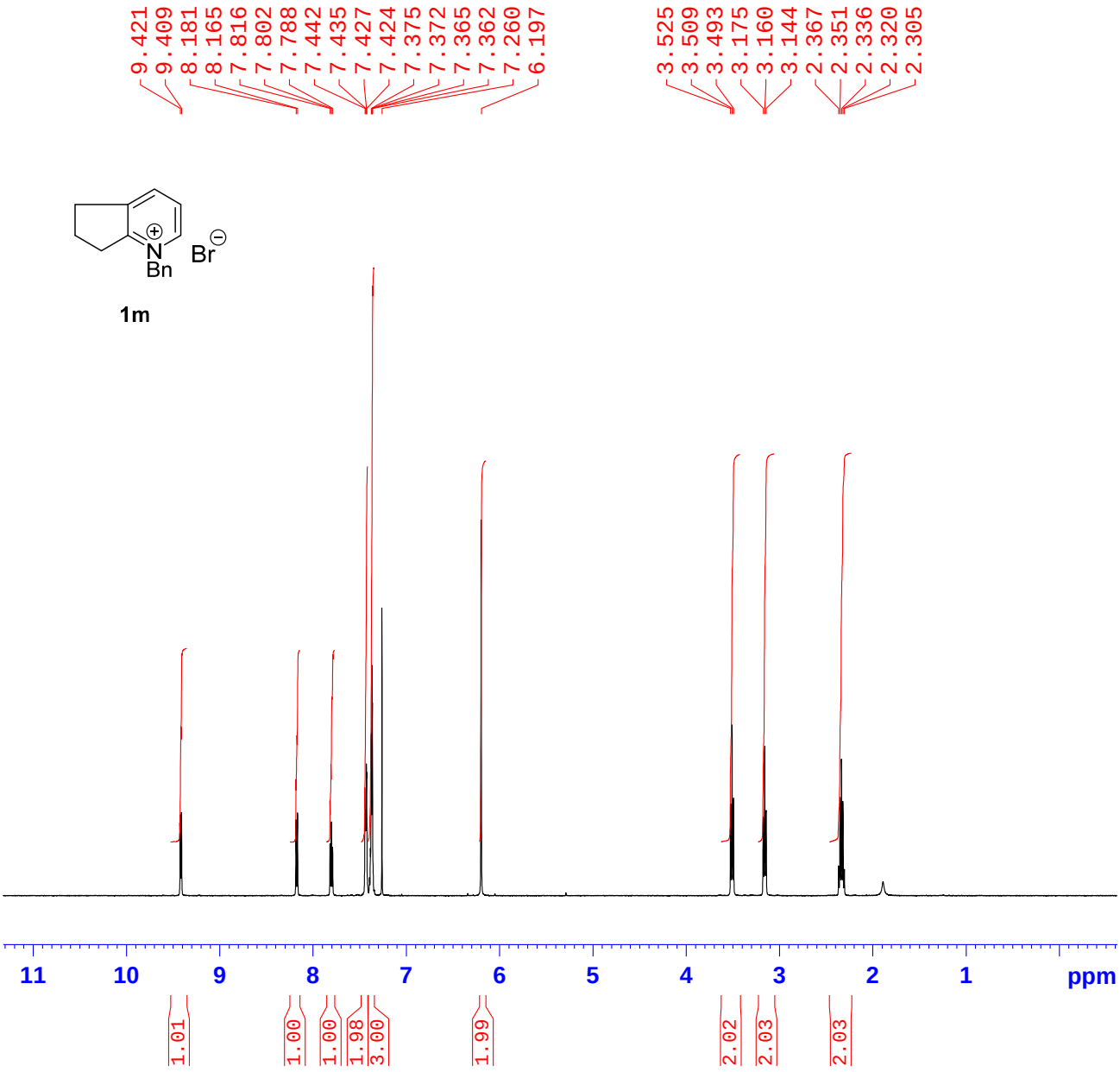
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7.260
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3.509
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2.351
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Bn
Br
1m
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10
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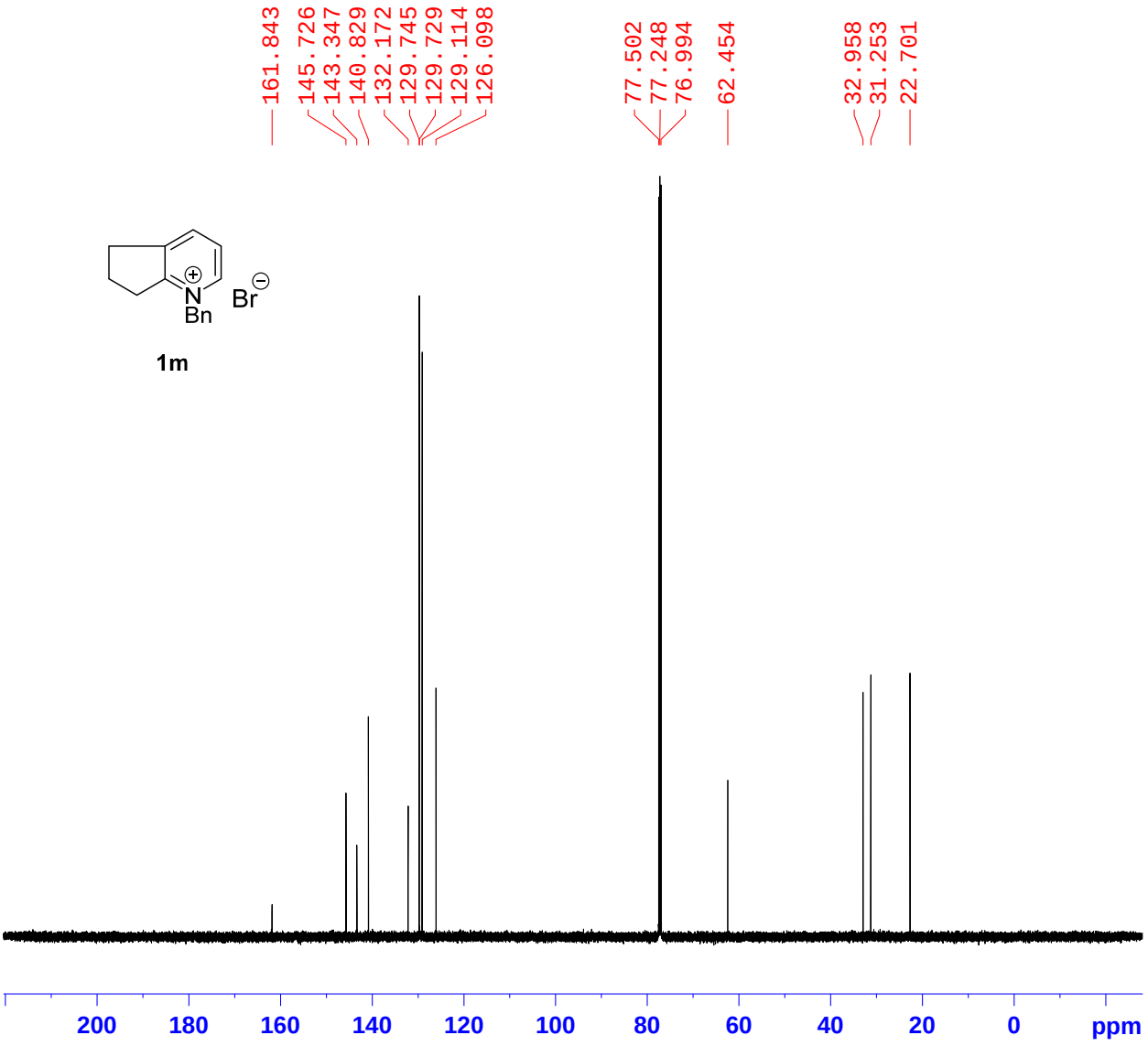
2.03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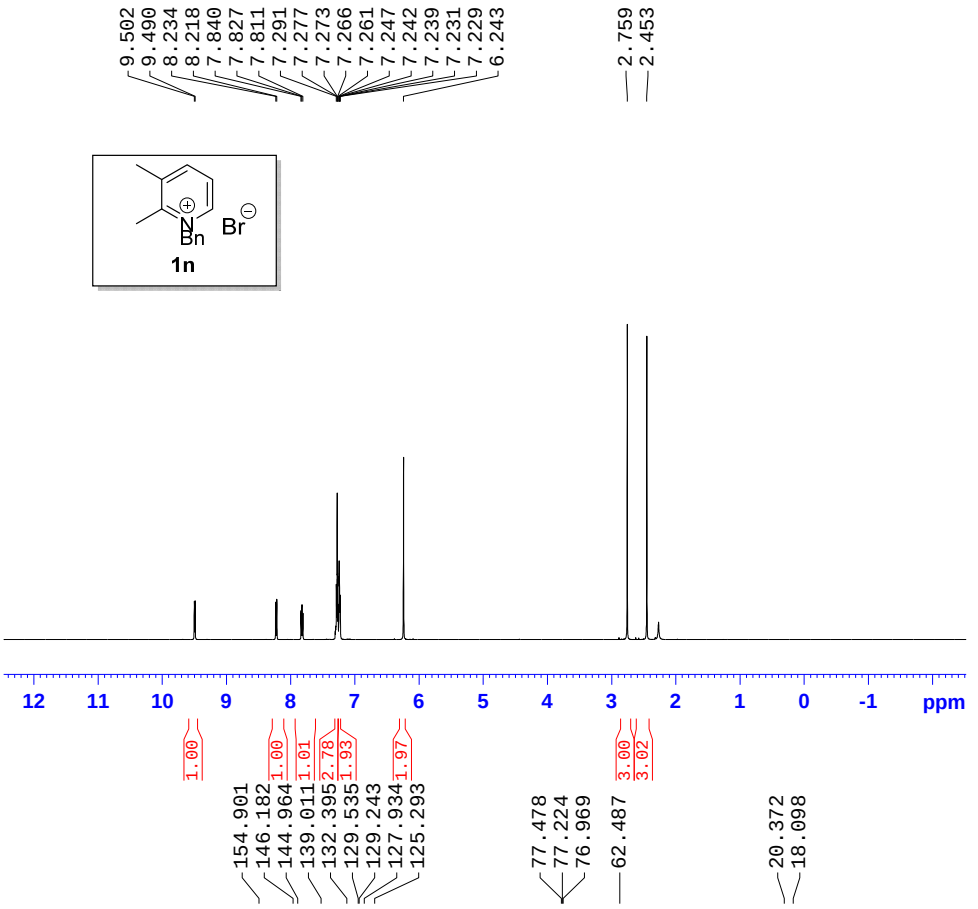


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EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
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PULPROG            zg10
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7500.000 Hz
FIDRES         0.228882 Hz
AQ             2.1845334 sec
RG                  228
DW                66.667 usec
DE                 6.50 usec
TE                299.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         500.1325007 MHz
NUC1                1H
P1                 11.75 usec
PLW1        18.39999962 W

F2 - Processing parameters
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LB                 0.30 Hz
GB       0
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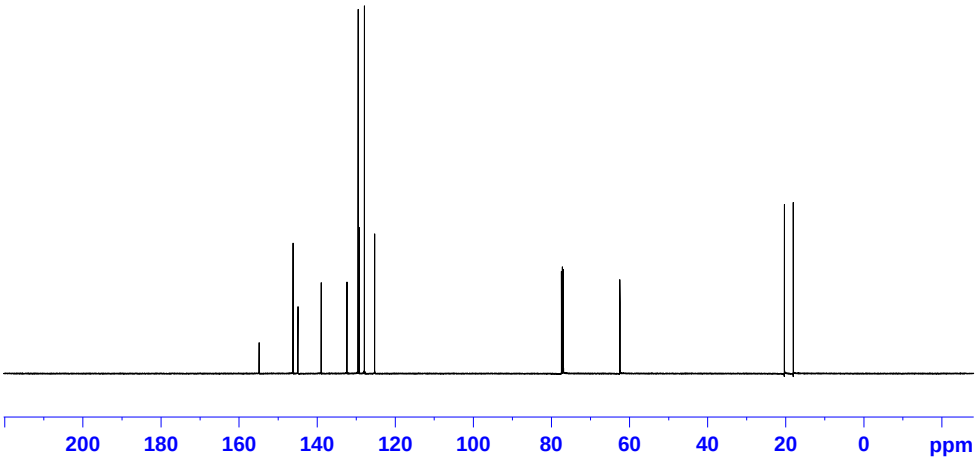


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Current Data Parameters
NAME          10933-060
EXPNO                 2
PROCNO                1

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PULPROG            zgpg
TD                262144
SOLVENT           CDCl3
NS                 2000
DS                    0
SWH           31250.000 Hz
FIDRES         0.119209 Hz
AQ             4.1943040 sec
RG                 2050
DW                16.000 usec
DE                 6.50 usec
TE                299.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
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NUC1                13C
P1                 9.75 usec
PLW1       126.00000000 W

======== CHANNEL f2 ========
SFO2         500.1325007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        18.39999962 W
PLW12        0.41056001 W
PLW13        0.20651001 W

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LB                 0.30 Hz
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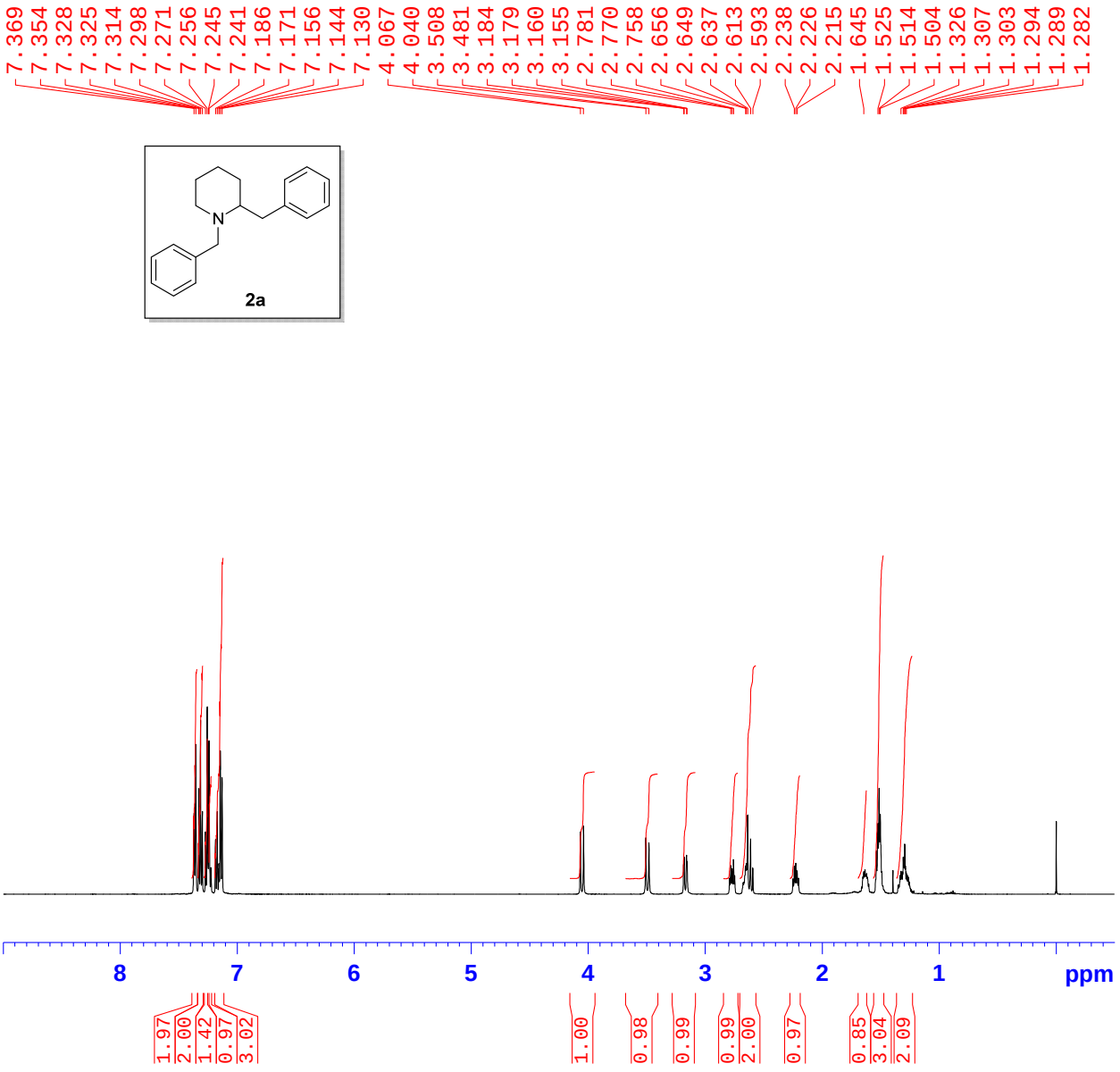
```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7.144
7.130
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3.155
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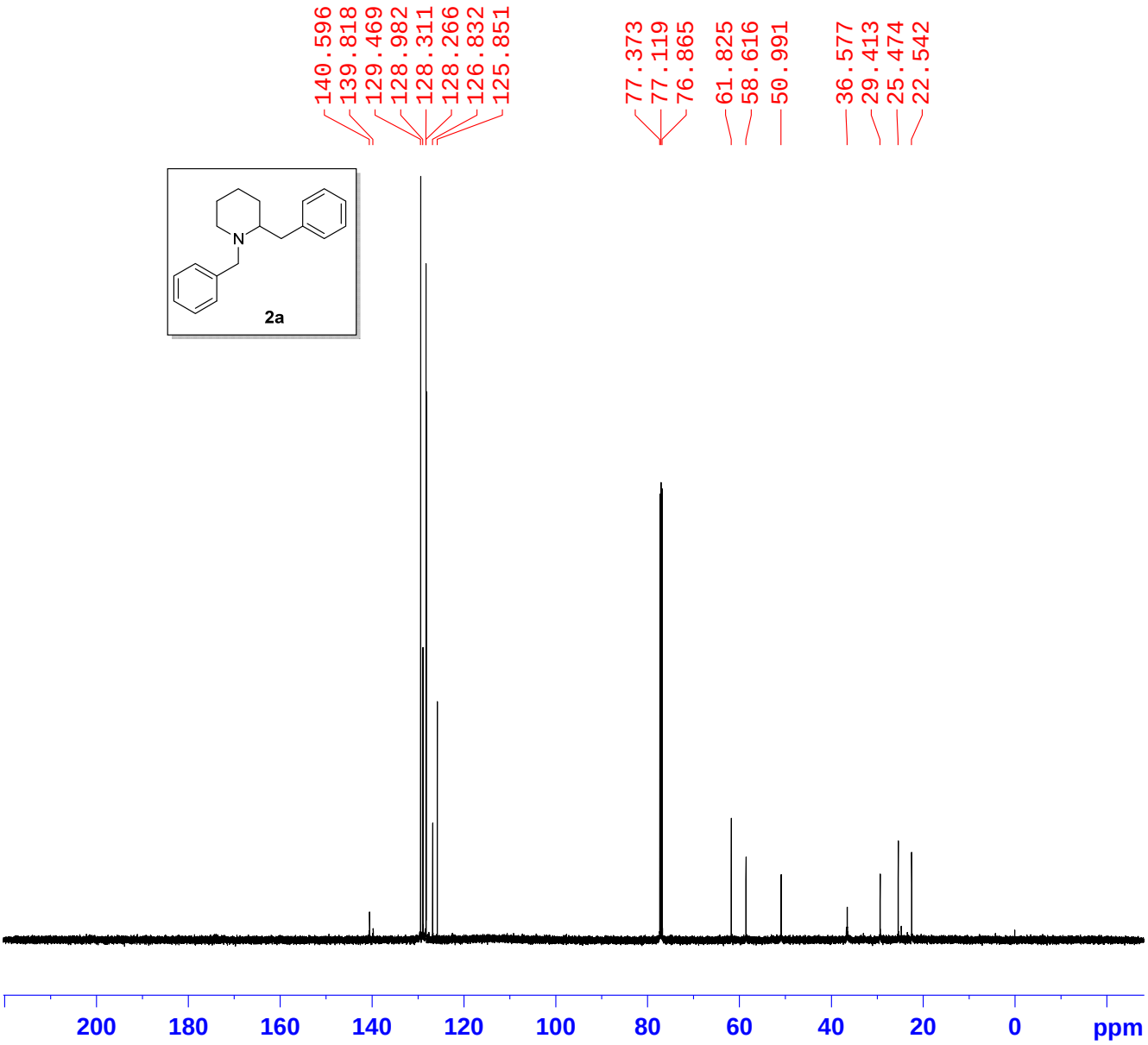
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120
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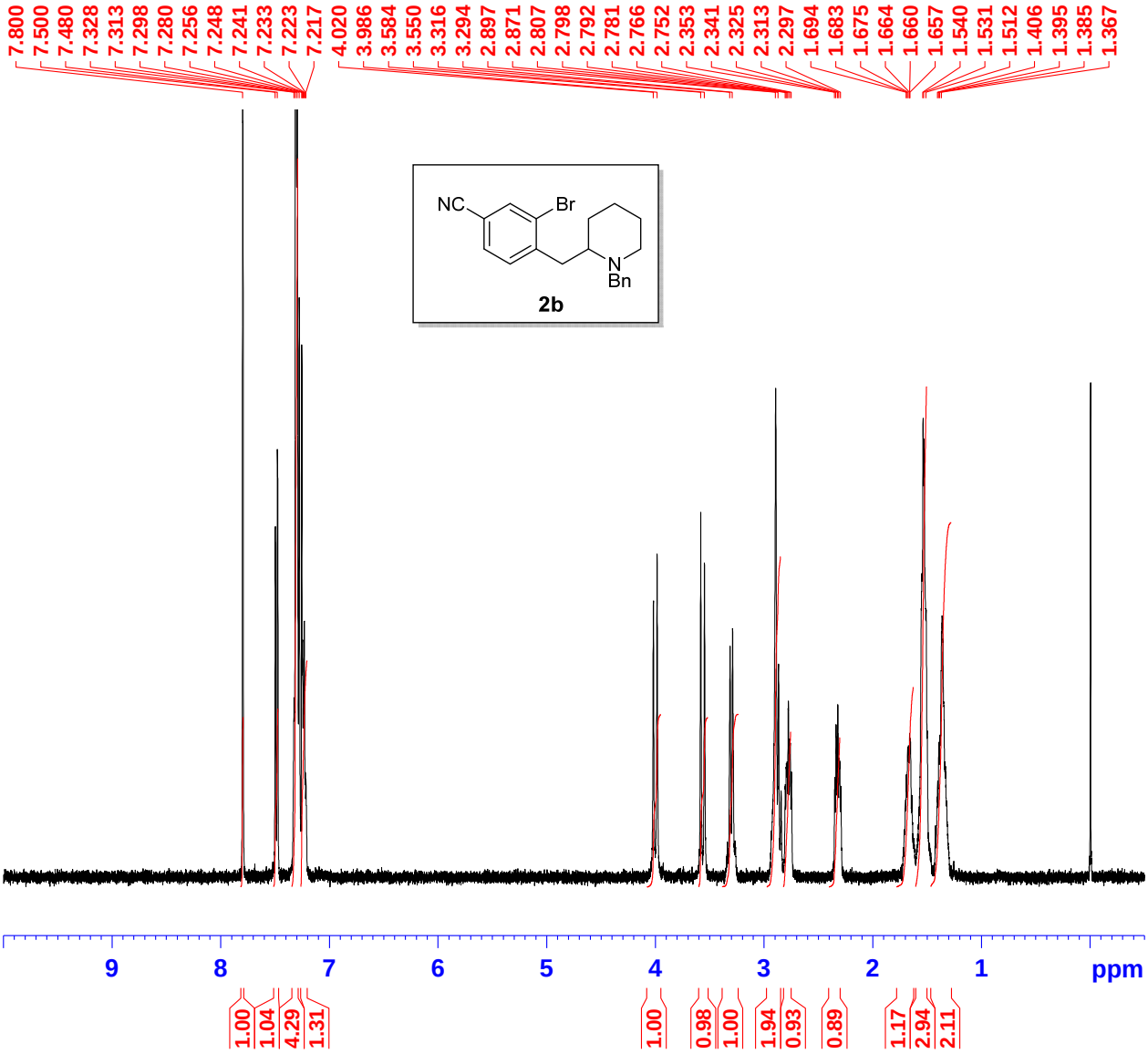
ppm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Bn
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8
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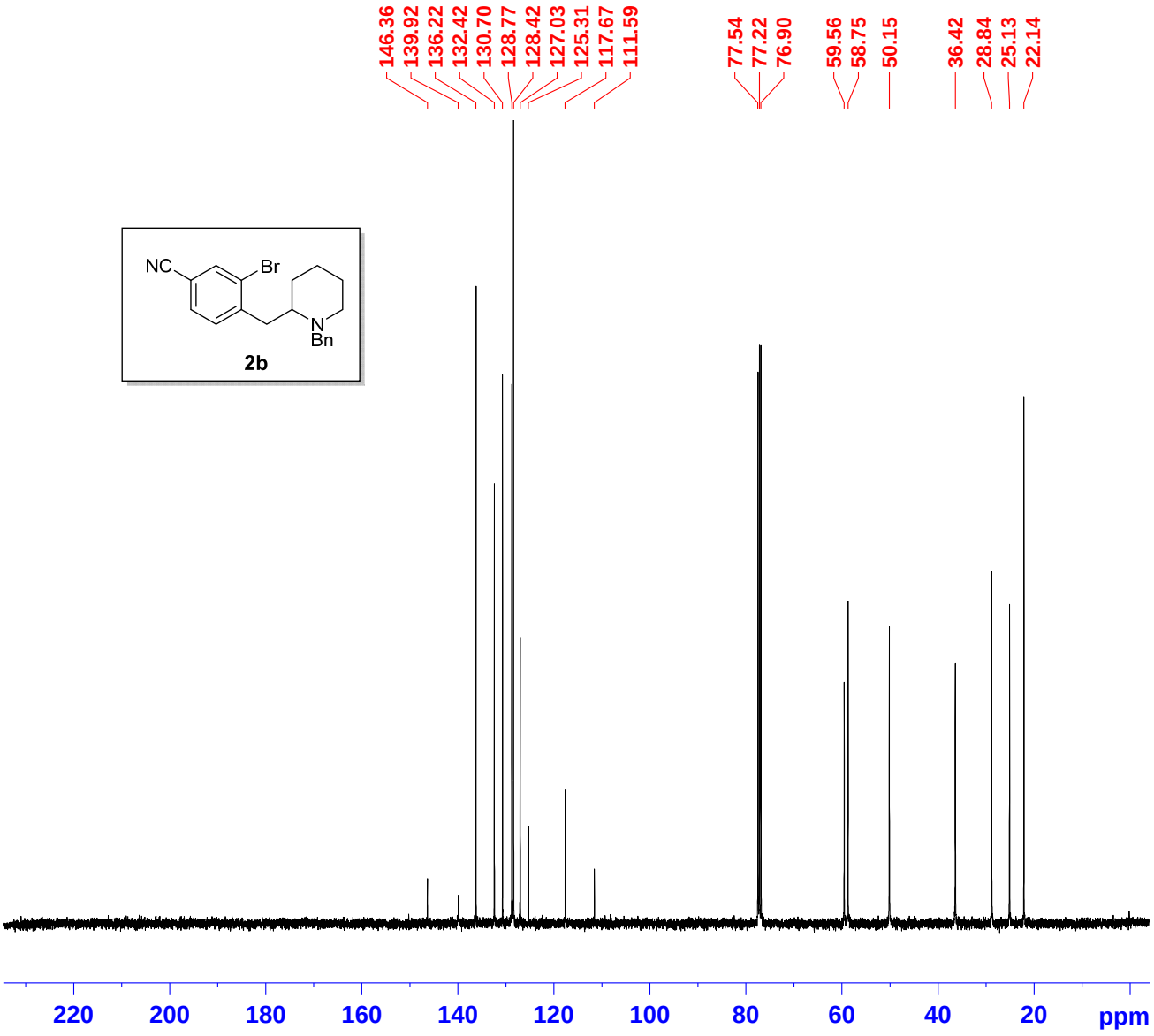
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50.15
36.42
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Bn
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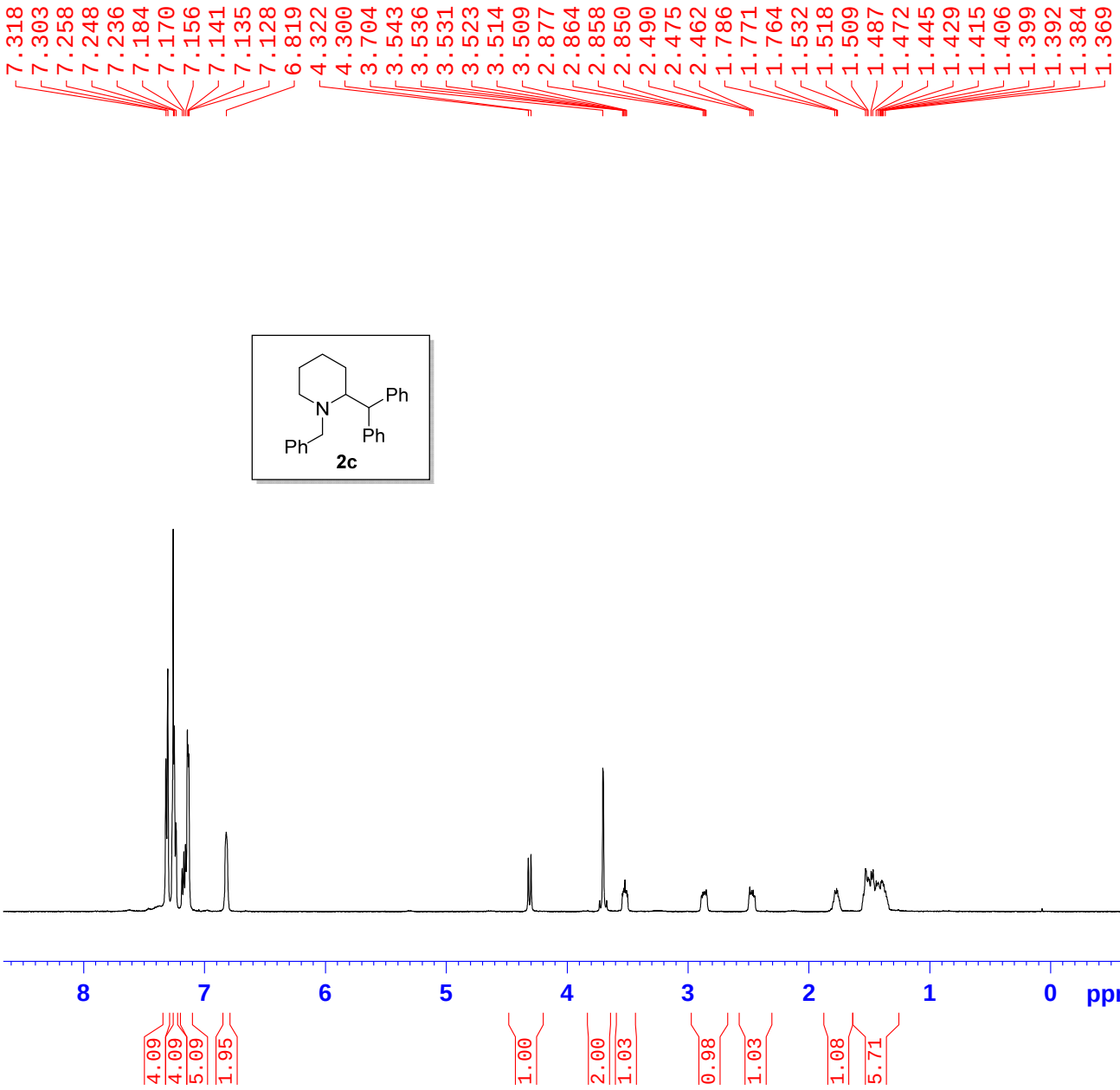
20
ppm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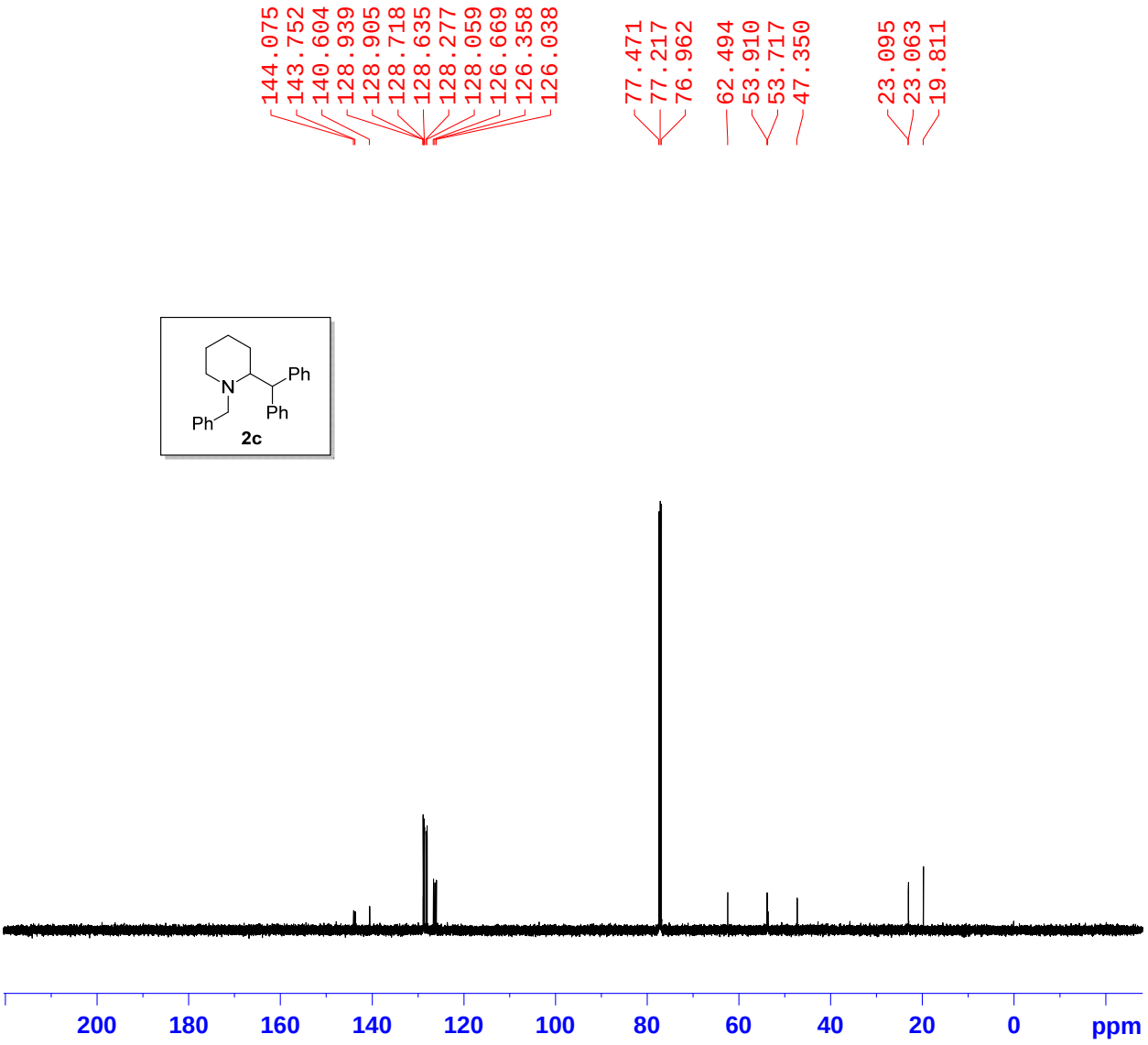
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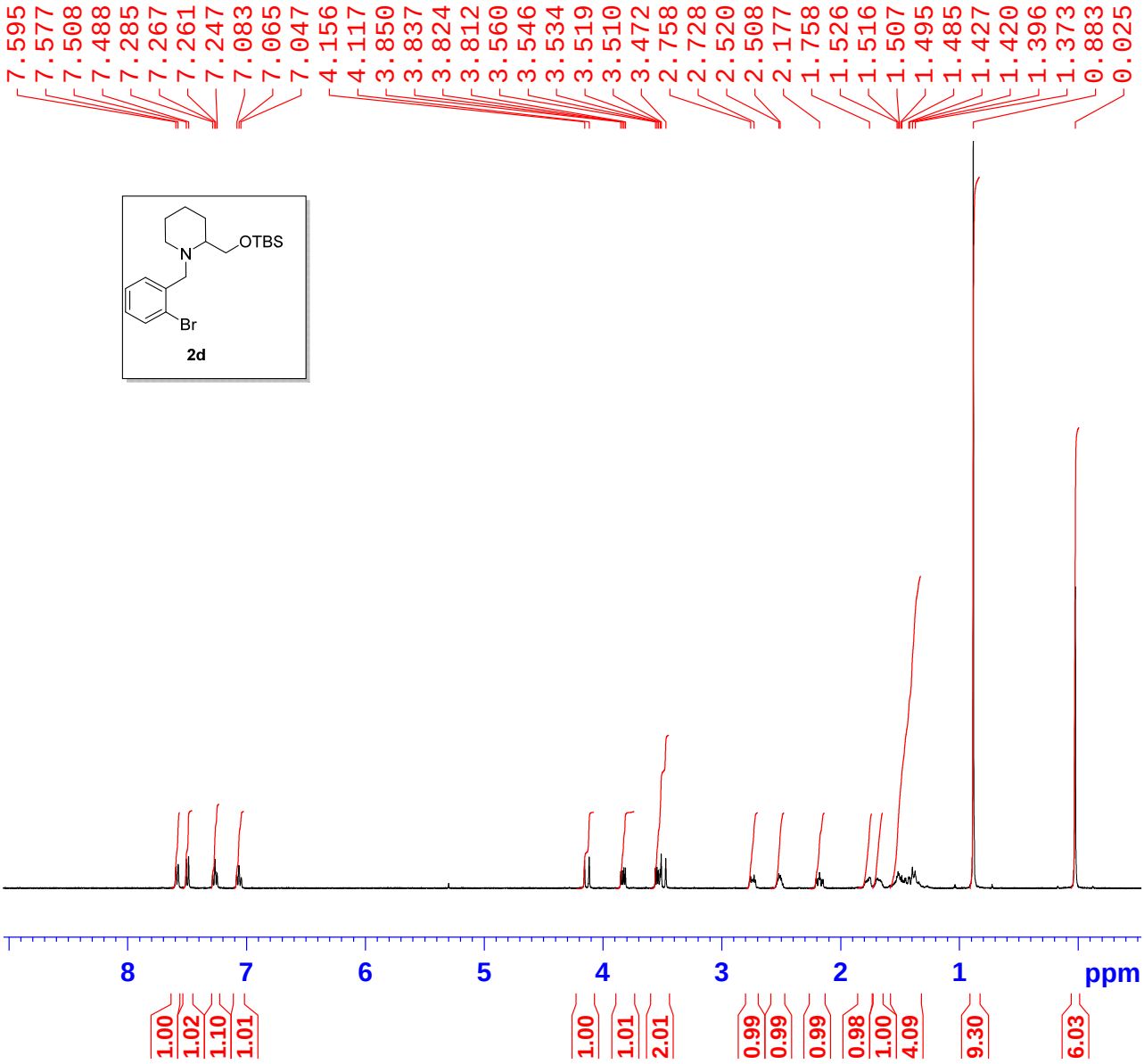
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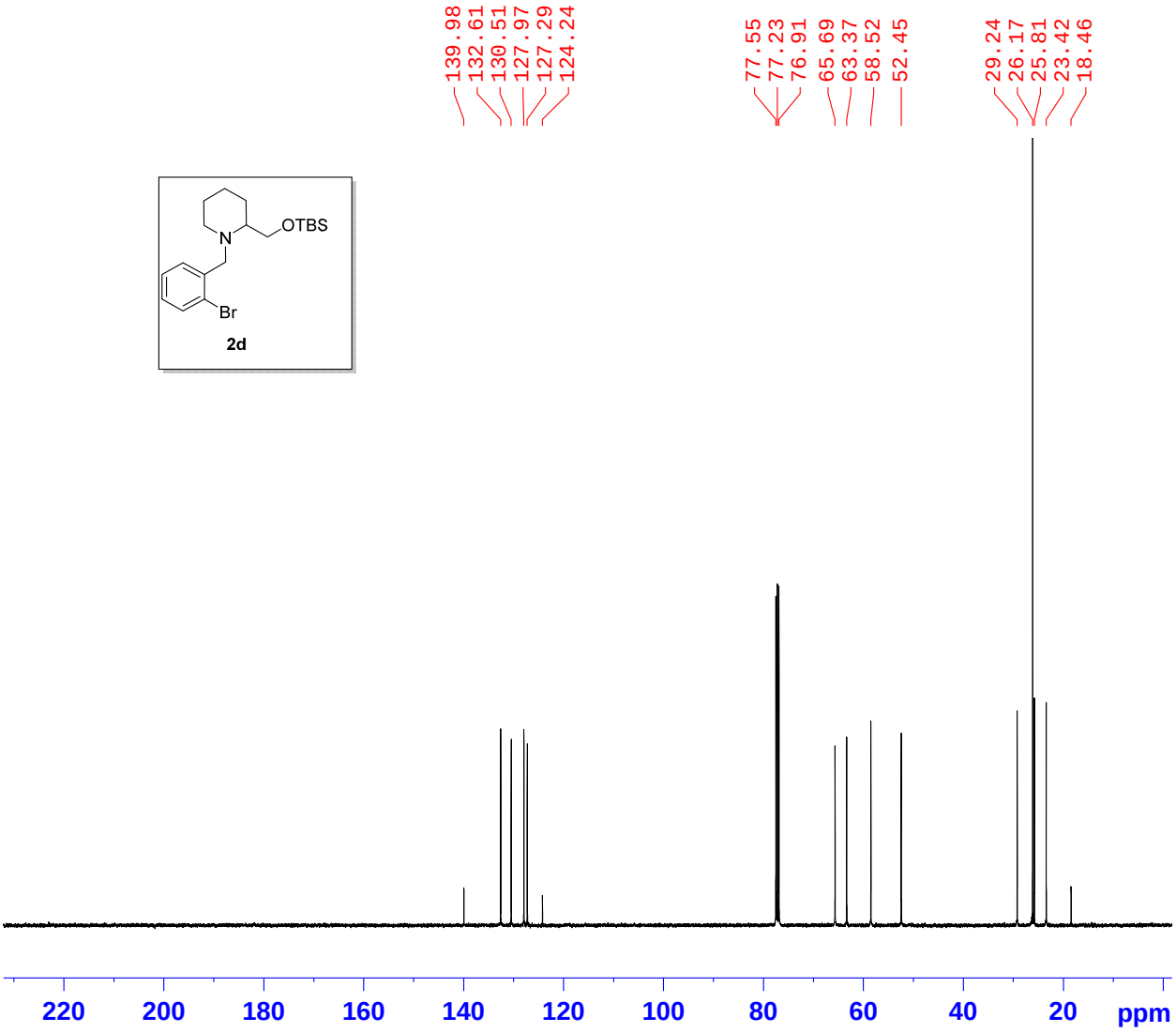
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76.91
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63.37
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29.24
26.17
25.81
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Br
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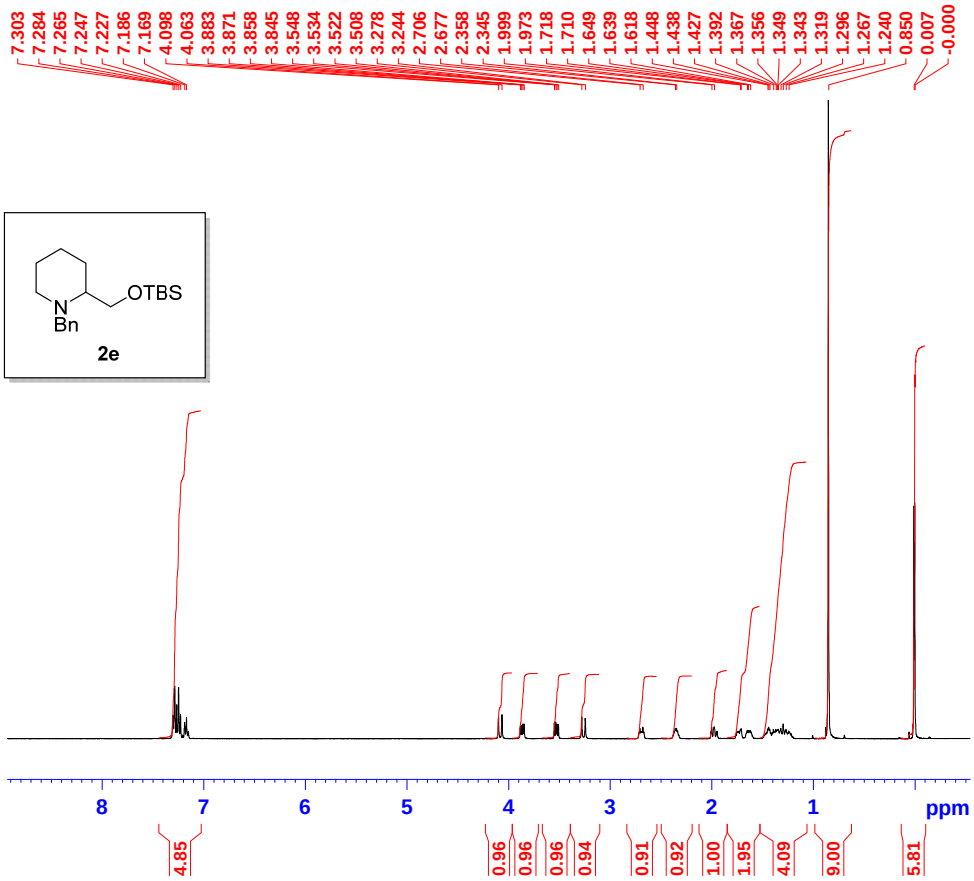
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-0.000
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Bn
2e
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2
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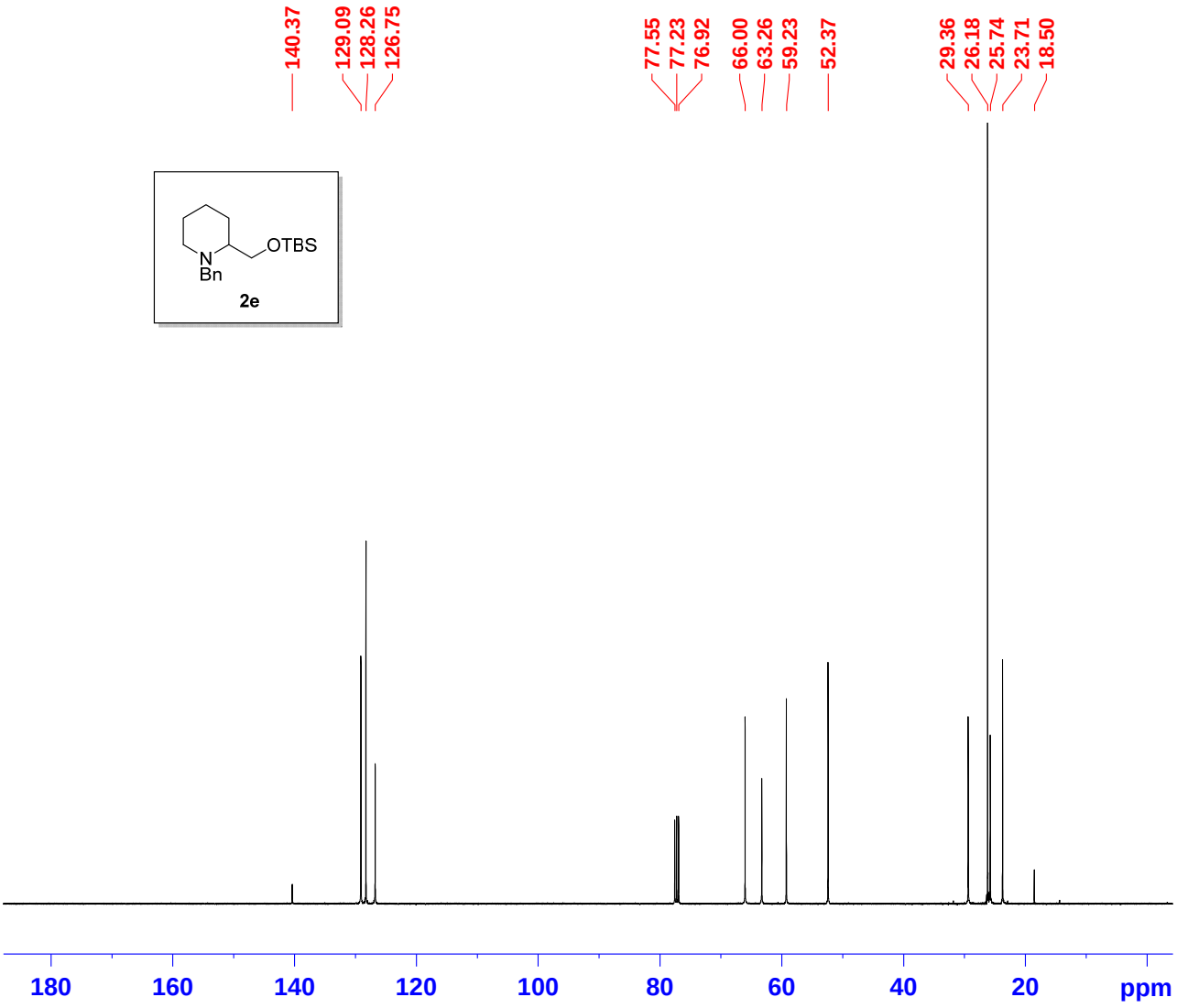
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Bn
2e
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120
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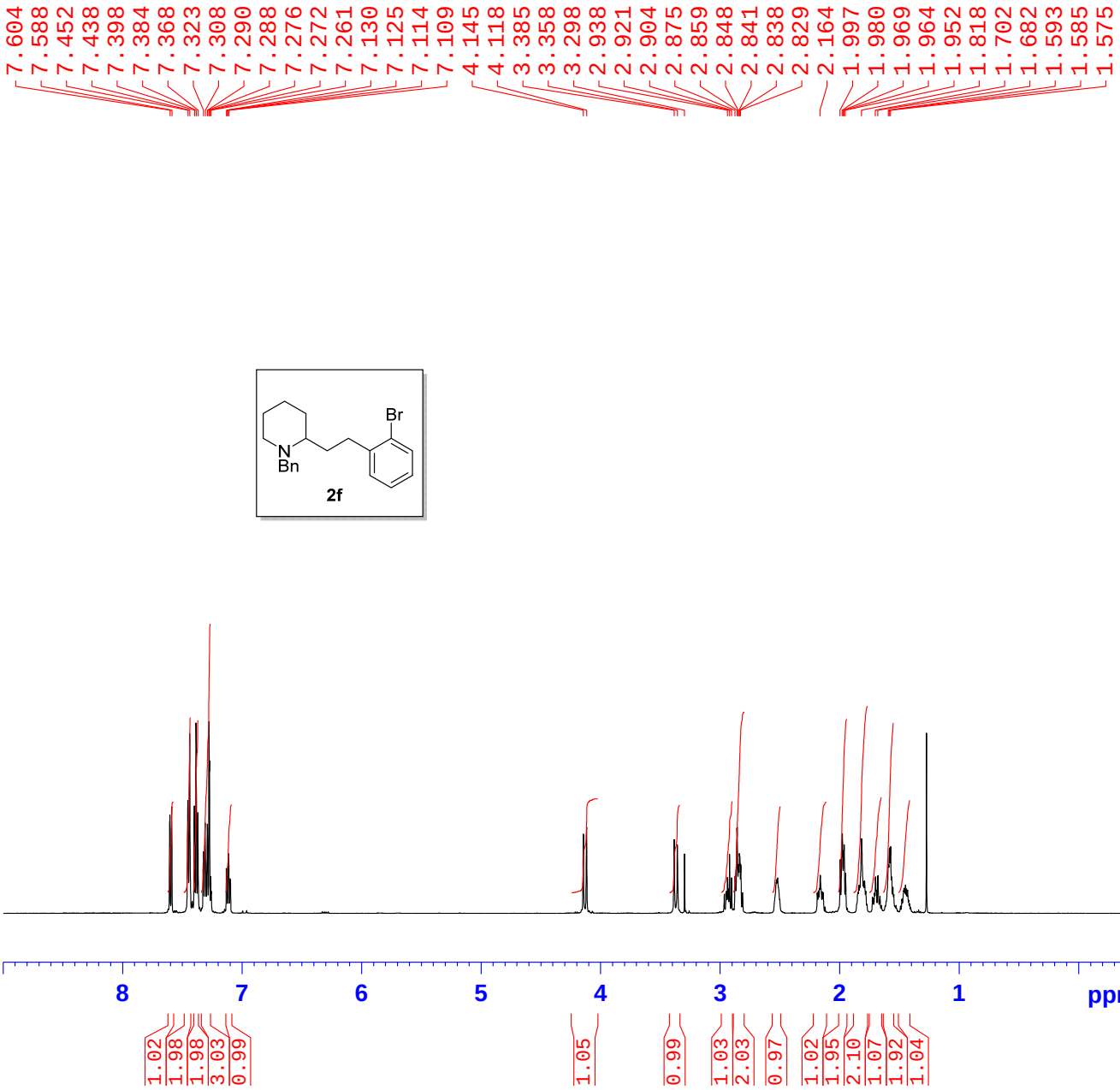
ppm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7.109
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4.118
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3.358
3.298
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2.921
2.904
2.875
2.859
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2.838
2.829
2.164
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1.585
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Bn
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7
6
5
4
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2
1
ppm
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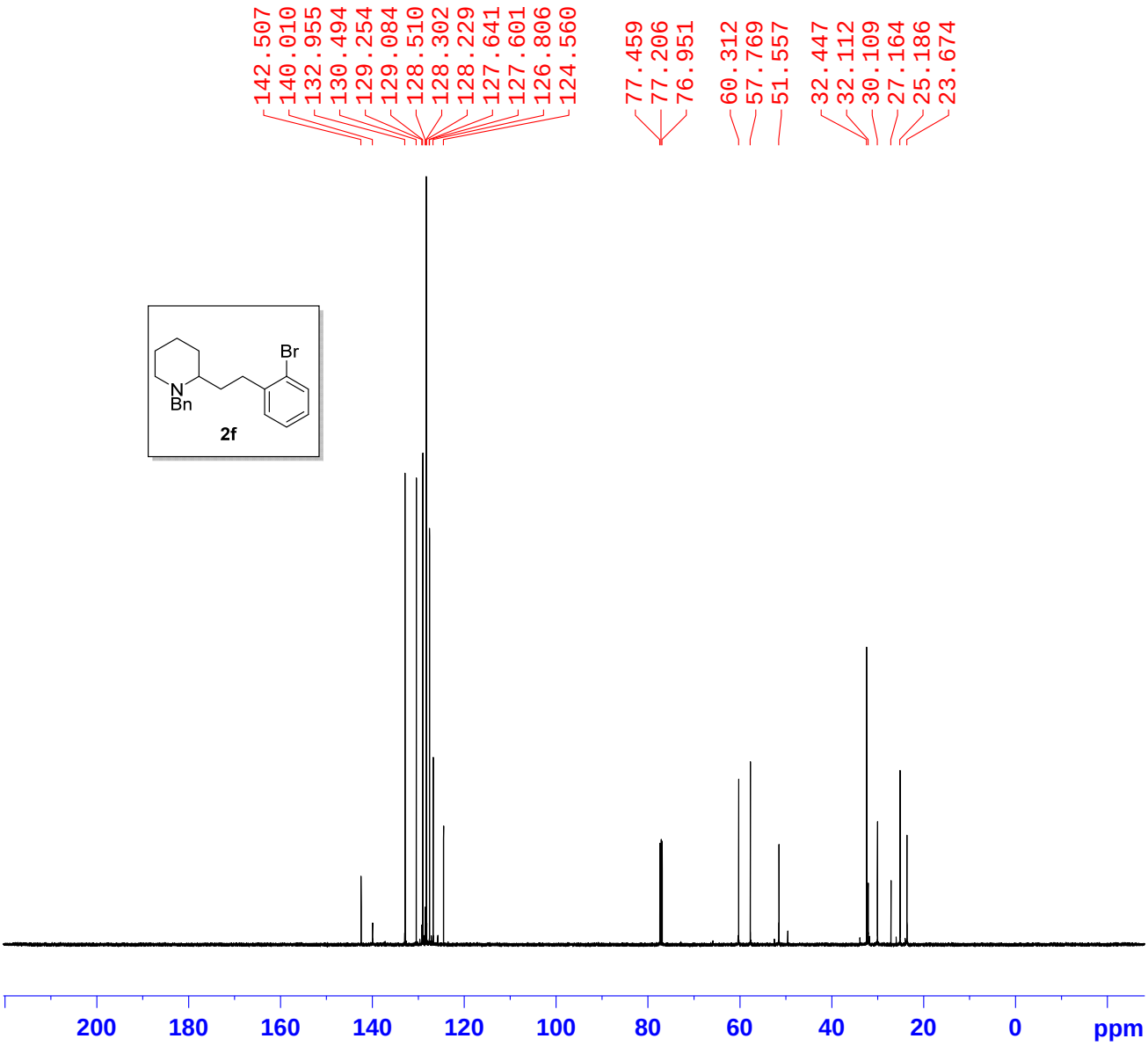
1.04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126.806
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77.206
76.951
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51.557
32.447
32.112
30.109
27.164
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Br
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Bn
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200
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120
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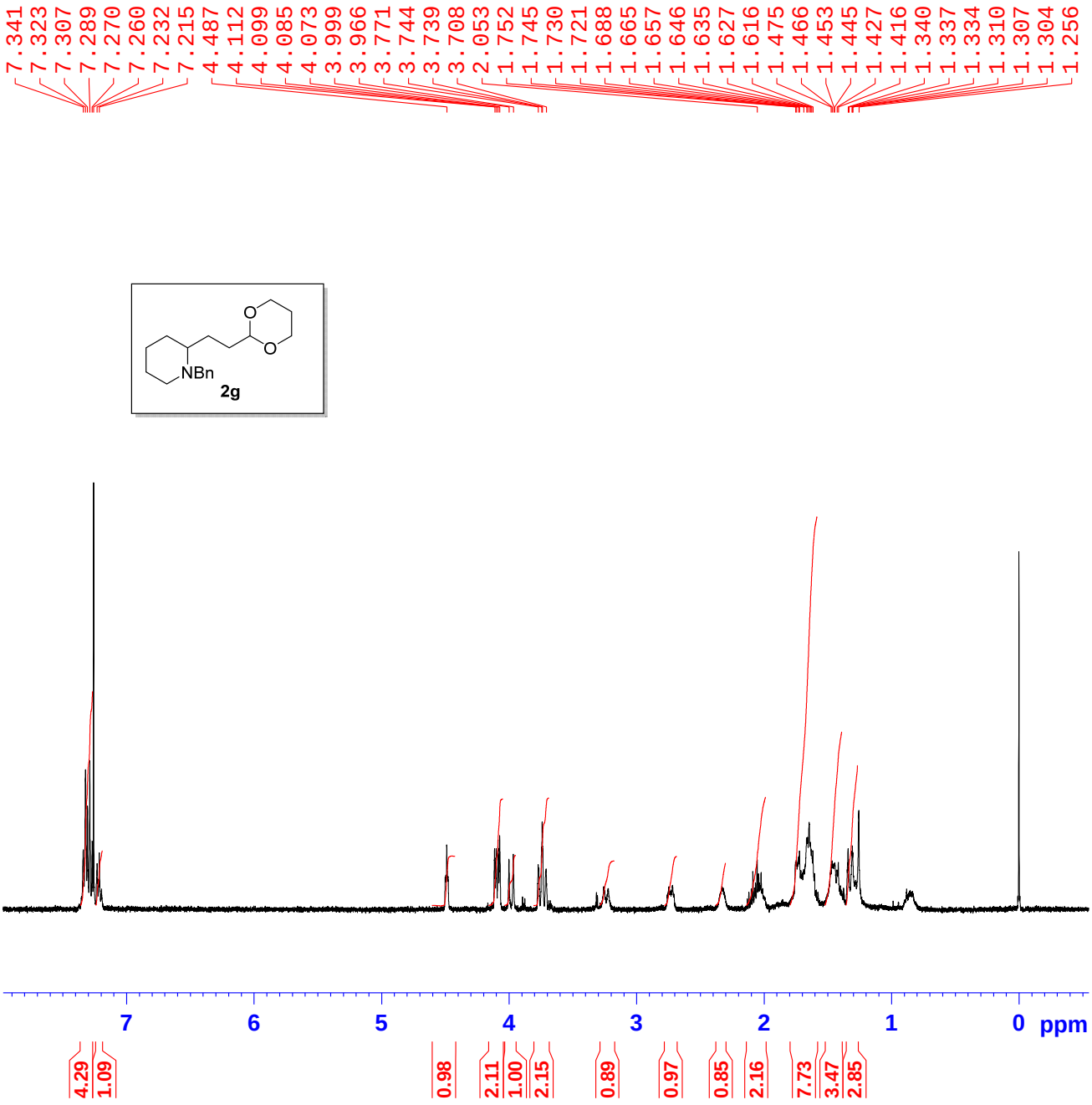
80
60
40
20
0
ppm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3.771
3.744
3.739
3.708
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1.745
1.730
1.721
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1.646
1.635
1.627
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1.475
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O
O
NBn
2g
7
6
5
4
3
2
1
0
ppm
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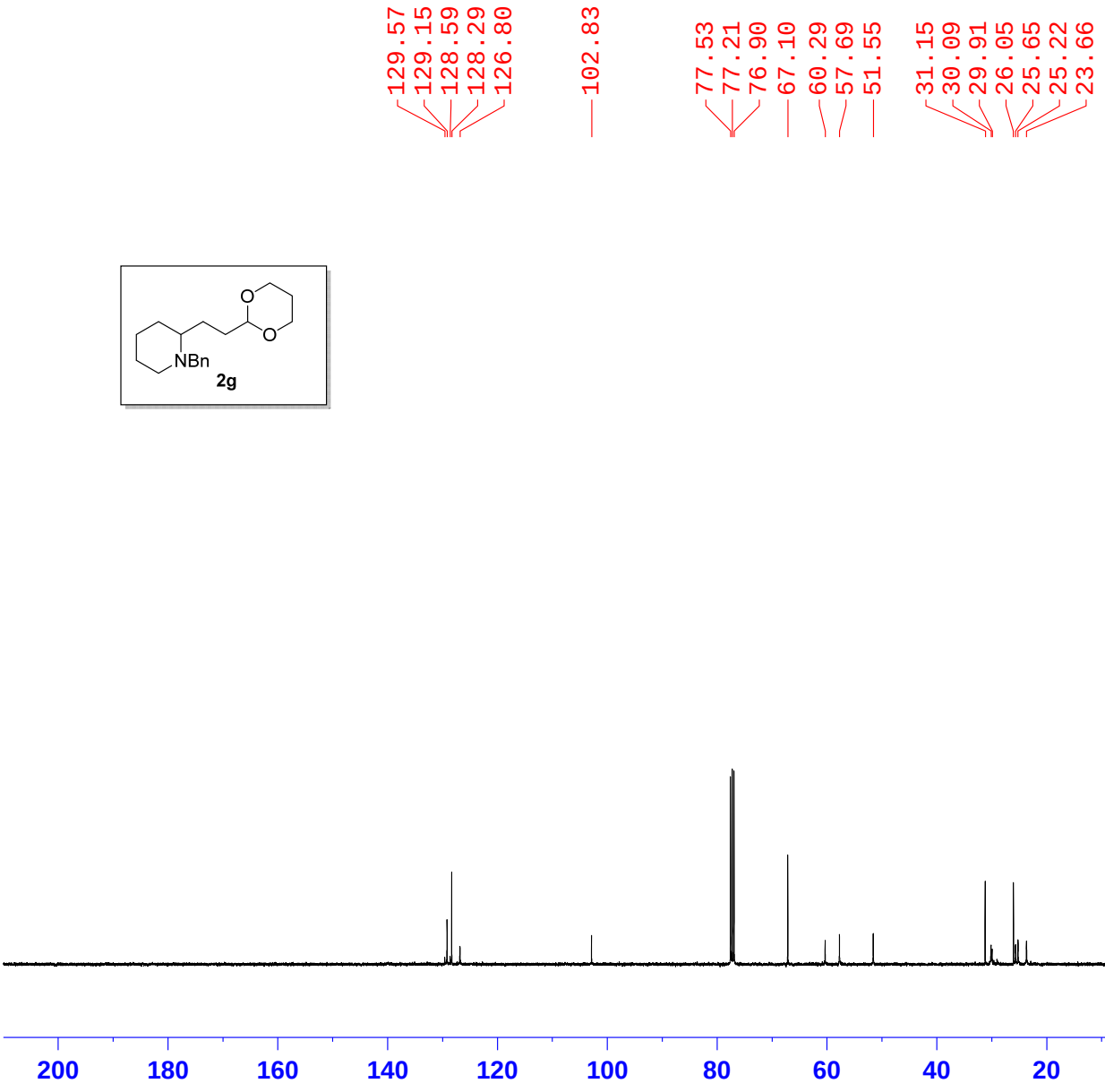
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77.21
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60.29
57.69
51.55
31.15
30.09
29.91
26.05
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25.22
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O
O
NBn
2g
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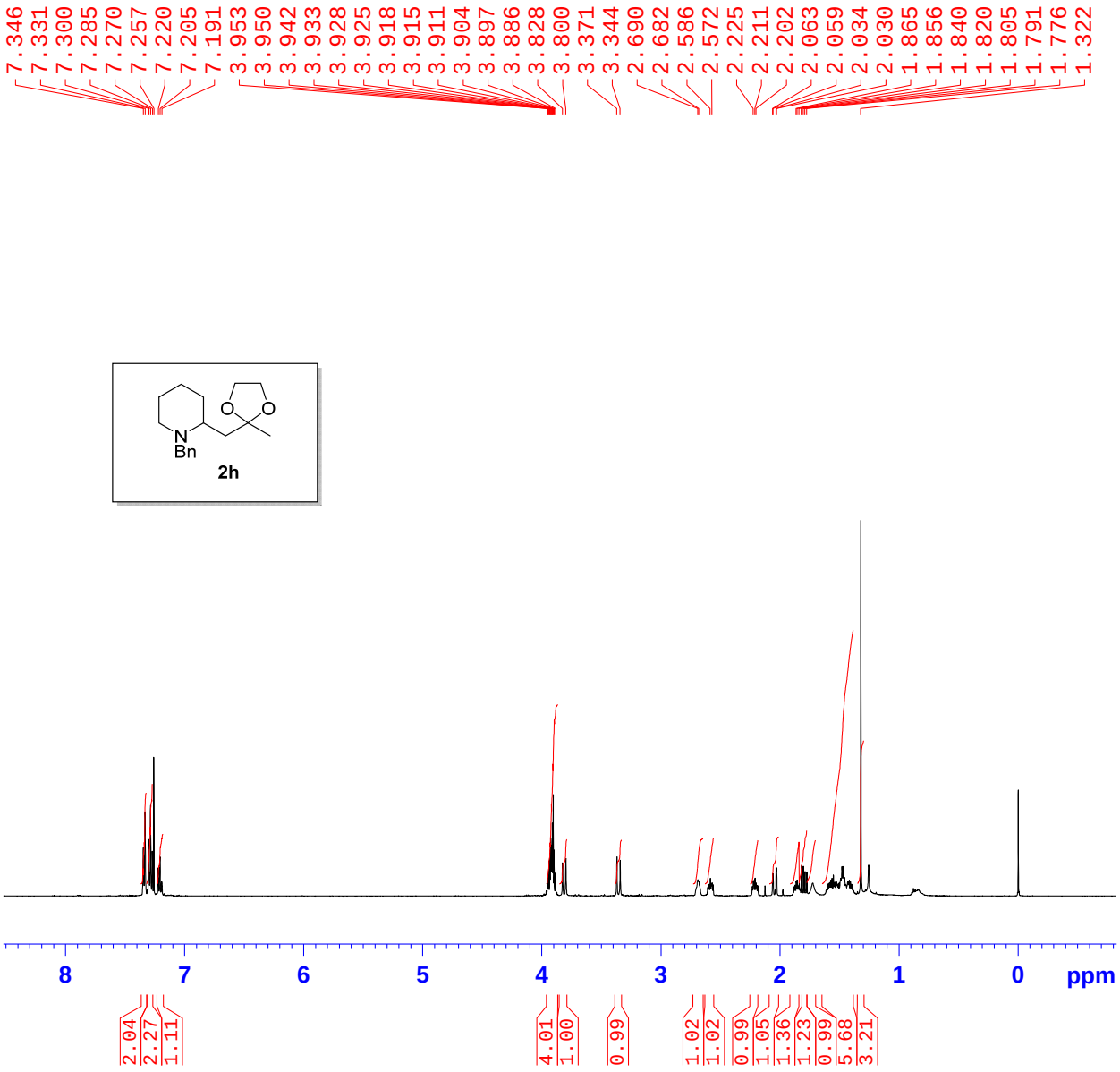
140
120
100
80
60
40
20
ppm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3.933
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3.925
3.918
3.915
3.911
3.904
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3.828
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2.572
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2.063
2.059
2.034
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1.856
1.840
1.820
1.805
1.791
1.776
1.322
N
Bn
O
O
2h
8
7
6
5
4
3
2
1
0
ppm
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2.27
1.11
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1.02
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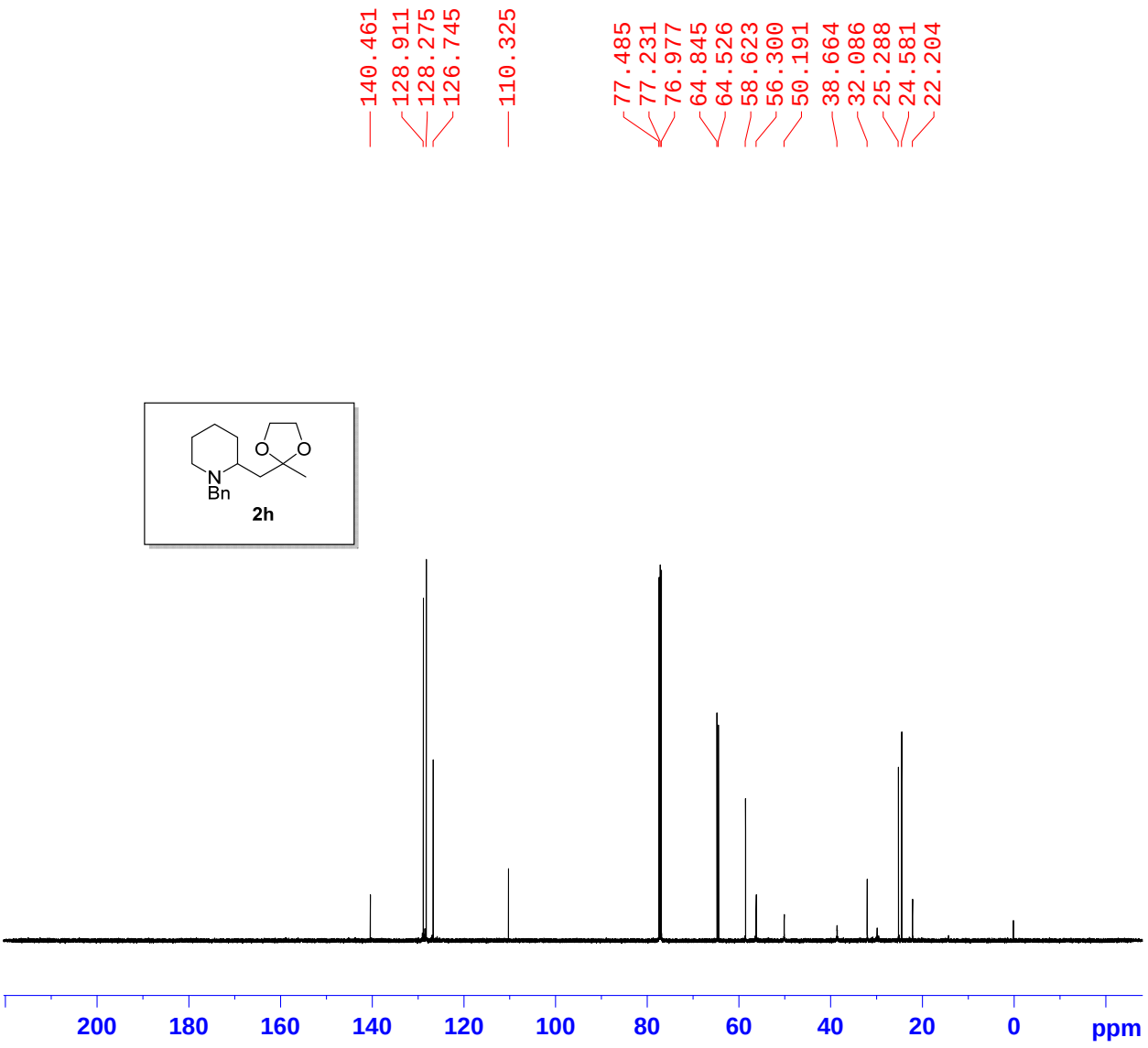
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56.300
50.191
38.664
32.086
25.288
24.581
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Bn
O
O
2h
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120
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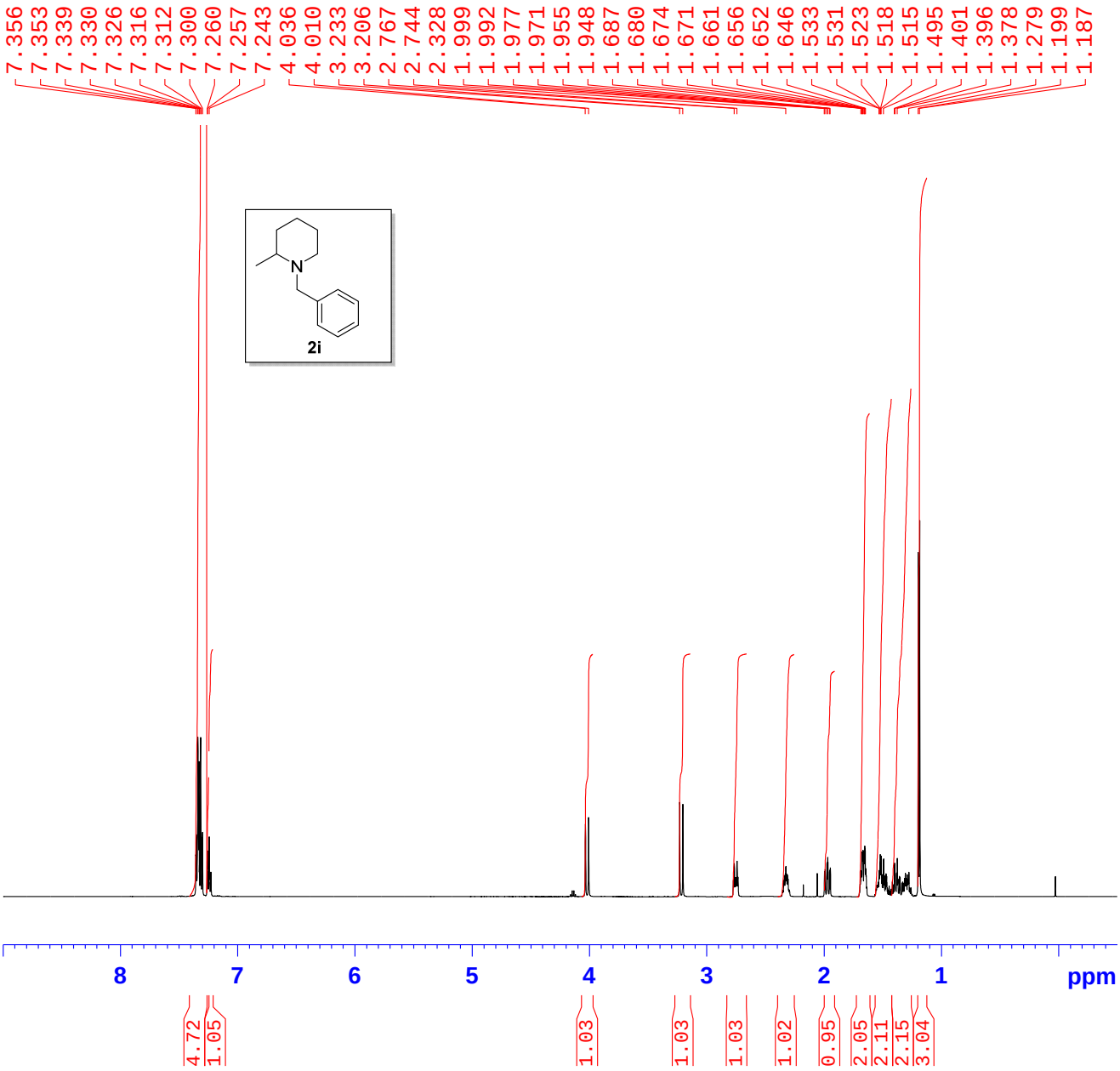
40
20
0
ppm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1.533
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1.523
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1.495
1.401
1.396
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1.279
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1.187
N
2i
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7
6
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4
3
2
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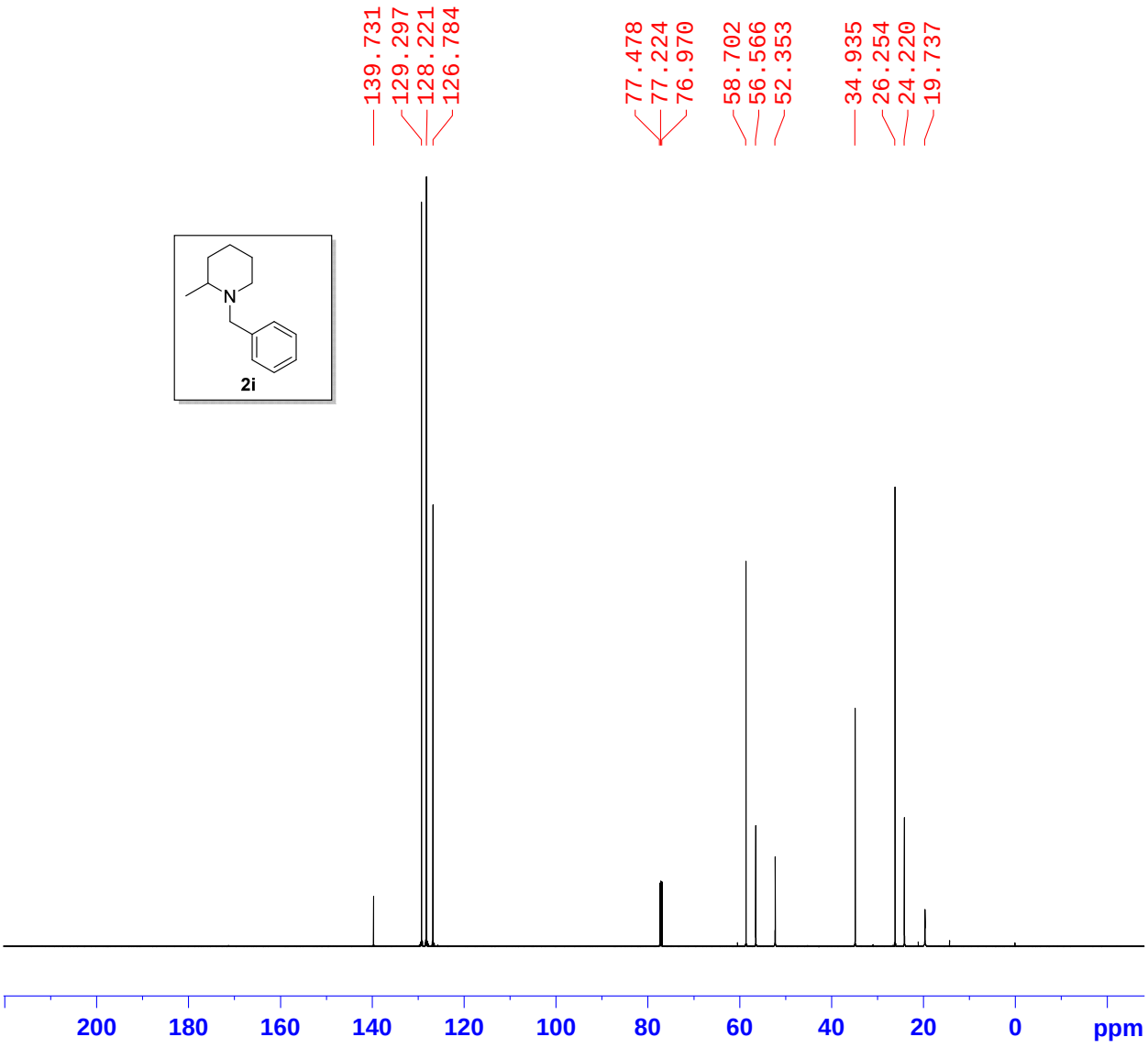
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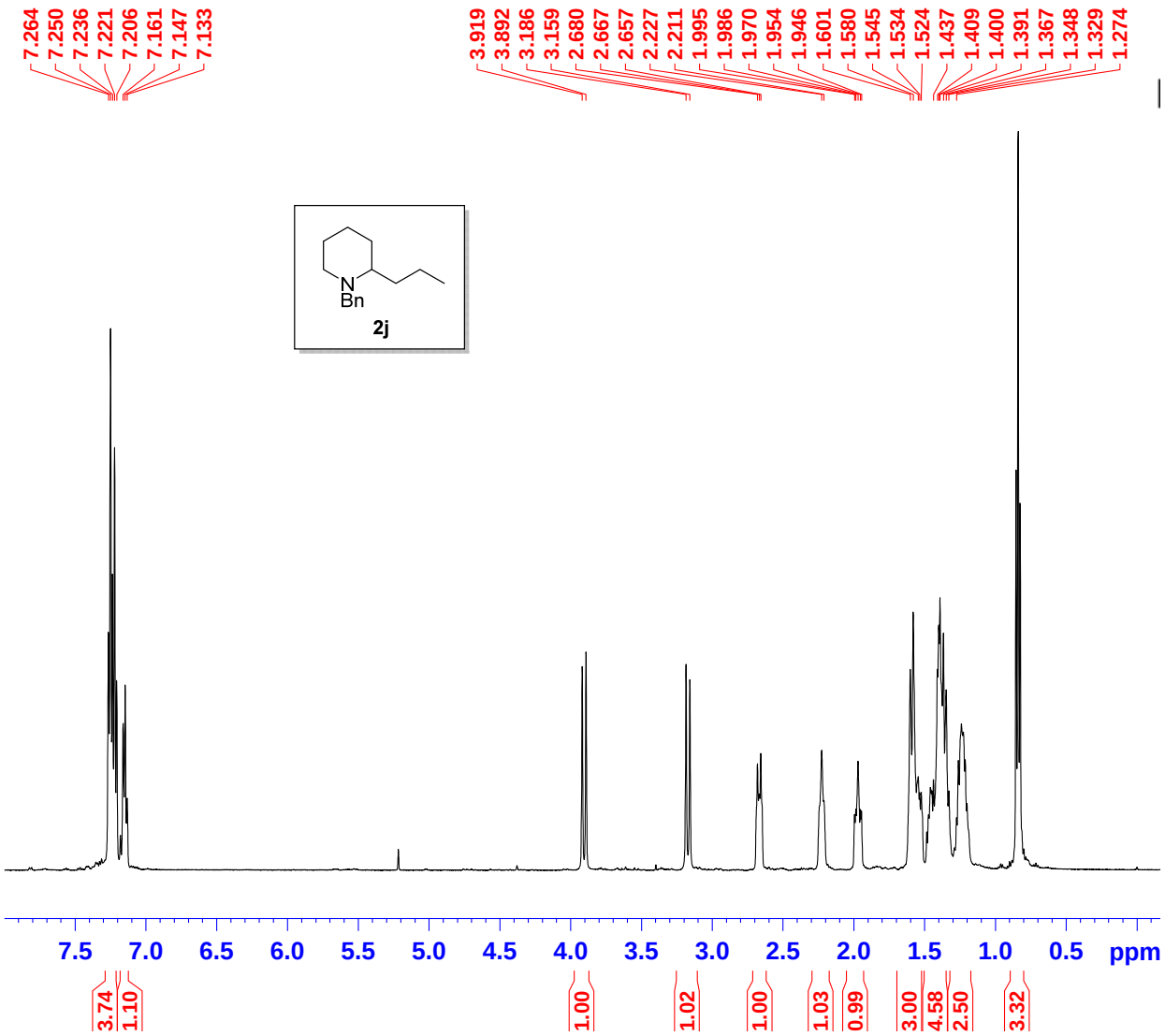
40
20
0
ppm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3.159
2.680
2.667
2.657
2.227
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1.986
1.970
1.954
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1.601
1.580
1.545
1.534
1.524
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Bn
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5.5
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4.0
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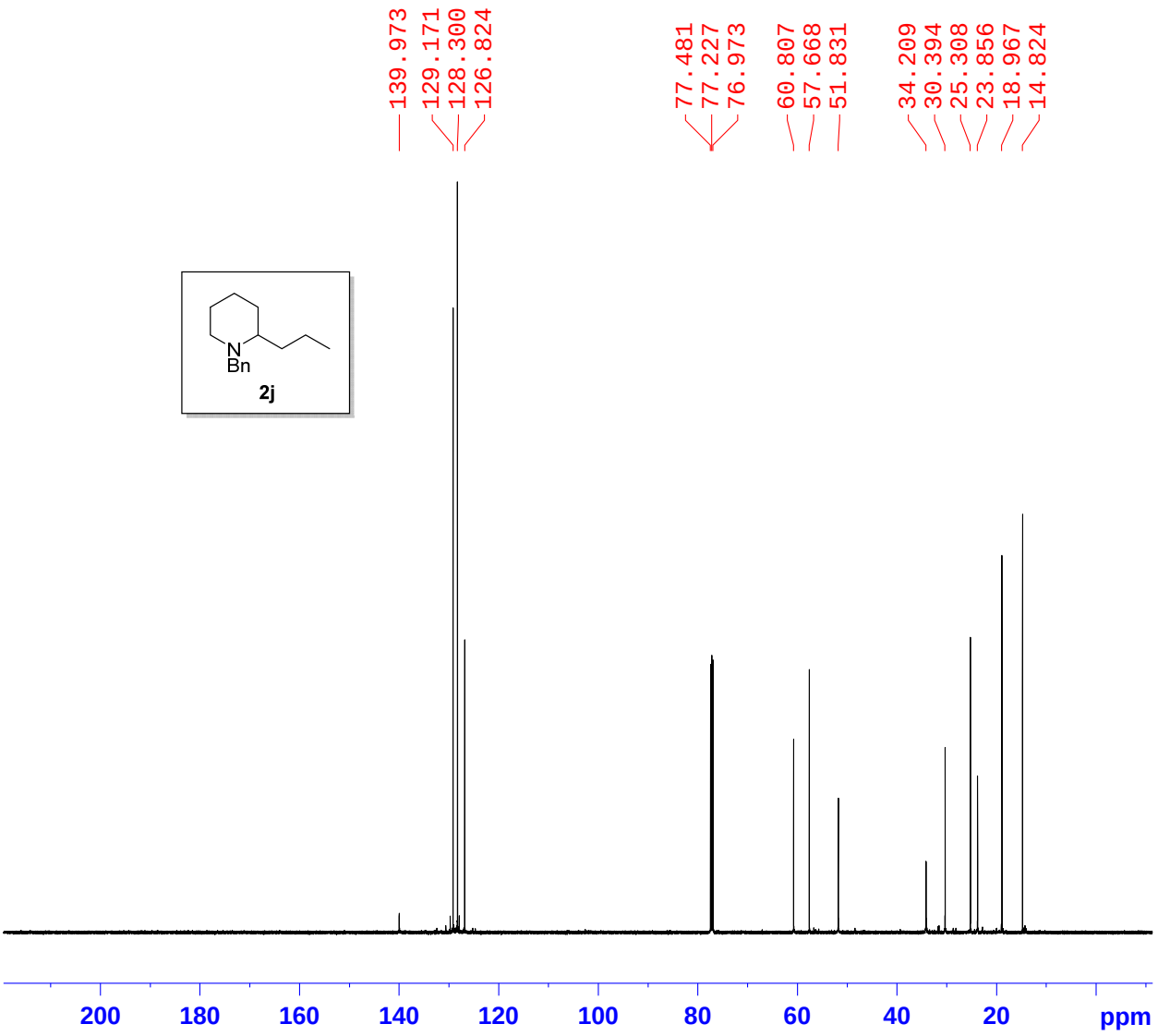
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25.308
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N
Bn
2j
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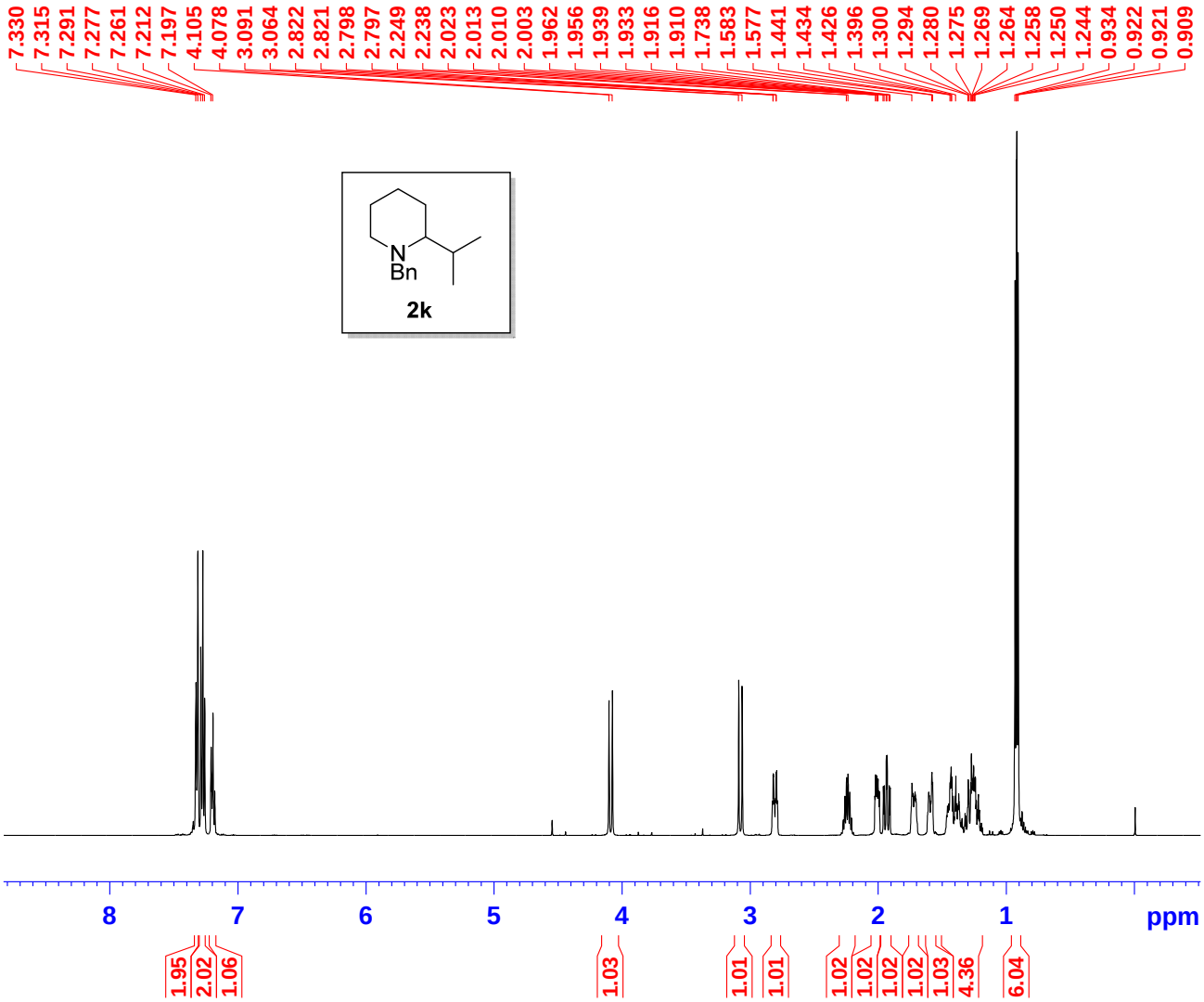
140
120
100
80
60
40
20
ppm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2.797
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Bn
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2
1
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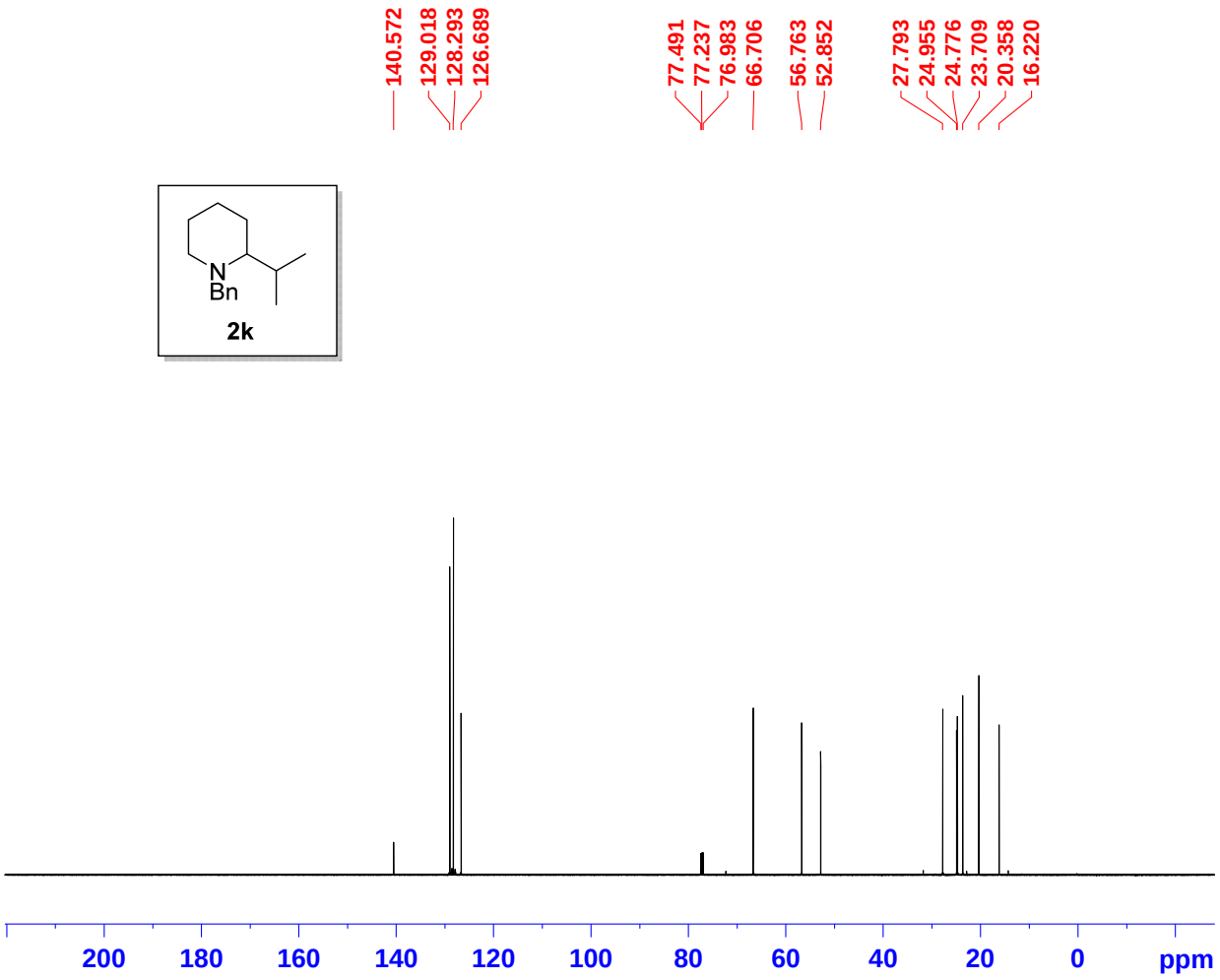
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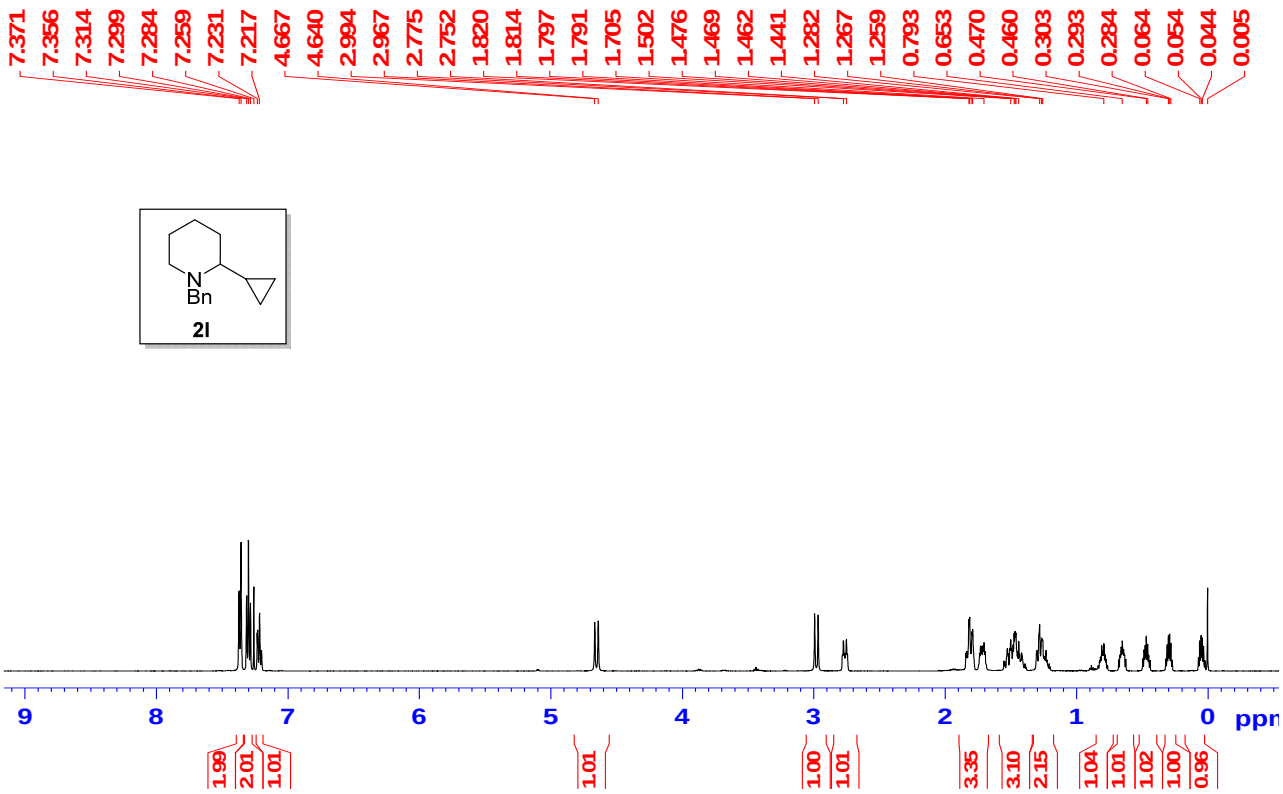
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0.293
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0.064
0.054
0.044
0.005
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Bn
2l
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8
7
6
5
4
3
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1.02
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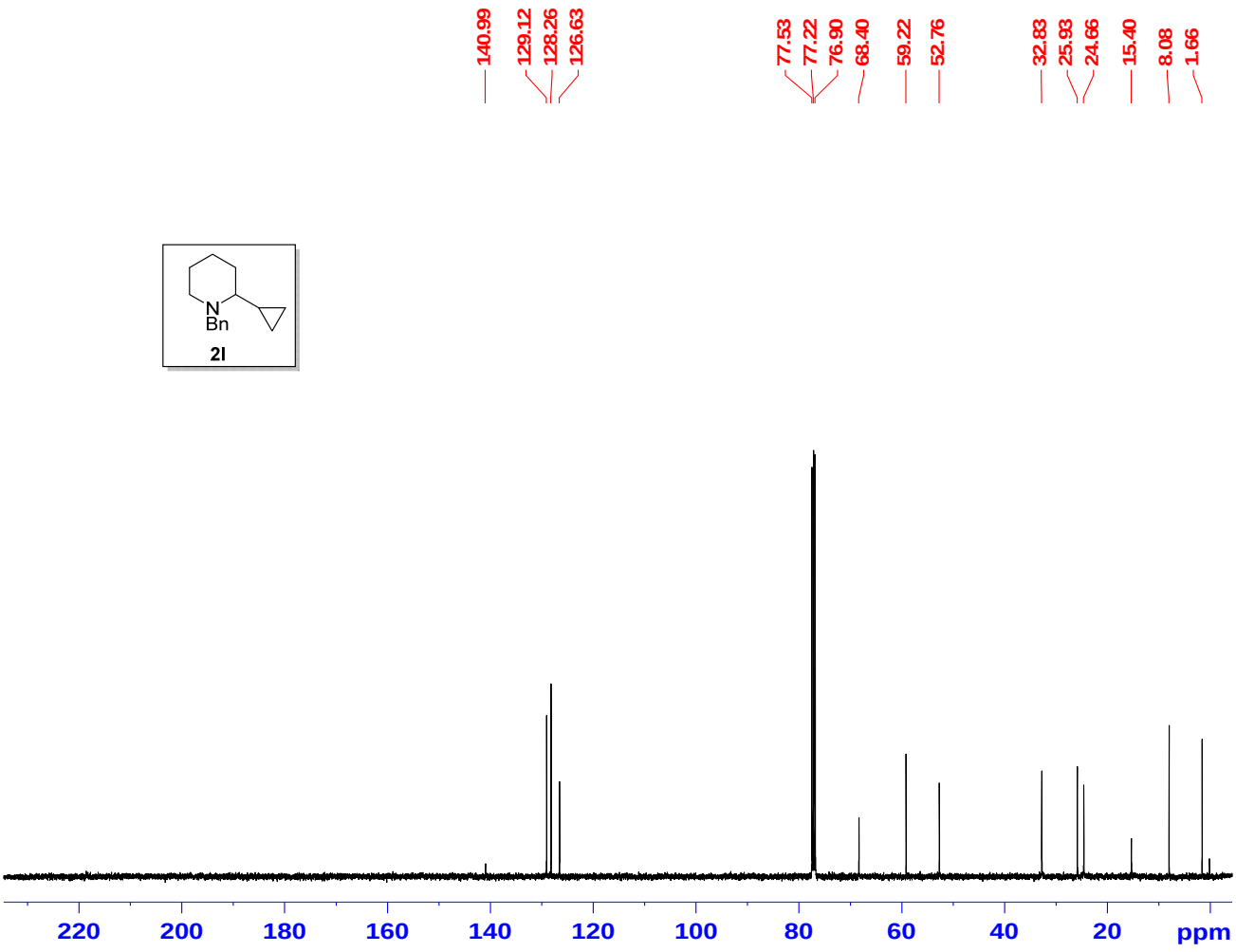
0.96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Bn
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20
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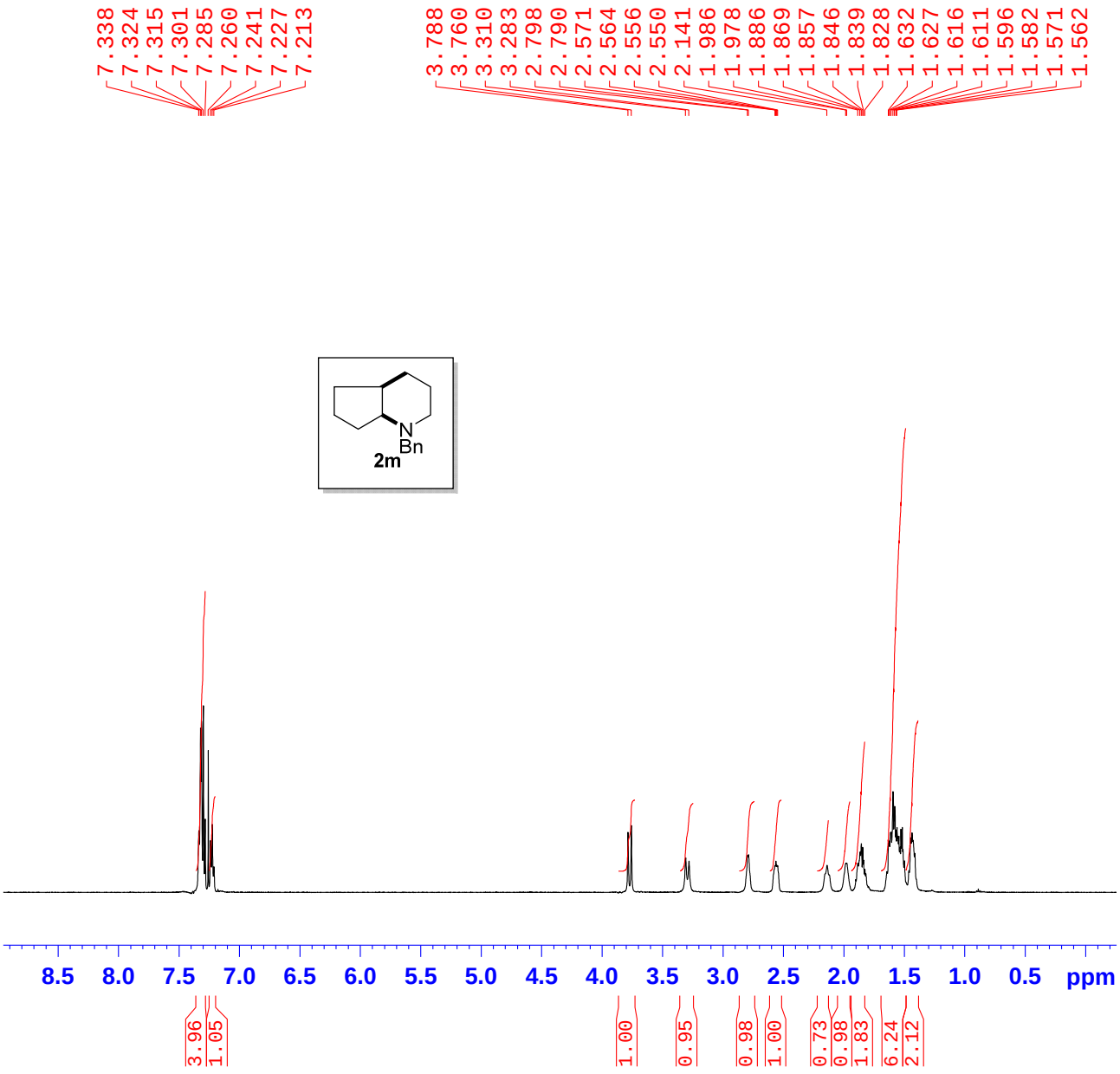
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2.798
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1.616
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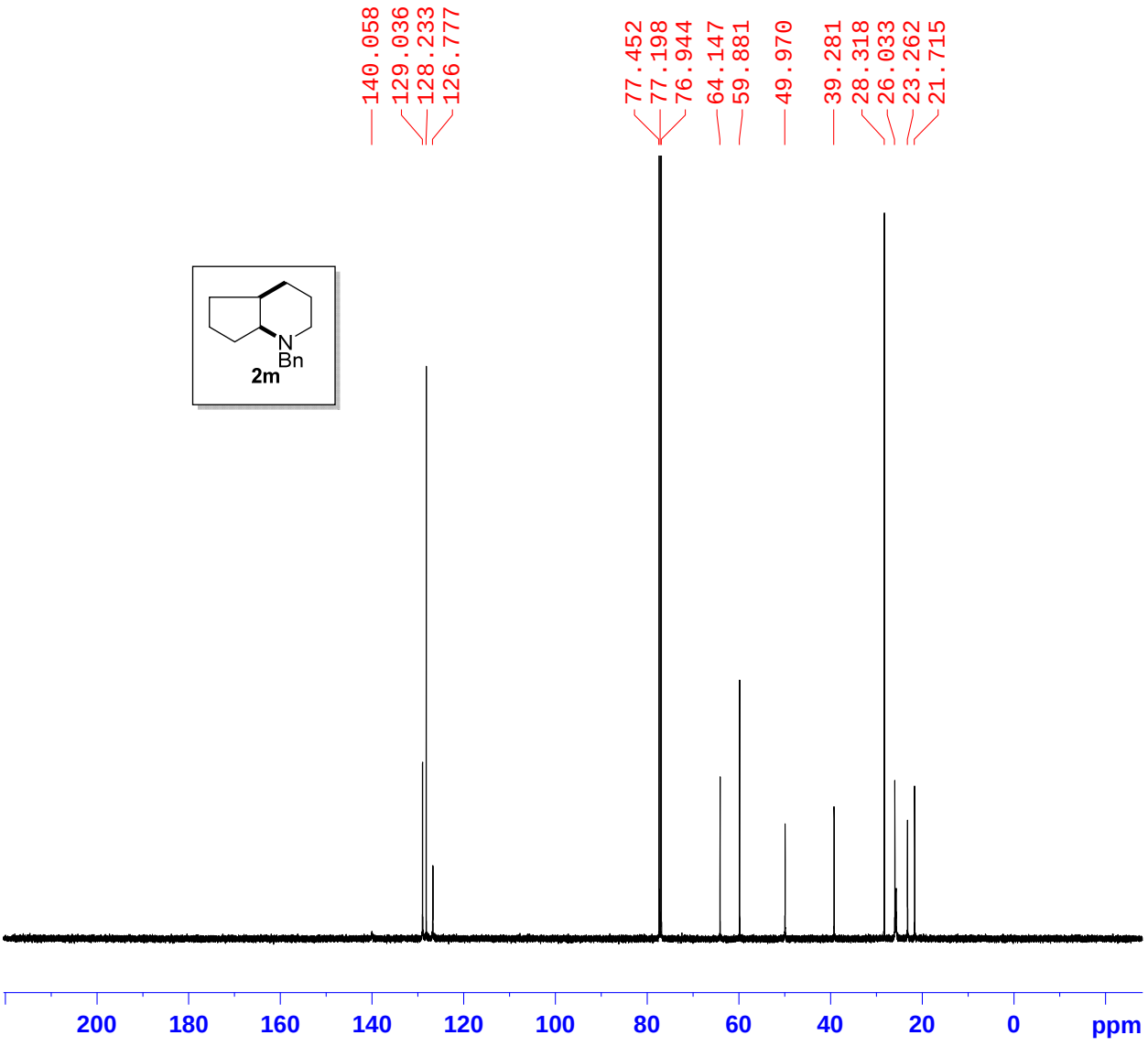
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Bn
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120
100
80
60
40
20
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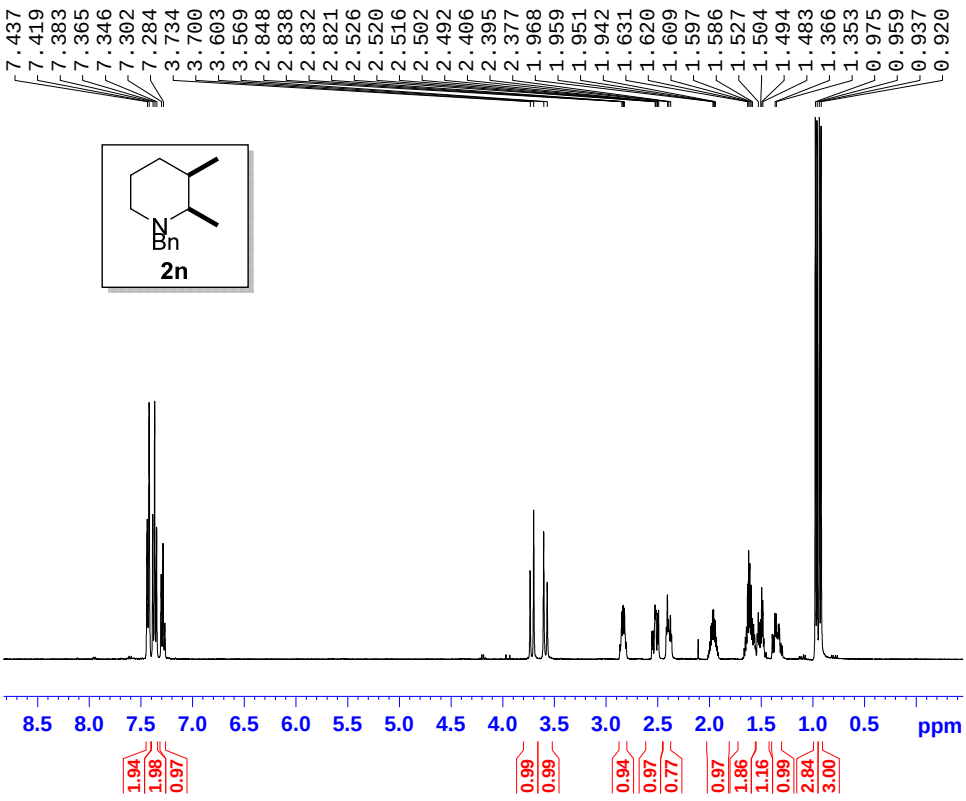
ppm

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EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
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Time              15.50
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT           CDCl3
NS                    4
DS                    4
SWH            5896.227 Hz
FIDRES        0.179939 Hz
AQ           2.7787263 sec
RG                 90.5
DW               84.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1327209 MHz
NUC1                1H
P1                15.00 usec
PLW1        10.50000000 W

F2 - Processing parameters
SI                65536
SF          400.1300000 MHz
WDW                  EM
SSB       0
LB                0.05 Hz
GB        0
PC                1.00
```

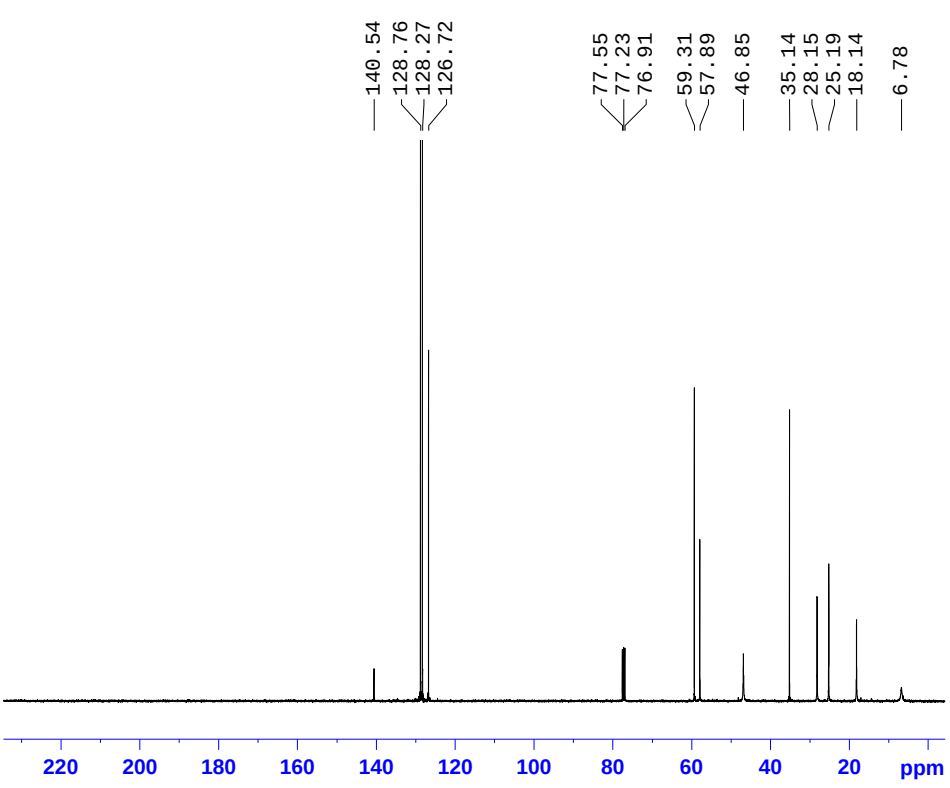


```
Current Data Parameters
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EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
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Time              16.17
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PROBHD   5 mm PABBO BB-
PULPROG           zgpg
TD                32768
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           24038.461 Hz
FIDRES        0.733596 Hz
AQ            0.6815744 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6243395 MHz
NUC1                13C
P1                10.90 usec
PLW1        43.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        10.50000000 W
PLW12        0.29166999 W
PLW13        0.14670999 W

F2 - Processing parameters
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SF          100.6127550 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
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```

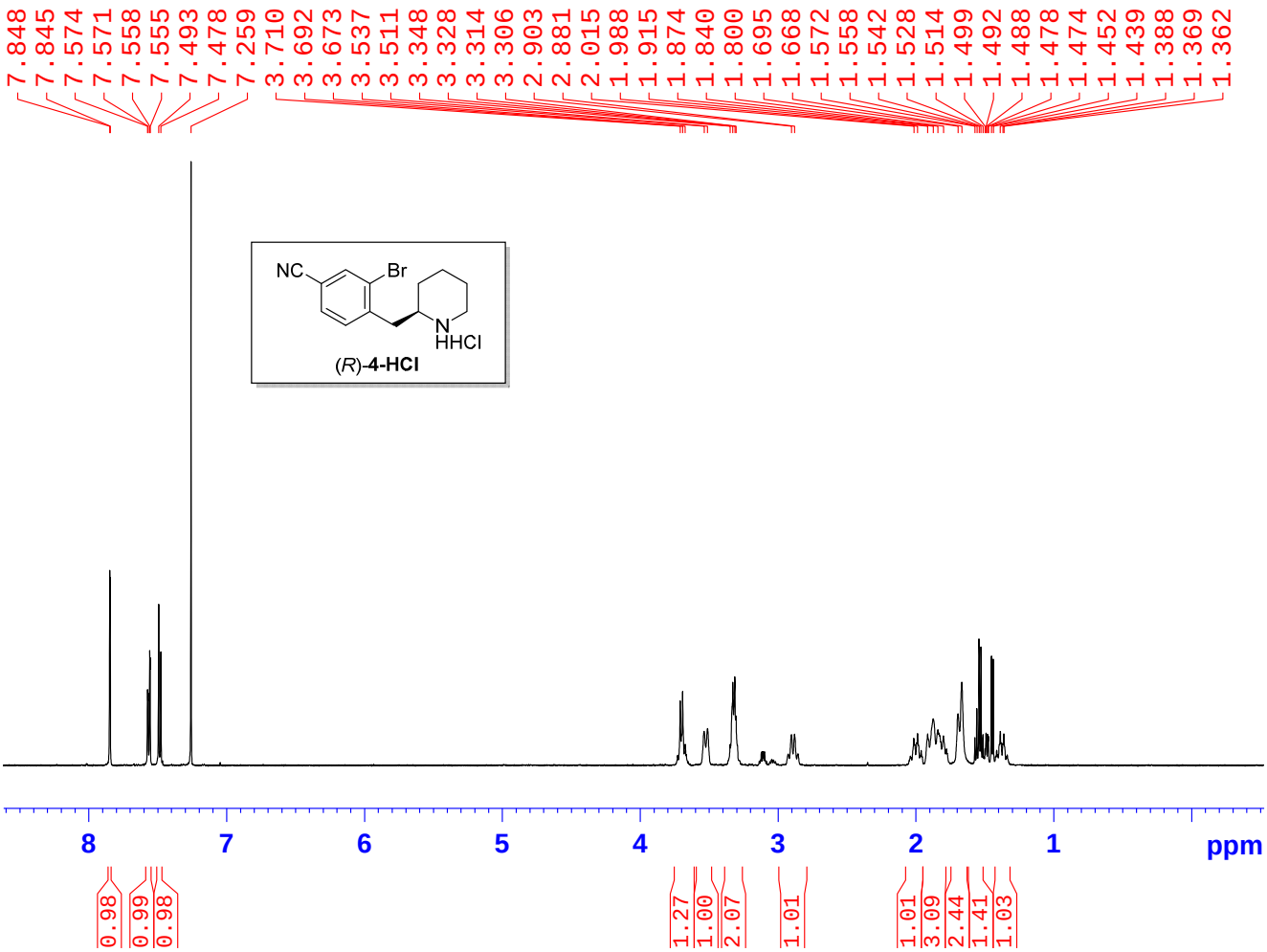
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3.673
3.537
3.511
3.348
3.328
3.314
3.306
2.903
2.881
2.015
1.988
1.915
1.874
1.840
1.800
1.695
1.668
1.572
1.558
1.542
1.528
1.514
1.499
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1.488
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1.474
1.452
1.439
1.388
1.369
1.362
NC
Br
N
HHCl
(R)-4-HCl
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7
6
5
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2
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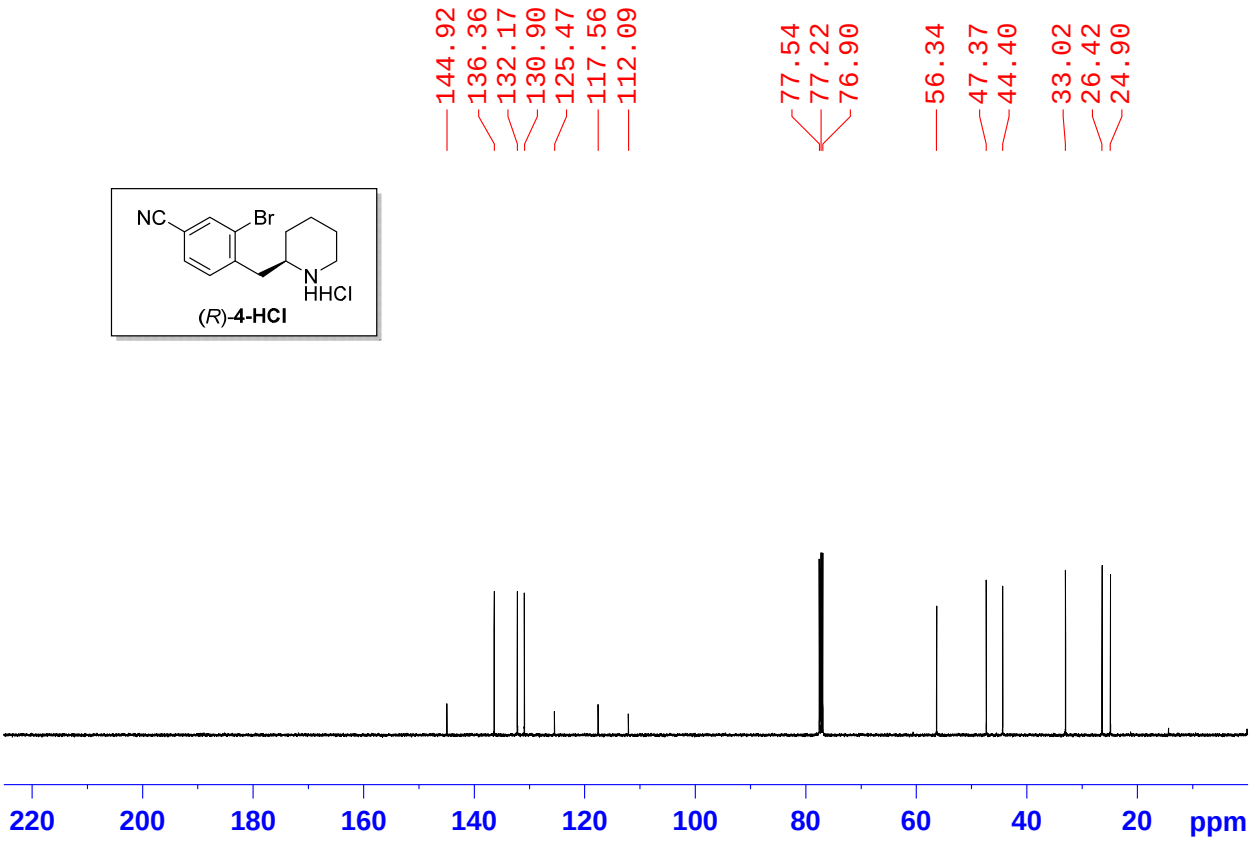
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117.56
112.09
77.54
77.22
76.90
56.34
47.37
44.40
33.02
26.42
24.90
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HHCl
(R)-4-HCl
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140
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80
60
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20
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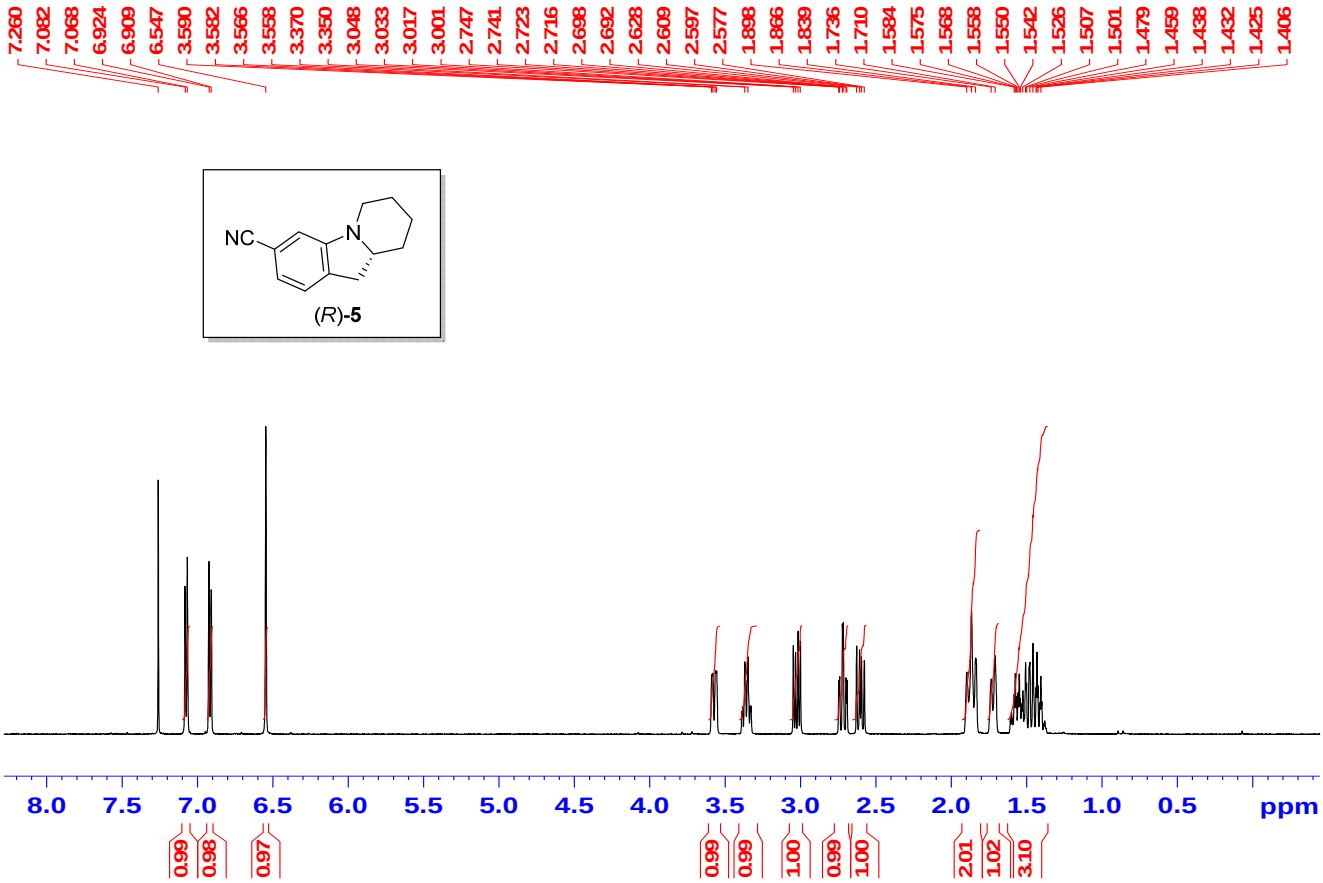
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3.582
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3.033
3.017
3.001
2.747
2.741
2.723
2.716
2.698
2.692
2.628
2.609
2.597
2.577
1.898
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1.839
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1.710
1.584
1.575
1.568
1.558
1.550
1.542
1.526
1.507
1.501
1.479
1.459
1.438
1.432
1.425
1.406
NC
N
(R)-5
8.0
7.5
7.0
6.5
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5.0
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3.5
3.0
2.5
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1.0
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2.01
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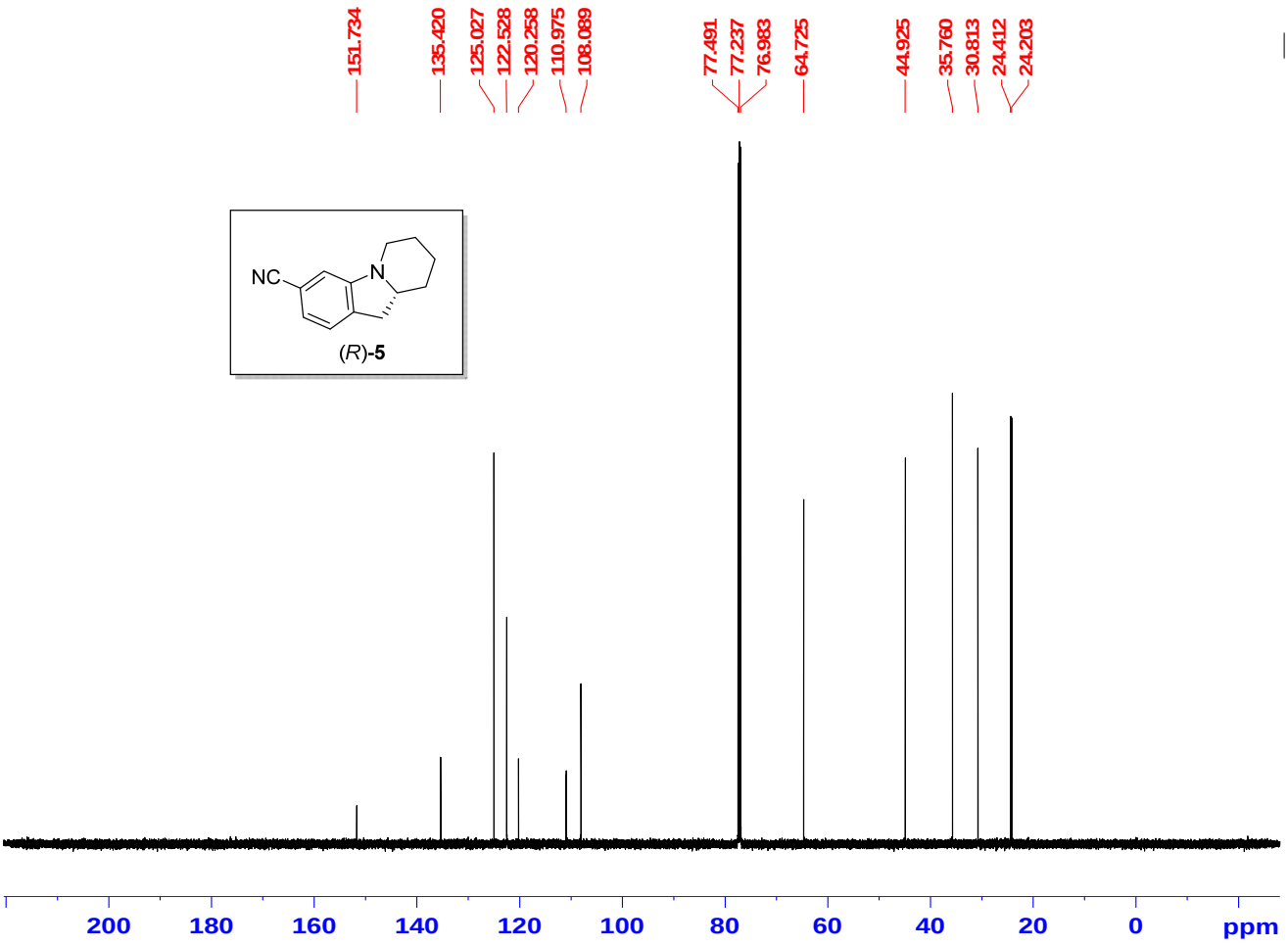
3.10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64.725
44.925
35.760
30.813
24.412
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N
(R)-5
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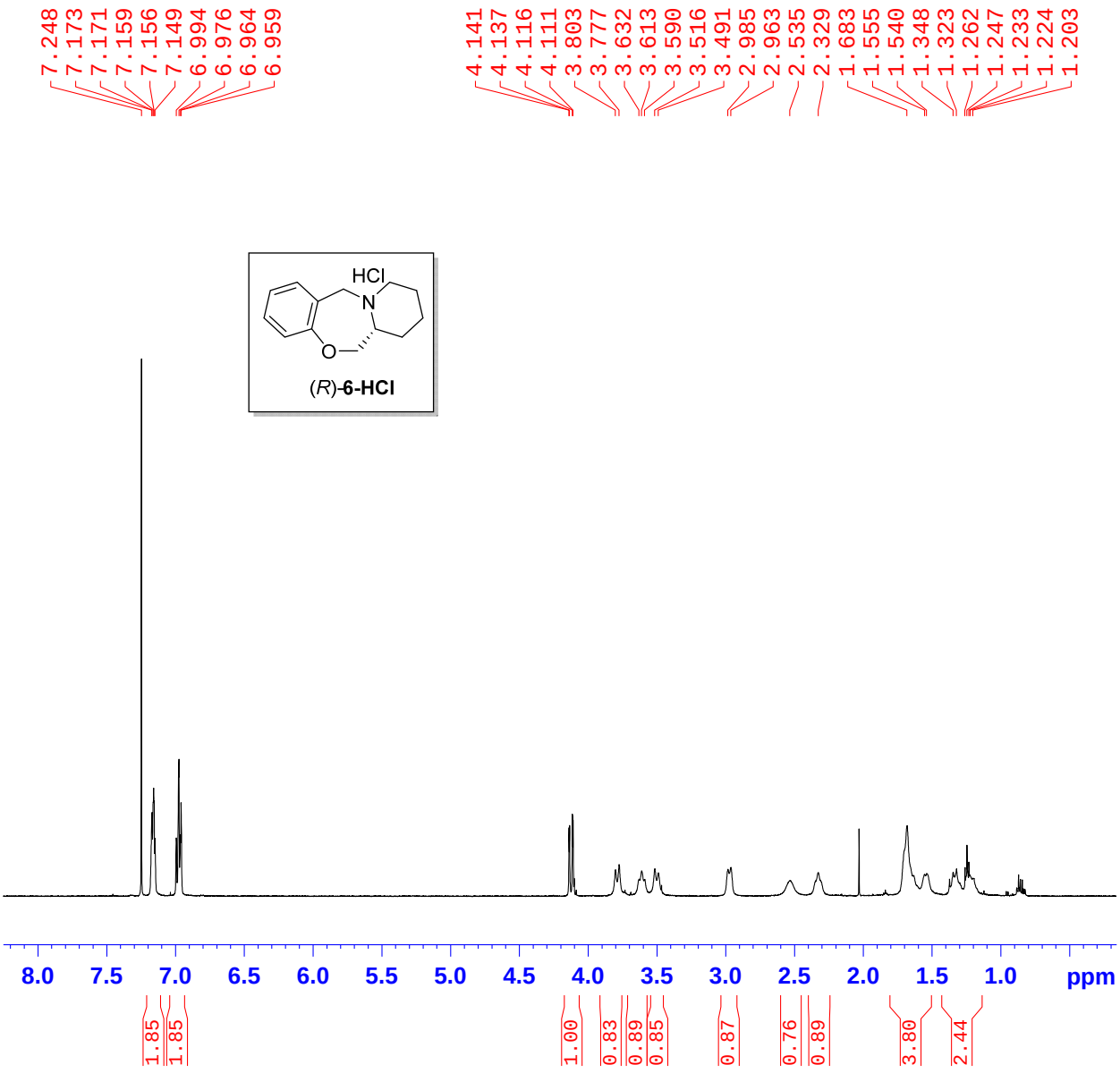
120
100
80
60
40
20
0
ppm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6.976
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4.137
4.116
4.111
3.803
3.777
3.632
3.613
3.590
3.516
3.491
2.985
2.963
2.535
2.329
1.683
1.555
1.540
1.348
1.323
1.262
1.247
1.233
1.224
1.203
HCl
N
O
(R)-6-HCl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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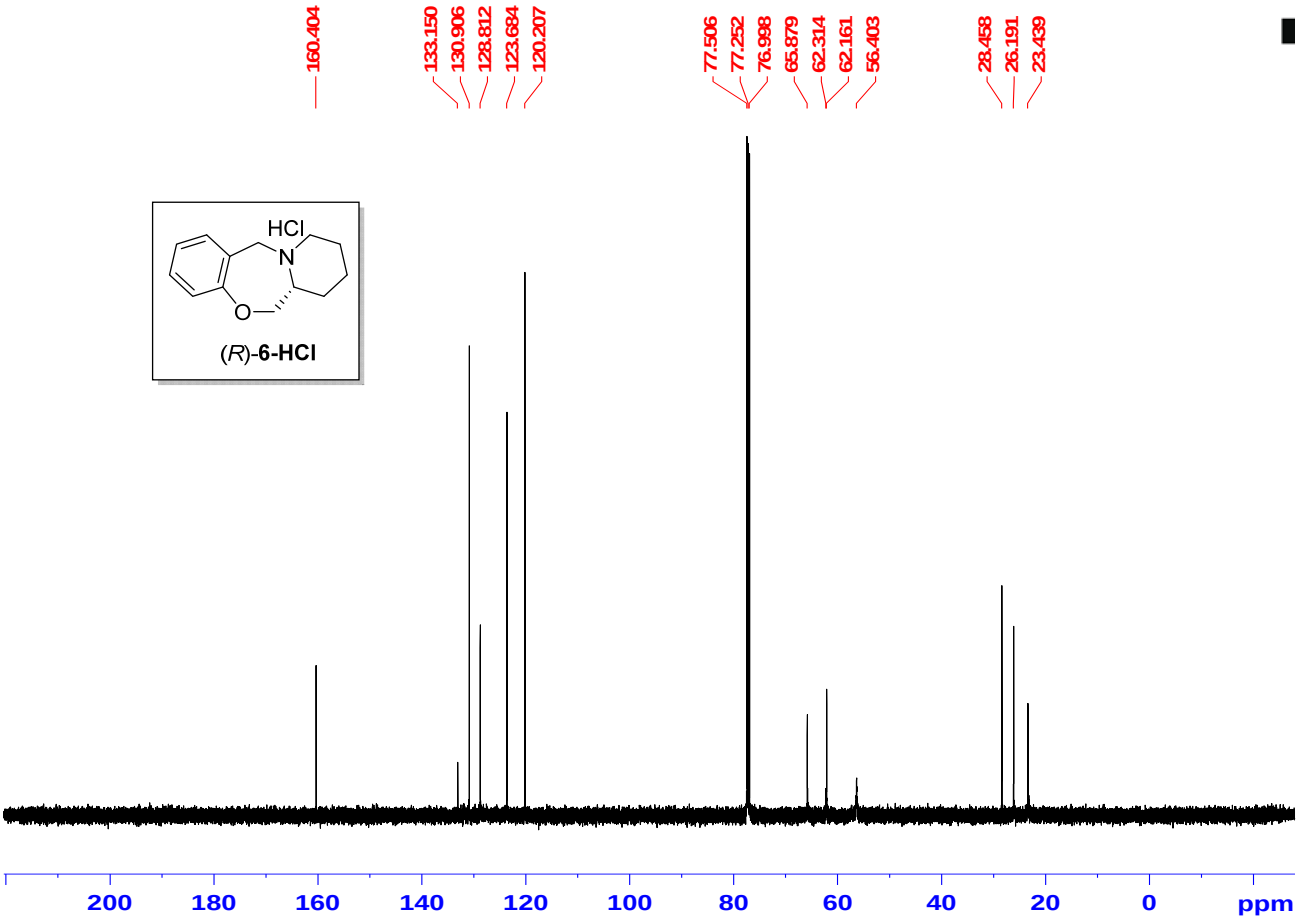
2.44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77.252
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65.879
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62.161
56.403
28.458
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O
(R)-6-HCl
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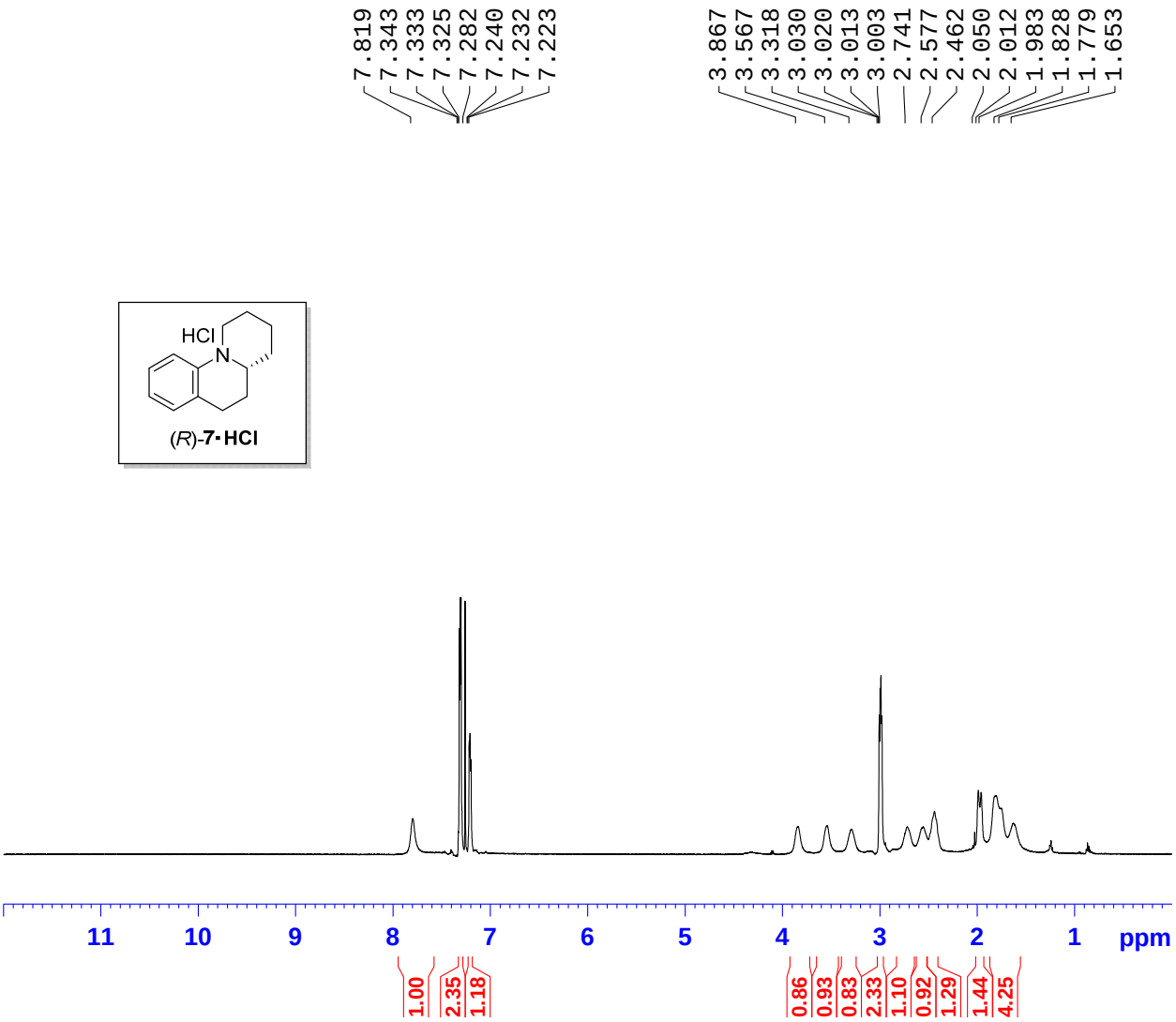
140
120
100
80
60
40
20
0
ppm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7.223
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3.318
3.030
3.020
3.013
3.003
2.741
2.577
2.462
2.050
2.012
1.983
1.828
1.779
1.653
HCl
N
(R)-7·HCl
11
10
9
8
7
6
5
4
3
2
1
ppm
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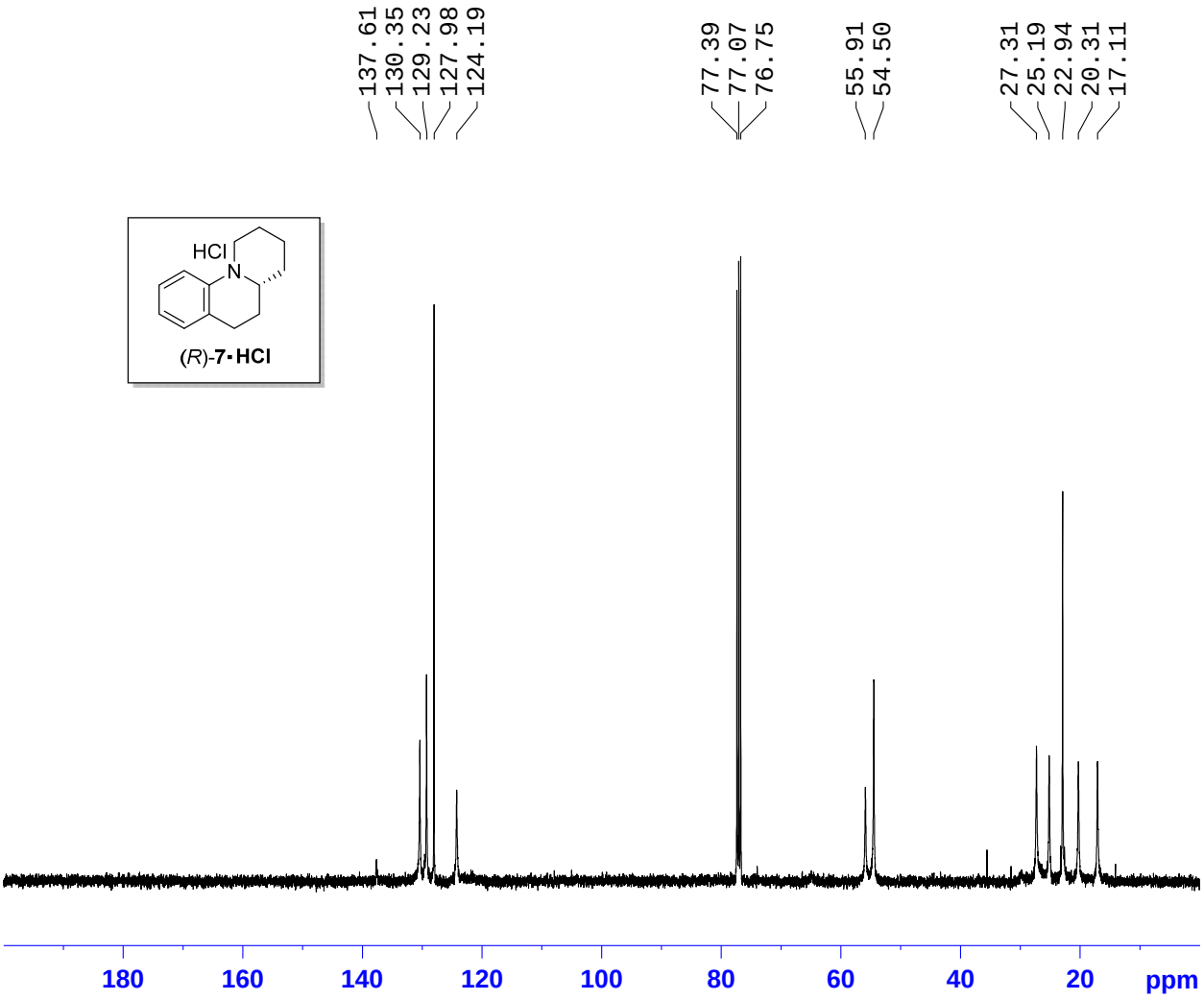
1.10
0.92
1.29
1.44
4.25


137.61
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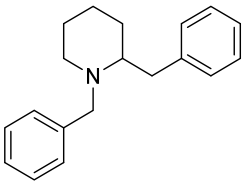
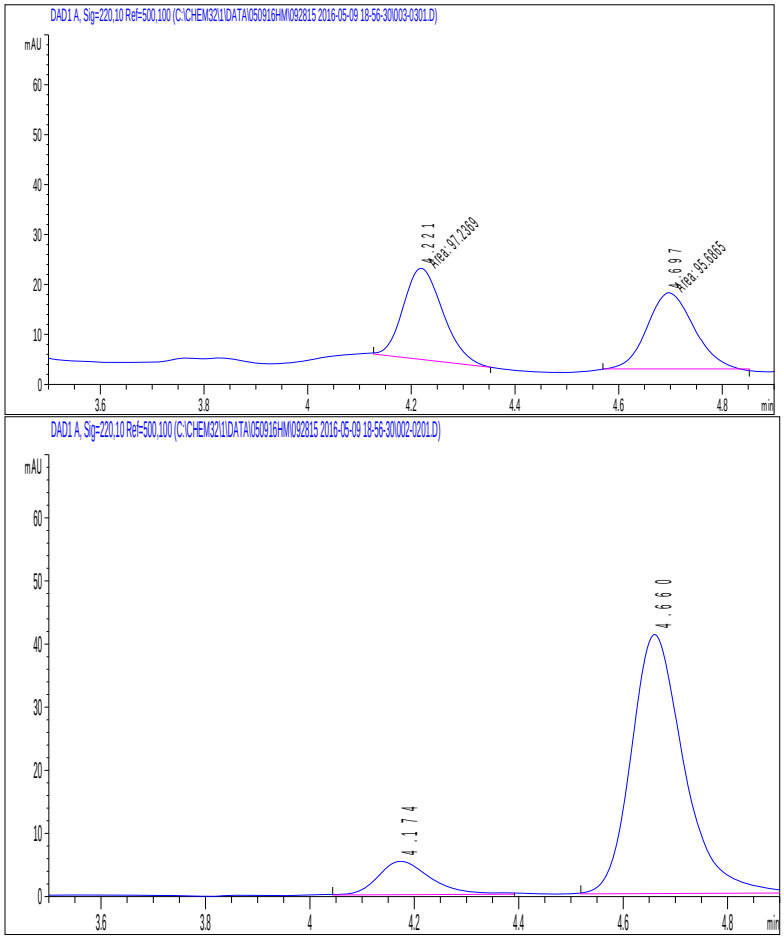
77.39
77.07
76.75
55.91
54.50
27.31
25.19
22.94
20.31
17.11
HCl
N
(R)-7·HCl
180
160
140
120
100
80
60
40
20
ppm

Chiral HPLC Data

1,2-dibenzylpiperidine 2a*

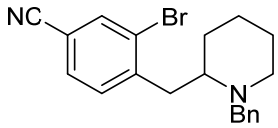


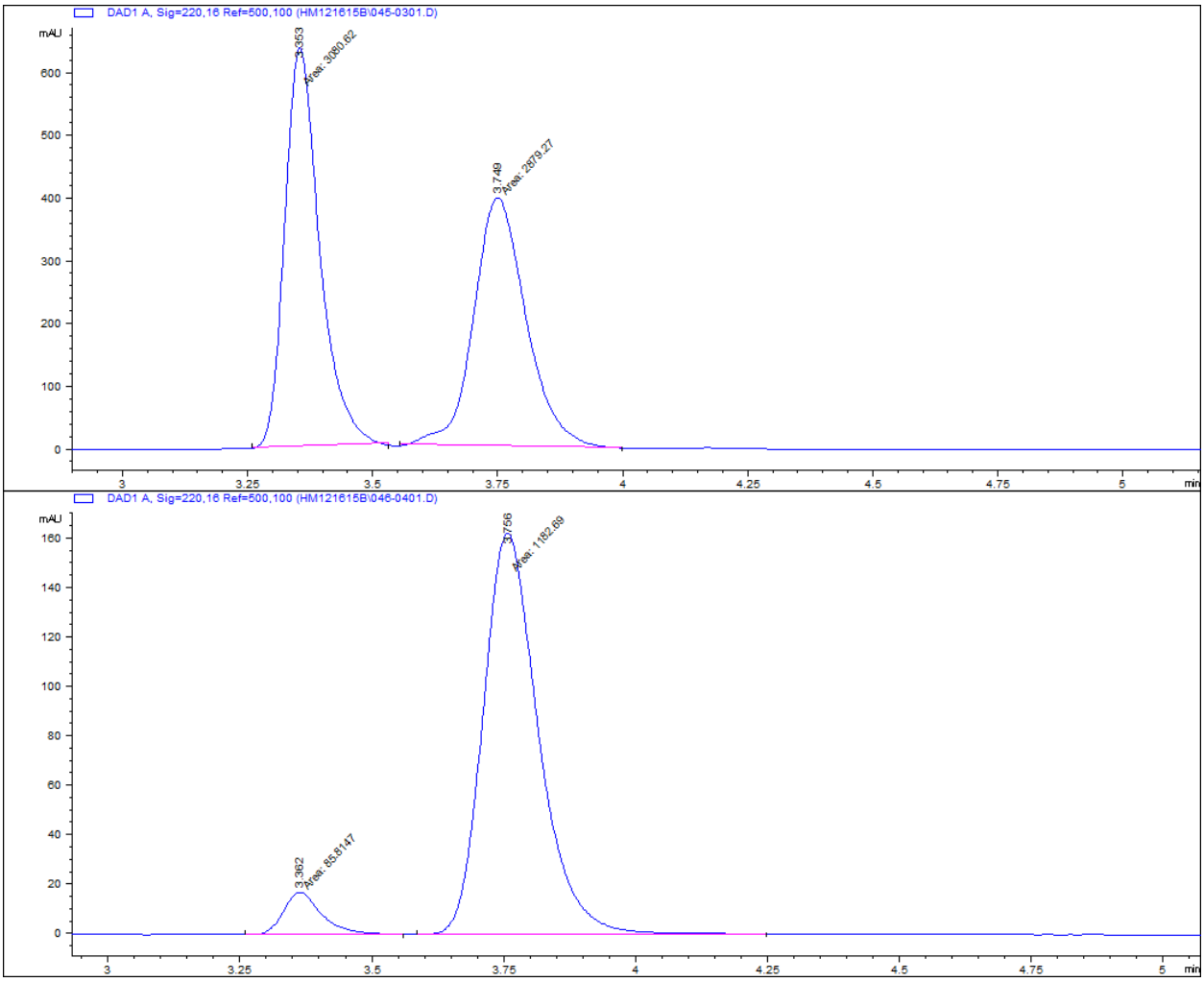


#	Time	Area	Height	Width	Area%	Symmetry
1	4.174	31.7	5	0.1049	9.819	0.836
2	4.66	291	41.2	0.1178	90.181	0.785

* For this HPLC spectrum, the sample was prepared from the reaction using the (*R*,*R*)-MeO-BoQPhos ligand. The major isomer at t = 4.66 min is the (*S*)-isomer.

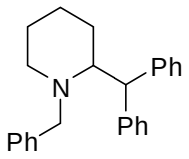
4-((1-benzylpiperidinyl)methyl)-3-bromobenzonitrile 2b

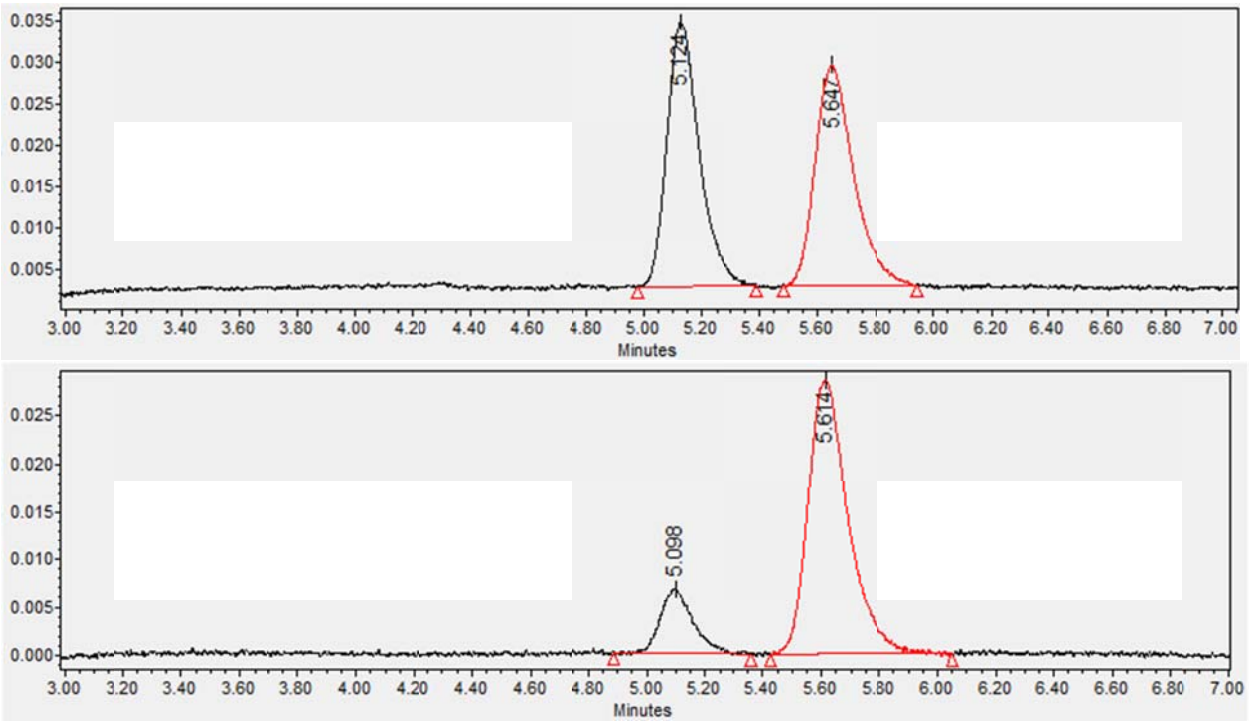




#	Time	Area	Height	Width	Area%	Symmetry
1	3.362	85.8	17.1	0.0839	6.763	0.722
2	3.756	1183	162.5	0.1213	93.237	0.761

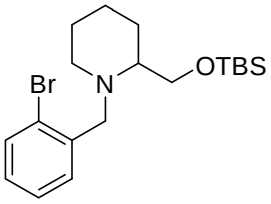
2-benzhydryl-1-benzylpiperidine 2c

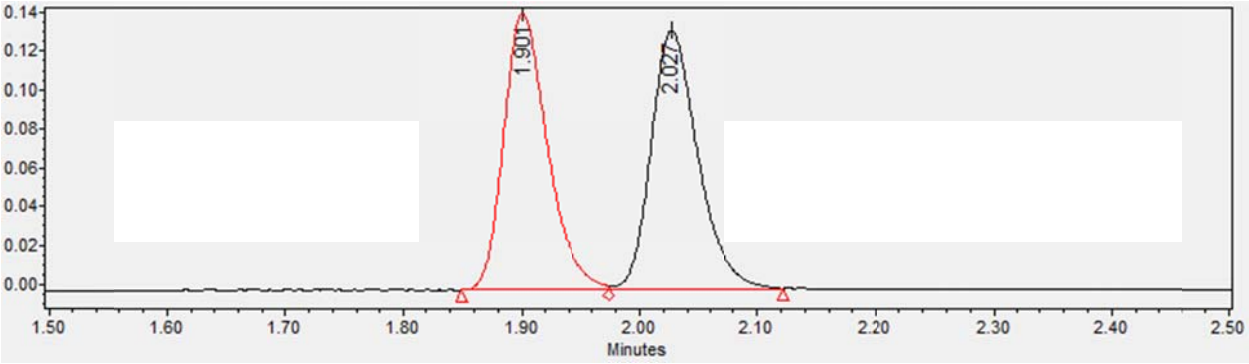


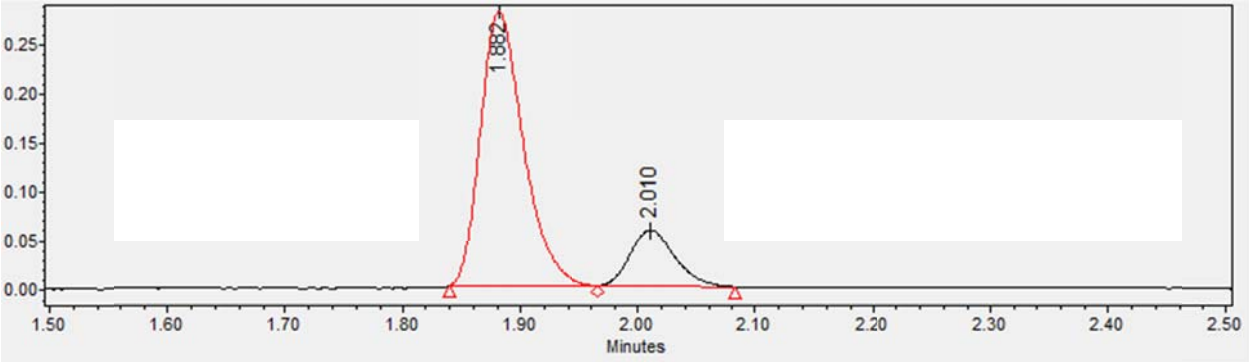


	RT	Area	% Area	Height
1	5.098	51057	15.79	6816
2	5.614	272262	84.21	28644

1-(2-bromobenzyl)-2-(((tert-butyldimethylsilyl)oxy)methyl)piperidine 2d

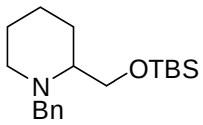


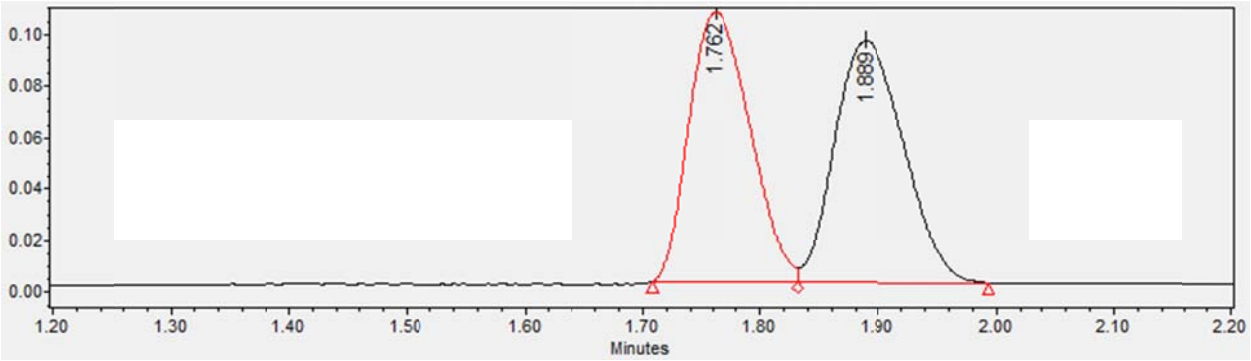


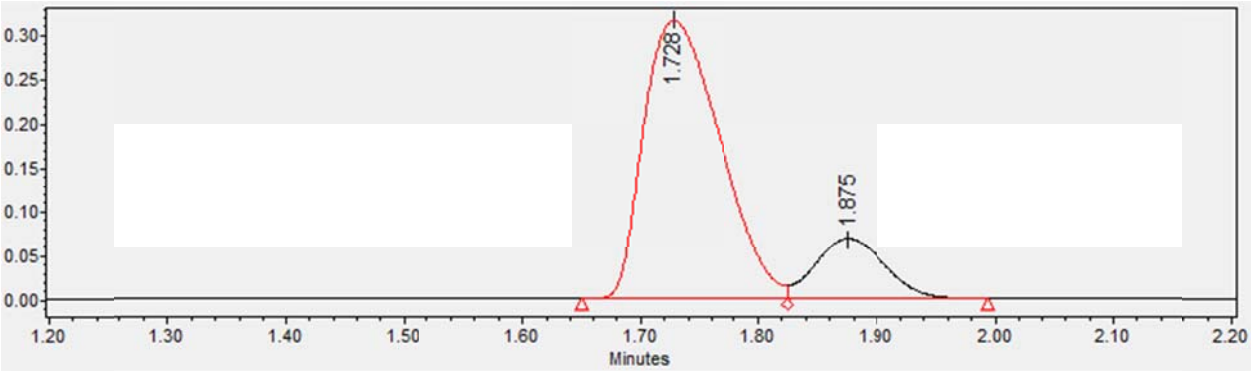


	RT	Area	% Area	Height
1	1.882	1131929	81.81	446676
2	2.010	251701	18.19	93443

1-benzyl-2-(((tert-butyldimethylsilyl)oxy)methyl)piperidine 2e

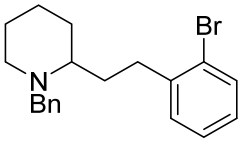


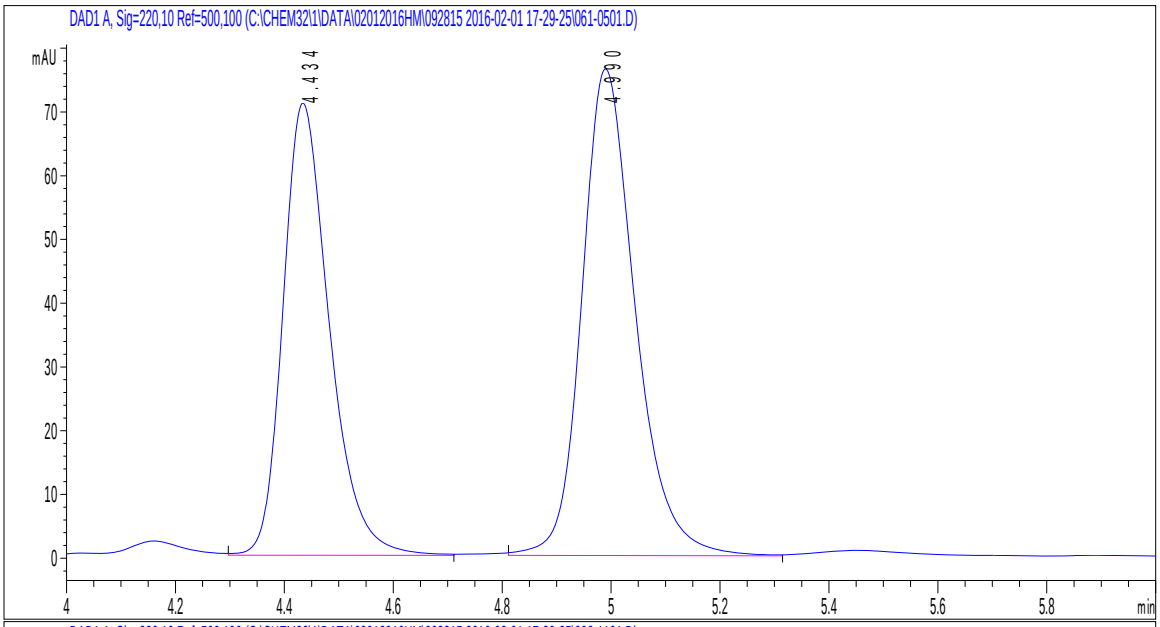


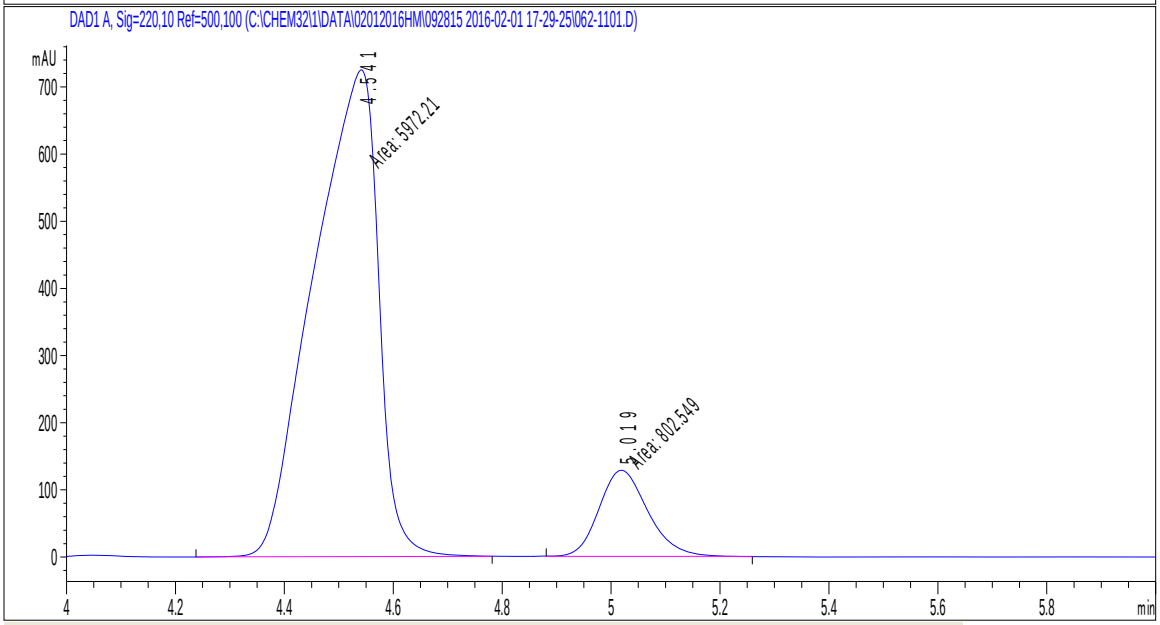


	RT	Area	% Area	Height
1	1.728	1279697	83.78	285672
2	1.875	247716	16.22	61464

1-benzyl-2-(2-bromophenethyl)piperidine 2f

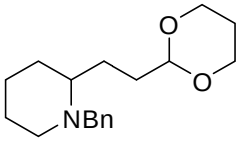


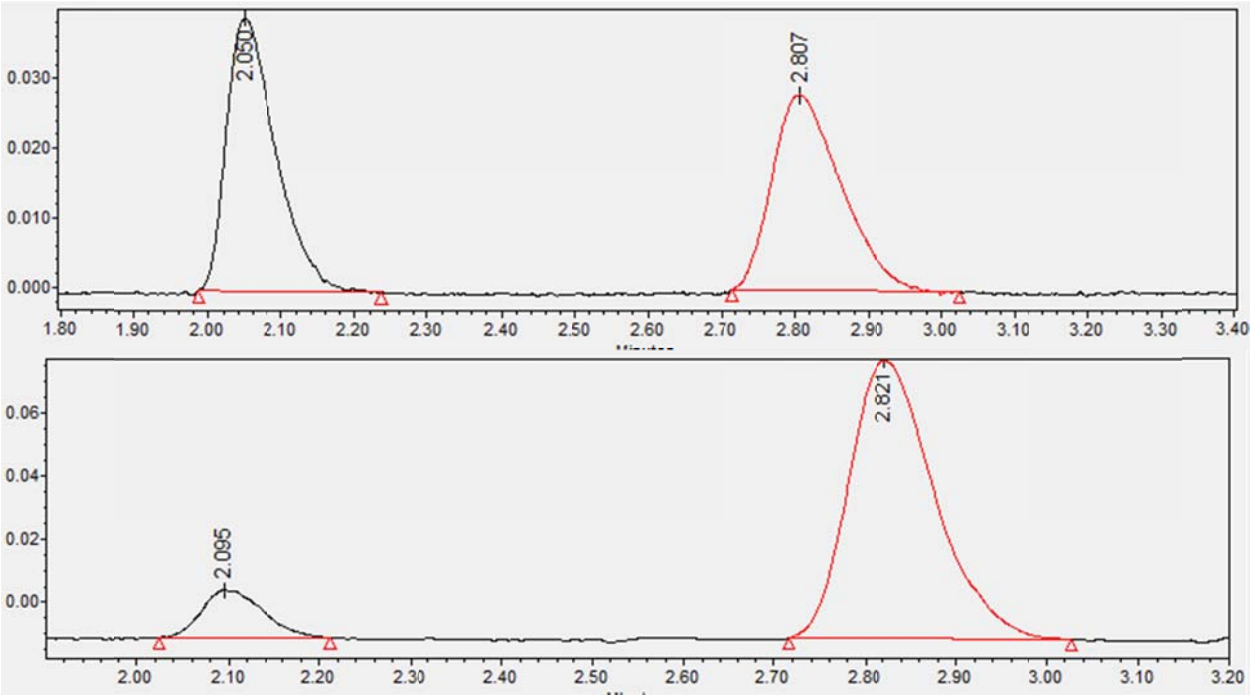




#	Time	Area	Height	Width	Area%	Symmetry
1	4.541	5972.2	725.1	0.1373	88.154	2.537
2	5.019	802.5	128.5	0.1041	11.846	0.809

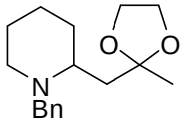
2-(2-(1,3-dioxan-2-yl)ethyl)-1-benzylpiperidine 2g

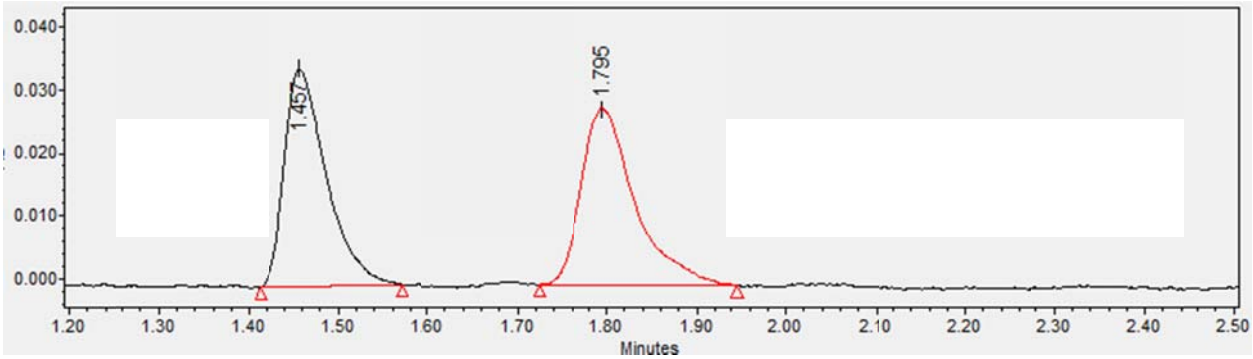


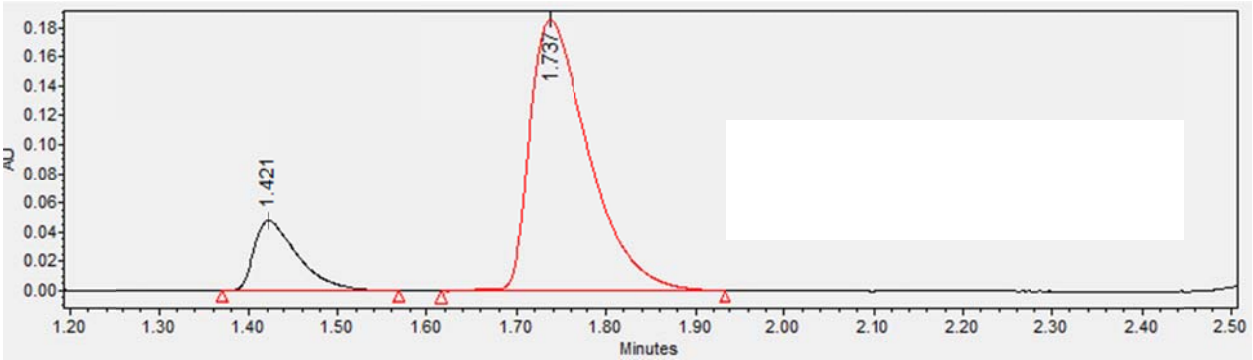


	RT	Area	% Area	Height
1	2.095	37038	10.97	8036
2	2.820	300723	89.03	45840

1-benzyl-2-((2-methyl-1,3-dioxolan-2-yl)methyl)piperidine 2h

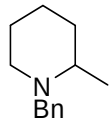


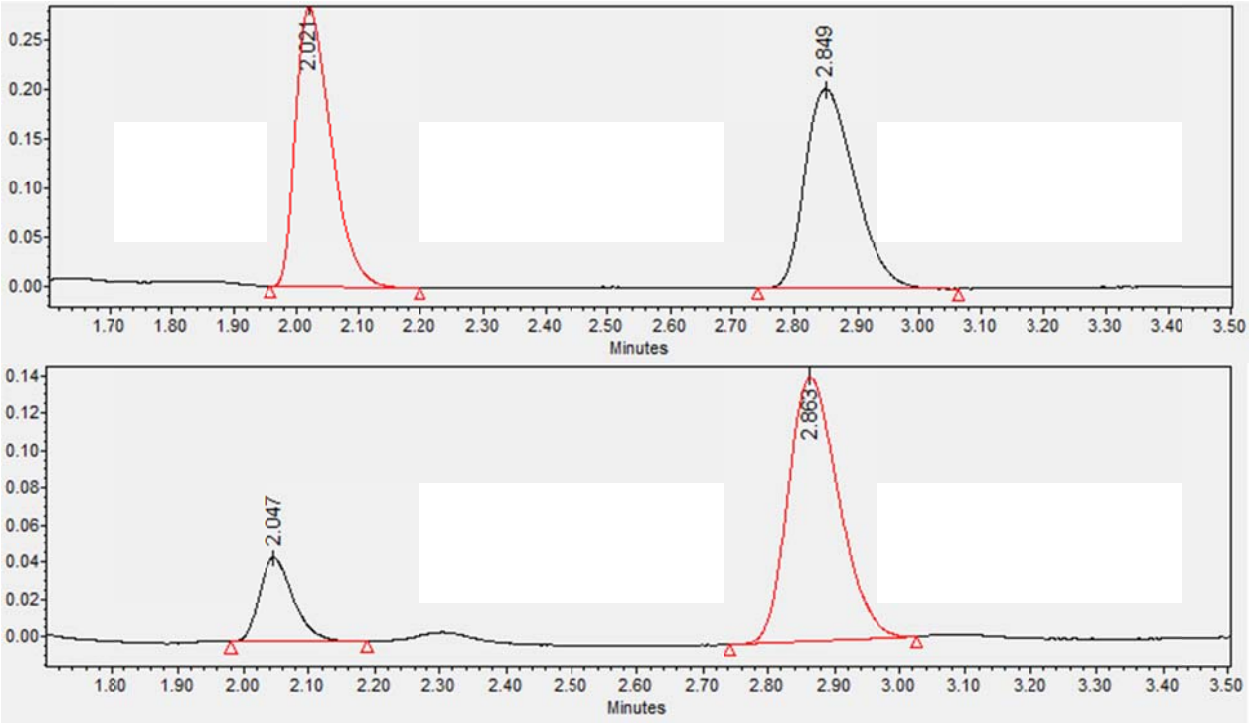




	RT	Area	% Area	Height
1	1.421	158705	16.49	46903
2	1.737	803567	83.51	176377

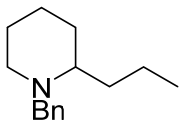
1-benzyl-2-methylpiperidine 2i

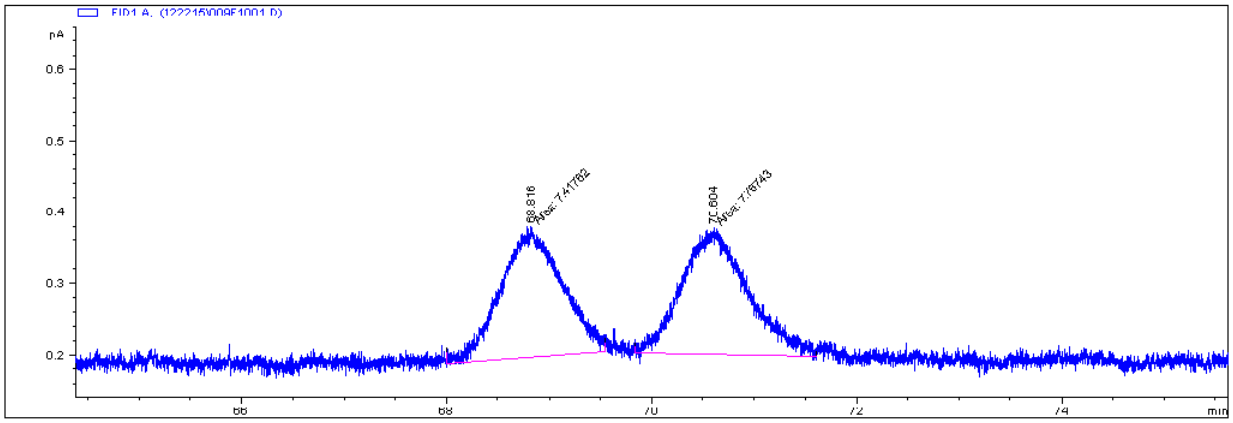


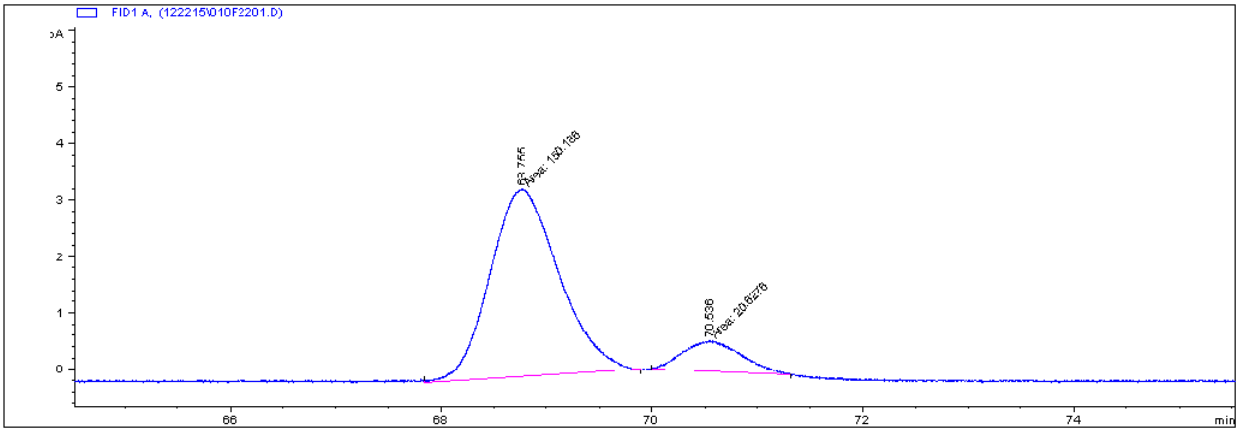


	RT	Area	% Area	Height
1	2.047	164346	18.00	45248
2	2.863	748934	82.00	141360

1-benzyl-2-propylpiperidine 2j

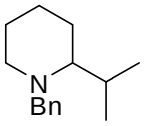


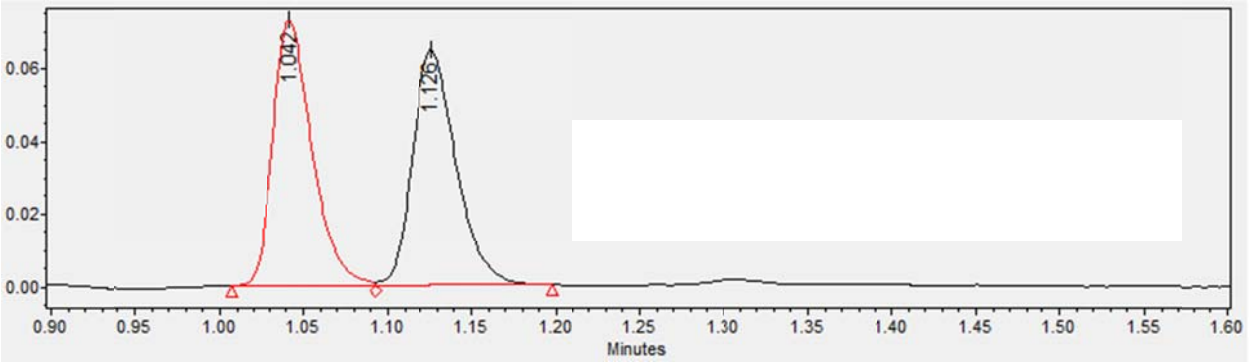


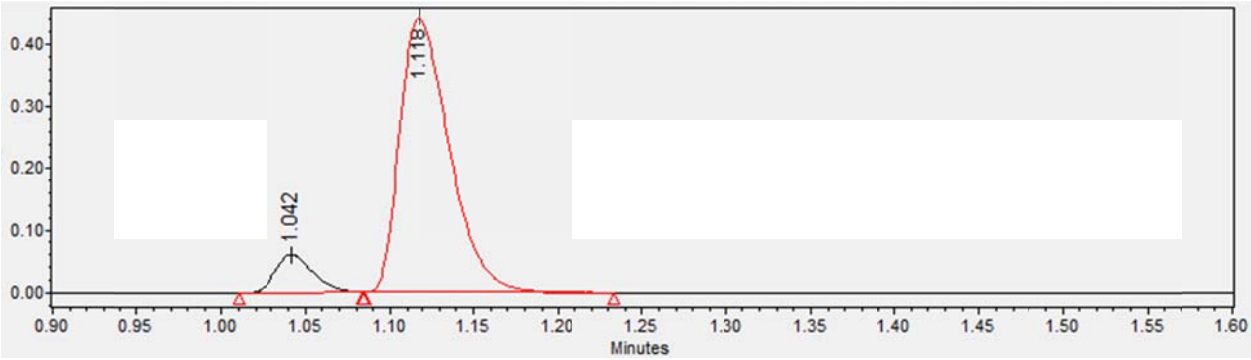


#	Time	Area	Height	Width	Area%	Symmetry
1	68.755	150.2	3.3	0.7559	87.924	0.812
2	70.536	20.6	5.4E-1	0.6411	12.076	0.756

1-benzyl-2-isopropylpiperidine 2k

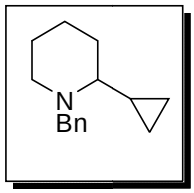


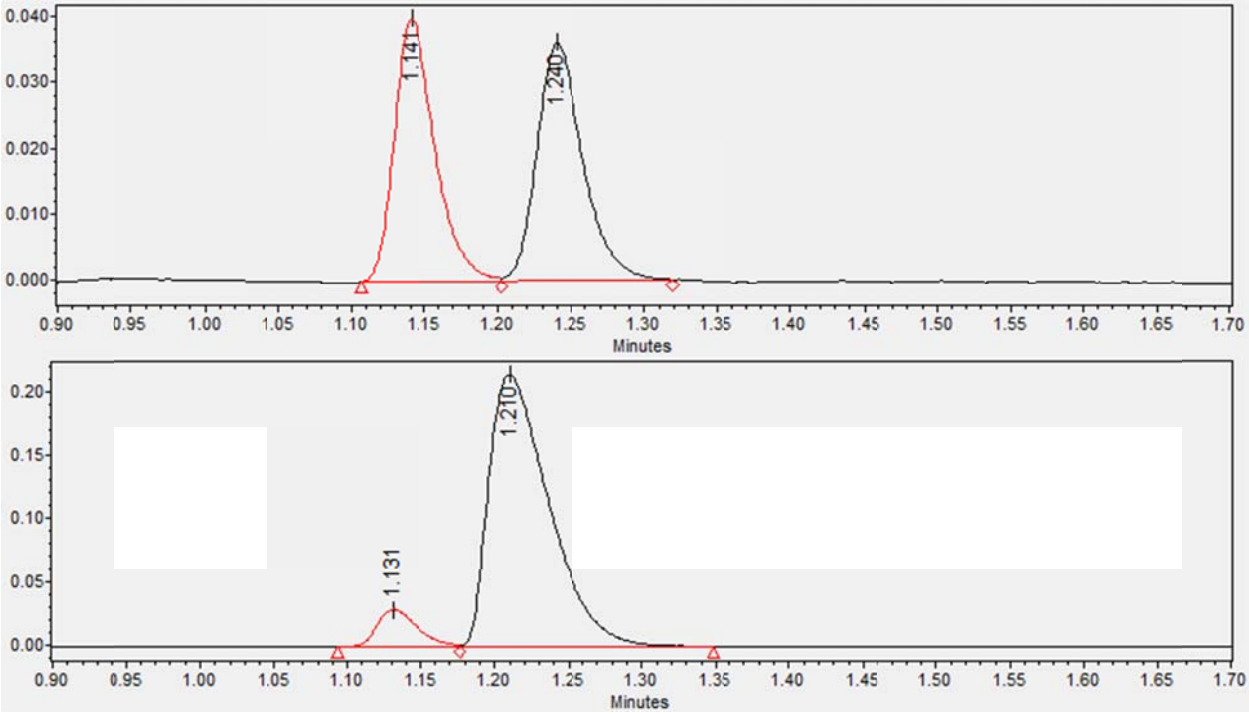




	RT	Area	% Area	Height
1	1.041	98324	9.38	63828
2	1.117	949888	90.62	457318

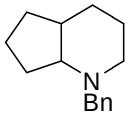
1-benzyl-2-cyclopropylpiperidine 2l

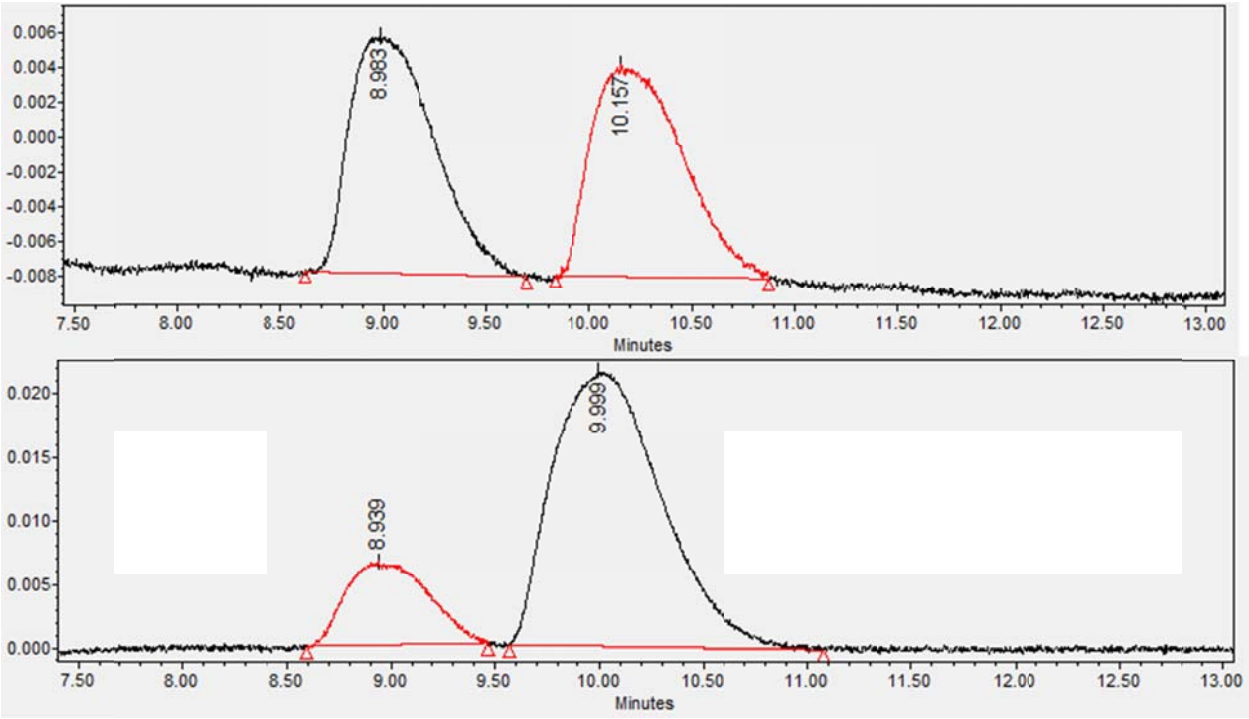




	RT	Area	% Area	Height
1	1.131	54888	8.38	29111
2	1.210	600165	91.62	213055

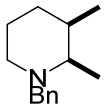
cis-1-Benzyloctahydro-1H-cyclopenta[b]pyridine 2m

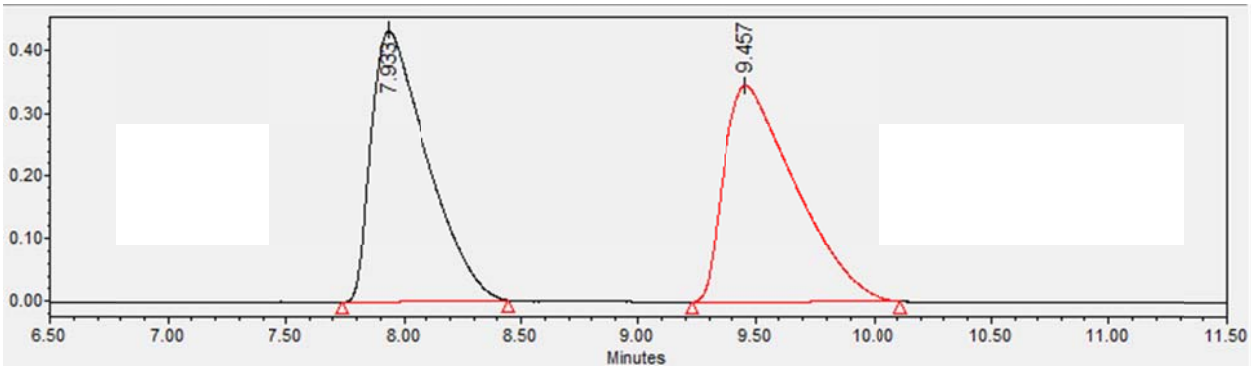


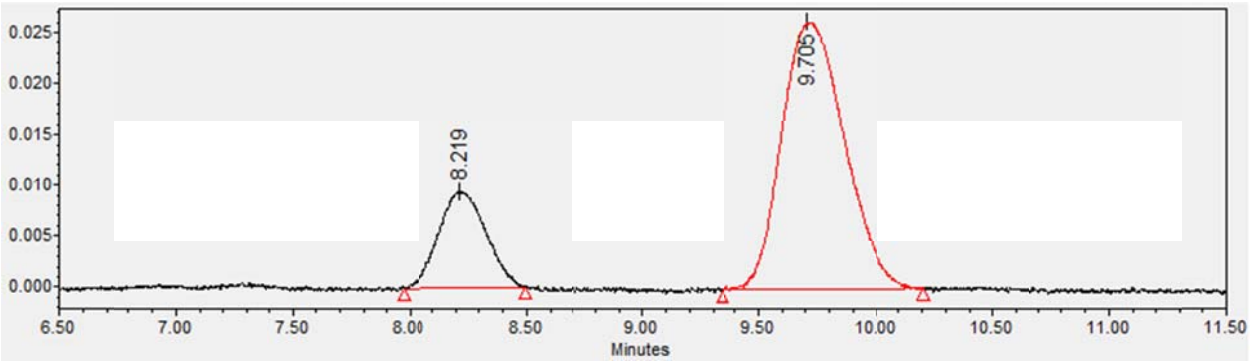


	RT	Area	% Area	Height
1	8.938	217332	18.93	7854
2	9.997	930935	81.07	25612

cis-1-Benzyl-2,3-dimethylpiperidine 2n

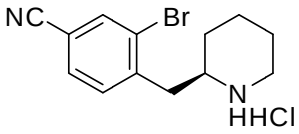


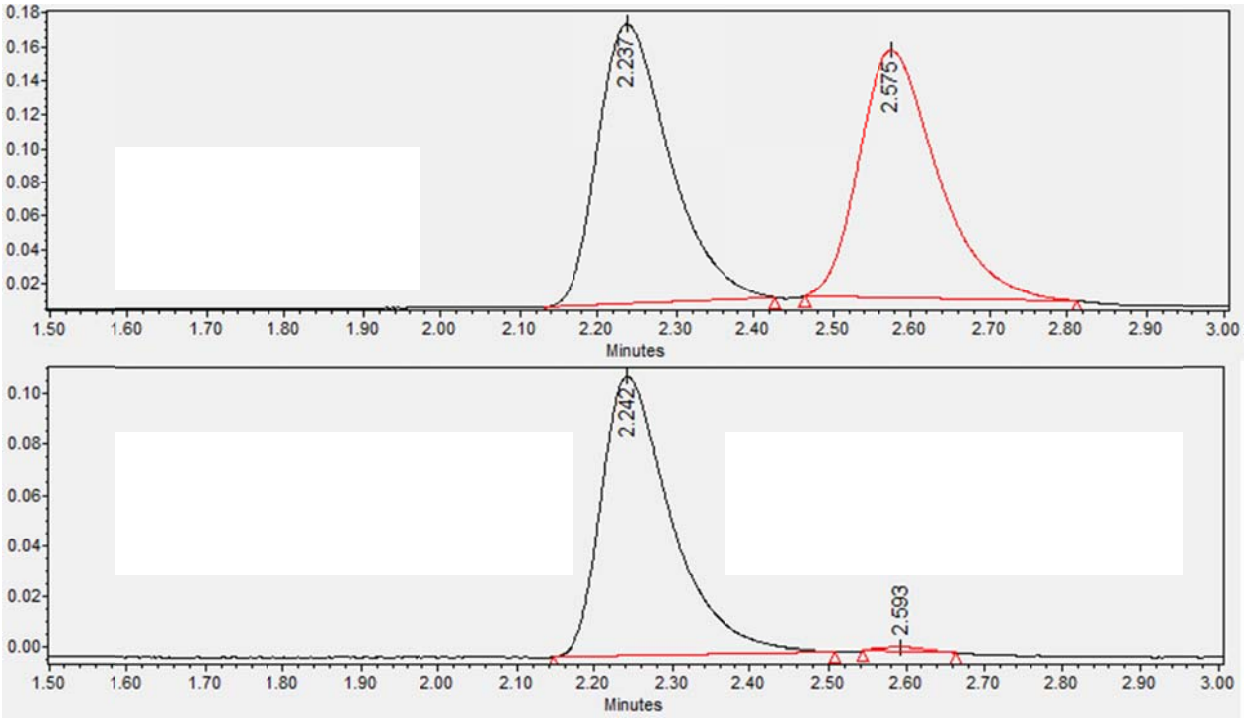




	RT	Area	% Area	Height
1	8.219	133999	21.58	9575
2	9.705	486919	78.42	26235

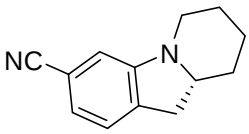
(*R*)-3-bromo-4-(piperidinylmethyl)benzonitrile hydrochloride 4-HCl

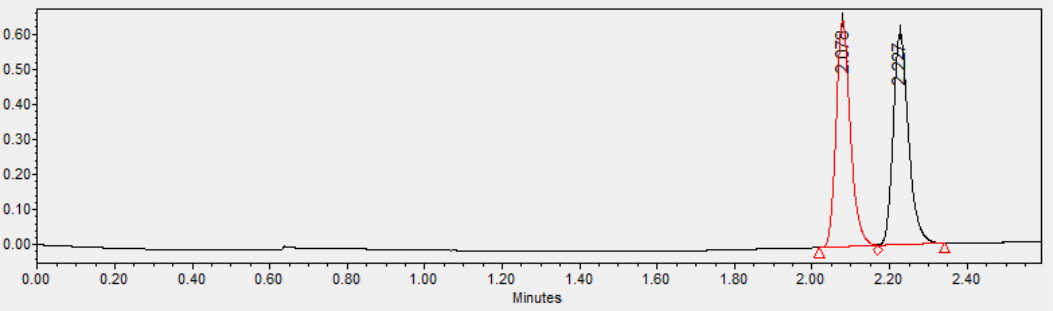


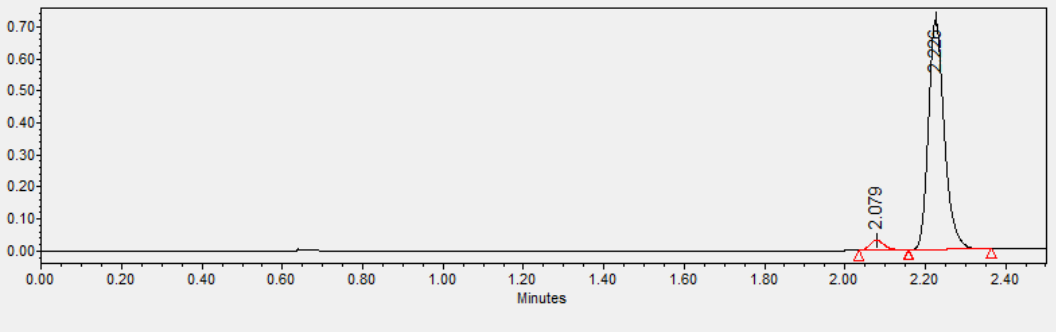


	RT	Area	% Area	Height
1	2.242	684729	99.08	110378
2	2.593	6385	0.92	1663

(*R*)-6,7,8,9,9a,10-hexahydropyridoindole-3-carbonitrile 5

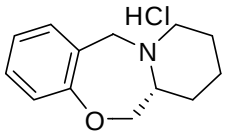


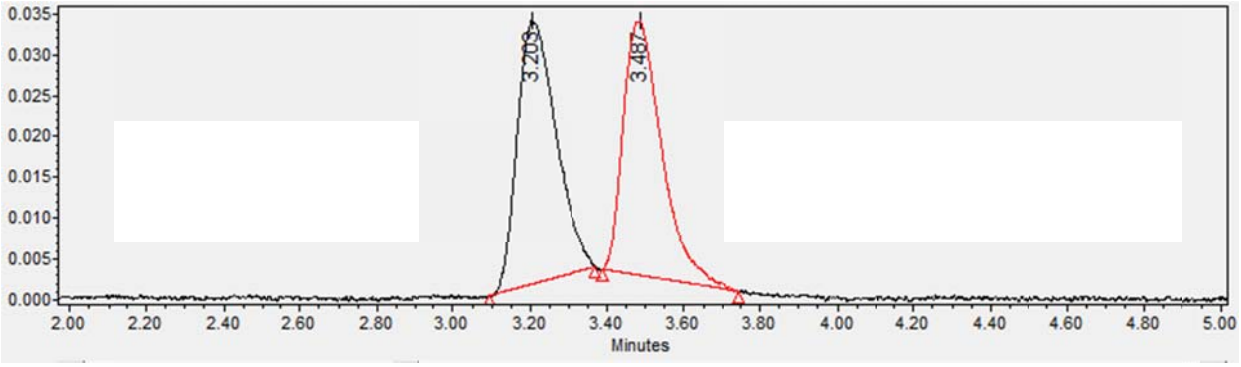


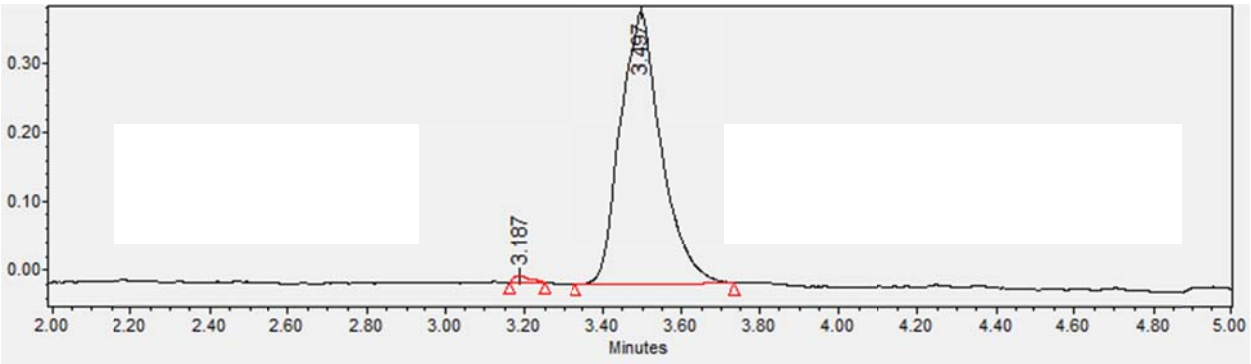


	RT	Area	% Area	Height
1	2.075	15655	0.76	12245
2	2.226	2035043	99.24	748037

(*R*)-6,6a,7,8,9,10-hexahydro-12H-benzo[f]pyrido[2,1-c][1,4]oxazepine 6

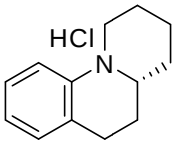


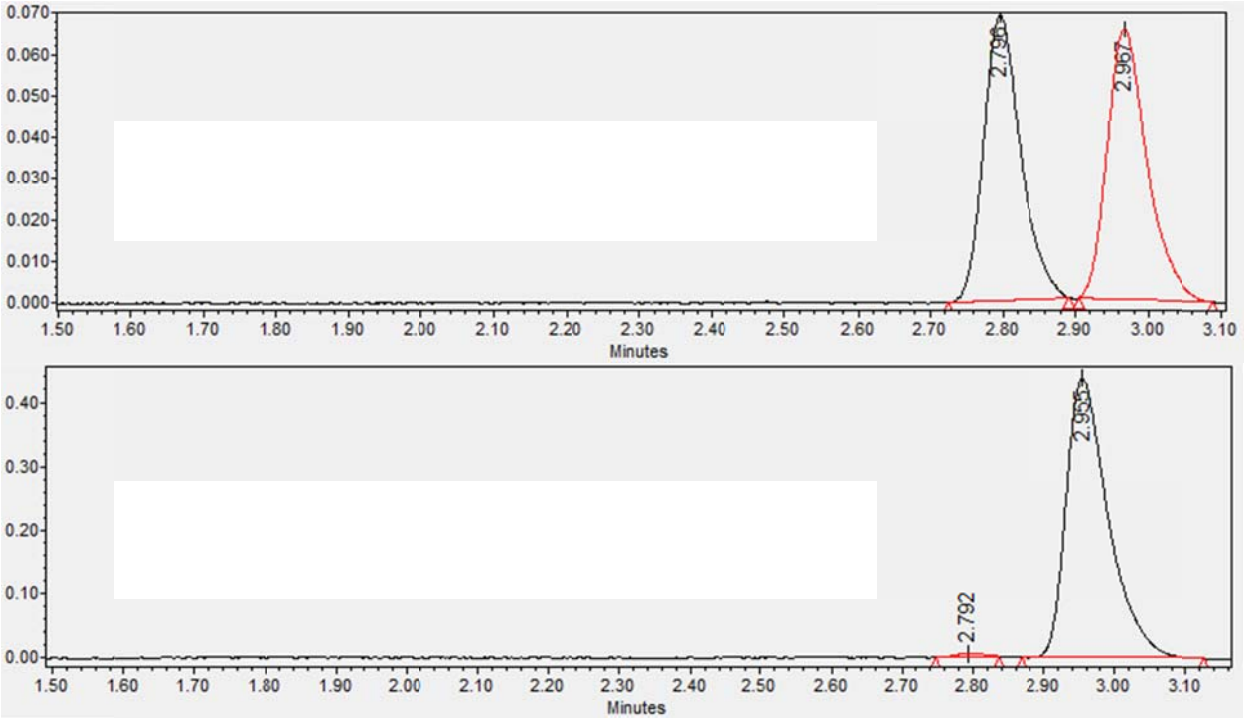




	RT	Area	% Area	Height
1	3.187	27486	0.96	9523
2	3.497	2822155	99.04	393504

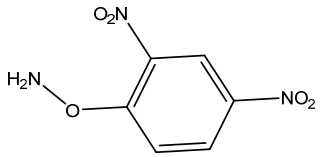
2,3,4,4a,5,6-hexahydro-1H-pyrido[1,2-a]quinolone 7



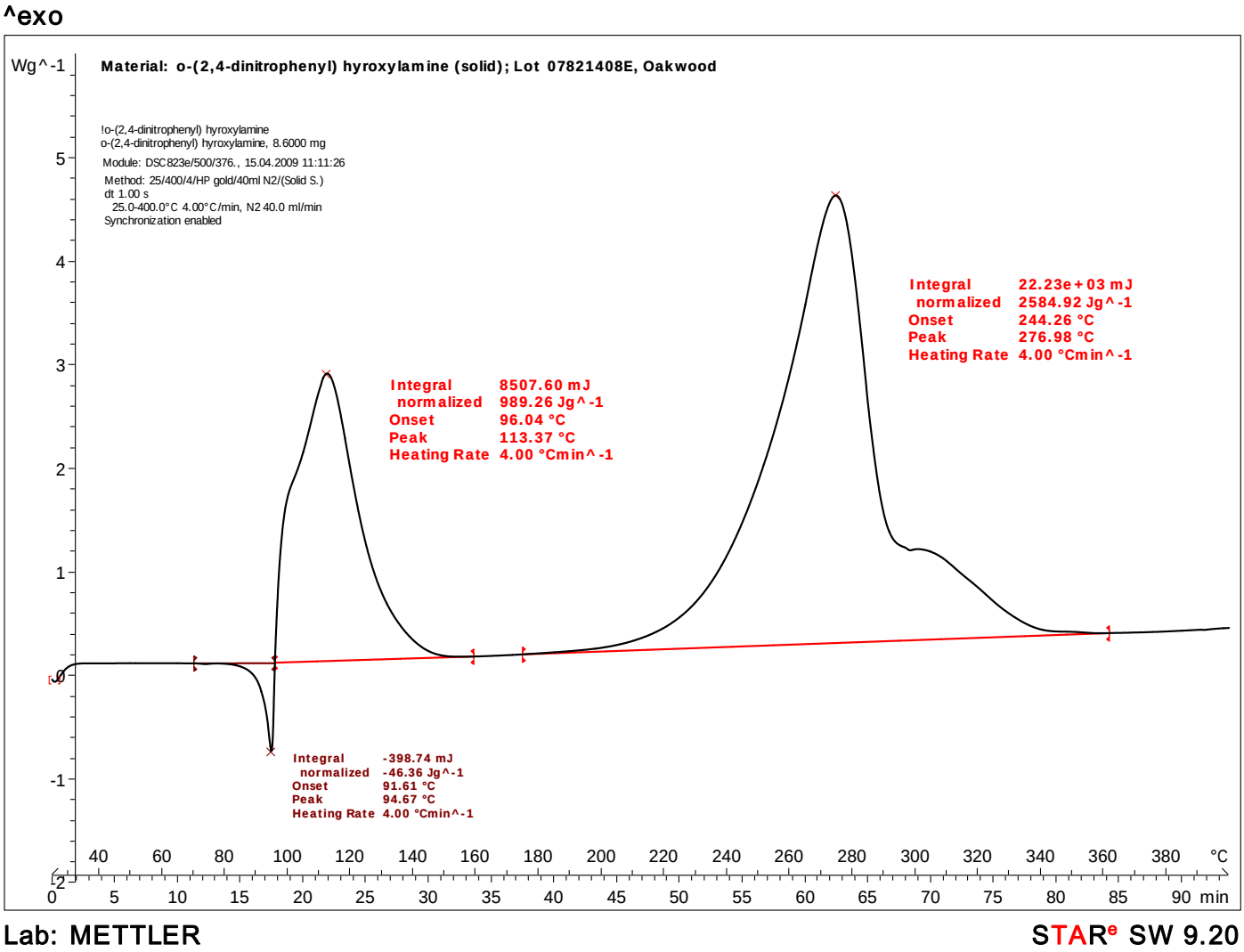


	RT	Area	% Area	Height
1	2.792	15165	0.84	5658
2	2.955	1781639	99.16	436675

DSC plot of o-(2,4-dinitrophenyl)hydroxylamine (solid); Lot # 07821408E, Oakwood:



O-(2,4-dinitrophenyl)hydroxylamine

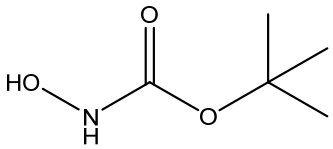


Method: 25 ºC to 400 ºC with 4 ºC/min heating rate, in a closed gold plated crucible.

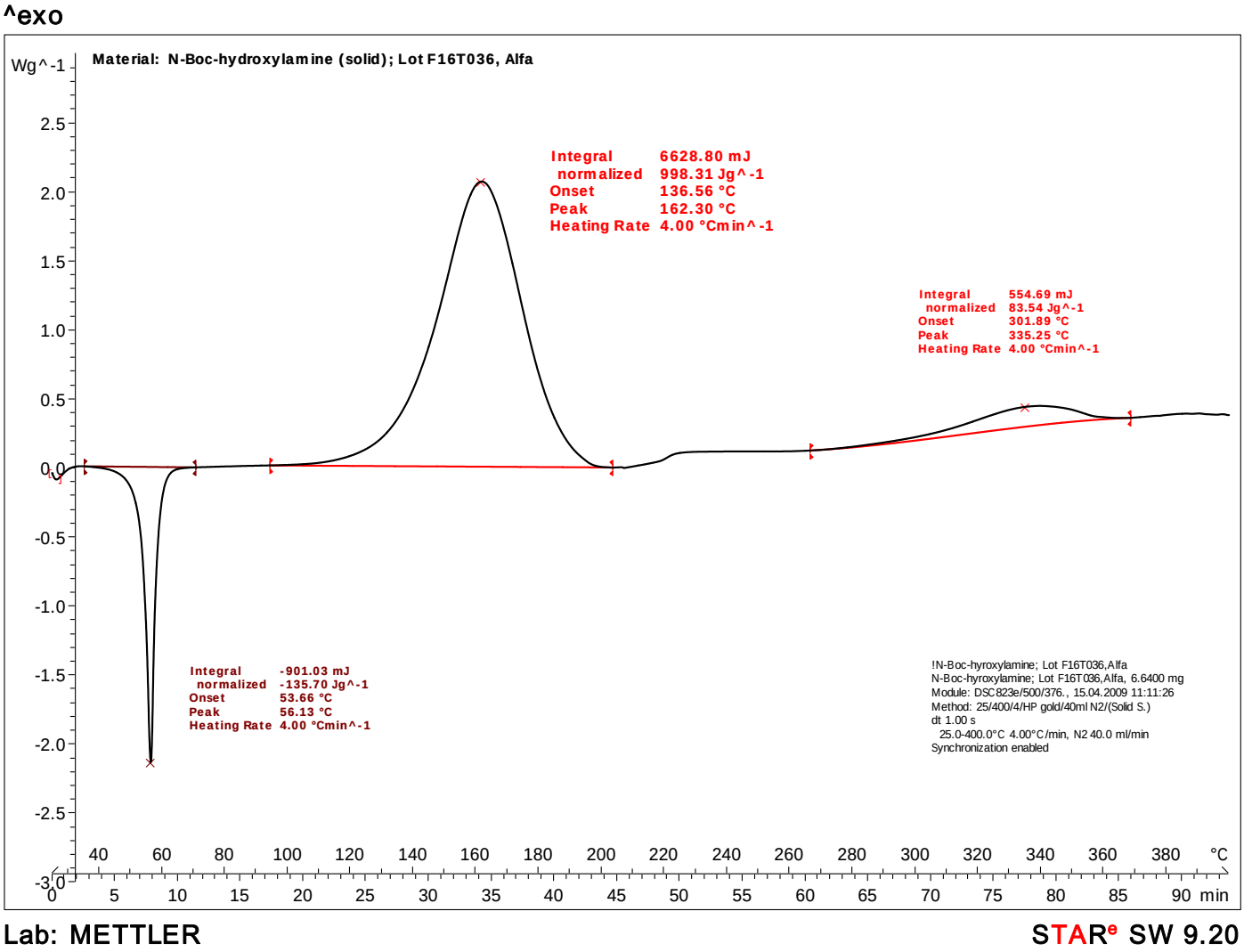
Module: Mettler Toledo DSC 823e; sensor FRS5+.

Sample preparation: As received.

DSC plot of N-Boc-hydroxylamine (solid); Lot # F16T036,Alfa:



N-Boc-hydroxylamine



Method: 25 ºC to 400 ºC with 4 ºC/min heating rate, in a closed gold plated crucible.

Module: Mettler Toledo DSC 823e; sensor FRS5+.

Sample preparation: As received.

Transition State Calculations

All optimizations and transition state searches were performed with the Gaussian 09 program[1] on a Unix HPC platform. All structures were optimized at the B3LYP level of theory employing the LANL2DZ basis set with ECP for Ir[3] and D95v for the remaining atoms.[4] All optimized structures were subjected to a frequency test to verify a single imaginary frequency was found (Transition states) and that the imaginary vibrational mode corresponds with the expected reaction pathway. All stable structures were subjected to a frequency test to verify no imaginary frequencies. The resulting transition state structures were subjected to an IRC calculation (B3LYP/LANL2DZ) to verify a clean reaction pathway from the starting material to the respected product. An outer-sphere dissociated mechanism[5] similar to the DFT computed Ir-hydrogenation mechanism of imines[6] was used as the basis for the computational studies of the asymmetric Ir-hydrogenation of the enamine intermediate (Figure 1). An iodo-Ir complex[7] was found to be a viable catalyst for the sequential protonation and hydride delivery pathway for the enamine hydrogenation with a maximum energy barrier of 22.1 kcal/mol.

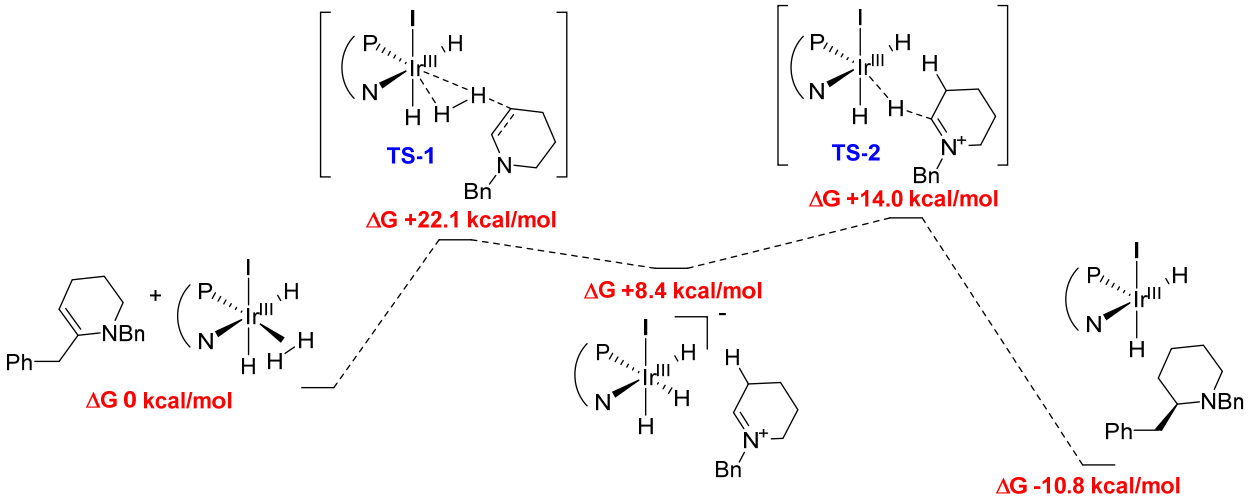
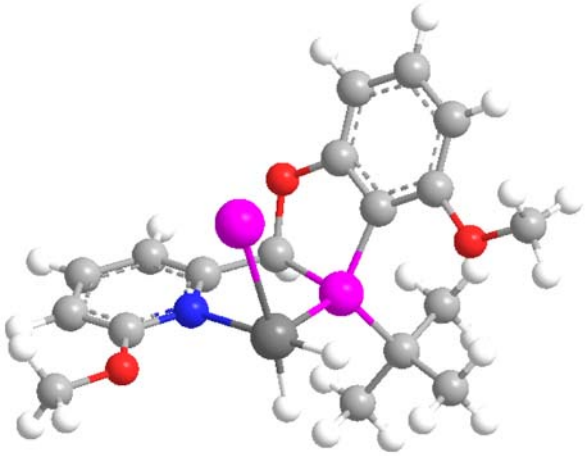


Figure 1. Reaction pathways for the Ir-**L4** catalyzed asymmetric reduction (B3LYP/LANL2DZ CPCM = THF, 298.15 K, 1 atm).

A



SCF Done: E(RB3LYP) = -1103.29465932

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.390330 (Hartree/Particle)
Thermal correction to Energy= 0.417522
Thermal correction to Enthalpy= 0.418466
Thermal correction to Gibbs Free Energy= 0.331744
Sum of electronic and zero-point Energies= -1102.904329
Sum of electronic and thermal Energies= -1102.877137
Sum of electronic and thermal Enthalpies= -1102.876193
Sum of electronic and thermal Free Energies= -1102.962915

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-9.629203015655	9.426970111035	3.102639345095
C	-8.770168061647	10.014148900830	2.149654171053
C	-8.600882831592	9.403449140794	0.891399715684
C	-9.283545327242	8.208096669312	0.609788796267
C	-10.145124078856	7.599779742616	1.534899797214
C	-10.302640408459	8.229732073697	2.781608329951
H	-9.777520295106	9.880580972412	4.075739439105
H	-10.657919821812	6.676734560158	1.288412215372
H	-10.960839335405	7.782945605492	3.521937410465
O	-8.052423901974	11.185946212940	2.353063404586
C	-8.134359430811	11.857056474342	3.655563852264
H	-7.782011629814	11.195165581296	4.455008045560
H	-7.476097031944	12.722733859319	3.571359399468

H	-9.160424629072	12.185198322957	3.859895482595
O	-9.065202220030	7.613156580860	-0.643728331748
C	-8.208923162929	8.425944256709	-1.548466880761
P	-7.483607982180	9.879794162226	-0.501197855788
C	-8.071001092458	11.537361425196	-1.330576069172
C	-7.398213749867	12.718354464537	-0.590830064431
H	-7.720374656950	13.655233516470	-1.064982673609
H	-7.681642333184	12.745859849367	0.465994982042
H	-6.306244714605	12.657346575225	-0.656715074323
C	-9.611684179224	11.632040682383	-1.226469706912
H	-9.938524492267	12.547303741828	-1.737572335657
H	-10.119040319822	10.786285248306	-1.707764348423
H	-9.945707693246	11.688089779622	-0.184852393940
C	-7.620722760455	11.515513303928	-2.812392168162
H	-6.536105477124	11.388843610878	-2.903494466086
H	-8.115738828903	10.726625367210	-3.392105946793
H	-7.889528369091	12.476652406809	-3.269392299843
C	-7.130488510452	7.548514669984	-2.148185917569
C	-7.478755566534	6.534179622134	-3.050719781256
C	-6.463082159401	5.726670553955	-3.596296810912
H	-8.518836518991	6.380953487791	-3.314415311594
C	-4.848134461248	7.016005687719	-2.350770101698
C	-5.126952827379	5.967162282365	-3.250511499449
H	-6.707733987289	4.927870213836	-4.289153352272
N	-5.825995104449	7.775517182594	-1.791129841859
Ir	-5.294848017088	9.327146352755	-0.339587266642
O	-3.587139969153	7.389710786875	-1.956329707971
C	-2.420950467355	6.618679178328	-2.415855600942
H	-2.327739003241	6.676857544898	-3.506001966879
H	-2.496817290608	5.575602031911	-2.089431704271
H	-1.565253385657	7.098421113106	-1.941085500882
H	-5.067902094983	10.420149917351	-1.473145150543
I	-5.095471417734	7.378223218293	1.788051819586
H	-4.936171784350	10.484610536786	0.709833853108
H	-4.330045068633	5.367047901972	-3.671233776206
H	-8.871236573729	8.803558248591	-2.333484732821

Iodide

SCF Done: E(RB3LYP) = -11.5603193090 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016848
Sum of electronic and zero-point Energies= -11.560319
Sum of electronic and thermal Energies= -11.558903
Sum of electronic and thermal Enthalpies= -11.557959
Sum of electronic and thermal Free Energies= -11.577168

Atomic Type	Coordinates (Angstroms) X	Y	Z
I	0.381558050000	1.359300460000	0.000000000000

Hydrogen

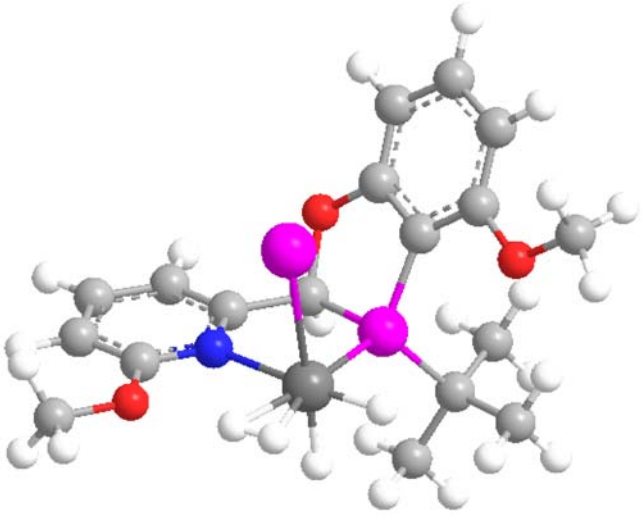
SCF Done: E(RB3LYP) = -1.17449948 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.010144 (Hartree/Particle)
Thermal correction to Energy= 0.012504
Thermal correction to Enthalpy= 0.013449
Thermal correction to Gibbs Free Energy= -0.001346
Sum of electronic and zero-point Energies= -1.164356
Sum of electronic and thermal Energies= -1.161995
Sum of electronic and thermal Enthalpies= -1.161051
Sum of electronic and thermal Free Energies= -1.175845

Atomic Type	Coordinates (Angstroms) X	Y	Z
H	0.000000000000	0.000000000000	0.371854993324
H	0.000000000000	0.000000000000	-0.371854993324

B



SCF Done: E(RB3LYP) = -1104.48278058 A.U.

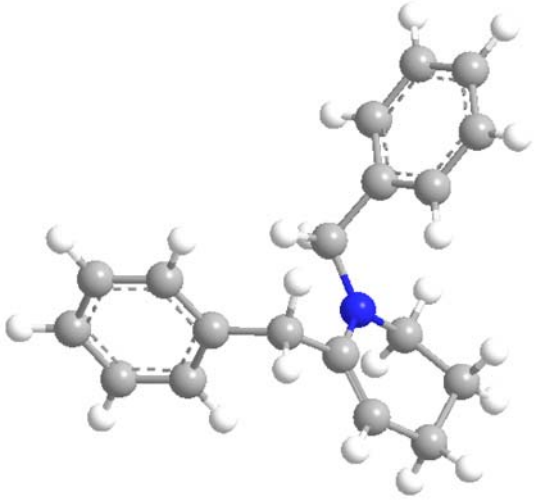
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.406320 (Hartree/Particle)
Thermal correction to Energy= 0.434508
Thermal correction to Enthalpy= 0.435452
Thermal correction to Gibbs Free Energy= 0.345711
Sum of electronic and zero-point Energies= -1104.076461
Sum of electronic and thermal Energies= -1104.048273
Sum of electronic and thermal Enthalpies= -1104.047328
Sum of electronic and thermal Free Energies= -1104.137070

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.960099544396	-1.372795389568	1.366443938687
C	3.204116183566	-0.696142969907	0.384874580152
C	2.185127534306	0.192564256616	0.778053924929
C	1.929714903089	0.381605130402	2.145302602188
C	2.663666772868	-0.272773276580	3.146180760983
C	3.679861049293	-1.150979220486	2.730691211412
H	4.749924640762	-2.060264739113	1.086832693822
H	2.441648324622	-0.105079958340	4.194239381209
H	4.265484685932	-1.676917172138	3.479998645238
O	3.392921867982	-0.833302671254	-0.984811012055
C	4.390131535430	-1.791501447014	-1.474606061699

H	4.151135198288	-2.806588883645	-1.136925523299
H	4.327435802149	-1.736863307987	-2.562263876607
H	5.396608003983	-1.509566603446	-1.142855352374
O	0.894686272424	1.265249980661	2.494850483768
C	0.184231302206	1.843505788517	1.322691760941
P	1.008184538440	1.160155734285	-0.271055371463
C	1.968458015423	2.652388181532	-1.071190080427
C	2.640512456659	2.148342374998	-2.372182352934
H	3.173183615702	2.987586792433	-2.839492357943
H	3.359667186241	1.347741176738	-2.170846403202
H	1.897652394504	1.773895722467	-3.085774913318
C	3.034321815800	3.170458902614	-0.076992340171
H	3.555675694304	4.020774974880	-0.536228286190
H	2.594529530806	3.524351169488	0.864214215371
H	3.779837319489	2.402995779024	0.157097010725
C	0.947822492747	3.768874787115	-1.402576387560
H	0.169988277427	3.415692896558	-2.088210144006
H	0.462371009693	4.177012329910	-0.507053844053
H	1.483198839699	4.593854718233	-1.890696002202
C	-1.294787619765	1.516593380455	1.424604259374
C	-1.982989553579	1.934495626344	2.573053460424
C	-3.353688807785	1.652371877817	2.693165439668
H	-1.448604830126	2.464794592627	3.352293852842
C	-3.255804580710	0.589905217102	0.525825159005
C	-4.004493735159	0.975034763426	1.656427457103
H	-3.907148037861	1.960512503012	3.574365187828
N	-1.919480620477	0.838989661534	0.406217463777
Ir	-0.774623717011	0.137005187293	-1.376946558976
O	-3.808240770499	-0.063621517984	-0.548429389393
C	-5.230097313229	-0.443940538554	-0.527931010342
H	-5.865949717802	0.446433602841	-0.475743507410
H	-5.434721394506	-1.117383330103	0.311145940367
H	-5.390140909080	-0.963542115482	-1.472661079594
H	-1.000041888949	1.513026786814	-2.144575925110
I	-0.499131451161	-2.510298258535	-0.172083574505
H	0.179696896725	-0.288918348613	-2.584819504609
H	-5.062061859659	0.754461652328	1.720810139833
H	0.326011095478	2.925901053613	1.394787405606
H	-2.377317125965	-0.417732586043	-1.938693929179
H	-1.841836787110	-0.612114596881	-2.564479796633

C



SCF Done: E(RB3LYP) = -791.285602263 A.U.

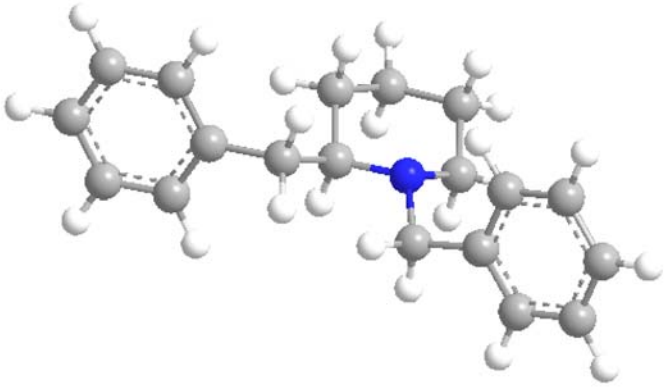
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.355723 (Hartree/Particle)
Thermal correction to Energy= 0.372917
Thermal correction to Enthalpy= 0.373861
Thermal correction to Gibbs Free Energy= 0.306314
Sum of electronic and zero-point Energies= -790.929879
Sum of electronic and thermal Energies= -790.912685
Sum of electronic and thermal Enthalpies= -790.911741
Sum of electronic and thermal Free Energies= -790.979288

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.753915001655	1.055387060371	-1.257736535987
C	3.415986812919	0.445292975767	-0.027606718558
H	4.499782843563	0.507166272470	-0.190222149172
H	3.212055415549	1.053269312217	0.865236885096
N	1.372604756334	1.314271727263	-1.217090254446
C	0.513076914367	1.109661193422	-0.048944876996
H	1.048899938221	0.520759708205	0.700876751894
H	-0.358898674351	0.501595519617	-0.336716110410
C	0.697447419618	1.730607213693	-2.463456098362
H	-0.233704634862	2.243916564435	-2.196117078805
H	0.425300567064	0.842066659297	-3.060003703211
C	1.588242169627	2.662446421120	-3.308869478886
H	1.765558420841	3.591022684197	-2.749598562155

H	1.061600181811	2.927467448743	-4.235083714472
C	2.937042178310	1.975445737386	-3.621200918757
H	3.648613759293	2.715136902087	-4.017232484102
H	2.795622652743	1.232304819465	-4.423546679072
C	3.503036696487	1.324836711510	-2.371653275339
H	4.561957492974	1.080256997542	-2.349753228259
C	-0.920424354732	4.742568014825	1.914775861227
H	-1.275443991317	5.640586671376	2.414696009426
C	0.333584491816	4.736050111290	1.270475264666
H	0.949594202542	5.632546755530	1.273435542281
C	0.791394158280	3.573318188664	0.620378716966
H	1.754431311543	3.575089668047	0.116072032610
C	0.005609915489	2.400504292332	0.606120041364
C	-1.252701894919	2.417254604637	1.247236178651
H	-1.874510062268	1.523195083311	1.234298724333
C	-1.713779742311	3.577475272805	1.900051235298
H	-2.685883384401	3.574975880528	2.387865521673
C	2.492730824814	-3.739553029824	0.850282595577
H	2.276831207823	-4.782108452508	1.071366692729
C	2.583699998163	-3.299450305273	-0.486111112115
H	2.438281476913	-4.005350795400	-1.300868341540
C	2.863183295131	-1.949059717238	-0.771667628051
H	2.932418276150	-1.614117402469	-1.804218954132
C	3.054411369984	-1.014564593736	0.270518035875
C	2.958462285308	-1.464765473615	1.606793487575
H	3.100471956704	-0.757894289141	2.422860536016
C	2.681818344697	-2.815442670656	1.897322298246
H	2.611680402426	-3.143169742293	2.932035491325

D



SCF Done: E(RB3LYP) = -792.501898325 A.U.

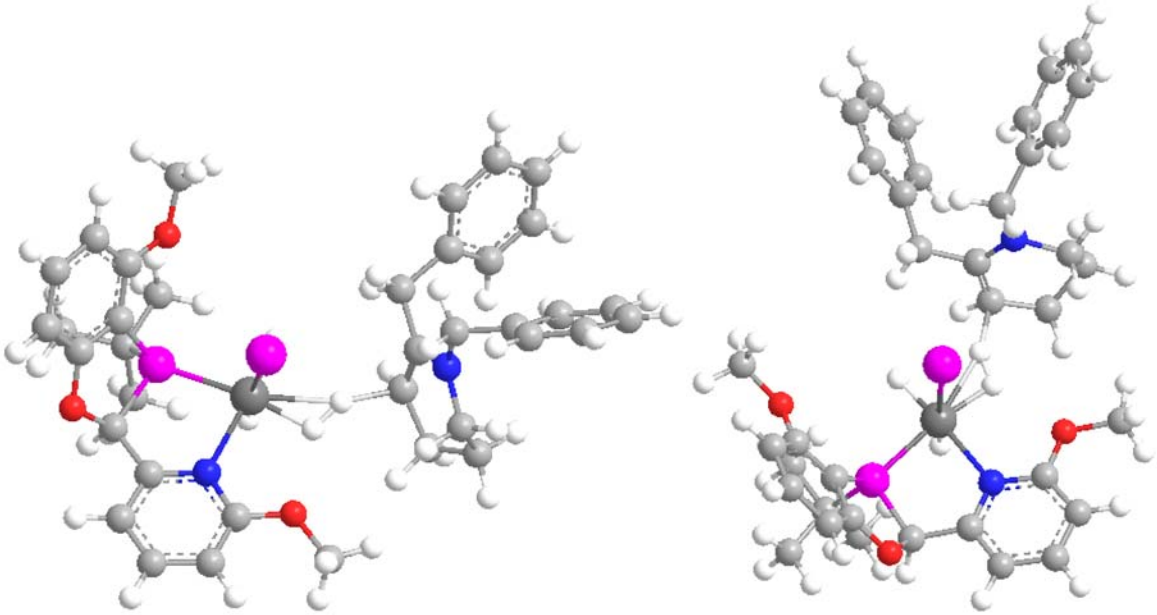
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.379402 (Hartree/Particle)
Thermal correction to Energy= 0.396701
Thermal correction to Enthalpy= 0.397645
Thermal correction to Gibbs Free Energy= 0.331303
Sum of electronic and zero-point Energies= -792.122496
Sum of electronic and thermal Energies= -792.105197
Sum of electronic and thermal Enthalpies= -792.104253
Sum of electronic and thermal Free Energies= -792.170596

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.454994395600	1.304067115475	-0.257300185271
H	2.834318259205	1.891806157156	0.607924716783
C	2.543530026001	-0.208180591097	0.111767735649
H	1.911468154305	-0.415530910268	0.982936451125
H	2.138797736021	-0.787323245704	-0.728732758621
N	1.046702480820	1.719990311109	-0.565857317145
C	0.073097412666	1.462878839682	0.528325968248
H	0.232547277546	2.154335082702	1.380707410049
H	0.234928053525	0.451519040316	0.912561027500
C	0.969280224722	3.152081919968	-0.975272389600
H	1.290635327130	3.807718549682	-0.136758575154
H	-0.079978330506	3.387297929429	-1.184744848974
C	1.830867933781	3.458903414858	-2.208750315506
H	1.747850583257	4.527676318954	-2.451124497855
H	1.447879048763	2.892551374376	-3.070054597352

C	3.294606617311	3.067209699412	-1.936981686563
H	3.708869589792	3.720286873999	-1.152683273352
H	3.912283438739	3.210967518100	-2.834180566887
C	3.362532020172	1.598630443793	-1.477040191220
H	3.049940810710	0.942912451081	-2.304352274819
H	4.394713478072	1.331170206817	-1.221692527714
C	-4.114843777290	1.618290295471	-0.690456262139
H	-5.161256027595	1.642196383496	-0.985472500915
C	-3.155627087148	1.000553710806	-1.520782041466
H	-3.464168096546	0.545616807415	-2.459542951957
C	-1.801619153343	0.969248239009	-1.138571550702
H	-1.058365132849	0.503097060598	-1.780147814737
C	-1.381713637942	1.556070222734	0.076789552453
C	-2.346595033224	2.176408656492	0.898879362764
H	-2.037279279526	2.638767133150	1.834708702599
C	-3.704949977644	2.207058169665	0.521858977715
H	-4.435290646207	2.690315732718	1.166845031210
C	6.587695825978	-1.536780394315	1.089221571456
H	7.593441594135	-1.867956825783	1.336624940722
C	5.889455349629	-0.672762435147	1.958205156123
H	6.356637889152	-0.337387606261	2.881465861655
C	4.586164109707	-0.248165760400	1.637433135382
H	4.052883547550	0.409360085219	2.321850529432
C	3.955096414242	-0.671829148135	0.443325605799
C	4.664084162407	-1.540123280665	-0.416730218439
H	4.194143137146	-1.881046402811	-1.337115662967
C	5.968289243537	-1.971015101686	-0.099454426306
H	6.495952038201	-2.640884041408	-0.774632301002

E



SCF Done: E(RB3LYP) = -1895.75554256 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

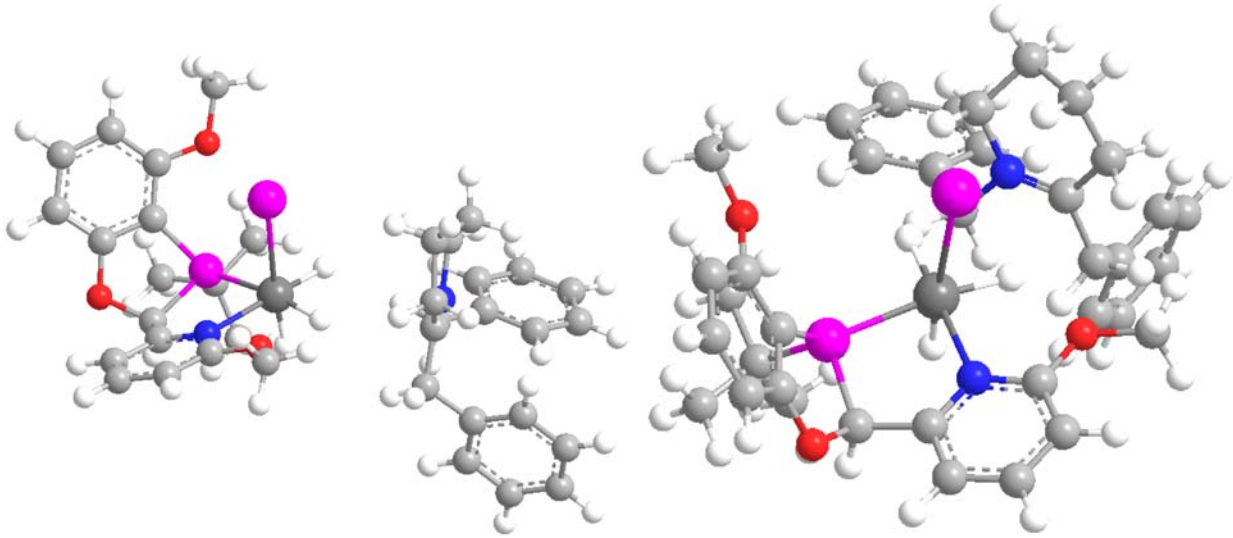
Zero-point correction= 0.761805 (Hartree/Particle)
Thermal correction to Energy= 0.808456
Thermal correction to Enthalpy= 0.809400
Thermal correction to Gibbs Free Energy= 0.674340
Sum of electronic and zero-point Energies= -1894.993737
Sum of electronic and thermal Energies= -1894.947086
Sum of electronic and thermal Enthalpies= -1894.946142
Sum of electronic and thermal Free Energies= -1895.081202

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.825168734398	3.296223254400	-0.284385588667
C	-4.601603040531	2.610376158238	-0.422695246404
C	-4.118708727586	1.778557284405	0.610655349926
C	-4.886463096908	1.648618529891	1.790762905736
C	-6.108307413762	2.331998670869	1.932782576894
C	-6.584001526624	3.159064001202	0.894202429441
H	-6.182578489888	3.931551294427	-1.091242410364
H	-4.021078554287	2.726856467406	-1.336134167105
H	-6.686096245522	2.222005777750	2.847559080980
C	-2.096408952204	-0.801501650273	2.012222819100

C	-2.291430968356	-2.191273658872	2.622872133806
C	-2.776825610610	-0.402963608554	0.848002807883
C	-3.431835171165	-2.948635281102	1.909533173022
H	-1.358942592292	-2.773978629875	2.560184771915
C	-3.330059735224	-2.753820136251	0.388043938168
H	-4.405141496135	-2.572287725804	2.251362878818
H	-4.154131326359	-3.261768840857	-0.121423654274
C	-2.765980063910	1.074198188024	0.472568868194
H	-2.376038629612	1.210474298312	-0.542601521392
H	-2.040517534027	1.558360238384	1.135761463712
H	-2.388020553558	-3.181506855179	0.010583600163
H	-3.392419434487	-4.020623969582	2.138781323875
H	-2.520770697191	-2.093990146919	3.692034726600
N	-3.386561221142	-1.313816517816	0.028786506949
C	-3.876219286356	-1.022911473118	-1.338036661615
H	-3.220099745511	-1.527424701518	-2.061879188190
H	-3.789135883359	0.048072515014	-1.527418254212
C	-5.320363004121	-1.461342614718	-1.575615862249
C	-6.347130718947	-1.110163356938	-0.670678361709
C	-5.652598928696	-2.192344283870	-2.735417032848
C	-7.679732461506	-1.484735417958	-0.922439672751
H	-6.102976351659	-0.546879368362	0.226529768294
C	-6.987568128151	-2.564308525553	-2.993415055344
H	-4.869457595459	-2.474456752680	-3.436710023372
C	-8.005770436352	-2.211869764538	-2.086488978576
H	-8.461145386042	-1.209579639748	-0.217983367079
H	-7.228865924455	-3.128120810147	-3.891293896482
H	-9.035942528100	-2.500145527639	-2.281096504751
H	-0.629270696553	-0.870920991791	1.474000212101
C	3.723317483652	3.221334888291	-2.965213131201
C	3.225962590279	2.852152565837	-1.695832652722
C	3.804296035860	1.771439368787	-1.002565927852
C	4.872453739277	1.078023510687	-1.593108788335
C	5.394775276579	1.420256658085	-2.850421170532
C	4.799471228868	2.501077896689	-3.523732585509
H	3.291294369276	4.048740817969	-3.516537047304
H	6.220796232628	0.861811086459	-3.277052190745
H	5.175717998007	2.790704905120	-4.501454877996
O	2.180624144460	3.502145355851	-1.047228420596
C	1.485831799284	4.593650650234	-1.736001941672
H	1.040864068717	4.241176337370	-2.674031163069
H	0.700480916518	4.911248599583	-1.048556414933
H	2.169287850913	5.428489347792	-1.933302691075
O	5.430539357870	0.012210657090	-0.867302906661

C	4.694549158329	-0.292611457937	0.388946700185
P	3.329847714259	1.034163253112	0.637088950241
C	4.030326211037	2.228151034576	2.012535647112
C	2.974354789737	3.334628476530	2.258239095204
H	3.348612301088	4.015454205585	3.035275428094
H	2.779602746983	3.914709870273	1.350001652940
H	2.025434720358	2.907672849026	2.603993831402
C	5.366906338726	2.853402791547	1.548940695409
H	5.757125834113	3.490064506090	2.354651839114
H	6.129334727114	2.095228420180	1.328507641994
H	5.236062651658	3.477255687858	0.657836271364
C	4.240846456308	1.411041691802	3.310871271320
H	3.317060323094	0.916313888037	3.629959412667
H	5.024108872206	0.649075919542	3.206454062647
H	4.555892571679	2.097502802481	4.108412832678
C	4.154564183786	-1.712179539913	0.321299158395
C	5.059260483041	-2.727246450260	-0.027034124062
C	4.615589327822	-4.057633468449	-0.070090609306
H	6.084169708630	-2.466673603927	-0.262050458253
C	2.429617193747	-3.272950708436	0.609837484095
C	3.286158619874	-4.339135517745	0.259780606229
H	5.292290206166	-4.860806335343	-0.344286787933
N	2.837139902753	-1.968365196537	0.621190741893
Ir	1.398978681032	-0.262747263822	0.989650065966
O	1.119213421550	-3.472534155731	0.972190736018
C	0.574202022803	-4.837680896496	0.974316380812
H	1.114787922753	-5.473178816479	1.685226108689
H	0.607372779344	-5.271781900076	-0.031350611345
H	-0.460996075338	-4.722017141565	1.295062319423
H	0.177933984122	-1.376060999777	1.360213610041
H	1.697719384507	-0.223101371267	2.552527005320
I	0.576034030347	-0.434296128218	-1.837478821191
H	0.475833571176	1.016774243068	1.239664485979
H	2.923345861485	-5.358356964944	0.247555621789
H	5.438181294656	-0.228977505351	1.189025482161
H	-1.843151610295	0.003061124764	2.701074938591
H	-4.527428843862	1.013795948679	2.597838542212
H	-7.528436287931	3.686705724619	1.002550104116

F



SCF Done: E(RB3LYP) = -1895.78227702 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.768183 (Hartree/Particle)
Thermal correction to Energy= 0.815262
Thermal correction to Enthalpy= 0.816206
Thermal correction to Gibbs Free Energy= 0.679274
Sum of electronic and zero-point Energies= -1895.014094
Sum of electronic and thermal Energies= -1894.967015
Sum of electronic and thermal Enthalpies= -1894.966071
Sum of electronic and thermal Free Energies= -1895.103003

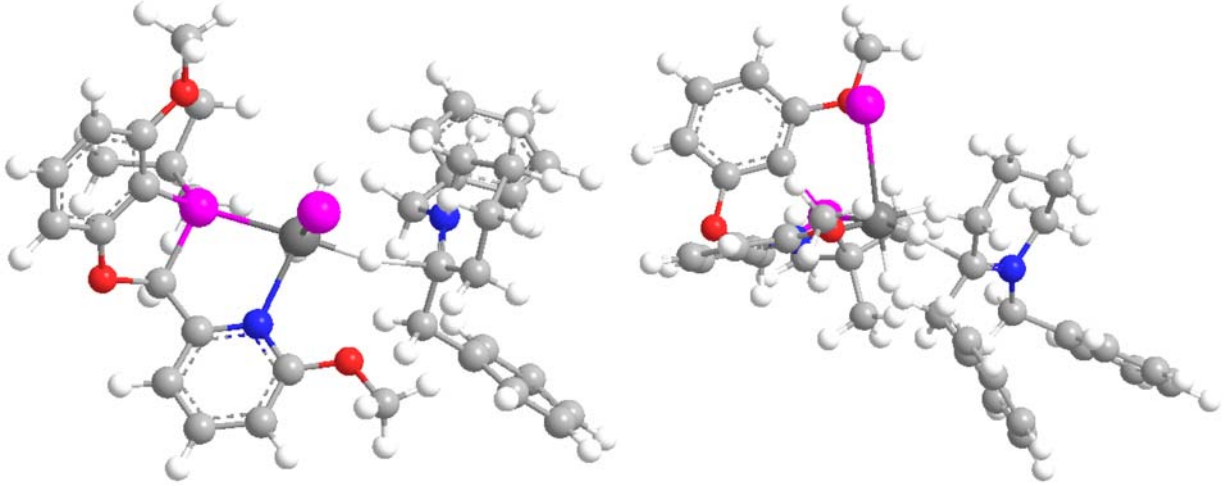
Zero-point correction= 0.768183 (Hartree/Particle)
Thermal correction to Energy= 0.815262
Thermal correction to Enthalpy= 0.816206
Thermal correction to Gibbs Free Energy= 0.679274
Sum of electronic and zero-point Energies= -1895.014094
Sum of electronic and thermal Energies= -1894.967015
Sum of electronic and thermal Enthalpies= -1894.966071
Sum of electronic and thermal Free Energies= -1895.103003

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	6.753778396002	-0.765723531020	-2.740843500448
C	5.441150251834	-0.939899782461	-2.260374889787
C	5.211363477241	-1.364855065566	-0.934229686098
C	6.320864028880	-1.619802848468	-0.096545798548

C	7.633012014991	-1.443368821387	-0.573791072135
C	7.854398173569	-1.014070221090	-1.898136885109
H	6.914076476066	-0.438881031885	-3.764955801989
H	4.598470445618	-0.752214742512	-2.922936960973
H	8.476885633251	-1.644171140810	0.081351062617
C	3.163493316268	-1.862634306991	2.035127401599
C	2.588651974537	-1.223817666357	3.311032331234
C	3.403675189541	-0.931536046507	0.869450489129
C	3.183248040814	0.179821462486	3.507601361907
H	1.497158509585	-1.151928873091	3.225799726632
C	2.882400188364	1.037801256531	2.277219041005
H	4.267786855864	0.122789569762	3.672363017401
H	3.408014479262	1.993899679483	2.318089769273
C	3.779949739378	-1.609068741912	-0.444470443759
H	3.058955641505	-1.317360176274	-1.215474849341
H	3.638004167751	-2.684219246484	-0.291754622117
H	1.806750412380	1.233793454220	2.183146898353
H	2.742753111647	0.670645905163	4.382587785627
H	2.809139886572	-1.866908286186	4.169833995664
N	3.296302302198	0.370580612039	0.991290343515
C	3.381880149376	1.327028821675	-0.168842636478
H	2.365131970321	1.713994000591	-0.299106199767
H	3.643533291540	0.764888293630	-1.063057730722
C	4.368620965001	2.465150021703	0.048662242583
C	5.750815203597	2.213056743939	0.200350609165
C	3.908380686492	3.798849996297	0.049466010643
C	6.654238895817	3.279294185409	0.359505855983
H	6.122838920059	1.191622057185	0.192321692013
C	4.813130139405	4.868077889036	0.200718272106
H	2.846415518606	4.003591382021	-0.068872651339
C	6.188668884546	4.610448910422	0.358538585301
H	7.715480406911	3.075171358442	0.476986037607
H	4.446801010739	5.891356445796	0.197265179398
H	6.888509823803	5.433743854690	0.477310611019
H	2.500639548786	-2.655628136088	1.665765673765
H	0.681025025239	-1.325698748273	0.016828515779
H	4.125230281976	-2.360823829441	2.237759666765
H	6.170994847266	-1.964666120592	0.924168159379
H	8.867776516257	-0.879720157946	-2.267352476326
Ir	-0.615167885512	-0.419863060541	-0.298152149177
I	-1.708574005534	-1.063226876393	2.448549737077
C	-6.039604617501	1.885687942688	0.961041563822
C	-4.663675042505	1.863570211752	0.635276132207
C	-4.213683215993	1.130776156805	-0.480616603990

C	-5.162741451947	0.456460144514	-1.268606524921
C	-6.536835788237	0.466360239400	-0.983351330451
C	-6.956324324206	1.187977883000	0.148533604220
H	-6.400640497949	2.435300030651	1.823054591100
H	-7.237277431521	-0.068722985639	-1.615619255424
H	-8.012383470488	1.210879211967	0.405093419818
O	-3.688842172277	2.560165506682	1.346616035817
C	-4.065158702093	3.240724475744	2.587826787639
H	-4.776909369080	4.052009578900	2.390787052753
H	-4.492930991223	2.532002679613	3.307035965004
H	-3.134545309327	3.652016234891	2.981802934042
O	-4.683667736618	-0.217961422358	-2.406785239607
C	-3.206823228481	-0.377405451260	-2.376104050803
P	-2.468697722028	0.896128361398	-1.136126360018
C	-2.172904454340	2.507874978495	-2.215032566240
C	-1.074163856454	2.210122569775	-3.263778422625
H	-0.839373732150	3.138631996995	-3.803450289691
H	-0.157729603057	1.841332733970	-2.791591524219
H	-1.397593631533	1.470762280936	-4.008170984991
C	-1.678030265421	3.610772364499	-1.245068893421
H	-1.498884820883	4.535222280434	-1.812459905003
H	-2.415907240744	3.821088268267	-0.462718205128
H	-0.738651571718	3.318646338243	-0.759757121545
C	-3.465988345854	2.970080336839	-2.925939439187
H	-3.239329106363	3.855567174613	-3.536797505347
H	-3.870761673490	2.199004888643	-3.592968343157
H	-4.246397221241	3.246854083100	-2.208377769027
C	-2.876417860189	-1.821699944821	-2.011113673245
C	-3.690087135842	-2.828689973722	-2.556533845459
C	-3.409715934161	-4.172128012489	-2.267341179755
H	-4.526919659313	-2.547601989770	-3.183347994439
C	-1.534307061079	-3.416061679511	-0.934376381531
C	-2.316570431549	-4.473436693839	-1.448555675877
H	-4.024649690135	-4.969024879529	-2.674299473415
N	-1.804056792407	-2.097922968966	-1.192019054726
O	-0.436996726430	-3.643431352932	-0.140148797141
C	-0.131719978424	-5.015284757002	0.282869684962
H	0.123946212269	-5.645998515239	-0.577115461510
H	-0.971552195635	-5.451170907135	0.836750538301
H	0.733072952534	-4.916721780155	0.939792754574
H	-2.074131179828	-5.502182252831	-1.216191403266
H	-2.861388255155	-0.163755183401	-3.392092555539
H	0.096635729469	-0.137323357150	-1.690179483728
H	0.247950692787	0.796667712692	0.303196531742

G



SCF Done: E(RB3LYP) = -1895.77530466 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.767175 (Hartree/Particle)
Thermal correction to Energy= 0.813280
Thermal correction to Enthalpy= 0.814224
Thermal correction to Gibbs Free Energy= 0.681268
Sum of electronic and zero-point Energies= -1895.008130
Sum of electronic and thermal Energies= -1894.962024
Sum of electronic and thermal Enthalpies= -1894.961080
Sum of electronic and thermal Free Energies= -1895.094036

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	6.695291170209	-1.296468022787	-1.995956137918
C	5.366039597649	-0.901189338000	-1.750278990612
C	4.502056181049	-1.703642947253	-0.970782805205
C	5.000611079161	-2.923331884018	-0.456242113794
C	6.329322694745	-3.321183030115	-0.696614626392
C	7.184502959318	-2.506127672833	-1.465189927292
H	7.341522510988	-0.666311315519	-2.601974690412
H	5.002411188819	0.026535958584	-2.185846059702
H	6.691756210340	-4.264183159863	-0.294740598105
C	2.860669355721	-1.482831589486	1.836429275612
C	2.524556849555	-0.812706502311	3.177631173646
C	2.814079065386	-0.570012831109	0.612710744691
C	3.261165346768	0.532368191418	3.284687647846
H	1.441898805860	-0.653047647879	3.245353289241

C	2.893337823624	1.413984869253	2.087476684644
H	4.348406420532	0.375074253439	3.314298831132
H	3.485864398383	2.331640609022	2.080890887967
C	3.044895115816	-1.294288064698	-0.727911965051
H	2.674054526897	-0.694196854892	-1.560080608726
H	2.411703412207	-2.183464908200	-0.689023681865
H	1.827699179169	1.688290846782	2.124858304120
H	2.979603201376	1.060983128960	4.203591313180
H	2.810721327488	-1.482062474668	3.998184701503
N	3.108990646670	0.735048156583	0.770015747082
C	3.150872803820	1.698331467093	-0.362653527630
H	2.192717251540	2.234953778891	-0.367557601547
H	3.205031261824	1.145787911304	-1.299880515415
C	4.309336327367	2.686420641303	-0.282768322436
C	5.610312770328	2.274367249873	0.081578736224
C	4.091551991627	4.036045153095	-0.631962791442
C	6.672335382602	3.197212111723	0.098404131552
H	5.791072772310	1.238955836135	0.359264165331
C	5.154958050786	4.959913314575	-0.624308071007
H	3.091983992578	4.367396259671	-0.906448742935
C	6.449668799995	4.543186205179	-0.257482439396
H	7.668084088632	2.868830493233	0.386137636916
H	4.972484630539	5.996742171230	-0.895596638928
H	7.270702304879	5.255670961462	-0.245042176419
H	2.194948572324	-2.326261059776	1.645190452675
H	1.053828163559	-0.618185139916	0.448154915285
H	3.886835070402	-1.882202177770	1.872721025756
H	4.345506656110	-3.574196460080	0.118503179028
H	8.209861347355	-2.813245448861	-1.655277335339
Ir	-0.456847272675	-0.030895608163	0.032532459607
I	-1.681596090181	-1.139037155774	2.525324627126
C	-6.194064090892	1.294445139921	0.896579536327
C	-4.810963212820	1.502674774237	0.690655384236
C	-4.168992868810	0.917459877810	-0.418155325992
C	-4.935154474110	0.160471103618	-1.320928888954
C	-6.311392303122	-0.056596612737	-1.154931882895
C	-6.923786044698	0.518456340995	-0.026985026509
H	-6.702769566909	1.726635275702	1.750794873445
H	-6.869169589208	-0.648693573666	-1.872425768129
H	-7.986928301160	0.363955187988	0.138297880344
O	-4.013386956372	2.292894179505	1.513510126383
C	-4.592052147971	2.859399029893	2.734909787003
H	-5.400941554603	3.560615200540	2.495602023036
H	-4.964104663960	2.066446519562	3.394525849349

H	-3.771494127352	3.390376571562	3.219611646012
O	-4.269924179892	-0.354201237107	-2.449408822832
C	-2.793774489252	-0.278372685405	-2.310922391551
P	-2.371133474568	0.994670743124	-0.935375349595
C	-2.214214324039	2.714855737277	-1.859819517352
C	-1.033478530682	2.648064892080	-2.858518269478
H	-0.900105195614	3.641436536119	-3.309229786696
H	-0.099790139130	2.365584610760	-2.361897038431
H	-1.216850549809	1.939338858730	-3.676456852135
C	-1.922162690484	3.786930725871	-0.779498821970
H	-1.830981858919	4.768432393461	-1.265804239256
H	-2.725660955789	3.841147201777	-0.036618725079
H	-0.983228681426	3.574445148995	-0.254249938120
C	-3.518957490721	3.060117651349	-2.615871963168
H	-3.379858403779	4.014847165167	-3.142117401315
H	-3.776631783486	2.301062727168	-3.365003347347
H	-4.368367375988	3.172055852157	-1.933194788211
C	-2.255133139843	-1.672544071952	-2.005799406926
C	-2.850524147518	-2.752739386691	-2.676986912326
C	-2.381162066458	-4.052644268578	-2.439100049941
H	-3.670956051543	-2.562988825025	-3.357380661561
C	-0.764733174749	-3.105997666122	-0.905269064976
C	-1.323294244231	-4.235288956460	-1.543430144459
H	-2.824733474457	-4.905615046292	-2.943285206788
N	-1.219373083567	-1.833656374405	-1.113043758138
O	0.291866918717	-3.217671379069	-0.030946091152
C	0.697351066906	-4.559386662840	0.414551189810
H	1.125762854195	-5.136159886655	-0.413374664946
H	-0.150914776178	-5.094455005361	0.855599485604
H	1.458133470738	-4.386882129146	1.175758640278
H	-0.937398241268	-5.227234753510	-1.349571013933
H	-2.418646261672	0.062582797715	-3.280324722866
H	0.331062808672	0.526439388462	-1.227548051919
H	0.023462314370	1.280631754640	0.808567430524

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