Supporting Information

Reductive *ortho* C-H Cyanoalkylation of Aryl(Heteroaryl) Sulfoxides: A General Approach to α-Aryl(Heteroaryl) Nitriles

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1 General information

Unless otherwise indicated, all glassware was oven dried by a heat gun before use and all reactions were performed under an atmosphere of Nitrogen. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on plastic plates coated with silica gel GF254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (160-200 mesh). Neat infra-red spectra were recorded using a NEXUS670 FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. Mass spectra were obtained using a TOF MS instrument ESI source. All ^{1}H NMR, ^{13}C NMR spectra were recorded on Bruker AV-400 or AV-600. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 77.16 (^{13}C NMR). Coupling constants were quoted in Hz(*J*). ^{1}H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quadruplet (q), pentet (p), septet (se), octet (o). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m).

2 General procedure for the synthesis of starting materials

Aryl sulfoxides **2a** and **2b** are commercially available. Aryl sulfoxides **1a**[1], **1q**[1], **1s**[1], **1t**[1], **2c**[2], **2d**[2], **2e**[3], **2f**[2], **2g**[2], **2h**[4], **2i**[5], **2j**[2], **2o**[2], **2p**[6], **2q**[7], **2r**[8], **2s**[3] and **2t**[9] are known compounds.

References:

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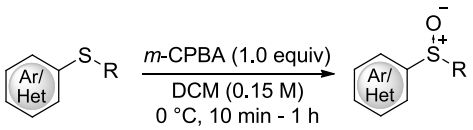
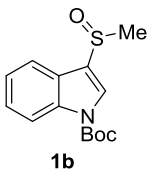
General procedure for the synthesis of aryl sulfoxide 1 and 2



To a solution of aryl sulfide (2.0 to 10.2 mmol) in DCM (0.3 M) was added a solution of *m*-CPBA (1.0 equiv) in DCM (0.3 M) dropwise at 0 ℃. The resulting solution was stirred at 0 ℃ for 10 min to 1h. Progress of the oxidation was checked by TLC. After completion of the reaction, saturated aqueous $NaHCO_3$ was added to the reaction mixture and the resulting solution was extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained residue was purified by silica gel chromatography eluting with an eluent (PE/EtOAc) to give the corresponding aryl sulfoxide **1** or **2**.



1b

tert-butyl 3-(methyl sulfinyl)-1H-indole-1-carboxylate (1b):

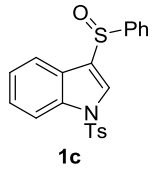
Following the general procedure, the title compound was prepared from corresponding sulfide (1.32 g, 5.0 mmol) and it was obtained as white solid, m.p. 106-108 ℃, 1.33 g, 95% yield. (Rf = 0.16, eluent: PE/EtOAc = 1/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.3 Hz, 1H), 7.99 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.36 – 7.29 (m, 1H), 3.00 (s, 3H), 1.67 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.9, 136.3, 126.3, 125.8, 125.4, 123.8, 123.7, 119.5, 116.1, 85.3, 41.8, 28.2.

IR (neat): 3122, 2992, 2915, 1726, 1578, 1534, 1447, 1371, 1250, 1146, 1037, 842, 764, 714.

HRMS (ESI-TOF): calculated for [$C_{14}H_{17}NO_3SNa$ ($M + Na^+$)]: 302.0821, found: 302.0824.



1c

3-(phenylsulfinyl)-1-tosyl-1H-indole (1c):

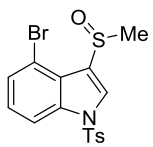
Following the general procedure, the title compound was prepared from corresponding sulfide (1.90 g, 5.0 mmol) and it was obtained as white solid, m.p. 151-154 ℃, 1.54 g, 78% yield. (Rf = 0.46, eluent: PE/EtOAc = 1/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (d, *J* = 0.8 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.67 (m, 2H), 7.51 – 7.45 (m, 3H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.1, 143.0, 135.6, 134.5, 131.2, 130.4, 129.4, 128.7, 127.3, 126.1, 125.9, 125.1, 124.7, 124.3, 120.6, 113.9, 21.8.

IR (neat): 3130, 1596, 1528, 1474, 1443, 1370, 1262, 1178, 1039, 814.

HRMS (ESI-TOF): calculated for [$C_{21}H_{17}NO_3S_2Na$ ($M + Na^+$)]: 418.0542, found: 418.0544.



1d

4-bromo-3-(methylsulfinyl)-1-tosyl-1H-indole (1d):

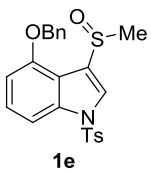
Following the general procedure, the title compound was prepared from corresponding sulfide (1.98 g, 5.0 mmol) and it was obtained as white solid, m.p. 140-142 ℃, 1.83 g, 89% yield. (Rf = 0.32, eluent: PE/EtOAc = 1/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.19 (m, 3H), 2.99 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.2, 136.8, 134.4, 130.4, 128.4, 127.79, 127.78, 127.3, 126.7, 126.5, 113.3, 113.1, 45.4, 21.8.

IR (neat): 3041, 2920, 1597, 1561, 1517, 1410, 1369, 1288, 1168, 1051, 813, 741, 696.

HRMS (ESI-TOF): calculated for [$C_{16}H_{14}BrNO_3S_2Na$ ($M + Na^+$)]: 433.9491, found: 433.9486.



1e

4-(benzyloxy)-3-(methylsulfinyl)-1-tosyl-1H-indole (1e):

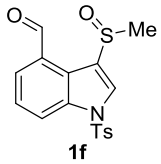
Following the general procedure, the title compound was prepared from corresponding sulfide (847.1 mg, 2.0 mmol) and it was obtained as white solid, m.p. 175-177 ℃, 747.2 mg, 86% yield. (Rf = 0.34, eluent: PE/EtOAc = 1/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.37 (m, 4H), 7.30 (t, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 3.8 Hz, 3H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.13 (q, *J* = 11.3 Hz, 2H), 2.76 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 151.8, 145.8, 137.3, 135.8, 134.7, 130.2, 128.9, 128.5, 127.7, 127.3, 127.1, 127.0, 125.0, 116.4, 107.4, 105.4, 70.7, 43.7, 21.8.

IR (neat): 3094, 3028, 1583, 1490, 1426, 1372, 1268, 1098, 1056, 1017, 815, 707, 661.

HRMS (ESI-TOF): calculated for [$C_{23}H_{21}NO_4S_2Na$ ($M + Na^+$)]: 462.0804, found: 462.0810.



1f

3-(methylsulfinyl)-1-tosyl-1H-indole-4-carbaldehyde (1f):

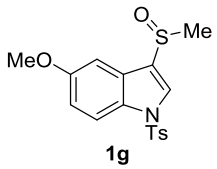
Following the general procedure, the title compound was prepared from corresponding sulfide (1.24 g, 3.59 mmol) and it was obtained as white solid, m.p. 201-203 ℃, 920.3 mg, 71% yield. (Rf = 0.58, eluent: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.43 (s, 1H), 8.42 – 8.37 (m, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 6.8 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.86 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 192.2, 146.3, 137.1, 134.4, 132.1, 130.9, 130.4, 129.5, 128.9, 127.3, 125.4, 121.9, 120.8, 46.0, 21.8.

IR (neat): 3119, 2843, 1691, 1596, 1568, 1509, 1370, 1093, 1036, 827, 788, 659.

HRMS (ESI-TOF): calculated for [$C_{17}H_{15}NO_4S_2Na$ ($M + Na^+$)]: 384.0335, found: 384.0337.



1g

5-methoxy-3-(methylsulfinyl)-1-tosyl-1H-indole (1g):

Following the general procedure, the title compound was prepared from corresponding sulfide (1.29 g, 3.70 mmol) and it was obtained as white solid, m.p. 89-91 ℃, 1.27 g, 95% yield. (Rf = 0.29, eluent: EtOAc)

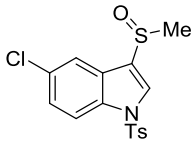
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 – 7.88 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.04 – 7.00 (m, 1H), 3.83 (s, 3H), 2.98 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.9, 145.9, 134.5, 130.3, 130.1, 127.1, 126.8, 126.7, 124.5, 115.6, 115.1, 102.1, 55.9, 41.4, 21.7.

IR (neat): 3130, 3106, 1592, 1525, 1471, 1377, 1305, 1218, 1166, 1025, 810, 765.

HRMS (ESI-TOF): calculated for [$C_{17}H_{17}NO_4S_2Na$ ($M + Na^+$)]: 386.0491, found: 386.0496

5-chloro-3-(methylsulfinyl)-1-tosyl-1H-indole (1h):



1h

Following the general procedure, and the title compound was prepared from corresponding sulfide (3.41 g, 9.70 mmol) and it was obtained as white solid, m.p. 141-142 ℃, 2.99 g, 84% yield. (Rf = 0.18, eluent: PE/EtOAc = 1/1)

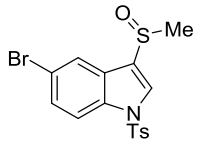
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.81 – 7.76 (m, 3H), 7.38 – 7.35 (m, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.97 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.4, 134.3, 133.9, 130.5, 130.3, 127.5, 127.2, 126.9, 126.5, 124.4, 119.9, 115.3, 41.8, 21.8.

IR (neat): 3125, 3093, 1594, 1572, 1494, 1442, 1375, 1288, 1031, 800, 752.

HRMS (ESI-TOF): calculated for [$C_{16}H_{14}ClNO_3S_2Na$ ($M + Na^+$)]: 389.9996, found: 389.9997.

5-bromo-3-(methylsulfinyl)-1-tosyl-1H-indole (1i):



1i

Following the general procedure, the title compound was prepared from corresponding sulfide (1.98 g, 5.0 mmol) and it was obtained as white solid, m.p. 134-136 ℃, 1.68 g, 81% yield. (Rf = 0.16, eluent: PE/EtOAc = 1/1)

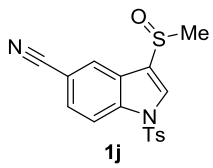
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (s, 2H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 3.00 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.2, 134.1, 134.0, 130.3, 129.0, 127.23, 127.17, 127.06, 124.2, 122.8, 117.7, 115.4, 41.6, 21.6.

IR (neat): 3124, 3093, 1593, 1566, 1494, 1439, 1375, 1287, 1030, 819, 737.

HRMS (ESI-TOF): calculated for [$C_{16}H_{14}BrNO_3S_2Na$ ($M + Na^+$)]: 433.9491, found: 433.9492.

3-(methylsulfinyl)-1-tosyl-1H-indole-5-carbonitrile (1j):



1j

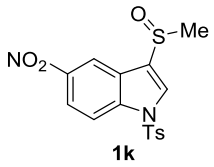
Following the general procedure, the title compound was prepared from corresponding sulfide (2.75 g, 8.03 mmol) and it was obtained as white solid, m.p. 180-182 ℃, 2.76 g, 96% yield. (Rf = 0.29, eluent: EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, *J* = 0.8 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 8.07 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.64 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.99 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.9, 137.1, 133.9, 130.6, 129.0, 128.1, 127.3, 125.9, 125.2, 125.0, 118.6, 115.1, 108.1, 42.0, 21.8.

IR (neat): 3131, 2915, 2223, 1597, 1569, 1494, 1454, 1381, 1291, 1168, 1028, 810, 767, 672.

HRMS (ESI-TOF): calculated for [$C_{17}H_{14}N_2O_3S_2Na$ (M + Na^+)]: 381.0338, found: 381.0342.



1k

3-(methylsulfinyl)-5-nitro-1-tosyl-1H-indole (1k):

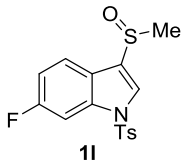
Following the general procedure, the title compound was prepared from corresponding sulfide (1.47 g, 4.05 mmol) and it was obtained as light yellow solid, m.p. 200-202 ℃, 1.44 g, 94% yield. (Rf = 0.44, eluent: EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.30 (d, *J* = 7.7 Hz, 1H), 8.20 – 8.08 (m, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.02 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.0, 144.5, 138.3, 133.9, 130.7, 129.0, 127.4, 126.2, 125.7, 121.2, 116.6, 114.6, 42.2, 21.8.

IR (neat): 3126, 2916, 1610, 1597, 1515, 1440, 1383, 1334, 1286, 1030, 814, 732.

HRMS (ESI-TOF): calculated for [$C_{16}H_{14}N_2O_5S_2Na$ (M + Na^+)]: 401.0236, found: 401.0230.



1l

6-fluoro-3-(methylsulfinyl)-1-tosyl-1H-indole (1l):

Following the general procedure, the title compound was prepared from corresponding sulfide (1.68 g, 5.0 mmol) and it was obtained as white solid, m.p. 170-172 ℃, 1.53 g, 87% yield. (Rf = 0.26, eluent: EtOAc)

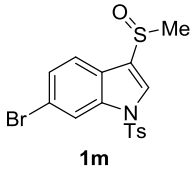
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.68 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.09 – 7.05 (m, 1H), 2.96 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.4 (d, *J* = 245.0 Hz), 146.3, 135.9 (d, *J* = 12.4 Hz), 134.2, 130.5, 127.2, 126.5 (d, *J* = 3.7 Hz), 124.8, 122.1 (d, *J* = 1.7 Hz), 121.2 (d, *J* = 10.0 Hz), 113.0 (d, *J* = 24.5 Hz), 101.6 (d, *J* = 28.5 Hz), 41.6, 21.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -113.33 (s).

IR (neat): 3134, 3090, 1581, 1479, 1375, 1287, 1213, 1172, 1101, 1040, 818, 761, 642.

HRMS (ESI-TOF): calculated for [$C_{16}H_{14}FNO_3S_2Na$ (M + Na^+)]: 374.0291, found: 374.0293.



1m

6-bromo-3-(methylsulfinyl)-1-tosyl-1H-indole (1m):

Following the general procedure, the title compound was prepared from

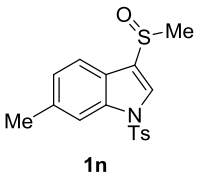
corresponding sulfide (1.61 g, 4.05 mmol) and it was obtained as white solid, m.p. 134-136 ℃, 1.57 g, 94% yield. (Rf = 0.38, eluent: EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, *J* = 1.3 Hz, 1H), 7.92 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.94 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.4, 136.1, 134.2, 130.5, 127.7, 127.2, 126.5, 125.0, 124.6, 121.2, 119.9, 117.2, 41.7, 21.7.

IR (neat): 3129, 3002, 2913, 1596, 1526, 1494, 1445, 1382, 1270, 1138, 1027, 800, 730, 666.

HRMS (ESI-TOF): calculated for [$C_{16}H_{14}BrNO_3S_2Na$ (M + Na^+)]: 433.9491, found: 433.9487.



1n

6-methyl-3-(methylsulfinyl)-1-tosyl-1H-indole (1n):

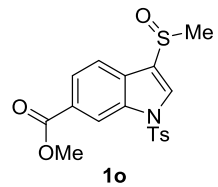
Following the general procedure, the title compound was prepared from corresponding sulfide (1.66 g, 5.0 mmol) and it was obtained as white solid, m.p. 151-153 ℃, 1.48 g, 85% yield. (Rf = 0.37, eluent: EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.84 – 7.77 (m, 3H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 1H), 2.95 (s, 3H), 2.49 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.9, 136.5, 136.0, 134.7, 130.3, 127.1, 125.8, 125.7, 125.0, 123.4, 119.6, 114.2, 41.6, 22.1, 21.7.

IR (neat): 3168, 2920, 1593, 1530, 1487, 1447, 1367, 1266, 1168, 1063, 1037, 815, 794, 671.

HRMS (ESI-TOF): calculated for [$C_{17}H_{17}NO_3S_2Na$ (M + Na^+)]: 370.0542, found: 370.0546.



1o

methyl 3-(methylsulfinyl)-1-tosyl-1H-indole-6-carboxylate(1o):

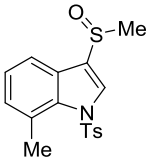
Following the general procedure, the title compound was prepared from corresponding sulfide (1.88 g, 5.0 mmol) and it was obtained as white solid, m.p. 162-163 ℃, 1.62 g, 83% yield. (Rf = 0.35, eluent: EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.10 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.79 (m, 3H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.97 (s, 3H), 2.98 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 146.3, 134.9, 134.1, 130.4, 129.1, 128.8, 127.8, 127.2, 125.1, 124.9, 119.8, 115.7, 52.5, 41.6, 21.6.

IR (neat): 3149, 2986, 2948, 1712, 1595, 1515, 1496, 1383, 1288, 1172, 1027, 812, 766, 666.

HRMS (ESI-TOF): calculated for [$C_{18}H_{17}NO_5S_2Na$ (M + Na^+)]: 414.0440, found: 414.0447.



1p

7-methyl-3-(methylsulfinyl)-1-tosyl-1H-indole (1p):

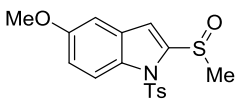
Following the general procedure, the title compound was prepared from corresponding sulfide (663.0 mg, 2.0 mmol) and it was obtained as white solid, m.p. 112-114 ℃, 498.2 mg, 72% yield. (Rf = 0.41, eluent: EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.26 – 7.24 (m, 2H), 7.20 – 7.16 (m, 1H), 7.09 – 7.06 (m, 1H), 2.99 (s, 3H), 2.49 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.5, 136.2, 135.4, 130.2, 129.50, 129.46, 127.6, 126.6, 125.4, 124.6, 123.9, 117.7, 41.3, 21.7, 21.6.

IR (neat): 3157, 2922, 2851, 1593, 1547, 1459, 1361, 1294, 1171, 1051, 815, 775.

HRMS (ESI-TOF): calculated for [$C_{17}H_{17}NO_3S_2Na$ ($M + Na^+$)]: 370.0542, found: 370.0548.



1r

5-methoxy-2-(methylsulfinyl)-1-tosyl-1H-indole (1r):

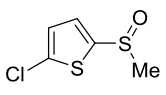
Following the general procedure, the title compound was prepared from corresponding sulfide (1.67 g, 4.80 mmol) and it was obtained as white solid, m.p. 202-204 ℃, 1.31 g, 75% yield. (Rf = 0.30, eluent: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 9.1 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.24 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.03 – 6.92 (m, 2H), 3.79 (s, 3H), 3.11 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.2, 145.9, 144.7, 133.8, 133.2, 130.13, 130.11, 127.0, 115.8, 115.3, 113.7, 103.9, 55.7, 45.4, 21.7.

IR (neat): 3001, 1595, 1526, 1492, 1464, 1357, 1299, 1063, 1027, 886, 695.

HRMS (ESI-TOF): calculated for [$C_{17}H_{17}NO_4S_2Na$ ($M + Na^+$)]: 386.0491, found: 386.0497.



1u

2-chloro-5-(methylsulfinyl)thiophene (1u):

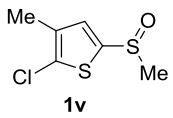
Following the general procedure, the title compound was prepared from corresponding sulfide (749.3 mg, 4.55 mmol) and it was obtained as colorless oil, 557.4 mg, 68% yield. (Rf = 0.31, eluent: PE/EtOAc = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 3.9 Hz, 1H), 6.89 (d, *J* = 3.9 Hz, 1H), 2.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.4, 136.0, 128.8, 126.5, 44.3.

IR (neat): 3072, 2995, 2910, 1636, 1518, 1414, 1296, 1209, 1038, 796, 680.

HRMS (ESI-TOF): calculated for [$C_5H_5ClOS_2Na$ (M + Na^+)]: 202.9363, found: 202.9366.



1v

2-chloro-3-methyl-5-(methylsulfinyl)thiophene (1v):

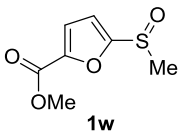
Following the general procedure, the title compound was prepared from corresponding sulfide (1.82 g, 10.2 mmol), and it was obtained as white solid, m.p. 181-183 ℃, 1.60 g, 81% yield. (Rf = 0.34, eluent: PE/EtOAc = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, 1H), 2.87 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 143.0, 135.3, 131.2, 131.0, 44. 5, 13.8.

IR (neat): 3035, 2999, 2980, 2903, 1552, 1414, 1383, 1303, 1206, 1014, 881, 691.

HRMS (ESI-TOF): calculated for [$C_6H_7ClOS_2Na$ (M + Na^+)]: 216.9519, found: 216.9518.



1w

methyl 5-(methylsulfinyl)furan-2-carboxylate (1w):

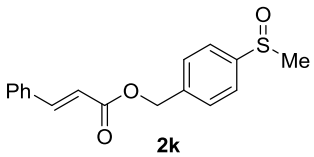
Following the general procedure, the title compound was prepared from corresponding sulfide (986.7 mg, 5.73 mmol) and it was obtained as white solid, m.p. 168-170 ℃, 937.8 mg, 87% yield. (Rf = 0.39, eluent: EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (d, *J* = 3.6 Hz, 1H), 7.02 (d, *J* = 3.6 Hz, 1H), 3.91 (s, 3H), 2.99 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.4, 157.4, 147.6, 118.5, 115.3, 52.5, 39.8.

IR (neat): 3118, 2993, 2964, 2915, 2852, 1716, 1577, 1479, 1436, 1122, 1035, 760, 691.

HRMS (ESI-TOF): calculated for [$C_7H_8O_4SNa$ (M + Na^+)]: 211.0036, found: 211.0038.



2k

4-(methylsulfinyl)benzyl cinnamate (2k):

Following the general procedure, the title compound was prepared from corresponding sulfide (853.1 mg, 3.0 mmol) and it was obtained as white solid, m.p. 80-82 ℃, 839.2 mg, 93% yield. (Rf = 0.22, eluent: PE/EtOAc = 1/1)

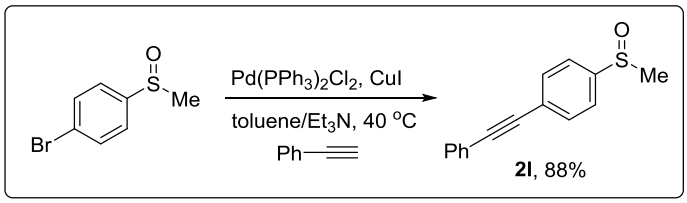
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 16.0 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.51 (m, 2H), 7.41 – 7.37 (m, 3H), 6.49 (d, *J* = 16.0 Hz, 1H), 5.30 (s, 2H), 2.73 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 145.8, 145.7, 139.5, 134.3, 130.7, 129.1, 128.3, 123.9, 117.5, 65.5, 44.1. One aromatic carbon peak is overlapped.

IR (neat): 3025, 2982, 2903, 1705, 1634, 1577, 1490, 1447, 1389, 1311, 1160, 1040, 770.

HRMS (ESI-TOF): calculated for [$C_{17}H_{16}O_3SNa$ ($M + Na^+$)]: 323.0712, found: 323.0716.

1-(methylsulfinyl)-4-(phenylethynyl)benzene (2l):



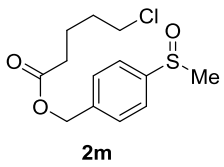
Air was removed from a solution of 1-bromo-4-(methylsulfinyl)benzene (219 mg, 1.0 mmol) and ethynylbenzene (110 μL, 1.0 mmol) in toluene/Et_3N (4:1, 20 mL) by blowing N_2 for 20 min. then CuI (3.8 mg, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol) were added. The mixture was stirred at 60 ℃ for 16 h. After evaporation of the solvents, the residue was purified by flash column chromatography on silica gel to give the title compound **2l** as a yellow solid, m.p. 117-118 ℃, 210.3 mg, 88% yield. (Rf = 0.27, eluent: PE/EtOAc = 1/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 – 7.66 (m, 2H), 7.64 – 7.62 (m, 2H) 7.57 – 7.52 (m, 2H), 7.41 – 7.34 (m, 3H), 2.76 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.5, 132.3, 131.7, 128.8, 128.4, 126.2, 123.5, 122.5, 91.5, 88.1, 43.9.

IR (neat): 3060, 2987, 2903, 2218, 1588, 1491, 1444, 1358, 1306, 1174, 1038, 827, 756.

HRMS (ESI-TOF): calculated for [$C_{15}H_{12}OSNa$ ($M + Na^+$)]: 263.0501, found: 263.0504.



2m

4-(methylsulfinyl)benzyl 4-chlorobutanoate (2m):

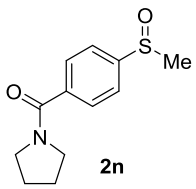
Following the general procedure, the title compound was prepared from corresponding sulfide (905.7 mg, 3.32 mmol) and it was obtained as white solid, m.p. 35-36 ℃, 880.3 mg, 92% yield. (Rf = 0.26, eluent: PE/EtOAc = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.05 (s, 2H), 3.43 –3.39 (m, 2H), 2.60 (s, 3H), 2.34 –2.27 (m, 2H), 1.71 – 1.65 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.4, 145.3, 138.9, 128.6, 123.5, 65.0, 44.2, 43.6, 32.9, 31.4, 21.8.

IR (neat): 2988, 2950, 2909, 2877, 1725, 1495, 1446, 1350, 1292, 1170, 1031, 817, 728.

HRMS (ESI-TOF): calculated for [$C_{13}H_{17}ClO_3SNa$ ($M + Na^+$)]: 311.0479, found: 311.0485.



2n

(4-(methylsulfinyl)phenyl)(pyrrolidin-1-yl)methanone (2n):

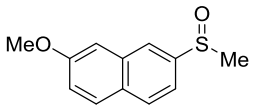
Following the general procedure, the title compound was prepared from corresponding sulfide (947.2 mg, 4.28 mmol) and it was obtained as white solid, m.p.109-111 ℃, 994.7 mg, 98% yield. (Rf = 0.57, eluent: DCM/MeOH = 9/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 4H), 3.75 – 3.65 (m, 2H), 3.48 – 3.31 (m, 2H), 2.72 (s, 3H), 2.03 – 1.82 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 147.5, 140.0, 128.2, 123.7, 77.4, 49.6, 44.0.

IR (neat): 2970, 2875, 1715, 1618, 1595, 1496, 1432, 1294, 1081, 1042, 830, 758, 697.

HRMS (ESI-TOF): calculated for [$C_{12}H_{15}NO_2SNa$ ($M + Na^+$)]: 260.0716, found: 260.0724.



2u

2-methoxy-7-(methylsulfinyl)naphthalene (2u):

Following the general procedure, the title compound was prepared from corresponding sulfide (1.21 g, 5.90 mmol) and it was obtained as white solid, m.p. 102-104 ℃, 720.1 mg, 55% yield. (Rf = 0.36, eluent: EtOAc)

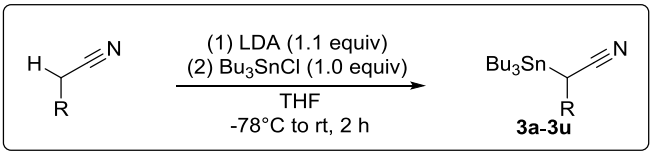
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.24 – 7.21 (m, 1H), 7.19 (d, *J* = 2.3 Hz, 1H), 3.91 (s, 3H), 2.77 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.7, 143.3, 134.4, 129.9, 129.5, 129.3, 122.7, 120.7, 117.3, 106.3, 55.5, 43.9.

IR (neat): 2994, 2935, 2909, 1622, 1594, 1504, 1451, 1383, 1130, 1023, 837, 695.

HRMS (ESI-TOF): calculated for [$C_{12}H_{12}O_2SNa$ ($M + Na^+$)]: 243.0450, found: 243.0451.

General procedure for the synthesis of α-stannyl nitrile 3



3a-3u

The synthesis of α-stannyl nitrile **3** was performed following the reported procedure[10]: To the

solution of (*i*-Pr)$_2$NH (1.54 mL, 11 mmol) in THF (10 mL) was added *n*-BuLi (4.4 mL, 2.5 M in hexane) slowly at -78 ℃. After stirring for 10 min, a solution of nitrile (10 mmol) in THF (7 mL) was added dropwise to the mixture at –78 ℃. The mixture was then stirred for 5min. After that, to the mixture was added a solution of Bu_3SnCl (2.7 mL, 10 mmol) in THF (6 mL) dropwise. After stirring for 1 h, the mixture was warmed to room temperature for another 1 h. The solvent was removed under vacuum, and the residue was diluted in petroleum ether (50 mL), filtered, concentrated, and purified by flash chromatography on Biotage Isolera Prime flash system with silica gel column (unless otherwise noted, gradient 0-5% EtOAc/PE, flow rate 50 mL/min).

[10] W. Qin, S. Long, A. Bongini and M. Panunzio, *Eur. J. Org. Chem*., 2015, 3495.

3a

2-(tributylstannyl)acetonitrile (3a):

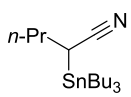
Following the general procedure, the title compound was obtained as light yellow oil, 1.82 g, 55% yield. (Rf = 0.18, eluent: PE/EtOAc = 100/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.61– 1.48 (m, 6H), 1.44 (s, 2H), 1.37– 1.28 (m, 6H), 1.16 – 1.02 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 122.1, 28.8, 27.3, 13.7, 10.6, 8.4.

IR (neat): 2955, 2920, 2871, 2851, 2217, 2181, 1465, 1376, 738.

HRMS (ESI-TOF): calculated for [$C_{14}H_{30}NSn$ ($M + H^+$)]: 332.1394, found: 332.1389.



3b

2-(tributylstannyl)pentanenitrile (3b):

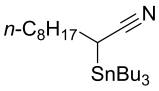
Following the general procedure, the title compound was prepared from pentanenitrile (40 mmol) and it was obtained as light yellow oil, 11.91 g, 80% yield. (Rf = 0.21, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.95-1.83 (m, 1H), 1.75 – 1.66 (m, 1H), 1.62 – 1.47 (m, 8H), 1.47 – 1.39 (m, 1H), 1.37-1.27(m, 6H), 1.15 – 0.99 (m, 6H), 0.99-0.85 (m, 12H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 125.0, 31.1, 28.9, 27.4, 24.1, 13.8, 13.5, 10.1, 9.3.

IR (neat): 2923, 2853, 2205, 1463, 1340, 744.

HRMS (ESI-TOF): calculated for [$C_{17}H_{36}NSn$ ($M + H^+$)]: 374.1864, found: 374.1885.



3c

2-(tributylstannyl)decanenitrile (3c):

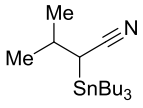
Following the general procedure, the title compound was obtained as light yellow oil, 2.39 g, 54% yield. (Rf = 0.24, eluent: PE/EtOAc = 100/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.94 – 1.81 (m, 1H), 1.75 – 1.66 (m, 1H), 1.62 – 1.45 (m, 8H), 1.37 – 1.20 (m, 17H), 1.14 – 1.00 (m, 6H), 0.96 – 0.84 (m, 12H).

^{13}C NMR (151 MHz, $CDCl_3$): 125.0, 31.9, 30.9, 29.4, 29.3, 29.03, 29.01, 28.9, 27.4, 22.8, 14.2, 13.7, 10.1, 9.5.

IR (neat): 2955, 2922, 2852, 2206, 1463, 1376, 722.

HRMS (ESI-TOF): calculated for [$C_{22}H_{46}NSn$ (M + H)]: 444.2647, found: 444.2643.



3d

3-methyl-2-(tributylstannyl)butanenitrile (3d):

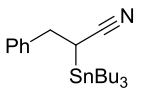
Following the general procedure, the title compound was obtained as light yellow oil, 2.08 g, 56% yield. (Rf = 0.18, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.06 – 1.95 (m, 1H), 1.93 – 1.81 (m, 1H), 1.60 – 1.45 (m, 6H), 1.39 – 1.29 (m, 6H), 1.13 – 1.02 (m, 12H), 0.91 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 123.6, 28.9, 28.5, 27.4, 24.2, 22.8, 19.8, 13.7, 10.7.

IR (neat): 2955, 2923, 2852, 2820, 2204, 1463, 1368, 1290, 1194, 1105, 840.

HRMS (ESI-TOF): calculated for [$C_{17}H_{36}NSn$ (M + H^+)]: 374.1864, found: 374.1863.



3e

3-phenyl-2-(tributylstannyl)propanenitrile (3e):

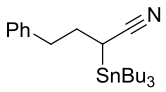
Following the general procedure, the title compound was obtained as light yellow oil, 1.85 g, 44% yield. (Rf = 0.29, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 – 7.29 (m, 2H), 7.28 – 7.22 (m, 3H), 3.09 – 2.96 (m, 1H), 2.97 – 2.86 (m, 1H), 2.22 – 2.09 (m, 1H), 1.60 – 1.44 (m, 6H), 1.38 – 1.29 (m, 6H), 1.12 – 0.98 (m, 6H), 0.91 (t, *J* = 7.3 Hz 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.5, 128.9, 128.3, 127.1, 124.5, 35.1, 28.8, 27.4, 13.7, 12.0, 10.3.

IR (neat): 2920, 2851, 2206, 1602, 1495, 1455, 698, 746.

HRMS (ESI-TOF): calculated for [$C_{21}H_{36}NSn$ (M + H)]: 422.1864, found: 422.1872.



3f

4-phenyl-2-(tributylstannyl)butanenitrile (3f):

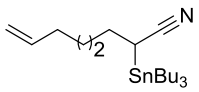
Following the general procedure, the title compound was obtained as light yellow oil, 938.3 mg, 22% yield. (Rf = 0.18, eluent: PE/EtOAc = 100/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.19 (m, 3H), 2.99 – 2.90 (m, 1H), 2.76 – 2.68 (m, 1H), 2.10 – 1.98 (m, 1H), 1.94 – 1.79 (m, 2H), 1.60 – 1.45 (m, 6H), 1.37 – 1.28 (m, 6H), 1.15 – 1.01 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.6, 128.67, 128.66, 126.4, 124.6, 36.8, 31.0, 28.8, 27.4, 13.7, 10.2, 8.8.

IR (neat): 2921, 2851, 2206, 1604, 1496, 1375, 745, 725.

HRMS (ESI-TOF): calculated for [$C_{22}H_{38}NSn$ ($M + H^+$)]: 436.2020, found: 436.2024.



3g

2-(tributylstannyl)oct-7-enenitrile (3g):

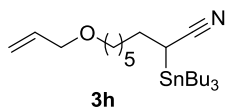
Following the general procedure, the title compound was obtained as light yellow oil, 2.43 g, 59% yield. (Rf = 0.35, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.83 – 5.74 (m, 1H), 5.03 – 4.90 (m, 2H), 2.10 – 2.01 (m, 2H), 1.93 – 1.81 (m, 1H), 1.76 – 1.65 (m, 1H), 1.62-1.48 (m, 8H), 1.47 – 1.36 (m, 3H), 1.36 – 1.28 (m, 6H), 1.14 – 0.99 (m, 6H), 0.90 (t, *J* = 7.3Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.6, 124.9, 114.8, 33.6, 30.4, 28.90, 28.88, 28.3, 27.4, 13.7, 10.2, 9.5.

IR (neat): 3076, 2923, 2853, 2205, 1640, 1457, 1340, 909, 746.

HRMS (ESI-TOF): calculated for [$C_{20}H_{40}NSn$ ($M + H^+$)]: 414.2177, found: 414.2163.



3h

8-(allyloxy)-2-(tributylstannyl)octanenitrile (3h):

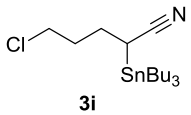
Following the general procedure, the title compound was obtained as light yellow oil, 3.20 g, 68% yield. (Rf = 0.33, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.95 – 5.85 (m, 1H), 5.30 – 5.13 (m, 2H), 3.97 (d, *J* = 5.6 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 1.92 – 1.80 (m, 1H), 1.75 – 1.65 (m, 1H), 1.62 – 1.46 (m, 10H), 1.45 – 1.26 (m, 11H), 1.15 – 0.98 (m, 6H), 0.92 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 135.1, 124.9, 116.8, 71.9, 70.4, 30.9, 29.8, 28.94, 28.90, 28.86, 27.4, 26.1, 13.7, 10.1, 9.5.

IR (neat): 3062, 2926, 2853, 2205, 1647, 1457, 1104, 919, 726.

HRMS (ESI-TOF): calculated for [$C_{20}H_{41}NOSn$ [(M-C_3H_5) + H^+]]: 416.2334, found: 416.2311.



3i

5-chloro-2-(tributylstannyl)pentanenitrile (3i):

Following the general procedure, the title compound was obtained as light yellow oil, 1.91 g, 47% yield. (Rf = 0.33, eluent: PE/EtOAc = 20/1)

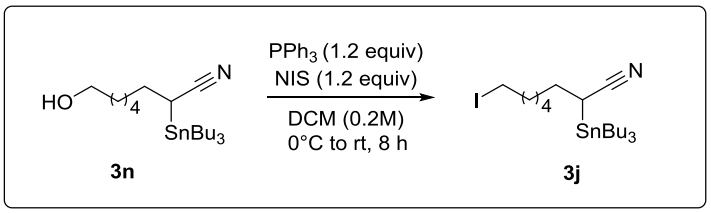
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.65 – 3.52 (m, 2H), 2.09 – 2.00 (m, 1H), 1.94 – 1.86 (m, 2H), 1.85 – 1.77 (m, 2H), 1.60 – 1.48 (m, 6H), 1.37 – 1.29 (m, 6H), 1.15 – 1.04 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 124.4, 43.9, 33.0, 28.8, 27.4, 26.0, 13.7, 10.2, 8.4.

IR (neat): 2921, 2852, 2205, 1457, 1376, 746, 669.

HRMS (ESI-TOF): calculated for [$C_{17}H_{34}ClNSnNa$ (M + Na^+)]: 430.1294, found: 430.1266.

8-iodo-2-(tributylstannyl)octanenitrile (3j):



3n **3j**

The synthesis of *α*-stannyl nitriles **3j** was conducted following the reported procedure.[11]

To the mixture of 8-hydroxy-2-(tributylstannyl)octanenitrile **3n** (1.29 g, 3 mmol) and PPh_3 (944 mg, 3.6 mmol) in DCM (0.2 M) was added NIS (810 mg, 3.6 mmol) in small portions at 0 ℃. After that, the reaction mixture was allowed to warm to room temperature and stirred for 8 h. The solvent was removed under vacuum, and the residue was dissolved in petroleum ether (10 mL), filtered, concentrated, and purified by flash chromatography on Biotage Isolera Prime flash system with silica gel column (gradient 0-2% EtOAc/PE, flow rate 25 mL/min). The title compound was obtained as light yellow oil, 761.6 mg, 47% yield. (Rf = 0.47, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.21 (t, *J* = 6.9 Hz, 2H), 2.37 (t, *J* = 7.1 Hz, 2H), 1.91 – 1.82 (m, 2H), 1.74 – 1.54 (m, 9H), 1.52 – 1.41 (m, 4H), 1.41– 1.29 (m, 9H), 1.18 – 1.07 (m, 3H), 1.01 – 0.86 (m, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 119.9, 33.3, 30.3, 28.9, 28.6, 27.8, 27.4, 25.4, 17.3, 13.8, 10.2,

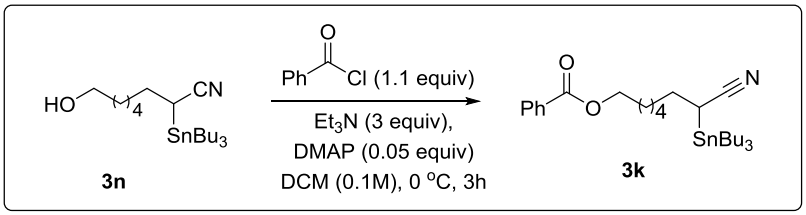
7.1.

IR (neat): 2927, 2855, 2157, 1458, 1375, 734, 502.

HRMS (ESI-TOF): calculated for [$C_{20}H_{41}INSn$ ($M + H^+$)]: 542.1300, found: 542.1300.

[11] R. Lagoutte, I. Šebesta, P. Jiroš, B. Kalinová, A. Jirošová, J. Straka, K. Černá, J. Šobotník, J. Cvačka and U. Jahn, *Chem. Eur. J.*, 2013, **26**, 8515.

7-cyano-7-(tributylstannyl)heptyl benzoate (3k):



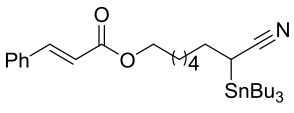
To the solution of 8-hydroxy-2-(tributylstannyl) octanenitrile **3n** (1.29g, 3 mmol), Et_3N (1.25 mL, 9 mmol) and DMAP (18 mg, 0.15 mmol) in DCM (30 mL) was added acyl chloride (1.1 equiv) dropwise at 0 ℃. The mixture was stirred at 0 ℃ for 3 h, after which the mixture was treated with $NaHCO_3$ (sat., 20 mL) solution and extracted by DCM (20 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting mixture was purified by flash chromatography on Biotage Isolera Prime flash system with silica gel column (gradient 0-20% EtOAc/PE, flow rate 50 mL/min). The title compound was obtained as light yellow oil, 1.06 g, 66 % yield. (Rf = 0.26, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 – 8.01 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 1.93 – 1.81 (m, 1H), 1.80 – 1.67 (m, 3H), 1.64 – 1.49 (m, 8H), 1.49 – 1.41 (m, 4H), 1.39 – 1.27 (m, 7H), 1.14 – 0.99 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 132.9, 130.5, 129.6, 128.4, 124.9, 65.0, 30.8, 28.9, 28.8, 28.73, 28.67, 27.4, 25.9, 13.7, 10.1, 9.5.

IR (neat): 2927, 2854, 2205, 1718, 1602, 1585, 1492, 1452, 1272, 712.

HRMS (ESI-TOF): calculated for [$C_{27}H_{46}NO_2Sn$ ($M + H^+$)]: 536.2545, found: 536.2538.



3l

7-cyano-7-(tributylstannyl)heptyl cinnamate (3l):

Following a similar procedure for synthesis of **3k**, the title compound

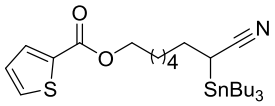
was obtained as light yellow oil, 1.18 g, 70% yield. (Rf = 0.50, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.42 – 7.35 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 1.94 – 1.81 (m, 1H), 1.77 – 1.65 (m, 3H), 1.63 – 1.48 (m , 8H), 1.48 – 1.37 (m, 4H), 1.37 – 1.29 (m, 7H), 1.15 – 1.00 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2, 144.8, 134.5, 130.4, 129.0, 128.2, 124.9, 118.3, 64.6, 30.9, 28.93, 28.86, 28.74, 28.68, 27.4, 25.9, 13.7, 10.1, 9.5.

IR (neat): 2925, 2853, 2205, 1711, 1637, 1540, 1377, 1165, 767.

HRMS (ESI-TOF): calculated for [$C_{29}H_{48}NO_2Sn$ ($M + H^+$)]: 562.2702, found: 562.2704.



3m

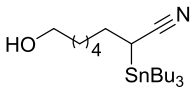
7-cyano-7-(tributylstannyl)heptyl thiophene-2-carboxylate(3m): Following a similar procedure for synthesis of **3k**, the title compound was obtained as light yellow oil, 1.13 g, 70% yield. (Rf = 0.38, eluent: PE/EtOAc = 15/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 – 7.60 (m, 1H), 7.56 – 7.50 (m, 1H), 7.11 – 7.05 (m, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 1.93 – 1.80 (m, 1H), 1.78 – 1.68 (m, 3H), 1.62 – 1.47 (m, 8H), 1.46 – 1.38 (m, 4H), 1.38 – 1.28 (m, 7H), 1.14 – 0.99 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.4, 134.1, 133.3, 132.3, 127.8, 124.9, 65.1, 30.8, 28.9, 28.8, 28.7, 28.6, 27.3, 25.8, 13.7, 10.1, 9.5.

IR (neat): 2926, 2854, 2205, 1732, 1463, 1418, 1145, 735, 691.

HRMS (ESI-TOF): calculated for [$C_{25}H_{44}NO_2SSn$ ($M + H^+$)]: 542.2109, found: 542.2132.



3n

8-hydroxy-2-(tributylstannyl)octanenitrile (3n): Following the general procedure, 2.2 equiv of LDA was used in the reaction, and the flash chromatography gradient was 0-30% EtOAc/PE. The title compound was obtained as yellow green oil, 2.62 g, 61% yield. (Rf = 0.26, eluent: PE/EtOAc = 3/1)

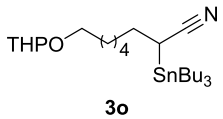
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.62 (dd, *J* = 12.0, 6.5 Hz, 2H), 1.92 – 1.80 (m, 1H), 1.74 – 1.62 (m, 1H), 1.61 – 1.49 (m, 10H), 1.44 – 1.26 (m, 11H), 1.16 – 0.98 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 125.0, 62.9, 32.7, 30.9, 28.90, 28.85, 28.80, 27.4, 25.6, 13.7,

10.1, 9.5.

IR (neat): 3366, 2925, 2853, 2248, 2206, 1463, 1376, 1060, 725.

HRMS (ESI-TOF): calculated for [$C_{20}H_{42}NOSn$ (M + H^+)]: 432.2283, found: 432.2282.



3o

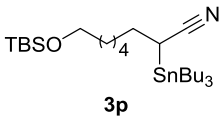
8-((tetrahydro-2H-pyran-2-yl)oxy)-2-(tributylstannyl)octanenitrile (3o): Following the general procedure, the title compound was obtained as light yellow oil, 3.19 g, 62% yield. (Rf = 0.41, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.59 – 4.53 (m, 1H), 3.88 – 3.82 (m, 1H), 3.75 – 3.69 (m, 1H), 3.53 – 3.46 (m, 1H), 3.40 – 3.33 (m, 1H), 1.92 – 1.76 (m, 2H), 1.74 – 1.67 (m, 2H), 1.62 – 1.45 (m, 14H), 1.44 – 1.27 (m, 11H), 1.13 – 0.98(m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 125.0, 99.0, 67.6, 62.47, 30.90, 30.86, 29.8, 28.94, 28.89, 28.86, 27.4, 26.2, 25.6, 19.8, 13.7, 10.1, 9.5.

IR (neat): 2924, 2853, 2205, 1456, 1352, 1022, 772.

HRMS (ESI-TOF): calculated for [$C_{25}H_{50}NO_2Sn$ (M + H^+)]: 516.2858, found: 516.2855.



3p

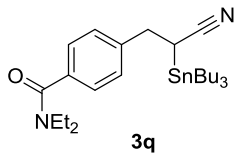
8-((tert-butyldimethylsilyl)oxy)-2-(tributylstannyl)octanenitrile (3p): Following the general procedure, the title compound was obtained as light yellow oil, 2.56 g, 47% yield. (Rf = 0.41, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.60 (t, *J* = 6.5 Hz, 2H), 1.93 – 1.80 (m, 1H), 1.76 – 1.64 (m, 1H), 1.60 – 1.47 (m, 10H), 1.45 – 1.38 (m, 1H), 1.37 – 1.27 (m, 10H), 1.14 – 0.99 (m, 6H), 0.94 – 0.85 (m, 18H), 0.04 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 125.0, 63.3, 32.9, 31.0, 29.0, 28.90, 28.89, 27.4, 26.1, 25.8, 18.5, 13.8, 10.2, 9.6, -5.1.

IR (neat): 2926, 2854, 2206, 1462, 1253, 1094, 773.

HRMS (ESI-TOF): calculated for [$C_{26}H_{56}NOSiSn$ (M + H^+)]: 546.3148, found: 546.3151.



3q

4-(2-cyano-2-(tributylstannyl)ethyl)-N,N-diethylbenzamide (3q): Following the general procedure, the flash chromatography gradient was 0-30% EtOAc/PE. The title compound was obtained as light yellow oil,

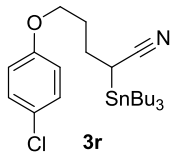
1.61 g, 31% yield. (Rf = 0.23, eluent: PE/EtOAc = 3/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.51 (d, *J* = 5.6 Hz, 2H), 3.22 (d, *J* = 5.3 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.44 (m, 6H), 1.34 – 1.26 (m, 6H), 1.24 – 1.03 (m, 10H), 0.98 – 0.92 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 170.9, 139.1, 136.3, 128.4, 126.9, 119.0, 43.3, 39.3, 31.4, 27.9, 27.2, 19.2, 13.7, 10.3.

IR (neat): 2245, 2205, 1620, 1513, 1425, 1286, 729

HRMS (ESI-TOF): calculated for [$C_{26}H_{45}N_2OSn$ (M + H^+)]: 521.2548, found: 521.2559



3r

5-(4-chlorophenoxy)-2-(tributylstannyl)pentanenitrile (3r):

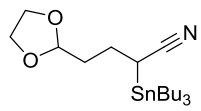
Following the general procedure, the flash chromatography gradient was 0-30% EtOAc/PE. The title compound was obtained as light yellow oil, 2.49 g, 50% yield. (Rf = 0.29, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 – 7.20 (m, 2H), 6.83 – 6.78 (m, 2H), 4.03 – 3.90 (m, 2H), 2.13 – 2.01 (m, 1H), 1.99 – 1.78 (m, 4H), 1.62 – 1.47 (m, 6H), 1.38 – 1.29 (m, 6H), 1.16-1.03 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.5, 129.4, 125.7, 124.6, 115.8, 66.9, 30.2, 28.8, 27.4, 25.6, 13.7, 10.2, 8.9.

IR (neat): 2205, 1596, 1581, 1491, 1465, 1376, 1241, 1169, 823.

HRMS (ESI-TOF): calculated for [$C_{23}H_{39}ClNOSn$ (M + H^+)]: 500.1737, found: 500.1741.



3s

4-(1,3-dioxolan-2-yl)-2-(2-iodophenyl)butanenitrile (3s):

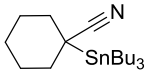
Following the general procedure, the flash chromatography gradient was 0-20% EtOAc/PE. The title compound was obtained as light yellow oil, 2.23 g, 52% yield. (Rf = 0.21, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.87 (t, *J* = 4.3 Hz, 1H), 4.00 – 3.90 (m, 2H), 3.90 – 3.79 (m, 2H), 1.99 – 1.86 (m, 2H), 1.85 – 1.68 (m, 3H), 1.61 – 1.43 (m, 6H), 1.37 – 1.27 (m, 6H), 1.19 – 0.98 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 124.6, 103.6, 65.1, 65.0, 34.7, 28.8, 27.4, 23.4, 13.7, 10.1, 9.3.

IR (neat): 2920, 2852, 2248, 2206, 1457, 1376, 1139, 768.

HRMS (ESI-TOF): calculated for [$C_{19}H_{38}NO_2Sn$ ($M + H^+$)]: 432.1919, found: 432.1920.



3t

1-(tributylstannyl)cyclohexane-1-carbonitrile (3t):

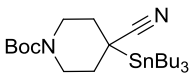
Following the general procedure, the title compound was obtained as light yellow oil, 3.19 g, 80% yield. (Rf = 0.47, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.97 (d, *J* = 13.0 Hz, 2H), 1.77 – 1.63 (m, 3H), 1.63 – 1.45 (m, 10H), 1.36 – 1.20 (m, 7H), 1.11 – 0.97 (m, 6H), 0.89 (t, *J* = 7.4 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 126.7, 33.0, 28.9, 27.5, 26.2, 24.2, 22.3, 13.7, 9.3.

IR (neat): 2924, 2852, 2195, 1447, 800.

HRMS (ESI-TOF): calculated for [$C_{19}H_{38}NSn$ ($M + H^+$)]: 400.2021, found: 400.2028.



3u

tert-butyl 4-cyano-4-(tributylstannyl)piperidine-1-carboxylate (3u):

Following the general procedure, the flash chromatography gradient was 0-30% EtOAc/PE. The title compound was obtained as light yellow oil, 4.06 g, 81% yield. (Rf = 0.39, eluent: PE/EtOAc = 5/1)

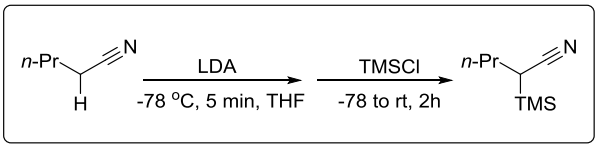
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.14 – 3.85 (m, 2H), 3.13 – 2.92 (m, 2H), 1.91 – 1.84 (m, 2H), 1.74 – 1.63 (m, 2H), 1.58 – 1.47 (m, 6H), 1.43 (s, 9H), 1.35 – 1.27 (m, 6H), 1.13 – 1.00 (m, 6H), 0.88 (t, *J* = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.8, 125.3, 79.9, 32.0, 28.9, 28.5, 27.5, 19.6, 13.7, 9.5, 8.0.

IR (neat): 2955, 2852, 2194, 1693, 1417, 1634, 1340, 1240, 1168, 1131.

HRMS (ESI-TOF): calculated for [$C_{23}H_{44}N_2O_2SnK$ ($M + K^+$)]: 539.2056, found: 539.2083.

2-(trimethylsilyl)pentanenitrile (3w):



To a solution of (i-Pr)$_2$NH (1.54 mL, 11 mmol) in THF (10 mL) was added *n*-BuLi (2.5 M, 4.4 mL) slowly at -78 °C. After stirring for 10 min, a solution of pentanenitrile (2.1 mL，10 mmol) in THF (7.0 mL) was added dropwise to the mixture at -78 ℃. The mixture was stirred for 5 min. Then a solution of TMSCl (1.0 mL, 12 mmol) in THF (6.0 mL) was added dropwise. After that,

the mixture was stirred at -78 ℃ for 1 h, then allowed to warm to room temperature. The reaction mixture was then stirred under room temperature for 1 h. After that, the solvent was removed under vacuum, and the residue was dissolved in petroleum ether (50 mL), filtered, concentrated, and purified by flash chromatography on Biotage Isolera Prime flash system with silica gel column (gradient 0-2% EtOAc/PE, flow rate 50 mL/min). The title compound was obtained as yellow oil, 1.5 g, 97% yield. (Rf = 0.38, eluent: PE/EtOAc = 40/1)

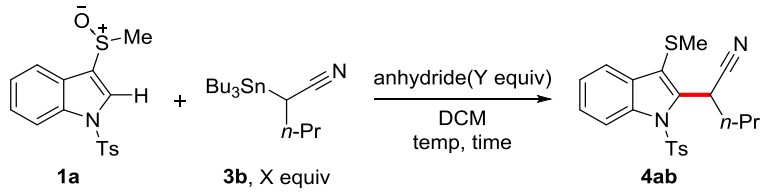
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76 – 1.69 (m, 1H), 1.69 – 1.57 (m, 1H), 1.57 – 1.31 (m, 3H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.13 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 122.2, 28.7, 23.0, 18.6, 13.3, -3.3.

IR (neat): 2959, 2874, 2219, 1465, 1381, 1252.

MS (EI): calculated for [$C_7H_{14}NSi$ (M – CH_3)]: 140.1, found: 140.1.

3 Optimization of reaction conditions

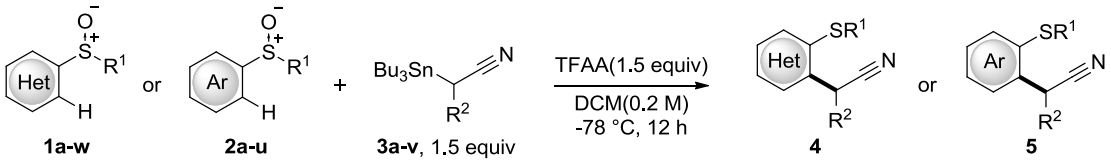


entry	anhydride	X equiv	temp(℃)	con.	time	yield (%)[a]
1	Tf_2O(1.5)	1.5	-78	0.2 M	12 h	trace
2	Ms_2O(1.5)	1.5	-78 to rt	0.2 M	12 h	trace [c]
3	Ts_2O(1.5)	1.5	-78 to rt	0.2 M	12 h	trace [c]
4	Ac_2O(1.5)	1.5	-78 to rt	0.2 M	12 h	0[c]
5	TFAA(1.5)	1.5	-78	0.2 M	12 h	90[b]
6	TFAA(1.5)	1.5	-100	0.2 M	12 h	80
7	TFAA(1.5)	1.5	-60	0.2 M	12 h	60
8	TFAA(1.5)	1.0	-78	0.2 M	12 h	69
9	TFAA(1.5)	1.2	-78	0.2 M	12 h	75
10	TFAA(1.5)	2.0	-78	0.2 M	12 h	94
11	TFAA(1.5)	1.5	-78	0.2 M	5 h	66
12	TFAA(1.5)	1.5	-78	0.2 M	24 h	90
13	TFAA(1.5)	1.5	-78	0.5 M	12 h	87
14	TFAA(1.5)	1.5	-78	0.1 M	12 h	90

[a] Isolated yield. [b]0.5 mmol of **1a** was used. [c]59% of **1a** (Ms_2O), 31% of 1a (Ts_2O) and 98% of **1a** (Ac_2O) were recovered, respectively.

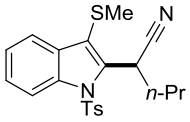
General procedure for optimization of reaction conditions: To a mixture of aryl sulfoxide **1a** (0.2 mmol) and α-stannyl nitrile **3b** in DCM was added anhydride under the indicated temperature. After stirring for the indicated time, to the mixture was added sat. aqueous $NaHCO_3$ (3 mL). The mixture was then extracted with DCM (3 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting mixture was purified by silica gel chromatography affording desired product **4ab**.

4 General procedure for *ortho* C-H cyanoalkylation of aryl(heteroaryl) sulfoxide 1 and 2



1a-w **2a-u** **3a-v**, 1.5 equiv **4** **5**

General procedure: To a mixture of aryl sulfoxide **1** or **2** (0.5 mmol) and α-stannyl nitrile **3** (0.75 mmol) in DCM (2.5 mL) was added TFAA (104 μL, 0.75 mmol) under -78 ℃. After stirring for 12 h, to the mixture was added sat. aqueous $NaHCO_3$ (3 mL). The mixture was then extracted with DCM (3 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting mixture was purified by silica gel chromatography affording α-aryl(heteroaryl) nitrile **4** or **5**.



4ab

2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4ab):

Following the general procedure, the title compound was obtained as white solid, m.p. 87-89 ℃, 179.2 mg, 90% yield. (Rf = 0.27, eluent: PE/EtOAc =10/1)

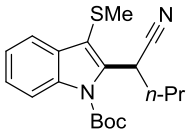
Following the general procedure, when **1a** (10 mmol) was used in this reaction, **4ab** was obtained 3.3 g, 83% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.66 (m, 3H), 7.42 – 7.38 (m, 1H), 7.35 – 7.32 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.25 (dd, *J* = 9.2, 6.2 Hz, 1H), 2.37 – 2.31 (m, 7H), 1.99 – 1.87 (m, 1H), 1.74 – 1.63 (m, 1H), 1.53 – 1.42 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.8, 137.0, 136.6, 135.0, 130.6, 130.3, 126.6, 126.2, 124.6, 119.8, 119.3, 118.7, 115.7, 36.0, 28.8, 21.7, 21.0, 18.3, 13.5.

IR (neat): 3125, 2980, 2964, 2925, 2865, 2239, 1647, 1593, 1448, 1372, 1165, 812, 747, 669.

HRMS (ESI-TOF): calculated for [$C_{21}H_{22}N_2O_2S_2Na$ ($M + Na^+$)]: 421.1015, found: 421.1020.



4bb

tert-butyl-2-(1-cyanobutyl)-3-(methylthio)-1H-indole-1-carboxylate (4bb):

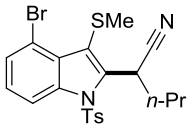
Following the general procedure, the title compound was obtained as colorless oil, 103.4 mg, 60% yield. (Rf = 0.31, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.35 – 7.32 (m, 1H), 5.25 (dd, *J* = 8.9, 6.5 Hz, 1H), 2.36 (s, 3H), 2.34 – 2.26 (m, 1H), 1.95 – 1.89 (m, 1H), 1.75 (s, 9H), 1.69 – 1.63 (m, 1H), 1.54 – 1.45 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 149.7, 137.0, 136.0, 129.7, 125.7, 123.6, 119.60, 119.58, 116.12, 116.07, 86.0, 35.0, 29.6, 28.3, 20.9, 18.7, 13.6.

IR (neat): 2963, 2928, 2874, 2242, 1735, 1450, 1369, 1310, 1152, 1127, 1102, 841, 758, 729.

HRMS (ESI-TOF): calculated for [$C_{19}H_{24}N_2O_2SNa$ ($M + Na^+$)]: 367.1451, found: 367.1456.



4db

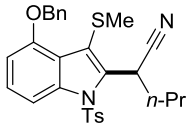
2-(4-bromo-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4db): Following the general procedure, the title compound was obtained as white solid, m.p. 102-104 ℃, 203.5 mg, 85% yield. (Rf = 0.23, eluent: PE/EtOAc = 20/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.19 (t, *J* = 8.2 Hz, 1H), 5.38 (t, *J* = 8.0 Hz, 1H), 2.43– 2.32 (m, 7H), 1.98 – 1.83 (m, 1H), 1.80 – 1.64 (m, 1H), 1.57 – 1.43 (m, 1H), 1.01 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.2, 139.9, 137.8, 134.6, 130.3, 129.9, 127.7, 126.6, 126.5, 119.1, 118.5, 114.7, 114.5, 35.9, 28.9, 21.7, 21.3, 20.9, 13.4.

IR (neat): 2985, 2964, 2920, 2870, 2237, 1595, 1460, 1375, 1361, 1158, 1087, 775, 743, 663.

HRMS (ESI-TOF): calculated for [$C_{21}H_{21}BrN_2O_2S_2Na$ ($M + Na^+$)]: 499.0120, found: 499.0115.



4eb

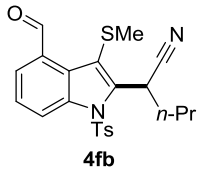
2-(4-(benzyloxy)-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4eb): Following the general procedure, the title compound was obtained as white solid, m.p. 110-112 ℃, 154.3 mg, 61% yield. (Rf = 0.33, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 6.4 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.42– 7.39 (m, 2H), 7.36– 7.33 (m, 1H), 7.31–7.27 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 5.37 – 5.29 (m, 1H), 5.22 – 5.17 (m, 2H), 2.41 – 2.31 (m, 4H), 2.28 (s, 3H), 2.01 – 1.91 (m, 1H), 1.74 – 1.64 (m, 1H), 1.53 – 1.43 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 153.0, 145.7, 138.4, 136.5, 135.7, 134.9, 130.1, 128.6, 128.0, 127.2, 126.8, 126.6, 120.2, 119.5, 118.1, 108.5, 106.6, 70.6, 35.9, 28.8, 21.7, 20.9, 19.9, 13.5.

IR (neat): 3056, 2960, 2929, 2860, 2237, 1597, 1453, 1370, 1350, 1264, 1113, 1074, 775, 734, 659.

HRMS (ESI-TOF): calculated for [$C_{28}H_{28}N_2O_3S_2Na$ (M + Na^+)]: 527.1434, found: 527.1439.



4fb

2-(4-formyl-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4fb):

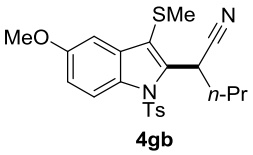
Similar to the general procedure, the reaction was performed in MeCN at -40 ℃ for 12 h, the title compound was obtained as white solid, m.p. 144-146 ℃, 189.2 mg, 89% yield. (Rf = 0.23, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.52 (s, 1H), 8.48 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.68 (s, 2H), 7.50 – 7.45 (m, 1H), 7.27 (d, 2H), 5.42 – 5.30 (m, 1H), 2.43 – 2.31 (m, 7H), 1.99 – 1.86 (m, 1H), 1.80 – 1.69 (m, 1H), 1.57 – 1.43 (m, 1H), 1.02 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 191.1, 146.5, 140.8, 137.3, 134.6, 130.6, 130.5, 130.0, 126.7, 125.7, 124.0, 121.0, 118.8, 116.8, 35.9, 28.9, 21.8, 21.1, 19.0, 13.4.

IR (neat): 2959, 2928, 2870, 2341, 1672, 1590, 1456, 1375, 1362, 1240, 1182, 1092, 792, 661.

HRMS (ESI-TOF): calculated for [$C_{22}H_{22}N_2O_3S_2Na$ (M + Na^+)]: 449.0964, found: 449.0972.



4gb

2-(5-methoxy-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4gb):

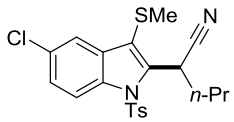
Following the general procedure, the title compound was obtained as white solid, m.p. 95-97 ℃, 206.2 mg, 96% yield. (Rf = 0.24, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 9.1 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.99 (dd, *J* = 9.1, 2.6 Hz, 1H), 5.23 (dd, *J* = 9.2, 6.3 Hz, 1H), 3.85 (s, 3H), 2.34 – 2.28 (m, 7H), 1.99 – 1.85 (m, 1H), 1.72 – 1.59 (m, 1H), 1.53 – 1.38 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.3, 145.7, 137.7, 134.8, 131.8, 130.9, 130.1, 126.5, 119.2, 118.7, 116.8, 115.2, 101.7, 55.7, 35.9, 28.7, 21.6, 20.8, 18.1, 13.4.

IR (neat): 2961, 2927, 2870, 2233, 1595, 1462, 1372, 1206, 1149, 1064, 865, 809, 661.

HRMS (ESI-TOF): calculated for [$C_{22}H_{24}N_2O_3S_2Na$ (M + Na^+)]: 451.1121, found: 451.1116.



4hb

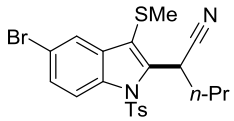
2-(5-chloro-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4hb): Following the general procedure, the title compound was obtained as white solid, m.p. 126-128 ℃, 175.7 mg, 81% yield. (Rf = 0.23, eluent: PE/EtOAc = 20/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.9 Hz, 1H), 7.73 – 7.58 (m, 3H), 7.37 – 7.32 (m, 1H), 7.26 (d, 2H), 5.22 (dd, *J* = 9.2, 6.1 Hz, 1H), 2.37 – 2.29 (m, 7H), 2.00 – 1.82 (m, 1H), 1.76 – 1.62 (m, 1H), 1.57 – 1.40 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.1, 138.5, 134.8, 134.7, 131.9, 130.6, 130.3, 126.5, 126.4, 119.4, 118.8, 117.9, 116.8, 35.9, 28.7, 21.7, 20.9, 18.2, 13.4.

IR (neat): 2981, 2962, 2928, 2870, 2233, 1609, 1595, 1446, 1372, 1350, 1084, 813, 767, 667.

HRMS (ESI-TOF): calculated for [$C_{21}H_{21}ClN_2O_2S_2Na$ ($M + Na^+$)]: 455.0625, found: 455.0629.



4ib

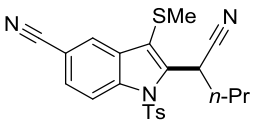
(2-(5-bromo-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4ib): Following the general procedure, the title compound was obtained as white solid, m.p. 116-118 ℃, 203.4 mg, 85% yield. (Rf = 0.20, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.7 Hz, 1H), 7.79 (s, 1H), 7.66 (d, *J* = 6.4 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.20 (dd, *J* = 8.8, 6.3 Hz, 1H), 2.38 – 2.29 (m, 7H), 1.96 – 1.84 (m, 1H), 1.74 – 1.63 (m, 1H), 1.52 – 1.39 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.2, 138.4, 135.3, 134.7, 132.4, 130.4, 129.1, 126.6, 122.5, 118.9, 118.3, 117.9, 117.2, 36.0, 28.8, 21.8, 21.0, 18.4, 13.4.

IR (neat): 3069, 2979, 2956, 2929, 2868, 2235, 1596, 1445, 1381, 1193, 1156, 1076, 812, 764, 665.

HRMS (ESI-TOF): calculated for [$C_{21}H_{21}BrN_2O_2S_2Na$ ($M + Na^+$)]: 499.0120, found: 499.0119.



4jb

2-(3-(methylthio)-5-nitro-1-tosyl-1H-indol-2-yl)pentanenitrile (4jb): Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min and then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 125-127 ℃, 201.6 mg, 95% yield. (Rf = 0.18, eluent: PE/EtOAc = 10/1)

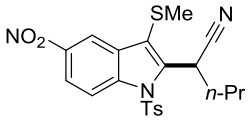
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.6 Hz, 1H), 8.01 (s, 1H), 7.69 (d, *J* = 6.8 Hz, 2H),

7.64 (d, *J* = 8.7 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.19 (dd, *J* = 9.3, 6.0 Hz, 1H), 2.38 (s, 3H), 2.36 – 2.29 (m, 4H), 1.94 – 1.83 (m, 1H), 1.74 – 1.66 (m, 1H), 1.53 – 1.42 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.7, 139.6, 138.2, 134.6, 130.8, 130.6, 129.0, 126.6, 124.7, 118.9, 118.6, 117.9, 116.5, 108.3, 35.9, 28.8, 21.8, 21.0, 18.4, 13.4.

IR (neat): 3070, 2974, 2936, 2873, 2234, 1609, 1595, 1446, 1372, 1350, 1084, 809.

HRMS (ESI-TOF): calculated for [$C_{22}H_{21}N_3O_2S_2Na$ (M + Na^+)]: 446.0967, found: 446.0960.



4kb

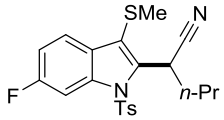
2-(1-cyanobutyl)-3-(methylthio)-1-tosyl-1H-indole-5-carbonitrile (4kb): Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min and then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 142-144 ℃, 189.1 mg, 85% yield. (Rf = 0.28, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.33 – 8.32 (m, 1H), 8.28 – 8.26 (m, 1H), 7.70 (s, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.20 (dd, *J* = 8.7, 6.2 Hz, 1H), 2.39 – 2.36 (m, 7H), 1.97 – 1.84 (m, 1H), 1.77 – 1.64 (m, 1H), 1.55 – 1.42 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.8, 144.9, 140.3, 139.2, 134.4, 130.8, 130.6, 126.6, 121.0, 118.7, 118.4, 115.9, 115.9, 35.8, 28.8, 21.7, 20.9, 18.5, 13.3.

IR (neat): 3087, 2969, 2922, 2864, 2236, 1596, 1444, 1382, 1347, 1196, 1160, 815, 735, 661.

HRMS (ESI-TOF): calculated for [$C_{21}H_{21}N_3O_4S_2Na$ (M + Na^+)]: 466.0866, found: 466.0870.



4lb

2-(6-fluoro-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4lb): Following the general procedure, the title compound was obtained as white solid, 156.8 mg, m.p. 102-104 ℃, 75% yield. (Rf = 0.31, eluent: PE/EtOAc = 10/1)

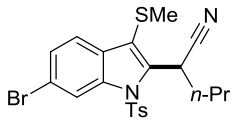
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (d, *J* = 9.3 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.60 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.11 – 7.07 (m, 1H), 5.19 (dd, *J* = 9.3, 6.1 Hz, 1H), 2.36 – 2.29 (m, 7H), 1.95 – 1.85 (m, 1H), 1.72 – 1.62 (m, 1H), 1.52 – 1.41 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.7 (d, *J* = 243.5 Hz), 146.1, 137.2 (d, *J* = 3.4 Hz), 136.6 (d, *J* = 12.6 Hz), 134.8, 130.3, 126.7, 126.6, 120.7 (d, *J* = 9.8 Hz), 119.0, 118.3, 113.0 (d, *J* = 24.3 Hz), 103.1 (d, *J* = 29.4 Hz), 35.9, 28.8, 21.7, 20.9, 18.2, 13.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -113.91 (s).

IR (neat): 3123, 2982, 2926, 2869, 2238, 1592, 1376, 1358, 1295, 1170, 1133, 812, 662, 634.

HRMS (ESI-TOF): calculated for [$C_{21}H_{21}FN_2O_2S_2Na$ (M + Na^+)]: 439.0921, found: 439.0923.



4mb

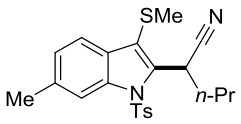
2-(6-bromo-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4mb): Following the general procedure, the title compound was obtained as white solid, m.p. 125-127 ℃, 174.5 mg, 73% yield. (Rf =0.18, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.27 (d, *J* = 9.4 Hz, 2H), 5.17 (dd, *J* = 9.3, 6.1 Hz, 1H), 2.36 (s, 3H), 2.33 – 2.26 (m, 4H), 1.96 – 1.81 (m, 1H), 1.73 – 1.61 (m, 1H), 1.53 – 1.40 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.2, 137.4, 137.1, 134.7, 130.4, 129.4, 127.9, 126.6, 120.9, 119.9, 118.8, 118.6, 118.4, 35.9, 28.7, 21.7, 20.9, 18.3, 13.4.

IR (neat): 3116, 2978, 2957, 2925, 2872, 2240, 1593, 1454, 1377, 1359, 1294, 1162, 1087, 814, 747, 661.

HRMS (ESI-TOF): calculated for [$C_{21}H_{21}BrN_2O_2S_2Na$ (M + Na^+)]: 499.0120, found: 499.0119.



4nb

2-(6-methyl-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4nb): Following the general procedure, the title compound was obtained as white solid, m.p. 150-151 ℃, 147.2 mg, 71% yield. (Rf = 0.32, eluent: PE/EtOAc = 10/1)

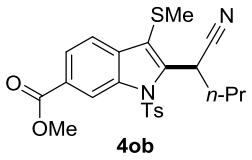
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 5.21 (dd, *J* = 9.0, 6.3 Hz, 1H), 2.51 (s, 3H), 2.36 – 2.27 (m, 7H), 1.96 – 1.88 (m, 1H), 1.72 – 1.61 (m, 1H), 1.52 – 1.41 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 137.0, 136.5, 136.1, 135.1, 130.2, 128.2, 126.5, 126.1,

119.4, 119.3, 118.8, 115.7, 36.0, 28.8, 22.2, 21.7, 20.9, 18.2, 13.4.

IR (neat): 3032, 2978, 2958, 2923, 2868, 2238, 1593, 1541, 1458, 1371, 1358, 1299, 1168, 1089, 812, 663, 635.

HRMS (ESI-TOF): calculated for [$C_{22}H_{24}N_2O_2S_2Na$ (M + Na^+)]: 435.1171, found: 435.1175.



4ob

methyl-2-(1-cyanobutyl)-3-(methylthio)-1-tosyl-1H-indole-6-carboxylate (4ob):

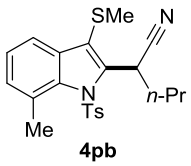
Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min and then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 153-155 ℃, 210.6 mg, 92% yield. (Rf = 0.22, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.01 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.68 – 7.71 (m, 3H), 7.24 (d, *J* = 8.3 Hz, 2H), 5.24 (dd, *J* = 9.4, 6.0 Hz, 1H), 3.96 (s, 3H), 2.35 – 2.29 (m, 7H), 1.95 – 1.87 (m, 1H), 1.74 – 1.63 (m, 1H), 1.52 – 1.42 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.9, 146.2, 139.9, 135.9, 134.7, 134.1, 130.3, 127.9, 126.6, 125.5, 119.5, 118.7, 118.2, 117.3, 52.4, 35.8, 28.8, 21.7, 20.9, 18.2, 13.3.

IR (neat): 2956, 2926, 2867, 2238, 1717, 1596, 1535, 1432, 1375, 1286, 1246, 1167, 1091, 767, 739, 661.

HRMS (ESI-TOF): calculated for [$C_{23}H_{24}N_2O_4S_2Na$ (M + Na^+)]: 479.1070, found: 479.1071.



4pb

2-(7-methyl-3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4pb):

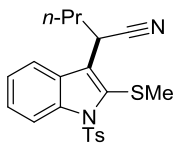
Following the general procedure, the title compound was obtained as white solid, m.p. 79-81 ℃, 140.3 mg, 68% yield. (Rf = 0.26, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.20 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 2H), 4.89 (dd, *J* = 9.2, 6.4 Hz, 1H), 2.72 (s, 3H), 2.28 (s, 3H), 2.25 – 2.16 (m, 1H), 2.07 (s, 3H), 1.94 – 1.86 (m, 1H), 1.67 – 1.55 (m, 1H), 1.48 – 1.37 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.2, 141.7, 139.7, 134.9, 131.9, 130.6, 130.1, 129.0, 127.0, 126.2, 125.9, 119.4, 117.5, 36.0, 30.7, 21.6, 21.4, 20.9, 17.6, 13.4.

IR (neat): 2988, 2966, 2939, 2867, 2239, 1593, 1445, 1368, 1342, 1288, 1154, 1084, 795, 762, 660.

HRMS (ESI-TOF): calculated for [$C_{22}H_{24}N_2O_2S_2Na$ ($M + Na^+$)]: 435.1171, found: 435.1173.



4qb

2-(2-(methylthio)-1-tosyl-1H-indol-3-yl)pentanenitrile (4qb):

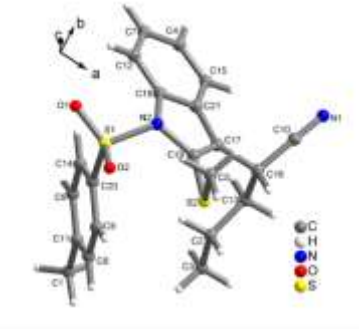
Simlar to general procedure, MeCN instead of DCM was used and the reaction was performed at -40 ℃ for 12 h. The title compound was obtained as white solid, m.p. 104-106 ℃, 197.8 mg, 99% yield. (Rf = 0.20, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.5 Hz, 1H), 7.75 (t, *J* = 8.4 Hz, 3H), 7.45 – 7.42 (m, 1H), 7.36 – 7.31 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 4.44 (t, *J* = 7.9 Hz, 1H), 2.49 (s, 3H), 2.35 (s, 3H), 2.11 – 2.01 (m, 1H), 1.79 – 1.69 (m, 1H), 1.46 – 1.36 (m, 1H), 1.31 – 1.20 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.3, 138.4, 135.7, 131.0, 129.8, 127.2, 126.9, 126.6, 125.0, 124.2, 120.1, 119.6, 116.0, 35.6, 28.5, 21.73, 21.70, 20.6, 13.4.

IR (neat): 2962, 2925, 2874, 2239, 1595, 1490, 1440, 1364, 1302, 1186, 1085, 752, 723, 669, .

HRMS (ESI-TOF): calculated for [$C_{21}H_{22}N_2O_2S_2$ Na ($M + Na^+$)]: 421.1015, found: 421.1016.



4qb

Single crystals of product **4qb** was obtained through slow evaporation at room temperature of a solution in ethyl acetate – dichloromethane.

Bond precision:	C-C = 0.0031 A		Wavelength=0.71073
Cell:	a=9.0286(6)	b=24.0830(16)	c=10.3285(7)
	alpha=90	beta=114.965(3)	gamma=90
Temperature:	296 K		
	Calculated		Reported

Volume	2036.0(2)	2036.0(2)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C21 H22 N2 O2 S2	C21 H22 N2 O2 S2
Sum formula	C21 H22 N2 O2 S2	C21 H22 N2 O2 S2
Mr	398.53	398.53
Dx,g cm-3	1.300	1.300
Z	4	4
Mu (mm-1)	0.280	0.280
F000	840.0	840.0
F000'	841.29	
h,k,lmax	11,31,13	11,31,13
Nref	4619	4618
Tmin,Tmax	0.925,0.956	0.925,0.956
Tmin'	0.925	

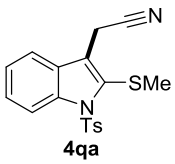
Correction method= # Reported T Limits: Tmin=0.925 Tmax=0.956 AbsCorr = EMPIRICAL

Data completeness= 1.000 Theta(max)= 27.360

R(reflections)= 0.0439(3954) wR2(reflections)= 0.1287(4618)

S = 1.065 Npar= 244

For more details please see the CIF file attached with ESI. The crystal data of **4qb** has already been deposited at Cambridge Crystallographic Data Center, UK, and the CCDC reference number is 1822813.



4qa

2-(2-(methylthio)-1-tosyl-1H-indol-3-yl)acetonitrile (4qa):

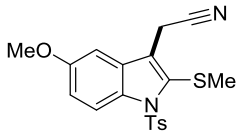
Simlar to general procedure, MeCN instead of DCM was used and the reaction was performed at -40 ℃ for 12 h. The title compound was obtained as white solid, m.p. 135-137 ℃, 154.6 mg, 87% yield. (Rf = 0.18, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.6 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.93 (s, 2H), 2.48 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.3, 137.9, 135.8, 131.5, 129.8, 127.5, 127.3, 126.8, 124.2, 119.9, 119.0, 116.9, 115.6, 21.7, 21.4, 14.3.

IR (neat): 3064, 2921, 2850, 2249, 1594, 1492, 1440, 1370, 1306, 1230, 1177, 813, 742.

HRMS (ESI-TOF): calculated for [$C_{18}H_{16}N_2O_2S_2Na$ ($M + Na^+$)]: 379.0545, found: 379.0534



4ra

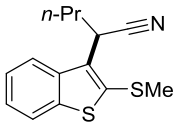
2-(5-methoxy-2-(methylthio)-1-tosyl-1H-indol-3-yl)acetonitrile (4ra): Simlar to general procedure, MeCN instead of DCM was used and the reaction was performed at -40 ℃ for 12 h. The title compound was obtained as white solid, m.p. 181-183 ℃, 155.1 mg, 80% yield. (Rf = 0.31, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.06 (dd, *J* = 9.2, 2.5 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 1H), 3.89 (s, 2H), 3.86 (s, 3H), 2.48 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.9, 145.3, 135.6, 132.4, 132.0, 129.8, 128.5, 127.2, 119.6, 116.9, 116.8, 116.0, 100.8, 55.8, 21.7, 21.4, 14.4.

IR (neat): 2925, 2849, 2248, 1611, 1595, 1453, 1371, 1339, 1291, 1217, 1178, 813, 742.

HRMS (ESI-TOF): calculated for [$C_{19}H_{18}N_2O_3S_2Na$ ($M + Na^+$)]: 409.0651, found: 409.0650.



4sb

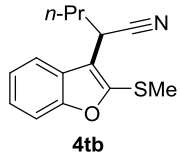
2-(2-(methylthio)benzo[b]thiophen-3-yl)pentanenitrile (4sb): Simlar to general procedure, MeCN instead of DCM and $(ClF_2CCO)_2O$ instead of TFAA were used, the reaction was performed at -40 ℃ for 12 h. The title compound was obtained as colorless oil, 95.3 mg, 73% yield. (Rf = 0.26, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.39 – 7.35 (m, 1H), 4.58 (t, *J* = 8.0 Hz, 1H), 2.55 (s, 3H), 2.25 – 2.13 (m, 1H), 1.94 – 1.83 (m, 1H), 1.62 – 1.52 (m, 1H), 1.49 – 1.38 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.5, 136.9, 136.8, 130.8, 125.1, 124.9, 122.5, 122.2, 120.0, 35.3, 29.9, 21.2, 20.8, 13.5.

IR (neat): 2958, 2924, 2871, 2237, 1459, 1425, 1381, 1313, 1261, 1121, 1099, 959, 750, 729.

HRMS (ESI-TOF): calculated for [$C_{14}H_{15}NS_2Na$ ($M + Na^+$)]: 284.0538, found: 284.0538.



4tb

2-(2-(methylthio)benzofuran-3-yl)pentanenitrile (4tb):

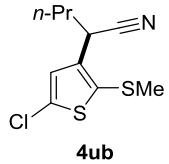
Simlar to general procedure, MeCN instead of DCM and $(ClF_2CCO)_2O$ instead of TFAA were used, the reaction was performed at -40 ℃ for 12 h. The title compound was obtained as colorless oil, 75.9 mg, 62% yield. (Rf = 0.26, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 – 7.69 (m, 1H), 7.49 – 7.45 (m, 1H), 7.36 – 7.32 (m, 1H), 7.31 – 7.27 (m, 1H), 4.15 (t, *J* = 7.8 Hz, 1H), 2.52 (s, 3H), 2.15 – 2.07 (m, 1H), 1.94 – 1.86 (m, 1H), 1.56 – 1.41 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.8, 148.7, 126.3, 125.4, 123.4, 119.9, 119.6, 117.6, 111.5, 35.7, 28.0, 20.6, 17.8, 13.4.

IR (neat): 2960, 2928, 2873, 2239, 1565, 1446, 1381, 1338, 1272, 1227, 1132, 1092, 744, 671.

HRMS (ESI-TOF): calculated for [$C_{14}H_{15}NOSNa$ ($M + Na^+$)]: 268.0767, found: 268.0769.



4ub

2-(5-chloro-2-(methylthio)thiophen-3-yl)pentanenitrile (4ub):

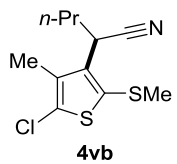
Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min and then -60 ℃ for 12 h. The title compound was obtained as colorless oil, 84.7 mg, 69% yield. (Rf = 0.22, eluent: PE/EtOAc = 20/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (s, 1H), 4.18 (dd, *J* = 8.4, 6.9 Hz, 1H), 2.39 (s, 3H), 1.98 – 1.83 (m, 1H), 1.79 – 1.66 (m, 1H), 1.58 – 1.36 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.6, 132.5, 131.8, 125.9, 120.2, 36.6, 30.6, 22.6, 20.4, 13.4.

IR (neat): 3086, 2960, 2924, 2873, 2239, 1530, 1464, 1419, 1387, 1314, 1184, 826, 732.

HRMS (ESI-TOF): calculated for [$C_{10}H_{12}ClNS_2Na$ ($M + Na^+$)]: 267.9992, found: 267.9990.



4vb

2-(5-chloro-4-methyl-2-(methylthio)thiophen-3-yl)pentanenitrile (4vb):

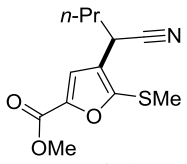
Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min and then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 31-32 ℃, 83.4 mg, 64% yield. (Rf = 0.39, eluent: PE/EtOAc = 20/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.37 (dd, *J* = 8.7, 7.3 Hz, 1H), 2.38 (s, 3H), 2.27 (s, 3H), 2.06 – 1.94 (m, 1H), 1.73 – 1.61 (m, 1H), 1.60 – 1.48 (m, 1H), 1.46 – 1.34 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.9, 133.4, 130.6, 128.2, 119.7, 35.0, 30.2, 22.7, 20.7, 13.4, 13.1.

IR (neat): 2959, 2943, 2923, 2899, 2872, 2233, 1542, 1453, 1435, 1386, 1159, 1016, 963, 735.

HRMS (ESI-TOF): calculated for [$C_{11}H_{14}ClNS_2Na$ ($M + Na^+$)]: 282.0148, found: 282.0151.



4wb

methyl-4-(1-cyanobutyl)-5-(methylthio)furan-2-carboxylate (4wb):

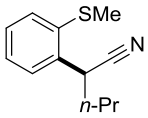
Similar to the general procedure, Tf_2O instead of TFAA was used, the reaction was performed at -78 ℃ for 10 min and then -60 ℃ for 12 h. The title compound was obtained as colorless oil, 66.1 mg, 52% yield. (Rf = 0.19, eluent: PE/EtOAc = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 1H), 3.92 – 3.76 (m, 4H), 2.47 (s, 3H), 1.95 – 1.82 (m, 1H), 1.79 – 1.66 (m, 1H), 1.53 – 1.36 (m, 2H), 1.01 – 0.89 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.2, 149.7, 146.1, 124.9, 119.8, 118.0, 52.3, 36.0, 28.1, 20.2, 17.7, 13.3.

IR (neat): 2959, 2932, 2874, 2244, 1721, 1497, 1435, 1385, 1302, 1198, 1122, 1096, 761, 730.

HRMS (ESI-TOF): calculated for [$C_{12}H_{15}NO_3SNa$ ($M + Na^+$)]: 276.0665, found: 276.0668.



5ab

2-(2-(methylthio)phenyl)pentanenitrile (5ab):

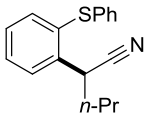
Following the general procedure, the title compound was obtained as colorless oil, 94.2 mg, 92% yield. (Rf = 0.32, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.48 (m, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 4.38 (dd, *J* = 8.9, 5.8 Hz, 1H), 2.49 (s, 3H), 1.89 – 1.77 (m, 2H), 1.66 – 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.4, 135.2, 128.7, 128.1, 127.8, 126.4, 121.1, 36.7, 34.4, 20.6, 17.1, 13.5.

IR (neat): 3061, 2959, 2924, 2873, 2238, 1589, 1468, 1437, 1382, 1185, 1042, 719, 696.

HRMS (ESI-TOF): calculated for [$C_{12}H_{15}NSNa$ ($M + Na^+$)]: 228.0817, found: 228.0823.



5bb

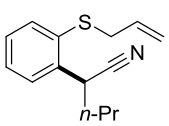
2-(2-(phenylthio)phenyl)pentanenitrile (5bb):

Following the general procedure, the title compound was obtained as colorless oil, 89.2 mg, 67% yield. (Rf = 0.31, eluent: PE/EtOAc = 20/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.34 – 7.26 (m, 3H), 7.26 – 7.14 (m, 3H), 4.52 (dd, *J* = 9.4, 5.3 Hz, 1H), 1.90 – 1.79 (m, 1H), 1.79 – 1.67 (m, 1H), 1.65 – 1.41 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.7, 135.9, 135.0, 132.6, 129.5, 129.4, 129.3, 129.0, 128.5, 126.9, 121.1, 37.4, 34.8, 20.6, 13.4.

The ^{1}H NMR and ^{13}C NMR of **5bb** are consistent with the reported spectra[2].



5cb

2-(2-(allylthio)phenyl)pentanenitrile (5cb):

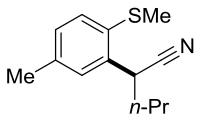
Following the general procedure, the title compound was obtained as colorless oil, 97.9 mg, 85% yield. (Rf = 0.26, eluent: PE/EtOAc = 40/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.50 (m, 1H), 7.48 – 7.41 (m, 1H), 7.32 – 7.22 (m, 2H), 5.88 – 5.78 (m, 1H), 5.11 – 4.96 (m, 2H), 4.54 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.50 (d, *J* = 7.1 Hz, 2H), 1.92 – 1.69 (m, 2H), 1.66 – 1.42 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 137.9, 133.7, 132.9, 132.6, 128.5, 127.9, 127.8, 121.3, 118.4, 38.7, 37.2, 34.6, 20.5, 13.5.

IR (neat): 3061, 2959, 2931, 2873, 2238, 1636, 1589, 1468, 1438, 1382, 1184, 919, 752, 705.

HRMS (ESI-TOF): calculated for [$C_{14}H_{17}NSNa$ ($M + Na^+$)]: 254.0974, found: 254.0983.



5db

2-(5-methyl-2-(methylthio)phenyl)pentanenitrile (5db):

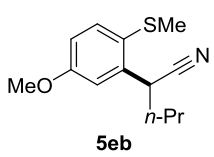
Following the general procedure, the title compound was obtained as colorless oil, 104.8 mg, 96% yield. (Rf = 0.38, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (d, *J* = 1.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.40 (dd, *J* = 9.2, 5.5 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H), 1.89 – 1.75 (m, 2H), 1.65 – 1.47 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.9, 135.8, 132.7, 129.6, 129.4, 128.5, 121.4, 37.1, 34.4, 21.1, 20.7, 17.9, 13.5.

IR (neat): 2959, 2923, 2873, 2238, 1602, 1478, 1465, 1437, 1381, 1170, 1053, 810, 735.

HRMS (ESI-TOF): calculated for [$C_{13}H_{17}NSNa$ ($M + Na^+$)]: 242.0974, found: 242.0982.



5eb

2-(5-methoxy-2-(methylthio)phenyl)pentanenitrile (5eb):

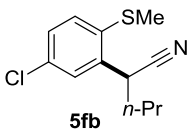
Following the general procedure, the title compound was obtained as colorless oil, 110.2 mg, 94% yield. (Rf = 0.37, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 2.8 Hz, 1H), 6.84 (dd, *J* = 8.6, 2.8 Hz, 1H), 4.51 (dd, *J* = 9.3, 5.6 Hz, 1H), 3.81 (s, 3H), 2.39 (s, 3H), 1.91 – 1.72 (m, 2H), 1.64 – 1.46 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.3, 138.7, 133.3, 126.6, 121.2, 114.6, 113.5, 55.5, 37.3, 34.7, 20.6, 19.5, 13.5.

IR (neat): 2959, 2923, 2873, 2836, 2238, 1597, 1475, 1438, 1382, 1288, 1232, 810, 649, 615.

HRMS (ESI-TOF): calculated for [$C_{13}H_{17}NOSNa$ ($M + Na^+$)]: 258.0923, found: 258.0923.



5fb

2-(5-chloro-2-(methylthio)phenyl)pentanenitrile (5fb):

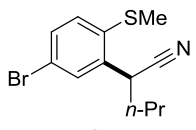
Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min and then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 30-31 ℃, 97.1 mg, 81% yield. (Rf = 0.32, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 2.2 Hz, 1H), 7.29 – 7.21 (m, 2H), 4.32 (dd, *J* = 9.1, 5.6 Hz, 1H), 2.47 (s, 3H), 1.88 – 1.75 (m, 2H), 1.64 – 1.46 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.9, 135.0, 132.3, 129.4, 128.9, 127.8, 120.4, 36.5, 34.3, 20.6, 17.2, 13.4.

IR (neat): 2956, 2943, 2925, 2863, 2239, 1753, 1582, 1460, 1384, 1269, 1111, 877, 800, 746.

HRMS (ESI-TOF): calculated for [$C_{12}H_{14}ClNSNa$ ($M + Na^+$)]: 262.0428, found: 262.0436.



5gb

2-(5-bromo-2-(methylthio)phenyl)pentanenitrile (5gb):

Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min and then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 49-51 ℃, 97.3 mg, 68% yield. (Rf = 0.35, eluent: PE/EtOAc = 40/1)

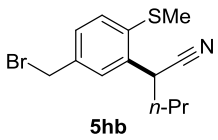
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 2.2 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.30 (dd, *J* = 9.2, 5.5 Hz, 1H), 2.47 (s, 3H), 1.88 – 1.74 (m, 2H), 1.64 – 1.47 (m,

2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 137.0, 135.7, 131.8, 130.7, 129.5, 120.4, 120.0, 36.5, 34.2, 20.6, 17.1, 13.4.

IR (neat): 3088, 2959, 2922, 2874, 2237, 1731, 1576, 1467, 1389, 1093, 1051, 867, 818, 746.

HRMS (ESI-TOF): calculated for [$C_{12}H_{14}BrNSNa$ (M + Na^+)]: 305.9923, found: 305.9926.



5hb

2-(5-(bromomethyl)-2-(methylthio)phenyl)pentanenitrile (5hb):

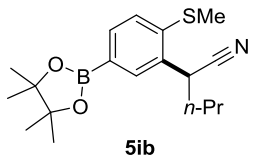
Following the general procedure, the title compound was obtained as colorless oil, 131.0 mg, 88% yield. (Rf = 0.15, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (d, *J* = 1.9 Hz, 1H), 7.33 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 4.50 – 4.45 (m, 2H), 4.31 (dd, *J* = 8.6, 6.0 Hz, 1H), 2.48 (s, 3H), 1.88 – 1.77 (m, 2H), 1.65 – 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.9, 135.7, 135.1, 129.3, 128.2, 127.7, 120.7, 36.4, 34.3, 32.7, 20.6, 16.6, 13.4.

IR (neat): 2960, 2926, 2873, 2239, 1602, 1475, 1435, 1382, 1227, 1209, 1051, 907, 818, 729.

HRMS (ESI-TOF): calculated for [$C_{13}H_{16}BrNSNa$ (M + Na^+)]: 320.0079, found: 320.0079.



5ib

2-(2-(methylthio)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pentanenitrile (5ib):

Following the general procedure, the title compound was obtained as yellow solid, m.p. 84-86 ℃, 134.1 mg, 81% yield. (Rf = 0.36, eluent: PE/EtOAc = 10/1)

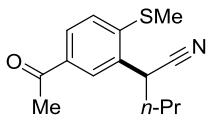
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (d, *J* = 0.9 Hz, 1H), 7.70 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 4.28 (dd, *J* = 9.6, 5.3 Hz, 1H), 2.49 (s, 3H), 1.94 – 1.85 (m, 1H), 1.85 – 1.76 (m, 1H), 1.67 – 1.57 (m, 1H), 1.57 – 1.47 (m, 1H), 1.33 (s, 12H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.2, 134.9, 133.7, 133.6, 125.7, 120.9, 84.0, 36.4, 34.1, 25.0, 24.9, 20.7, 16.1, 13.4.

^{11}B NMR (193 MHz, $CDCl_3$): δ 30.82.

IR (neat): 2965, 2924, 2863, 2235, 2162, 1599, 1371, 1354, 1103, 854, 734, 679.

HRMS (ESI-TOF): calculated for [$C_{18}H_{27}BNO_2S$ (M + H^+)]: 331.1886, found: 331.1879.



5jb

2-(5-acetyl-2-(methylthio)phenyl)pentanenitrile (5jb):

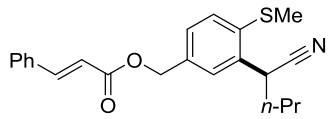
Simlar to general procedure, MeCN instead of DCM, the reaction was performed at -40 ℃ for 12 h. The title compound was obtained as white solid, m.p. 65-67 ℃, 95.2 mg, 77% yield. (Rf = 0.24, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 1.8 Hz, 1H), 7.87 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 4.25 (dd, *J* = 9.2, 5.4 Hz, 1H), 2.59 (s, 3H), 2.55 (s, 3H), 1.93 – 1.79 (m, 2H), 1.67 – 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 196.9, 143.4, 134.2, 133.9, 128.4, 127.4, 125.3, 120.4, 36.0, 34.2, 26.6, 20.7, 15.7, 13.5.

IR (neat): 2992, 2961, 2933, 2874, 2237, 1677, 1592, 1556, 1464, 1408, 1354, 1242, 812, 751, 612.

HRMS (ESI-TOF): calculated for [$C_{14}H_{17}NOSNa$ (M + Na^+)]: 270.0923, found: 270.0928.



5kb

3-(1-cyanobutyl)-4-(methylthio)benzyl cinnamate (5kb):

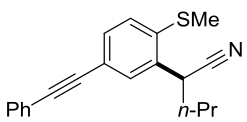
Following the general procedure, the title compound was obtained as colorless oil, 160.8 mg, 88% yield. (Rf = 0.19, eluent: PE/EtOAc = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 16.0 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.44 – 7.31 (m, 5H), 6.51 (d, *J* = 16.0 Hz, 1H), 5.31 – 5.20 (m, 2H), 4.38 (dd, *J* = 8.9, 5.7 Hz, 1H), 2.52 (s, 3H), 1.96 – 1.78 (m, 2H), 1.71 – 1.48 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 145.5, 136.6, 135.3, 134.4, 134.3, 130.5, 129.0, 128.7, 128.3, 128.0, 127.6, 120.9, 117.7, 65.7, 36.6, 34.4, 20.7, 16.9, 13.5.

IR (neat): 2959, 2927, 2873, 2239, 1708, 1635, 1578, 1496, 1449, 1372, 1308, 1156, 815, 729.

HRMS (ESI-TOF): calculated for [$C_{22}H_{23}NO_2SNa$ (M + Na^+)]: 388.1342, found: 388.1348.



5lb

2-(2-(methylthio)-5-(phenylethynyl)phenyl)pentanenitrile (5lb):

Following the general procedure, the title compound was obtained as white solid, m.p. 110-112 ℃, 122.1 mg, 80% yield. (Rf = 0.39, eluent: PE/EtOAc = 10/1)

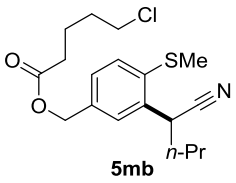
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 (d, *J* = 1.7 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.45 (dd, *J* = 8.2,

1.8 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 1H), 4.31 (dd, *J* = 8.8, 5.7 Hz, 1H), 2.50 (s, 3H), 1.92 – 1.79 (m, 2H), 1.69 – 1.49 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 137.0, 134.7, 131.7, 131.6, 130.6, 128.52, 128.47, 126.8, 123.0, 120.9, 120.7, 90.5, 88.5, 36.3, 34.2, 20.6, 16.4, 13.5.

IR (neat): 3061, 2956, 2924, 2867, 2237, 1985, 1492, 1383, 1262, 818, 760, 692.

HRMS (ESI-TOF): calculated for [$C_{20}H_{19}NSNa$ ($M + Na^+$)]: 328.1130, found: 328.1128.



5mb

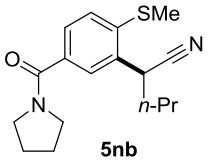
3-(1-cyanobutyl)-4-(methylthio)benzyl 5-chloropentanoate (5mb): Following the general procedure, the title compound was obtained as colorless oil, 163.2 mg, 92% yield. (Rf = 0.39, eluent: PE/EtOAc = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.28 (d, *J* = 0.9 Hz, 2H), 5.13 – 5.04 (m, 2H), 4.33 (dd, *J* = 8.6, 6.0 Hz, 1H), 3.53 (dd, *J* = 8.0, 4.1 Hz, 2H), 2.48 (s, 3H), 2.43 – 2.37 (m, 2H), 1.89 – 1.73 (m, 6H), 1.68 – 1.46 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.9, 136.5, 135.2, 134.1, 128.5, 127.8, 127.4, 120.8, 65.5, 44.5, 36.5, 34.3, 33.4, 31.8, 22.2, 20.6, 16.8, 13.4.

IR (neat): 2959, 2873, 2239, 1732, 1606, 1477, 1437, 1381, 1351, 1169, 1051, 815, 729.

HRMS (ESI-TOF): calculated for [$C_{18}H_{24}ClNO_2SNa$ ($M + Na^+$)]: 376.1108, found: 376.1115.



5nb

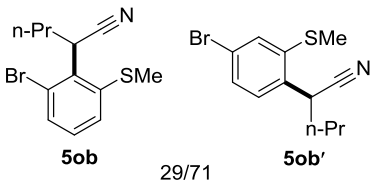
2-(2-(methylthio)-5-(pyrrolidine-1-carbonyl)phenyl)pentanenitrile (5nb): Following the general procedure, the title compound was obtained as colorless oil, 120.1 mg, 79% yield. (Rf = 0.19, eluent: PE/EtOAc = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 1.5 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 4.29 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.68 – 3.34 (m, 4H), 2.51 (s, 3H), 2.00 – 1.77 (m, 6H), 1.66 – 1.44 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.5, 138.7, 134.5, 134.0, 127.6, 126.5, 126.4, 120.6, 49.6, 46.4, 36.1, 34.2, 26.4, 24.4, 20.5, 16.2, 13.3.

IR (neat): 2960, 2874, 2238, 1616, 1553, 1422, 1391, 1341, 1228, 1051, 830, 726.

HRMS (ESI-TOF): calculated for [$C_{17}H_{22}N_2OSNa$ ($M + Na^+$)]: 325.1345, found: 325.1350.



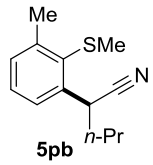
2-(2-bromo-6-(methylthio)phenyl)pentanenitrile(5ob) and 2-(4-bromo-2-(methylthio)phenyl)pentane nitrile(5ob′): Following the general procedure, the title compound was obtained as colorless oil, 64.3 mg, 45% yield. (Rf = 0.20, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$), mixture of **5ob** and **5ob′**: δ 7.66 (dd, *J* = 8.0, 1.3 Hz, 0.71H), 7.54 (dd, *J* = 7.8, 1.3 Hz, 0.71H), 7.52 – 7.50 (m, 0.29H), 7.32 (dd, *J* = 6.7, 1.4 Hz, 0.47H), 7.29 – 7.26 (m, 0.36H), 7.26 – 7.23 (m, 0.71H), 4.88 (dd, *J* = 9.3, 5.5 Hz, 0.71H), 4.39 (dd, *J* = 8.9, 5.7 Hz, 0.29H), 2.51 (s, 0.87H), 2.43 (s, 2.12H), 1.93 – 1.74 (m, 2H), 1.66 – 1.48 (m, 2H), 1.03 – 0.97 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) , mixture of **5ob** and **5ob′**: δ 142.9, 136.4, 135.6, 135.3, 133.6, 132.8, 130.6, 128.7, 128.1, 127.8, 127.3, 126.4, 121.3, 121.1, 77.4, 77.2, 76.9, 38.0, 36.7, 36.7, 34.4, 29.8, 20.6, 19.5, 17.1, 13.5, 13.5.

IR (neat): 2960, 2924, 2873, 2238, 1555, 1465, 1442, 1382, 1315, 1265, 1175, 784, 728.

HRMS (ESI-TOF): calculated for [$C_{12}H_{14}BrNSNa$ (M + Na^+)]: 305.9923, found: 305.9920.



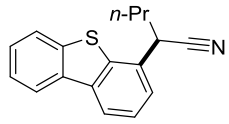
2-(3-methyl-2-(methylthio)phenyl)pentanenitrile (5pb): Following the general procedure, the title compound was obtained as colorless oil, 54.2 mg, 49% yield. (Rf = 0.29, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.21 (m, 2H), 4.87 (dd, *J* = 9.3, 5.6 Hz, 1H), 2.59 (s, 3H), 2.25 (s, 3H), 1.92 – 1.84 (m, 1H), 1.82 – 1.73 (m, 1H), 1.66 – 1.47 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 143.9, 140.9, 134.2, 130.4, 129.2, 125.8, 121.9, 38.1, 35.5, 21.7, 20.7, 19.2, 13.5.

IR (neat): 3055, 2959, 2923, 2873, 2237, 1578, 1460, 1379, 1314, 1170, 785, 736.

HRMS (ESI-TOF): calculated for [$C_{13}H_{17}NSNa$ (M + Na^+)]: 242.0974, found: 242.0971.



5qb

2-(dibenzo[b,d]thiophen-4-yl)pentanenitrile (5qb):

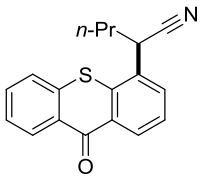
Following the general procedure, the title compound was obtained as white solid, m.p. 60-62 ℃, 106.6 mg, 80% yield. (Rf = 0.25, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 – 8.14 (m, 1H), 8.14 – 8.11 (m, 1H), 7.89 – 7.85 (m, 1H), 7.60 – 7.56 (m, 1H), 7.54 – 7.46 (m, 3H), 4.11 (dd, *J* = 8.5, 6.1 Hz, 1H), 2.13 – 2.02 (m, 2H), 1.68 – 1.53 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.6, 137.7, 136.7, 135.8, 130.5, 127.4, 125.5, 125.4, 125.0, 122.9, 122.0, 121.5, 120.1, 36.7, 35.5, 20.7, 13.5.

IR (neat): 3061, 2966, 2929, 2868, 2243, 1597, 1582, 1460, 1441, 1403, 1378, 802, 754.

HRMS (ESI-TOF): calculated for [$C_{17}H_{15}NSK$ (M + K^+)]: 304.0557, found: 304.0550.



5rb

2-(9-oxo-9H-thioxanthen-4-yl)pentanenitrile (5rb):

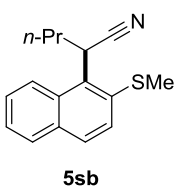
Simlar to general procedure, MeCN instead of DCM, the reaction was performed at -40 ℃ for 12 h. The title compound was obtained as white solid, m.p. 128-130 ℃, 108.4 mg, 74% yield. (Rf = 0.23, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.63 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.58 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.87 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.63 – 7.59 (m, 1H), 7.58 – 7.49 (m, 2H), 4.31 (t, *J* = 7.2 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.74 – 1.59 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 180.0, 135.2, 134.7, 132.9, 132.4, 131.8, 130.4, 130.2, 130.0, 128.7, 127.2, 126.44, 126.37, 120.0, 36.1, 34.2, 20.8, 13.5.

IR (neat): 3060, 2954, 2924, 2853, 2243, 1632, 1583, 1459, 1415, 1377, 1317, 815, 741.

HRMS (ESI-TOF): calculated for [$C_{18}H_{16}NOS$ (M + H^+)]: 294.0947, found: 294.0948.



5sb

2-(2-(methylthio)naphthalen-1-yl)pentanenitrile (5sb):

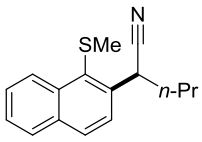
Following the general procedure, the title compound was obtained as white solid, m.p. 86-88 ℃, 99.8 mg, 78% yield. (Rf = 0.20, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.45 (m, 2H), 5.32 (s, 1H), 2.57 (s, 3H), 2.44 – 2.25 (m, 1H), 1.93 – 1.83 (m, 1H), 1.79 – 1.67 (m, 1H), 1.56 – 1.45 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 135.2, 133.0, 131.0, 130.8, 129.5, 129.3, 127.3, 127.0, 126.0, 124.2, 121.2, 35.4, 31.9, 21.1, 18.7, 13.6.

IR (neat): 3053, 2966, 2920, 2860, 2231, 1619, 1585, 1505, 1453, 1367, 1268, 802, 743.

HRMS (ESI-TOF): calculated for [$C_{16}H_{17}NSNa$ (M + Na^+)]: 278.0974, found: 278.0975.



5tb

2-(1-(methylthio)naphthalen-2-yl)pentanenitrile (5tb):

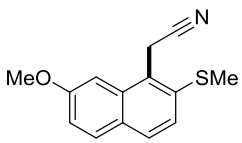
Following the general procedure, the title compound was obtained as colorless oil, 103.7 mg, 81% yield. (Rf = 0.20, eluent: PE/EtOAc = 40/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.5 Hz, 1H), 7.93– 7.85 (m, 2H), 7.71 – 7.62 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 5.20 (dd, *J* = 9.1, 6.1 Hz, 1H), 2.36 (s, 3H), 2.07 – 1.97 (m, 1H), 1.89 – 1.79 (m, 1H), 1.69 – 1.49 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.9, 134.5, 133.7, 132.2, 130.4, 128.9, 127.8, 126.9, 126.6, 124.9, 121.7, 37.9, 35.8, 20.7, 20.2, 13.6

IR (neat): 3055, 2959, 2922, 2873, 2237, 1593, 1556, 1503, 1463, 1381, 1314, 817, 730.

HRMS (ESI-TOF): calculated for [$C_{16}H_{17}NSNa$ (M + Na^+)]: 287.0974, found: 287.0974.



5ua

2-(7-methoxy-2-(methylthio)naphthalen-1-yl)acetonitrile (5ub):

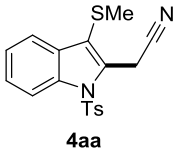
Following the general procedure, the title compound was obtained as white solid, m.p. 97-99 ℃, 92.1 mg, 76% yield. (Rf = 0.23, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.18 – 7.11 (m, 2H), 4.34 (s, 2H), 3.97 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.2, 136.7, 133.0, 130.6, 129.3, 127.6, 123.9, 123.5, 118.5, 117.6, 101.8, 55.6, 18.3, 17.9.

IR (neat): 3003, 2963, 2926, 2247, 1619, 1592, 1506, 1458, 1386, 1233, 1125, 833, 735.

HRMS (ESI-TOF): calculated for [$C_{14}H_{13}NOSNa$ (M + Na^+)]: 266.0610, found: 266.0601.



4aa

2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)acetonitrile (4aa):

Similar to the general procedure, the reaction was performed at -78 ℃ for 10

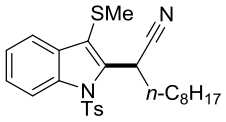
min then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 164-166 ℃, 133.3 mg, 75% yield. (Rf = 0.19, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 8.2 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.35 – 7.31 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 4.52 (s, 2H), 2.36 – 2.32 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.9, 136.2, 135.0, 131.6, 130.2, 130.0, 127.2, 126.3, 124.4, 120.2, 118.9, 116.6, 114.9, 21.8, 18.8, 16.5.

IR (neat): 3052, 2922, 2852, 2255, 1595, 1494, 1449, 1361, 1291, 1254, 1163, 818, 746.

HRMS (ESI-TOF): calculated for [$C_{18}H_{16}N_2O_2S_2Na$ (M + Na^+)]: 379.0545, found: 379.0541.



4ac

2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)decanenitrile (4ac):

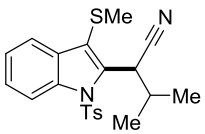
Following the general procedure, the title compound was obtained as white solid, m.p. 66-68 ℃, 191.8 mg, 82% yield. (Rf = 0.17, eluent: PE/EtOAc = 20/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.74 – 7.64 (m, 3H), 7.42 – 7.38 (m, 1H), 7.37 – 7.32 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.24 (dd, *J* = 9.3, 6.2 Hz, 1H), 2.33 (br s, 7H), 2.04 – 1.89 (m, 1H), 1.71 – 1.60 (m, 1H), 1.49 – 1.40 (m, 1H), 1.39 – 1.34 (m, 2H), 1.33 – 1.22 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 137.0, 136.5, 135.0, 130.5, 130.2, 126.6, 126.1, 124.5, 119.8, 119.2, 118.6, 115.6, 34.0, 31.8, 29.3, 29.2, 29.0, 28.9, 27.6, 22.7, 21.6, 18.2, 14.2.

IR (neat): 2992, 2956, 2921, 2848, 2238, 1597, 1447, 1371, 1304, 1269, 1146, 815, 745.

HRMS (ESI-TOF): calculated for [$C_{26}H_{32}N_2O_2S_2Na$ (M + Na^+)]: 491.1797, found: 491.1805.



4ad

3-methyl-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)butanenitrile (4ad):

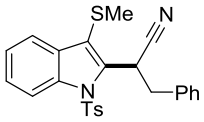
Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 111-113 ℃, 157.1 mg, 79% yield. (Rf = 0.32, eluent: PE/EtOAc = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 3H), 7.44 – 7.30 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.97 (d, *J* = 9.8 Hz, 1H), 2.86 – 2.72 (m, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.35 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 136.6, 136.5, 134.7, 130.5, 130.1, 126.6, 126.2, 124.6, 119.9, 119.3, 119.0, 115.9, 36.4, 33.2, 21.7, 21.5, 20.0, 18.2.

IR (neat): 2966, 2922, 2236, 1595, 1445, 1373, 1350, 1340, 1303, 1192, 1166, 815, 762.

HRMS (ESI-TOF): calculated for [$C_{21}H_{22}N_2O_2S_2Na$ (M + Na^+)]: 421.1015, found: 421.1021.



4ae

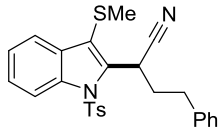
2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)-3-phenylpropanenitrile (4ae): Following the general procedure, the title compound was obtained as colorless oil, 208.2 mg, 93% yield. (Rf = 0.24, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 6.8 Hz, 3H), 7.46 – 7.27 (m, 7H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.53 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.67– 3.55 (m, 1H), 3.49 – 3.34 (m, 1H), 2.41 – 2.08 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.8, 136.51, 136.45, 135.8, 134.9, 130.2, 129.3, 128.9, 127.6, 126.6, 126.3, 124.5, 119.9, 118.7, 115.5, 39.8, 31.9, 21.6, 18.0. Two aromatic carbon peaks are overlapped.

IR (neat): 2924, 2241, 1596, 1495, 1447, 1373, 1303, 1267, 1171, 1091, 812, 731.

HRMS (ESI-TOF): calculated for [$C_{25}H_{22}N_2O_2S_2Na$ (M + Na^+)]: 469.1015, found: 469.1021.



4af

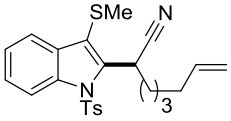
2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)-4-phenylbutanenitrile (4af): Similar to the general procedure, the reaction was performed at -78 ℃ for 10 min then -60 ℃ for 12 h. The title compound was obtained as white solid, m.p. 127-129 ℃, 172.3 mg, 75% yield. (Rf = 0.28, eluent: PE/EtOAc = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 6.5 Hz, 2H), 7.44 – 7.30 (m, 4H), 7.29 – 7.16 (m, 5H), 5.14 (dd, *J* = 9.5, 5.7 Hz, 1H), 3.08 – 2.95 (m, 1H), 2.87 – 2.62 (m, 2H), 2.39 – 2.16 (m, 7H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.8, 139.7, 136.6, 136.4, 135.1, 130.4, 130.3, 128.75, 128.74, 126.6, 126.3, 124.5, 119.8, 118.9, 115.6, 35.4, 33.7, 28.6, 21.7, 18.2. Two aromatic carbon peaks are overlapped.

IR (neat): 3114, 3048, 2960, 2926, 2239, 1595, 1493, 1446, 1373, 1333, 1305, 1171, 819, 743, 665.

HRMS (ESI-TOF): calculated for [$C_{26}H_{24}N_2O_2S_2Na$ (M + Na^+)]: 483.1171, found: 483.1180.



4ag

2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)oct-7-enenitrile (4ag):

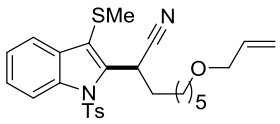
Following the general procedure, the title compound was obtained as colorless oil, 201.2 mg, 92% yield. (Rf = 0.32, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.62 (m, 3H), 7.44 – 7.38 (m, 1H), 7.37 – 7.31 (m, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.85 – 5.74 (m, 1H), 5.24 (dd, *J* = 9.3, 6.2 Hz, 1H), 5.05 – 4.99 (m, 1H), 4.98 – 4.92 (m, 1H), 2.33 (br s, 7H), 2.11 – 2.05 (m, 2H), 2.03 – 1.93 (m, 1H), 1.74 – 1.62 (m, 1H), 1.53 – 1.41 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 138.3, 136.8, 136.5, 134.9, 130.4, 130.2, 126.5, 126.2, 124.5, 119.8, 119.1, 118.6, 115.6, 114.9, 33.8, 33.4, 29.0, 28.1, 27.0, 21.6, 18.2.

IR (neat): 3071, 2925, 2858, 2240, 1640, 1596, 1447, 1374, 1305, 1268, 1168, 1691, 812, 747.

HRMS (ESI-TOF): calculated for [$C_{24}H_{26}N_2O_2S_2Na$ (M + Na^+)]: 461.1328, found: 461.1332.



4ah

8-(allyloxy)-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)octanenitrile (4ah):

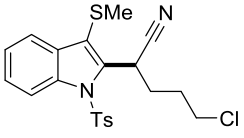
Following the general procedure, the title compound was obtained as white solid, m.p. 53-55 ℃, 227.4 mg, 91% yield. (Rf = 0.21, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.73 – 7.62 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.96 – 5.85 (m, 1H), 5.29 – 5.20 (m, 2H), 5.16 (d, *J* = 10.4 Hz, 1H), 3.95 (d, *J* = 5.6 Hz, 2H), 3.42 (t, *J* = 6.6 Hz, 2H), 2.32 (br s, 6H), 2.03 – 1.90 (m, 1H), 1.72 – 1.56 (m, 3H), 1.50 – 1.32 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 136.8, 136.5, 135.0, 134.9, 130.4, 130.1, 126.5, 126.1, 124.5, 119.7, 119.1, 118.6, 116.7, 115.6, 71.8, 70.2, 33.9, 29.6, 28.9, 28.7, 27.5, 25.9, 21.6, 18.1.

IR (neat): 2990, 2930, 2851, 2238, 1959, 1447, 1376, 1356, 1304, 1269, 1145, 1088, 808, 759, 662.

HRMS (ESI-TOF): calculated for [$C_{27}H_{32}N_2O_3S_2Na$ (M + Na^+)]: 519.1747, found: 519.1756.



4ai

5-chloro-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4ai):

Following the general procedure, the title compound was obtained as colorless oil, 186.8 mg, 86% yield. (Rf = 0.22, eluent: PE/EtOAc = 10/1)

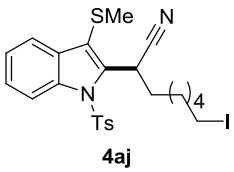
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.69 (t, *J* = 8.5 Hz, 3H), 7.45 – 7.38 (m,

1H), 7.37 –7.34 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.30 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.67 – 3.55 (m, 2H), 2.54 – 2.42 (m, 1H), 2.39 – 2.30 (m, 6H), 2.28 – 2.19 (m, 1H), 2.18 – 2.09 (m, 1H), 1.95 – 1.86 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.9, 136.5, 136.0, 134.8, 130.4, 130.3, 126.6, 126.4, 124.7, 119.9, 119.1, 118.8, 115.7, 43.8, 31.3, 30.3, 28.4, 21.7, 18.2.

IR (neat): 2924, 2241, 1596, 1493, 1447, 1374, 1305, 1266, 1168, 1091, 812, 731.

HRMS (ESI-TOF): calculated for [$C_{21}H_{21}ClN_2O_2S_2Na$ (M + Na^+)]: 455.0625, found: 455.0631.



4aj

8-iodo-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)octanenitrile (4aj):

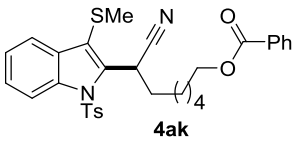
Following the general procedure, 0.3 mmol of aryl sulfoxide was used in the reaction, the title compound was obtained as colorless oil, 105.3 mg, 62% yield. (Rf = 0.25, eluent: PE/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 3H), 7.43 – 7.31 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.23 (dd, *J* = 9.2, 6.2 Hz, 1H), 3.18 (t, *J* = 7.0 Hz, 2H), 2.41 – 2.24 (m, 7H), 2.07 – 1.90 (m, 1H), 1.88 – 1.76 (m, 2H), 1.73 – 1.60 (m, 1H), 1.52 – 1.33 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.8, 136.8, 136.6, 134.9, 130.5, 130.3, 126.6, 126.3, 124.6, 119.8, 119.2, 118.7, 115.7, 33.9, 33.4, 30.3, 29.0, 27.8, 27.5, 21.8, 18.3, 7.1.

IR (neat): 2924, 2854, 2240, 1735, 1597, 1493, 1447, 1372, 1301, 1239, 1092, 812, 747, 661.

HRMS (ESI-TOF): calculated for [$C_{24}H_{27}IN_2O_2S_2Na$ (M + Na^+)]: 589.0451, found: 589.0453.



4ak

7-cyano-7-(3-(methylthio)-1-tosyl-1H-indol-2-yl)heptyl benzoate (4ak):

Following the general procedure, the title compound was obtained as colorless oil, 262.1 mg, 93% yield. (Rf = 0.34, eluent: PE/EtOAc = 5/1)

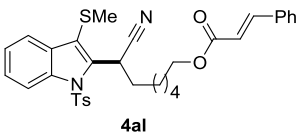
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.75 – 7.63 (m, 3H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.26 (dd, *J* = 9.2, 6.2 Hz, 1H), 4.32 (t, *J* = 6.5 Hz, 2H), 2.39 – 2.29 (m, 7H), 2.05 – 1.95 (m, 1H), 1.83 – 1.65 (m, 3H), 1.55 – 1.40 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 145.8, 136.8, 136.5, 134.9, 132.9, 130.4, 130.2, 129.5, 128.4, 126.5, 126.2, 124.5, 119.8, 119.1, 118.6, 115.6, 64.9, 33.9, 28.9, 28.6, 28.5, 27.5, 25.8, 21.6,

18.2. One aromatic carbon peak is overlapped.

IR (neat): 2927, 2859, 2250, 1713, 1598, 1493, 1449, 1375, 1314, 1272, 1173, 1092, 812, 711.

HRMS (ESI-TOF): calculated for [$C_{31}H_{33}N_2O_4S_2$ ($M + H^+$)]: 561.1876, found: 561.1873.



4al

7-cyano-7-(3-(methylthio)-1-tosyl-1H-indol-2-yl)heptyl cinnamate (4al):

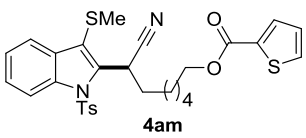
Following the general procedure, the title compound was obtained as colorless oil, 270.4 mg, 92% yield. (Rf = 0.23, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.73 – 7.63 (m, 4H), 7.56 – 7.50 (m, 2H), 7.42 – 7.30 (m, 5H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 12.0 Hz, 1H), 5.25 (dd, *J* = 9.3, 6.2 Hz, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 2.39 – 2.29 (m, 7H), 2.05 – 1.94 (m, 1H), 1.77 – 1.65 (m, 3H), 1.53 – 1.40 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.1, 145.8, 144.7, 136.8, 136.5, 134.9, 134.4, 130.4, 130.3, 130.2, 128.9, 128.1, 126.5, 126.2, 124.5, 119.8, 119.1, 118.6, 118.2, 115.6, 64.5, 33.9, 28.9, 28.6, 28.5, 27.5, 25.8, 21.6, 18.2.

IR (neat): 2927, 2858, 2240, 1734, 1708, 1636, 1597, 1448, 1373, 1166, 762, 661.

HRMS (ESI-TOF): calculated for [$C_{33}H_{34}N_2O_4S_2Na$ ($M + Na^+$)]: 609.1852, found: 609.1854.



4am

7-cyano-7-(3-(methylthio)-1-tosyl-1H-indol-2-yl)heptyl thiophene -2-carboxylate (4am):

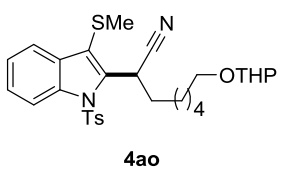
Following the general procedure, the title compound was obtained as colorless oil, 268.8 mg, 95% yield. (Rf = 0.28, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.79 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.72 – 7.63 (m, 3H), 7.51 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.36 – 7.31 (m, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.07 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.24 (dd, *J* = 9.3, 6.2 Hz, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 2.38 – 2.27 (m, 7H), 2.03 – 1.93 (m, 1H), 1.79 – 1.64 (m, 3H), 1.53 – 1.40 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.3, 145.8, 136.8, 136.5, 134.9, 133.9, 133.3, 132.3, 130.4, 130.2, 127.8, 126.5, 126.2, 124.5, 119.8, 119.1, 118.6, 115.6, 65.1, 33.8, 28.9, 28.6, 28.5, 27.5, 25.7, 21.6, 18.2.

IR (neat): 2928, 2859, 2240, 1734, 1705, 1596, 1447, 1372, 1090, 749, 728, 661.

HRMS (ESI-TOF): calculated for [$C_{29}H_{30}N_2O_4S_3Na$ ($M + Na^+$)]: 589.1260, found: 589.1262.



4ao

2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)-8-((tetrahydro-2H-pyran-2-yl)oxy)octanenitrile (4ao):

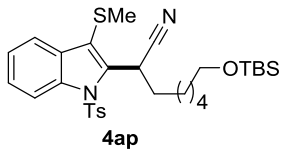
Following the general procedure, the title compound was obtained as colorless oil, 151.5 mg, 56% yield. (Rf = 0.32, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.62 (m, 3H), 7.41 – 7.37 (m, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.21 (dd, *J* = 9.2, 6.2 Hz, 1H), 4.59 – 4.55 (m, 1H), 3.89 – 3.83 (m, 1H), 3.76 – 3.69 (m, 1H), 3.53 – 3.46 (m, 1H), 3.41 – 3.34 (m, 1H), 2.35 – 2.29 (m, 6H), 2.01 – 1.91 (m, 1H), 1.86 – 1.77 (m, 1H), 1.74 – 1.47 (m, 9H), 1.46 – 1.36 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.8, 136.9, 136.6, 135.0, 130.5, 130.2, 126.6, 126.2, 124.6, 119.8, 119.2, 115.7, 98.9, 67.54, 67.52, 62.4, 34.0, 30.9, 29.7, 29.0, 28.81, 28.80, 27.65, 27.64, 26.1, 25.6, 21.7, 19.8, 18.2. One aromatic carbon peak is overlapped.

IR (neat): 2931, 2859, 2243, 1597, 1494, 1448, 1376, 1307, 1252, 1132, 1097, 812, 730, 661.

HRMS (ESI-TOF): calculated for [$C_{29}H_{36}N_2O_4S_2Na$ ($M + Na^+$)]: 563.2009, found: 563.2009.



4ap

8-((tert-butyldimethylsilyl)oxy)-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)octanenitrile (4ap):

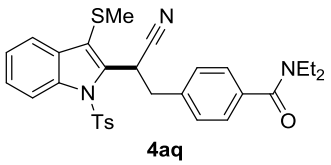
Following the general procedure, the title compound was obtained as colorless oil, 273.8 mg, 96% yield. (Rf = 0.32, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 3H), 7.42 – 7.36 (m, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.24 (dd, *J* = 9.3, 6.2 Hz, 1H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.32 (br s, 6H), 2.01 – 1.93 (m, 1H), 1.72 – 1.62 (m, 1H), 1.57 – 1.32 (m, 8H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 136.9, 136.5, 135.0, 130.5, 130.2, 126.5, 126.2, 124.5, 119.8, 119.2, 118.6, 115.6, 63.2, 34.0, 32.7, 29.0, 28.7, 27.6, 26.0, 25.6, 21.6, 18.4, 18.2, -5.2.

IR (neat): 2927, 2855, 2240, 1597, 1494, 1448, 1377, 1305, 1254, 1170, 1090, 834, 743, 660.

HRMS (ESI-TOF): calculated for [$C_{30}H_{43}N_2O_3S_2Si$ ($M + H^+$)]: 571.2479, found: 571.2485.



4aq

4-(2-cyano-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)ethyl)-N,N-diethylbenzamide (4aq):

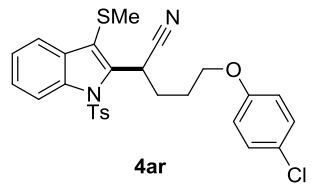
Following the general procedure, the title compound was obtained as colorless oil, 186.6 mg, 68% yield. (Rf = 0.39, eluent: PE/EtOAc = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 3H), 7.42 – 7.32 (m, 6H), 7.23 (d, *J* = 8.2 Hz, 2H), 5.46 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.67 – 3.10 (m, 6H), 2.41 – 2.11 (m, 6H), 1.31 – 1.01 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.0, 145.9, 137.5, 136.6, 136.5, 134.9, 130.3, 129.4, 126.9, 126.7, 126.4, 124.6, 120.0, 118.5, 115.5, 43.4, 39.6, 39.3, 31.6, 21.7, 18.1, 14.3, 13.0. Three aromatic carbon peaks are overlapped.

IR (neat): 2977, 2928, 2242, 1734, 1626, 1446, 1372, 1287, 1239, 1174, 1091, 811, 731.

HRMS (ESI-TOF): calculated for [$C_{30}H_{32}N_3O_3S_2$ (M + H^+)]: 546.1880, found: 546.1885.



4ar

(5-(4-chlorophenoxy)-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4ar):

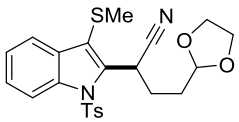
Following the general procedure, the title compound was obtained as colorless oil, 189.2 mg, 72% yield. (Rf = 0.21, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 3H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.21 (dd, *J* = 7.6, 5.7 Hz, 4H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.37 (t, *J* = 7.6 Hz, 1H), 4.05 – 3.95 (m, 2H), 2.58 – 2.48 (m, 1H), 2.38 – 2.24 (m, 7H), 2.16 – 2.07 (m, 1H), 2.01 – 1.91 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.4, 145.9, 136.6, 136.4, 134.9, 130.5, 130.2, 129.4, 126.6, 126.3, 125.7, 124.6, 119.9, 119.0, 115.8, 115.7, 67.1, 31.0, 28.7, 27.2, 21.7, 18.2. One aromatic carbon peak is overlapped.

IR (neat): 2925, 2240, 1733, 1596, 1491, 1446, 1373, 1239, 1168, 1090, 822, 732.

HRMS (ESI-TOF): calculated for [$C_{27}H_{25}ClN_2O_3S_2Na$ (M + Na^+)]: 547.0887, found: 544.0891.



4as

4-(1,3-dioxolan-2-yl)-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)butanenitrile (4as):

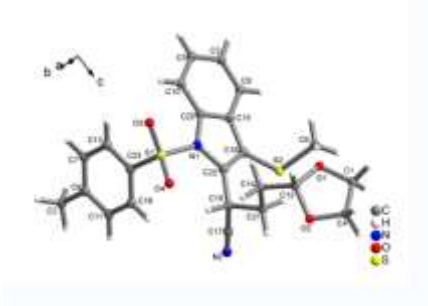
Following the general procedure, the title compound was obtained as white solid, m.p. 121-123 ℃, 177.1 mg, 78% yield. (Rf = 0.31, eluent: PE/EtOAc = 3/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.40 (dd, *J* = 9.3, 6.4 Hz, 1H), 4.96 (t, *J* = 4.2 Hz, 1H), 4.04 – 3.96 (m, 2H), 3.93 – 3.82 (m, 2H), 2.50 – 2.41 (m, 1H), 2.33 (d, *J* = 5.1 Hz, 6H), 2.24 – 2.15 (m, 1H), 2.07 – 1.97 (m, 1H), 1.90 – 1.80 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.8, 136.63, 136.57, 134.9, 130.5, 130.2, 126.6, 126.2, 124.6, 119.8, 119.0, 115.7, 103.4, 65.2, 65.1, 31.2, 28.8, 28.2, 21.7, 18.2.

IR (neat): 2993, 2979, 2957, 2921, 2877, 2237, 1599, 1447, 1376, 1307, 1252, 1132, 1097, 814, 750, 660.

HRMS (ESI-TOF): calculated for [$C_{23}H_{24}N_2O_4S_2Na$ ($M + Na^+$)]: 479.1070, found: 479.1078.



4as

Single crystals of product **4as** was obtained through slow evaporation at room temperature of a solution in ethyl acetate – dichloromethane.

Bond precision:	C-C = 0.0038 A		Wavelength=0.71073
Cell:	a=12.143(3)	b=10.204(2)	c=18.499(4)
	alpha=90	beta=94.972(12)	gamma=90
Temperature:	296 K		
	Calculated		Reported
Volume	2283.5(9)		2283.4(8)
Space group	P 21/c		P2(1)/c
Hall group	-P 2ybc		?
Moiety formula	C23 H24 N2 O4 S2		C23 H24 N2 O4 S2

Sum formula	C23 H24 N2 O4 S2	C23 H24 N2 O4 S2
Mr	456.56	456.56
Dx,g cm-3	1.328	1.328
Z	4	4
Mu (mm-1)	0.265	0.265
F000	960.0	960.0
F000'	961.39	
h,k,lmax	15,13,24	15,13,24
Nref	5276	5261
Tmin,Tmax	0.915,0.943	0.905,0.943
Tmin'	0.909	

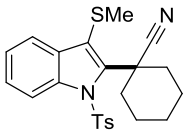
Correction method= # Reported T Limits: Tmin=0.905 Tmax=0.943 AbsCorr = EMPIRICAL

Data completeness= 0.997 Theta(max)= 27.550

R(reflections)= 0.0564(3670) wR2(reflections)= 0.1367(5261)

S = 1.052 Npar= 280

For more details please see the CIF file attached with ESI. The crystal data of **4as** has already been deposited at Cambridge Crystallographic Data Center, UK, and the CCDC reference number is 1822811.



4at

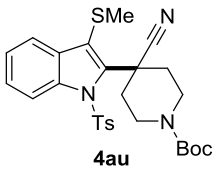
1-(3-(methylthio)-1-tosyl-1H-indol-2-yl)cyclohexane-1-carbonitrile (4at): Following the general procedure, the title compound was obtained as white solid, m.p. 138-140 ℃, 197.4 mg, 93% yield. (Rf = 0.23, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 2H), 2.77 – 2.60 (m, 4H), 2.29 (s, 3H), 2.21 (s, 3H), 1.95 – 1.66 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 144.9, 142.4, 139.7, 133.4, 131.7, 128.8, 127.4, 127.1, 126.4, 125.4, 121.6, 119.9, 118.2, 42.8, 35.8, 24.6, 23.2, 21.5, 18.4.

IR (neat): 2933, 2860, 2235, 1594, 1495, 1440, 1373, 1354, 1311, 1176, 818, 753, 659.

HRMS (ESI-TOF): calculated for [$C_{23}H_{24}N_2O_2S_2Na$ ($M + Na^+$)]: 447.1171, found: 447.1179.



4au

tert-butyl 4-cyano-4-(3-(methylthio)-1-tosyl-1H-indol-2-yl)piperidine-1-carboxylate (4au):

Following the general procedure, the title compound was obtained as colorless oil, 165.1 mg, 63% yield. (Rf = 0.27, eluent: PE/EtOAc = 5/1)

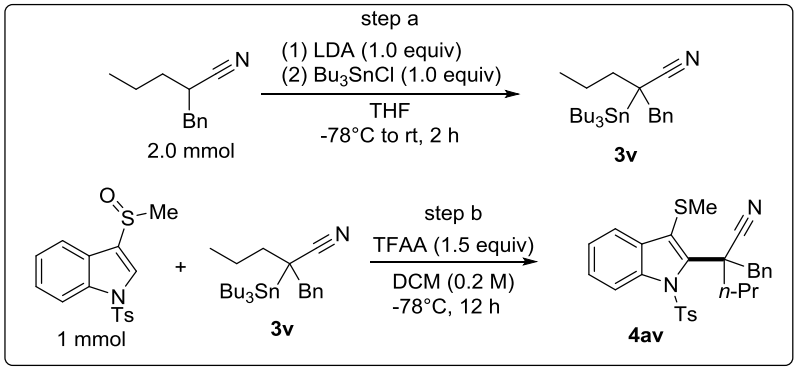
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.29 (m, 4H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 2H), 4.17 – 3.93 (m, 2H), 3.47 – 3.26 (m, 2H), 2.92 – 2.59 (m, 4H), 2.32 – 2.18 (m, 6H), 1.45 (s, 9H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.6, 145.2, 139.9, 139.6, 133.3, 131.5, 128.9, 128.3, 127.3, 126.8, 125.6, 120.4, 120.2, 118.2, 80.1, 41.3, 40.9, 40.3, 35.6, 35.3, 28.4, 21.6, 18.8.

IR (neat): 2977, 2928, 2248, 1687, 1596, 1446, 1366, 1248, 1169, 1150, 812, 726, 660.

HRMS (ESI-TOF): calculated for [$C_{27}H_{31}N_3O_4S_2Na$ (M + Na^+)]: 548.1648, found: 548.1656.

2-benzyl-2-(3-(methylthio)-1-tosyl-1H-indol-2-yl)pentanenitrile (4av):



Step a: To the solution of (*i*-Pr)$_2$NH (280 μL, 2.0 mmol) in THF (2 mL) was added *n*-BuLi (0.8 mL, 2.5 M in hexane) at -78 ℃. After stirring for 10 min, to the mixture was added a solution of 2-benzylpentanenitrile (346 mg, 2.0 mmol) in THF (2 mL). The mixture was sirred for 5 min. Under the same temperature, to the mixture was added dropwise a solution of Bu_3SnCl (523μL, 2.0 mmol) in THF (2 mL). The resulting mixture was stirred for 2 h, after which the reaction mixture was allowed to warm to room temperture. The mixture was then concentrated and diluted with petroleum ether (15 mL). After filtration and concentration, the crude product **3v** was obtained which was directly used without further purification.

Step b: Following the general procedure, the title compound was obtained as white solid, m.p. 101-103 ℃, 308 mg, 63% yield. (Rf = 0.20, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.49 (d, *J* = 7.7

Hz, 1H), 7.39 – 7.29 (m, 6H), 7.27 – 7.22 (m, 1H), 7.04 (d, *J* = 8.2 Hz, 2H), 3.98 (d, *J* = 13.2 Hz, 1H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.20 – 3.15 (m, 1H), 2.33 (s, 3H), 2.26 (s, 3H), 1.94 – 1.89 (m, 1H), 1.62 – 1.50 (m, 1H), 1.29 – 1.17 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.1, 140.6, 139.4, 135.3, 133.3, 132.4, 131.1, 129.2, 128.3, 127.5, 126.8, 126.4, 126.3, 125.3, 121.6, 120.0, 117.7, 47.9, 44.3, 39.8, 21.6, 18.8, 17.6, 13.9.

IR (neat): 3031, 2961, 2929, 2872, 2241, 1595, 1496, 1448, 1360, 1300, 1166, 763, 725, 702.

HRMS (ESI-TOF): calculated for [$C_{28}H_{28}N_2O_2S_2Na$ ($M + Na^+$)]: 511.1484, found: 511.1496.

5 Density functional theory (DFT) mechanistic study

5.1 Computational details

All structures were optimized in the gas phase at M06[12]/BSI level, where BSI represents a basis set with SDD[13] for Sn and 6-31G(d,p) for other non-metal atoms. Harmonic frequency analysis calculations were subsequently performed to verify the optimized geometries to be minima (no imaginary frequency) or transition states (TSs, having unique one imaginary frequency). The energies were then improved by M06/BSII//M06/BSI single-point calculations with solvent effects accounted by the SMD[14] solvent model, using the experimental solvent (dichloromethane). BSII denotes a basis set with SDD for Sn and 6-311++G(d,p) for other non-metal atoms. The refined energies were then corrected to enthalpies and free energies at experimental temperature (195.15K) and 1 atm, using the gas phase M06/BSI harmonic frequencies. Total energies and Cartesian coordinates of all optimized structures are given below in this Supporting Information. All standard DFT calculations were carried out using Gaussian 09 program.[15]

Reference

[12] a) A. D. Kulkarni, D. G. Truhlar, *J. Chem. Theory Comput.*, 2011, **7**, 2325; b) P. Sliwa, J. Handzlik, *J. Chem. Phys. Lett.*, 2010, **493**, 273; c) Y. Zhao, D. G. Truhlar, *J. Chem. Theory Comput.*, 2009, **5**, 324; d) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41,** 157.

[13] a) D. Andrae, U. Häussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta.*, 1990, **77**, 123; b) M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866.

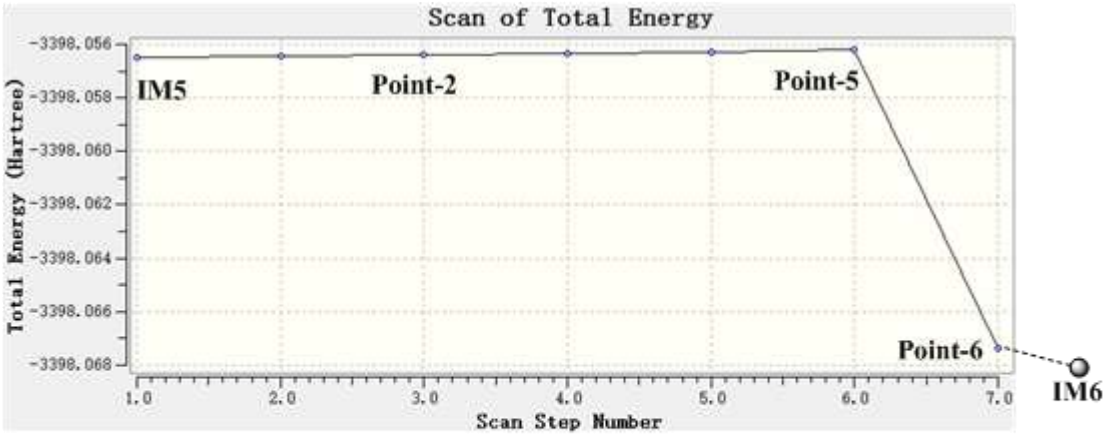
[14] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B.*, 2009, **113**, 6378.

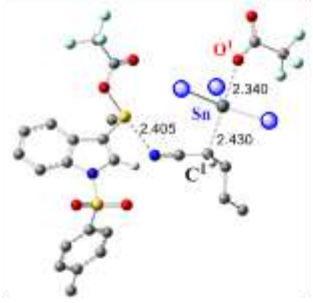
[15] Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D.

Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

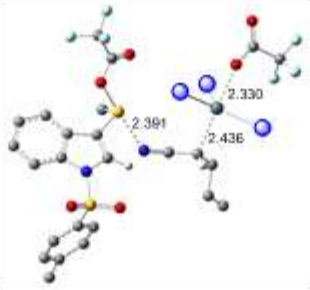
5.2 Results for potential energy surface (PES) scan

The PES scan was carried out strating **IM5** toward **IM6,** using the Sn···O[C(O)CCF$_3$] distance as the scan/reaction coordinate by an interval of 0.005 angstroms. As shown by the PES below, the energy rises very slowly at first five points then goes down rapidly, reaching **Point-6**, which is close to **IM6**, as shown by the broken C^1-Sn bond and formed Sn-O^1 bond. These results indicate that the OC(O)CF$_3$ can easily extract the SnBu$_3$ group, giving **IM6** without an appreicable barrier. The PES explains why a S_N2 transition state could not be located.

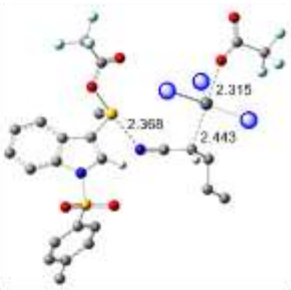




IM5

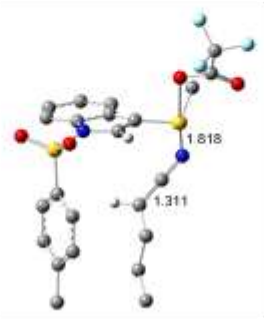


Point-2



Point-5

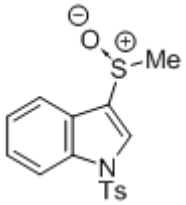
Point-6



IM6

5.3: Cartesian Coordinates in Å, SCF Energies and Free Energies (in a.u.) at 195.15 K and 1 atm for the Optimized Structures [BSI=6-31G(d,p), BSII=6-311++G(d,p)]

1a



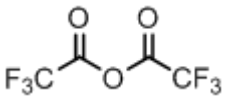
M06/BS1 SCF energy: -1694.786256 a.u.

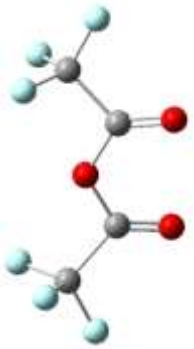
M06/BS2 SCF energy in solution: -1695.057078 a.u.

M06/BS2 Free energy in solution: -1694.805290 a.u.

H	3.693443	0.681794	-1.875890
C	2.746753	1.131607	-1.587730
C	0.304858	2.345848	-0.768588
C	2.027233	0.615281	-0.503301
C	2.230520	2.229197	-2.256833
C	1.024181	2.823404	-1.854675
C	0.825917	1.238373	-0.102708
H	2.771877	2.646380	-3.102663
H	0.648614	3.687876	-2.396936
H	-0.611793	2.828465	-0.443474
C	2.242846	-0.485566	0.401656
N	0.358159	0.544626	1.023028
C	1.227185	-0.500998	1.307337
H	1.037593	-1.154303	2.150594
S	-1.170227	0.727287	1.763516
S	3.616331	-1.616904	0.411973
O	-1.091925	-0.091663	2.960827
O	-1.419594	2.156010	1.832738
C	-2.278810	-0.004501	0.605264
C	-4.022853	-1.176382	-1.209427
C	-3.111500	0.809164	-0.155174
C	-2.296529	-1.394657	0.481259

TFAA





M06/BS1 SCF energy: -976.776506 a.u.

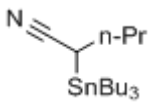
M06/BS2 SCF energy in solution: -977.061761 a.u.

M06/BS2 Free energy in solution: -977.030338 a.u.

C	-0.131698	1.191902	0.699607
O	0.000000	0.000000	0.038926
C	0.131698	-1.191902	0.699607
C	0.101646	2.310951	-0.328900
C	-0.101646	-2.310951	-0.328900
F	-0.800953	2.227735	-1.300562
F	1.311943	2.187322	-0.861408
F	0.000000	3.486761	0.260433
F	-1.311943	-2.187322	-0.861408
F	0.000000	-3.486761	0.260433
F	0.800953	-2.227735	-1.300562
O	-0.408456	1.357914	1.841735
O	0.408456	-1.357914	1.841735

C	-3.169240	-1.967819	-0.427571
C	-3.982180	0.211215	-1.058434
H	-3.086374	1.888658	-0.029878
H	-1.646011	-2.015994	1.093534
H	-3.200252	-3.050759	-0.534909
H	-4.645844	0.832844	-1.656163
C	-4.954590	-1.817800	-2.187475
H	-4.397395	-2.300876	-2.999864
H	-5.636127	-1.087047	-2.633632
H	-5.554279	-2.599566	-1.706563
O	4.838328	-0.852180	-0.034649
C	3.085118	-2.597149	-1.019841
H	2.948762	-1.944899	-1.888292
H	3.873154	-3.328626	-1.222986
H	2.151927	-3.115091	-0.775800

3b

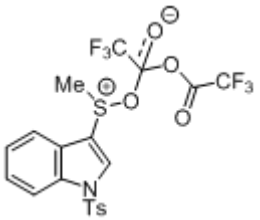


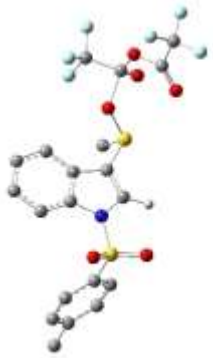
M06/BS1 SCF energy: -726.467157 a.u.

M06/BS2 SCF energy in solution: -726.643061 a.u.

M06/BS2 Free energy in solution: -726.192550 a.u.

TS1





M06/BS1 SCF energy: -2671.578887 a.u.

M06/BS2 SCF energy in solution: -2672.132456 a.u.

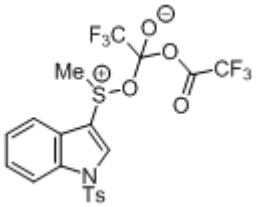
M06/BS2 Free energy in solution: -2671.830859 a.u.

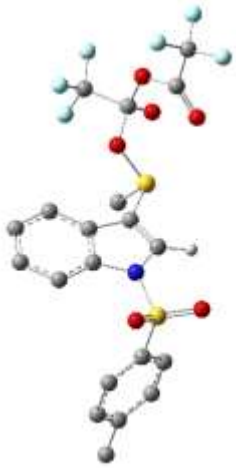
H	-0.051251	-2.012595	1.535493
C	-0.854955	-1.470942	1.015319
Sn	0.176258	0.053872	-0.264667
C	1.727543	-1.023214	-1.333869
H	1.256776	-1.705896	-2.055108
C	-1.339201	0.975716	-1.518290
H	-0.822303	1.663295	-2.203992
H	-1.804413	0.204676	-2.148073
C	-2.391207	1.725777	-0.706753
H	-1.901340	2.451871	-0.035551

H	-0.759320	-2.192126	1.329435
C	0.189678	-1.756240	1.635707
C	2.622637	-0.542603	2.488487
C	0.735968	-0.681313	0.924371
C	0.875532	-2.221066	2.745258
C	2.076563	-1.625227	3.161441
C	1.933198	-0.082932	1.368064
H	0.471897	-3.055634	3.313182
H	2.585052	-2.010933	4.041620
H	3.534888	-0.064857	2.833104

H	-2.926539	1.028105	-0.041202	C	0.331669	0.059482	-0.243961
C	-3.407236	2.458393	-1.574898	N	2.212234	0.983597	0.499495
H	-2.875359	3.165115	-2.230534	C	1.236959	1.054997	-0.472427
H	-3.894322	1.733382	-2.245147	H	1.272165	1.820200	-1.238917
C	-4.454679	3.195637	-0.758209	S	3.631106	1.956439	0.487291
H	-3.990291	3.941800	-0.100231	S	-1.073975	-0.236924	-1.243396
H	-5.017637	2.503301	-0.118653	O	3.320237	3.016454	-0.454313
H	-5.177324	3.719744	-1.394381	O	3.935661	2.231402	1.878789
C	1.004693	1.527755	1.096345	C	4.852173	0.884504	-0.188820
H	1.588920	1.004346	1.867097	C	6.769414	-0.799920	-1.276008
H	0.164120	2.008489	1.619492	C	5.808079	0.319930	0.649088
H	2.290200	-0.287447	-1.926641	C	4.831676	0.630509	-1.561612
C	2.662066	-1.784298	-0.400845	C	5.791517	-0.213507	-2.092339
H	3.096881	-1.096187	0.344389	C	6.764628	-0.520339	0.092297
H	2.091362	-2.528579	0.180138	H	5.811622	0.546668	1.712038
C	3.793649	-2.494175	-1.134791	H	4.083526	1.094047	-2.201501
H	4.367087	-1.751315	-1.710277	H	5.794277	-0.423791	-3.160502
H	3.362361	-3.183699	-1.876743	H	7.524445	-0.965924	0.731218
C	4.717918	-3.251246	-0.196900	C	7.797022	-1.705290	-1.875567
H	5.173437	-2.575247	0.538743	H	8.495615	-2.080227	-1.121662
H	5.531563	-3.750535	-0.735576	H	8.374898	-1.185080	-2.649110
H	4.170446	-4.021571	0.362364	H	7.324045	-2.567104	-2.362179
C	1.861879	2.569887	0.384483	O	-2.134809	-0.570178	-0.133840
H	2.698396	2.077317	-0.140909	C	-0.622368	-1.844407	-1.928385
H	1.271693	3.070144	-0.403113	H	-0.326907	-2.526618	-1.127481
C	2.428620	3.627220	1.323383	H	-1.498489	-2.219804	-2.463017
H	3.008306	3.127056	2.114552	H	0.203909	-1.682030	-2.627209
H	1.596546	4.135477	1.834369	C	-4.348809	1.295027	-0.521739
C	3.299760	4.644588	0.606506	O	-4.527921	0.023672	-0.174500
H	4.150976	4.157472	0.112181	C	-3.758560	-0.994183	-0.840864
H	3.703615	5.396954	1.293861	C	-5.437926	2.139824	0.159906
H	2.733034	5.175373	-0.169973	C	-3.916554	-2.247852	0.033898
C	-1.691566	-2.429718	0.160356	F	-5.401642	1.974383	1.479927
H	-1.033152	-2.863083	-0.609460	F	-6.640831	1.767391	-0.273385
H	-2.461159	-1.858301	-0.382922	F	-5.264712	3.422597	-0.114201
C	-2.351520	-3.550071	0.953272	F	-3.743769	-2.030202	1.331937
H	-1.574826	-4.110000	1.495758	F	-3.056230	-3.186659	-0.354493
H	-3.003875	-3.109927	1.722327	F	-5.153395	-2.721548	-0.143677
C	-3.152189	-4.488752	0.067978	O	-3.503913	1.765996	-1.227698
H	-2.513529	-4.956087	-0.692988	O	-3.731894	-1.069127	-2.048880
H	-3.950723	-3.950491	-0.459160				
H	-3.621460	-5.292884	0.645732				
C	-1.629804	-0.764764	1.999024				
N	-2.255966	-0.144349	2.764977				

IM1





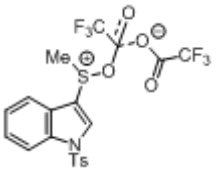
M06/BS1 SCF energy: -2671.582093 a.u.

M06/BS2 SCF energy in solution: -2672.136612 a.u.

M06/BS2 Free energy in solution: -2671.834991 a.u.

H	-0.709444	-2.235689	1.526526
C	0.205124	-1.713814	1.800708
C	2.551413	-0.297368	2.577858
C	0.696724	-0.666584	1.013198
C	0.902239	-2.051076	2.948815
C	2.059774	-1.354895	3.328608
C	1.853380	0.031975	1.418293
H	0.540715	-2.862662	3.575237
H	2.578636	-1.639082	4.240614
H	3.428176	0.259589	2.894143
C	0.265876	-0.035476	-0.209724
N	2.084521	1.044494	0.471909
C	1.123810	0.986511	-0.508315
H	1.128845	1.682119	-1.339477
S	3.506642	2.016005	0.342469
S	-1.045858	-0.471649	-1.267247
O	3.175404	2.989836	-0.680775
O	3.837494	2.407941	1.698691
C	4.705675	0.879559	-0.263385
C	6.569594	-0.932261	-1.232734
C	5.640119	0.337566	0.614055
C	4.678959	0.538132	-1.616333

TS2

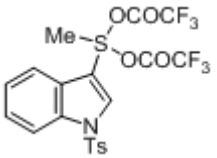
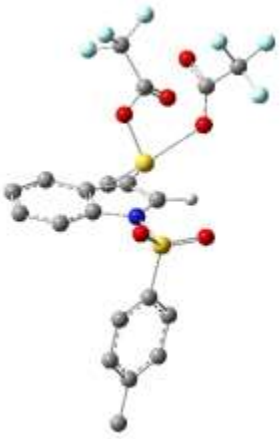
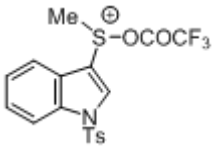


M06/BS1 SCF energy: -2671.577603 a.u.

M06/BS2 SCF energy in solution: -2672.135913 a.u.

M06/BS2 Free energy in solution: -2671.836227 a.u.

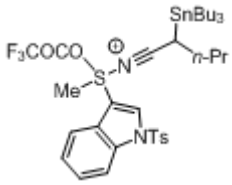
H	-0.566785	-3.135326	1.104833
C	0.305081	-2.578257	1.438676
C	2.524880	-1.089069	2.416504
C	0.657171	-1.363088	0.843573
C	1.077476	-3.043928	2.490140
C	2.175751	-2.313304	2.966751
C	1.749694	-0.631693	1.354614
H	0.820755	-3.987593	2.964650
H	2.756611	-2.704130	3.798137
H	3.350299	-0.504131	2.811456
C	0.121060	-0.562406	-0.230633
N	1.837576	0.562365	0.618149
C	0.854546	0.593336	-0.330063
H	0.743724	1.438026	-1.000126
S	3.114345	1.732291	0.695514
S	-1.155622	-0.870306	-1.349249
O	2.622729	2.831984	-0.111896
O	3.418784	1.883564	2.104627
C	4.437489	0.912918	-0.123515
C	6.506972	-0.389828	-1.431934
C	5.471904	0.364488	0.627984
C	4.409398	0.825991	-1.516579

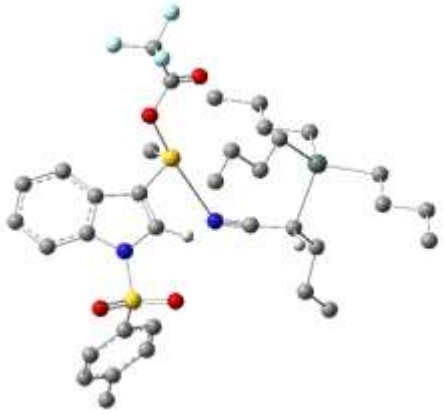
C	5.613076	-0.368467	-2.088488	C	5.447247	0.172294	-2.158013
C	6.568841	-0.567200	0.115929	C	6.503532	-0.284112	-0.039080
H	5.647733	0.627452	1.661585	H	5.476441	0.456510	1.710793
H	3.944627	0.979938	-2.286942	H	3.595476	1.270737	-2.085304
H	5.609286	-0.646838	-3.140777	H	5.446332	0.096167	-3.243847
H	7.309641	-0.998364	0.786391	H	7.323798	-0.715607	0.530937
C	7.584514	-1.891137	-1.767101	C	7.625381	-1.074246	-2.149419
H	8.358978	-1.358417	-2.333766	H	7.244336	-1.817806	-2.859098
H	7.128985	-2.614034	-2.453055	H	8.304716	-1.575181	-1.453356
H	8.082358	-2.440470	-0.962030	H	8.211750	-0.352634	-2.731998
O	-2.149859	-0.759177	-0.115017	O	-2.372278	-1.235403	-0.280878
C	-0.561468	-2.137370	-1.741680	C	-0.805596	-2.541668	-1.905901
H	-0.321893	-2.731616	-0.856660	H	-0.651089	-3.221738	-1.066359
H	-1.400212	-2.557514	-2.300239	H	-1.664834	-2.851777	-2.507727
H	0.314703	-2.038736	-2.390133	H	0.089046	-2.490260	-2.534141
C	-4.059486	1.318203	-0.504485	C	-3.320004	1.568247	-0.267698
O	-4.358160	0.082208	-0.181021	O	-4.145842	0.619295	-0.107388
C	-3.503230	-1.031944	-0.759911	C	-3.636541	-1.065695	-0.887570
C	-5.143723	2.257310	0.053897	C	-3.914853	2.916038	0.197729
C	-3.990034	-2.238564	0.069623	C	-4.647246	-1.826407	-0.024078
F	-5.180636	2.176780	1.384478	F	-3.027124	3.905996	0.141667
F	-6.345714	1.921215	-0.412622	F	-4.363731	2.840309	1.454528
F	-4.895644	3.514334	-0.283696	F	-4.951665	3.253917	-0.578485
F	-3.928605	-2.047763	1.387715	F	-4.483485	-1.659049	1.280039
F	-3.232550	-3.300451	-0.222670	F	-4.483494	-3.130155	-0.292724
F	-5.249155	-2.528068	-0.251176	F	-5.882797	-1.488602	-0.356368
O	-3.108149	1.741900	-1.111006	O	-2.182844	1.567802	-0.734479
O	-3.481937	-1.143942	-1.990816	O	-3.742120	-1.001365	-2.091608
IM2  				**IM3**  			

M06/BS1 SCF energy: -2671.578695 a.u. M06/BS2 SCF energy in solution: -2672.139086 a.u. M06/BS2 Free energy in solution: -2671.839332 a.u.				M06/BS1 SCF energy: -2145.409590 a.u. M06/BS2 SCF energy in solution: -2145.801947 a.u. M06/BS2 Free energy in solution: -2145.525815 a.u.			
H	-0.456981	-3.437230	0.941703	H	1.846306	2.097403	-1.786399
C	0.390553	-2.844097	1.275201	C	0.920048	2.163818	-1.222141
C	2.564203	-1.298893	2.264526	C	-1.473666	2.424473	0.295944
C	0.653517	-1.578988	0.740855	C	0.402462	1.066993	-0.528844
C	1.223060	-3.326413	2.272498	C	0.229152	3.363934	-1.163096
C	2.298925	-2.568634	2.755267	C	-0.951346	3.491811	-0.419016
C	1.727935	-0.824229	1.259242	C	-0.779370	1.221933	0.225083
H	1.031558	-4.308343	2.697632	H	0.617208	4.226924	-1.697578
H	2.928894	-2.974252	3.542563	H	-1.462177	4.450414	-0.388021
H	3.373545	-0.694663	2.663819	H	-2.368880	2.531185	0.901212
C	0.039287	-0.737047	-0.261013	C	0.814264	-0.303280	-0.310110
N	1.733548	0.414713	0.595121	N	-1.049852	-0.007751	0.856145
C	0.714880	0.461433	-0.305943	C	-0.094345	-0.907905	0.548033
H	0.521082	1.343961	-0.904233	H	-0.116989	-1.919835	0.939374
S	2.947625	1.650619	0.727322	S	-2.446918	-0.391293	1.852269
S	-1.240126	-1.001293	-1.377457	S	2.128104	-1.230679	-0.854251
O	2.409881	2.743888	-0.058551	O	-2.122889	-1.704243	2.373319
O	3.222416	1.780294	2.144401	O	-2.624771	0.761488	2.709706
C	4.317657	0.911030	-0.089029	C	-3.732439	-0.482782	0.664370
C	6.460641	-0.267608	-1.396011	C	-5.754657	-0.642315	-1.223113
C	5.399179	0.459136	0.660469	C	-4.670991	0.542646	0.595187
C	4.280798	0.793359	-1.479794	C	-3.779031	-1.591381	-0.184076
C	5.354882	0.200922	-2.120437	C	-4.793069	-1.658933	-1.122653
C	6.467281	-0.127955	-0.006381	C	-5.681224	0.447906	-0.352750
H	5.409133	0.573644	1.741203	H	-4.621074	1.389075	1.274889
H	3.428742	1.161877	-2.047440	H	-3.039122	-2.385608	-0.105118
H	5.346069	0.098191	-3.204027	H	-4.848596	-2.513790	-1.794021
H	7.324302	-0.483422	0.562059	H	-6.429208	1.235147	-0.419849
C	7.612060	-0.896597	-2.112155	C	-6.845184	-0.741228	-2.240128
H	7.272779	-1.704101	-2.771648	H	-6.434550	-0.906515	-3.243111
H	8.345874	-1.307502	-1.412318	H	-7.458096	0.164845	-2.262854
H	8.123467	-0.163157	-2.747807	H	-7.503035	-1.591521	-2.022288
O	-2.499875	-1.350902	-0.315600	O	3.431127	-0.270952	-0.267959
C	-0.956208	-2.684586	-1.940309	C	2.343236	-0.876163	-2.597743
H	-0.922427	-3.393377	-1.111660	H	2.506106	0.189955	-2.767155
H	-1.776802	-2.927251	-2.621452	H	3.199915	-1.465930	-2.936459
H	-0.010268	-2.680026	-2.491292	H	1.431868	-1.221911	-3.096323
C	-3.140948	1.664134	-0.257985	C	4.612514	-0.920727	-0.208849
O	-4.099930	0.885622	-0.065496	C	5.652127	0.018089	0.430799
C	-3.726443	-1.169033	-0.901477	F	5.251914	0.371535	1.644489
C	-3.445764	3.105681	0.213415	F	5.776979	1.110633	-0.313087

C	-4.814409	-1.657776	0.058642	F	6.815397	-0.595312	0.511205
F	-2.441160	3.955675	-0.005330	O	4.819137	-2.030929	-0.597871
F	-3.707970	3.125545	1.528042				
F	-4.526871	3.593435	-0.412036				
F	-4.562159	-1.413119	1.332236				
F	-4.877622	-2.990622	-0.096777				
F	-5.986432	-1.149543	-0.274278				
O	-2.018198	1.462674	-0.748928				
O	-3.889344	-1.043066	-2.083950				

IM4



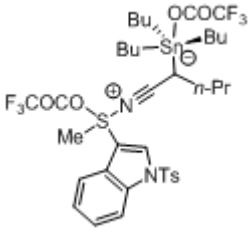


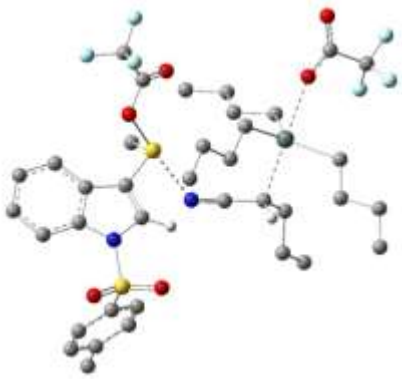
M06/BS1 SCF energy: -2871.901942 a.u.

M06/BS2 SCF energy in solution: -2872.468731 a.u.

M06/BS2 Free energy in solution: -2871.719298 a.u.

IM5





M06/BS1 SCF energy: -3398.056988 a.u.

M06/BS2 SCF energy in solution: -3398.792834 a.u.

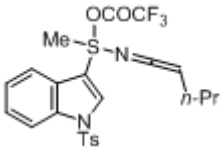
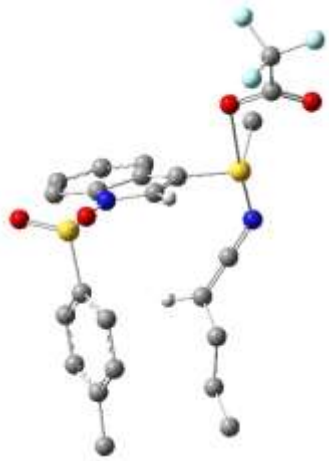
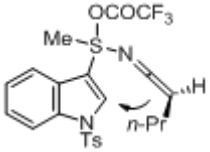
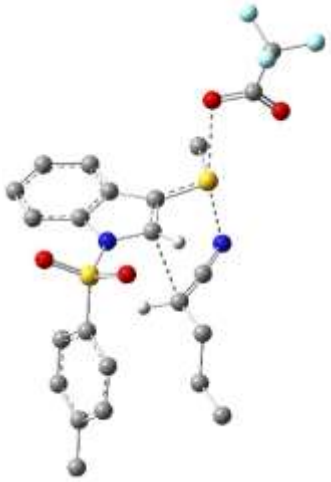
M06/BS2 Free energy in solution: -3398.020030 a.u.

H	-3.142995	3.685703	-1.257740	H	-3.599819	3.807026	-1.067832
C	-3.785798	2.979581	-0.737877	C	-4.307677	3.153265	-0.565816
C	-5.502947	1.219835	0.697197	C	-6.181310	1.533133	0.831437
C	-3.266230	1.844422	-0.108489	C	-3.907861	1.928640	-0.019566
C	-5.151335	3.203734	-0.665308	C	-5.632164	3.535963	-0.431857
C	-5.997800	2.333491	0.035672	C	-6.557604	2.734324	0.251396
C	-4.132180	0.994940	0.612742	C	-4.850888	1.149008	0.686335
H	-5.573698	4.079048	-1.151974	H	-5.957880	4.483127	-0.854176
H	-7.063099	2.544223	0.077625	H	-7.588267	3.066937	0.343052
H	-6.152279	0.565785	1.271593	H	-6.887547	0.926618	1.389890
C	-1.947213	1.277166	0.060837	C	-2.665522	1.192668	0.059557
N	-3.347942	-0.019173	1.192857	N	-4.181004	0.017006	1.179471
C	-2.044361	0.155370	0.853455	C	-2.874087	0.048012	0.784431
H	-1.279207	-0.542928	1.173765	H	-2.193485	-0.758793	1.031169
S	-3.923541	-1.486975	1.939078	S	-4.906611	-1.419166	1.827570

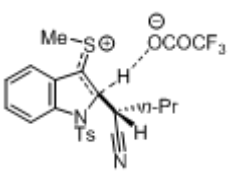
S	-0.425805	1.725687	-0.595559	S	-1.101402	1.564647	-0.599496
O	-2.726108	-2.054190	2.528993	O	-3.782697	-2.149155	2.382120
O	-5.063860	-1.092523	2.740441	O	-6.007895	-0.962754	2.652111
C	-4.439561	-2.425538	0.547125	C	-5.511407	-2.216815	0.382156
C	-5.230233	-3.909111	-1.656121	C	-6.442725	-3.471418	-1.908884
C	-5.795172	-2.666690	0.349833	C	-6.879560	-2.235707	0.132973
C	-3.464652	-2.902653	-0.332384	C	-4.591680	-2.806252	-0.488859
C	-3.871988	-3.641004	-1.428803	C	-5.069041	-3.428059	-1.628930
C	-6.177543	-3.414387	-0.757074	C	-7.333554	-2.869961	-1.017064
H	-6.532996	-2.286113	1.051202	H	-7.575811	-1.777014	0.830230
H	-2.408980	-2.693328	-0.165625	H	-3.524227	-2.778103	-0.278064
H	-3.129689	-4.022330	-2.127958	H	-4.369241	-3.894021	-2.320486
H	-7.232698	-3.618345	-0.927071	H	-8.400918	-2.900438	-1.226052
C	-5.642412	-4.717124	-2.844101	C	-6.931173	-4.158653	-3.143130
H	-5.245172	-4.286206	-3.770787	H	-6.475135	-3.724678	-4.041167
H	-6.731042	-4.780555	-2.932237	H	-8.018418	-4.087709	-3.242361
H	-5.247175	-5.738211	-2.776567	H	-6.658452	-5.221018	-3.131904
O	-0.485729	3.378412	-0.097456	O	-1.185009	3.233500	-0.095459
C	-0.729826	1.979370	-2.349452	C	-1.416059	1.862426	-2.352899
H	-1.627964	2.581903	-2.498245	H	-2.211847	2.601400	-2.464025
H	0.159295	2.465549	-2.762103	H	-0.476562	2.221427	-2.782742
H	-0.851458	0.976625	-2.769458	H	-1.701318	0.901096	-2.783738
C	0.668495	4.047860	-0.261210	C	-0.079475	3.946511	-0.339671
C	0.569745	5.394918	0.476148	C	-0.203289	5.295317	0.389602
F	0.509890	5.159189	1.782097	F	-0.216773	5.076638	1.700082
F	-0.523143	6.048960	0.108186	F	-1.336180	5.900405	0.047707
F	1.631766	6.129086	0.210748	F	0.816396	6.073367	0.084964
O	1.630445	3.656232	-0.855851	O	0.860400	3.602128	-0.997577
H	1.942867	-2.593245	0.541042	H	1.077167	-2.662902	0.487742
C	2.130574	-2.153749	-0.449797	C	1.274563	-2.158310	-0.468870
Sn	3.732707	-0.587198	-0.125633	Sn	3.035797	-0.628853	0.078155
C	5.315242	-1.696691	0.856491	C	4.186188	-2.114766	1.177613
H	5.752507	-2.401989	0.136331	H	4.862590	-2.621447	0.474687
C	4.172569	0.162886	-2.111345	C	3.431907	-0.094721	-1.991942
H	5.035367	0.838373	-2.029011	H	4.339778	0.520356	-1.994714
H	4.500401	-0.683512	-2.731626	H	3.670822	-1.013353	-2.547853
C	2.994456	0.884726	-2.758533	C	2.283198	0.652304	-2.659089
H	2.653889	1.706896	-2.105773	H	2.014639	1.541765	-2.062263
H	2.132044	0.201791	-2.853449	H	1.376138	0.023039	-2.683689
C	3.330858	1.451864	-4.132640	C	2.611300	1.095279	-4.080753
H	4.201004	2.119049	-4.040139	H	3.520834	1.714355	-4.060242
H	3.648476	0.629593	-4.791748	H	2.862956	0.208789	-4.683482
C	2.170739	2.203797	-4.760864	C	1.478941	1.865415	-4.737572
H	1.875592	3.061088	-4.138573	H	1.241682	2.775970	-4.168283

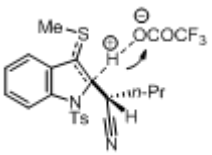
H	1.291166	1.555279	-4.876704
H	2.423332	2.594328	-5.753263
C	2.856841	0.927223	1.172676
H	2.518070	1.757203	0.533962
H	3.674786	1.332733	1.784942
H	6.108547	-0.980330	1.112369
C	4.829886	-2.425218	2.104983
H	4.358458	-1.710809	2.801799
H	4.039650	-3.147535	1.839828
C	5.943840	-3.165797	2.835403
H	6.729170	-2.446701	3.113862
H	6.416290	-3.874923	2.138562
C	5.449028	-3.900749	4.069470
H	5.000444	-3.205273	4.791068
H	6.258856	-4.431733	4.582710
H	4.681463	-4.640832	3.807401
C	1.727319	0.438210	2.073174
H	0.942884	-0.062127	1.476863
H	2.103267	-0.336528	2.762161
C	1.086748	1.558560	2.886388
H	0.620811	2.289970	2.201254
H	1.877476	2.116257	3.410627
C	0.060128	1.055529	3.885516
H	-0.740732	0.487773	3.391180
H	-0.412304	1.877021	4.435487
H	0.523093	0.385494	4.621147
C	2.620491	-3.212994	-1.446021
H	3.592441	-3.590981	-1.092824
H	2.812436	-2.737289	-2.420774
C	1.658231	-4.379891	-1.626225
H	1.464308	-4.838930	-0.645245
H	0.689078	-3.999000	-1.984007
C	2.196016	-5.419466	-2.593481
H	3.150377	-5.831159	-2.240672
H	2.372742	-4.982966	-3.585042
H	1.500213	-6.256213	-2.719577
C	0.944705	-1.482907	-0.876204
N	0.003702	-0.884644	-1.234090

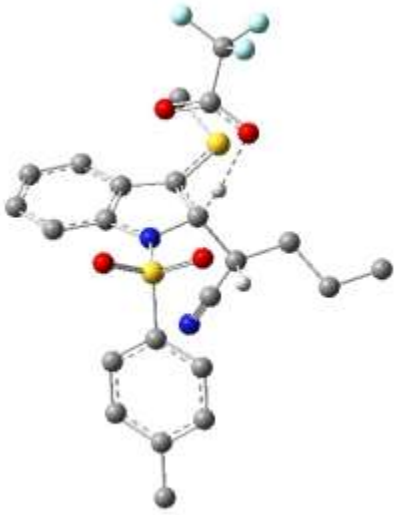
H	0.564411	1.258067	-4.793530
H	1.729049	2.175742	-5.758806
C	1.951101	0.825522	1.278822
H	1.628842	1.630721	0.599128
H	2.715975	1.272808	1.926711
H	4.827569	-1.524856	1.845836
C	3.381528	-3.129464	1.976798
H	2.661534	-2.613573	2.635727
H	2.771764	-3.758792	1.306729
C	4.257494	-4.042943	2.827417
H	4.864324	-3.426492	3.508014
H	4.973807	-4.562198	2.172137
C	3.450654	-5.054950	3.622399
H	2.746004	-4.553572	4.299071
H	4.090159	-5.702691	4.233329
H	2.860943	-5.701751	2.959046
C	0.784661	0.316065	2.112282
H	0.021224	-0.154337	1.468448
H	1.124858	-0.485344	2.789092
C	0.121058	1.411027	2.942371
H	-0.259920	2.202685	2.272295
H	0.888515	1.902969	3.558737
C	-0.996719	0.893269	3.831230
H	-1.784571	0.394771	3.247638
H	-1.473073	1.698999	4.401251
H	-0.615939	0.157428	4.551452
C	1.811872	-3.121735	-1.530549
H	2.839418	-3.415042	-1.261634
H	1.895836	-2.594942	-2.494037
C	0.966622	-4.377271	-1.708828
H	0.888916	-4.895140	-0.740131
H	-0.060090	-4.086228	-1.981203
C	1.539824	-5.314430	-2.756957
H	2.555798	-5.632240	-2.488574
H	1.600048	-4.822949	-3.736782
H	0.930983	-6.217926	-2.875091
C	0.119331	-1.459414	-0.859734
N	-0.827579	-0.838223	-1.187010
C	6.069417	1.204417	0.327716
O	4.874291	0.903141	0.598552
C	6.949832	-0.013778	-0.050439
F	8.124495	0.330242	-0.580341
F	6.346586	-0.829326	-0.934850
F	7.211471	-0.756885	1.040468

				O	6.633940	2.294567	0.363536
IM6  				**TS4**  			
M06/BS1 SCF energy: -2395.475565 a.u. M06/BS2 SCF energy in solution: -2395.948734 a.u. M06/BS2 Free energy in solution: -2395.557193 a.u.				M06/BS1 SCF energy: -2395.463942 a.u. M06/BS2 SCF energy in solution: -2395.938115 a.u. M06/BS2 Free energy in solution: -2395.549704 a.u.			
H	-1.206603	1.183420	3.675706	H	2.037820	2.521358	-2.431304
C	-0.570629	1.761542	3.010271	C	1.176108	2.754142	-1.816322
C	1.115787	3.289226	1.306033	C	-1.073110	3.432746	-0.226620
C	-0.468398	1.443068	1.651056	C	0.661077	1.825082	-0.902841
C	0.162518	2.830673	3.497125	C	0.568258	3.993954	-1.927526
C	0.990064	3.586747	2.654425	C	-0.541192	4.328591	-1.142628
C	0.387496	2.202862	0.823303	C	-0.460364	2.187561	-0.123471
H	0.093493	3.090581	4.550444	H	0.963227	4.718564	-2.634790
H	1.545238	4.426940	3.063971	H	-0.995595	5.310738	-1.245842
H	1.748320	3.880688	0.651742	H	-1.921546	3.699716	0.395681
C	-1.046521	0.430291	0.802736	C	1.025886	0.480839	-0.501405
N	0.316705	1.651687	-0.467504	N	-0.781648	1.093272	0.701661
C	-0.530904	0.566134	-0.453623	C	0.080079	0.055928	0.437091
H	-0.718768	-0.011607	-1.351295	H	0.088703	-0.830715	1.061898
S	1.361281	1.961111	-1.801600	S	-1.999610	1.005115	1.919852
S	-1.980581	-0.979536	1.235718	S	2.213529	-0.630254	-0.991678
O	0.615431	1.522961	-2.965599	O	-1.537730	-0.026602	2.829798
O	1.785700	3.338356	-1.637395	O	-2.190725	2.375724	2.355080
C	2.721001	0.870713	-1.531180	C	-3.437732	0.422523	1.077722
C	4.927835	-0.781445	-1.187315	C	-5.801201	-0.445012	-0.098262
C	3.618589	1.142704	-0.496373	C	-3.906055	1.072676	-0.063177
C	2.890253	-0.218133	-2.381493	C	-4.134503	-0.639197	1.654041
C	4.000352	-1.035872	-2.202124	C	-5.316515	-1.058664	1.062098

C	4.707684	0.303218	-0.326580	C	-5.080832	0.620842	-0.649028
H	3.475514	1.999143	0.159371	H	-3.369483	1.913840	-0.498517
H	2.176435	-0.408934	-3.178833	H	-3.751994	-1.126685	2.547721
H	4.157897	-1.879981	-2.871296	H	-5.873873	-1.883808	1.502666
H	5.420090	0.500436	0.472939	H	-5.453039	1.107487	-1.548293
C	6.155206	-1.621704	-1.035267	C	-7.044908	-0.955443	-0.750833
H	6.064187	-2.575499	-1.564709	H	-6.853689	-1.924388	-1.232174
H	6.375927	-1.825268	0.019291	H	-7.413438	-0.267497	-1.517868
H	7.028583	-1.098419	-1.445870	H	-7.841817	-1.118251	-0.016512
O	-3.655201	-0.086728	-0.284971	O	4.312225	0.208946	0.392310
C	-3.162596	-0.418537	2.483907	C	3.100642	0.181225	-2.325985
H	-3.377812	0.635740	2.304237	H	3.623885	1.049898	-1.921241
H	-4.057913	-1.023009	2.316258	H	3.834972	-0.560291	-2.647696
H	-2.733225	-0.593518	3.472573	H	2.410352	0.429384	-3.135507
C	-4.562973	-0.957334	-0.367841	C	5.075715	-0.750827	0.133307
C	-5.554989	-0.659519	-1.517652	C	6.328179	-0.770026	1.046301
F	-4.926406	-0.678861	-2.703511	F	5.978770	-0.851541	2.339962
F	-6.099488	0.558211	-1.380498	F	7.043149	0.358241	0.906083
F	-6.557423	-1.537265	-1.585892	F	7.152874	-1.790380	0.796729
O	-4.758078	-1.970077	0.309477	O	4.983377	-1.654839	-0.707857
H	2.211849	-0.768996	2.026826	H	-1.926351	-0.561307	-1.467385
C	1.616750	-1.617837	1.680268	C	-1.314380	-1.441927	-1.252687
C	2.254899	-2.642494	0.786135	C	-1.897762	-2.534880	-0.414949
H	2.420714	-2.184386	-0.204025	H	-2.104300	-2.143011	0.593849
H	1.565855	-3.482726	0.627544	H	-1.174165	-3.352295	-0.299908
C	3.588240	-3.146236	1.326127	C	-3.206595	-3.057162	-1.013761
H	4.274077	-2.290292	1.431362	H	-3.906573	-2.214031	-1.116899
H	3.444703	-3.552225	2.337249	H	-3.015369	-3.429084	-2.029712
C	4.193656	-4.199440	0.415787	C	-3.822516	-4.147457	-0.156381
H	4.308074	-3.814841	-0.607136	H	-3.979383	-3.799942	0.873331
H	3.553106	-5.088860	0.361120	H	-3.173332	-5.030626	-0.108911
H	5.181578	-4.522014	0.763999	H	-4.793545	-4.467392	-0.552210
C	0.367585	-1.679917	2.071628	C	-0.221198	-1.633200	-2.022686
N	-0.816834	-1.724360	2.416581	N	0.854939	-1.699848	-2.543484
IM7				**TS5**			





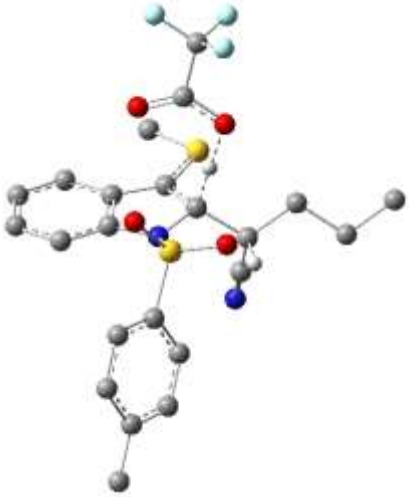


M06/BS1 SCF energy: -2395.531990 a.u.

M06/BS2 SCF energy in solution: -2396.007137 a.u.

M06/BS2 Free energy in solution: -2395.615897 a.u.

H	-1.844252	2.265804	3.326493
C	-1.208990	2.527267	2.489898
C	0.485586	3.255440	0.322774
C	-0.786024	1.549235	1.556073
C	-0.783396	3.821738	2.337553
C	0.046272	4.175333	1.253115
C	0.081265	1.924835	0.484671
H	-1.090963	4.582886	3.048035
H	0.356855	5.211868	1.145159
H	1.108128	3.560455	-0.510329
C	-1.058929	0.177613	1.418314
N	0.399169	0.817991	-0.259595
C	-0.273543	-0.375054	0.271705
H	-1.018126	-0.759100	-0.473777
S	1.233050	0.784472	-1.757225
S	-2.123204	-0.877246	2.216407
O	0.701296	-0.369085	-2.458606
O	1.126277	2.124781	-2.303630
C	2.904539	0.459868	-1.290486
C	5.520955	-0.073922	-0.518367
C	3.617345	1.429980	-0.585236
C	3.479352	-0.760898	-1.634076
C	4.787617	-1.016590	-1.243741
C	4.919466	1.151360	-0.203367
H	3.168223	2.388886	-0.335551
H	2.912191	-1.496078	-2.200195
H	5.250606	-1.965270	-1.508460
H	5.487328	1.897155	0.349674



M06/BS1 SCF energy: -2395.528141 a.u.

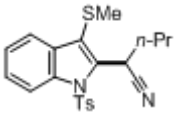
M06/BS2 SCF energy in solution: -2395.998016 a.u.

M06/BS2 Free energy in solution: -2395.610662 a.u.

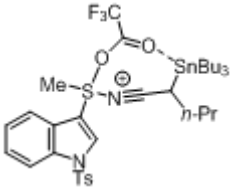
H	1.489354	-1.580800	3.929323
C	0.699061	-1.766251	3.212812
C	-1.382250	-2.327712	1.356278
C	0.473121	-0.898959	2.119021
C	-0.105783	-2.869790	3.363297
C	-1.135555	-3.144035	2.440299
C	-0.578457	-1.192323	1.209075
H	0.054913	-3.545506	4.198310
H	-1.754348	-4.026009	2.586189
H	-2.176011	-2.558957	0.653723
C	1.109122	0.273636	1.646208
N	-0.639996	-0.218311	0.239915
C	0.499262	0.683939	0.393441
H	1.354776	0.338618	-0.471847
S	-1.333363	-0.522219	-1.310267
S	2.446103	1.181393	2.227840
O	-0.853614	0.572557	-2.139472
O	-1.075028	-1.899996	-1.688329
C	-3.055200	-0.327230	-0.970556
C	-5.782023	0.026330	-0.573655
C	-3.929865	-1.352245	-1.318059
C	-3.514356	0.876775	-0.436223
C	-4.875424	1.041093	-0.239270
C	-5.291443	-1.164993	-1.113674
H	-3.548515	-2.278823	-1.740065
H	-2.823207	1.673172	-0.166327
H	-5.250003	1.973343	0.179704
H	-5.987771	-1.957214	-1.381861

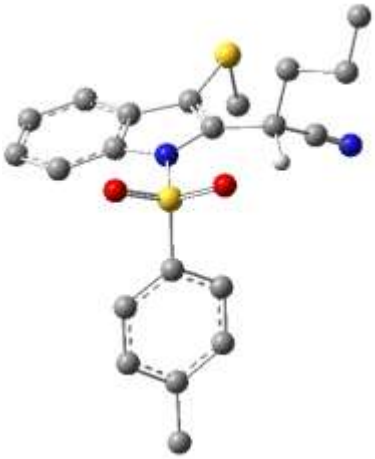
C	6.913515	-0.370503	-0.062940	C	-7.245247	0.213835	-0.330207
H	6.909454	-0.722255	0.976921	H	-7.553447	1.245961	-0.529468
H	7.545206	0.523759	-0.096420	H	-7.492824	0.001201	0.718035
H	7.379736	-1.151380	-0.671989	H	-7.847132	-0.455932	-0.952605
O	-2.570286	-1.254741	-1.341507	O	2.191141	-1.989703	-0.315269
C	-3.138290	0.152515	3.303323	C	2.942750	0.434897	3.800348
H	-3.553265	0.993688	2.741213	H	3.355038	-0.566117	3.653365
H	-3.956061	-0.502881	3.614929	H	3.736980	1.089482	4.170130
H	-2.588159	0.474033	4.190648	H	2.122406	0.441126	4.521820
C	-3.227190	-0.203074	-1.167485	C	2.665096	-1.200217	-1.120990
C	-4.676274	-0.311931	-1.704110	C	3.879997	-1.632595	-1.968375
F	-5.375817	-1.204136	-0.979020	F	3.634865	-1.495541	-3.276451
F	-4.705341	-0.737993	-2.975022	F	4.222750	-2.900565	-1.750596
F	-5.352485	0.840291	-1.660743	F	4.944014	-0.870427	-1.680146
O	-2.912131	0.864342	-0.619535	O	2.319309	0.000007	-1.381305
H	1.268323	-1.681235	-0.371141	H	-0.612079	2.190732	-0.624940
C	0.734376	-1.508236	0.574749	C	0.186363	2.169699	0.128602
C	0.114271	-2.854788	0.968410	C	1.350029	2.969944	-0.473999
H	-0.739590	-3.040489	0.301092	H	1.650403	2.443376	-1.389895
H	-0.275496	-2.814633	1.994790	H	2.221372	2.959639	0.195047
C	1.122986	-3.990211	0.857634	C	0.970018	4.407453	-0.793420
H	1.482073	-4.050141	-0.180379	H	0.072953	4.410186	-1.430685
H	2.003669	-3.757750	1.475366	H	0.691317	4.931433	0.132746
C	0.528025	-5.319516	1.284829	C	2.102376	5.147087	-1.483171
H	-0.344433	-5.578798	0.671693	H	2.373660	4.660978	-2.428678
H	0.198339	-5.288087	2.331053	H	3.002151	5.168336	-0.854938
H	1.255380	-6.133084	1.190237	H	1.830226	6.184247	-1.707567
C	1.733950	-1.064079	1.547266	C	-0.372738	2.804918	1.324458
N	2.521907	-0.694718	2.316781	N	-0.822333	3.305036	2.272315

4ab



TS3



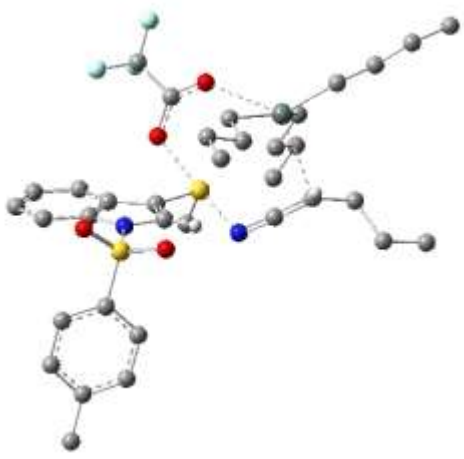


M06/BS1 SCF energy: -1868.958204 a.u.

M06/BS2 SCF energy in solution: -1869.266006 a.u.

M06/BS2 Free energy in solution: -1868.908909 a.u.

H	-1.535999	4.254016	0.447439
C	-0.754999	3.735980	-0.106649
C	1.251104	2.367260	-1.579258
C	-0.770229	2.341780	-0.202081
C	0.264997	4.430801	-0.734301
C	1.257321	3.749896	-1.454929
C	0.219906	1.673866	-0.945090
H	0.299503	5.515867	-0.671983
H	2.050135	4.315533	-1.938814
H	2.014719	1.858131	-2.157574
C	-1.653208	1.343433	0.336692
N	-0.069622	0.295487	-0.879246
C	-1.199797	0.112594	-0.054461
S	0.982574	-0.888809	-1.538239
S	-3.133911	1.672805	1.239156
O	0.238780	-2.138538	-1.541982
O	1.478296	-0.336405	-2.785147
C	2.298208	-0.966917	-0.365457
C	4.374710	-1.119879	1.471986
C	3.566630	-0.538112	-0.740319
C	2.040543	-1.469796	0.911442
C	3.082511	-1.538839	1.819738
C	4.598797	-0.622303	0.187079
H	3.743909	-0.154732	-1.741931
H	1.043260	-1.801288	1.196745
H	2.900098	-1.927107	2.820379
H	5.598591	-0.295618	-0.092486
C	5.485878	-1.220942	2.467206
H	5.232414	-0.698851	3.397586



M06/BS1 SCF energy: -2871.878381 a.u.

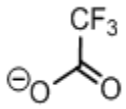
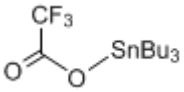
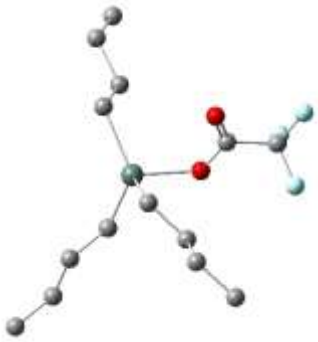
M06/BS2 SCF energy in solution: -2872.451271 a.u.

M06/BS2 Free energy in solution: -2871.701371 a.u.

H	1.698666	3.678141	1.077825
C	2.521559	3.200719	0.557155
C	4.648563	2.015174	-0.911848
C	2.448653	1.850797	0.186347
C	3.649717	3.923695	0.209735
C	4.700025	3.340606	-0.514452
C	3.518652	1.286637	-0.546648
H	3.716105	4.971033	0.493753
H	5.566242	3.941139	-0.780607
H	5.445589	1.568886	-1.498746
C	1.495019	0.777262	0.362080
N	3.201640	-0.052890	-0.799060
C	1.989415	-0.351874	-0.230452
H	1.585212	-1.354358	-0.301337
S	4.233493	-1.252885	-1.492294
S	-0.081268	0.773619	1.170239
O	3.362660	-2.404208	-1.647906
O	4.870629	-0.614627	-2.627695
C	5.416795	-1.548039	-0.223949
C	7.263400	-2.018172	1.791921
C	6.705957	-1.042996	-0.358565
C	5.026196	-2.287413	0.893971
C	5.955541	-2.514021	1.894117
C	7.621716	-1.286241	0.657854
H	6.990974	-0.486617	-1.247478
H	4.016260	-2.683877	0.973191
H	5.672633	-3.090848	2.773057
H	8.636402	-0.903988	0.567448
C	8.250779	-2.282730	2.882623

H	6.416074	-0.796239	2.077823
H	5.676786	-2.268016	2.733312
C	-2.430092	2.047291	2.880059
H	-1.667786	2.827884	2.801230
H	-3.250294	2.410852	3.505706
H	-2.005166	1.145793	3.332221
H	-1.038018	-2.008029	0.111680
C	-1.800538	-1.230833	0.244153
C	-2.964794	-1.583215	-0.701995
H	-2.612227	-1.394354	-1.725708
H	-3.801994	-0.894751	-0.519155
C	-3.414601	-3.028333	-0.565734
H	-2.558391	-3.686608	-0.777661
H	-3.708796	-3.227390	0.475657
C	-4.567080	-3.350852	-1.499680
H	-4.290664	-3.169723	-2.546345
H	-5.441797	-2.726594	-1.277373
H	-4.876166	-4.398334	-1.413895
C	-2.187362	-1.332749	1.652617
N	-2.457640	-1.499147	2.770588

H	8.439700	-3.358287	2.986463
H	7.871020	-1.933822	3.850406
H	9.207517	-1.787263	2.691154
O	-0.378856	2.866741	0.515459
C	0.330615	1.407942	2.816351
H	1.313967	1.022242	3.095575
H	0.312496	2.497406	2.771345
H	-0.439932	1.035492	3.496491
C	-1.312760	3.065443	-0.319645
C	-1.355911	4.546557	-0.758598
F	-2.258430	4.763053	-1.708130
F	-0.164348	4.933600	-1.221118
F	-1.658696	5.325531	0.285244
O	-2.150258	2.295156	-0.792299
H	-1.766846	-2.994921	0.016001
C	-1.975468	-2.362538	0.886547
Sn	-2.898338	-0.340370	-0.640719
C	-4.324641	-1.575387	-1.712215
H	-4.274351	-1.250528	-2.762528
C	-3.931968	0.584229	1.020093
H	-4.504145	1.397027	0.550858
H	-4.663365	-0.179501	1.320659
C	-3.169812	1.092255	2.229989
H	-2.521609	1.935865	1.947727
H	-2.513937	0.299446	2.633031
C	-4.103899	1.548646	3.345717
H	-4.778483	2.322969	2.951838
H	-4.746235	0.704880	3.640932
C	-3.350127	2.077939	4.553140
H	-2.702542	2.921401	4.278028
H	-2.713450	1.301233	4.997781
H	-4.032159	2.428529	5.335735
C	-1.169293	-0.243425	-1.937408
H	-0.375528	0.383796	-1.517475
H	-1.571634	0.318366	-2.794335
H	-3.928356	-2.602250	-1.695386
C	-5.758447	-1.542070	-1.200409
H	-5.795956	-1.880144	-0.151473
H	-6.137756	-0.507652	-1.191951
C	-6.697493	-2.409315	-2.030724
H	-6.311278	-3.440044	-2.048554
H	-6.677582	-2.061397	-3.074632
C	-8.122828	-2.398794	-1.505882
H	-8.168749	-2.776946	-0.476065

				H	-8.786594	-3.021222	-2.116687
				H	-8.535477	-1.381510	-1.499724
				C	-0.649880	-1.599797	-2.389840
				H	-0.229425	-2.161841	-1.536501
				H	-1.476527	-2.218329	-2.776971
				C	0.418844	-1.475856	-3.471095
				H	1.257675	-0.874932	-3.084203
				H	0.005683	-0.907428	-4.317644
				C	0.922633	-2.827846	-3.942475
				H	1.349652	-3.399798	-3.109151
				H	1.705123	-2.726528	-4.703129
				H	0.109475	-3.423217	-4.378101
				C	-3.134637	-2.738619	1.786882
				H	-4.054907	-2.758086	1.183947
				H	-3.274212	-1.965836	2.556819
				C	-2.928852	-4.102637	2.440538
				H	-2.769658	-4.857888	1.658056
				H	-2.006612	-4.076428	3.037976
				C	-4.113882	-4.486012	3.308177
				H	-5.037575	-4.536239	2.717686
				H	-4.272632	-3.752314	4.108606
				H	-3.966944	-5.464408	3.778063
				C	-0.922327	-1.667521	1.331340
				N	0.018945	-0.990883	1.709687
$CF_3(O)CO^-$   M06/BS1 SCF energy: -526.124794 a.u. M06/BS2 SCF energy in solution: -526.306215 a.u. M06/BS2 Free energy in solution: -526.298462 a.u.				**$Bu_3SnOCOCF_3$**   M06/BS1 SCF energy: -1002.590817 a.u. M06/BS2 SCF energy in solution: -1002.859897 a.u. M06/BS2 Free energy in solution: -1002.499652 a.u.			
C	1.040686	0.013243	-0.007573	Sn	0.420370	0.559797	-0.483130
O	1.501934	-1.141823	-0.003998	C	1.283029	-1.064547	-1.605345
C	-0.515568	0.017788	-0.002400	H	0.602380	-1.322103	-2.425997
F	-0.997930	-0.556359	1.119132	C	1.729532	1.252594	1.087118

F	-1.020508	-0.690520	-1.032441	H	1.300040	2.164782	1.524060
F	-1.073336	1.236956	-0.073050	H	1.712707	0.486725	1.875824
O	1.582474	1.129712	-0.003868	C	-0.842272	2.067793	-1.360502
				H	-1.306037	1.653964	-2.264309
				H	2.214390	-0.695161	-2.057033
				H	-0.180713	2.885159	-1.679949
				O	-0.892263	-0.535937	0.822642
				C	-1.815687	-1.150842	0.171154
				C	-2.643704	-2.066407	1.087270
				O	-2.051325	-1.089452	-1.023514
				F	-3.625464	-2.669855	0.428885
				F	-1.856966	-3.010129	1.615061
				F	-3.181316	-1.373890	2.094142
				C	3.157086	1.502478	0.610273
				H	3.578409	0.580776	0.175022
				H	3.165213	2.245505	-0.204096
				C	4.076996	1.985774	1.724553
				H	4.074717	1.243018	2.536719
				H	3.661122	2.908907	2.156625
				C	5.496864	2.229745	1.243846
				H	6.150403	2.578810	2.051506
				H	5.938240	1.311754	0.834000
				H	5.519105	2.986778	0.448859
				C	1.560172	-2.275506	-0.718475
				H	0.620247	-2.658967	-0.288632
				H	2.179220	-1.980998	0.146219
				C	2.256652	-3.405077	-1.467215
				H	1.645873	-3.685596	-2.338883
				H	3.209762	-3.032107	-1.872452
				C	2.501980	-4.621550	-0.591473
				H	1.557336	-5.026851	-0.205769
				H	3.008233	-5.425283	-1.138390
				H	3.125943	-4.366717	0.275325
				C	-1.896851	2.583961	-0.387125
				H	-1.420202	2.926962	0.546390
				H	-2.574949	1.766500	-0.095924
				C	-2.723906	3.724303	-0.969967
				H	-2.051386	4.547500	-1.255930
				H	-3.197661	3.381288	-1.902285
				C	-3.781810	4.228888	-0.004249
				H	-3.327152	4.595891	0.925354
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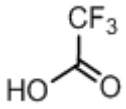
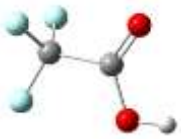
				H	-4.481719	3.428305	0.268234
CF_3COOH							





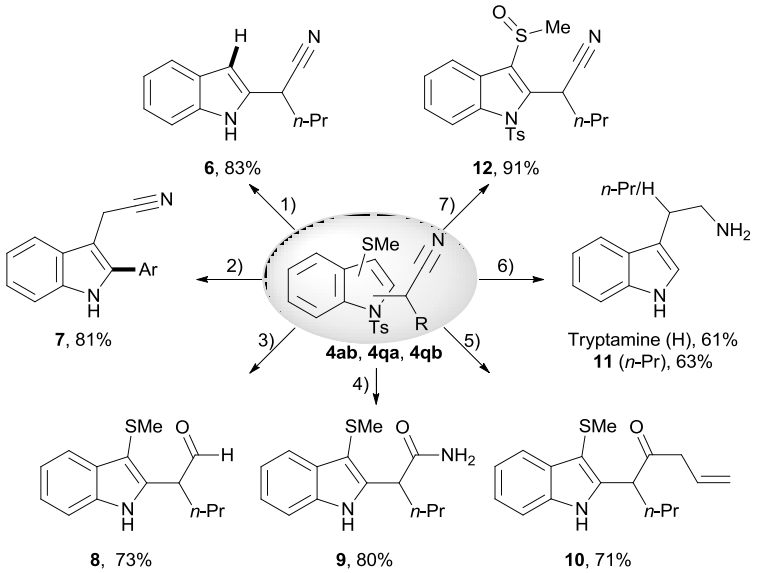
M06/BS1 SCF energy: -526.599981 a.u.

M06/BS2 SCF energy in solution: -526.758137 a.u.

M06/BS2 Free energy in solution: -526.736911 a.u.

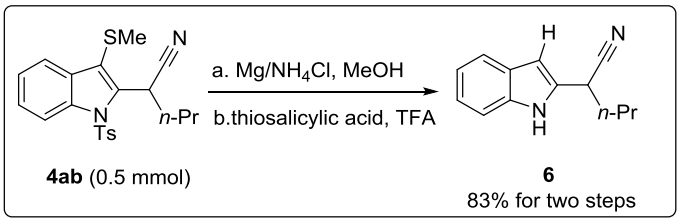
C	0.934675	-0.129630	-0.009915
O	1.437553	-1.220987	-0.004522
C	-0.593159	0.025870	-0.003374
F	-1.062879	-0.402267	1.166908
F	-1.109874	-0.736177	-0.961866
F	-0.994976	1.275343	-0.188780
O	1.555349	1.036252	-0.004725
H	2.517239	0.868348	0.007348

6 Elaboration of products and synthesis of Trptamine



(1) a. Mg/NH_4Cl, MeOH; b.thiosalicylic acid, TFA; (2) a. Mg/NH_4Cl, MeOH; b. Pd-PEPPSI-SIPr, ArZnI·LiCl, CH_3CN, (Ar=4-EtO_2C-Ph); (3) a. Mg/NH4Cl, MeOH; b. DIBAL-H, toluene; (4) a. Mg/NH_4Cl, MeOH; b. K_2CO_3/H_2O_2, DMSO; (5) a. Mg/NH_4Cl, MeOH; b. $Zn/AlCl_3$, allyl bromide, THF; (6) a. Mg/NH_4Cl, MeOH; b. $PdCl_2$, Et_3SiH, TMSCl, THF; c. $LiAlH_4$, Et_2O; (7) m-CPBA, DCM.

2-(1H-indol-2-yl)pentanenitrile (6)



Step a: To an oven-dried 100 mL flask were added indole **4ab** (199 mg, 0.5 mmol), MeOH (13 mL), Mg powder (600 mg, 25 mmol) and NH_4Cl (1.34 g, 25 mmol) in sequence. The mixture was stirred at 50 ℃ until **4ab** was completely consumed. Then to the mixture was added silica gel (3 g). After 10 min, the mixture was filtrated and washed with EtOAc. The resulting mixture was then concentrated and purified by flash column chromatography on silica gel to give 2-(3-(methylthio)-1H-indol-2-yl) pentanenitrile as a white solid, 112.4 mg, 92% yield. (Rf = 0.31, eluent: PE/EtOAc = 10/1). (**caution:** NH_4Cl was added in small portion to avoid liquid flooding and rapid foaming)

2-(3-(methylthio)-1H-indol-2-yl)pentanenitrile:

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.19 (m, 2H), 4.64 (t, *J* = 7.6 Hz, 1H), 2.32 (s, 3H), 2.12 – 2.02 (m, 1H), 1.98 – 1.89 (m, 1H), 1.58 – 1.44 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 135.9, 134.9, 129.2, 123.5, 121.0, 120.0, 119.4, 111.7, 106.4, 36.3, 28.9, 20.4, 19.9, 13.4.

IR (neat): 3330, 3057, 2967, 2916, 2859, 2242, 1600, 1578, 1450, 1380, 1115, 750, 694.

HRMS: calculated for [$C_{14}H_{16}N_2SNa$ (M + Na^+)]: 267.0926, found: 267.0925.

Step b: A suspension of the obtained product 2-(3-(methylthio)-1H-indol-2-yl)pentanenitrile and thiosalicylic acid (141.9 mg, 0.92 mmol, 2.0 equiv) in TFA (3 mL) was stirred at 50 ℃. After 5 h, TFA was removed under reduced pressure. The residue was dissolved in EtOAc, washed twice with NaOH aq. (1 M) and then three times with water. The mixture was then dried, concentrated, purified by flash column chromatography to give the title compound **6** as colorless oil, 82.2 mg, 83% yield for the two steps. (Rf = 0.14, eluent: PE/EtOAc = 10/1)

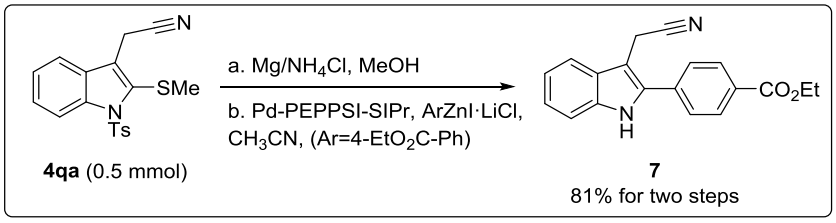
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.15 – 7.11 (m, 1H), 6.48 – 6.45 (m, 1H), 4.07 (dd, *J* = 7.9, 6.7 Hz, 1H), 2.09 – 1.94 (m, 2H), 1.62 – 1.50 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.3, 131.6, 128.1, 122.7, 120.7, 120.5, 119.7, 111.1, 101.7, 35.6, 31.1, 20.4, 13.5.

IR (neat): 3381, 3056, 2957, 2962, 2875, 2247, 1579, 1547, 1456, 1380, 1295, 783, 760, 658.

HRMS: calculated for [$C_{13}H_{14}N_2$ Na (M + Na^+)]: 221.1049, found: 221.1046.

ethyl 4-(3-(cyanomethyl)-1H-indol-2-yl)benzoate (7)



4qa (0.5 mmol) **7** 81% for two steps

Step a: The deprotection of Ts group from **4qa** (178 mg, 0.5 mmol) was performed following the step a in the synthesis of compound **6**. 2-(2-(methylthio)-1H-indol-3-yl)acetonitrile was obtained as white solid, 94.0 mg, 93% yield.

2-(2-(methylthio)-1H-indol-3-yl)acetonitrile:

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.22 – 7.18 (m, 1H), 3.96 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.3, 128.7, 126.6, 123.8, 120.7, 118.5, 118.1, 111.2, 109.1,

20.0, 13.7.

IR (neat): 3415, 3052, 2922, 2241, 1446, 1404, 1340, 1315, 1287, 1209, 746, 664.

HRMS: calculated for [$C_{11}H_{10}N_2SNa$ ($M + Na^+$)]: 225.0457, found: 225.0450.

Step b: the Negishi cross coupling was conducted following the reported procedure.[17]

Pd-PEPPSI-SIPr (31.6 mg, 0.046 mmol) was placed in a 20 mL Schlenk tube. 4-EtO_2C-PhZnI ŁLiCl[18 and 19](1.86 mL, 0.93 mmol, 0.5 M in THF) was added at 20 ℃. After 3 min, the mixture became black. After addition of acetonitrile (1.5 mL) and the obtained product 2-(2-(methylthio)-1H-indol-3-yl)acetonitrile at 0 ℃, the resulting mixture was stirring at 20 ℃ for 7 h, to the mixture was added NH_4Cl(sat., 10 mL). The resulting mixture was extracted with ethyl acetate (10 mL × 3), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the title compound **7** as white solid, m.p. 169-170 ℃, 123.2 mg, 81% yield for the two steps. (Rf = 0.27, eluent: PE/EtOAc = 5/1)

[17] S. Otsuka, D. Fujino, K. Murakami, H. Yorimitsu and A. Osuka, *Chem. Eur. J.*, 2014, **20**, 13146.

[18] A. Krasovskiy, V. Malakhov, A. Gavryushin and P. Knochel, *Angew. Chem., Int. Ed..*, 2006, **45**, 6040.

[19] A. Krasovskiy, P. Knochel, *Synthesis.* 2006, 890**.**

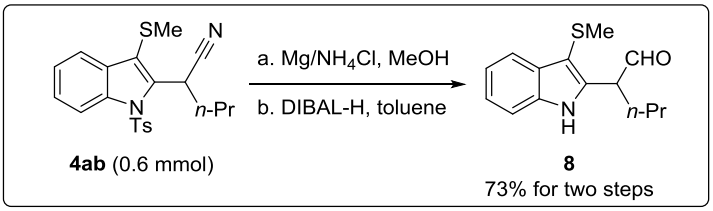
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.22 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.2, 136.0, 135.8, 135.1, 130.6, 130.4, 128.0, 127.8, 123.9, 121.0, 118.7, 118.1, 111.5, 102.3, 61.5, 14.5, 14.0.

IR (neat): 3333, 3063, 2987, 2957, 2922, 2850, 2258, 1708, 1496, 1448, 1103, 773, 749, 688.

HRMS: calculated for [$C_{19}H_{16}N_2O_2Na$ ($M + Na^+$)]: 327.1104, found: 327.1097.

2-(3-(methylthio)-1H-indol-2-yl)pentanal (8)



Step a: The deprotection of Ts group from **4ab** (239 mg, 0.6 mmol) was performed following the step a in the synthesis of compound **6**. 2-(3-(methylthio)-1H-indol-2-yl) pentanenitrile was obtained as a white solid, 134.9 mg.

Step b: To a solution of the obtained product 2-(3-(methylthio)-1H-indol-2-yl)pentanenitrile in toluene (2 mL) was added DIBAL-H (1.5 M in toluene, 0.74 mL) at -60 ℃. After stirring for 3 h, the mixture was gradually warmed to 0 ℃. Then HCl (1M, 2.2 mL) was added dropwise. The resulting mixture was stirred for 30 min and then extracted with DCM. The organic layer was washed with NaCl (sat.), dried over Na_2SO_4. The mixture was then filtrated, concentrated under vacuum, and purified by flash column chromatography on silica gel to give the title compound **8** as colorless oil, 108.3 mg, 73% yield for the two steps. (Rf = 0.23, eluent: PE/EtOAc = 10/1)

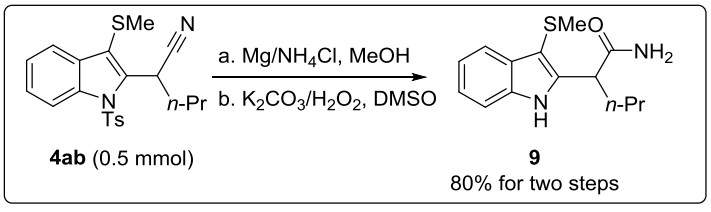
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (d, *J* = 0.8 Hz, 1H), 8.53 (s, 1H), 7.78 – 7.75 (m, 1H), 7.40 – 7.33 (m, 1H), 7.25 – 7.19 (m, 2H), 4.48 (dd, *J* = 8.8, 5.9 Hz, 1H), 2.31 (s, 3H), 2.16 – 2.07 (m, 1H), 1.86 – 1.76 (m, 1H), 1.39 – 1.25 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.2, 136.9, 136.2, 129.6, 122.9, 120.7, 119.2, 111.4, 107.4, 50.1, 31.4, 20.44, 20.39, 14.0.

IR (neat): 3380, 3058, 2957, 2919, 2870, 1713, 1580, 1453, 1229, 742, 699.

HRMS: calculated for [$C_{14}H_{17}NOSNa$ ($M + Na^+$)]: 270.0923, found: 270.0916.

2-(3-(methylthio)-1H-indol-2-yl)pentanamide (9)



Step a: The deprotection of Ts group from **4ab** (199 mg, 0.5 mmol) was performed following the step a in the synthesis of compound **6**. 2-(3-(methylthio)-1H-indol-2-yl) pentanenitrile was

obtained as a white solid, 112.0 mg.

Step b: To a solution of the obtained product 2-(3-(methylthio)-1H-indol-2-yl)pentanenitrile in DMSO (1 mL) was sequentially added H_2O_2 (30% aq., 130 μL) and K_2CO_3 (13.6 mg, 0.092 mmol) at 25 ℃. After stirring for 12 h, the mixture was diluted with H_2O (7 mL), extracted with DCM (3 × 15 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. After removal of the solvent in vacuo, the crude material was purified by flash column chromatography on silica gel to give the title compound **9** as a white solid, m.p. 155-156 ℃, 105.0 mg, 80% yield for the two steps. (Rf = 0.44, eluent: PE/EtOAc = 1/1)

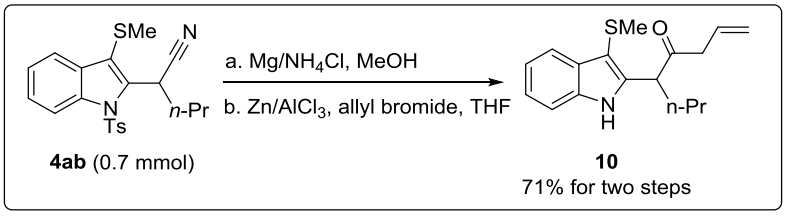
^{1}H NMR (600 MHz, $CDCl_3$): δ 9.34 (s, 1H), 7.75 – 7.68 (m, 1H), 7.38 – 7.30 (m, 1H), 7.22 – 7.15 (m, 2H), 5.89 (s, 2H), 4.22 (t, *J* = 7.6 Hz, 1H), 2.29 (s, 3H), 2.13 – 2.04 (m, 1H), 1.90 – 1.80 (m, 1H), 1.41 – 1.27 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 175.6, 139.9, 135.9, 129.4, 122.6, 120.4, 118.9, 111.6, 104.7, 43.4, 35.4, 20.8, 20.3, 13.9.

IR (neat): 3427, 3187, 3058, 2957, 2921, 2874, 1673, 1654, 1578, 1452, 740, 676.

HRMS: calculated for [$C_{14}H_{18}N_2OSNa$ ($M + Na^+$)]: 285.1032, found: 285.1035.

5-(3-(methylthio)-1H-indol-2-yl)oct-1-en-4-one (10)



4ab (0.7 mmol) → **10** 71% for two steps

Step a: The deprotection of Ts group from **4ab** (279 mg, 0.7mmol) was performed following the step a in the synthesis of compound **6**. 2-(3-(methylthio)-1H-indol-2-yl) pentanenitrile was obtained as a white solid, 157.3 mg.

Step b: To a mixture of the obtained product 2-(3-(methylthio)-1H-indol-2-yl)pentanenitrile, allyl bromide (83μL, 0.966 mmol) and Zn (powder, 168 mg, 2.58 mmol) in THF (3 mL) was added anhydrous $AlCl_3$ (35 mg, 0.257 mmol) at -40 ℃ under N_2 atmosphere. The mixture was stirred for 3 h at the same temperature. Then to the mixture was added HCl (2 M, 3.9 mL) dropwise. After stirring for 30 min, the mixture was neutralized with $NaHCO_3$ (sat.), extracted with DCM and dried over Na_2SO_4. Then the mixture was filtrated and concentrated under vacuum. The obtained

residue was further purified by flash column chromatography on silica gel to give the title compound **10** as a white solid, m.p. 29-31 ℃, 142.5 mg, 71% yield for the two steps. (Rf = 0.35, eluent: PE/EtOAc = 10/1)

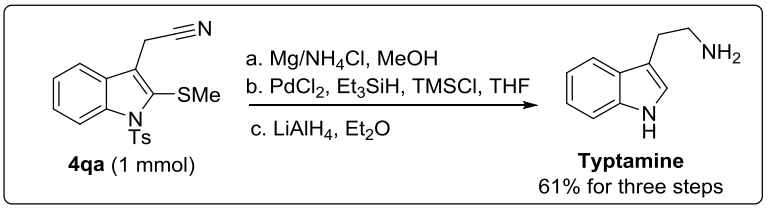
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.79 – 7.72 (m, 1H), 7.39 – 7.32 (m, 1H), 7.27 – 7.16 (m, 2H), 5.97 – 5.80 (m, 1H), 5.24 – 5.10 (m, 2H), 4.71 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.43 – 3.24 (m, 2H), 2.34 (s, 3H), 2.08 – 1.95 (m, 1H), 1.87 – 1.74 (m, 1H), 1.37 – 1.18 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.2, 138.6, 136.1, 129.7, 129.5, 122.8, 120.5, 119.7, 119.1, 111.5, 106.2, 48.2, 47.8, 34.4, 20.6, 20.2, 14.0.

IR (neat): 3352, 3058, 2957, 2920, 2871, 1704, 1636, 1579, 1454, 1380, 741, 701.

HRMS: calculated for [$C_{17}H_{21}NOSNa$ ($M + Na^+$)]: 310.1236, found: 310.1232.

Tryptamine



Step a: The deprotection of Ts group from **4qa** (356 mg, 1 mmol) was performed following the step a in the synthesis of compound **6**. 2-(2-(methylthio)-1H-indol-3-yl)acetonitrile was obtained as white solid, 188.2 mg. (Rf = 0.23, eluent: PE/EtOAc = 3/1)

Step b: To a mixture of the obtained product 2-(2-(methylthio)-1H-indol-3-yl)acetonitrile, Et_3SiH (226 mg, 1.95 mmol) and TMSCl (100 mg, 0.93 mmol) in THF (6 mL) was added $PdCl_2$ (8.2 mg, 5% mmol) at 25 ℃. After stirring for 3 h, the mixture was concentrated under vacuum. The obtained residue was further purified by flash column chromatography on silica gel to give 2-(1H-indol-3-yl)acetonitrile as a white solid, 126.3 mg. (Rf = 0.29, eluent: PE/EtOAc = 3/1)

2-(1H-indol-3-yl)acetonitrile:

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.23 (d, *J* = 1.2 Hz, 1H), 7.22– 7.18 (m, 1H), 3.85 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.4, 126.1, 123.0, 122.9, 120.4, 118.3, 118.2, 111.7, 104.9, 14.6.

The ^{1}H NMR and ^{13}C NMR of 2-(1H-indol-3-yl)acetonitrile is consistent with the reported spectra[20].

[20] T. Matsumura, T. Niwa and M. Nakada, *Tetrahedron Letters.*, 2012, **53**, 4313.

Step c: To a suspension of $LiAlH_4$ (123 mg, 3.24 mmol) in Et_2O (2 mL) at 0 ℃ was added the obtained product 2-(1H-indol-3-yl)acetonitrile in Et_2O (2 mL) dropwise for 5 min under N_2 atmosphere. Then the mixture was gradually warmed to room temperature. After stirring for 12 h, to the mixture was added Rochelle salt (sat., 5 mL). The resulting mixture was stirred for 30 min, then extracted with EtOAc (3×10 mL) dried over Na_2SO_4, filtered and concentrated to approximately 1 mL under reduced pressure. Then petroleum ether (30 mL) was added. The obtained mixture was cooled to -50 ℃ for solidification. After filtration, the title compound Tryptamine was obtained as a white solid, 97.7 mg, 61% yield for the three steps.

Typtamine:

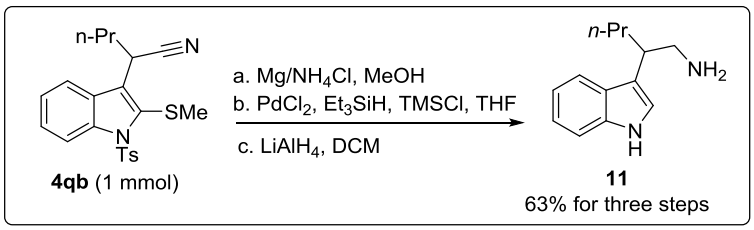
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.45 (br s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.30 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 3.05 (t, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 1.40 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.5, 127.6, 122.2, 122.0, 119.3, 118.9, 113.7, 111.3, 42.4, 29.6.

The ^{1}H NMR and ^{13}C NMR of Tryptamine is consistent with the reported spectra[21].

[21] A. Abdelwaly, I. Salama, M. S. Gomaa and M. A. Helal, *Med. Chem. Res*., 2017, **26**, 3173.

2-(1H-indol-3-yl)pentan-1-amine (11)



The deprotection of Ts group and desulfenylation from **4qb** (398 mg, 1 mmol) was performed following the steps in the synthesis of Tryptamine.

2-(2-(methylthio)-1H-indol-3-yl)pentanenitrile：

The title compound was obtained as a colorless oil, 217.0 mg, 89% yield. (Rf = 0.31, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H),

7.29 – 7.23 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 4.36 (t, *J* = 7.9 Hz, 1H), 2.39 (s, 3H), 2.23 – 2.13 (m, 1H), 1.98 – 1.90 (m, 1H), 1.60 – 1.51 (m, 1H), 1.50 – 1.41 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.7, 128.0, 125.6, 123.5, 121.2, 120.4, 119.0, 114.3, 111.2, 36.2, 28.1, 20.7, 20.1, 13.5.

IR (neat): 3323, 2958, 2925, 2872, 2238, 1490, 1447, 1381, 1343, 1314, 1241, 740, 677.

HRMS: calculated for [$C_{14}H_{16}N_2SNa$ ($M + Na^+$)]: 267.0926, found: 267.0932.

2-(1H-indol-3-yl)pentanenitrile:

The title compound was obtained as a colorless oil, 153.5 mg, 87% yield. (Rf = 0.35, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 4.11 (dd, *J* = 8.3, 6.4 Hz, 1H), 2.14 – 1.97 (m, 2H), 1.69 – 1.51 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.4, 125.2, 122.5, 122.4, 121.5, 119.9, 118.3, 111.8, 110.2, 35.8, 28.5, 20.4, 13.4.

IR (neat): 3407, 3058, 2959, 2931, 2872, 2238, 1490, 1457, 1380, 763, 738, 653.

HRMS: calculated for [$C_{13}H_{14}N_2Na$ ($M + Na^+$)]: 221.1049, found: 221.1046.

2-(1H-indol-3-yl)pentan-1-amine (11):

The title compound was obtained as a colorless oil, 127.4 mg, 63% yield for the three steps. (Rf = 0.11, eluent: MeOH)

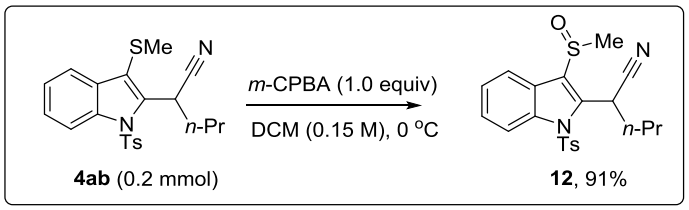
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.65 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 3.03 – 2.90 (m, 3H), 1.77 – 1.64 (m, 2H), 1.56 (s, 2H), 1.35 – 1.22 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.8, 127.1, 121.9 119.5, 119.1, 117.5, 111.4, 47.0, 40.6, 35.6, 20.9, 14.3. One aromatic carbon peak is overlapped.

IR (neat): 3411, 2954, 2920, 2851, 1582, 1456, 1376, 1258, 1011, 799, 737.

HRMS: calculated for [$C_{13}H_{19}N_2$ ($M + H^+$)]: 203.1548, found: 203.1541.

2-(3-(methylsulfinyl)-1-tosyl-1H-indol-2-yl)pentanenitrile (12)



To a solution of **4ab** (79.6 mg, 0.2 mmol) in DCM (8 mL) was added a solution of *m*-CPBA (34 mg, 0.2 mmol, 1.0 equiv) in DCM (8 mL) dropwise at 0 ℃. The resulting mixture was stirred at 0 ℃ for 0.5 h .Then to the mixture was added $NaHCO_3$ (sat., 4 mL). After extracted with DCM (3×10 mL), dried over Na_2SO_4 concentrated under vacucum, the residue was further purified by flash column chromatography on silica gel affording the title compound **12** as a white solid, m.p. 143-145 ℃, 75.4 mg, 91% yield. (Rf = 0.34, eluent: PE/EtOAc = 1/1)

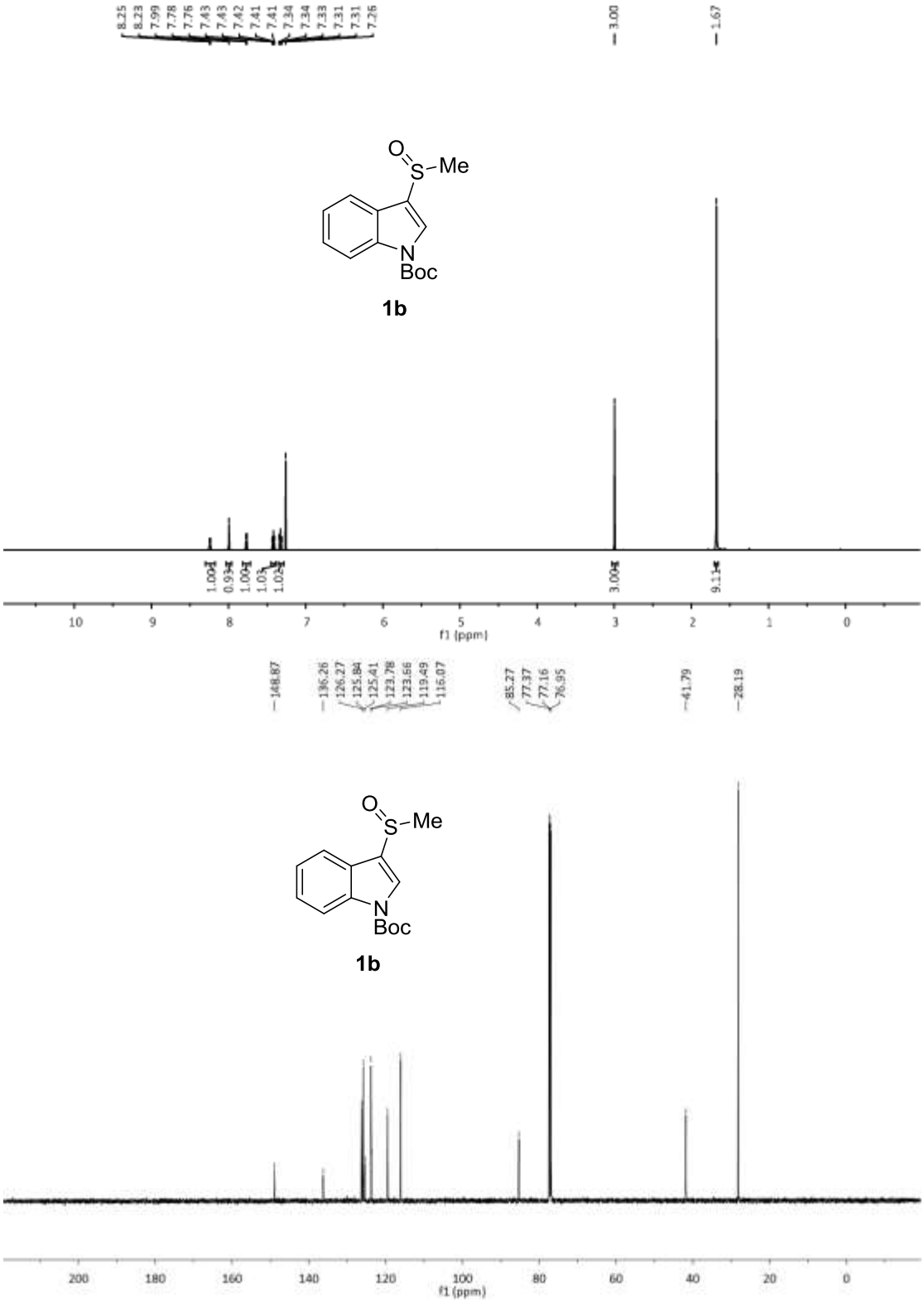
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 5.7 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.27 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.06 (s, 3H), 2.41 – 2.27 (m, 4H), 1.93 – 1.85 (m, 1H), 1.77 – 1.69 (m, 1H), 1.57 – 1.49 (m, 1H), 1.01 (t, *J* = 7.3 Hz, 3H).

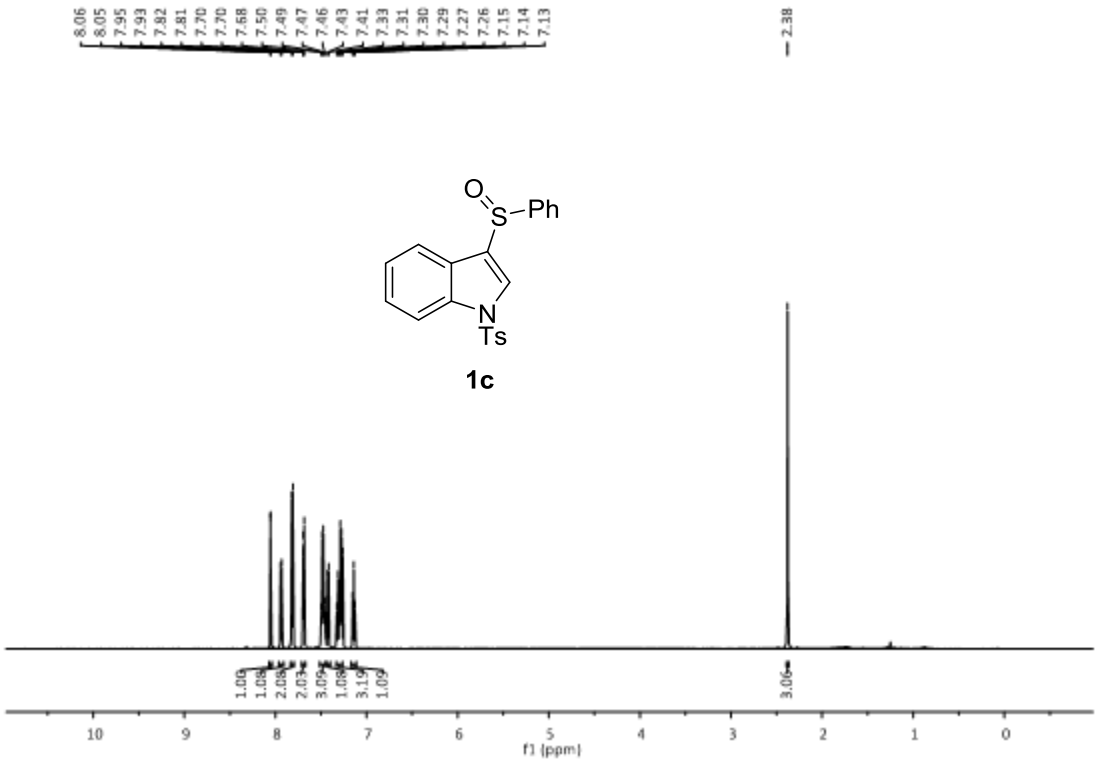
^{13}C NMR (151 MHz, $CDCl_3$): δ 146.6, 136.8, 134.9, 133.9, 130.6, 126.8, 126.5, 125.1, 124.9, 124.7, 121.1, 119.1, 115.9, 38.9, 35.9, 28.2, 21.8, 21.1, 13.3.

IR (neat): 2963, 2920, 2870, 2238, 1597, 1548, 1441, 1386, 1046, 1027, 811, 756, 663.

HRMS: calculated for [$C_{21}H_{23}N_2O_3S_2$ ($M + H^+$)]: 415.1145, found: 415.1153.

7 NMR spectra

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7.93
7.82
7.81
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7.70
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2.03
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f1 (ppm)

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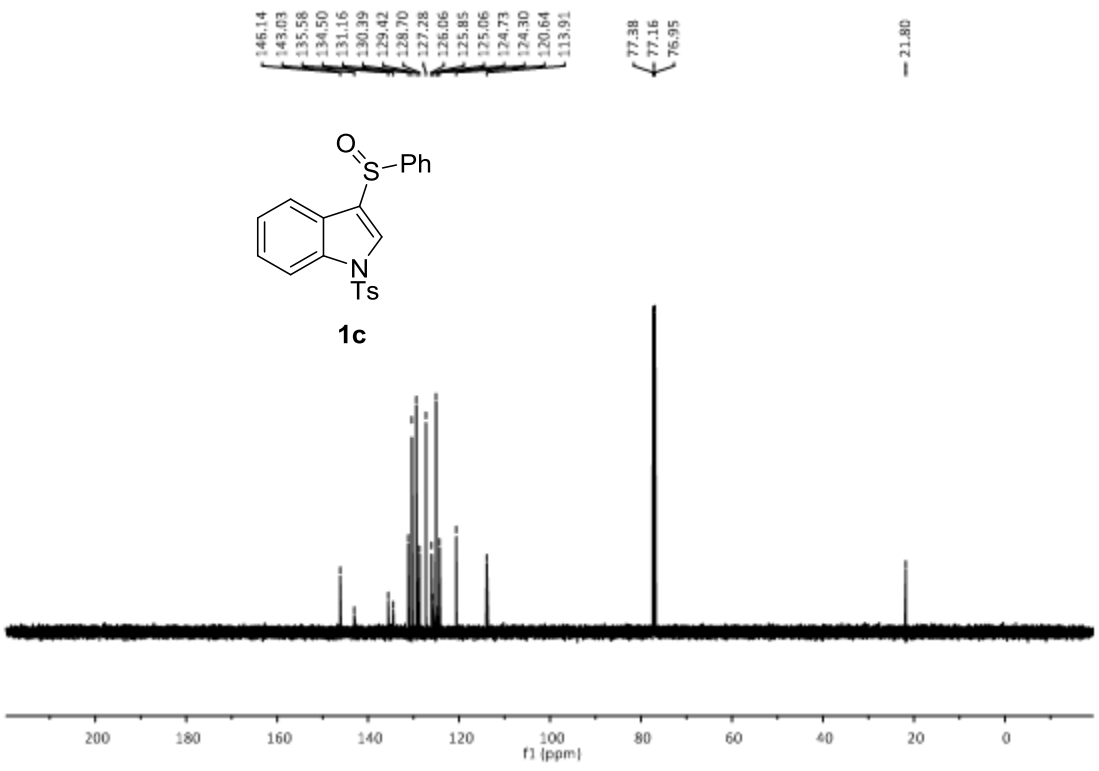
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77.16
76.95
21.80
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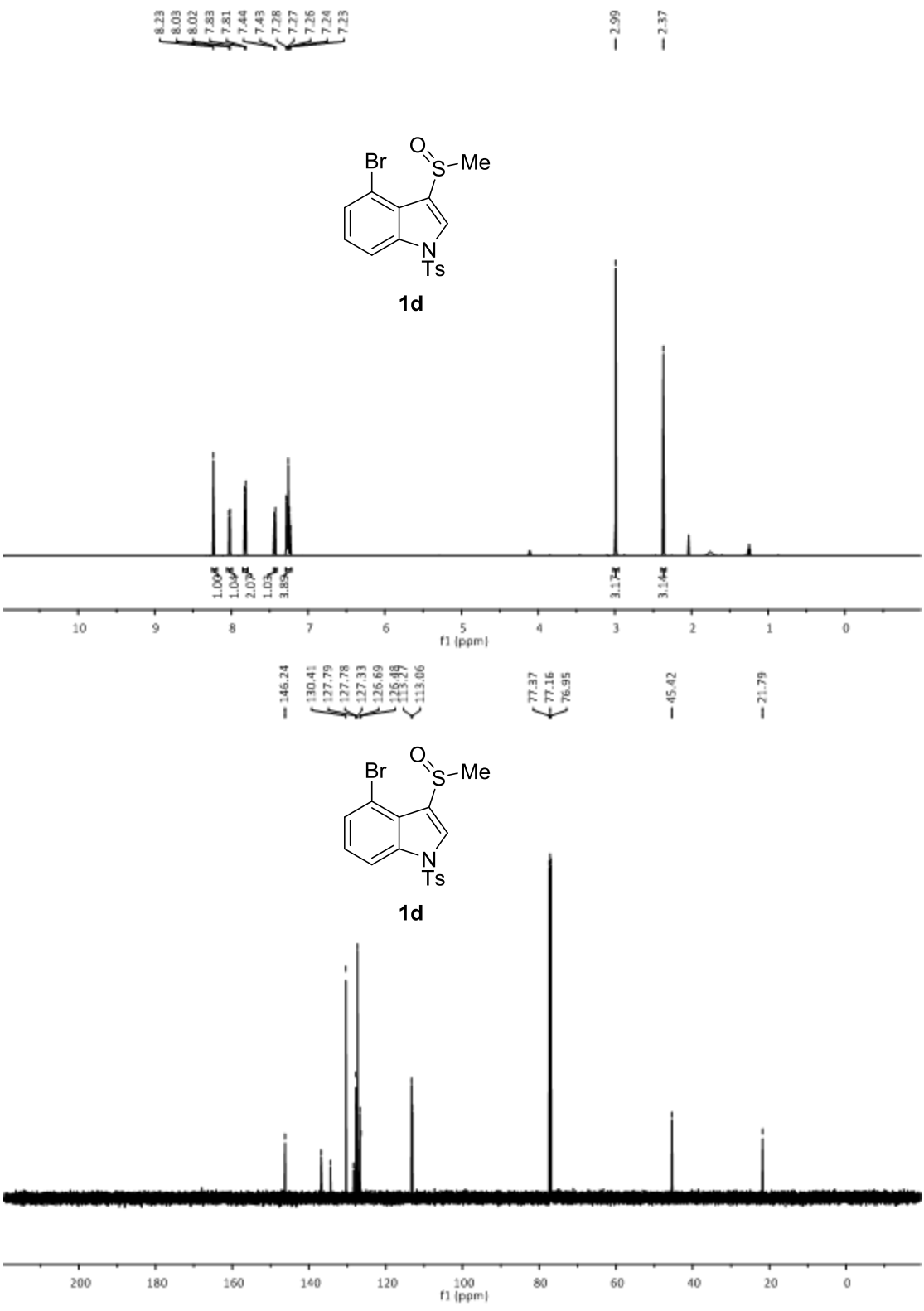
20
0
f1 (ppm)

1c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2.37
Br
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S
Me
N
Ts
1d
1.00
1.04
2.07
1.03
3.89
3.17
3.14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
146.24
130.41
127.79
127.78
127.33
126.69
113.06
77.37
77.16
76.95
45.42
21.79
Br
O
S
Me
N
Ts
1d
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180
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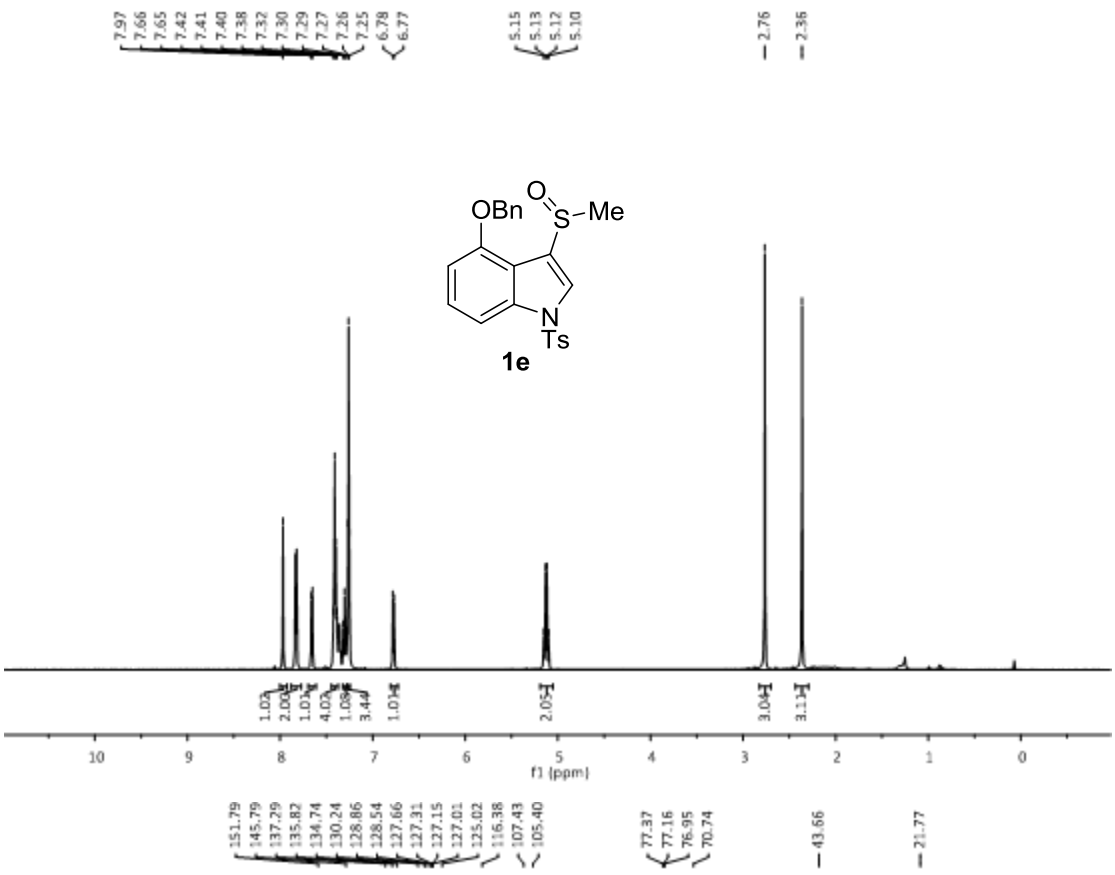
140
120
100
80
60
40
20
0
f1 (ppm)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7.38
7.32
7.30
7.29
7.27
7.26
7.25
6.78
6.77
5.15
5.13
5.12
5.10
2.76
2.36
OBn
O
S
Me
N
Ts
1e
1.03
2.00
1.01
4.03
1.08
3.44
1.01
2.05
3.04
3.11
10
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7
6
5
4
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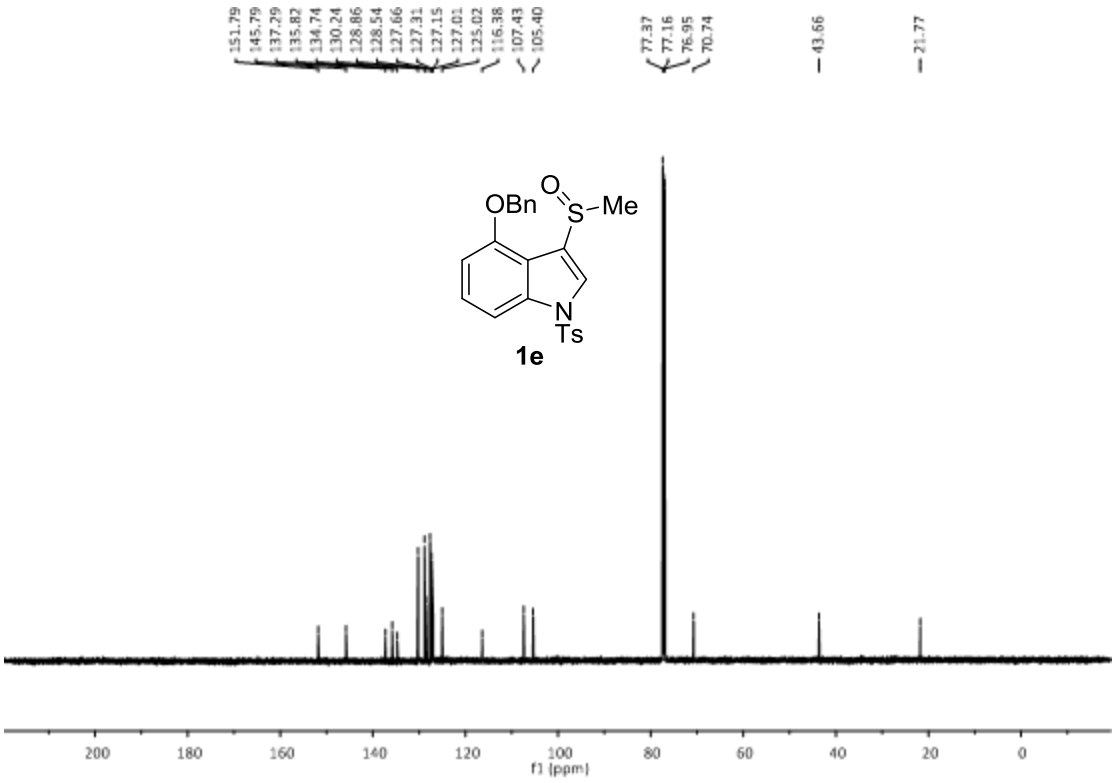
1
0
f1 (ppm)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145.79
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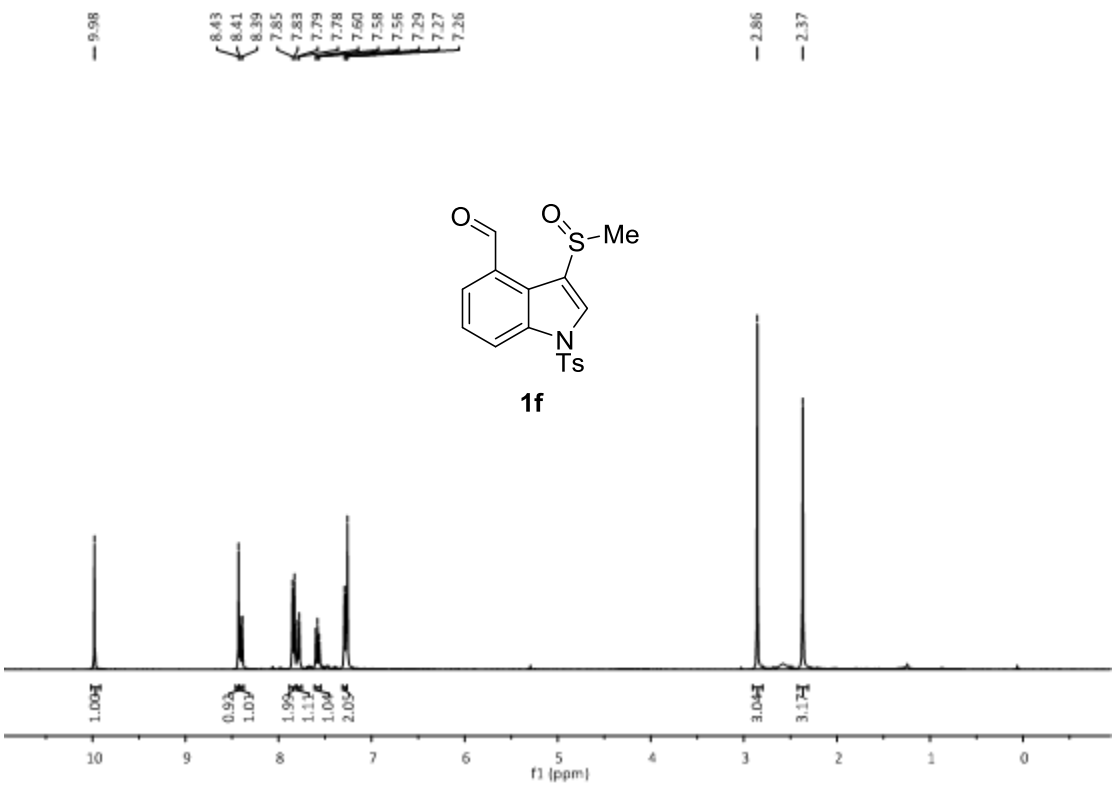
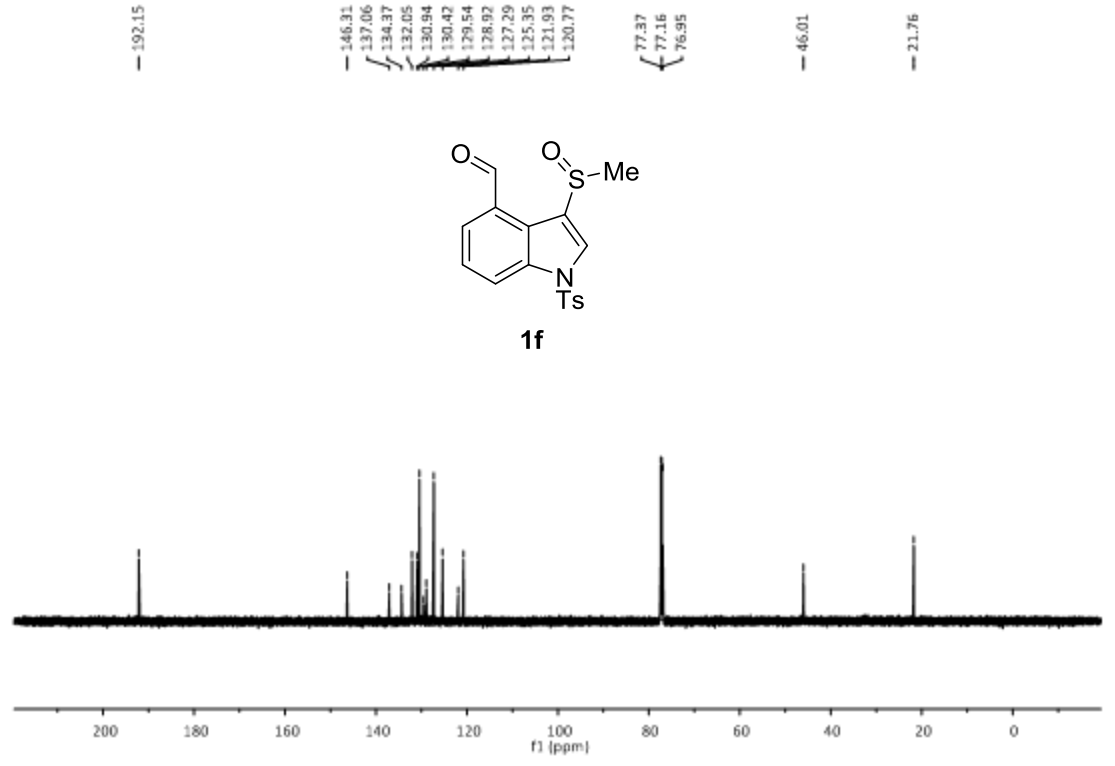
135.82
134.74
130.24
128.86
128.54
127.66
127.31
127.15
127.01
125.02
116.38
107.43
105.40
77.37
77.16
76.95
70.74
43.66
21.77
OBn
O
S
Me
N
Ts
1e
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


9.98
8.43
8.41
8.39
7.85
7.83
7.79
7.78
7.60
7.58
7.56
7.29
7.27
7.26
2.86
2.37
O
O
S
Me
N
Ts
1.00
0.93
1.01
1.99
1.11
1.04
2.05
3.04
3.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

1f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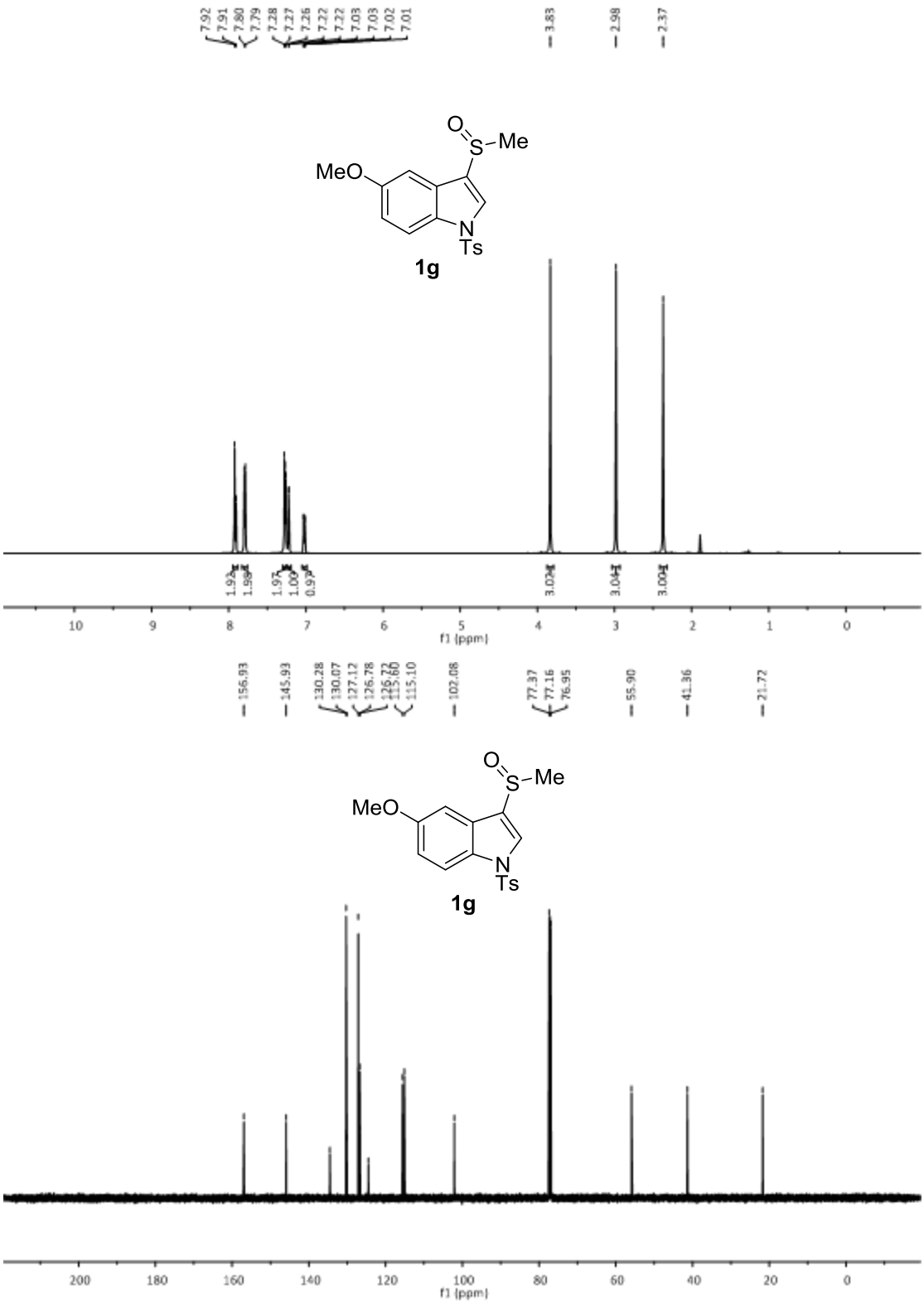
146.31
137.06
134.37
132.05
130.94
130.42
129.54
128.92
127.29
125.35
121.93
120.77
77.37
77.16
76.95
46.01
21.76
O
O
S
Me
N
Ts
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1f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7.91
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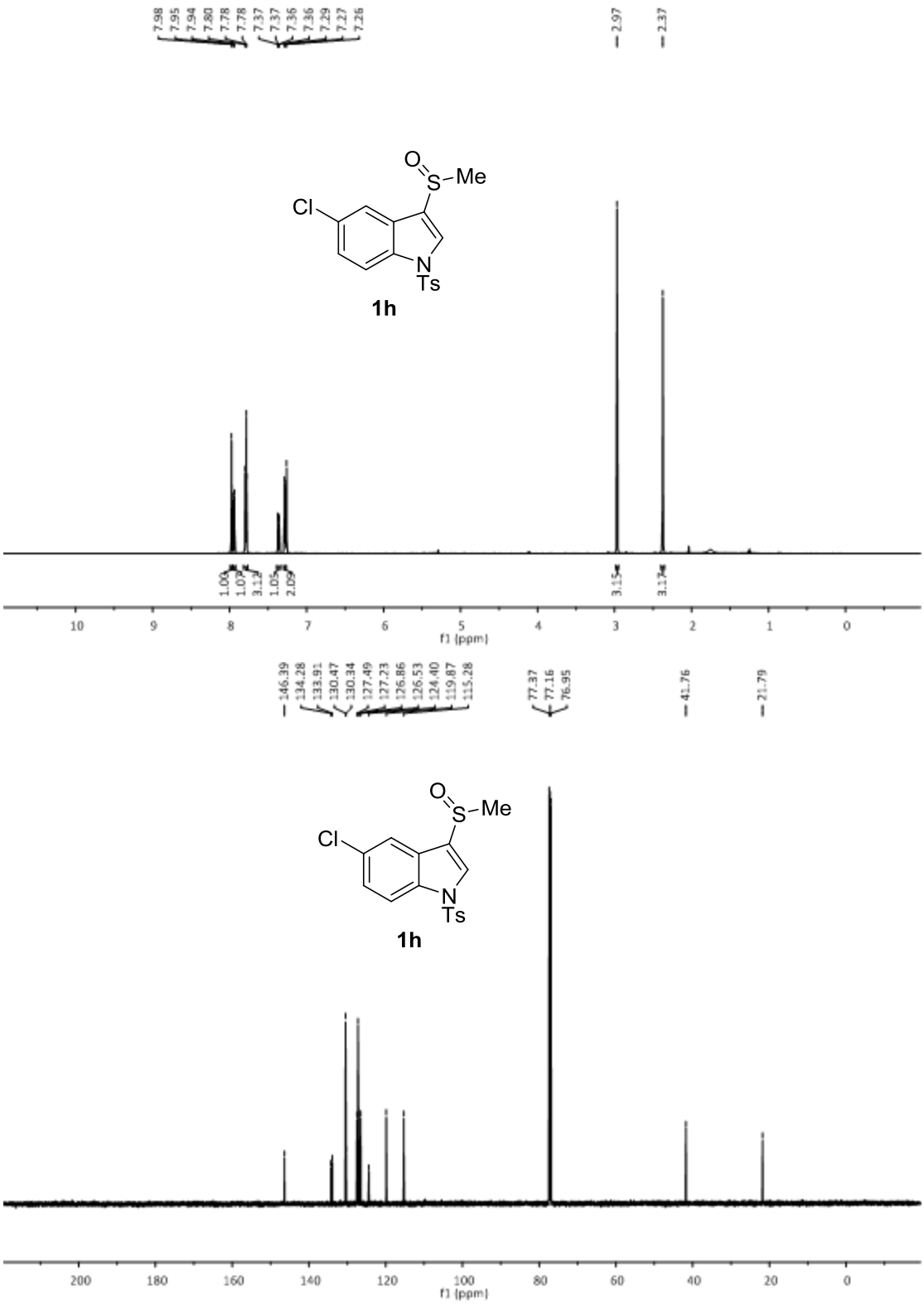
7.79
7.28
7.27
7.26
7.22
7.22
7.03
7.03
7.02
7.01
3.83
2.98
2.37
O
S
Me
MeO
N
Ts
1g
1.92
1.98
1.97
1.00
0.97
3.02
3.04
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
156.93
145.93
130.28
130.07
127.12
126.78
126.72
125.60
115.10
102.08
77.37
77.16
76.95
55.90
41.36
21.72
O
S
Me
MeO
N
Ts
1g
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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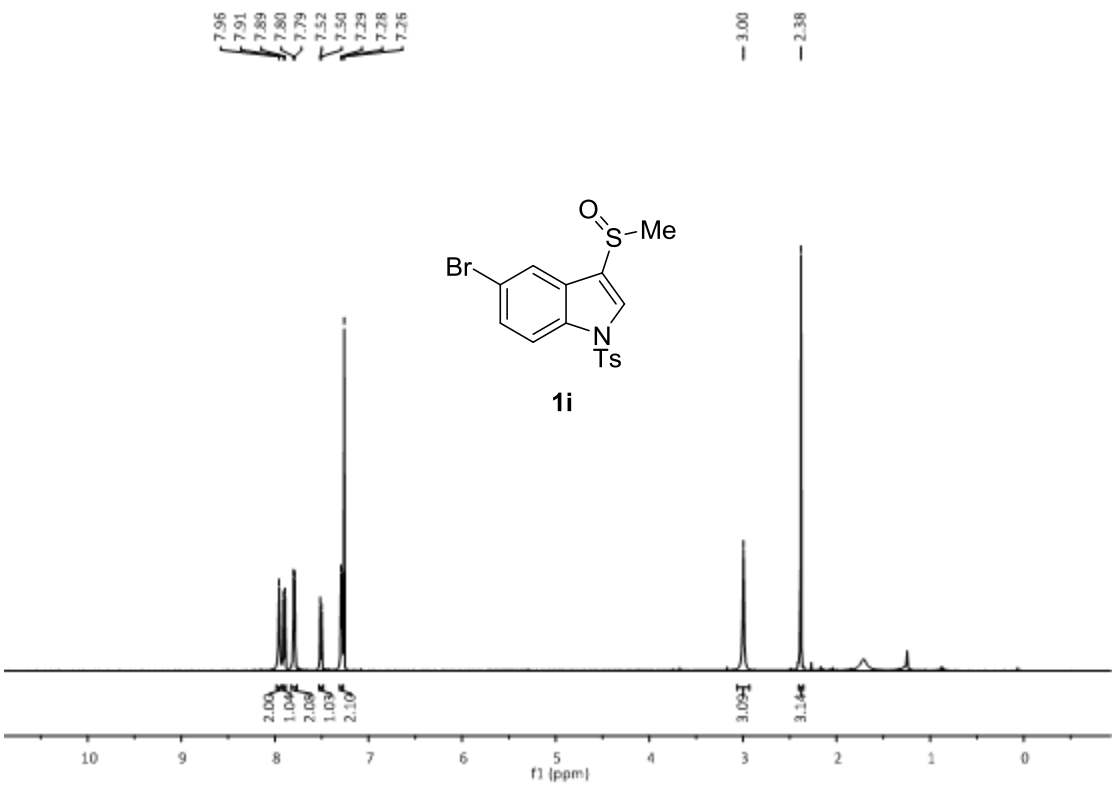
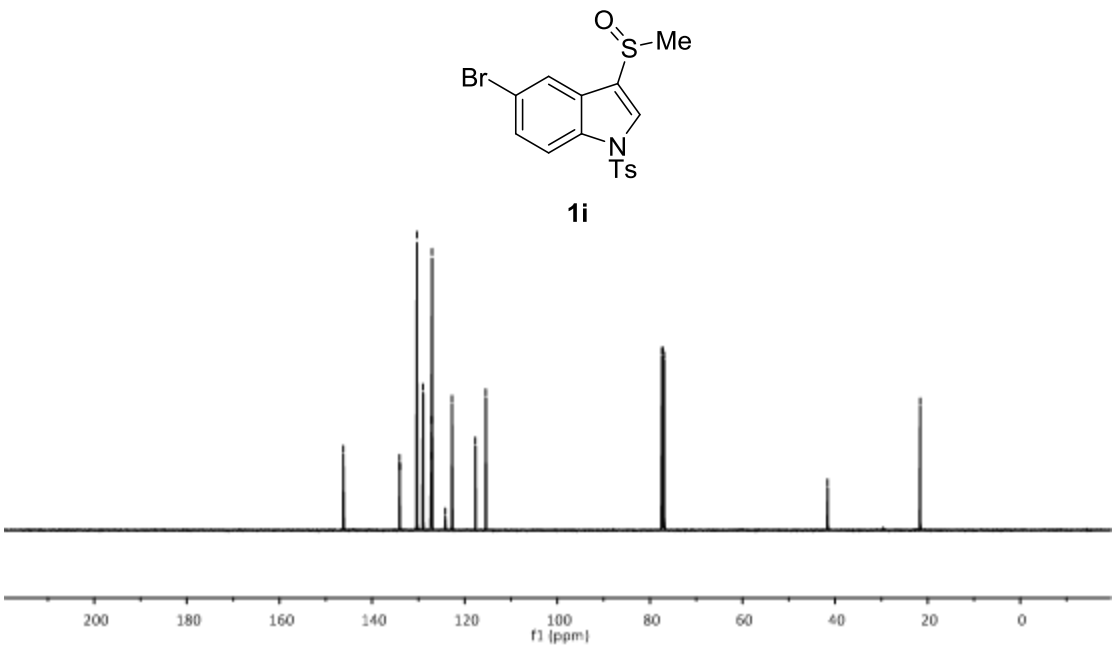
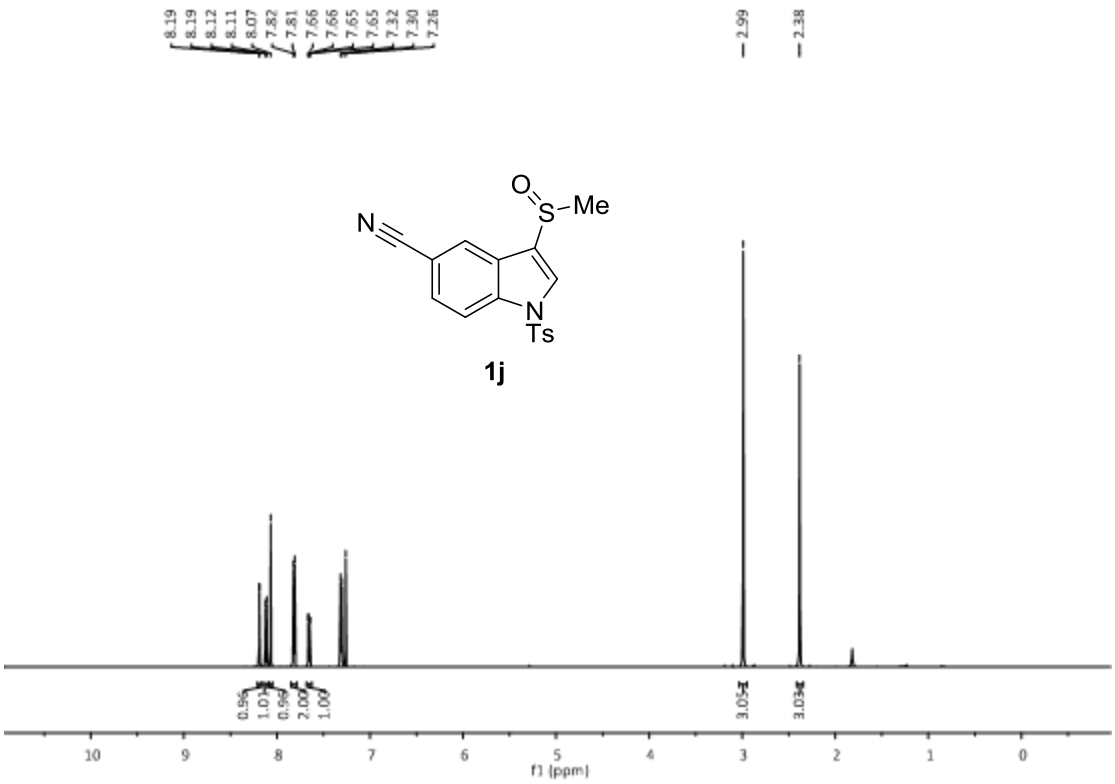
7.95
7.94
7.80
7.78
7.78
7.37
7.37
7.36
7.36
7.29
7.27
7.26
2.97
2.37
O
S
Me
Cl
N
Ts
1h
1.00
1.07
3.12
1.05
2.09
3.15
3.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
146.39
134.28
133.91
130.47
130.34
127.49
127.23
126.86
126.53
124.40
119.87
115.28
77.37
77.16
76.95
41.76
21.79
O
S
Me
Cl
N
Ts
1h
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.96
7.91
7.89
7.80
7.79
7.52
7.50
7.29
7.28
7.26
3.00
2.38
O
S
Me
Br
N
Ts
2.00
1.04
2.08
1.03
2.10
3.09
3.14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

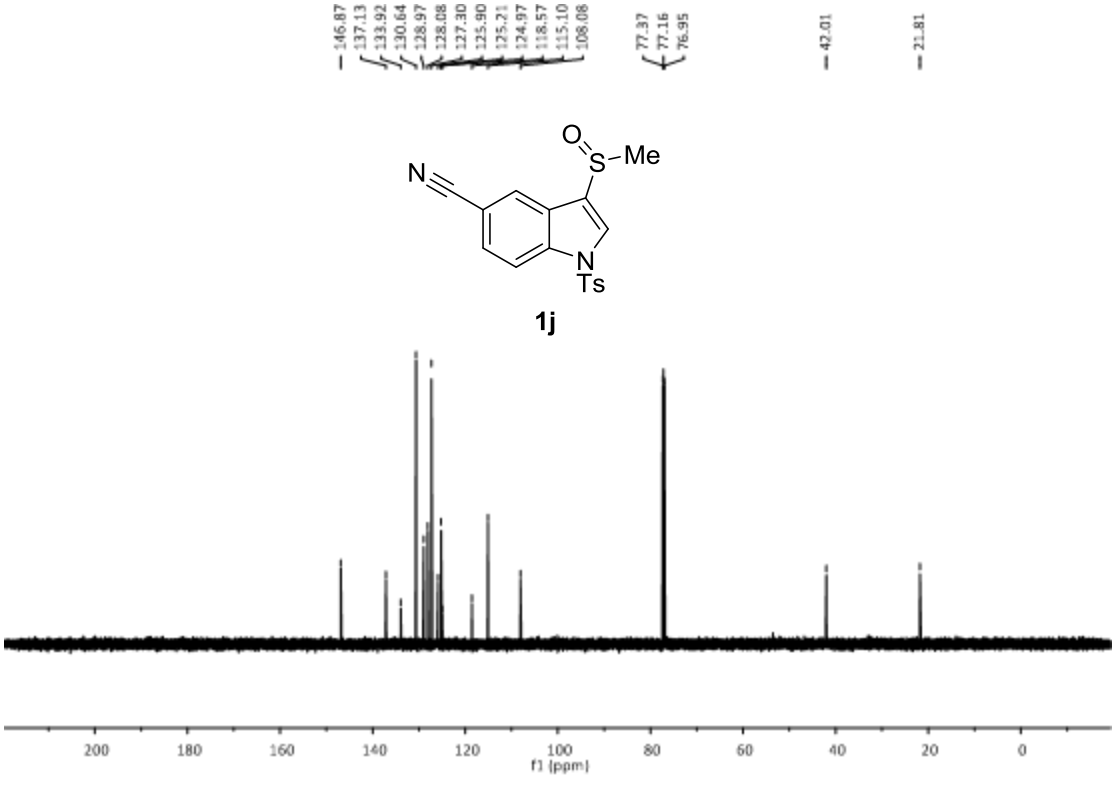
1i


146.24
134.07
134.03
130.31
128.98
127.23
127.17
127.06
124.20
122.75
117.71
115.44
77.37
77.16
76.95
41.64
21.62
O
S
Me
Br
N
Ts
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1i


8.19
8.19
8.12
8.11
8.07
7.82
7.81
7.66
7.66
7.65
7.65
7.32
7.30
7.26
2.99
2.38
O
S
Me
N
N
Ts
0.95
1.01
0.99
2.00
1.00
3.05
3.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

1j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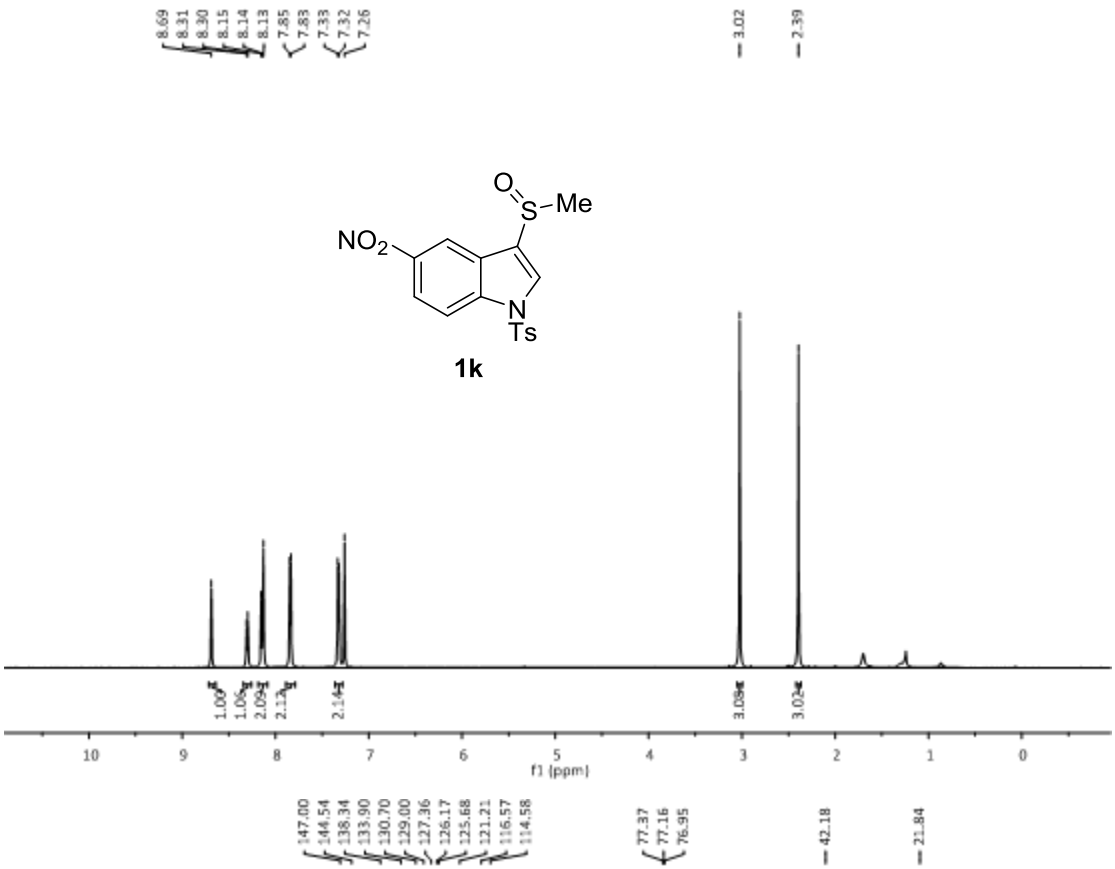
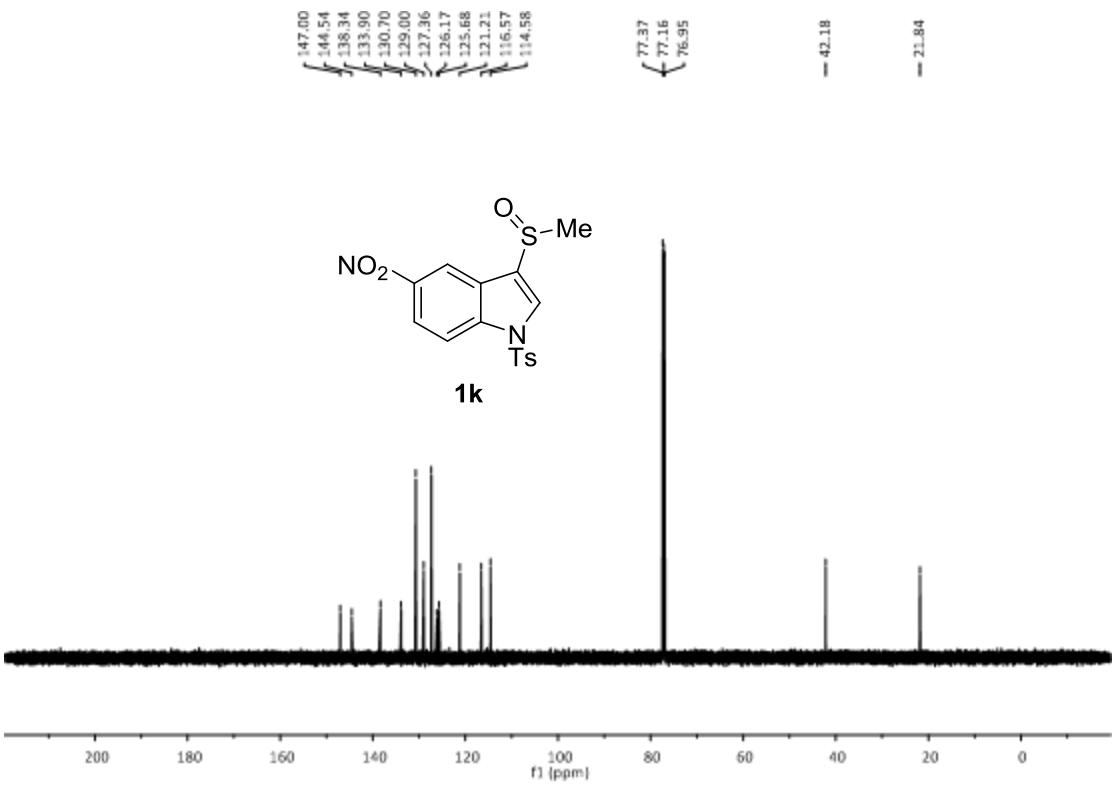
137.13
133.92
130.64
128.97
128.08
127.30
125.90
125.21
124.97
118.57
115.10
108.08
77.37
77.16
76.95
42.01
21.81
O
S
Me
N
N
Ts
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1j


8.69
8.31
8.30
8.15
8.14
8.13
7.85
7.83
7.33
7.32
7.26
3.02
2.39
O
S
Me
NO2
N
Ts
1k
1.00
1.06
2.09
2.13
2.14
3.09
3.02
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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144.54
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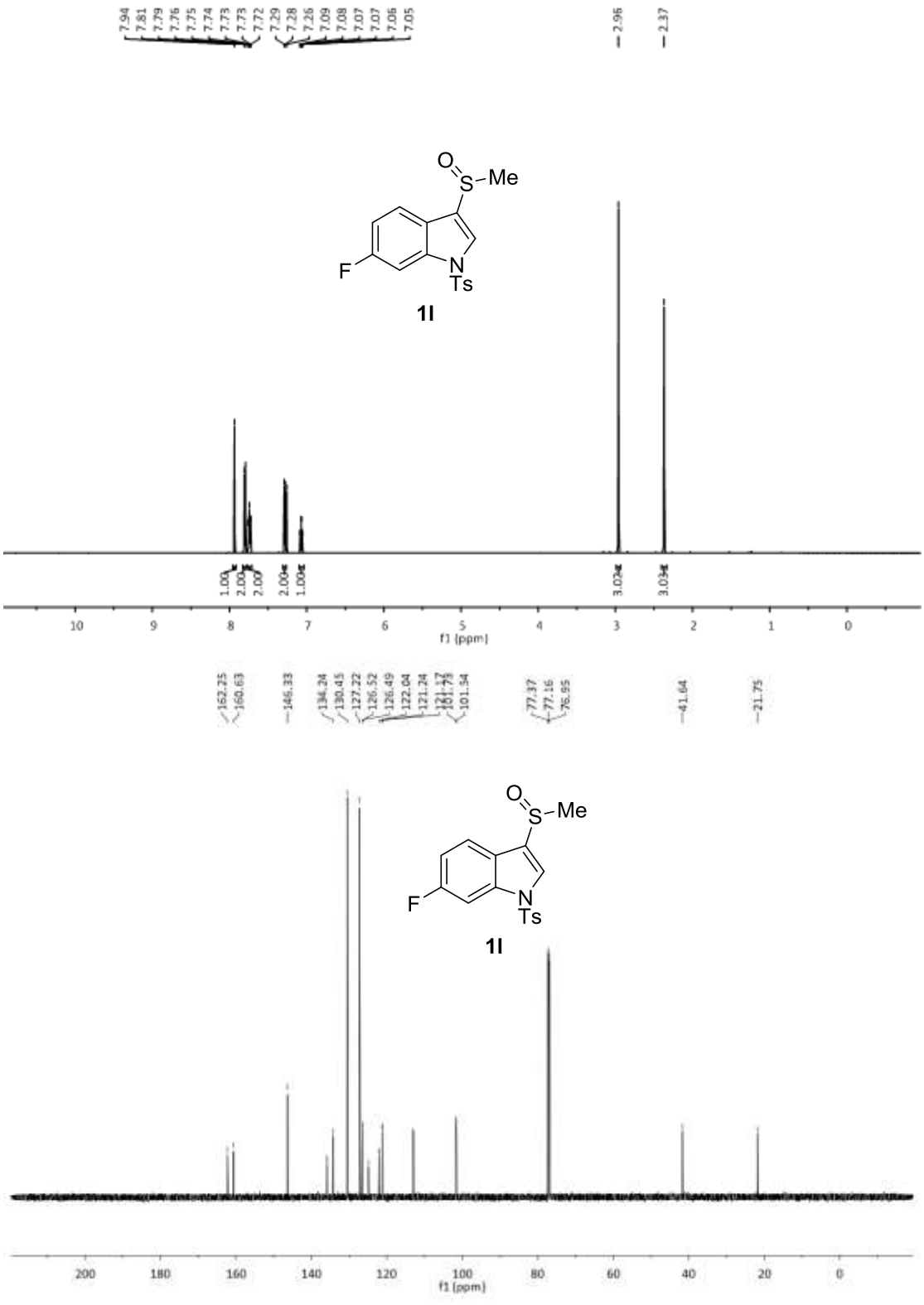
133.90
130.70
129.00
127.36
126.17
125.68
121.21
116.57
114.58
77.37
77.16
76.95
42.18
21.84
O
S
Me
NO2
N
Ts
1k
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.94
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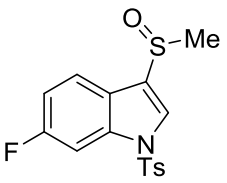
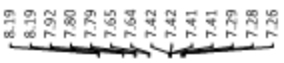
7.76
7.75
7.74
7.73
7.73
7.72
7.29
7.28
7.26
7.09
7.08
7.07
7.07
7.06
7.05
2.96
2.37
O
S
Me
F
N
Ts
1l
1.00
2.00
2.07
2.00
1.00
3.02
3.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
162.25
160.63
146.33
134.24
130.45
127.22
126.52
126.49
122.04
121.24
101.54
77.37
77.16
76.95
41.64
21.75
O
S
Me
F
N
Ts
1l
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


O
S
Me
F
N
Ts

1l

-113.33
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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8.19
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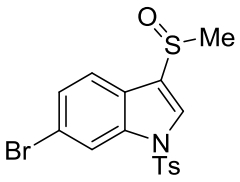
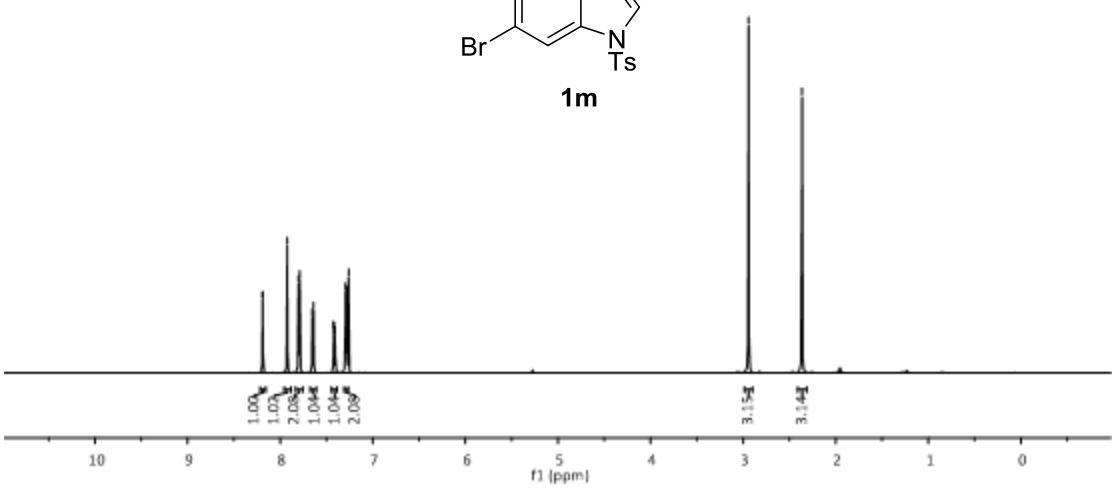
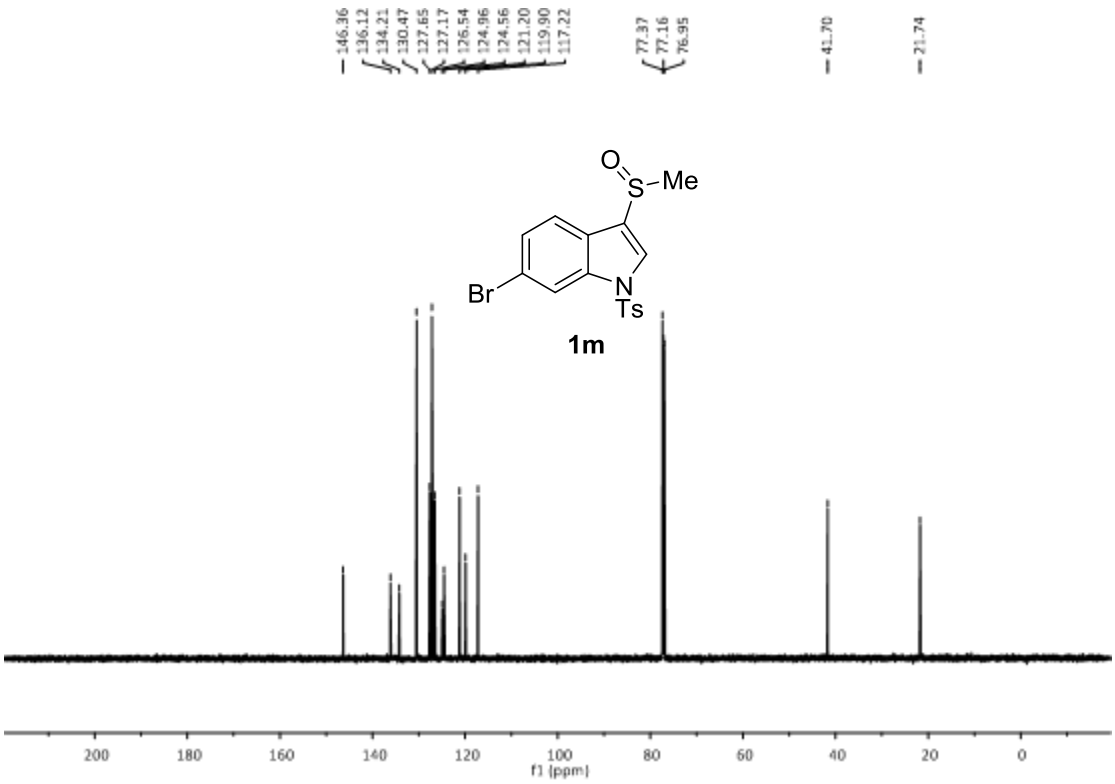
7.64
7.42
7.42
7.41
7.41
7.29
7.28
7.26


2.94
2.36


O
S
Me
Br
N
Ts

1m


1.00
1.03
2.08
1.04
1.04
2.09
3.15
3.14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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136.12
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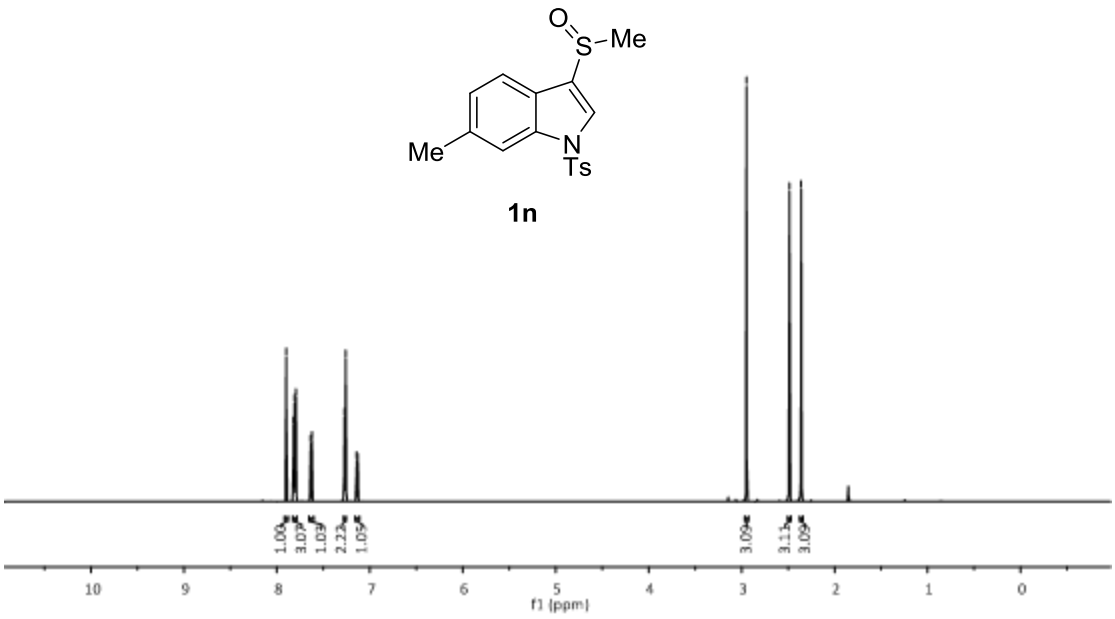
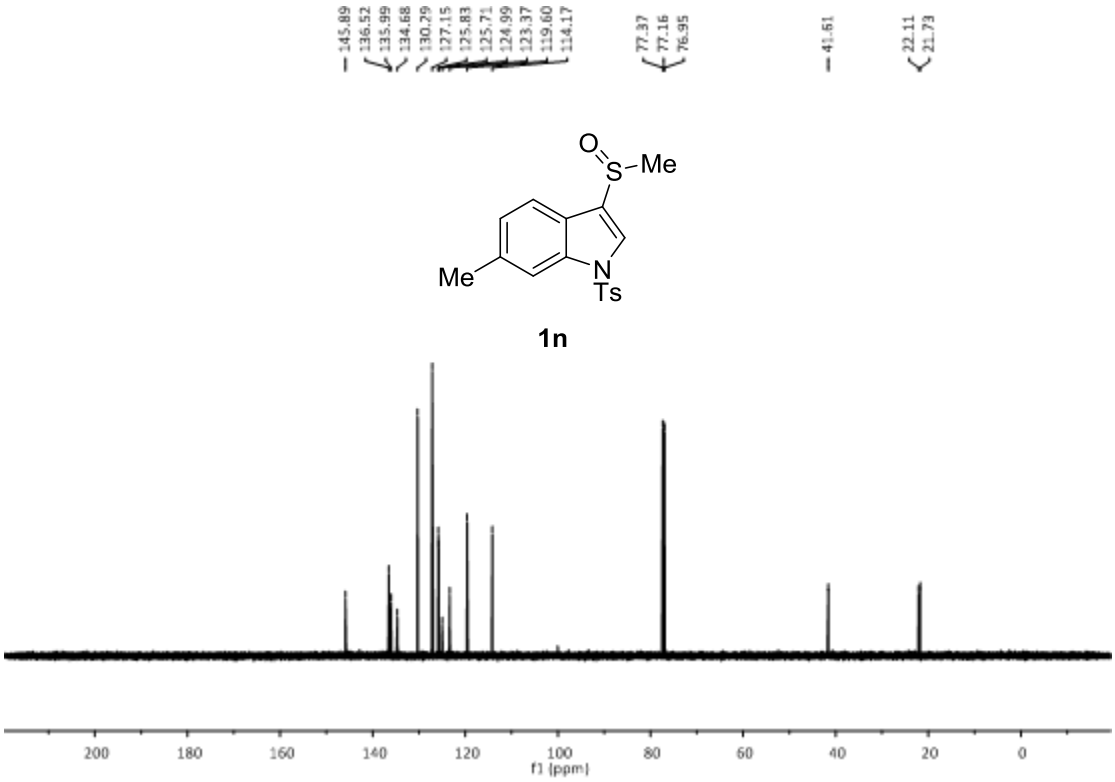
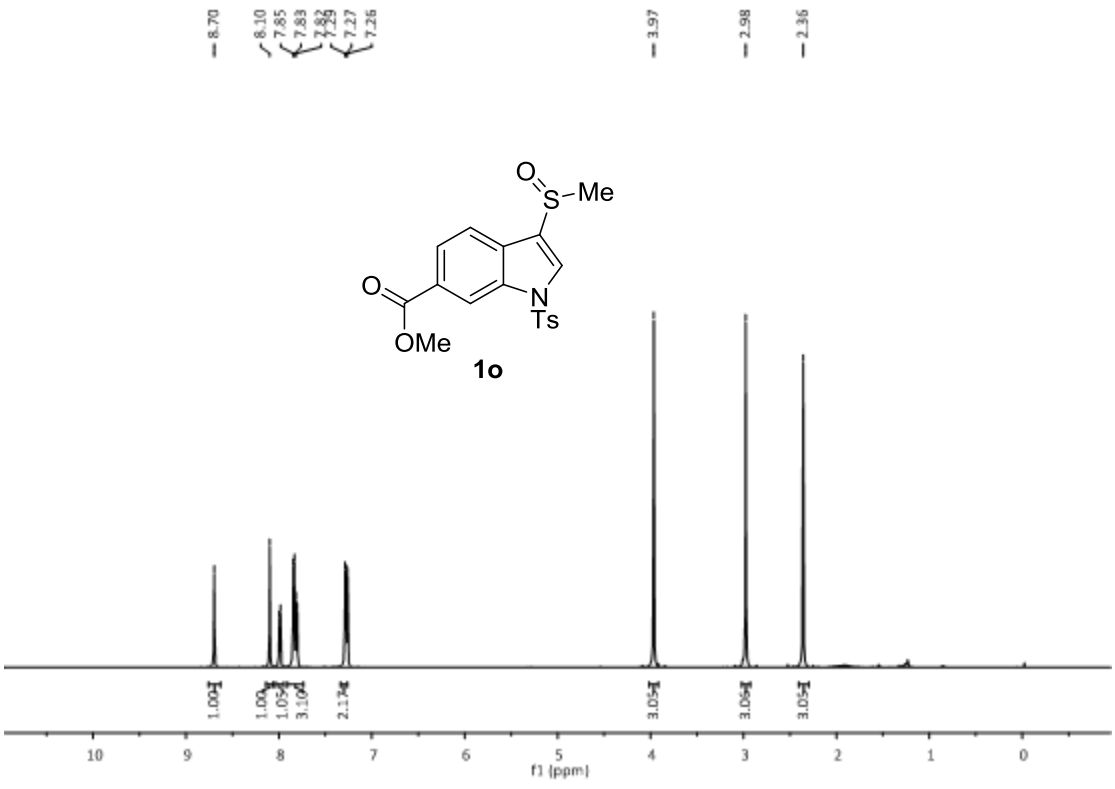
130.47
127.65
127.17
126.54
124.96
124.56
121.20
119.90
117.22
77.37
77.16
76.95
41.70
21.74
O
S
Me
Br
N
Ts
1m
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)
7.90
7.82
7.81
7.80
7.64
7.62
7.27
7.26
7.14
7.13
2.95
2.49
2.36

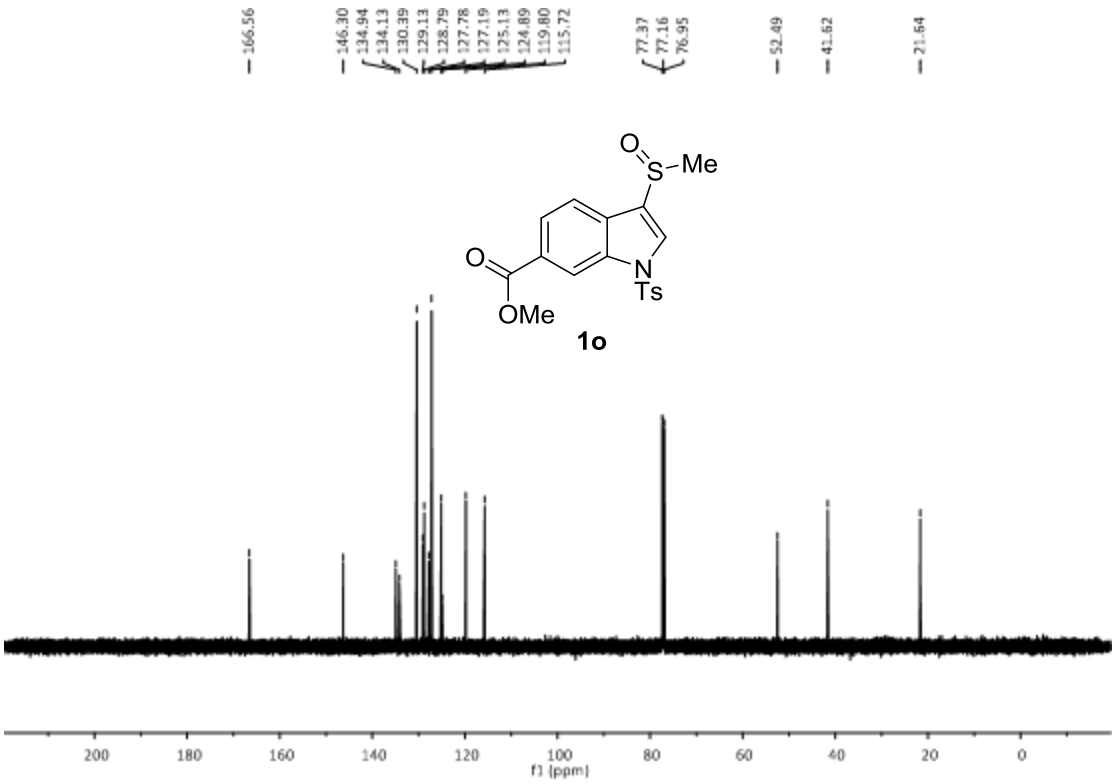

O
S
Me
Me
N
Ts
1n
1.00
3.07
1.03
2.22
1.05
3.09
3.11
3.09
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


145.89
136.52
135.99
134.68
130.29
127.15
125.83
125.71
124.99
123.37
119.60
114.17
77.37
77.16
76.95
41.61
22.11
21.73
O
S
Me
Me
N
Ts
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1n


8.70
8.10
7.85
7.83
7.82
7.29
7.27
7.26
3.97
2.98
2.36
O
S
Me
O
N
Ts
OMe
1.00
1.00
1.05
3.10
2.17
3.05
3.06
3.05
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

1o


166.56
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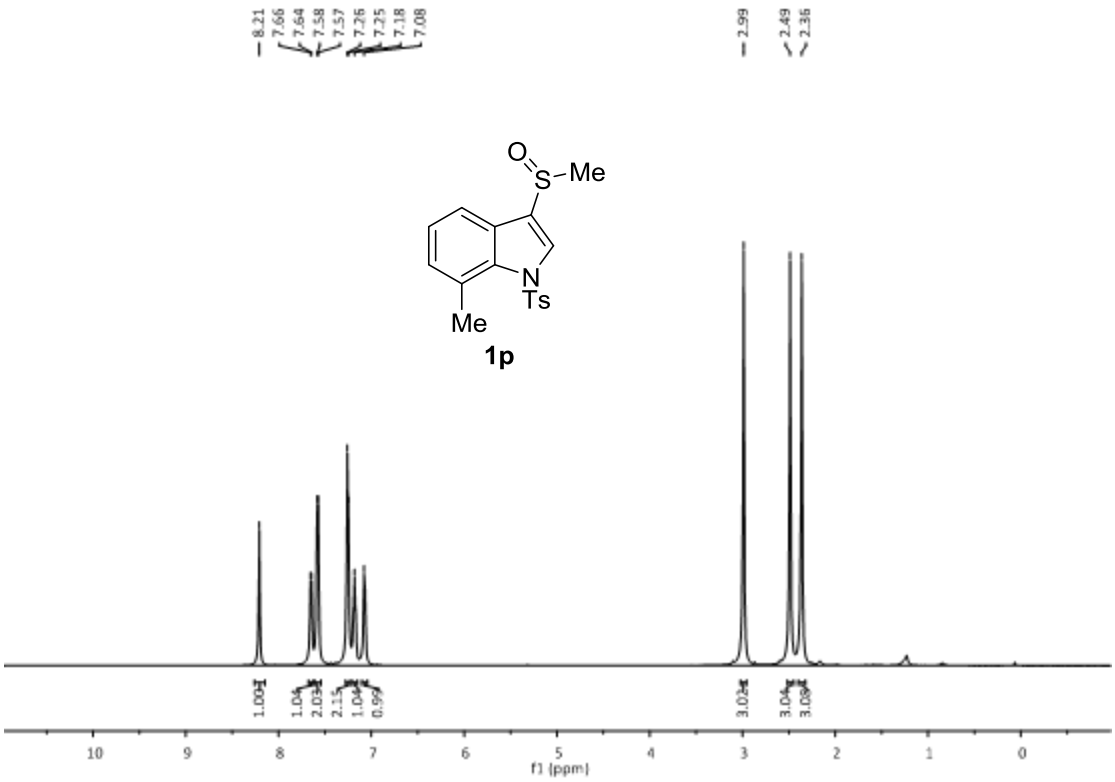
134.13
130.39
129.13
128.79
127.78
127.19
125.13
124.89
119.80
115.72
77.37
77.16
76.95
52.49
41.62
21.64
O
S
Me
O
N
Ts
OMe
1o
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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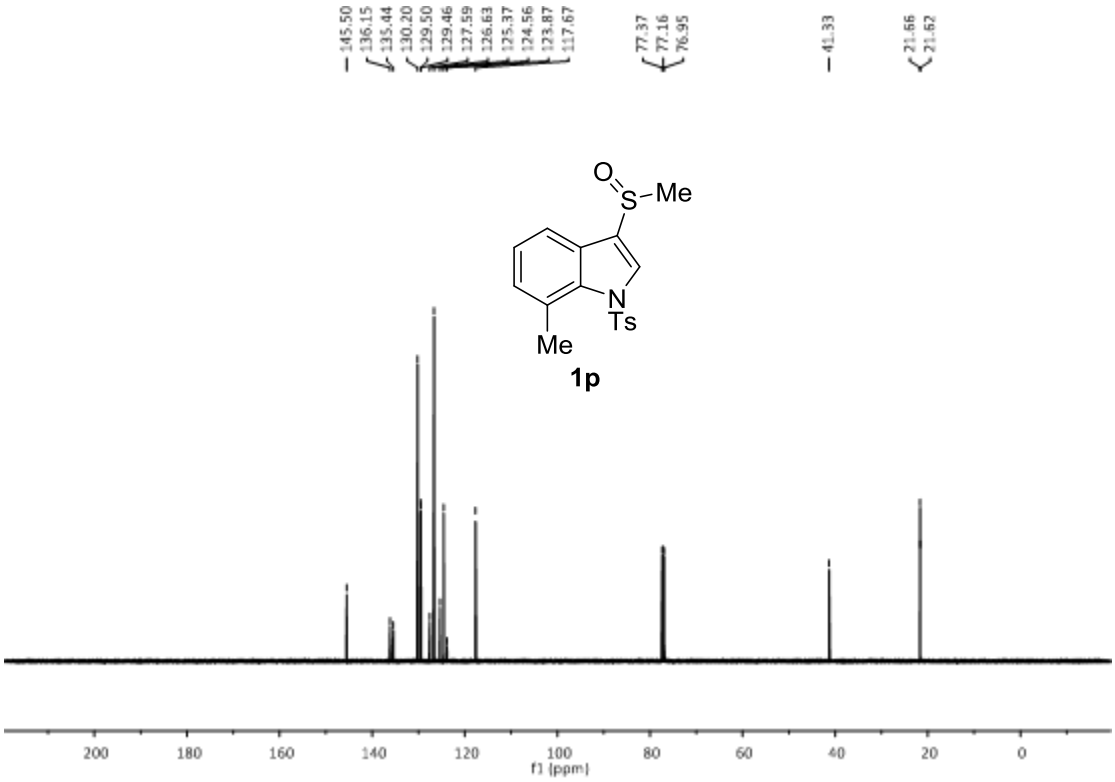
7.58
7.57
7.26
7.25
7.18
7.08
2.99
2.49
2.36
O
S
Me
N
Ts
Me
1p
1.00
1.04
2.03
2.15
1.04
0.99
3.02
3.04
3.09
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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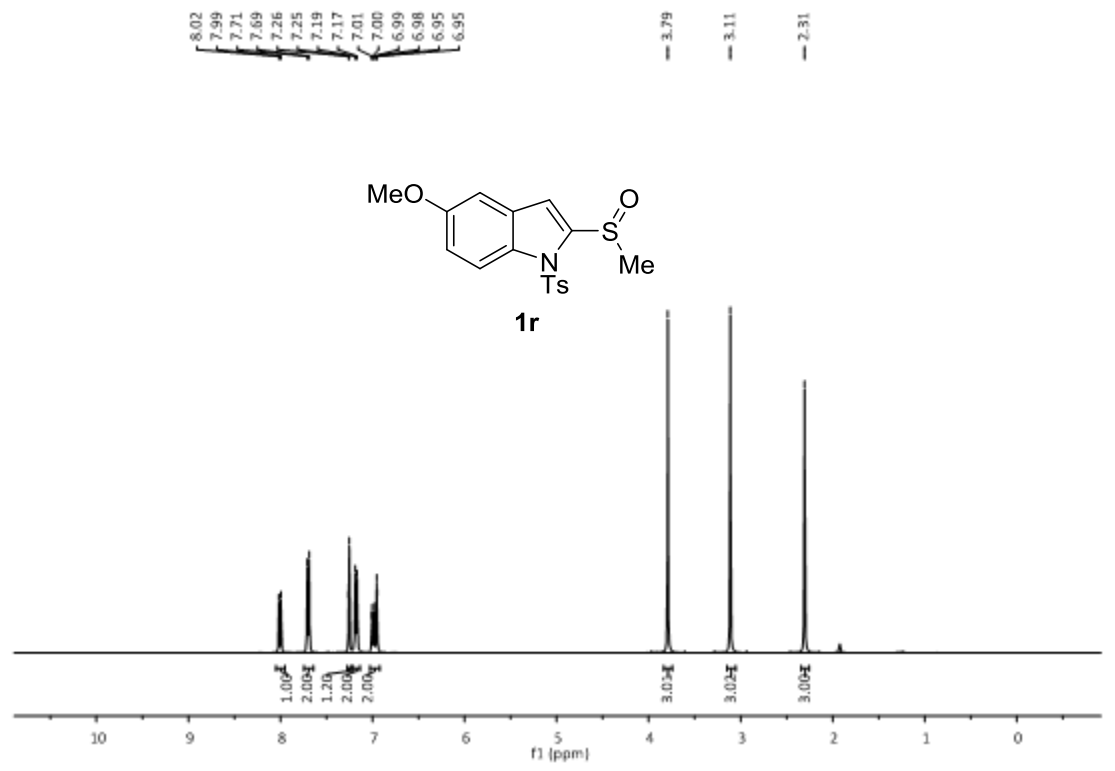
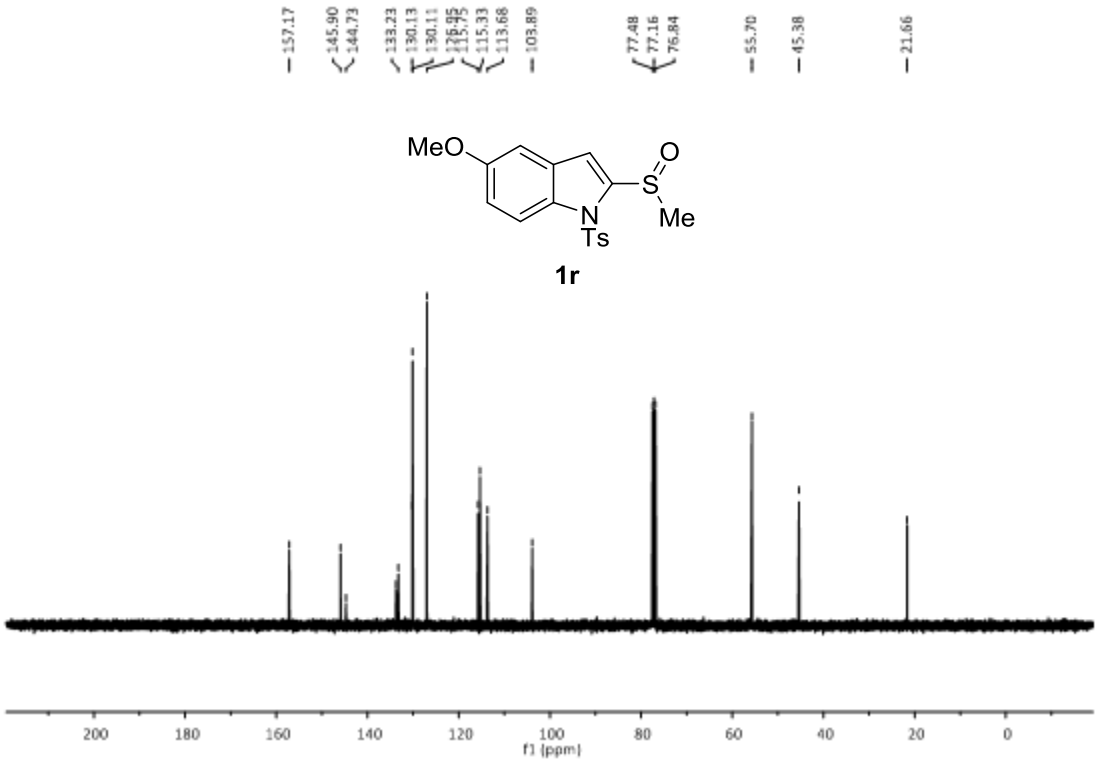
129.46
127.59
126.63
125.37
124.56
123.87
117.67
77.37
77.16
76.95
41.33
21.66
21.62
O
S
Me
N
Ts
Me
1p
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.02
7.99
7.71
7.69
7.26
7.25
7.19
7.17
7.01
7.00
6.99
6.98
6.95
6.95
3.79
3.11
2.31
MeO
O
S
Me
N
Ts
1r
1.00
2.09
1.20
2.00
2.00
3.03
3.02
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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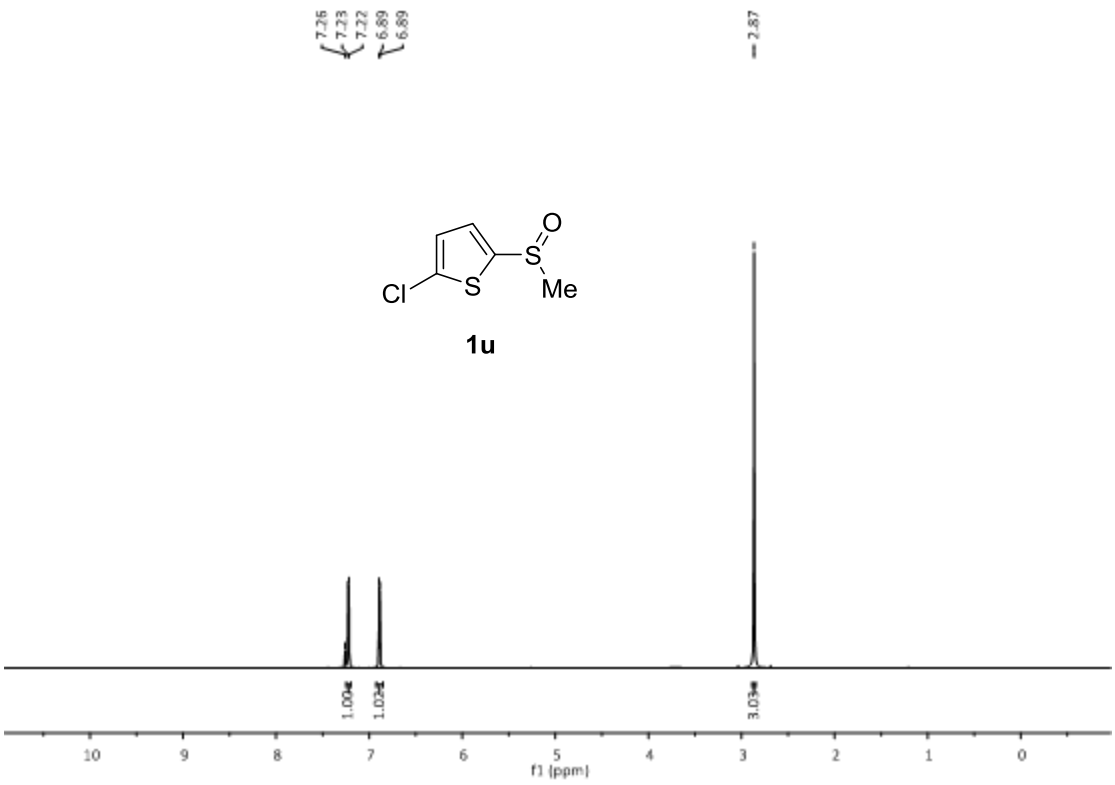
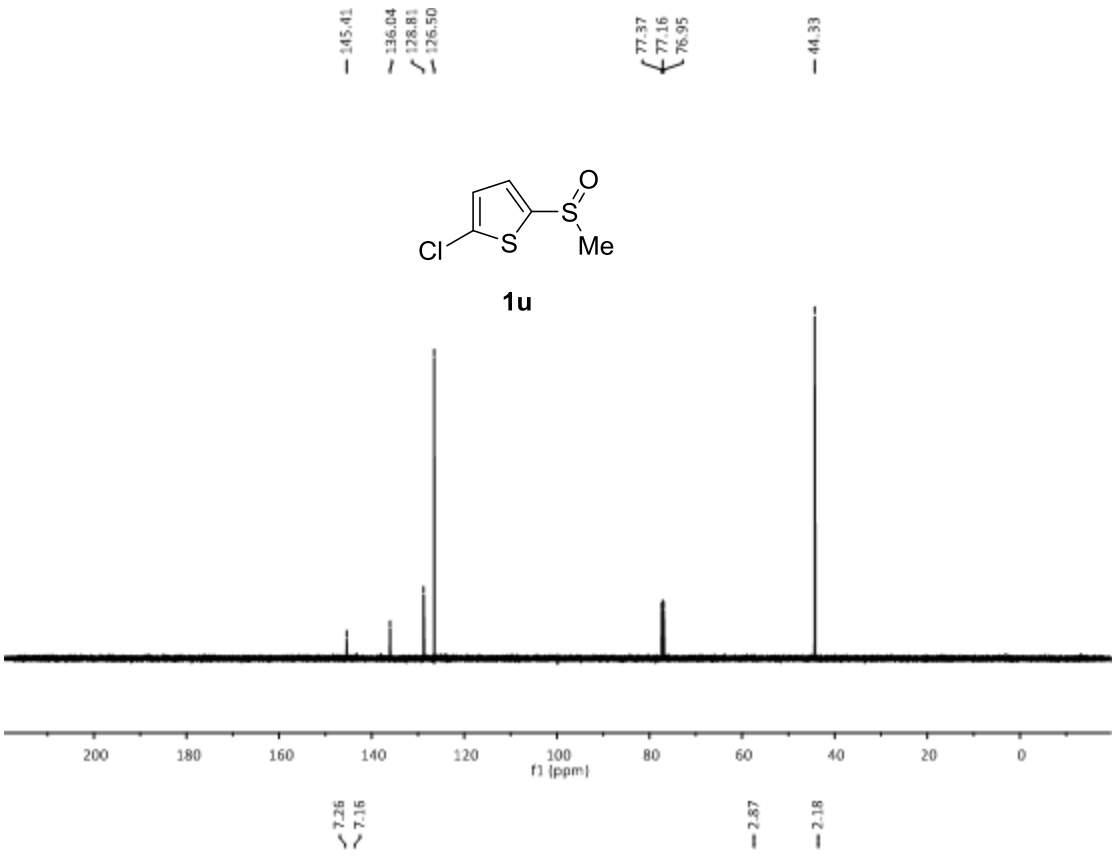
130.11
126.95
115.75
115.33
113.68
103.89
77.48
77.16
76.84
55.70
45.38
21.66
MeO
O
S
Me
N
Ts
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

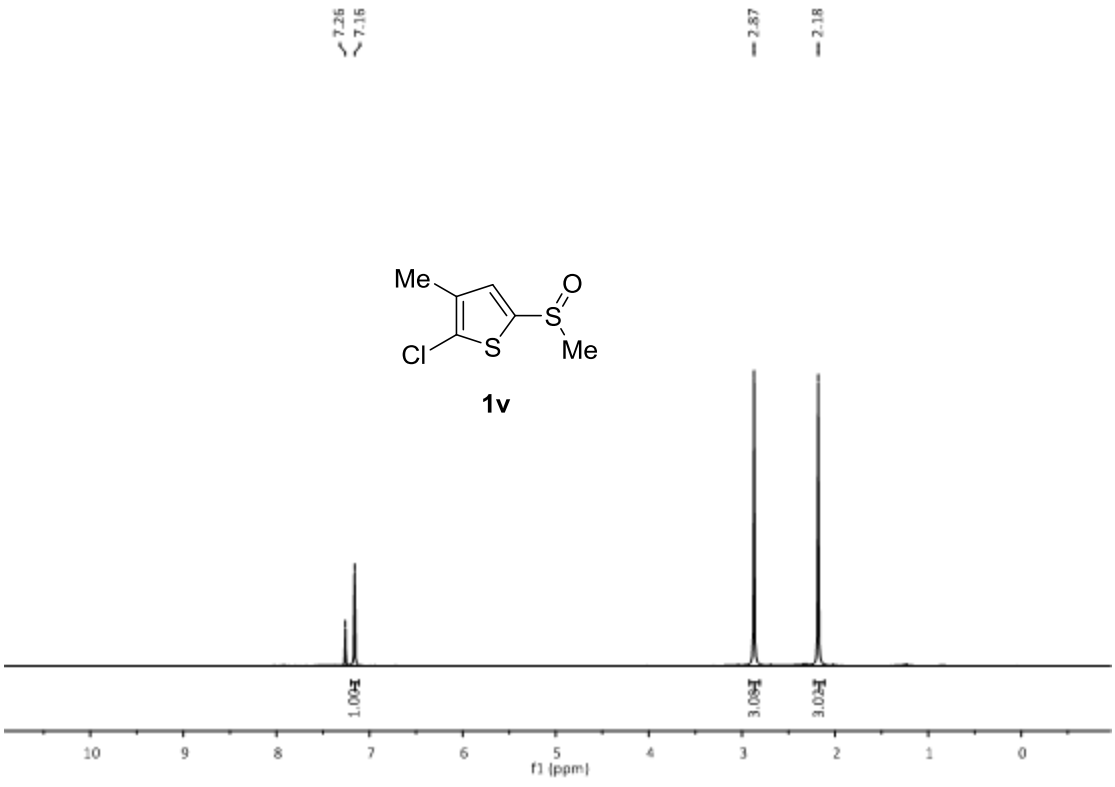
1r


7.26
7.23
7.22
6.89
6.89
2.87
Cl
S
O
S
Me
1.00
1.02
3.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

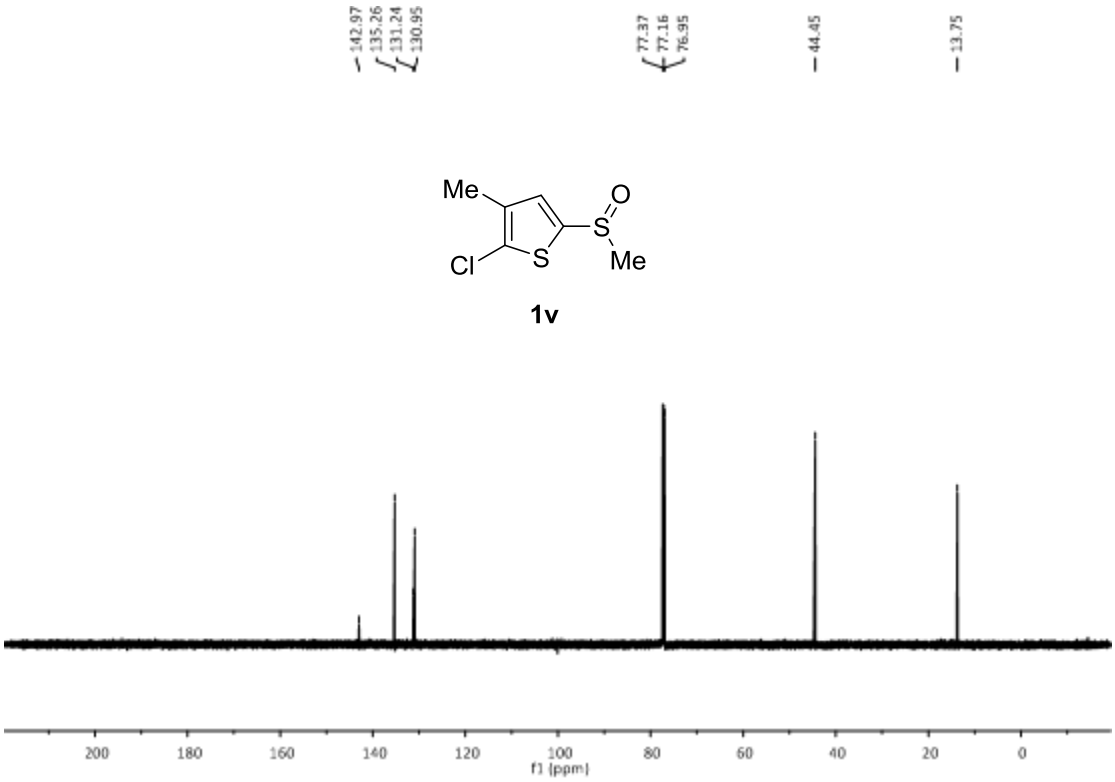
1u


145.41
136.04
128.81
126.50
77.37
77.16
76.95
44.33
O
S
Cl
S
Me
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

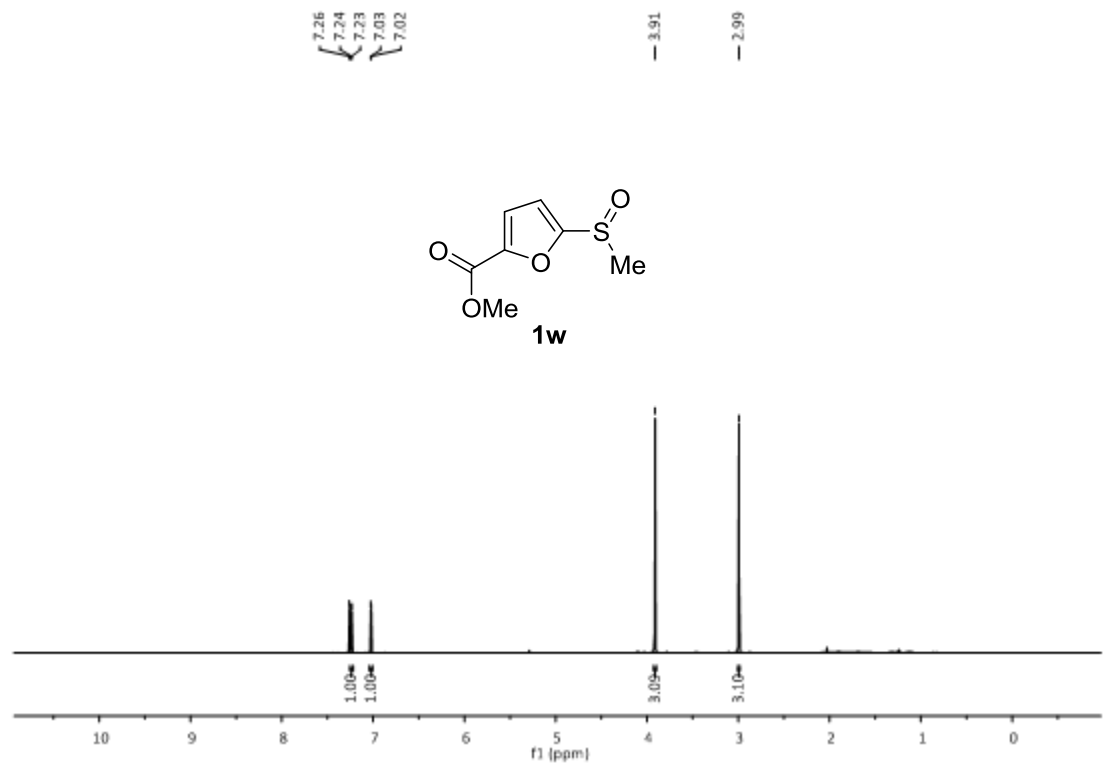
1u


7.26
7.16
2.87
2.18
Me
O
S
Cl
S
Me
1.00
3.08
3.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

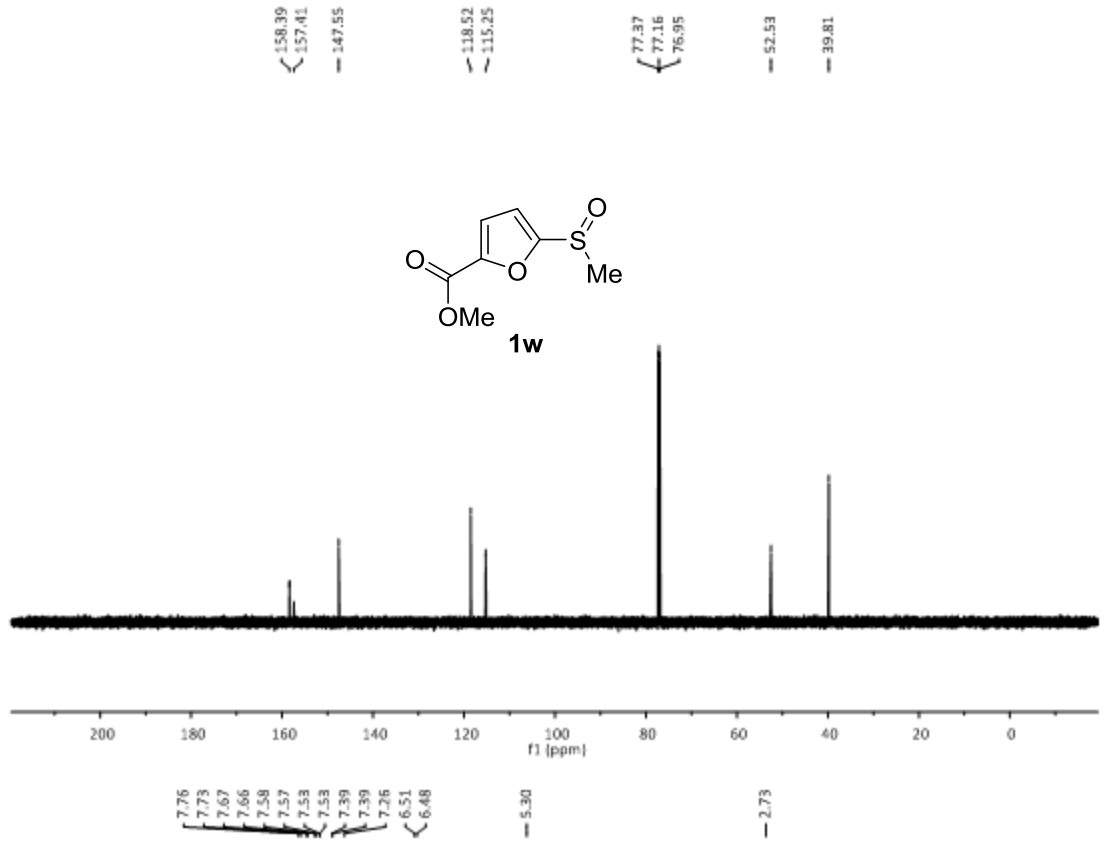
1v


142.97
135.26
131.24
130.95
77.37
77.16
76.95
44.45
13.75
Me
O
S
Cl
S
Me
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

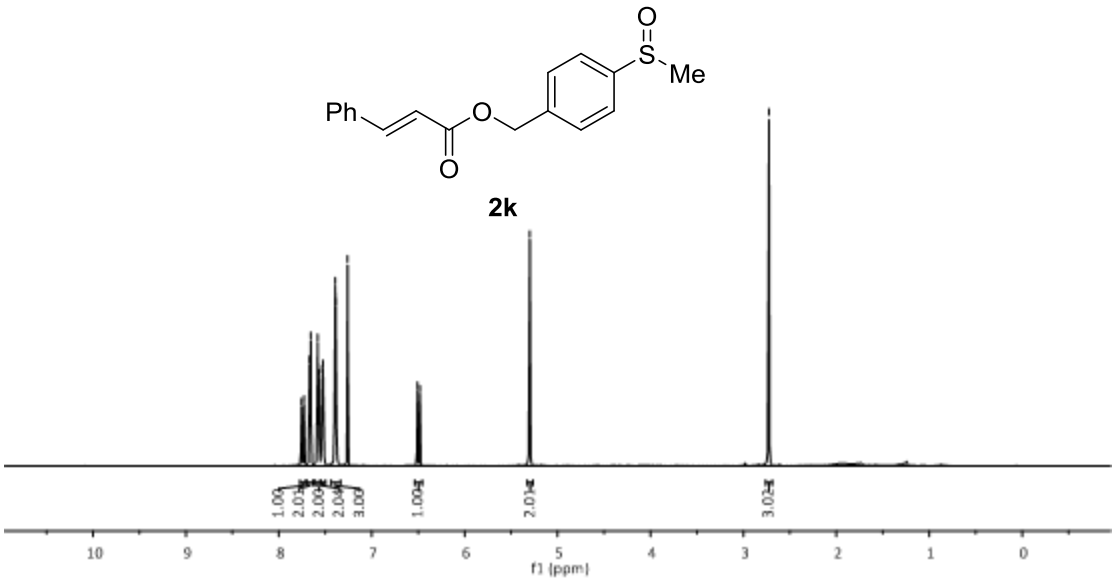
1v


7.26
7.24
7.23
7.03
7.02
3.91
2.99
O
O
S
O
Me
OMe
1.00
1.00
3.09
3.10
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

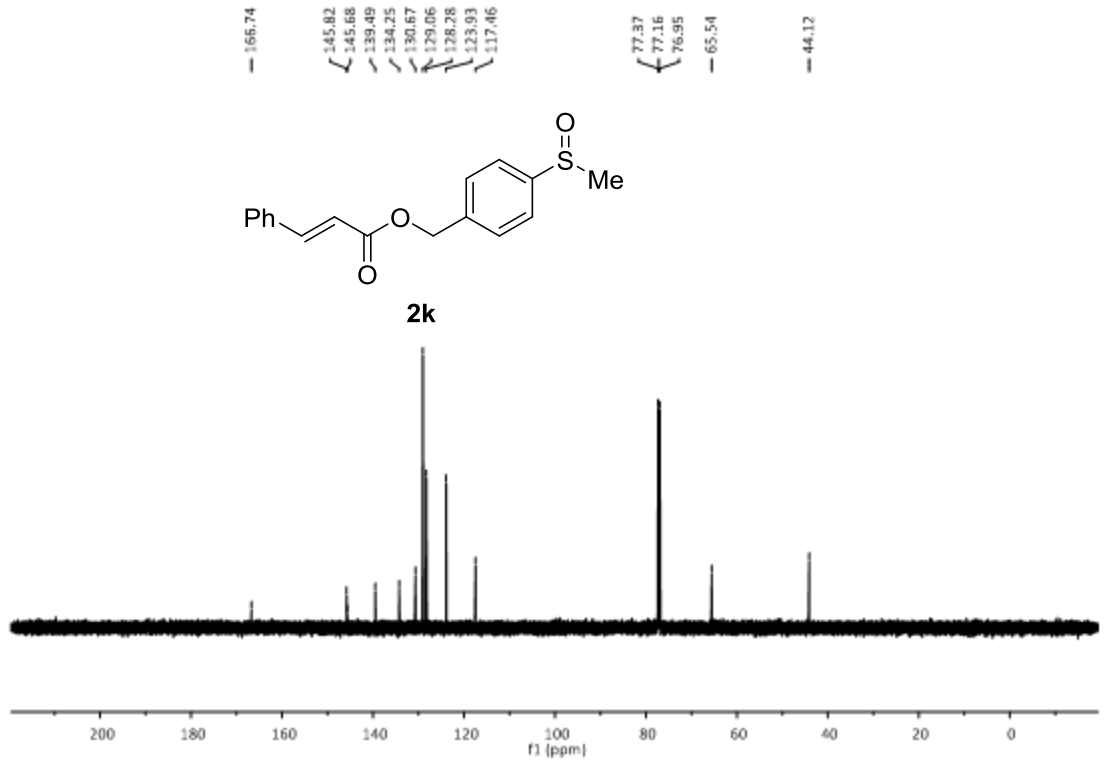
1w


158.39
157.41
147.55
118.52
115.25
77.37
77.16
76.95
52.53
39.81
O
O
S
Me
O
O
OMe
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)
7.76
7.73
7.67
7.66
7.58
7.57
7.53
7.53
7.39
7.39
7.26
6.51
6.48
5.30
2.73

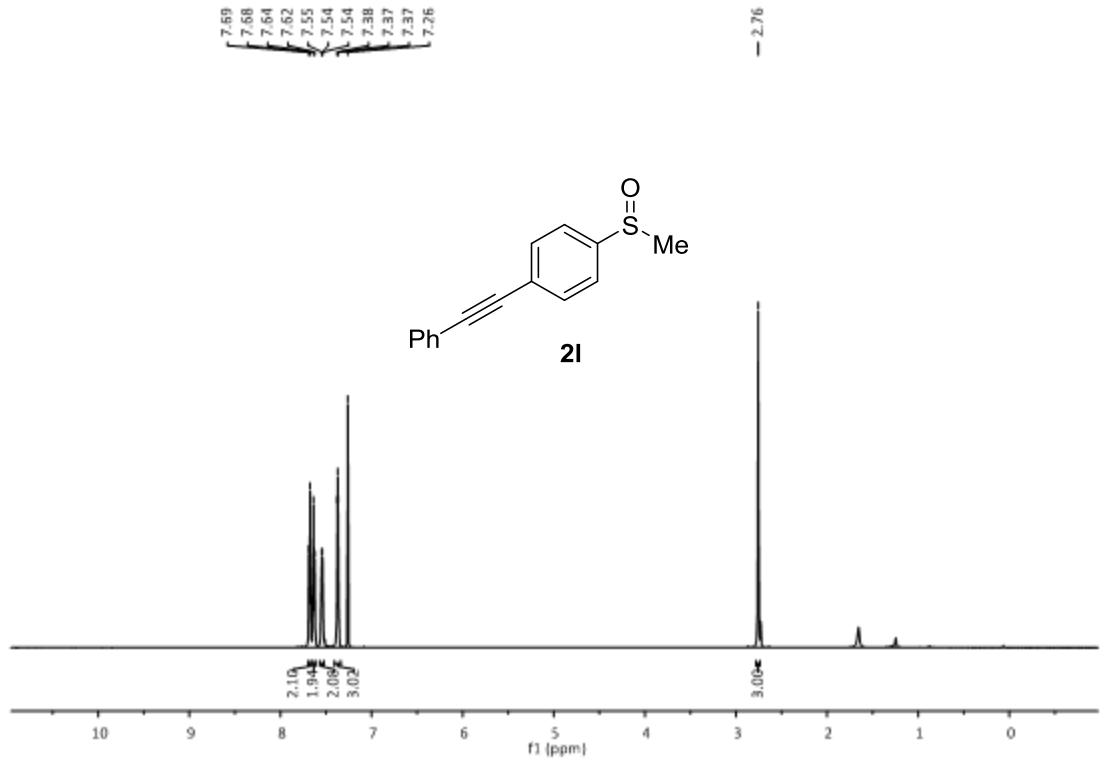
1w


O
S
Me
Ph
O
O
1.00
2.01
2.00
2.04
3.00
1.00
2.01
3.02
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

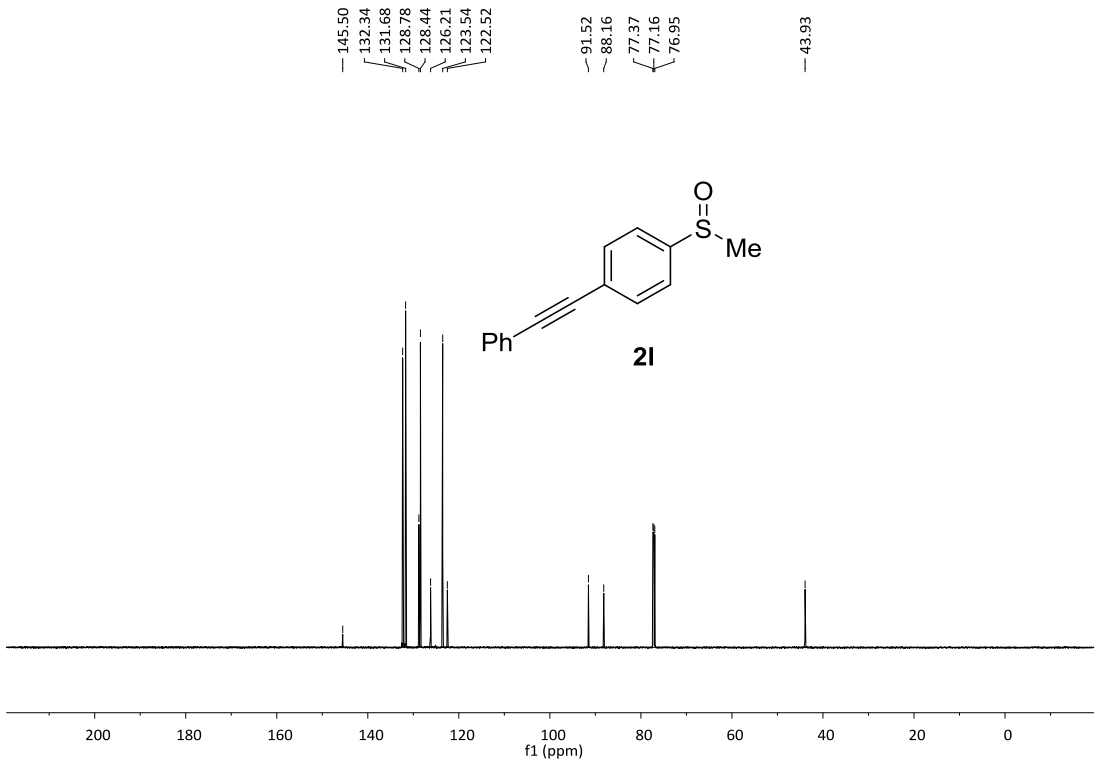
2k

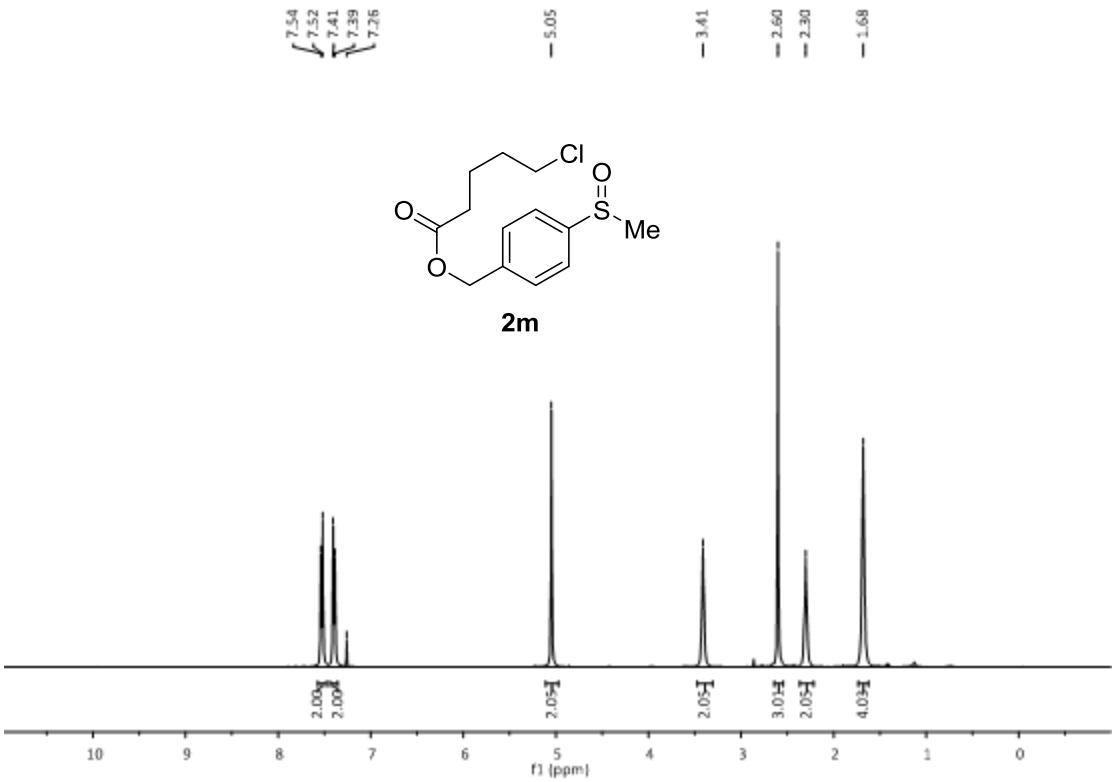

166.74
145.82
145.68
139.49
134.25
130.67
129.06
128.28
123.93
117.46
77.37
77.16
76.95
65.54
44.12
O
S
Me
Ph
O
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

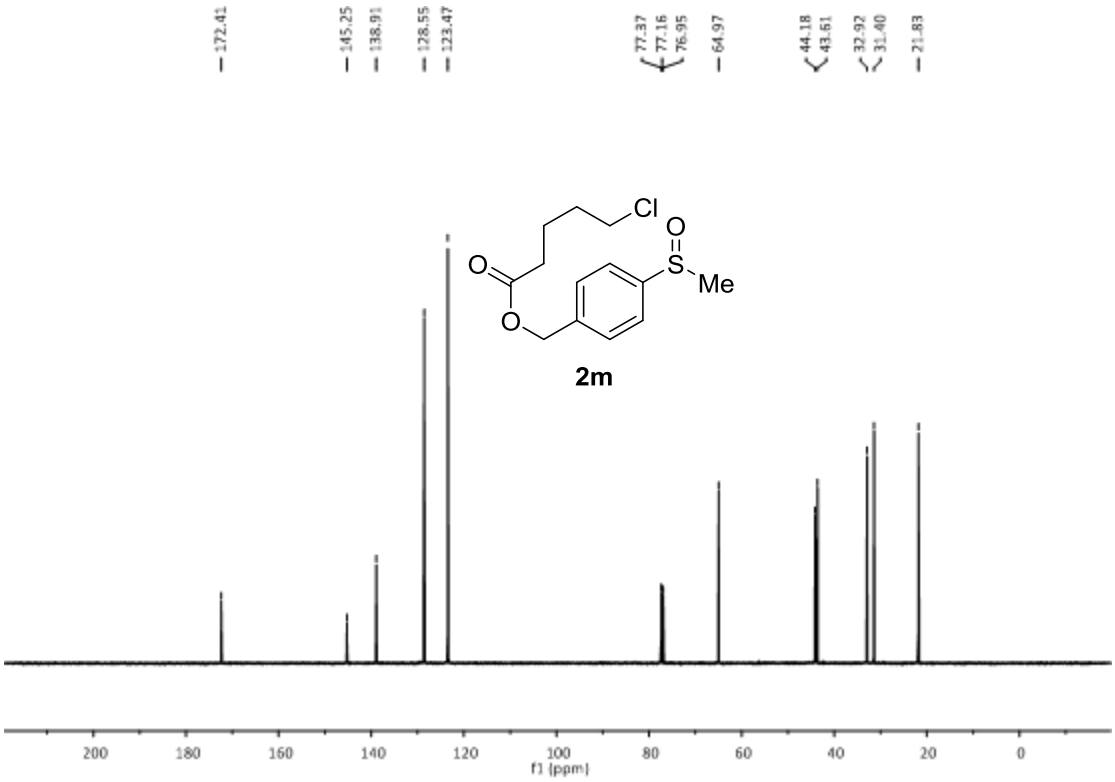
2k

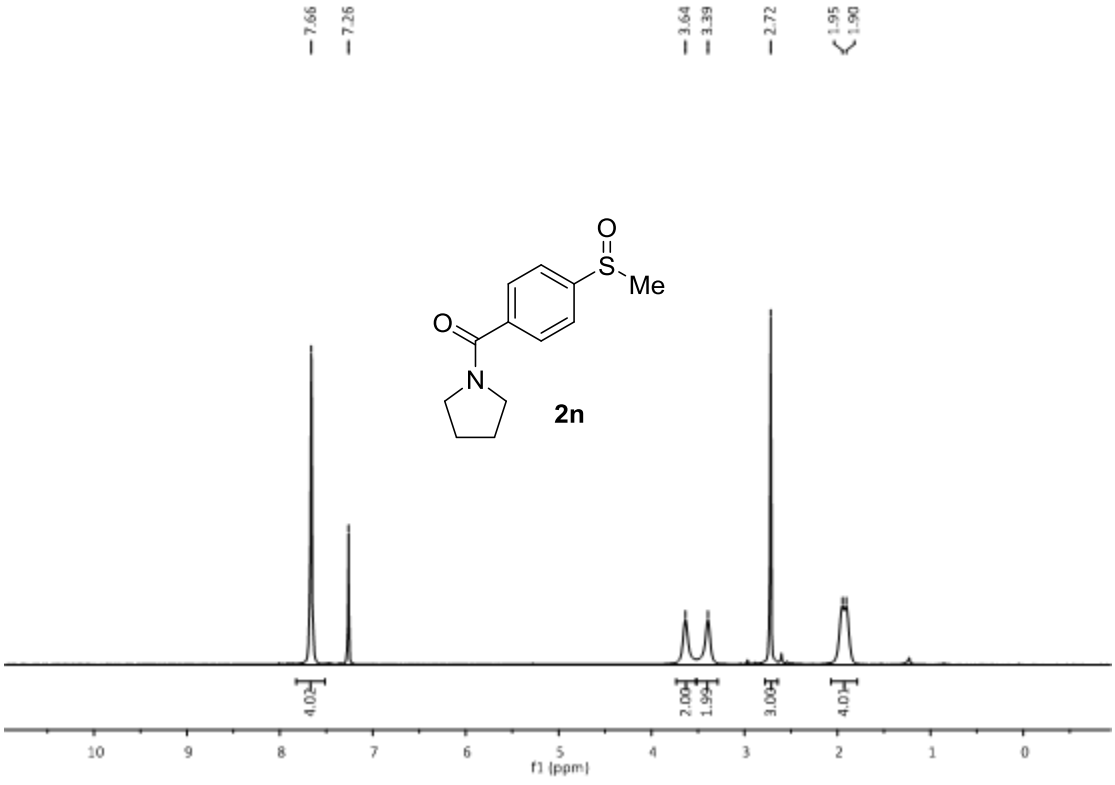

7.69
7.68
7.64
7.62
7.55
7.54
7.54
7.38
7.37
7.37
7.26
2.76
O
S
Me
Ph
2.10
1.94
2.09
3.02
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

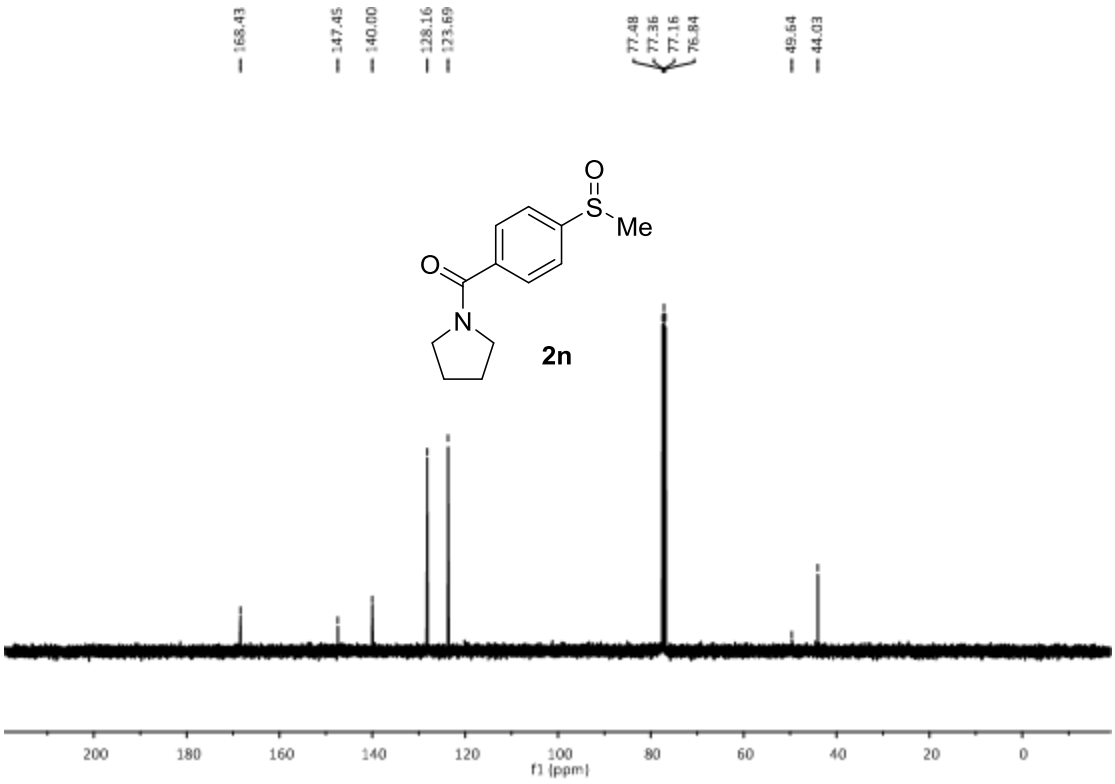
2l

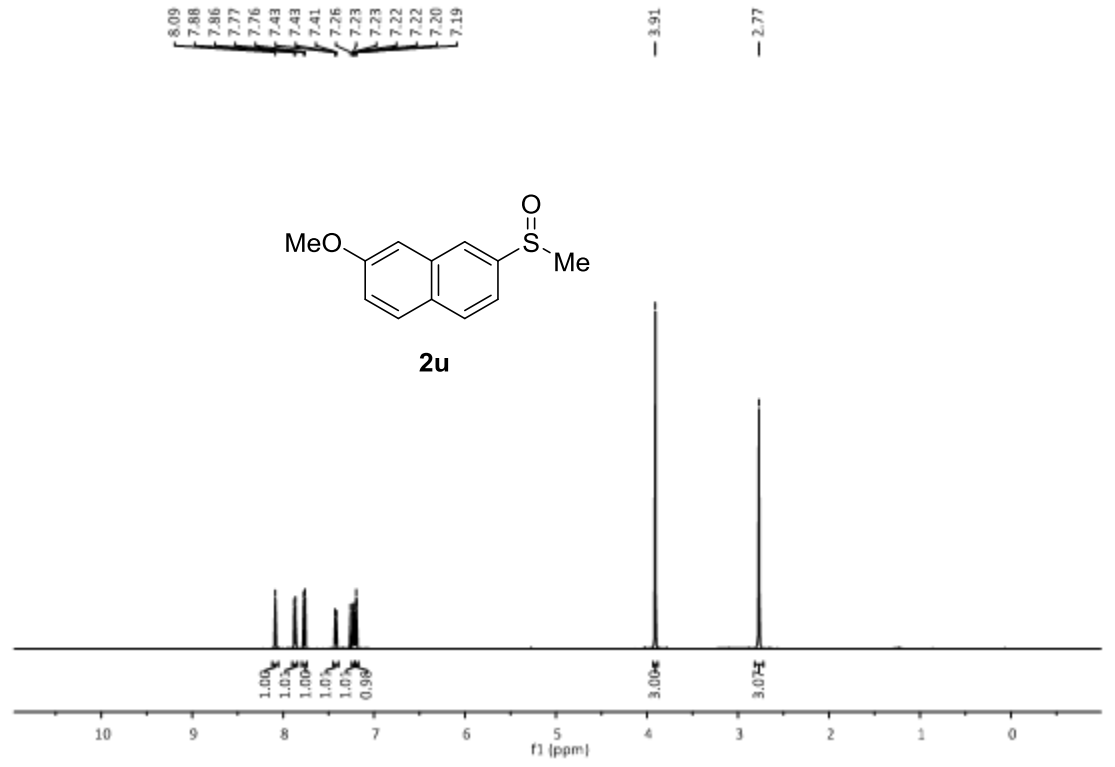

145.50
132.34
131.68
128.78
128.44
126.21
123.54
122.52
91.52
88.16
77.37
77.16
76.95
43.93
O
S
Me
Ph
2l
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

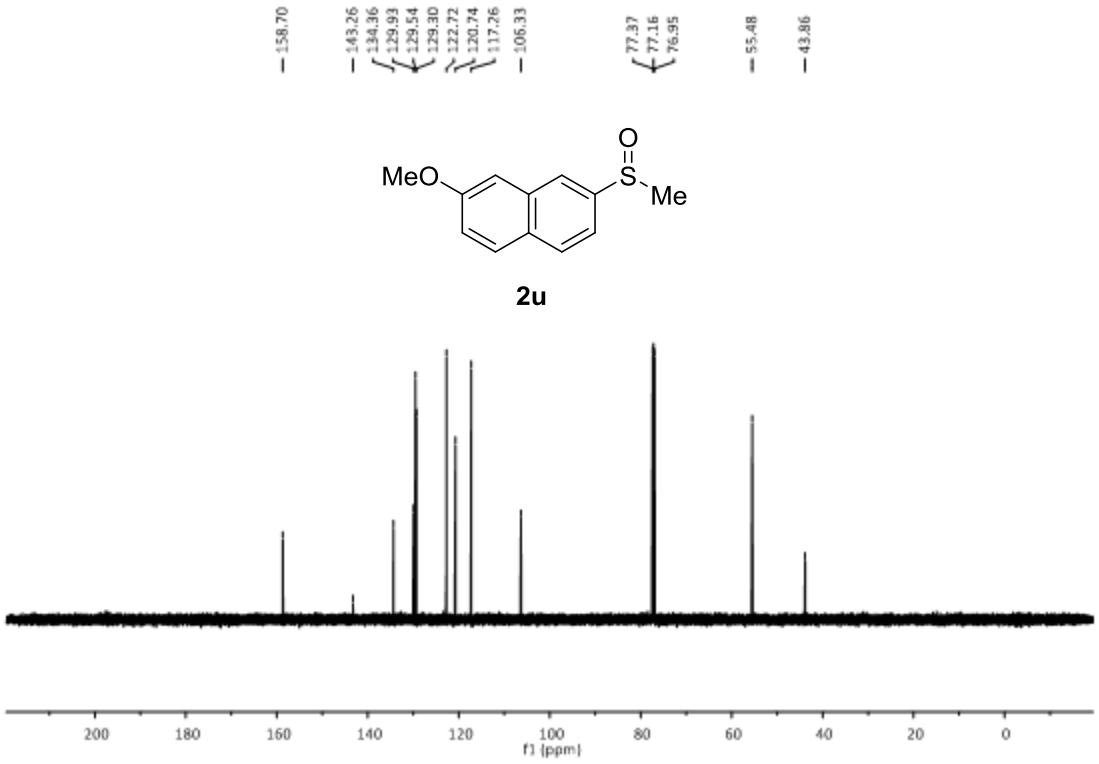

7.54
7.52
7.41
7.39
7.26
5.05
3.41
2.60
2.30
1.68
Cl
O
O
S
Me
O
2m
2.00
2.00
2.05
2.05
3.01
2.05
4.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


172.41
145.25
138.91
128.55
123.47
77.37
77.16
76.95
64.97
44.18
43.61
32.92
31.40
21.83
Cl
O
S
Me
O
O
2m
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

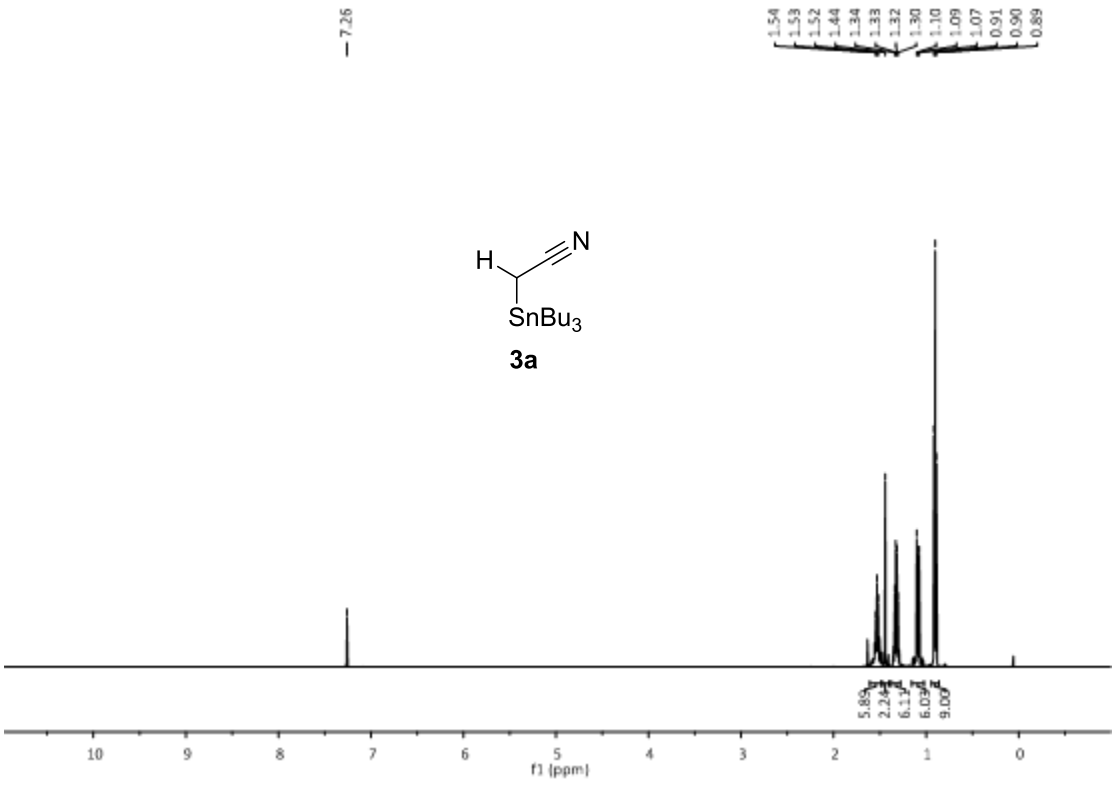

7.66
7.26
3.64
3.39
2.72
1.95
1.90
O
S
Me
O
N
2n
4.02
2.00
1.99
3.00
4.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


168.43
147.45
140.00
128.16
123.69
77.48
77.36
77.16
76.84
49.64
44.03
O
S
Me
O
N
2n
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

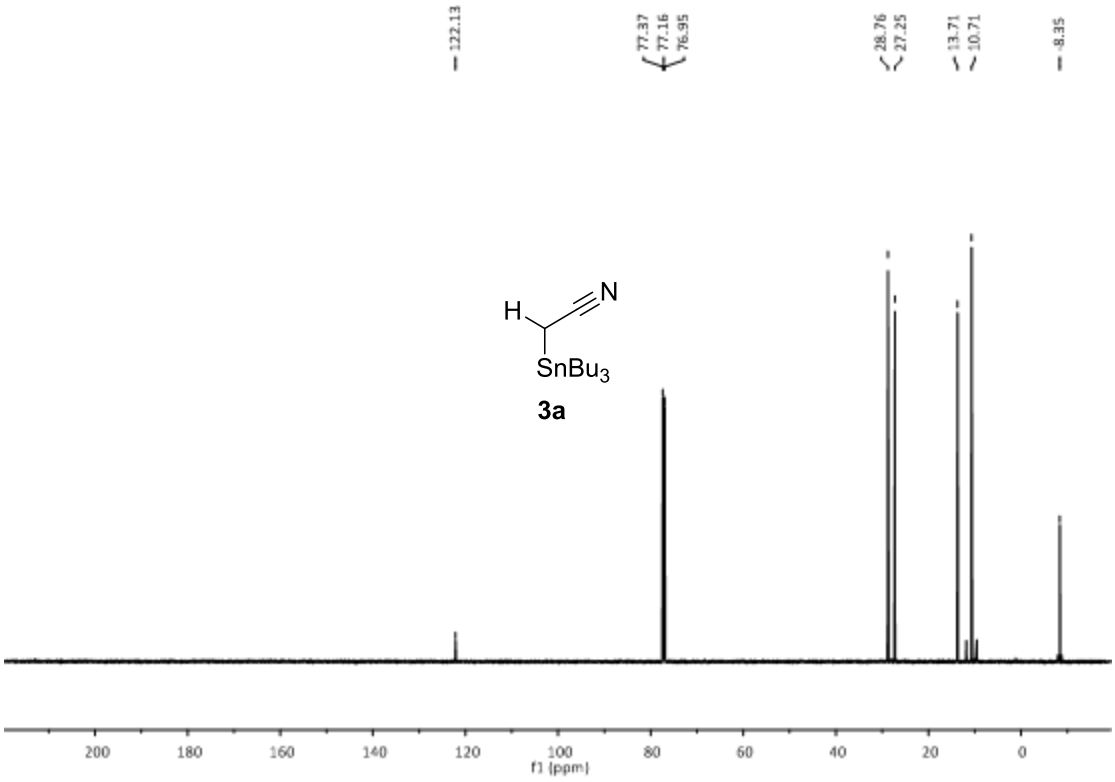

8.09
7.88
7.86
7.77
7.76
7.43
7.43
7.41
7.26
7.23
7.23
7.22
7.22
7.20
7.19
3.91
2.77
MeO
O
S
Me
2u
1.00
1.00
1.00
1.01
1.01
0.98
3.00
3.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

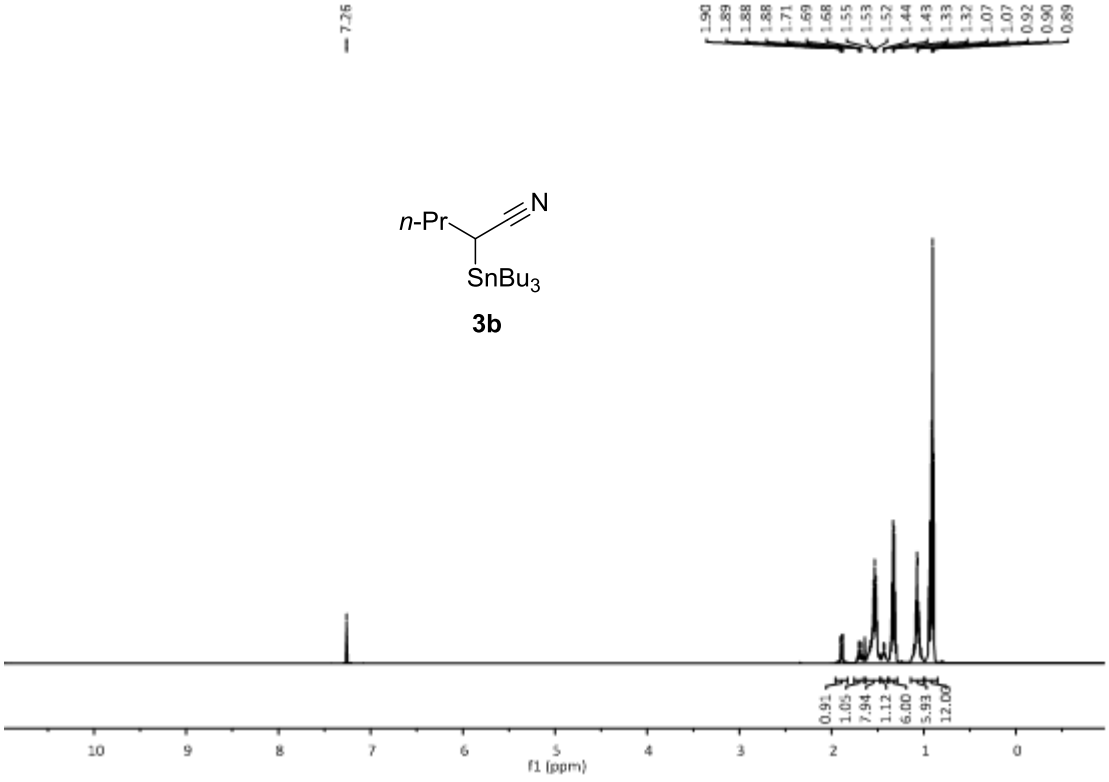

158.70
143.26
134.36
129.93
129.54
129.30
122.72
120.74
117.26
106.33
77.37
77.16
76.95
55.48
43.86
MeO
S
O
Me
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

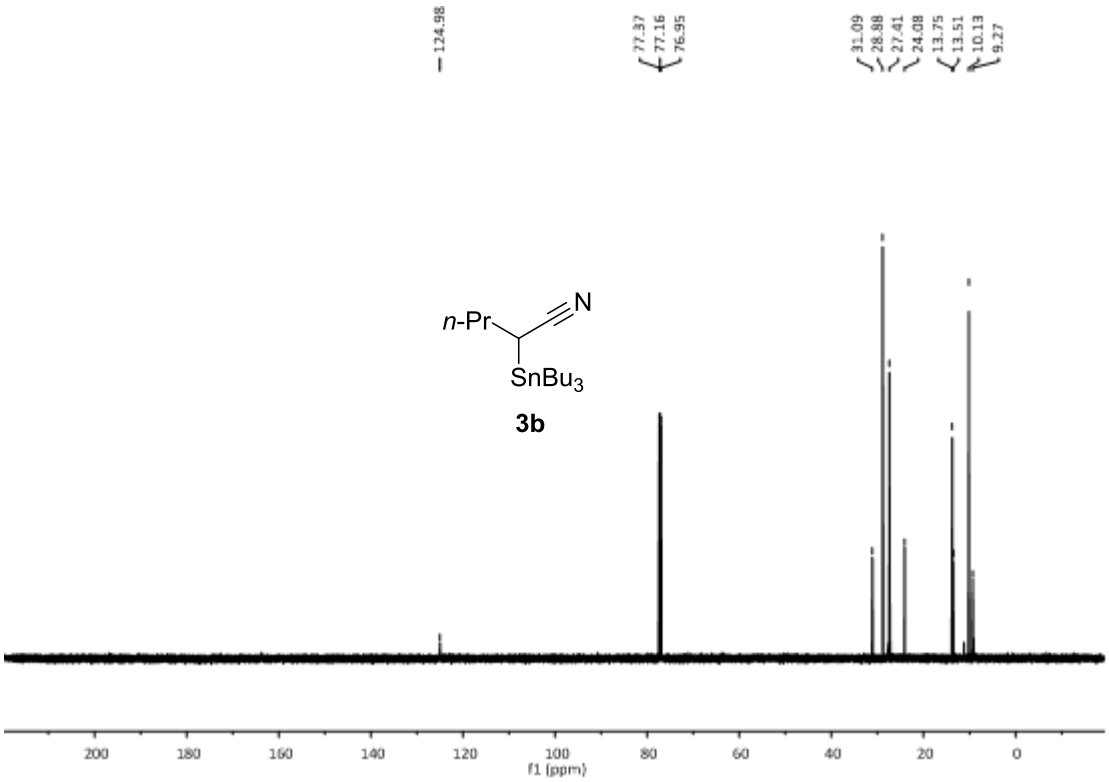
2u

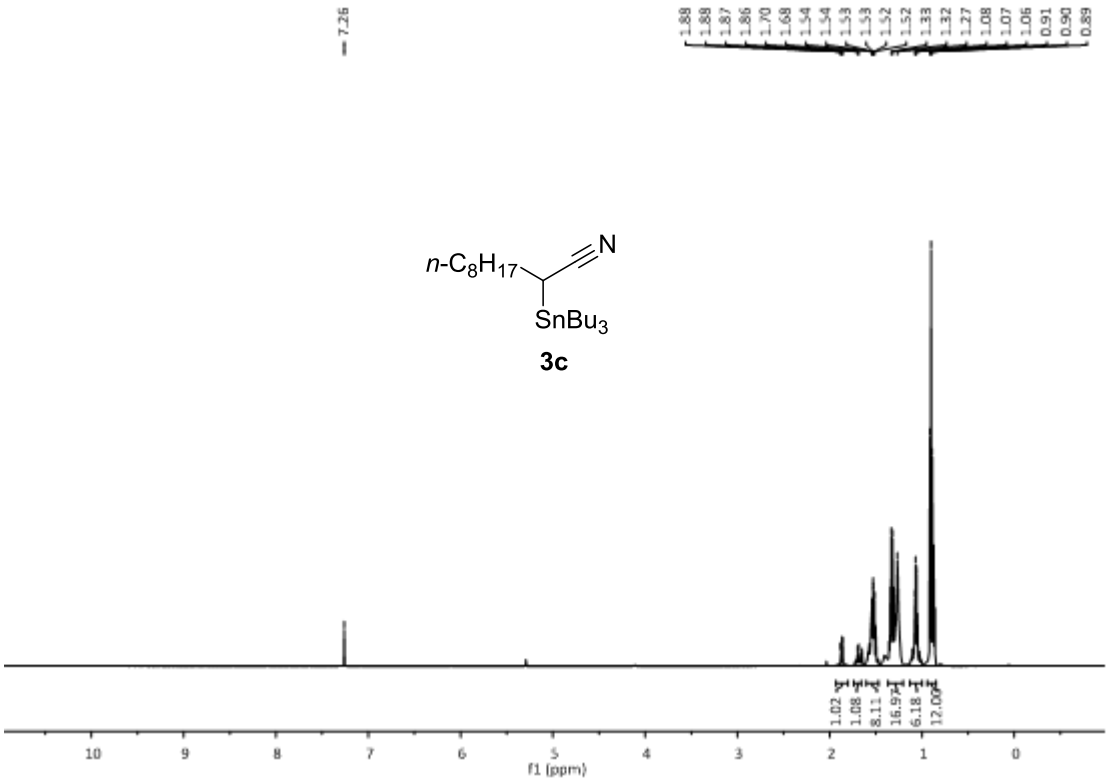

7.26
1.54
1.53
1.52
1.44
1.34
1.33
1.32
1.30
1.10
1.09
1.07
0.91
0.90
0.89
H
N
SnBu3
5.89
2.24
6.11
6.03
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

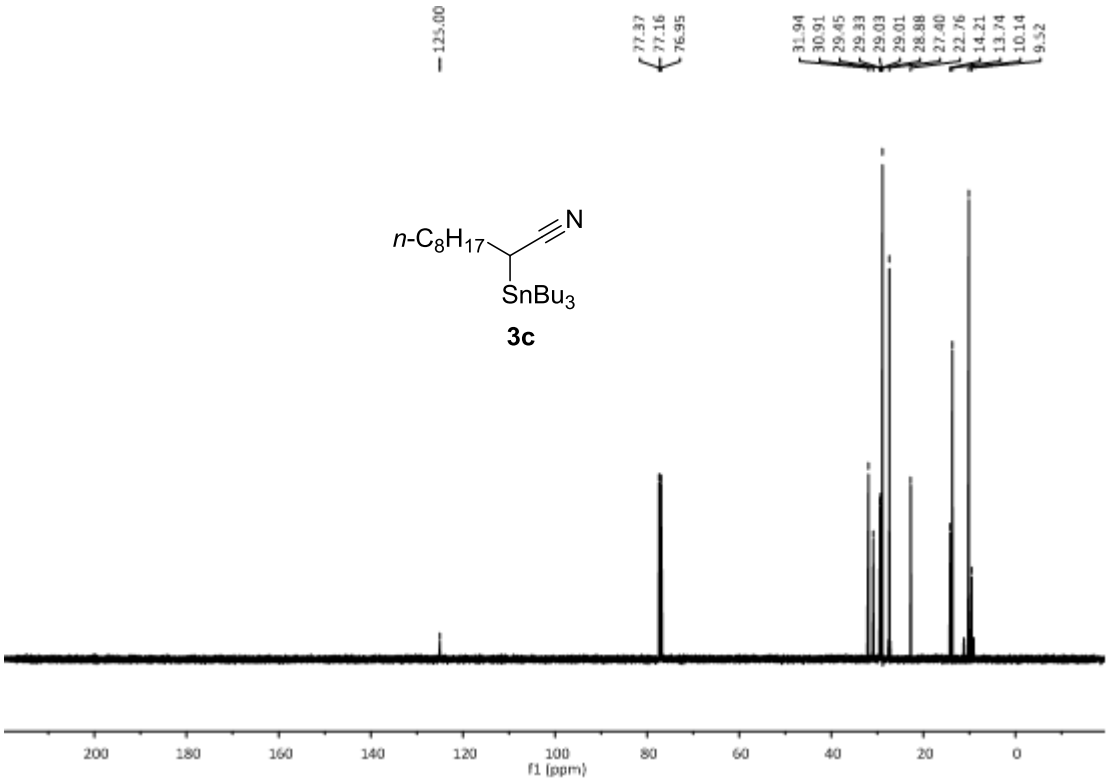
3a


122.13
77.37
77.16
76.95
28.76
27.25
13.71
10.71
8.35
H
N
SnBu3
3a
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

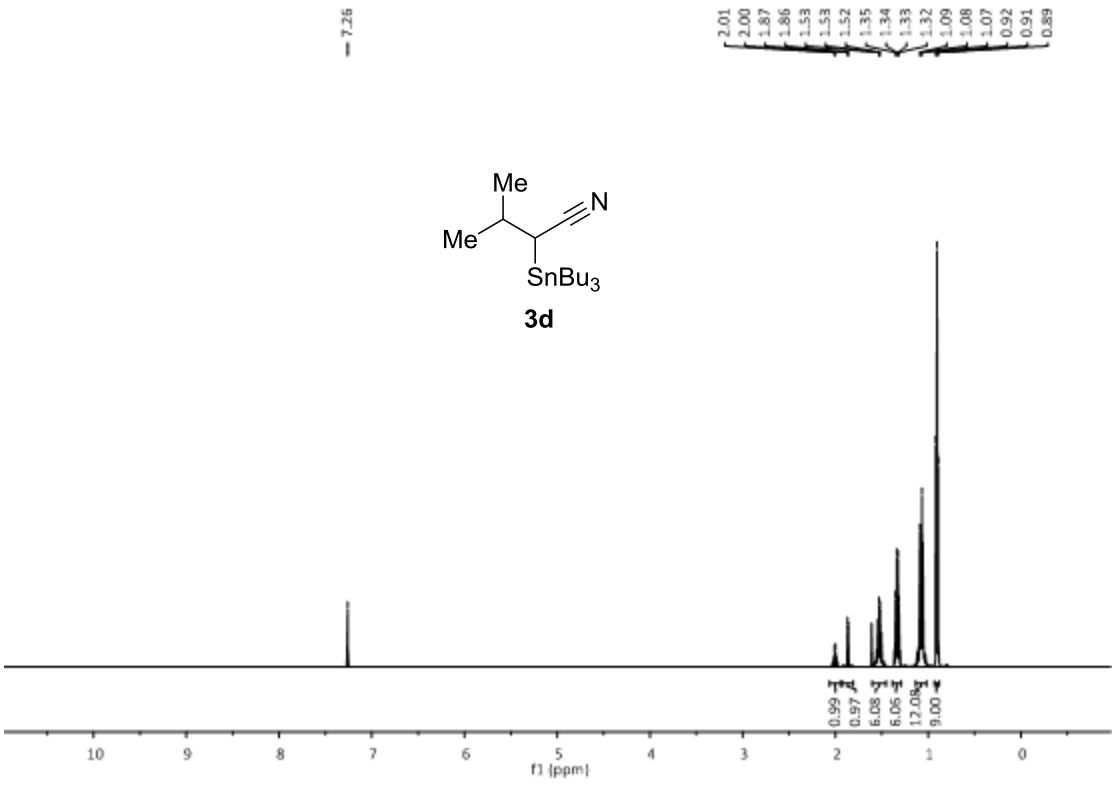

7.26
1.90
1.89
1.88
1.88
1.71
1.69
1.68
1.55
1.53
1.52
1.44
1.43
1.33
1.32
1.07
1.07
0.92
0.90
0.89
n-Pr
N
SnBu3
3b
0.91
1.05
7.94
1.12
6.00
5.93
12.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


124.98
77.37
77.16
76.95
31.09
28.88
27.41
24.08
13.75
13.51
10.13
9.27
n-Pr
N
SnBu3
3b
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

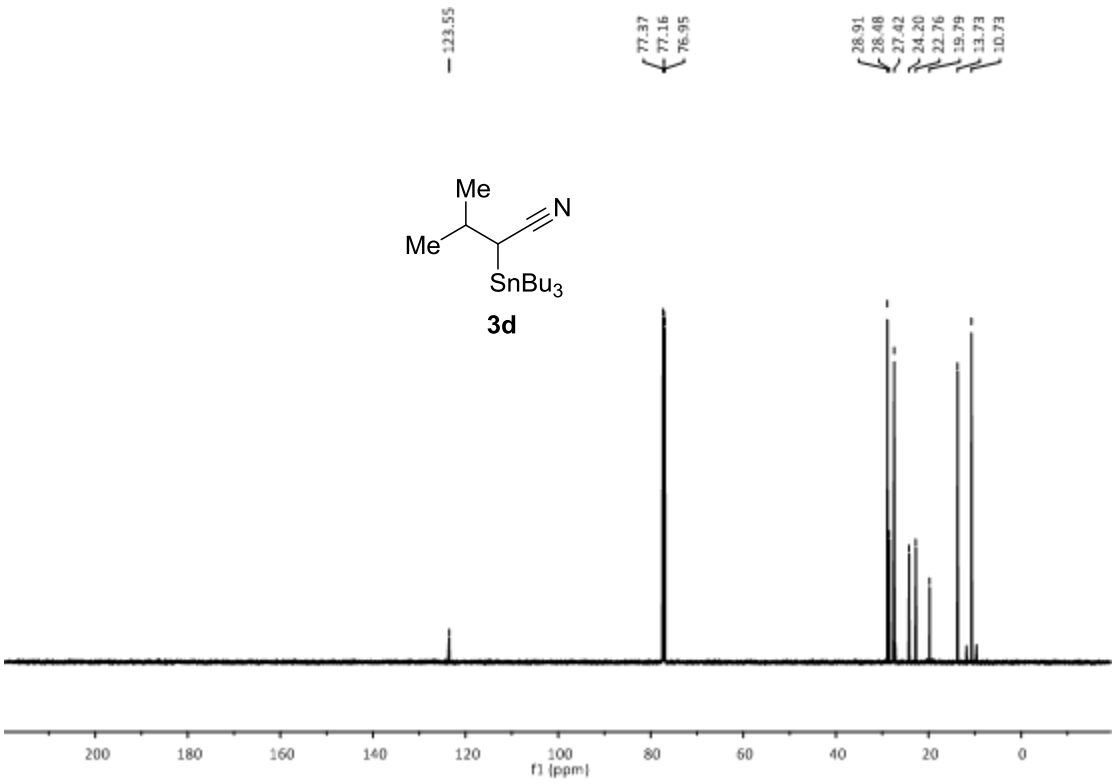

7.26
1.89
1.88
1.87
1.86
1.70
1.68
1.54
1.54
1.53
1.53
1.52
1.52
1.33
1.32
1.27
1.08
1.07
1.06
0.91
0.90
0.89
n-C8H17
N
SnBu3
3c
1.02
1.08
8.11
16.97
6.18
12.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

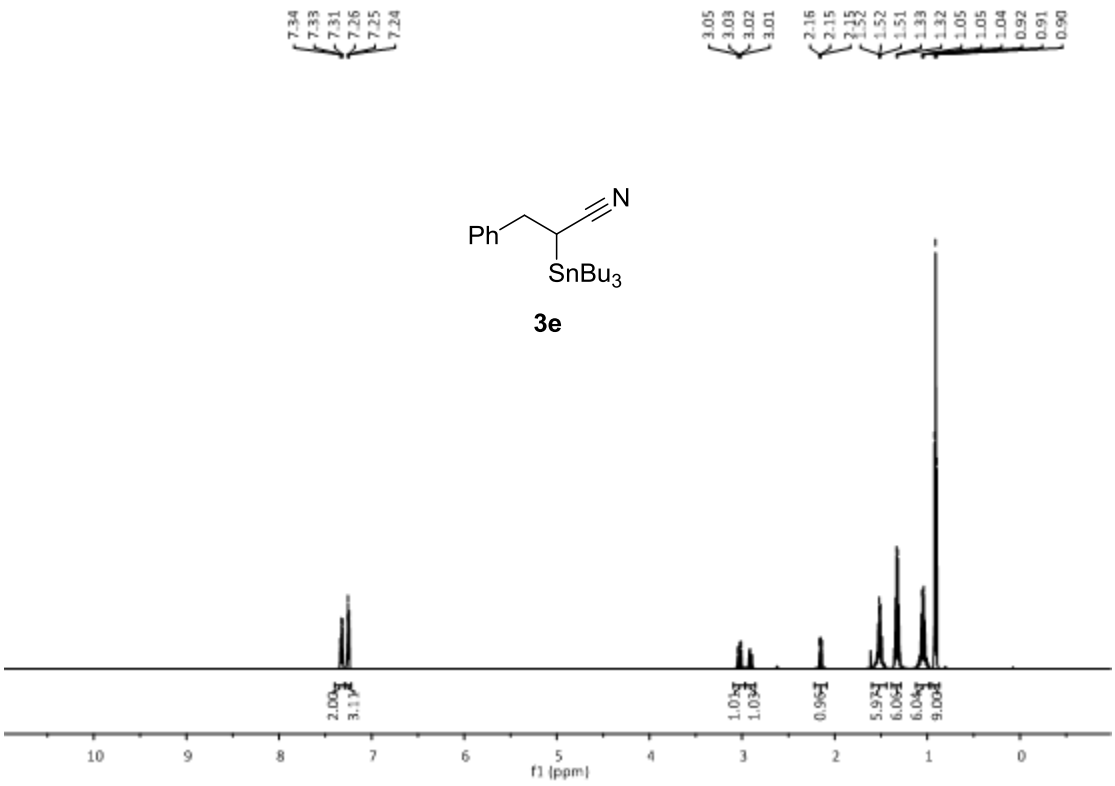

125.00
77.37
77.16
76.95
31.94
30.91
29.45
29.33
29.03
29.01
28.88
27.40
22.76
14.21
13.74
10.14
9.52
n-C8H17
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

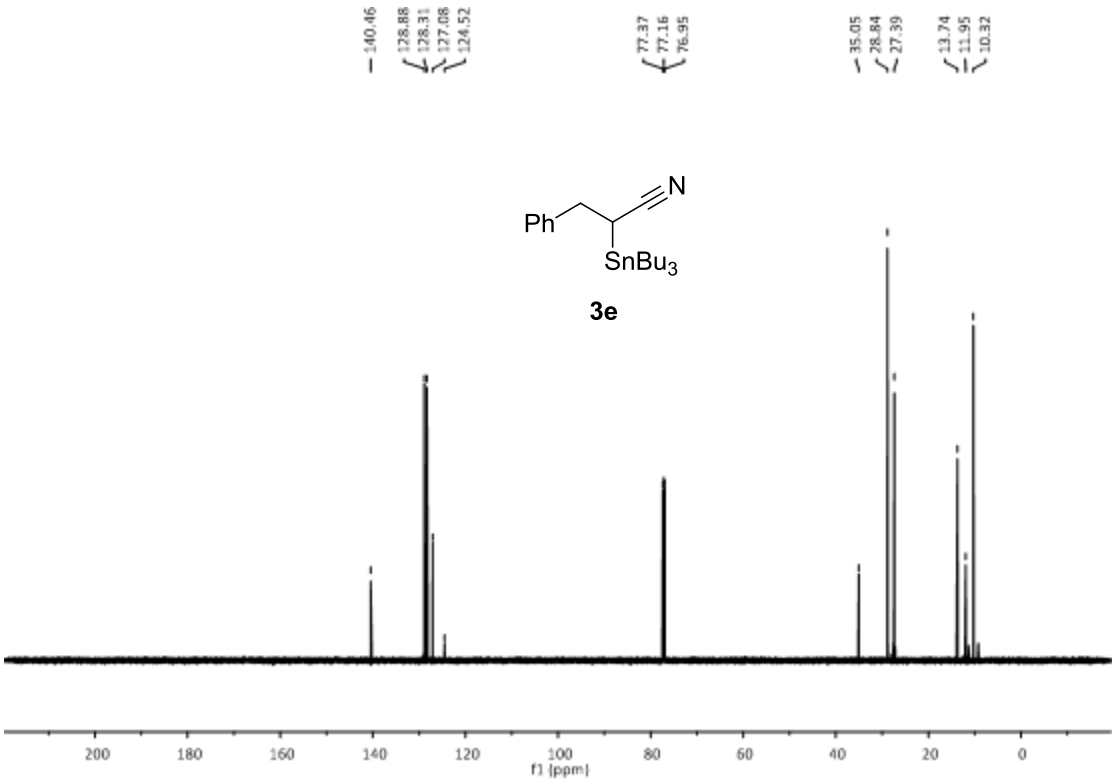
3c


7.26
2.01
2.00
1.87
1.86
1.53
1.53
1.52
1.35
1.34
1.33
1.32
1.09
1.08
1.07
0.92
0.91
0.89
Me
Me
N
SnBu3
0.99
0.97
6.08
6.06
12.08
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

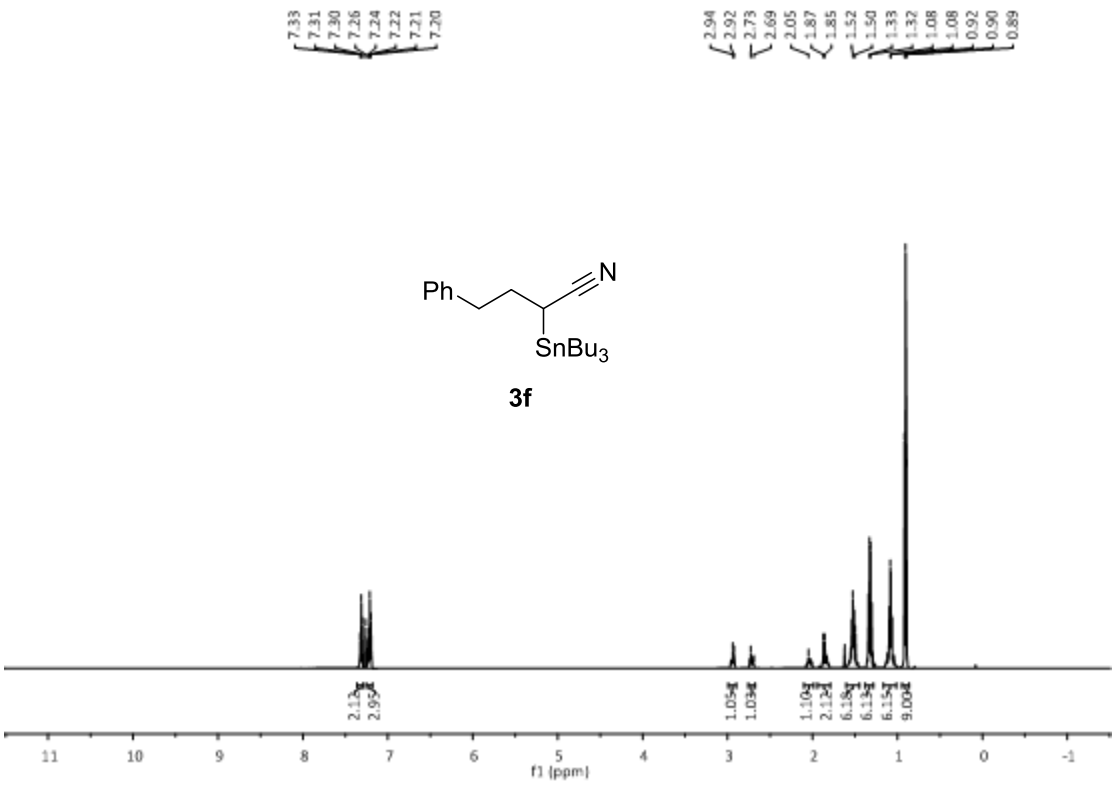
3d


123.55
77.37
77.16
76.95
28.91
28.48
27.42
24.20
22.76
19.79
13.73
10.73
Me
Me
N
SnBu3
3d
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

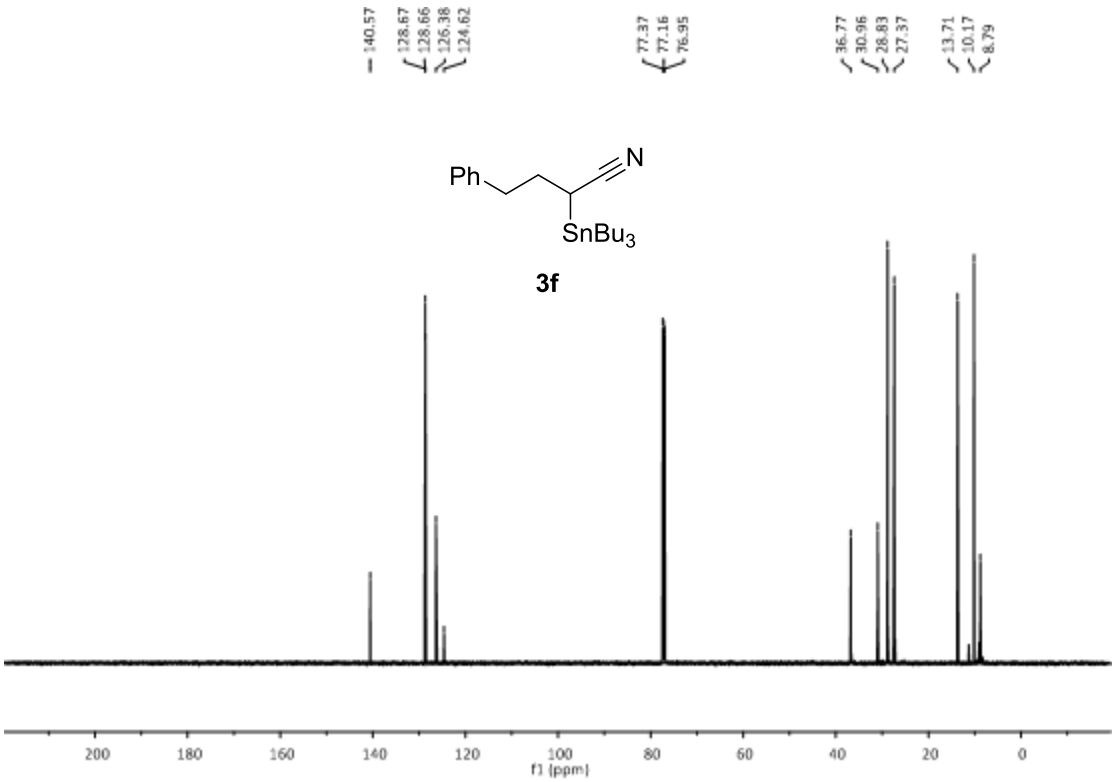

7.34
7.33
7.31
7.26
7.25
7.24
3.05
3.03
3.02
3.01
2.16
2.15
1.52
1.51
1.33
1.32
1.05
1.05
1.04
0.92
0.91
0.90
Ph
N
SnBu3
3e
2.00
3.11
1.01
1.03
0.96
5.97
6.06
6.04
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


140.46
128.88
128.31
127.08
124.52
77.37
77.16
76.95
35.05
28.84
27.39
13.74
11.95
10.32
N
Ph
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

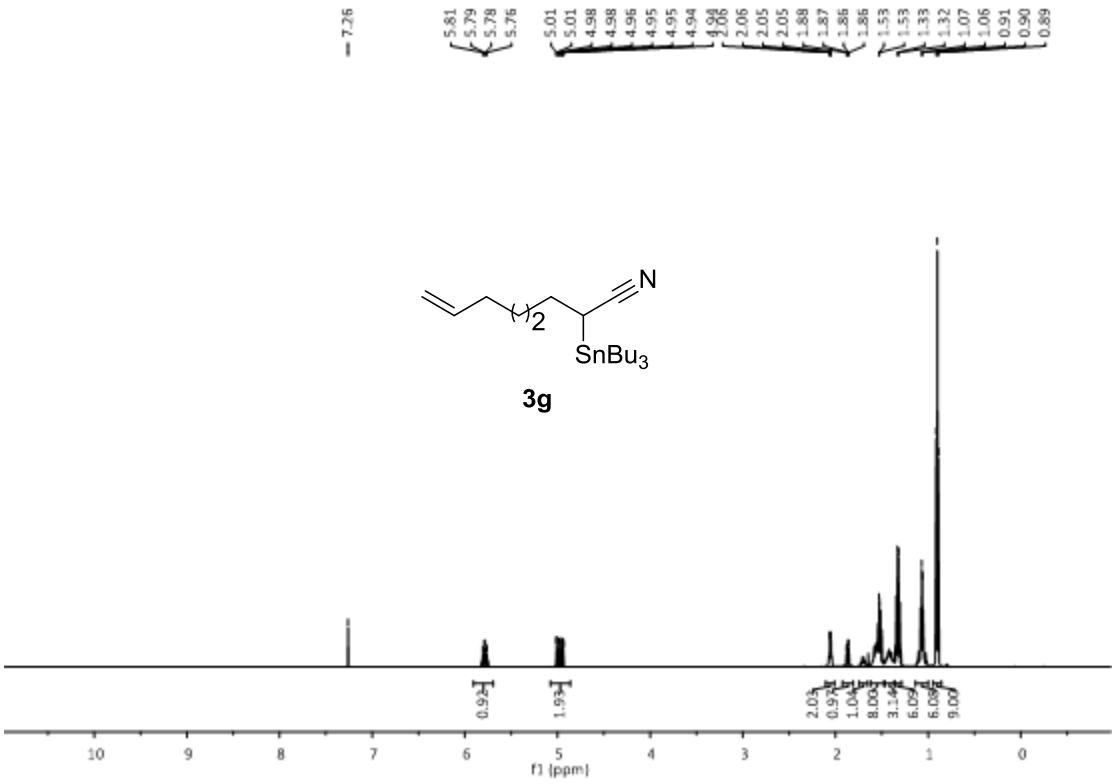
3e


7.33
7.31
7.30
7.26
7.24
7.22
7.21
7.20
2.94
2.92
2.73
2.69
2.05
1.87
1.85
1.52
1.50
1.33
1.32
1.08
1.08
0.92
0.90
0.89
N
Ph
SnBu3
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

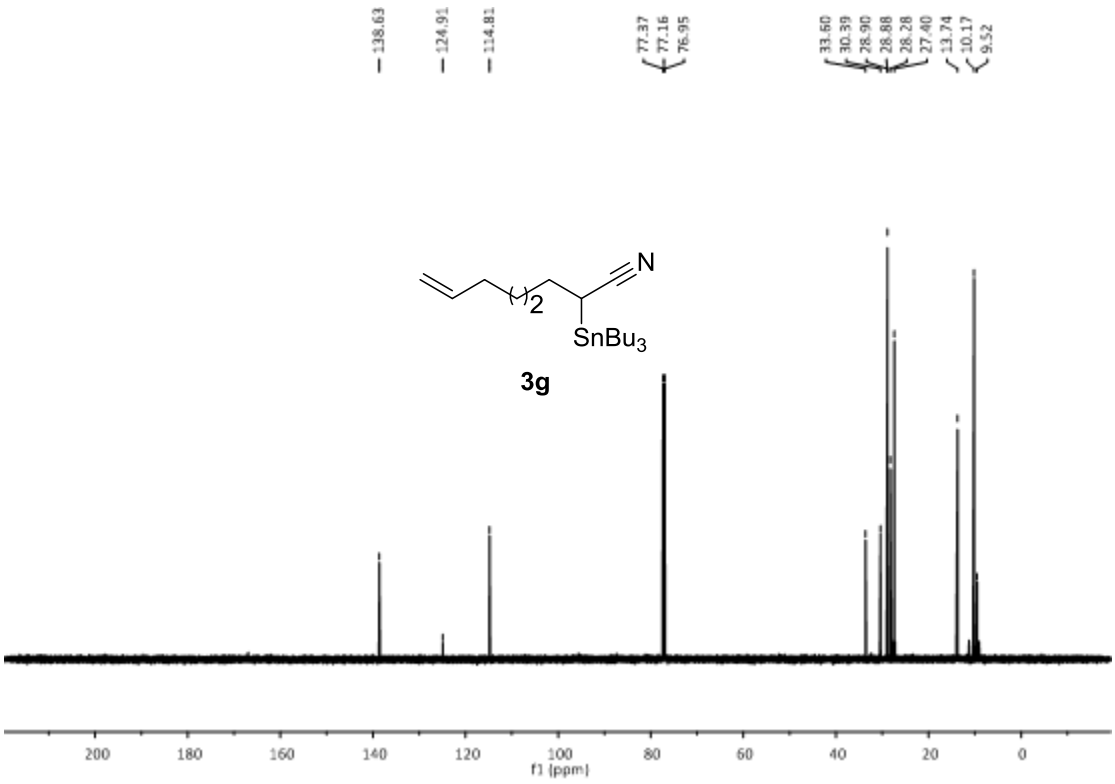
3f


140.57
128.67
128.66
126.38
124.62
77.37
77.16
76.95
36.77
30.96
28.83
27.37
13.71
10.17
8.79
Ph
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

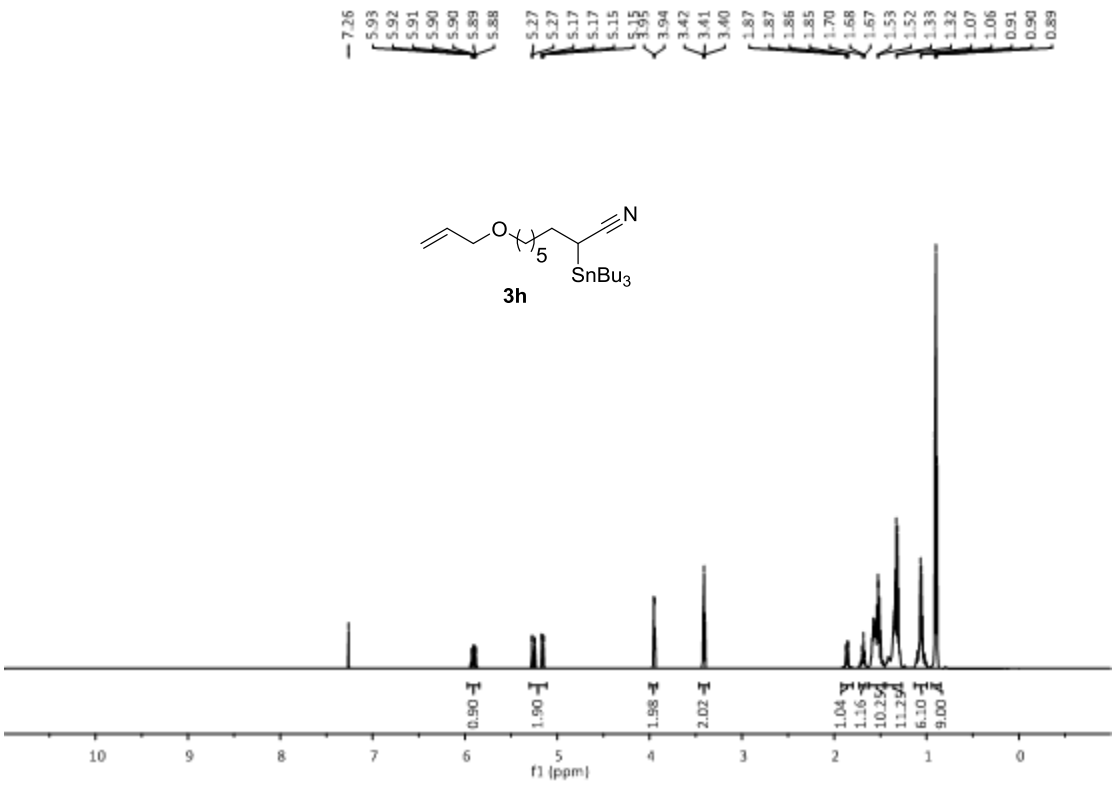
3f


7.26
5.81
5.79
5.78
5.76
5.01
5.01
4.98
4.98
4.96
4.95
4.95
4.94
4.94
2.06
2.05
2.05
1.88
1.87
1.86
1.86
1.53
1.53
1.33
1.32
1.07
1.06
0.91
0.90
0.89
N
2
SnBu3
0.92
1.93
2.03
0.97
1.04
8.00
3.14
6.09
6.08
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

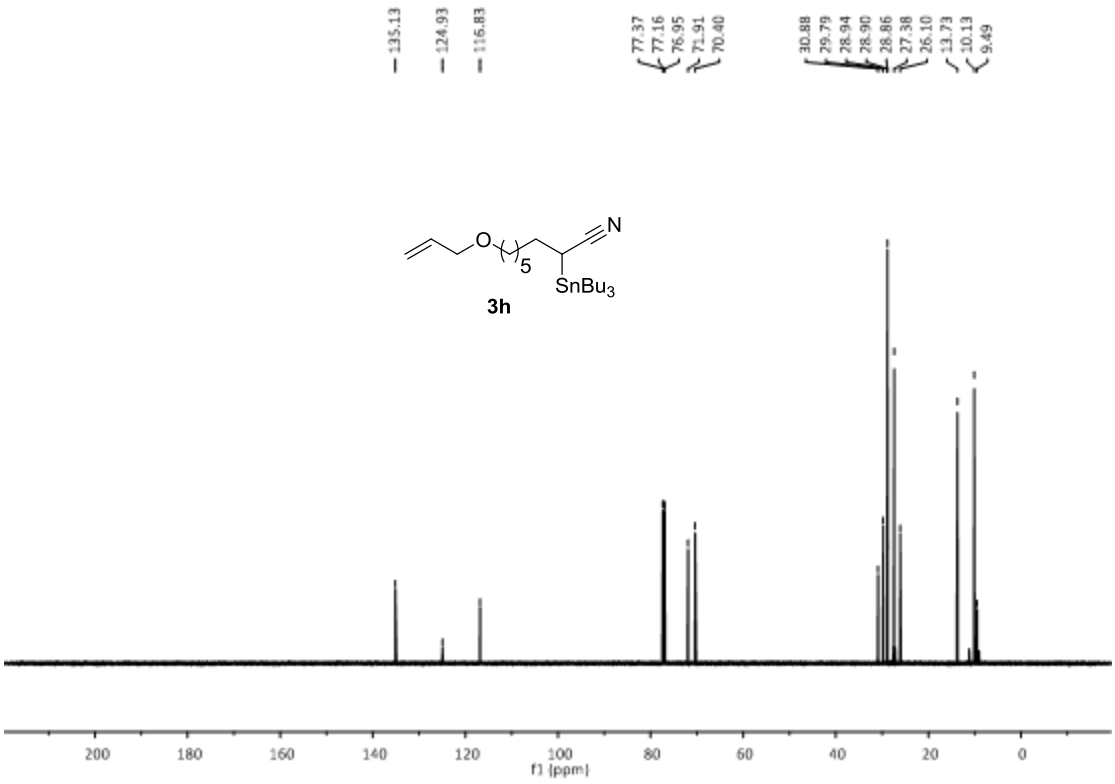
3g

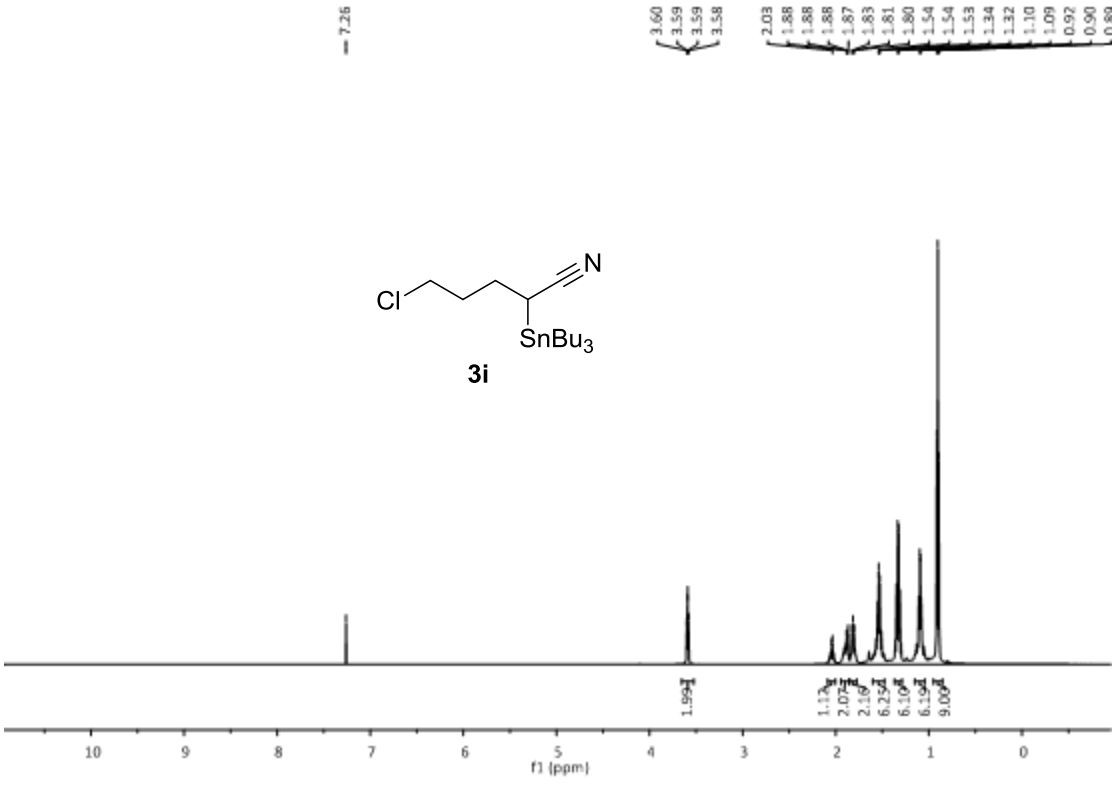

138.63
124.91
114.81
77.37
77.16
76.95
33.60
30.39
28.90
28.88
28.28
27.40
13.74
10.17
9.52
N
2
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

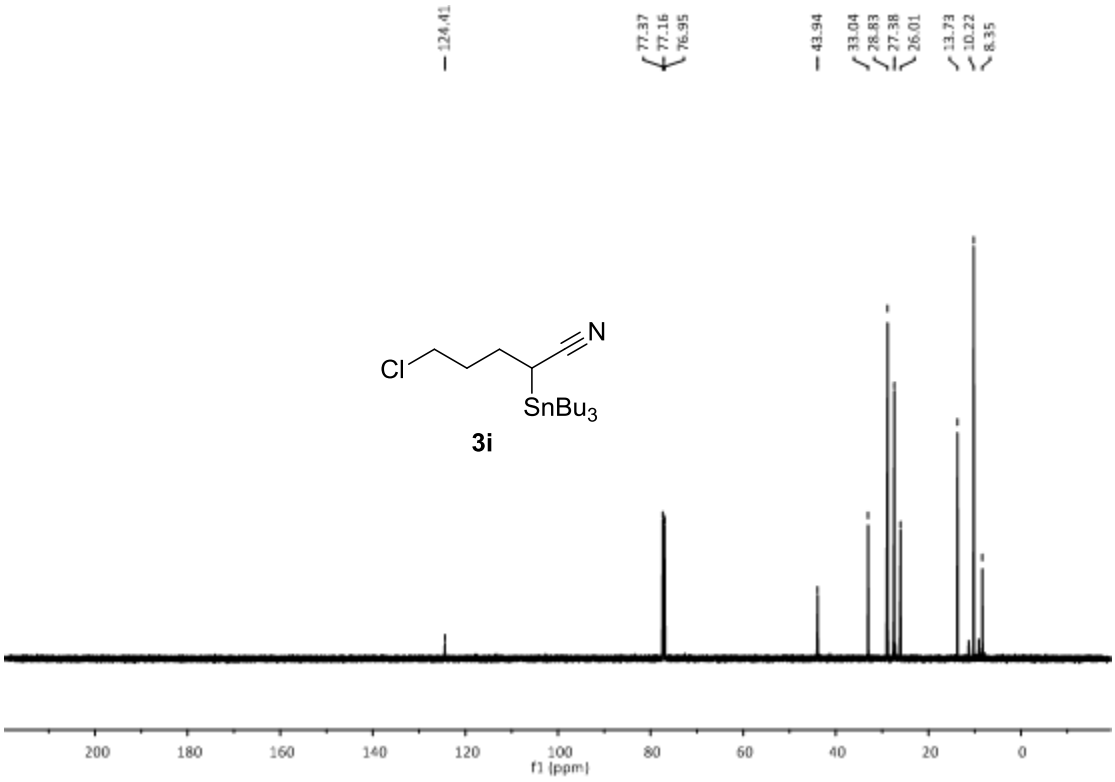
3g


7.26
5.93
5.92
5.91
5.90
5.90
5.89
5.88
5.27
5.27
5.17
5.17
5.15
5.15
3.95
3.94
3.42
3.41
3.40
1.87
1.87
1.86
1.85
1.70
1.68
1.67
1.53
1.52
1.33
1.32
1.07
1.06
0.91
0.90
0.89
O
5
N
SnBu3
0.90
1.90
1.98
2.02
1.04
1.16
10.25
11.29
6.10
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

3h


135.13
124.93
116.83
77.37
77.16
76.95
71.91
70.40
30.88
29.79
28.94
28.90
28.86
27.38
26.10
13.73
10.13
9.49
O
5
N
SnBu3
3h
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.26
3.60
3.59
3.59
3.58
2.03
1.88
1.88
1.88
1.87
1.83
1.81
1.80
1.54
1.54
1.53
1.34
1.32
1.10
1.09
0.92
0.90
Cl
N
SnBu3
3i
1.99
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


124.41
77.37
77.16
76.95
43.94
33.04
28.83
27.38
26.01
13.73
10.22
8.35
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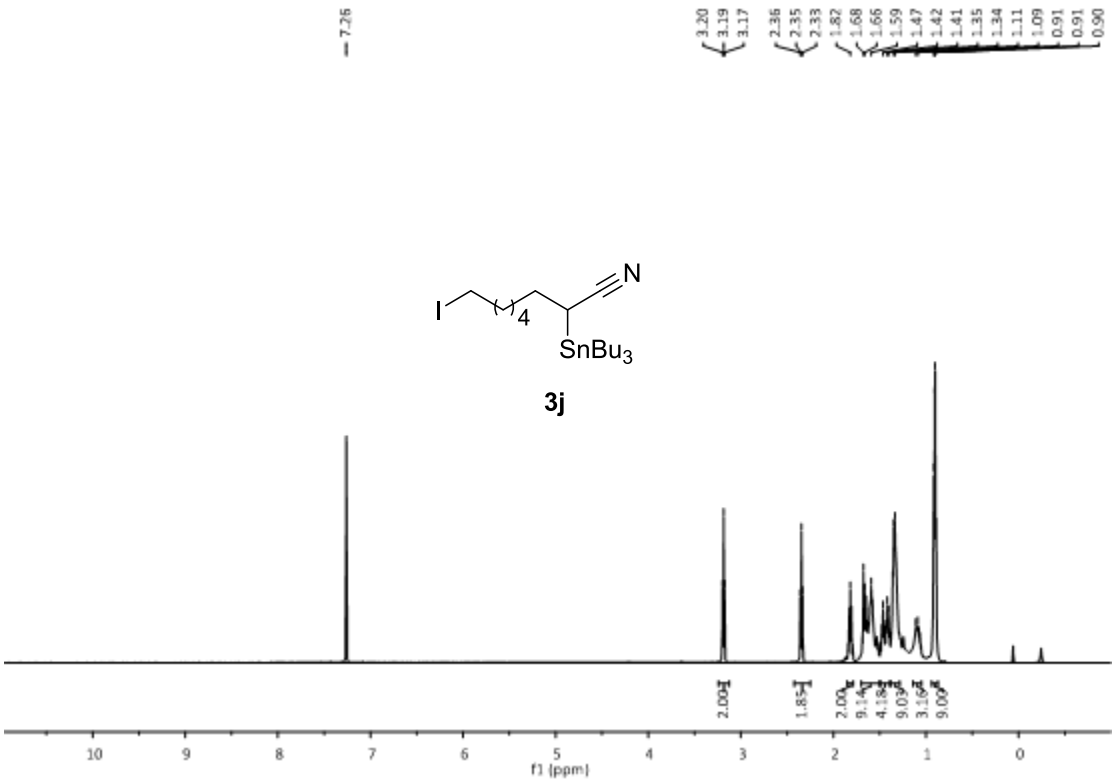
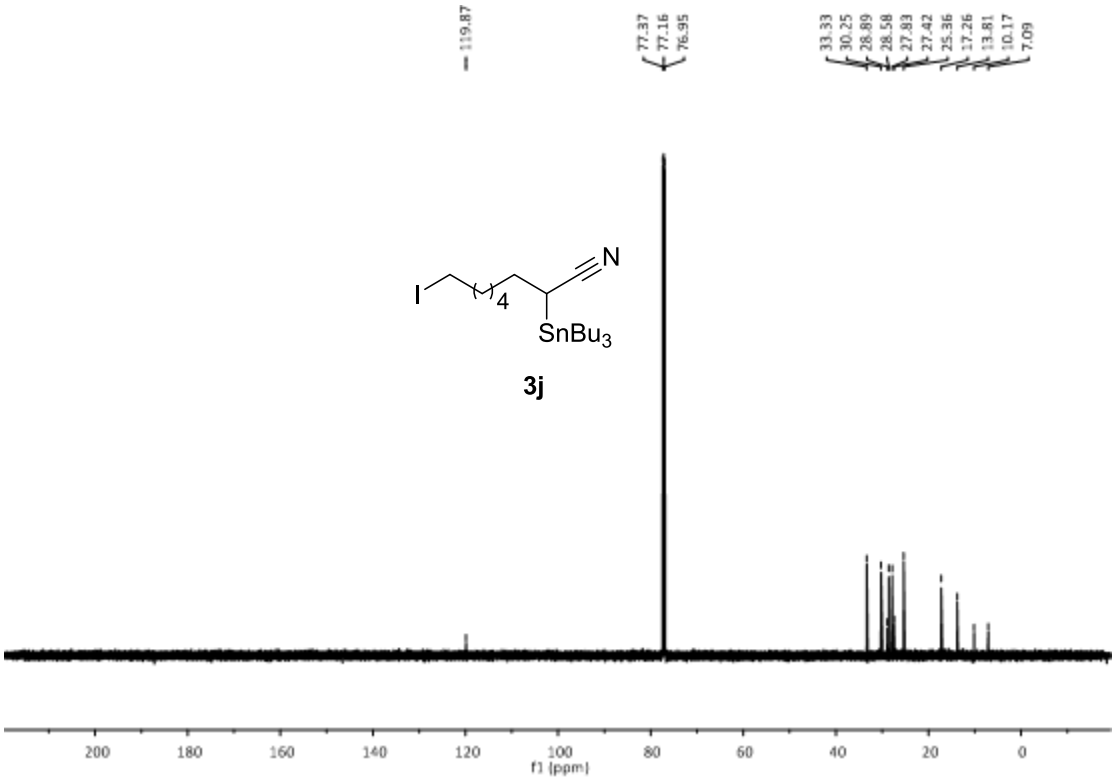
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

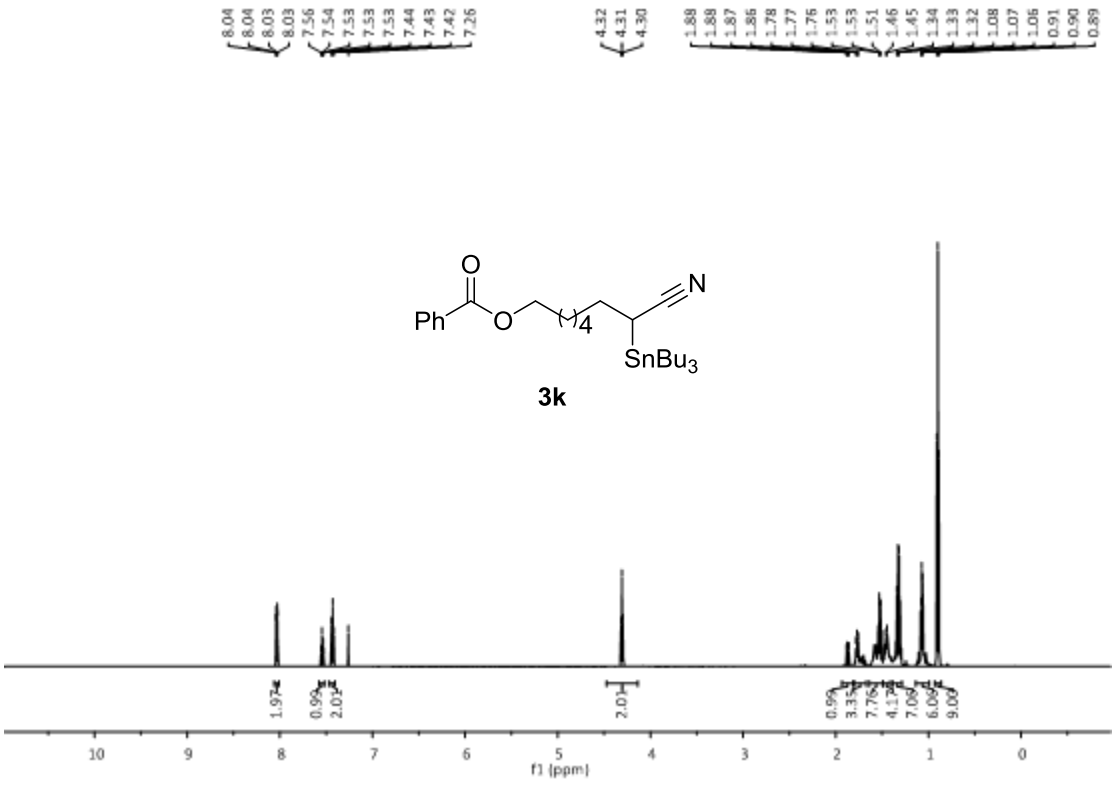
3i


7.26
3.20
3.19
3.17
2.36
2.35
2.33
1.82
1.68
1.66
1.59
1.47
1.42
1.41
1.35
1.34
1.11
1.09
0.91
0.91
0.90
I
4
N
SnBu3
2.00
1.85
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

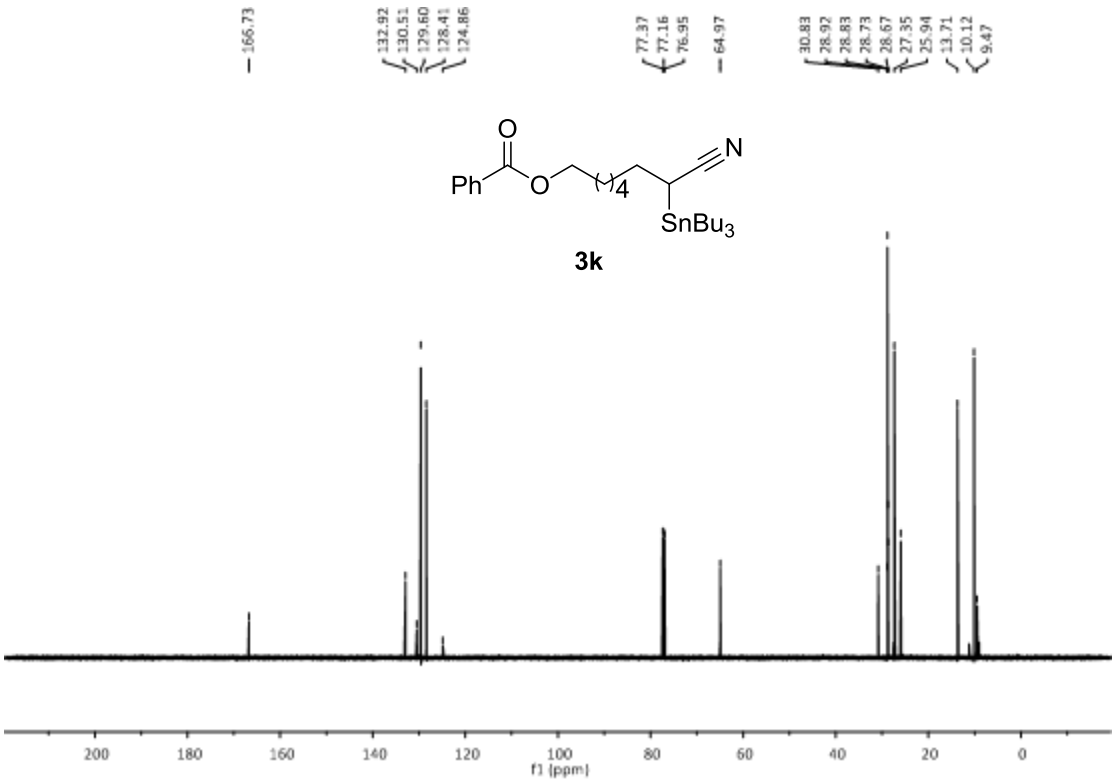
3j


119.87
77.37
77.16
76.95
33.33
30.25
28.89
28.58
27.83
27.42
25.36
17.26
13.81
10.17
7.09
I
4
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

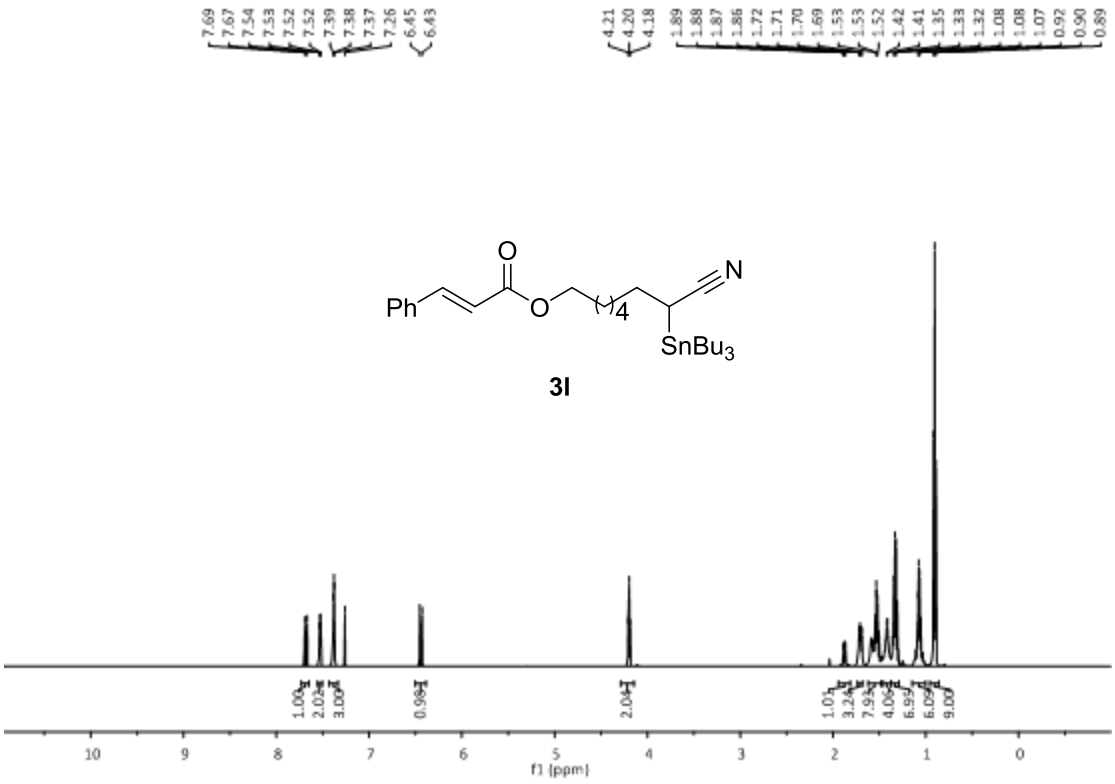
3j


8.04
8.04
8.03
8.03
7.56
7.54
7.53
7.53
7.53
7.44
7.43
7.42
7.26
4.32
4.31
4.30
1.88
1.88
1.87
1.86
1.78
1.77
1.76
1.53
1.53
1.51
1.46
1.45
1.34
1.33
1.32
1.08
1.07
1.06
0.91
0.90
0.89
O
Ph
O
4
N
SnBu3
1.97
0.99
2.02
2.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

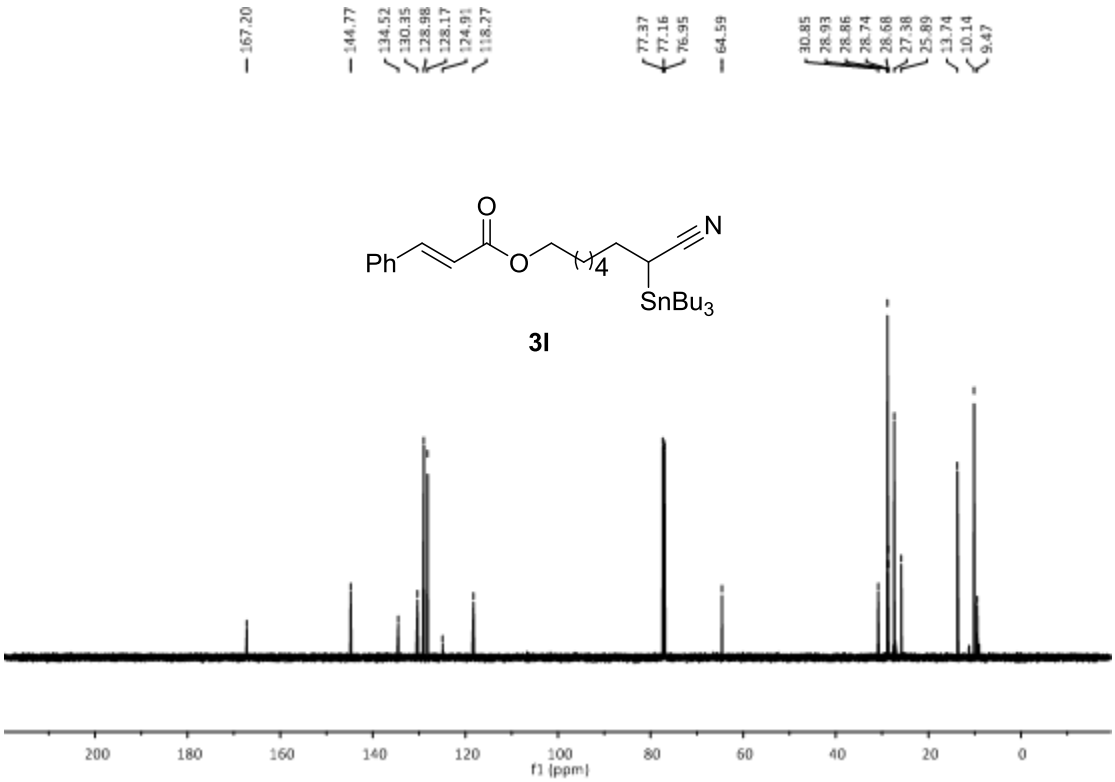
3k


166.73
132.92
130.51
129.60
128.41
124.86
77.37
77.16
76.95
64.97
30.83
28.92
28.83
28.73
28.67
27.35
25.94
13.71
10.12
9.47
O
Ph
O
4
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

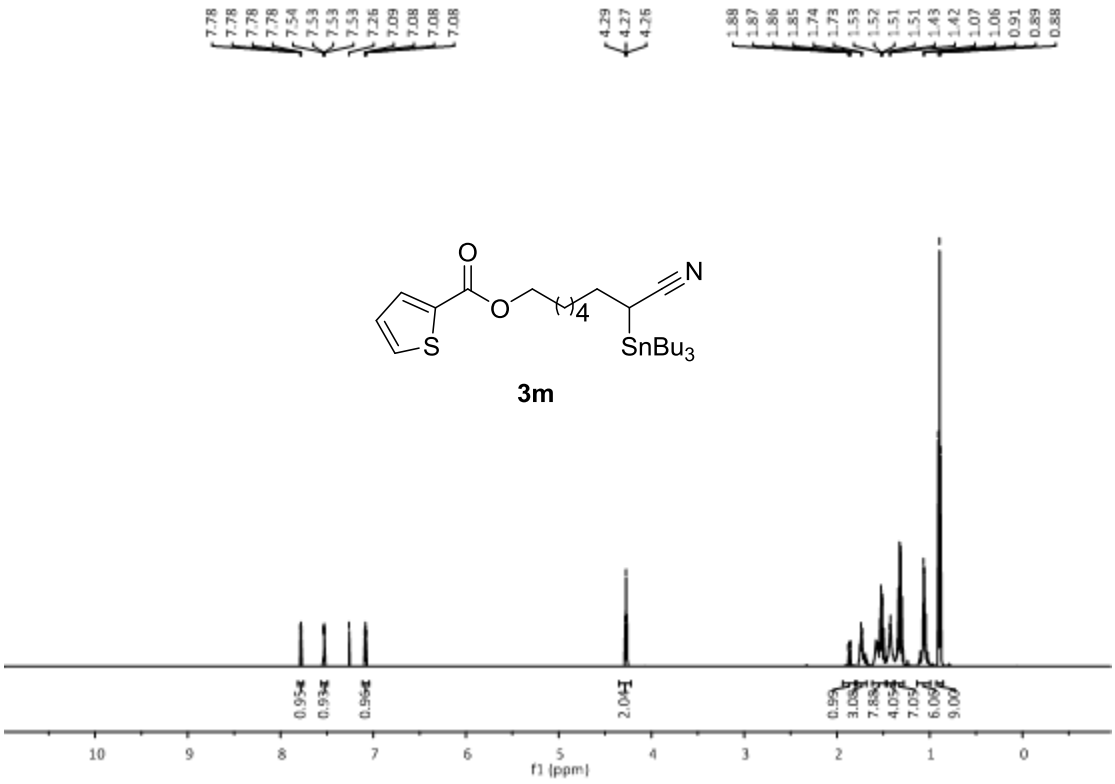
3k


7.69
7.67
7.54
7.53
7.52
7.52
7.39
7.38
7.37
7.26
6.45
6.43
4.21
4.20
4.18
1.89
1.88
1.87
1.86
1.72
1.71
1.70
1.69
1.53
1.53
1.52
1.42
1.41
1.35
1.33
1.32
1.08
1.08
1.07
0.92
0.90
0.89
O
Ph
O
4
N
SnBu3
1.00
2.02
3.00
0.99
2.04
1.01
3.24
7.93
4.04
6.99
6.09
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

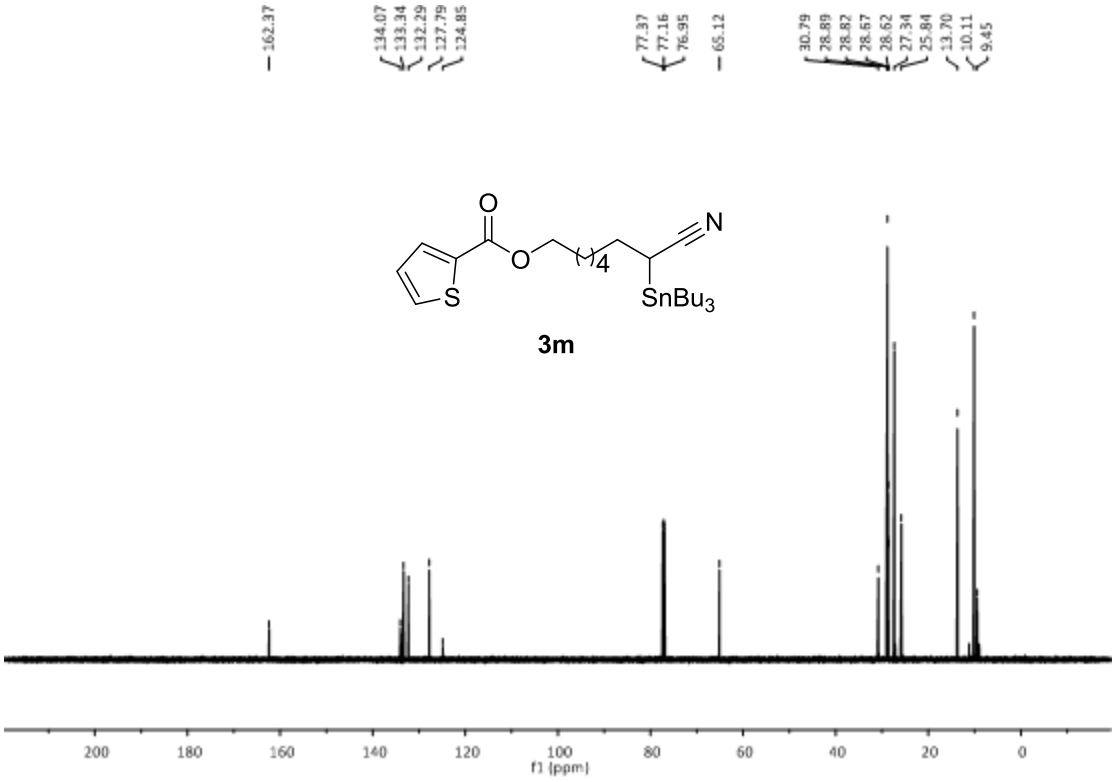
3l


167.20
144.77
134.52
130.35
128.98
128.17
124.91
118.27
77.37
77.16
76.95
64.59
30.85
28.93
28.86
28.74
28.68
27.38
25.89
13.74
10.14
9.47
O
Ph
O
4
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

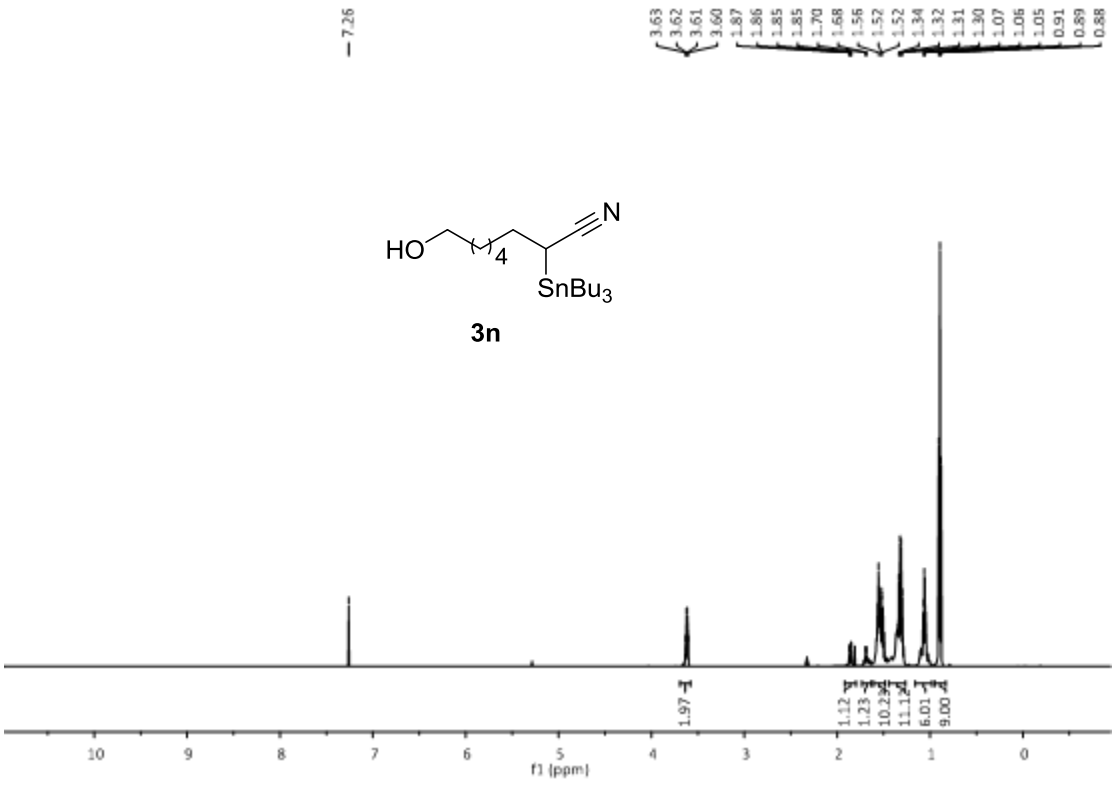
3l


7.78
7.78
7.78
7.78
7.54
7.53
7.53
7.53
7.53
7.26
7.09
7.08
7.08
7.08
4.29
4.27
4.26
1.88
1.87
1.86
1.85
1.74
1.73
1.53
1.52
1.51
1.51
1.43
1.42
1.07
1.06
0.91
0.89
0.88
O
O
4
N
S
SnBu3
0.95
0.93
0.89
2.04
0.99
3.05
7.88
4.05
7.05
6.09
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

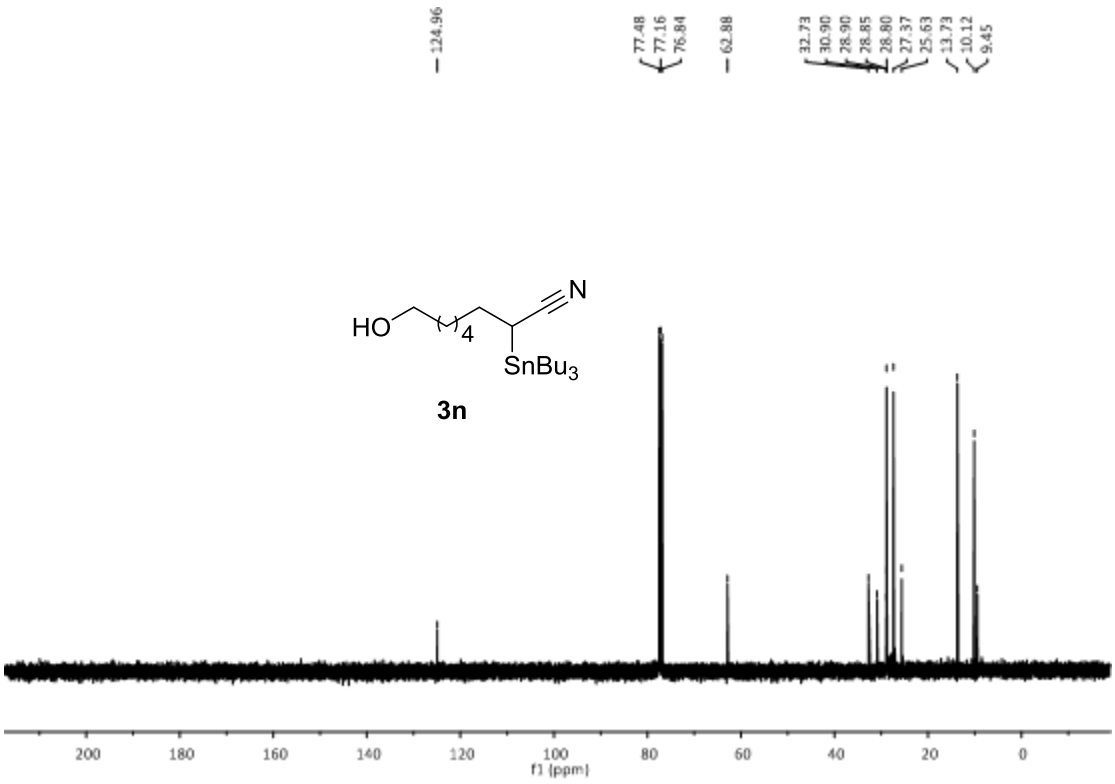
3m


162.37
134.07
133.34
132.29
127.79
124.85
77.37
77.16
76.95
65.12
30.79
28.89
28.82
28.67
28.62
27.34
25.84
13.70
10.11
9.45
O
O
S
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

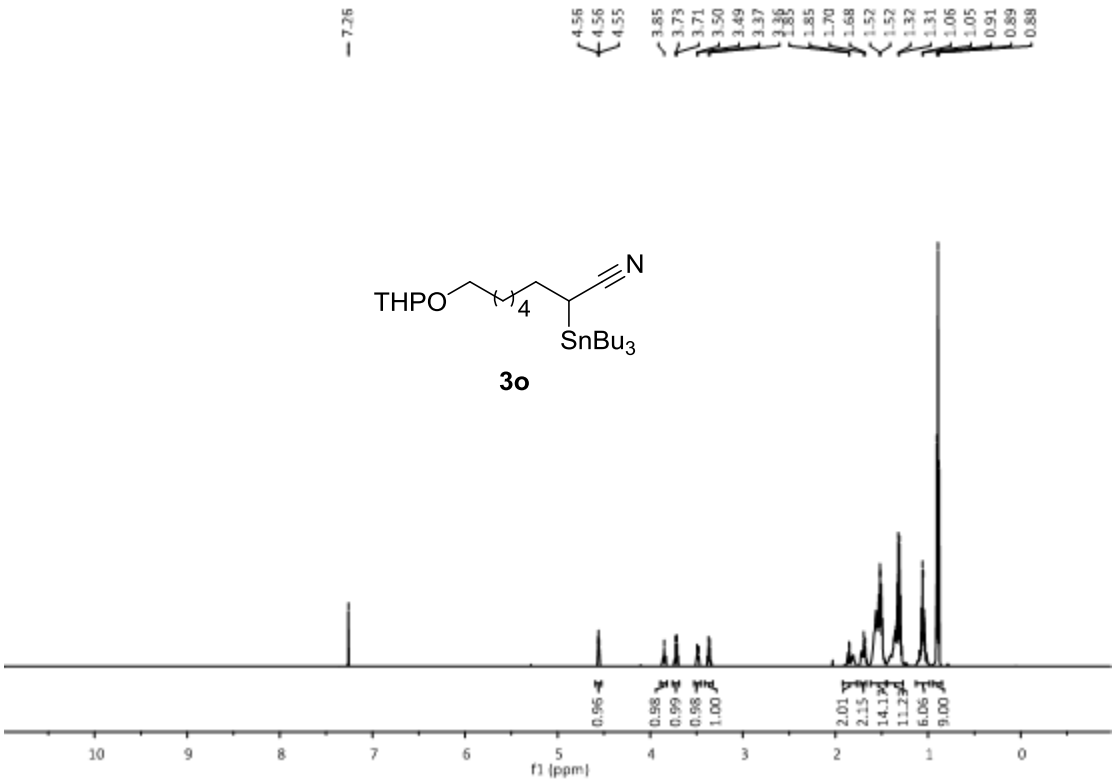
3m


7.26
3.63
3.62
3.61
3.60
1.87
1.86
1.85
1.85
1.70
1.68
1.56
1.52
1.52
1.34
1.32
1.31
1.30
1.07
1.06
1.05
0.91
0.89
0.88
HO
N
SnBu3
1.97
1.12
1.23
10.29
11.12
6.01
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

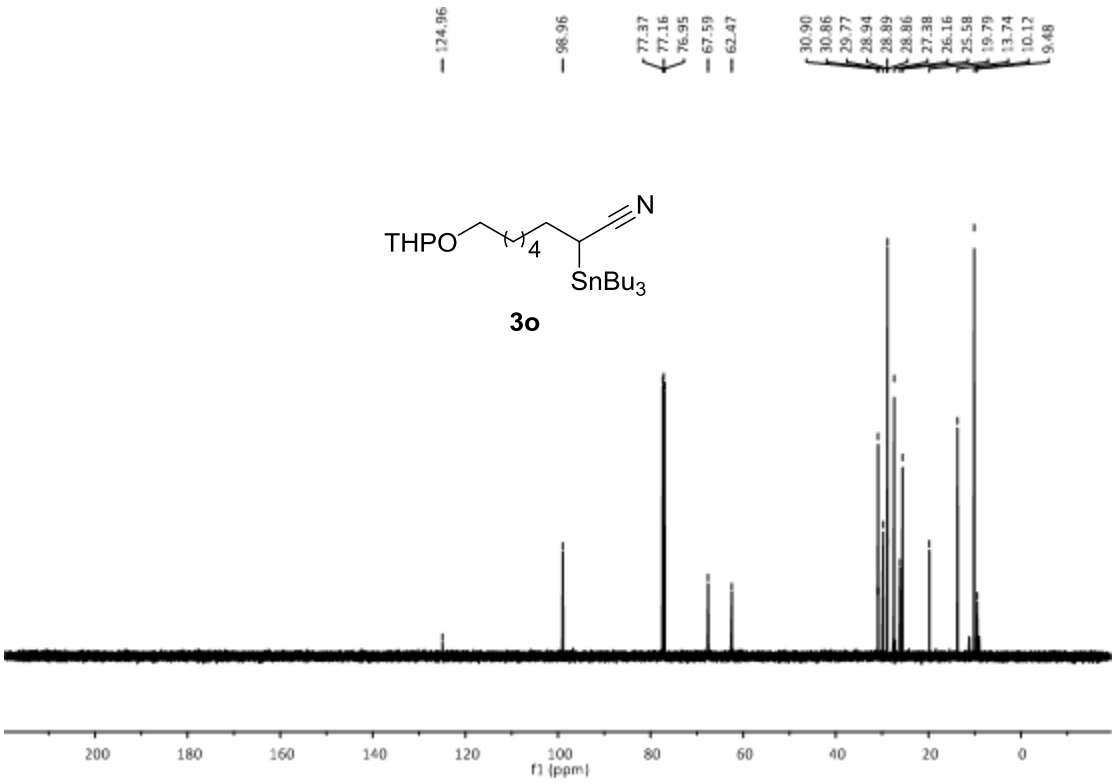
3n


124.96
77.48
77.16
76.84
62.88
32.73
30.90
28.90
28.85
28.80
27.37
25.63
13.73
10.12
9.45
HO
4
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

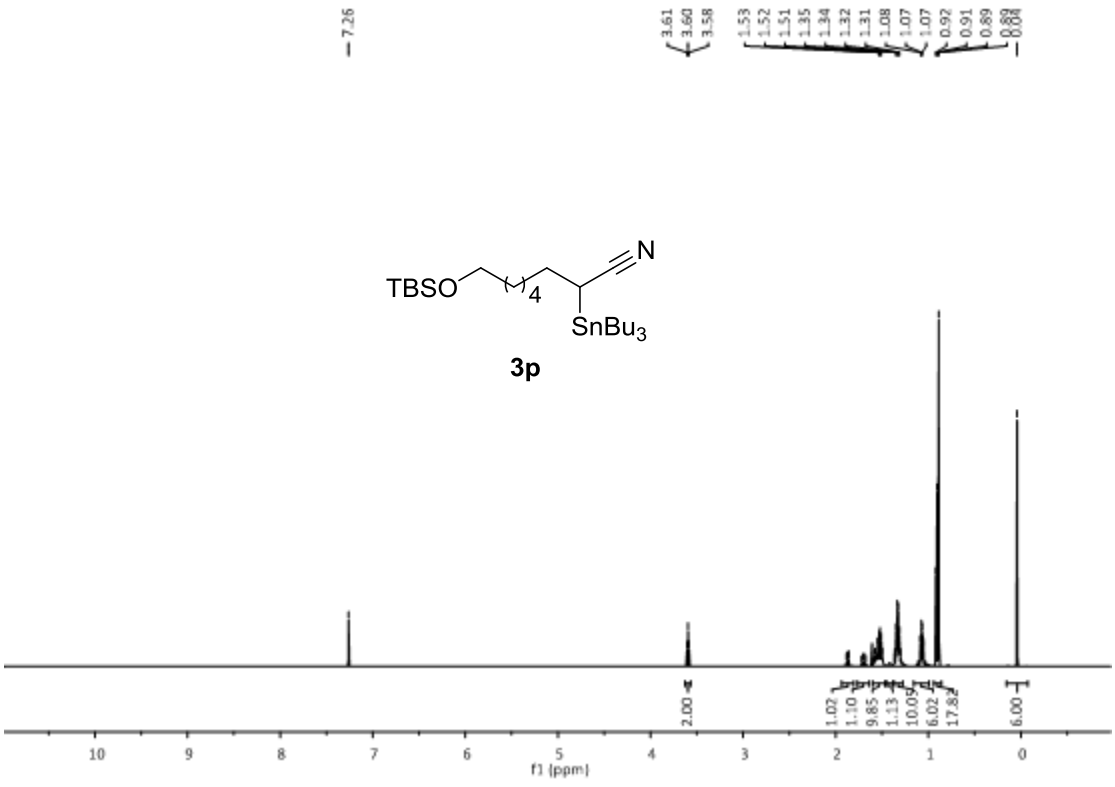
3n


7.26
4.56
4.56
4.55
3.85
3.73
3.71
3.50
3.49
3.37
1.85
1.70
1.68
1.52
1.52
1.32
1.31
1.06
1.05
0.91
0.89
0.88
THPO
4
N
SnBu3
0.96
0.98
0.99
0.98
1.00
2.01
2.15
14.17
11.23
6.06
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

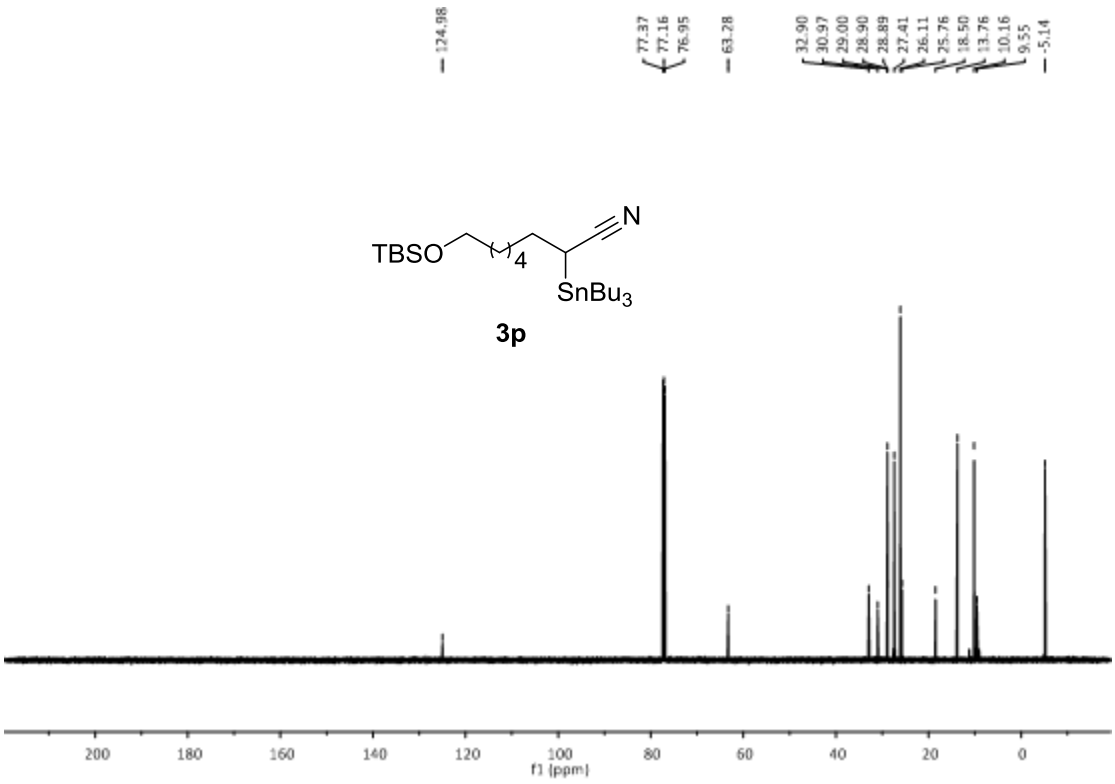
3o


124.96
98.96
77.37
77.16
76.95
67.59
62.47
30.90
30.86
29.77
28.94
28.89
28.86
27.38
26.16
25.58
19.79
13.74
10.12
9.48
THPO
4
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

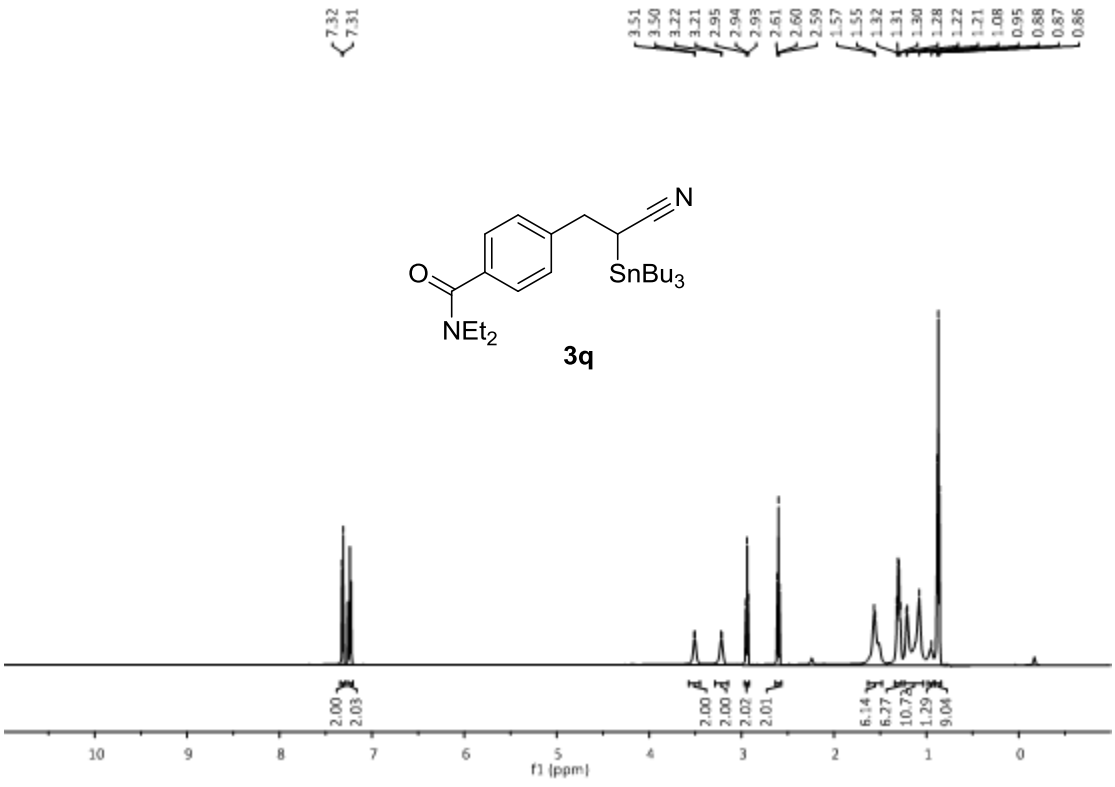
3o


7.26
3.61
3.60
3.58
1.53
1.52
1.51
1.35
1.34
1.32
1.31
1.08
1.07
1.07
0.92
0.91
0.89
TBSO
4
N
SnBu3
2.00
1.02
1.10
9.85
1.13
10.09
6.02
17.82
6.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

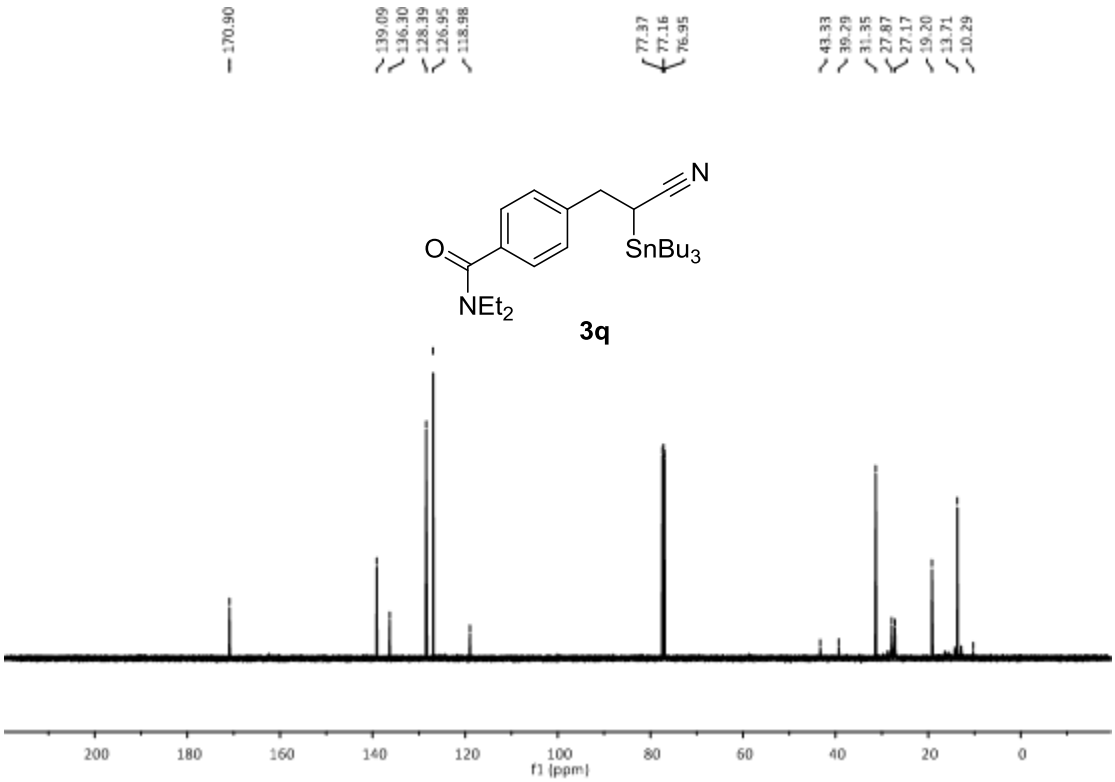
3p

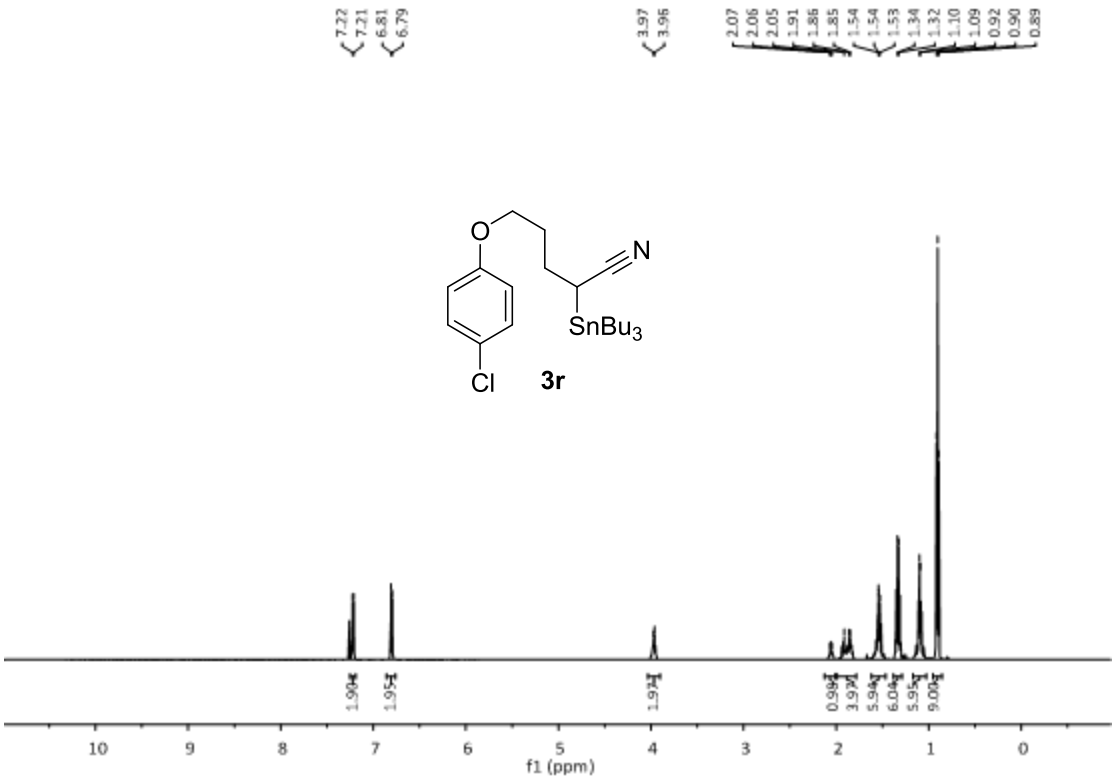

124.98
77.37
77.16
76.95
63.28
32.90
30.97
29.00
28.90
28.89
27.41
26.11
25.76
18.50
13.76
10.16
9.55
-5.14
TBSO
4
N
SnBu3
f1 (ppm)

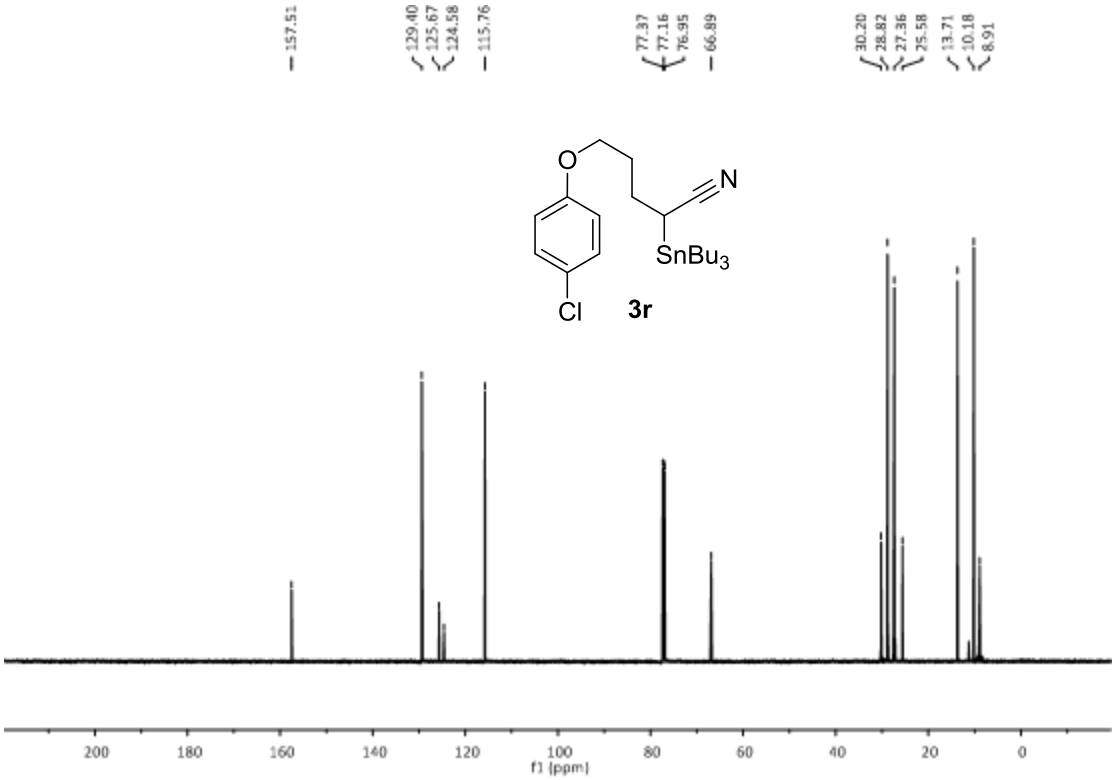
3p

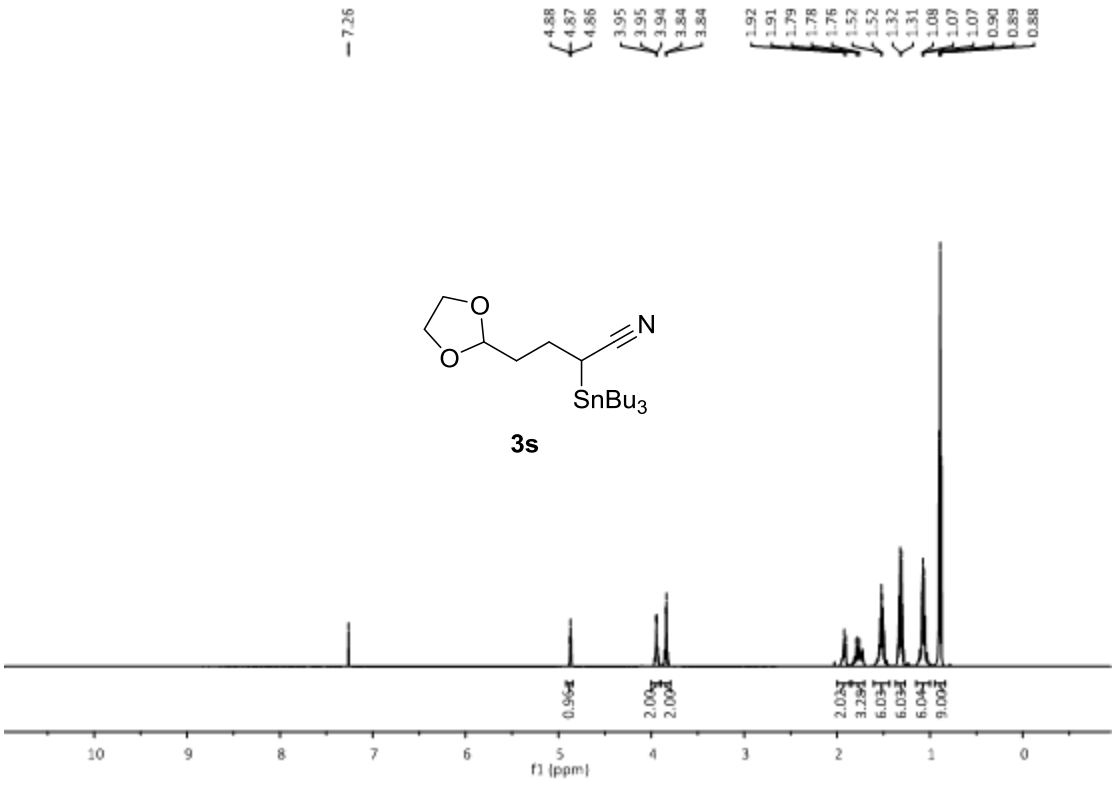

7.32
7.31
3.51
3.50
3.22
3.21
2.95
2.94
2.93
2.61
2.60
2.59
1.57
1.55
1.32
1.31
1.30
1.28
1.22
1.21
1.08
0.95
0.88
0.87
0.86
O
NEt2
N
SnBu3
2.00
2.03
2.00
2.00
2.02
2.01
6.14
6.27
10.78
1.29
9.04
f1 (ppm)

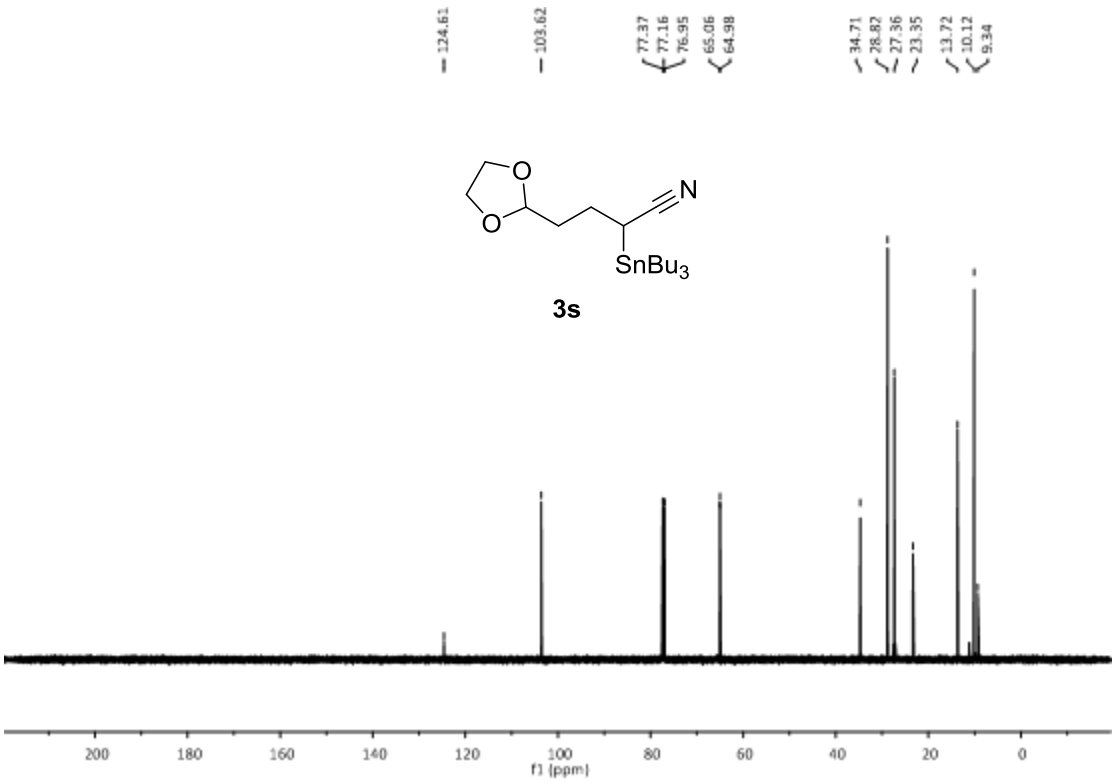
3q


170.90
139.09
136.30
128.39
126.95
118.98
77.37
77.16
76.95
43.33
39.29
31.35
27.87
27.17
19.20
13.71
10.29
N
O
SnBu3
NEt2
3q
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

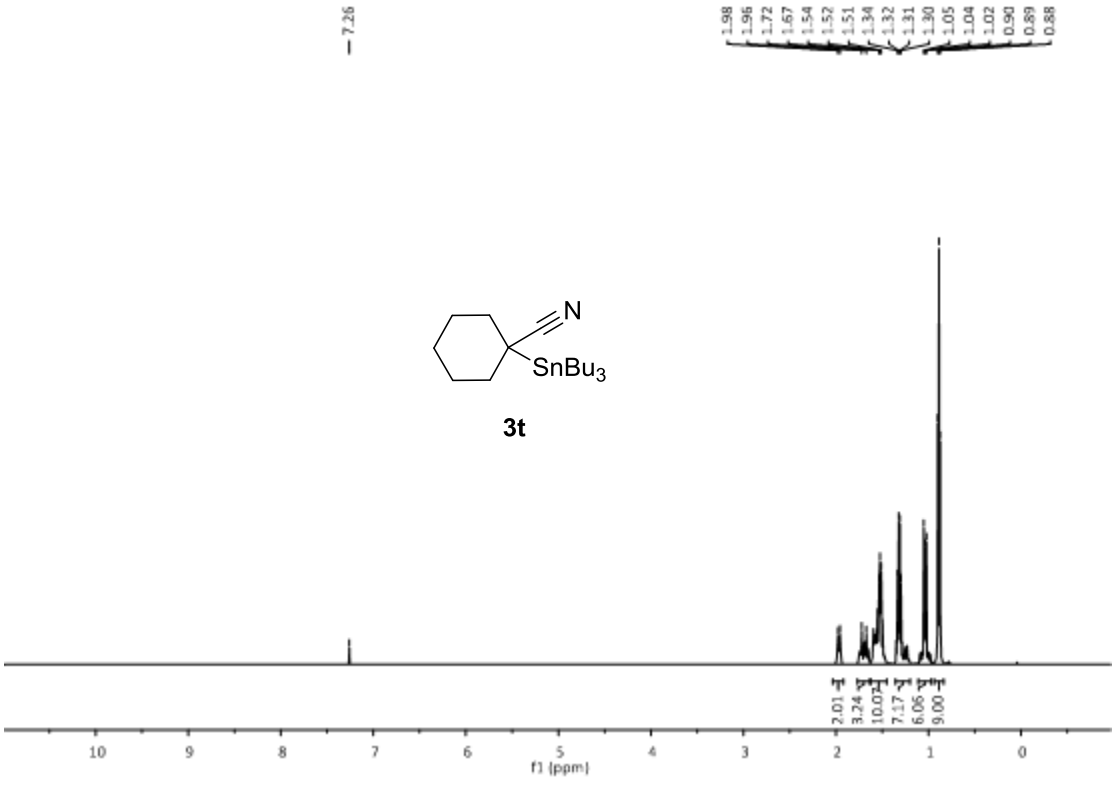

7.22
7.21
6.81
6.79
3.97
3.96
2.07
2.06
2.05
1.91
1.86
1.85
1.54
1.54
1.53
1.34
1.32
1.10
1.09
0.92
0.90
0.89
O
N
SnBu3
Cl
3r
1.90
1.95
1.93
0.98
3.92
5.94
6.04
5.95
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


157.51
129.40
125.67
124.58
115.76
77.37
77.16
76.95
66.89
30.20
28.82
27.36
25.58
13.71
10.18
8.91
O
N
SnBu3
Cl
3r
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

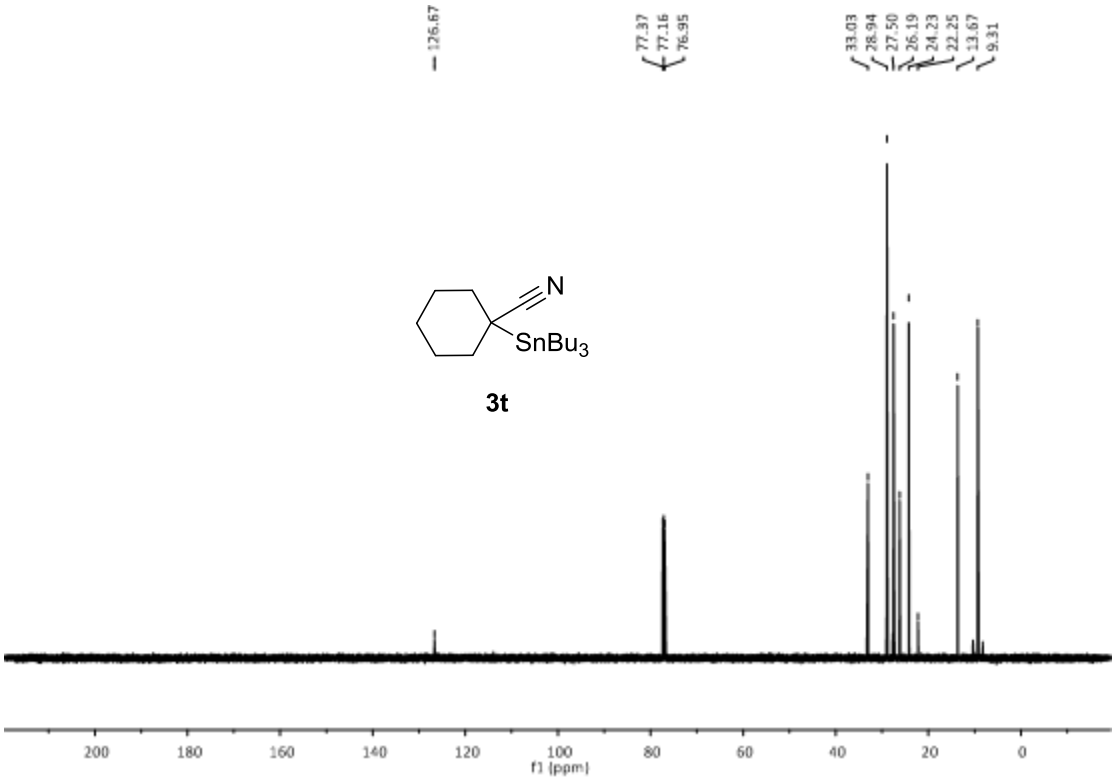

7.26
4.88
4.87
4.86
3.95
3.95
3.94
3.84
3.84
1.92
1.91
1.79
1.78
1.76
1.52
1.52
1.32
1.31
1.08
1.07
1.07
0.90
0.89
0.88
O
O
N
SnBu3
3s
0.96
2.00
2.00
2.03
3.29
6.03
6.03
6.04
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


124.61
103.62
77.37
77.16
76.95
65.06
64.98
34.71
28.82
27.36
23.35
13.72
10.12
9.34
O
O
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

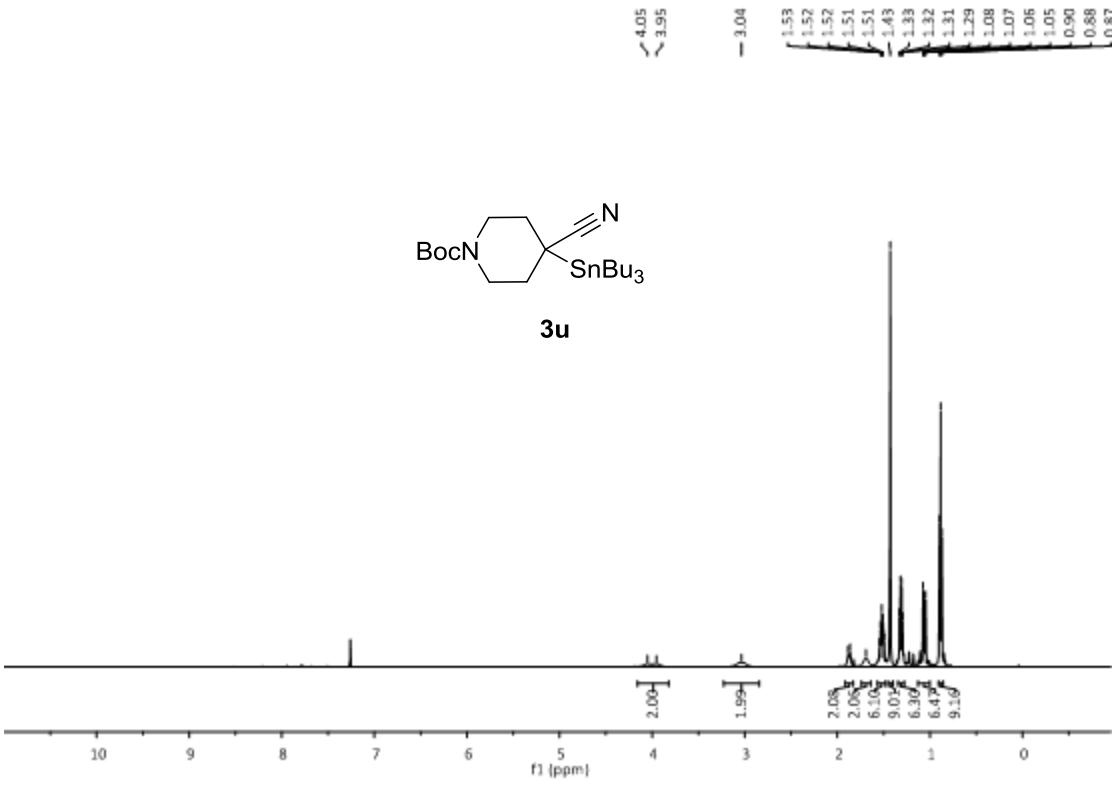
3s


7.26
1.98
1.96
1.72
1.67
1.54
1.52
1.51
1.34
1.32
1.31
1.30
1.05
1.04
1.02
0.90
0.89
0.88
N
SnBu3
2.01
3.24
10.03
7.17
6.06
9.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

3t


126.67
77.37
77.16
76.95
33.03
28.94
27.50
26.19
24.23
22.25
13.67
9.31
N
SnBu3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

3t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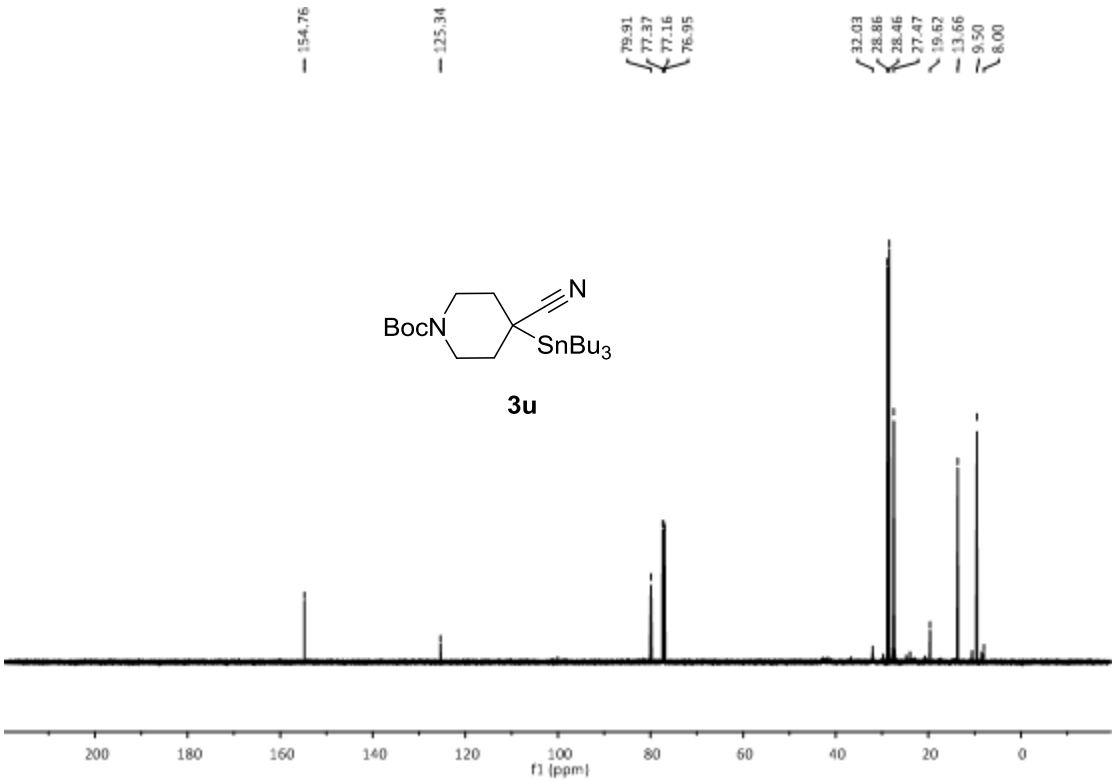
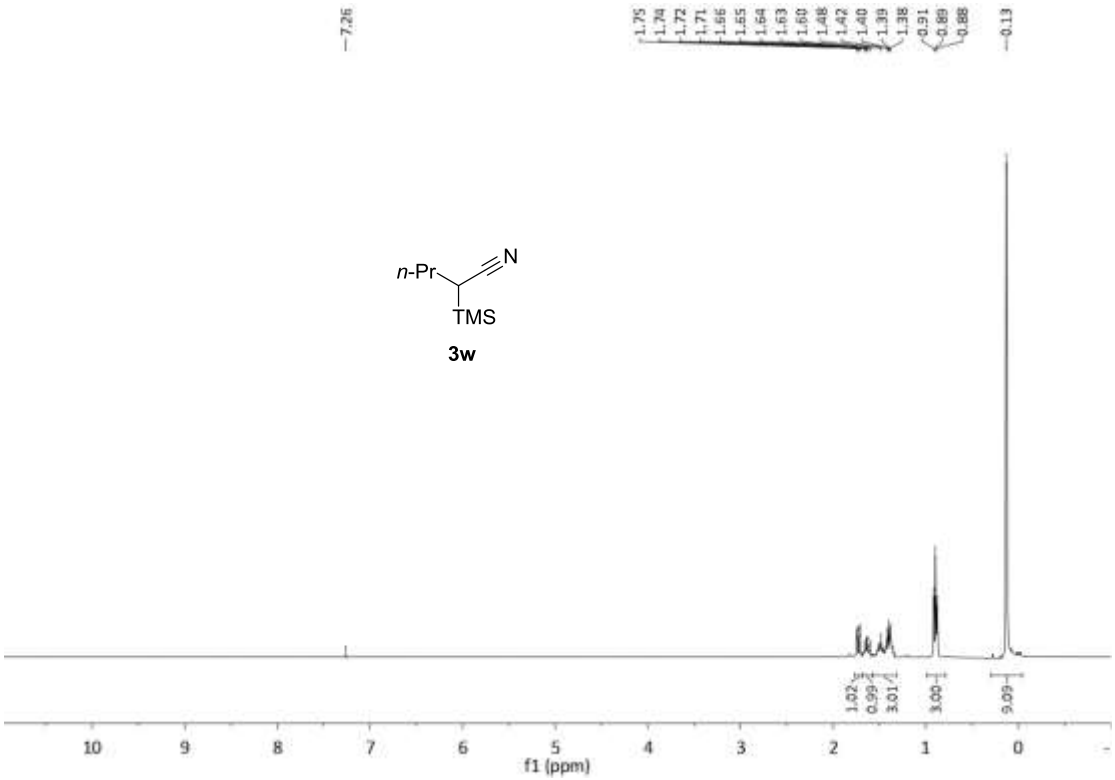
3.95
3.04
1.53
1.52
1.52
1.51
1.51
1.43
1.33
1.32
1.31
1.29
1.08
1.07
1.06
1.05
0.90
0.88
N
BocN
SnBu3
2.00
1.89
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

3u


154.76
125.34
79.91
77.37
77.16
76.95
32.03
28.86
28.46
27.47
19.62
13.66
9.50
8.00
BocN
N
SnBu3
3u
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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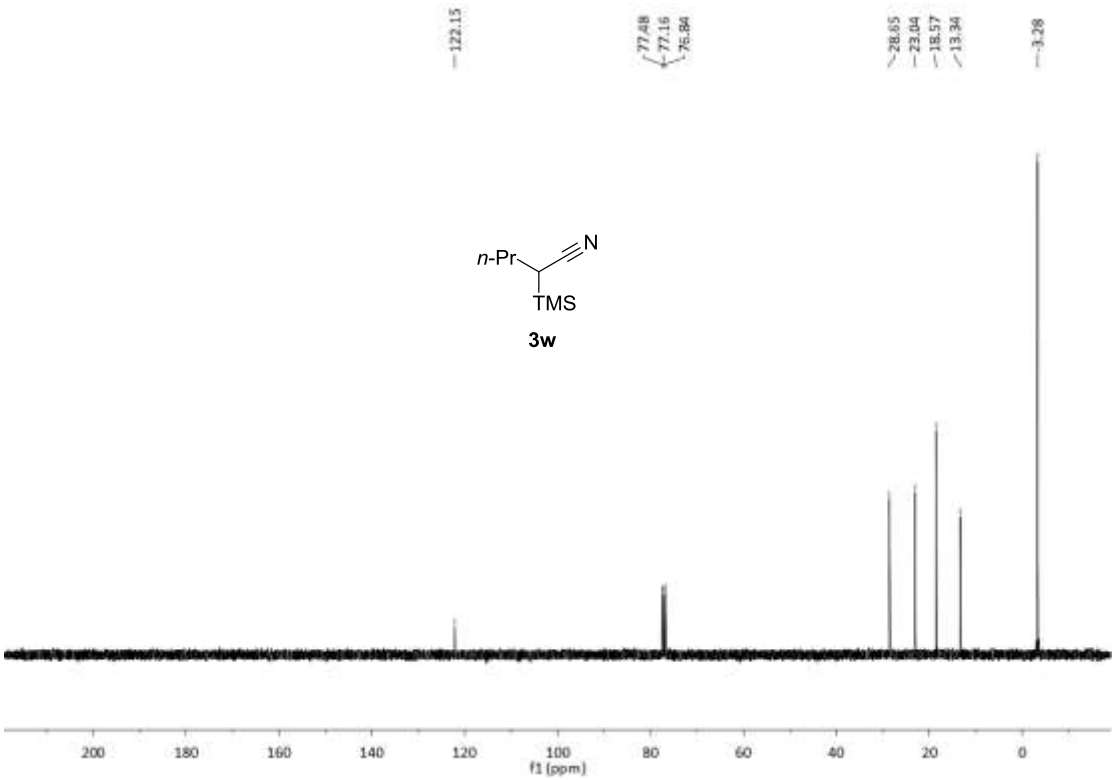
1.75
1.74
1.72
1.71
1.66
1.65
1.64
1.63
1.60
1.48
1.42
1.40
1.39
1.38
0.91
0.89
0.88
0.13
n-Pr
N
TMS
3w
1.02
0.99
3.01
3.00
9.09
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


122.15
77.48
77.16
76.84
28.65
23.04
18.57
13.34
-3.28
n-Pr
N
TMS
3w
200
180
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140
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100
80
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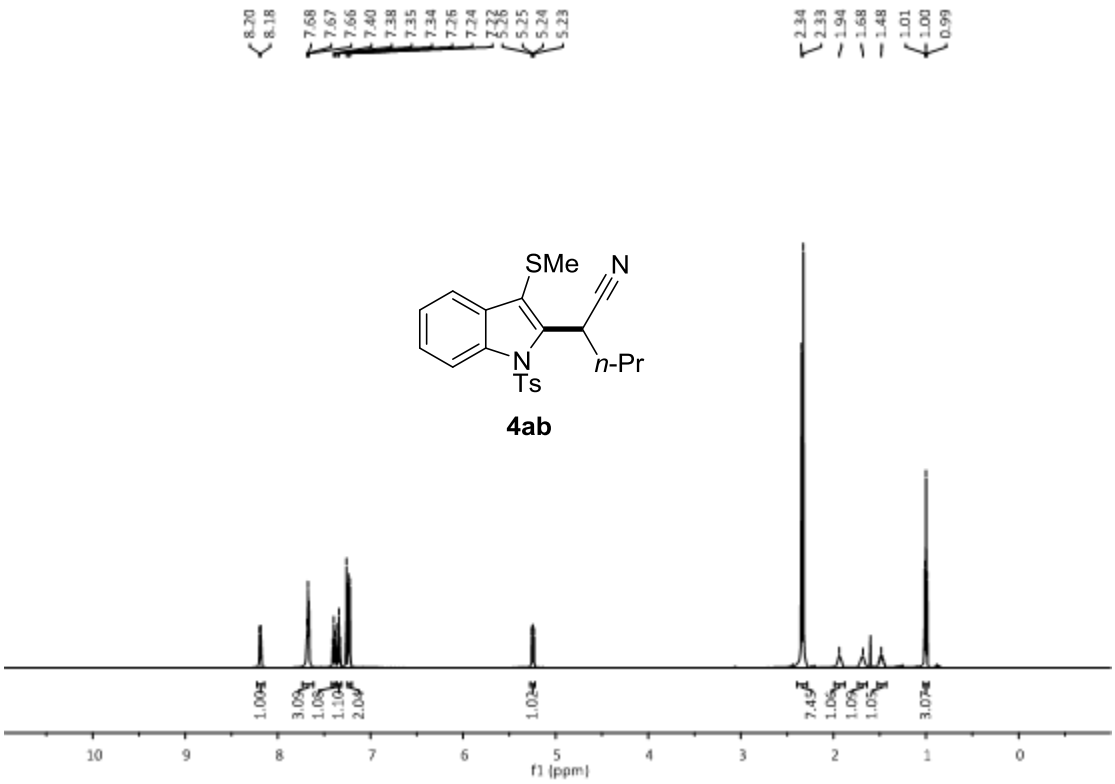
40
20
0
f1 (ppm)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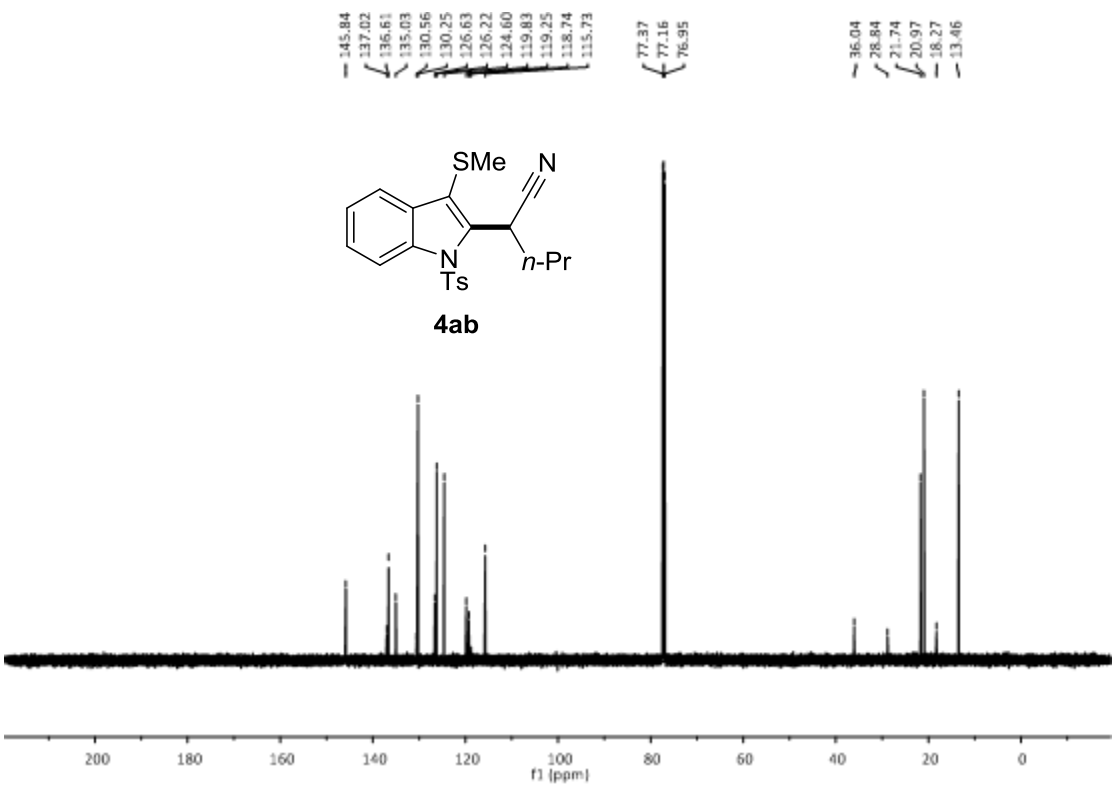
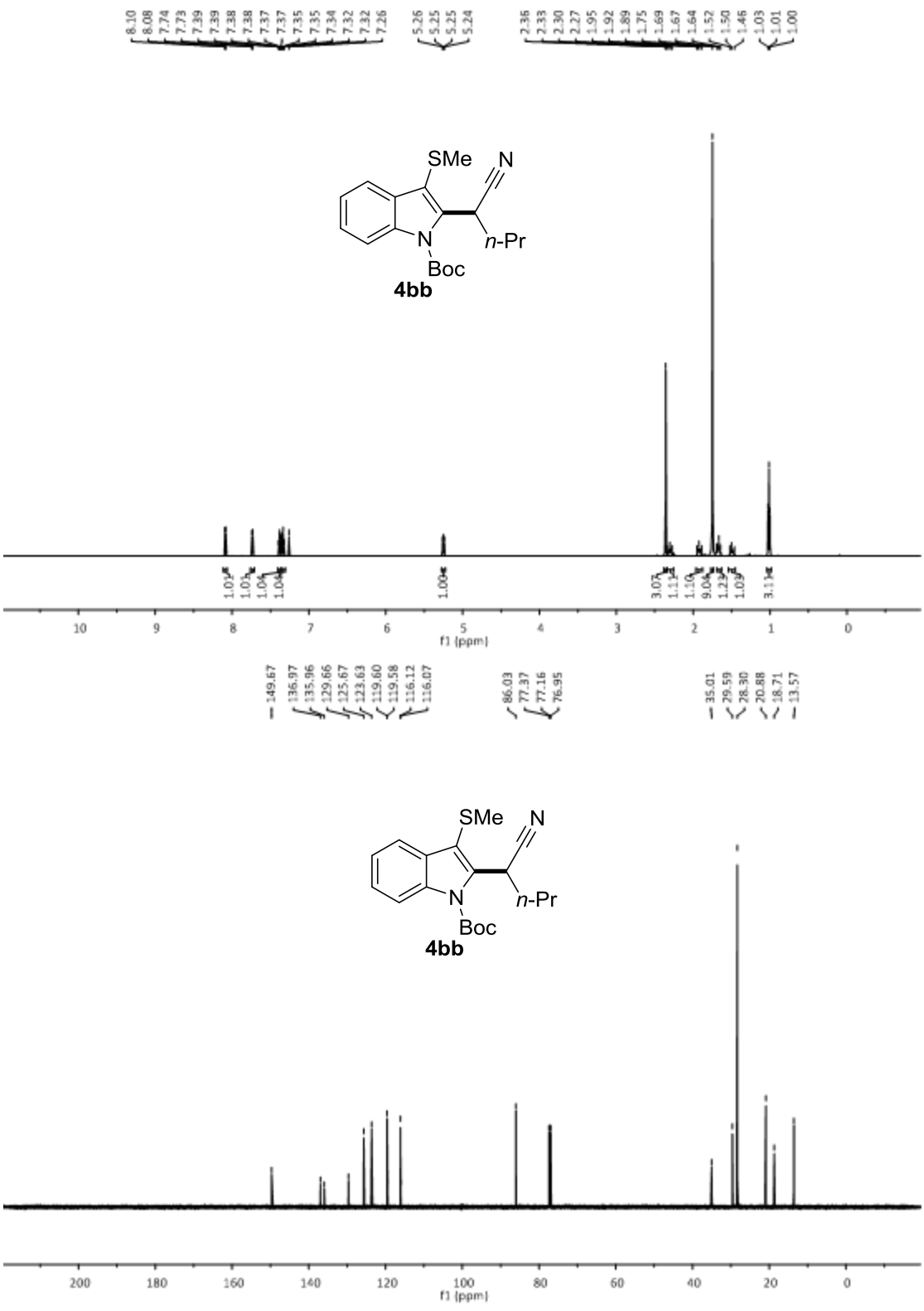
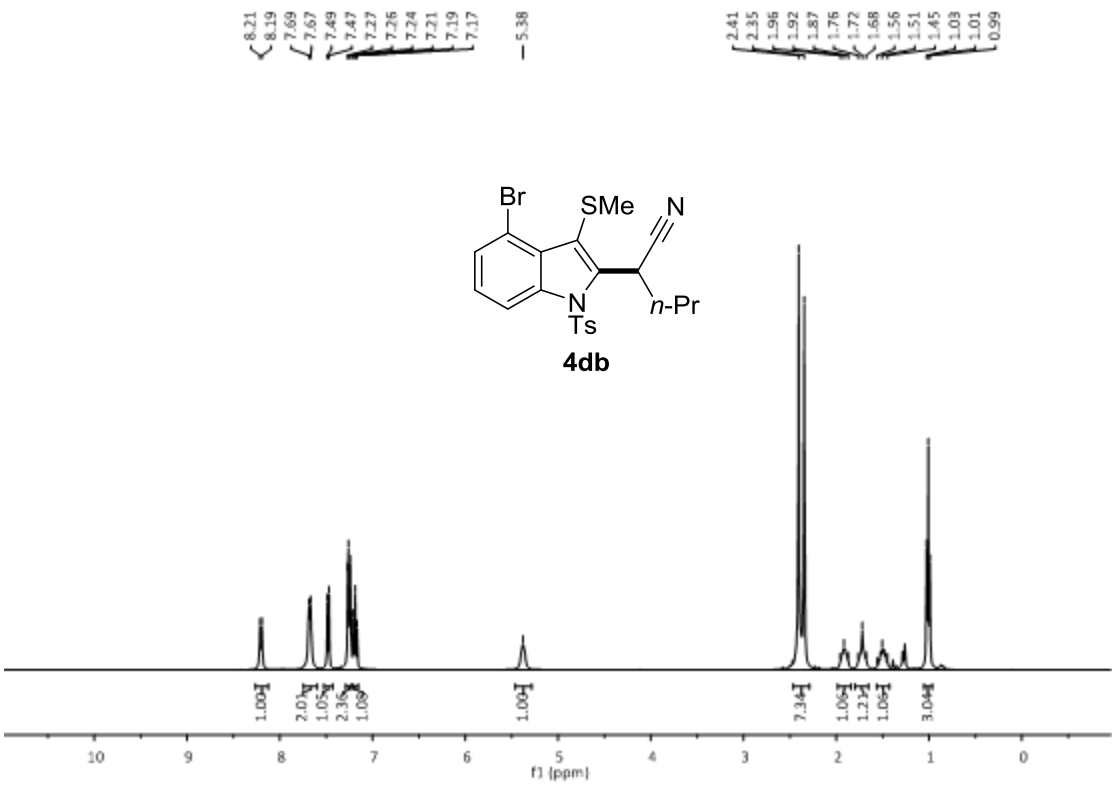
7.35
7.34
7.26
7.24
5.26
5.25
5.24
5.23
2.34
2.33
1.94
1.68
1.48
1.01
1.00
0.99
SMe
N
N
Ts
n-Pr
4ab
1.00
3.09
1.08
1.10
2.04
1.02
7.45
1.06
1.09
1.05
3.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


145.84
137.02
136.61
135.03
130.56
130.25
126.63
126.22
124.60
119.83
119.25
118.74
115.73
77.37
77.16
76.95
36.04
28.84
21.74
20.97
18.27
13.46
SMe
N
N
Ts
n-Pr
4ab
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


SMe
N
n-Pr
N
Boc
4bb
f1 (ppm)
SMe
N
n-Pr
N
Boc
4bb
f1 (ppm)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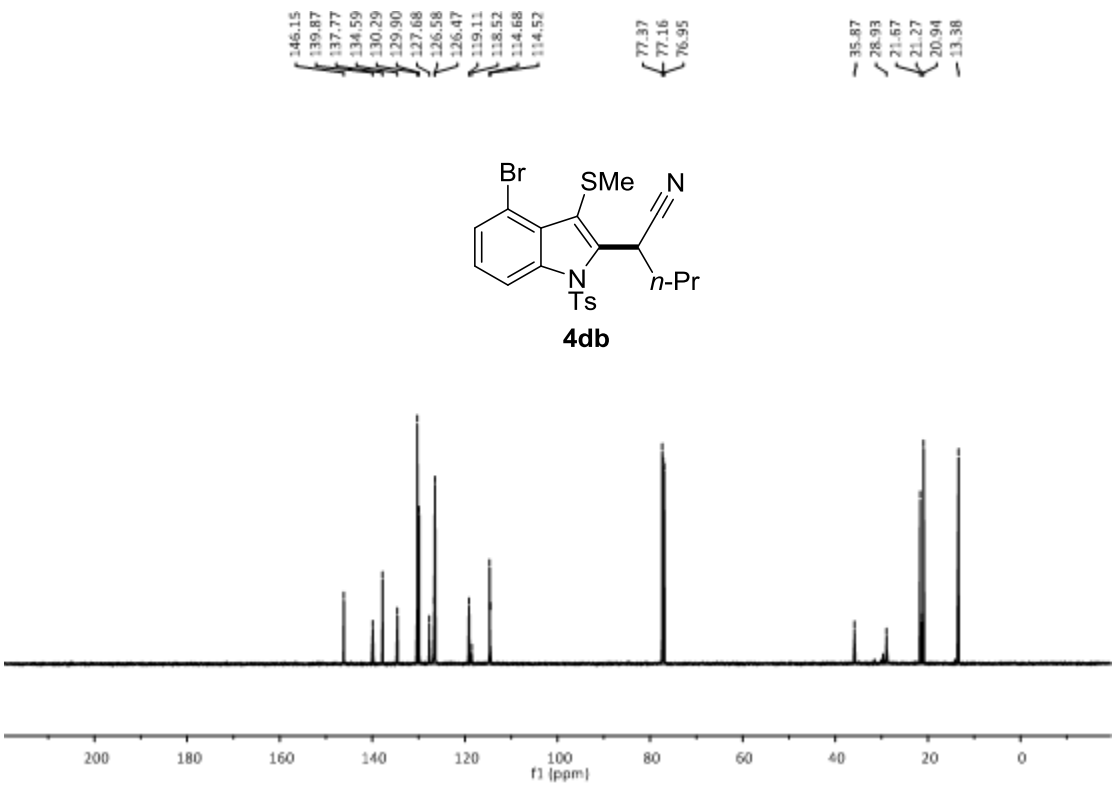
8.19
7.69
7.67
7.49
7.47
7.27
7.26
7.24
7.21
7.19
7.17
5.38
2.41
2.35
1.96
1.92
1.87
1.76
1.72
1.68
1.56
1.51
1.45
1.03
1.01
0.99
Br
SMe
N
N
Ts
n-Pr
4db
1.00
2.01
1.05
2.36
1.09
1.00
7.34
1.06
1.21
1.06
3.04
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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139.87
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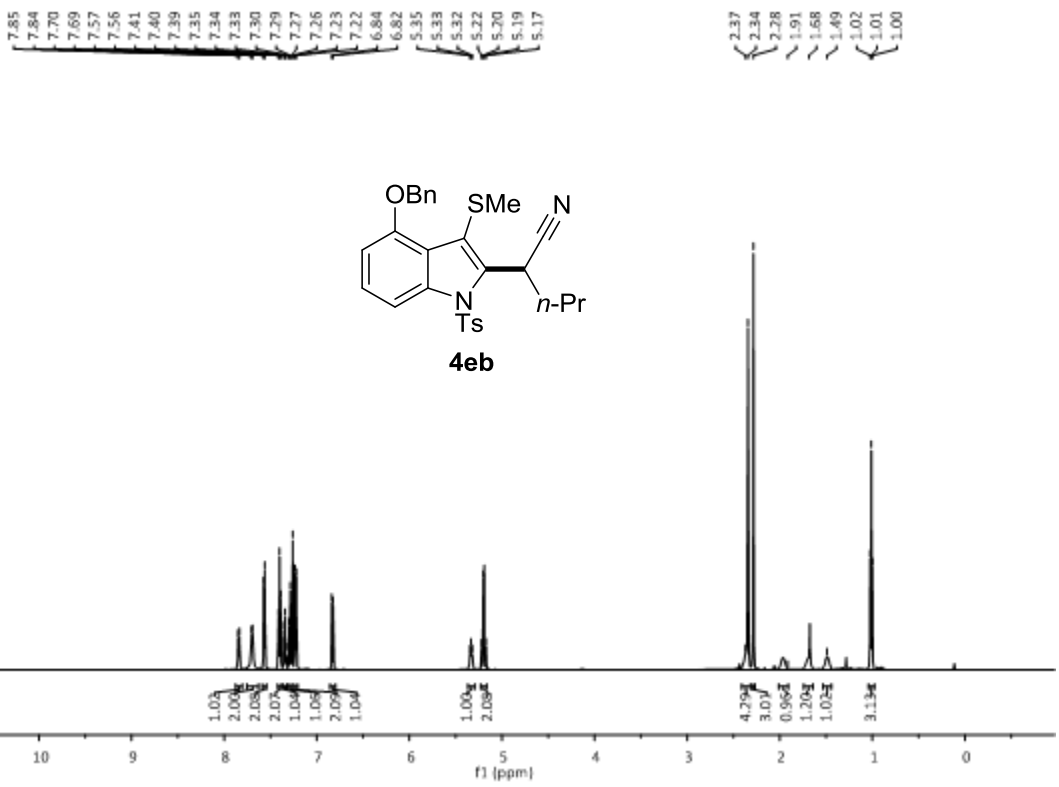
129.90
127.68
126.58
126.47
119.11
118.52
114.68
114.52
77.37
77.16
76.95
35.87
28.93
21.67
21.27
20.94
13.38
Br
SMe
N
N
Ts
n-Pr
4db
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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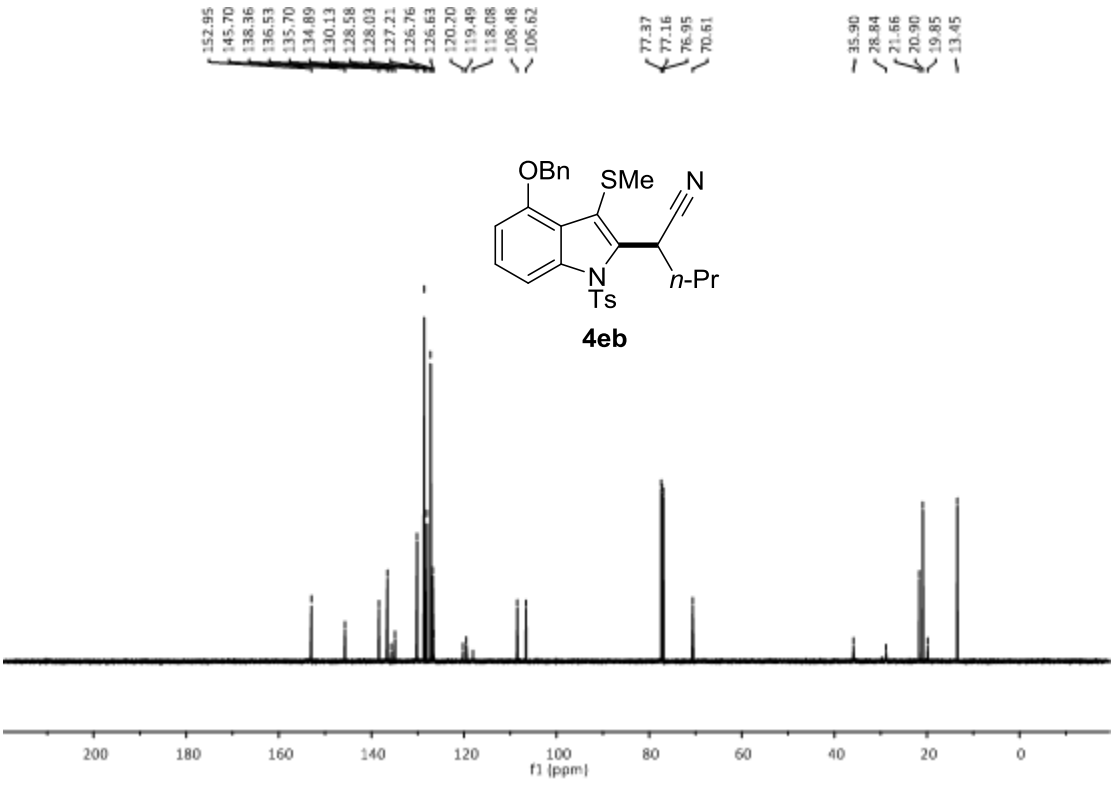
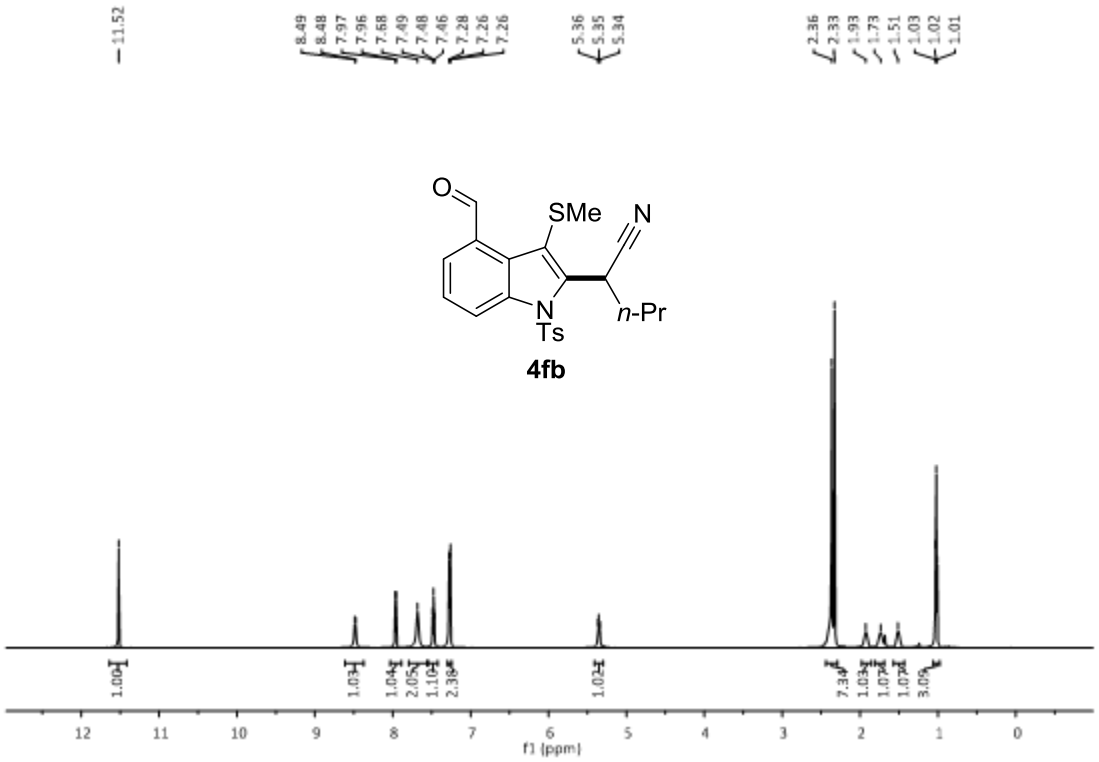
7.84
7.70
7.69
7.57
7.56
7.41
7.40
7.39
7.35
7.34
7.33
7.30
7.29
7.27
7.26
7.23
7.22
6.84
6.82
5.35
5.33
5.32
5.22
5.20
5.19
5.17
2.37
2.34
2.28
1.91
1.68
1.49
1.02
1.01
1.00
OBn
SMe
N
N
Ts
n-Pr
4eb
f1 (ppm)


152.95
145.70
138.36
136.53
135.70
134.89
130.13
128.58
128.03
127.21
126.76
126.63
120.20
119.49
118.08
108.48
106.62
77.37
77.16
76.95
70.61
35.90
28.84
21.66
20.90
19.85
13.45
OBn
SMe
N
N
Ts
n-Pr
4eb
f1 (ppm)


11.52
8.49
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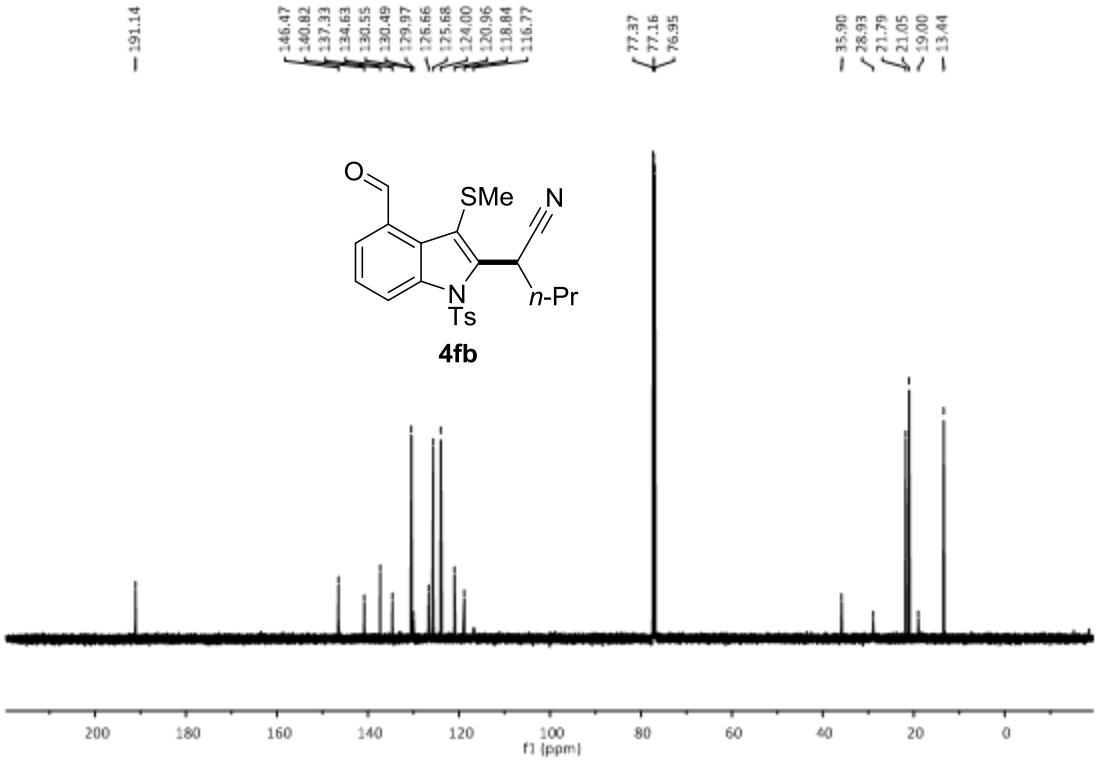
7.97
7.96
7.68
7.49
7.48
7.46
7.28
7.26
7.26
5.36
5.35
5.34
2.36
2.33
1.93
1.73
1.51
1.03
1.02
1.01
O
SMe
N
N
Ts
n-Pr
4fb
1.00
1.03
1.04
2.05
1.10
2.38
1.02
7.34
1.03
1.07
1.07
3.05
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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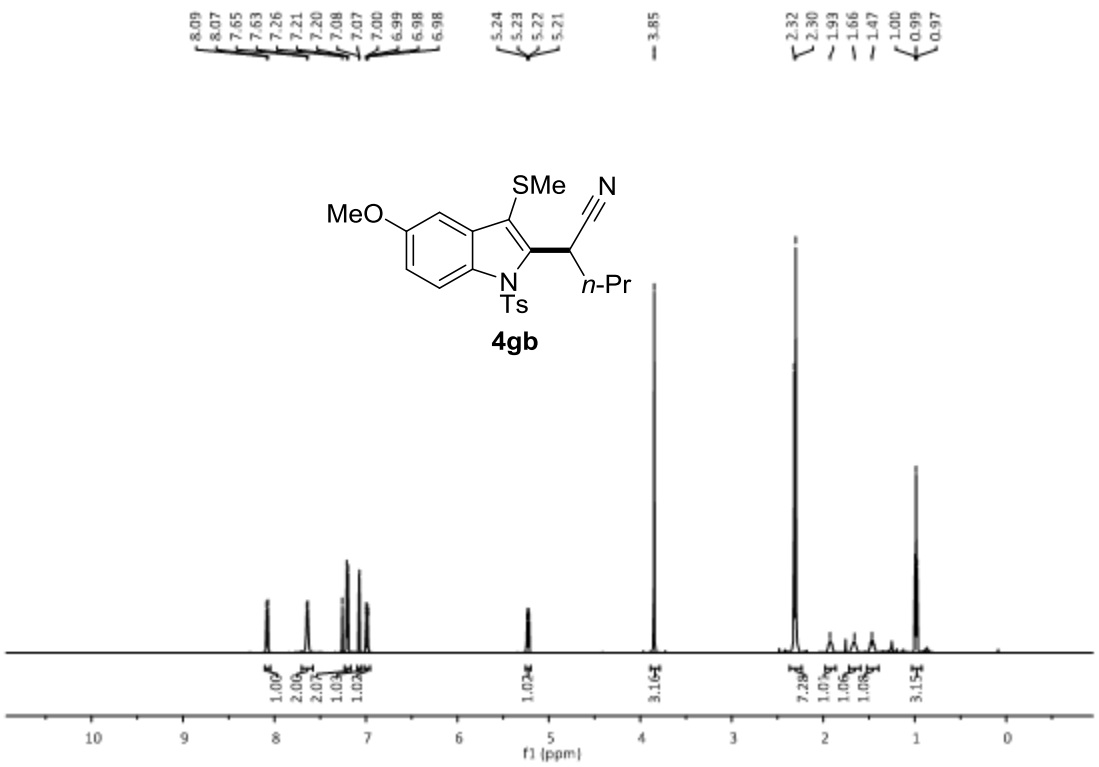
130.55
130.49
129.97
126.66
125.68
124.00
120.96
118.84
116.77
77.37
77.16
76.95
35.90
28.93
21.79
21.05
19.00
13.44
O
SMe
N
N
Ts
n-Pr
4fb
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.09
8.07
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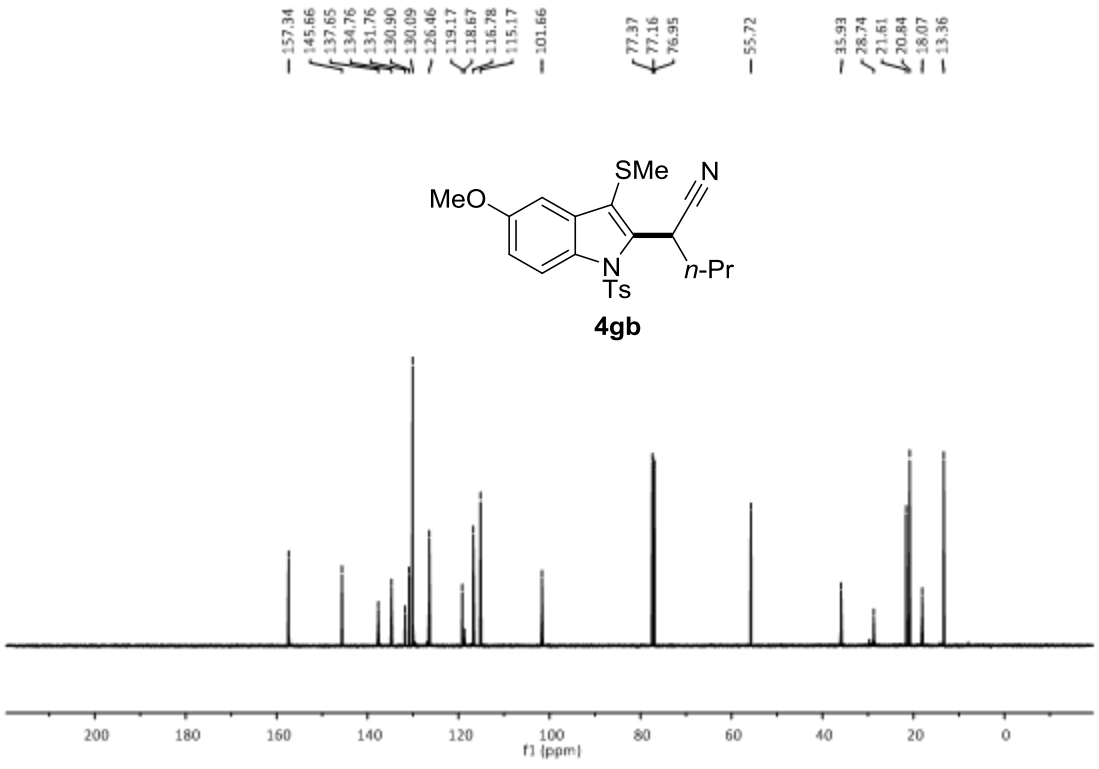
7.63
7.26
7.21
7.20
7.08
7.07
7.00
6.99
6.98
6.98
5.24
5.23
5.22
5.21
3.85
2.32
2.30
1.93
1.66
1.47
1.00
0.99
0.97
SMe
N
MeO
n-Pr
N
Ts
4gb
f1 (ppm)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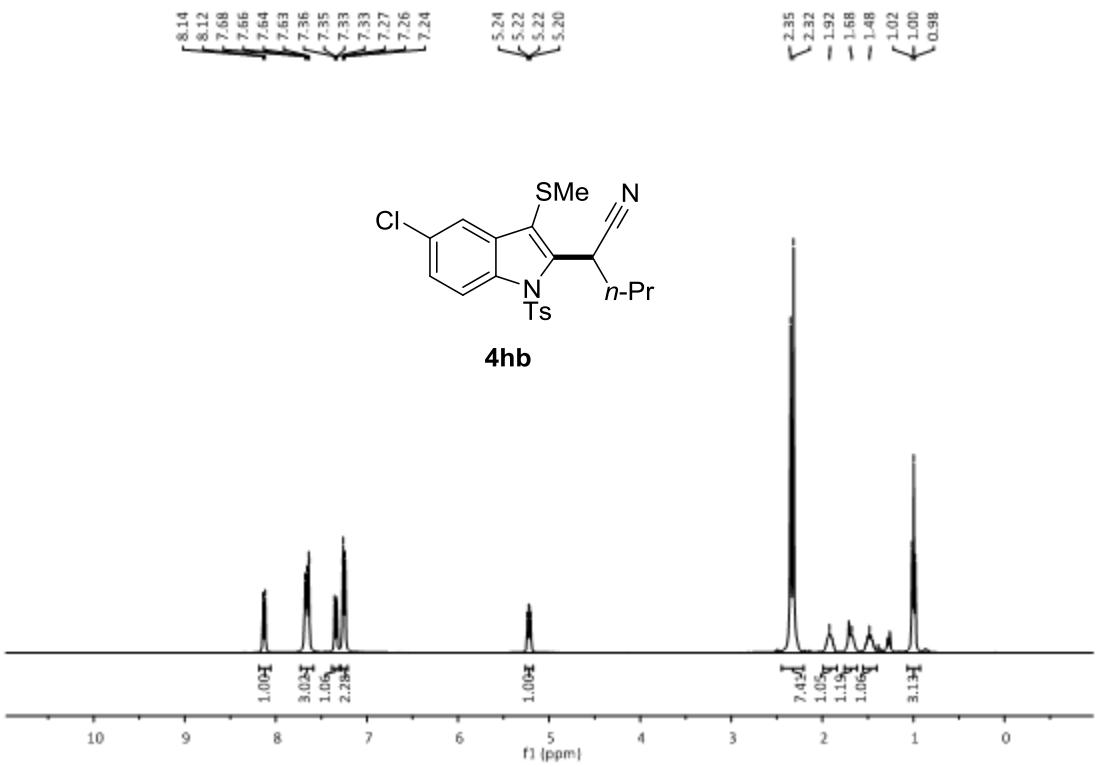
134.76
131.76
130.90
130.09
126.46
119.17
118.67
116.78
115.17
101.66
77.37
77.16
76.95
55.72
35.93
28.74
21.61
20.84
18.07
13.36
SMe
N
MeO
n-Pr
N
Ts
4gb
f1 (ppm)


8.14
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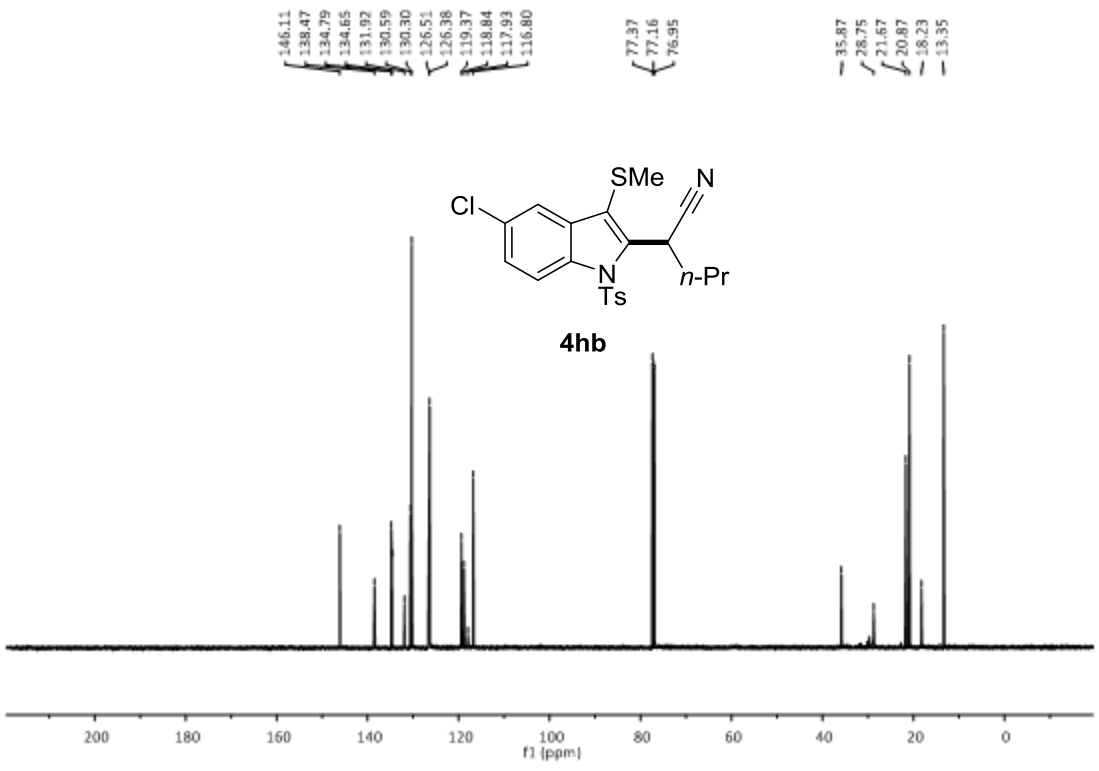
7.35
7.33
7.33
7.27
7.26
7.24
5.24
5.22
5.22
5.20
2.35
2.32
1.92
1.68
1.48
1.02
1.00
0.98
SMe
N
Cl
N
Ts
n-Pr
4hb
1.00
3.03
1.05
2.28
1.00
7.45
1.05
1.19
1.06
3.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


146.11
138.47
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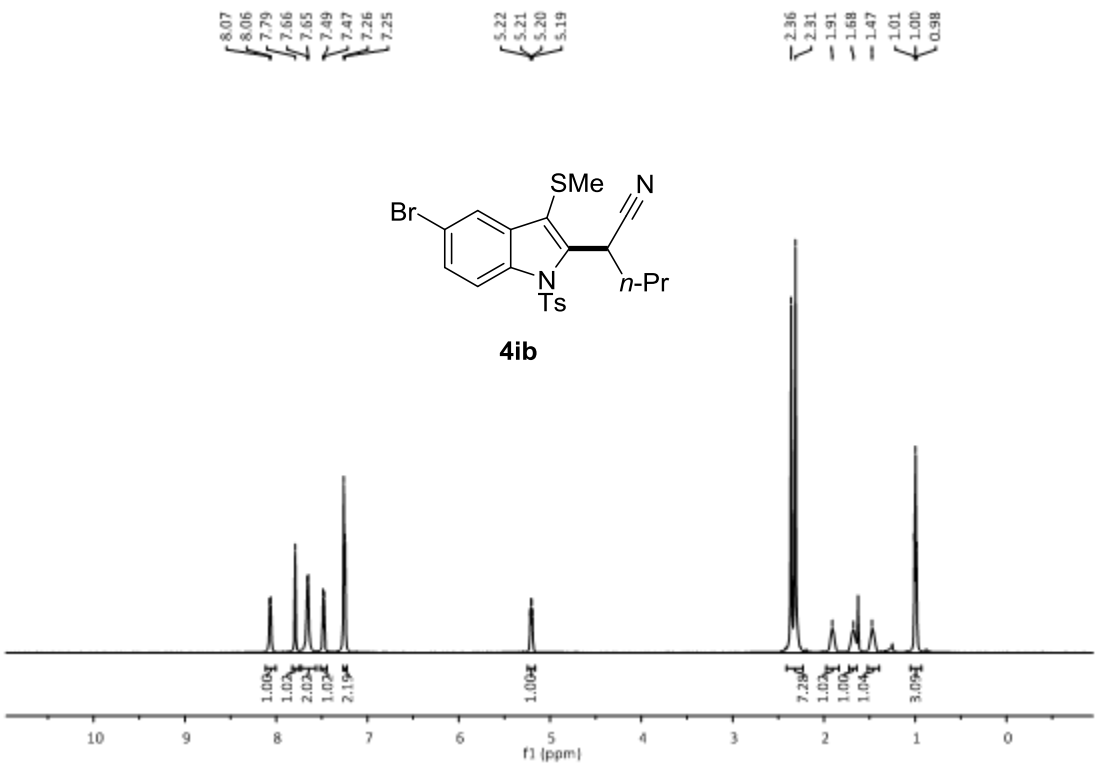
131.92
130.59
130.30
126.51
126.36
119.37
118.84
117.93
116.80
77.37
77.16
76.95
35.87
28.75
21.67
20.87
18.23
13.35
SMe
N
Cl
N
Ts
n-Pr
4hb
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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8.06
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7.66
7.65
7.49
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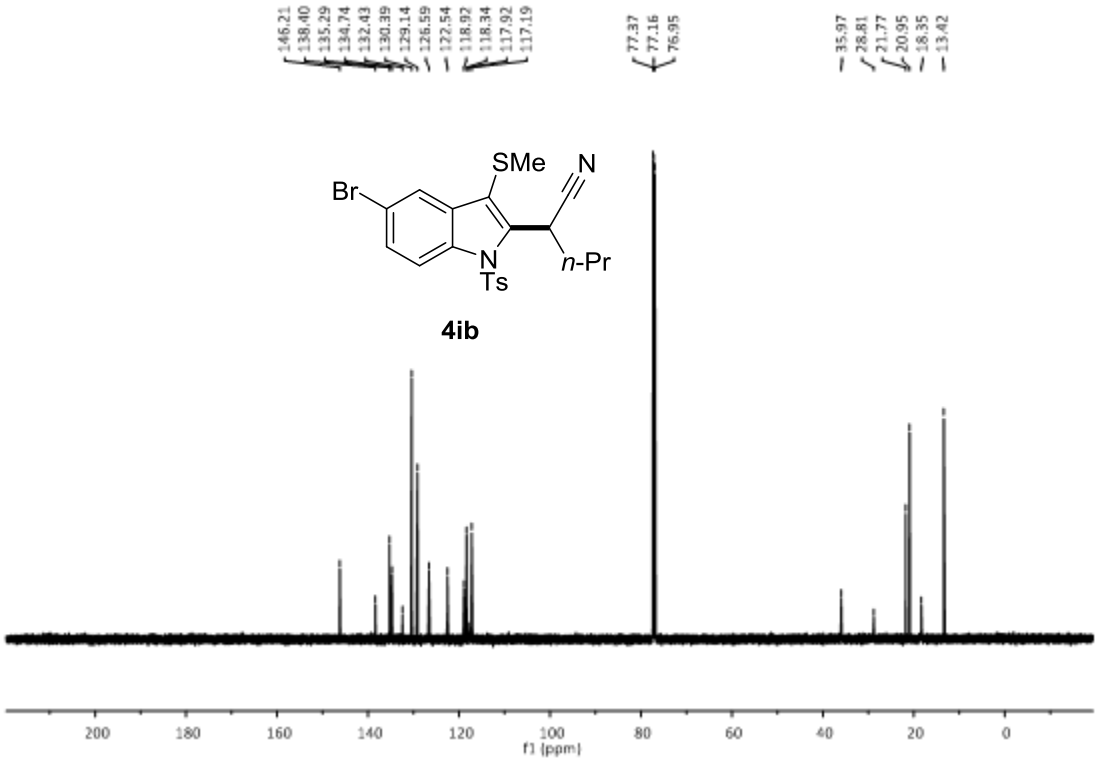
7.26
7.25
5.22
5.21
5.20
5.19
2.36
2.31
1.91
1.68
1.47
1.01
1.00
0.98
SMe
N
Br
N
Ts
n-Pr
4ib
f1 (ppm)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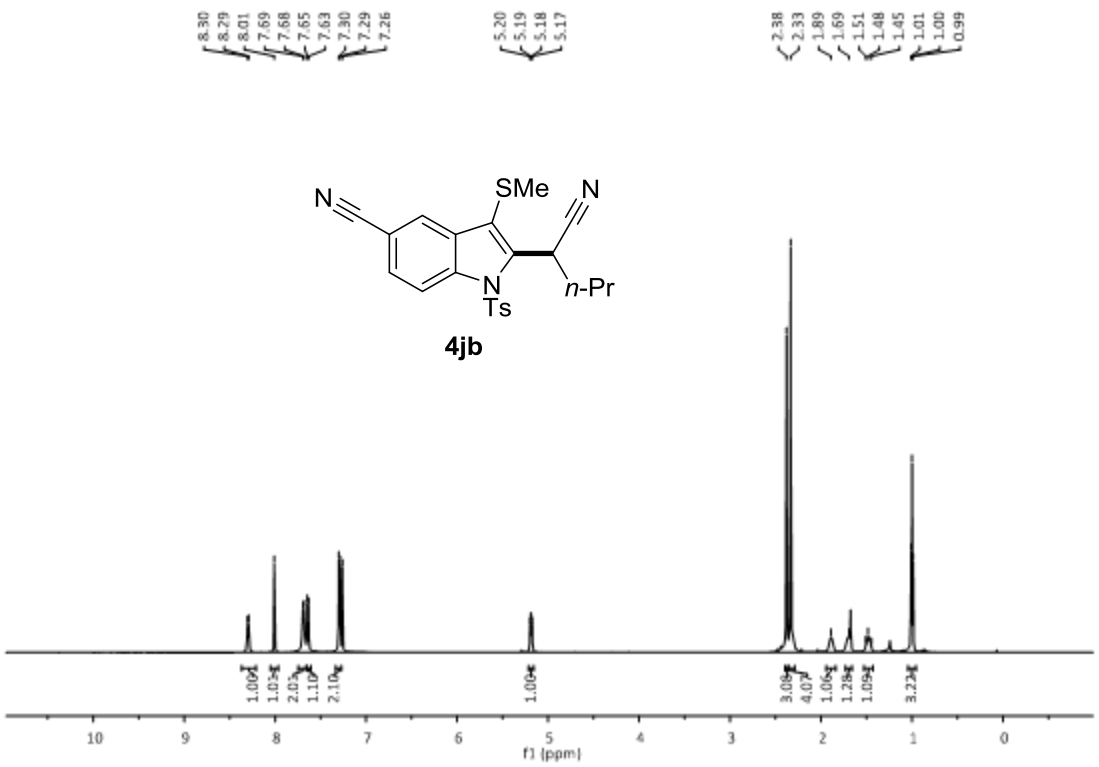
130.39
129.14
126.59
122.54
118.92
118.34
117.92
117.19
77.37
77.16
76.95
35.97
28.81
21.77
20.95
18.35
13.42
SMe
N
Br
N
Ts
n-Pr
4ib
f1 (ppm)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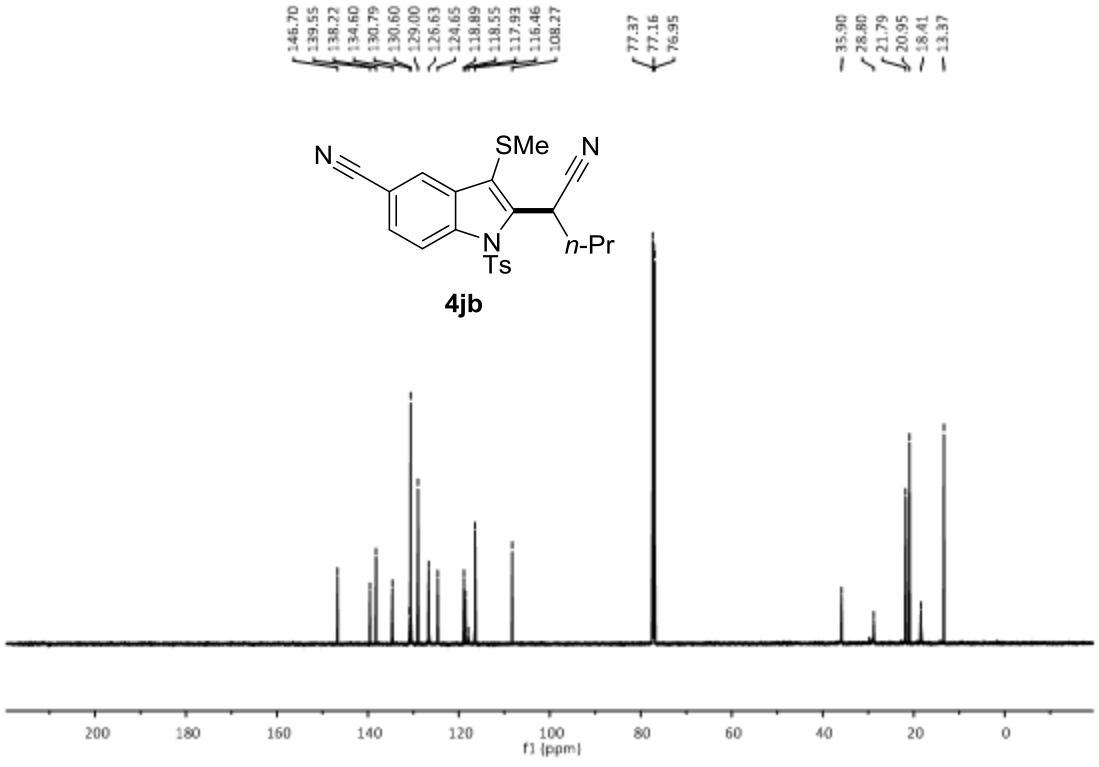
8.29
8.01
7.69
7.68
7.65
7.63
7.30
7.29
7.26
5.20
5.19
5.18
5.17
2.38
2.33
1.89
1.69
1.51
1.48
1.45
1.01
1.00
0.99
SMe
N
N
N
Ts
n-Pr
1.00
1.03
2.03
1.10
2.10
1.00
3.08
4.07
1.06
1.28
1.05
3.22
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

4jb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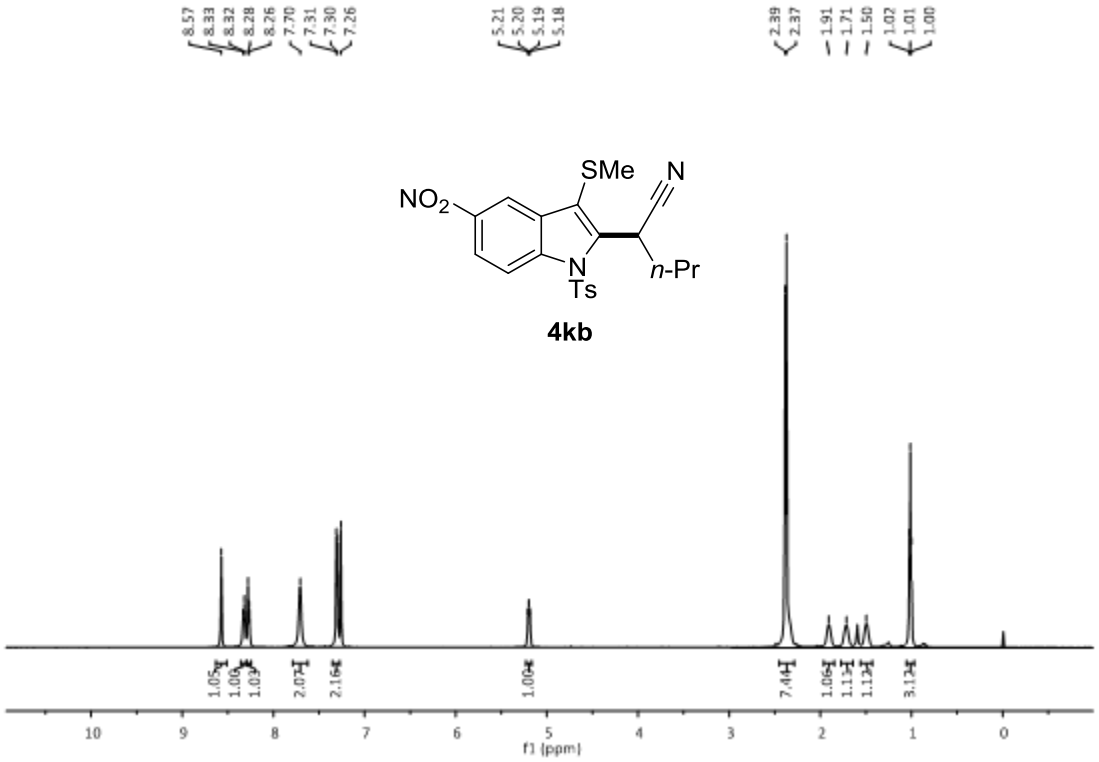
130.79
130.60
129.00
126.63
124.65
118.89
118.55
117.93
116.46
108.27
77.37
77.16
76.95
35.90
28.80
21.79
20.95
18.41
13.37
SMe
N
N
N
Ts
n-Pr
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

4jb


8.57
8.33
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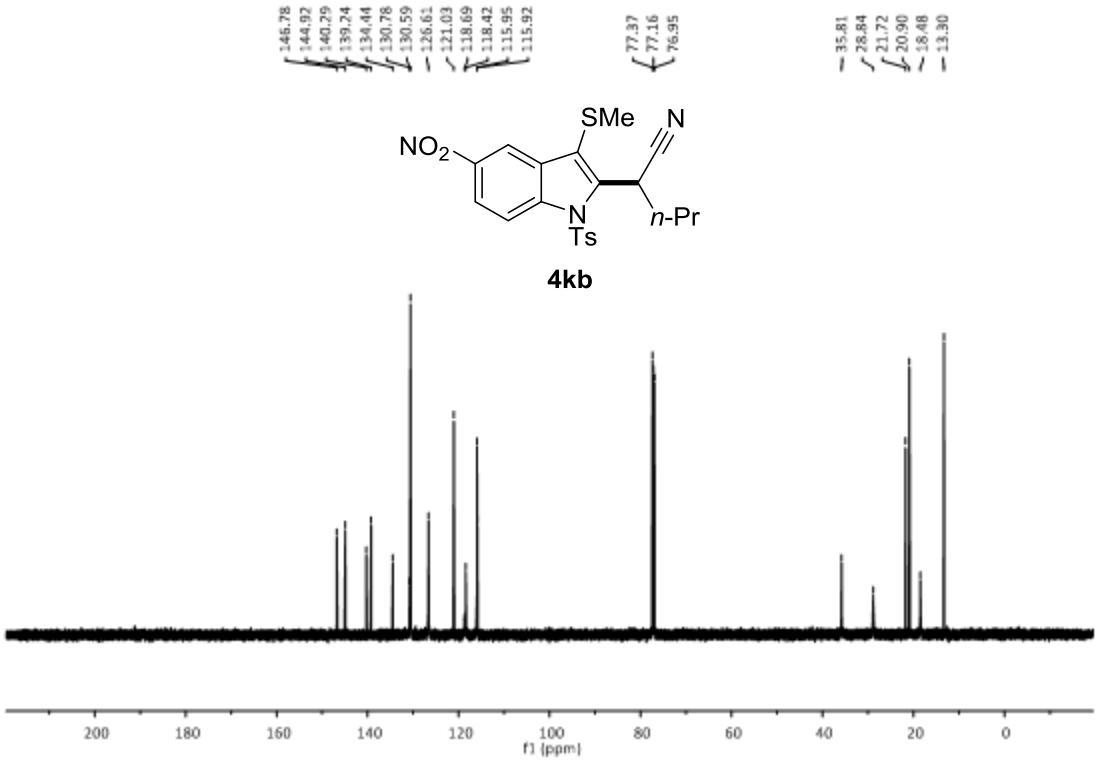
7.70
7.31
7.30
7.26
5.21
5.20
5.19
5.18
2.39
2.37
1.91
1.71
1.50
1.02
1.01
1.00
SMe
N
NO2
N
Ts
n-Pr
4kb
1.05
1.00
1.03
2.07
2.16
1.00
7.44
1.06
1.13
1.13
3.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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130.78
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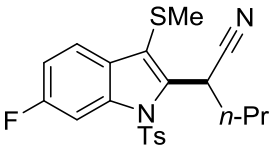
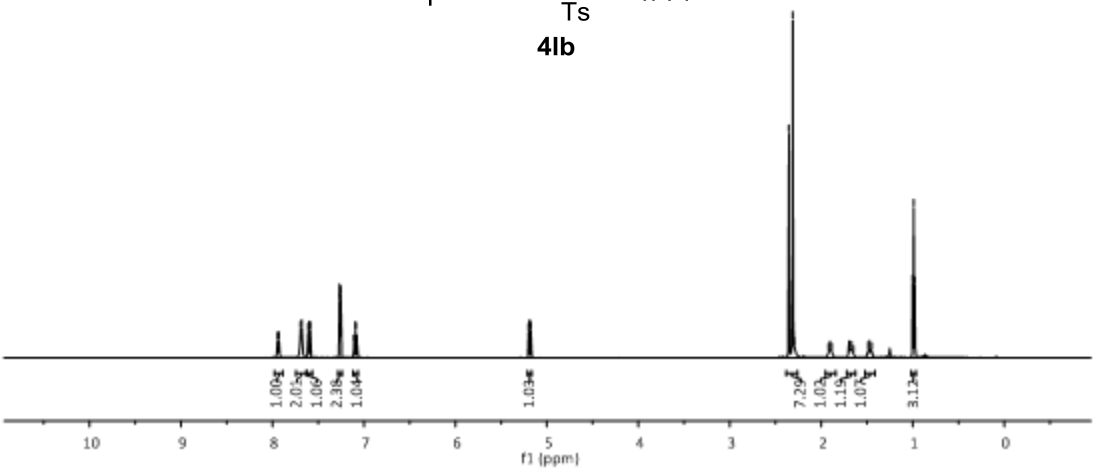
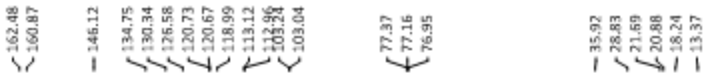
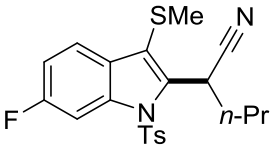
126.61
121.03
118.69
118.42
115.95
115.92
77.37
77.16
76.95
35.81
28.84
21.72
20.90
18.48
13.30
SMe
N
NO2
N
Ts
n-Pr
4kb
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



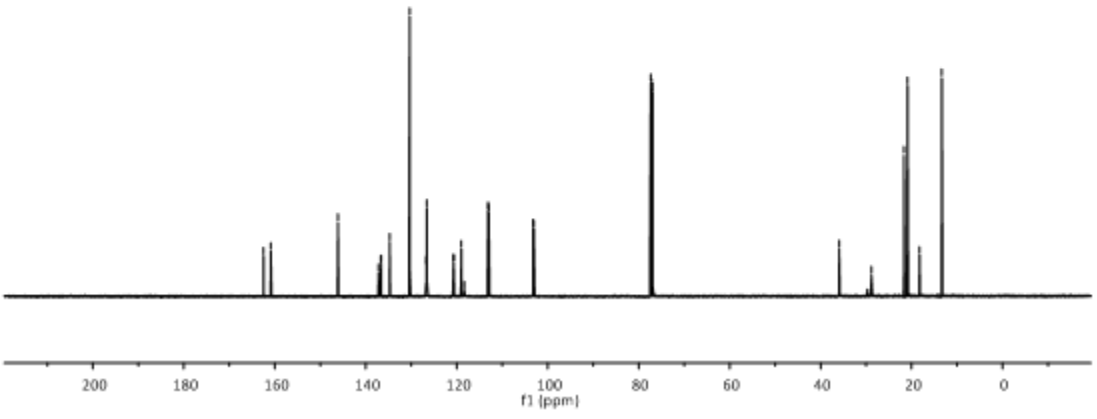
4lb

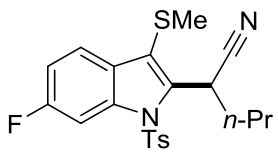






4lb

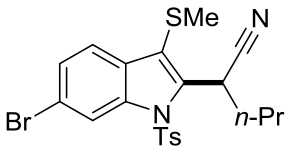



SMe
N
F
N
Ts
n-Pr

4lb

-113.91
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


8.39
7.68
7.67
7.53
7.52
7.46
7.46
7.44
7.44
7.28
7.26
5.18
5.17
5.17
5.16
2.36
2.30
1.89
1.67
1.49
1.47
1.45
1.43
1.00
0.99
0.98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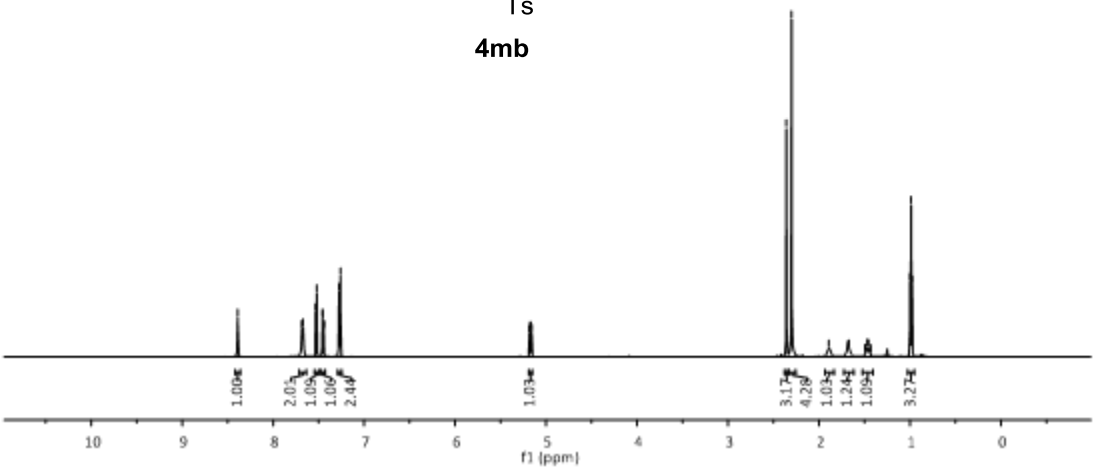
Br
N
Ts
n-Pr

4mb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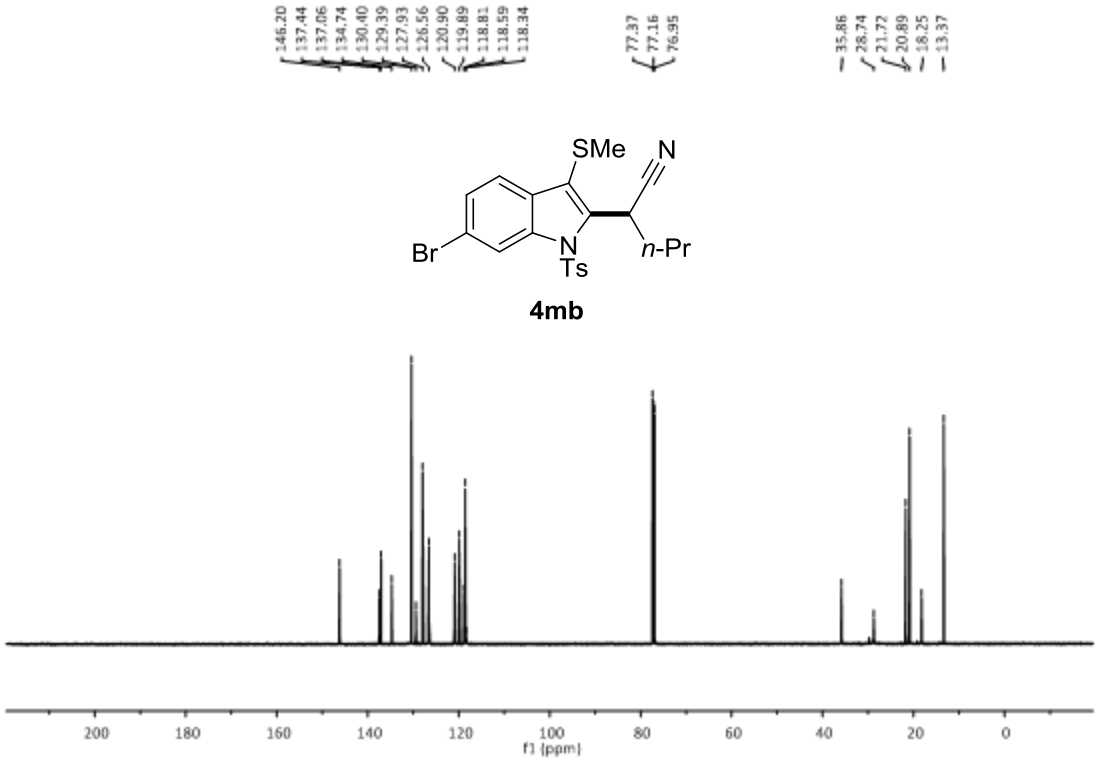
f1 (ppm)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118.81
118.59
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77.16
76.95
35.86
28.74
21.72
20.89
18.25
13.37
SMe
N
Br
N
Ts
n-Pr
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60
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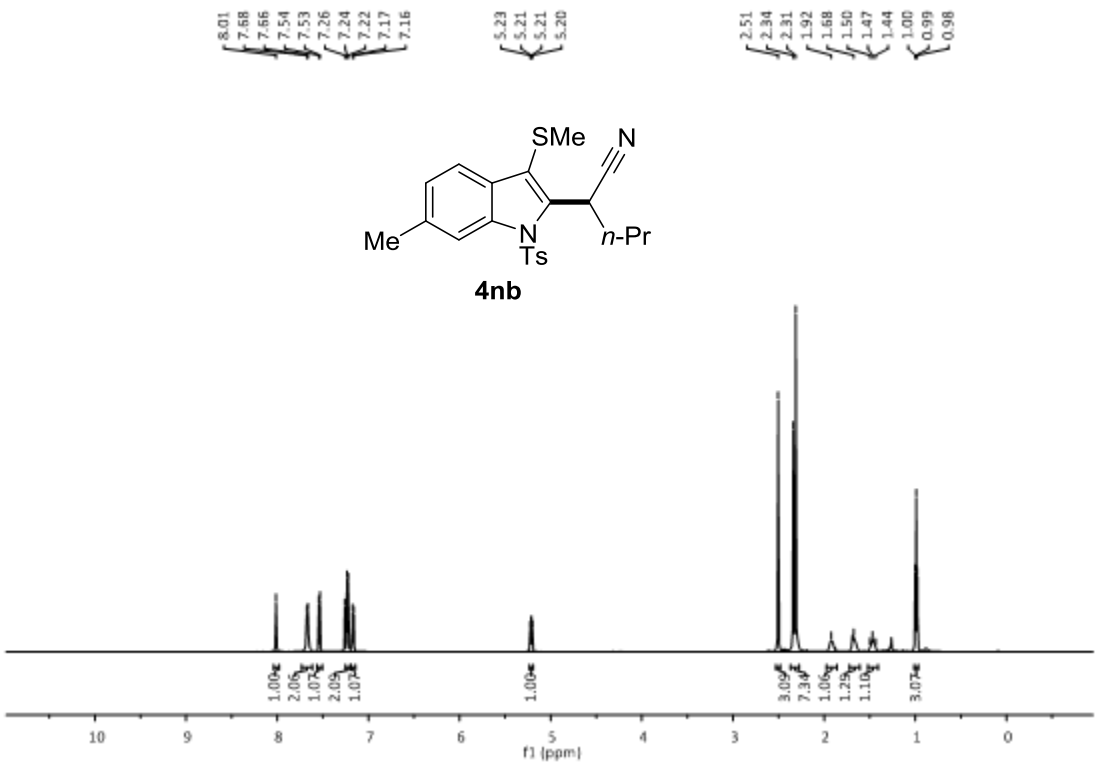
f1 (ppm)

4mb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5.21
5.20
2.51
2.34
2.31
1.92
1.68
1.50
1.47
1.44
1.00
0.99
0.98
SMe
N
Me
N
Ts
n-Pr
1.00
2.05
1.07
2.05
1.07
1.00
3.09
7.34
1.06
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3
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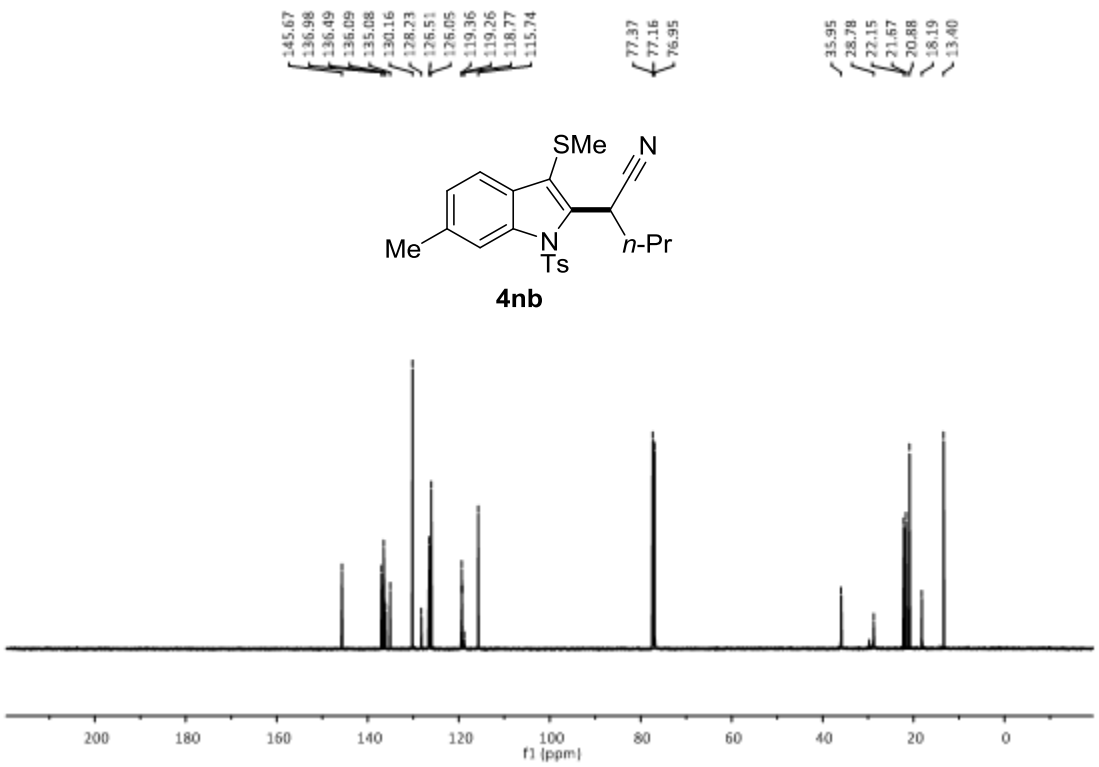
0
f1 (ppm)

4nb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77.37
77.16
76.95
35.95
28.78
22.15
21.67
20.88
18.19
13.40
SMe
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Me
N
Ts
n-Pr
4nb
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100
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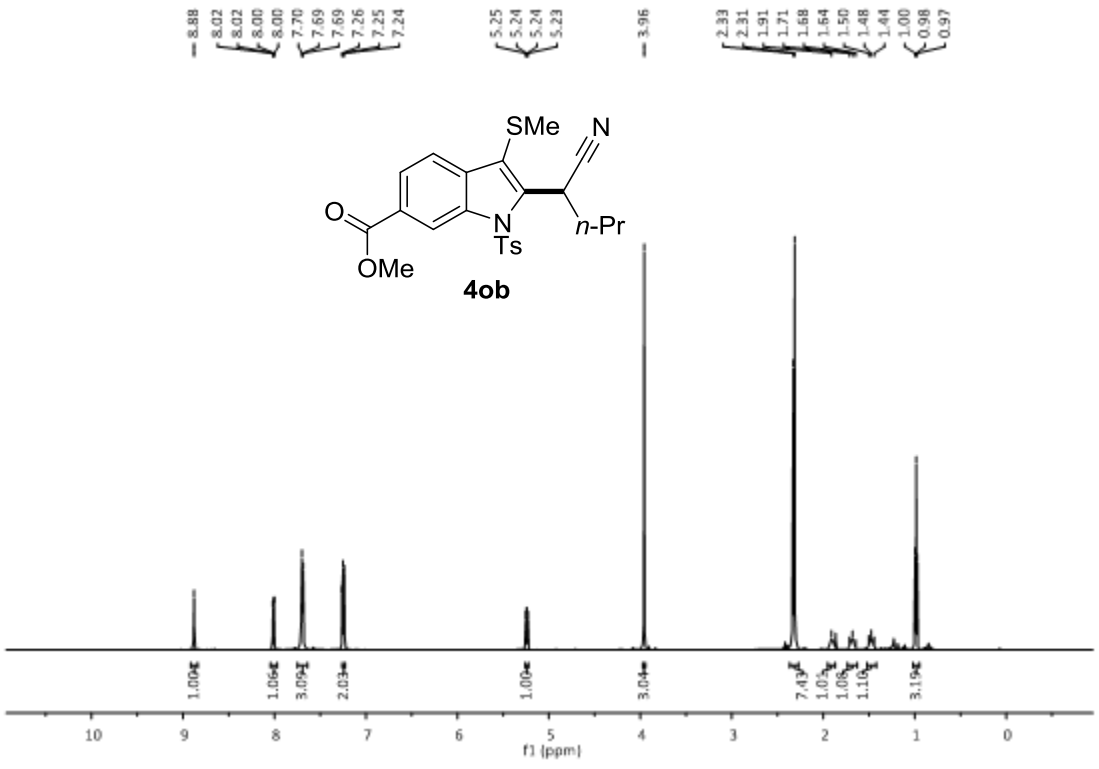
f1 (ppm)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7.24
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5.24
5.24
5.23
3.96
2.33
2.31
1.91
1.71
1.68
1.64
1.50
1.48
1.44
1.00
0.98
0.97
SMe
N
O
N
Ts
n-Pr
OMe
4ob
1.00
1.06
3.09
2.03
1.00
3.04
7.49
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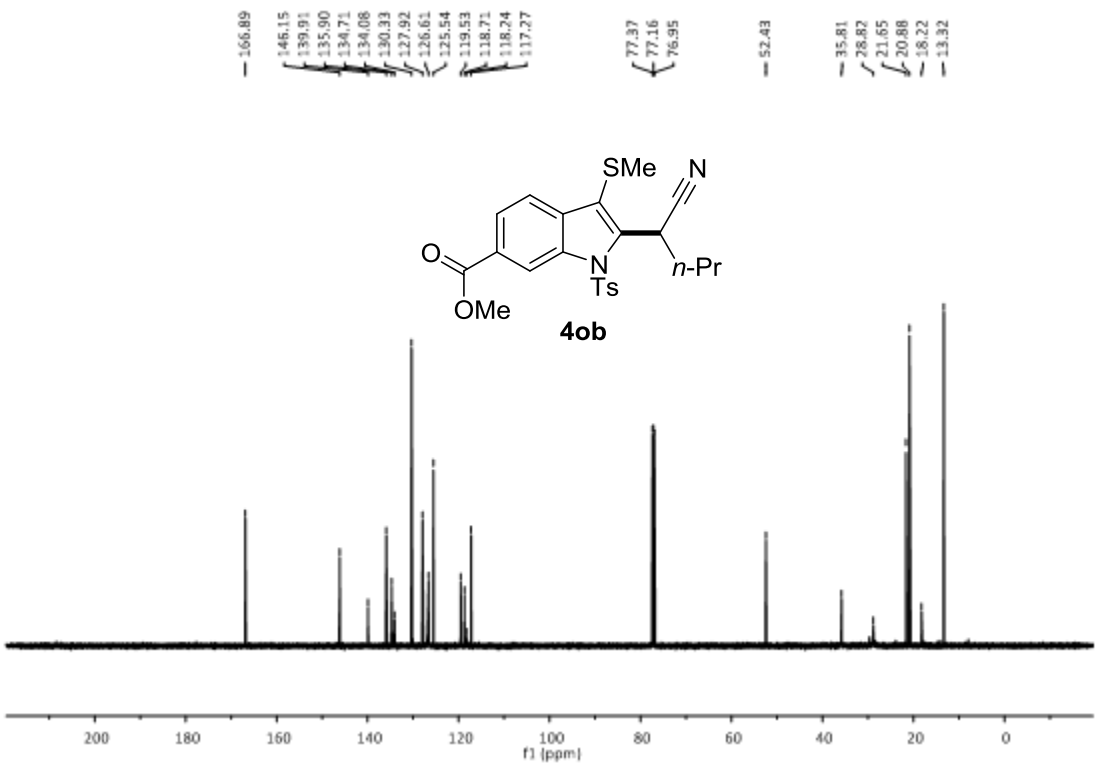
f1 (ppm)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117.27
77.37
77.16
76.95
52.43
35.81
28.82
21.65
20.88
18.22
13.32
SMe
N
O
N
n-Pr
Ts
OMe
4ob
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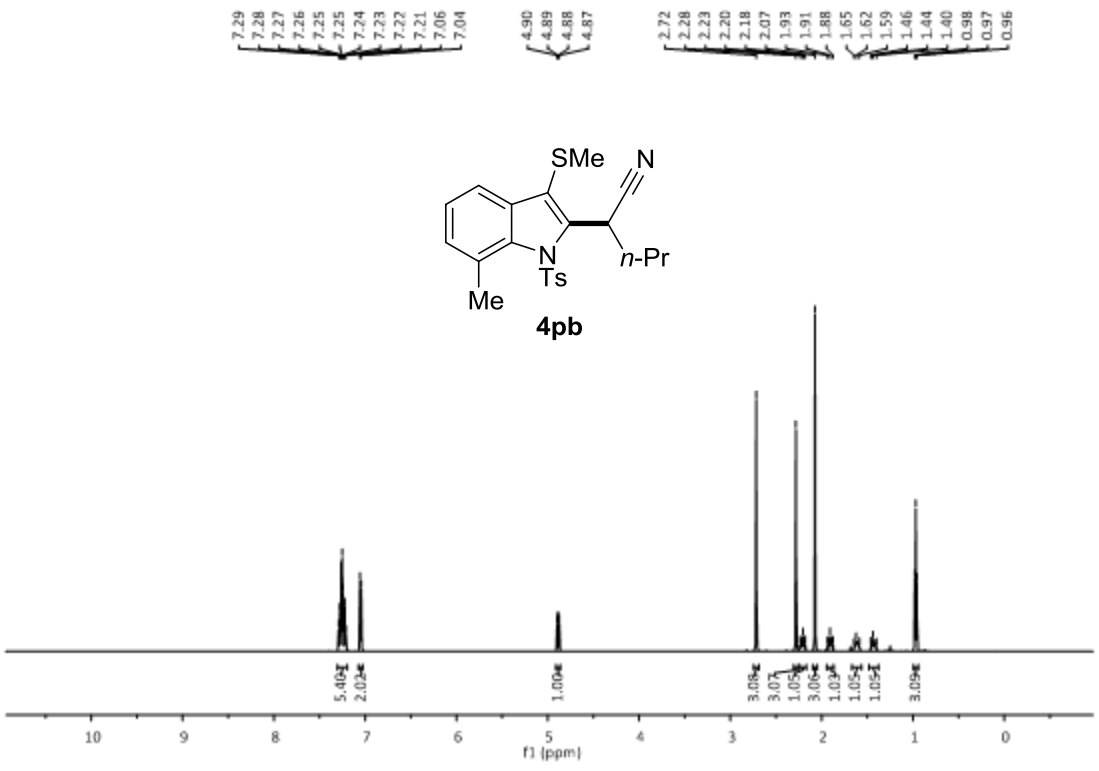
f1 (ppm)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7.23
7.22
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7.06
7.04
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4.89
4.88
4.87
2.72
2.28
2.23
2.20
2.18
2.07
1.93
1.91
1.88
1.65
1.62
1.59
1.46
1.44
1.40
0.98
0.97
0.96
SMe
N
N
n-Pr
Ts
Me
4pb
5.40
2.02
1.00
3.08
3.07
1.05
3.06
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3.09
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9
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7
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5
4
3
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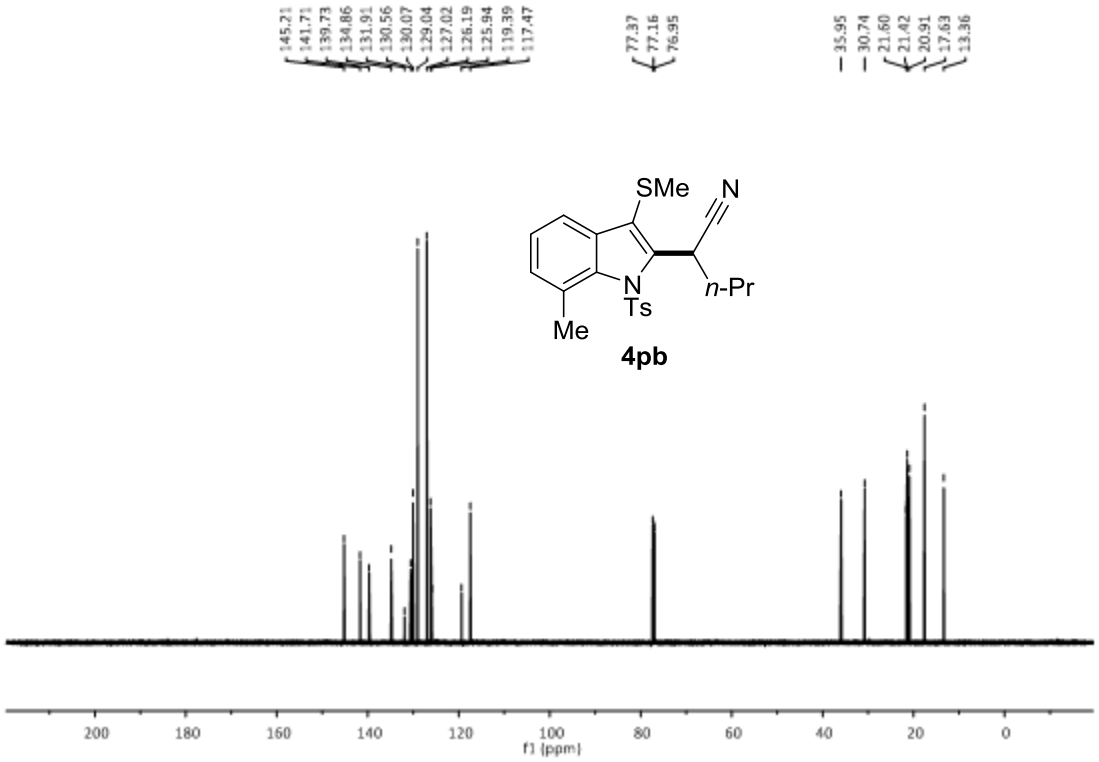
0
f1 (ppm)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77.37
77.16
76.95
35.95
30.74
21.60
21.42
20.91
17.63
13.36
SMe
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Ts
Me
4pb
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140
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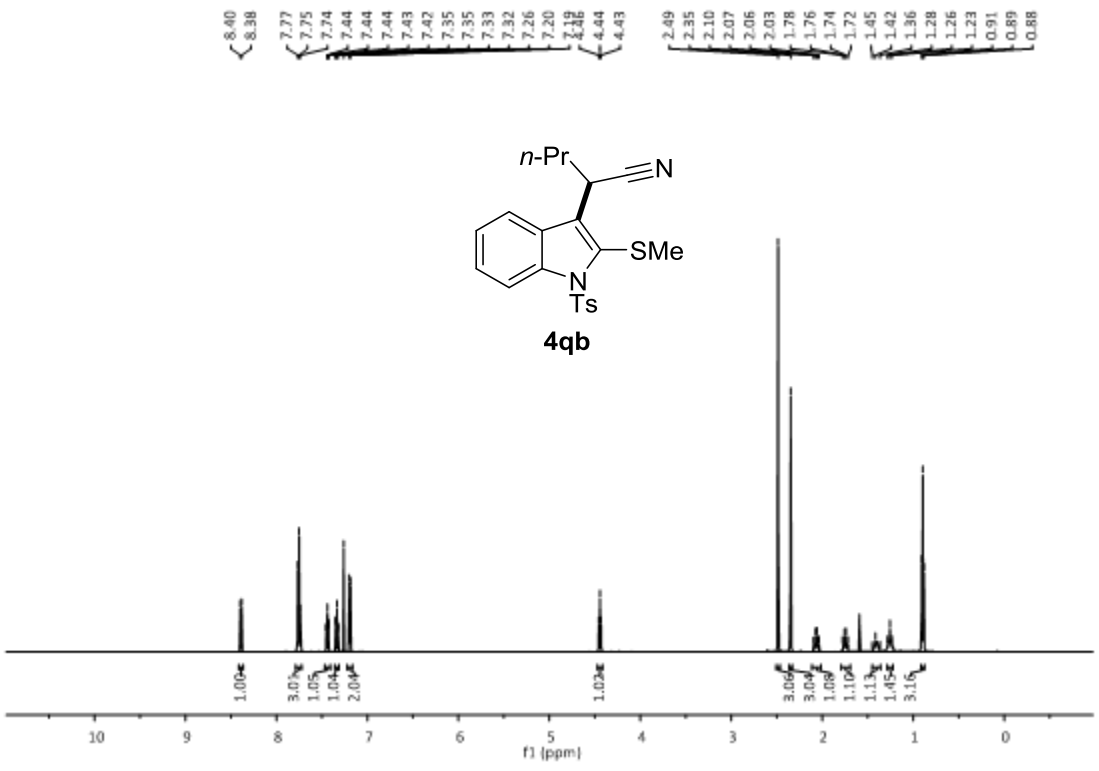
f1 (ppm)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7.42
7.35
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7.33
7.32
7.26
7.20
7.19
4.44
4.43
2.49
2.35
2.10
2.07
2.06
2.03
1.78
1.76
1.74
1.72
1.45
1.42
1.36
1.28
1.26
1.23
0.91
0.89
0.88
n-Pr
N
SMe
N
Ts
4qb
1.00
3.01
1.05
1.04
2.04
1.03
3.09
3.04
1.09
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9
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5
4
3
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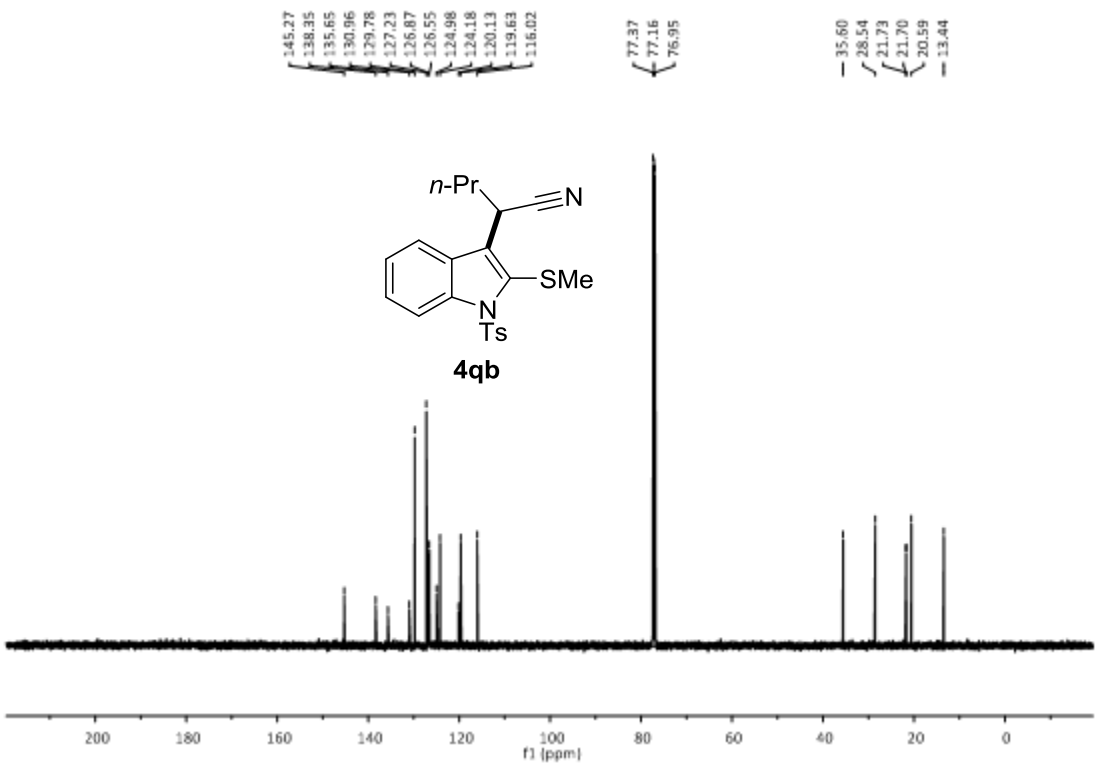
f1 (ppm)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120.13
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116.02
77.37
77.16
76.95
35.60
28.54
21.73
21.70
20.59
13.44
n-Pr
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4qb
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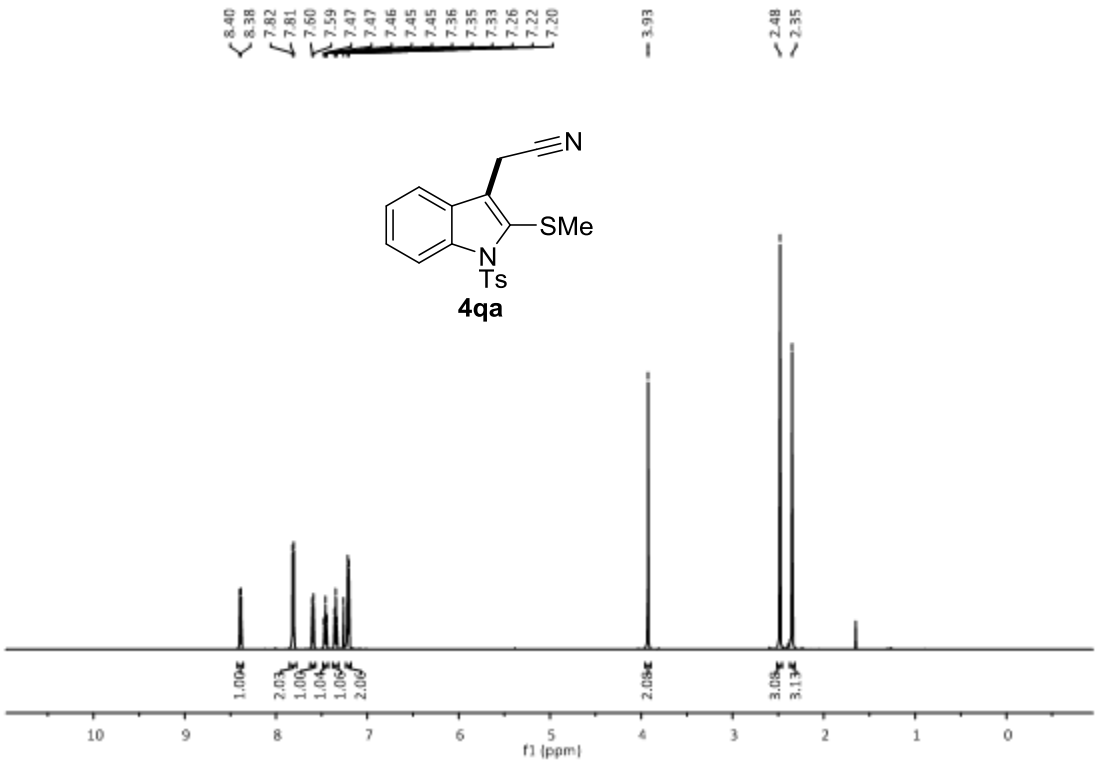
f1 (ppm)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7.35
7.33
7.26
7.22
7.20
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2.48
2.35
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SMe
N
Ts
4qa
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2.03
1.00
1.04
1.06
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3.13
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7
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5
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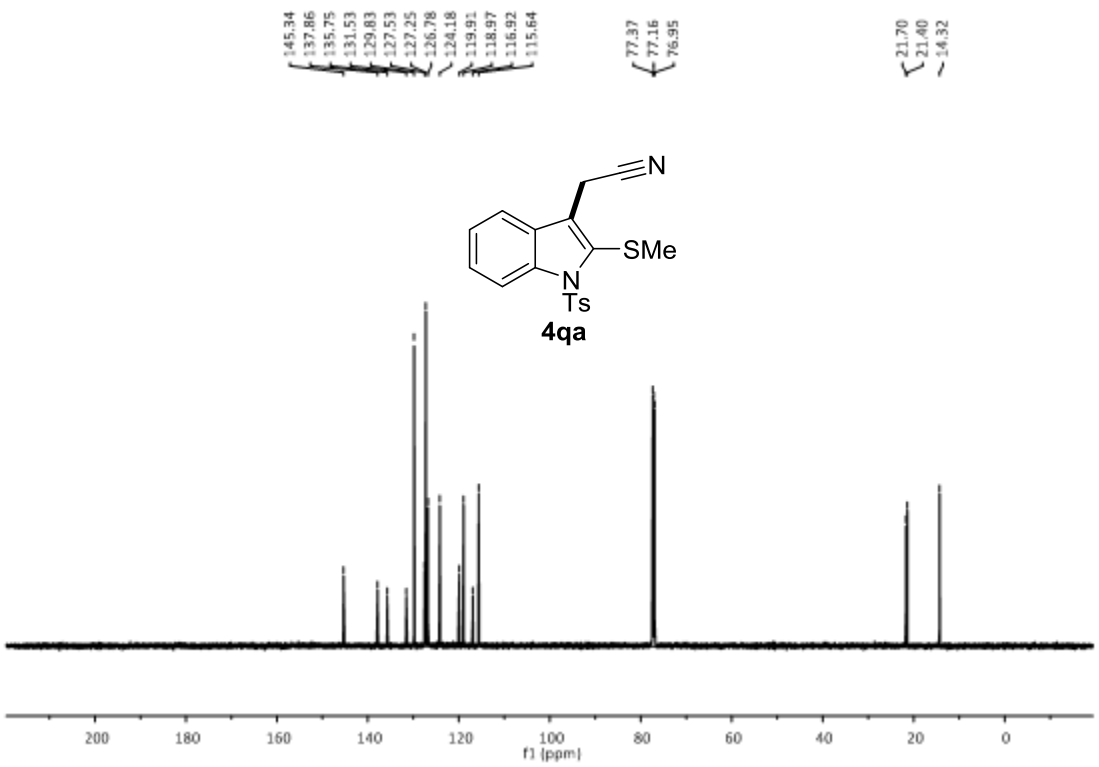
f1 (ppm)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77.16
76.95
21.70
21.40
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N
Ts
4qa
200
180
160
140
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100
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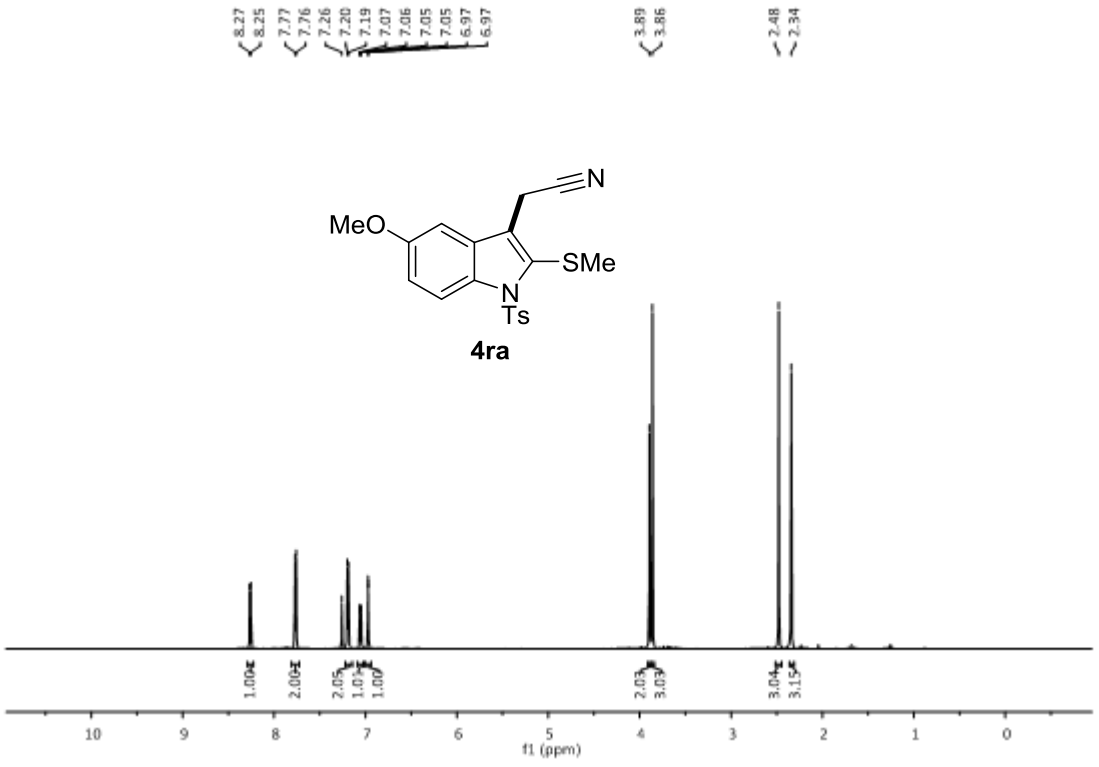
20
0
f1 (ppm)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7.05
7.05
6.97
6.97
3.89
3.86
2.48
2.34
N
MeO
SMe
N
Ts
4ra
1.00
2.00
2.05
1.03
1.00
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3.04
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7
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5
4
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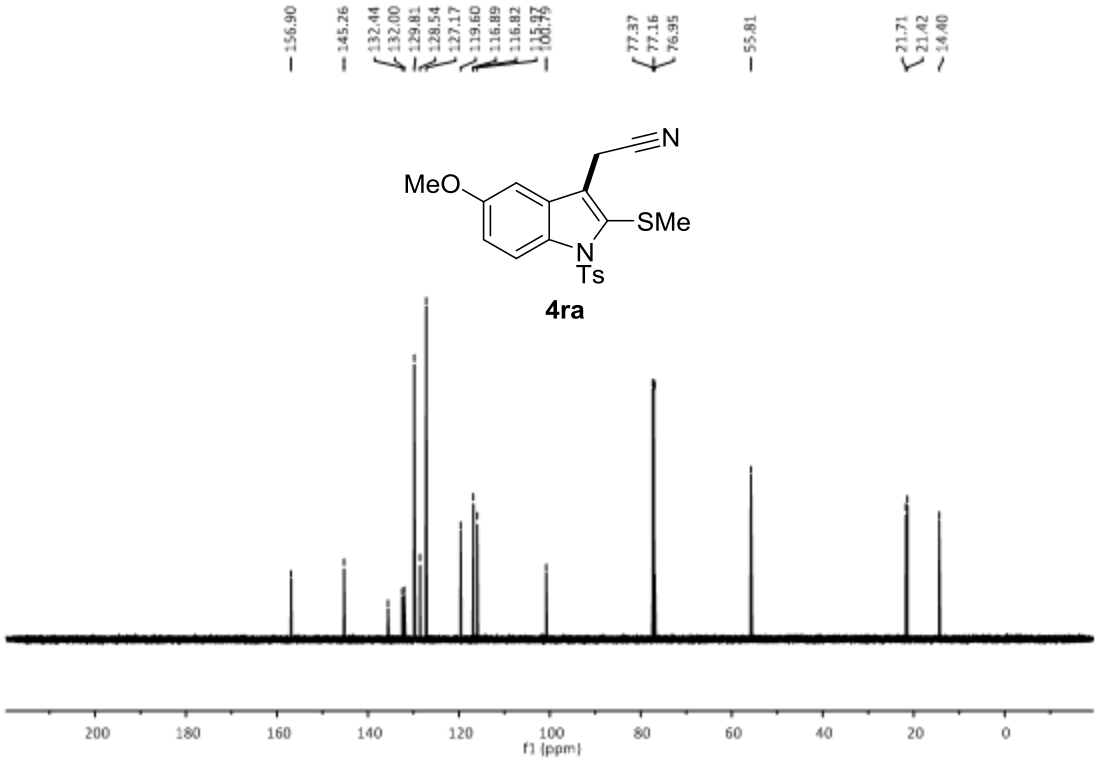
f1 (ppm)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100.79
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77.16
76.95
55.81
21.71
21.42
14.40
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SMe
N
Ts
200
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160
140
120
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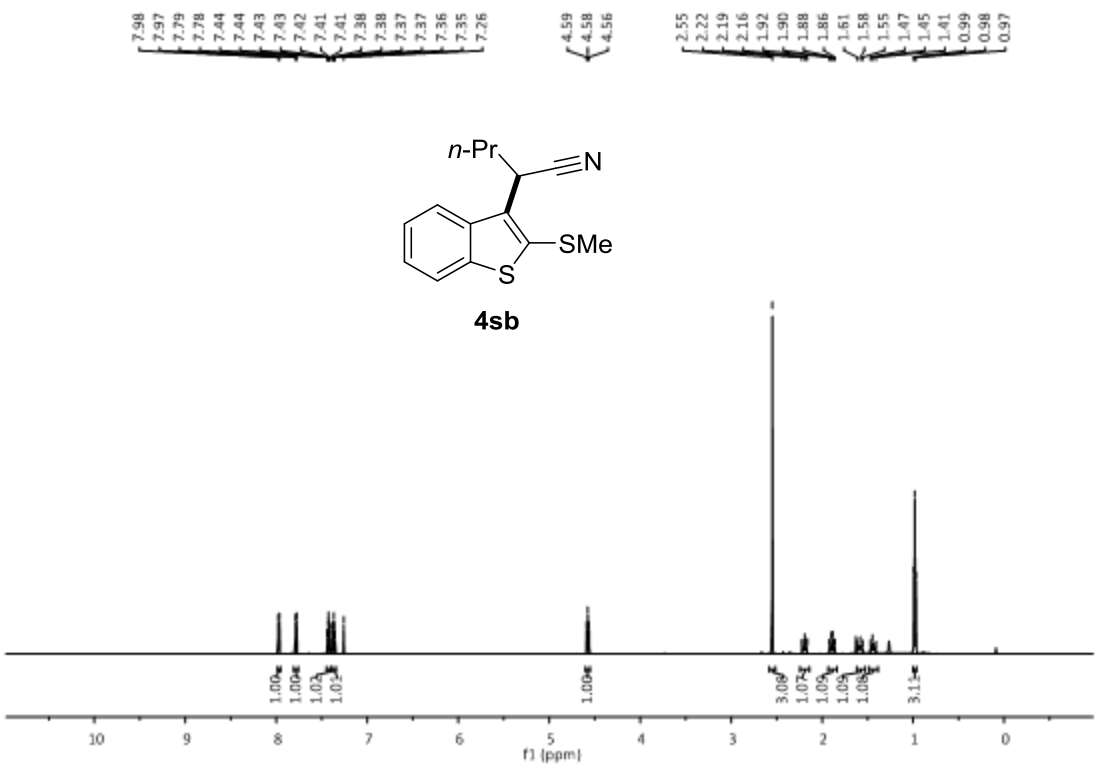
80
60
40
20
0
f1 (ppm)

4ra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7.37
7.37
7.36
7.35
7.26
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4.58
4.56
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2.22
2.19
2.16
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1.90
1.88
1.86
1.61
1.58
1.55
1.47
1.45
1.41
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0.98
0.97
n-Pr
N
SMe
S
1.00
1.00
1.02
1.03
1.00
3.09
1.07
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3
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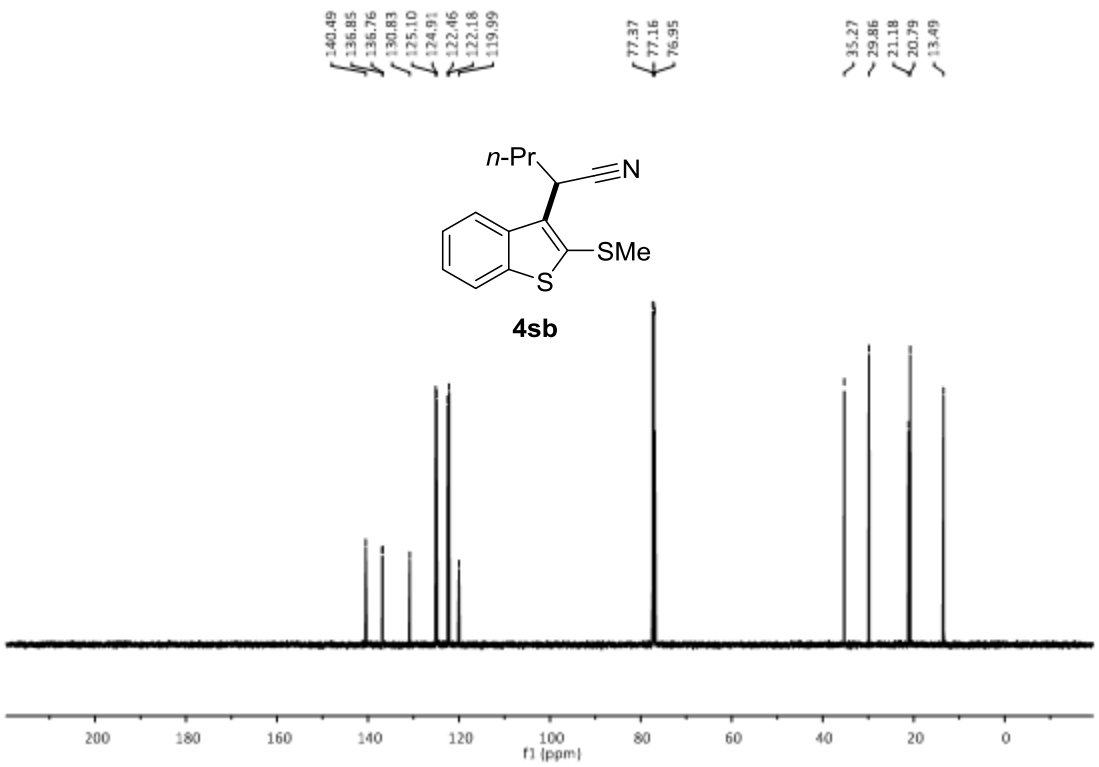
f1 (ppm)

4sb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122.18
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77.37
77.16
76.95
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29.86
21.18
20.79
13.49
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S
4sb
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100
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20
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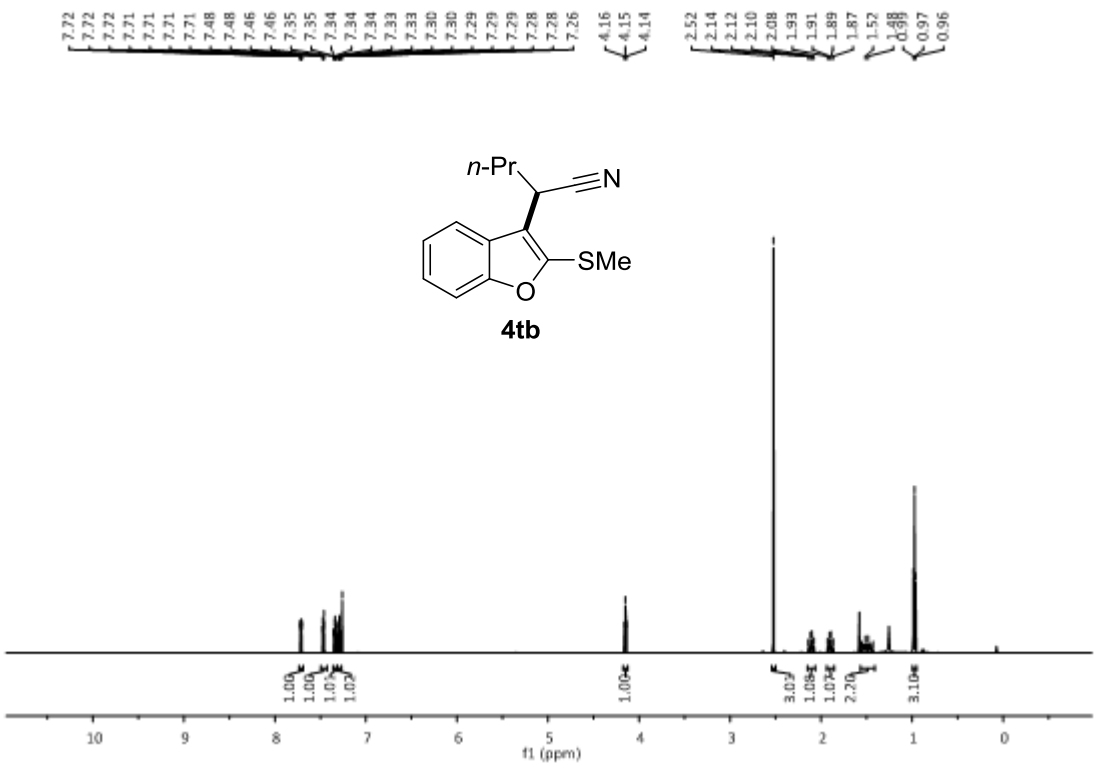
f1 (ppm)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7.46
7.46
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4.15
4.14
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2.14
2.12
2.10
2.08
1.93
1.91
1.89
1.87
1.52
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0.96
n-Pr
N
SMe
O
4tb
1.00
1.00
1.03
1.02
1.00
3.03
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3.10
10
9
8
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5
4
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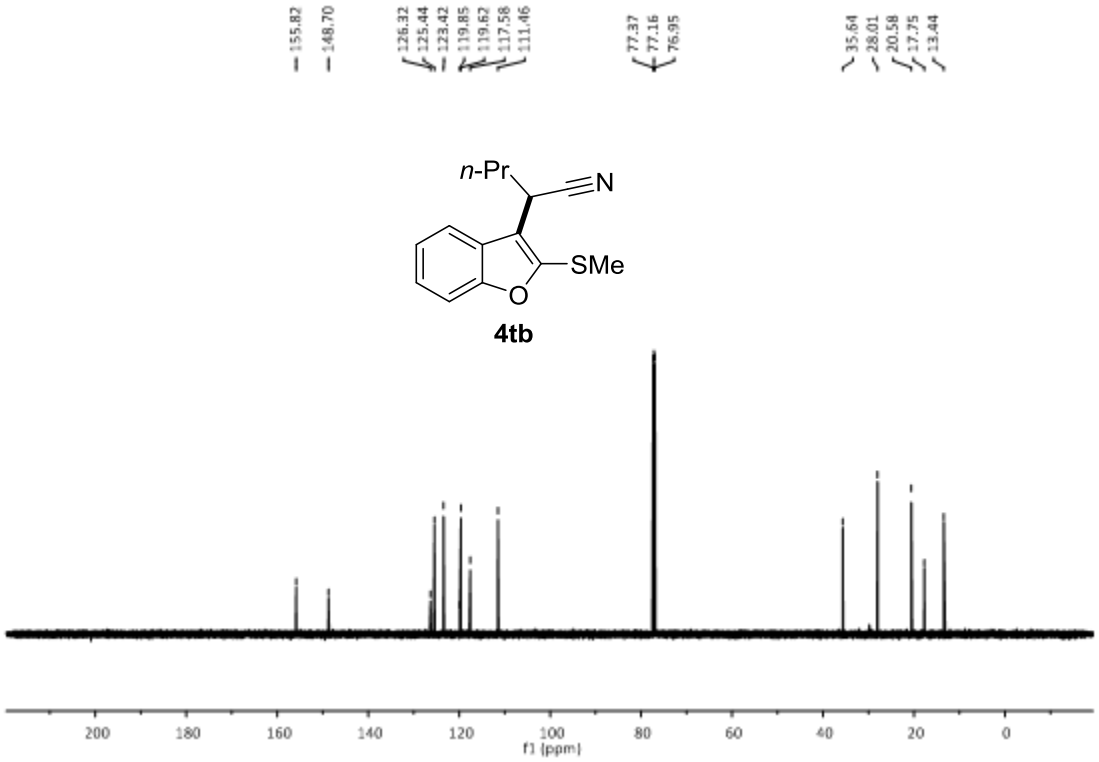
f1 (ppm)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117.58
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77.37
77.16
76.95
35.64
28.01
20.58
17.75
13.44
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N
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O
4tb
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180
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140
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100
80
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20
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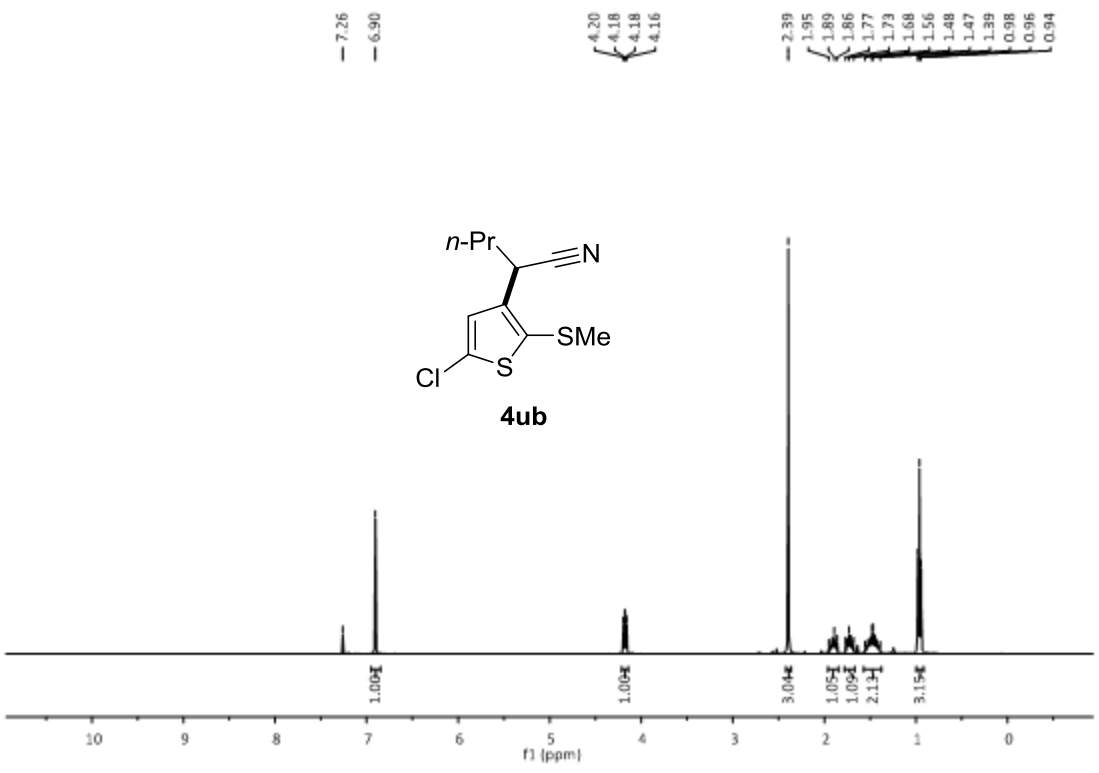
f1 (ppm)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4.16
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1.77
1.73
1.68
1.56
1.48
1.47
1.39
0.98
0.96
0.94
n-Pr
N
SMe
Cl
S
4ub
1.00
1.00
3.04
1.05
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2.13
3.15
10
9
8
7
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5
4
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1
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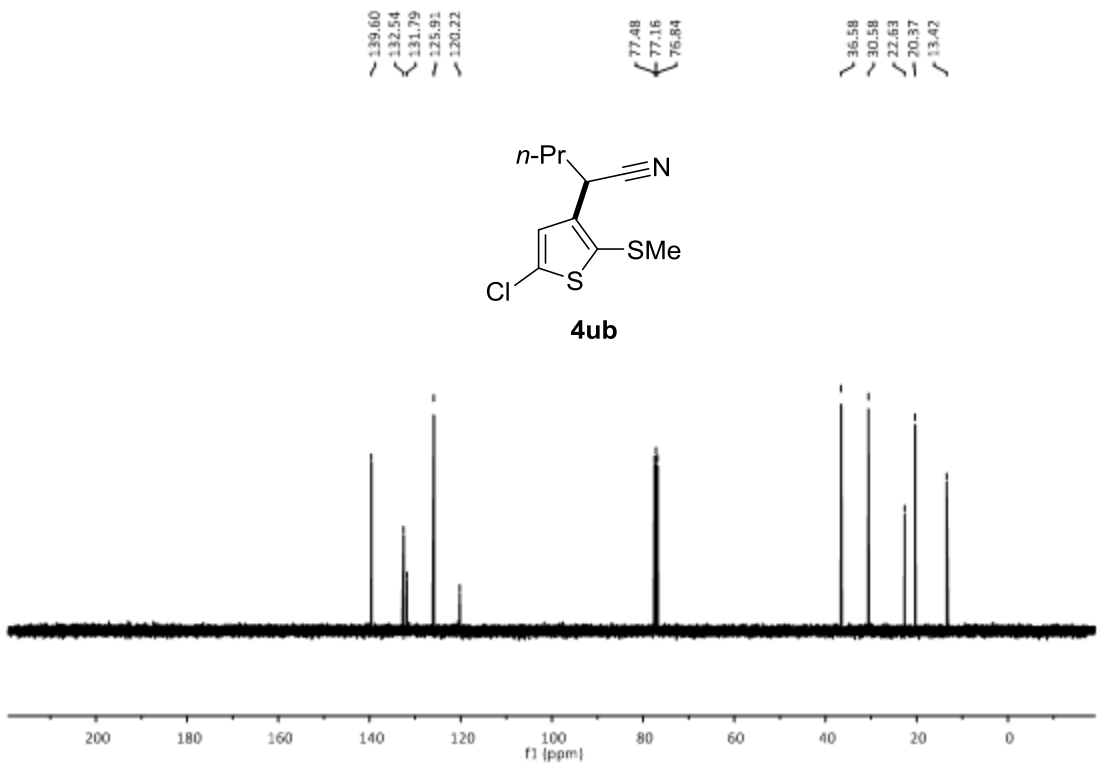
f1 (ppm)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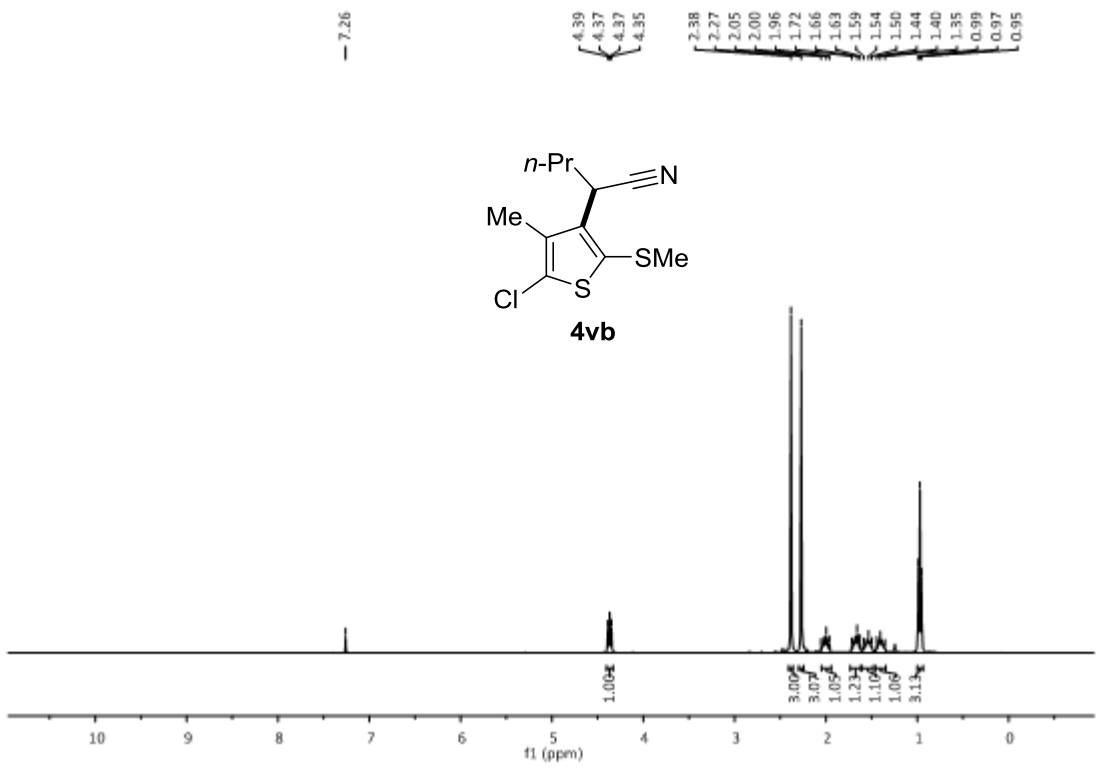
77.48
77.16
76.84
36.58
30.58
22.63
20.37
13.42
n-Pr
N
SMe
Cl
S
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

4ub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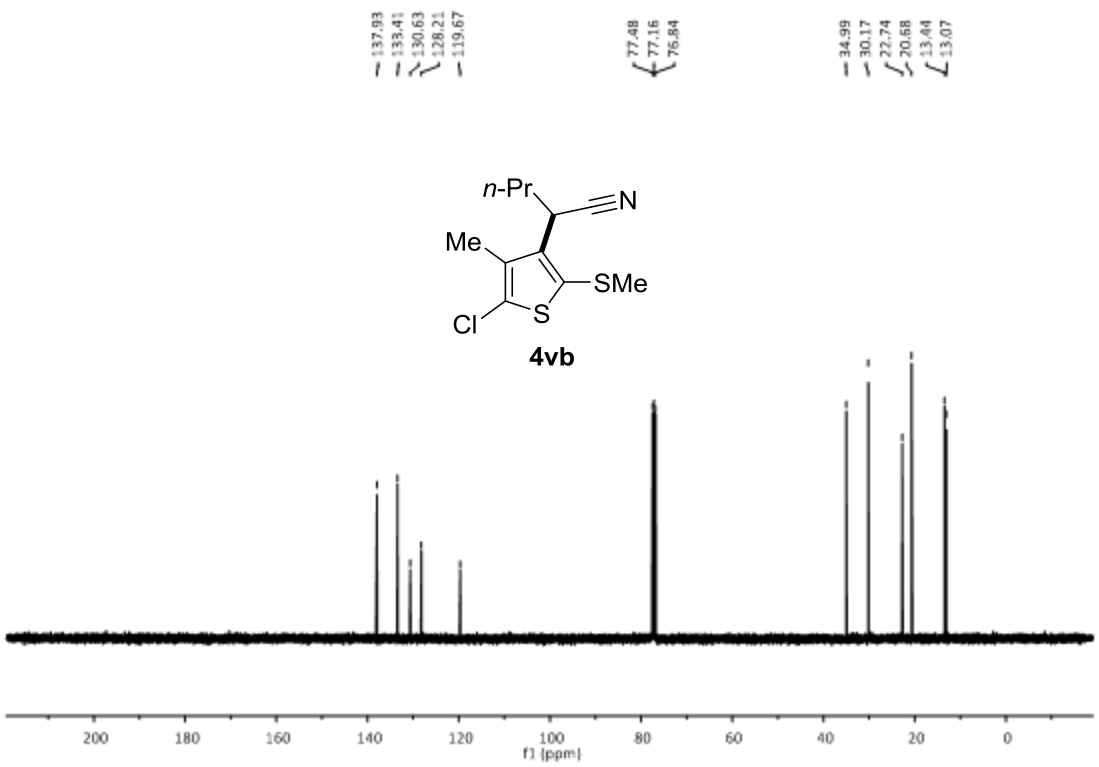
4.37
4.35
2.38
2.27
2.05
2.00
1.96
1.72
1.66
1.63
1.59
1.54
1.50
1.44
1.40
1.35
0.99
0.97
0.95
n-Pr
N
Me
SMe
Cl
S
1.00
3.00
3.07
1.09
1.21
1.10
1.06
3.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

4vb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133.41
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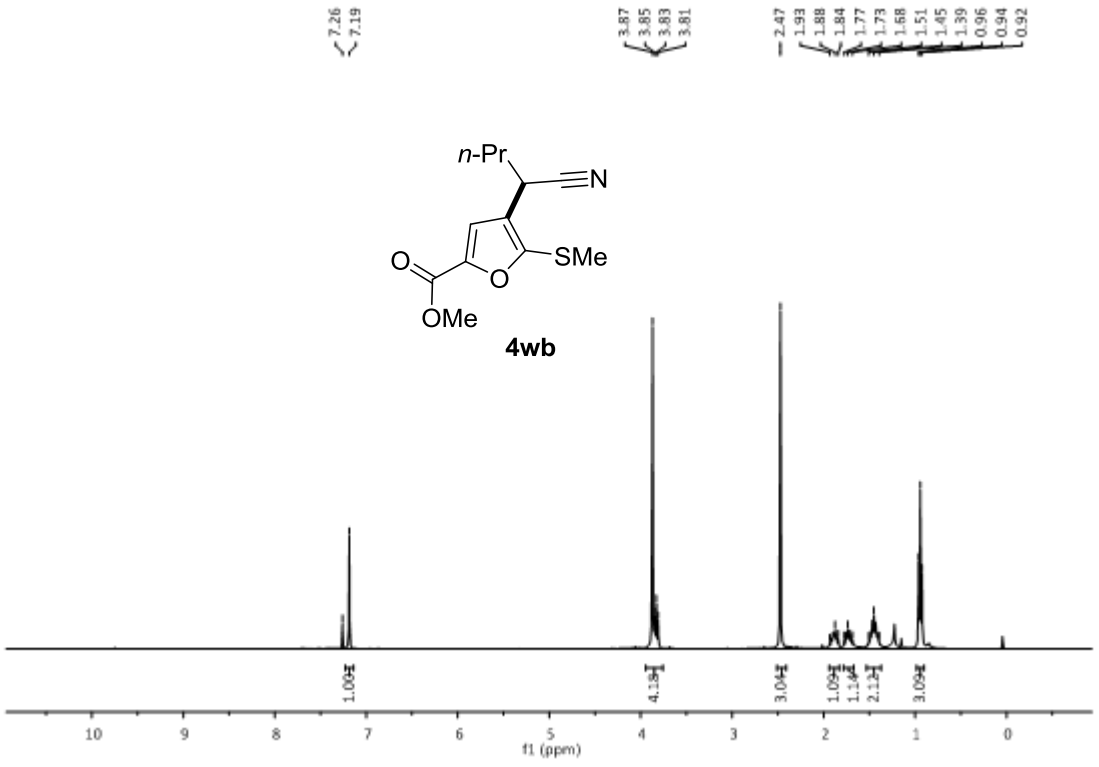
128.21
119.67
77.48
77.16
76.84
34.99
30.17
22.74
20.68
13.44
13.07
n-Pr
N
Me
SMe
Cl
S
4vb
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.19
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3.81
2.47
1.93
1.88
1.84
1.77
1.73
1.68
1.51
1.45
1.39
0.96
0.94
0.92
n-Pr
N
SMe
O
O
OMe
4wb
1.00
4.19
3.04
1.09
1.14
2.13
3.09
10
9
8
7
6
5
4
3
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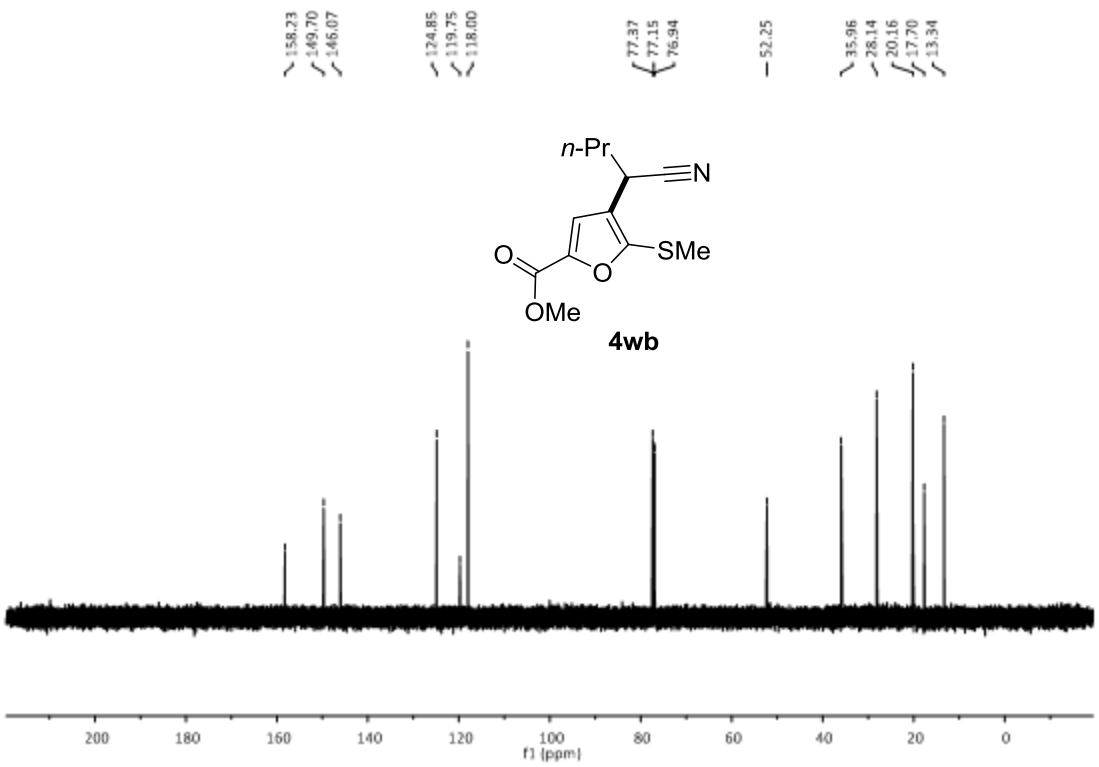
f1 (ppm)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119.75
118.00
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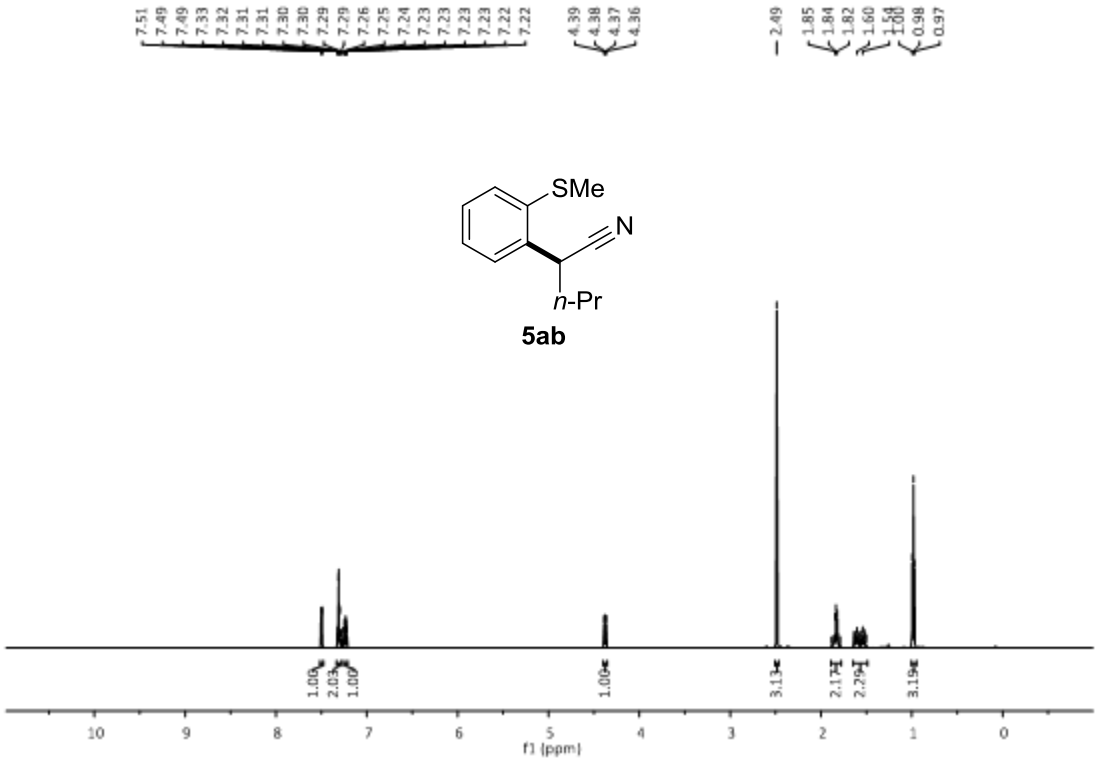
77.15
76.94
52.25
35.96
28.14
20.16
17.70
13.34
n-Pr
N
SMe
O
O
OMe
4wb
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.23
7.23
7.23
7.23
7.22
7.22
4.39
4.38
4.37
4.36
2.49
1.85
1.84
1.82
1.60
1.54
1.00
0.98
0.97
SMe
N
n-Pr
5ab
1.00
2.03
1.00
1.00
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2.29
3.19
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5
4
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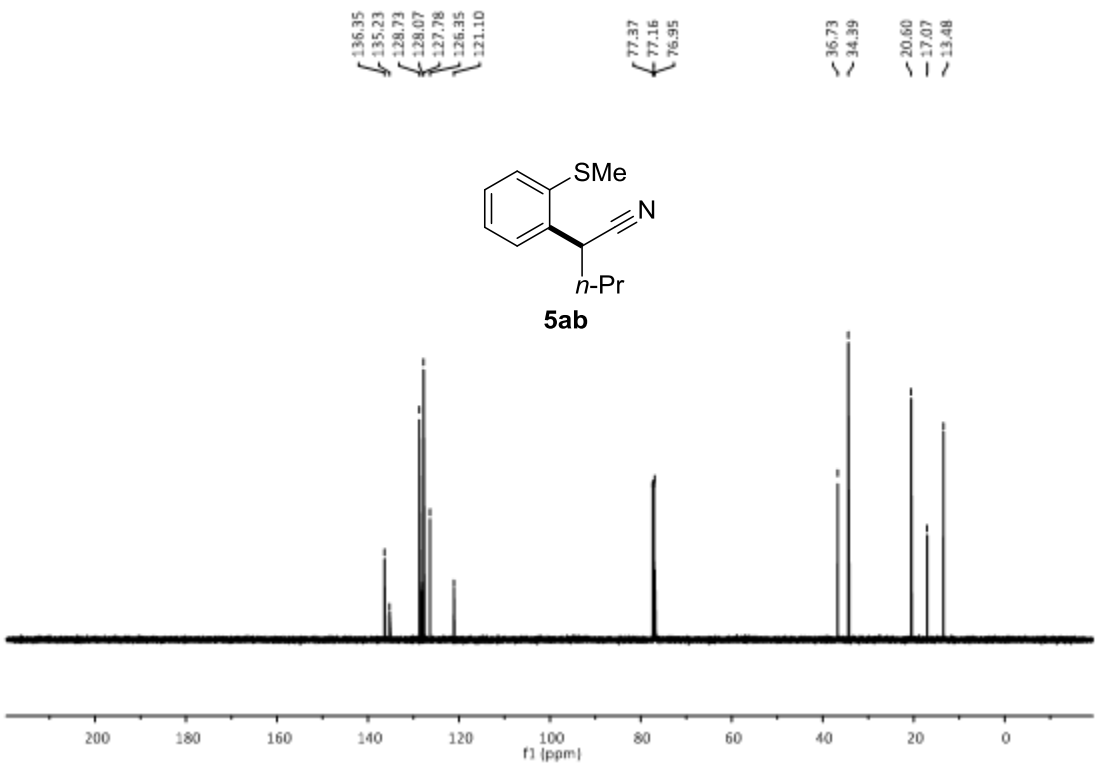
f1 (ppm)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36.73
34.39
20.60
17.07
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n-Pr
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60
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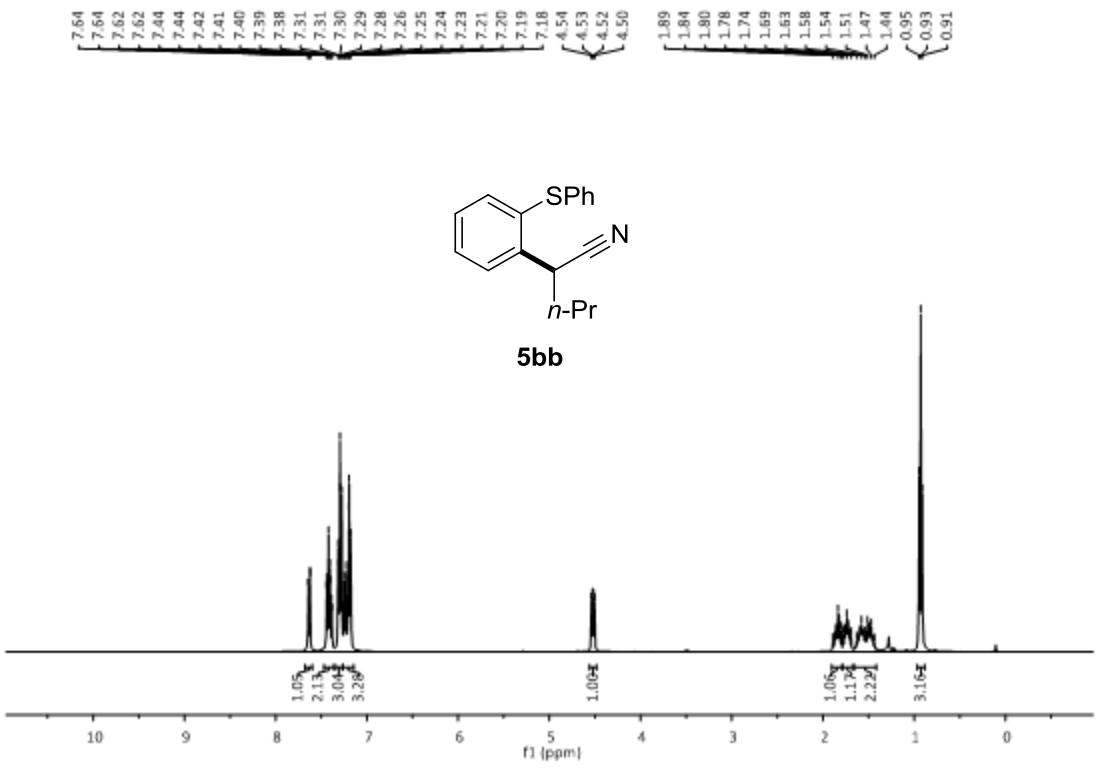
20
0
f1 (ppm)

5ab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7.23
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7.19
7.18
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4.53
4.52
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1.69
1.63
1.58
1.54
1.51
1.47
1.44
0.95
0.93
0.91
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N
n-Pr
1.05
2.13
3.04
3.28
1.00
1.06
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3
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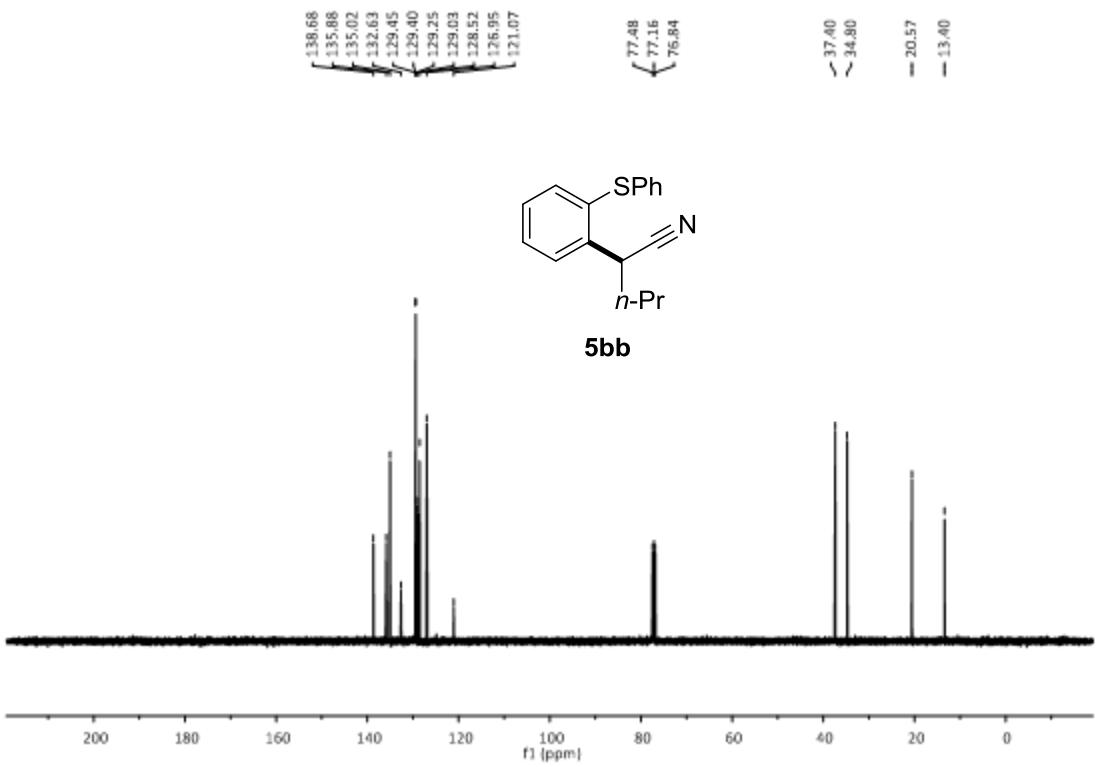
f1 (ppm)

5bb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77.48
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37.40
34.80
20.57
13.40
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n-Pr
200
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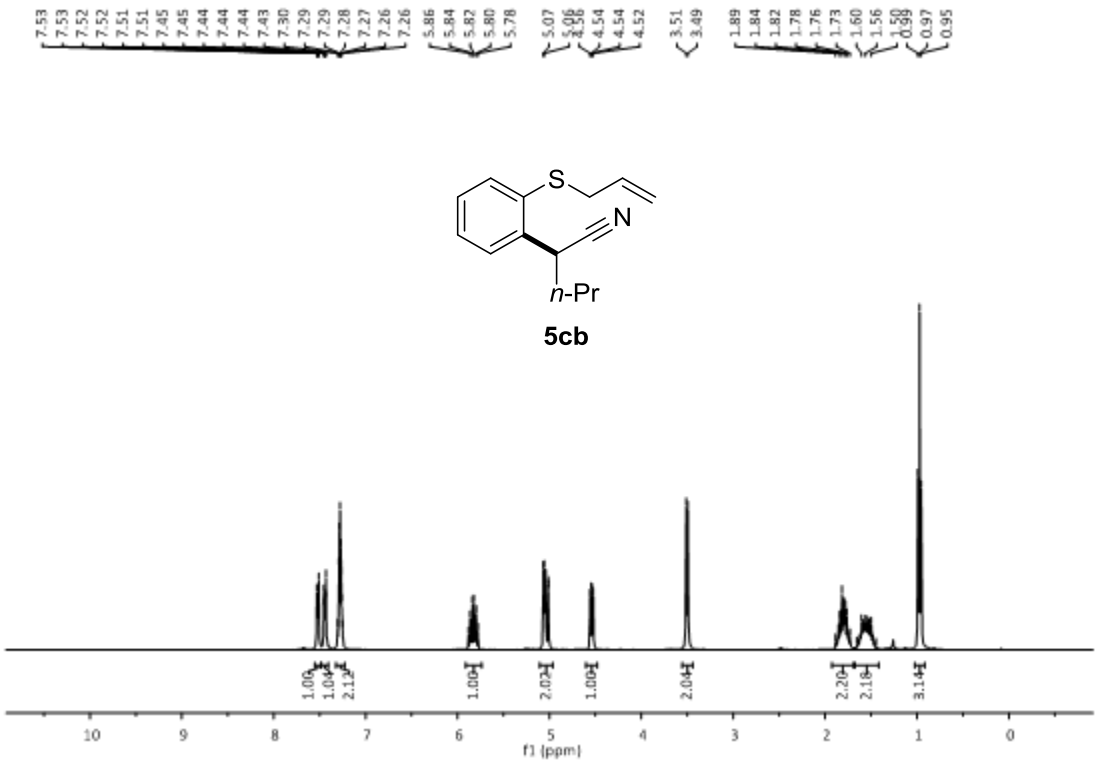
140
120
100
80
60
40
20
0
f1 (ppm)

5bb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7.29
7.29
7.28
7.27
7.26
7.26
5.86
5.84
5.82
5.80
5.78
5.07
4.54
4.54
4.52
3.51
3.49
1.89
1.84
1.82
1.78
1.76
1.73
1.60
1.56
0.97
0.95
S
N
n-Pr
1.00
1.04
2.12
1.00
2.02
1.00
2.04
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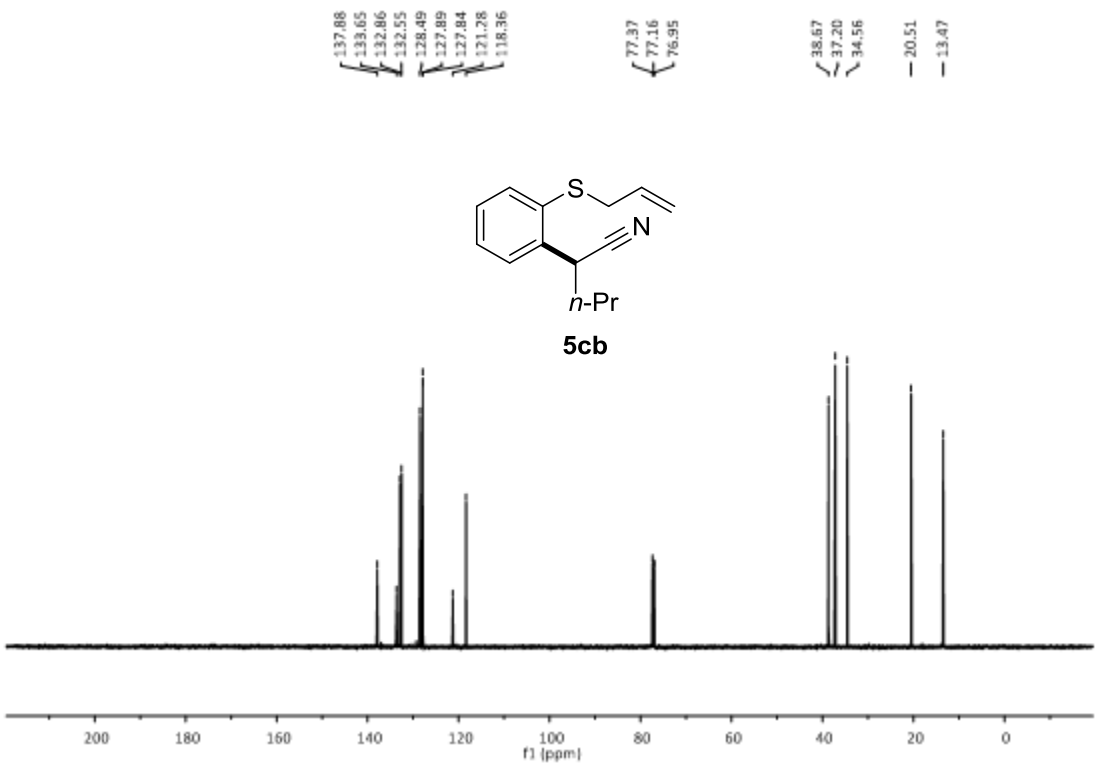
0
f1 (ppm)

5cb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127.89
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121.28
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77.37
77.16
76.95
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37.20
34.56
20.51
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n-Pr
200
180
160
140
120
100
80
60
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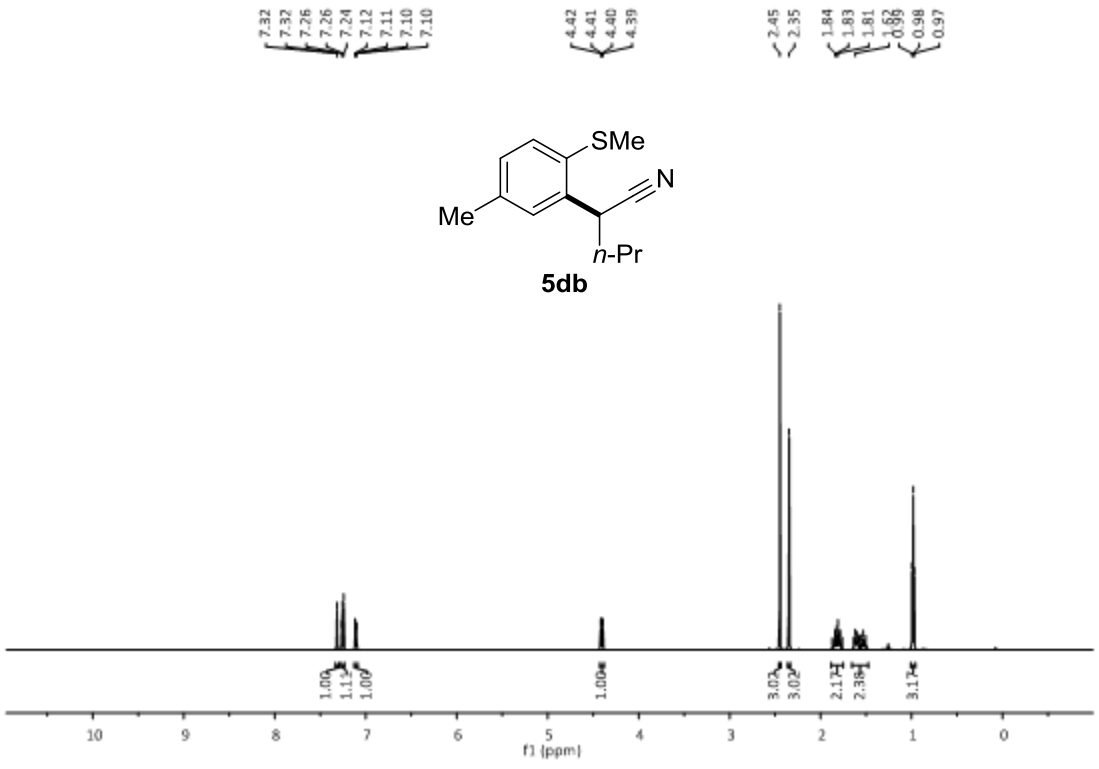
20
0
f1 (ppm)

5cb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7.10
4.42
4.41
4.40
4.39
2.45
2.35
1.84
1.83
1.81
1.62
0.98
0.98
0.97
SMe
N
Me
n-Pr
1.00
1.13
1.00
1.00
3.02
3.02
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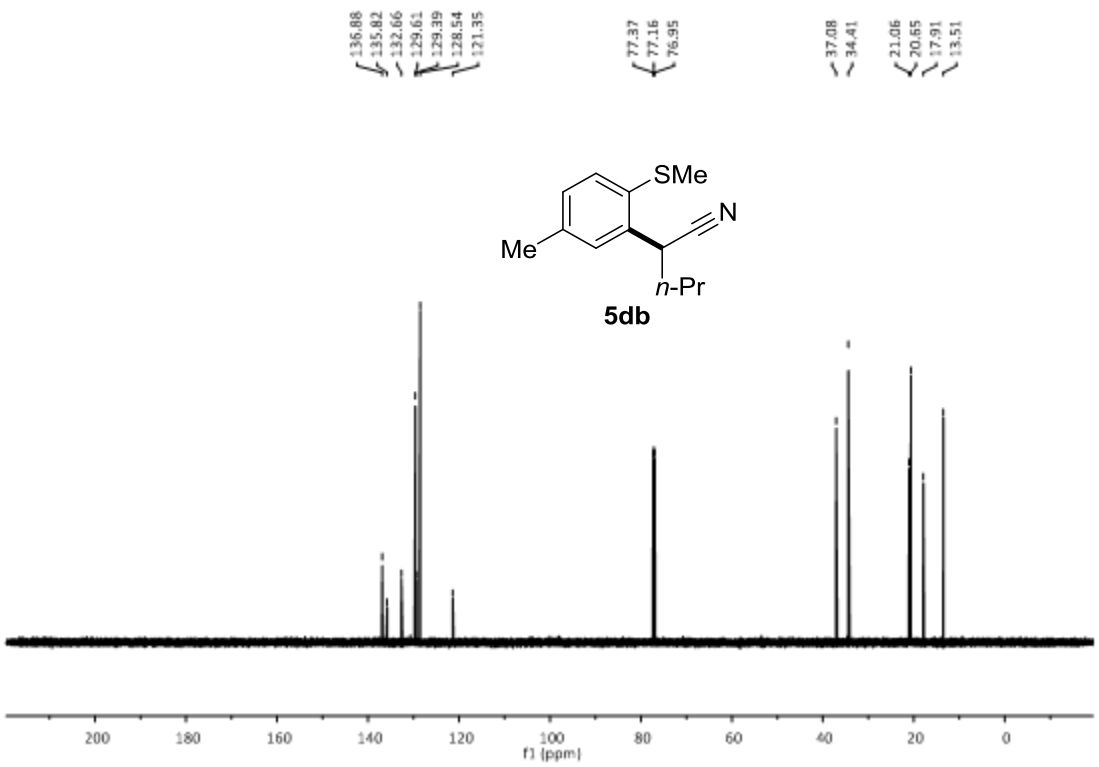
2.38
3.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

5db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128.54
121.35
77.37
77.16
76.95
37.08
34.41
21.06
20.65
17.91
13.51
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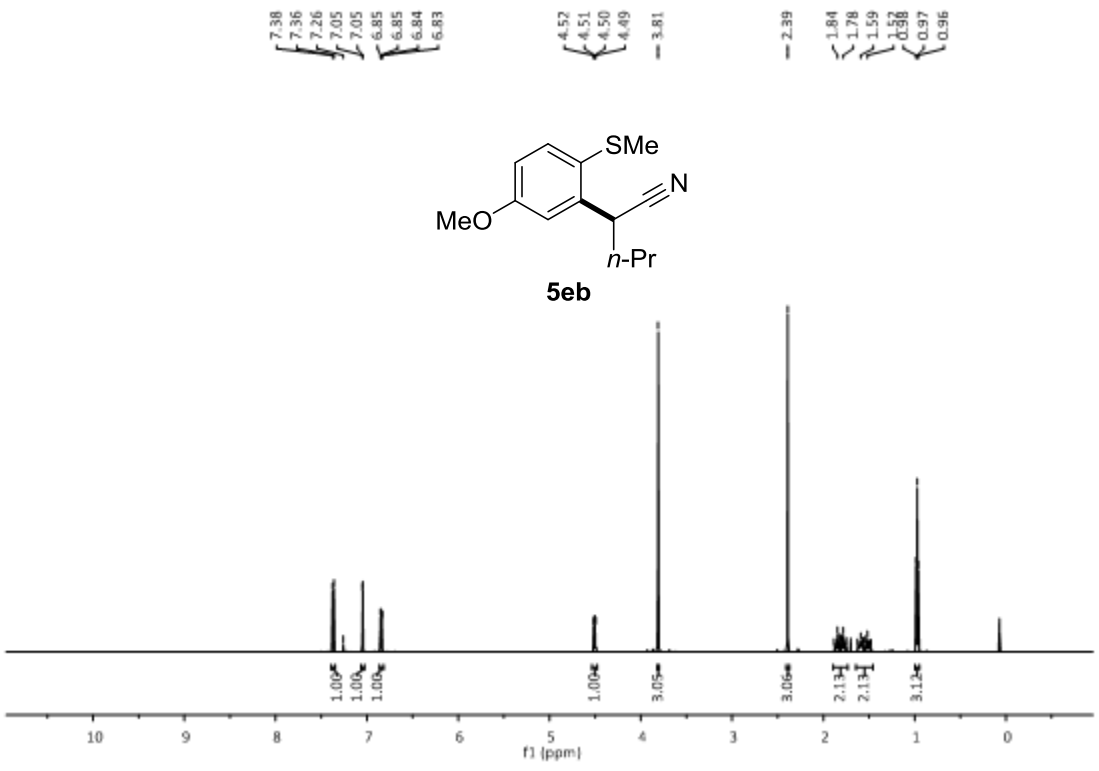
N
Me
n-Pr
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

5db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7.05
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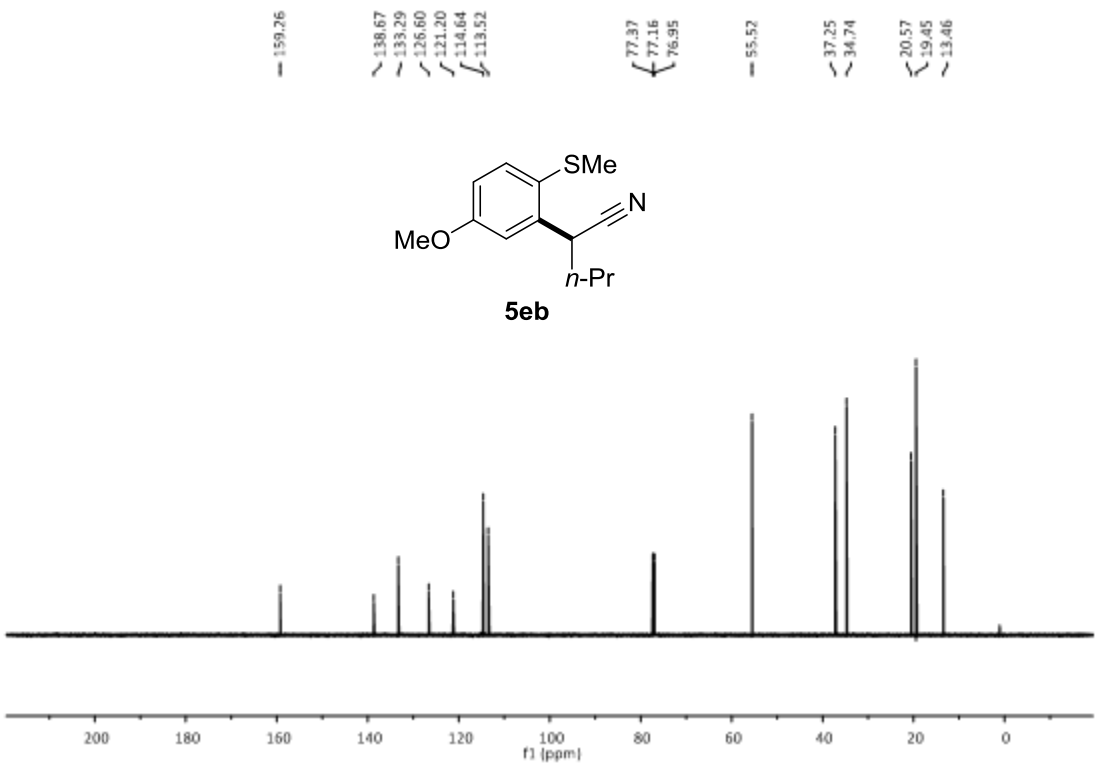
6.85
6.84
6.83
4.52
4.51
4.50
4.49
3.81
2.39
1.84
1.78
1.59
0.98
0.97
0.96
SMe
N
MeO
n-Pr
1.00
1.00
1.00
1.00
3.05
3.06
2.13
2.13
3.12
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

5eb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121.20
114.64
113.52
77.37
77.16
76.95
55.52
37.25
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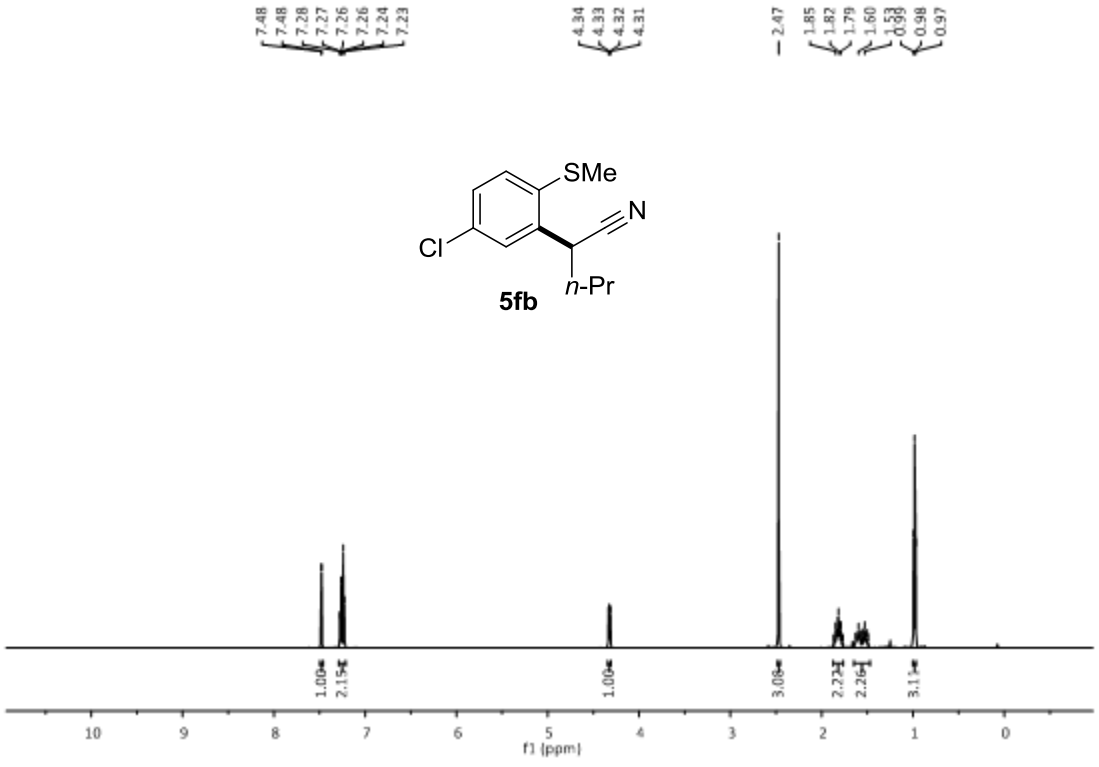
20.57
19.45
13.46
SMe
N
MeO
n-Pr
5eb
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.26
7.24
7.23
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4.33
4.32
4.31
2.47
1.85
1.82
1.79
1.60
1.53
0.98
0.97
SMe
N
Cl
n-Pr
5fb
1.00
2.15
1.00
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3.13
10
9
8
7
6
5
4
3
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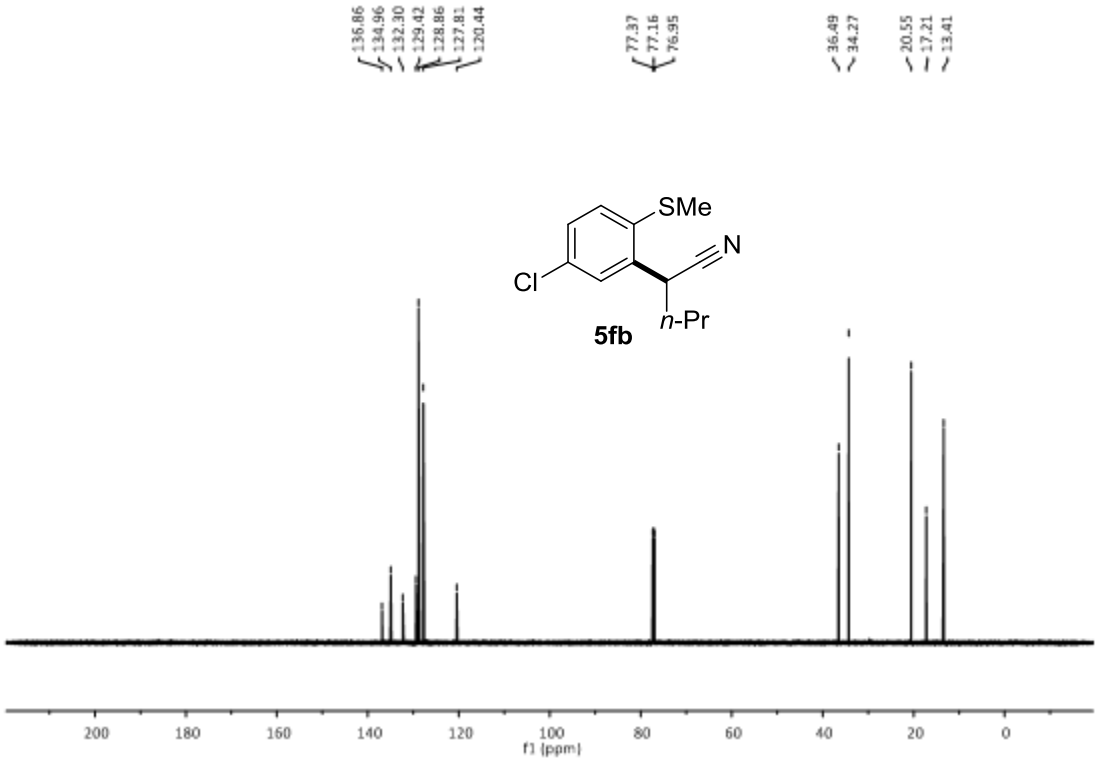
1
0
f1 (ppm)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77.37
77.16
76.95
36.49
34.27
20.55
17.21
13.41
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N
Cl
n-Pr
5fb
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180
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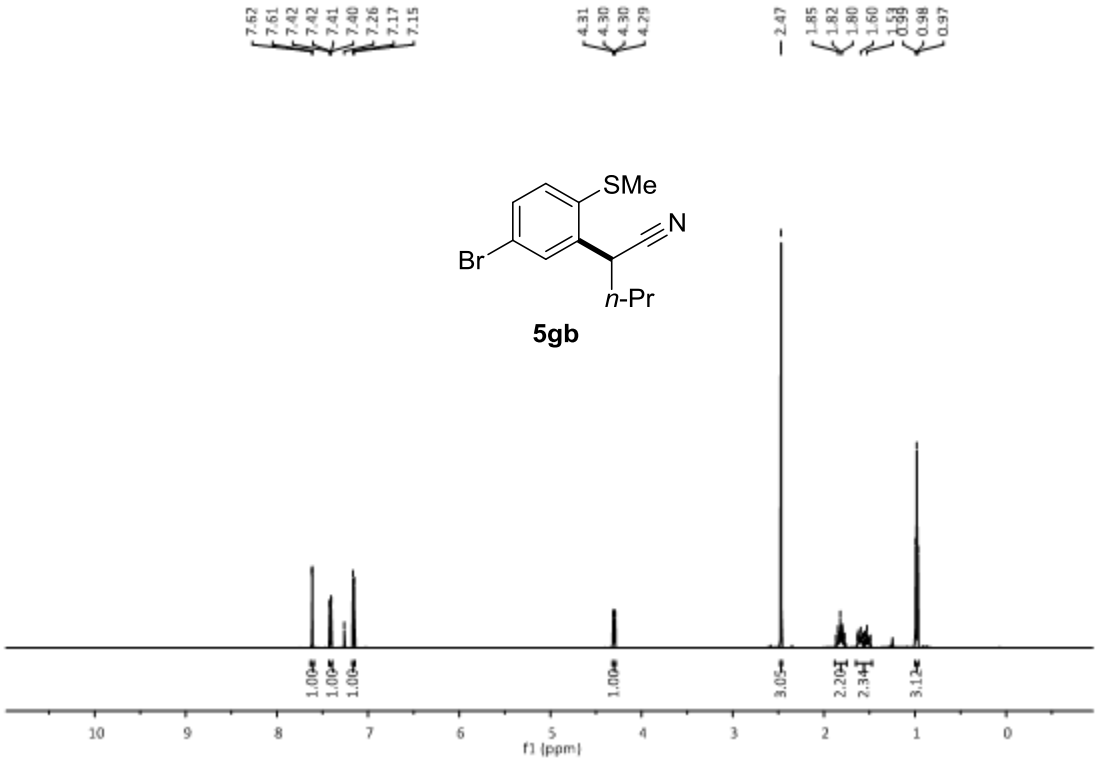
140
120
100
80
60
40
20
0
f1 (ppm)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7.42
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7.26
7.17
7.15
4.31
4.30
4.30
4.29
2.47
1.85
1.82
1.80
1.60
0.99
0.98
0.97
SMe
N
Br
n-Pr
5gb
1.00
1.00
1.00
1.00
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3.12
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9
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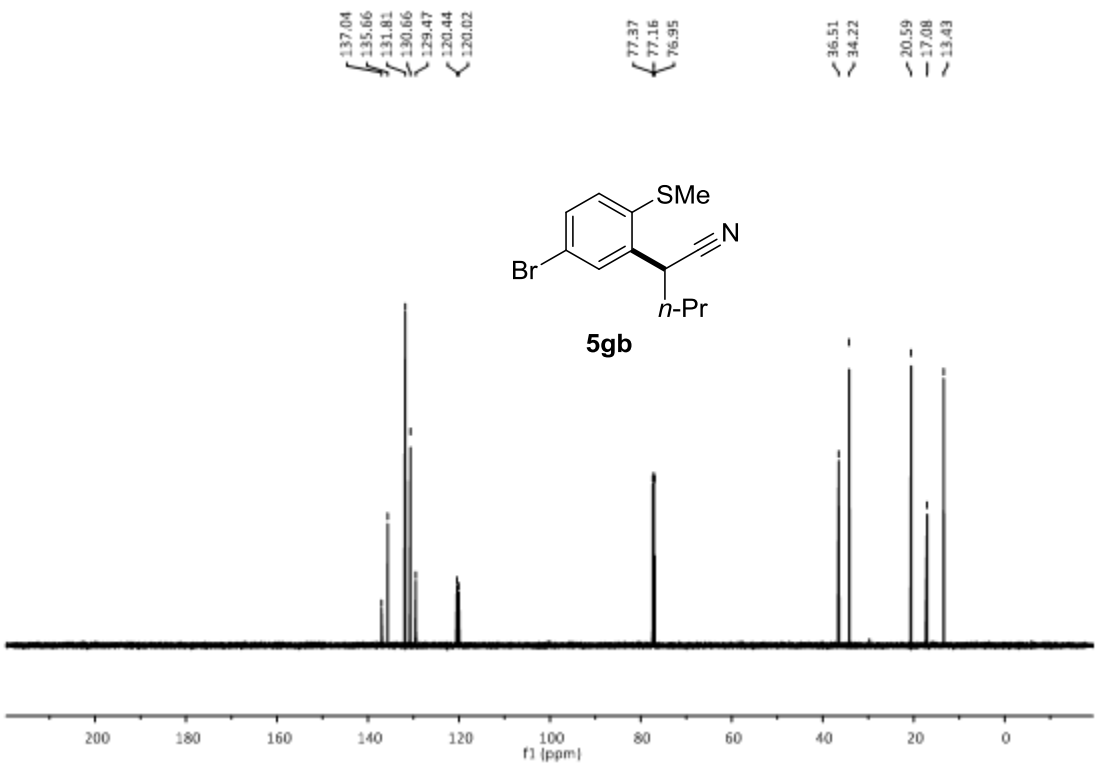
5
4
3
2
1
0
f1 (ppm)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36.51
34.22
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17.08
13.43
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N
Br
n-Pr
5gb
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180
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140
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100
80
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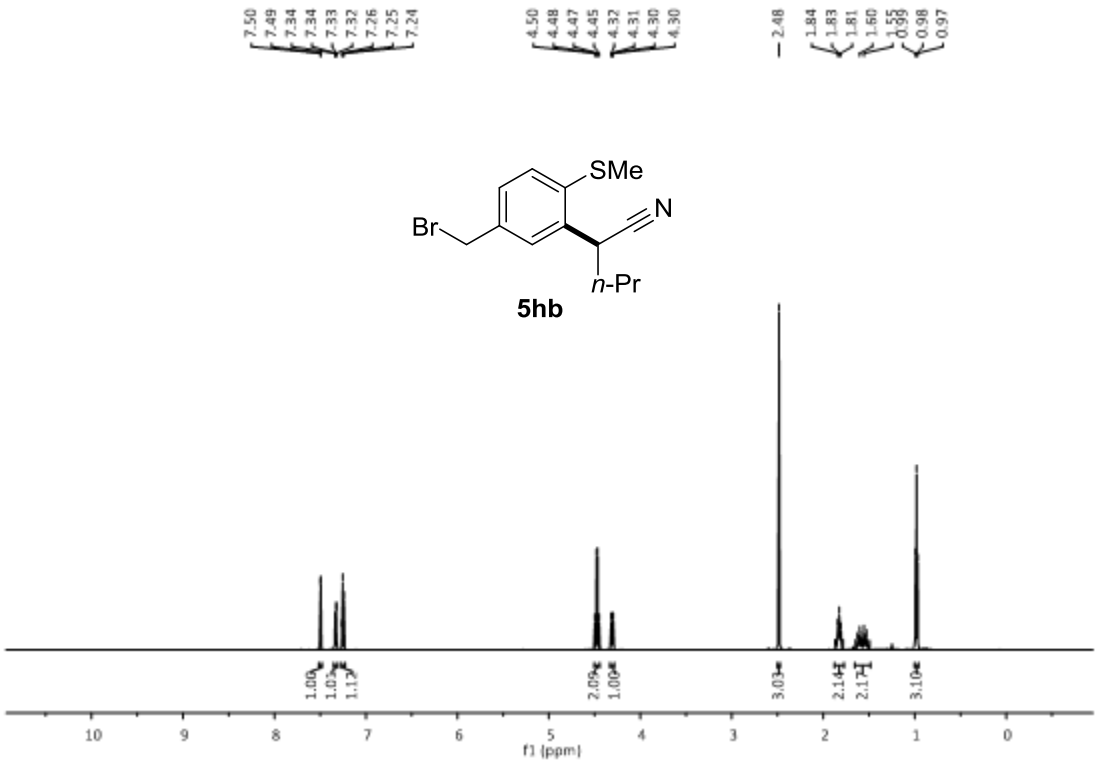
40
20
0
f1 (ppm)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4.47
4.45
4.32
4.31
4.30
4.30
2.48
1.84
1.83
1.81
1.60
1.55
0.99
0.98
0.97
SMe
N
Br
n-Pr
5hb
1.00
1.03
1.17
2.09
1.00
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3.10
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5
4
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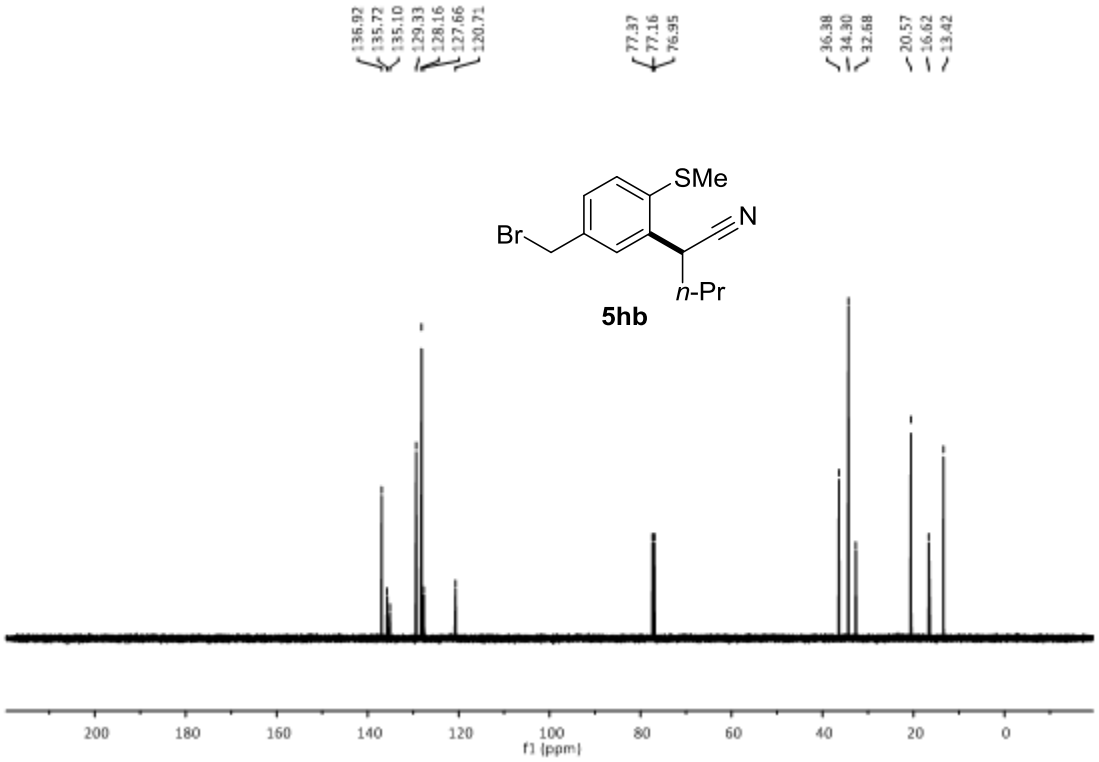
1
0
f1 (ppm)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127.66
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77.37
77.16
76.95
36.38
34.30
32.68
20.57
16.62
13.42
SMe
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Br
n-Pr
200
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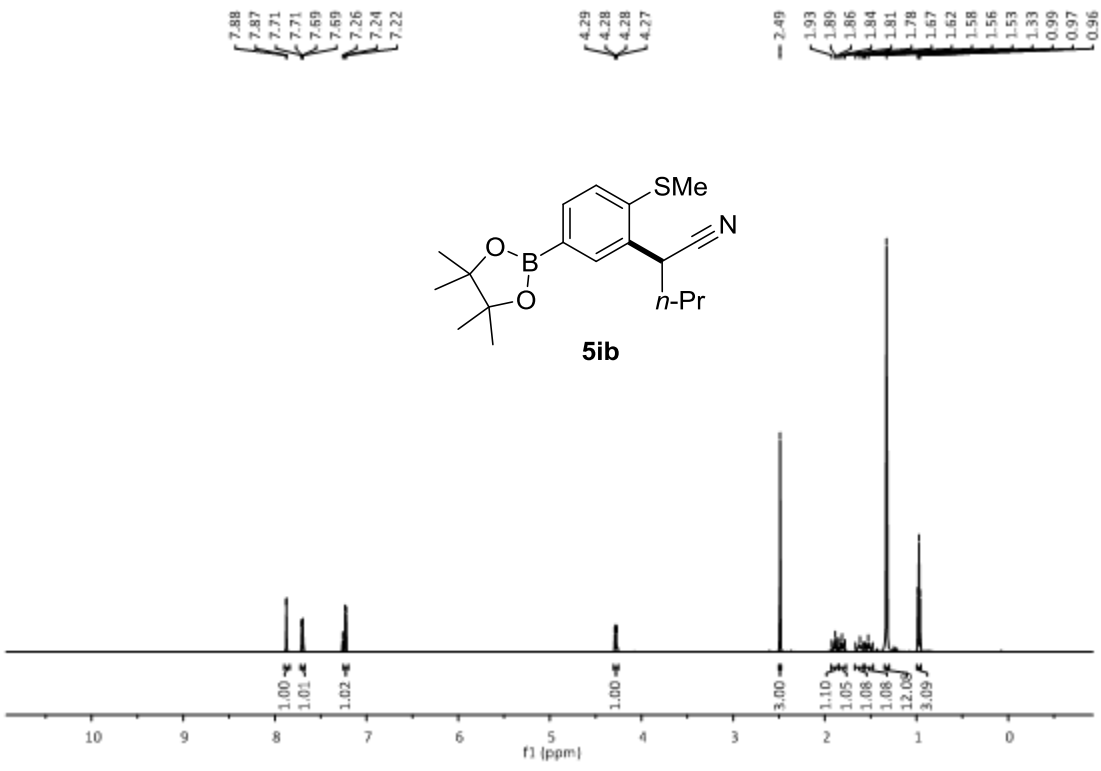
160
140
120
100
80
60
40
20
0
f1 (ppm)

5hb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7.22
4.29
4.28
4.28
4.27
2.49
1.93
1.89
1.86
1.84
1.81
1.78
1.67
1.62
1.58
1.56
1.53
1.33
0.99
0.97
0.96
SMe
N
O
B
O
n-Pr
1.00
1.01
1.02
1.00
3.00
1.10
1.05
1.08
1.08
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10
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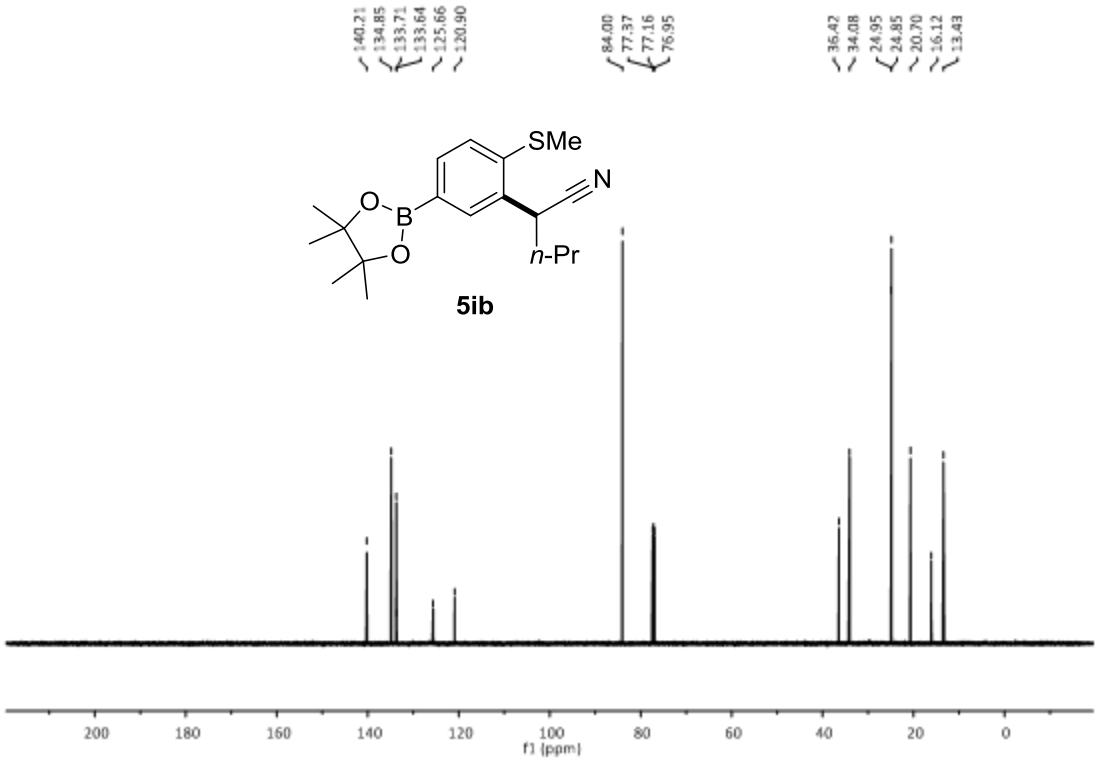
6
5
4
3
2
1
0
f1 (ppm)

5ib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77.16
76.95
36.42
34.08
24.95
24.85
20.70
16.12
13.43
SMe
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B
O
n-Pr
200
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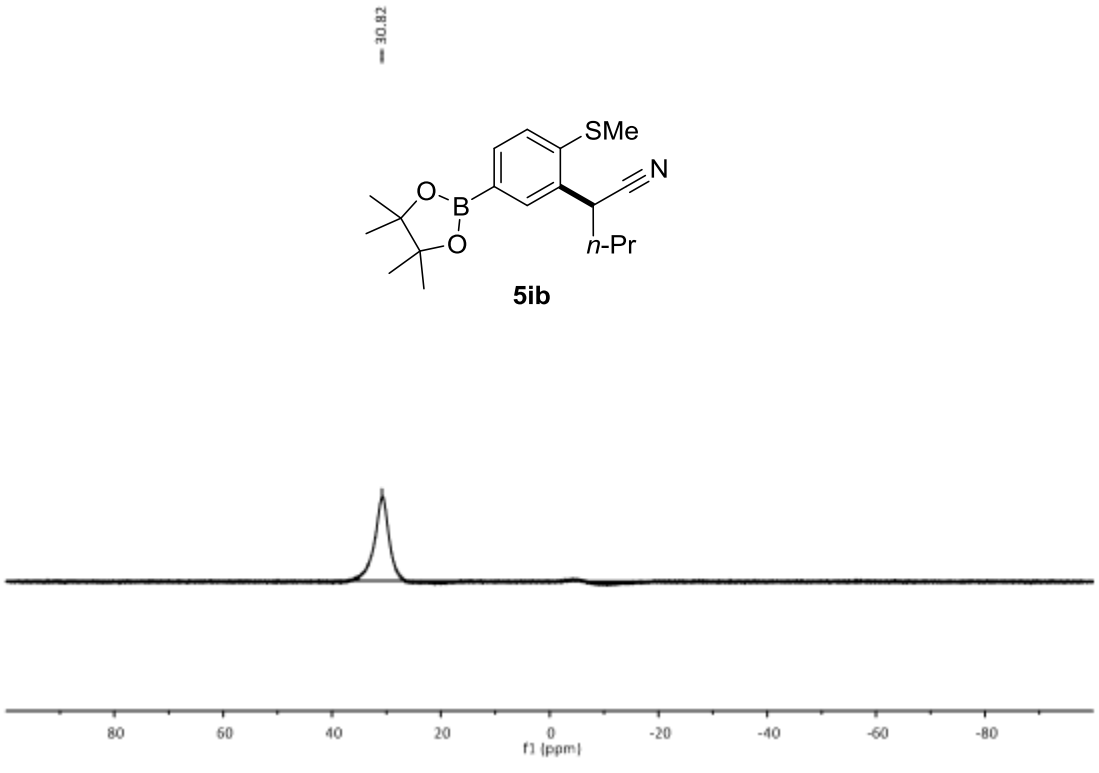
160
140
120
100
80
60
40
20
0
f1 (ppm)

5ib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B
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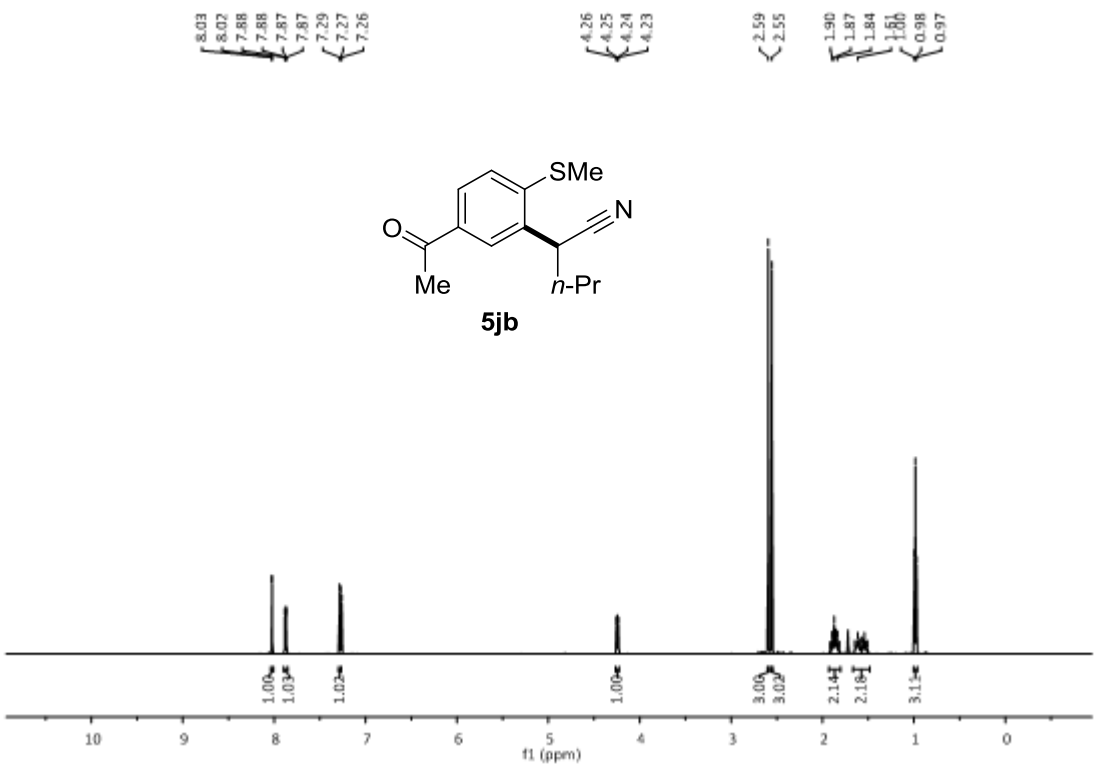
80
60
40
20
0
-20
-40
-60
-80
f1 (ppm)

5ib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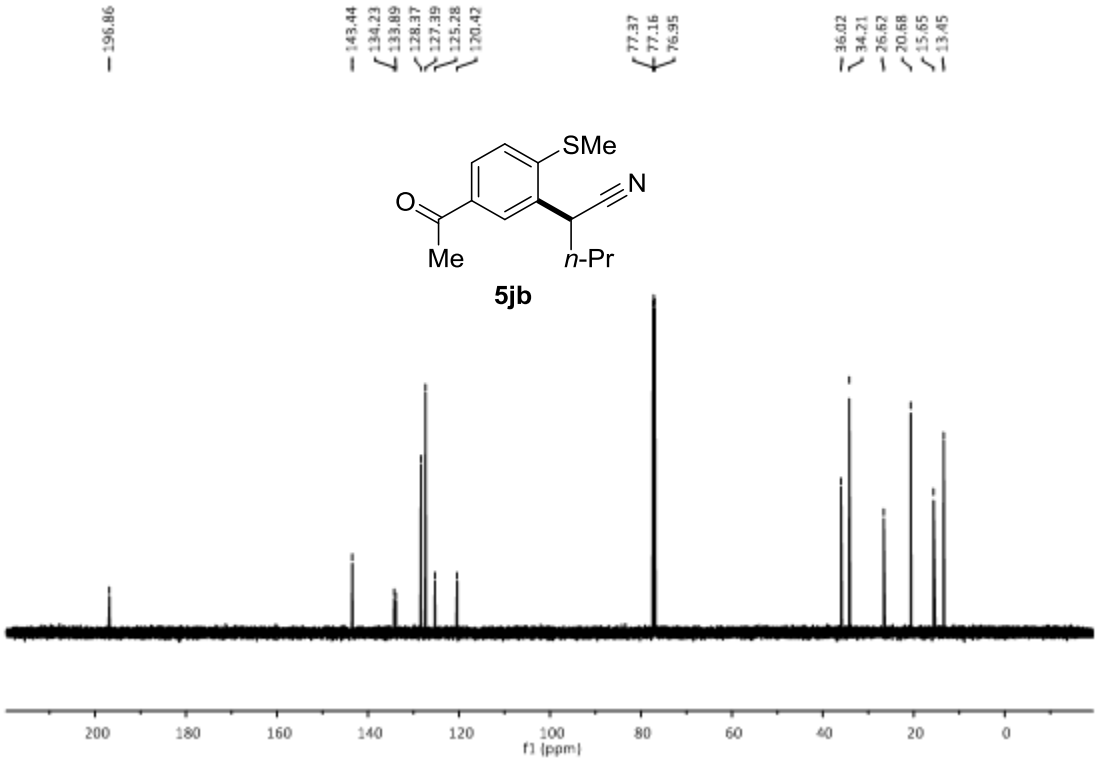
7.26
4.26
4.25
4.24
4.23
2.59
2.55
1.90
1.87
1.84
1.51
1.00
0.98
0.97
SMe
N
O
Me
n-Pr
1.00
1.03
1.02
1.00
3.00
3.02
2.14
2.18
3.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

5jb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120.42
77.37
77.16
76.95
36.02
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26.62
20.68
15.65
13.45
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O
Me
n-Pr
200
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140
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100
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60
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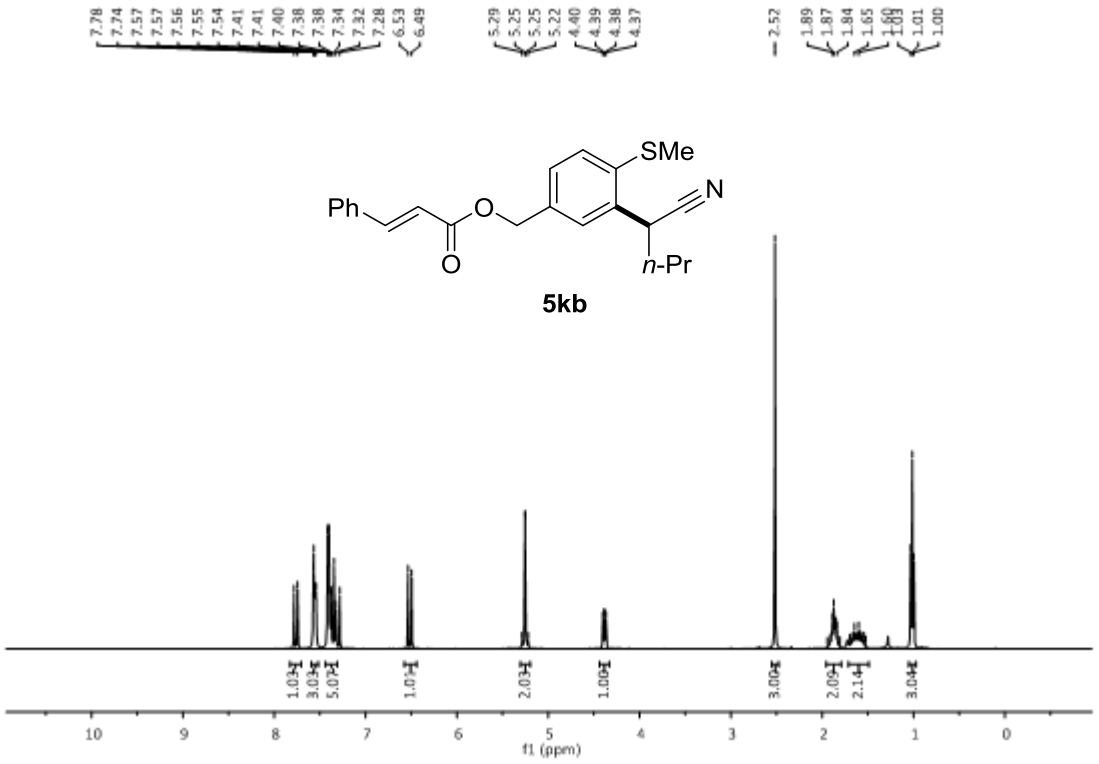
20
0
f1 (ppm)

5jb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7.40
7.38
7.38
7.34
7.32
7.28
6.53
6.49
5.29
5.25
5.25
5.22
4.40
4.39
4.38
4.37
2.52
1.89
1.87
1.84
1.65
1.01
1.00
SMe
N
Ph
O
O
n-Pr
1.03
3.03
5.07
1.01
2.03
1.00
3.00
2.09
2.14
3.04
10
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8
7
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5
4
3
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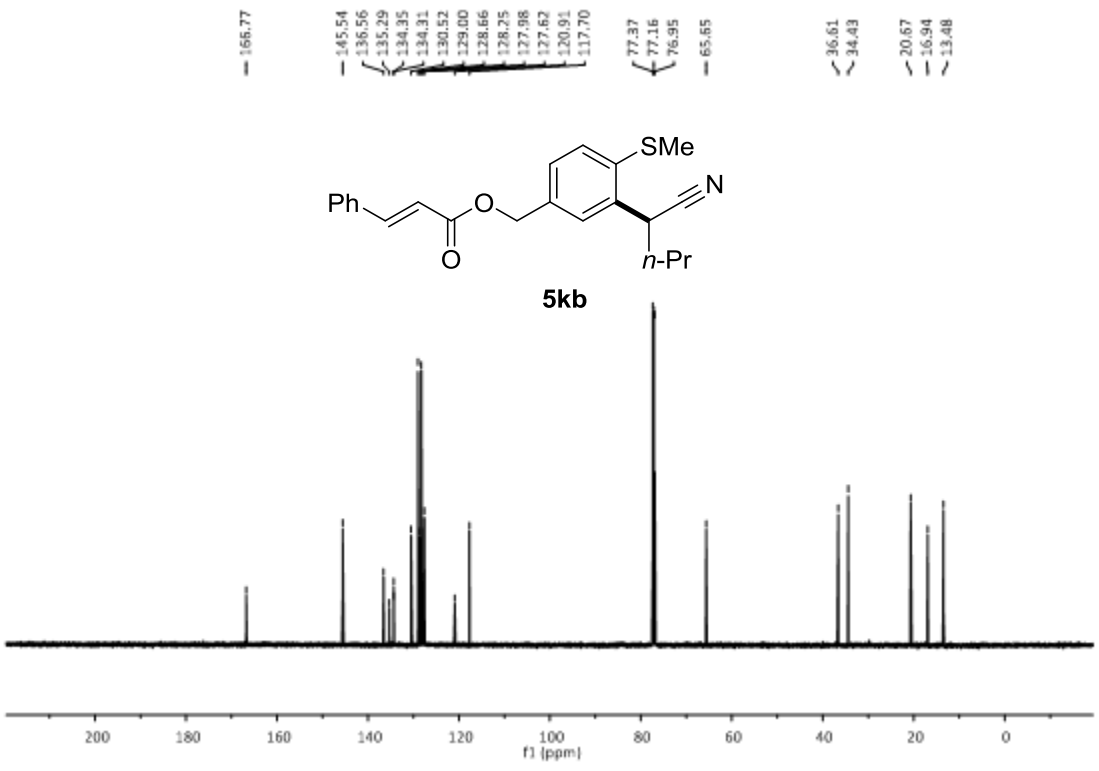
1
0
f1 (ppm)

5kb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128.25
127.98
127.62
120.91
117.70
77.37
77.16
76.95
65.65
36.61
34.43
20.67
16.94
13.48
SMe
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Ph
O
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n-Pr
200
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160
140
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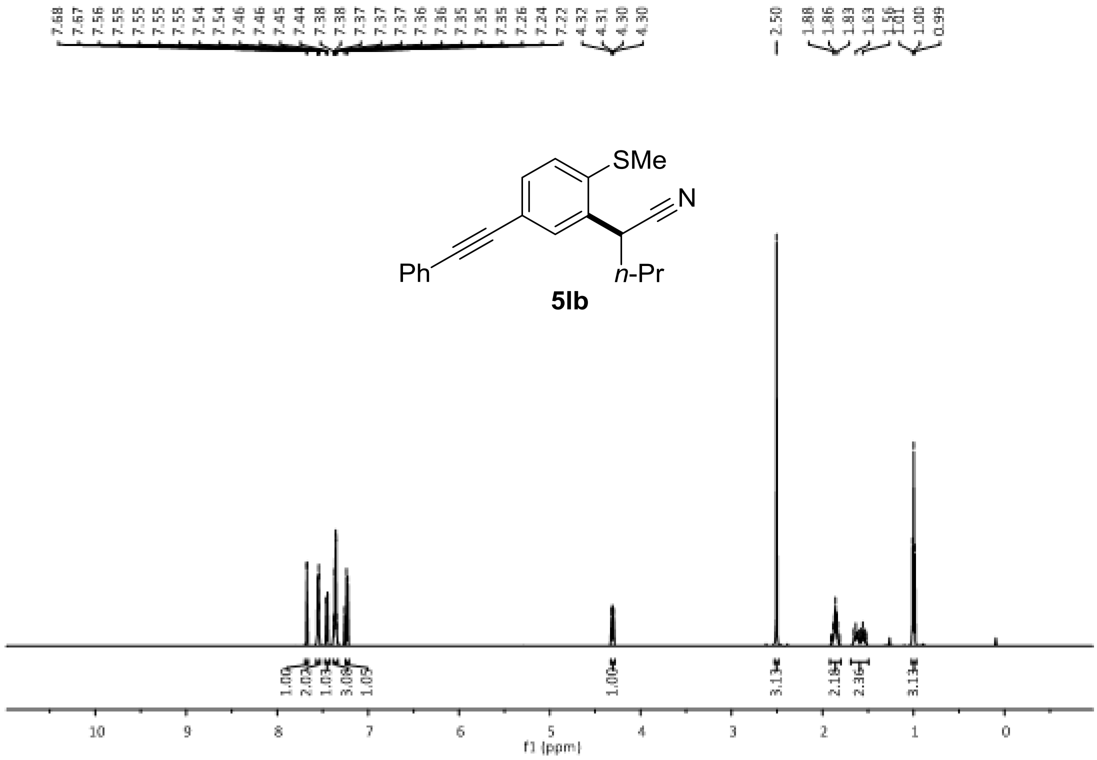
100
80
60
40
20
0
f1 (ppm)

5kb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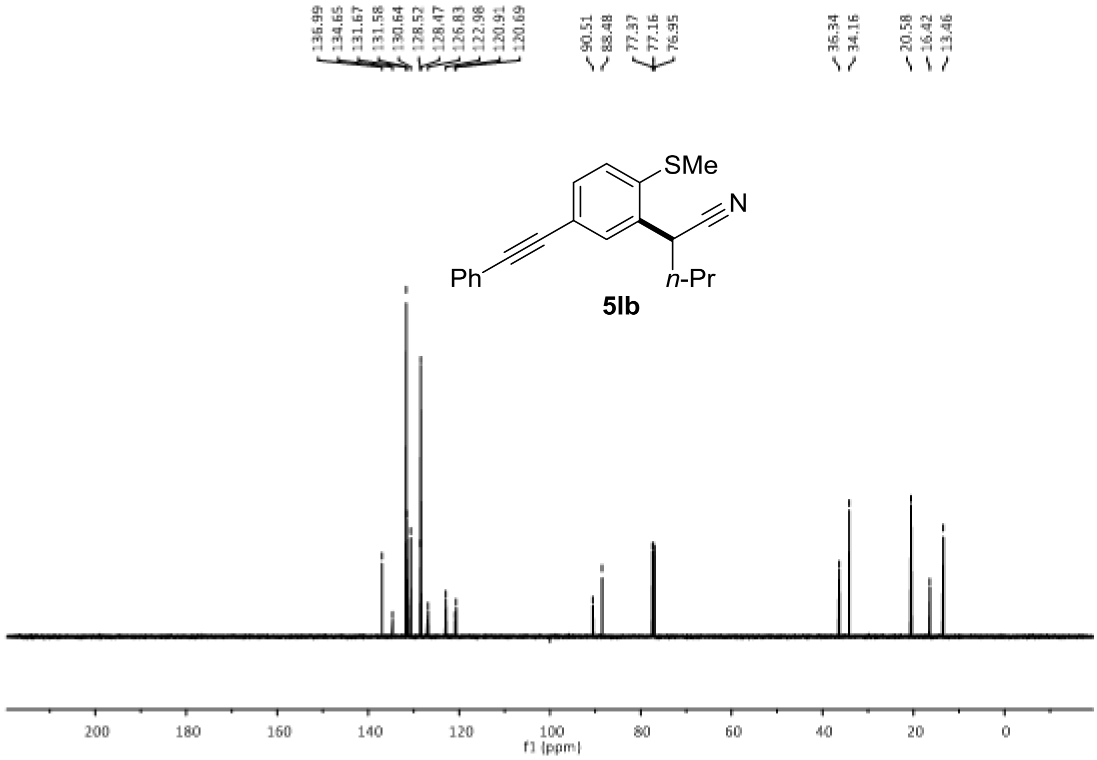
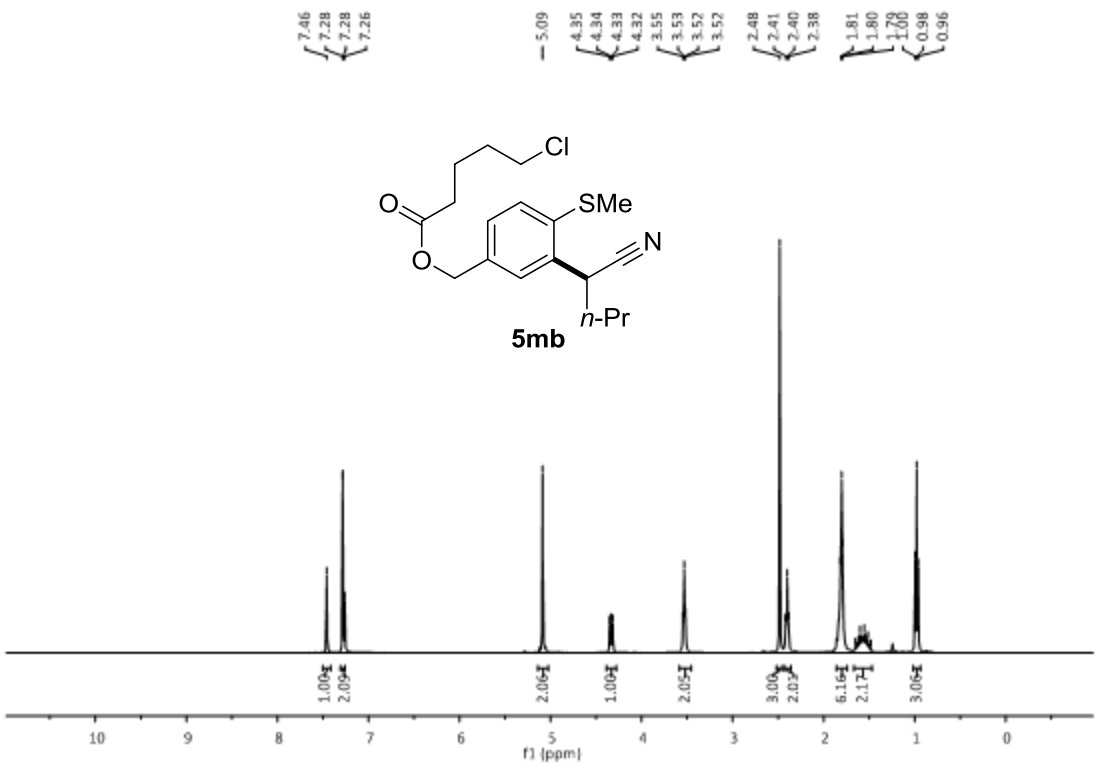
2.50 1.88 1.86 1.83 1.63 1.56 1.01 1.00 0.99
SMe
N
Ph
n-Pr
5lb
1.00 2.03 1.03 3.08 1.05
1.00
3.13
2.18 2.36
3.13
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


136.99 134.65 131.67 131.58 130.64 128.52 128.47 126.83 122.98 120.91 120.69
90.51 88.48 77.37 77.16 76.95
36.34 34.16
20.58 16.42 13.46
SMe
N
Ph
n-Pr
5lb
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)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7.26
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4.34
4.33
4.32
3.55
3.53
3.52
3.52
2.48
2.41
2.40
2.38
1.81
1.80
1.78
1.00
0.98
0.96
Cl
O
O
SMe
N
n-Pr
5mb
1.00
2.09
2.06
1.00
2.05
3.00
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2.17
3.06
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5
4
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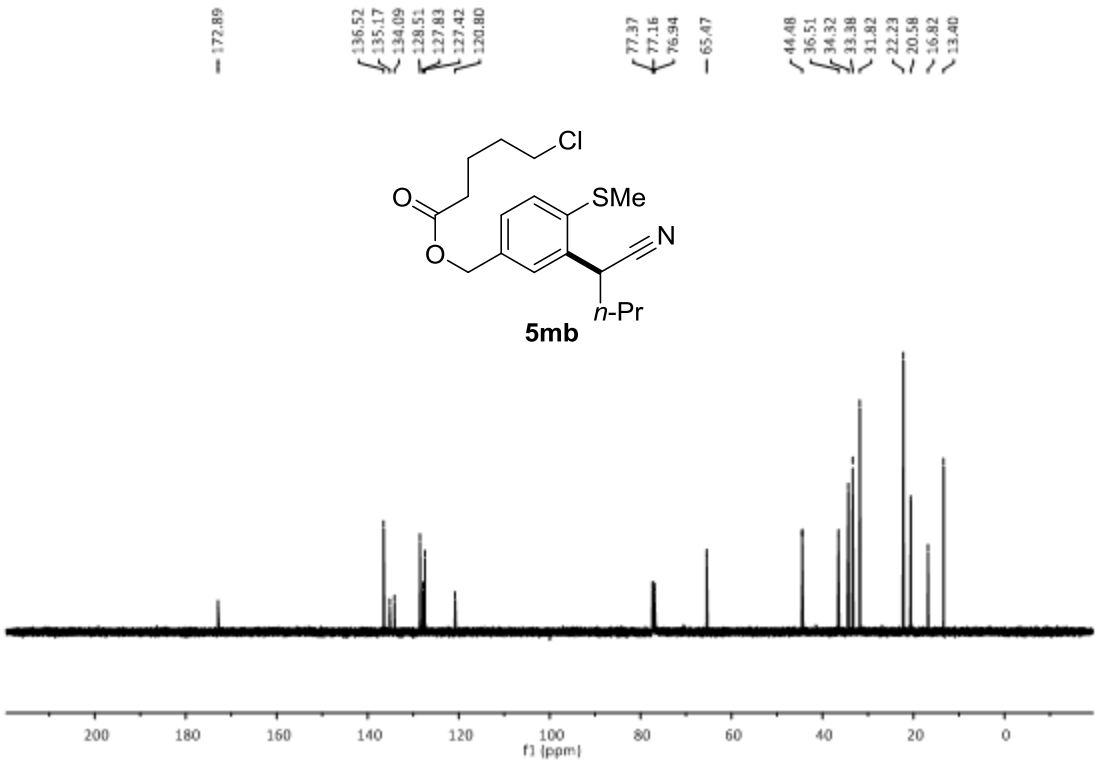
f1 (ppm)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127.83
127.42
120.80
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77.16
76.94
65.47
44.48
36.51
34.32
33.38
31.82
22.23
20.58
16.82
13.40
Cl
O
O
SMe
N
n-Pr
5mb
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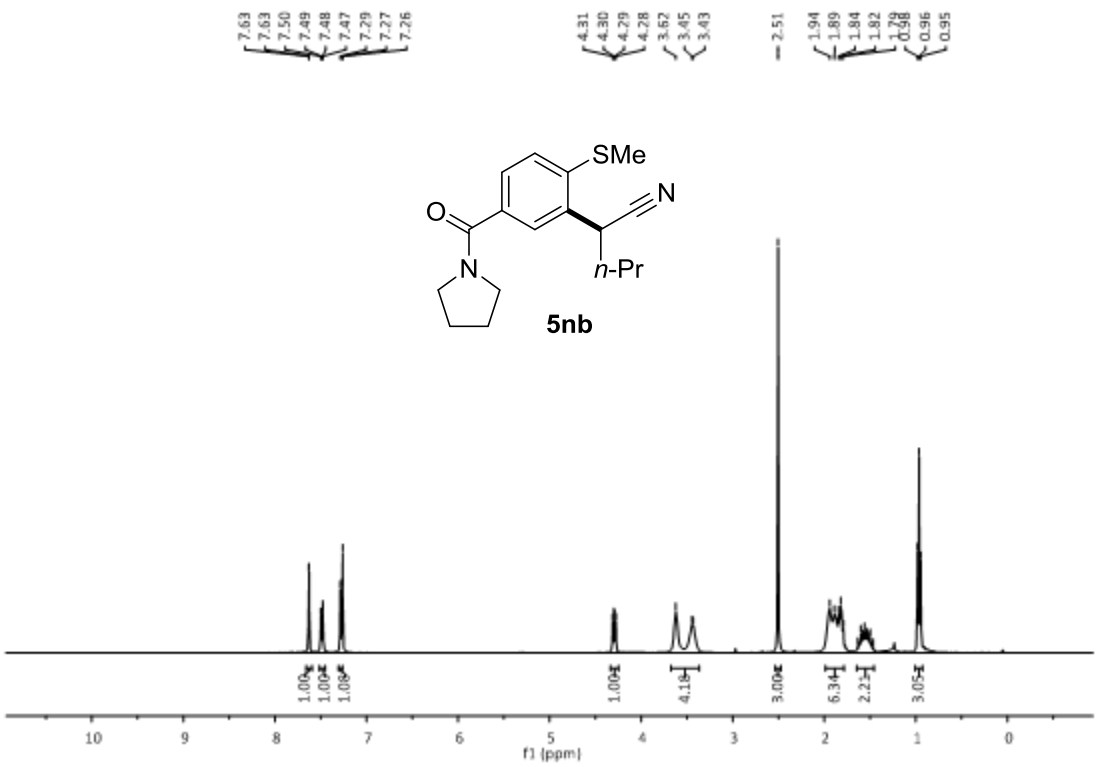
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4.28
3.52
3.45
3.43
2.51
1.94
1.89
1.84
1.82
1.79
0.98
0.96
0.95
SMe
N
O
N
n-Pr
5nb
1.00
1.00
1.08
1.00
4.18
3.00
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3.05
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5
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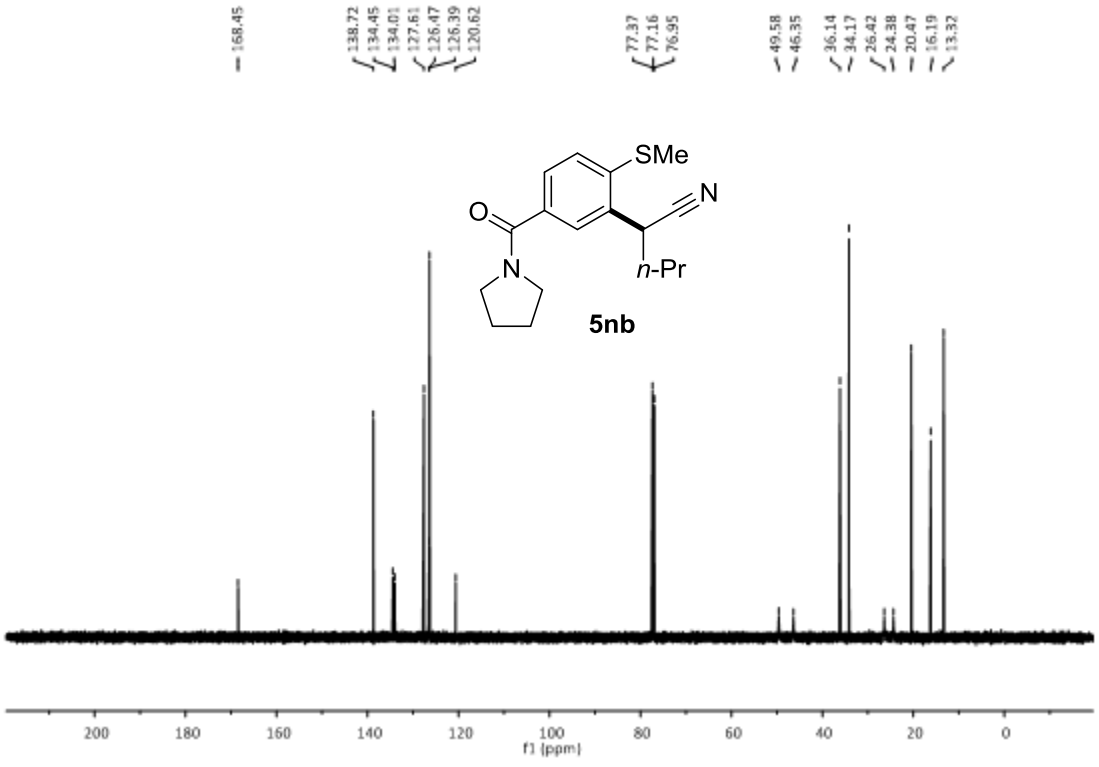
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77.16
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49.58
46.35
36.14
34.17
26.42
24.38
20.47
16.19
13.32
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N
O
N
n-Pr
5nb
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140
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100
80
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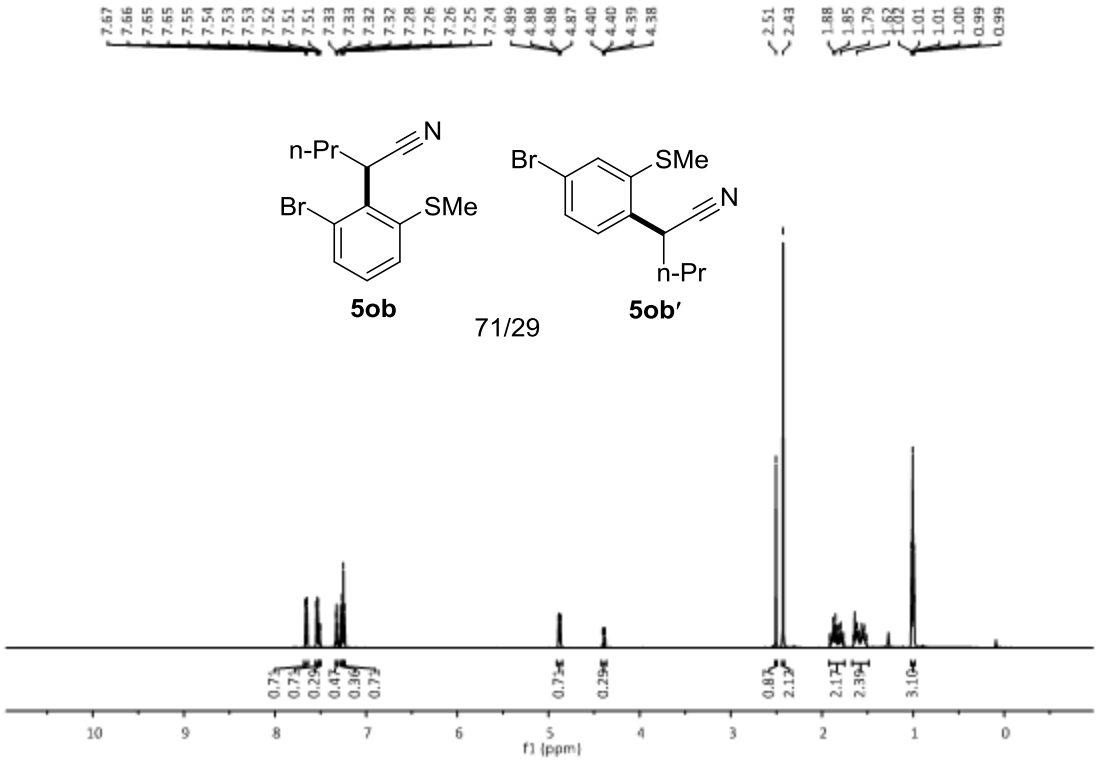
20
0
f1 (ppm)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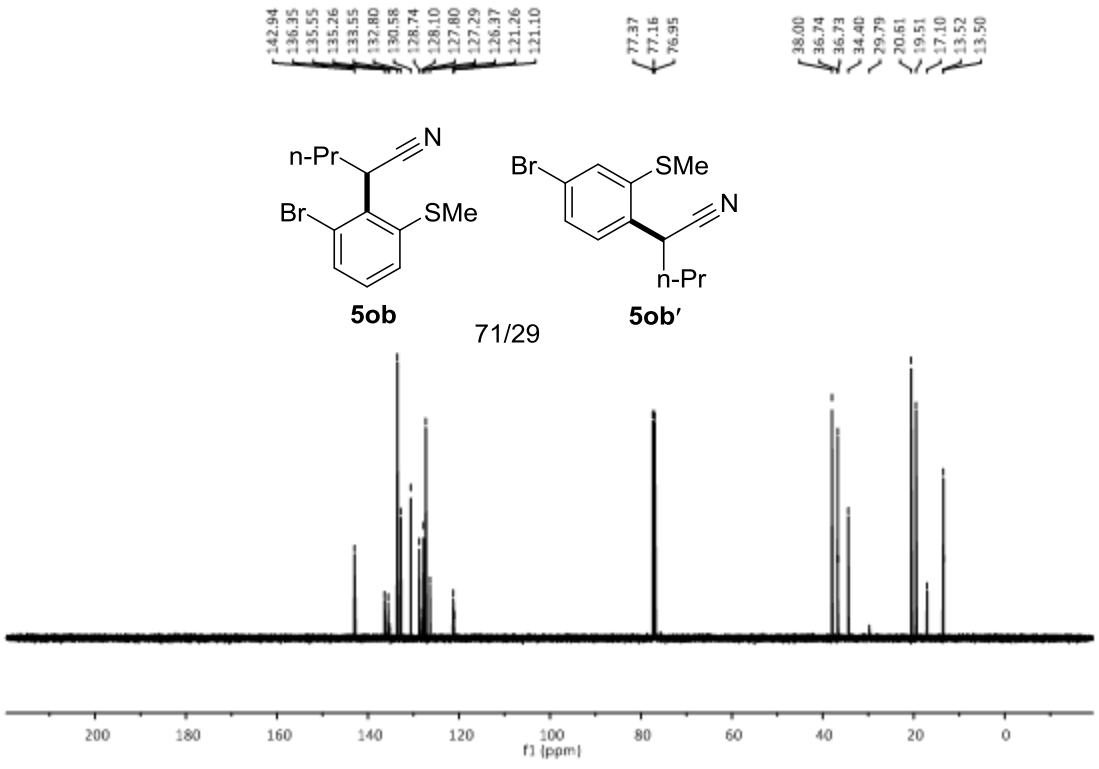
N
Br
SMe
5ob
Br
SMe
N
n-Pr
5ob′
71/29
f1 (ppm)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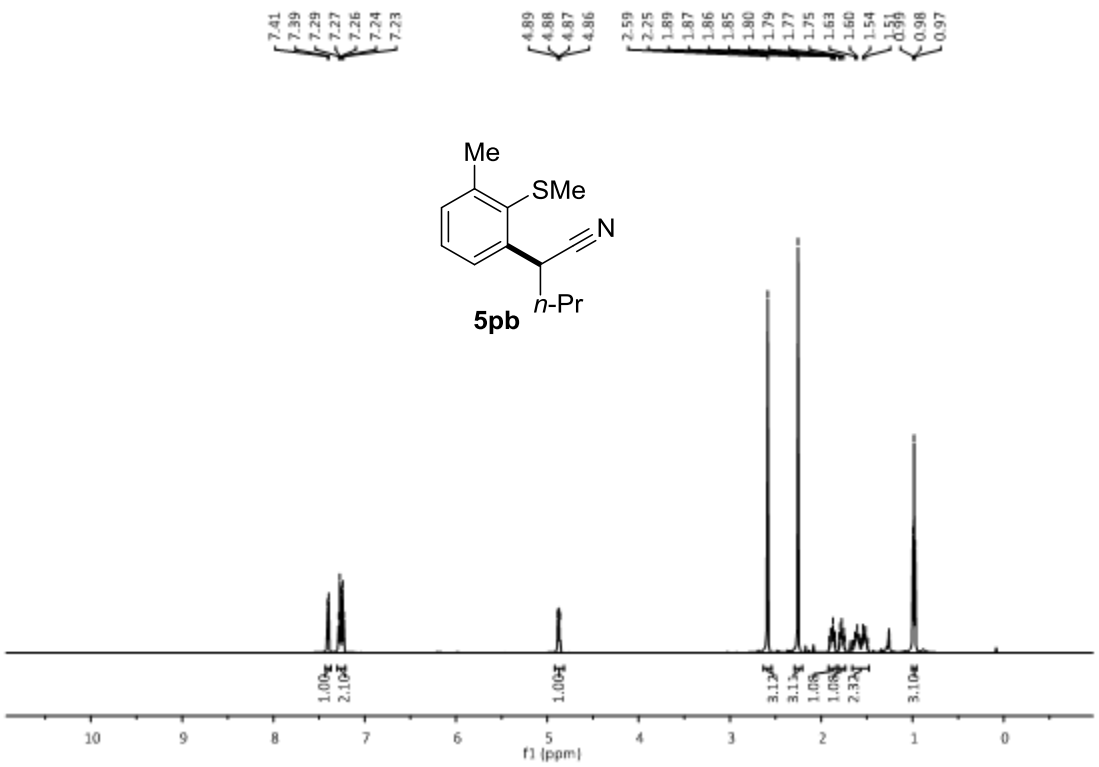
N
Br
SMe
5ob
Br
SMe
N
n-Pr
5ob′
71/29
f1 (ppm)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7.23
4.89
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4.87
4.86
2.59
2.25
1.89
1.87
1.86
1.85
1.80
1.79
1.77
1.75
1.63
1.60
1.54
1.51
0.99
0.98
0.97
Me
SMe
N
n-Pr
5pb
1.00
2.10
1.00
3.12
3.13
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3.10
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9
8
7
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5
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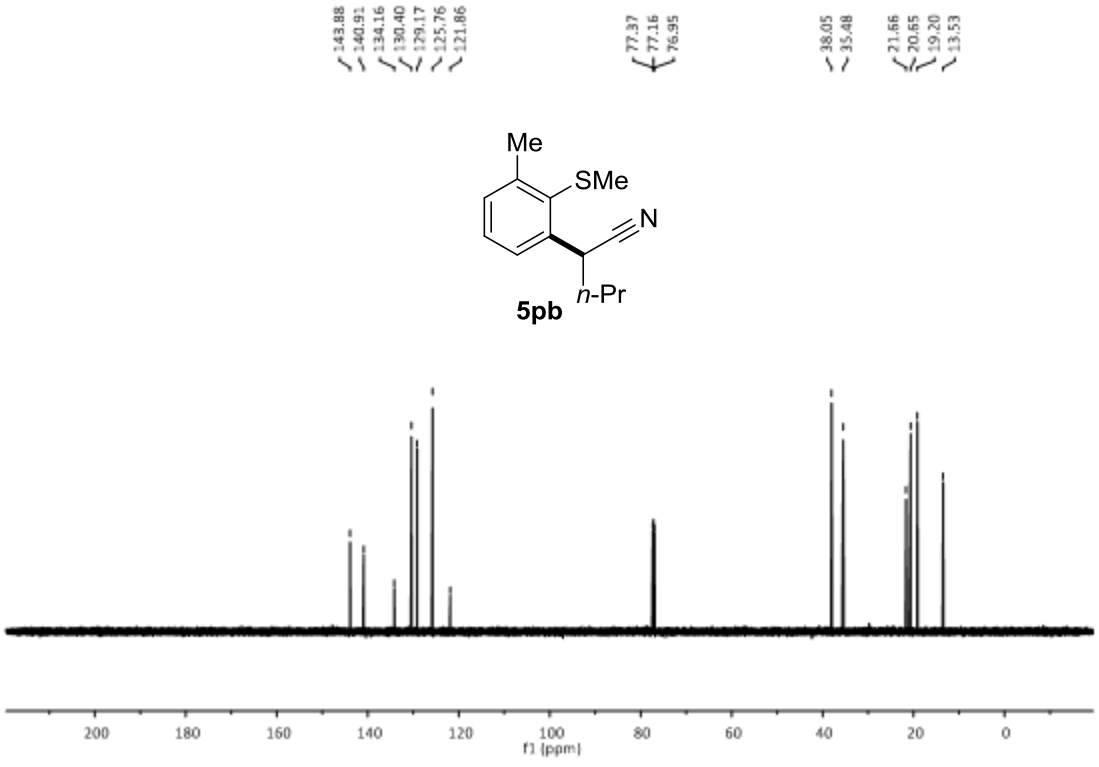
f1 (ppm)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125.76
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77.37
77.16
76.95
38.05
35.48
21.66
20.65
19.20
13.53
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SMe
N
n-Pr
5pb
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140
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100
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20
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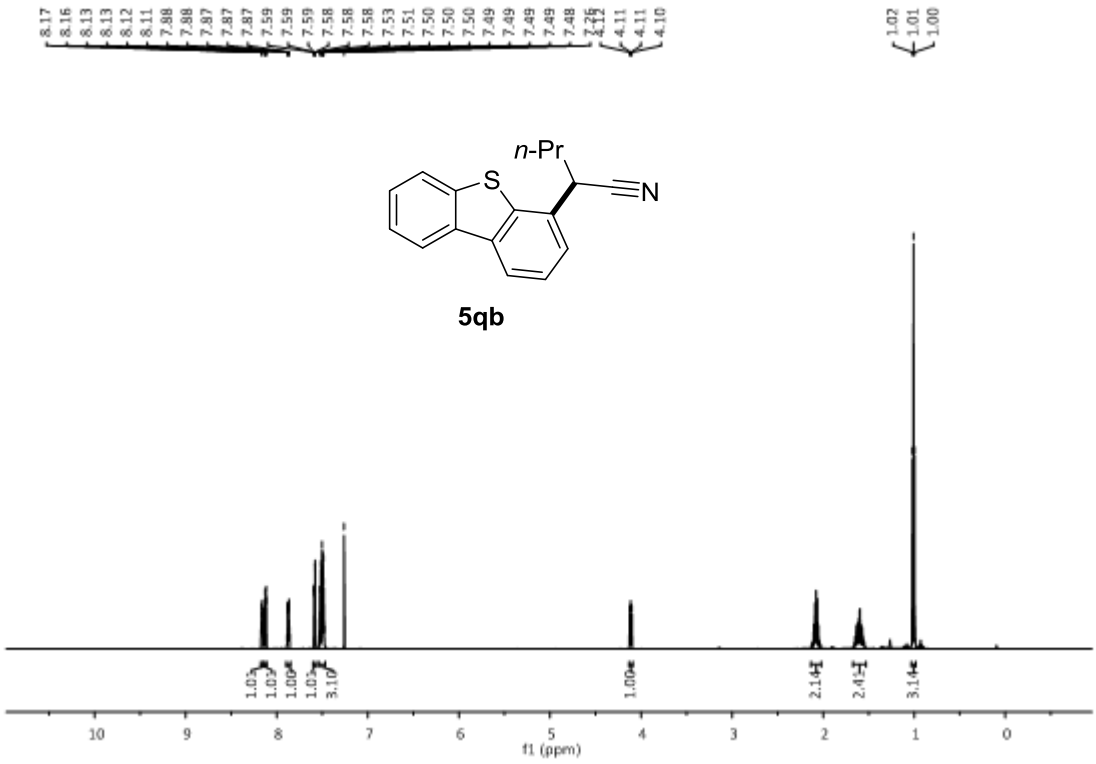
f1 (ppm)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7.88
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7.87
7.87
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7.59
7.59
7.58
7.58
7.58
7.53
7.51
7.50
7.50
7.50
7.49
7.49
7.49
7.49
7.48
4.11
4.11
4.10
1.02
1.01
1.00
n-Pr
S
N
1.03
1.03
1.00
1.03
3.10
1.00
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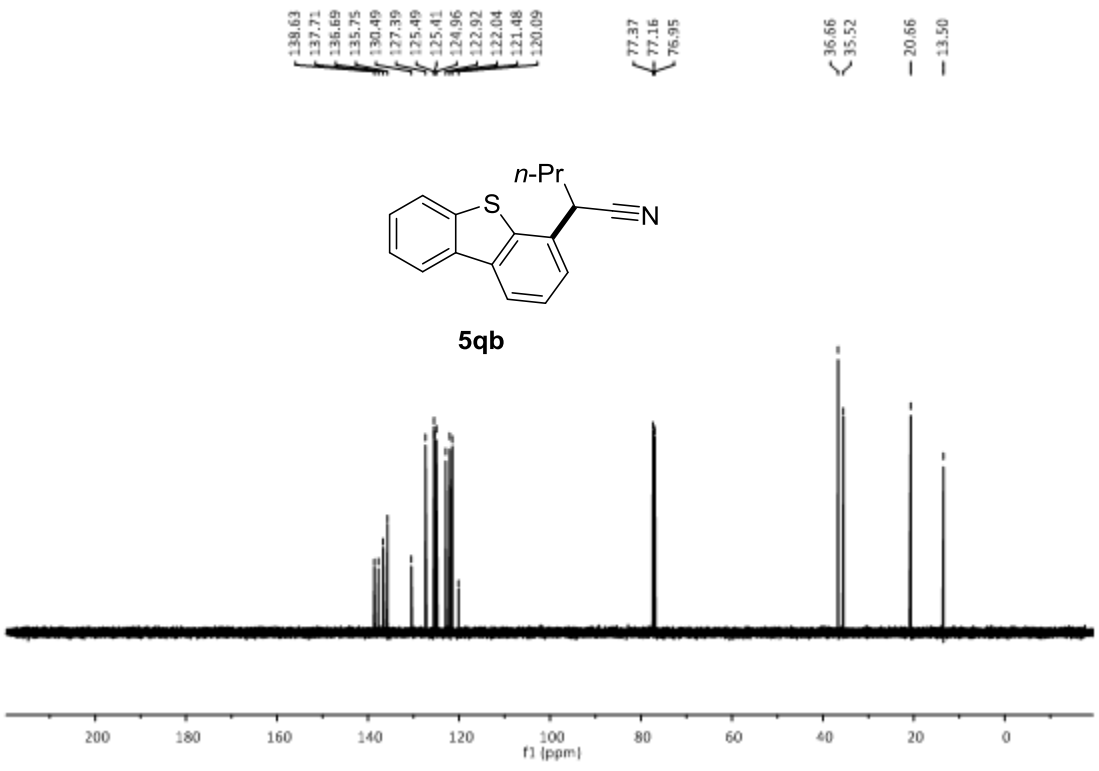
3.14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

5qb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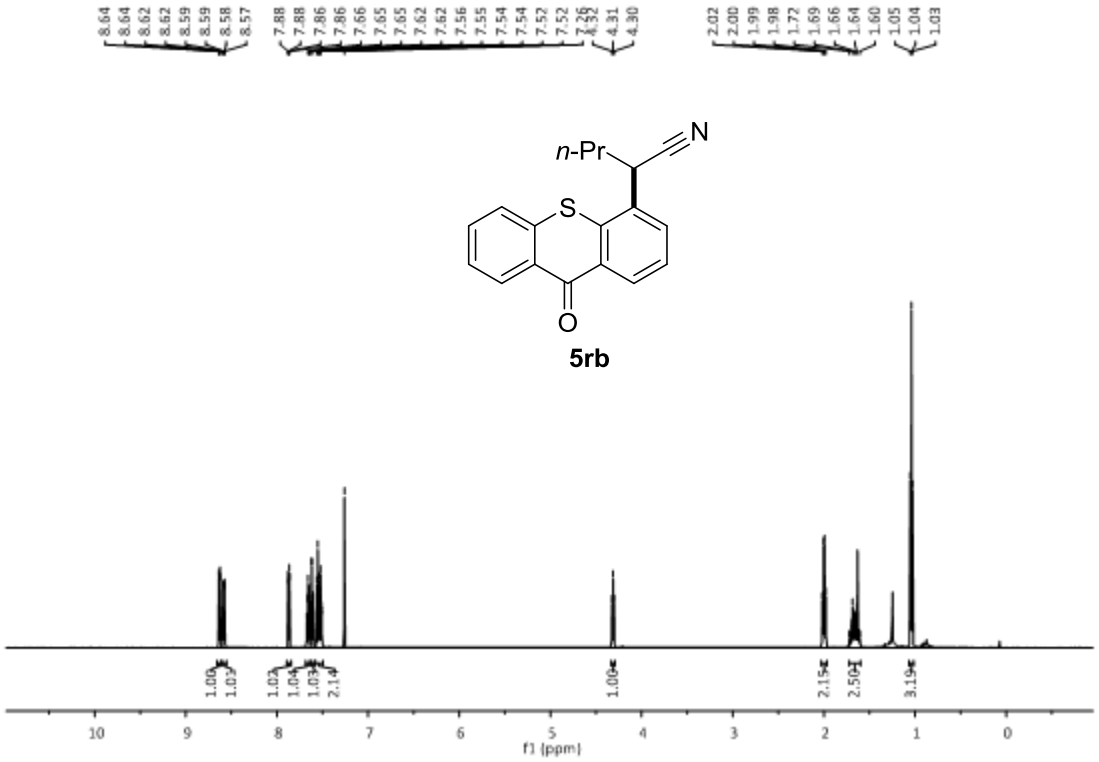
125.49
125.41
124.96
122.92
122.04
121.48
120.09
77.37
77.16
76.95
36.66
35.52
20.66
13.50
n-Pr
S
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

5qb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8.58
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7.88
7.86
7.86
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7.62
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7.54
7.52
7.52
4.32
4.31
4.30
2.02
2.00
1.99
1.98
1.72
1.69
1.66
1.64
1.60
1.05
1.04
1.03
n-Pr
N
S
O
1.00
1.03
1.02
1.04
1.03
2.14
1.00
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7
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3
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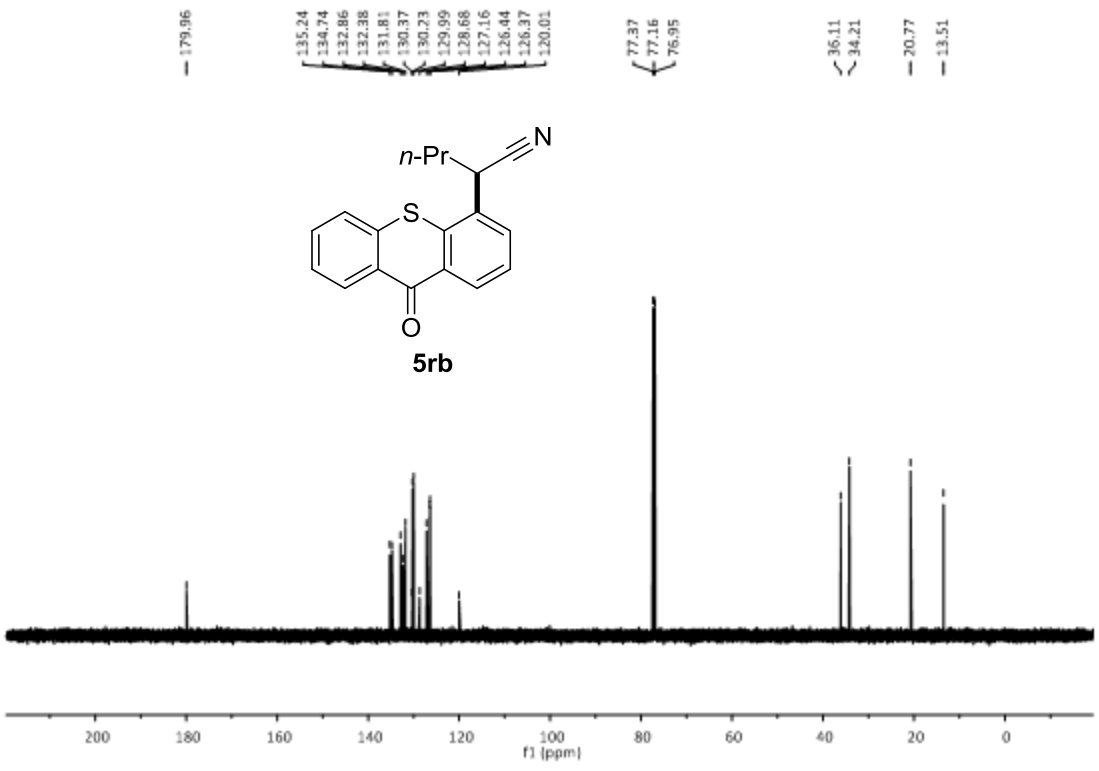
0
f1 (ppm)

5rb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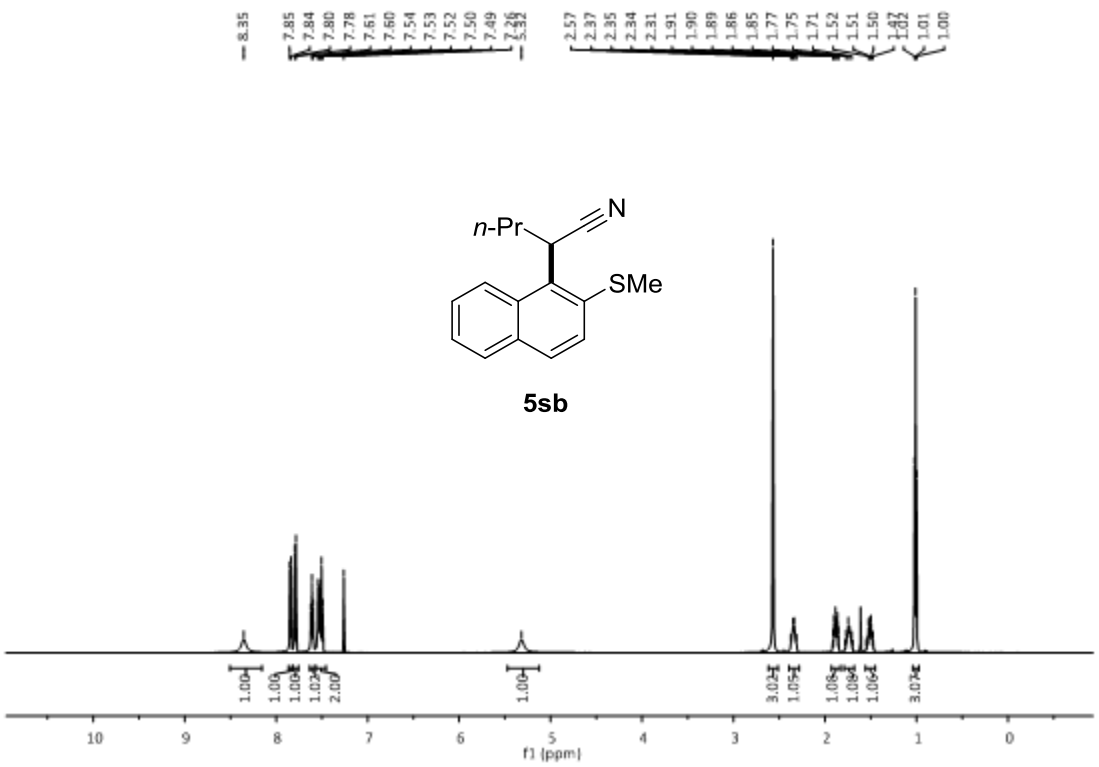
130.23
129.99
128.68
127.16
126.44
126.37
120.01
77.37
77.16
76.95
36.11
34.21
20.77
13.51
n-Pr
N
S
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

5rb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7.54
7.53
7.52
7.50
7.49
7.26
5.32
2.57
2.37
2.35
2.34
2.31
1.91
1.90
1.89
1.86
1.85
1.77
1.75
1.71
1.52
1.51
1.50
1.02
1.01
1.00
n-Pr
N
SMe
5sb
1.00
1.00
1.00
1.02
2.00
1.00
3.02
1.05
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1.08
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3.07
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5
4
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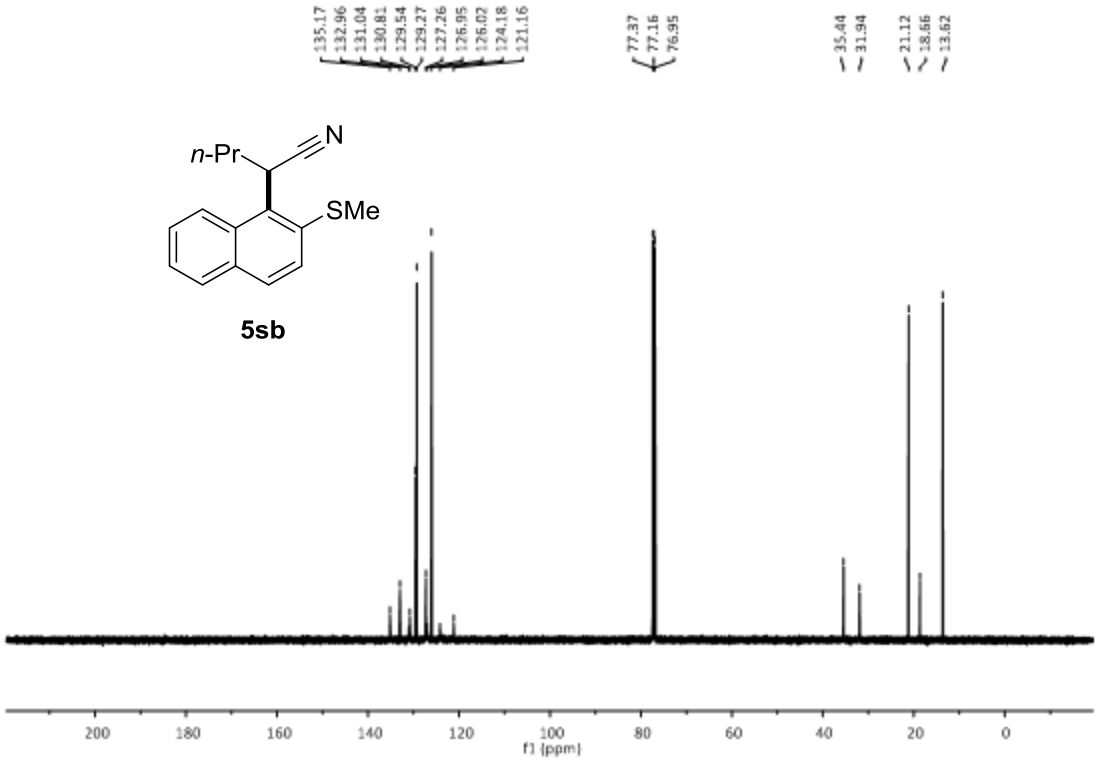
2
1
0
f1 (ppm)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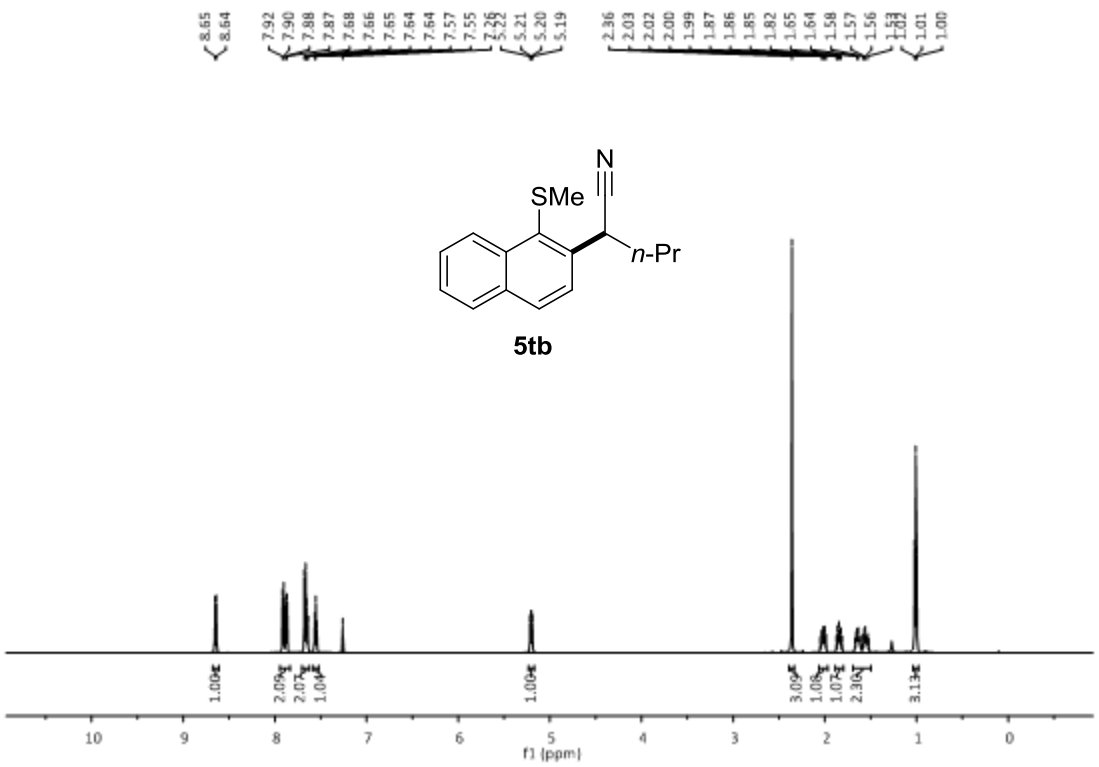
129.54
129.27
127.26
126.95
126.02
124.18
121.16
77.37
77.16
76.95
35.44
31.94
21.12
18.66
13.62
n-Pr
N
SMe
5sb
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.88
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7.66
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7.64
7.64
7.57
7.55
5.21
5.20
5.19
2.36
2.03
2.02
2.00
1.99
1.87
1.86
1.85
1.82
1.65
1.64
1.58
1.57
1.56
1.01
1.00
N
SMe
n-Pr
5tb
1.00
2.09
2.07
1.04
1.00
3.09
1.08
1.07
2.30
3.13
10
9
8
7
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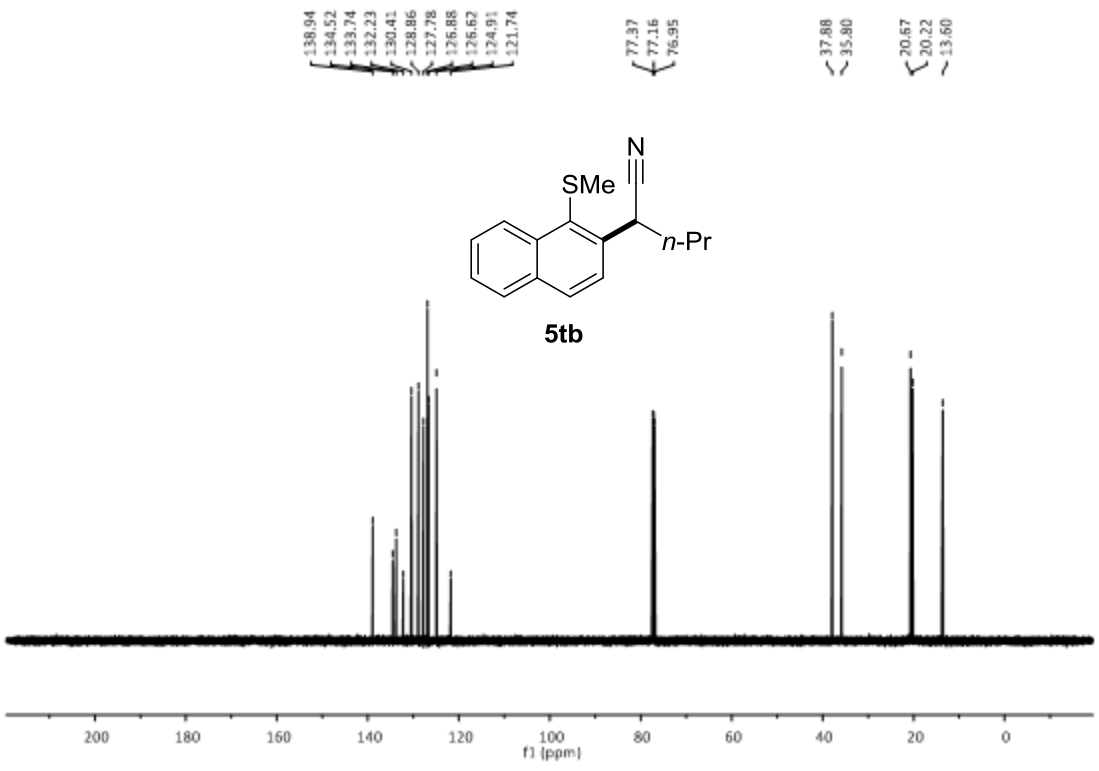
5
4
3
2
1
0
f1 (ppm)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126.88
126.62
124.91
121.74
77.37
77.16
76.95
37.88
35.80
20.67
20.22
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n-Pr
5tb
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100
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20
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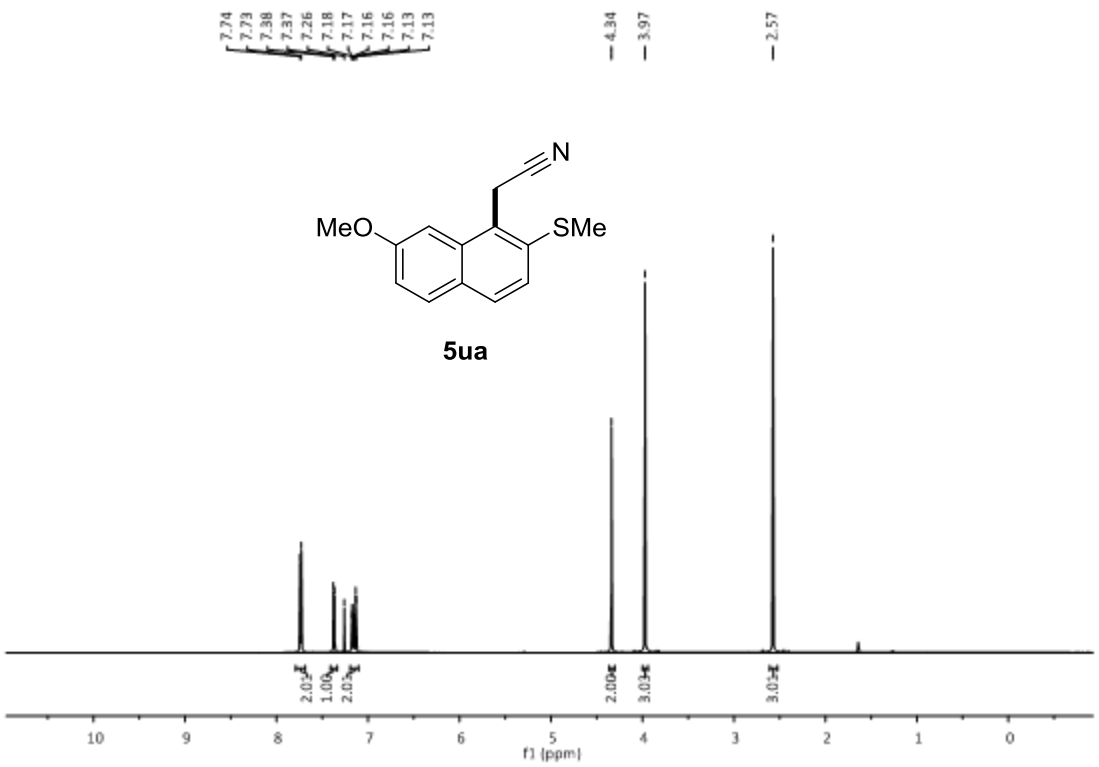
f1 (ppm)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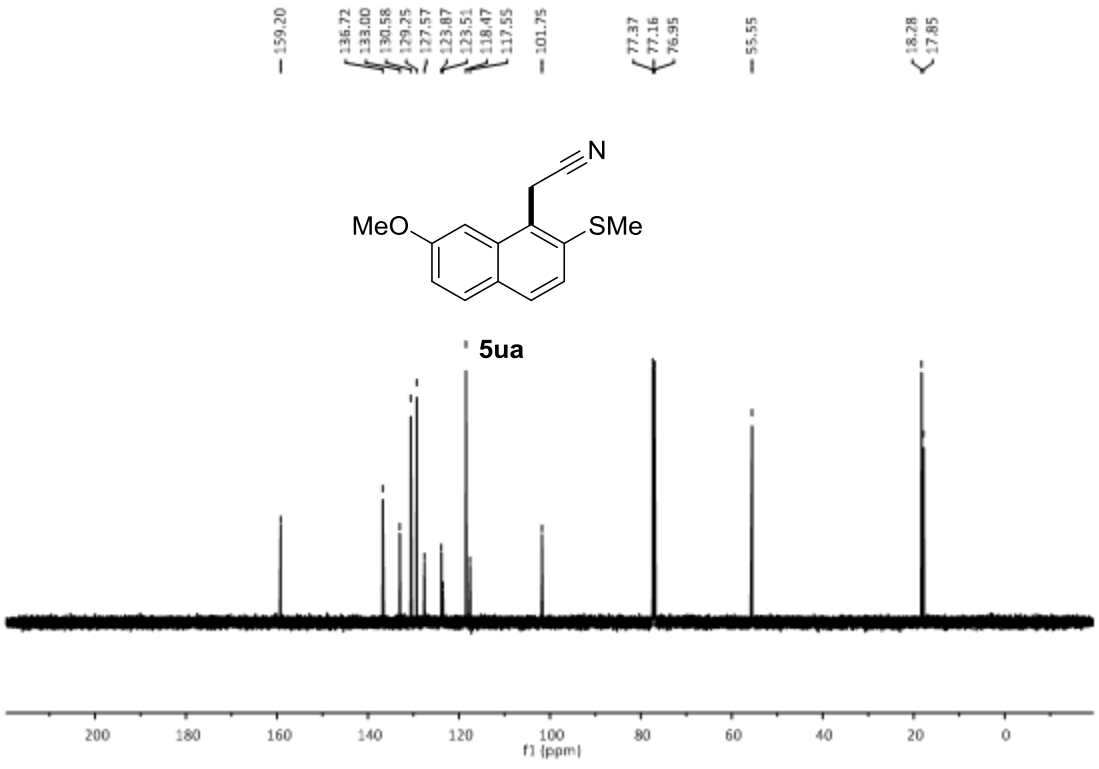
7.37
7.26
7.18
7.17
7.16
7.16
7.13
7.13
4.34
3.97
2.57
N
MeO
SMe
2.02
1.00
2.02
2.00
3.03
3.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

5ua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123.51
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117.55
101.75
77.37
77.16
76.95
55.55
18.28
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SMe
200
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120
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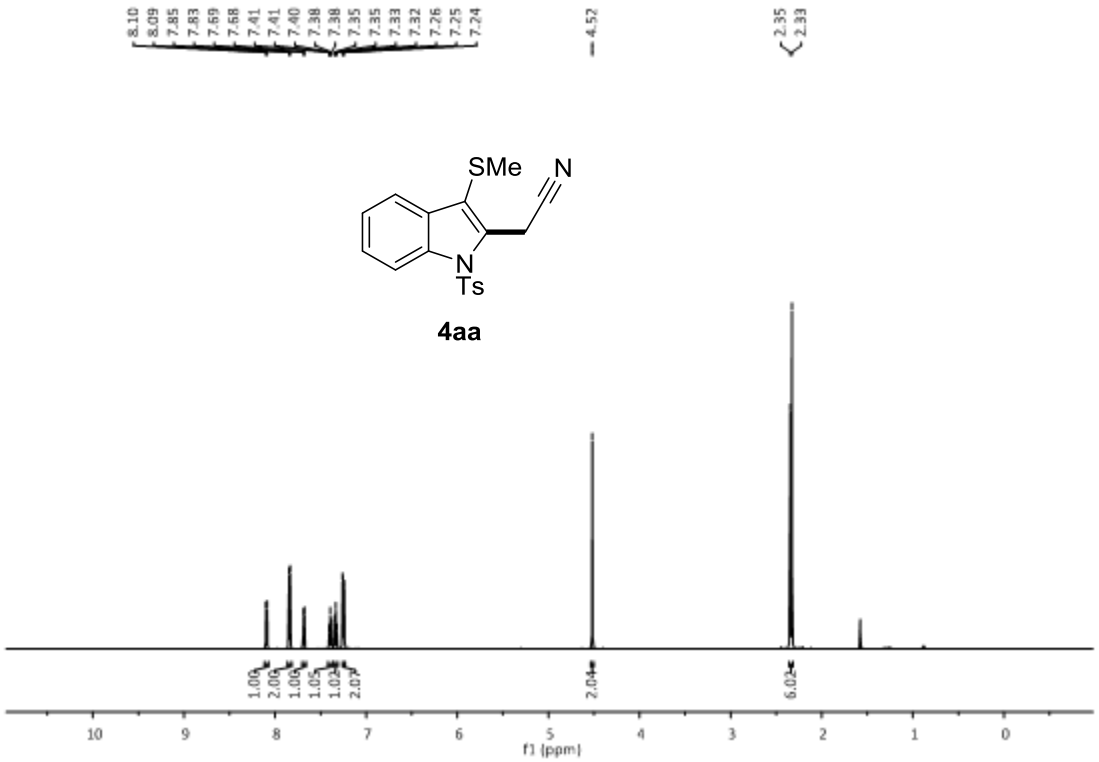
80
60
40
20
0
f1 (ppm)

5ua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7.38
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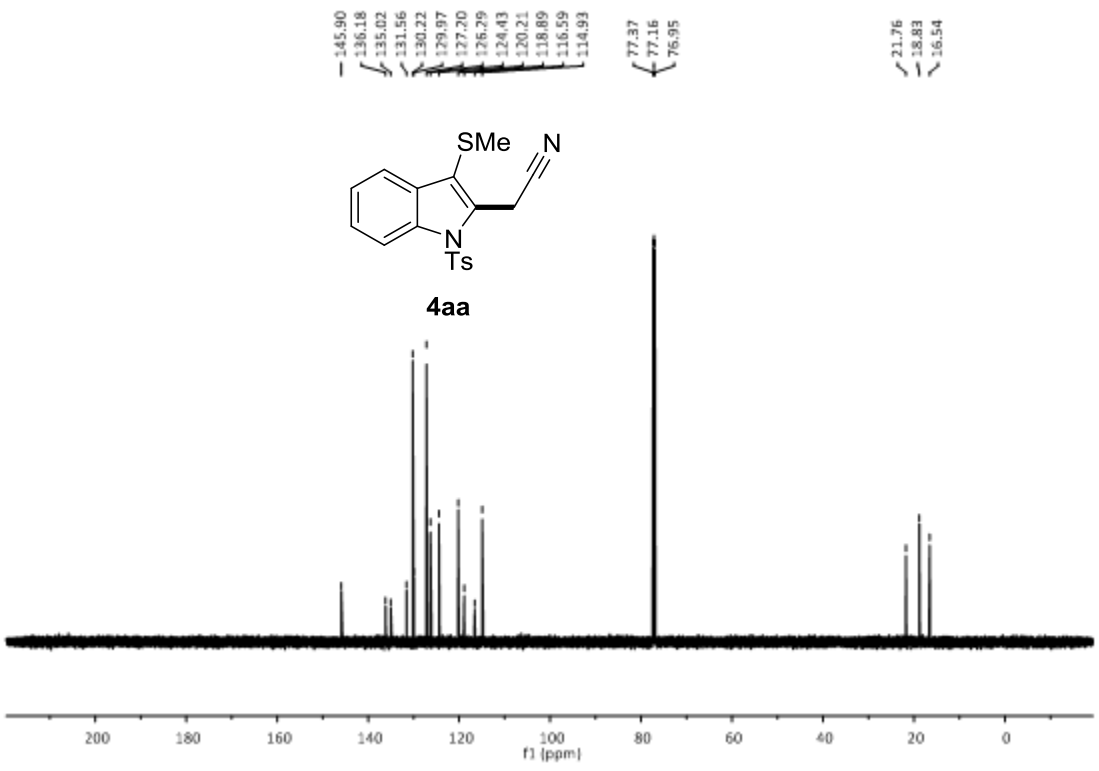
7.35
7.35
7.33
7.32
7.26
7.25
7.24
4.52
2.35
2.33
SMe
N
N
Ts
1.00
2.00
1.00
1.05
1.02
2.07
2.04
6.02
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

4aa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126.29
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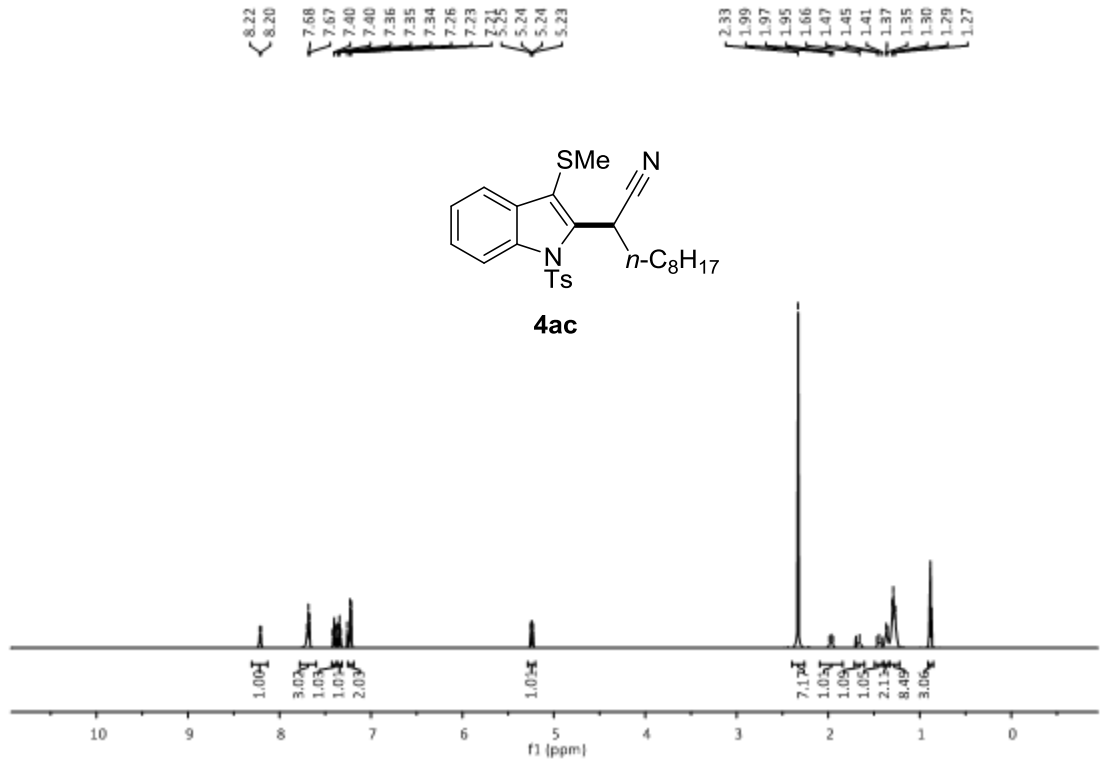
120.21
118.89
116.59
114.93
77.37
77.16
76.95
21.76
18.83
16.54
SMe
N
N
Ts
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

4aa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7.21
5.25
5.24
5.24
5.23
2.33
1.99
1.97
1.95
1.66
1.47
1.45
1.41
1.37
1.35
1.30
1.29
1.27
SMe
N
N
Ts
n-C8H17
1.00
3.02
1.03
1.01
2.09
1.01
7.17
1.03
1.09
1.05
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10
9
8
7
6
5
4
3
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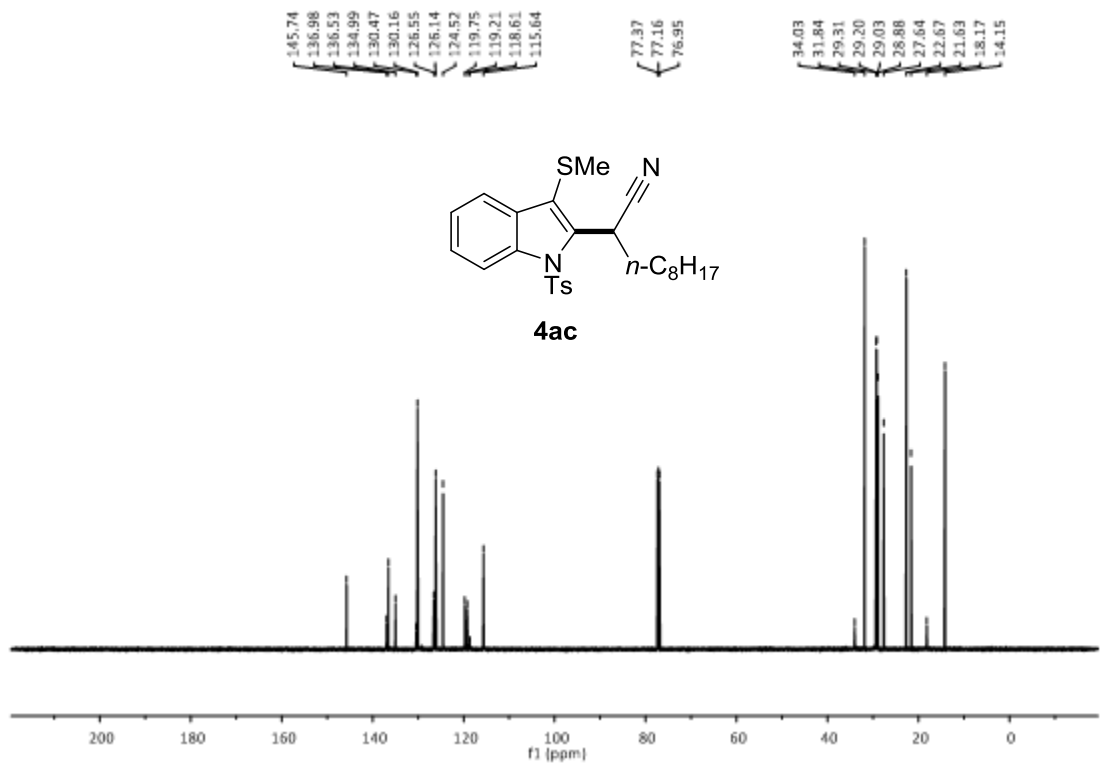
0
f1 (ppm)

4ac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77.37
77.16
76.95
34.03
31.84
29.31
29.20
29.03
28.88
27.64
22.67
21.63
18.17
14.15
SMe
N
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Ts
n-C8H17
200
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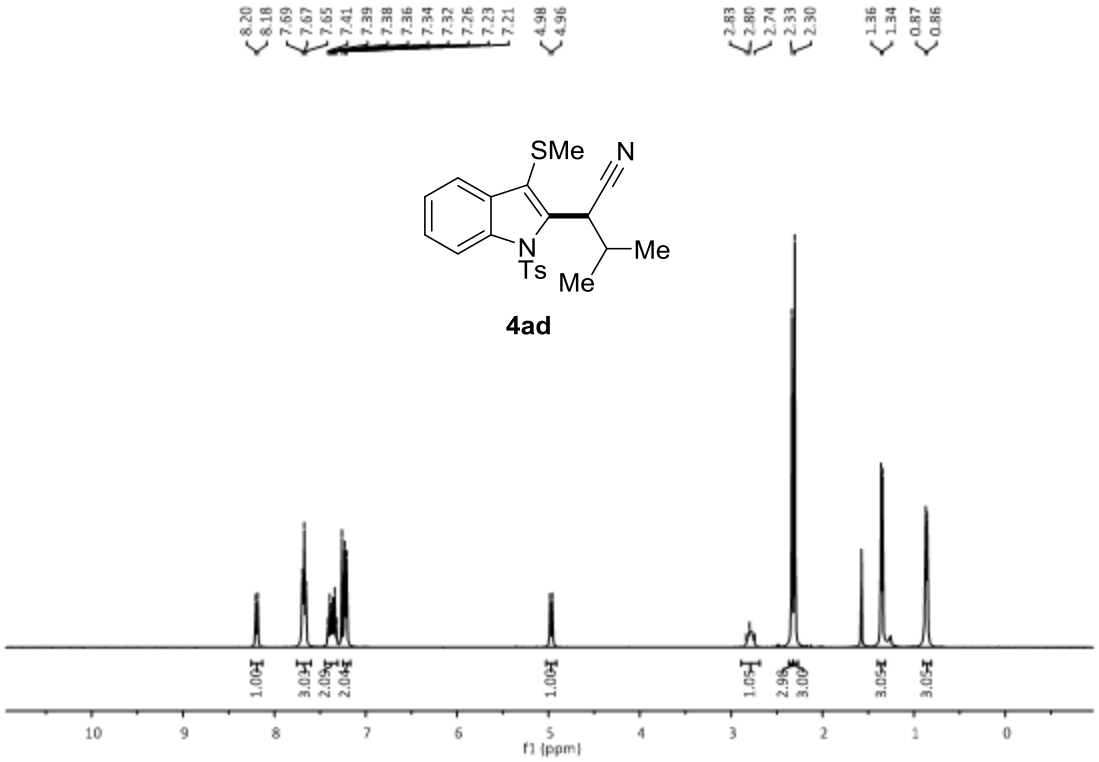
160
140
120
100
80
60
40
20
0
f1 (ppm)

4ac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7.32
7.26
7.23
7.21
4.98
4.96
2.83
2.80
2.74
2.33
2.30
1.36
1.34
0.87
0.86
SMe
N
N
Ts
Me
Me
1.00
3.03
2.09
2.04
1.00
1.05
2.98
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3.05
10
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8
7
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5
4
3
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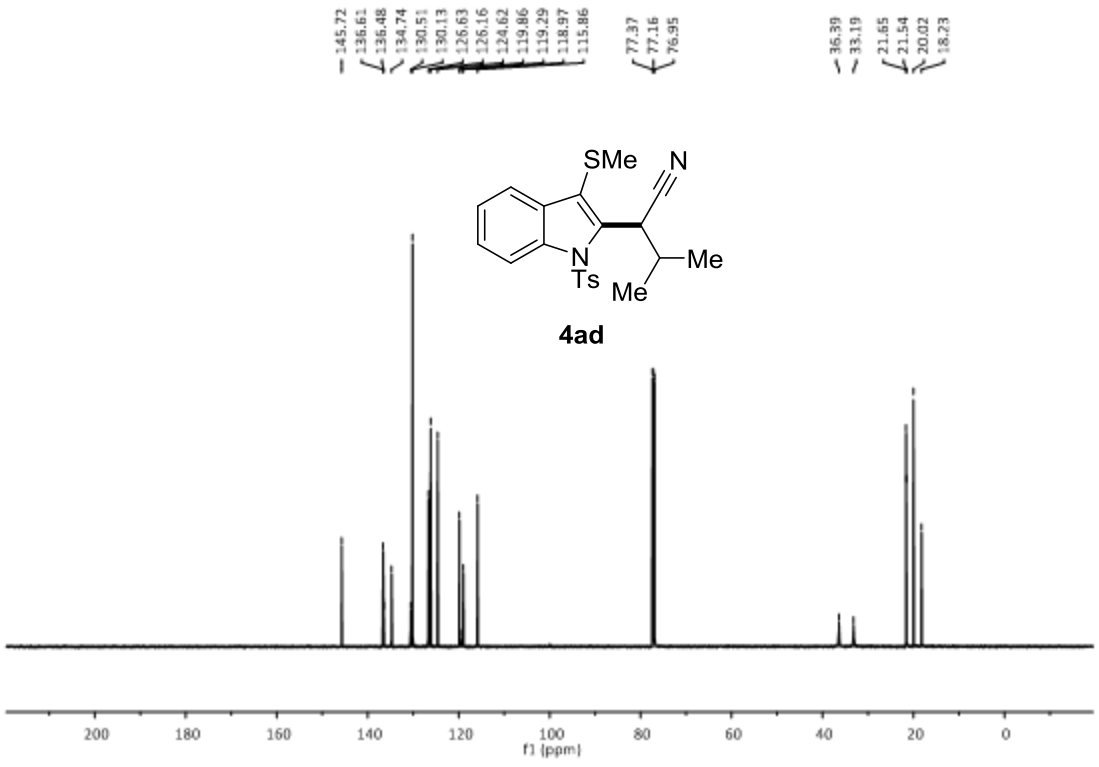
0
f1 (ppm)

4ad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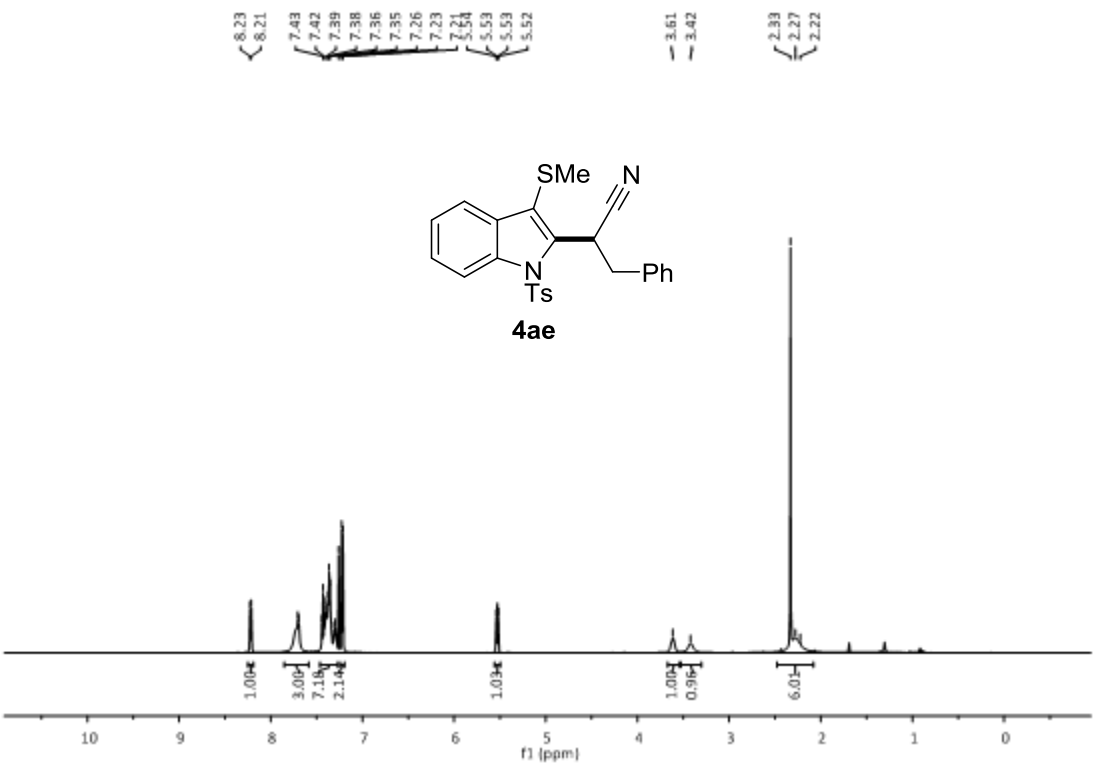
119.86
119.29
118.97
115.86
77.37
77.16
76.95
36.39
33.19
21.65
21.54
20.02
18.23
SMe
N
N
Ts
Me
Me
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

4ad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7.35
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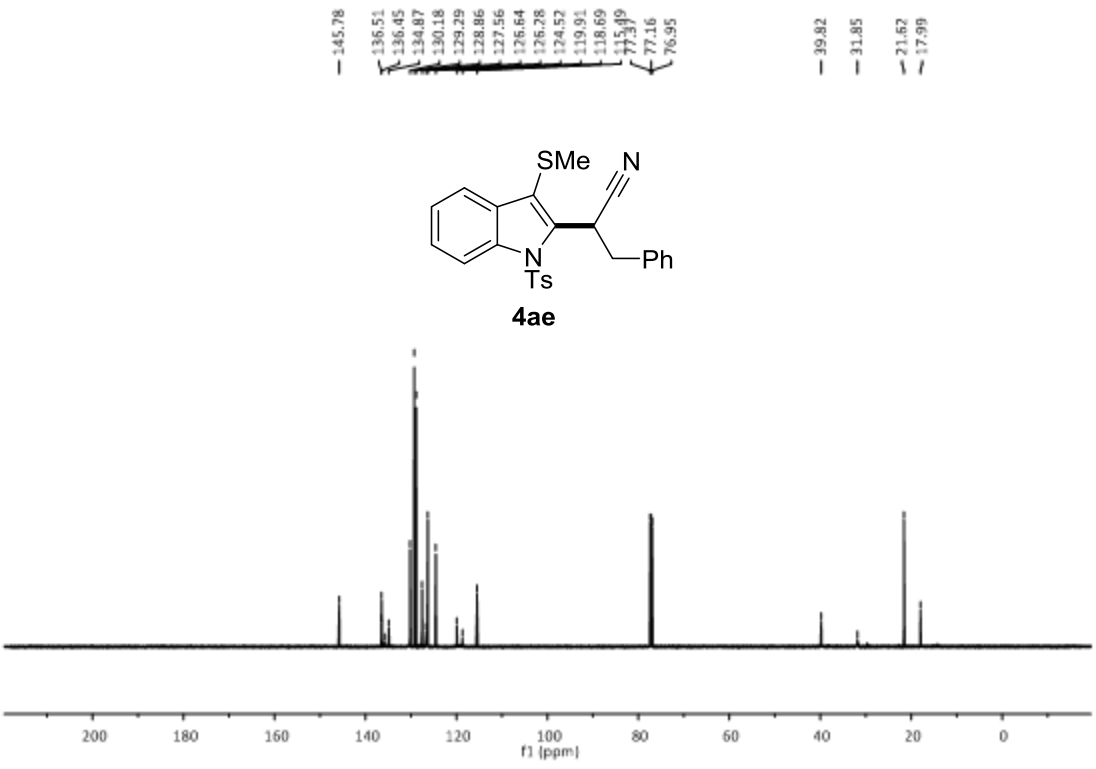
7.21
5.54
5.53
5.53
5.52
3.61
3.42
2.33
2.27
2.22
SMe
N
N
Ts
Ph
1.00
3.00
7.18
2.14
1.03
1.00
0.96
6.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

4ae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128.86
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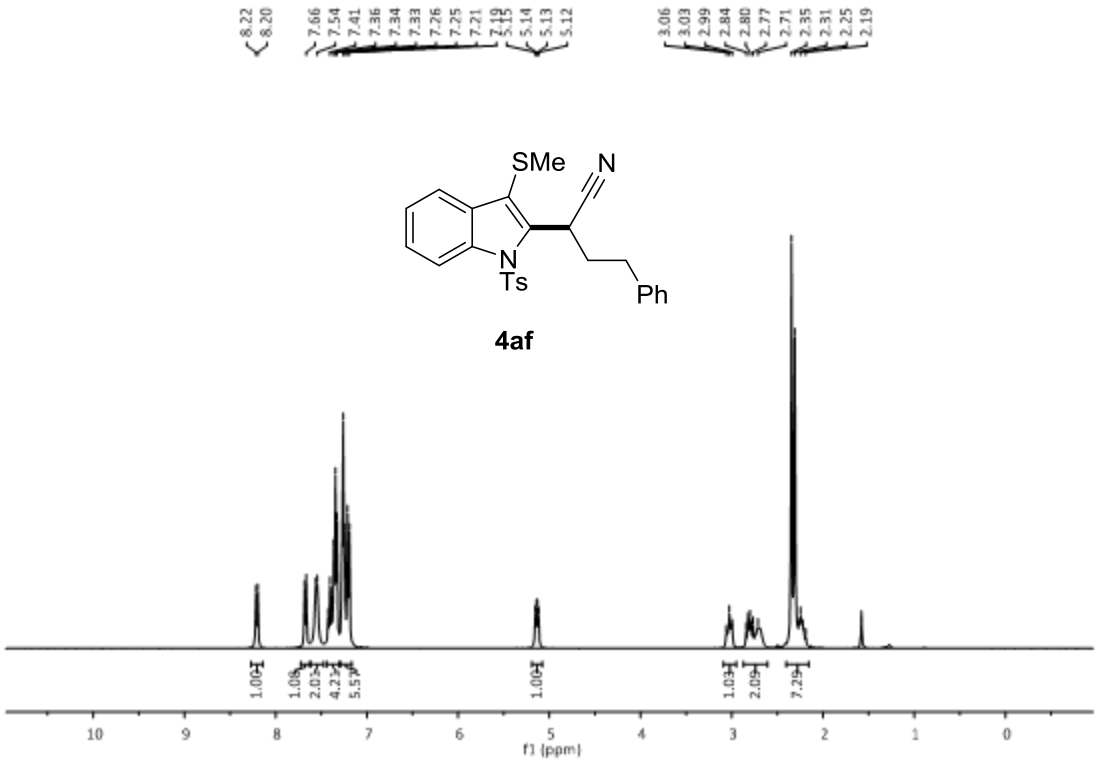
126.64
126.28
124.52
119.91
118.69
115.49
77.31
77.16
76.95
39.82
31.85
21.62
17.99
SMe
N
N
Ts
Ph
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

4ae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5.14
5.13
5.12
3.06
3.03
2.99
2.84
2.80
2.77
2.71
2.35
2.31
2.25
2.19
SMe
N
N
Ts
Ph
4af
1.00
1.08
2.03
4.23
5.57
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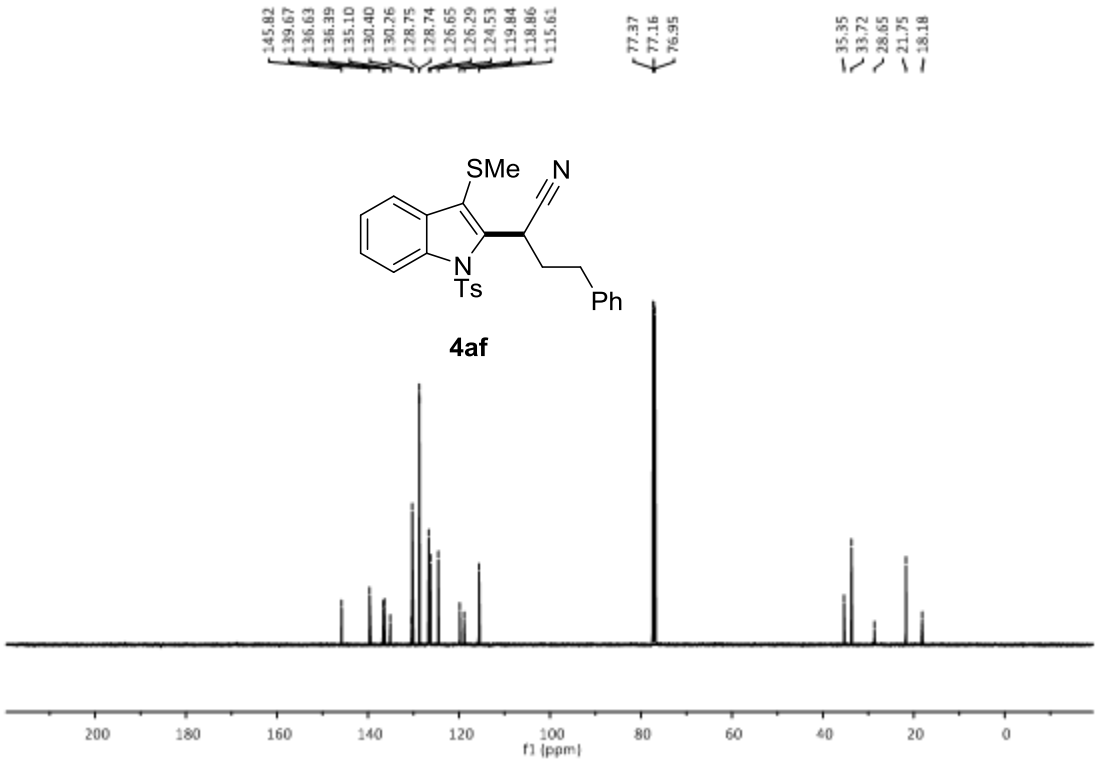
f1 (ppm)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118.86
115.61
77.37
77.16
76.95
35.35
33.72
28.65
21.75
18.18
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Ts
Ph
4af
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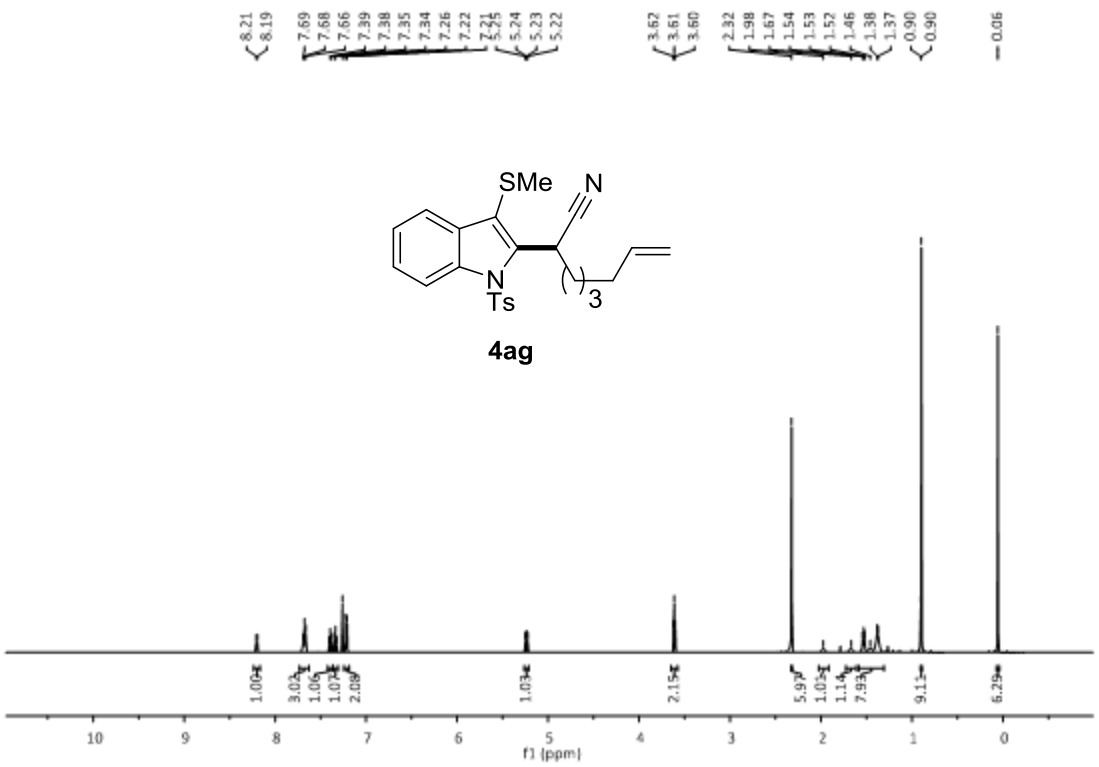
f1 (ppm)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5.23
5.22
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3.61
3.60
2.32
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1.67
1.54
1.53
1.52
1.46
1.38
1.37
0.90
0.90
0.06
SMe
N
N
Ts
3
1.00
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1.05
1.07
2.09
1.03
2.15
5.97
1.03
1.14
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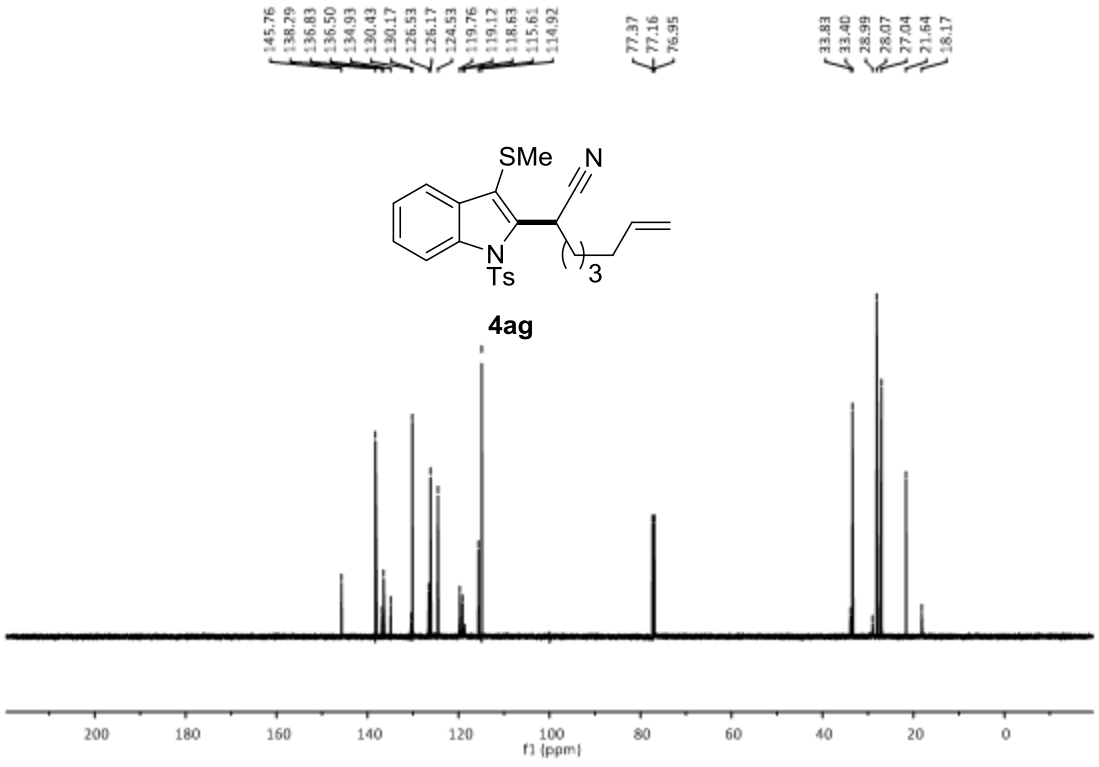
f1 (ppm)

4ag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115.61
114.92
77.37
77.16
76.95
33.83
33.40
28.99
28.07
27.04
21.64
18.17
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N
N
Ts
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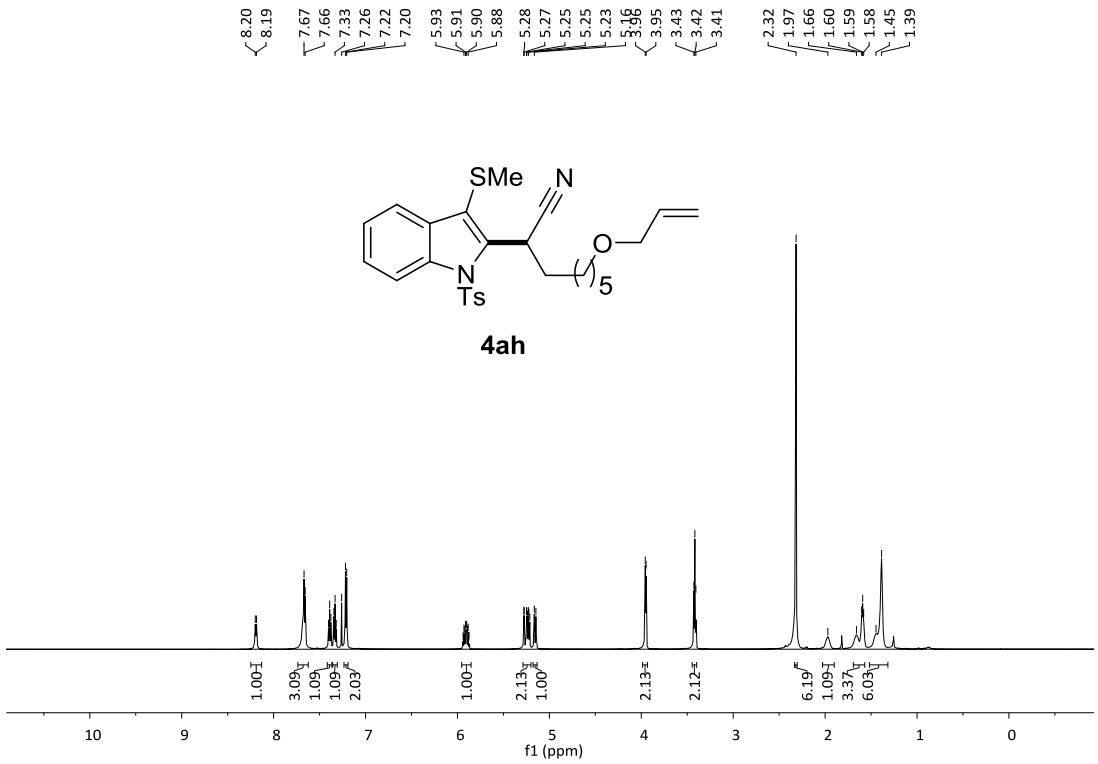
0
f1 (ppm)

4ag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5.25
5.23
3.96
3.95
3.43
3.42
3.41
2.32
1.97
1.66
1.60
1.59
1.58
1.45
1.39
SMe
N
O
N
Ts
5
4ah
1.00
3.09
1.05
1.09
2.03
1.00
2.13
1.00
2.13
2.12
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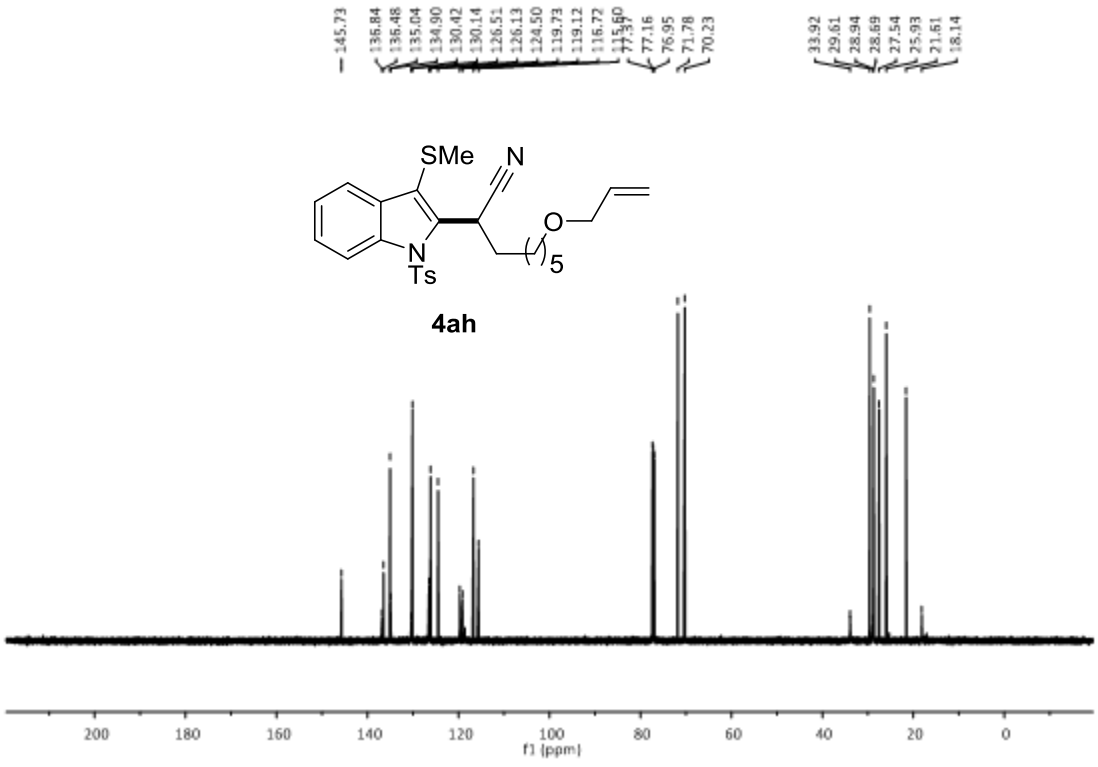
f1 (ppm)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126.13
124.50
119.73
119.12
116.72
115.60
77.37
77.16
76.95
71.78
70.23
33.92
29.61
28.94
28.69
27.54
25.93
21.61
18.14
SMe
N
O
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Ts
5
4ah
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100
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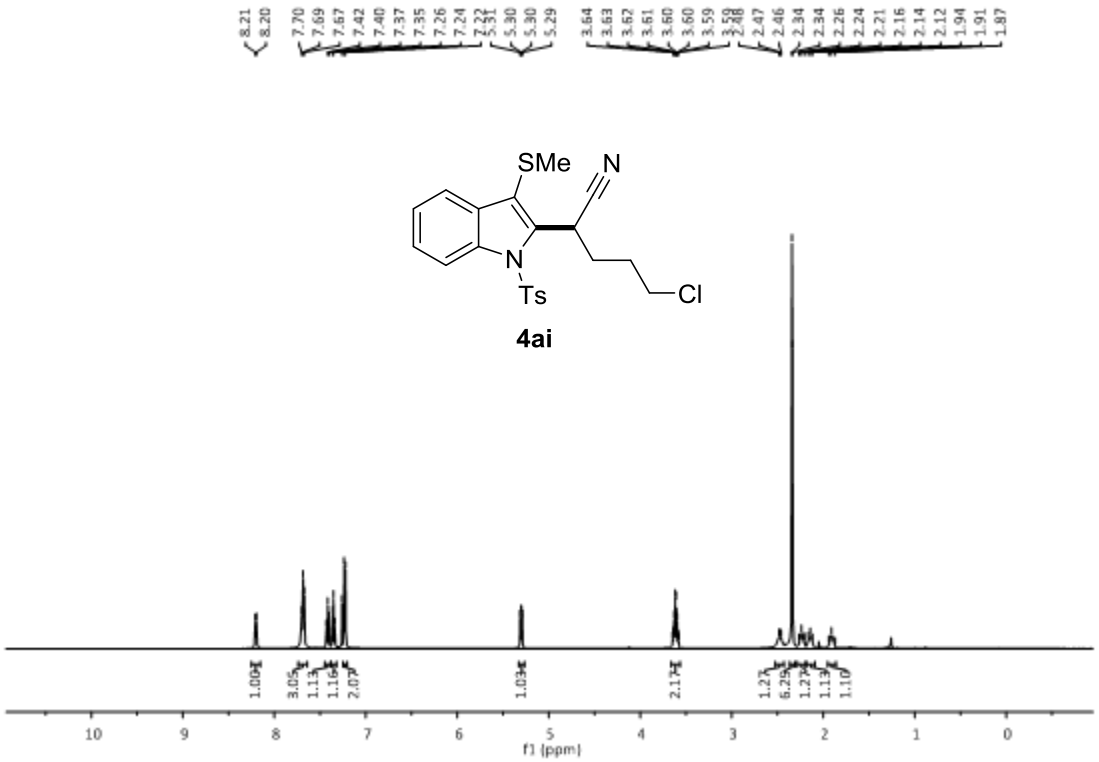
f1 (ppm)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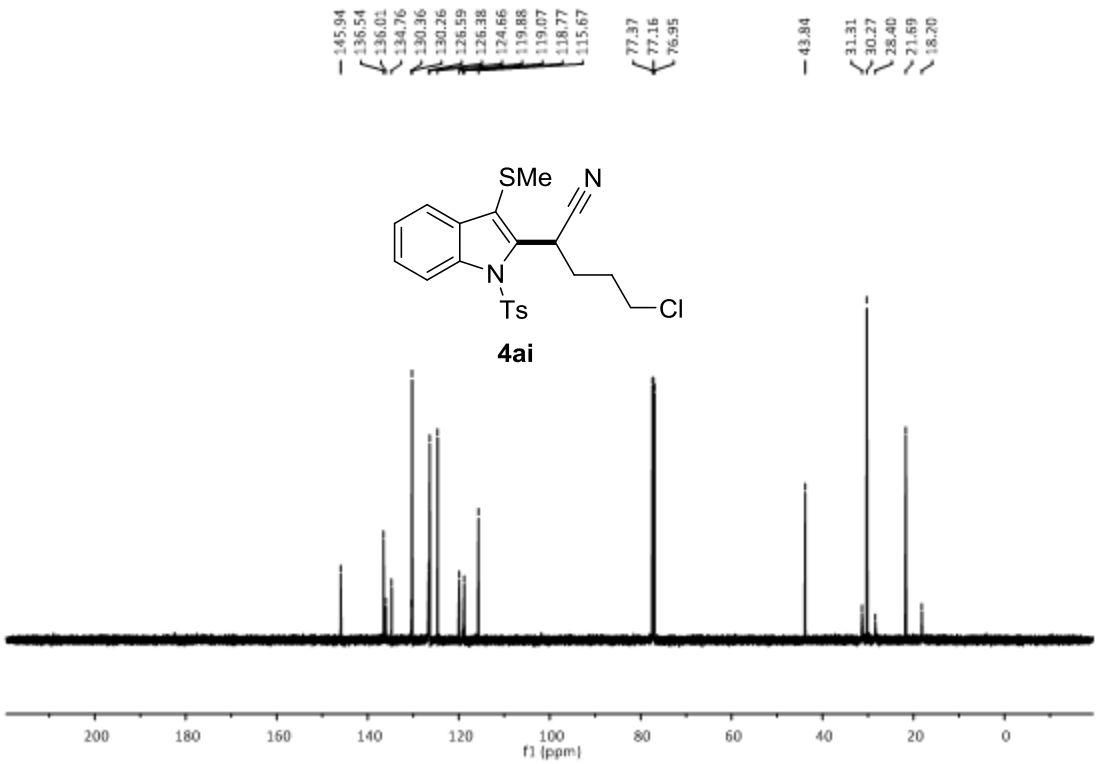
N
Ts
Cl
4ai
f1 (ppm)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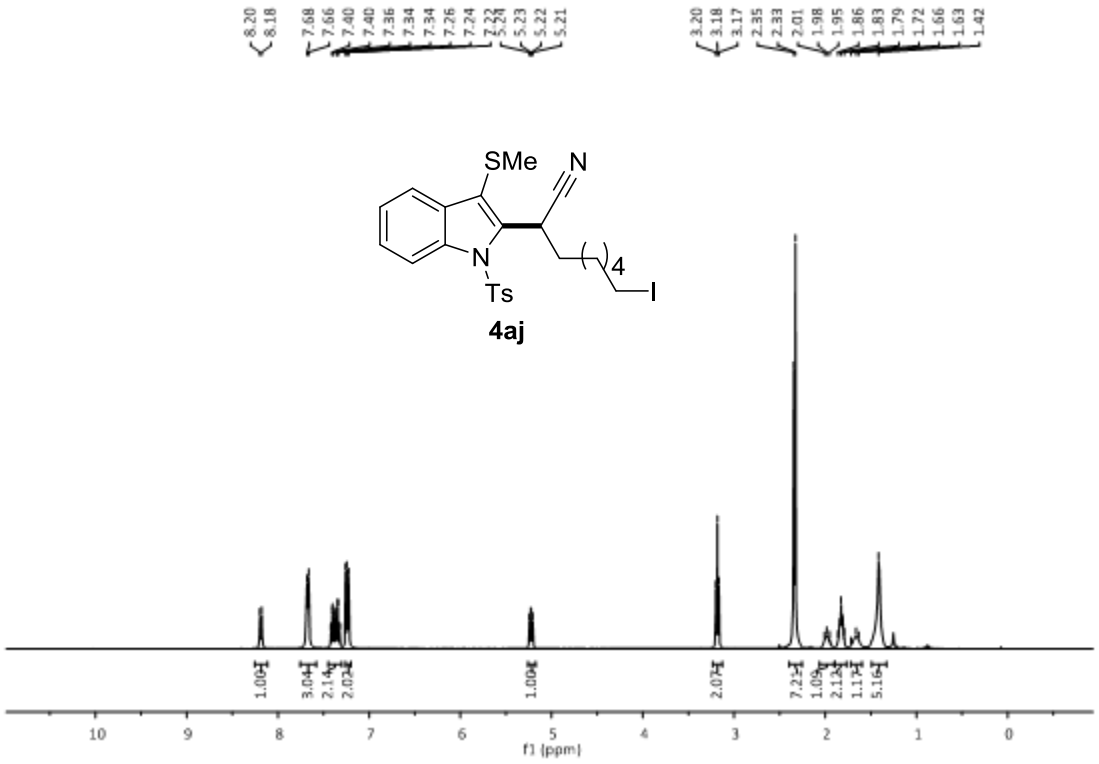
Ts
Cl
4ai
f1 (ppm)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Ts
4
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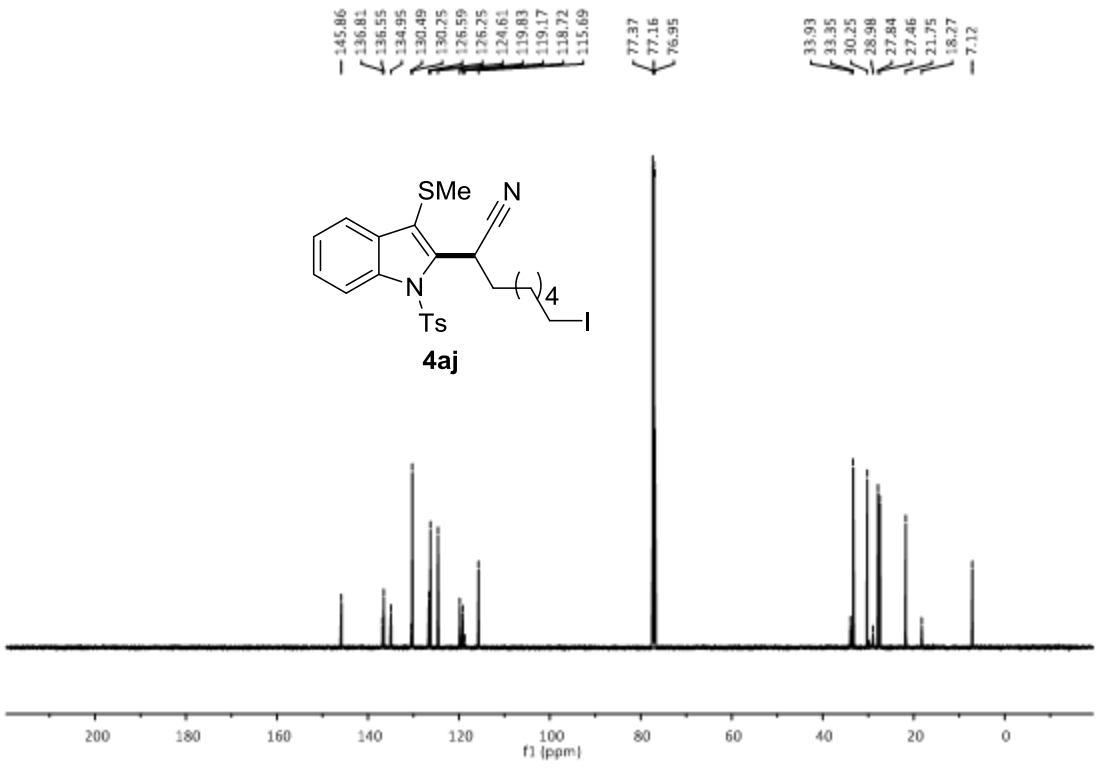
4aj
f1 (ppm)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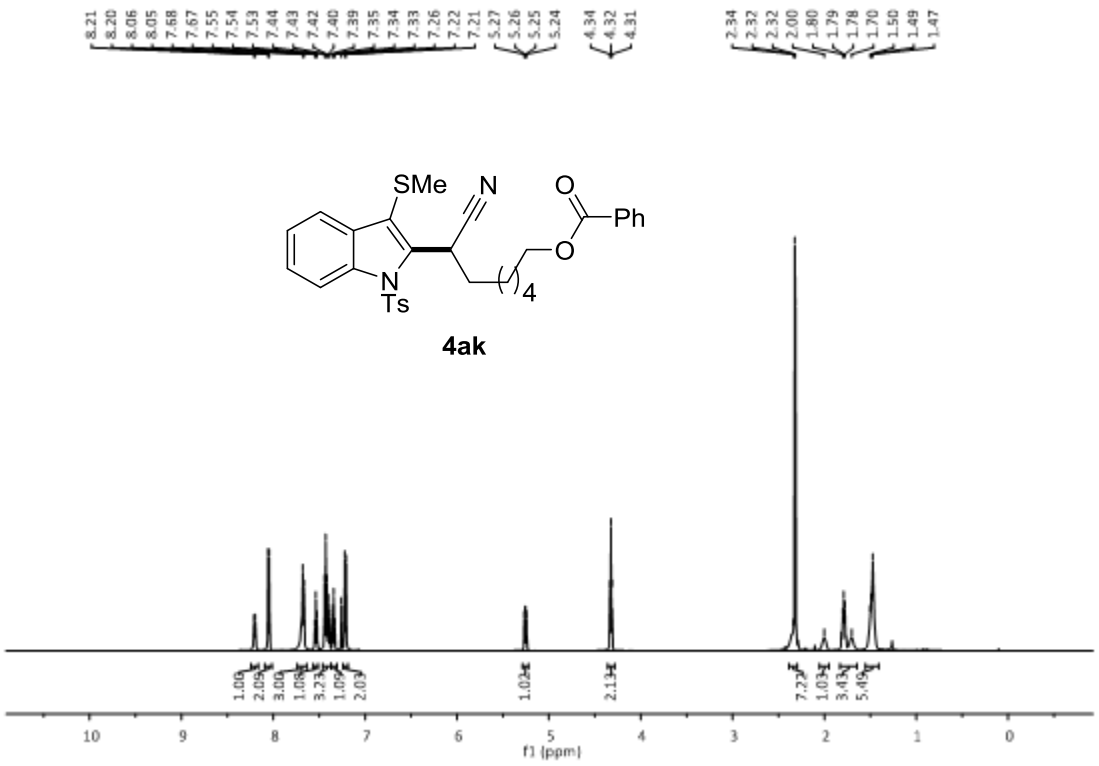
N
Ts
4
I
4aj
f1 (ppm)



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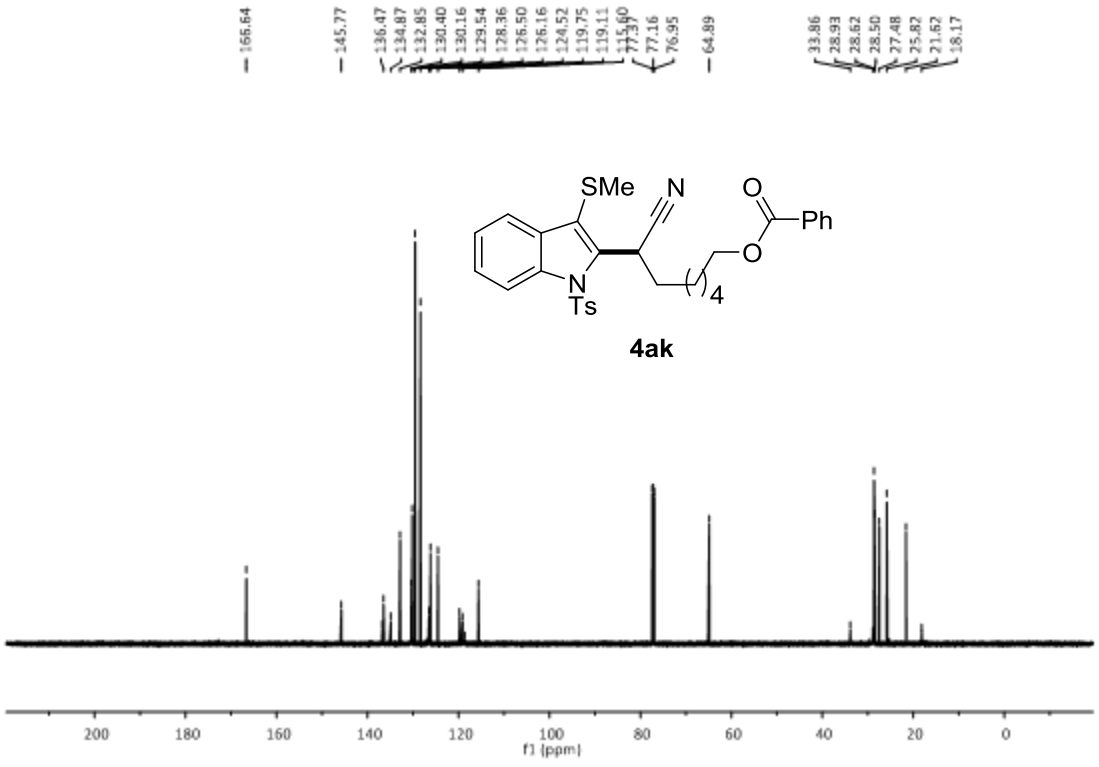

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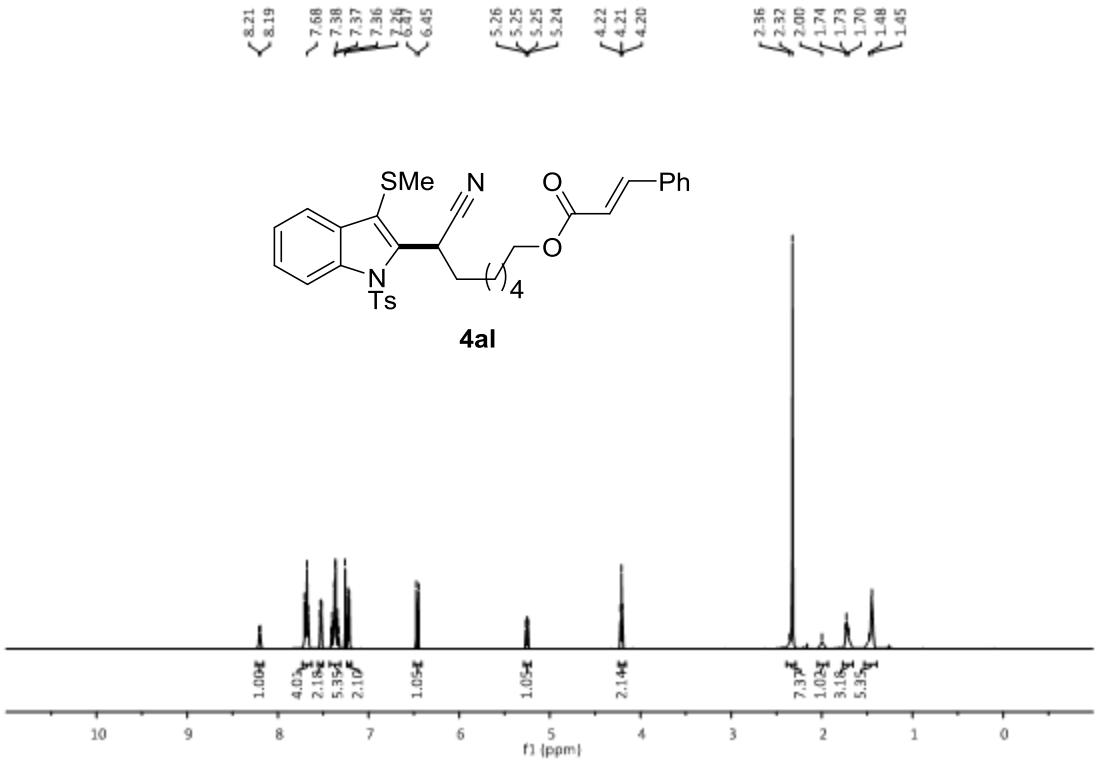
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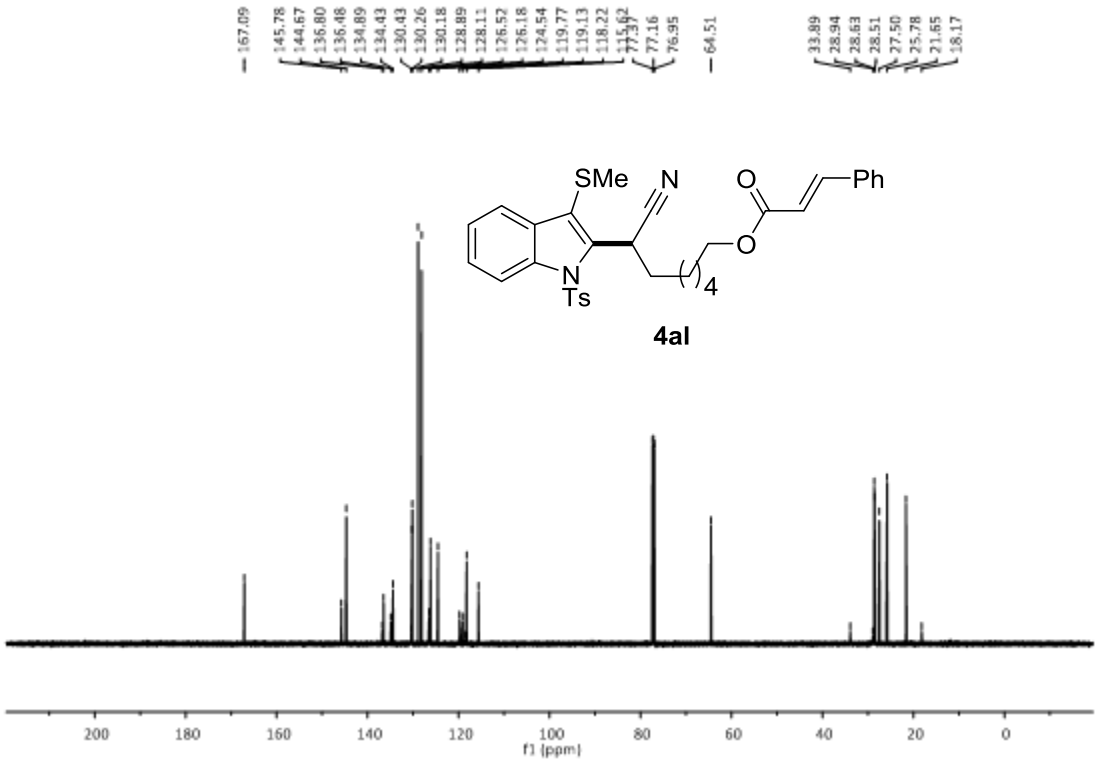
Ph
O
N
Ts
4
4al
f1 (ppm)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Ph
O
N
Ts
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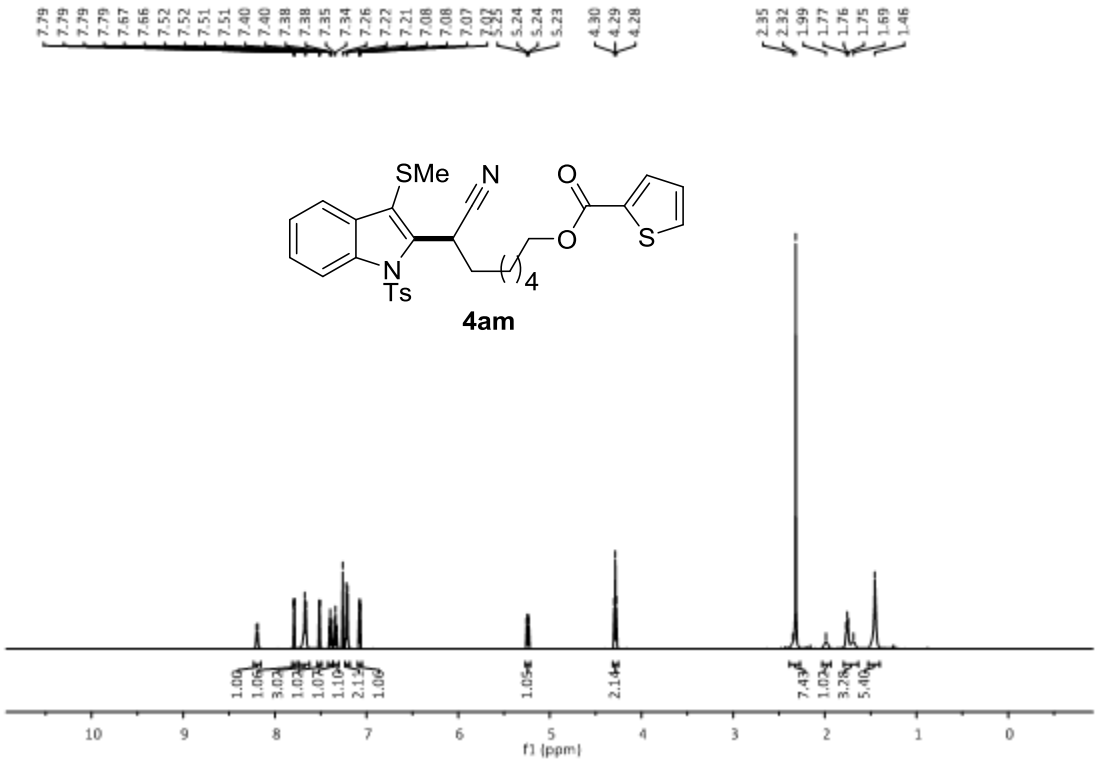
4al
f1 (ppm)



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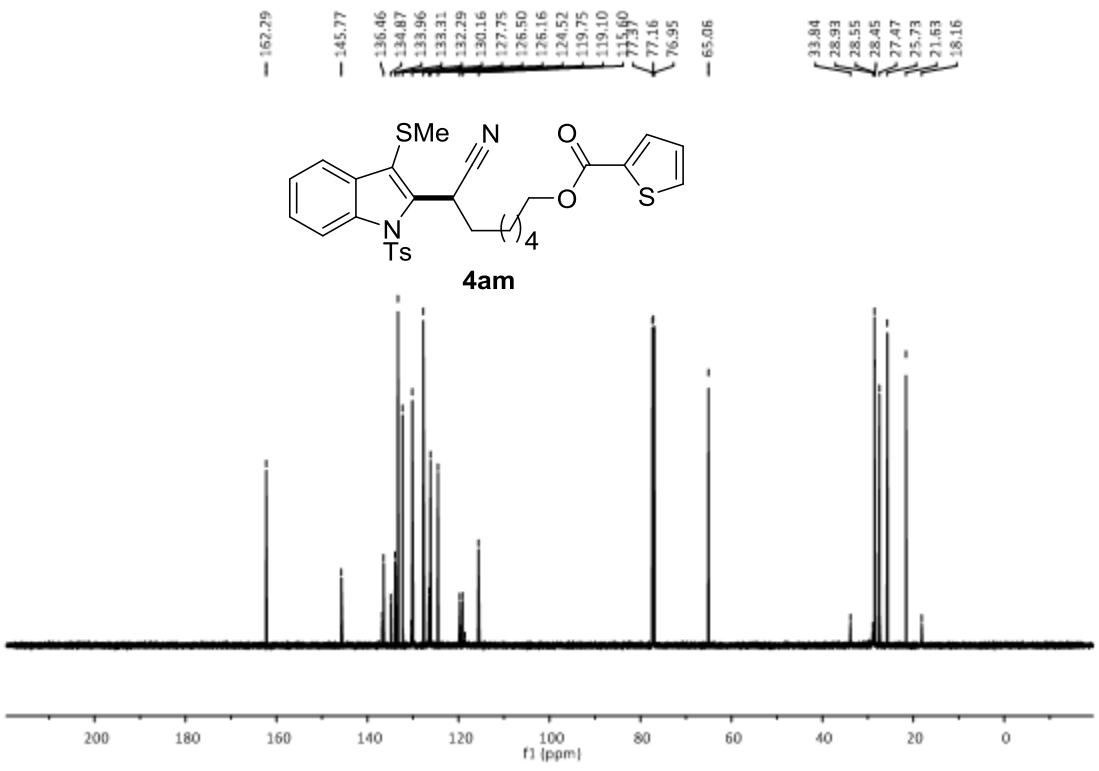

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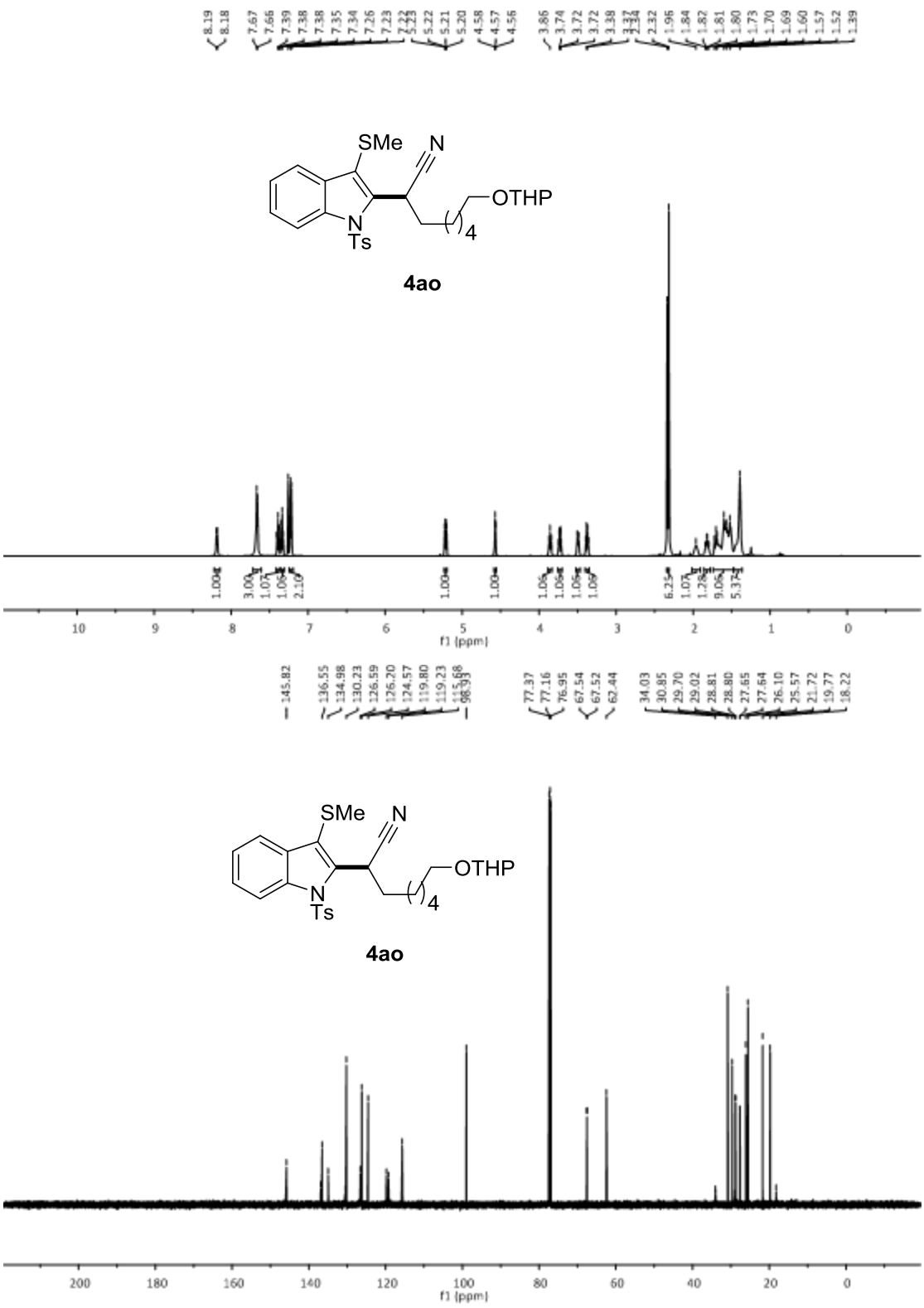
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OTHP
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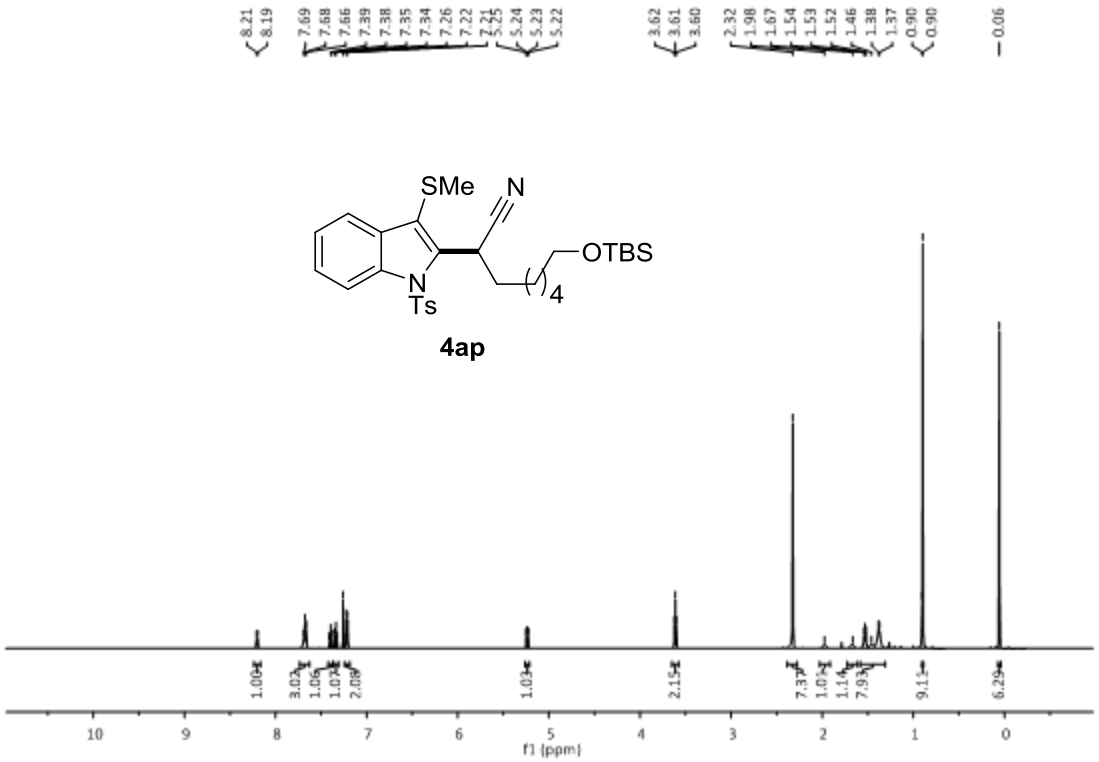
Ts
4
4ao
f1 (ppm)
SMe
N
OTHP
N
Ts
4
4ao
f1 (ppm)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Ts
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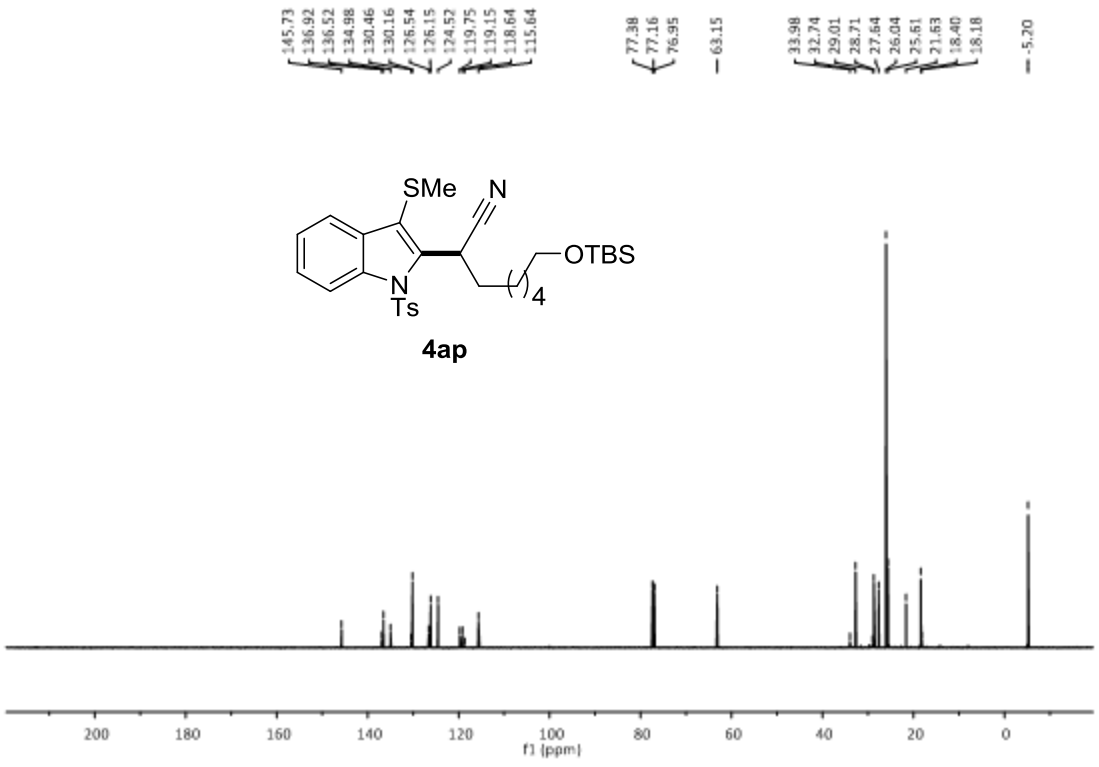
f1 (ppm)


SMe
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OTBS
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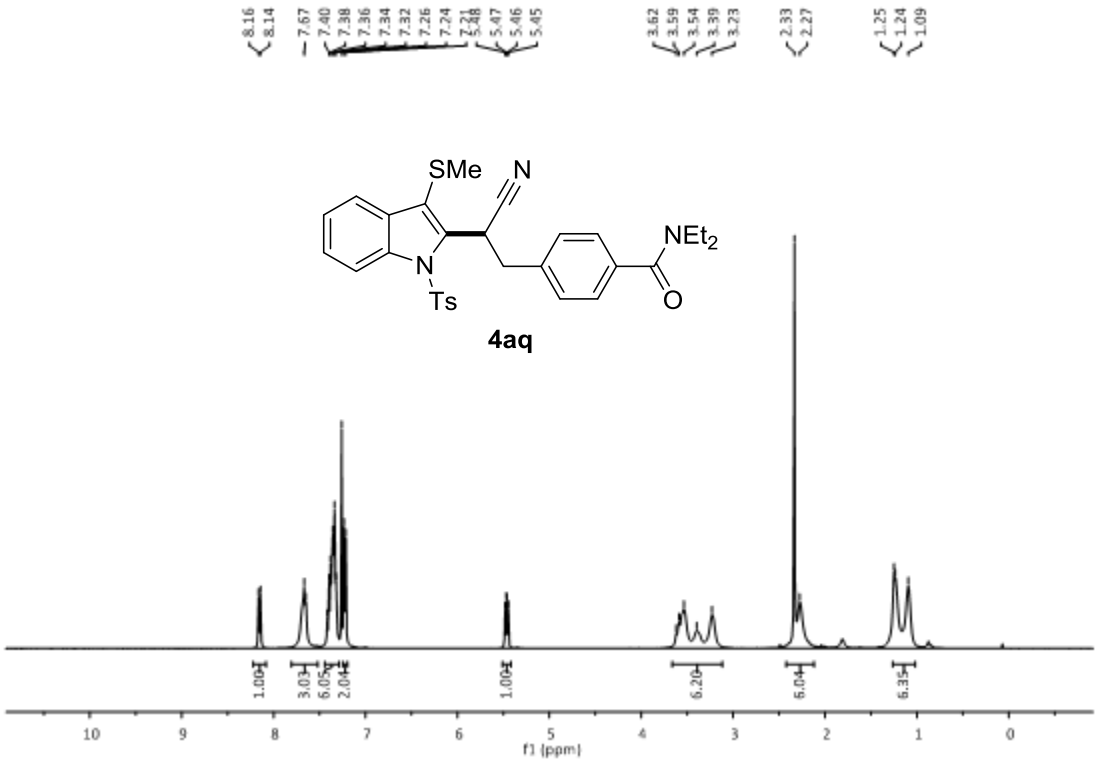
Ts
4
4ap
f1 (ppm)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7.24
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5.48
5.47
5.46
5.45
3.62
3.59
3.54
3.39
3.23
2.33
2.27
1.25
1.24
1.09
SMe
N
NEt2
N
Ts
O
4aq
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3.03
6.05
2.04
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6.36
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9
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7
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5
4
3
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1
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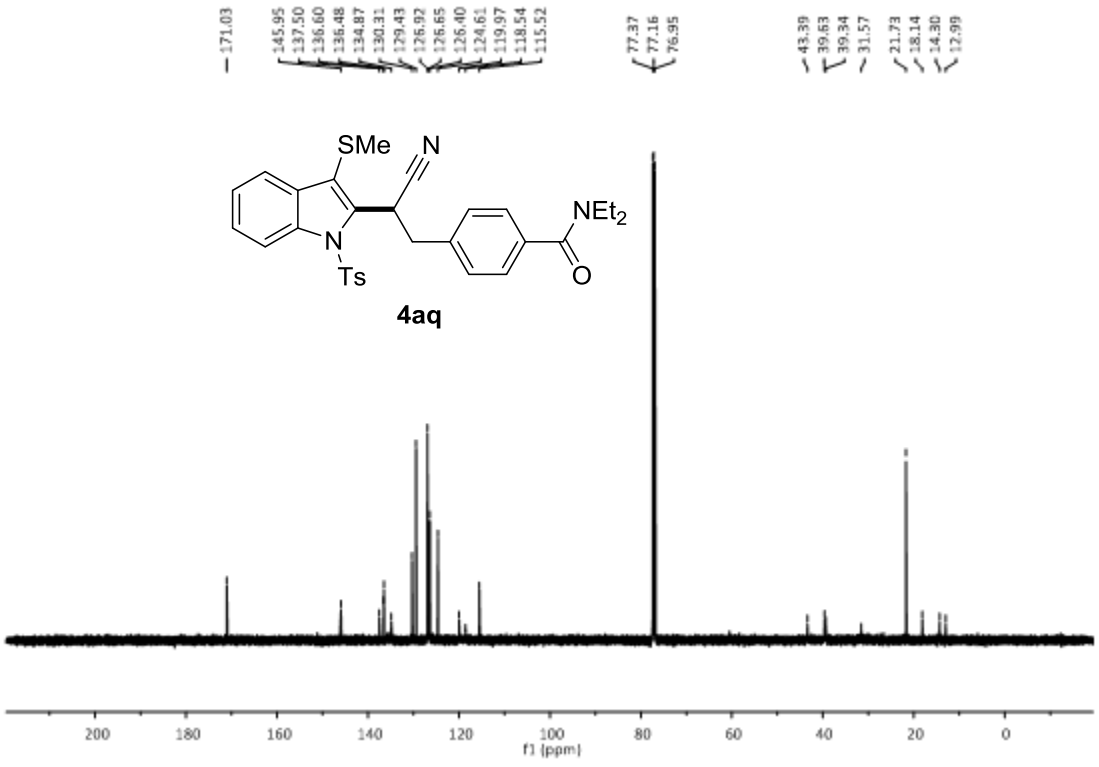
f1 (ppm)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126.65
126.40
124.61
119.97
118.54
115.52
77.37
77.16
76.95
43.39
39.63
39.34
31.57
21.73
18.14
14.30
12.99
SMe
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NEt2
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Ts
O
4aq
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140
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100
80
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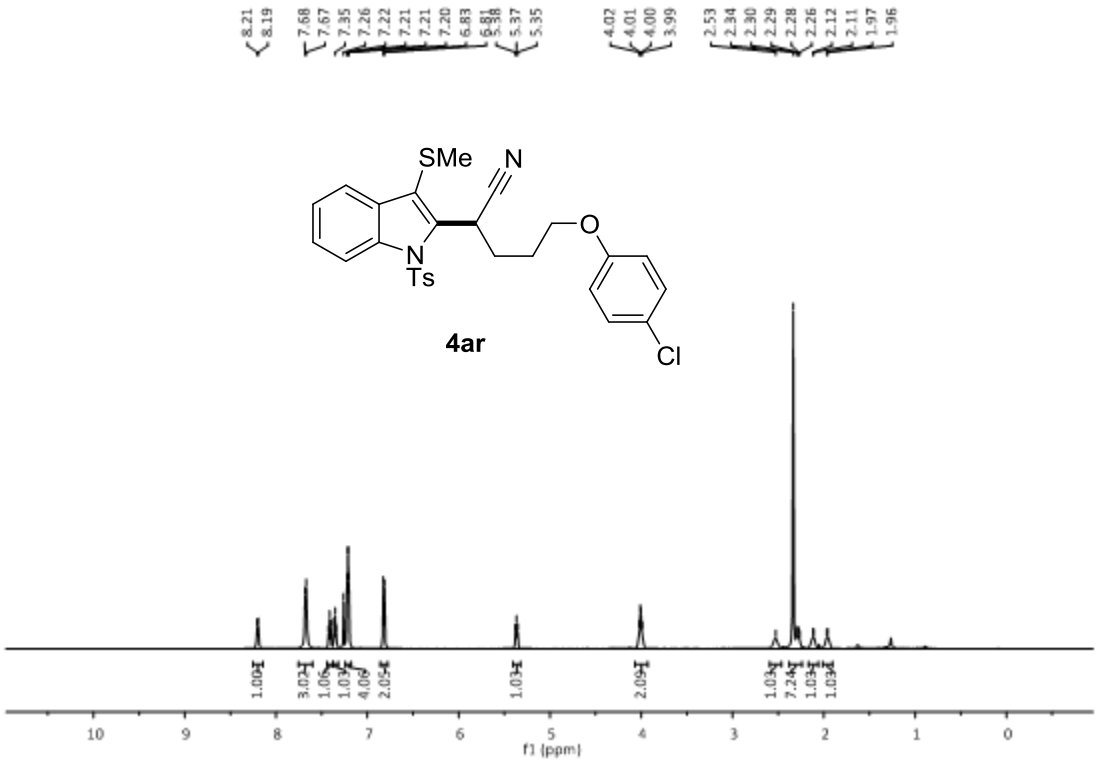
20
0
f1 (ppm)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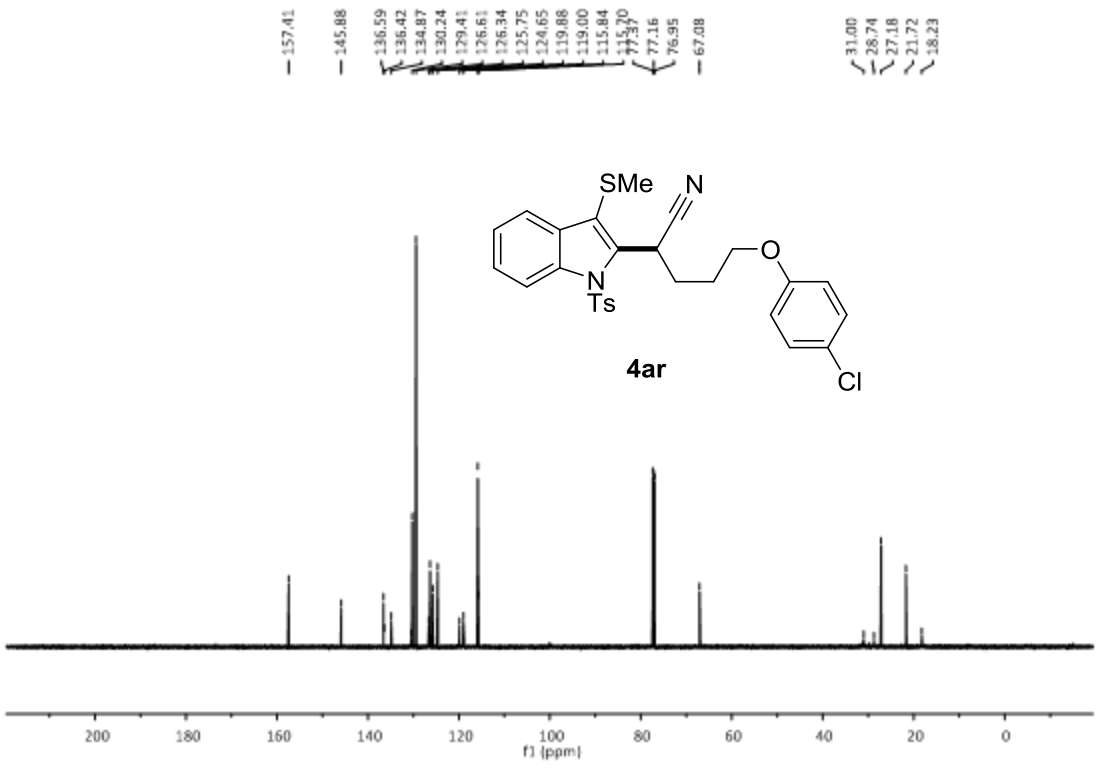
O
N
Ts
Cl
4ar
f1 (ppm)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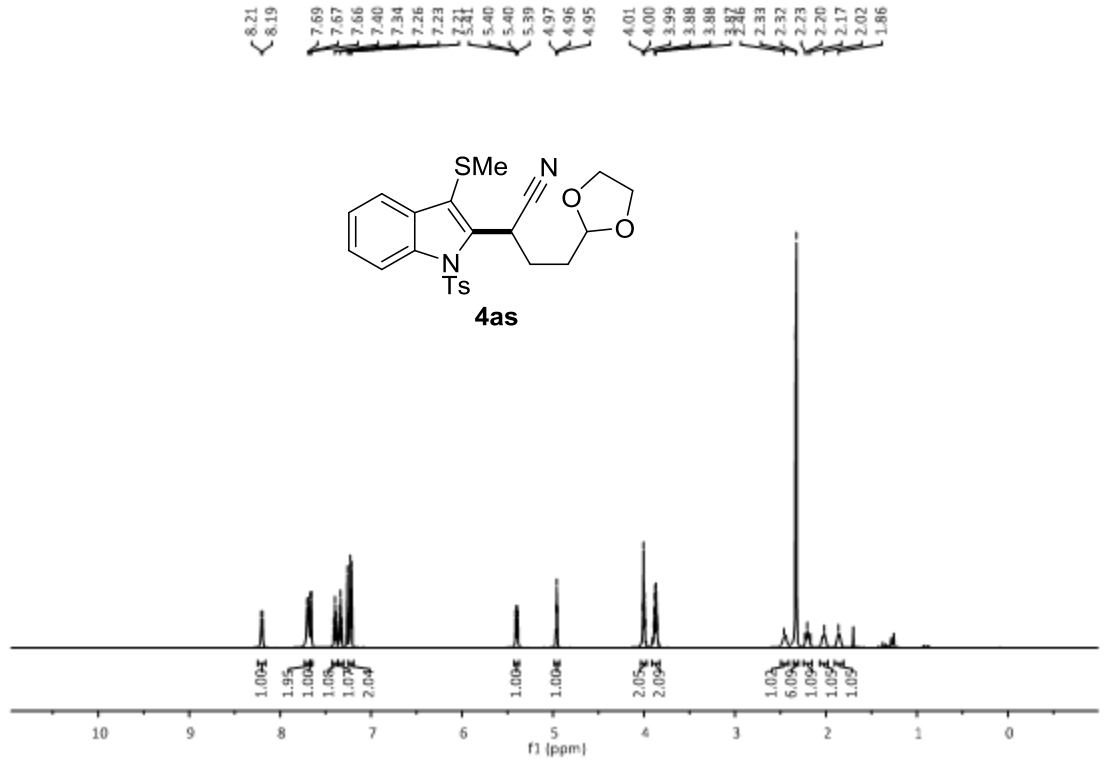
Ts
Cl
4ar
f1 (ppm)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7.23
5.40
5.40
5.39
4.97
4.96
4.95
4.01
4.00
3.99
3.88
3.88
2.33
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2.17
2.02
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SMe
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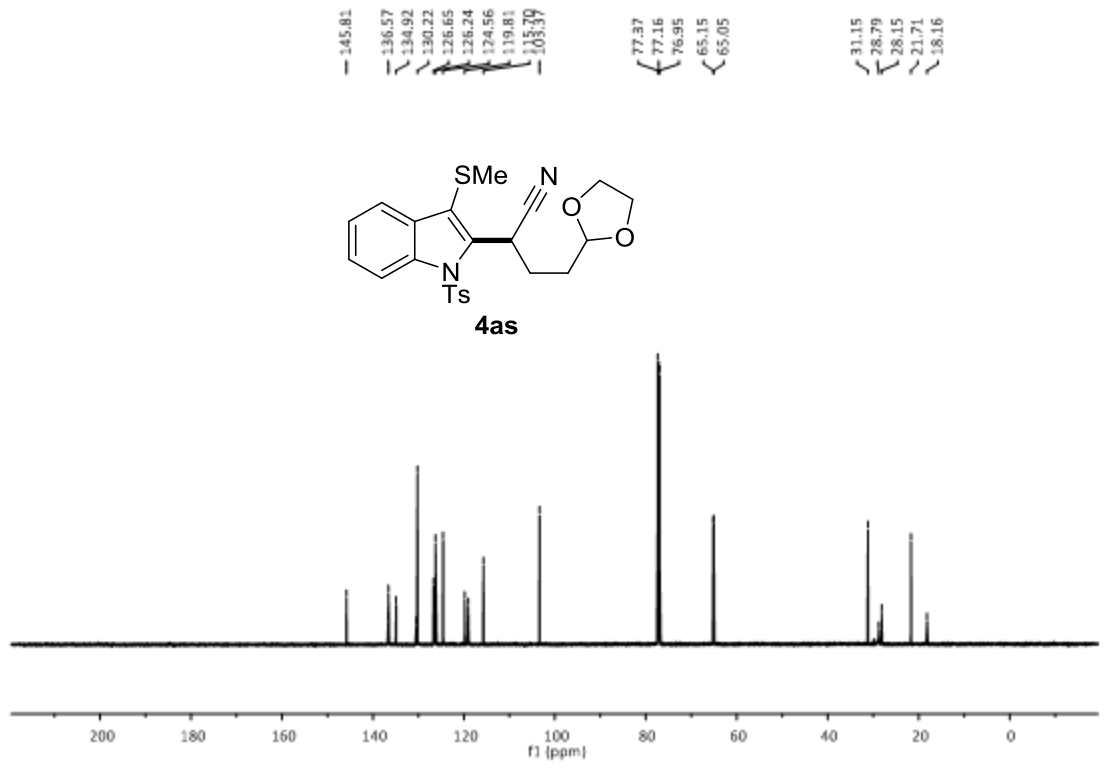
O
O
N
Ts
4as
f1 (ppm)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77.16
76.95
65.15
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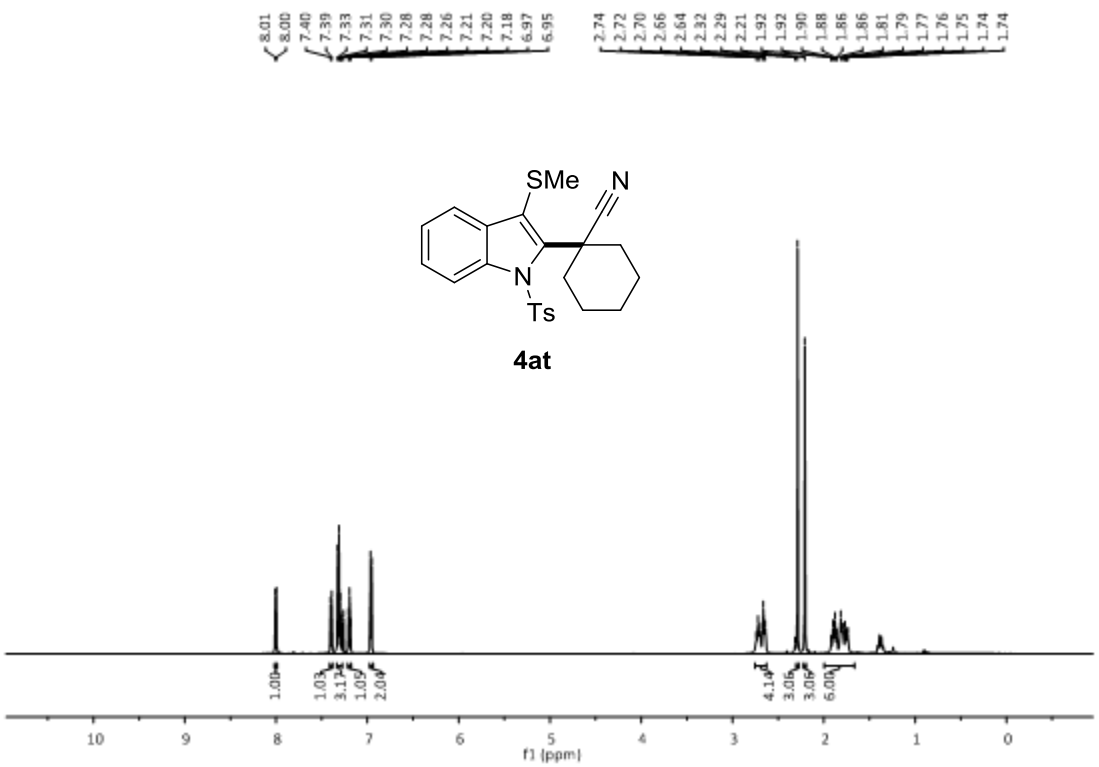
28.15
21.71
18.16
SMe
N
O
O
N
Ts
4as
f1 (ppm)


SMe
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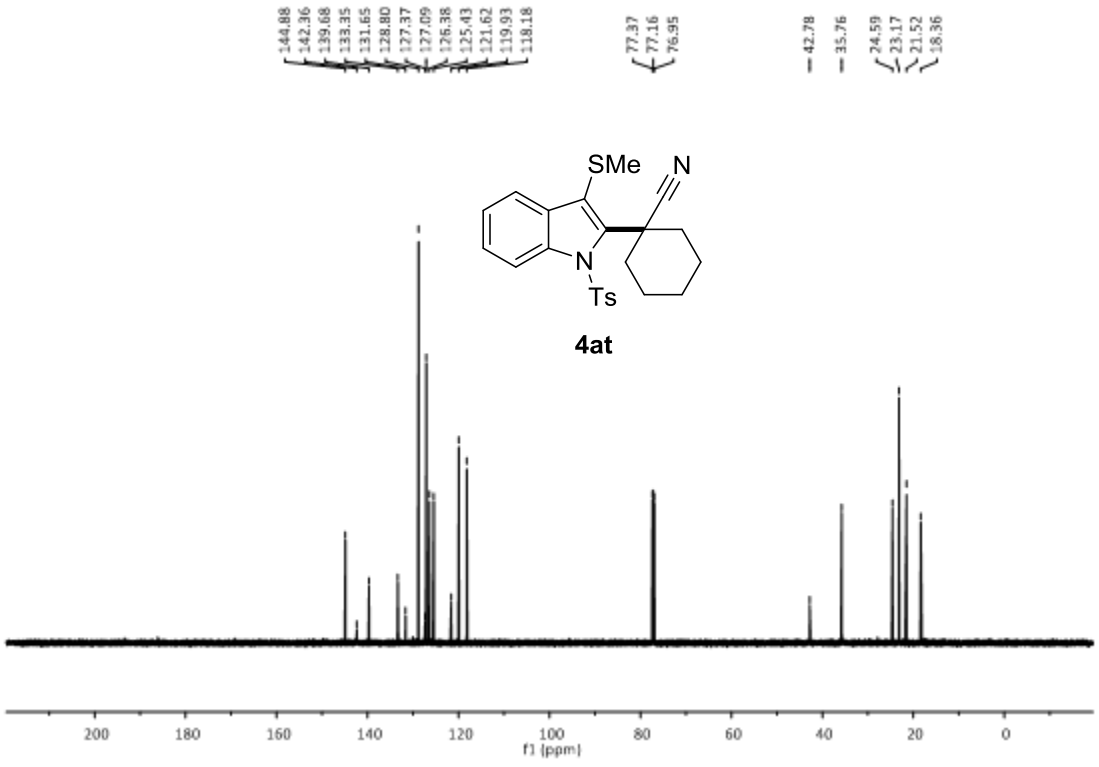
N
Ts
4at
f1 (ppm)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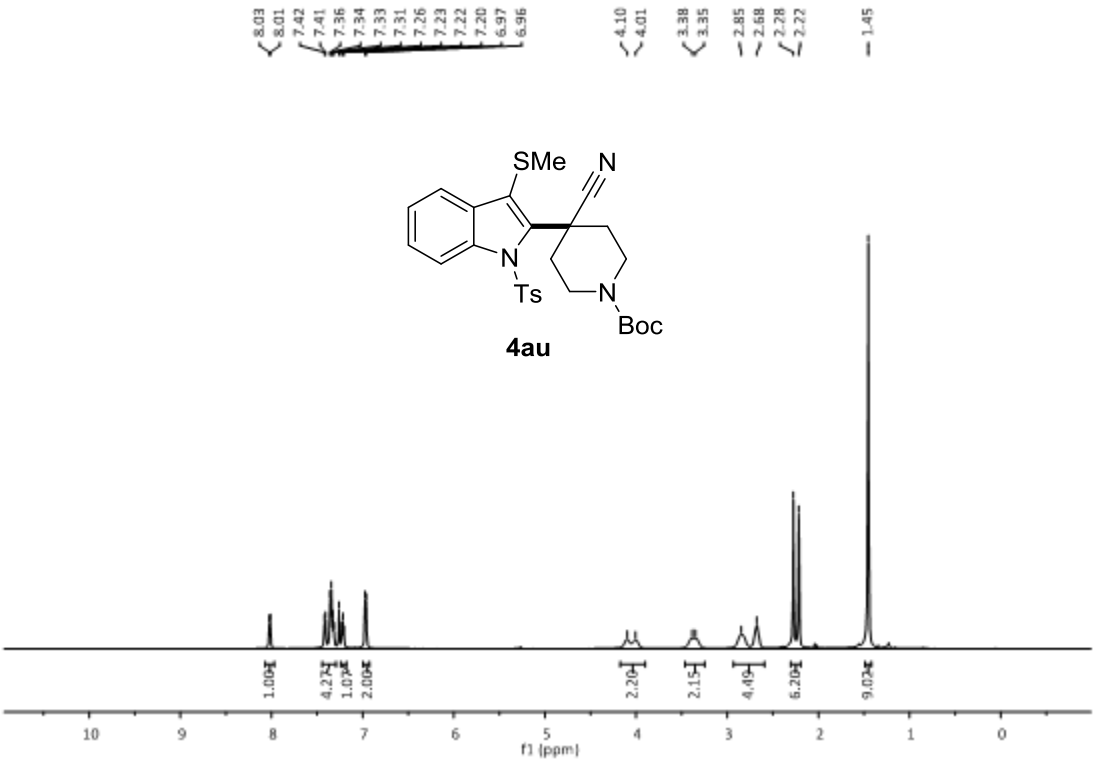
4at
f1 (ppm)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7.23
7.22
7.20
6.97
6.96
4.10
4.01
3.38
3.35
2.85
2.68
2.28
2.22
1.45
SMe
N
N
Ts
N
Boc
4au
1.00
4.27
1.07
2.00
2.20
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9.02
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9
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7
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5
4
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1
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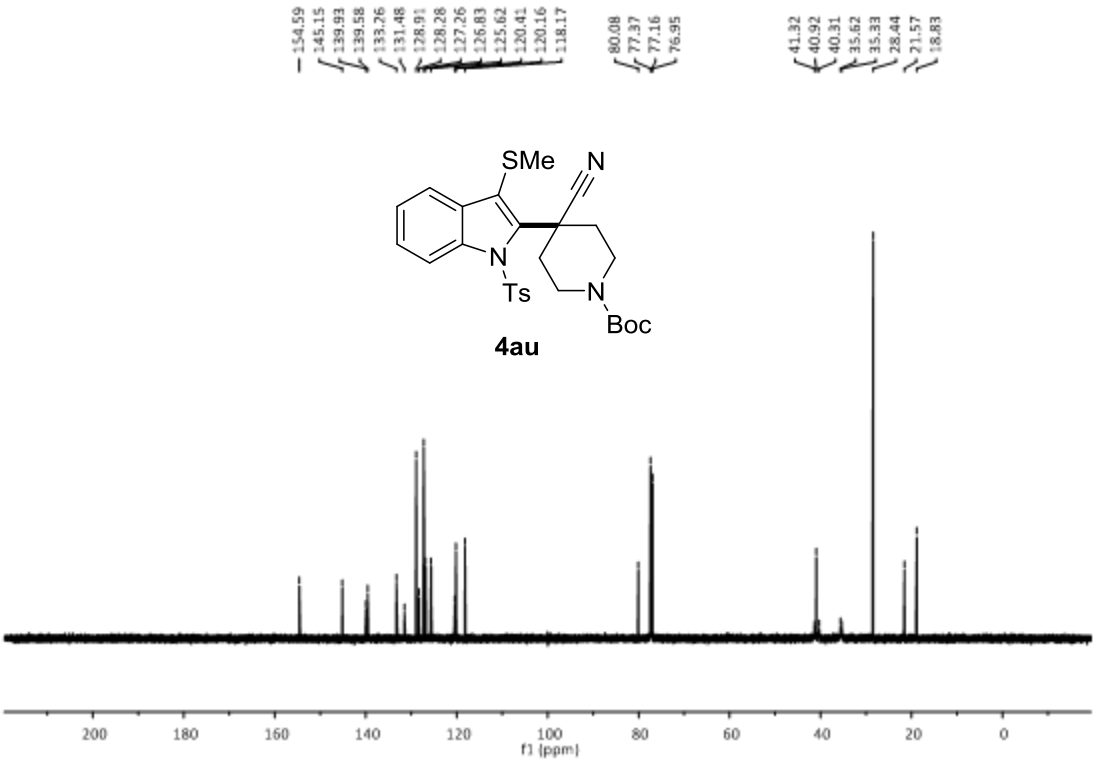
f1 (ppm)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120.41
120.16
118.17
80.08
77.37
77.16
76.95
41.32
40.92
40.31
35.62
35.33
28.44
21.57
18.83
SMe
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Ts
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Boc
4au
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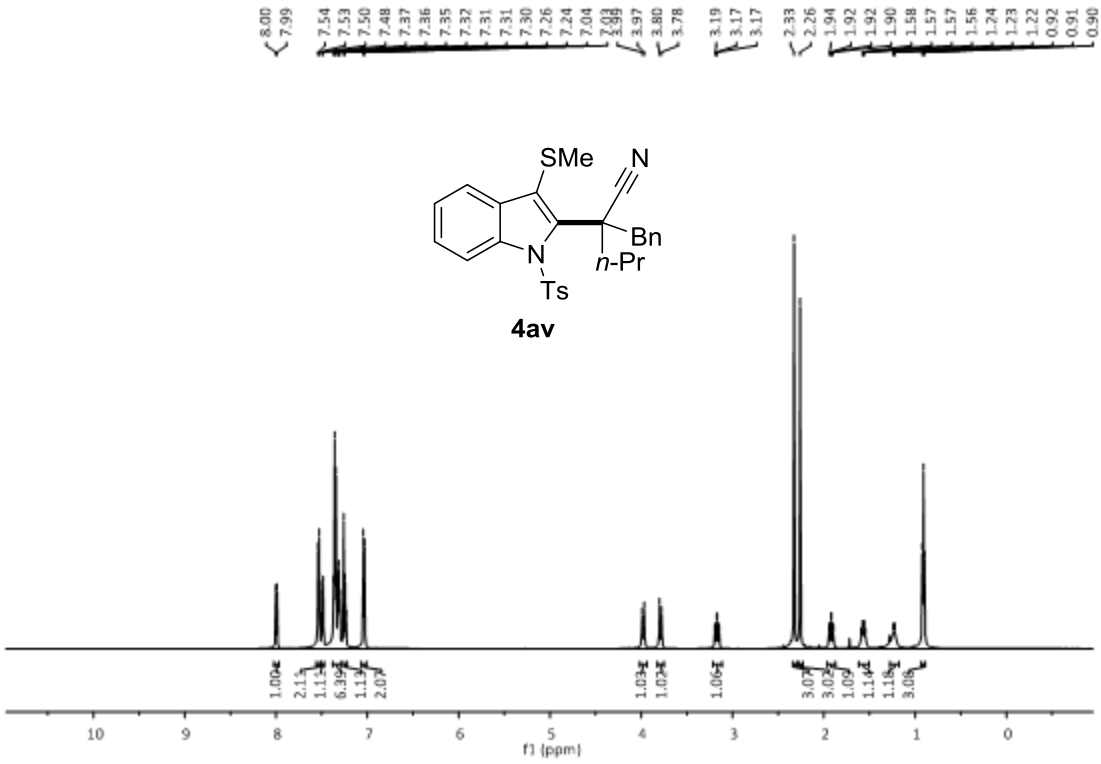
f1 (ppm)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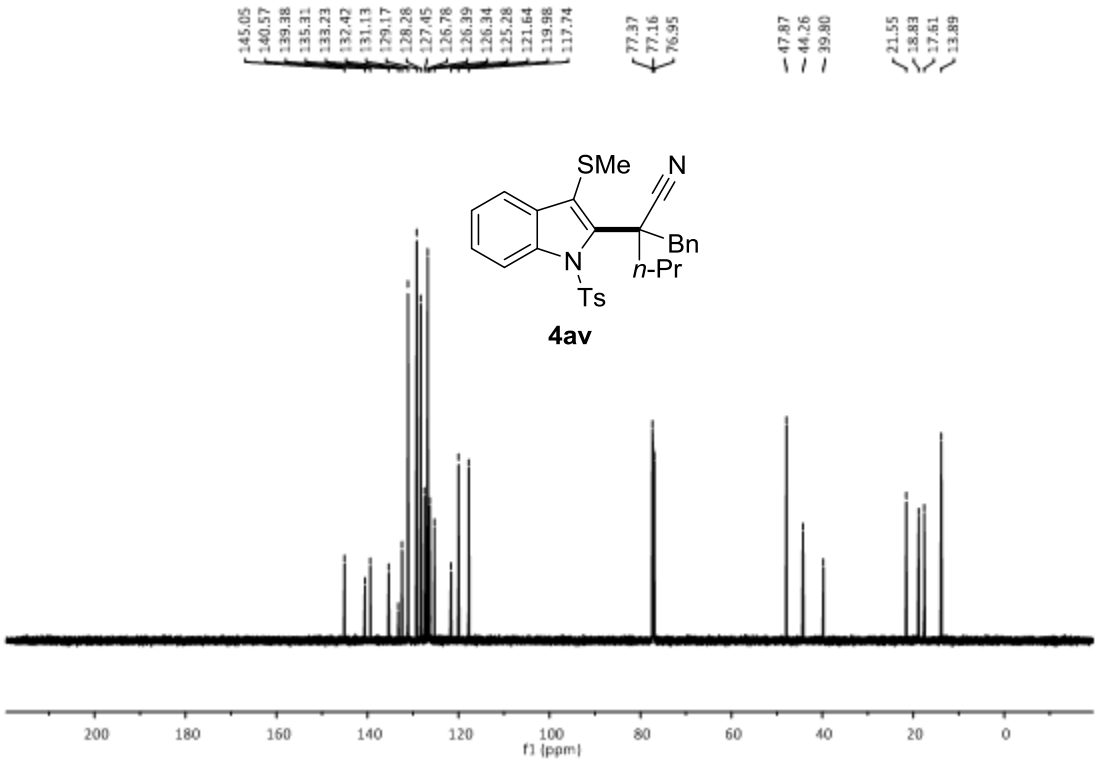
Bn
n-Pr
N
Ts
4av
f1 (ppm)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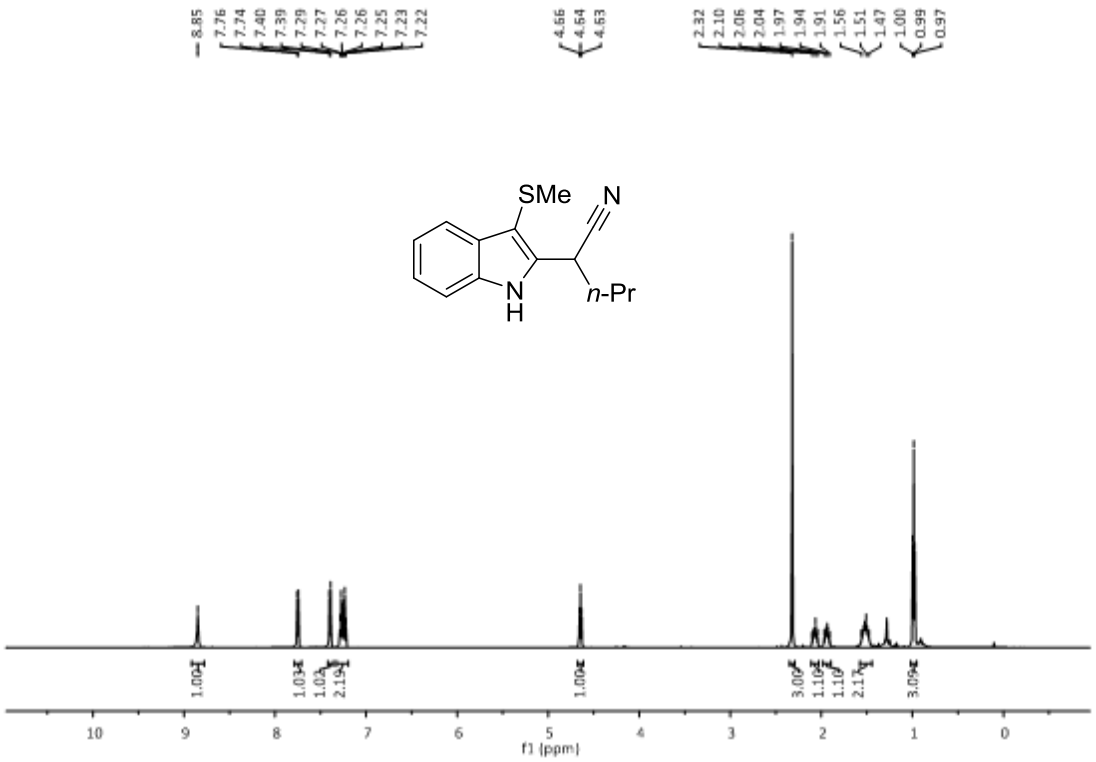
Bn
n-Pr
N
Ts
4av
f1 (ppm)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4.66
4.64
4.63
2.32
2.10
2.06
2.04
1.97
1.94
1.91
1.56
1.51
1.47
1.00
0.99
0.97
SMe
N
N
H
n-Pr
1.00
1.03
1.02
2.19
1.00
3.00
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3.09
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9
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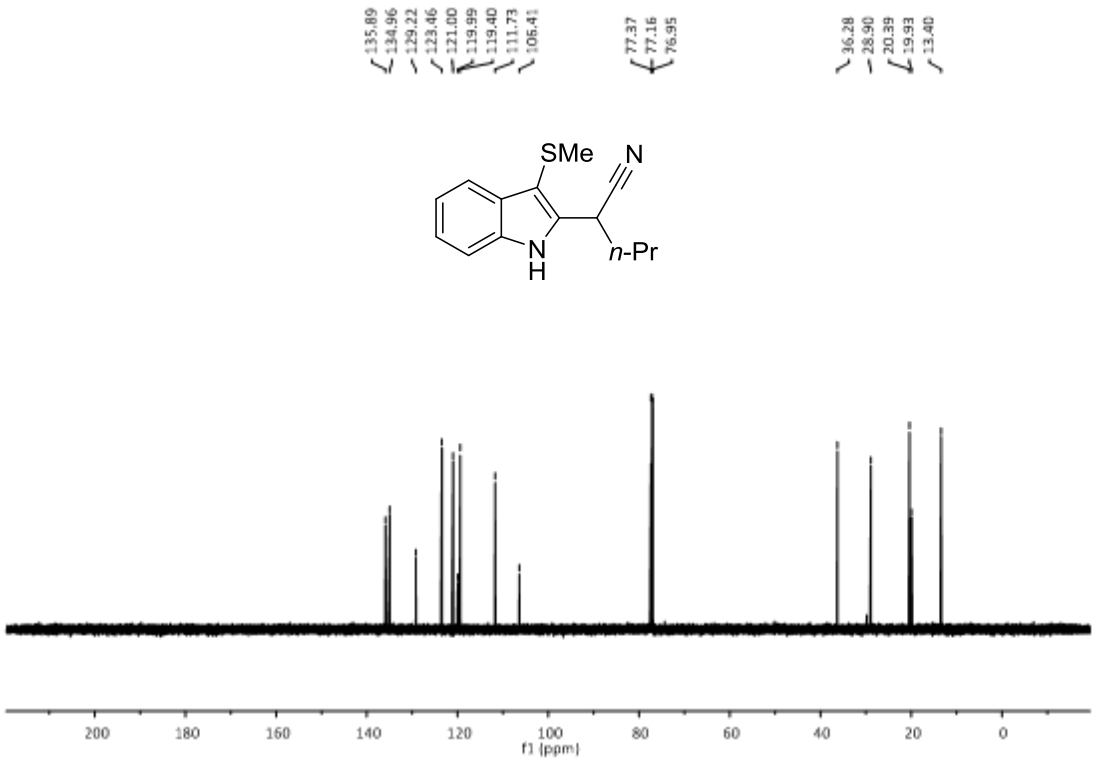
f1 (ppm)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77.37
77.16
76.95
36.28
28.90
20.39
19.93
13.40
SMe
N
N
H
n-Pr
200
180
160
140
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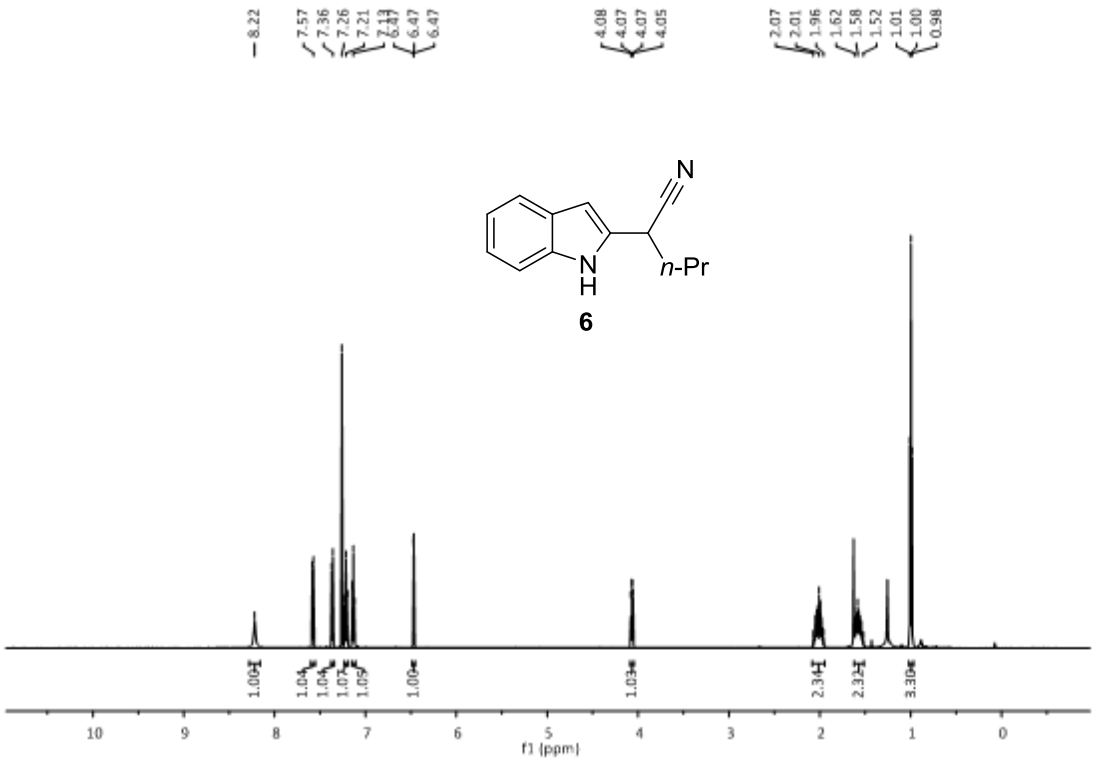
100
80
60
40
20
0
f1 (ppm)


8.22
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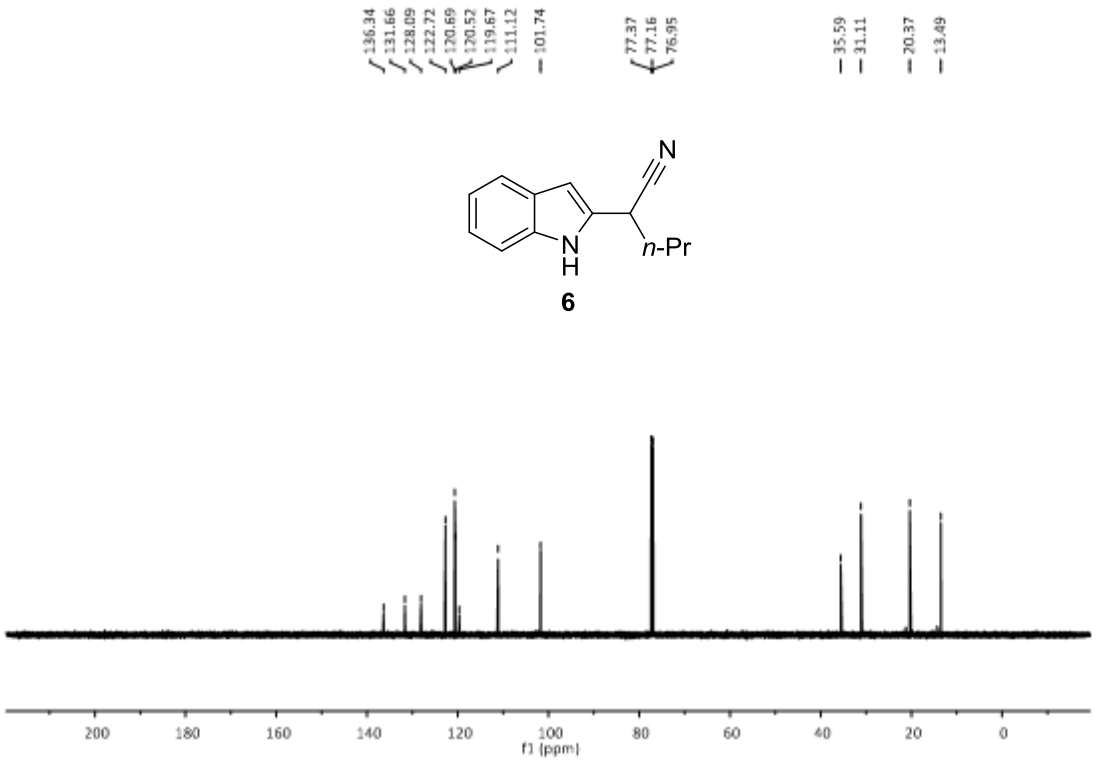
7.36
7.26
7.21
7.13
6.47
6.47
4.08
4.07
4.07
4.05
2.07
2.01
1.96
1.62
1.58
1.52
1.01
1.00
0.98
N
N
H
n-Pr
1.00
1.04
1.04
1.07
1.05
1.00
1.03
2.34
2.33
3.30
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

6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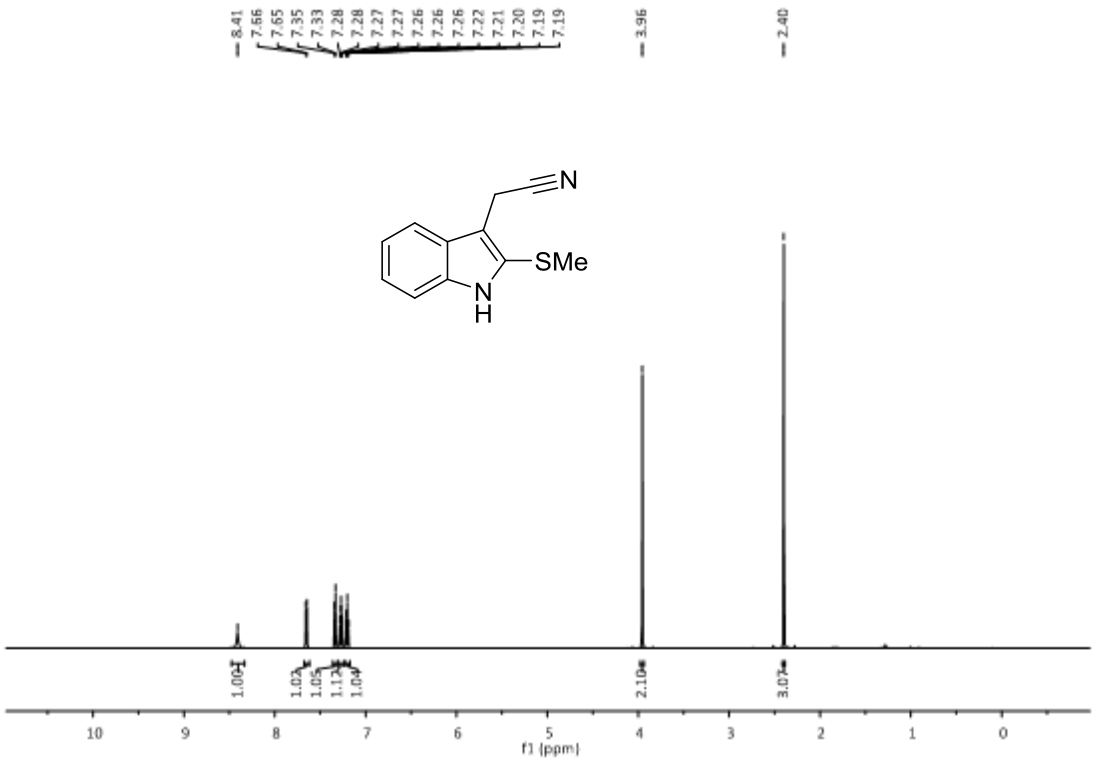
122.72
120.69
120.52
119.67
111.12
101.74
77.37
77.16
76.95
35.59
31.11
20.37
13.49
N
N
H
n-Pr
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

6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7.65
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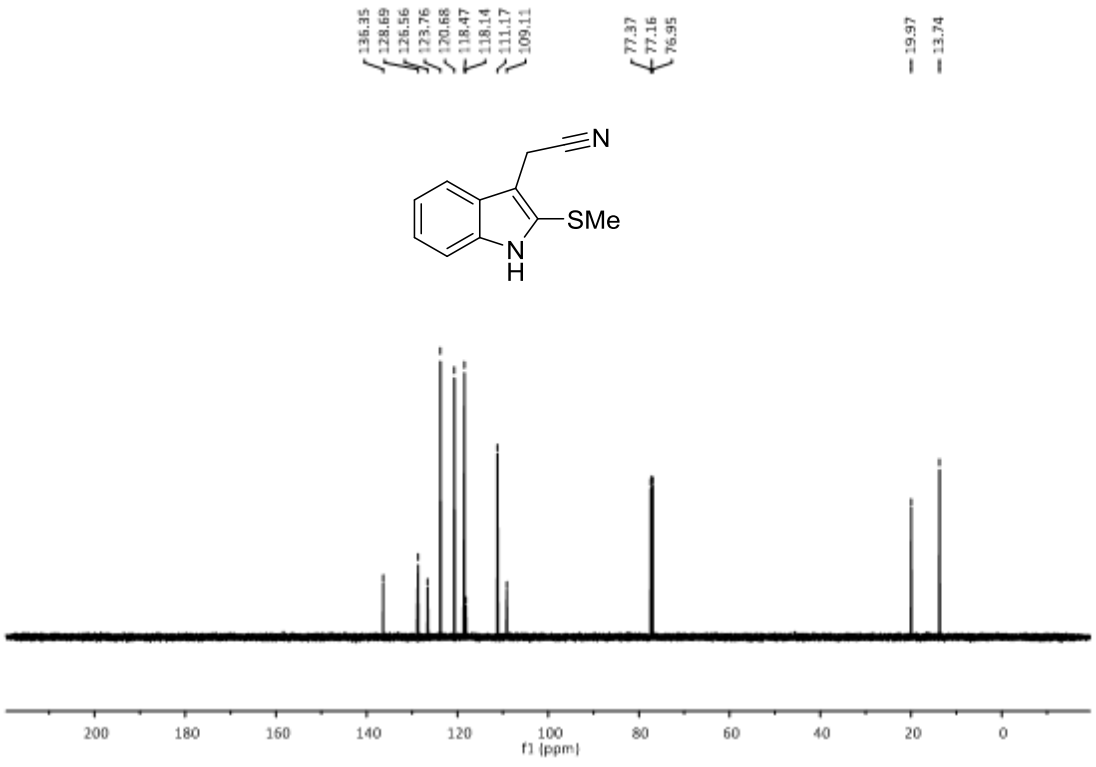
7.28
7.27
7.27
7.26
7.26
7.26
7.22
7.21
7.20
7.19
7.19
3.96
2.40
N
SMe
N
H
1.00
1.02
1.05
1.12
1.04
2.10
3.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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128.69
126.56
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118.47
118.14
111.17
109.11
77.37
77.16
76.95
19.97
13.74
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SMe
N
H
200
180
160
140
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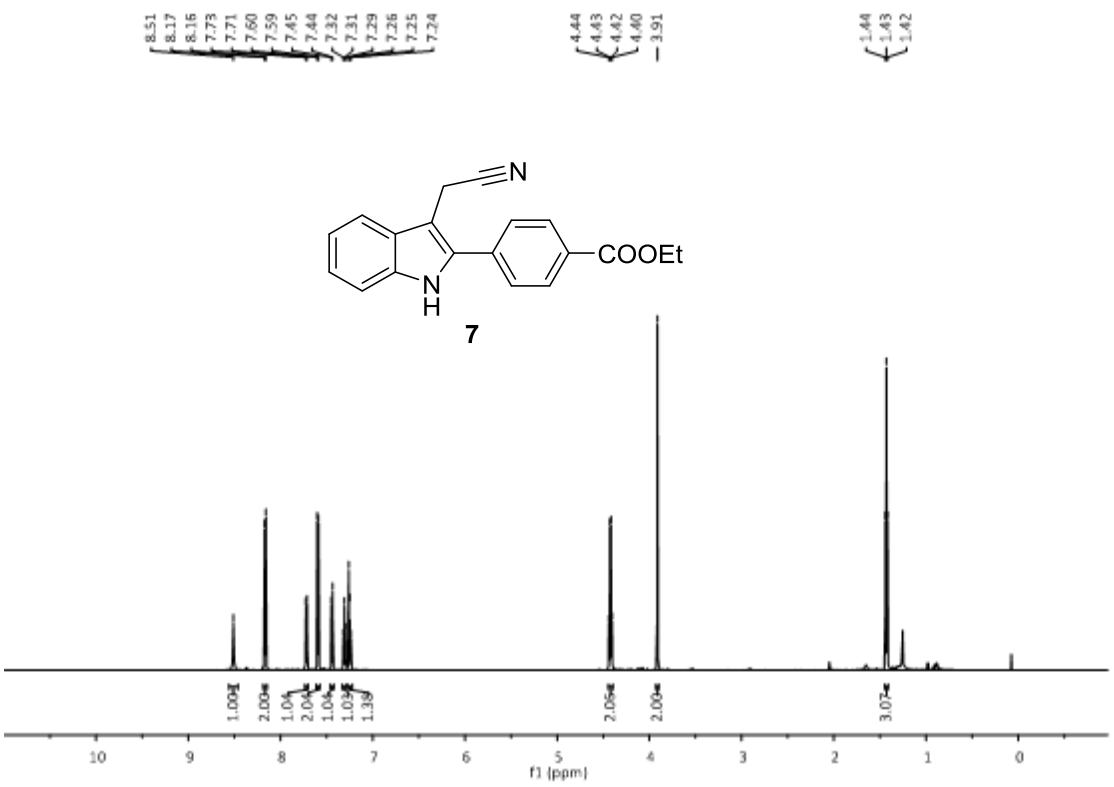
100
80
60
40
20
0
f1 (ppm)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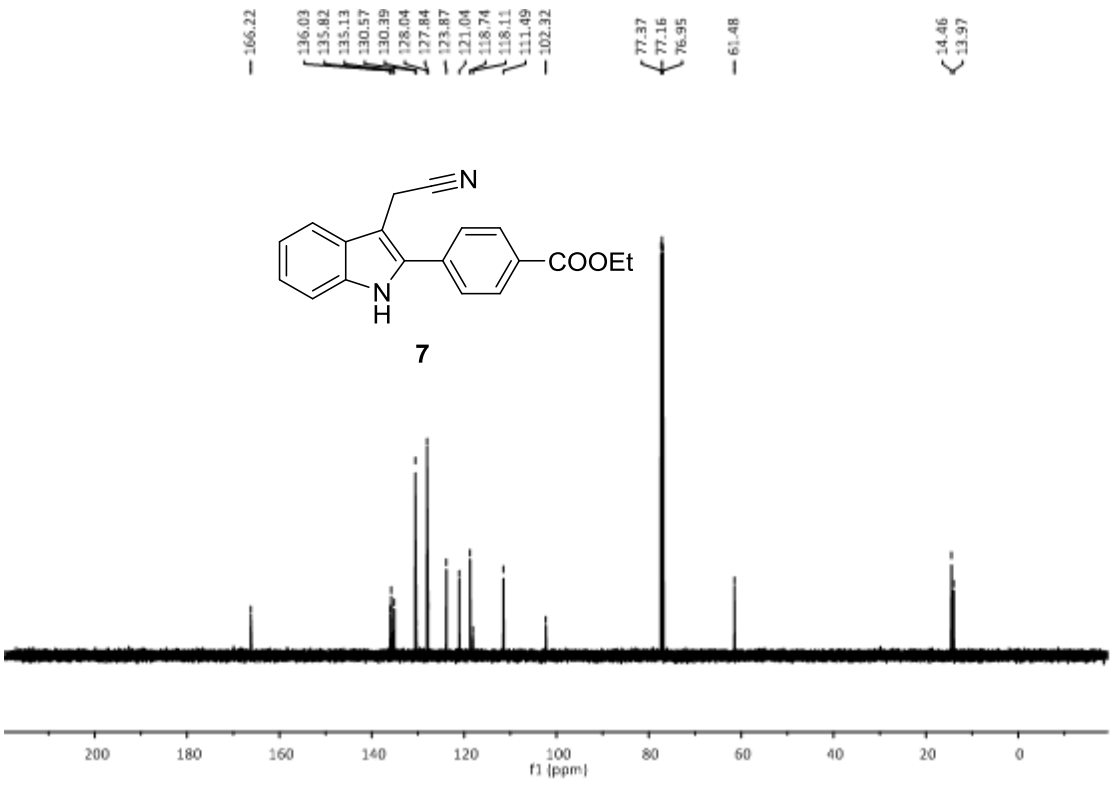
8.17
8.16
7.73
7.71
7.60
7.59
7.45
7.44
7.32
7.31
7.29
7.26
7.25
7.24
4.44
4.43
4.42
4.40
3.91
1.44
1.43
1.42
N
COOEt
N
H
7
1.00
2.00
1.04
2.04
1.04
1.03
1.39
2.05
2.00
3.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


166.22
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135.82
135.13
130.57
130.39
128.04
127.84
123.87
121.04
118.74
118.11
111.49
102.32
77.37
77.16
76.95
61.48
14.46
13.97
N
COOEt
N
H
7
200
180
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140
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100
80
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20
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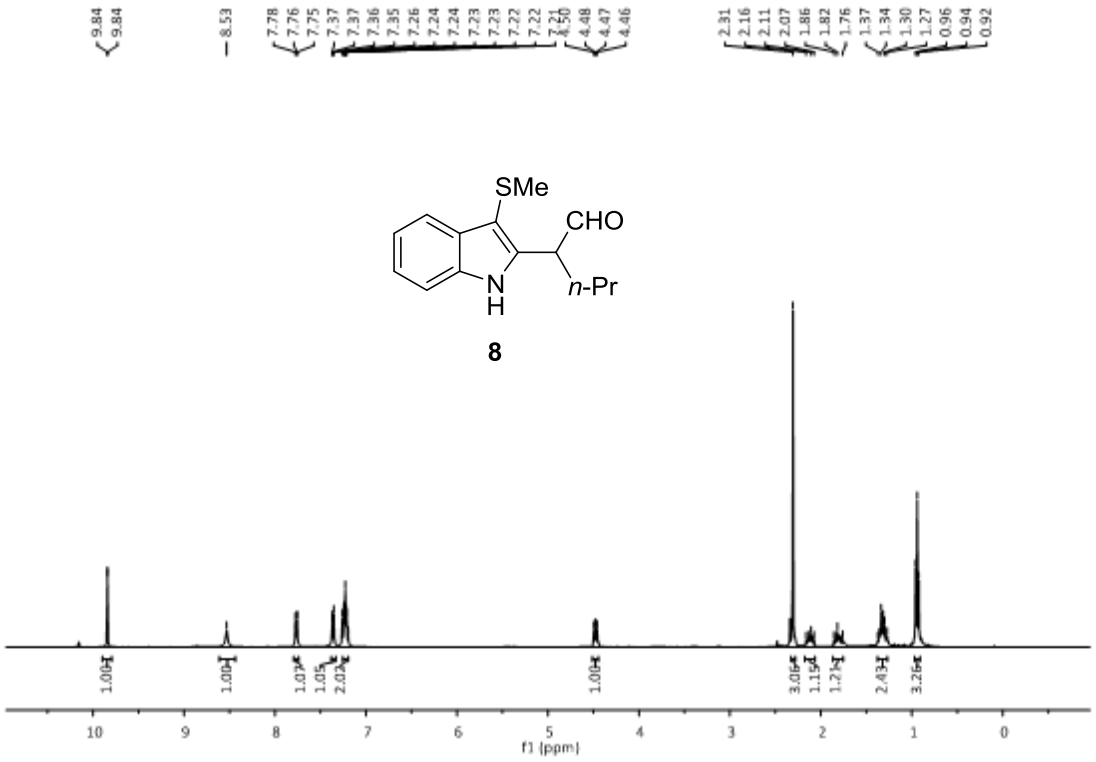
f1 (ppm)



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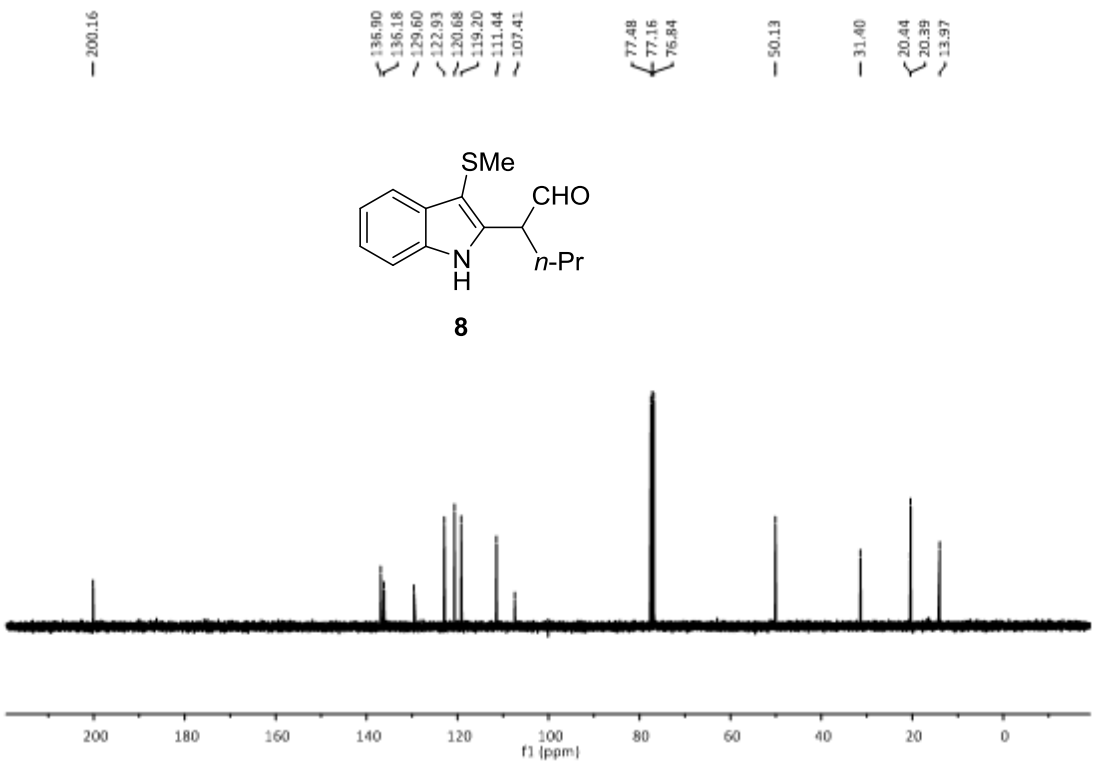

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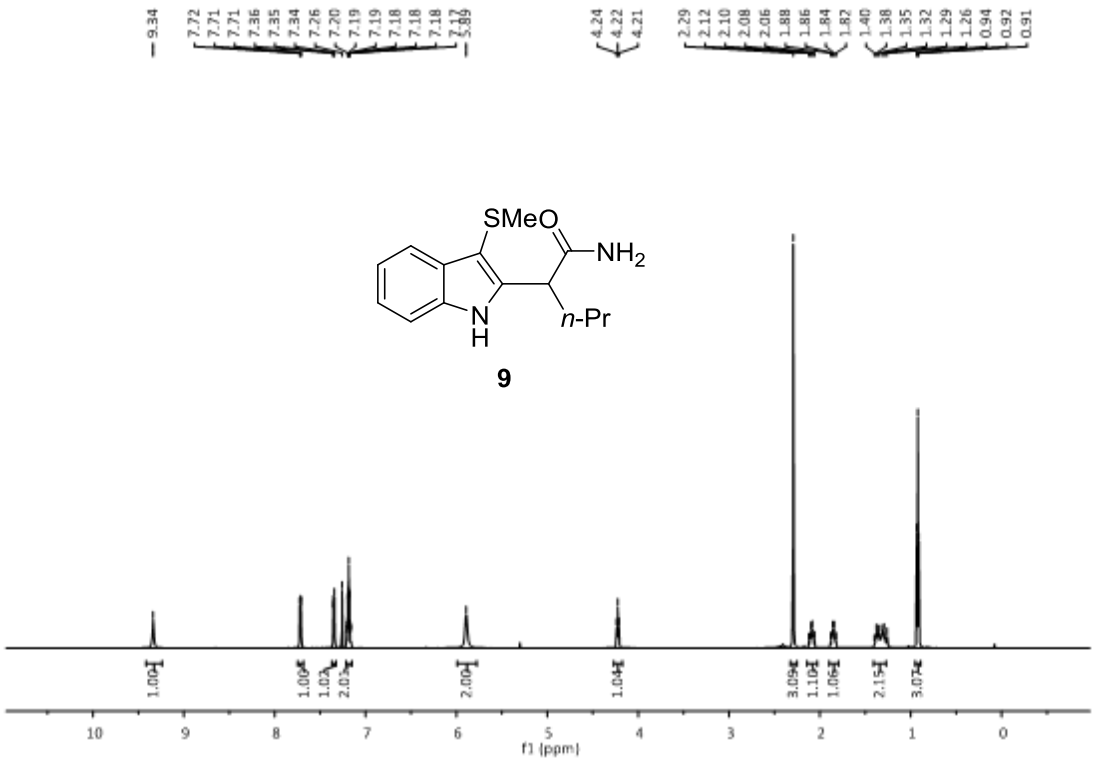
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7.72
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7.71
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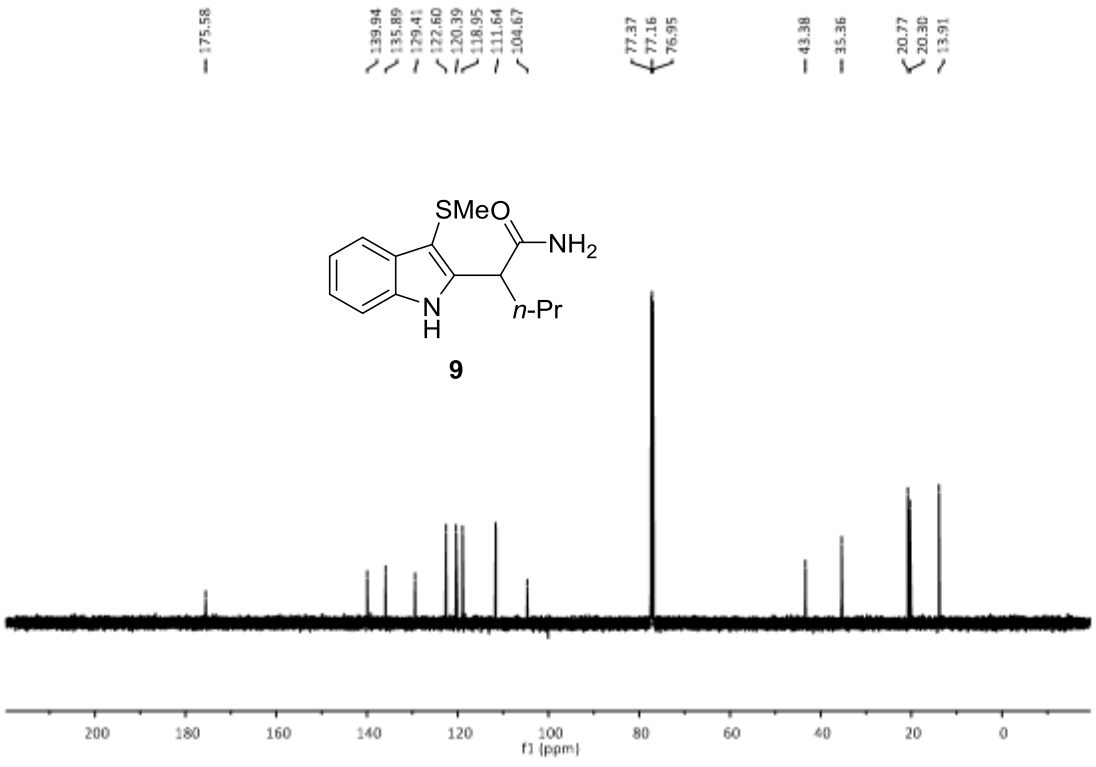
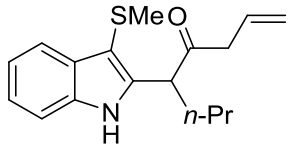
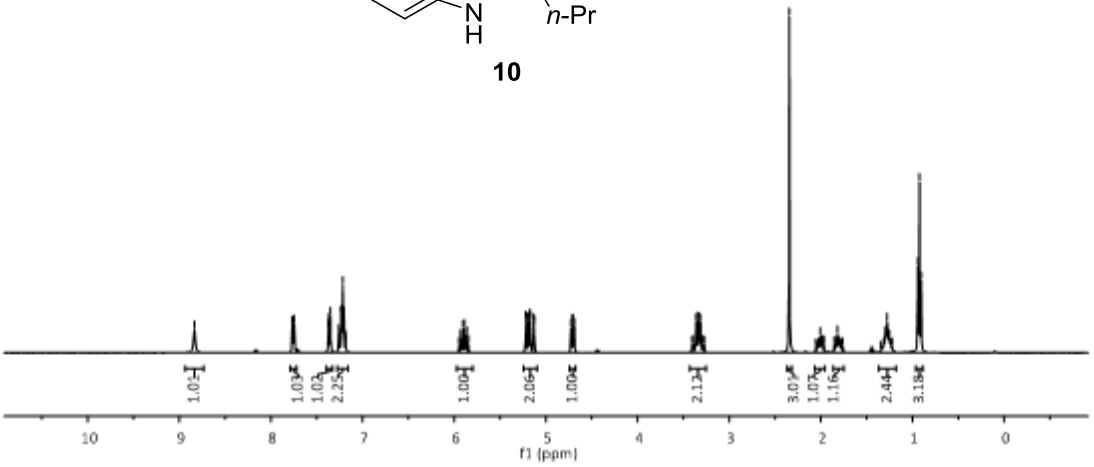
7.35
7.34
7.26
7.20
7.19
7.19
7.18
7.18
7.18
7.17
5.89
4.24
4.22
4.21
2.29
2.12
2.10
2.08
2.06
1.88
1.86
1.84
1.82
1.40
1.38
1.35
1.32
1.29
1.26
0.94
0.92
0.91
SMeO
NH2
N
H
n-Pr
9
1.00
1.00
1.02
2.03
2.00
1.04
3.09
1.10
1.06
2.15
3.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


175.58
139.94
135.89
129.41
122.60
120.39
118.95
111.64
104.67
77.37
77.16
76.95
43.38
35.36
20.77
20.30
13.91
SMeO
NH2
N
H
n-Pr
9
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


SMe
O
N
H
n-Pr

10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1.03
1.02
2.25
1.00
2.06
1.00
2.13
3.07
1.07
1.16
2.44
3.18
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


209.24
138.58
136.05
129.73
129.47
122.75
120.49
119.71
119.12
111.51
106.22
77.37
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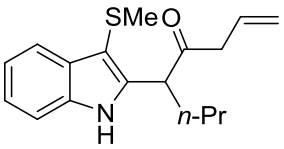
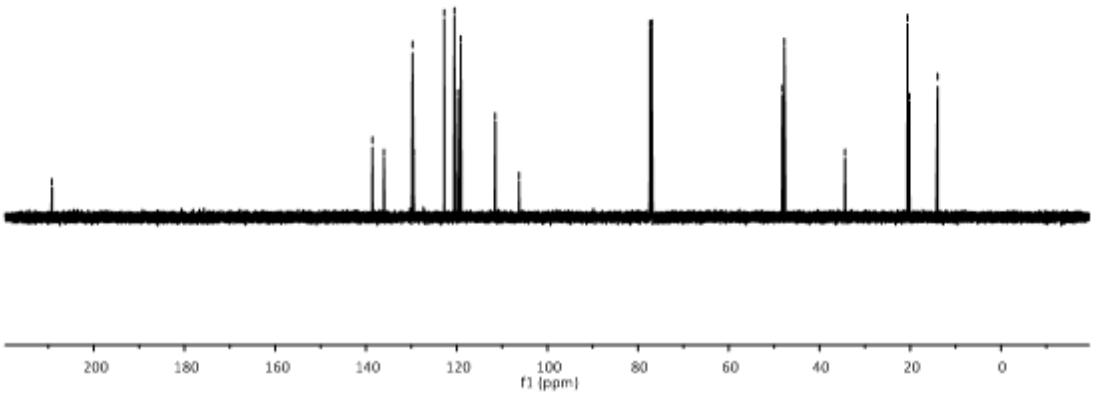
76.95
48.21
47.77
34.37
20.62
20.18
13.97


SMe
O
N
H
n-Pr

10


200
180
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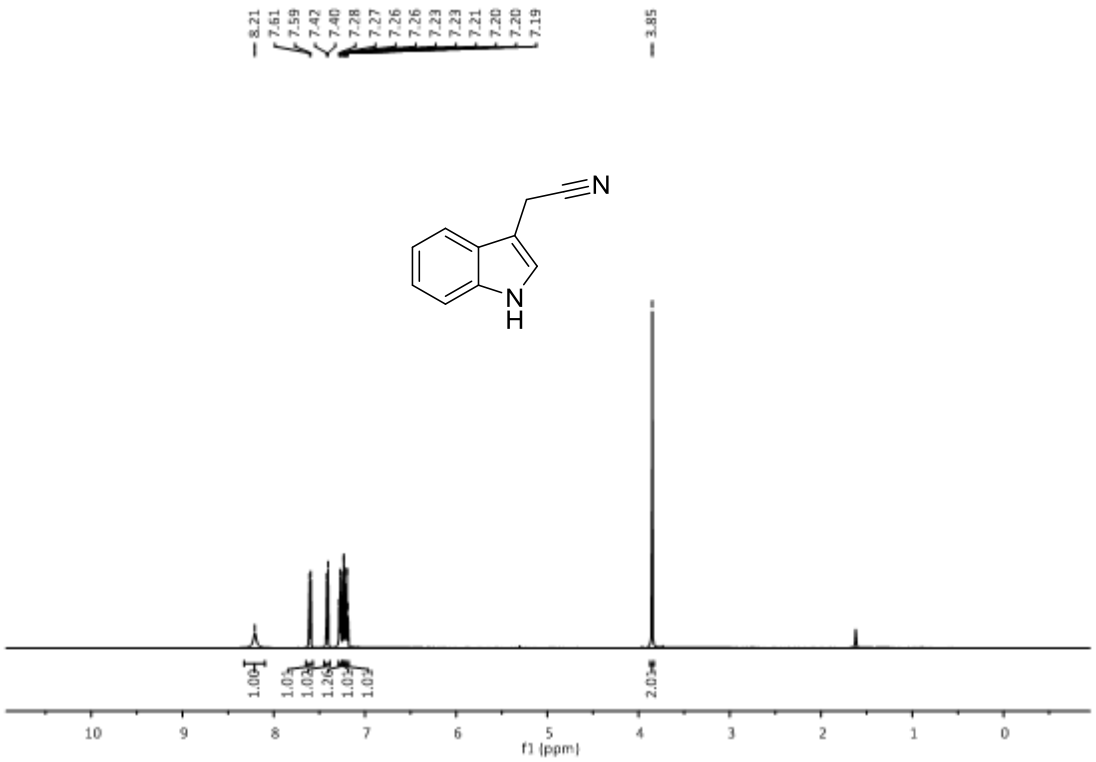
140
120
100
80
60
40
20
0
f1 (ppm)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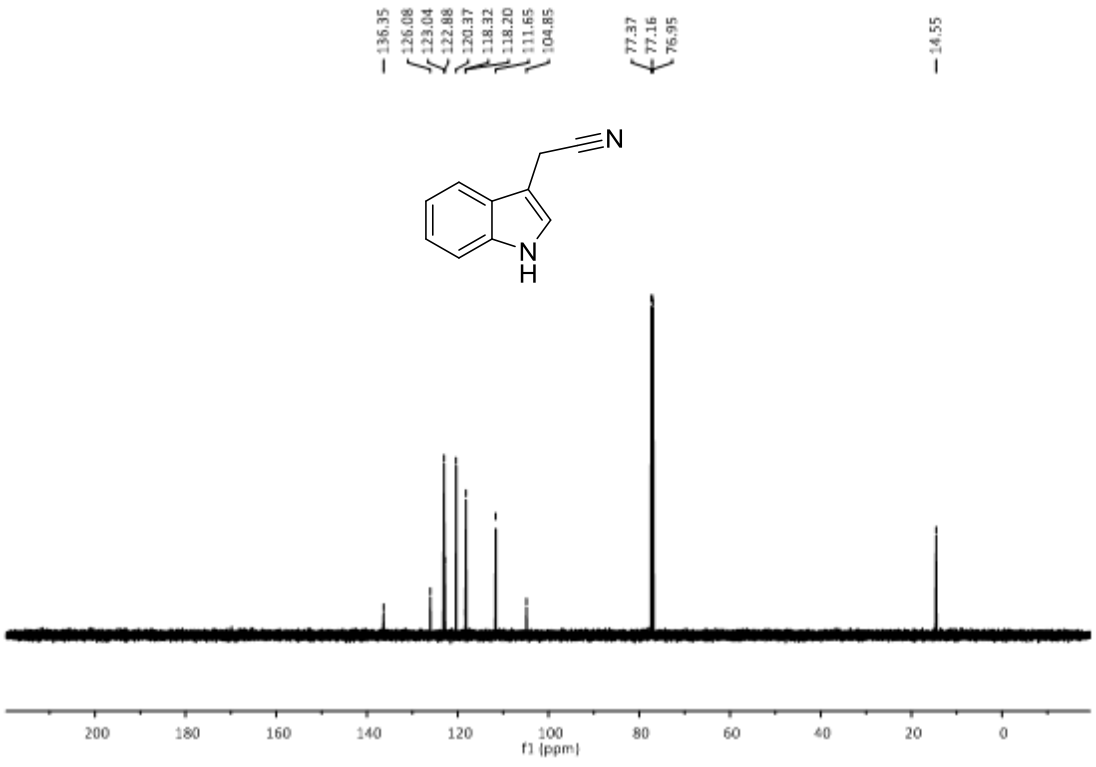
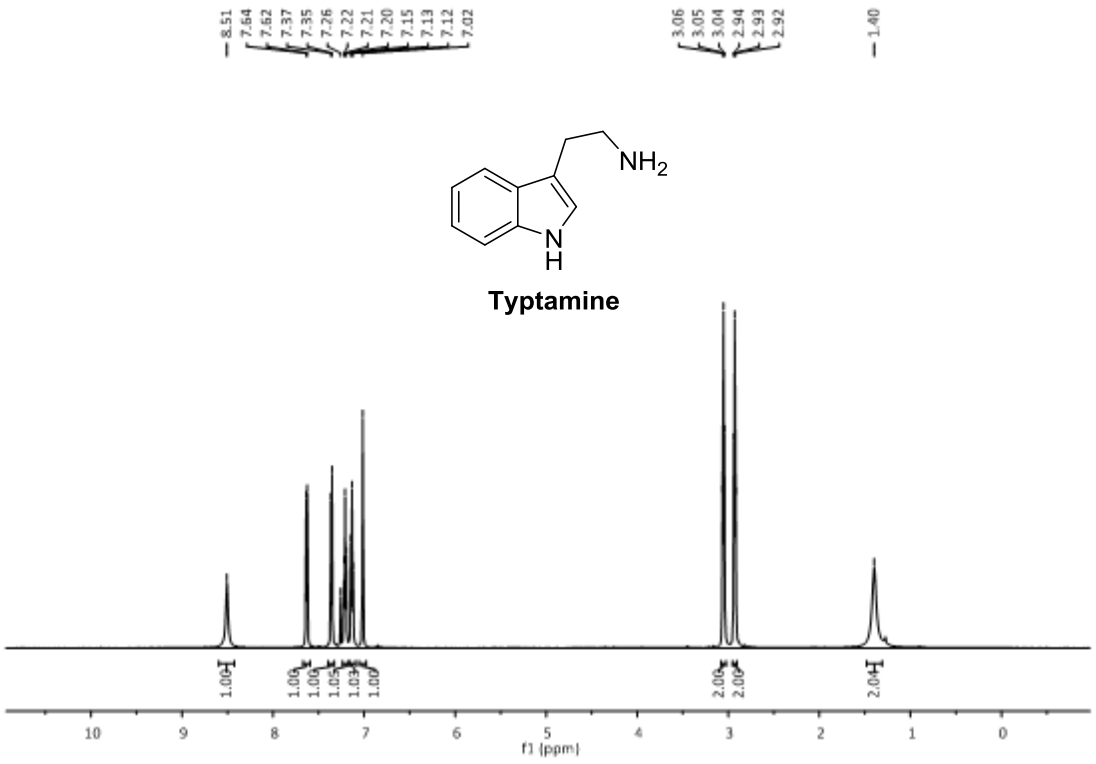
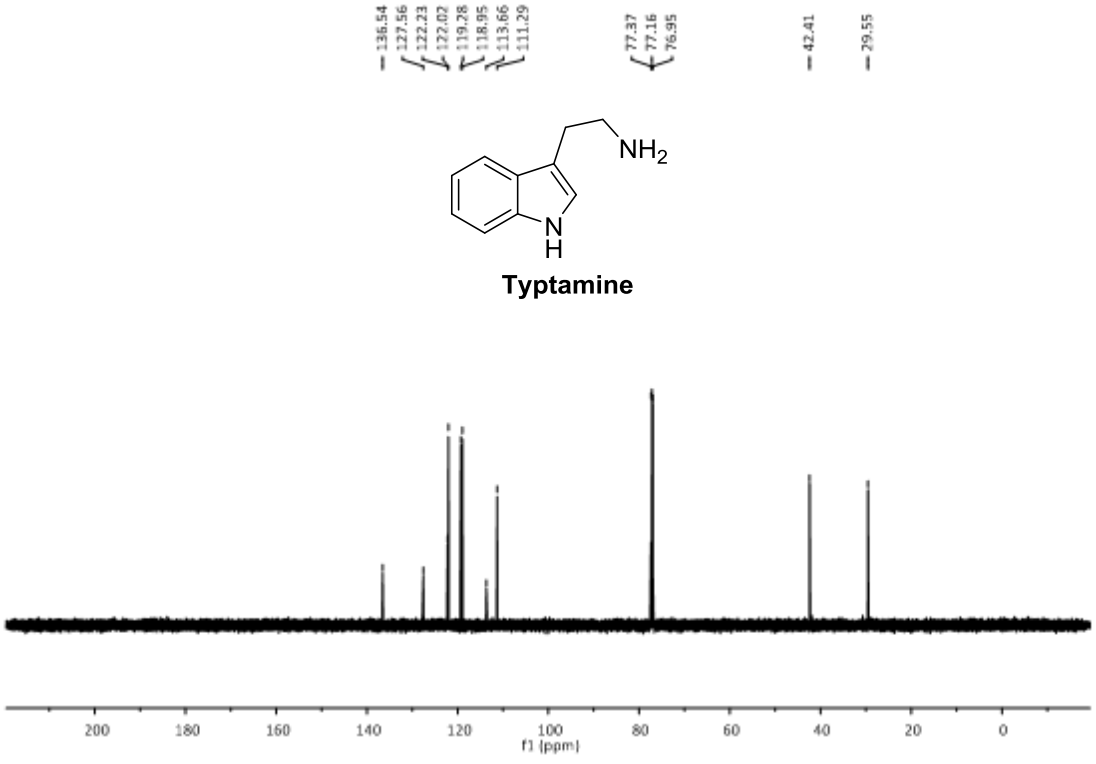
7.61
7.59
7.42
7.40
7.28
7.27
7.26
7.26
7.23
7.23
7.21
7.20
7.20
7.19
3.85
N
N
H
1.00
1.01
1.02
1.26
1.02
1.02
2.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

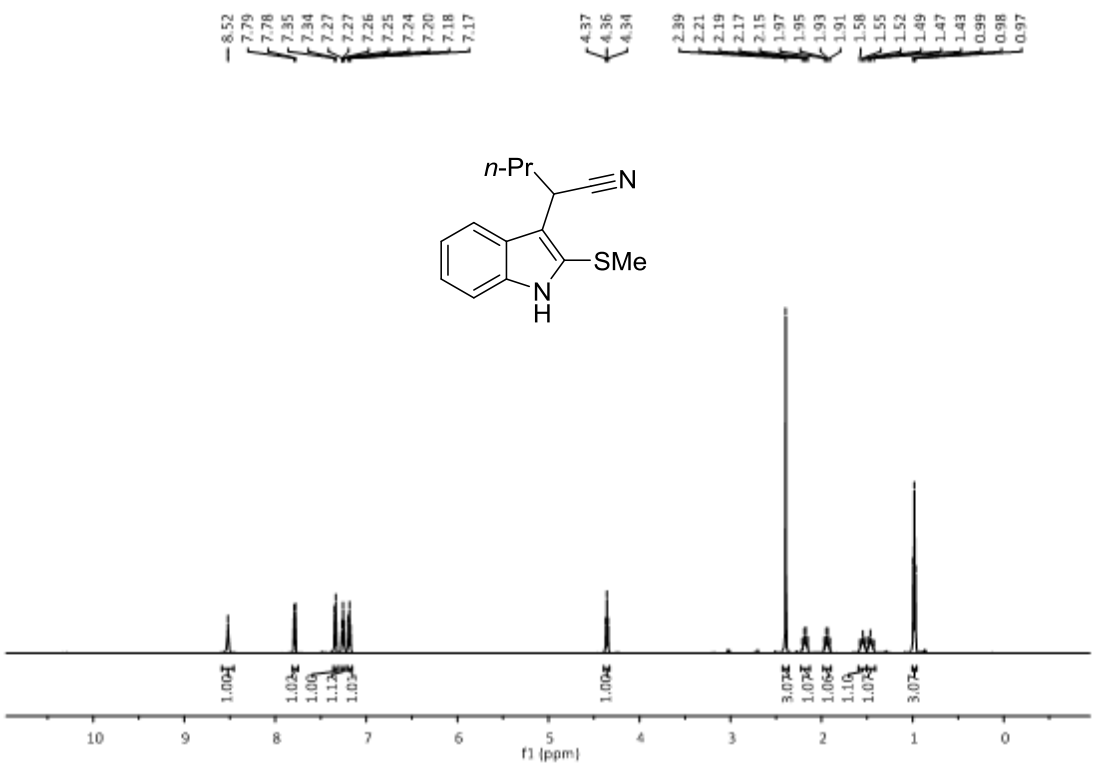

136.35
126.08
123.04
122.88
120.37
118.32
118.20
111.65
104.85
77.37
77.16
76.95
14.55
N
N
H
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



Typtamine



Typtamine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7.24
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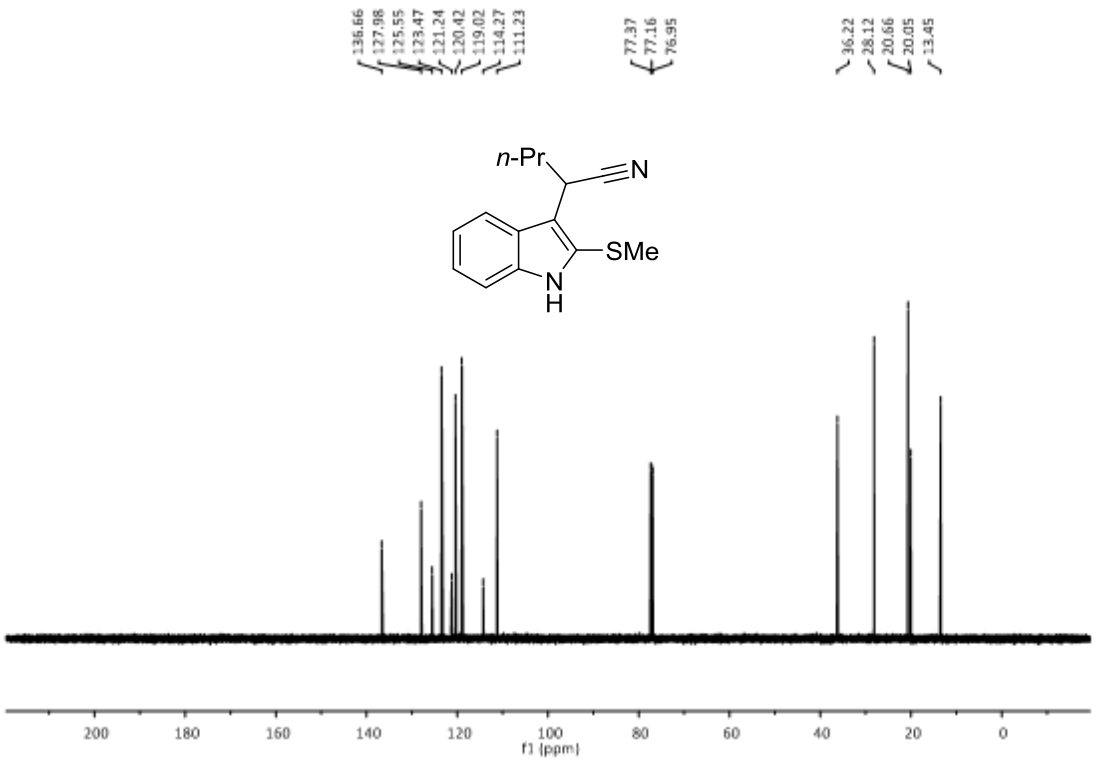
7.18
7.17
4.37
4.36
4.34
2.39
2.21
2.19
2.17
2.15
1.97
1.95
1.93
1.91
1.58
1.55
1.52
1.49
1.47
1.43
0.99
0.98
0.97
n-Pr
N
SMe
N
H
1.00
1.02
1.00
1.12
1.03
1.00
3.07
1.07
1.06
1.10
1.07
3.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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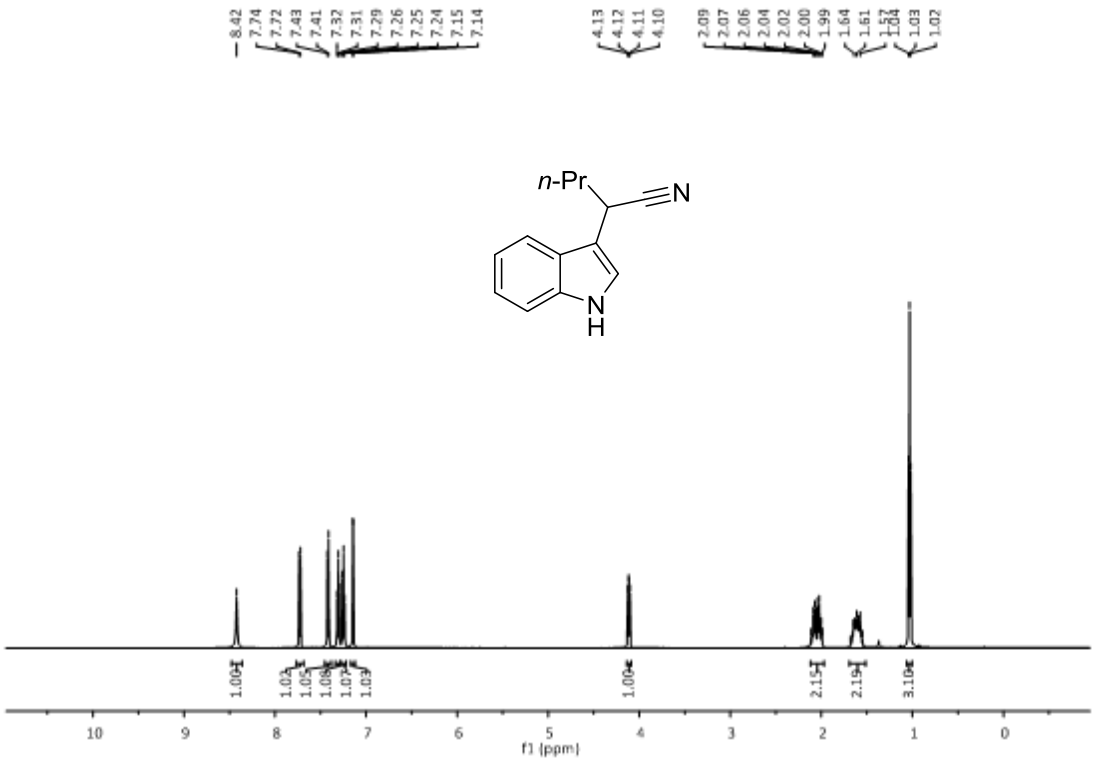
125.55
123.47
121.24
120.42
119.02
114.27
111.23
77.37
77.16
76.95
36.22
28.12
20.66
20.05
13.45
n-Pr
N
SMe
N
H
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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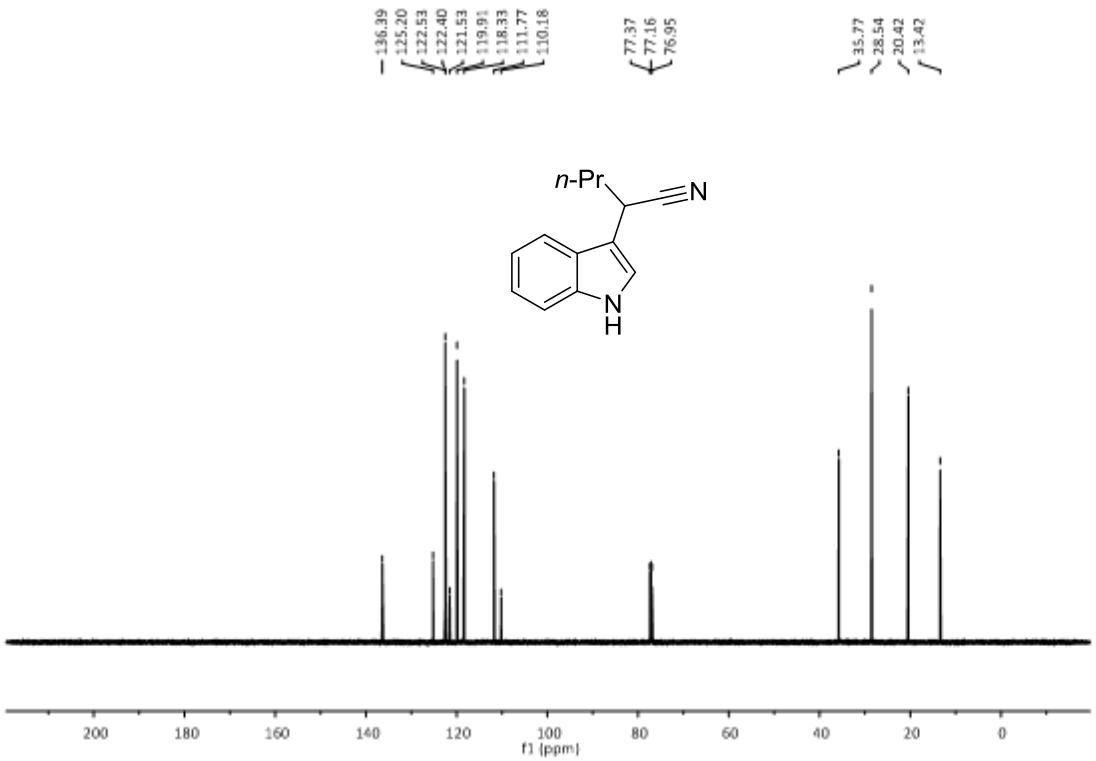
7.24
7.15
7.14
4.13
4.12
4.11
4.10
2.09
2.07
2.06
2.04
2.02
2.00
1.99
1.64
1.61
1.04
1.03
1.02
n-Pr
N
N
H
1.00
1.02
1.05
1.08
1.07
1.03
1.00
2.15
2.19
3.10
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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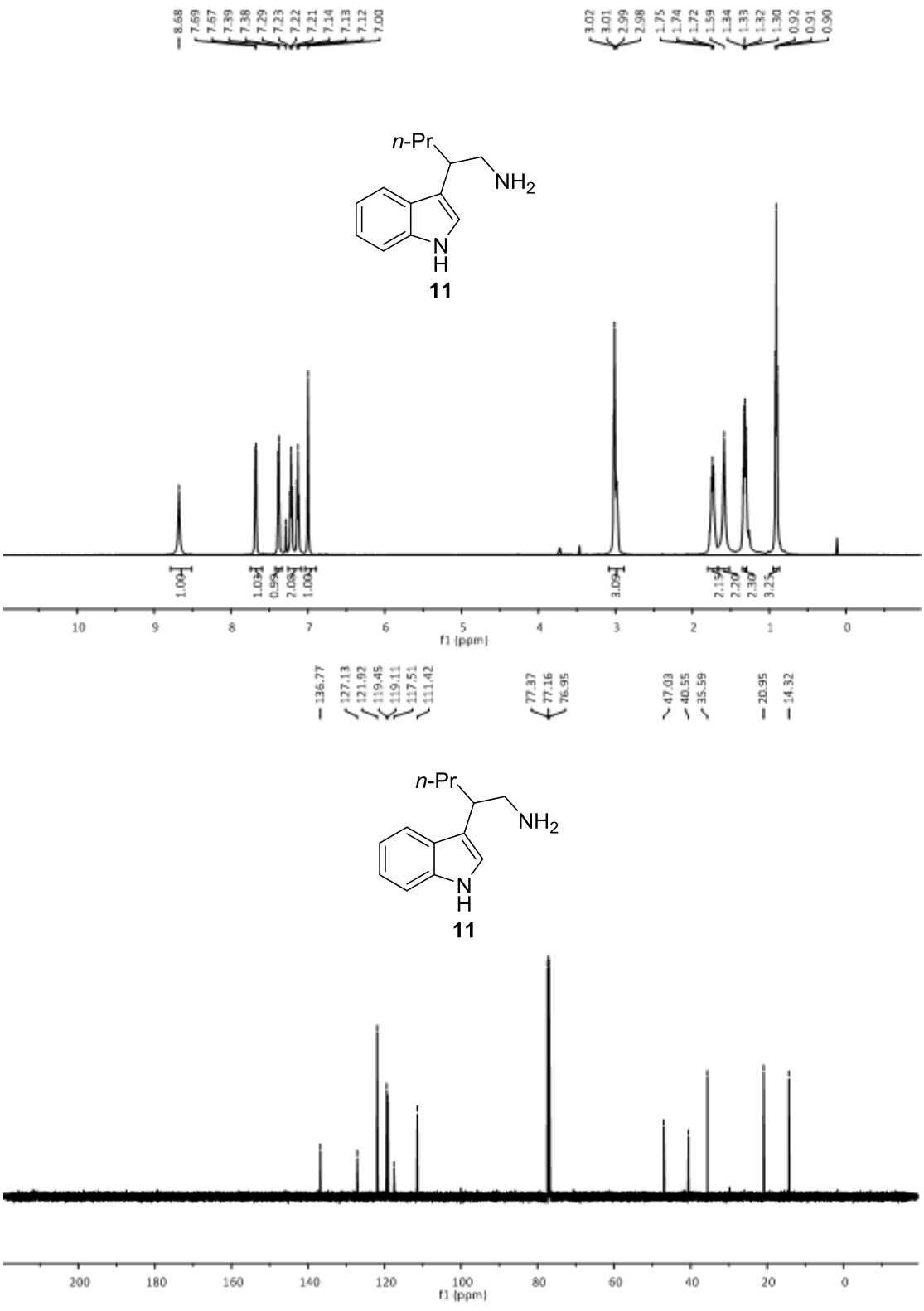
118.33
111.77
110.18
77.37
77.16
76.95
35.77
28.54
20.42
13.42
n-Pr
N
N
H
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.22
7.21
7.14
7.13
7.12
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3.01
2.99
2.98
1.75
1.74
1.72
1.59
1.34
1.33
1.32
1.30
0.92
0.91
0.90
n-Pr
NH2
N
H
11
1.00
1.09
0.99
2.08
1.00
3.09
2.19
2.20
2.30
3.25
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
136.77
127.13
121.92
119.45
119.11
117.51
111.42
77.37
77.16
76.95
47.03
40.55
35.59
20.95
14.32
n-Pr
NH2
N
H
11
200
180
160
140
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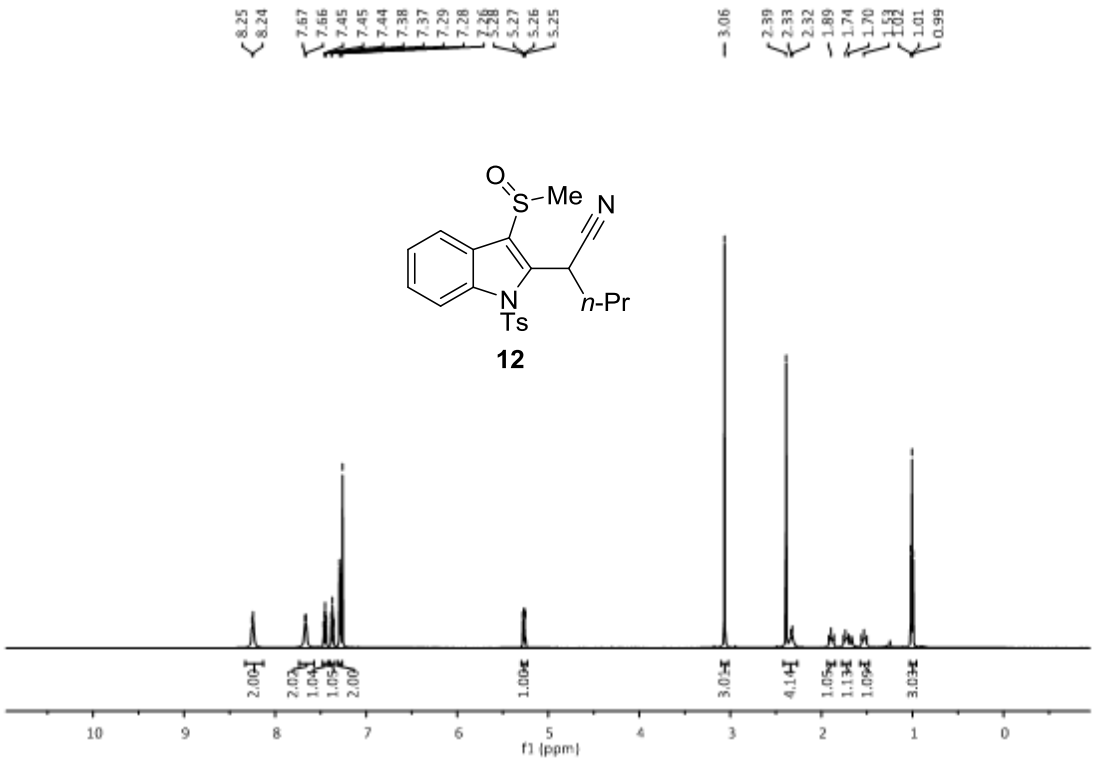
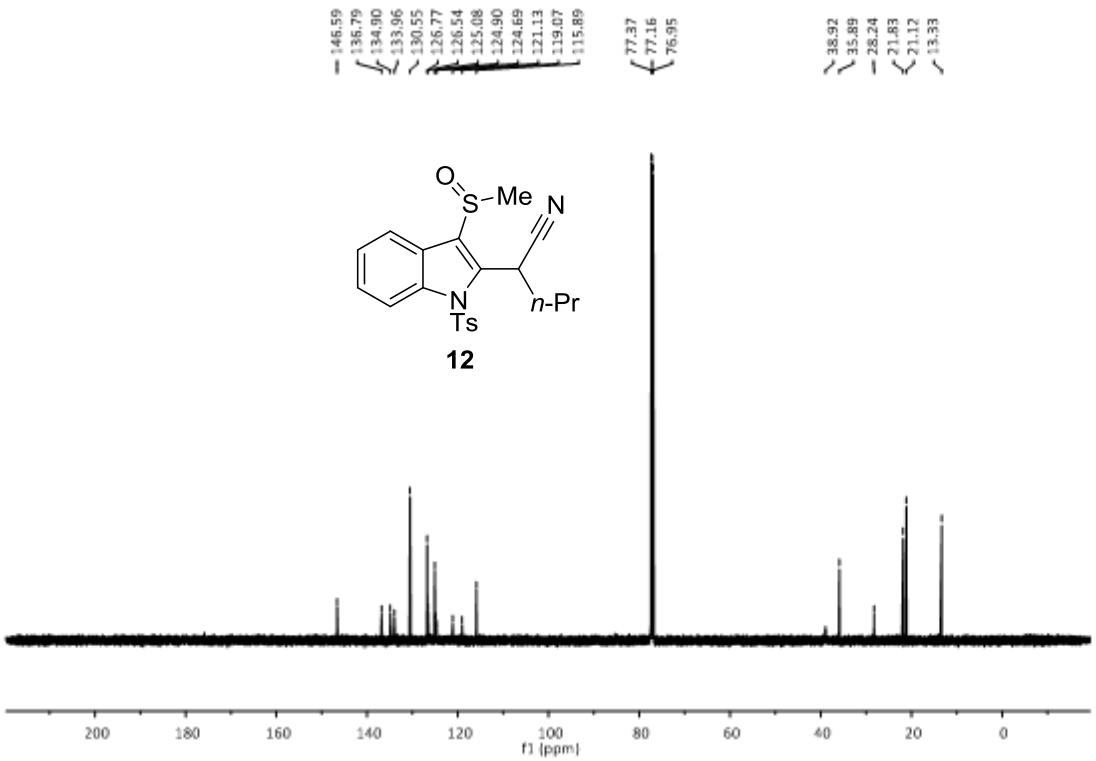
100
80
60
40
20
0
f1 (ppm)


8.25
8.24
7.67
7.66
7.45
7.45
7.44
7.38
7.37
7.29
7.28
5.27
5.26
5.25
3.06
2.39
2.33
2.32
1.89
1.74
1.70
1.01
0.99
O
S
Me
N
N
Ts
n-Pr
12
f1 (ppm)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119.07
115.89
77.37
77.16
76.95
38.92
35.89
28.24
21.83
21.12
13.33
O
S
Me
N
N
Ts
n-Pr
12
f1 (ppm)