Supporting Information for

Ligand-Free Iridium-Catalyzed Regioselective C-H Borylation of Indoles

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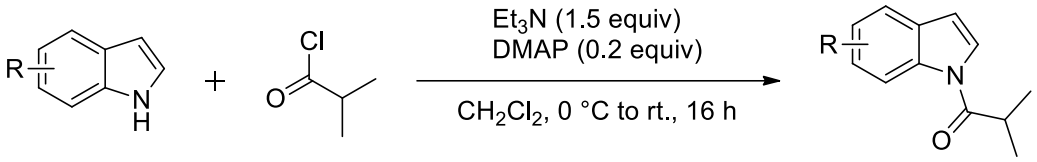
1. General

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

THF, CH_2Cl_2, *n*-heptane, *n*-hexane, and 1,4-dioxane were purified by passing through a neutral alumina column under argon. All other chemicals and solvents were used as received. Compounds **S1** (CAS: 576-15-8),[1] **S2** (CAS: 73747-53-2),[2] **S3** (CAS: 70957-04-9),[3] **S4** (CAS: 39203-20-8),[4] **S5** (CAS: 119668-50-7)[5] were prepared according to the literature procedures[1-5] and the characterization data are consistent with the literature reported.[1-5]

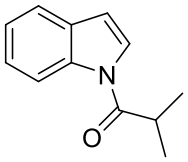
^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{11}B NMR spectra were recorded on Zhongke-Niujin 400, and Bruker DRX400 spectrometers at ambient temperature with $CDCl_3$ as solvent. ^{13}C shifts were obtained with ^{1}H decoupling. Chemical shifts and coupling constants are listed in ppm and Hz, respectively. High-resolution mass spectroscopy data were obtained on Agilent 6530, Agilent 6224 TOF LC/MS, and Agilent 7205 GCQTOF spectrometers. X-ray crystallography was measured on an XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. Melting points were determined on an Electrothermal IA9000 Series Digital Melting Point Apparatus.

2. General procedure for the Synthesis of N- isobutyryl substrates (GP1)

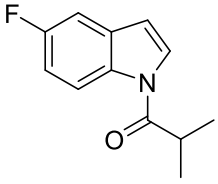


1

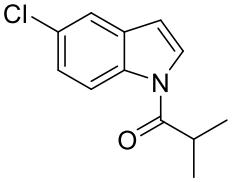
The synthesis of compound 1 was adapted from the literature procedures.[6] To a 50-mL flask charged with indole (2 mmol), DMAP (0.4 mmol), Et_3N (0.4 mL. 3 mmol) and DCM (10 mL) was slowly added isobutyryl chloride (1.5 eq.) at 0 °C. The reaction was then warmed to room temperature and allowed to stir at this temperature for additional 16 h. After the conclusion of the reaction, H_2O (20 mL) was then added. The biphasic mixture was then extracted with DCM 3 times (3 X 10 mL). The combined organic phase was washed with 1 M HCl (20 mL) and then dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was then purified by chromatography on silica gel using PE/EtOAc as the eluent to afford **1**.



Compound **1a** (CAS: 343773-85-3): Rf = 0.4 (PE/EtOAc = 50:1), white solid, mp = 76 -78 ˚C, 0.34 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 3.6 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.31 – 7.27 (m, 1H), 6.66 (d, *J* = 4.0 Hz, 1H), 3.56 – 3.05 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.8, 135.8, 130.4, 125.1, 124.5, 123.6, 120.7, 116.8, 109.0, 33.8, 19.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{13}NNaO$ 210.0889, found 210.0881.

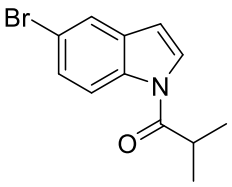


Compound **1b**: Rf = 0.5 (PE/EtOAc = 40:1), white solid, mp = 62 -66 ˚C, 0.37 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 9.2, 4.8 Hz, 1H), 7.45 (d, *J* = 4.0 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.98 (td, *J* = 9.2, 2.8 Hz, 1H), 6.52 (dd, *J* = 4.0, 0.4 Hz, 1H), 3.30 – 3.15 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.6, 159.6 (d, *J* = 238.7 Hz), 132.2 , 131.4 (d, *J* = 10.0 Hz), 126.0, 117.9 (d, *J* = 9.1 Hz), 112.8 (d, *J* = 24.7 Hz), 108.7 (d, *J* = 3.8 Hz), 106.2 (d, *J* = 23.7 Hz), 33.6, 19.5; ^{19}F NMR (376 MHz, CDCl3) δ -119.5; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}FNO$ 206.0976, found 206.0972.

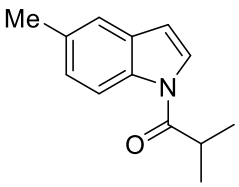


Compound **1c** (CAS: 1855896-84-2): Rf = 0.5 (PE/EtOAc = 40:1), white solid, mp = 72 - 75 ˚C, 0.40 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.8 Hz, 1H), 7.53 (s, 1H), 7.52 (d, *J* = 3.6 Hz, 2H), 7.31 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.60 (d, *J* = 3.6 Hz, 1H), 3.48 – 3.10 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.6, 134.2, 131.6, 129.2, 125.8, 125.3, 120.3, 117.9, 108.3, 33.7, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}ClNO$ 222.0680, found 222.0675.

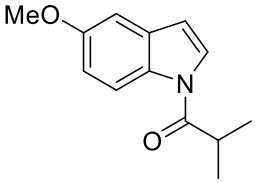
Compound **1d** (CAS: 1855896-77-3): Rf = 0.5 (PE/EtOAc = 40:1), white solid, mp = 80 -83 ˚C, 0.47 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 4.0 Hz, 1H), 7.44 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.58 (dd, *J* = 3.6, 0.4 Hz, 1H), 3.68 – 3.00 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.7, 134.5, 132.1, 127.9, 125.7, 123.4, 118.3, 116.9, 108.2, 33.8, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}BrNO$ 266.0175, found 266.0174.



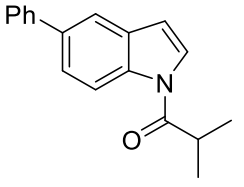
Compound **1e** (CAS: 1855896-67-1): Rf = 0.5 (PE/EtOAc = 30:1), white solid, mp = 65 -68 ˚C, 0.35 g, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 4.0 Hz, 1H), 7.37 (s, 1H), 7.19 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H), 3.39 – 3.20 (m, 1H), 2.46 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.6, 133.9, 133.1, 130.6, 126.3, 124.5, 120.6, 116.4, 108.8, 33.6, 21.3, 19.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}NNaO$ 224.1046, found 224.1058.



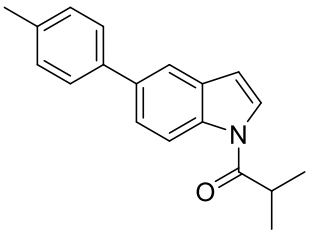
Compound **1f** (CAS: 1855896-72-8): Rf = 0.3 (PE/EtOAc = 30:1), white solid, mp = 76 -80 ˚C, 0.40 g, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 9.2 Hz, 1H), 7.48 (d, *J* = 4.0 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.58 (d, *J* = 3.6 Hz, 1H), 3.86 (s, 3H), 3.37 – 3.22 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.5, 156.4, 131.4, 130.5, 125.2, 117.6, 113.5, 108.9, 103.5, 55.7, 33.5, 19.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}NNaO_2$ 240.0995, found 240.0990.



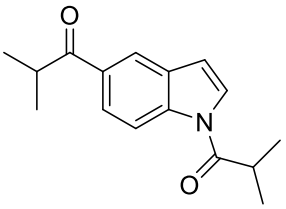
Compound **1g**: Rf = 0.4 (PE/EtOAc = 30:1), white solid, mp = 151 -154 ˚C, 0.48 g, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.54 (d, *J* = 4.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.38 – 7.32 (m, 1H), 6.71 (dd, *J* = 3.6, 0.4 Hz, 1H), 3.47 – 3.21 (m, 1H), 1.38 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.7, 141.5, 137.0, 135.2, 131.0, 128.8, 127.4, 127.0, 125.2, 124.7, 119.2, 117.0, 109.3, 33.8, 19.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}NNaO$ 286.1202, found 286.1204.



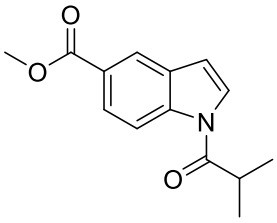
Compound **1h**: Rf = 0.4 (PE/EtOAc = 40:1), white solid, mp = 158 -163 ˚C, 0.53 g, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.59 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 3.51 – 3.13 (m, 1H), 2.41 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.7, 138.6, 136.7, 130.9, 129.5, 127.2, 125.1, 124.5, 118.9, 117.0, 109.3, 77.3, 77.0, 76.7, 33.8, 21.1, 19.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO$ 300.1359, found 300.1370.



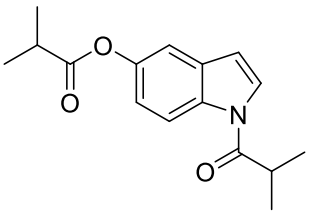
Compound **1i**: Rf = 0.4 (PE/EtOAc = 1:1), white solid, mp = 115 -120 ˚C, 0.31 g, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.8 Hz, 1H), 8.22 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 3.6 Hz, 1H), 6.75 (d, *J* = 4.0 Hz, 1H), 3.72 – 3.58 (m, 1H), 3.41 – 3.22 (m, 1H), 1.38 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 204.3, 175.8, 138.3, 131.9, 130.4, 125.9, 125.5, 121.7, 116.7, 109.6, 35.4, 33.9, 19.4, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NO_2$ 258.1489, found 258.1490.



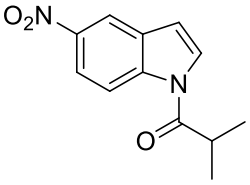
Compound **1j**: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 101 - 104 ˚C, 0.44 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.8 Hz, 1H), 8.29 (d, *J* = 1.6 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.56 (d, *J* = 4.0 Hz, 1H), 6.72 (d, *J* = 3.6 Hz, 1H), 3.94 (s, 3H), 3.37 – 3.26 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.9, 167.4, 138.4, 130.2, 126.4, 125.8, 125.5, 123.0, 116.5, 109.4, 52.1, 33.9, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{16}NO_3$ 246.1125, found 246.1129.



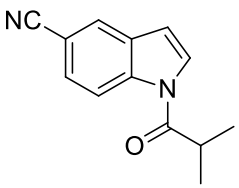
Compound **1k**: Rf = 0.4 (PE/EtOAc = 10:1), colorless oil, 0.46 g, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 3.6 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.61 (d, *J* = 3.6 Hz, 1H), 3.38 – 3.23 (m, 1H), 2.89 – 2.76 (m, 1H), 1.39 – 1.28 (m, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 175.6, 147.1, 133.4, 131.0, 125.6, 118.7, 117.4, 113.1, 108.9, 34.2, 33.6, 19.4, 19.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NO_3$ 274.1438, found 274.1445.



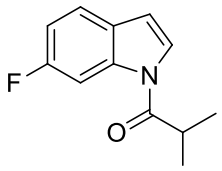
Compound **1l**: Rf = 0.3 (PE/EtOAc = 10:1), yellow solid, mp = 121 -124 ˚C, 0.40 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 9.2 Hz, 1H), 8.49 – 8.47 (m, 1H), 8.25 – 8.21 (m, 1H), 7.67 (d, *J* = 3.6 Hz, 1H), 6.80 (d, *J* = 4.k0 Hz, 1H), 3.42 – 3.26 (m, 1H), 1.39 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.8, 144.3, 138.8, 130.2, 127.4, 120.3, 117.0, 116.9, 109.4, 34.0, 19.3; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}N_2O_3$ 233.0921, found 233.0932.



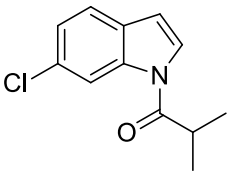
Compound **1m**: Rf = 0.3 (PE/EtOAc = 10:1), white solid, mp = 72 -80 ˚C, 5.72 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 0.8 Hz, 1H), 7.63 (d, *J* = 4.0 Hz, 1H), 7.60 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.72 (dd, *J* = 4.0, 0.4 Hz, 1H), 3.39 – 3.26 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.9, 137.6, 130.3, 128.3, 126.7, 125.5, 119.6, 117.7, 108.6, 107.0, 34.0, 19.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{12}N_2NaO$ 235.0842, found 235.0841.



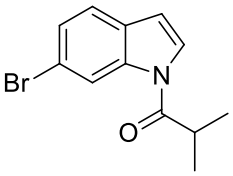
Compound **1n**: Rf = 0.6 (PE/EtOAc = 10:1), white solid, mp = 46 -49 ˚C, 0.34 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 10.8, 2.4 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.05 – 6.98 (m, 1H), 6.61 (dd, *J* = 4.0, 0.8 Hz, 1H), 3.34 – 3.21 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.8, 161.3 (d, *J* = 240.5 Hz), 135.9 (d, *J* = 13.1 Hz), 126.6, 124.89 (d, *J* = 4.1 Hz), 121.2 (d, *J* = 10.0 Hz), 111.8 (d, *J* = 24.2 Hz), 108.8 , 104.2 (d, *J* = 28.6 Hz), 33.7 , 19.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.9; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}FNO$ 206.0976, found 206.0967.



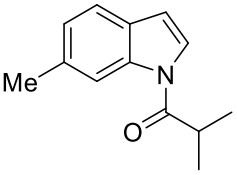
Compound **1o**: Rf = 0.6 (PE/EtOAc = 10:1), white solid, mp = 61 -65 ˚C, 0.38 g, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.6 Hz, 1H), 7.49 (d, *J* = 4.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 3.35 – 3.22 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.7, 136.1, 131.1, 128.8, 125.1, 124.2, 121.3, 117.2, 108.7, 33.8, 19.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{12}ClNNaO$ 244.0500, found 244.0501.



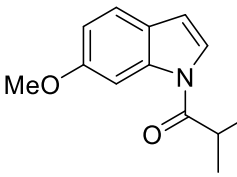
Compound **1p**: Rf = 0.5 (PE/EtOAc = 40:1), white solid, mp = 68 -71 ˚C, 0.45 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.47 (d, *J* = 3.6 Hz, 1H), 7.44 – 7.35 (m, 1H), 7.26 (s, 1H), 6.61 (d, *J* = 3.6 Hz, 1H), 3.35 – 3.20 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.7, 136.4, 129.1, 126.9, 125.0, 121.7, 120.0, 118.9, 108.8, 33.8, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}BrNO$ 266.0175, found 266.0186.



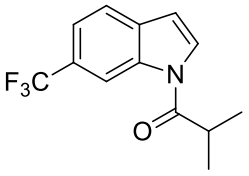
Compound **1q**: Rf = 0.4 (PE/EtOAc = 40:1), white solid, 0.35 g, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 4.0 Hz, 1H), 7.12 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.61 (dd, *J* = 3.6, 0.4 Hz, 1H), 3.40 – 3.19 (m, 1H), 2.50 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.9, 136.1, 135.6, 128.0, 125.0, 123.9, 120.2, 117.1, 108.9, 33.7, 21.9, 19.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}NNaO$ 224.1046, found 224.1045.



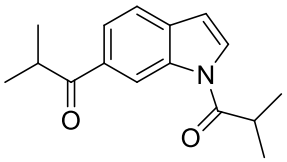
Compound **1r**: Rf = 0.4 (PE/EtOAc = 30:1), white oil, 0.35 g, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 4.0 Hz, 1H), 6.92 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.57 (dd, *J* = 4.0, 0.8 Hz, 1H), 3.88 (s, 3H), 3.35 – 3.21 (m, 1H), 1.35 (d, J = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2, 158.4, 136.8, 124.0, 123.3, 121.1, 113.2, 109.0, 100.7, 55.6, 33.8, 19.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}NNaO_2$ 240.0995, found 240.0987.



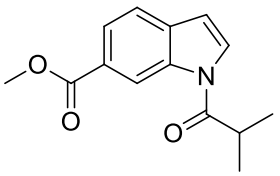
Compound **1s**: Rf = 0.5 (PE/EtOAc = 10:1), white solid, mp = 65 -68 ˚C, 0.46 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 0.8 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.52 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.71 (dd, *J* = 3.6, 0.4 Hz, 1H), 3.39 – 3.25 (m, 1H), 1.38 (d, *J* = 6.8 Hz,



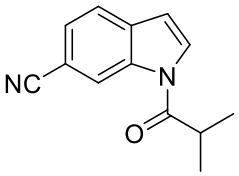
6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.8, 135.0, 132.8, 127.2 (q, *J* = 32.0 Hz), 126.9, 124.8 (q, *J* = 270.2 Hz), 121.0, 120.4 (q, *J* = 3.6 Hz), 114.5 (q, *J* = 4.4 Hz), 108.7, 33.8, 19.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.1; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NO$ 256.0944, found 256.0946.



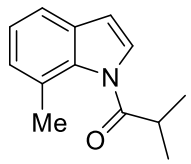
Compound **1t**: Rf = 0.2 (PE/EtOAc = 30:1), colorless oil, 0.26 g, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 3.6 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 4.0 Hz, 1H), 3.81 – 3.68 (m, 1H), 3.47 – 3.26 (m, 1H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.28 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 204.6, 175.9, 135.4, 133.9, 133.3, 127.6, 123.7, 120.8, 117.6, 108.9, 35.3, 33.8, 19.5, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NO_2$ 258.1489, found 258.1491.



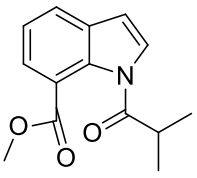
Compound **1u**: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 108 - 113 ˚C, 0.43 g, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, *J* = 0.4 Hz, 1H), 7.98 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.65 (d, *J* = 3.6 Hz, 1H), 7.60 (dd, *J* = 8.4, 0.4 Hz, 1H), 6.69 (dd, *J* = 4.0, 0.8 Hz, 1H), 3.93 (s, 3H), 3.41 – 3.20 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.7, 167.6, 135.2, 134.1, 127.4, 126.9, 124.9, 120.4, 118.6, 108.8, 52.1, 33.9, 19.4; HRMS (ESI-TOF) m/z: [M+H]+ calcd for $C_{14}H_{16}NO_3$ 246.1125, found 246.1126.



Compound **1v**: Rf = 0.5 (PE/EtOAc = 10:1), white solid, mp = 147 -150 ˚C, 0.36 g, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.70 (d, *J* = 3.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.73 (dd, *J* = 3.6, 0.4 Hz, 1H), 3.40 – 3.26 (m, 1H), 1.38 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.7, 134.8, 133.6, 127.8, 126.8, 121.5, 121.4, 119.8, 108.8, 108.0, 33.9, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}N_2O$ 213.1022, found 213.1023.

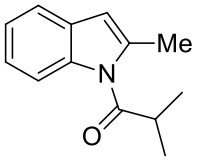


Compound **1w**: Rf = 0.4 (PE/EtOAc = 30:1), 0.35 g, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 3.6 Hz, 1H), 3.47 – 3.27 (m, 1H), 2.52 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.6, 134.2, 130.9, 126.8, 125.4, 124.8, 122.8, 117.4, 107.6, 33.8, 21.1, 18.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}NNaO$ 224.1046, found 224.1040.

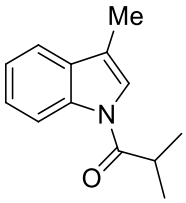


Compound **1x**: Rf = 0.3 (PE/EtOAc = 10:1), white solid, mp = 96 -100 ˚C, 5.72 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 3.6 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H), 3.89 (s, 3H), 3.38 – 3.21 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.4, 168.5, 131.9, 131.4, 126.0, 125.3, 123.8, 123.3, 122.4, 108.7, 52.0, 34.1, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{16}NO_3$ 246.1125, found 246.1129.

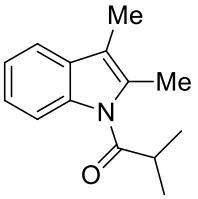
Compound **3a** [CAS: 1451075-03-8][7]: Rf = 0.3 (PE/EtOAc = 10:1), colorless oil, 0.34 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.26 – 7.17 (m, 2H), 6.38 (s, 1H), 3.60 – 3.49 (m, 1H), 2.63 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.6, 137.5, 136.2, 129.8, 123.3, 122.8, 119.9, 114.6, 109.2, 35.5, 19.6, 17.0.



Compound **3b** [CAS: 1824689-93-1][8]: Rf = 0.3 (PE/EtOAc = 10:1), white solid, mp = 70 – 73 ˚C, 0.35 g, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.30 – 7.26 (m, 2H), 3.32 – 3.24 (m, 1H), 2.30 (d, *J* = 1.2 Hz, 3H), 1.35 (d, J = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.4, 136.1, 131.4, 125.2, 123.3, 121.5, 118.7, 118.2, 116.9, 33.7, 19.5, 9.7.

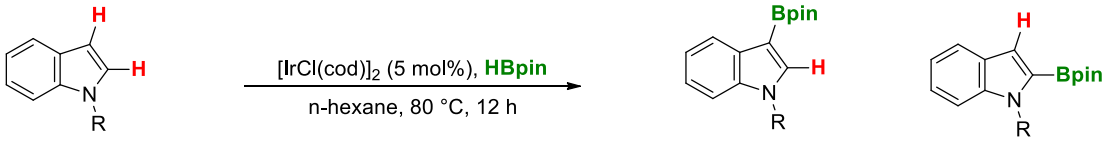


Compound **3c**: Rf = 0.3 (PE/EtOAc = 10:1), colorless oil, 0.35 g, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 1H), 7.47 – 7.43 (m, 1H), 7.26 – 7.23 (m, 2H), 3.61 – 3.50 (m, 1H), 2.55 (s, 3H), 2.21 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.5, 135.4, 132.7, 131.2, 123.5, 122.5, 118.2, 115.0, 114.2, 35.6, 19.6, 13.9, 8.7.



3. Effect of N-substituent on regioselectivity

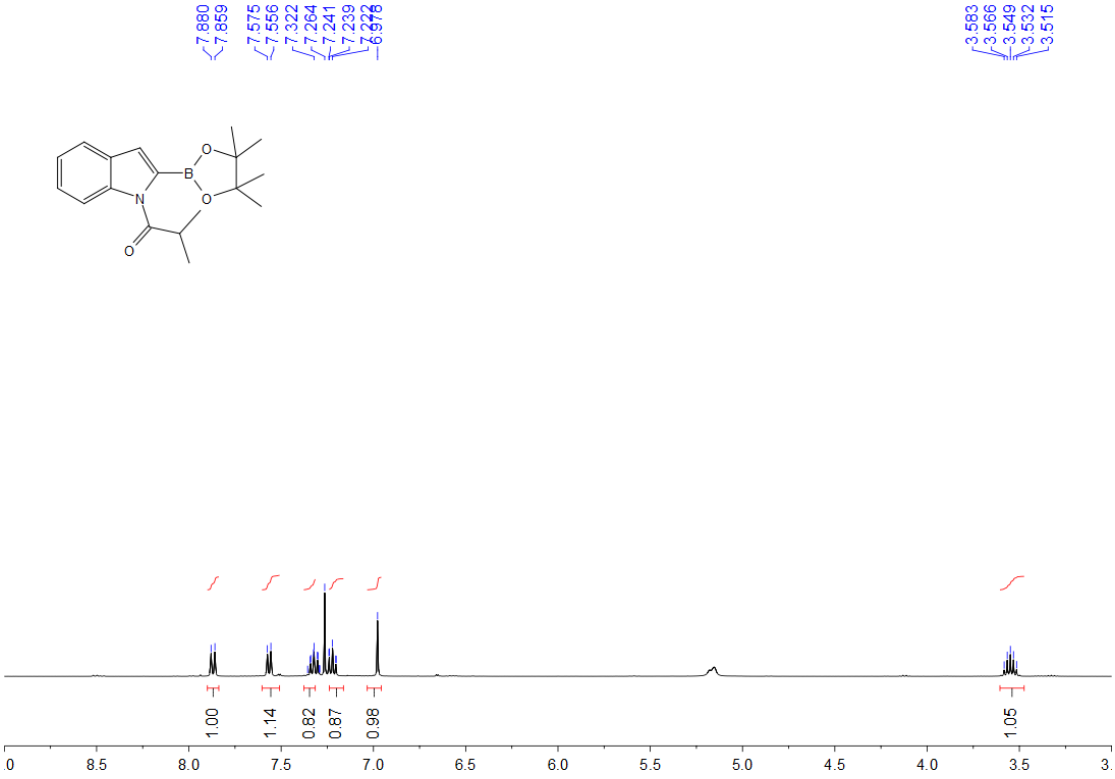
Table S1. Assessment of N-substituent of regioselectivity



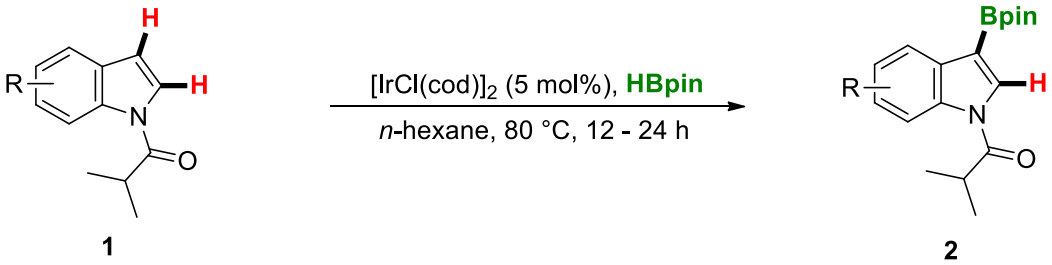
Entry	R	C3/C2
1	H	n.d. (trace)
2	C(O)Me (**S1**)	90:10
3	C(O)Et (**S2**)	65:35
4	C(O)-*i*-Pr (**1a**)	97:3
5	C(O)-*t*-Bu (**S3**)	94:6
6	C(O)OMe (**S4**)	79:21
7	C(O)NEt_2 (**S5**)	58:42

Conclusion: C(O)-*i*-Pr is optimal in terms of regioselectivity.

4. Crude ^{1}H NMR of C2-borylated product 2a' from Table 1, entry 4

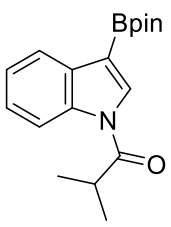


5. General procedure for the catalytic C-H borylation (*GP2*)



1 **2**

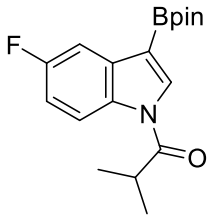
In a N_2-filled glovebox, to a 25-mL flame-dried Schlenk tube charged with $[IrCl(cod)]_2$ (6.7 mg, 0.01 mmol), HBpin (38.4 mg, 0.3 mmol), *N*-isobutyryl indole **1** (0.2 mmol) was added *n*-hexane (1 mL). The resulting mixture allowed to stir at 80 °C for 12 - 24 h. After the completion of the reaction, the regioselectivity was determined by GC analysis or ^{1}H NMR of crude reaction mixture. After removal of the solvent, the residue was purified by flash column chromatography on silica gel using PE/EtOAc as the eluent to afford desired borylated product **2**.



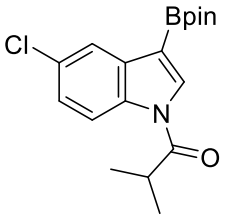
Compound **2a**: Rf = 0.5 (PE/EtOAc = 40:1), white solid, mp = 114 -116 ˚C, 49.6 mg, 79% yield, C3:C2 = 97:3 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.01 – 7.96 (m, 1H), 7.93 (s, 1H), 7.37 – 7.28 (m, 2H), 3.47 – 3.33 (m, 1H), 1.38 (s, 12H), 1.36 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.01, 136.7, 133.7, 133.6, 125.0, 123.8, 122.4, 116.6, 83.5, 77.0, 33.8, 24.9, 19.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; HRMS (ESI-

TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{25}BNO_3$ 314.1922, found 314.1923.

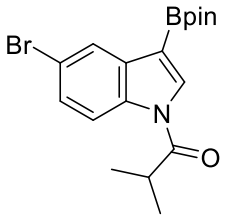
Compound **2b**: Rf = 0.45 (PE/EtOAc = 40:1), white solid, mp = 98 -100 ˚C, 48.7 mg, 77% yield, C3:C2 = 98:2 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.88 (s, 1H), 7.57 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.06 – 6.93 (m, 1H), 3.52 – 3.00 (m, 1H), 1.31 (s, 12H), 1.28 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.8, 159.9 (d, *J* = 239.9 Hz), 134.9, 134.6 (d, *J* = 10.1 Hz), 133.0, 117.5 (d, *J* = 9.1 Hz), 112.7 (d, *J* = 25.0 Hz), 108.1 (d, *J* = 23.7 Hz), 83.7, 33.6, 24.9, 19.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{23}BFNNaO_3$ 354.1647, found 354.1649.



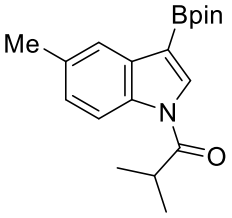
Compound **2c**: Rf = 0.5 (PE/EtOAc = 40:1), white solid, mp = 132 -138 ˚C, 57.7 mg, 83% yield, C3:C2 = 98:2 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.94 (s, 1H), 7.30 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.44 – 3.31 (m, 1H), 1.38 (s, 12H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.9, 139.0, 135.0, 134.7, 129.5, 125.2, 122.1, 117.6, 83.7, 33.7, 24.9, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}BClNO_3$ 348.1532, found 348.1538.



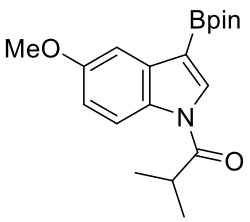
Compound **2d**: Rf = 0.45 (PE/EtOAc = 40:1), white solid, mp = 122 -125 ˚C, 62.7 mg, 80% yield, C3:C2 = 96:4 (GC).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.8 Hz, 1H), 8.10 (d, *J* = 2.0 Hz, 1H), 7.92 (s, 1H), 7.44 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.44 – 3.28 (m, 1H), 1.38 (s, 12H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.9, 135.4, 135.1, 134.6, 127.9, 125.1, 118.0, 117.3, 83.8, 33.7, 24.9, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.3; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}BBrNO_3$ 392.1027, found 392.1023.



Compound **2e**: Rf = 0.4 (PE/EtOAc = 30:1), white solid, mp = 159 -163 ˚C, 45.2 mg, 69% yield, C3:C2 = 95:5 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.75 (t, *J* = 0.8 Hz, 1H), 7.16 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.47 – 3.31 (m, 1H), 2.47 (s, 3H), 1.39 (s, 12H), 1.34 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.9, 134.9, 133.87, 133.5, 133.4, 126.3, 122.2, 116.2, 83.5, 33.6, 24.9, 21.5, 19.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2; HRMS (ESI-TOF) m/z: [M+H]+ calcd for $C_{16}H_{25}N2O_3$ 293.1860, found 293.1860.

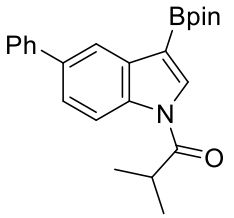


Compound **2f**: Rf = 0.2 (PE/EtOAc = 30:1), white solid, mp = 110 -114 ˚C, 62.7 mg, 91% yield, C3:C2 = 96:4 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 9.6 Hz, 1H), 7.90 (s, 1H), 7.47 (d, *J* = 2.8 Hz, 1H), 6.95 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.89 (s, 3H), 3.50 – 3.09 (m, 1H), 1.38 (s, 12H), 1.34 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.7, 156.6, 134.5, 134.3, 131.4, 117.2, 113.0, 105.67, 83.5, 55.7, 33.5, 24.9, 19.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for

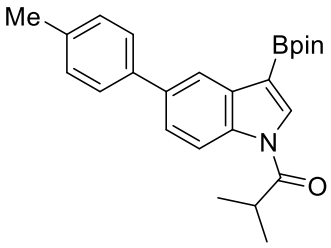


$C_{19}H_{26}BNNaO_4$ 366.1847, found 366.1850.

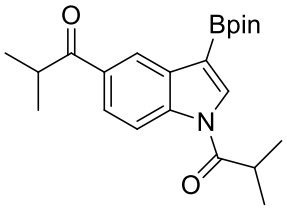
Compound **2g**: Rf = 0.4 (PE/EtOAc = 30:1), white solid, mp = 178-180 ˚C, 58.4 mg, 75% yield, C3:C2 = 92:8 (^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 2.0 Hz, 1H), 7.97 (s, 1H), 7.75 – 7.65 (m, 2H), 7.59 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 3.58 – 3.28 (m, 1H), 1.39 (s, 12H), 1.37 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 142.0, 137.2, 136.1, 134.3, 133.9, 128.7, 127.6, 126.8, 124.6, 120.9, 116.7, 83.6, 33.7, 24.9, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{29}BNO_3$ 390.2235, found 390.2234.



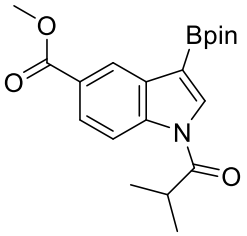
Compound **2h**: Rf = 0.5 (PE/EtOAc = 40:1), white solid, mp = 184 -188 ˚C, 52.4 mg, 65% yield, C3:C2 = 94:6 (^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 1.6 Hz, 1H), 7.97 (s, 1H), 7.62 – 7.55 (m, 3H), 7.30 (s, 1H), 7.28 (s, 1H), 3.49 – 3.31 (m, 1H), 2.42 (s, 3H), 1.39 (s, 12H), 1.38 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 139.1, 137.2, 136.5, 136.0, 134.3, 133.9, 129.4, 127.5, 124.5, 120.7, 116.7, 83.6, 33.7, 24.9, 21.1, 19.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{31}BNO_3$ 404.2392, found 404.2381.



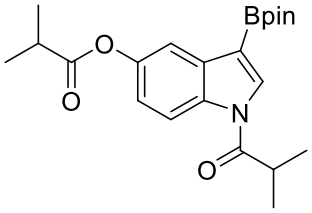
Compound **2i**: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 135 - 140 ˚C, 42.9 mg, 56% yield, C3:C2 = 99:1 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.6 Hz, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 7.98 (s, 1H), 7.97 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.74 – 3.61 (m, 1H), 3.46 – 3.33 (m, 1H), 1.39 (s, 12H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.26 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 204.6, 176.0, 139.2, 134.8, 133.4, 132.3, 125.4, 123.4, 116.4, 83.8, 35.5, 33.9, 24.9, 19.5, 19.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{30}BNNaO_4$ 406.2160, found 406.2162.



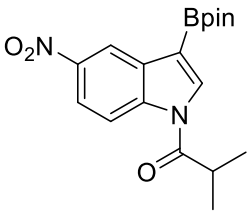
Compound **2j**: Rf = 0.35 (PE/EtOAc = 10:1), white solid, mp = 130 - 135 ˚C, 55.0 mg, 74% yield, C3:C2 = 98:2 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 1.2 Hz, 1H), 8.51 (dd, *J* = 8.8, 0.4 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.99 (s, 1H), 3.96 (s, 3H), 3.48 – 3.31 (m, 1H), 1.39 (s, 12H), 1.37 (d, *J* = 2.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.1, 167.7, 139.4, 134.8, 133.1, 126.4, 125.8, 124.6, 116.3, 83.8, 52.1, 33.9, 24.9, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{26}BNNaO_5$ 394.1796, found 394.1795.



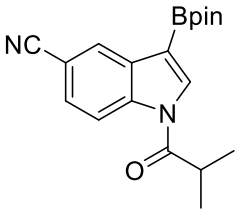
Compound **2k**: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 149 -152 ˚C, 69.5 mg, 87% yield, C3:C2 = 98:2 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.8 Hz, 1H), 7.95 (s, 1H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.03 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.48 – 3.29 (m, 1H), 2.94 – 2.70 (m, 1H), 1.37 (s, 12H),1.36(d,*J*=6.8 Hz,6H), 1.34(d, *J*=6.8 Hz, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2, 175.9, 147.4, 134.7, 134.4, 134.2, 118.9, 117.1, 114.8, 83.6, 34.2, 33.6, 24.9, 19.6, 19.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{31}BNO_5$ 400.2290, found 400.2288.



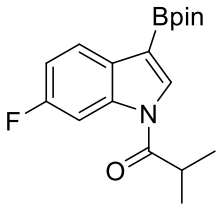
Compound **2l**: Rf = 0.3 (PE/EtOAc = 10:1), white solid, mp = 208 - 210 ˚C, 46.6 mg, 65% yield, C3:C2 = 99:1 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 2.4 Hz, 1H), 8.58 (d, *J* = 9.2 Hz, 1H), 8.23 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.06 (s, 1H), 3.49 – 3.32 (m, 1H), 1.40 (s, 12H), 1.38 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 144.6, 139.8, 136.1, 133.4, 120.4, 118.7, 116.7, 84.1, 34.0, 24.9, 19.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}BN_2O_5$ 359.1776, found 359.1786.



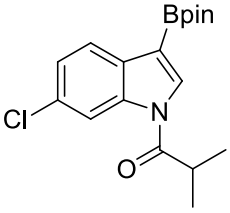
Compound **2m**: Rf = 0.2 (PE/EtOAc = 10:1), white solid, mp = 166 - 170 ˚C, 41.3 mg, 61% yield, C3:C2 = 97:3 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.8 Hz, 1H), 8.34 (d, *J* = 1.2 Hz, 1H), 8.02 (s, 1H), 7.59 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.54 – 3.22 (m, 1H), 1.39 (s, 12H), 1.36 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 138.6, 135.3, 133.5, 128.2, 127.5, 119.9, 117.4, 107.2, 84.0, 34.0, 24.9, 19.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.5; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{24}BN_2O_3$ 339.1874, found 339.1870.



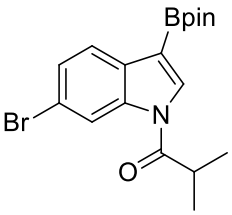
Compound **2n**: Rf = 0.6 (PE/EtOAc = 10:1), white solid, mp = 116 -120 ˚C, 40.4 mg, 61% yield, C3:C2 = 96:4 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 10.4, 2.4 Hz, 1H), 7.90 (s, 1H), 7.89 (dd, *J* = 12.4, 5.6 Hz, 3H), 7.10 – 6.99 (m, 2H), 3.45 – 3.28 (m, 1H), 1.38 (s, 12H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 161.3 (d, *J* = 240.4 Hz), 136.7 (d, *J* = 13.0 Hz), 133.8 (d, *J* = 3.5 Hz), 129.5 , 123.0 (d, *J* = 9.8 Hz), 111.9 (d, *J* = 23.8 Hz), 103.9 (d, *J* = 28.7 Hz), 83.6, 33.7, 24.9, 19.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.9; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{23}BFNNaO_3$ 354.1647, found 354.1657.



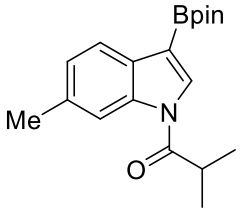
Compound **2o**: Rf = 0.4 (PE/EtOAc = 40:1), white solid, mp = 134 -140 ˚C, 58.4 mg, 84% yield, C3:C2 = 97:3 (GC).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 1.6 Hz, 1H), 7.90 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 3.42 – 3.29 (m, 1H), 1.38 (s, 12H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 137.0, 134.1, 131.8, 131.0, 124.6, 123.1, 116.9, 83.7, 33.8, 24.9, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$)



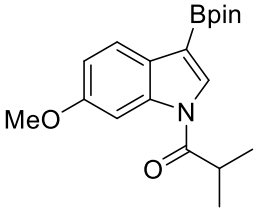
δ 29.7; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}BClNO_3$ 348.1532, found 348.1532.



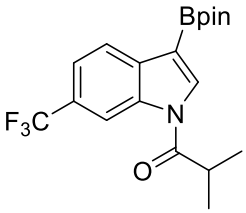
Compound **2p**: Rf = 0.4 (PE/EtOAc = 40:1), white solid, mp = 146 -150 ˚C, 57.3 mg, 73% yield, C3:C2 = 92:8 (GC).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 1.6 Hz, 1H), 7.89 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.47 – 3.23 (m, 1H), 1.37 (s, 12H), 1.35 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.0, 137.3, 134.0, 132.2, 127.1, 123.6, 119.7, 118.8, 83.7, 33.8, 24.9, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}BBrNO_3$ 392.1027, found 392.1026.



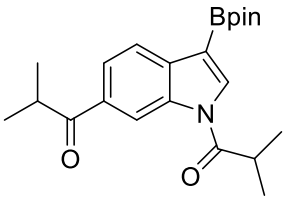
Compound **2q**: Rf = 0.4 (PE/EtOAc = 40:1), white solid, mp = 132 -136 ˚C, 55.6 mg, 85% yield, C3:C2 = 95:5 (GC).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.86 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 3.50 – 3.27 (m, 1H), 2.48 (s, 3H), 1.37 (s, 12H), 1.34 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.2, 135.1, 133.2, 125.2, 121.9, 116.2, 83.4, 33.7, 24.9, 21.9, 19.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for$C_{19}H_{26}BNNaO_3$ 350.1898, found 350.1894.



Compound **2r**: Rf = 0.4 (PE/EtOAc = 30:1), white solid, mp = 116 -120 ˚C, 54.9 mg, 80% yield, C3:C2 = 96:4 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 1H), 6.94 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.88 (s, 3H), 3.46 – 3.32 (m, 1H), 1.37 (s, 12H), 1.35 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.4, 158.3, 137.6, 132.4, 126.9, 122.8, 113.4, 100.4, 83.5, 55.6, 33.8, 24.9, 19.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{26}BNNaO_4$ 366.1847, found 366.1858.



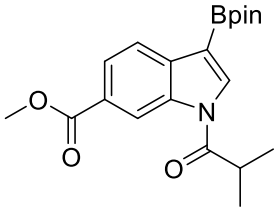
Compound **2s**: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 158 -162 ˚C, 68.6 mg, 90% yield, C3:C2 = 97:3 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.04 (s, 1H), 7.54 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.46 – 3.35 (m, 1H), 1.39 (s, 12H), 1.37 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.0, 135.9, 135.8, 135.7, 127.0 (q, *J* = 32.0 Hz), 124.9 (q, *J* = 270.0 Hz), 122.8, 120.6 (q, *J* = 3.4 Hz), 114.2 (q, *J* = 4.2 Hz), 83.8, 33.8, 24.9, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9; ^{19}F NMR (376MHz, $CDCl_3$) δ -61.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{24}BF_3NO_3$ 382.1796, found 382.1803.



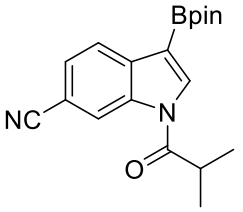
Compound **2t**: Rf = 0.2 (PE/EtOAc = 30:1), white solid, mp = 131 -135 ˚C, 46.0 mg, 60% yield, C3:C2 = 98:2 (GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (d, *J* = 1.2 Hz, 1H), 8.06 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.97 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.77 – 3.65 (m, 1H), 3.49 – 3.36 (m, 1H), 1.39 (s, 15H), 1.37 (s, 3H), 1.25 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$

NMR (100 MHz, $CDCl_3$) δ 204.7, 176.1, 137.2, 136.4, 136.3, 133.3, 124.0, 122.5, 117.3, 83.8, 35.3, 33.8, 24.9, 19.5, 19.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{30}BNNaO_4$ 406.2160, found 406.2155.

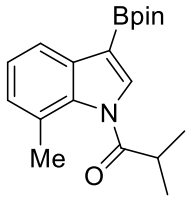
Compound **2u**: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 207 - 210 ˚C, 46.8 mg, 63% yield, C3:C2 = 98:2 (GC). ^1H NMR (400 MHz, $CDCl_3$) δ 9.15 (t, *J* = 1.2 Hz, 1H), 8.05 (s, 1H), 8.01 (d, *J* = 1.2 Hz, 2H), 3.93 (s, 3H), 3.50 – 3.28 (m, 1H), 1.38 (s, 12H), 1.37 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.9, 167.7, 137.3, 136.3, 136.2, 126.8, 125.2, 122.2, 118.3, 83.8, 52.0, 33.8, 24.9, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{26}BNNaO_5$ 394.1796, found 394.1808.



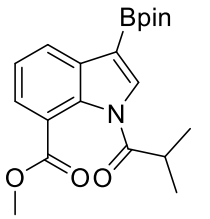
Compound **2v**: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 117 -121 ˚C, 42.6 mg, 63% yield, C3:C2 = 99:1 (GC). ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 0.8 Hz, 1H), 8.07 (s, 1H), 8.05 (d, *J* = 0.4 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.46 – 3.31 (m, 1H), 1.38 (s, 12H), 1.37 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.8, 136.8, 136.4, 135.7, 127.0, 123.4, 121.1, 120.0, 108.0, 83.9, 33.9, 24.9, 19.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.5; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{24}BN_2O_3$ 339.1874, found 339.1872.



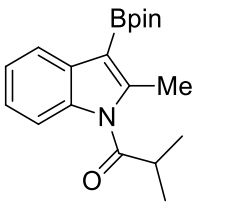
Compound **2w**: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 116 -118 ˚C, 57.6 mg, 88% yield, C3:C2 = 93:7 (GC). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 3.51 – 3.35 (m, 1H), 2.46 (s, 3H), 1.37 (s, 12H), 1.37 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.8, 136.0, 135.1, 134.8, 127.7, 125.9, 123.9, 120.2, 83.4, 35.0, 24.9, 22.0, 19.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{26}BNNaO_3$ 350.1898, found 350.1900.



Compound **2x**: Rf = 0.3 (PE/EtOAc = 10:1), white solid, mp = 128 -130 ˚C, 65.3 mg, 88% yield, C3:C2 = 94:6 (GC). ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.94 (s, 1H), 7.59 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.38 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.38 (s, 12H), 1.34 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)δ 175.6, 168.5, 135.2, 134.9, 132.3, 125.7, 125.2, 123.4, 122.0, 83.6, 51.9, 34.2, 24.9, 19.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{26}BNNaO_5$ 394.1796, found 394.1790.

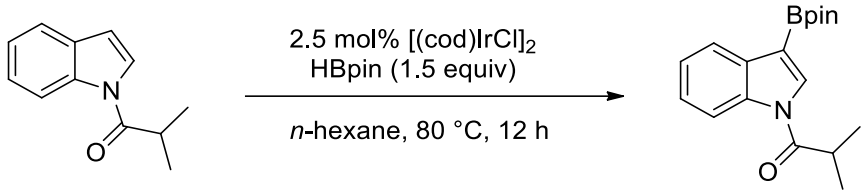


Compound **4a**: Rf = 0.3 (PE/EtOAc = 10:1), white solid, mp = 80 – 83 ˚C, 26.0 mg, 40% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 1H), 7.66 – 7.63 (m, 1H), 726 – 7.20 (m, 2H), 3.61 – 3.54 (m, 1H), 2.79 (s, 3H), 1.37 (s, 12H), 1.32 (d, J = 6.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 179.5, 147.6, 136.4, 133.5, 123.1, 122.7, 122.2, 113.2, 83.0,



36.2, 25.0, 19.4, 15.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{26}BNNaO_3$ 350.1898, found 350.1900.

6. Gram-scale prepration of 2a

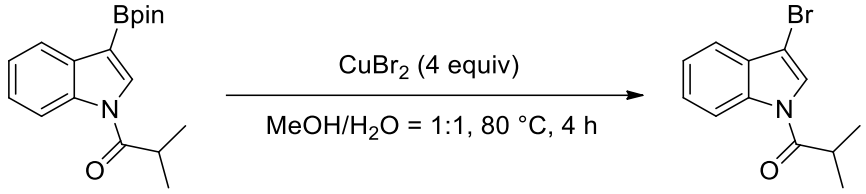


1a **2a**

In a nitrogen filled glovebox, to a 75-mL flame-dried tube charged with $[IrCl(cod)]_2$ (89.8 mg, 0.13 mmol), HBpin (1.04 g, 8.1 mmol, 1.5 equiv), *N*-isobutyryl indole **1a** (1.00 g, 5.3 mmol) was added *n*-hexane (25 mL). The mixture was allowed to stir at 80 °C for 16 h. The regioselectivity was determined by GC analysis of crude reaction mixture after completion. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (40:1) as the eluent to afford desired borylated product **2a** (1.32 g, 79% yield).

7. Synthetic Application of 2a

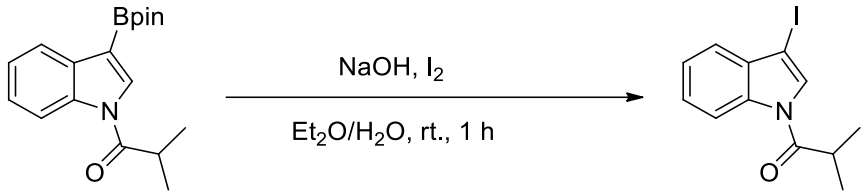
a) Bromination



2a **5**

The reaction was adapted from the literature procedures.[9] To a 15 mL seal bottle charged with $CuBr_2$ (4 equiv., 0.8 mmol, 179 mg), water (1 mL), methanol (1 mL) and **2a** (1 equiv., 0.2 mmol, 62.6 mg). The mixture was heated at 80 °C for 4 h. After cooling to room temperature, the mixture was extracted with Et2O four times. The combined organic layers were washed with water and brine, dried and concentrated. The residue was purified by column chromatography to give the product **5** as white solid. Rf = 0.4 (PE/EtOAc = 40:1), white solid, mp = 148 – 150 ˚C, 37 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.56 – 7.52 (m, 1H), 7.46 – 7.40 (m, 1H), 7.40 – 7.34 (m, 1H), 3.34 – 3.21 (m, 1H), 1.37 (d, J = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.0, 135.2, 129.3, 126.4, 124.2, 123.5, 119.4, 116.9, 100.1, 33.8, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}BrNO$ 266.0175, found 266.0170.

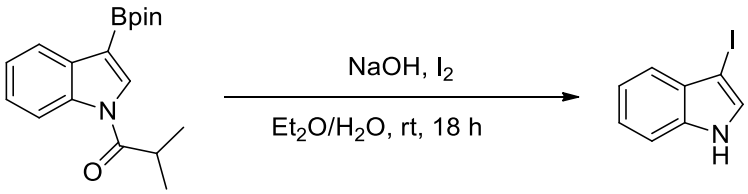
b) Iodination



2a **6**

The reaction was adapted from the literature procedures.[10] NaOH (3.0 M in water, 1 mL) was added to a solution of **2a** (62.6 mg, 0.20 mmol) in diethyl ether (1.2 mL). After stirring for 10 min at room temperature, a solution of iodine (254 mg, 1.0 mmol) in diethyl ether 3 mL) was added over 5 min. The resulting mixture was allowed to stir at room temperature for 1 h. The mixture was then quenched with saturated aqueous $Na_2S_2O_3$ (10 mL). The mixture was diluted by H_2O (10 mL) and extracted with diethyl ether (3 × 15 mL), the combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography to give the product **4** as yellow oil. Rf = 0.4 (PE/EtOAc = 40:1), vinicolor oil, 44.0 mg, 70% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.39 (m, 1H), 7.66 (s, 1H), 7.49 – 7.32 (m, 3H), 3.34 – 3.20 (m, 1H), 1.36 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 135.3, 132.0, 128.9, 126.3, 124.3, 121.4, 116.7, 67.8, 33.9, 19.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}INO$ 314.0039, found 314.0039.

c) Iodination/deacylation

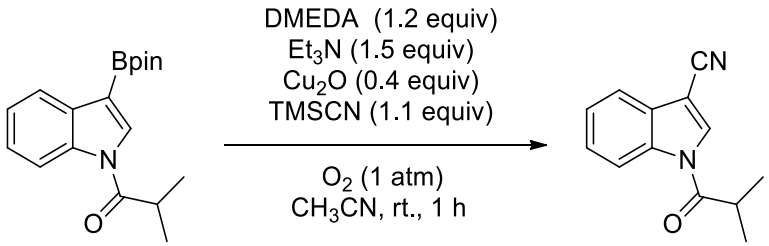


2a **7**

The reaction was adapted from the literature procedures.[10] NaOH (3.0 M in water, 1 mL) was added to a solution of **2a** (62.6 mg, 0.20 mmol) in diethyl ether (1.2 mL). After stirring for 10 min at room temperature, a solution of iodine (254 mg, 1.0 mmol) in diethyl ether 3 mL) was added over 5 min. The resulting mixture was allowed to stir at room temperature for 18 h. The mixture was then quenched with saturated aqueous $Na_2S_2O_3$ (10 mL). The mixture was diluted by H_2O (10 mL) and extracted with diethyl ether (3 × 15 mL), the combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography to give the product **7** (CAS: 26340-47-6) as a white solid in 80% yield: Rf = 0.4 (PE/EtOAc = 10:1), white solid, mp = 66 – 68 ˚C, 34.0 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.55 – 7.43 (m, 1H), 7.39 – 7.34 (m, 1H), 7.27 – 7.18 (m, 3H). The characterization data is consistent

with the literature reported.[11]

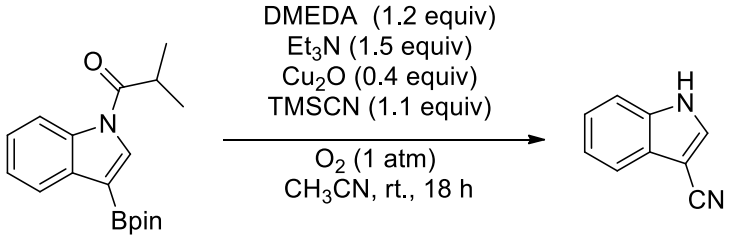
d) Cynantion



2a **8**

The reaction was adapted from the literature procedures.[12] To a flame-dried Schlenck tube was charged with **2a** (0.2 mmol, 1.0 equiv), *N*,*N*'-Dimethylenediamine (0.24 mmol, 1.2 equiv), Cu_2O (0.08 mmol, 40 mol %) and triethylamine (0.3 mmol, 1.5 equiv). The tube was evacuated three times under vacuum and backfilled with O_2, and then connected with an oxygen balloon via a needle. Dried CH_3CN (3 mL) and TMSCN (0.22 mmol, 1.1 equiv) were injected via syringe. The mixture was stirred at rt. for 1 hours. The resultant mixture was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **8** as white solid. Rf = 0.4 (PE/EtOAc = 20:1), white solid, mp = 122 – 123 ˚C, 38.0 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.54 – 7.38 (m, 2H), 3.43 – 3.21 (m, 1H), 1.39 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 133.6, 130.4, 126.6, 125.8, 123.9, 118.3, 115.9, 112.6, 92.7, 32.7, 18.1; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}N_2O$ 213.1022, found 213.1026.

e) Cycnation/deacylation

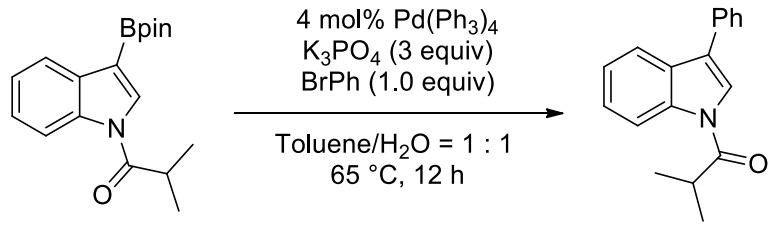


2a **9**

The reaction was adapted from the literature procedures.[12] To a flame-dried Schlenck tube was charged with **2a** (0.2 mmol, 1.0 equiv), *N*,*N*'-Dimethylenediamine (0.24 mmol, 1.2 equiv), Cu_2O (0.08 mmol, 40 mol %) and triethylamine (0.3 mmol, 1.5 equiv). The tube was evacuated three times under vacuum and backfilled with O_2, and then connected with an oxygen balloon via a needle. Dried CH_3CN (3 mL) and TMSCN (0.22 mmol, 1.1 equiv) were injected via syringe. The mixture was stirred at rt. for 18 hours. The resultant mixture was evaporated under reduced

pressure. The residue was purified by column chromatography to give the product **9** (CAS: 5437-28-3) as white solid. Rf = 0.4 (PE/EtOAc = 8:1), white solid, mp = 76 – 78 ˚C, 23.0 mg, 80% yield.[1]H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 2.8 Hz, 1H), 7.48 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.37 – 7.27 (m, 3H). The characterization data is consistent with the literature reported.[13]

f) Suzuki-Miyaura coupling

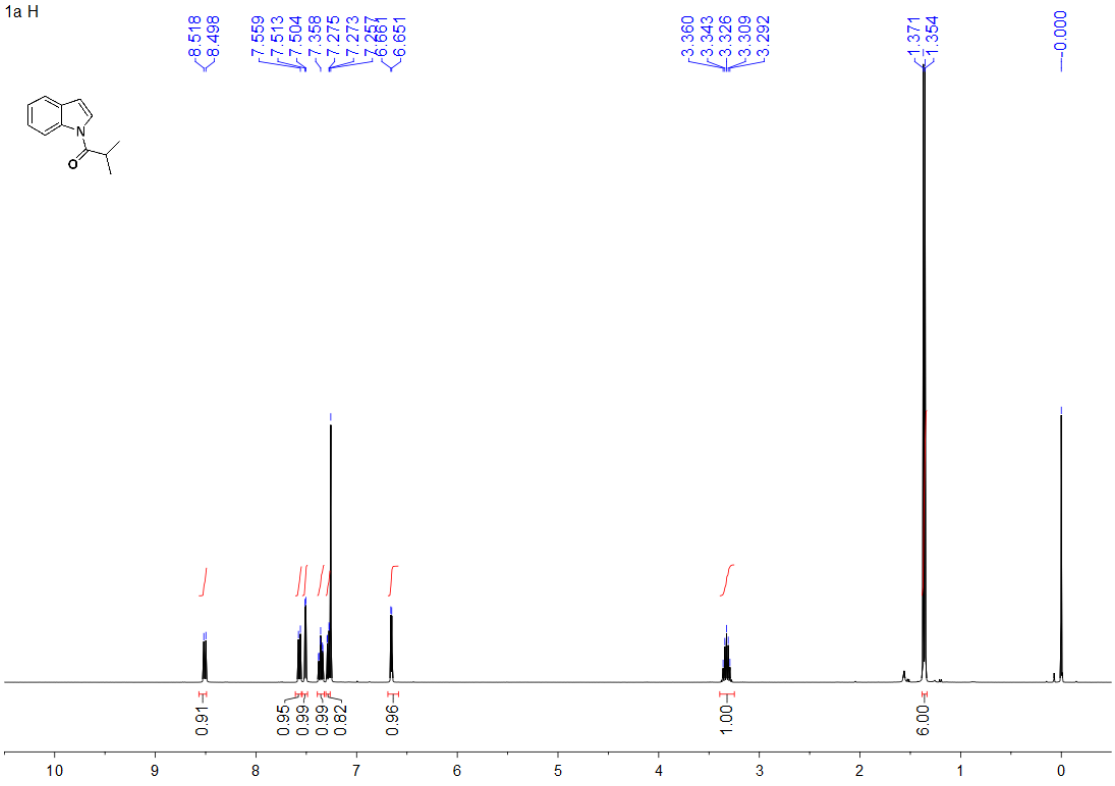


2a **10**

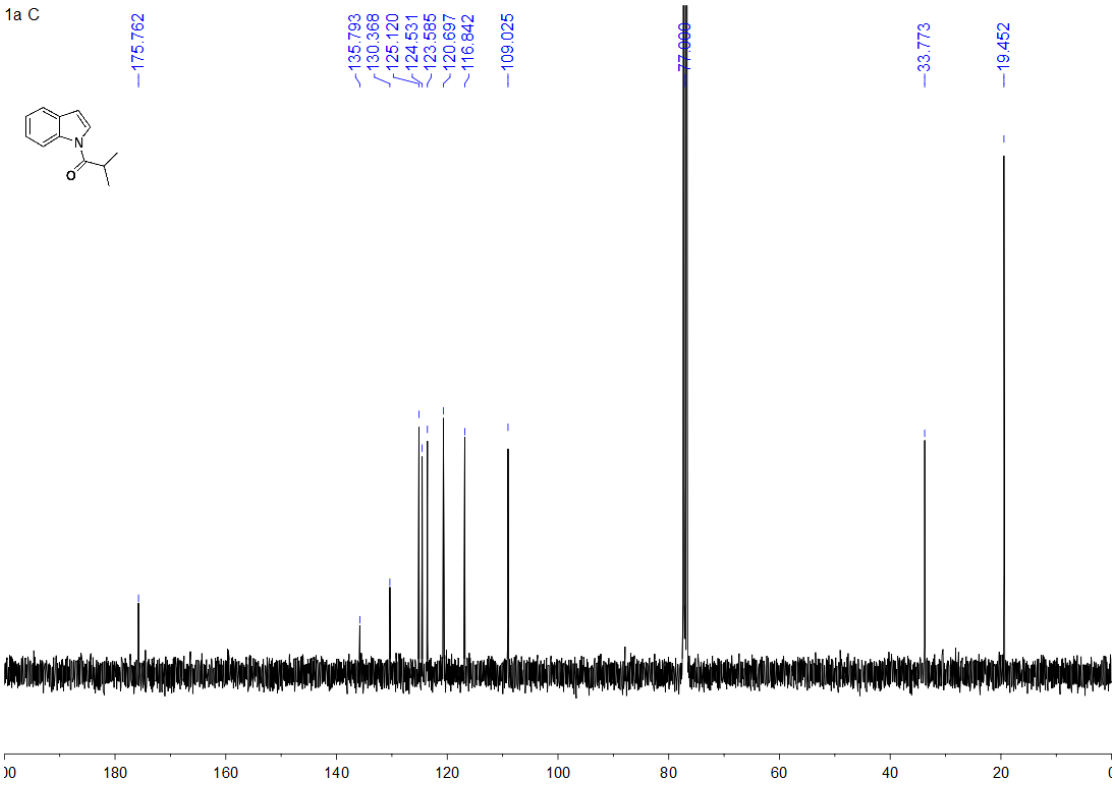
The reaction was adapted from the literature procedures.[14] To a flame-dried Schlenck tube was charged with **2a** (75.0 mg, 0.24 mmol, 1.2 equiv), $Pd(Ph_3)_4$ (9.2 mg, 4 mol%), K_3PO_4 (127.0 mg, 0.6 mmol) and bromobenzene (31.4 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated three times under vacuum and backfilled with N_2. Degassed toluene (1 mL) and H_2O (1 mL) were injected via syringe. The mixture was stirred at 65 °C for 12 hours. After cooling to the room temperature, the mixture was extracted with diethyl ether (3 × 15 mL). The combined organic layers were evaporated under reduced pressure. The residue was purified by column chromatography to give the product **10** as white solid. Rf = 0.4 (PE/EtOAc = 1:1), white solid, mp = 66 – 68 ˚C, 57.2 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.60 (s, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.30 (m, 3H), 3.67 – 3.10 (m, 1H), 1.39 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 136.6, 133.5, 129.0, 128.9, 128.0, 127.5, 125.6, 124.0, 123.9, 121.4, 119.8, 117.2, 33.9, 19.5; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}NO$ 264.1383, found 264.1386.

8. NMR Spectra for all New and Key Compounds

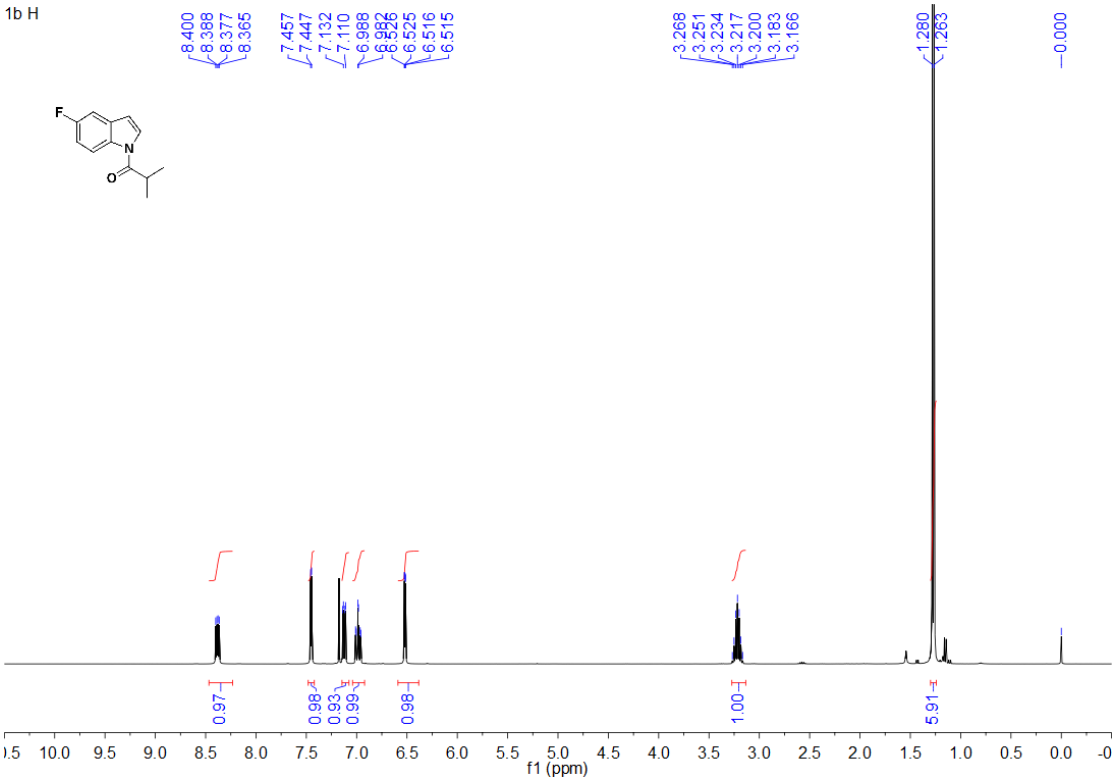
^{1}H NMR spectrum of 1a



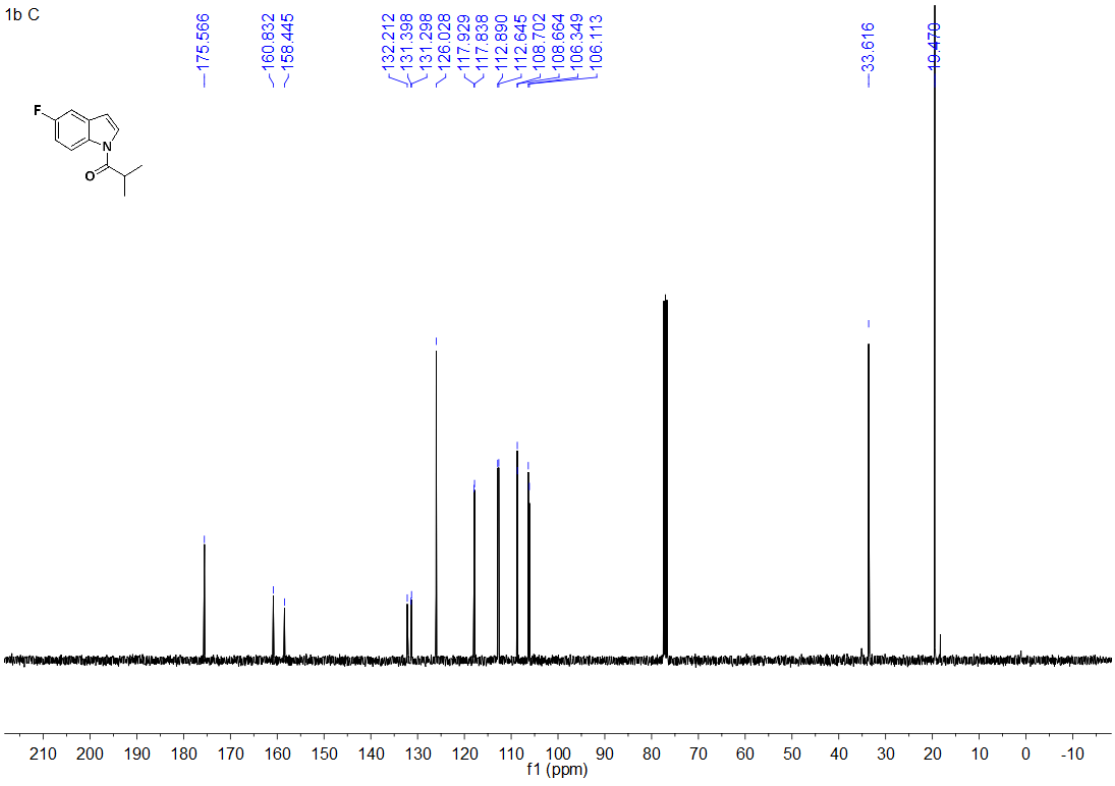
^{13}C NMR spectrum of 1a



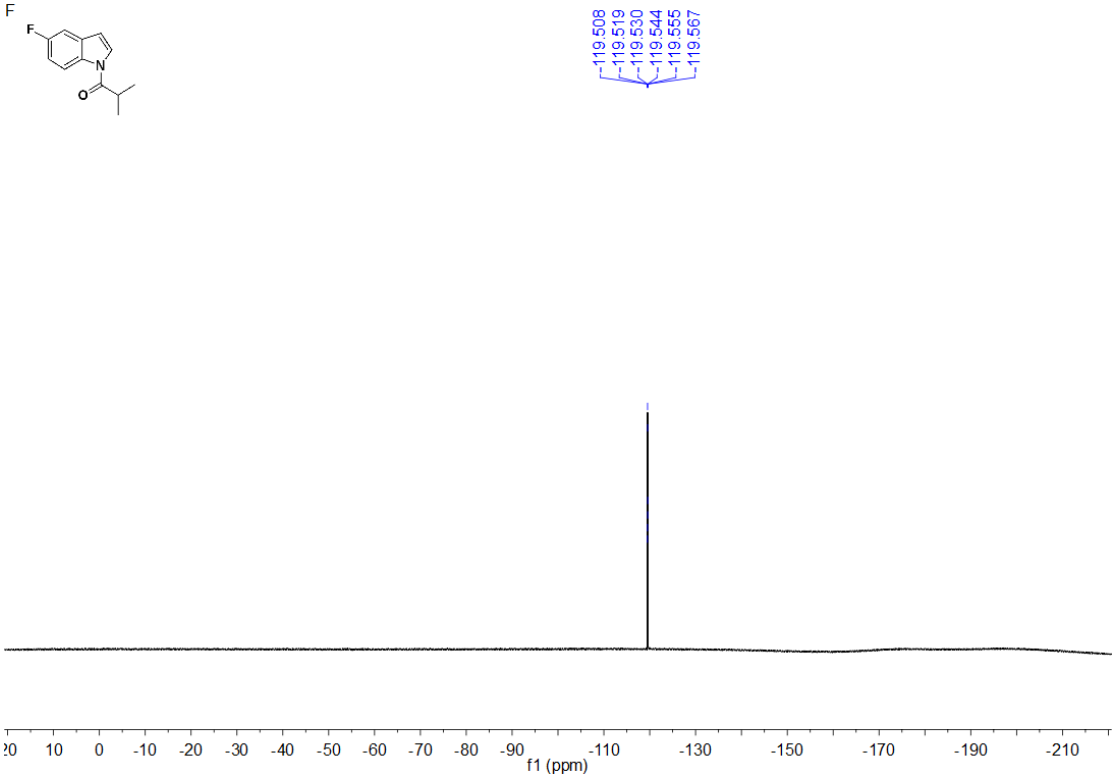
^{1}H NMR spectrum of 1b



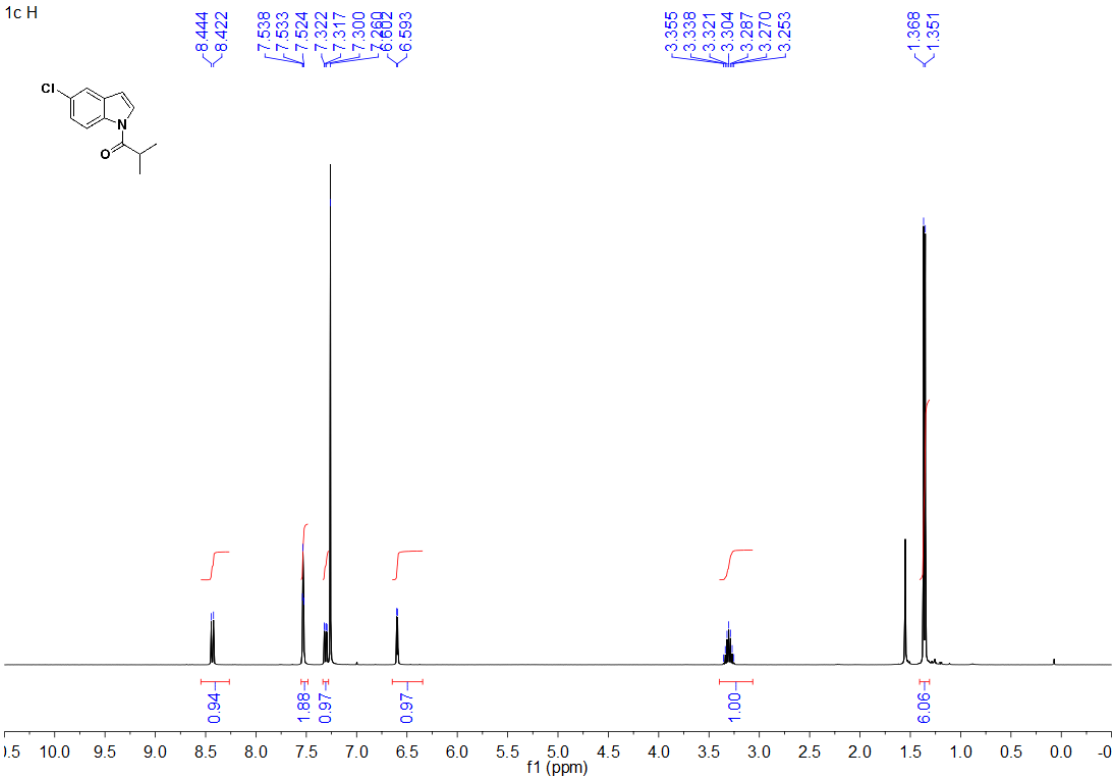
^{13}C NMR spectrum of 1b



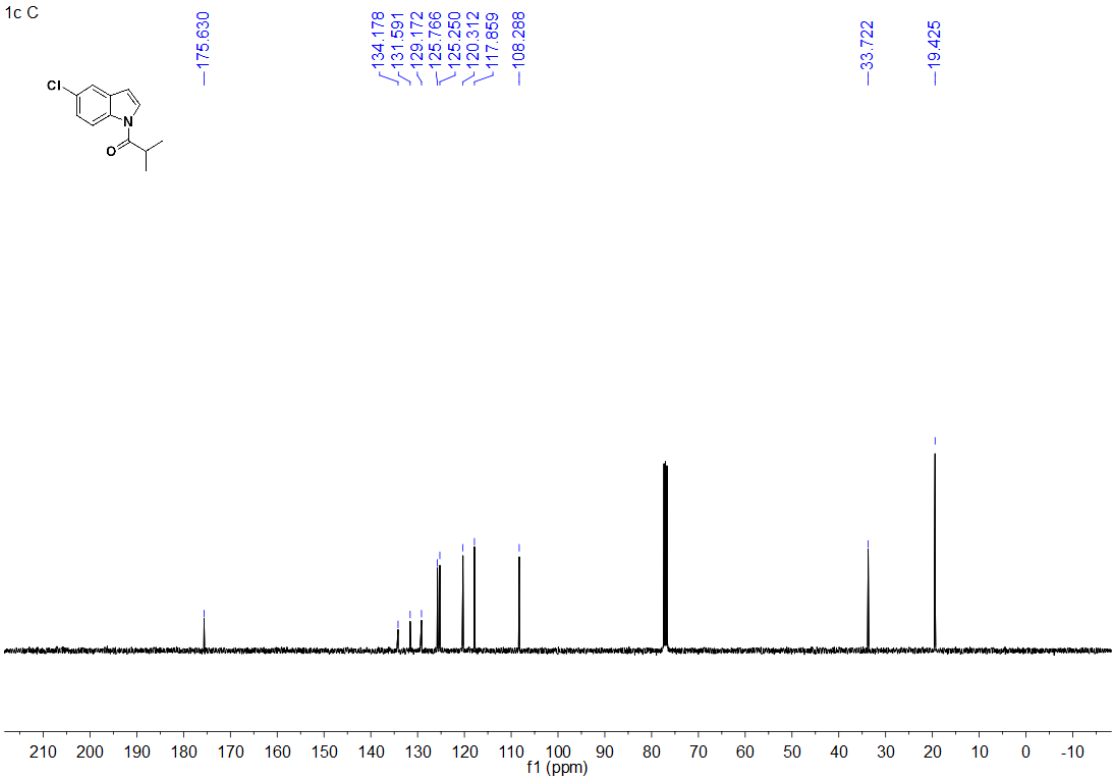
^{19}F NMR spectrum of 1b



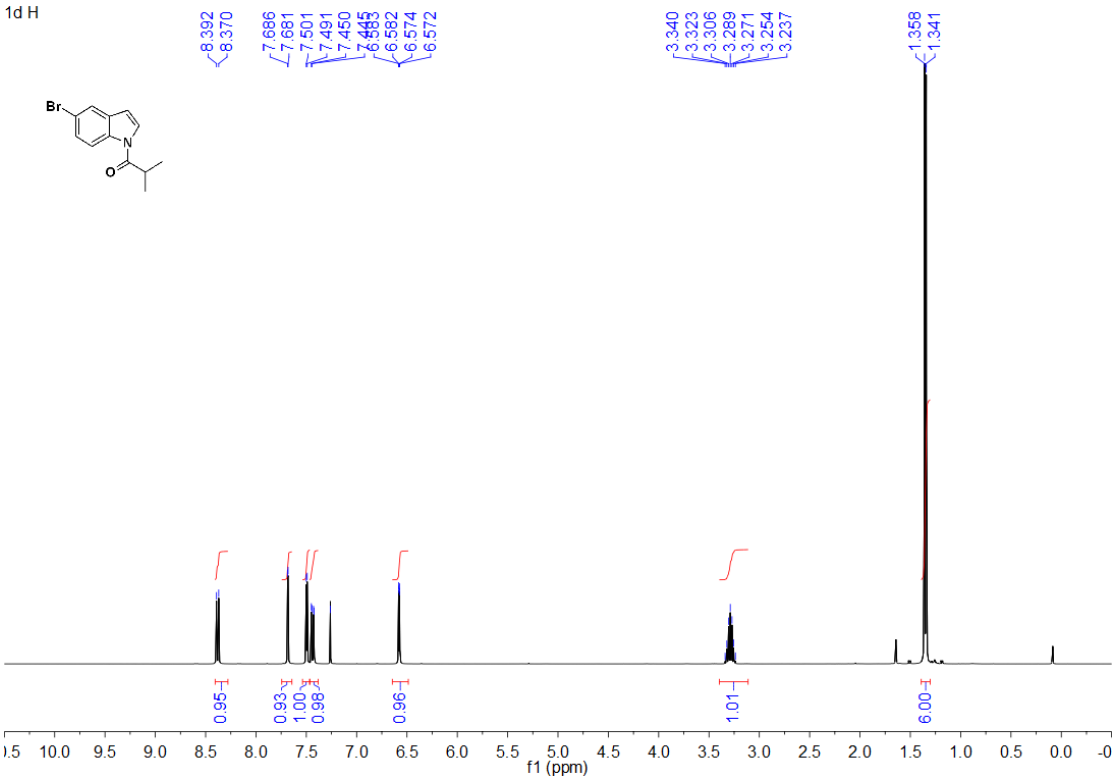
^{1}H NMR spectrum of 1c



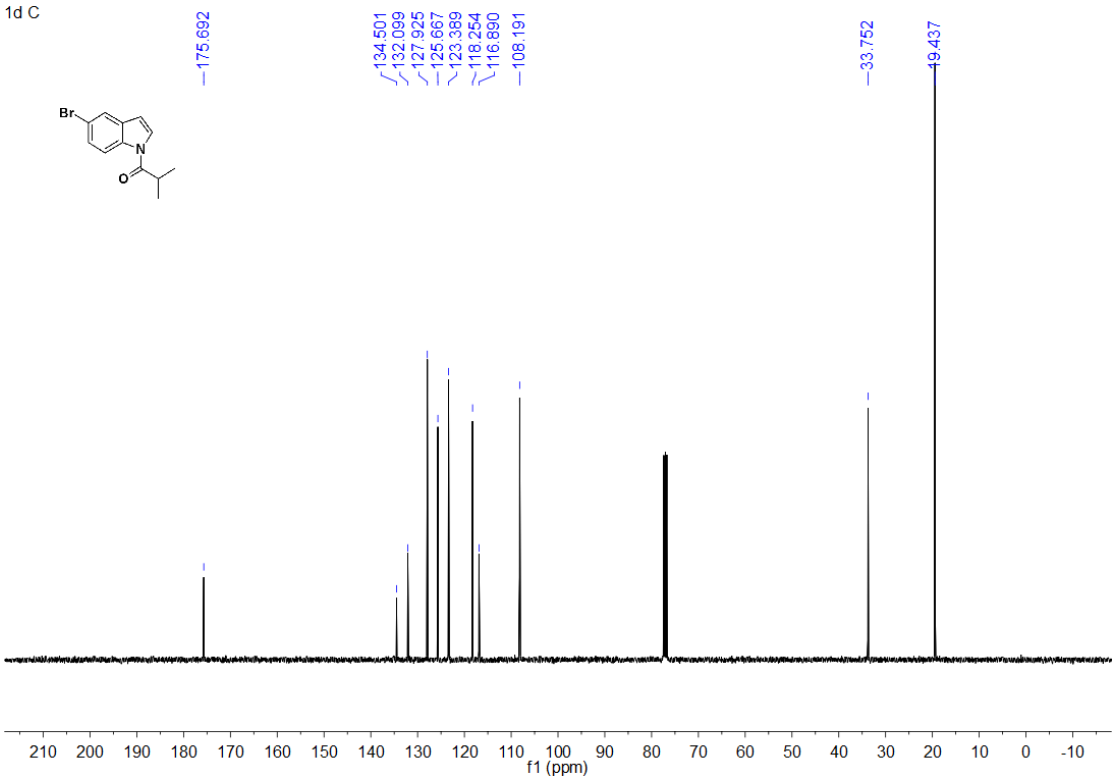
^{13}C NMR spectrum of 1c



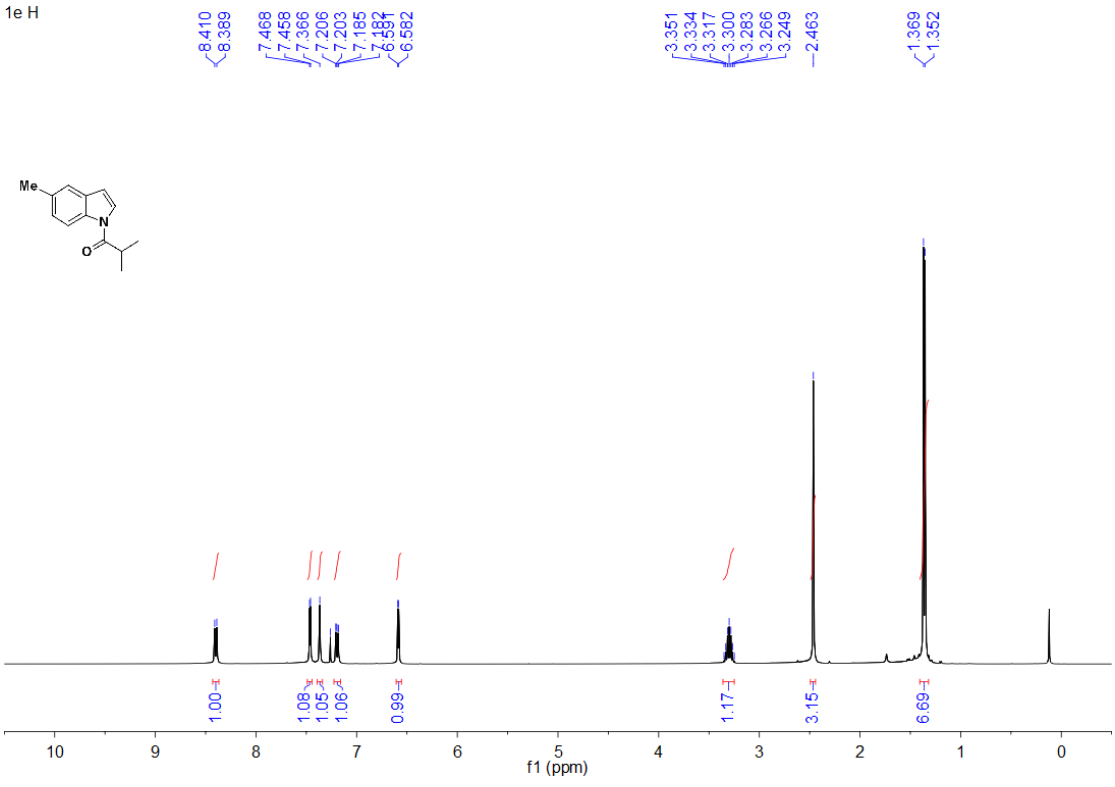
^{1}H NMR spectrum of 1d



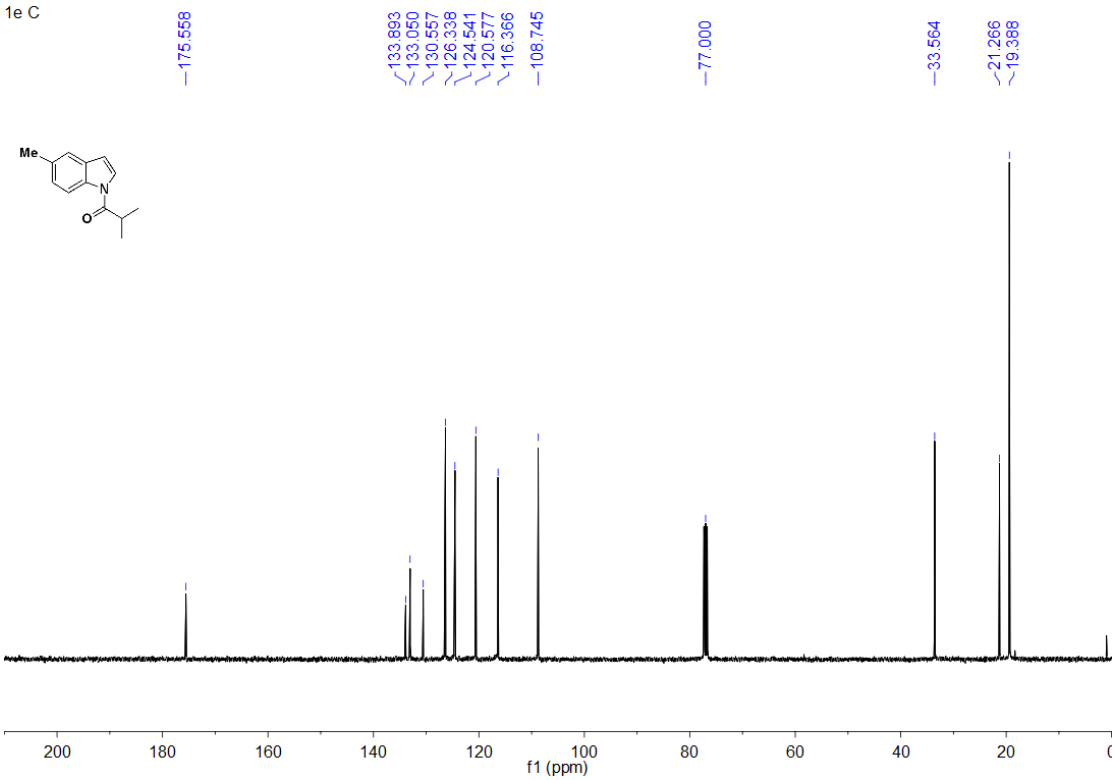
^{13}C NMR spectrum of 1d



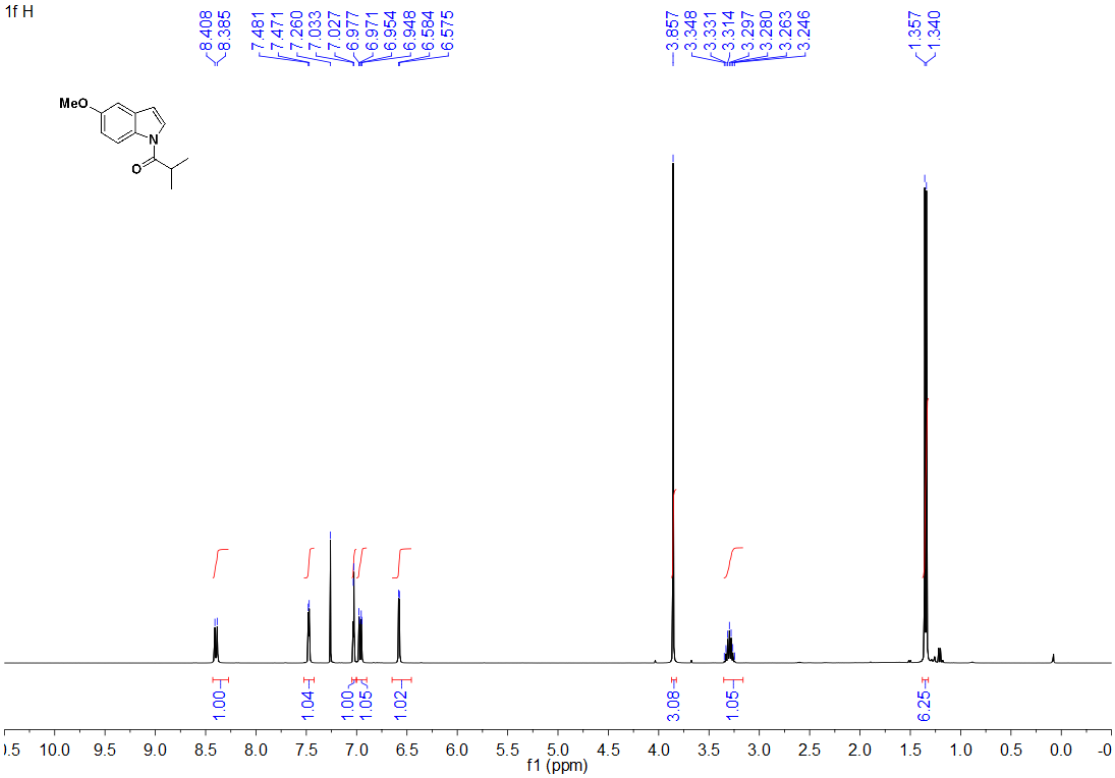
^{1}H NMR spectrum of 1e



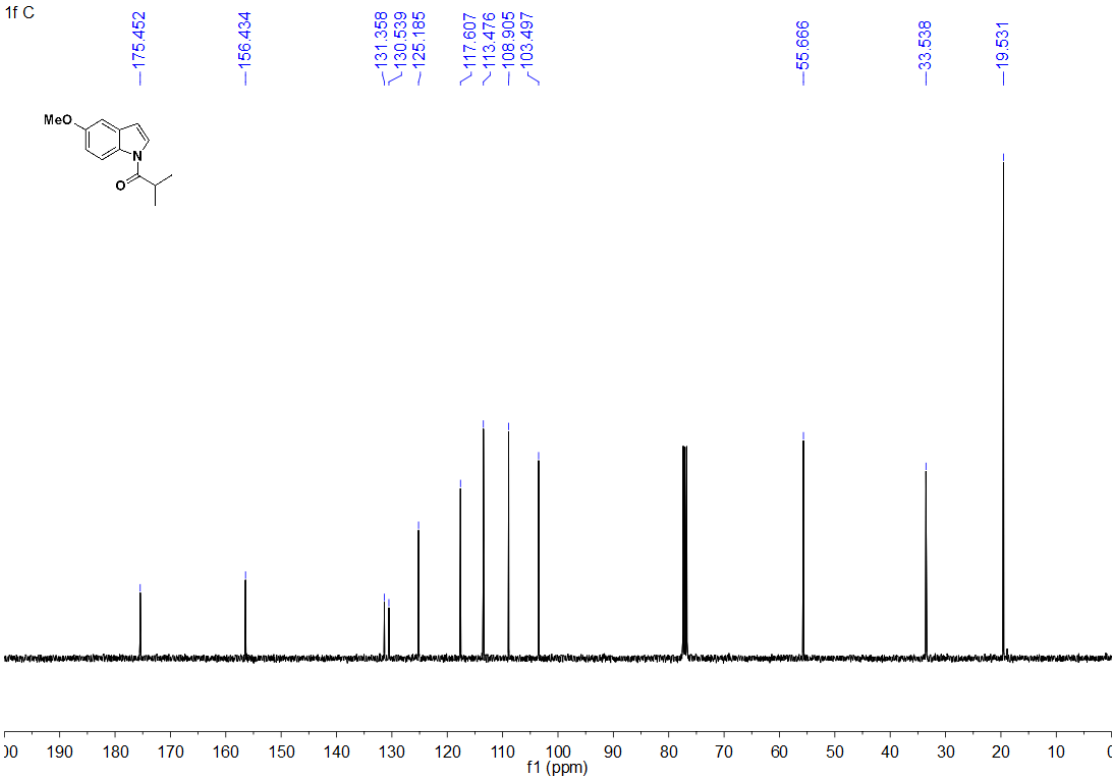
^{13}C NMR spectrum of 1e



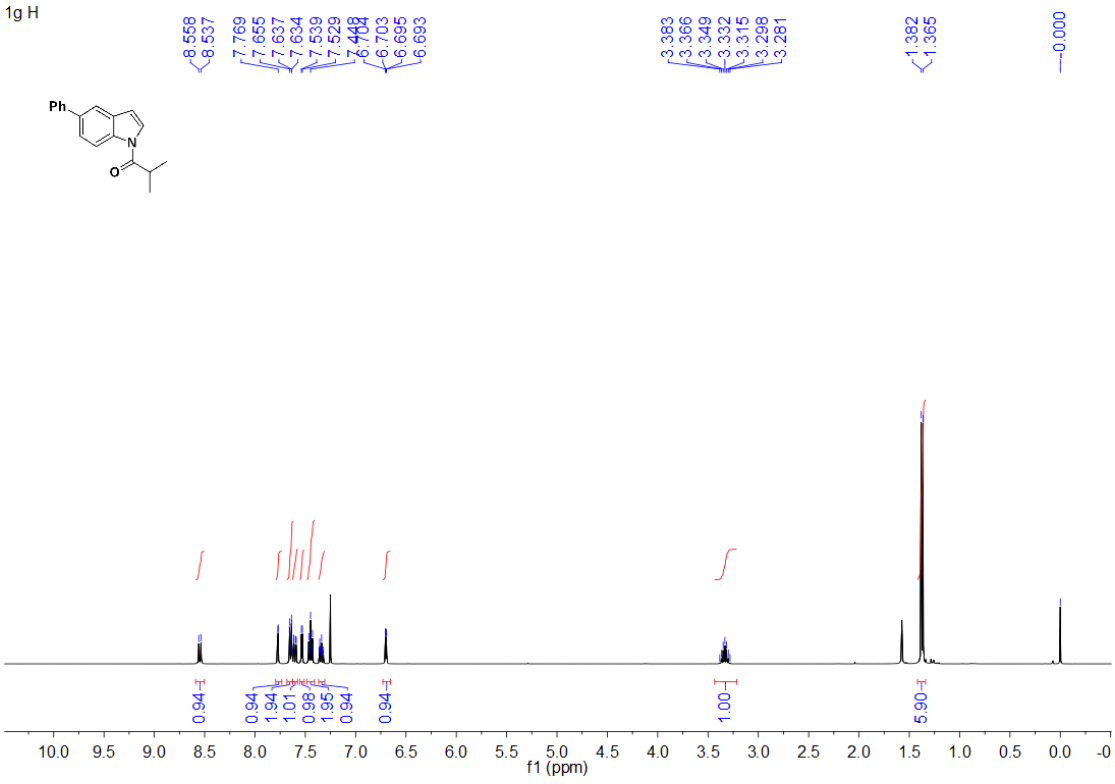
^{1}H NMR spectrum of 1f



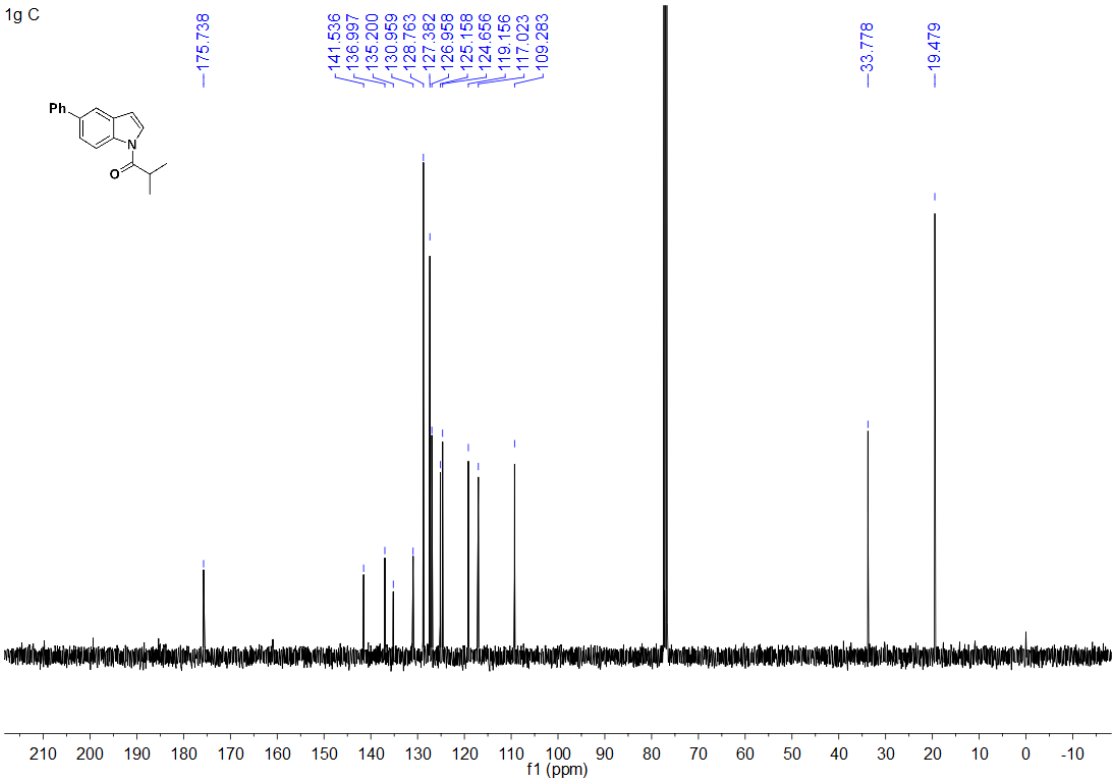
^{13}C NMR spectrum of 1f



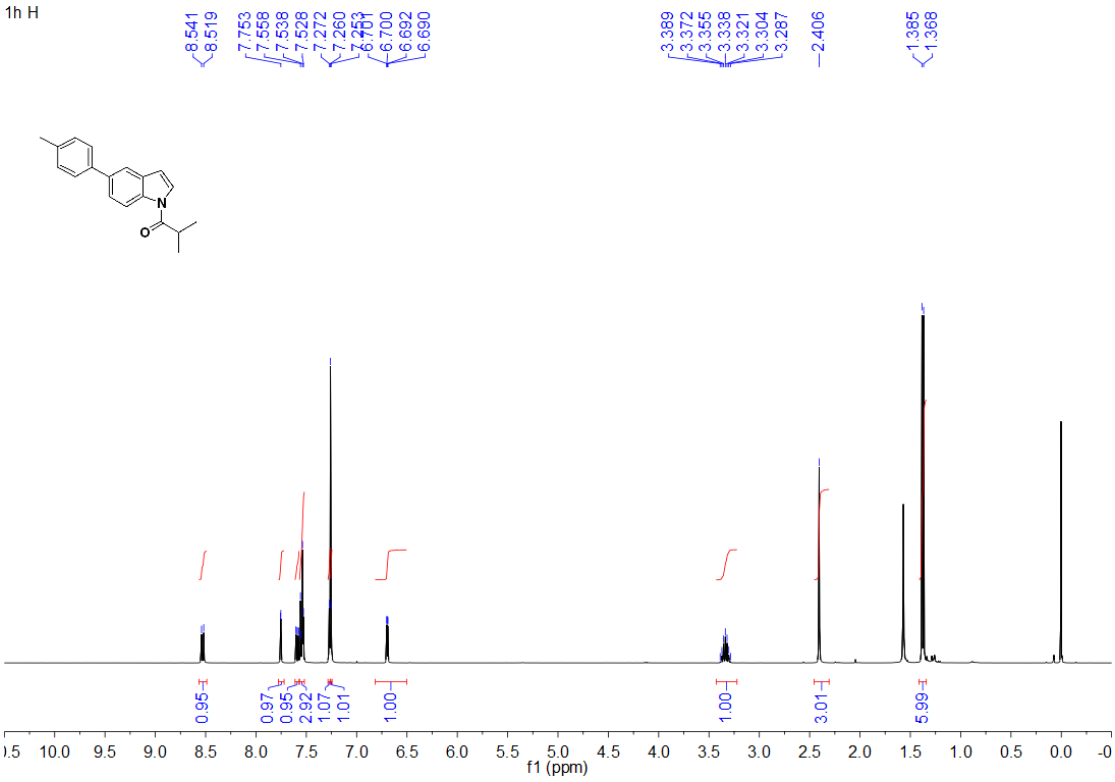
^{1}H NMR spectrum of 1g



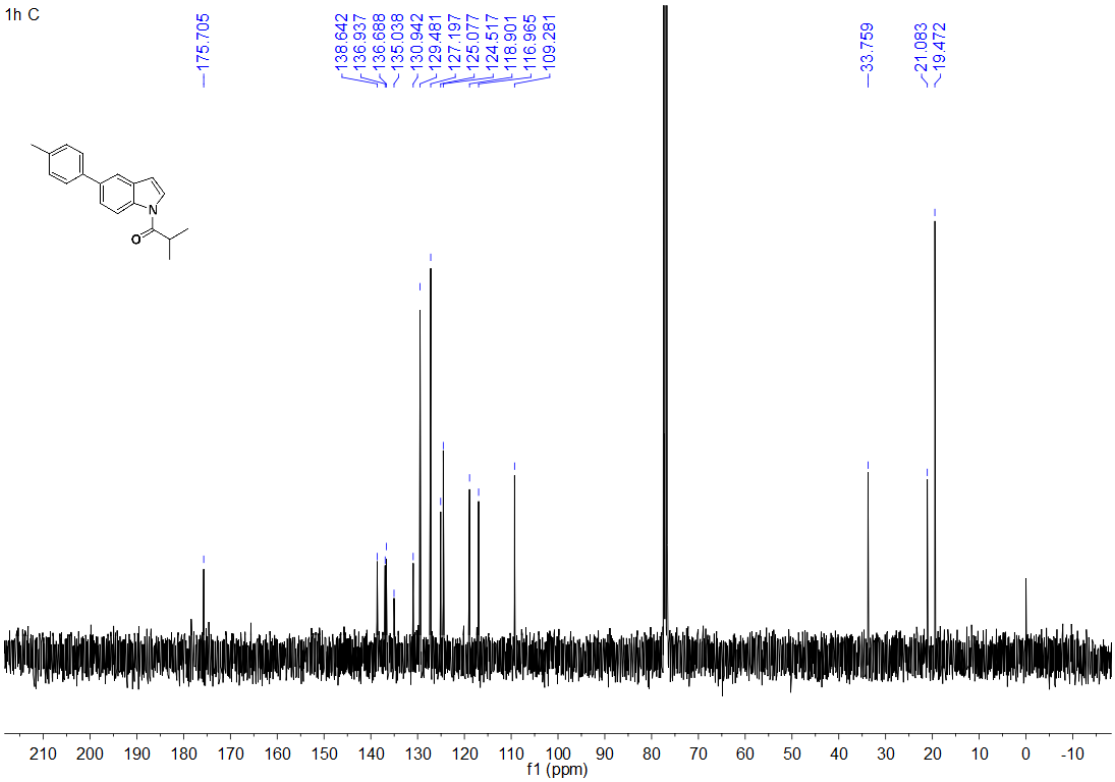
^{13}C NMR spectrum of 1g



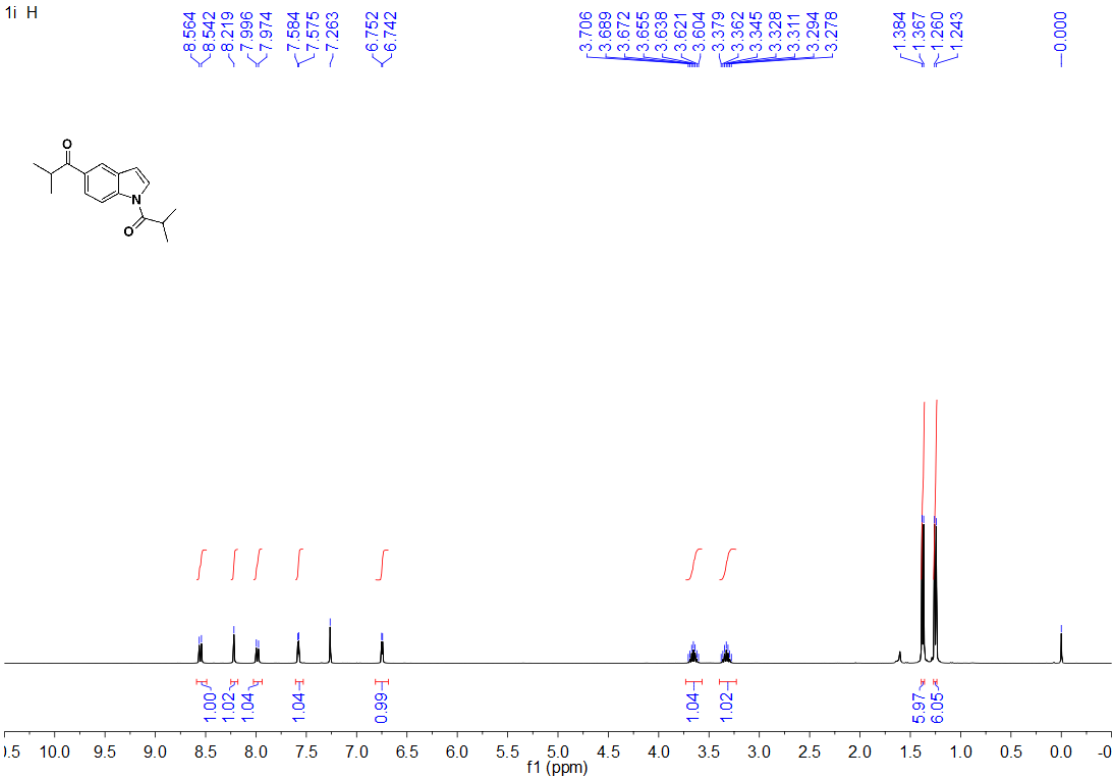
^{1}H NMR spectrum of 1h



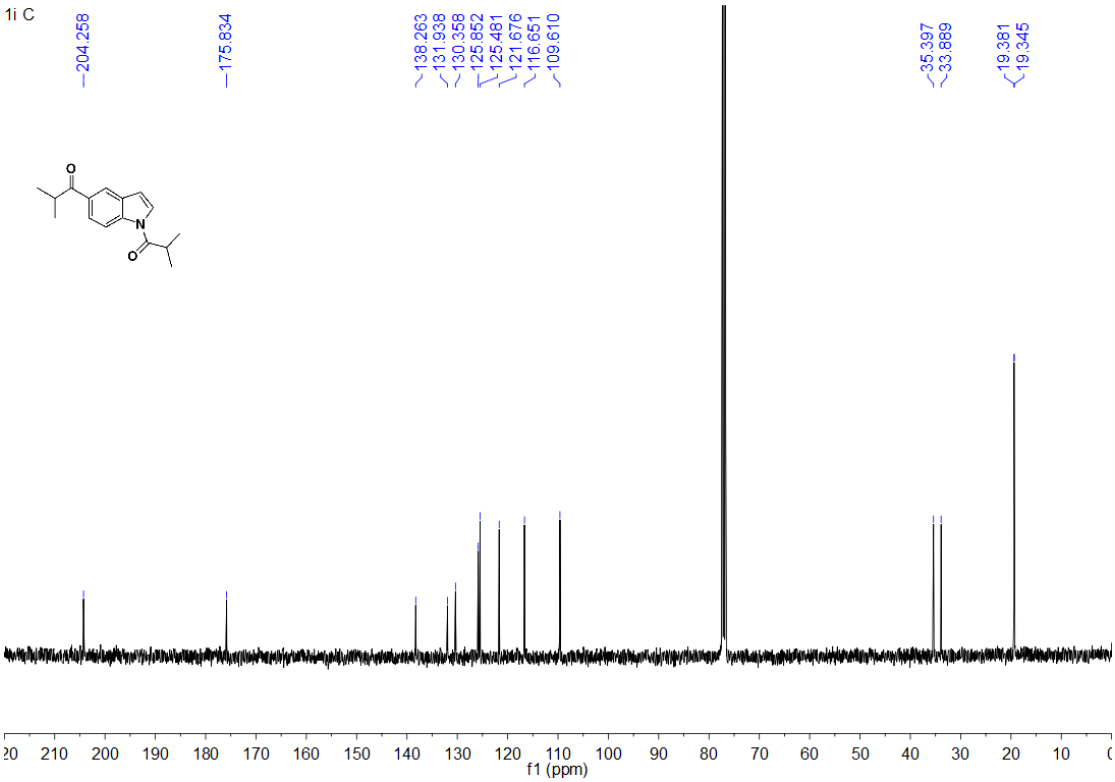
^{13}C NMR spectrum of 1h



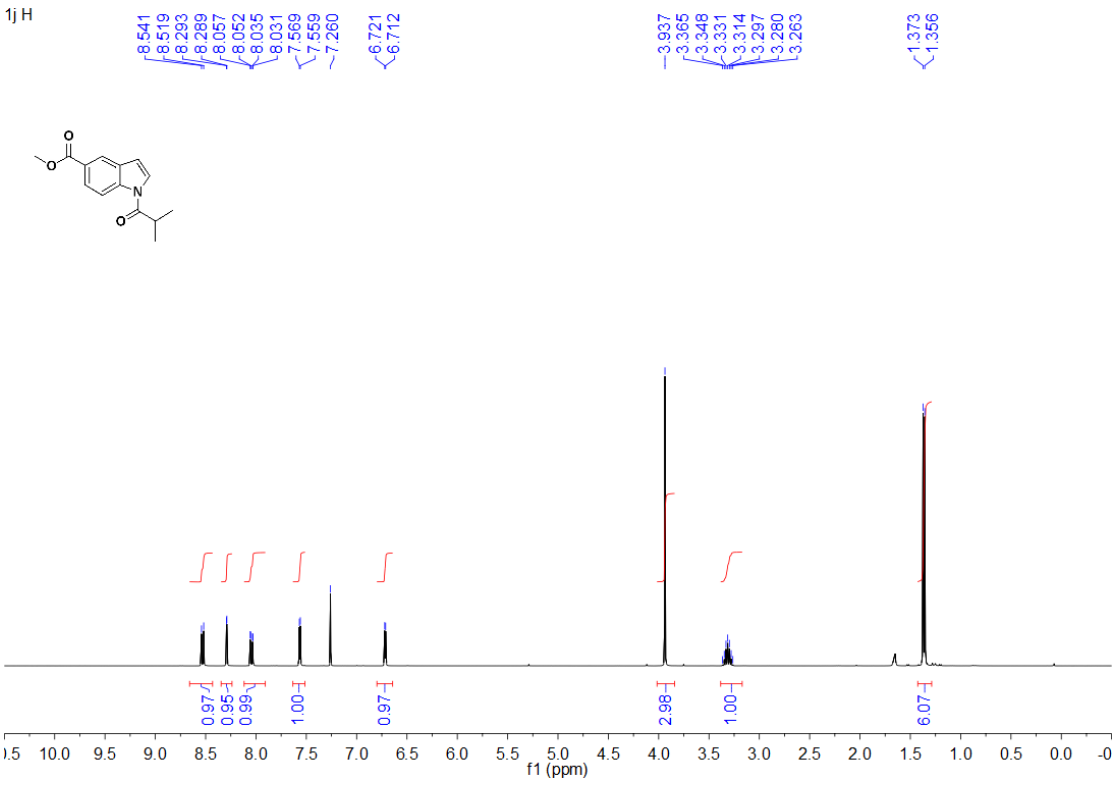
^{1}H NMR spectrum of 1i



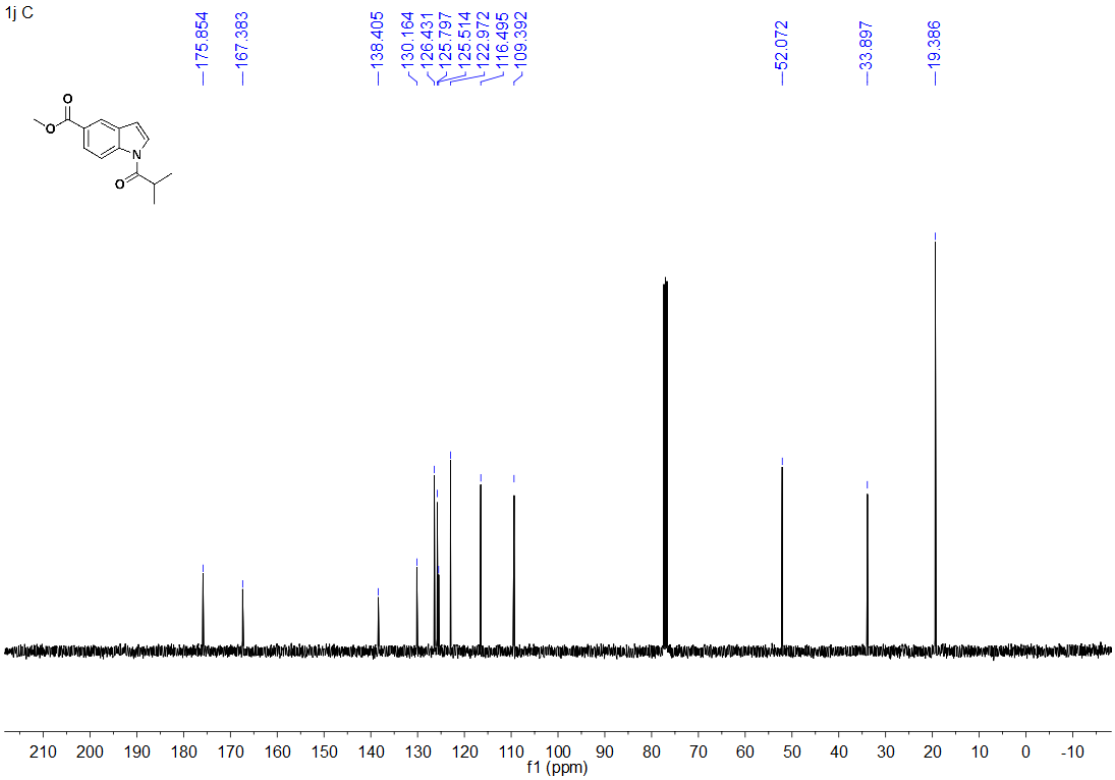
^{13}C NMR spectrum of 1i



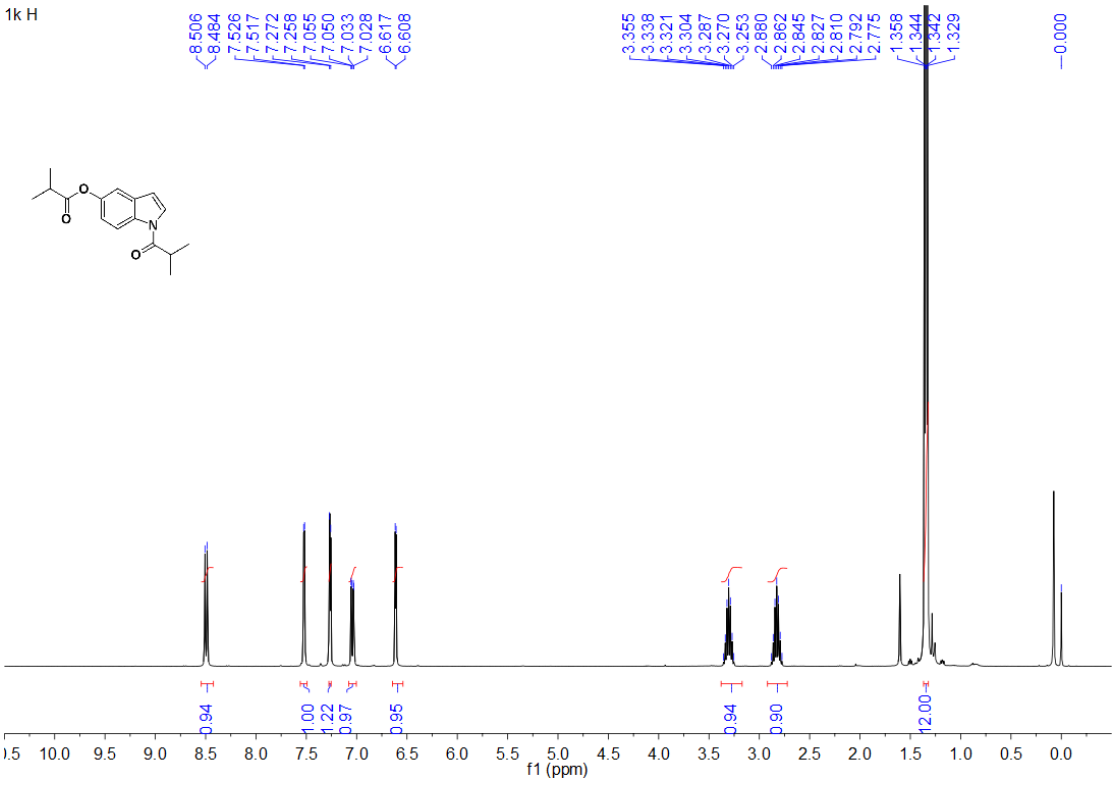
^{1}H NMR spectrum of 1j



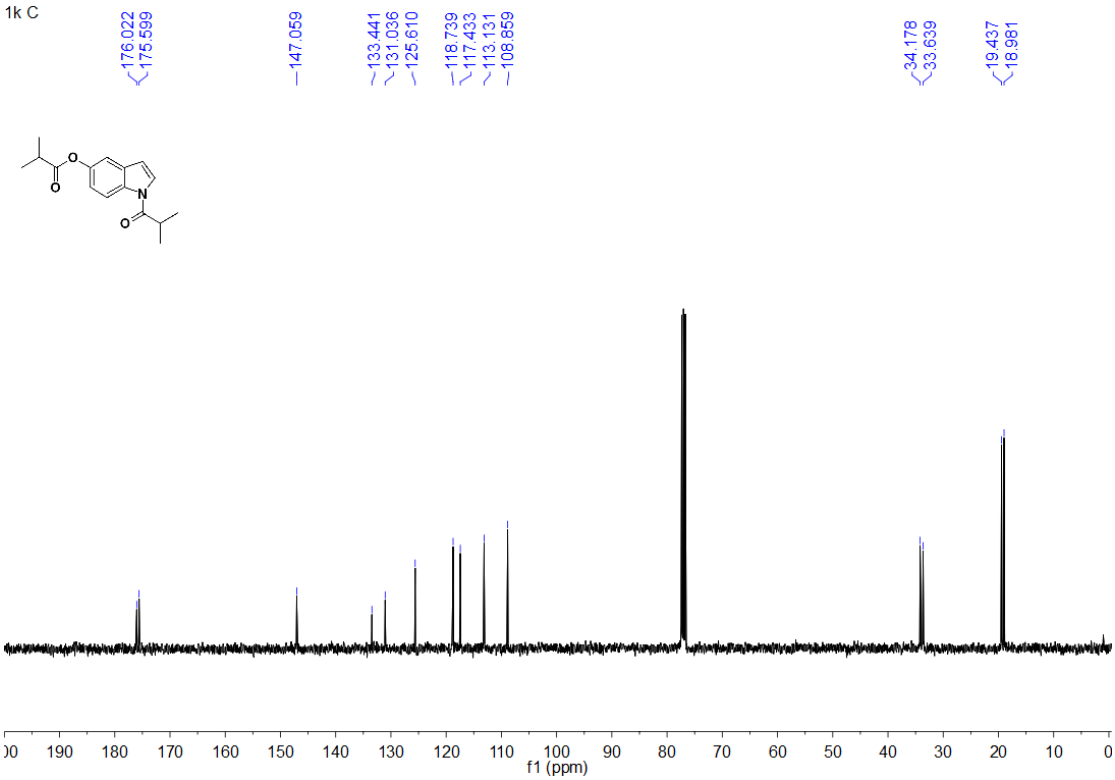
^{13}C NMR spectrum of 1j



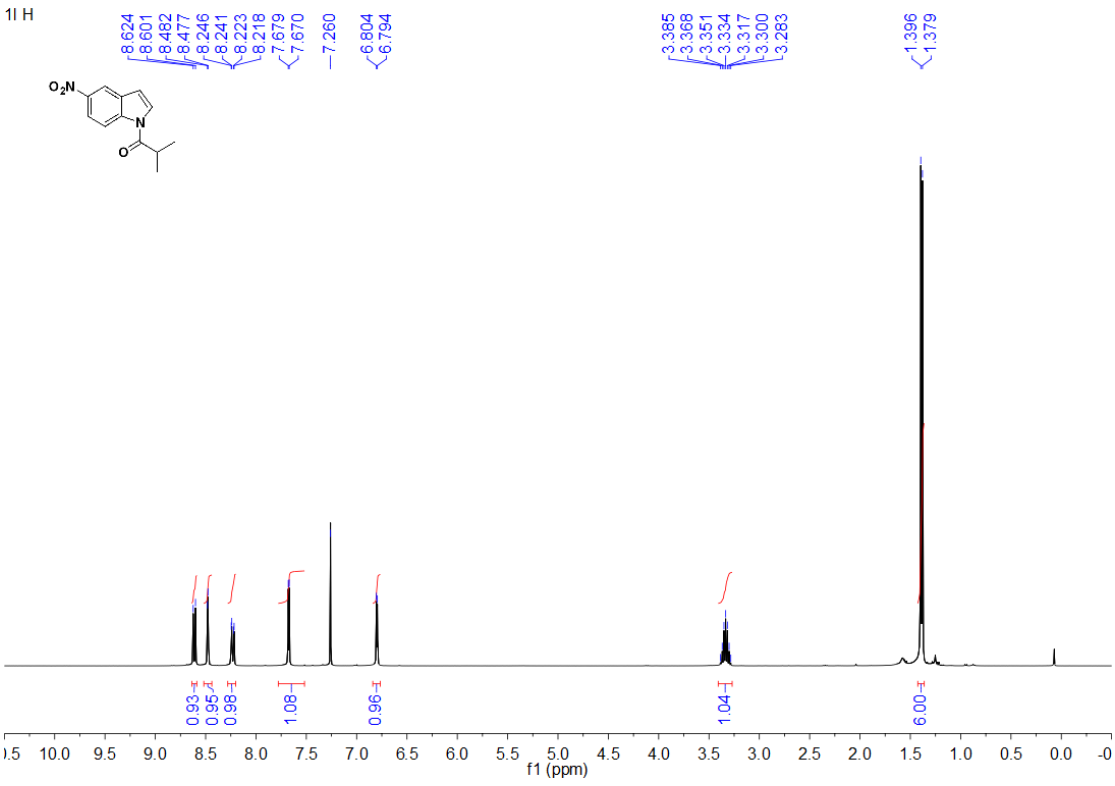
^{1}H NMR spectrum of 1k



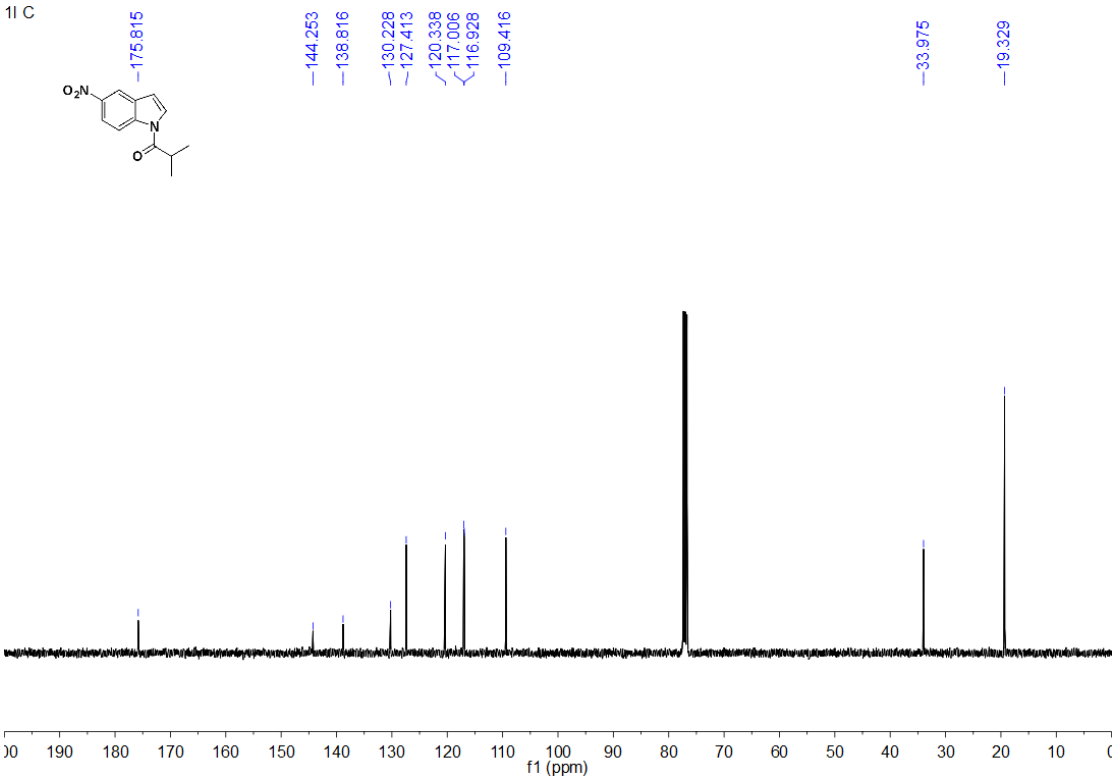
^{13}C NMR spectrum of 1k



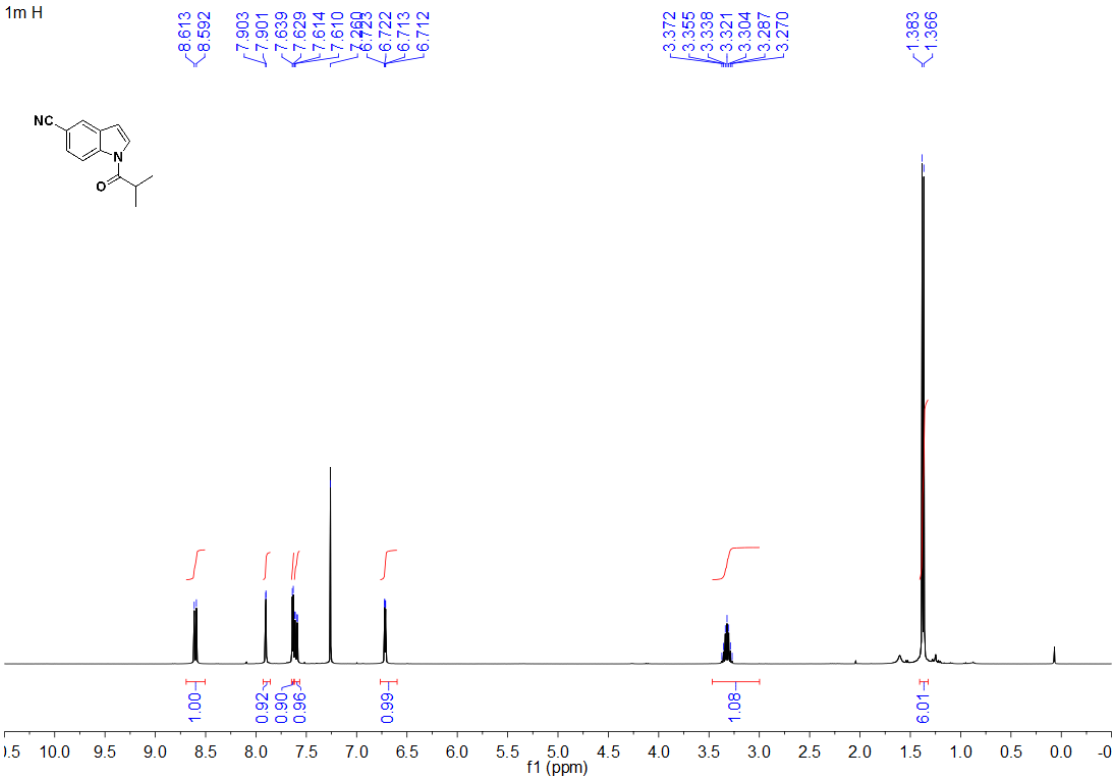
^{1}H NMR spectrum of 1l



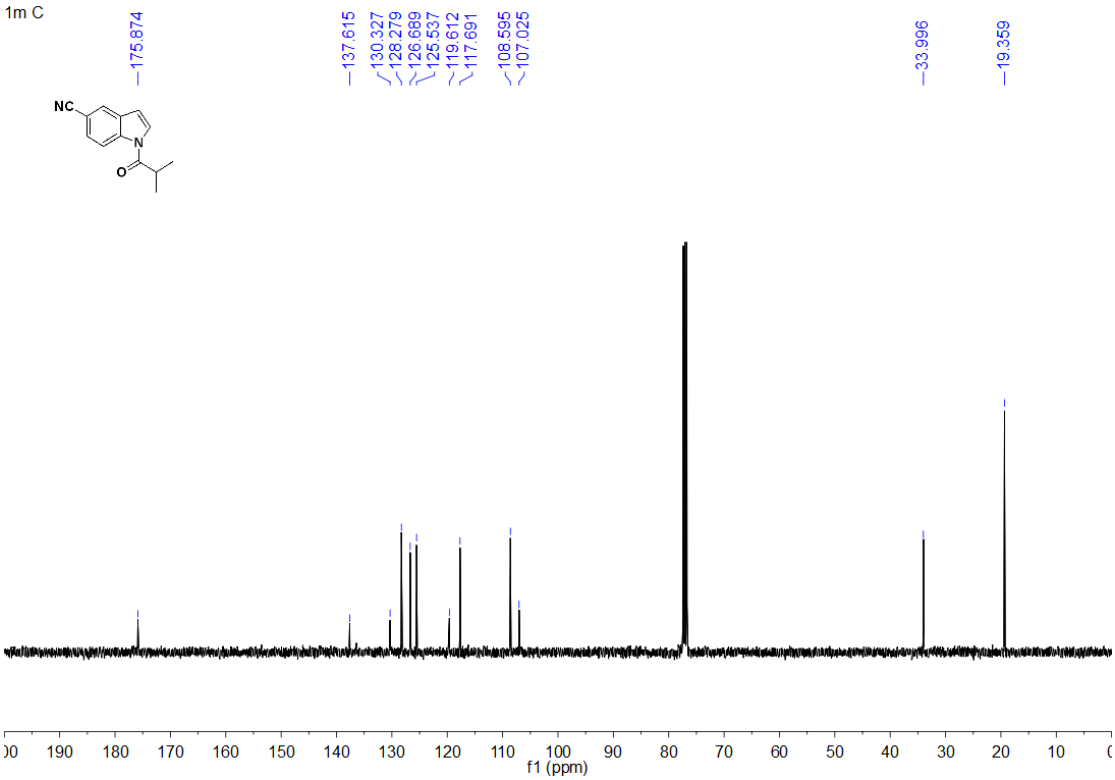
^{13}C NMR spectrum of 1l



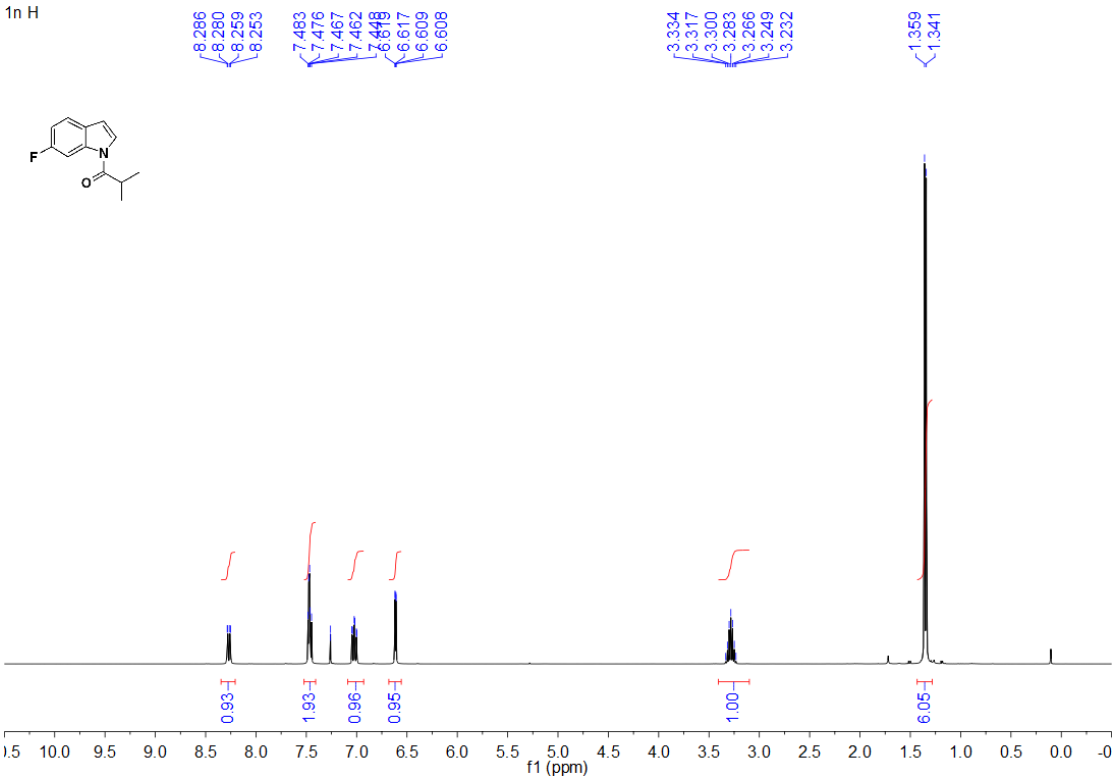
^{1}H NMR spectrum of 1m



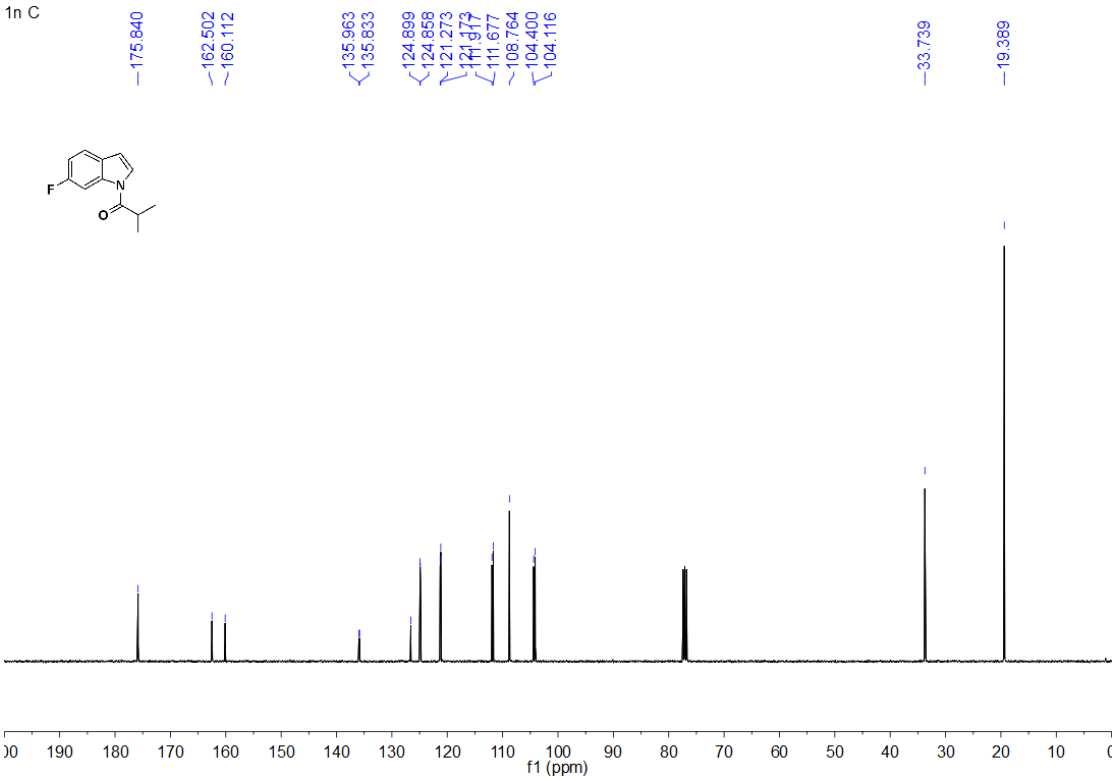
^{13}C NMR spectrum of 1m



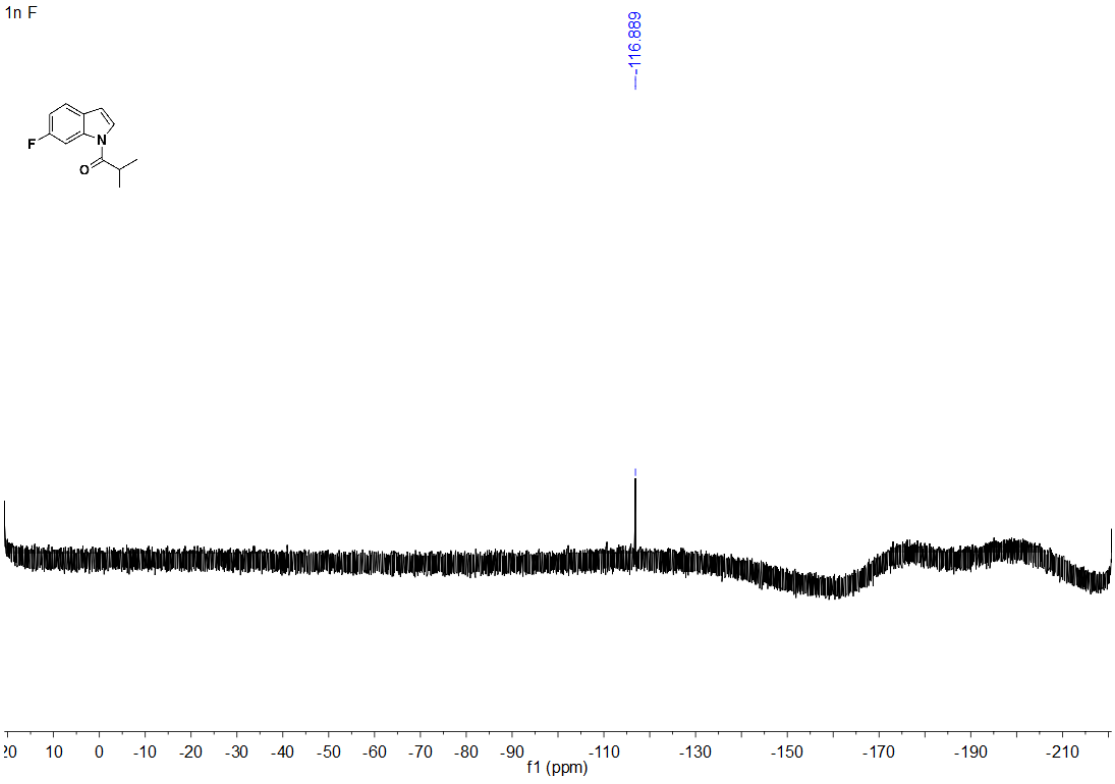
^{1}H NMR spectrum of 1n



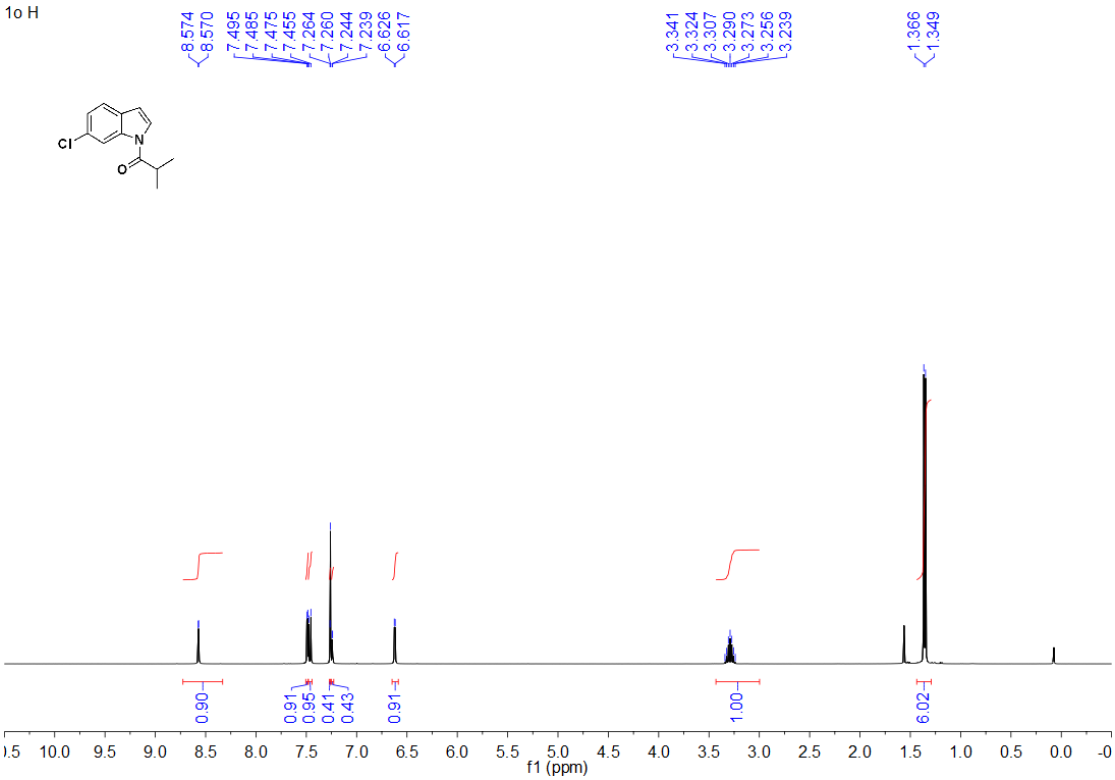
^{13}C NMR spectrum of 1n



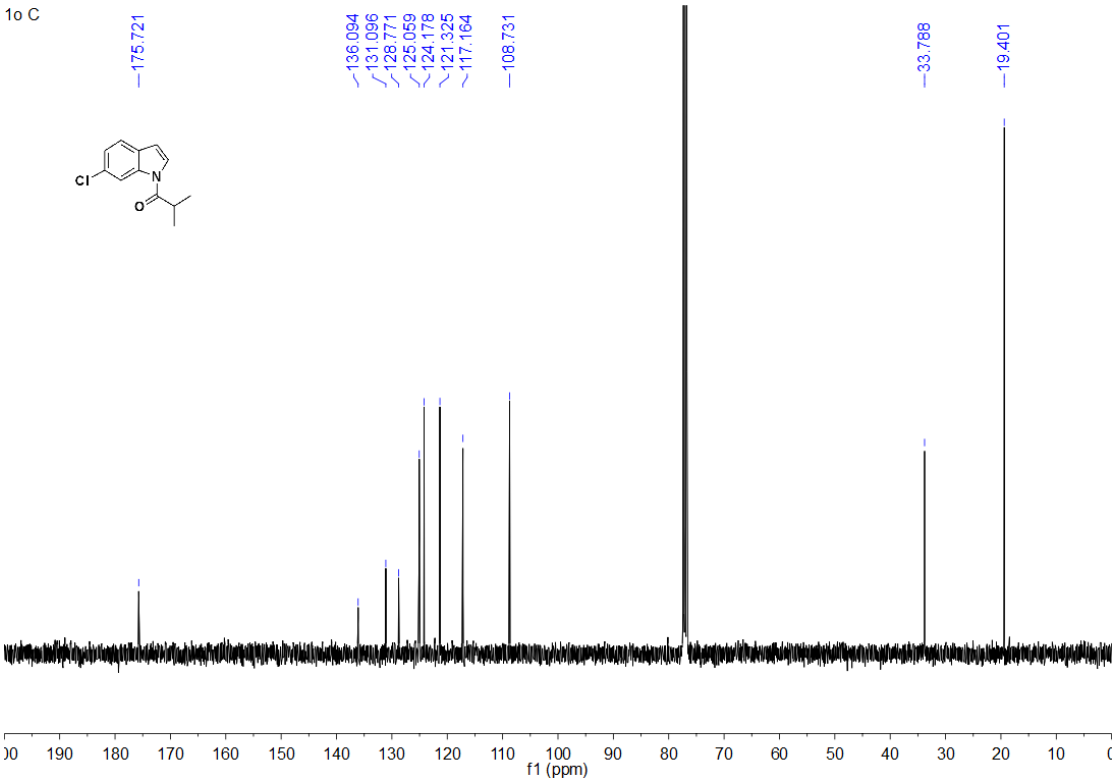
^{19}F NMR spectrum of 1n



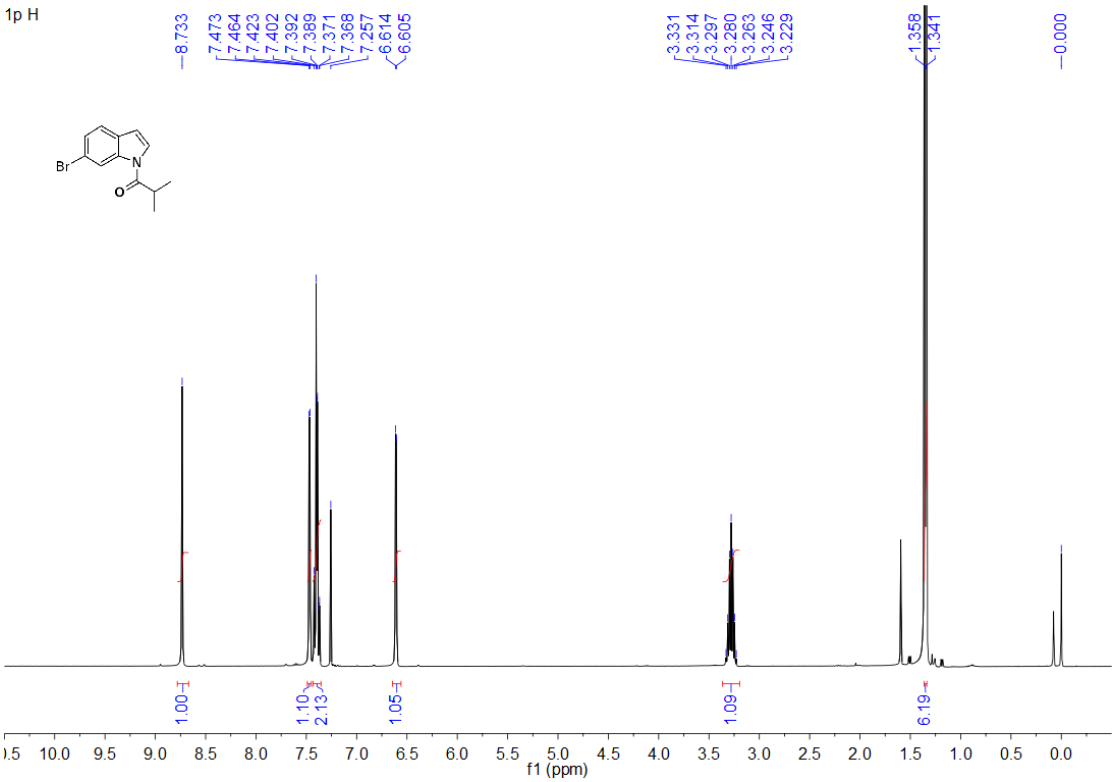
^{1}H NMR spectrum of 1o



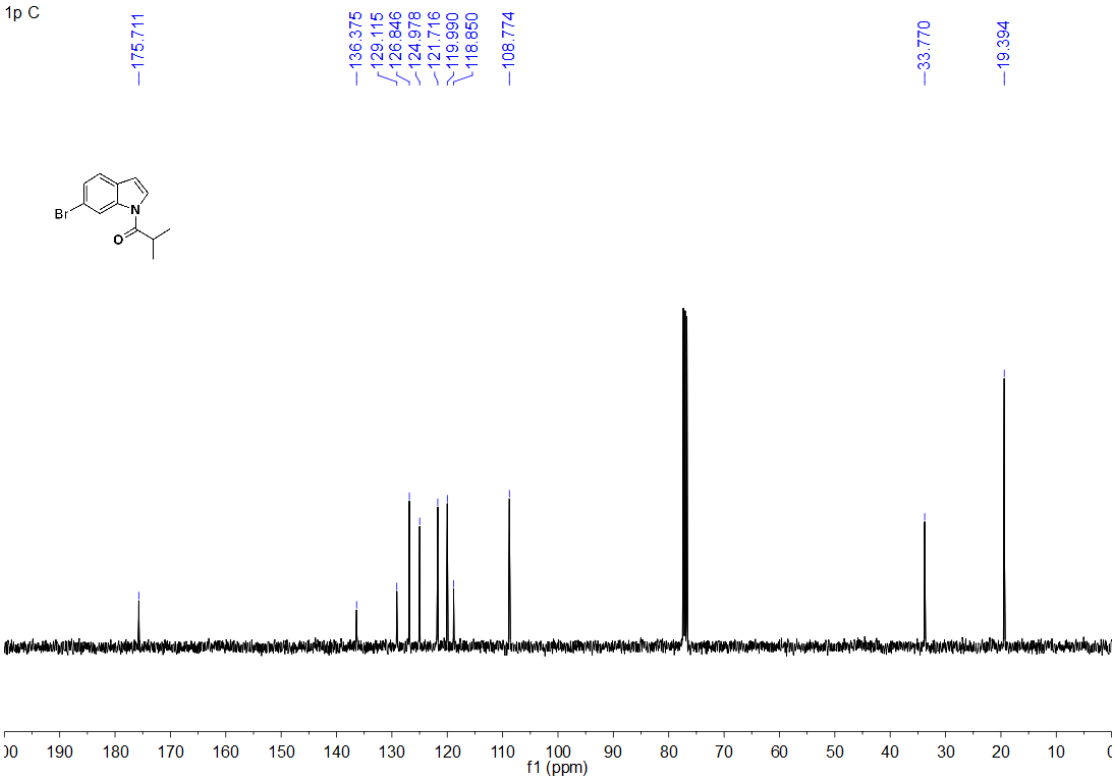
^{13}C NMR spectrum of 1o



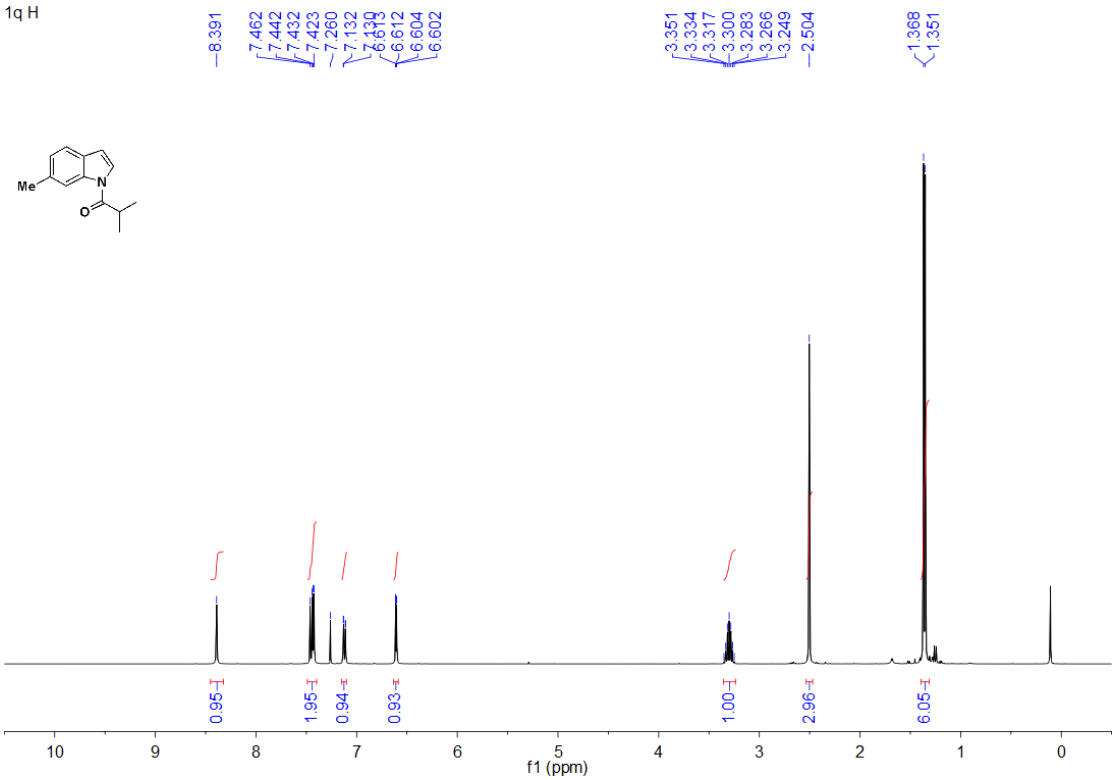
^{1}H NMR spectrum of 1p



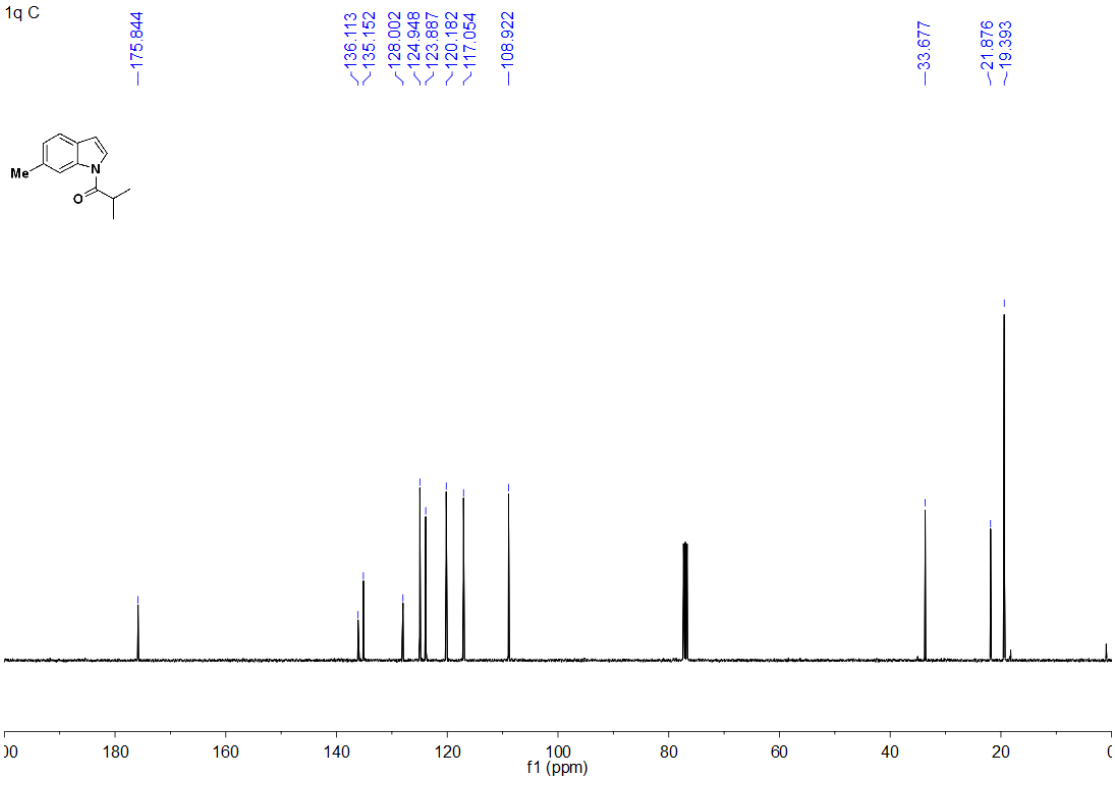
^{13}C NMR spectrum of 1p



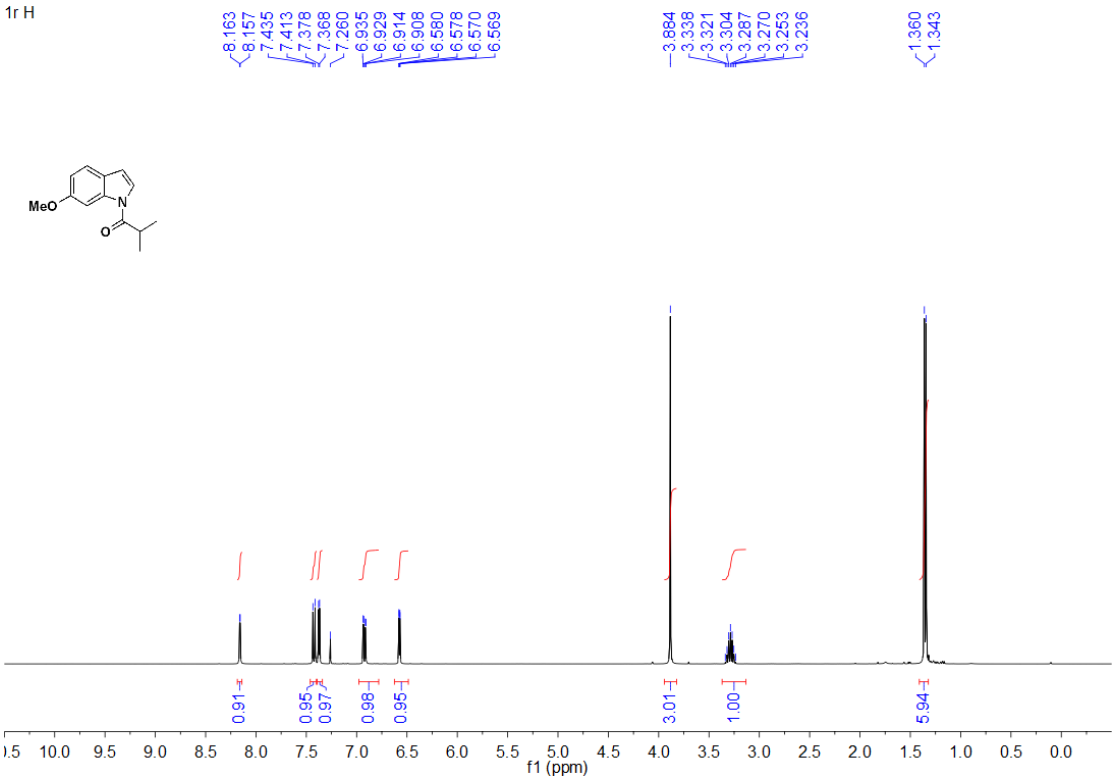
^{1}H NMR spectrum of 1q



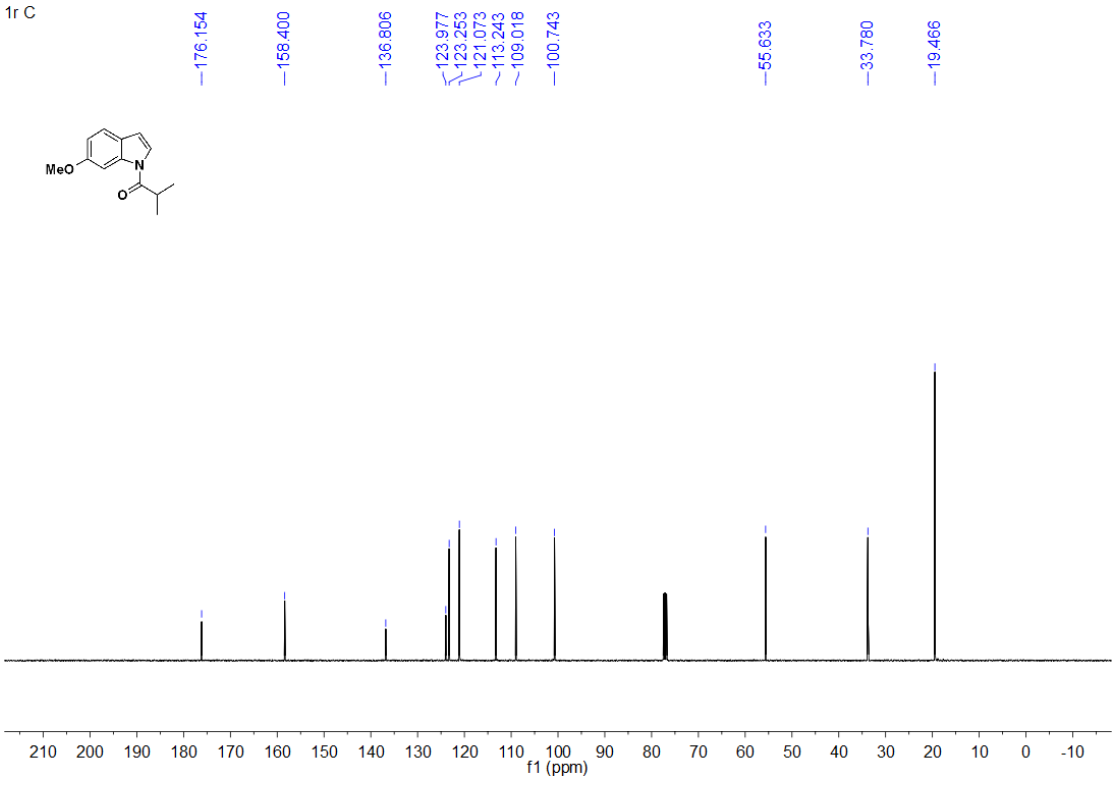
^{13}C NMR spectrum of 1q



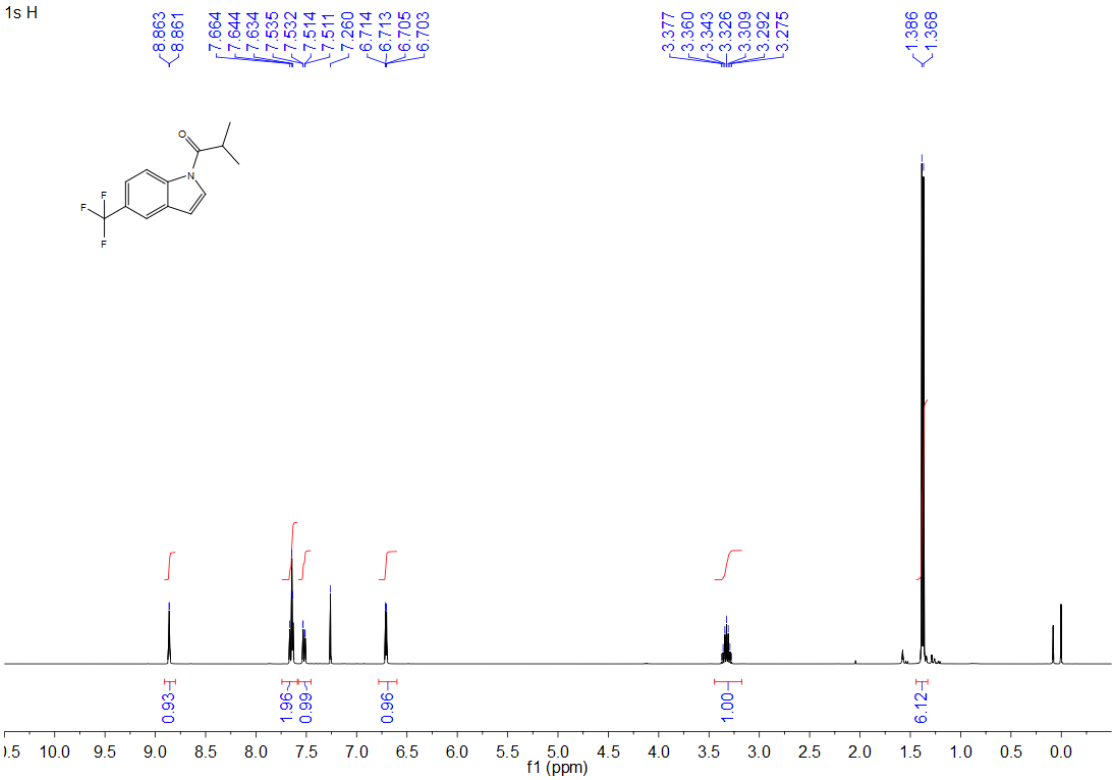
^{1}H NMR spectrum of 1r



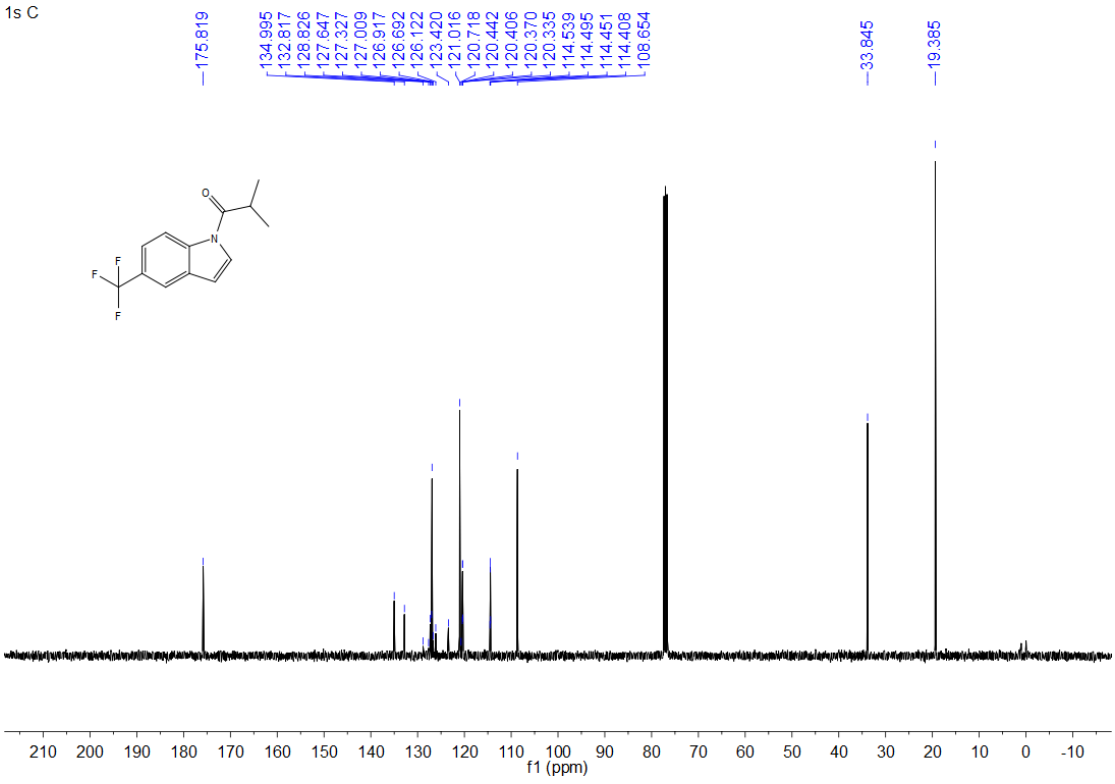
^{13}C NMR spectrum of 1r



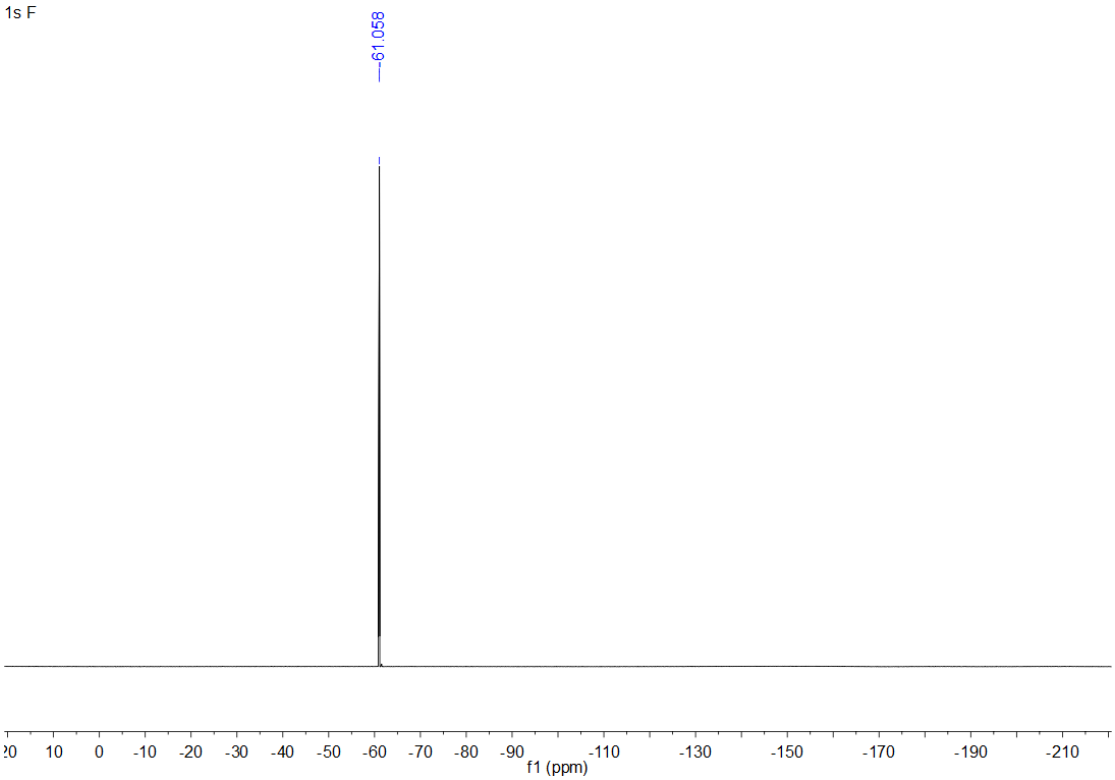
^{1}H NMR spectrum of 1s



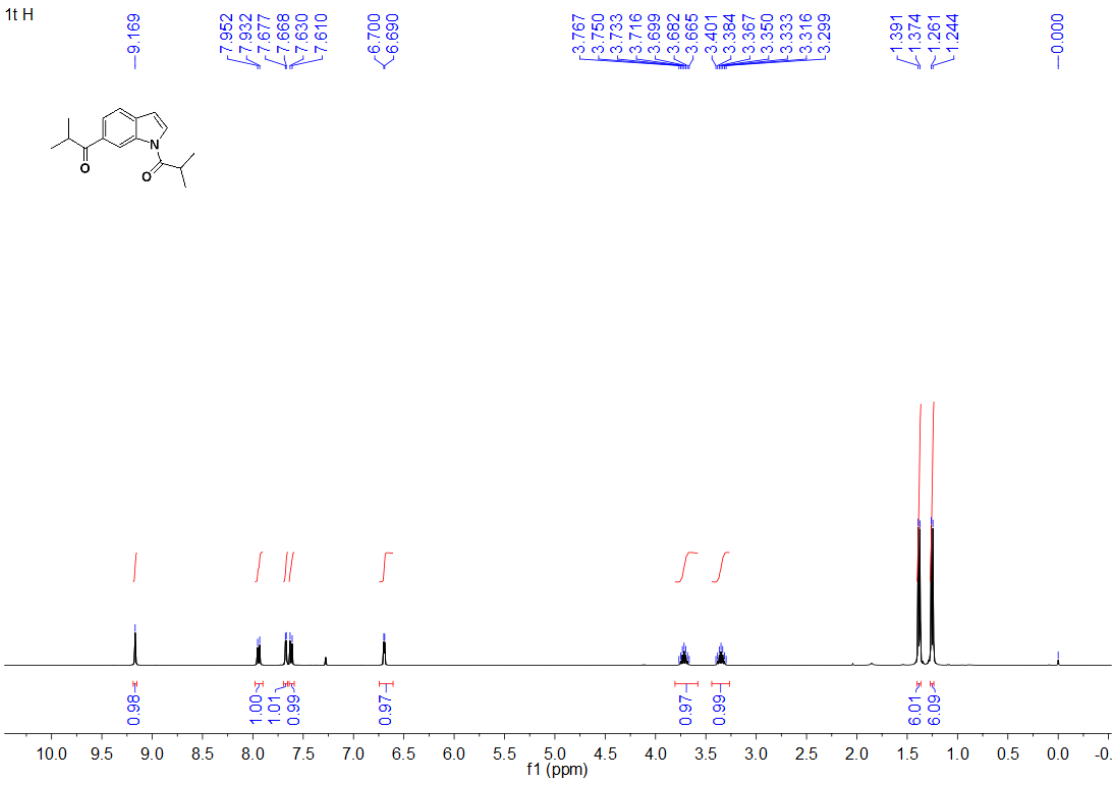
^{13}C NMR spectrum of 1s



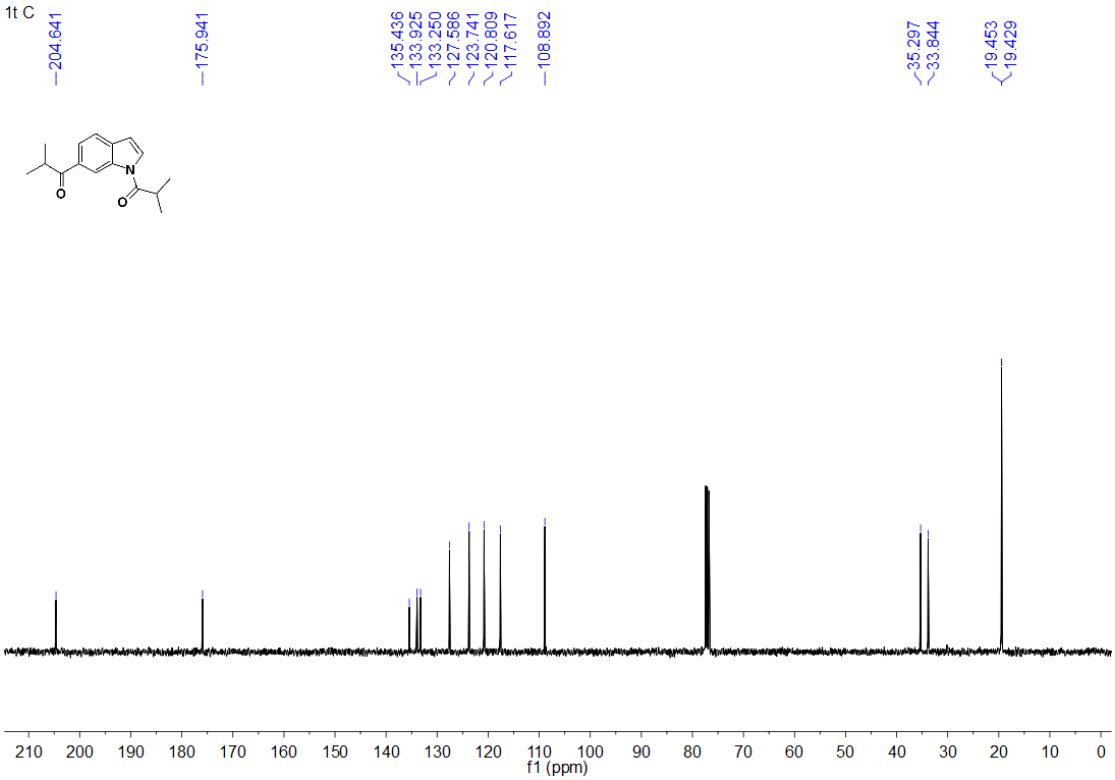
^{19}F NMR spectrum of 1s



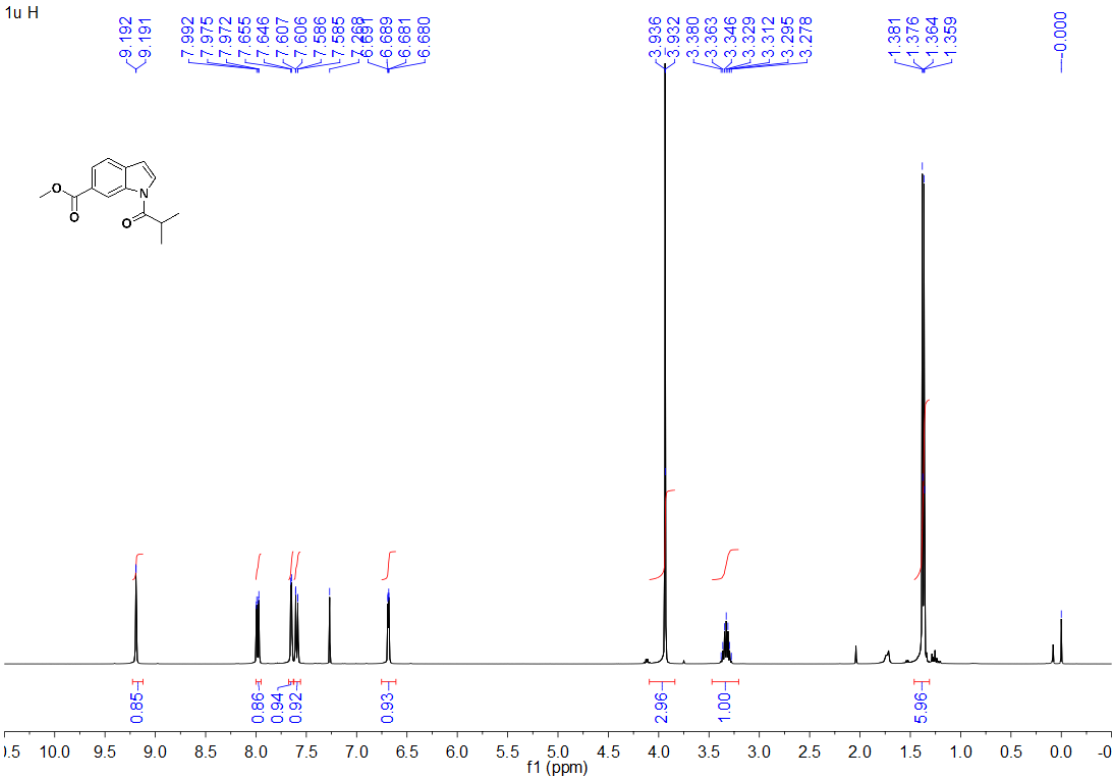
^{1}H NMR spectrum of 1t



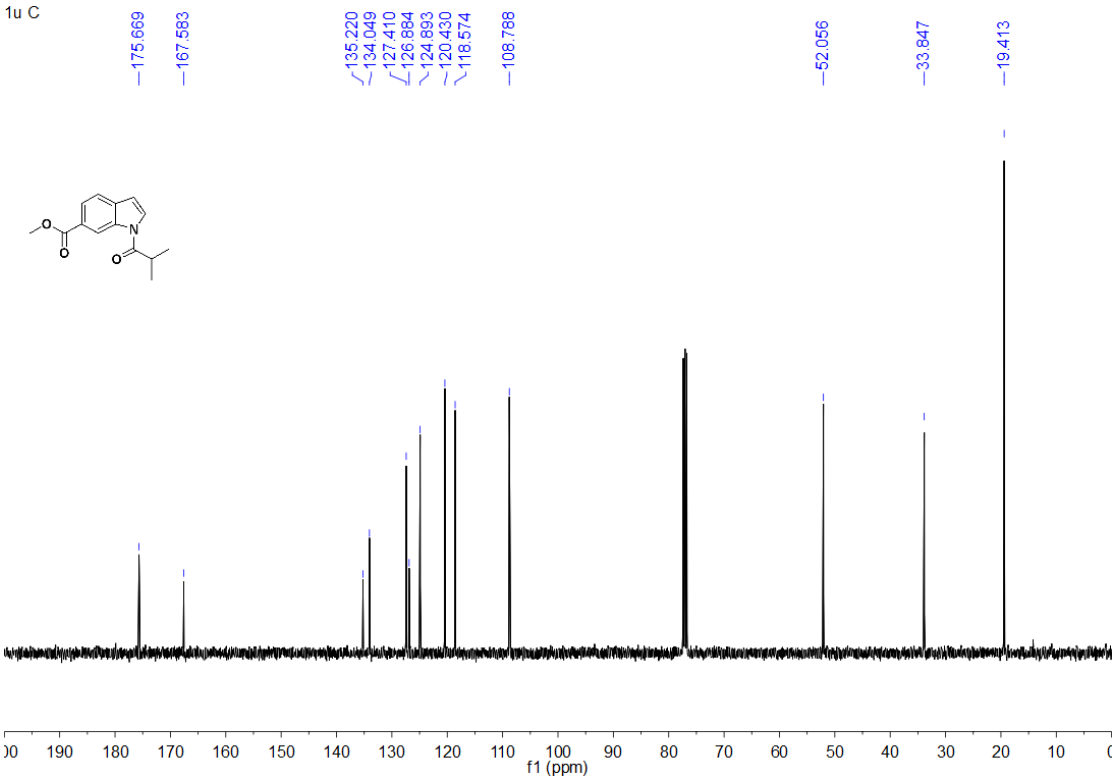
^{13}C NMR spectrum of 1t



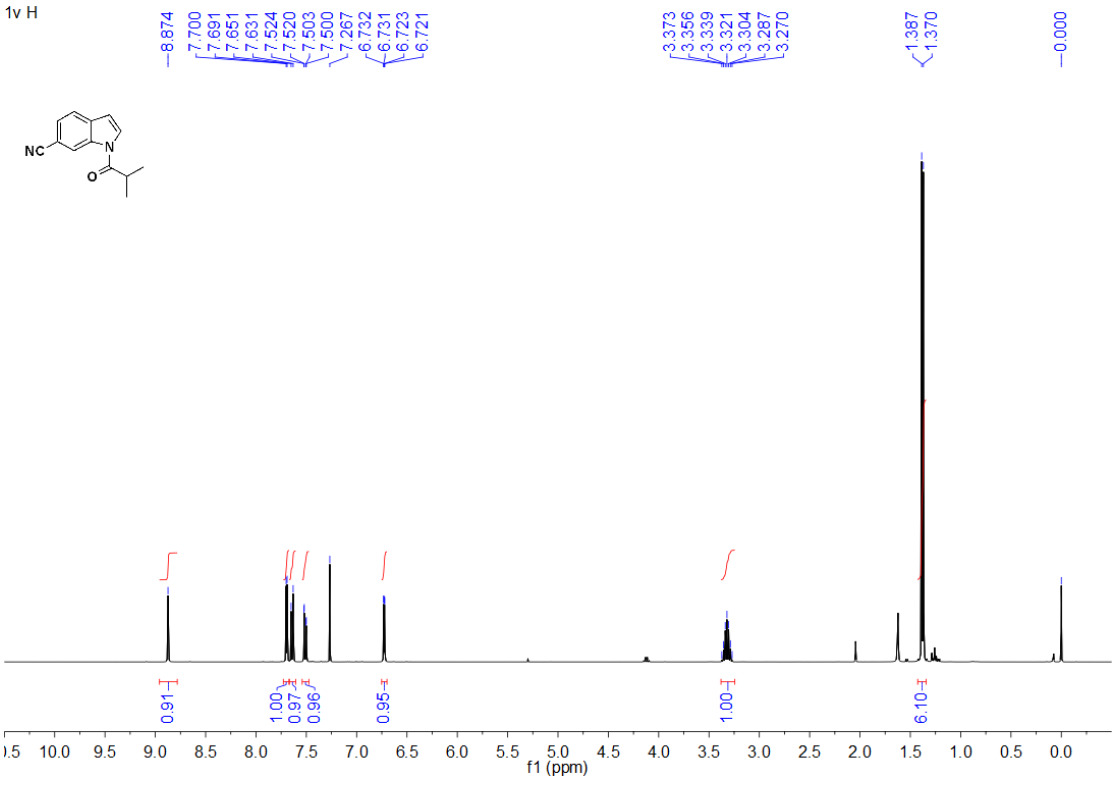
^{1}H NMR spectrum of 1u



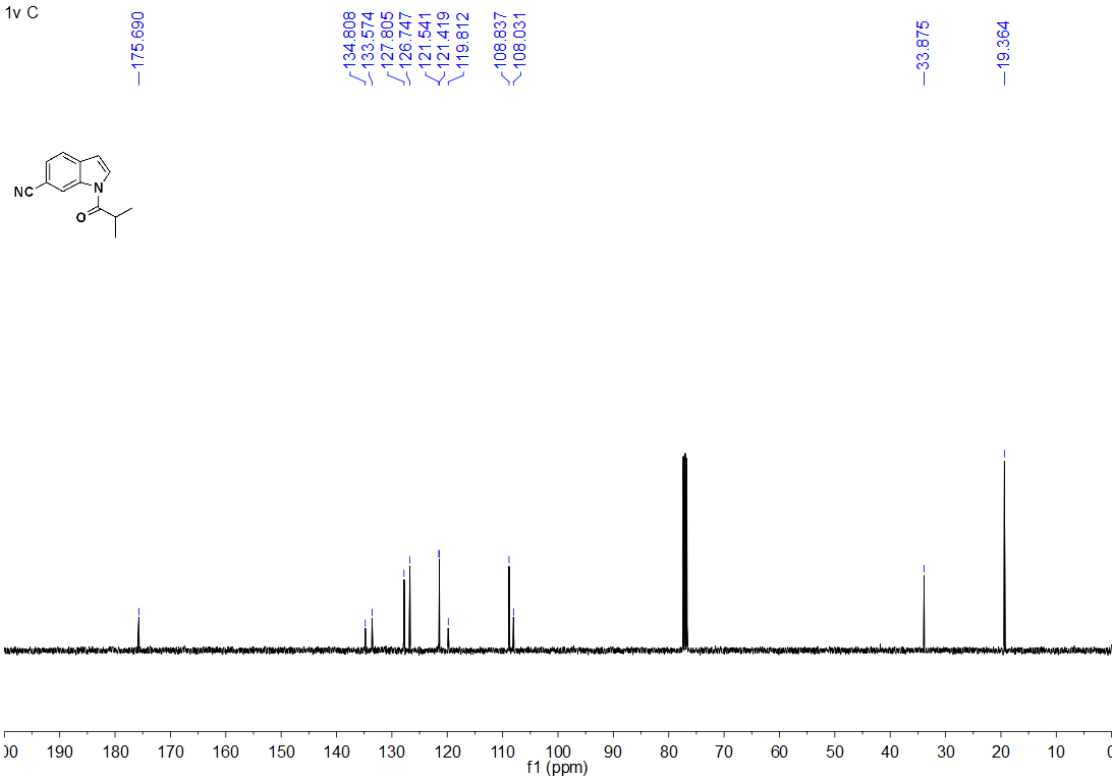
^{13}C NMR spectrum of 1u



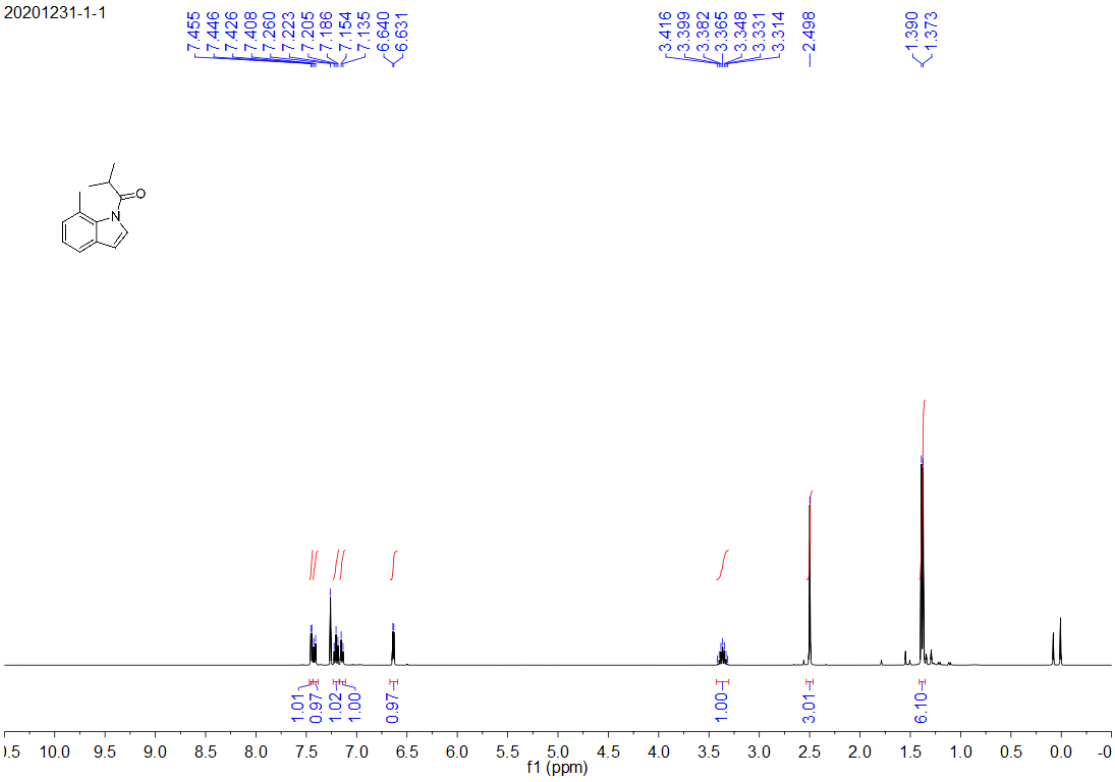
^{1}H NMR spectrum of 1v



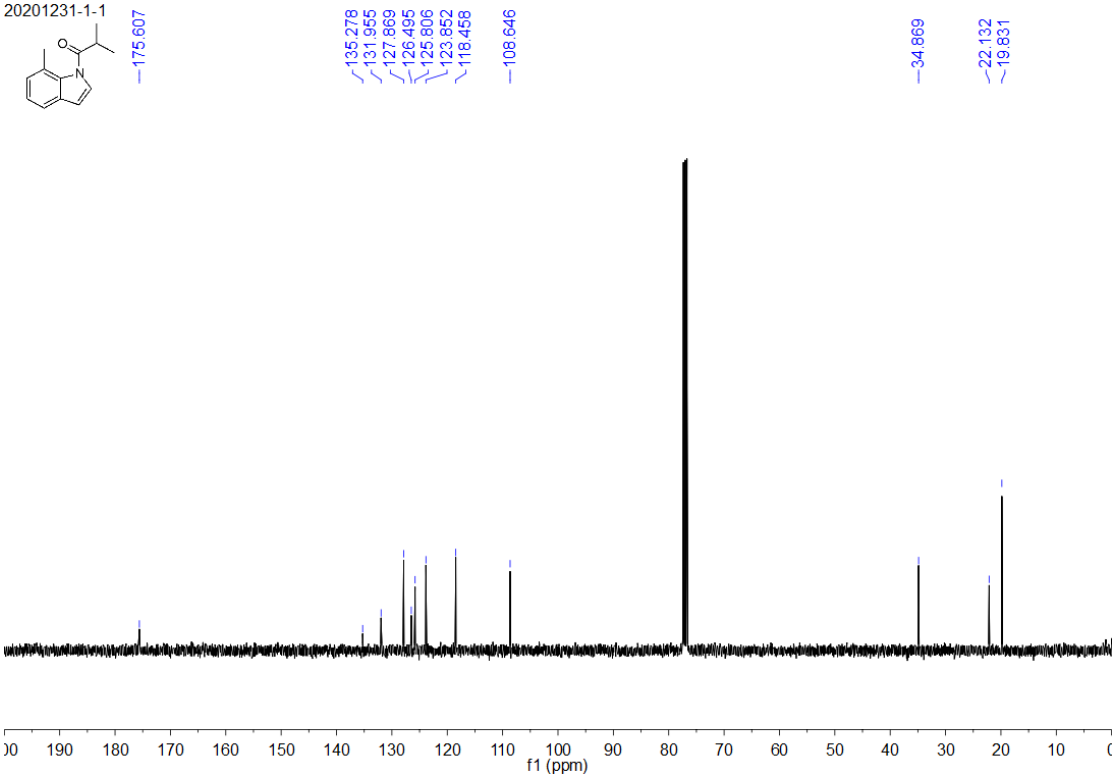
^{13}C NMR spectrum of 1v



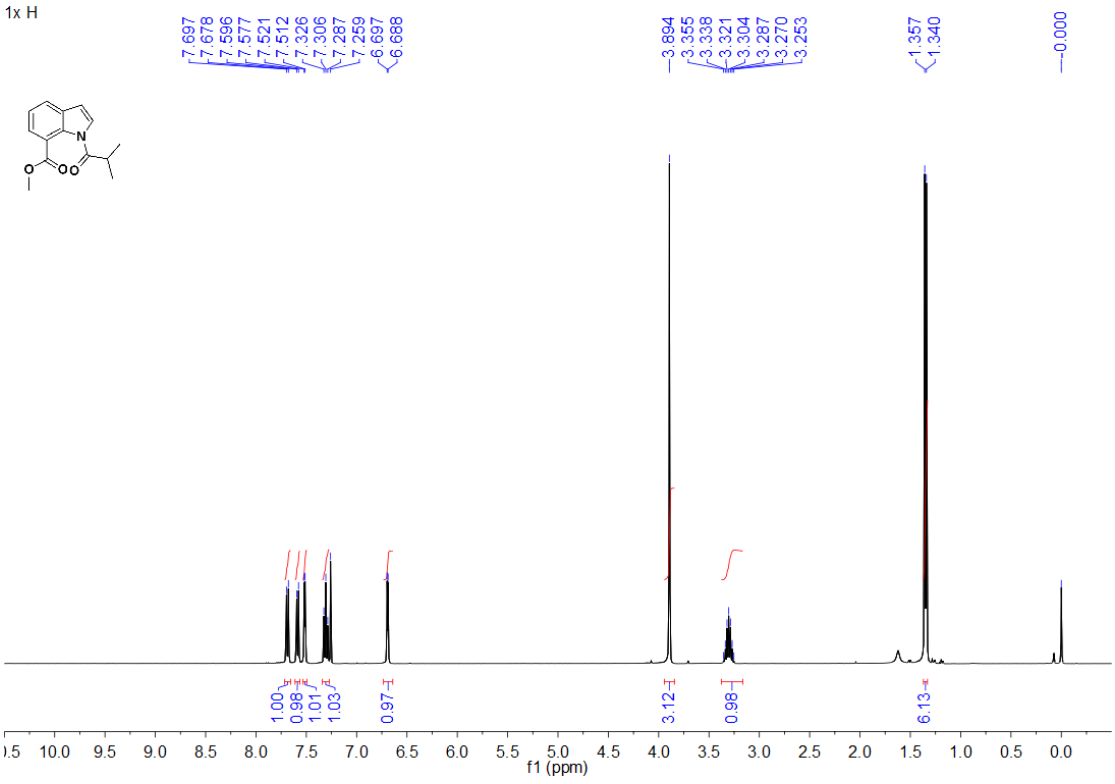
^{1}H NMR spectrum of 1w



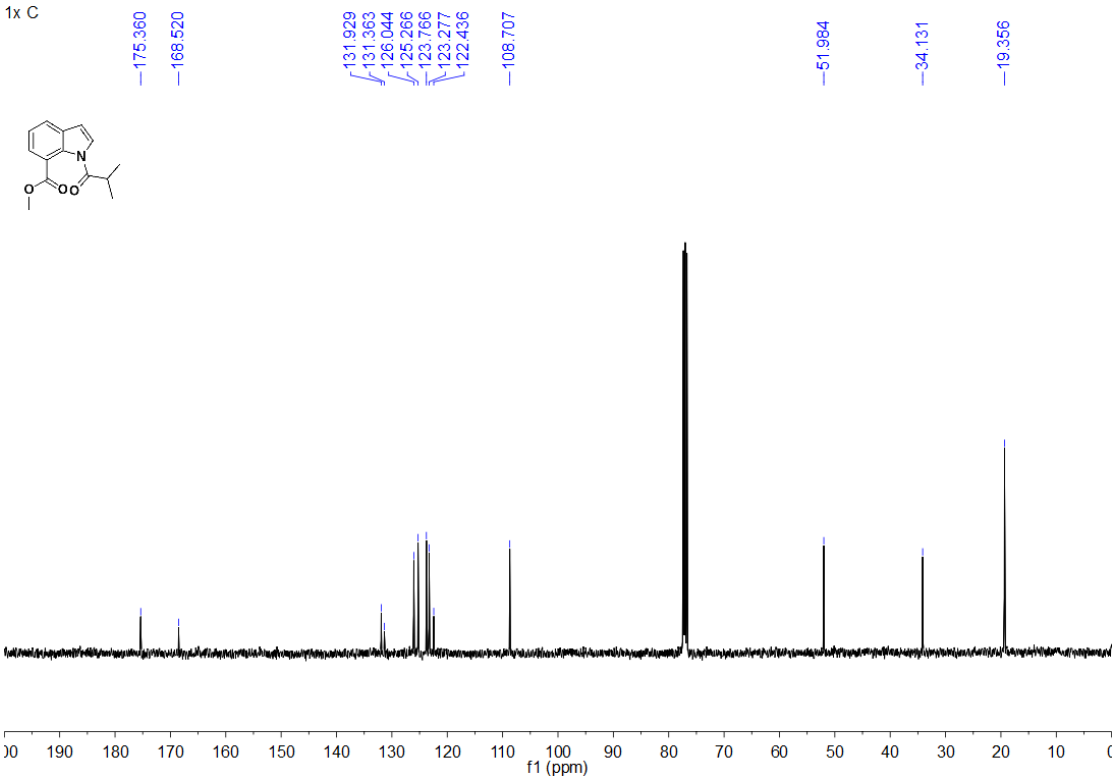
^{13}C NMR spectrum of 1w



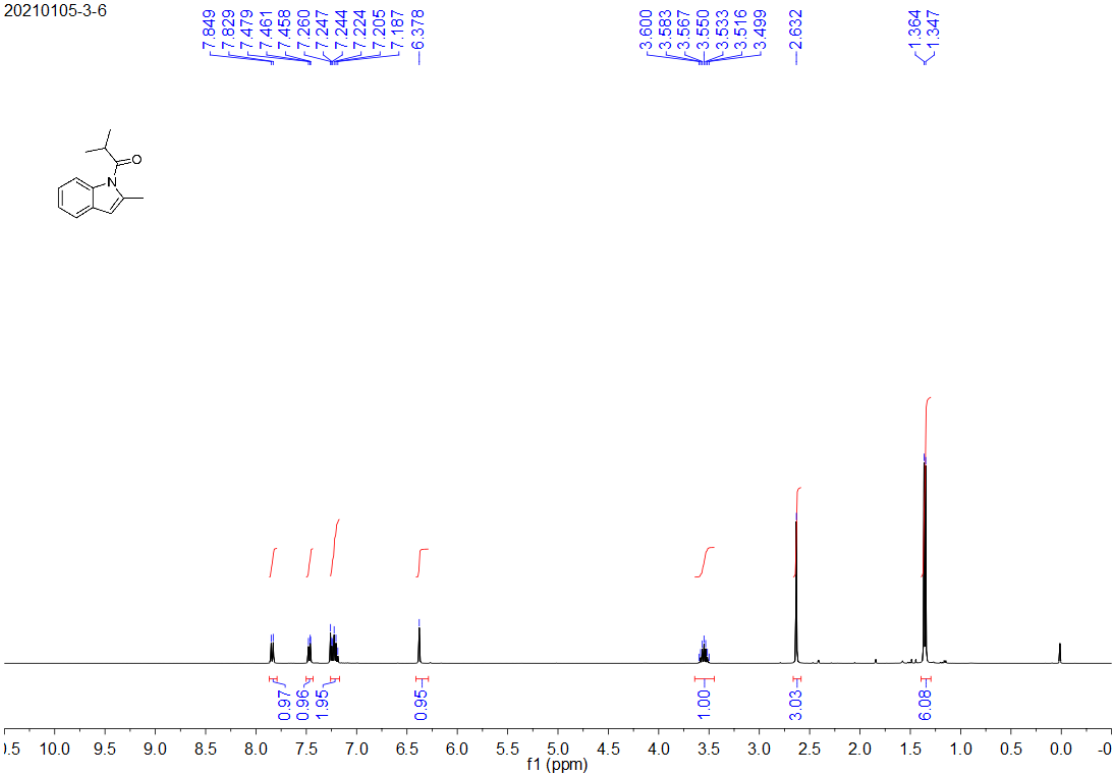
^{1}H NMR spectrum of 1x



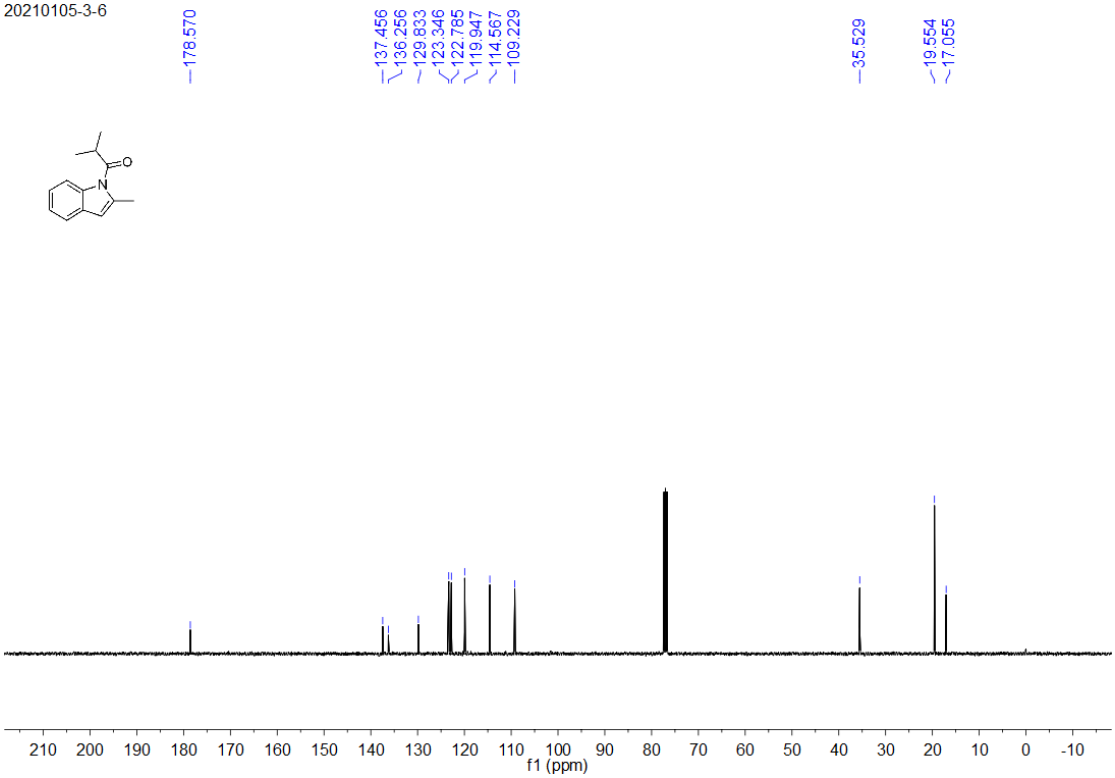
^{13}C NMR spectrum of 1x



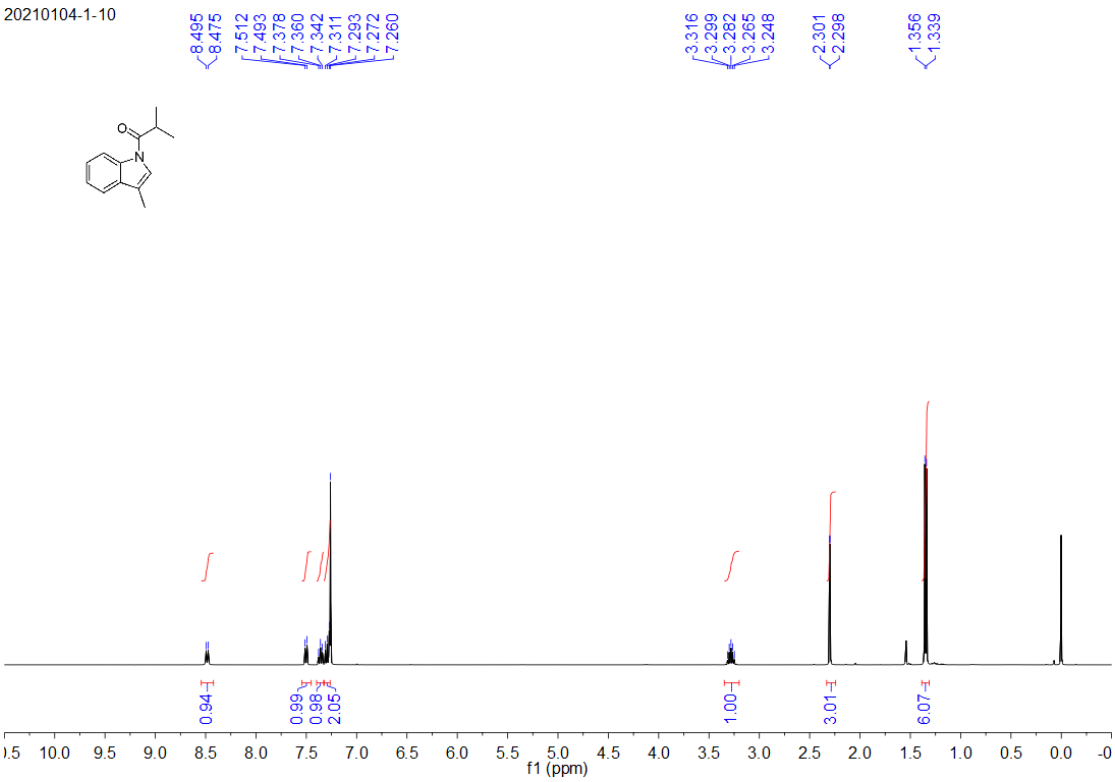
^{1}H NMR spectrum of 3a



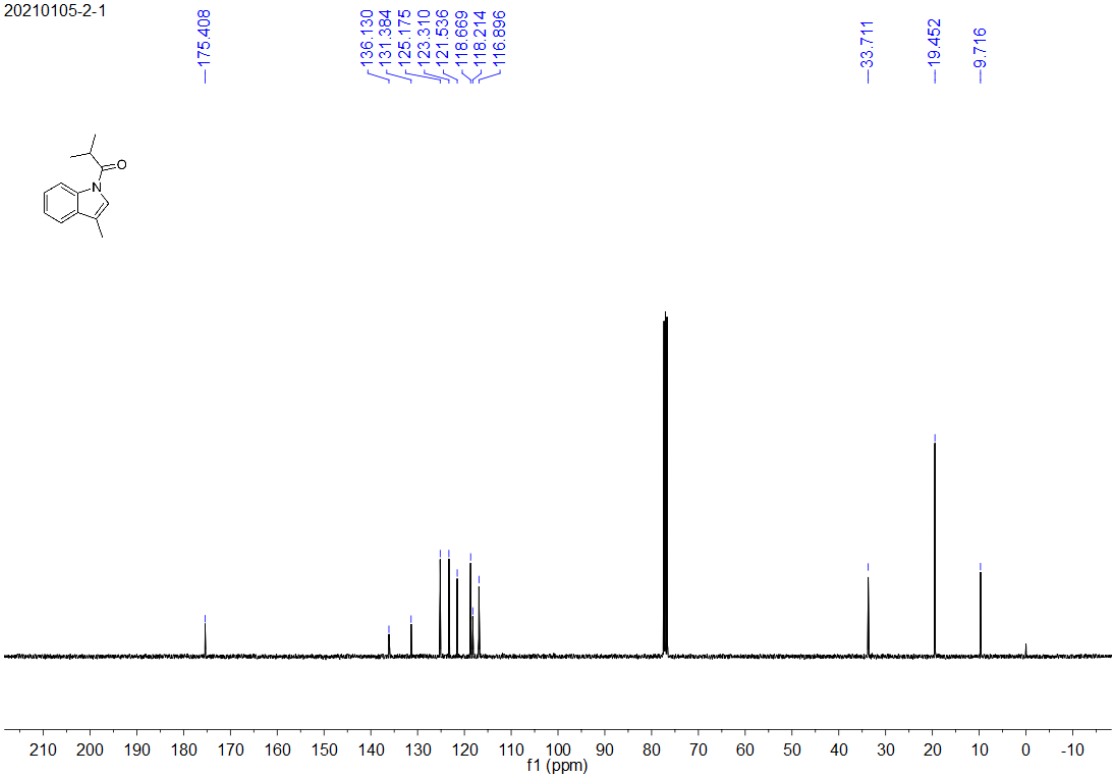
^{13}C NMR spectrum of 3a



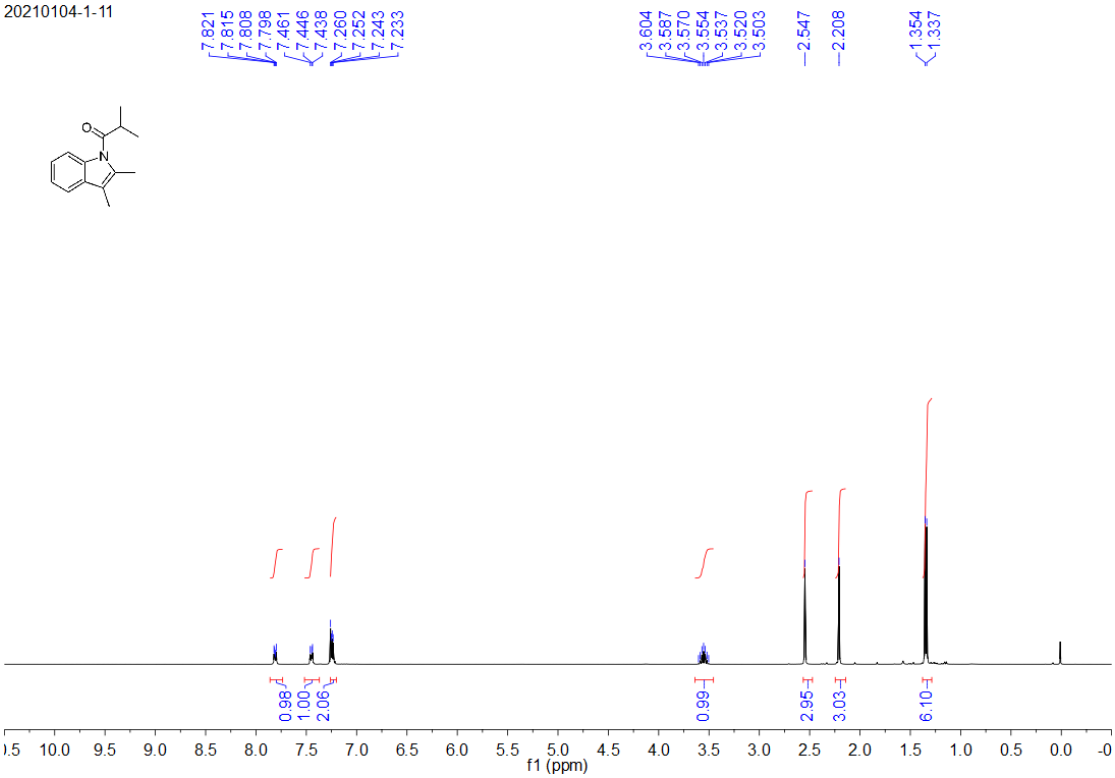
^{1}H NMR spectrum of 3b



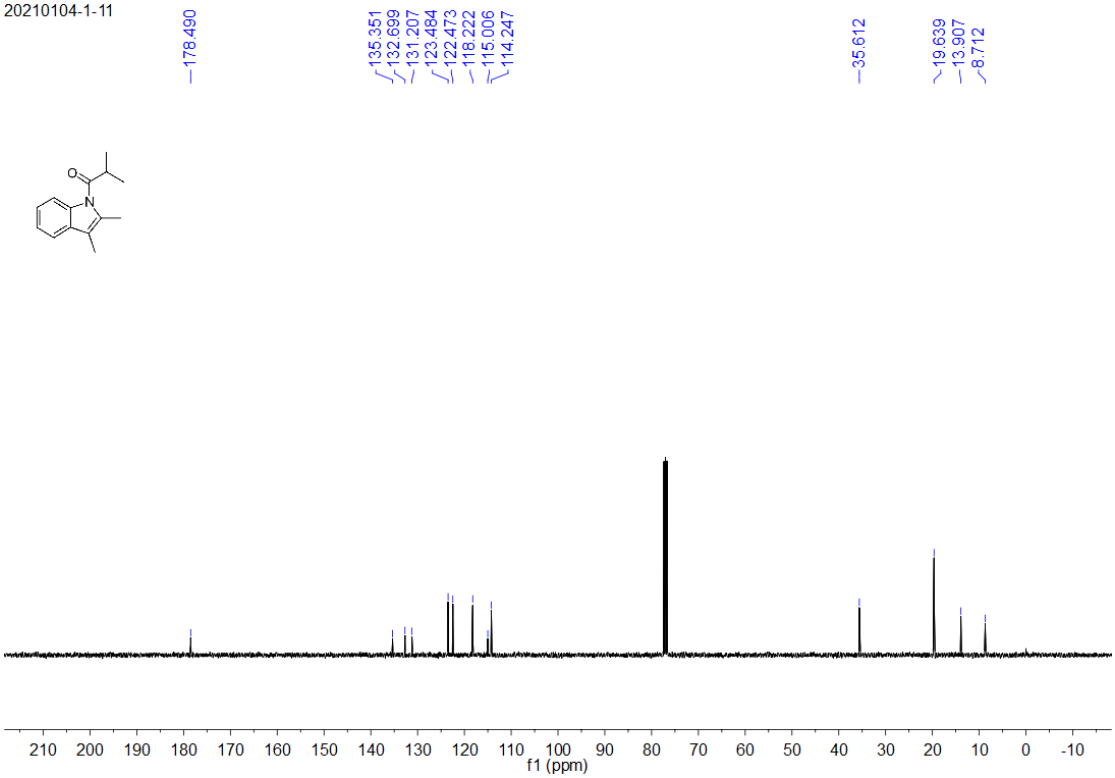
^{13}C NMR spectrum of 3b



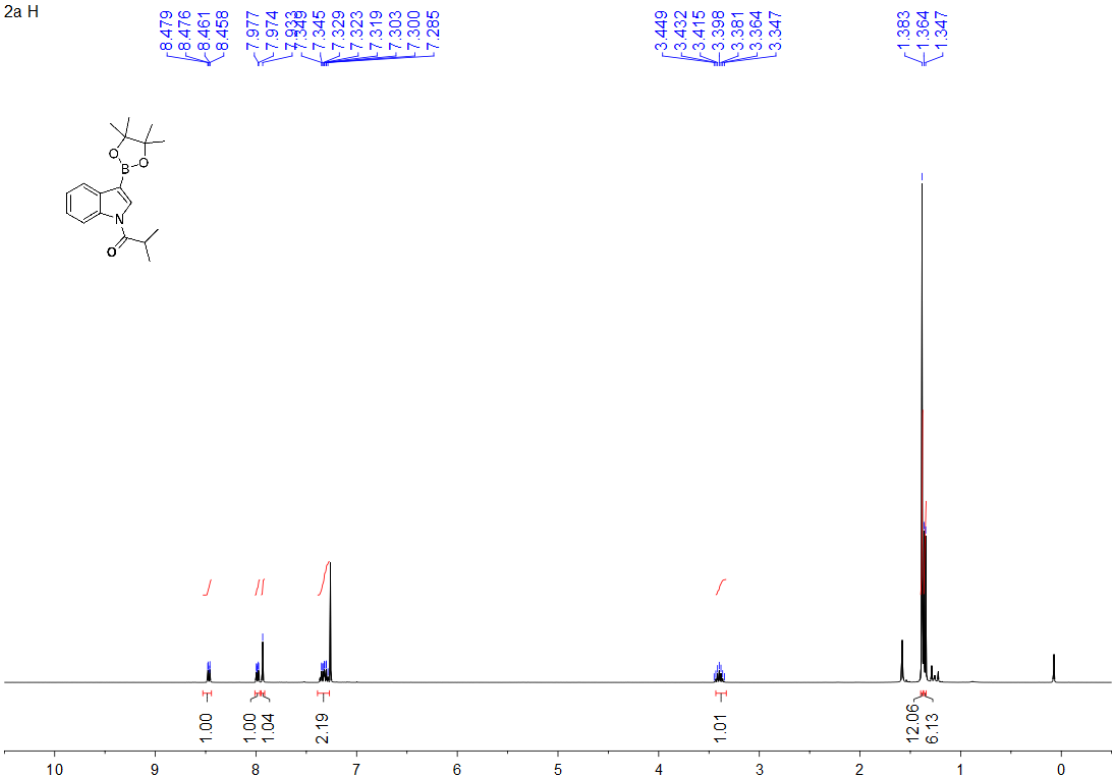
^{1}H NMR spectrum of 3c



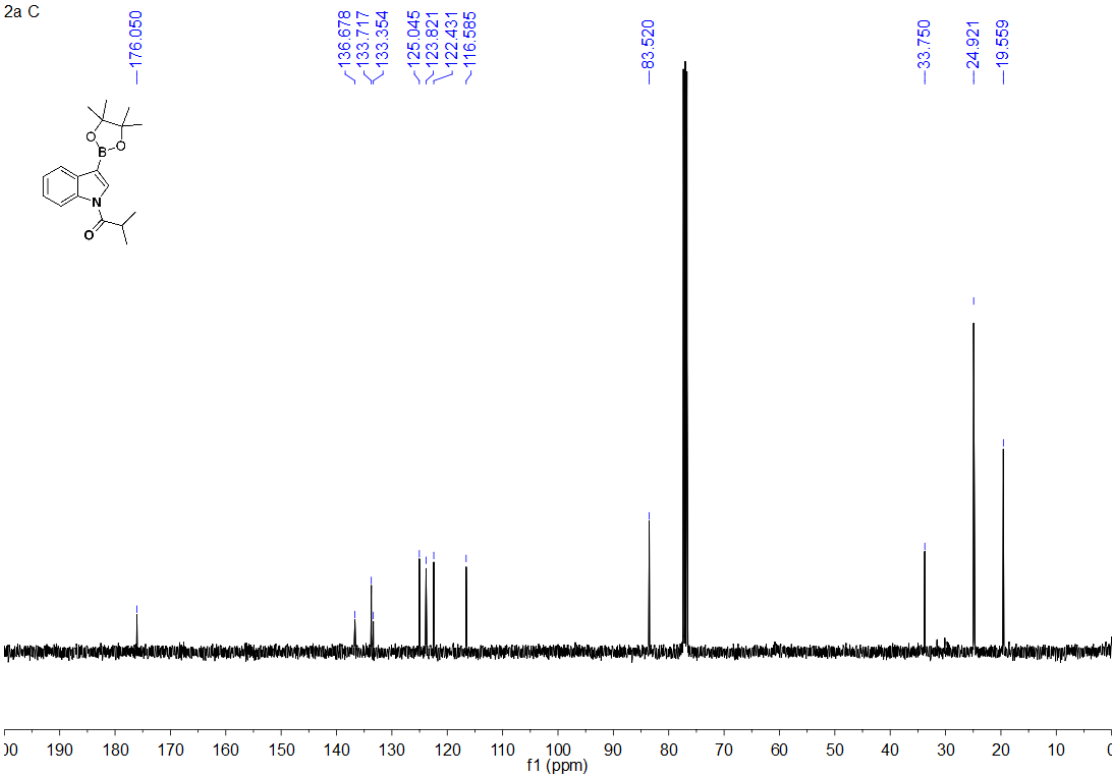
^{13}C NMR spectrum of 3c



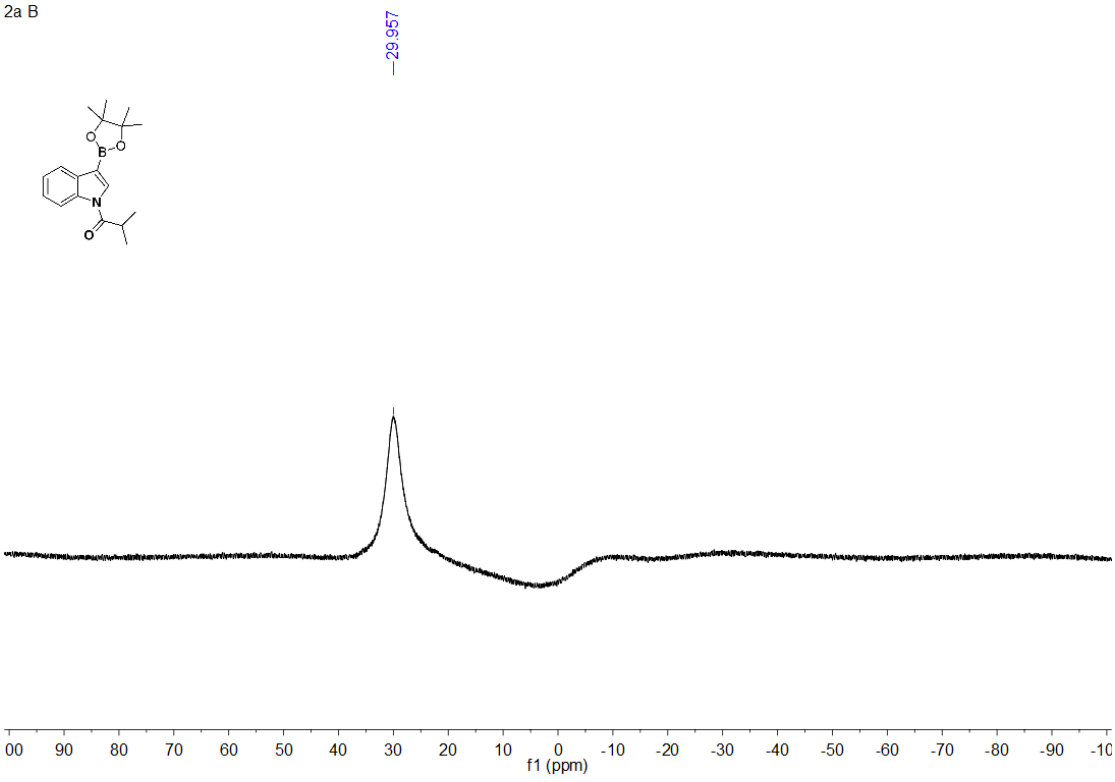
^{1}H NMR spectrum of 2a



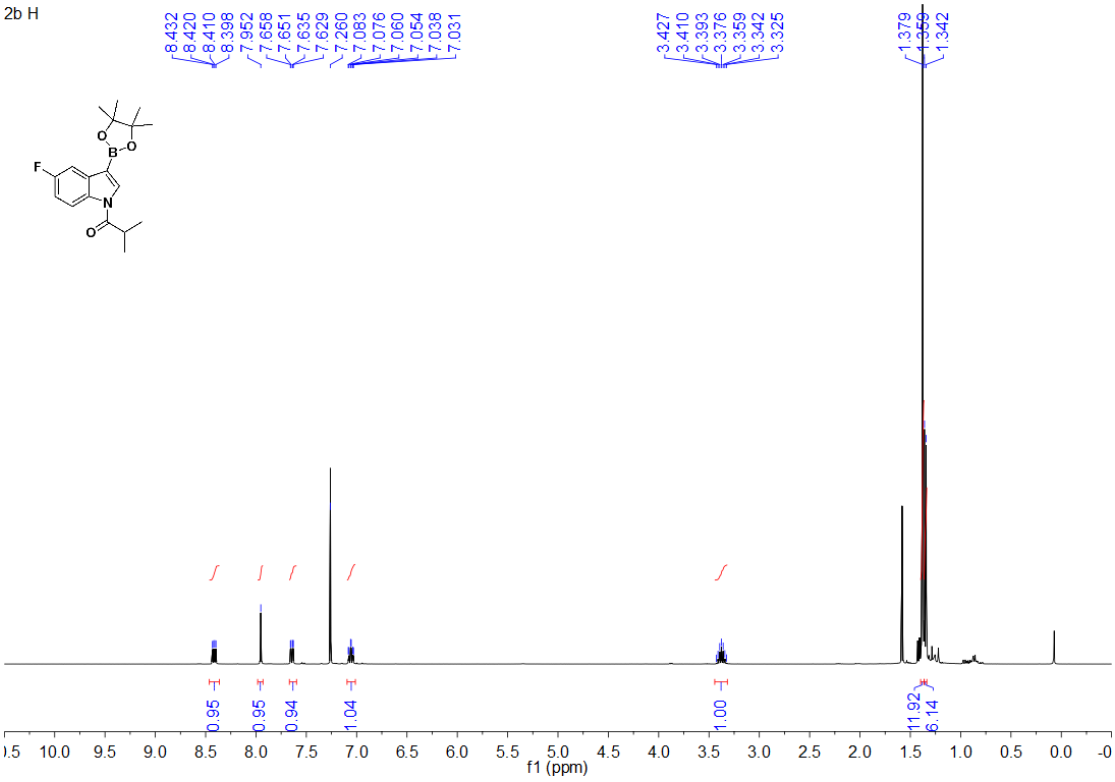
^{13}C NMR spectrum of 2a



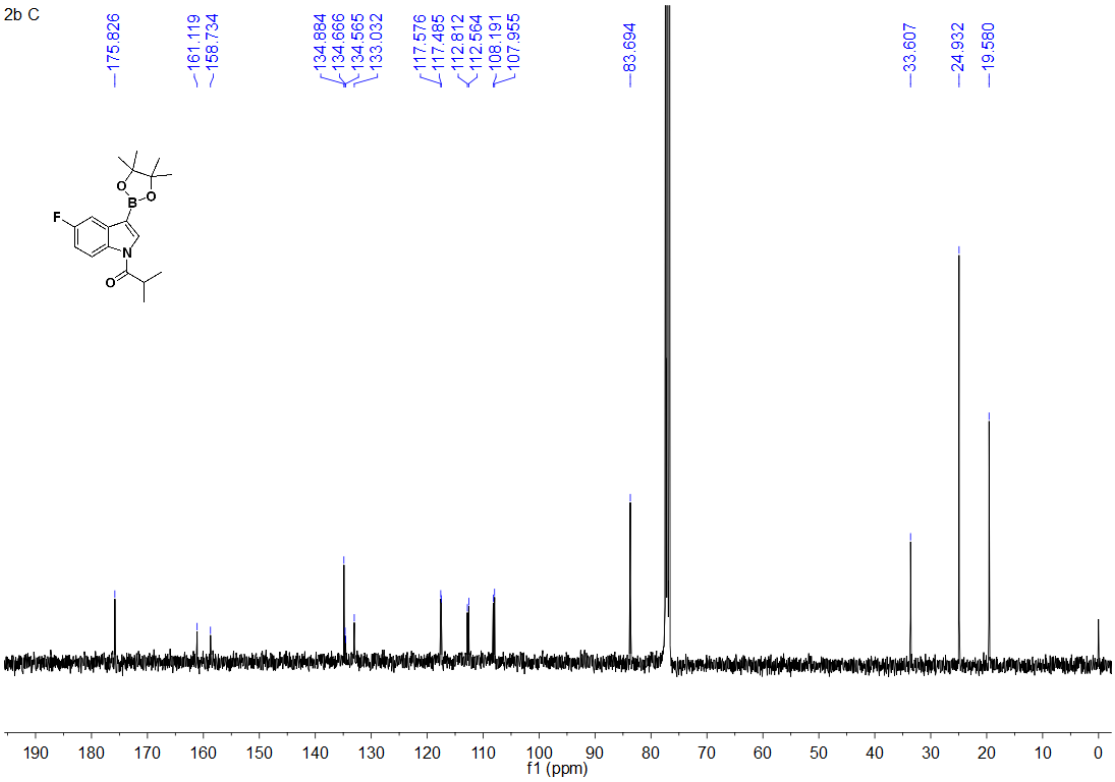
^{11}B NMR spectrum of 2a



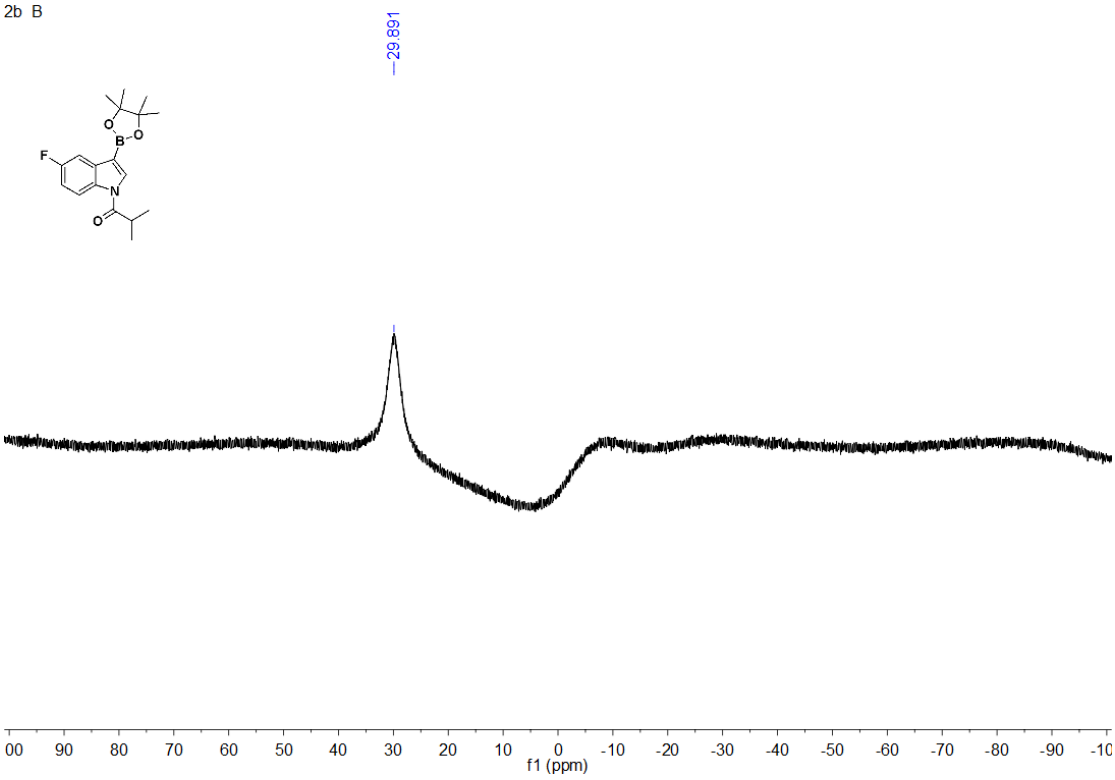
^{1}H NMR spectrum of 2b



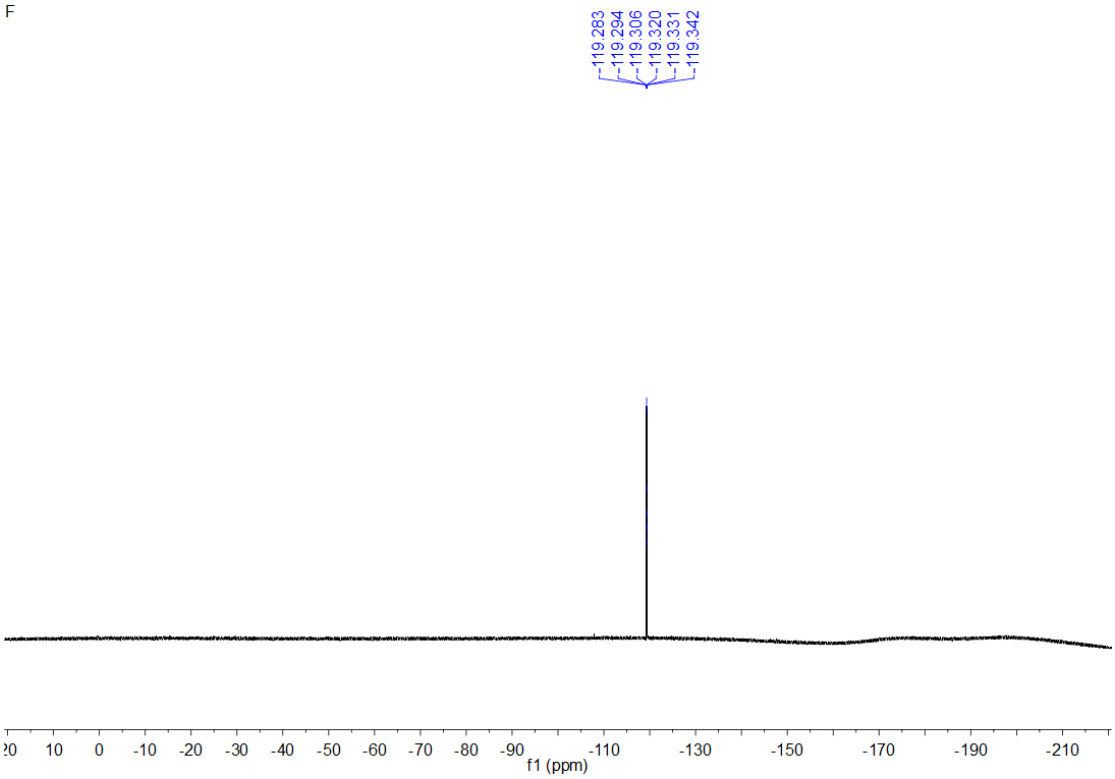
^{13}C NMR spectrum of 2b



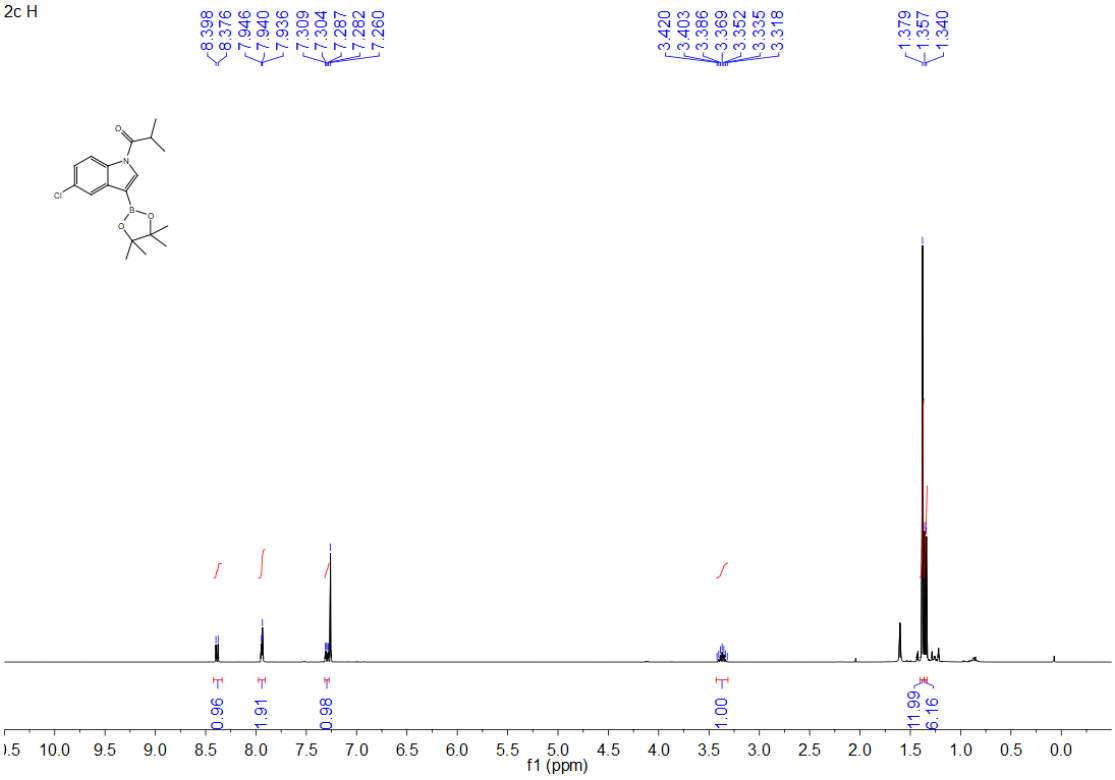
^{11}B NMR spectrum of 2b



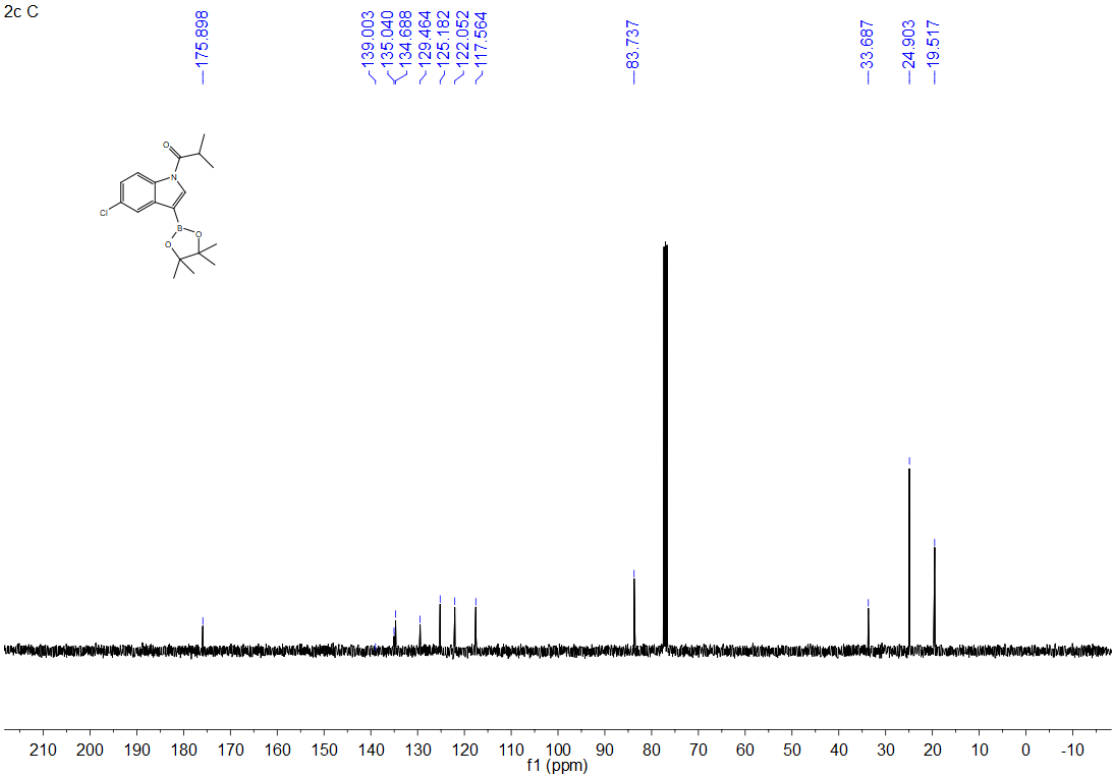
^{19}F NMR spectrum of 2b



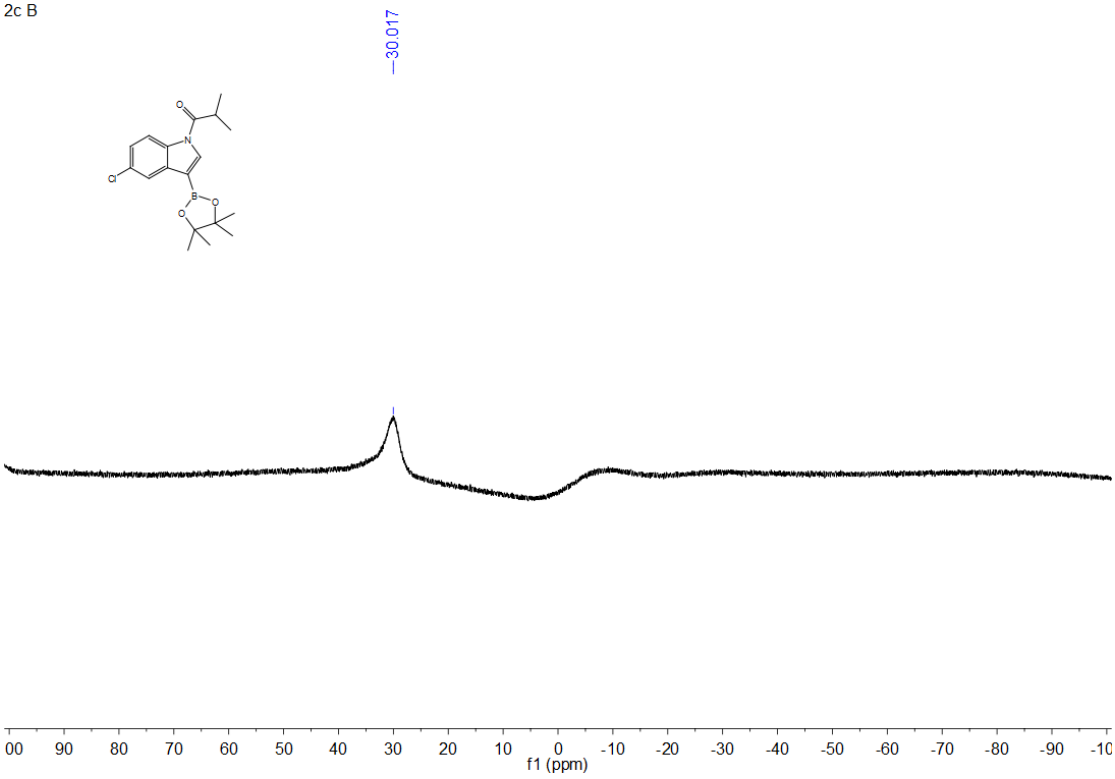
^{1}H NMR spectrum of 2c



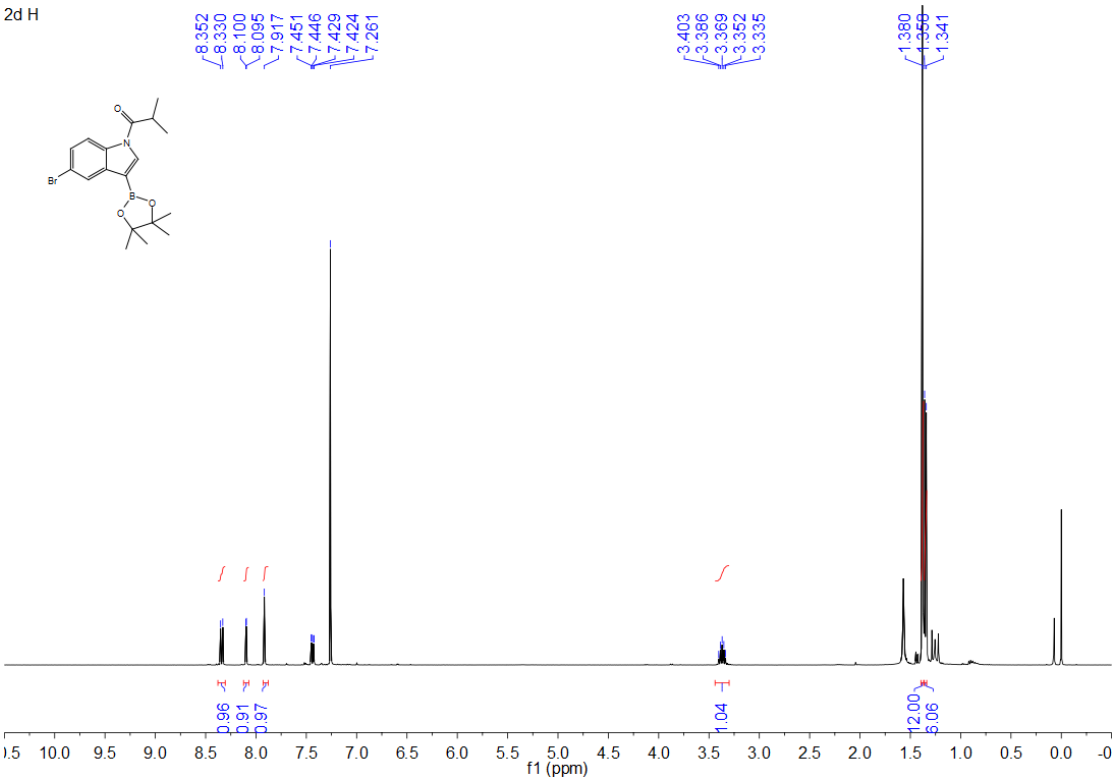
^{13}C NMR spectrum of 2c



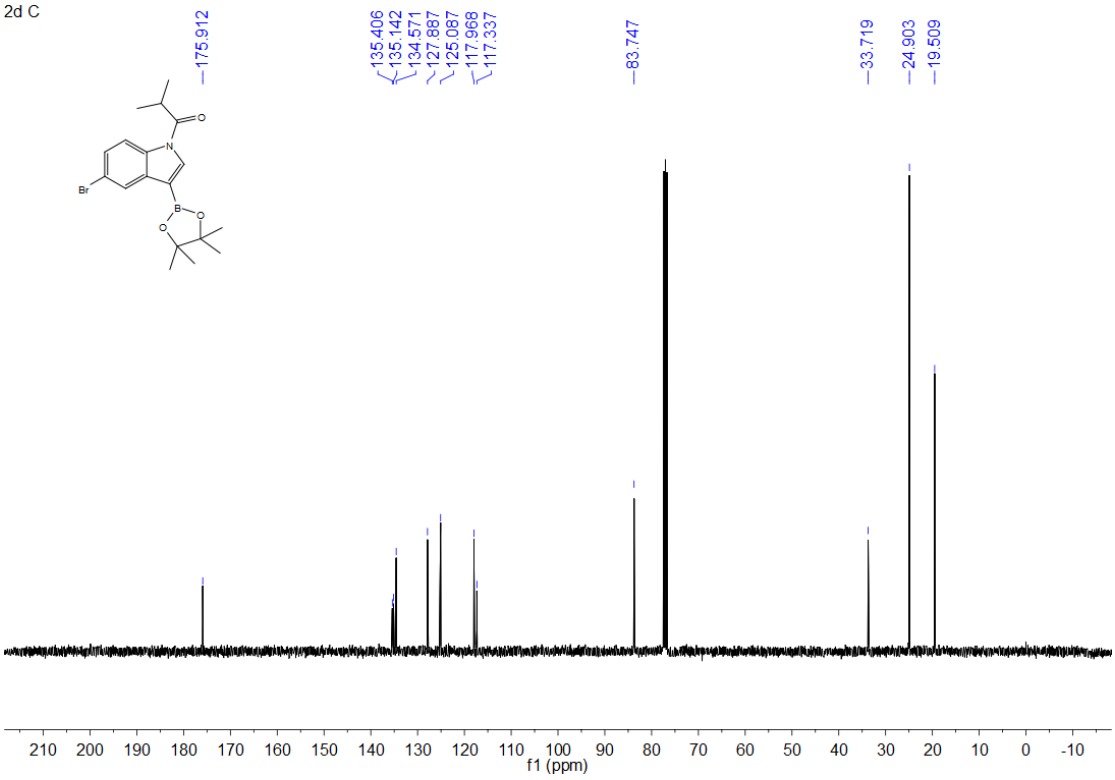
^{11}B NMR spectrum of 2c



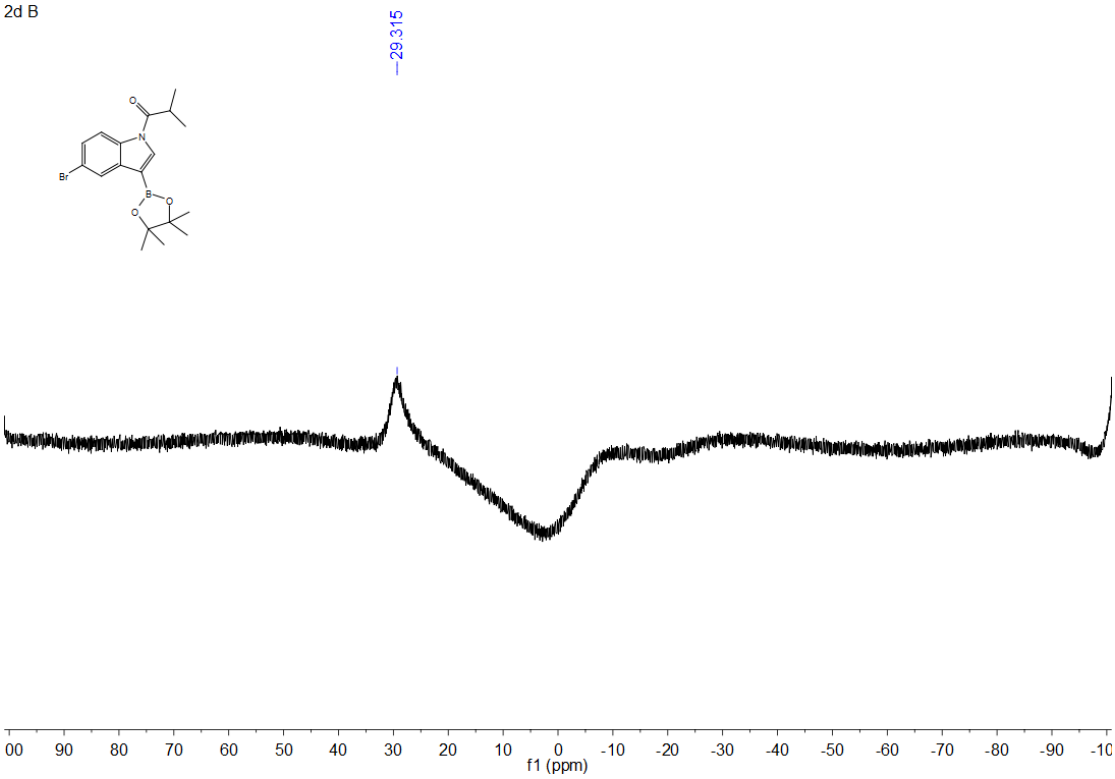
^{1}H NMR spectrum of 2d



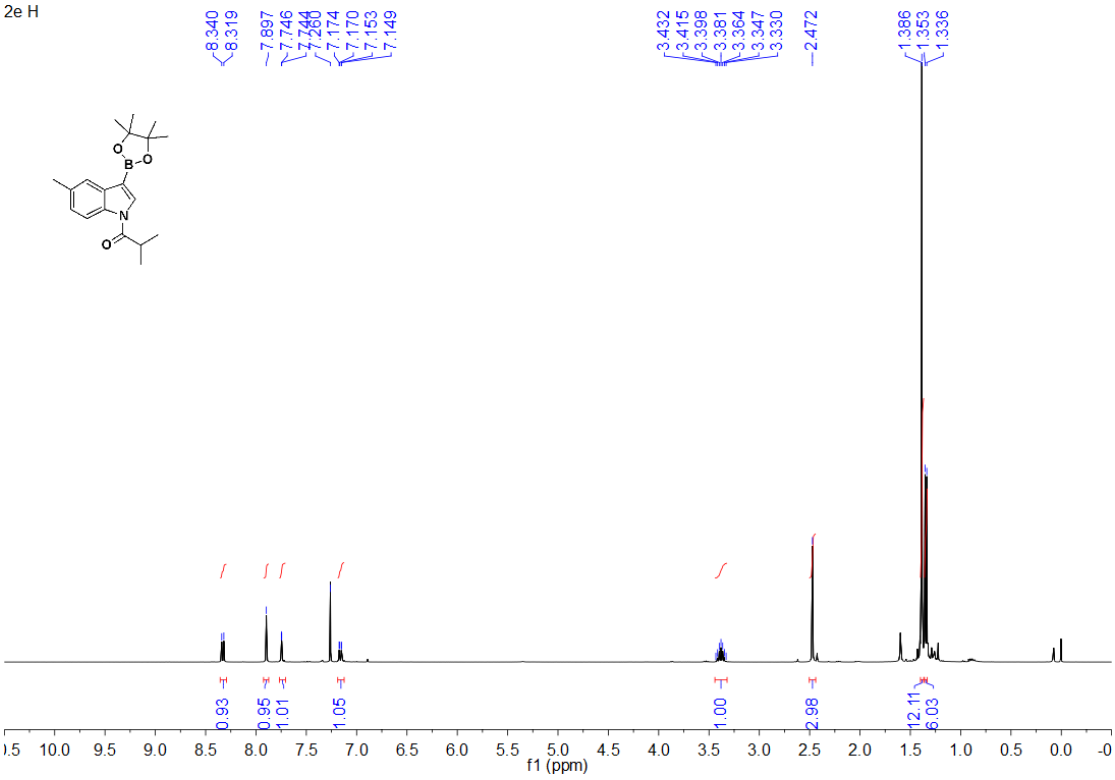
^{13}C NMR spectrum of 2d



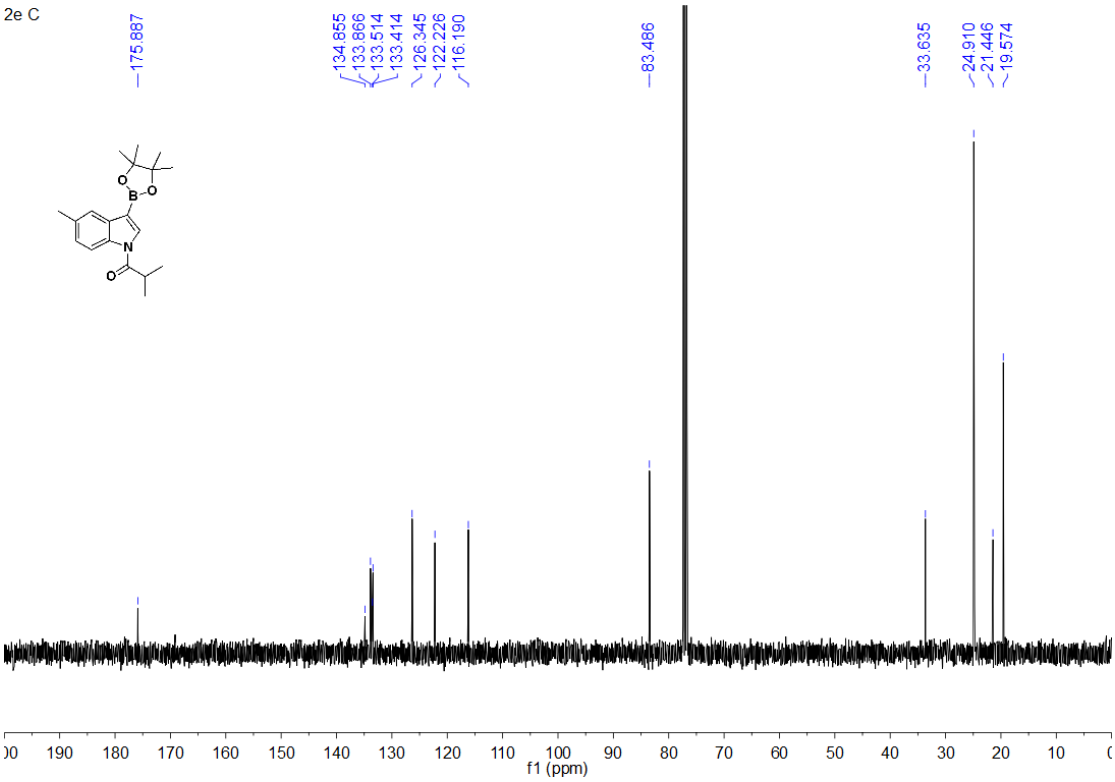
^{11}B NMR spectrum of 2d



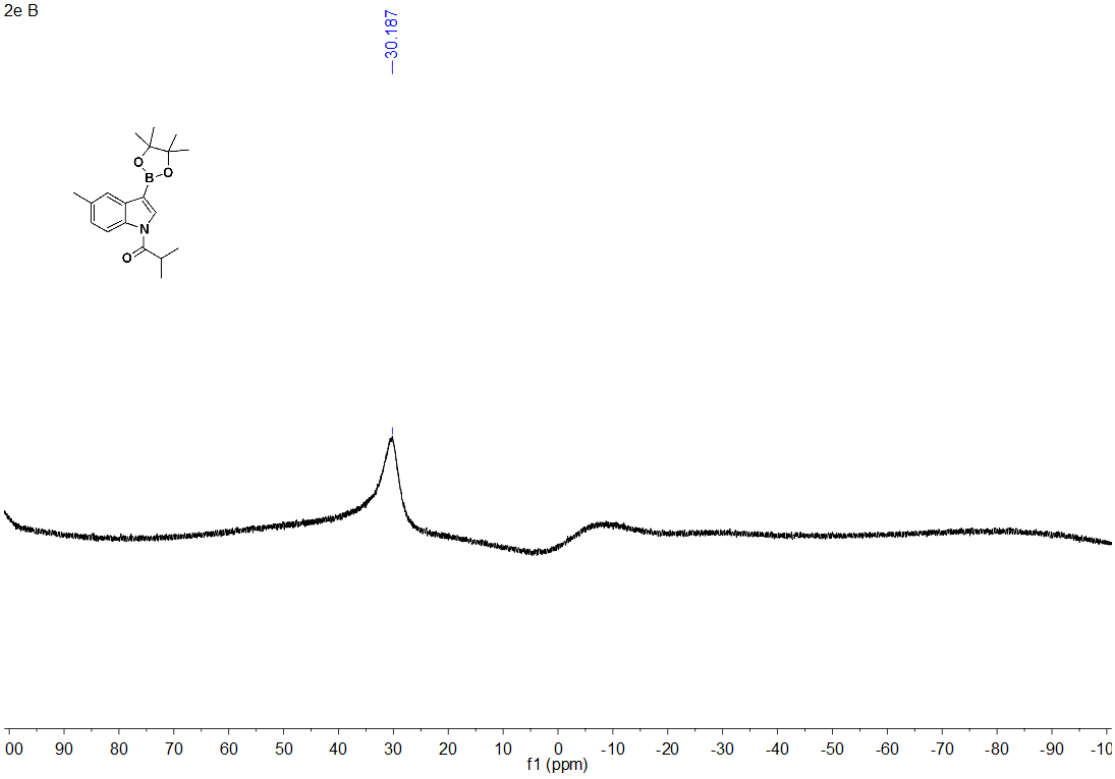
^{1}H NMR spectrum of 2e



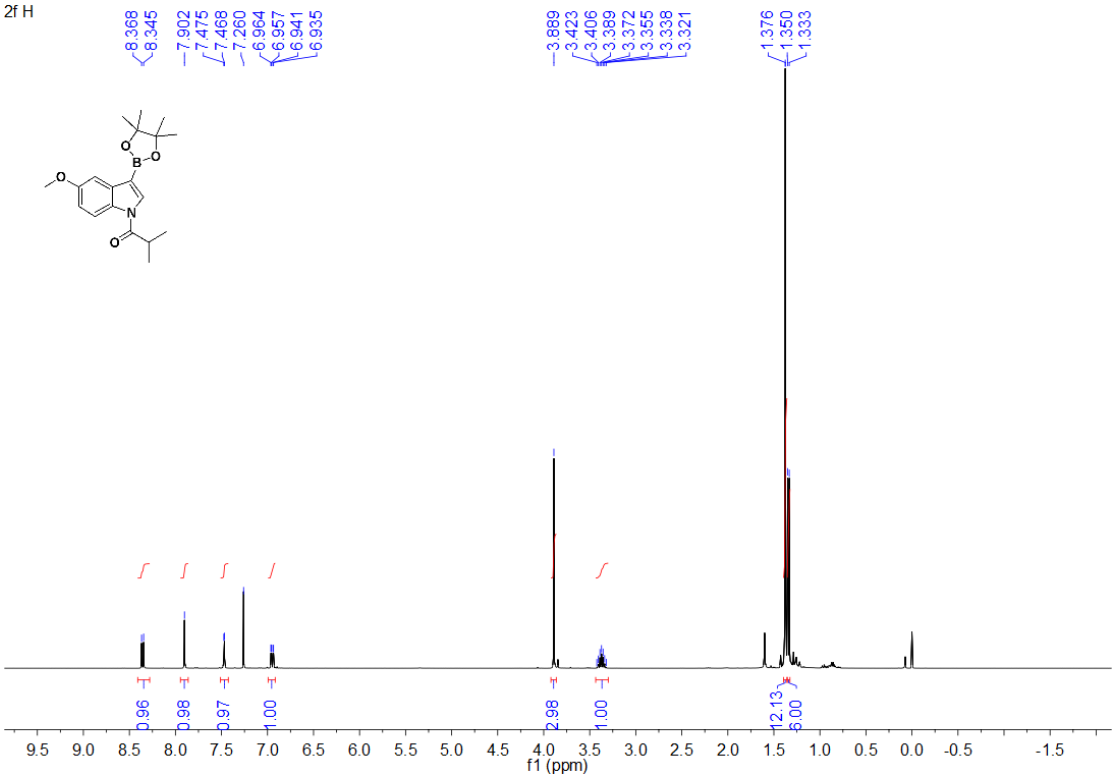
^{13}C NMR spectrum of 2e



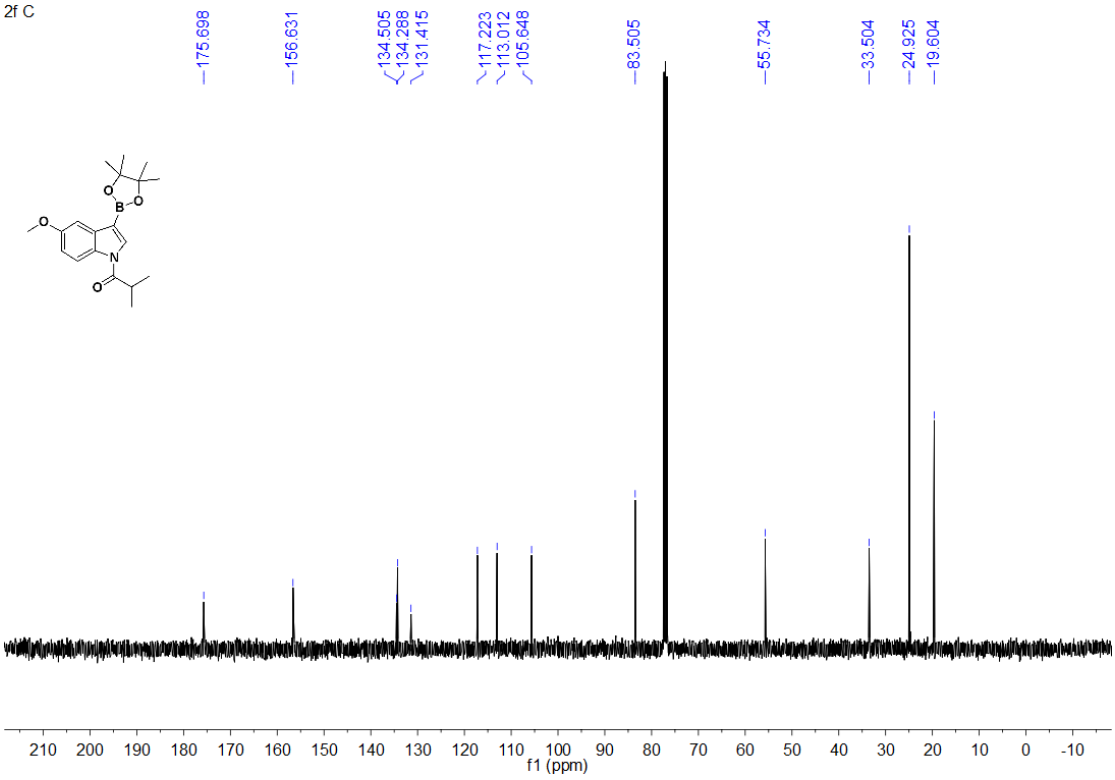
^{11}B NMR spectrum of 2e



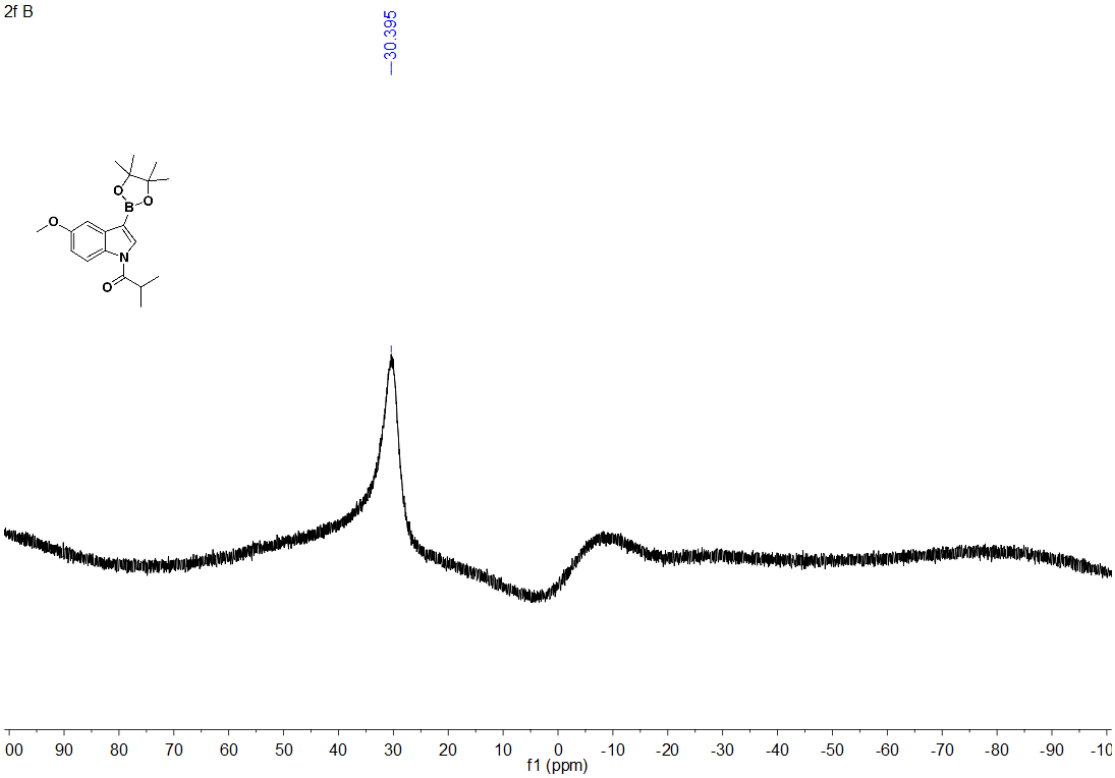
^{1}H NMR spectrum of 2f



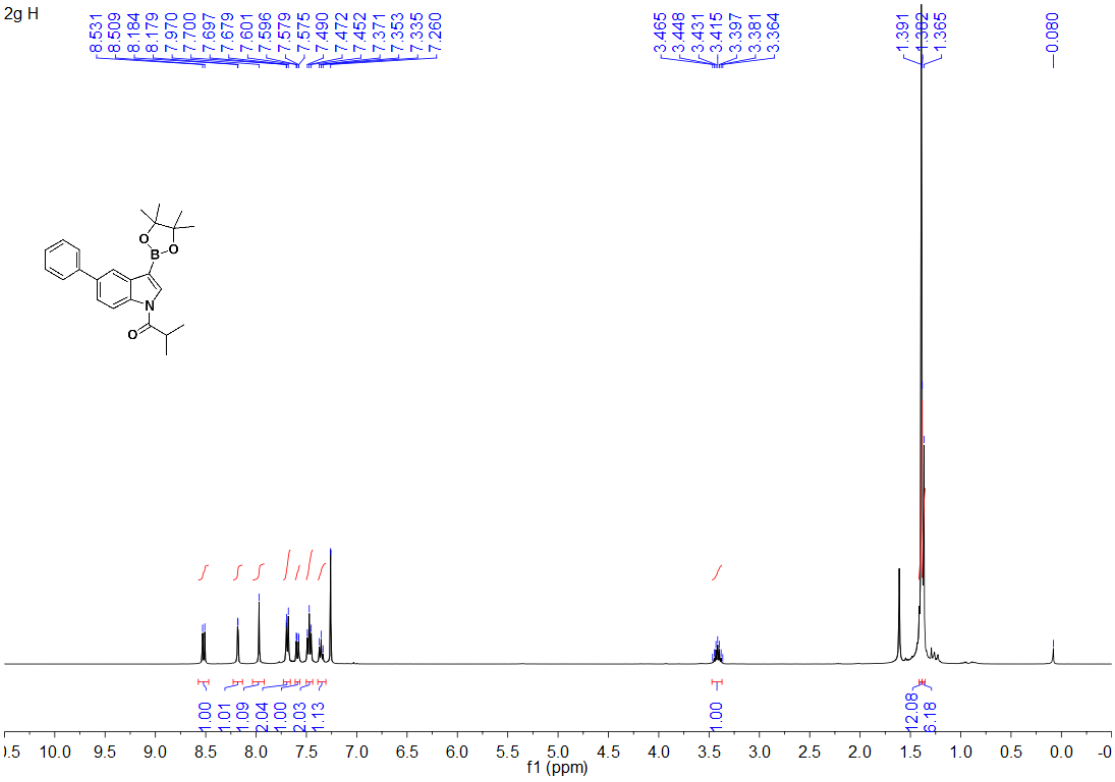
^{13}C NMR spectrum of 2f



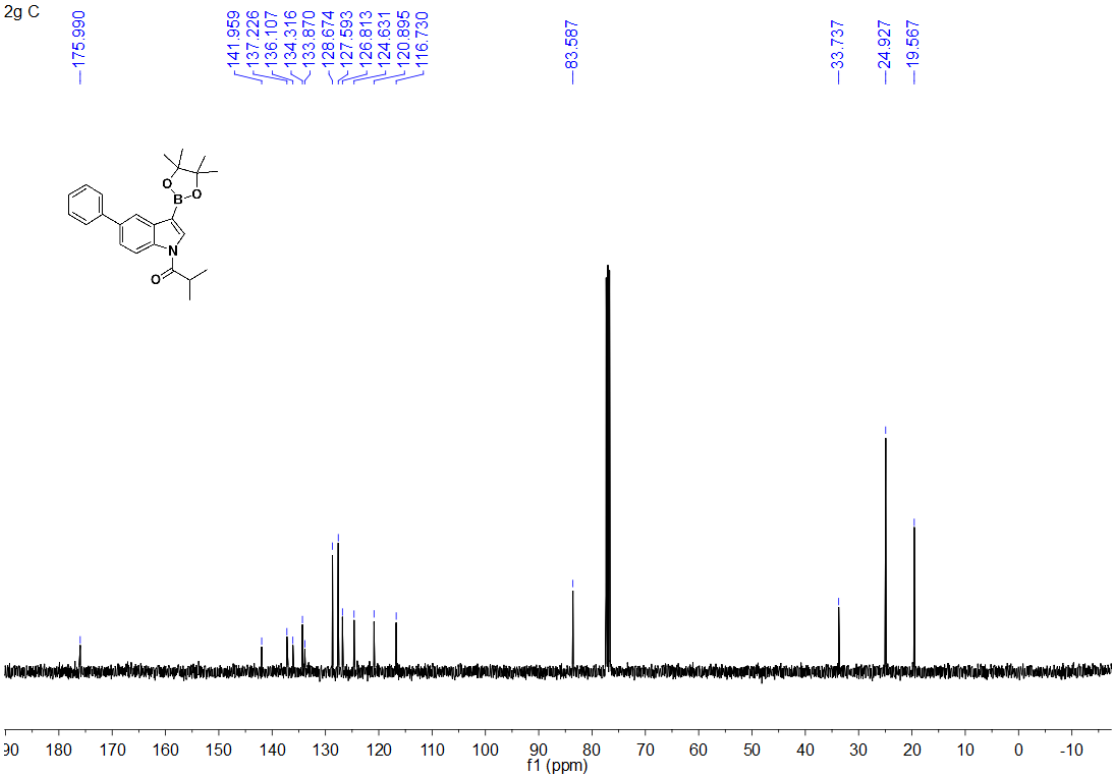
^{11}B NMR spectrum of 2f



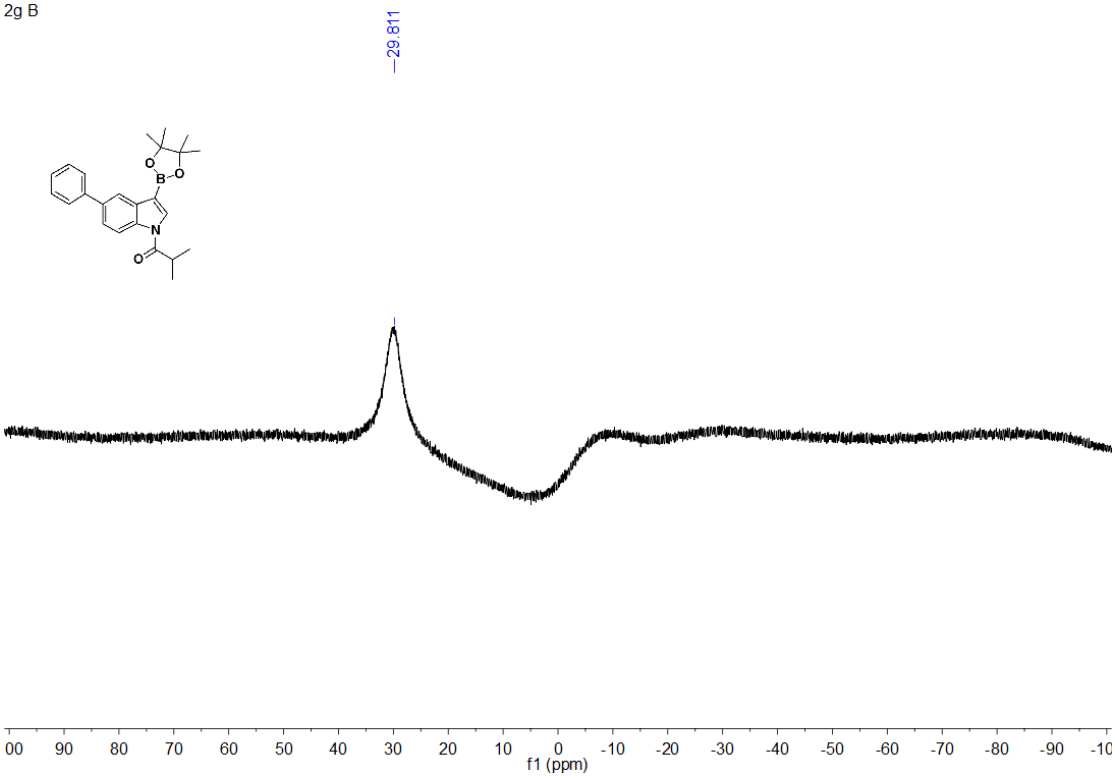
^{1}H NMR spectrum of 2g



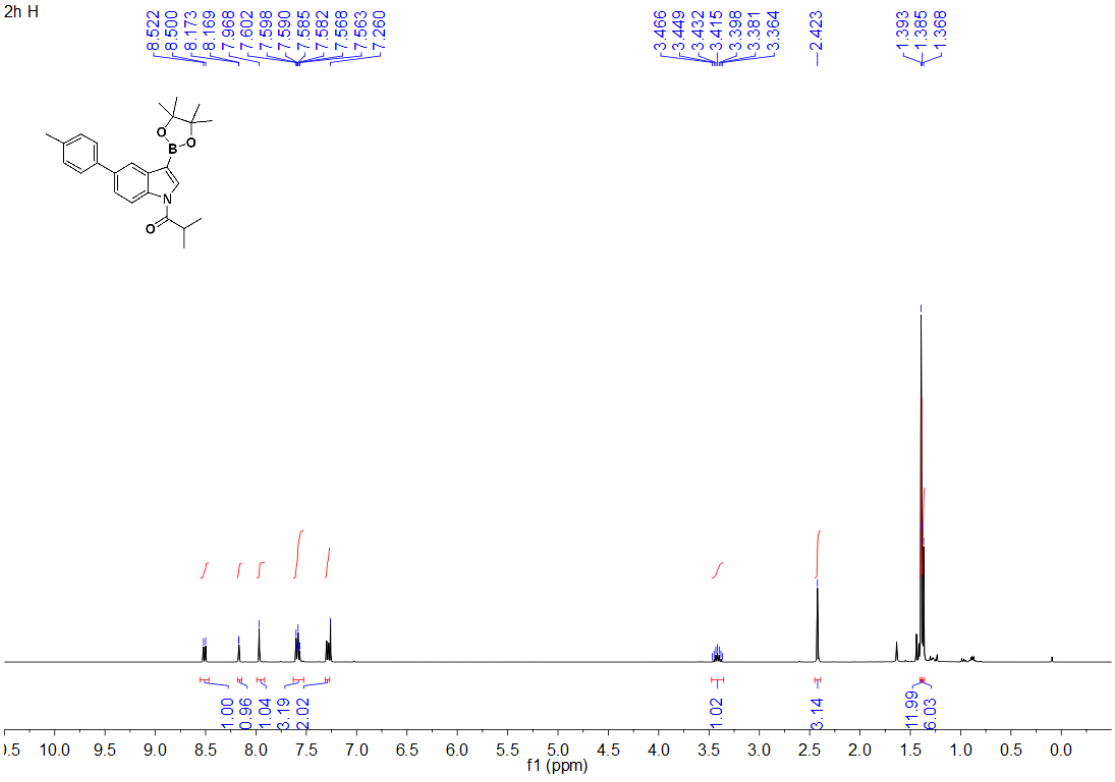
^{13}C NMR spectrum of 2g



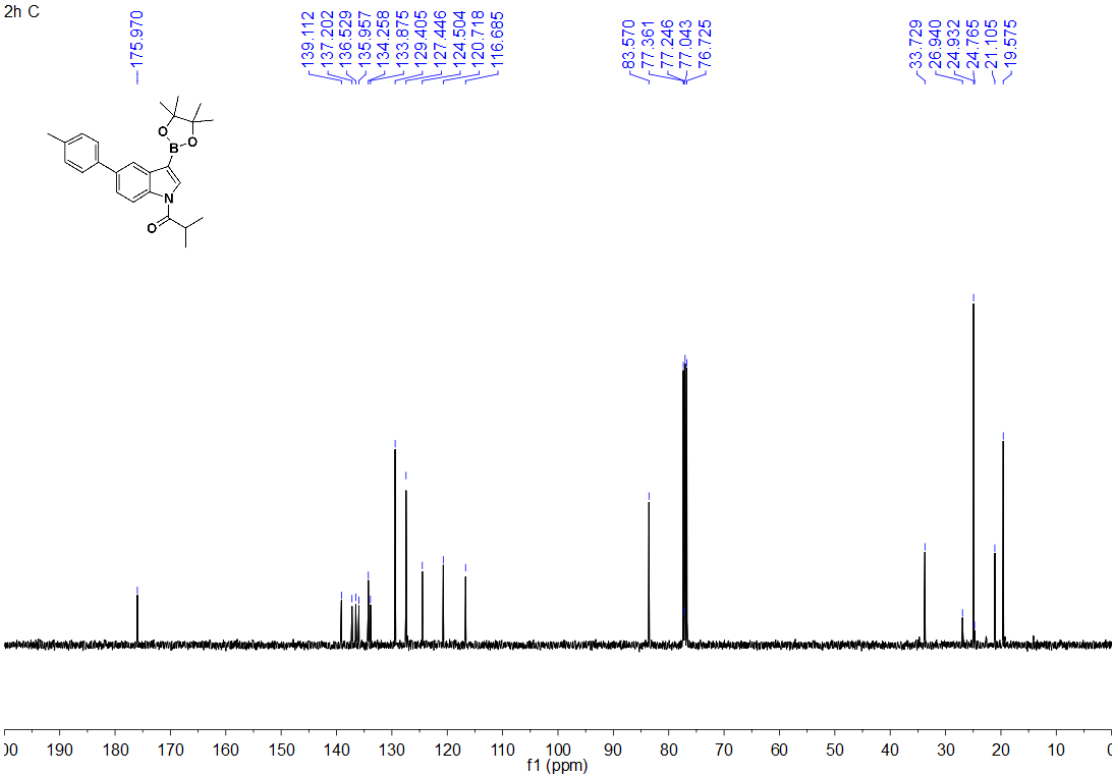
^{11}B NMR spectrum of 2g



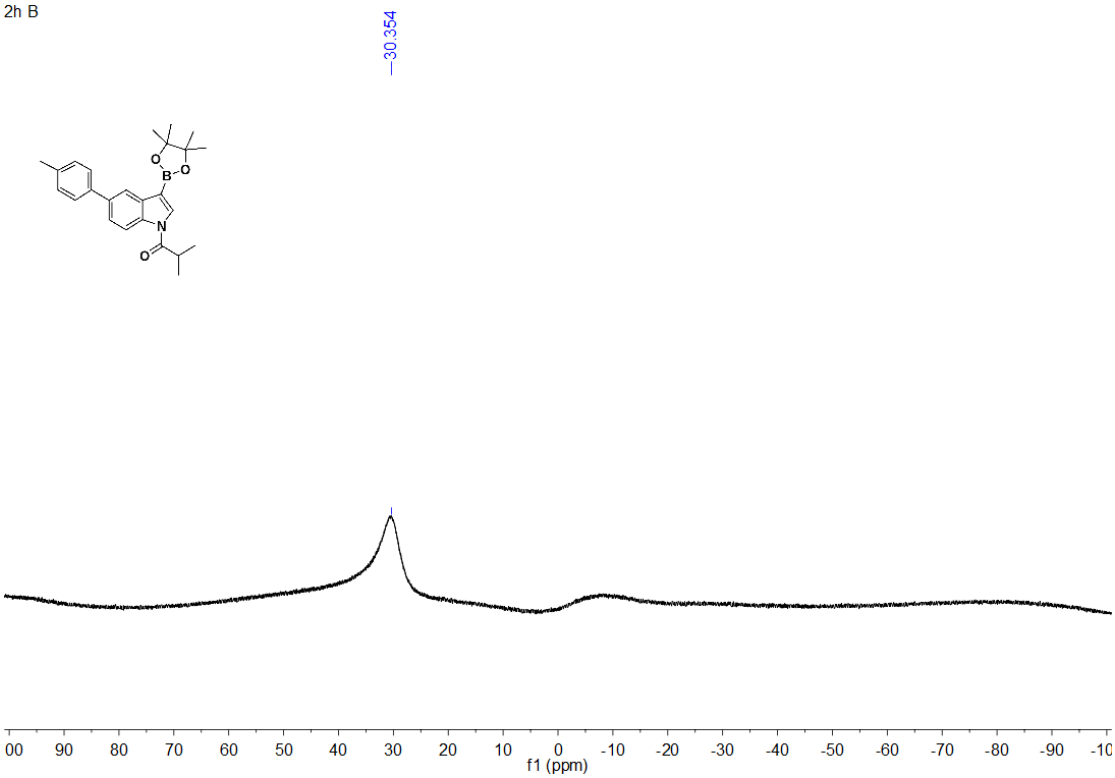
^{1}H NMR spectrum of 2h



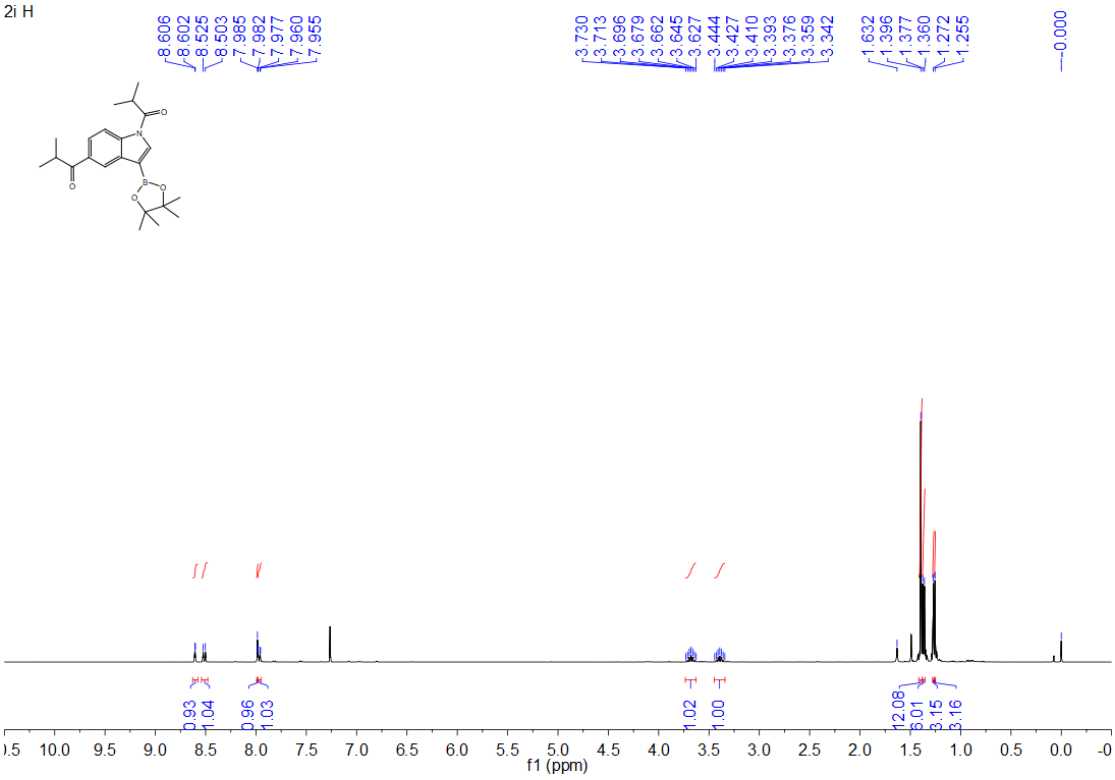
^{13}C NMR spectrum of 2h



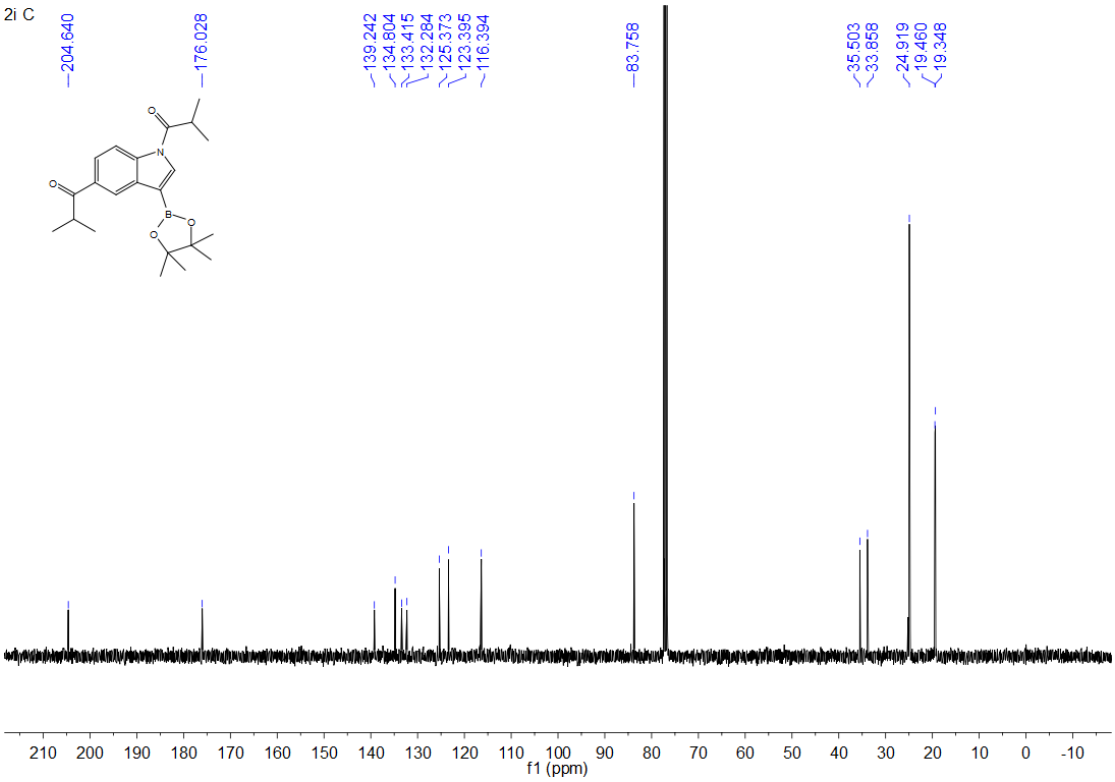
^{11}B NMR spectrum of 2h



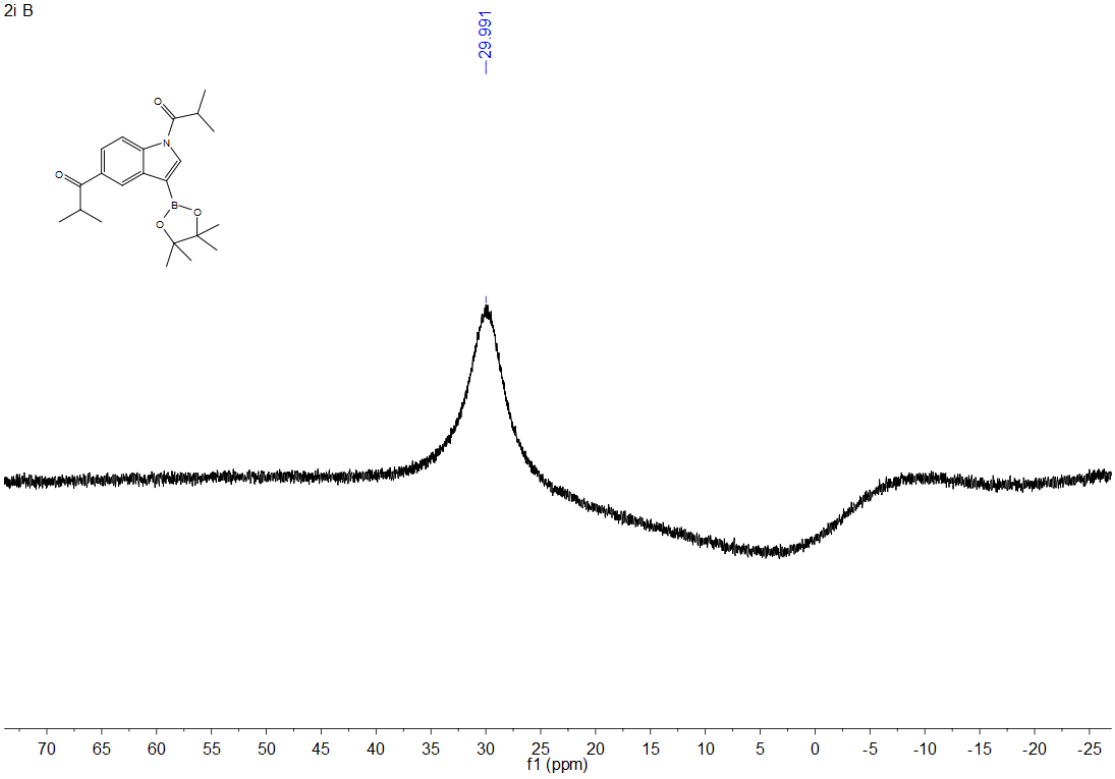
^{1}H NMR spectrum of 2i



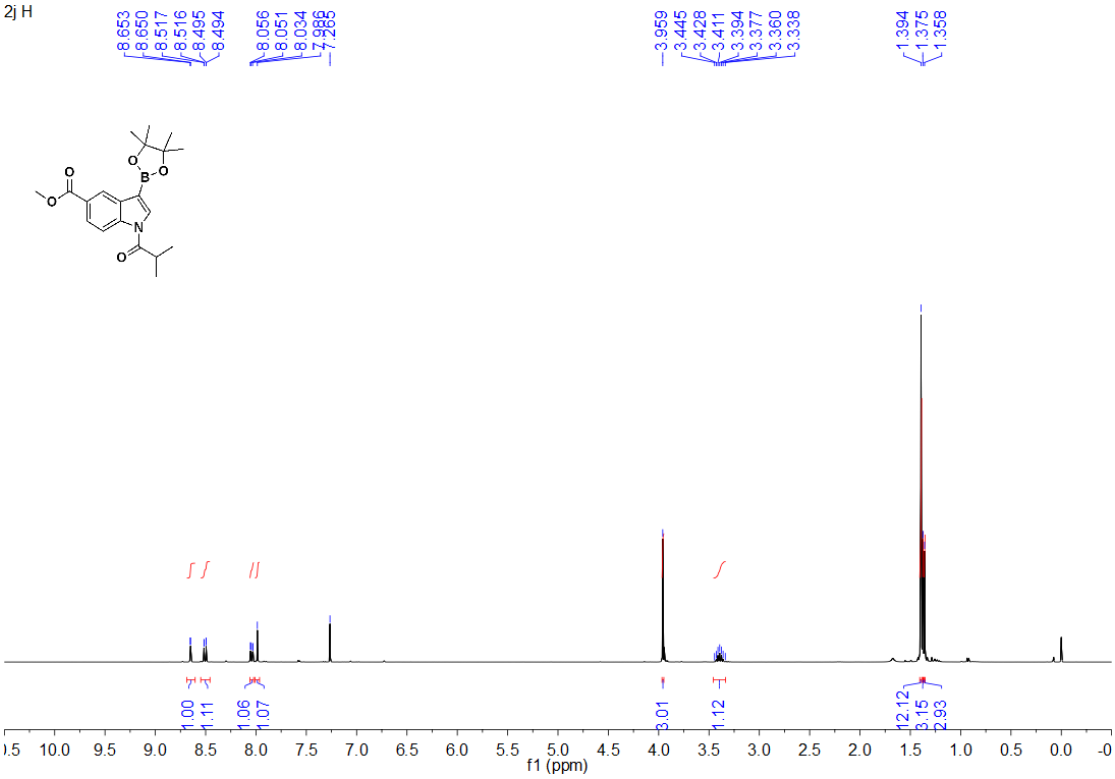
^{13}C NMR spectrum of 2i



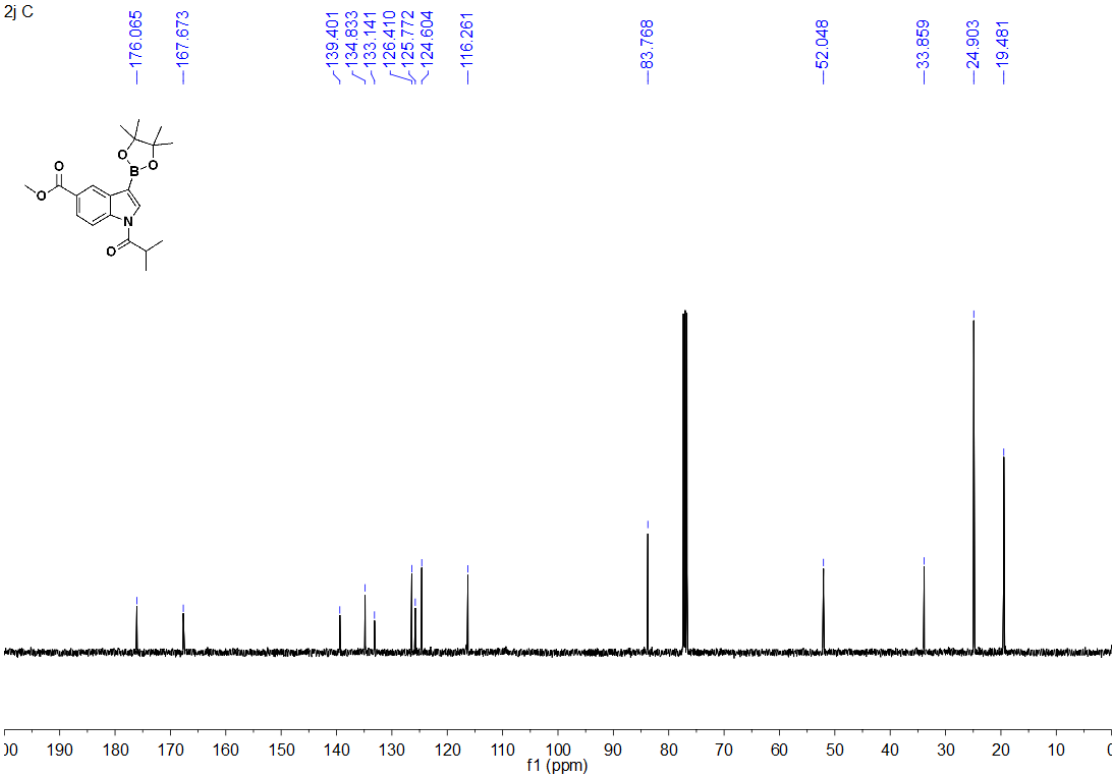
^{11}B NMR spectrum of 2i



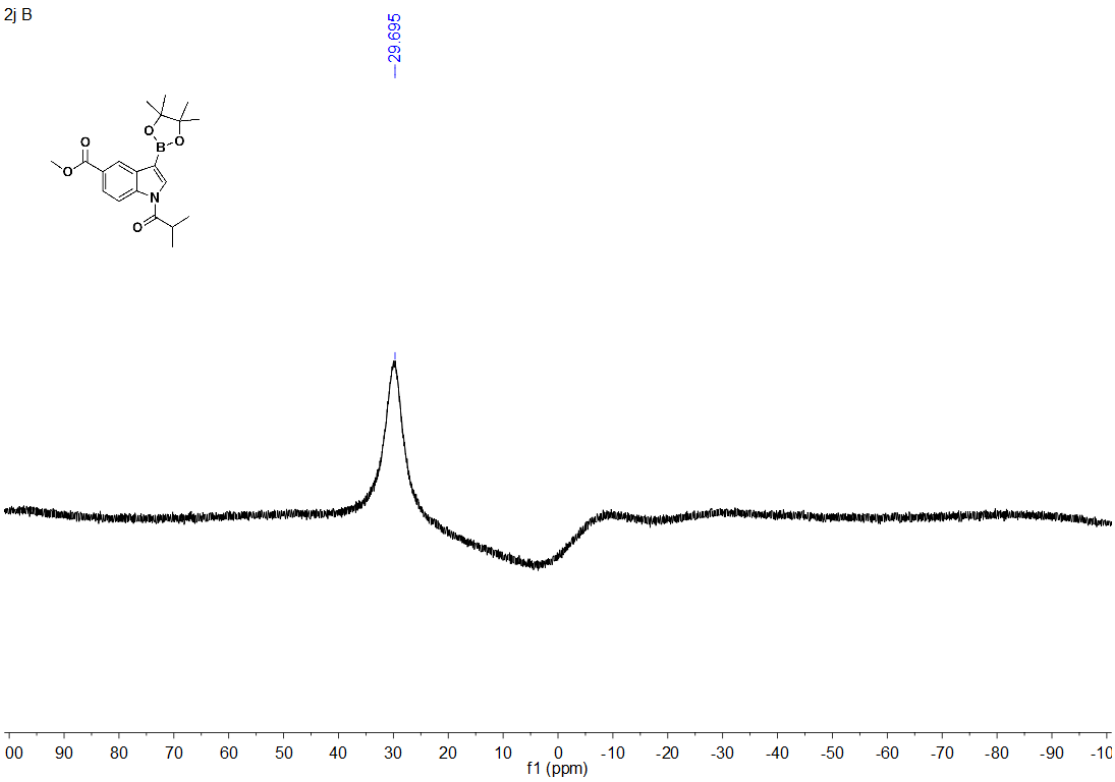
^{1}H NMR spectrum of 2j



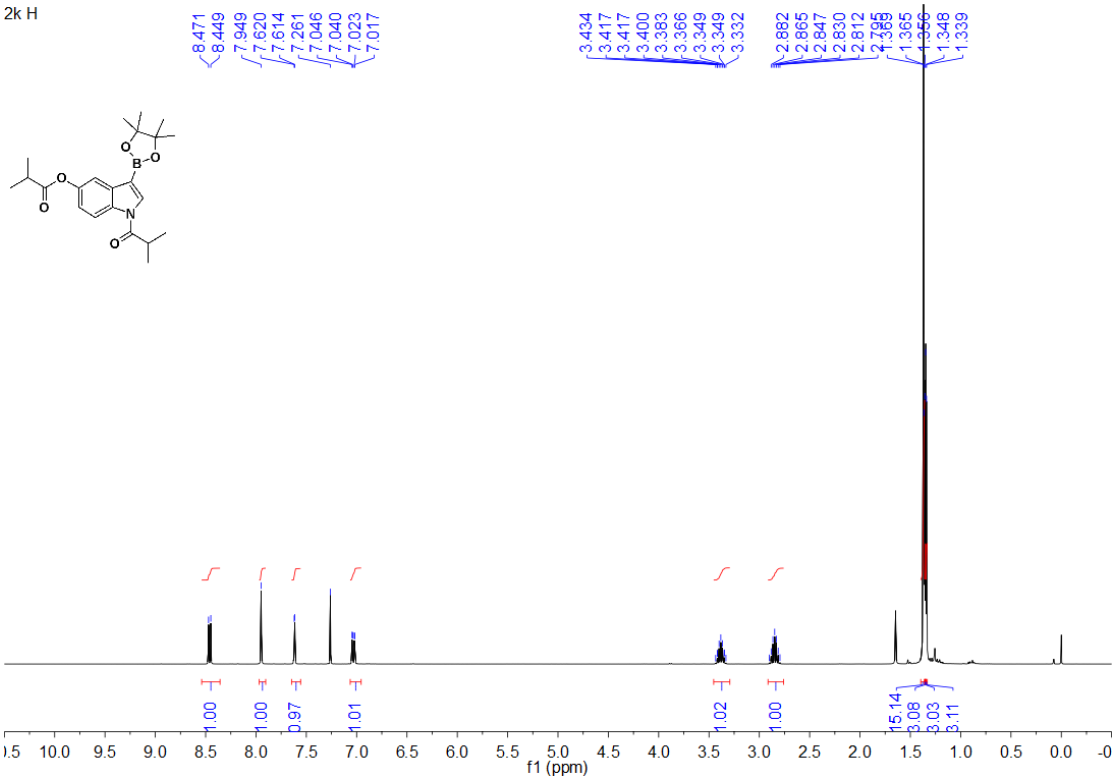
^{13}C NMR spectrum of 2j



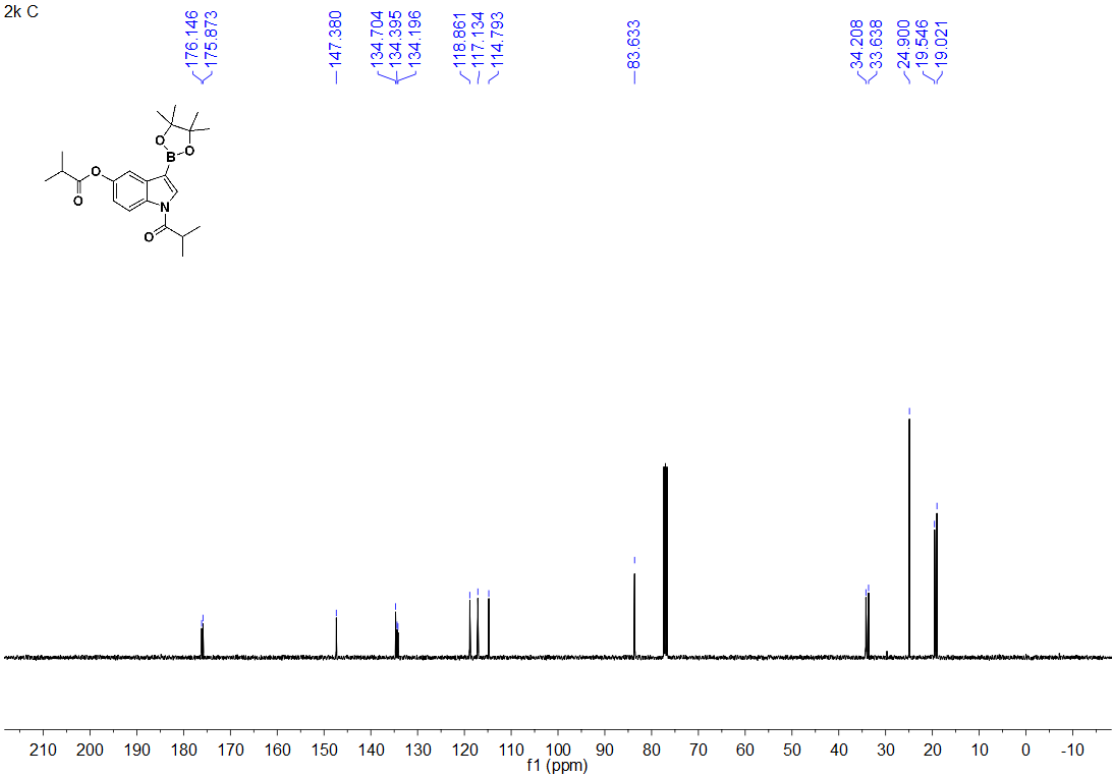
^{11}B NMR spectrum of 2j



^{1}H NMR spectrum of 2k

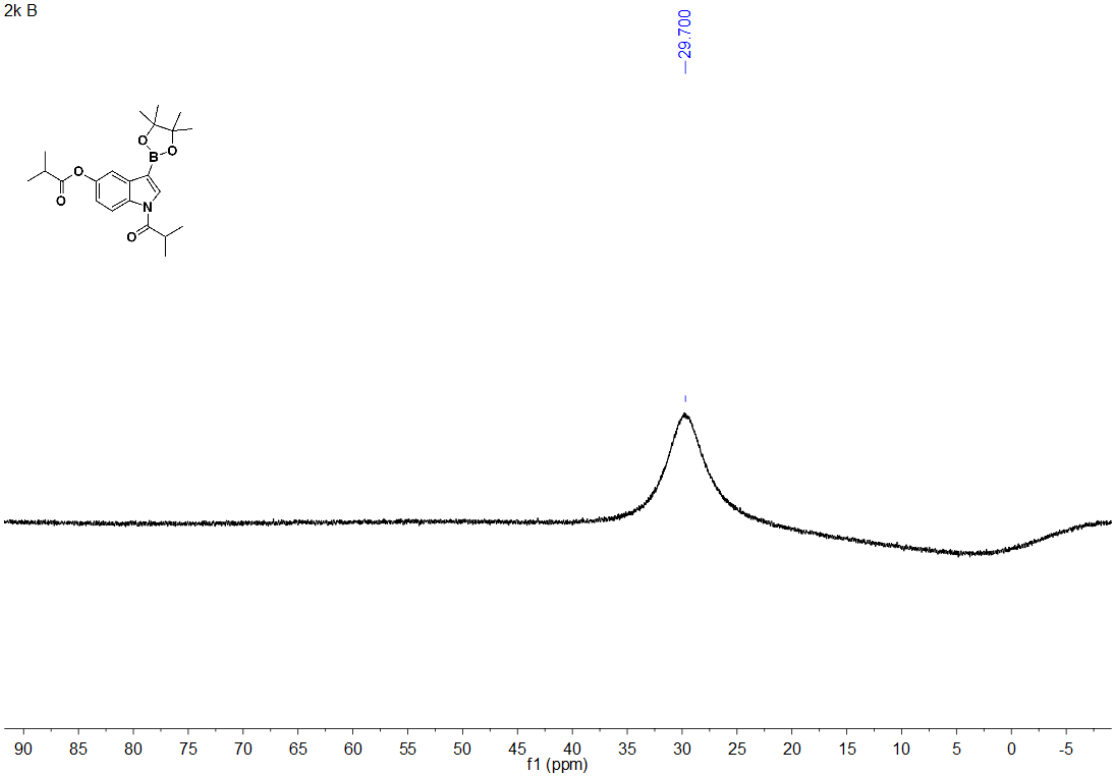


^{13}C NMR spectrum of 2k



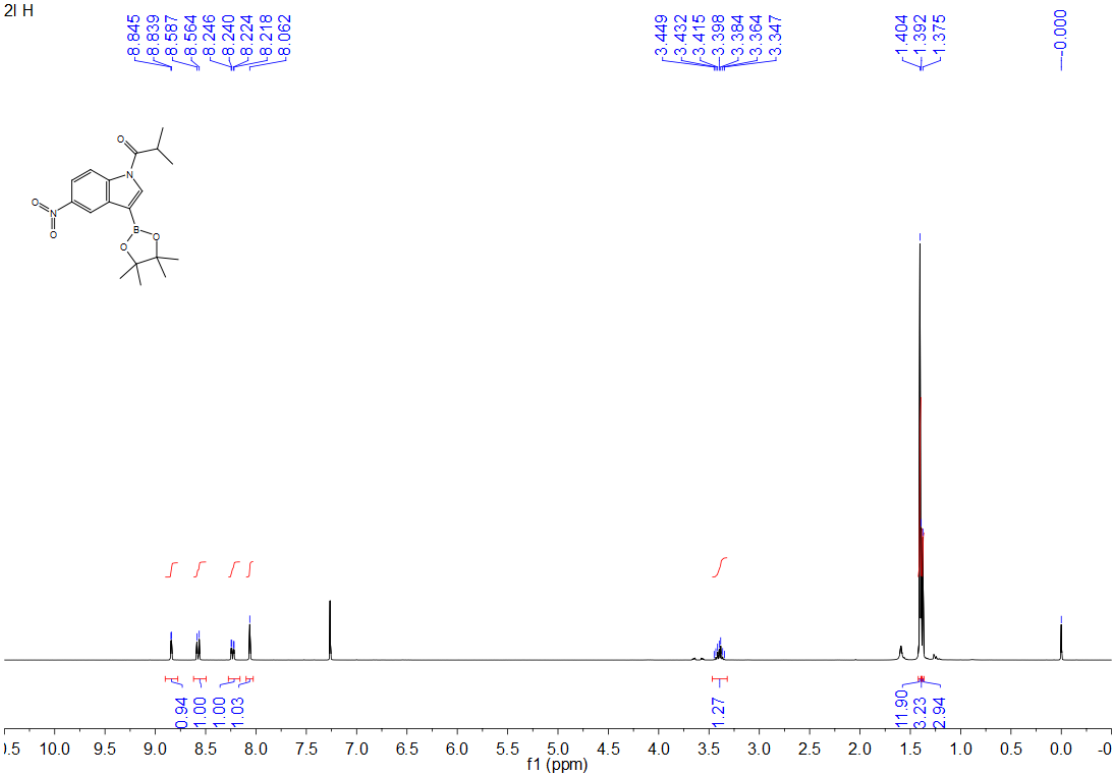
^{11}B NMR spectrum of 2k

2k B

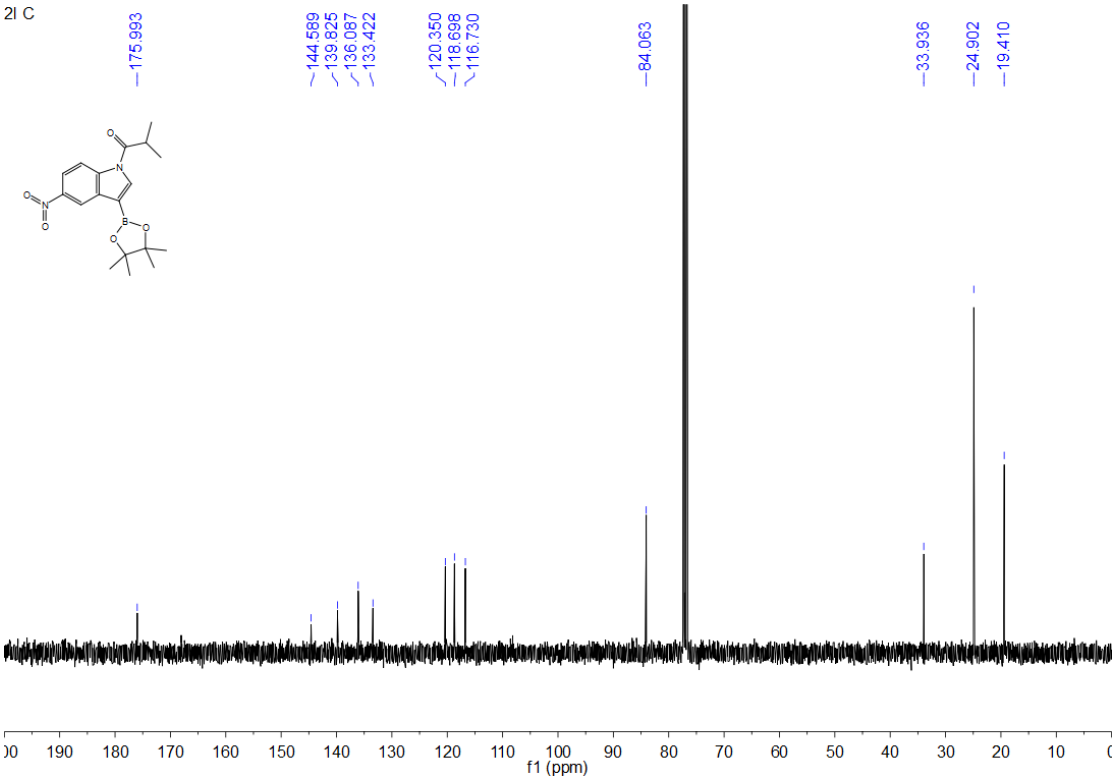


^{1}H NMR spectrum of 2l

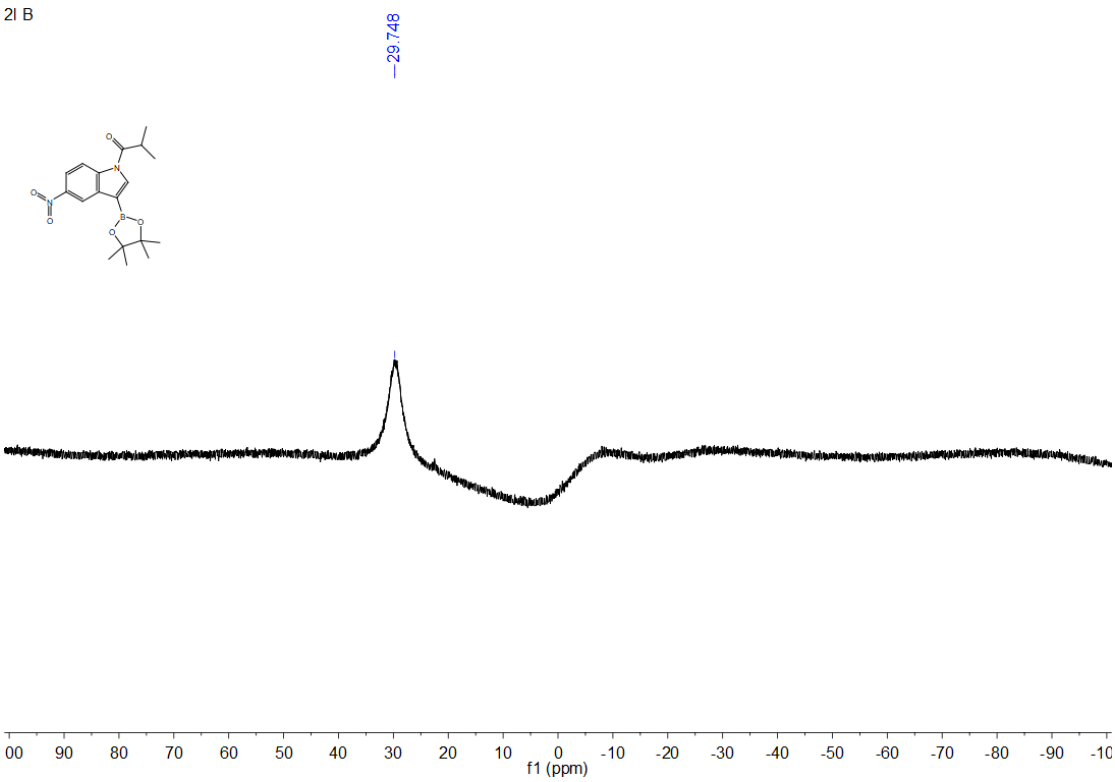
2l H



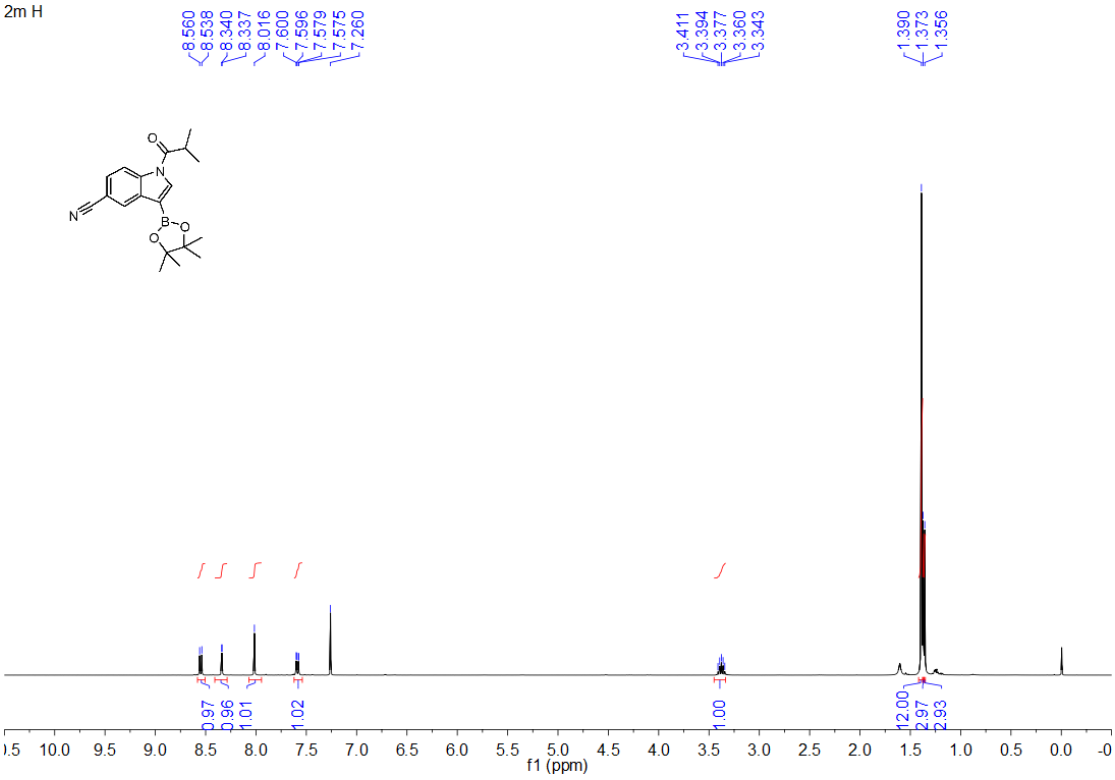
^{13}C NMR spectrum of 2l



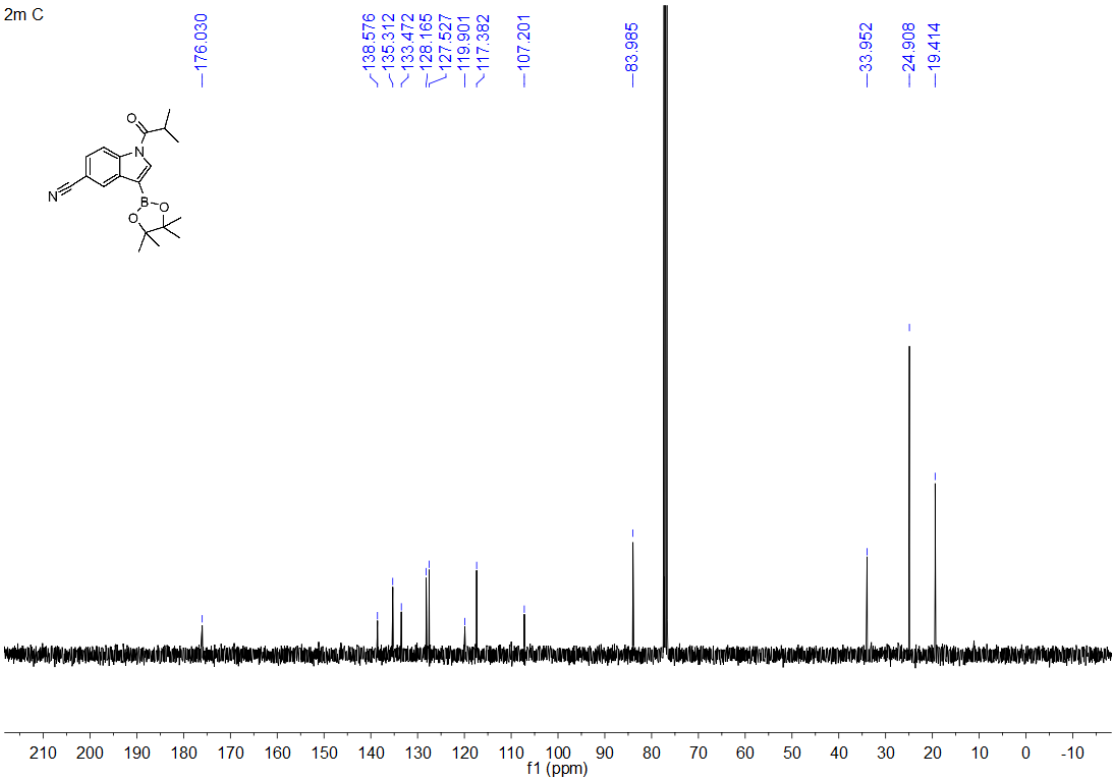
^{11}B NMR spectrum of 2l



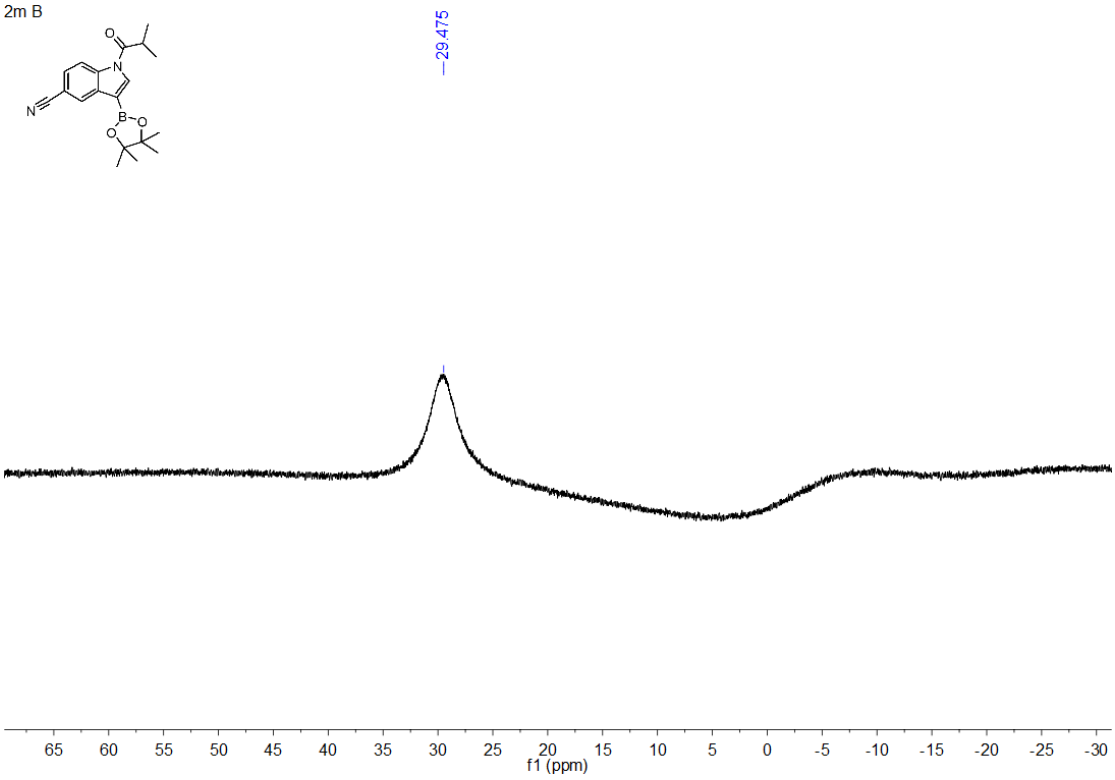
^{1}H NMR spectrum of 2m



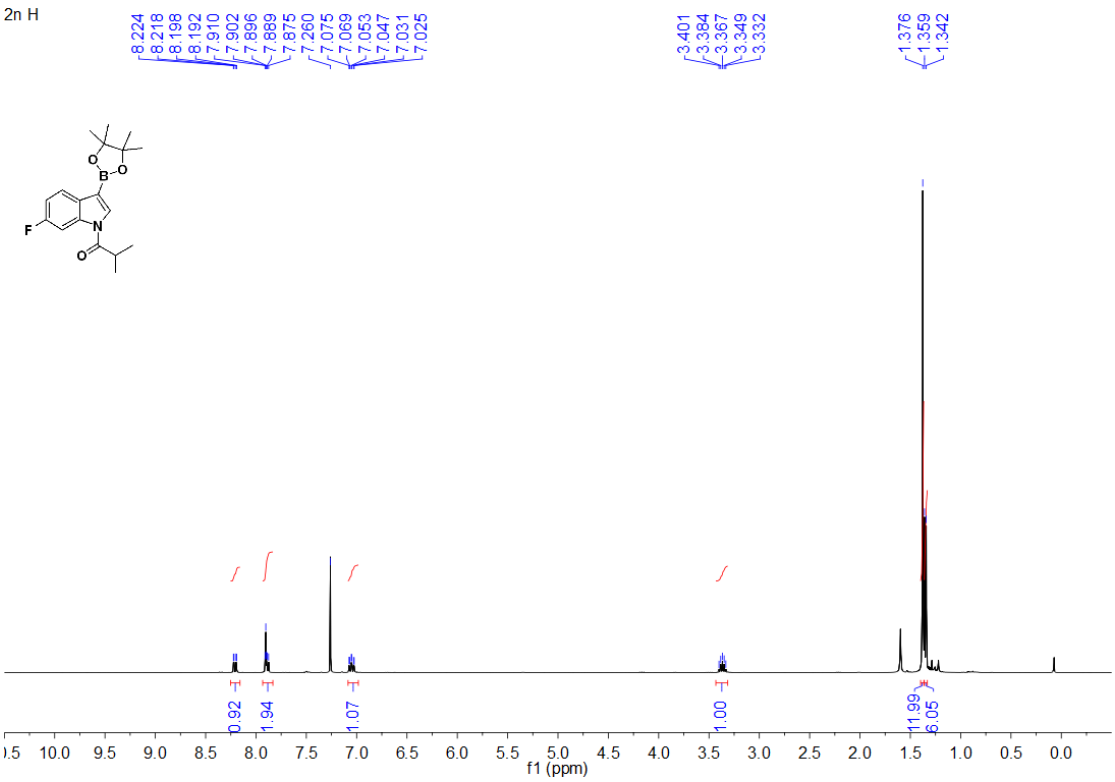
^{13}C NMR spectrum of 2m



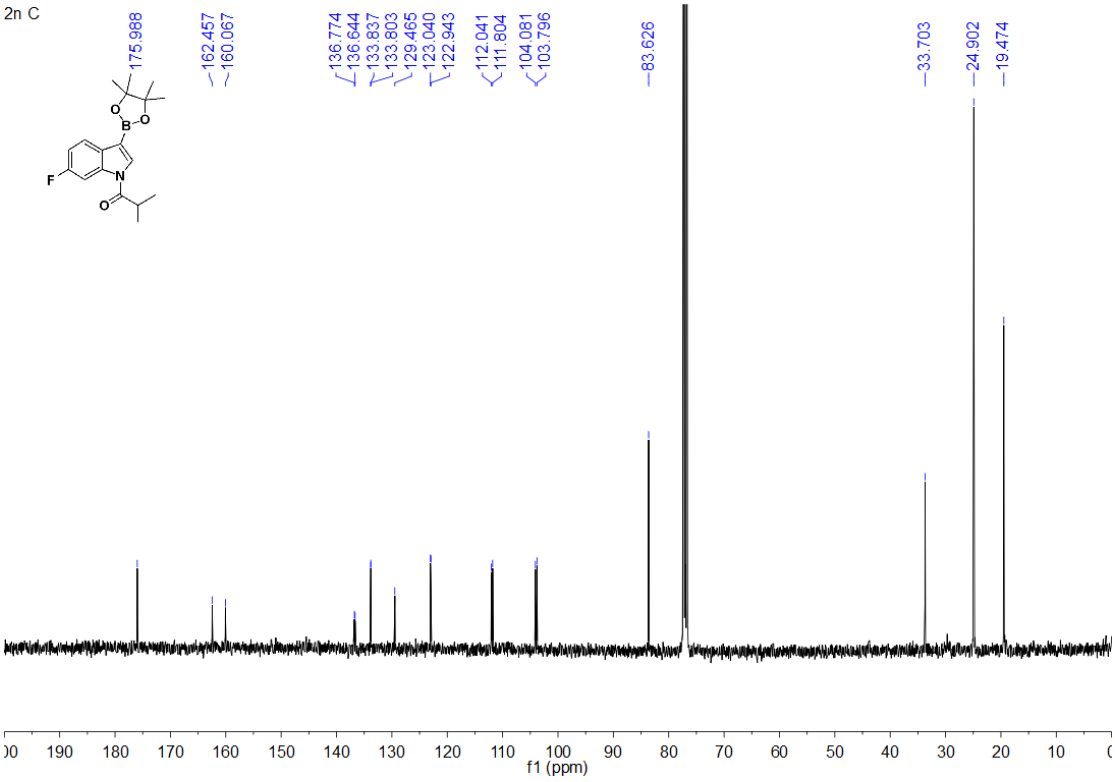
^{11}B NMR spectrum of 2m



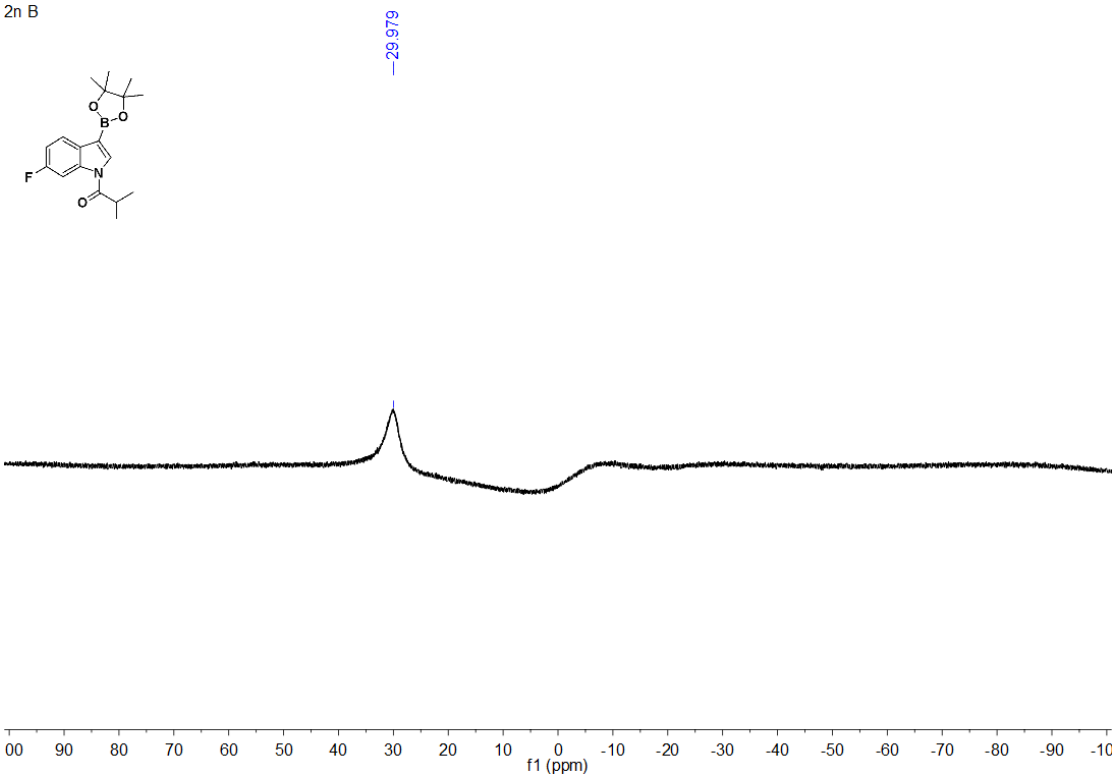
^{1}H NMR spectrum of 2n



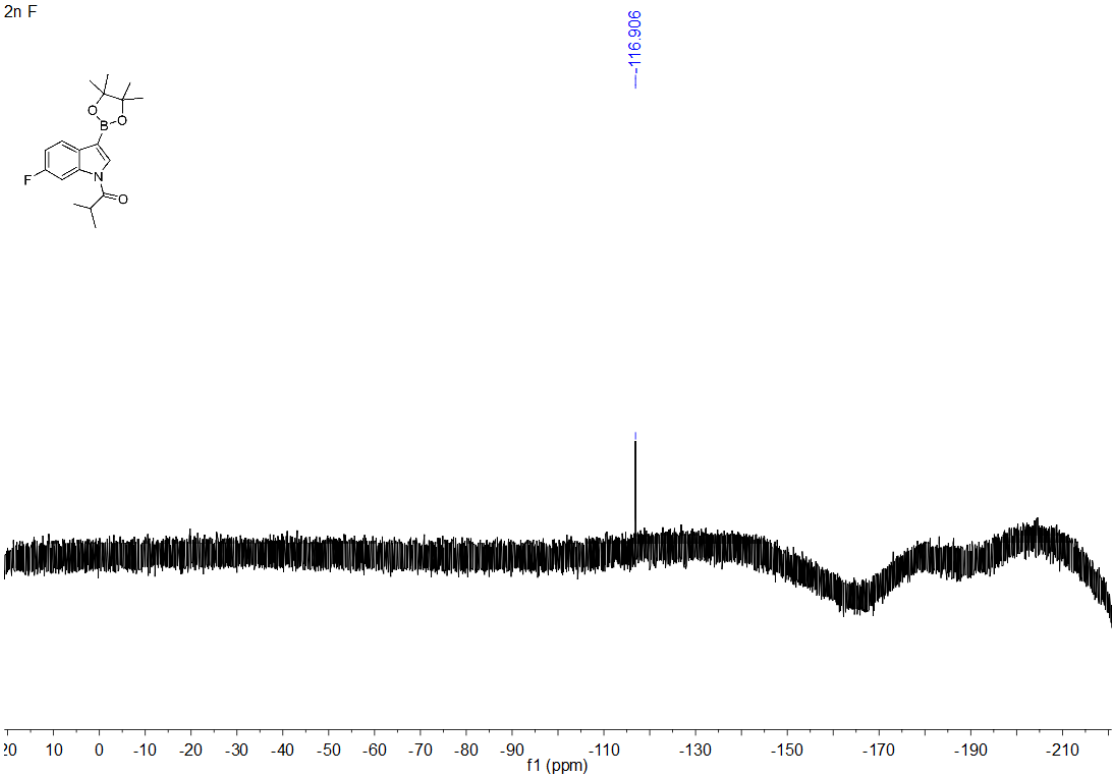
^{13}C NMR spectrum of 2n



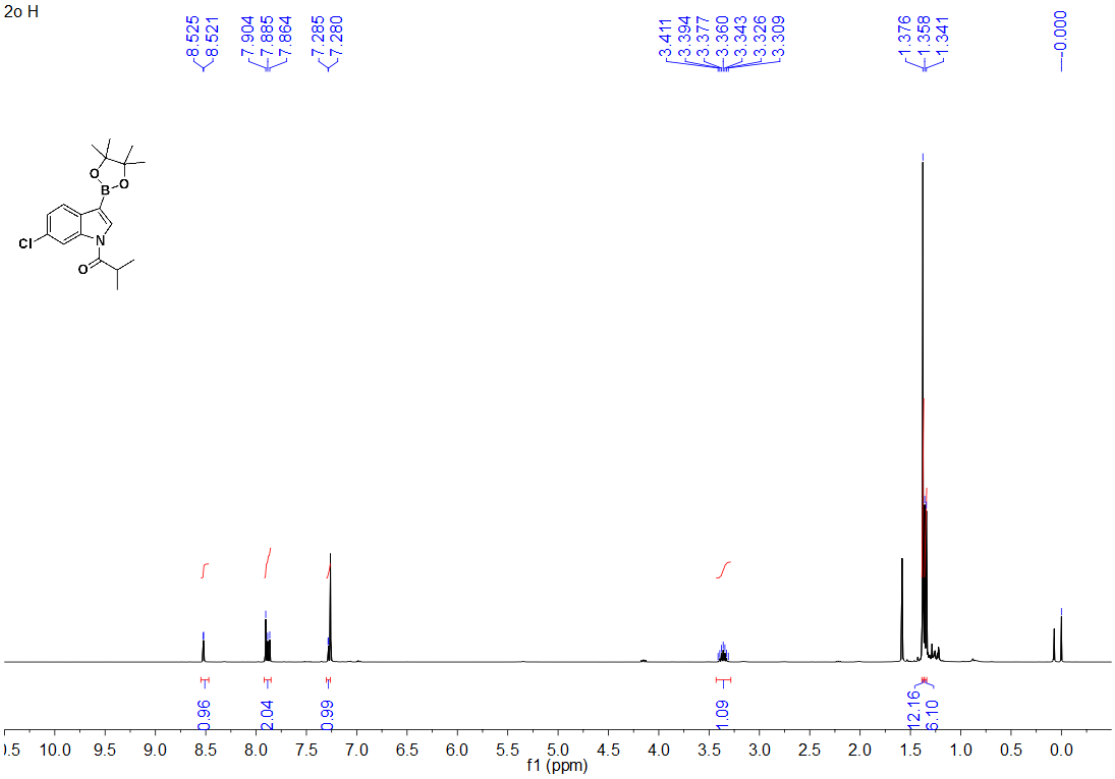
^{11}B NMR spectrum of 2n



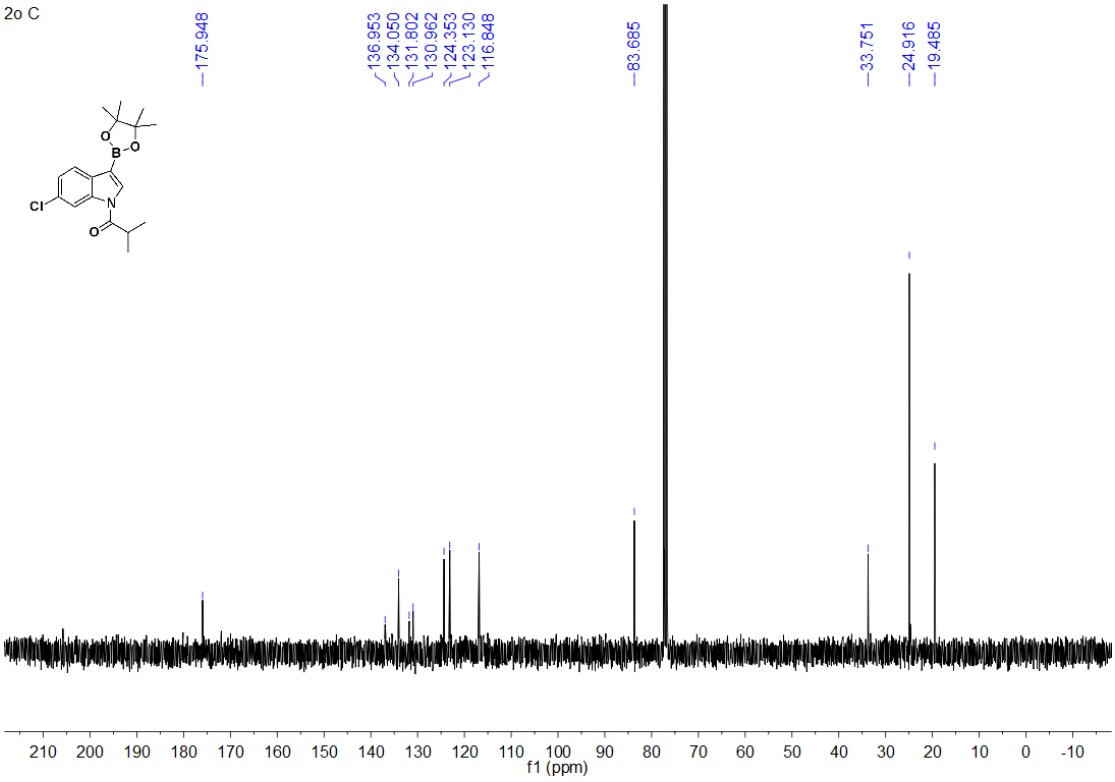
^{19}F NMR spectrum of 2n



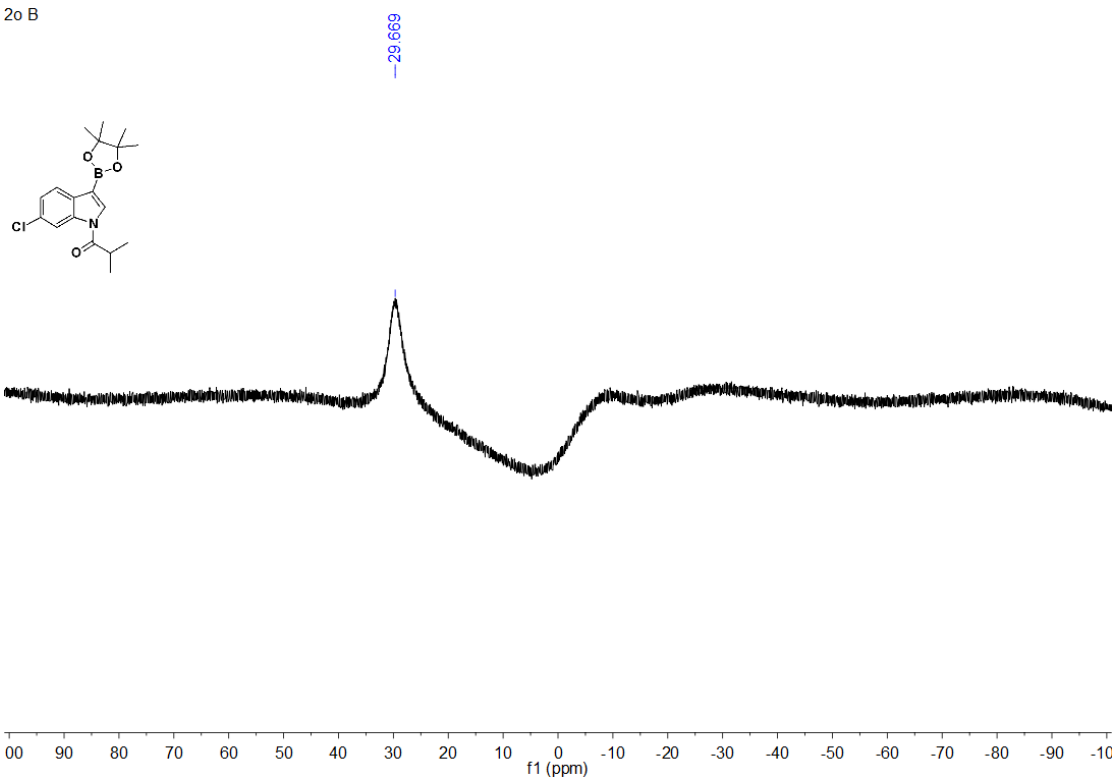
^{1}H NMR spectrum of 2o



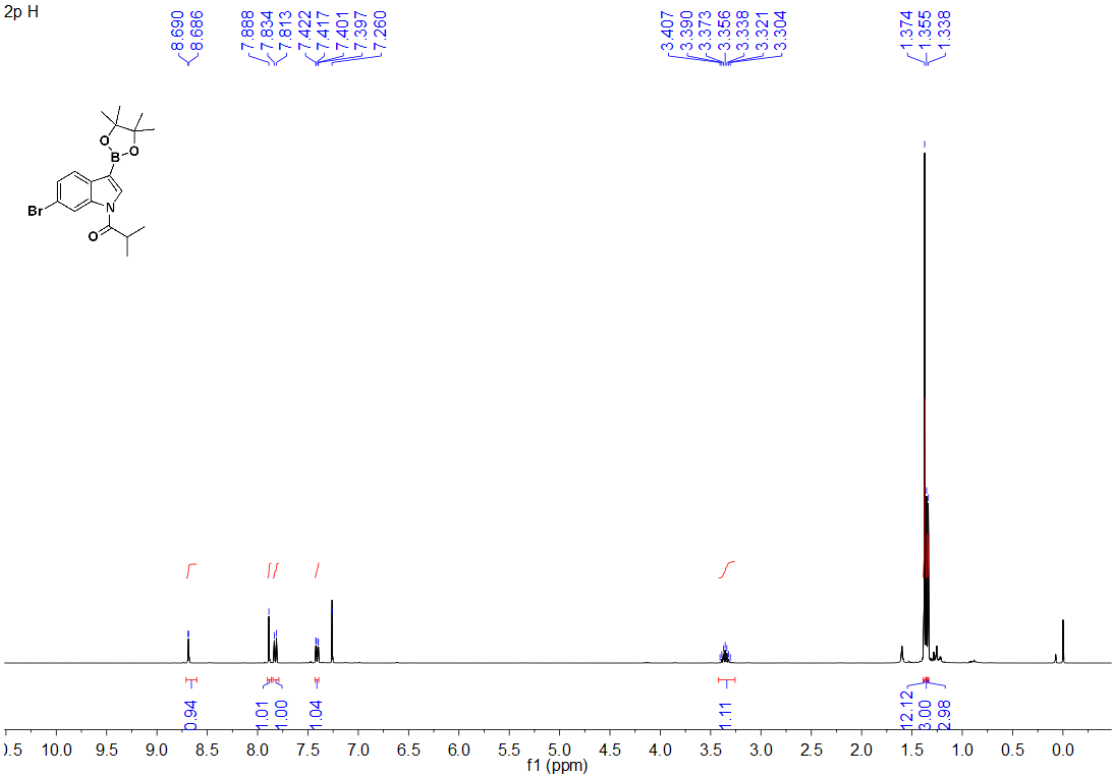
^{13}C NMR spectrum of 2o



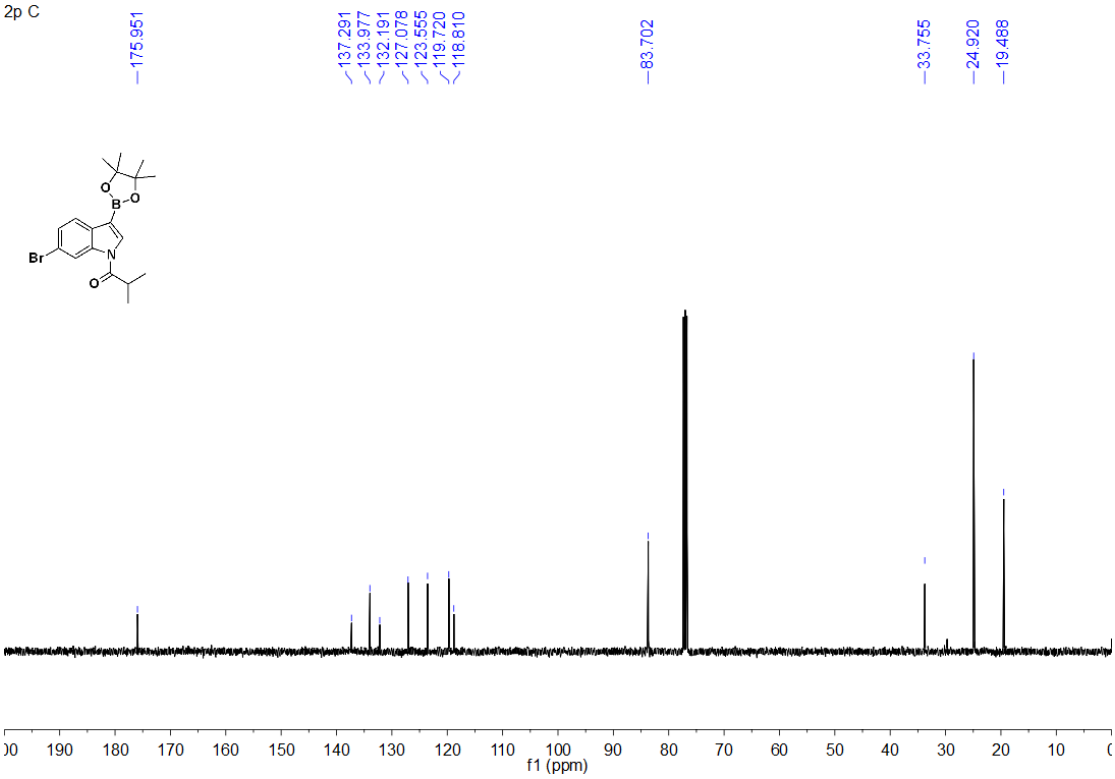
^{11}B NMR spectrum of 2o



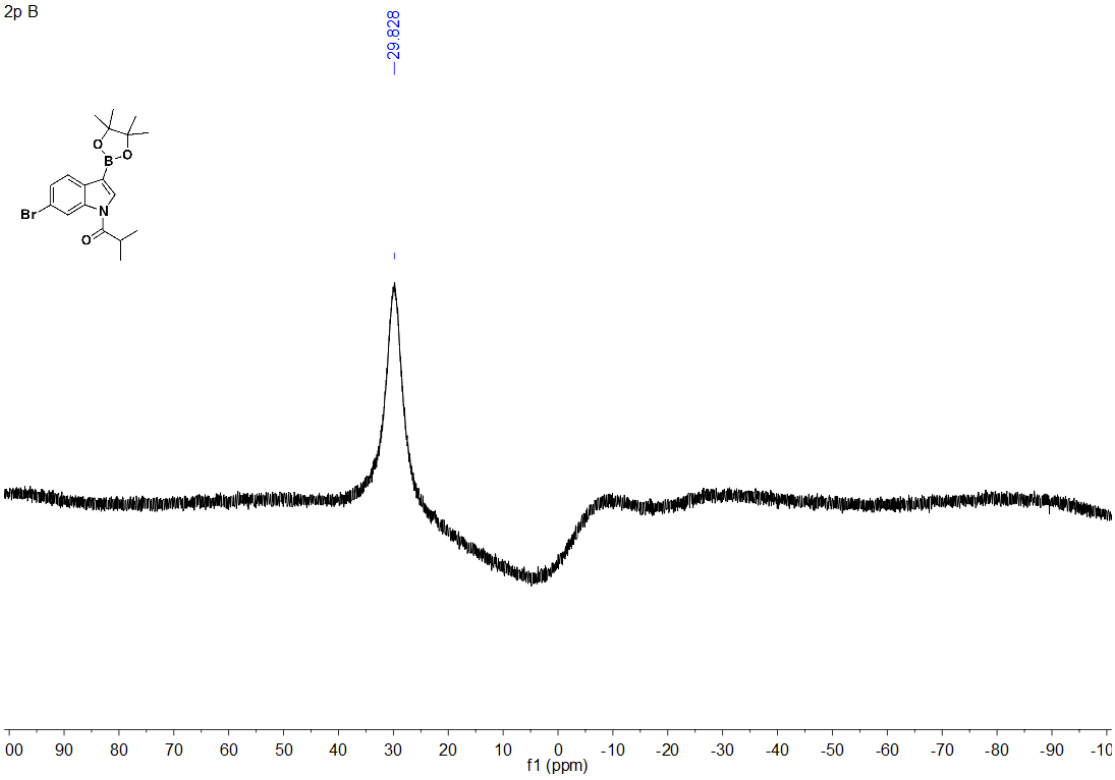
^{1}H NMR spectrum of 2p



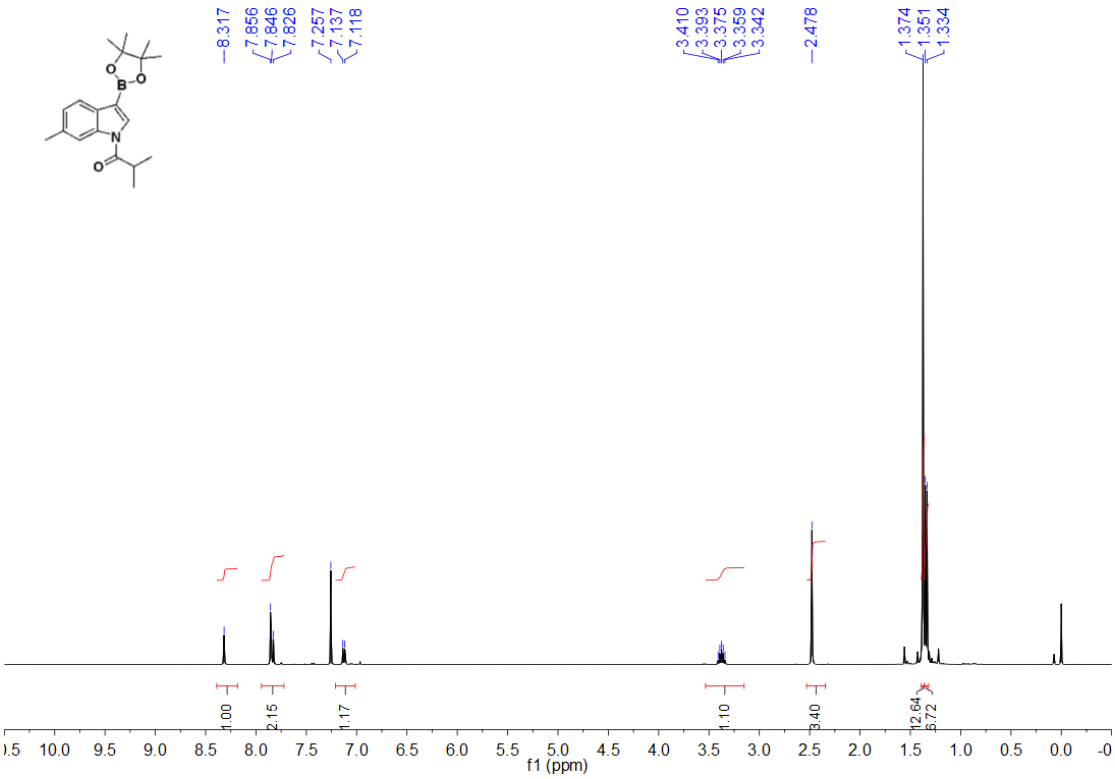
^{13}C NMR spectrum of 2p



^{11}B NMR spectrum of 2p

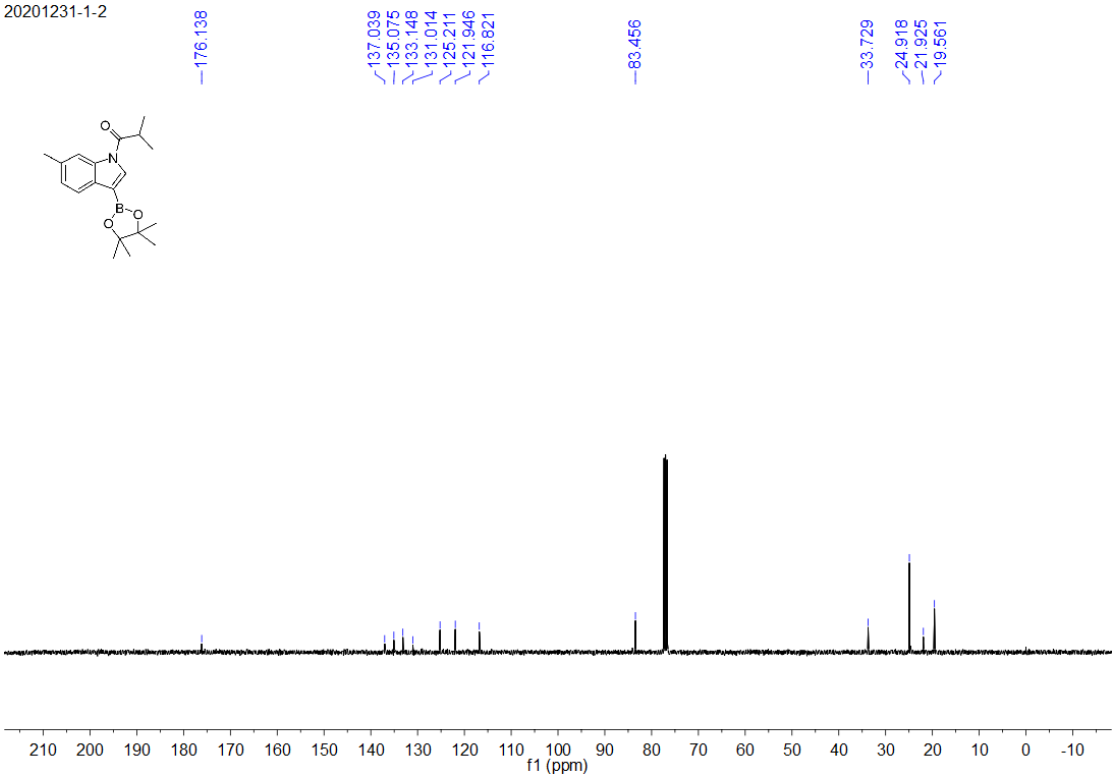


^{1}H NMR spectrum of 2q



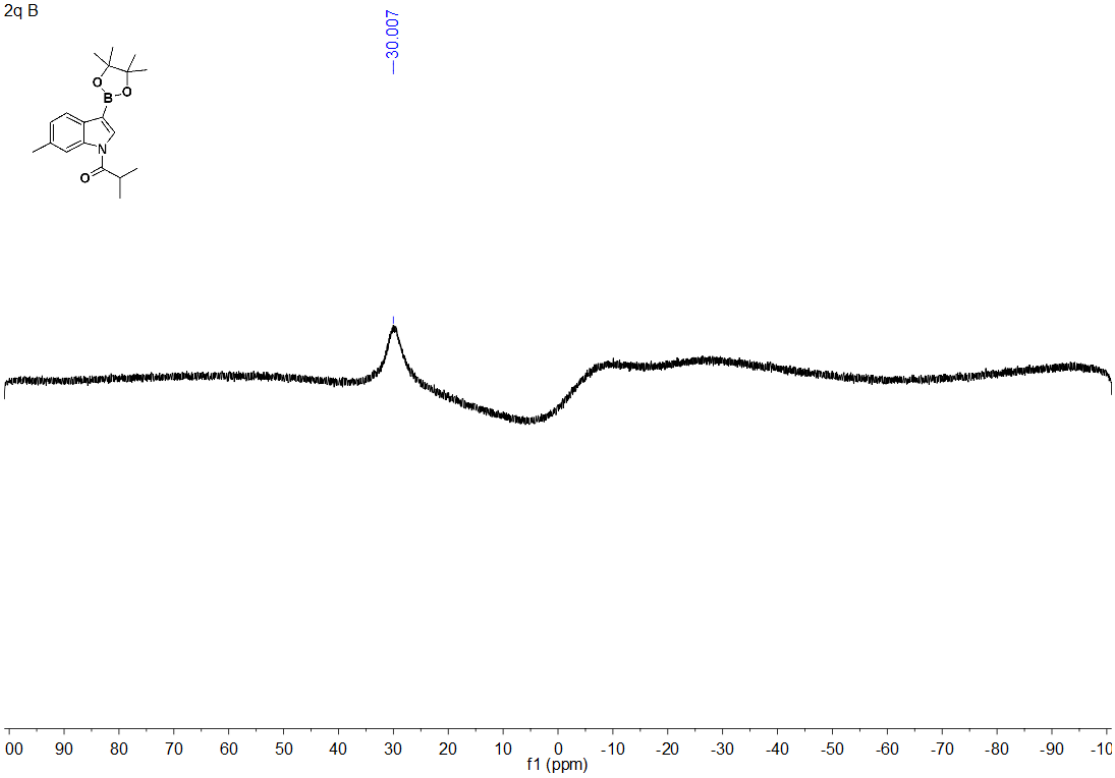
^{13}C NMR spectrum of 2q

20201231-1-2

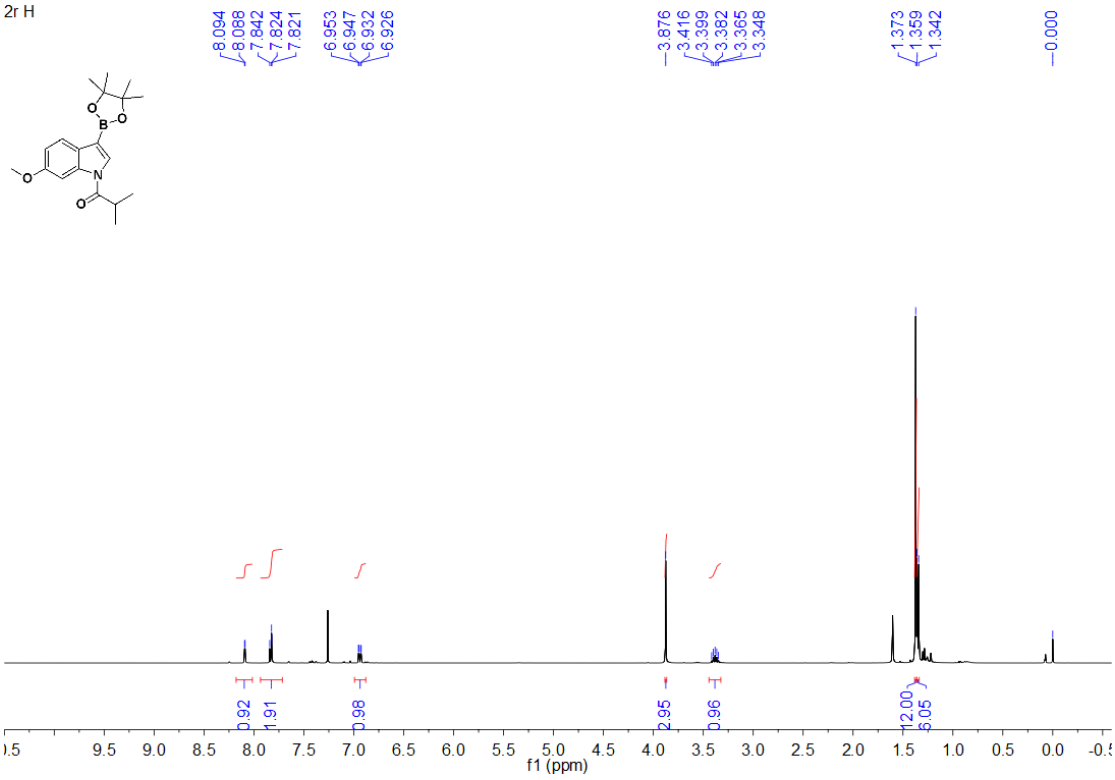


^{11}B NMR spectrum of 2q

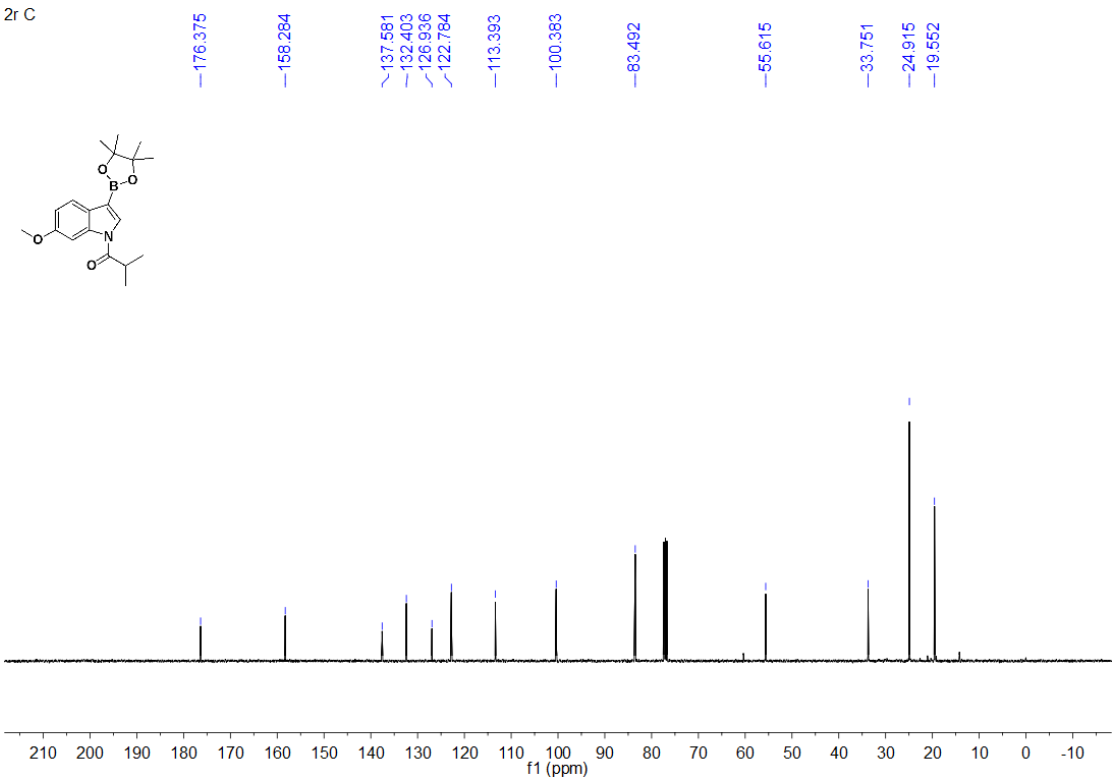
2q B



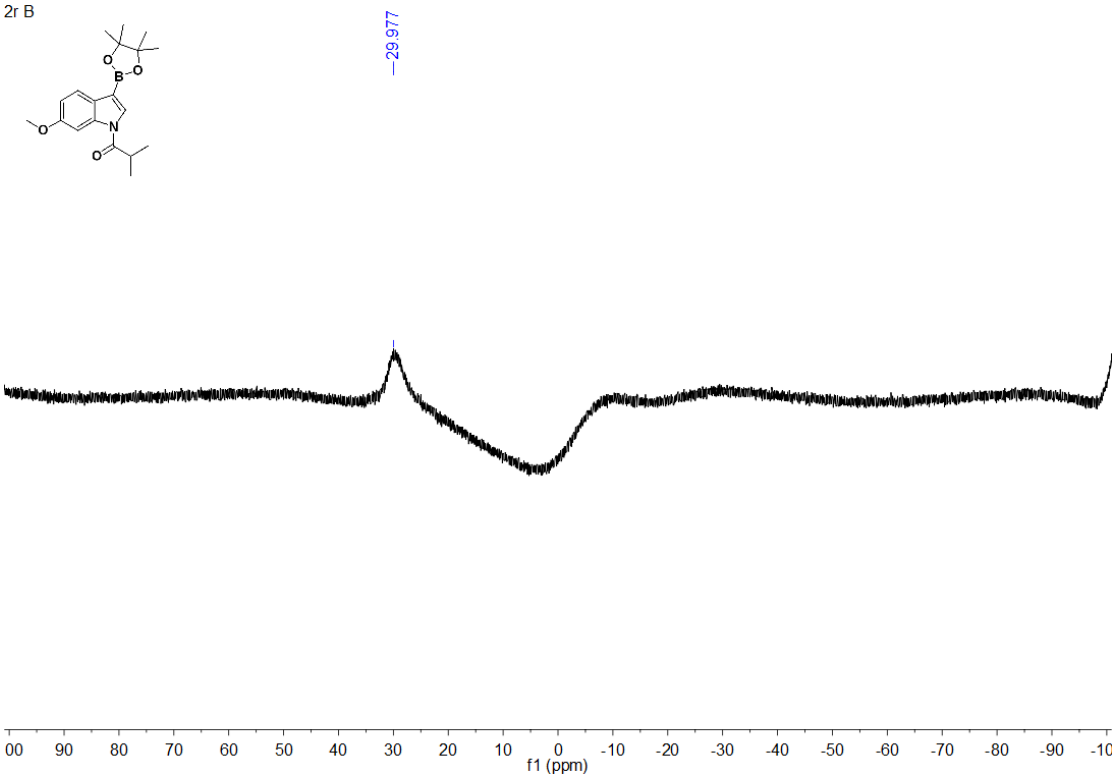
^{1}H NMR spectrum of 2r



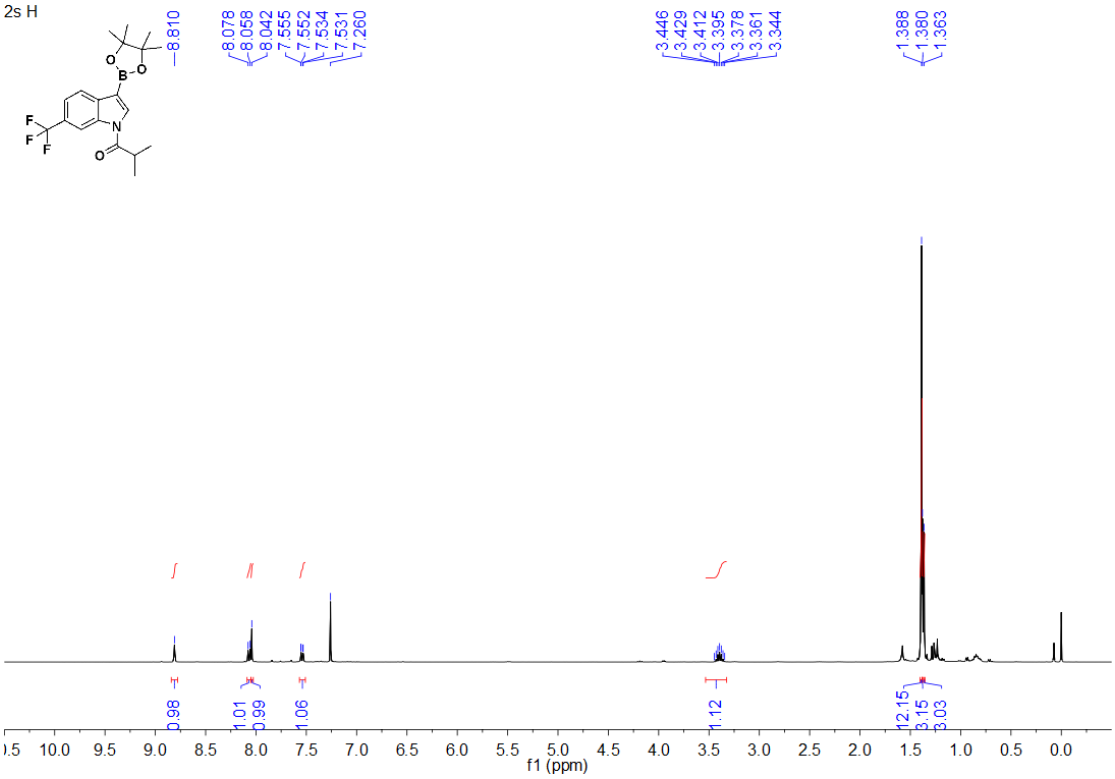
^{13}C NMR spectrum of 2r



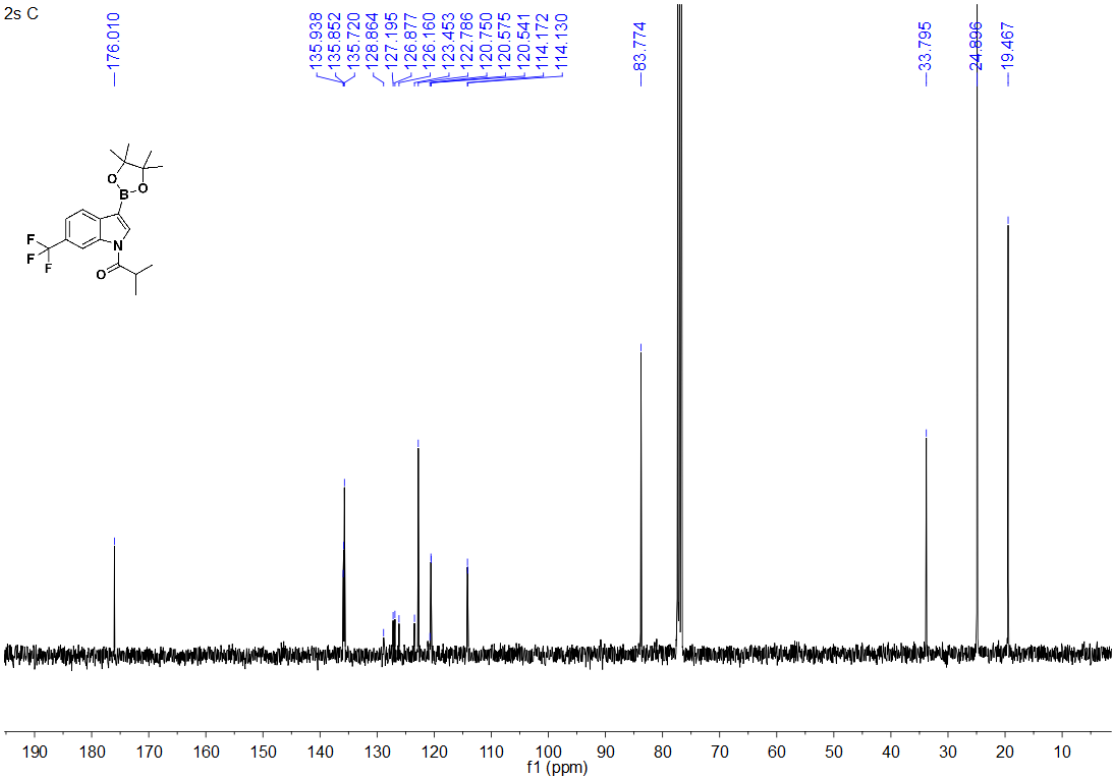
^{11}B NMR spectrum of 2r



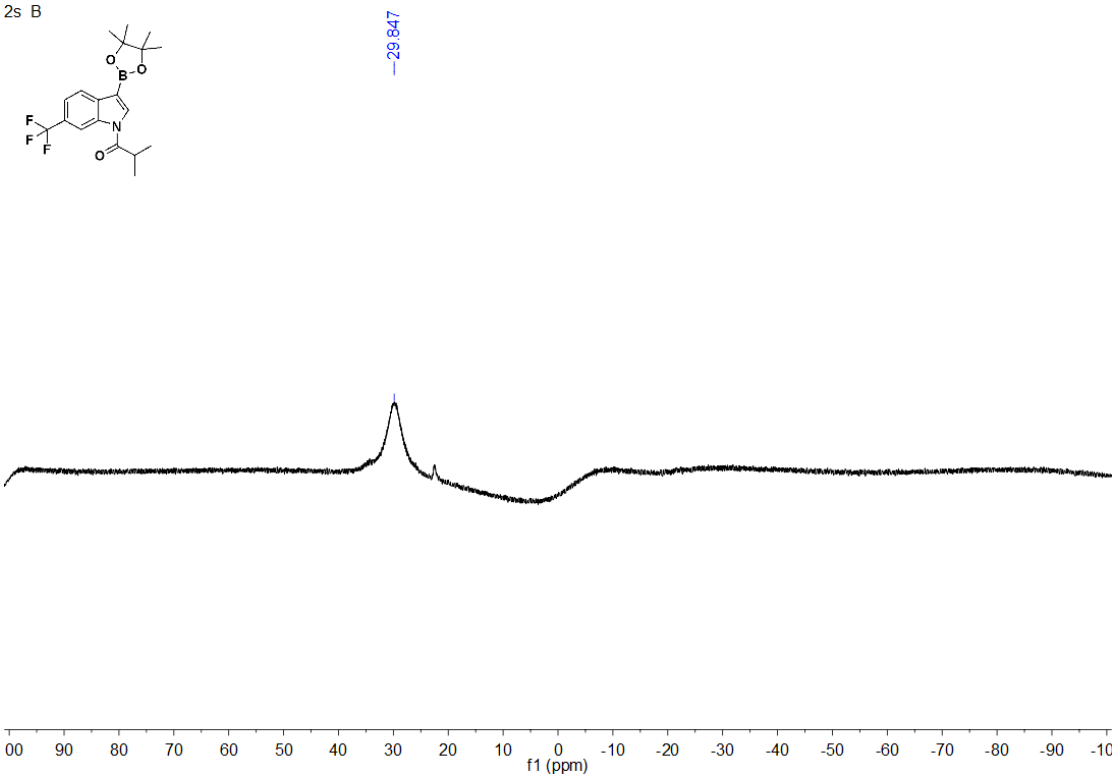
^{1}H NMR spectrum of 2s



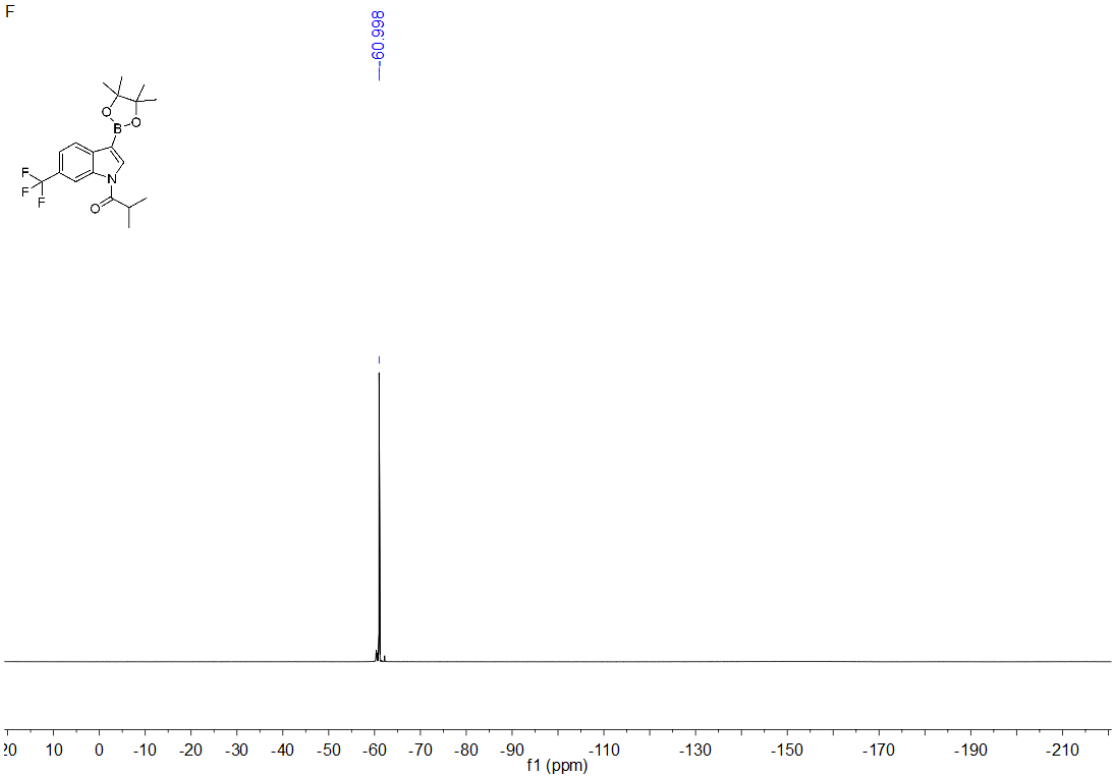
^{13}C NMR spectrum of 2s



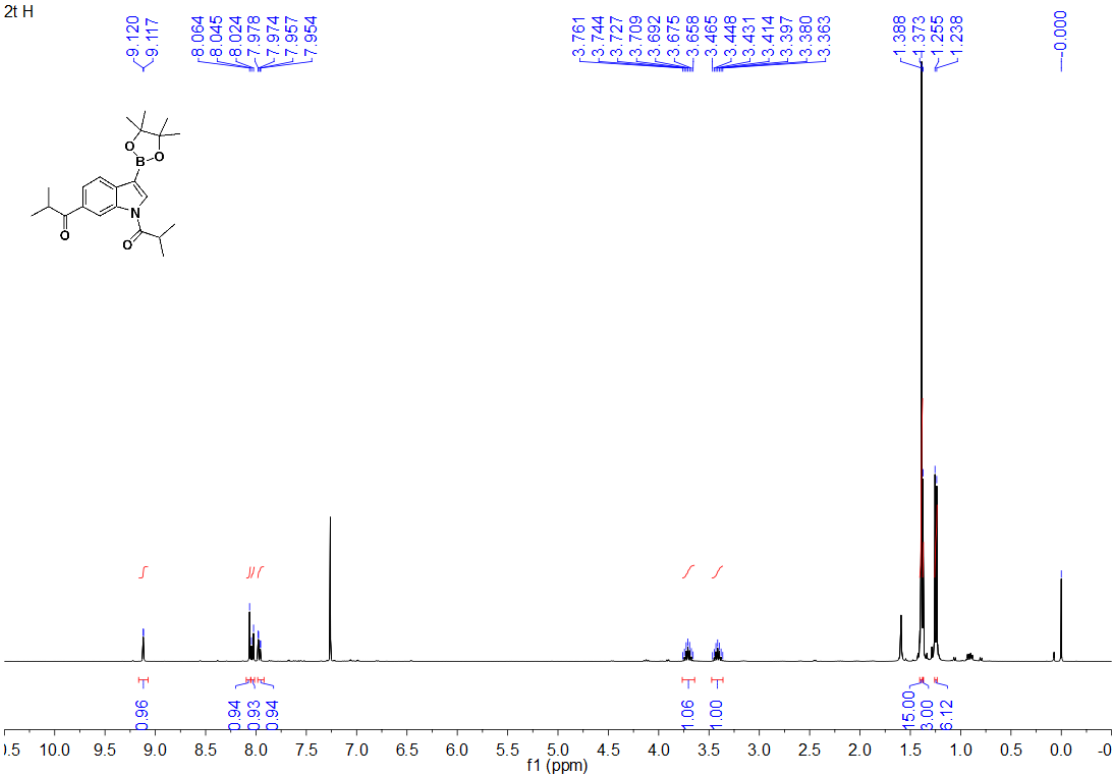
^{11}B NMR spectrum of 2s



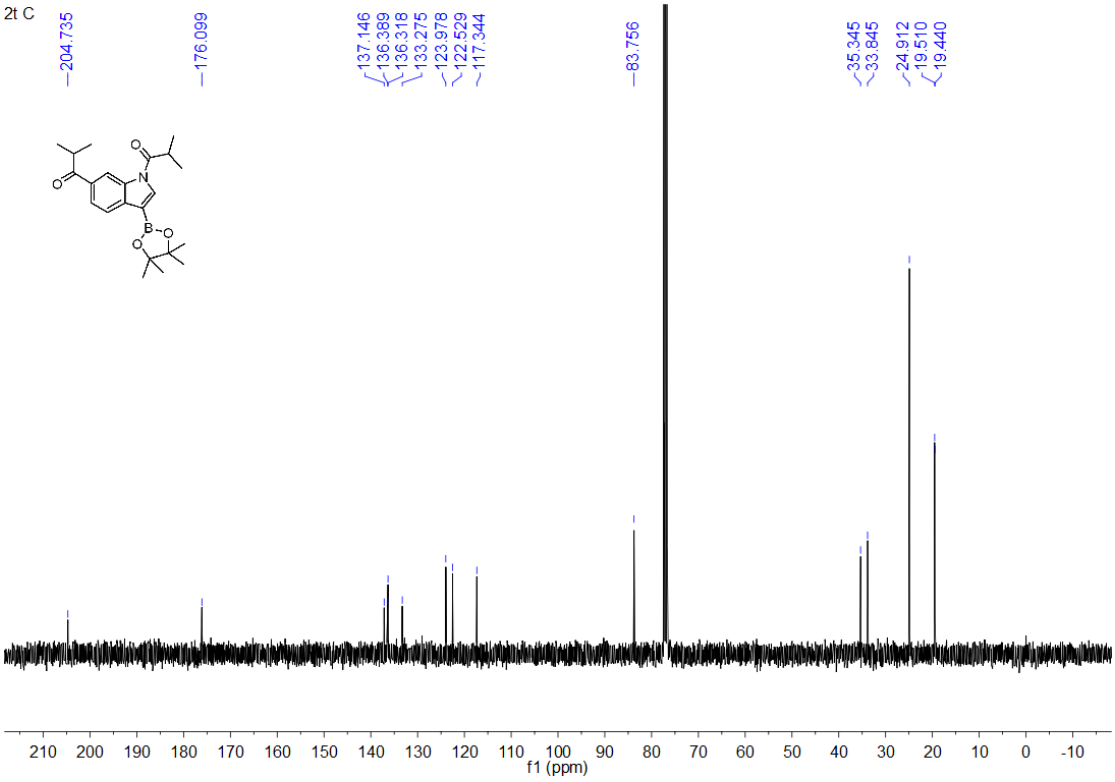
^{19}F NMR spectrum of 2s



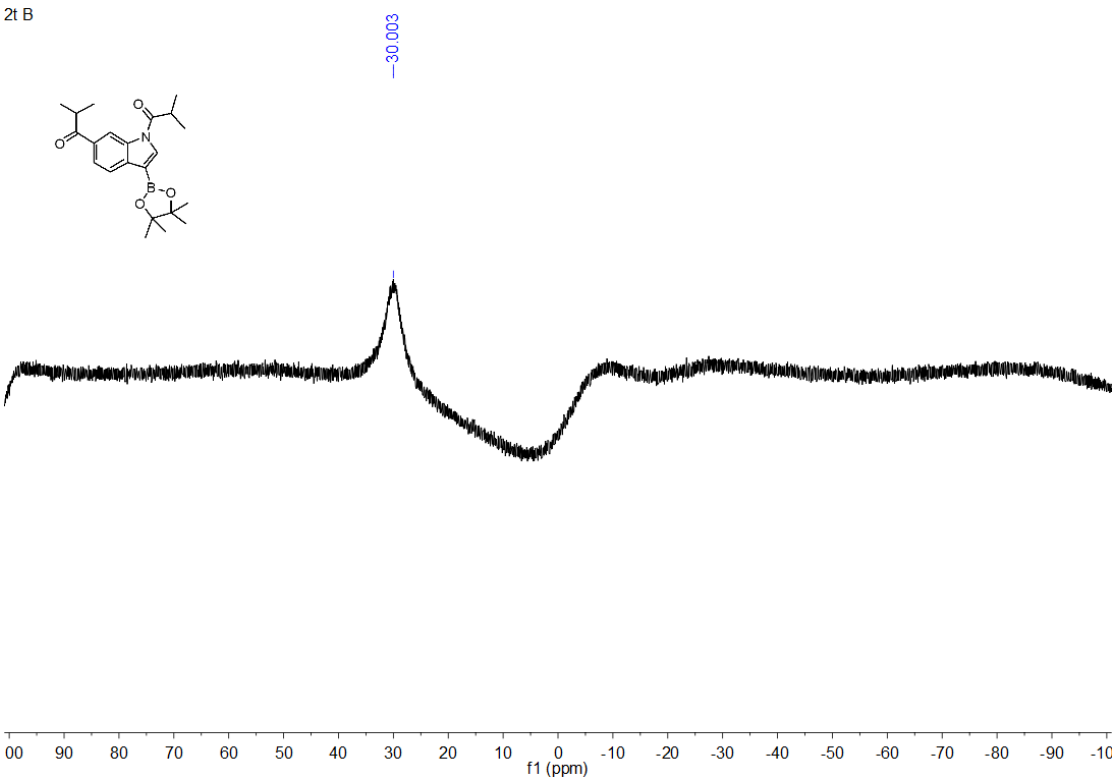
^{1}H NMR spectrum of 2t



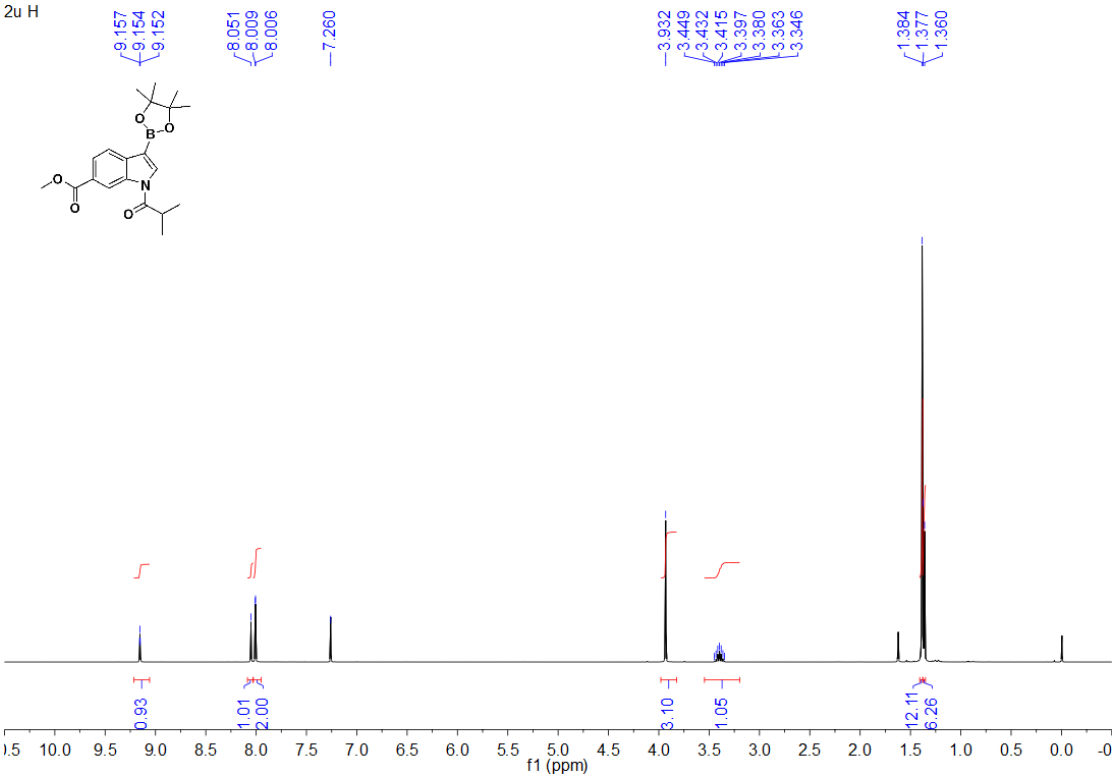
^{13}C NMR spectrum of 2t



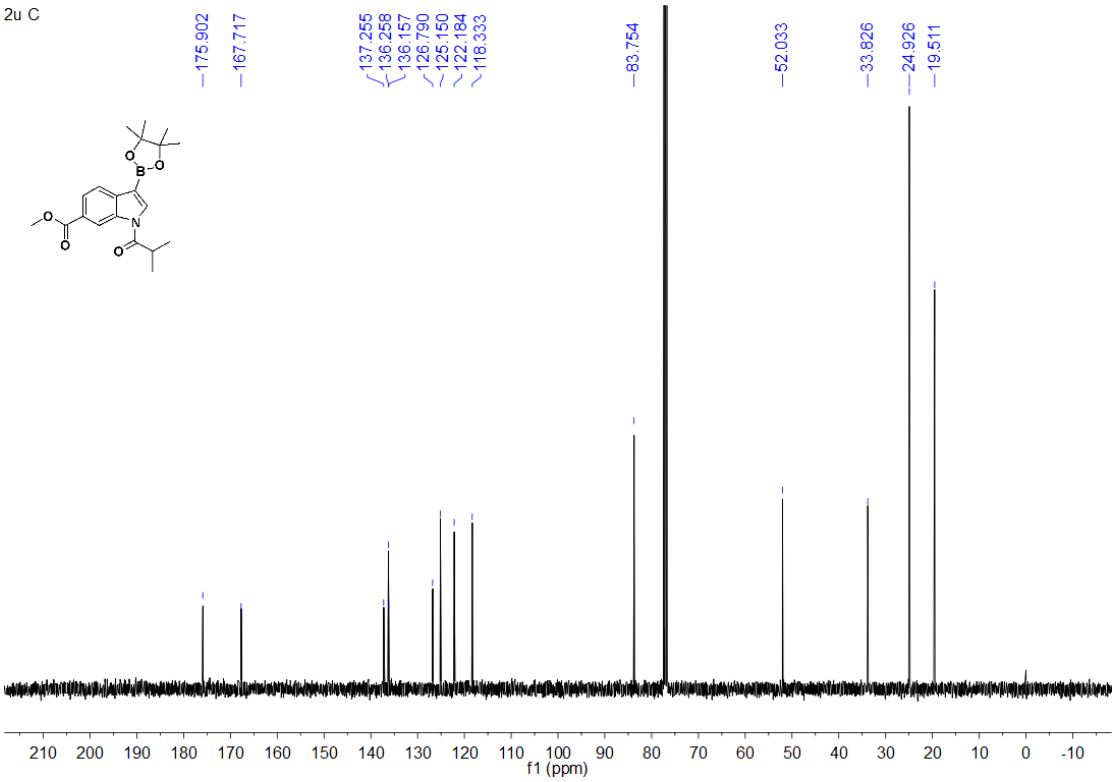
^{11}B NMR spectrum of 2t



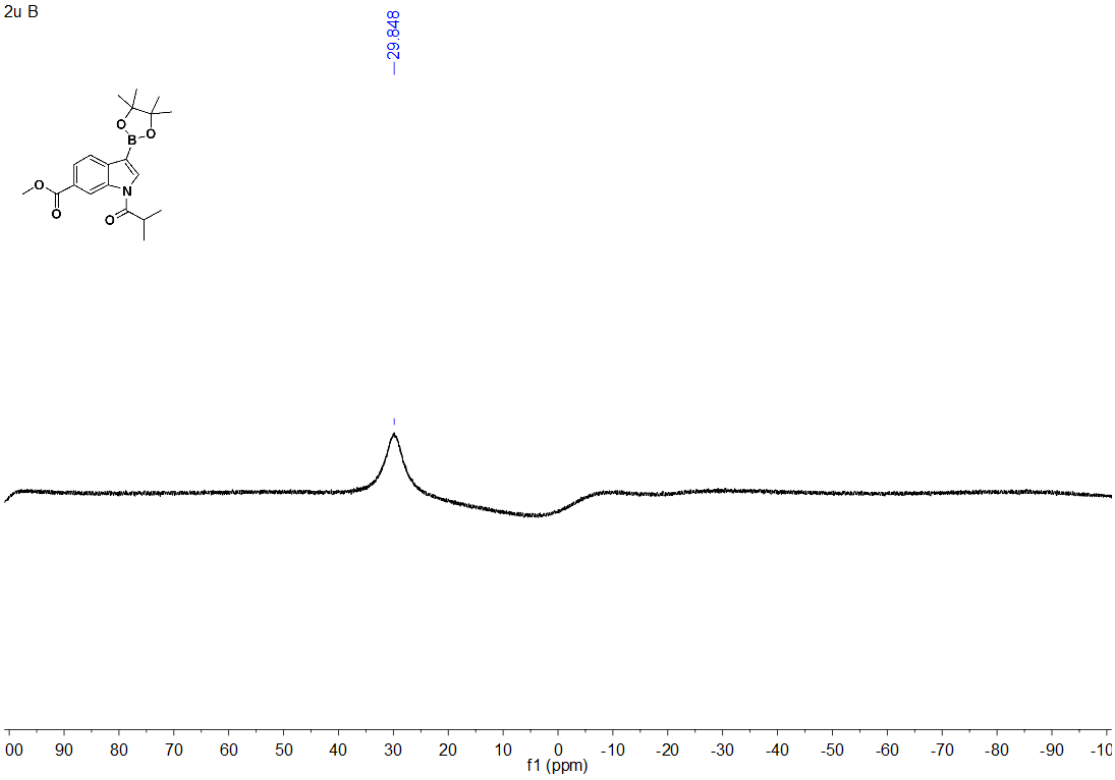
^{1}H NMR spectrum of 2u



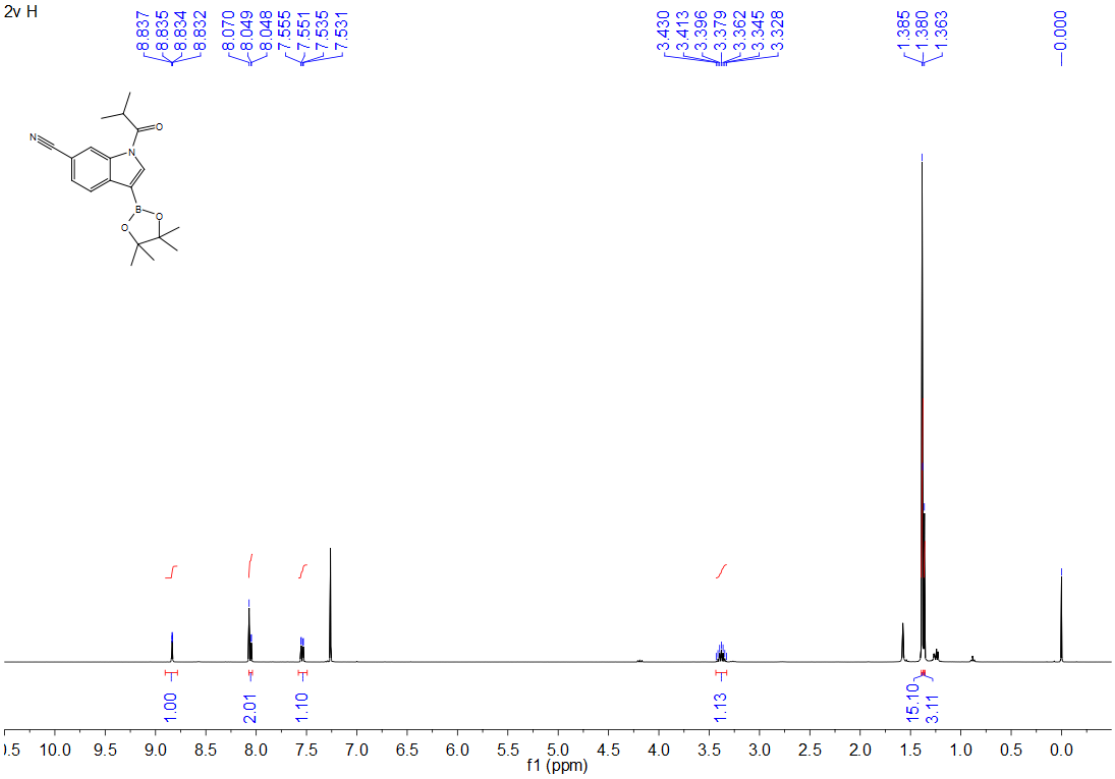
^{13}C NMR spectrum of 2u



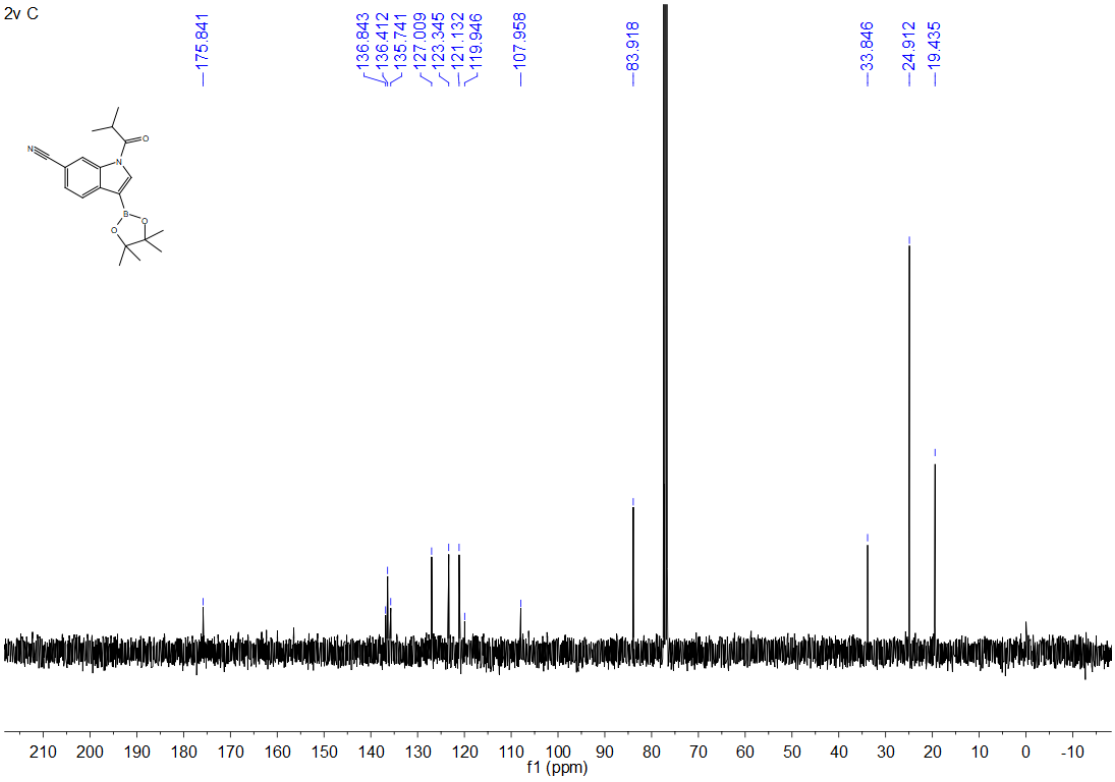
^{11}B NMR spectrum of 2u



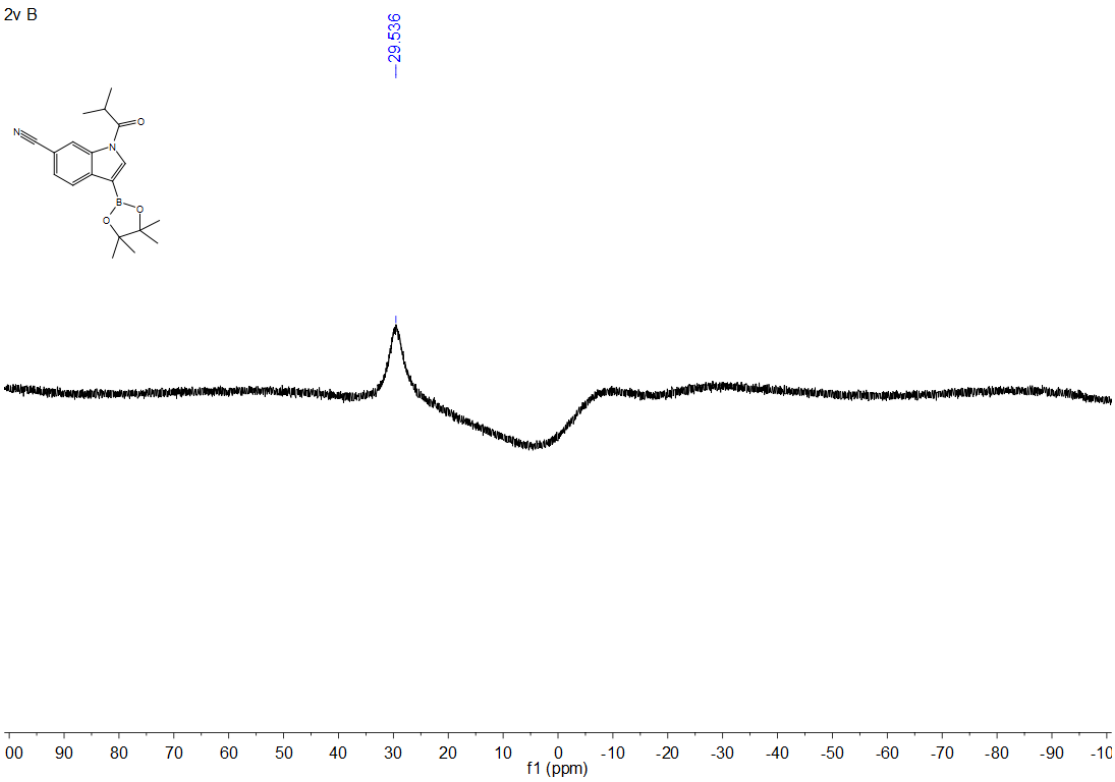
^{1}H NMR spectrum of 2v



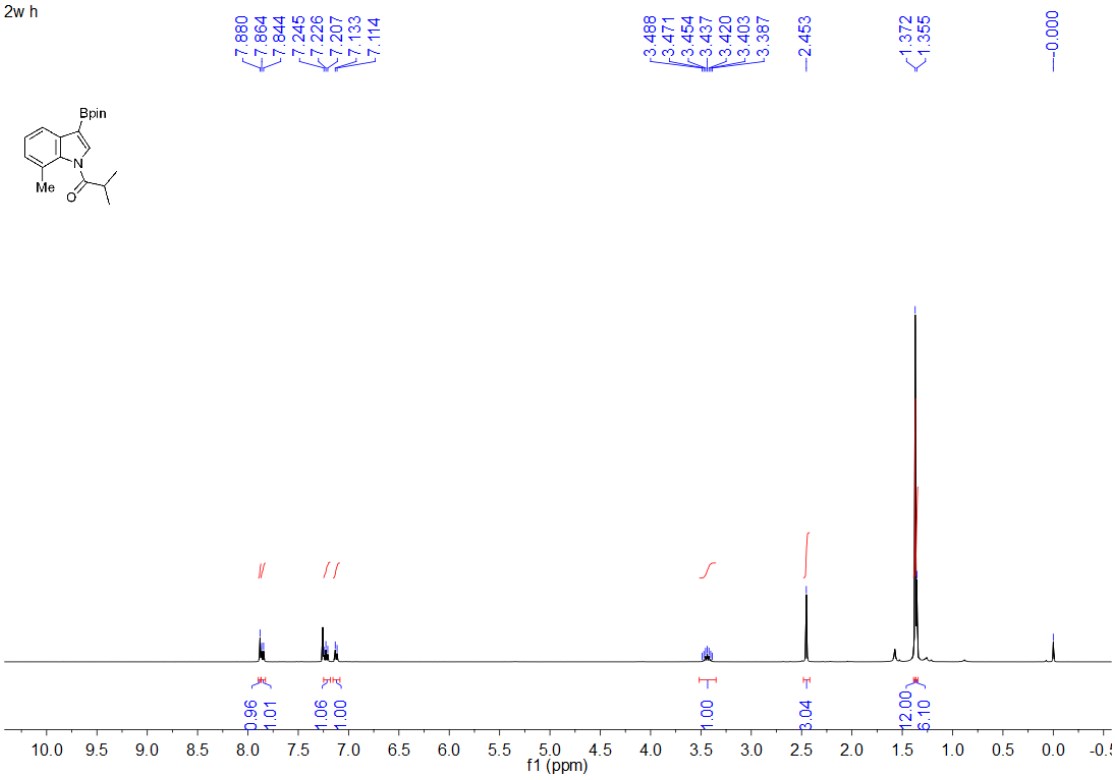
^{13}C NMR spectrum of 2v



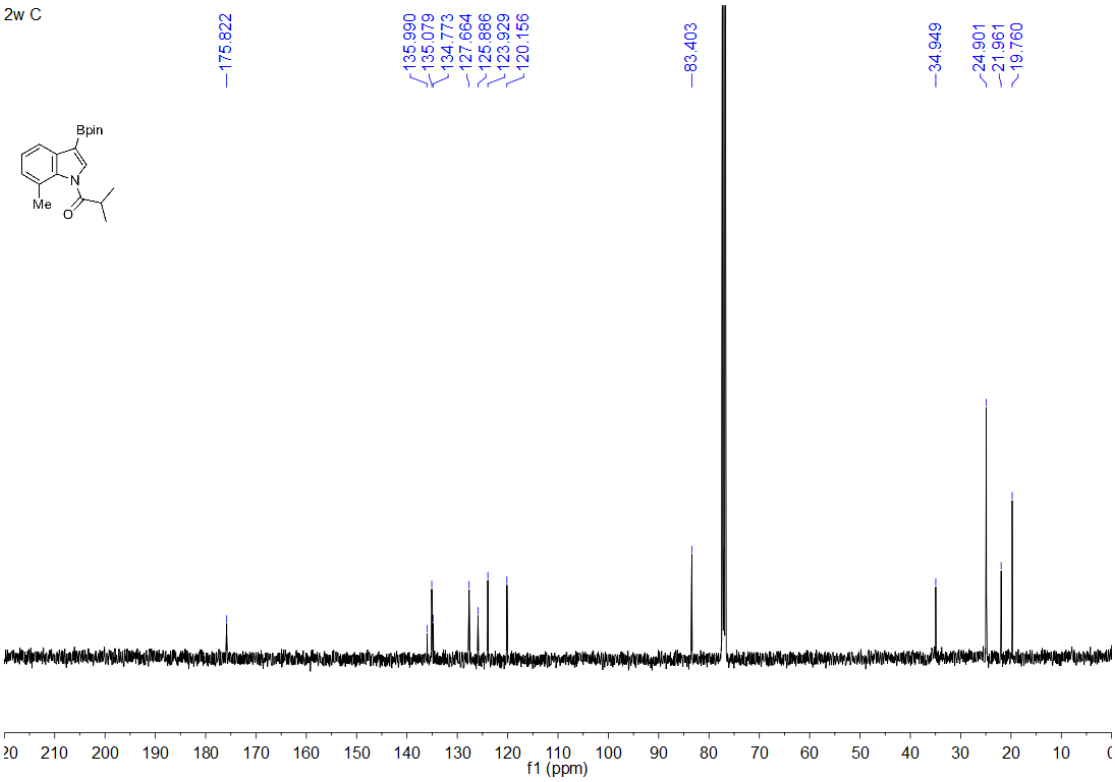
^{11}B NMR spectrum of 2v



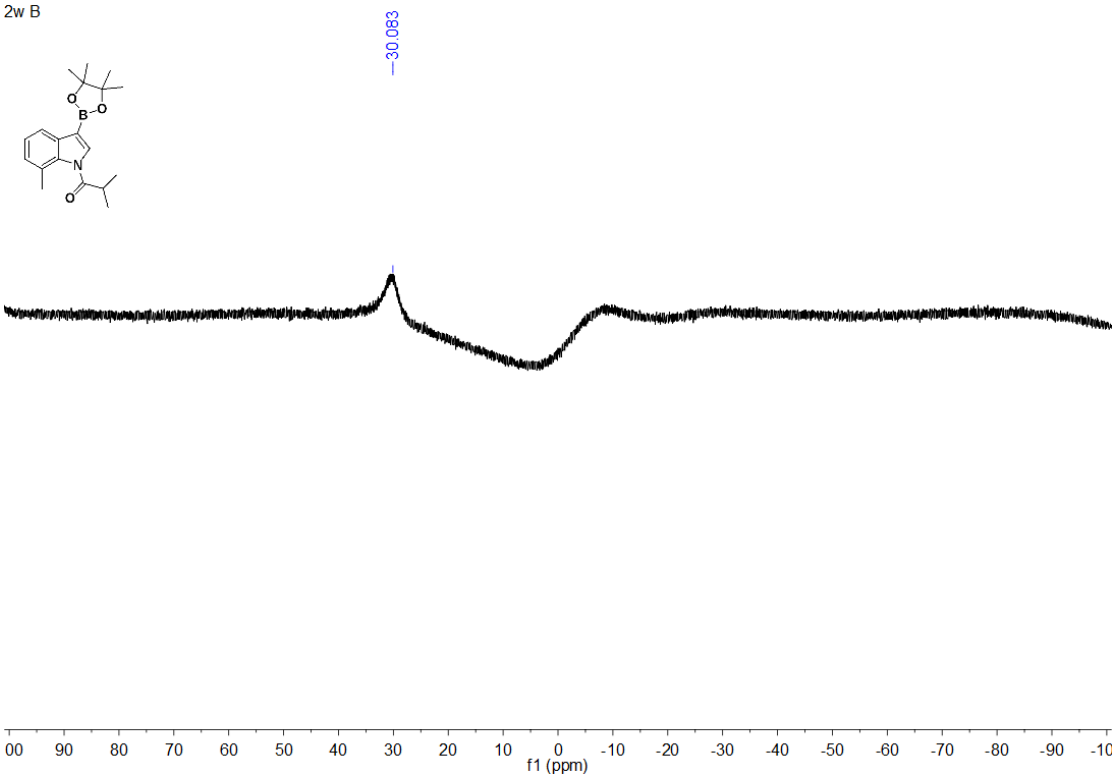
^{1}H NMR spectrum of 2w



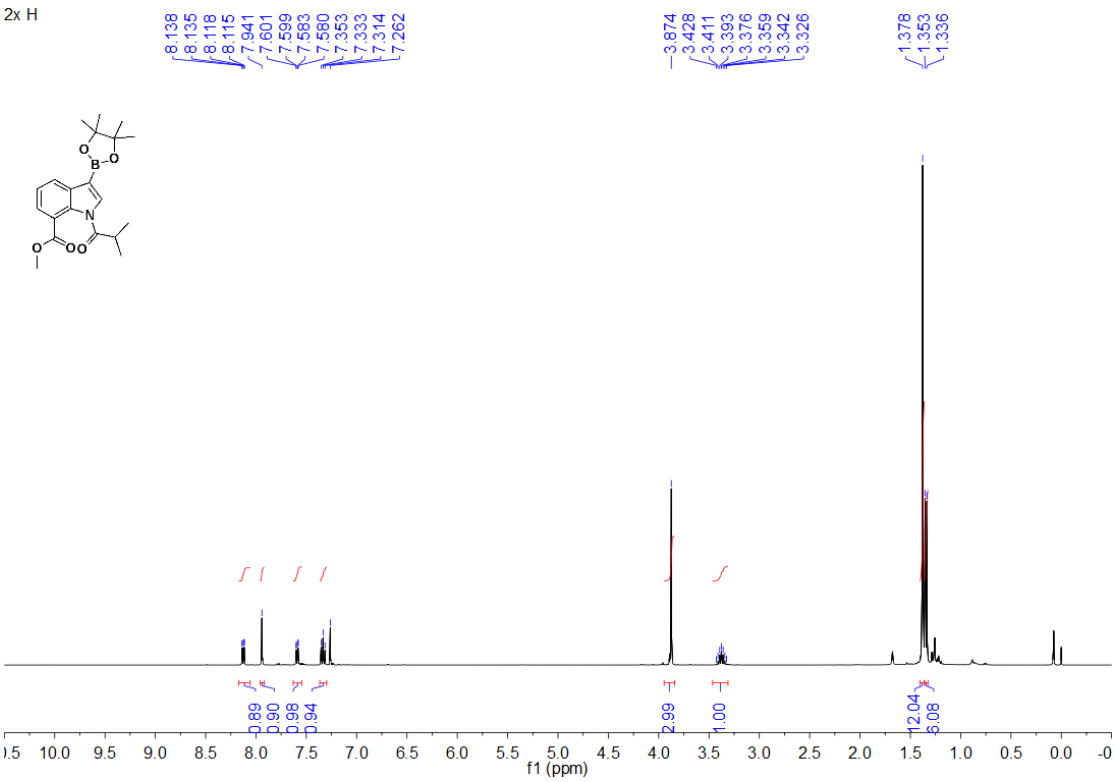
^{13}C NMR spectrum of 2w



^{11}B NMR spectrum of 2w

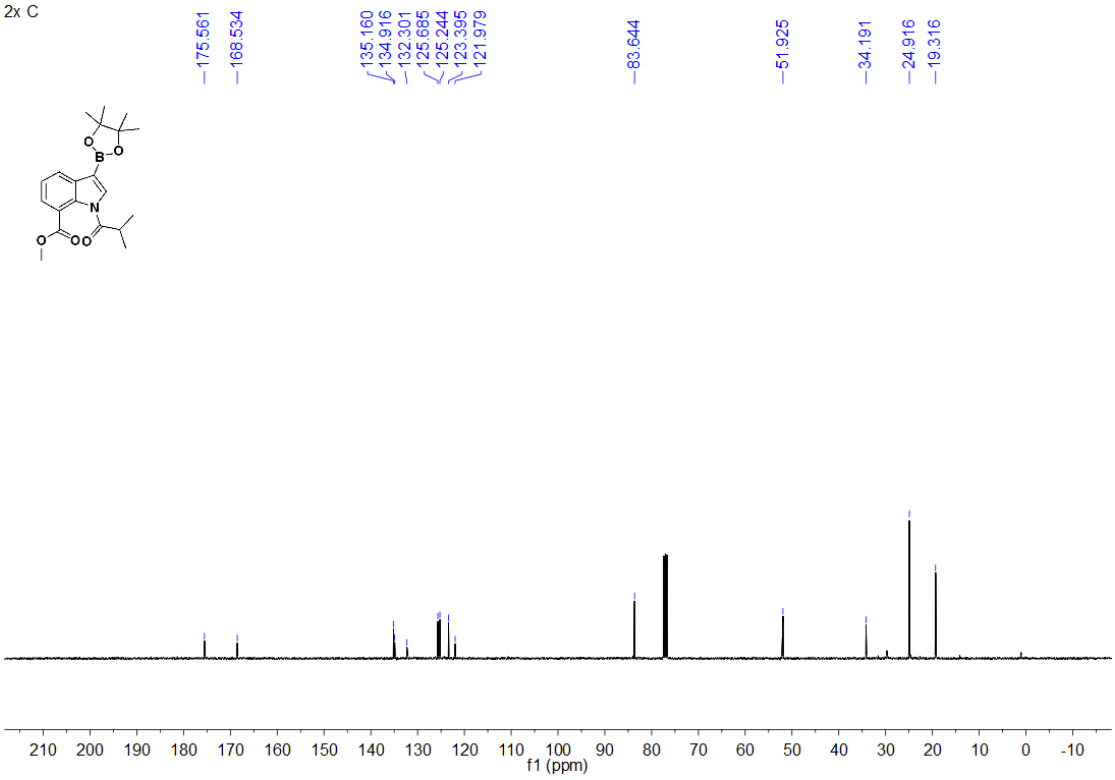


^{1}H NMR spectrum of 2x



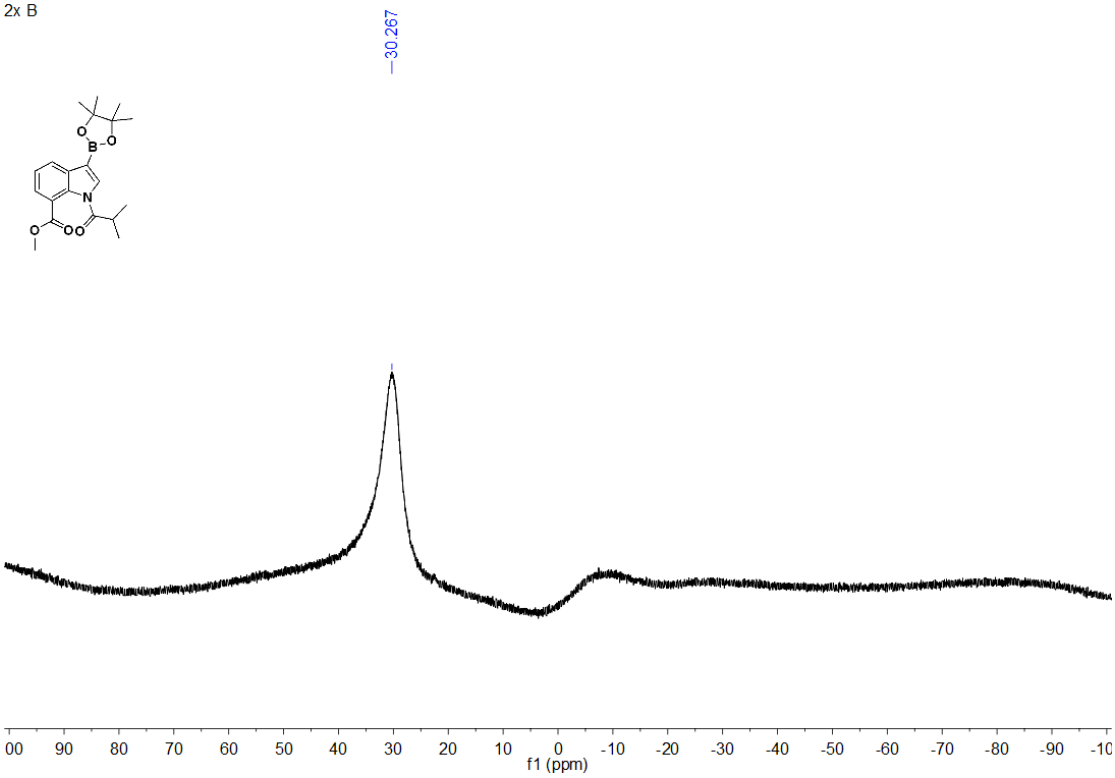
^{13}C NMR spectrum of 2x

2x C

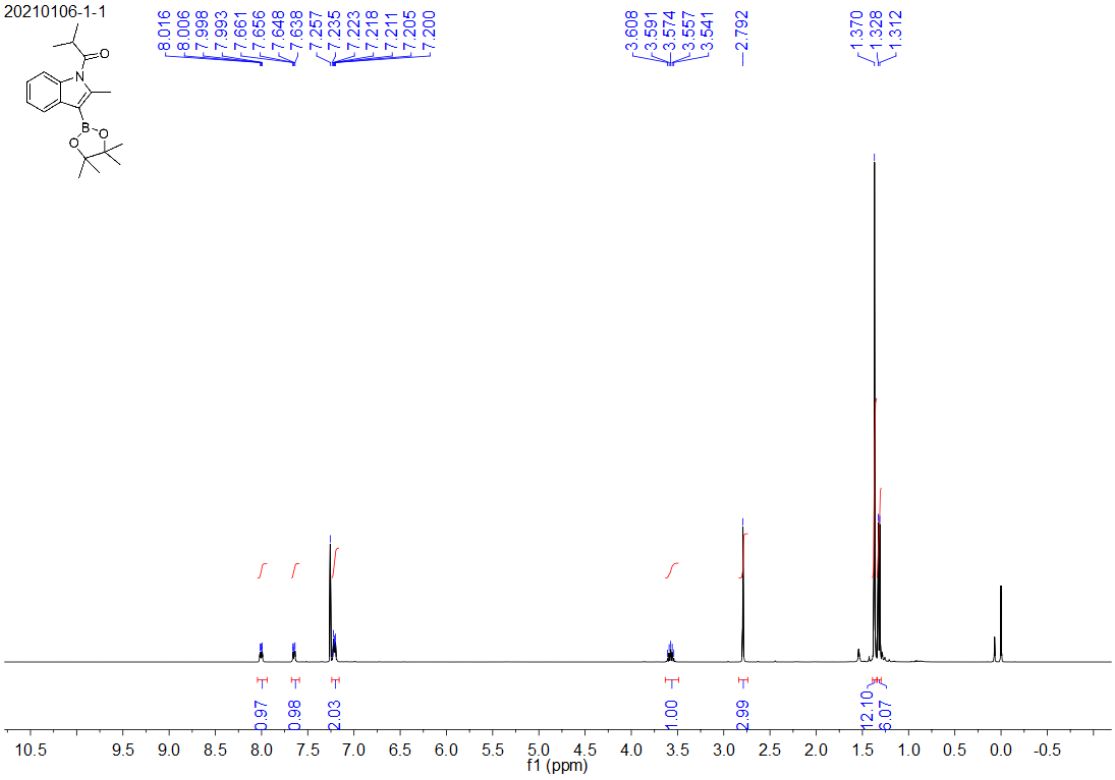


^{11}B NMR spectrum of 2x

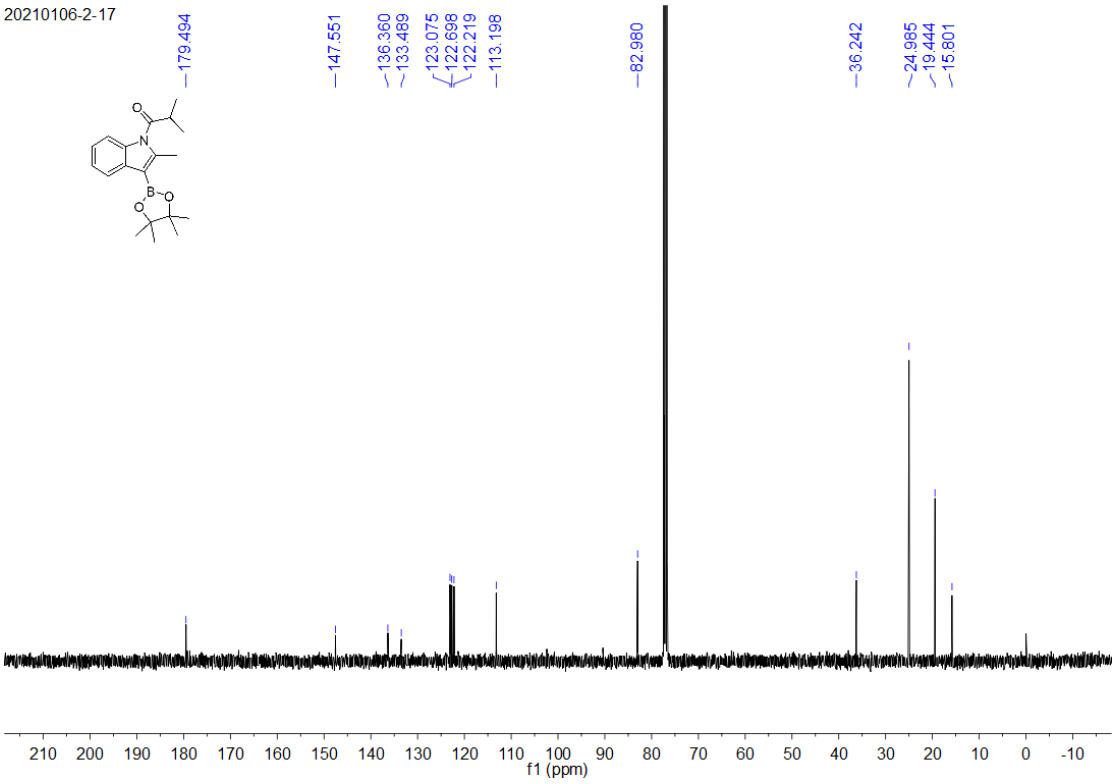
2x B



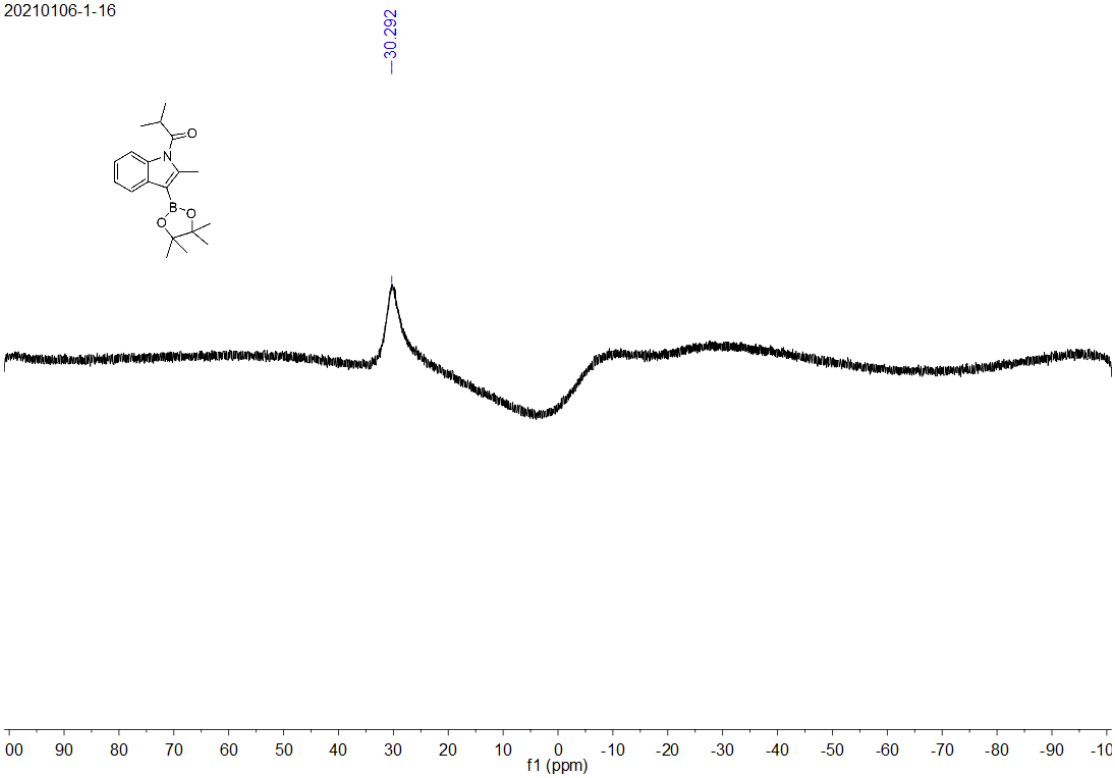
^{1}H NMR spectrum of 4a



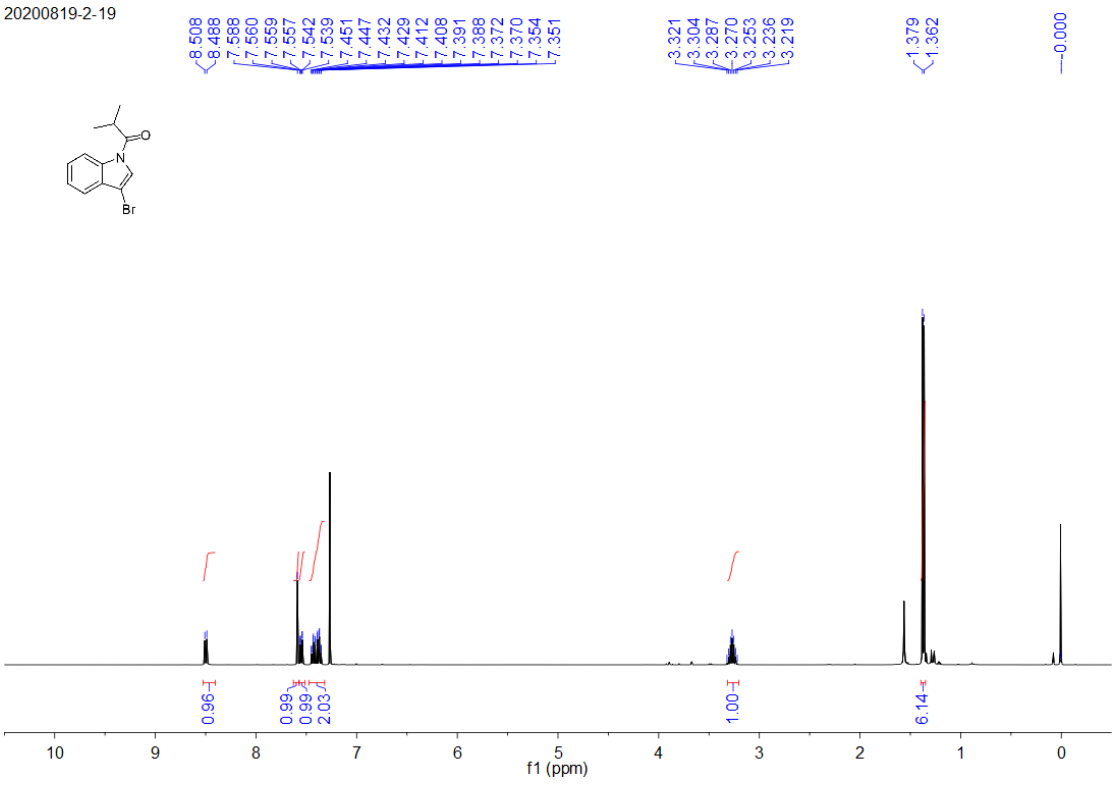
^{13}C NMR spectrum of 4a



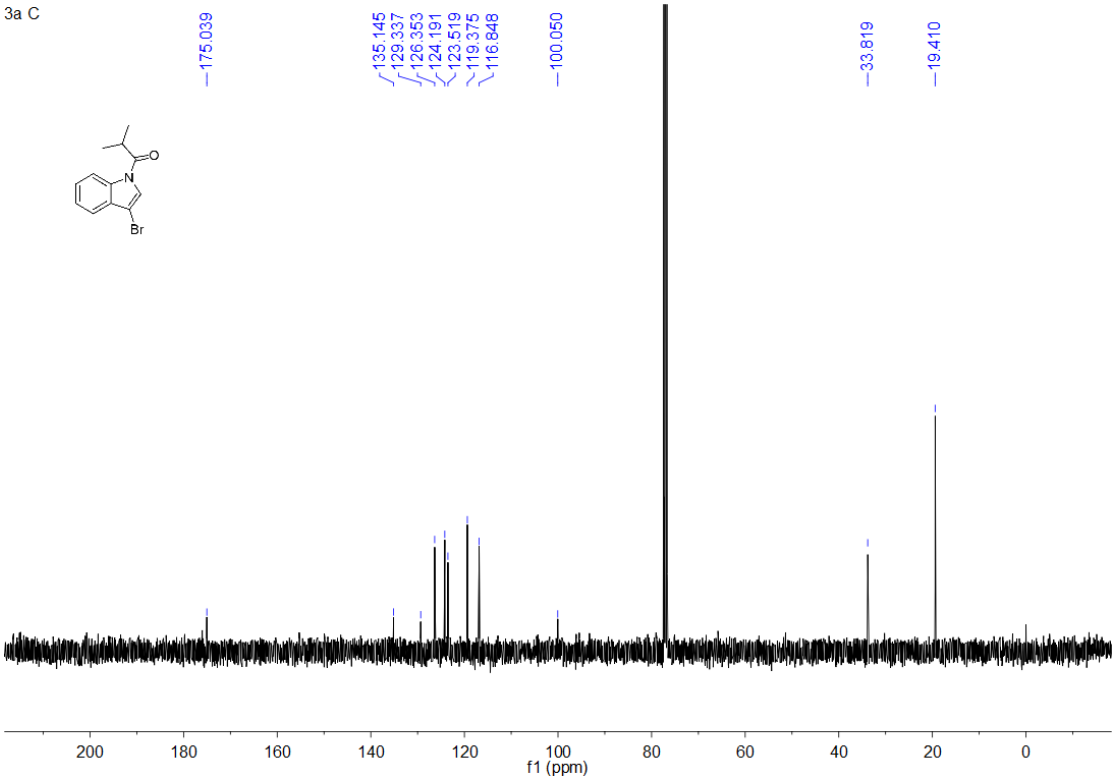
^{11}B NMR spectrum of 4a



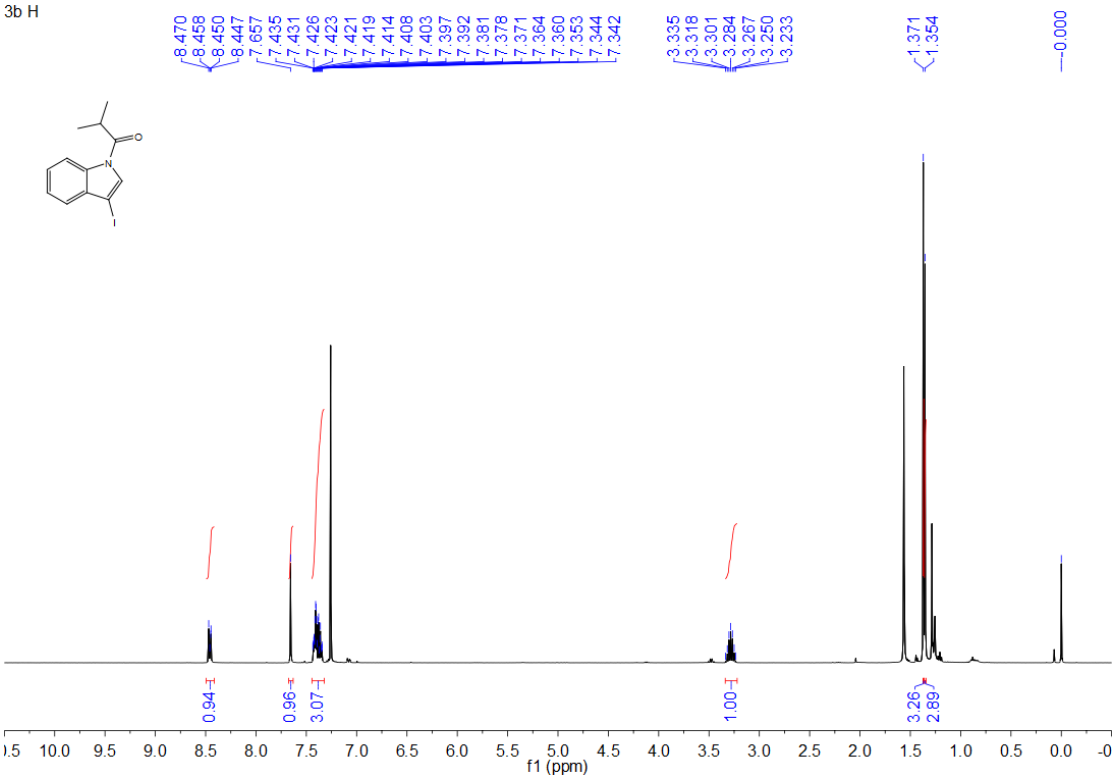
^{1}H NMR spectrum of 5



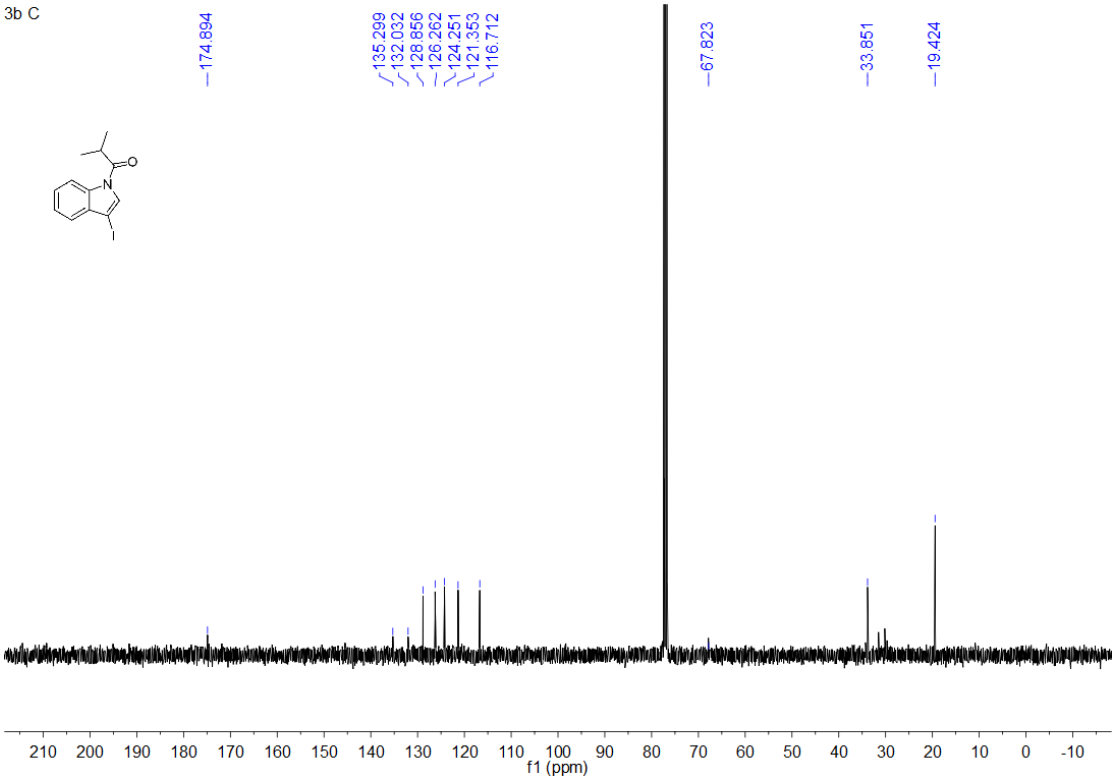
^{13}C NMR spectrum of 5



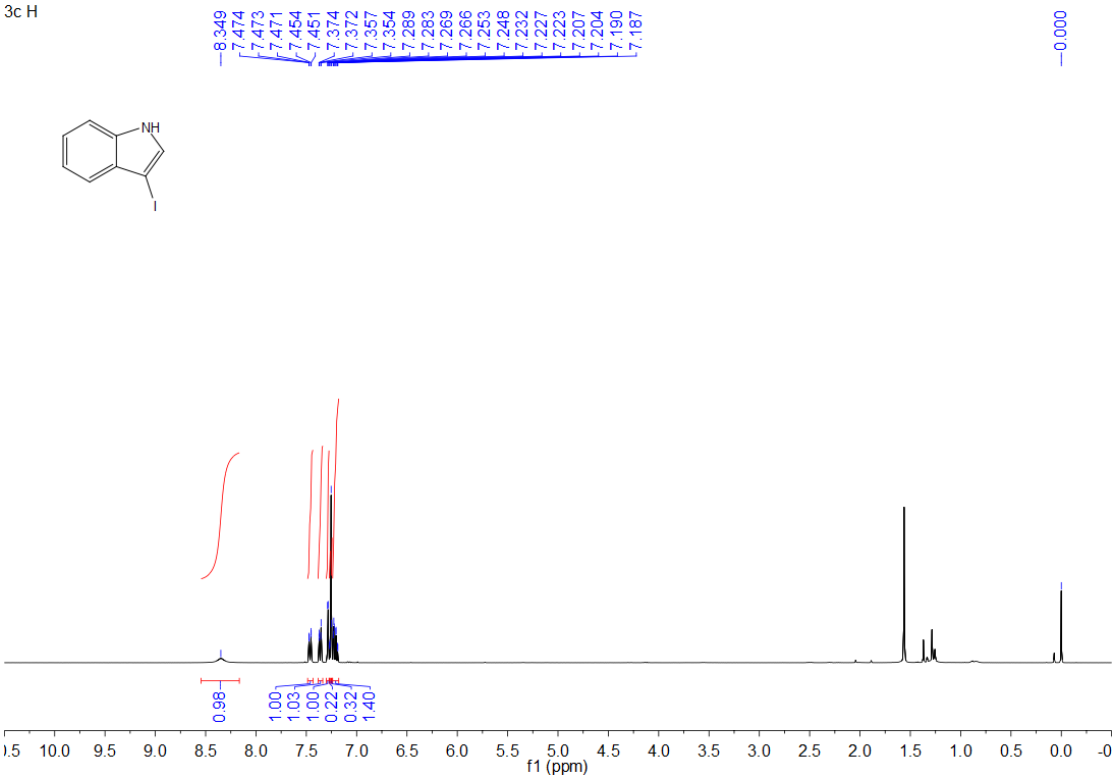
^{1}H NMR spectrum of 6



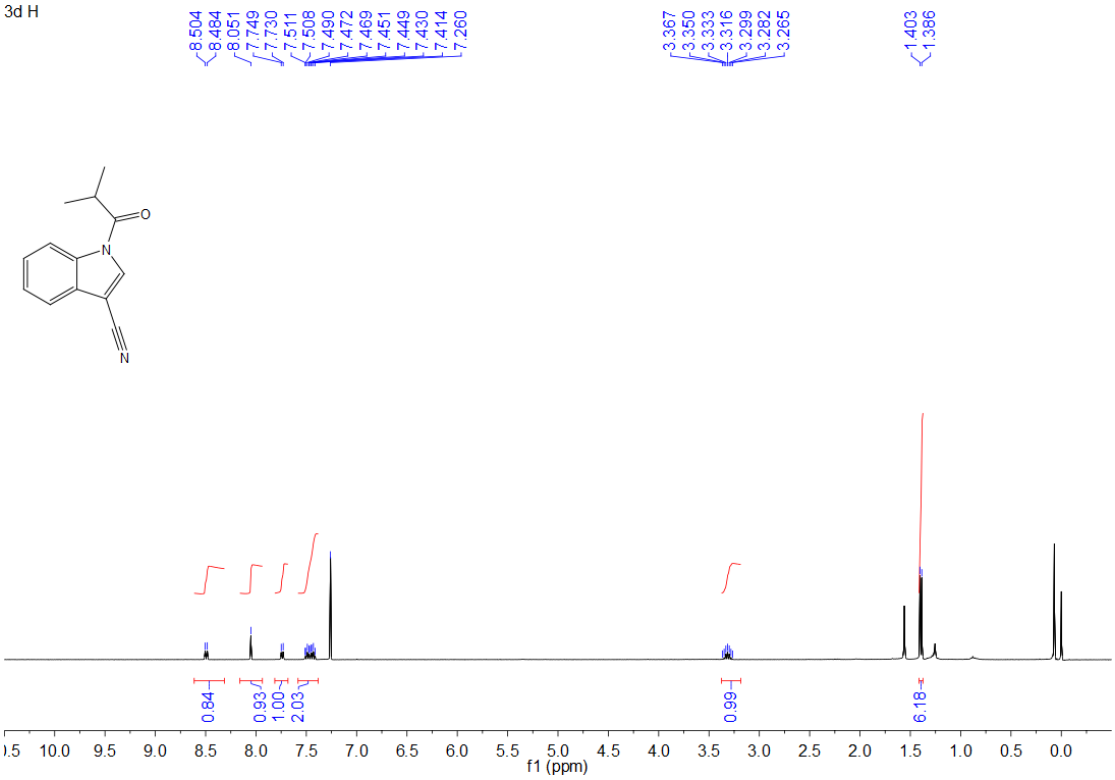
^{13}C NMR spectrum of 6



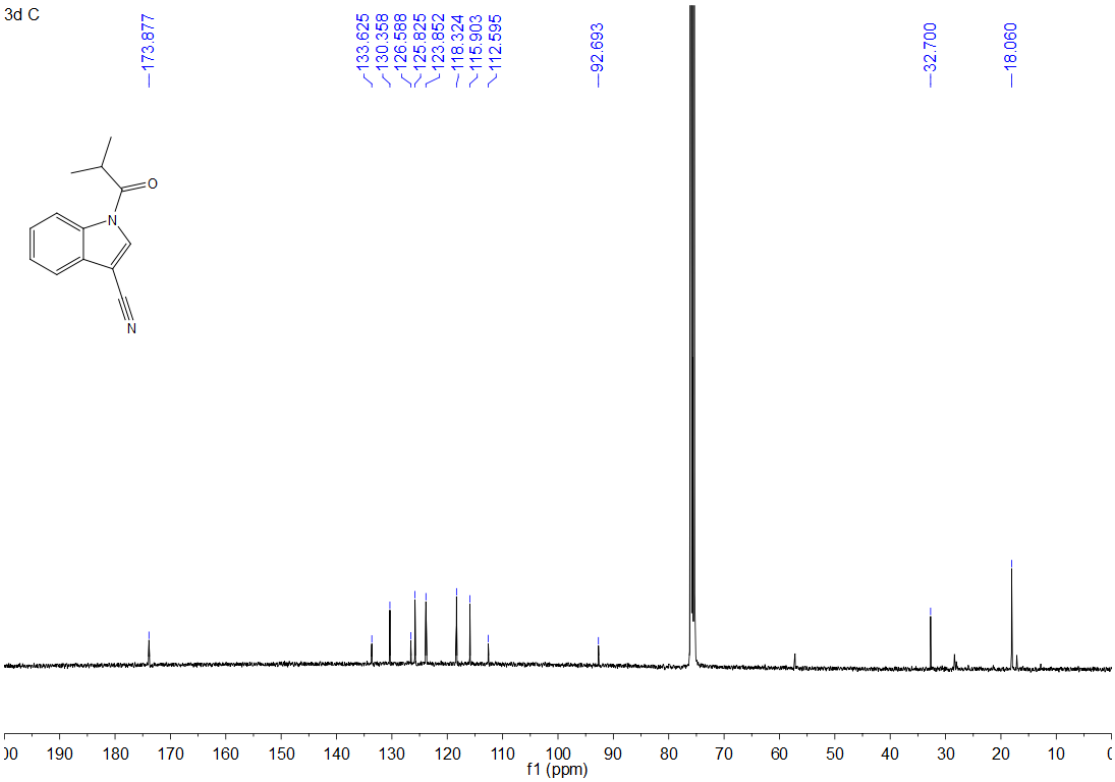
^{1}H NMR spectrum of 7



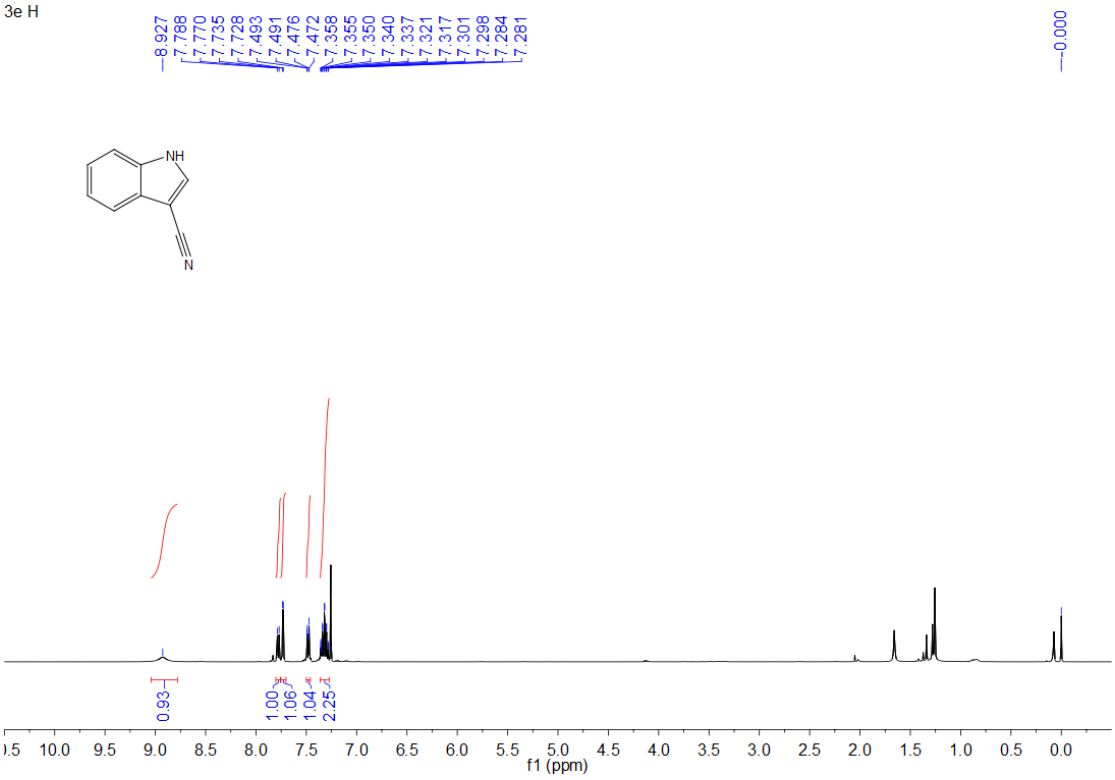
^{1}H NMR spectrum of 8



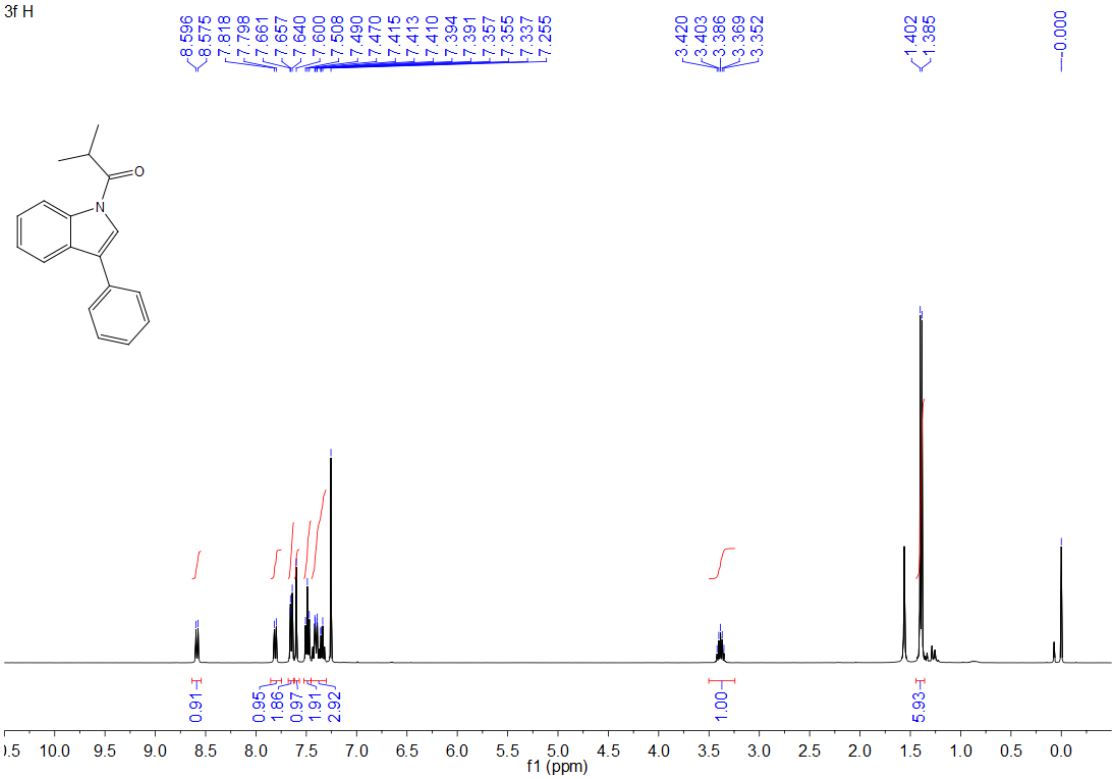
^{13}C NMR spectrum of 8



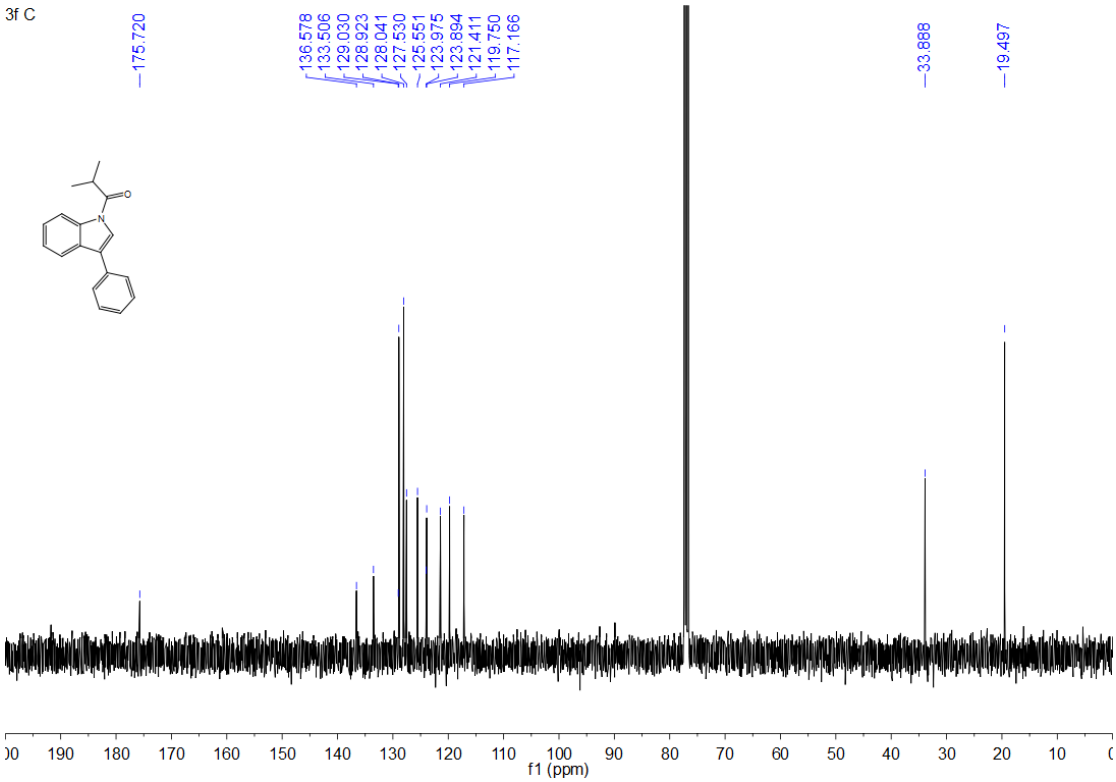
^{1}H NMR spectrum of 9



^{1}H NMR spectrum of 10



^{13}C NMR spectrum of 10



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