Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of Benzothiophenes via Sulfonium-[3,3]-Rearrangement of Aryl Sulfoxides with Allenenitriles

Lei Zhang, Kun Wan, Huanhuan Wang, Mengyao Wang, Ao Cui, Xin Huang and Bo Peng*

*pengbo@zjnu.cn

Table of Contents

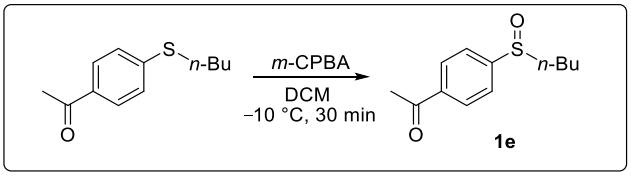
1 General information

Unless otherwise indicated, all glassware was oven dried 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. 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. Compound isolation was performed on chromatography column using silica gel 60 (160-200 mesh). Neat infrared spectra were recorded using a NEXUS670 FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. MS (EI) analysis was performed on Agilent GC-MS instrument. High-resolution mass spectrometry (HRMS) analysis was carried out using a TOF MS instrument with ESI or APCI source. All ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 or AV-600. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.16). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz).

2 General procedure for the synthesis of starting materials

Aryl sulfoxide **1u** and **1v** are commercially available. Aryl sulfoxides **1a-1d**[1], **1f**[l],**1g**[2], **1i-1k**[3], **1l**[4],**1m**[3], **1n**[5], **1o**[4], **1s**[2], **1t**[2], **1w**[6] and allenenitriles **2b**[7], **2c**[8], **2d**[8], **2e**[10], **2i**[11], **2u**[11] are all known compounds.

1-(4-(butylsulfinyl)phenyl)ethan-1-one (1e)



To a solution of aryl sulfide (5 mmol) in DCM (0.3 M) was added a solution of *m*-CPBA (1.0 equiv) in DCM (0.3 M) dropwise at –10 °C. Progress of the oxidation was checked by TLC. After

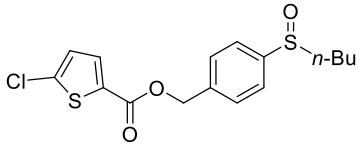
completion of the reaction, saturated aqueous $NaHCO_3$ was added to the reaction mixture and the resulting solution was extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained residue was further purified by column chromatography on silica gel to afford compound **1e** in 75% yield (1.7 g) as a white solid. m.p. 52 − 53 °C. (Rf = 0.33, eluent: PE/EtOAc = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 2.82 – 2.62 (m, 2H), 2.53 (s, 3H), 1.72 – 1.57 (m, 1H), 1.50 – 1.39 (m, 1H), 1.39 – 1.23 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.9, 149.1, 138.7, 128.8, 124.0, 56.5, 26.6, 23.7, 21.6, 13.5.

IR (neat):2929, 2871, 1676, 1590, 1394, 1263, 1032, 824, 590.

HRMS (ESI-TOF): calculated for [$C_{12}H_{17}O_2S$ (M + H^+)]: 225.0944, found: 225.0945.



1h

4-(butylsulfinyl)benzyl 5-chlorothiophene-2-carboxylate (1h)

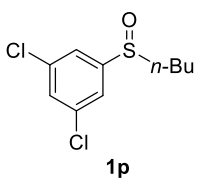
Following a procedure similar to the synthesis of **1e**, the title compound was prepared on 7 mmol scale and obtained as colorless oil, 2.0 g, 80% yield. (Rf = 0.40, eluent: PE/EtOAc = 1/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 – 7.61 (m, 3H), 7.56 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 4.0 Hz, 1H), 5.36 (s, 2H), 2.81 – 2.78 (m, 2H), 1.78 – 1.70 (m, 1H), 1.63 – 1.56 (m, 1H), 1.51 – 1.37 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.0, 138.7, 138.1, 133.7, 131.3, 128.9, 127.6, 124.5, 100.1, 66.2, 57.2, 24.3, 22.0, 13.8.

IR (neat):2957, 2871, 1707, 1421, 1246, 1082, 1057, 809, 743.

HRMS (ESI-TOF): calculated for [$C_{16}H_{18}ClO_3S_2$ (M + H^+)]: 357.0380, found: 357.0381.



1p

1-(butylsulfinyl)-3,5-dichlorobenzene (1p)

Following a procedure similar to the synthesis of **1e**, the title compound was prepared on 5 mmol scale and obtained as colorless oil, 662 mg, 53% yield. (Rf = 0.26, eluent: PE/EtOAc = 2/1)

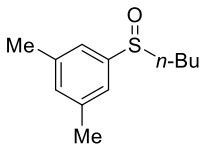
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 − 7.46 (m, 3H), 2.87 – 2.73 (m, 2H), 1.84 – 1.73 (m, 1H), 1.66

−1.54 (m, 1H), 1.53 – 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.0, 136.4, 131.1, 122.5, 57.3, 24.1, 22.0, 13.8.

IR (neat): 3021, 2920, 2853, 2247, 1658, 1467, 1376, 969, 721.

HRMS (ESI-TOF): calculated for [$C_{10}H_{13}Cl_2OS$ (M + H^+)]: 251.0017, found: 251.0016.



1q

1-(butylsulfinyl)-3,5-dimethylbenzene (1q)

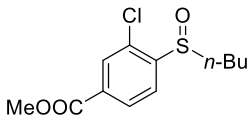
Following a procedure similar to the synthesis of **1e**, the title compound was prepared on 8 mmol scale and obtained as colorless oil, 1.4 g, 85% yield. (Rf = 0.34, eluent: PE/EtOAc = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (s, 2H), 7.05 (s, 1H), 2.77 – 2.69 (m, 2H), 2.33 (s, 3H) 2.32 (s, 3H), 1.72 – 1.63 (m, 1H), 1.61 – 1.53 (m, 1H), 1.47 – 1.33 (m, 2H), 0.89 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 139.1, 132.6, 121.4, 57.1, 24.3, 21.9, 21.3, 13.7.

IR (neat):2956, 2828, 1605, 1458, 1102, 1034, 992, 849.

HRMS (ESI-TOF): calculated for [$C_{12}H_{19}OS$ (M + H^+)]: 211.1151, found: 211.1150.



1r

methyl 4-(butylsulfinyl)-3-chlorobenzoate (1r)

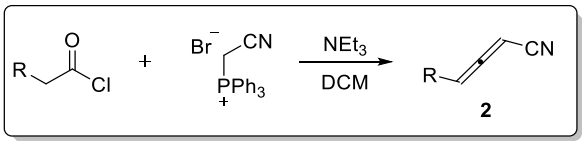
Following a procedure similar to the synthesis of **1e**, the title compound was prepared on 6 mmol scale and obtained as white solid, 1.2 g, 71% yield. m.p. 53 − 54 °C (Rf = 0.30, eluent: PE/EtOAc = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.66 (s, 1H), 7.47 (d, *J* = 9.4 Hz, 1H), 3.89 (s, 3H), 2.82 – 2.70 (m, 2H), 1.76 – 1.68 (m, 1H), 1.53 – 1.47 (m, 1H), 1.44 – 1.32 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): **δ** 165.4, 149.4, 135.0, 132.3, 132.1, 126.5, 122.1, 56.9, 52.9, 23.9, 21.9, 13.8.

IR (neat):2954, 1730, 1586, 1433, 1233, 1046, 770, 666.

HRMS (ESI-TOF): calculated for [$C_{12}H_{16}ClO_3S$ (M + H^+)]: 275.0503, found: 275.0506.



General procedure: To a solution of (cyanomethyl)triphenylphosphonium bromide (3-13 mmol) in dry DCM (0.3 M) was added dropwise NEt_3 (2.0 equiv) at 0 °C. The reaction mixture was stirred for 30 min. After that, a solution of acyl chloride (1.0 equiv) in DCM was added to the mixture dropwise in 10 min using syringe pump. After stirring for 3 h, water (5-15 mL) was added to the mixture and allowed to stir for 10 min. The aqueous phase was then extracted with DCM. Then the organic layers were combined, dried over Na_2SO_4 and concentrated. The residue was washed with diethyl ether to precipitate triphenylphosphine oxide. After filtration, the filtrate was concentrated and then purified by silica gel column chromatography to afford allenenitrile **2**.

2a

dodeca-2,3-dienenitrile (2a)

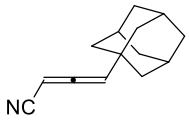
Following the general procedure, the title compound was prepared on 10 mmol scale and obtained as colorless oil, 1.2 g, 67% yield. (Rf = 0.46, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.72 – 5.68 (m, 1H), 5.20 – 5.18 (m, 1H), .2.14 – 2.10 (m, 2H), 1.47 – 1.42 (m, 2H), 1.32 – 1.24 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.1, 172.5, 113.4, 95.9, 68.7, 52.0, 32.4, 22.5.

IR (neat): 2924, 2854, 2225, 1960, 1465, 866, 722.

HRMS (ESI-TOF): calculated for [$C_{12}H_{20}N$ (M + H^+)]: 178.1517, found: 178.1591.



2f

4-((3r,5r,7r)-adamantan-1-yl)buta-2,3-dienenitrile (2f)

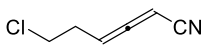
Following the general procedure, the title compound was prepared on 5 mmol scale and obtained as white solid, 0.55 g, 55% yield. m.p. 45-46 °C. (Rf = 0.40, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.56 (d, *J* = 6.4 Hz, 1H), 5.24 (d, *J* = 6.4 Hz, 1H), 2.03 – 1.99 (m, 3H), 1.74 – 1.71 (m, 3H), 1.67 – 1.65 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 214.3, 114.2, 107.8, 68.6, 42.4, 36.5, 35.0, 28.5.

IR (neat): 2975, 2904, 2845, 2221, 1952, 1450, 1316, 877, 812, 720.

HRMS (ESI-TOF): calculated for [$C_{14}H_{17}NNa$ (M + Na^+)]: 222.1253, found: 222.1253.



2g

6-chlorohexa-2,3-dienenitrile (2g)

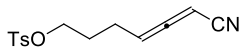
Following the general procedure, the title compound was prepared on 10 mmol scale and obtained as colorless oil, 572 mg, 45% yield. (Rf = 0.30, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.82 – 5.79 (m, 1H), 5.36 – 5.29 (m, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.64 – 2.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.4, 113.2, 93.7, 68.7, 42.7, 30.6.

IR (neat): 3018, 2226, 1964, 1444, 1297, 854, 717, 657.

HRMS (ESI-TOF): calculated for [C_6H_7ClN (M + H^+)]: 128.0262, found: 128.0257.



2h

6-cyanohexa-4,5-dien-1-yl 4-methylbenzenesulfonate (2h)

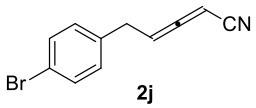
Following the general procedure, the title compound was prepared on 7 mmol scale and obtained as colorless oil, 1.4 g, 61% yield. (Rf = 0.36, eluent: PE/EtOAc = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.70 – 5.66 (m, 1H), 5.23 – 5.20 (m, 1H), 4.06 (t, *J* = 6.1 Hz, 2H), 2.45 (s, 3H), 2.23 – 2.19 (m, 2H), 1.84 – 1.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 215.1, 145.1, 132.9, 130.1, 128.0, 113.4, 95.7, 69.1, 68.4, 27.7, 23.4, 21.8.

IR (neat): 2983, 2225, 1961, 1715, 1294, 1256, 1152, 1028, 976, 774.

HRMS (ESI-TOF): calculated for [$C_{14}H_{16}NO_3S$ (M + H^+)]: 278.0845, found: 278.0845.



2j

5-(4-bromophenyl)penta-2,3-dienenitrile (2j)

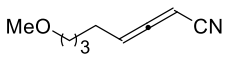
Following the general procedure, the title compound was prepared on 3 mmol scale and obtained as colorless oil, 420 mg, 60% yield. (Rf = 0.37, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.89 – 5.86 (m, 1H), 5.25 – 5.23 (m, 1H), 3.43 (dd, *J* = 7.2, 3.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.6, 136.5, 131.9, 130.3, 121.1, 113.3, 96.3, 68.6, 33.3.

IR (neat): 2921, 2225, 1962, 1486, 1070, 1010, 853, 513.

HRMS (ESI-TOF): calculated for [$C_{11}H_8BrNNa$ (M + Na^+)]: 255.9732, found: 255.9728.



2k

8-methoxyocta-2,3-dienenitrile (2k)

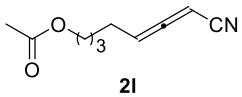
Following the general procedure, the title compound was prepared on 5 mmol scale and obtained as colorless oil, 393 mg, 52% yield. (Rf = 0.32, eluent: PE/EtOAc = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 – 5.69 (m, 1H), 5.23 – 5.19 (m, 1H), 3.38 (t, *J* = 6.1 Hz, 2H), 3.33 (s, 3H), 2.20 – 2.13 (m, 2H), 1.65 – 1.50 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 215.4, 113.9, 96.9, 72.3, 67.6, 58.8, 29.1, 27.2, 25.3.

IR (neat): 2930, 2225, 1960, 1452, 1114, 864.

HRMS (ESI-TOF): calculated for [$C_{10}H_{13}NONa$ ($M + Na^+$)]: 174.0889, found: 174.0889.



2l

7-cyanohepta-5,6-dien-1-yl acetate (2l)

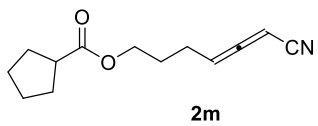
Following the general procedure, the title compound was prepared on 5 mmol scale and obtained as colorless oil, 493 mg, 55 % yield. (Rf = 0.30, eluent: PE/EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 – 5.69 (m, 1H), 5.25 – 5.21 (m, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 2.21 – 2.14 (m, 2H), 2.05 (s, 3H), 1.72 – 1.63 (m, 2H), 1.59 – 1.49 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 215.3, 171.3, 113.7, 96.6, 67.8, 64.0, 28.0, 27.0, 24.9, 21.1.

IR (neat): 2943, 2225, 1960, 1365, 1235, 1039, 866.

HRMS (ESI-TOF): calculated for [$C_{10}H_{14}NO_2$ ($M + H^+$)]: 180.1019, found: 180.1014.



2m

6-cyanohexa-4,5-dien-1-yl cyclopentanecarboxylate (2m)

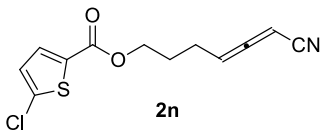
Following the general procedure, the title compound was prepared on 12 mmol scale and obtained as colorless oil, 1.7 g, 65 % yield. (Rf = 0.42, eluent: PE/EtOAc = 8/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.77 – 5.74 (m, 1H), 5.26 – 5.24 (m, 1H), 4.11 (t, *J* = 6.3 Hz, 2H), 2.75 – 2.70 (m, 1H), 2.24 – 2.20 (m, 2H), 1.90 – 1.86 (m, 2H), 1.84 – 1.74 (m, 4H), 1.73 – 1.66 (m, 2H), 1.61 – 1.54 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.3, 176.9, 113.6, 96.2, 68.2, 63.1, 43.9, 30.2, 27.6, 25.9, 24.1.

IR (neat): 2956, 2225, 1959, 1724, 1151, 859.

HRMS (ESI-TOF): calculated for [$C_{13}H_{18}NO_2$ ($M + H^+$)]: 220.1332, found: 220.1334.



2n

6-cyanohexa-4,5-dien-1-yl 4-chlorothiophene-2-carboxylate (2n)

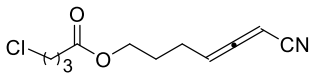
Following the general procedure, the title compound was prepared on 13 mmol scale and obtained as colorless oil, 2.1 g, 60 % yield. (Rf = 0.40, eluent: PE/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, *J* = 4.0 Hz, 1H), 6.93 (d, *J* = 4.0 Hz, 1H), 5.79 – 5.76 (m, 1H), 5.28 – 5.26 (m, 1H), 4.32 (t, *J* = 6.3 Hz, 2H), 2.30 – 2.26 (m, 2H), 1.93 – 1.88 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.2, 161.2, 137.6, 133.3, 131.7, 127.5, 113.5, 96.1, 68.3, 64.1, 27.5, 24.0.

IR (neat): 2958, 2225, 1961, 1704, 1421, 1249, 1096, 1058, 743.

HRMS (ESI-TOF): calculated for [$C_{12}H_{11}ClNO_2S$ (M + H^+)]: 268.0194, found: 268.0193.



2o

6-cyanohexa-4,5-dien-1-yl 4-chlorobutanoate (2o)

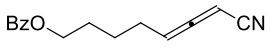
Following the general procedure, the title compound was prepared on 11 mmol scale and obtained as colorless oil, 1.4 g, 56 % yield. (Rf = 0.30, eluent: PE/EtOAc = 4/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.77 – 5.74 (m, 1H), 5.27 – 5.25 (m, 1H), 4.13 (t, *J* = 6.4 Hz, 2H), 3.60 (t, *J* = 6.3 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.25 – 2.21 (m, 2H), 2.13 – 2.06 (m, 2H), 1.85 – 1.78 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.2, 172.7, 113.6, 96.2, 68.3, 63.4, 44.2, 31.2, 27.7, 27.5, 24.0.

IR (neat): 2960, 2225, 1959, 1728, 1173, 1144, 871, 728.

HRMS (ESI-TOF): calculated for [$C_{11}H_{14}ClNO_2Na$ (M + Na^+)]: 250.0605, found: 250.0608.



2p

7-cyanohepta-5,6-dien-1-yl benzoate (2p)

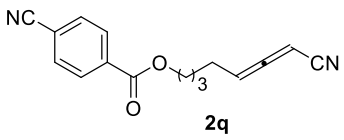
Following the general procedure, the title compound was prepared on 11 mmol scale and obtained as colorless oil, 1.6 g, 62 % yield. (Rf = 0.40, eluent: PE/EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 – 8.02 (m, 2H), 7.47 – 7.43 (m, 1H), 7.49 – 7.42 (m, 2H), 5.77 – 5.72 (m, 1H), 5.25 – 5.22 (m, 1H), 4.34 (t, *J* = 6.4 Hz, 2H), 2.27 – 2.20 (m, 2H), 1.87 – 1.80 (m, 2H), 1.70 – 1.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 215.4, 166.7, 133.1, 130.4, 129.7, 128.5, 113.8, 96.6, 67.9, 64.5, 28.2, 27.1, 25.1.

IR (neat): 2944, 2364, 1711, 1269, 1069, 1112, 708.

HRMS (ESI-TOF): calculated for [$C_{15}H_{16}NO_2$ (M + H^+)]: 242.1176, found:242.1173.



2q

7-cyanohepta-5,6-dien-1-yl 4-cyanobenzoate (2q)

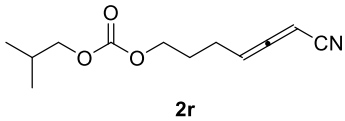
Following the general procedure, the title compound was prepared on 6 mmol scale and obtained as colorless oil, 910 mg, 57 % yield. (Rf = 0.42, eluent: PE/EtOAc = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 5.76 – 5.73 (m, 1H), 5.26 – 5.23 (m, 1H), 4.37 (t, *J* = 6.5 Hz, 2H), 2.25 – 2.21 (m, 2H), 1.87 – 1.80 (m, 2H), 1.66 – 1.61 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.3, 165.0, 134.1, 132.4, 130.2, 118.1, 116.5, 113.7, 96.5, 68.0, 65.4, 28.1, 27.0, 25.0.

IR (neat): 2943, 2229, 1959, 1716, 1421, 1259, 1107, 1018, 860, 766.

HRMS (ESI-TOF): calculated for [$C_{16}H_{15}N_2O_2$ (M + H^+)]: 267.1128, found: 267.1130.



2r

6-cyanohexa-4,5-dien-1-yl isobutyl carbonate (2r)

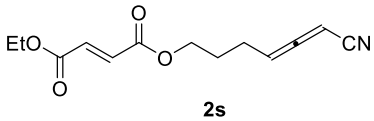
Following the general procedure, the title compound was prepared on 7 mmol scale and obtained as colorless oil, 812 mg, 52 % yield. (Rf = 0.46, eluent: PE/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.77 – 5.73 (m, 1H), 5.26 – 5.24 (m, 1H), 4.17 (t, *J* = 6.3 Hz, 2H), 3.91 (d, *J* = 6.7 Hz, 2H), 2.27 – 2.23 (m, 2H), 2.00 – 1.93 (m, 1H), 1.87 – 1.82 (m, 2H), 0.94 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.2, 155.4, 113.5, 96.1, 74.3, 68.3, 66.6, 27.9, 27.6, 23.8, 19.0.

IR (neat): 2962, 2225, 1960, 1739, 1245, 1259, 972, 790.

HRMS (ESI-TOF): calculated for [$C_{12}H_{18}NO_3$ (M + H^+)]: 224.1281, found: 224.1280.



2s

6-cyanohexa-4,5-dien-1-yl ethyl fumarate (2s)

Following the general procedure, the title compound was prepared on 11 mmol scale and obtained as colorless oil, 1.5 g,

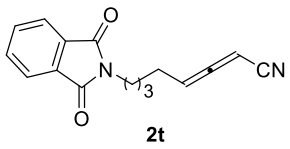
56 % yield. (Rf = 0.36, eluent: PE/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.76 (s, 2H), 5.73 – 5.69 (m, 1H), 5.23 – 5.21 (m, 1H), 4.20 – 4.15 (m, 4H), 2.21 – 2.16 (m, 2H), 1.82 – 1.76 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 214.9, 164.69, 164.67, 133.9, 133.0, 113.3, 95.8, 68.0, 63.9, 61.3, 27.1, 23.7, 14.0.

IR (neat): 2983, 2225, 1961, 1715, 1245, 1294, 1256, 1152, 1029, 977, 774.

HRMS (ESI-TOF): calculated for [$C_{13}H_{16}NO_4$ (M + H^+)]: 250.1074, found: 250.1078.



2t

8-(1,3-dioxoisoindolin-2-yl)octa-2,3-dienenitrile (2t)

Following the general procedure, the title compound was prepared on 11 mmol scale and obtained as colorless oil, 1.5 g, 56 % yield. (Rf = 0.36, eluent: PE/EtOAc = 5/1).

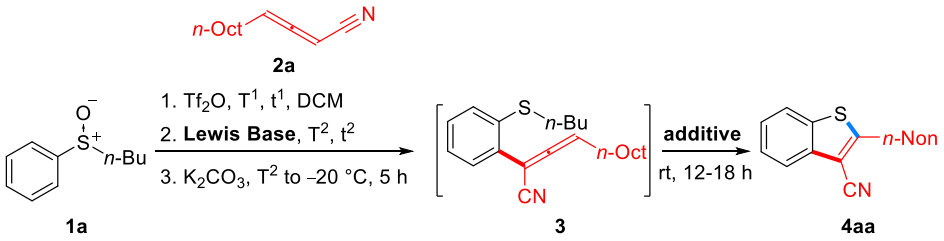
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 – 7.82 (m, 2H), 7.71 – 7.70 (m, 2H), 5.71 – 5.68 (m, 1H), 5.23 – 5.21 (m, 1H), 3.69 (t, *J* = 7.2 Hz, 2H), 2.21 – 2.17 (m, 2H), 1.75 – 1.70 (m, 2H), 1.54 – 1.49 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 215.2, 168.5, 134.1, 132.1, 123.3, 113.7, 96.5, 67.8, 37.5, 27.9, 26.9, 25.7.

IR (neat): 2952, 2221, 1957, 1693, 1438, 1135, 881, 714.

HRMS (ESI-TOF): calculated for [$C_{16}H_{15}N_2O_2$ (M + H^+)]: 267.1128, found: 267.1131.

3 Development and optimization of the reaction

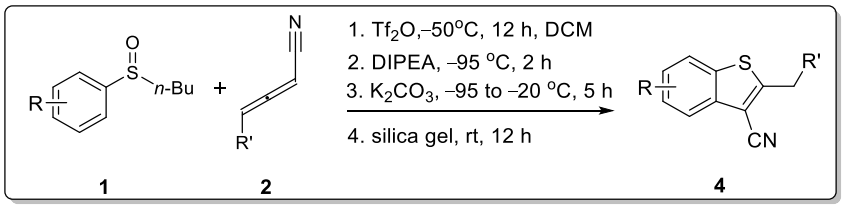


Entry	Base	T^1, t^1	T^2, t^2	Additive	Yield(%)
1	2-chloropyridine	–50 °C, 12 h	–95 °C, 2 h	none	31
2	2-methylpyridine	–50 °C, 12 h	–95 °C, 2 h	none	25
3	NEt_3	–50 °C, 12 h	–95 °C, 2 h	none	40
4	DABCO	–50 °C, 12 h	–95 °C, 2 h	none	13
5	*N*-ethylmorpholine	–50 °C, 12 h	–95 °C, 2 h	none	35
6	DIPEA	–50 °C, 12 h	–95 °C, 2 h	none	57
7	DIPEA	–60 °C, 12 h	–95 °C, 2 h	none	40
8	DIPEA	–40 °C, 12 h	–95 °C, 2 h	none	15
9	DIPEA	–50 °C, 6 h	–95 °C, 2 h	none	40
10	DIPEA	–50 °C, 18 h	–95 °C, 2 h	none	48
11	DIPEA	–50 °C, 12 h	–78 °C, 2 h	none	51
12	DIPEA	–50 °C, 12 h	–95 °C, 30 min	none	53
13	DIPEA	–50 °C, 12 h	–95 °C, 2 h	HOAc	61
14	DIPEA	–50 °C, 12 h	–95 °C, 2 h	TsOH	39
15	DIPEA	–50 °C, 12 h	–95 °C, 2 h	TFA	41
16	DIPEA	–50 °C, 12 h	–95 °C, 2 h	$BF_3{\cdot}Et_2O$	20
17	DIPEA	–50 °C, 12 h	–95 °C, 2 h	Silica gel	74(71)
18	DIPEA	–50 °C, 12 h	–95 °C, 2 h	NEt_3	21

General procedure: To a mixture of aryl sulfoxide (**1a**, 0.5 mmol) and allenenitrile (**2a**, 0.75 mmol, 1.5 equiv) in DCM (3 mL) was added Tf_2O (126 μL, 0.75 mmol, 1.5 equiv) at –78 °C under N_2 atomsphere. The reaction mixture was gradually warmed to T^1. After stirring for t^1, the reaction mixture was cooled to T^2. A solution of Lewis Base (1.5 equiv) in DCM (1 mL) was added to the mixture dropwise in 10 min using syringe pump. After stirring at T^2 for t^2, K_2CO_3 (345.5 mg, 5.0 equiv) was added, and the resulting reaction mixture was warm up to –20 °C and kept stirring for 5 h. The mixture was filtrated and concentrated under vacuum and then was dissolved in DCM (3 mL). For cases of entries 1-12, after stirring for 18 h at room temperature, the resulting mixture was

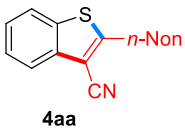
concentrated. Then, the obtained residue was used to determine the NMR yield of **4aa** using internal standard dibromomethane (86.9 mg, 0.5 mmol). For cases of entries 13-18, to this mixture was added additive (1.1 equiv). After stirring for 12 h, the resulting mixture was filtrated and concentrated under vacuum. Then, the obtained residue was used to determine the NMR yield of **4aa** using internal standard dibromomethane (86.9 mg, 0.5 mmol).

4 General procedure for the synthesis of benzothiophenes 4



General procedure: To a mixture of aryl sulfoxide (**1**, 0.5 mmol) and allenenitrile (**2**, 0.75 mmol, 1.5 equiv) in DCM (3 mL) was added Tf_2O (126 μL, 0.75 mmol, 1.5 equiv) at –78 °C under N_2 atomsphere. The reaction mixture was gradually warmed to –50 °C. After stirring for 12 h, the reaction mixture was cooled to –95 °C. A solution of DIPEA (96.9 mg, 0.75 mmol, 1.5 equiv) in DCM (1 mL) was added to the mixture dropwise in 10 min using syringe pump. After stirring at –95 °C for 2 h, K_2CO_3 (345.5 mg, 5.0 equiv) was added, and the resulting reaction mixture was warm up to –20 °C and kept stirring for 5 h. The mixture was then filtrated and concentrated under vacuum. To the obtained residue was added DCM (3 mL) and silica gel (1 g). The mixture was stirred for 12 h at rt. After that, the mixture was filtrated and concentrated under vacuum, and purified obtained by silica gel flash chromatography to give compound **4**. Products **4ab**, **4ia**, **4ka** and **4ma-4oa** were further purified by preparative HPLC with a reverse C18 column using MeOH/H_2O as eluent.

Note: Tf_2O and the solution of DIPEA in DCM were injected on the inner wall of Schlenk bottle lying a few centimeters higher than the reaction mixture. So that, the chemicals (Tf_2O and DIPEA) could be sufficiently cooled prior to their flowing into the reaction mixture.



4aa

2-nonylbenzo[*b*]thiophene-3-carbonitrile (4aa)

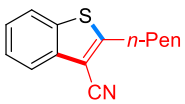
Following the general procedure, the title compound was obtained as colorless oil, 101 mg, 71% yield. (Rf = 0.36, eluent: PE/EtOAc = 40/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.42 – 7.38 (dd, *J* = 22.8, 12.0 Hz, 1H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.47 – 1.39 (m, 2H), 1.33 – 1.21 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.2, 138.0, 137.4, 125.9, 125.6, 122.5, 122.1, 114.5, 104.5, 32.0, 31.3, 30.5, 29.54, 29.38, 29.35, 29.2, 22.8, 14.2.

IR (neat): 3329, 2973, 2360, 2341, 1456, 1087, 1014, 879.

HRMS (ESI-TOF): calculated for [$C_{18}H_{24}NS$ (M + H^+)]: 286.1624, found: 286.1621.



4ab

2-pentylbenzo[*b*]thiophene-3-carbonitrile (4ab)

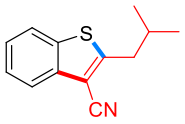
Following the general procedure, the title compound was obtained as colorless oil, 75 mg, 65% yield. (Rf = 0.36, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.41 – 7.39 (m, 1H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.77 (m, 2H), 1.44 – 1.35 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.2, 138.0, 137.4, 125.9, 125.6, 122.5, 122.1, 114.5, 104.5, 31.2, 31.0, 30.5, 22.4, 14.0.

IR (neat): 2955, 2927, 2857,2360, 2341, 2221, 1525,1460, 754, 728.

HRMS (ESI-TOF): calculated for [$C_{14}H_{16}NS$ (M + H^+)]: 230.0998, found: 230.0994.



4ac

2-isobutylbenzo[*b*]thiophene-3-carbonitrile (4ac)

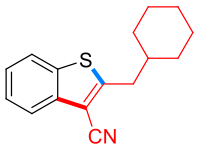
Following the general procedure, the title compound was obtained as light yellow oil, 73 mg, 68% yield. (Rf = 0.40, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 15.0, 7.8 Hz, 1H), 7.40 (dd, *J* = 15.0, 7.2 Hz, 1H), 3.00 (d, *J* = 7.3 Hz, 2H), 2.13 – 2.08 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8, 137.9, 137.7, 125.9, 125.6, 122.5, 122.1, 114.6, 105.3, 39.5, 31.1, 22.4.

IR (neat): 2957, 2926, 2870, 2360, 2341, 2220, 1461, 1435, 754, 729.

HRMS (ESI-TOF): calculated for [$C_{13}H_{13}NSNa$ (M + Na^+)]: 238.0661, found: 238.0666.



4ad

2-(cyclohexylmethyl)benzo[*b*]thiophene-3-carbonitrile (4ad)

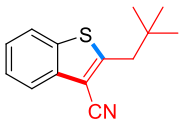
Following the general procedure, the title compound was obtained as white solid, 79 mg, 62% yield. m.p. 95 − 96 °C. (Rf = 0.48, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.41 – 7.38 (m, 1H), 3.01 (d, *J* = 7.0 Hz, 2H), 1.80 – 1.70 (m, 6H), 1.25 – 1.21 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.6, 137.9, 137.7, 125.9, 125.6, 122.5, 122.1, 114.7, 105.3, 40.4, 38.2, 33.0, 26.3, 26.1.

IR (neat): 3337, 2922, 2851, 2360, 2341, 2218, 1459, 1435, 754, 730.

HRMS (ESI-TOF): calculated for [$C_{16}H_{18}NS$ (M + H^+)]: 256.1154, found: 256.1153.



4ae

2-neopentylbenzo[*b*]thiophene-3-carbonitrile (4ae)

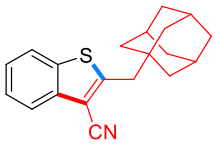
Following the general procedure, the title compound was obtained as white solid, 54 mg, 47% yield. m.p. 63 − 64 °C. (Rf = 0.40, eluent: PE/EtOAc = 40/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.44 – 7.39 (m, 1H), 3.03 (s, 2H), 1.09 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.2, 138.0, 137.8, 125.8, 125.7, 122.3, 122.2, 115.0, 106.6, 44.4, 33.4, 29.6.

IR (neat): 2953, 2920, 2850, 2221, 1460, 1434, 1046, 755, 729.

HRMS (ESI-TOF): calculated for [$C_{14}H_{16}NS$ (M + H^+)]: 230.0998, found: 230.0997.



4af

2-(((3r,5r,7r)-adamantan-1-yl)methyl)benzo[*b*]thiophene-3-carbonitrile (4af)

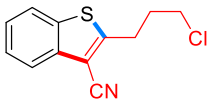
Following the general procedure, the title compound was obtained as colorless solid, 77 mg, 50% yield. m.p. 188 − 189 °C. (Rf = 0.45, eluent: PE/EtOAc = 40/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.43 – 7.39 (m, 1H), 2.90 (s, 2H), 2.04 – 1.97 (m, 3H), 1.71 – 1.57 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.1, 138.1, 138.0, 125.8, 125.6, 122.2, 122.1, 115.1, 106.6, 45.1, 42.4, 36.8, 35.2, 28.8.

IR (neat): 2895**,** 2843, 2223, 2223, 1460, 1433, 758, 731.

HRMS (ESI-TOF): calculated for [$C_{20}H_{22}NS$ (M + H^+)]: 308.1467, found: 308.1470



4ag

2-(3-chloropropyl)benzo[*b*]thiophene-3-carbonitrile (4ag)

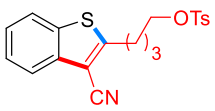
Following the general procedure, the title compound was obtained as colorless oil, 66 mg, 56% yield. (Rf = 0.36, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.49 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.42 (dd, *J* = 11.2, 4.1 Hz, 1H), 3.63 (t, *J* = 6.3 Hz, 2H), 3.32 (t, *J* = 9.0 Hz, 2H), 2.31 – 2.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.3, 137.9, 137.5, 126.1, 125.9, 122.6, 122.2, 114.1, 105.3, 43.4, 33.5, 27.6.

IR (neat): 2957, 2221, 1461, 1435, 1265, 754, 728, 657.

HRMS (ESI-TOF): calculated for [$C_{12}H_{11}ClNS$ (M + H^+)]: 236.0295, found: 236.0228.



4ah

4-(3-cyanobenzo[*b*]thiophen-2-yl)butyl 4-methylbenzenesulfonate (4ah)

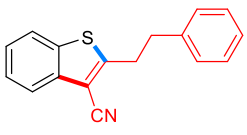
Following the general procedure, the title compound was obtained as white solid, 135 mg, 70% yield. m.p. 84 − 86 °C. (Rf = 0.45, eluent: PE/EtOAc = 3/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.81 – 7.76 (m, 3H), 7.51 – 7.46 (m, 1H), 7.44 – 7.39 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.09 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 1.89 – 1.80 (m, 2H), 1.79 – 1.73 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 145.0, 137.8, 137.4, 133.1, 130.0, 128.0, 126.0, 125.9, 122.6, 122.1, 114.2, 105.0, 69.8, 29.7, 28.3, 27.1, 21.8.

IR (neat): 2226, 1343, 1188, 1174, 1096, 939, 870, 757.

HRMS (ESI-TOF): calculated for [$C_{20}H_{20}NO_3S_2$ (M + H^+)]: 386.0879, found: 386.0874.



4ai

2-phenethylbenzo[*b*]thiophene-3-carbonitrile (4ai)

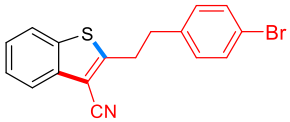
Following the general procedure, the title compound was obtained as white solid, 75 mg, 57% yield. m.p. 64 − 66 °C. (Rf = 0.36, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.42 – 7.39 (m, 1H), 7.32 – 7.30 (m, 2H), 7.26 – 7.22 (m, 3H), 3.47 – 3.43 (m, 2H), 3.13 – 3.09 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.3, 139.5, 137.8, 137.5, 128.8, 128.6, 126.8, 125.9, 125.7, 122.6, 122.1, 114.3, 105.0, 37.2, 32.3.

IR (neat): 2219, 1454, 1435, 1261, 759, 732, 698.

HRMS (ESI-TOF): calculated for [$C_{17}H_{14}NS$ (M + H^+)]: 264.0841, found: 264.0840.



4aj

2-(4-bromophenethyl)benzo[*b*]thiophene-3-carbonitrile (4aj)

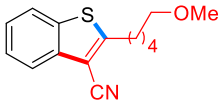
Following the general procedure, the title compound was obtained as white solid, 90 mg, 53% yield. m.p. 78 − 79 °C. (Rf = 0.30, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 15.0, 7.8 Hz, 1H), 7.42 – 7.40 (m, 3H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.42 (t, *J* = 7.7 Hz, 2H), 3.06 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.7, 138.4, 137.7, 137.4, 131.8, 130.3, 126.0, 125.8, 122.6, 122.2, 120.7, 114.2, 105.1, 36.5, 32.0.

IR (neat): 2216, 1485, 1460, 1009, 800, 754, 727, 698.

HRMS (ESI-TOF): calculated for [$C_{17}H_{13}BrNS$ (M + H^+)]: 340.9947, found: 341.9964.



4ak

2-(5-methoxypentyl)benzo[*b*]thiophene-3-carbonitrile (4ak)

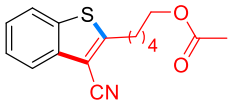
Following the general procedure, the title compound was obtained as yellow oil, 79 mg, 61% yield. (Rf = 0.26, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.41 – 7.37 (m, 1H), 3.38 (t, *J* = 6.4 Hz, 2H), 3.32 (s, 3H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.85 – 1.80 (m, 2H), 1.64 – 1.61 (m, 2H), 1.52 – 1.46 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.8, 137.9, 137.4, 125.9, 125.6, 122.5, 122.0, 114.4, 104.5, 72.5, 58.7, 31.1, 30.4, 29.3, 25.8.

IR (neat): 2929, 2858, 2220, 1460, 1435, 1116, 754, 729, 657.

HRMS (ESI-TOF): calculated for [$C_{15}H_{18}NOS$ (M + H^+)]: 260.1104, found: 260.1102.



4al

5-(3-cyanobenzo[*b*]thiophen-2-yl)pentyl acetate (4al)

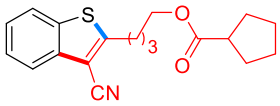
Following the general procedure, the title compound was obtained as light yellow oil, 93 mg, 65% yield. (Rf = 0.29, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.42 – 7.38 (m, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 3.14 (t, *J* = 6.0 Hz, 2H), 2.04 (s, 3H), 1.86 – 1.81 (m, 2H), 1.72 – 1.67 (m, 2H), 1.52 – 1.48 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.3, 159.4, 137.9, 137.4, 126.0, 125.7, 122.5, 122.1, 114.4, 104.7, 64.2, 30.8, 30.3, 28.3, 25.5, 21.1.

IR (neat): 2935, 2220, 1732, 1435, 1233, 1042, 756, 730, 606.

HRMS (ESI-TOF): calculated for [$C_{16}H_{18}NO_2S$ (M + H^+)]: 288.1053, found: 288.1050.



4am

4-(3-cyanobenzo[*b*]thiophen-2-yl)butyl cyclopentanecarboxylate (4am)

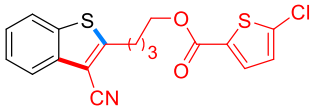
Following the general procedure, the title compound was obtained as yellow oil, 105 mg, 64% yield. (Rf = 0.37, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 15.0, 7.2 Hz, 1H), 7.41 (dd, *J* = 15.0, 7.2 Hz,1H), 4.12 (t, *J* = 6.3 Hz, 2H), 3.17 (t, *J* = 7.6 Hz, 2H), 2.76 – 2.70 (m, 1H), 1.92 – 1.85 (m, 4H), 1.81 – 1.74 (m, 4H), 1.71 – 1.67 (m, 2H), 1.59 – 1.55 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 177.0, 159.1, 137.9, 137.4, 126.0, 125.8, 122.6, 122.1, 114.3, 104.9, 63.7, 44.0, 30.2, 30.1, 28.2, 27.8, 25.9.

IR (neat): 2951, 2222, 1725, 1400, 1436, 1152, 1042, 754, 730.

HRMS (ESI-TOF): calculated for [$C_{19}H_{22}NO_2S$ (M + H^+)]: 328.1366, found: 328.1363.



4an

4-(3-cyanobenzo[*b*]thiophen-2-yl)butyl 5-chlorothiophene-2-carboxylate (4an)

Following the general procedure, the title compound was obtained as white solid, 128 mg, 68% yield. m.p. 70 − 71 °C. (Rf = 0.29, eluent: PE/EtOAc = 10/1).

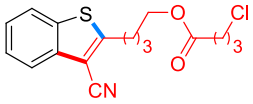
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 4.0 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.44 – 7.38 (m, 1H), 6.92 (d, *J* = 4.0 Hz, 1H), 4.33 (t, *J* = 6.2 Hz, 2H),

3.20 (t, *J* = 7.3 Hz, 2H), 1.99 – 1.91 (m, 2H), 1.91 – 1.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.3, 158.8, 137.9, 137.5, 137.4, 133.2, 131.9, 127.4, 126.0, 125.8, 122.6, 122.2, 114.3, 105.0, 64.7, 30.0, 28.2, 27.7.

IR (neat): 2917, 2221, 1706, 1423, 1333, 1252, 1087, 753, 728.

HRMS (ESI-TOF): calculated for [$C_{18}H_{15}ClNO_2S_2$ (M + H^+)]: 376.0227, found: 376.0222.



4ao

4-(3-cyanobenzo[*b*]thiophen-2-yl)butyl 4-chlorobutanoate (4ao)

Following the general procedure, the title compound was obtained as colorless oil, 101 mg, 60% yield. (Rf = 0.5, eluent: PE/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 15.0, 7.8 Hz, 1H), 7.41 (dd, *J* = 11.2, 4.0 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 3.60 (t, *J* = 6.3 Hz, 2H), 3.17 (t, *J* = 7.6 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.12 – 2.07 (m, 2H), 1.91 – 1.86 (m, 2H), 1.80 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.8, 158.9, 137.9, 137.4, 126.0, 125.8, 122.6, 122.1, 114.3, 104.9, 64.0, 44.2, 31.3, 30.0, 28.1, 27.7.

IR (neat): 2952, 2221, 1729, 1436, 1171, 1144, 755, 730, 647.

HRMS (ESI-TOF): calculated for [$C_{17}H_{19}ClNO_2S$ (M + H^+)]: 336.0820, found: 336.0816.

4ap

5-(3-cyanobenzo[*b*]thiophen-2-yl)pentyl benzoate (4ap)

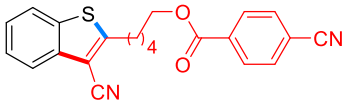
Following the general procedure, the title compound was obtained as yellow solid, 106 mg, 61% yield. m.p. 71 − 72 °C. (Rf = 0.5, eluent: PE/EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 8.00 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.50 – 7.46 (m, 1H), 7.44 – 7.38 (m, 3H), 4.34 (t, *J* = 6.5 Hz, 2H), 3.17 (t, *J* = 7.6 Hz, 2H), 1.94 – 1.81 (m, 4H), 1.65 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.8, 159.5, 137.9, 137.4, 133.0, 130.4, 129.7, 128.5, 126.0, 125.7, 122.6, 122.1, 114.4, 104.7, 64.7, 30.8, 30.3, 28.5, 25.6.

IR (neat): 2938, 2223, 1707, 1291, 1275, 1126, 762, 755, 674.

HRMS (ESI-TOF): calculated for [$C_{21}H_{20}NO_2S$ (M + H^+)]: 350.1209, found: 350.1207.



4aq

5-(3-cyanobenzo[*b*]thiophen-2-yl)pentyl 4-cyanobenzoate (4aq)

Following the general procedure, the title compound was obtained as white solid, 122 mg, 65% yield. m.p. 90 − 91 °C. (Rf = 0.42, eluent: PE/EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.43 – 7.39 (m, 1H), 4.36 (t, *J* = 6.5 Hz, 2H), 3.17 (t, *J* = 7.5 Hz, 2H), 1.91 – 1.82 (m, 4H), 1.63 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.0, 159.2, 137.8, 137.3, 134.2, 132.3, 130.1, 126.0, 125.7, 122.5, 122.1, 118.1, 116.4, 114.4, 104.8, 65.4, 30.7, 30.2, 28.3, 25.4.

IR (neat): 2906, 2220, 1713, 1270, 1245, 1117, 863, 754, 690.

HRMS (ESI-TOF): calculated for [$C_{22}H_{19}N_2O_2S$ (M + H^+)]: 375.1162, found: 375.1162.

4ar

4-(3-cyanobenzo[*b*]thiophen-2-yl)butyl isobutyl carbonate (4ar)

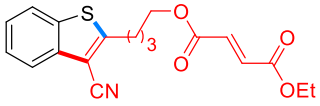
Following the general procedure, the title compound was obtained as colorless oil, 103 mg, 62% yield. (Rf = 0.45, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.43 – 7.39 (m, 1H), 4.19 (t, *J* = 6.3 Hz, 2H), 3.92 (d, *J* = 6.7 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 2H), 2.00 – 1.95 (m, 1H), 1.94 – 1.89 (m, 2H), 1.84 – 1.79 (m, 2H), 0.95 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 155.5, 137.9, 137.5, 126.0, 125.8, 122.6, 122.2, 114.3, 105.0, 74.3, 67.2, 30.1, 28.3, 27.9, 27.6, 19.1.

IR (neat): 2958, 2222, 1739, 1460, 1245, 967, 790, 754, 729.

HRMS (ESI-TOF): calculated for [$C_{18}H_{22}NO_3S$ (M + H^+)]: 332.1315, found: 332.1314.



4as

4-(3-cyanobenzo[*b*]thiophen-2-yl)butyl ethyl fumarate (4as)

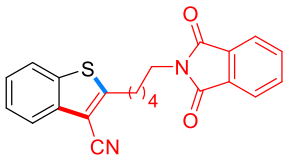
Following the general procedure, the title compound was obtained as white solid, 100 mg, 56% yield. m.p. 56 − 57 °C. (Rf = 0.26, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.42 – 7.39 (m, 1H), 6.85 (s, 2H), 4.27 – 4.23 (m, 4H), 3.18 (t, *J* = 7.5 Hz, 2H), 1.93 – 1.88 (m, 2H), 1.85 – 1.80 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.11, 165.05, 158.7, 137.9, 137.4, 134.1, 133.4, 126.0, 125.8, 122.6, 122.2, 114.3, 105.0, 64.7, 61.5, 30.0, 28.0, 27.7, 14.2.

IR (neat): 2221, 1731, 1717, 1644, 1253, 1178, 1037, 977, 757, 730.

HRMS (ESI-TOF): calculated for [$C_{19}H_{20}NO_4S$ (M + H^+)]: 358.1108, found:358.1107.



4at

2-(4-(1,3-dioxoisoindolin-2-yl)butyl)benzo[*b*]thiophene-3-carbonitrile (4at)

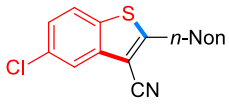
Following the general procedure, the title compound was obtained as white solid, 129 mg, 69% yield. m.p. 107 − 108 °C. (Rf = 0.30, eluent: PE/EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.82 (m, 3H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.70 (m, 2H), 7.50 – 7.45 (m, 1H), 7.42 – 7.37 (m, 1H), 3.70 (t, *J* = 7.2 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H), 1.90 – 1.82 (m, 2H), 1.79 – 1.72 (m, 2H), 1.54 – 1.45 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.6, 159.4, 137.9, 137.4, 134.1, 132.2, 125.9, 125.7, 123.4, 122.6, 122.1, 114.4, 104.7, 37.8, 30.8, 30.3, 28.3, 26.4.

IR (neat): 2952, 2221, 1728, 1460, 1436, 1172, 1144, 755, 730.

HRMS (ESI-TOF): calculated for [$C_{22}H_{19}N_2O_2S$ (M + H^+)]: 375.1162, found:375.1158.



4ba

5-chloro-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4ba)

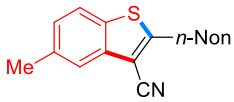
Following the general procedure, the title compound was obtained as light yellow solid, 102 mg, 64% yield. m.p. 66 − 67 °C. (Rf = 0.5, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (d, *J* = 1.9 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.37 (dd, *J* = 8.6, 2.0 Hz, 1H), 3.12 (t, *J* = 7.8 Hz, 2H), 1.81 – 1.76 (m, 2H), 1.44 – 1.39 (m, 2H), 1.28 – 1.24 (m, 10H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.1, 139.1, 135.5, 132.5, 126.2, 123.6, 121.8, 113.9, 104.0, 32.0, 31.2, 30.6, 29.5, 29.4, 29.3, 29.2, 22.8, 14.3.

IR (neat): 2924, 2849, 2219, 1462, 1416, 1081, 871, 815, 730.

HRMS (ESI-TOF): calculated for [$C_{18}H_{23}ClNS$ (M + H^+)]: 320.1234, found: 320.1255.



4ca

5-methyl-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4ca)

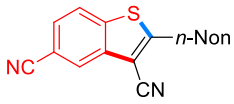
Following the general procedure, the title compound was obtained as colorless oil, 90 mg, 60% yield. (Rf = 0.32, eluent: PE/EtOAc = 40/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.64 (m, 2H), 7.22 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.10 (t, *J* = 7.6 Hz, 2H), 2.50 (s, 3H), 1.82 – 1.75 (m, 2H), 1.45 – 1.38 (m, 2H), 1.31 – 1.22 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.2, 138.3, 136.0, 134.6, 127.3, 122.1, 122.0, 114.7, 104.1, 32.0, 31.3, 30.6, 29.6, 29.39, 29.37, 29.2, 22.8, 21.6, 14.3.

IR (neat): 2921, 2852, 2218, 1450, 1377, 1151, 871, 797, 721.

HRMS (ESI-TOF): calculated for [$C_{19}H_{26}NS$ (M + H^+)]: 300.1780, found: 300.1781.



4da

2-nonylbenzo[*b*]thiophene-3,5-dicarbonitrile (4da)

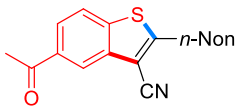
Following the general procedure, the title compound was obtained as white solid, 87 mg, 56% yield. m.p. 74 − 75 °C. (Rf = 0.36, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 (d, *J* = 0.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 8.4, 1.3 Hz, 1H), 3.15 (t, *J* = 7.7 Hz, 2H), 1.84 – 1.78 (m, 2H), 1.45 – 1.39 (m, 2H), 1.36 – 1.32 (m, 2H), 1.29 – 1.24 (m, 8H), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.9, 141.4, 137.9, 127.8, 126.3, 123.7, 118.5, 113.9, 110.0, 104.6, 31.9, 31.2, 30.6, 29.5, 29.33, 29.27, 29.1, 22.8, 14.2.

IR (neat): 2924, 2849, 2219, 1417, 1081,871, 816, 759, 730.

HRMS (ESI-TOF): calculated for [$C_{19}H_{23}N_2S$ (M + H^+)]: 311.1576, found: 311.1585.



4ea

5-acetyl-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4ea)

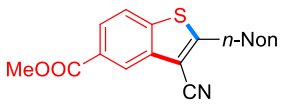
Following the general procedure, the title compound was obtained as white solid, 119 mg, 73% yield. m.p. 56 − 57 °C. (Rf = 0.36, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40 (d, *J* = 1.2 Hz, 1H), 8.02 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 3.15 (t, *J* = 7.8 Hz, 2H), 2.71 (s, 3H), 1.84 – 1.78 (m, 2H), 1.45 – 1.40 (m, 2H), 1.36 – 1.33 (m, 2H), 1.29 – 1.24 (m, 8H), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 197.5, 161.8, 141.8, 137.8, 135.1, 124.8, 122.8, 122.6, 114.0, 105.2, 32.0, 31.2, 30.7, 29.5, 29.4, 29.3, 29.1, 27.0, 22.8, 14.3.

IR (neat): 2914, 2851, 2217, 1687, 1432, 1358, 1230, 897, 817.

HRMS (ESI-TOF): calculated for [$C_{20}H_{26}NOS$ (M + H^+)]: 328.1730, found: 328.1736.



4fa

methyl 3-cyano-2-nonylbenzo[*b*]thiophene-5-carboxylate (4fa)

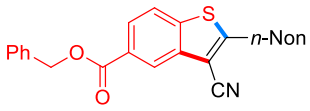
Following the general procedure, the title compound was obtained as white solid, 120 mg, 70% yield. m.p. 54 − 55 °C. (Rf = 0.34, eluent: PE/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 – 8.53 (m, 1H), 8.08 – 8.05 (m, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 3.98 (s, 3H), 3.14 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.77 (m, 2H), 1.45 – 1.39 (m, 2H), 1.31 – 1.23 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 161.6, 141.6, 137.8, 128.2, 126.2, 123.7, 122.6, 114.0, 105.1, 52.6, 32.0, 31.2, 30.6, 29.5, 29.4, 29.3, 29.2, 22.8, 14.3.

IR (neat): 2914, 2851, 2217, 1712, 1435, 1277, 1243, 1099, 757.

HRMS (ESI-TOF): calculated for [$C_{20}H_{26}NO_2S$ (M + H^+)]: 344.1679, found: 344.1677.



4ga

benzyl 3-cyano-2-nonylbenzo[*b*]thiophene-5-carboxylate (4ga)

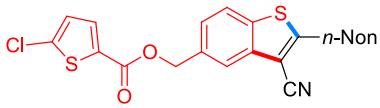
Following the general procedure, the title compound was obtained as colorless oil, 147 mg, 70% yield. (Rf = 0.42, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.57 (d, *J* = 1.0 Hz, 1H), 8.09 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.83 (dd, *J* = 8.5, 0.4 Hz, 1H), 7.50 – 7.48 (m, 2H), 7.42 – 7.39 (m, 2H), 7.37 – 7.35 (m, 1H), 5.43 (s, 2H), 3.14 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.45 – 1.40 (m, 2H), 1.36 – 1.27 (m, 2H), 1.30 – 1.25 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 161.6, 141.7, 137.7, 135.9, 128.8, 128.52, 128.49, 128.2, 126.3, 123.8, 122.5, 113.9, 105.1, 67.2, 31.9, 31.2, 30.6, 29.5, 29.34, 29.30, 29.1, 22.8, 14.2.

IR (neat): 2921, 2847, 2214, 1712, 1439, 1238, 1243, 1096, 754, 698.

HRMS (ESI-TOF): calculated for [$C_{26}H_{30}NO_2S$ (M + H^+)]: 420.1992, found: 420.2102.



4ha

(3-cyano-2-nonylbenzo[*b*]thiophen-5-yl)methyl 5-chlorothiophene-2-carboxylate (4ha)

Following the general procedure, the title compound was obtained as colorless oil, 152 mg, 66% yield. (Rf = 0.36, eluent: PE/EtOAc = 20/1).

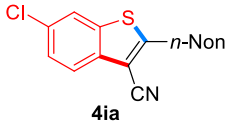
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, *J* = 0.7 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 4.0 Hz, 1H), 7.46 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.94 (d, *J* = 4.0 Hz, 1H), 5.44 (s, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.82 – 1.77 (m, 2H), 1.44 – 1.39 (m, 2H), 1.35 – 1.32 (m, 2H), 1.30 – 1.278 (m, 8H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.2, 161.1, 138.2, 138.0, 137.4, 133.7, 133.6, 131.6, 127.5, 125.8, 122.9, 121.8, 114.3, 104.5, 66.8, 32.0, 31.3, 30.6, 29.5, 29.4, 29.3, 29.1, 22.8, 14.3.

IR (neat): 2917, 2851, 2217, 1707, 1423, 1245, 1076, 1057, 745.

HRMS (ESI-TOF): calculated for [$C_{24}H_{26}ClNO_2S_2Na$ (M + Na^+)]: 482.0986, found: 482.0998.

Following the general procedure, a mixture of **4ia** and **4ia'** were obtained from the reaction of sulfoxide **1i** (0.5 mmol) and allenenitrile **2a**.



4ia

6-chloro-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4ia)

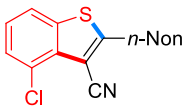
The title compound was obtained as colorless oil, 80 mg, 50% yield. (Rf = 0.32, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, *J* = 1.7 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.44 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.10 (t, *J* = 7.2 Hz, 2H), 1.81 – 1.76 (m, 2H), 1.44 – 1.39 (m, 2H), 1.36 – 1.32 (m, 2H), 1.28 – 1.24 (m, 8H), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.7, 138.4, 136.4, 131.8, 126.8, 122.9, 122.2, 114.1, 104.3, 32.0, 31.2, 30.6, 29.5, 29.4, 29.3, 29.2, 22.8, 14.3.

IR (neat): 2920, 2852, 2221, 1704, 1455, 1055, 808, 787, 721.

HRMS (ESI-TOF): calculated for [$C_{18}H_{23}ClNS$ (M + H^+)]: 320.1234, found: 320.1245.



4ia'

4-chloro-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4ia')

The title compound was obtained as colorless oil, 26 mg, 16% yield. (Rf = 0.30, eluent: PE/EtOAc = 40/1).

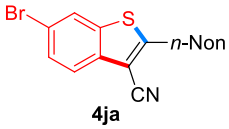
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 – 7.72 (m, 1H), 7.62 – 7.61 (m, 1H), 7.22 (dd, *J* = 15.8, 7.9 Hz, 1H), 3.14 (t, *J* = 7.8 Hz, 2H), 1.82 – 1.77 (m, 2H), 1.46 – 1.40 (m, 2H), 1.36– 1.32 (m, 2H), 1.31 – 1.25 m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.2, 137.9, 137.4, 125.9, 125.6, 122.5, 122.1, 114.5, 104.5, 32.0, 31.3, 30.5, 29.6, 29.39, 29.36, 29.2, 22.8, 14.3.

IR (neat): 2922, 2853, 2221, 1461, 1434, 754, 729.

HRMS (ESI-TOF): calculated for [$C_{18}H_{23}ClNS$ (M + H^+)]: 320.1234, found: 320.1245.

Following the general procedure, **4ja** and **4ja'** were obtained from the reaction of sulfoxide **1j** (0.5 mmol) and allenenitrile **2a**.



4ja

6-bromo-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4ja)

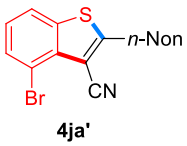
The title compound was obtained as colorless oil, 96 mg, 53% yield. (Rf = 0.36, eluent: PE/EtOAc = 40/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.10 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.41 – 1.38 (m, 2H), 1.36 – 1.25 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.7, 138.8, 136.7, 129.4, 125.1, 123.2, 119.5, 114.0, 104.4, 32.0, 31.2, 30.5, 29.5, 29.4, 29.3, 29.1, 22.8, 14.3.

IR (neat): 2921, 2852, 2360, 2341, 2222, 1454, 1386, 810, 767, 670.

HRMS (ESI-TOF): calculated for [$C_{18}H_{23}BrNS$ (M + H^+)]: 386.0549, found: 386.0544.



4ja'

4-bromo-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4ja')

The title compound was obtained as colorless oil, 47 mg, 26% yield. (Rf = 0.36, eluent: PE/EtOAc = 40/1).

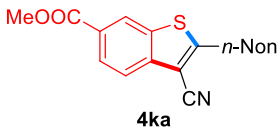
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.61 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.24 – 7.21 (m, 1H), 3.14 (t, *J* = 7.8 Hz, 2H), 1.82 – 1.77 (m, 2H), 1.46 – 1.41 (m, 2H), 1.36 – 1.32 (m, 2H), 1.31 – 1.25 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 163.1, 138.8, 135.4, 130.7, 126.2, 121.8, 116.4, 115.2, 105.1, 53.6, 32.0, 31.1, 30.6, 29.5, 29.4, 29.2, 22.8, 14.3.

IR (neat): 2919, 2850, 2363, 2215, 1459, 1078, 769, 735.

HRMS (ESI-TOF): calculated for [$C_{18}H_{23}BrNS$ (M + H^+)]: 386.0549, found: 386.0544.

Following the general procedure, **4ka** and **4ka'** were obtained from the reaction of sulfoxide **1k** (0.5 mmol) and allenenitrile **2a**.



4ka

3-cyano-2-nonylbenzo[*b*]thiophen-6-yl acetate (4ka)

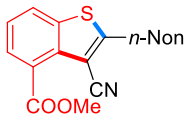
The title compound was obtained as yellow oil, 82 mg, 48% yield. (Rf = 0.52, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H), 3.15 (t, *J* = 7.7 Hz, 2H), 1.85 – 1.79 (m, 2H), 1.46 – 1.40 (m, 2H), 1.37 – 1.33 (m, 2H), 1.29 – 1.27 (m, 8H), 0.88 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 163.9, 141.3, 137.1, 127.5, 126.8, 124.6, 121.9, 114.0, 104.7, 52.6, 32.0, 31.2, 30.8, 29.5, 29.4, 29.3, 29.2, 22.8, 14.2.

IR (neat): 2918, 2852, 2226, 1713, 1426, 1234, 1122, 973, 767, 726.

HRMS (ESI-TOF): calculated for [$C_{20}H_{26}NO_2S$ (M + H^+)]: 344.1679, found: 344.1677.



4ka'

methyl 3-cyano-2-nonylbenzo[*b*]thiophene-4-carboxylate (4ka')

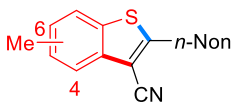
The title compound was obtained as colorless oil, 22 mg, 13% yield. (Rf = 0.38, eluent: PE/EtOAc = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.89 (m, 2H), 7.45 – 7.41 (m, 1H), 4.04 (s, 3H), 3.18 (t, *J* = 7.6 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.47 – 1.40 (m, 2H), 1.37 – 1.33 (m, 2H), 1.31 – 1.26 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 163.9, 138.8, 134.3, 128.2, 126.9, 126.2, 124.7, 114.8, 104.9, 52.0, 32.0, 31.1, 30.8, 29.5, 29.4, 29.2, 22.8, 14.2.

IR (neat): 2913, 2849, 2215, 1732, 1470, 1435, 1415, 1131, 1087, 752.

HRMS (ESI-TOF): calculated for [$C_{20}H_{26}NO_2S$ (M + H^+)]: 344.1679, found: 344.1677.



4la
(C6/C4 = 55/45)

6-methyl-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4la)

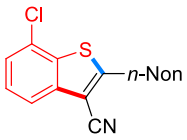
Following the general procedure, the title compound was obtained as colorless oil, 91 mg, 61% yield. (Rf = 0.32, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 0.55H, C6), 7.62 (d, *J* = 8.0 Hz, 0.45H, C4), 7.58 (s, 0.55H, C6), 7.28 (d, *J* = 8.3 Hz, 0.55H, C6), 7.27 – 7.24 (m, 0.45H, C4), 7.19 – 7.17 (m, 0.45H, C4), 3.13 – 3.07 (m, 2H), 2.86 (s, 1.35H, C4), 2.48 (s, 1.65H, C6), 1.81 – 1.75 (m, 2H), 1.45 – 1.38 (m, 2H), 1.35 – 1.34 (m, 2H), 1.31 – 1.26 (m, 8H), 0.89 – 0.86 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.0, 159.0, 137.74, 137.69, 135.9, 135.8, 135.7, 133.1, 127.5, 125.4, 122.3, 121.6, 120.3, 116.7, 114.7, 104.2, 103.8, 32.0, 31.3, 31.2, 30.5, 29.6, 29.39, 29.36, 29.2, 29.1, 22.8, 21.7, 20.1, 14.3.

IR (neat): 2922, 2853, 2218, 1452, 1377, 810, 766,746, 722.

HRMS (ESI-TOF): calculated for [$C_{19}H_{25}NSNa$ (M + Na^+)]: 322.1600, found: 322.1594.



4ma

7-chloro-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4ma)

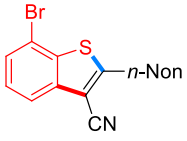
Following the general procedure, the title compound was obtained as colorless oil, 86 mg, 54% yield. (Rf = 0.45, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 1.8 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.44 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.10 (t, *J* = 7.8 Hz, 2H), 1.81 – 1.76 (m, 2H), 1.44 – 1.38 (m, 2H), 1.35 – 1.33 (m, 2H), 1.30 – 1.25 (m, 8H), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.6, 138.4, 136.4, 131.8, 126.8, 122.9, 122.2, 114.0, 104.4, 32.0, 31.2, 30.6, 29.5, 29.4, 29.3, 29.1, 22.8, 14.2.

IR (neat): 2921, 2851, 2221, 1466, 1456, 1391, 1094, 808, 787.

HRMS (ESI-TOF): calculated for [$C_{18}H_{23}ClNS$ (M + H^+)]: 320.1234, found: 320.1240.



4na

7-bromo-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4na)

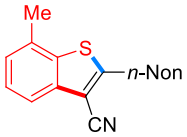
Following the general procedure, the title compound was obtained as white solid, 80 mg, 44% yield. m.p. 53 − 54 °C. (Rf = 0.42, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81 (d, *J* = 6.0, Hz, 1H), 7.54 (d, *J* = 6.0, Hz, 1H), 7.36 (dd, *J* = 15.6, 7.8 Hz, 1H), 3.13 (t, *J* = 7.6 Hz, 2H), 1.84 – 1.79 (m, 2H), 1.44 – 1.41 (m, 2H), 1.36 – 1.33 (m, 2H), 1.30 – 1.25 (m, 8H), 0.87 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0, 139.3, 138.8, 128.4, 127.3, 121.0, 115.9, 114.2, 105.5, 32.0, 31.2, 30.6, 29.5, 29.4, 29.3, 29.2, 22.8, 14.2.

IR (neat): 2920, 2849, 2221, 1546, 1454, 1395, 1097, 853, 740, 7181, 454.

HRMS (ESI-TOF): calculated for [$C_{18}H_{22}BrNSNa$ (M + Na^+)]: 386.0549, found: 386.0543.



4oa

7-methyl-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4oa)

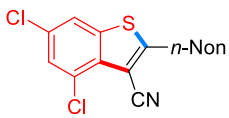
Following the general procedure, the title compound was obtained as white solid, 51 mg, 34% yield. m.p. 57 − 59 °C. (Rf = 0.42, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.54 (s, 3H), 1.83 – 1.78 (m, 2H), 1.44 – 1.40 (m, 2H), 1.37 – 1.33 (m, 2H), 1.29 – 1.24 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.6, 137.8, 137.7, 132.2, 126.3, 125.8, 119.7, 114.7, 105.2, 32.0, 31.3, 30.6, 29.6, 29.39, 29.38, 29.2, 22.8, 20.2, 14.3.

IR (neat): 2921, 2850, 2213, 1464, 1429, 1162, 888, 788.

HRMS (ESI-TOF): calculated for [$C_{19}H_{26}NS$ (M + H^+)]: 300.1780, found: 300.1778.



4pa

4,6-dichloro-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4pa)

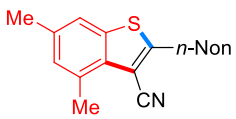
Following the general procedure, the title compound was obtained as white solid, 111 mg, 63% yield. m.p. 68 − 69 °C. (Rf = 0.40, eluent: PE/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 1.8 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 3.12 (t, *J* = 8.0 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.45 – 1.40 (m, 2H), 1.29 – 1.26 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 163.0, 139.5, 132.9, 131.6, 128.8, 127.4, 120.9, 114.5, 103.6, 32.0, 31.0, 30.5, 29.5, 29.4, 29.3, 29.2, 22.8, 14.3.

IR (neat): 2914, 2849, 2218, 1470, 1438, 1365, 1076, 855, 817, 831.

HRMS (ESI-TOF): calculated for [$C_{18}H_{21}Cl_2NSNa$ (M + Na^+)]: 376.0664, found: 376.0660.



4qa

4,6-dimethyl-2-nonylbenzo[*b*]thiophene-3-carbonitrile (4qa)

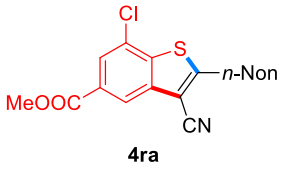
Following the general procedure, the title compound was obtained as white solid, 63 mg, 40% yield. m.p. 52 − 53 °C. (Rf = 0.42, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (s, 1H), 7.00 (s, 1H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.81 (s, 3H), 2.41 (s, 3H), 1.79 – 1.74 (m, 2H), 1.44 – 1.38 (m, 2H), 1.34 – 1.32 (m, 2H), 1.30 – 1.26 (m, 8H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.8, 138.1, 135.5, 133.6, 132.6, 129.3, 120.1, 116.8, 103.5, 32.0, 31.2, 30.4, 29.6, 29.4, 29.2, 22.8, 21.4, 19.9, 14.3.

IR (neat): 2915, 2848, 2213, 1463, 1449, 1379, 1166, 847, 720.

HRMS (ESI-TOF): calculated for [$C_{20}H_{28}NS$ (M + H^+)]: 314.1937, found: 314.1934.



4ra

methyl 7-chloro-3-cyano-2-nonylbenzo[*b*]thiophene-5-carboxylate (4ra)

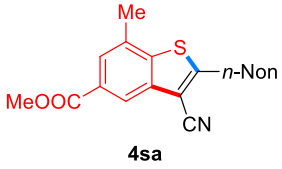
Following the general procedure, the title compound was obtained as white solid, 102 mg, 54% yield. m.p. 66 − 67 °C. (Rf = 0.36, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.89 (s, 1H), 3.98 (s, 3H), 3.12 (t, *J* = 6.0 Hz, 2H), 1.82 – 1.77 (m, 2H), 1.44 – 1.39 (m, 2H), 1.35 – 1.32 (m, 2H), 1.30 – 1.22 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 165.7, 162.1, 140.9, 136.1, 130.8, 128.0, 125.0, 124.6, 113.6, 104.7, 52.9, 32.0, 31.1, 30.7, 29.5, 29.4, 29.3, 29.1, 22.8, 14.3.

IR (neat): 2920, 2850, 2219, 1734, 1432, 1310, 1239, 1082, 774.

HRMS (ESI-TOF): calculated for [$C_{20}H_{25}ClNO_2S$ (M + H^+)]: 378.1289, found: 378.1285.



4sa

methyl 3-cyano-7-methyl-2-nonylbenzo[*b*]thiophene-5-carboxylate (4sa)

Following the general procedure, the title compound was obtained as white solid, 63 mg, 35% yield. m.p. 76 − 77 °C. (Rf = 0.45, eluent: PE/EtOAc = 10/1).

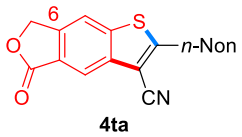
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.87 (s, 1H), 3.97 (s, 3H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H), 1.85 – 1.78 (m, 2H), 1.45 – 1.40 (m, 2H), 1.37 – 1.33 (m, 2H), 1.36– 1.33 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.0, 160.9, 142.0, 137.6, 132.4, 128.5, 126.3, 121.4, 114.1, 105.8, 52.5, 32.0, 31.2, 30.7, 29.5, 29.4, 29.3, 29.2, 22.8, 20.1, 14.2.

IR (neat): 2915, 2846, 2225, 1711, 1451, 1440, 1269,1115, 1082, 767.

HRMS (ESI-TOF): calculated for [$C_{21}H_{28}NO_2S$ (M + H^+)]: 358.1835, found: 358.1835.

Following the general procedure, **4ta** and **4ta'** were obtained from the reaction of sulfoxide **1t** (0.5 mmol) and allenenitrile **2a**.



4ta

2-nonyl-5-oxo-5,7-dihydrothieno[2,3-f]isobenzofuran-3-carbonitrile (4ta)

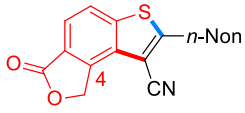
The title compound was obtained as white solid, 65 mg, 38% yield. m.p. 145 − 146 °C. (Rf = 0.29, eluent: PE/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.91 (s, 1H), 5.43 (s, 2H), 3.17 – 3.14 (m, 2H), 1.84 – 1.79 (m, 2H), 1.45 – 1.40 (m, 2H), 1.36 – 1.32 (m, 2H), 1.29 – 1.23 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2, 162.4, 143.3, 142.3, 138.7, 124.2, 119.6, 116.3, 113.4, 105.1, 69.3, 31.9, 31.1, 30.8, 29.5, 29.31, 29.27, 29.1, 22.7, 14.2.

IR (neat): 2920, 2854, 2218, 1751, 1446, 1362, 1068, 1001, 888, 768.

HRMS (ESI-TOF): calculated for [$C_{20}H_{24}NO_2S$ (M + H^+)]: 342.1522, found: 342.1516.



4ta'

7-nonyl-3-oxo-1,3-dihydrothieno[3,2-e]isobenzofuran-8-carbonitrile (4ta')

The title compound was obtained as white solid, 41 mg, 24% yield. m.p. 154 − 155 °C. (Rf = 0.46, eluent: PE/EtOAc = 5/1).

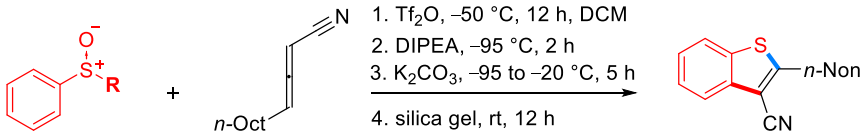
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 5.78 (s, 2H), 3.17 (t, *J* = 7.6 Hz, 2H), 1.85 – 1.80 (m, 2H), 1.46 – 1.41 (m, 2H), 1.37 – 1.33 (m, 2H), 1.30 – 1.24 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 163.4, 142.8, 141.5, 132.0, 124.1, 123.7, 121.7, 114.3, 102.3, 68.6, 31.9, 31.3, 30.6, 29.5, 29.34, 29.28, 29.1, 22.8, 14.2.

IR (neat): 2923, 2849, 2219, 1752, 1451, 1335, 1077, 903, 753, 723.

HRMS (ESI-TOF): calculated for [$C_{20}H_{24}NO_2S$ (M + H^+)]: 342.1522, found: 342.1516.

5 The investigation of "R" group of sulfoxides 1

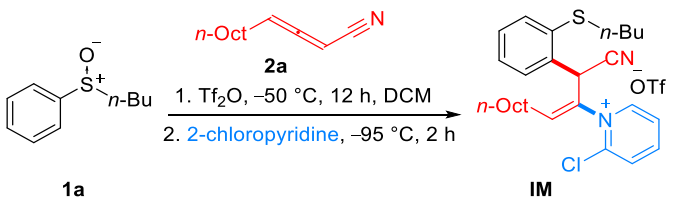


1	**2a**	**4aa**
1u, R = methyl		trace
1v, R = ethyl		64%
1w, R = *i*-Pr		67%

General procedure: To a mixture of aryl sulfoxide (**1**, 0.5 mmol) and allenenitrile (**2a**, 0.75 mmol, 1.5 equiv) in DCM (3 mL) was added Tf_2O (126 μL, 0.75 mmol, 1.5 equiv) at –78 °C under N_2 atomsphere. The reaction mixture was gradually warmed to –50 °C. After stirring for 12 h, the reaction mixture was cooled to –95 °C. A solution of DIPEA (96.9 mg, 0.75 mmol, 1.5 equiv) in DCM (1 mL) was added to the mixture dropwise in 10 min using syringe pump. After stirring at –95 °C for 2 h, K_2CO_3 (345.5 mg, 5.0 equiv) was added, and the resulting reaction mixture was warm up to –20 °C and kept stirring for 5 h. The mixture was then filtrated and concentrated under vacuum. To the obtained residue was added DCM (3 mL) and silica gel (1 g). The mixture was stirred for 12 h at rt. After that, the mixture was filtrated and concentrated under vacuum, and purified obtained by silica gel flash chromatography to afford compound **4aa** as colorless oil. (Rf = 0.36, eluent: PE/EtOAc = 40/1).

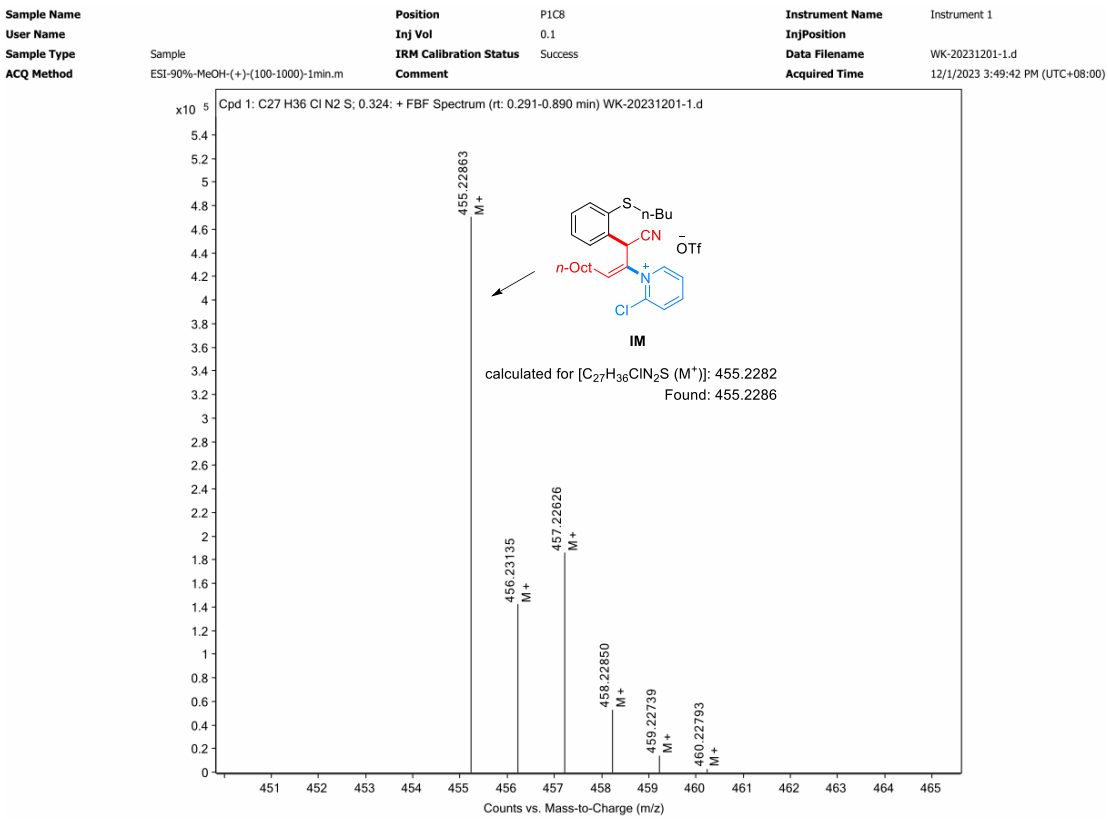
For the characterization of **4aa,** see S13.

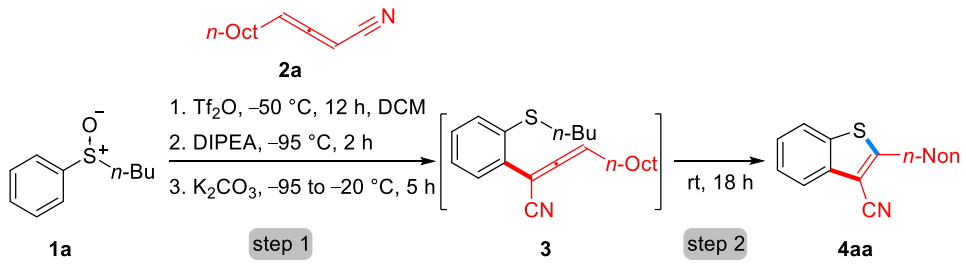
6 Mechanistic studies



To a mixture of aryl sulfoxide (**1a**, 0.5 mmol) and allenenitrile (**2a**, 0.75 mmol, 1.5 equiv) in DCM (3 mL) was added Tf_2O (126 μL, 0.75 mmol, 1.5 equiv) at –78 °C under N_2 atomsphere. The reaction mixture was gradually warmed to –50 °C. After stirring for 12 h, the reaction mixture was cooled to –95 °C. A solution of 2-chloropyridine (85.2 mg, 0.75 mmol, 1.5 equiv) in DCM (1 mL) was added to the mixture dropwise in 10 min using syringe pump. After stirring at –95 °C for 2 h, the sample was detected by ESI-MS.

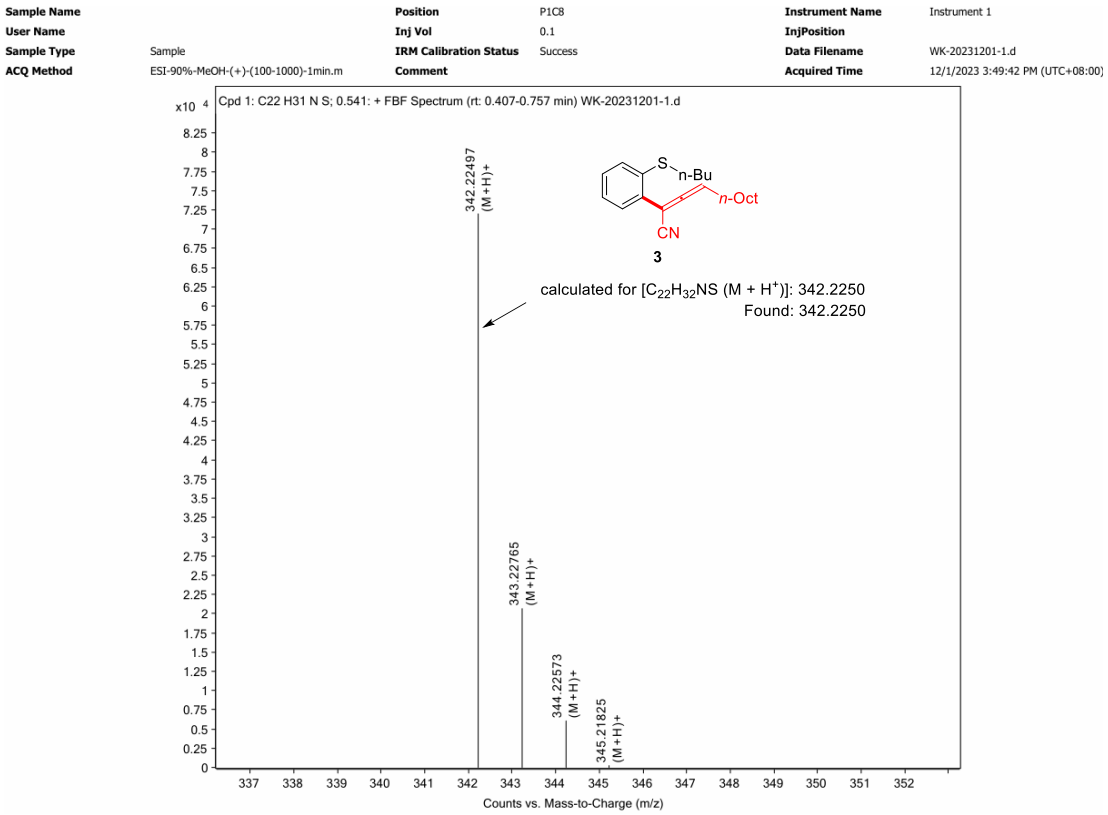
The MS spectra of key intermediated **IM** is given below.



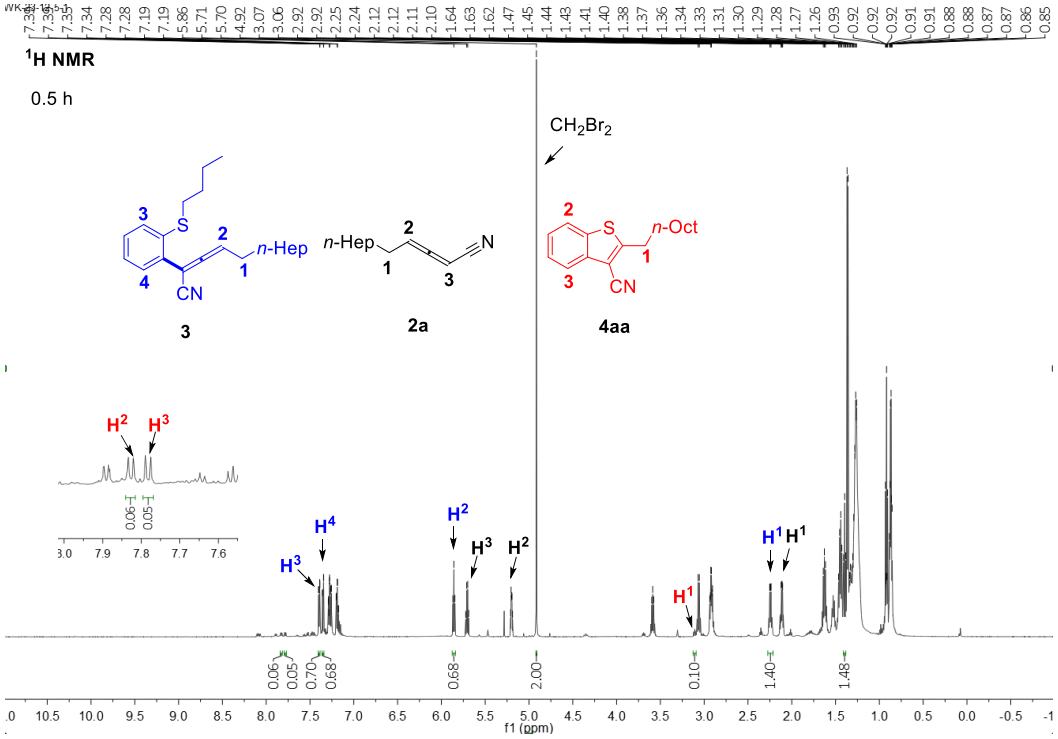


Step1: To a mixture of aryl sulfoxide (**1a**, 0.5 mmol) and allenenitrile (**2a**, 0.75 mmol, 1.5 equiv) in DCM (3 mL) was added Tf_2O (126 μL, 0.75 mmol, 1.5 equiv) at –78 °C under N_2 atomsphere. The reaction mixture was gradually warmed to –50 °C. After stirring for 12 h, the reaction mixture was cooled to –95 °C. A solution of DIPEA (96.9 mg, 0.75 mmol, 1.5 equiv) in DCM (1 mL) was added to the mixture dropwise in 10 min using syringe pump. After stirring at –95 °C for 2 h, K_2CO_3 (345.5 mg, 5.0 equiv) was added to the mixture. The resulted mixture was warm up to –20 °C and kept stirring for 5 h. After that, the mixture was filtrated and concentrated under vacuum. The obtained residue was detected by ESI-MS and NMR.

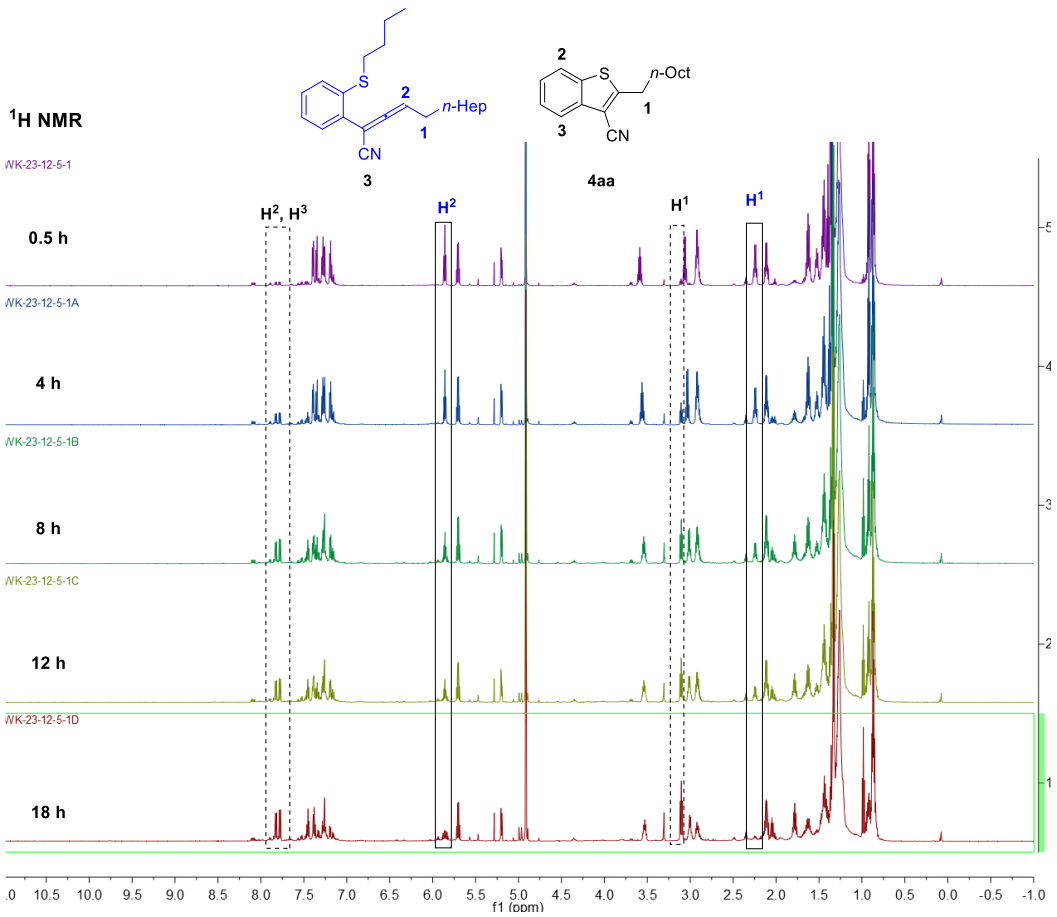
The MS spectra of compound **3** is given below.



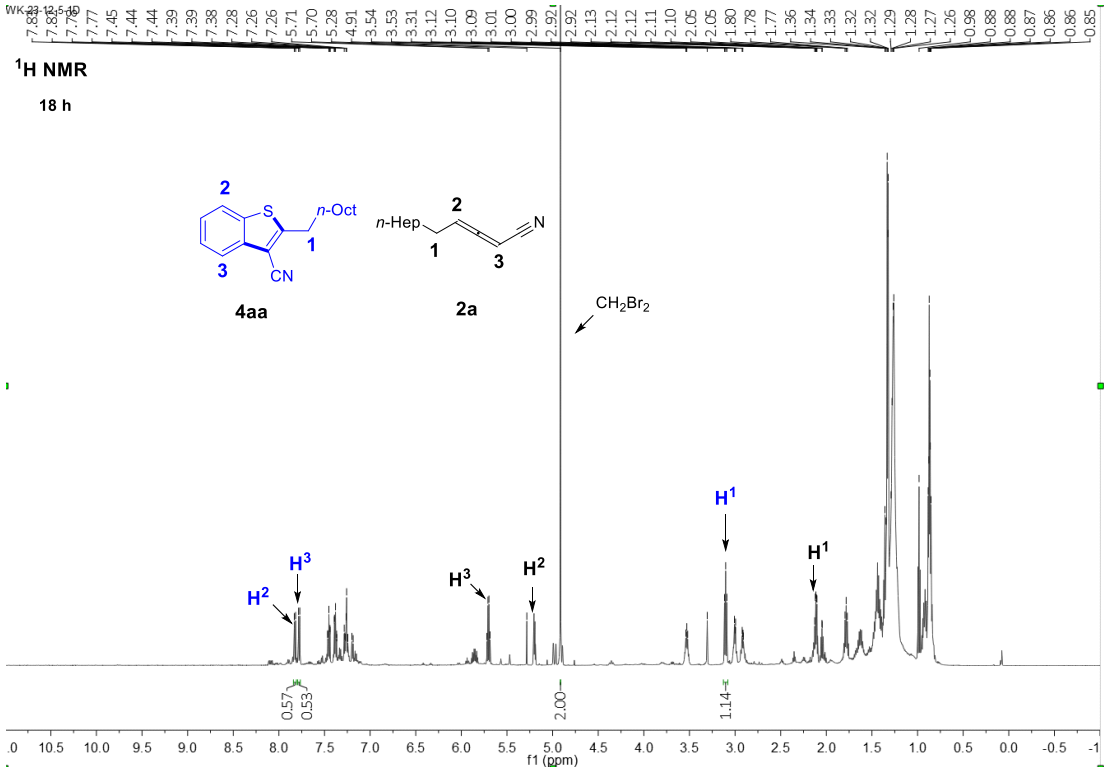
The ^{1}H NMR spectrum of the mixture provided below indicates that step 1 yielded compound **3** (68%) and **4aa** (5%).



Step 2: The sample obtained from step 1 was measured by NMR spectroscopy at 0.5 h, 4 h, 8 h, 12 h and 18 h, respectively. The in situ NMR indicated that the rearrangement product **3** could undergo cyclization and isomerization to form the final product **4aa** (57%) gradually. However, *ortho*-allenic phenyl sulfide **3** partially deteriorated in NMR tube, resulting in **4aa** with low efficiency.

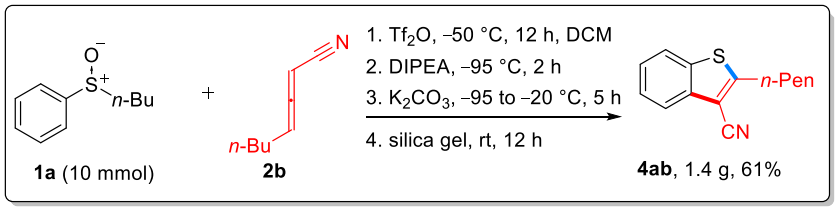


The ^{1}H NMR given below indicates that, after 18 hours, **4aa** was produced in 57% yield.



7 Gram-scale reaction and elaboration of product 4ab

7.1 Gram-scale reaction

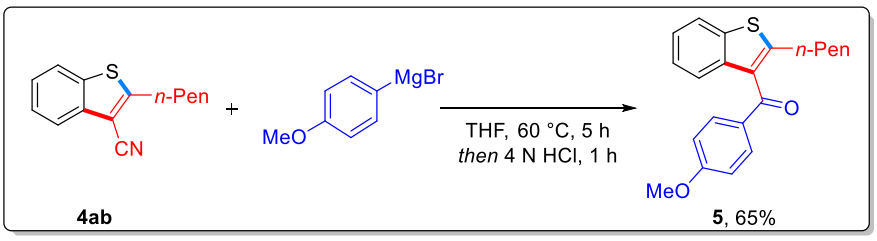


To a mixture of aryl sulfoxide (**1a**, 10 mmol) and allenenitrile (**2b**, 15 mmol, 1.5 equiv) in DCM (30 mL) was added Tf_2O (2.52 mL, 15 mmol, 1.5 equiv) at –78 °C under N_2 atomsphere. The reaction mixture was gradually warmed to –50 °C. After stirring for 12 h, the reaction mixture was cooled to –95 °C. A solution of DIPEA (1.9 g, 15mmol, 1.5 equiv) in DCM (5 mL) was added to the mixture dropwise in 1 h using syringe pump. After stirring at –95 °C for 2 h, K_2CO_3 (6.9 g, 50 mmol, 5.0 equiv) was added, and the resulting reaction mixture was warm up to –20 °C and kept stirring for 5 h. The mixture was then filtrated and concentrated under vacuum. To the obtained residue in DCM (10 mL) was added silica gel (4 g) and stirring for 12 h at rt. After that, the mixture was filtrated and concentrated under vacuum. The obtained residue was further purified obtained by silica gel flash chromatography to give compound **4ab** in 61% yield (1.4 g) as colorless oil.

Note: Tf_2O and the solution of DIPEA in DCM were injected on the inner wall of Schlenk bottle lying a few centimeters higher than the reaction mixture. So that, the chemicals (Tf_2O and DIPEA) could be sufficiently cooled prior to their flowing into the reaction mixture.

7.2 Elaboration of product 4ab

(4-methoxyphenyl)(2-pentylbenzo[*b*]thiophen-3-yl)methanone (5)



To a solution of **4ab** (115 mg, 0.5 mmol) in THF (1 mL) were added (4-methoxyphenyl)magnesium bromide (1.1 equiv) at rt. The reaction was warmed to 60 °C and stirred for 5 h. Then to the mixture was added 4 N HCl dropwise. After stirring for another 1 h, the mixture was neutralized with sat. aq. $NaHCO_3$, extracted with EtOAc. The combined organic layer was dried over Na_2SO_4 and

concentrated. The resulting residue was further purified by column chromatography on silica gel to afford compound **5** in 65% yield (110 mg) as colorless oil. (Rf = 0.29 eluent: Petroleum ether /EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 – 7.82 (m, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 6.94 – 6.91 (m, 2H), 3.88 (s, 3H), 2.85 (t, *J* = 7.7 Hz, 2H), 1.70 – 1.66 (m, 2H), 1.27 – 1.25 (m, 4H), 0.82 (t, *J* = 7.0 Hz, 3H).

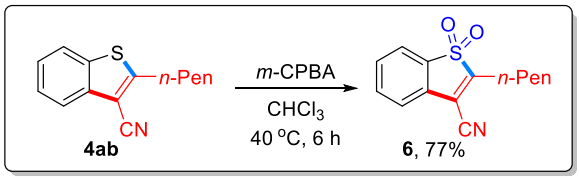
^{13}C NMR (151 MHz, $CDCl_3$): δ 192.6, 164.0, 150.2, 139.2, 138.1, 132.4, 131.5, 130.0, 124.6, 124.2, 123.3, 122.1, 114.0, 55.7, 31.5, 31.4, 29. 8, 22.4, 14.0.

IR (neat): 2927, 1617, 1597, 1258, 1163, 1024, 842, 730, 606.

HRMS (ESI-TOF): calculated for [$C_{21}H_{22}O_2SNa$ ($M + Na^+$)]: 361.1233, found: 361.1234.

Compound **5** is a known compound and the NMR data is consistent with the reported spectra[12].

2-pentylbenzo[*b*]thiophene-3-carbonitrile 1,1-dioxide (6)



To a solution of **4ab** (115 mg, 0.5 mmol) in $CHCl_3$ (1.5 mL) was added *m*-CPBA (224 mg, 2.2 equiv). The resulting solution was stirred at 40 °C for 6 h. After completion of the reaction, the reaction was quenched with sat. aq. $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel to afford compound **6** in 77% yield (100 mg) as colorless oil. (Rf = 0.4, eluent: Petroleum ether /EtOAc = 3/1).

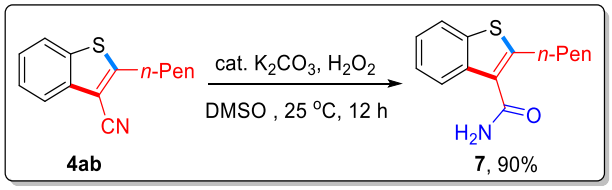
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.61 – 7.58 (m, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 2.86 – 2.82 (t, *J* = 7.6 Hz, 2H), 1.91 – 1.86 (m, 2H), 1.47 – 1.37 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.2, 135.0, 134.6, 131.2, 127.5, 123.3, 122.2, 112.2, 111.2, 31.5, 27.2, 25.9, 22.2, 14.0.

IR (neat): 2956, 1452, 1313, 1153, 1120, 761, 611, 559.

HRMS (ESI-TOF): calculated for [$C_{14}H_{16}NO_2S$ (M + H^+)]: 262.0896, found: 262.0896.

2-pentylbenzo[*b*]thiophene-3-carboxamide (7)



To a solution of **4ab** (115 mg, 0.5 mmol) in DMSO (1 mL) were sequentially added H_2O_2 (30% aq., 140 µL) and K_2CO_3 (14 mg, 0.1 mmol) at 25 °C. After stirring for 12 h, the mixture was diluted with H_2O, extracted with DCM and dried with Na_2SO_4. Then the mixture was filtered and concentrated under vacuum. The resulting residue was further purified by column chromatography on silica gel to afford compound **7** in 90% yield (99 mg) as white solid, m.p. 167 − 168 °C (Rf = 0.30, eluent: PE/EtOAc = 2/1)

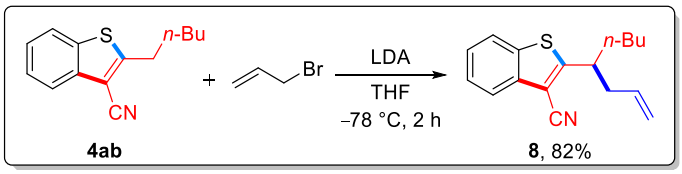
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.33 – 7.31 (m, 1H), 6.08 (brs, 1H), 5.82 (brs, 1H), 3.13 (t, *J* = 7.6 Hz, 2H), 1.80 – 1.75 (m, 2H), 1.42 – 1.33 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.0, 150.6, 138.2, 137.9, 127.5, 125.0, 124.4, 122.5, 122.3, 31.6, 31.5, 29.6, 22.5, 14.1.

IR (neat): 3355, 3172, 1643, 1613, 1432, 735, 717, 678.

HRMS (ESI-TOF): calculated for [$C_{14}H_{18}NOS$ (M + H^+)]: 248.1104, found: 248.1104.

2-(oct-1-en-4-yl)benzo[*b*]thiophene-3-carbonitrile (8)



To the solution of (*i*-Pr)$_2$NH (84 µL, 0.6 mmol) in THF (1.5 mL) was added *n*-BuLi (1.6 M, 0.37 mL) slowly at –78 °C. After stirring for 10 min, **4ab** (115 mg, 0.5 mmol) was added dropwise to the mixture at –78 °C. After 30 min, allyl bromide (50 µL, 0.6 mmol) was added. After stirring for 1 h, the mixture was quenched with NH_4Cl (sat.), extracted with EtOAc and dried over Na_2SO_4. Then the mixture was filtered and concentrated under vacuum. The

resulting residue was further purified by column chromatography on silica gel to afford compound **8** in 82% (110 mg) as colorless oil. (Rf = 0.36, eluent: Petroleum ether /EtOAc = 40/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.42 – 7.38 (m, 1H), 5.78 – 5.68 (m, 1H), 5.06 – 4.97 (m, 2H), 3.49 – 3.39 (m, 1H), 2.60 – 2.53 (m, 1H), 2.49 – 2.39 (m, 1H), 1.90 – 1.83 (m, 1H), 1.73 – 1.63 (m, 1H), 1.37 – 1.21 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.3, 137.6, 137.3, 135.0, 125.8, 125.6, 122.7, 122.2, 117.8, 114.7, 104.8, 42.3, 42.0, 36.9, 29.6, 22.6, 14.0.

IR (neat): 2955, 2927, 2856, 2363, 2221, 1641, 1524, 1460, 1437, 991, 916, 756.

HRMS (ESI-TOF): calculated for [$C_{17}H_{19}NSNa$ ($M + Na^+$)]: 292.1130, found: 292.1132.

8 References

[1] M. Chen, Y. Liang, T. Dong, Z.-X. Wang and B. Peng. *Angew. Chem. Int. Ed*., 2021, **60**, 2339.

[2] M. Hu, Y. Liu, Y. Liang, T. Dong, L. Kong, M. Bao, Z.-X. Wang and B. Peng. *Nat. Commun*., 2022, **13**, 4719.

[3] L. Zhang, J.-N. He, Y. Liang, M. Hu, L. Shang, X. Huang, L. Kong, Z.-X. Wang and B. Peng. *Angew. Chem. Int. Ed*., 2019, **58**, 5316.

[4] Z.-Y. Tian and C-P. Zhang. *Chem. Commun*., 2019, **55**, 11936.

[5] S. Ruppenthal and R. Brueckner, *J. Org. Chem*., 2015, **80**, 897.

[6] H.-J. Xu, Y.-C. Lin, X. Wan, C.-Y. Yang and Y.-S. Feng, *Tetrahedron.,* 2010, **66**, 8823.

[7] S. Ma, H. Xie, G. Wang, J. Zhang and Z. Shi, *Synthesis.*, 2001, 713.

[8] P. M. Greaves, S. R. Landor and D. R. J. Laws, *J. Chem. Soc. C*., 1968, 291.

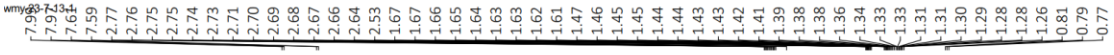
[9] Q. Liu, J. Zheng, X. Zhang and S. Ma, *Nat. Commun*., 2022, **13**, 3302.

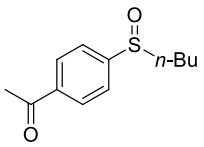
[10] F.-D. Fu, Z.-C. Shu, G.-F. He, J.-C. Bai, L.-Q. Lu and W.-J. Xiao, *Org. Chem. Front.*, 2022, **9**, 5259.

[11] Y.-F. Ao, D.-X. Wang, L. Zhao and M.-X. Wang, *J. Org. Chem*., 2014, **79**, 3103.

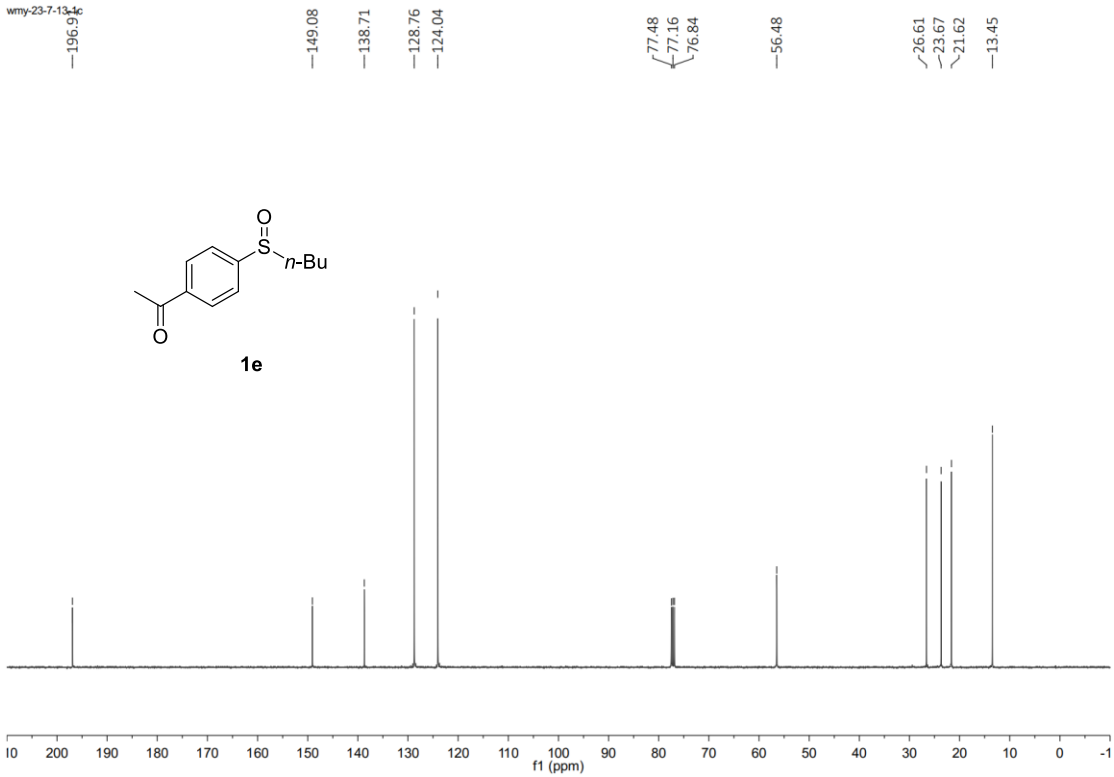
[12] J. Romero-Parra, J. Mella-Raipán, V. Palmieri, M. Allará, M. J. Torres, H. Pessoa-Mahana, P. Iturriaga-Vásquez, R. Escobar, M. Faúndez, V. Di Marzo, and C. D. Pessoa-Mahana, *Eur. J. Med. Chem*., 2016, **124**, 17.

9 NMR spectra

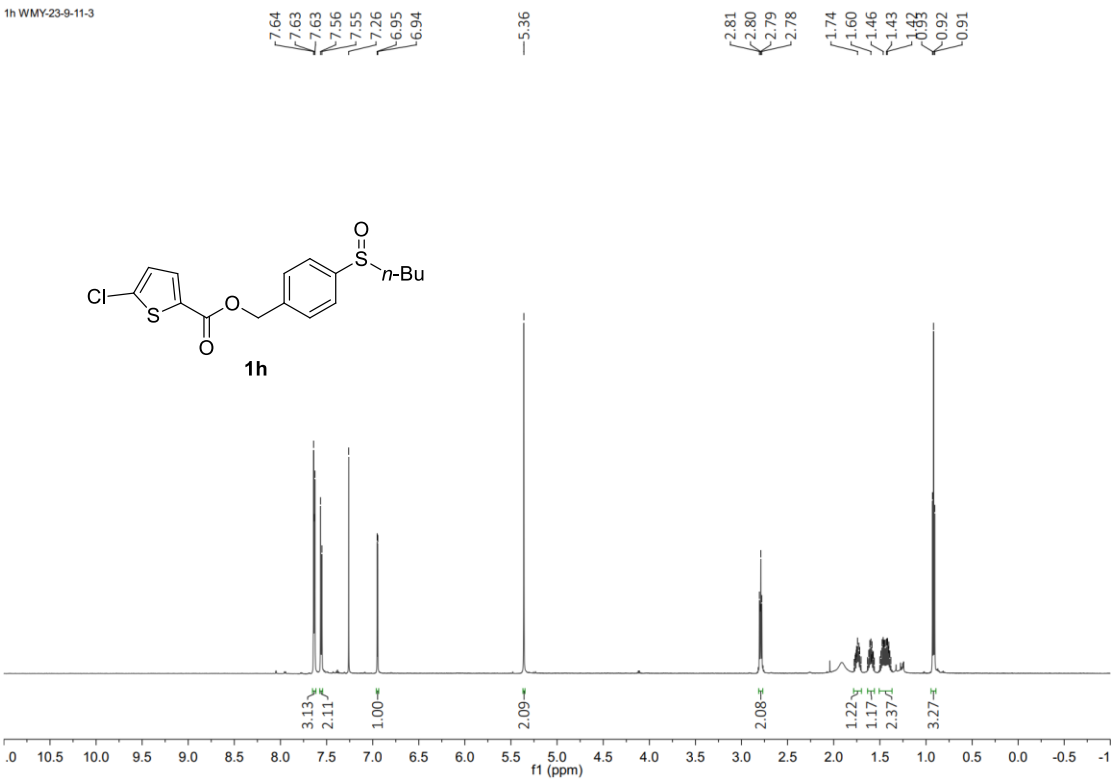


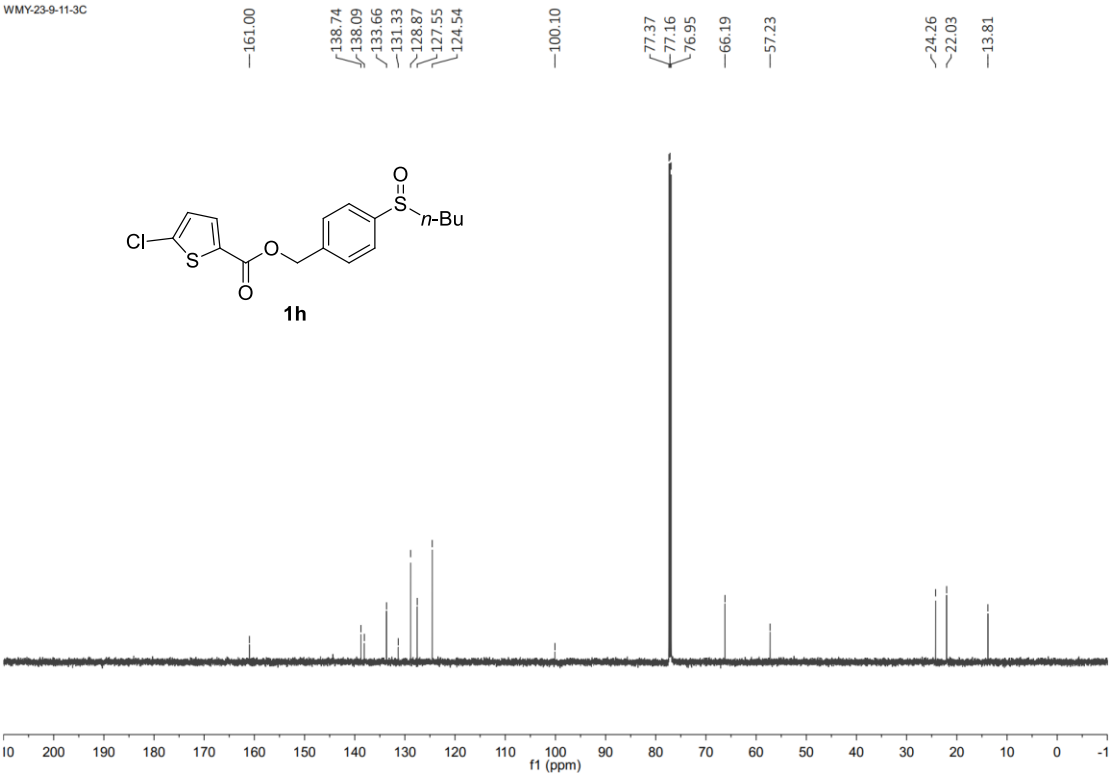


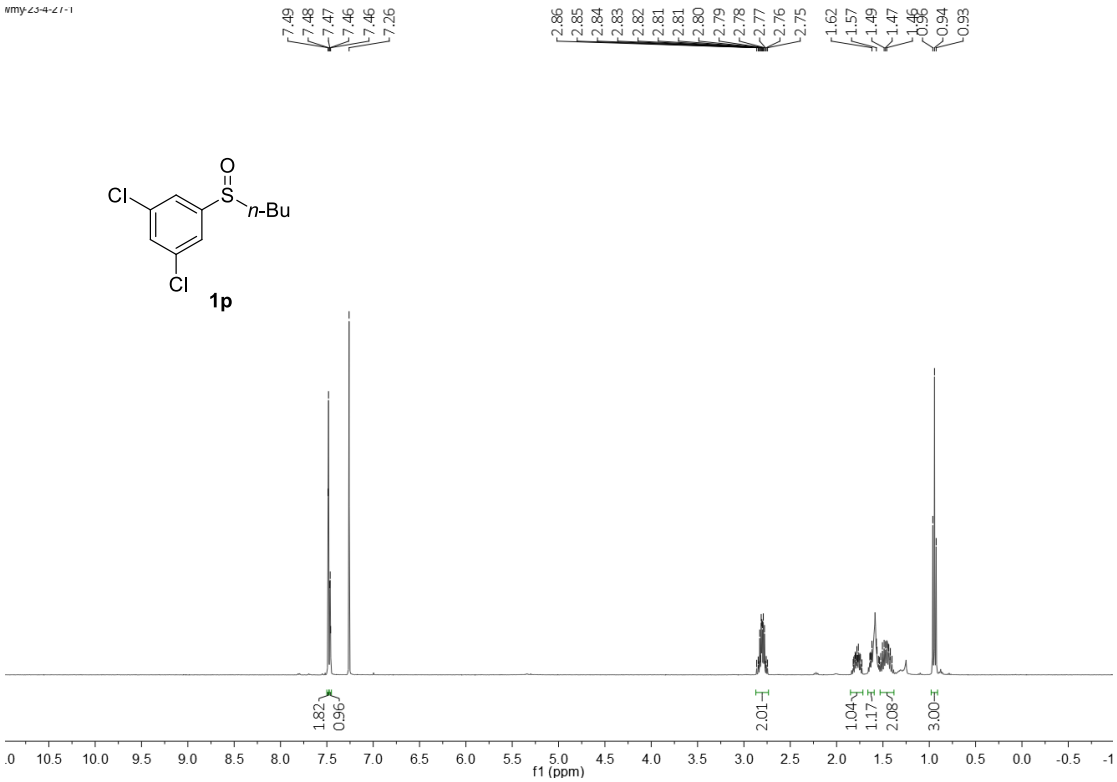
1e

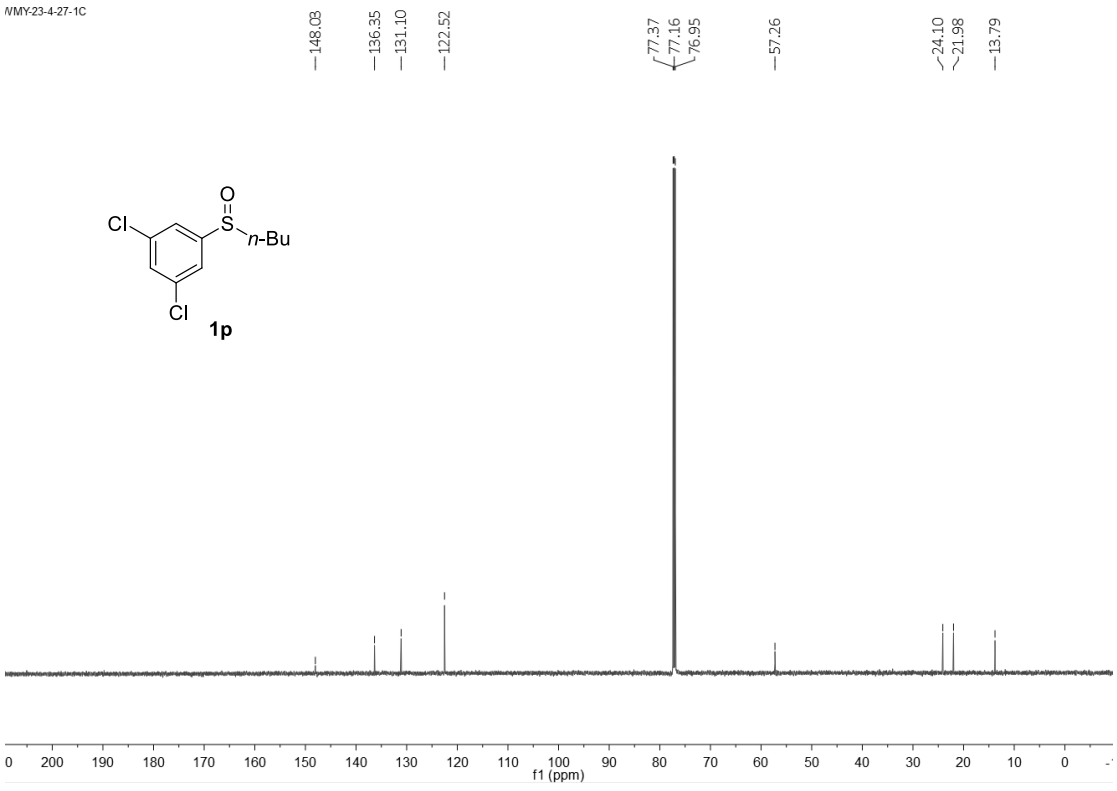


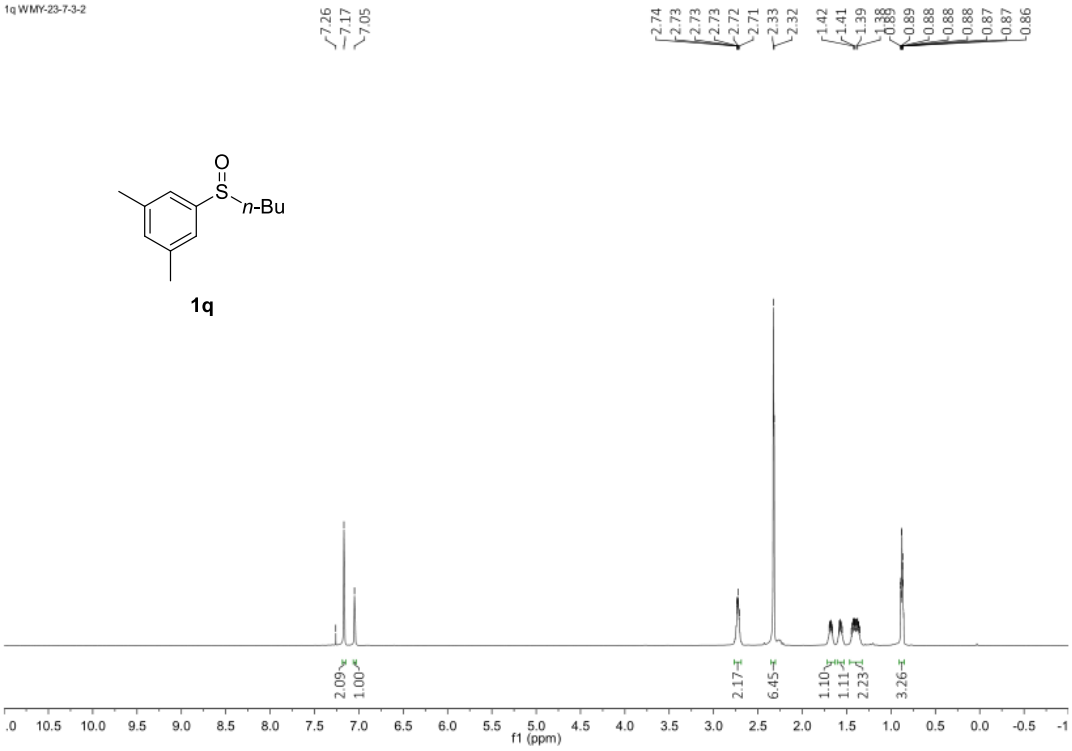
1e


1h WMY-23-9-11-3
7.64
7.63
7.63
7.56
7.55
7.26
6.95
6.94
5.36
2.81
2.80
2.79
2.78
1.74
1.60
1.46
1.43
0.93
0.92
0.91
Cl
S
O
O
O
S
n-Bu
1h
3.13
2.11
1.00
2.09
2.08
1.22
1.17
2.37
3.27
f1 (ppm)

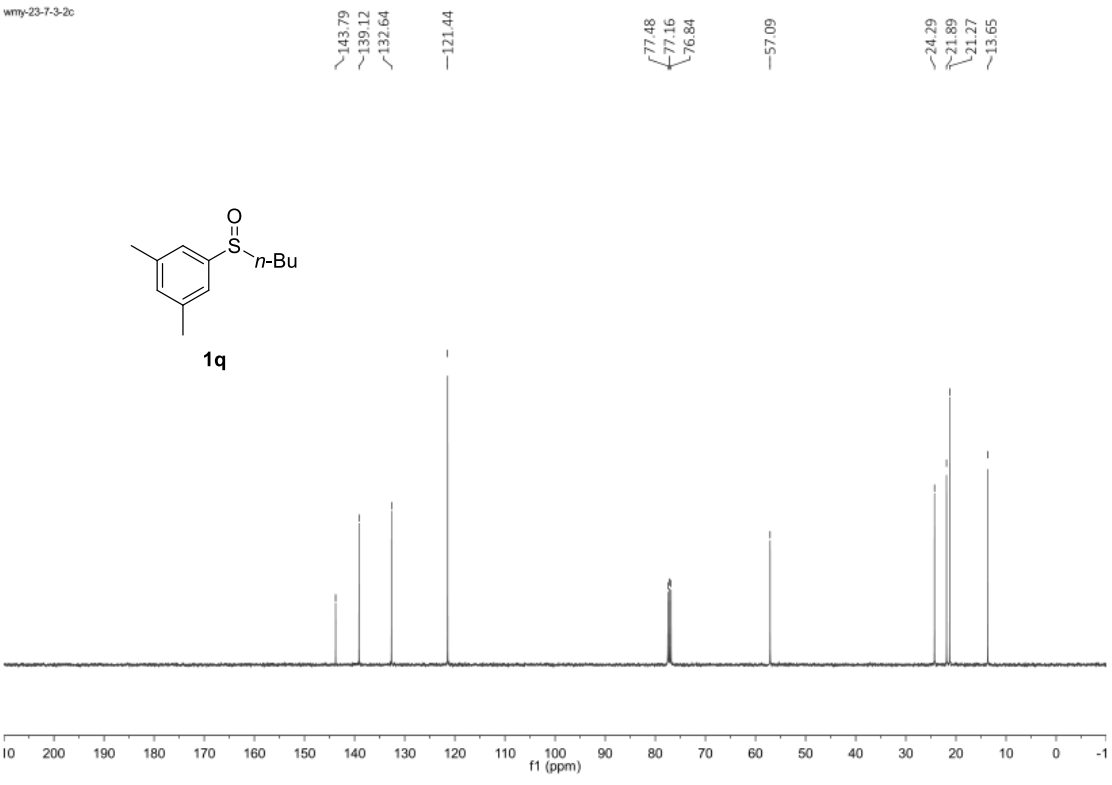

WMY-23-9-11-3C
161.00
138.74
138.09
133.66
131.33
128.87
127.55
124.54
100.10
77.37
77.16
76.95
66.19
57.23
24.26
22.03
13.81
Cl
S
O
O
O
S
n-Bu
1h
f1 (ppm)


7.49
7.48
7.47
7.46
7.46
7.26
2.86
2.85
2.84
2.83
2.82
2.81
2.81
2.80
2.79
2.78
2.77
2.76
2.75
1.62
1.57
1.49
1.47
0.96
0.94
0.93
Cl
O
S
n-Bu
Cl
1p
1.82
0.96
2.01
1.04
1.17
2.08
3.00
f1 (ppm)

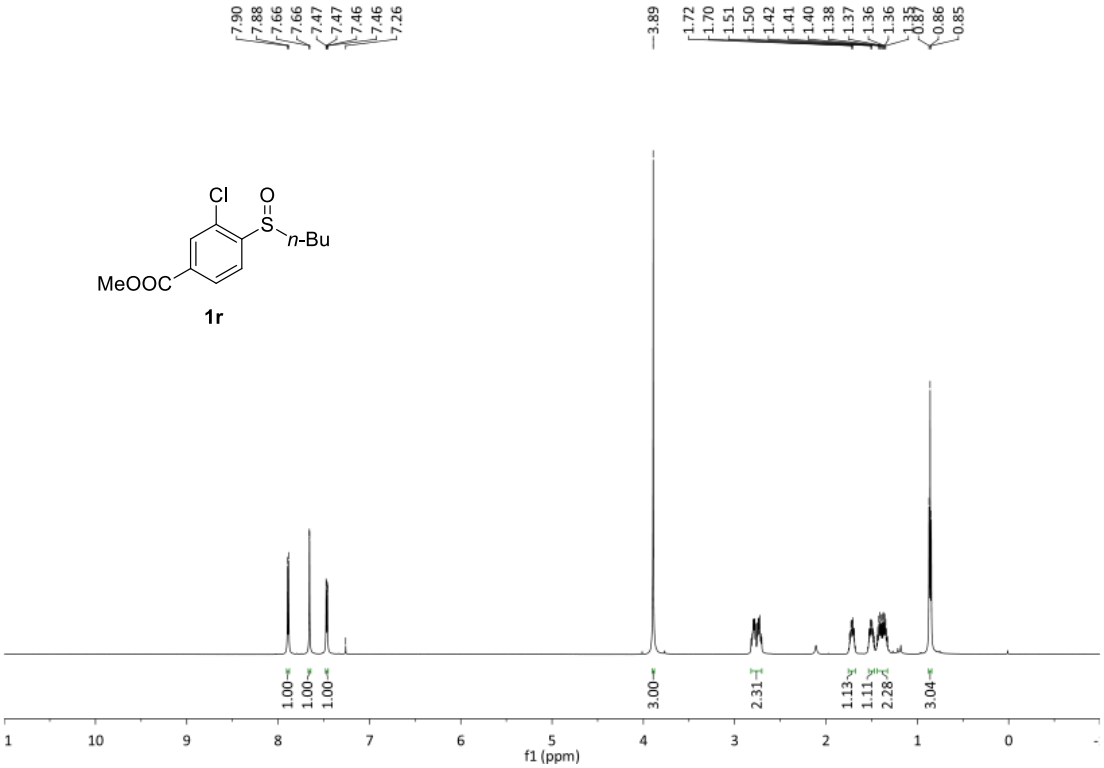

148.03
136.35
131.10
122.52
77.37
77.16
76.95
57.26
24.10
21.98
13.79
Cl
O
S
n-Bu
Cl
1p
f1 (ppm)

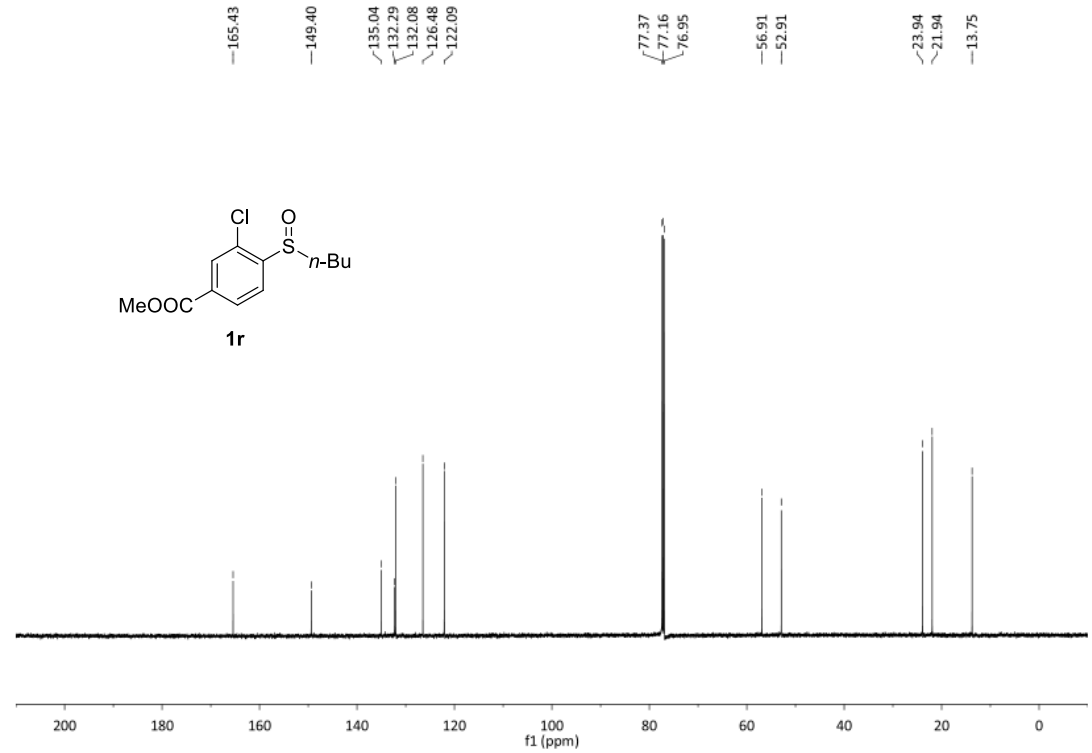

1q WMY-23-7-3-2
7.26
7.17
7.05
2.74
2.73
2.73
2.73
2.72
2.71
2.33
2.32
1.42
1.41
1.39
0.89
0.89
0.88
0.88
0.88
0.87
0.87
0.86
O
S
n-Bu
2.09
1.00
2.17
6.45
1.10
1.11
2.23
3.26
f1 (ppm)

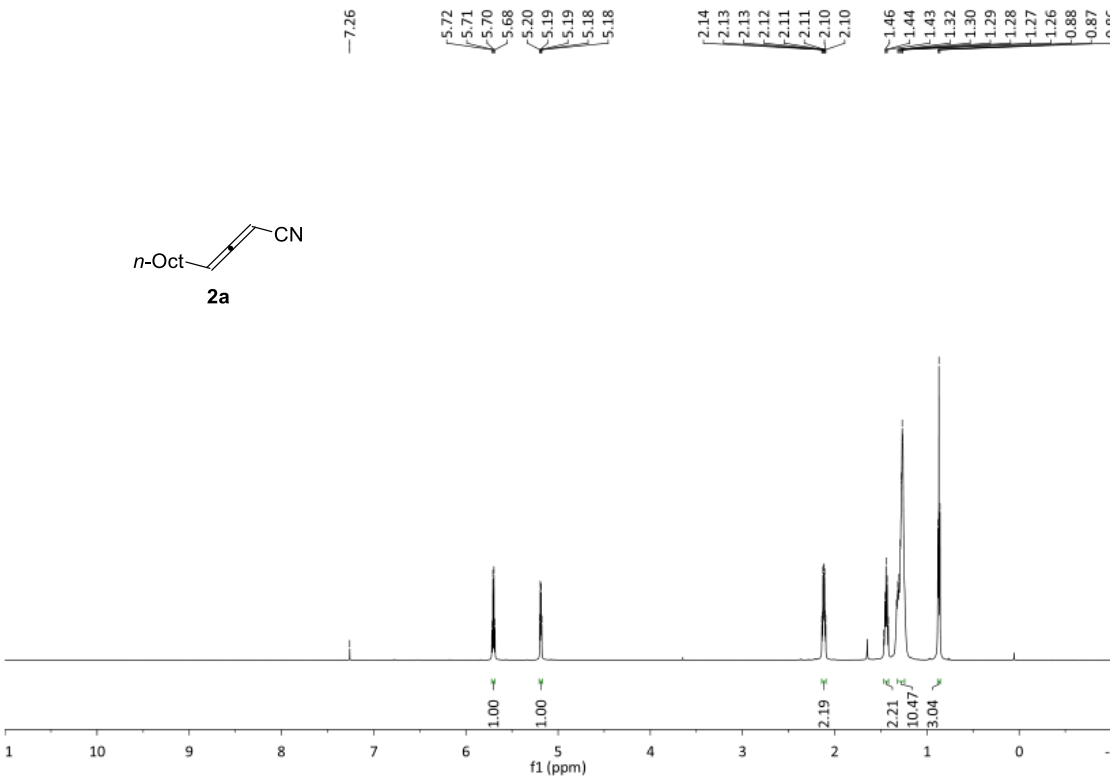
1q

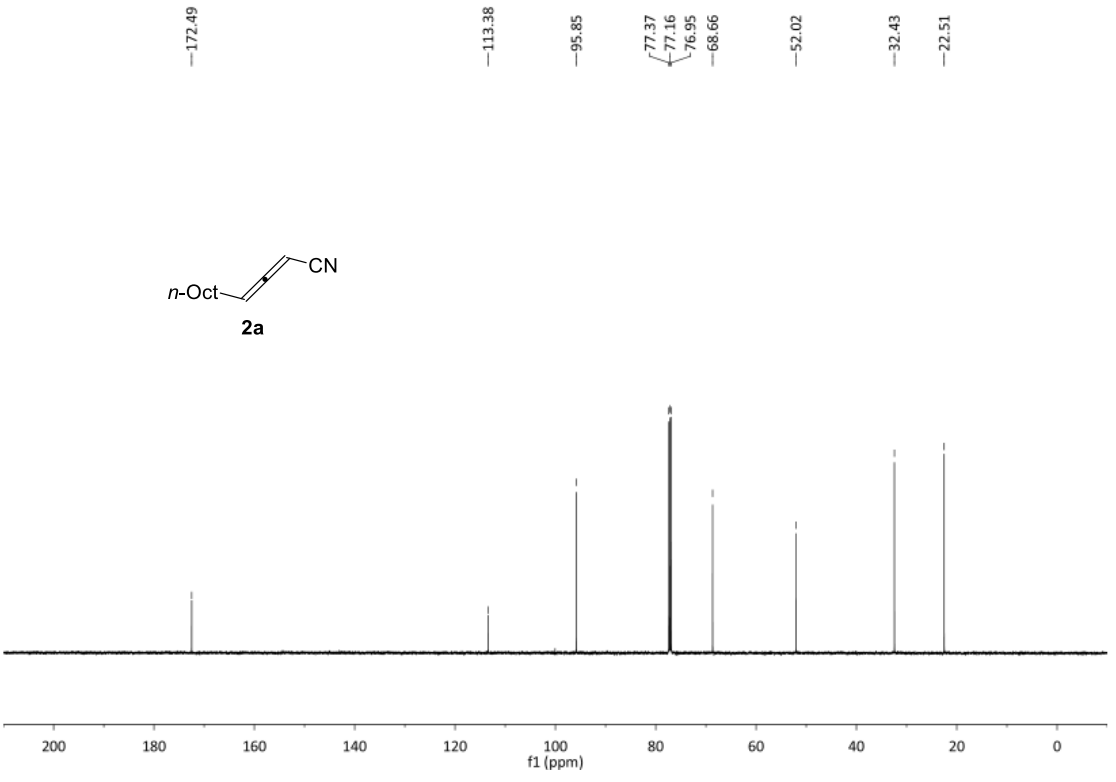

wmy-23-7-3-2c
143.79
139.12
132.64
121.44
77.48
77.16
76.84
57.09
24.29
21.89
21.27
13.65
O
S
n-Bu
f1 (ppm)

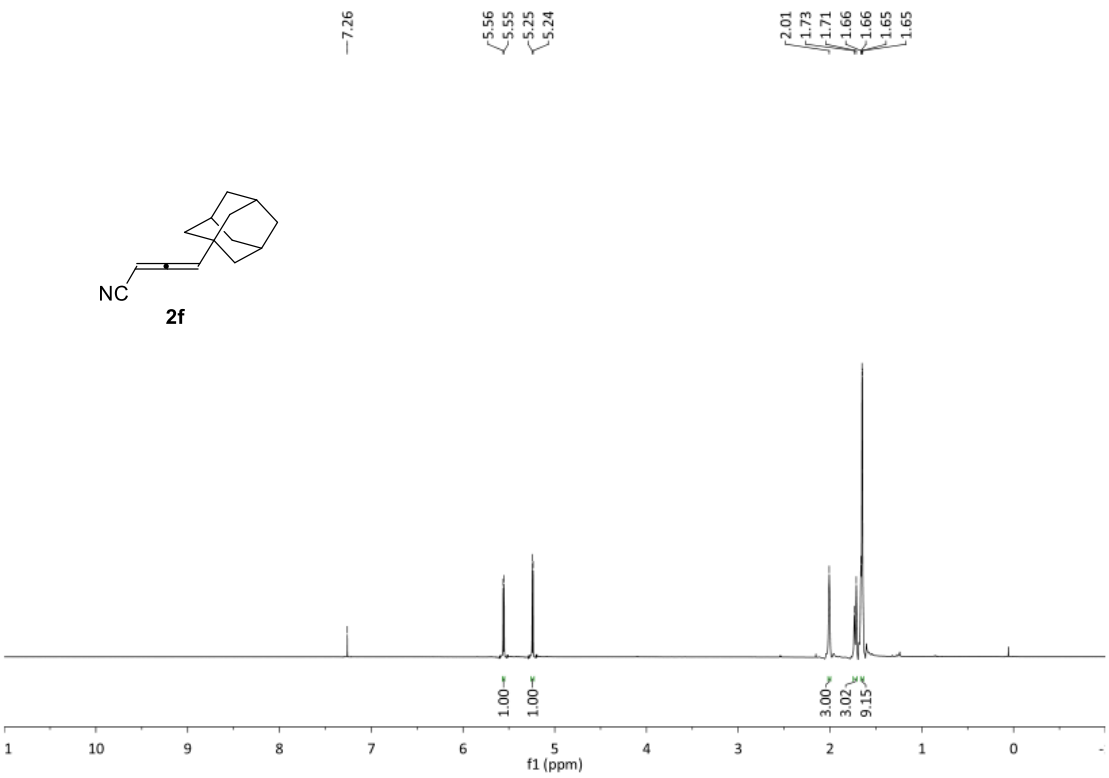
1q

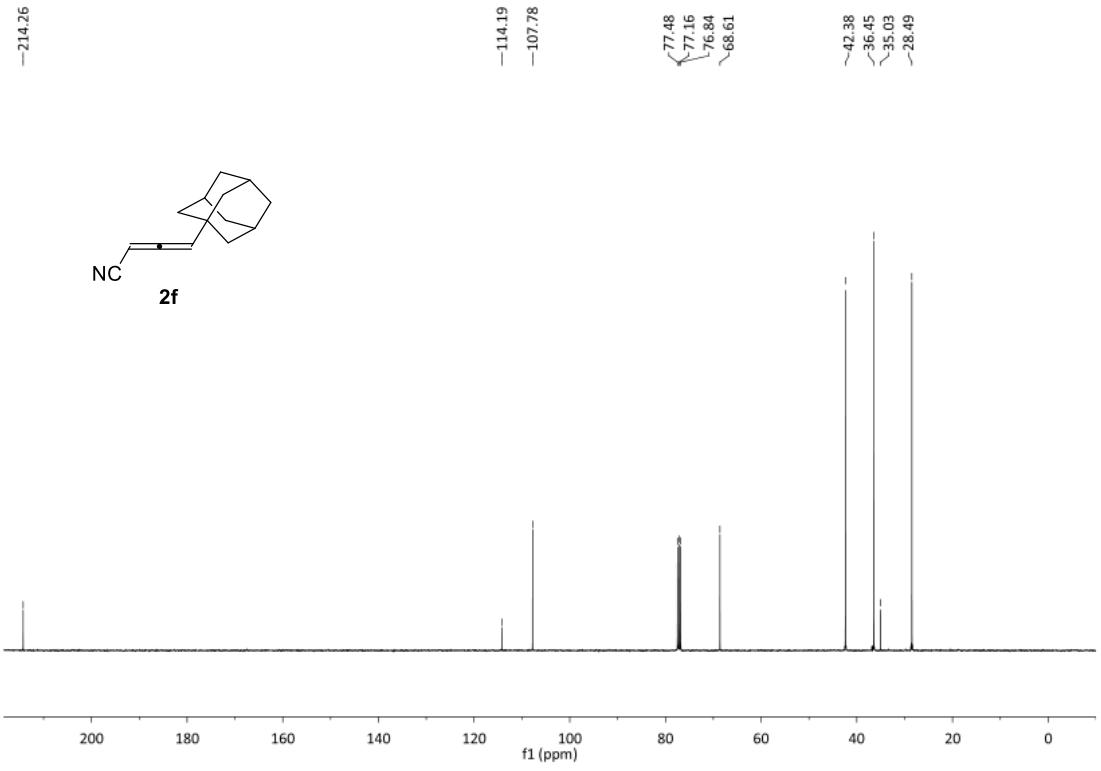

7.90
7.88
7.66
7.66
7.47
7.47
7.46
7.46
7.26
3.89
1.72
1.70
1.51
1.50
1.42
1.41
1.40
1.38
1.37
1.36
1.36
0.87
0.86
0.85
Cl
O
S
n-Bu
MeOOC
1r
1.00
1.00
1.00
3.00
2.31
1.13
1.11
2.28
3.04
f1 (ppm)


165.43
149.40
135.04
132.29
132.08
126.48
122.09
77.37
77.16
76.95
56.91
52.91
23.94
21.94
13.75
Cl
O
S
n-Bu
MeOOC
1r
f1 (ppm)

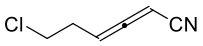

7.26
5.72
5.71
5.70
5.68
5.20
5.19
5.19
5.18
5.18
2.14
2.13
2.13
2.12
2.11
2.11
2.10
2.10
1.46
1.44
1.43
1.32
1.30
1.29
1.28
1.27
1.26
0.88
0.87
n-Oct
CN
2a
1.00
1.00
2.19
2.21
10.47
3.04
f1 (ppm)


172.49
113.38
95.85
77.37
77.16
76.95
68.66
52.02
32.43
22.51
n-Oct
CN
2a
f1 (ppm)

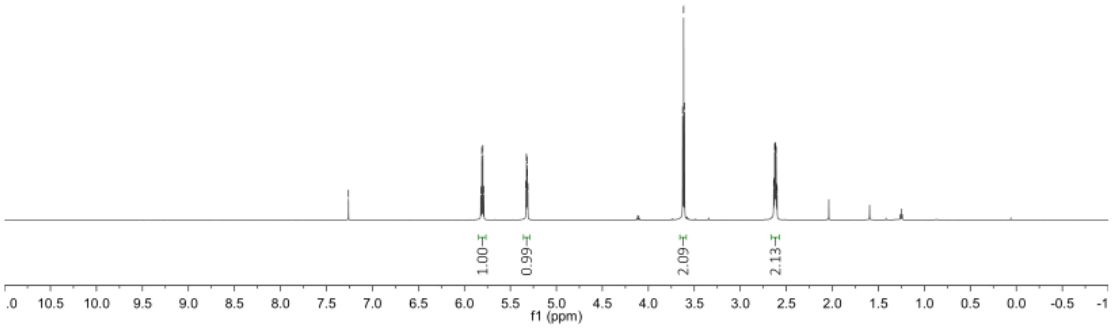

7.26
5.56
5.55
5.25
5.24
2.01
1.73
1.71
1.66
1.66
1.65
1.65
NC
2f
1.00
1.00
3.00
3.02
9.15
f1 (ppm)


214.26
114.19
107.78
77.48
77.16
76.84
68.61
42.38
36.45
35.03
28.49
NC
2f
f1 (ppm)

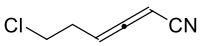

PWJ-201218-C
7.26
5.82
5.81
5.80
5.79
5.33
5.33
5.32
5.31
5.31
3.63
3.62
3.61
2.64
2.63
2.63
2.62
2.62
2.61
2.61
2.60


Cl
CN

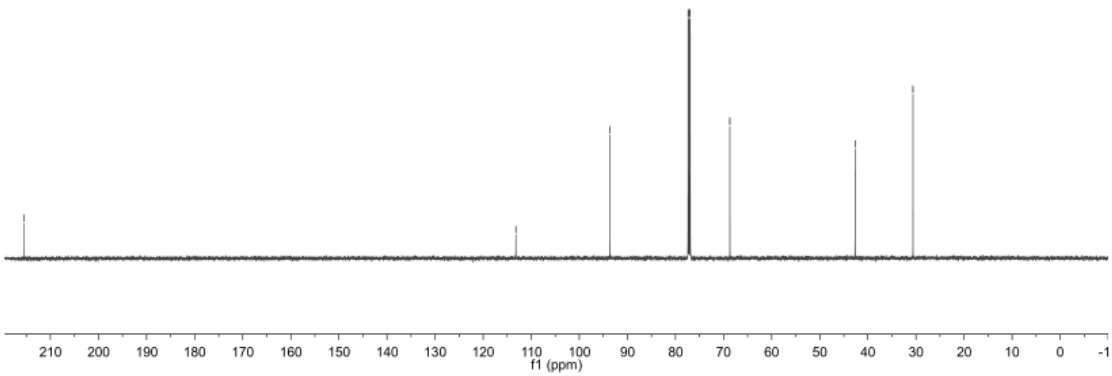
2g

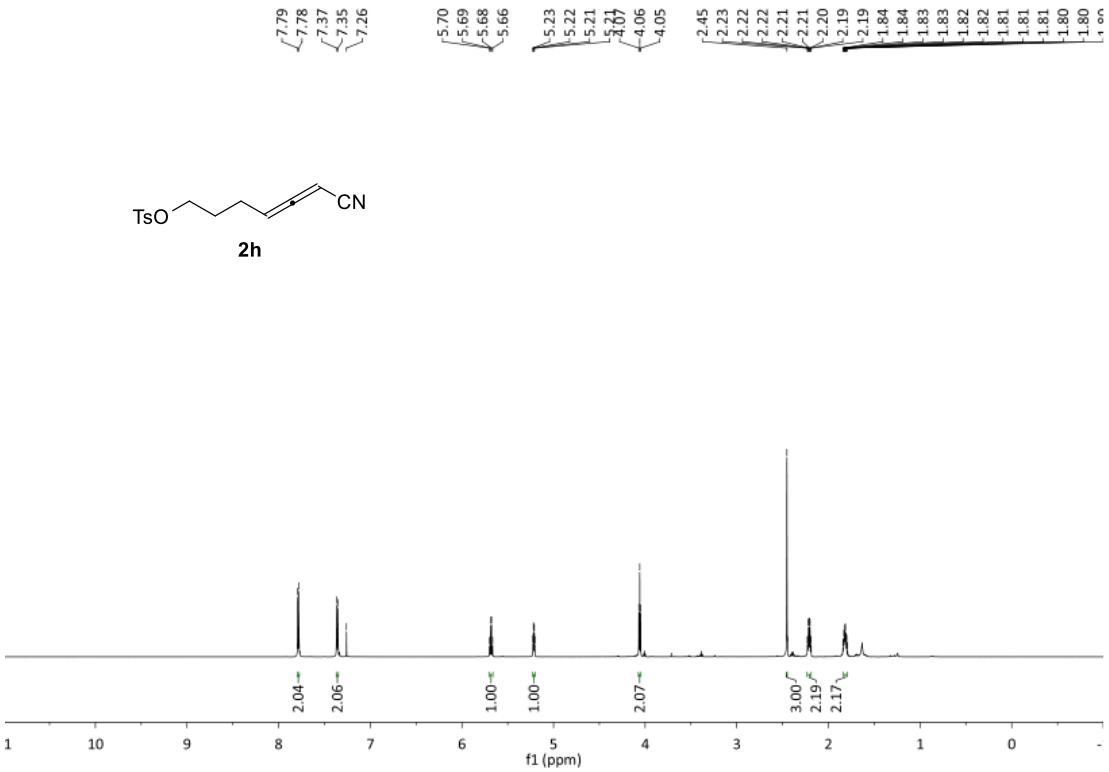

1.00
0.99
2.09
2.13
f1 (ppm)

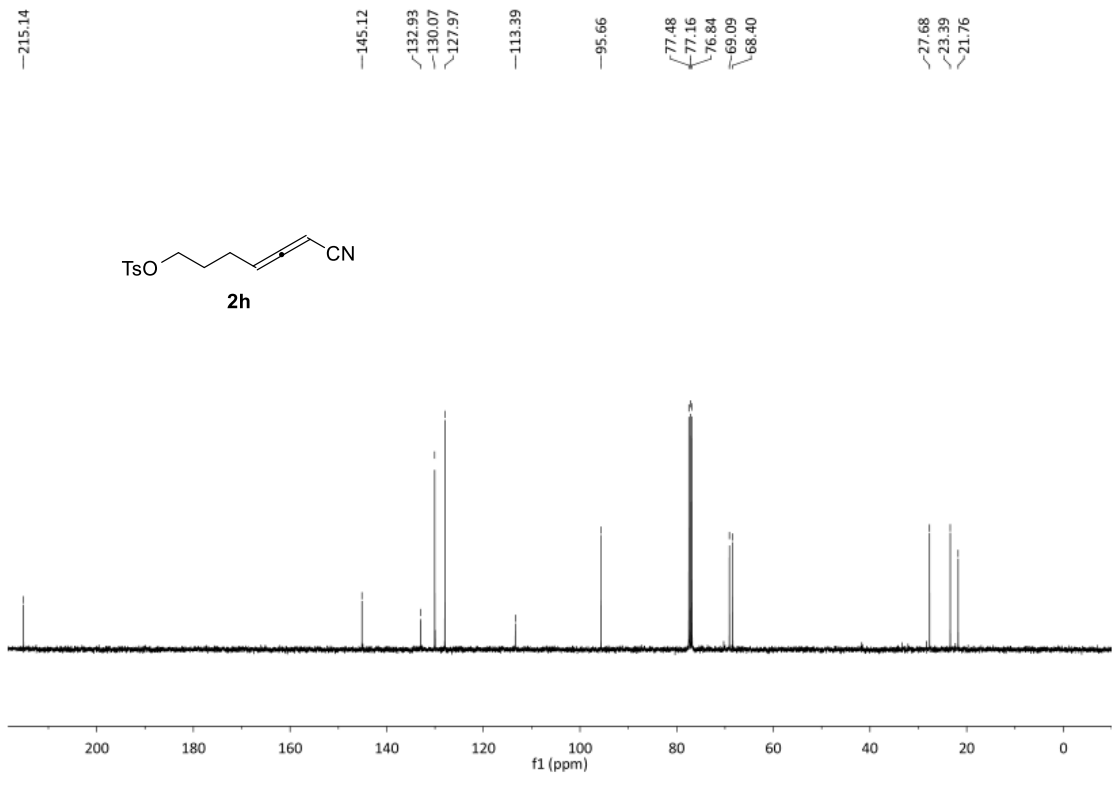

PWJ-201218-C
215.44
113.19
93.65
77.37
77.16
76.95
68.69
42.65
30.62

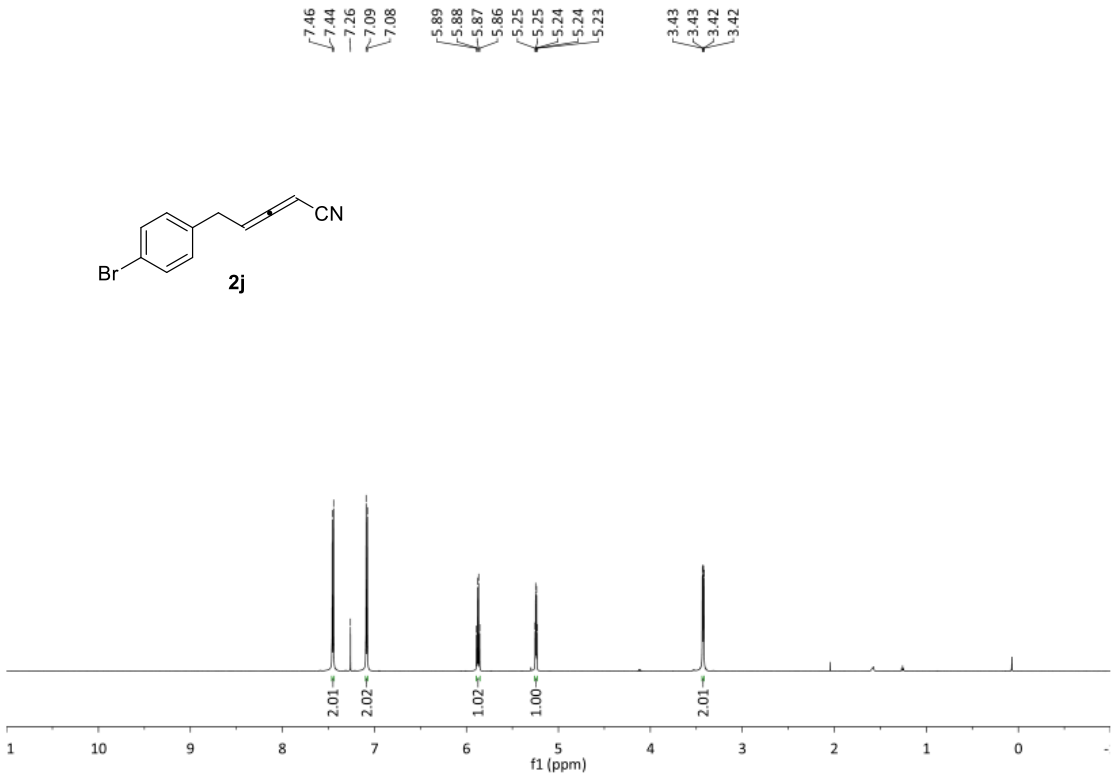

Cl
CN

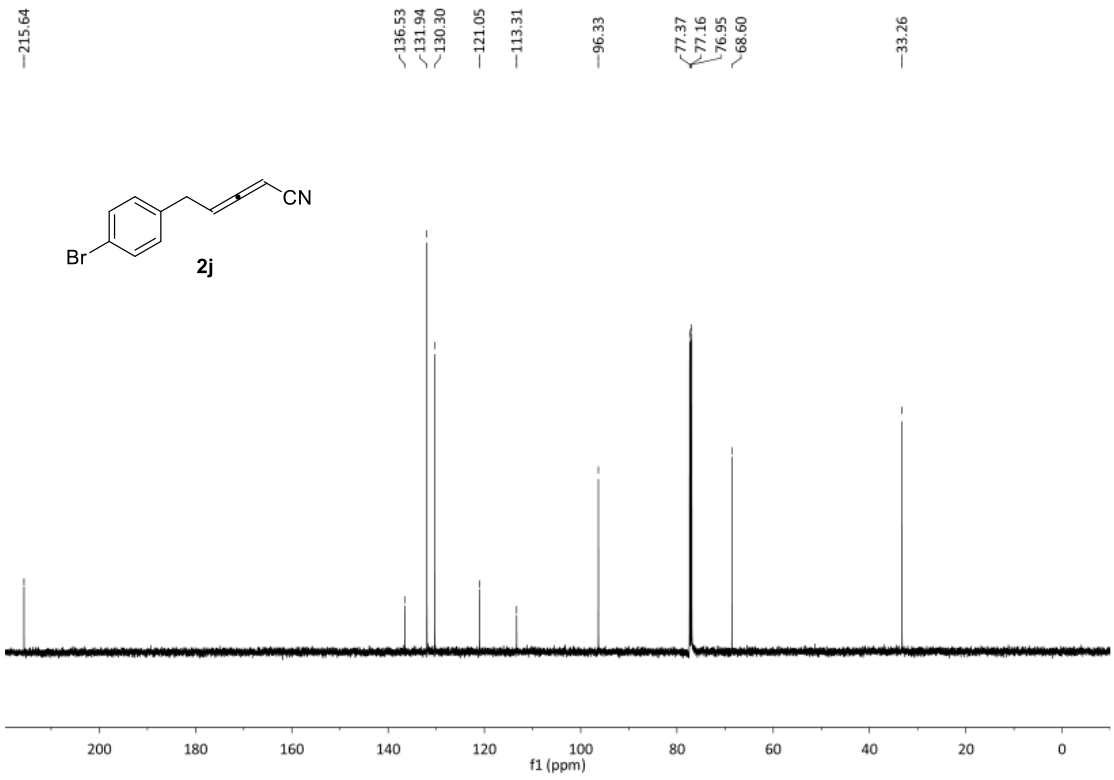
2g

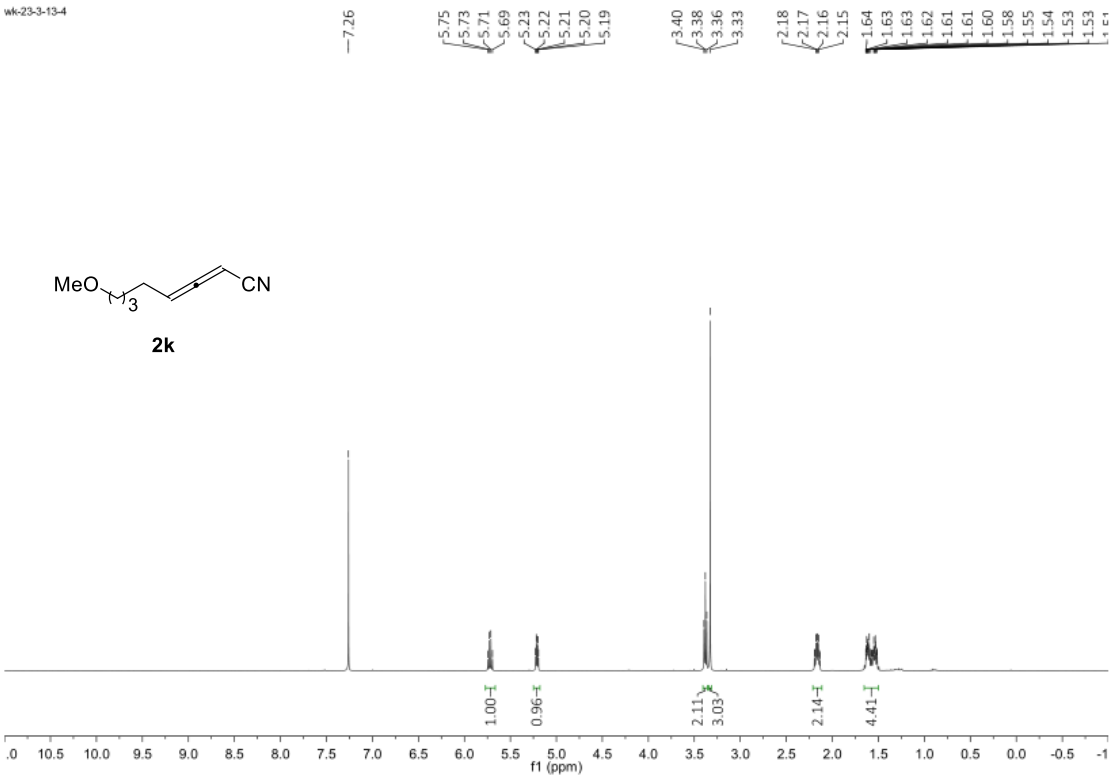

f1 (ppm)

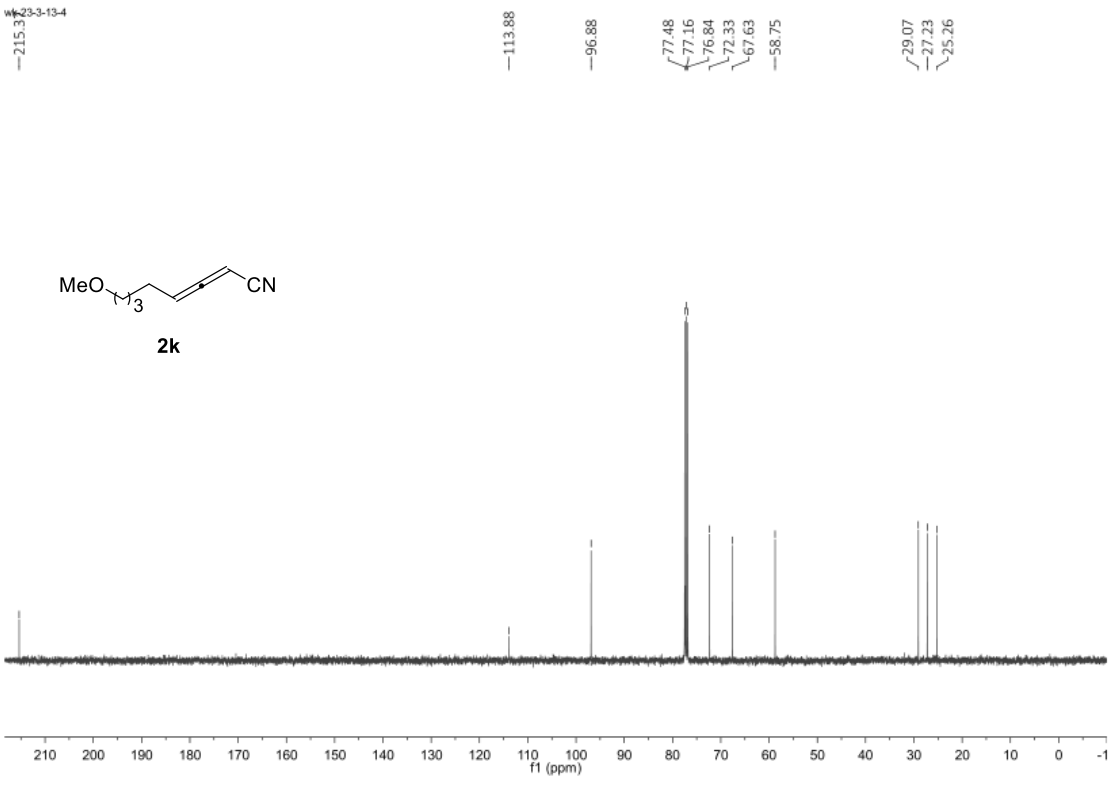

7.79
7.78
7.37
7.35
7.26
5.70
5.69
5.68
5.66
5.23
5.22
5.21
4.07
4.06
4.05
2.45
2.23
2.22
2.22
2.21
2.21
2.20
2.19
2.19
1.84
1.84
1.83
1.83
1.82
1.82
1.81
1.81
1.81
1.80
1.80
TsO
CN
2h
2.04
2.06
1.00
1.00
2.07
3.00
2.19
2.17
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

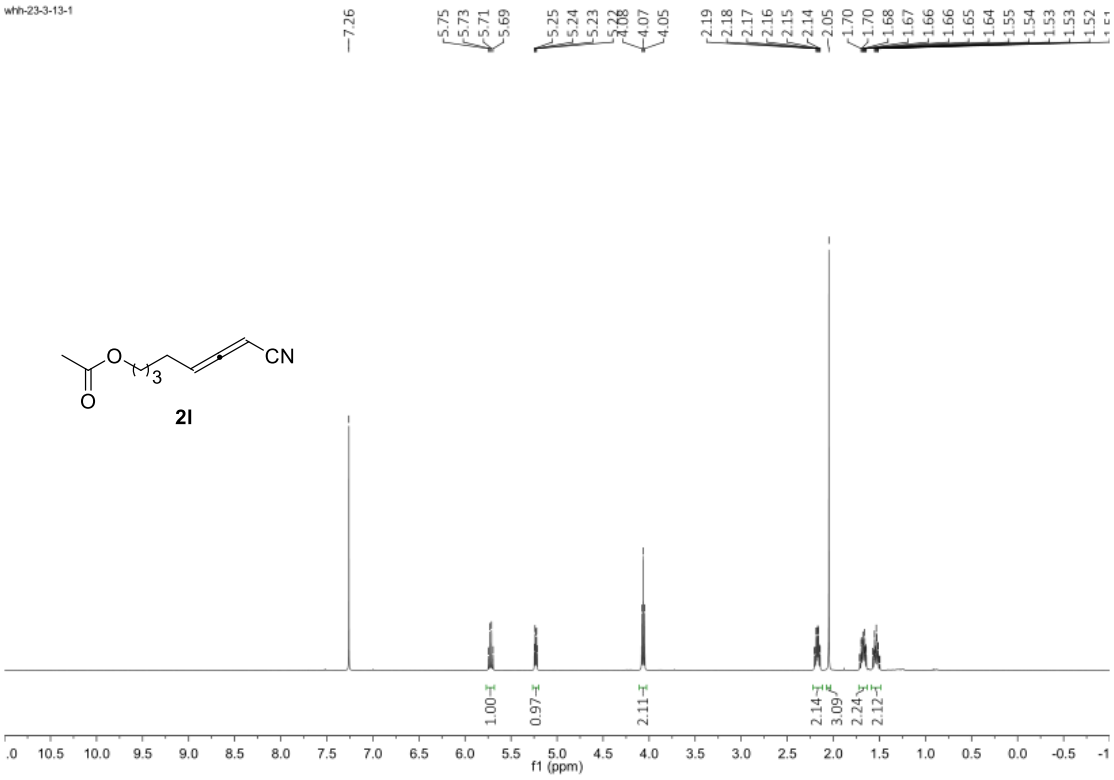

215.14
145.12
132.93
130.07
127.97
113.39
95.66
77.48
77.16
76.84
69.09
68.40
27.68
23.39
21.76
TsO
CN
2h
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

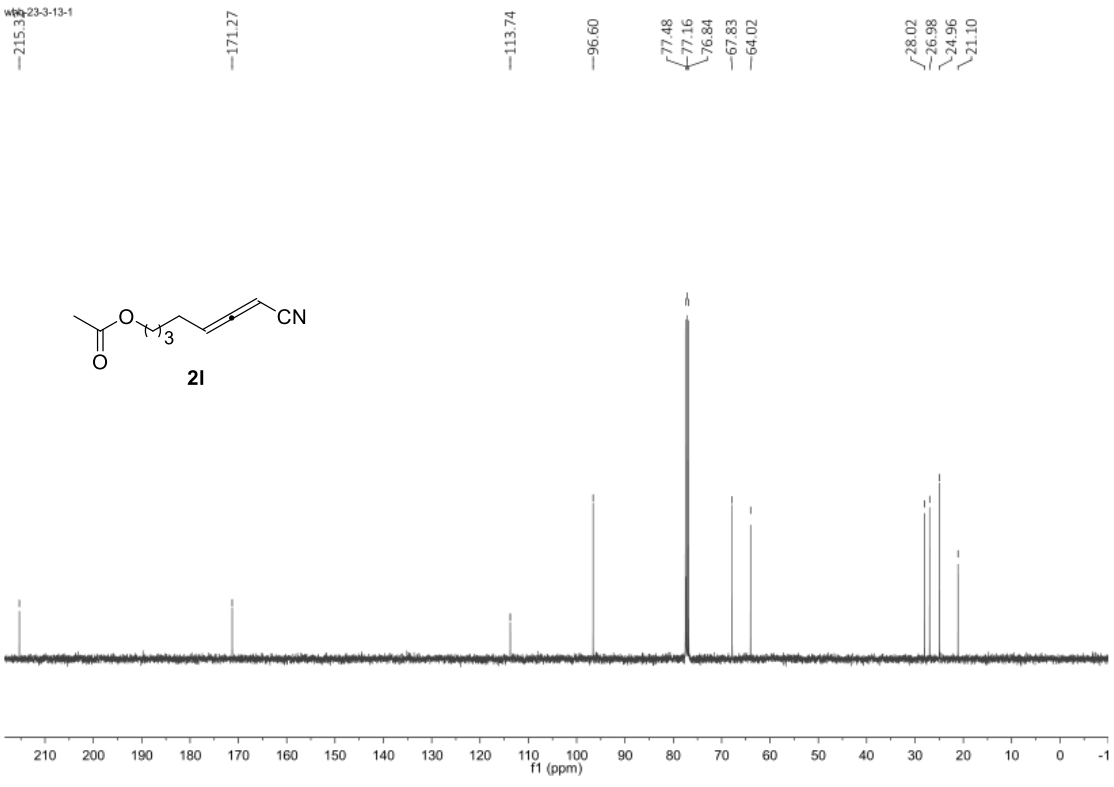

7.46
7.44
7.26
7.09
7.08
5.89
5.88
5.87
5.86
5.25
5.25
5.24
5.24
5.23
3.43
3.43
3.42
3.42
CN
Br
2j
2.01
2.02
1.02
1.00
2.01
f1 (ppm)

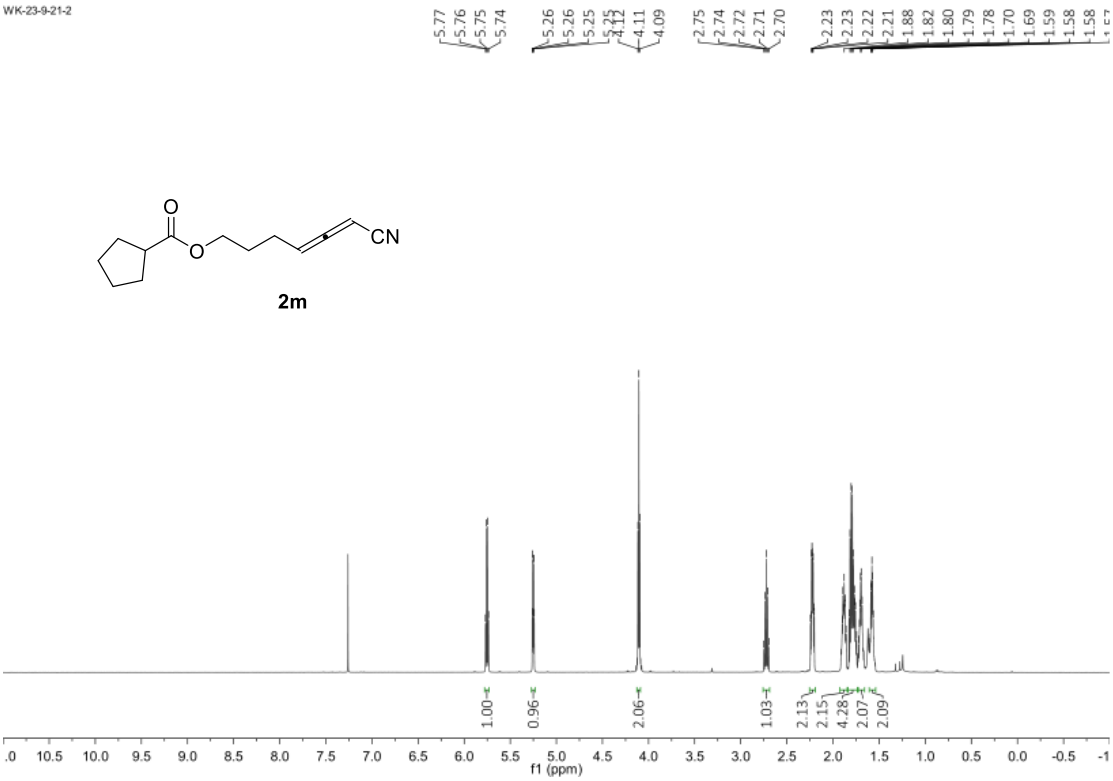

215.64
136.53
131.94
130.30
121.05
113.31
96.33
77.37
77.16
76.95
68.60
33.26
CN
Br
2j
f1 (ppm)

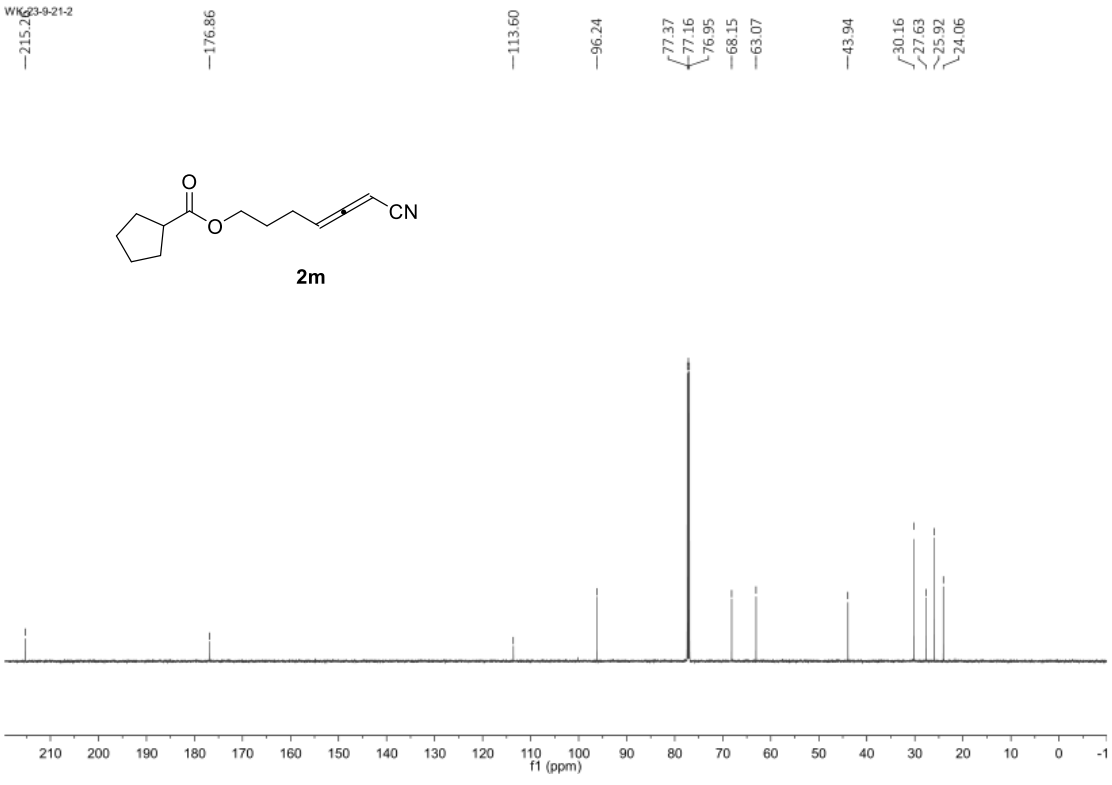

wk-23-3-13-4
7.26
5.75
5.73
5.71
5.69
5.23
5.22
5.21
5.20
5.19
3.40
3.38
3.36
3.33
2.18
2.17
2.16
2.15
1.64
1.63
1.63
1.62
1.61
1.61
1.60
1.58
1.55
1.54
1.53
1.53
MeO
3
CN
2k
1.00
0.96
2.11
3.03
2.14
4.41
f1 (ppm)

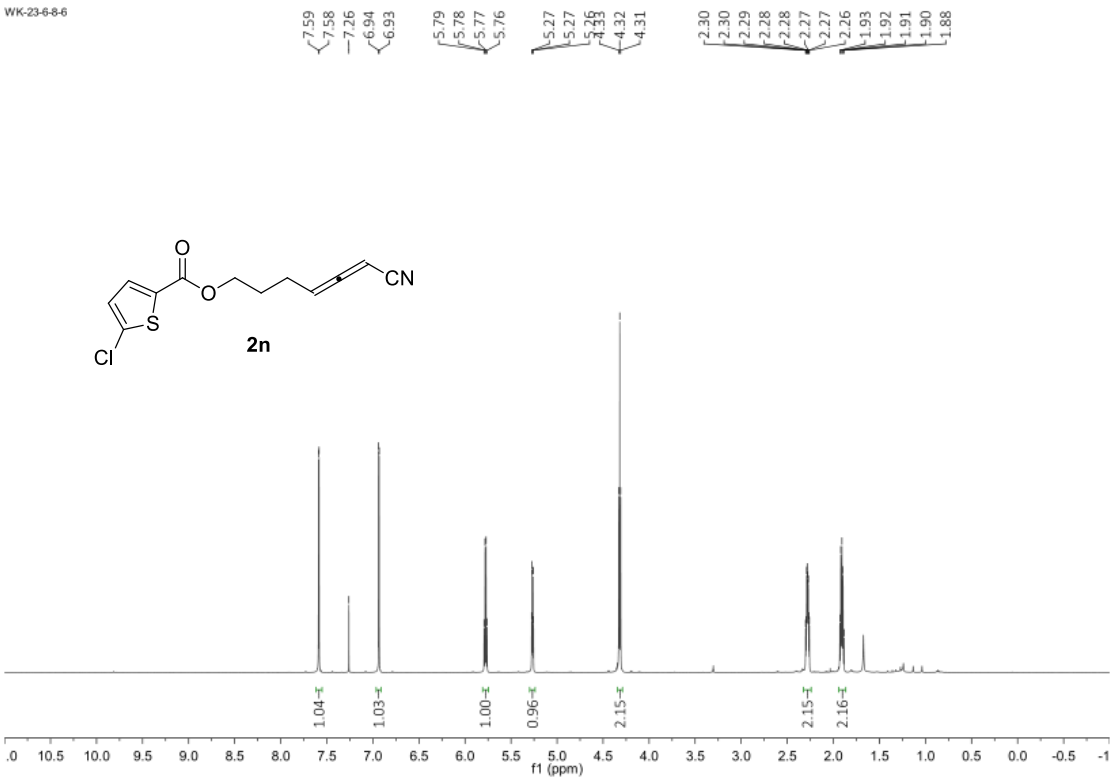

wk-23-3-13-4
215.37
113.88
96.88
77.48
77.16
76.84
72.33
67.63
58.75
29.07
27.23
25.26
MeO
3
CN
2k
f1 (ppm)

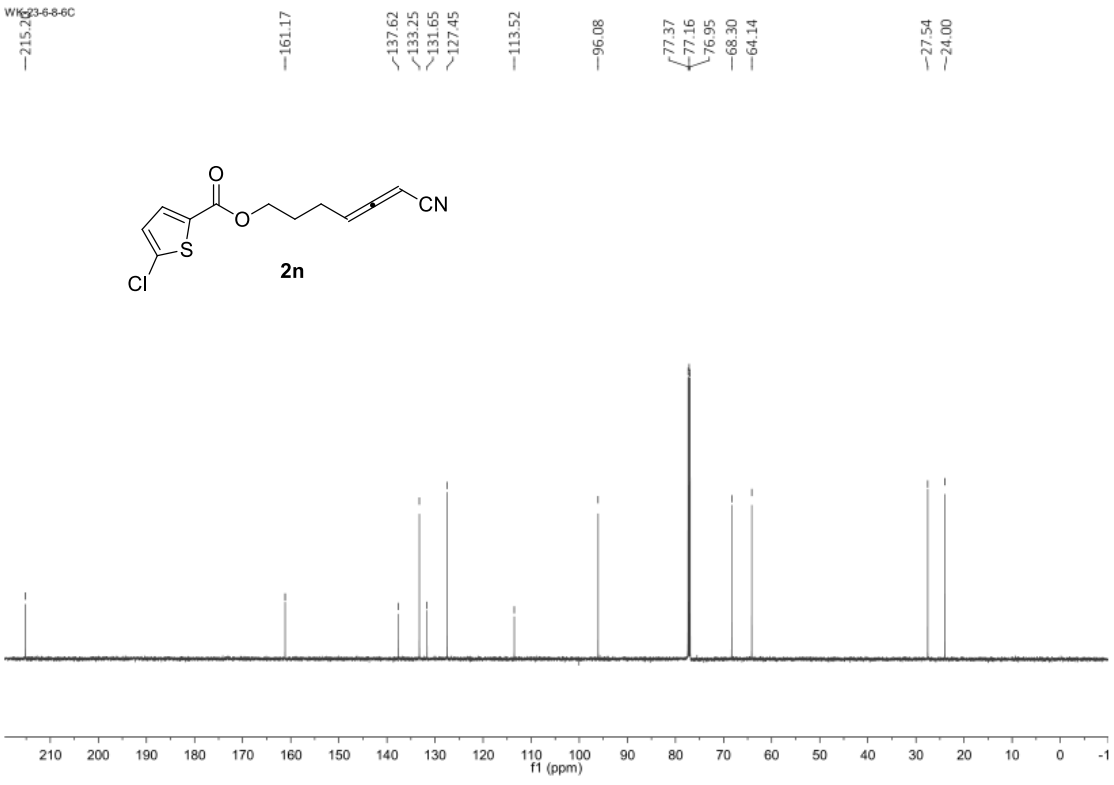

whh-23-3-13-1
7.26
5.75
5.73
5.71
5.69
5.25
5.24
5.23
4.08
4.07
4.05
2.19
2.18
2.17
2.16
2.15
2.14
2.05
1.70
1.68
1.67
1.66
1.65
1.64
1.55
1.54
1.53
1.52
O
O
3
CN
2l
1.00
0.97
2.11
2.14
3.09
2.24
2.12
f1 (ppm)

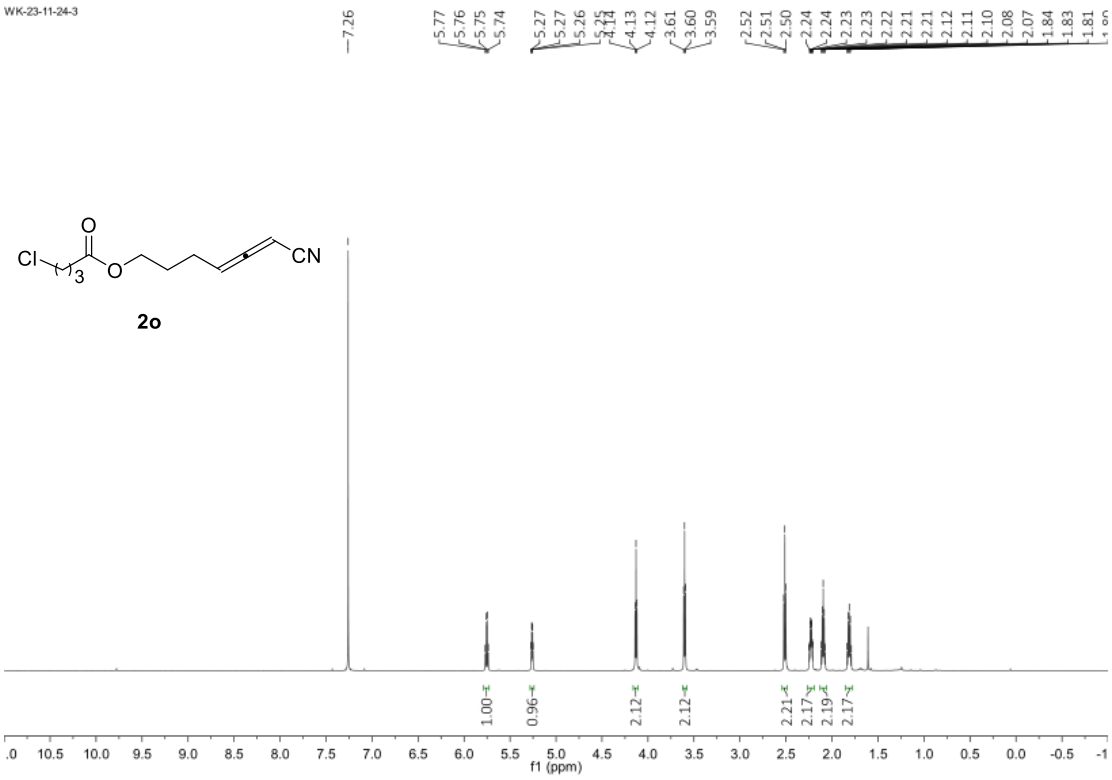

whh-23-3-13-1
215.32
171.27
113.74
96.60
77.48
77.16
76.84
67.83
64.02
28.02
26.98
24.96
21.10
O
O
3
CN
2l
f1 (ppm)

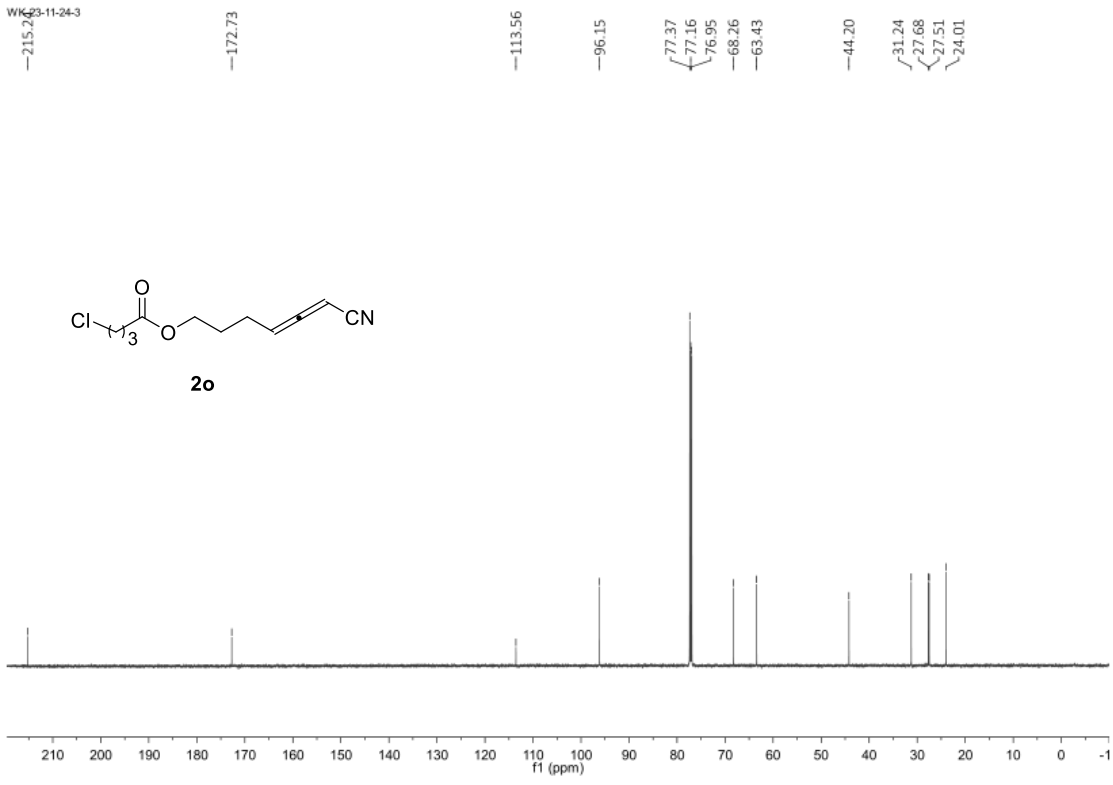

WK-23-9-21-2
5.77
5.76
5.75
5.74
5.26
5.26
5.25
4.11
4.09
2.75
2.74
2.72
2.71
2.70
2.23
2.23
2.22
2.21
1.88
1.82
1.80
1.79
1.78
1.70
1.69
1.59
1.58
1.58
O
O
CN
2m
1.00
0.96
2.06
1.03
2.13
2.15
4.28
2.07
2.09
f1 (ppm)

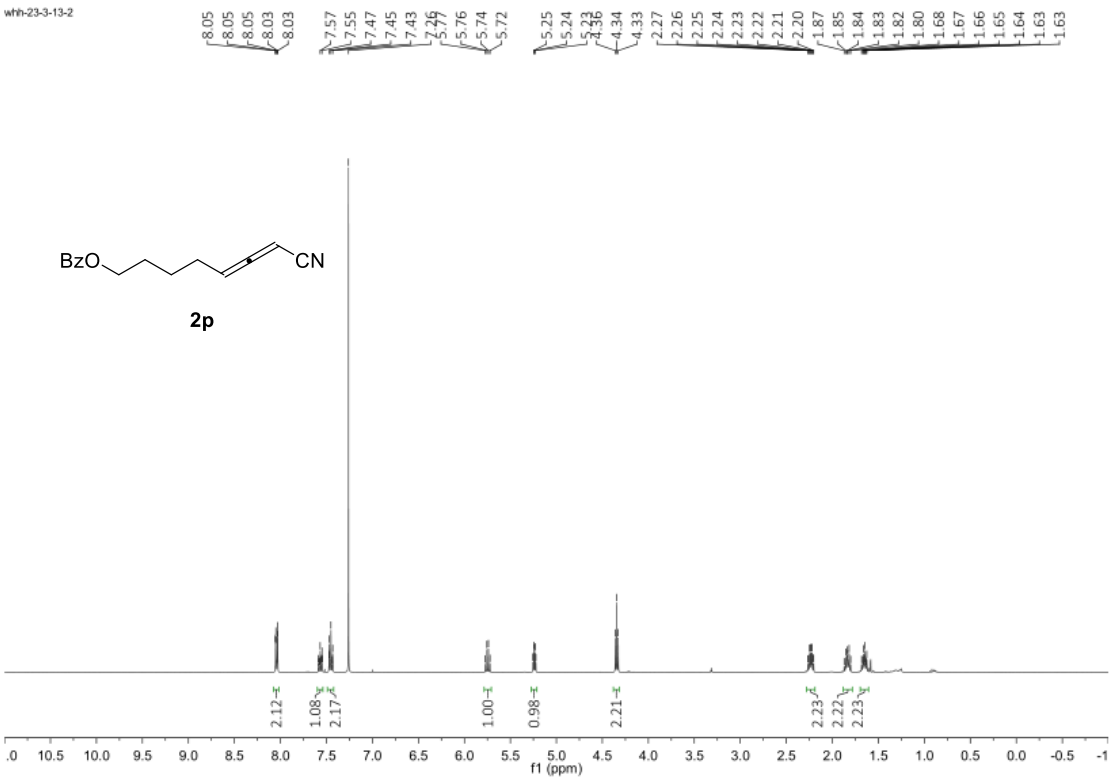

WK-23-9-21-2
215.26
176.86
113.60
96.24
77.37
77.16
76.95
68.15
63.07
43.94
30.16
27.63
25.92
24.06
O
O
CN
2m
f1 (ppm)

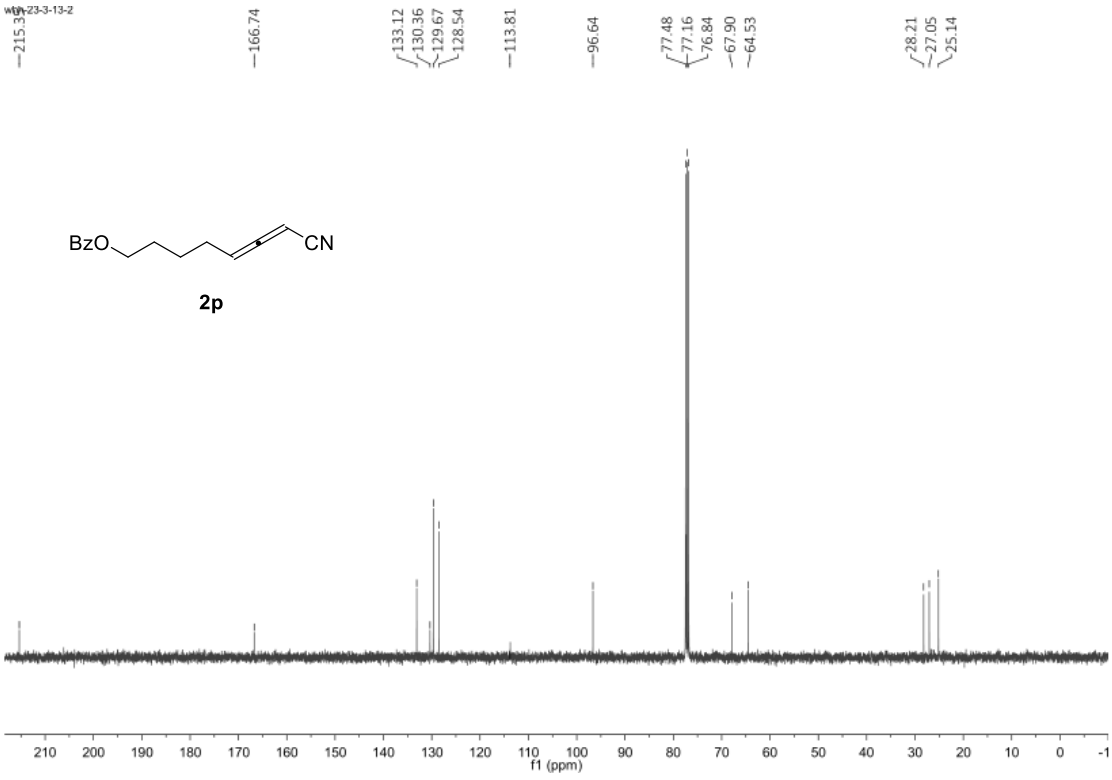

WK-23-6-8-6
7.59
7.58
7.26
6.94
6.93
5.79
5.78
5.77
5.76
5.27
5.27
5.25
4.33
4.32
4.31
2.30
2.30
2.29
2.28
2.28
2.27
2.27
2.26
1.93
1.92
1.91
1.90
1.88
O
O
CN
S
Cl
2n
1.04
1.03
1.00
0.96
2.15
2.15
2.16
f1 (ppm)

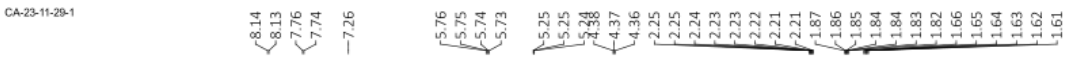

WK-23-6-8-6C
215.26
161.17
137.62
133.25
131.65
127.45
113.52
96.08
77.37
77.16
76.95
68.30
64.14
27.54
24.00
O
O
CN
S
Cl
2n
f1 (ppm)

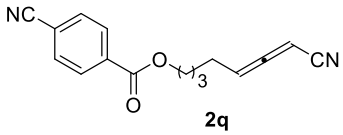

WK-23-11-24-3
7.26
5.77
5.76
5.75
5.74
5.27
5.27
5.26
4.13
4.12
3.61
3.60
3.59
2.52
2.51
2.50
2.24
2.24
2.23
2.23
2.22
2.21
2.21
2.12
2.11
2.10
2.08
2.07
1.84
1.83
1.81
Cl
O
O
3
O
CN
2o
1.00
0.96
2.12
2.12
2.21
2.17
2.19
2.17
f1 (ppm)


WK-23-11-24-3
215.24
172.73
113.56
96.15
77.37
77.16
76.95
68.26
63.43
44.20
31.24
27.68
27.51
24.01
Cl
O
O
3
O
CN
2o
f1 (ppm)

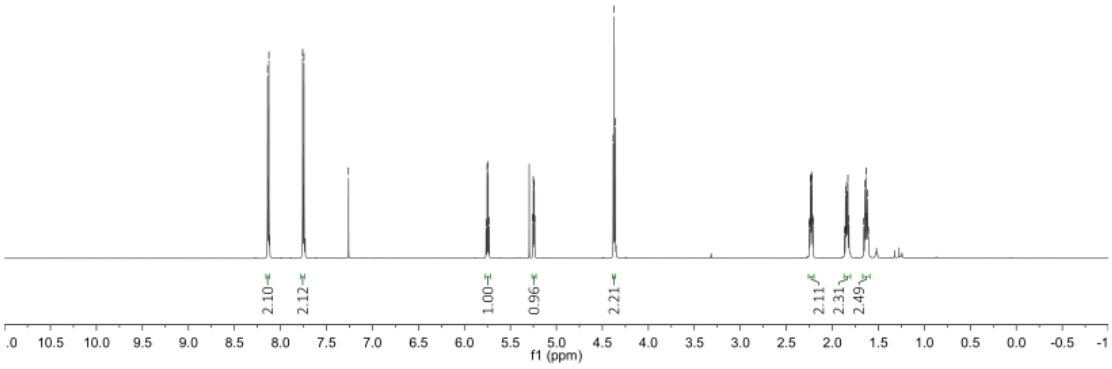

whh-23-3-13-2
8.05
8.05
8.05
8.03
8.03
7.57
7.55
7.47
7.45
7.43
7.26
5.76
5.74
5.72
5.25
5.24
4.34
4.33
2.27
2.26
2.25
2.24
2.23
2.22
2.21
2.20
1.87
1.85
1.84
1.83
1.82
1.80
1.68
1.67
1.66
1.65
1.64
1.63
1.63
BzO
CN
2p
2.12
1.08
2.17
1.00
0.98
2.21
2.23
2.22
2.23
f1 (ppm)


whh-23-3-13-2
166.74
133.12
130.36
129.67
128.54
113.81
96.64
77.48
77.16
76.84
67.90
64.53
28.21
27.05
25.14
BzO
CN
2p
f1 (ppm)

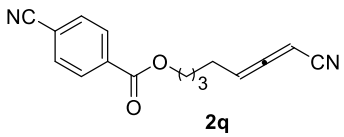

CA-23-11-29-1
8.14
8.13
7.76
7.74
7.26
5.76
5.75
5.74
5.73
5.25
5.25
5.24
4.38
4.37
4.36
2.25
2.25
2.24
2.23
2.23
2.22
2.21
2.21
1.87
1.86
1.85
1.84
1.84
1.83
1.82
1.66
1.65
1.64
1.63
1.62
1.61


NC
O
3
CN
O

2q

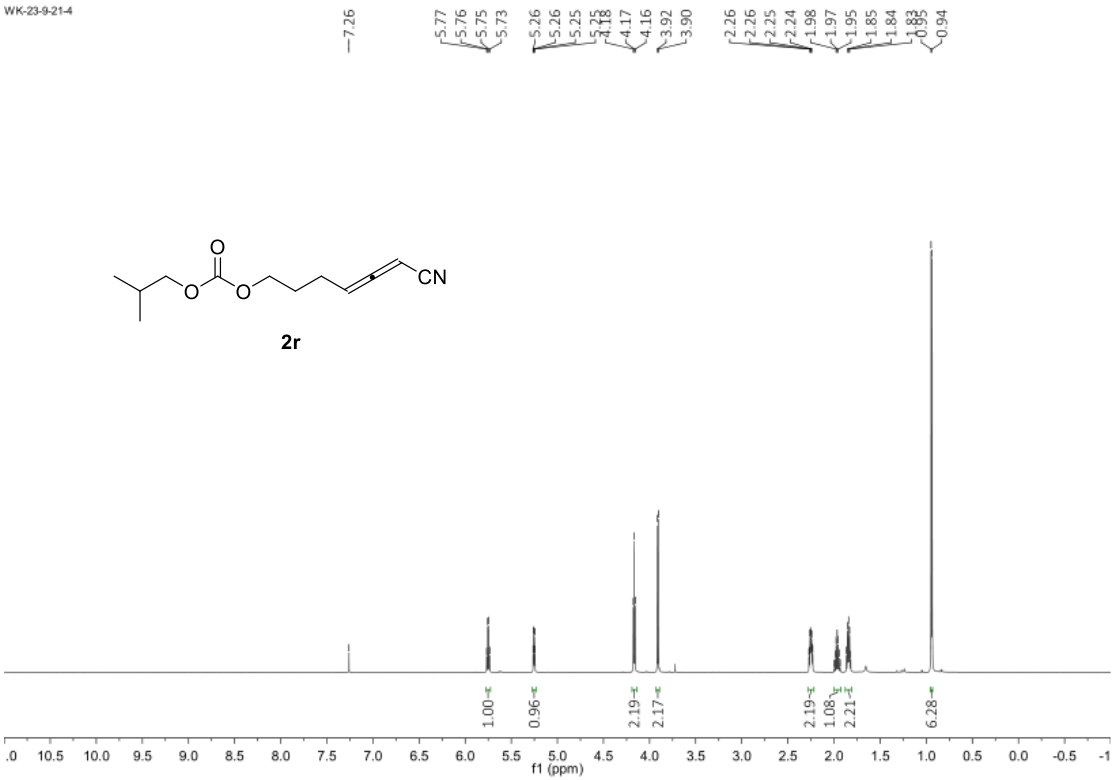

2.10
2.12
1.00
0.96
2.21
2.11
2.31
2.49
f1 (ppm)

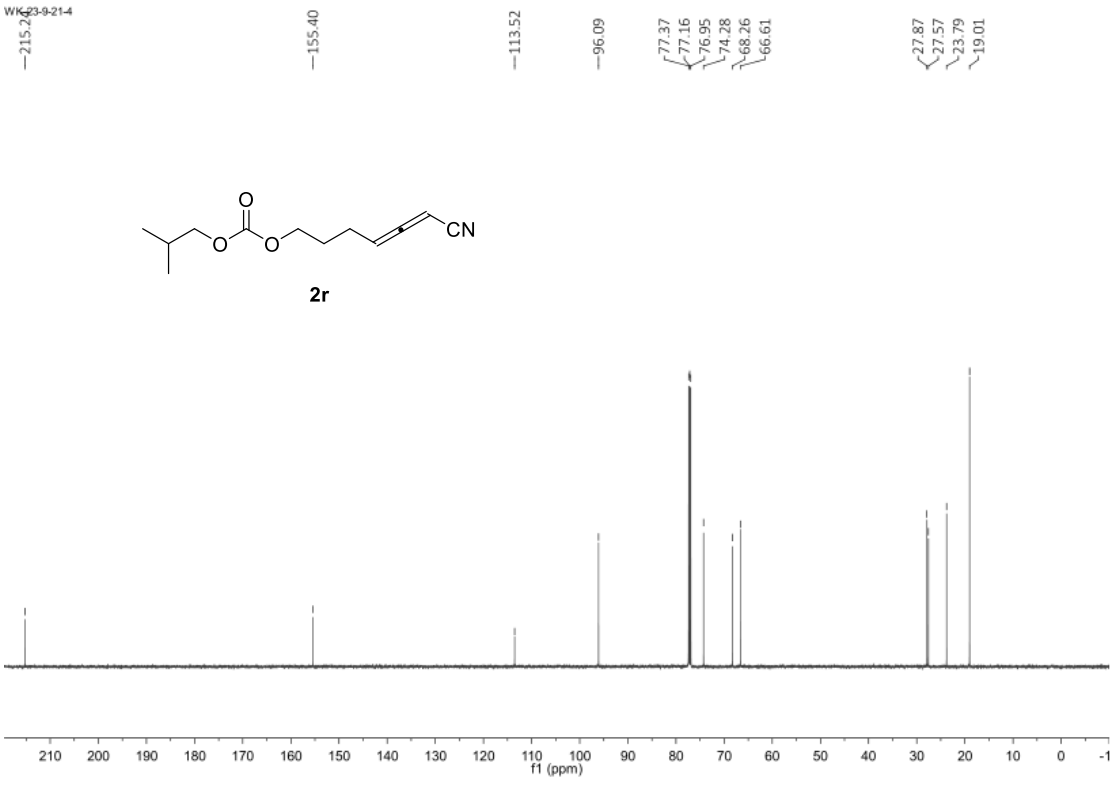

CA-23-11-29-1
215.31
165.04
134.14
132.38
130.19
118.09
116.54
113.66
96.50
77.37
77.16
76.95
68.01
65.35
28.09
26.97
25.00

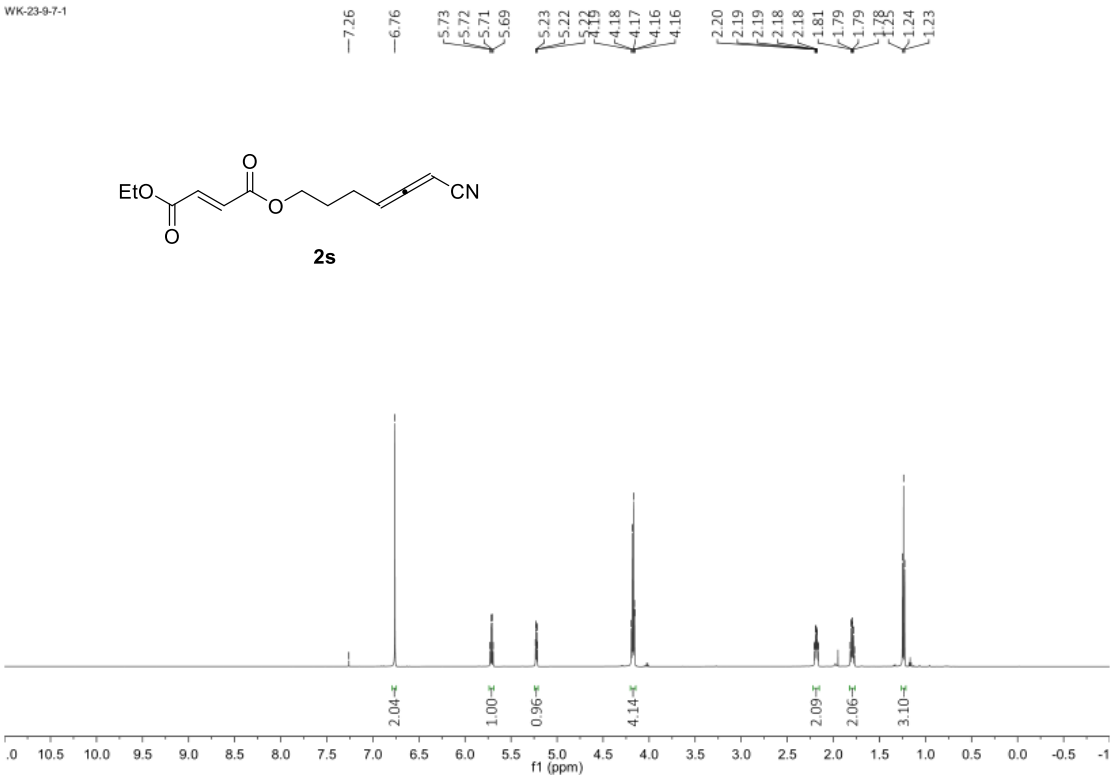

NC
O
3
CN
O

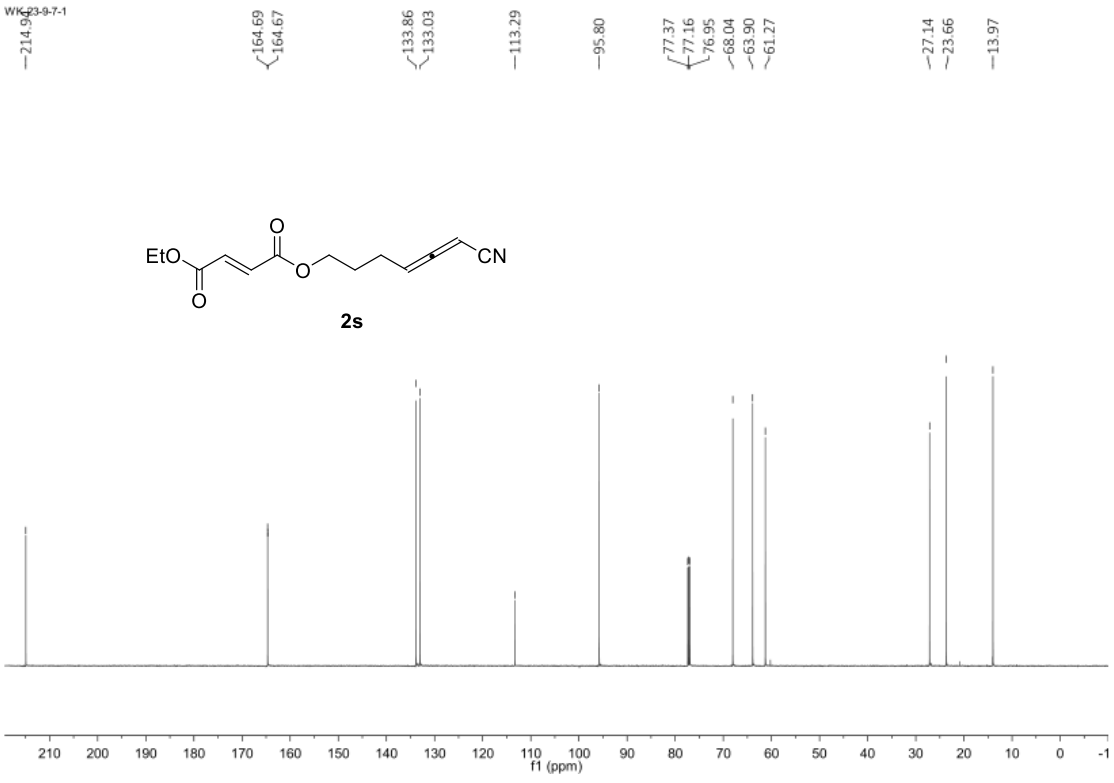
2q

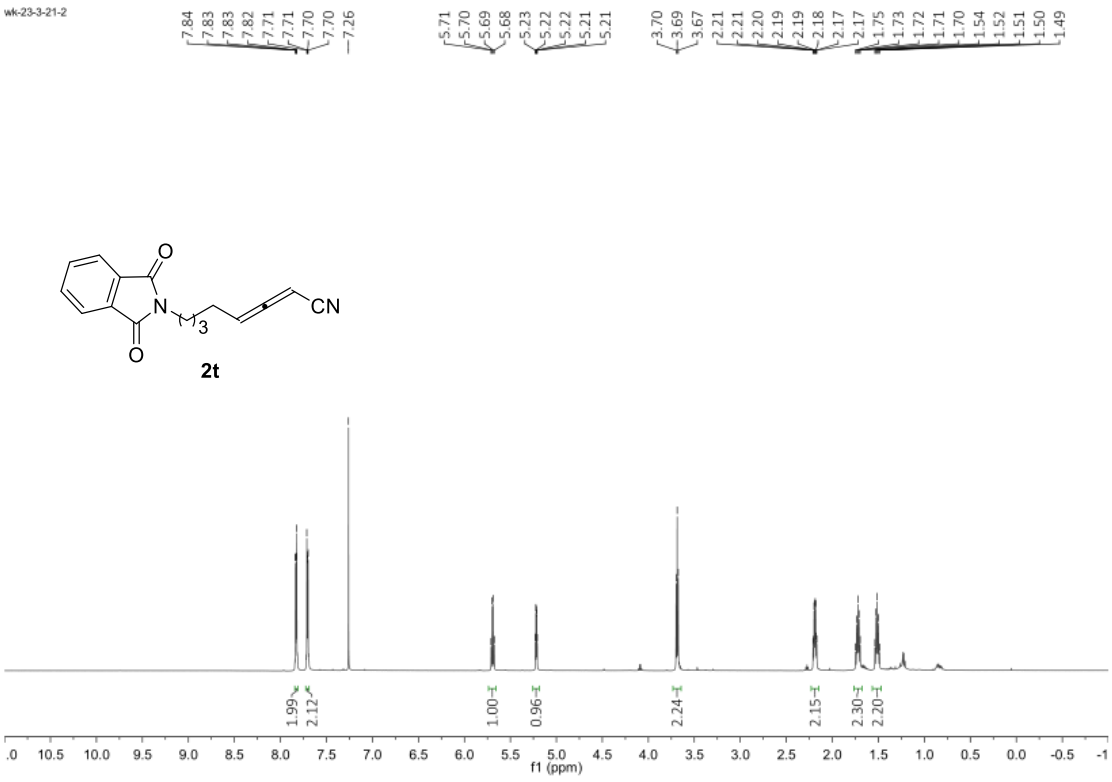
f1 (ppm)

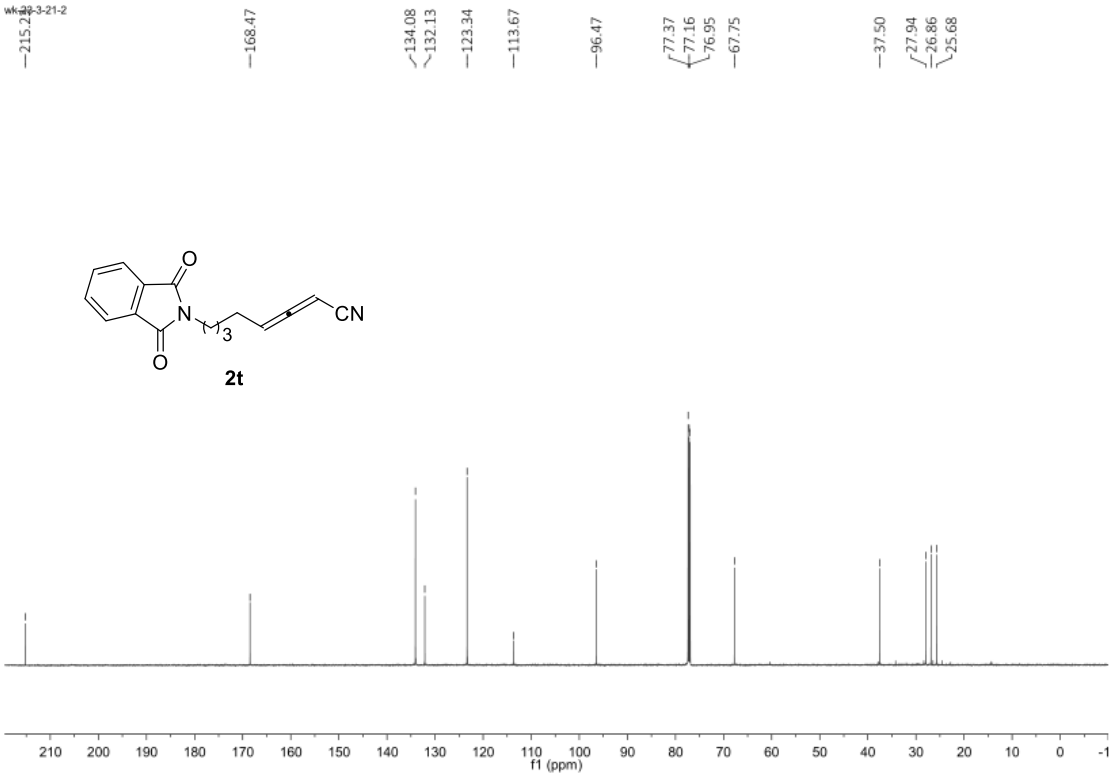

WK-23-9-21-4
7.26
5.77
5.76
5.75
5.73
5.26
5.26
5.25
5.25
4.18
4.17
4.16
3.92
3.90
2.26
2.26
2.25
2.24
1.98
1.97
1.95
1.85
1.84
0.95
0.94
O
O
O
CN
2r
1.00
0.96
2.19
2.17
2.19
1.08
2.21
6.28
f1 (ppm)

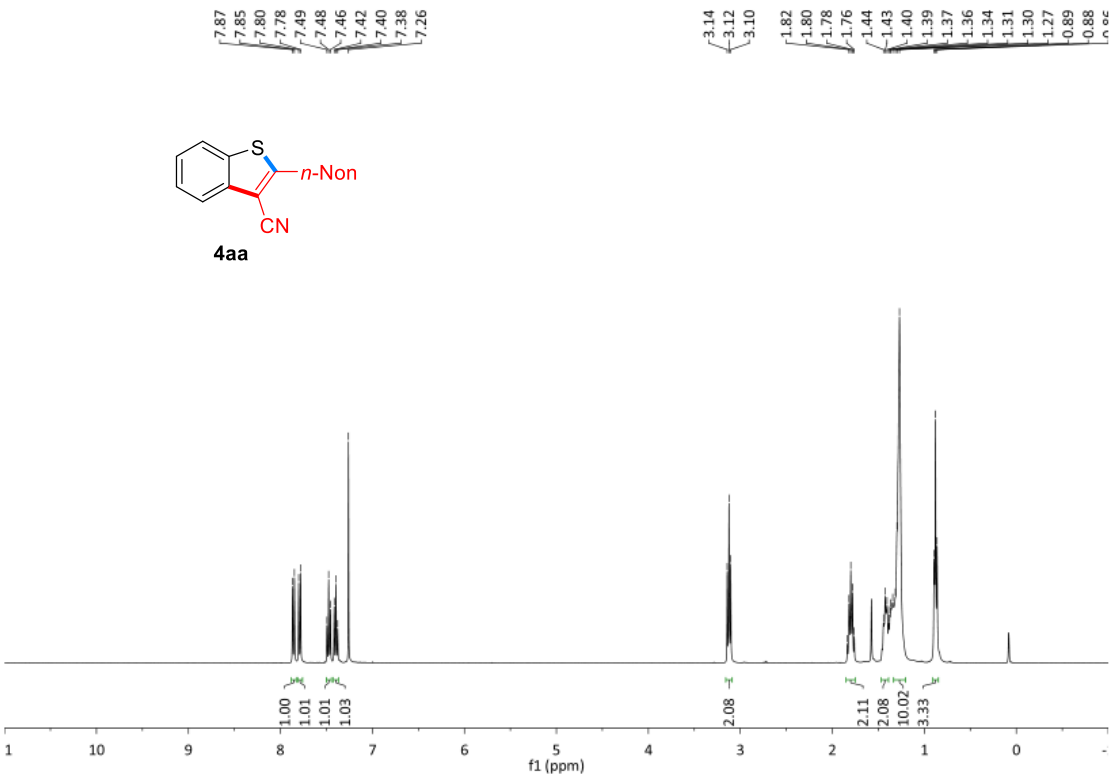

WK-23-9-21-4
215.26
155.40
113.52
96.09
77.37
77.16
76.95
74.28
68.26
66.61
27.87
27.57
23.79
19.01
O
O
O
CN
2r
f1 (ppm)

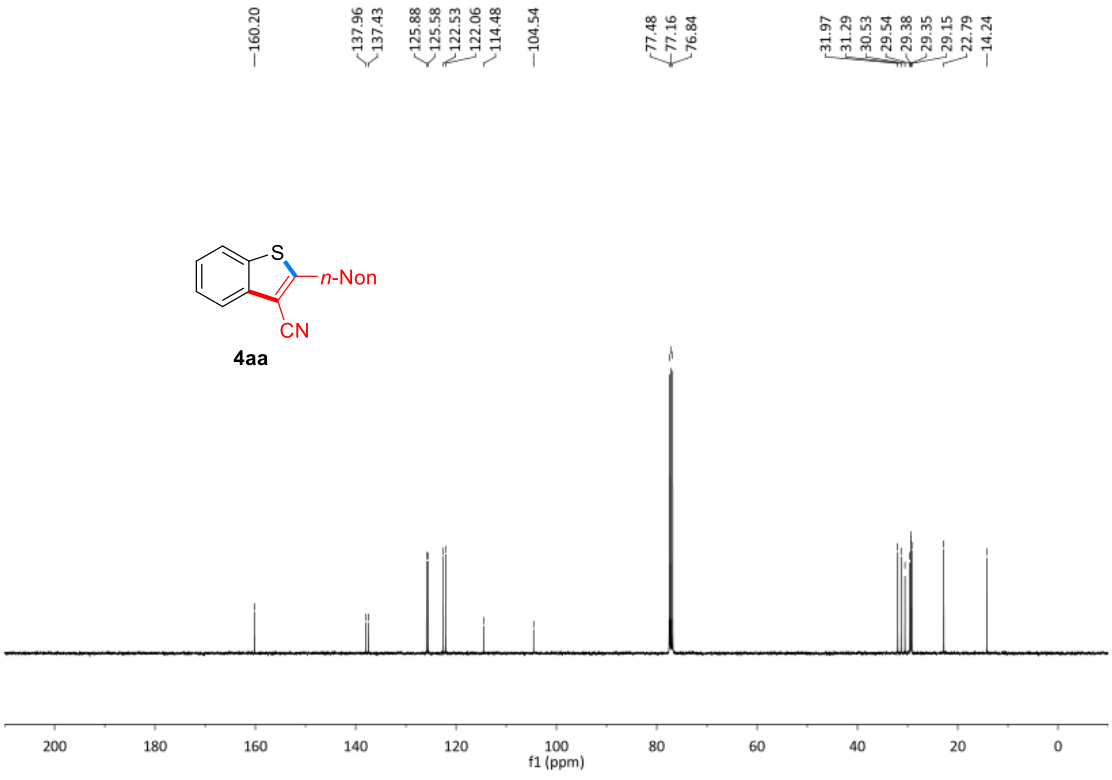

WK-23-9-7-1
7.26
6.76
5.73
5.72
5.71
5.69
5.23
5.22
5.22
4.19
4.18
4.17
4.16
4.16
2.20
2.19
2.19
2.18
2.18
1.81
1.79
1.79
1.78
1.25
1.24
1.23
EtO
O
O
O
CN
2s
2.04
1.00
0.96
4.14
2.09
2.06
3.10
f1 (ppm)

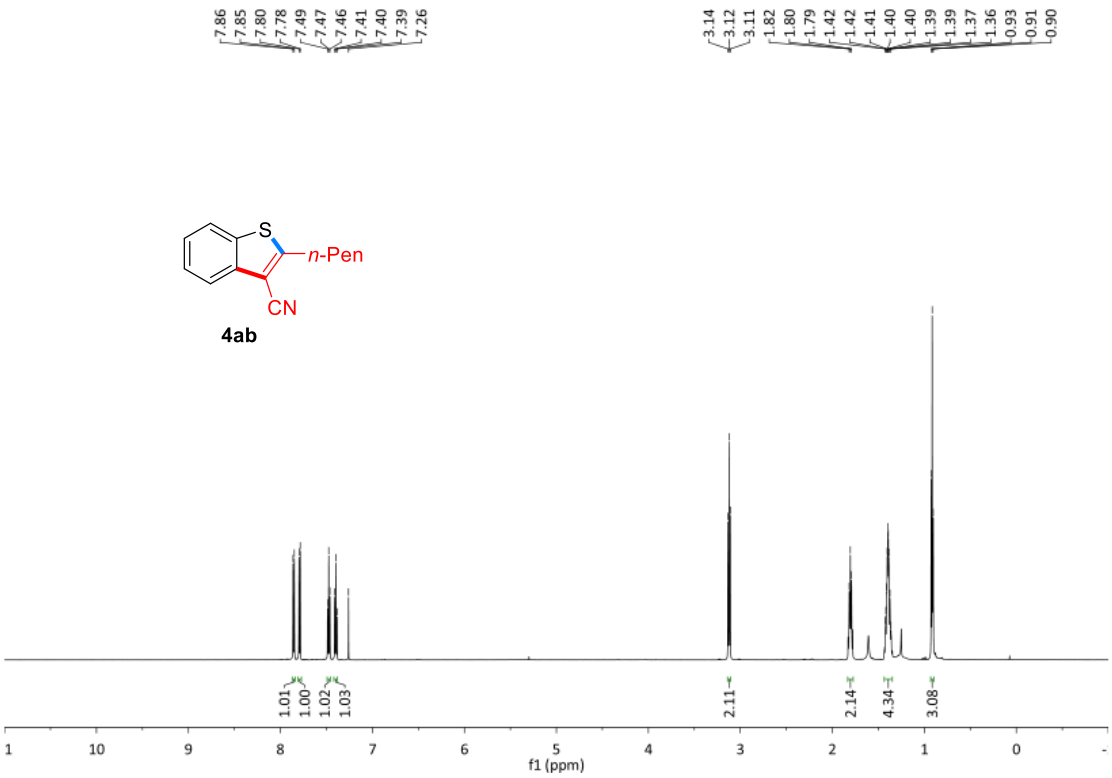

WK-23-9-7-1
214.94
164.69
164.67
133.86
133.03
113.29
95.80
77.37
77.16
76.95
68.04
63.90
61.27
27.14
23.66
13.97
EtO
O
O
O
CN
2s
f1 (ppm)

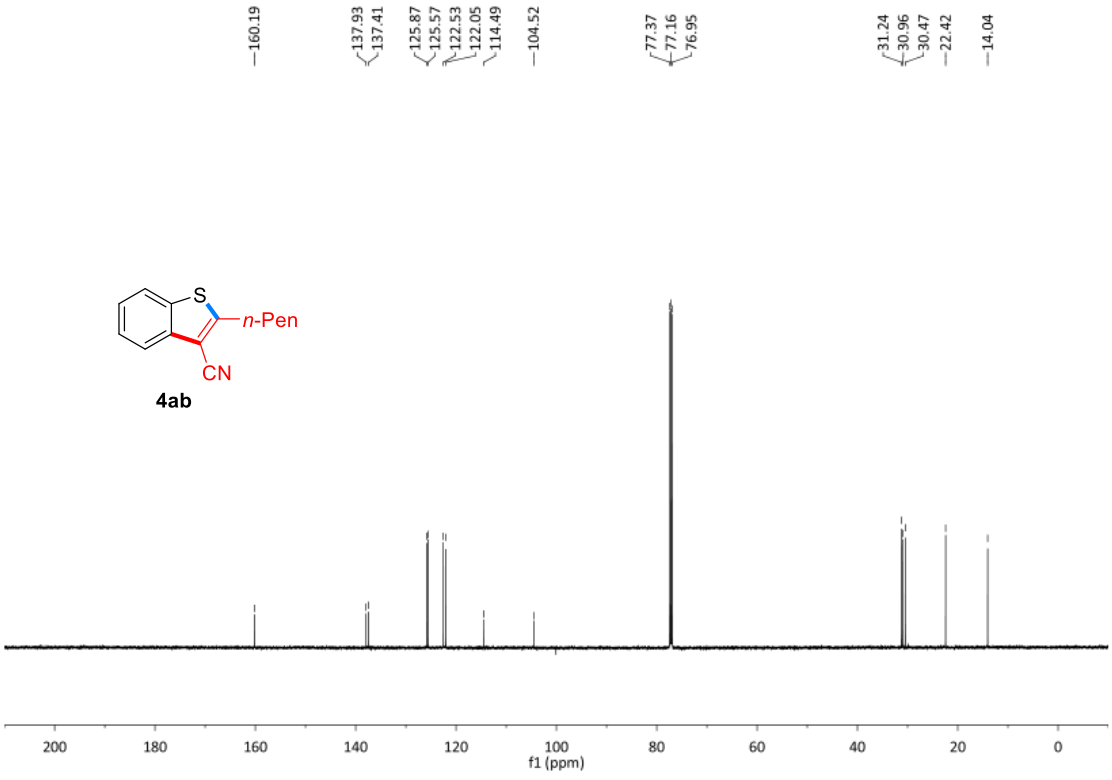

wk-23-3-21-2
7.84
7.83
7.83
7.82
7.71
7.71
7.70
7.70
7.26
5.71
5.70
5.69
5.68
5.23
5.22
5.22
5.21
5.21
3.70
3.69
3.67
2.21
2.21
2.20
2.19
2.19
2.18
2.17
2.17
1.75
1.73
1.72
1.71
1.70
1.54
1.52
1.51
1.50
1.49
O
N
3
CN
O
2t
1.99
2.12
1.00
0.96
2.24
2.15
2.30
2.20
f1 (ppm)

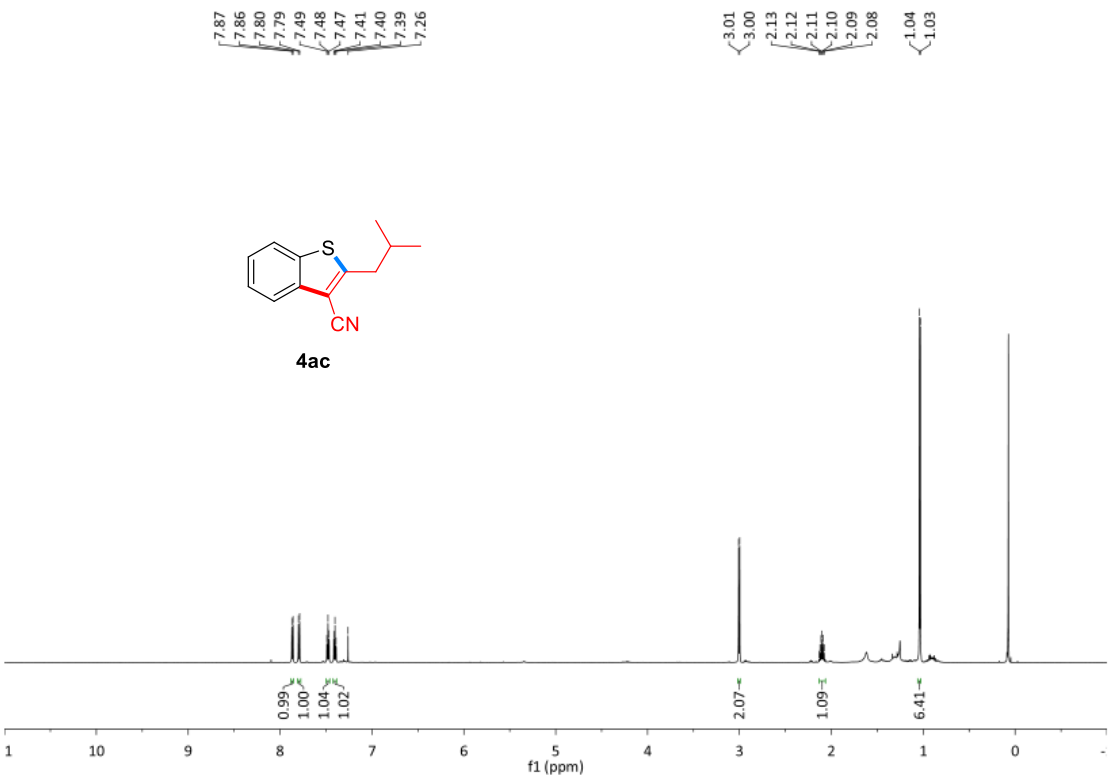

wk-23-3-21-2
215.23
168.47
134.08
132.13
123.34
113.67
96.47
77.37
77.16
76.95
67.75
37.50
27.94
26.86
25.68
O
N
3
CN
O
2t
f1 (ppm)


7.87
7.85
7.80
7.78
7.49
7.48
7.46
7.42
7.40
7.38
7.26
3.14
3.12
3.10
1.82
1.80
1.78
1.76
1.44
1.43
1.40
1.39
1.37
1.36
1.34
1.31
1.30
1.27
0.89
0.88
S
n-Non
CN
4aa
1.00
1.01
1.01
1.03
2.08
2.11
2.08
10.02
3.33
f1 (ppm)

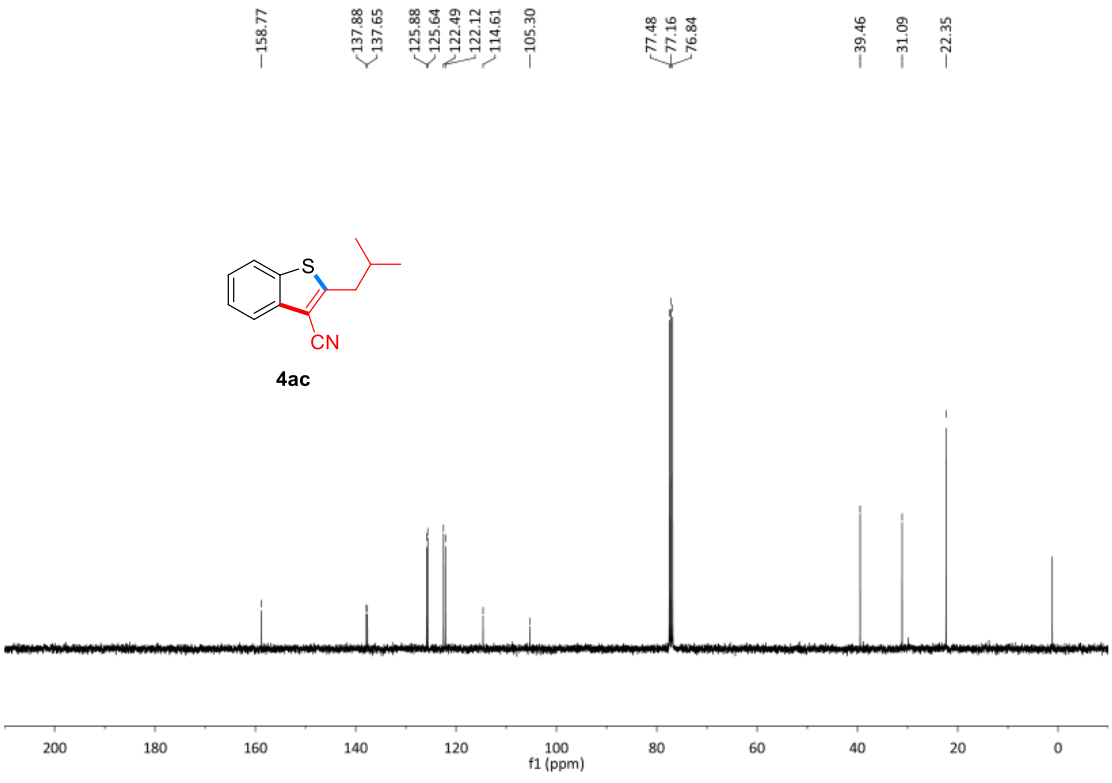

160.20
137.96
137.43
125.88
125.58
122.53
122.06
114.48
104.54
77.48
77.16
76.84
31.97
31.29
30.53
29.54
29.38
29.35
29.15
22.79
14.24
S
n-Non
CN
4aa
f1 (ppm)


7.86
7.85
7.80
7.78
7.49
7.47
7.46
7.41
7.40
7.39
7.26
3.14
3.12
3.11
1.82
1.80
1.79
1.42
1.42
1.41
1.40
1.40
1.39
1.39
1.37
1.36
0.93
0.91
0.90
S
n-Pen
CN
4ab
1.01
1.00
1.02
1.03
2.11
2.14
4.34
3.08
f1 (ppm)

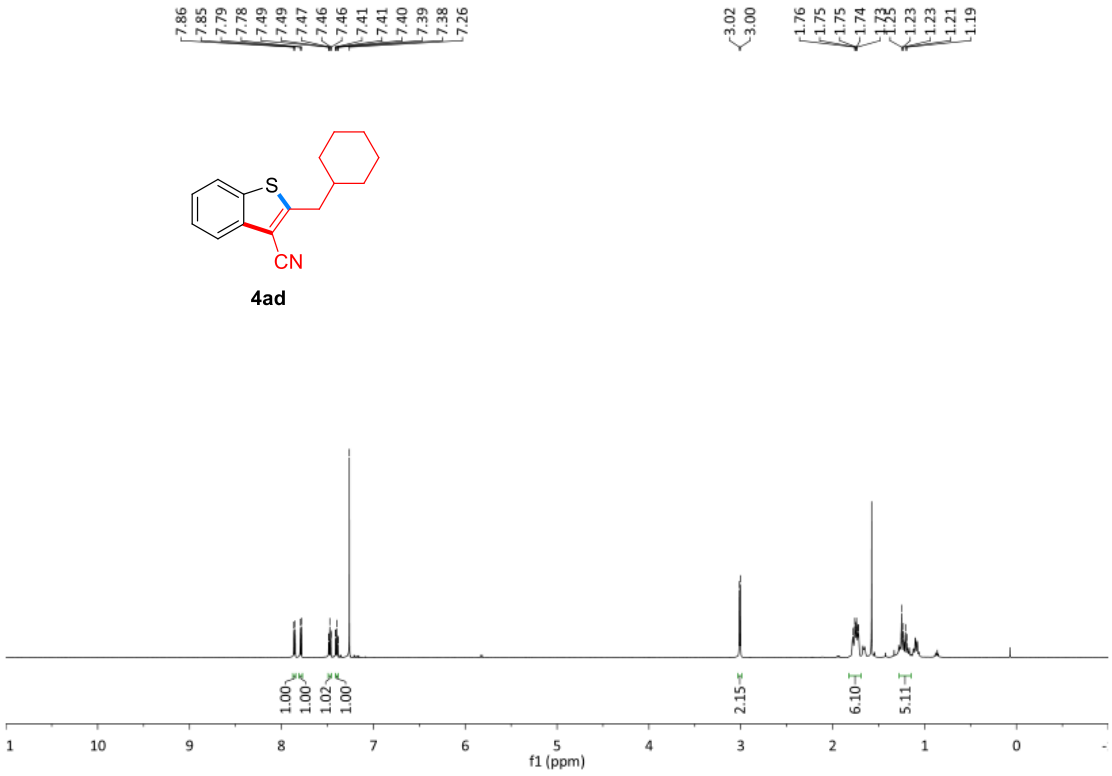

160.19
137.93
137.41
125.87
125.57
122.53
122.05
114.49
104.52
77.37
77.16
76.95
31.24
30.96
30.47
22.42
14.04
S
n-Pen
CN
4ab
f1 (ppm)

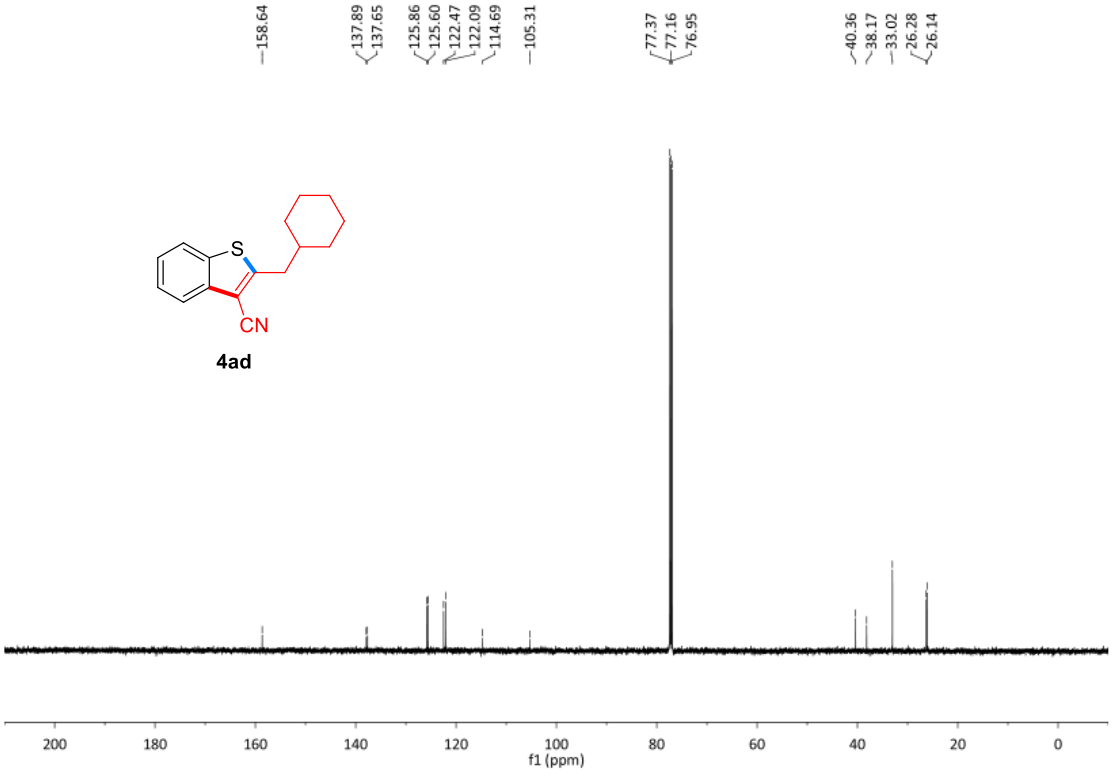

7.87
7.86
7.80
7.79
7.49
7.48
7.47
7.41
7.40
7.39
7.26
3.01
3.00
2.13
2.12
2.11
2.10
2.09
2.08
1.04
1.03
S
CN
0.99
1.00
1.04
1.02
2.07
1.09
6.41
f1 (ppm)

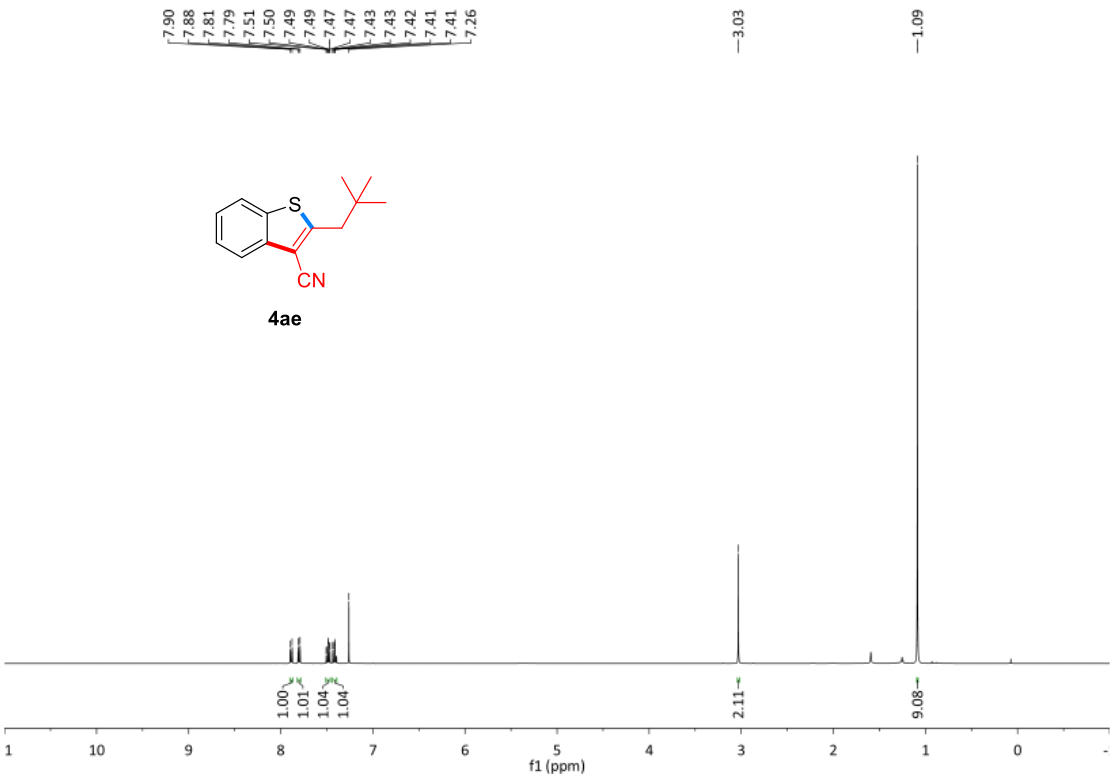
4ac


158.77
137.88
137.65
125.88
125.64
122.49
122.12
114.61
105.30
77.48
77.16
76.84
39.46
31.09
22.35
S
CN
f1 (ppm)

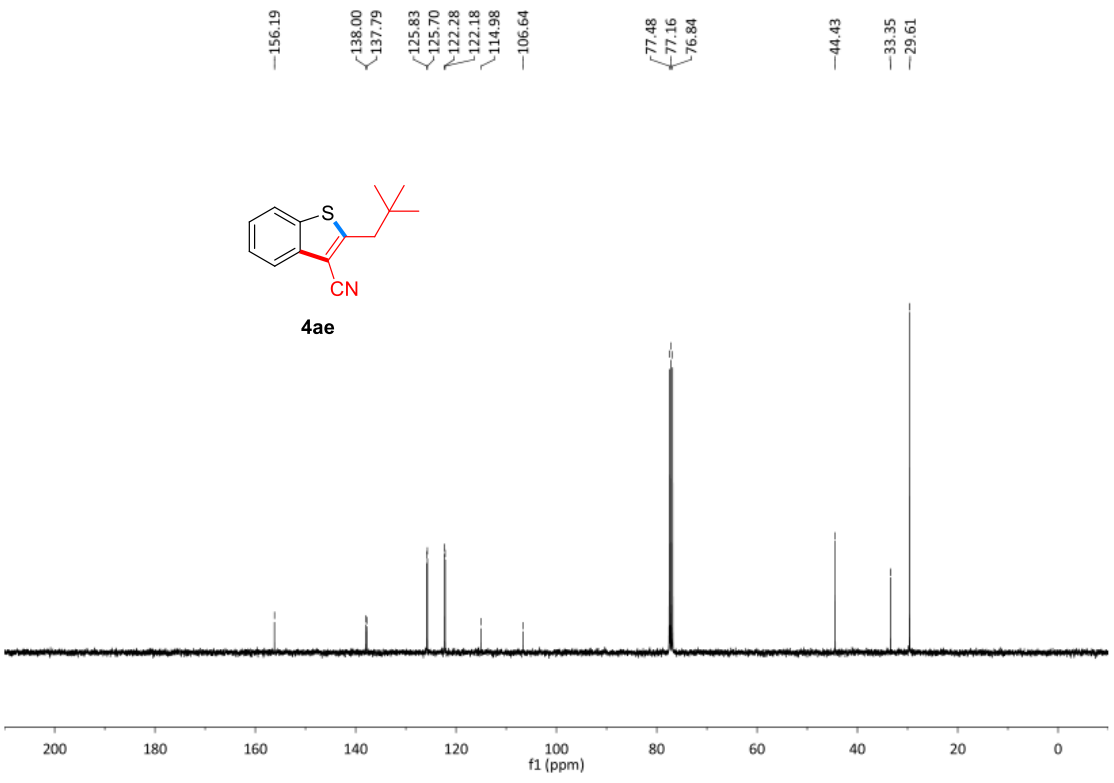
4ac


7.86
7.85
7.79
7.78
7.49
7.49
7.47
7.46
7.46
7.41
7.41
7.40
7.39
7.38
7.26
3.02
3.00
1.76
1.75
1.75
1.74
1.23
1.23
1.21
1.19
S
CN
4ad
1.00
1.00
1.02
1.00
2.15
6.10
5.11
f1 (ppm)

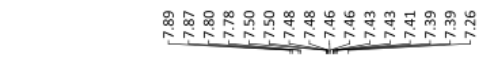

158.64
137.89
137.65
125.86
125.60
122.47
122.09
114.69
105.31
77.37
77.16
76.95
40.36
38.17
33.02
26.28
26.14
S
CN
4ad
f1 (ppm)

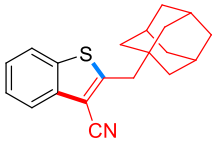

7.90
7.88
7.81
7.79
7.51
7.50
7.49
7.49
7.47
7.47
7.43
7.43
7.42
7.41
7.41
7.26
3.03
1.09
S
CN
1.00
1.01
1.04
1.04
2.11
9.08
f1 (ppm)

4ae

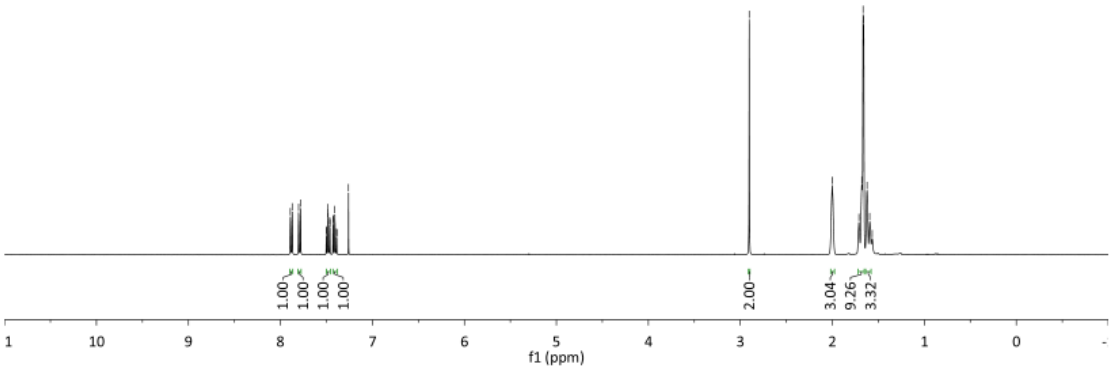

156.19
138.00
137.79
125.83
125.70
122.28
122.18
114.98
106.64
77.48
77.16
76.84
44.43
33.35
29.61
S
CN
f1 (ppm)

4ae

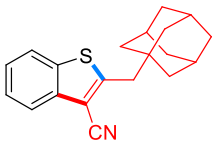

7.89
7.87
7.80
7.78
7.50
7.50
7.48
7.48
7.46
7.46
7.43
7.43
7.41
7.39
7.39
7.26
2.90
2.00
1.71
1.68
1.67
1.66
1.62
1.59
1.57


S
CN

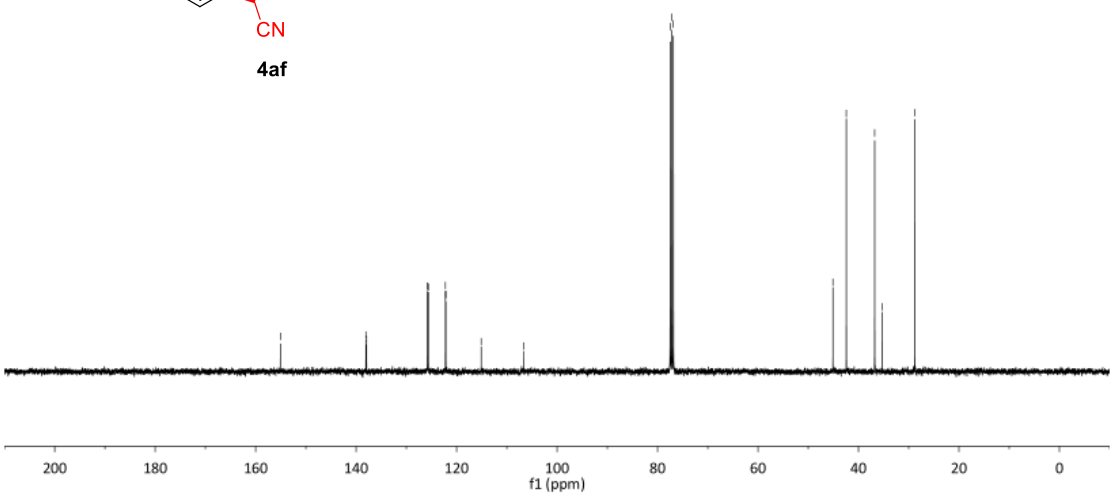
4af

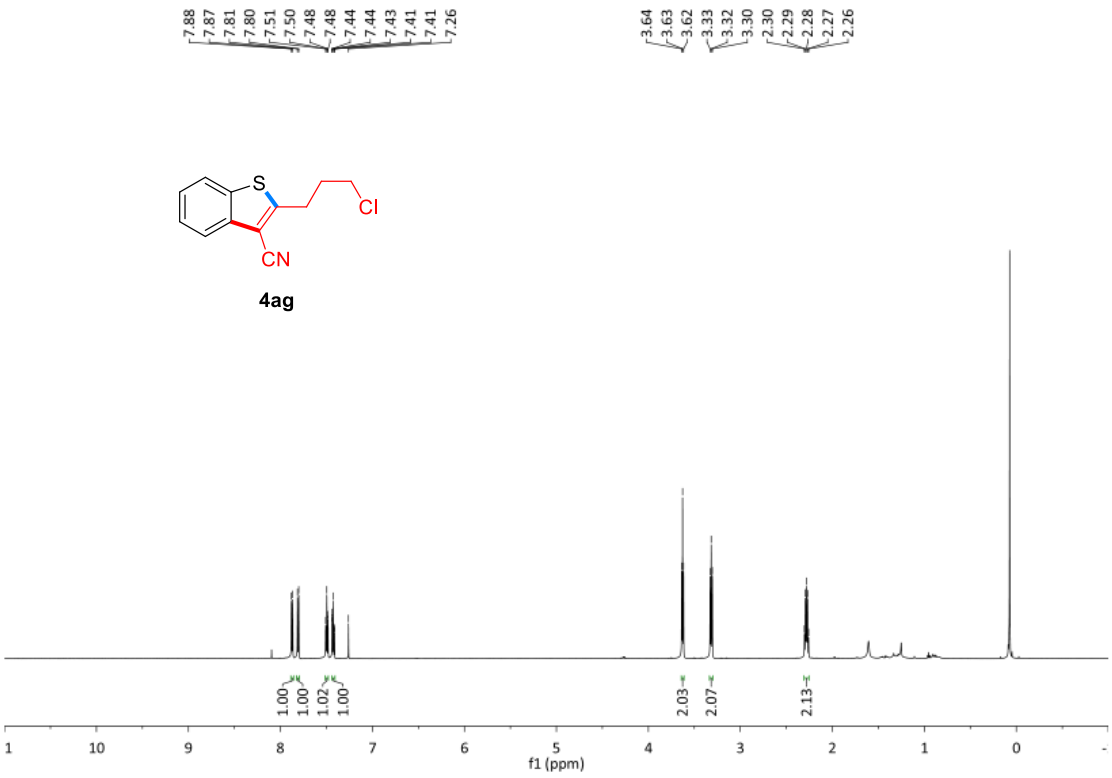

1.00
1.00
1.00
1.00
2.00
3.04
9.26
3.32
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


155.07
138.06
137.92
125.80
125.62
122.22
122.14
115.10
106.62
77.48
77.16
76.84
45.09
42.42
36.78
35.24
28.79

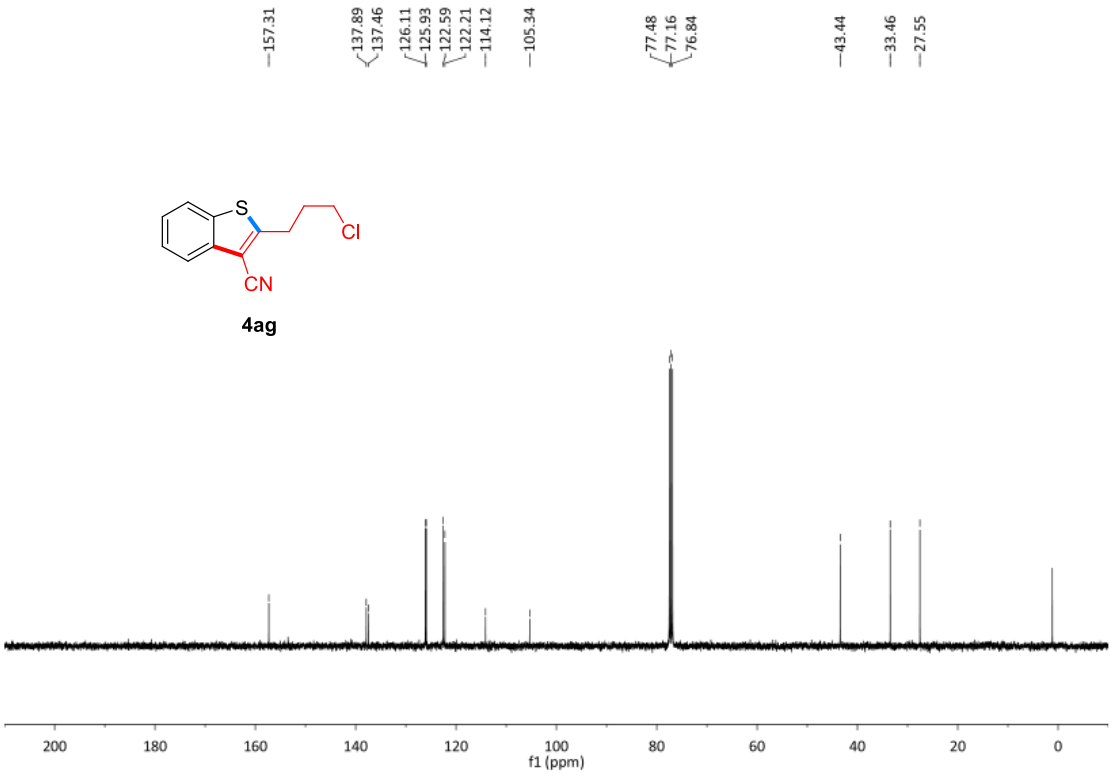

S
CN

4af

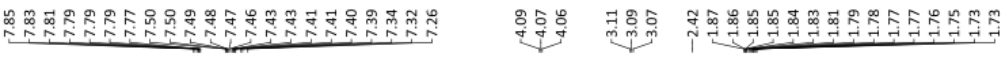

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

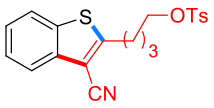

7.88
7.87
7.81
7.80
7.51
7.50
7.48
7.48
7.44
7.44
7.43
7.41
7.41
7.26
3.64
3.63
3.62
3.33
3.32
3.30
2.30
2.29
2.28
2.27
2.26
S
Cl
CN
1.00
1.00
1.02
1.00
2.03
2.07
2.13
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

4ag

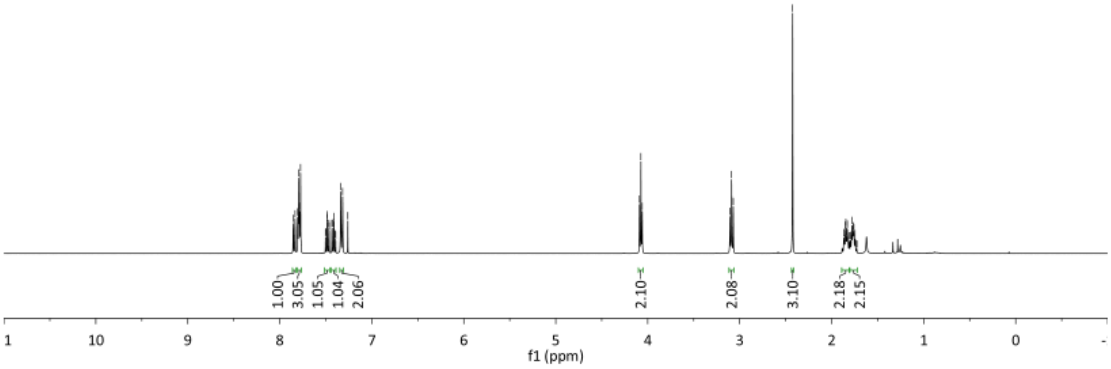

157.31
137.89
137.46
126.11
125.93
122.59
122.21
114.12
105.34
77.48
77.16
76.84
43.44
33.46
27.55
S
Cl
CN
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

4ag

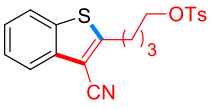

7.85
7.83
7.81
7.79
7.79
7.79
7.77
7.50
7.50
7.49
7.48
7.47
7.46
7.43
7.43
7.41
7.41
7.40
7.39
7.34
7.32
7.26
4.09
4.07
4.06
3.11
3.09
3.07
2.42
1.87
1.86
1.85
1.85
1.84
1.83
1.81
1.79
1.78
1.77
1.77
1.76
1.75
1.73
1.73


S
OTs
3
CN

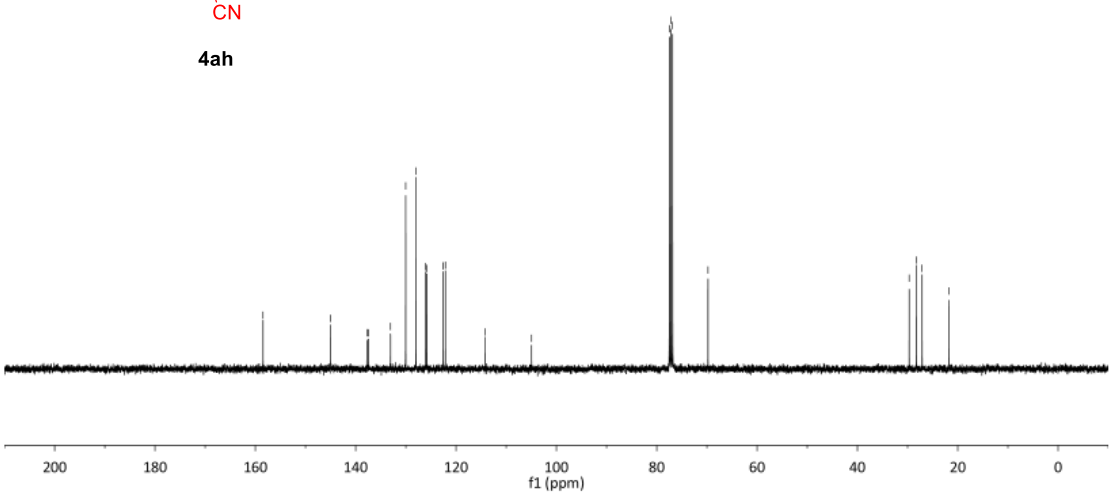
4ah

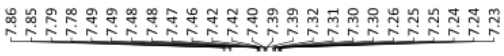

1.00
3.05
1.05
1.04
2.06
2.10
2.08
3.10
2.18
2.15
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

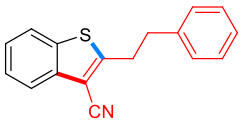

158.46
145.00
137.77
137.42
133.05
130.04
128.00
126.04
125.84
122.60
122.12
114.24
104.95
77.48
77.16
76.84
69.77
29.69
28.26
27.11
21.76


S
OTs
3
CN

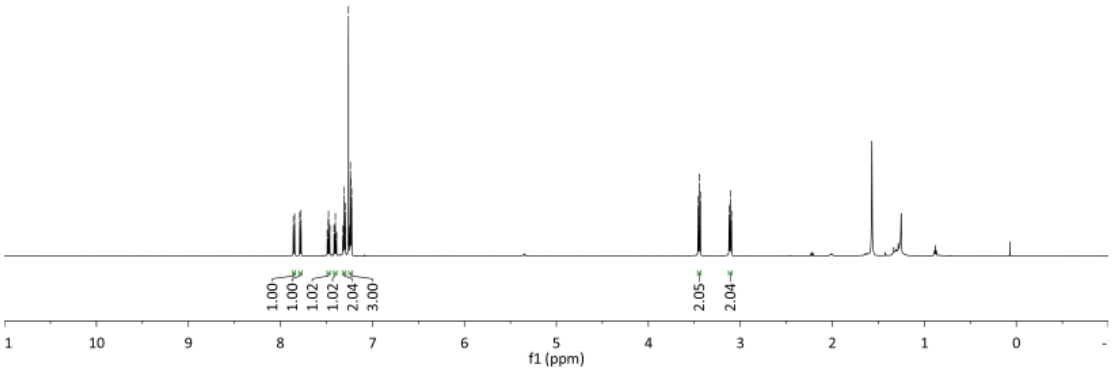
4ah

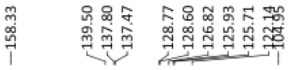

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

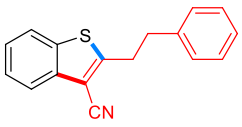

7.86
7.85
7.79
7.78
7.49
7.49
7.48
7.48
7.47
7.46
7.42
7.42
7.40
7.39
7.39
7.32
7.31
7.30
7.30
7.26
7.25
7.25
7.24
7.24
7.23
3.46
3.45
3.43
3.12
3.11
3.10


S
CN

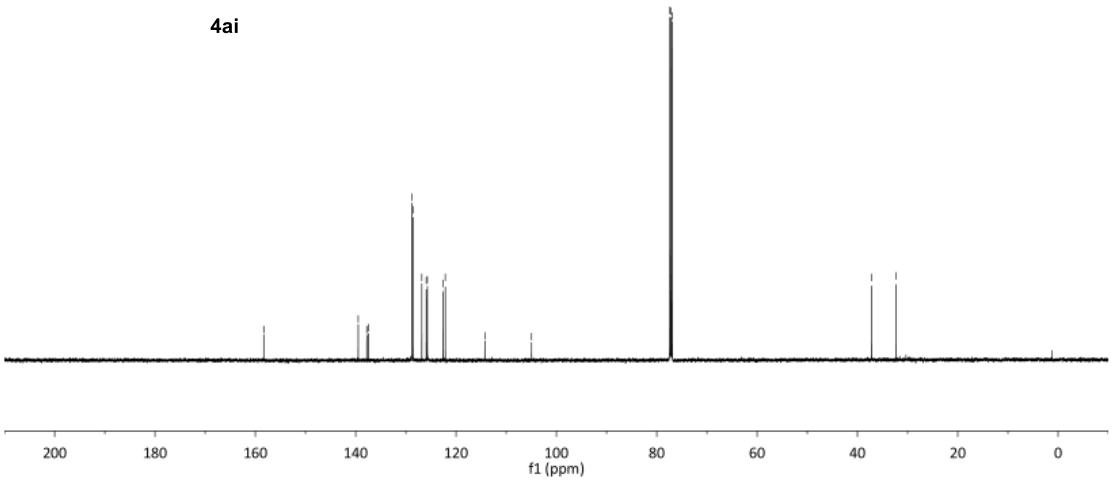
4ai

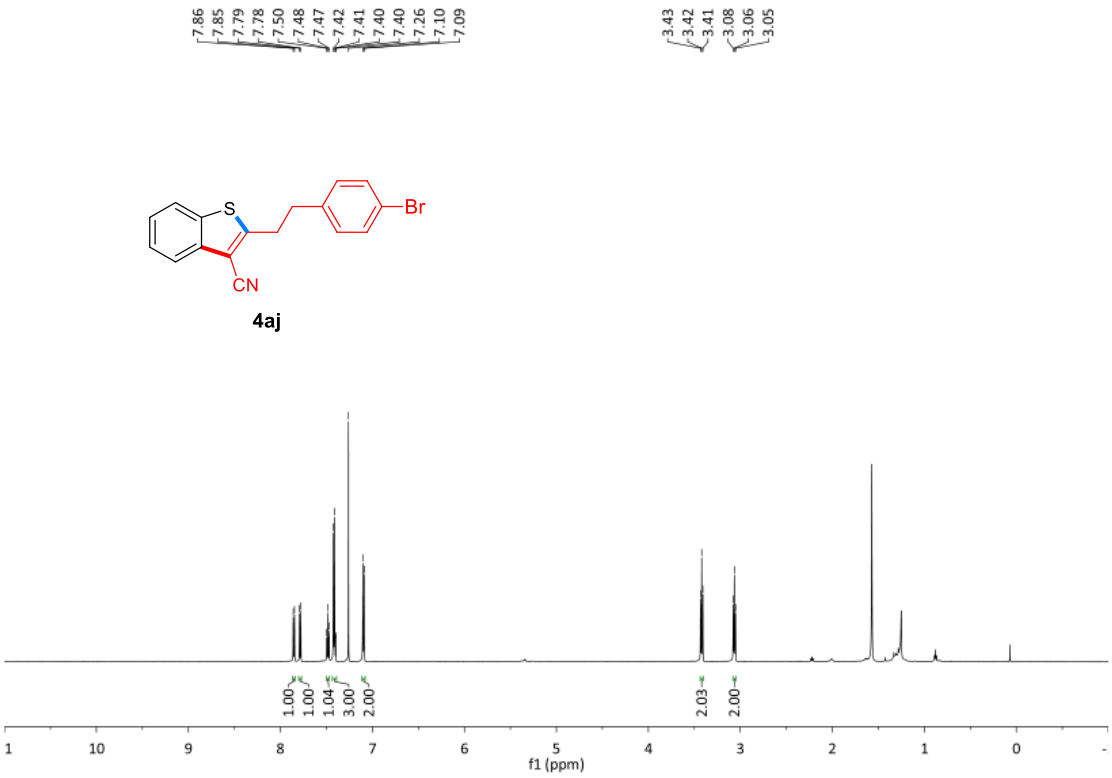

1.00
1.00
1.02
2.04
3.00
2.05
2.04
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


158.33
139.50
137.80
137.47
128.77
128.60
126.82
125.93
125.71
122.14
104.95
77.37
77.16
76.95
37.16
32.27

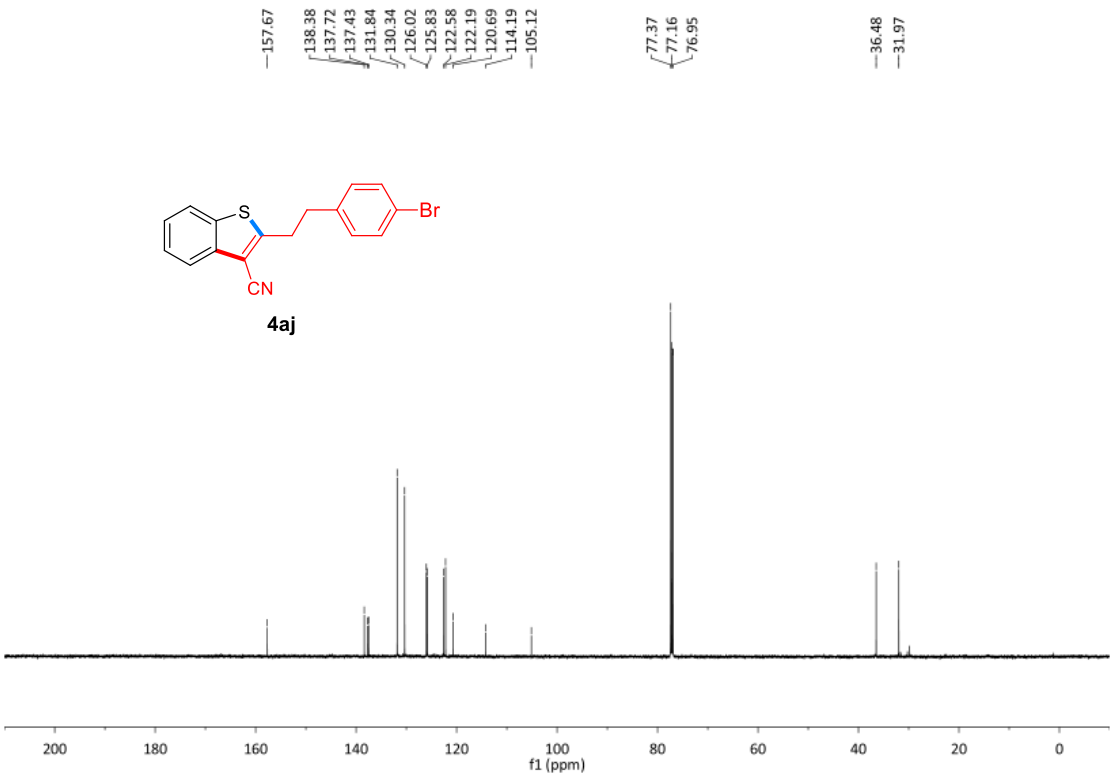

S
CN

4ai

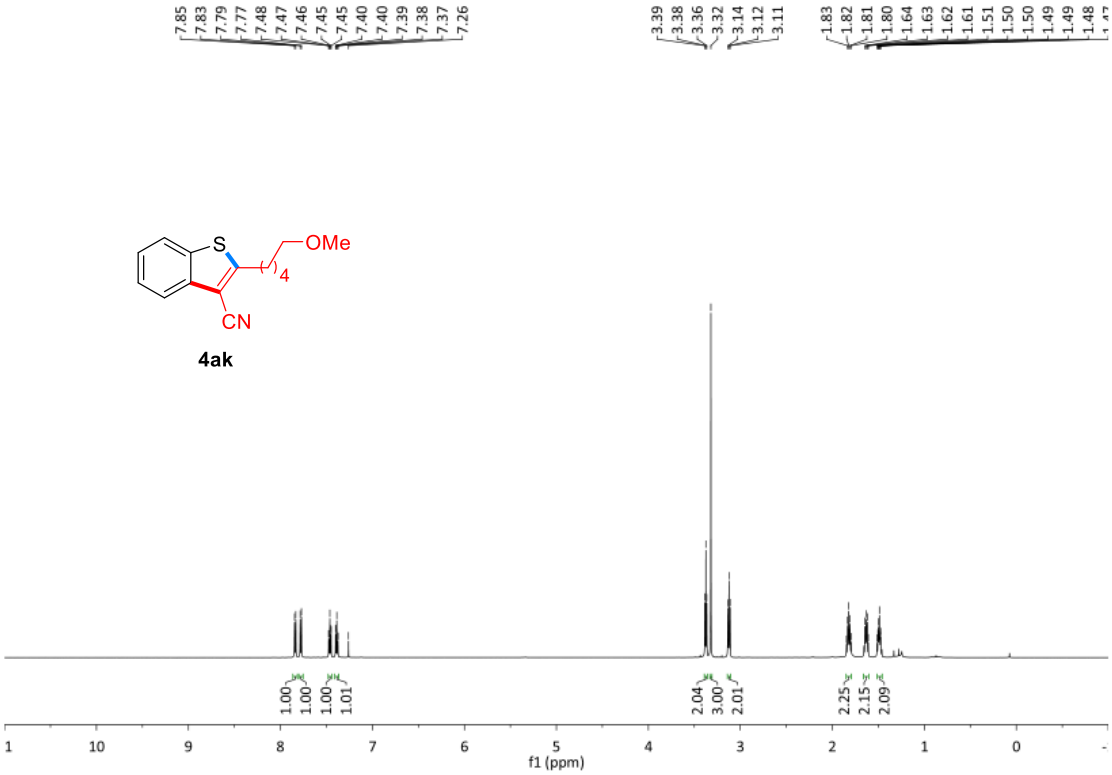

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

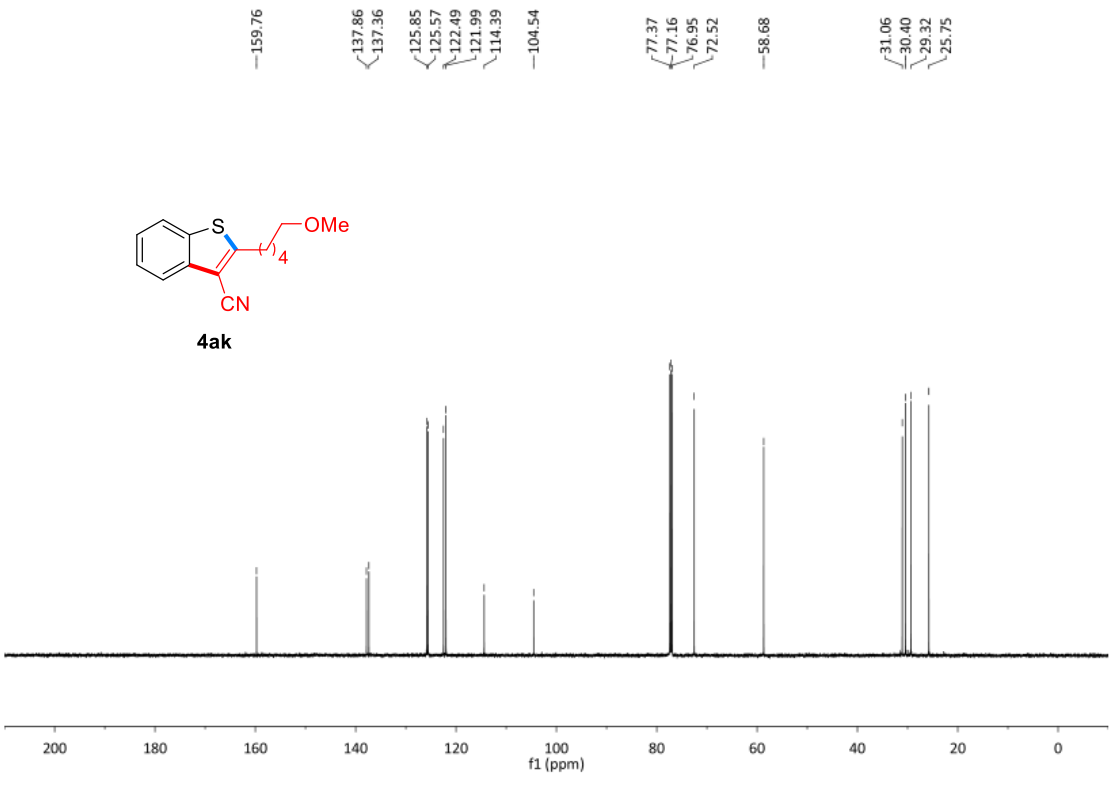

7.86
7.85
7.79
7.78
7.50
7.48
7.47
7.42
7.41
7.40
7.40
7.26
7.10
7.09
3.43
3.42
3.41
3.08
3.06
3.05
S
Br
CN
1.00
1.00
1.04
3.00
2.00
2.03
2.00
f1 (ppm)

4aj

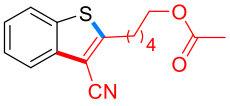

157.67
138.38
137.72
137.43
131.84
130.34
126.02
125.83
122.58
122.19
120.69
114.19
105.12
77.37
77.16
76.95
36.48
31.97
S
Br
CN
f1 (ppm)

4aj


7.85
7.83
7.79
7.77
7.48
7.47
7.46
7.45
7.45
7.40
7.40
7.39
7.38
7.37
7.26
3.39
3.38
3.36
3.32
3.14
3.12
3.11
1.83
1.82
1.81
1.80
1.64
1.63
1.62
1.61
1.51
1.50
1.50
1.49
1.49
1.48
S
OMe
4
CN
4ak
1.00
1.00
1.00
1.01
2.04
3.00
2.01
2.25
2.15
2.09
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


159.76
137.86
137.36
125.85
125.57
122.49
121.99
114.39
104.54
77.37
77.16
76.95
72.52
58.68
31.06
30.40
29.32
25.75
S
OMe
4
CN
4ak
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

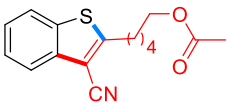

7.86
7.85
7.80
7.78
7.49
7.49
7.48
7.48
7.46
7.46
7.41
7.41
7.40
7.40
7.39
7.39
7.26
4.08
4.07
4.06
3.15
3.14
3.13
2.04
1.85
1.84
1.82
1.81
1.71
1.70
1.68
1.67
1.67
1.51
1.51
1.50
1.50
1.49
1.49


S
O
4
O
CN

4al

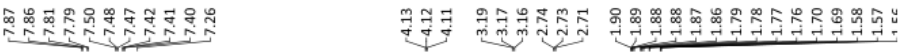
1.00
1.00
1.00
1.00
2.04
2.00
3.00
2.09
2.38
2.12
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

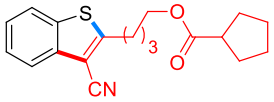

171.27
159.41
137.86
137.38
125.94
125.68
122.53
122.07
114.37
104.71
77.37
77.16
76.95
64.24
30.82
30.31
28.32
25.52
21.10


S
O
4
O
CN

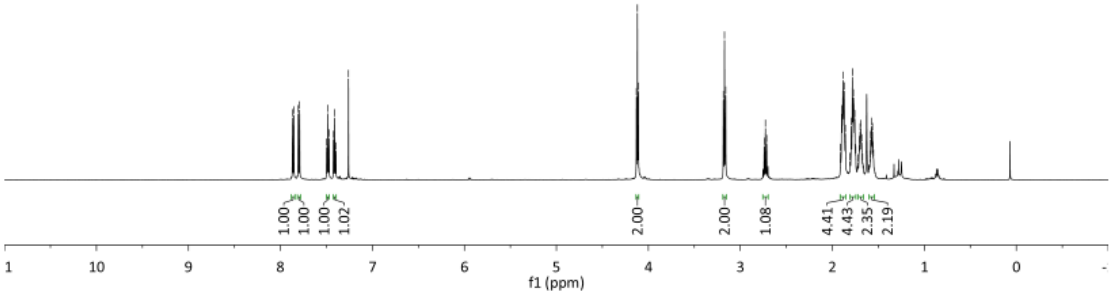
4al

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

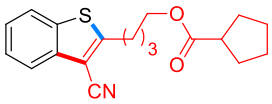

7.87
7.86
7.81
7.79
7.50
7.48
7.47
7.42
7.41
7.40
7.26
4.13
4.12
4.11
3.19
3.17
3.16
2.74
2.73
2.71
1.90
1.89
1.88
1.88
1.87
1.86
1.79
1.78
1.77
1.76
1.70
1.69
1.58
1.57


S
O
3
O
CN

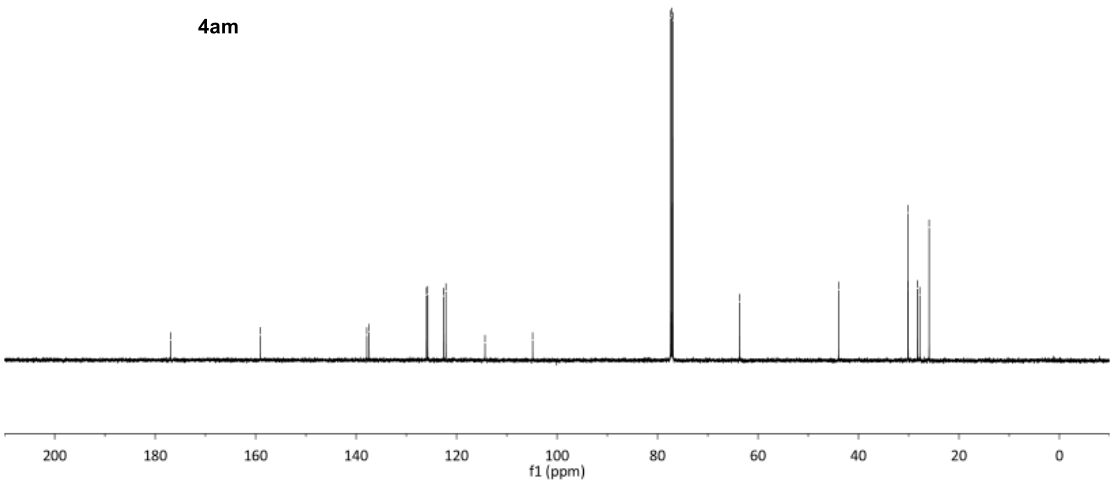
4am

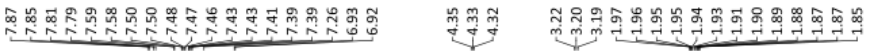

1.00
1.00
1.00
1.02
2.00
2.00
1.08
4.41
4.43
2.35
2.19
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

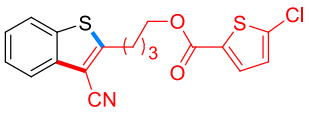

176.95
159.06
137.87
137.40
125.99
125.75
122.57
122.13
114.34
104.86
77.37
77.16
76.95
63.65
43.96
30.16
30.10
28.21
27.80
25.93


S
O
3
O
CN

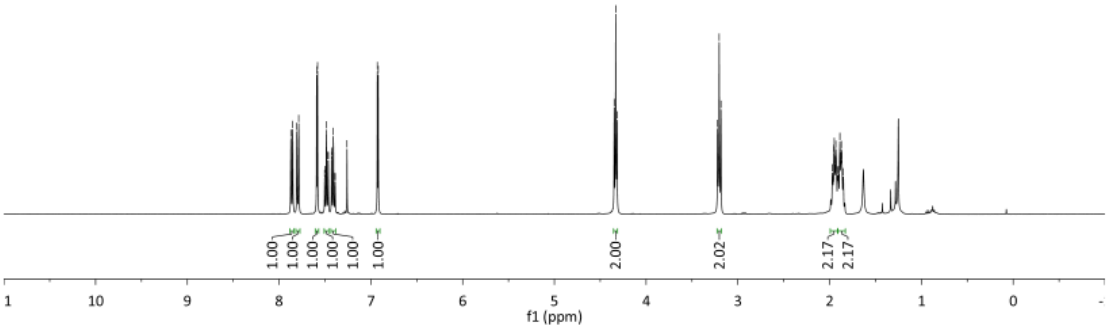
4am


200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

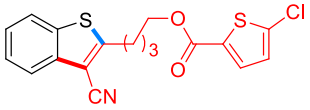

7.87
7.85
7.81
7.79
7.59
7.58
7.50
7.50
7.48
7.47
7.46
7.43
7.43
7.41
7.39
7.39
7.26
6.93
6.92
4.35
4.33
4.32
3.22
3.20
3.19
1.97
1.96
1.95
1.95
1.94
1.93
1.91
1.90
1.89
1.88
1.87
1.87
1.85


S
O
3
S
Cl
O
CN

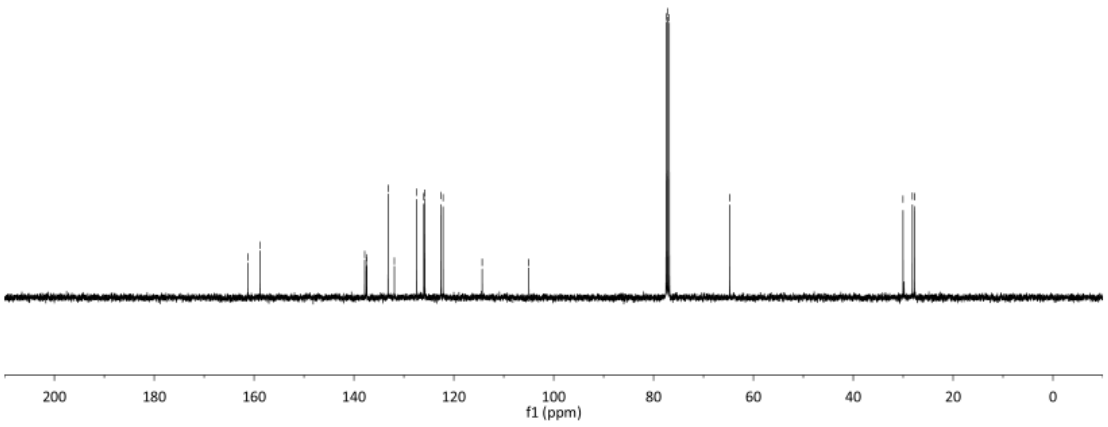
4an


1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.02
2.17
2.17
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

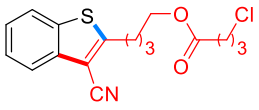

161.28
158.79
137.86
137.53
137.41
133.17
131.90
127.42
126.02
125.79
122.58
122.15
114.32
104.97
77.48
77.16
76.84
64.74
30.03
28.16
27.69


S
O
3
S
Cl
O
CN

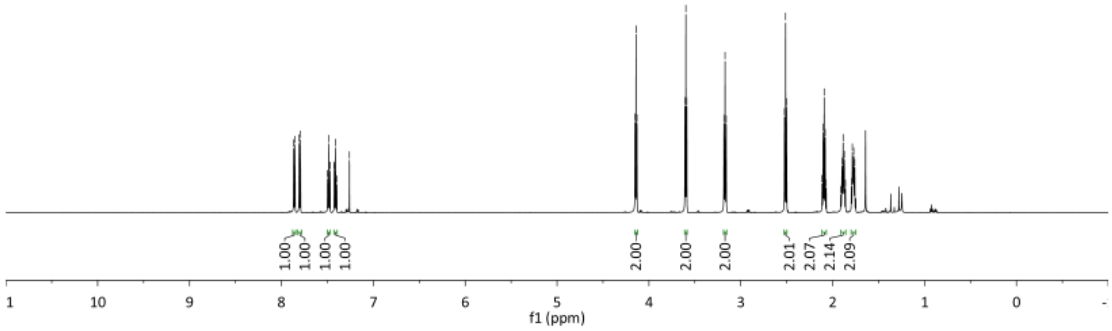
4an

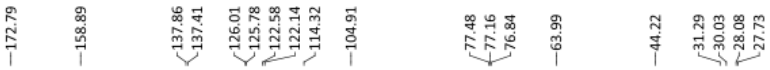

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

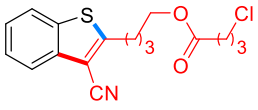

7.87
7.85
7.81
7.79
7.50
7.48
7.47
7.42
7.42
7.41
7.40
7.26
4.15
4.14
4.13
3.61
3.60
3.59
3.17
2.52
2.51
2.50
2.12
2.10
2.09
2.08
2.07
1.90
1.89
1.88
1.87
1.80
1.79
1.77
1.77


S
O
Cl
3
3
O
CN

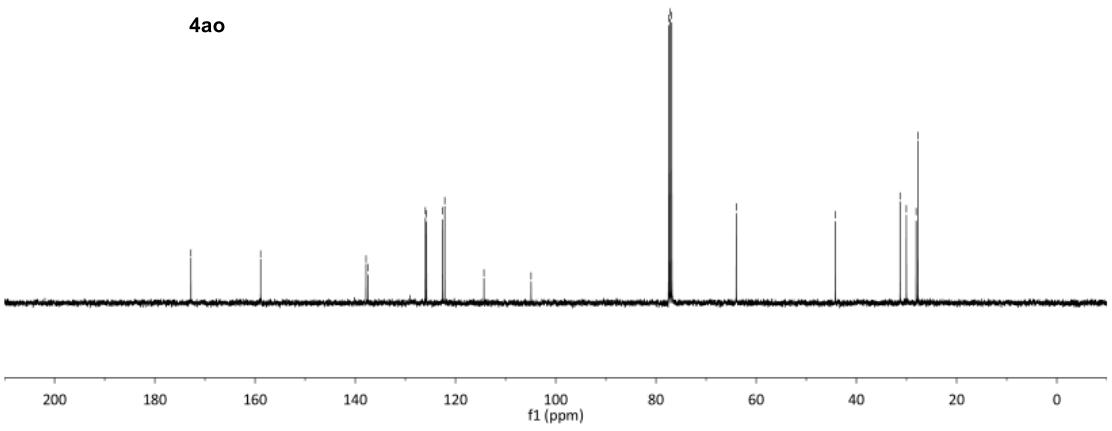
4ao

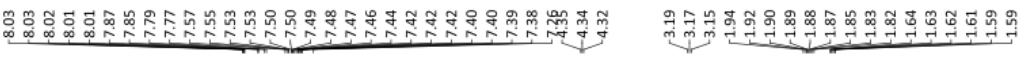

1.00
1.00
1.00
1.00
2.00
2.00
2.00
2.01
2.07
2.14
2.09
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


172.79
158.89
137.86
137.41
126.01
125.78
122.58
122.14
114.32
104.91
77.48
77.16
76.84
63.99
44.22
31.29
30.03
28.08
27.73


S
O
Cl
3
3
O
CN

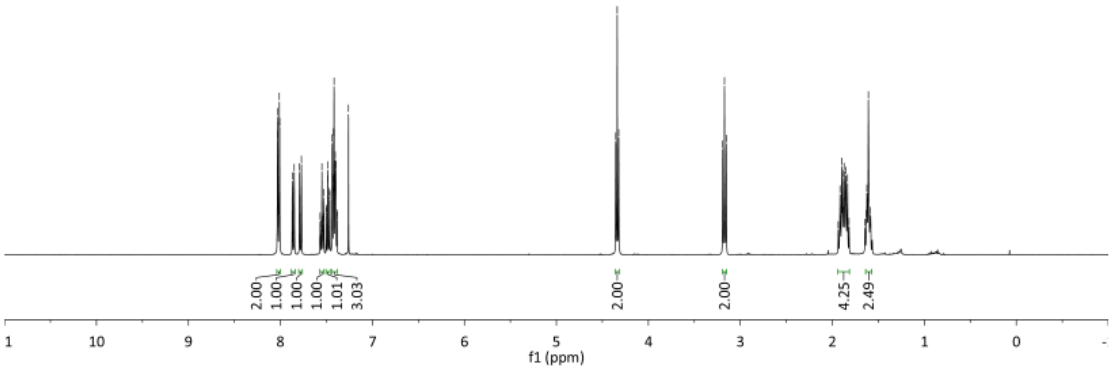
4ao


200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.03
8.03
8.02
8.01
8.01
7.87
7.85
7.79
7.77
7.57
7.55
7.53
7.53
7.50
7.50
7.49
7.48
7.47
7.46
7.44
7.42
7.42
7.42
7.40
7.40
7.39
7.38
7.35
4.35
4.34
4.32
3.19
3.17
3.15
1.94
1.92
1.90
1.89
1.88
1.87
1.85
1.83
1.82
1.64
1.63
1.62
1.61
1.59
1.59


S
O
4
O
CN

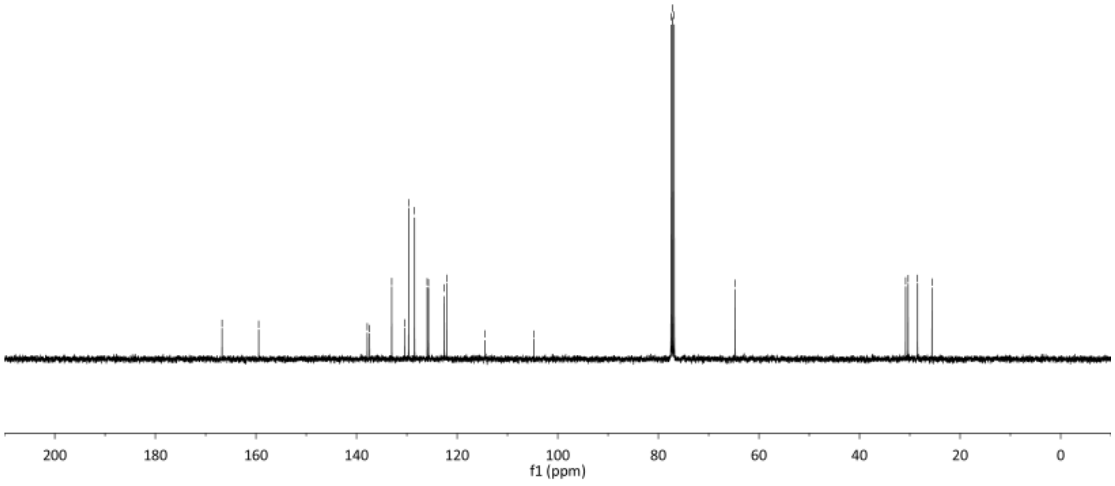
4ap

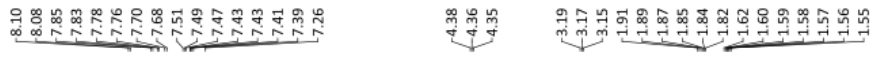

2.00
1.00
1.00
1.00
1.01
3.03
2.00
2.00
4.25
2.49
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

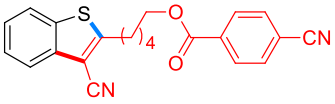

166.75
159.46
137.87
137.39
133.01
130.42
129.66
128.47
125.96
125.69
122.56
122.10
114.43
104.74
77.48
77.16
76.84
64.70
30.83
30.33
28.46
25.61


S
O
4
O
CN

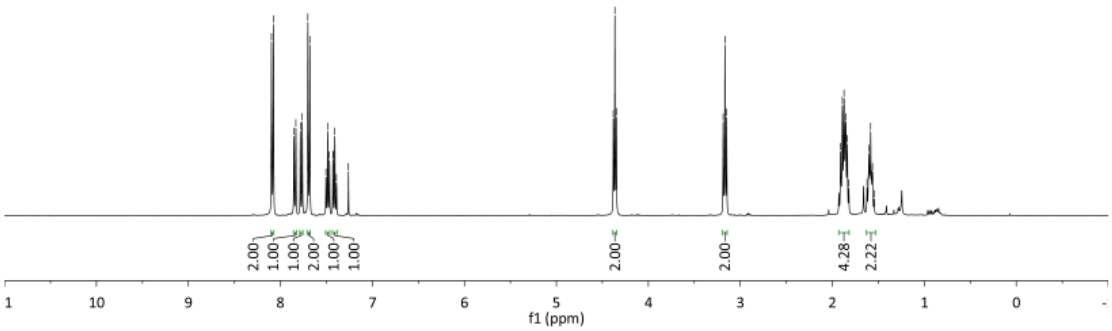
4ap

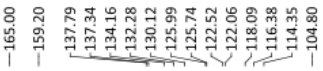

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

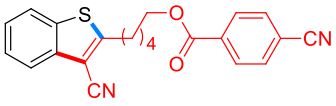

8.10
8.08
7.85
7.83
7.78
7.76
7.70
7.68
7.51
7.49
7.47
7.43
7.43
7.41
7.39
7.26
4.38
4.36
4.35
3.19
3.17
3.15
1.91
1.89
1.87
1.85
1.84
1.82
1.62
1.60
1.59
1.58
1.57
1.56
1.55


S
O
4
O
CN
CN

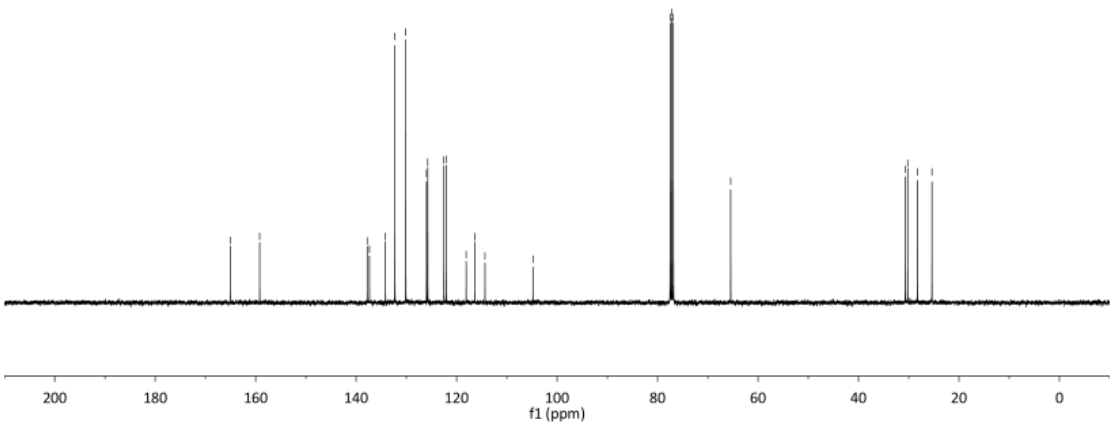
4aq


2.00
1.00
1.00
2.00
1.00
1.00
2.00
2.00
4.28
2.22
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


165.00
159.20
137.79
137.34
134.16
132.28
130.12
125.99
125.74
122.52
122.06
118.09
116.38
114.35
104.80
77.48
77.16
76.84
65.44
30.67
30.21
28.27
25.38


S
O
4
O
CN
CN

4aq


200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.87
7.85
7.80
7.79
7.50
7.50
7.48
7.47
7.47
7.42
7.42
7.41
7.40
7.40
7.26
4.20
4.19
4.18
3.92
3.91
3.19
3.18
3.16
1.97
1.96
1.92
1.90
1.83
1.82
0.95
0.94


S
O
3
O
O
CN

4ar

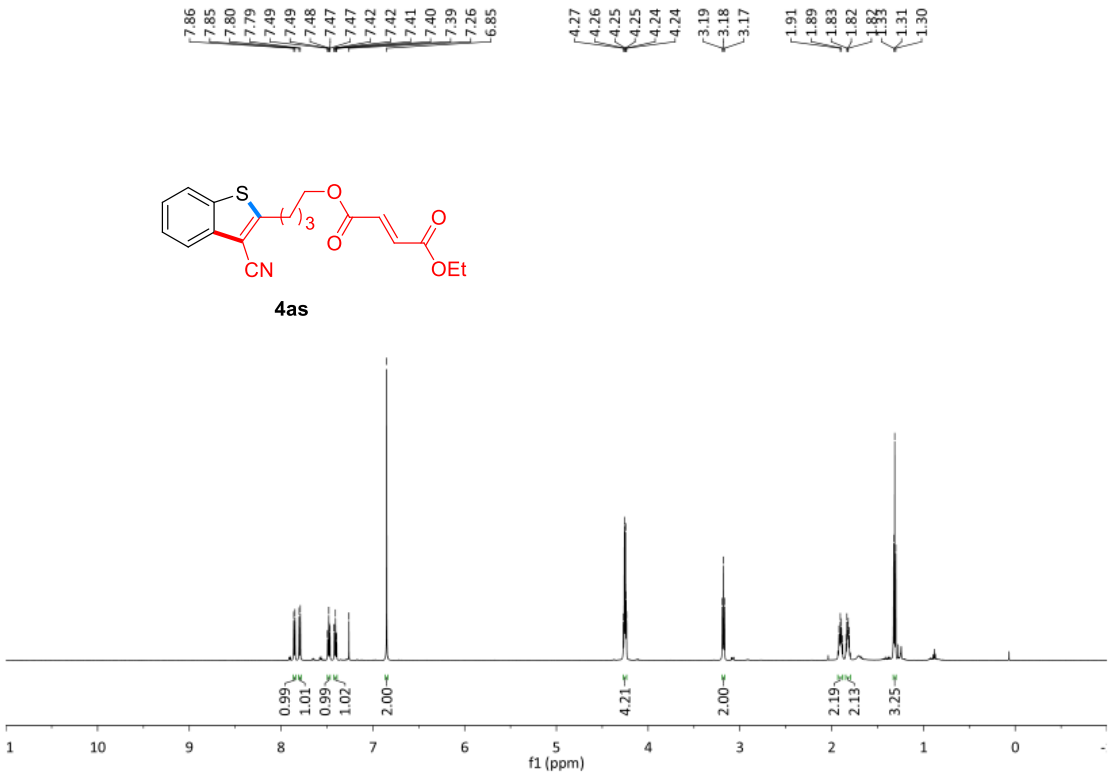
1.00
1.01
1.00
1.00
2.01
2.00
2.00
1.05
2.16
2.14
6.11
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


158.85
155.50
137.88
137.45
126.01
125.78
122.58
122.17
114.32
104.95
77.48
77.16
76.84
74.25
67.24
30.05
28.25
27.91
27.55
19.06

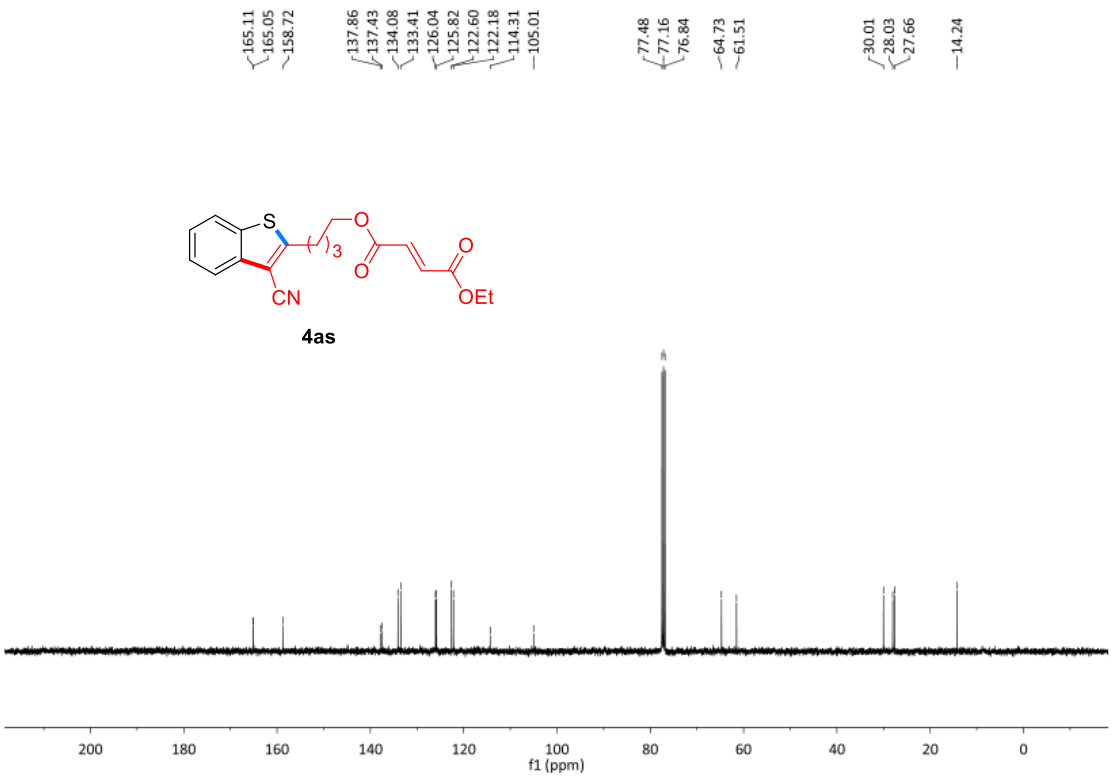

S
O
3
O
O
CN

4ar

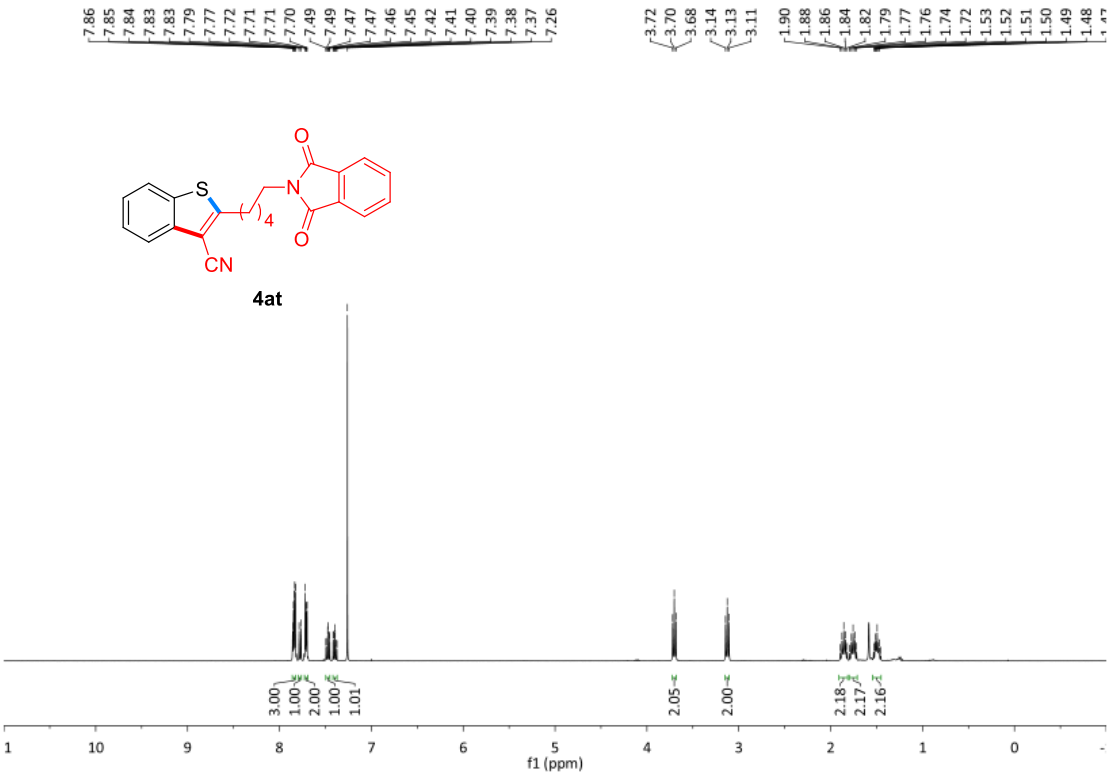
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

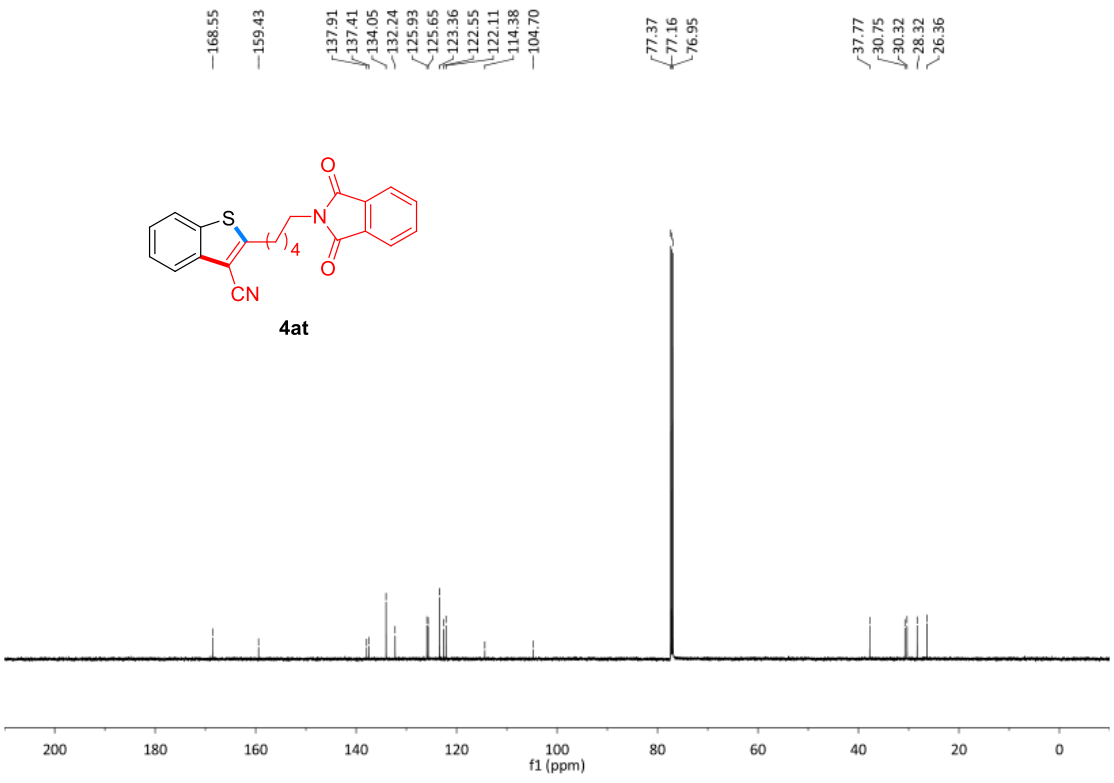

7.86
7.85
7.80
7.79
7.49
7.49
7.48
7.47
7.47
7.42
7.42
7.41
7.40
7.39
7.26
6.85
4.27
4.26
4.25
4.25
4.24
4.24
3.19
3.18
3.17
1.91
1.89
1.83
1.82
1.33
1.31
1.30
S
O
3
O
O
CN
OEt
0.99
1.01
0.99
1.02
2.00
4.21
2.00
2.19
2.13
3.25
f1 (ppm)

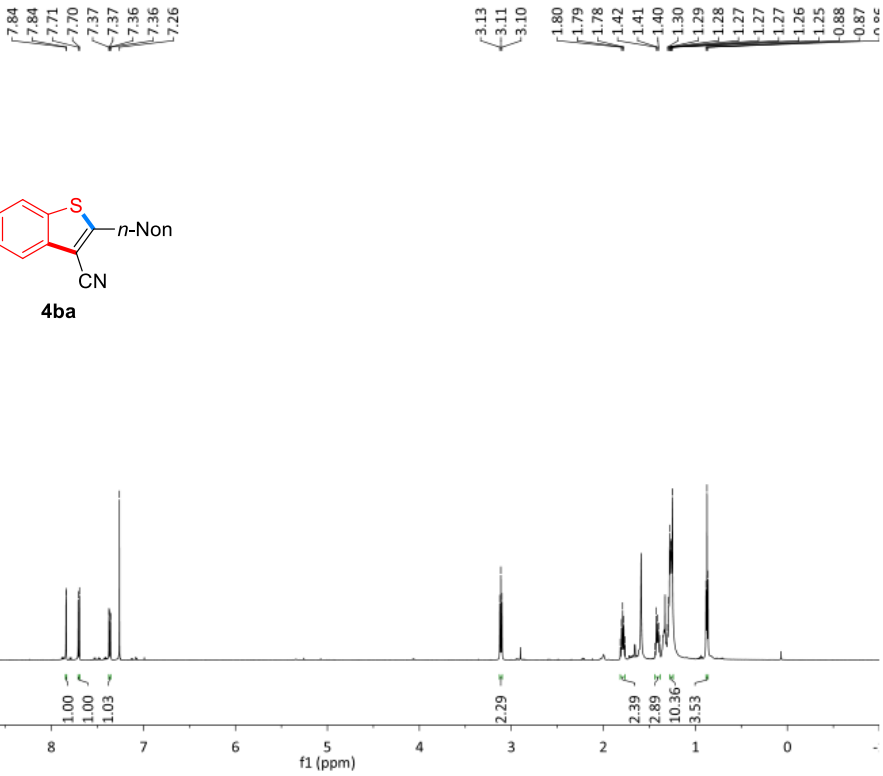
4as

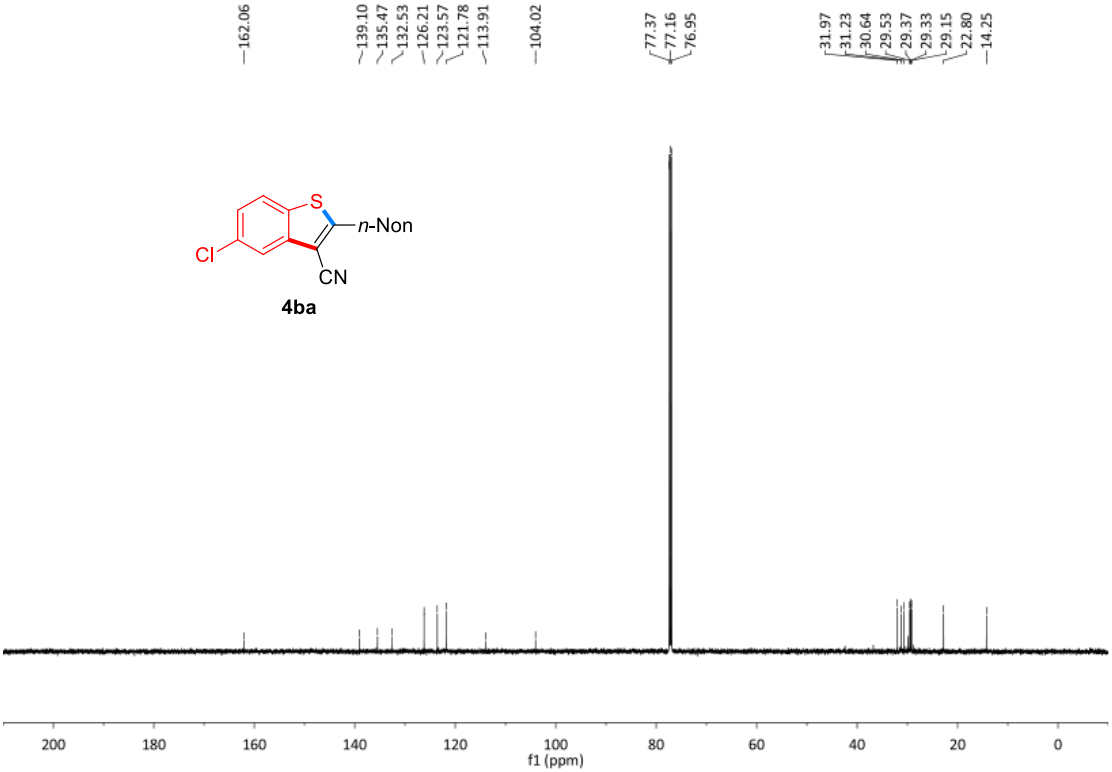

165.11
165.05
158.72
137.86
137.43
134.08
133.41
126.04
125.82
122.60
122.18
114.31
105.01
77.48
77.16
76.84
64.73
61.51
30.01
28.03
27.66
14.24
S
O
3
O
O
CN
OEt
f1 (ppm)

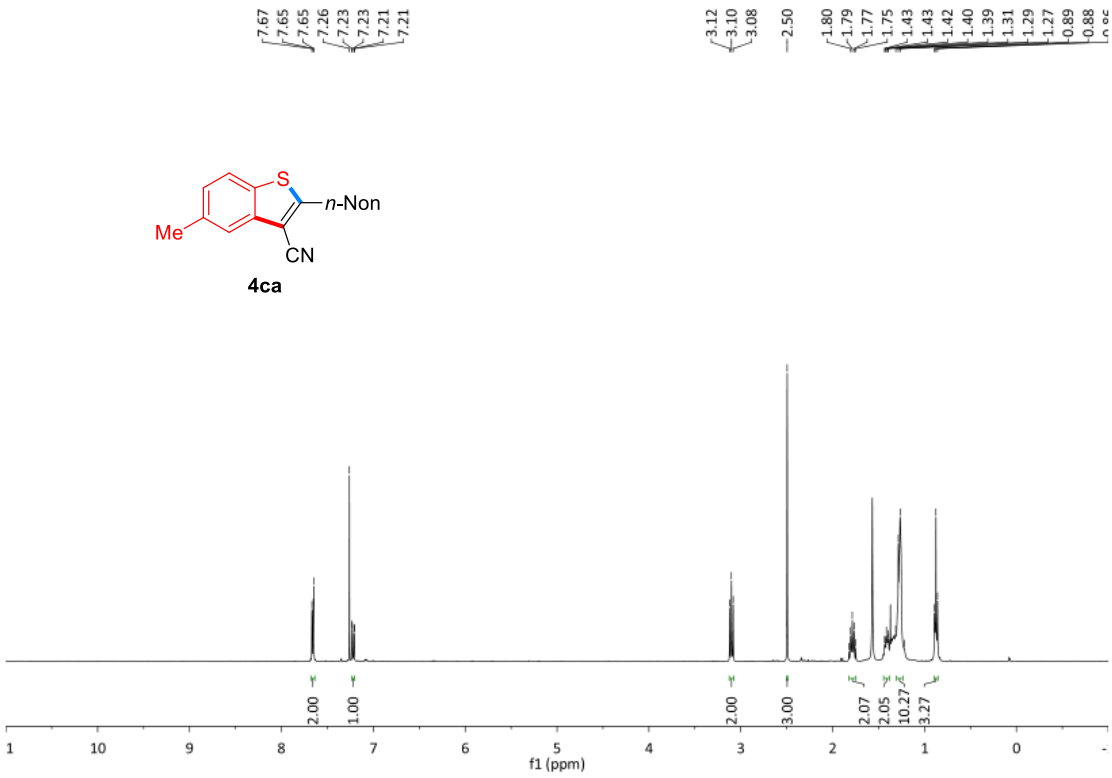
4as

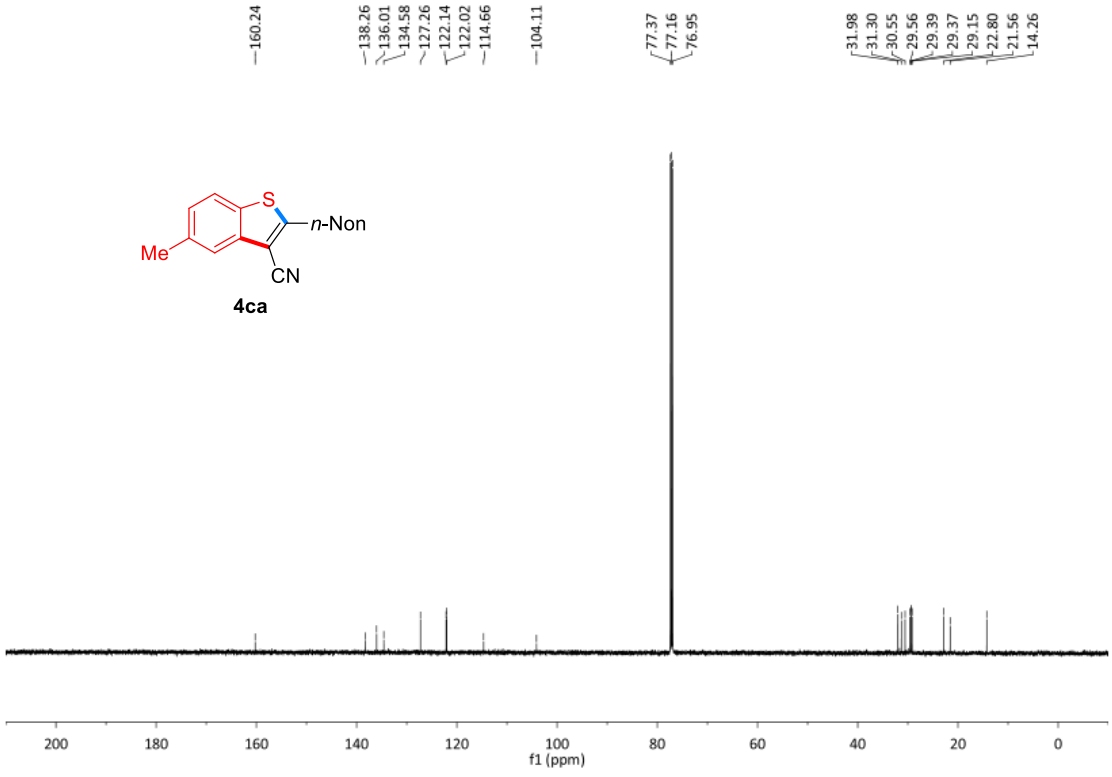

7.86
7.85
7.84
7.83
7.83
7.79
7.77
7.72
7.71
7.71
7.70
7.49
7.49
7.47
7.47
7.46
7.45
7.42
7.41
7.40
7.39
7.38
7.37
7.26
3.72
3.70
3.68
3.14
3.13
3.11
1.90
1.88
1.86
1.84
1.82
1.79
1.77
1.76
1.74
1.72
1.53
1.52
1.51
1.50
1.49
1.48
S
N
O
O
4
CN
4at
3.00
1.00
2.00
1.00
1.01
2.05
2.00
2.18
2.17
2.16
f1 (ppm)

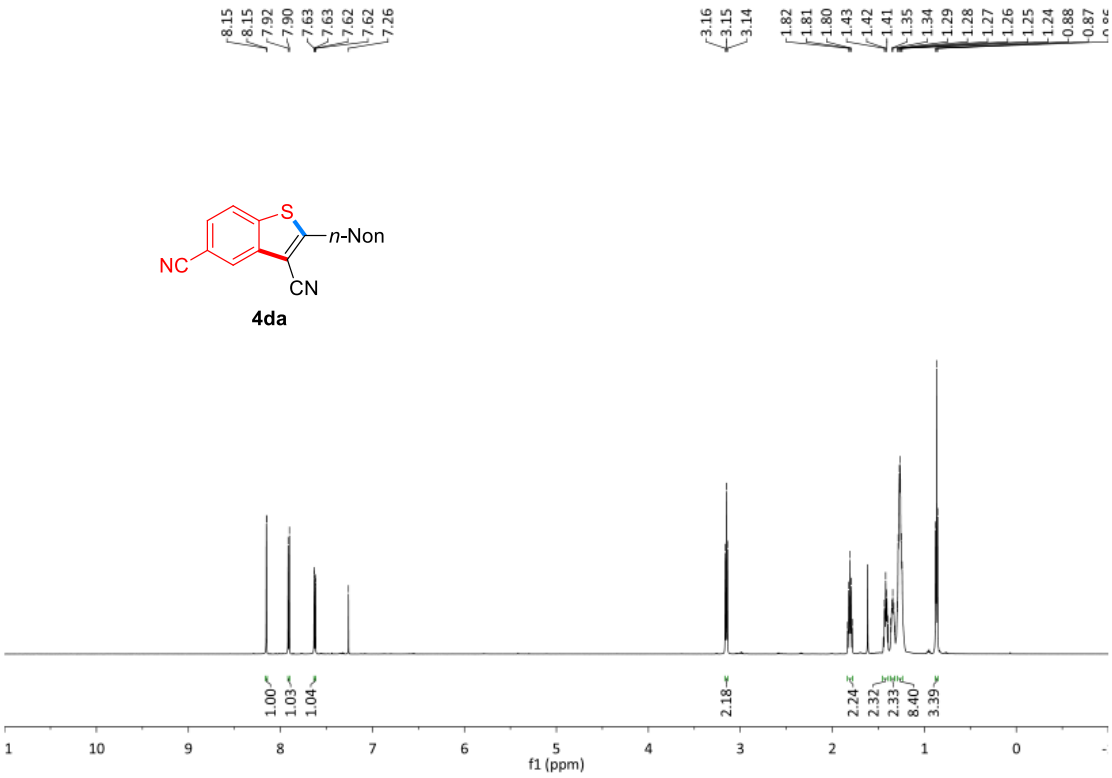

168.55
159.43
137.91
137.41
134.05
132.24
125.93
125.65
123.36
122.55
122.11
114.38
104.70
77.37
77.16
76.95
37.77
30.75
30.32
28.32
26.36
S
N
O
O
4
CN
4at
f1 (ppm)

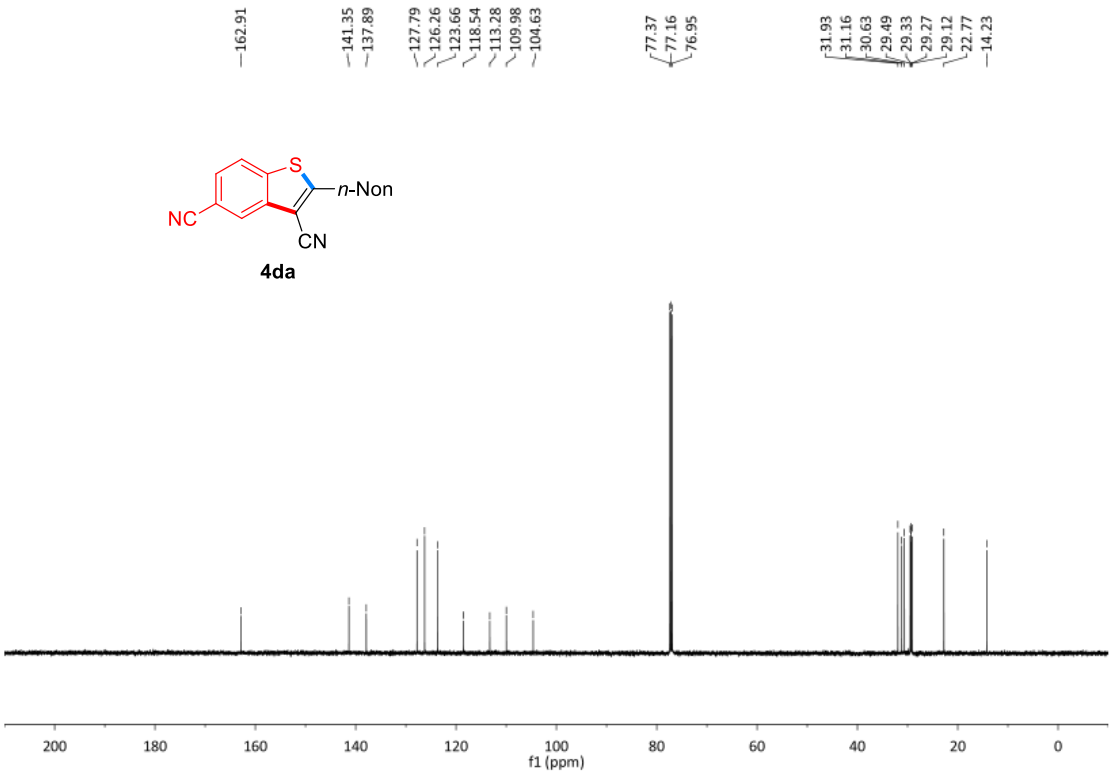

7.84
7.84
7.71
7.70
7.37
7.37
7.36
7.36
7.26
3.13
3.11
3.10
1.80
1.79
1.78
1.42
1.41
1.40
1.30
1.29
1.28
1.27
1.27
1.27
1.26
1.25
0.88
0.87
S
n-Non
Cl
CN
4ba
1.00
1.00
1.03
2.29
2.39
2.89
10.36
3.53
f1 (ppm)

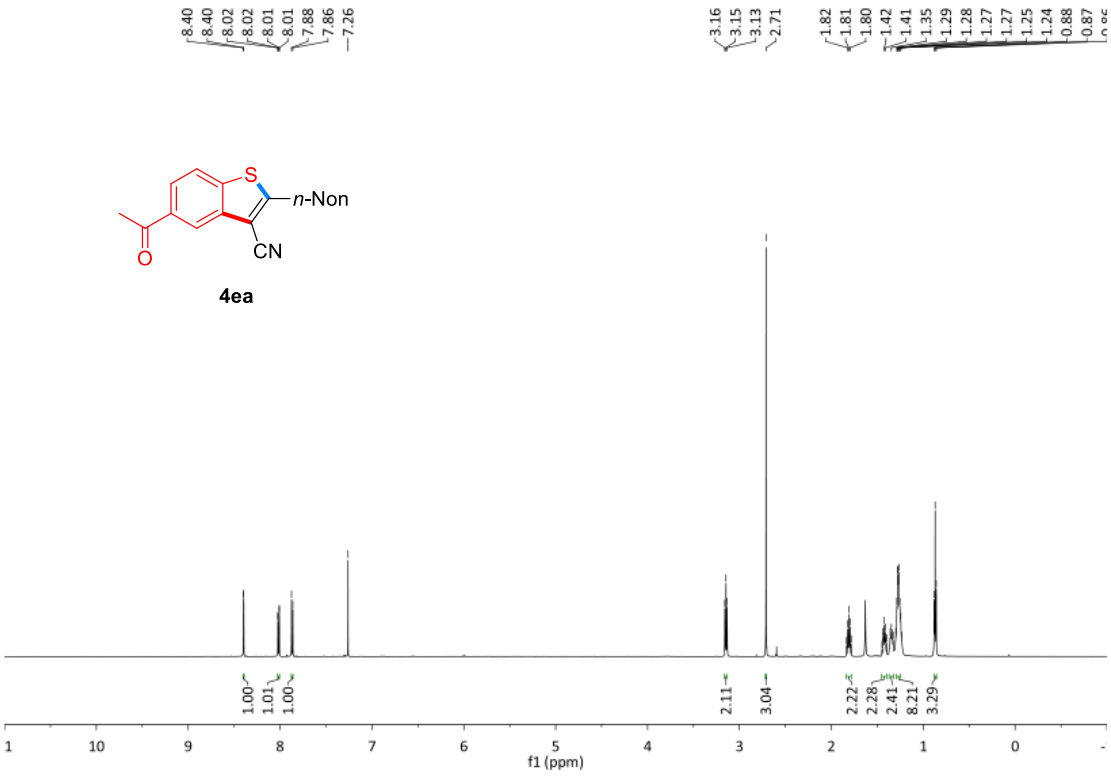

162.06
139.10
135.47
132.53
126.21
123.57
121.78
113.91
104.02
77.37
77.16
76.95
31.97
31.23
30.64
29.53
29.37
29.33
29.15
22.80
14.25
S
n-Non
Cl
CN
4ba
f1 (ppm)

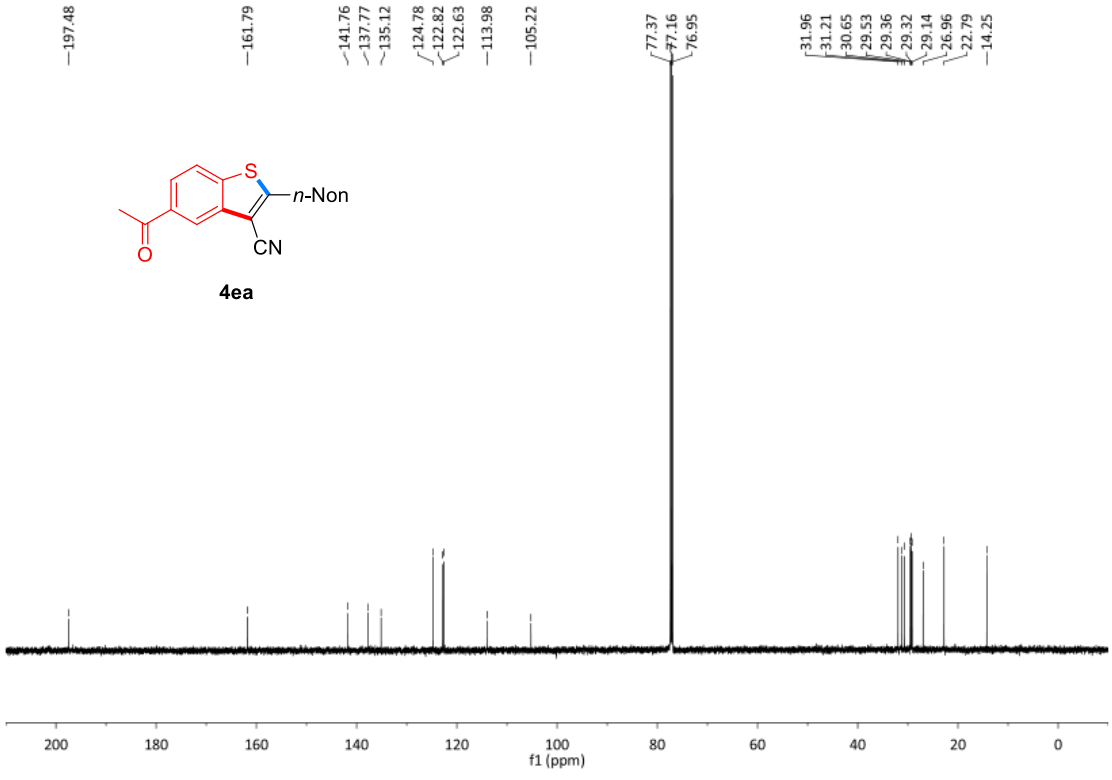

7.67
7.65
7.65
7.26
7.23
7.23
7.21
7.21
3.12
3.10
3.08
2.50
1.80
1.79
1.77
1.75
1.43
1.42
1.40
1.39
1.31
1.29
1.27
0.89
0.88
S
n-Non
Me
CN
4ca
2.00
1.00
2.00
3.00
2.07
2.05
10.27
3.27
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

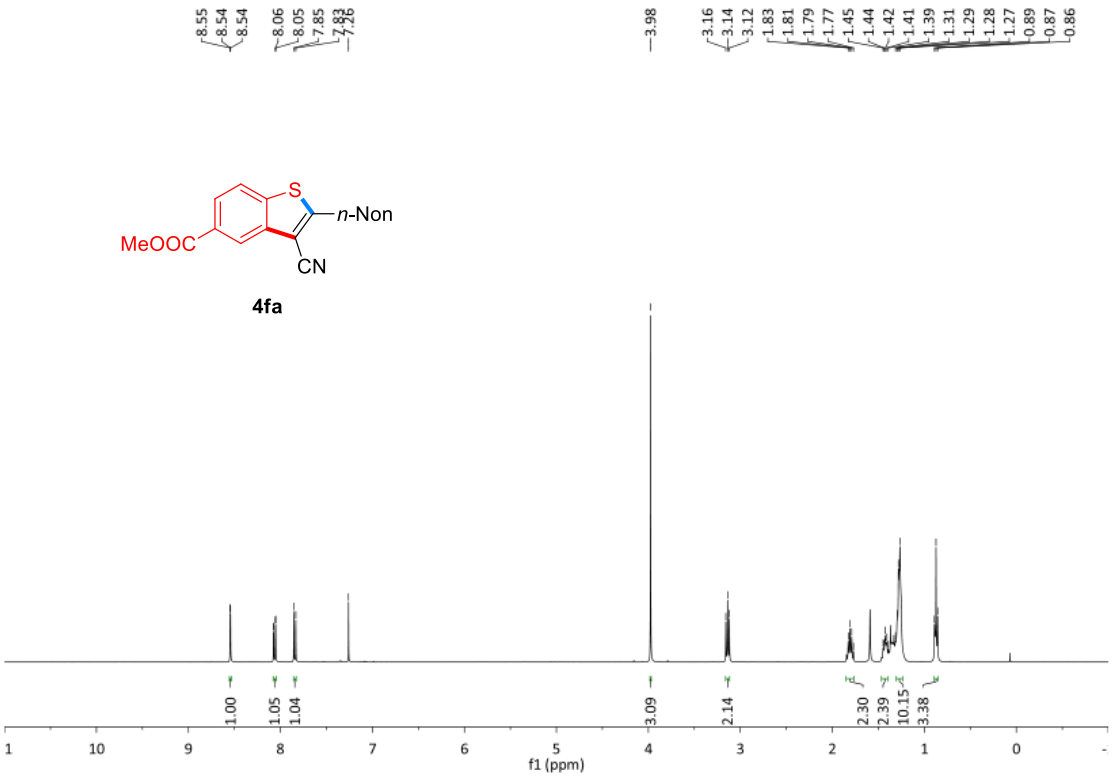

160.24
138.26
136.01
134.58
127.26
122.14
122.02
114.66
104.11
77.37
77.16
76.95
31.98
31.30
30.55
29.56
29.39
29.37
29.15
22.80
21.56
14.26
S
n-Non
Me
CN
4ca
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

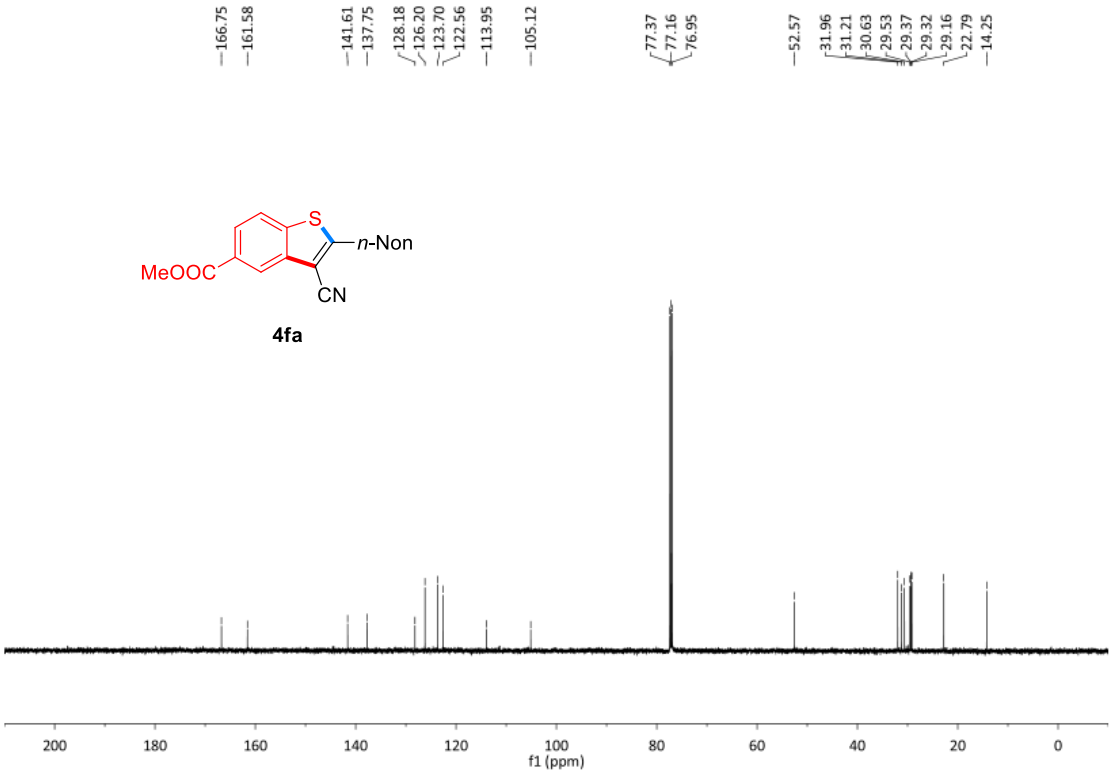

8.15
8.15
7.92
7.90
7.63
7.63
7.62
7.62
7.26
3.16
3.15
3.14
1.82
1.81
1.80
1.43
1.42
1.41
1.35
1.34
1.29
1.28
1.27
1.26
1.25
1.24
0.88
0.87
S
n-Non
NC
CN
4da
1.00
1.03
1.04
2.18
2.24
2.32
2.33
8.40
3.39
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

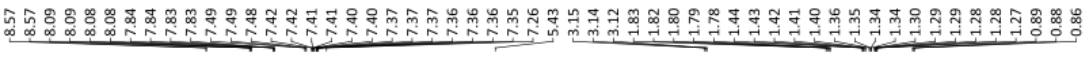

162.91
141.35
137.89
127.79
126.26
123.66
118.54
113.28
109.98
104.63
77.37
77.16
76.95
31.93
31.16
30.63
29.49
29.33
29.27
29.12
22.77
14.23
S
n-Non
NC
CN
4da
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

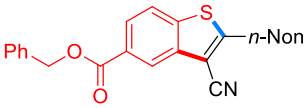

8.40
8.40
8.02
8.02
8.01
8.01
7.88
7.86
7.26
3.16
3.15
3.13
2.71
1.82
1.81
1.80
1.42
1.41
1.35
1.29
1.28
1.27
1.27
1.25
1.24
0.88
0.87
S
n-Non
CN
O
4ea
1.00
1.01
1.00
2.11
3.04
2.22
2.28
2.41
8.21
3.29
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


197.48
161.79
141.76
137.77
135.12
124.78
122.82
122.63
113.98
105.22
77.37
77.16
76.95
31.96
31.21
30.65
29.53
29.36
29.32
29.14
26.96
22.79
14.25
S
n-Non
CN
O
4ea
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

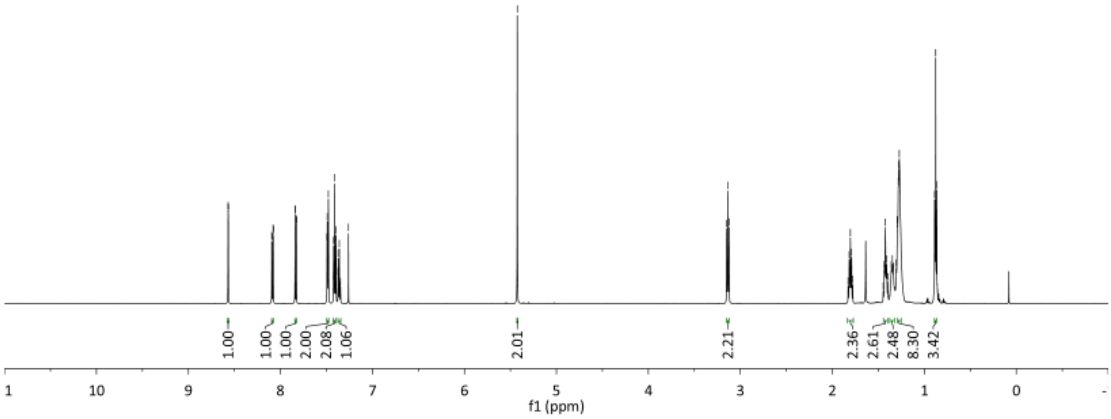

8.55
8.54
8.54
8.06
8.05
7.85
7.83
7.26
3.98
3.16
3.14
3.12
1.83
1.81
1.79
1.77
1.45
1.44
1.42
1.41
1.39
1.31
1.29
1.28
1.27
0.89
0.87
0.86
S
n-Non
MeOOC
CN
4fa
1.00
1.05
1.04
3.09
2.14
2.30
2.39
10.15
3.38
f1 (ppm)


166.75
161.58
141.61
137.75
128.18
126.20
123.70
122.56
113.95
105.12
77.37
77.16
76.95
52.57
31.96
31.21
30.63
29.53
29.37
29.32
29.16
22.79
14.25
S
n-Non
MeOOC
CN
4fa
f1 (ppm)

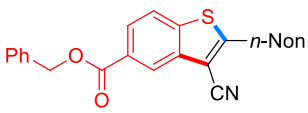

8.57
8.57
8.09
8.09
8.08
8.08
7.84
7.84
7.83
7.83
7.49
7.49
7.48
7.42
7.42
7.41
7.41
7.40
7.40
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.26
5.43
3.15
3.14
3.12
1.83
1.82
1.80
1.79
1.78
1.44
1.43
1.42
1.41
1.40
1.36
1.35
1.34
1.34
1.30
1.29
1.29
1.28
1.28
1.27
0.89
0.88
0.86


Ph
O
O
S
n-Non
CN

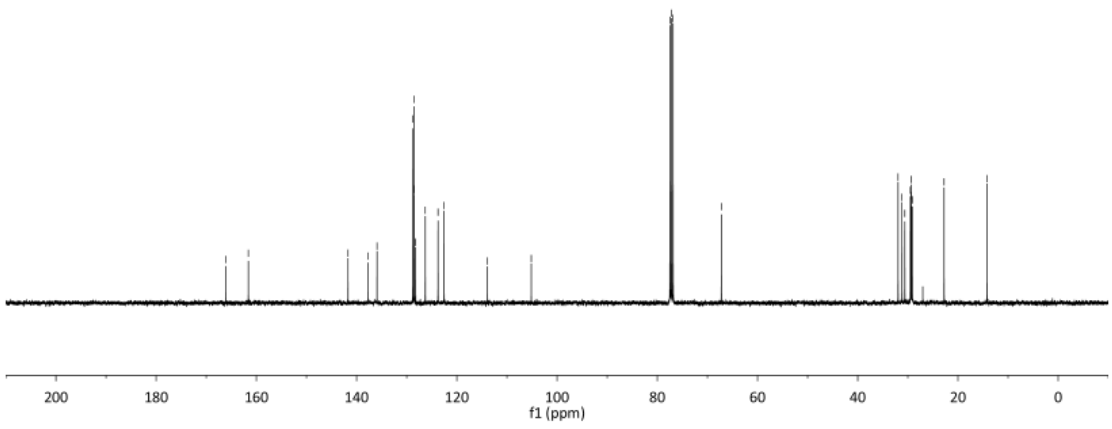
4ga

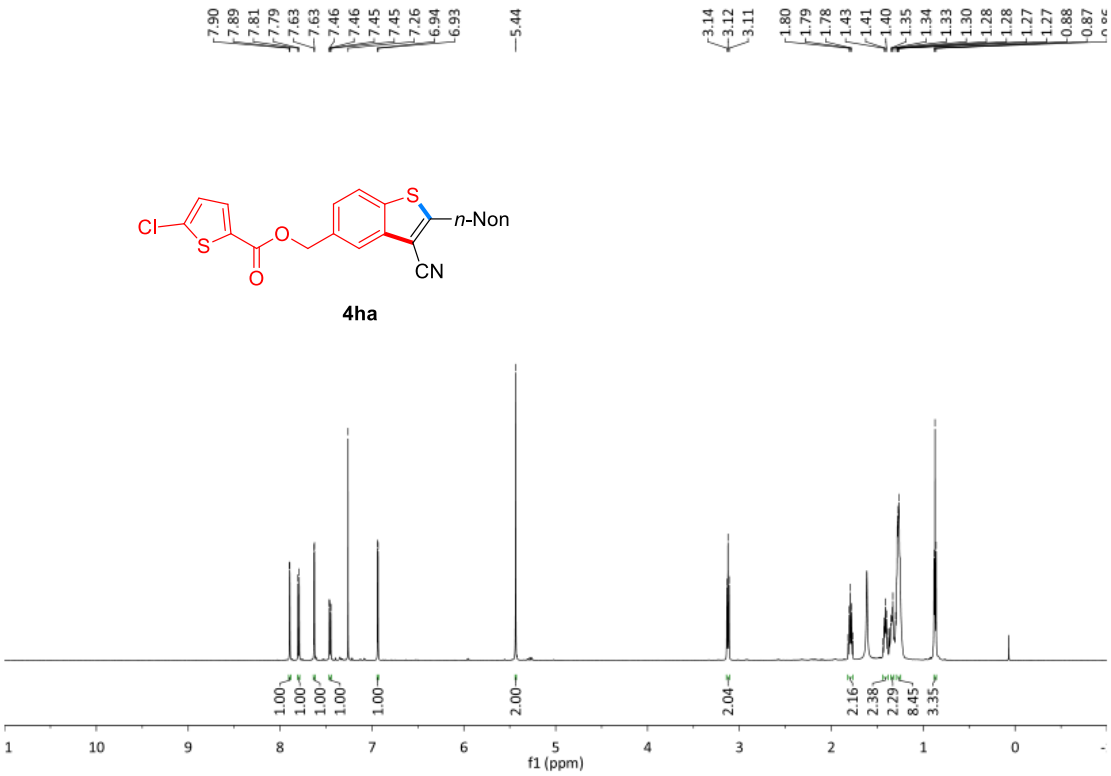

1.00
1.00
1.00
2.08
1.06
2.01
2.21
2.36
2.61
2.48
8.30
3.42
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


166.09
161.60
141.71
137.72
135.93
128.80
128.52
128.49
128.21
126.29
123.76
122.54
113.89
105.14
77.48
77.16
76.84
67.22
31.94
31.17
30.60
29.50
29.34
29.30
29.12
22.76
14.22

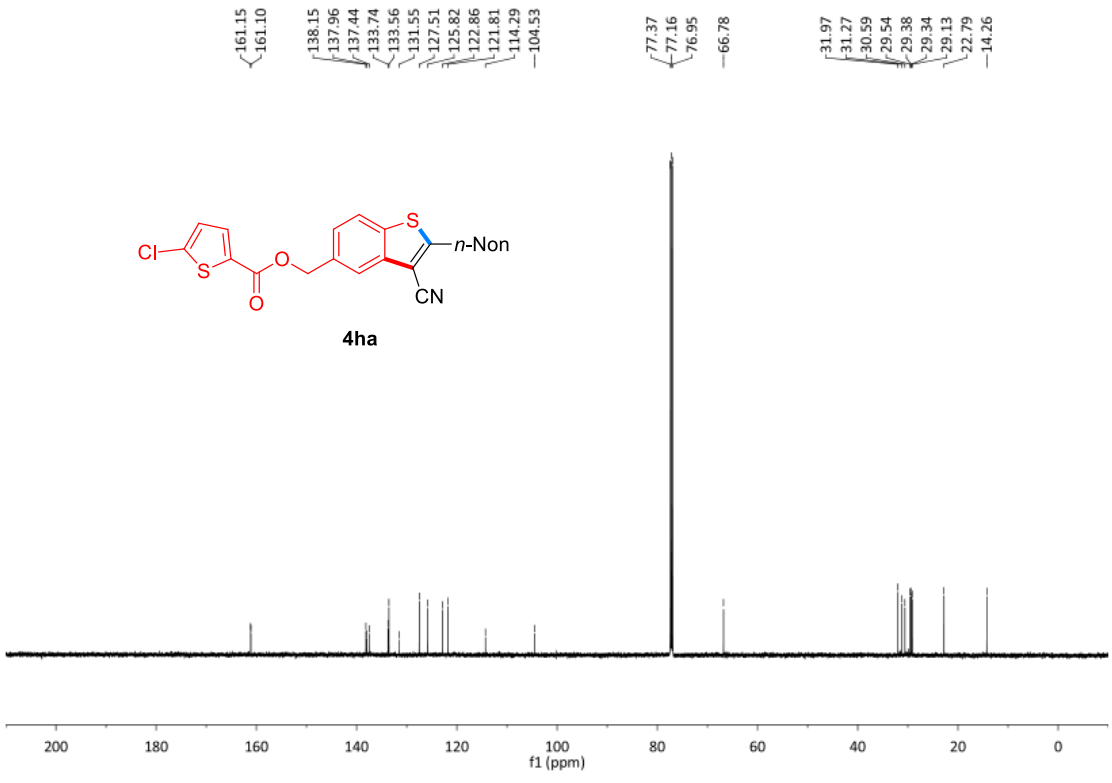

Ph
O
O
S
n-Non
CN

4ga

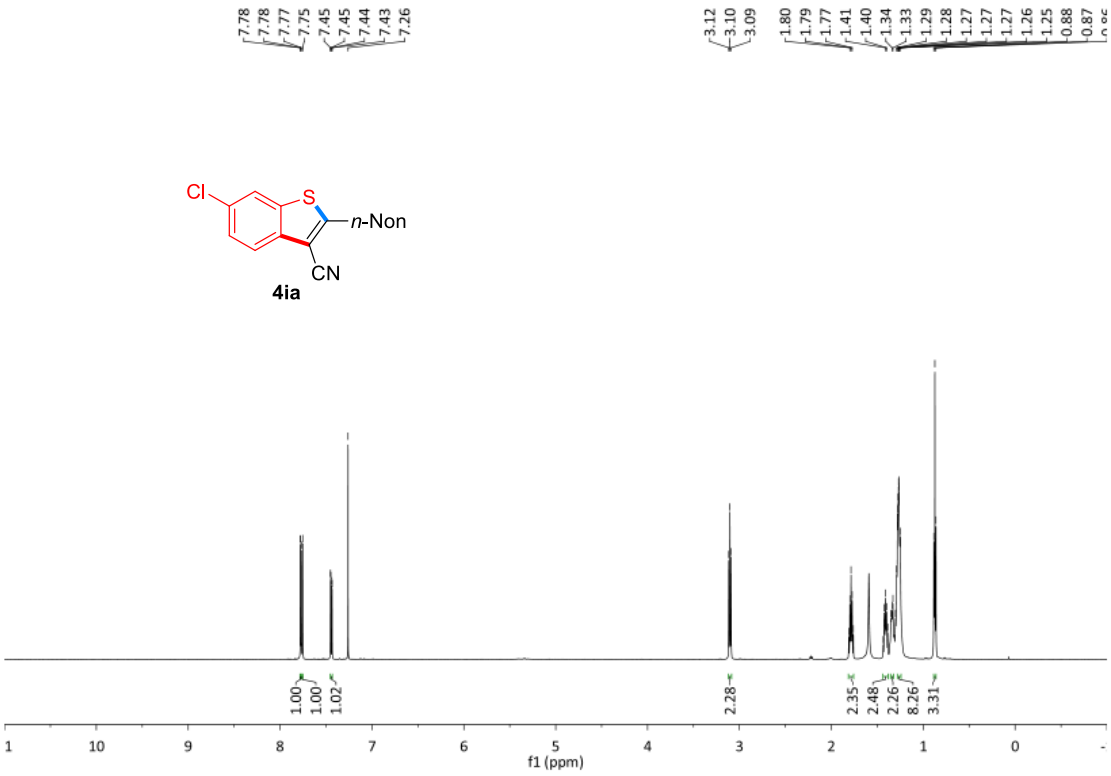

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

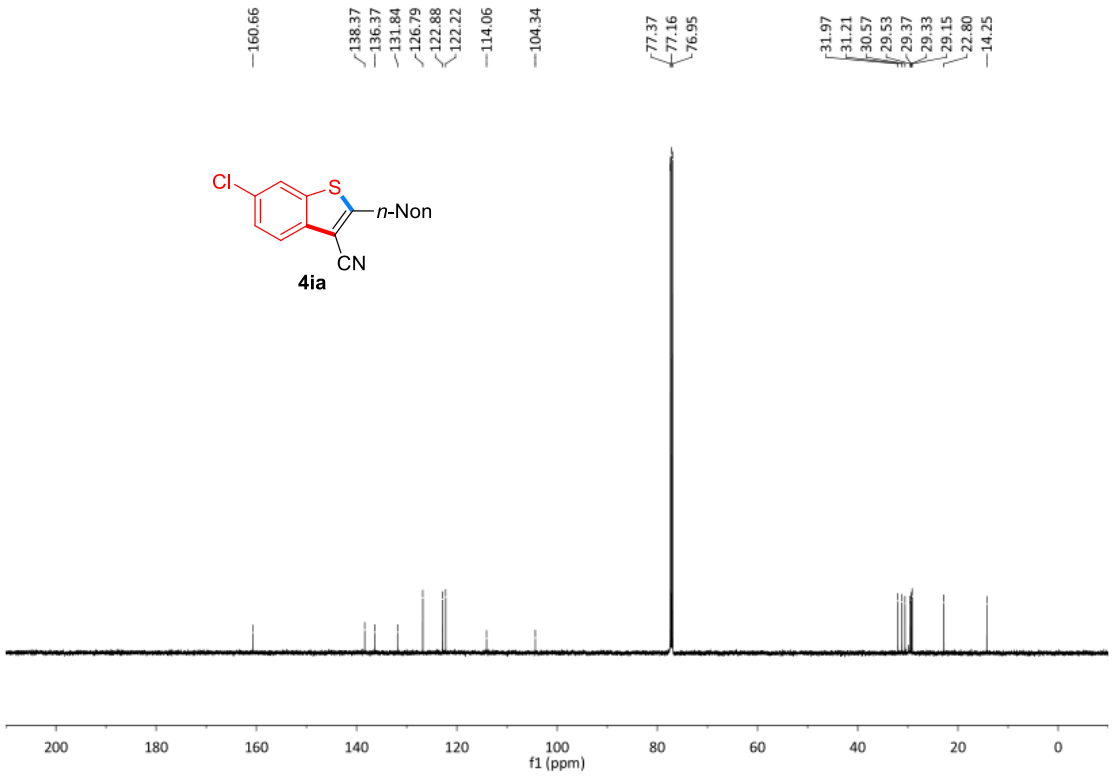

7.90
7.89
7.81
7.79
7.63
7.63
7.46
7.46
7.45
7.45
7.26
6.94
6.93
5.44
3.14
3.12
3.11
1.80
1.79
1.78
1.43
1.41
1.40
1.35
1.34
1.33
1.30
1.28
1.28
1.27
1.27
0.88
0.87
Cl
S
O
O
S
n-Non
CN
1.00
1.00
1.00
1.00
1.00
2.00
2.04
2.16
2.38
2.29
8.45
3.35
f1 (ppm)

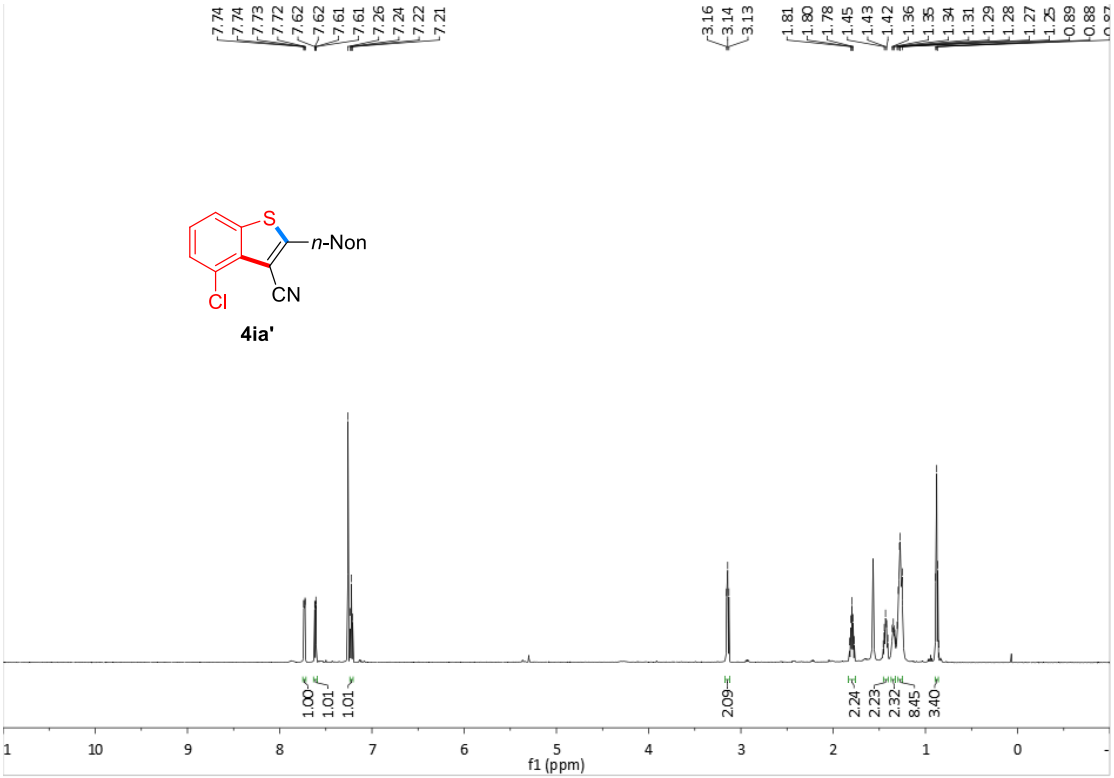
4ha

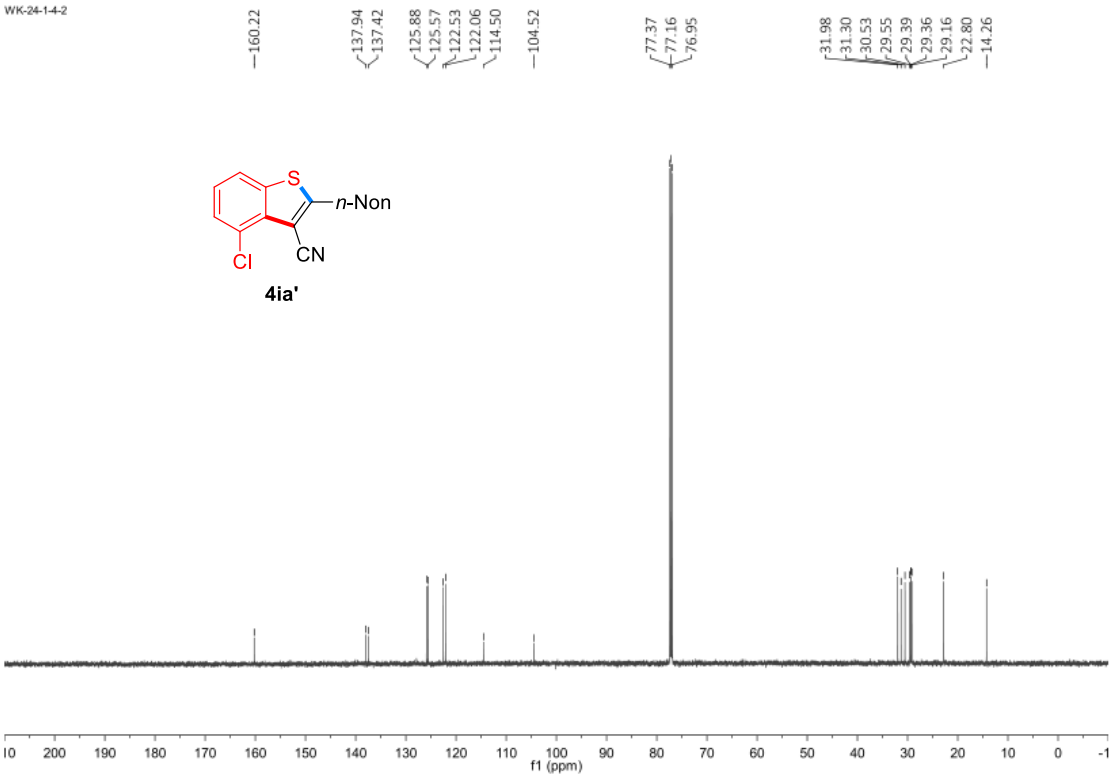

161.15
161.10
138.15
137.96
137.44
133.74
133.56
131.55
127.51
125.82
122.86
121.81
114.29
104.53
77.37
77.16
76.95
66.78
31.97
31.27
30.59
29.54
29.38
29.34
29.13
22.79
14.26
Cl
S
O
O
S
n-Non
CN
f1 (ppm)

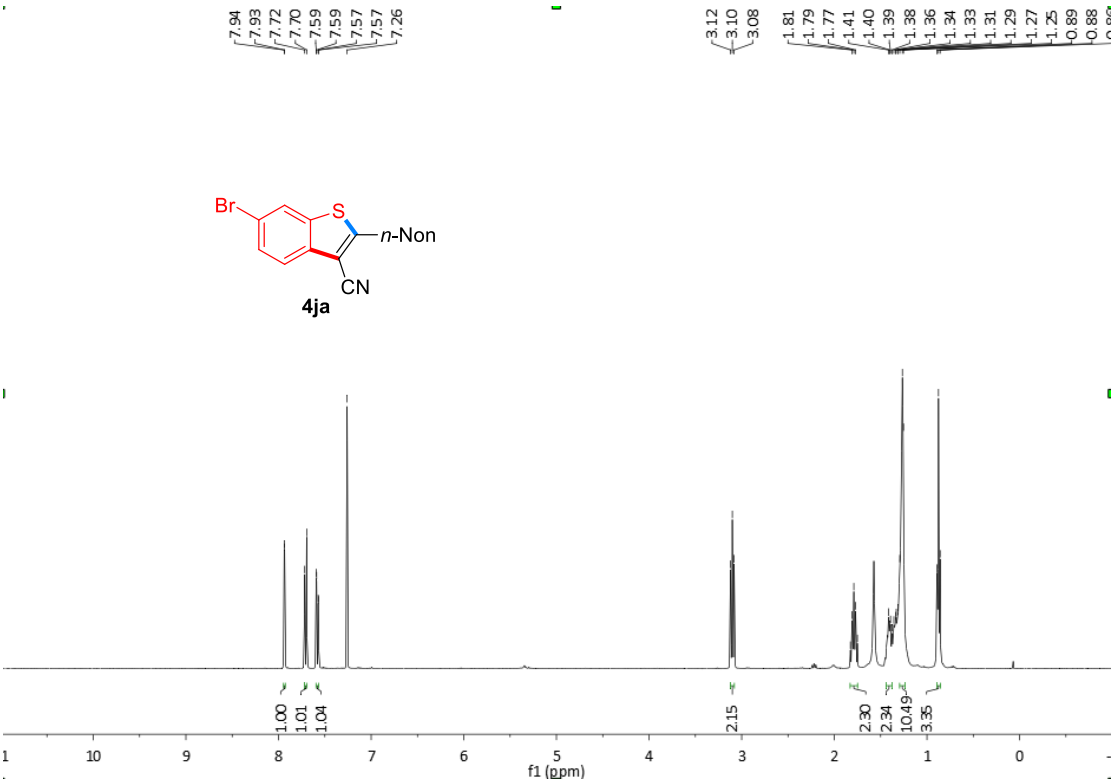
4ha

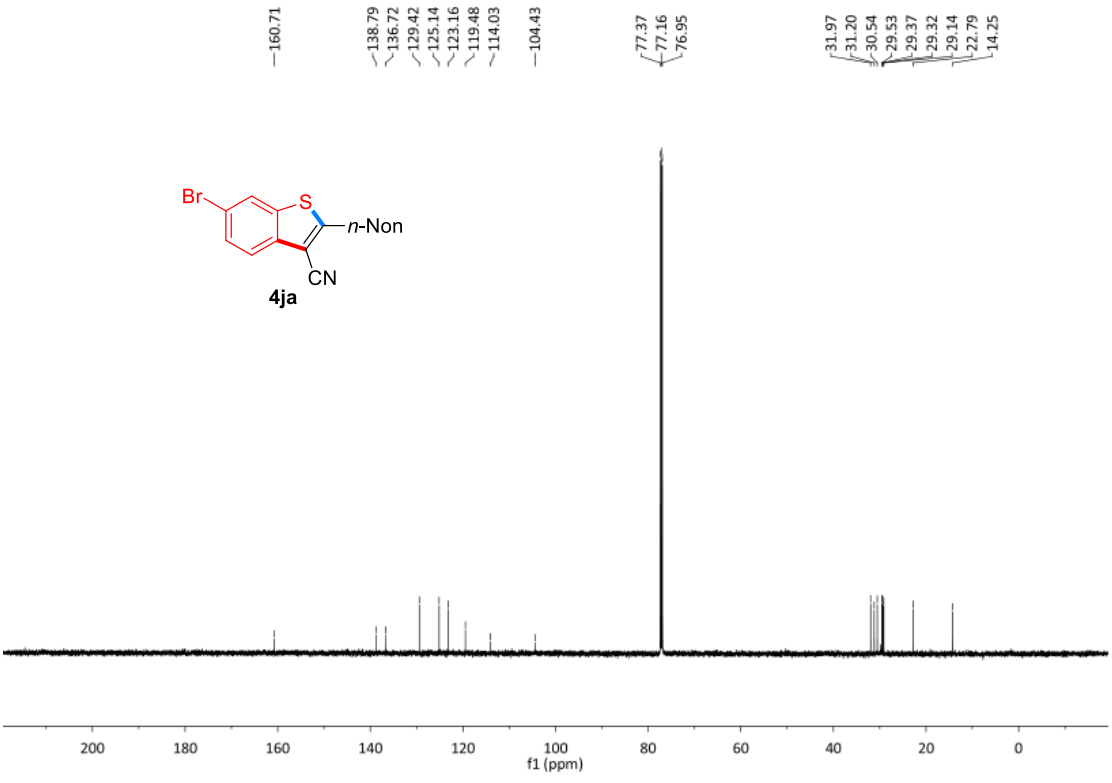

7.78
7.78
7.77
7.75
7.45
7.45
7.44
7.43
7.26
3.12
3.10
3.09
1.80
1.79
1.77
1.41
1.40
1.34
1.33
1.29
1.28
1.27
1.27
1.27
1.26
1.25
0.88
0.87
Cl
S
n-Non
CN
4ia
1.00
1.00
1.02
2.28
2.35
2.48
2.26
8.26
3.31
f1 (ppm)

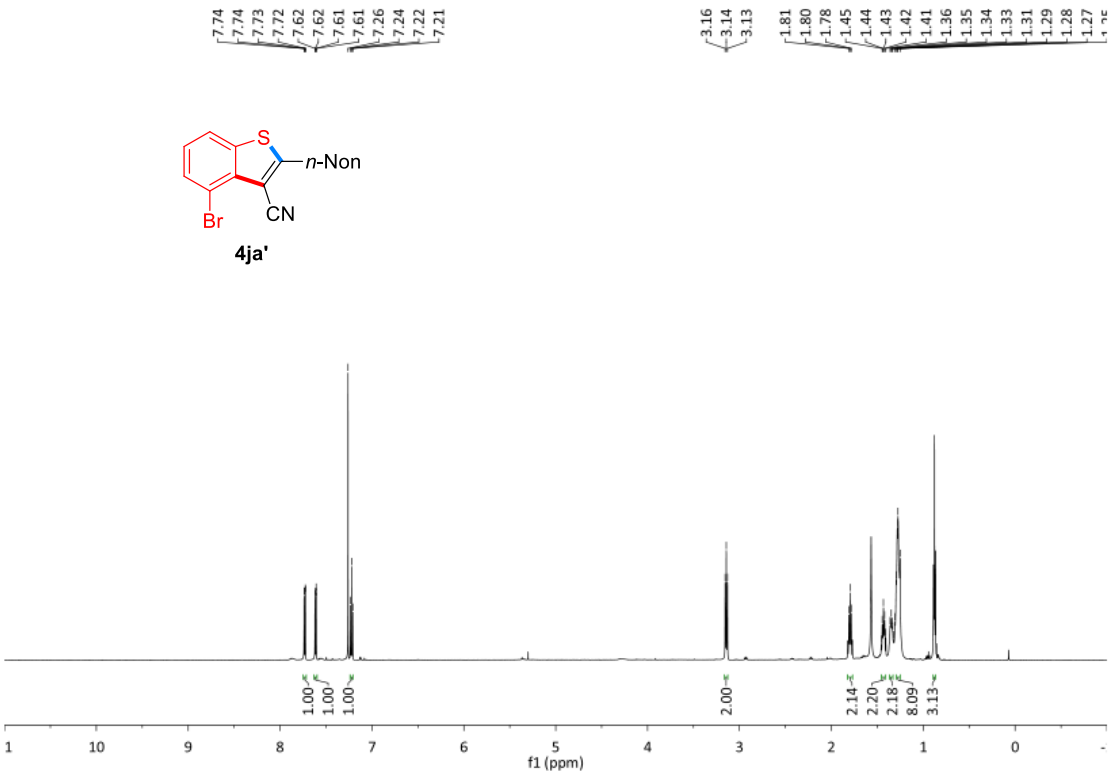

160.66
138.37
136.37
131.84
126.79
122.88
122.22
114.06
104.34
77.37
77.16
76.95
31.97
31.21
30.57
29.53
29.37
29.33
29.15
22.80
14.25
Cl
S
n-Non
CN
4ia
f1 (ppm)

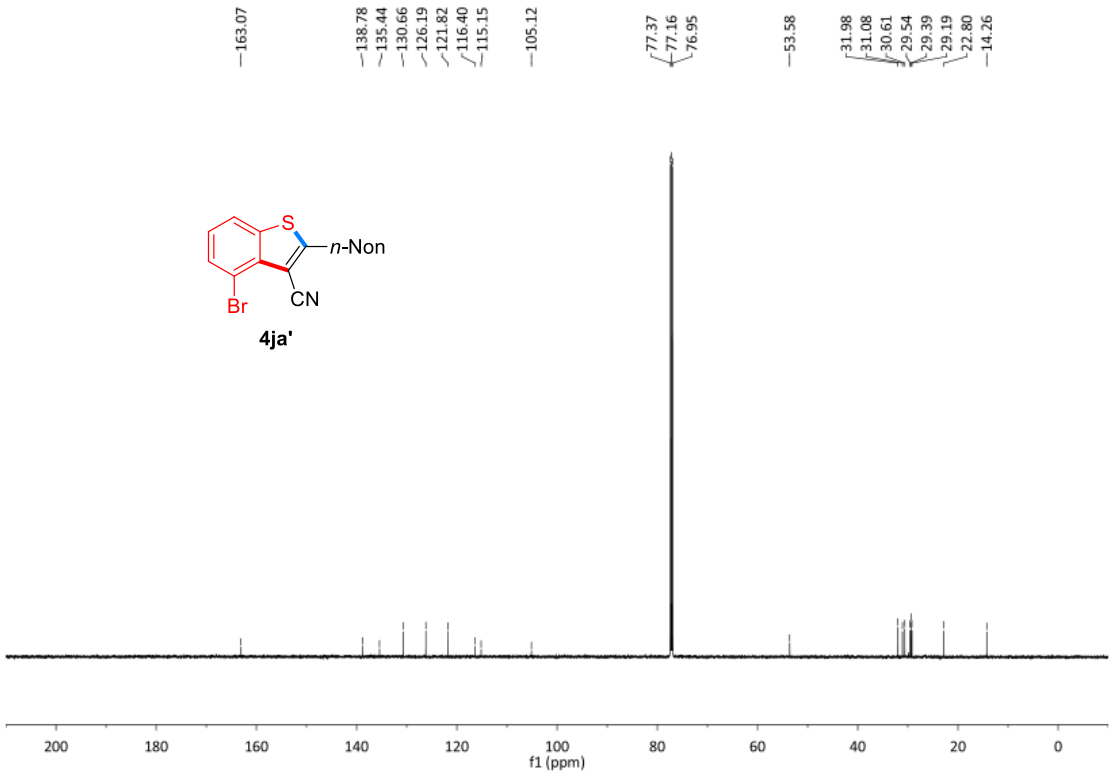

7.74
7.74
7.73
7.72
7.62
7.62
7.61
7.61
7.26
7.24
7.22
7.21
3.16
3.14
3.13
1.81
1.80
1.78
1.45
1.43
1.42
1.36
1.35
1.34
1.31
1.29
1.28
1.27
1.25
0.89
0.88
S
n-Non
Cl
CN
4ia'
1.00
1.01
1.01
2.09
2.24
2.23
2.32
8.45
3.40
f1 (ppm)

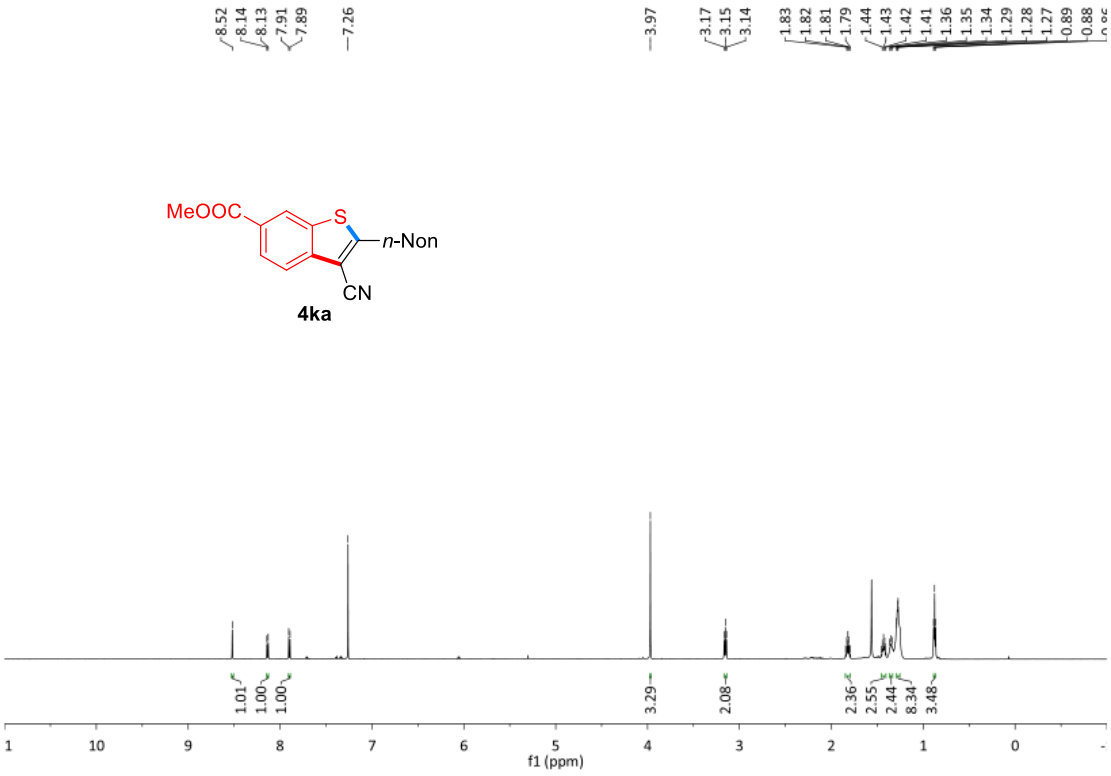

WK-24-1-4-2
160.22
137.94
137.42
125.88
125.57
122.53
122.06
114.50
104.52
77.37
77.16
76.95
31.98
31.30
30.53
29.55
29.39
29.36
29.16
22.80
14.26
S
n-Non
Cl
CN
4ia'
f1 (ppm)

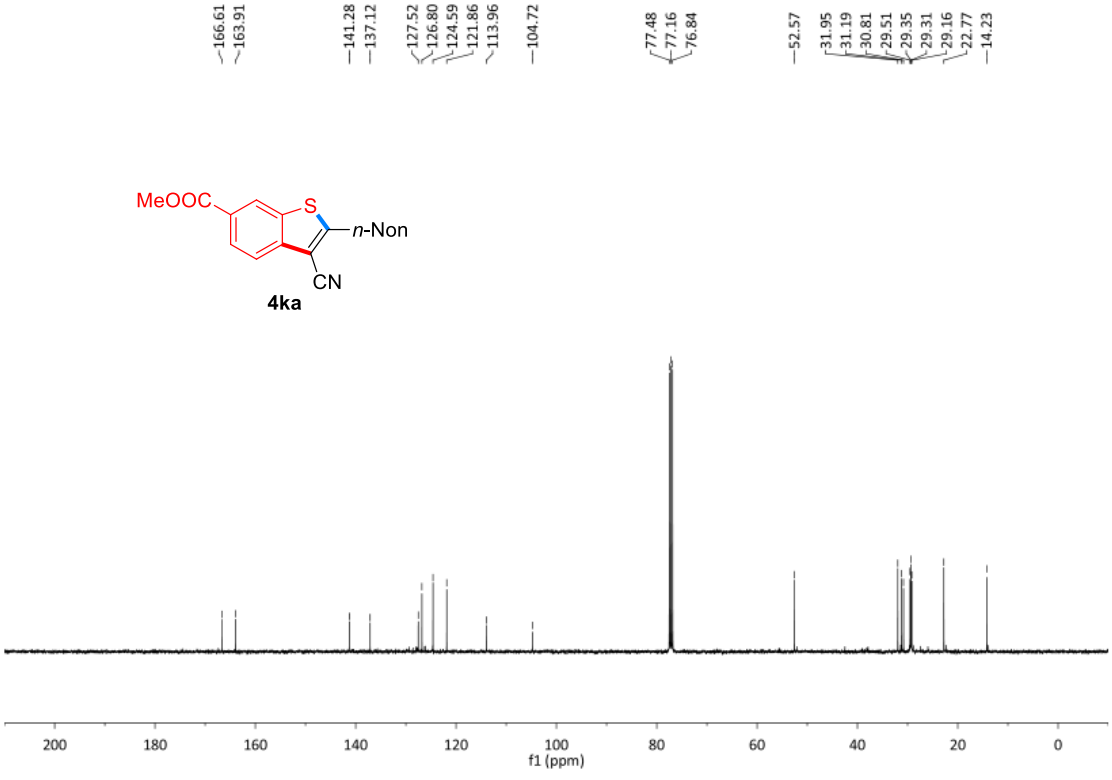

7.94
7.93
7.72
7.70
7.59
7.59
7.57
7.57
7.26
3.12
3.10
3.08
1.81
1.79
1.77
1.41
1.40
1.39
1.38
1.36
1.34
1.33
1.31
1.29
1.27
1.25
0.89
0.88
Br
S
n-Non
CN
4ja
1.00
1.01
1.04
2.15
2.30
2.34
10.49
3.35
f1 (ppm)

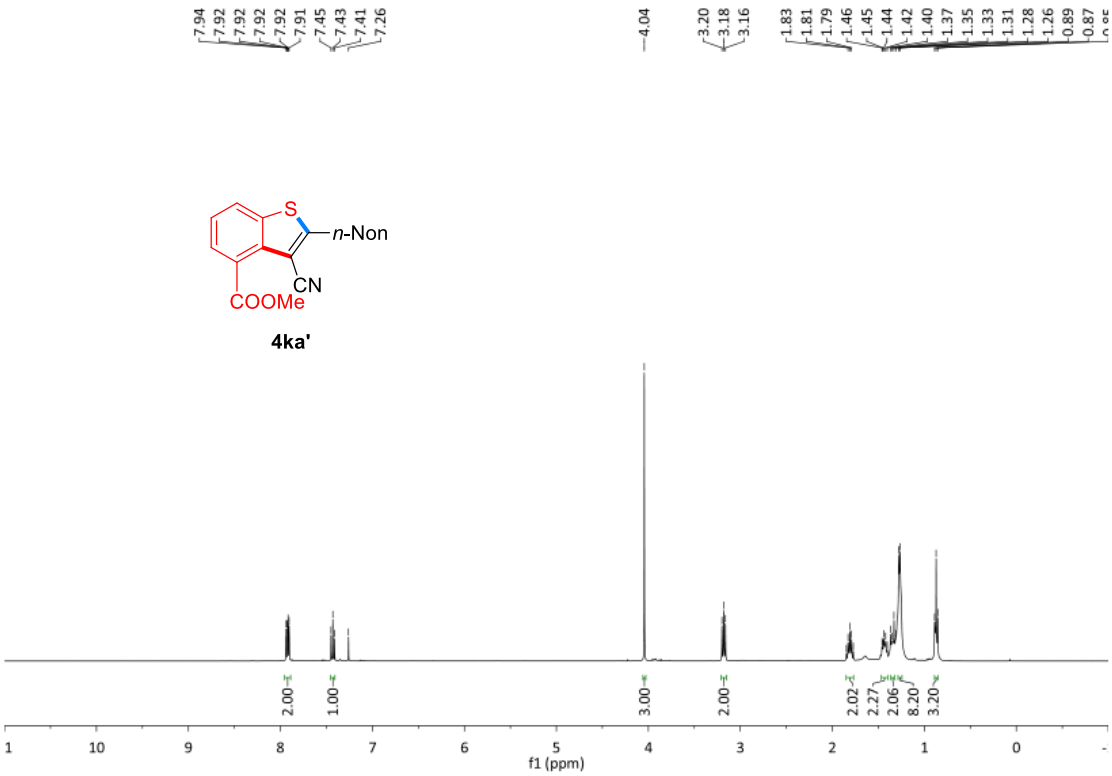

160.71
138.79
136.72
129.42
125.14
123.16
119.48
114.03
104.43
77.37
77.16
76.95
31.97
31.20
30.54
29.53
29.37
29.32
29.14
22.79
14.25
Br
S
n-Non
CN
4ja
f1 (ppm)

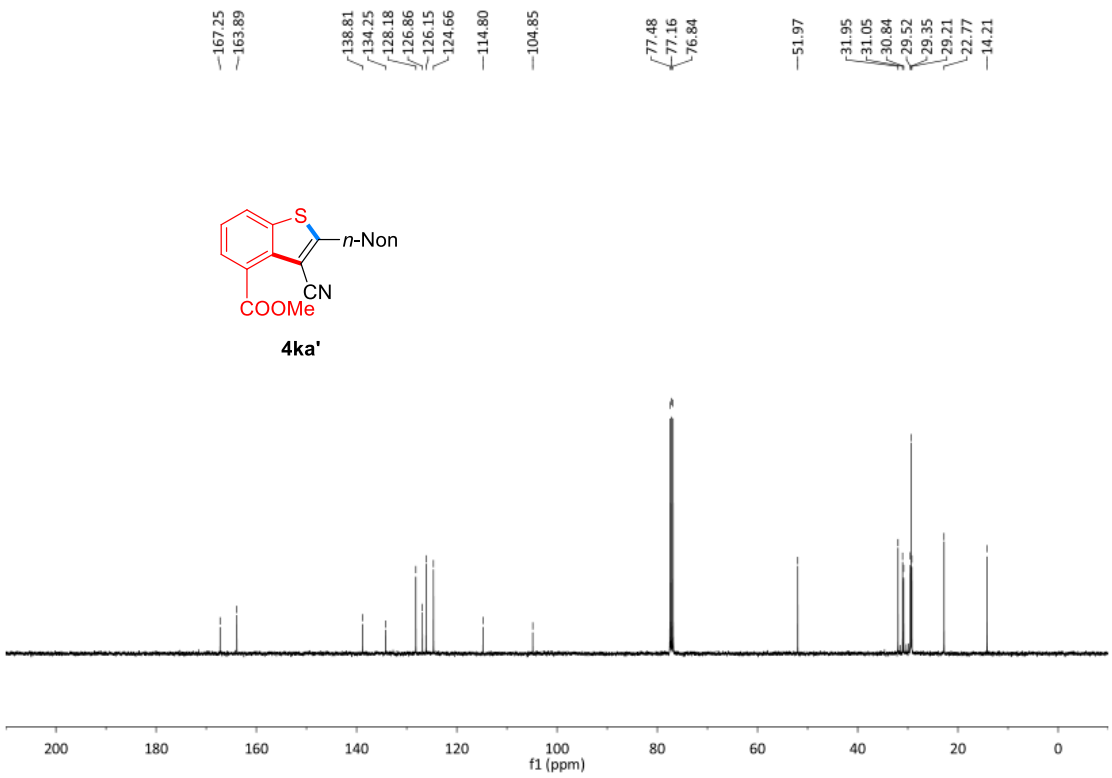

7.74
7.74
7.73
7.72
7.62
7.62
7.61
7.61
7.26
7.24
7.22
7.21
3.16
3.14
3.13
1.81
1.80
1.78
1.45
1.44
1.43
1.42
1.41
1.36
1.35
1.34
1.33
1.31
1.29
1.28
1.27
S
n-Non
CN
Br
4ja'
1.00
1.00
1.00
2.00
2.14
2.20
2.18
8.09
3.13
f1 (ppm)

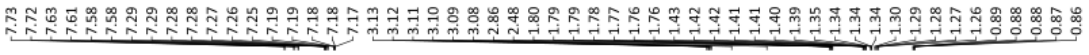

163.07
138.78
135.44
130.66
126.19
121.82
116.40
115.15
105.12
77.37
77.16
76.95
53.58
31.98
31.08
30.61
29.54
29.39
29.19
22.80
14.26
S
n-Non
CN
Br
4ja'
f1 (ppm)

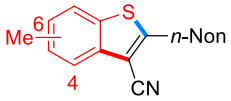

8.52
8.14
8.13
7.91
7.89
7.26
3.97
3.17
3.15
3.14
1.83
1.82
1.81
1.79
1.44
1.43
1.42
1.41
1.36
1.35
1.34
1.29
1.28
1.27
0.89
0.88
MeOOC
S
n-Non
CN
4ka
1.01
1.00
1.00
3.29
2.08
2.36
2.55
2.44
8.34
3.48
f1 (ppm)


166.61
163.91
141.28
137.12
127.52
126.80
124.59
121.86
113.96
104.72
77.48
77.16
76.84
52.57
31.95
31.19
30.81
29.51
29.35
29.31
29.16
22.77
14.23
MeOOC
S
n-Non
CN
4ka
f1 (ppm)

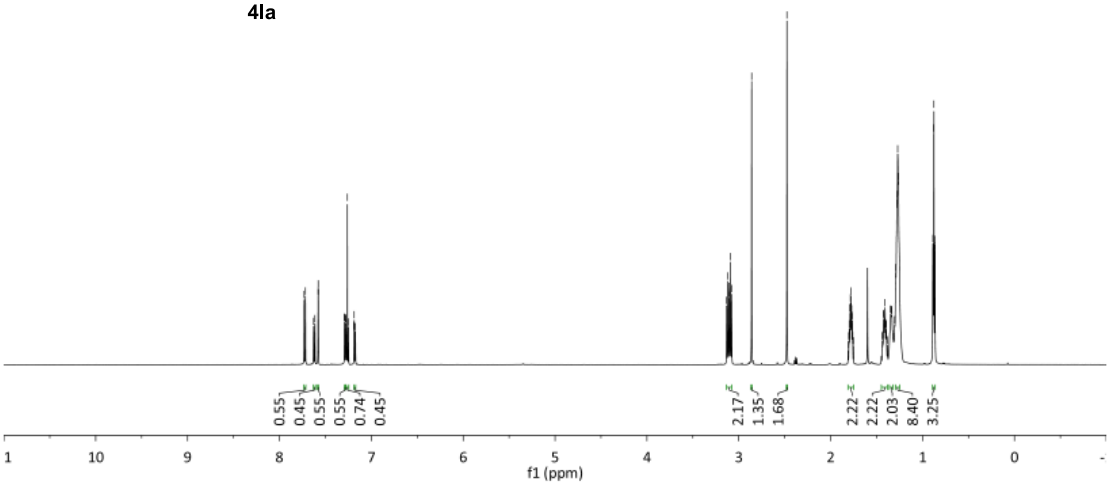

7.94
7.92
7.92
7.92
7.92
7.91
7.45
7.43
7.41
7.26
4.04
3.20
3.18
3.16
1.83
1.81
1.79
1.46
1.45
1.44
1.42
1.40
1.37
1.35
1.33
1.31
1.28
1.26
0.89
0.87
S
n-Non
CN
COOMe
4ka'
2.00
1.00
3.00
2.00
2.02
2.27
2.06
8.20
3.20
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

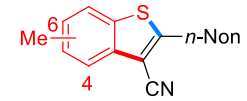

167.25
163.89
138.81
134.25
128.18
126.86
126.15
124.66
114.80
104.85
77.48
77.16
76.84
51.97
31.95
31.05
30.84
29.52
29.35
29.21
22.77
14.21
S
n-Non
CN
COOMe
4ka'
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



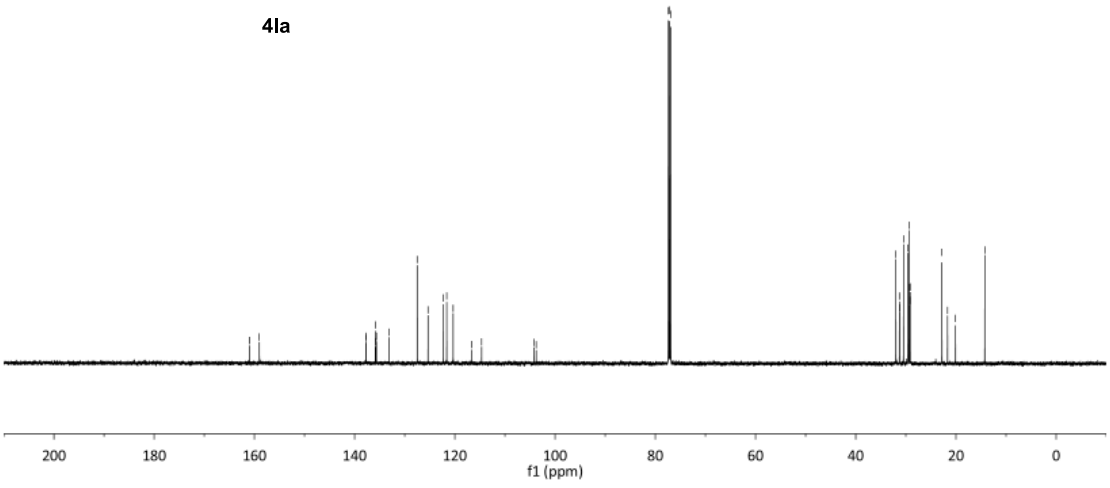

Me
6
S
n-Non
4
CN

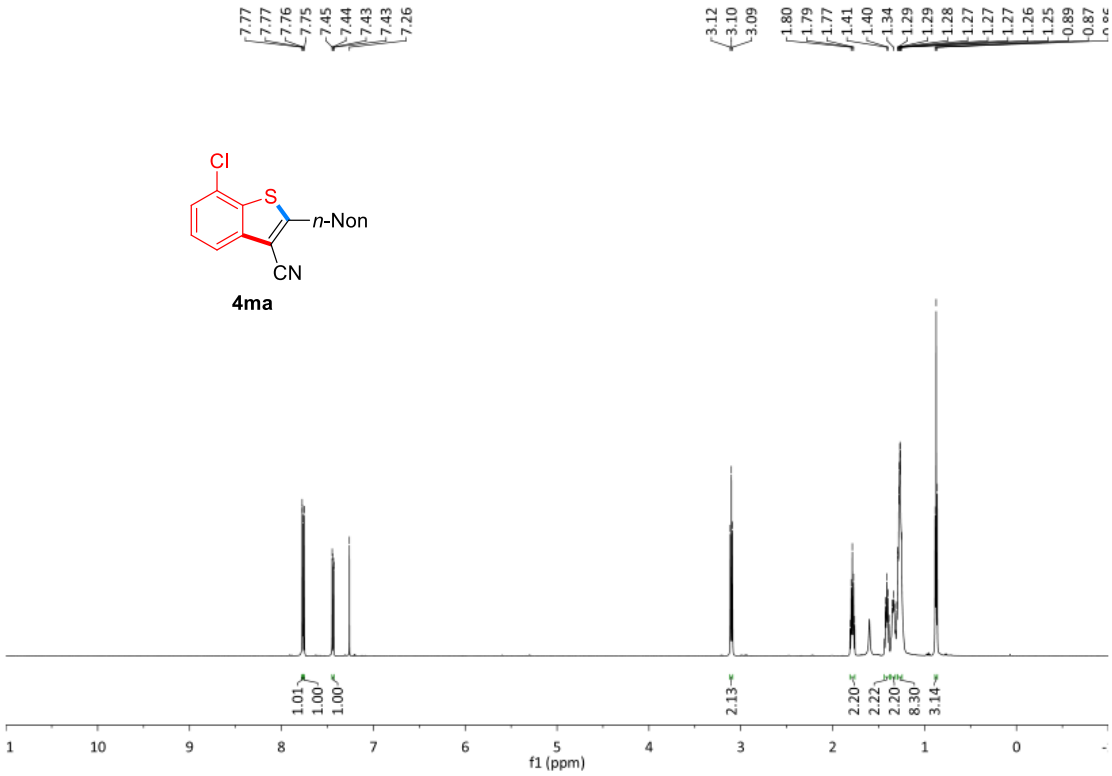
4la

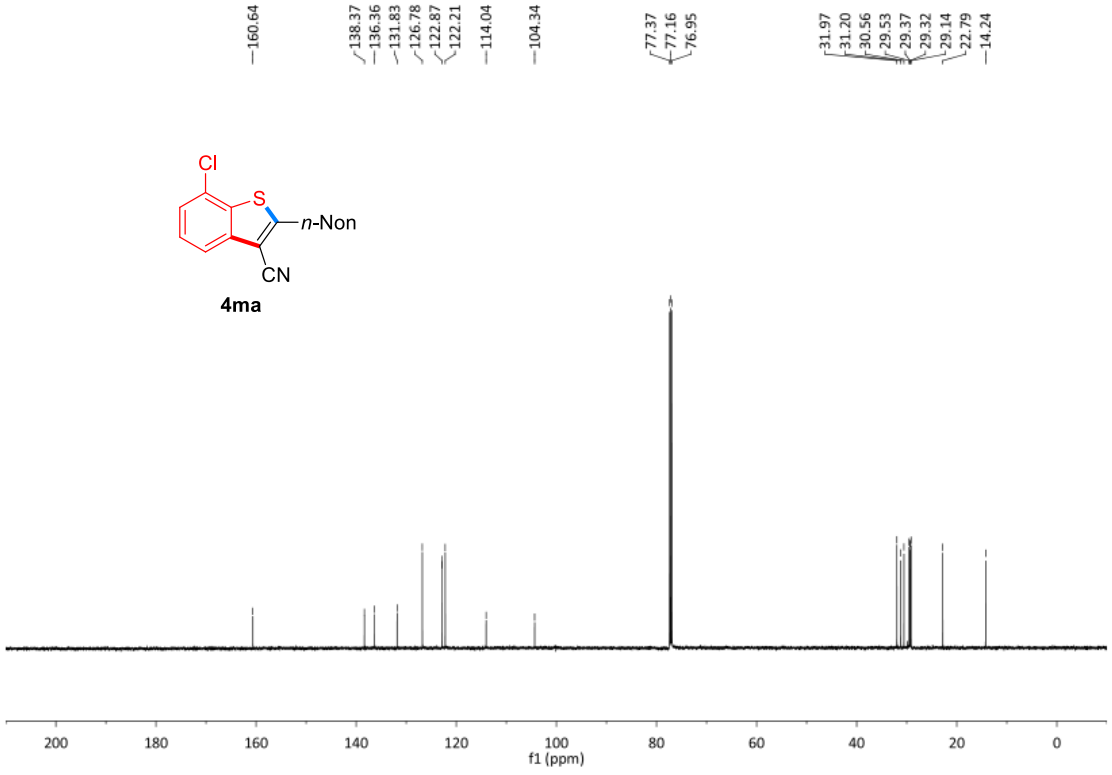

0.55
0.45
0.55
0.55
0.74
0.45
2.17
1.35
1.68
2.22
2.22
2.03
8.40
3.25
f1 (ppm)

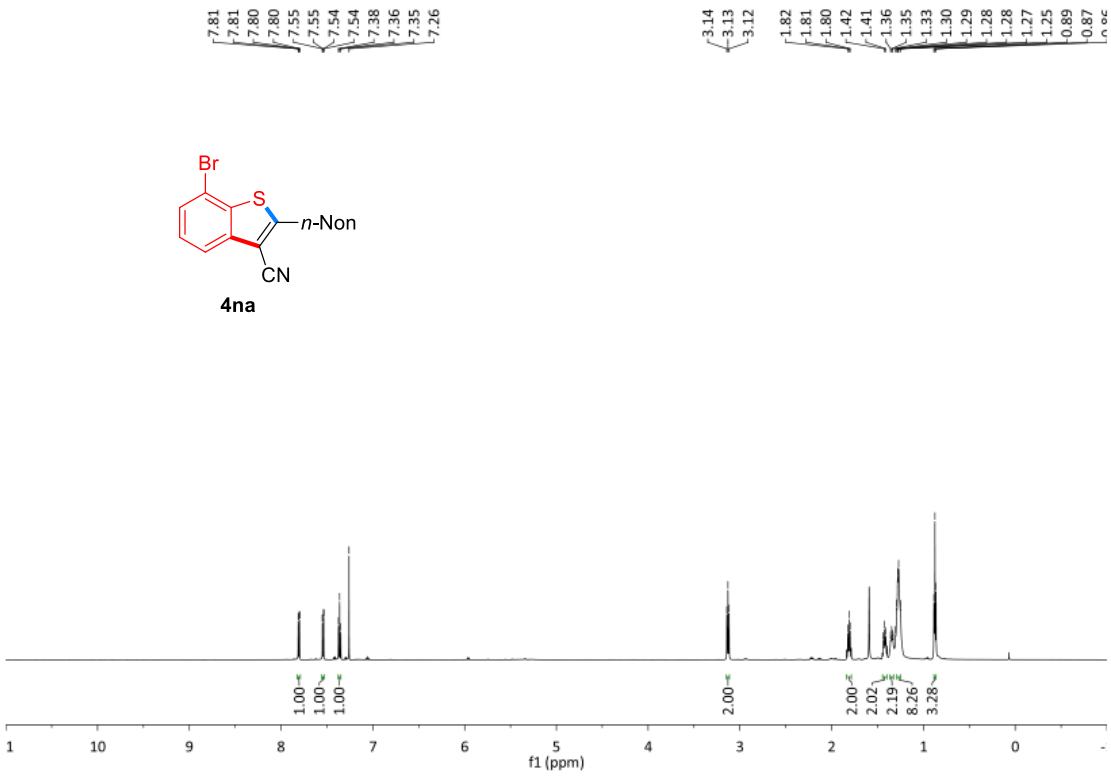

Me
6
S
n-Non
4
CN

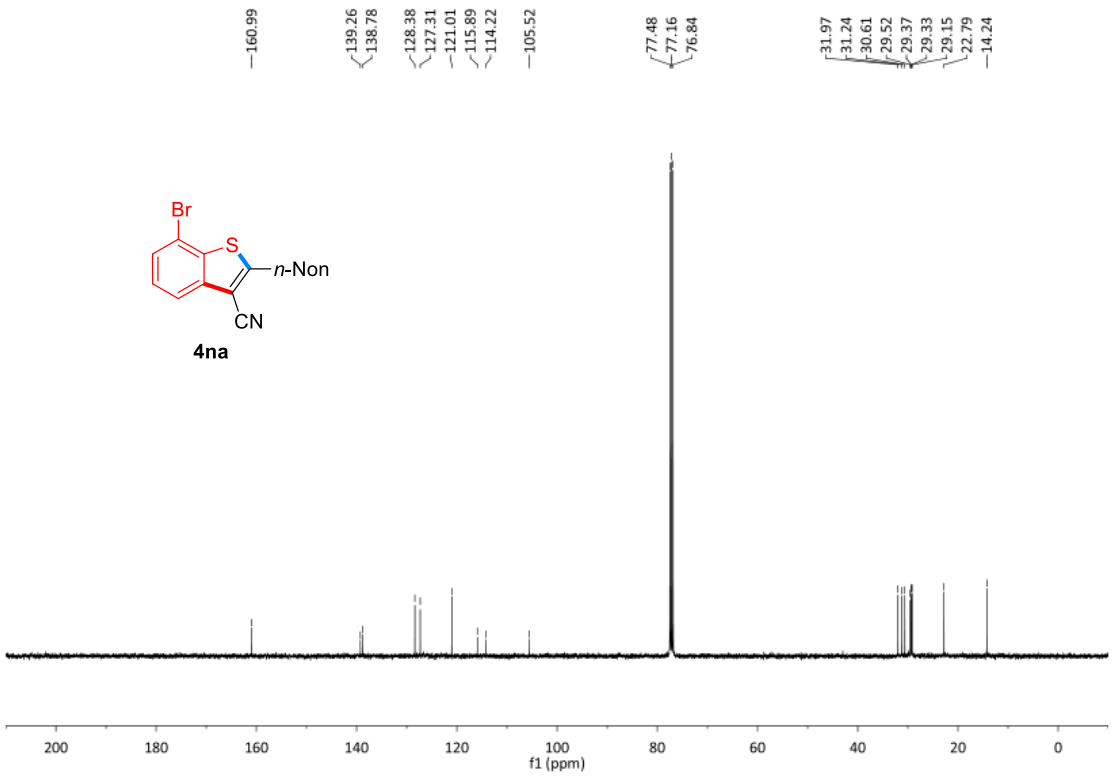
4la

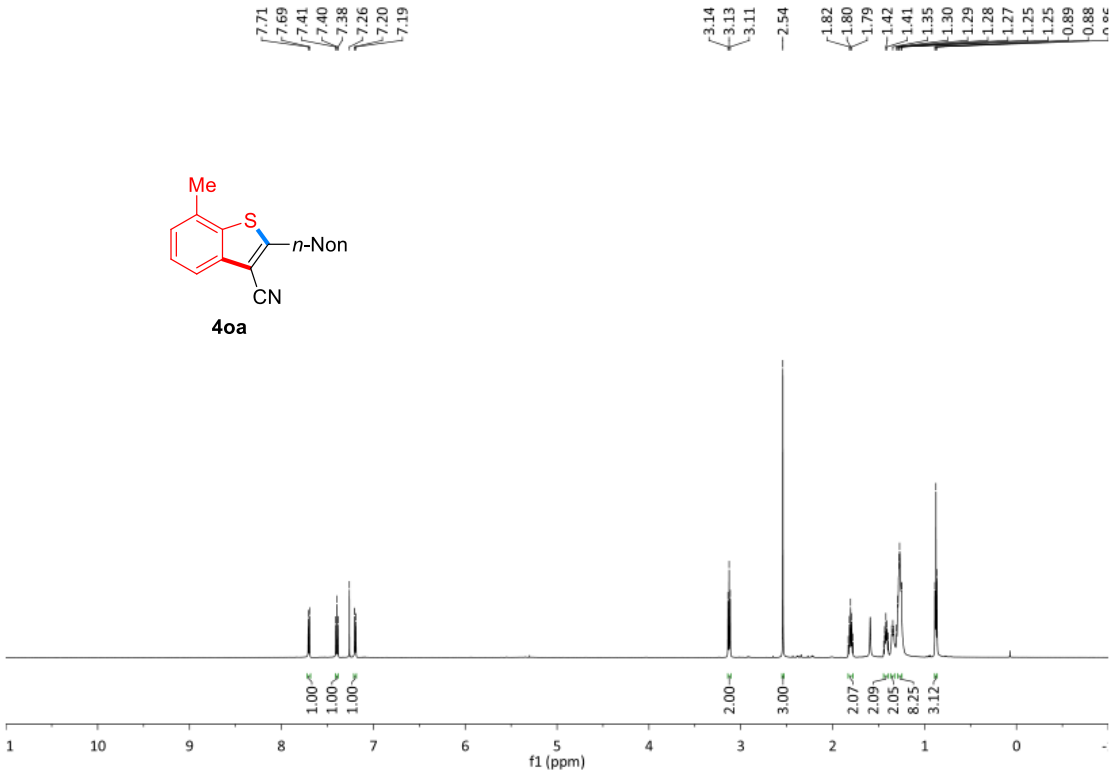

f1 (ppm)

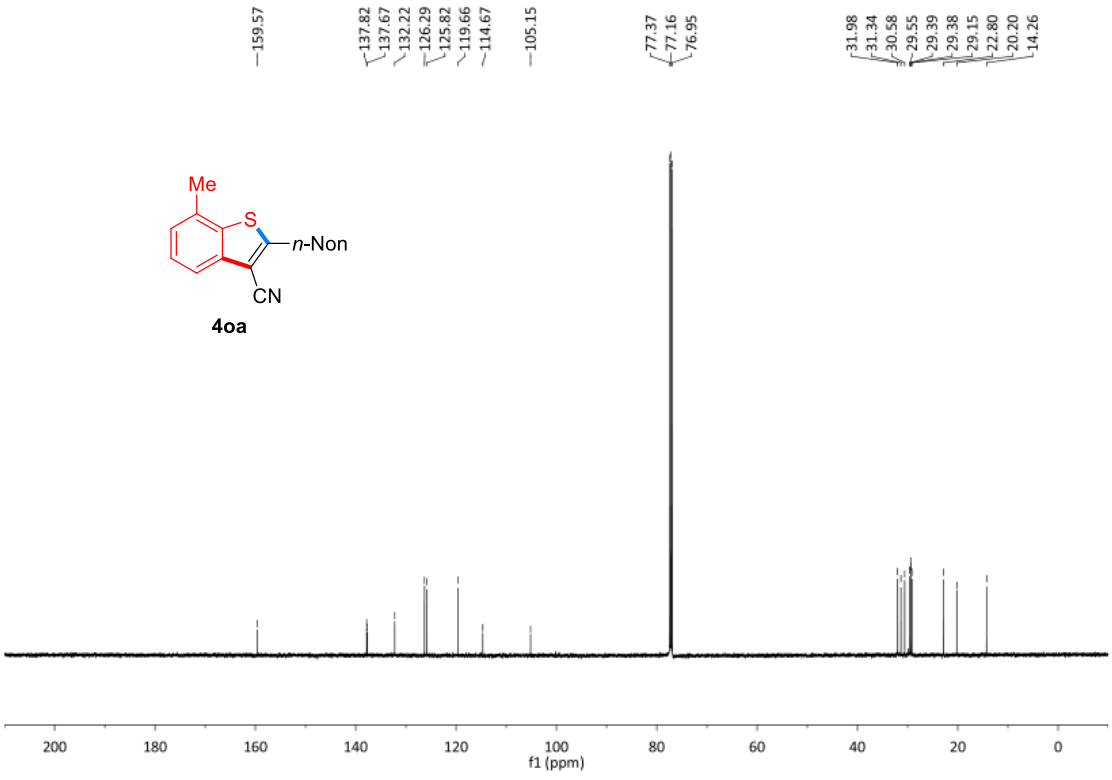

7.77
7.77
7.76
7.75
7.45
7.44
7.43
7.43
7.26
3.12
3.10
3.09
1.80
1.79
1.77
1.41
1.40
1.34
1.29
1.29
1.28
1.27
1.27
1.27
1.26
1.25
0.89
0.87
Cl
S
n-Non
CN
4ma
1.01
1.00
1.00
2.13
2.20
2.22
2.20
8.30
3.14
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

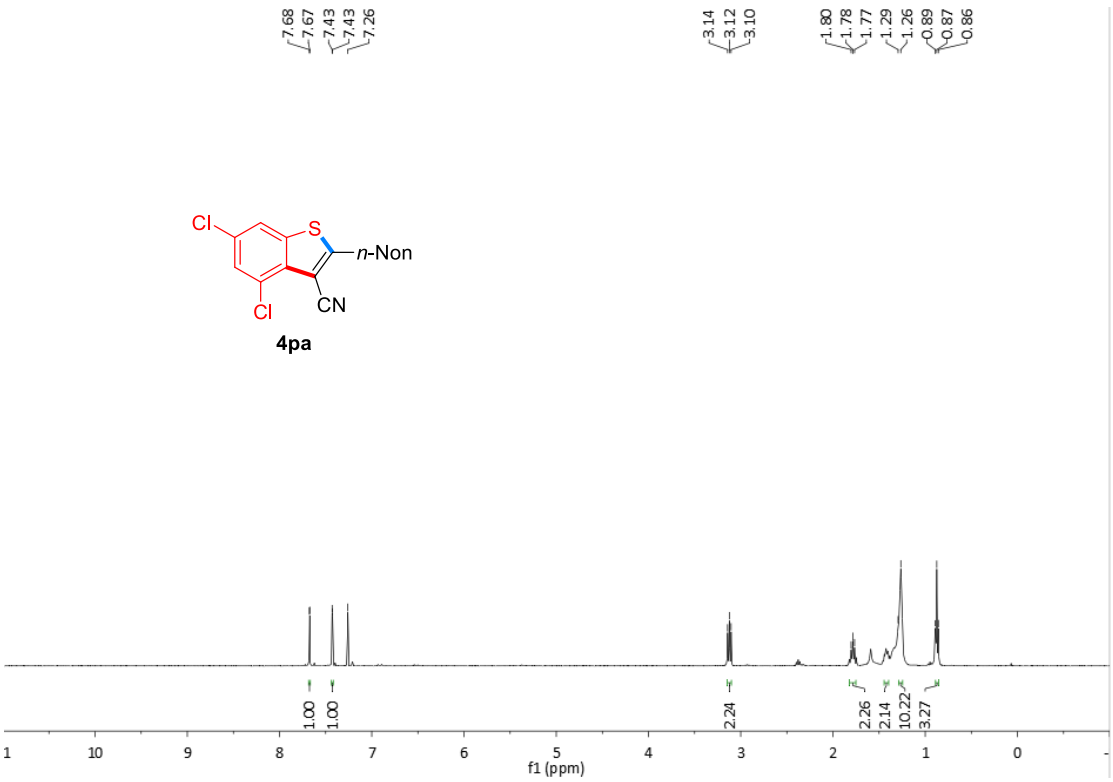

160.64
138.37
136.36
131.83
126.78
122.87
122.21
114.04
104.34
77.37
77.16
76.95
31.97
31.20
30.56
29.53
29.37
29.32
29.14
22.79
14.24
Cl
S
n-Non
CN
4ma
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

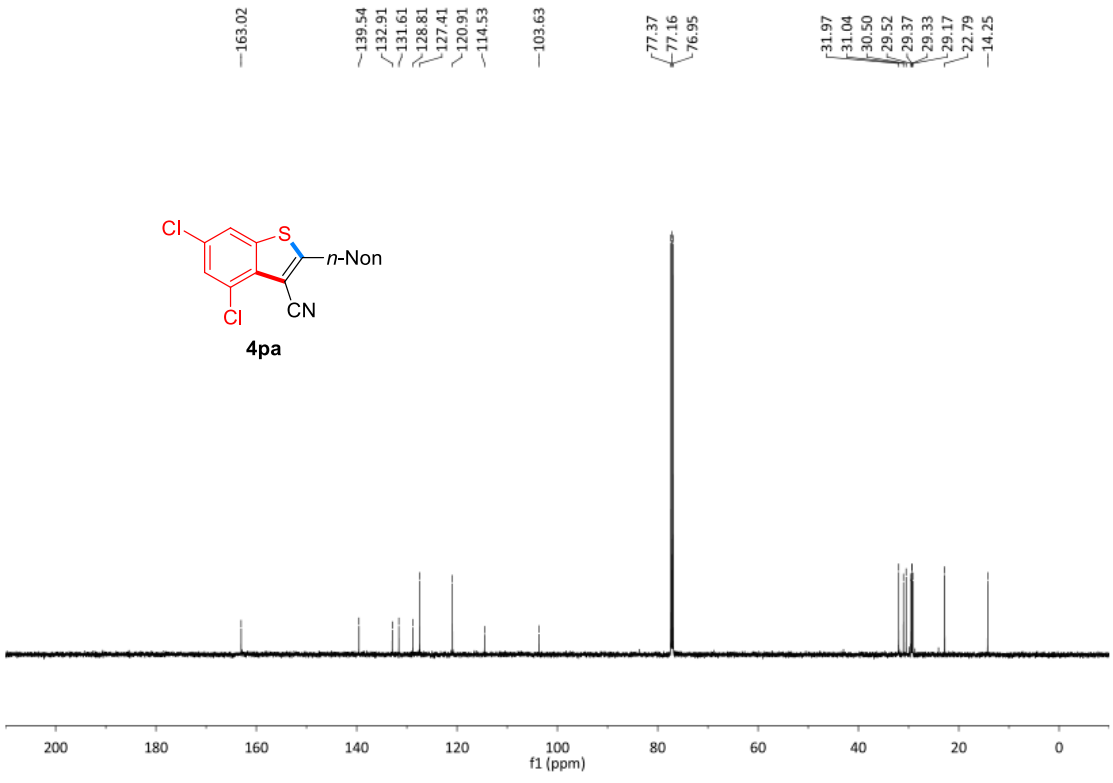

7.81
7.81
7.80
7.80
7.55
7.55
7.54
7.54
7.38
7.36
7.35
7.26
3.14
3.13
3.12
1.82
1.81
1.80
1.42
1.41
1.36
1.35
1.33
1.30
1.29
1.28
1.28
1.27
1.25
0.89
0.87
Br
S
n-Non
CN
4na
1.00
1.00
1.00
2.00
2.00
2.02
2.19
8.26
3.28
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

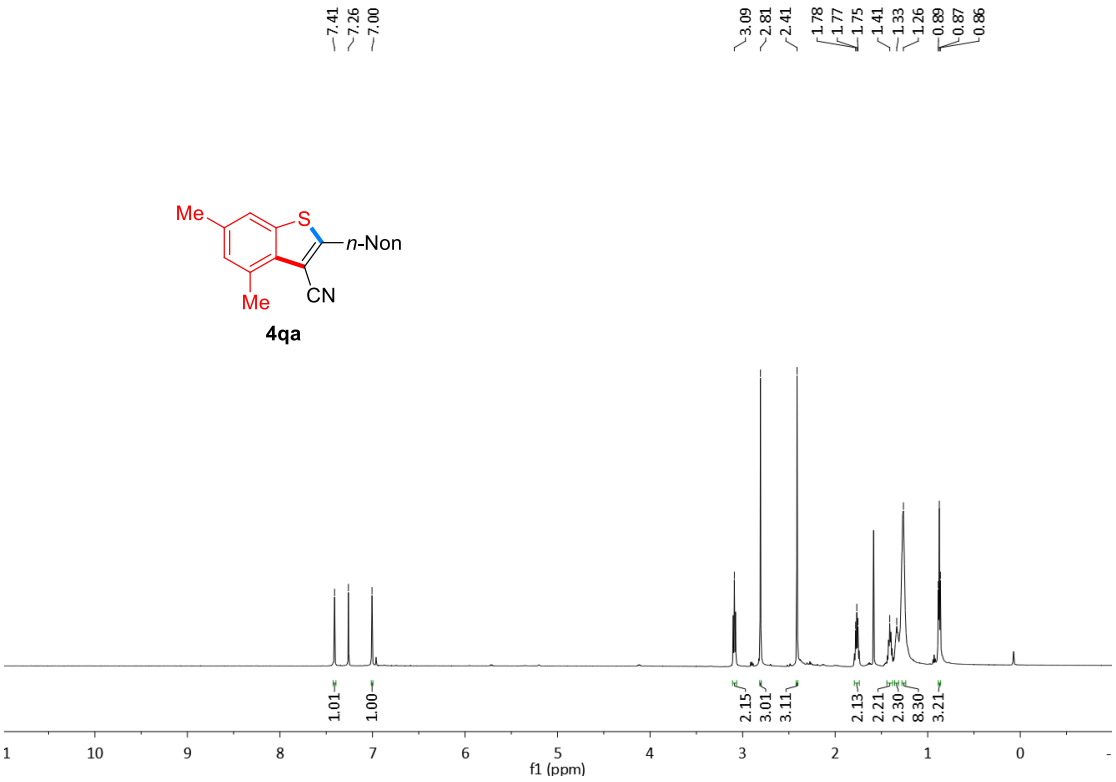

160.99
139.26
138.78
128.38
127.31
121.01
115.89
114.22
105.52
77.48
77.16
76.84
31.97
31.24
30.61
29.52
29.37
29.33
29.15
22.79
14.24
Br
S
n-Non
CN
4na
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

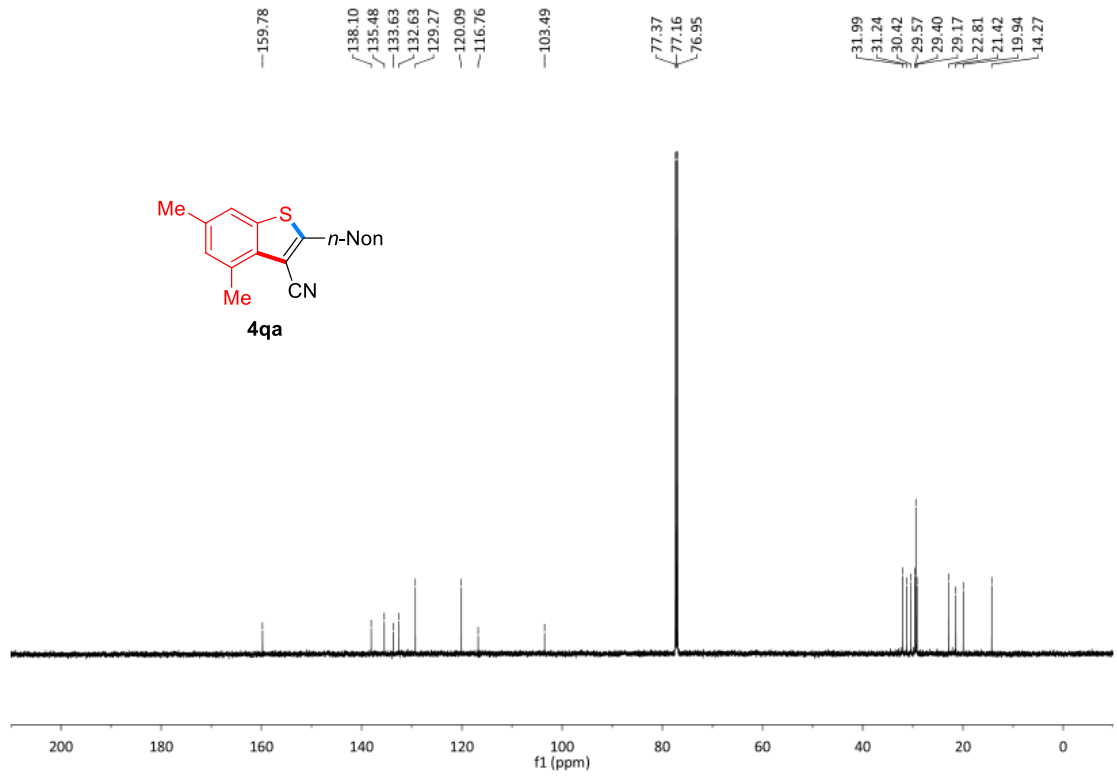

7.71
7.69
7.41
7.40
7.38
7.26
7.20
7.19
3.14
3.13
3.11
2.54
1.82
1.80
1.79
1.42
1.41
1.35
1.30
1.29
1.28
1.27
1.25
1.25
0.89
0.88
Me
S
n-Non
CN
4oa
1.00
1.00
1.00
2.00
3.00
2.07
2.09
2.05
8.25
3.12
f1 (ppm)

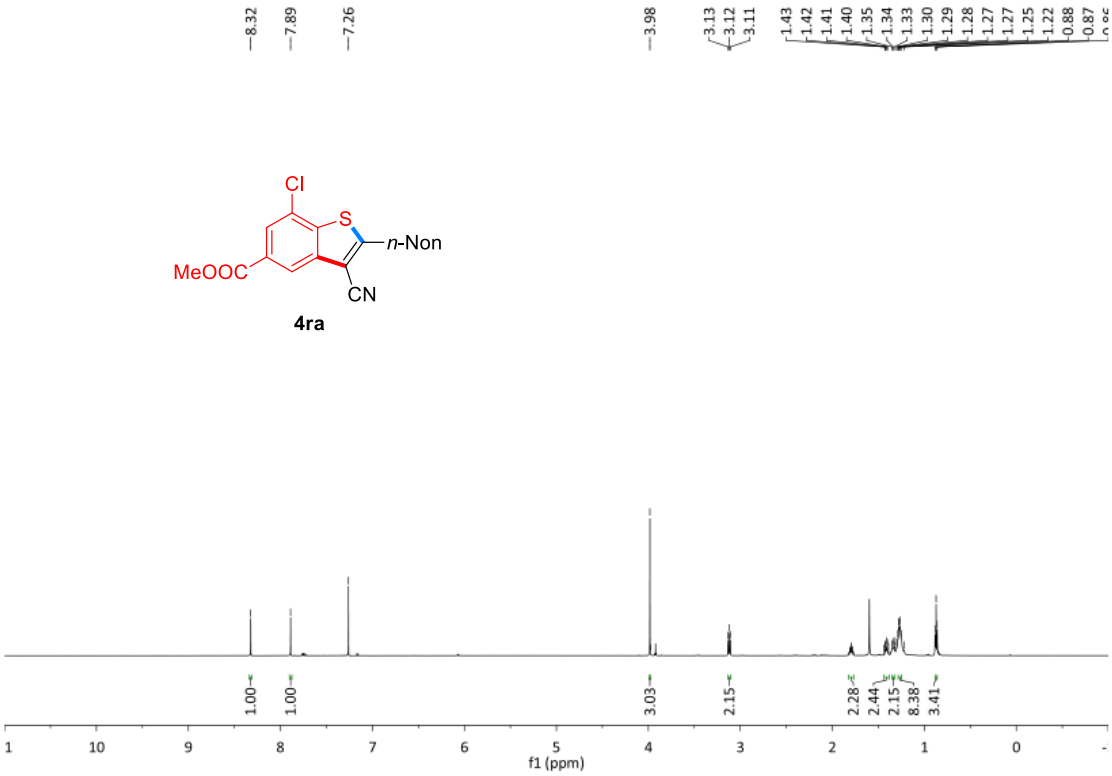

159.57
137.82
137.67
132.22
126.29
125.82
119.66
114.67
105.15
77.37
77.16
76.95
31.98
31.34
30.58
29.55
29.39
29.38
29.15
22.80
20.20
14.26
Me
S
n-Non
CN
4oa
f1 (ppm)

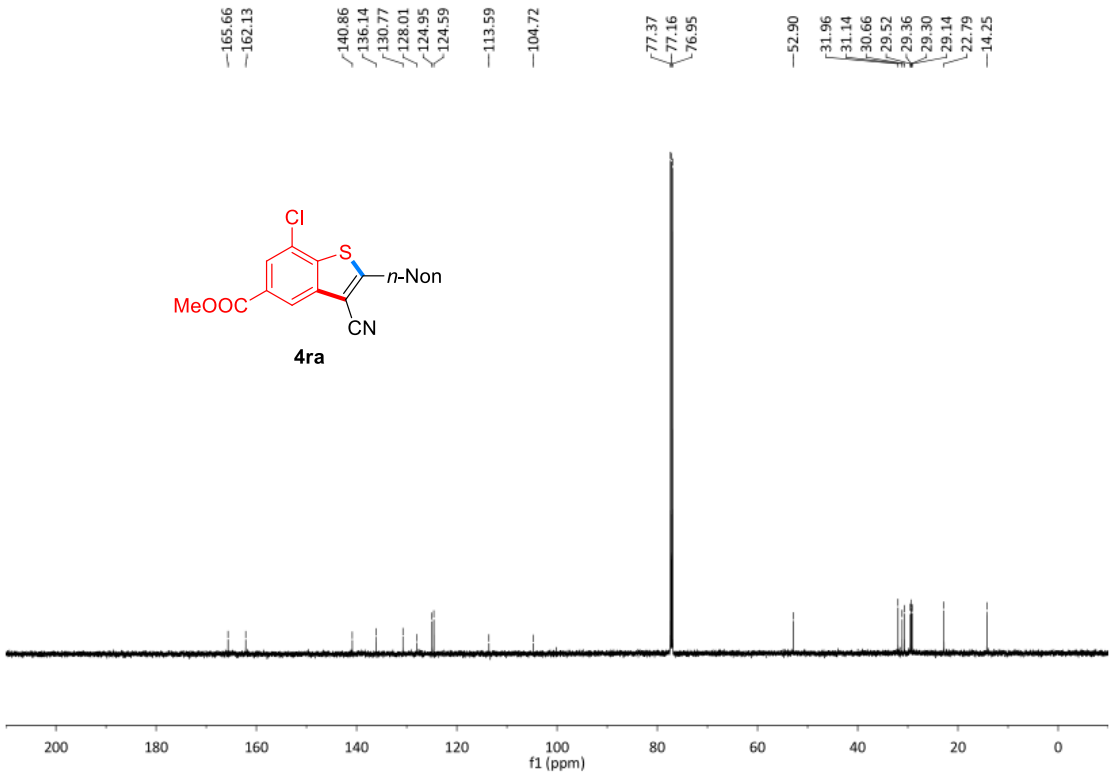

7.68
7.67
7.43
7.43
7.26
3.14
3.12
3.10
1.80
1.78
1.77
1.29
1.26
0.89
0.87
0.86
Cl
S
n-Non
Cl
CN
4pa
1.00
1.00
2.24
2.26
2.14
10.22
3.27
f1 (ppm)

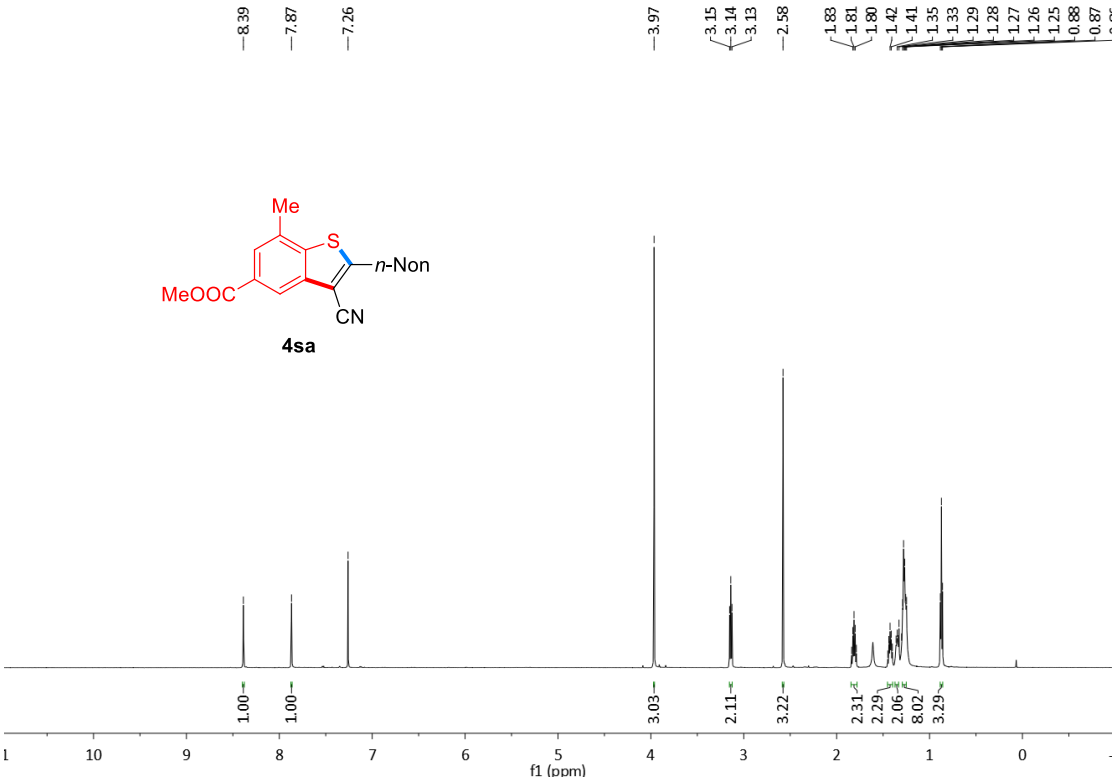

163.02
139.54
132.91
131.61
128.81
127.41
120.91
114.53
103.63
77.37
77.16
76.95
31.97
31.04
30.50
29.52
29.37
29.33
29.17
22.79
14.25
Cl
S
n-Non
Cl
CN
4pa
f1 (ppm)

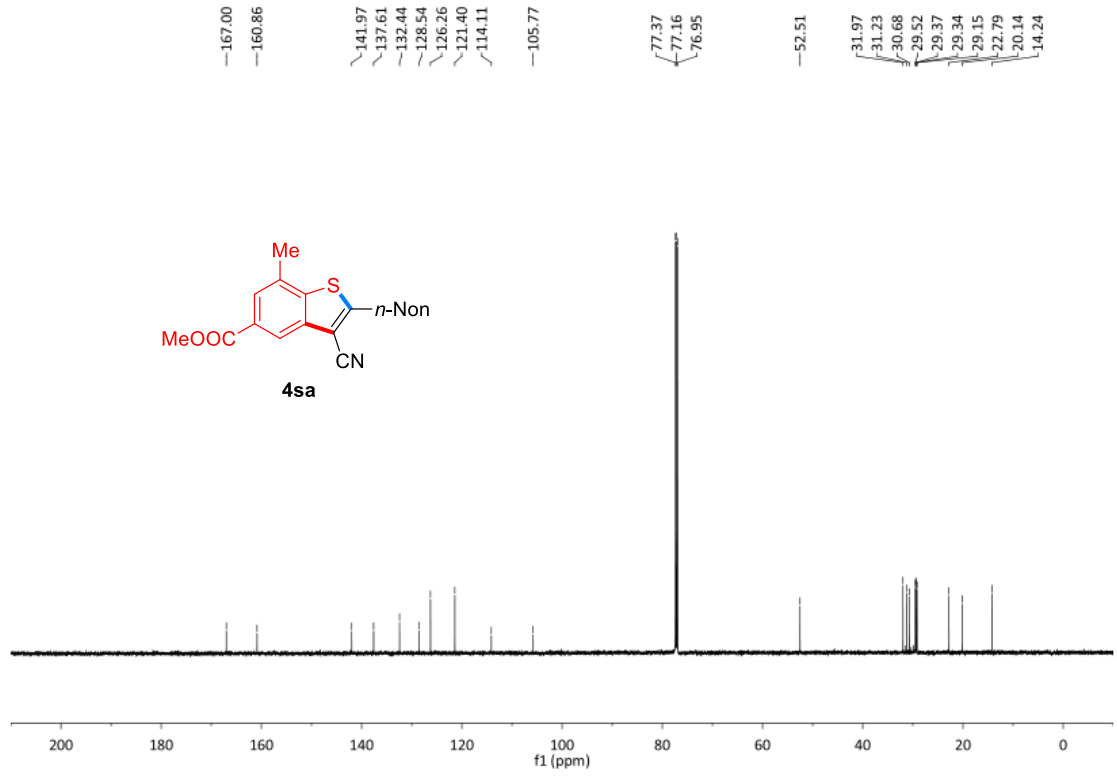

7.41
7.26
7.00
3.09
2.81
2.41
1.78
1.77
1.75
1.41
1.33
1.26
0.89
0.87
0.86
Me
S
n-Non
Me
CN
4qa
1.01
1.00
2.15
3.01
3.11
2.13
2.21
2.30
8.30
3.21
f1 (ppm)

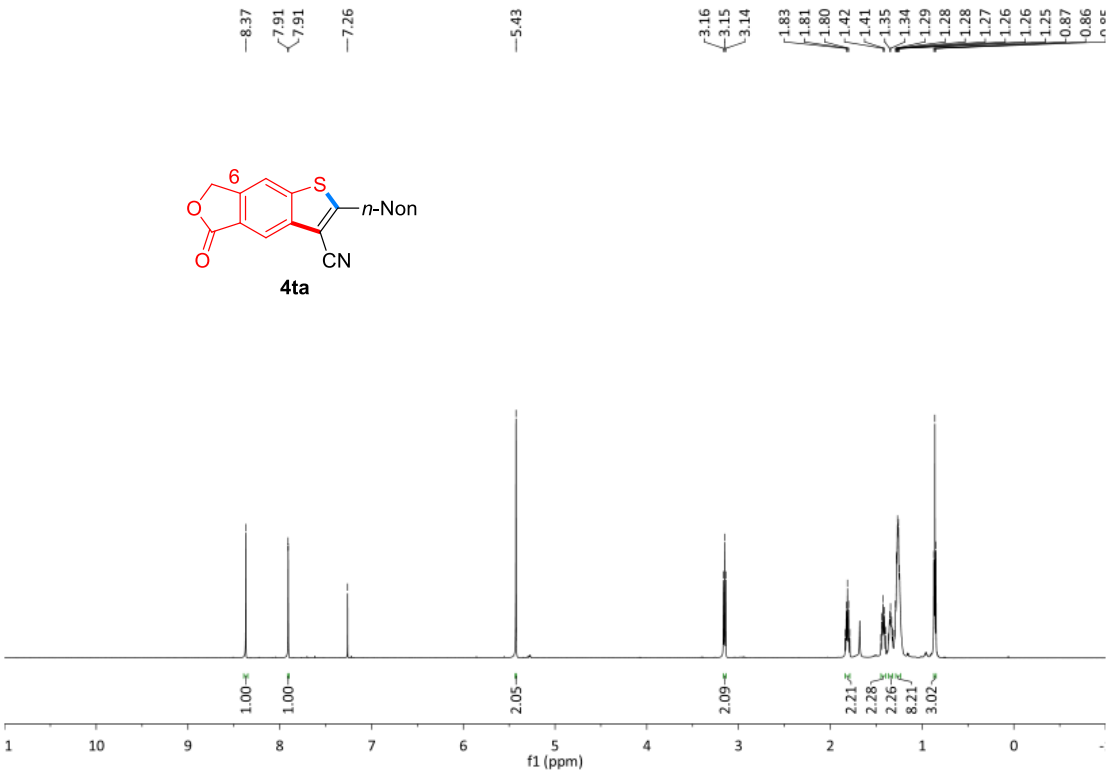

159.78
138.10
135.48
133.63
132.63
129.27
120.09
116.76
103.49
77.37
77.16
76.95
31.99
31.24
30.42
29.57
29.40
29.17
22.81
21.42
19.94
14.27
Me
S
n-Non
Me
CN
4qa
f1 (ppm)

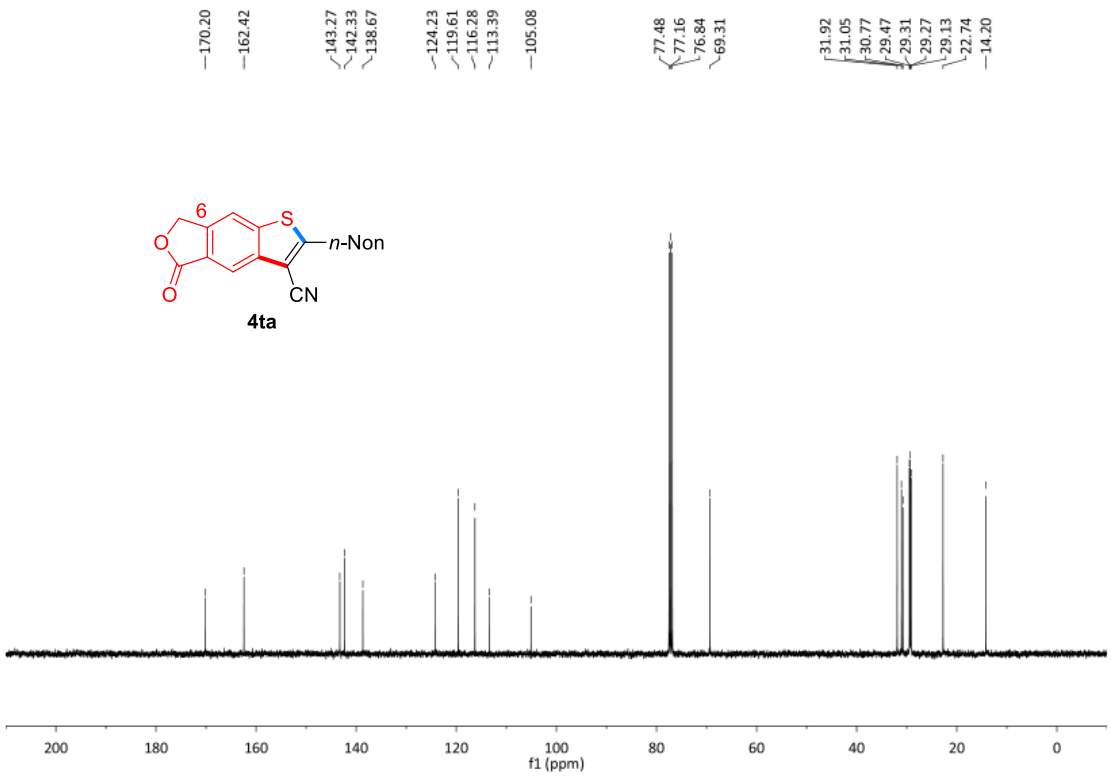

8.32
7.89
7.26
3.98
3.13
3.12
3.11
1.43
1.42
1.41
1.40
1.35
1.34
1.33
1.30
1.29
1.28
1.27
1.27
1.25
1.22
0.88
0.87
Cl
S
n-Non
MeOOC
CN
4ra
1.00
1.00
3.03
2.15
2.28
2.44
2.15
8.38
3.41
f1 (ppm)

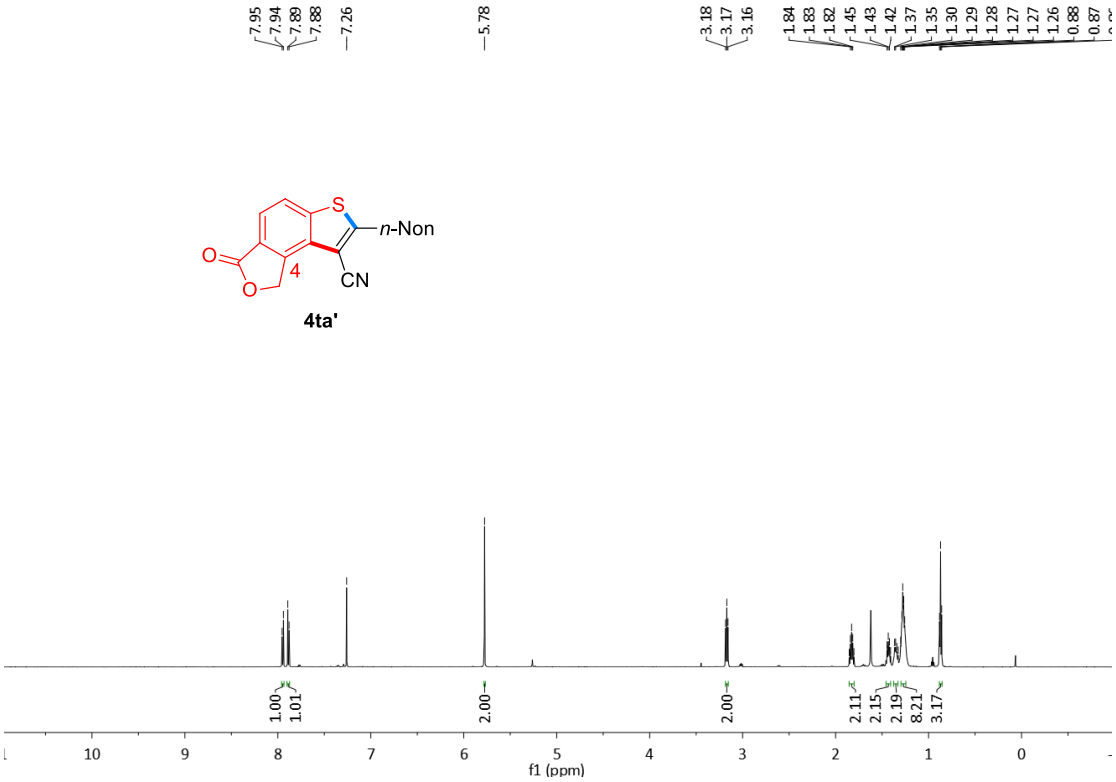

165.66
162.13
140.86
136.14
130.77
128.01
124.95
124.59
113.59
104.72
77.37
77.16
76.95
52.90
31.96
31.14
30.66
29.52
29.36
29.30
29.14
22.79
14.25
Cl
S
n-Non
MeOOC
CN
4ra
f1 (ppm)

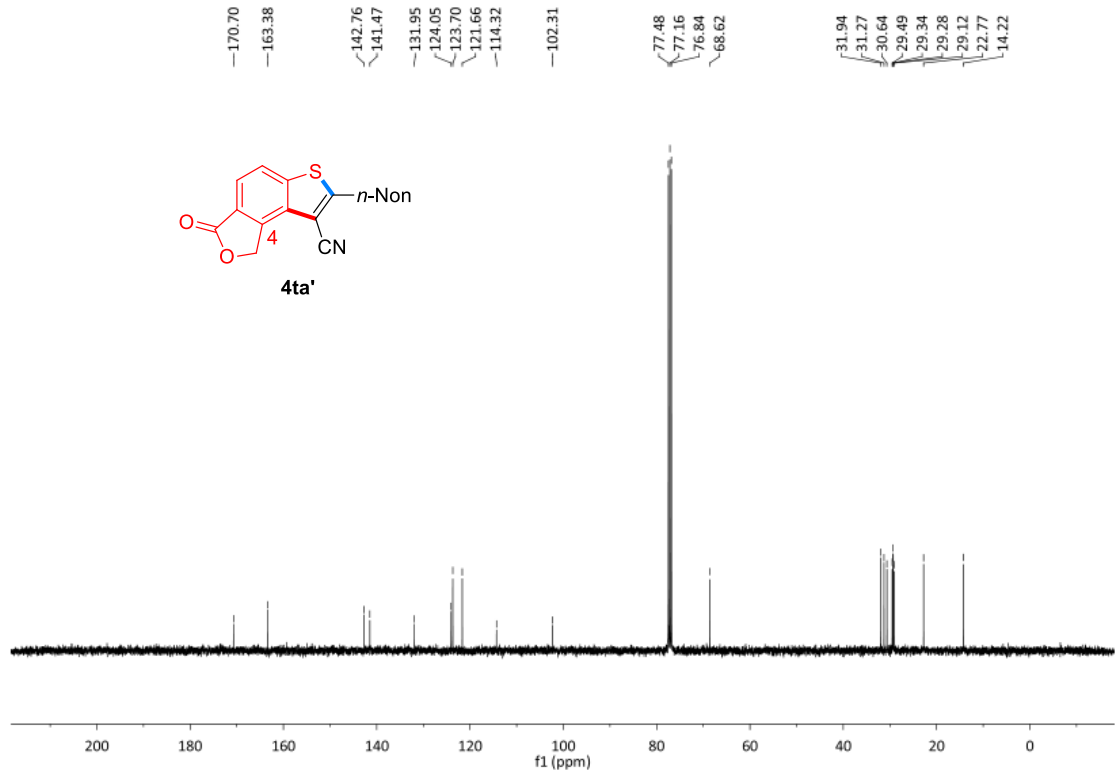

8.39
7.87
7.26
3.97
3.15
3.14
3.13
2.58
1.83
1.81
1.80
1.42
1.41
1.35
1.33
1.29
1.28
1.27
1.26
1.25
0.88
0.87
Me
S
n-Non
MeOOC
CN
4sa
1.00
1.00
3.03
2.11
3.22
2.31
2.29
2.06
8.02
3.29
f1 (ppm)

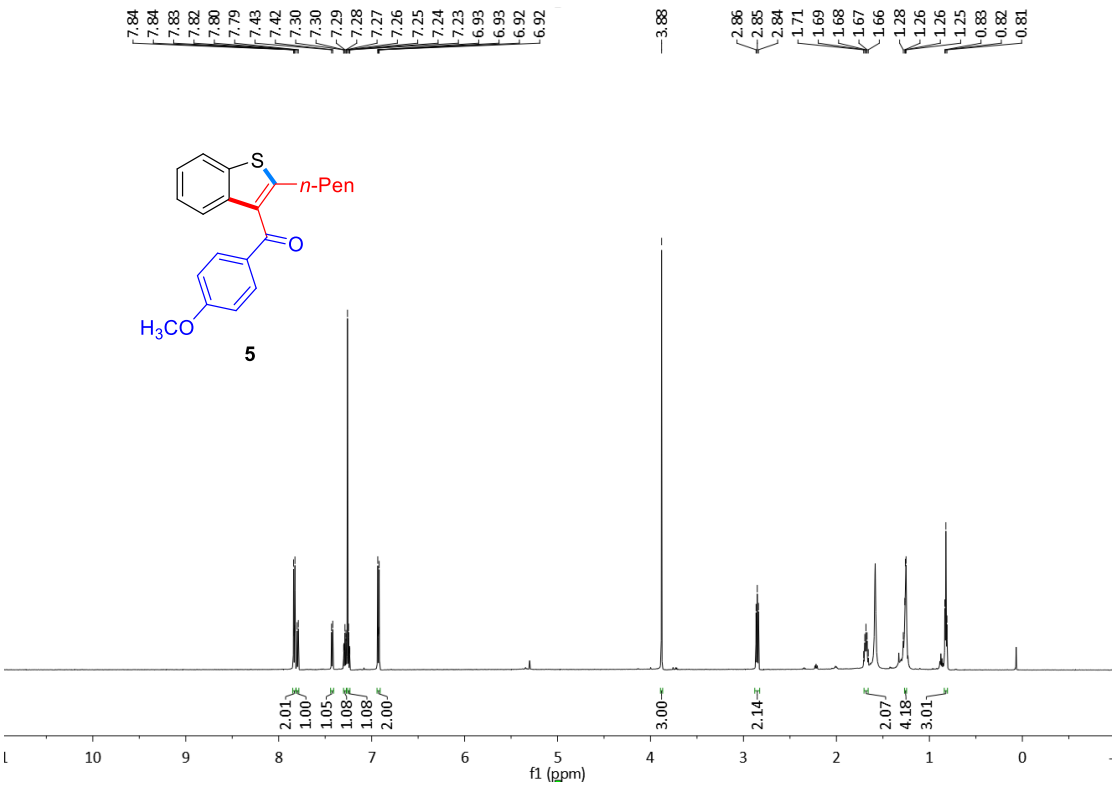

167.00
160.86
141.97
137.61
132.44
128.54
126.26
121.40
114.11
105.77
77.37
77.16
76.95
52.51
31.97
31.23
30.68
29.52
29.37
29.34
29.15
22.79
20.14
14.24
Me
S
n-Non
MeOOC
CN
4sa
f1 (ppm)

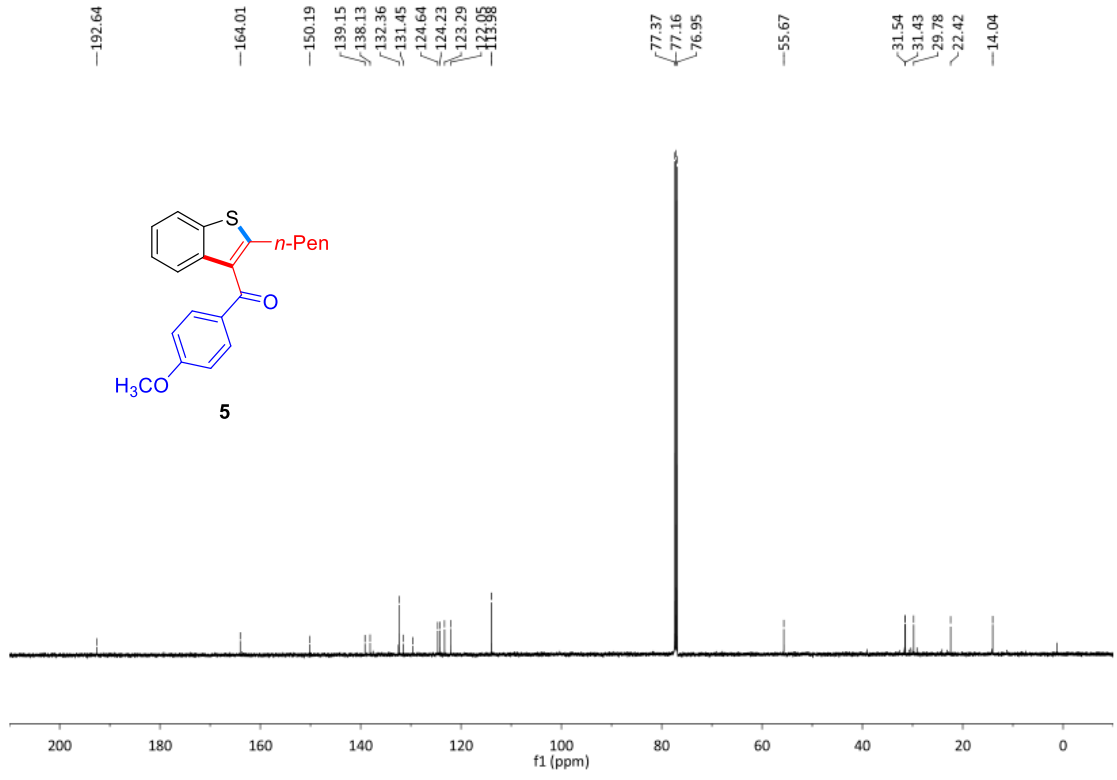

8.37
7.91
7.91
7.26
5.43
3.16
3.15
3.14
1.83
1.81
1.80
1.42
1.41
1.35
1.34
1.29
1.28
1.28
1.27
1.26
1.26
1.25
0.87
0.86
6
S
O
O
n-Non
CN
4ta
1.00
1.00
2.05
2.09
2.21
2.28
2.26
8.21
3.02
f1 (ppm)

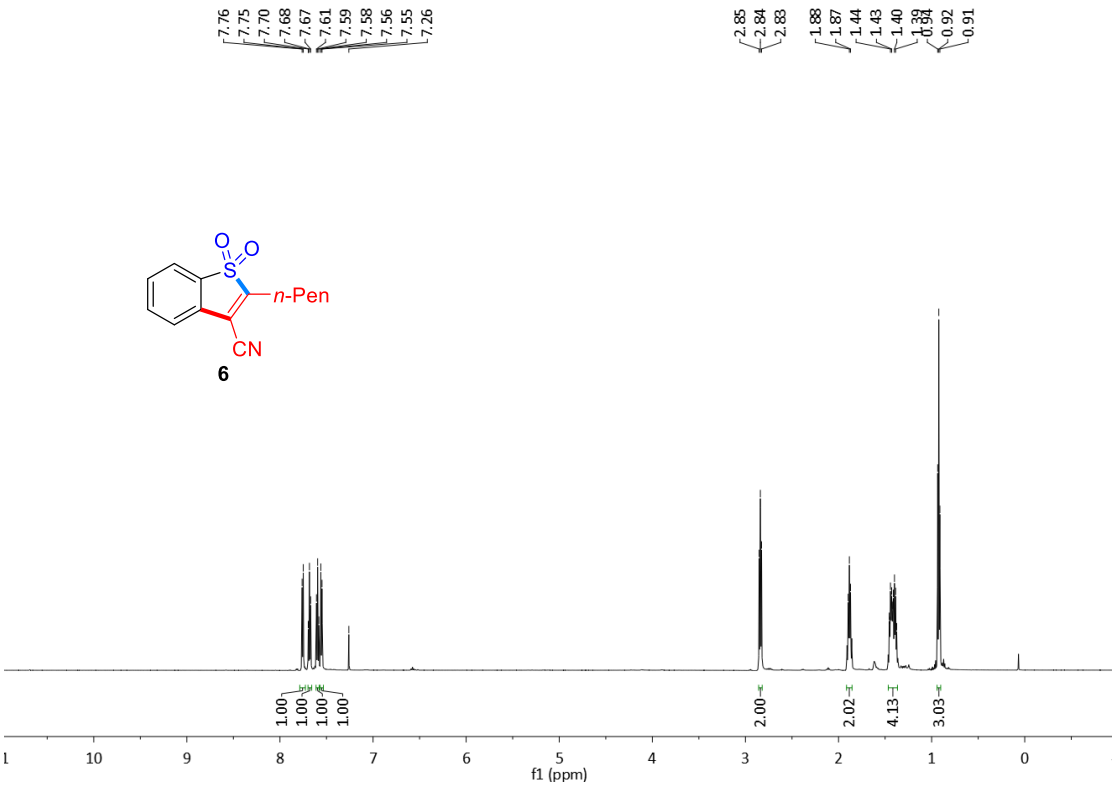

170.20
162.42
143.27
142.33
138.67
124.23
119.61
116.28
113.39
105.08
77.48
77.16
76.84
69.31
31.92
31.05
30.77
29.47
29.31
29.27
29.13
22.74
14.20
6
S
O
O
n-Non
CN
4ta
f1 (ppm)

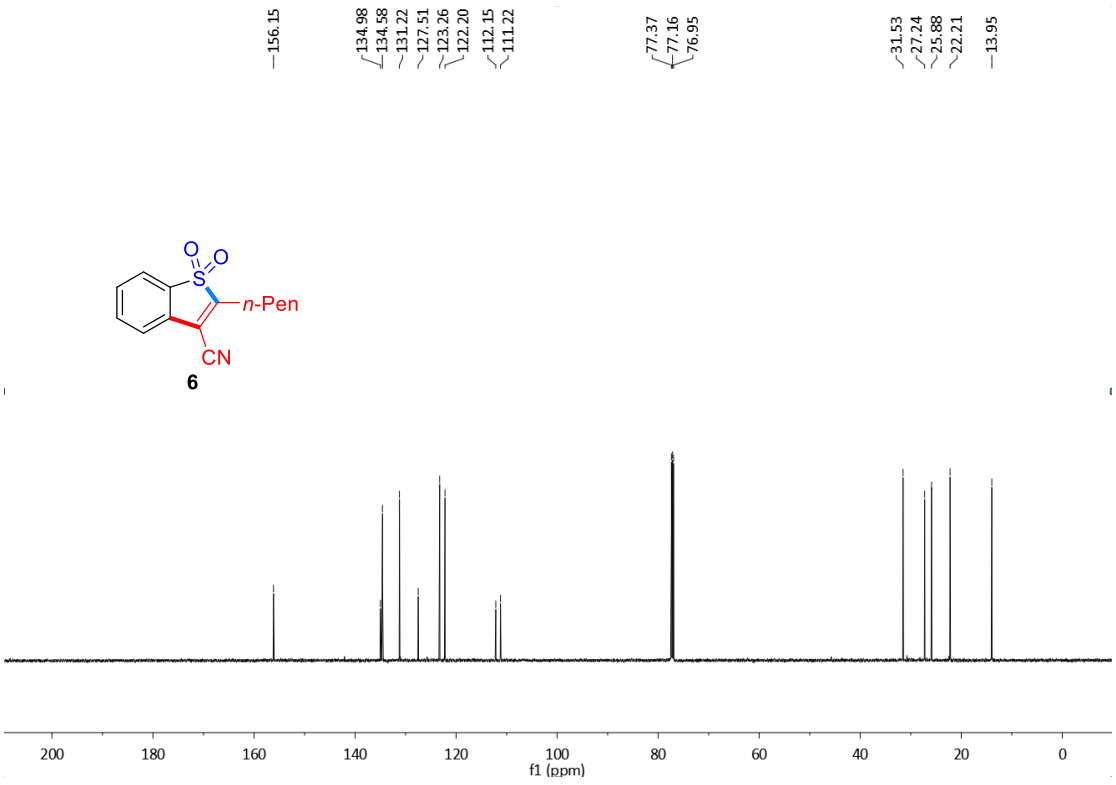

7.95
7.94
7.89
7.88
7.26
5.78
3.18
3.17
3.16
1.84
1.83
1.82
1.45
1.43
1.42
1.37
1.35
1.30
1.29
1.28
1.27
1.27
1.26
0.88
0.87
S
n-Non
O
4
O
CN
4ta'
1.00
1.01
2.00
2.00
2.11
2.15
2.19
8.21
3.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

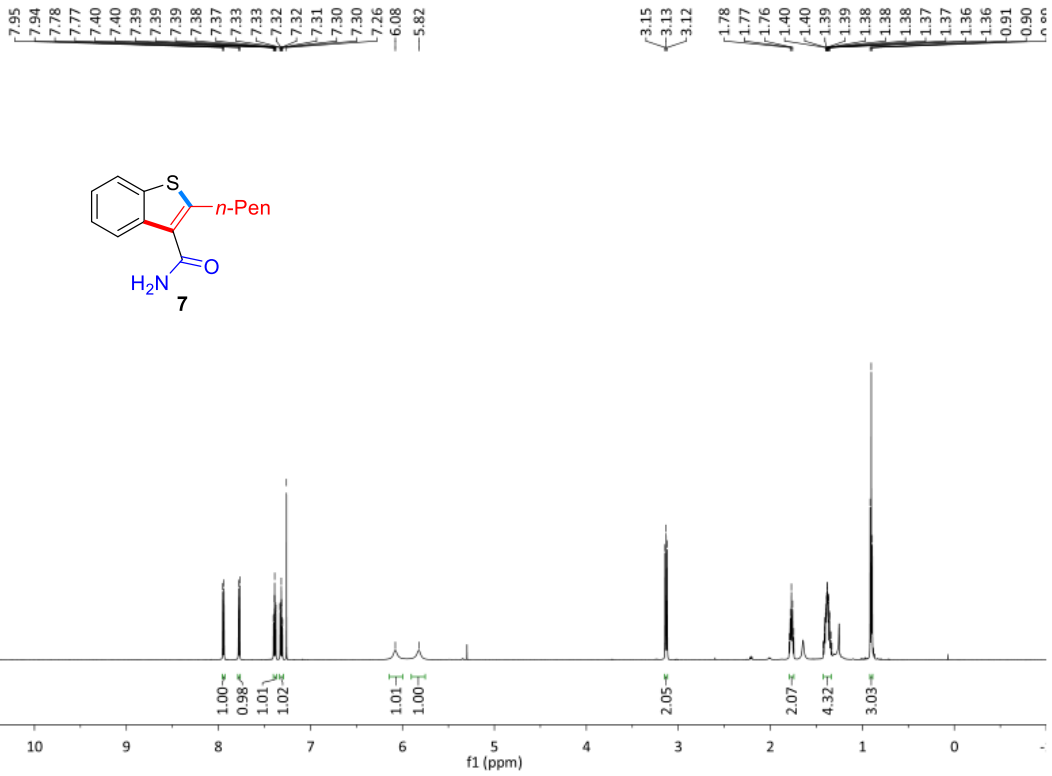

170.70
163.38
142.76
141.47
131.95
124.05
123.70
121.66
114.32
102.31
77.48
77.16
76.84
68.62
31.94
31.27
30.64
29.49
29.34
29.28
29.12
22.77
14.22
S
n-Non
O
4
O
CN
4ta'
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

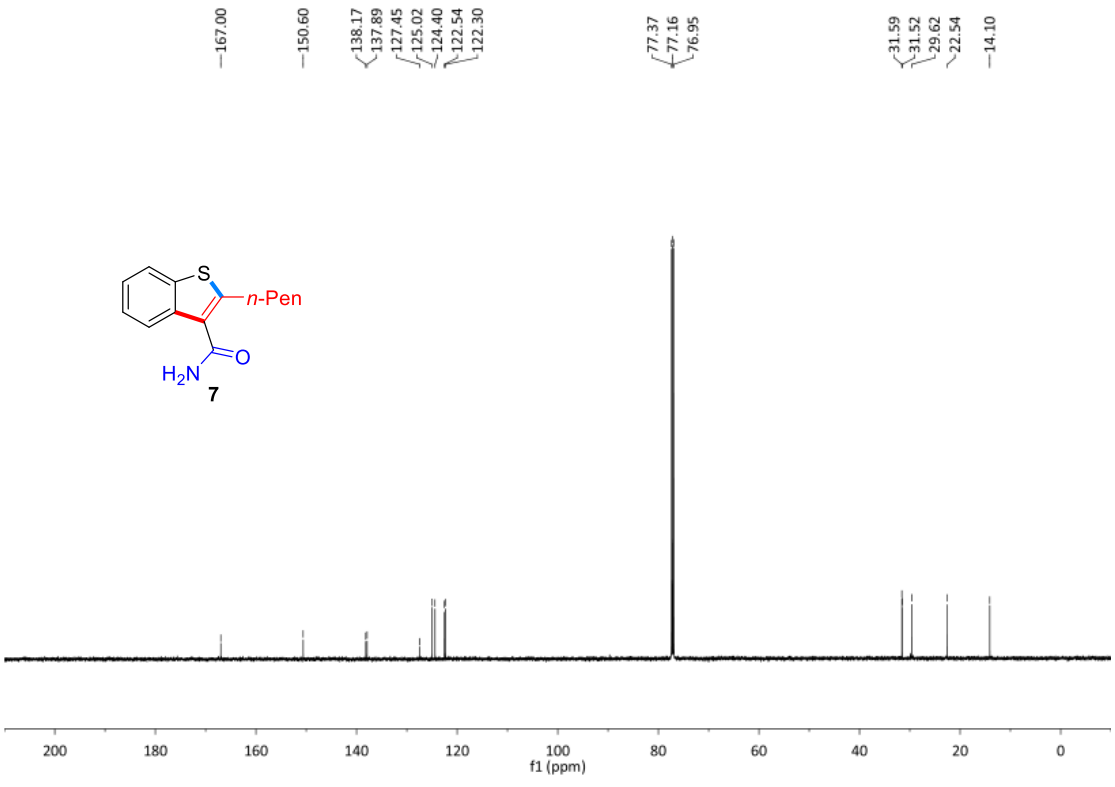

7.84
7.84
7.83
7.82
7.80
7.79
7.43
7.42
7.30
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
6.93
6.93
6.92
6.92
3.88
2.86
2.85
2.84
1.71
1.69
1.68
1.67
1.66
1.28
1.26
1.26
1.25
0.83
0.82
0.81
S
n-Pen
O
H3CO
5
2.01
1.00
1.05
1.08
1.08
2.00
3.00
2.14
2.07
4.18
3.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

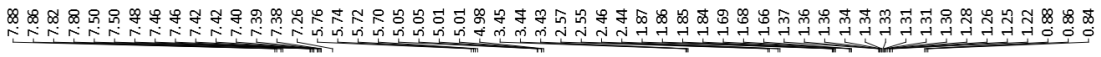

192.64
164.01
150.19
139.15
138.13
132.36
131.45
124.64
124.23
123.29
113.98
77.37
77.16
76.95
55.67
31.54
31.43
29.78
22.42
14.04
S
n-Pen
O
H3CO
5
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

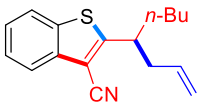

7.76
7.75
7.70
7.68
7.67
7.61
7.59
7.58
7.56
7.55
7.26
2.85
2.84
2.83
1.88
1.87
1.44
1.43
1.40
0.92
0.91
n-Pen
CN
6
1.00
1.00
1.00
1.00
2.00
2.02
4.13
3.03
f1 (ppm)


156.15
134.98
134.58
131.22
127.51
123.26
122.20
112.15
111.22
77.37
77.16
76.95
31.53
27.24
25.88
22.21
13.95
n-Pen
CN
6
f1 (ppm)

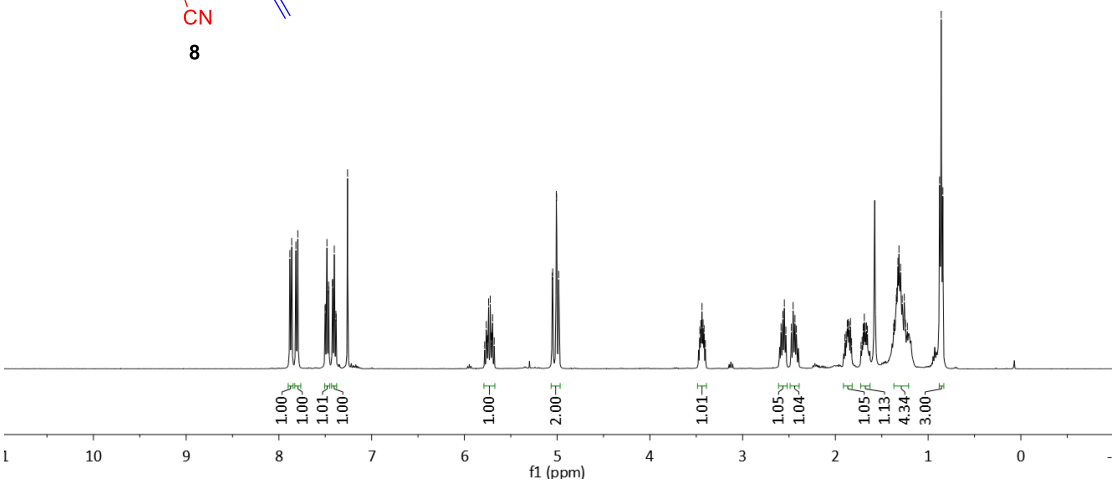

7.95
7.94
7.78
7.77
7.40
7.40
7.39
7.39
7.39
7.38
7.37
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.26
6.08
5.82
3.15
3.13
3.12
1.78
1.77
1.76
1.40
1.40
1.39
1.39
1.38
1.38
1.38
1.37
1.37
1.36
1.36
0.91
0.90
S
n-Pen
O
H2N
7
1.00
0.98
1.01
1.02
1.01
1.00
2.05
2.07
4.32
3.03
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

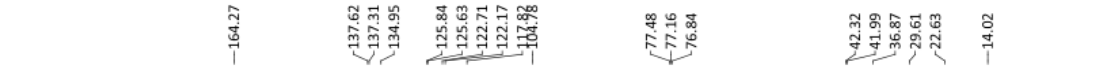

167.00
150.60
138.17
137.89
127.45
125.02
124.40
122.54
122.30
77.37
77.16
76.95
31.59
31.52
29.62
22.54
14.10
S
n-Pen
O
H2N
7
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

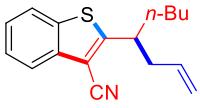

7.88
7.86
7.82
7.80
7.50
7.50
7.48
7.46
7.46
7.42
7.42
7.40
7.39
7.38
7.26
5.76
5.74
5.72
5.70
5.05
5.05
5.01
5.01
4.98
3.45
3.44
3.43
2.57
2.55
2.46
2.44
1.87
1.86
1.85
1.84
1.69
1.68
1.66
1.37
1.36
1.36
1.34
1.34
1.33
1.31
1.31
1.30
1.28
1.26
1.25
1.22
0.88
0.86
0.84


S
n-Bu
CN

8


1.00
1.00
1.01
1.00
1.00
2.00
1.01
1.05
1.04
1.05
1.13
4.34
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


164.27
137.62
137.31
134.95
125.84
125.63
122.71
122.17
117.82
104.78
77.48
77.16
76.84
42.32
41.99
36.87
29.61
22.63
14.02


S
n-Bu
CN

8

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)