Supplementary Information

Dihalo(imidazolium)sulfuranes: A Versatile Platform for the Synthesis of New Electrophilic Group-Transfer Reagents

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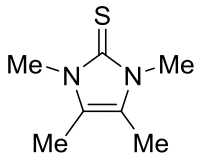
Experimental procedures and characterizations.

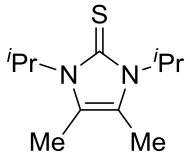
General: All solvents were purified by distillation over the drying agents indicated. All reactions were carried out under Ar atmosphere unless other way stated. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker AV 400 or DPX 300; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. All flash chromatography was performed on Merck 60 silica gel (40-63 µm). Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates and visualized by UV irradiation and/or ceric ammonium molybdate, $KMnO_4$ or *p*-anysaldehyde dip. All commercially available compounds (Acros, ABCR, Alfa Aesar, Aldrich) were used as received. Compounds **1**, **2** and **4** were synthetized following optimized versions of the procedures described in the literature; spectroscopic data are in agreement with those reported.[1, 2]

Compound 1



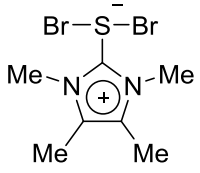
Acetoin (5.92 mL, 68.09 mmol) was added to a stirred solution of dimethylthiourea (7.09 g, 68.09 mmol) in 1-hexanol (80 mL) and the reaction mixture was heated to 158 °C for 12h. Then, the solution was allowed to cool to room temperature and the solid was filtered and washed with cold ethanol to afford compound **1** as a white solid (10.64 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.98 (6H, s), 3.42 (6H, s). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 9.1, 31.8, 120.7, 159.9. IR (neat, cm^{-1}) = 854, 1099, 1175, 1219, 1378, 1427, 1463, 1657, 2942.

Compound 2



Acetoin (20.62 mL, 237.08 mmol) was added to a stirred solution of diisopropylthiourea (38.00 g, 237.08 mmol) in 1-hexanol (225 mL), and the reaction mixture was heated to 158 °C for 12h. Subsequently, the solution was cooled down to room temperature and the solid formed was filtered and washed with cold ethanol to afford compound **2** as a white solid (37.20 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.42 (12H, d, *J* = 7.3Hz), 2.16 (6H, s), 5.17 – 6.22 (2H, br s). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ =10.5, 20.9, 49.5, 121.5, 159.8. IR (neat, cm^{-1}) = 906, 980, 1025, 1089, 1105, 1138, 1206, 1338, 1368, 1412, 1464, 1643, 2937, 2974. HRMS: calcd. for $C_{11}H_{21}N_2S$ $[M^+]$ = 213.1419; found = 213.1419.

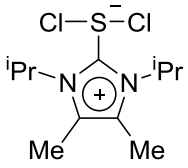
Compound 3



Bromine (655 µL, 12.81 mmol) was added at 0ºC to a solution of compound **1** (2.00 g, 12.81 mmol) in dry DCM (21 mL), and the reaction slowly warmed up to RT during 3 hours. After removal of all volatiles under vacuum, compound **3** was obtained as an orange solid (3.88 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 2.27 (6H, s), 3.81 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 9.7, 33.8, 127.8. IR (neat, cm^{-1}) = 783, 855, 1032, 1230, 1372, 1429, 1490, 1624, 2944. HRMS: calcd. for $C_7H_{12}N_2BrS$ [M-Br] = 234.9898; found = 234.9899.

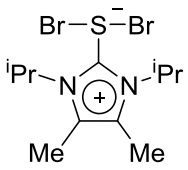
[1] Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.
[2] Roesky, H. W.; Nehete, U. N.; Singh, S.; Schmidt, H.-G.; Shermolovich, Y. G. *Main Group Chem.* **2005**, *4*, 11.

Compound 4



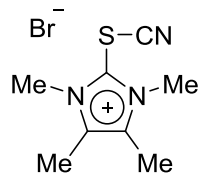
Following the procedure described in the literature, SO_2Cl_2 (517 µL, 5.18 mmol) was added to a solution of compound **2** (1.00 g, 4.71 mmol) in 20 mL of toluene at 0 ºC. The reaction mixture was left to warm up to RT for 1 hour. The precipitate was filtered off, washed with cold toluene and dried under vacuum to afford compound **4** as a yellowish solid (979 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 1.67 (12H, d, *J* = 7.1Hz), 2.37 (6H, s), 5.69 (2H, hept, *J* = 7.1Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ =10.5, 21.0, 53.5, 127.8, 147.6. IR (neat, cm^{-1}) = 978, 1032, 1110, 1137, 1215, 1369, 1420, 1610, 2878, 2935. HRMS: calcd. for $C_{11}H_{20}N_2ClS$ [M]= 247.1030; found = 247.1030.

Compound 5



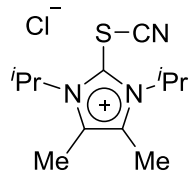
To a solution of compound **2** (20.13 g, 94.77 mmol) in dry DCM (100 mL) bromine (4.9 mL, 94.77 mmol) was added at 0 ºC and the reaction was allowed to warm up to RT for 3 hours. After removal of all volatiles under vacuum, compound **5** was obtained as an orange solid (33.05 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 1.68 (12H, d, *J* = 7.1 Hz), 2.37 (6H, s), 5.67 (2H, hept, *J* = 7.1Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ =10.7, 20.6, 53.7, 128.3, 146.0. IR (neat, cm^{-1}) = 907, 980, 1028, 1112, 1137, 1217, 1371, 1423, 1606, 2877, 2936, 2972. HRMS: calcd. for $C_{11}H_{20}BrN_2S$ [M] = 291.0523; found = 291.0525.

Compound 6



Trimethylsilyl cyanide (252 µL, 2 mmol) was added to a solution of **3** (632 mg, 2 mmol) in dry DCM (5 mL) at room temperature. After stirring for 30 minutes all the volatiles were removed under vacuum and the obtained solid washed with dry ether to afford **6** as a white solid (501 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 2.35 (6H, s), 3.96 (6H, s). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 9.9, 34.7, 106.6, 130.3, 131.8. IR (neat, cm^{-1}) = 774, 860, 1032, 1102, 1232, 1374, 1439, 1508, 1631, 2168, 2930, 2969. HRMS: calcd. for $C_8H_{12}N_3S$ [M-Br] = 182.0748; found =182.0746.

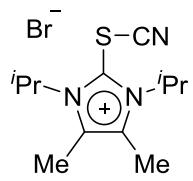
Compound 7



TMSCN (252 µL, 2 mmol) was added dropwise to a solution of **4** (454 mg, 2 mmol) in dry DCM (5 mL) at 0°C, and the reaction mixture stirred at room temperature for 1 hour. After that the solvent was evaporated and the remaining solid washed twice with diethyl ether and dried under vacuum to afford compound **7** as an off-white solid (409 mg, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.72 (12H, d, *J* = 6.9 Hz), 2.40 (6H, s), 5.40 (2H, hept, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 10.1, 20.1, 54.0, 108.1, 129.3, 131.4. IR (neat, cm^{-1}) = 907, 980, 1114, 1140, 1216, 1342, 1371, 1393, 1457, 1607, 2151, 2938, 2971.

HRMS: calcd. for $C_{11}H_{14}N_2$ [M-Cl] = 238.1373; found = 238.1372.

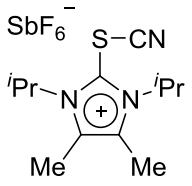
Compound 8



TMSCN (5.60 mL, 45.16 mmol) was added dropwise at 0°C to a solution of compound **5** (14.01 g, 37.64 mmol) in dry DCM (50 mL) and the reaction mixture was stirred at RT for 3h. The solvent was then evaporated and the remaining solid washed twice with diethyl ether and dried under vacuum to afford compound **8** as a pale yellow solid (10.66 g, 89

%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 1.72 (12H, d, *J* = 7.1 Hz), 2.40 (6H, s), 5.38, (2H, hept, *J* = 7.1Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 10.9, 20.9, 55.0, 107.7, 130.4, 131.7. IR (neat, cm^{-1}) = 910, 1109, 1220, 1372, 1396, 1619, 2154, 2939, 3003, 3467. HRMS: calcd. for $C_{12}H_{20}N_3S$ [M]= 238.1372; found = 238.1372. Anal. Calcd for $C_{12}H_{20}BrN_3S$: C, 45.29; H, 6.33; N, 13.20. Found: C, 45.55; H, 6.47; N, 12.99.

Compound 9

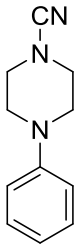


Solid $AgSbF_6$ (4.34 g, 12.63 mmol) was added to a solution of **8** (4.02 g, 12.63 mmol) in dry MeCN (25 mL) and the reaction mixture was allowed to stir at RT for 1h. The formed AgBr was then removed by filtration, affording **9** as a pale yellow solid (5.68 g, 95 %). ^{1}H NMR (400 MHz, CD_3CN, ppm) δ = 1.64 (12H, d, *J* = 7.0 Hz), 2.40 (6H, s), 5.19 (2H, hept, *J* = 6.9 Hz). ^{13}C NMR (101 MHz, CD_3CN, ppm) δ =10.7, 20.9, 55.1, 106.8, 124.7, 133.7. IR (neat, cm^{-1}) = 905, 1114, 1139, 1217, 1381, 1397, 1460, 1600, 2173, 2999. ^{19}F NMR (282 MHz, CD_3CN) δ= -124.05 (sext, $J_{F\text{-}121Sb}$= 1947 Hz). HRMS: calcd. for $C_{12}H_{20}N_3S_1$ [M-SbF_6] = 238.1373; found = 238.1372. Anal. Calcd for $C_{12}H_{20}F_6N_3SSb$: C, 30.40; H, 4.25; N, 8.86. Found: C, 30.45; H, 4.21; N, 8.85.

General procedure for electrophilic cyanation of amines and thiols (Method A):

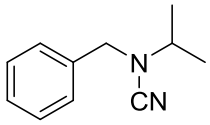
To a solution of the desired substrate (0.30-0.38 mmol) and DIPEA (1.0 eq) in DCM (0.15 M), **8** (1.2 eq) was added and the reaction mixture stirred at room temperature for the specified time (see Chart 1). The reaction was quenched with saturated NH_4Cl and extracted with DCM. The organic layers were dried over anhydrous Na_2SO_4, filtered, and the volatiles were removed under vacuum. The crude was purified by flash chromatography on silica gel (*n*-Hexane/EtOAc) affording the desired products.

Compound 10



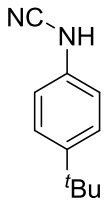
Using the general procedure, compound **10** was prepared from 1-phenylpiperazine (45 µL, 0.30 mmol), DIPEA (52 µL, 0.30 mmol) and **8** (114 mg, 0.36 mmol), to obtain after flash chromatography (*n*-Hexane/EtOAc 7/3) a colorless oil (49 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 3.18 – 3.27 (4H, m), 3.34 – 3.46 (4H, m), 6.88 – 6.99 (3H, m), 7.23 – 7.36 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 48.1, 48.3, 116.4, 116.8, 120.5, 128.6, 150.0. IR (neat, cm^{-1}) = 910, 998, 1139, 1173, 1229, 1266, 1326, 1380, 1448, 1494, 1597, 1721, 2209, 2822. HRMS: calcd. for $C_{11}H_{13}N_3Na_1$ [M+Na] = 210.1001; found = 210.1001.

Compound 11



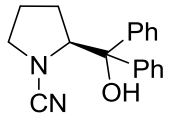
Using the general procedure, compound **11** was prepared from *N*-isopropylbenzylamine (55 µL, 0.33 mmol), DIPEA (57 µL, 0.33 mmol) and **8** (124 mg, 0.39 mmol) to obtain after flash chromatography (*n*-Hexane/EtOAc 7/3) a colorless oil (52 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.24 (3H, s), 1.26 (3H, s), 3.11 (1H, hept, *J* = 6.5 Hz), 4.21 (2H, s), 7.30 – 7.42 (5H, m). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 19.7, 50.2, 53.5, 115.93, 127.5, 127.6, 128.1, 134.5. IR (neat, cm^{-1}) = 958, 1028, 1077, 1095, 1127, 1172, 1209, 1370, 1388, 1454, 1496, 1604, 2202, 2874, 2929, 2973, 3031. HRMS: calcd. for $C_{11}H_{14}N_2Na_1$ [M+Na] = 197.1049; found = 197.1049

Compound 12



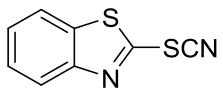
Using the general procedure, compound **12** was prepared from 4-tert-butylaniline (53 µL, 0.34 mmol), DIPEA (59 µL, 0.34 mmol) and **8** (129 mg, 0.40 mmol) to obtain after flash chromatography (*n*-Hexane/EtOAc 7/3) a white solid (47 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.30 (9H, s), 5.99 (1H, s), 6.92 – 6.99 (2H, m), 7.32 – 7.40 (2H, dd, *J* = 10.7, 5.4 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 30.6, 33.6, 110.4, 114.3, 125.9, 133.6, 146.1. IR (neat, cm^{-1}) = 1023, 1248, 1426, 1514, 1615, 2224, 2959, 3066, 3156. HRMS: calcd. for $C_{11}H_{14}N_2$ [M-H] = 173.1084; found = 173.1084.

Compound 13



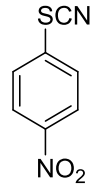
Using the general procedure, compound **13** was prepared from (*S*)-(-)-α,α-diphenylprolinol (76 mg, 0.30 mmol), DIPEA (52 µL, 0.30 mmol) and **8** (114 mg, 0.36 mmol) to obtain after flash chromatography (*n*-Hexane/EtOAc 7/3) a white solid (70 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.70 – 1.87 (2H, m), 1.88 – 1.96 (2H, m), 2.60 (1H, s), 3.41 – 3.46 (1H, m), 4.81 (1H, t, *J* = 6.9 Hz), 7.19 – 7.41 (6H, m), 7.43 – 7.49 (2H, m), 7.56 – 7.62 (2H, m) . ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 25.3, 28.2, 54.2, 69.3, 79.2, 117.4, 126.1, 127.2, 128.3, 143.6. IR (neat, cm^{-1}) = 961, 987, 1034, 1270, 1386, 1449, 1493, 1754, 2004, 2026, 2146, 2968, 3057, 3490. HRMS: calcd. for $C_{18}H_{19}N_2O_1$ [M+H] = 279.1493; found = 279.1491.

Compound 14



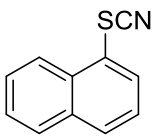
Using the general procedure, compound **14** was prepared from 2-mercaptobenzothiazole (63 mg, 0.38 mmol), DIPEA (66 µL, 0.38 mmol) and **8** (145 mg, 0.45 mmol) to obtain after flash chromatography (*n*-Hexane/EtOAc 8/2) as yellow solid (66 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.47 (1H, ddd, *J* = 8.1, 7.3, 1.3 Hz), 7.54 (1H, ddd, *J* = 8.3, 7.3, 1.3 Hz), 7.88 (1H, ddd, *J* = 8.0, 1.2, 0.5 Hz), 8.00 (1H, brdd, *J* = 8.2, 0.6 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 106.2, 120.6, 122.4, 125.6, 126.4, 135.7, 152.2, 152.6. IR (neat, cm^{-1}) = 1075, 1163, 1235, 1273, 1309, 1419, 1461, 1554, 1586, 1619, 1789, 1911, 1946, 2166, 2920, 2987, 3051. HRMS: calcd. for $C_8H_4N_2S_2Na_1$ [M+Na] = 214.9705; found = 214.9708.

Compound 15



Using the general procedure, compound **15** was prepared from 4-nitrobenzenethiol (54 mg, 0.35 mmol), DIPEA (61 µL, 0.35 mmol) and compound **8** (133 mg, 0.42 mmol) to obtain after flash chromatography (*n*-Hexane/EtOAc 8/2) a white solid (48 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.63 – 7.72 (2H, m), 8.28 – 8.34 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 108.0, 125.1, 128.7, 133.3, 148.0. IR (neat, cm^{-1}) = 956, 1009, 1081, 1106, 1120, 1187, 1278, 1316, 1398, 1417, 1475, 1514, 1578, 1601, 1664, 1922, 2161, 2445, 2844, 3104. HRMS: calcd. for $C_7H_4N_2O_2S_1$ [M] = 179.9991; found = 179.9993.

Compound 16



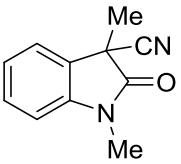
Using the general procedure, compound **16** was prepared from 1-naphthalenethiol (50 µL, 0.36 mmol), DIPEA (62 µL, 0.36 mmol) and **8** (136 mg, 0.43 mmol) to obtain after flash chromatography (*n*-Hexane/EtOAc 9/1) a pale yellow solid (56 mg, 85%). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ = 7.54 (1H, dd, *J* = 8.3, 7.3 Hz), 7.64 (1H, ddd, *J* = 8.2, 6.9, 1.2 Hz), 7.73 (1H, ddd, *J* = 8.5, 7.0, 1.4 Hz), 7.93 – 7.99 (2H, m), 8.02 (1H, br d, *J* = 8.0 Hz), 8.27 (1H, dd, *J* = 8.5, 0.9

Hz). ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ = 111.0, 121.1, 124.5, 126.3, 127.5, 128.4, 129.3, 131.9, 132.5, 133.0, 134.7. IR (neat, cm^{-1}) = 965, 1058, 1143, 1200, 1255, 1338, 1369, 1501, 1590, 1720, 1823, 1935, 2151, 2832, 3056. HRMS: calcd. $C_{11}H_7N_1S_1$ [M] = 185.0298; found = 185.0299.

General procedure for electrophilic cyanation of activated methylenes (Method A):

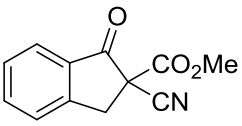
DIPEA (1.0 eq.) was added to a solution of the desired substrate (0.30 mmol) in dry DCM (0.15 M). After stirring 30 min, solid **8** (1.2 eq.) was added and the reaction was allowed to stir for the specified time (see Chart 1). Quenched with HCl (1N) and extraction with EtOAc afforded a crude product that was purified by flash chromatography on silica gel (*n*-Hexane/EtOAc).

Compound 17



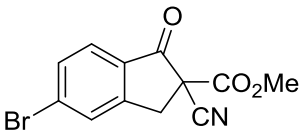
NaH (8 mg, 0.33 mmol) was added to a solution of 1,3-dimethylindolin-2-one (48 mg, 0.29 mmol.) in dry THF (2.0 mL) at 0ºC. After stirring for 30 minutes, solid **8** (143 mg, 0.45 mmol) was added, and the reaction mixture was left to warm up to room temperature for 12 h. Quenching with HCl (1N) and extraction with EtOAc afforded a crude that was purified by flash chromatography on silica gel (n-Hexane/EtOAc 7/3). Compound **17** was obtained as a colorless solid (39 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 1.67 (3H, s), 2.97 (3H, s), 6.61 (1H, d, *J* = 7.4 Hz), 6.71 (1H, d, *J* = 7.8 Hz), 6.86 (1H, td, *J* = 7.4, 1.1 Hz), 7.20 – 7.28 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 17.5, 26.0, 51.8, 108.0, 121.7, 123.8, 128.6, 129.8, 131.3, 143.9, 177.8. IR (neat, cm^{-1}) = 758, 1027, 1093, 1156, 1263, 1303, 1346, 1373, 1453, 1473, 1607, 1697, 2935, 2967. HRMS: calcd. for $C_{11}H_{10}N_2ONa$ [M+Na]= 209.0685; found 209.0685.

Compound 18



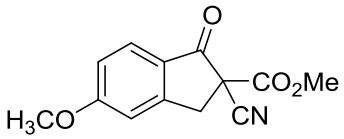
Using the general procedure, compound **18** was prepared from methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (57 mg, 0.30 mmol.), DIPEA (52 µL, 0.30 mmol) and **8** (114 mg, 0.36 mmol). Purification by flash chromatography (*n*-Hexane/EtOAc 8/2) afforded a colorless oil (60 mg, 93%). ^{1}H NMR (400 MHz, CDCl3, ppm) δ = 3.71 (1H, d, *J* = 17.3 Hz), 3.89 (3H, s), 3.96 (1H, d, *J* = 17.3 Hz), 7.51 (1H, t, *J* = 7.5 Hz), 7.56 (1H, dt, *J* = 7.8, 0.9 Hz), 7.75 (1H, t, *J* = 7.7 Hz), 7.86 (1H, m). HRMS: calcd. $C_{12}H_9N_1O_3Na_1$ [M+Na] = 238.0476; found = 238.0474.

Compound 19



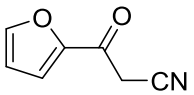
Using the general procedure, compound **19** was prepared from methyl 5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (81 mg, 0.30 mmol.), DIPEA (78 µL, 0.45 mmol) and compound **6** (118 mg, 0.45 mmol) to obtain after flash chromatography (*n*-Hexane/EtOAc 7/3) a colorless oil (69 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 3.65 (1H, d, *J* = 17.4Hz), 3.87 (3H, s), 3.91 (1H, d, *J* = 17.4 Hz), 7.62 (1H, ddt, *J* = 8.6, 1.6, 0.8 Hz), 7.69 (1H, dd, *J* = 8.6, 0.8 Hz), 7.72 (1H, dd, *J* = 1.6, 0.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 37.2, 54.4, 55.0, 115.4, 127.4, 130.0, 131.0, 133.0, 133.1, 152.9, 164.4, 189.5. IR (neat, cm^{-1}) = 958, 1018, 1092, 1236, 1308, 1329, 1445, 1490, 1651, 1720, 1741, 2252, 2890. HRMS: calcd. for $C_{12}H_8NO_3BrNa$ [M+Na] = 315.9578; found = 315.9579.

Compound 20



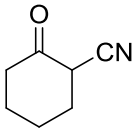
Using the general procedure, compound **20** was prepared from methyl 5-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate[3] (60 mg, 0.27 mmol), DIPEA (72 µL, 0.41 mmol) and compound **8** (135 mg, 0.42 mmol) to obtain, after flash chromatography (*n*-Hexane/EtOAc 8/2) a colorless oil (39 mg, 59%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 3.60 (1H, d, *J* = 17.2 Hz), 3.83 – 3.93 (7H, m), 6.86 – 6.95 (1H, m), 6.99 (1H, dd, *J* = 8.6, 2.2 Hz), 7.75 (1H, d, *J* = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 37.6, 54.7, 54.7, 56.2, 109.7, 116.2, 117.4, 125.1, 128.3, 154.9, 165.1, 167.3, 188.5. IR (neat, cm^{-1}) = 952, 1019, 1090, 1240, 1308, 1340, 1443, 1492, 1650, 1716, 1745, 2247, 2844, 2956. HRMS: calcd. for $C_{13}H_{11}NO_4Na$ [M+Na] = 268.0578; found = 268.0580.

Compound 21



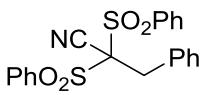
Using the general procedure, compound **21** was prepared from 4,4,4-trifluoro-1-(furan-2-yl)butane-1,3-dione (45 µL, 0.30 mmol), DIPEA (89 µL, 0.51 mmol) and **8** (147 mg, 0.46 mmol) to obtain after flash chromatography (*n*-Hexane/EtOAc 8/2) as a yellow solid (40 mg, 99%). ^{1}H NMR (300 MHz, CDCl3, ppm) δ = 3.88 (2H,s), 6.57 (1H, dd, *J* = 3.7, 1.7 Hz), 7.31 (1H, dd, *J* = 3.7, 0.7 Hz), 7.59 (1H, dd, *J* = 1.7, 0.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 29.8, 113.5, 119.4, 147.8, 147.9, 150.6, 175.8. IR (neat, cm^{-1}) = 881, 903, 941, 995, 1015, 1082, 1163, 1259, 1330, 1387, 1461, 1561, 1671, 1850, 2258, 2927, 2957, 3126, 3140. HRMS: calcd. for $C_7H_5N_1O_2Na$ [M+Na] = 158.0212; found = 158.0212.

Compound 22



In a 2-necked round bottom flask, compound **8** (1.79 g, 5.59 mmol) was added to a solution of freshly distilled 1-cyclohexene-pyrrolidine (0.9 mL, 5.59 mmol) and DIPEA (1.0 mL, 5.59 mmol) in DCM (18 mL) at RT. After stirring 1 hour, the reaction was quenched with HCl (1N) and thoroughly extracted with Et_2O. The organic layers were dried over Na_2SO_4, filtered and all the volatiles were removed under vacuum. The pure product was obtained by distillation (88ºC, 0.1 mbar) as a colorless oil (379 mg, 55%). ^{1}H NMR (ketone form) (300 MHz, $CDCl_3$, ppm) δ = 1.65 – 1.89 (3H, m), 1.96 – 2.15 (3H, m), 2.31 – 2.48 (2H, m), 3.50 (1H, dd, J = 10.7, 5.4 Hz). ^{13}C NMR (ketone) (75 MHz, $CDCl_3$, ppm) δ = 23.6, 26.7, 32.0, 40.6, 43.3, 116.5, 200.3. ^{1}H NMR (enol form) (300 MHz, $CDCl_3$, ppm) δ = 1.90 – 1.95 (4H, m), 3.35 – 3.45 (4H, m). ^{13}C NMR (enol) (75 MHz, $CDCl_3$, ppm) δ = 23.7, 25.8, 26.9, 32.2, 40.7, 43.4, 50.6, 116.7, 200.4. IR (neat, ketone/enol, cm^{-1}) = 949, 1036, 1073, 1127, 1160, 1205, 1300, 1352, 1379, 1425, 1450, 1666, 1690, 2202, 2250, 2869, 2945. HRMS: calcd. for C_7H_9NONa [M+Na] = 146.0576; found = 146.0576.

Compound 23



NaH (20 mg, 0.86 mmol) was added to a solution of 2-phenyl-1,1-diphenylsulfonethane[4] (103 mg, 0.27 mmol) in dry THF (1.9 mL) at 0ºC. After stirring for 5 minutes, **8** (131 mg, 0.41 mmol) was added and the reaction mixture warmed up to room temperature for 24 h. Then it was quenched with HCl (1N) and extracted with EtOAc. The organic layers were dried over anhydrous Na_2SO_4, filtered and the volatiles removed under vacuum. The crude oil thus obtained was purified

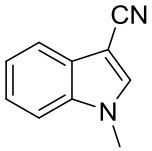
[3] Emelen, K. V.; De Wit, T.; Hoornaert, G. J.; Compernolle, F. *Tetrahedron* **2002**, *58*, 4225.
[4] Wang Ya-pin, H. X. *Chem. Res. Chin. Univ.* **1993**, *9*, 91.

by flash chromatography on silica gel (n-Hexane/EtOAc 8/2) affording **24** (90 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 3.68 (2H, s), 7.03 – 7.23 (5H, m), 7.43 – 7.56 (4H, m), 7.61 – 7.71 (3H, m), 7.86 – 7.96 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 36.2, 84.4, 113.0, 128.5, 128.7, 129.3, 130.8, 131.5, 131.6, 135.8, 135.9. IR (neat, cm^{-1}) = 910, 999, 1024, 1076, 1170, 1314, 1354, 1448, 1497, 1582, 2256, 2924, 3065. HRMS: calcd. for $C_{21}H_{17}NO_4S_2Na$ [M+Na] = 434.0493; found = 434.0491.

General procedure for electrophilic cyanation of aromatic substrates (Method B).

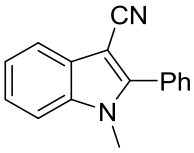
A Young flask charged with the aromatic substrate (0.3-0.4 mmol), cyano source **9** (1.2 eq), $BF_3{\cdot}Et_2O$ (0.2 eq.) and dry DCE (0.10 M) was heated to 80 °C and stirred for the specified time. The reaction was quenched with $NaHCO_3$ (sat.) and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and all the volatiles removed in vacuum. The crude product was purified by flash chromatography on silica gel (*n*-Hexane/EtOAc).

Compound 24



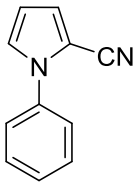
Using the general procedure, compound **24** was obtained as a colorless oil (51 mg, 87%) from 1-methylindole (48 µL, 0.38 mmol), $BF_3{\cdot}Et_2O$ (9 µL, 0.076 mmol) and **9** (216 mg, 0.45 mmol). Flash chromatography (*n*-Hexane/EtOAc 1/1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 3.84 (3H, s), 7.27 – 7.35 (2H, m), 7.40 (1H, d, *J* = 7.5 Hz), 7.43 (1H, s), 7.65 (1H, d, *J* = 7.2 Hz). HRMS: calcd. for $C_{10}H_8N_2$ [M] = 156.0687; found = 156.0689

Compound 25



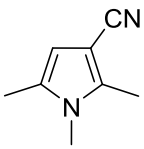
Using the general procedure, compound **25** was prepared from 1-methyl-2-phenylindole (62 mg, 0.30 mmol), $BF_3{\cdot}Et_2O$ (7 µL, 0.060 mmol) and **9** (170 mg, 0.36 mmol), and purified by flash chromatography (*n*-Hexane/EtOAc 7/3) to obtain a white solid (64 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 3.77 (3H, s), 7.33 (1H, ddd, *J* = 7.4, 7.0, 1.3 Hz), 7.38 (1H, ddd, *J* = 7.2, 6.9, 1.4 Hz), 7.43 (1H, brd, *J* = 7.8 Hz), 7.50 – 7.62 (5H, m), 7.79 (1H, brd, *J* = 7.6 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 31.7, 85.6, 110.4, 116.5, 119.6, 122.4, 123.8, 127.6, 128.7, 129.0, 129.8, 129.9, 136.8, 148.0. HRMS: calcd. for $C_{16}H_{12}N_2Na_1$ [M+Na] = 255.0891; found = 255.0892.

Compound 26



Using the general procedure, compound **26** was prepared from 1-phenylpyrrole (51 µL, 0.35 mmol), $BF_3{\cdot}Et_2O$ (8 µL, 0.070 mmol) and **9** (199 mg, 0.42 mmol). After flash chromatography (*n*-Hexane/EtOAc 7/3) a white solid was obtained (44 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 6.36 (1H, dd, *J* = 3.9, 2.8 Hz), 7.00 (1H, dd, *J* = 4.0, 1.5 Hz), 7.09 (1H, dd, *J* = 2.8, 1.6 Hz), 7.41 – 7.52 (5H, m). HRMS: calcd. for $C_{11}H_8N_2$ [M] = 168.0687; found = 168.0689.

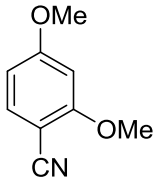
Compound 27



Using the general procedure, compound **27** was prepared from 1,2,5-trimethylpyrrole (54 µL, 0.40 mmol), $BF_3{\cdot}Et_2O$ (10 µL, 0.080 mmol) and compound **9** (227 mg, 0.48 mmol). After flash chromatography (*n*-Hexane/EtOAc 8/2) a pale yellow solid was obtained (45 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 2.19 (3H, s), 2.33 (3H, s), 3.40 (3H, s), 6.02 (1H, q, *J* = 1.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 10.1, 10.2, 20.8, 94.6, 110.7, 117.3, 128.0, 136.6. IR (neat, cm^{-1}) = 1239, 1342, 1369, 1416, 1437, 1535, 1702, 1737, 2148, 2207, 2850, 2919, 2961. HRMS: calcd. for $C_8H_{10}N_2$

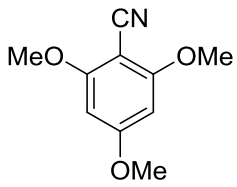
[M] = 134.0844; found = 134.0845

Compound 28



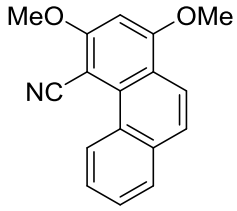
Using the general procedure, compound **28** was prepared from 1,3-dimethoxybenzene (47 µL, 0.36 mmol), $BF_3{\cdot}Et_2O$ (9 µL, 0.072 mmol) and **9** (204 mg, 0.43 mmol). After flash chromatography (*n*-Hexane/EtOAc 8/2) a white solid was obtained (50 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 3.84 (3H, s), 3.88 (3H, s), 6.45 (1H, d, *J* = 2.0 Hz), 6.51 (1H, dd, *J* = 8.4, 2.2 Hz), 7.47 (1H, d, *J* = 8.7 Hz). HRMS: calcd. for $C_9H_9NO_2$ [M] = 163.0633; found = 163.0634.

Compound 29



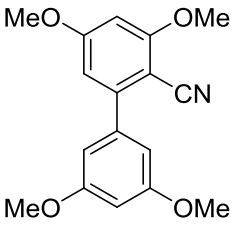
Using the general procedure, compound **29** was prepared from 1,3,5-trimethoxybenzene (59 mg, 0.35 mmol), $BF_3{\cdot}Et_2O$ (9 µL, 0.072 mmol) and **9** (200 mg, 0.42 mmol). After flash chromatography (*n*-Hexane/EtOAc 8/2) a white solid was obtained (63 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 3.85 (3H, s), 3.88 (6H, s), 6.06 (2H, s). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 54.9, 55.3, 83.2, 89.5, 113.9, 163.0, 164.5. IR (neat, cm^{-1}) = 917, 951, 1022, 1051, 1157, 1211, 1227, 1347, 1413, 1467, 1496, 1579, 1603, 1940, 2211, 2848, 2946, 2979. HRMS: calcd. for $C_{10}H_{11}N_1O_3Na_1$ [M+Na] = 216.0629; found = 216.0631

Compound 30



Using the general procedure, compound **30** was prepared from 1,3-dimethoxyphenanthrene[5] (71 mg, 0.30 mmol), $BF_3{\cdot}Et_2O$ (7 µL, 0.060 mmol) and **9** (170 mg, 0.36 mmol). After flash chromatography (*n*-Hexane/EtOAc 8/2) a yellow solid was obtained (73 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ = 4.04 (3H, s), 4.07 (3H, s), 6.62 (1H, s), 7.61 – 7.71 (3H, m), 7.86 – 7.90 (1H, m), 8.06 (1H, d, *J* = 9.0 Hz), 9.79 – 9.83 (1H, m). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ = 56.1, 56.6, 86.7, 91.9, 118.5, 119.5, 119.8, 125.5, 125. 8, 126.5, 128.1, 128.3, 128.8, 131.8, 134.0, 160.8, 165.1. IR (neat, cm^{-1}) = 1122, 1244, 1279, 1309, 1346, 1384, 1416, 1427, 1459, 1506, 1526, 1568, 1591, 1620, 2206, 2940. HRMS: calcd. for $C_{17}H_{13}N_1O_2Na_1$ [M+Na] = 286.0837; found = 286.0838

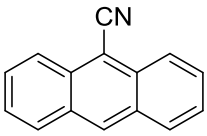
Compound 31



Using the general procedure, compound **31** was prepared from 3,3',5,5'-tetramethoxy-1,1'-biphenyl[6] (82 mg, 0.30 mmol), $BF_3{\cdot}Et_2O$ (7 µL, 0.060 mmol) and **9** (170 mg, 0.36 mmol). After flash chromatography (*n*-Hexane/EtOAc 8/2) a pale yellow solid (62 mg, 70%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 3.83 (6H, s), 3.88 (3H, s), 3.94 (3H, s), 6.46 (1H, d, *J* = 2.2 Hz), 6.52 (1H, t, *J* = 2.3 Hz), 6.56 (1H, d, *J* = 2.2 Hz.)6.67 (1H, d, *J* = 2.3 Hz). HRMS: calcd. for $C_{17}H_{17}N_1O_4Na_1$ [M+Na] = 322.1046; found = 322.1049.

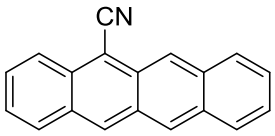
[5] Fürstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264.
[6] Yamamoto, Y. *Synlett* **2007**, 1913.

Compound 32



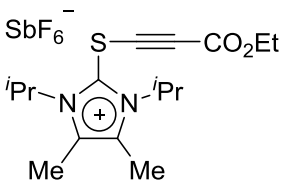
Using the general procedure, compound **32** was prepared from anthracene (55 mg, 0.31 mmol), $BF_3{\cdot}Et_2O$ (7 µL, 0.062 mmol) and **9** (175 mg, 0.37 mmol). After flash chromatography (*n*-Hexane/EtOAc 7/3) a yellow solid (29 mg, 46%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.60 (2H, ddd, *J* = 8.6, 6.6, 1.1 Hz), 7.73 (2H, ddd, *J* = 8.7, 6.6, 1.2 Hz), 8.09 (2H, d, *J* = 8.5 Hz), 8.42 (2H, brdd, *J* = 8.6, 1.0 Hz), 8.70 (1H, s). HRMS: calcd. for $C_{15}H_9N_1$ [M] = 203.0736; found = 203.0734.

Compound 33



Using the general procedure, compound **33** was prepared from tetracene (75 mg, 0.33 mmol), $BF_3{\cdot}Et_2O$ (8 µL, 0.066 mmol) and **9** (188 mg, 0.39 mmol). After flash chromatography (*n*-Hexane/EtOAc from 9:1 to 7:3) a red solid was obtained (70 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.47 – 7.55 (3H, m), 7.68 (1H, ddd, *J* = 8.9, 6.6, 1.2 Hz), 7.97 – 8.18 (3H, m), 8.39 (1H, dd, *J* = 8.8, 1.0 Hz), 8.76 (1H, s), 8.92 (1H, s), 9.06 (1H, s). HRMS: calcd. for $C_{19}H_{11}N_1Na_1$ [M+Na] = 276.0784; found = 276.0783.

Compound 35

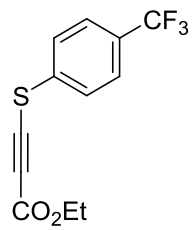


Silver ethyl propiolate (1.41 g, 6.87 mmol) was added to a solution of compound **5** (2.56 g, 6.87 mmol) in dry DCM (20 mL) at RT (note: the reaction is slightly exothermic and may cause DCM to boil). After 5 min $AgSbF_6$ (2.32 g, 6.75 mmol) was added and the reaction mixture stirred at RT for 45 min. Silver salts were then filtered off and the solvent removed under vacuum. The remaining solid was washed twice with diethyl ether to afford compound **36** as a pale yellow solid (3.48 g, 93%). ^{1}H NMR (400 MHz, CD_3CN, ppm) δ = 1.24 (3H, t, *J* = 7.1 Hz), 1.62 (12H, d, *J* = 7.0 Hz), 2.38 (6H, s), 4.21 (2H, q, *J* = 7.1 Hz), 5.17 (2H, hept, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, CD_3CN, ppm) δ = 10.6, 14.1, 21.0, 54.8, 63.7, 73.4, 87.8, 128.6, 132.6, 152.5. ^{19}F NMR (282 MHz, CD_3CN) δ= -124.00 (sext, $J_{F\text{-}121Sb}$= 1931 Hz). IR (neat, cm^{-1}) = 1026, 1115, 1140, 1219, 1261, 1380, 1397, 1460, 1615, 1707, 2178, 2989. HRMS: calcd. for $C_{16}H_{25}N_2O_2S_1$ [M-SbF_6] = 309.1629; found = 309.1631

General procedure for alkynylation reaction:

Reagent **35** (1.2 eq) was added to a solution of initial substrate (0.30 mmol) and DIPEA (1.0 eq) in dry DCM (0.15 M) and the reaction was stirred at room temperature for the specified time (see Chart 2). The reaction was quenched with NH_4Cl (1.0 M) and extracted with DCM. The organic layers were dried over anhydrous Na_2SO_4, filtered and all the volatiles removed under vacuum. The crude was purified by flash chromatography on silica gel (*n*-Hexane/EtOAc) affording the desired products.

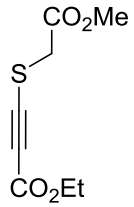
Compound 36



Using the general procedure, compound **36** was prepared from 4-(trifluoromethyl)benzenethiol (50 µL, 0.36 mmol), DIPEA (63 µL, 0.36 mmol) and **35** (235 mg, 0.43 mmol), obtaining after flash chromatography (*n*-Hexane/EtOAc 8/2) a yellow oil (97 mg, 98%). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ = 1.32 (3H, t, *J* = 7.1 Hz), 4.26 (2H, q, *J* = 7.2 Hz), 7.61 (2H, d, *J* = 8.4 Hz), 7.67 (2H, d, *J* = 8.4 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ = 14.2, 62.6, 77.2, 93.2, 125.6 (q, $J_{C\text{-}F}$ = 272.0 Hz) 126.8 (q, $J_{C\text{-}F}$ = 3.7 Hz) 127.3,

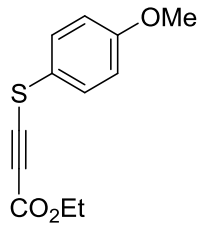
130.0 (q, $J_{C\text{-}F}$ = 32.7 Hz), 152.8, 163.2; IR (neat, cm^{-1}) = 1013, 1032, 1085, 1165, 1367, 1403, 1466, 1541, 1606, 1703, 2153, 2984. HRMS calcd. for $C_{12}H_{10}O_2SF_3$ [M+H] = 275.0346; found = 275.0348

Compound 37



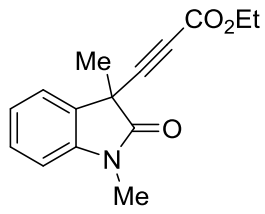
Using the general procedure, compound **37** was prepared from methyl thioglycolate (34 µL, 0.38 mmol), DIPEA (66 µL, 0.38 mmol) and compound **35** (248 mg, 0.45 mmol) obtaining after flash chromatography (*n*-Hexane/EtOAc 8/2) an orange oil (72 mg, 94%).^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.30 (3H, t, *J* = 7.2 Hz), 3.66 (2H, s), 3.81 (3H, s), 4.23 (2H, q, *J* = 7.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 13.9, 36.7, 52.9, 61.7, 80.9, 88.4, 152.5, 167.5. IR (neat, cm^{-1}) = 1030, 1163, 1296, 1366, 1391, 1436, 1698, 1738, 2149, 2955, 2983. HRMS calcd. for $C_8H_{10}O_4S_1Na_1$ [M+Na] = 225.0191; found = 225.0192.

Compound 38



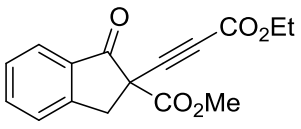
Using the general procedure, compound **38** was prepared from 4-methoxybenzenethiol (39 µL, 0.32 mmol), DIPEA (56 µL, 0.32 mmol) and compound **36** (209 mg, 0.38 mmol) obtaining after flash chromatography (*n*-Hexane/EtOAc 8/2) a yellow oil (74 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.31 (3H, t, *J* = 7.1 Hz), 3.81 (3H, s), 4.24 (2H, q, *J* = 7.1 Hz), 6.88 – 6.97 (2H, m), 7.35 – 7.46 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 13.0, 54.4, 60.8, 80.6, 88.8, 114.3, 118.1, 129.4, 151.9, 158.9. IR (neat, cm^{-1}): 914, 1023, 1054, 1091, 1120, 1239, 1378, 1411, 1426, 1551, 1624, 1719, 2158, 2975. HRMS calcd. for $C_{12}H_{12}O_3S_1Na_1$ [M+Na] = 259.0397; found = 259.0399**.**

Compound 39



NaH (21 mg, 0.76 mmol) was added to a solution of 1,3-dimethylindolin-2-one (111 mg, 0.69 mmol) in dry THF (4.6mL) at 0ºC. After stirring for 30 minutes, **35** (569 mg, 1.04 mmol) was added and the reaction mixture was left to warm up to room temperature for 3 h. Then it was quenched with HCl (1N) and extracted with EtOAc. The organic layers were dried over anhydrous Na_2SO_4, filtered and the volatiles were removed in vacuum. The crude was purified by flash chromatography on silica gel (n-Hexane/EtOAc 8/2) affording **40** (140 mg, 79%).^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.24 (3H, t, *J* = 7.1 Hz), 1.69 (3H, s), 3.20 (3H, s), 4.16 (2H, q, *J* = 7.1 Hz), 6.84 (1H, d, *J* = 7.7 Hz), 7.09 (1H, dt, *J* = 7.4, 0.9 Hz), 7.26 – 7.38 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 14.0, 24.7, 26.9, 42.7, 62.2, 74.1, 85.2, 108.8, 123.5, 123.6, 129.4, 130.1, 142.4, 153.3, 174.0. IR (neat, cm^{-1}) = 729, 791, 909, 1030, 1093, 1223, 1256, 1278, 1345, 1367, 1470, 1491, 1610, 1709, 2234, 2964.

Compound 40

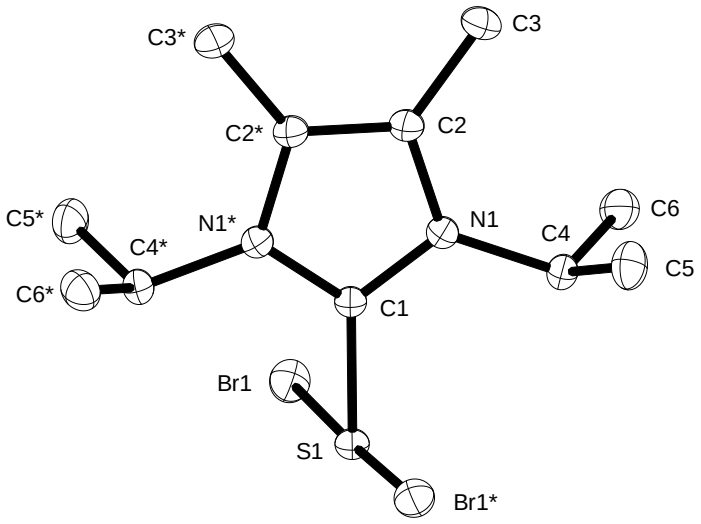


DIPEA (61µL, 0.35 mmol) was added to a solution of methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (66 mg, 0.35 mmol) in dry DCM (0.15 M). After stirring for 15 min, compound **35** (229 mg, 0.42 mmol) was added and the reaction was allowed to stir for 30 min. The reaction was then quenched with NH_4Cl and extracted with DCM. The organic layers were dried over anhydrous Na_2SO_4, filtered and the volatiles were removed in vacuum. The crude was purified by flash chromatography on silica gel (*n*-Hexane/EtOAc from 9/1 to 7/3) affording **40** as an orange oil (89 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.29 (3H, t, *J* =

7.1Hz), 3.58 (1H, d, = 17.2 Hz), 3.83 (3H,s), 3.97 (1H, d, *J* = 17.2 Hz), 4.22 (2H, q, *J* = 7.2 Hz), 7.45 (1H, ddd, *J* = 7.9, 7.1, 0.9 Hz), 7.50 (1H, dt, *J* = 7.9, 0.9 Hz), 7.69 (1H, td, *J* = 7.5, 1.2 Hz), 7.82 (1H, dt, *J* = 7.5, 1.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 14.1, 40.0, 54.3, 62.4, 75.6, 82.8, 126.2, 126.6, 128.4, 128.7, 132.9, 136.5, 152.1, 153.2, 167.2, 194.2. IR (neat, cm^{-1}) = 956, 1021, 1103, 1211, 1235, 1291, 1342, 1368, 1418, 1435, 1463, 1604, 1740, 2973. HRMS: calcd. for $C_{16}H_{14}O_5Na$ [M+Na] = 309.0734; found = 309.0733.

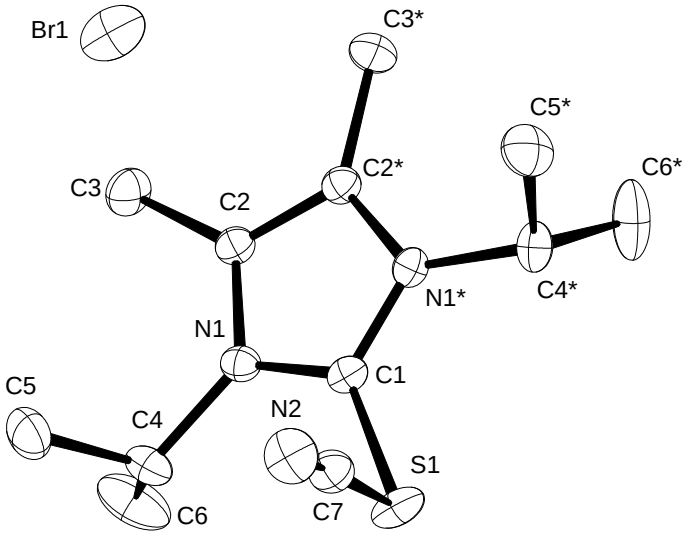
X-Ray structures.

Compound 5.



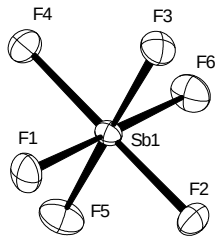
Empirical formula	C_{11} H_{20} Br_2 N_2 S	
Color	orange	
Formula weight	372.17 g·mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	C2/c, (no. 15)	
Unit cell dimensions	a = 10.9428(7) Å	α= 90°.
	b = 12.0932(9) Å	β= 110.582(8)°.
	c = 11.9149(13) Å	γ = 90°.
Volume	1476.1(2) Å3	
Z	4	
Density (calculated)	1.675 Mg·m-3	
Absorption coefficient	5.612 mm-1	
F(000)	744 e	
Crystal size	0.06 x 0.05 x 0.04 mm3	
θ range for data collection	2.606 to 33.125°.	
Index ranges	-16 ≤ h ≤ 16, -17≤ k ≤ 18, -18≤ l ≤ 18	
Reflections collected	15473	
Independent reflections	2818 [Rint = 0.0460]	
Reflections with I>2σ(I)	2411	
Completeness to θ = 27.500°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.84518 and 0.70105	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	2818 / 0 / 77	
Goodness-of-fit on F2	1.068	
Final R indices [I>2σ(I)]	R1 = 0.0286	wR2 = 0.0690
R indices (all data)	R1 = 0.0367	wR2 = 0.0731
Extinction coefficient	0	
Largest diff. peak and hole	0.633 and -0.927 e·Å-3	

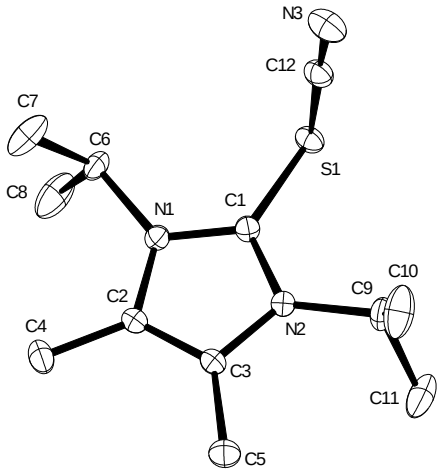
Compound 8.



Empirical formula	$C_{12}H_{20}BrN_3S$	
Color	yellow	
Formula weight	318.28 g · mol^{-1}	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	Pnma, (no. 62)	
Unit cell dimensions	a = 12.3841(9) Å	α= 90°.
	b = 10.5701(12) Å	β= 90°.
	c = 11.6763(13) Å	γ = 90°.
Volume	1528.4(3) Å^3	
Z	4	
Density (calculated)	1.383 Mg · m^{-3}	
Absorption coefficient	2.811 mm^{-1}	
F(000)	656 e	
Crystal size	0.10 x 0.08 x 0.04 mm^3	
θ range for data collection	3.076 to 33.135°.	
Index ranges	-14 ≤ h ≤ 19, -16≤ k ≤ 16, -17 ≤ l ≤ 17	
Reflections collected	28801	
Independent reflections	3027 [R_{int} = 0.0506]	
Reflections with I>2σ(I)	2610	
Completeness to θ = 25.242°	99.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.90 and 0.79	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3027 / 0 / 88	
Goodness-of-fit on F^2	1.104	
Final R indices [I>2σ(I)]	R_1 = 0.0311	wR^2 = 0.0754
R indices (all data)	R_1 = 0.0389	wR^2 = 0.0794
Largest diff. peak and hole	0.5 and -0.5 e · Å^{-3}	

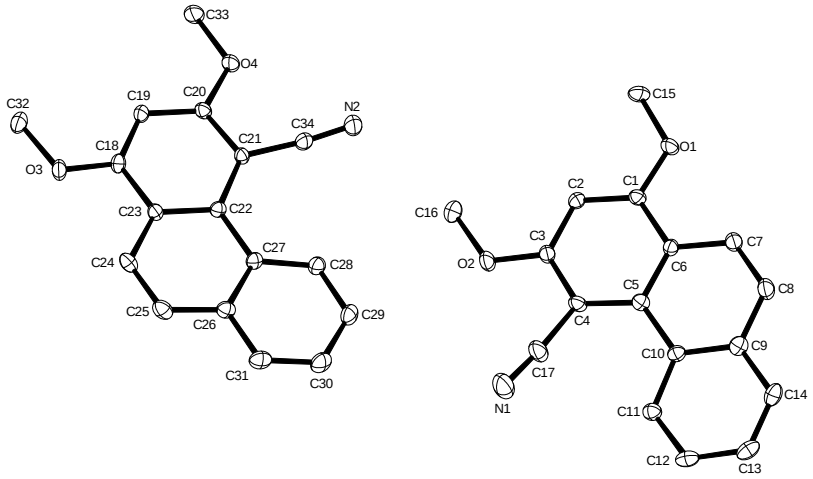
Compound 9.





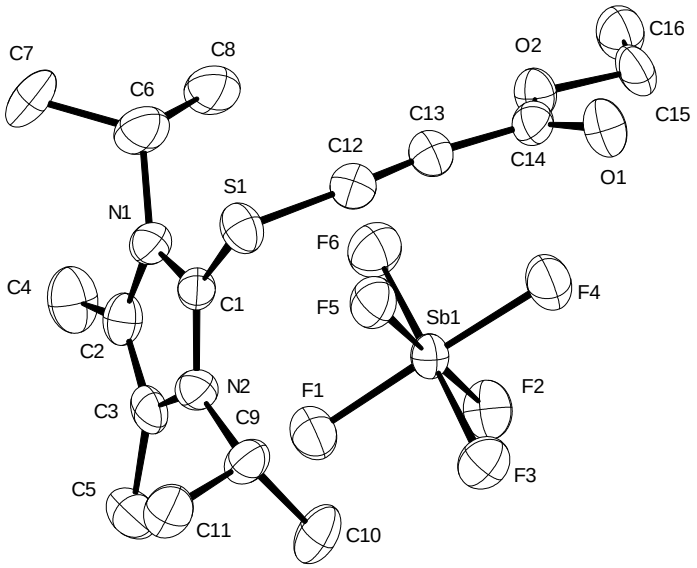
Empirical formula	C_{12} H_{20} F_6 N_3 S Sb	
Color	yellow	
Formula weight	474.12 g · mol-1	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P21/n, (no. 14)	
Unit cell dimensions	a = 10.8037(9) Å	α= 90°.
	b = 9.0136(5) Å	β= 92.334(8)°.
	c = 17.8195(14) Å	γ = 90°.
Volume	1733.8(2) Å3	
Z	4	
Density (calculated)	1.816 Mg · m-3	
Absorption coefficient	1.770 mm-1	
F(000)	936 e	
Crystal size	0.18 x 0.14 x 0.09 mm3	
θ range for data collection	2.944 to 30.045°.	
Index ranges	-15 ≤ h ≤ 15, -12≤ k ≤ 12, -22 ≤ l ≤ 25	
Reflections collected	26540	
Independent reflections	5054 [Rint = 0.0320]	
Reflections with I>2σ(I)	4566	
Completeness to θ = 25.242°	99.3 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.84 and 0.76	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	5054 / 0 / 214	
Goodness-of-fit on F2	1.056	
Final R indices [I>2σ(I)]	R1 = 0.0321	wR2 = 0.0886
R indices (all data)	R1 = 0.0352	wR2 = 0.0923
Largest diff. peak and hole	4.023 and -1.112 e · Å-3	

Compound 30.



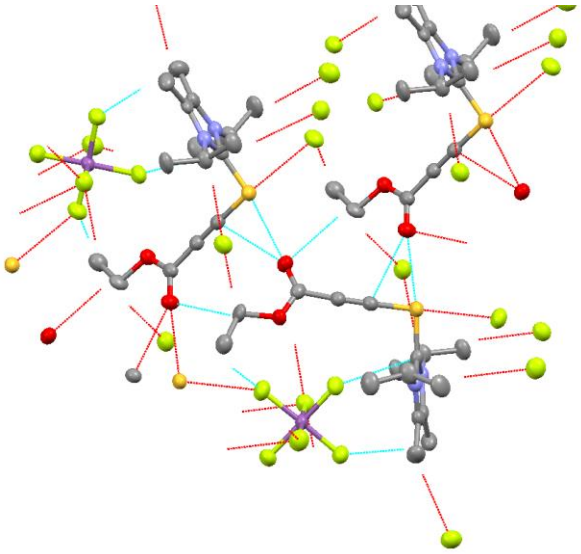
Empirical formula	$C_{17}H_{13}NO_2$	
Color	colourless	
Formula weight	263.28 g·mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P21/n, (no. 14)	
Unit cell dimensions	a = 19.351(3) Å	α= 90°.
	b = 7.2231(14) Å	β= 110.331(14)°.
	c = 19.351(3) Å	γ = 90°.
Volume	2536.3(8) Å3	
Z	8	
Density (calculated)	1.379 Mg·m-3	
Absorption coefficient	0.091 mm-1	
F(000)	1104 e	
Crystal size	0.58 x 0.06 x 0.04 mm3	
θ range for data collection	2.820 to 33.162°.	
Index ranges	-29 ≤ h ≤ 29, -11≤ k ≤ 10, -29 ≤ l ≤ 29	
Reflections collected	54028	
Independent reflections	9643 [Rint = 0.0628]	
Reflections with I>2σ(I)	6931	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99482 and 0.97055	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	9643 / 0 / 366	
Goodness-of-fit on F2	1.022	
Final R indices [I>2σ(I)]	R1 = 0.0533	wR2 = 0.1334
R indices (all data)	R1 = 0.0891	wR2 = 0.1485
Extinction coefficient	n/a	
Largest diff. peak and hole	0.573 and -0.316 e·Å-3	

Compound 35.



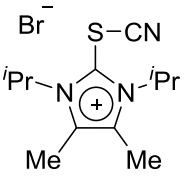
Empirical formula	C_{16} H_{25} F_6 N_2 O_2 S Sb	
Color	colorless	
Formula weight	545.19 g · mol-1	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	ORTHORHOMBIC	
Space group	P212121, (no. 19)	
Unit cell dimensions	a = 9.0118(3) Å	α= 90°.
	b = 9.0638(3) Å	β= 90°.
	c = 26.0781(8) Å	γ = 90°.
Volume	2130.09(12) Å3	
Z	4	
Density (calculated)	1.700 Mg · m-3	
Absorption coefficient	11.805 mm-1	
F(000)	1088 e	
Crystal size	0.37 x 0.04 x 0.035 mm3	
θ range for data collection	3.389 to 67.555°.	
Index ranges	-10 ≤ h ≤ 10, -10≤ k ≤ 10, -29 ≤ l ≤ 30	
Reflections collected	50968	
Independent reflections	3826 [Rint = 0.0748]	
Reflections with I>2σ(I)	3526	
Completeness to θ = 67.555°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.73 and 0.19	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3826 / 0 / 260	
Goodness-of-fit on F2	1.059	
Final R indices [I>2σ(I)]	R1 = 0.0410	wR2 = 0.0983
R indices (all data)	R1 = 0.0467	wR2 = 0.1023
Absolute structure parameter	0.005(5)	
Largest diff. peak and hole	0.3 and -1.4 e · Å-3	

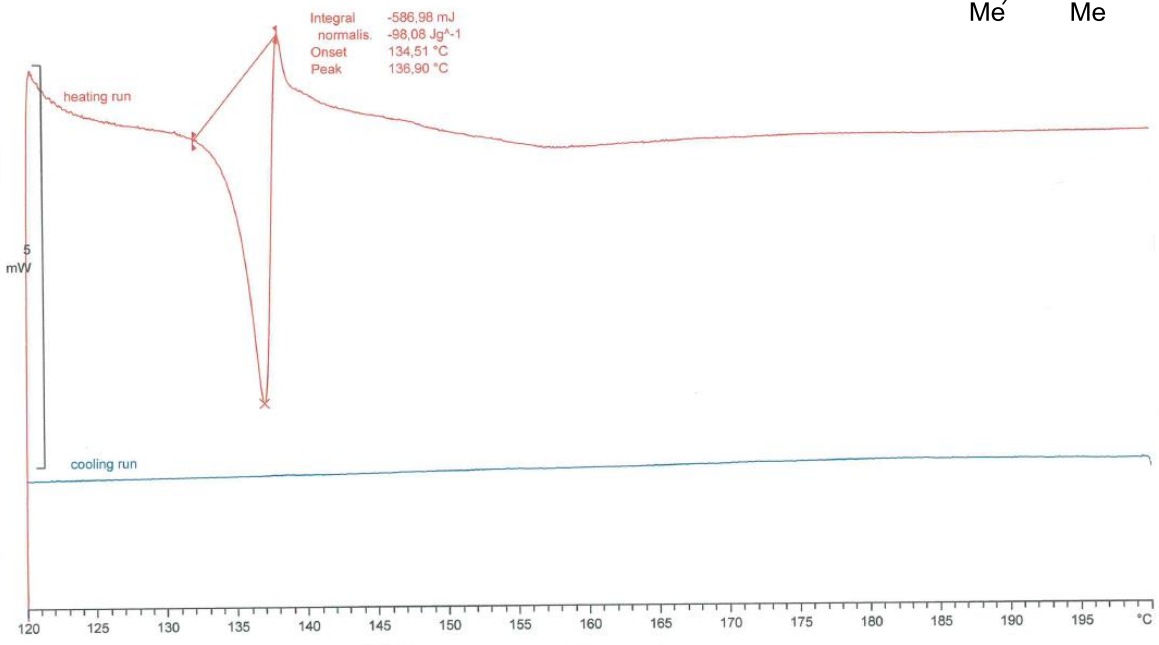
Intermolecular interaction in 35.



Differential scanning calorimetry (DSC).

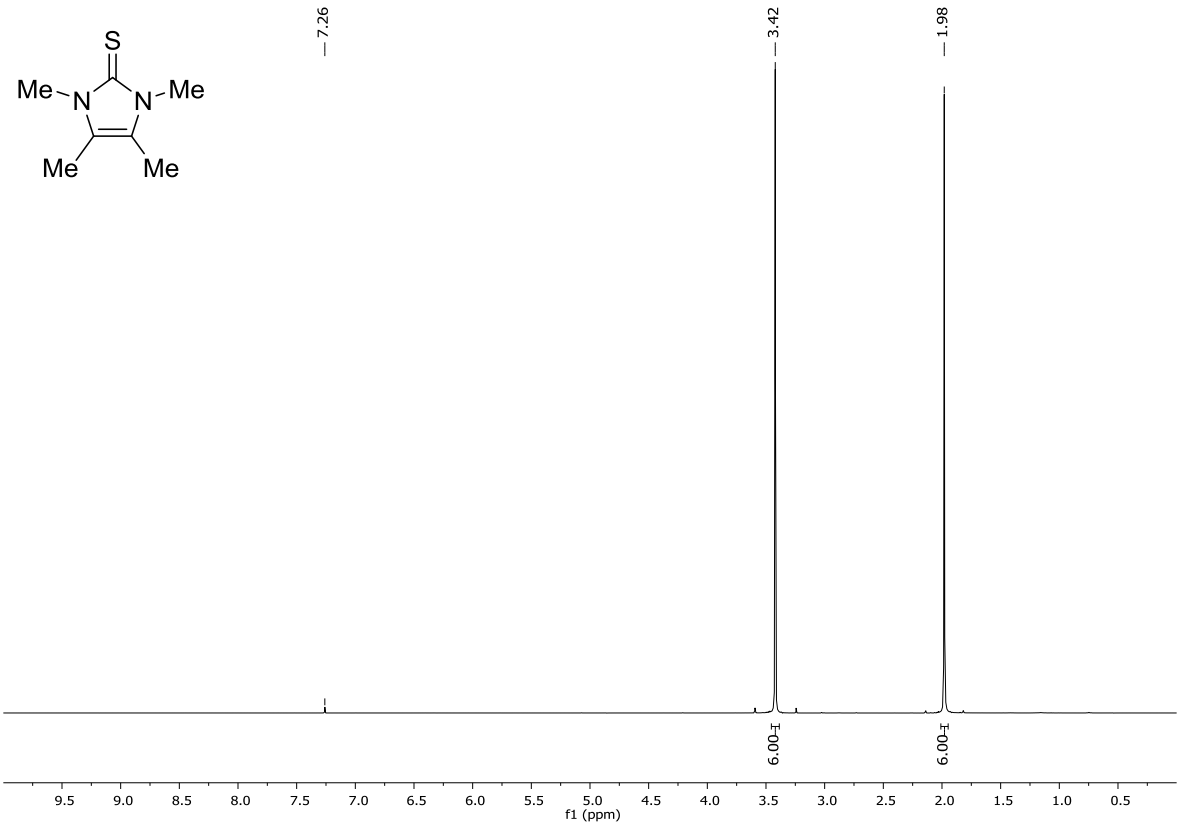
Compound 8.



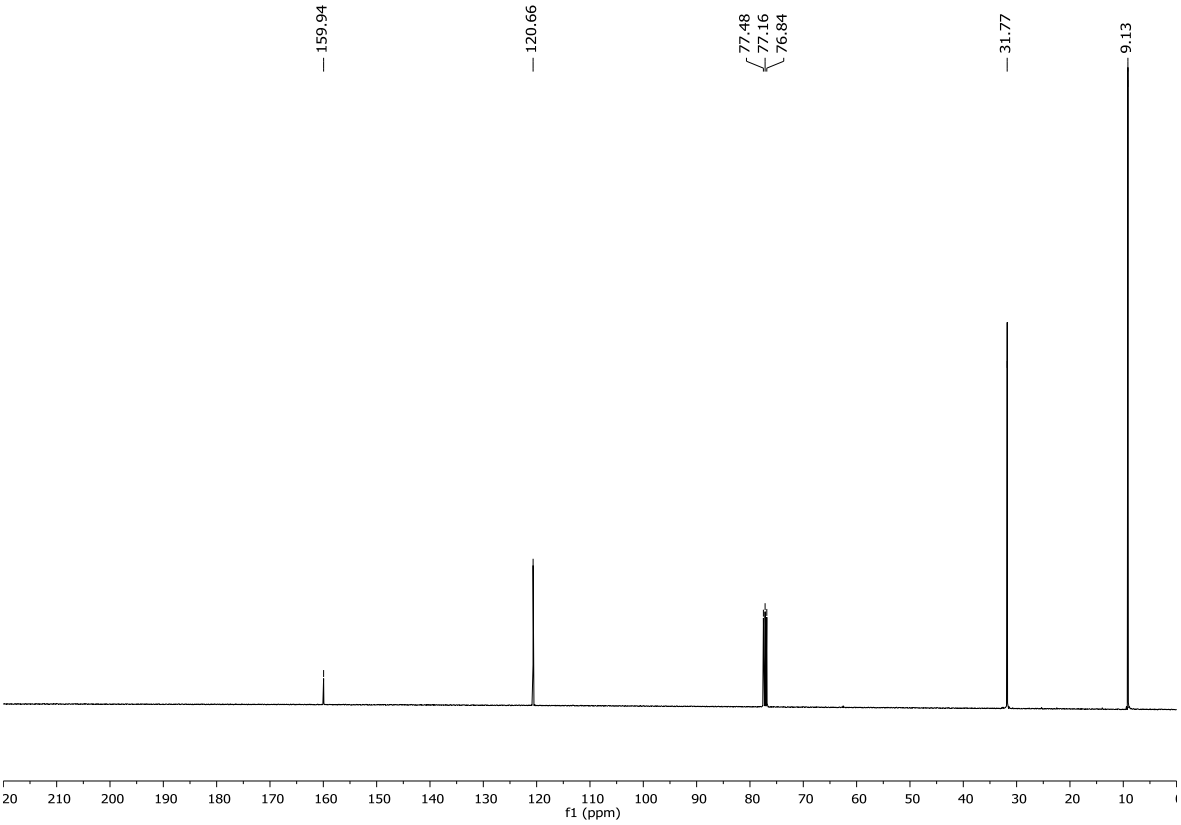


NMR Spectra.

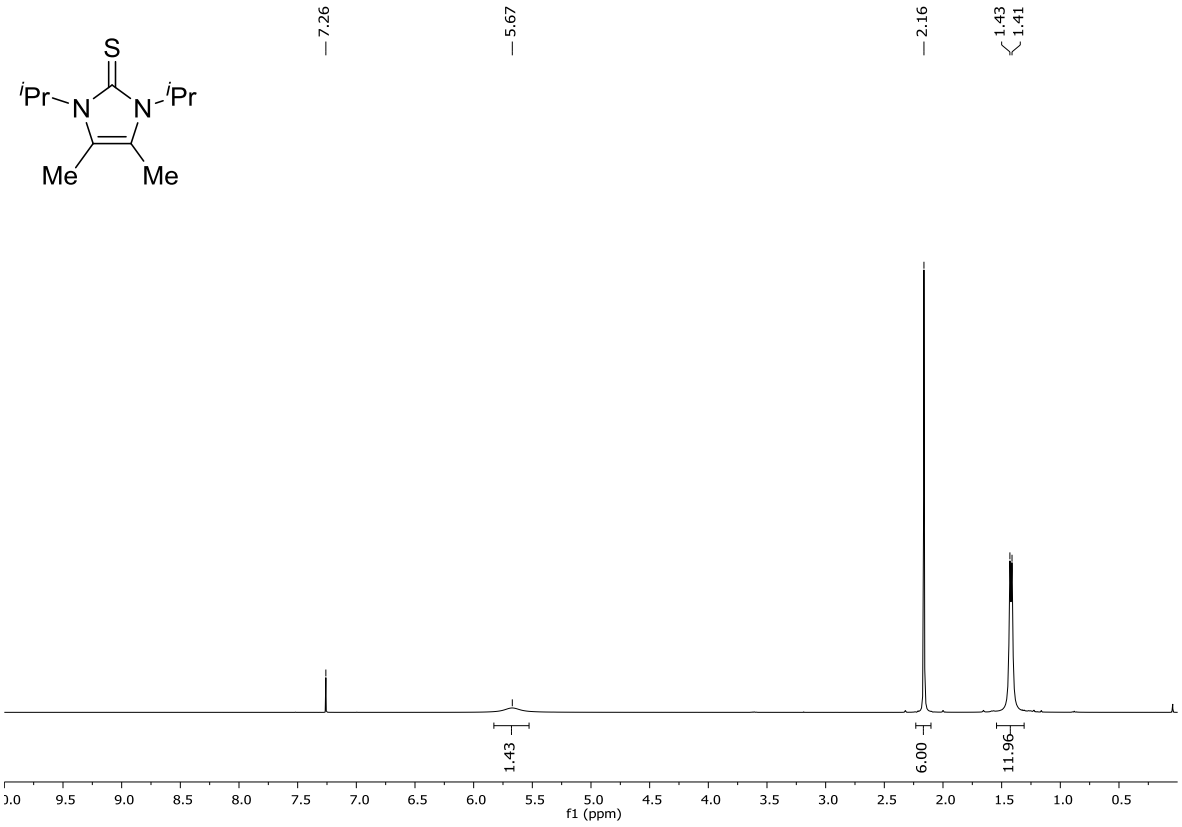
^{1}H NMR (400 MHz, $CDCl_3$) **1**



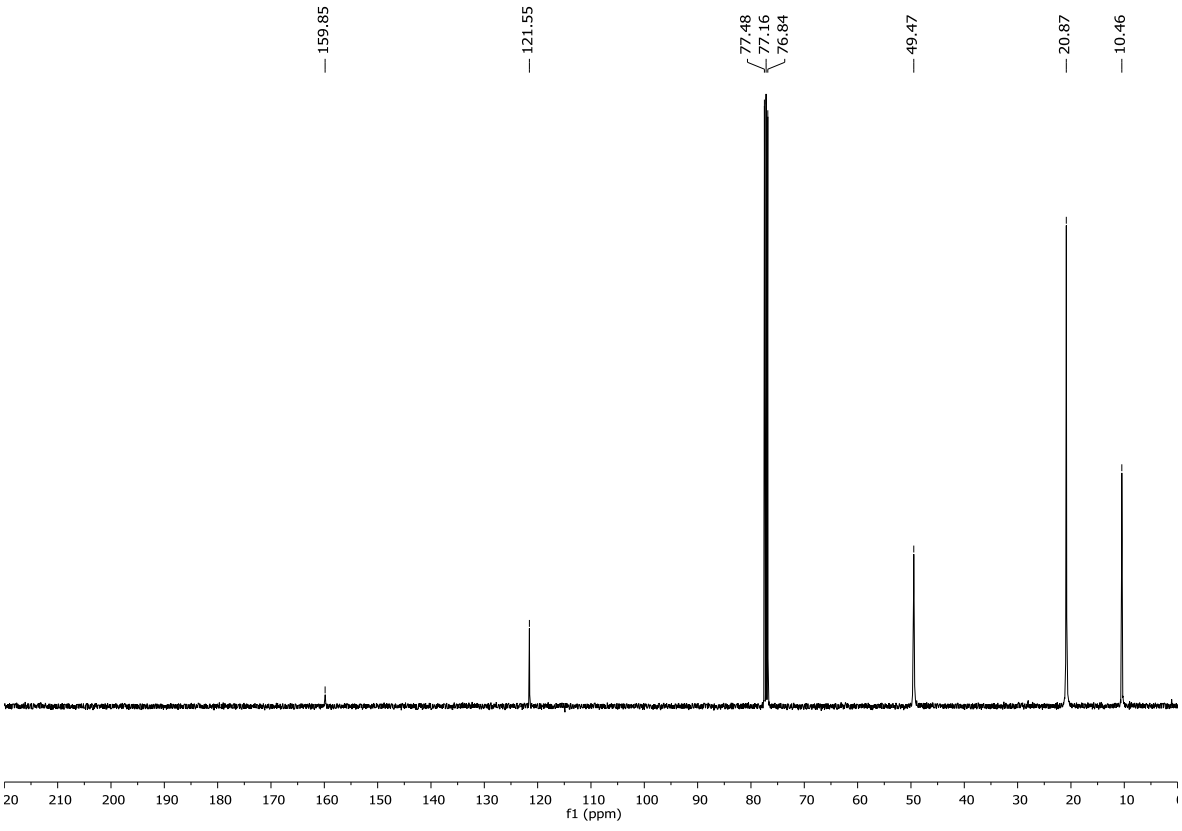
^{13}C NMR (101 MHz, $CDCl_3$) **1**



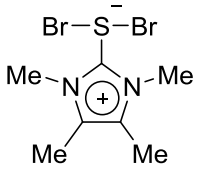
^{1}H NMR (400 MHz, $CDCl_3$) **2**



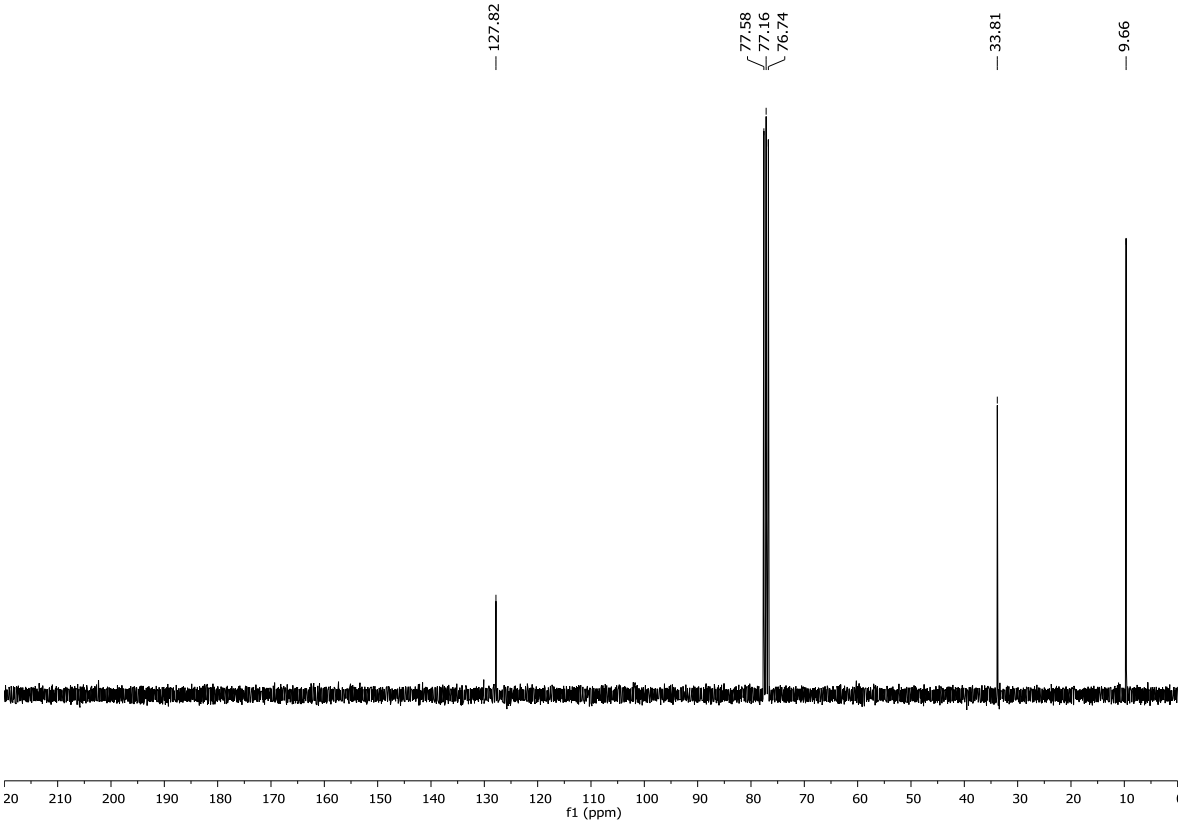
^{13}C NMR (101 MHz, $CDCl_3$) **2**



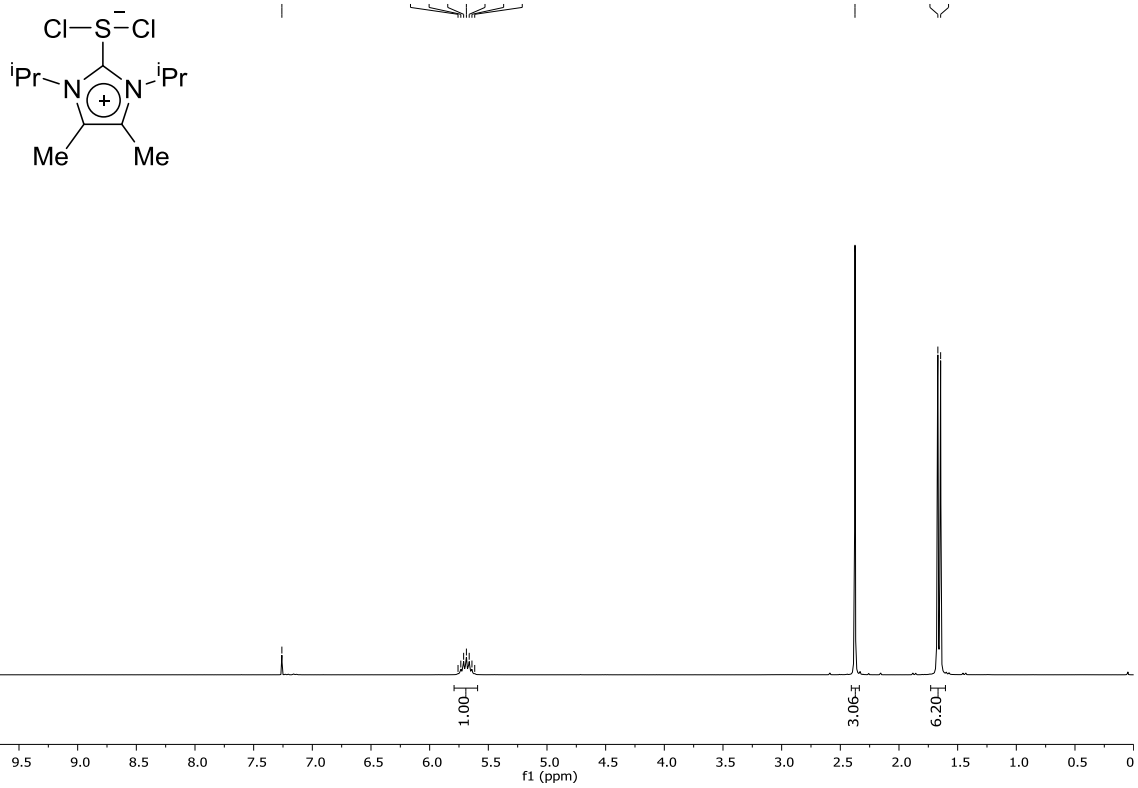
^{1}H NMR (300 MHz, $CDCl_3$) **3**



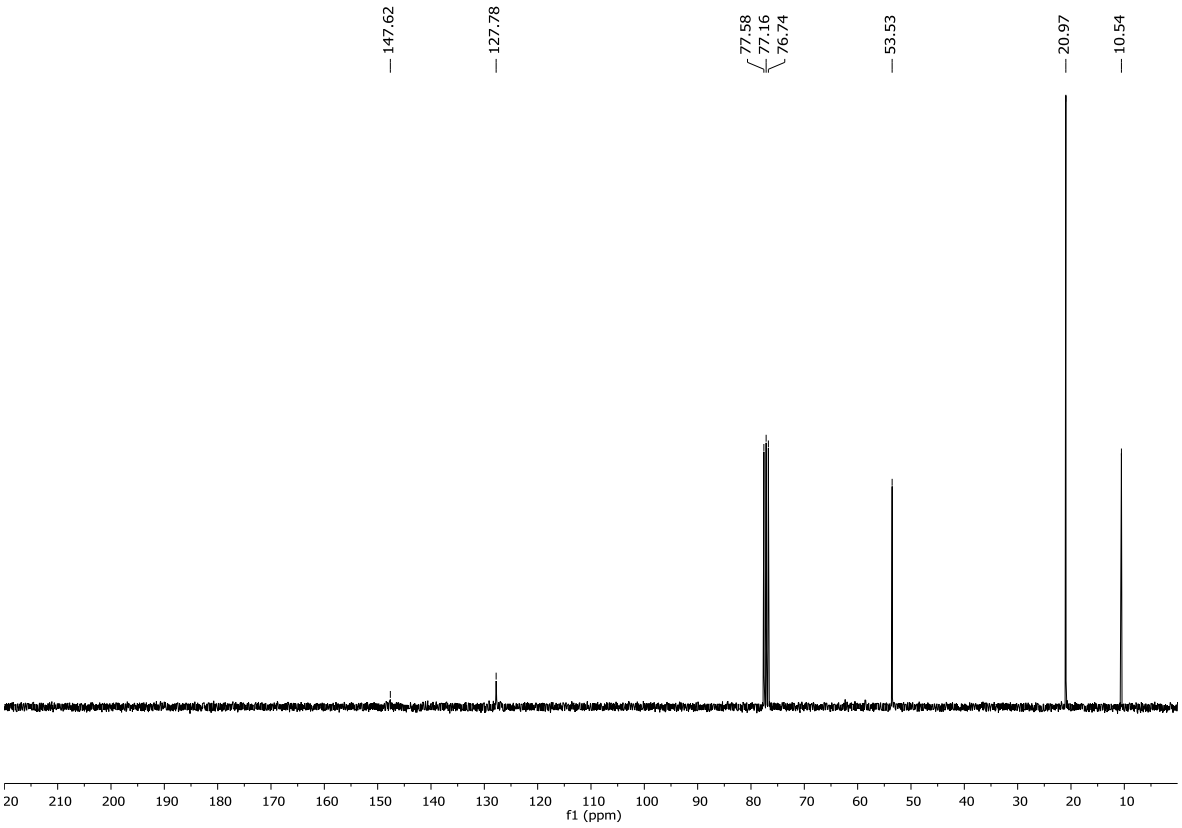
^{13}C NMR (75 MHz, $CDCl_3$) **3**



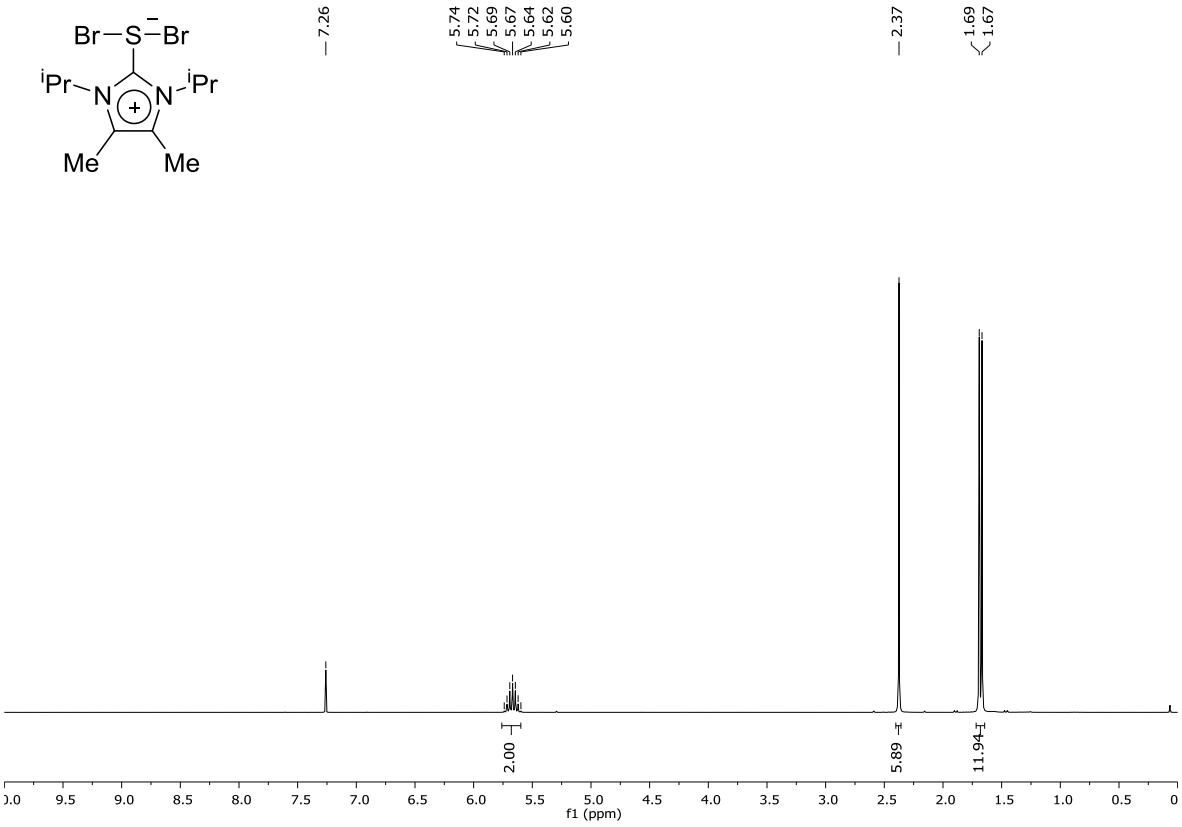
^{1}H NMR (300 MHz, $CDCl_3$) **4**



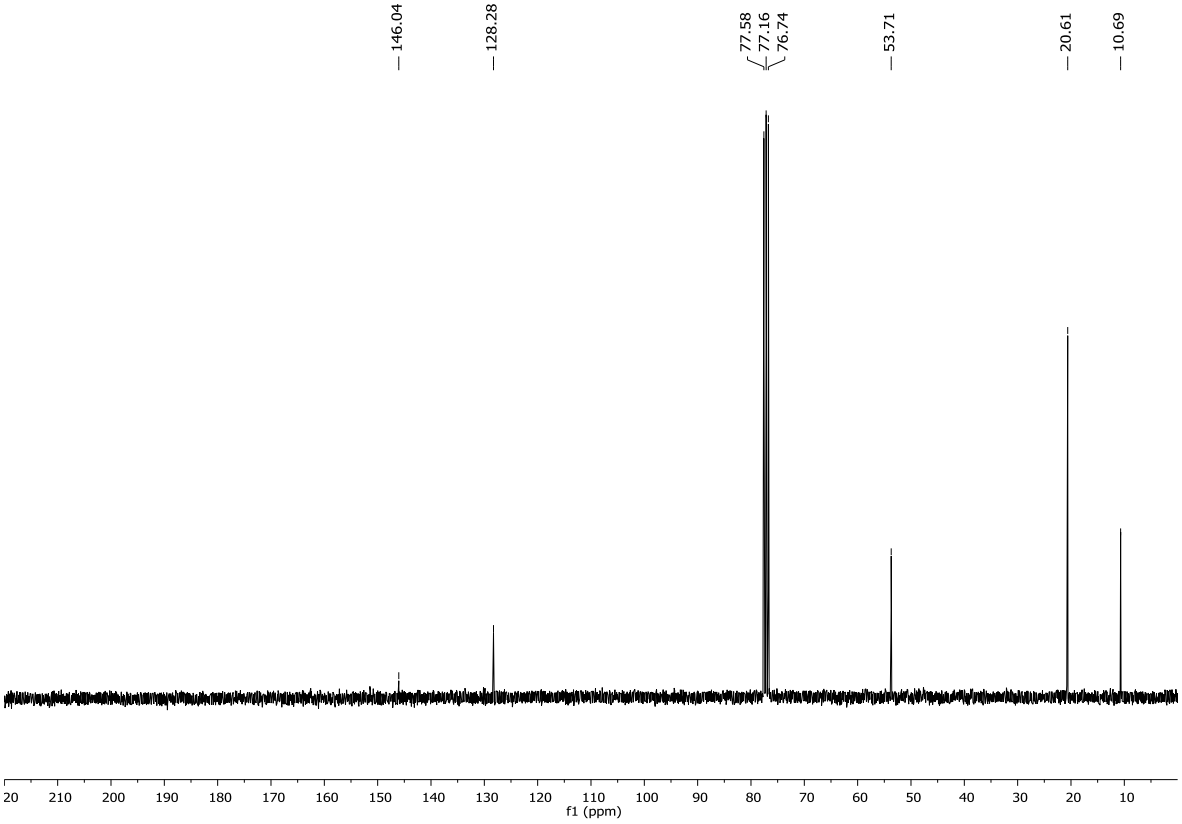
^{13}C NMR (75 MHz, $CDCl_3$) **4**



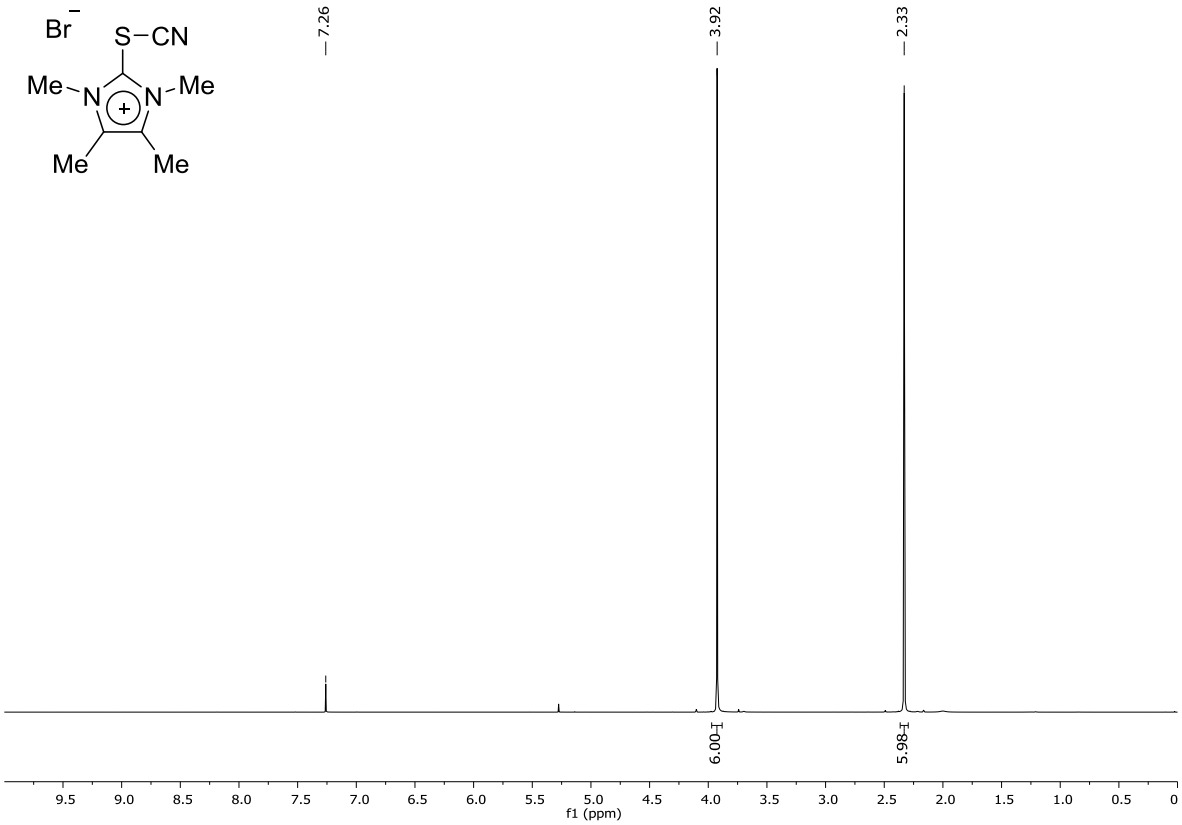
^{1}H NMR (300 MHz, $CDCl_3$) **5**



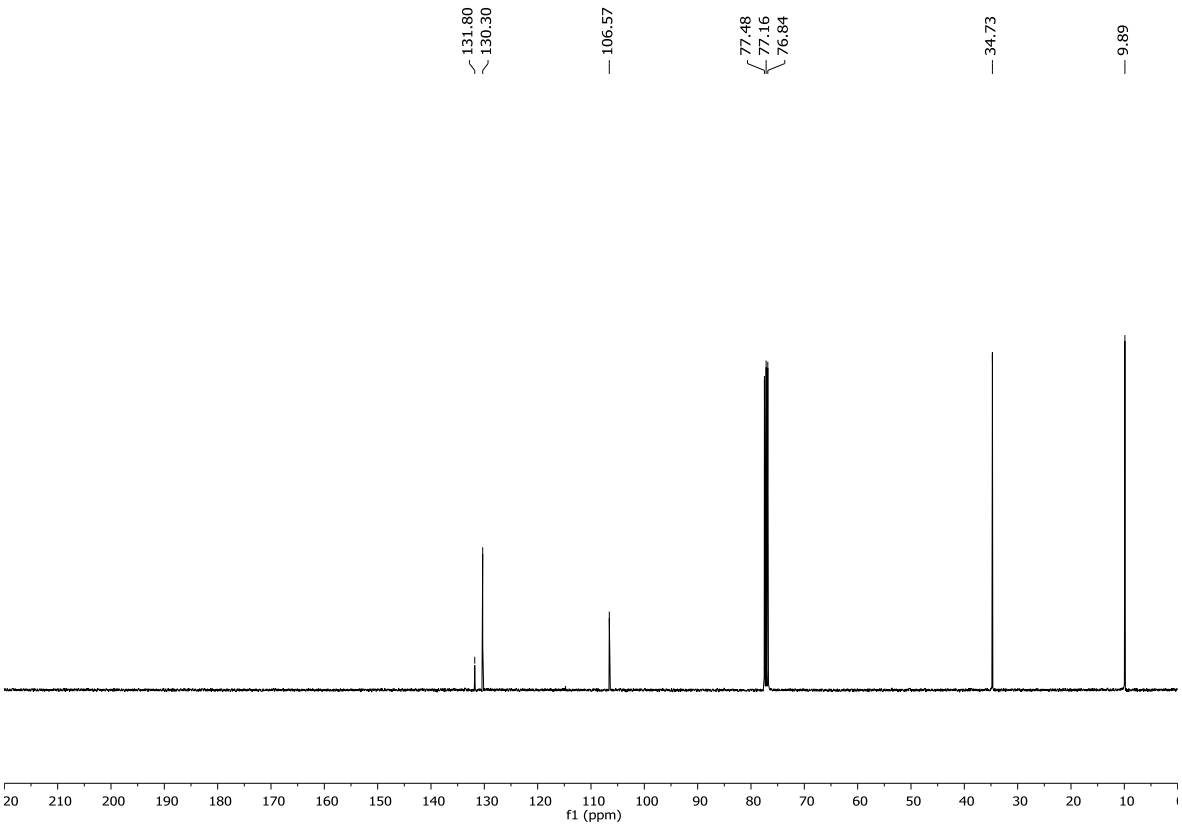
^{13}C NMR (75 MHz, $CDCl_3$) **5**



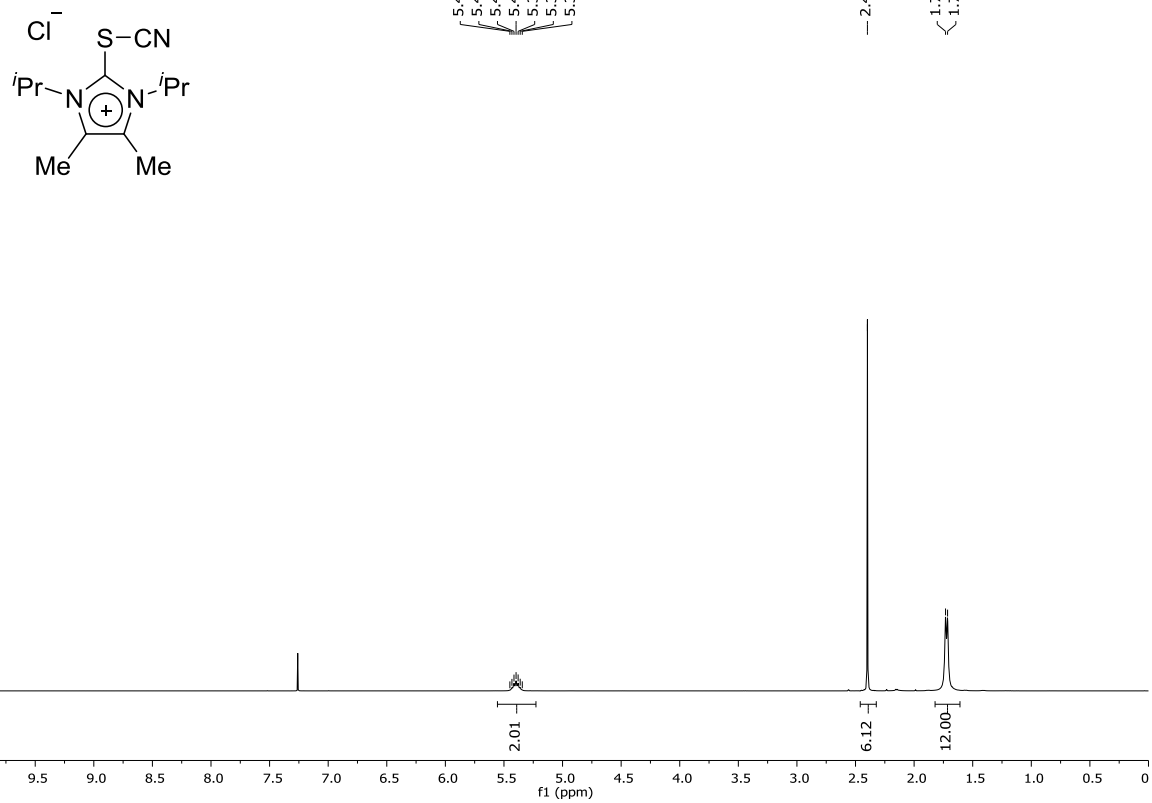
^{1}H NMR (400 MHz, $CDCl_3$) **6**



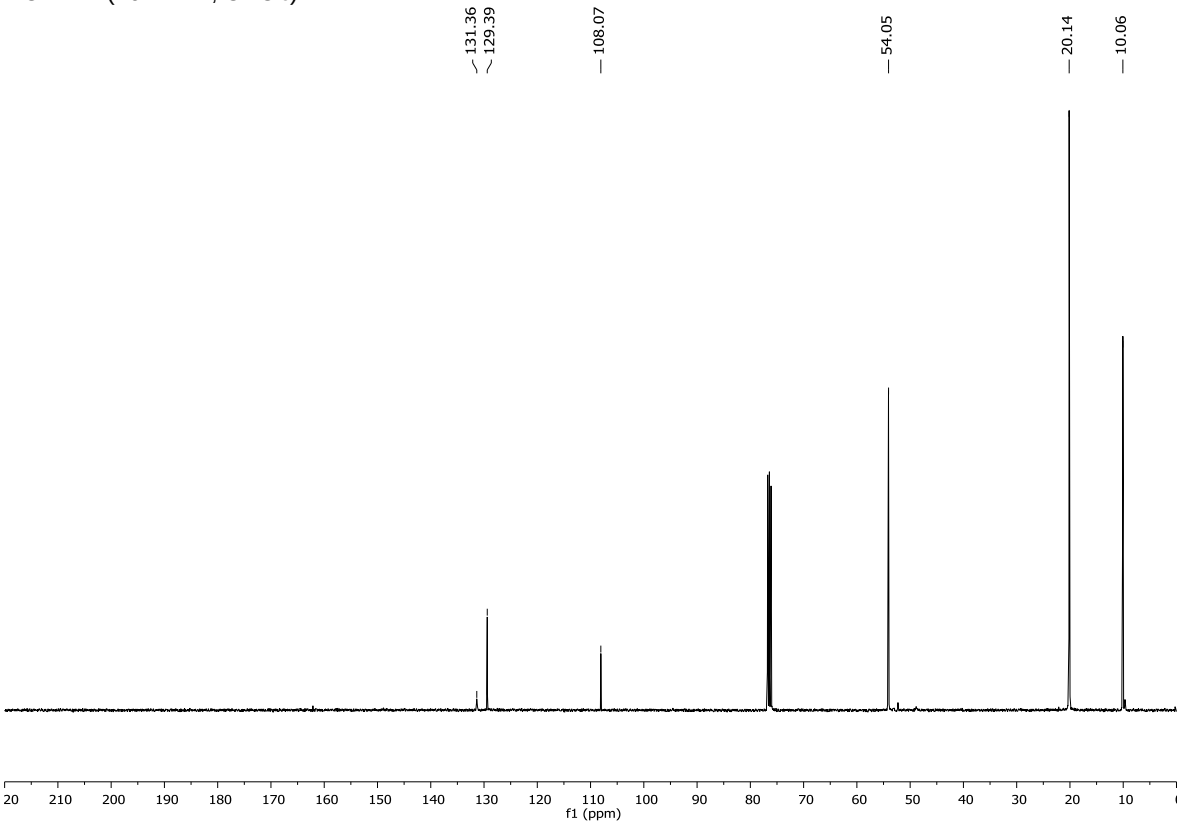
^{13}C NMR (101 MHz, $CDCl_3$) **6**



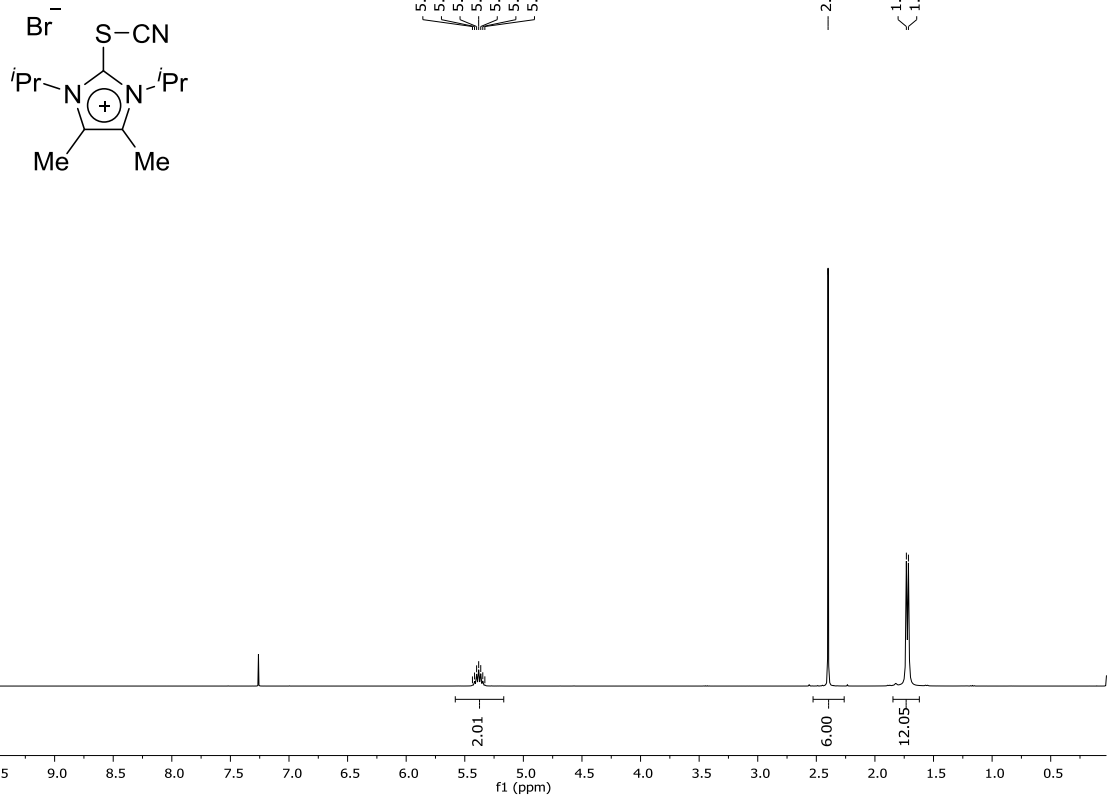
^{1}H NMR (400 MHz, $CDCl_3$) **7**



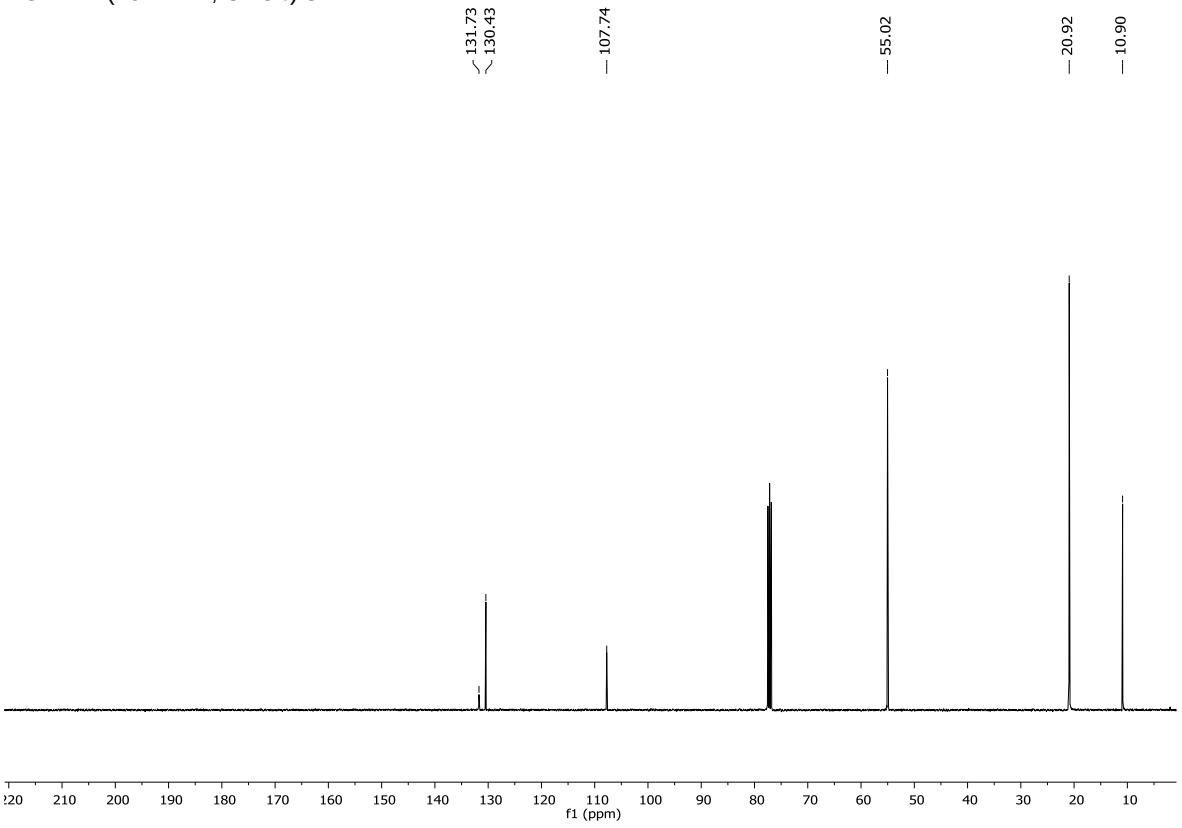
^{13}C NMR (101 MHz, $CDCl_3$) **7**



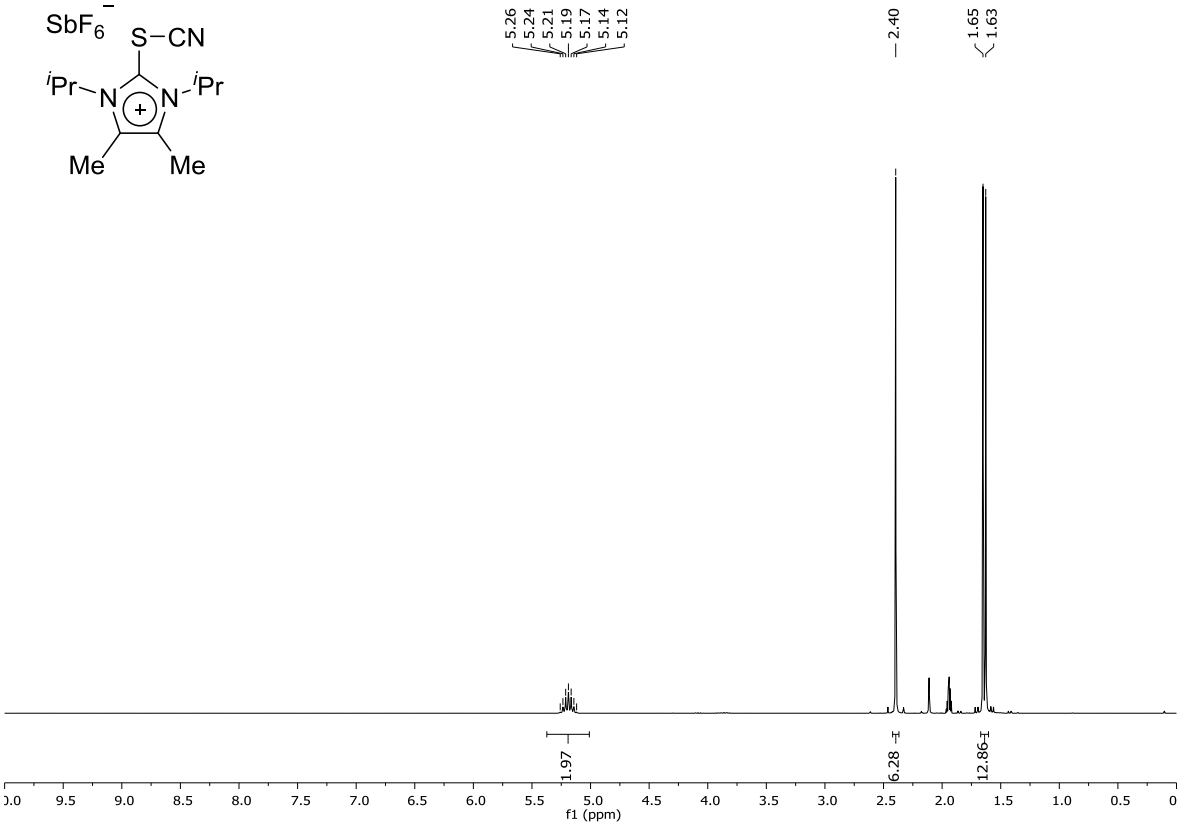
^{1}H NMR (400 MHz, $CDCl_3$) **8**



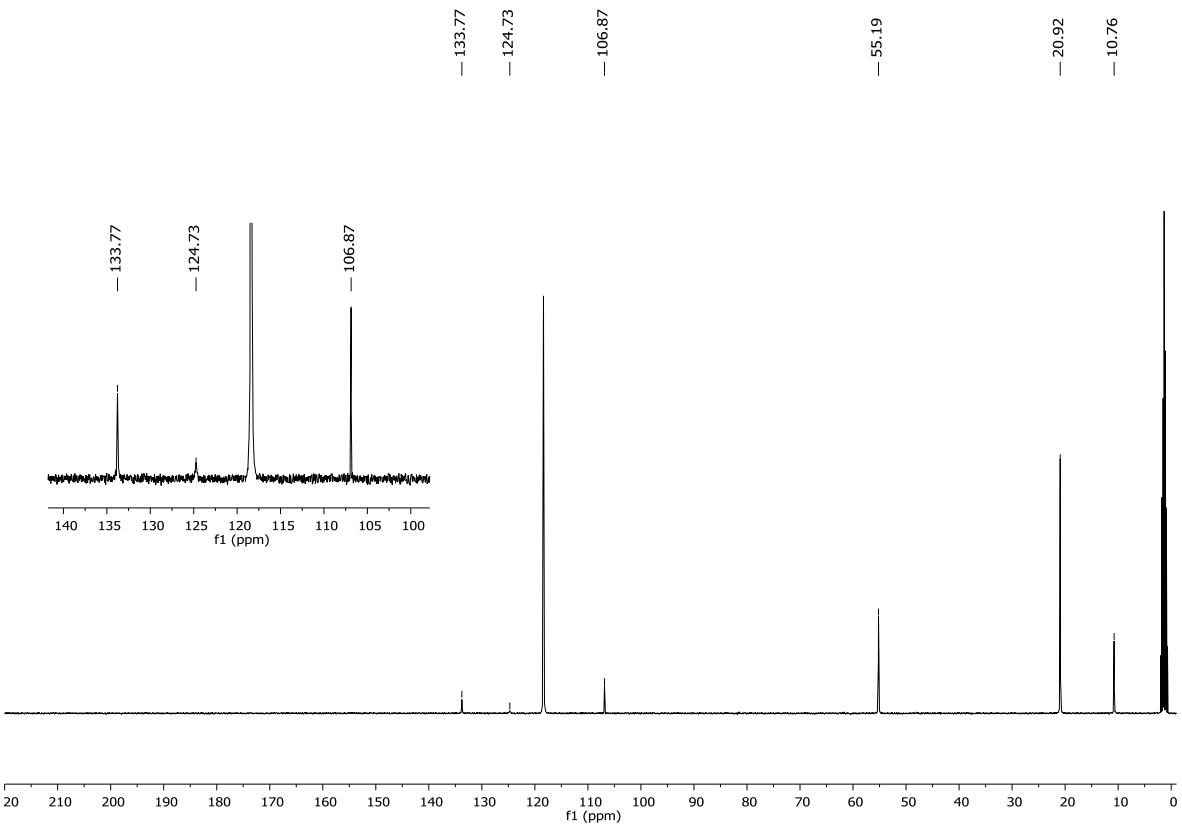
^{13}C NMR (101 MHz, $CDCl_3$) **8**



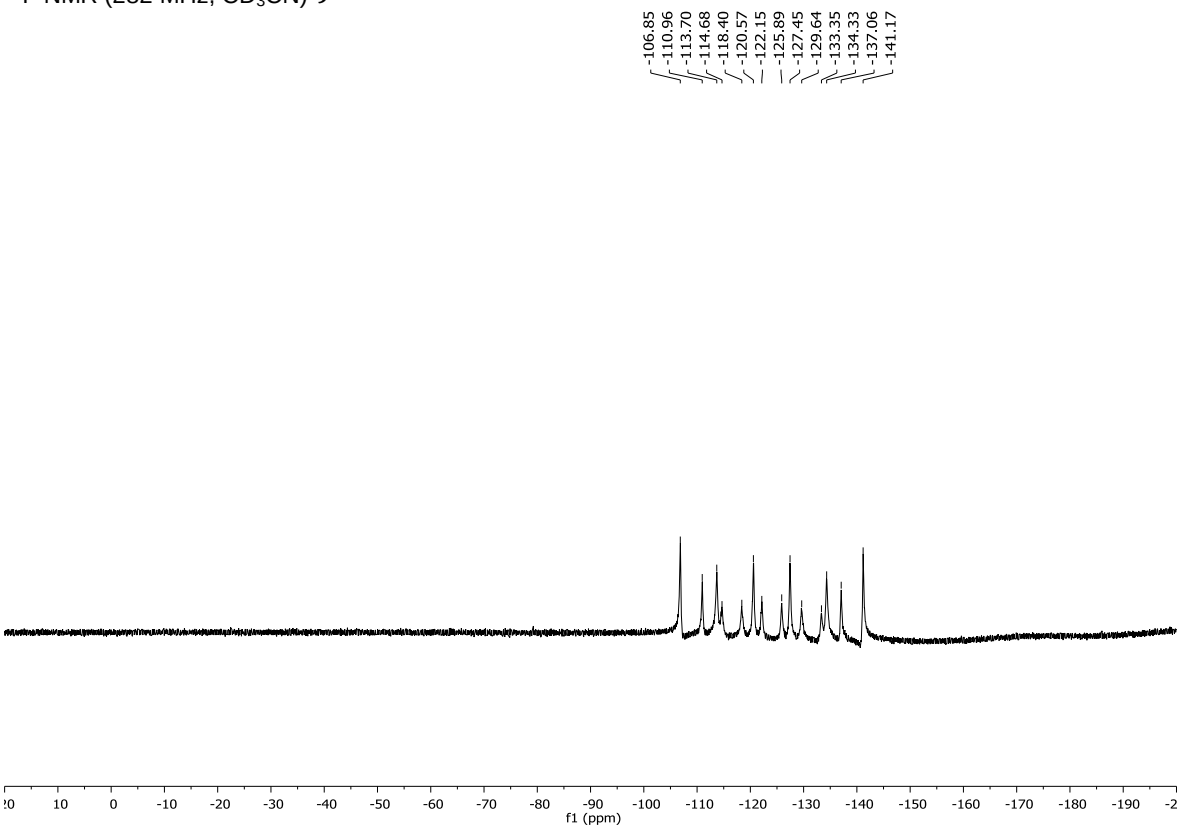
^{1}H NMR (400 MHz, CD_3CN) **9**



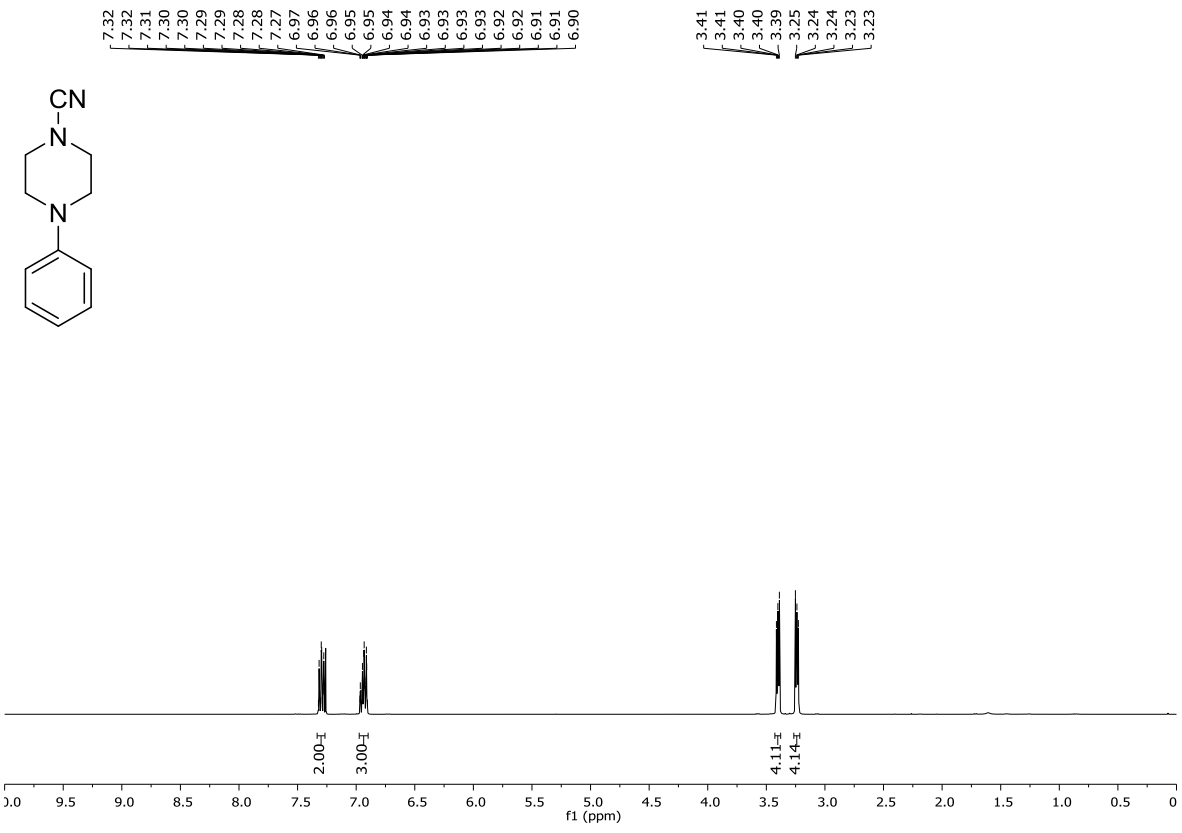
^{13}C NMR (101 MHz, $CDCl_3$) **9**



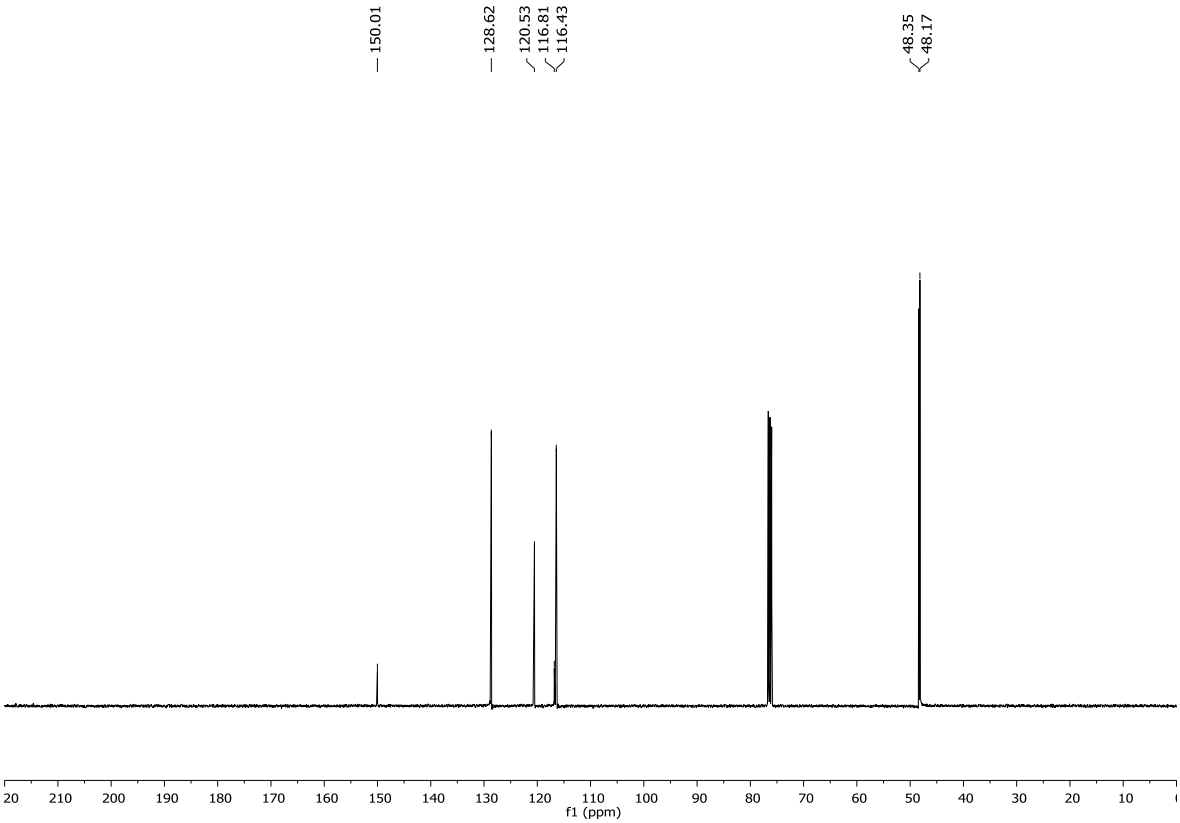
^{19}F NMR (282 MHz, CD_3CN) **9**



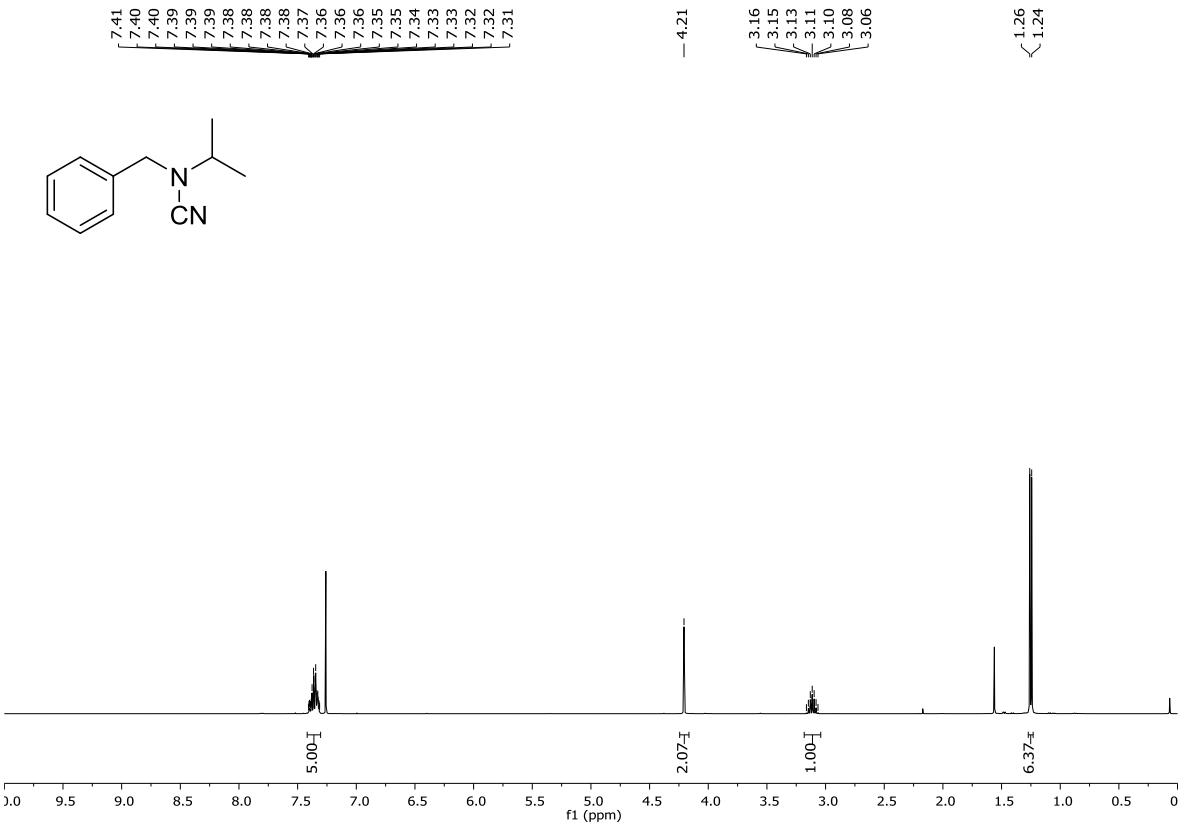
^{1}H NMR (400 MHz, $CDCl_3$) **10**



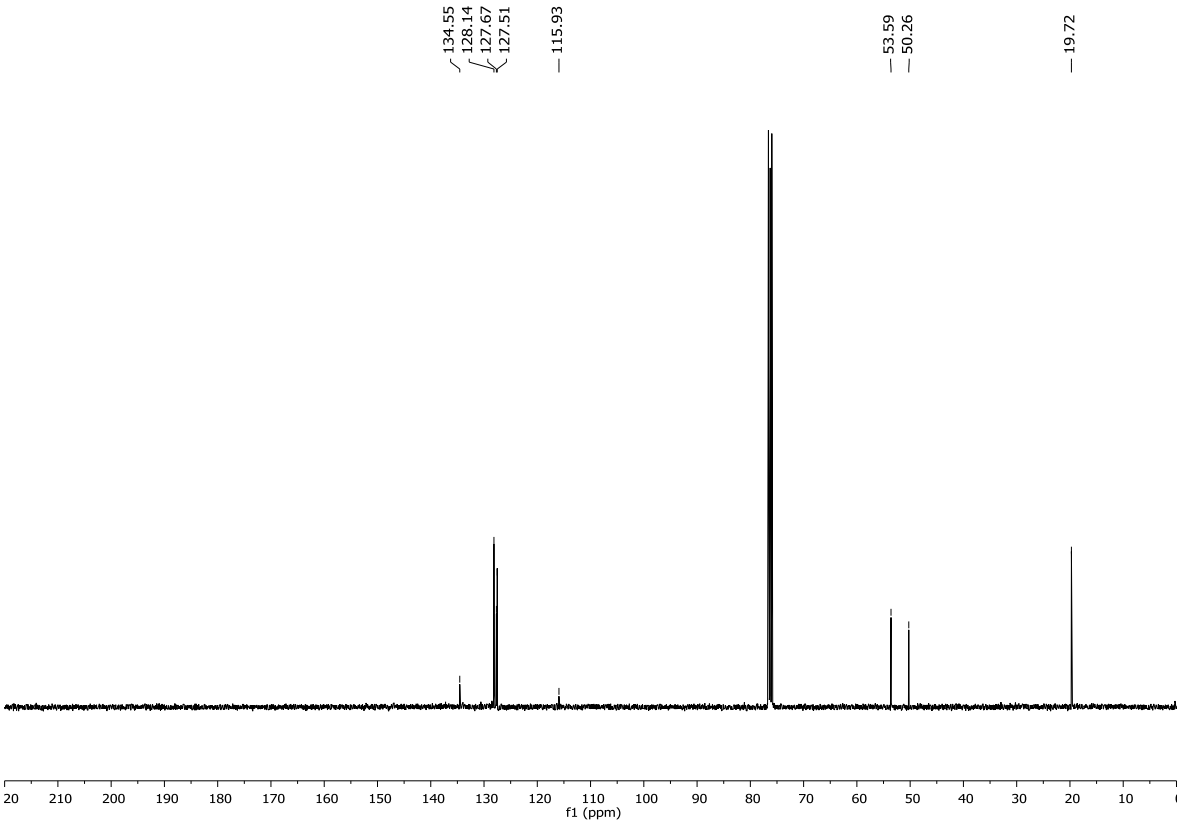
^{13}C NMR (101 MHz, $CDCl_3$) **10**



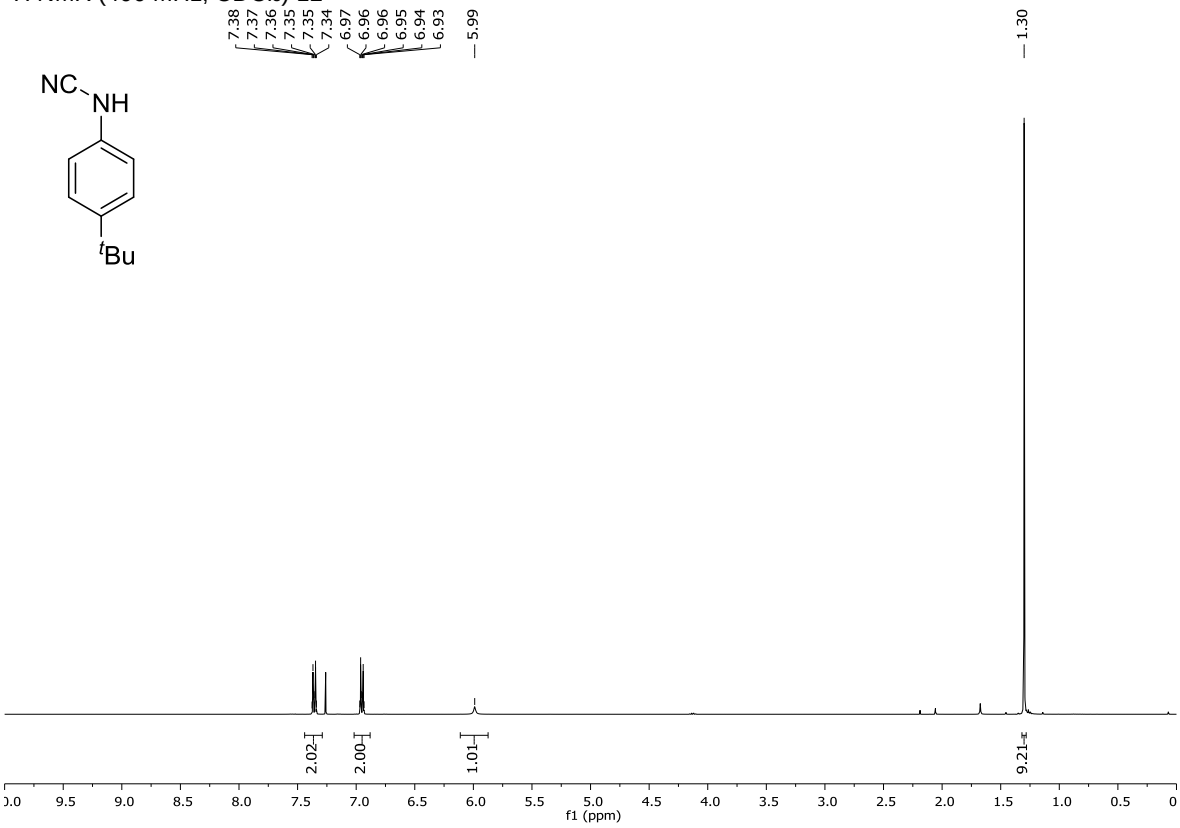
^{1}H NMR (400 MHz, $CDCl_3$) **11**



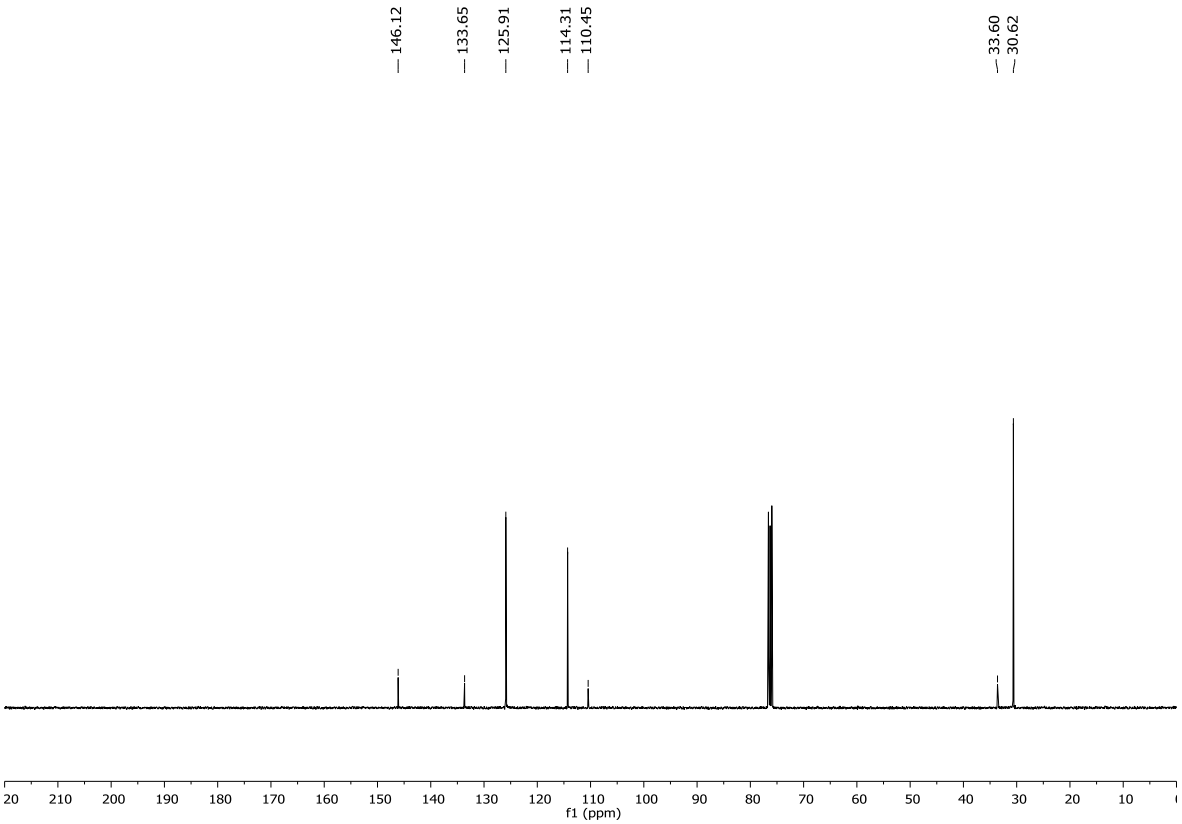
^{13}C NMR (101 MHz, $CDCl_3$) **11**



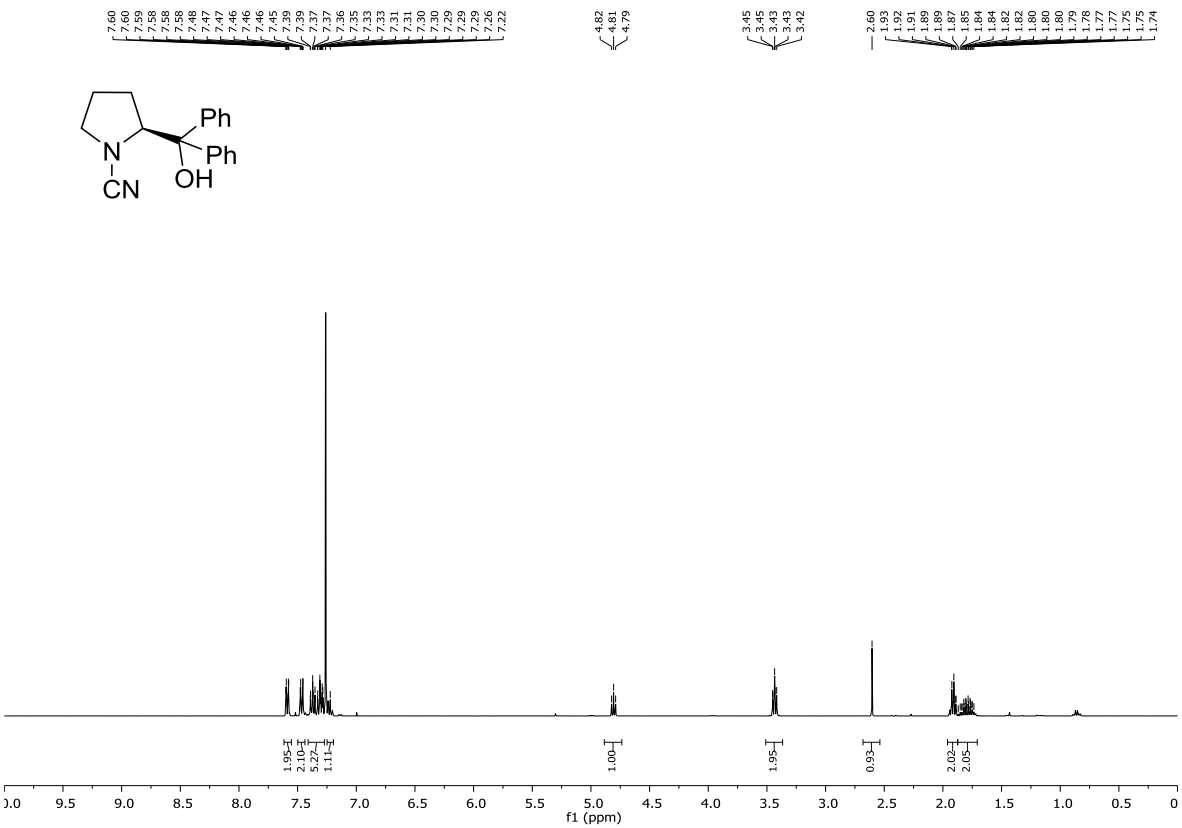
^{1}H NMR (400 MHz, $CDCl_3$) **12**



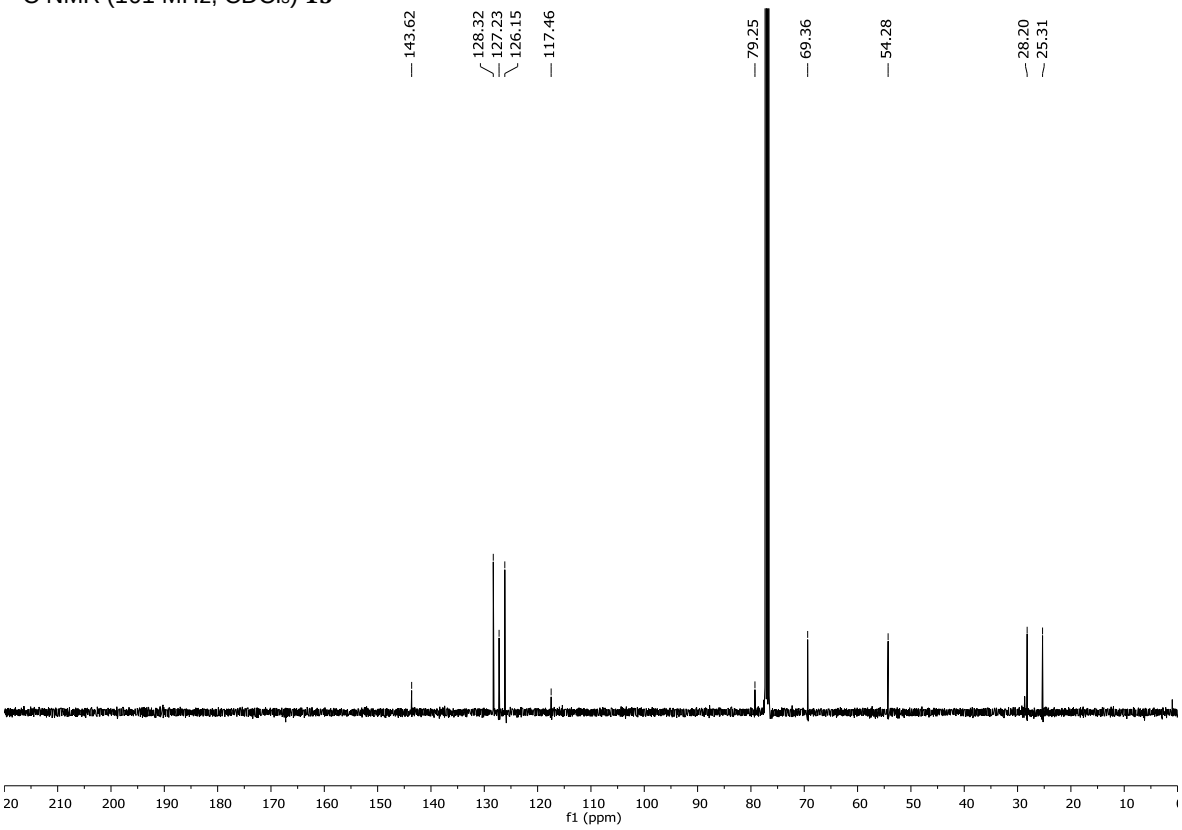
^{13}C NMR (101 MHz, $CDCl_3$) **12**



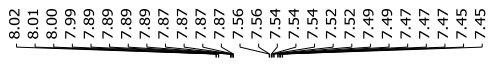
^{1}H NMR (400 MHz, $CDCl_3$) **13**

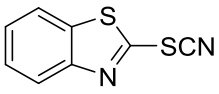


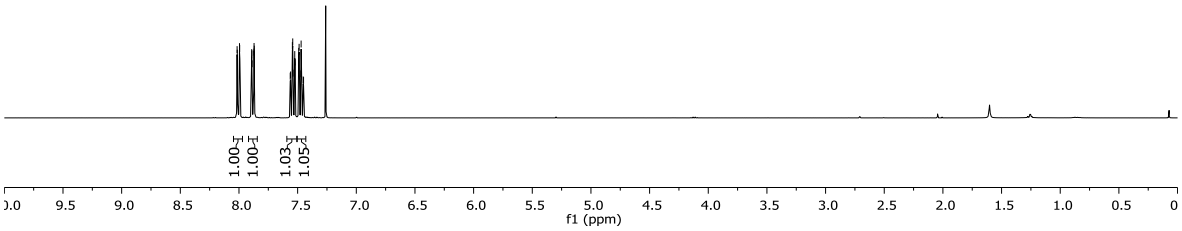
^{13}C NMR (101 MHz, $CDCl_3$) **13**



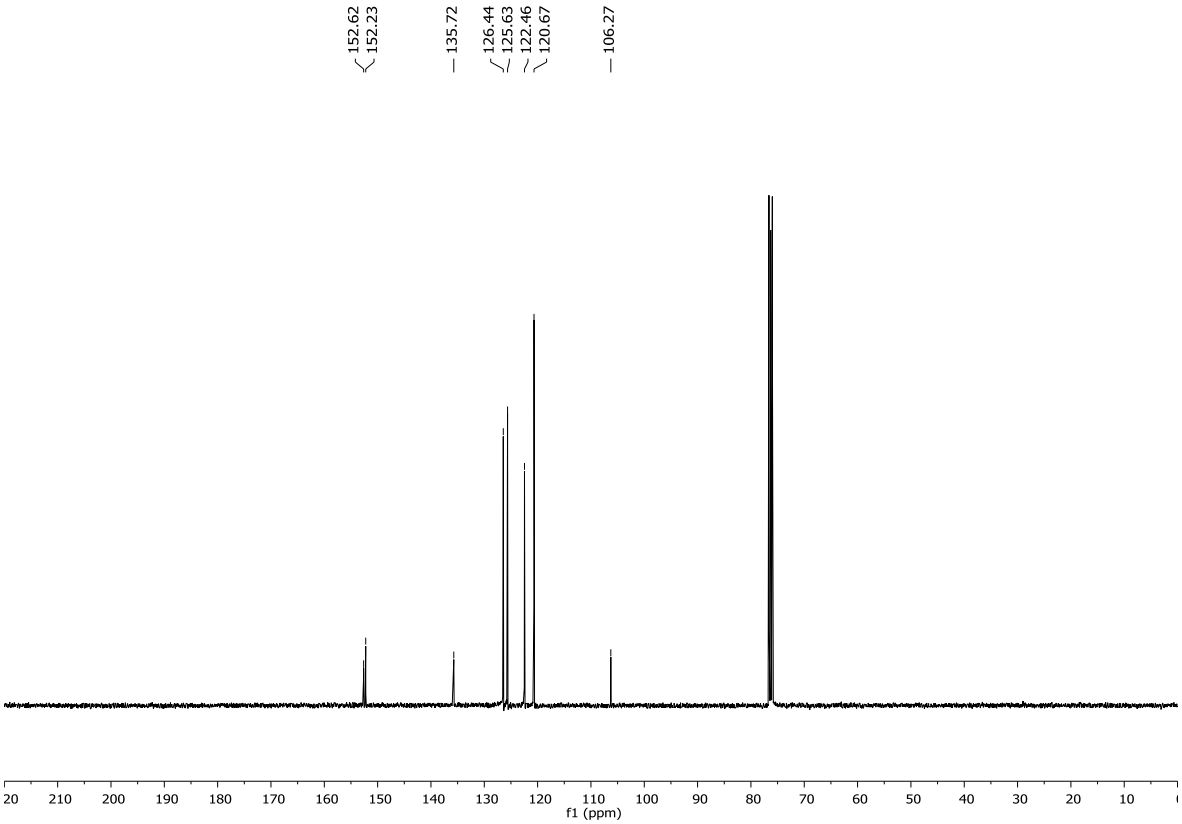
^{1}H NMR (400 MHz, $CDCl_3$) **14**



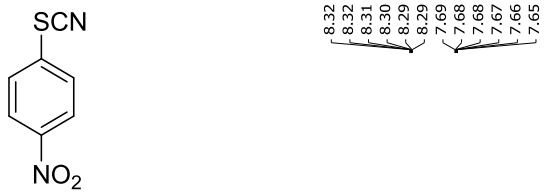


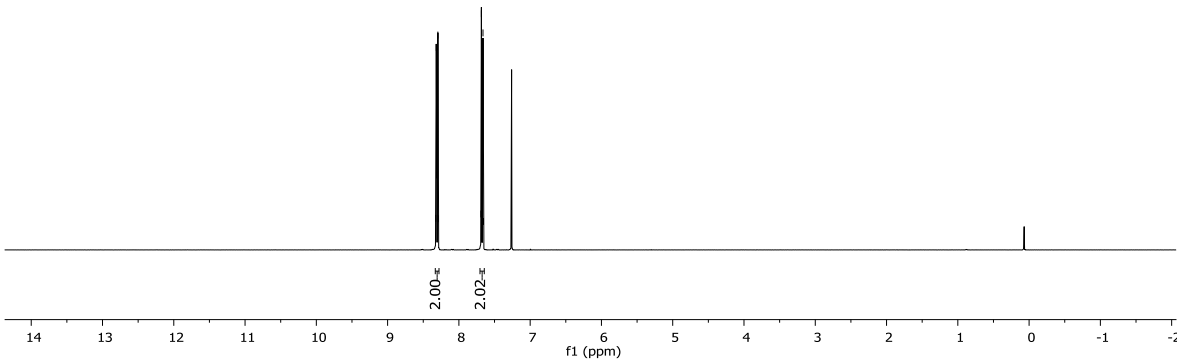


^{13}C NMR (101 MHz, $CDCl_3$) **14**

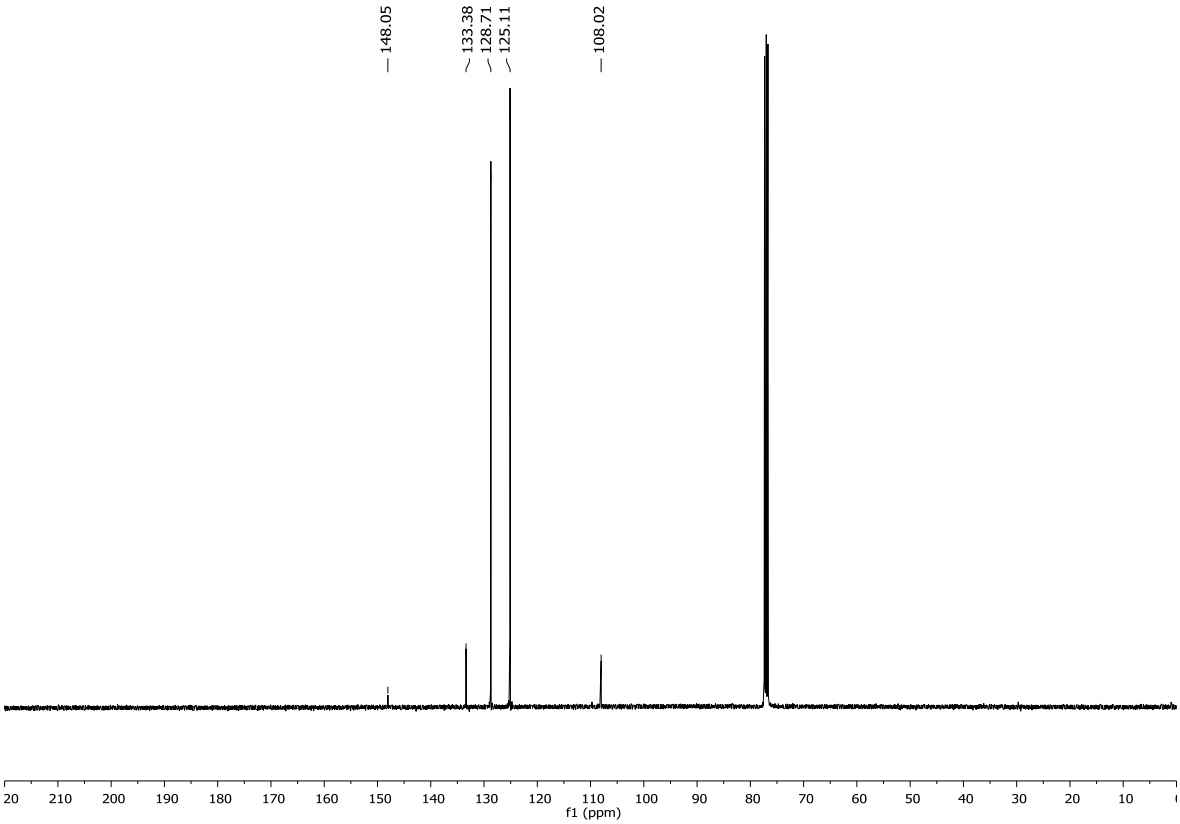


^{1}H NMR (400 MHz, $CDCl_3$) **15**

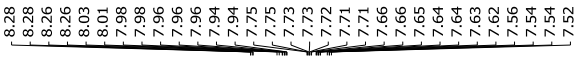


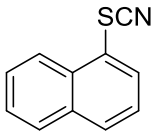


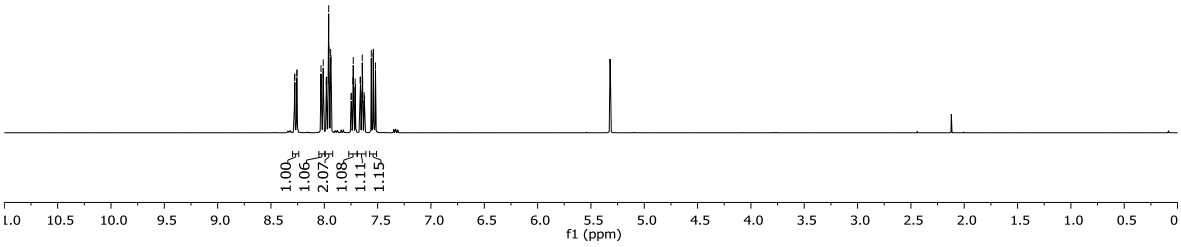
^{13}C NMR (101 MHz, $CDCl_3$) **15**



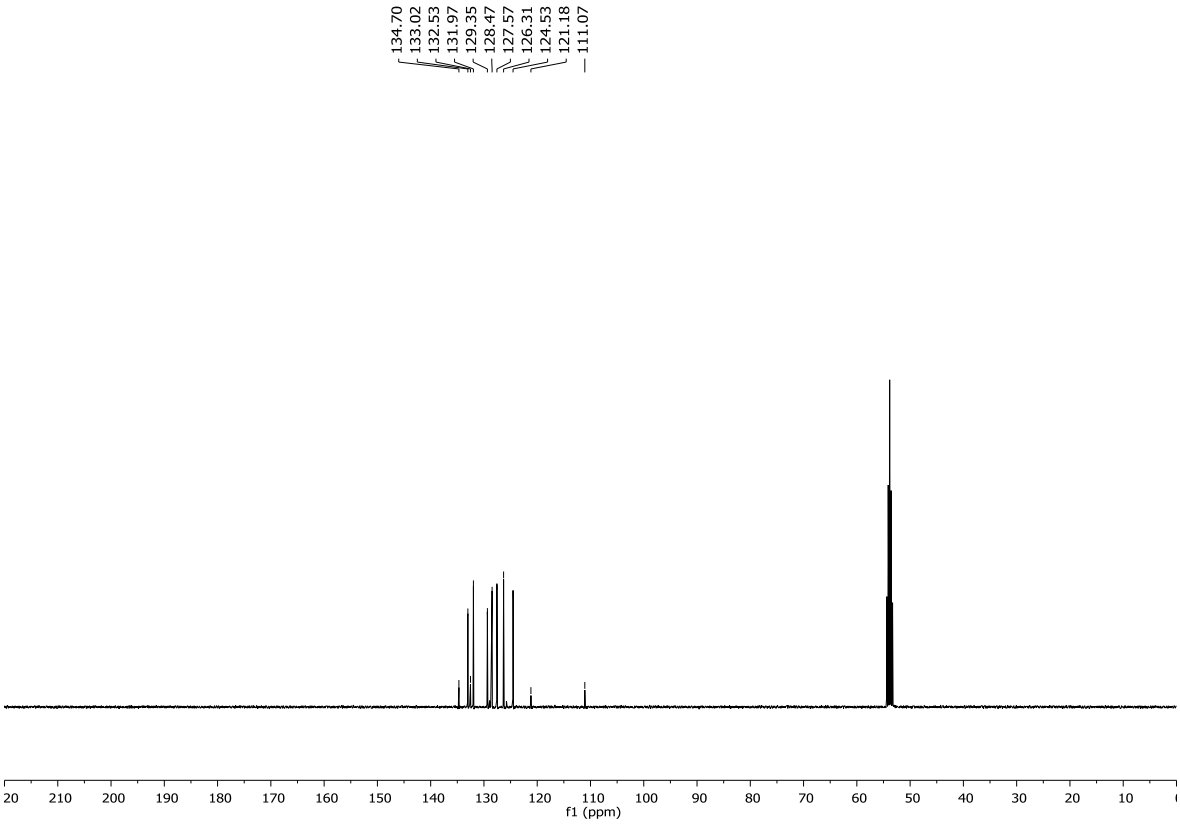
^{1}H NMR (400 MHz, $CDCl_3$) **16**



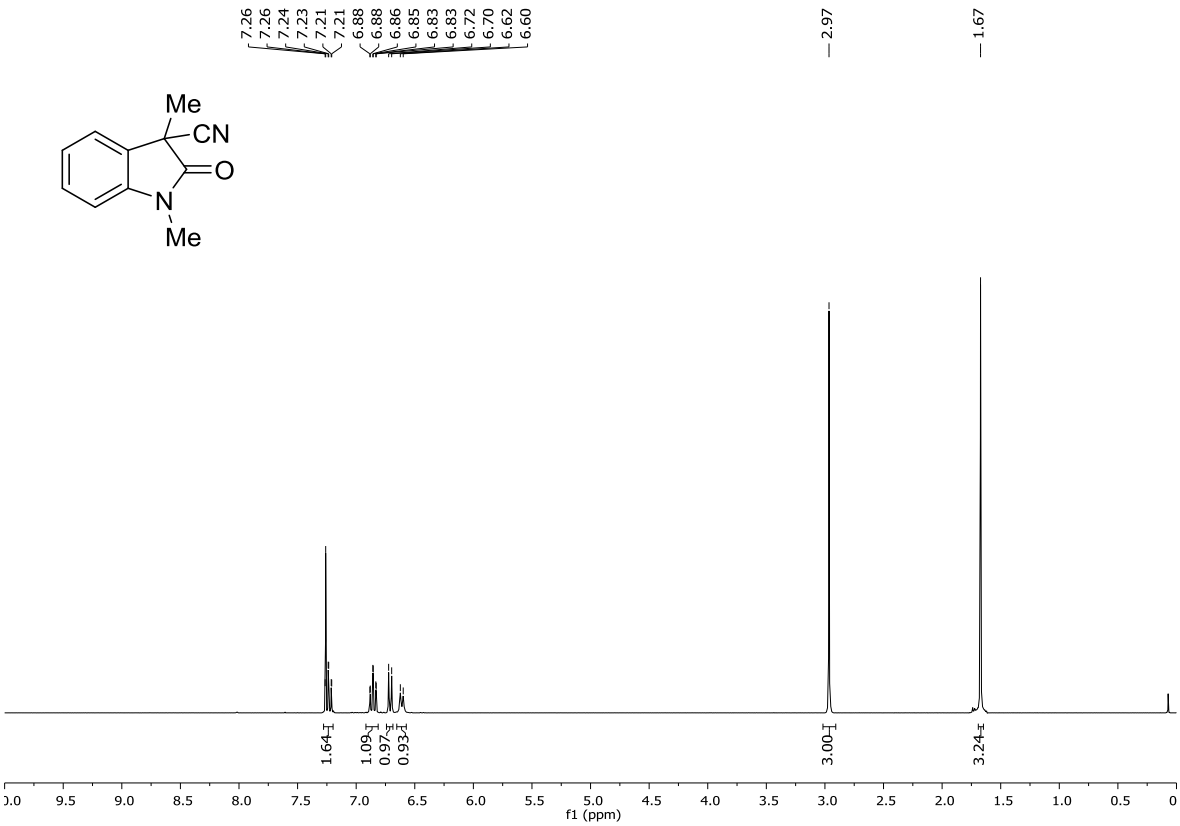




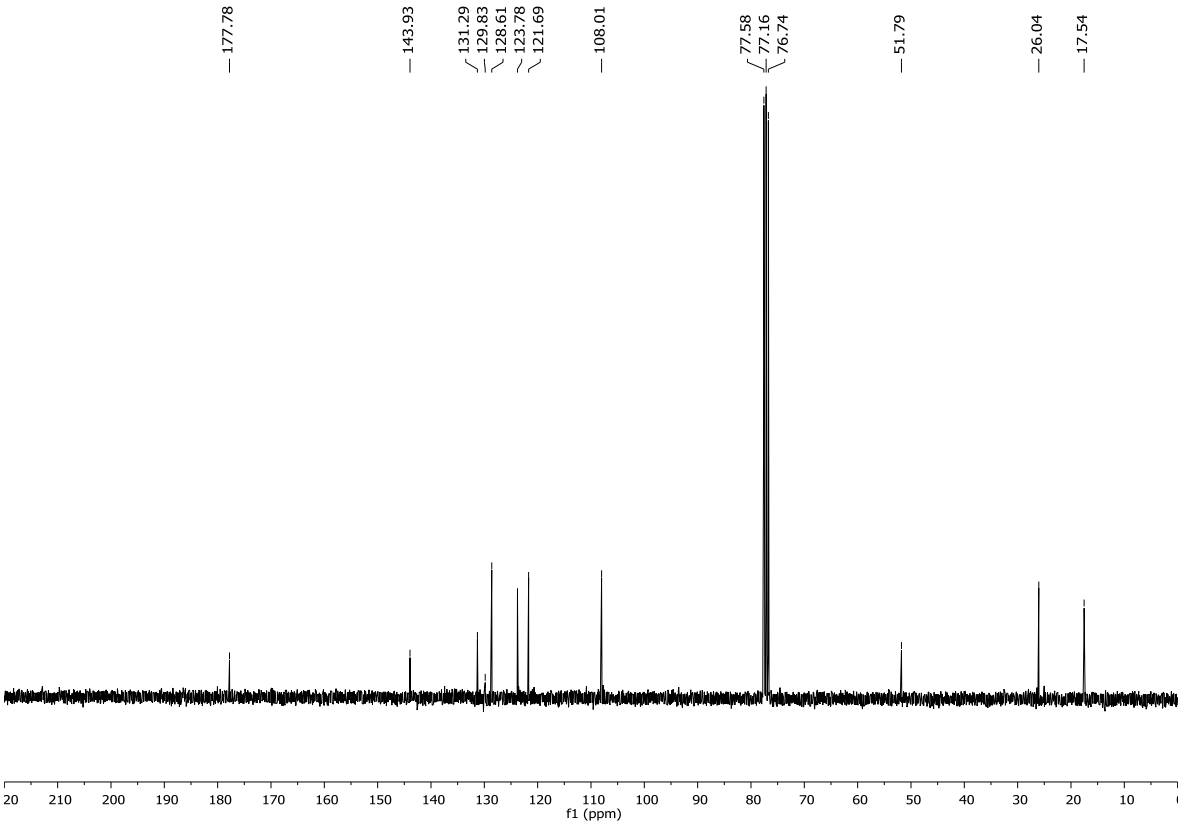
^{13}C NMR (101 MHz, $CDCl_3$) **16**



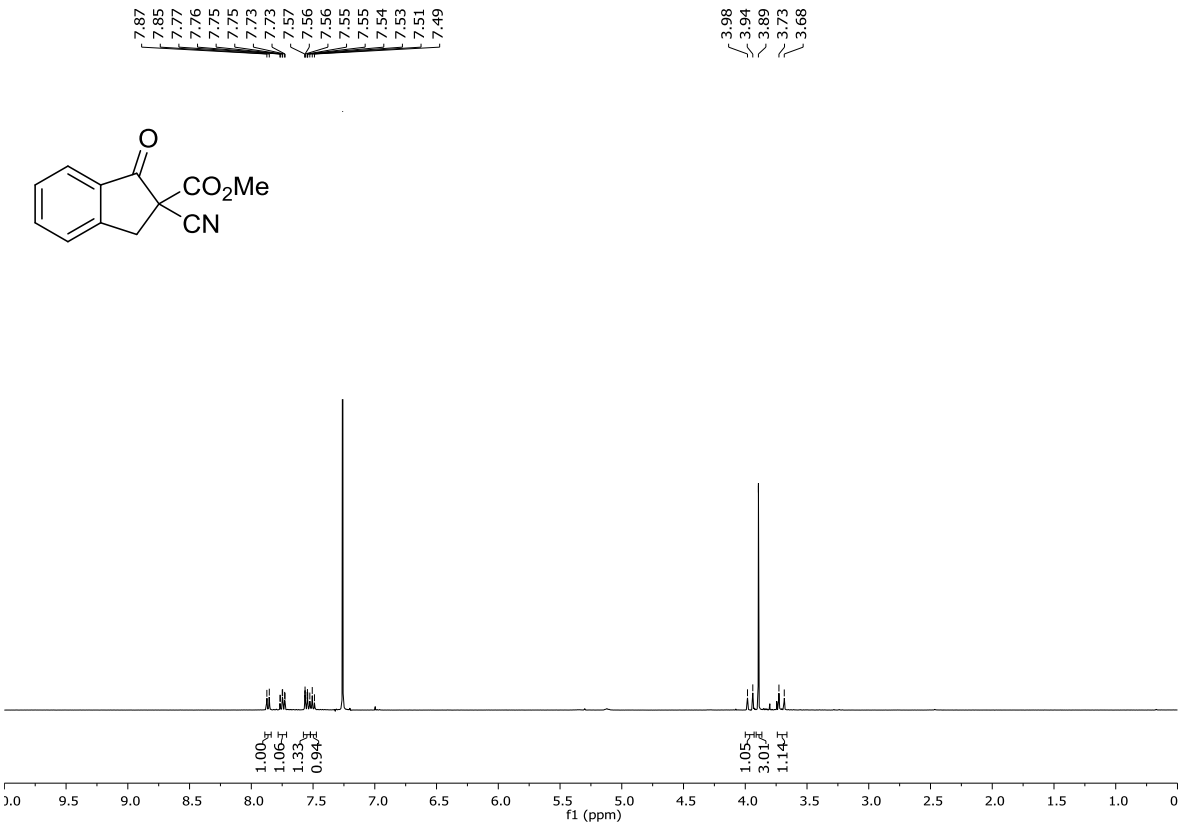
^{1}H NMR (300 MHz, $CDCl_3$) **17**



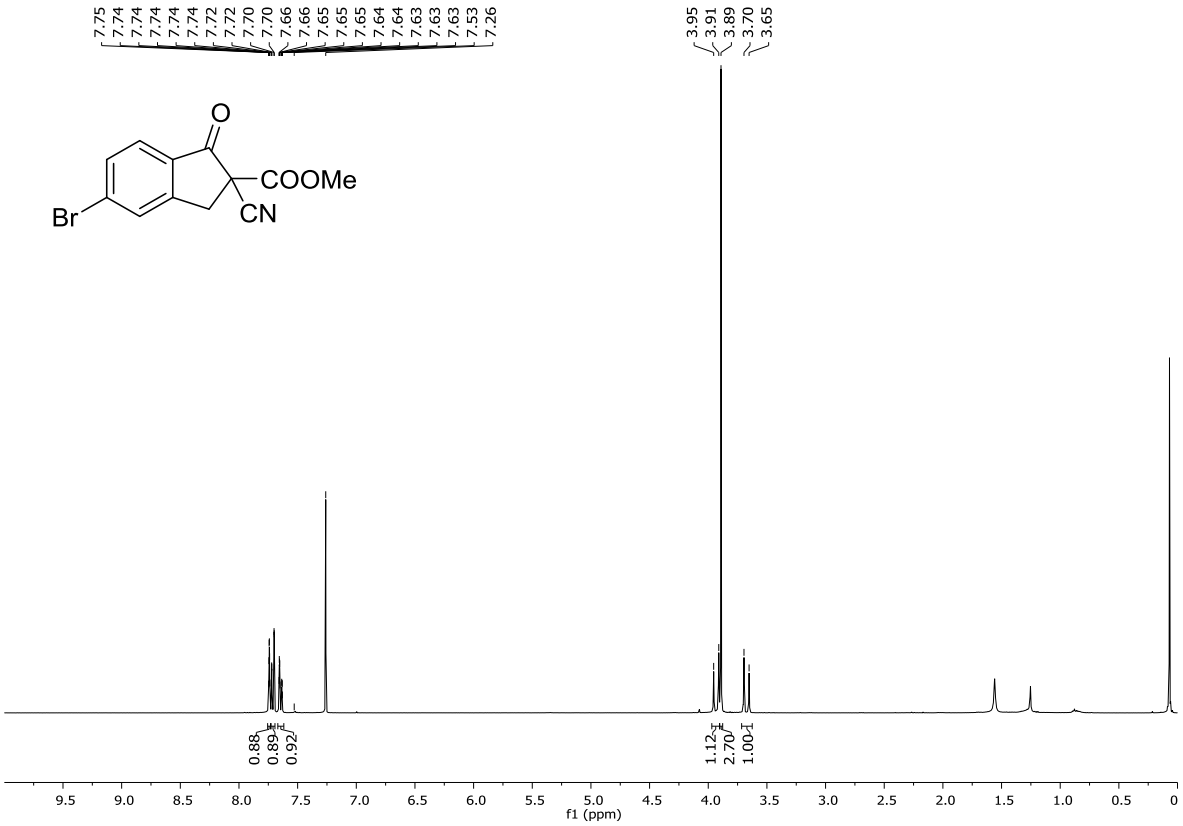
^{13}C NMR (75 MHz, $CDCl_3$) **17**



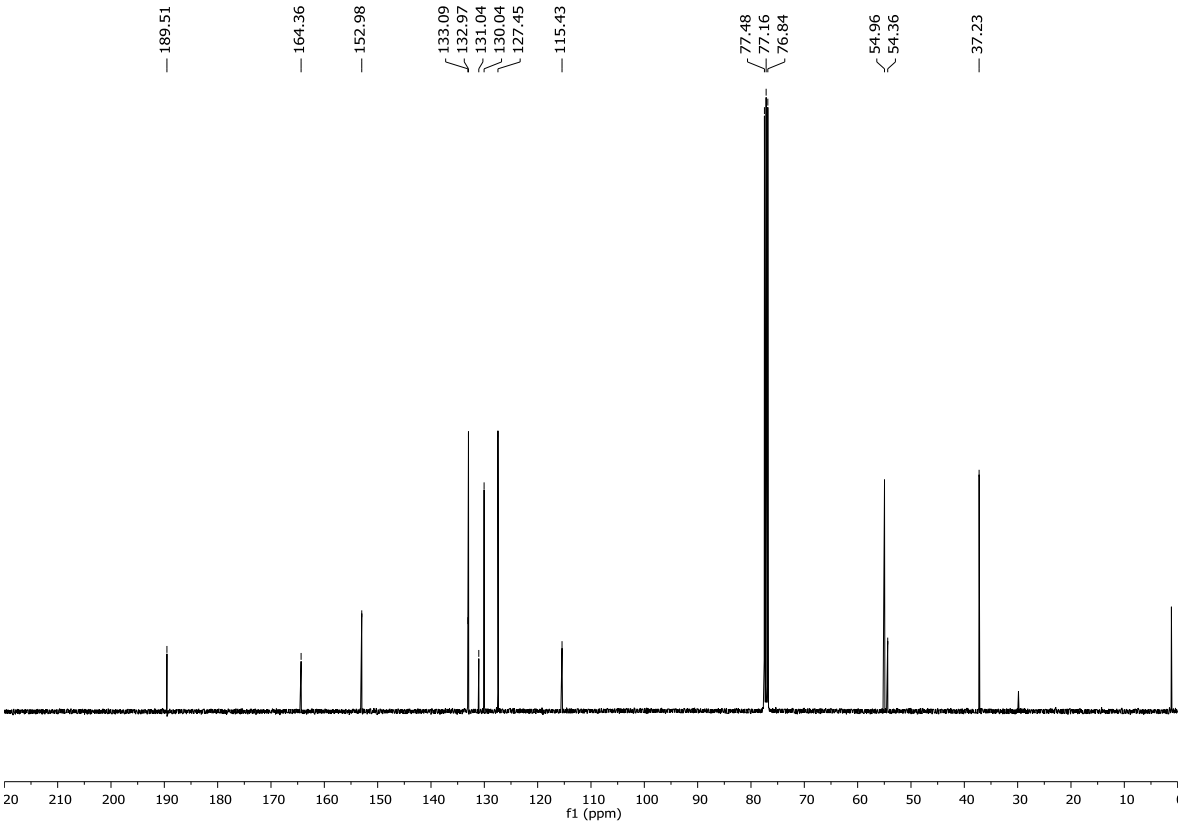
^{1}H NMR (400 MHz, $CDCl_3$) **18**



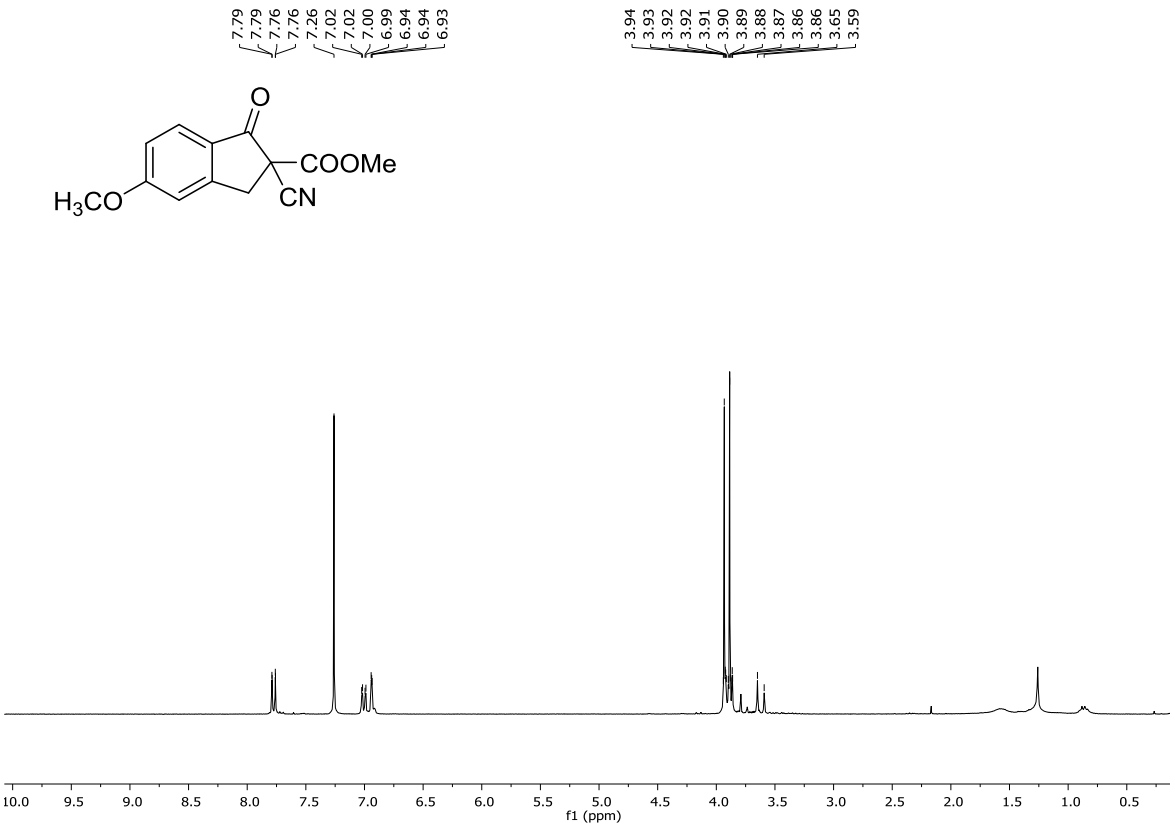
^{1}H NMR (400 MHz, $CDCl_3$) **19**



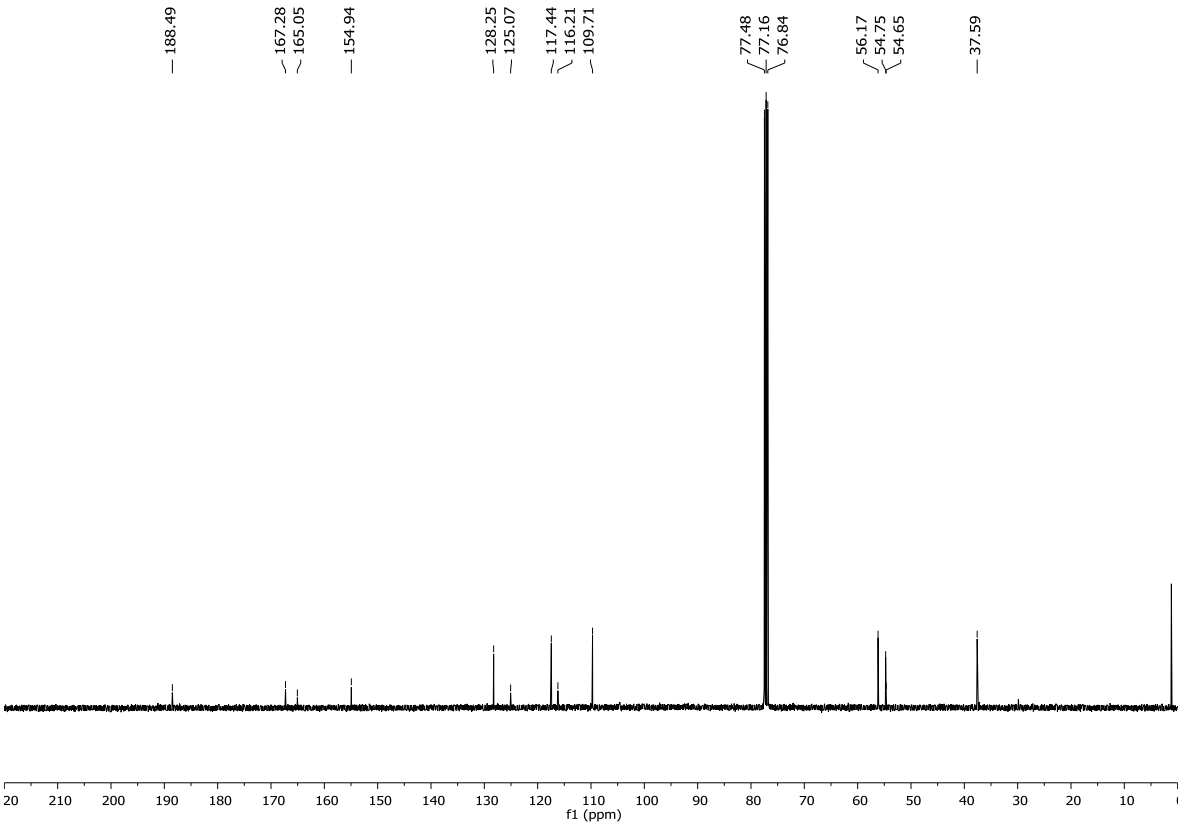
^{1}H NMR (400 MHz, $CDCl_3$) **19**



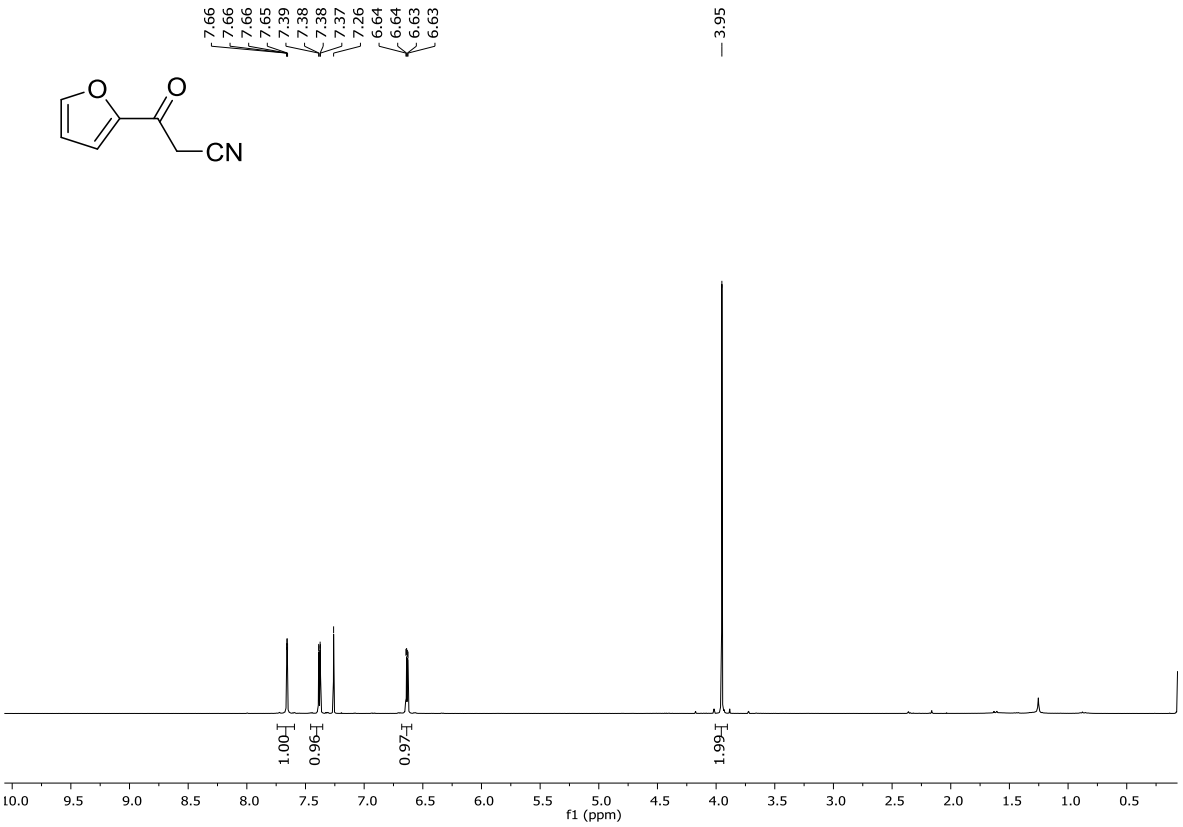
^{1}H NMR (400 MHz, $CDCl_3$) **20**



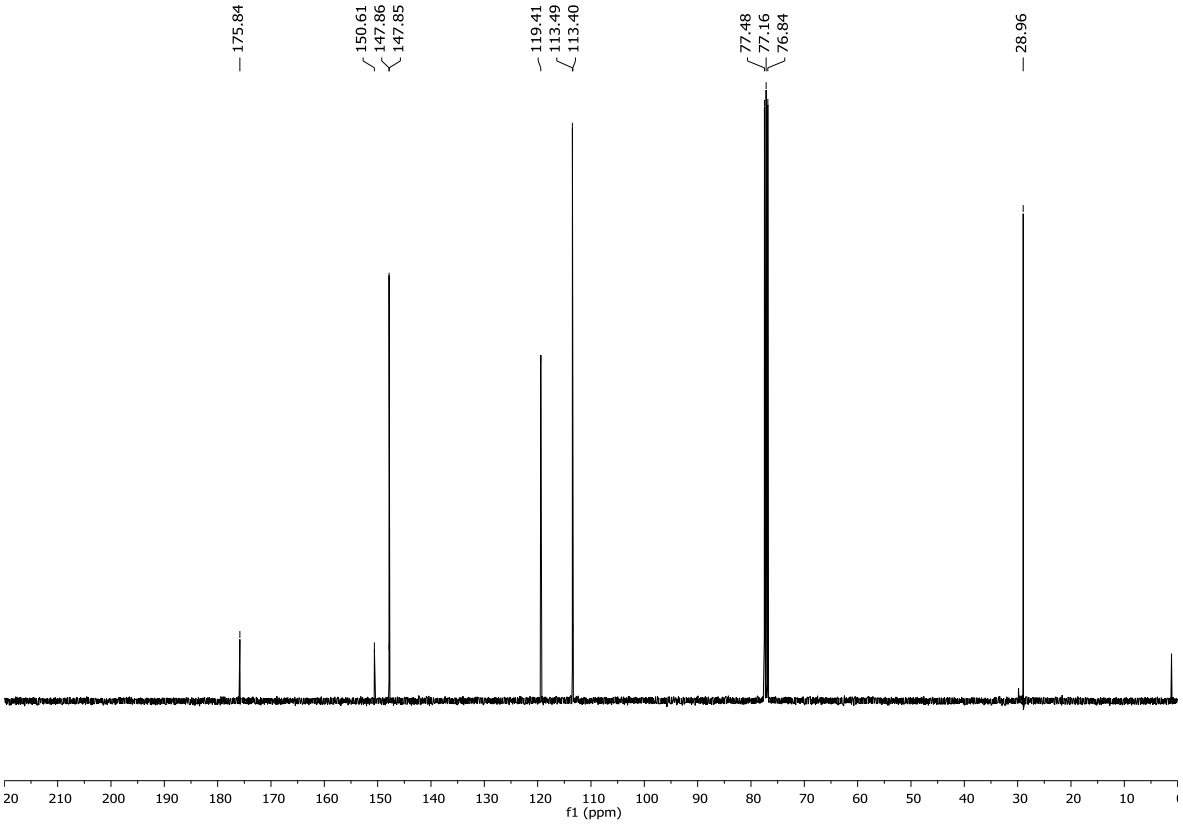
^{13}C NMR (101 MHz, $CDCl_3$) **20**



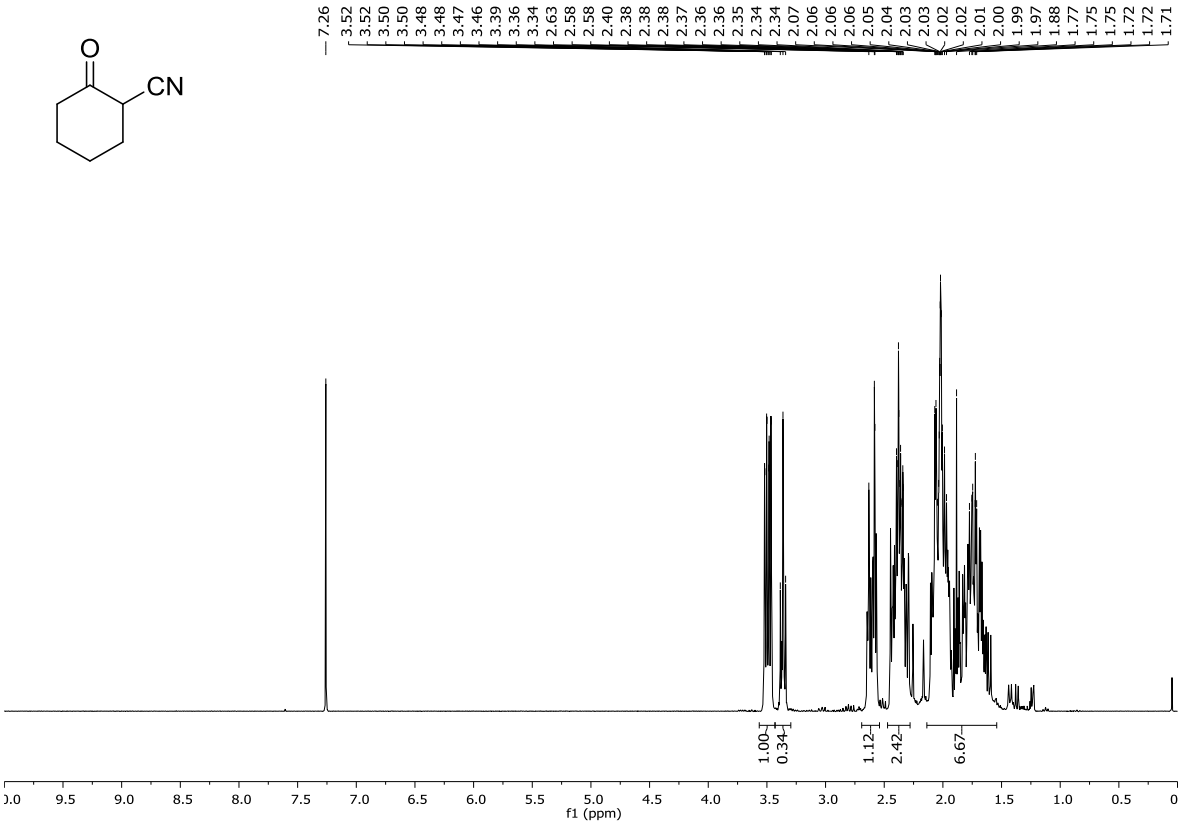
^{1}H NMR (400 MHz, $CDCl_3$) **21**



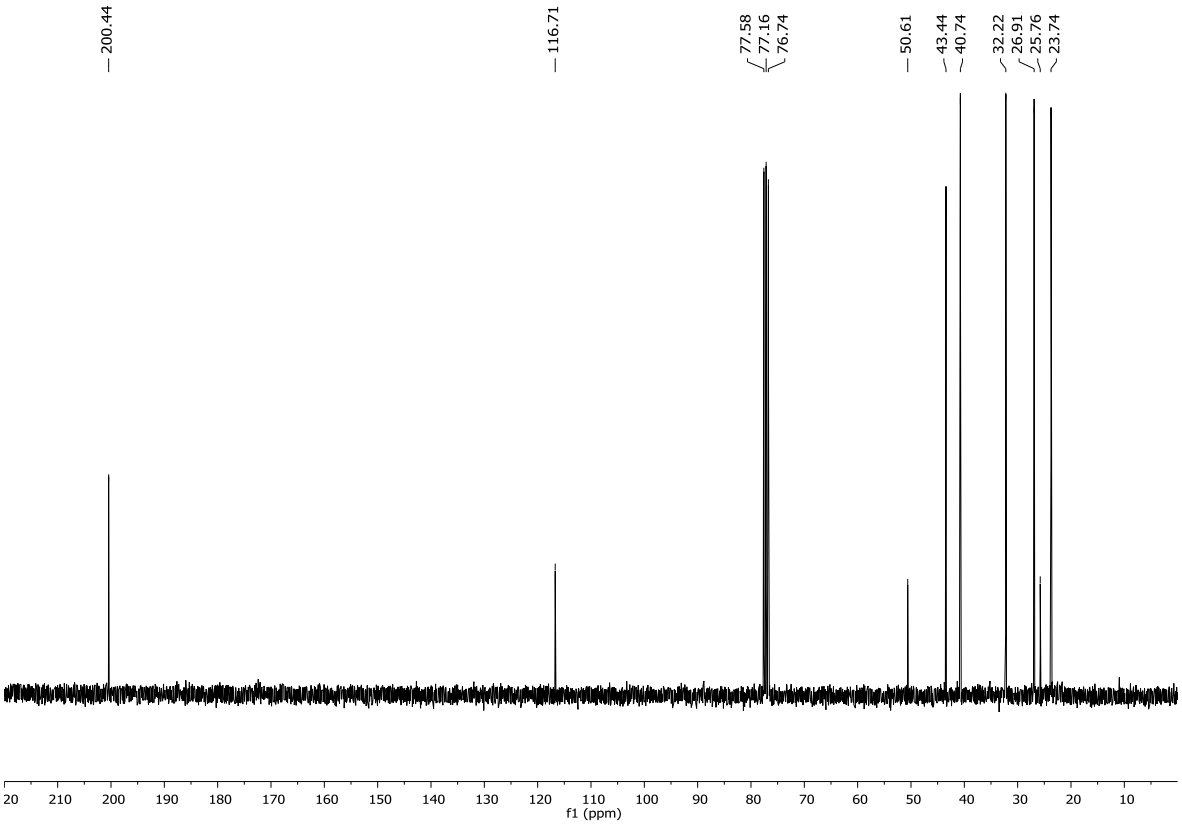
^{13}C NMR (101 MHz, $CDCl_3$) **21**



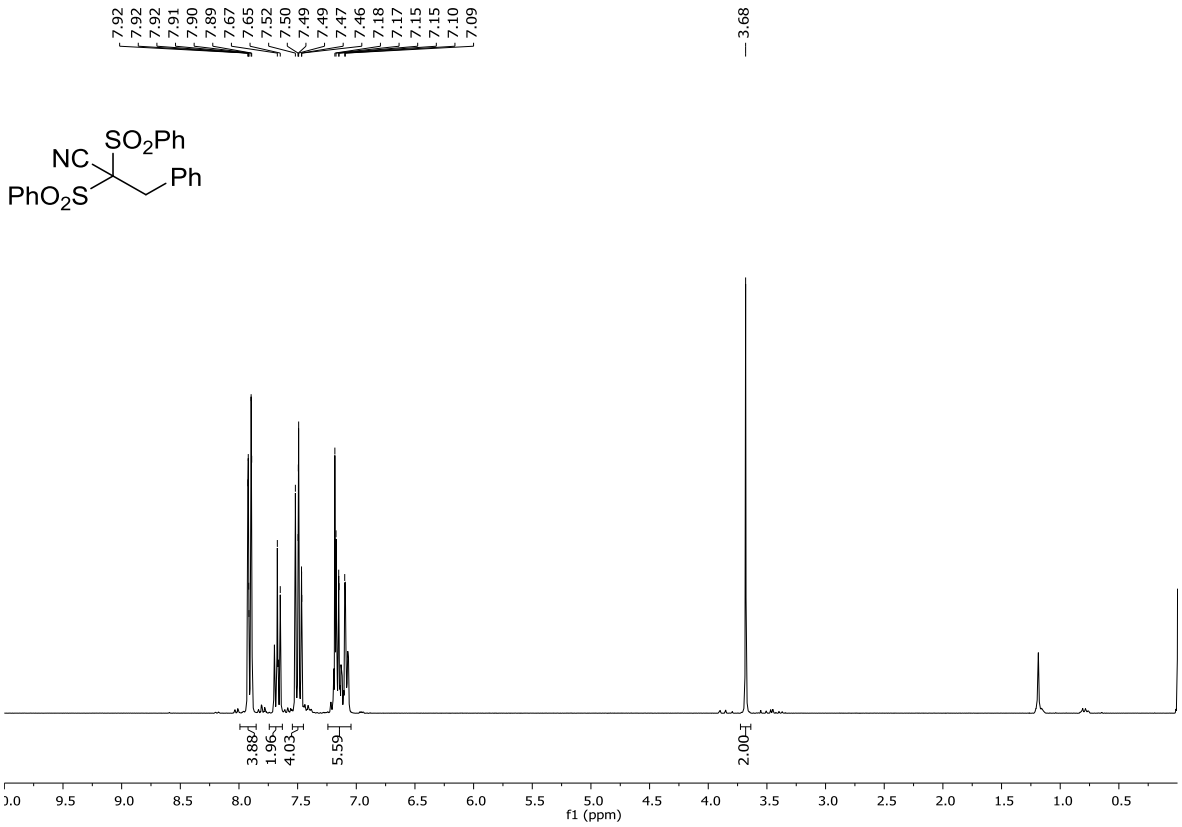
^{1}H NMR (300 MHz, $CDCl_3$) **22**



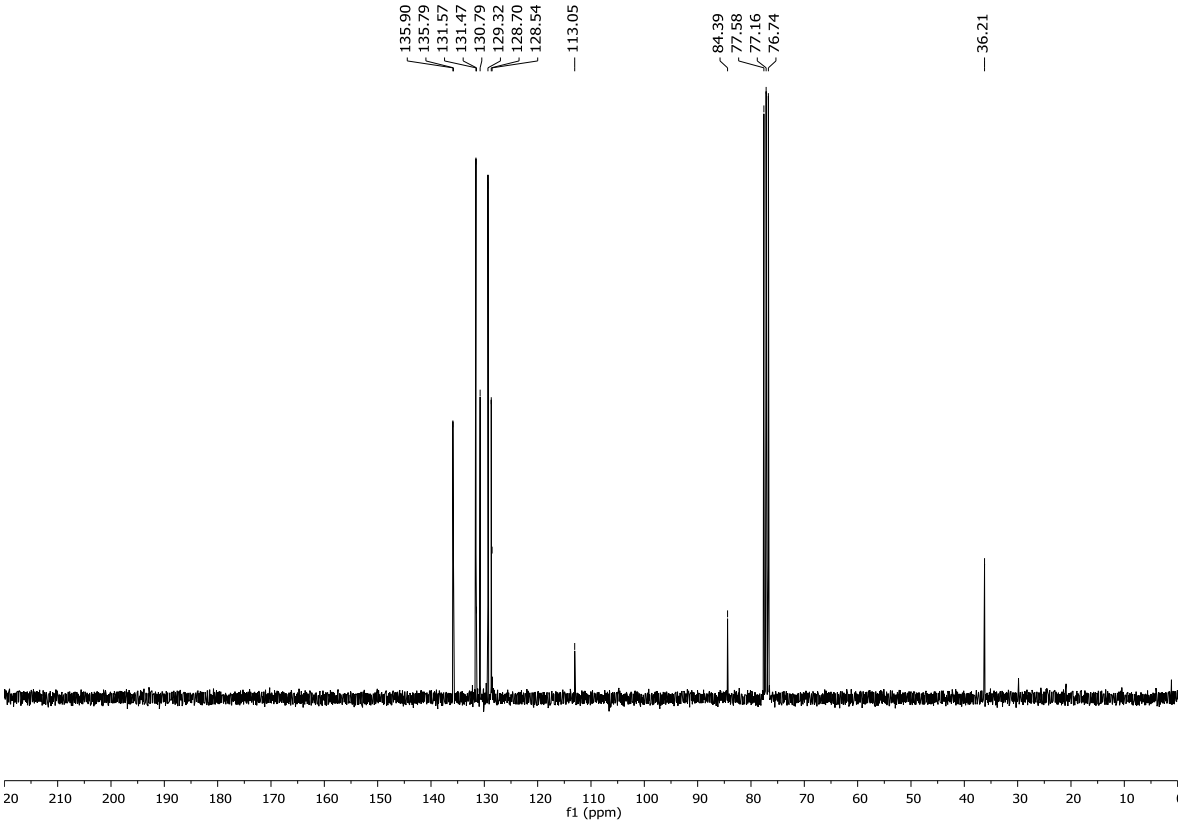
^{13}C NMR (75 MHz, $CDCl_3$) **22**



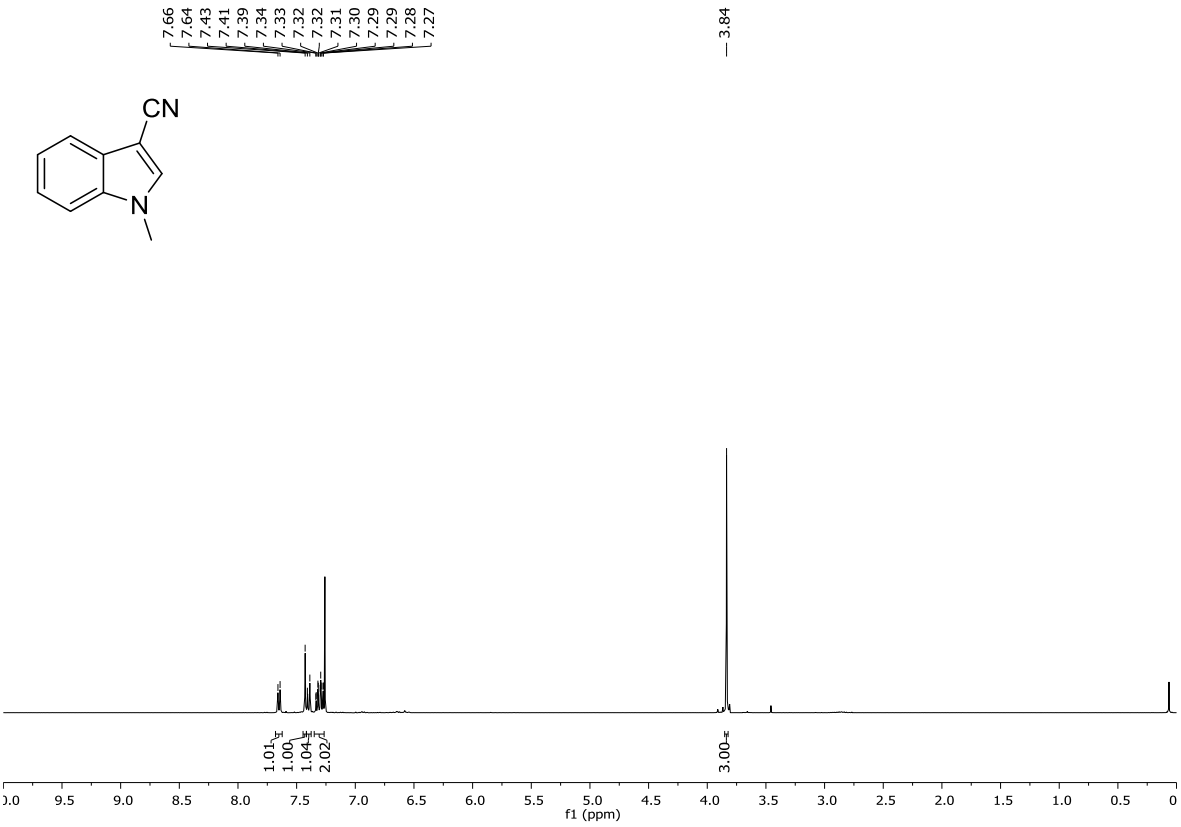
^{1}H NMR (300 MHz, $CDCl_3$) **23**



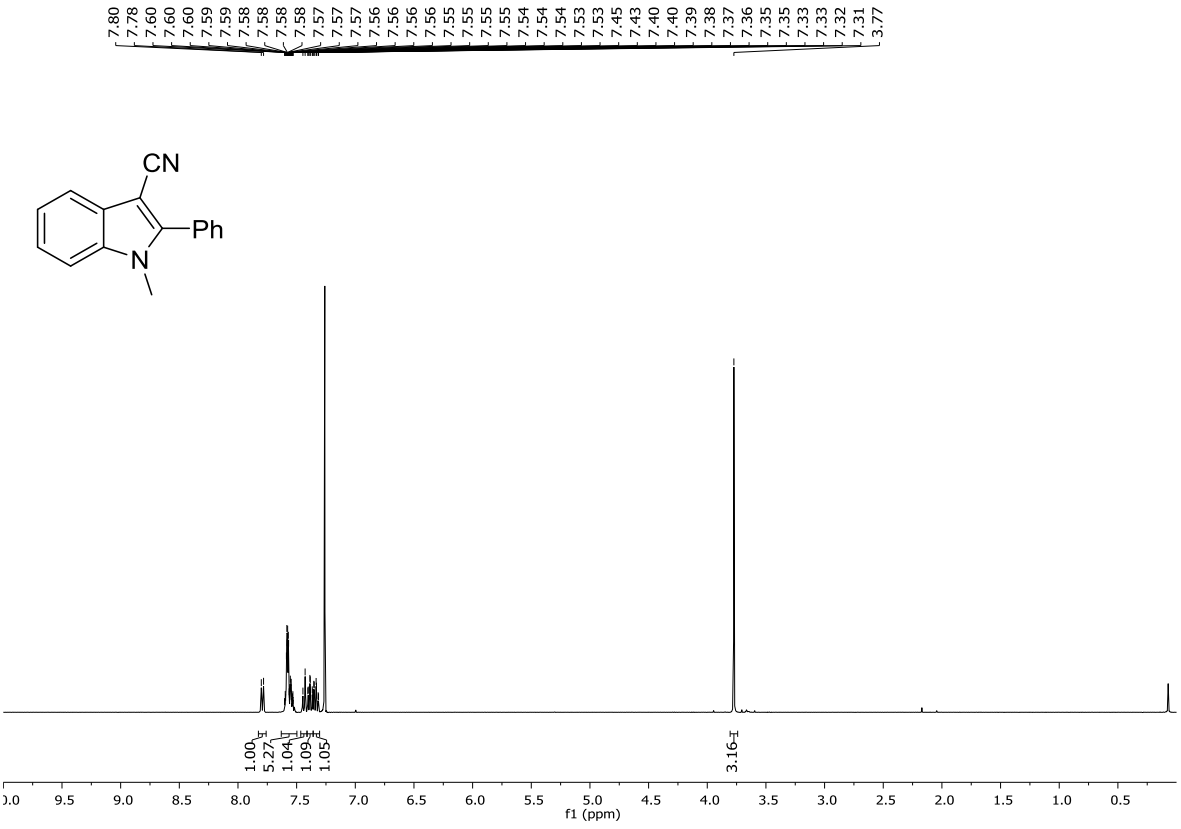
^{13}C NMR (75 MHz, $CDCl_3$) **23**



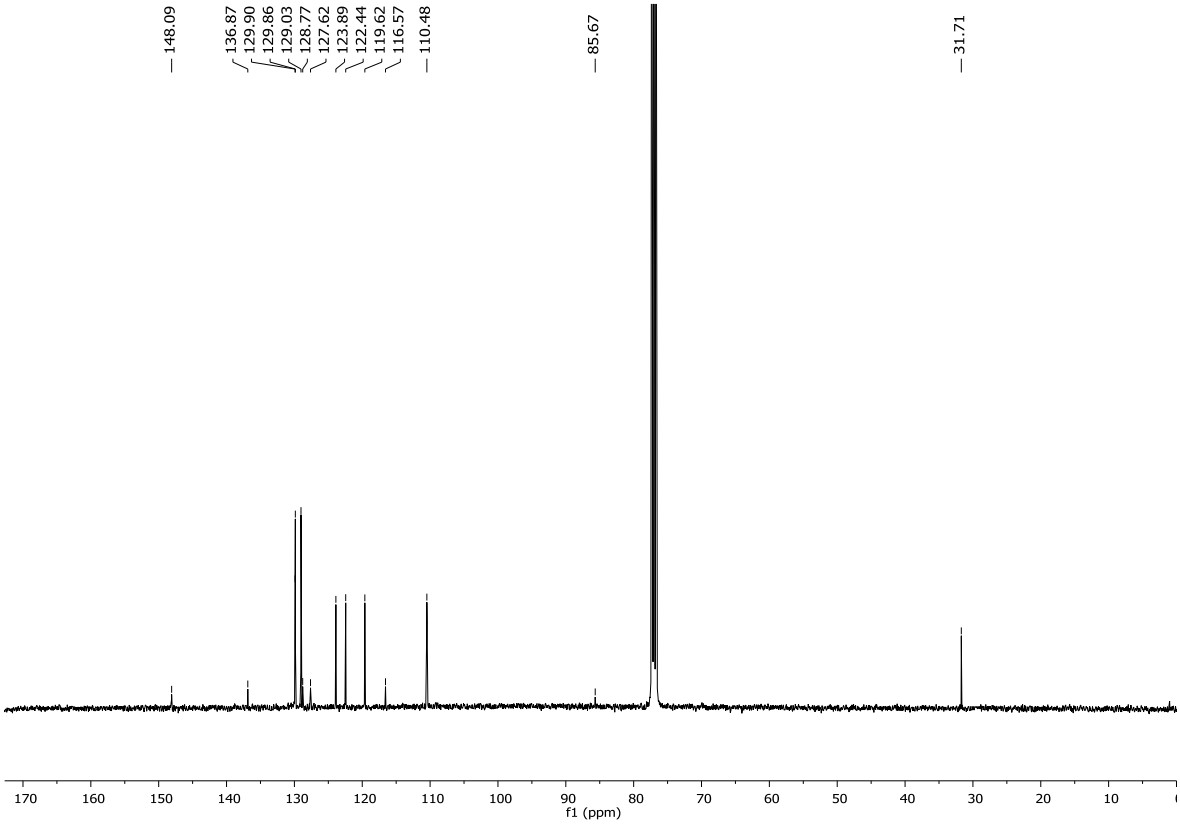
^{1}H NMR (400 MHz, $CDCl_3$) **24**



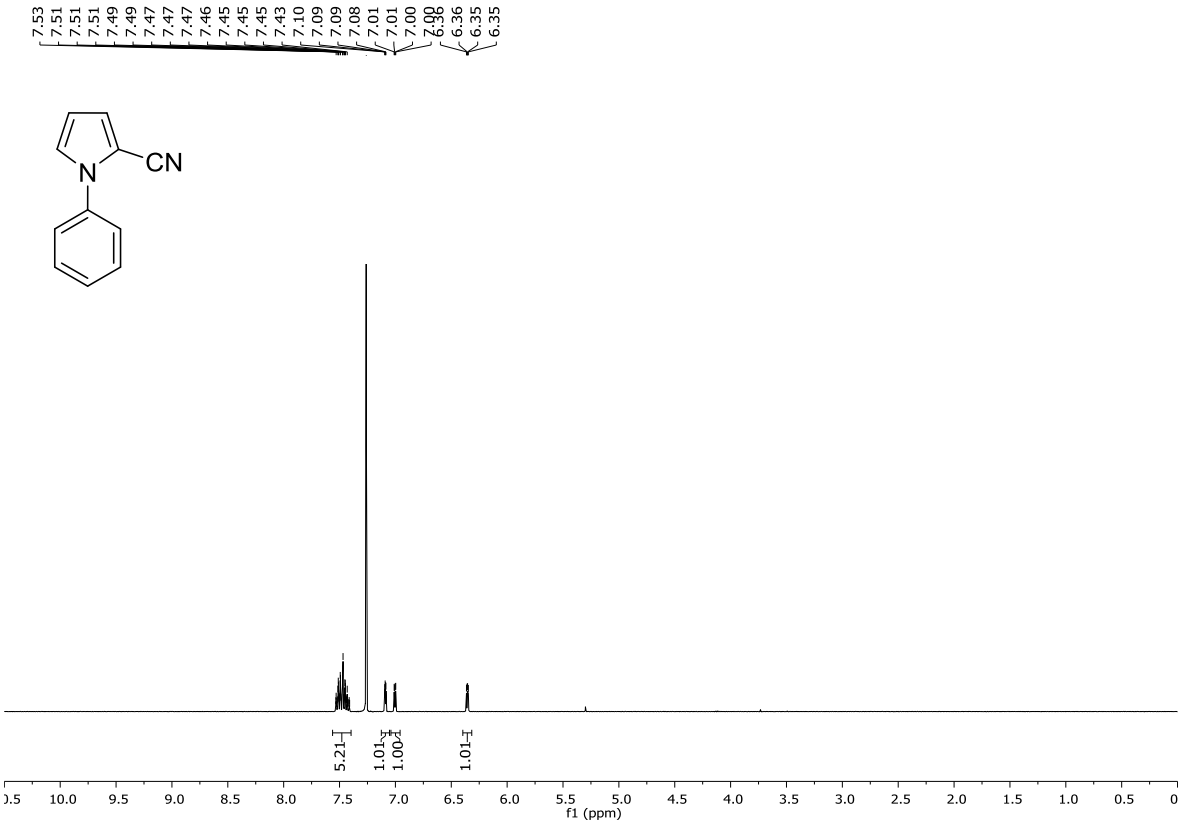
^{1}H NMR (400 MHz, $CDCl_3$) **25**



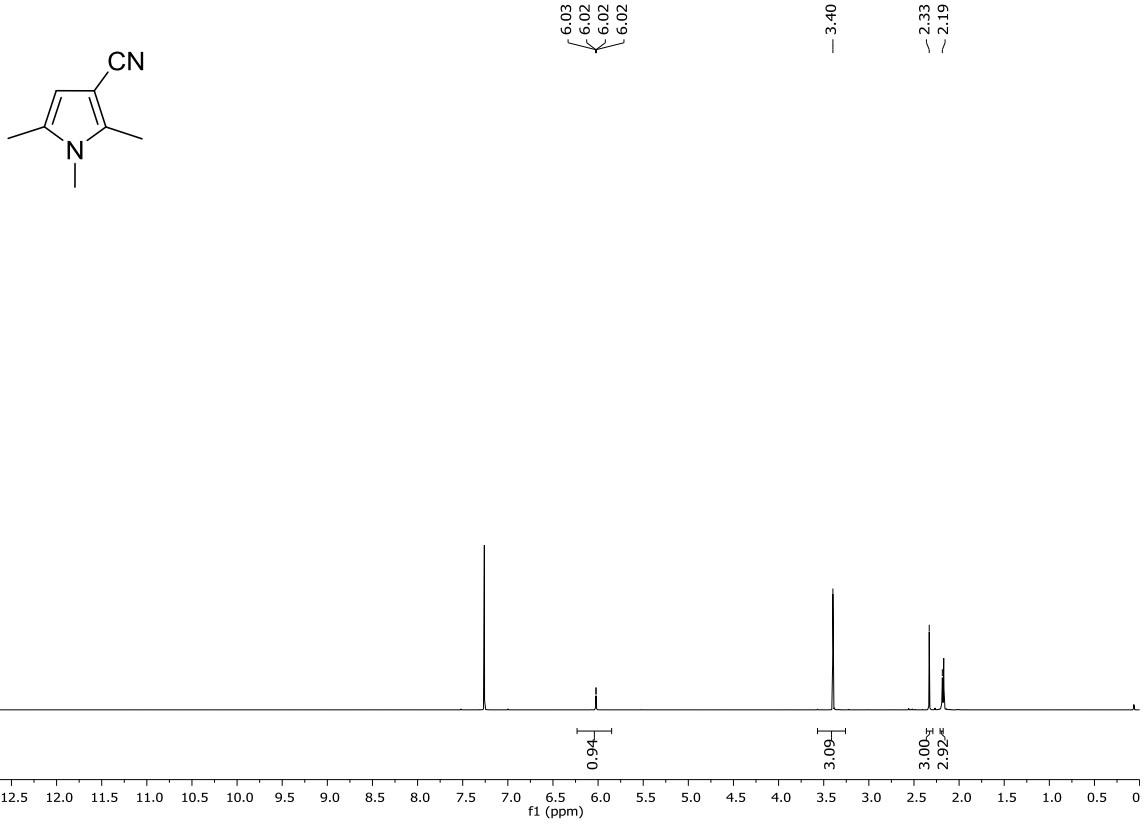
^{13}C NMR (101 MHz, $CDCl_3$) **25**



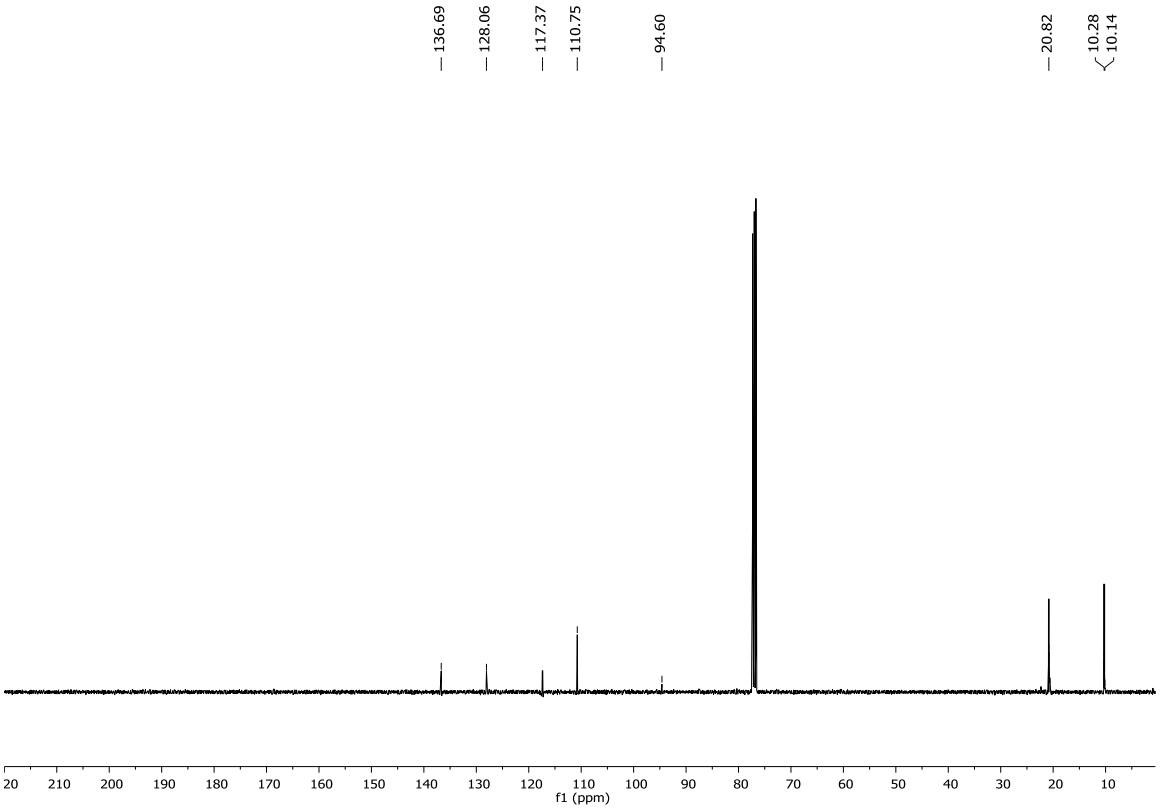
^{1}H NMR (400 MHz, $CDCl_3$) **26**



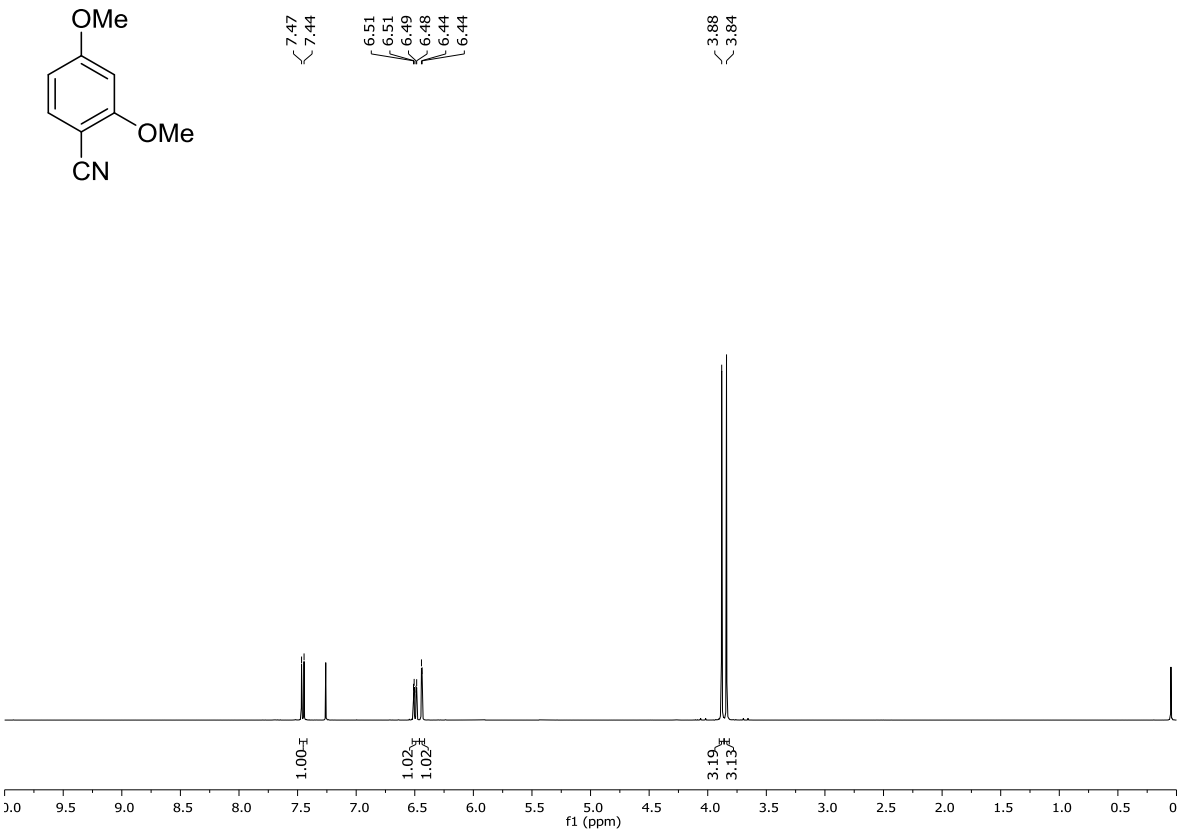
^{1}H NMR (400 MHz, $CDCl_3$) **27**



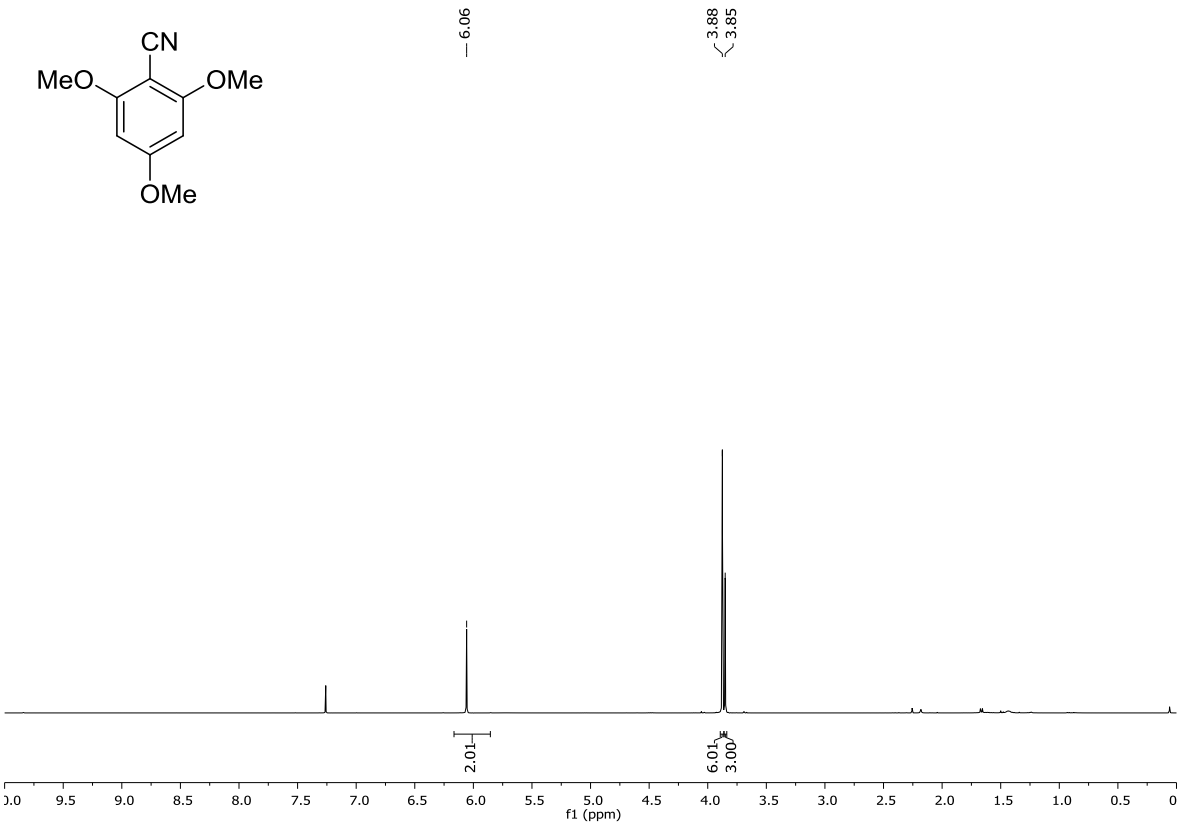
^{13}C NMR (101 MHz, $CDCl_3$) **27**



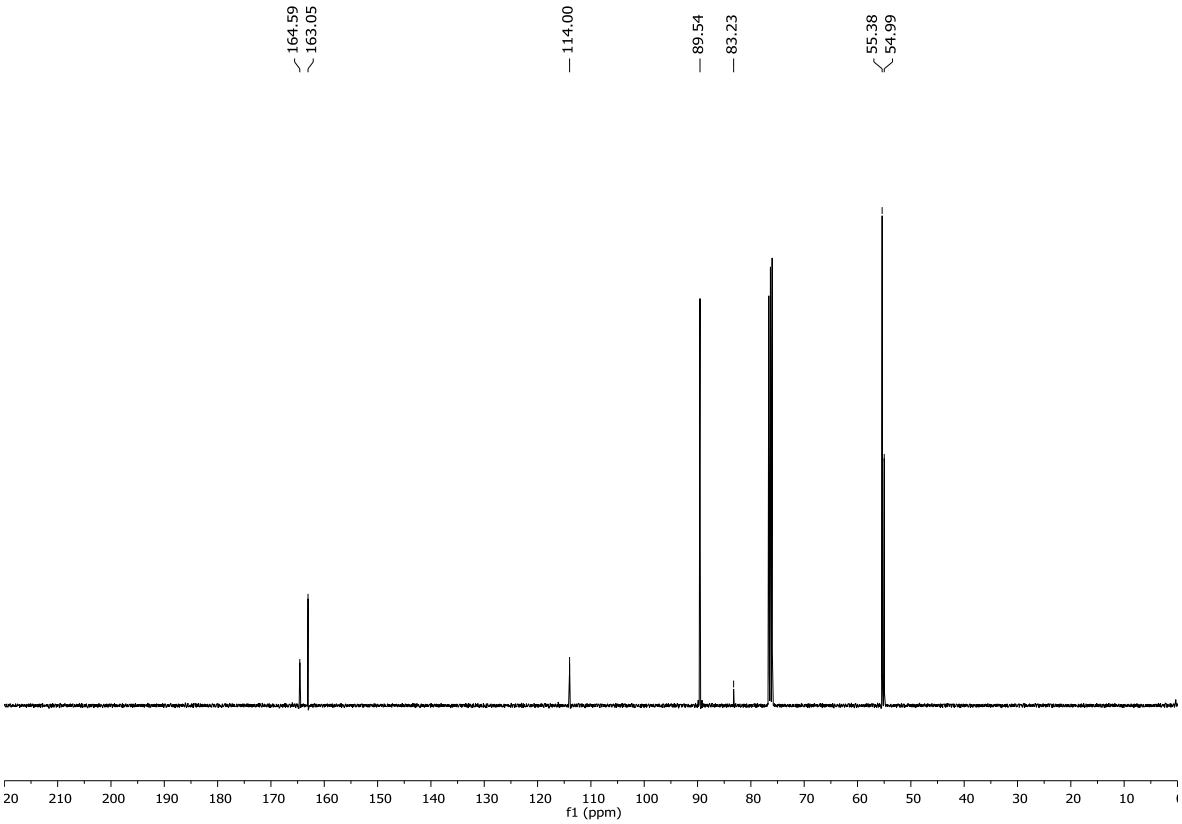
^{1}H NMR (400 MHz, $CDCl_3$) **28**



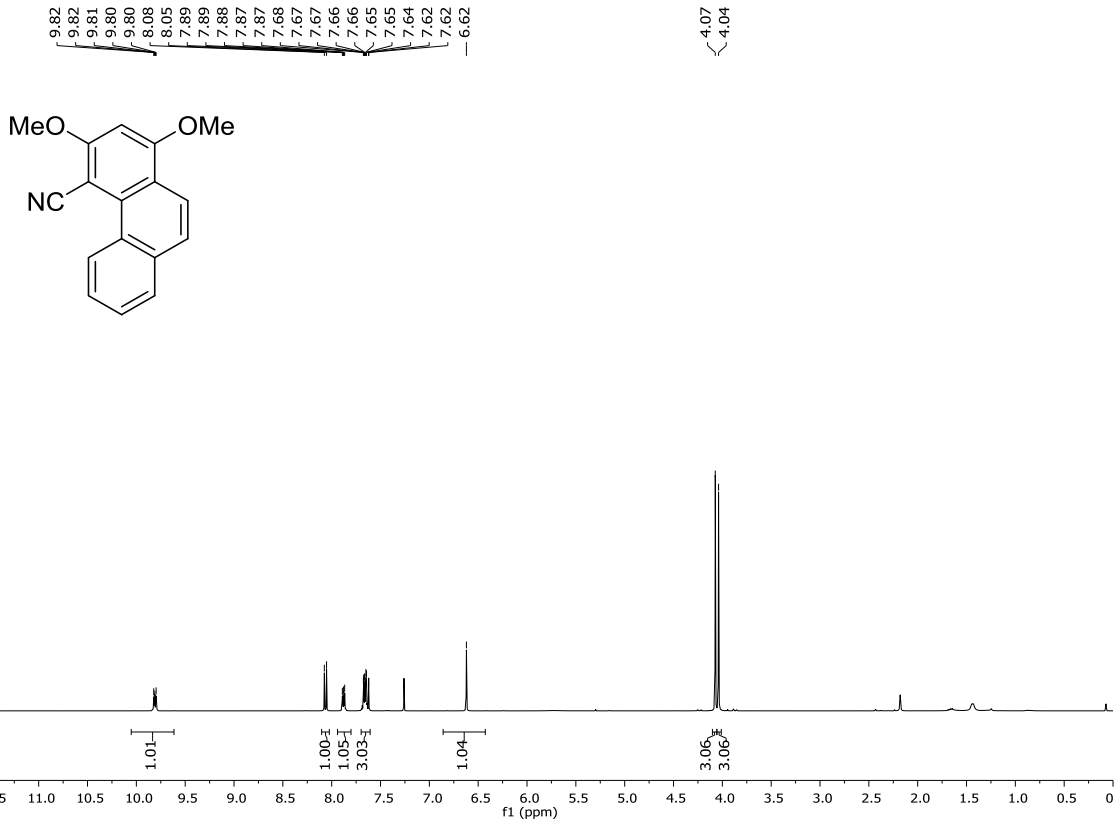
^{1}H NMR (400 MHz, $CDCl_3$) **29**



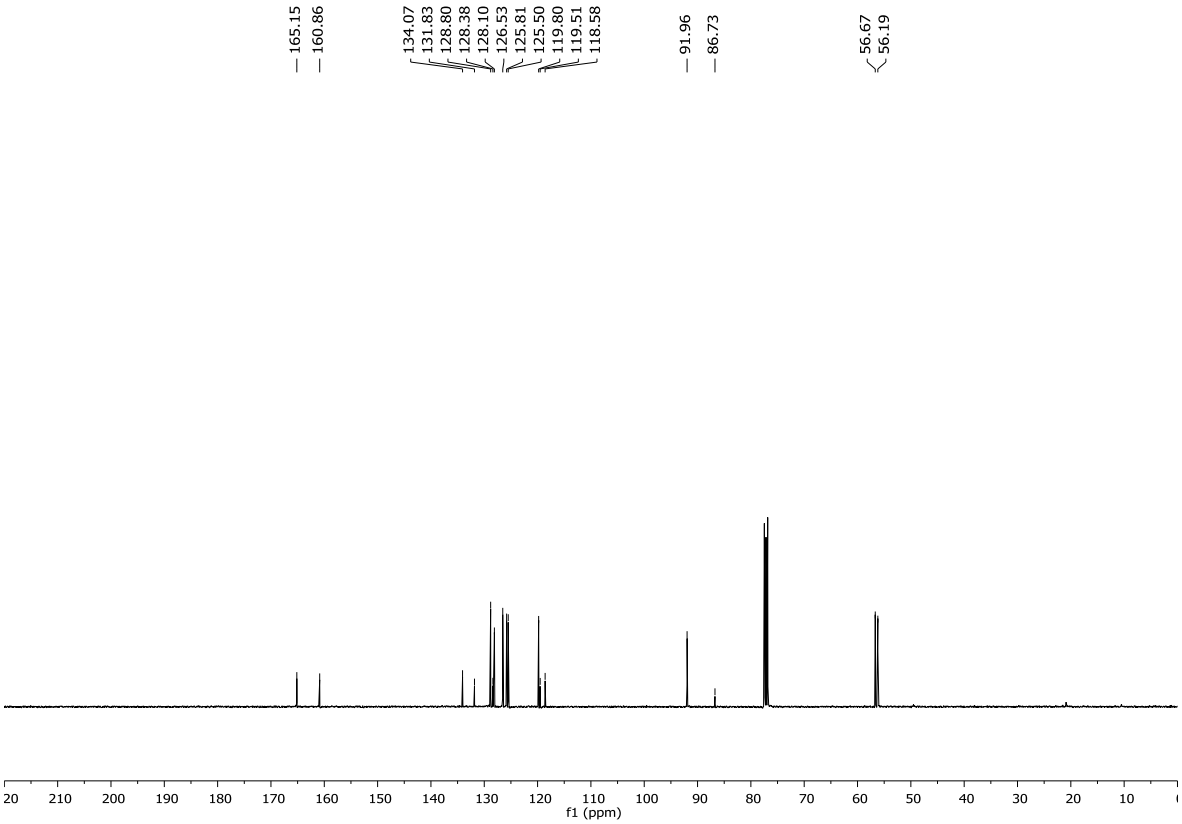
^{13}C NMR (101 MHz, $CDCl_3$) **29**



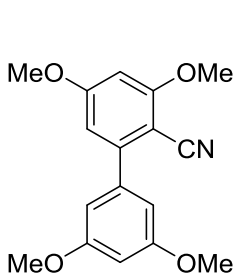
^{1}H NMR (400 MHz, $CDCl_3$) **30**



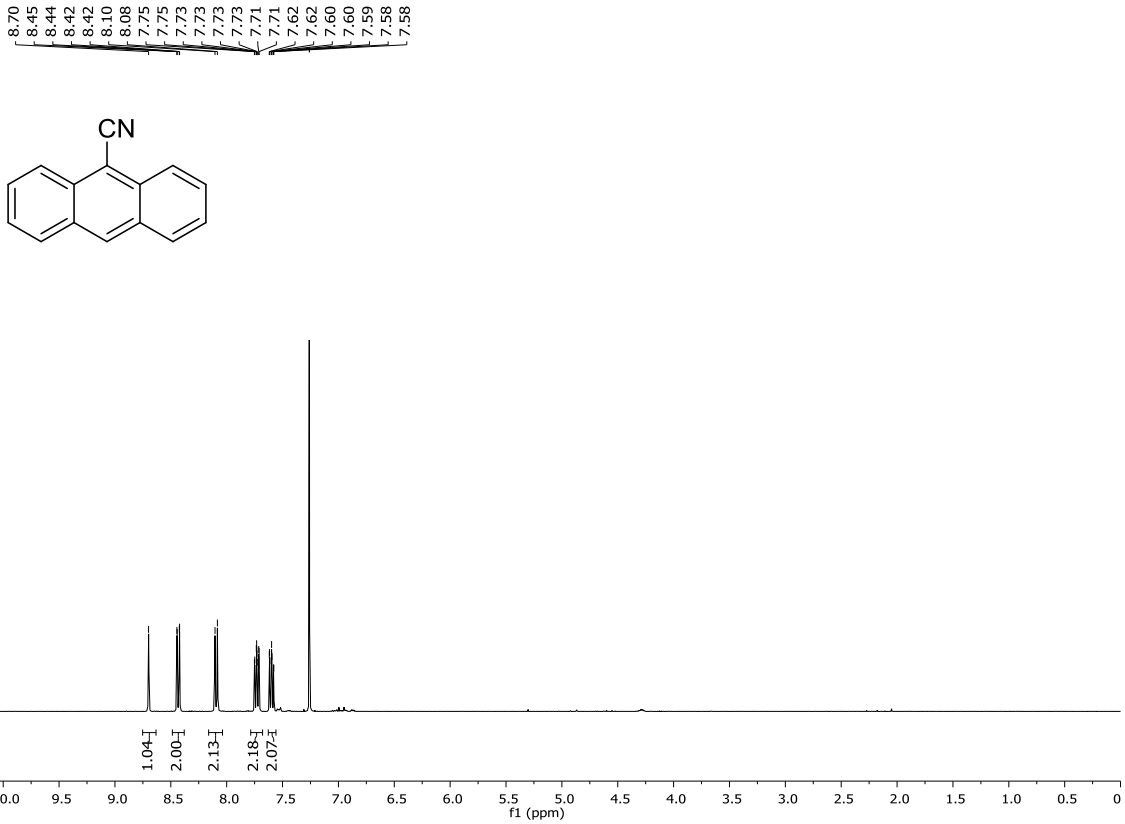
^{13}C NMR (101 MHz, $CDCl_3$) **30**



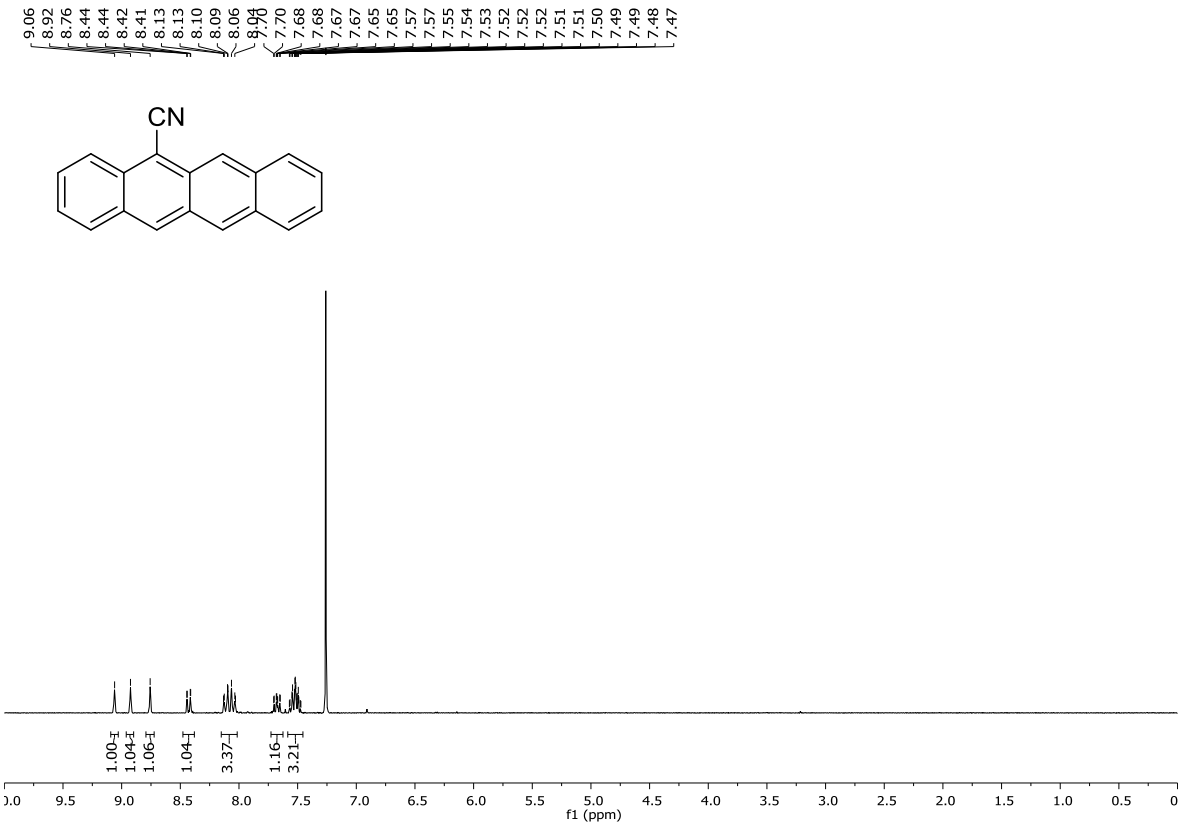
^{1}H NMR (400 MHz, $CDCl_3$) **31**



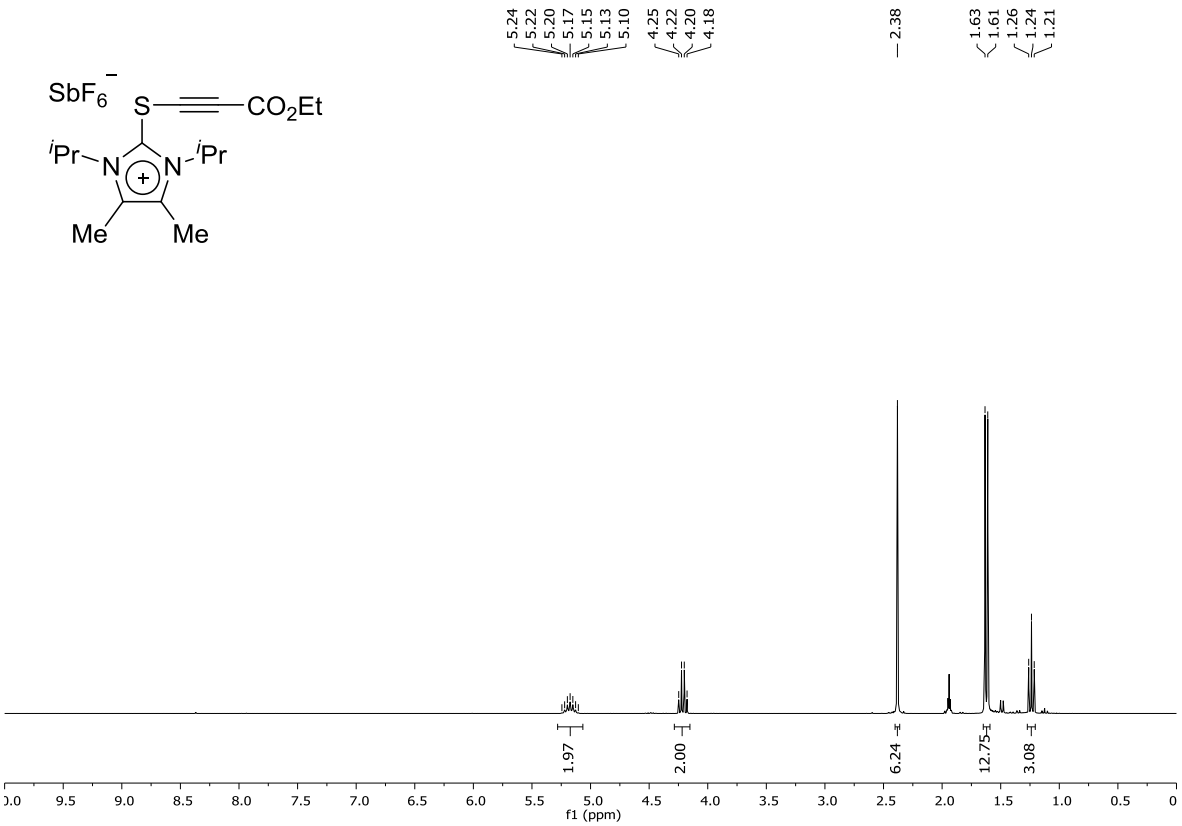
^{1}H NMR (400 MHz, $CDCl_3$) **32**



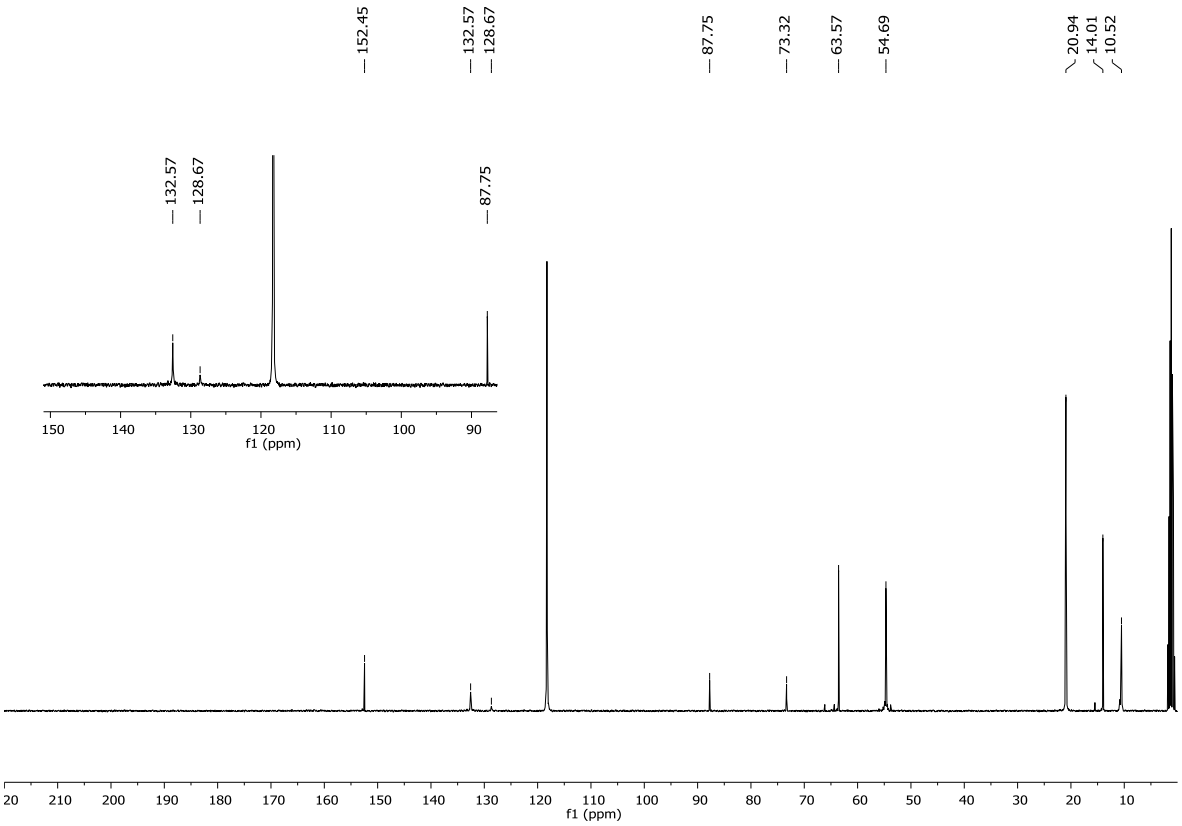
^{1}H NMR (400 MHz, $CDCl_3$) **33**



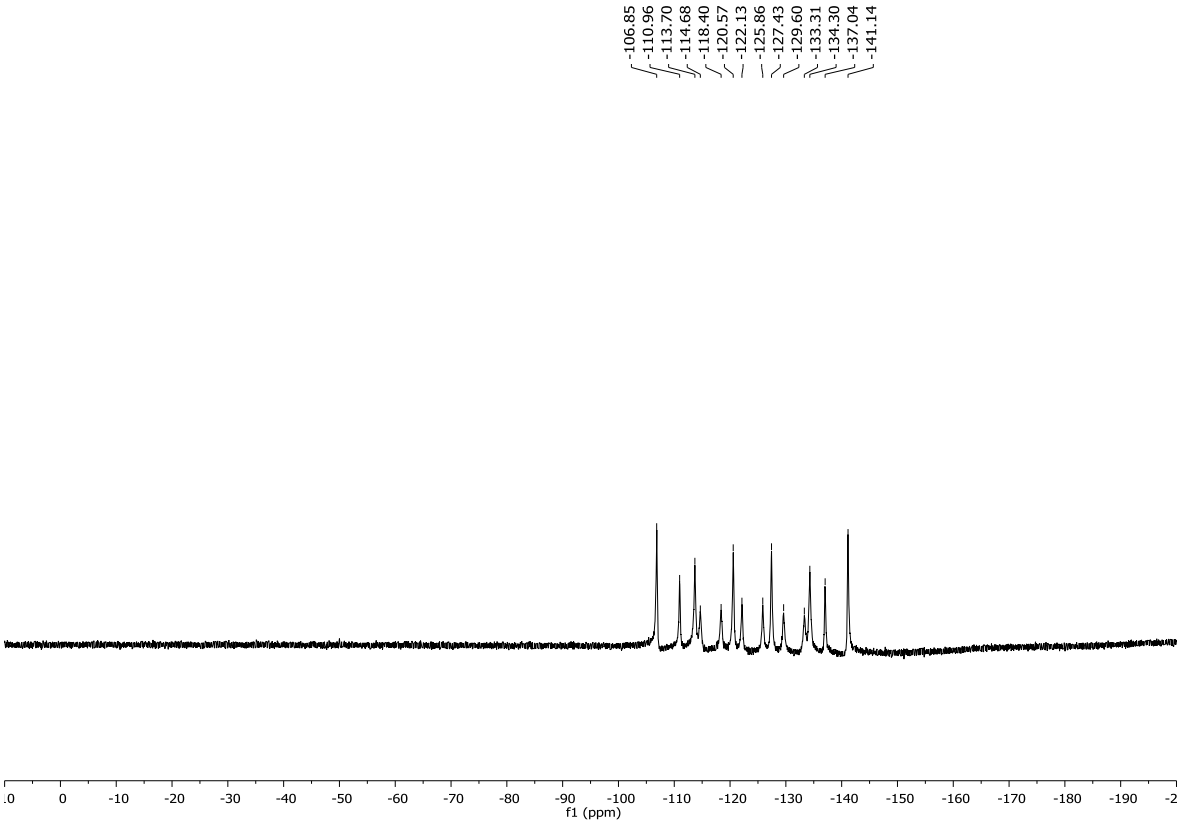
^{1}H NMR (400 MHz, CD_3CN) **35**



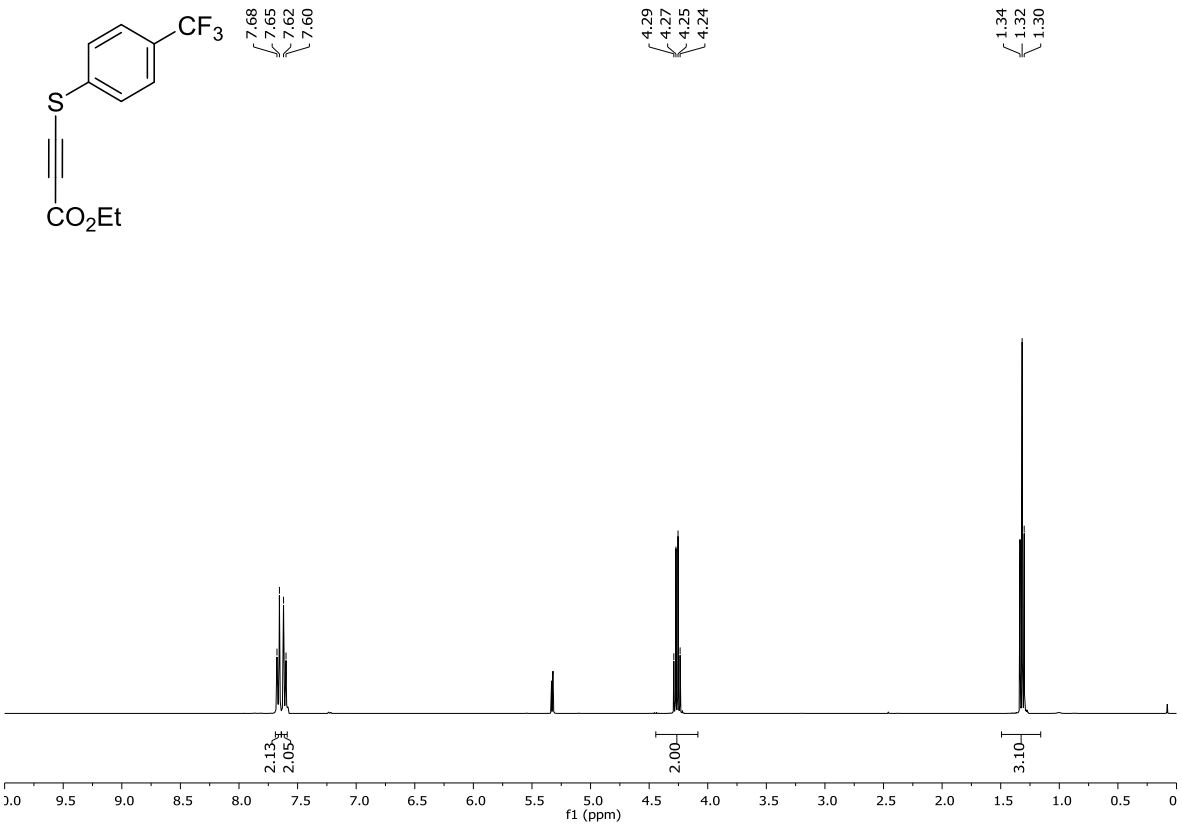
^{13}C NMR (101 MHz, CD_3CN) **35**



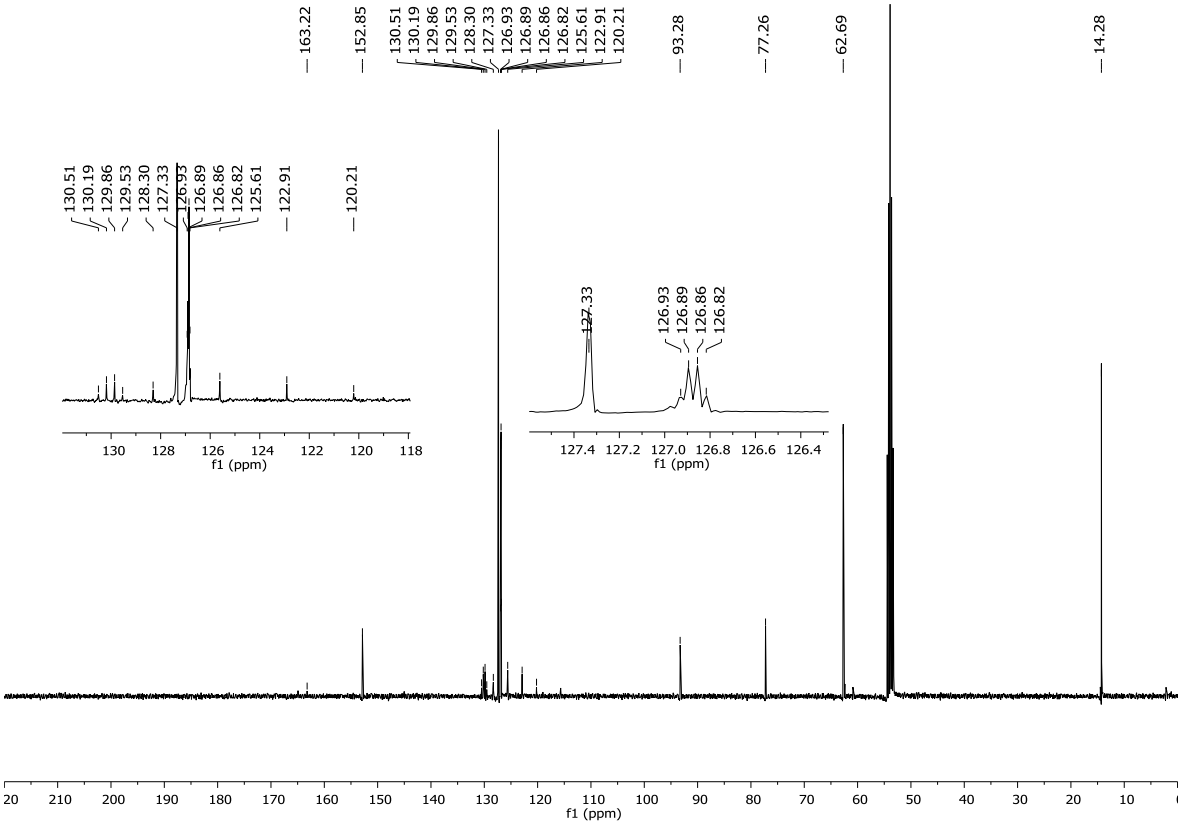
^{19}F NMR (282 MHz, CD_3CN) **35**



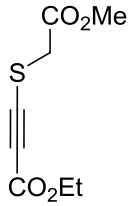
^{1}H NMR (400 MHz, CD_2Cl_2) **36**



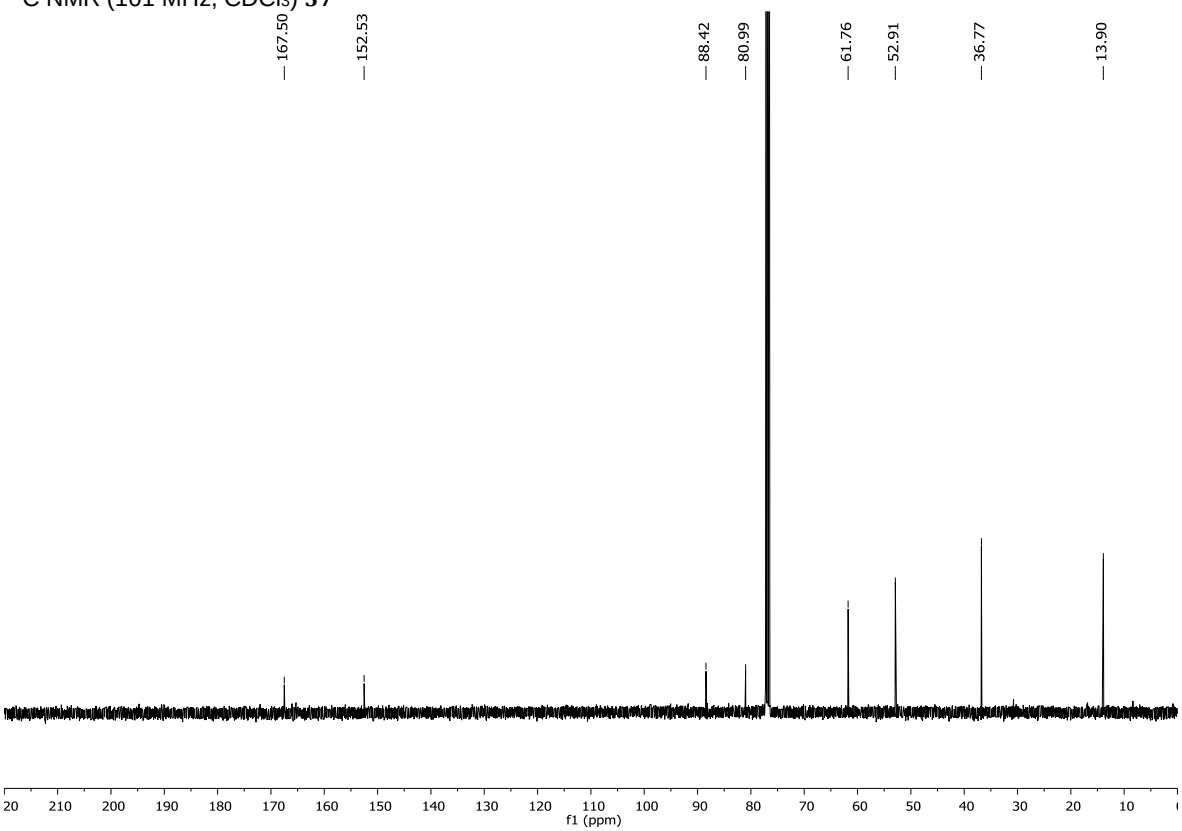
^{13}C NMR (101 MHz, CD_2Cl_2) **36**



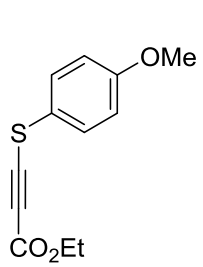
^{1}H NMR (400 MHz, $CDCl_3$) **37**



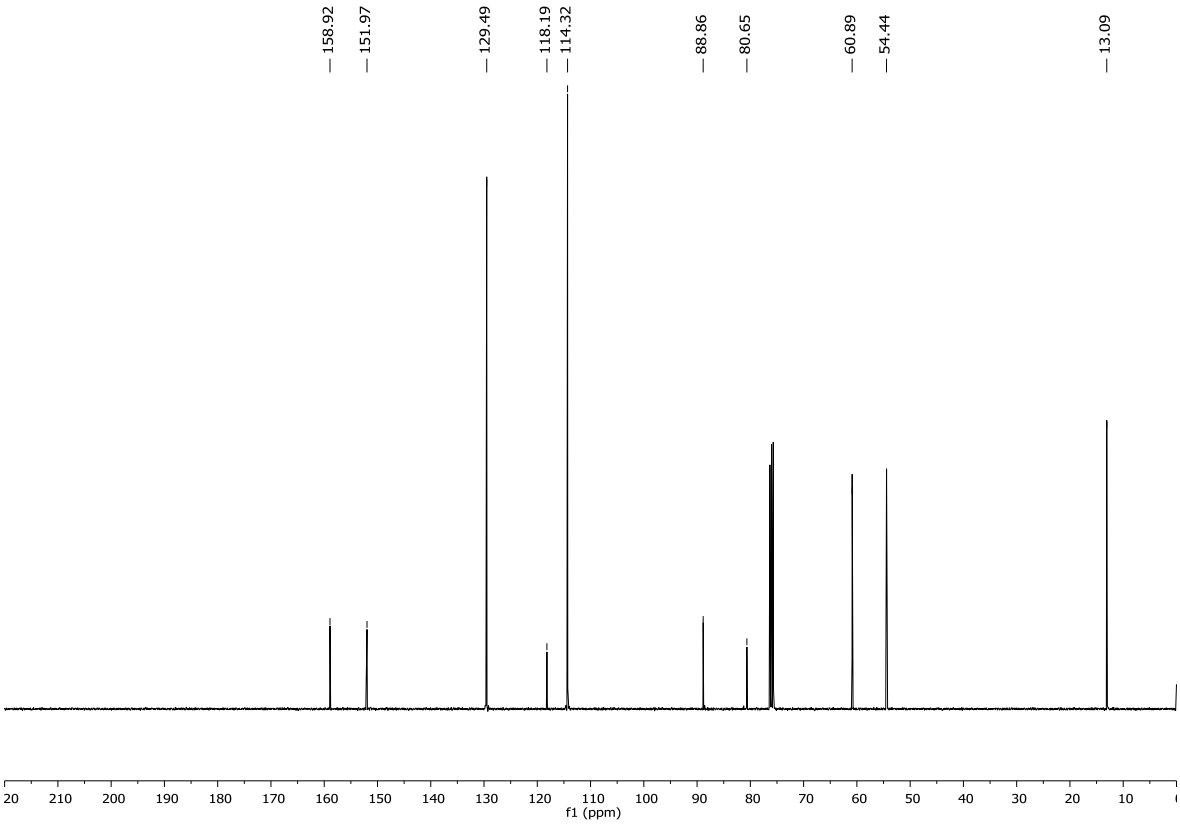
^{13}C NMR (101 MHz, $CDCl_3$) **37**



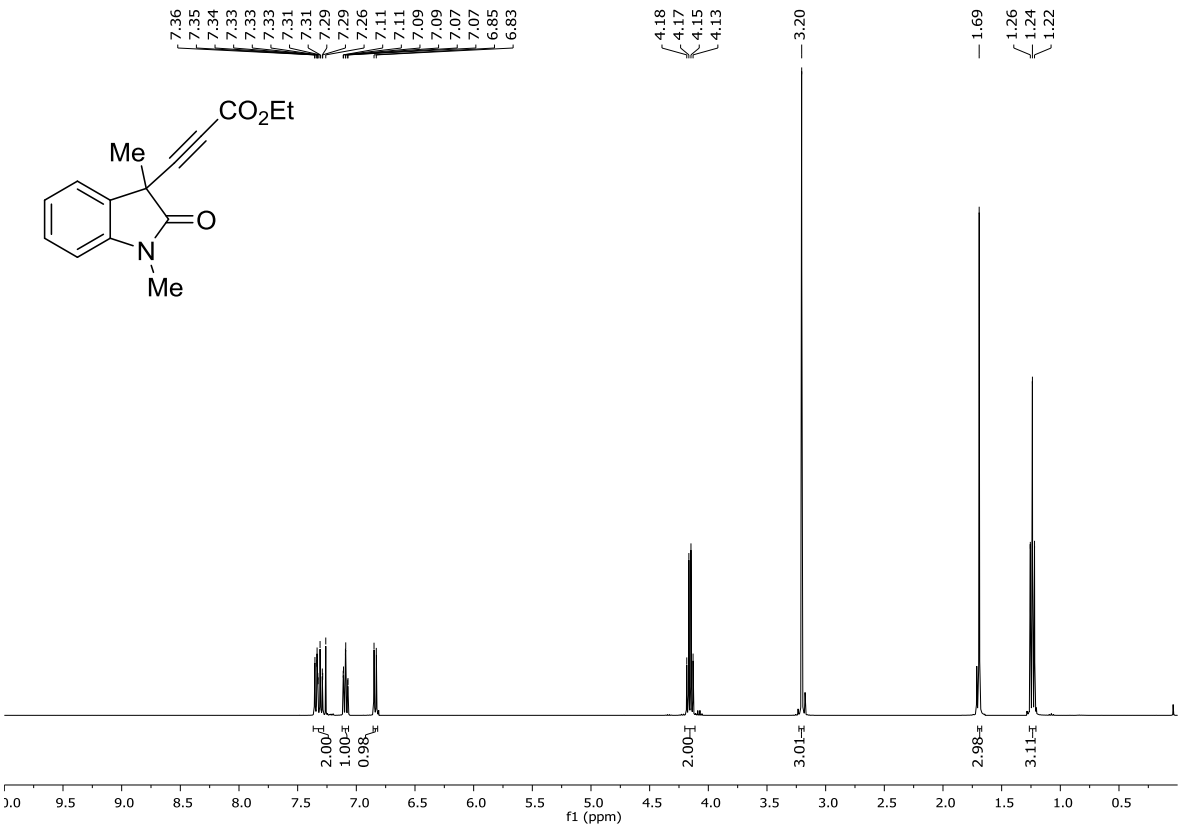
^{1}H NMR (400 MHz, $CDCl_3$) **38**



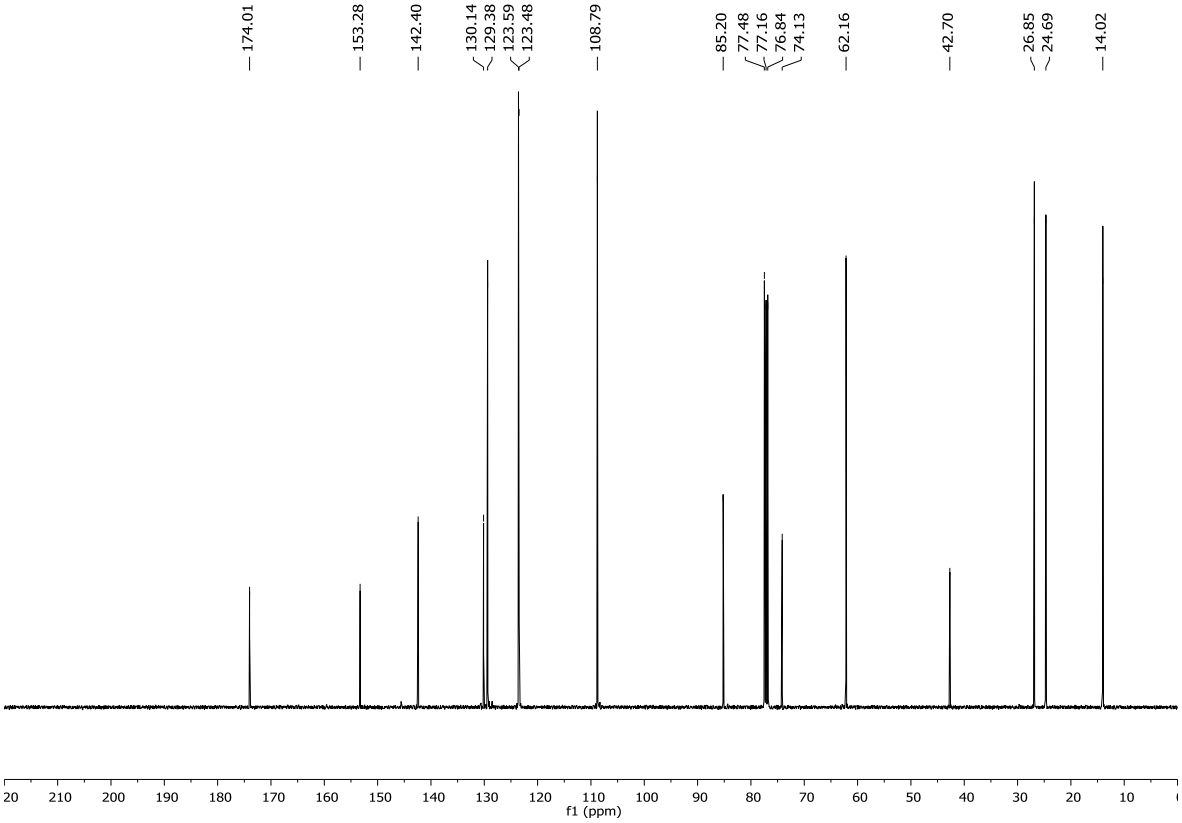
^{13}C NMR (101 MHz, $CDCl_3$) **38**



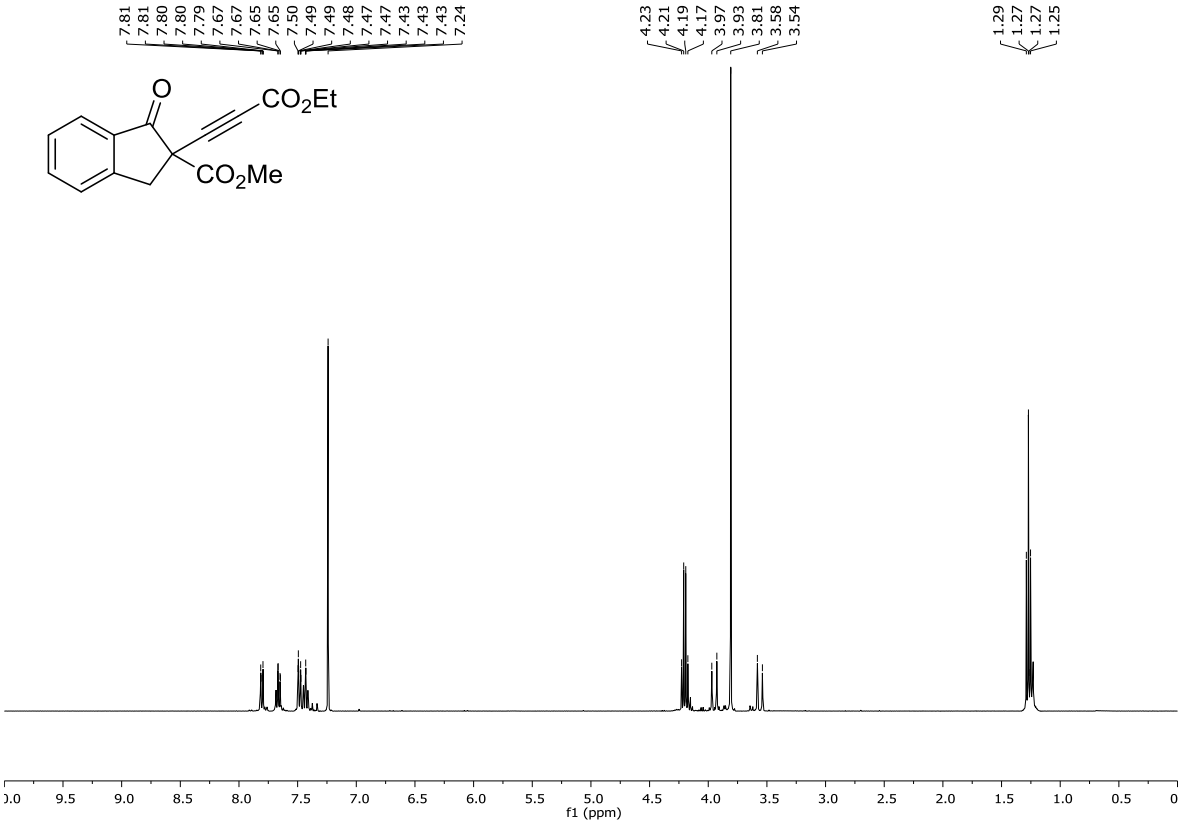
^{1}H NMR (400 MHz, $CDCl_3$) **39**



^{13}C NMR (101 MHz, $CDCl_3$) **39**



^{1}H NMR (400 MHz, $CDCl_3$) **40**



^{13}C NMR (101 MHz, $CDCl_3$) **40**