Supporting Information for

Synthesis of Cyclic Chiral α-Amino Boronates by Copper-catalyzed Asymmetric Dearomative Borylation of Indoles

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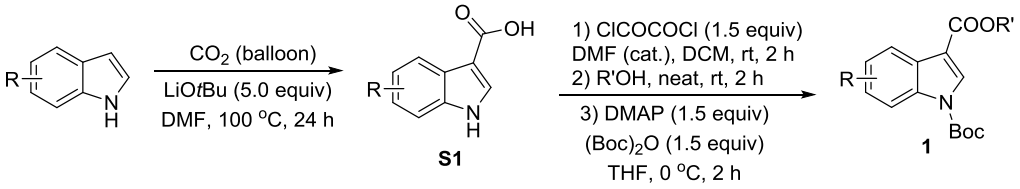
1. General

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using standard Schlenk techniques or glovebox.

THF, Et_2O, CH_2Cl_2, toluene, CH_3CN, and 1,4-dioxane were purified by passing through a neutral alumina column under argon. All other chemicals and solvents were purchased and used as received.

^1H NMR, ^{13}C NMR and ^{11}B NMR spectra were recorded on Zhongke-Niujin 400, Bruker 400, Bruker 600 NMR spectrometer at ambient temperature. ^{13}C shifts were obtained with ^1H decoupling. ^{11}B NMR chemical shifts are externally referenced to BF_3 OEt_2 (δ 0). HPLC data were collected on a Shimadzu LC-20AT spectrometer. Optical Rotation was recorded on a Perkin Elmer 341 polarimerter. High-resolution mass spectroscopy data were obtained on Agilent 6530, Agilent 6224 TOF LC/MS spectrometer. X-ray crystallography was measured on Burker Smart APEX II.

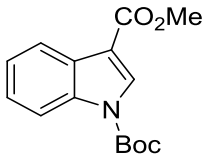
2. General procedures for the synthesis of N-Boc indole-3-carboxylate 1 (GP1)



The preparation of indole-3-carboxylic acid **S1** was according to literature procedures.[1] To a 100mL flame-dried two-necked flask was charged with Li*O*t*Bu (2.0 g, 25 mmol, 5.0 equiv) was added indole (5 mmol, 1.0 equiv). The reaction vessel was evacuated under high vacuum and the atmosphere was replaced with a balloon of CO_2. Then DMF (25 mL) was added and the mixture was allowed to stir for 24 h at 100 ℃. Then the resulting mixture was cooled and carefully quenched by a solution of HCl (2 M, 50 mL) and extracted with EtOAc 3 times (3×30 mL). The combined organic layers were washed with water (50 mL), brine (50 mL) and dry over $MgSO_4$. The dried organic phase was concentrated under reduced pressure and the residue (**S1**) was used in the next step without further purification.

Steps 2 and 3 were adapted from literature procedures.[2,3] To a 100-mL flask charged with crude **S1**, DCM (50 mL) and DMF (0.1 mL) was added $(COCl)_2$ (0.96 g, 7.5 mmol) slowly at 0 ℃. The resulting mixture was then allowed to warm to room temperature and stir at same temperature for 2 h. After concentration, alcohol (30 mL) was introduced and the mixture was continued to stir at room temperature for additional 2 h. The alcohol was then removed and the residue was dissolved in THF (5 mL) followed by addition of DMAP (0.92 g, 7.5 mmol) and Boc_2O (1.64 g, 7.5 mmol) at 0 ℃. The reaction was then allowed to warm to room temperature and stir for 2 h. After concentration, the residue was purified by column chromatography on silica gel using PE/EtOAc (20:1) as the eluent to afford corresponding product **1**.

Compound 1a



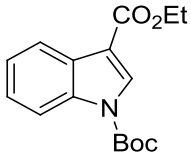
White solid, 1.32 g, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.19-8.15 (m, 2H), 7.39-7.32 (m, 2H), 3.94 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 148.9, 135.5, 132.0, 127.4, 125.1, 123.9, 121.6, 115.1, 112.1, 85.0, 51.4, 28.0; HRMS (ESI) calcd for $C_{15}H_{18}NO_4$ ($[M+H]^+$): 276.1236, found: 276.1232.

1. W.-J. Yoo, M. G. Capdevila, X. Du and S. Kobayashi, *Org. Lett.* 2012, **14**, 5326.

2. E. C. Linton and M. C. Kozlowski, *J. Am. Chem. Soc.* 2008, **130**, 16162.

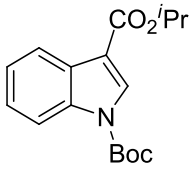
3. C. Fang, M. Li, X. Hu, W. Mo, B. Hu, N. Sun, L. Jin and Z. Shen *Adv. Syn. Catal.* 2016, **358**, 1157.

Compound 1b



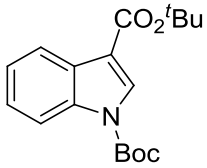
White solid, 1.39 g, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27(s, 1H), 8.18-8.15 (m, 2H), 7.39-7.32(m, 2H), 4.41 (q, *J* = 6.8 Hz, 2H), 1.69 (s, 9H), 1.43 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 149.0, 135.5, 132.0, 127.5, 125.0, 123.8, 121.7, 115.1, 112.5, 85.0, 60.3, 28.0, 14.4; HRMS (ESI) calcd for $C_{16}H_{20}NO_4$ ($[M+H]^+$): 290.1392, found: 290.1389.

Compound 1c



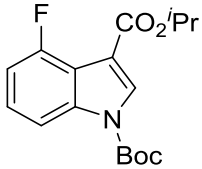
White solid, 1.48 g, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.18-8.16 (m, 2H), 7.38-7.32 (m, 2H), 5.33-5.27 (m, 1H), 1.69 (s, 9H), 1.41 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 149.0, 135.5, 131.9, 127.6, 125.0, 123.8, 121.7, 115.1, 112.9, 85.0, 67.7, 28.1, 22.1; HRMS (ESI) calcd for $C_{17}H_{22}NO_4$ ($[M+H]^+$): 304.1549, found: 304.1546.

Compound 1d



White solid, 1.47 g, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.15-8.12 (m, 2H), 7.38-7.30 (m, 2H), 1.68 (s, 9H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 149.1, 135.6, 131.8, 127.6, 124.9, 123.7, 121.7, 115.1, 114.1, 84.8, 80.9, 28.4, 28.1; HRMS (ESI) calcd for $C_{18}H_{24}NO_4$ ($[M+H]^+$): 318.1705, found: 318.1701.

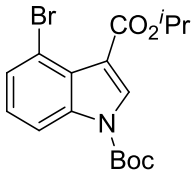
Compound 1g



White solid, 0.66 g, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.33-7.29 (m, 1H), 7.05-7.00 (m, 1H), 5.32-5.23 (m, 1H), 1.69 (s, 9H), 1.39 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 155.9 (d, *J* = 252.0 Hz), 148.7, 138.0 (d, *J* = 8.8 Hz), 132.5, 126.0 (d, *J* = 7.7 Hz), 115.5 (d, *J* = 19.6 Hz),

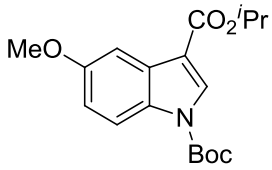
112.3 (d, *J* = 3.8 Hz), 111.2 (d, *J* = 4.0 Hz), 110.3 (d, *J* = 20.8 Hz), 85.5, 68.2, 28.0, 21.9; HRMS (ESI) calcd for $C_{17}H_{21}FNO_4$ ($[M+H]^+$): 322.1455, found: 322.1451.

Compound 1h



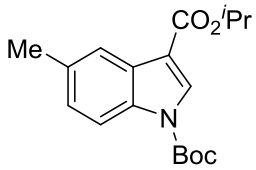
Colorless oil, 0.77 g, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.11 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.22-7.18 (m, 1H), 5.33-5.24 (m, 1H), 1.68 (s, 9H), 1.41 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 148.5, 136.7, 131.3, 128.8, 126.4, 125.9, 114.6, 114.3, 114.2, 85.4, 68.7, 28.0, 21.9; HRMS (ESI) calcd for $C_{17}H_{21}{}^{79}BrNO_4$ ($[M+H]^+$): 382.0654, found: 382.0650.

Compound 1i



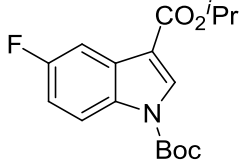
White solid, 0.69 g, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 1.6 Hz, 1H), 6.98-6.95 (m, 1H), 5.32-5.25 (m, 1H), 3.89 (s, 3H), 1.68 (s, 9H), 1.40 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 156.7, 149.0, 132.1, 130.1, 128.7, 115.9, 114.3, 112.5, 103.7, 84.9, 67.7, 55.6, 28.1, 22.1; HRMS (ESI) calcd for $C_{18}H_{24}NO_5$ ($[M+H]^+$): 334.1654, found: 334.1650.

Compound 1j



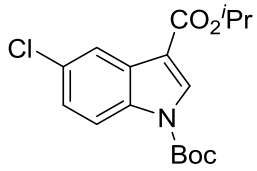
White solid, 0.68 g, 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.96 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 5.34-5.24 (m, 1H), 2.48 (s, 3H), 1.68 (s, 9H), 1.41 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 149.1, 133.7, 133.5, 131.9, 127.8, 126.4, 121.5, 114.7, 112.5, 84.8, 67.7, 28.1, 22.1, 21.5; HRMS (ESI) calcd for $C_{18}H_{24}NO_4$ ($[M+H]^+$): 318.1705, found: 318.1703.

Compound 1k



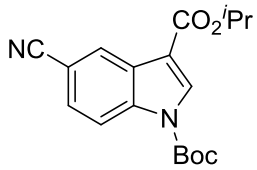
White solid, 0.69 g, 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.13-8.10 (m, 1H), 7.82-7.79 (m, 1H), 7.11-7.06 (m, 1H), 5.33-5.26 (m, 1H), 1.69 (s, 9H), 1.41 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, *J* = 242.2 Hz), 158.7, 148.8, 133.1, 131.9, 128.6, 116.2 (d, *J* = 9.2 Hz), 113.0 (d, *J* = 25.2 Hz), 112.7 (d, *J* = 3.8 Hz), 107.5 (d, *J* = 25.1 Hz), 85.3, 68.0, 28.1, 22.0; HRMS (ESI) calcd for $C_{17}H_{21}FNO_4$ ($[M+H]^+$): 322.1455, found: 322.1451.

Compound 1l



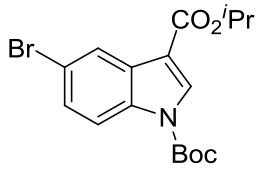
White solid, 1.23 g, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.13 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.33-7.30 (m, 1H), 5.34-5.25 (m, 1H), 1.69 (s, 9H), 1.41 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 148.7, 133.9, 132.8, 129.7, 128.7, 125.3, 121.4, 116.2, 112.3, 85.4, 68.1, 28.0, 22.0; HRMS (ESI) calcd for $C_{17}H_{21}{}^{35}ClNO_4$ ($[M+H]^+$): 338.1159, found: 338.1154.

Compound 1m



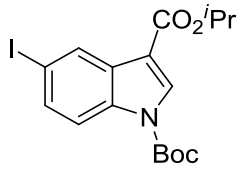
White solid, 0.66 g, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.33 (s, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 5.37-5.27 (m, 1H), 1.71 (s, 9H), 1.43 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 148.3, 137.3, 133.6, 128.1, 127.6, 126.8, 119.5, 116.1, 112.8, 107.5, 86.3, 68.5, 28.0, 22.0; HRMS (ESI) calcd for $C_{18}H_{21}N_2O_4$ ($[M+H]^+$): 329.1501, found: 329.1495.

Compound 1n



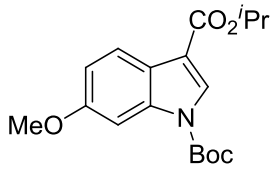
White solid, 0.92 g, 48% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.6 Hz, 1H), 8.22 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.47-7.44 (m, 1H), 5.34-5.24 (m, 1H), 1.68 (s, 9H), 1.41 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 148.6, 134.2, 132.6, 129.2, 127.9, 124.4, 117.5, 116.5, 112.2, 85.5, 68.0, 28.0, 22.0; HRMS (ESI) calcd for $C_{17}H_{21}{}^{81}BrNO_4$ ($[M+H]^+$): 384.0633, found: 384.0640.

Compound 1o



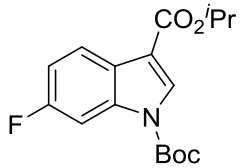
White solid, 0.90 g, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 1.6 Hz, 1H), 8.18 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.65-7.63 (m, 1H), 5.33-5.24 (m, 1H), 1.68 (s, 9H), 1.41 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 148.6, 134.8, 133.6, 132.2, 130.6, 129.7, 116.9, 112.0, 88.4, 85.5, 68.1, 28.0, 22.0; HRMS (ESI) calcd for $C_{17}H_{20}INNaO_4$ ($[M+Na]^+$): 452.0335, found: 452.0330.

Compound 1p



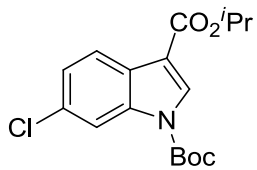
White solid, 0.55 g, 33% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.75 (s, 1H), 6.98-6.96 (m, 1H), 5.33-5.24 (m, 1H), 3.88 (s, 3H), 1.69 (s, 9H), 1.40 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 158.1, 149.1, 136.6, 130.6, 122.2, 121.3, 113.3, 113.0, 99.0, 84.8, 67.7, 55.6, 28.1, 22.1; HRMS (ESI) calcd for $C_{18}H_{23}NNaO_5$ ($[M+Na]^+$): 356.1474, found: 356.1472.

Compound 1q



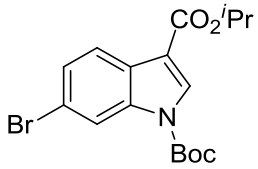
White solid, 0.85 g, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.10-8.07 (m, 1H), 7.90-7.88 (m, 1H), 7.11-7.06 (m, 1H), 5.34-5.24 (m, 1H), 1.69 (s, 9H), 1.40 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.1 (d, *J* = 240.0 Hz), 148.7, 135.7 (d, *J* = 12.9 Hz), 131.9 (d, *J* = 3.2 Hz), 123.9, 122.6 (d, *J* = 9.7 Hz), 112.8, 112.2 (d, *J* = 23.8 Hz), 102.5 (d, *J* = 28.5 Hz), 85.4, 67.9, 28.0, 22.0; HRMS (ESI) calcd for $C_{17}H_{21}FNO_4$ ($[M+H]^+$): 322.1455, found: 322.1450.

Compound 1r



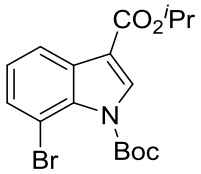
White solid, 0.62 g, 37% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.32-7.29 (m, 1H), 5.33-5.24 (m, 1H), 1.69 (s, 9H), 1.40 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 148.6, 135.8, 132.1, 131.0, 126.1, 124.4, 122.5, 115.4, 112.8, 85.5, 67.9, 28.0, 22.0; HRMS (ESI) calcd for $C_{17}H_{21}{}^{35}ClNO_4$ ($[M+H]^+$): 338.1159, found: 338.1153.

Compound 1s



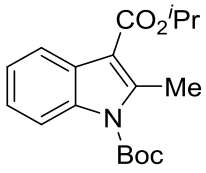
White solid, 1.24 g, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.19 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 5.32-5.26 (m, 1H), 1.69 (s, 9H), 1.41 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 148.6, 136.1, 132.0, 127.1, 126.4, 122.8, 118.8, 118.3, 112.8, 85.6, 68.0, 28.0, 22.0; HRMS (ESI) calcd for $C_{17}H_{20}{}^{81}BrNNaO_4$ ($[M+Na]^+$): 406.0453, found: 406.0449.

Compound 1t



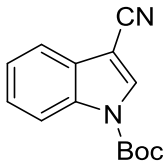
White solid, 0.99 g, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.16(m, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.22-7.19 (m, 1H), 5.32-5.26 (m, 1H), 1.68 (s, 9H), 1.41 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 147.8, 135.0, 133.8, 130.9, 130.3, 125.0, 121.0, 112.3, 107.4, 85.7, 67.9, 27.8, 22.0; HRMS (ESI) calcd for $C_{17}H_{21}{}^{79}BrNO_4$ ($[M+H]^+$): 382.0654, found: 382.0651.

Compound 1u



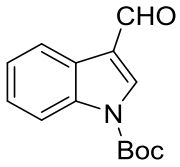
White solid, 0.16 g, 10% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.06 (m, 2H), 7.29-7.27 (m, 2H), 5.35-5.29 (m, 1H), 2.98 (s, 3H), 1.70 (s, 9H), 1.43 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 150.0, 145.6, 135.4, 127.2, 124.0, 123.5, 121.3, 114.8, 110.6, 84.9, 67.5, 28.1, 22.2, 15.0; HRMS (ESI) calcd for $C_{18}H_{24}NO_4$ ($[M+H]^+$): 318.1705, found: 318.1704.

Compound 1v



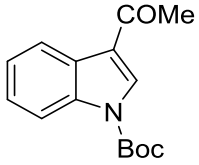
White solid, 1.20 g, 99% yield; ^{1}H NMR (400 MHz, CDCl3) δ 8.17 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.46-7.35 (m, 2H), 1.70 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 134.2, 133.2, 128.0, 126.2, 124.2, 119.7, 115.6, 114.1, 92.2, 85.9, 27.9; HRMS (ESI) calcd for $C_{14}H_{14}N_2NaO_2$ ($[M+Na]^+$): 265.0947, found: 265.0949.

Compound 1w



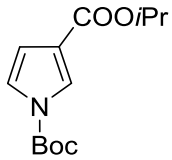
White solid, 1.04 g, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 8.24 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.44-7.36 (m, 2H), 1.71 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 156.6, 148.8, 136.5, 135.9, 126.1, 124.6, 122.1, 121.5, 115.1, 85.6, 28.1; HRMS (ESI) calcd for $C_{14}H_{16}NO_3$ ($[M+H]^+$): 246.1125, found: 246.1127.

Compound 1x



White solid, 1.17 g, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.36 (m, 1H), 8.23 (s, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 7.40-7.33 (m, 2H), 2.57 (s, 3H), 1.72 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 149.1, 135.5, 132.4, 127.3, 125.4, 124.3, 122.7, 120.6, 114.9, 85.4, 28.1, 27.7; HRMS (ESI) calcd for $C_{15}H_{17}NNaO_3$ ($[M+Na]^+$): 282.1101, found: 282.1105.

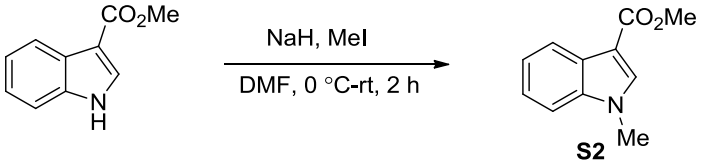
Compound 1y



Colorless oil, 0.77 g, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.20-7.19 (m, 1H), 6.60-6.59 (m, 1H), 5.23-5.13 (m, 1H), 1.61 (s, 9H), 1.32 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 148.1, 124.5, 120.5, 111.9, 84.8, 81.0,

67.4, 27.8, 21.9; HRMS (ESI) calcd for $C_{13}H_{20}NO_4$ ($[M+H]^+$): 254.1387, found: 254.1390.

3. Synthesis of Compound S2

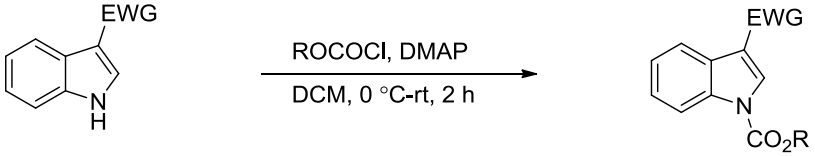


S2

The preparation of compound **S2** was adapted from the literature procedures.[4] To a 50-mL flask charged with methyl indole-3-carboxylate (1.75 g, 10 mmol) and DMF (10 mL) was added NaH (0.80 g, 60% in mineral oil, 20 mmol) in 5 portions at 0 ℃. The resulting mixture was allowed to stir at same temperature for 0.5 h. Methyl iodide (1.24 mL, 20 mmol) was then introduced slowly at 0 ℃. The reaction was then warmed to room temperature and continued to stir for 2 h. Water (10 mL) was then added slowly at 0 ℃ to quench the reaction. The mixture was then extracted with EtOAc 3 times (3 X 30 mL). The combined organic phase was then washed with water 3 times (3 X 20 mL). After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (20:1) as the eluent to afford *N*-Methyl indole **S2** as white solid (1.88 g, 99% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.16 (m, 1H), 7.75 (s, 1H), 7.33-7.27 (m, 3H), 3.90 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 137.1, 135.1, 126.5, 122.7, 121.8, 121.5, 109.7, 106.7, 50.9, 33.4; HRMS (ESI) calcd for $C_{11}H_{12}NO_2$ ($[M+H]^+$): 190.0868, found: 190.0861.

4. General Procedures for the synthesis of compounds 1e and S3-S6 (GP2)



The synthesis of compounds **1e** and **S3-S6** was adapted from literature procedures.[5] To a 100-mL flask charged with 3-subsitiuted indole (10 mmol, carboxylic esters were prepared according to the GP1) and DCM (20 mL) was introduced DMAP (1.8 g, 15 mmol, 1.5 equiv) followed by slow addition of chloro methylformate or CbzCl (15 mmol, 1.5 equiv) at 0 ℃. The resulting mixture was allowed to warm to room temperature and stir for 2 h. The reaction was then diluted by 1 M HCl (20 mL) and extracted with DCM 3 times (3 X 20 mL). The combined organic phase was dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (10:1) as the eluent to afford corresponding 1,3-disubtituted indole.

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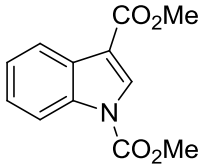
4. M. Kitano, A. Kojima, K. Nakano, A. Miyagishi, T. Noguchi and N. Ohashi, *Chem. Pharm. Bull.* 1999, **47**, 1538.

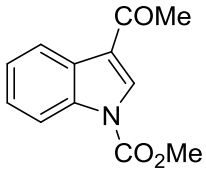
5. C. N. Rao, D. Lentz and H.-U. Reissig, *Angew. Chem., Int. Ed.* 2015, **54**, 2750.

Compound 1e



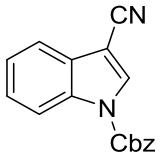
White solid, 2.05 g, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.18-8.15 (m, 2H), 7.41-7.34 (m, 2H), 4.07 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.8, 135.4, 131.5, 127.3, 125.3, 124.2, 121.6, 115.0, 112.9, 54.3, 51.5; HRMS (ESI) calcd for $C_{12}H_{12}NO_4$ ($[M+H]^+$): 234.0766, found: 234.0763.

Compound S3



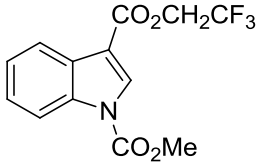
White solid, 1.98 g, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.8 Hz, 1H), 8.24 (s, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.43-7.36 (m, 2H), 4.12 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 151.0, 135.5, 131.9, 127.2, 125.8, 124.7, 122.7, 121.3, 114.8, 54.5, 27.7; HRMS (ESI) calcd for $C_{12}H_{12}NO_3$ ($[M+H]^+$): 218.0817, found: 218.0811.

Compound S4



White solid, 2.23 g, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 8.14 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.50-7.37 (m, 7H), 5.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 134.3, 134.0, 132.8, 129.2, 128.9, 128.8, 127.9, 126.6, 124.6, 119.9, 115.6, 113.8, 93.3, 69.9; HRMS (ESI) calcd for $C_{17}H_{13}N_2O_2$ ($[M+H]^+$): 277.0977, found: 277.0974.

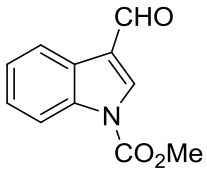
Compound S5



White solid, 2.80 g, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 7.45-7.38 (m, 2H), 4.76-4.70 (m, 2H), 4.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 150.7, 135.5, 132.6, 127.0, 125.8, 124.6,

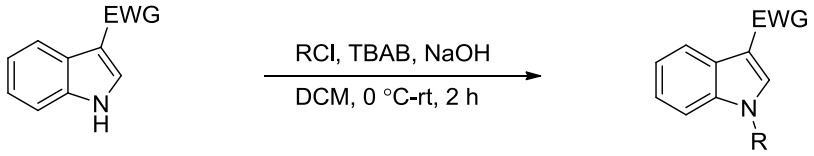
123.1 (q, J = 275.7 Hz), 121.5, 115.2, 111.3, 60.1 (q, J = 36.4 Hz), 54.6; HRMS (ESI) calcd for $C_{13}H_{11}F_3NO_4$ ($[M+H]^+$): 302.0640, found: 302.0636.

Compound S6



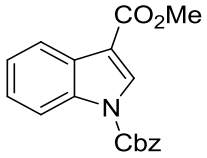
White solid, 1.87 g, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H), 8.22 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.45-7.36 (m, 2H), 4.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 150.6, 136.0, 135.8, 126.3, 125.9, 124.8, 122.1, 115.0, 54.6 (two aromatic carbon signals overlap); HRMS (ESI) calcd for $C_{11}H_9NNaO_3$ ($[M+Na]^+$): 226.0480, found: 226.0479.

5. General Procedures for the synthesis of compounds 1f and S7-S10 (GP3)



The synthesis of compounds **1f** and **S7-S10** was adapted from the literature procedures.[6] To a 100-mL flask charged with 3-subsitiuted indole (10 mmol, carboxylic esters were prepared according to the GP1), DCM (10 mL), TBAB (0.32 g, 1.0 mmol), and NaOH (0.80 g, 20 mmol) was added corresponding CbzCl (15 mmol, 1.5 equiv), acyl chloride (15 mmol, 1.5 equiv) or TsCl (15 mmol, 1.5 equiv) slowly at 0 ℃. The resulting mixture was allowed to warm to room temperature and stir for 3 h. The reaction was then diluted by 1 M HCl (20 mL) and extracted with DCM 3 times (3 X 10 mL). The combined organic phase was dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (10:1) as the eluent to afford corresponding 1,3-disubtituted indole.

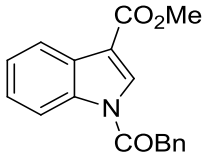
Compound 1f



White solid, 2.93 g, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.20-8.14 (m, 2H), 7.49-7.32 (m, 7H), 5.46 (s, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.2, 135.5, 134.4, 131.5, 129.0, 128.8, 128.7, 127.4, 125.4, 124.2, 121.7, 115.1, 113.0, 69.4, 51.5; HRMS (ESI) calcd for $C_{18}H_{16}NO_4$ ($[M+H]^+$): 310.1079, found: 310.1078.

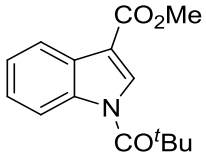
6. E. Reimann *Pharmazie* 2000, **55**, 907-912.

Compound S7



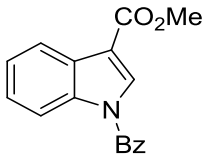
White solid, 2.46 g, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.4 Hz, 1H), 8.21 (s, 1H), 8.13 (d, *J* = 7.2 Hz, 1H), 7.42 - 7.32 (m, 7H), 4.28 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 164.3, 136.1, 132.5, 130.7, 129.1, 129.0, 127.7, 127.2, 126.1, 124.9, 121.5, 116.6, 114.0, 51.6, 42.6; HRMS (ESI) calcd for $C_{18}H_{16}NO_3$ ($[M+H]^+$): 294.1130, found: 294.1126.

Compound S8



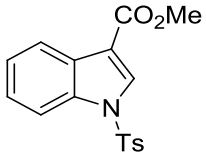
White solid, 1.86 g, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.0 Hz, 1H), 8.42 (s, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.43-7.36 (m, 2H), 3.96 (s, 3H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 164.6, 137.2, 131.5, 126.4, 125.9, 124.6, 121.2, 117.1, 112.9, 51.6, 41.6, 28.7; HRMS (ESI) calcd for $C_{15}H_{18}NO_3$ ($[M+H]^+$): 260.1287, found: 260.1281.

Compound S9



White solid, 2.18 g, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 7.2 Hz, 1H), 7.99 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.68-7.65 (m, 1H), 7.59-7.55 (m, 2H), 7.46-7.41(m, 2H), 3.91(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 164.4, 136.3, 133.4, 133.3, 132.7, 129.4, 128.9, 127.6, 125.7, 125.0, 121.6, 116.2, 113.2, 51.6; HRMS (ESI) calcd for $C_{17}H_{13}NNaO_3$ ($[M+Na]^+$): 302.0793, found: 302.0787.

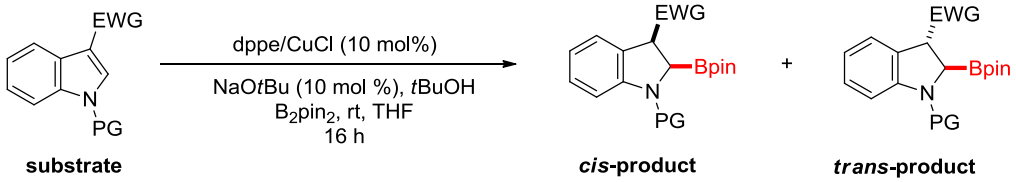
Compound S10



White solid, 2.30 g, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.13(d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H) 7.82 (d, *J* = 7.2 Hz, 2H), 7.38-7.31 (m, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 3.92 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 145.7, 134.7, 134.5, 132.0, 130.1, 127.7, 127.0, 125.3, 124.3, 122.0, 113.4,

113.2, 51.5, 21.5; HRMS (ESI) calcd for $C_{17}H_{16}NO_4S$ ($[M+H]^+$): 330.0800, found: 330.0797.

6. *Table S1. Initial Survey of Copper-catalyzed Dearomative Borylation Using Achiral ligand (dppe).*

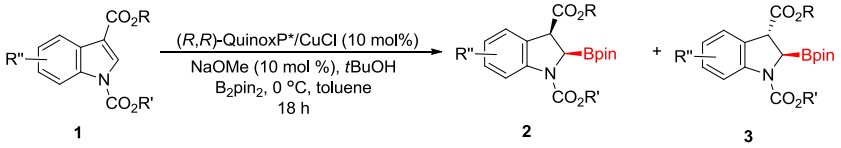


To entry	substrate	PG, EWG	results
1	**S2**	Me, CO_2Me	no reaction
2	**S3**	CO_2Me, COMe	yes, major *trans*-product.
3	**S4**	Cbz, CN	no reaction
4	**S5**	CO_2Me, $CO_2CH_2CF_3$	yes, major *trans*-product
5	**S6**	CO_2Me, CHO	messy
6	**S7**	COBn, CO_2Me	trace
7	**S8**	CO*t*Bu, CO_2Me	trace
8	**S9**	Bz, CO_2Me	trace
9	**S10**	Ts, CO_2Me	no reaction
10	***1a***	*Boc, CO_2Me*	*yes, major cis-product*
11	**1e**	CO_2Me, CO_2Me	yes, major *trans*-product
12	**1f**	Cbz, CO_2Me	yes, major *trans*-product

Conclusions: 1) When indole substrate bearing electron-withdrawing group such as acyl, formyl, or alkoxycarbonyl in its 3-position was used, alkoxycarbonyl substitution in nitrogen was responsible for the reaction to take place; 2) In the presence of achiral ligand dppe, only substrate **1a** could give *cis*-product preferentially; 3) *Trans*-product was not stable towards isolation by chromatography on either silica gel or alumina whereas *cis*-one was isolable.

Therefore, we chose indole **1a** as model substrate to further evaluate reactivity and stereoselectivity in the presence of chiral catalyst.

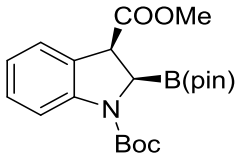
7. *General procedures for the catalytic asymmetric dearomative borylation of indole 1*



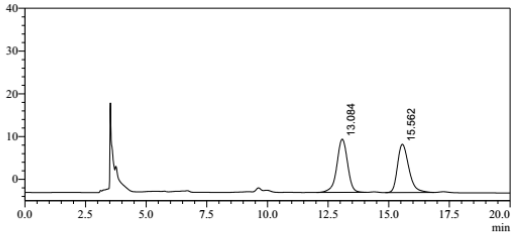
In a nitrogen-filled grovebox, to a 25-mL flame-dried Schlenk tube charged with CuCl (2.0 mg, 0.02 mmol), NaOMe (1.1 mg, 0.02 mmol) and (*R*,*R*)-QunioxP* (6.7 mg, 0.02 mmol) was added toluene (0.5 mL). The resulting mixture was allowed to

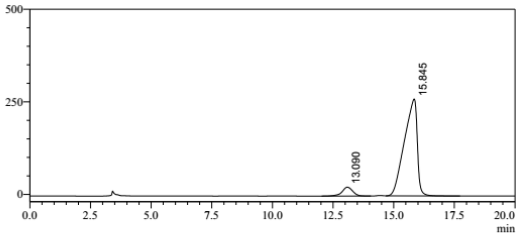
stir at room temperature for 0.5 h. B_2pin_2 (0.30 mmol in 0.5 mL) was then introduced and the reaction was allowed to stir at room temperature for 10 min followed by addition of indole **1** (0.20 mmol in 1 mL toluene) and *t*BuOH (37.5 μL, 0.4 mmol) at 0 ^oC. The resulting mixture was continued to stir at 0 ^oC for 18-48 hours. After removal of the solvent, the ^1H NMR of crude mixture was taken to determine the d.r. value. The residue was purified by column chromatography on silica gel using PE/EtOAc (12:1) as the eluent to affording corresponding 2-boryl indoline **2** or **3**.

Compound 2a



Colorless oil, 70.9 mg, 88% yield, 95:5 *d.r.*, 86% *ee*, $[\alpha]_D^{25}$ = -57.7 (*c* 0.40, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (brs, 1H), 7.27-7.17 (m, 2H), 6.93-6.90 (m, 1H), 4.44 (brs, 1H), 4.11 (d, *J* = 11.6 Hz, 1H), 3.74 (s, 3H), 1.58 (s, 9H), 1.31 (s, 6H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 152.4, 142.1, 128.6, 128.3, 125.1, 121.8, 114.8, 83.8, 81.4, 52.4, 48.8, 47.2, 28.3, 25.3, 24.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6; HRMS (ESI) calcd for $C_{21}H_{31}BNO_6$ ($[M+H]^+$): 404.2244, found: 404.2245. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98: 2, flow rate = 1.0 mL/min., wavelength = 230 nm, t_R = 13.09 (minor), 15.85 (major).





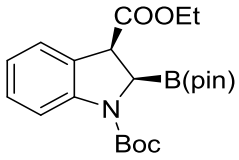
???A 230nm

Peak ID	Ret. Time	Height	Area	Area%
1	13.084	12441	382199	51.065
2	15.562	11280	366262	48.935
Total				100.000

???A 230nm

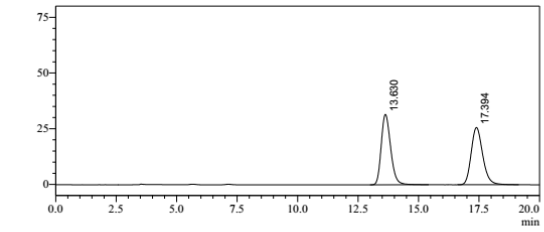
Peak ID	Ret. Time	Height	Area	Area%
1	13.090	23995	735536	7.036
2	15.845	261743	9718475	92.964
Total				100.000

Compound 2b



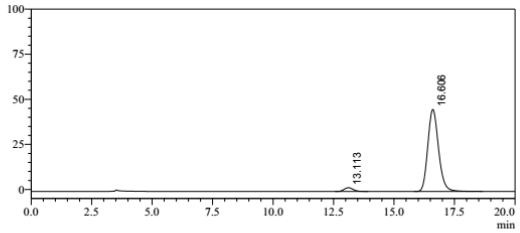
Colorless oil, 72.6 mg, 87% yield, 95:5 *d.r.*, 93% *ee* $[\alpha]_D^{25}$ = -66.5 (*c* 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (brs, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.20-7.17 (m, 1H), 6.92-6.89 (m, 1H), 4.47 (d, *J* = 11.2 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, *J* = 14.0 Hz, 2H), 4.11 (d, *J* = 12.0 Hz, 1H), 1.58 (s, 9H), 1.32-1.26 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 152.4, 142.3, 128.5, 128.3, 124.8, 121.8, 115.1, 83.8, 81.2, 61.4, 48.6, 47.5, 28.3, 25.3, 24.8, 14.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6; HRMS (ESI) calcd for $C_{22}H_{32}BNNaO_6$ ($[M+Na]^+$): 440.2220, found: 440.2216. The enantiopurity was

determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98: 2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 13.11 (minor), 16.61 (major).



A Channel 2 254nm

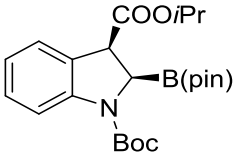
Peak ID	Ret. Time	Height	Area	Area%
1	13.630	31563	858121	50.123
2	17.394	25686	853909	49.877
Total				100.000



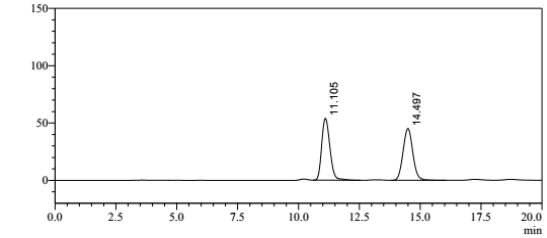
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	13.113	2088	54564	3.737
2	16.606	45474	1405573	96.263
Total				100.000

Compound 2c

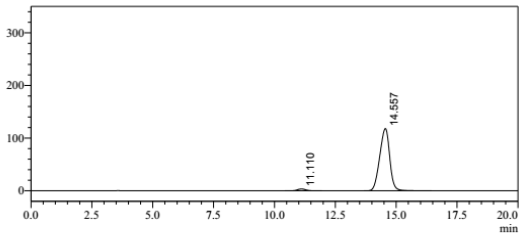


Colorless oil, 75.0 mg, 87% yield, 95:5 *d.r.*, 95% *ee*, $[\alpha]_D^{25}$ = -66.3 (*c* 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (brs, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.20-7.16 (m, 1H), 6.91-6.88 (m, 1H), 5.07-5.01 (m, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.10 (d, *J* = 12.0 Hz, 1H), 1.58 (s, 9H), 1.32-1.25 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 152.4, 142.3, 128.5, 128.3, 124.7, 121.7, 115.0, 83.8, 81.2, 69.2, 48.7, 47.8, 28.4, 25.3, 24.9, 21.8, 21.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8; HRMS (ESI) calcd for $C_{23}H_{34}BNNaO_6$ ($[M+Na]^+$): 454.2377, found: 454.2376. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 11.11 (minor), 14.56 (major).



A Channel 2 254nm

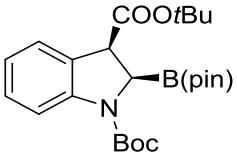
Peak ID	Ret. Time	Height	Area	Area%
1	11.105	53905	1271940	50.246
2	14.497	45158	1259484	49.754
Total				100.000



A Channel 2 254nm

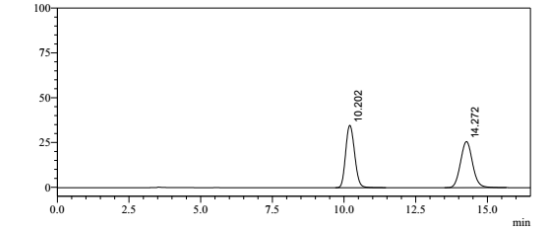
Peak ID	Ret. Time	Height	Area	Area%
1	11.110	3398	80128	2.318
2	14.557	118234	3376668	97.682
Total				100.000

Compound 2d



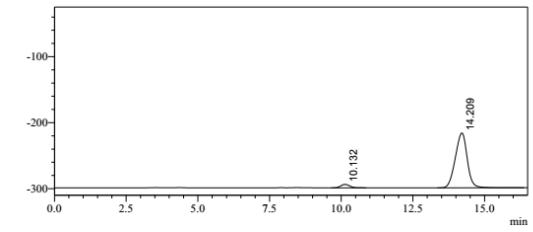
Colorless oil, 80.1 mg, 90% yield, 96:4 *d.r.*, 91% *ee*, $[\alpha]_D^{25}$ = -30.9 (*c* 0.19, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.19-7.15 (m, 1H), 6.91-6.87 (m, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.06 (d, *J* = 12.0 Hz, 1H), 1.57 (s, 9H), 1.47 (s, 9H), 1.33 (s, 6H), 1.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 152.2, 141.9, 128.3, 124.5, 121.5, 114.9, 83.5, 81.8, 80.8, 48.4, 28.2, 27.8, 25.2, 24.7

(two aromatic carbons overlap; *B*-adjacent carbon overlaps with C3-carbon); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.5; HRMS (ESI) calcd for $C_{24}H_{36}BNNaO_6$ ($[M+Na]^+$): 468.2535, found: 468.2531. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 10.13 (minor), 14.21 (major).



A Channel 2 254nm

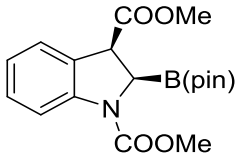
Peak ID	Ret. Time	Height	Area	Area%
1	10.202	34788	756284	50.143
2	14.272	25710	751965	49.857
Total				100.000



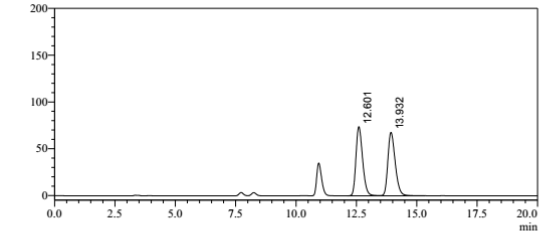
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	10.132	5107	110594	4.408
2	14.209	83001	2398070	95.592
Total				100.000

Compound 2e

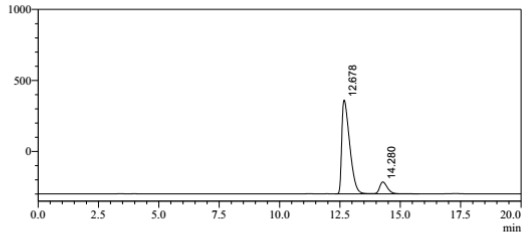


Colorless oil, 54.1 mg, 75% yield, 90:10 *d.r.*, 78% *ee*, $[\alpha]_D^{25}$ = -9.2 (*c* 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (brs, 1H), 7.29-7.21 (m, 2H), 6.97 - 6.94 (m, 1H), 4.50 (s, 1H), 4.12 (d, *J* = 11.6 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 1.31 (s, 6H), 1.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 153.3, 142.8, 128.8, 127.5, 124.6, 122.4, 115.1, 84.0, 60.3, 52.6, 48.4, 25.2, 24.8 (*B*-adjacent carbon overlaps with C3-carbon); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.9; HRMS (ESI) calcd for $C_{18}H_{24}BNNaO_6$ ($[M+Na]^+$): 384.1594, found: 384.1592. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IC column, Hexane/*i*PrOH = 90: 10, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 12.68 (major), 14.28 (minor).



A Channel 2 254nm

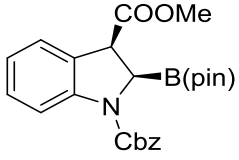
Peak ID	Ret. Time	Height	Area	Area%
1	12.601	73894	1421992	49.750
2	13.932	67847	1436279	50.250
Total				100.000



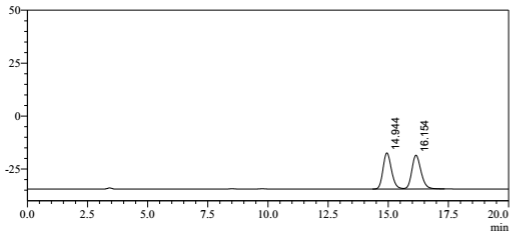
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	12.678	660197	15046107	88.926
2	14.280	83589	1873714	11.074
Total				100.000

Compound 2f

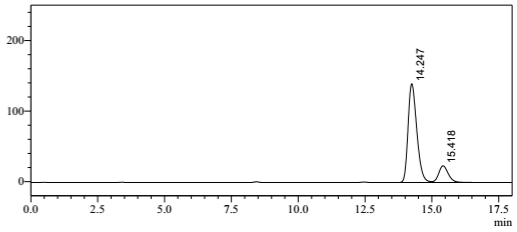


White solid, 66.4 mg, 76% yield, 95:5 *d.r.*, 68% *ee*, $[\alpha]_D^{25}$ = -49.2 (*c* 0.24, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.41 (m 1H), 7.41-7.28 (m, 7H), 6.94 (s, 1H), 5.39-5.07 (m, 2H), 4.50 (brs, 1H), 4.20 (brs, 1H), 3.74 (s, 3H), 1.18 (brs, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 152.8, 142.7, 136.0, 128.8, 128.4, 127.9, 127.7, 125.3, 124.5, 122.5, 115.3, 84.0, 66.9, 52.5, 48.5, 47.4, 25.1, 24.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8; HRMS (ESI) calcd for $C_{24}H_{29}BNO_6$ ($[M+H]^+$): 438.2088, found: 438.2090; The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IC column, Hexane/*i*PrOH = 90: 10, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 14.25 (major), 15.42 (minor).



A Channel 2 254nm

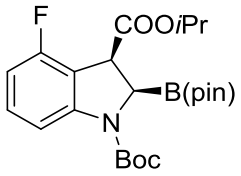
Peak ID	Ret. Time	Height	Area	Area%
1	14.944	17051	418543	49.672
2	16.154	15918	424064	50.328
Total				100.000



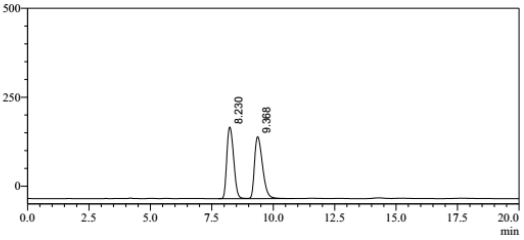
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	14.247	139948	3188373	84.111
2	15.418	23682	602281	15.889
Total				100.000

Compound 2g

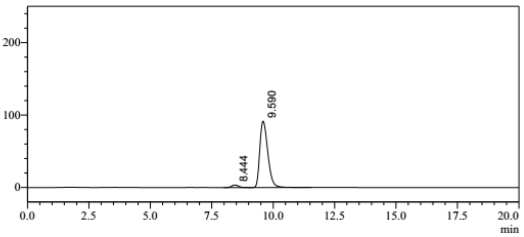


Colorless oil, 83.5 mg, 93% yield, >98:2 *d.r.*, 94% *ee*, $[\alpha]_D^{25}$ = -73.8 (*c* 0.14, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (brs, 1H), 7.18-7.13 (m, 1H), 6.64-6.59 (m, 1H), 5.04-5.01(m, 1H), 4.45 (d, *J* = 10.0 Hz, 1H), 4.16 (d, *J* = 12.0 Hz, 1H), 1.57 (s, 9H), 1.30-1.22 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 159.1 (d, *J* = 245.6 Hz), 152.1, 145.0, 130.3 (d, *J* = 8.1 Hz), 115.7 (d, *J* = 17.9 Hz), 110.6, 108.7 (d, *J* = 20.2 Hz), 84.0, 81.7, 69.1, 50.0, 44.9, 28.3, 25.2, 24.7, 21.6, 21.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.5 ppm; HRMS (ESI) calcd for $C_{23}H_{33}BFNNaO_6$ ($[M+Na]^+$): 472.2283, found: 472.2290. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 8.44 (minor), 9.59 (major).



A Channel 2 254nm

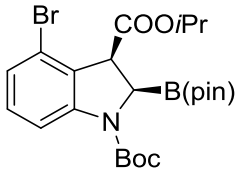
Peak ID	Ret. Time	Height	Area	Area%
1	8.230	201046	3893239	49.695
2	9.368	173998	3941045	50.305
Total				100.000



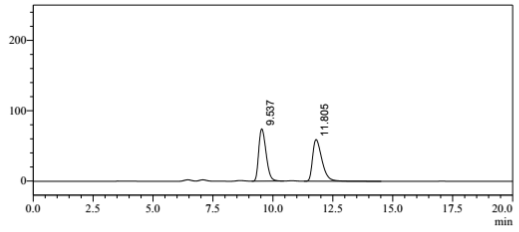
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	8.444	3402	65656	3.058
2	9.590	91522	2081466	96.942
Total				100.000

Compound 2h

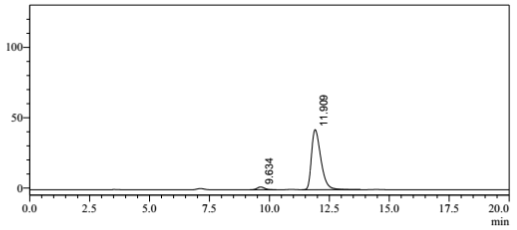


Colorless oil, 65.4 mg, 64% yield, 94:6 *d.r.*, 93% *ee*, $[\alpha]_D^{25}$ = -17.5 (*c* 0.16, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (brs, 1H), 7.07-7.06 (m, 2H), 5.01 (s, 1H), 4.27 (brs, 1H), 4.09 (brs, 1H), 1.57 (s, 9H), 1.29-1.23 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 152.5, 140.0, 130.6, 130.0, 125.0, 120.2, 113.5, 84.2, 82.2, 69.0, 49.1, 49.0, 28.3, 25.4, 24.6, 21.6, 21.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1; HRMS (ESI) calcd for $C_{23}H_{33}B^{81}BrNNaO_6$ ($[M+Na]^+$): 534.1462, found: 534.1464. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 9.63 (minor), 11.91 (major).



A Channel 2 254nm

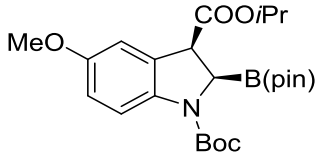
Peak ID	Ret. Time	Height	Area	Area%
1	9.537	74289	1589982	49.704
2	11.805	59218	1608896	50.296
Total				100.000



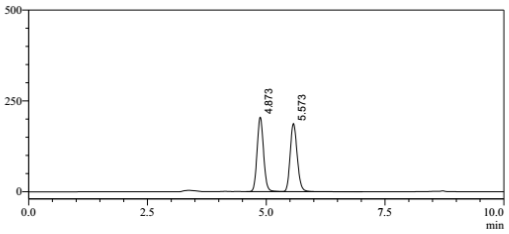
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	9.634	1933	41372	3.427
2	11.909	42664	1166028	96.573
Total				100.000

Compound 2i

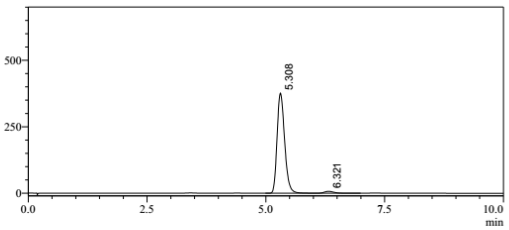


Colorless oil, 77.4 mg, 84% yield, 95:5 *d.r.*, 95% *ee*, $[\alpha]_D^{25}$ = -46.6 (*c* 0.38, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 6.88 (s, 1H), 6.75-6.72 (m, 1H), 5.08-5.02 (m, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.10 (d, *J* = 12.0 Hz, 1H), 3.74 (s, 3H), 1.56 (s, 9H), 1.32-1.27 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 155.0, 152.3, 136.0, 129.5, 115.5, 113.7, 110.7, 83.8, 81.0, 69.2, 55.6, 48.9, 47.8, 28.4, 25.3, 24.8, 21.8(2), 21.8(0); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5; HRMS (ESI) calcd for $C_{24}H_{37}BNO_7$ ($[M+H]^+$):462.2663, found:462.2665. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IC column, Hexane/*i*PrOH = 90:10, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 5.31 (major), 6.32 (minor).



A Channel 2 254nm

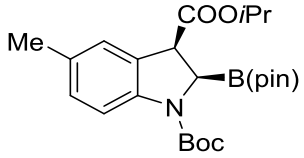
Peak ID	Ret. Time	Height	Area	Area%
1	4.873	205064	1949896	50.130
2	5.573	187695	1939776	49.870
Total				100.000



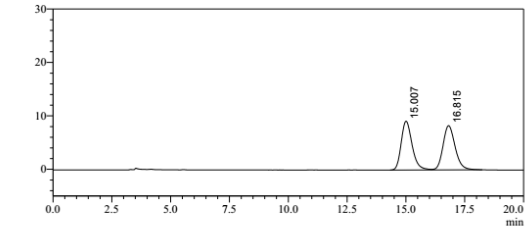
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	5.308	376486	4157665	97.554
2	6.321	7279	104258	2.446
Total				100.000

Compound 2j

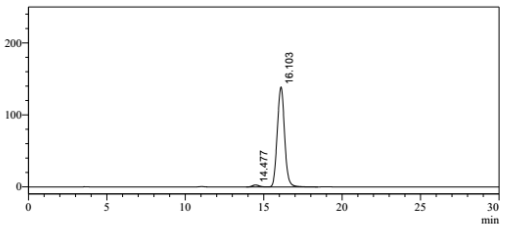


Colorless oil, 81.0 mg, 91% yield, 97:3 *d.r.*, 96% *ee*, $[\alpha]_D^{25}$ = -39.7 (*c* 0.08, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.08 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.07-5.01(m, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 4.09 (d, *J* = 12.0 Hz, 1H), 2.26 (s, 3H), 1.57 (s, 9H), 1.32-1.26 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 152.4, 139.9, 131.1, 129.0, 128.5, 125.3, 114.7, 83.7, 81.1, 69.1, 48.7, 47.8, 28.4, 25.3, 24.9, 21.8, 21.7, 20.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8; HRMS (ESI) calcd for $C_{24}H_{37}BNO_6$ ($[M+H]^+$): 446.2714, found: 446.2710. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 14.48 (minor), 16.10 (major).



A Channel 2 254nm

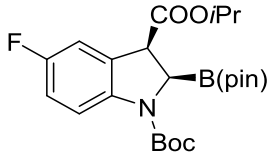
Peak ID	Ret. Time	Height	Area	Area%
1	15.007	9134	294351	49.857
2	16.815	8281	296039	50.143
Total				100.000



A Channel 2 254nm

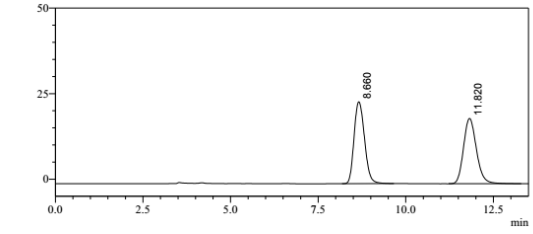
Peak ID	Ret. Time	Height	Area	Area%
1	14.477	2753	84206	1.829
2	16.103	139084	4518703	98.171
Total				100.000

Compound 2k



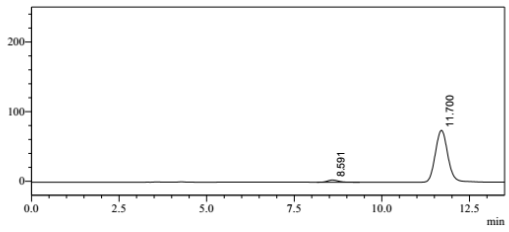
Colorless oil, 60.2 mg, 67% yield, 85:15 *d.r.*, 93% *ee*, $[\alpha]_D^{25}$ = -32.8 (*c* 0.14, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (brs, 1H), 7.01 (d, *J* = 6.8 Hz, 1H), 6.90-6.86 (m, 1H), 5.07-5.02 (m, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.13 (d, *J* = 12.0 Hz, 1H), 1.57 (s, 9H), 1.32-1.27(m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 158.2 (d, *J* = 238.1 Hz), 152.2, 138.4, 129.8, 115.5, 114.9 (d, *J* = 22.7 Hz), 112.1, 83.9, 81.4, 69.6, 49.0, 47.6, 28.3, 25.3, 24.8, 21.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.3; HRMS (ESI) calcd for $C_{23}H_{34}BFNO_6$ ($[M+H]^+$): 450.2463, found: 450.2462. The enantiopurity was

determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 8.59 (minor), 11.70 (major).



A Channel 2 254nm

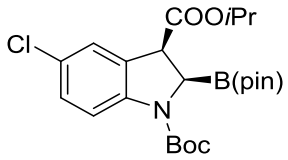
Peak ID	Ret. Time	Height	Area	Area%
1	8.660	23909	497734	50.435
2	11.820	19085	489140	49.565
Total				100.000



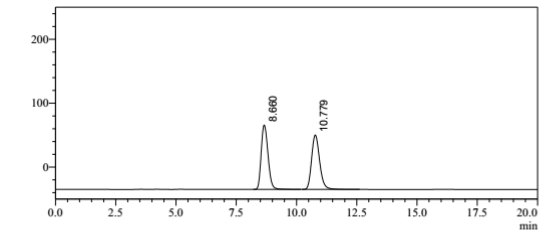
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	8.591	3103	65004	3.392
2	11.700	74413	1851254	96.608
Total				100.000

Compound 2l

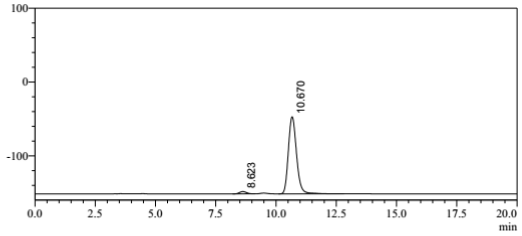


Colorless oil, 77.2 mg, 83% yield, 94:6 *d.r.*, 95% *ee*, $[\alpha]_D^{25}$ = -25.0 (*c* 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.25 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 5.08-5.02 (m, 1H), 4.41 (d, *J* = 11.6 Hz, 1H), 4.12 (d, *J* = 12.0 Hz, 1H), 1.57 (s, 9H), 1.32-1.27 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 152.1, 140.8, 130.0, 128.5, 126.6, 124.9, 115.9, 83.9, 81.6, 69.6, 49.1, 47.6, 28.3, 25.3, 25.0, 21.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.4; HRMS (ESI) calcd for $C_{23}H_{33}BClNO_6$ ($[M+Na]^+$): 488.1987, found: 488.1982. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 8.62 (minor), 10.67 (major).



A Channel 2 254nm

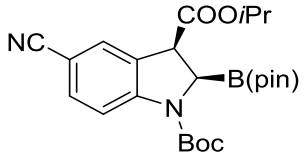
Peak ID	Ret. Time	Height	Area	Area%
1	8.660	100610	1985308	50.019
2	10.779	85104	1983776	49.981
Total				100.000



A Channel 2 254nm

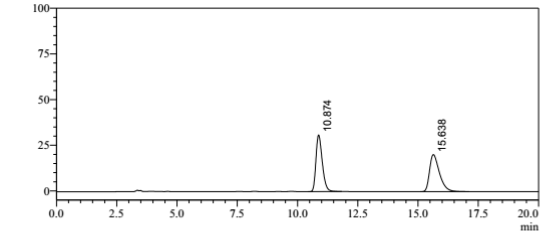
Peak ID	Ret. Time	Height	Area	Area%
1	8.623	3129	61767	2.439
2	10.670	104513	2470440	97.561
Total				100.000

Compound 2m



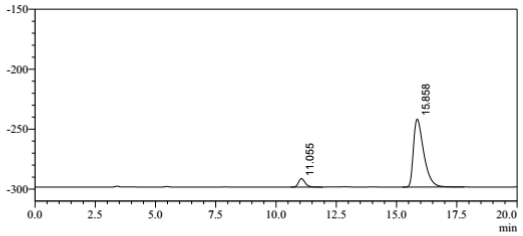
Colorless oil, 45.6 mg, 50% yield, 71:29 *d.r.*, 85% *ee*, $[\alpha]_D^{25}$ = -57.1 (*c* 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (brs, 1H), 7.56 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 5.10-5.03(m, 1H), 4.44 (d, *J* = 12.4 Hz, 1H), 4.16 (d, *J* = 12.0 Hz, 1H), 1.58 (s, 9H), 1.32-1.27 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 151.7, 145.7, 133.6, 129.4,, 128.5, 119.4, 115.2, 104.4, 84.0, 82.5, 70.0, 49.2, 47.3, 28.2, 25.2, 24.9, 21.7; ^{11}B

NMR (128 MHz, $CDCl_3$) δ 31.2 ppm; HRMS (ESI) calcd for $C_{24}H_{33}BN_2NaO_6$ ($[M+Na]^+$): 479.2329, found: 479.2332. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 90: 10, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 11.06 (minor), 15.86 (major).



A Channel 2 254nm

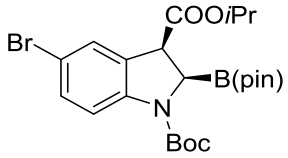
Peak ID	Ret. Time	Height	Area	Area%
1	10.874	31020	568824	49.559
2	15.638	20277	578952	50.441
Total				100.000



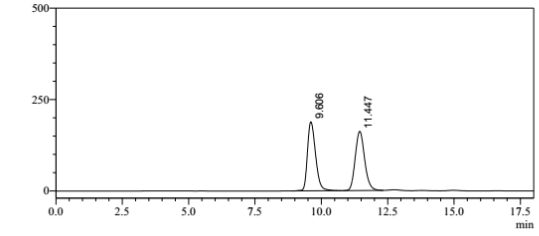
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	11.055	7058	135862	7.444
2	15.858	56668	1689323	92.556
Total				100.000

Compound 2n

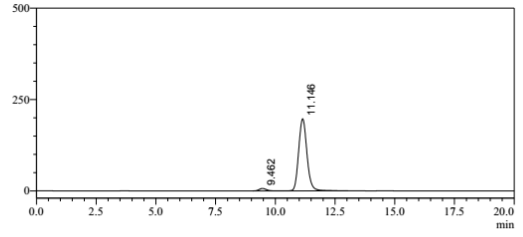


Colorless oil, 89.9 mg, 88% yield, 95:5 *d.r.*, 94% *ee*, $[\alpha]_D^{25}$ = -20.0 (*c* 0.76, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70-7.27 (m, 3H), 5.08-5.02 (m, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 1.57 (s, 9H), 1.31-1.26(m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 152.1, 141.4, 131.4, 130.5, 127.8, 116.4, 113.9, 83.9, 81.7, 69.6, 49.0, 47.5, 28.3, 25.3, 25.0, 21.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.4; HRMS (ESI) calcd for $C_{23}H_{33}B^{81}BrNNaO_6$ ($[M+Na]^+$): 534.1462, found: 534.1466. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 9.46 (minor), 11.15 (major).



A Channel 2 254nm

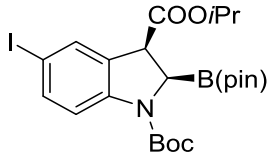
Peak ID	Ret. Time	Height	Area	Area%
1	9.606	188850	4019210	50.116
2	11.447	162045	4000625	49.884
Total				100.000



A Channel 2 254nm

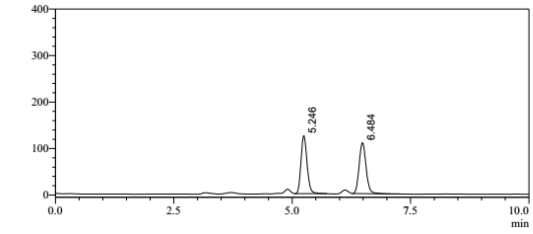
Peak ID	Ret. Time	Height	Area	Area%
1	9.462	6511	139556	2.843
2	11.146	197044	4769558	97.157
Total				100.000

Compound 2o



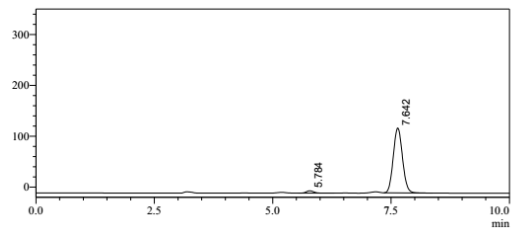
Colorless oil, 95.8 mg, 86% yield, 97:3 *d.r.*, 94% *ee*, $[\alpha]_D^{25}$ = -4.0 (*c* 0.30, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.27 (brs, 1H), 5.08-5.02 (m, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.09 (d, *J* = 12.0 Hz, 1H), 1.56 (s, 9H),

1.31-1.26 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 152.1, 141.9, 137.3, 133.6, 130.9, 117.0, 83.9, 83.6, 81.6, 69.6, 48.8, 47.2, 28.3, 25.3, 24.9, 21.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7; HRMS (ESI) calcd for $C_{23}H_{34}BINO_6$ ($[M+H]^+$): 558.1524, found: 558.1520. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IF column, Hexane/*i*PrOH = 95:5, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 5.78 (minor), 7.64 (major).



A Channel 2 254nm

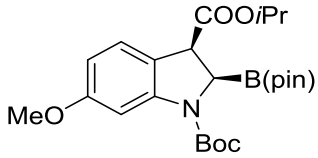
Peak ID	Ret. Time	Height	Area	Area%
1	5.246	124380	1115190	49.715
2	6.484	109524	1127969	50.285
Total				100.000



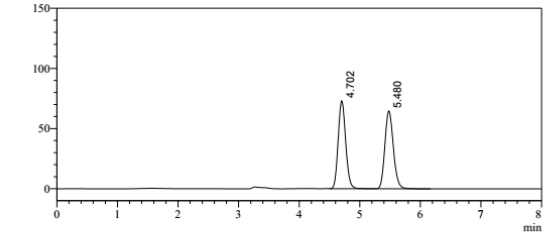
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	5.784	4537	50407	2.835
2	7.642	127565	1727511	97.165
Total				100.000

Compound 2p

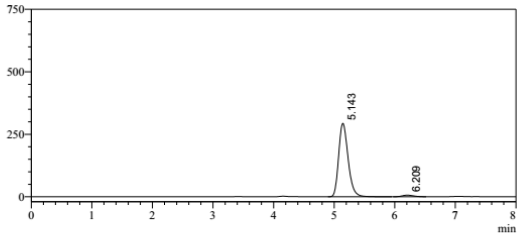


Colorless oil, 81.1 mg, 88% yield, 98:2 *d.r.*, 95% *ee*, $[\alpha]_D^{25}$ = -73.8 (*c* 0.13, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.14 (m, 2H), 6.47-6.44 (m, 1H), 5.07-4.98 (m, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 3.77 (s, 3H), 1.58 (s, 9H), 1.32-1.24 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 160.4, 152.3, 143.3, 124.9, 120.3, 107.6, 101.1, 83.8, 81.2, 69.1, 55.3, 49.8, 47.1, 28.4, 25.3, 24.8, 21.8, 21.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8; HRMS (ESI) calcd for $C_{24}H_{36}BNNaO_7$ ($[M+Na]^+$): 484.2483, found: 484.2484. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IC column, Hexane/*i*PrOH = 90: 10, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 5.14 (major), 6.21 (minor).



A Channel 2 254nm

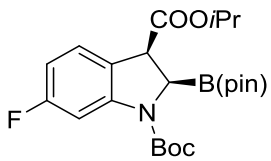
Peak ID	Ret. Time	Height	Area	Area%
1	4.702	73014	630066	49.939
2	5.480	64724	631615	50.061
Total				100.000



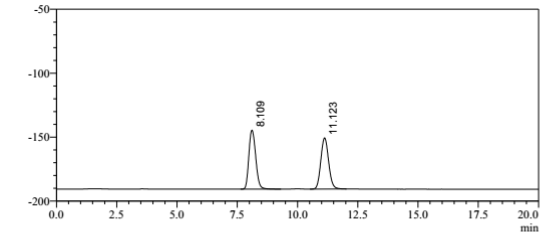
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	5.143	293570	3184424	97.504
2	6.209	6351	81521	2.496
Total				100.000

Compound 2q

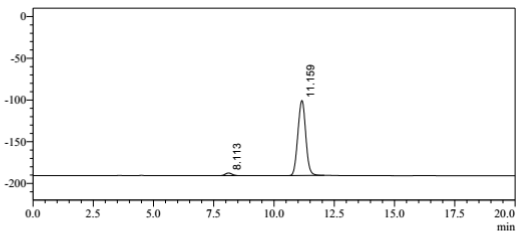


Colorless oil, 72.7 mg, 81% yield, 97:3 *d.r.*, 94% *ee*, $[\alpha]_D^{25}$ = -73.6 (*c* 0.38, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59-7.18 (m, 2H), 6.60-6.56 (m, 1H), 5.07-5.01 (m, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.13 (d, *J* = 12.0 Hz, 1H), 1.58 (s, 9H), 1.32-1.24 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 163.4 (d, *J* = 241.0 Hz), 152.1, 143.6, 125.4, 123.7, 108.2 (d, *J* = 23.5 Hz), 103.1 (d, *J* = 22.6 Hz), 83.9, 81.8, 69.4, 49.6, 47.0, 28.3, 25.3, 24.8, 21.8, 21.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1; HRMS (ESI) calcd for $C_{23}H_{33}BFNNaO_6$ ($[M+Na]^+$): 472.2283, found: 472.2285. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 8.11 (minor), 11.16 (major).



A Channel 2 254nm

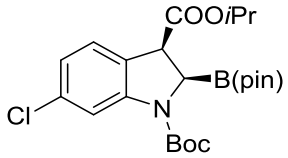
Peak ID	Ret. Time	Height	Area	Area%
1	8.109	46109	914435	50.412
2	11.123	39966	899488	49.588
Total				100.000



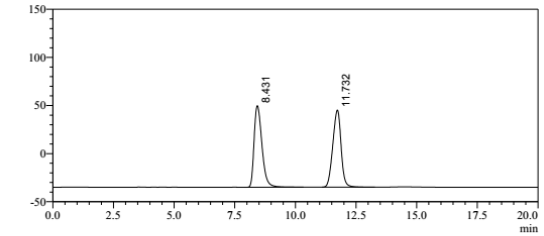
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	8.113	3106	63341	3.003
2	11.159	89892	2045712	96.997
Total				100.000

Compound 2r

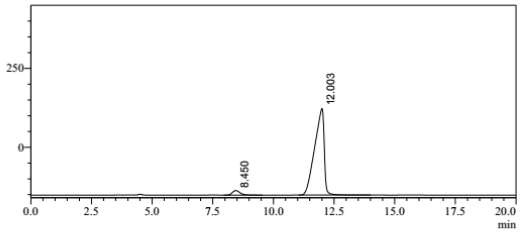


Colorless oil, 78.1 mg, 84% yield, 93:7 *d.r.*, 92% *ee*, $[\alpha]_D^{25}$ = -67.6 (*c* 0.21, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (brs, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.07-5.02(m, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 4.12 (d, *J* = 12.0 Hz, 1H), 1.58 (s, 9H), 1.32-1.25 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 151.9, 143.1, 134.3, 126.8, 125.4, 121.6, 115.4, 83.8, 81.6, 69.4, 49.2, 47.2, 28.2, 25.2, 24.9, 21.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.5; HRMS (ESI) calcd for $C_{23}H_{33}BClNNaO_6$ ($[M+Na]^+$): 488.1987, found: 488.1992. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 8.45 (minor), 12.00 (major).



A Channel 2 254nm

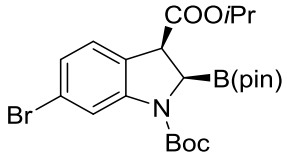
Peak ID	Ret. Time	Height	Area	Area%
1	8.431	84762	1917072	50.101
2	11.732	80202	1909363	49.899
Total				100.000



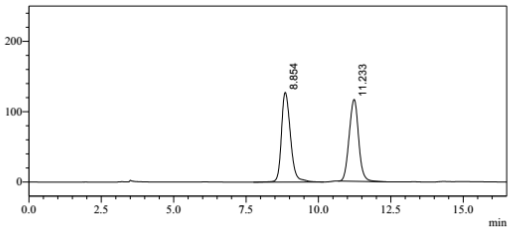
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	8.450	14384	319448	4.063
2	12.003	274260	7543034	95.937
Total				100.000

Compound 2s

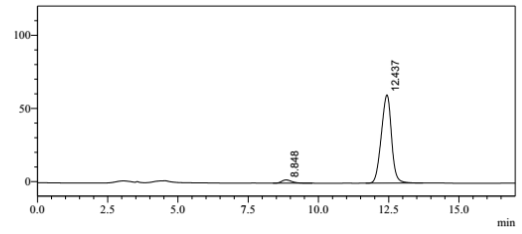


White solid, 74.3 mg, 73% yield, 94:6 *d.r.*, 93% *ee*, $[\alpha]_D^{25}$ = -49.5 (*c* 0.15, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 5.07-5.01(m, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 1.58 (s, 9H), 1.32-1.24 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 152.0, 127.4, 125.9, 124.6, 122.4, 118.4, 83.9, 82.0, 69.5, 49.2, 47.3, 28.3, 25.3, 25.0, 21.8 (one aromatic carbon signal does not show.); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8; HRMS (ESI) calcd for $C_{23}H_{33}B^{79}BrNNaO_6$ ($[M+Na]^+$): 532.1482, found: 532.1478. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 8.85 (minor), 12.44 (major).



???A 230nm

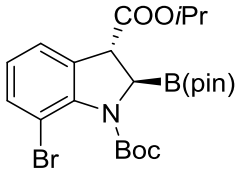
Peak ID	Ret. Time	Height	Area	Area%
1	8.854	127443	2771900	51.098
2	11.233	116293	2652743	48.902
Total				100.000



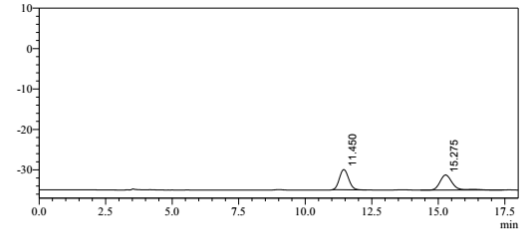
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	8.848	2236	56832	3.597
2	12.437	60315	1523194	96.403
Total				100.000

Compound 3t

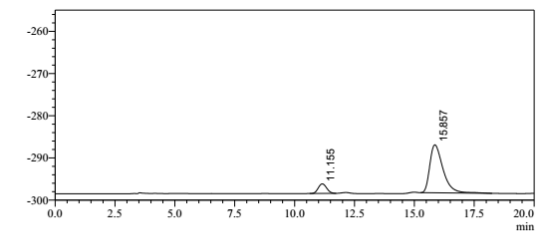


Colorless oil, 52.9 mg, 52% yield, 16:84 *d.r.*, 78% *ee*, $[\alpha]_D^{25}$ = -50.0 (*c* 0.16, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 6.92-6.88 (m, 1H), 5.07-5.00 (m, 1H), 4.09-4.04 (m, 2H), 1.56 (s, 9H), 1.26-1.24 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 155.4, 142.5, 136.5, 132.9, 125.7, 122.9, 112.5, 83.4, 82.9, 68.8, 54.3, 49.6, 28.3, 24.8, 24.7, 21.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.6 ppm; HRMS (ESI) calcd for $C_{23}H_{33}B^{81}BrNNaO_6$ ($[M+Na]^+$): 534.1462, found: 534.1467. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 11.16 (minor), 15.86 (major).



A Channel 2 254nm

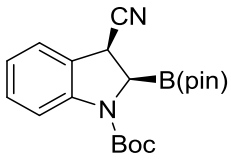
Peak ID	Ret. Time	Height	Area	Area%
1	11.450	5007	120558	50.270
2	15.275	3737	119262	49.730
Total				100.000



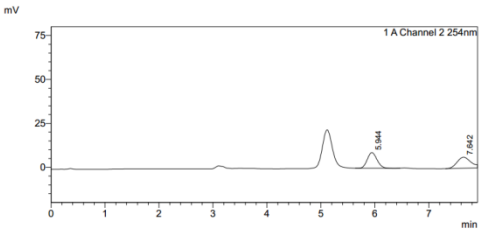
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	11.155	2262	55462	11.209
2	15.857	11371	439339	88.791
Total				100.000

Compound 2v

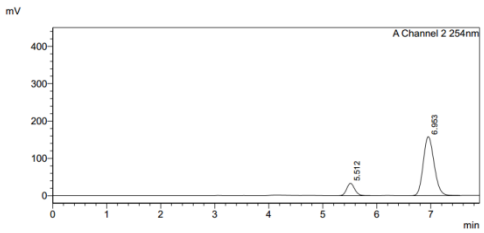


Colorless oil, 62.2 mg, 84% yield, 92:8 *d.r.*, 73% *ee*, $[\alpha]_D^{25}$ = -35.0 (*c* 0.37, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.46 (m, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.28-7.25 (m, 1H), 7.02-6.98 (m, 1H), 4.50 (br s, 1H), 4.05 (br s, 1H), 1.59 (s, 9H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 141.5, 129.8, 125.3, 122.7, 118.3, 115.0, 84.8, 82.6, 47.4, 30.8, 28.3, 25.4, 24.4; HRMS (ESI) calcd for $C_{20}H_{27}BN_2NaO_4$([M+Na]$^+$): 393.1956, found: 393.1963. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IC column, Hexane/*i*PrOH = 90:10, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 5.51 (minor), 6.95 (major).



A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	5.944	8872	109485	49.926
2	7.642	6240	109809	50.074
Total				100.000



A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	5.512	32945	341806	13.408
2	6.953	157893	2207447	86.592
Total				100.000

8. Method to determine diastereoselective ratio (d.r.) by NMR (reaction of 1c at room temperature as an example)

To determine the d.r. value (**2c**/**3c**), $H^{a\text{-}c}$ and $H^{a'\text{-}c'}$ were chosen as diagnostic signals. Apparently, H^a and $H^{a'}$ overlap at δ 5.07 ppm. In order to assign H^b, H^c, $H^{b'}$, and $H^{c'}$, a deuterium experiment was conducted. The reaction was carried out with MeOD instead of normal alcohol. Therefore by combination of ^1H NMR spectra from normal reaction we could elucidate the assignments of these diagnostic protons as shown in Figures S1 and S2. The disappearance of singal at δ 4.48 ppm upon use of MeOD indicates that H^c (or $H^{c'}$)is C3-proton in **2c** (or **3c**) (Figures S1 and S2, right spectra). Another information could be obtained is that H^b and $H^{b'}$ overlap at δ 4.10 ppm (Figure S1). Lastly, the integration differnce (0.12) of singal at δ 4.10 ppm minus that of signal at δ 4.48 ppm is twice as much as difference (0.06) between signals at δ 5.07

ppm and δ 4.48 ppm, which indicates that $H^{b'}$ and $H^{c'}$ overap at δ 4.10 ppm. Therefore the chemical of 4.48 ppm belongs to H^{c}. With that, d.r. value coud be obtained from singals at δ 5.07 ppm (H^{a} and $H^{a'}$) and δ 4.48 ppm (H^{c}). A total integration of H^{a} and $H^{a'}$ is denoted $I^{a+a'}$. The integration of H^{c} is denoted I^{c}. Therefore we could deduce the $I^{a'}$ by substraction I^{c} from $I^{a+a'}$. Thus the d.r. could be caculated as $100*I^{c}/I^{a+a'}$:$100*I^{a'}/I^{a+a'}$. The d.r values of the rest substrate scope could be calculated by analogue.

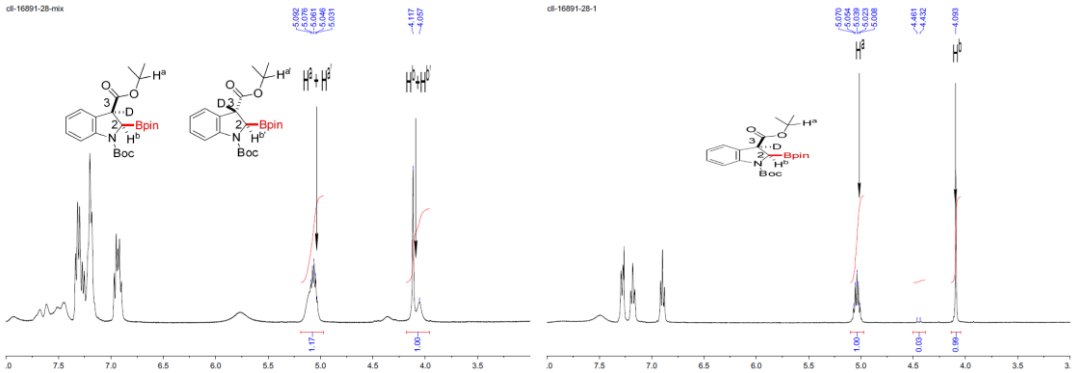


Figure S1. Partial ^{1}H NMR spectra of deterium experiment. Left: ^{1}H NMR of crude reaction mixture; right: pure C3-D *cis* product.

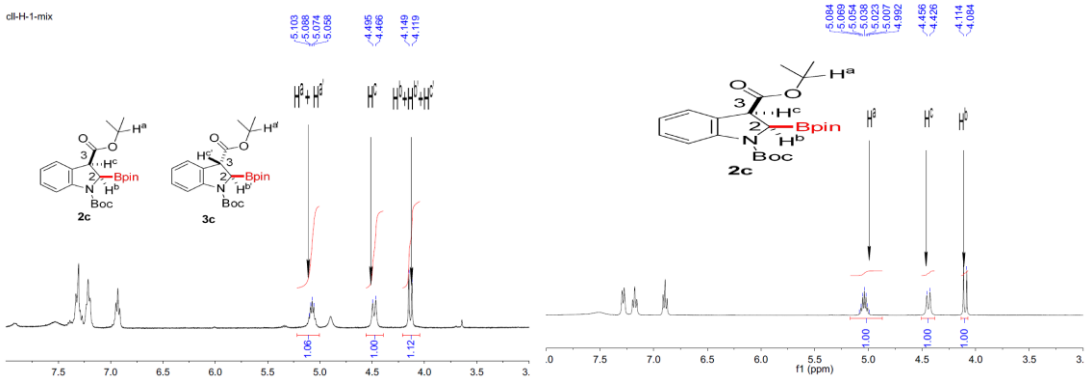
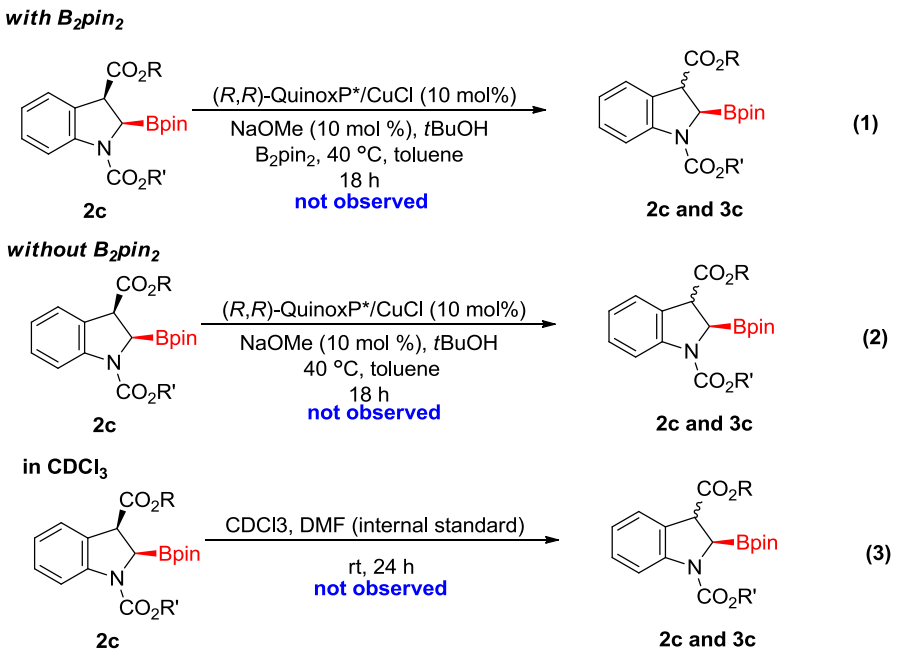


Figure S2. Partial ^{1}H NMR spectra of crude mixture and **2c**. Left: crude ^{1}H NMR of crude mixture; right: pure *cis* product **2c**.

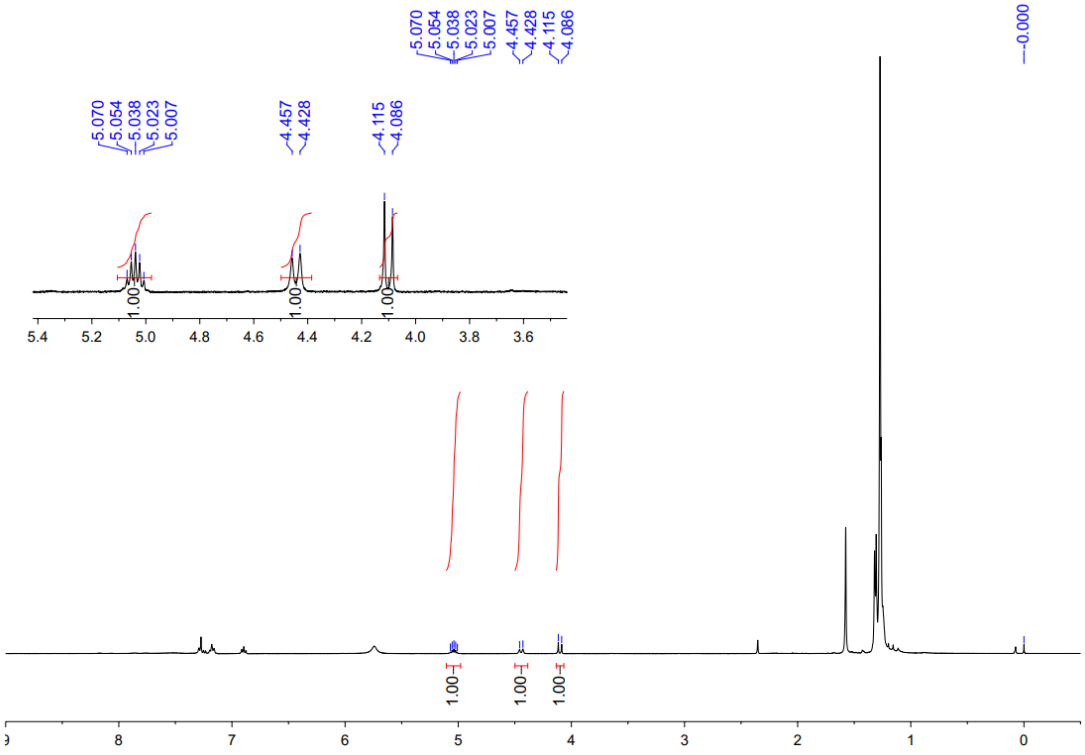
9. Control experiments for isomerization test and NMR spectrum

In order to know possibility of isomerization of product, three control experiments were conducted: 1) **2c** under reaction conditions at 40 ˚C for 18 h; 2) **2c** under reaction conditions without B_2pin_2 at 40 ˚C for 18 h; 3) **2c** in $CDCl_3$ for 24 hours. The results of these experiments show that no isomerization was observed under these

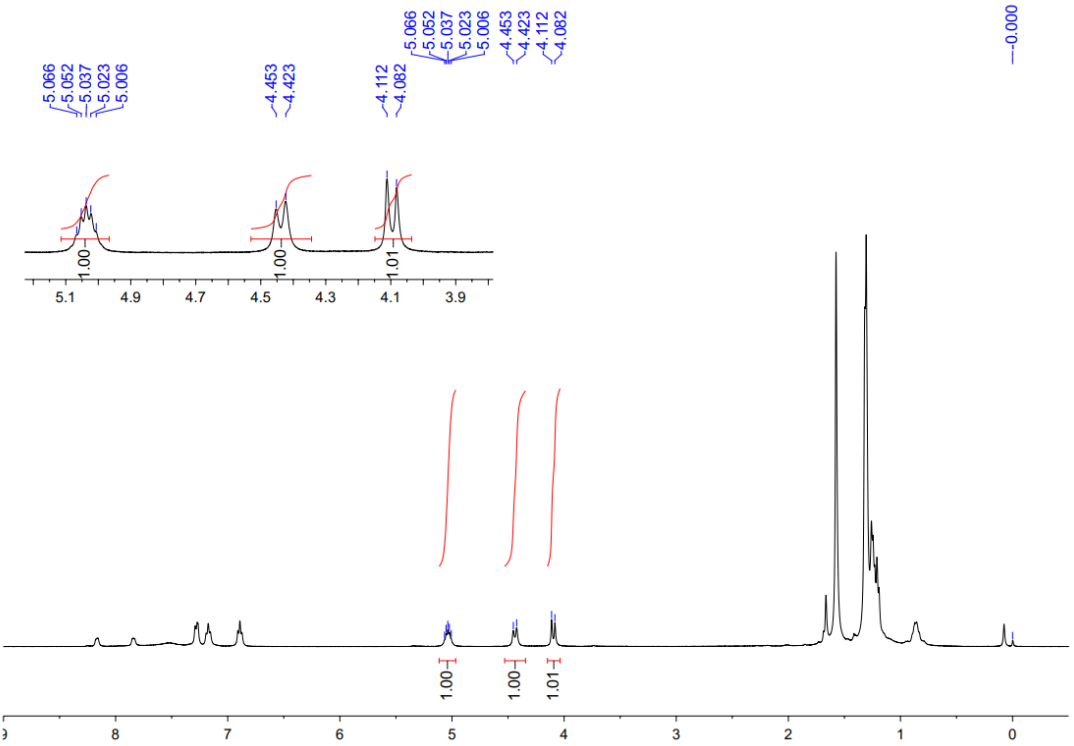
conditions, demonstrating relative stability of stereochemistry of **2c**. Additionally, the ee value of each control experiment was not changed.



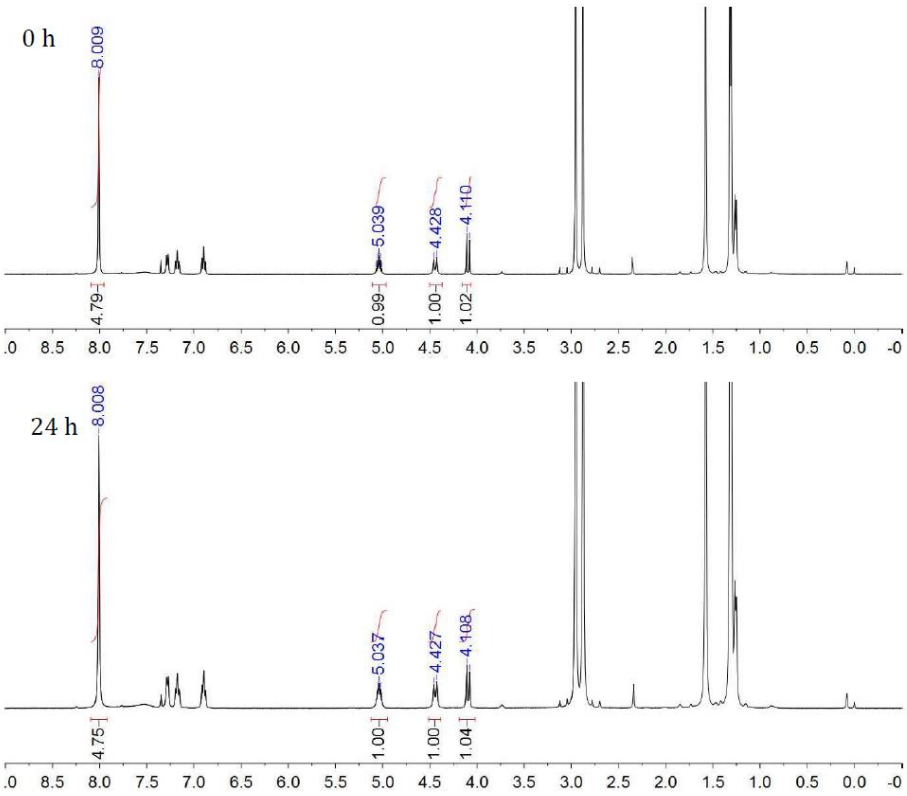
NMR of control experiment (1)



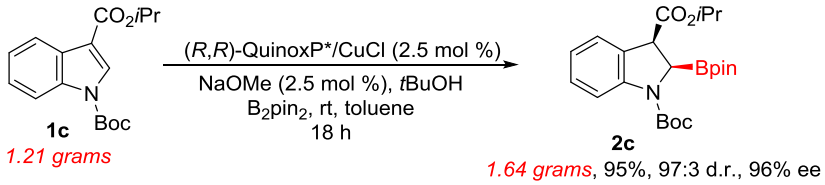
NMR of control experiment (2)



NMR of control experiment (3)

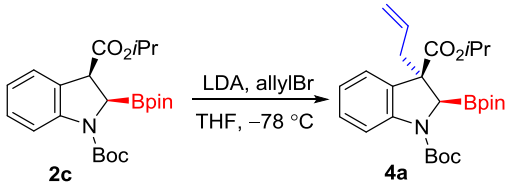


10. Gram-scale dearomative borylation of indole 2c



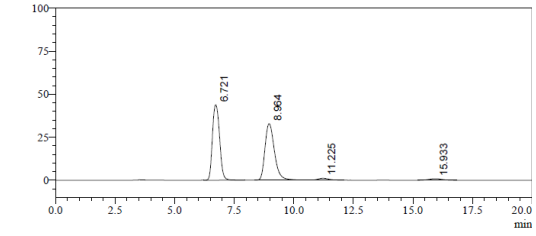
To a 100-mL flame-dried flask charged with CuCl (9.9 mg, 0.10 mmol), NaOMe (5.4 mg, 0.10 mmol) and (*R*,*R*)-QunioxP* (33.5 mg, 0.10 mmol) was added toluene (10 mL). The resulting mixture was allowed to stir at room temperature for 0.5 h. B_2pin_2 (1.53 g, 6.0 mmol in 10 mL) was then introduced and the reaction was allowed to stir at same temperature for 10 min followed by addition of indole **1c** (1.21 g, 4.0 mmol in 20 mL toluene) and *t*BuOH (0.77 mL, 8.0 mmol) at same temperature. The resulting mixture was continued to stir at room temperature for 12 h. After removal of the solvent, the ^{1}H NMR of crude mixture was taken to determine the d.r. value (97:3). The residue was purified by column chromatography on silica gel using PE/EtOAc (12:1) as the eluent to affording corresponding 2-boryl indoline **2c** as colorless oil (1.64 g, 95% yield, 97:3 d.r., 96% ee).

11. C3 functionalzation of 2-borylindoline 4



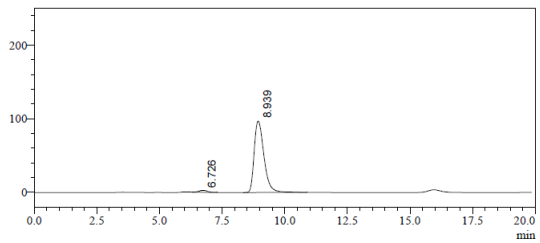
To a 50-mL flame-dried flask charged with 2-borylindoline **2c** (1.64 g, 3.80 mmol) and THF (30 mL) was added LDA (2.85 mL, 2M in hep/ethylbenzene, 5.7 mmol, 1.5 equiv) at -78 ℃ dropwisely. The resulting mixture was allowed at same temperature for 30 min. The allyl bromide (0.49 mL, 5.7 mmol, 1.5 equiv) was then added slowly at -78 ℃. The reaction mixuture was then allowed to warm to room temerature and continued to stir at same temperature for 3 h. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (20: 1) as the eluent to afford C3 allylated 2-borylindoline **4a** as colorless oil (1.75 g, 98%). The relative configuration was determined by 2D NMR NOSEY spectrum.

96:4 *d.r.*, 95% *ee*, $[\alpha]_D^{25}$ = -50.0 (*c* 0.16, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.47 (m, 1H), 7.35-7.33 (m, 1H), 7.18 (s, 1H), 6.91 (s, 1H), 5.60 (s, 1H), 5.13-5.05 (m, 3H), 3.87 (s, 1H), 2.60-2.66 (m, 2H), 1.57 (s, 9H), 1.27 (brs, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 152.3, 142.1, 132.6, 132.0, 128.6, 124.4, 121.7, 119.2, 114.9, 83.4, 81.1, 69.5, 54.1, 45.1, 28.4, 28.0, 25.3, 24.9, 21.7, 21.6; HRMS (ESI) calcd for $C_{26}H_{38}BNNaO_6$ ($[M+Na]^+$): 494.2690, found: 494.2689. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 6.73 (minor), 8.94 (major)



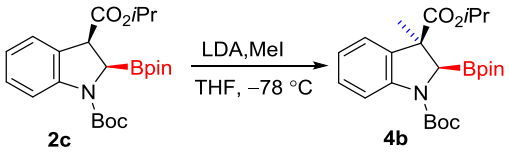
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	6.721	43844	914598	48.310
2	8.964	32843	908995	48.015
3	11.225	1170	37569	1.984
4	15.933	864	32004	1.691
Total				100.000



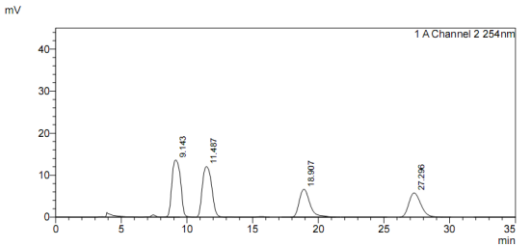
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	6.726	2751	61834	2.301
2	8.939	97067	2625960	97.699
Total				100.000



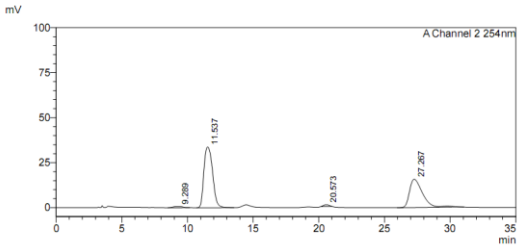
2c **4b**

To a 25-mL flame-dried flask charged with 2-borylindoline **2c** (86.2 mg, 0.20 mmol) and THF (1 mL) was added LDA (150 μL, 2M in hep/ethylbenzene, 0.3 mmol, 1.5 equiv) at -78 ℃ dropwisely. The resulting mixture was allowed at same temperature for 10 min. The iodomethane (24.4 μL, 0.4 mmol, 2.0 equiv) was then added slowly at -78 ℃. The reaction mixuture was then allowed to warm to room temerature and continued to stir at same temperature for 10 min. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (15: 1) as the eluent to afford C3 methylated 2-borylindoline **8** as colorless oil (59.6 mg, 67%).d.r. = 2:1, 96% *ee*, $[\alpha]_D^{25}$ = -18.0 (*c* 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.28-7.27 (m, 1H), 7.20-7.16 (m, 1H), 6.93-6.90 (m, 1H), 5.00-4.97 (m, 1H), 4.38 (s, 0.3H), 3.68 (s, 0.6H), 1.58 (s, 9H), 1.29-1.20 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ174.0, 173.5, 152.6, 129.0, 128.5, 124.6, 123.7, 122.7, 121.9, 121.8, 115.3, 114.9, 83.5, 81.1, 69.3, 68.8, 57.7, 28.4, 28.0, 27.2, 25.3, 24.9, 21.7, 21.5; HRMS (ESI) calcd for $C_{24}H_{36}BNNaO_6$ ($[M+Na]^+$): 468.2528, found: 468.2542. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 99:1, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 9.29 (minor), 11.54 (major)



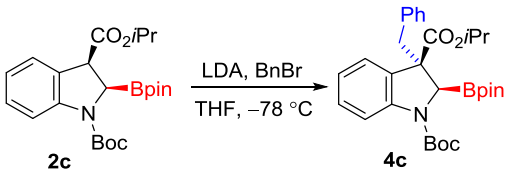
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	9.143	13600	620927	31.529
2	11.487	12051	599850	30.459
3	18.907	6656	377384	19.163
4	27.296	5803	371196	18.849
Total				100.000



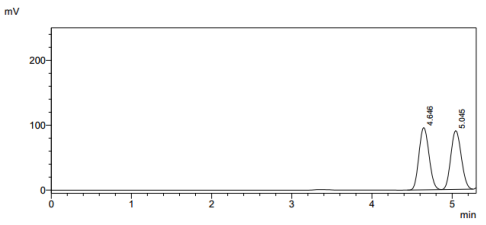
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	9.289	620	30547	1.132
2	11.537	33727	1552561	57.516
3	20.573	955	28520	1.057
4	27.267	15725	1087721	40.296
Total				100.000



2c **4c**

To a 25-mL flame-dried flask charged with 2-borylindoline **2c** (86.2 mg, 0.20 mmol) and THF (1 mL) was added LDA (150 μL, 2M in hep/ethylbenzene, 0.3 mmol, 1.5 equiv) at -78 ℃ dropwisely. The resulting mixture was allowed at same temperature for 10 min. The benzyl bromide (35.6 μL, 0.3 mmol, 1.5 equiv) was then added slowly at -78 ℃. The reaction mixuture was then allowed to warm to room temerature and continued to stir at same temperature for 10 min. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (15: 1) as the eluent to afford C3 benzylated 2-borylindoline **4c** as colorless oil (67.8 mg, 65%). 95% *ee*, $[\alpha]_D^{25}$ = -23.0 (*c* 0.57, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68-7.34 (m, 2H), 7.19-7.09 (m, 4H), 6.94-6.74 (m, 3H), 5.09 (s, 1H), 3.97 (s, 1H), 3.27 (d, J = 6.8 Hz, 1H), 3.10-3.02 (m, 1H), 1.46 (s, 9H), 1.31-1.23 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 151.7, 142.9, 135.7, 131.8, 129.9, 128.7, 127.7, 126.6, 124.9, 121.4, 115.1, 83.3, 80.9, 69.7, 58.9, 53.6, 46.3, 28.3, 25.2, 24.7, 21.7; HRMS (ESI) calcd for $C_{30}H_{41}BNO_6$ ($[M+H]^+$): 522.3021, found: 522.3030. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 99:1, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 4.67 (minor), 5.08 (major)



A Channel 2 254nm

Peak #	Ret. Time	Height	Area	Area%
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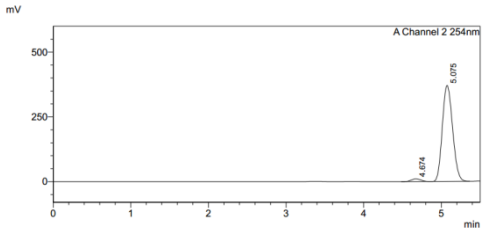
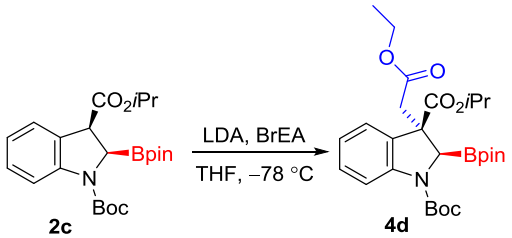
2	5.045	90261	817349	49.422
Total				100.000

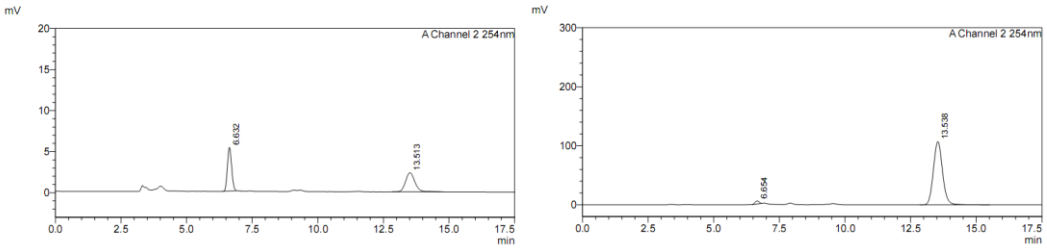


Peak #	Ret. Time	Height	Area	Area%
1	4.674	10683	92113	2.625
2	5.075	371127	3416866	97.375
Total				100.000



To a 25-mL flame-dried flask charged with 2-borylindoline **2c** (86.2 mg, 0.20 mmol) and THF (1 mL) was added LDA (150 μL, 2M in hep/ethylbenzene, 0.3 mmol, 1.5 equiv) at -78 ℃ dropwisely. The resulting mixture was allowed at same temperature for 10 min. The Ethyl bromoacetate (35.6 μL, 0.3 mmol, 1.5 equiv) was then added slowly at -78 ℃. The reaction mixuture was then allowed to warm to room temerature and continued to stir at same temperature for 10 min. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (12: 1) as the eluent to afford C3-alkylate 2-borylindoline **4d** as colorless oil (64.2mg, 62%). 96% *ee*, $[\alpha]_D^{25}$ = -32.0 (*c* 0.32, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89-7.48 (m, 1H), 7.27-7.18 (m, 2H), 6.91-6.89 (m, 1H), 5.08-5.05 (m, 1H), 4.13 (q, J = 6.6 Hz, 2H), 3.97 (s, 1H), 3.06(brs, 1H), 2.83 (d, *J* = 12.8 Hz, 1H), 1.58 (s, 9H), 1.27-1.22 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.9, 152.2, 141.3, 131.8, 129.1, 123.9, 121.8, 115.0, 83.4, 81.4, 69.7, 60.9, 56.2, 54.7, 45.2, 28.4, 25.4,

24.8, 21.7, 21.5, 14.0; HRMS (ESI) calcd for $C_{27}H_{41}BNO_8$ ($[M+H]^+$): 518.2920, found: 518.2927. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak ODH column, Hexane/*i*PrOH = 90:10, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 6.65 (minor), 13.54 (major).



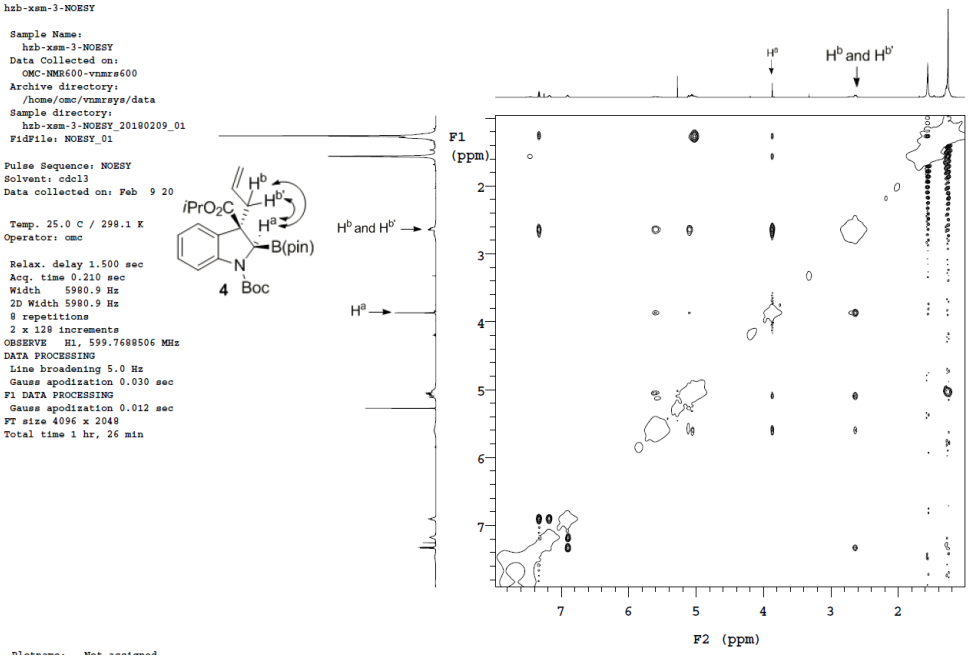
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	6.632	5313	59878	50.540
2	13.513	2330	58599	49.460
Total				100.000

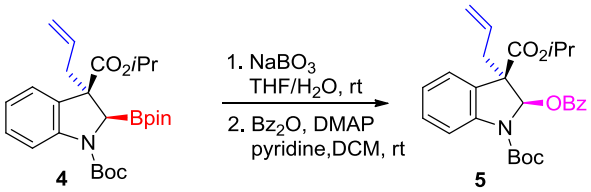
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	6.654	5111	56304	2.122
2	13.538	107000	2597254	97.878
Total				100.000

12. NOSEY spectrum of allylated 2-borylindoline 4



13. Oxidation of 2-borylindoline 4

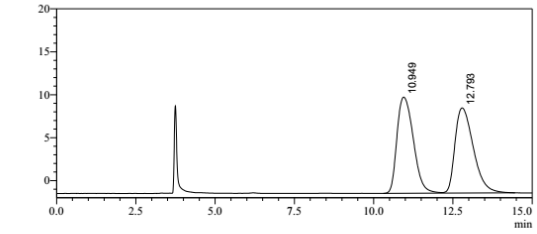


The oxidation of 2-borylindoline was adapted from literature procedures.[7] To a 25-mL flask charged with 4 (95 mg, 0.20 mmol), THF (2 mL) and H_2O (2 mL) was added $NaBO_3$ $4H_2O$ (123.2 mg, 0.80 mmol, 4.0 equiv) at room temperature. The

7. F. Meng, K. P. McGrath and A. H. Hoveyda *Nature* 2014, **513**, 367.

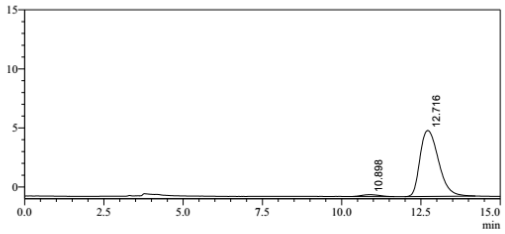
resulting mixture was allowed to stir at same temperature for 2 h. The reaction was then quenched with saturated $Na_2S_2O_3$ (5 mL) and diluted with water (20 mL). The biphasic solution was extracted with DCM 3 times (3 X 10 mL). The combined organic phase was then concentrated. The residue was dissolved in anhydrous DCM (5 mL) and cooled to 0 ℃. Bz_2O (68.0 mg, 0.30 mmol) and DMAP (2.7 mg, 0.02 mmol) were then introduced followed by slow addition of pyridine (24 μL, 0.30 mmol). The resulting mixture was then continued to stir at room temperature for 2 hours. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (10:1) as the eluent to afford corresponding indoline **5** as colorless oil (55.8 mg, 60% yield).

95% *ee*, $[\alpha]_D^{25}$ = +82.7 (*c* 0.38, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.93 (m, 2H), 7.53-7.49 (m, 2H), 7.37-7.26 (m, 3H), 7.16-7.10 (m, 2H), 5.62-5.55 (m, 1H), 5.12 -5.05 (m, 2H), 4.88-4.85 (m, 1H), 2.97-2.92 (m, 1H), 2.55-2.50 (m, 1H), 1.45 (s, 9H), 1.17 (d, *J* = 6.0 Hz, 3H), 0.92 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 164.2, 151.1, 141.2, 134.5, 133.3, 131.2, 130.6, 129.8, 129.6, 128.9, 128.7, 128.4, 126.8, 122.8, 119.9, 114.7, 87.0, 82.5, 69.2, 59.7, 42.4, 28.2, 21.7, 21.3; HRMS (ESI) calcd for $C_{20}H_{26}NO_4$ ($[M\text{-}OBz]^+$): 344.1862, found: 344.1849. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 99:1, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 10.90(minor), 12.72 (major)



A Channel 2 254nm

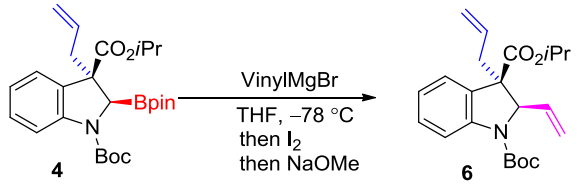
Peak ID	Ret. Time	Height	Area	Area%
1	10.949	11191	402907	50.247
2	12.793	9912	398950	49.753
Total				100.000



A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	10.898	158	5971	2.566
2	12.716	5578	226683	97.434
Total				100.000

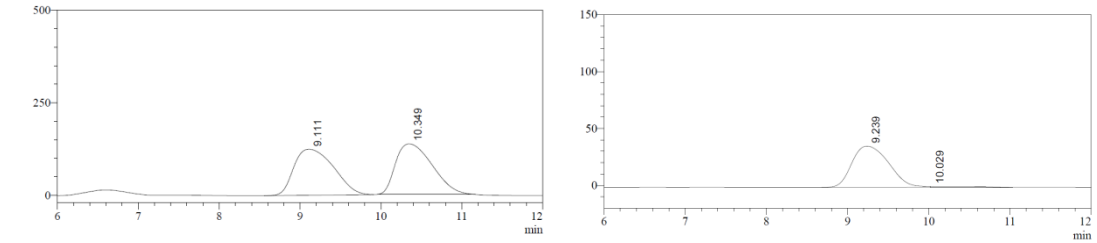
14. Stereospecific vinylation of 2-borylindoline 4.



This reaction was adapted from the literature procedures.[8] To a 25-mL flame-dried Schlenk tube charged with **4** (110 mg, 0.23 mmol) and THF (2 mL) was added vinylMgBr (0.35 mL, 1 M in THF, 0. 35 mmol, 1.5 equiv) at room temperature. The resulting mixture was allowed to stir at same temperature for 0.5 h. Methanolic

8. R. P. Sonawane, V. Jheengut, C. Rabalakos, R. Larouche-Gauthier, H. K. Scott and V. K. Aggarwal, *Angew. Chem., Int. Ed.* **2011**, 50, 3760.

solution of I_2 (292 mg, 1.15 mmol, 3 mL MeOH) was then introduced slowly to the reaction mixture at -78 ℃. The reaction was then allowed to stir at this temperature for additional 0.5 h. Methanolic solution of NaOMe (62.1 mg, 1.15 mmol, 3 mL MeOH) was then added slowly at -78 ℃. The resulting mixture was then warmed to room temperature and continued to stir at this temperature for 1 h. Saturated aqueous $Na_2S_2O_3$ (5 mL) was then added quench the reaction. After dilution with H_2O (20 mL), the mixture was extracted with EtOAc 3 times (3 X 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (20:1) as the eluent to afford corresponding 2-vinylindoline 6 as colorless oil (83.5 mg, 98% yield). 95% *ee*, $[\alpha]_D^{25}$ = +99.4 (*c* 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) 7.84 (brs, 1H), 7.30-7.24 (m, 2H), 7.01-6.98 (m, 1H), 5.73-5.64 (m, 1H), 5.57-5.48 (m, 1H), 5.25-5.21 (m, 1H), 5.14-5.11 (m, 1H), 5.05-5.03 (m, 2H), 4.59 (brs, 1H), 2.82-2.79 (m, 1H), 2.53-2.48 (m, 1H), 1.53 (s, 9H), 1.26-1.22 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 151.8, 141.0 133.0, 132.2, 128.4, 126.8, 122.2, 119.3, 118.2, 115.0, 82.3, 70.5, 68.6, 59.1, 43.9, 28.3, 21.8, 21.7 (one sp^2 carbon signal does not show.) HRMS (ESI) calcd for $C_{22}H_{33}N_2O_4$ ($[M+NH_4]^+$): 389.2435, found: 389.2429. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 99:1, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 9.23 (major), 10.03 (minor)



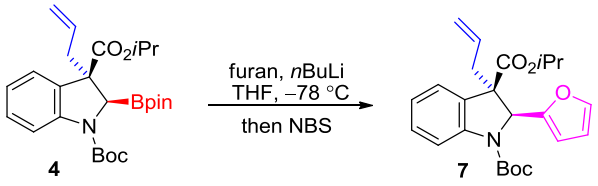
A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	9.111	124775	4254435	49.585
2	10.349	136902	4325599	50.415
Total				100.000

A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	9.239	36276	1141264	97.614
2	10.029	739	27896	2.386
Total				100.000

15. Stereospecific arylation of 2-borylindoline 4.

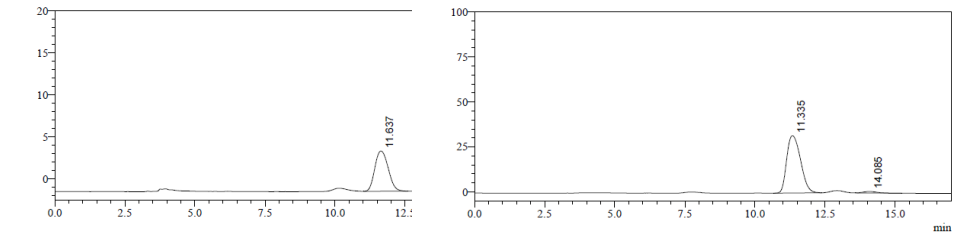


This reaction was adapted by the literature procedures.[9] To a 25-mL Schlenk tube charged with 4 (94 mg, 0.20 mmol) and THF (2 mL) was added freshly prepared fur-2-yl lithium (0.20 mL, 1.0 M in THF/hexanes, 0.20 mmol) slowly at -78 ℃. The resulting mixture was then allowed to stir at this temperature for 1.5 h. NBS (36 mg, 0.20 mmol) in THF (2 mL) was then added slowly to the reaction mixture at -78 ℃. The reaction was continued to stir at -78 ℃ for 0.5 h. Saturated aqueous $Na_2S_2O_3$ (2.5

9. A. Bonet, M. Odachowski, D. Leonori, S. Essafi and V. K. Aggarwal, *Nat. Chem.* 2014, **6**, 584.

mL) was then introduced to quench the reaction at room temperature. The organic phase was separated and the rest was extracted with EtOAc 3 times (3 X 10 mL). The combined organic phase was then dired over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (20:1) as the eluent to afford corresponding 2-(2-furyl)-indoline **7** as colorless oil (32.9 mg, 40% yield).

Colorless oil, 32.9 mg, 40% yield, 95% *ee*, $[\alpha]_D^{25}$ = +72.8 (*c* 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (brs, 1H), 7.41-7.45 (m, 1H), 7.23-7.21 (m, 1H), 7.06-7.03 (m, 1H), 6.21 (s, 1H), 6.03 (brs, 1H), 5.62-5.52(m, 1H), 5.25 (s, 1H), 5.09-5.02(m, 2H), 4.83-4.78 (m, 1H), 2.86-2.81 (m, 1H), 2.64-2.58 (m, 1H), 1.41 (s, 9H), 1.09 (d, *J* = 6.0 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 152.8, 151.6, 141.1, 132.0, 128.5, 126.8, 122.3, 119.5, 114.7, 110.3, 106.9, 81.1, 68.5, 65.1, 45.1, 29.3, 28.2, 21.6, 21.3; HRMS (ESI) calcd for $C_{24}H_{33}N_2O_5$ ($[M+NH_4]^+$): 429.2384, found: 429.2380. The enantiopurity was determined by HPLC analysis (Daicel Chiralpak IE column, Hexane/*i*PrOH = 99:1, flow rate = 1.0 mL/min., wavelength = 254 nm, t_R = 11.34 (major), 14.09 (minor).



A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	11.637	4792	158914	49.953
2	14.551	4450	159211	50.047
Total				100.000

A Channel 2 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	11.335	31882	1093605	97.568
2	14.085	841	27257	2.432
Total				100.000

16. Crystallographic data of compound 2s

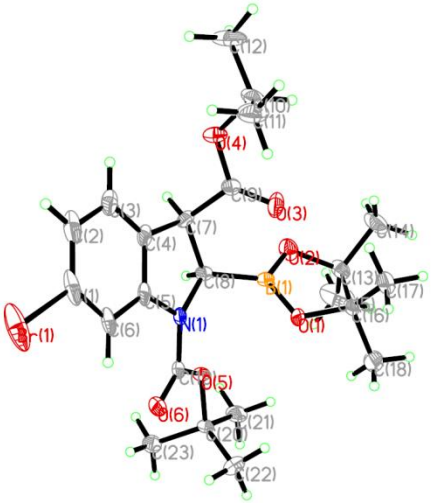


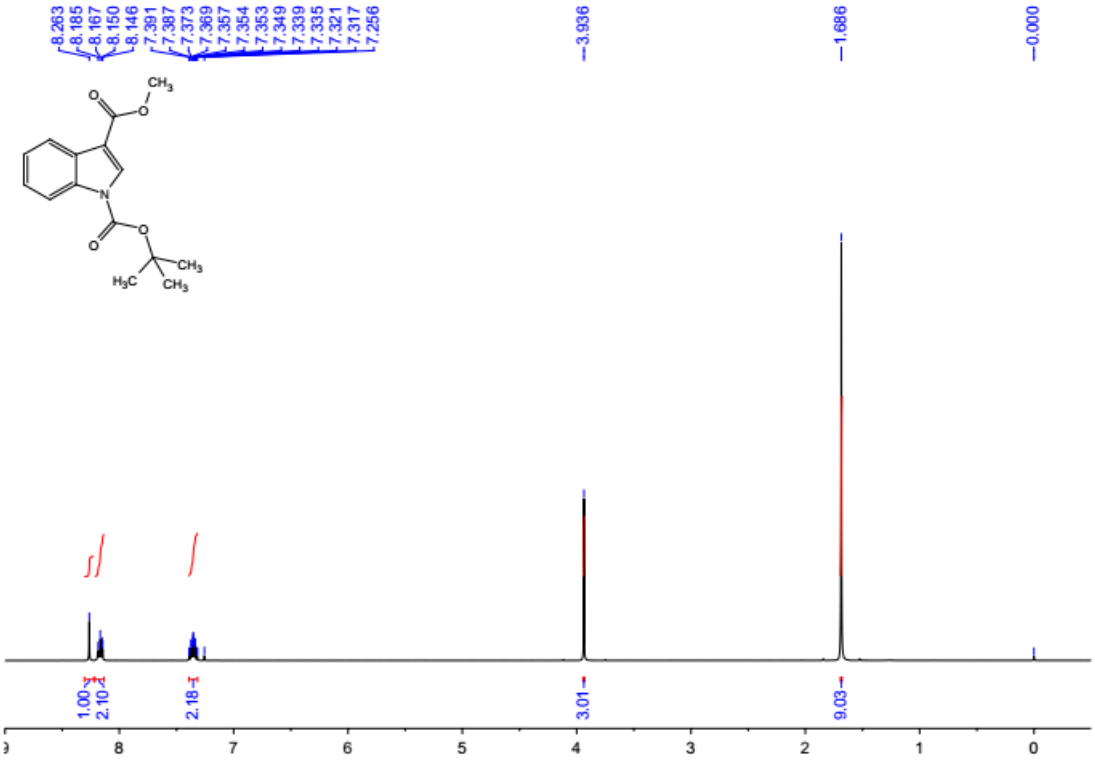
Table S2. Crystal data and structure refinement for **2s**.

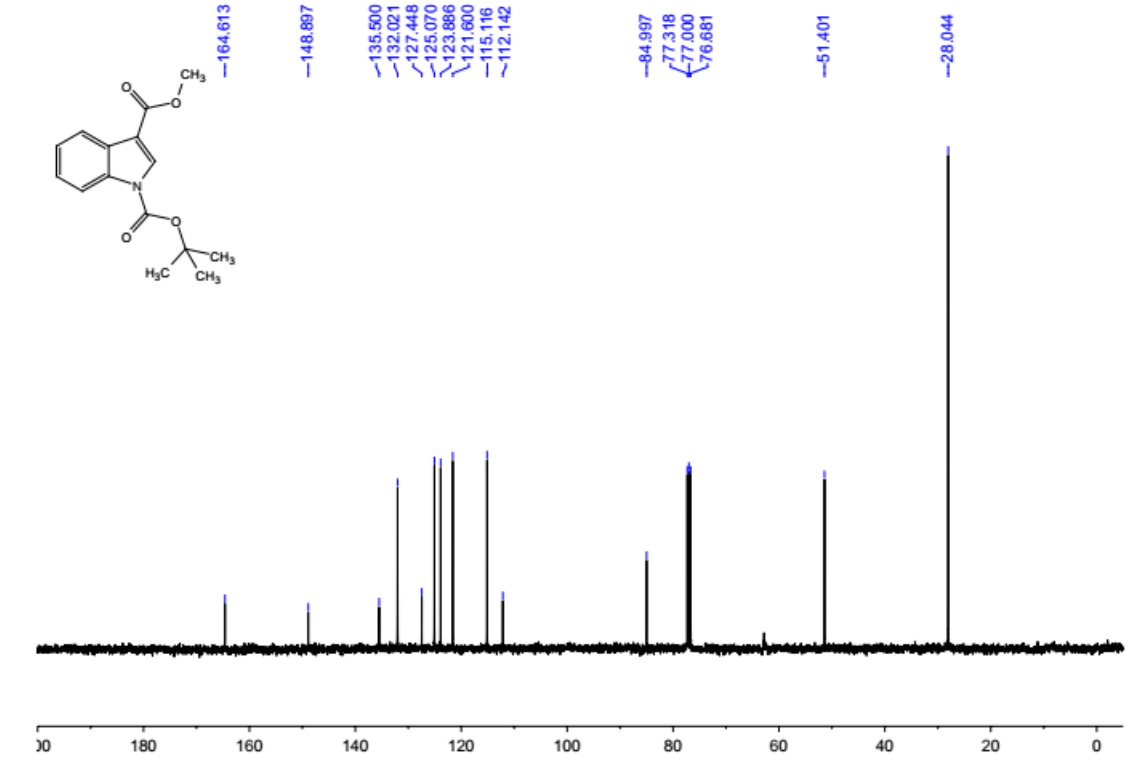
Identification code	1
Empirical formula	C23 H33 B Br N O6

Formula weight	510.22	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.0308(12) Å	α= 90˚
	b = 12.6903(16) Å	β= 90˚
	c = 19.943(2) Å	γ = 90˚
Volume	2538.6(5) $Å^3$	
Z	4	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	1.655 mm^{-1}	
F(000)	1064	
Crystal size	0.30 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.90 to 25.00 °.	
Index ranges	-11<=h<=11, -15<=k<=11, -23<=l<=22	
Reflections collected	12877	
Independent reflections	4452 [R(int) = 0.0382]	
Completeness to theta = 25.00˚	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7331 and 0.6365	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4452 / 0 / 298	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.1040	
R indices (all data)	R1 = 0.0506, wR2 = 0.1091	
Absolute structure parameter	0.029(10)	
Largest diff. peak and hole	0.584 and -0.841 $e.Å^{-3}$	

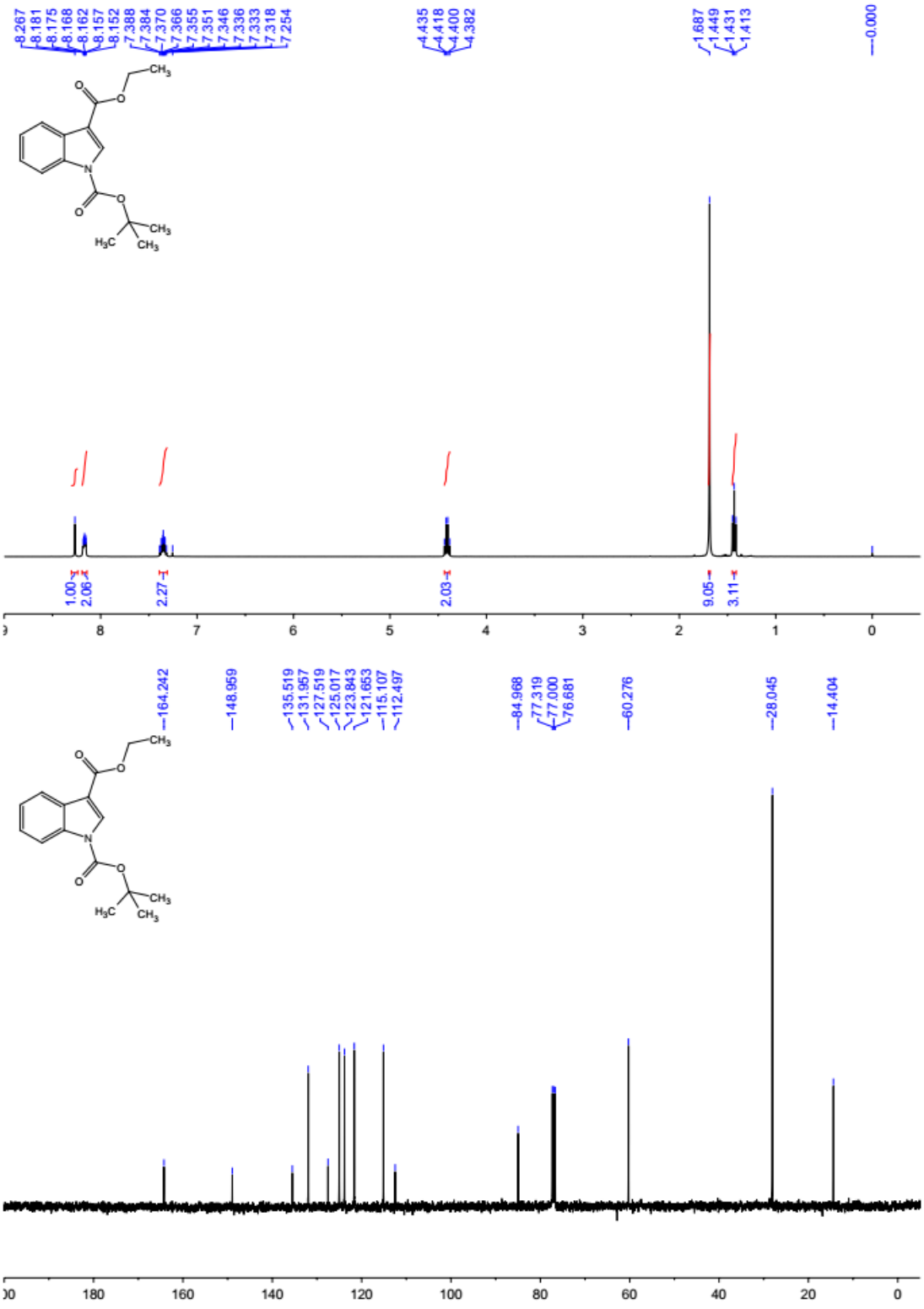
17. NMR spectra of all new compounds

Compound 1a

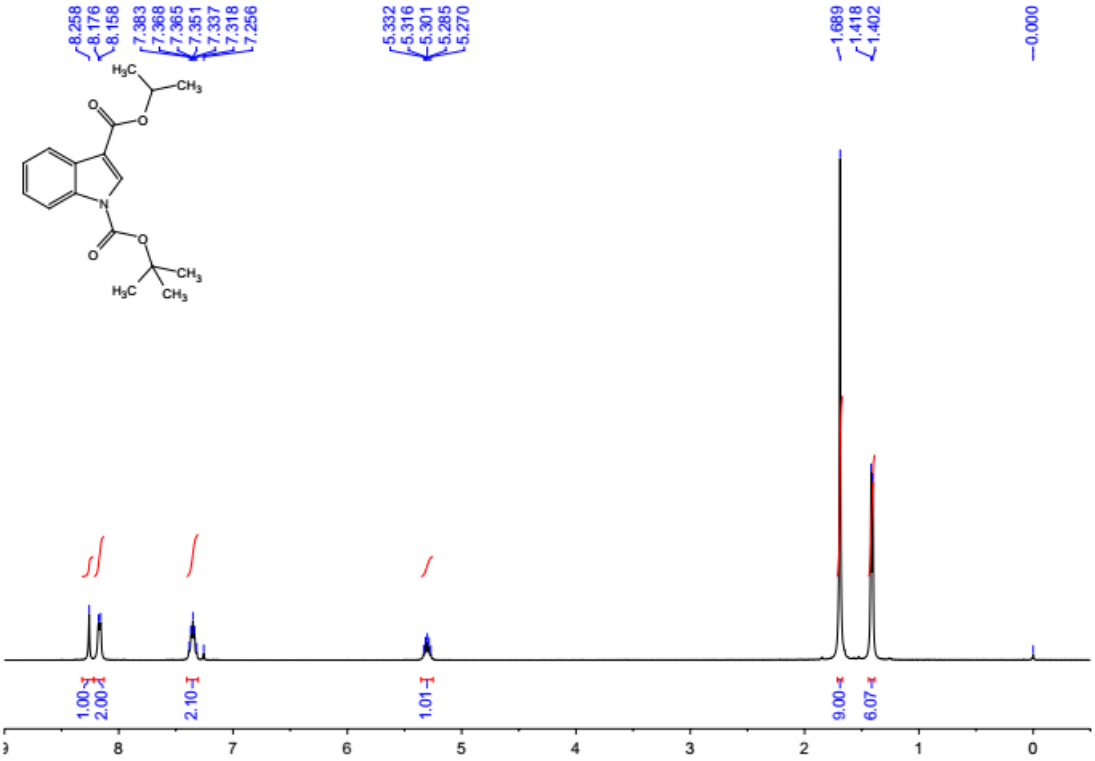


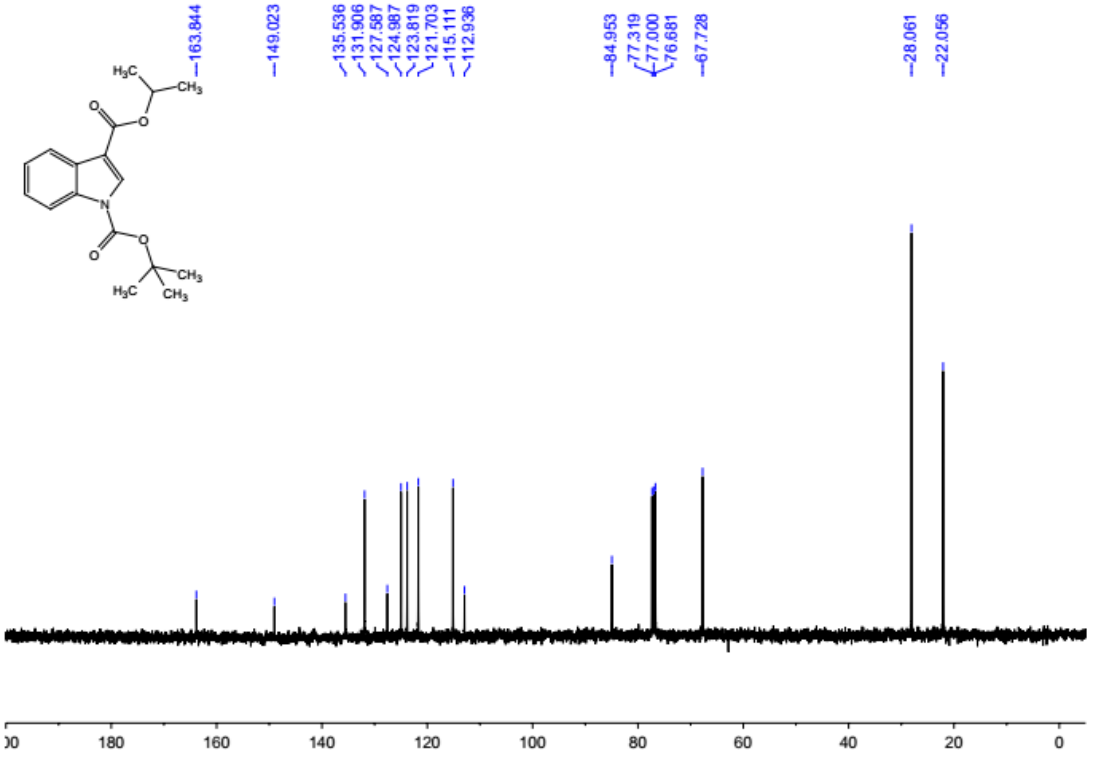


Compound 1b

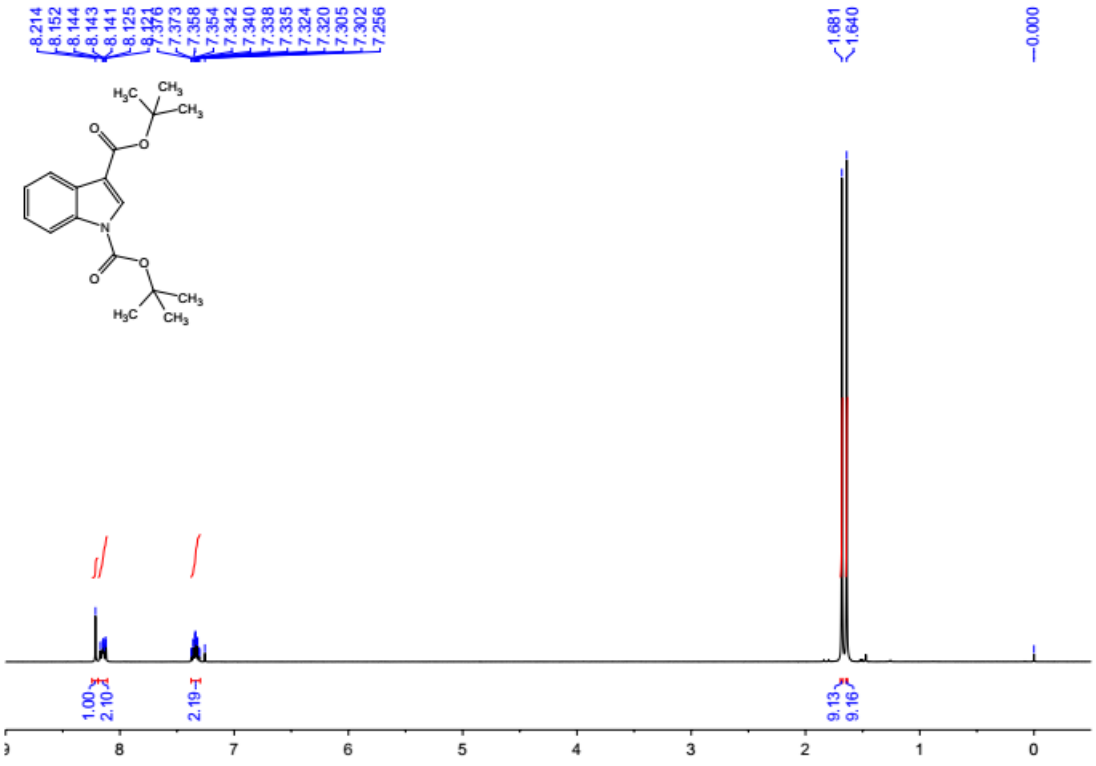

8.267
8.181
8.175
8.168
8.162
8.157
8.152
7.388
7.384
7.370
7.366
7.355
7.351
7.346
7.336
7.333
7.318
7.254
4.435
4.418
4.400
4.382
1.687
1.449
1.431
1.413
0.000
1.00
2.06
2.27
2.03
9.05
3.11
164.242
148.959
135.519
131.957
127.519
125.017
123.843
121.653
115.107
112.497
84.968
77.319
77.000
76.681
60.276
28.045
14.404

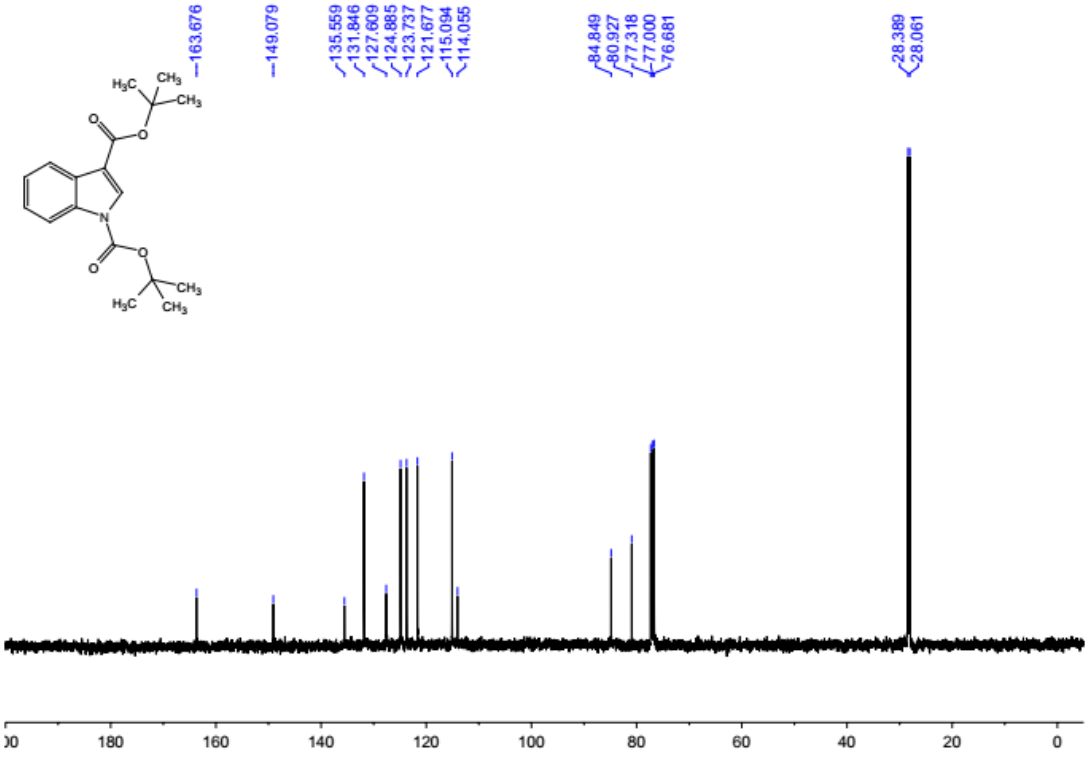
Compound 1c


8.258
8.176
8.158
7.383
7.368
7.365
7.351
7.337
7.318
7.256
5.332
5.316
5.301
5.285
5.270
1.689
1.418
1.402
0.000
1.00
2.00
2.10
1.01
9.00
6.07


163.844
149.023
135.536
131.906
127.587
124.987
123.819
121.703
115.111
112.936
84.953
77.319
77.000
76.681
67.728
28.061
22.056

Compound 1d


8.214
8.152
8.144
8.143
8.141
8.125
7.376
7.373
7.358
7.354
7.342
7.340
7.338
7.335
7.324
7.320
7.305
7.302
7.256
1.681
1.640
0.000
1.00
2.10
2.19
9.13
9.16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124.885
123.737
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114.055
84.849
80.927
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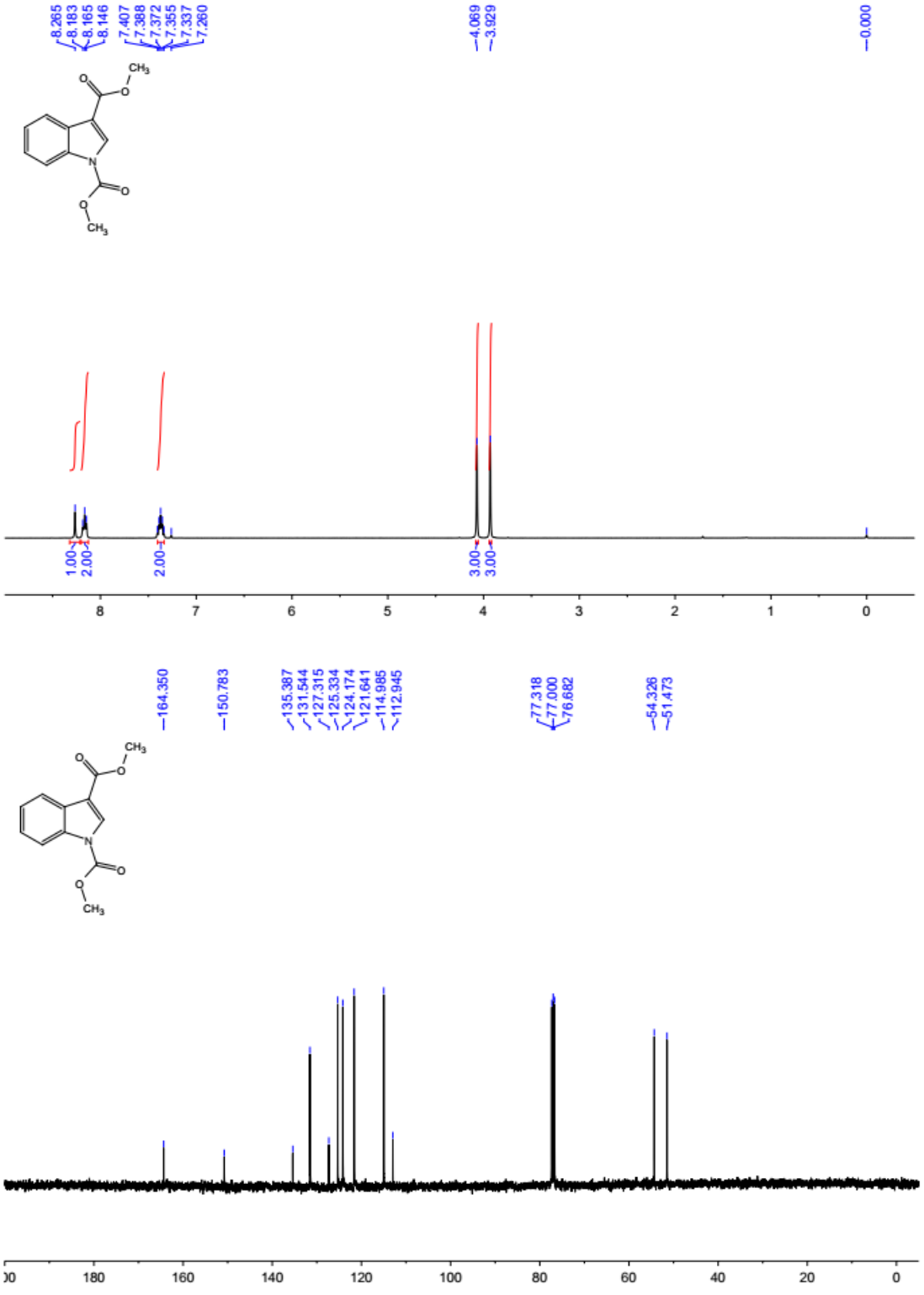
77.000
76.681
28.389
28.061

Compound 1e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8.165
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7.388
7.372
7.355
7.337
7.260
4.069
3.929
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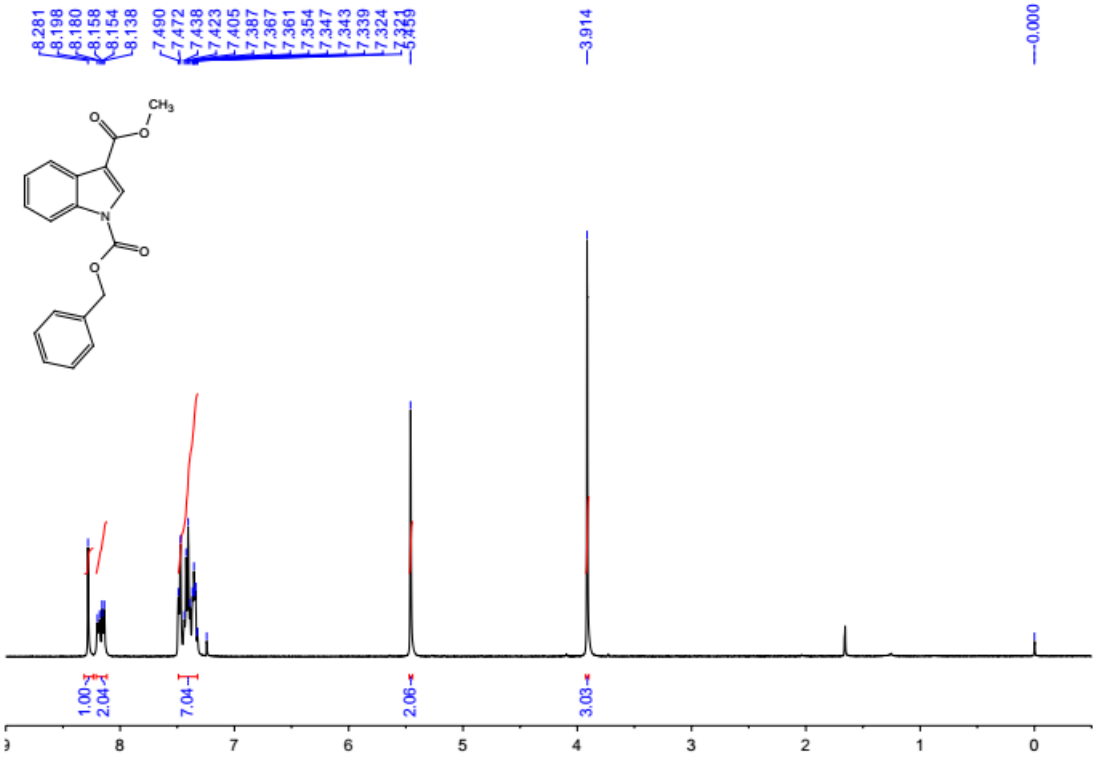
1.00
2.00
2.00
3.00
3.00
164.350
150.783
135.387
131.544
127.315
125.334
124.174
121.641
114.985
112.945
77.318
77.000
76.682
54.326
51.473

Compound 1f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8.154
8.138
7.490
7.472
7.438
7.423
7.405
7.387
7.367
7.361
7.354
7.347
7.343
7.339
7.324
7.321
5.459
3.914
0.000
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2.04
7.04
2.06
3.03
8
7
6
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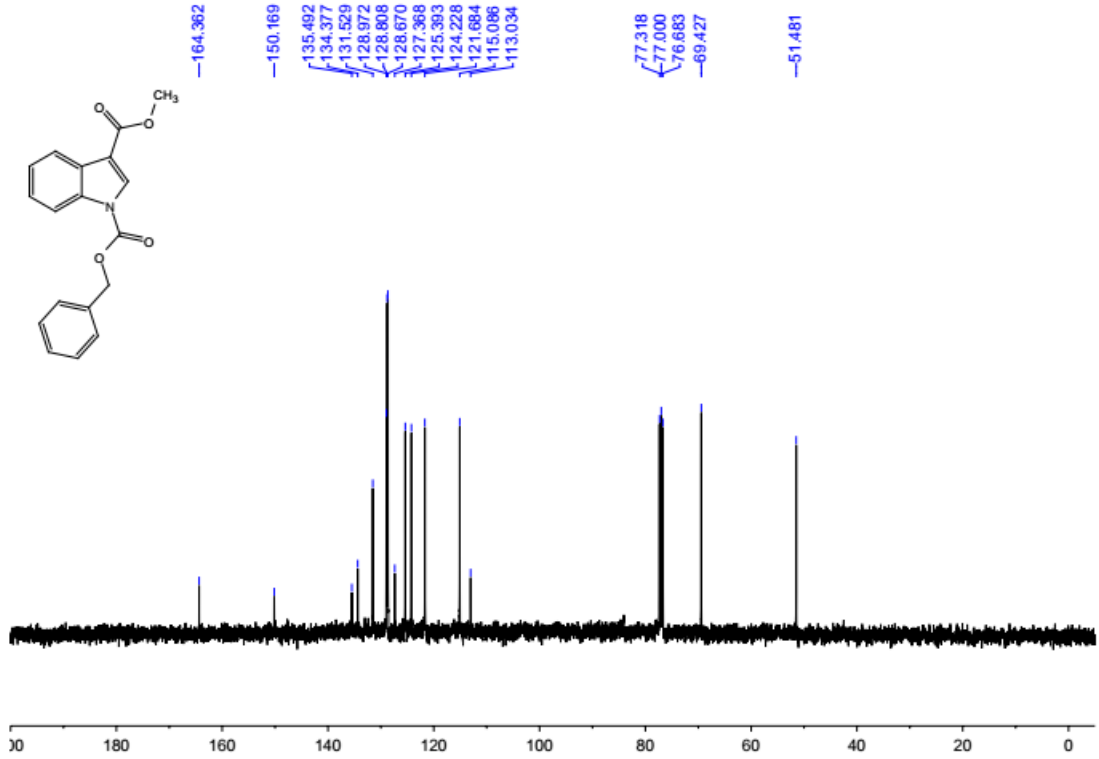
4
3
2
1
0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128.670
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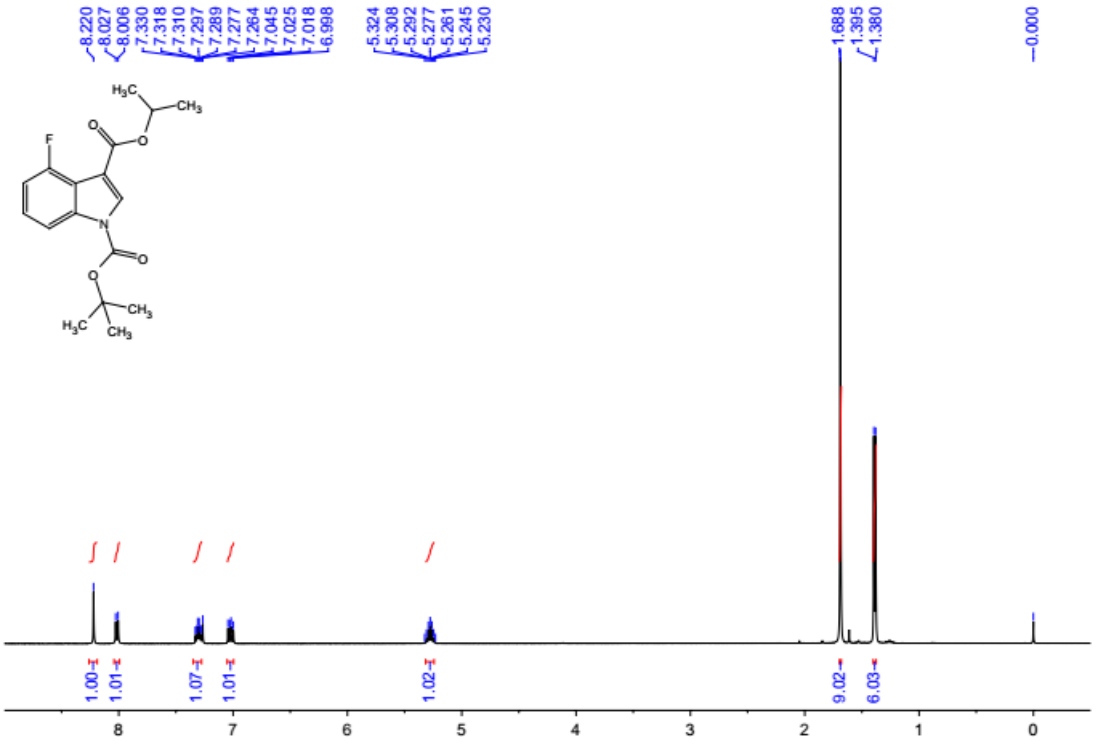
125.393
124.228
121.684
115.086
113.034
77.318
77.000
76.683
69.427
51.481
180
160
140
120
100
80
60
40
20
0

Compound 1g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7.297
7.289
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7.264
7.045
7.025
7.018
6.998
5.324
5.308
5.292
5.277
5.261
5.245
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1.380
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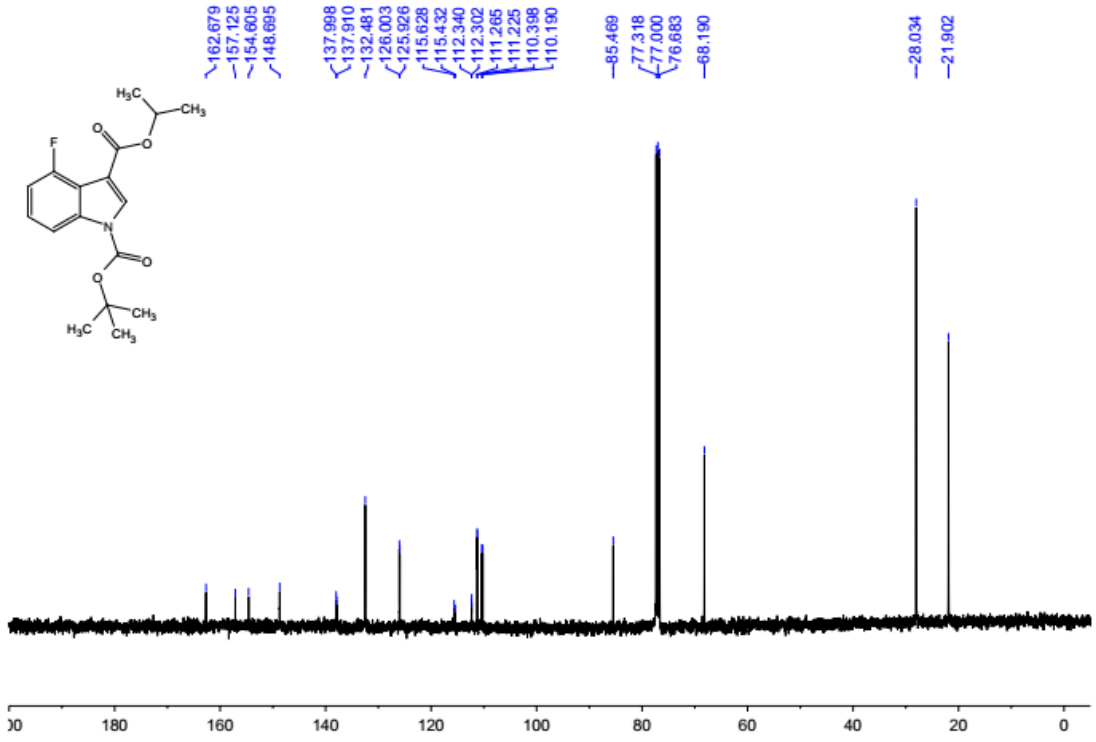
1.01
1.07
1.01
1.02
9.02
6.03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137.910
132.481
126.003
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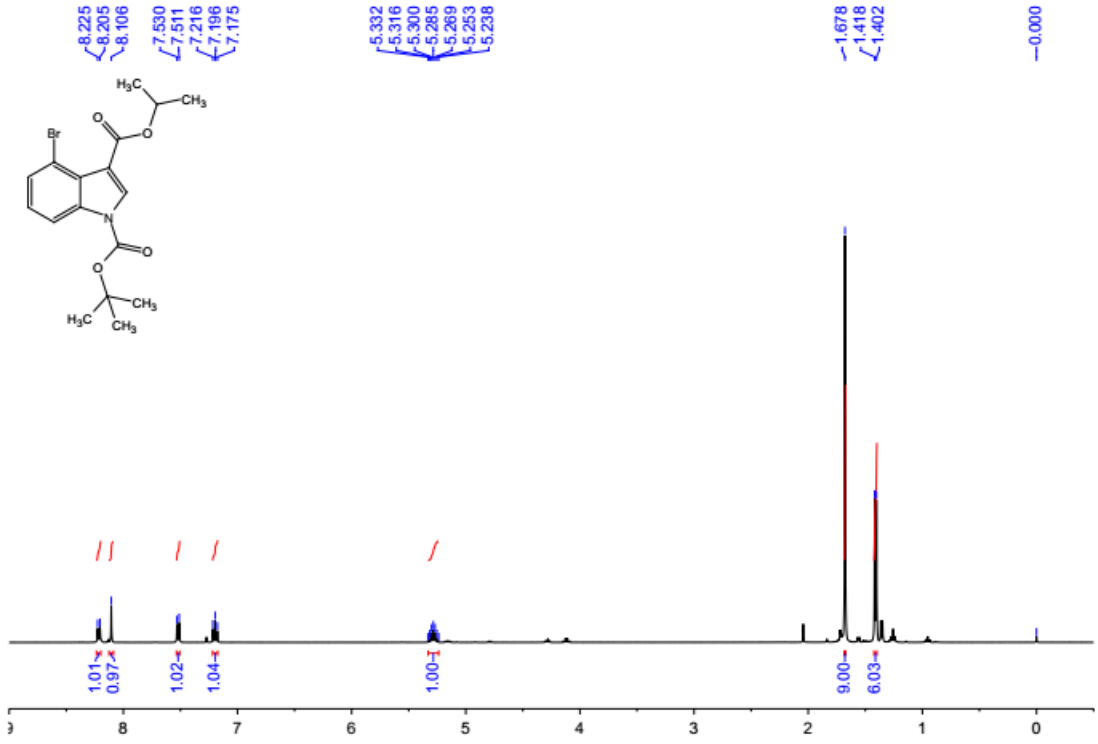
115.628
115.432
112.340
112.302
111.265
111.225
110.398
110.190
85.469
77.318
77.000
76.683
68.190
28.034
21.902

Compound 1h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8.106
7.530
7.511
7.216
7.196
7.175
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5.316
5.300
5.285
5.269
5.253
5.238
1.678
1.418
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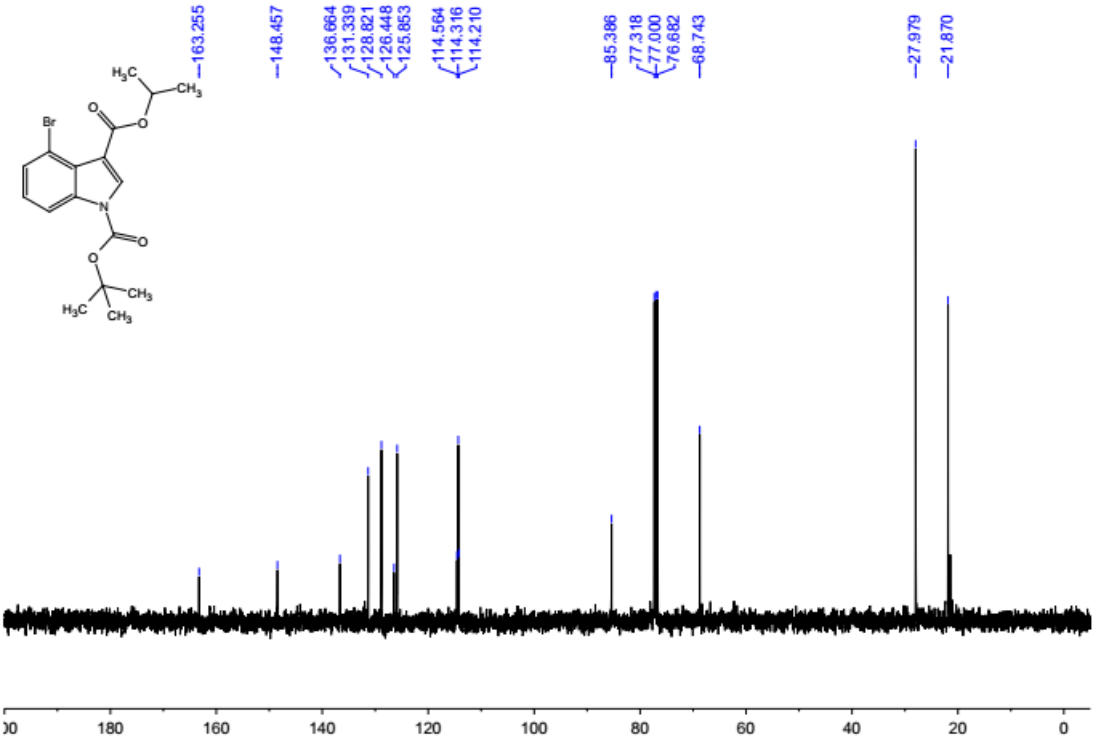
0.97
1.02
1.04
1.00
9.00
6.03
Br
N
O
H3C
CH3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125.853
114.564
114.316
114.210
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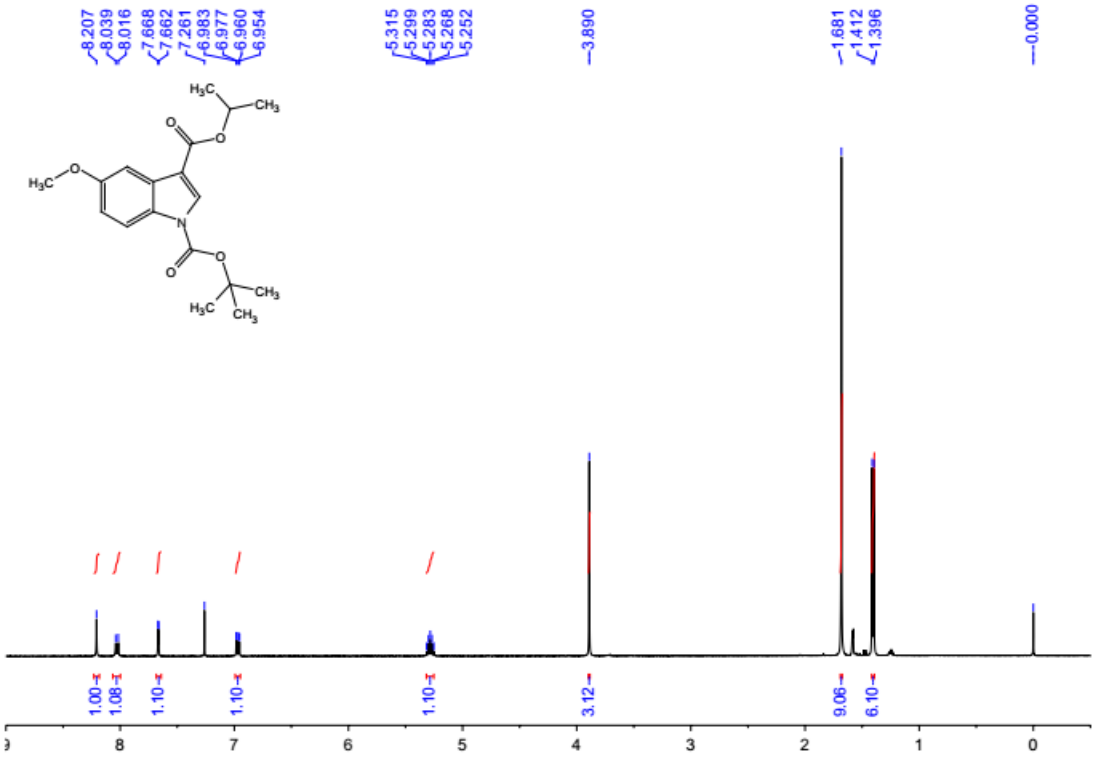
77.000
76.682
68.743
27.979
21.870
Br
N
O
H3C
CH3

Compound 1i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7.662
7.261
6.983
6.977
6.960
6.954
5.315
5.299
5.283
5.268
5.252
3.890
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1.412
1.396
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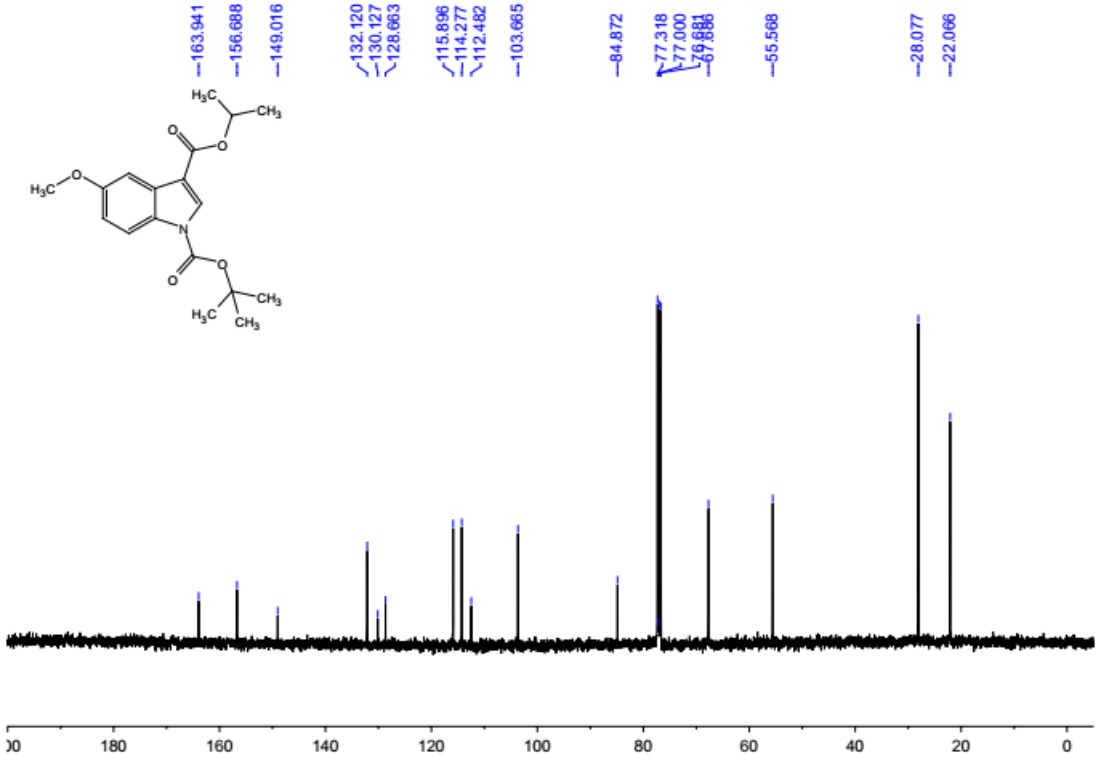
1.08
1.10
1.10
1.10
3.12
9.06
6.10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149.016
132.120
130.127
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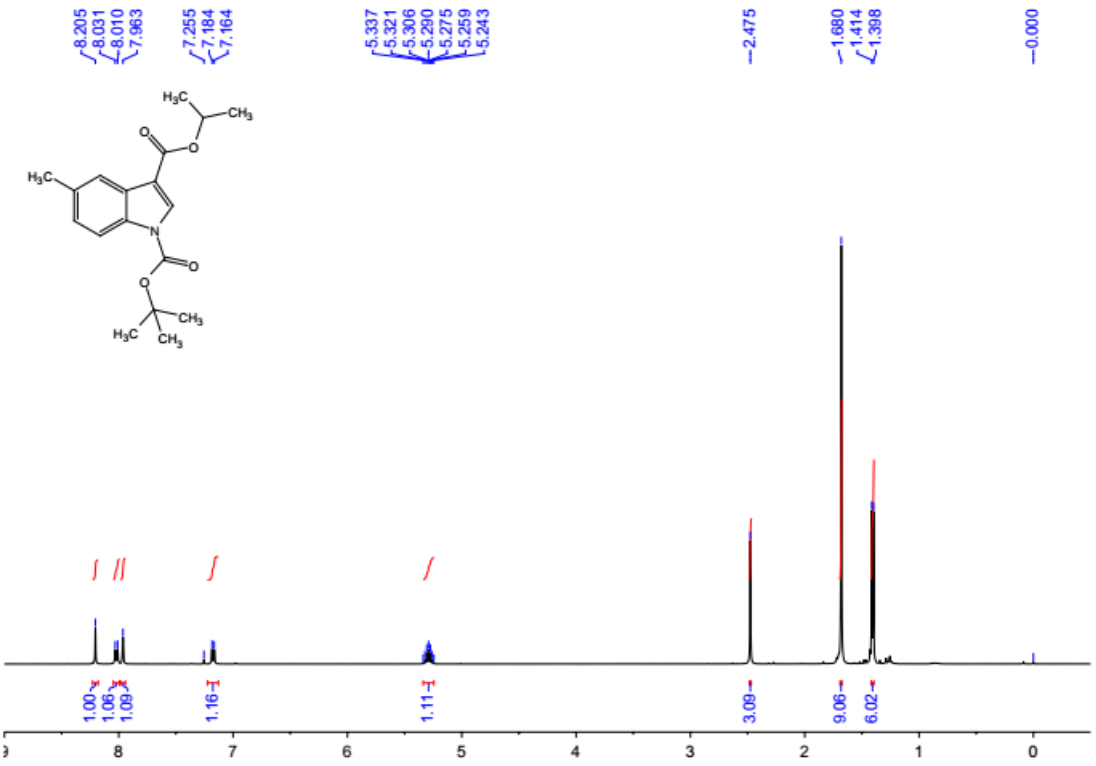
114.277
112.482
103.665
84.872
77.318
77.000
55.568
28.077
22.066

Compound 1j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8.031
8.010
7.963
7.255
7.184
7.164
5.337
5.321
5.306
5.290
5.275
5.259
5.243
2.475
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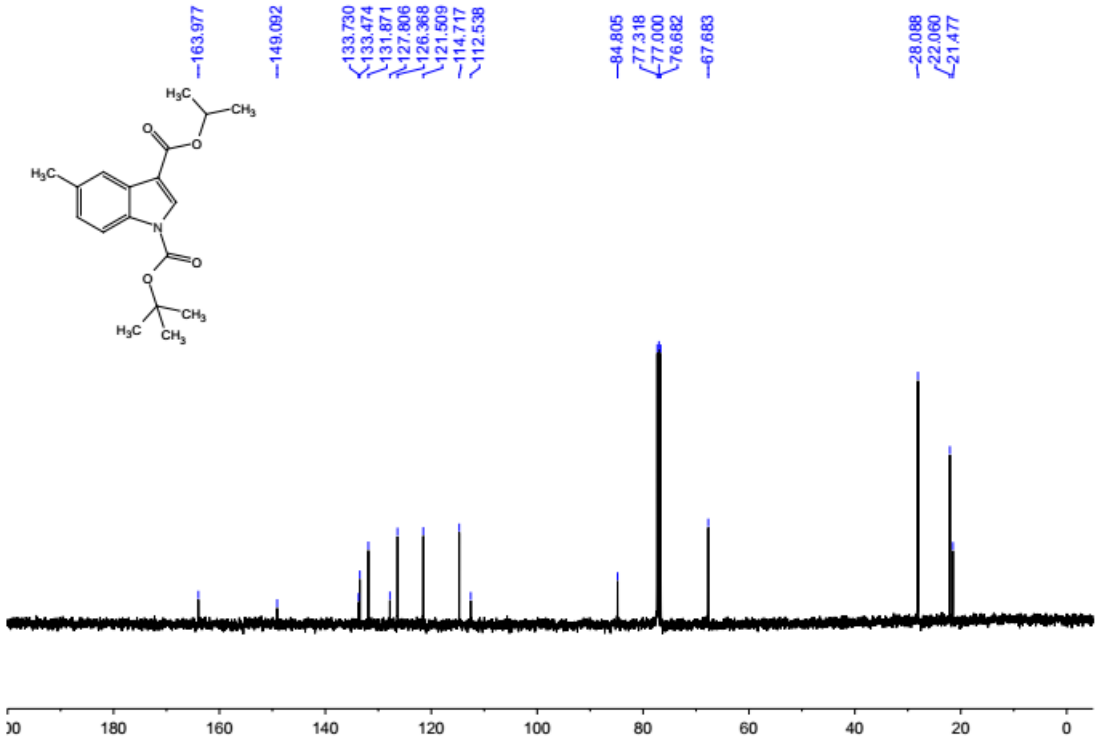
1.398
0.000
1.00
1.06
1.09
1.16
1.11
3.09
9.06
6.02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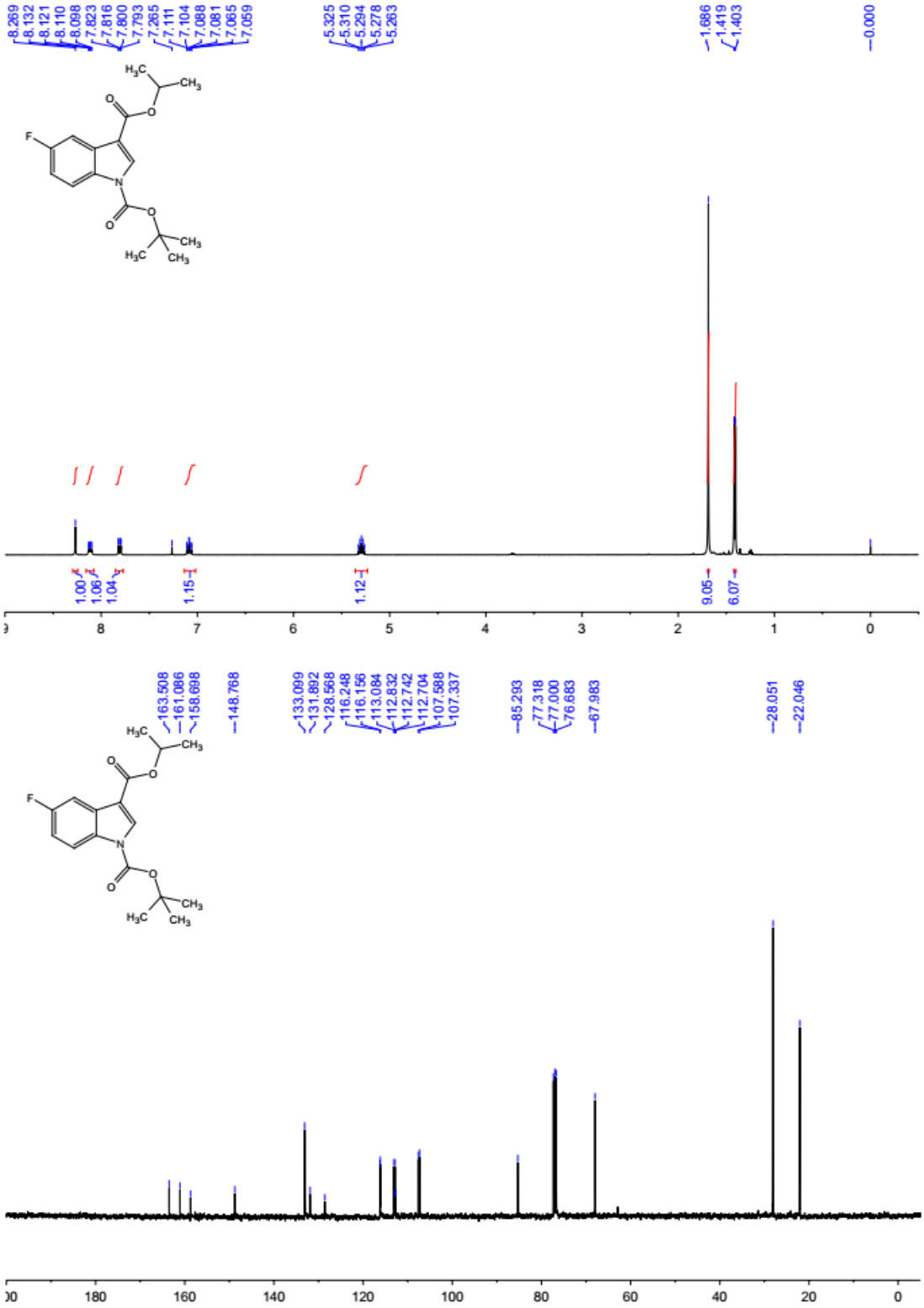
127.806
126.368
121.509
114.717
112.538
84.805
77.318
77.000
76.682
67.683
28.088
22.060
21.477

Compound 1k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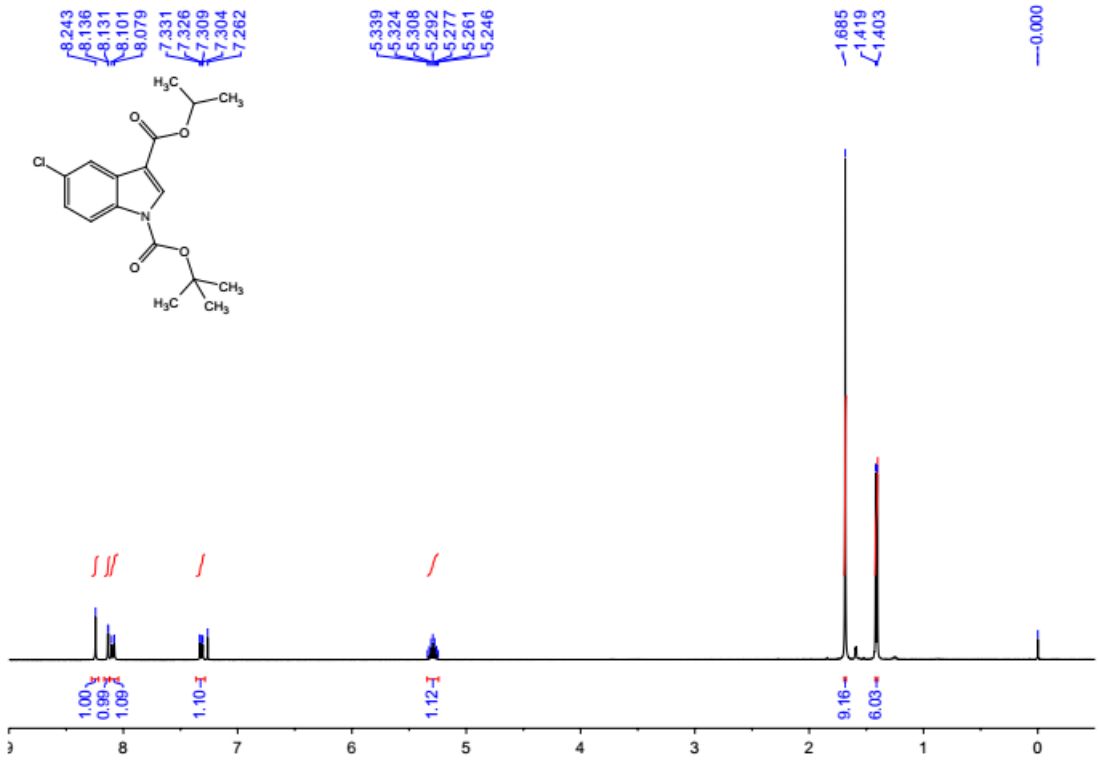
7.823
7.816
7.800
7.793
7.265
7.111
7.104
7.088
7.081
7.065
7.059
5.325
5.310
5.294
5.278
5.263
1.686
1.419
1.403
0.000
1.00
1.06
1.04
1.15
1.12
9.05
6.07
163.508
161.086
158.698
148.768
133.099
131.892
128.568
116.248
116.156
113.084
112.832
112.742
112.704
107.588
107.337
85.293
77.318
77.000
76.683
67.983
28.051
22.046

Compound 1l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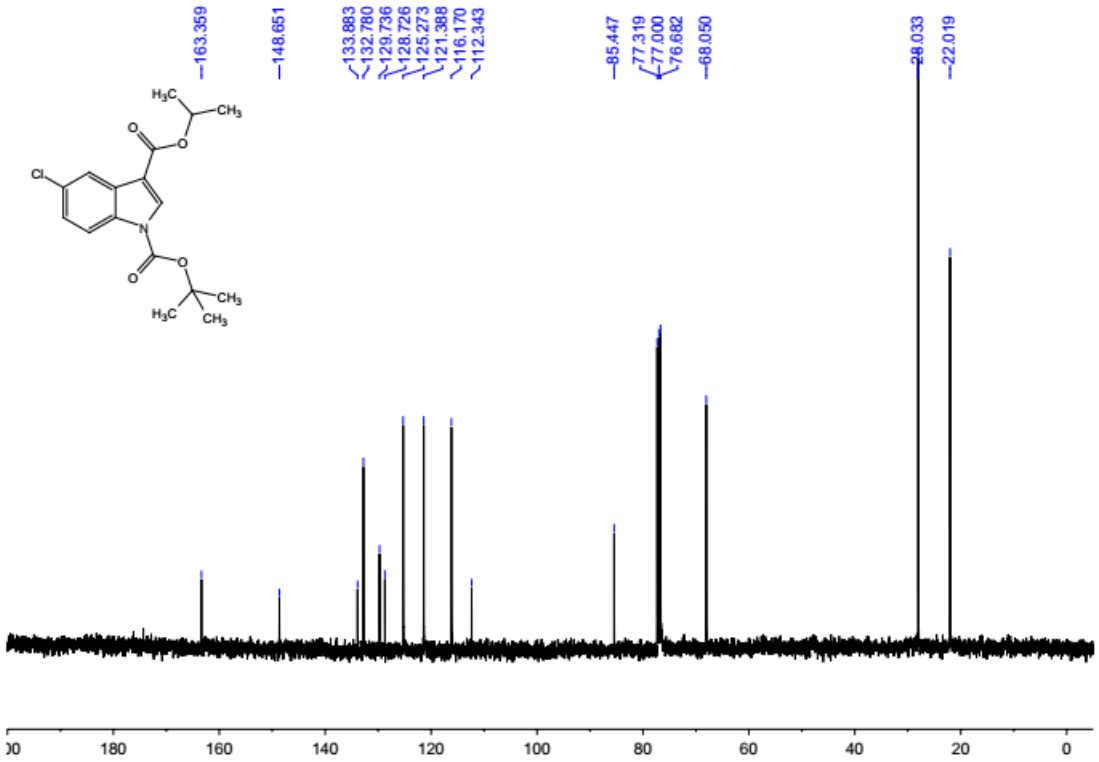
8.131
8.101
8.079
7.331
7.326
7.309
7.304
7.262
5.339
5.324
5.308
5.292
5.277
5.261
5.246
1.685
1.419
1.403
0.000
1.00
0.99
1.09
1.10
1.12
9.16
6.03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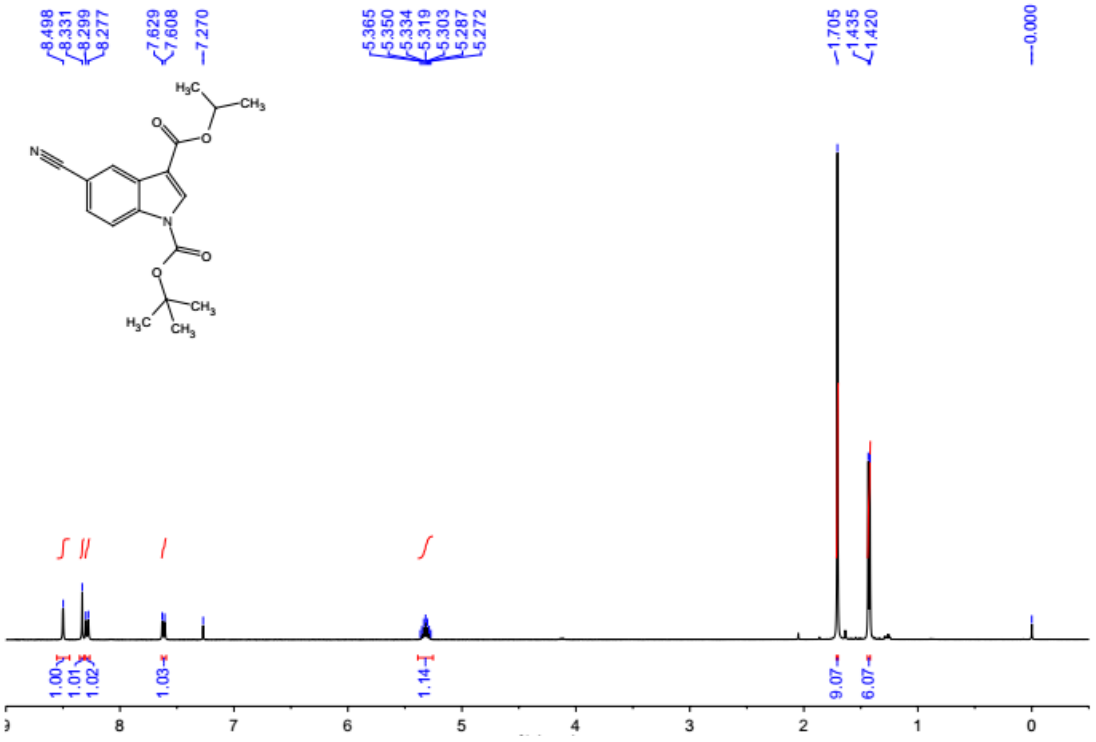
77.319
77.000
76.682
68.050
28.033
22.019

Compound 1m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8.277
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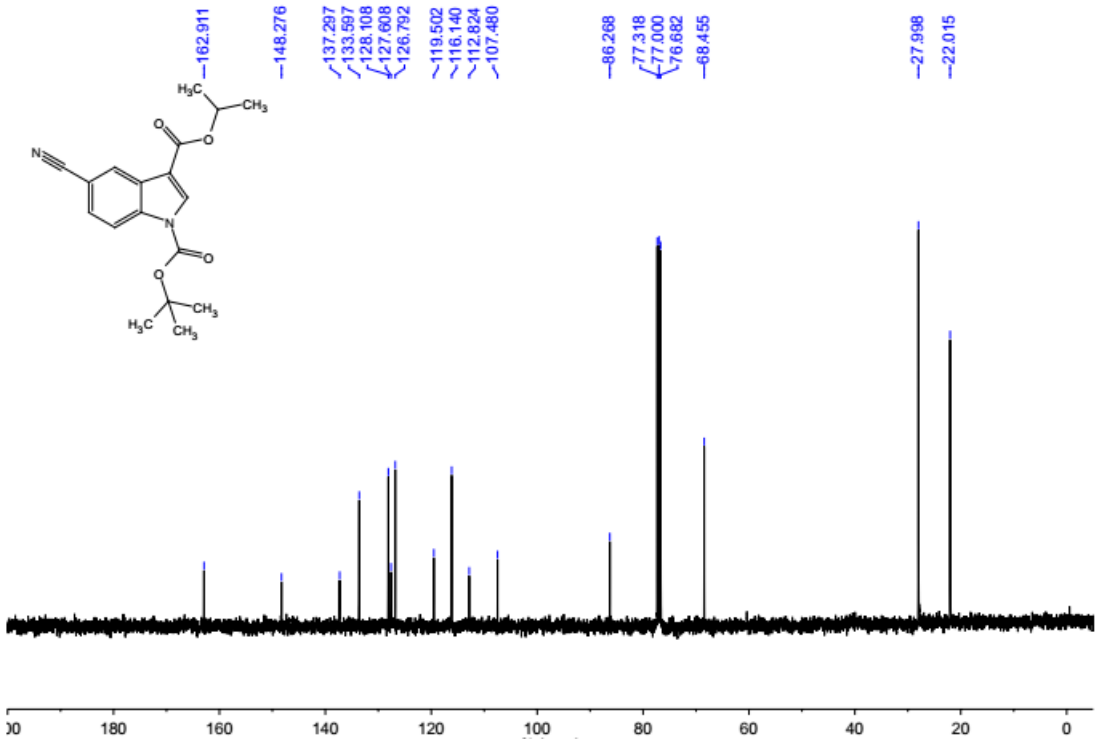
7.608
7.270
5.365
5.350
5.334
5.319
5.303
5.287
5.272
1.705
1.435
1.420
0.000
1.00
1.01
1.02
1.03
1.14
9.07
6.07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133.597
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127.608
126.792
119.502
116.140
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107.480
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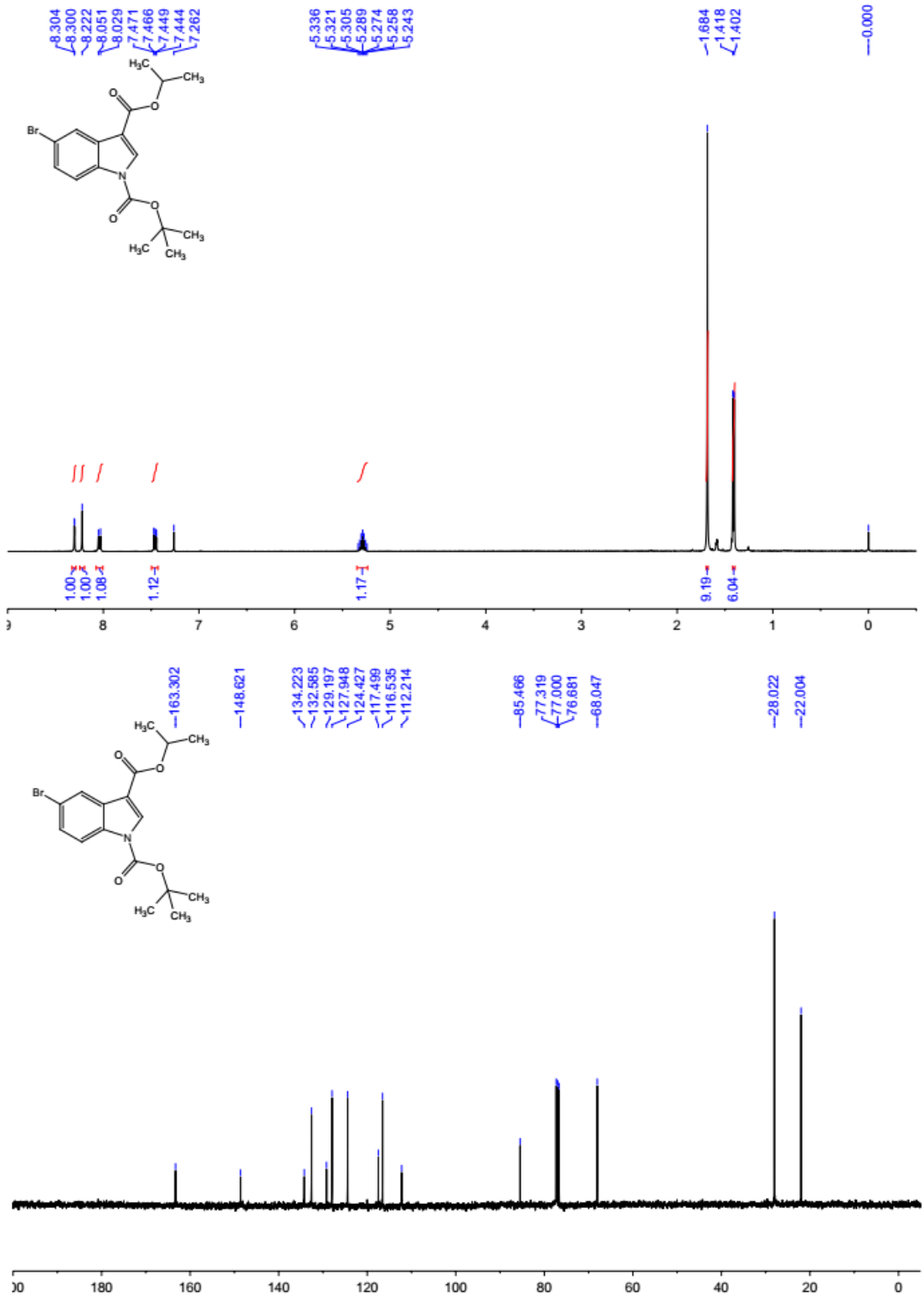
77.000
76.682
68.455
27.998
22.015

Compound 1n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7.466
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7.444
7.262
5.336
5.321
5.305
5.289
5.274
5.258
5.243
1.684
1.418
1.402
0.000
1.00
1.00
1.08
1.12
1.17
9.19
6.04
163.302
148.621
134.223
132.585
129.197
127.948
124.427
117.499
116.535
112.214
85.466
77.319
77.000
76.681
68.047
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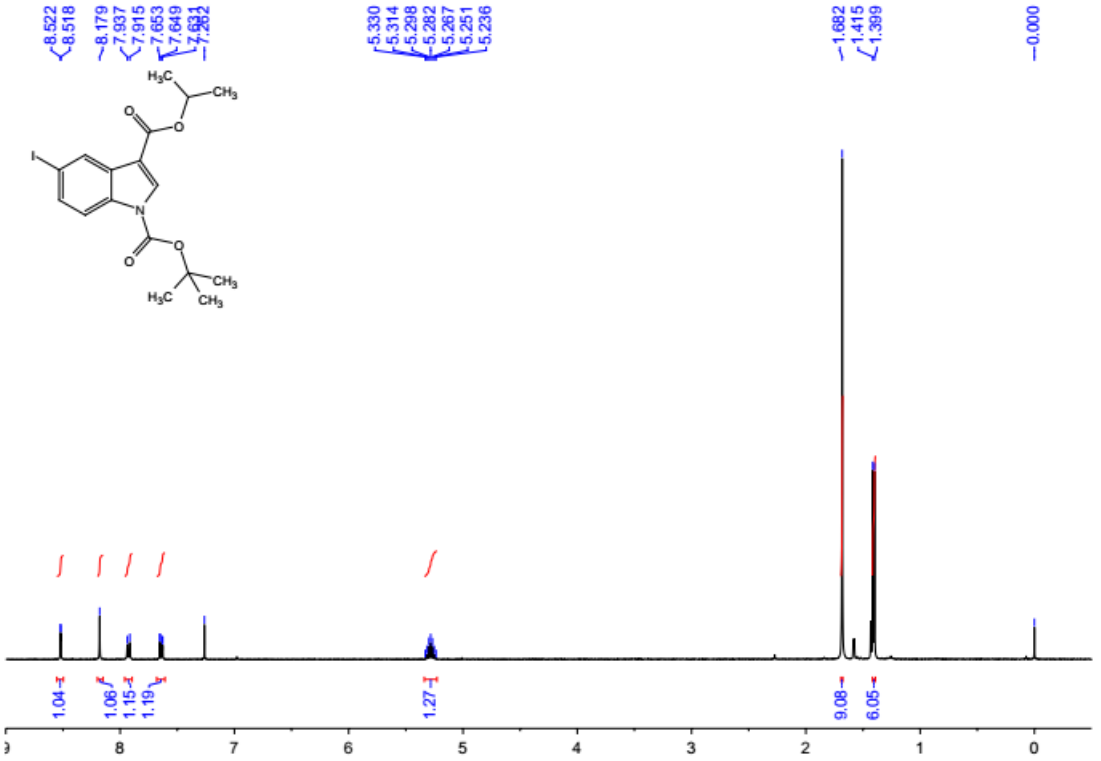
22.004
Br
N
O
O
O
O
H3C
CH3
H3C
CH3
H3C
CH3

Compound 1o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5.314
5.298
5.282
5.267
5.251
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1.682
1.415
1.399
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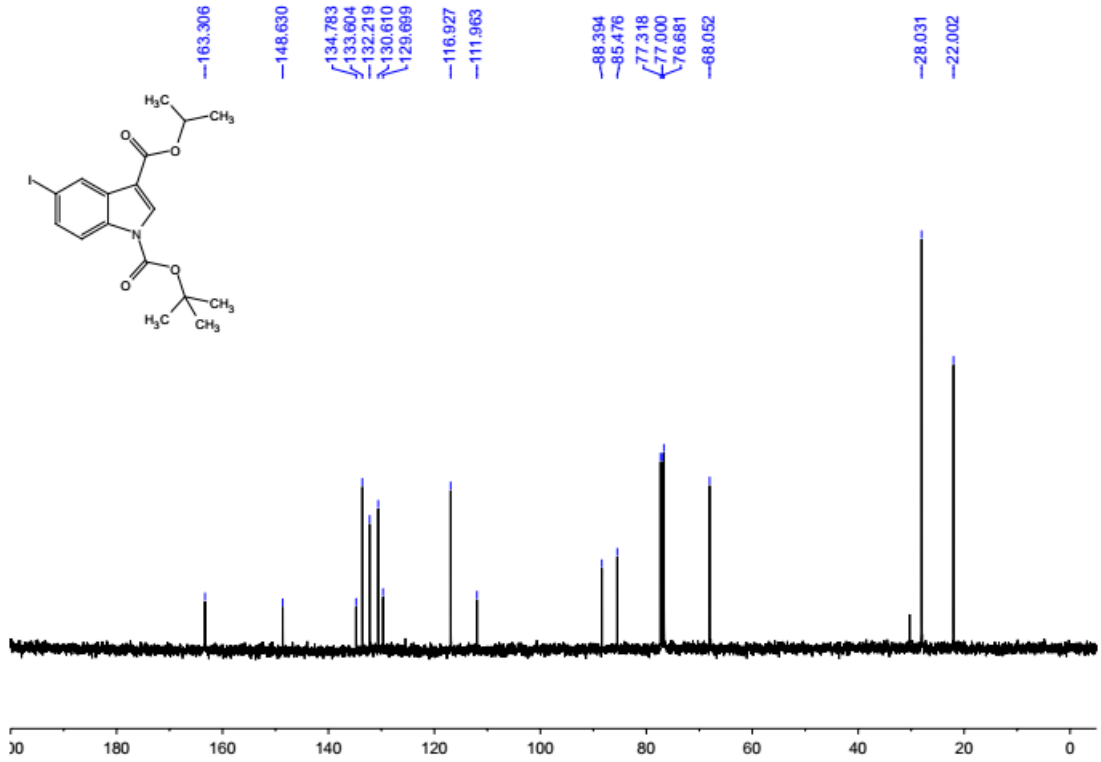
1.06
1.15
1.19
1.27
9.08
6.05


163.306
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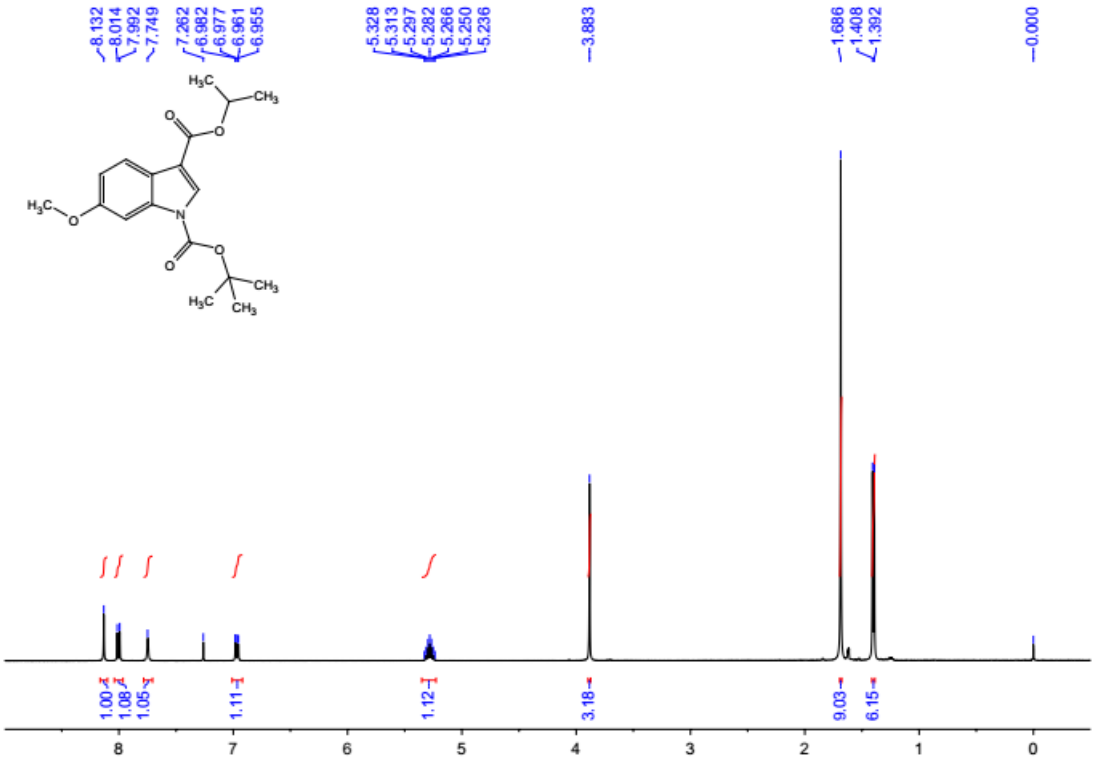
133.604
132.219
130.610
129.699
116.927
111.963
88.394
85.476
77.318
77.000
76.681
68.052
28.031
22.002

Compound 1p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7.749
7.262
6.982
6.977
6.961
6.955
5.328
5.313
5.297
5.282
5.266
5.250
5.236
3.883
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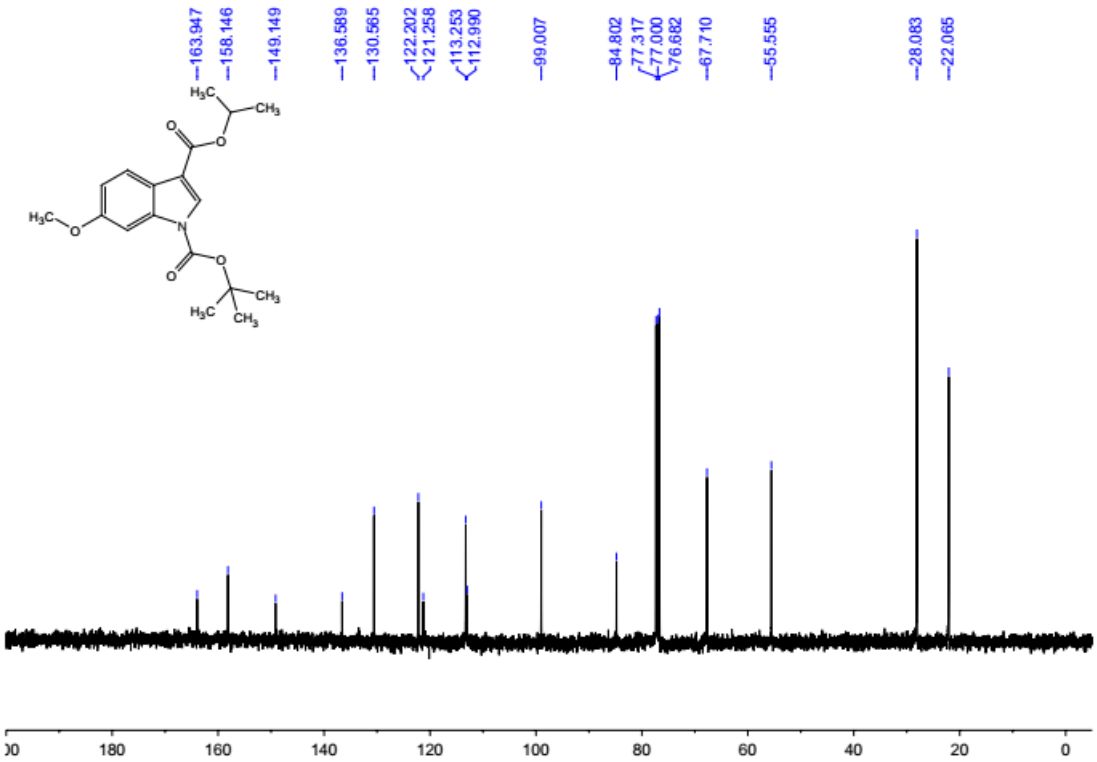
1.408
1.392
0.000
1.00
1.08
1.05
1.11
1.12
3.18
9.03
6.15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122.202
121.258
113.253
112.990
99.007
84.802
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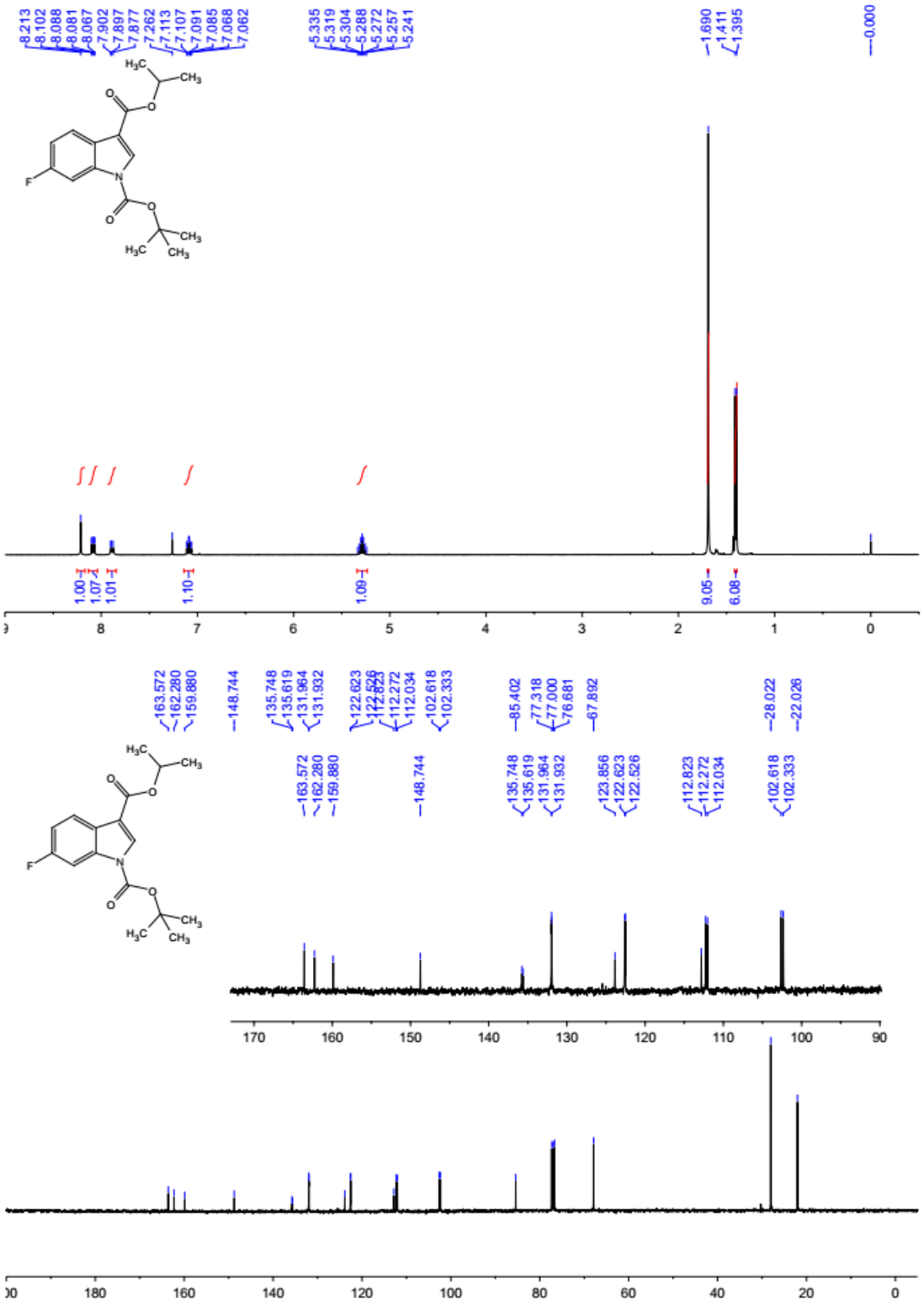
77.000
76.682
67.710
55.555
28.083
22.065

Compound 1q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8.081
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7.897
7.877
7.262
7.113
7.107
7.091
7.085
7.068
7.062
5.335
5.319
5.304
5.288
5.272
5.257
5.241
1.690
1.411
1.395
0.000
1.00
1.07
1.01
1.10
1.09
9.05
6.08
163.572
162.280
159.880
148.744
135.748
135.619
131.964
131.932
122.623
112.272
112.034
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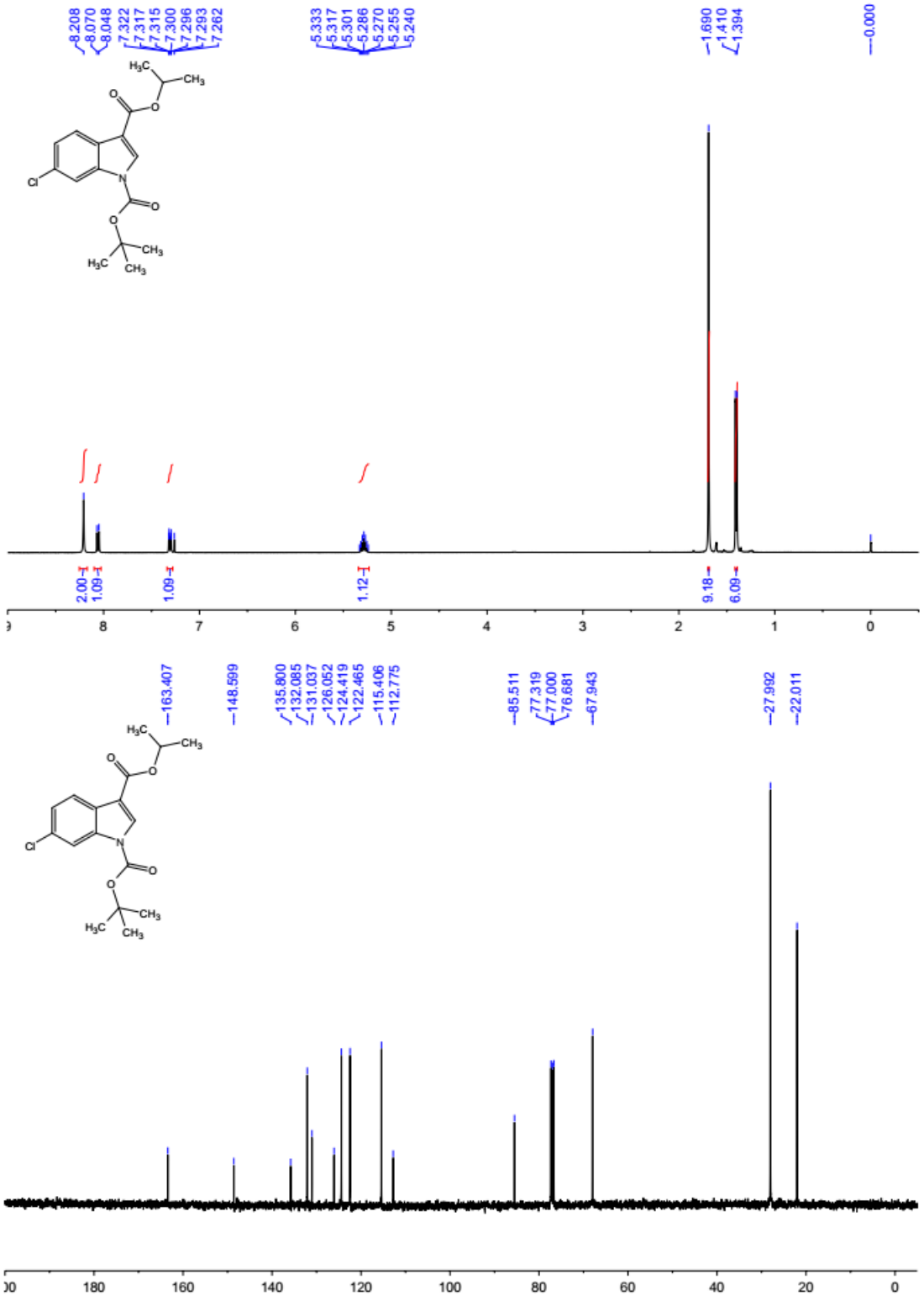
77.000
76.681
67.892
28.022
22.026

Compound 1r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8.070
8.048
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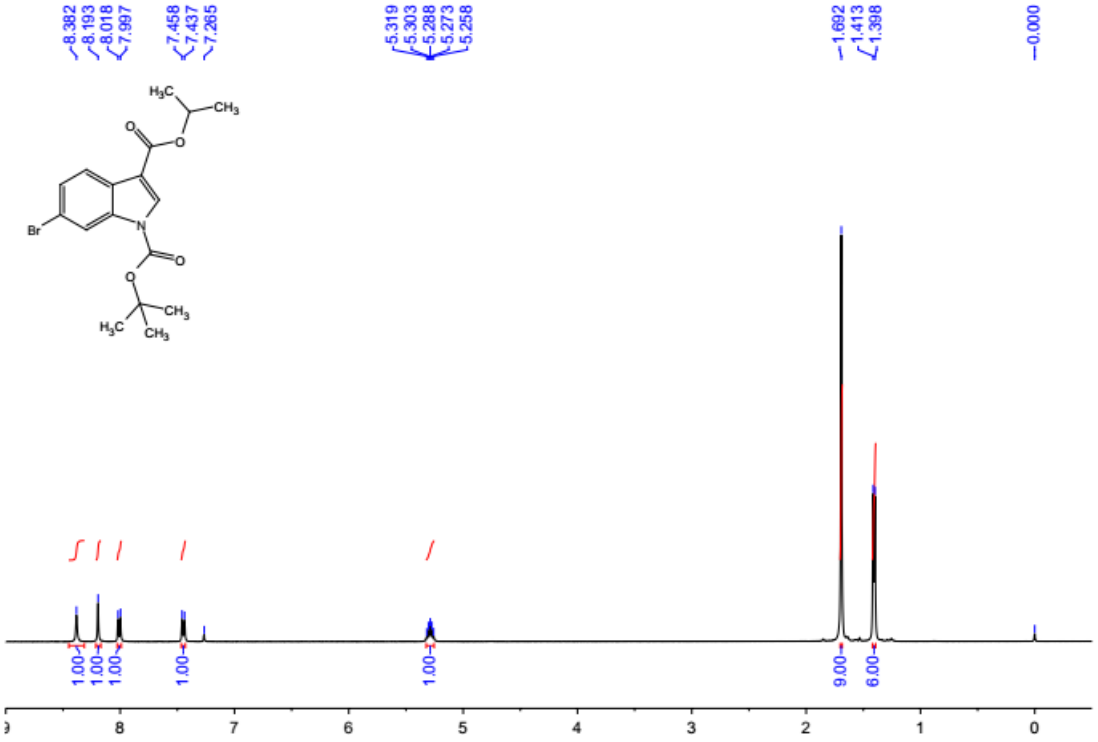
7.317
7.315
7.300
7.296
7.293
7.262
5.333
5.317
5.301
5.286
5.270
5.255
5.240
1.690
1.410
1.394
0.000
2.00
1.09
1.09
1.12
9.18
6.09
163.407
148.599
135.800
132.085
131.037
126.052
124.419
122.465
115.406
112.775
85.511
77.319
77.000
76.681
67.943
27.992
22.011

Compound 1s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7.437
7.265
5.319
5.303
5.288
5.273
5.258
1.692
1.413
1.398
0.000
1.00
1.00
1.00
1.00
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9.00
6.00
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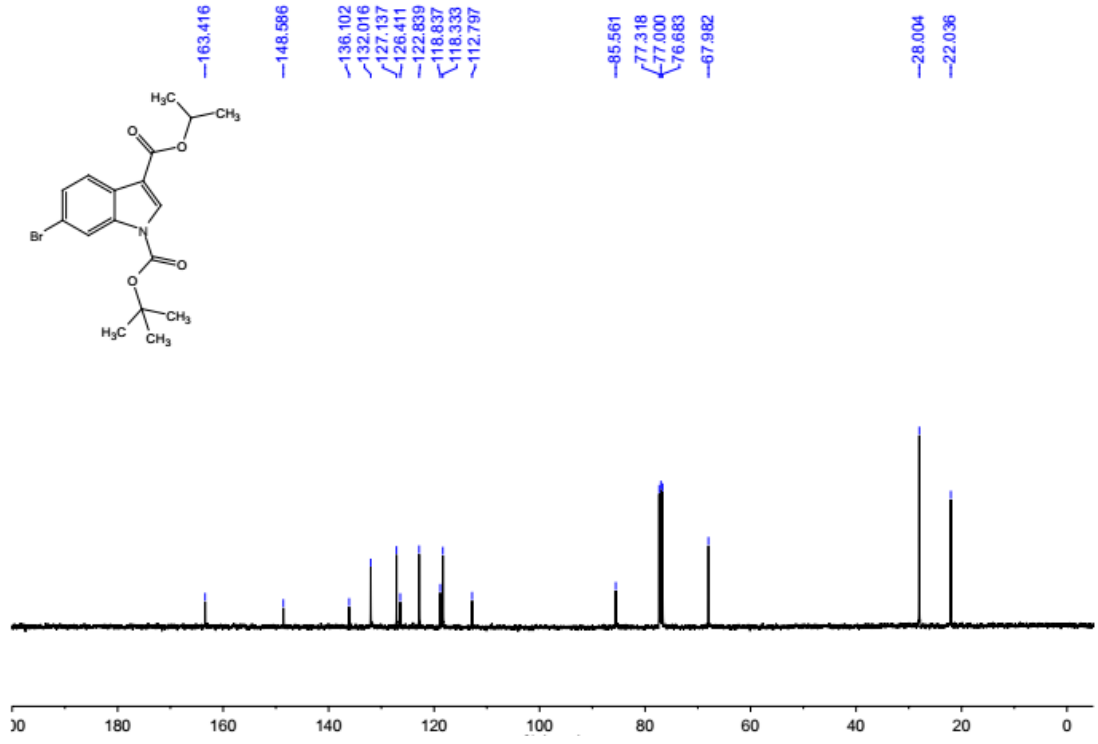
O
O
O
CH3
H3C
CH3
H3C
CH3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126.411
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118.837
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112.797
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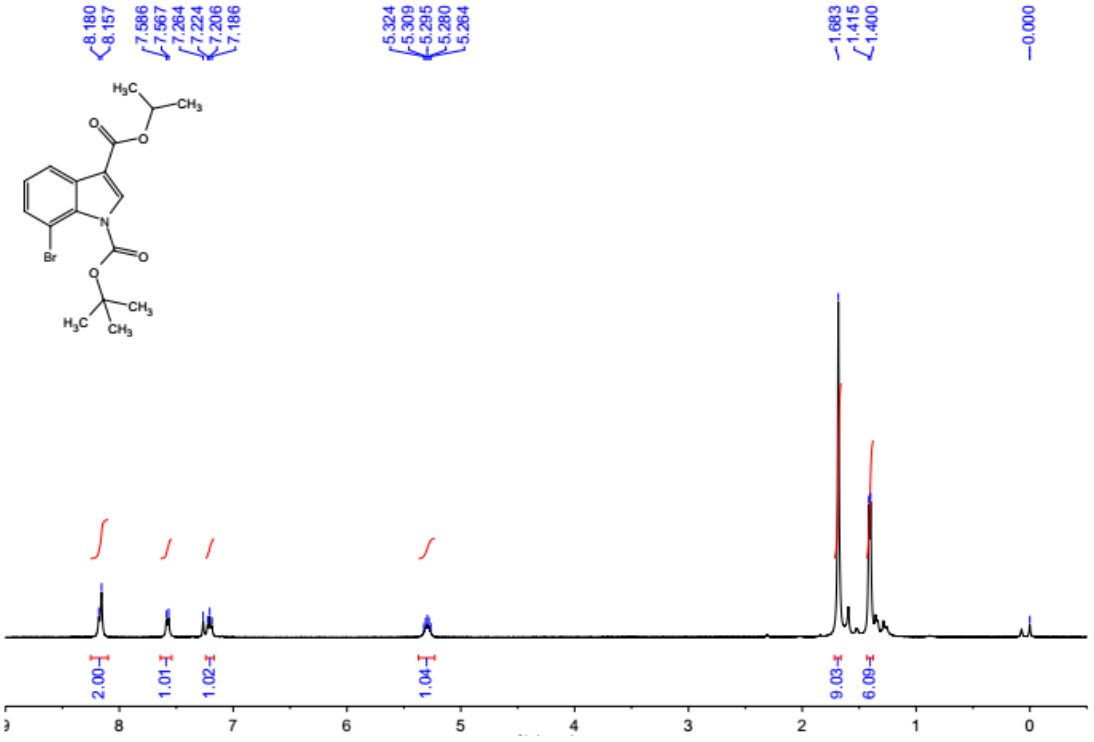
77.000
76.683
67.982
28.004
22.036
Br
N
O
O
O
O
CH3
H3C
CH3
H3C
CH3

Compound 1t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8.157
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7.224
7.206
7.186
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5.309
5.295
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5.264
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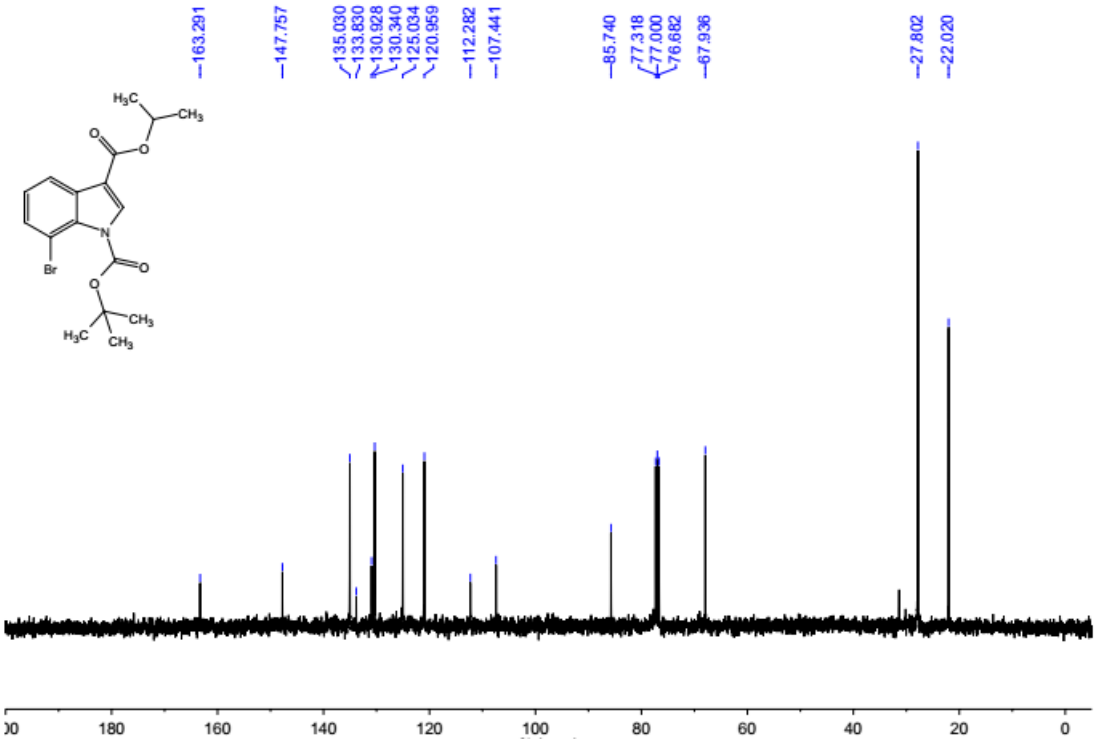
1.415
1.400
0.000
2.00
1.01
1.02
1.04
9.03
6.09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107.441
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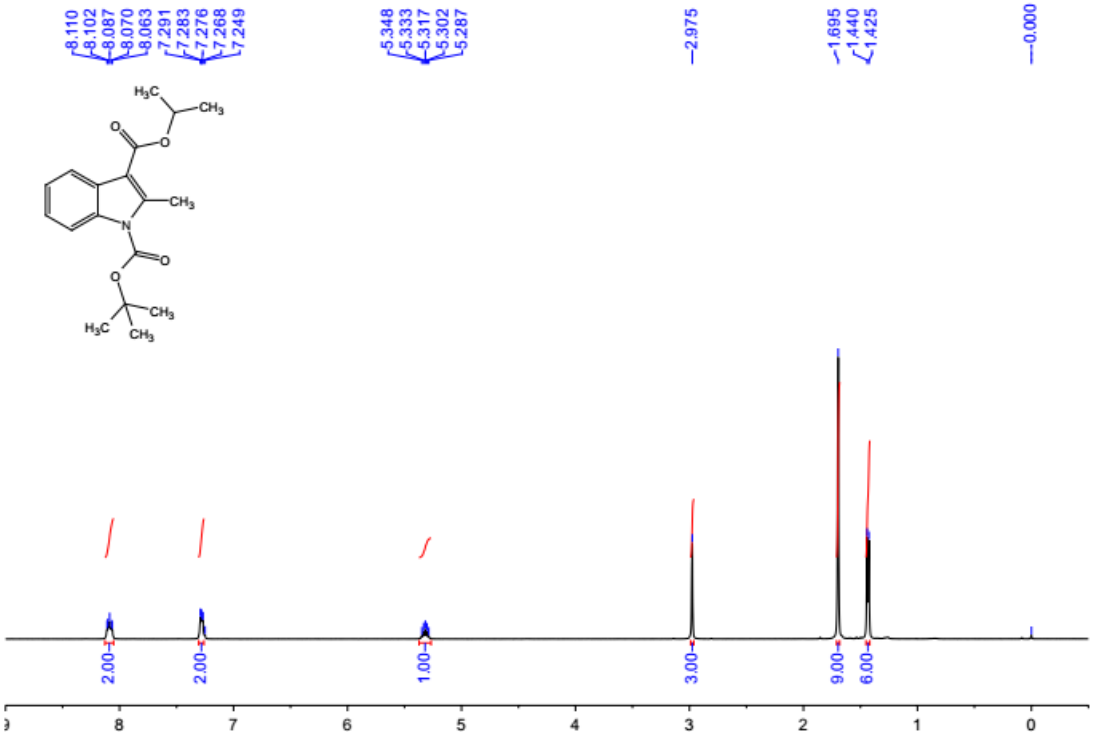
77.000
76.682
67.936
27.802
22.020

Compound 1u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8.063
7.291
7.283
7.276
7.268
7.249
5.348
5.333
5.317
5.302
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1.440
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2.00
1.00
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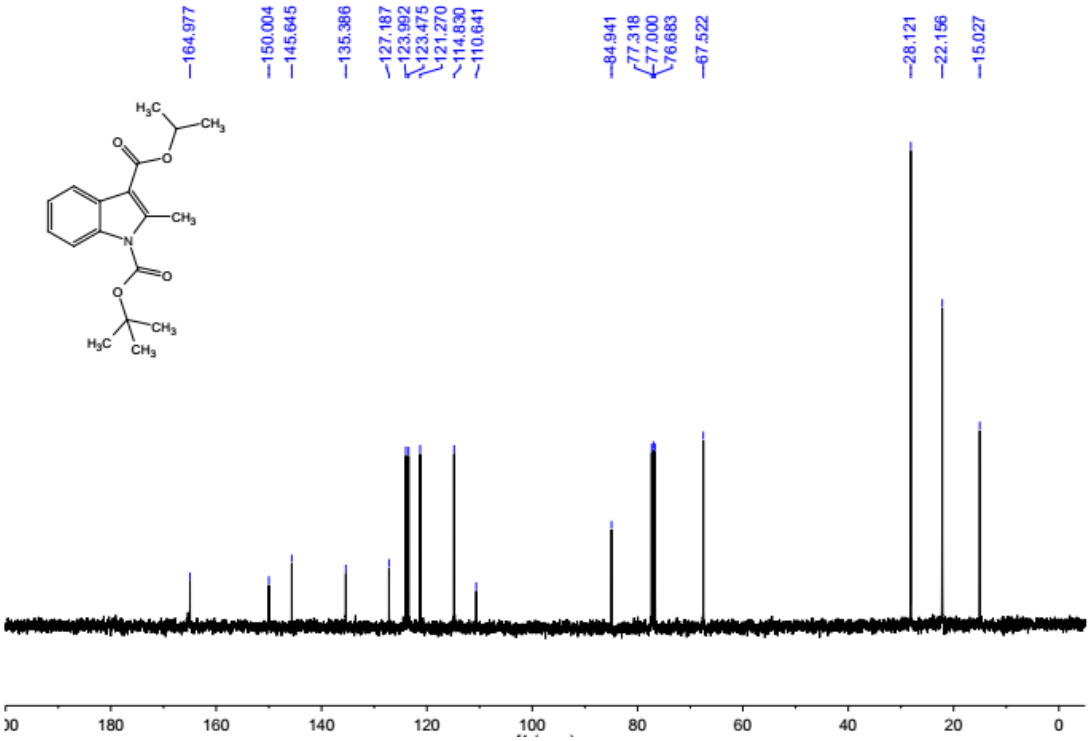
9.00
6.00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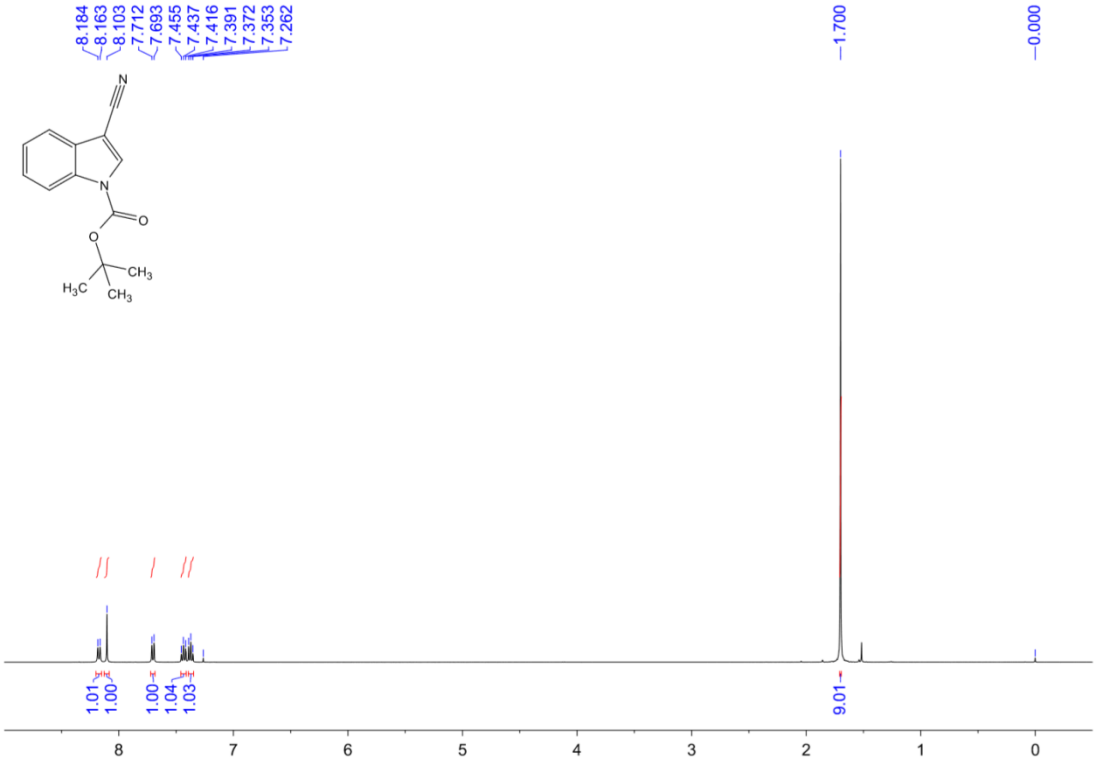
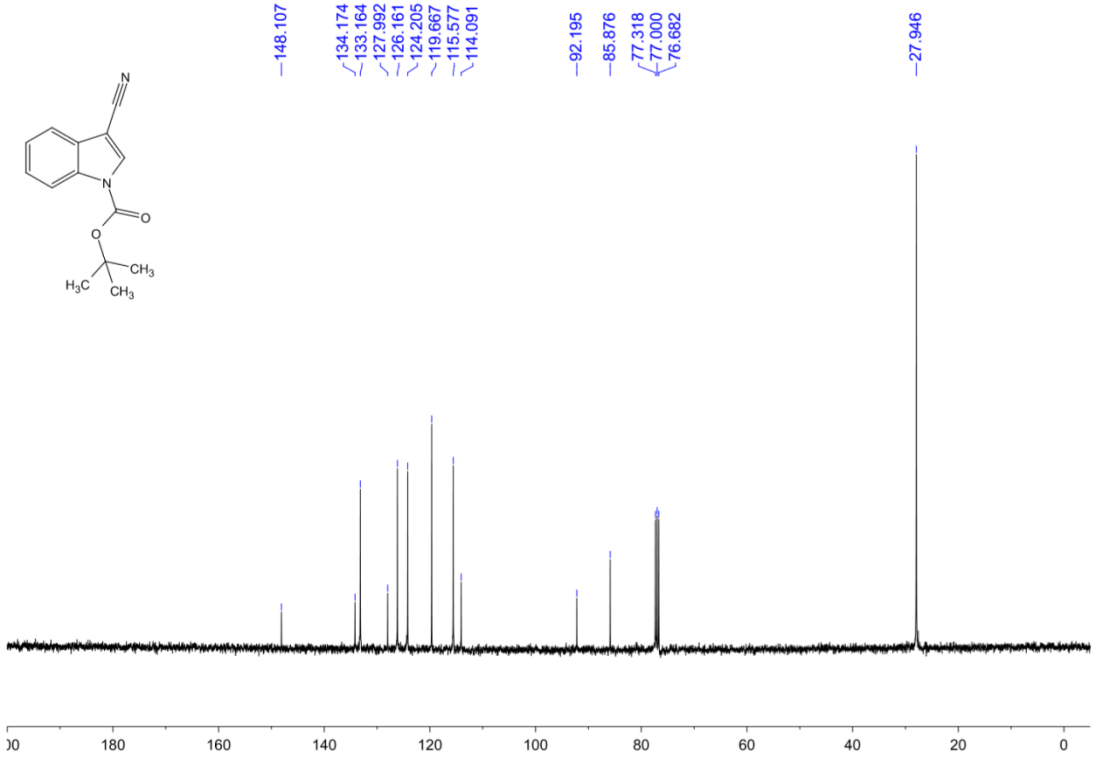
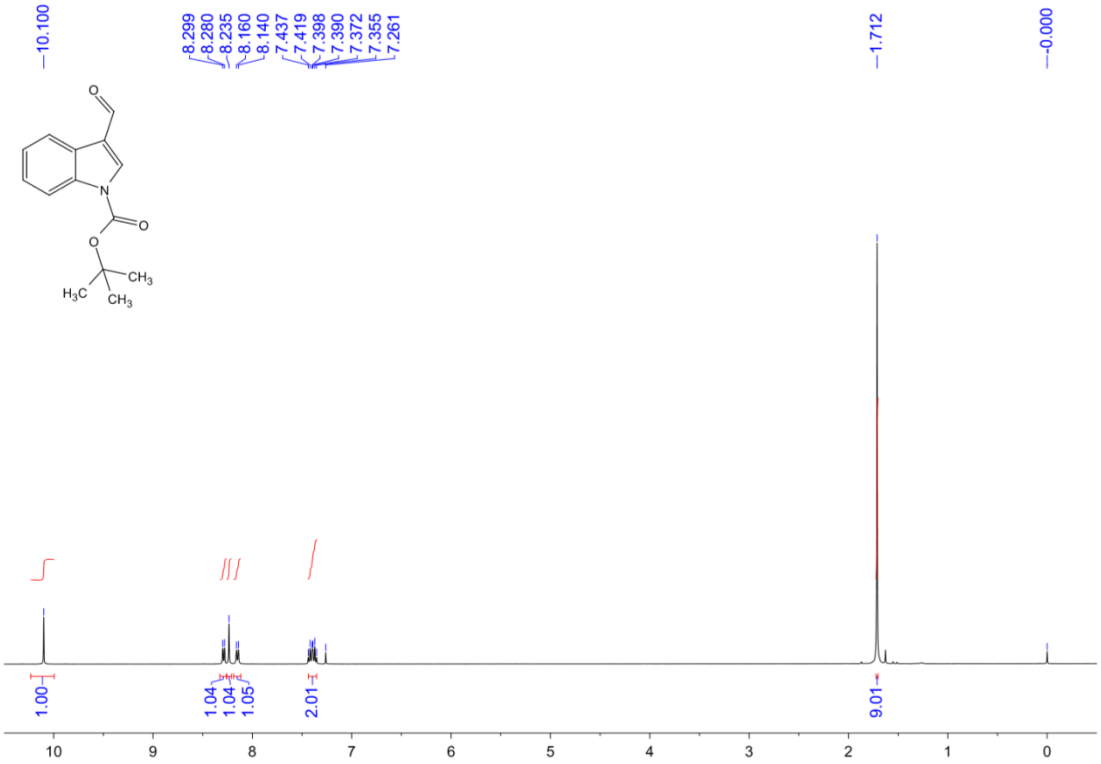
123.475
121.270
114.830
110.641
84.941
77.318
77.000
76.683
67.522
28.121
22.156
15.027

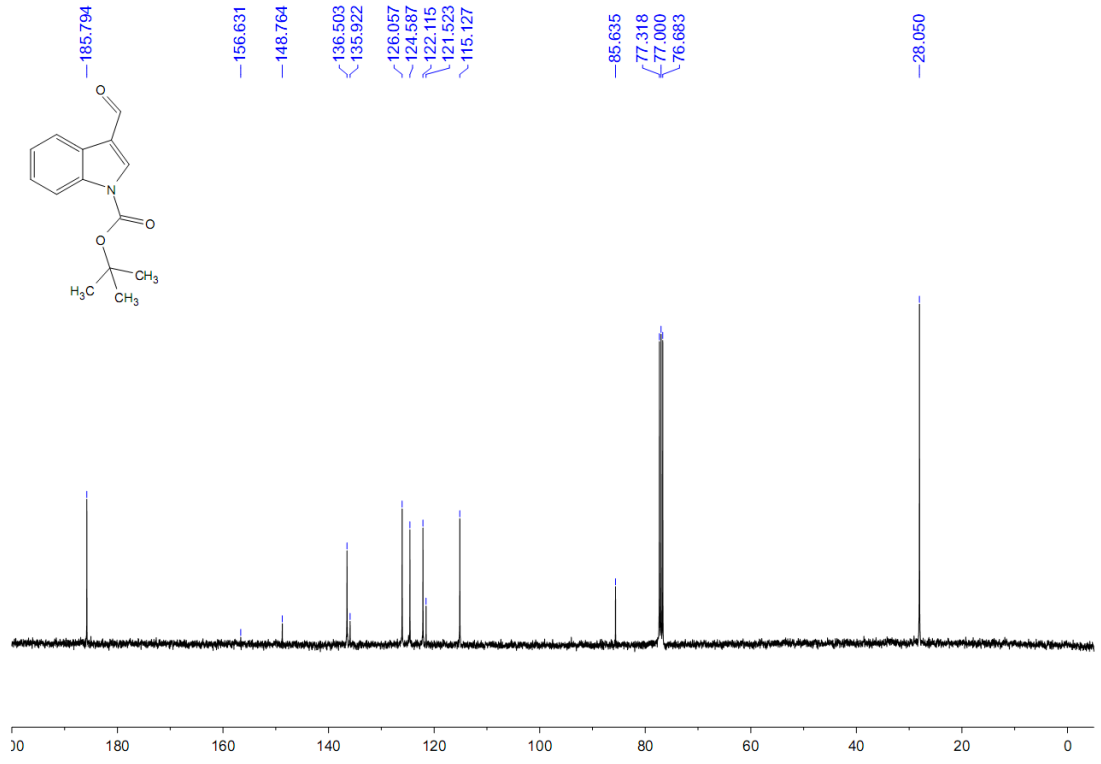
Compound 1v


8.184
8.163
8.103
7.712
7.693
7.455
7.437
7.416
7.391
7.372
7.353
7.262
1.700
0.000
1.01
1.00
1.00
1.04
1.03
9.01
8
7
6
5
4
3
2
1
0

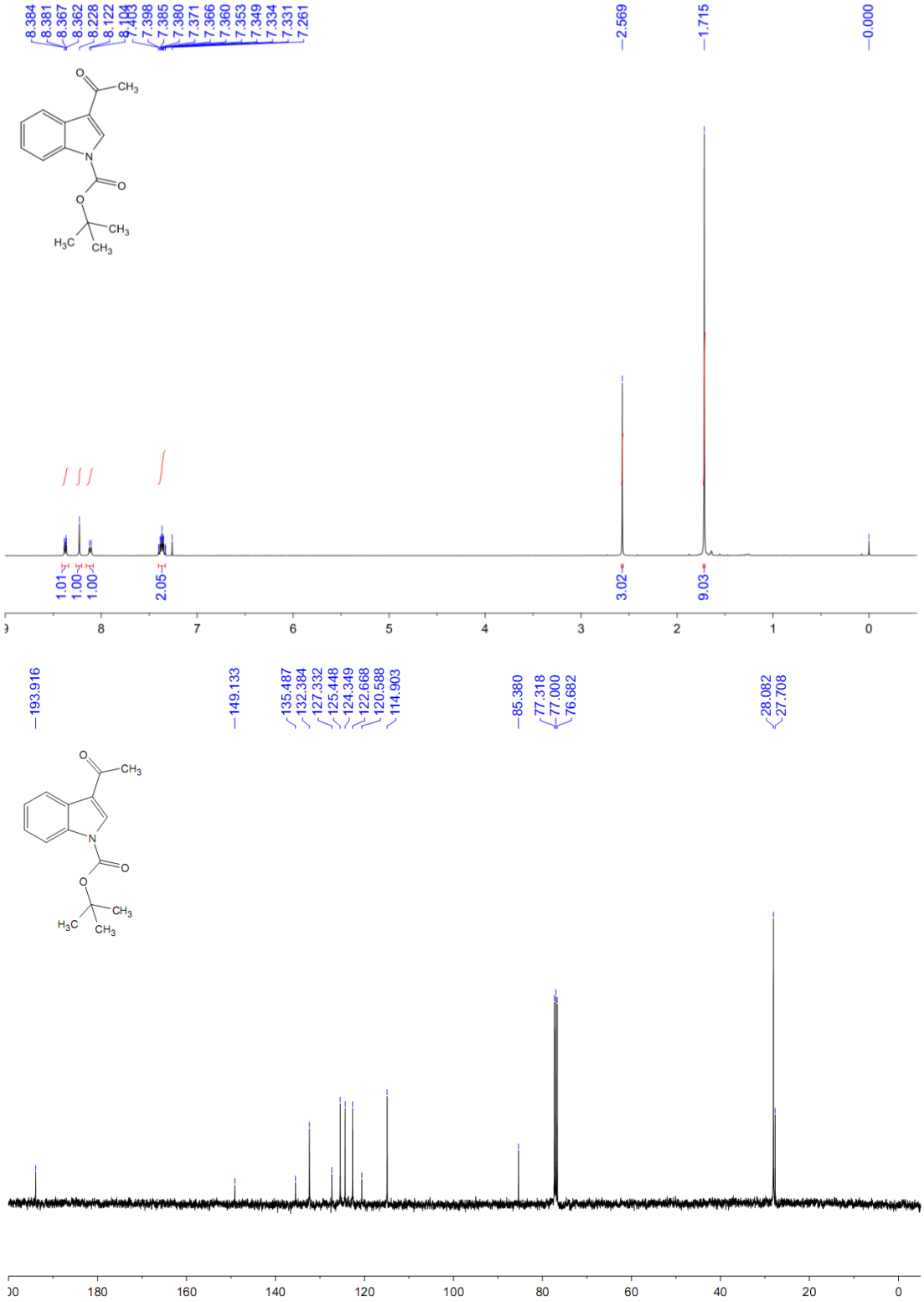

148.107
134.174
133.164
127.992
126.161
124.205
119.667
115.577
114.091
92.195
85.876
77.318
77.000
76.682
27.946
180
160
140
120
100
80
60
40
20
0

Compound 1w

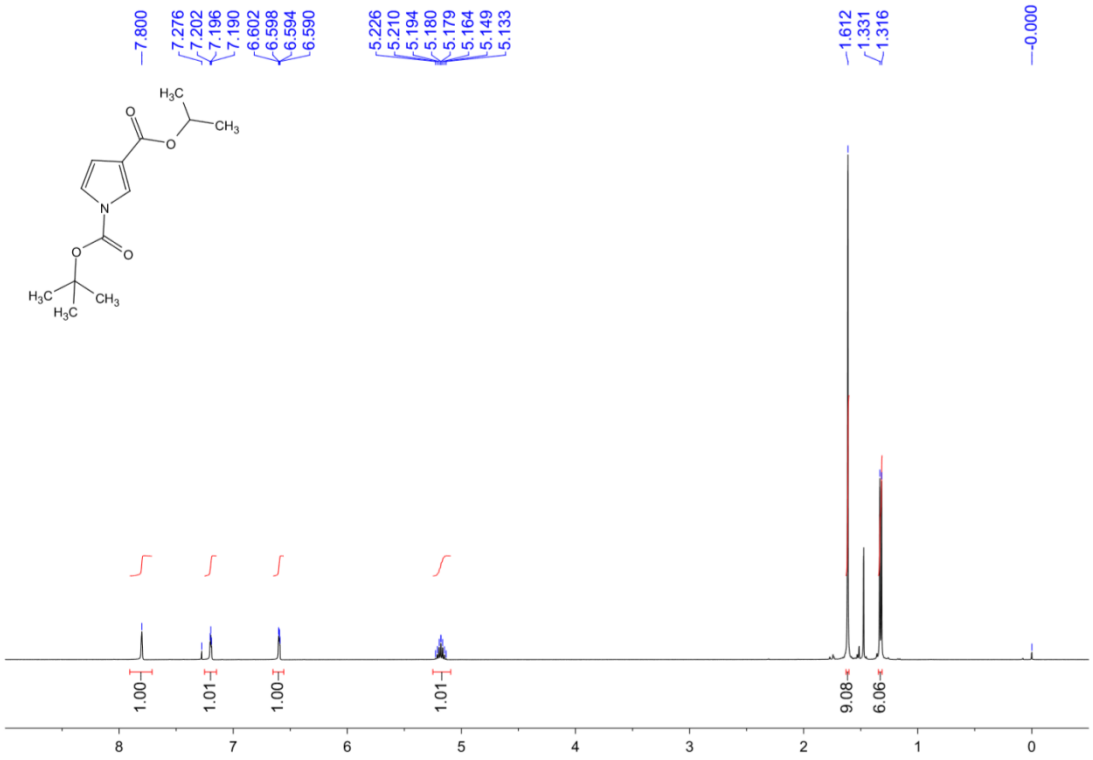

10.100
8.299
8.280
8.235
8.160
8.140
7.437
7.419
7.398
7.390
7.372
7.355
7.261
1.712
0.000
1.00
1.04
1.04
1.05
2.01
9.01
10
9
8
7
6
5
4
3
2
1
0

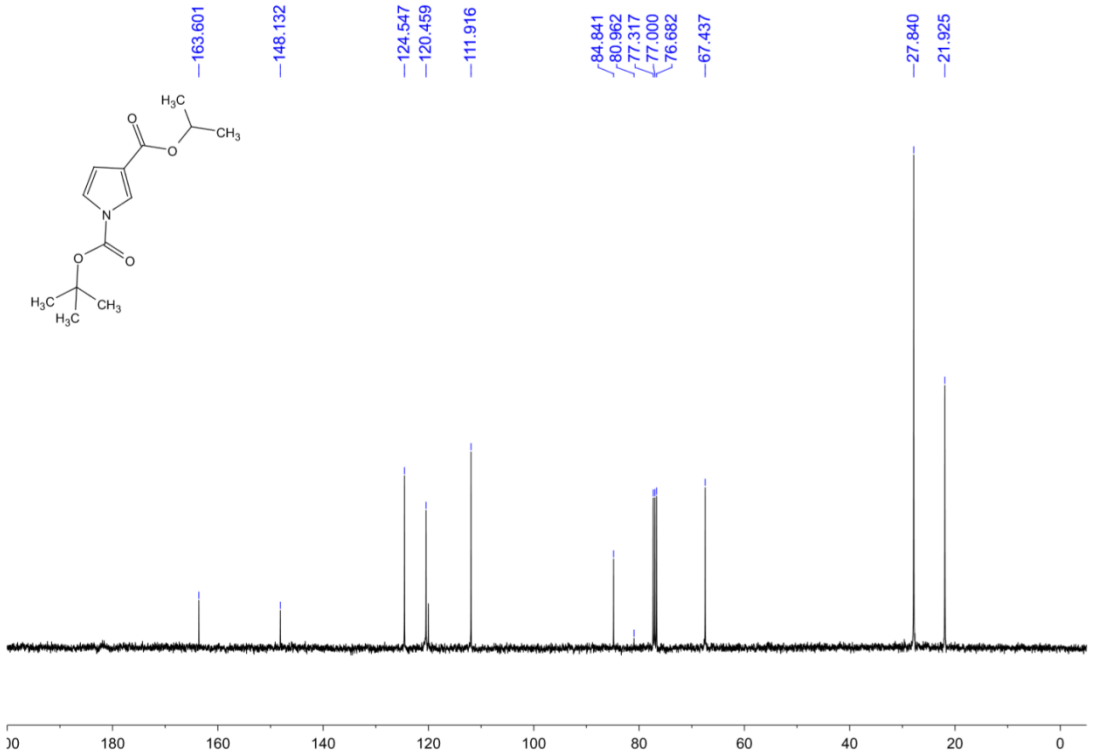

185.794
156.631
148.764
136.503
135.922
126.057
124.587
122.115
121.523
115.127
85.635
77.318
77.000
76.683
28.050
180
160
140
120
100
80
60
40
20
0

Compound 1x

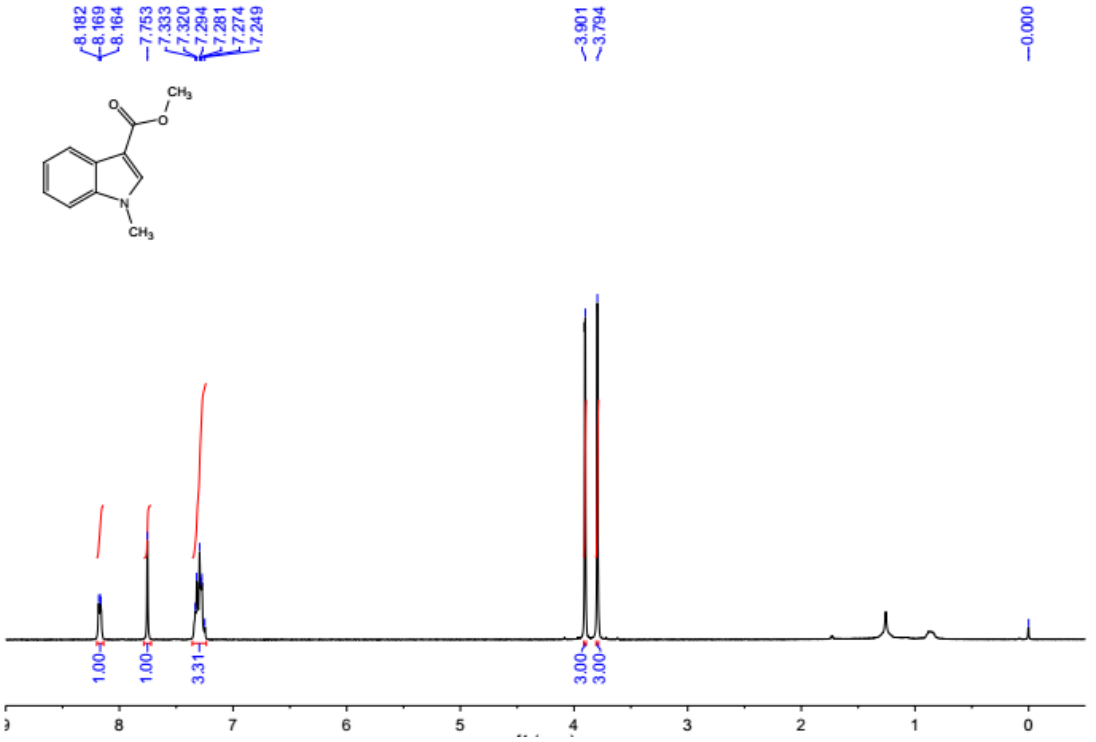

8.384
8.381
8.367
8.362
8.228
8.122
7.398
7.385
7.380
7.371
7.366
7.360
7.353
7.349
7.334
7.331
7.261
2.569
1.715
0.000
1.01
1.00
1.00
2.05
3.02
9.03
193.916
149.133
135.487
132.384
127.332
125.448
124.349
122.668
120.588
114.903
85.380
77.318
77.000
76.682
28.082
27.708

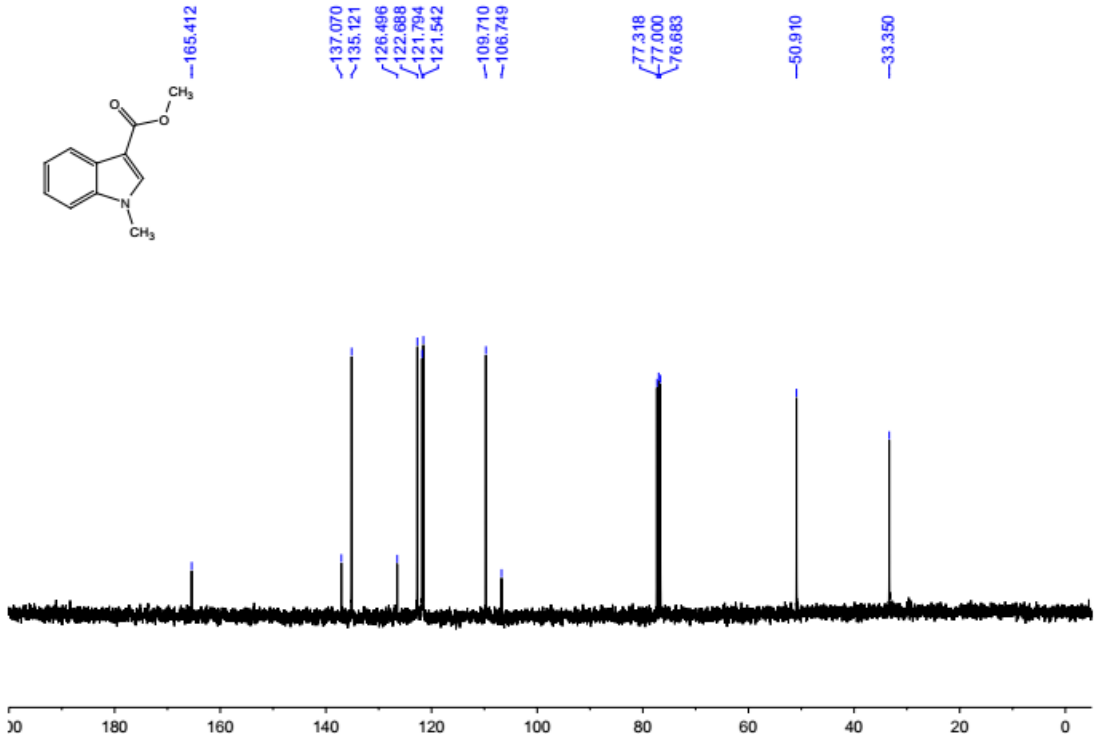
Compound 1y


7.800
7.276
7.202
7.196
7.190
6.602
6.598
6.594
6.590
5.226
5.210
5.194
5.180
5.179
5.164
5.149
5.133
1.612
1.331
1.316
0.000
1.00
1.01
1.00
1.01
9.08
6.06

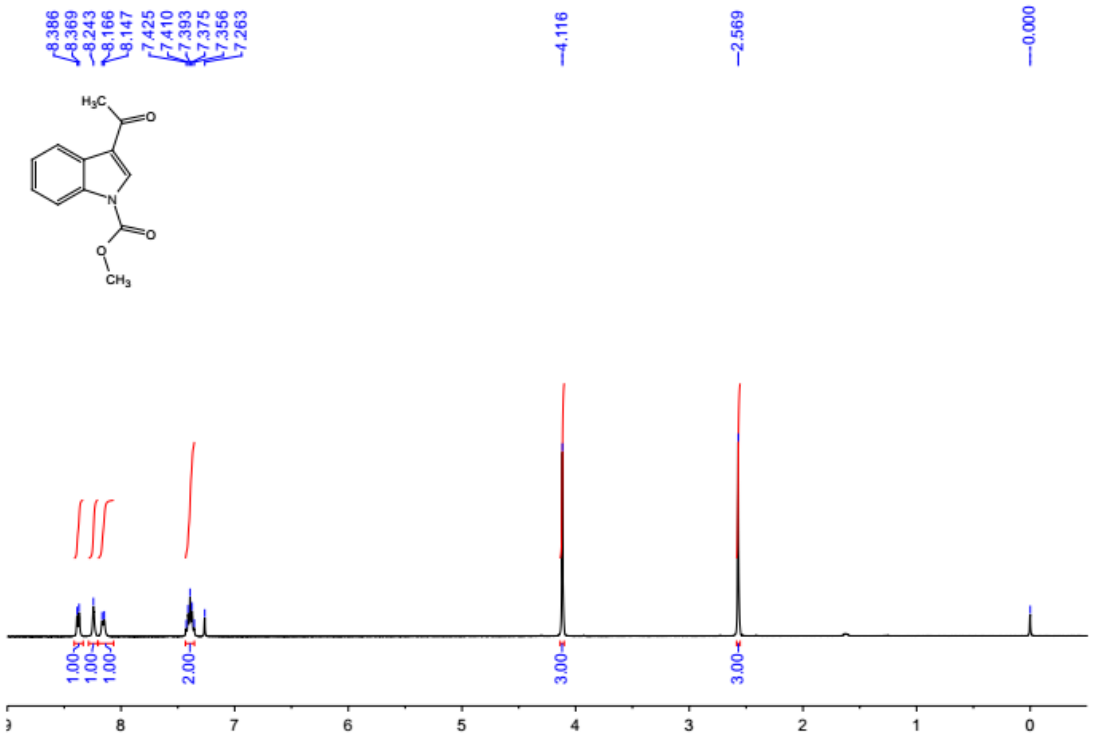

163.601
148.132
124.547
120.459
111.916
84.841
80.962
77.317
77.000
76.682
67.437
27.840
21.925

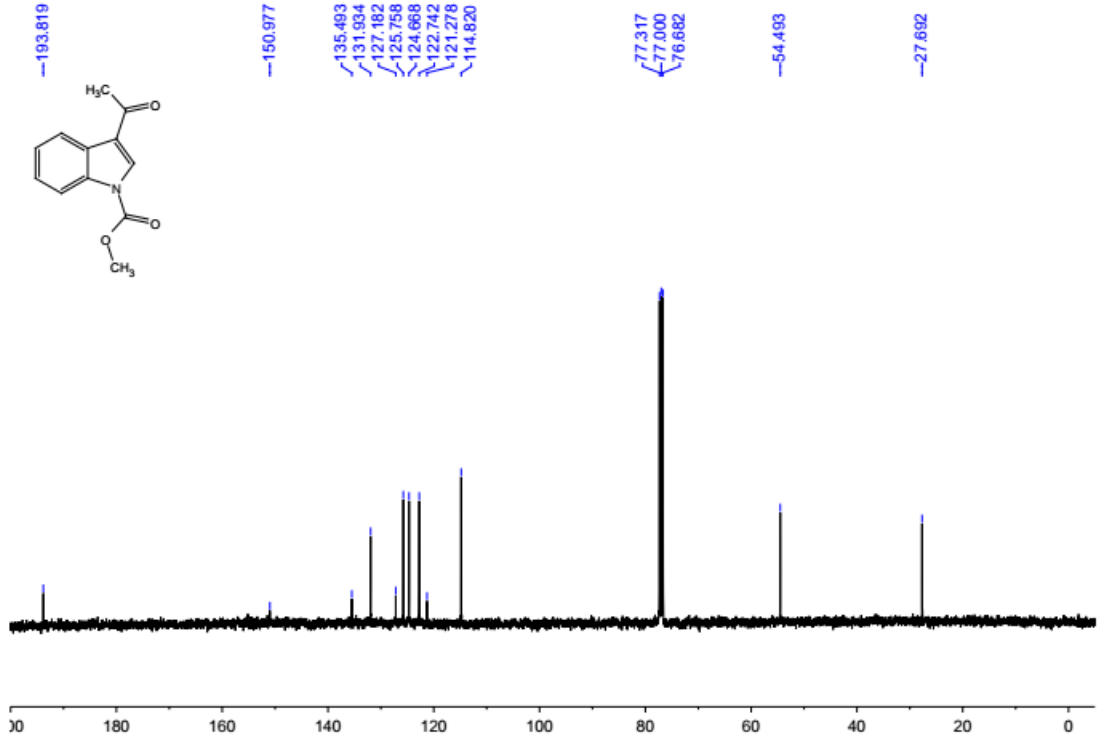
Compound S2


8.182
8.169
8.164
7.753
7.333
7.320
7.294
7.281
7.274
7.249
3.901
3.794
0.000
1.00
1.00
3.31
3.00
3.00

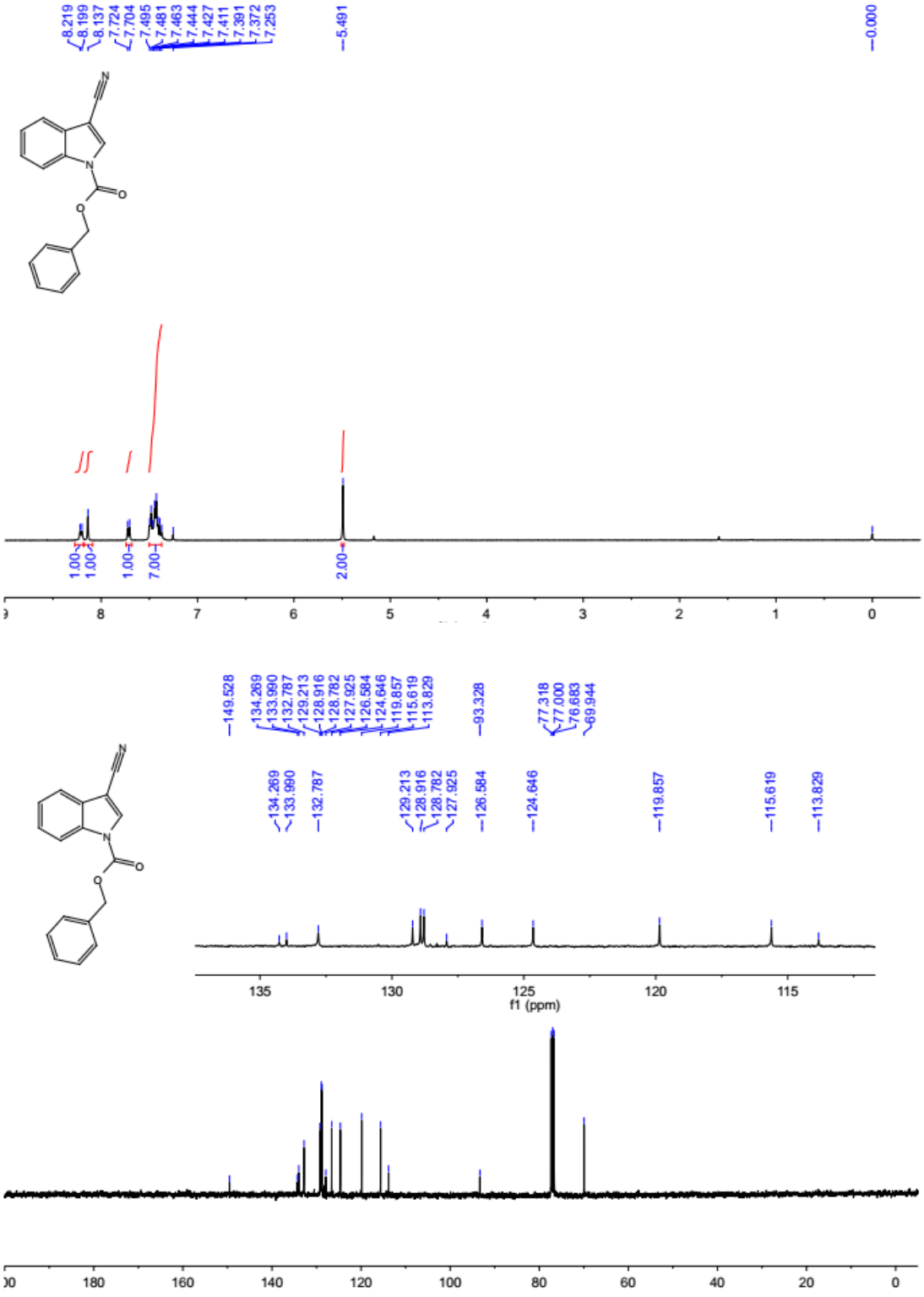

165.412
137.070
135.121
126.496
122.688
121.794
121.542
109.710
106.749
77.318
77.000
76.683
50.910
33.350

Compound S3

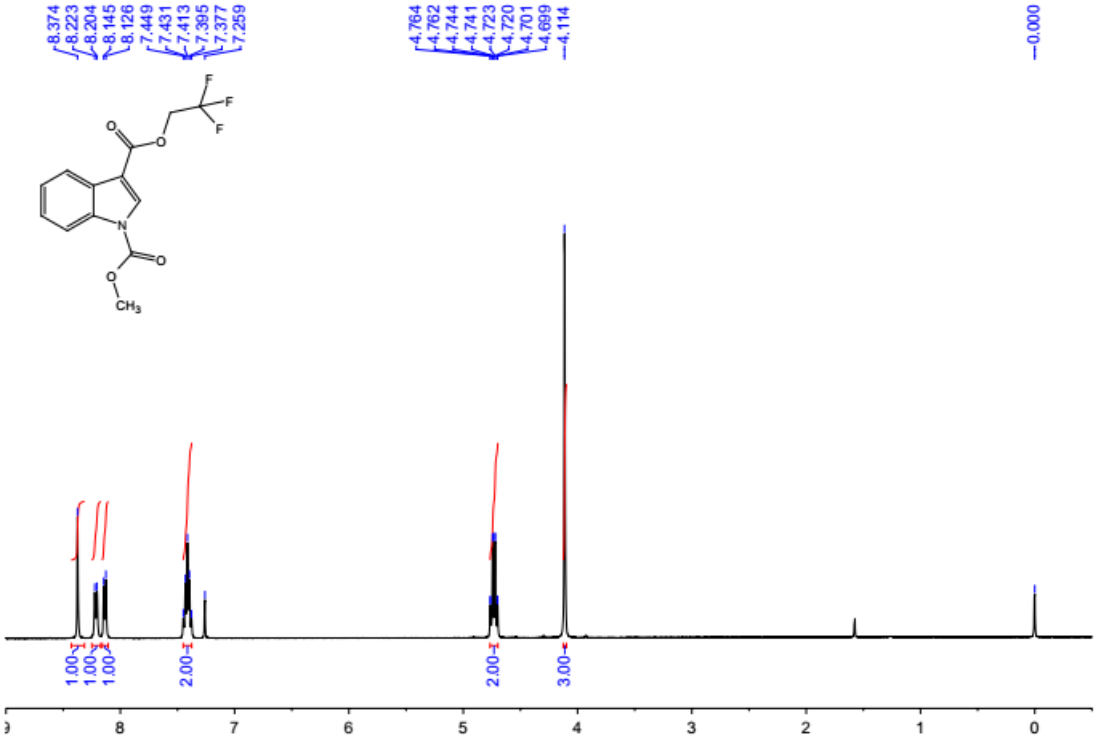

8.386
8.369
8.243
8.166
8.147
7.425
7.410
7.393
7.375
7.356
7.263
4.116
2.569
0.000
1.00
1.00
1.00
2.00
3.00
3.00

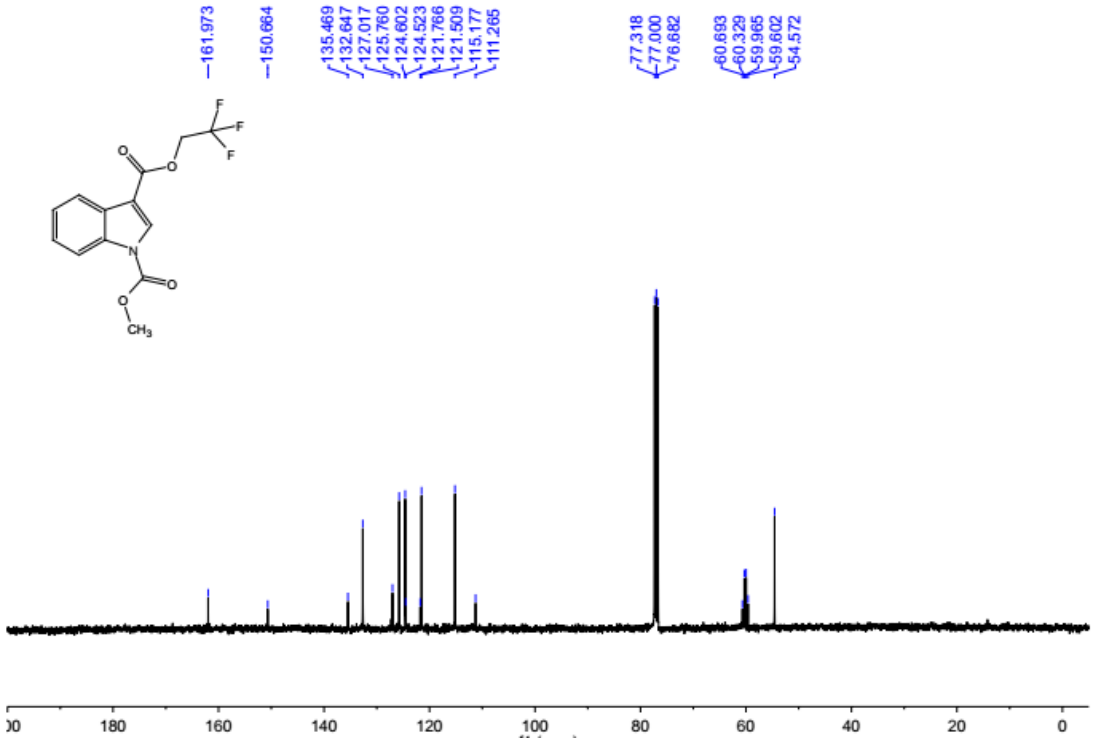

193.819
150.977
135.493
131.934
127.182
125.758
124.668
122.742
121.278
114.820
77.317
77.000
76.682
54.493
27.692

Compound S4

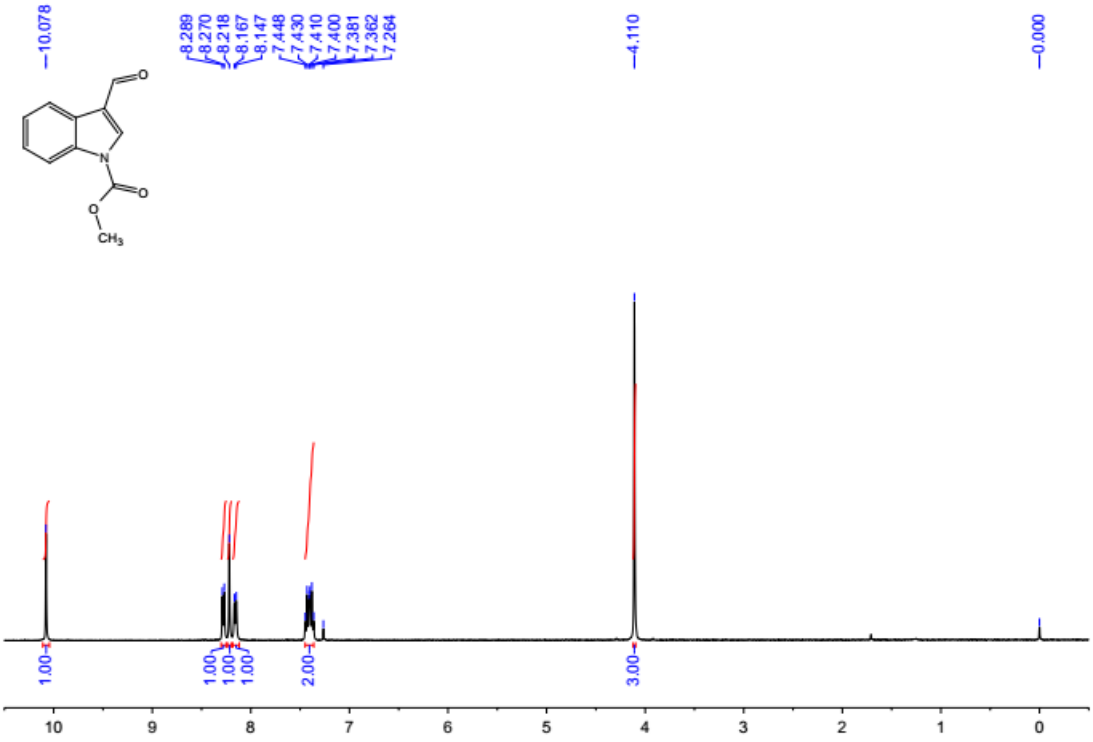

8.219
8.199
8.137
7.724
7.704
7.495
7.481
7.463
7.444
7.427
7.411
7.391
7.372
7.253
5.491
0.000
1.00
1.00
1.00
7.00
2.00
149.528
134.269
133.990
132.787
129.213
128.916
128.782
127.925
126.584
124.646
119.857
115.619
113.829
93.328
77.318
77.000
76.683
69.944
f1 (ppm)

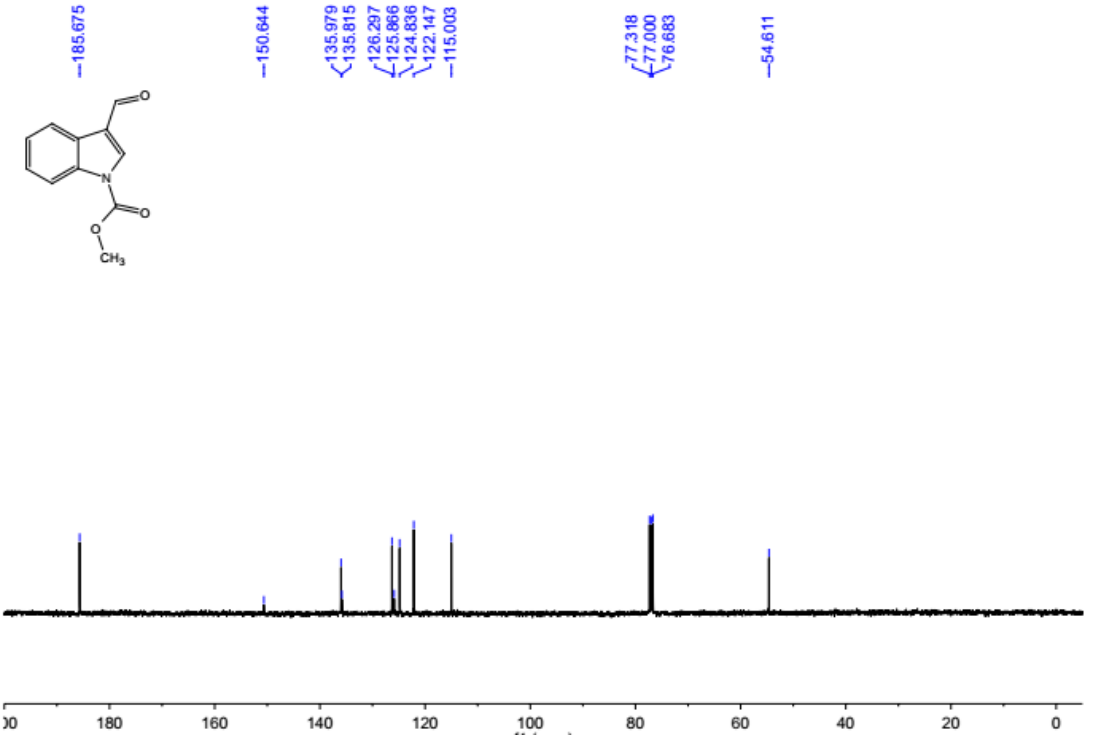
Compound S5


8.374
8.223
8.204
8.145
8.126
7.449
7.431
7.413
7.395
7.377
7.259
4.764
4.762
4.744
4.741
4.723
4.720
4.701
4.699
4.114
0.000
1.00
1.00
1.00
2.00
2.00
3.00

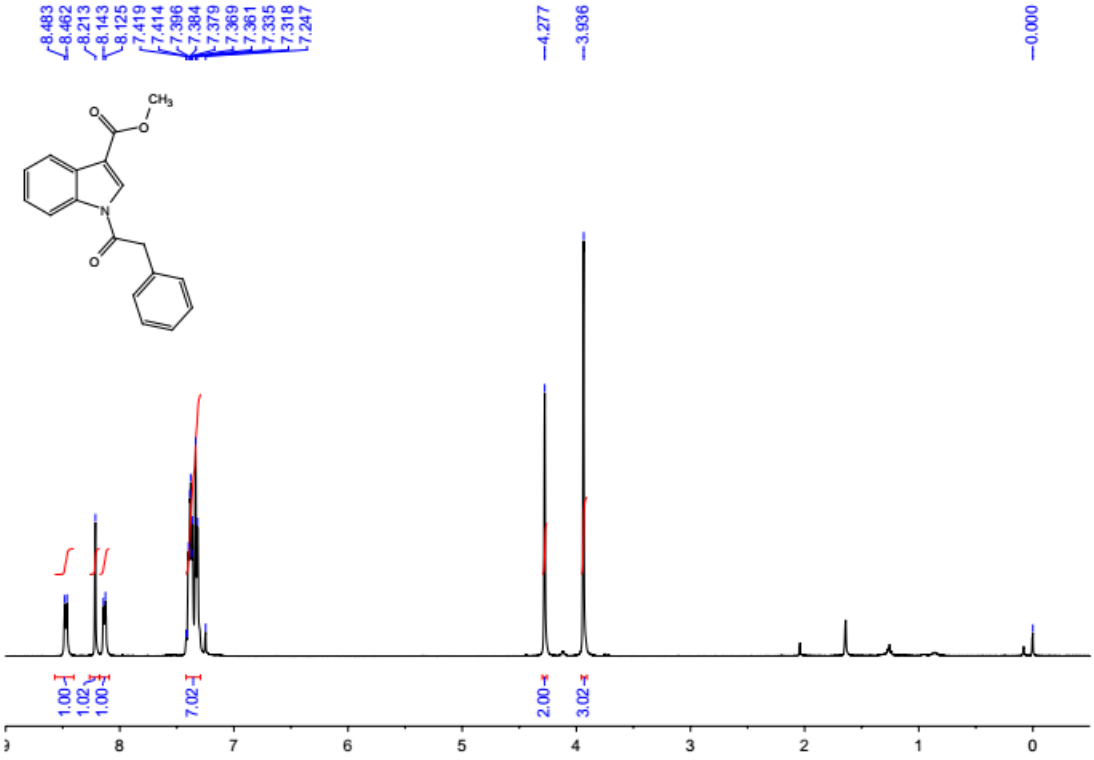

161.973
150.664
135.469
132.647
127.017
125.760
124.602
124.523
121.766
121.509
115.177
111.265
77.318
77.000
76.682
60.693
60.329
59.965
59.602
54.572

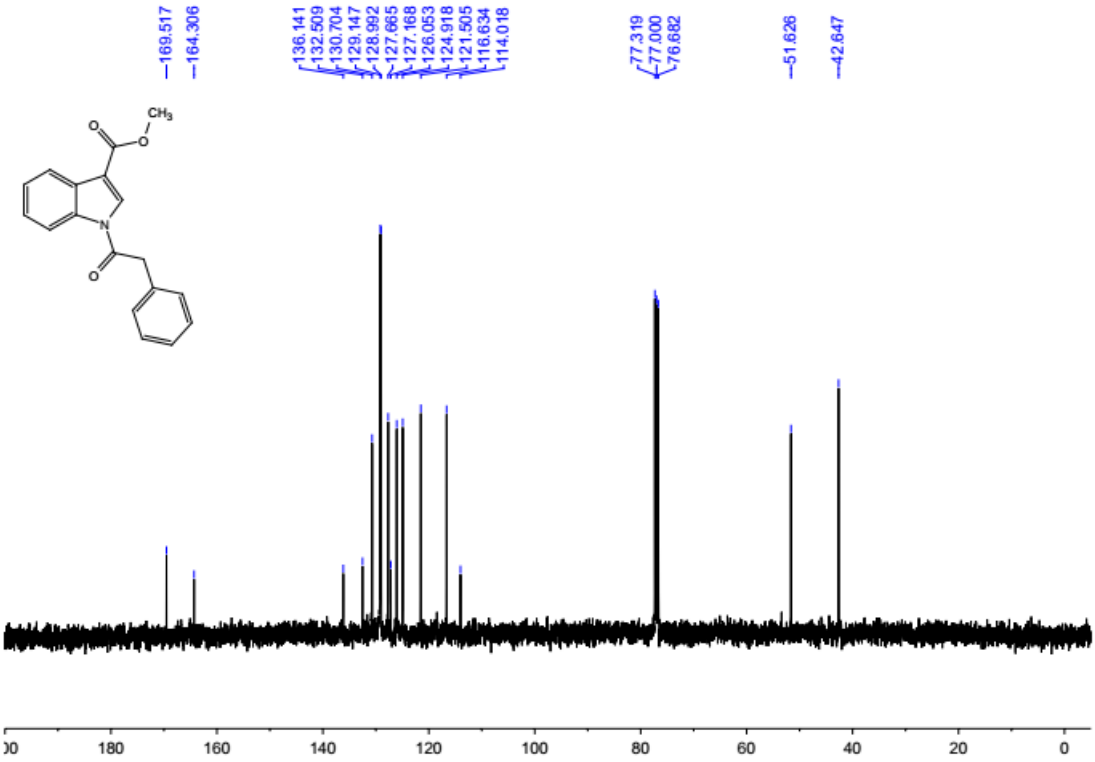
Compound S6


10.078
8.289
8.270
8.218
8.167
8.147
7.448
7.430
7.410
7.400
7.381
7.362
7.264
4.110
0.000
1.00
1.00
1.00
1.00
2.00
3.00
10
9
8
7
6
5
4
3
2
1
0

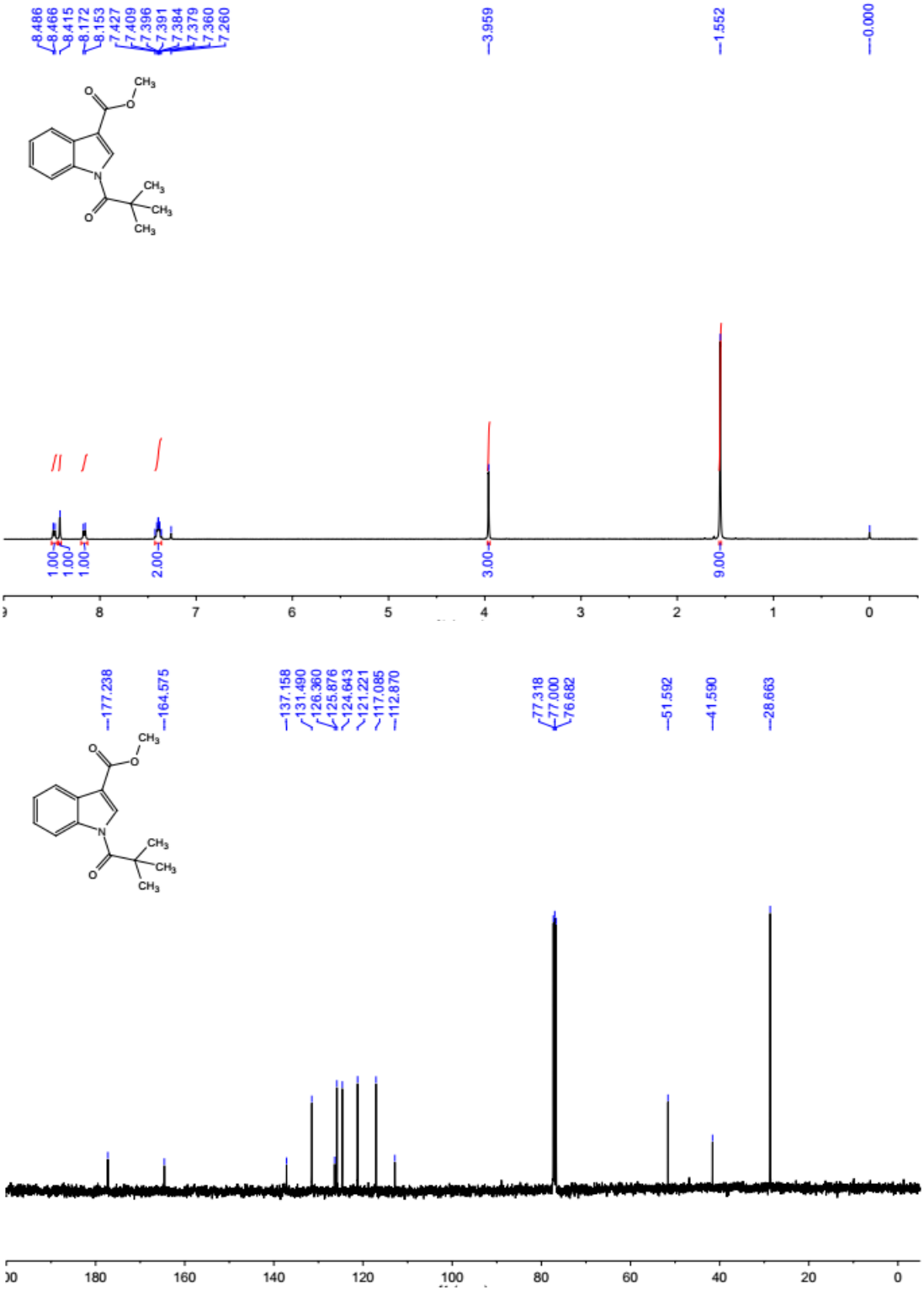

185.675
150.644
135.979
135.815
126.297
125.866
124.836
122.147
115.003
77.318
77.000
76.683
54.611
180
160
140
120
100
80
60
40
20
0

Compound S7

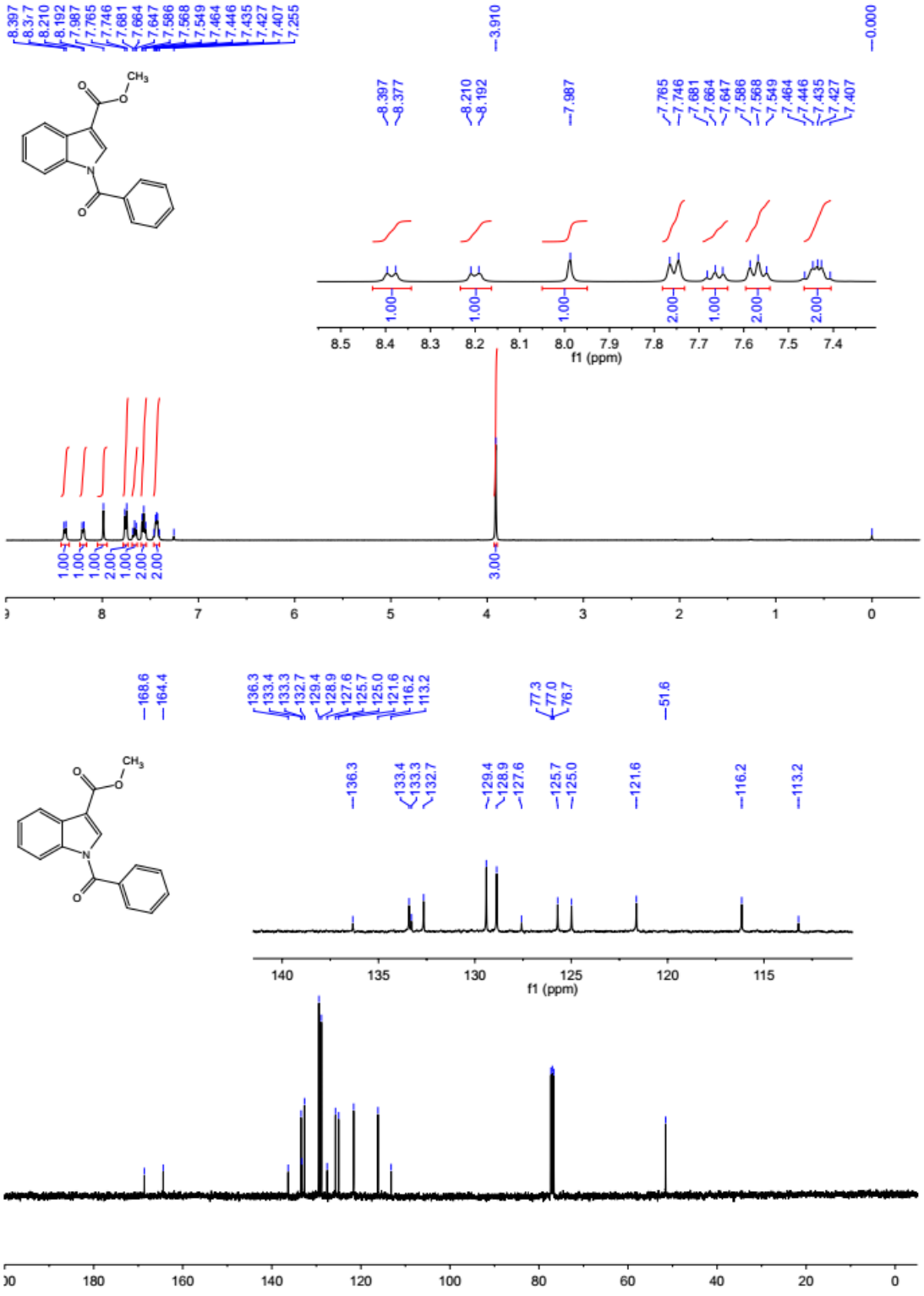

8.483
8.462
8.213
8.143
8.125
7.419
7.414
7.396
7.384
7.379
7.369
7.361
7.335
7.318
7.247
4.277
3.936
0.000
1.00
1.02
1.00
7.02
2.00
3.02


169.517
164.306
136.141
132.509
130.704
129.147
128.992
127.665
127.168
126.053
124.918
121.505
116.634
114.018
77.319
77.000
76.682
51.626
42.647

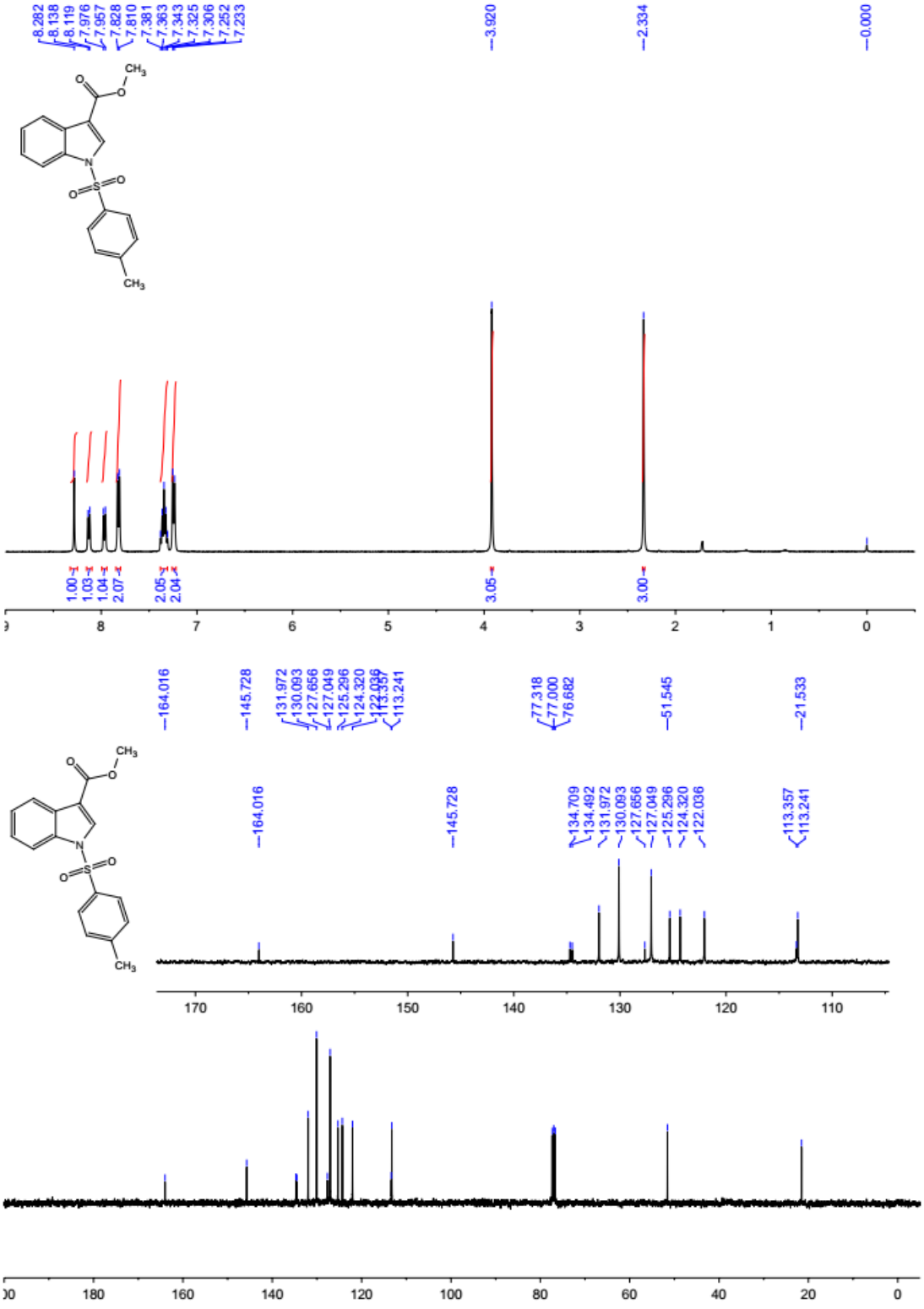
Compound S8


8.486
8.466
8.415
8.172
8.153
7.427
7.409
7.396
7.391
7.384
7.379
7.360
7.260
3.959
1.552
0.000
1.00
1.00
1.00
2.00
3.00
9.00
177.238
164.575
137.158
131.490
126.360
125.876
124.643
121.221
117.085
112.870
77.318
77.000
76.682
51.592
41.590
28.663

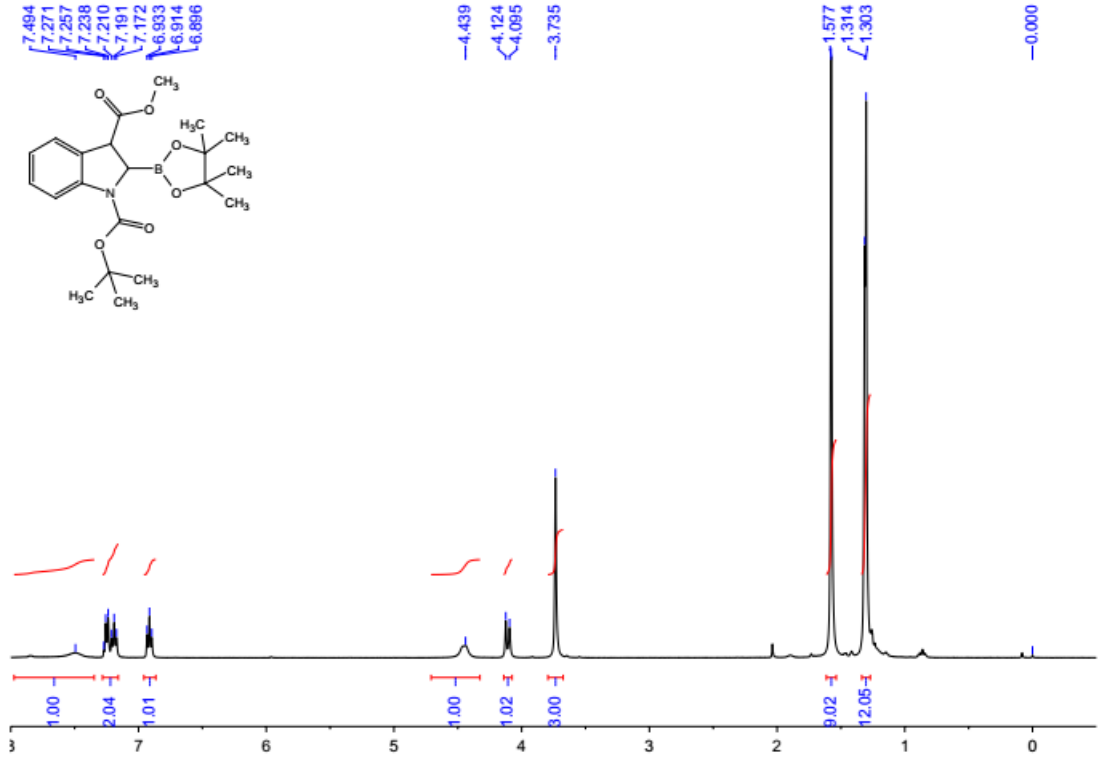
Compound S9

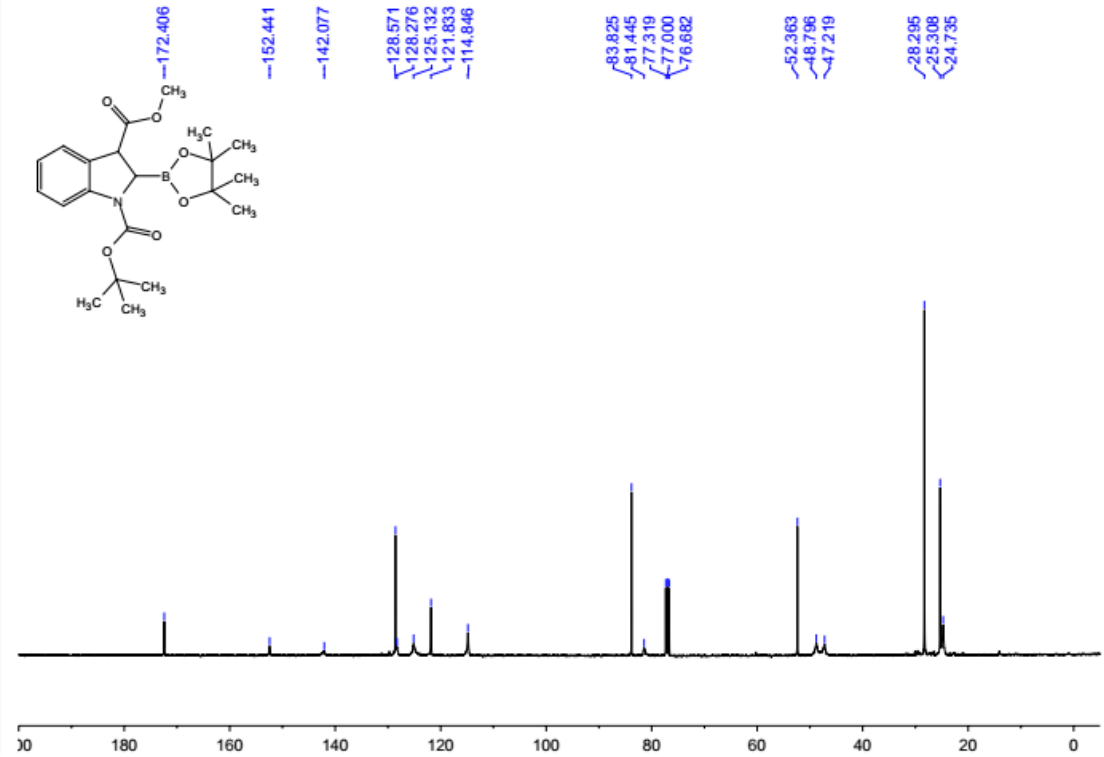


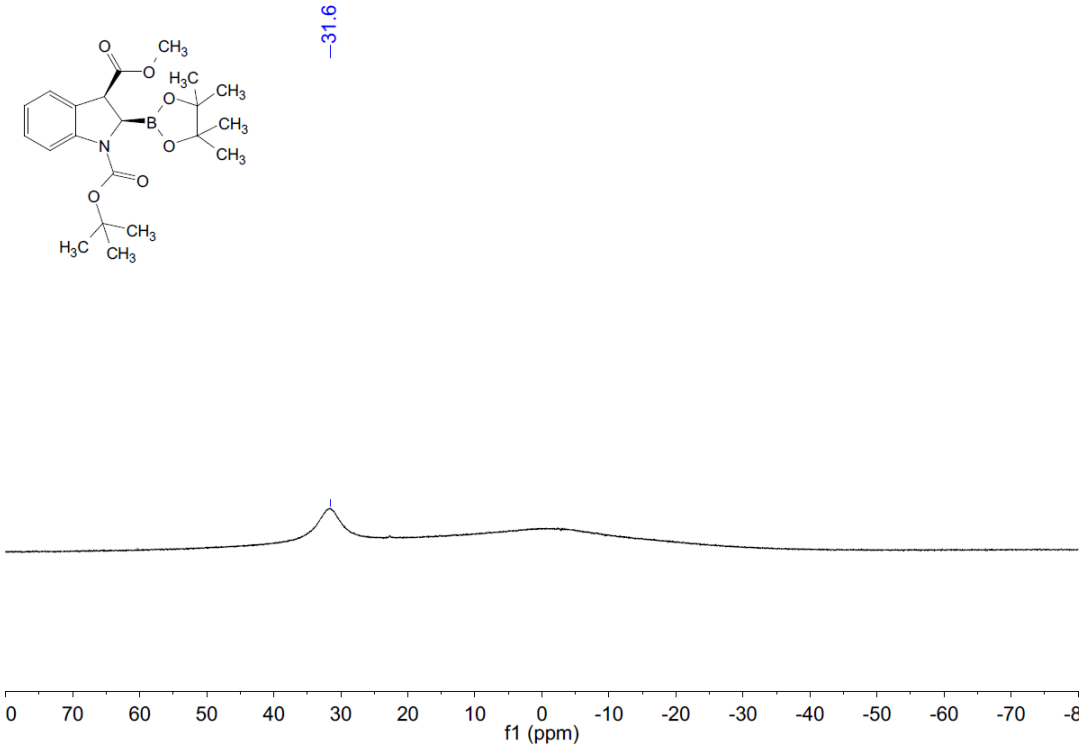
Compound S10



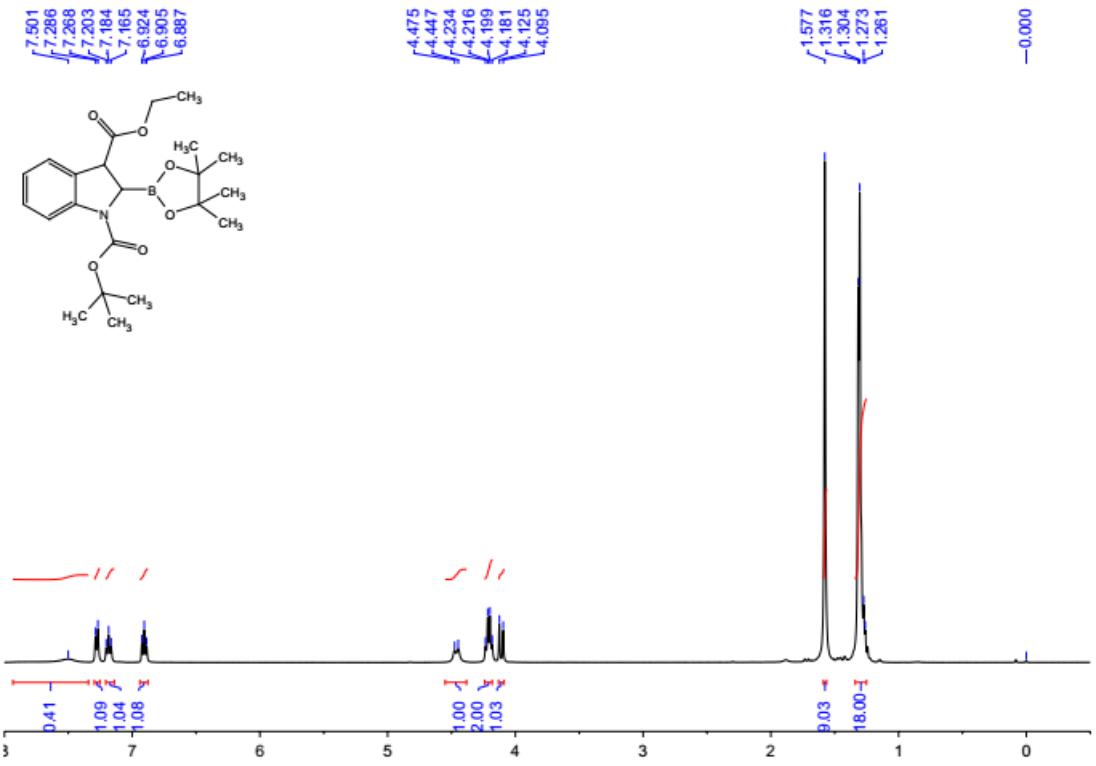
Compound 2a

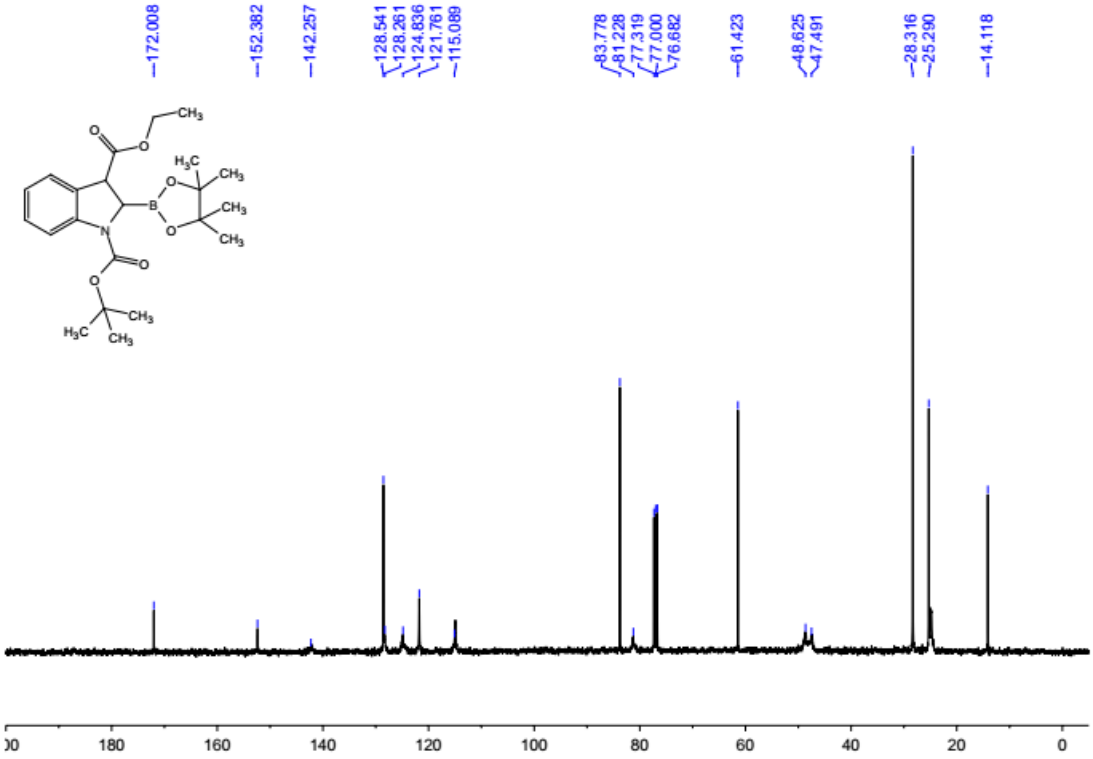

7.494
7.271
7.257
7.238
7.210
7.191
7.172
6.933
6.914
6.896
4.439
4.124
4.095
3.735
1.577
1.314
1.303
0.000
1.00
2.04
1.01
1.00
1.02
3.00
9.02
12.05

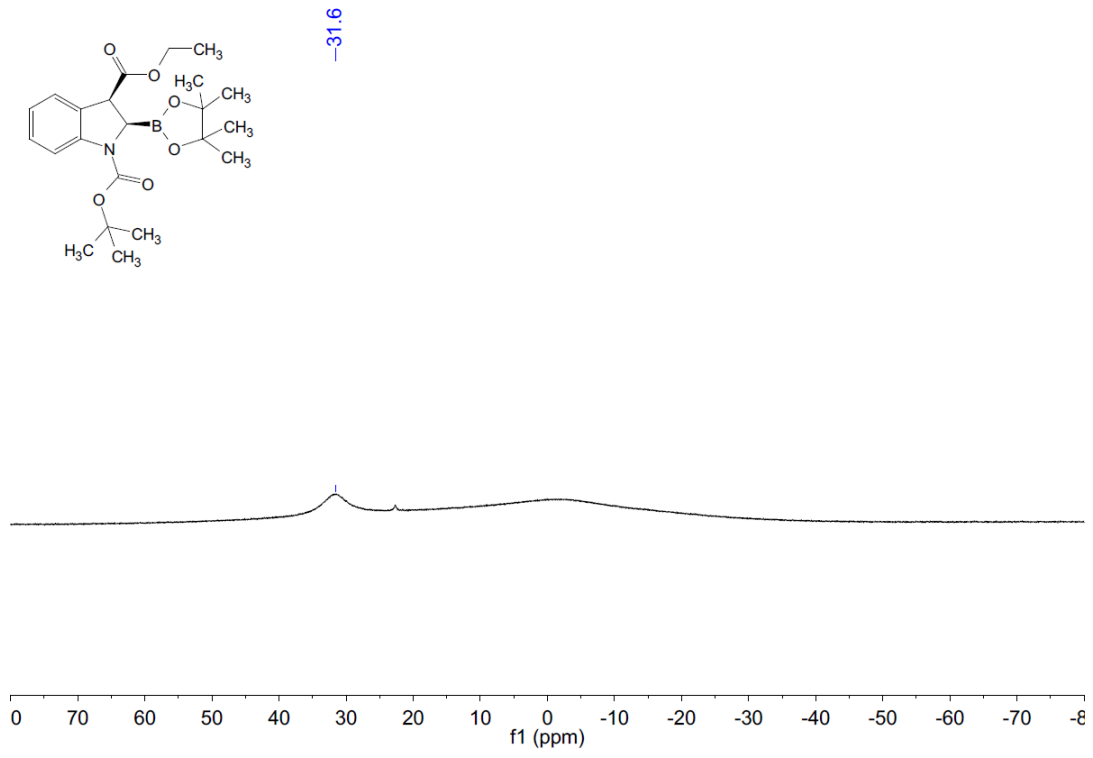

172.406
152.441
142.077
128.571
128.276
125.132
121.833
114.846
83.825
81.445
77.319
77.000
76.682
52.363
48.796
47.219
28.295
25.308
24.735


31.6
f1 (ppm)

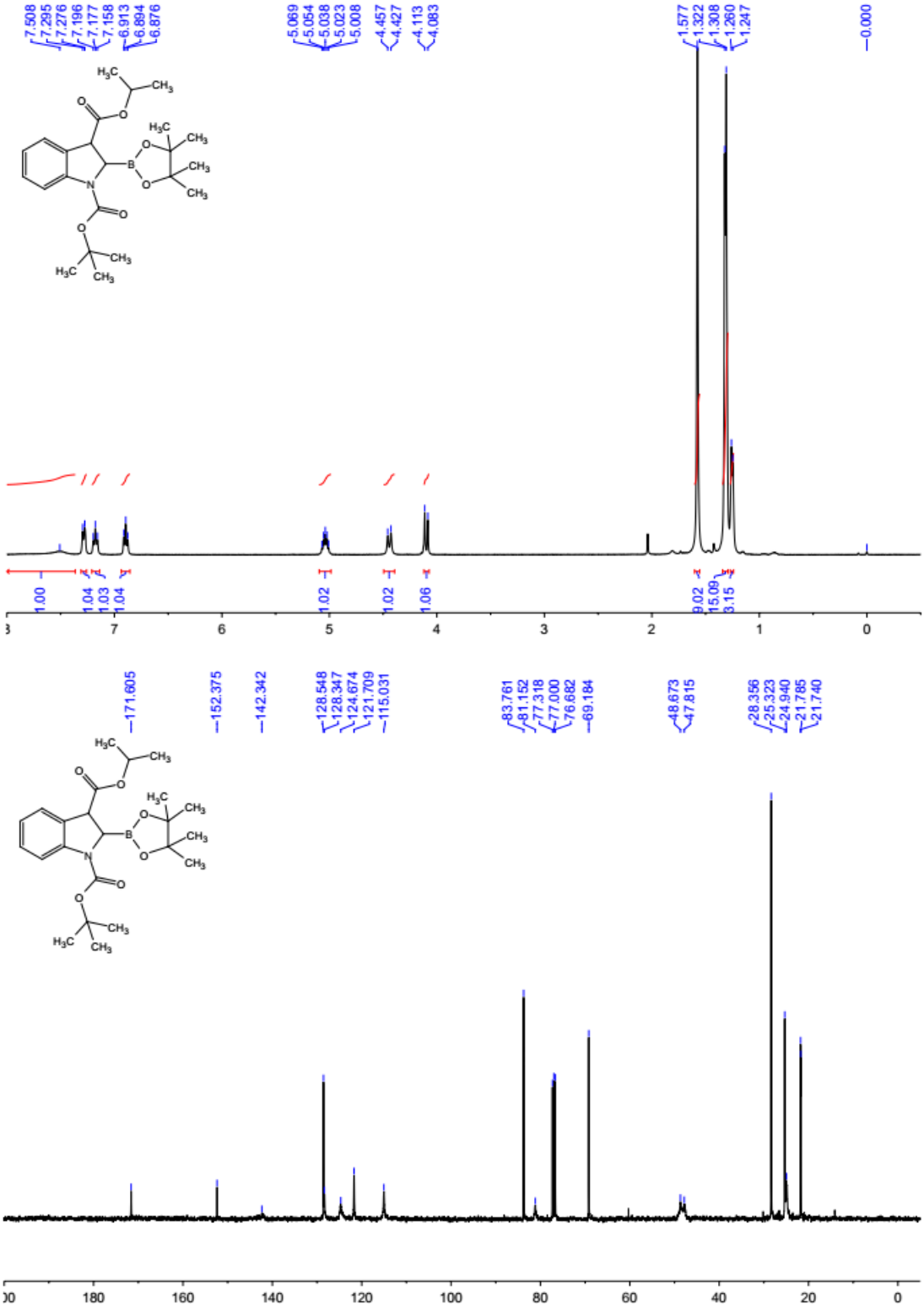
Compound 2b

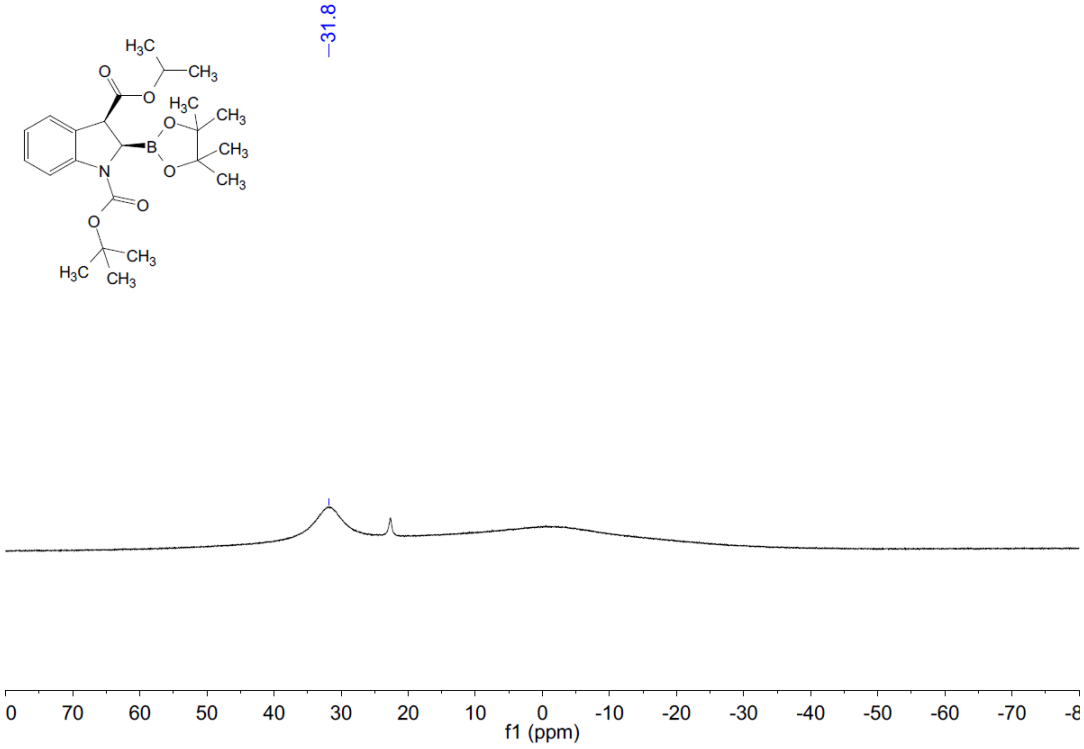

7.501
7.286
7.268
7.203
7.184
7.165
6.924
6.905
6.887
4.475
4.447
4.234
4.216
4.199
4.181
4.125
4.095
1.577
1.316
1.304
1.273
1.261
0.000
0.41
1.09
1.04
1.08
1.00
2.00
1.03
9.03
18.00


172.008
152.382
142.257
128.541
128.261
124.836
121.761
115.089
83.778
81.228
77.319
77.000
76.682
61.423
48.625
47.491
28.316
25.290
14.118
180
160
140
120
100
80
60
40
20
0

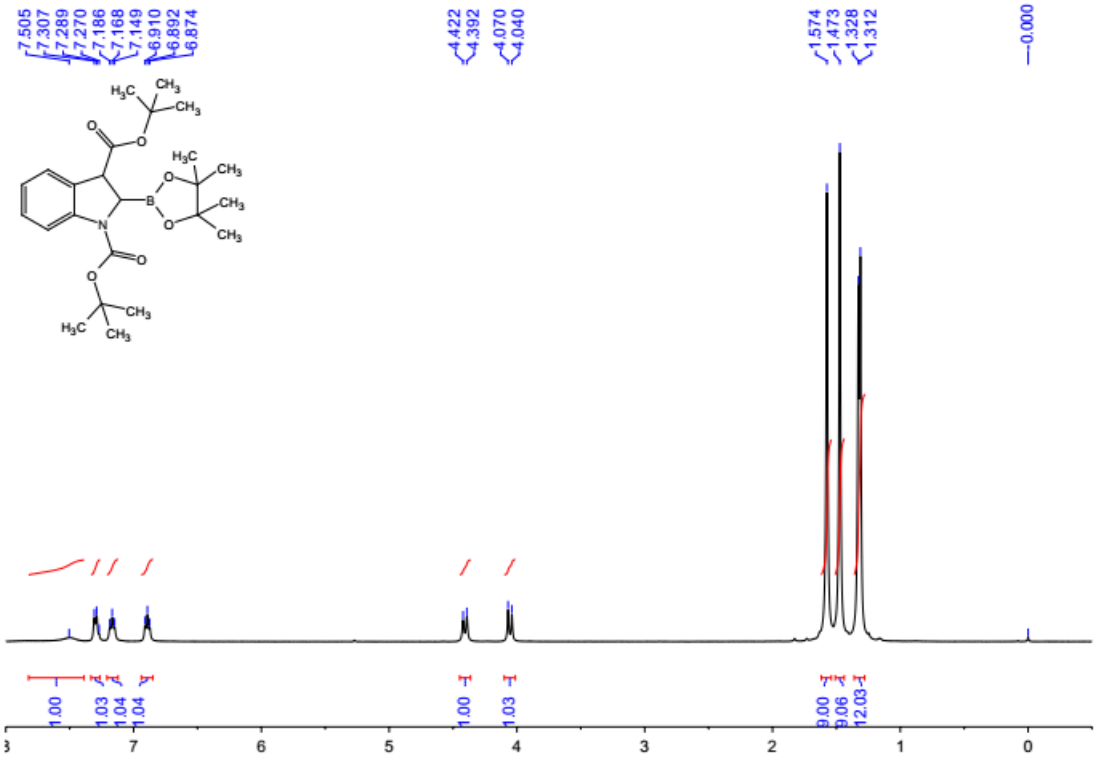

31.6
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

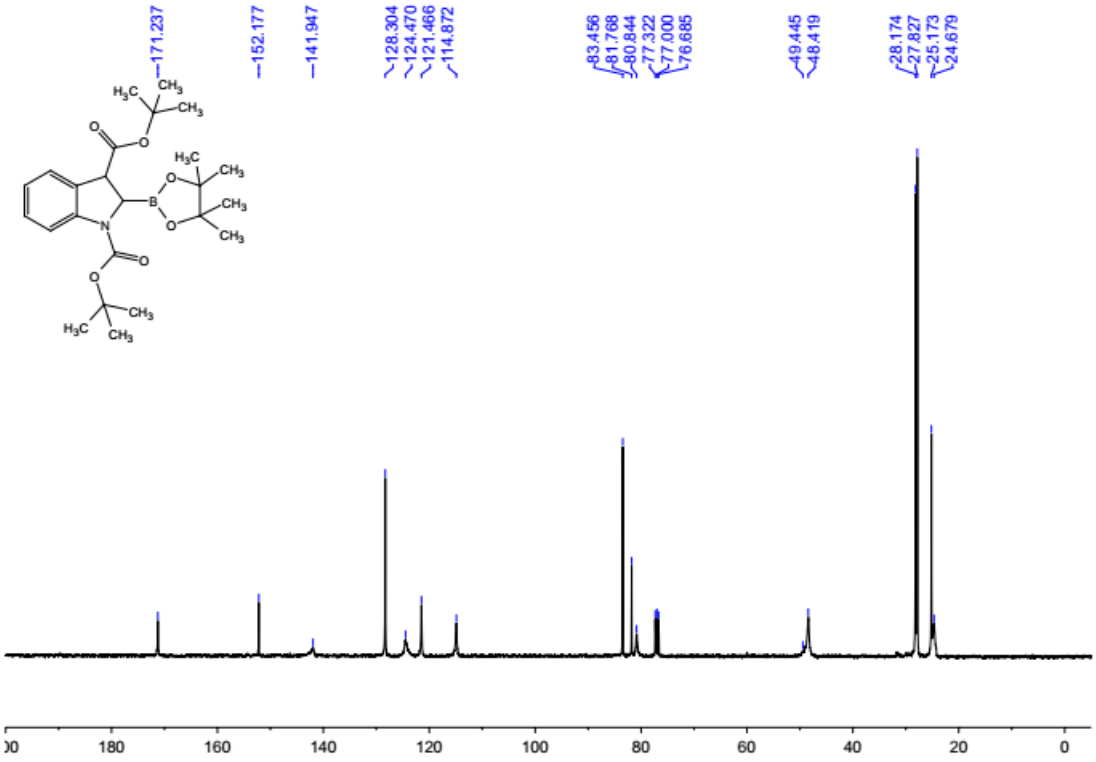
Compound 2c

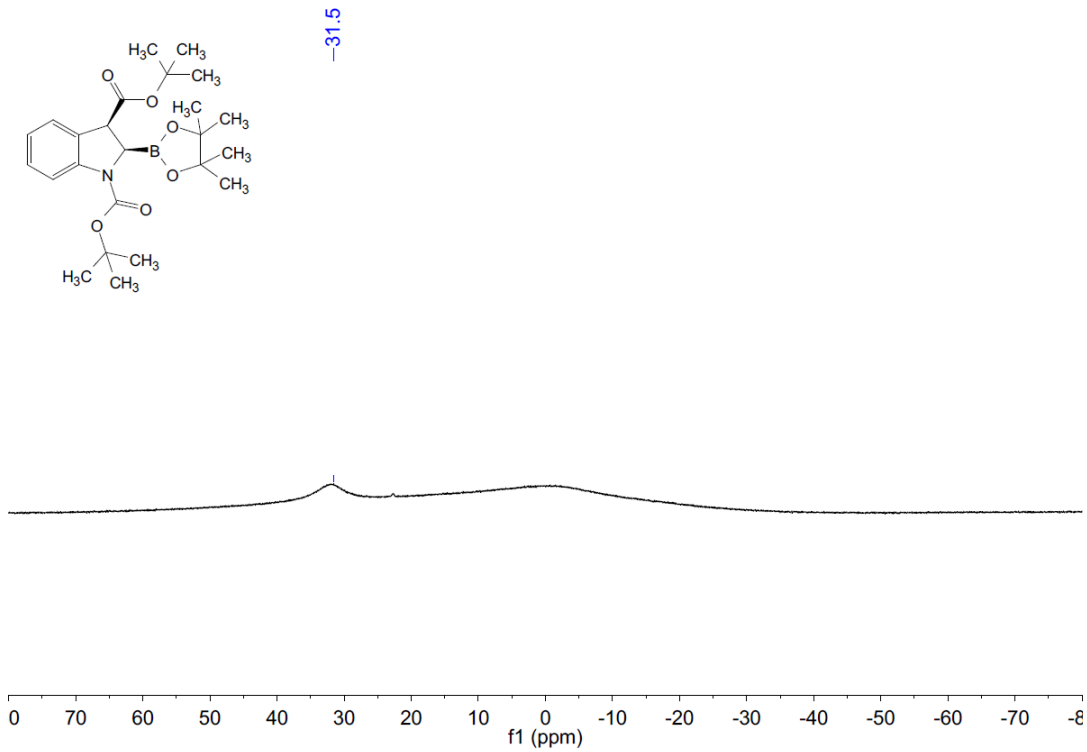

7.508
7.295
7.276
7.196
7.177
7.158
6.913
6.894
6.876
5.069
5.054
5.038
5.023
5.008
4.457
4.427
4.113
4.083
1.577
1.322
1.308
1.260
1.247
0.000
1.00
1.04
1.03
1.04
1.02
1.02
1.06
9.02
15.09
3.15
171.605
152.375
142.342
128.548
128.347
124.674
121.709
115.031
83.761
81.152
77.318
77.000
76.682
69.184
48.673
47.815
28.356
25.323
24.940
21.785
21.740


31.8
f1 (ppm)

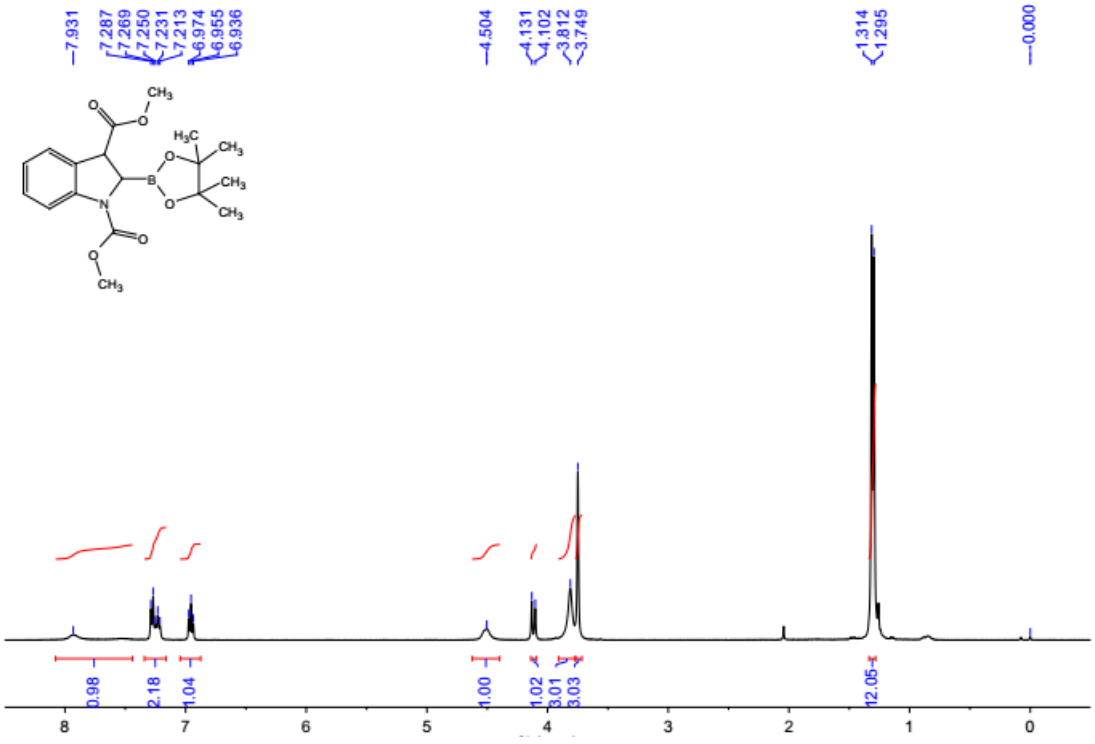
Compound 2d

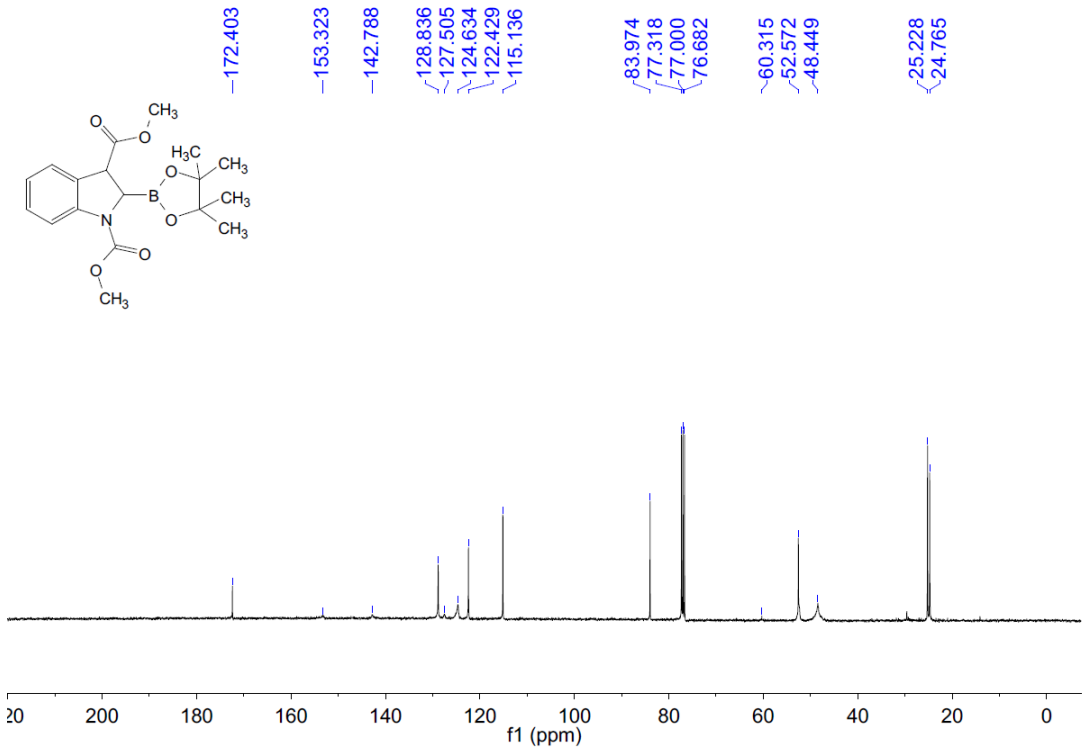

7.505
7.307
7.289
7.270
7.186
7.168
7.149
6.910
6.892
6.874
4.422
4.392
4.070
4.040
1.574
1.473
1.328
1.312
0.000
1.00
1.03
1.04
1.04
1.00
1.03
9.00
9.06
12.03

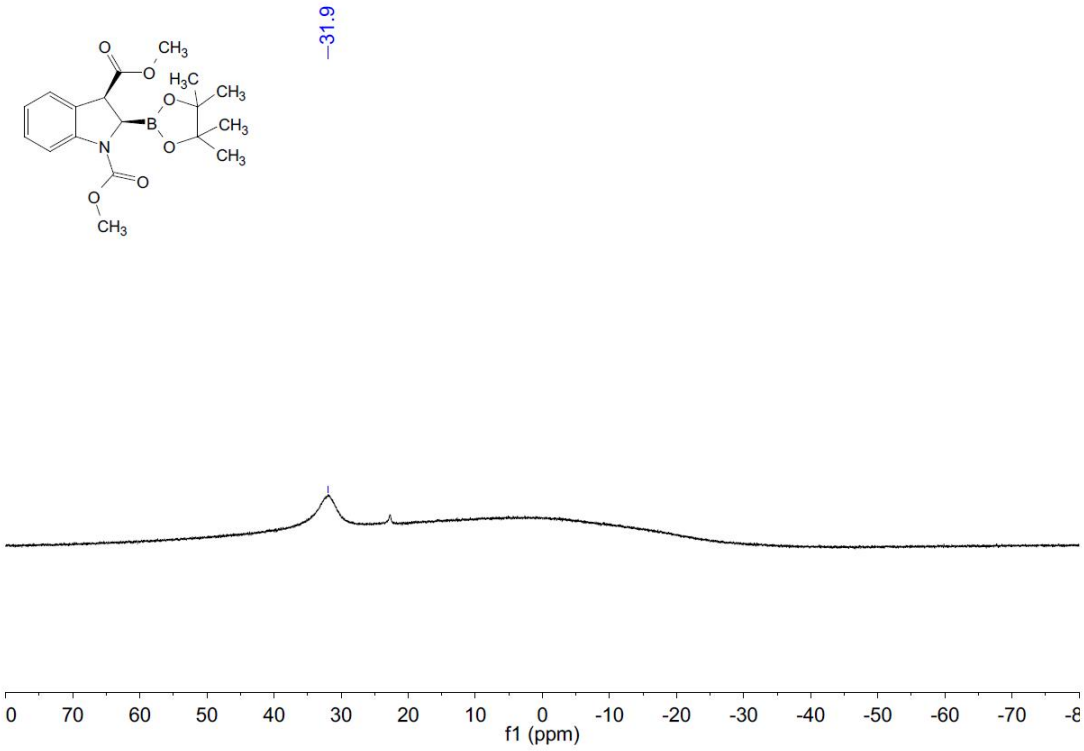

171.237
152.177
141.947
128.304
124.470
121.466
114.872
83.456
81.768
80.844
77.322
77.000
76.685
49.445
48.419
28.174
27.827
25.173
24.679
180
160
140
120
100
80
60
40
20
0


31.5
0
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

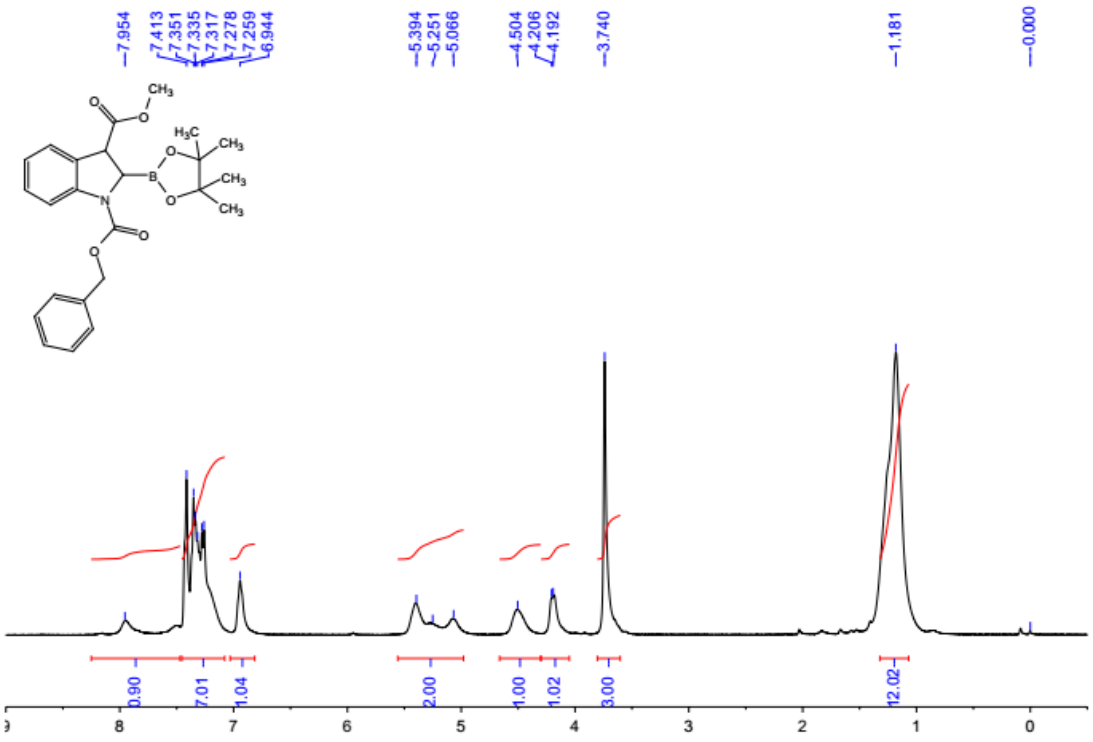
Compound 2e

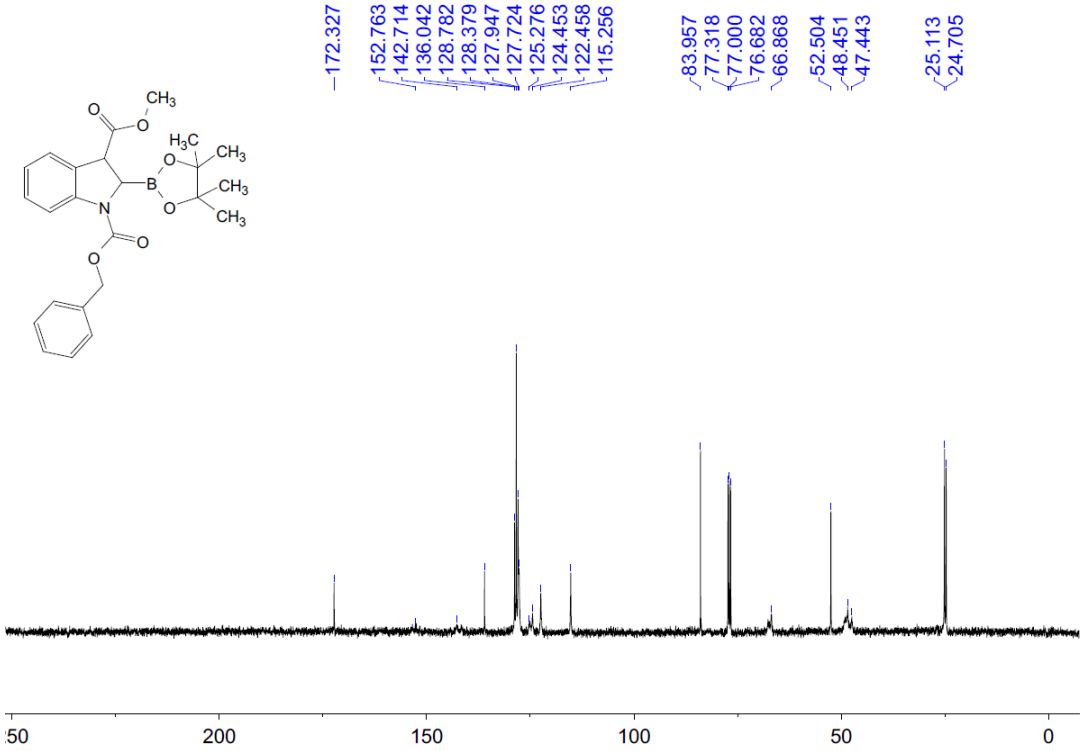

7.931
7.287
7.269
7.250
7.231
7.213
6.974
6.955
6.936
4.504
4.131
4.102
3.812
3.749
1.314
1.295
0.000
0.98
2.18
1.04
1.00
1.02
3.01
3.03
12.05

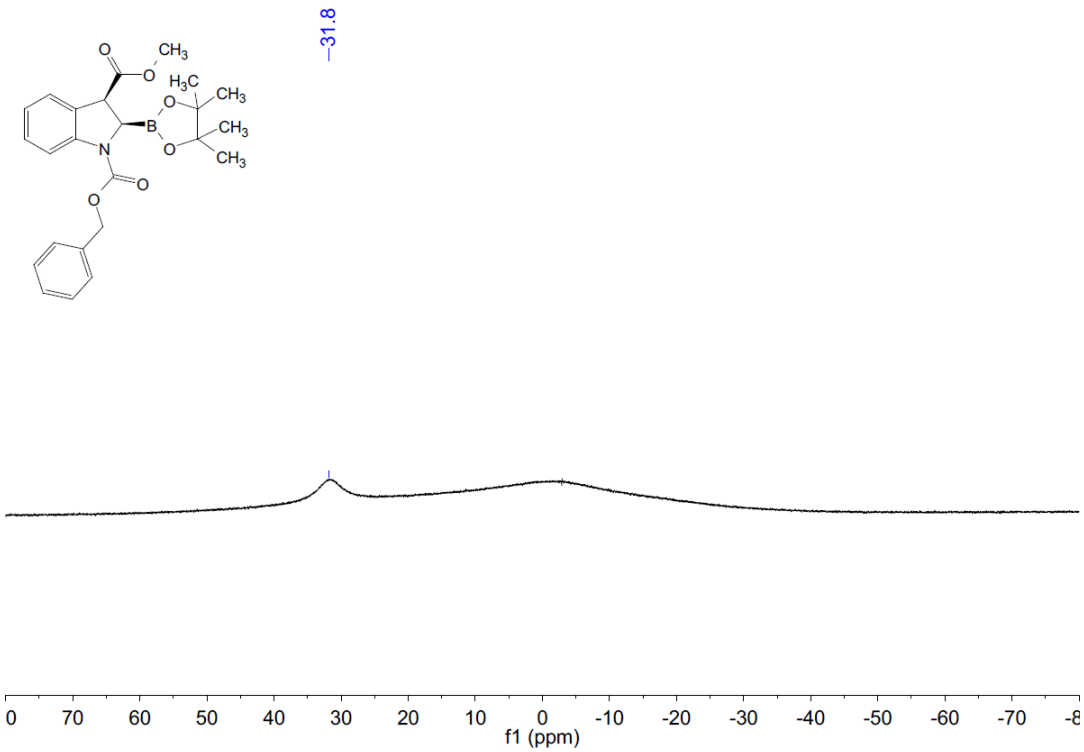

172.403
153.323
142.788
128.836
127.505
124.634
122.429
115.136
83.974
77.318
77.000
76.682
60.315
52.572
48.449
25.228
24.765
f1 (ppm)


31.9
f1 (ppm)

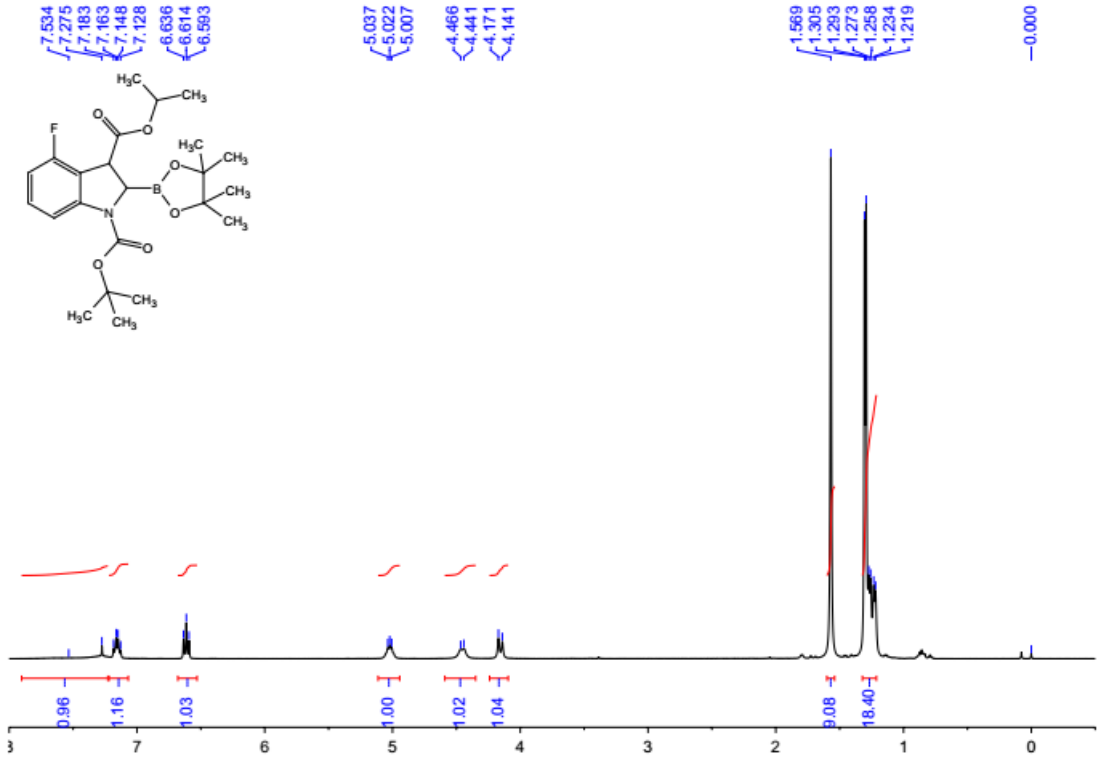
Compound 2f

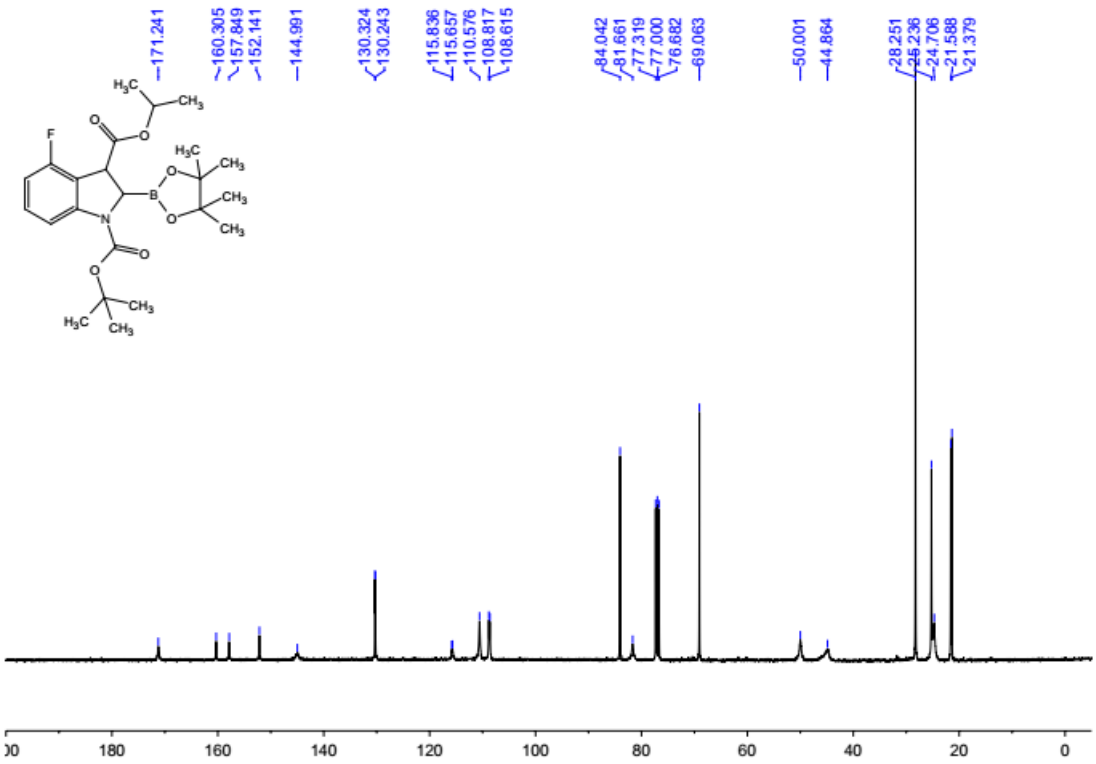

7.954
7.413
7.351
7.335
7.317
7.278
7.259
6.944
5.394
5.251
5.066
4.504
4.206
4.192
3.740
1.181
0.000
0.90
7.01
1.04
2.00
1.00
1.02
3.00
12.02

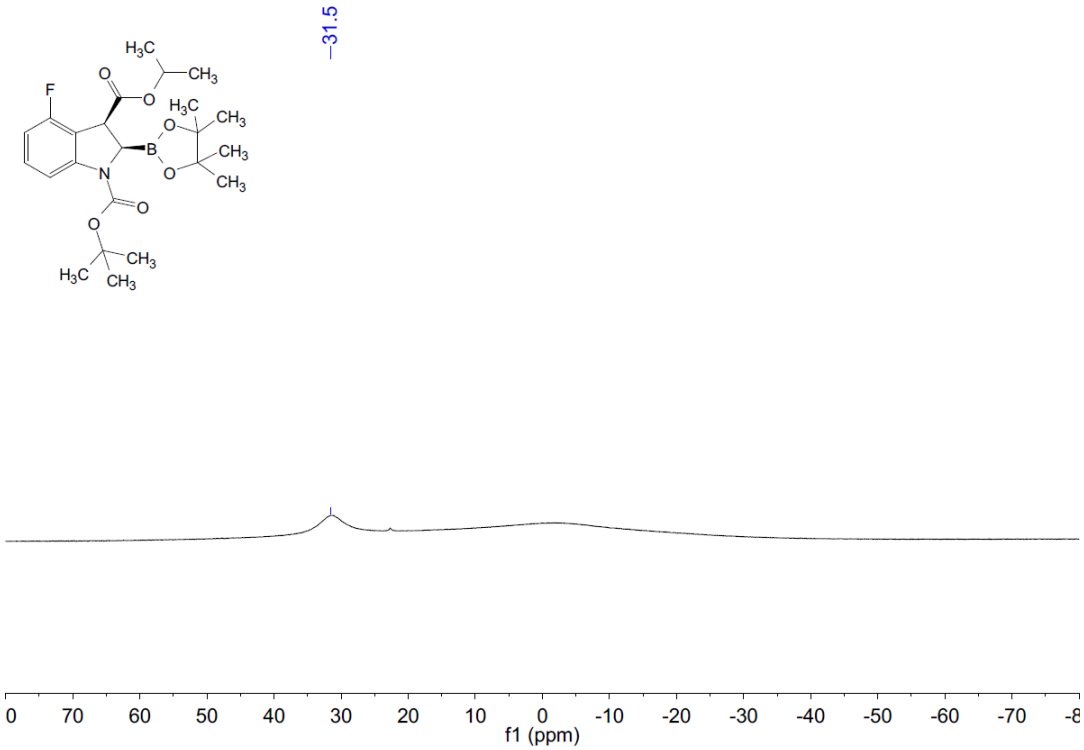

172.327
152.763
142.714
136.042
128.782
128.379
127.947
127.724
125.276
124.453
122.458
115.256
83.957
77.318
77.000
76.682
66.868
52.504
48.451
47.443
25.113
24.705
50
200
150
100
50
0


31.8
0
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

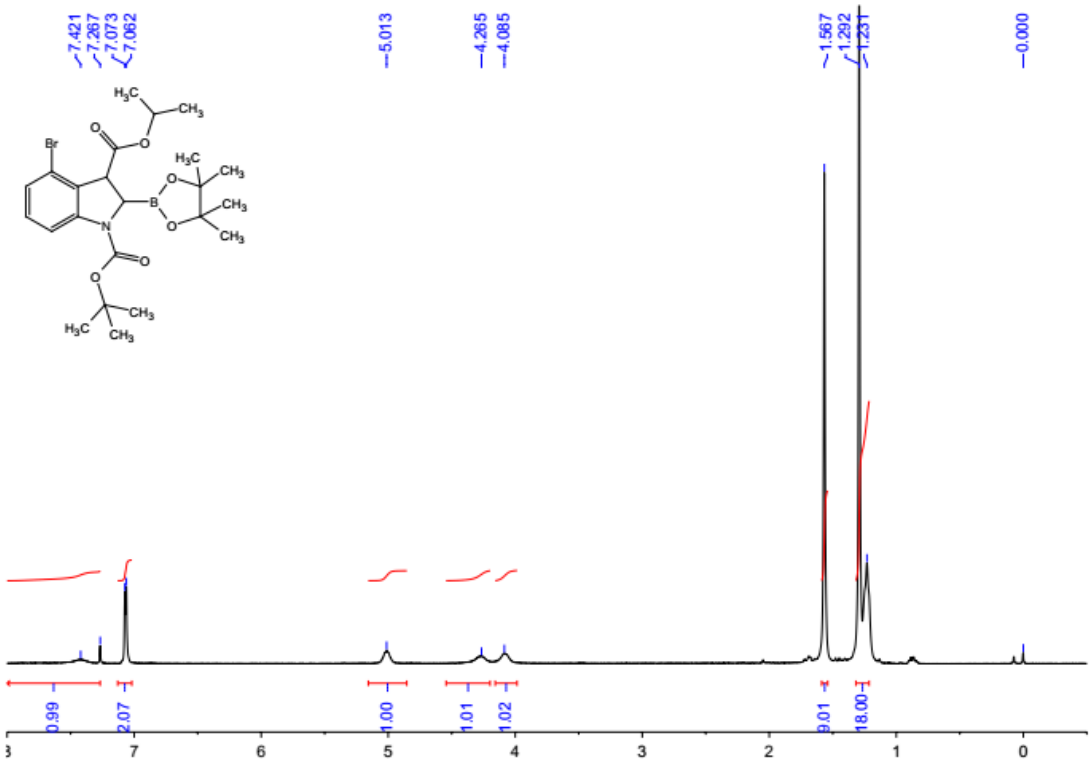
Compound 2g

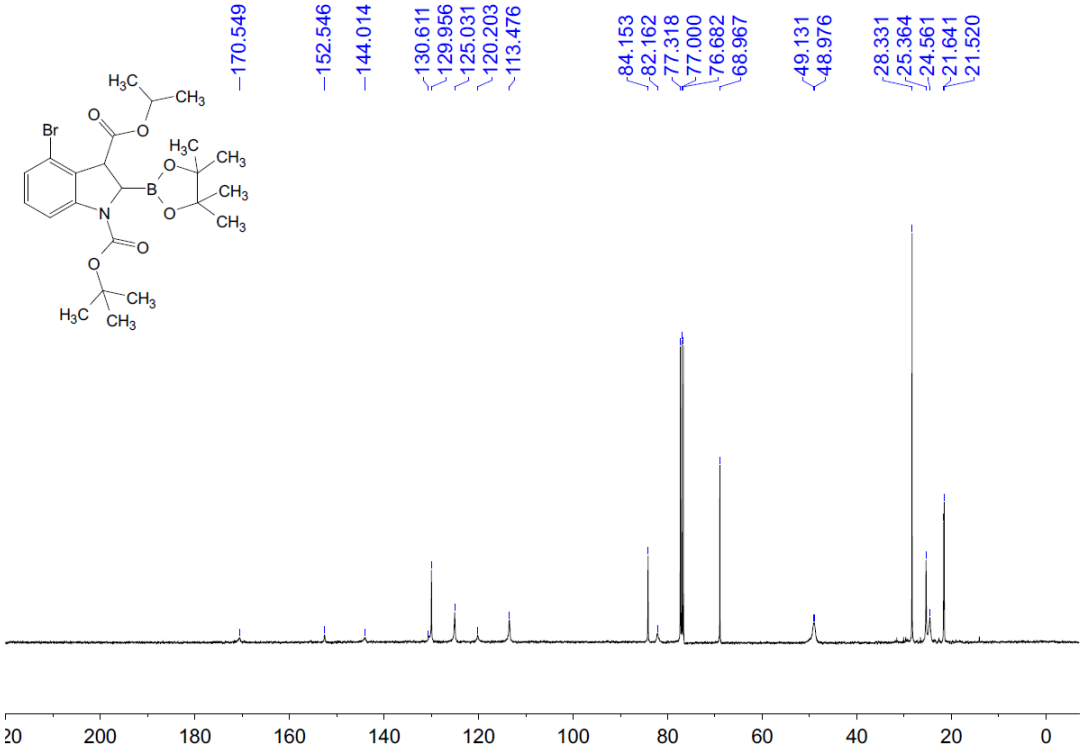

7.534
7.275
7.183
7.163
7.148
7.128
6.636
6.614
6.593
5.037
5.022
5.007
4.466
4.441
4.171
4.141
1.569
1.305
1.293
1.273
1.258
1.234
1.219
0.000
0.96
1.16
1.03
1.00
1.02
1.04
9.08
18.40

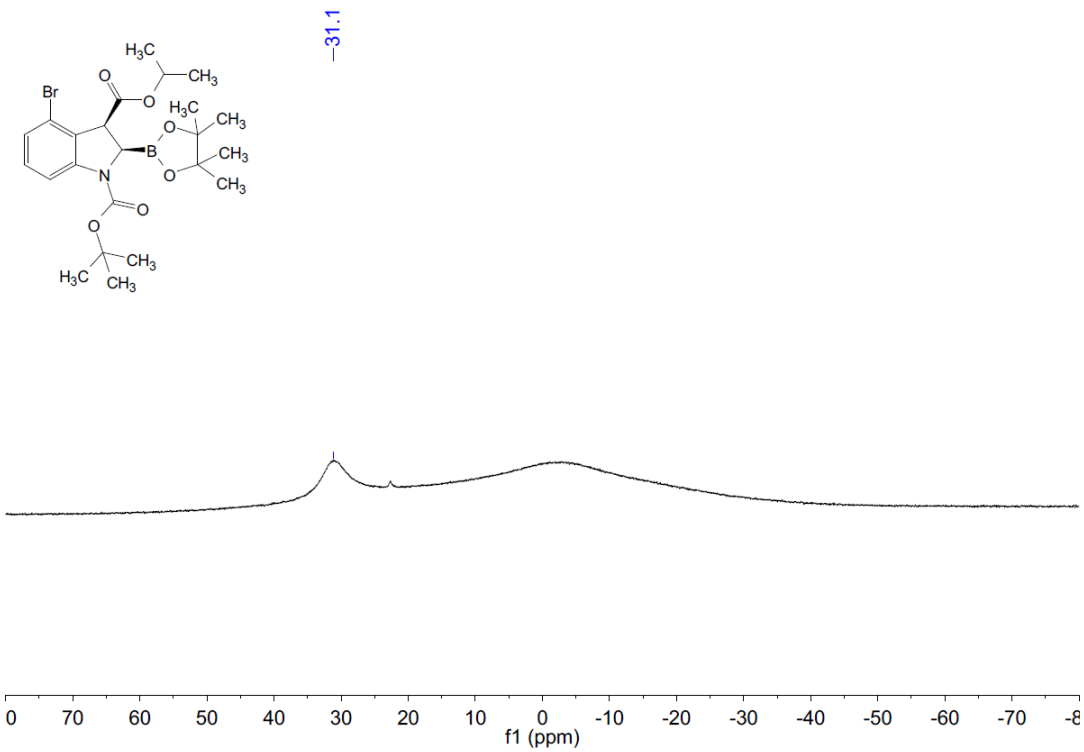

171.241
160.305
157.849
152.141
144.991
130.324
130.243
115.836
115.657
110.576
108.817
108.615
84.042
81.661
77.319
77.000
76.682
69.063
50.001
44.864
28.251
25.236
24.706
21.588
21.379


31.5
f1 (ppm)

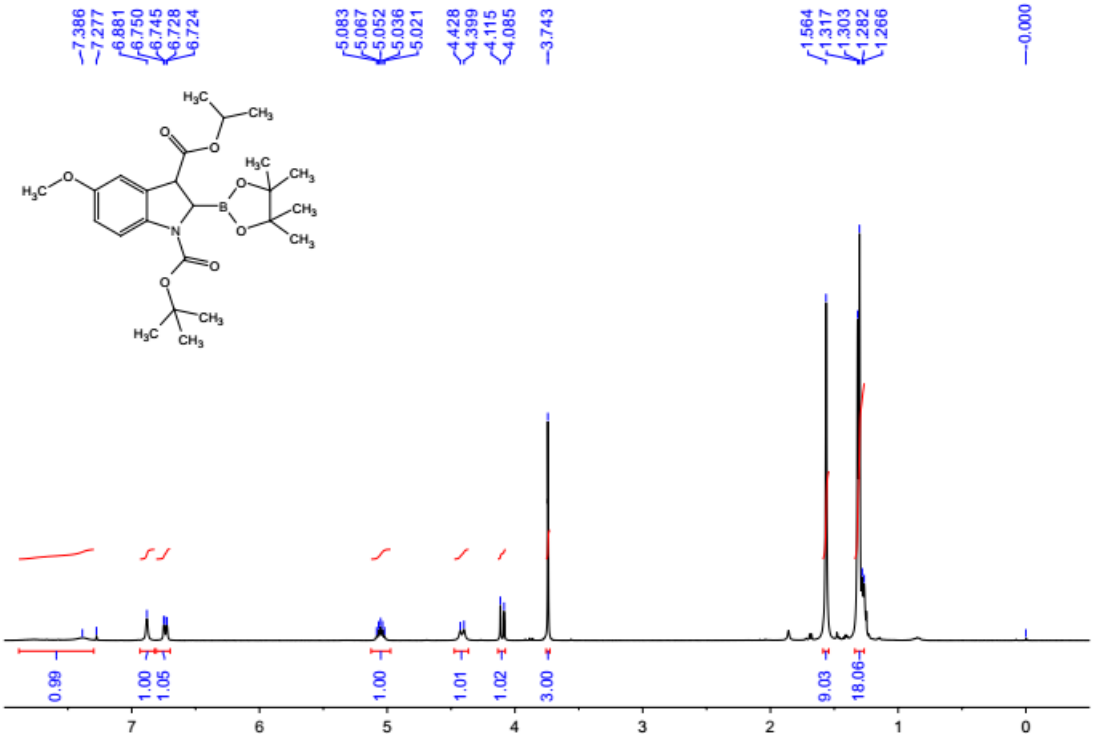
Compound 2h

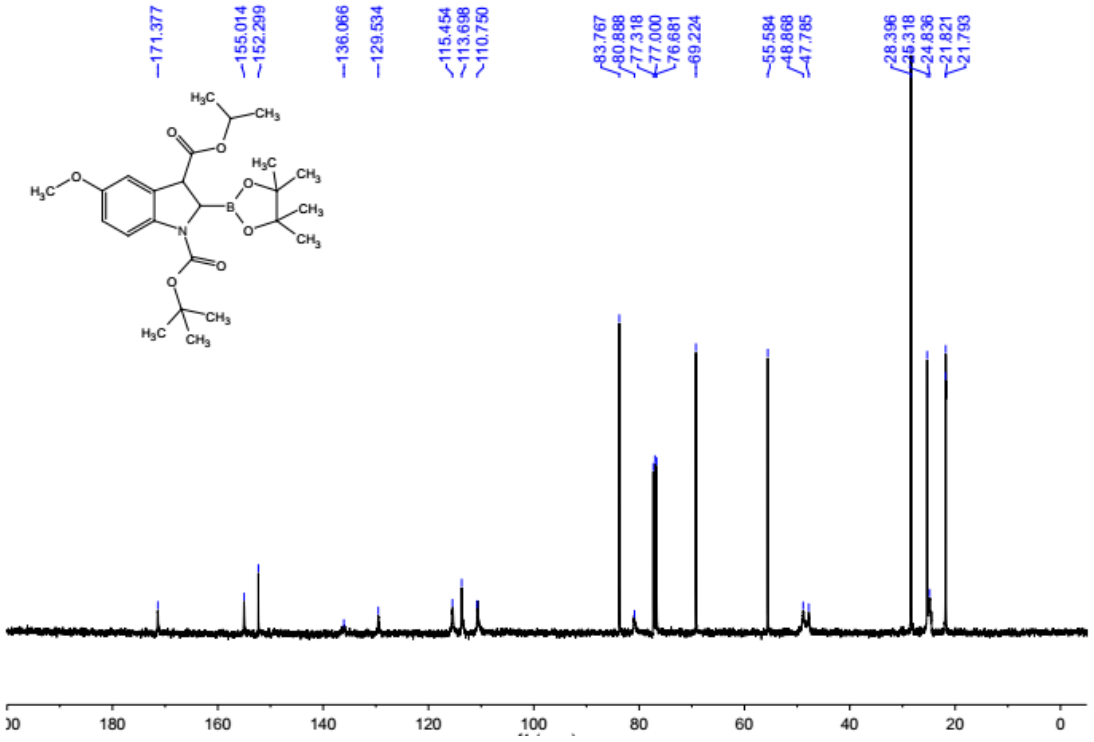

7.421
7.267
7.073
7.062
5.013
4.265
4.085
1.567
1.292
1.231
0.000
0.99
2.07
1.00
1.01
1.02
9.01
18.00

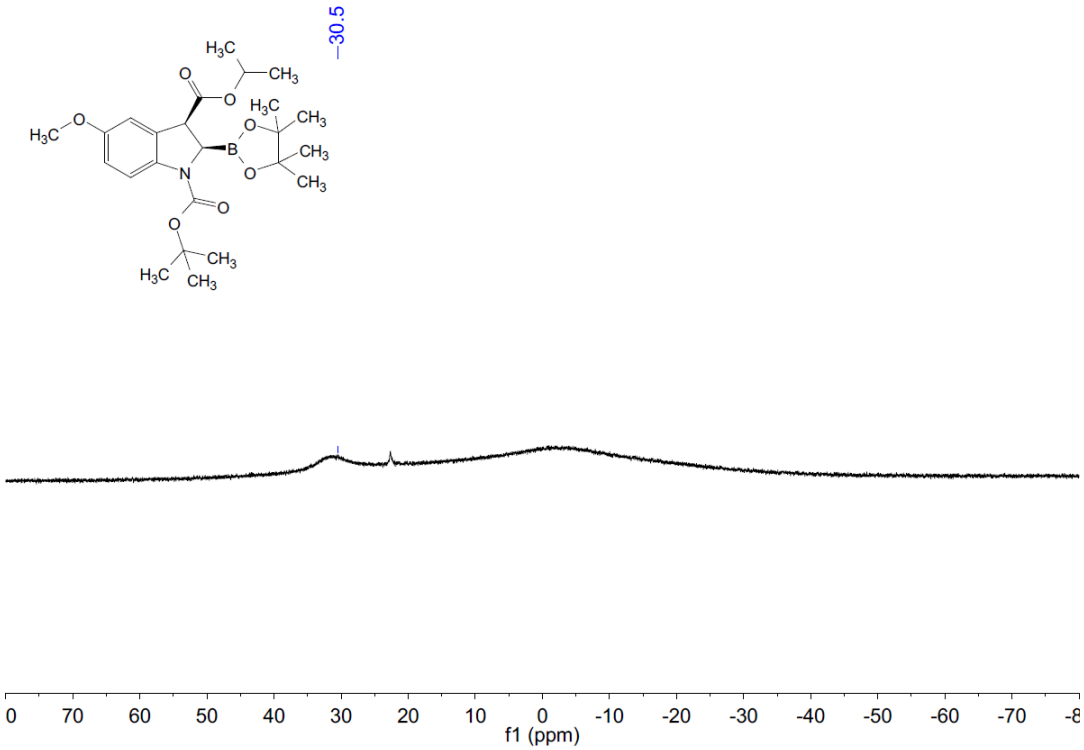

170.549
152.546
144.014
130.611
129.956
125.031
120.203
113.476
84.153
82.162
77.318
77.000
76.682
68.967
49.131
48.976
28.331
25.364
24.561
21.641
21.520
Br
O
O
B
N
O
O
O
CH3
CH3
CH3
CH3
CH3
CH3
H3C
H3C
H3C
H3C
H3C
H3C
200
180
160
140
120
100
80
60
40
20
0


31.1
Br
O
O
B
N
O
O
O
CH3
CH3
CH3
CH3
CH3
CH3
H3C
H3C
H3C
H3C
H3C
H3C
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

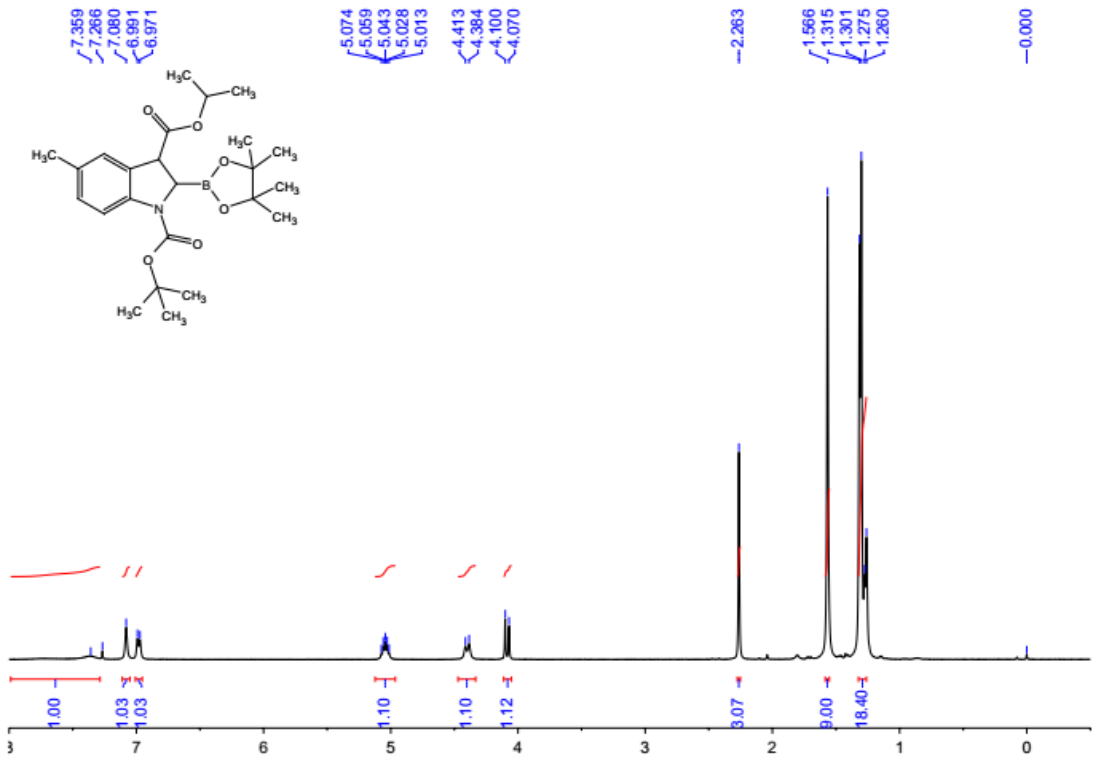
Compound 2i

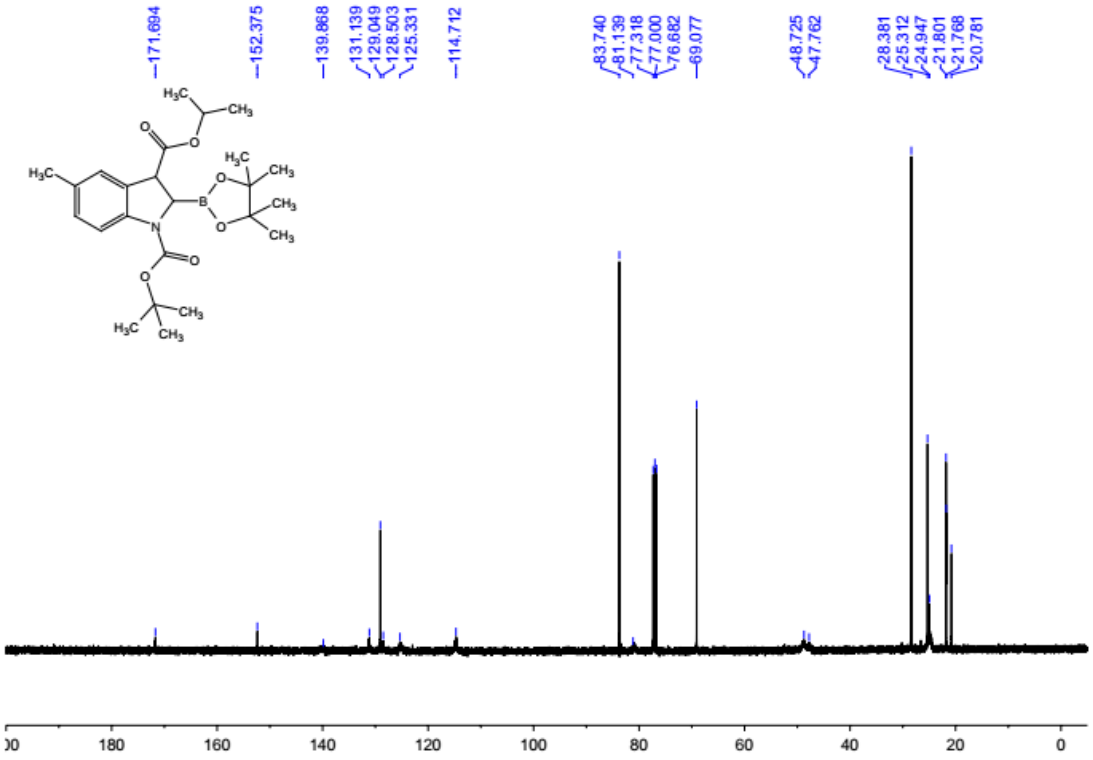

7.386
7.277
6.881
6.750
6.745
6.728
6.724
5.083
5.067
5.052
5.036
5.021
4.428
4.399
4.115
4.085
3.743
1.564
1.317
1.303
1.282
1.266
0.000
0.99
1.00
1.05
1.00
1.01
1.02
3.00
9.03
18.06

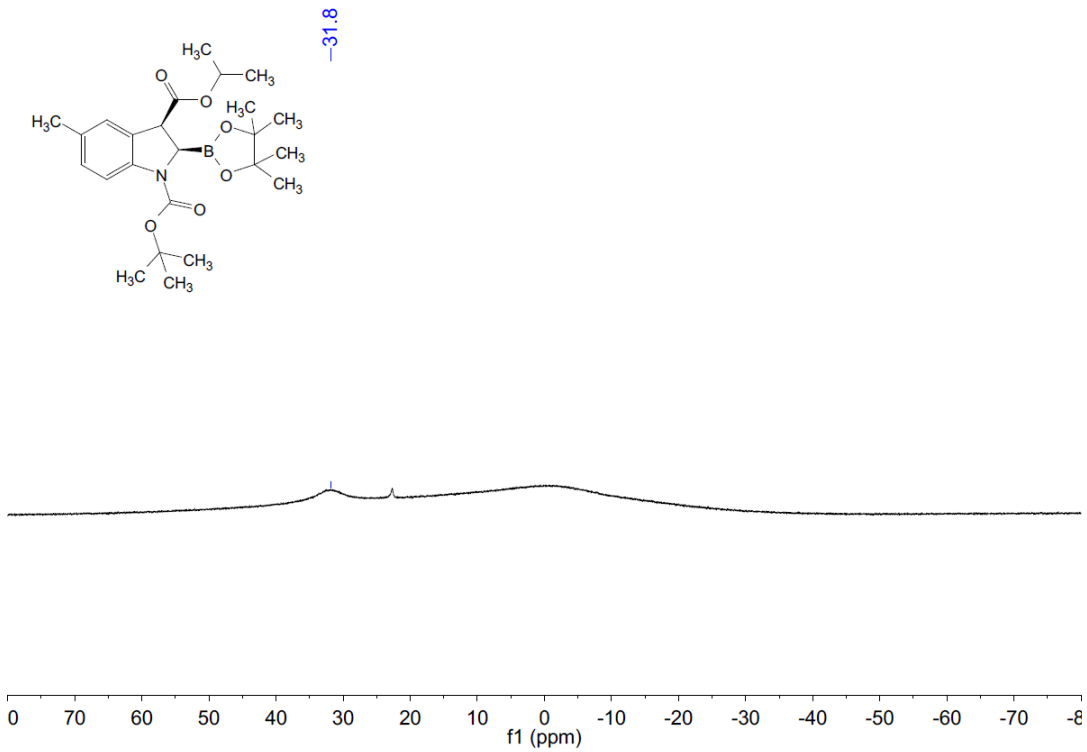

171.377
155.014
152.299
136.066
129.534
115.454
113.698
110.750
83.767
80.888
77.318
77.000
76.681
69.224
55.584
48.868
47.785
28.396
25.318
24.836
21.821
21.793


30.5
f1 (ppm)

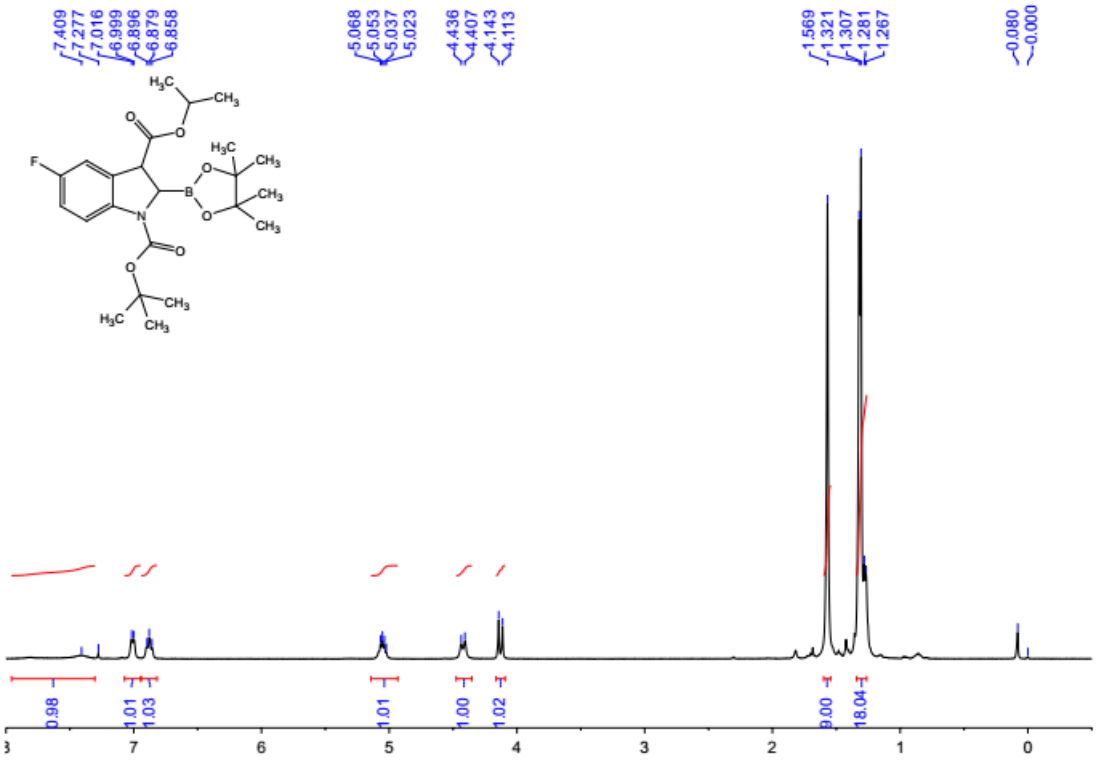
Compound 2j

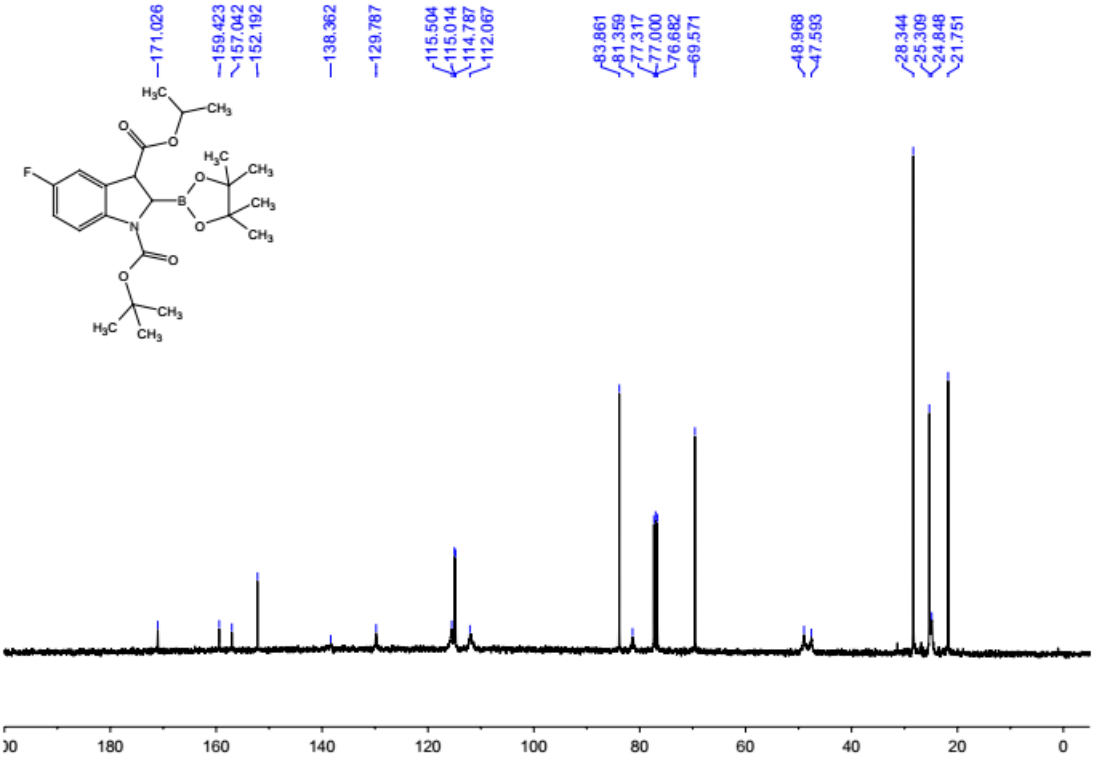

7.359
7.266
7.080
6.991
6.971
5.074
5.059
5.043
5.028
5.013
4.413
4.384
4.100
4.070
2.263
1.566
1.315
1.301
1.275
1.260
0.000
1.00
1.03
1.03
1.10
1.10
1.12
3.07
9.00
18.40

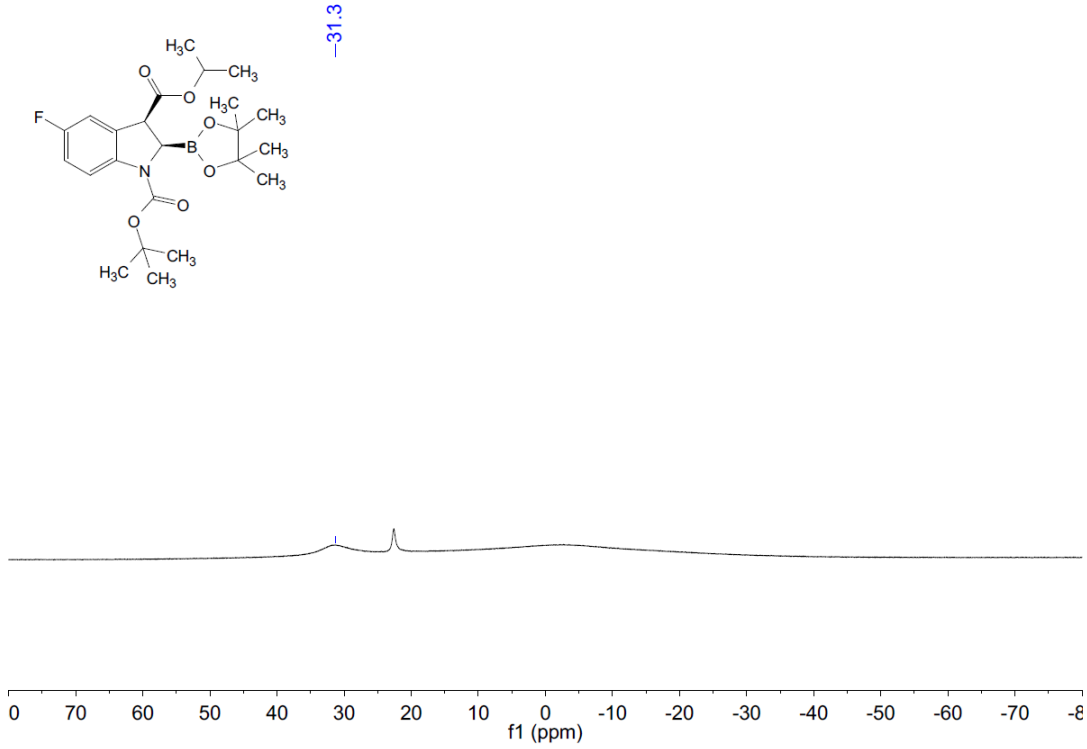

171.694
152.375
139.868
131.139
129.049
128.503
125.331
114.712
83.740
81.139
77.318
77.000
76.682
69.077
48.725
47.762
28.381
25.312
24.947
21.801
21.768
20.781
180
160
140
120
100
80
60
40
20
0


31.8
0
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

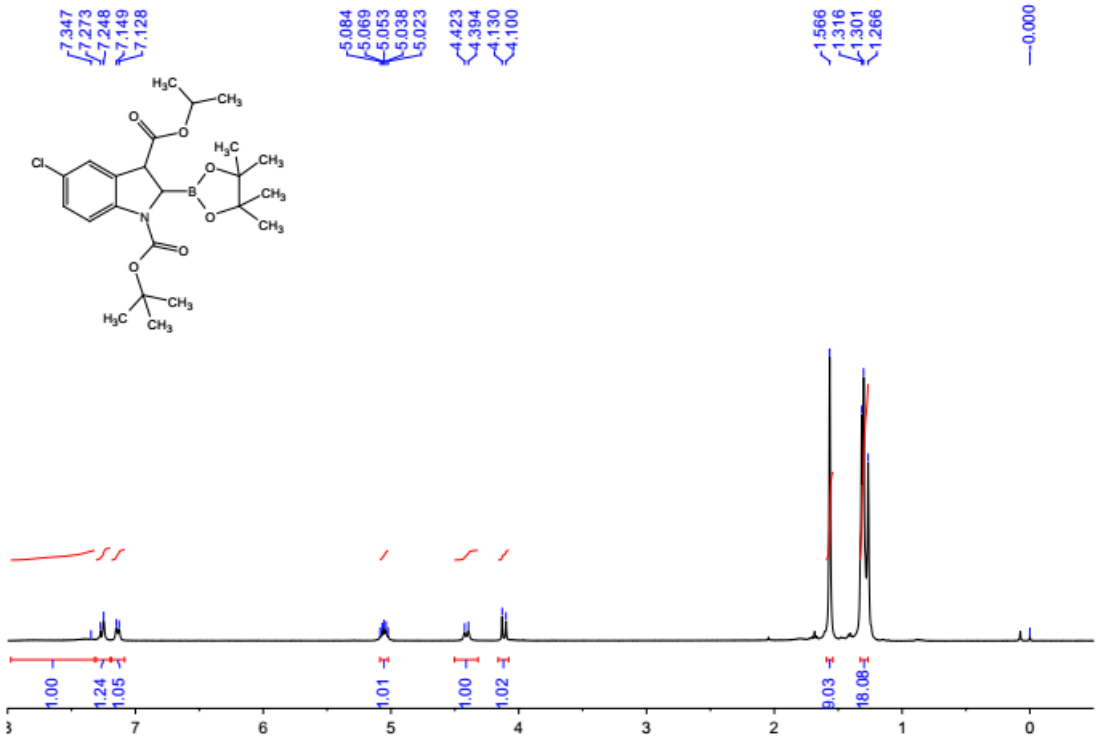
Compound 2k

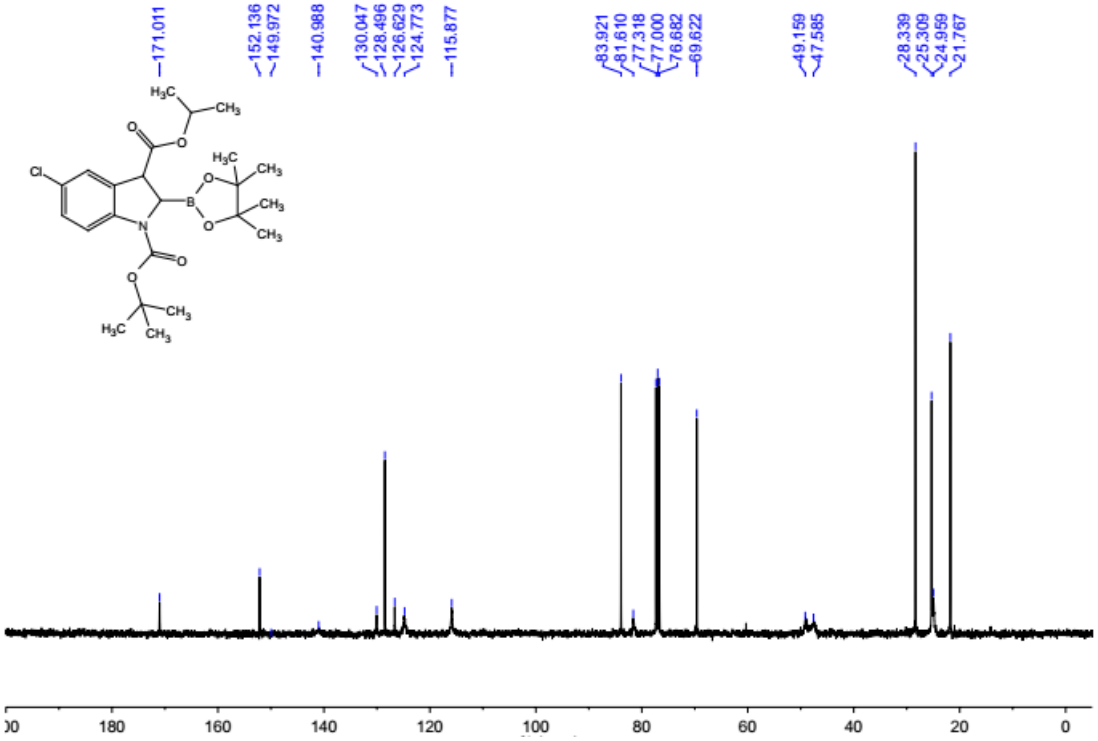

7.409
7.277
7.016
6.999
6.896
6.879
6.858
5.068
5.053
5.037
5.023
4.436
4.407
4.143
4.113
1.569
1.321
1.307
1.281
1.267
0.080
0.000
0.98
1.01
1.03
1.01
1.00
1.02
9.00
18.04

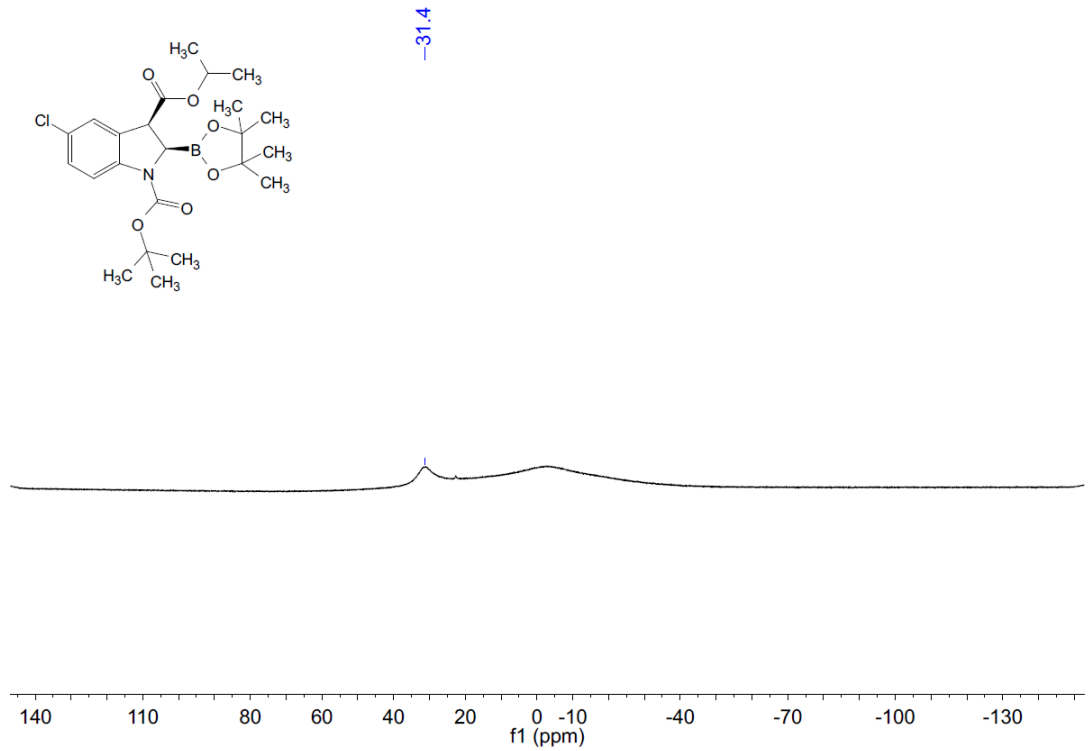

171.026
159.423
157.042
152.192
138.362
129.787
115.504
115.014
114.787
112.067
83.861
81.359
77.317
77.000
76.682
69.571
48.968
47.593
28.344
25.309
24.848
21.751


-31.3
f1 (ppm)

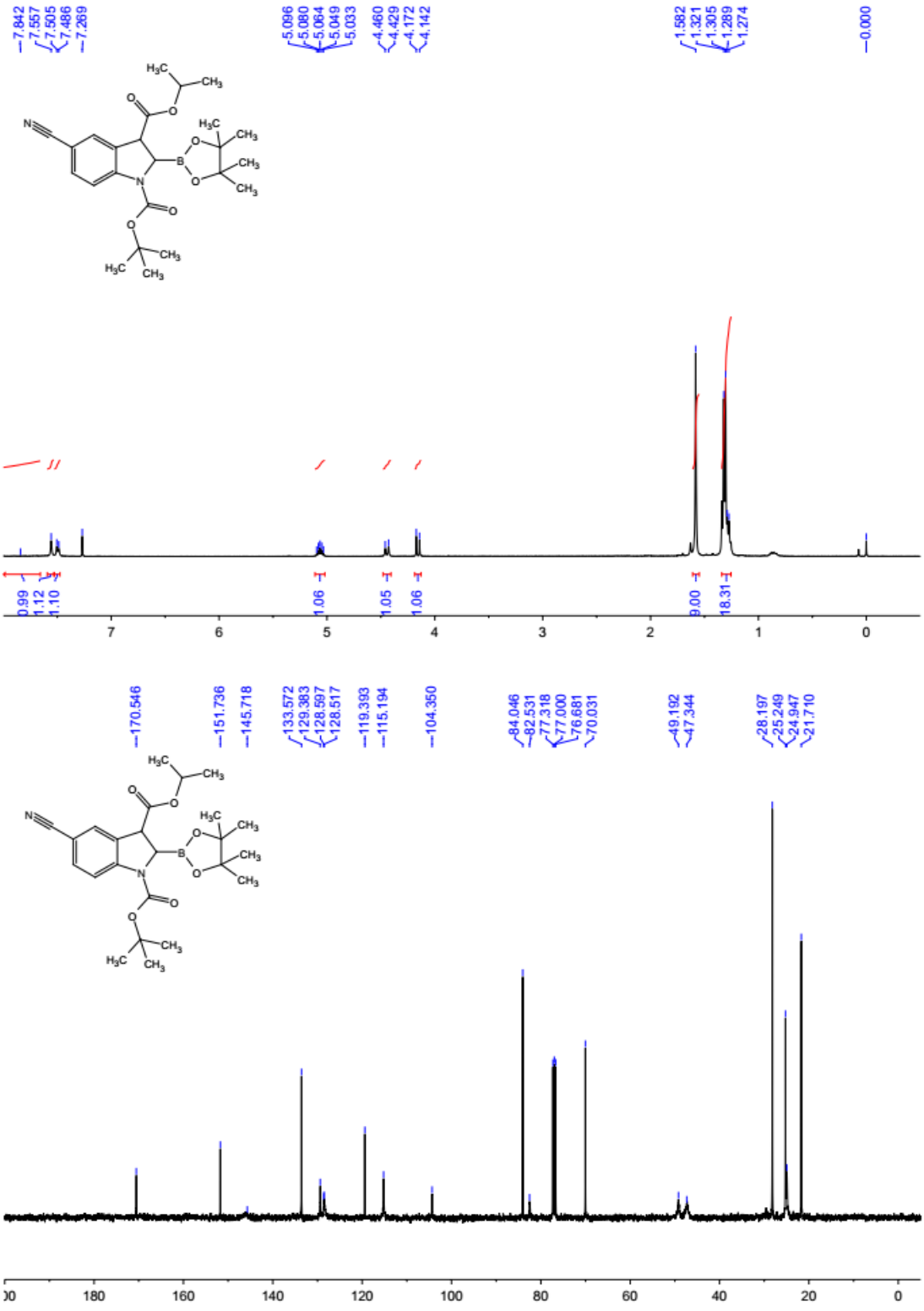
Compound 2l

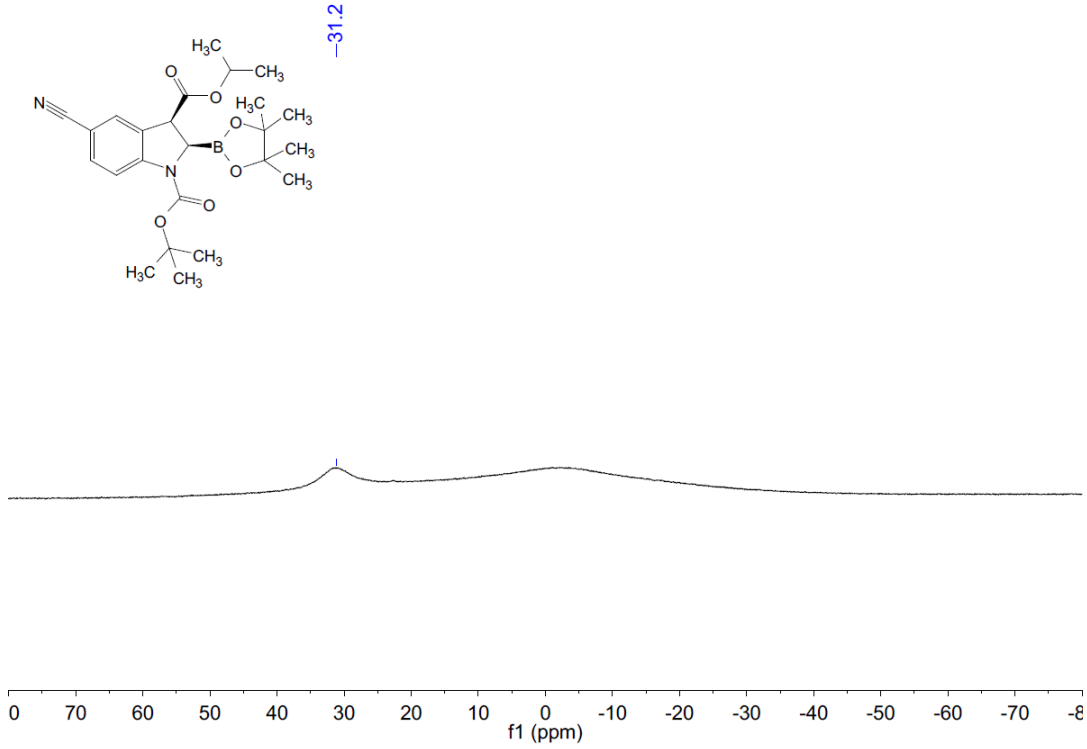

7.347
7.273
7.248
7.149
7.128
5.084
5.069
5.053
5.038
5.023
4.423
4.394
4.130
4.100
1.566
1.316
1.301
1.266
0.000
1.00
1.24
1.05
1.01
1.00
1.02
9.03
18.08


171.011
152.136
149.972
140.988
130.047
128.496
126.629
124.773
115.877
83.921
81.610
77.318
77.000
76.682
69.622
49.159
47.585
28.339
25.309
24.959
21.767
Cl
B
N
O
CH3
H3C
180
160
140
120
100
80
60
40
20
0

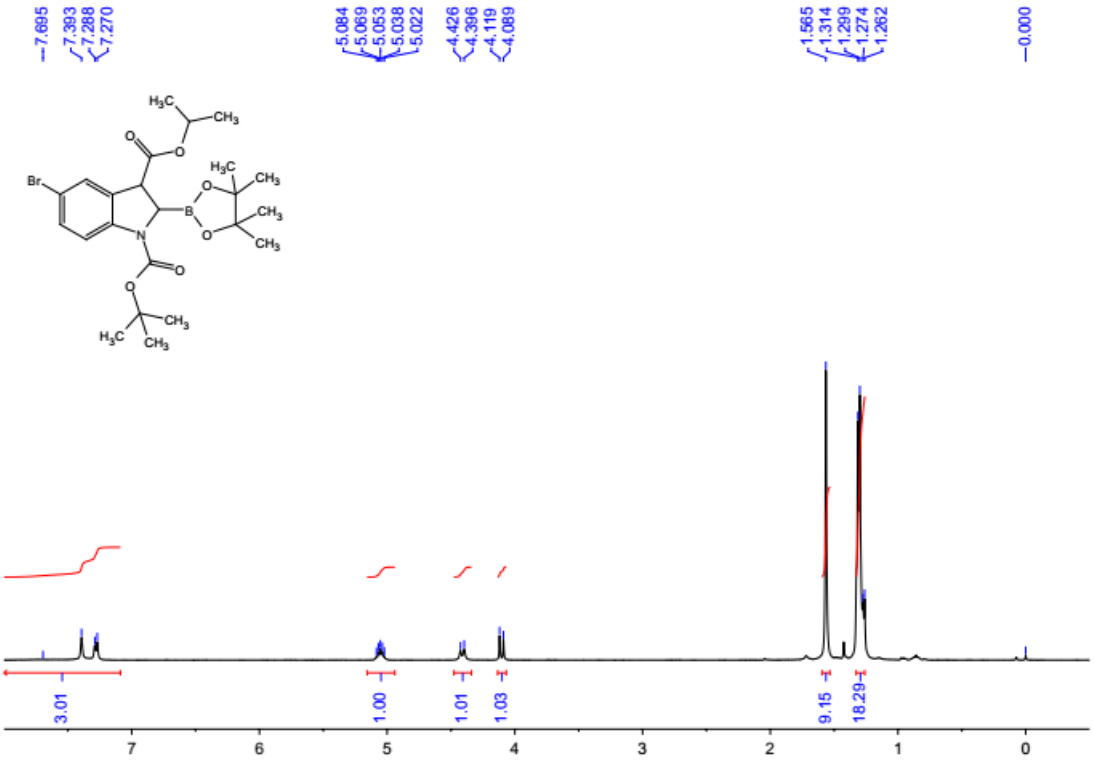

31.4
Cl
B
N
O
CH3
H3C
140
110
80
60
40
20
0
-10
-40
-70
-100
-130
f1 (ppm)

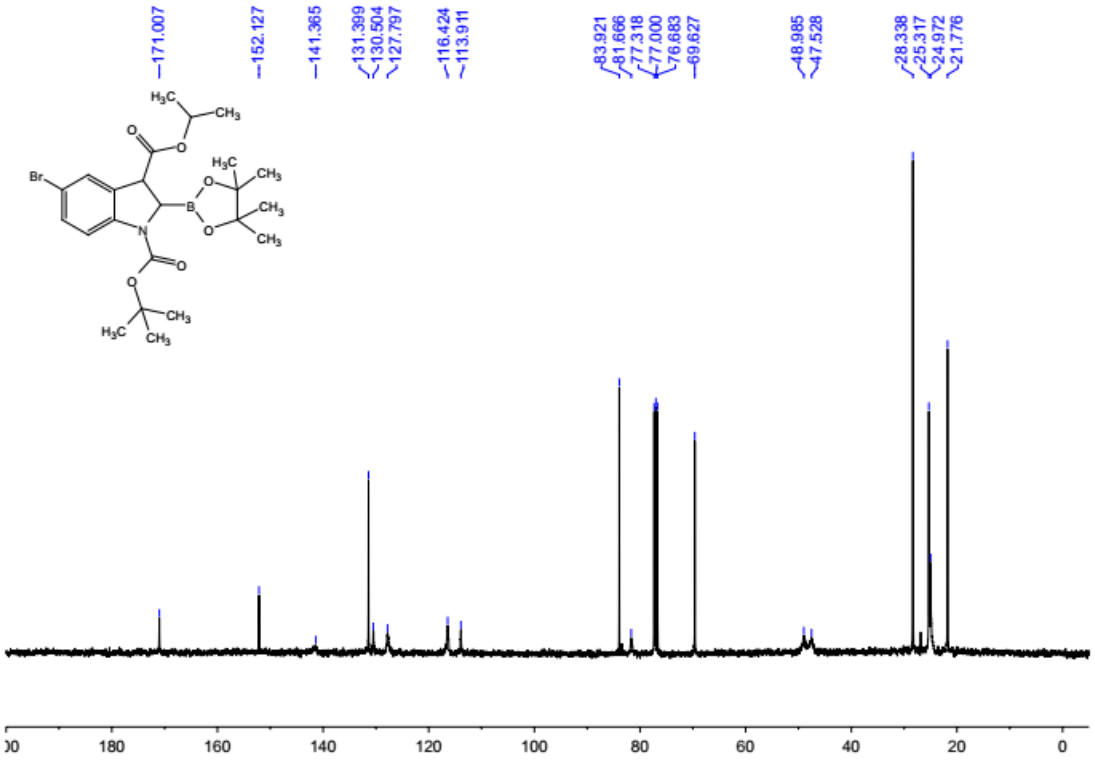
Compound 2m

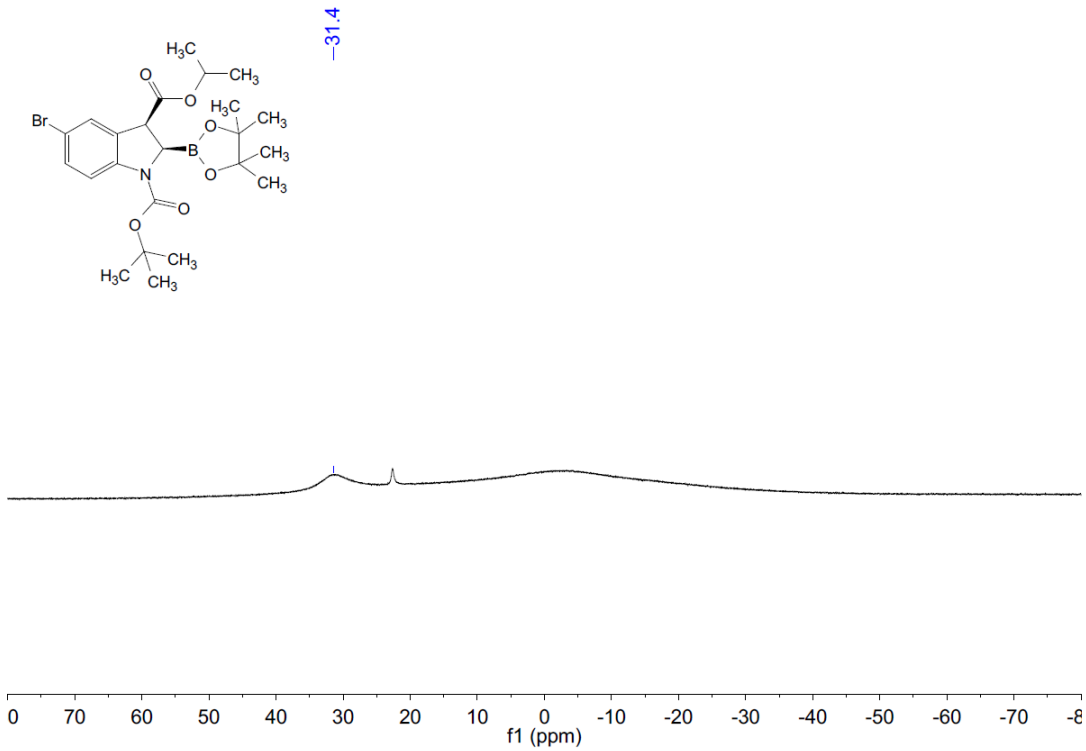

7.842
7.557
7.505
7.486
7.269
5.096
5.080
5.064
5.049
5.033
4.460
4.429
4.172
4.142
1.582
1.321
1.305
1.289
1.274
0.000
0.99
1.12
1.10
1.06
1.05
1.06
9.00
18.31
170.546
151.736
145.718
133.572
129.383
128.597
128.517
119.393
115.194
104.350
84.046
82.531
77.318
77.000
76.681
70.031
49.192
47.344
28.197
25.249
24.947
21.710


31.2
f1 (ppm)

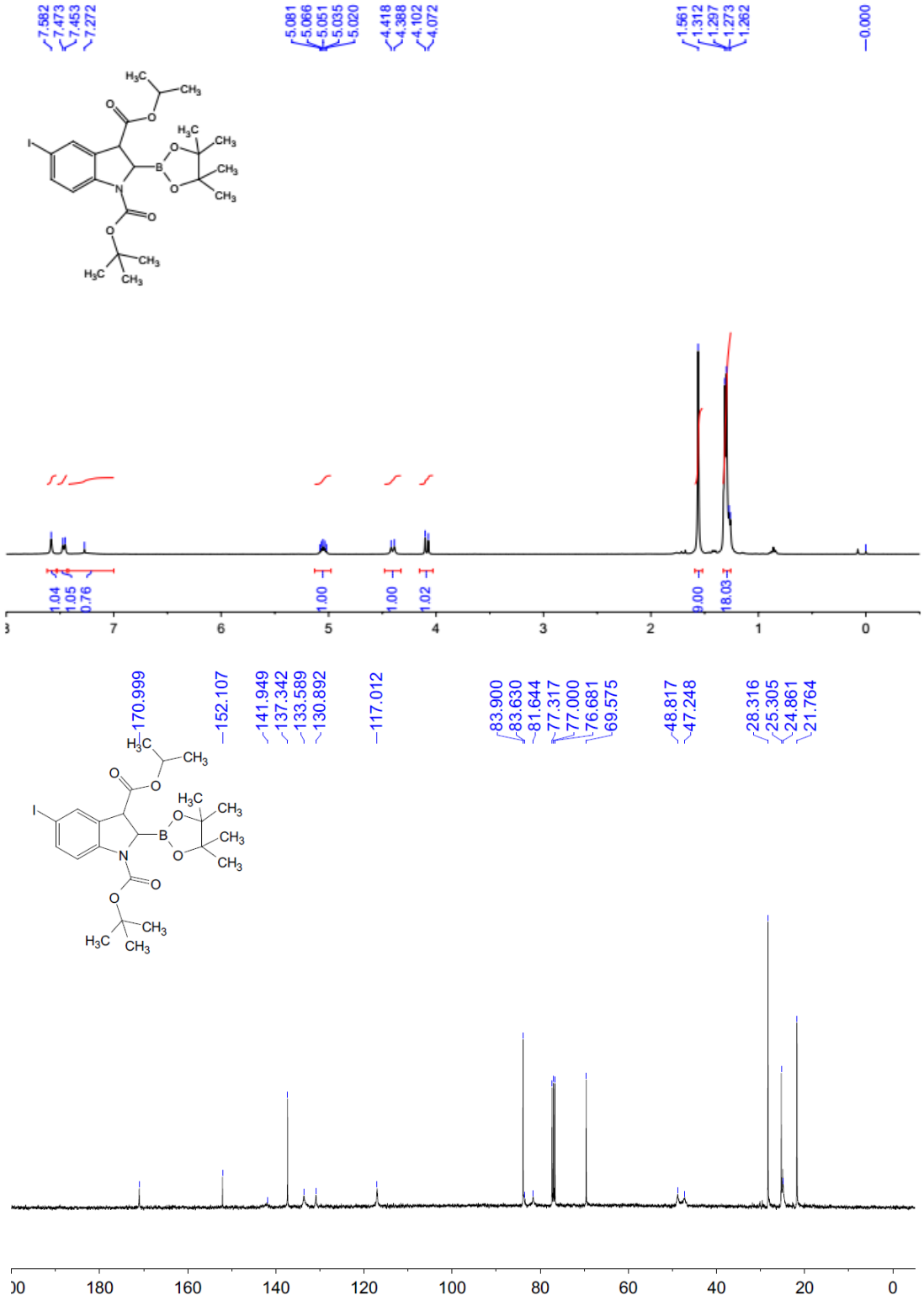
Compound 2n

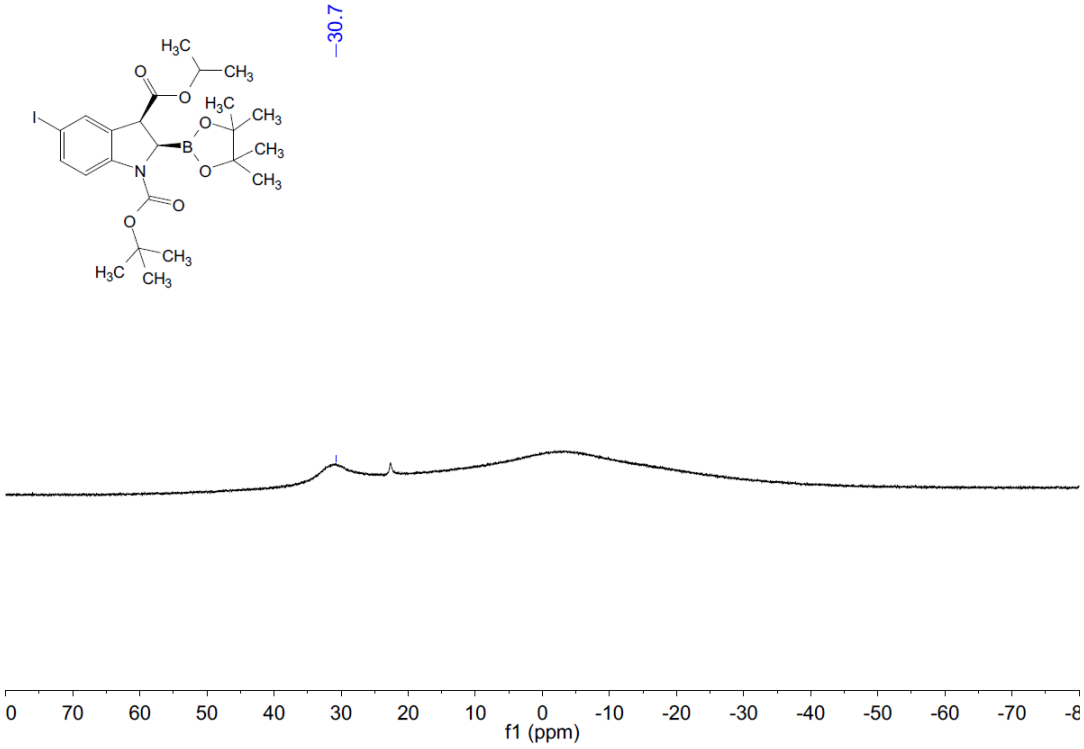

7.695
7.393
7.288
7.270
5.084
5.069
5.053
5.038
5.022
4.426
4.396
4.119
4.089
1.565
1.314
1.299
1.274
1.262
0.000
3.01
1.00
1.01
1.03
9.15
18.29


171.007
152.127
141.365
131.399
130.504
127.797
116.424
113.911
83.921
81.666
77.318
77.000
76.683
69.627
48.985
47.528
28.338
25.317
24.972
21.776
Br
B
N
O
CH3
H3C
180
160
140
120
100
80
60
40
20
0

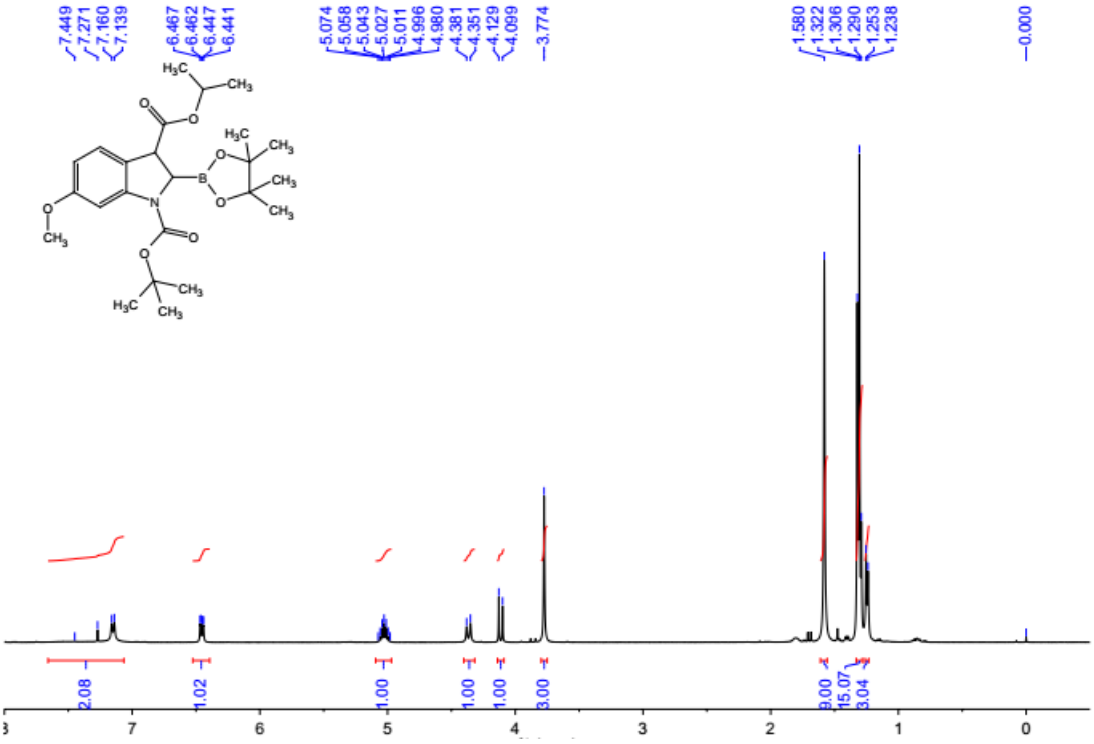

31.4
Br
B
N
O
CH3
H3C
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

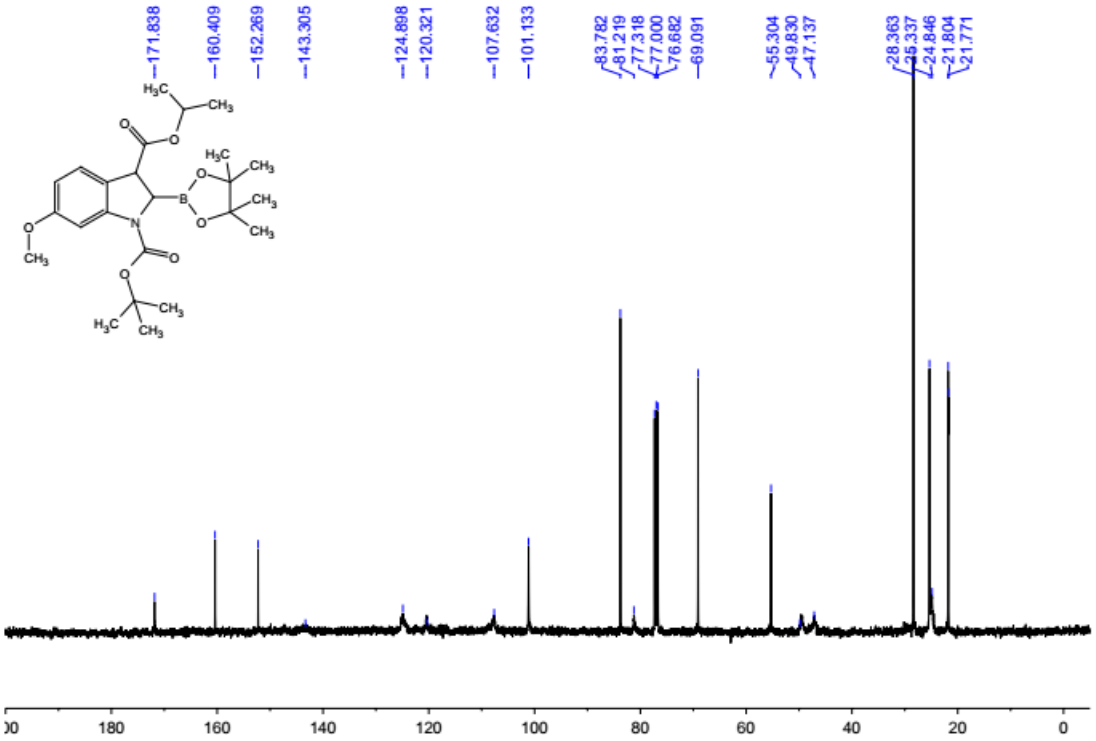
Compound 2o

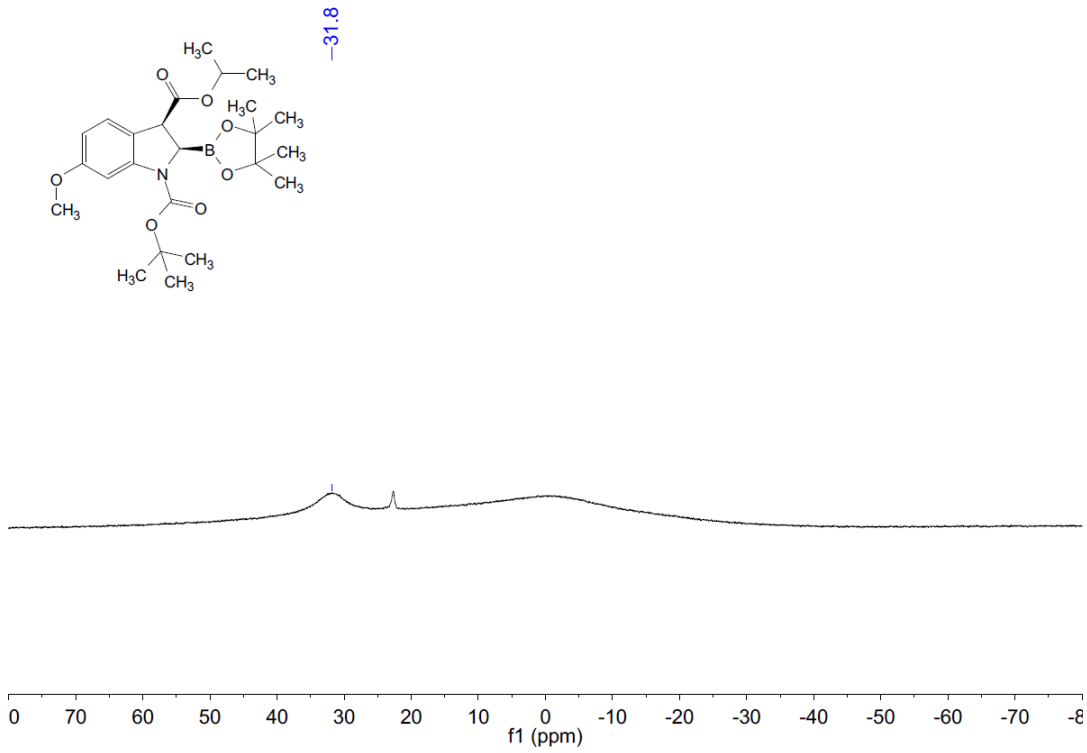

7.582
7.473
7.453
7.272
5.081
5.066
5.051
5.035
5.020
4.418
4.388
4.102
4.072
1.561
1.312
1.297
1.273
1.262
0.000
1.04
1.05
0.76
1.00
1.00
1.02
9.00
18.03
170.999
152.107
141.949
137.342
133.589
130.892
117.012
83.900
83.630
81.644
77.317
77.000
76.681
69.575
48.817
47.248
28.316
25.305
24.861
21.764


30.7
f1 (ppm)

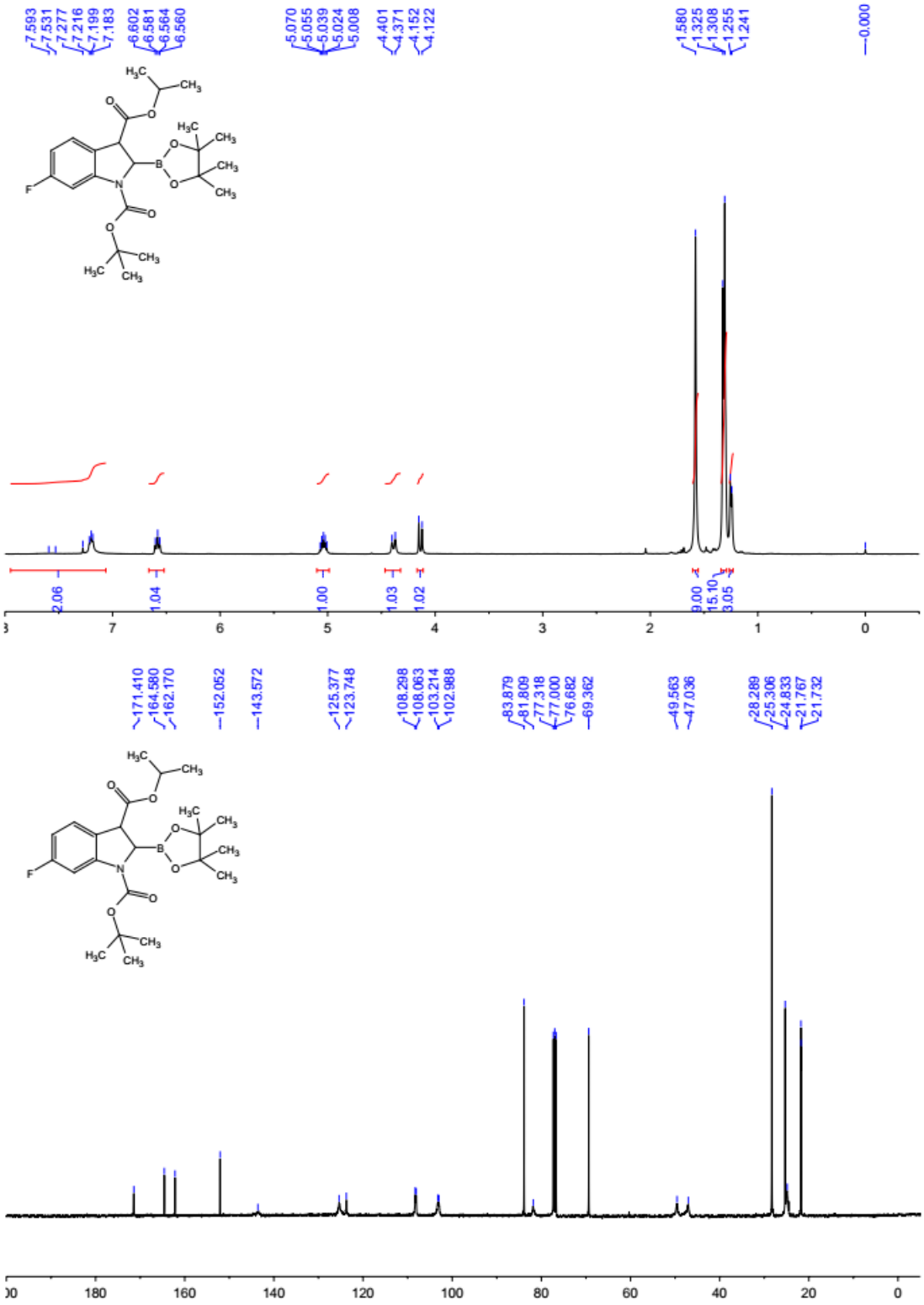
Compound 2p

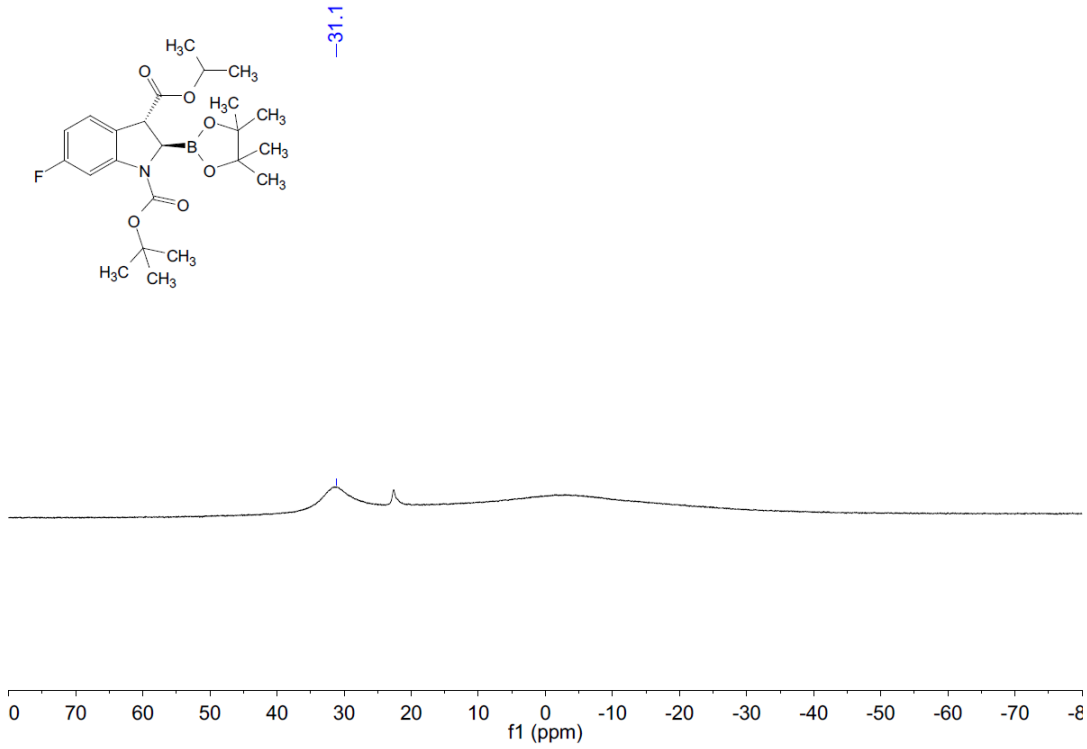

7.449
7.271
7.160
7.139
6.467
6.462
6.447
6.441
5.074
5.058
5.043
5.027
5.011
4.996
4.980
4.381
4.351
4.129
4.099
3.774
1.580
1.322
1.306
1.290
1.253
1.238
0.000
2.08
1.02
1.00
1.00
1.00
3.00
3.00
15.07
3.04


171.838
160.409
152.269
143.305
124.898
120.321
107.632
101.133
83.782
81.219
77.318
77.000
76.682
69.091
55.304
49.830
47.137
28.363
25.337
24.846
21.804
21.771
180
160
140
120
100
80
60
40
20
0

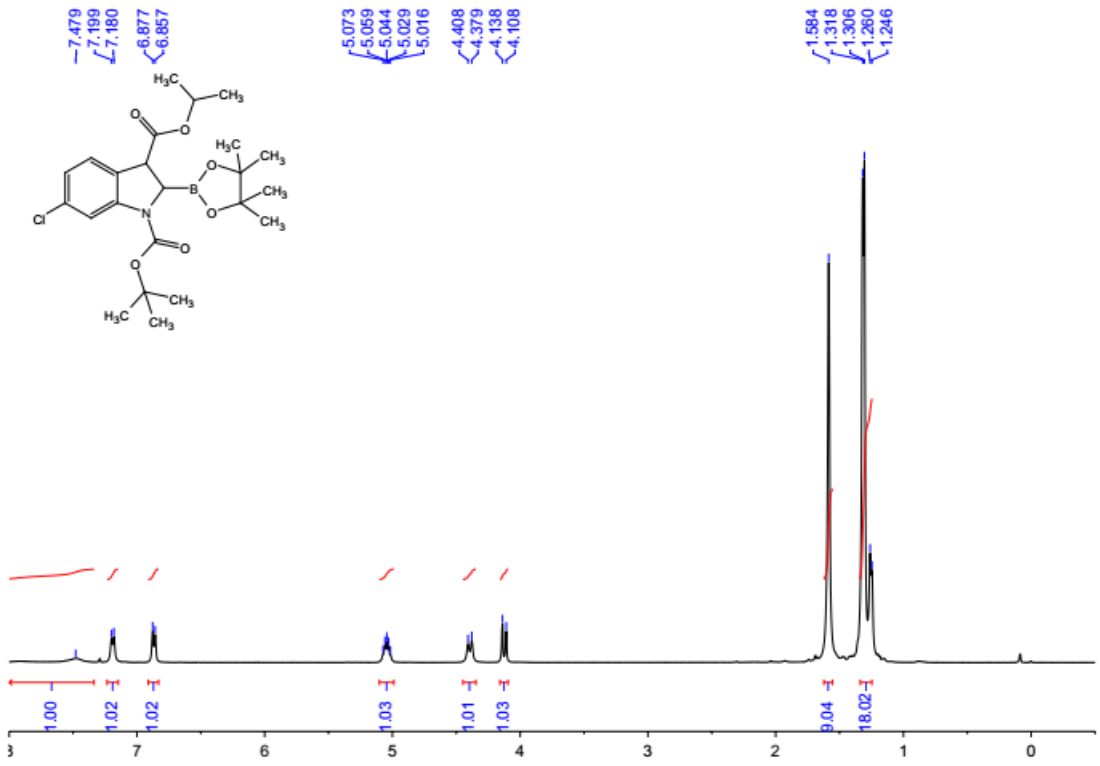

31.8
0
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

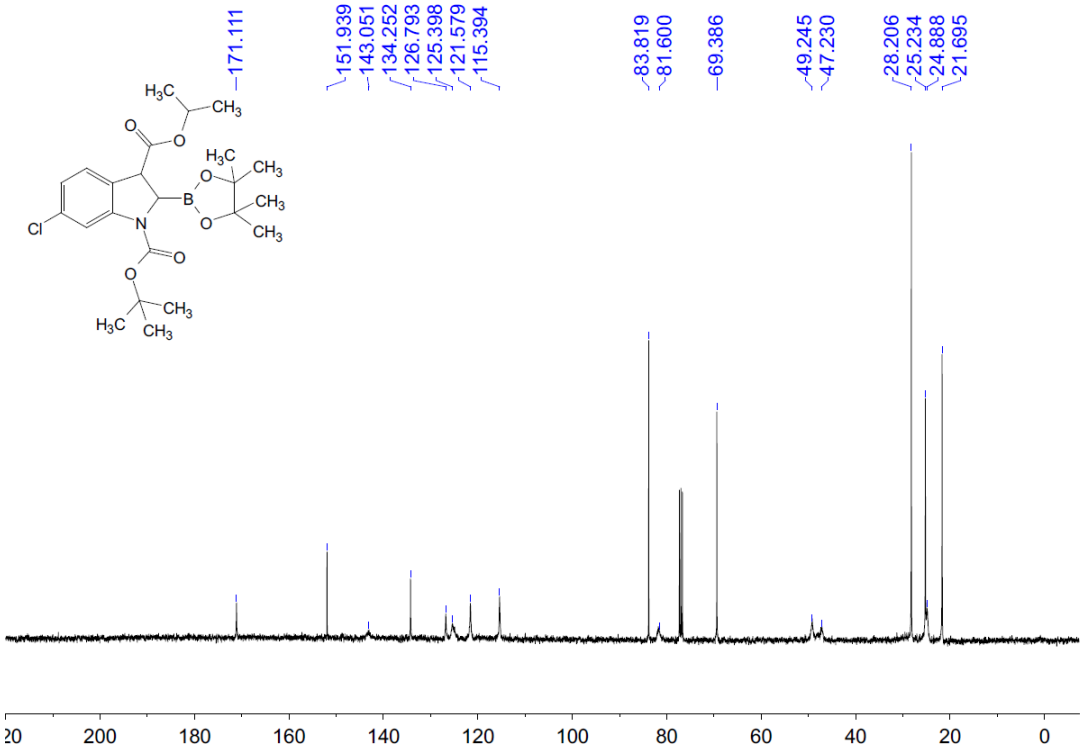
Compound 2q

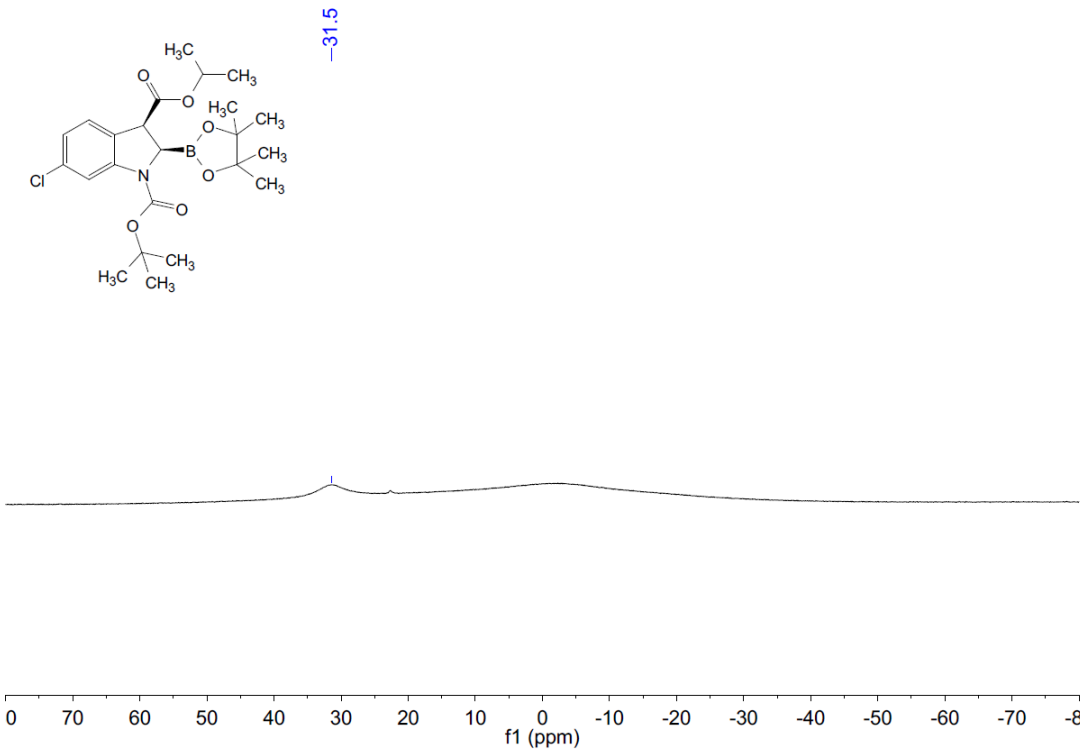

7.593
7.531
7.277
7.216
7.199
7.183
6.602
6.581
6.564
6.560
5.070
5.055
5.039
5.024
5.008
4.401
4.371
4.152
4.122
1.580
1.325
1.308
1.255
1.241
0.000
2.06
1.04
1.00
1.03
1.02
9.00
15.10
3.05
171.410
164.580
162.170
152.052
143.572
125.377
123.748
108.298
108.063
103.214
102.988
83.879
81.809
77.318
77.000
76.682
69.362
49.563
47.036
28.289
25.306
24.833
21.767
21.732


31.1
f1 (ppm)

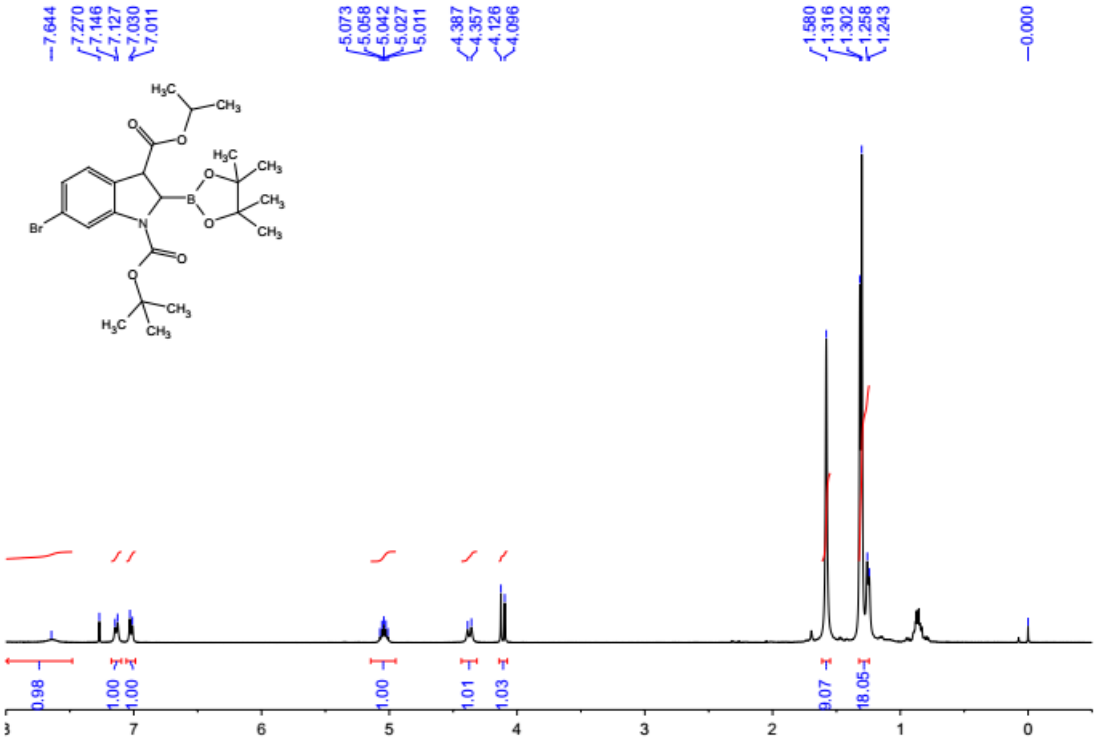
Compound 2r

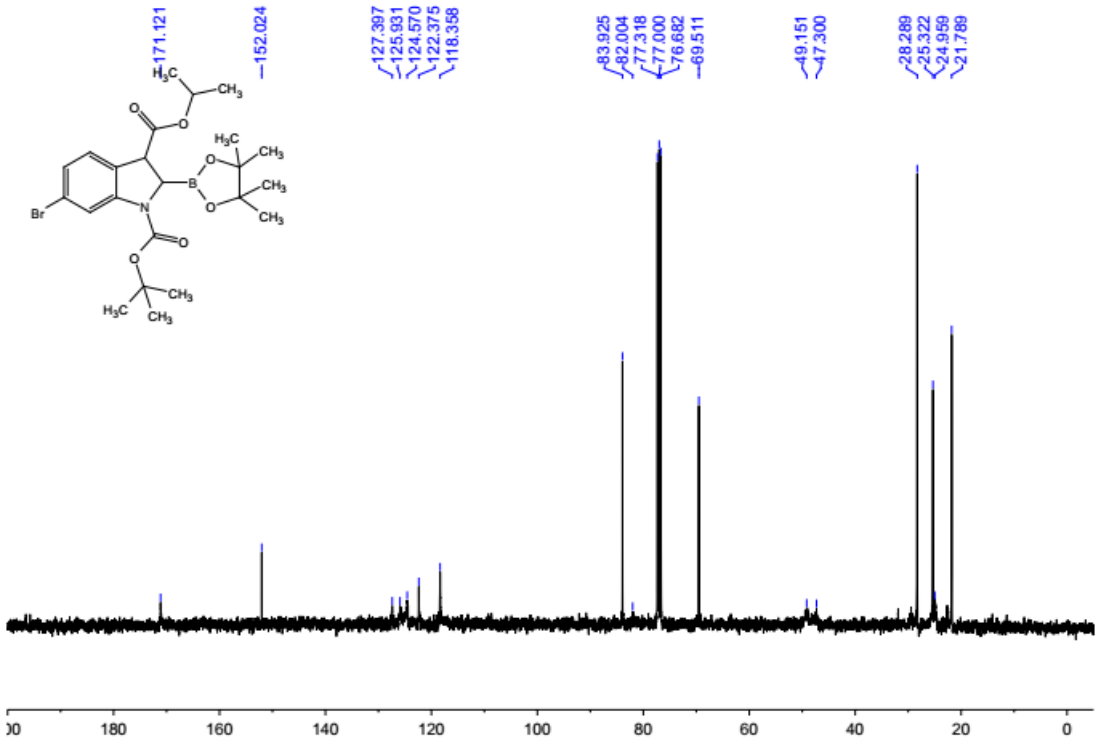

7.479
7.199
7.180
6.877
6.857
5.073
5.059
5.044
5.029
5.016
4.408
4.379
4.138
4.108
1.584
1.318
1.306
1.260
1.246
1.00
1.02
1.02
1.03
1.01
1.03
9.04
18.02

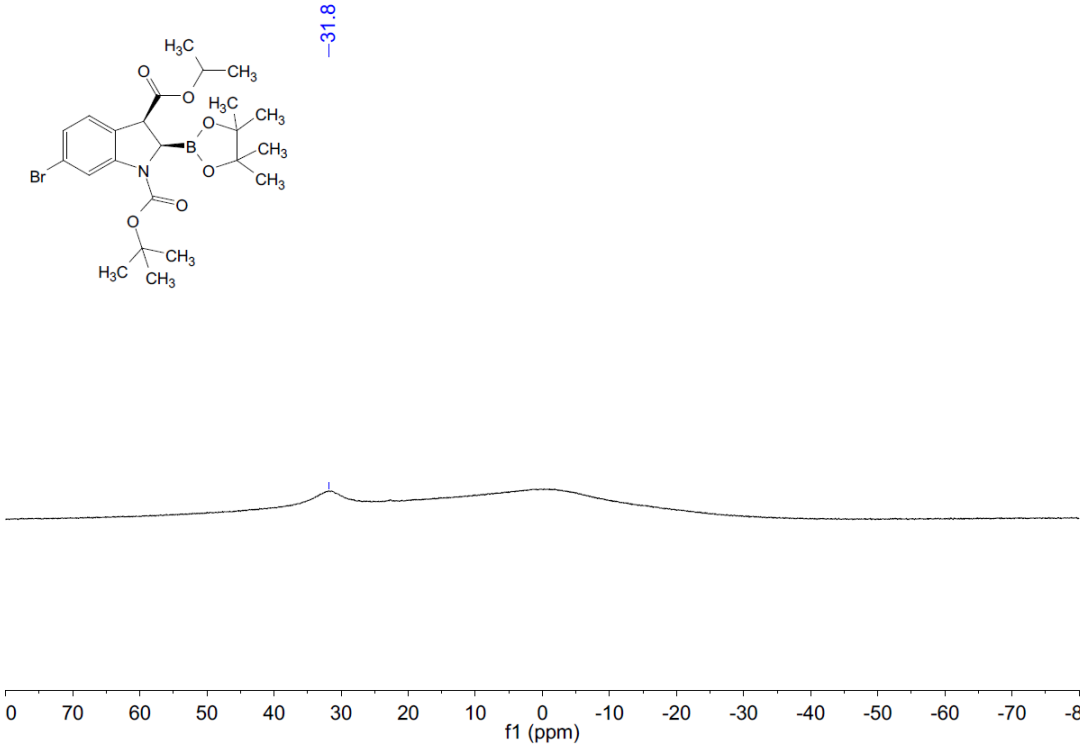

171.111
151.939
143.051
134.252
126.793
125.398
121.579
115.394
83.819
81.600
69.386
49.245
47.230
28.206
25.234
24.888
21.695
Cl
B
N
O
CH3
H3C
200
180
160
140
120
100
80
60
40
20
0


31.5
Cl
B
N
O
CH3
H3C
0
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

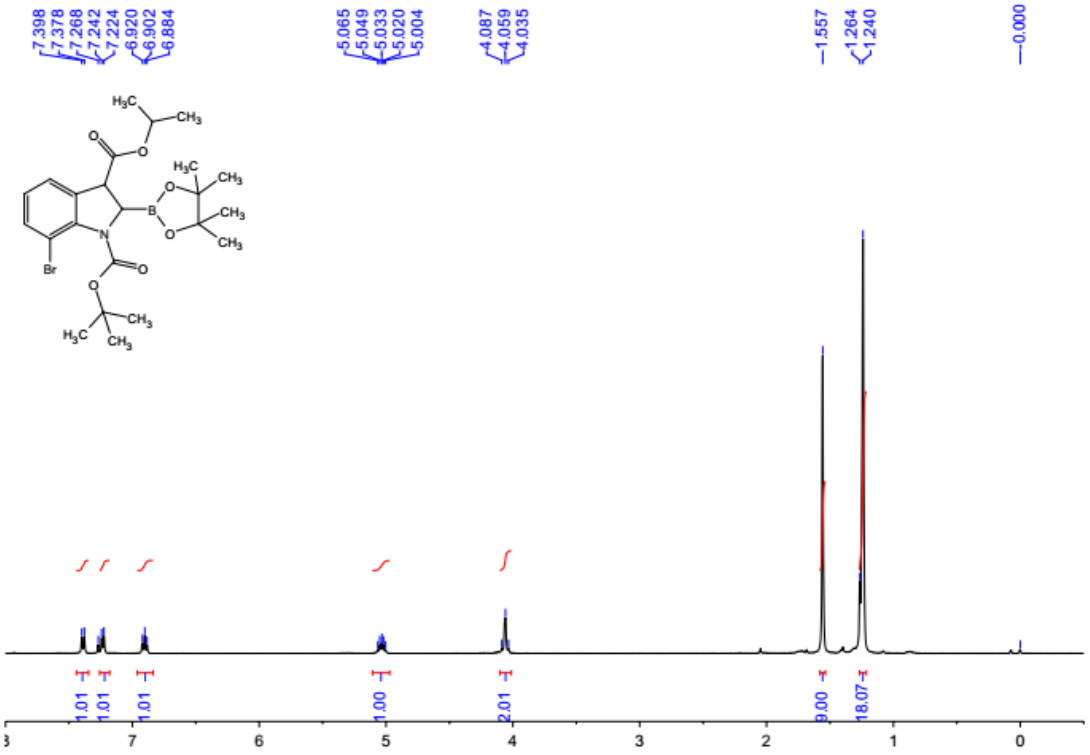
Compound 2s

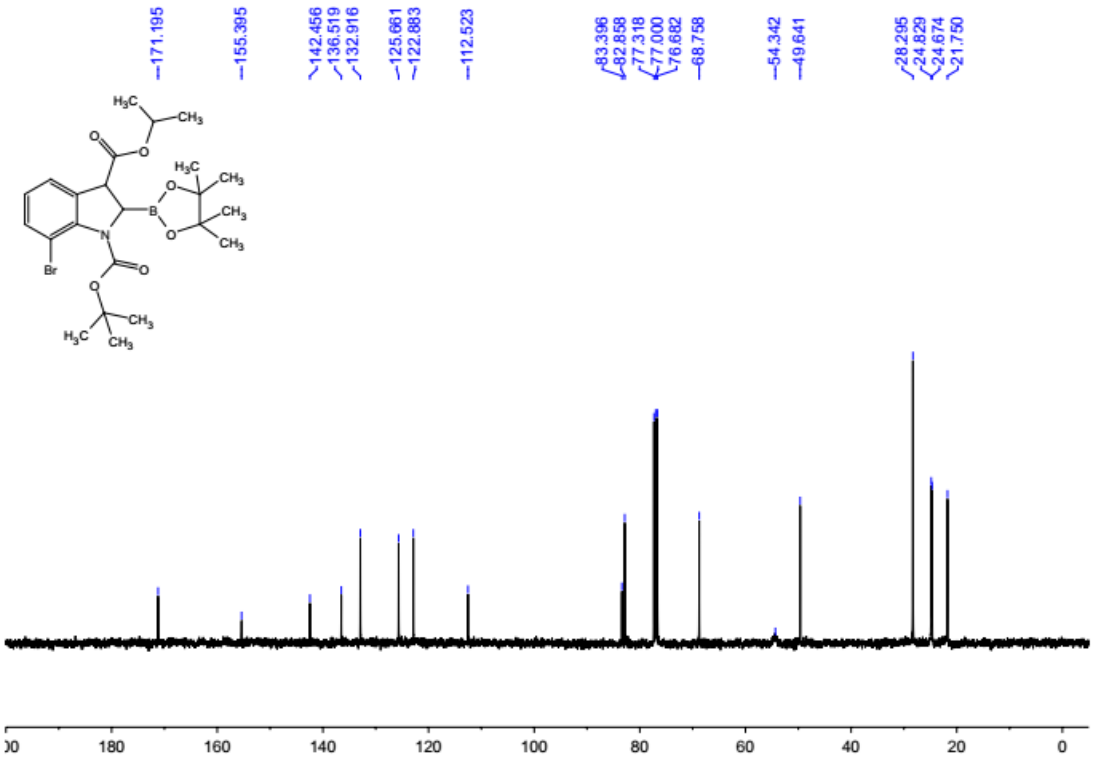

7.644
7.270
7.146
7.127
7.030
7.011
5.073
5.058
5.042
5.027
5.011
4.387
4.357
4.126
4.096
1.580
1.316
1.302
1.258
1.243
0.000
0.98
1.00
1.00
1.00
1.01
1.03
9.07
18.05

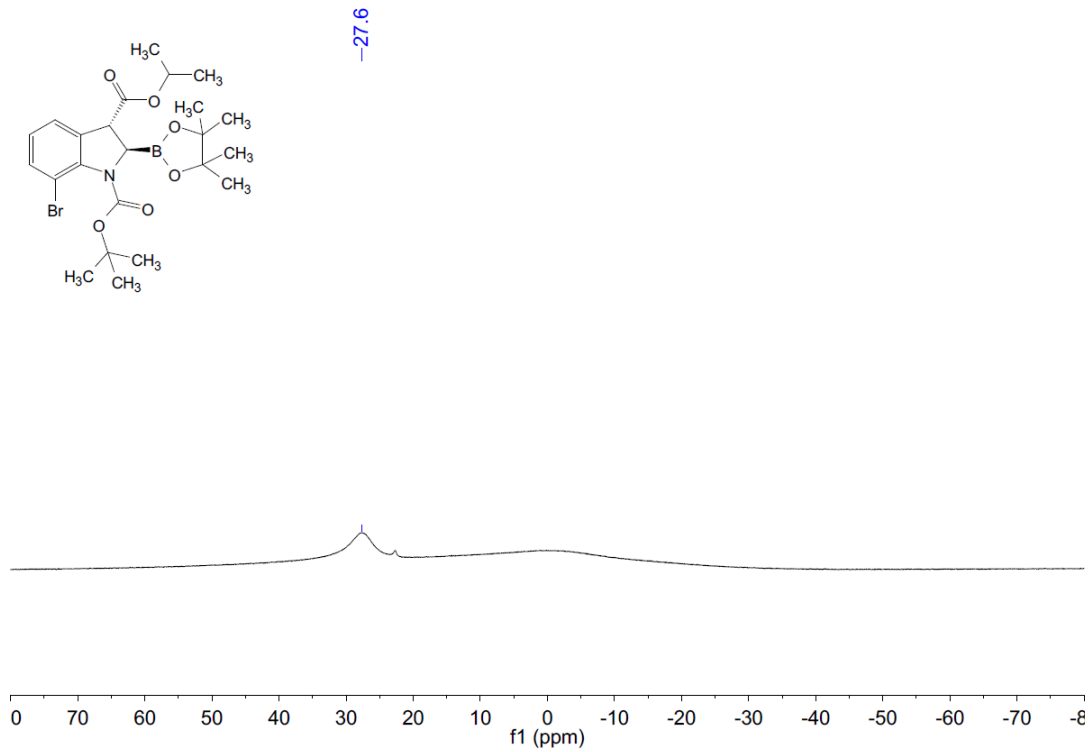

171.121
152.024
127.397
125.931
124.570
122.375
118.358
83.925
82.004
77.318
77.000
76.682
69.511
49.151
47.300
28.289
25.322
24.959
21.789


31.8
f1 (ppm)

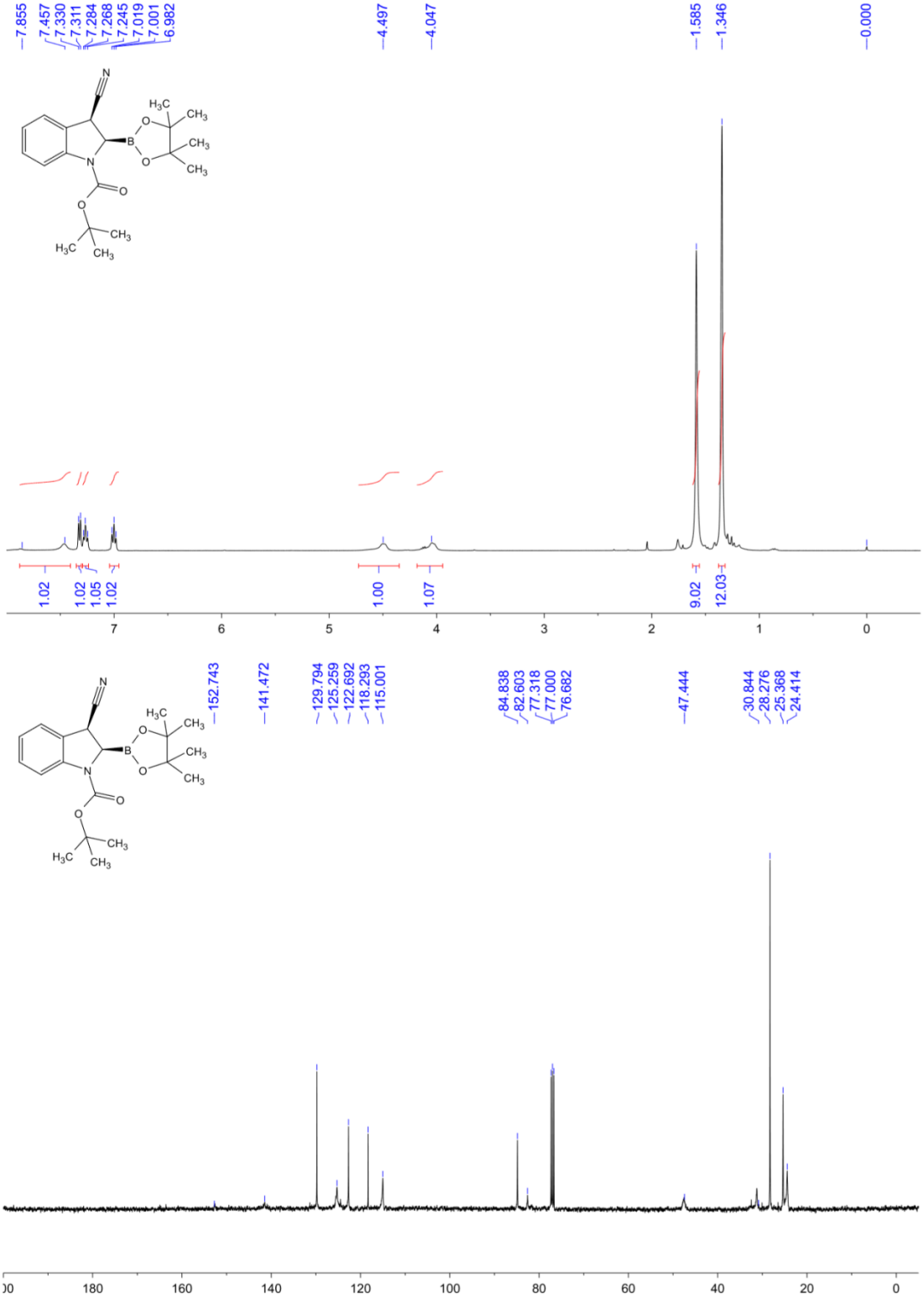
Compound 3t


7.398
7.378
7.268
7.242
7.224
6.920
6.902
6.884
5.065
5.049
5.033
5.020
5.004
4.087
4.059
4.035
1.557
1.264
1.240
0.000
1.01
1.01
1.01
1.00
2.01
9.00
18.07

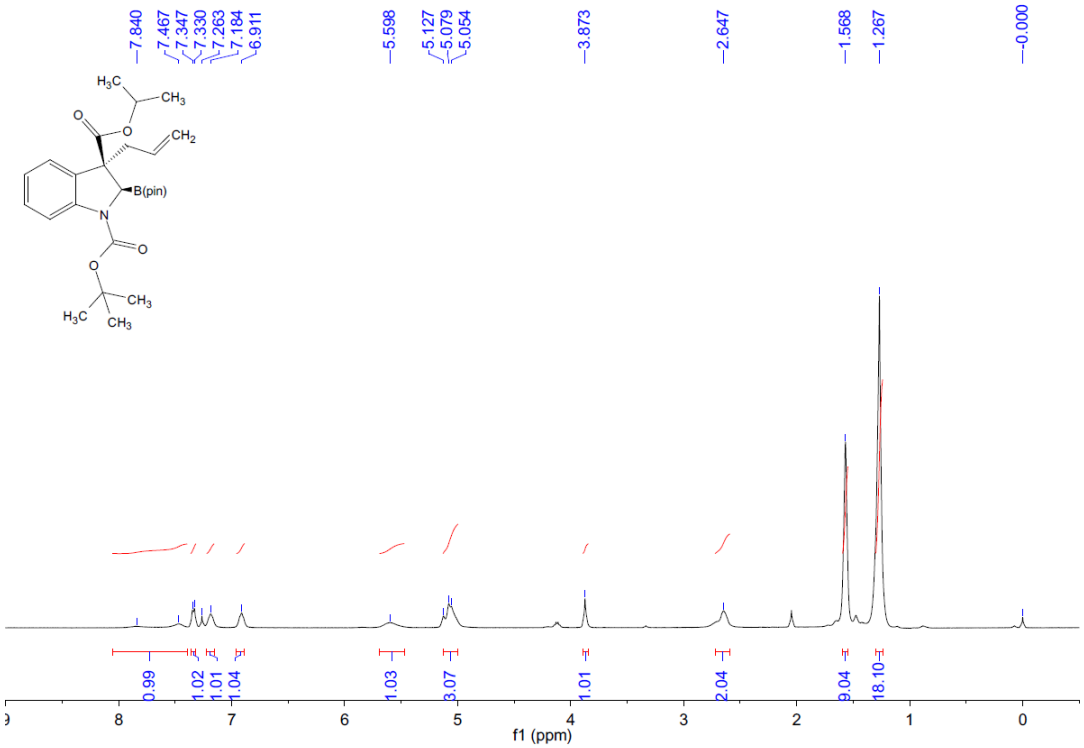

171.195
155.395
142.456
136.519
132.916
125.661
122.883
112.523
83.396
82.858
77.318
77.000
76.682
68.758
54.342
49.641
28.295
24.829
24.674
21.750
Br
180
160
140
120
100
80
60
40
20
0

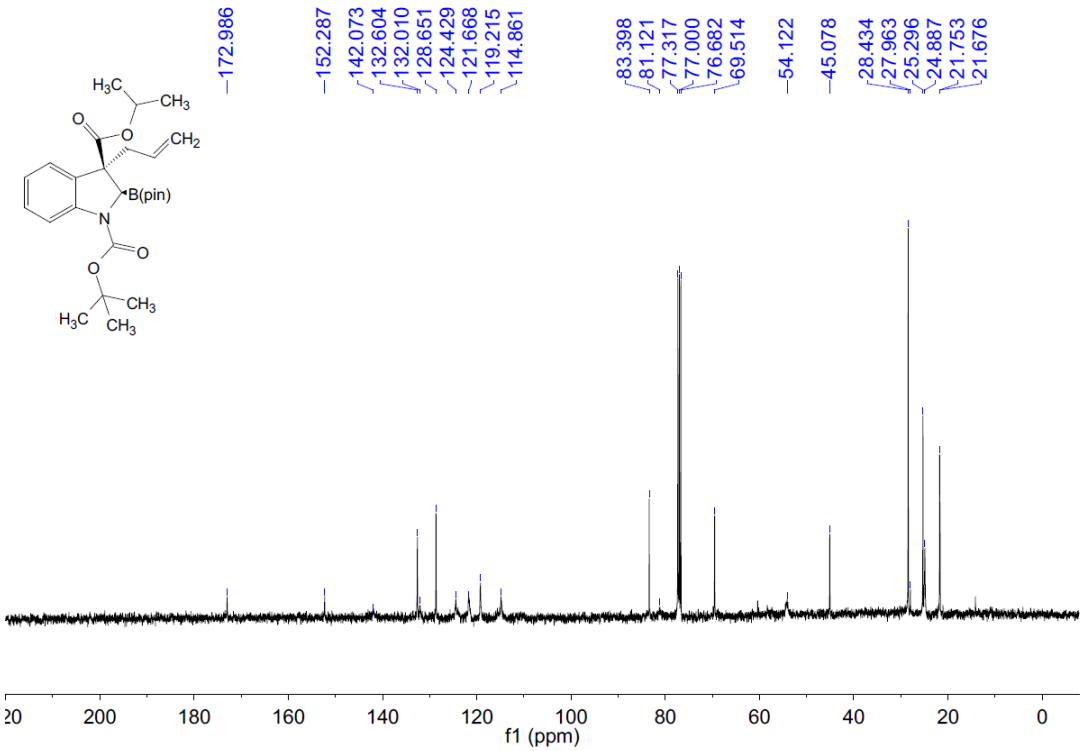

27.6
Br
0
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

Compound 2v

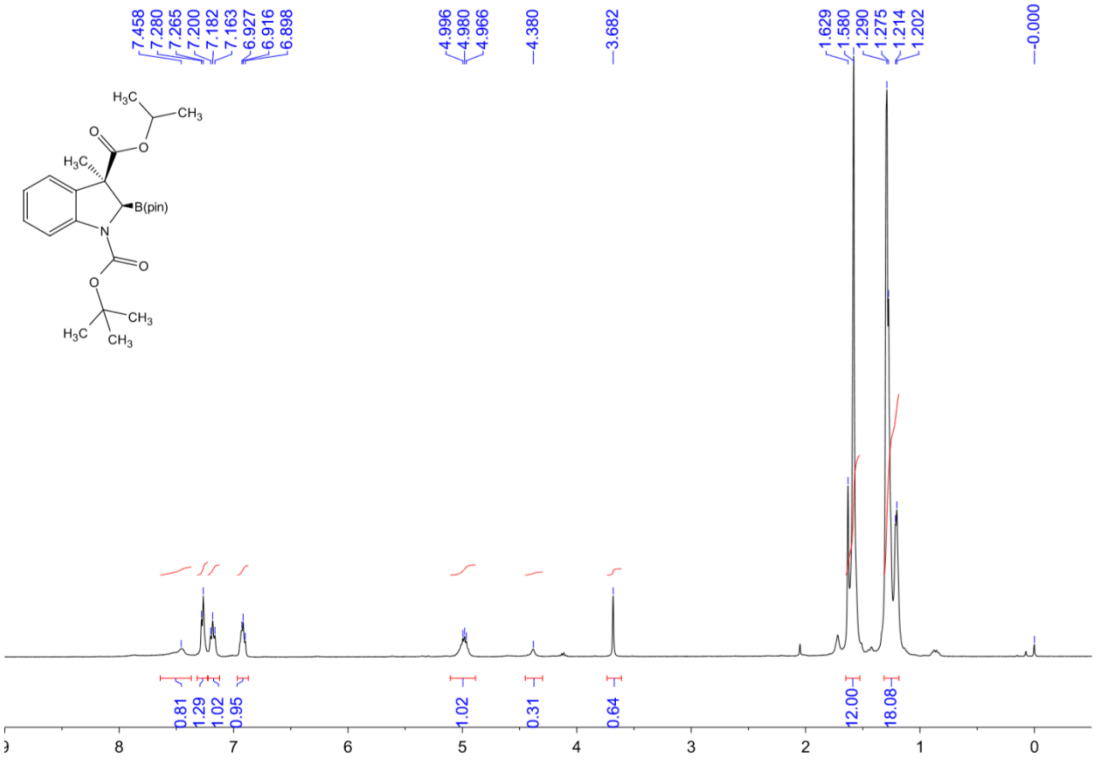

7.855
7.457
7.330
7.311
7.284
7.268
7.245
7.019
7.001
6.982
4.497
4.047
1.585
1.346
0.000
1.02
1.02
1.05
1.02
1.00
1.07
9.02
12.03
152.743
141.472
129.794
125.259
122.692
118.293
115.001
84.838
82.603
77.318
77.000
76.682
47.444
30.844
28.276
25.368
24.414

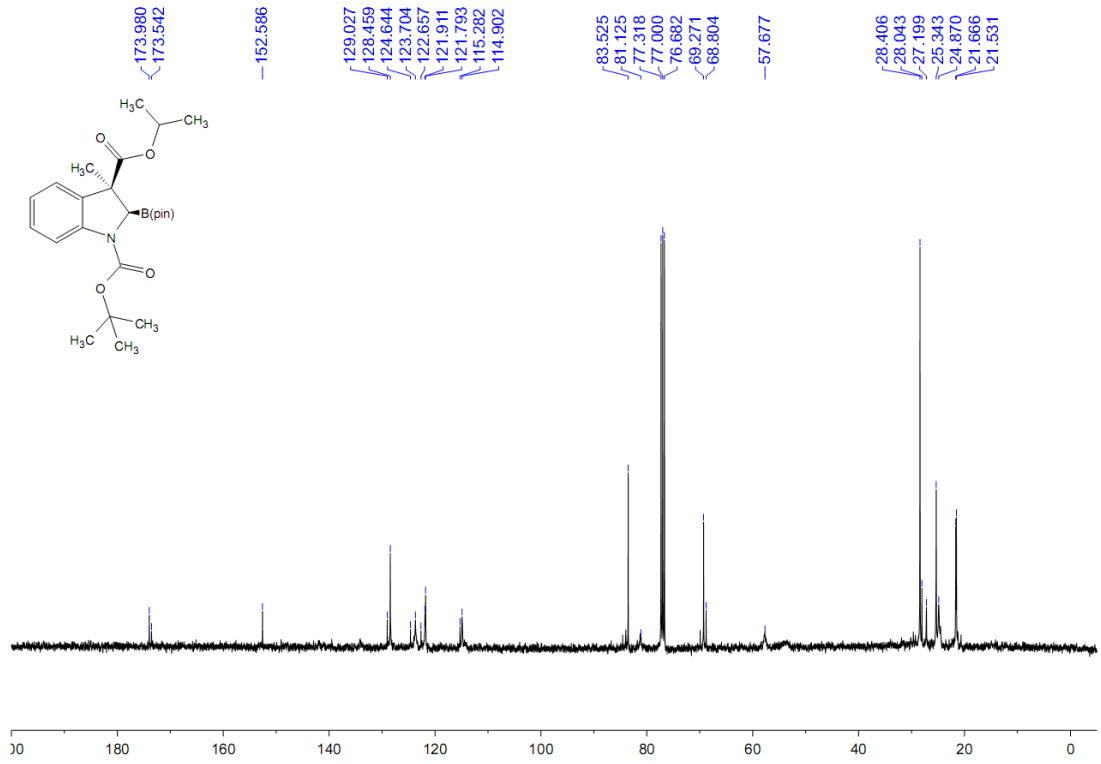
Compound 4a


7.840
7.467
7.347
7.330
7.263
7.184
6.911
5.598
5.127
5.079
5.054
3.873
2.647
1.568
1.267
0.000
B(pin)
0.99
1.02
1.01
1.04
1.03
3.07
1.01
2.04
9.04
18.10
f1 (ppm)

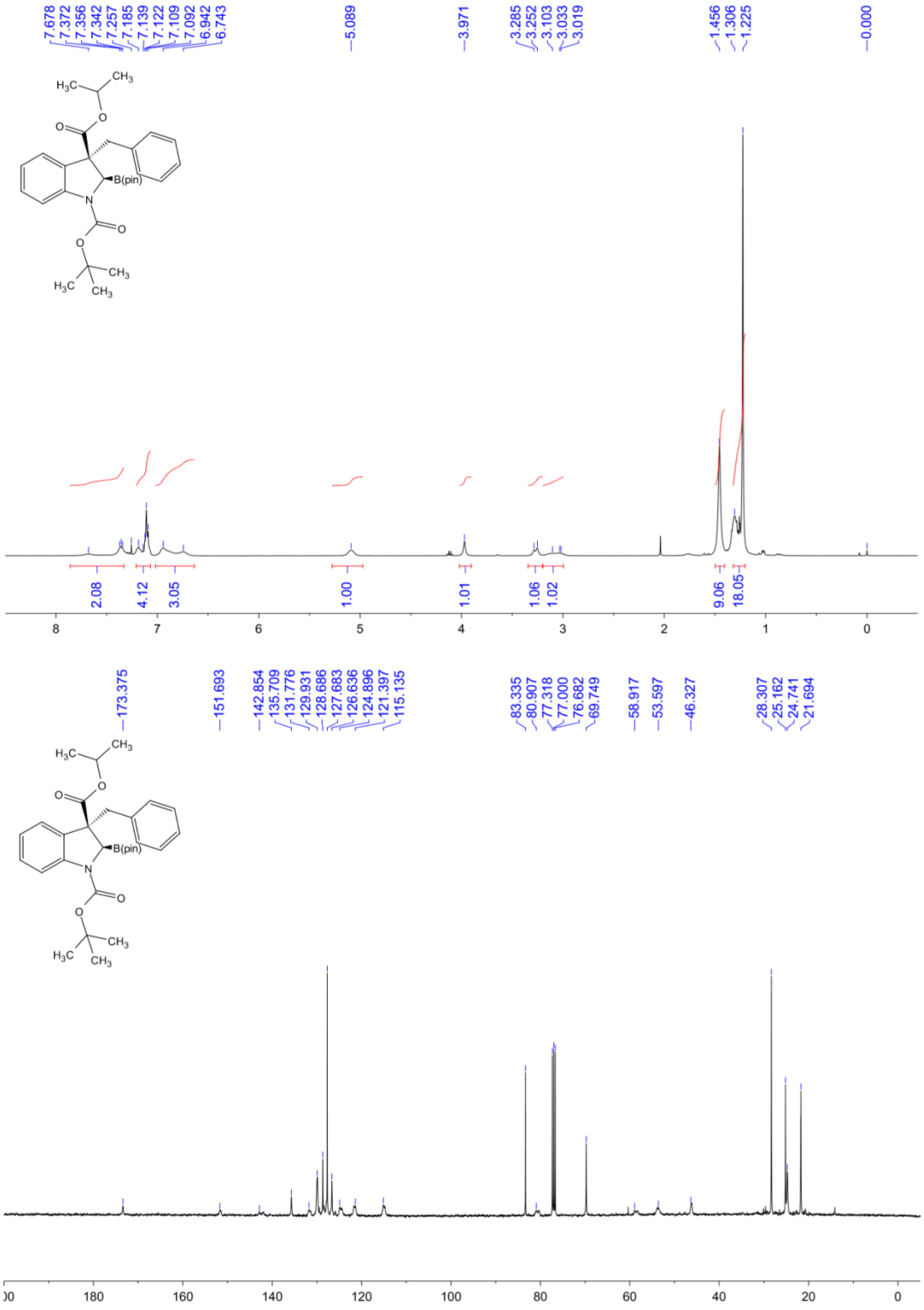

172.986
152.287
142.073
132.604
132.010
128.651
124.429
121.668
119.215
114.861
83.398
81.121
77.317
77.000
76.682
69.514
54.122
45.078
28.434
27.963
25.296
24.887
21.753
21.676
B(pin)
f1 (ppm)

Compound 4b

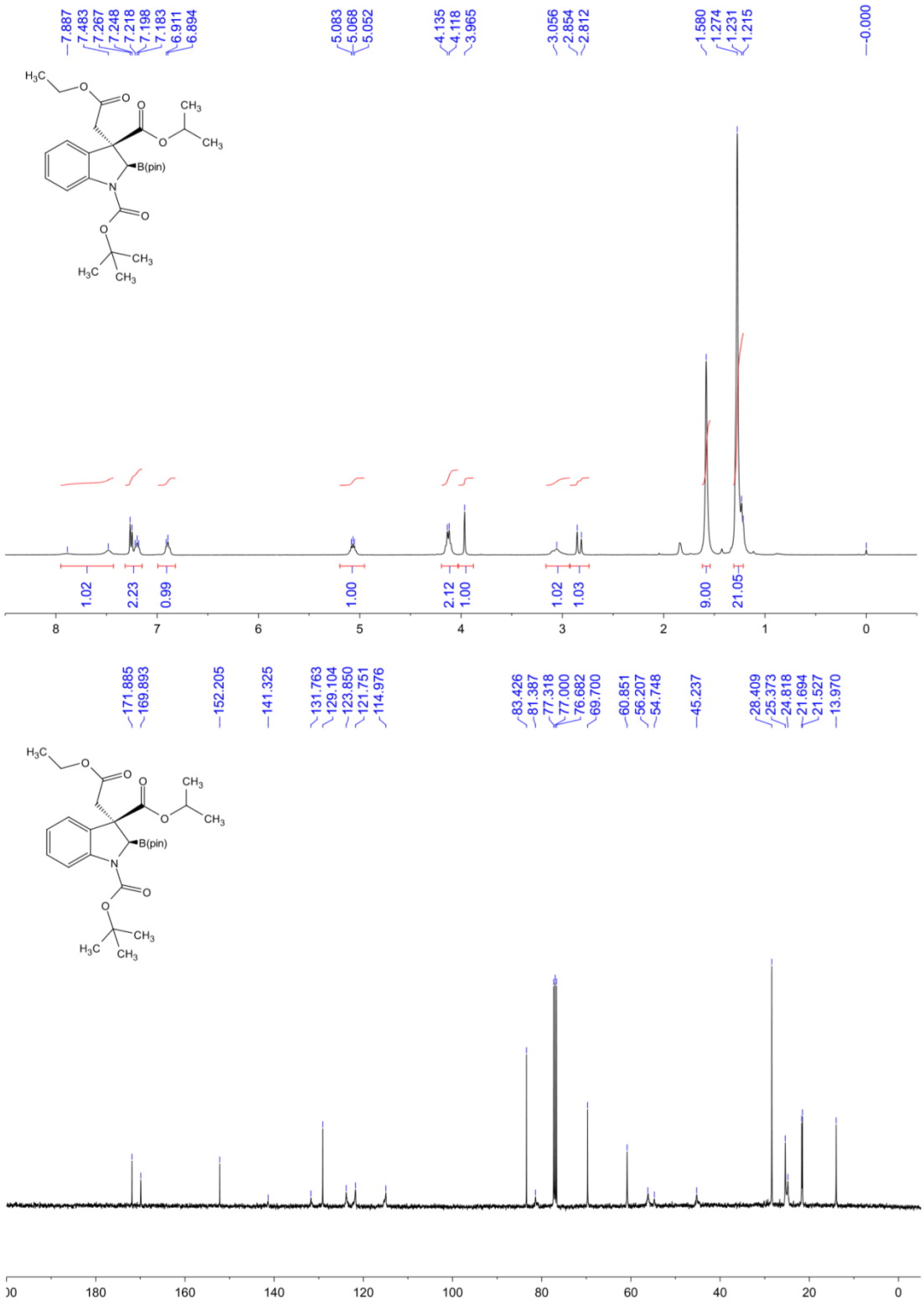

7.458
7.280
7.265
7.200
7.182
7.163
6.927
6.916
6.898
4.996
4.980
4.966
4.380
3.682
1.629
1.580
1.290
1.275
1.214
1.202
0.000
B(pin)
0.81
1.29
1.02
0.95
1.02
0.31
0.64
12.00
18.08


173.980
173.542
152.586
129.027
128.459
124.644
123.704
122.657
121.911
121.793
115.282
114.902
83.525
81.125
77.318
77.000
76.682
69.271
68.804
57.677
28.406
28.043
27.199
25.343
24.870
21.666
21.531
B(pin)

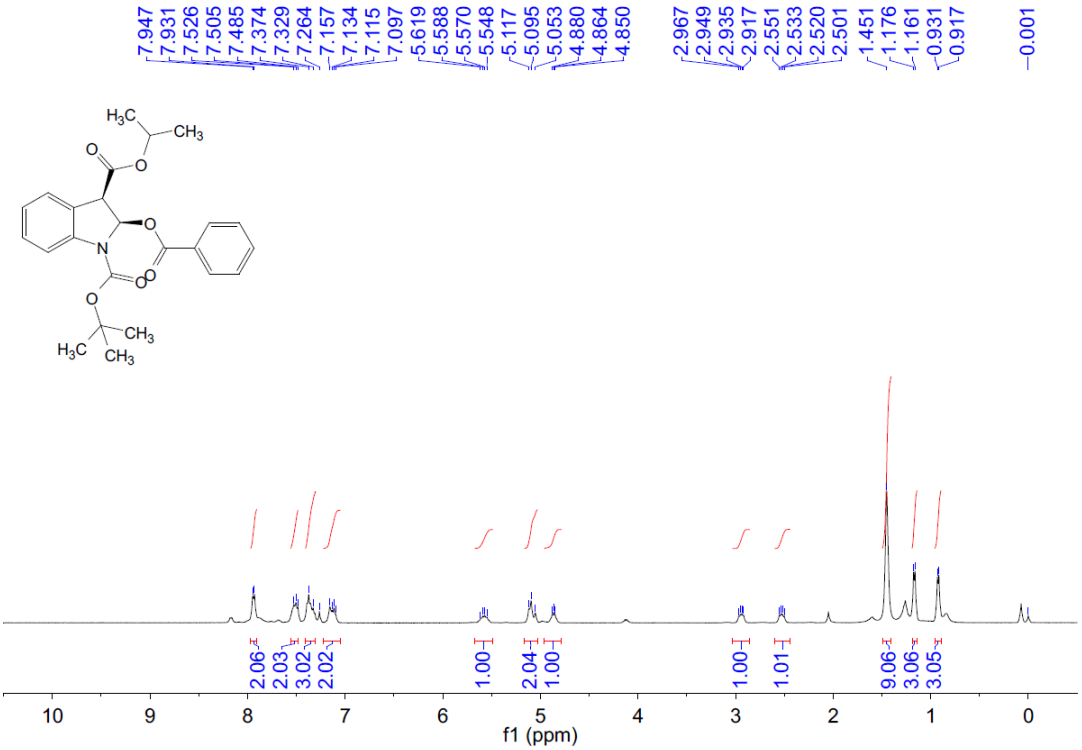
Compound 4c

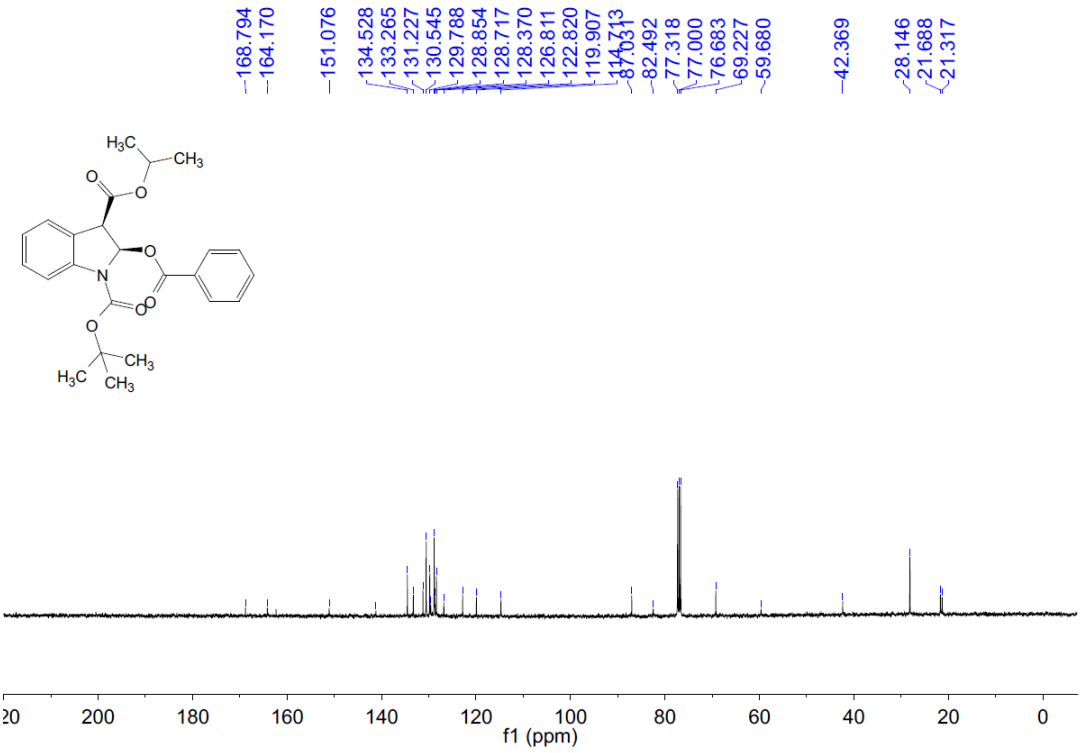

7.678
7.372
7.356
7.342
7.257
7.185
7.139
7.122
7.109
7.092
6.942
6.743
5.089
3.971
3.285
3.252
3.103
3.033
3.019
1.456
1.306
1.225
0.000
B(pin)
2.08
4.12
3.05
1.00
1.01
1.06
1.02
9.06
18.05
173.375
151.693
142.854
135.709
131.776
129.931
128.686
127.683
126.636
124.896
121.397
115.135
83.335
80.907
77.318
77.000
76.682
69.749
58.917
53.597
46.327
28.307
25.162
24.741
21.694

Compound 4d

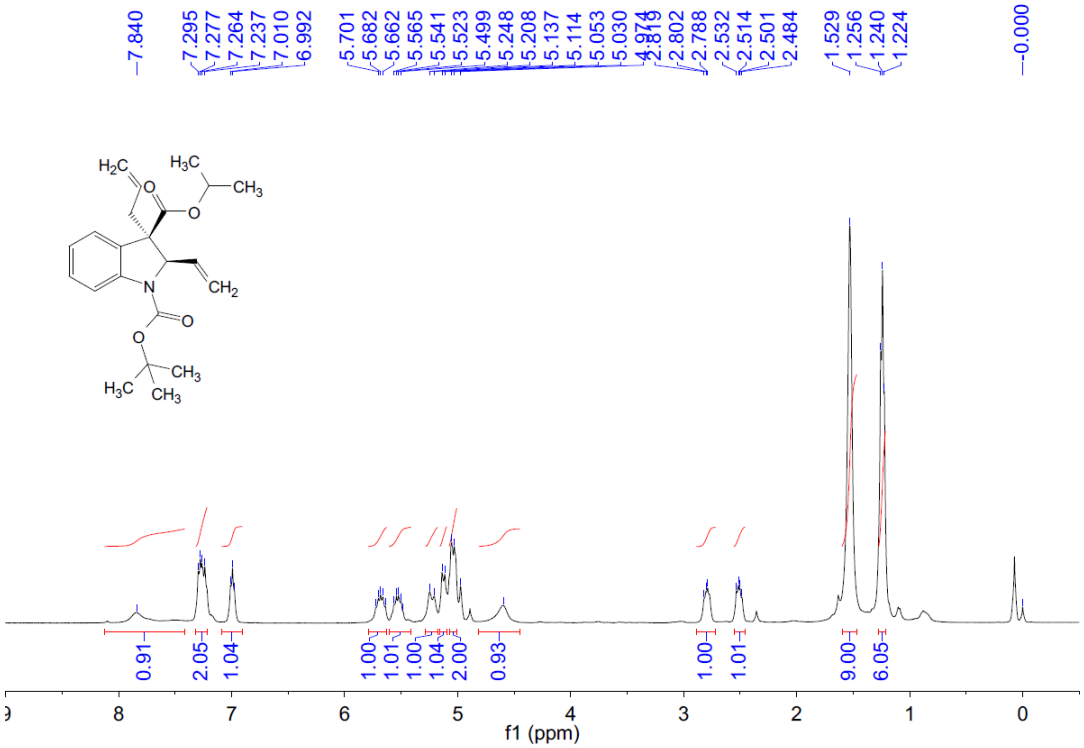

7.887
7.483
7.267
7.248
7.218
7.198
7.183
6.911
6.894
5.083
5.068
5.052
4.135
4.118
3.965
3.056
2.854
2.812
1.580
1.274
1.231
1.215
0.000
B(pin)
1.02
2.23
0.99
1.00
2.12
1.00
1.02
1.03
9.00
21.05
171.885
169.893
152.205
141.325
131.763
129.104
123.850
121.751
114.976
83.426
81.387
77.318
77.000
76.682
69.700
60.851
56.207
54.748
45.237
28.409
25.373
24.818
21.694
21.527
13.970

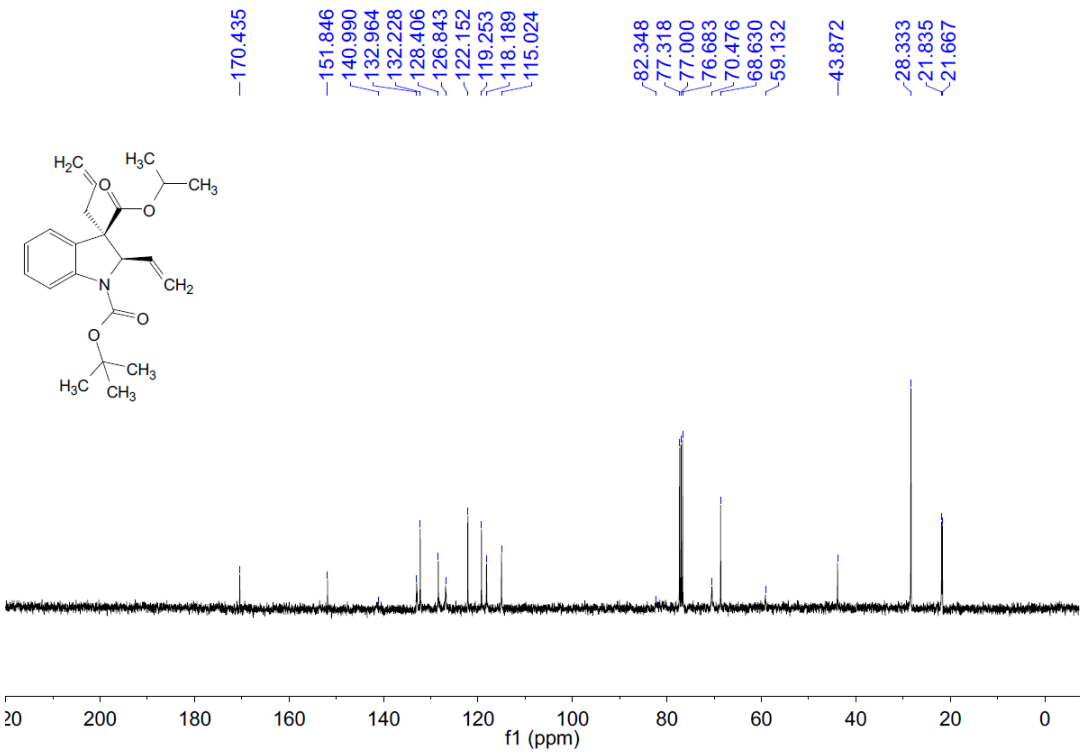
Compound 5


7.947
7.931
7.526
7.505
7.485
7.374
7.329
7.264
7.157
7.134
7.115
7.097
5.619
5.588
5.570
5.548
5.117
5.095
5.053
4.880
4.864
4.850
2.967
2.949
2.935
2.917
2.551
2.533
2.520
2.501
1.451
1.176
1.161
0.931
0.917
0.001
2.06
2.03
3.02
2.02
1.00
2.04
1.00
1.00
1.01
9.06
3.06
3.05
f1 (ppm)

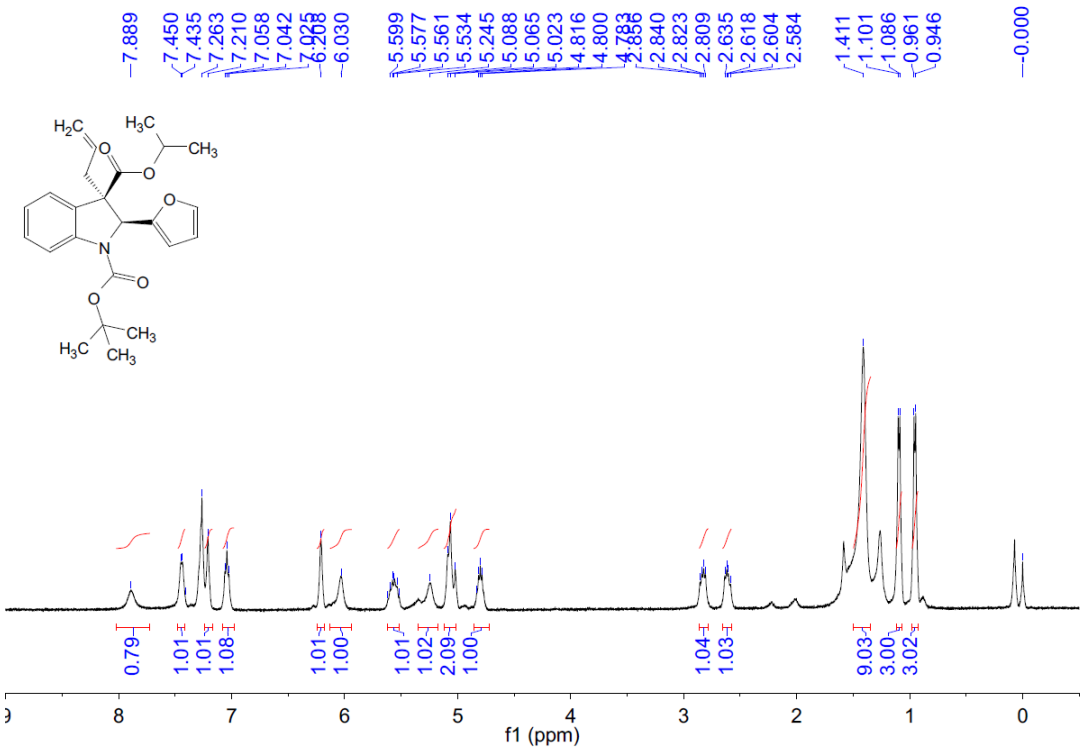

168.794
164.170
151.076
134.528
133.265
131.227
130.545
129.788
128.854
128.717
128.370
126.811
122.820
119.907
114.713
87.031
82.492
77.318
77.000
76.683
69.227
59.680
42.369
28.146
21.688
21.317
f1 (ppm)

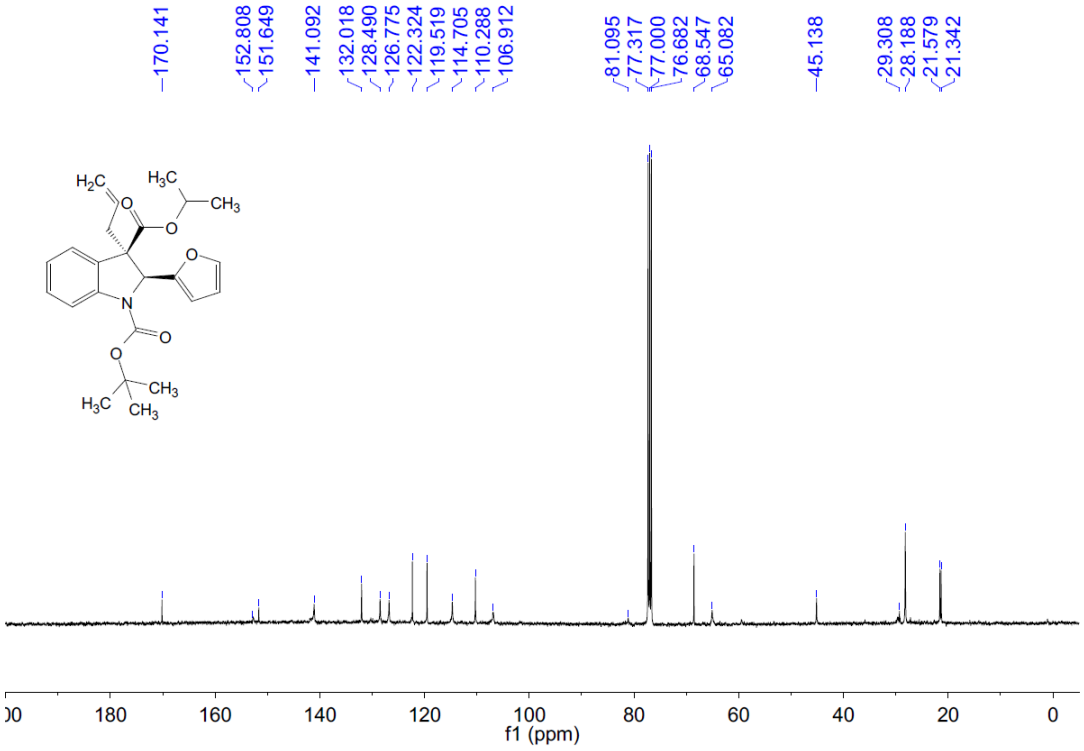
Compound 6


7.840
7.295
7.277
7.264
7.237
7.010
6.992
5.701
5.682
5.662
5.565
5.541
5.523
5.499
5.248
5.208
5.137
5.114
5.053
5.030
4.974
2.813
2.802
2.788
2.532
2.514
2.501
2.484
1.529
1.256
1.240
1.224
0.000
0.91
2.05
1.04
1.00
1.01
1.00
1.04
2.00
0.93
1.00
1.01
9.00
6.05
f1 (ppm)


170.435
151.846
140.990
132.964
132.228
128.406
126.843
122.152
119.253
118.189
115.024
82.348
77.318
77.000
76.683
70.476
68.630
59.132
43.872
28.333
21.835
21.667
f1 (ppm)

Compound 7


7.889
7.450
7.435
7.263
7.210
7.058
7.042
6.268
6.030
5.599
5.577
5.561
5.534
5.245
5.088
5.065
5.023
4.816
4.800
2.840
2.823
2.809
2.635
2.618
2.604
2.584
1.411
1.101
1.086
0.961
0.946
0.000
0.79
1.01
1.01
1.08
1.01
1.00
1.01
1.02
2.09
1.00
1.04
1.03
9.03
3.00
3.02
f1 (ppm)


170.141
152.808
151.649
141.092
132.018
128.490
126.775
122.324
119.519
114.705
110.288
106.912
81.095
77.317
77.000
76.682
68.547
65.082
45.138
29.308
28.188
21.579
21.342
f1 (ppm)