Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Ring-Closing Metathesis of *N*-Alkenyl-Cyanamides

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General Information

All reactions were carried out in oven-dried glassware under an argon atmosphere employing standard techniques in handling air-sensitive materials.

All solvents were reagent grade. Dichloromethane, 1,2-dichloroethane, *N*,*N*-dimethylformamide, *tert*-butanol and triethylamine were freshly distilled from calcium hydride and degassed by three cycles of "freeze-pump-thaw" using argon as inert gas when required. Tetrahydrofuran was freshly distilled from sodium/benzophenone. *tert*-Amyl alcohol was freshly distilled from iodine-activated Mg turnings and degassed by three cycles of "freeze-pump-thaw" using argon as inert gas when required. Methanol (99.8% purity, extra dry over molecular sieves, Acroseal™), 1,4-dioxane (99.5% purity, extra dry over molecular sieves, Acroseal™) and chloroform (99.9% purity, extra dry over molecular sieves, stabilized, AcroSeal™) were purchased from Acros Organics.

Copper(I) iodide (99,999% purity), *tert*-butyl XPhos (97% purity), Grubbs 2nd generation catalyst™ and Hoveyda-Grubbs 2nd generation catalyst™ were purchased from Sigma-Aldrich. 2,2'-Bisimidazole (95% purity) and Pd_2dba_3 were purchased from Fluorochem. Finely powdered anhydrous cesium carbonate (99% purity, metal basis) purchased from Alfa-Aesar was used for copper-mediated coupling reactions. All other reagents were used as supplied.

Reactions were magnetically stirred and monitored by thin layer chromatography using Merck-Kieselgel 60F_{254} plates. Flash chromatography and filtrations were performed with silica gel 60 (particle size 35-70 µm) supplied by Merck. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated.

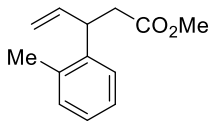
Proton NMR spectra were recorded using an internal deuterium lock at ambient temperature on Jeol 400 and 600 MHz spectrometers or on a Bruker 300 MHz spectrometer. Internal reference of δ_H 7.26 was used for $CDCl_3$, and δ_H 3.31 was used for CD_3OD. Data are presented as follows: chemical shift (in ppm on the δ scale relative to δ_{TMS} = 0), multiplicity (*s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, sext. = sextuplet, m = multiplet, br. = broad, app. = apparent*), coupling constants (*J*/Hz) and integration. Resonances that are

either partially or fully obscured are denoted obscured (obs.). Carbon-13 NMR spectra were recorded at 75, 100 or 150 MHz using $CDCl_3$ (δ_C 77.16) or CD_3OD (δ_C 49.00) as internal reference. Fluorine-19 NMR spectra were recorded at 376 MHz using fluorobenzene (δ_F -113.15) as internal reference.

Melting points were recorded on a Stuart Scientific Analogue SMP11. Infrared spectra were recorded on a Brucker Alpha Spectrometer (ATR) or a Nicolet OPUS IR Spectrometer. High-resolution mass spectra in positive mode were recorded using a 6520 series quadrupole time-of-flight (Q-TOF) mass spectrometer (Agilent) fitted with a multimode ion source.

Experimental Procedures and Characterization Data:

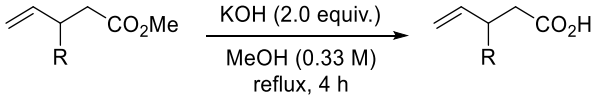
Synthesis of Unreported Amine Hydrochlorides and Related Precursors



S1j

Methyl 3-(*ortho*-tolyl)pent-4-enoate S1j. To a stirred solution of (*E*)-*ortho*-methylcinnamyl alcohol (1.98 g, 13.4 mmol) in toluene (40 mL) at room temperature were sequentially added trimethyl orthoacetate (8.5 mL, 67 mmol) and propionic acid (50 µL, 67 µmol). The resulting mixture was stirred for 12 hours at 150 °C. The reaction medium was then cooled down to room temperature and was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 99/01 to 95/05) to give methyl ester **S1j** (2.2 g, 10.8 mmol, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.10 (m, 4H), 5.93 (ddd, *J* = 17.1, 10.3 and 6.7 Hz, 1H), 5.06 (dt, *J* = 10.3 and 1.3 Hz, 1H), 5.06 (dt, *J* = 17.1 and 1.4 Hz, 1H), 4.17-4.10 (m, 1H), 3.63 (s, 3H), 2.78 (dd, *J* = 15.4 and 8.5 Hz, 1H), 2.71 (dd, *J* = 15.4 and 6.9 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 140.5, 140.0, 136.1, 130.7, 126.6, 126.4 (2C), 114.9, 51.7, 41.1, 39.6, 19.6; IR (ATR): ν_{max} 3072, 3021, 2952, 1739, 1436, 1259, 1166, 758, 729 cm^{-1}; ESIHRMS: *m/z* calcd. for $C_{13}H_{17}O_2$ $[M+H]^+$ 205.1223, found 205.1221.

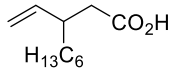
General Procedure for the Saponification of Methyl Esters:



S1 **S2**

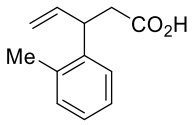
To a stirred solution of the appropriate methyl ester (10.0 mmol) in methanol (30 mL) at room temperature was added potassium hydroxide (1.22 g, 20.0 mmol). The resulting suspension was stirred for 4 hours at reflux and was cooled down to room temperature. The reaction mixture was diluted with water (*ca.* 50 mL) and then washed with diethyl ether (2 x 30 mL). The aqueous layer was then acidified to pH 1-2 with 35% aqueous hydrochloric acid and extracted with ethyl acetate

(3 x 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 90/10 to 80/20) to give the acid **S2**.



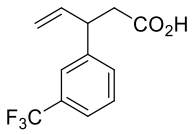
S2f

3-Hexylpent-4-enoic acid S2f. Yield: 88% (1.6 g, 8.8 mmol). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.39 (br. s, 1H), 5.64 (ddd, *J* = 17.2, 10.3 and 8.3 Hz, 1H), 5.08-5.00 (m, 2H), 2.57-2.46 (m, 1H), 2.41 (dd, *J* = 15.0 and 6.0 Hz, 1H), 2.32 (dd, *J* = 15.0 and 8.3 Hz, 1H), 1.46-1.19 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 141.0, 115.4, 40.3, 40.0, 34.6, 31.9, 29.3, 27.0, 22.8, 14.2; IR (ATR): ν_{max} 2958, 2927, 2857, 1709, 1420, 1292, 1224, 993, 917, 672 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{11}H_{21}O_2$ $[M+H]^+$ 185.1536, found 185.1536.



S2j

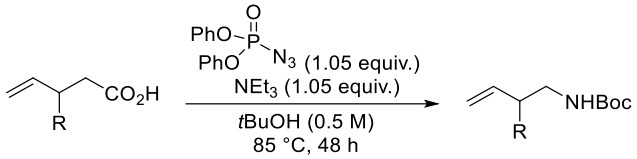
3-*ortho*-Tolylpent-4-enoic acid S2j. Yield: quant. (1.9 g, 10 mmol). White solid; Mp: 47-49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.33 (br. s, 1H), 7.22-7.11 (m, 4H), 5.94 (ddd, *J* = 17.0, 10.3 and 6.6 Hz, 1H), 5.09 (dt, *J* = 10.4 and 1.3 Hz, 1H), 5.03 (dt, *J* = 17.2 and 1.4 Hz, 1H), 4.16-4.09 (m, 1H), 2.82 (obs. dd, *J* = 15.8 and 8.3 Hz, 1H), 2.75 (obs. dd, *J* = 15.8 and 6.7 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 140.2, 139.7, 136.1, 130.8, 126.7, 126.5, 126.4, 115.2, 40.7, 39.4, 19.6; IR (ATR): ν_{max} 3021, 2981, 1708, 1490, 1462, 1416, 1292, 917, 755, 727 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{12}H_{13}O_2$ $[M-H]^-$ 189.0921, found 189.0914.



S2l

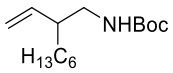
3-*meta*-(Trifluoromethyl)phenylpent-4-enoic acid S2l. Yield: 95% (2.3 g, 9.5 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.95 (br. s, 1H), 7.52-7.39 (m, 4H), 5.97 (ddd, *J* = 17.2, 10.4 and 6.8 Hz, 1H), 5.15 (obs. dt, *J* = 10.4 and 1.1 Hz, 1H), 5.11 (obs. dt, *J* = 17.2 and 1.2 Hz, 1H), 3.97-3.90 (m, 1H), 2.84 (dd, *J* = 15.8 and 7.9 Hz, 1H), 2.75 (dd, *J* = 15.8 and 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 143.2, 139.1, 131.1, 131.1 (q, *J* = 32.2 Hz), 129.3, 124.6 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.3 Hz), 123.9 (q, *J* = 3.8 Hz), 116.1, 45.0, 39.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7; IR (ATR): ν_{max} 3065, 2920, 1712, 1448, 1418, 1329, 1164, 1124, 1074, 923, 802, 704 cm^{-1}; ESIHRMS: *m/z* calcd. for $C_{12}H_{10}F_3O_2$ $[M-H]^-$ 243.0638, found 243.0644.

General Procedure for the Curtius Rearrangement of δ,ε-Unsaturated Acids:



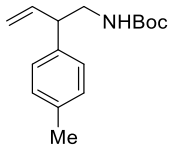
S2 **S3**

To a stirred solution of the appropriate acid **S2** (8.0 mmol) and triethylamine (1.2 mL, 8.4 mmol) in *tert*-butanol (16 mL) at room temperature was added dropwise diphenylphosphoryl azide (1.83 mL, 8.4 mmol). The resulting mixture was then stirred for 48 hours at 85 °C. The reaction was quenched with water (20 mL) and the aqueous phase was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed sequentially with a saturated aqueous solution of sodium hydrogen carbonate and with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 95/05 to 90/10) to give the desired carbamate **S3**.



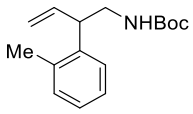
S3f

***N*-Boc-2-hexylbut-3-enylamine S3f**. Yield: 63% (1.3 g, 5.0 mmol). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (ddd, J = 17.0, 10.4 and 8.8 Hz, 1H), 5.10-5.02 (m, 2H), 4.52 (br. s, 1H), 3.30-3.19 (m, 1H), 2.87 (ddd, J = 13.4, 8.9 and 4.8 Hz, 1H), 2.18-2.07 (m, 1H), 1.43 (s, 9H), 1.39-1.19 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 140.7, 116.6, 79.2, 44.8, 44.6, 32.3, 31.9, 29.4, 28.6, 27.1, 22.8, 14.2; IR (ATR): ν_{max} 3354, 2959, 2928, 2858, 1698, 1509, 1366, 1270, 1250, 1173, 995, 914, 774 cm^{-1}; ESIHRMS: m/z calcd. for $C_{15}H_{29}NNaO_2$ $[M+Na]^+$ 278.2091, found 278.2088.



S3i

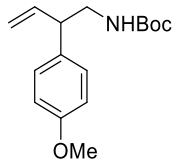
***N*-Boc-2-*para*-tolylbut-3-enylamine S3i**. Yield: 62% (1.3 g, 5.0 mmol). White solid; Mp: 41-43 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 5.94 (ddd, J = 17.2, 10.4 and 6.9 Hz, 1H), 5.16-5.07 (m, 2H), 4.49 (br. s, 1H), 3.51-3.31 (m, 3H), 2.33 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 139.3, 138.3, 136.6, 129.6, 127.8, 116.3, 79.4, 49.5, 45.0, 28.5, 21.1; IR (ATR): ν_{max} 3377, 2978, 2927, 2883, 1702, 1510, 1456, 1391, 1366, 1269, 1250, 1170, 773 cm^{-1}; ESIHRMS: m/z calcd. for $C_{16}H_{24}NO_2$ $[M+H]^+$ 262.1802, found 262.1811.



S3j

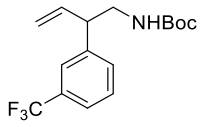
***N*-Boc-2-(*ortho*-tolyl)but-3-enylamine S3j**. Yield: 61% (1.3 g, 5.0 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.11 (m, 4H), 5.91 (ddd, J = 17.4, 10.3 and 7.3 Hz, 1H), 5.13 (dt, J = 10.3 and 1.3 Hz, 1H), 5.07 (dt, J = 17.2 and 1.4 Hz, 1H), 4.52 (br. s, 1H), 3.77 (q, J = 7.2 Hz, 1H), 3.58-3.47

(m, 1H), 3.36 (ddd, *J* = 13.3, 7.5 and 5.6 Hz, 1H), 2.34 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.0, 139.4, 138.9, 130.8, 130.2, 126.7, 126.5 (2C), 116.3, 79.4, 45.3, 44.4, 28.5, 19.7; IR (ATR): ν_{max} 3360, 2977, 2929, 1703, 1507, 1491, 1366, 1270, 1251, 1170, 772 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{16}H_{24}NO_2$ $[M+H]^+$ 262.1802, found 262.1799.



S3k

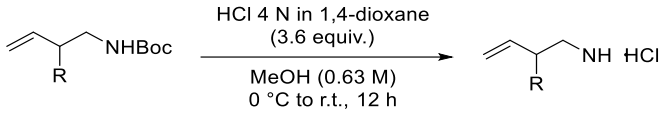
***N*-Boc-2-*para*-methoxyphenylbut-3-enylamine S3k**. Yield: 72% (1.6 g, 5.8 mmol). Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.12 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.93 (ddd, *J* = 17.1, 10.4 and 6.8 Hz, 1H), 5.16-5.06 (m, 2H), 4.49 (br. s, 1H), 3.79 (s, 3H), 3.50-3.29 (m, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.6, 156.0, 139.4, 133.4, 128.9, 116.2, 114.3, 79.4, 55.4, 49.0, 45.1, 28.5; IR (ATR): ν_{max} 3387, 2977, 2928, 2836, 1706, 1511, 1391, 1366, 1247, 1172, 1036, 830, 774 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{16}H_{24}NO_3$ $[M+H]^+$ 278.1751, found 278.1749.



S3l

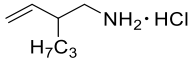
***N*-Boc-2-*meta*-(trifluoromethyl)phenylbut-3-enylamine S3l**. Yield: 67% (1.7 g, 5.4 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.50 (d, *J* = 7.5 Hz, 1H), 7.47-7.36 (m, 3H), 5.95 (ddd, *J* = 17.2, 10.4 and 7.6 Hz, 1H), 5.21 (dt, *J* = 10.4 and 1.2 Hz, 1H), 5.15 (dt, *J* = 17.1 and 1.3 Hz, 1H), 4.52 (br. s, 1H), 3.59 (q, *J* = 7.3 Hz, 1H), 3.50-3.37 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 155.9, 142.5, 138.1, 131.4, 131.1 (q, *J* = 32.4 Hz), 129.3, 124.8 (q, *J* = 3.9 Hz), 124.3 (q, *J* = 272.3 Hz), 123.9 (q, *J* = 3.9 Hz), 117.4, 79.6, 49.7, 45.0, 28.5; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -62.6; IR (ATR): ν_{max} 3362, 2977, 2931, 2871, 1693, 1513, 1366, 1271, 1251, 1172, 994, 916 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{16}H_{24}NO_2$ $[M+H]^+$ 316.1519, found 316.1517.

General Procedure for the Cleavage of Homoallylic *tert*-Butyl Carbamates:



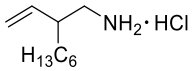
S3 **S4**

To a stirred solution of the appropriate carbamate **S3** (5.0 mmol) in methanol (8 mL) at 0 °C was added dropwise hydrochloric acid (4 M solution in 1,4-dioxane, 4.5 mL, 18.0 mmol). The resulting mixture was warmed up to room temperature and further stirred for 12 hours. The reaction mixture was concentrated under reduced pressure. The obtained solid was triturated in diethyl ether (*ca.* 5 mL), filtered and then washed with diethyl ether (2 x 5 mL) to afford the desired amine hydrochloride **S4**.



S4e

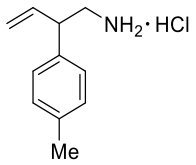
2-Propylbut-3-enylamine hydrochloride S4e. Yield: 75% (560 mg, 3.8 mmol). White solid; Mp: 77-80 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 5.60 (ddd, J = 17.0, 10.3 and 9.2 Hz, 1H), 5.30-5.23 (m, 2H), 3.00 (dd, J = 12.6 and 4.9 Hz, 1H), 2.80 (dd, J = 12.6 and 10.0 Hz, 1H), 2.44-2.34 (m, 1H), 1.51-1.27 (m, 4H), 0.96 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 139.1, 119.7, 44.2, 43.9, 35.2, 20.9, 14.1; IR (ATR): ν_{max} 2956, 2926, 2857, 1595, 1507, 1220, 1006, 961, 947, 772 cm^{-1}; ESIHRMS: m/z calcd. for $C_7H_{16}N$ $[M+H]^+$ 114.1277, found 114.1283.



S4f

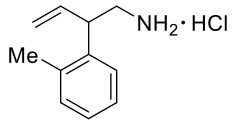
2-Hexylbut-3-enylamine hydrochloride S4f. Yield: 79% (757 mg, 4.0 mmol). White solid; Mp: 62-65 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 5.60 (ddd, J = 17.0, 10.3 and 9.2 Hz, 1H), 5.30-5.22 (m, 2H), 3.01 (dd, J = 12.7 and 5.0 Hz, 1H), 2.80 (dd, J = 12.6 and 10.0 Hz, 1H), 2.42-2.32 (m, 1H), 1.54-1.26 (m, 10H), 0.92 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 139.2, 119.7, 44.2, 33.1, 32.9, 30.2,

27.8, 23.6, 14.4 (1 carbon is not observed); IR (ATR): ν_{max} 3391, 2957, 2926, 2855, 1639, 1466, 1117, 971, 772 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{10}H_{22}N$ $[M+H]^+$ 156.1747, found 156.1750.



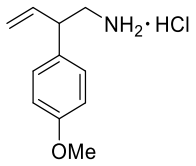
S4i

2-*para*-Tolylbut-3-enylamine hydrochloride S4i. Yield: 88% (875 mg, 4.4 mmol). White solid; Mp: 134-136 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 7.24-7.18 (m, 4H), 6.07-5.97 (m, 1H), 5.28 (d, *J* = 1.0 Hz, 1H), 5.25 (dt, *J* = 6.1 and 1.2 Hz, 1H), 3.64 (q, *J* = 7.9 Hz, 1H), 3.30-3.20 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 138.7, 138.6, 137.5, 130.8, 128.6, 118.4, 49.1, 44.5, 21.1; IR (ATR): ν_{max} 3001, 2865, 1606, 1510, 1219, 1143, 992, 939, 811, 772, 662 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{11}H_{16}N$ $[M+H]^+$ 162.1277, found 162.1283.



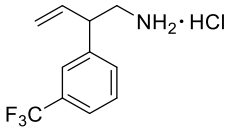
S4j

2-*ortho*-Tolylbut-3-enylamine hydrochloride S4j. Yield: 73% (718 mg, 3.6 mmol). White solid; Mp: 127-130 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 7.28-7.17 (m, 4H), 5.97 (ddd, *J* = 17.1, 10.2 and 8.0 Hz, 1H), 5.28 (dt, *J* = 10.2 and 1.1 Hz, 1H), 5.23 (dt, *J* = 17.1 and 1.2 Hz, 1H), 3.96 (q, *J* = 7.8 Hz, 1H), 3.32 (obs. dd, *J* = 12.8 and 8.8 Hz, 1H), 3.26 (dd, *J* = 12.8 and 6.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 138.5, 138.2, 137.5, 132.1, 128.4, 127.8, 127.1, 118.7, 44.9, 43.8, 19.5; IR (ATR): ν_{max} 3020, 2972, 2864, 1491, 1219, 1147, 979, 939, 767, 729, 670 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{11}H_{16}N$ $[M+H]^+$ 162.1277, found 162.1273.



S4k

2-*para*-Methoxyphenylbut-3-enylamine hydrochloride S4k. Yield: 81% (867 mg, 4.1 mmol). White solid; Mp: 132-134 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 7.24 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.01 (ddd, J = 16.9, 10.5 and 8.0 Hz, 1H), 5.28-5.26 (m, 1H), 5.24 (dt, J = 9.5 and 1.2 Hz, 1H), 3.81 (s, 3H), 3.62 (q, J = 7.9 Hz, 1H), 3.26 (dd, J = 12.7 and 8.2 Hz, 1H), 3.22 (dd, J = 12.7 and 7.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 160.7, 138.8, 132.4, 129.8, 118.2, 115.6, 55.7, 48.6, 44.6; IR (ATR): ν_{max} 3099, 3066, 2950, 2865, 1593, 1551, 1270, 1252, 1181, 1145, 1034, 948, 834, 773, 666 cm^{-1}; ESIHRMS: m/z calcd. for $C_{11}H_{15}NO$ $[M+H]^+$ 178.1226, found 178.1233.



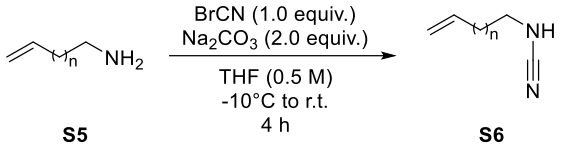
S4l

2-*meta*-(Trifluoromethyl)phenylbut-3-enylamine hydrochloride S4l. Yield: 66% (830 mg, 3.3 mmol). White solid; Mp: 168-170 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 7.66-7.59 (m, 4H), 6.11-6.01 (m, 1H), 5.36 (d, J = 0.8 Hz, 1H), 5.33 (dt, J = 7.4 and 1.1 Hz, 1H), 3.82 (q, J = 8.0 Hz, 1H), 3.39-3.29 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 142.2, 137.7, 132.6, 132.4 (q, J = 32.3 Hz), 131.1, 125.6 (m, 2C), 125.5 (q, J = 271.5 Hz), 119.6, 49.2, 44.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.8; IR (ATR): ν_{max} 2942, 2881, 1598, 1522, 1335, 1327, 1161, 1111, 1095, 1075, 953, 797, 773, 702 cm^{-1}; ESIHRMS: m/z calcd. for $C_{11}H_{12}F_3N$ $[M+H]^+$ 216.0995, found 216.0997.

Experimental Procedures and Characterization Data:

Synthesis of Monosubstituted Cyanamides

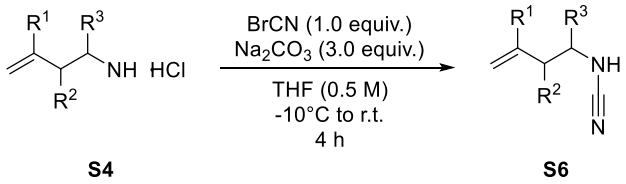
General Procedure I: Synthesis of Monosubstituted Cyanamides from Free Amines



ⓘ ***Caution**: cyanogen bromide is highly toxic and should be handled with care in a fume hood. Goggles, labcoat and gloves should be worn at all times to prevent eye and skin contact.*

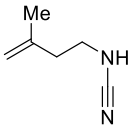
To a stirred suspension of cyanogen bromide (265 mg, 2.5 mmol) and sodium carbonate (530 mg, 5.0 mmol) in freshly distilled tetrahydrofuran (5 mL) at -10 °C was added dropwise the appropriate amine **S5** (2.5 mmol). The resulting mixture was stirred at -10 °C for 2 hours, warmed up to room temperature and stirred for 2 additional hours. The reaction was then filtered over a short pad of Celite®, which was thoroughly washed with diethyl ether. The filtrate was concentrated under reduced pressure to afford the desired cyanamide **S6** which was used for the next step without further purification.

General Procedure II: Synthesis of Monosubstituted Cyanamides from Amine Hydrochlorides



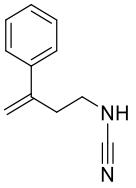
To a stirred suspension of cyanogen bromide (265 mg, 2.5 mmol) and sodium carbonate (795 mg, 7.5 mmol) in freshly distilled tetrahydrofuran (5 mL) at -10 °C was added portionwise the appropriate amine hydrochloride **S4** (2.5 mmol). The resulting mixture was stirred at -10 °C for 2 hours, warmed up to room temperature and stirred for 2 additional hours. The reaction was then filtered over a short pad of Celite®, which was thoroughly washed with diethyl ether. The

filtrate was concentrated under reduced pressure to afford the desired cyanamide **S6** which was used for the next step without further purification.



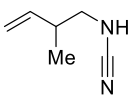
S6b

***N*-3-Methylbut-3-enyl cyanamide S6b**. Prepared according to general procedure II. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 (app. t, J = 1.4 Hz, 1H), 4.79 (app. s, 1H), 3.46 (br. s, 1H), 3.22 (q, J = 5.6 Hz, 2H), 2.32 (t, J = 6.9 Hz, 2H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 116.0, 113.8, 44.1, 37.7, 22.1; IR (ATR): ν_{max} 3209, 2220, 1456, 894 cm^{-1}; ESIHRMS *m/z* calcd. for $C_6H_{11}N_2$ $[M+H]^+$ 111.0917, found 111.0922.



S6c

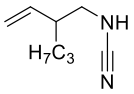
***N*-3-Phenylbut-3-enyl cyanamide S6c**. Prepared according to general procedure II. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 5H), 5.43 (app. s, 1H), 5.19 (app. s, 1H), 3.46 (br. s, 1H), 3.19 (q, J = 6.6 Hz, 2H), 2.83 (t, J = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 139.6, 128.8, 128.2, 126.2, 121.4, 115.8, 44.8, 35.7; IR (ATR): ν_{max} 3326, 2941, 2219, 1444, 904, 779, 702 cm^{-1}; ESIHRMS *m/z* calcd. for $C_{11}H_{13}N_2$ $[M+H]^+$ 173.1073, found 173.1073.



S6d

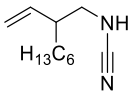
***N*-2-Methylbut-3-enyl cyanamide S6d**. Prepared according to general procedure II. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (ddd, J = 17.2, 10.3 and 7.6 Hz, 1H), 5.16 (ddd, J = 8.2, 1.5 and

1.0 Hz, 1H), 5.12-5.10 (m, 1H), 3.65 (br. s, 1H), 3.04 (ddd, *J* = 12.7, 6.7 and 6.0 Hz, 1H), 2.94 (ddd, *J* = 12.8, 7.9 and 5.2 Hz, 1H), 2.51-2.36 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.8, 116.8, 116.4, 51.5, 38.5, 17.1; IR (ATR): ν_{max} 3394, 2967, 2931, 2220, 1598, 1458, 1127, 915 cm^{-1}; ESIHRMS *m/z* calcd. for $C_6H_{11}N_2$ $[M+H]^+$ 111.0917, found 111.0920.



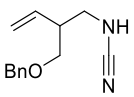
S6e

***N*-2-Propylbut-3-enyl cyanamide S6e**. Prepared according to general procedure II. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.50 (ddd, *J* = 16.9, 10.4 and 8.8 Hz, 1H), 5.21-5.13 (m, 2H), 3.43 (br. s, 1H), 3.12 (ddd, *J* = 12.5, 7.5 and 5.0 Hz, 1H), 2.91 (ddd, *J* = 12.6, 9.1 and 4.4 Hz, 1H), 2.34-2.24 (m, 1H), 1.43-1.22 (m, 4H), 0.90 (t, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 138.9, 118.5, 116.2, 50.3, 44.6, 34.0, 20.1, 14.1; IR (ATR): ν_{max} 3202, 2958, 2931, 2222, 1466, 1160, 994, 919 cm^{-1}; ESIHRMS *m/z* calcd. for $C_8H_{15}N_2$ $[M+H]^+$ 139.1230, found 139.1231.



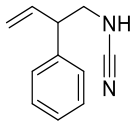
S6f

***N*-2-Hexylbut-3-enyl cyanamide S6f**. Prepared according to general procedure II. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.50 (ddd, *J* = 16.9, 10.4 and 8.8 Hz, 1H), 5.21-5.13 (m, 2H), 3.47 (br. s, 1H), 3.11 (dd, *J* = 12.7 and 5.0 Hz, 1H), 2.90 (dd, *J* = 12.7 and 9.1 Hz, 1H), 2.33-2.21 (m, 1H), 1.45-1.17 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.0, 118.4, 116.2, 50.2, 44.8, 31.8 (2C), 29.3, 26.9, 22.7, 14.2; IR (ATR): ν_{max} 3389, 2960, 2926, 2856, 2220, 1601, 1465, 1127, 994, 914, 757 cm^{-1}; ESIHRMS *m/z* calcd. for $C_{11}H_{21}N_2$ $[M+H]^+$ 181.1699, found 181.1700.



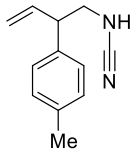
S6g

***N*-2-Benzyloxymethylbut-3-enyl cyanamide S6g**. Prepared according to general procedure II. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.33-7.28 (m, 3H), 5.68 (ddd, *J* = 16.8, 11.0 and 7.9 Hz, 1H), 5.22 (app. s, 1H), 5.19 (dt, *J* = 8.0 and 1.2 Hz, 1H), 4.51 (s, 2H), 3.95 (br. s, 1H), 3.59 (dd, *J* = 9.4 and 4.4 Hz, 1H), 3.47 (dd, *J* = 9.4 and 7.7 Hz, 1H), 3.29 (ddd, *J* = 12.5, 6.7 and 5.6 Hz, 1H), 3.19 (dt, *J* = 12.5 and 6.1 Hz, 1H), 2.70-2.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 135.1, 128.7, 128.1, 127.9, 118.7, 116.4, 73.6, 72.0, 49.1, 43.7; IR (ATR): ν_{max} 3217, 2921, 2866, 2221, 1496, 1454, 1363, 1100 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{13}H_{17}N_2O$ $[M+H]^+$ 217.1335, found 217.1337.



S6h

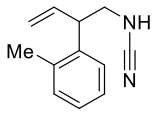
***N*-2-Phenylbut-3-enyl cyanamide S6h**. Prepared according to general procedure II. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 7.30-7.27 (m, 1H), 7.23-7.19 (m, 2H), 5.95 (ddd, *J* = 17.2, 10.4 and 7.6 Hz, 1H), 5.26-5.18 (m, 2H), 3.60 (q, *J* = 7.5 Hz, 1H), 3.47-3.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.4, 129.2, 127.8, 127.6, 117.9, 115.7, 50.7, 50.0; IR (ATR): ν_{max} 3391, 3075, 3026, 2927, 2222, 1602, 1464, 1218, 920, 753, 700 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{11}H_{13}N_2$ $[M+H]^+$ 173.1073, found 173.1070.



S6i

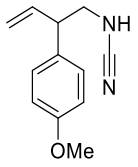
***N*-2-*para*-Tolylbut-3-enyl cyanamide S6i**. Prepared according to general procedure II. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 5.93 (ddd, *J* = 17.2, 10.4 and 7.6 Hz, 1H), 5.24-5.16 (m, 2H), 3.56 (q, *J* = 7.4 Hz, 1H), 3.41-3.28 (m, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.4, 136.6, 129.9, 127.7, 117.6, 115.8, 50.7, 49.5, 21.1; IR

(ATR): ν_{max} 3215, 2924, 2222, 1514, 1456, 1168, 994, 912, 732 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{12}H_{15}N_2$ $[M+H]^+$ 187.1230, found 187.1234.



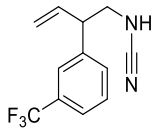
S6j

***N*-2-*ortho*-Tolylbut-3-enyl cyanamide S6j**. Prepared according to general procedure II. Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.14 (m, 3H), 7.12-7.09 (m, 1H), 5.89 (ddd, *J* = 17.4, 10.3 and 7.4 Hz, 1H), 5.22 (dt, *J* = 10.3 and 1.2 Hz, 1H), 5.16 (dt, *J* = 17.1 and 1.2 Hz, 1H), 3.87 (q, *J* = 7.5 Hz, 1H), 3.44 (obs. br. s, 1H), 3.41-3.36 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 137.3, 136.8, 131.2, 127.3, 126.8, 126.1, 117.8, 115.8, 50.0, 45.4, 19.6; IR (ATR): ν_{max} 3217, 2926, 2222, 1637, 1490, 1461, 1166, 921, 769, 757, 728 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{12}H_{15}N_2$ $[M+H]^+$ 187.1230, found 187.1234.



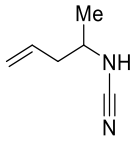
S6k

***N*-2-*para*-Methoxyphenylbut-3-enyl cyanamide S6k**. Prepared according to general procedure II. Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.92 (ddd, *J* = 17.2, 10.4 and 7.5 Hz, 1H), 5.22 (dt, *J* = 10.4 and 1.1 Hz, 1H), 5.17 (dt, *J* = 17.2 and 1.3 Hz, 1H), 3.80 (s, 3H), 3.55 (q, *J* = 7.6 Hz, 1H), 3.36 (obs. dd, *J* = 12.9 and 7.4 Hz, 1H), 3.30 (obs. dd, *J* = 12.9 and 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 137.7, 131.6, 128.9, 117.5, 115.8, 114.6, 55.4, 50.8, 49.1; IR (ATR): ν_{max} 3231, 2917, 2838, 2222, 1610, 1512, 1248, 1179, 1034, 919, 811,732 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{12}H_{15}N_2O$ $[M+H]^+$ 203.1179, found 203.1185.



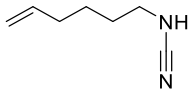
S6l

***N*-2-*meta*-(Trifluoromethyl)phenylbut-3-enyl cyanamide S6l**. Prepared according to general procedure II. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.40 (m, 4H), 5.94 (ddd, J = 17.1, 10.3 and 7.6 Hz, 1H), 5.30 (dt, J = 10.4 and 1.0 Hz, 1H), 5.24 (dt, J = 17.1 and 1.2 Hz, 1H), 3.68 (q, J = 7.6 Hz, 1H), 3.56 (br. s, 1H), 3.40 (obs. dd, J = 13.1 and 7.6 Hz, 1H), 3.36 (obs. dd, J = 13.2 and 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.5, 131.5 (q, J = 32.3 Hz), 131.4, 129.7, 124.5 (q, J = 3.8 Hz, 2C), 124.0 (q, J = 272.3 Hz), 118.8, 115.4, 50.4, 49.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7; IR (ATR): ν_{max} 3212, 2935, 2224, 1449, 1328, 1164, 1124, 1074, 704 cm^{-1}; ESIHRMS: m/z calcd. for $C_{12}H_{12}F_3N_2$ $[M+H]^+$ 241.0947, found 241.0939.



S6m

***N*-1-Methylbut-3-enyl cyanamide S6m**. Prepared according to general procedure II. Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84-5.67 (m, 1H), 5.21-5.14 (m, 2H), 3.62 (br. s, 1H), 3.33 (app. sept., J = 6.6 Hz, 1H), 2.34-2.17 (m, 2H), 1.27 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 119.5, 117.8, 51.4, 41.0, 20.0; IR (ATR): ν_{max} 3197, 2215, 919 cm^{-1}. ESIHRMS m/z calcd for $C_6H_{11}N_2$ $[M+H]^+$ 111.0917, found 111.0924.



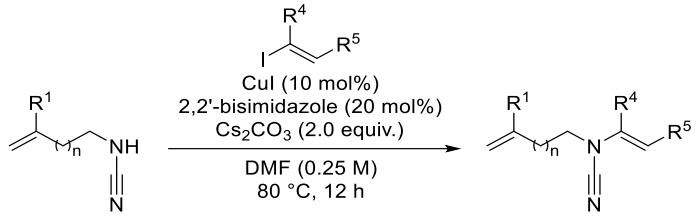
S6r

***N*-Hex-5-enyl cyanamide S6r**. Prepared according to general procedure I. Pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.78 (ddt, J = 17.0, 10.2 and 6.7 Hz, 1H), 5.02 (dq, J = 17.0 and 1.6 Hz, 1H), 4.99-4.96 (m, 1H), 3.59 (br. s, 1H), 3.09 (t, J = 7.1 Hz, 2H), 2.09 (q, J = 7.1 Hz, 2H), 1.63 (quint., J = 7.5 Hz, 2H), 1.46 (quint., J = 7.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.1, 116.2, 115.3, 46.3, 33.2, 29.2, 25.6; IR (ATR): ν_{max} 2932, 2220, 1639, 911 cm^{-1}; ESIHRMS: m/z calcd. for $C_7H_{16}N_3$ $[M+NH_4]^+$ 142.1339, found 142.1337.

Experimental Procedures and Characterization Data:

Synthesis of *N*-Alkenyl-Cyanamides

General Procedure I: Copper-Catalyzed *N*-Alkenylation of Cyanamides[S1]

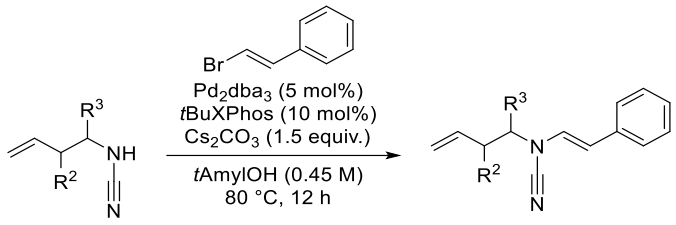


S6 (1.5 equiv.) **1**

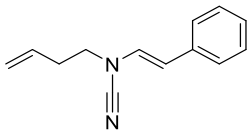
An oven dried pressure tube was charged with copper(I) iodide (32 mg, 0.17 mmol), 2,2'-bisimidazole (46 mg, 0.34 mmol), cesium carbonate (1.11 g, 3.4 mmol) and the appropriate (*E*)-iodoalkene (1.67 mmol). The tube was fitted with a rubber septum, evacuated under vacuum, backfilled with argon and *N*,*N*-dimethylformamide (3.3 mL) was next added. The resulting reaction mixture was stirred 5 minutes at room temperature before dropwise addition of a solution of the appropriate cyanamide **S6** (2.5 mmol) in *N*,*N*-dimethylformamide (3.3 mL). The tube was then closed with a Teflon-coated screw cap and the resulting suspension was stirred for 12 hours at 80 °C. The crude reaction mixture was cooled down to room temperature and diluted with diethyl ether. The organic layer was washed with water, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 95/05 to 90/10) to give the desired *N*-alkenyl-cyanamide **1**.

[S1] Nitelet, A.; Wouters, J.; Dewez, D.F.; Evano, G. *Org. Lett.* **2017**, *19*, 6276.

General Procedure II: Palladium-Catalyzed *N*-Alkenylation of Cyanamides[S2]



An oven dried pressure tube was charged with Pd_2dba_3 (101 mg, 0.11 mmol), *tert*-Butyl Xphos (93 mg, 0.22 mmol) and cesium carbonate (1.11 g, 3.4 mmol). The tube was fitted with a rubber septum, evacuated under vacuum, backfilled with argon and a solution of the appropriate cyanamide **S6** (2.5 mmol) and (*E*)-β-bromostyrene (416 mg, 2.27 mmol) in degassed *tert*-amyl alcohol (5 mL) was next added. The resulting mixture was then stirred for 12 hours at 80 °C. The reaction was filtered over a short pad of Celite®, which was thoroughly washed with dichloromethane. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 95/05 to 90/10) to give the desired *N*-alkenyl-cyanamide **1**.

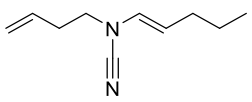


1a

(*E*)-*N*-But-3-enyl-*N*-styrylcyanamide 1a. Prepared according to general procedure I using (*E*)-β-iodostyrene[S3] (384 mg, 1.67 mmol). Yield: 67% (222 mg, 1.12 mmol). Pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.26-7.23 (m, 2H), 7.19 (tt, *J* = 7.2 and 1.3 Hz, 1H), 6.39 (d, *J* = 14.2 Hz, 1H), 6.17 (d, *J* = 14.2 Hz, 1H), 5.82 (ddt, *J* = 17.1, 10.2 and 6.8 Hz, 1H), 5.22 (dq, *J* = 17.1 and 1.5 Hz, 1H), 5.18 (dq, *J* = 10.2 and 1.2 Hz, 1H), 3.44 (t, *J* = 7.2 Hz, 2H), 2.53 (qt, *J* = 7.2 and 1.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.2, 133.0, 128.9, 128.3, 127.0, 125.6, 118.9, 113.2, 112.8,

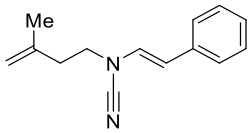
[S2] Stolley, R.M.; Guo, W.; Louie, J. *Org. Lett.* **2012**, *14*, 322.
[S3] Prepared according to a procedure described in: Bull, J.; Mousseau, J.; Charette, A. *Org. Lett.* **2008**, *10*, 5485.

51.0, 32.4; IR (ATR): ν_{max} 2218, 1719, 1649, 925, 748, 694 cm^{-1}; ESIHRMS *m/z* calcd for $C_{13}H_{15}N_2$ $[M+H]^+$ 199.1230, found 199.1228.



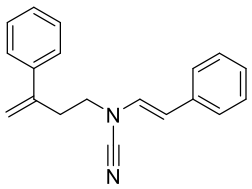
3

(*E*)-*N*-But-3-enyl-*N*-(pent-1-enyl)cyanamide 3. Prepared according to general procedure I using (*E*)-1-iodopent-1-ene (327 mg, 1.67 mmol). Yield: 40% (110 mg, 0.67 mmol). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddt, *J* = 17.0, 10.2 and 6.8 Hz, 1H), 5.68 (dt, *J* = 13.8 and 1.3 Hz, 1H), 5.22-5.12 (m, 3H), 3.26 (t, *J* = 7.2 Hz, 2H), 2.44 (tq, *J* = 7.2 and 1.3 Hz, 2H), 1.99 (qd, *J* = 7.2 and 1.3 Hz, 2H), 1.39 (app. sext., *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 127.8, 118.5, 114.2, 113.0, 50.3, 32.2, 31.5, 23.1, 13.6; IR (ATR): ν_{max} 2960, 2928, 2972, 2217, 1666, 1458, 1383, 1164, 1118, 929, 772 cm^{-1}; ESIHRMS *m/z* calcd for $C_{10}H_{17}N_2$ $[M+H]^+$ 165.1386, found 165.1396.



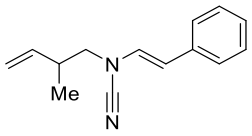
1b

(*E*)-*N*-3-Methylbut-3-enyl-*N*-styrylcyanamide 1b. Prepared according to general procedure I using (*E*)-β-iodostyrene (384 mg, 1.67 mmol). Yield: 47% (167 mg, 0.78 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.17 (m, 5H), 6.40 (d, *J* = 14.2 Hz, 1H), 6.17 (d, *J* = 14.2 Hz, 1H), 4.91 (m, 1H), 4.83 (m, 1H), 3.49 (t, *J* = 7.3 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 135.2, 128.9, 128.2, 127.0, 125.6, 113.7, 113.1, 112.7, 49.8, 35.9, 22.5; IR (ATR): ν_{max} 2217, 1649, 1144, 928, 747, 693 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1386, found 213.1386.



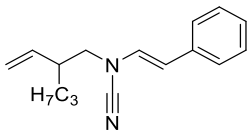
1c

(*E*)-*N*-3-Phenylbut-3-enyl-*N*-styrylcyanamide 1c. Prepared according to general procedure I using (*E*)-β-iodostyrene (384 mg, 1.67 mmol). Yield: 40% (183 mg, 0.67 mmol). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.13 (m, 10H), 6.26 (d, *J* = 14.3 Hz, 1H), 6.10 (d, *J* = 14.3 Hz, 1H), 5.43 (app. s, 1H), 5.25 (app. s, 1H), 3.45 (t, *J* = 7.1 Hz, 2H), 2.98 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 139.7, 135.2, 128.9, 128.8, 128.4, 128.2, 127.0, 126.4, 125.6, 116.3, 113.1, 112.5, 50.3, 34.3; IR (ATR): ν_{max} 2218, 1649, 1147, 928, 747, 694 cm^{-1}; ESIHRMS *m/z* calcd for $C_{19}H_{19}N_2$ $[M+H]^+$ 275.1543, found 275.1546.



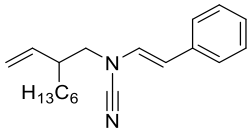
1d

(*E*)-*N*-2-Methylbut-3-enyl-*N*-styrylcyanamide 1d. Prepared according to general procedure II. Yield: 33% (159 mg, 0.75 mmol). Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.17 (m, 5H), 6.35 (d, *J* = 14.0 Hz, 1H), 6.18 (d, *J* = 14.0 Hz, 1H), 5.74 (ddd, *J* = 17.6, 10.3 and 7.5 Hz, 1H), 5.22-5.12 (m, 2H), 3.30 (obs. dd, *J* = 13.8 and 7.7 Hz, 1H), 3.26 (obs. dd, *J* = 13.8 and 7.1 Hz, 1H), 2.68 (app. sept., *J* = 7.0 Hz, 1H), 1.13 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 135.3, 128.9, 128.7, 127.0, 125.6, 116.8, 113.5, 112.6, 57.3, 37.4, 17.3; ESIHRMS *m/z* calcd for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1386, found 213.1387.



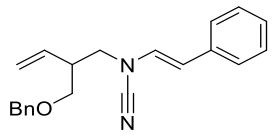
1e

(*E*)-*N*-2-Propylbut-3-enyl-*N*-styrylcyanamide 1e. Prepared according to general procedure II. Yield: 36% (196 mg, 0.82 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.17 (m, 5H), 6.34 (d, *J* = 14.2 Hz, 1H), 6.15 (d, *J* = 14.2 Hz, 1H), 5.59 (ddd, *J* = 16.9, 10.4 and 8.8 Hz, 1H), 5.22-5.15 (m, 2H), 3.36 (dd, *J* = 13.8 and 6.2 Hz, 1H), 3.24 (dd, *J* = 13.8 and 8.5 Hz, 1H), 2.57-2.47 (m, 1H), 1.50-1.22 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 135.3, 128.9, 128.8, 127.0, 125.6, 118.5, 113.6, 112.5, 56.2, 43.3, 34.0, 20.1, 14.1; IR (ATR): ν_{max} 3081, 2959, 2930, 2872, 2219, 1650, 1449, 1387, 1146, 925, 747, 693 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{21}N_2$ $[M+H]^+$ 241.1699, found 241.1697.



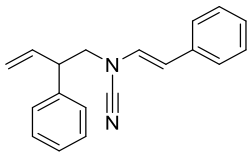
1f

(*E*)-*N*-2-Hexylbut-3-enyl-*N*-styrylcyanamide 1f. Prepared according to general procedure II. Yield: 41% (262 mg, 0.93 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.17 (m, 5H), 6.34 (d, *J* = 14.1 Hz, 1H), 6.15 (d, *J* = 14.1 Hz, 1H), 5.59 (ddd, *J* = 16.5, 10.7 and 8.7 Hz, 1H), 5.22-5.15 (m, 2H), 3.36 (dd, *J* = 13.8 and 6.2 Hz, 1H), 3.42 (dd, *J* = 13.8 and 8.6 Hz, 1H), 2.56-2.45 (m, 1H), 1.52-1.20 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 135.3, 128.9, 128.8, 127.0, 125.6, 118.5, 113.6, 112.5, 56.2, 43.6, 31.8 (2C), 29.3, 26.9, 22.7, 14.2; IR (ATR): ν_{max} 2956, 2927, 2856, 2220, 1717, 1650, 1451, 1220, 922, 771, 695 cm^{-1}; ESIHRMS *m/z* calcd for $C_{19}H_{27}N_2$ $[M+H]^+$ 283.2169, found 283.2166.



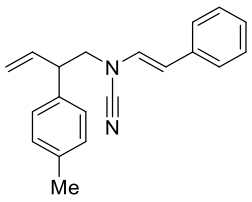
1g

(*E*)-*N*-2-Benzyloxymethylbut-3-enyl-*N*-styrylcyanamide 1g. Prepared according to general procedure II. Yield: 42% (304 mg, 0.95 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 7H), 7.22-7.17 (m, 3H), 6.38 (d, *J* = 14.2 Hz, 1H), 6.18 (d, *J* = 14.2 Hz, 1H), 5.82 (ddd, *J* = 17.2, 10.4 and 8.3 Hz, 1H), 5.29-5.25 (m, 1H), 5.23 (app. s, 1H), 4.52 (s, 2H), 3.64 (obs. dd, *J* = 13.9 and 6.4 Hz, 1H), 3.60 (obs. dd, *J* = 9.5 and 4.4 Hz, 1H), 3.51 (dd, *J* = 9.4 and 6.3 Hz, 1H), 3.42 (dd, *J* = 14.0 and 7.6 Hz, 1H), 2.87-2.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 135.3, 135.2, 128.9 (2C), 128.6, 128.0, 127.8, 126.9, 125.6, 119.2, 113.5, 112.5, 73.5, 70.1, 53.0, 43.5; IR (ATR): ν_{max} 3061, 3027, 2861, 2219, 1650, 1452, 1385 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{21}H_{23}N_2O$ $[M+H]^+$ 319.1805, found 319.1802.



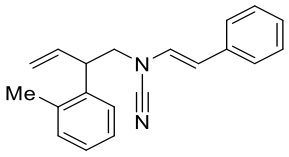
1h

(*E*)-*N*-2-Phenylbut-3-enyl-*N*-styrylcyanamide 1h. Prepared according to general procedure II. Yield: 20% (125 mg, 0.45 mmol). Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 2H), 7.31-7.23 (m, 5H), 7.21-7.14 (m, 3H), 6.21 (d, *J* = 14.1 Hz, 1H), 6.11 (d, *J* = 14.1 Hz, 1H), 6.05 (obs. ddd, *J* = 17.1, 10.3 and 7.1 Hz, 1H), 5.29-5.21 (m, 2H), 3.80 (q, *J* = 7.7 Hz, 1H), 3.67 (dd, *J* = 13.8 and 7.8 Hz, 1H), 3.61 (dd, *J* = 13.8 and 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 137.0, 135.2, 129.2, 128.9, 128.4, 127.9, 127.8, 127.0, 125.6, 118.2, 113.1, 112.8, 56.5, 48.8; IR (ATR): ν_{max} 3063, 3026, 2925, 2851, 2219, 1650, 1601, 1151, 927, 771, 748, 699 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{19}H_{19}N_2$ $[M+H]^+$ 275.1543, found 275.1539.



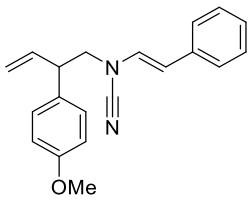
1i

(*E*)-*N*-2-*para*-Tolylbut-3-enyl-*N*-styrylcyanamide 1i. Prepared according to general procedure II. Yield: 26% (170 mg, 0.59 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.11 (m, 7H), 6.19 (d, *J* = 14.1 Hz, 1H), 6.10 (d, *J* = 14.1 Hz, 1H), 6.03 (ddd, *J* = 17.1, 10.4 and 7.5 Hz, 1H), 5.27-5.19 (m, 2H), 3.76 (q, *J* = 7.7 Hz, 1H), 3.65 (dd, *J* = 13.7 and 7.7 Hz, 1H), 3.58 (dd, *J* = 13.7 and 7.7 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 137.2, 136.5, 135.3, 129.9, 128.9, 128.5, 127.8, 127.0, 125.6, 118.0, 113.2, 112.7, 56.5, 48.4, 21.2; IR (ATR): ν_{max} 3033, 2924, 2219, 1650, 1387, 1219, 927, 772, 693 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{20}H_{21}N_2$ $[M+H]^+$ 289.1699, found 289.1710.



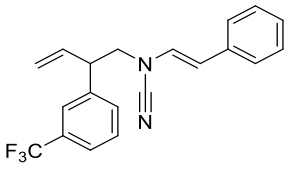
1j

(*E*)-*N*-2-*ortho*-Tolylbut-3-enyl-*N*-styrylcyanamide 1j. Prepared according to general procedure II. Yield: 29% (190 mg, 0.66 mmol). Brownish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.14 (m, 7H), 6.23 (d, *J* = 14.2 Hz, 1H), 6.13 (d, *J* = 14.2 Hz, 1H), 6.00 (ddd, *J* = 17.1, 10.3 and 7.4 Hz, 1H), 5.25 (dt, *J* = 10.3 and 1.1 Hz, 1H), 5.19 (dt, *J* = 17.1 and 1.2 Hz, 1H), 4.07 (q, *J* = 7.7 Hz, 1H), 3.69 (dd, *J* = 13.8 and 8.1 Hz, 1H), 3.63 (dd, *J* = 13.7 and 7.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.0, 136.5, 135.2, 131.2, 128.9, 128.5, 127.4, 127.0, 126.7, 126.5, 125.6, 118.1, 113.2, 112.6, 55.9, 44.1, 19.7; IR (ATR): ν_{max} 3025, 2917, 2850, 2219, 1650, 1491, 1449, 1384, 1153, 926, 771, 745, 693 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{20}H_{21}N_2$ $[M+H]^+$ 289.1699, found 289.1702.



1k

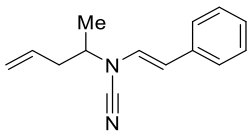
(*E*)-*N*-2-*para*-Methoxyphenylbut-3-enyl-*N*-styrylcyanamide 1k. Prepared according to general procedure II. Yield: 22% (152 mg, 0.50 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.14 (m, 5H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.20 (d, *J* = 14.2 Hz, 1H), 6.10 (d, *J* = 14.2 Hz, 1H), 6.02 (ddd, *J* = 17.2, 10.4 and 7.4 Hz, 1H), 5.25 (dt, *J* = 10.4 and 1.1 Hz, 1H), 5.21 (dt, *J* = 17.2 and 1.2 Hz, 1H), 3.78 (s, 3H), 3.75 (obs. q, *J* = 7.6 Hz, 1H), 3.64 (dd, *J* = 13.7 and 7.7 Hz, 1H), 3.56 (dd, *J* = 13.7 and 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 137.3, 135.2, 131.5, 129.0, 128.9, 128.5, 127.0, 125.6, 117.8, 114.6, 113.2, 112.7, 56.5, 55.4, 47.9; IR (ATR): ν_{max} 3029, 2934, 2219, 1650, 1610, 1512, 1248, 1179, 1124, 1034, 926, 748, 694 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{20}H_{18}F_3N_2$ $[M+H]^+$ 343.1417, found 343.1408.



1l

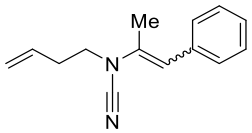
(*E*)-*N*-2-*meta*-(Trifluoromethyl)phenylbut-3-enyl-*N*-styrylcyanamide 1l. Prepared according to general procedure II. Yield: 24% (185 mg, 0.54 mmol). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.53-7.44 (m, 3H), 7.31-7.26 (m, 2H), 7.22-7.15 (m, 3H), 6.22 (d, *J* = 14.2 Hz, 1H), 6.12 (d, *J* = 14.2 Hz, 1H), 6.04 (ddd, *J* = 17.1, 10.4 and 7.5 Hz, 1H), 5.33 (dt, *J* = 10.4 and 1.0 Hz, 1H), 5.27 (dt, *J* = 17.1 and 1.1 Hz, 1H), 3.88 (q, *J* = 7.7 Hz, 1H), 3.70 (dd, *J* = 13.8 and 7.8 Hz, 1H), 3.62 (dd, *J* = 13.8 and 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 136.1, 134.9, 131.6 (q, *J* = 32.2 Hz), 131.5, 129.7, 128.9, 128.1, 127.2, 125.7, 124.7 (m, 2C), 124.1 (q, *J* = 272.4 Hz), 119.1, 113.3, 112.9, 56.1, 48.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; IR (ATR): ν_{max} 3027, 2919, 2221, 1650,

1449, 1329, 1164, 1124, 1074, 927, 747, 694 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{20}H_{21}N_2O$ $[M+H]^+$ 305.1648, found 305.1654.



1m

(*E*)-*N*-1-Methylbut-3-enyl-*N*-styrylcyanamide 1m. Prepared according to general procedure II. Yield: 54% (260 mg, 1.23 mmol). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.16 (m, 5H), 6.36 (d, *J* = 14.2 Hz, 1H), 6.25 (d, *J* = 14.2 Hz, 1H), 5.79 (ddt, *J* = 17.2, 10.2 and 7.1 Hz, 1H), 5.24-5.14 (m, 2H), 3.47 (sext., *J* = 7.1 Hz, 1H), 2.56-2.47 (m, 1H), 2.41-2.32 (m, 1H), 1.40 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 133.0, 128.9, 128.0, 127.0, 125.6, 119.3, 113.0, 111.6, 57.9, 39.6, 18.9; IR (ATR): ν_{max} 2214, 1721, 1399, 1123, 926, 747, 693 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1386, found 213.1392.

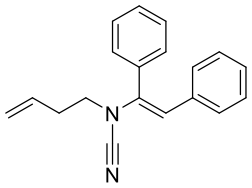


1n (*E*/*Z*: 83/17)

(*E*)-*N*-But-3-enyl-*N*-(1-phenylprop-1-en-2-yl)cyanamide 1n. Prepared according to general procedure I using (*E*)-β-iodo-β-methylstyrene (408 mg, 1.67 mmol). Yield: 32% (113 mg, 0.53 mmol). Obtained after purification as an inseparable mixture of *E* and *Z* isomers with a *E*/*Z* ratio of 83/17; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 2H), 7.26-7.21 (m, 1H), 7.21-7.16 (m, 2H), 5.98 (app. s, 1H, *E* + *Z* isomers), 5.85 (ddt, *J* = 17.0, 10.2 and 6.8 Hz, 0.83H, *E* isomer), 5.64 (ddt, *J* = 17.0, 10.2 and 6.8 Hz, 0.17H, *Z* isomer), 5.27-5.15 (m, 1.66H, *E* isomer), 5.13-5.05 (m, 0.34H, *Z* isomer), 3.52 (t, *J* = 7.3 Hz, 1.66H, *E* isomer), 3.09 (t, *J* = 7.1 Hz, 0.34H, *Z* isomer), 2.58 (app. qt, *J* = 7.3 and 1.2 Hz, 1.66H, *E* isomer), 2.34 (app. qt, *J* = 7.1 and 1.3 Hz, 0.34H, *Z* isomer), 2.15 (d, *J* = 0.9 Hz, 2.49H, *E* isomer), 2.13 (d, *J* = 1.2 Hz, 0.51H, *Z* isomer); ^{13}C NMR (100 MHz, $CDCl_3$)

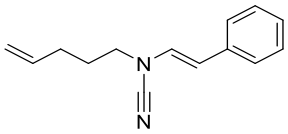
δ 136.4 (*E* isomer), 135.6 (*E* isomer), 135.0 (*Z* isomer), 134.6 (*Z* isomer), 133.7 (*Z* isomer), 133.4 (*E* isomer), 129.0 (*E* isomer), 128.6 (2C, *Z* isomer), 128.4 (*E* isomer), 127.5 (*Z* isomer), 126.6 (*E* isomer), 119.5 (*Z* isomer), 118.5 (*E* isomer), 118.3 (*Z* isomer), 113.9 (2C, *E* + Z isomers), 110.2 (*E* isomer), 51.7 (*Z* isomer), 48.5 (*E* isomer), 32.4 (*Z* isomer), 31.7 (*E* isomer), 22.1 (*Z* isomer), 16.1 (*E* isomer); IR (ATR): ν_{max} 2971, 2211, 1621, 1450, 1158, 703 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1386, found 213.1389.

*The E configuration of the major isomer has been attributed by analogy with the configuration of compound **1o**.*



1o

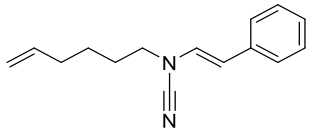
(*E*)-*N*-But-3-enyl-*N*-(1,2-diphenylvinyl)cyanamide 1o. Prepared according to general procedure I using (*E*)-β-iodo-β-phenylstyrene (511 mg, 1.67 mmol). Yield: 38% (174 mg, 0.63 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.42-7.29 (m, 5H), 7.13-7.03 (m, 3H), 6.93-6.84 (m, 2H), 6.48 (s, 1H), 5.76 (ddt, *J* = 17.1, 10.2 and 6.8 Hz, 1H), 5.24-5.11 (m, 2H), 3.28 (t, *J* = 7.2 Hz, 2H), 2.47 (app. qt, *J* = 7.2 and 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.6, 135.3, 133.4, 132.6, 130.4, 129.8, 129.2, 129.0, 128.2, 126.8, 118.6, 116.5, 114.7, 49.3, 32.3; IR (ATR): ν_{max} 2214, 919, 757, 695 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{19}H_{19}N_2$ $[M+H]^+$ 275.1543, found 275.1547.



1q

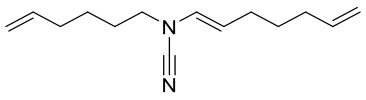
(*E*)-*N*-Pent-4-enyl-*N*-styrylcyanamide 1q. Prepared according to general procedure I using (*E*)-β-iodostyrene (384 mg, 1.67 mmol). Yield: 50% (177 mg, 0.84 mmol). Orange oil; ^{1}H NMR (600 MHz,

$CDCl_3$) δ 7.32-7.28 (m, 2H), 7.26-7.23 (m, 2H), 7.21 (tt, *J* = 7.2 and 1.3 Hz, 1H), 6.39 (d, *J* = 14.2 Hz, 1H), 6.17 (d, *J* = 14.2 Hz, 1H), 5.79 (ddt, *J* = 17.0, 10.2 and 6.7 Hz, 1H), 5.10 (dt, *J* = 17.0 and 1.5 Hz, 1H), 5.07 (dt, *J* = 10.2 and 1.2 Hz, 1H), 3.38 (t, *J* = 7.2 Hz, 2H), 2.21 (qd, *J* = 7.2 and 1.2 Hz, 2H), 1.88 (app. quint., *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.6, 135.3, 128.9, 128.4, 127.0, 125.6, 116.5, 113.3, 112.7, 50.8, 30.3, 27.2. IR (ATR): ν_{max} 3076, 2934, 2217, 1649, 925, 747, 693 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1386, found 213.1387.



1r

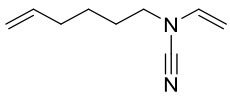
(*E*)-*N*-Hex-5-enyl-*N*-styrylcyanamide 1r. Prepared according to general procedure I using (*E*)-β-iodostyrene (384 mg, 1.67 mmol). Yield: 51% (192 mg, 0.85 mmol). Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.08 (m, 5H), 6.40 (d, *J* = 14.2 Hz, 1H), 6.16 (d, *J* = 14.2 Hz, 1H), 5.79 (ddt, *J* = 16.9, 10.2 and 6.7 Hz, 1H), 5.08-4.97 (m, 2H), 3.37 (t, *J* = 7.2 Hz, 2H), 2.13 (app. q, *J* = 7.2 Hz, 2H), 1.79 (app. quint., *J* = 7.5 Hz, 2H), 1.52 (obs. quint., *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.3, 128.9, 128.4, 127.0, 125.6, 115.5, 113.4, 112.6, 51.5, 33.3, 27.5, 25.7; IR (ATR): ν_{max} 3070, 2931, 2217, 1599, 926, 748 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{19}N_2$ $[M+H]^+$ 227.1543, found 227.1544.



1s

(*E*)-*N*-Hex-5-enyl-*N*-(hept-1,6-dienyl)cyanamide 1s. Prepared according to general procedure I using (*E*)-1-iodohepta-1,6-diene (371 mg, 1.67 mmol). Yield: 40% (146 mg, 0.67 mmol). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (obs. ddt, *J* = 16.9, 10.1 and 6.7 Hz, 1H), 5.77 (obs. ddt, *J* = 16.9, 10.1 and 6.7 Hz, 1H), 5.67 (dt, *J* = 13.8 and 1.3 Hz, 1H), 5.15 (dt, *J* = 13.8 and 7.2 Hz, 1H), 5.03 (dq, *J* = 9.1 and 1.7 Hz, 1H), 5.01-4.93 (m, 3H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.13-1.97 (m, 6H), 1.74-

1.65 (m, 2H), 1.51-1.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.0, 128.1, 115.4, 114.9, 114.3, 112.5, 50.8, 33.2, 33.1, 29.1, 28.8, 27.3, 25.7; IR (ATR): ν_{max} 3076, 2976, 2931, 2859, 2217, 1665, 1641, 1459, 1387, 1158, 929, 912 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{23}N_2$ $[M+H]^+$ 219.1856, found 219.1862.



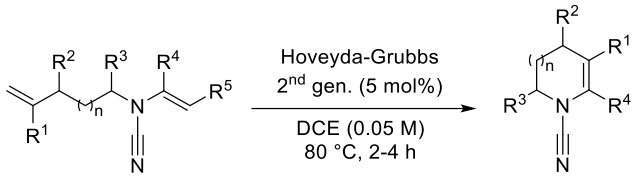
1t

***N*-Hex-5-enyl-*N*-vinylcyanamide 1t**. An oven dried pressure tube was charged with copper(I) iodide (114 mg, 0.6 mmol), 2,2'-bisimidazole (161 mg, 1.2 mmol) and cesium carbonate (3.9 g, 12.0 mmol). The tube was fitted with a rubber septum, evacuated under vacuum, backfilled with argon, and *N*,*N*-dimethylformamide (2 mL) and vinyl iodide (4 mL) were then sequentially added. The resulting reaction mixture was stirred 5 minutes at room temperature before dropwise addition of a solution of *N*-hex-5-enyl cyanamide **S6r** (300 mg, 3.0 mmol) in *N*,*N*-dimethylformamide (2 mL). The tube was then closed with a Teflon-coated screw cap and the resulting suspension was stirred for 12 hours at 80 °C. The crude reaction mixture was cooled down to room temperature and diluted with diethyl ether. The organic layer was washed with water, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 98/02 to 95/05) to give *N*-vinylcyanamide **1t** (250 mg, 1.7 mmol, 55%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (dd, *J* = 15.3 and 8.6 Hz, 1H), 5.78 (ddt, *J* = 16.9, 10.2 and 6.7 Hz, 1H), 5.06-4.96 (m, 2H), 4.63 (dd, *J* = 15.3 and 2.2 Hz, 1H), 4.46 (dd, *J* = 8.6 and 2.2 Hz, 1H), 3.25 (t, *J* = 7.2 Hz, 2H), 2.10 (q, *J* = 7.1 Hz, 2H), 1.72 (quint., *J* = 7.5 Hz, 2H), 1.48 (quint., *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 134.5, 115.4, 113.4, 94.7, 50.3, 33.2, 27.2, 25.6; IR (ATR): ν_{max} 3078, 2938, 2863, 2220, 1634, 1385, 1155, 914, 847, 772 cm^{-1}; ESIHRMS *m/z* calcd for $C_9H_{15}N_2$ $[M+H]^+$ 151.1230, found 151.1231.

Experimental Procedures and Characterization Data:

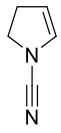
Ring-Closing Metathesis of *N*-Alkenyl-Cyanamides

General Procedure: Ring-Closing Metathesis of *N*-Alkenyl-Cyanamides



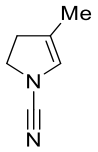
1 (n = 0 or 1) **2**

An oven dried pressure tube was charged with Hoveyda-Grubbs 2nd generation catalyst™ (16 mg, 25 µmol). The tube was fitted with a rubber septum, evacuated under vacuum, backfilled with argon and a solution of the appropriate *N*-alkenyl-cyanamide **1** (0.50 mmol) in degassed 1,2-dichloroethane (10 mL) was next added. The tube was then closed with a Teflon-coated screw cap and the resulting suspension was stirred at 80 °C until no starting material was detected by TLC (*ca.* 2-4 hours). The reaction mixture was cooled down to room temperature and was then concentrated under reduced pressure. The obtained residue was finally purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 95/05 to 90/10) to afford the desired heterocyclic cyanamide **2**.



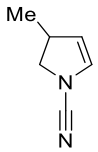
2a

***N*-Cyano-2,3-dihydropyrrole 2a**. Prepared according to general procedure. Yield: 68% (32 mg, 0.34 mmol). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (dt, J = 4.1 and 2.2 Hz, 1H), 5.08-5.04 (m, 1H), 3.82 (t, J = 9.3 Hz, 2H), 2.68 (tt, J = 9.4 and 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.9, 114.5, 108.3, 50.0, 29.5; IR (ATR): ν_{max} 2922, 2853, 2214, 1620, 703 cm^{-1}; ESIHRMS: m/z calcd. for $C_5H_{10}N_3$ $[M+NH_4]^+$ 112.0869, found 112.0872.



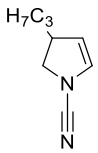
2b

***N*-Cyano-4-methyl-2,3-dihydropyrrole 2b**. Prepared according to general procedure using a reaction temperature of 120 °C. Yield: 62% (34 mg, 0.32 mmol). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (q, J = 1.8 Hz, 1H), 3.81 (t, J = 9.2 Hz, 2H), 2.55 (t, J = 9.3 Hz, 2H), 1.68 (d, J = 1.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.6, 118.9, 115.2, 50.4, 34.0, 13.1; IR (ATR): ν_{max} 2917, 2210, 1365, 1320, 1177 cm^{-1}; ESIHRMS: m/z calcd. for $C_6H_9N_2$ $[M+H]^+$ 109.0760, found 109.0764.



2d

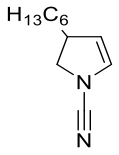
***N*-Cyano-3-methyl-2,3-dihydropyrrole 2d**. Prepared according to general procedure. Yield: 69% (38 mg, 0.34 mmol). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (dd, J = 4.1 and 1.9 Hz, 1H), 5.01 (dd, J = 4.0 and 2.5 Hz, 1H), 3.92 (t, J = 9.8 Hz, 1H), 3.35 (dd, J = 9.5 and 6.4 Hz, 1H), 3.13-3.01 (m, 1H), 1.11 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.0, 114.5, 114.4, 57.3, 37.2, 20.4; IR (ATR): ν_{max} 2964, 2927, 2217, 1649, 1618, 1449, 1339, 1189, 930, 695 cm^{-1}; ESIHRMS: m/z calcd. for $C_6H_9N_2$ $[M+H]^+$ 109.0760, found 109.0763.



2e

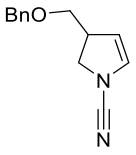
***N*-Cyano-3-propyl-2,3-dihydropyrrole 2e**. Prepared according to general procedure. Yield: 72% (50 mg, 0.36 mmol). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (dd, J = 4.1 and 2.0 Hz, 1H), 5.03

(dd, *J* = 4.1 and 2.5 Hz, 1H), 3.89 (t, *J* = 9.9 Hz, 1H), 3.43 (dd, *J* = 9.6 and 6.6 Hz, 1H), 3.06-2.92 (m, 1H), 1.51-1.18 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.2, 114.5, 113.0, 55.7, 42.5, 37.4, 20.3, 14.1; IR (ATR): ν_{max} 2959, 2929, 2873, 2216, 1618, 1467, 1382 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_8H_{13}N_2$ $[M+H]^+$ 137.1073, found 137.1072.



2f

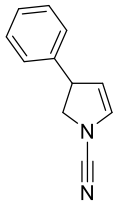
***N*-Cyano-3-hexyl-2,3-dihydropyrrole 2f**. Prepared according to general procedure. Yield: 69% (62 mg, 0.35 mmol). Note: Compound **2f** was also prepared in 63% yield (158 mg, 0.88 mmol) and using scaled-up substrate **1f** (395 mg, 1.40 mmol), catalyst and solvent quantities from general procedure. Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (dd, *J* = 4.1 and 2.0 Hz, 1H), 5.03 (dd, *J* = 4.1 and 2.6 Hz, 1H), 3.89 (t, *J* = 9.9 Hz, 1H), 3.43 (dd, *J* = 9.6 and 6.6 Hz, 1H), 3.02-2.93 (m, 1H), 1.48-1.35 (m, 2H), 1.35-1.21 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.2, 114.5, 113.0, 55.7, 42.8, 35.2, 31.8, 29.3, 27.1, 22.7, 14.2; IR (ATR): ν_{max} 2956, 2927, 2856, 2218, 1619, 1467, 1382, 1167, 850, 772, 721 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{11}H_{22}N_3$ $[M+NH_4]^+$ 196.1808, found 196.1811.



2g

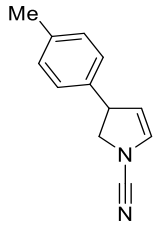
***N*-Cyano-3-(benzyloxy)methyl-2,3-dihydropyrrole 2g**. Prepared according to general procedure. Yield: 55% (58 mg, 0.28 mmol). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 7.32-7.28 (m, 3H), 6.12 (dd, *J* = 4.1 and 1.7 Hz, 1H), 4.99 (dd, *J* = 4.1 and 2.4 Hz, 1H), 4.52 (s, 2H), 3.88 (t, *J* = 9.9 Hz, 1H), 3.68 (dd, *J* = 9.9 and 5.6 Hz, 1H), 3.44 (dd, *J* = 8.6 and 4.9 Hz, 1H), 3.33 (obs. t, *J*

= 7.9 Hz, 1H), 3.32-3.24 (obs. m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 131.0, 128.7, 128.0, 127.9, 114.1, 109.2, 73.5, 72.1, 53.4, 43.4; IR (ATR): ν_{max} 2921, 2855, 2216, 1619, 1454, 1383, 1363 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{13}H_{15}N_2O$ $[M+H]^+$ 215.1179, found 215.1178.



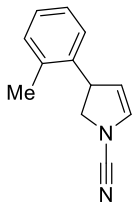
2h

***N*-Cyano-3-phenyl-2,3-dihydropyrrole 2h**. Prepared according to general procedure. Yield: 61% (52 mg, 0.31 mmol). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.22-7.18 (m, 2H), 6.28 (dd, *J* = 4.1 and 1.7 Hz, 1H), 5.17 (dd, *J* = 4.0 and 2.1 Hz, 1H), 4.26-4.16 (m, 2H), 3.76-3.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 130.4, 129.1, 127.7, 127.3, 113.9, 112.4, 58.1, 48.0; IR (ATR): ν_{max} 3029, 2918, 2850, 2217, 1619, 1454, 1379, 1274, 1168, 910, 731, 700 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{11}H_{11}N_2$ $[M+H]^+$ 171.0917, found 171.0920.



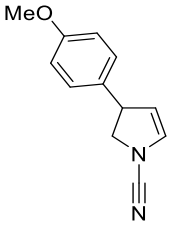
2i

***N*-Cyano-3-*para*-tolyl-2,3-dihydropyrrole 2i**. Prepared according to general procedure. Yield: 65% (60 mg, 0.33 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.26 (dd, *J* = 4.1 and 1.9 Hz, 1H), 5.14 (dd, *J* = 4.0 and 2.4 Hz, 1H), 4.23-4.13 (m, 2H), 3.73-3.63 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.4, 130.2, 129.8, 127.2, 114.0, 112.6, 58.2, 47.7, 21.2; IR (ATR): ν_{max} 3095, 3025, 2921, 2216, 1618, 1514, 1379, 1273, 1164, 818, 744 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{12}H_{16}N_3$ $[M+NH_4]^+$ 202.1339, found 202.1333.



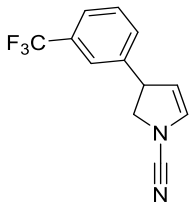
2j

***N*-Cyano-3-*ortho*-tolyl-2,3-dihydropyrrole 2j**. Prepared according to general procedure. Yield: 56% (52 mg, 0.28 mmol). Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.16 (m, 4H), 6.31 (dd, *J* = 4.1 and 2.1 Hz, 1H), 5.17 (dd, *J* = 4.0 and 2.6 Hz, 1H), 4.43 (ddt, *J* = 11.4, 6.9 and 2.4 Hz, 1H), 4.25 (dd, *J* = 11.0 and 9.6 Hz, 1H), 3.61 (dd, *J* = 9.6 and 6.9 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 135.3, 130.7, 130.6, 127.5, 126.9, 126.8, 114.0, 111.8, 57.3, 44.2, 19.8; IR (ATR): ν_{max} 3101, 2962, 2216, 1621, 1488, 1464, 1380, 1273, 1169, 758 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{12}H_{16}N_3$ $[M+NH_4]^+$ 202.1339, found 202.1340.



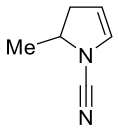
2k

***N*-Cyano-3-*para*-methoxyphenyl-2,3-dihydropyrrole 2k**. Prepared according to general procedure. Yield: 66% (66 mg, 0.33 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.26 (dd, *J* = 4.0 and 1.9 Hz, 1H), 5.14 (dd, *J* = 4.0 and 2.4 Hz, 1H), 4.21-4.12 (m, 2H), 3.80 (s, 3H), 3.65 (app. q, *J* = 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 134.2, 130.1, 128.3, 114.5, 114.0, 112.7, 58.3, 55.5, 47.3; IR (ATR): ν_{max} 3095, 2959, 2837, 2216, 1614, 1512, 1465, 1378, 1247, 1178, 1033, 832, 747, 699 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{12}H_{13}N_3O$ $[M+H]^+$ 201.1022, found 201.1023.



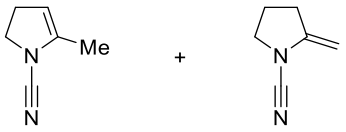
2l

***N*-Cyano-3-*meta*-(Trifluoromethyl)phenyl-2,3-dihydropyrrole 2l**. Prepared according to general procedure. Yield: 76% (91 mg, 0.38 mmol). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.44 (s, 1H), 7.40 (d, J = 7.7 Hz, 1H), 6.35 (dd, J = 4.1 and 1.9 Hz, 1H), 5.17 (dd, J = 4.0 and 2.4 Hz, 1H), 4.31-4.22 (m, 2H), 3.73-3.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 131.8 (q, J = 32.2 Hz), 131.3, 130.7, 129.7, 124.6 (q, J = 3.8 Hz), 124.2 (q, J = 3.9 Hz), 124.1 (q, J = 272.4 Hz), 113.5, 111.4, 57.9, 47.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; IR (ATR): ν_{max} 2918, 2850, 2219, 1621, 1450, 1325, 1273, 1164, 1123, 1074, 805, 703 cm^{-1}; ESIHRMS: m/z calcd. for $C_{12}H_{10}F_3N_2$ $[M+H]^+$ 239.0791, found 239.0799.



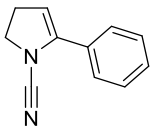
2m

***N*-Cyano-2-methyl-2,3-dihydropyrrole 2m**. Prepared according to general procedure. Yield: 58% (31 mg, 0.29 mmol). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (app. quint., J = 2.1 Hz, 1H), 4.98-4.93 (m, 1H), 4.17 (dquint., J = 10.0 and 6.5 Hz, 1H), 2.84 (ddt, J = 16.1, 10.1 and 2.5 Hz, 1H), 2.26 (ddt, J = 16.2, 6.9 and 2.4 Hz, 1H), 1.41 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.1, 113.9, 106.9, 58.3, 37.2, 19.9; IR (ATR): ν_{max} 2972, 2211, 1621, 1369, 1289, 1158, 702 cm^{-1}; ESIHRMS: m/z calcd. for $C_6H_9N_2$ $[M+H]^+$ 109.0760, found 109.0765.



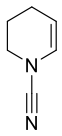
(*endo*)-**2n** (90/10) (*exo*)-**2n'**

***N*-Cyano-5-methyl-2,3-dihydropyrrole 2n**. Prepared according to general procedure. Yield: 18% (10 mg, 0.09 mmol). Obtained after purification as an inseparable mixture of *endo* and *exo* isomers with a *endo*/*exo* ratio of 90/10; Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (app. nonet, J = 1.3 Hz, 0.9H, *endo* isomer), 4.53 (app. quint., J = 1.9 Hz, 0.1H, *exo* isomer), 4.35 (app. quint., J = 1.9 Hz, 0.1H, *exo* isomer), 3.84 (t, J = 9.1 Hz, 1.8H, *endo* isomer), 3.65 (t, J = 6.8 Hz, 0.2H, *exo* isomer), 2.63-2.55 (m, 1.8H, *endo* isomer), 2.52 (tt, J = 7.5 and 1.8 Hz, 0.2H, *exo* isomer), 1.98 (quint., J = 7.1 Hz, 0.2H, *exo* isomer), 1.92-1.89 (m, 2.7H, *endo* isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1 (*exo* isomer), 137.7 (*endo* isomer), 114.1 (2C, *endo* + *exo* isomers), 51.1 (*exo* isomer), 50.5 (*endo* isomer), 29.2 (*exo* isomer), 28.9 (*endo* isomer), 23.5 (*exo* isomer), 12.2 (*endo* isomer); IR (ATR): ν_{max} 2920, 2215, 1659, 1162, 696 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_6H_9N_2$ $[M+H]^+$ 109.0760, found 109.0763.



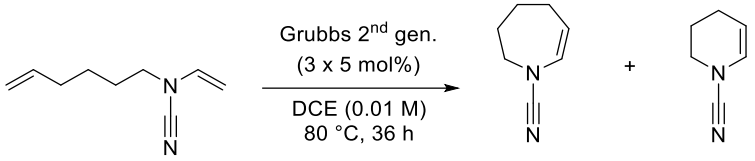
2o

***N*-Cyano-5-phenyl-2,3-dihydropyrrole 2o**. Prepared according to general procedure. Yield: 20% (17 mg, 0.10 mmol). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.42-7.35 (m, 3H), 5.25 (t, J = 2.9 Hz, 1H), 4.04 (dd, J = 9.6 and 8.8 Hz, 2H), 2.81 (dt, J = 9.2 and 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 129.5, 129.2, 128.8, 126.8, 114.4, 106.5, 51.8, 29.6; IR (ATR): ν_{max} 2215, 1681, 1279, 755, 696 cm^{-1}; ESIHRMS: *m*/*z* calcd. for $C_{11}H_{11}N_2$ $[M+H]^+$ 171.0916, found 171.0917.



2q

***N*-Cyano-3,4-dihydropyridine 2q**. Prepared according to general procedure. Yield: 59% (32 mg, 0.30 mmol). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (dt, J = 8.0 and 2.0 Hz, 1H), 4.95 (dt, J = 8.0 and 4.0 Hz, 1H), 3.50 (t, J = 5.6 Hz, 2H), 2.07-2.00 (m, 2H), 1.89 (quint., J = 5.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.8, 115.7, 107.6, 47.3, 21.0, 20.1; IR (ATR): ν_{max} 2932, 2217, 1656, 990, 718 cm^{-1}; ESIHRMS: m/z calcd. for $C_6H_9N_2$ $[M+H]^+$ 109.0760, found 109.0767.



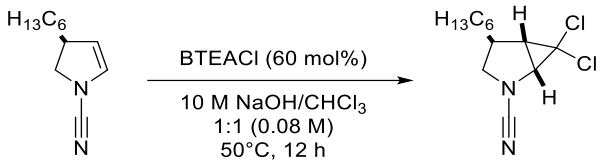
1t **2r** (55/45) **2q**

***N*-Cyano-2,3,4,5-tetrahydroazepine 2r** and ***N*-Cyano-3,4-dihydropyridine 2q**. An oven dried pressure tube was charged with Grubbs 2nd generation catalyst™ (21 mg, 25 µmol). The tube was fitted with a rubber septum, evacuated under vacuum, backfilled with argon and a solution of *N*-vinyl-cyanamide **1t** (61 mg, 0.50 mmol) in degassed 1,2-dichloroethane (50 mL) was next added. The tube was then closed with a Teflon-coated screw cap and the resulting suspension was stirred at 80 °C. After 12 hours, the reaction mixture was cooled down to room temperature and a second portion of Grubbs 2nd generation catalyst™ (21 mg, 25 µmol) was quickly added. After a further 12 hours at 80 °C, a third portion of Grubbs 2nd generation catalyst™ (21 mg, 25 µmol) was quickly added and the resulting mixture was further stirred at 80 °C for 12 hours (36 hours total reaction time). The reaction mixture was cooled down to room temperature and was then concentrated under reduced pressure. The obtained residue was finally purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 95/05 to 90/10) to afford an inseparable mixture of 7- and 6-membered rings, respectively compounds **2r** and **2q**, with a ratio of 55/45. Yield: 40% (24 mg, 0.21 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (dt, J = 8.0 and 2.0 Hz,

0.45H, compound **2q**), 6.02 (dt, *J* = 8.7 and 1.6 Hz, 0.55H, compound **2r**), 5.08 (dt, *J* = 8.8 and 5.7 Hz, 0.55H, compound **2r**), 4.95 (dt, *J* = 8.0 and 4.0 Hz, 0.45H, compound **2q**), 3.51 (obs. t, *J* = 5.6 Hz, 0.9H, compound **2q**), 3.48 (obs. t, *J* = 5.7 Hz, 1.1H, compound **2r**), 2.19 (ddd, *J* = 11.8, 5.7 and 1.5 Hz, 1.1H, compound **2r**), 2.07-2.00 (m, 0.9H, compound **2q**), 1.89 (quint., *J* = 5.7 Hz, 0.9H, compound **2q**), 1.87-1.81 (m, 1.1H, compound **2r**), 1.69-1.62 (m, 1.1H, compound **2r**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.9 (compound **2r**), 125.8 (compound **2q**), 116.8 (compound **2r**), 116.7 (compound **2r**), 115.7 (compound **2q**), 107.6 (compound **2q**), 54.7 (compound **2r**), 47.3 (compound **2q**), 29.3 (compound **2r**), 26.9 (compound **2r**), 25.8 (compound **2r**), 21.0 (compound **2q**), 20.1 (compound **2q**); ESIHRMS for compound **2r**: *m*/*z* calcd. for $C_7H_{14}N_3$ $[M+NH_4]^+$ 140.1182, found 140.1177.

Experimental Procedures and Characterization Data:

Diversification Reactions

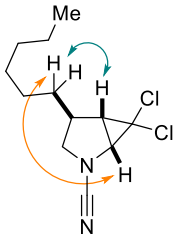


2f **4**

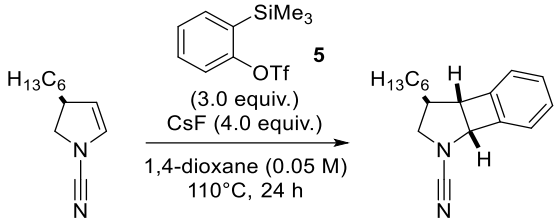
***N*-Cyano-3-hexyl-6,6-dichloro-2-azabicyclo[3.1.0]hexane 4**.[S4] To a stirred solution of *N*-cyano-3-hexyl-2,3-dihydropyrrole **2f** (35 mg, 0.20 mmol) and benzyltriethylammonium chloride (27 mg, 0.12 mmol) in chloroform (1.2 mL) at room temperature was added dropwise a 10 M aqueous solution of sodium hydroxyde (1.2 mL). The resulting mixture was then vigorously stirred for 12 hours at 50 °C. The reaction medium was then cooled down to room temperature and the organic and aqueous layers were separated. The aqueous layer was extracted with chloroform (2 x 2 mL) and the combined organic layers were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 95/05 to 90/10) to give the desired bicyclic cyanamide **4** (26 mg, 0.10 mmol, 50%) as a yellow oil. The diastereomeric ratio was determined by analysis of ^{1}H NMR spectra of the crude reaction mixture and was found to be higher than 95/5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (obs. d, J = 7.5 Hz, 1H), 3.63-3.58 (m, 1H), 3.42 (dd, J = 9.5 and 4.7 Hz, 1H), 2.58 (qd, J = 7.5 and 4.6 Hz, 1H), 2.17 (d, J = 7.5 Hz, 1H), 1.62-1.44 (m, 2H), 1.38-1.21 (m, 8H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.0, 63.5, 59.8, 51.3, 40.9, 40.0, 34.5, 31.7, 29.2, 27.5, 22.7, 14.2; IR (ATR): ν_{max} 2956, 2927, 2856, 2220, 1465, 1376, 1202, 1168, 822 cm^{-1}; ESIHRMS: m/z calcd. for $C_{12}H_{19}Cl_2N_2$ $[M+H]^+$ 261.0920, found 261.0911.

[S4] The protocol was adapted from : Chen, C.; Kattanguru, P.; Tomashenko, O. A.; Karpowicz, R.; Siemiaszko, G.; Bhattacharya, A.; Calasans, V.; Six, Y. *Org. Biomol. Chem.* **2017**, *15*, 5364.

The configuration of the obtained anti addition isomer has been attributed on the basis of NOESY experiments (see page S115 for NOESY spectrum).



4



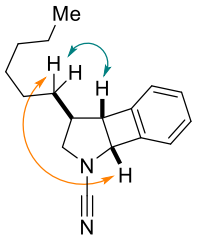
2f **6**

***N*-Cyano-3-hexyl-2,3,3a,7b-tetrahydro-1*H*-benzo[3,4]cyclobuta[1,2-*b*]pyrrole 6**.[S5] A scintillation vial fitted with a rubber septum was charged with *N*-cyano-3-hexyl-2,3-dihydropyrrole **2f** (35 mg, 0.20 mmol) and cesium fluoride (122 mg, 0.80 mmol). The scintillation vial was evacuated under high vacuum, backfilled with argon and then 1,4-dioxane (4 mL) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **5** (146 µL, 0.60 mmol) were sequentially added. The scintillation vial was then sealed, heated up to 110 °C and stirred for 24 hours. The resulting mixture was cooled down to room temperature, diluted with ethyl acetate (5 mL) and filtered over a short pad of Celite®, which was thoroughly washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc: 98/02 to 90/10) to give the desired tricyclic cyanamide **6** (31 mg, 0.12 mmol, 61%) as a yellow oil. The diastereomeric ratio was determined by analysis of ^{1}H NMR spectra of the crude reaction mixture and was found to be higher than 95/5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (obs. td, J = 7.5 and 1.2 Hz, 1H), 7.31 (obs. t, J = 7.0 Hz, 1H), 7.29-7.26 (m, 1H), 7.11 (d, J = 7.0 Hz, 1H), 5.18 (d, J = 3.8 Hz, 1H), 3.91 (d, J = 3.8 Hz, 1H), 3.35 (d, J = 10.2 Hz, 1H), 3.22 (dd, J = 10.2 and 5.4 Hz, 1H), 2.15 (q, J = 6.8 Hz, 1H), 1.47-1.27 (m, 10H), 0.91

[S5] The protocol was adapted from : Feltenberger, J. B.; Hayashi, R.; Tang, Y.; Babiash, E. S. C.; Hsung, R. P. *Org. Lett.* **2009**, *11*, 3666.

(t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 141.2, 130.3, 129.0, 123.5, 122.5, 117.2, 65.3, 55.2, 54.8, 40.8, 32.7, 31.9, 29.4, 27.7, 22.8, 14.2; IR (ATR): ν_{max} 2927, 2855, 2210, 1468, 1457, 1366, 1345, 1245, 1120, 745 cm^{-1}; ESIHRMS: m/z calcd. for $C_{17}H_{23}N_2$ $[M+H]^+$ 255.1856, found 255.1850.

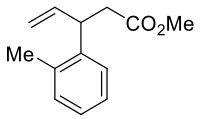
The configuration of the obtained anti addition isomer has been attributed on the basis of NOESY experiments (see page S117 for NOESY spectrum).



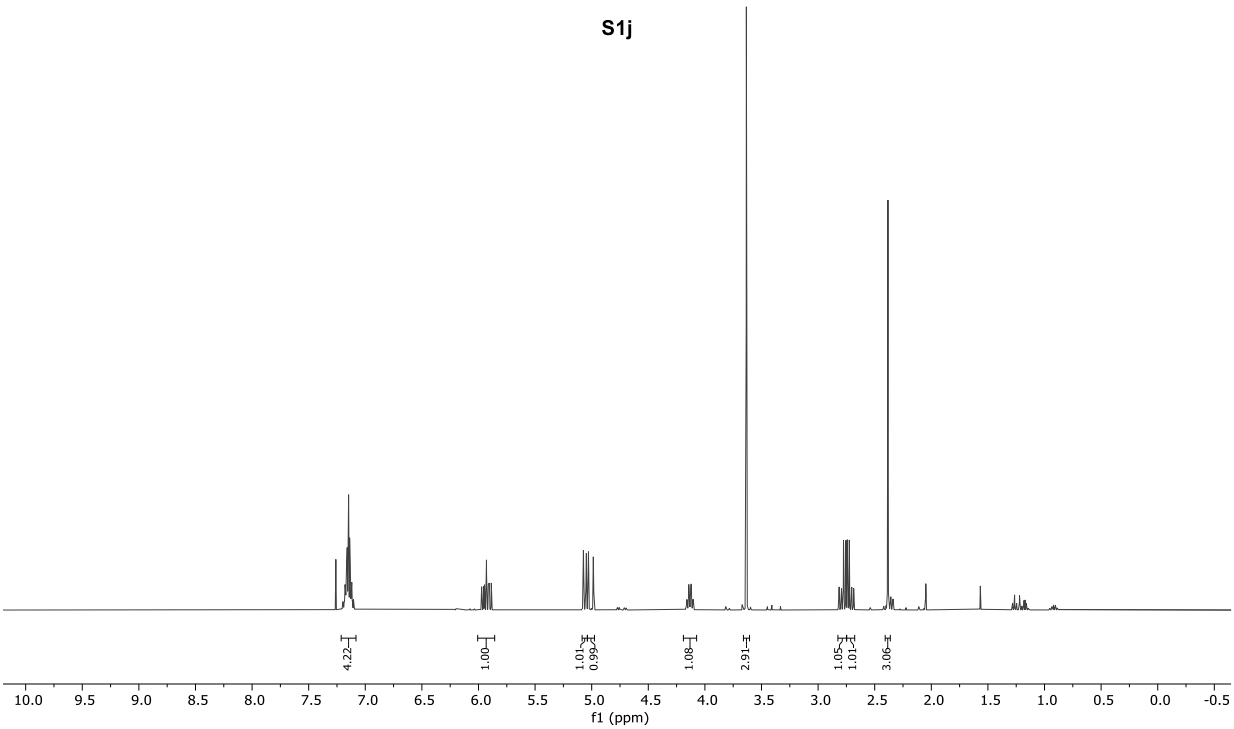
6

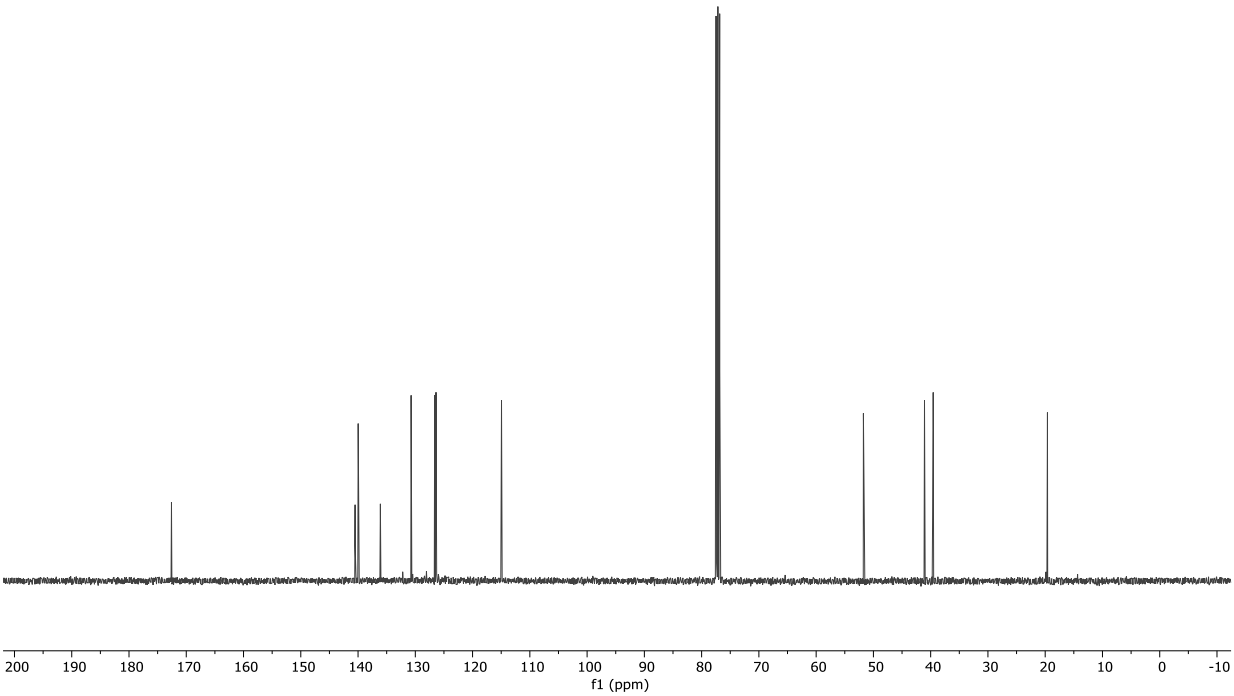
Supporting information

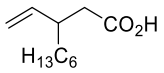
^{1}H, ^{13}C and ^{19}F NMR Spectra and NOESY Experiments


CO2Me
Me

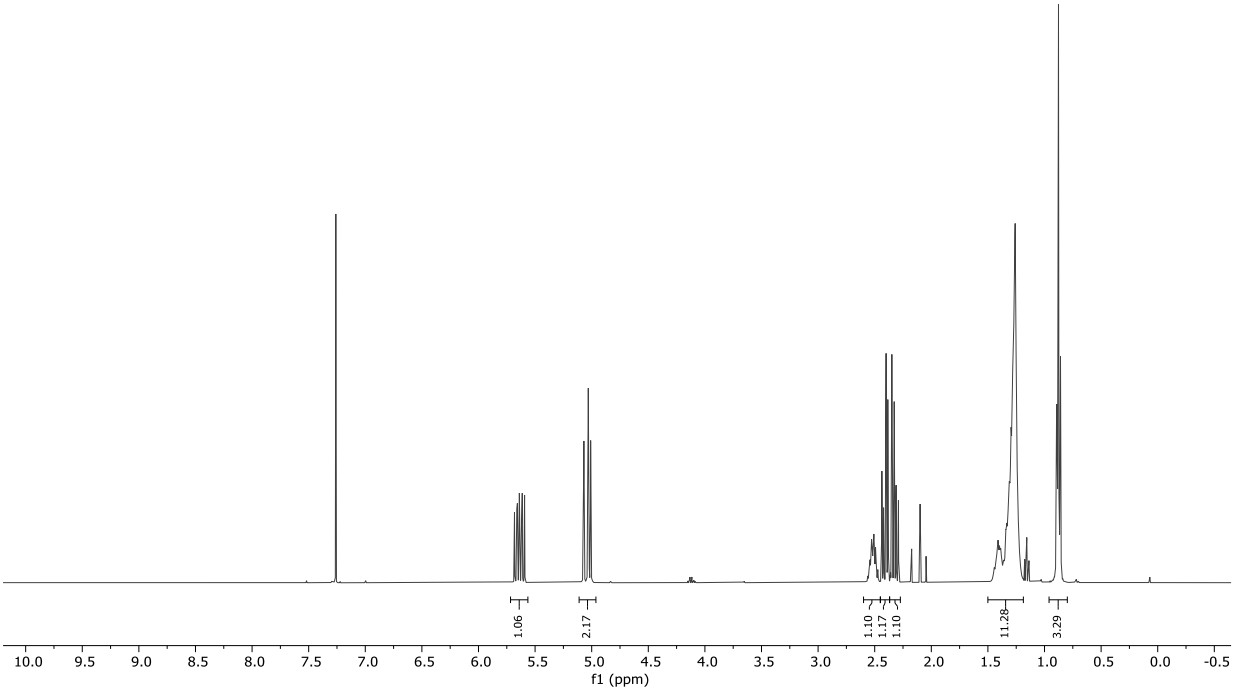
S1j

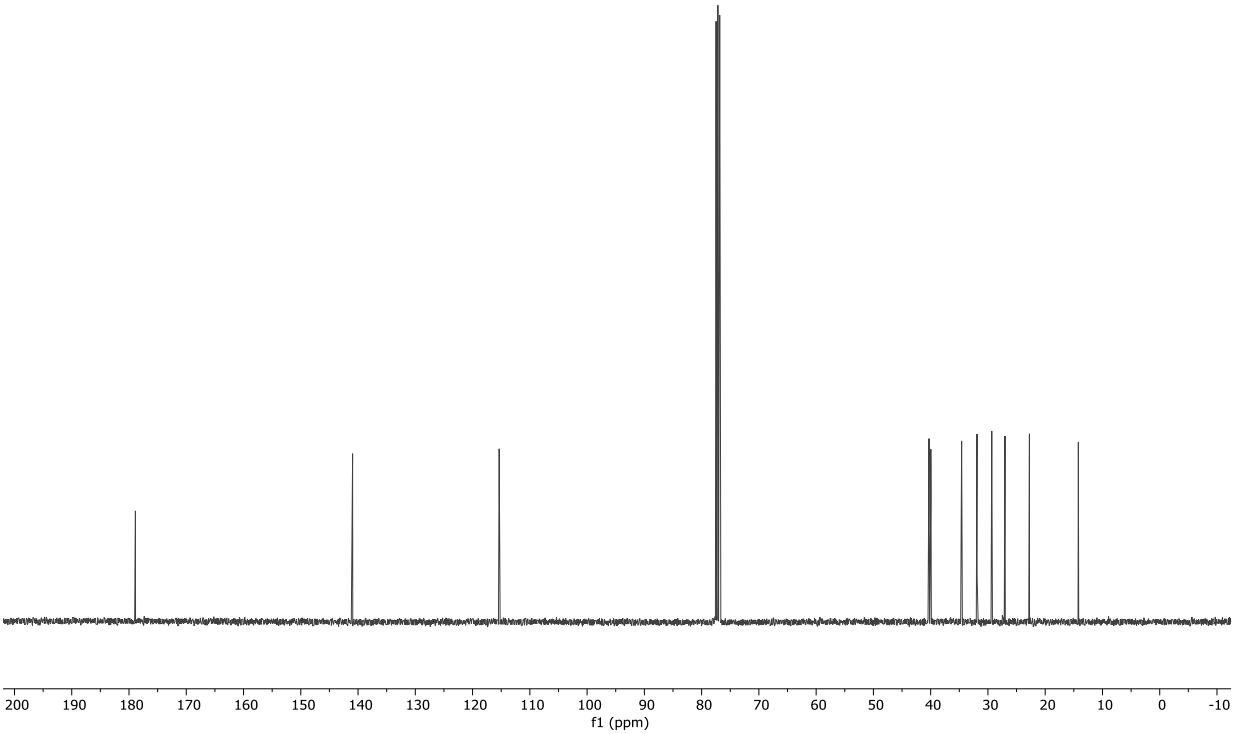

4.22
1.00
1.01
0.99
1.08
2.91
1.05
1.01
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

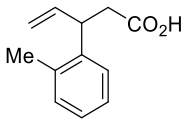

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CO2H
H13C6

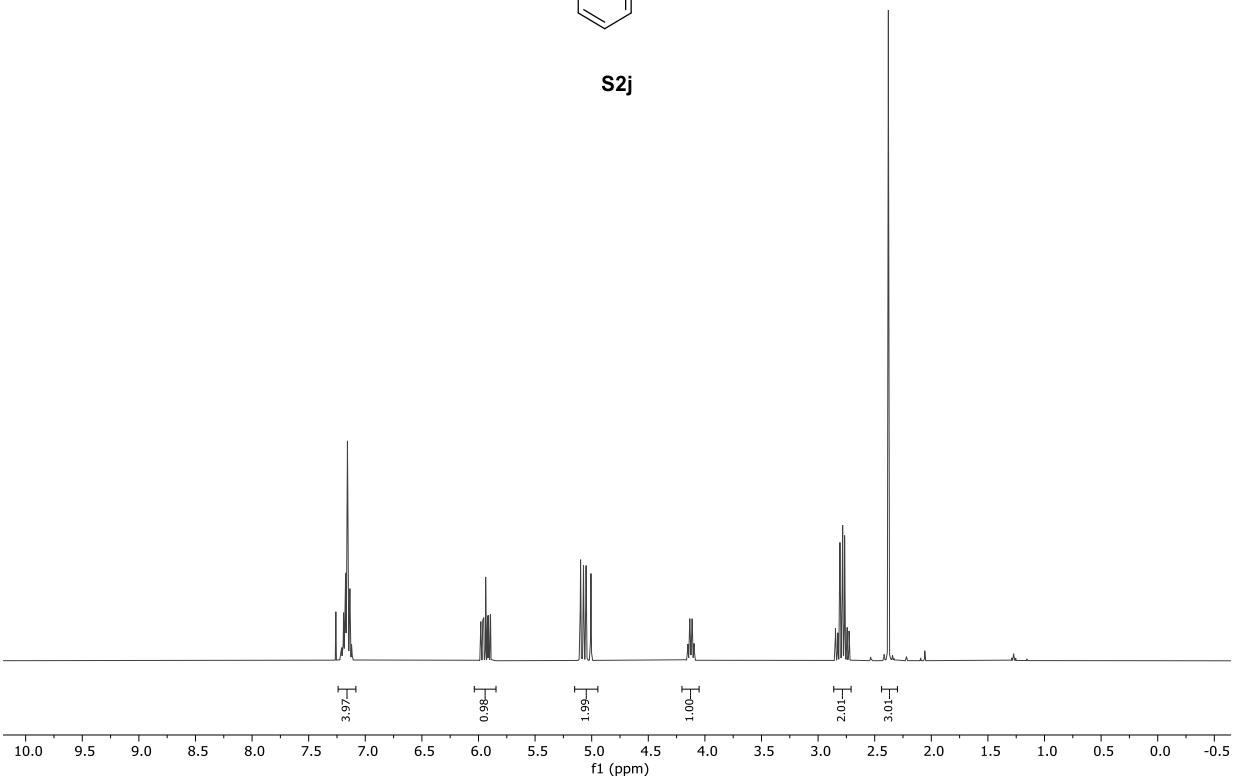
S2f

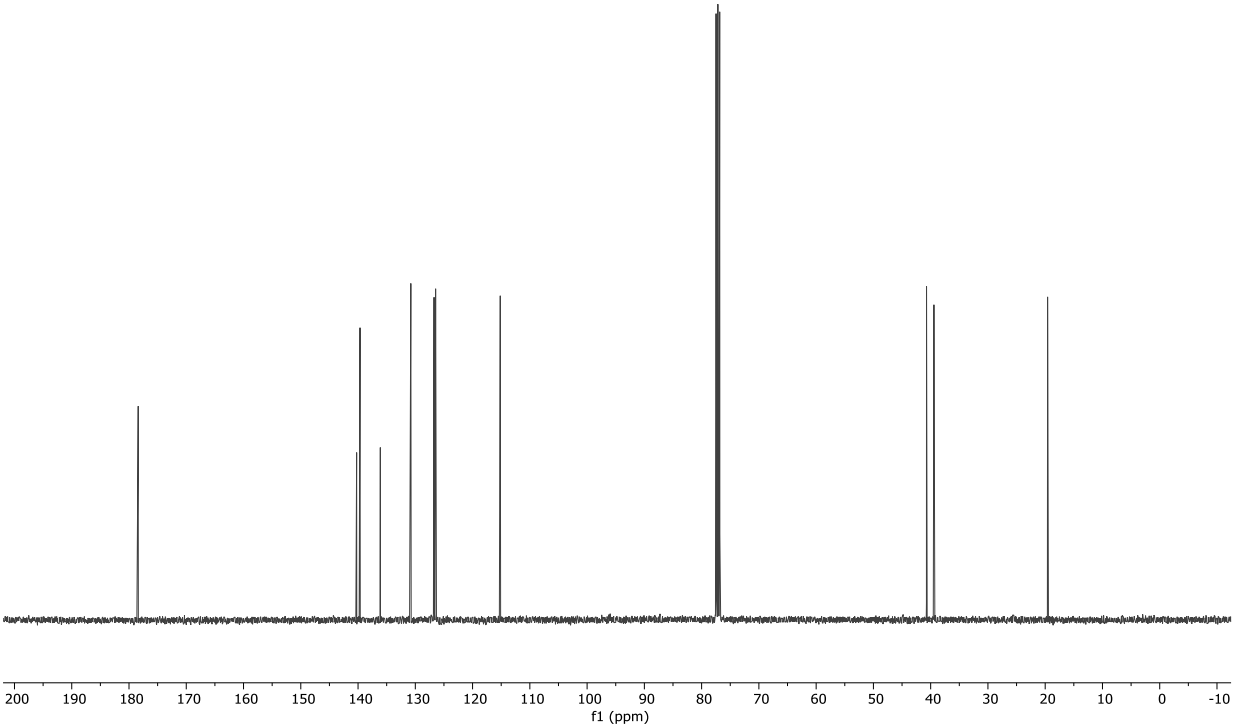

1.06
2.17
1.10
1.17
1.10
11.28
3.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

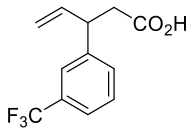

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CO2H
Me

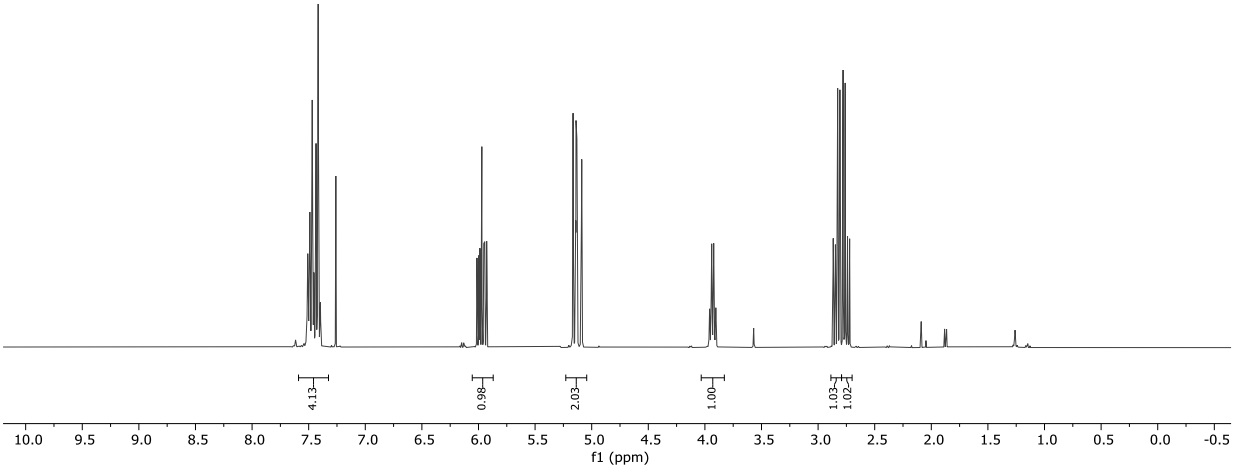
S2j

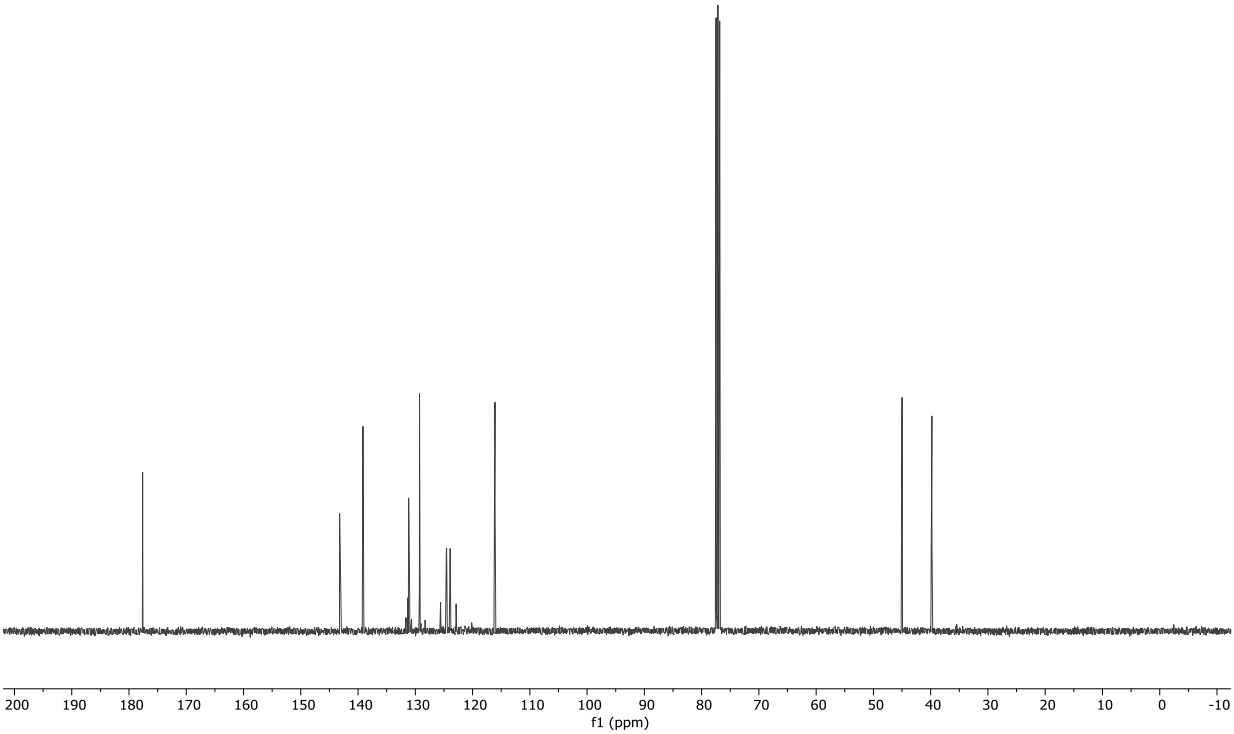

3.97
0.98
1.99
1.00
2.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

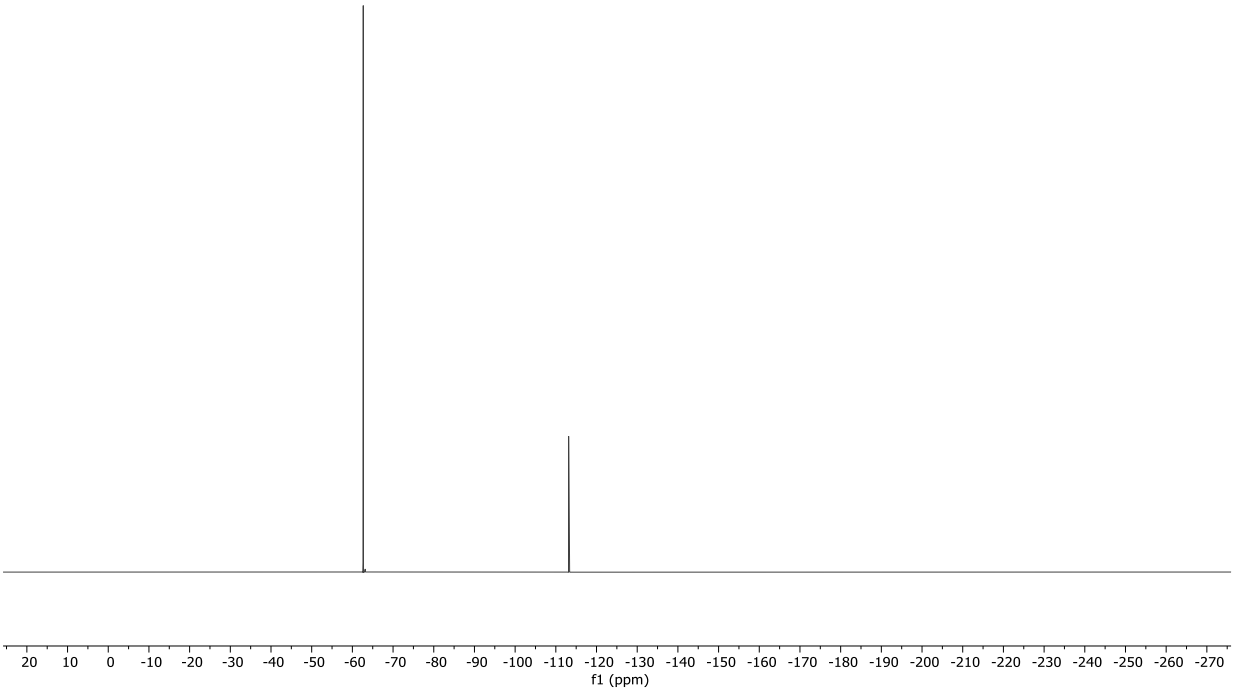

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

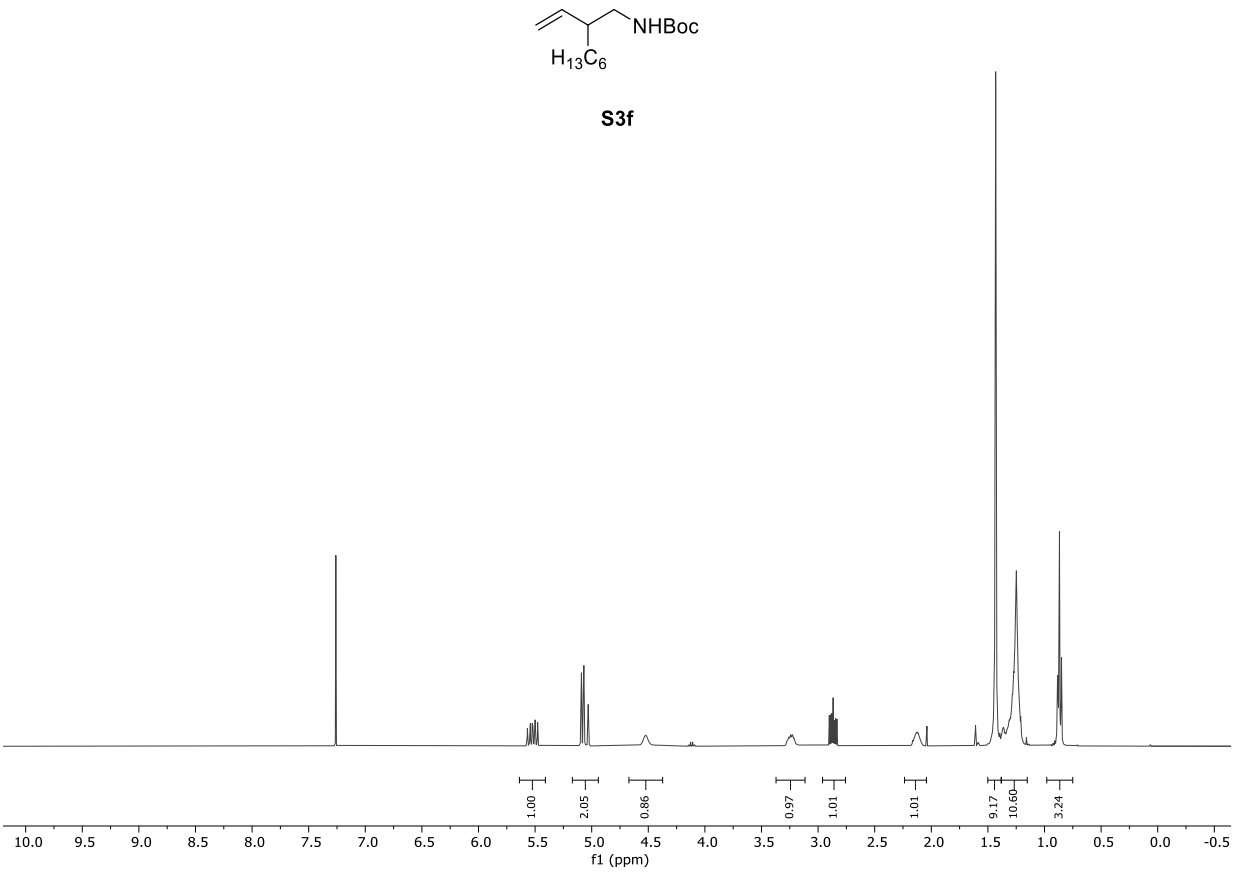

CO2H
F3C

S2l

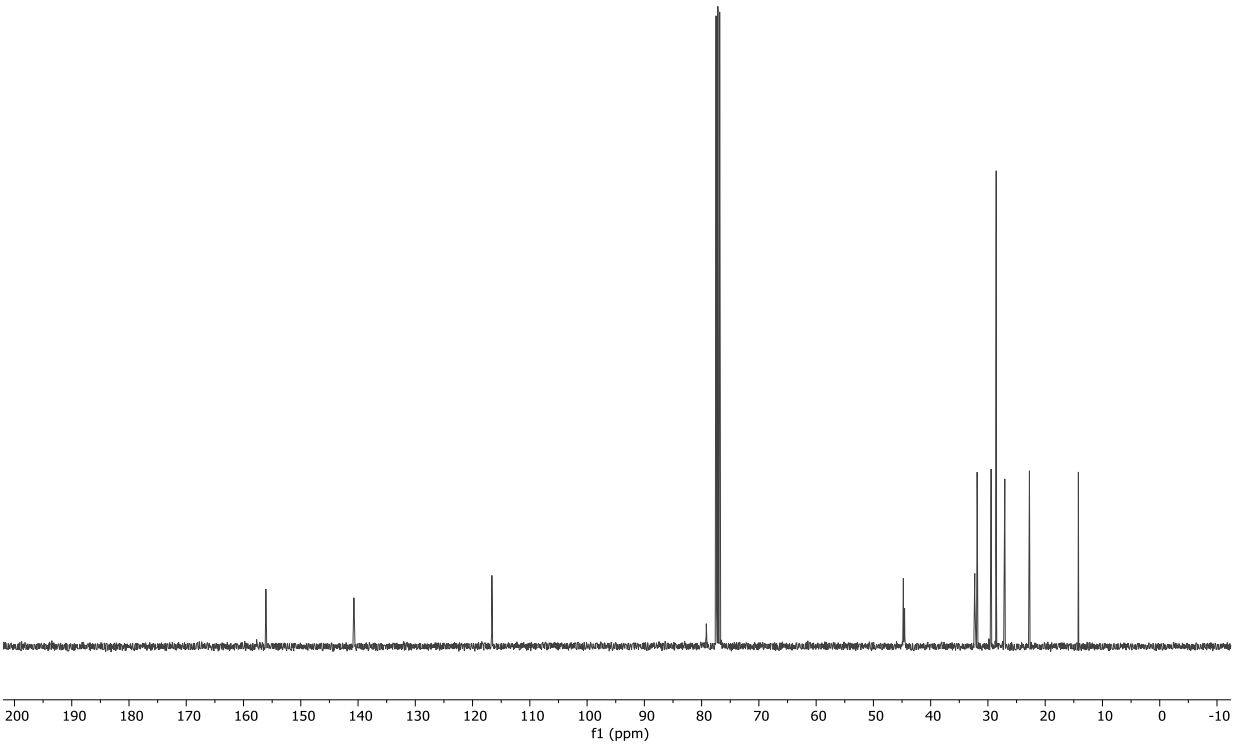

4.13
0.98
2.03
1.00
1.03
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

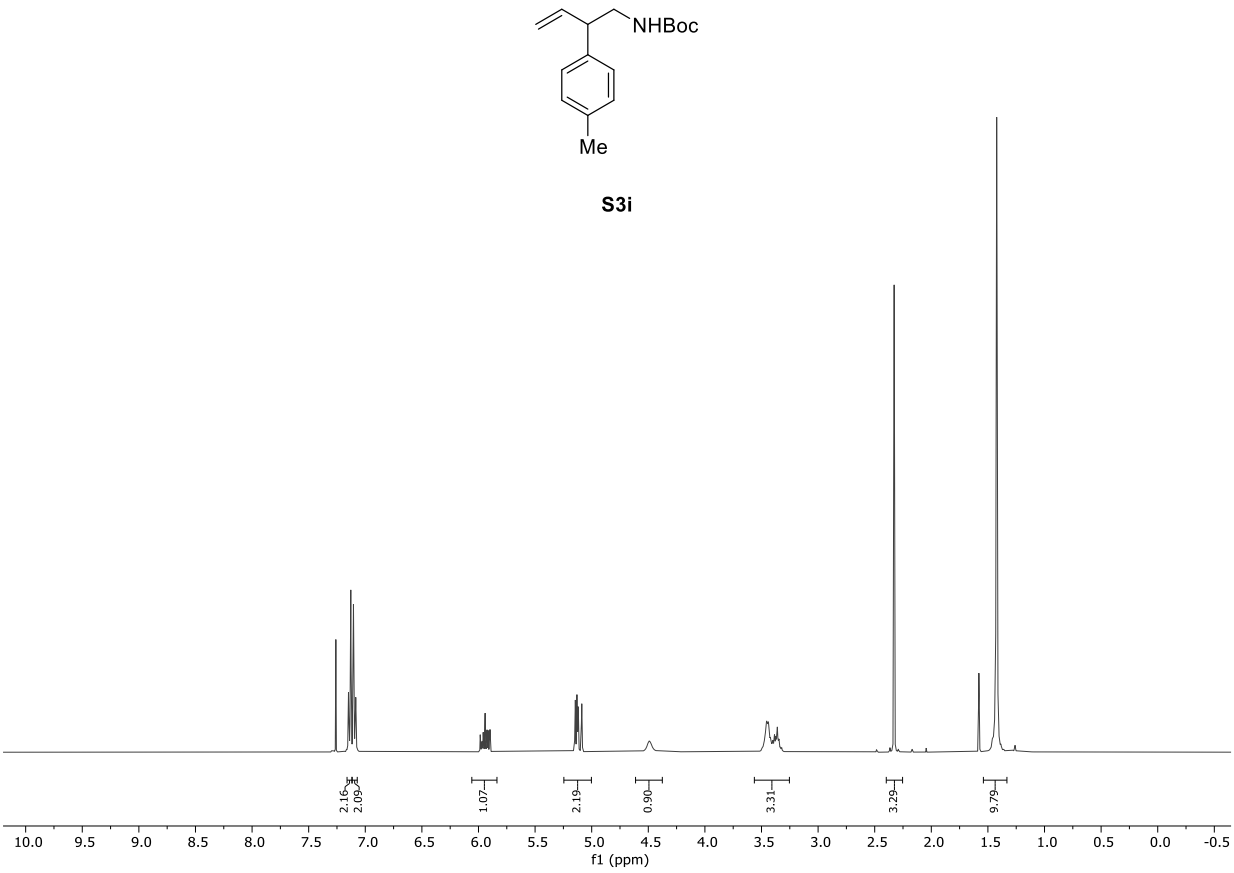

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)

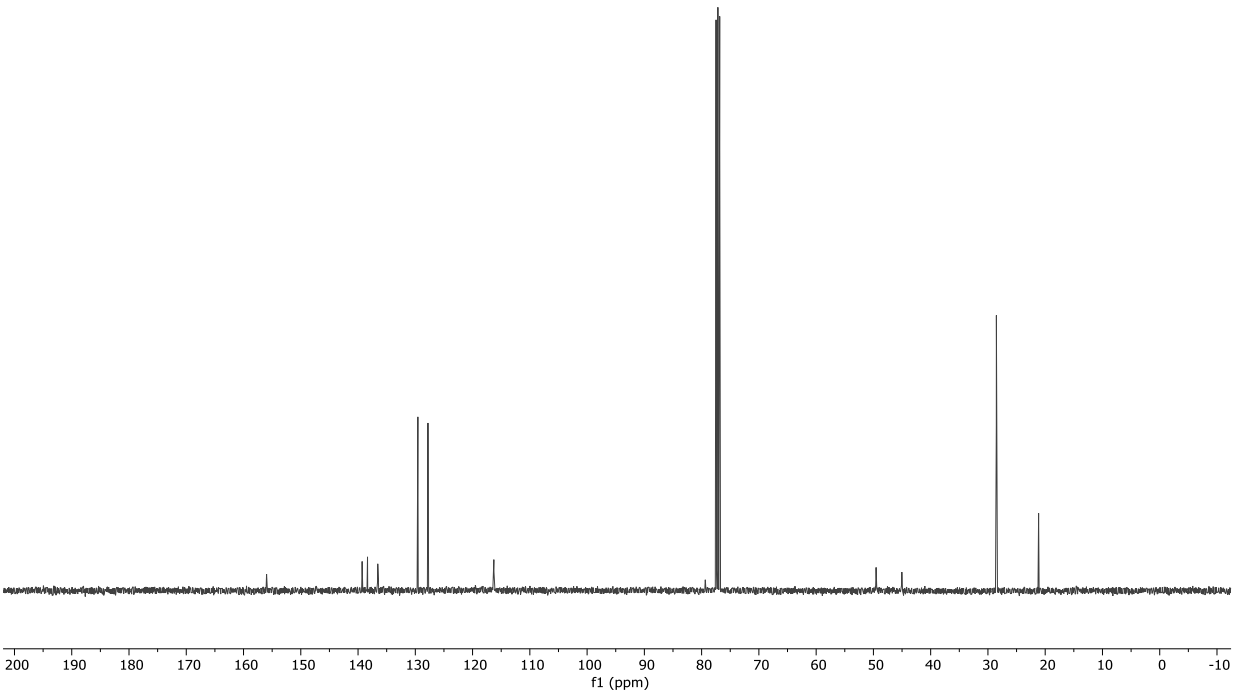

NHBoc
$H_{13}C_6$
1.00
2.05
0.86
0.97
1.01
1.01
9.17
10.60
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

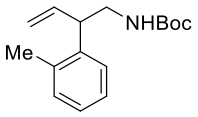
S3f


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

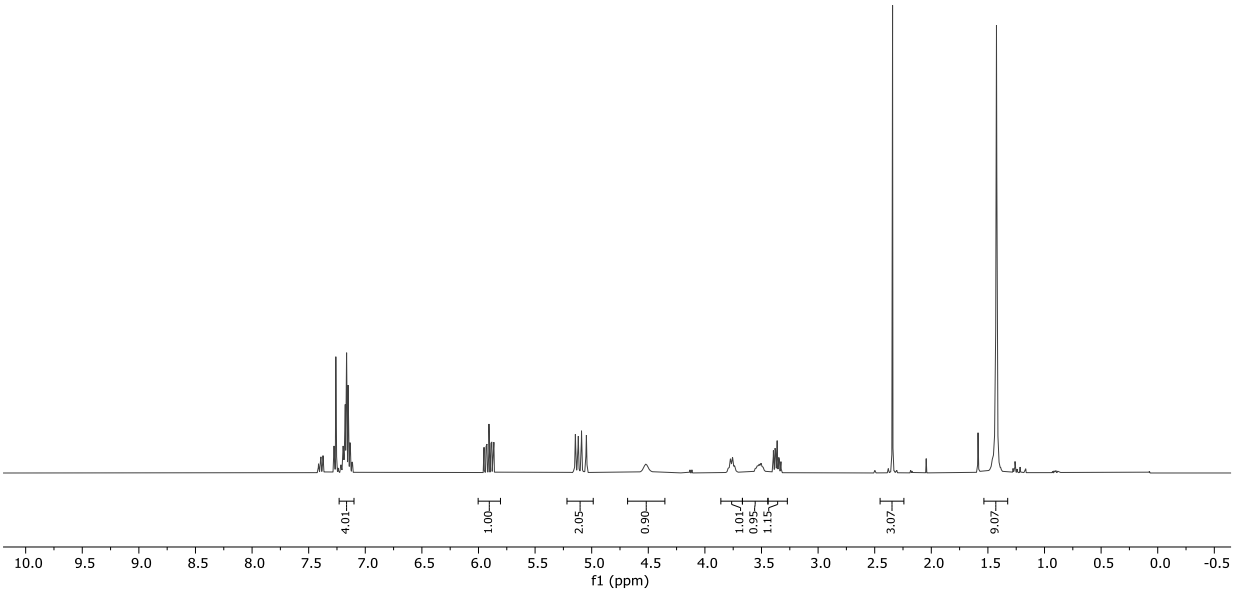

NHBoc
Me
2.16
2.09
1.07
2.19
0.90
3.31
3.29
9.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

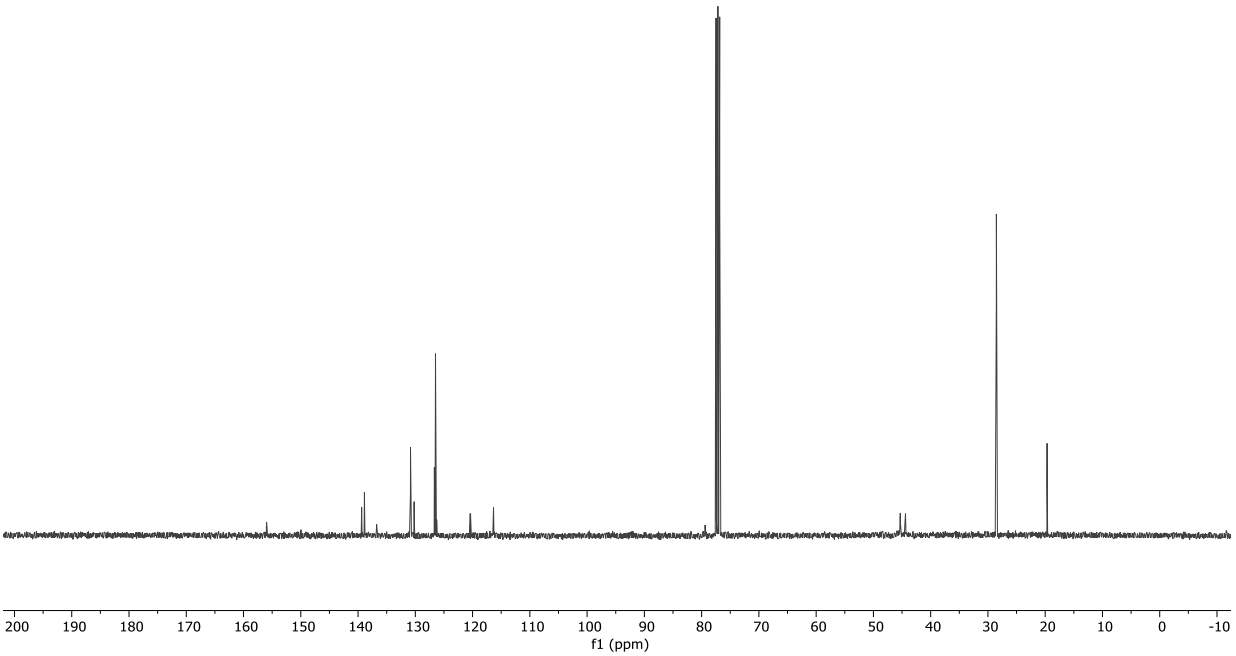
S3i


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NHBoc
Me

S3j


4.01
1.00
2.05
0.90
1.01
0.95
1.15
3.07
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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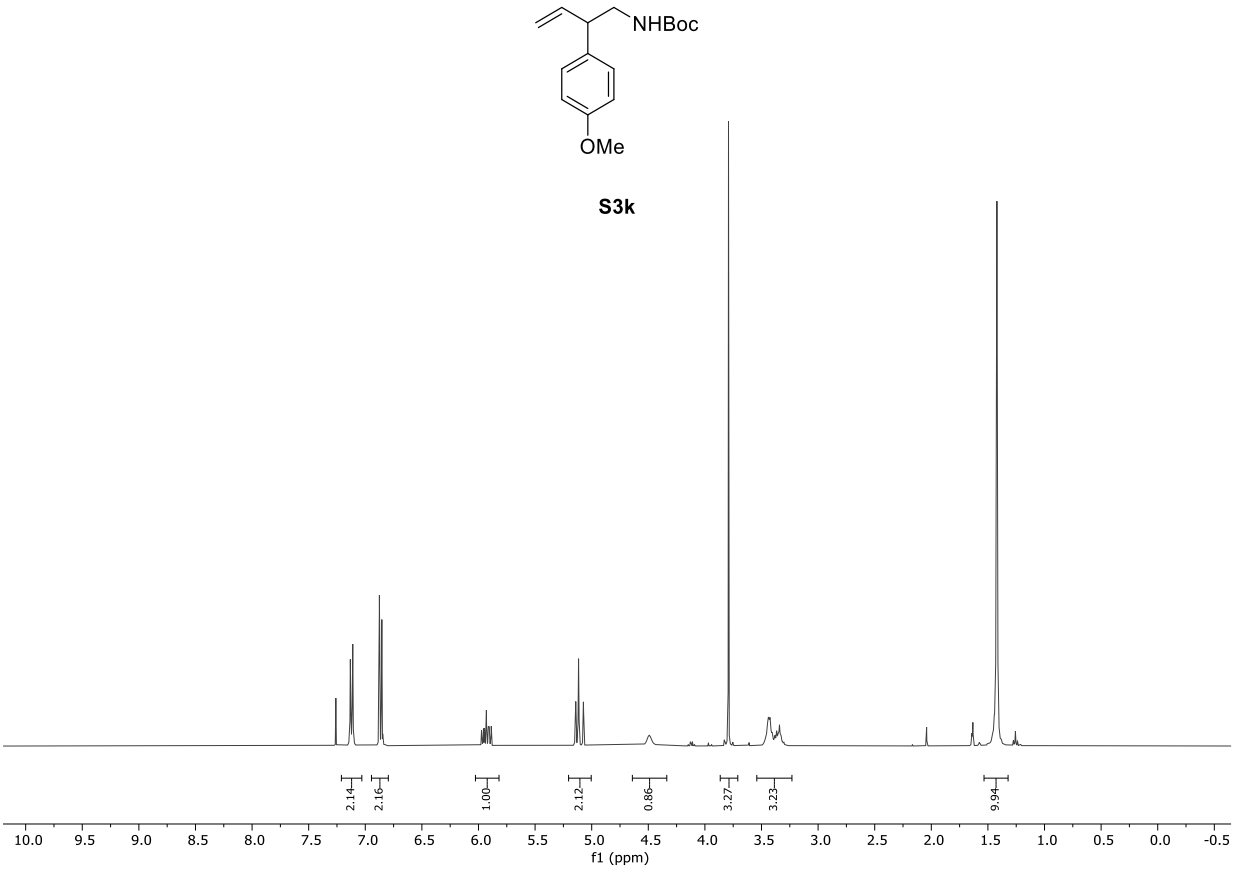
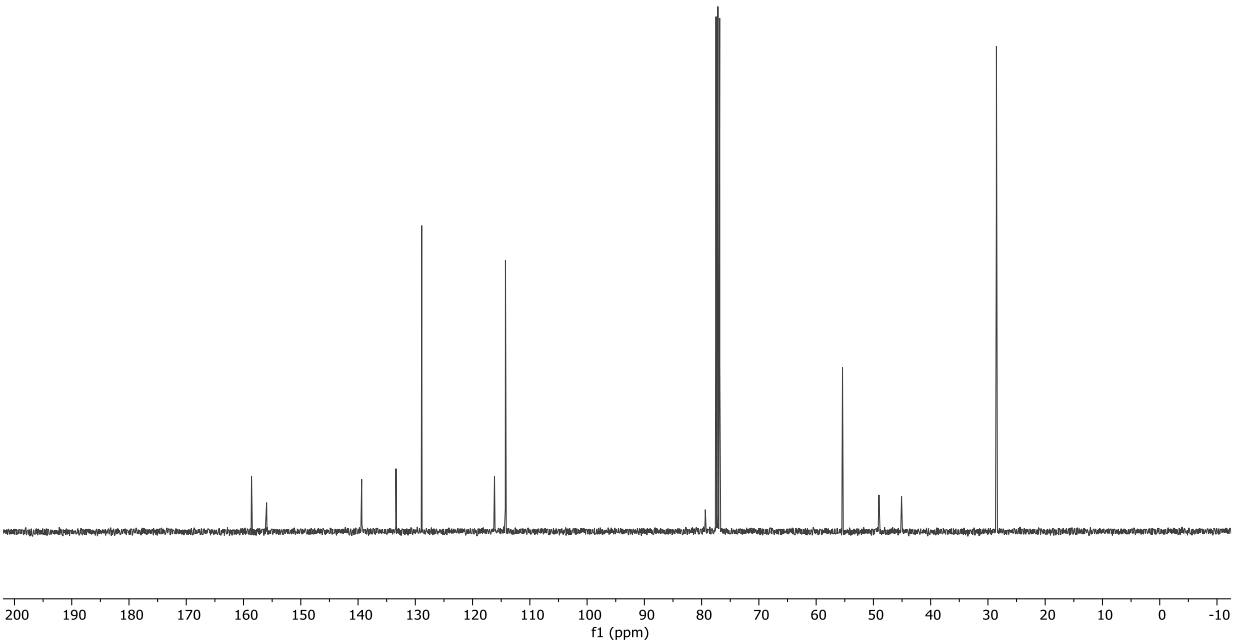
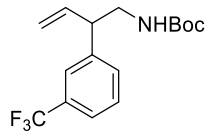
f1 (ppm)


NHBoc
OMe
2.14
2.16
1.00
2.12
0.86
3.27
3.23
9.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

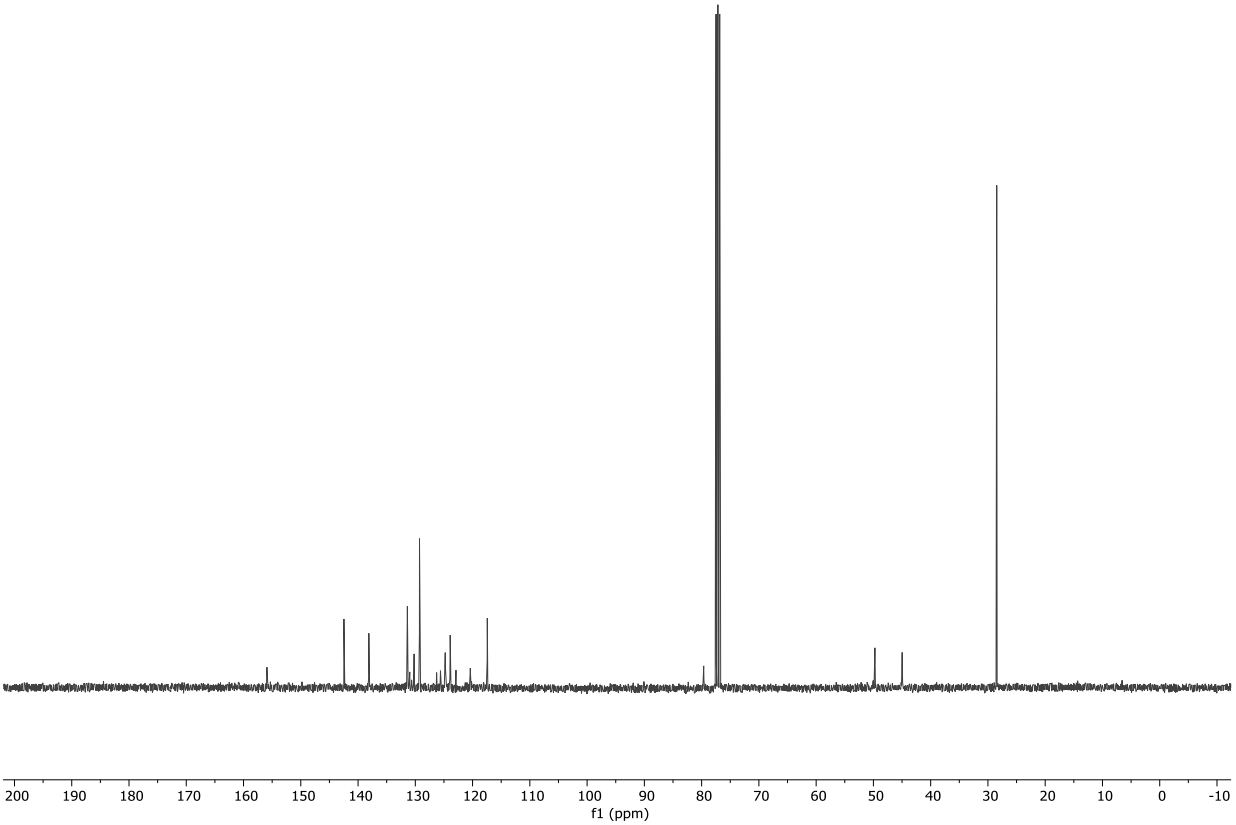
S3k

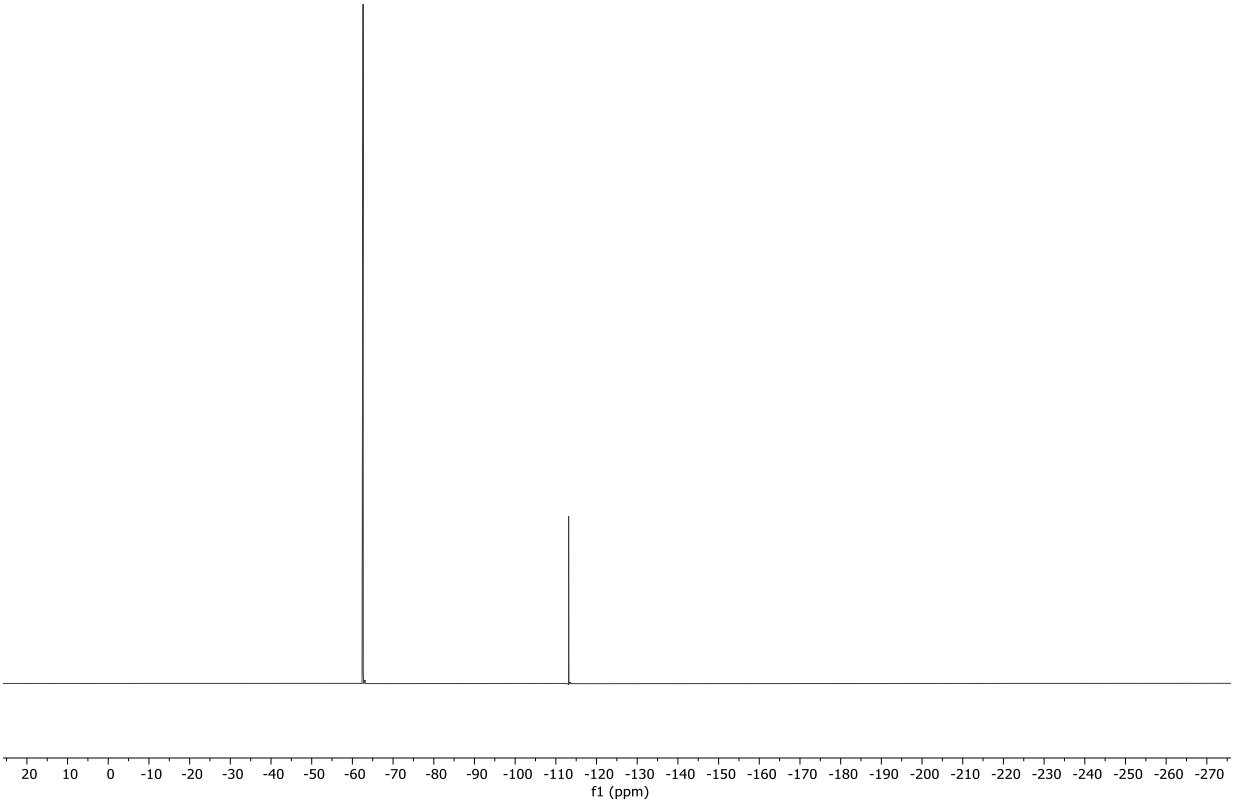

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

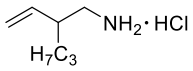

NHBoc
F3C

S3l

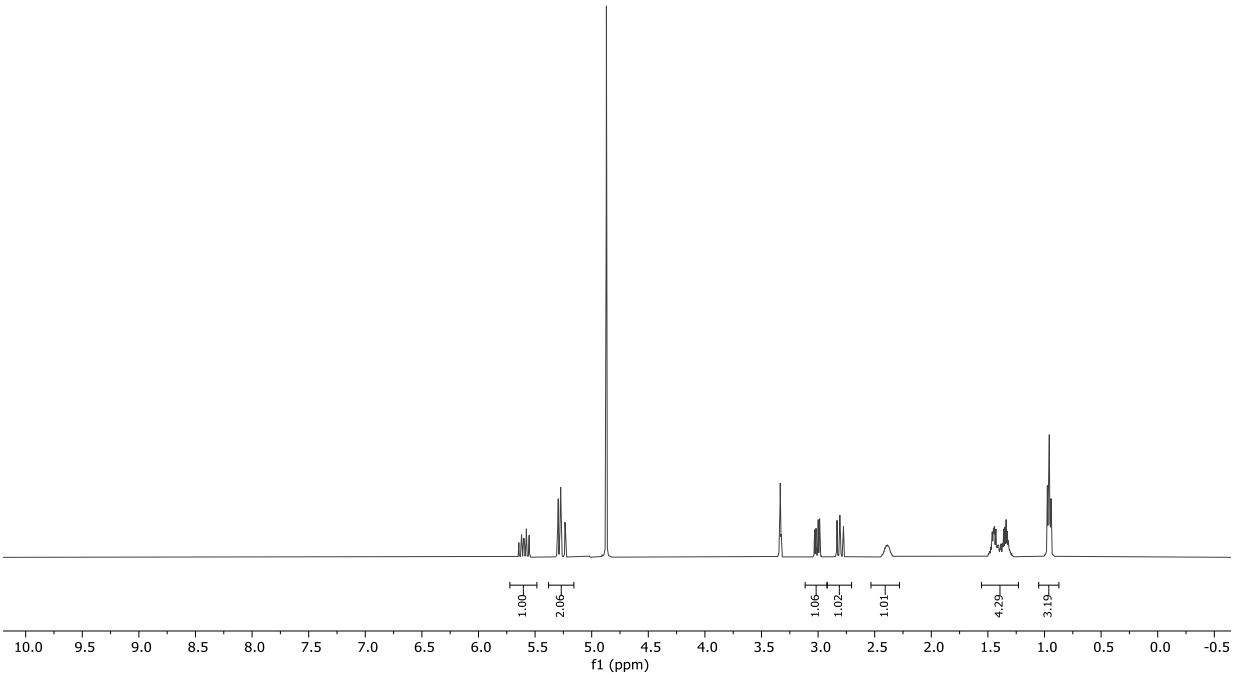
1.07
3.41
1.06
2.13
0.94
1.06
2.17
9.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

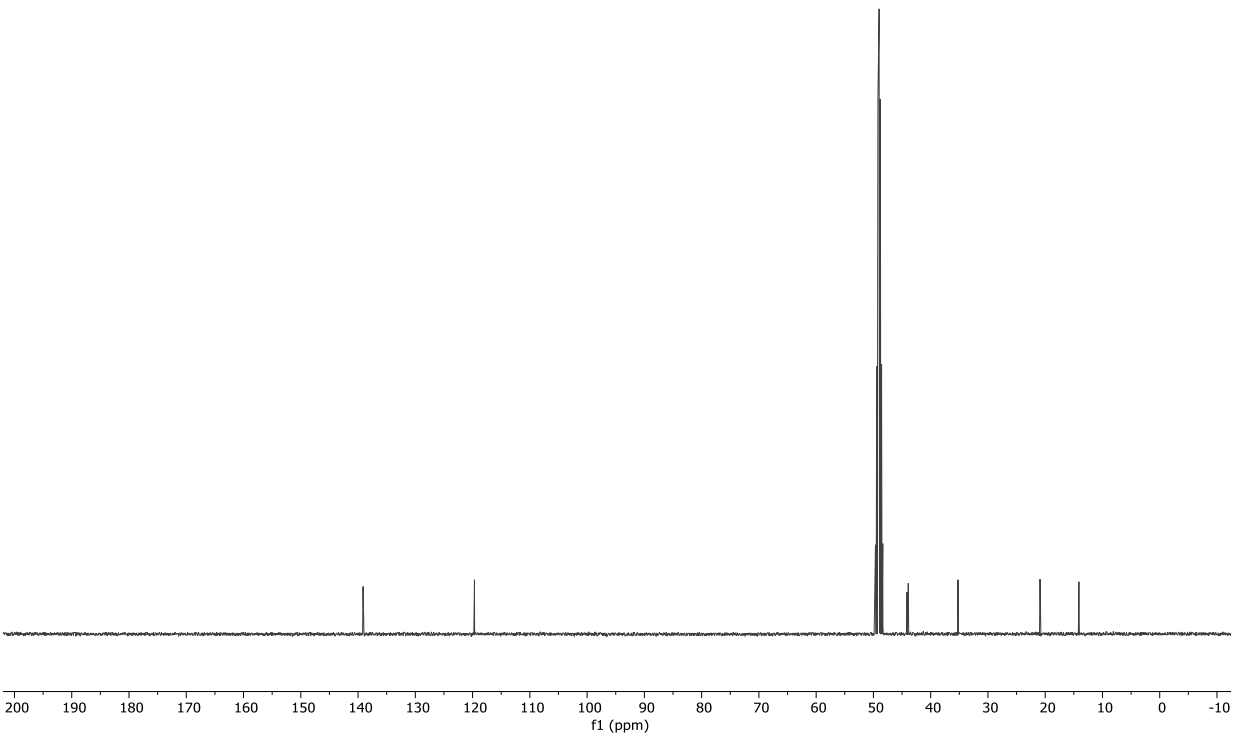

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

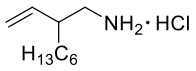

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)


NH2· HCl
H7C3

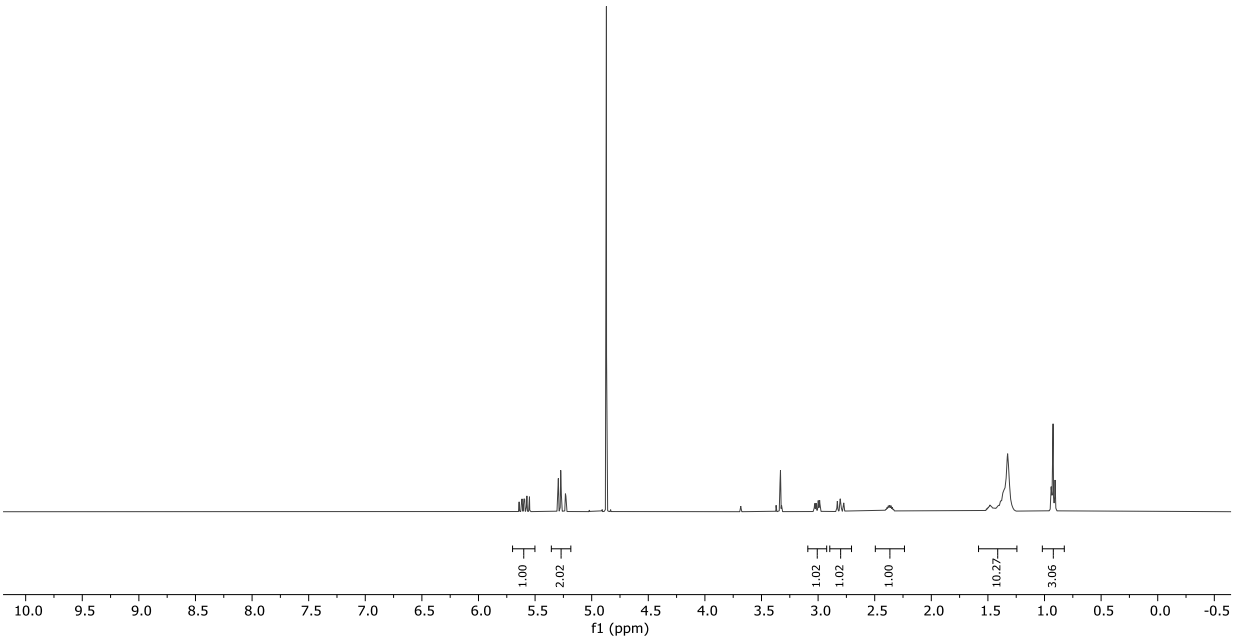
S4e

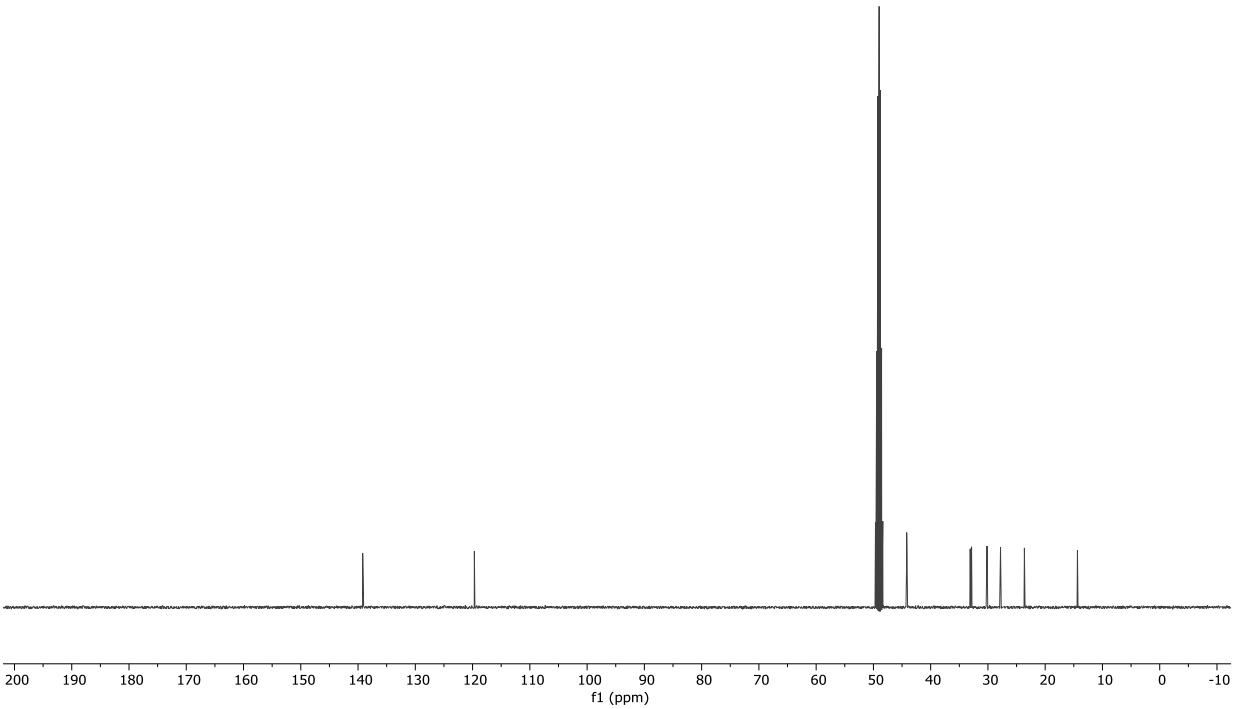

1.00
2.06
1.06
1.02
1.01
4.29
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

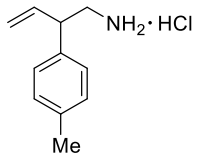

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH2· HCl
H13C6

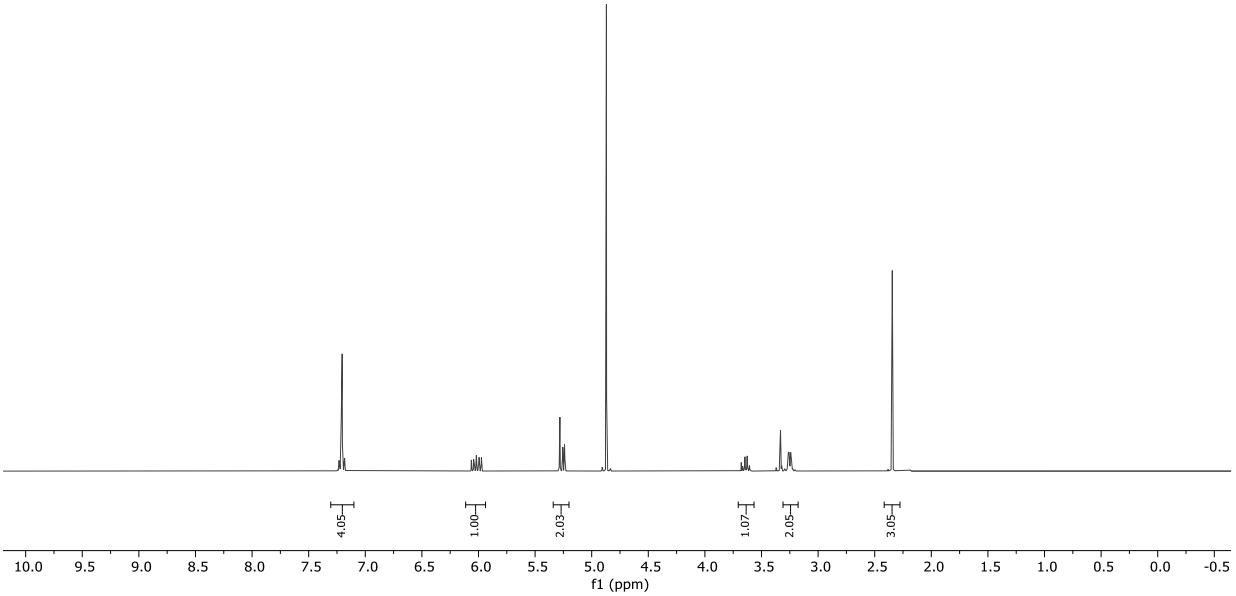
S4f

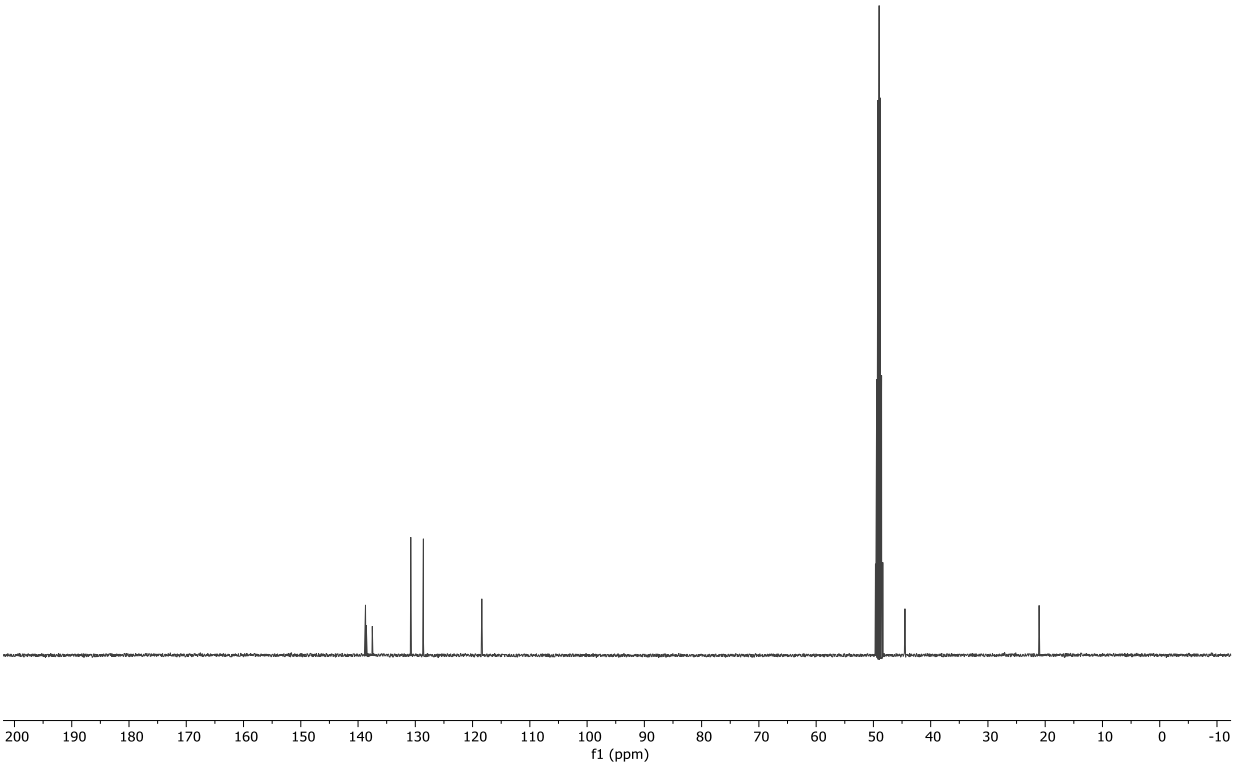

1.00
2.02
1.02
1.02
1.00
10.27
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

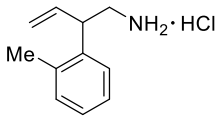

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH2· HCl
Me

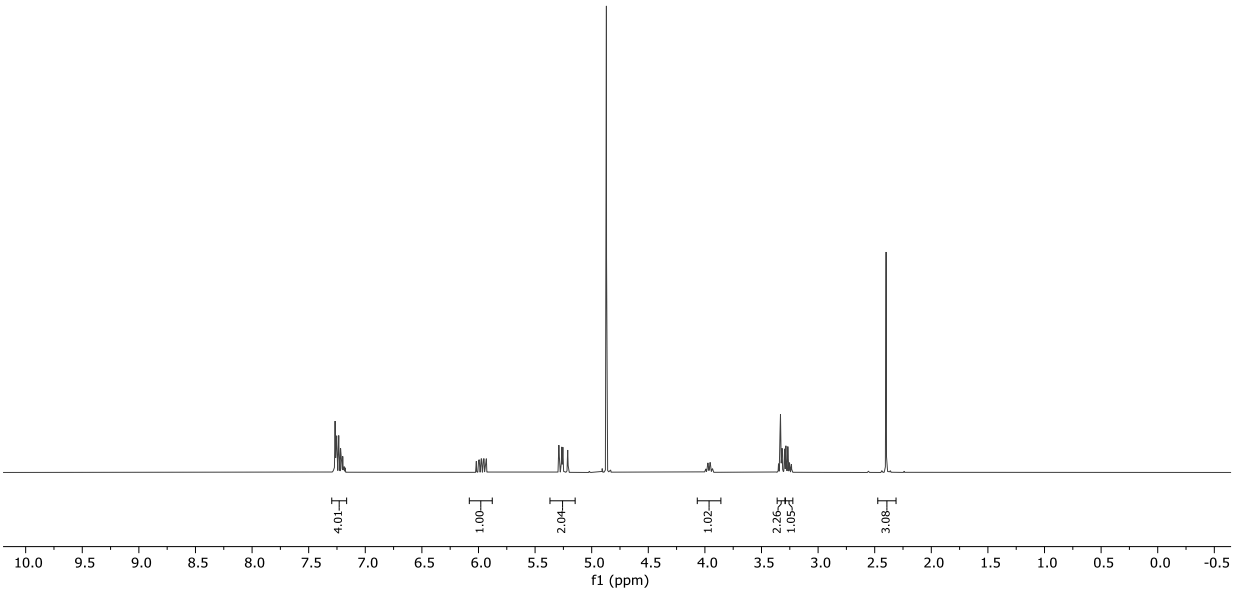
S4i

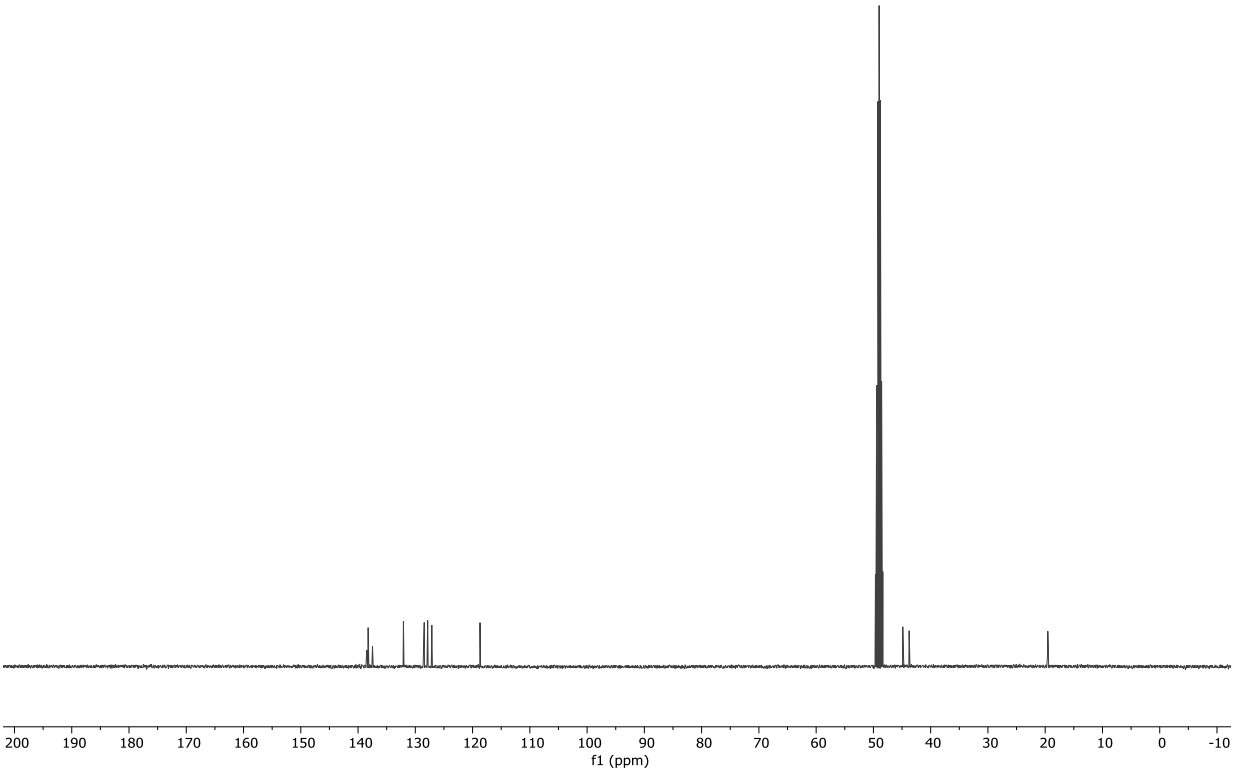

4.05
1.00
2.03
1.07
2.05
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

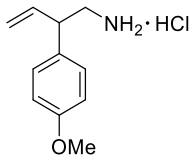

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH2· HCl
Me

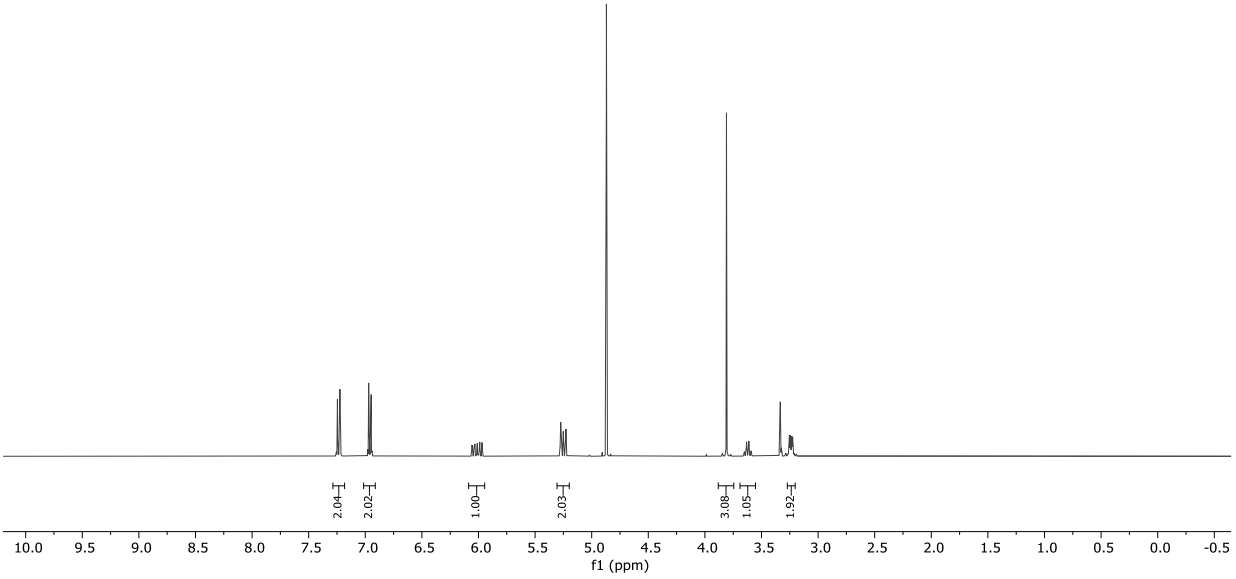
S4j

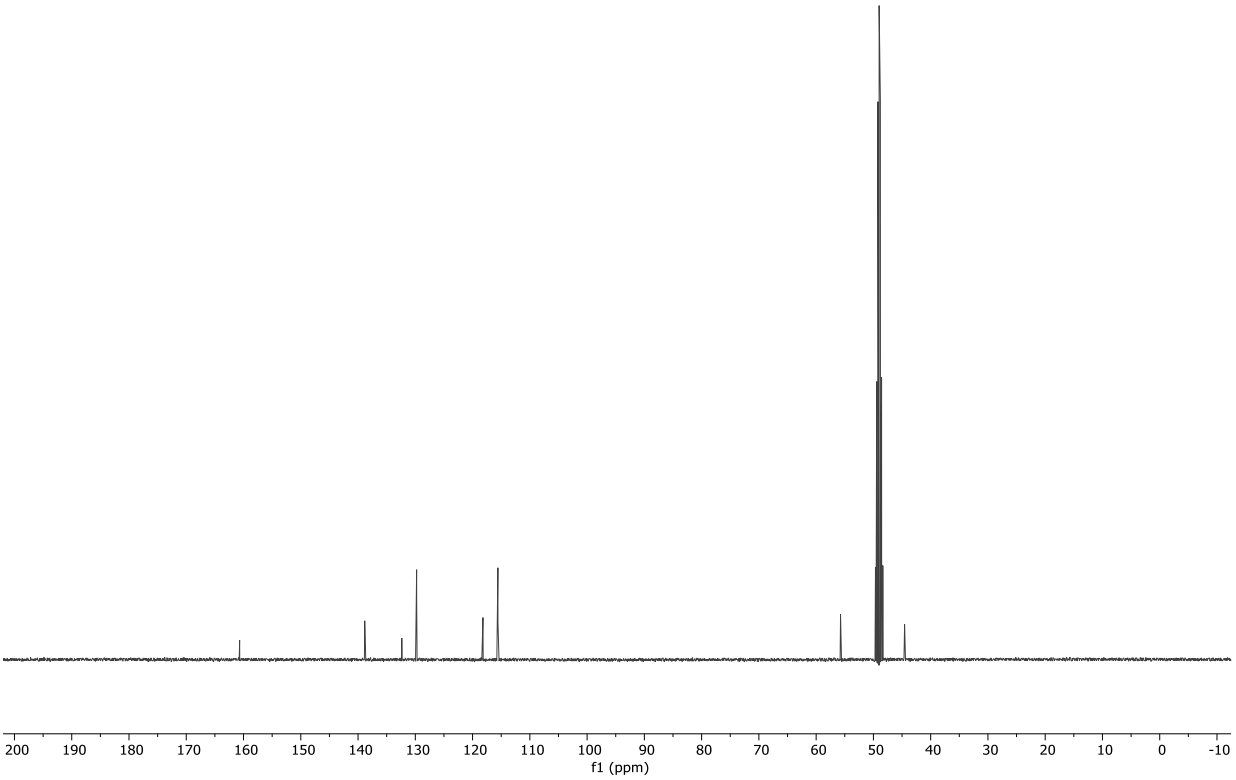

4.01
1.00
2.04
1.02
2.26
1.05
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

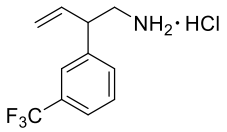

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH2· HCl
OMe

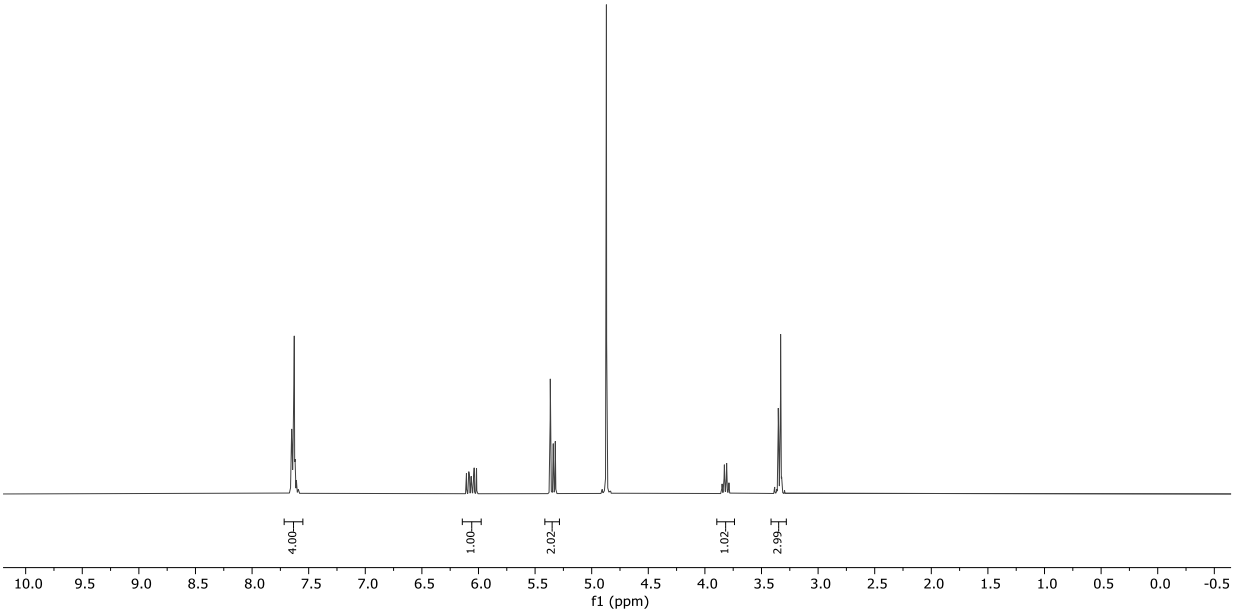
S4k

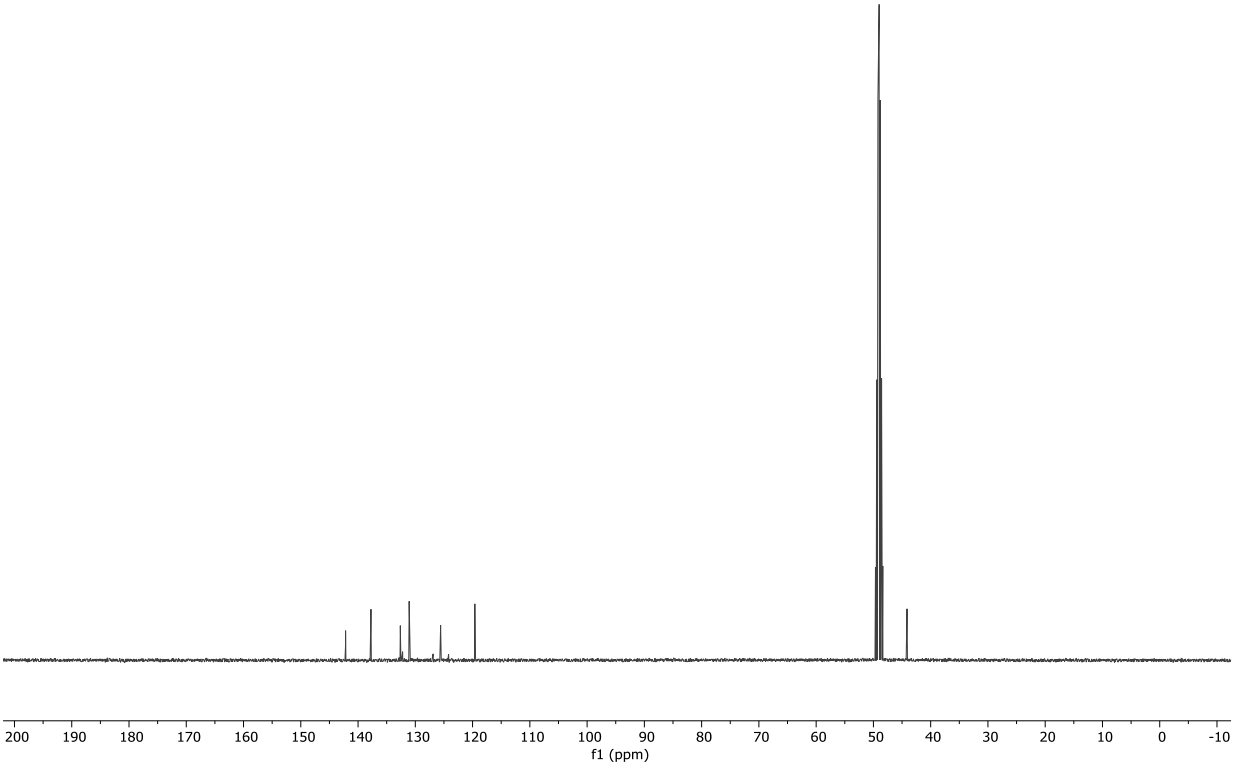

2.04
2.02
1.00
2.03
3.08
1.05
1.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

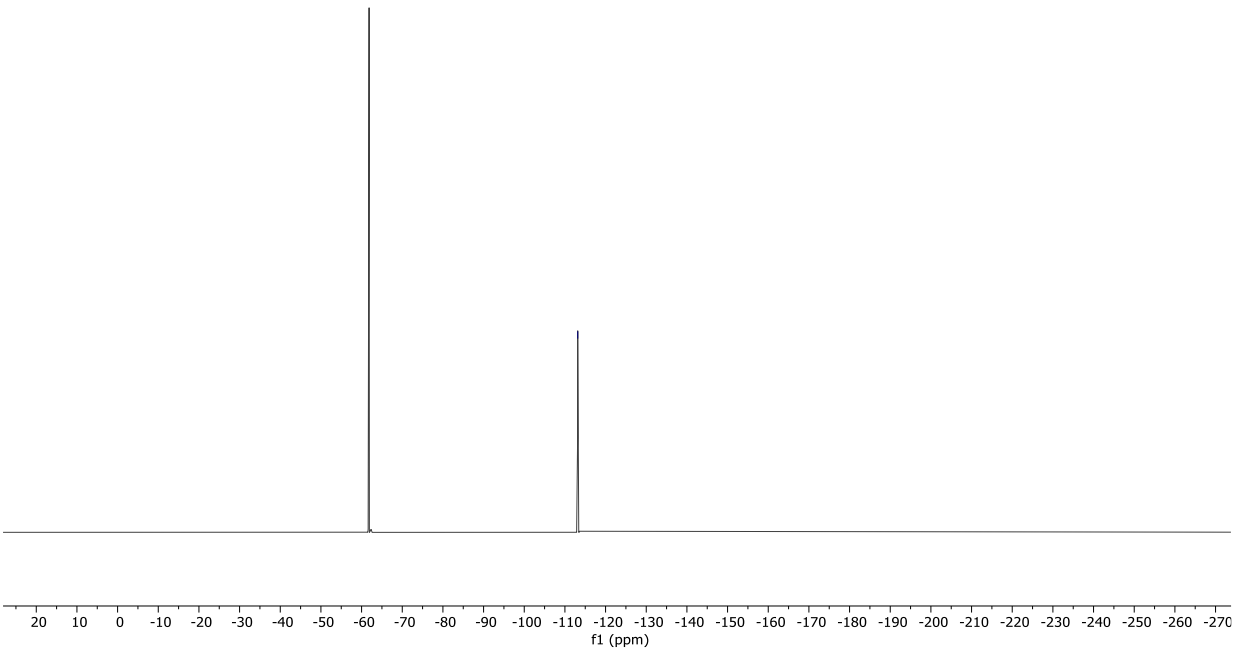

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

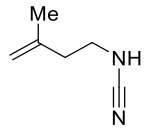

NH2· HCl
F3C

S4l

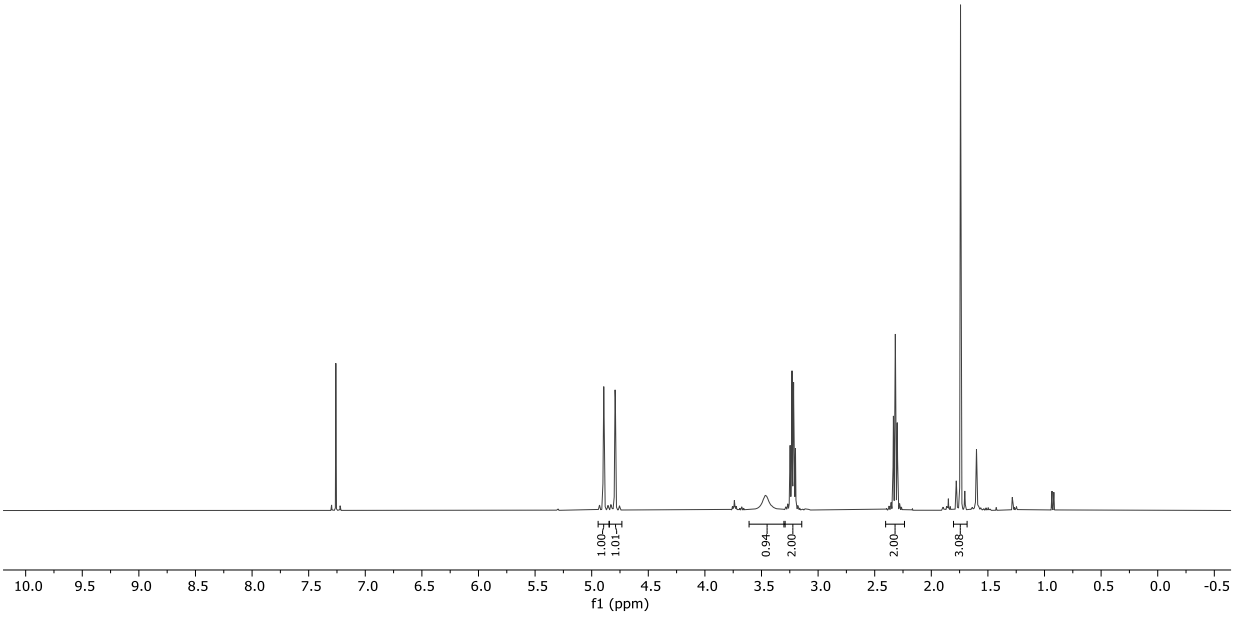

4.00
1.00
2.02
1.02
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

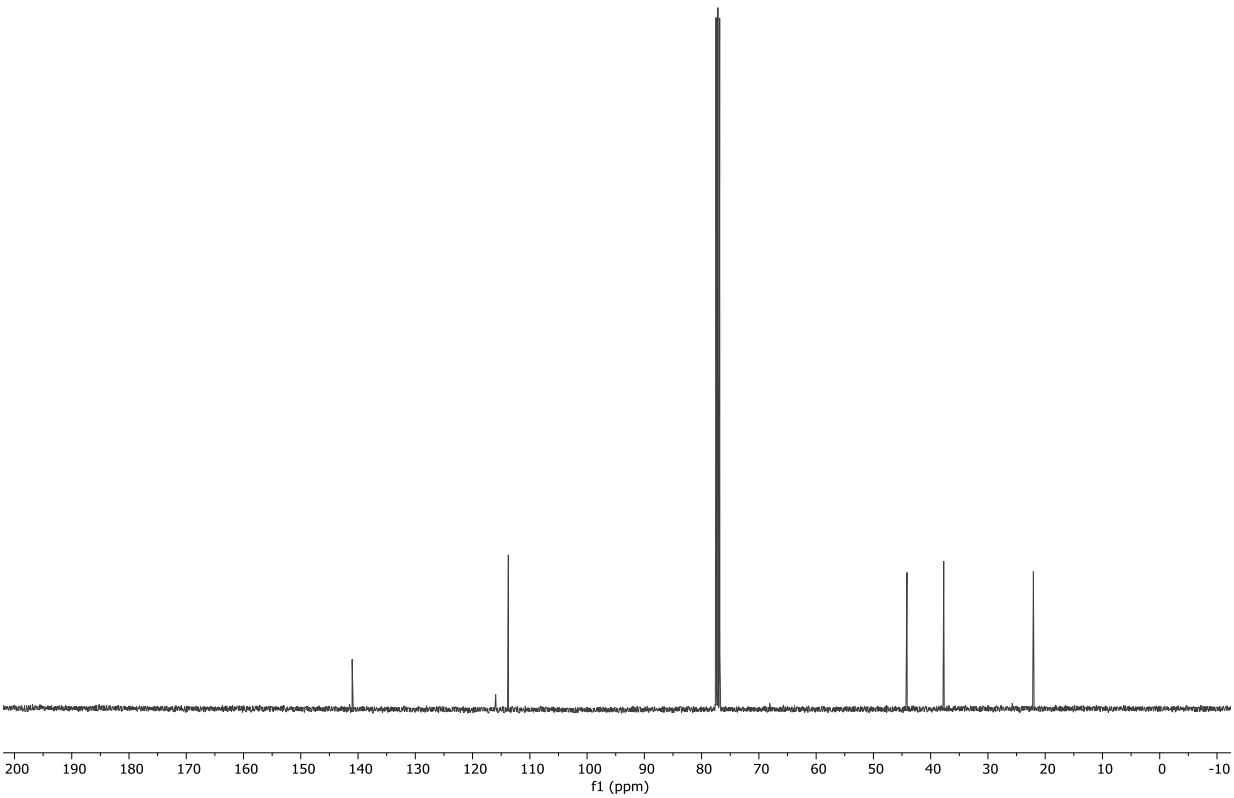

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

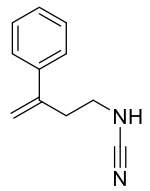

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)


Me
NH
N

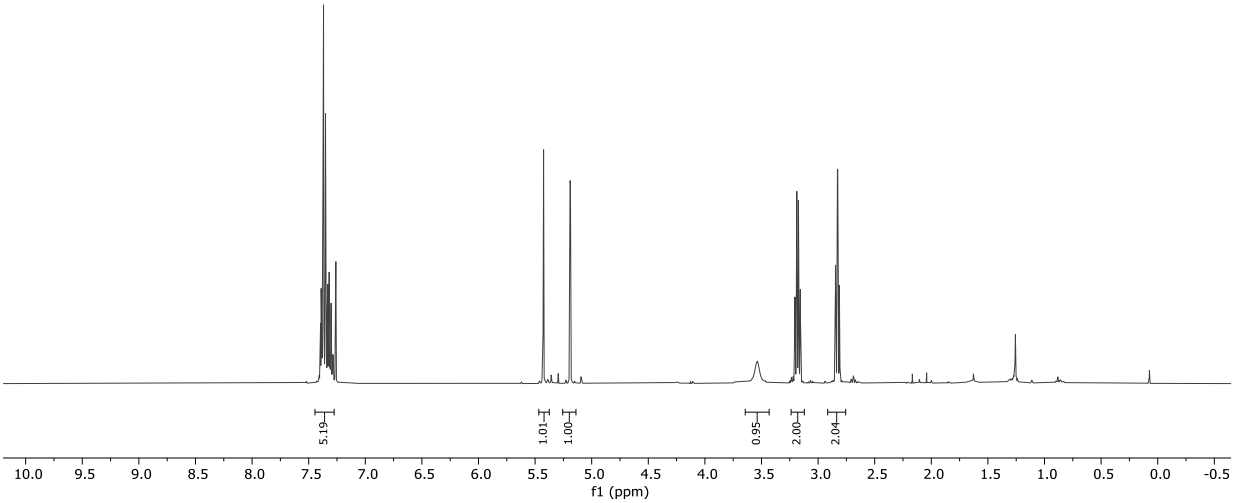
S6b

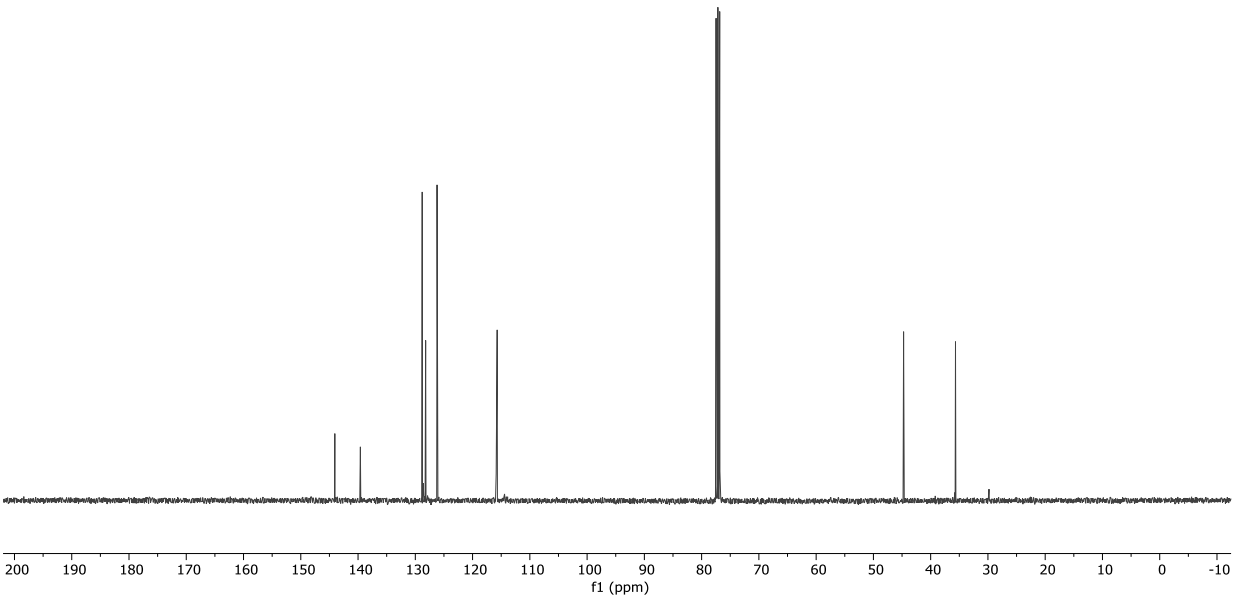

1.00
1.01
0.94
2.00
2.00
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

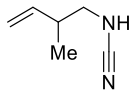

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
N

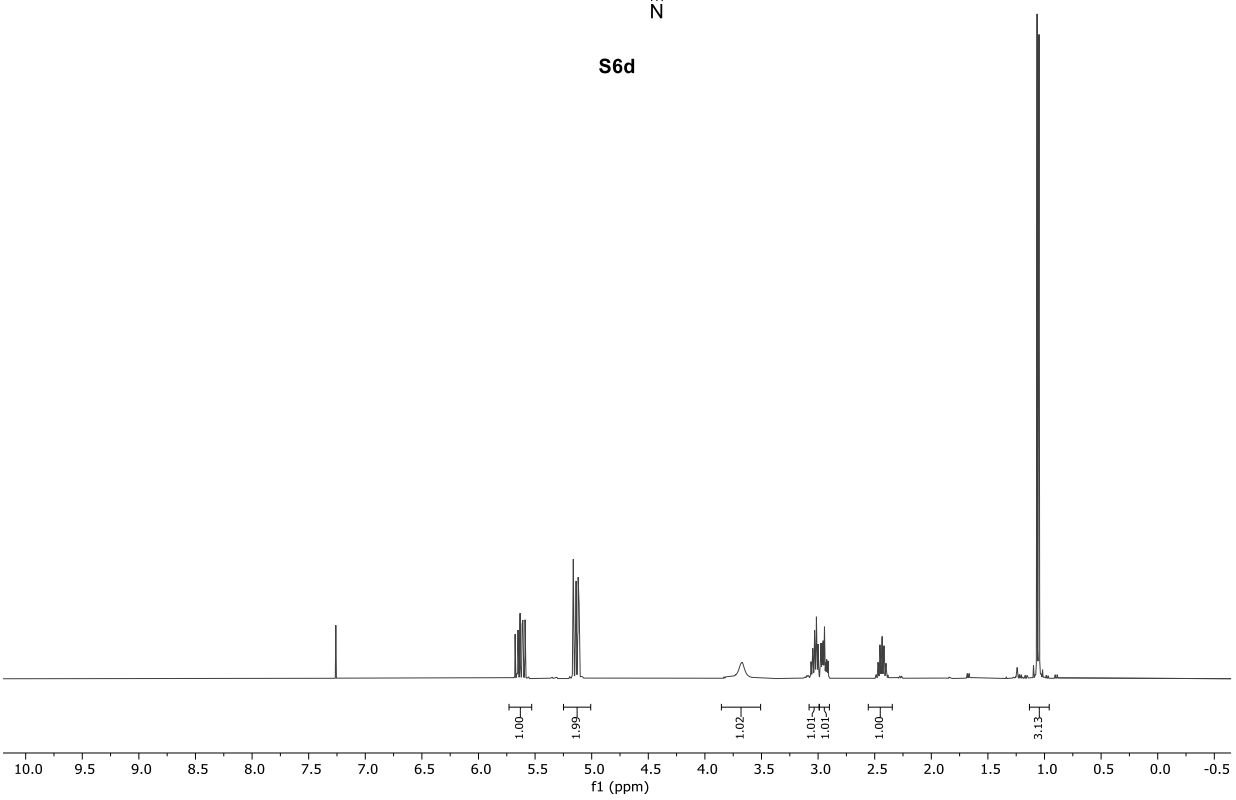
S6c

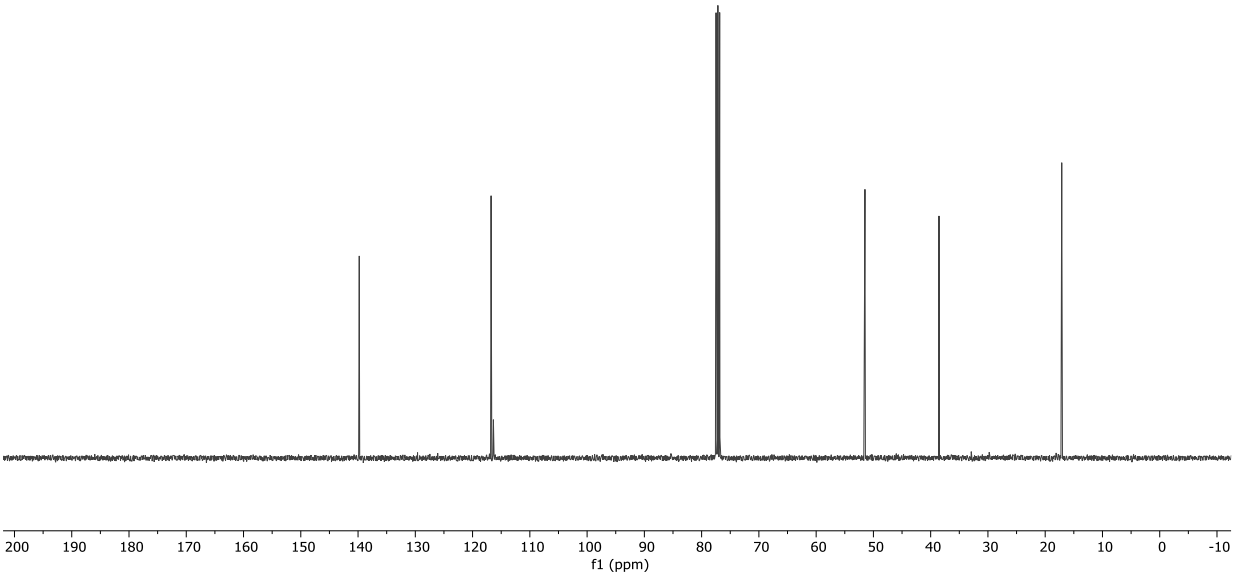

5.19
1.01
1.00
0.95
2.00
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

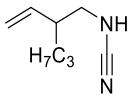

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
Me
N

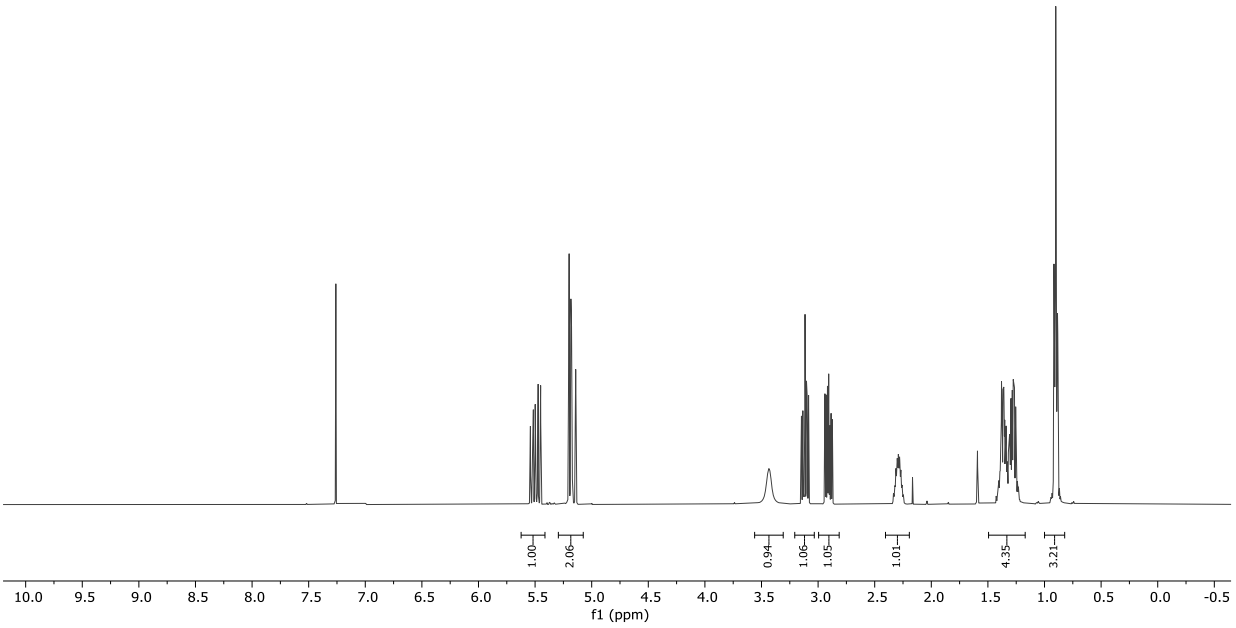
S6d

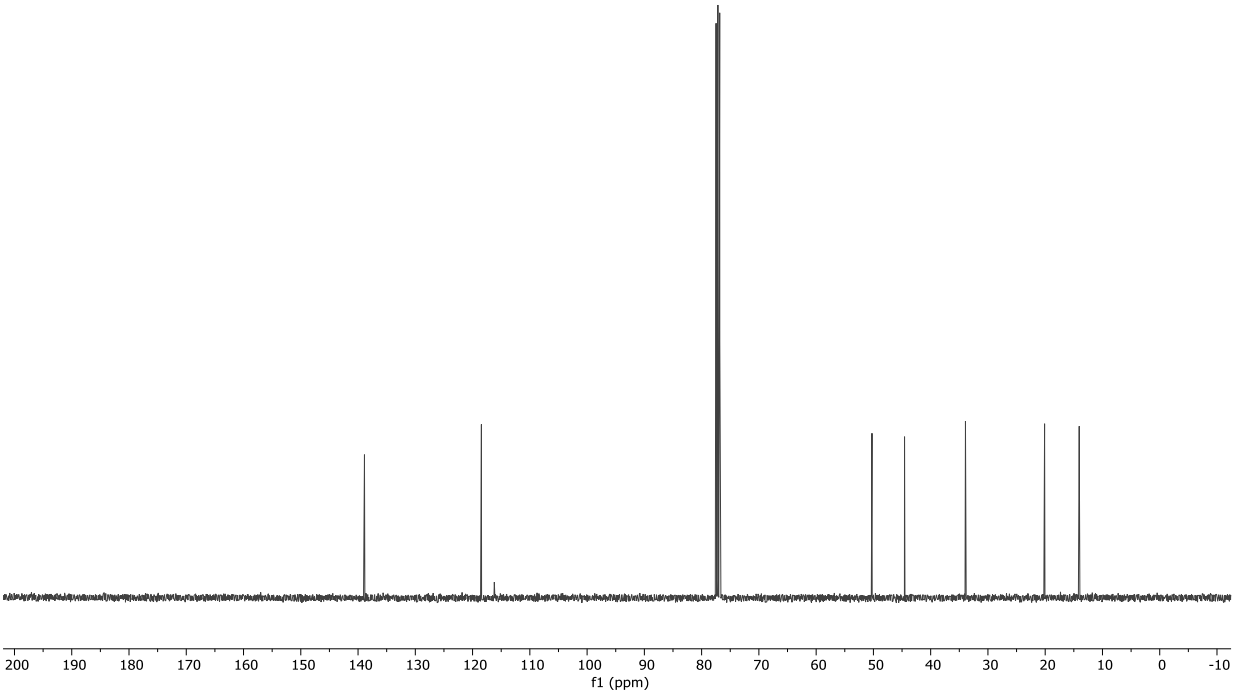

1.00
1.99
1.02
1.01
1.01
1.00
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

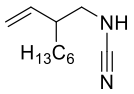

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
H_7C_3
N

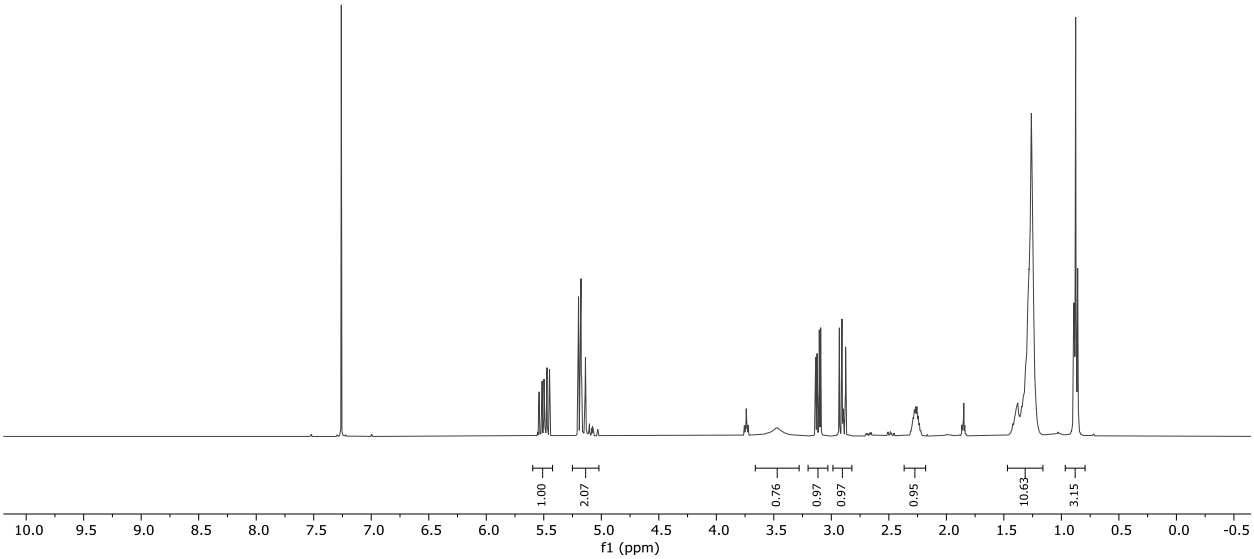
S6e

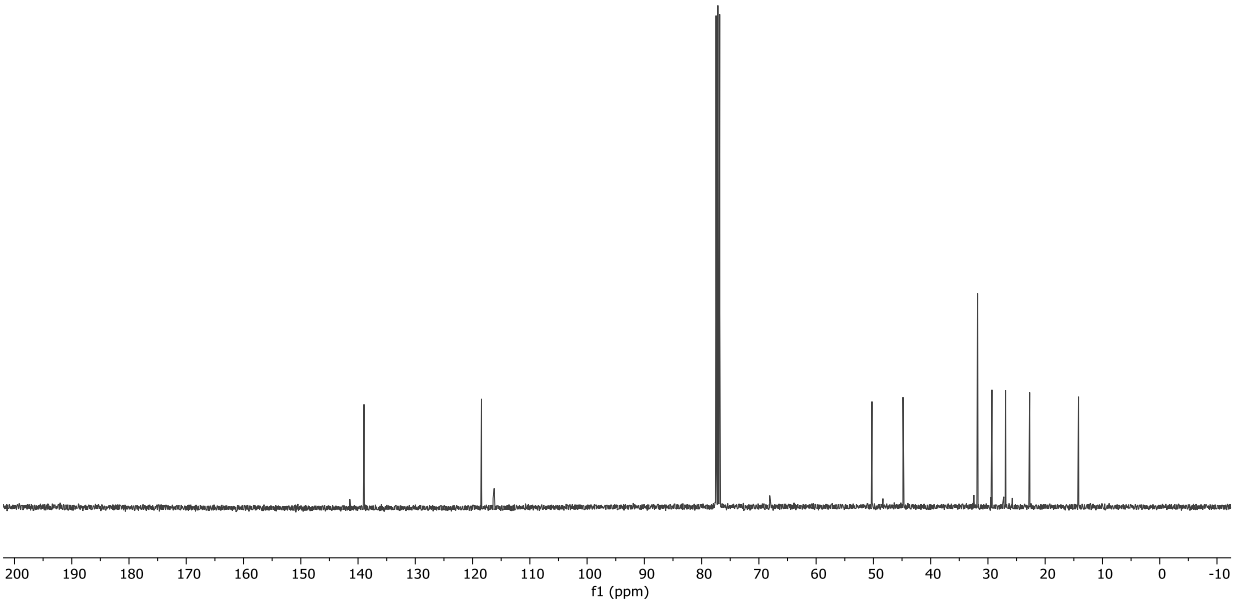

1.00
2.06
0.94
1.06
1.05
1.01
4.35
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

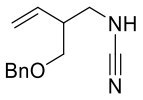

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
$H_{13}C_6$
N

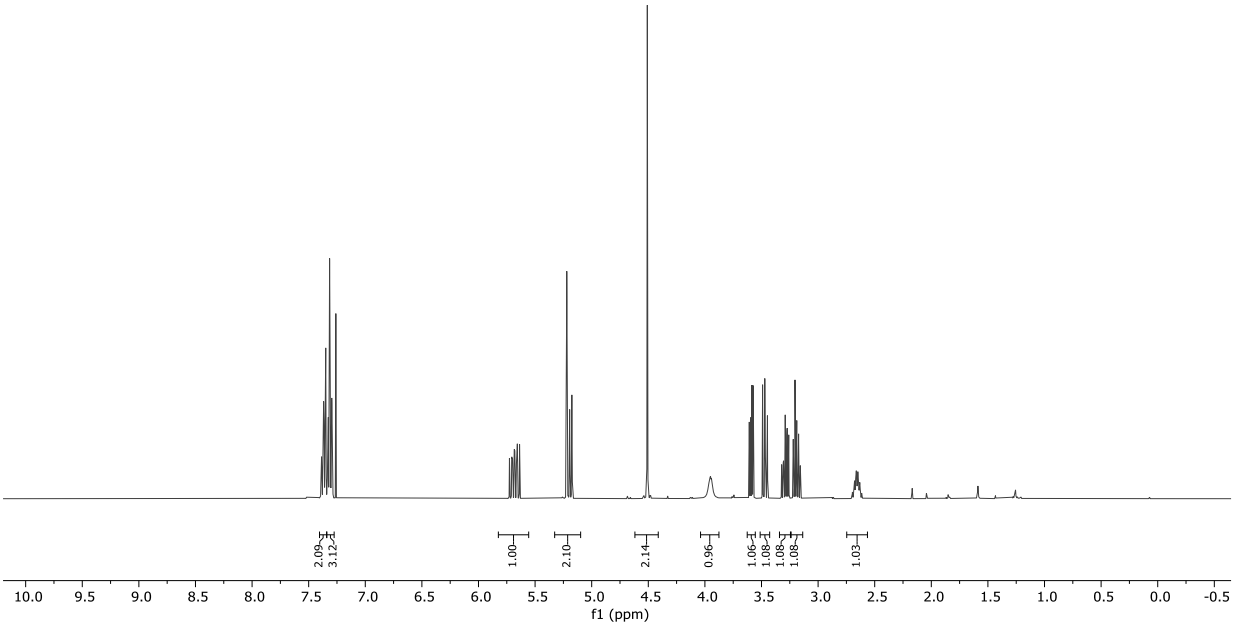
S6f

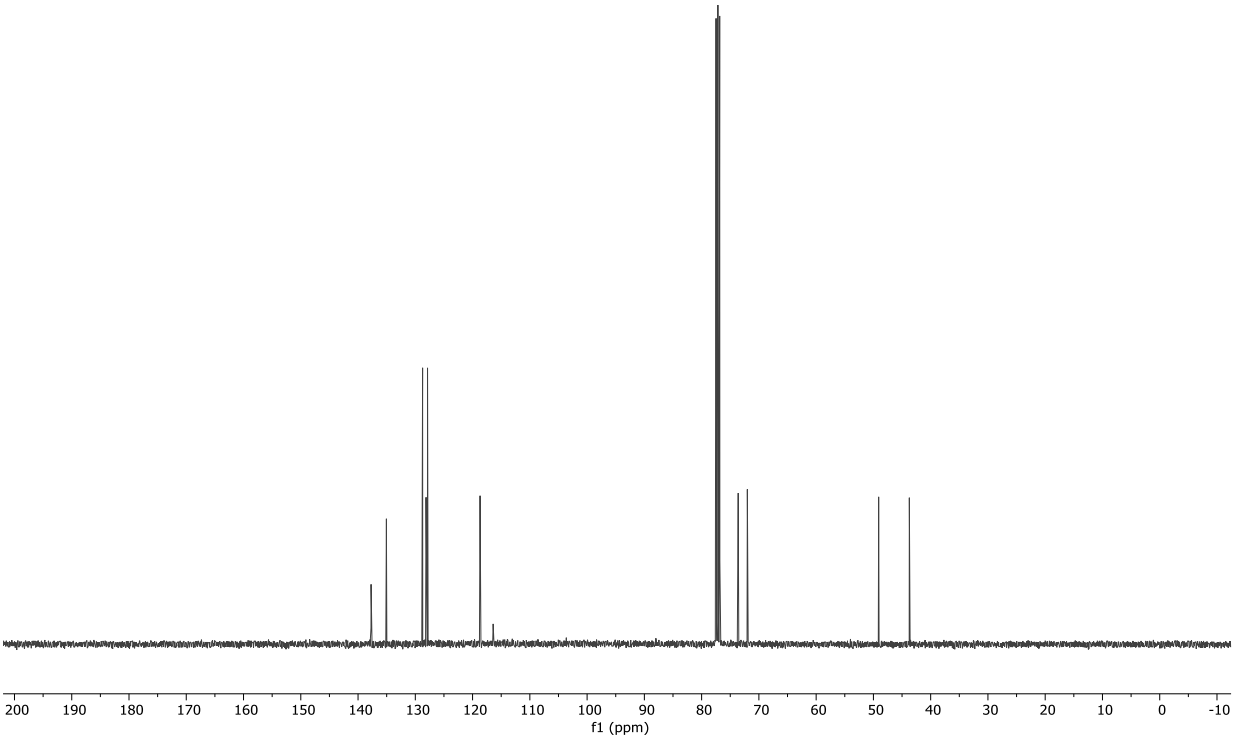

1.00
2.07
0.76
0.97
0.97
0.95
10.63
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

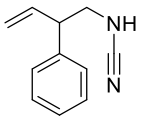

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
BnO
N

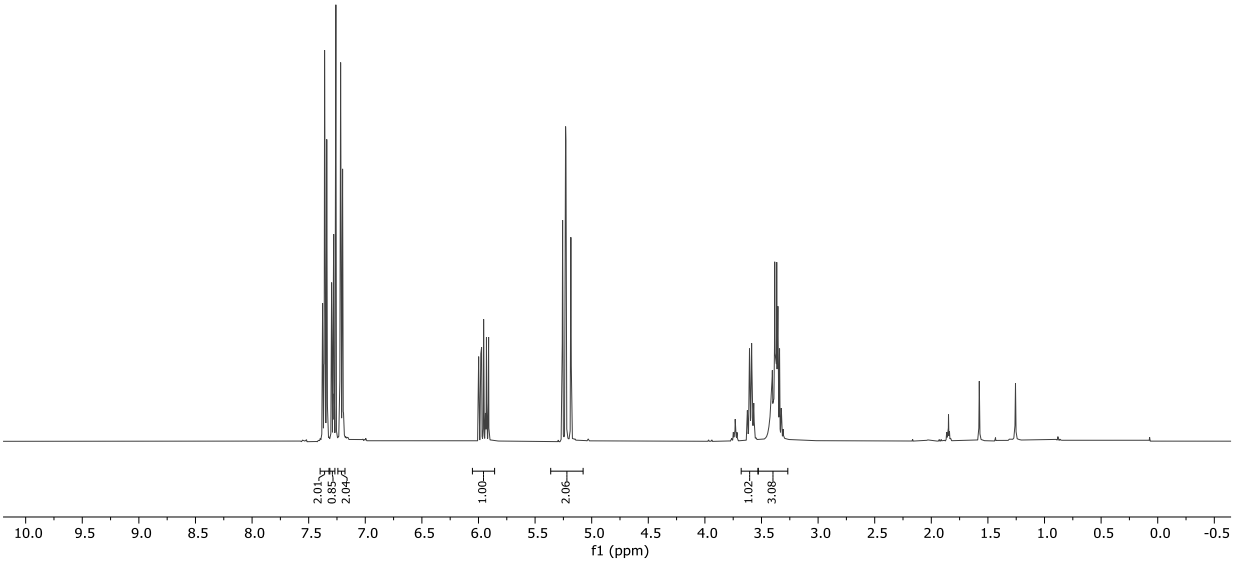
S6g

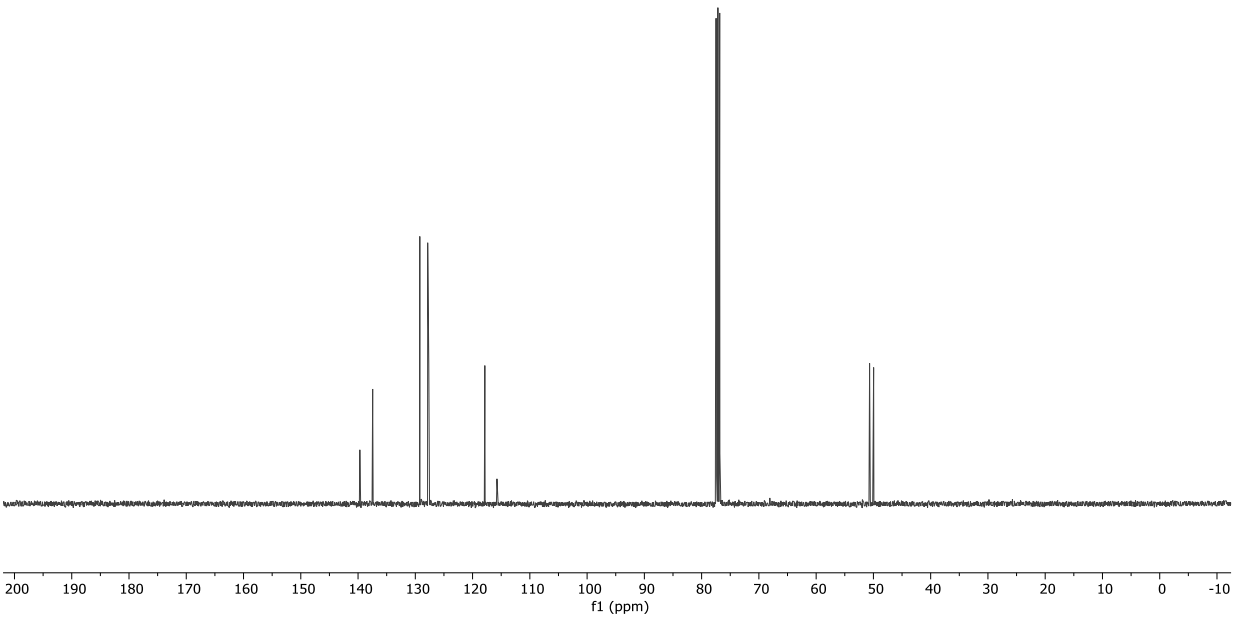

2.09
3.12
1.00
2.10
2.14
0.96
1.06
1.08
1.08
1.08
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

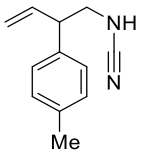

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
N

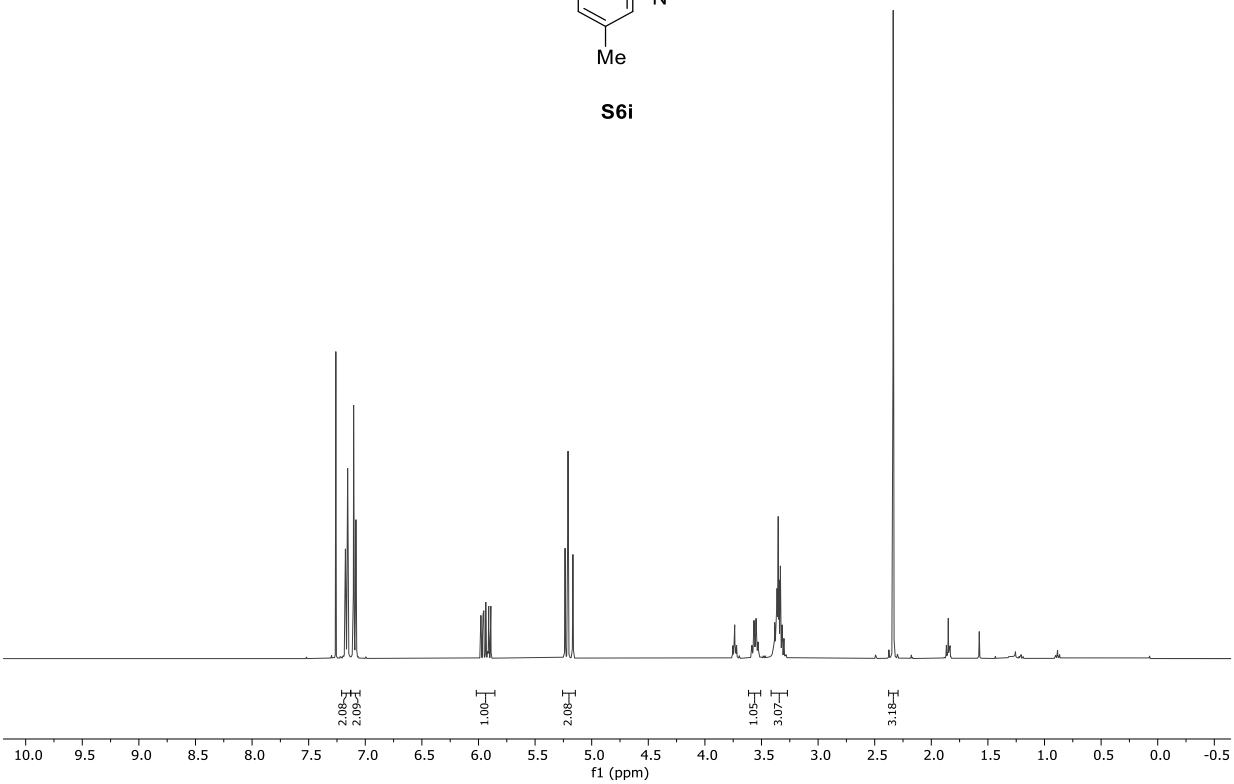
S6h

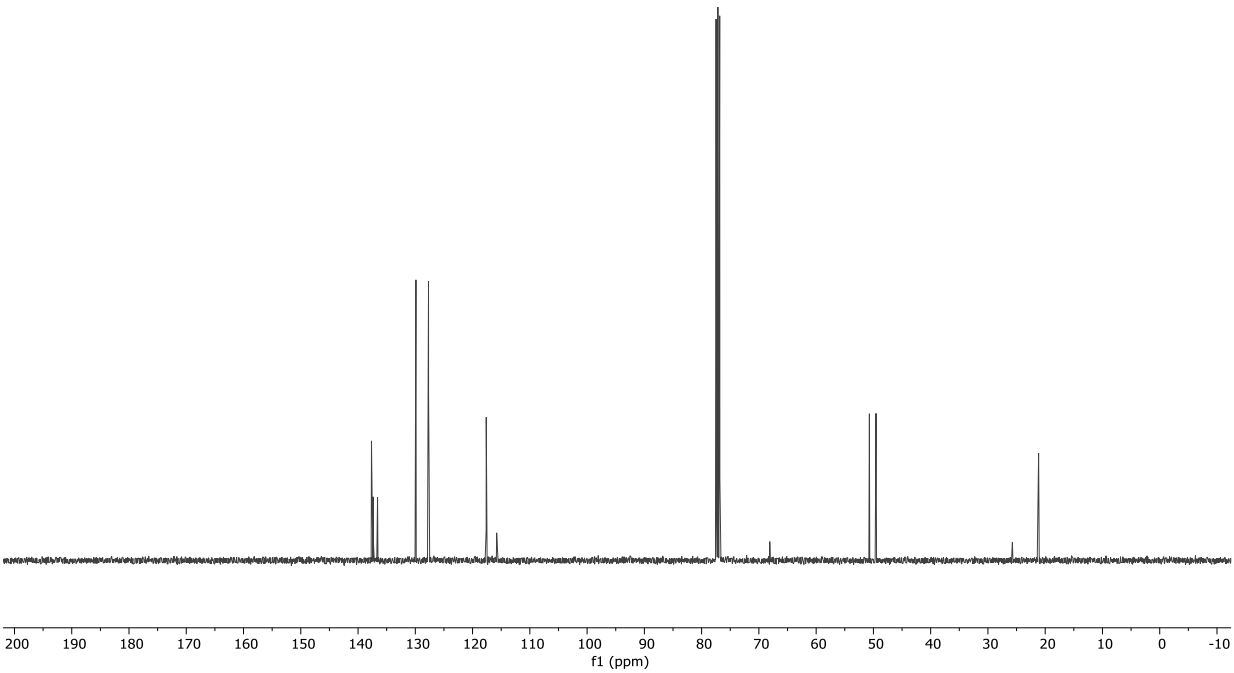

2.01
0.85
2.04
1.00
2.06
1.02
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

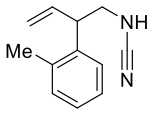

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
N
Me

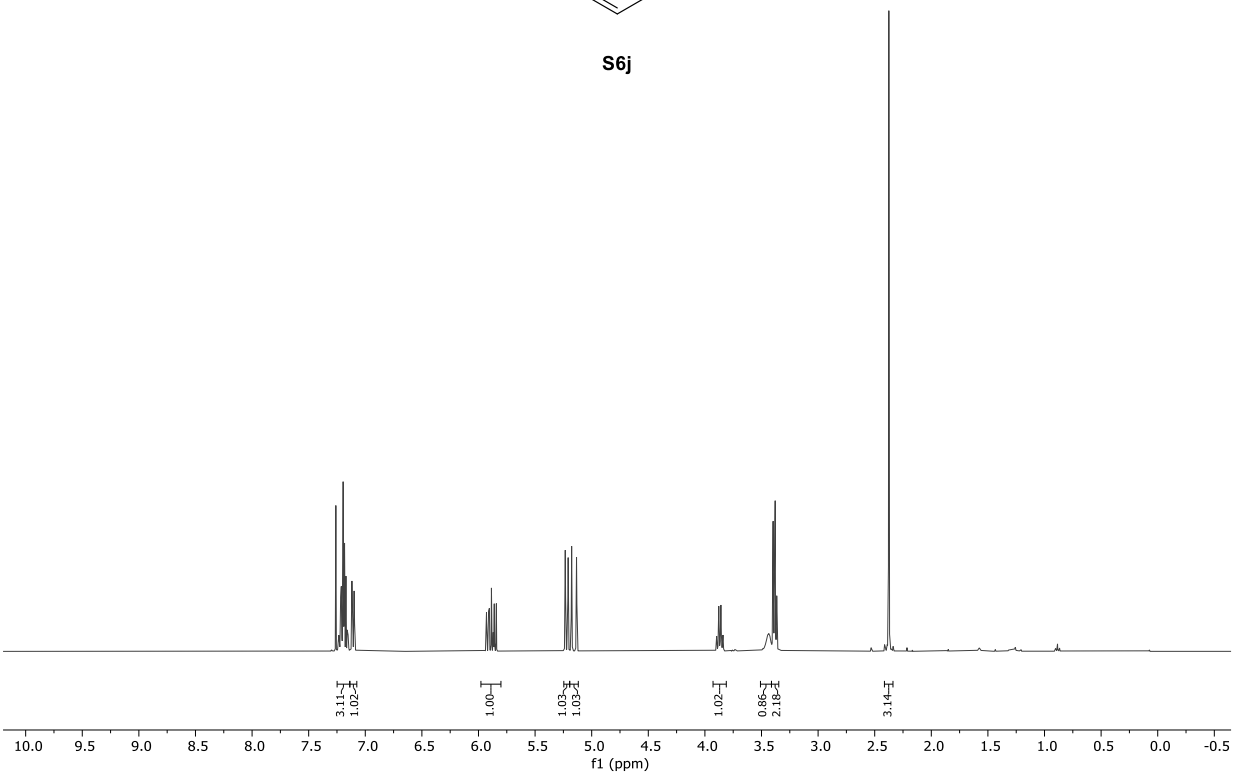
S6i

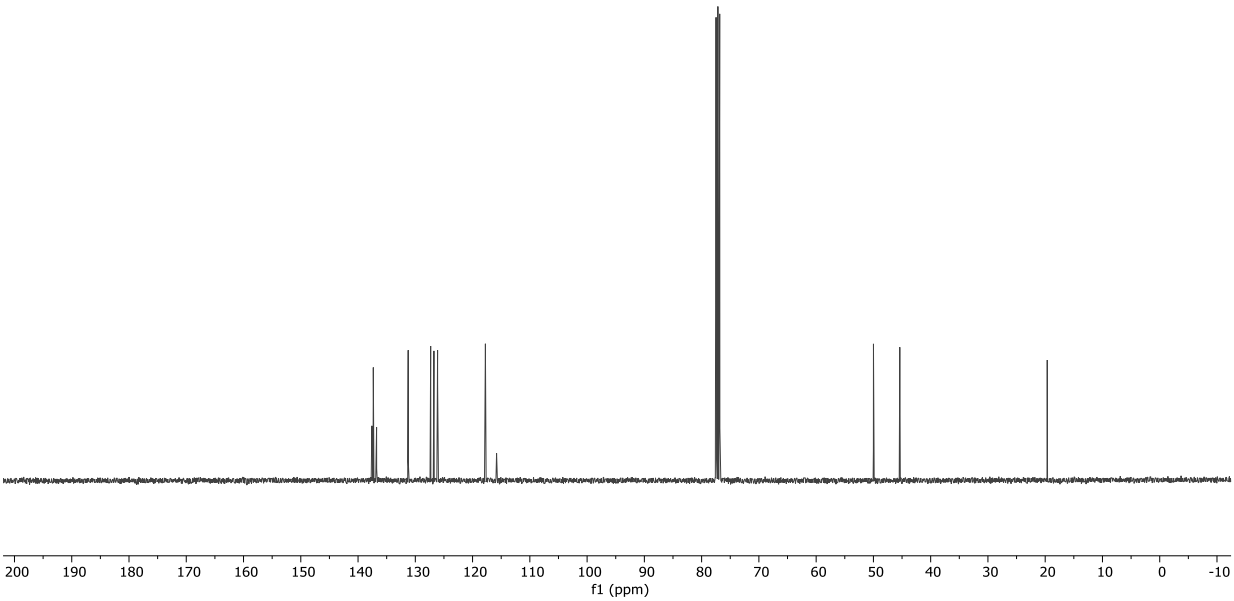

2.08
2.09
1.00
2.08
1.05
3.07
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

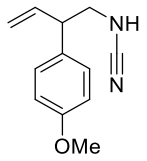

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
Me
N

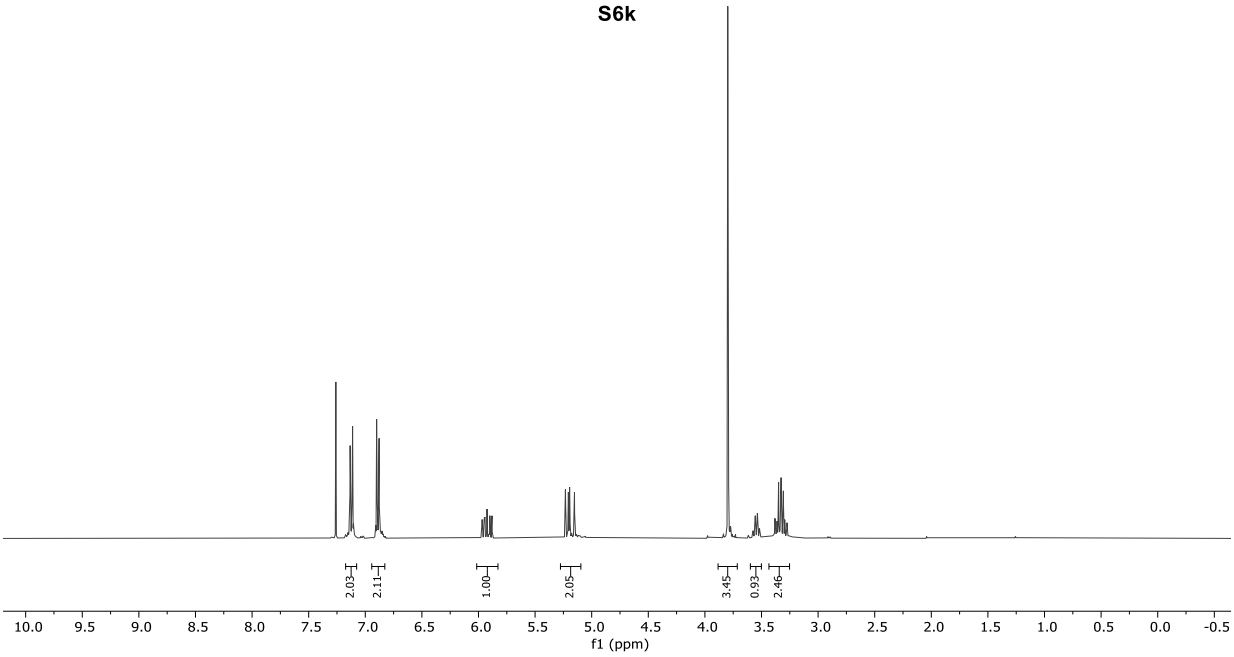
S6j

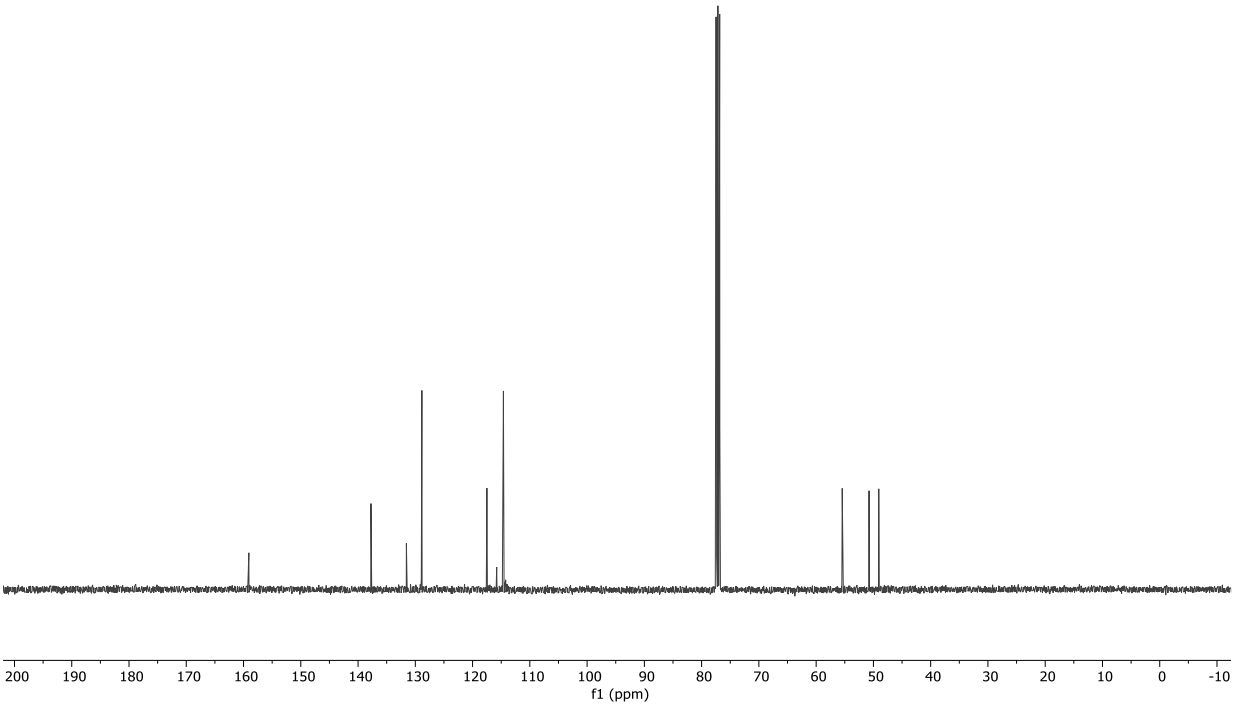

3.11
1.02
1.00
1.03
1.03
1.02
0.86
2.18
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

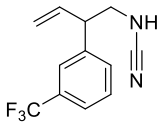

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
N
OMe

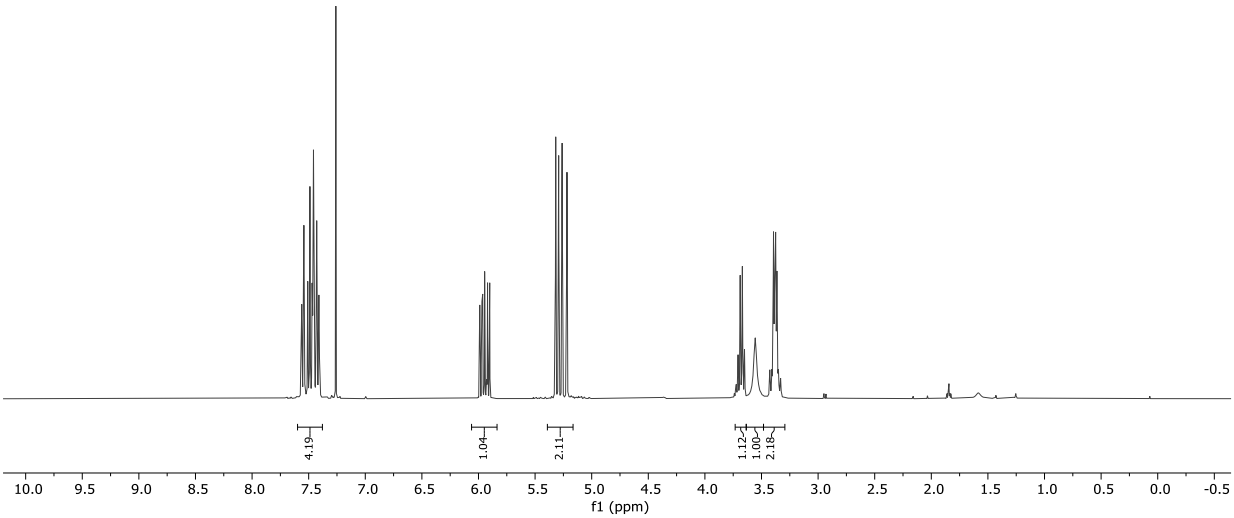
S6k

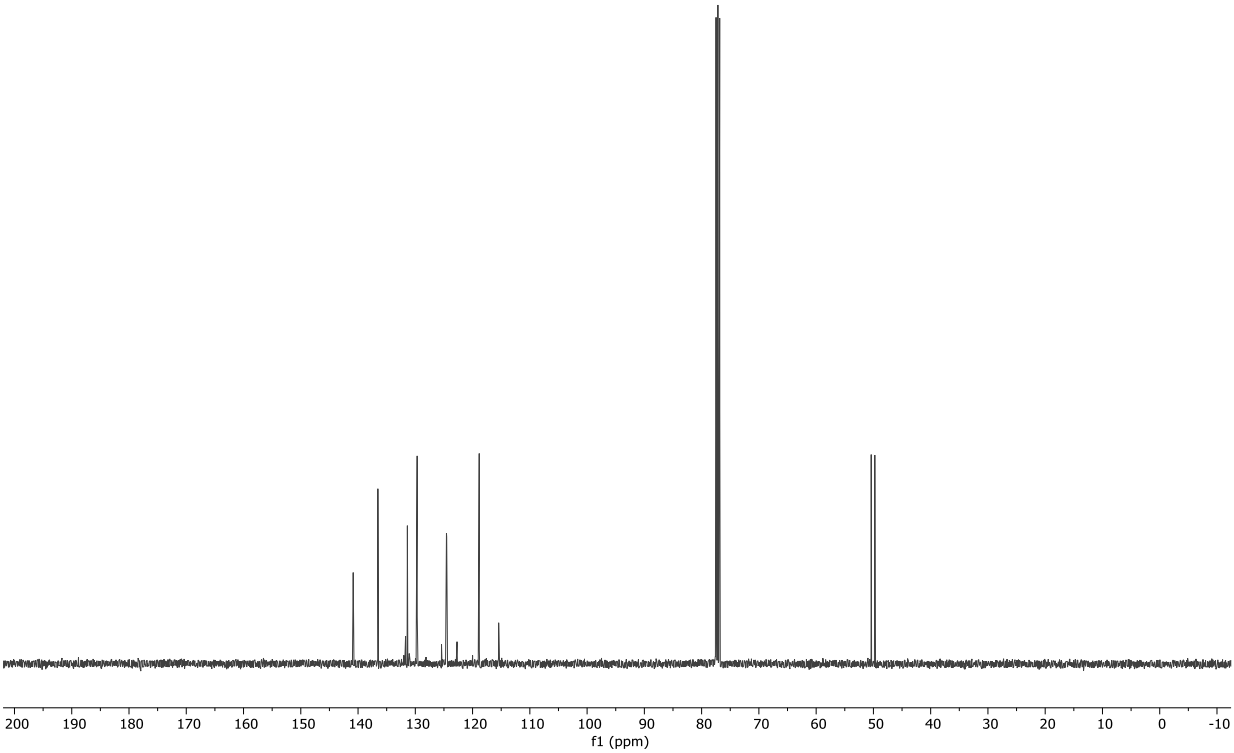

2.03
2.11
1.00
2.05
3.45
0.93
2.46
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

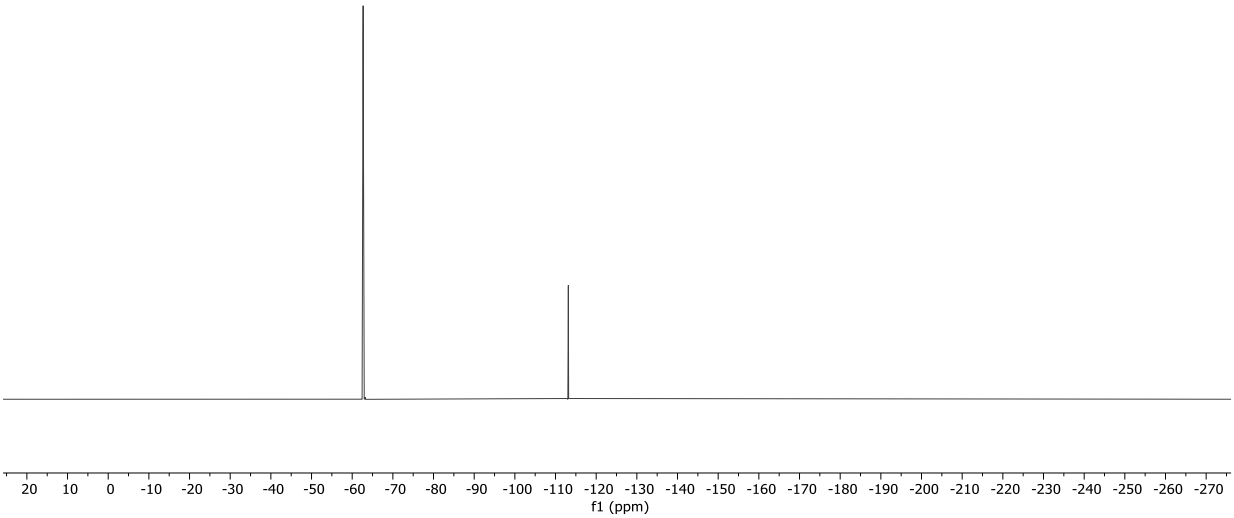

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

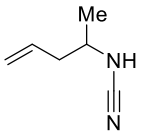

NH
N
F3C

S6l

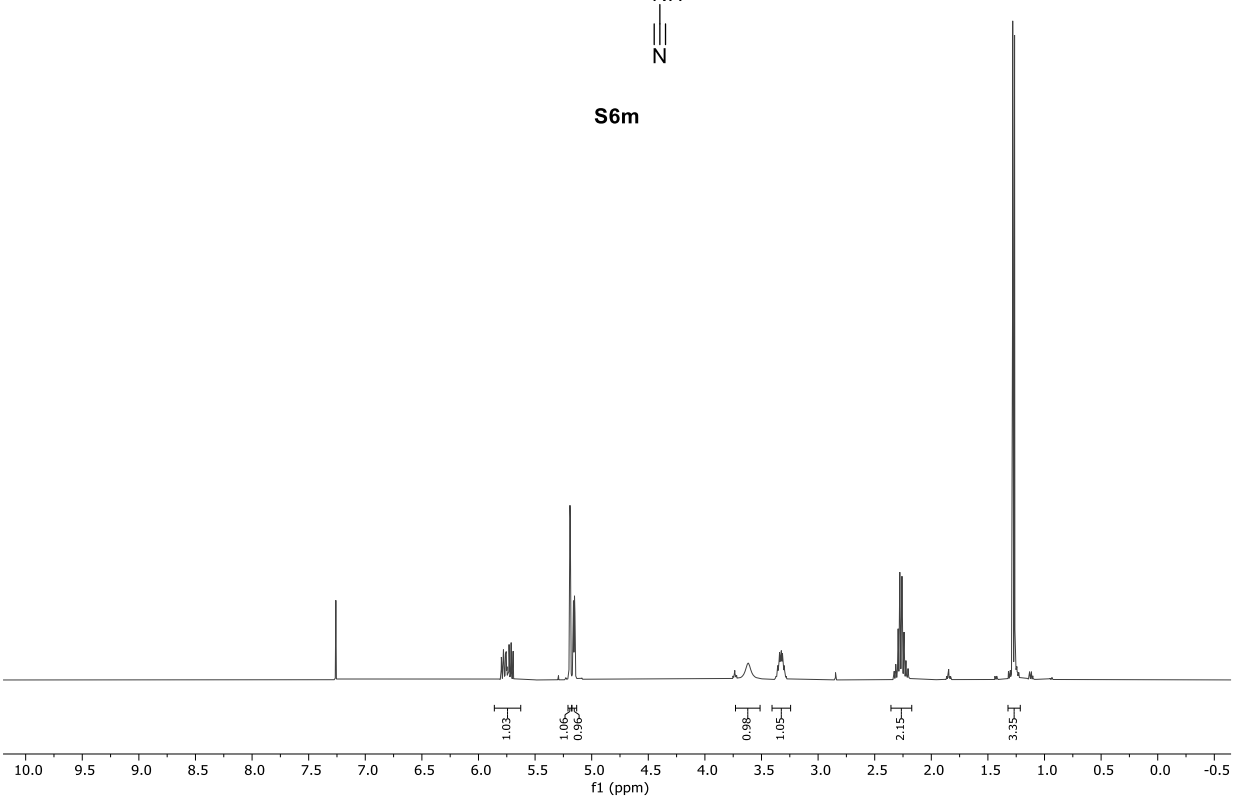

4.19
1.04
2.11
1.12
1.00
2.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

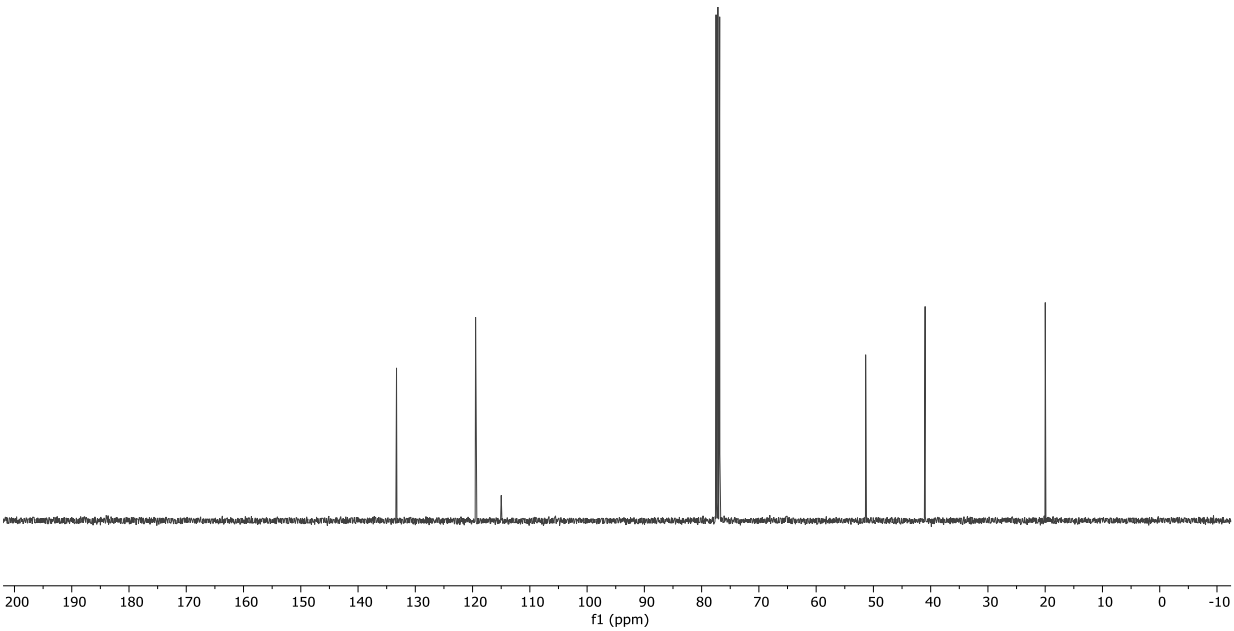

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

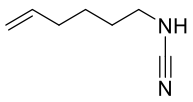

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)


Me
NH
N

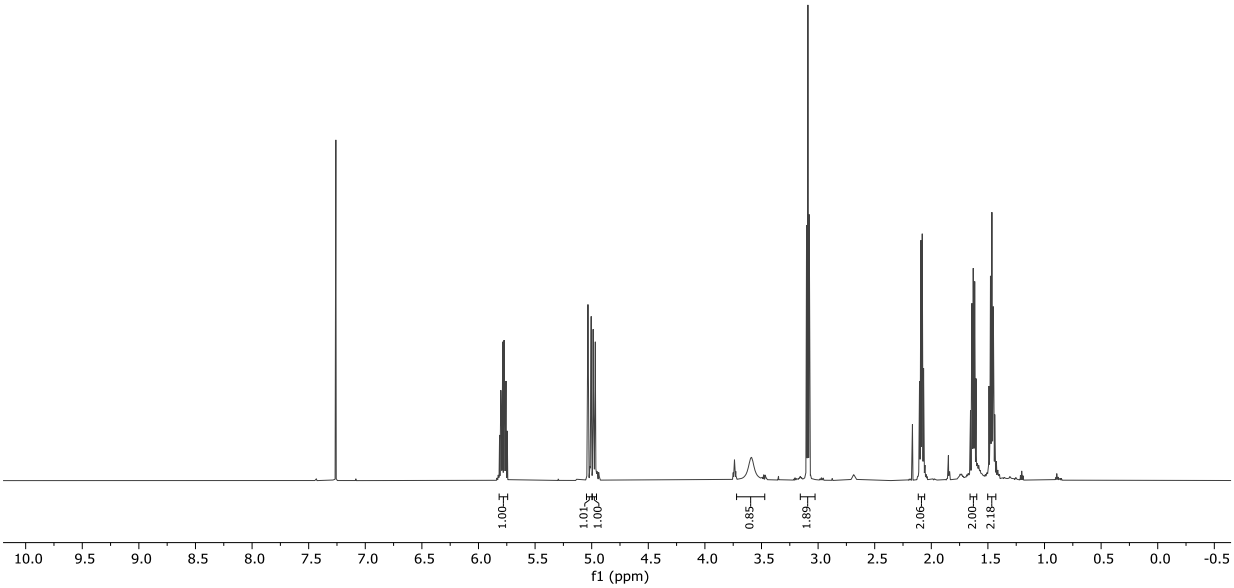
S6m

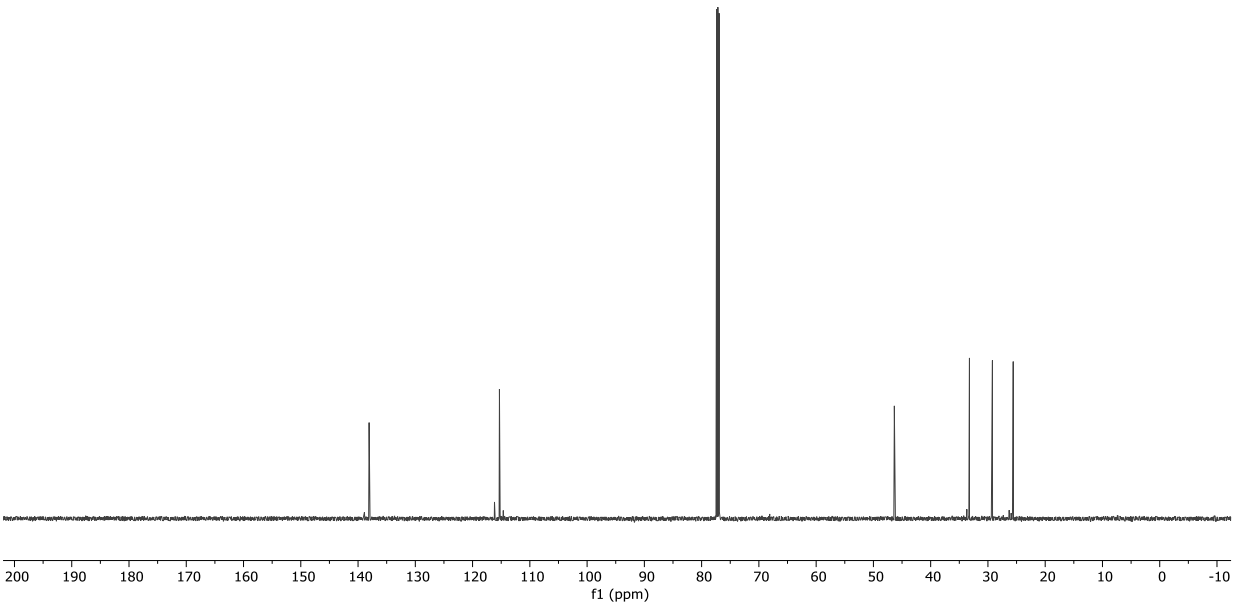

1.03
1.06
0.96
0.98
1.05
2.15
3.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

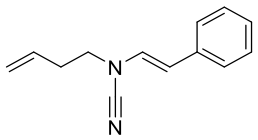

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH
N

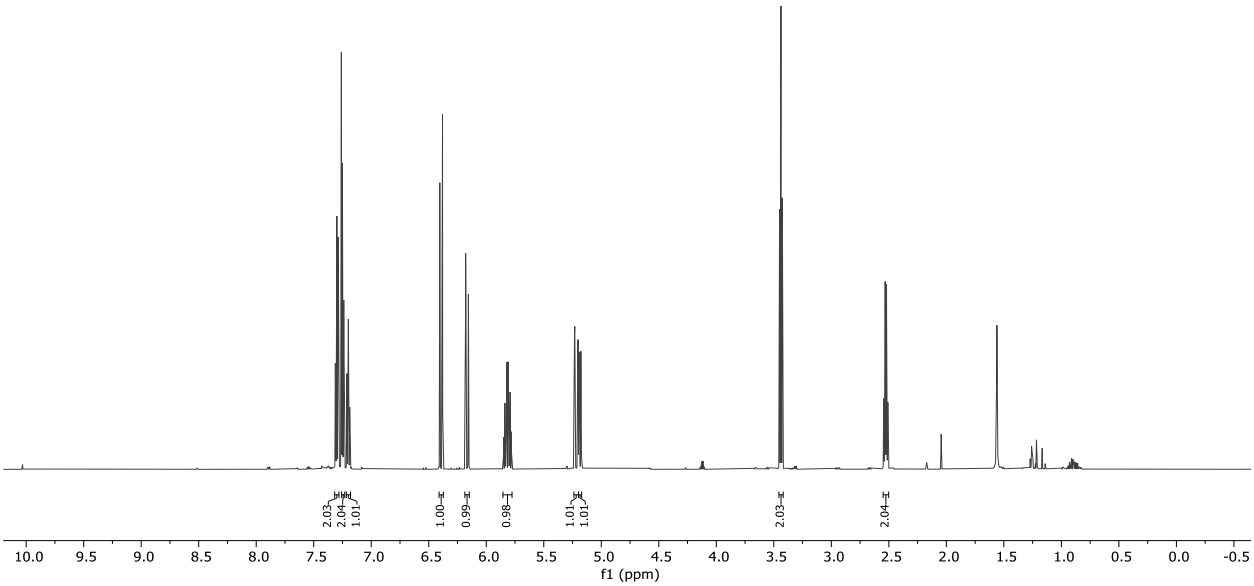
S6r

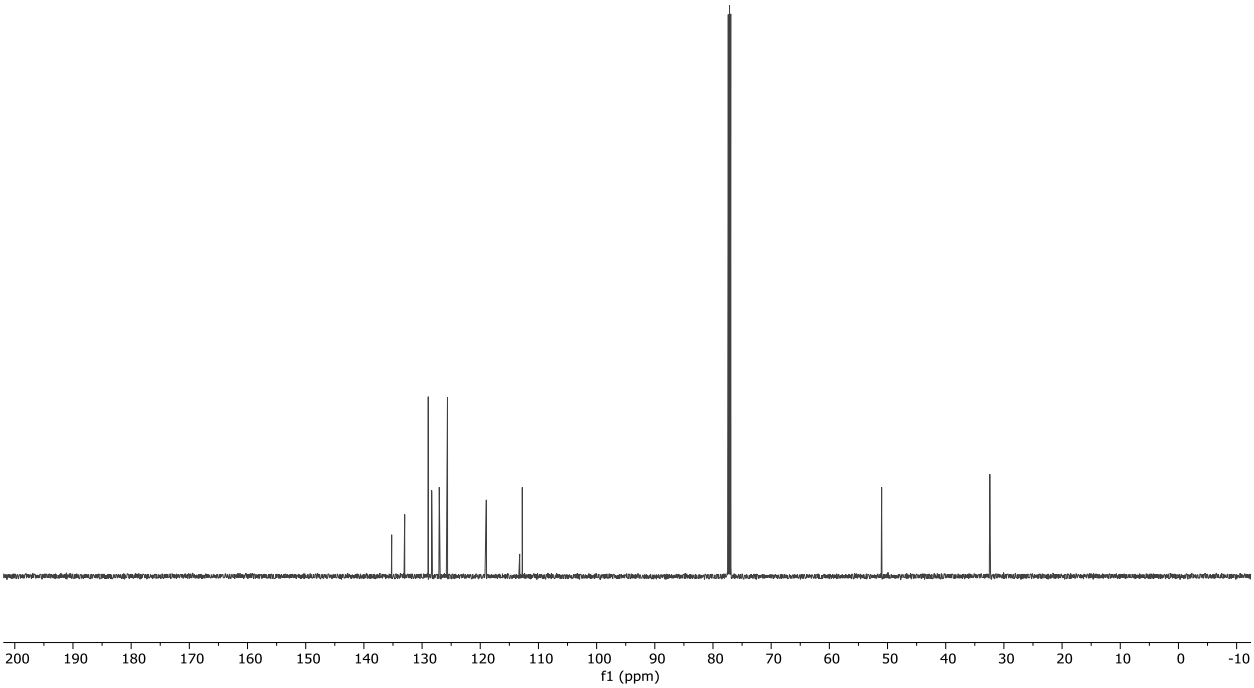

1.00
1.01
1.00
0.85
1.89
2.06
2.00
2.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

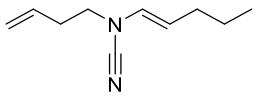

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



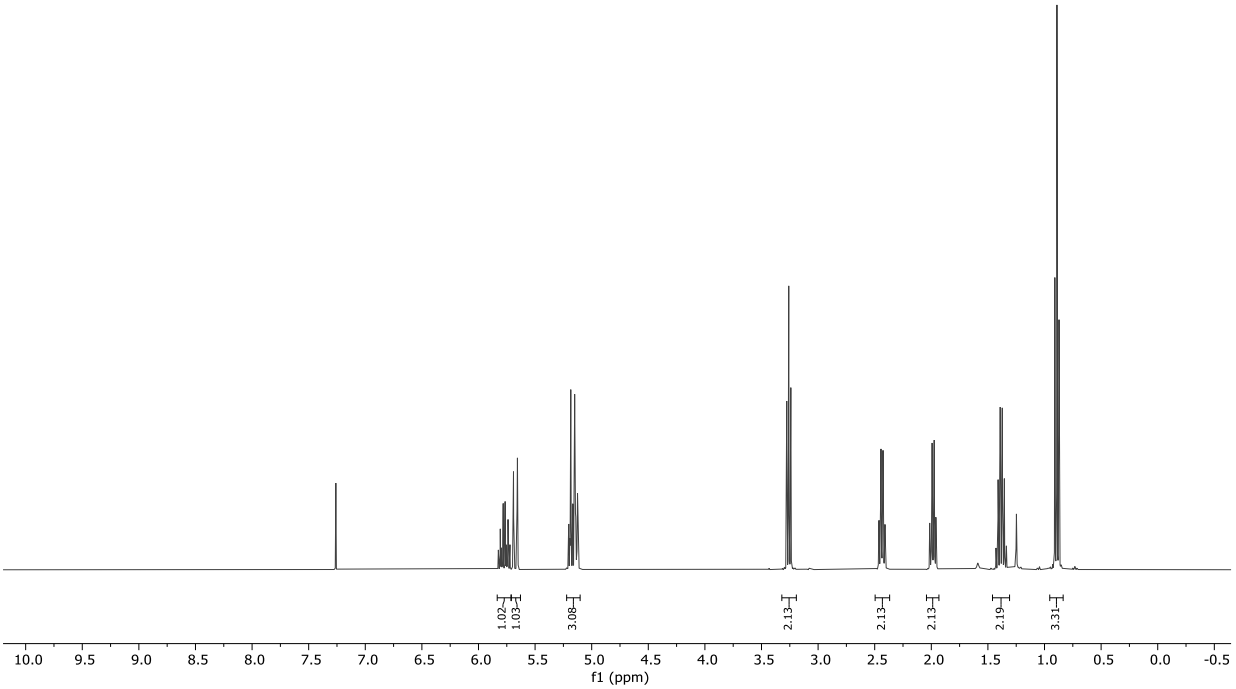
1a

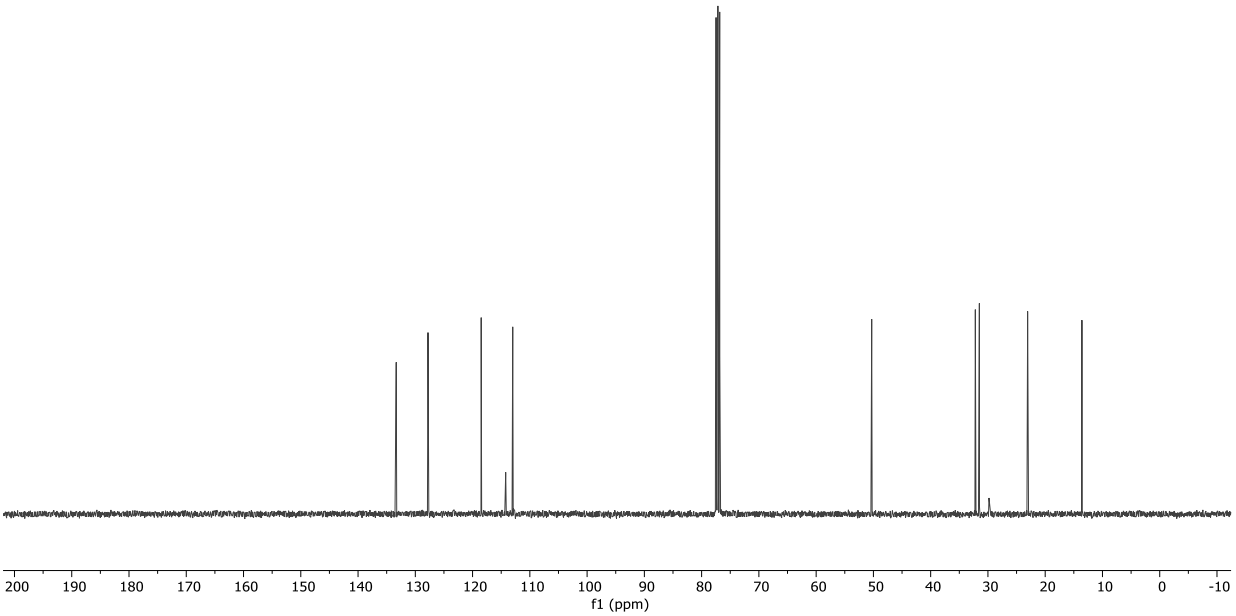

2.03
2.04
1.01
1.00
0.99
0.98
1.01
1.01
2.03
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

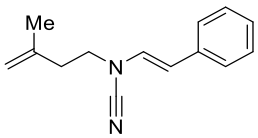

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



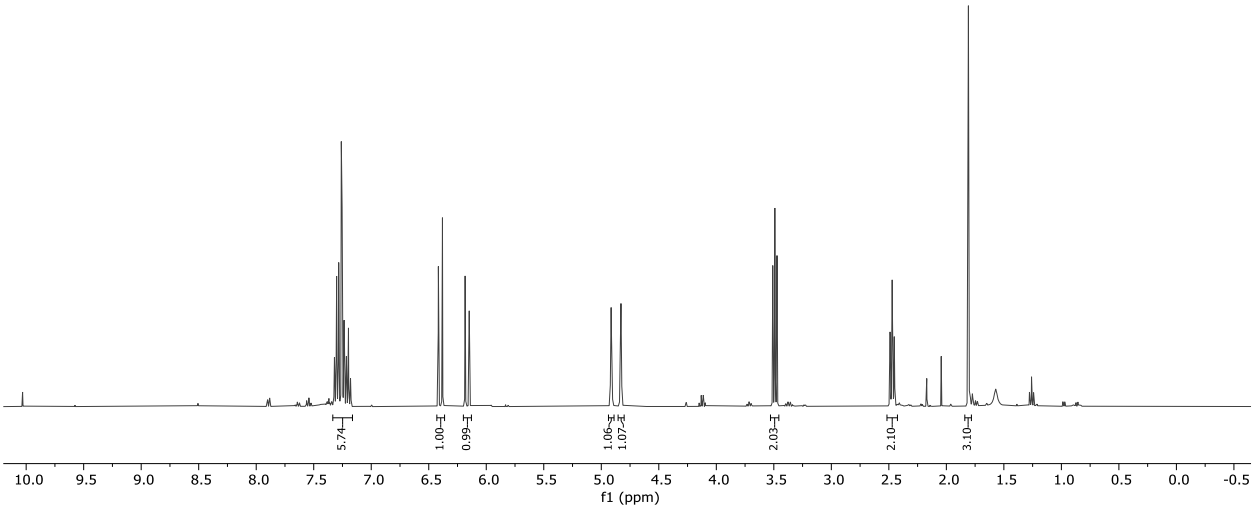
3a

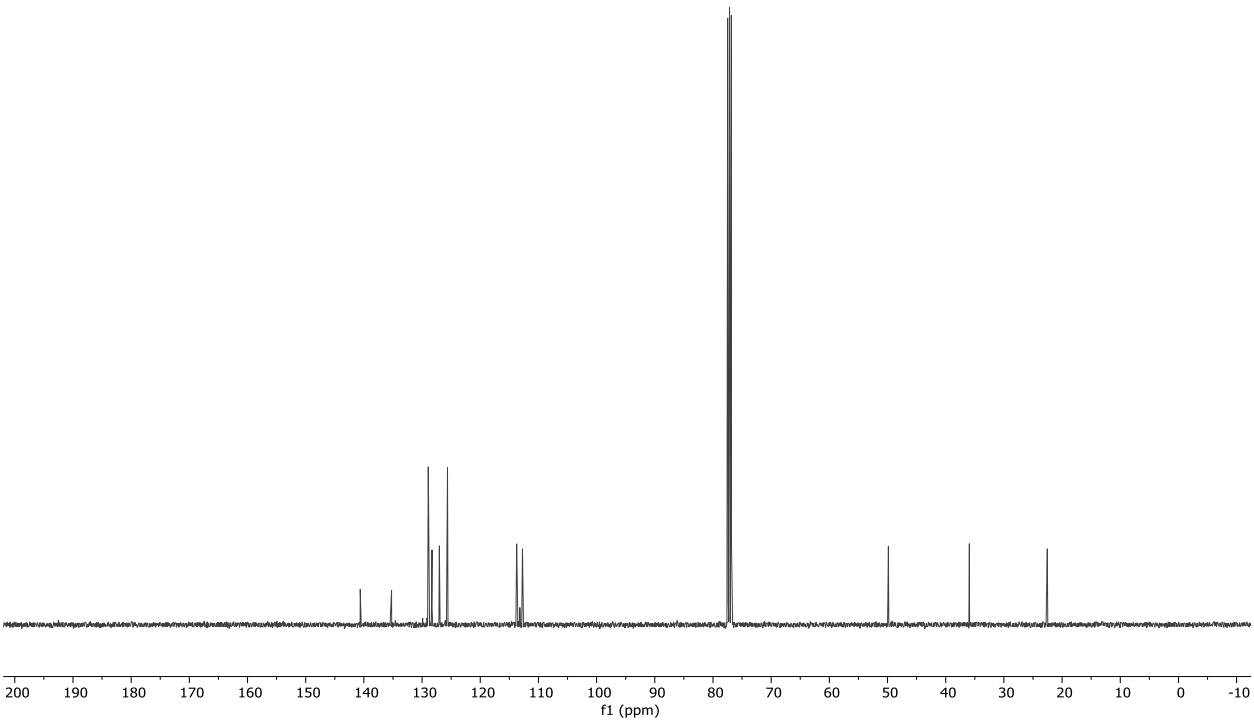

1.02
1.03
3.08
2.13
2.13
2.13
2.19
3.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

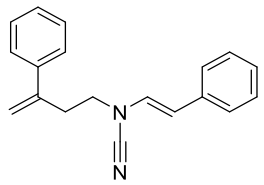

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
N
N

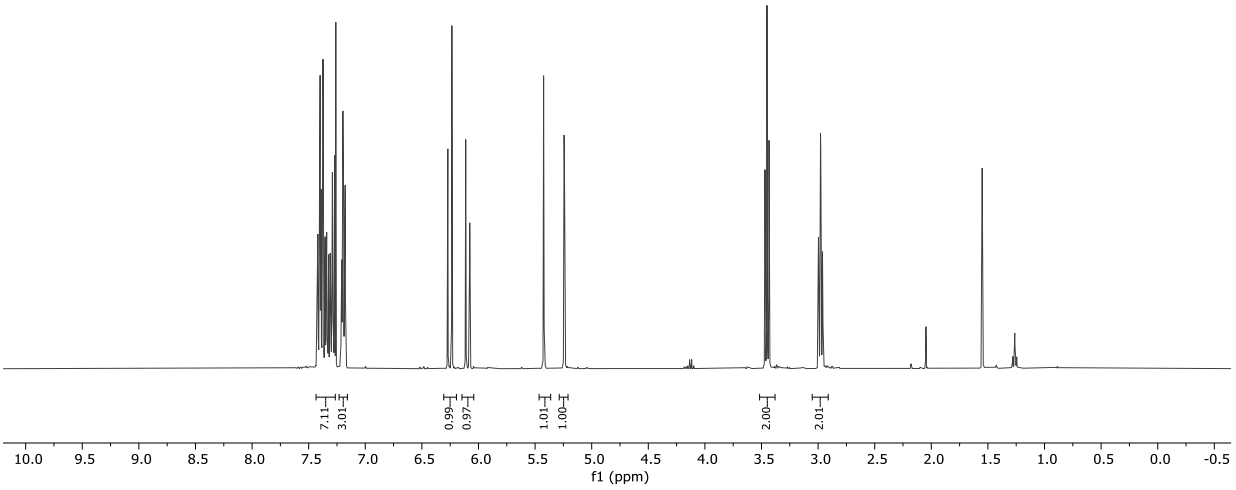
1b

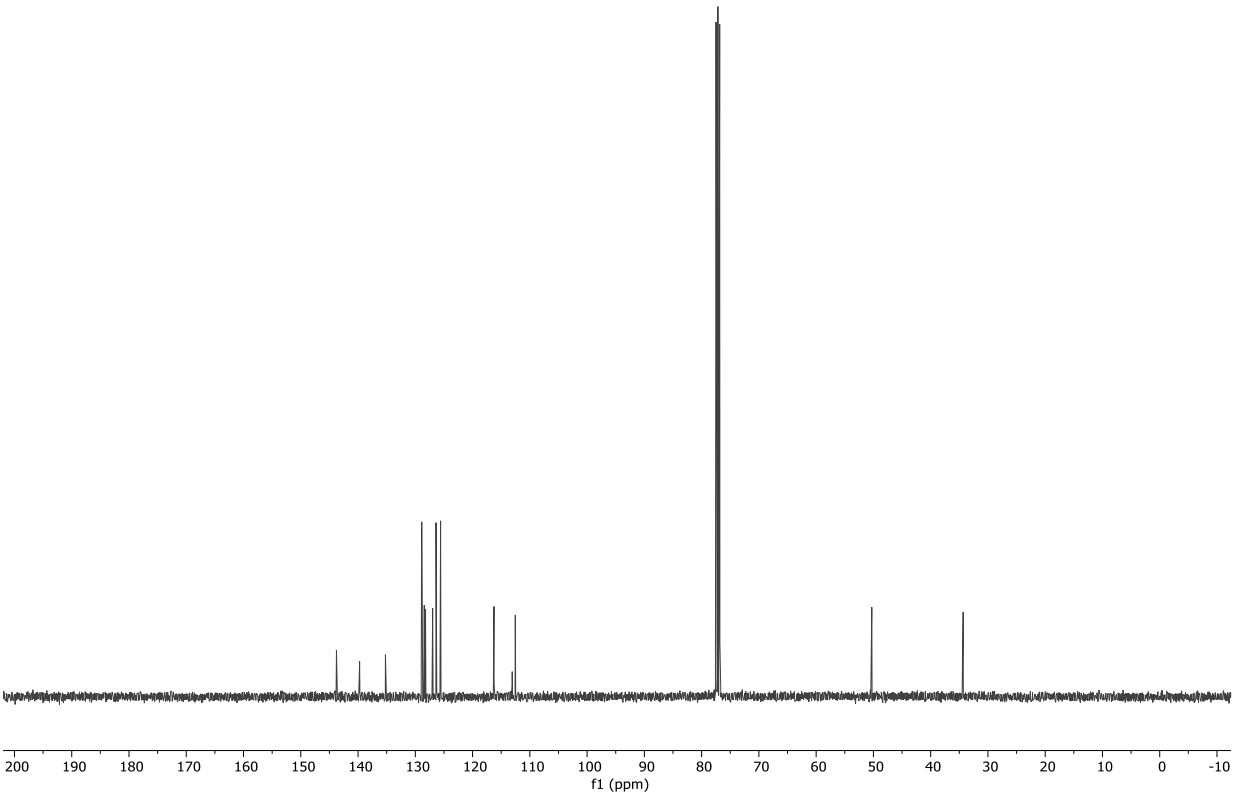

5.74
1.00
0.99
1.06
1.07
2.03
2.10
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

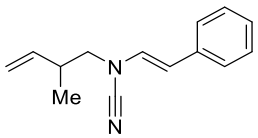

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



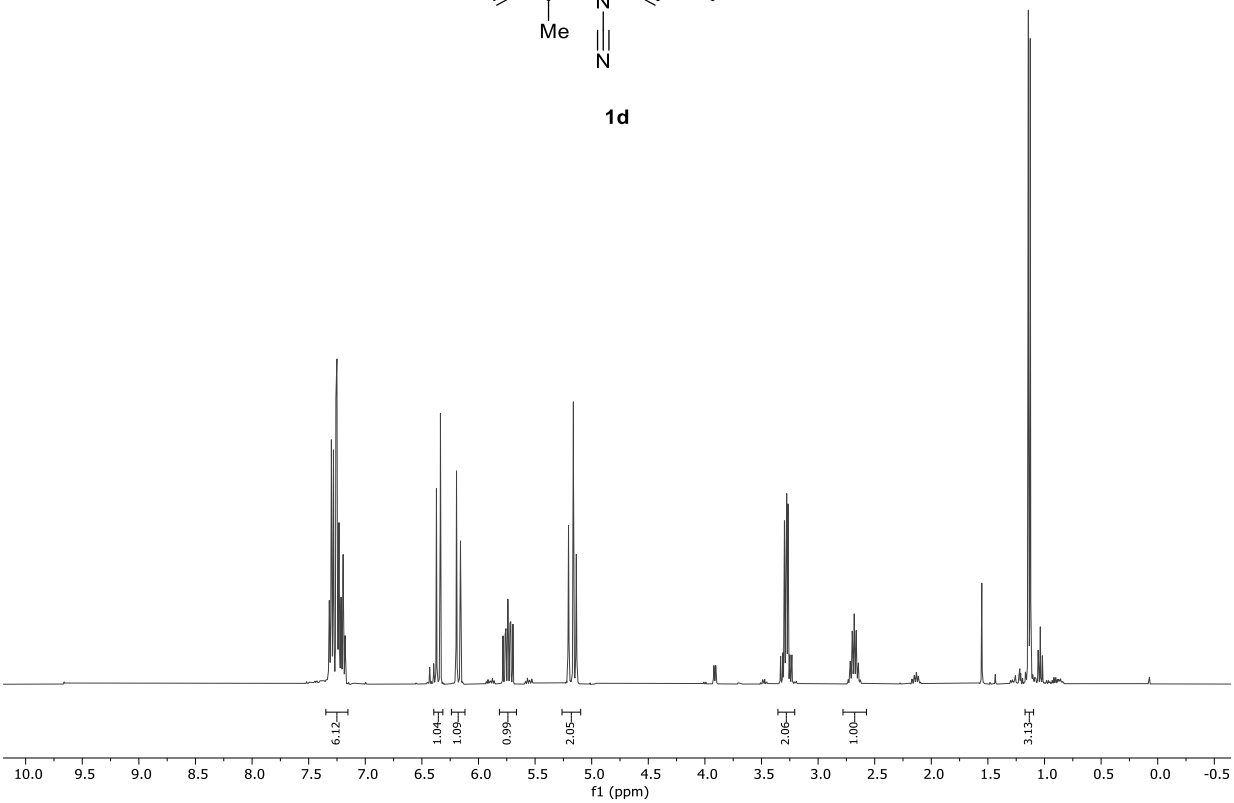
1c

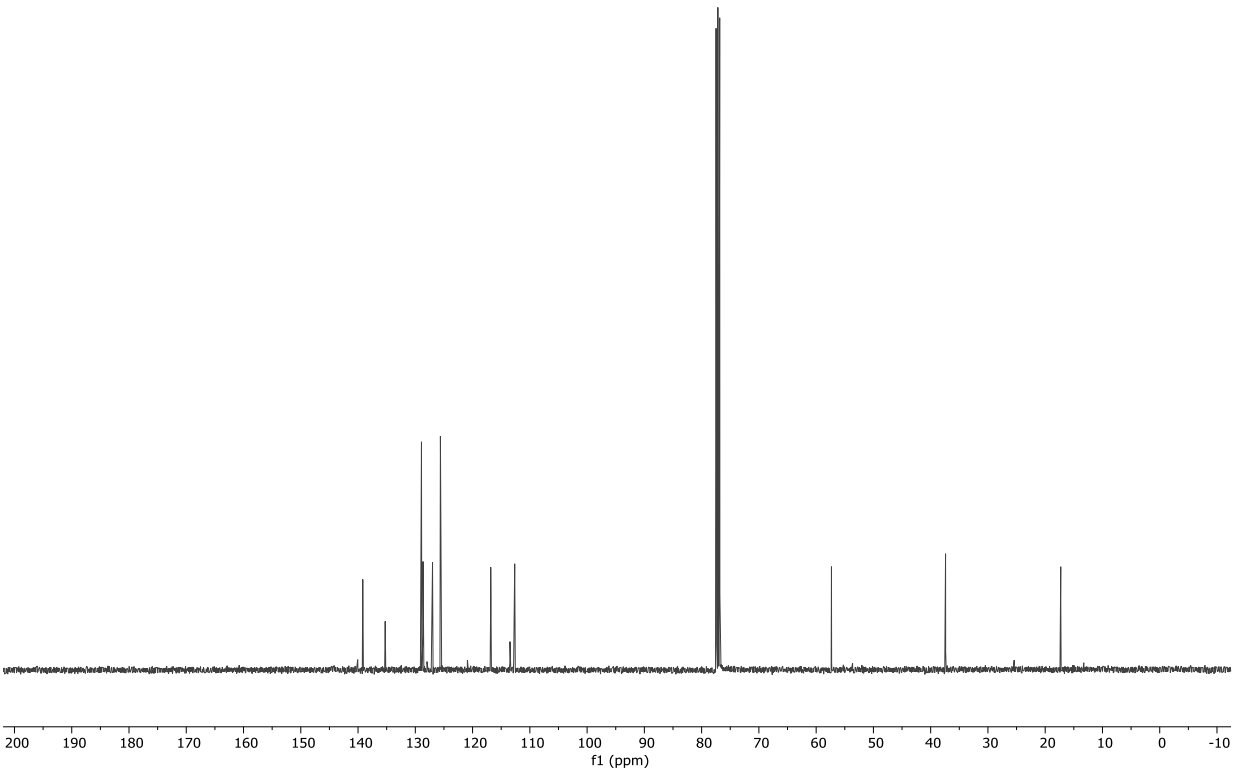

7.11
3.01
0.99
0.97
1.01
1.00
2.00
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

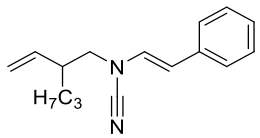

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
N
N

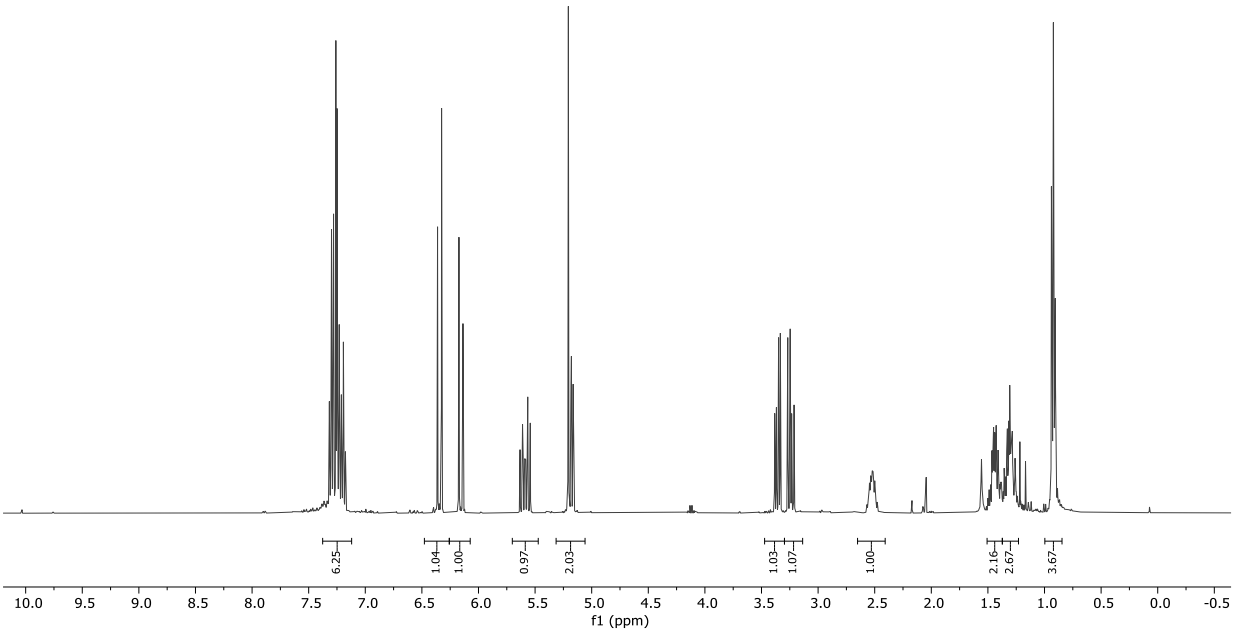
1d

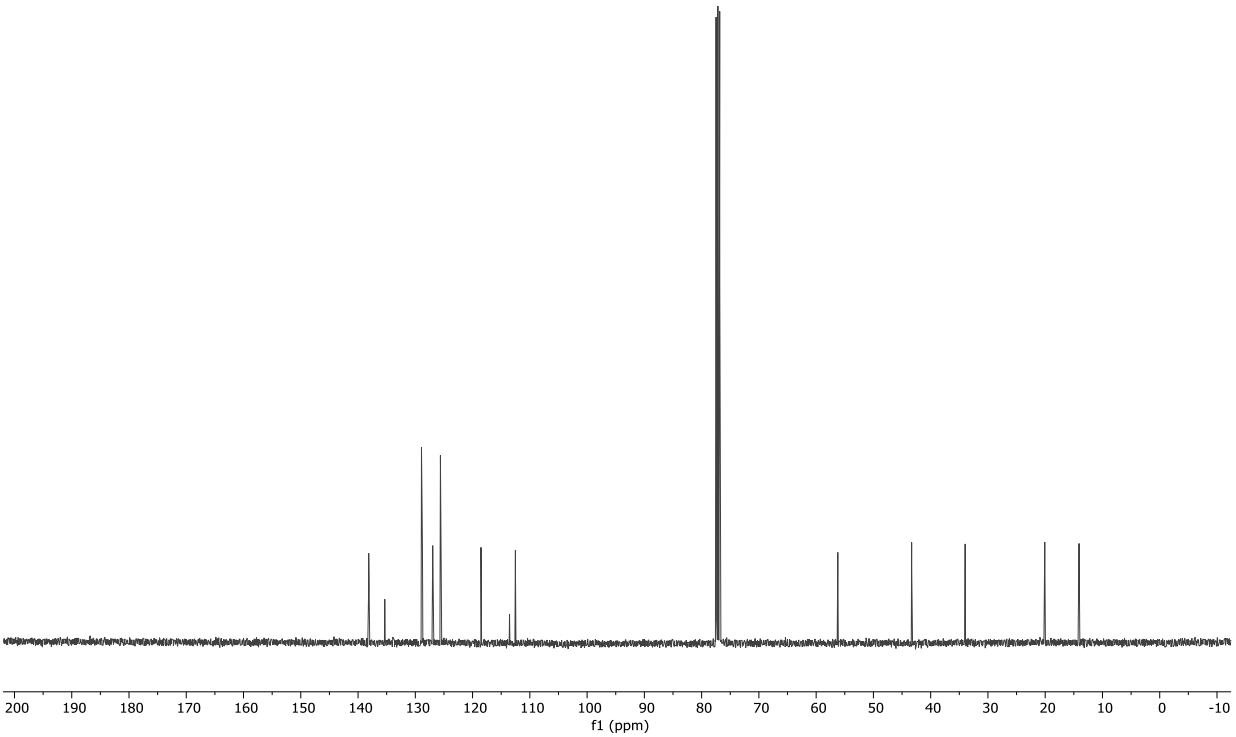

6.12
1.04
1.09
0.99
2.05
2.06
1.00
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

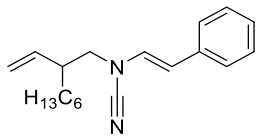

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
H_7C_3
N

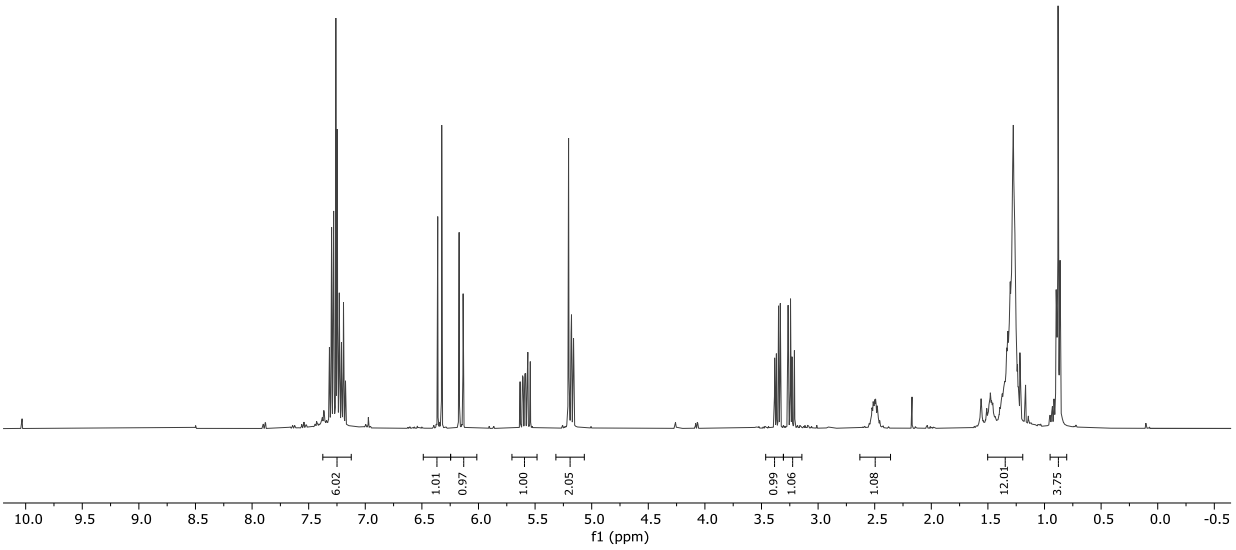
1e

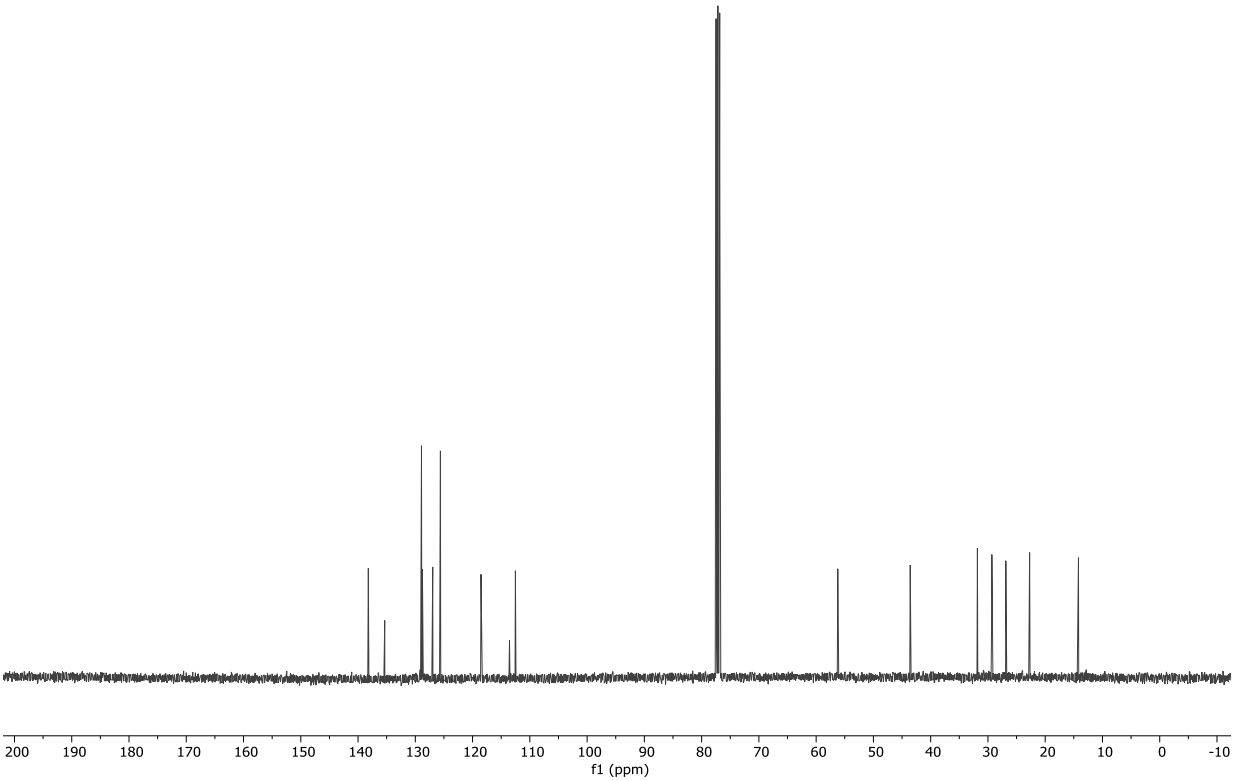

6.25
1.04
1.00
0.97
2.03
1.03
1.07
1.00
2.16
2.67
3.67
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

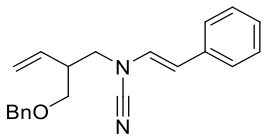

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
$H_{13}C_6$
N

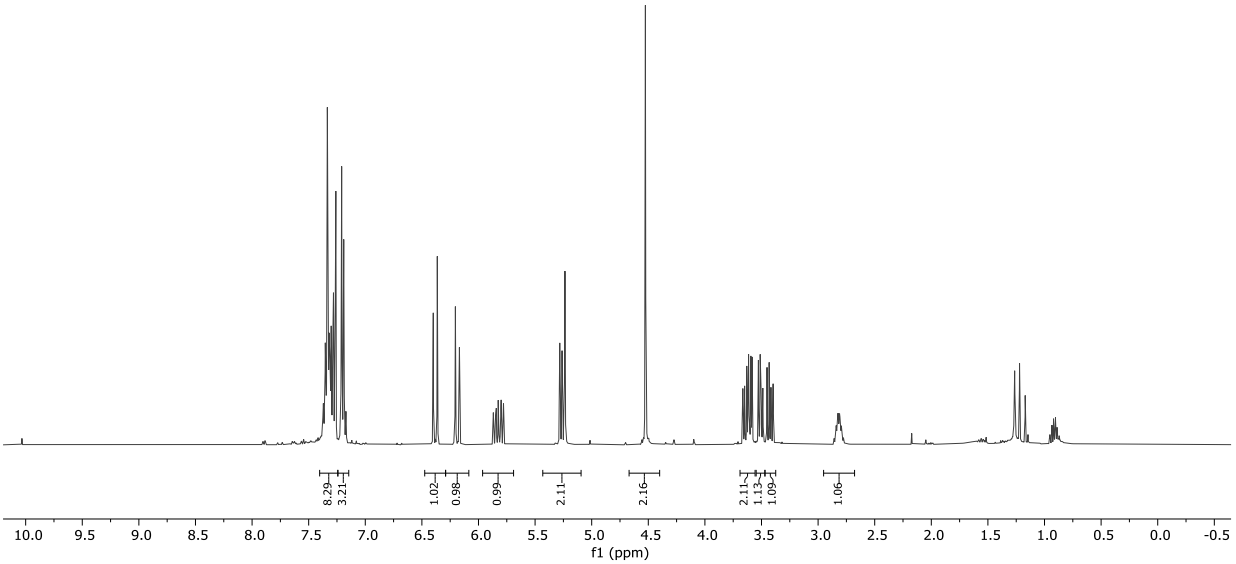
1f

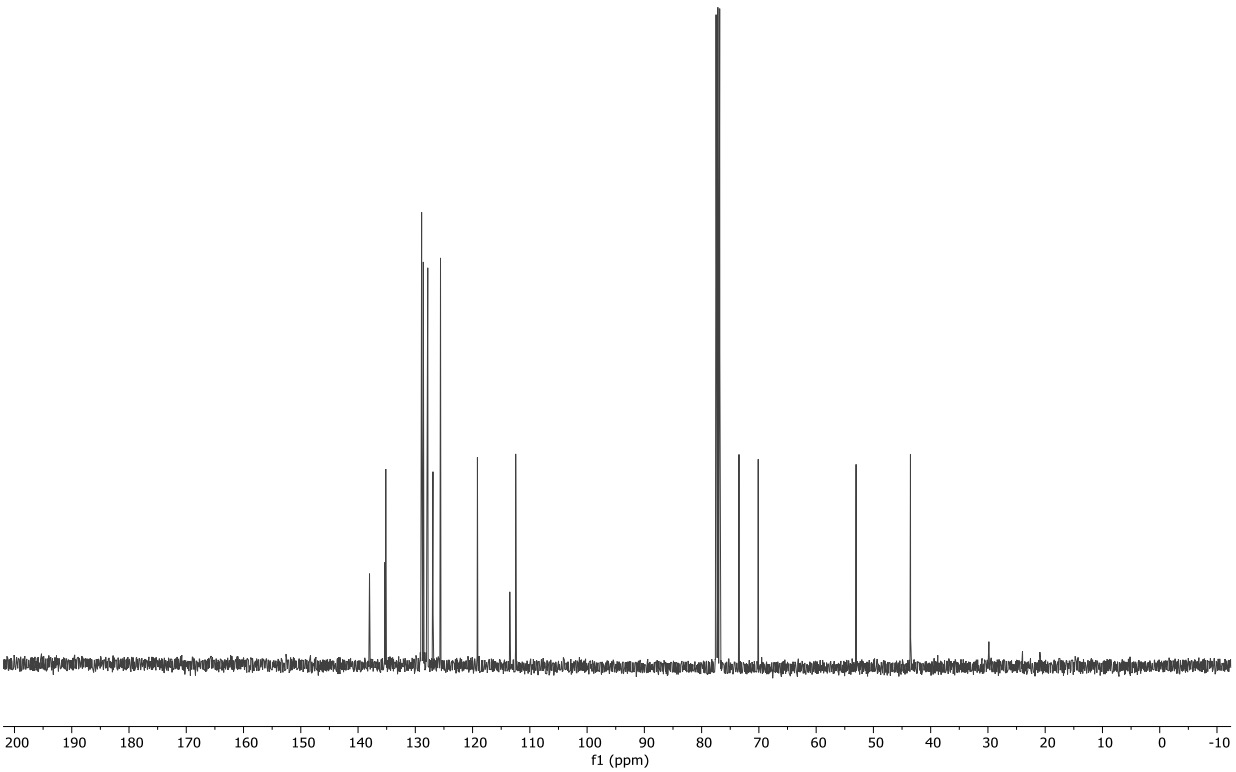

6.02
1.01
0.97
1.00
2.05
0.99
1.06
1.08
12.01
3.75
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

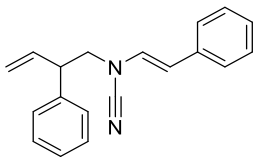

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


BnO
N
N

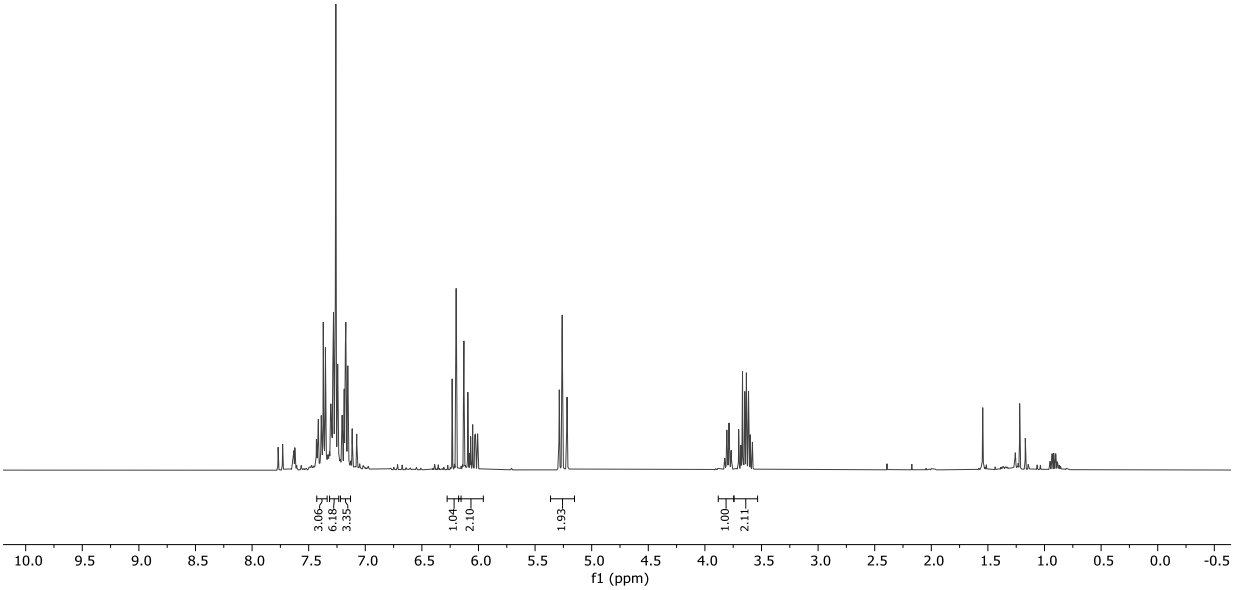
1g

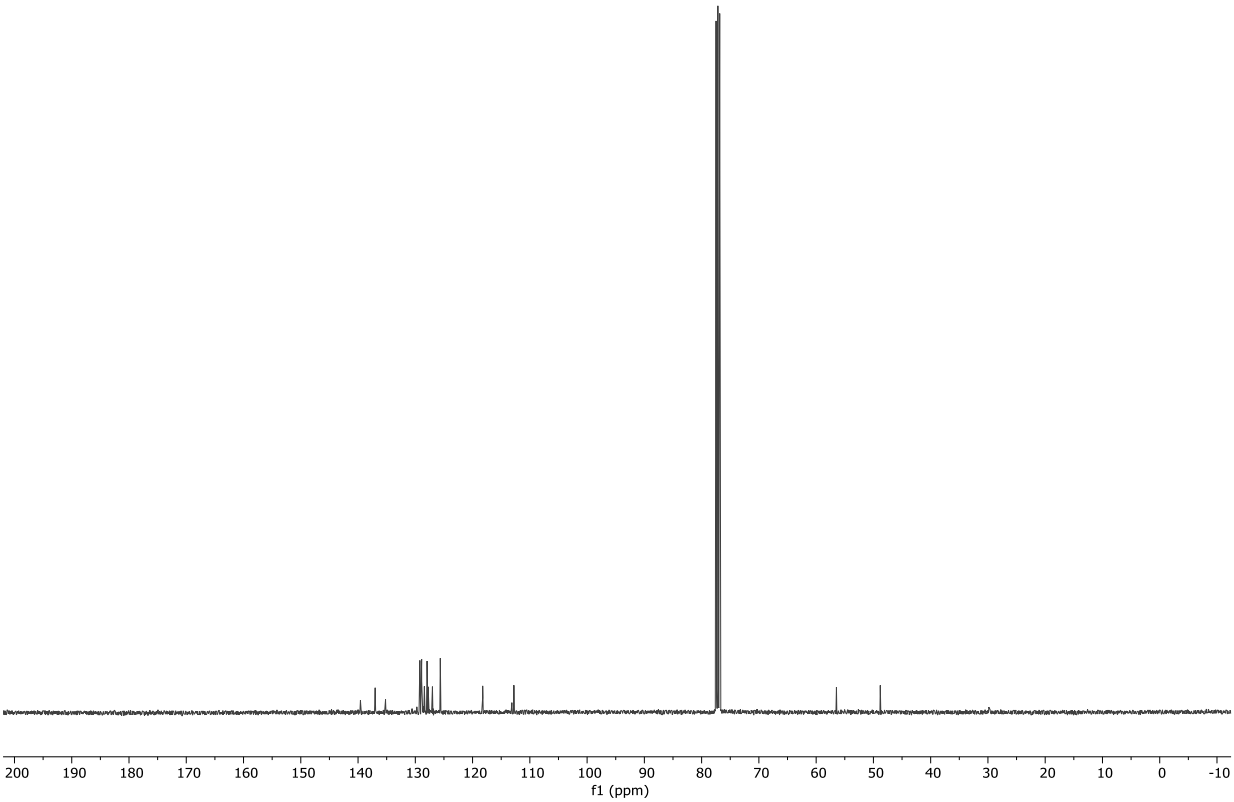

8.29
3.21
1.02
0.98
0.99
2.11
2.16
2.11
1.13
1.09
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

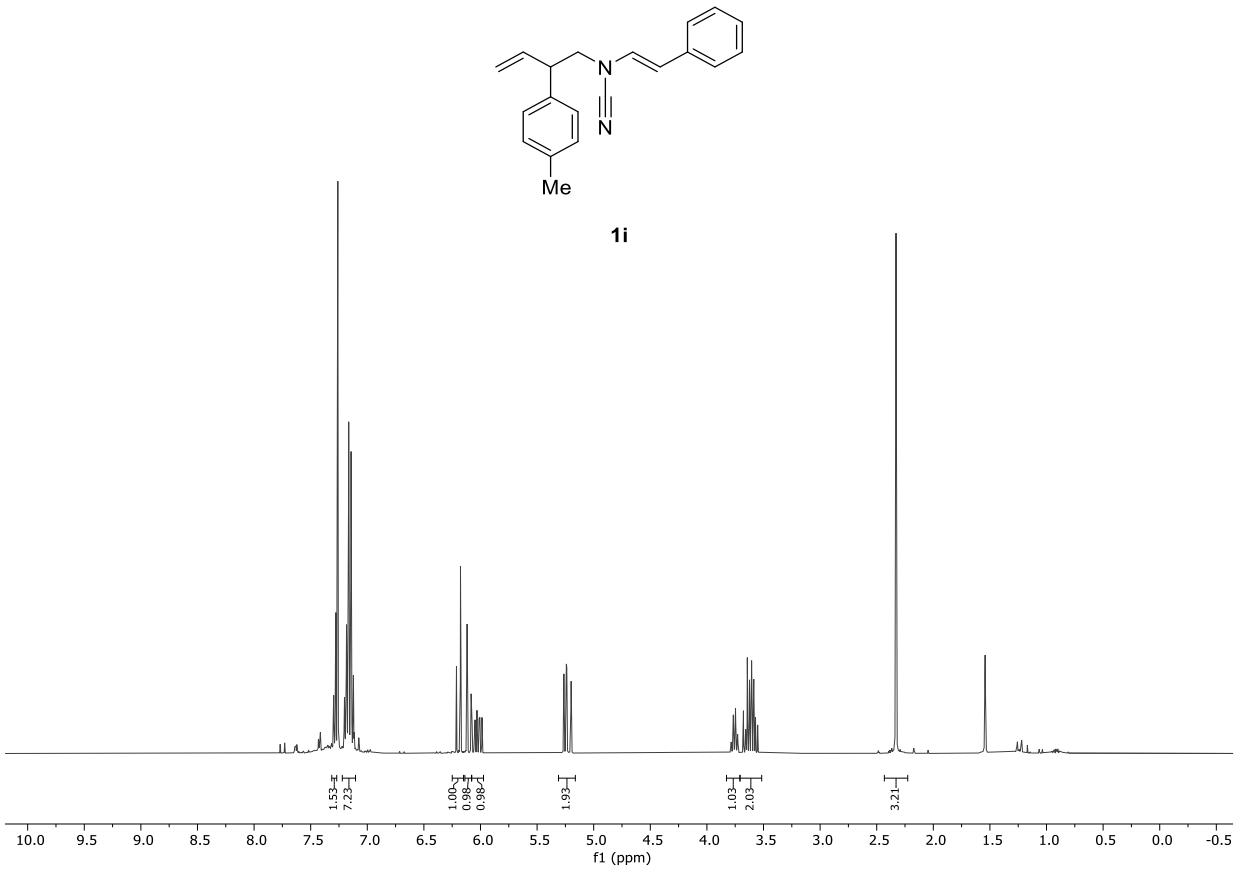

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



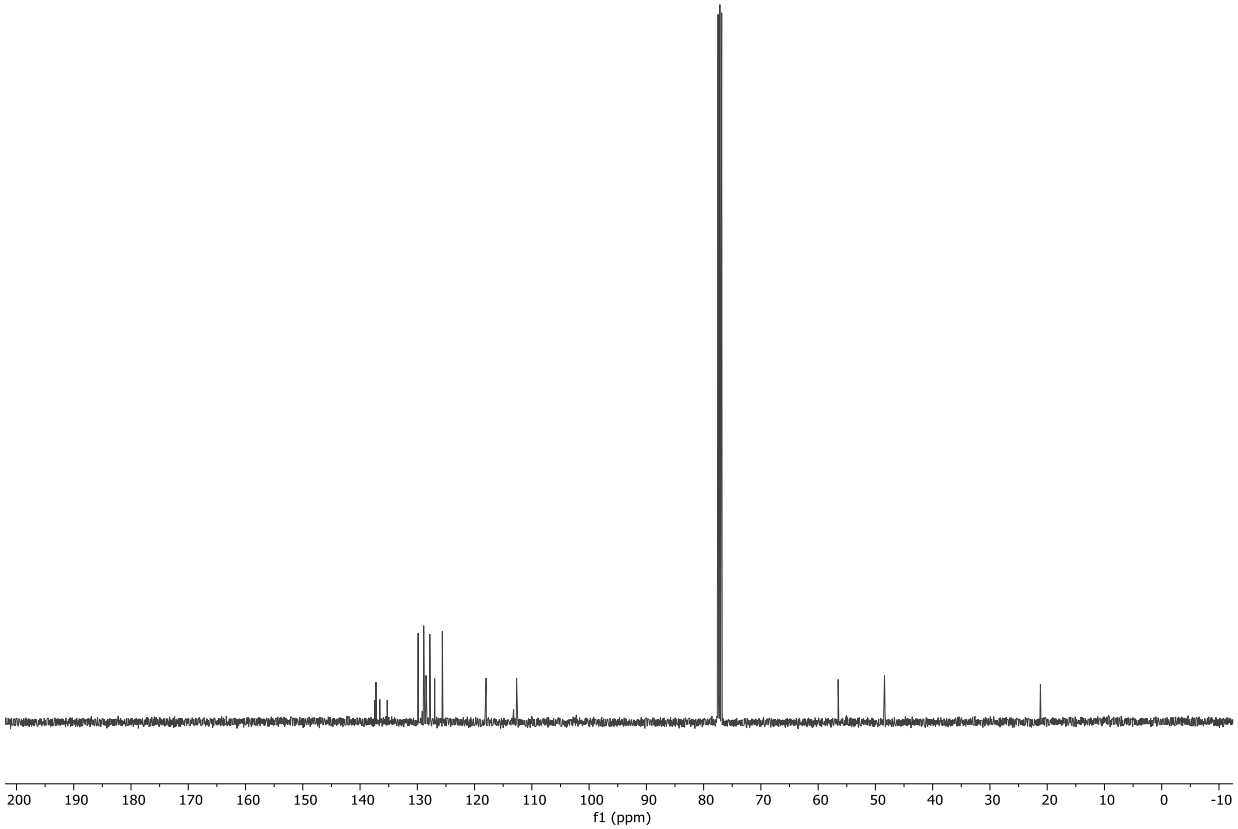
1h

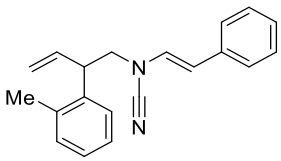

3.06
6.18
3.35
1.04
2.10
1.93
1.00
2.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

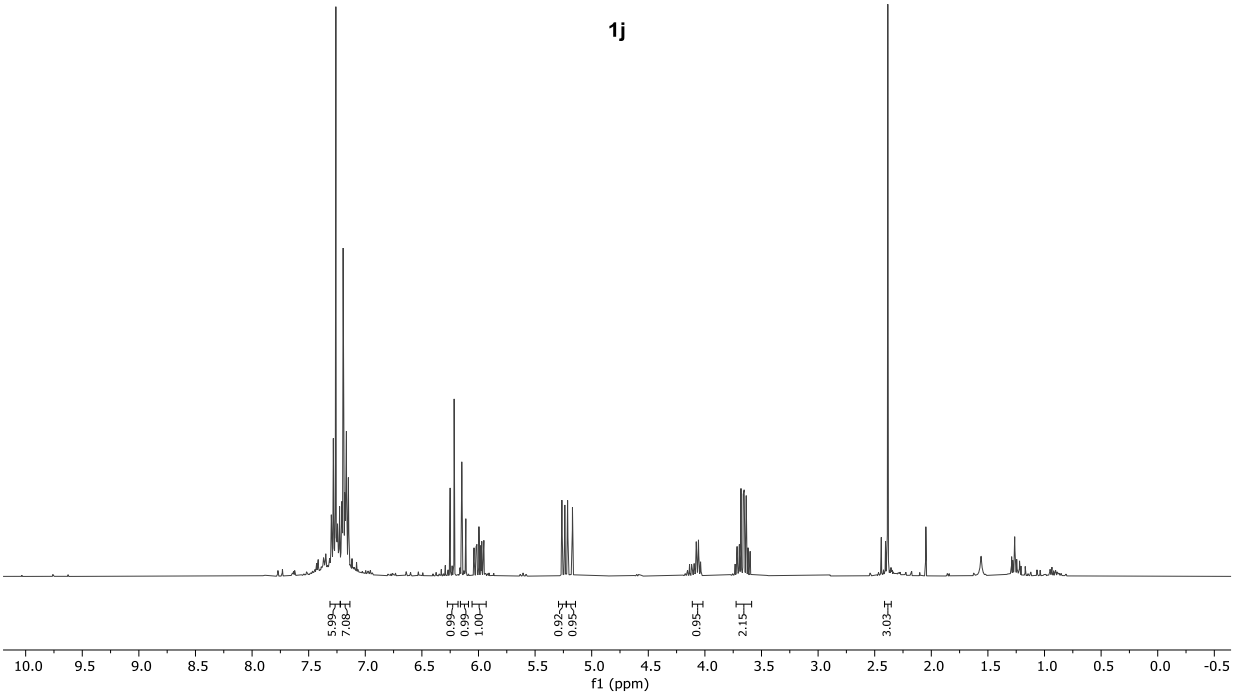

N
N
Me
1.53
7.23
1.00
0.98
0.98
1.93
1.03
2.03
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

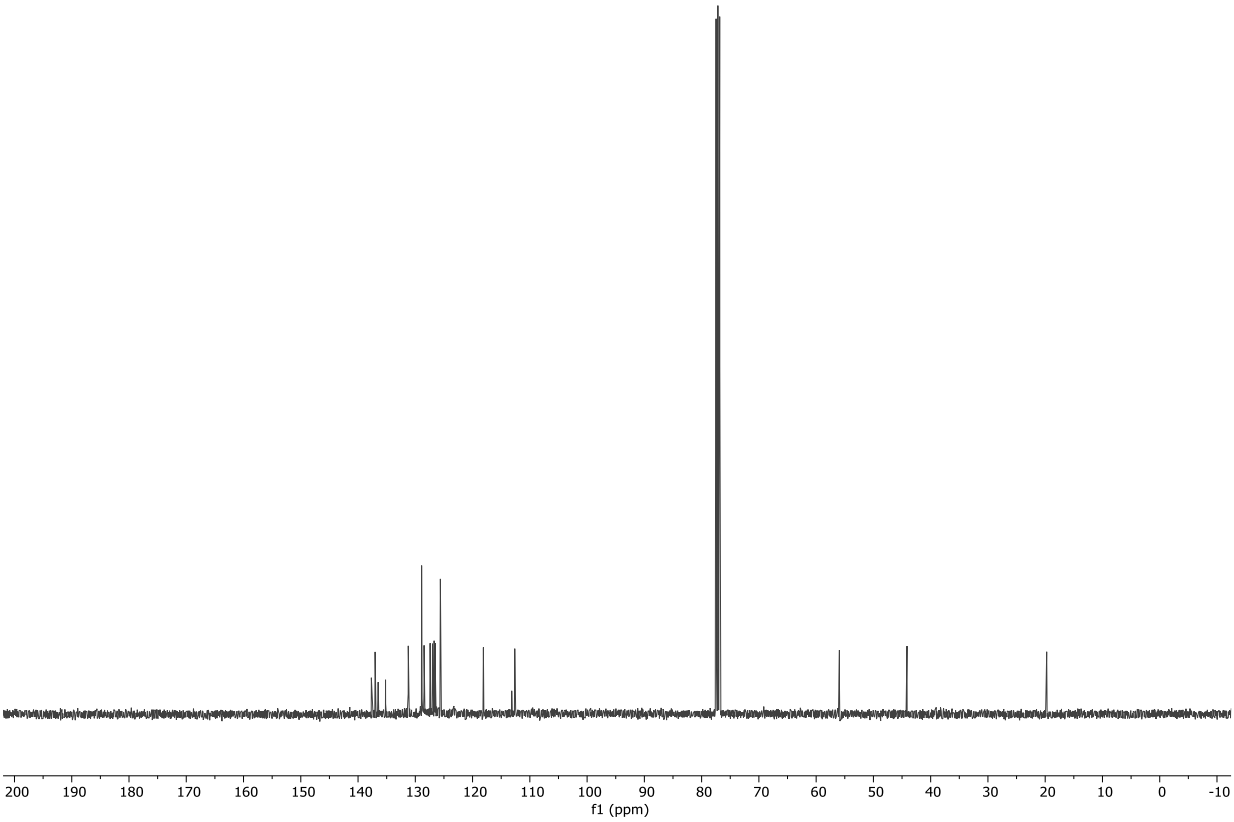
1i

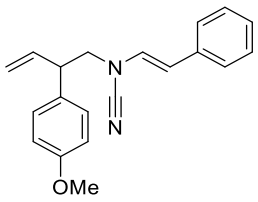

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
N
N

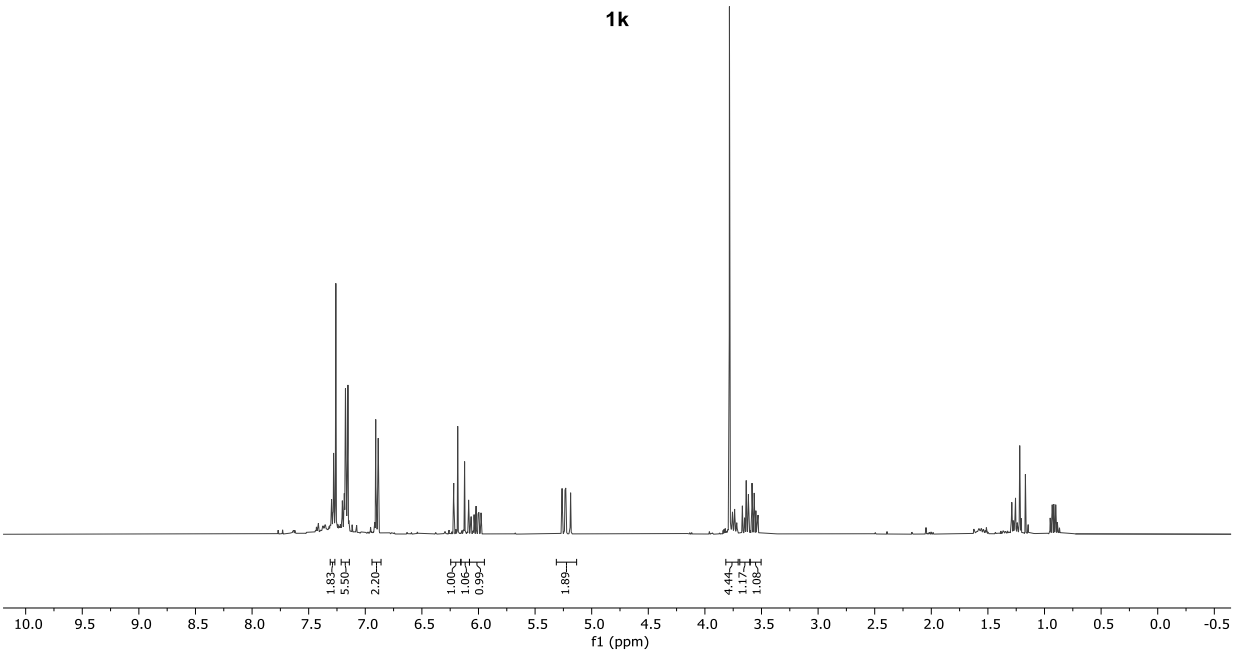
1j

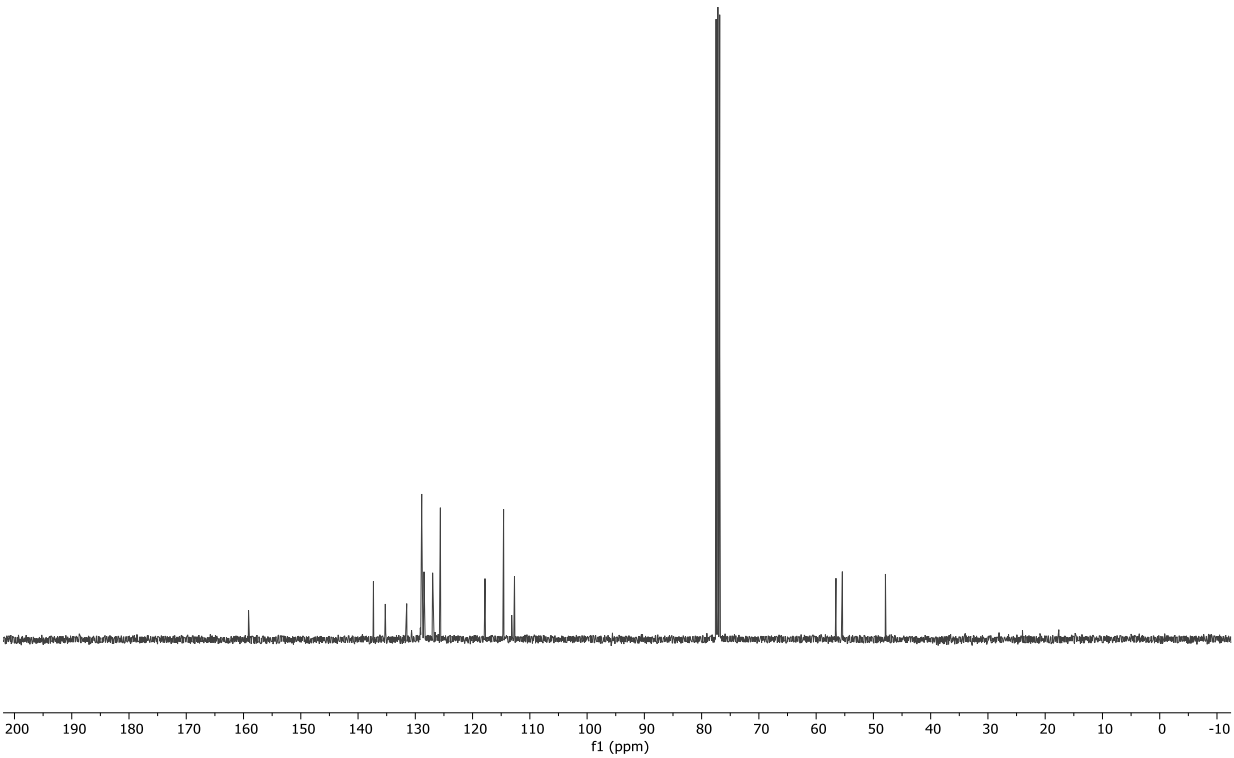

5.99
7.08
0.99
0.99
1.00
0.92
0.95
0.95
2.15
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

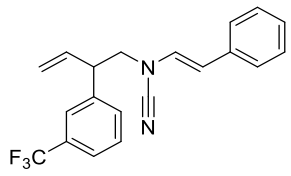

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N
OMe

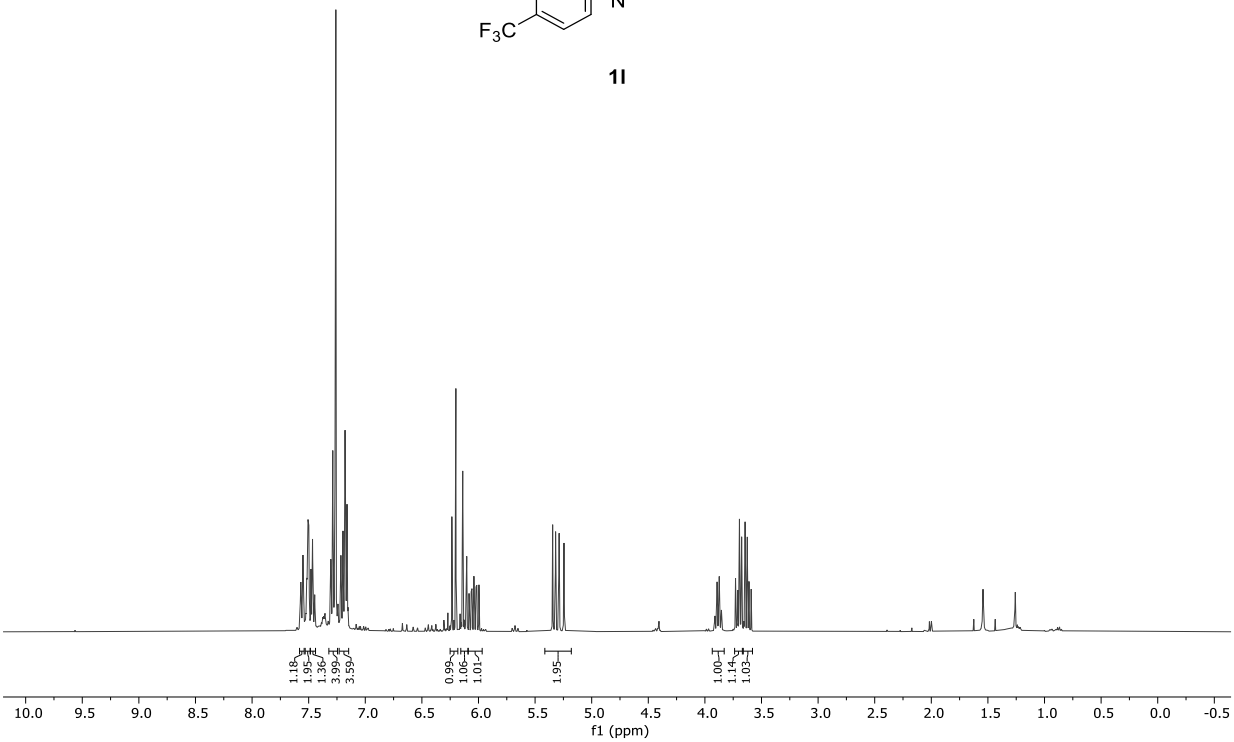
1k

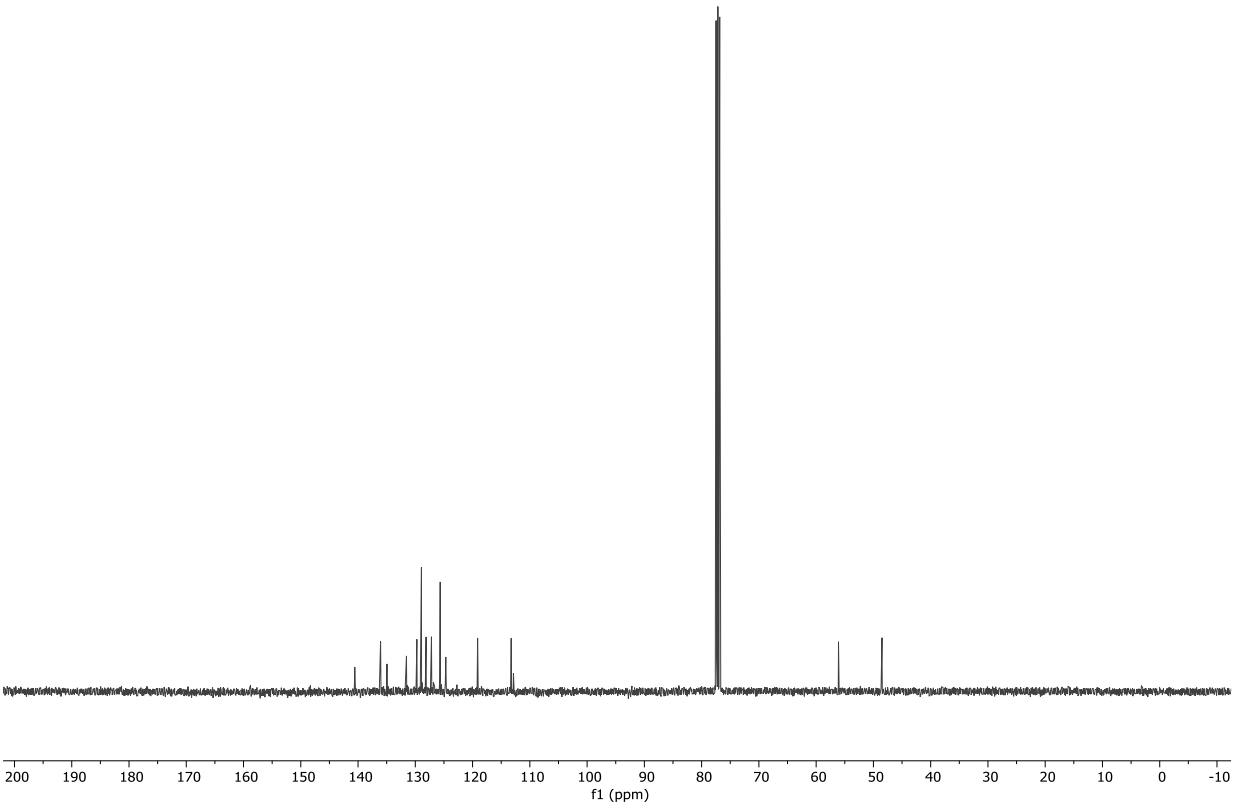

1.83
5.50
2.20
1.00
1.06
0.99
1.89
4.44
1.17
1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

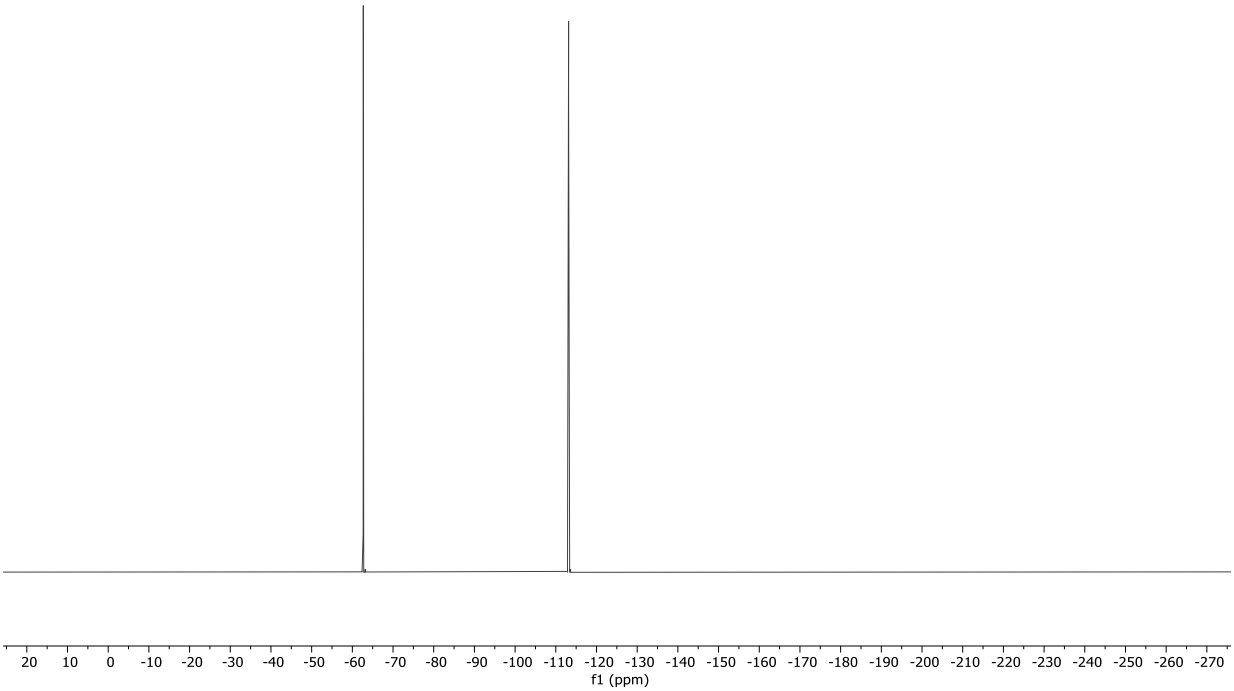

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

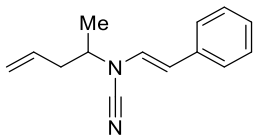

N
N
F3C

1l

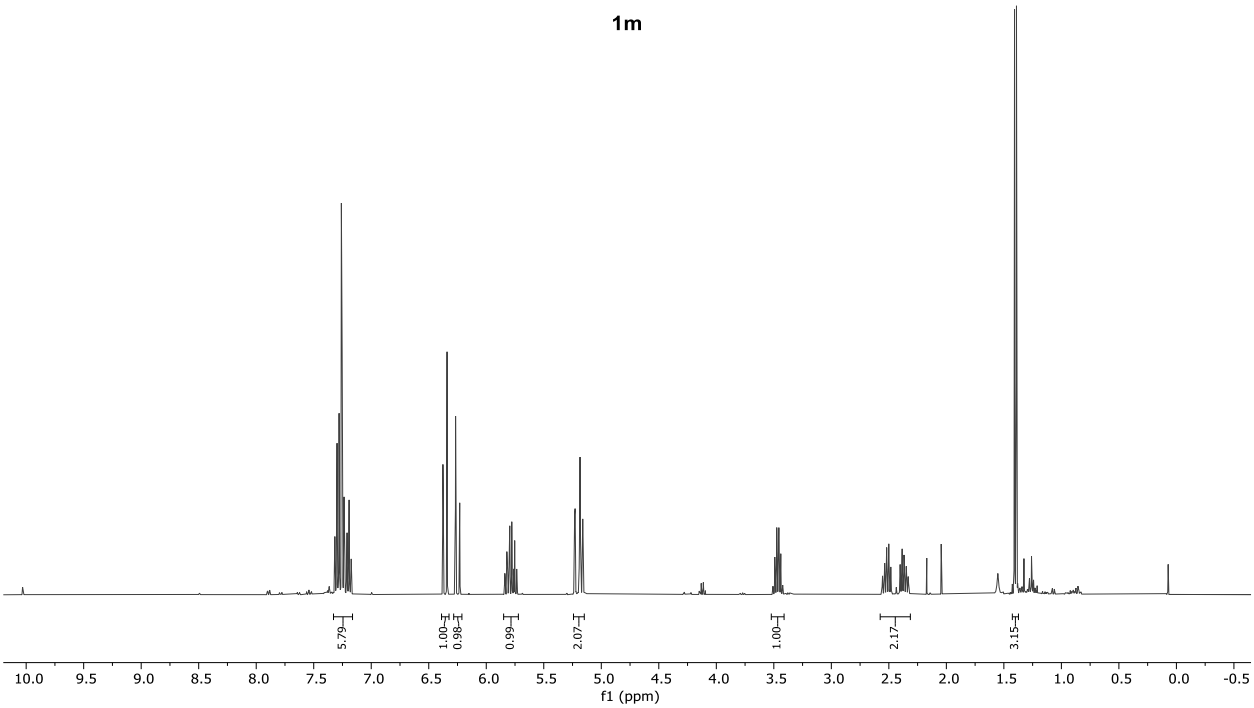

1.18
1.95
1.36
3.99
3.59
0.99
1.06
1.01
1.95
1.00
1.14
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

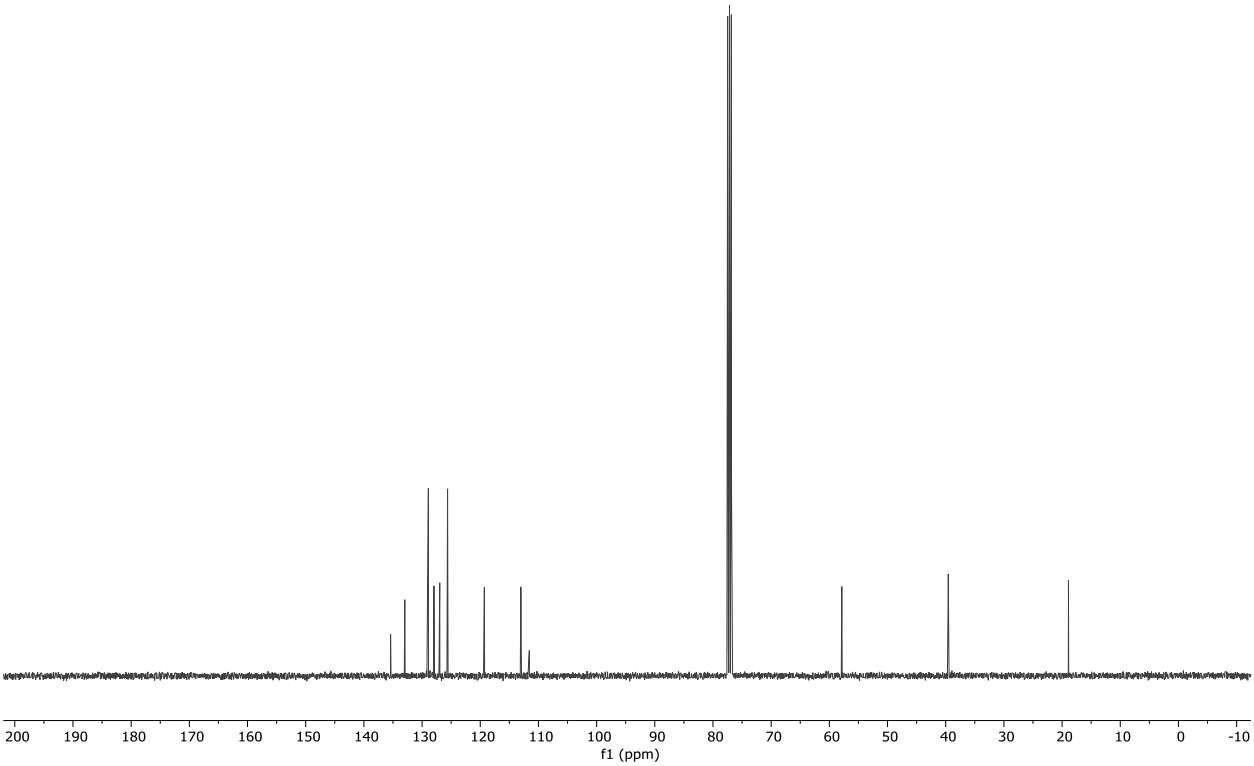

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

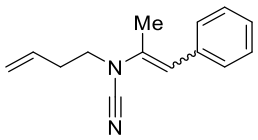

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)


Me
N
N

1m

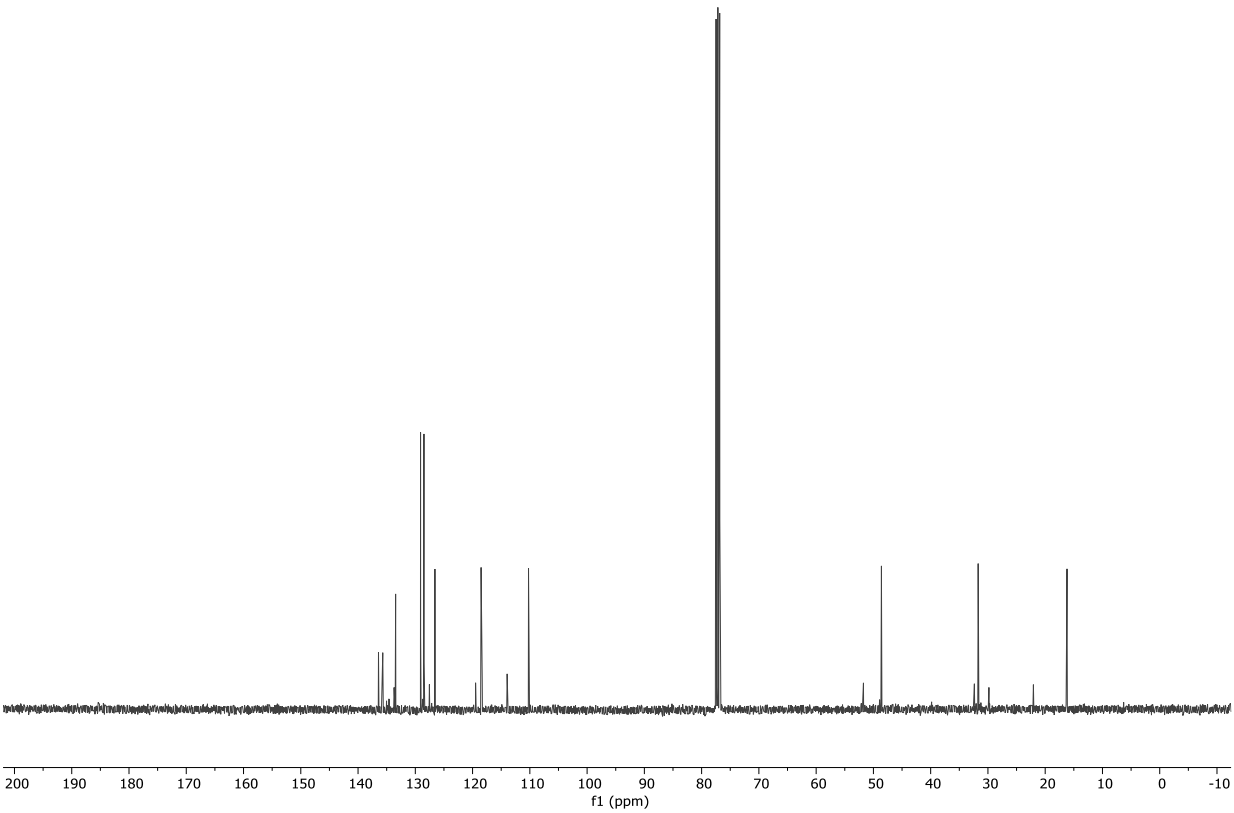

5.79
1.00
0.98
0.99
2.07
1.00
2.17
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

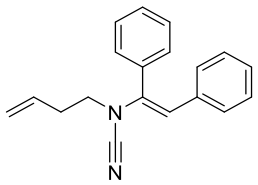

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
N
N

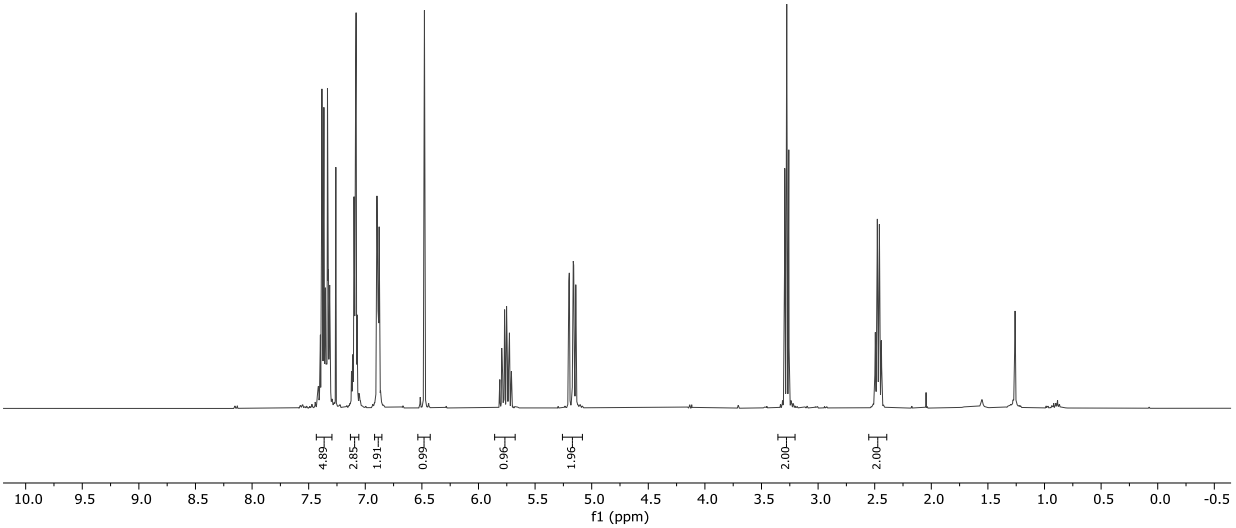
1n (*E*/*Z*: 83/17)

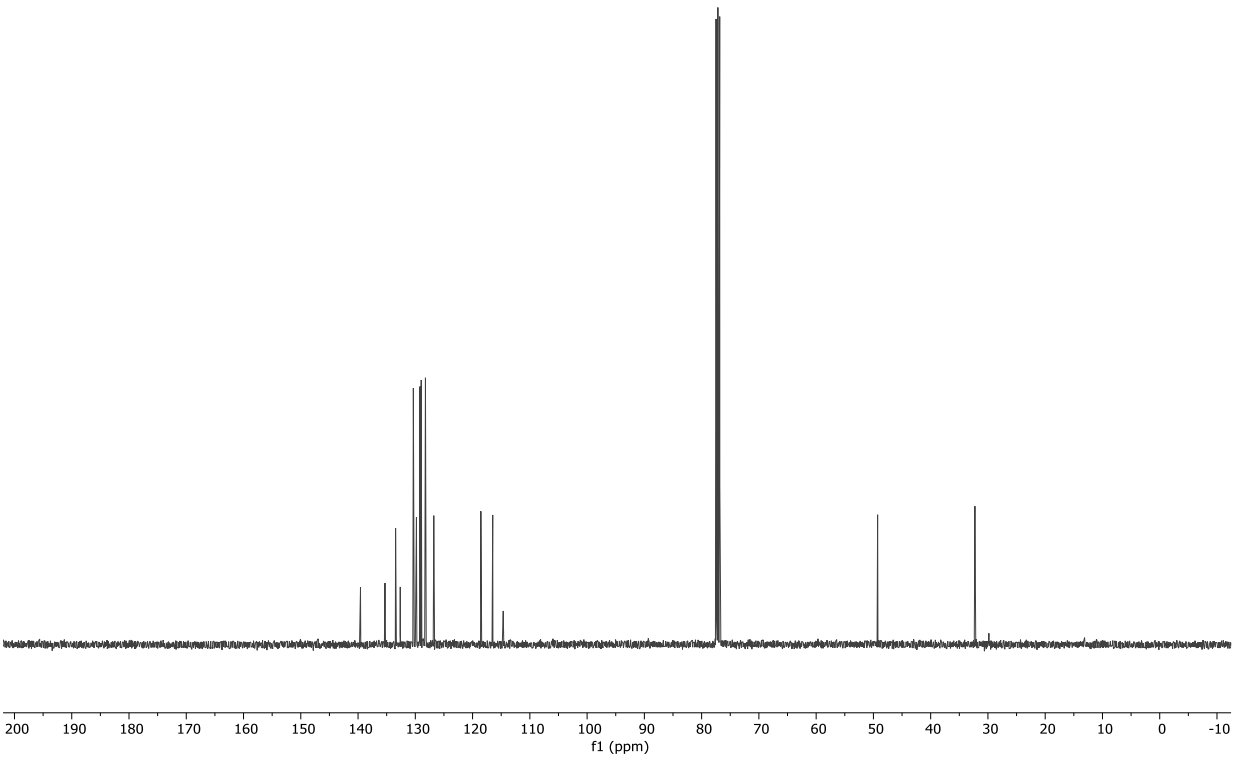
2.35
0.87
1.78
1.00
0.80
0.18
1.63
0.40
1.67
0.31
1.66
0.34
2.45
0.47
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

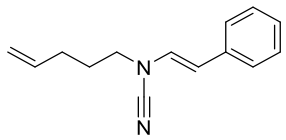

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



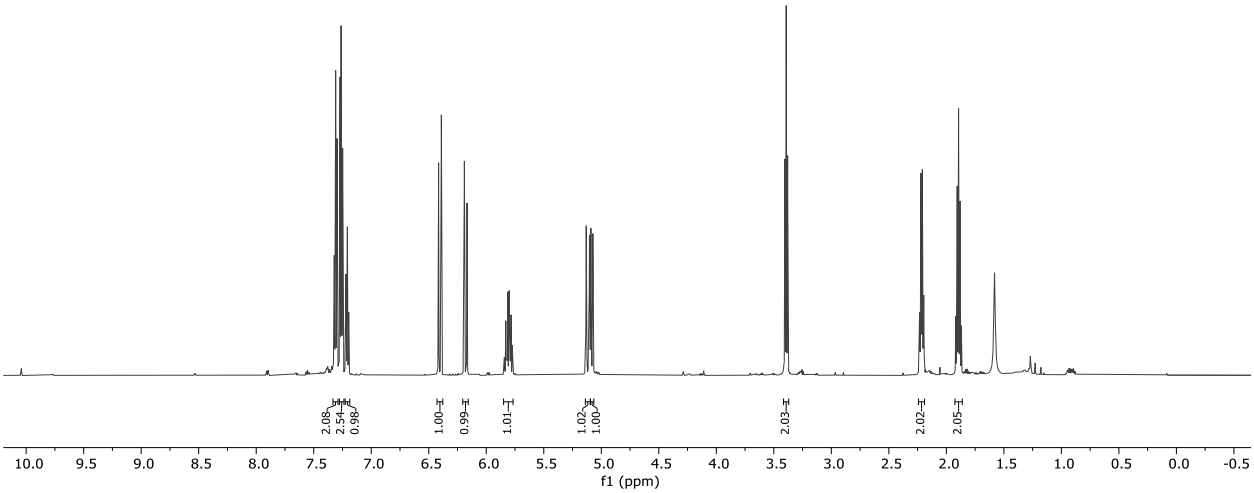
1o

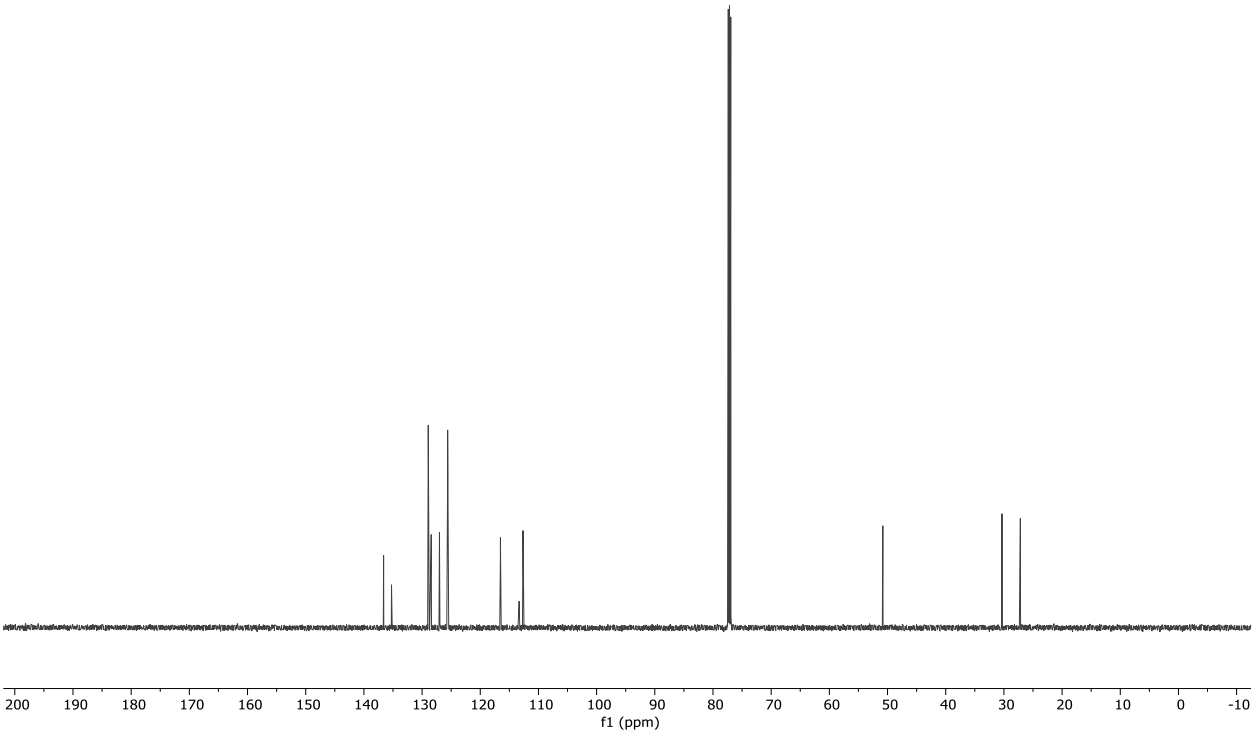

4.89
2.85
1.91
0.99
0.96
1.96
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

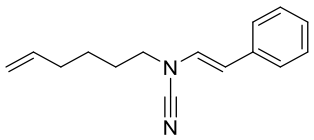

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



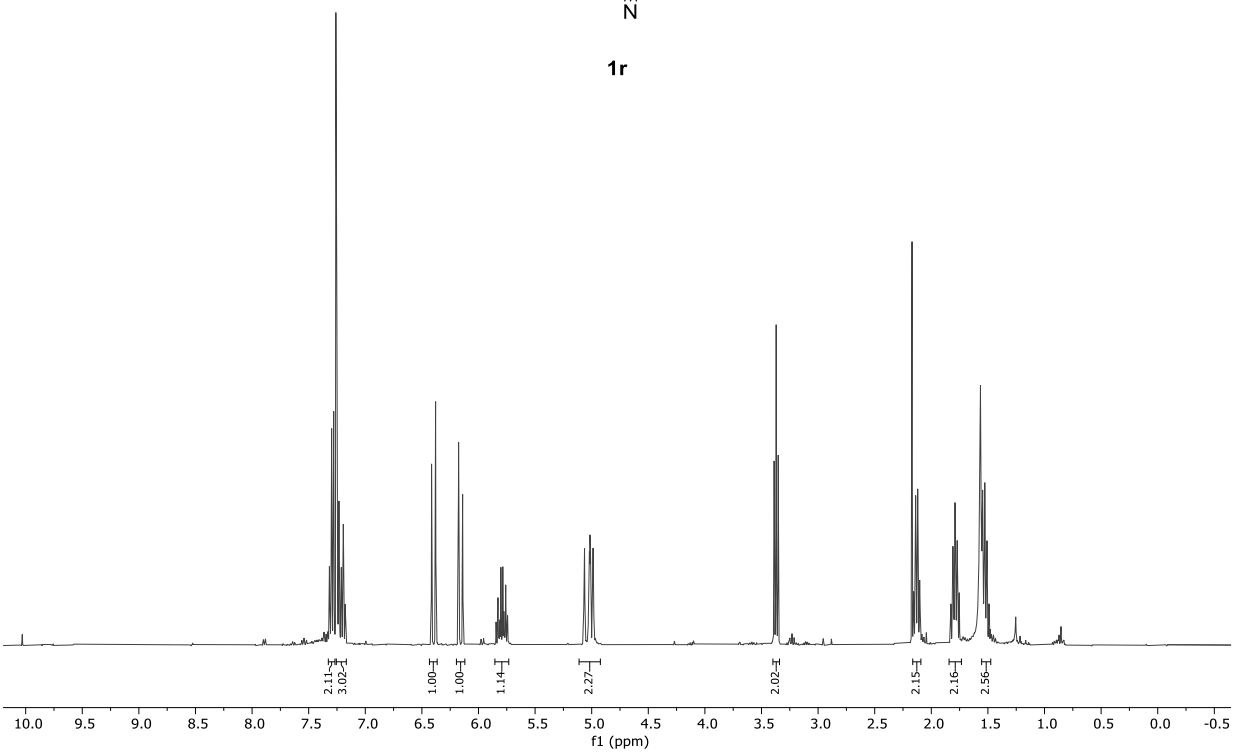
1q

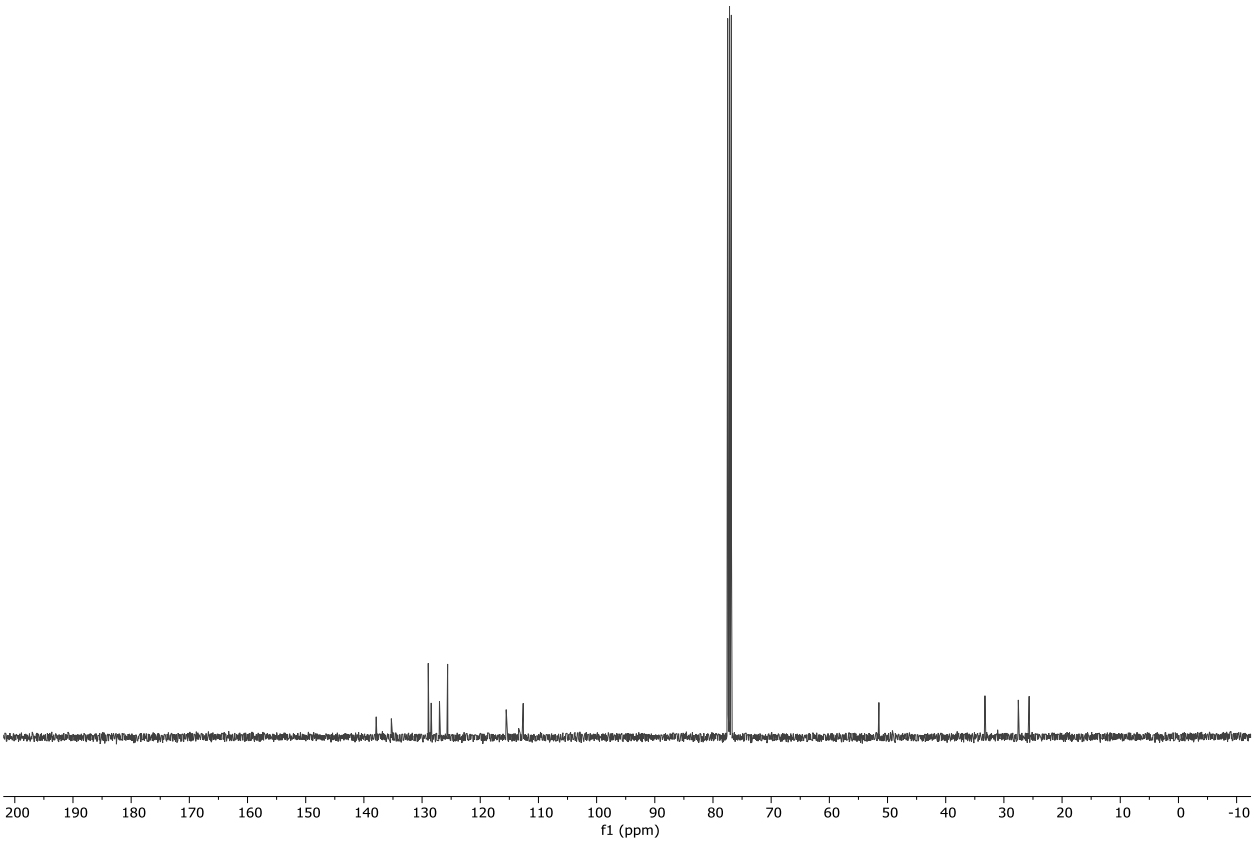

2.08
2.54
0.98
1.00
0.99
1.01
1.02
1.00
2.03
2.02
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1r


2.11
3.02
1.00
1.00
1.14
2.27
2.02
2.15
2.16
2.56
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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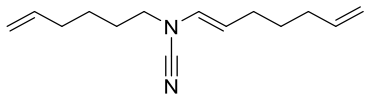
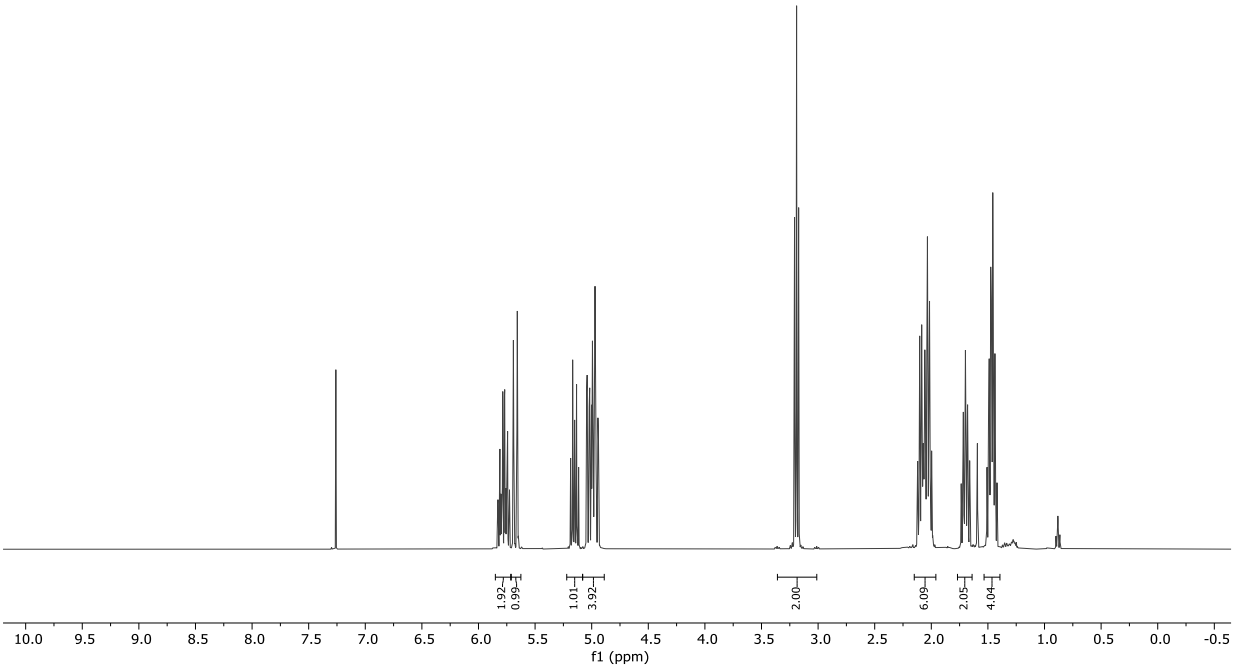
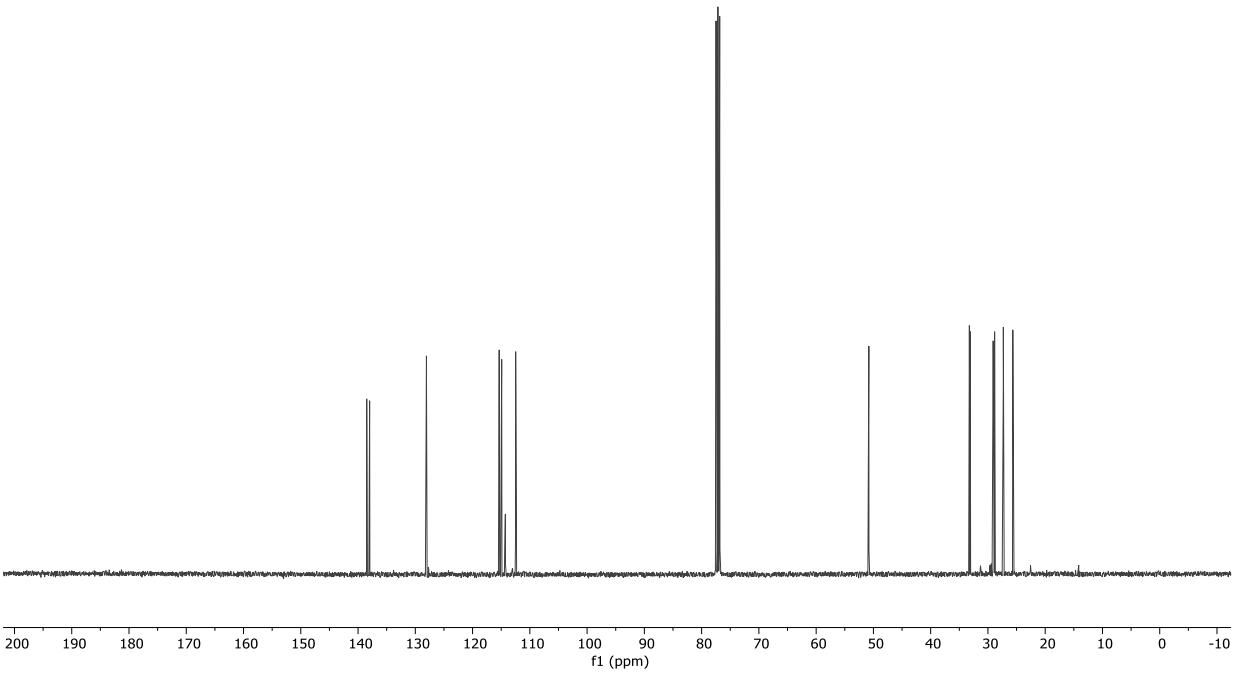
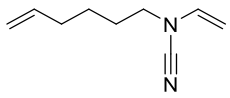
f1 (ppm)



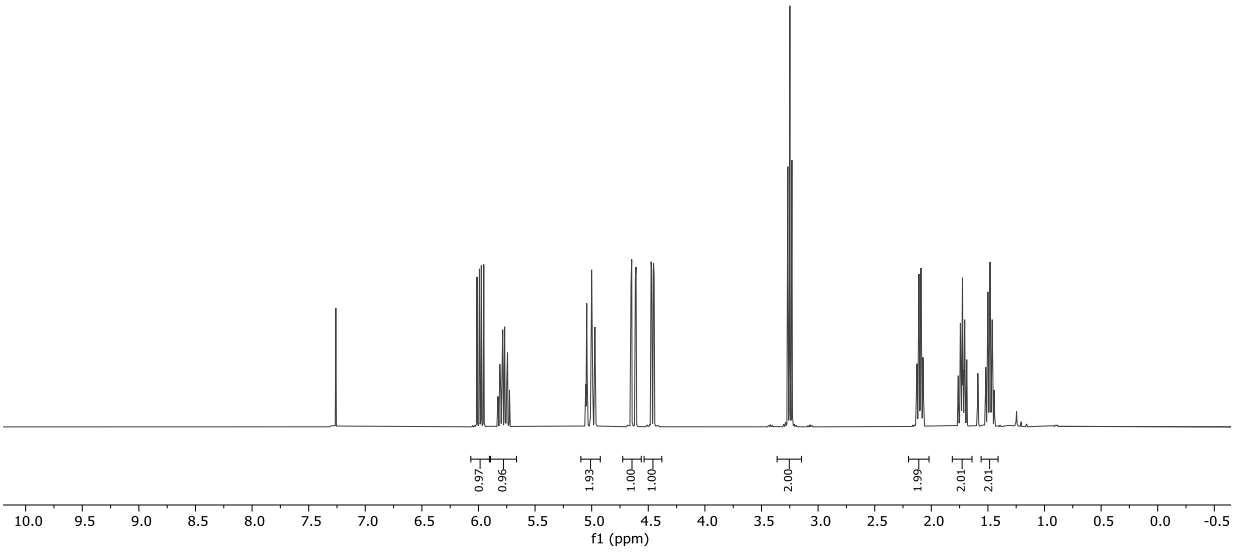
1s

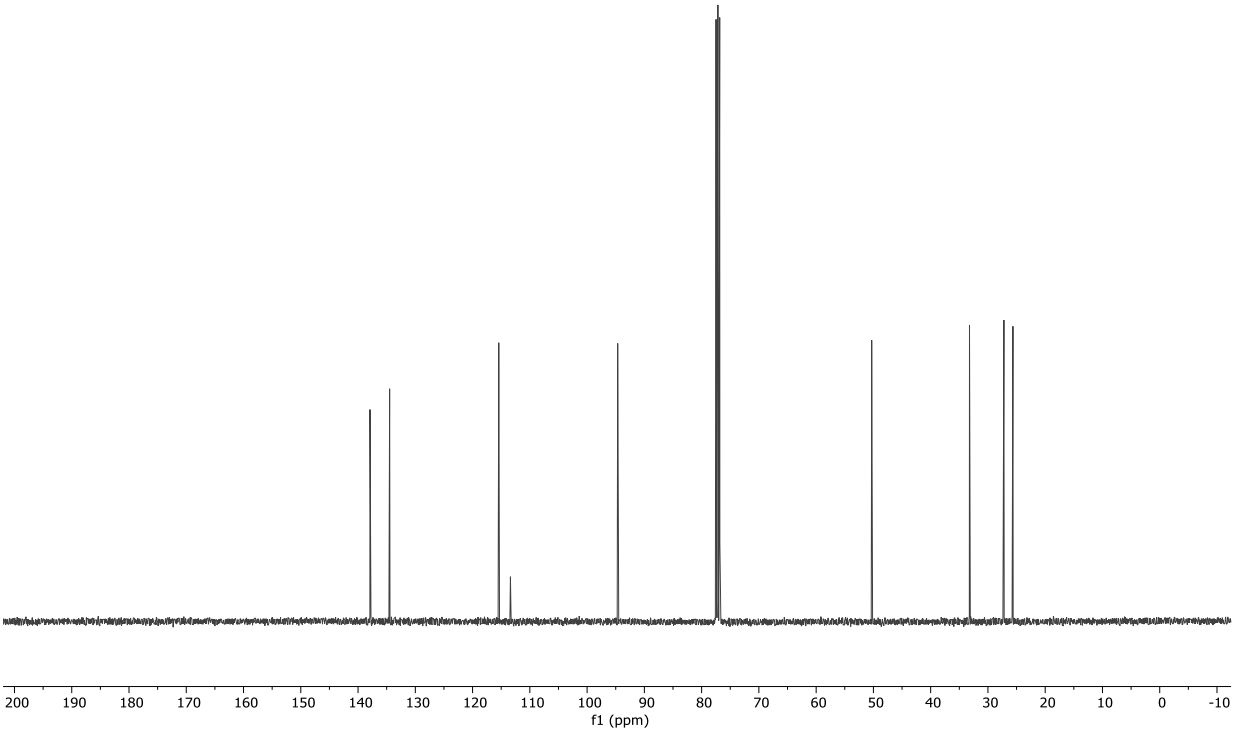

1.92
0.99
1.01
3.92
2.00
6.09
2.05
4.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

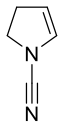

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N

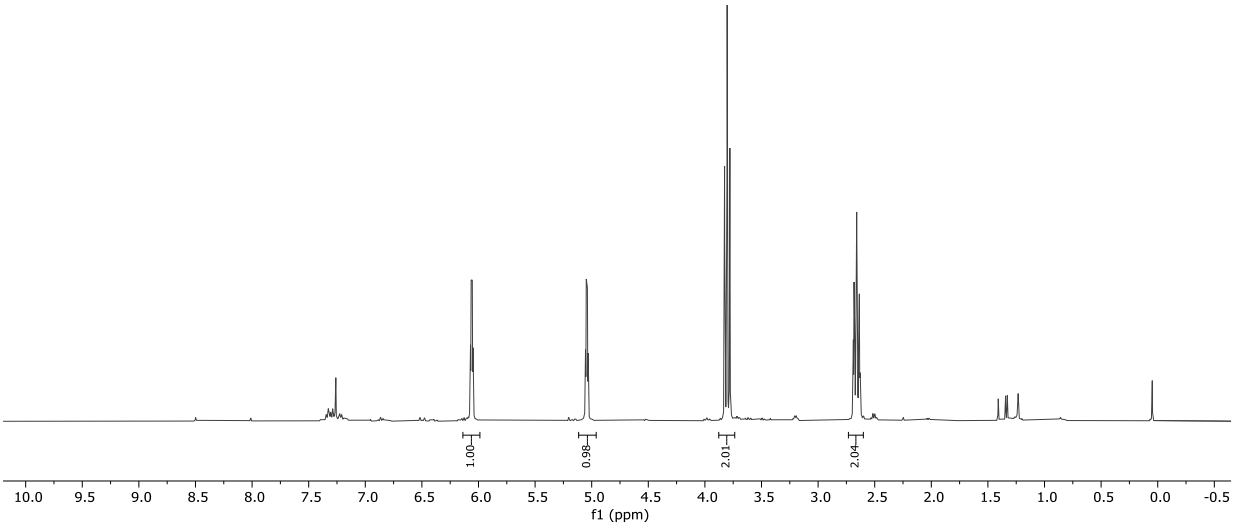
1t

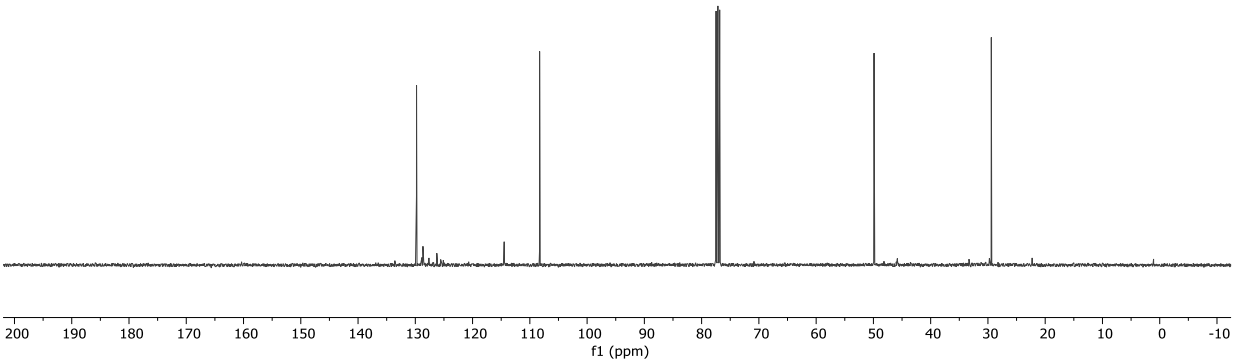

0.97
0.96
1.93
1.00
1.00
2.00
1.99
2.01
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

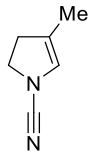

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



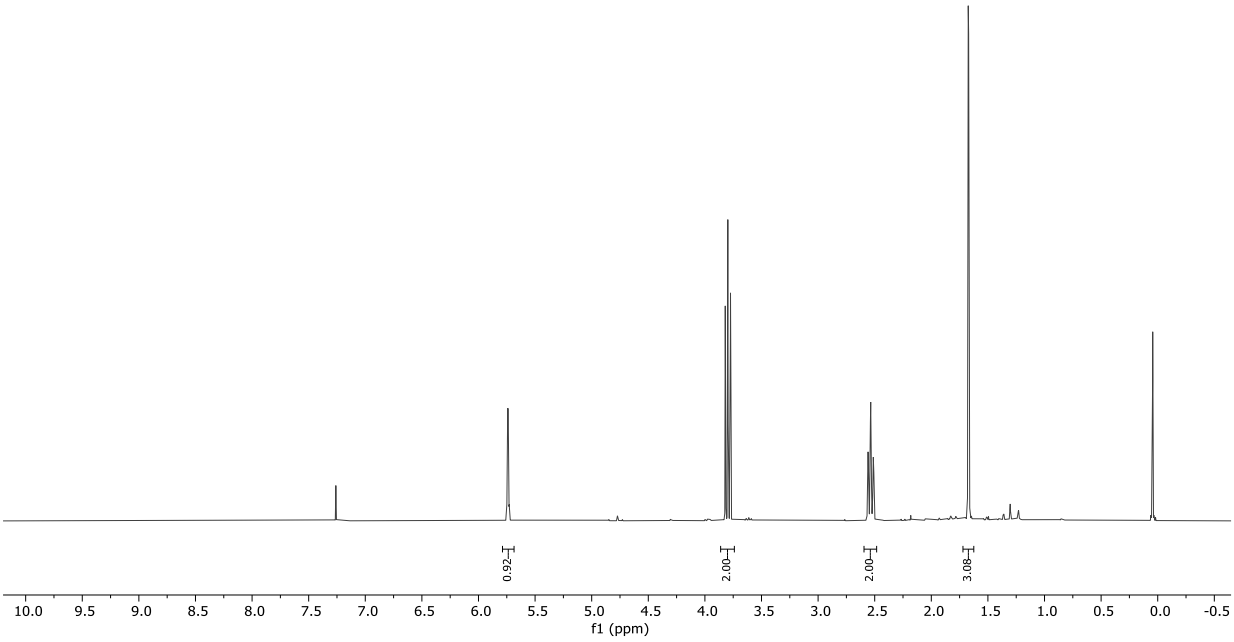
2a

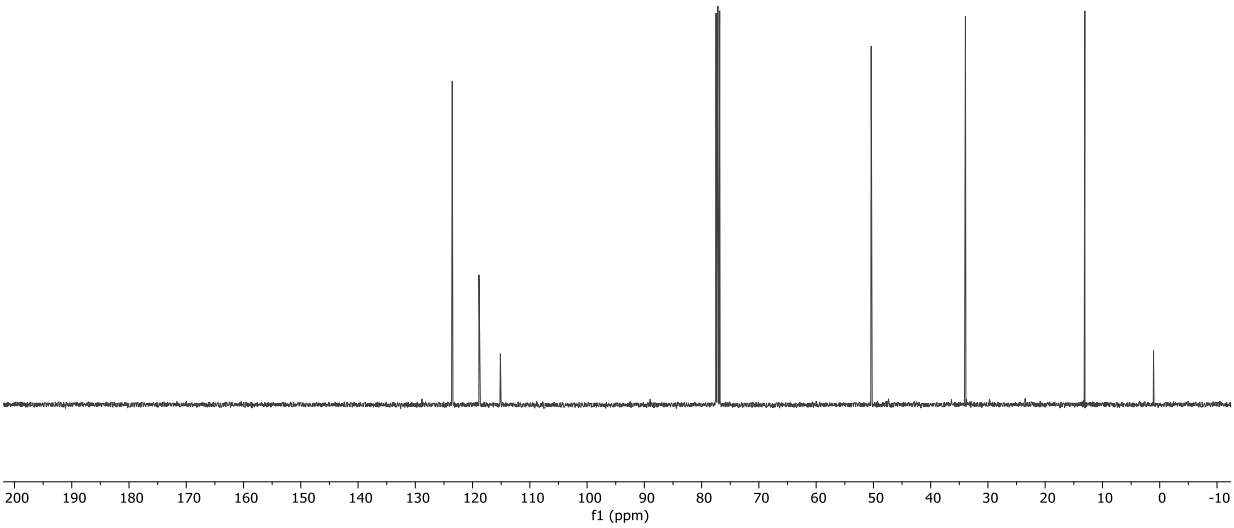

1.00
0.98
2.01
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
N
N

2b


0.92
2.00
2.00
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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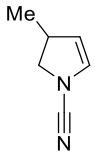
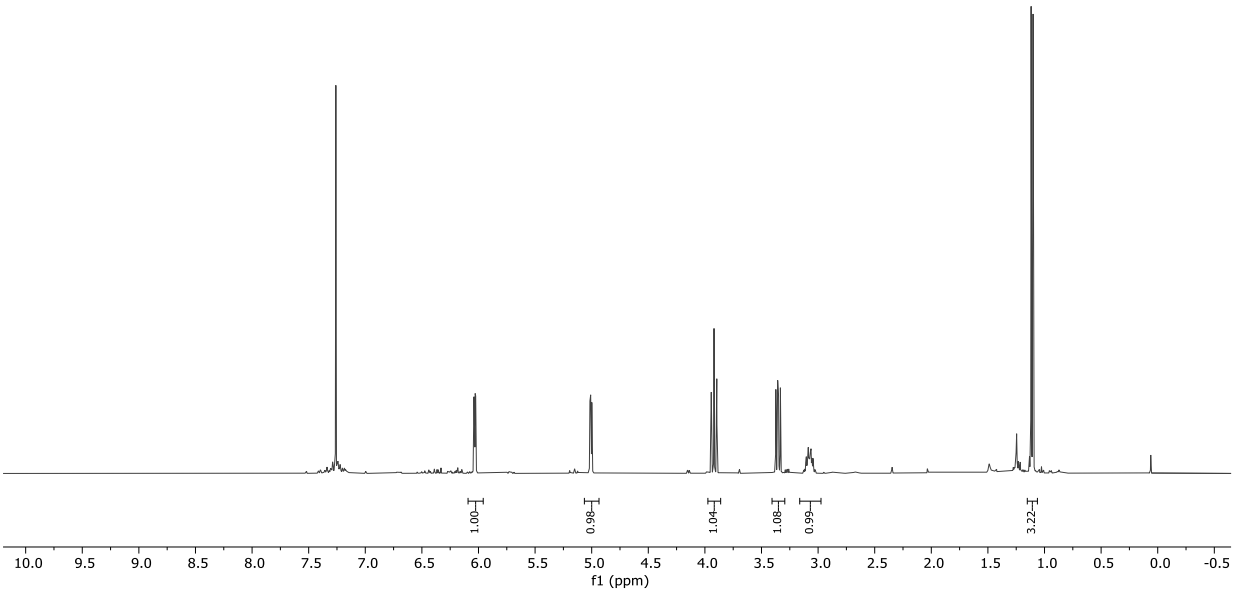
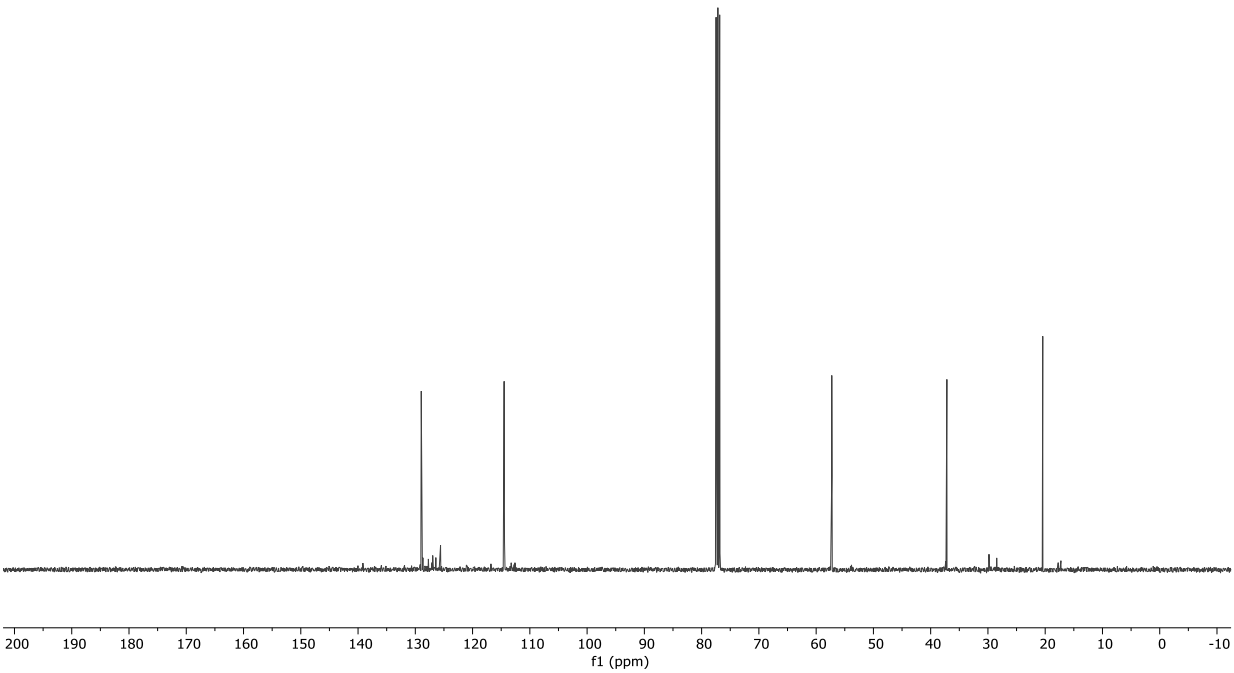
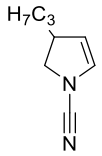
f1 (ppm)


Me
N
N

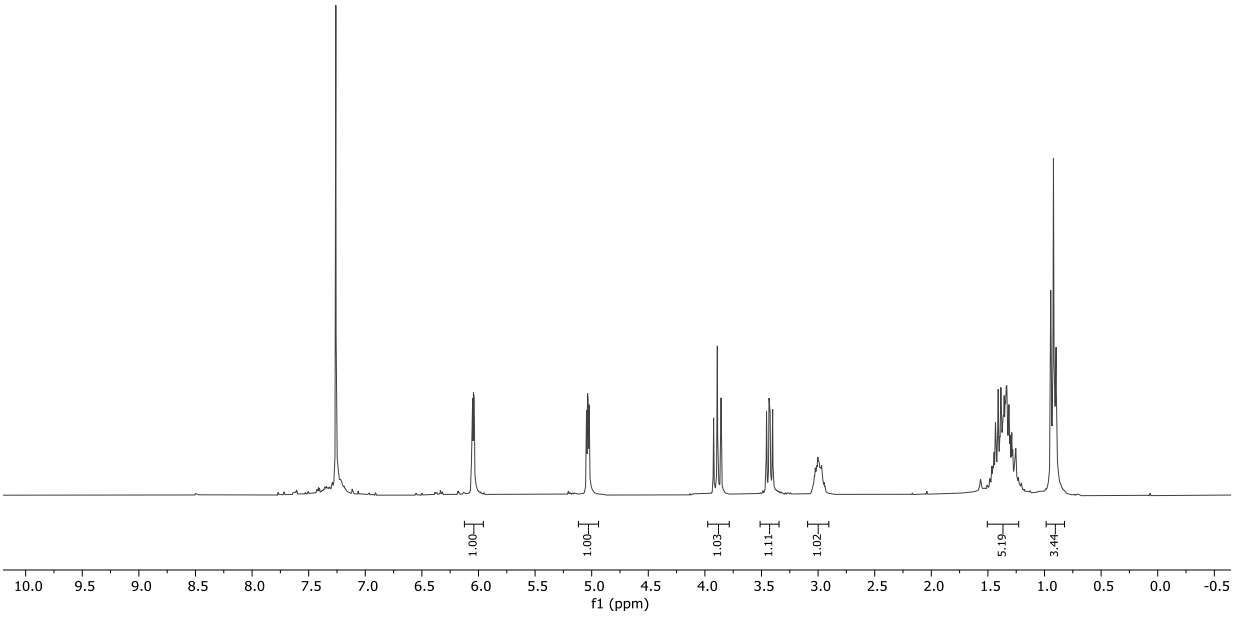
2d

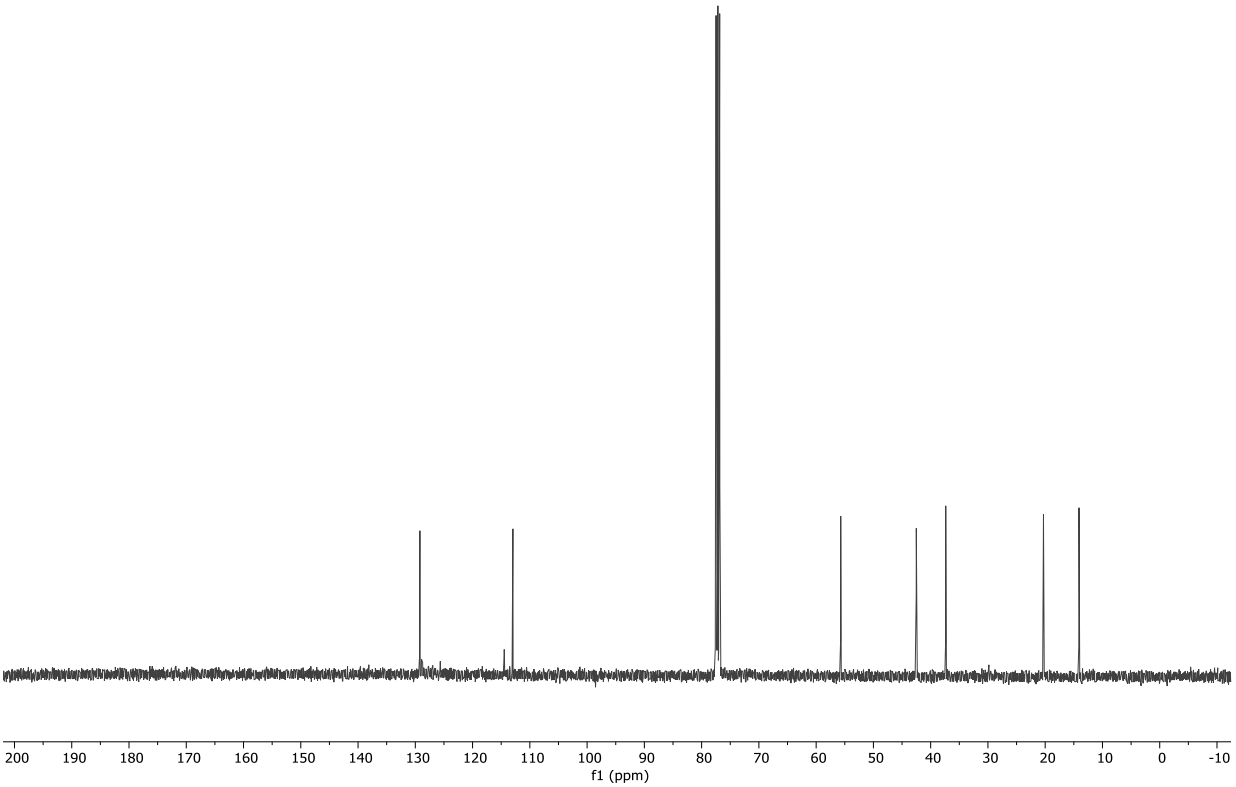

1.00
0.98
1.04
1.08
0.99
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

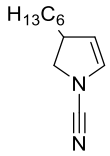

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H7C3
N
N

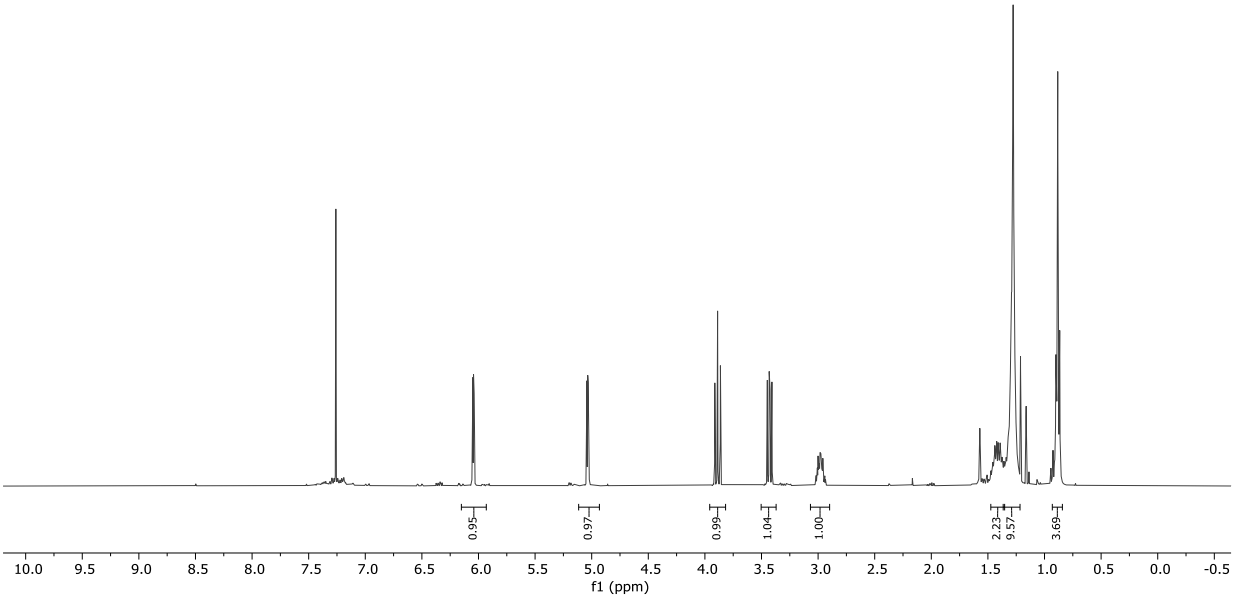
2e

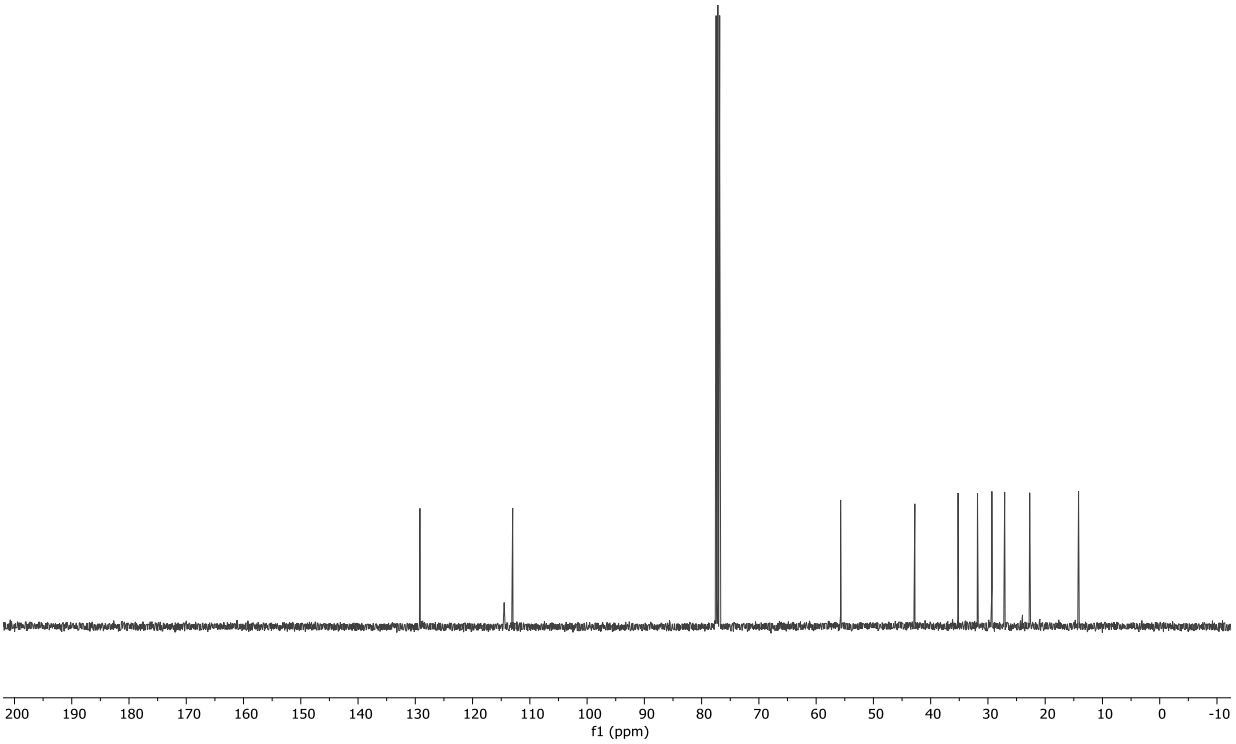

1.00
1.00
1.03
1.11
1.02
5.19
3.44
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

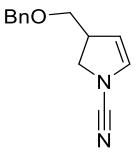

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H13C6
N
N

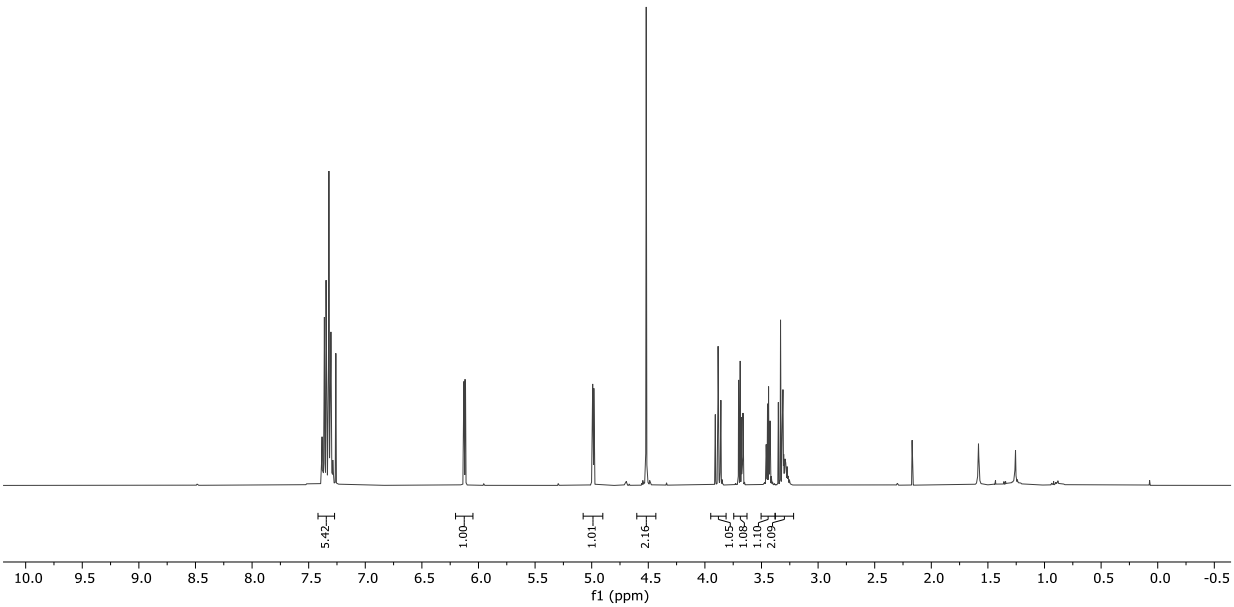
2f

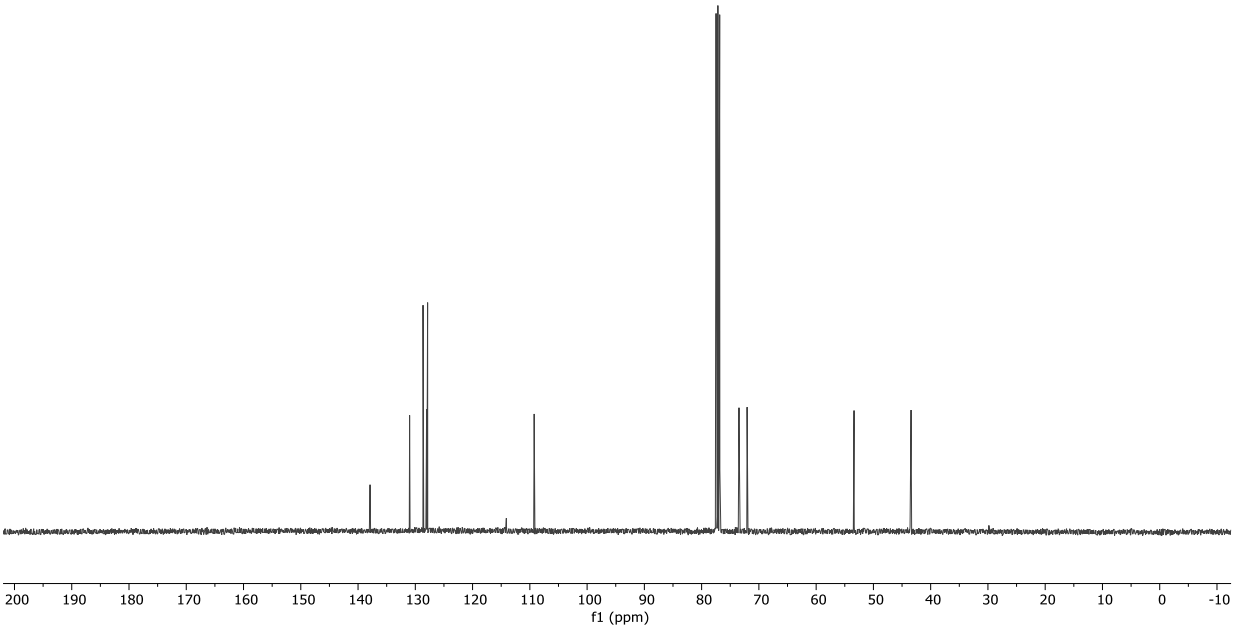

0.95
0.97
0.99
1.04
1.00
2.23
9.57
3.69
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

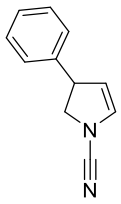

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


BnO
N
N

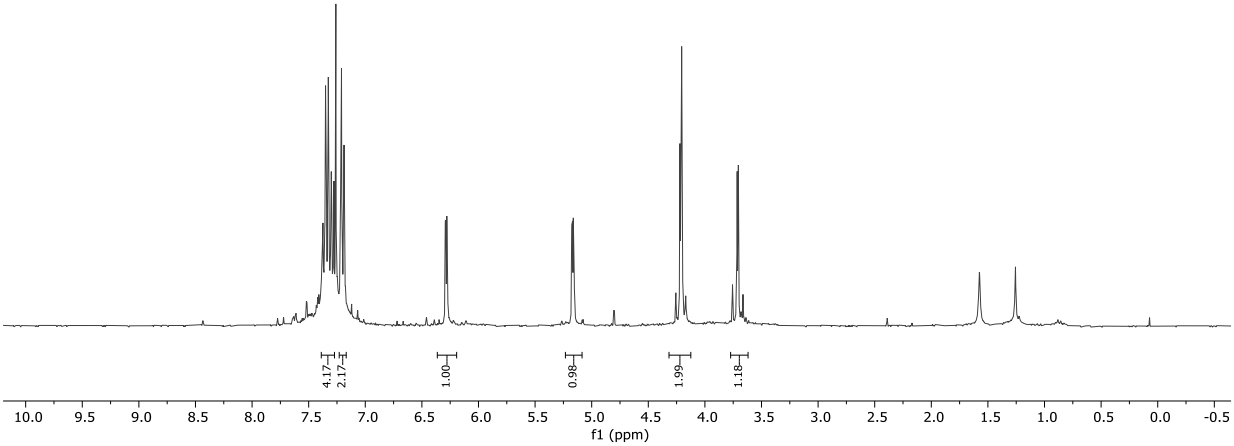
2g

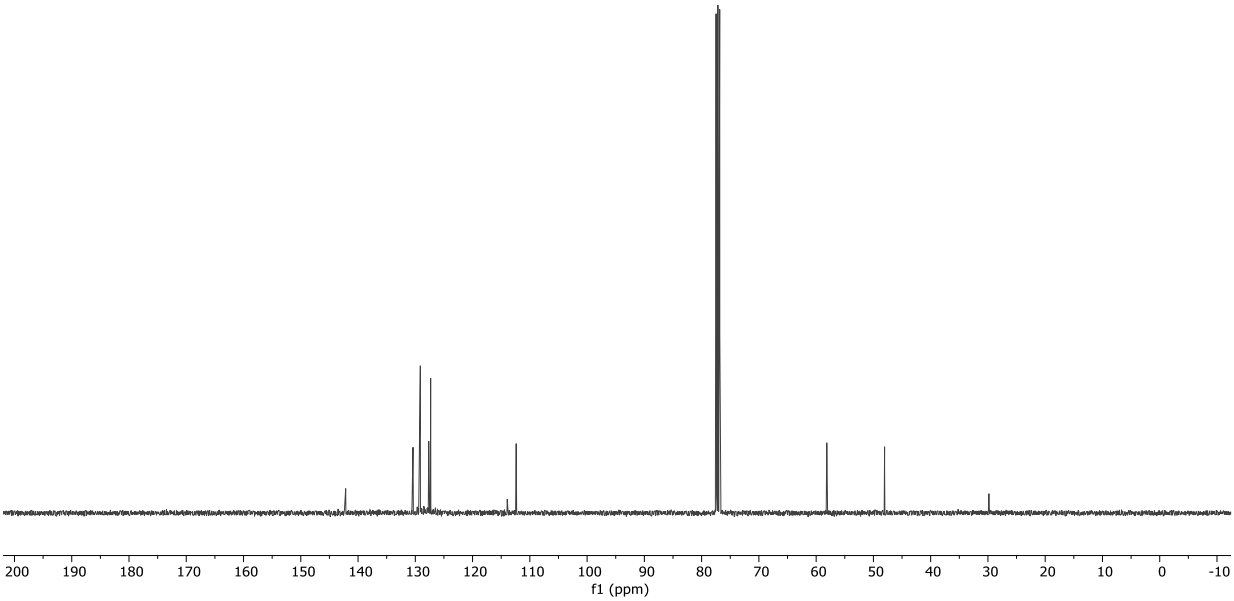

5.42
1.00
1.01
2.16
1.05
1.08
1.10
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

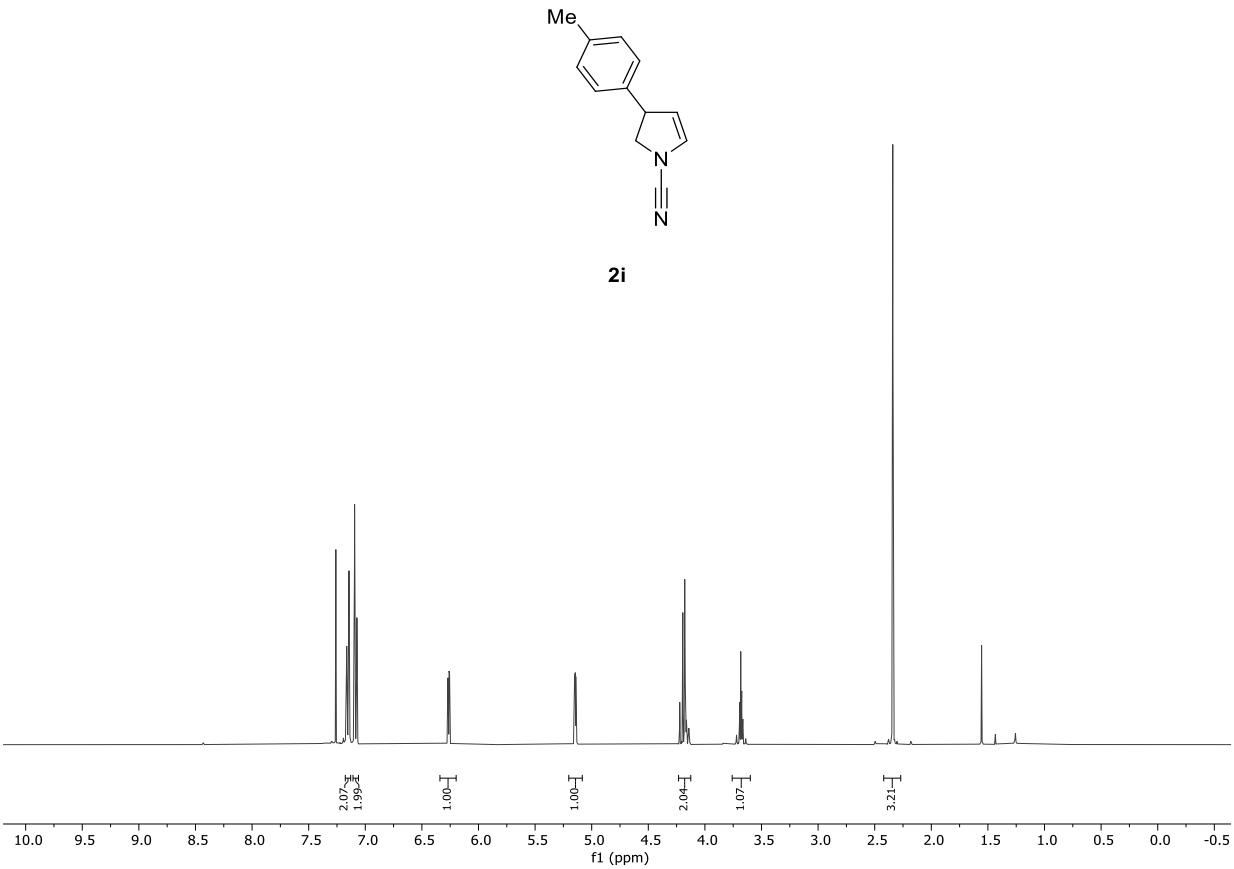

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N

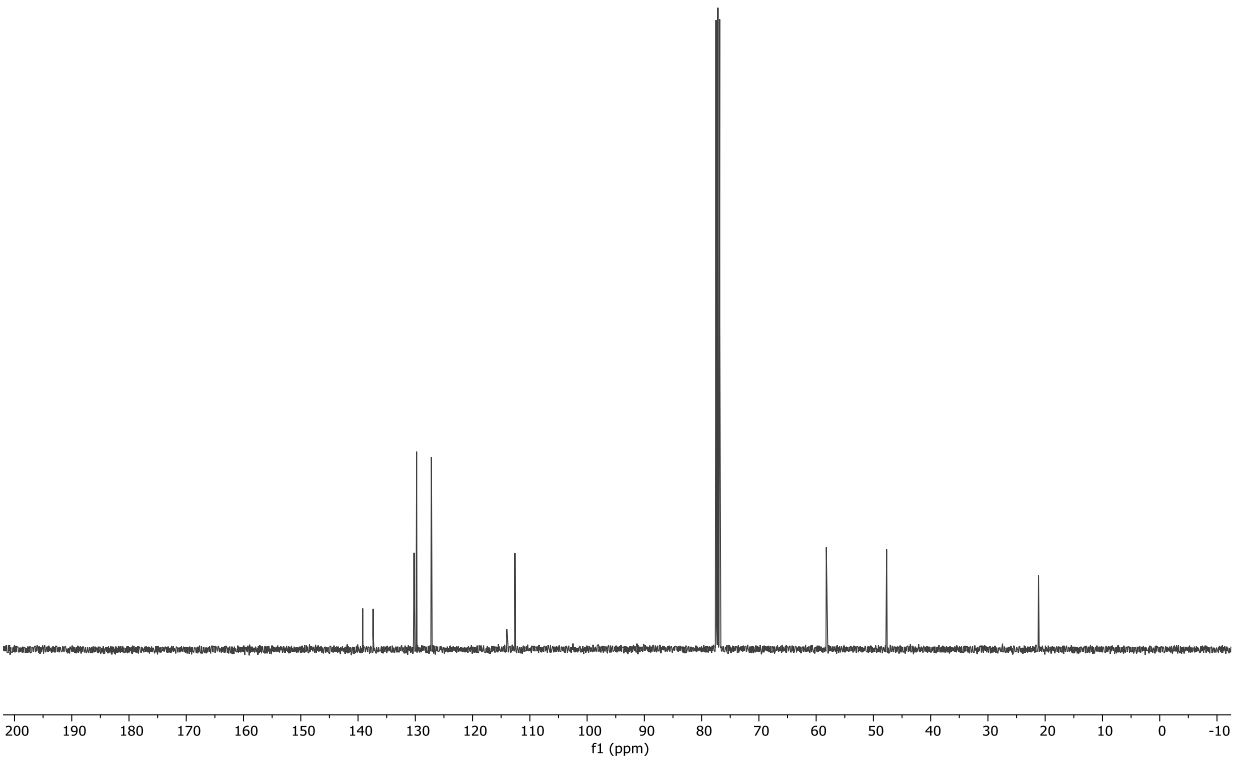
2h

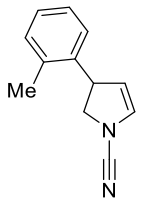

4.17
2.17
1.00
0.98
1.99
1.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

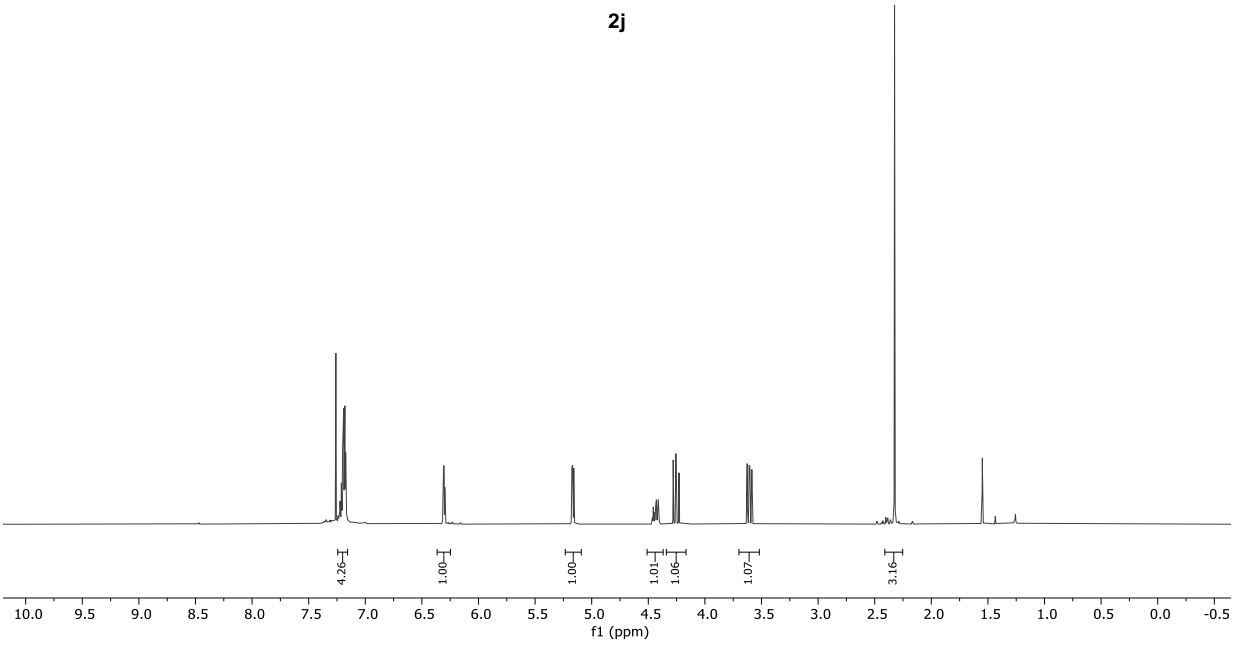

Me
N
N
2.07
1.99
1.00
1.00
2.04
1.07
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

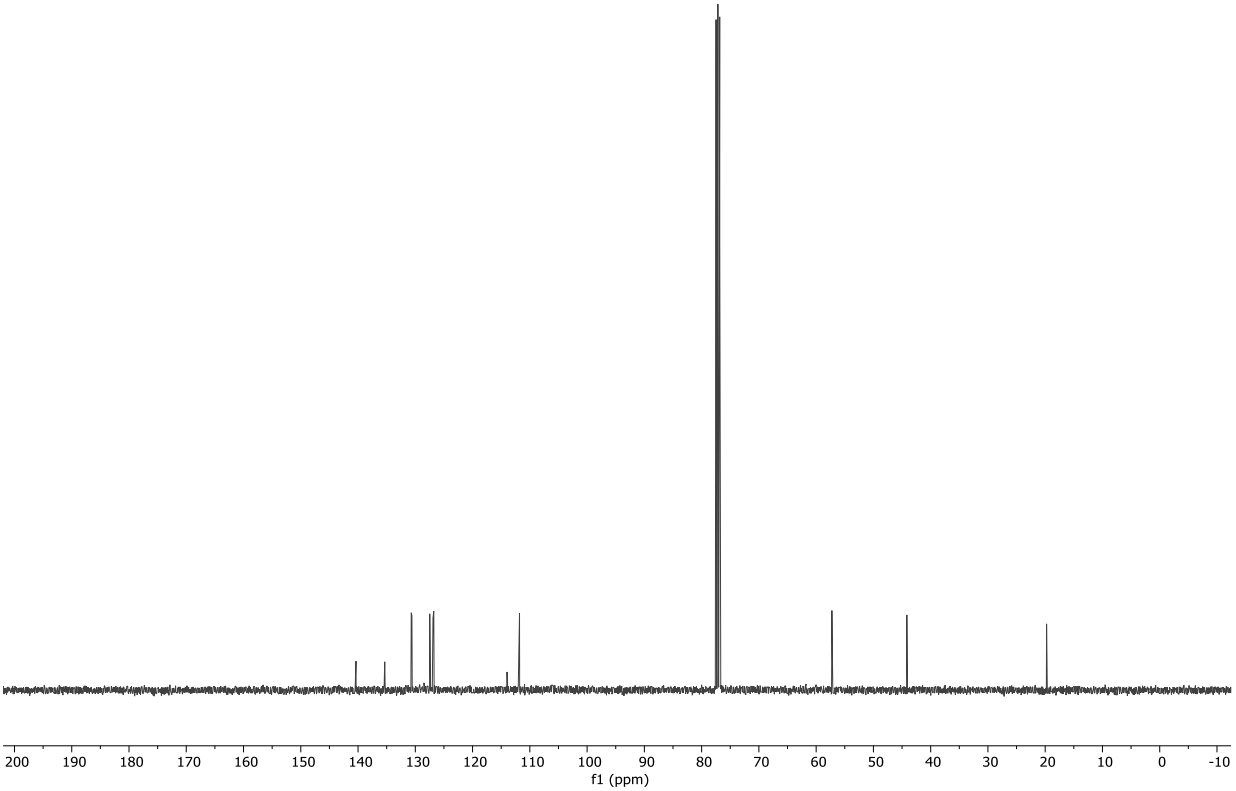
2i

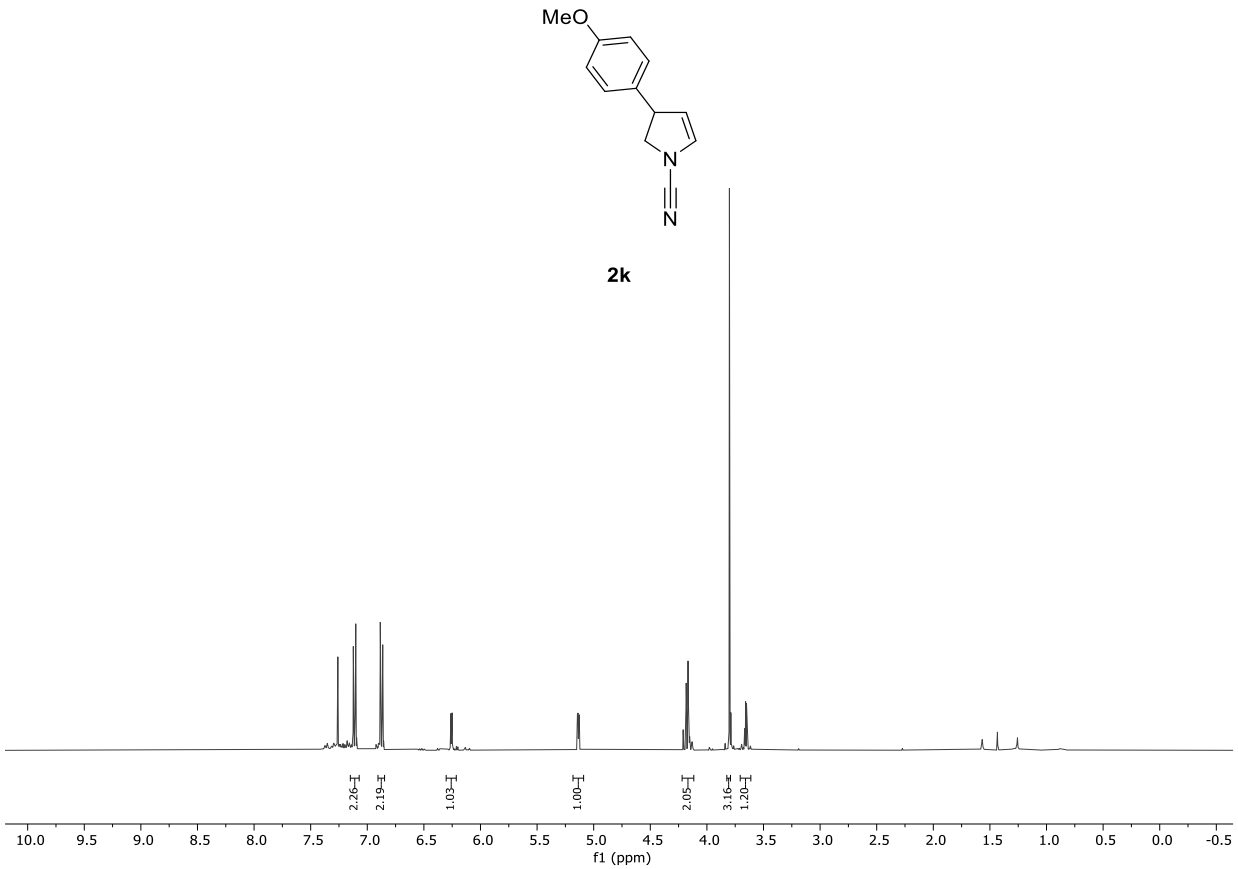

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
N
N

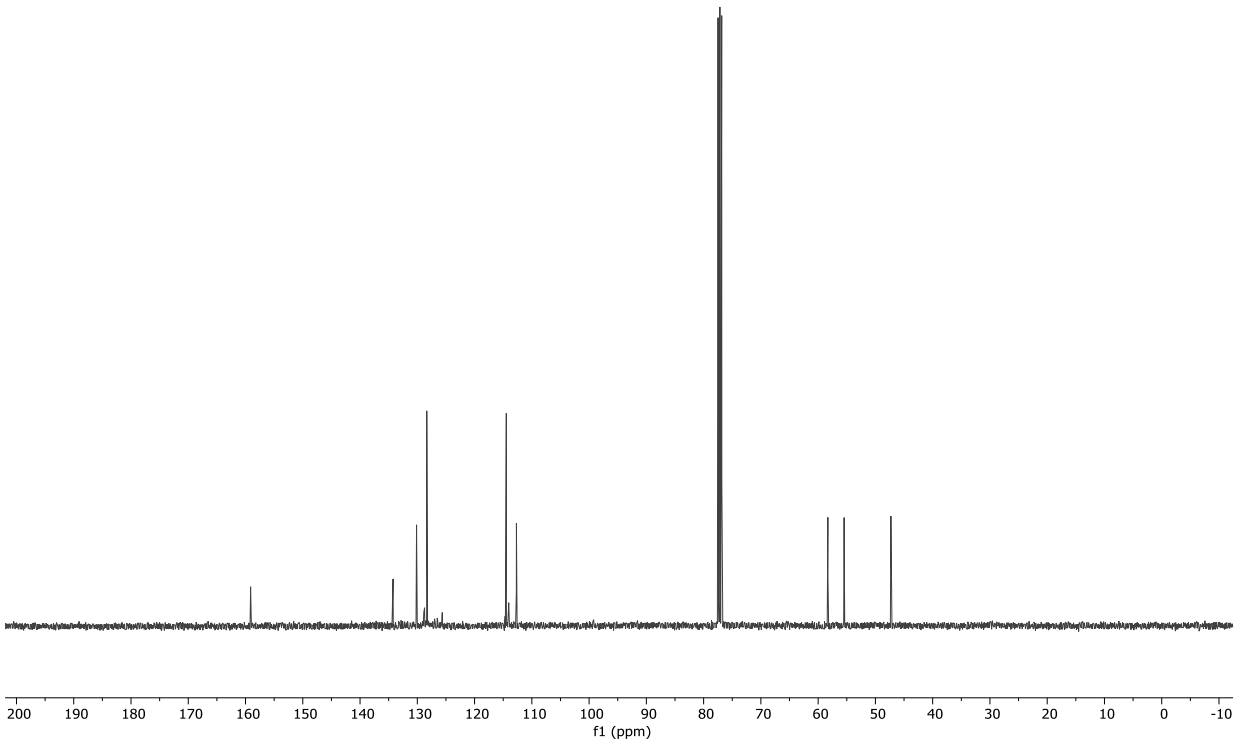
2j

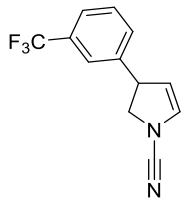

4.26
1.00
1.00
1.01
1.06
1.07
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

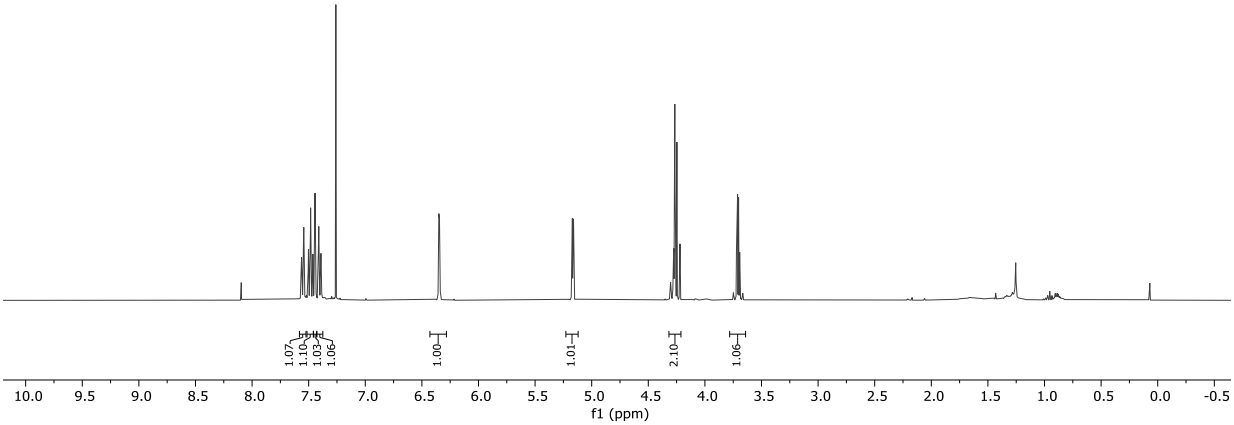

MeO
N
N
2.26
2.19
1.03
1.00
2.05
3.16
1.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

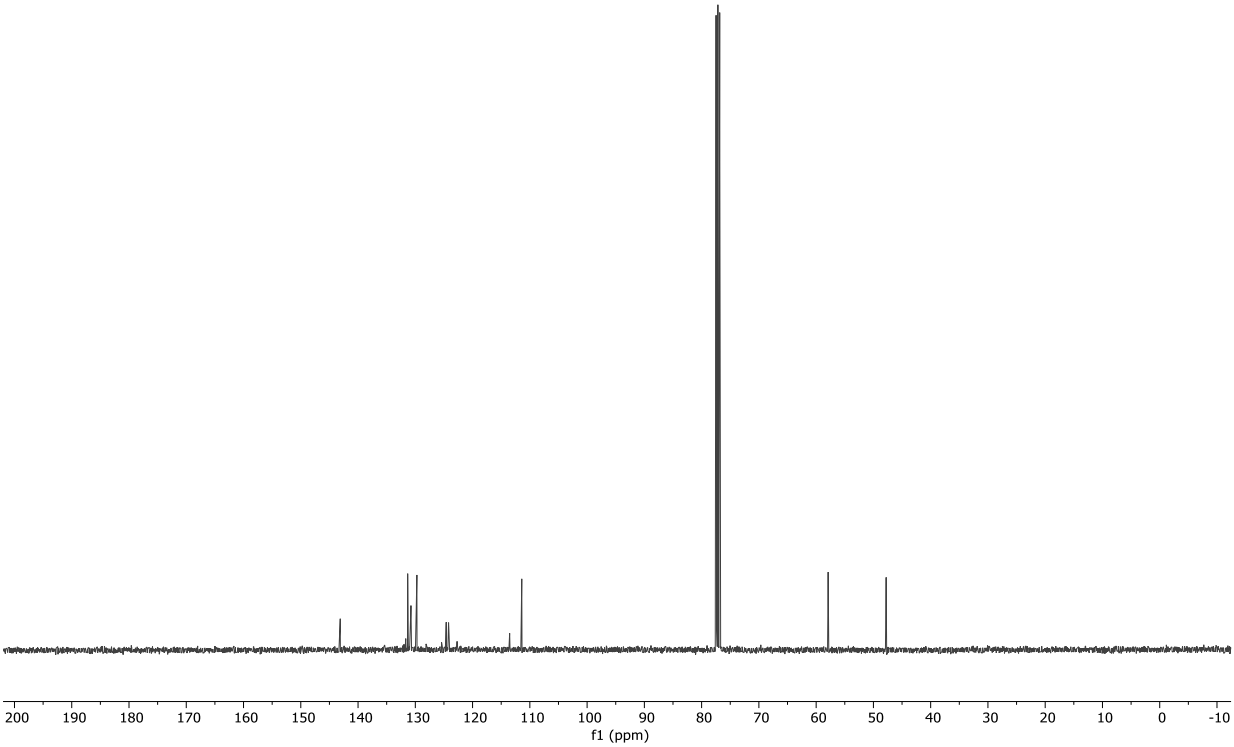
2k

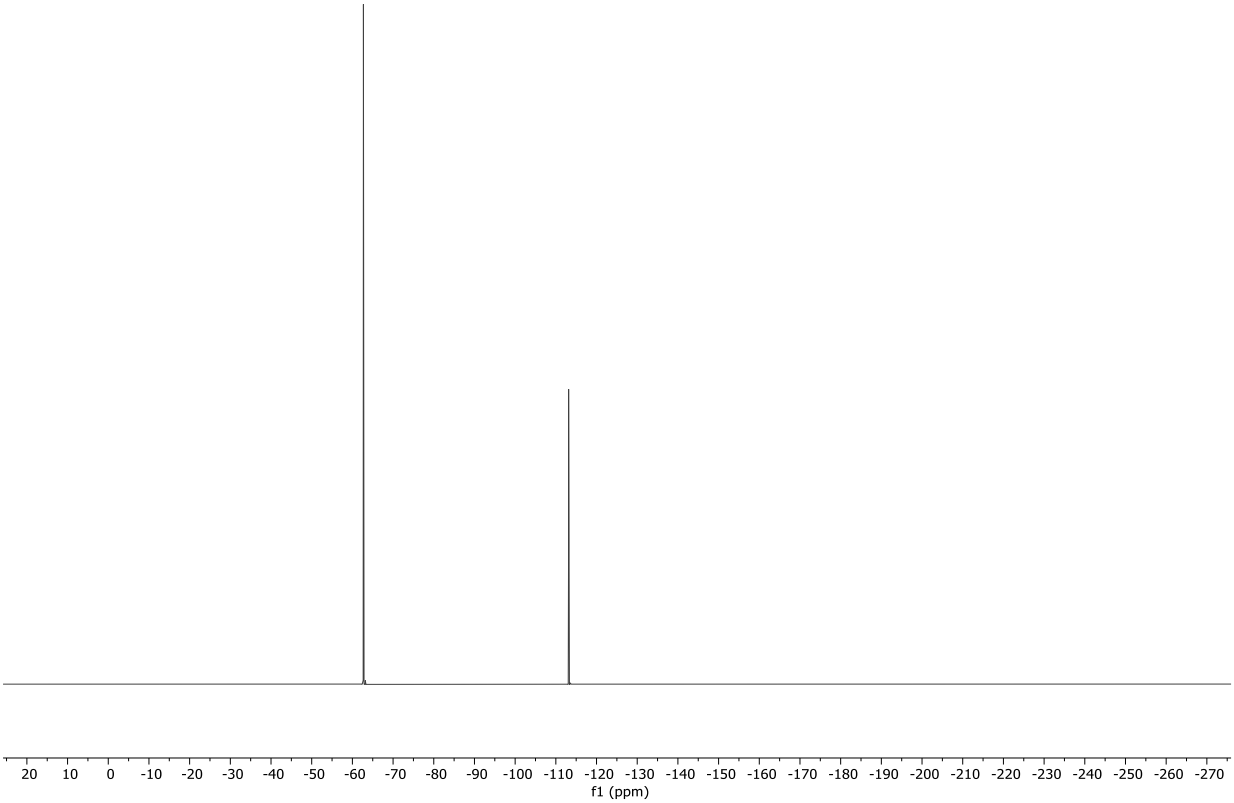

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

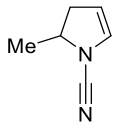

F3C
N
N

2l

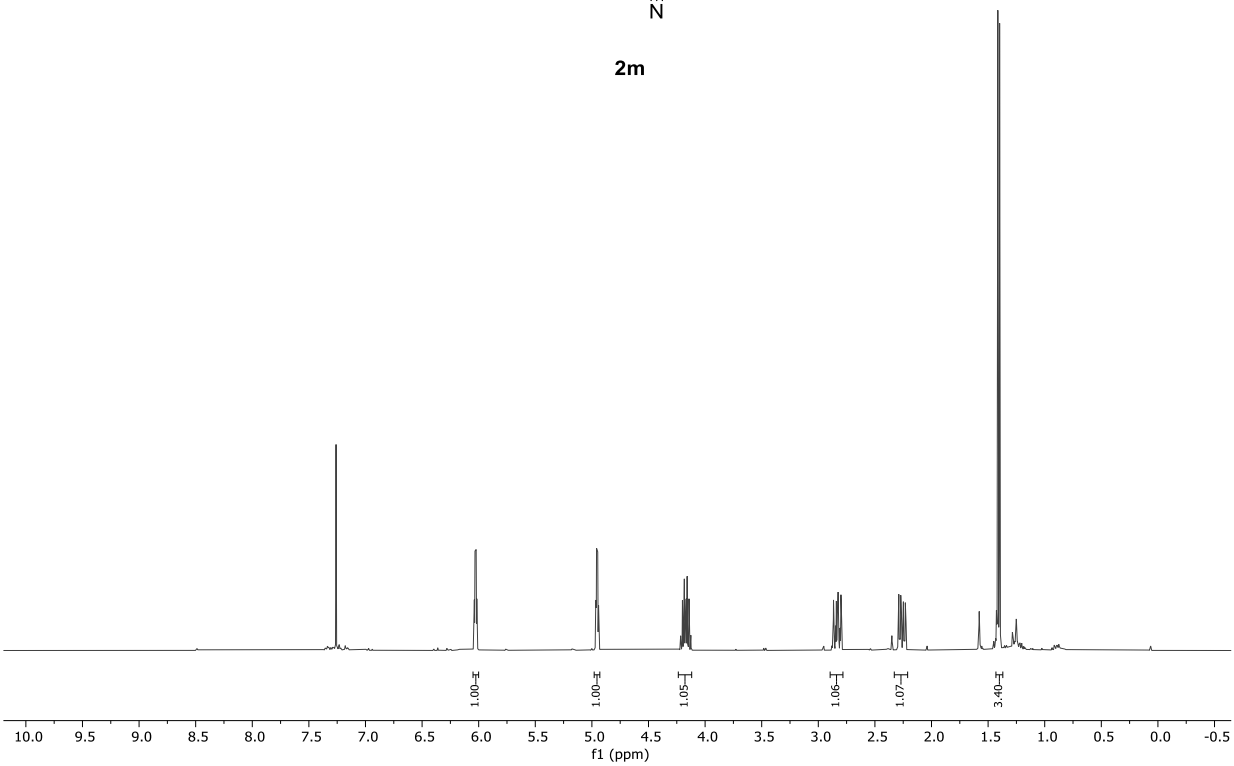

1.07
1.10
1.03
1.06
1.00
1.01
2.10
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

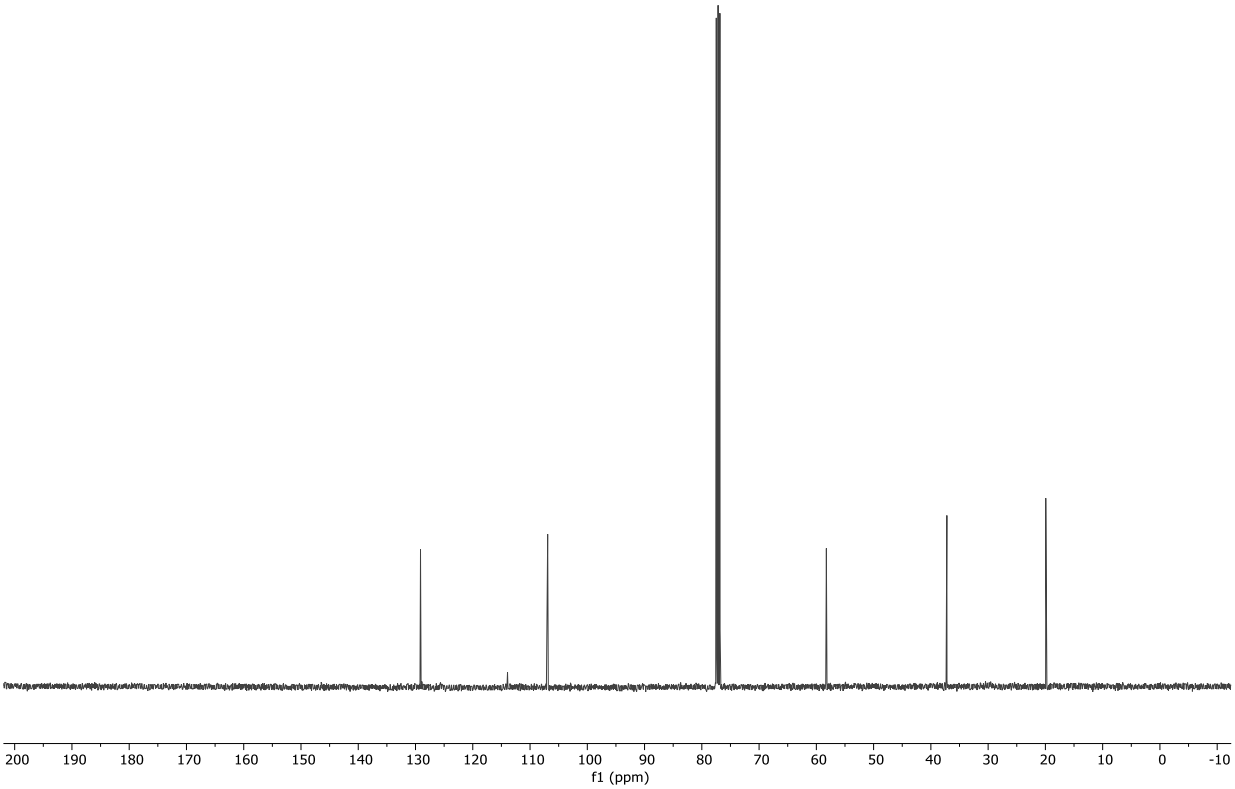

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

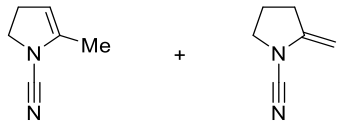

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)


Me
N
N

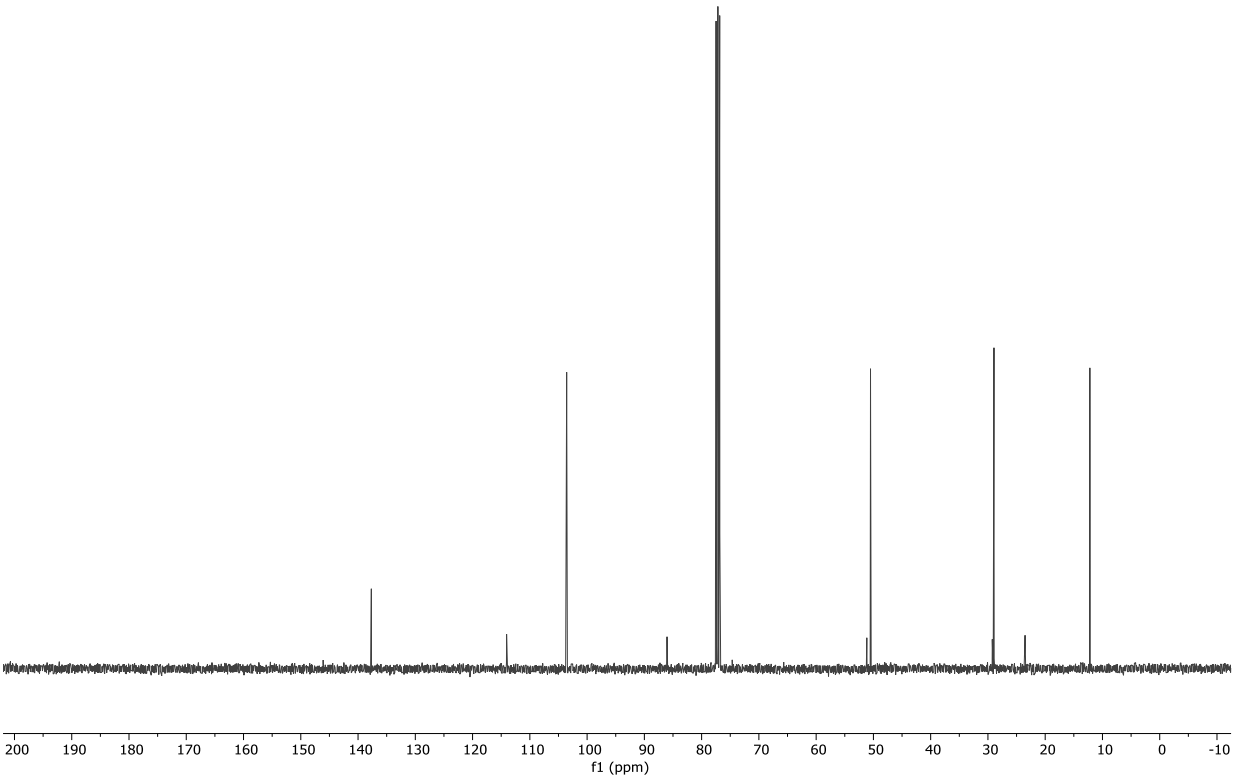
2m

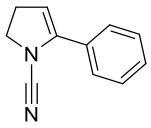

1.00
1.00
1.05
1.06
1.07
3.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

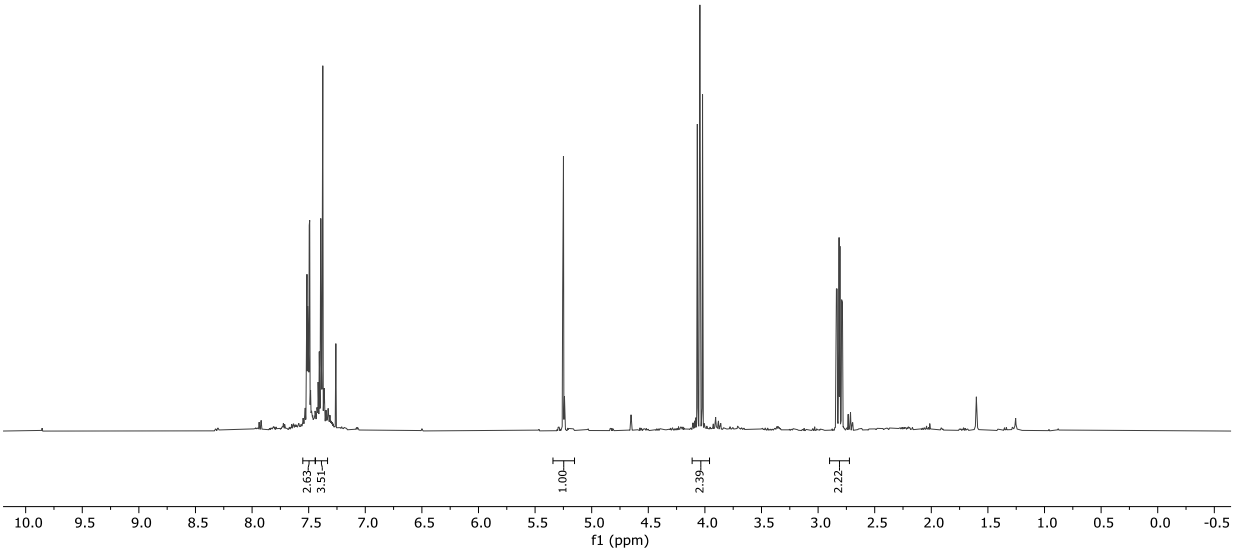


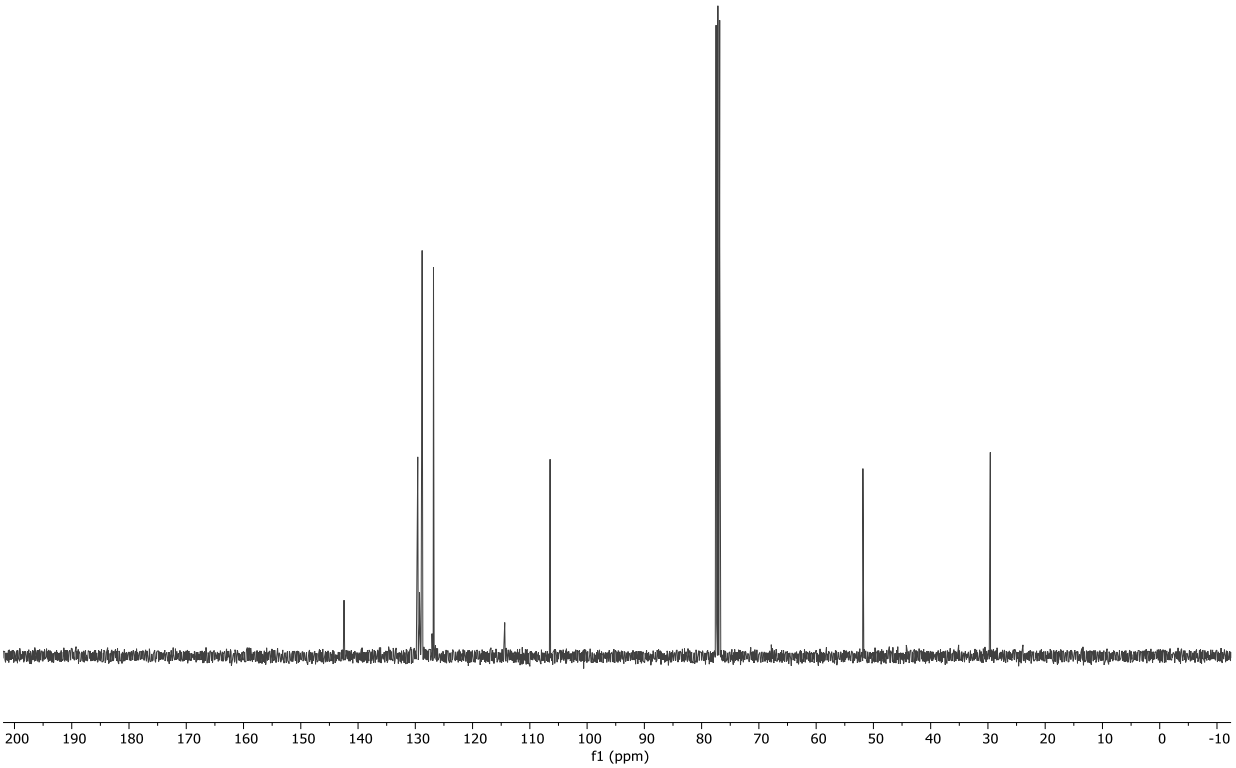
(*endo*)-**2n** (90/10) (*exo*)-**2n'**

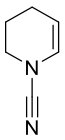




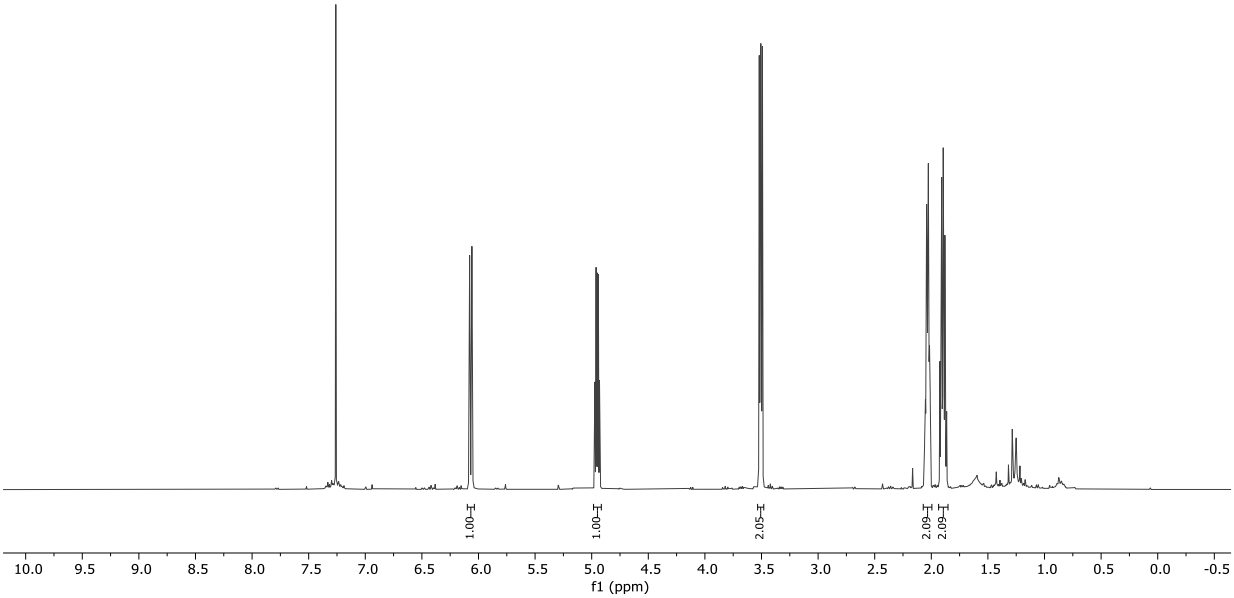
2o

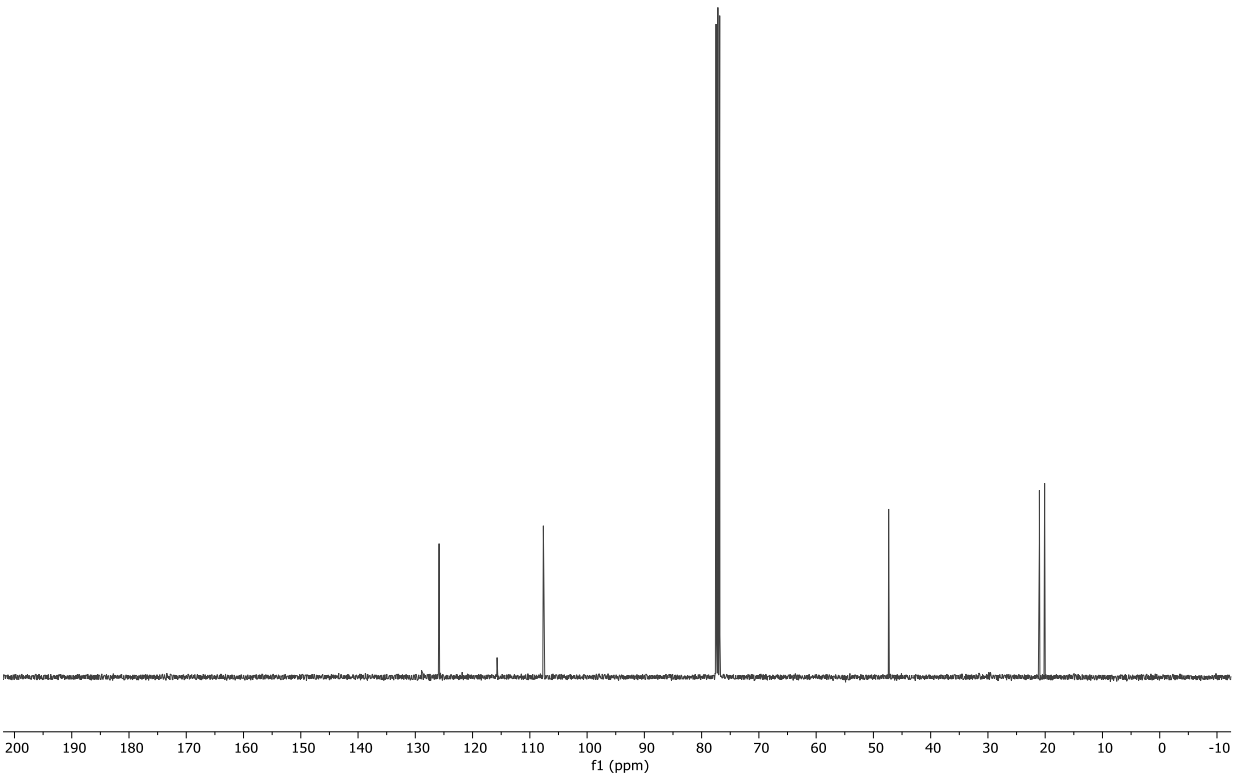

2.63
3.51
1.00
2.39
2.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

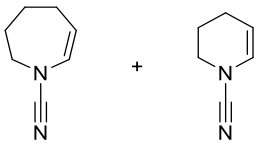

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



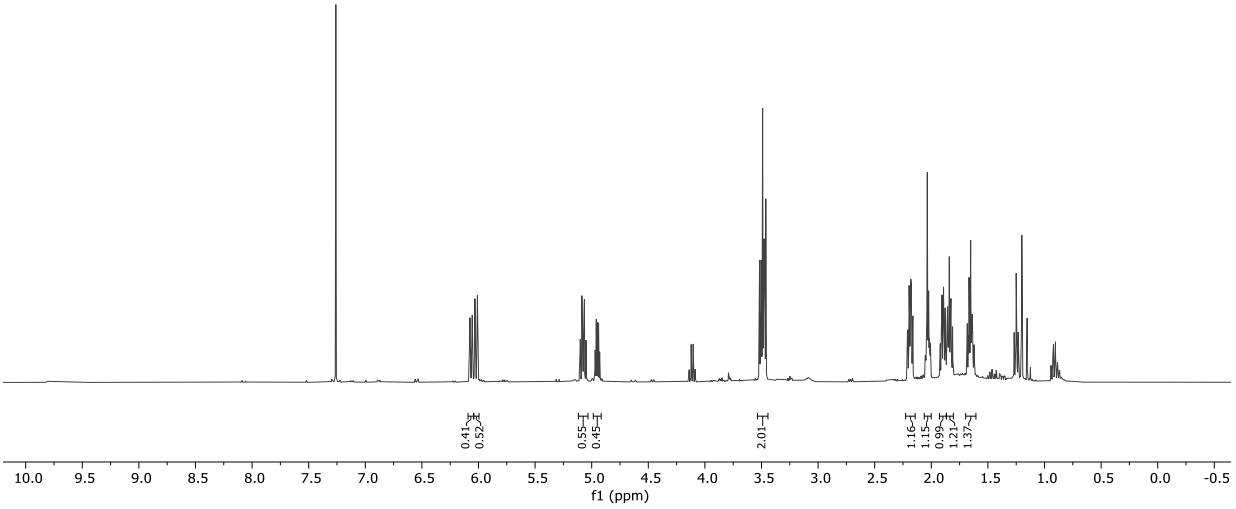
2q

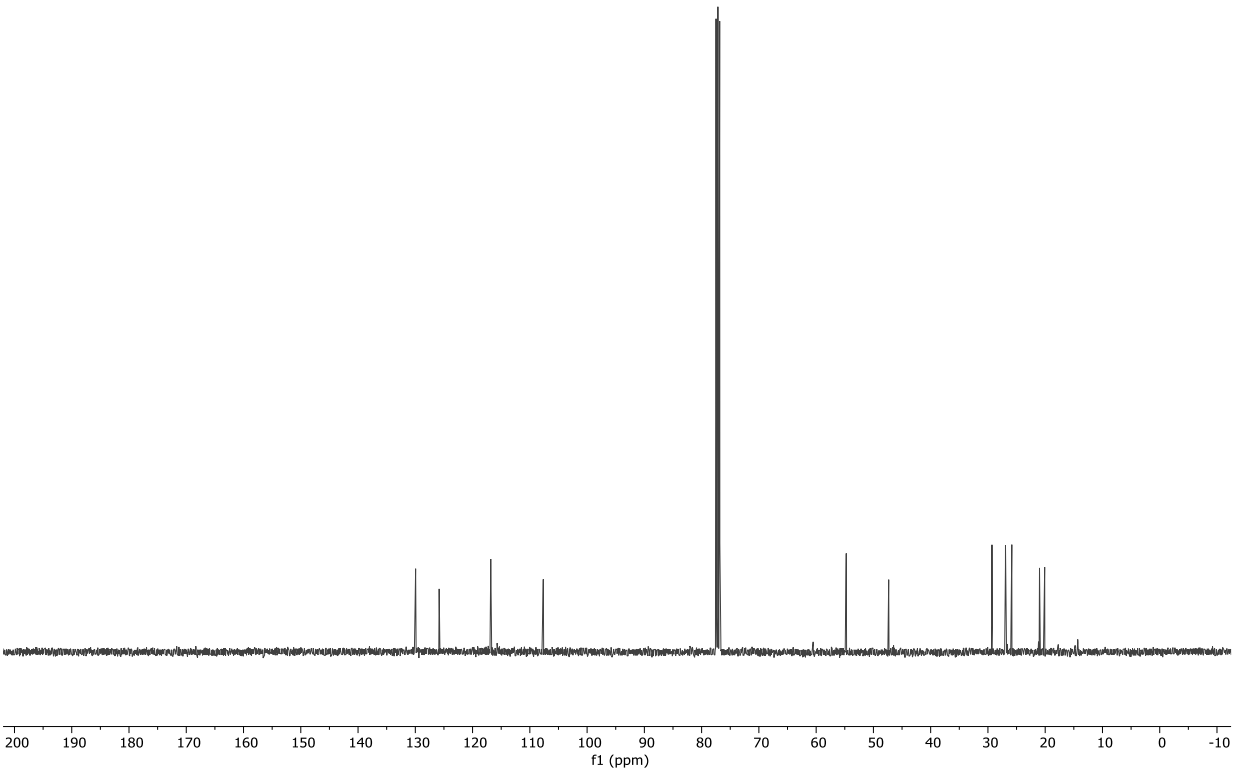

1.00
1.00
2.05
2.09
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

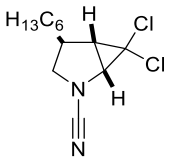

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



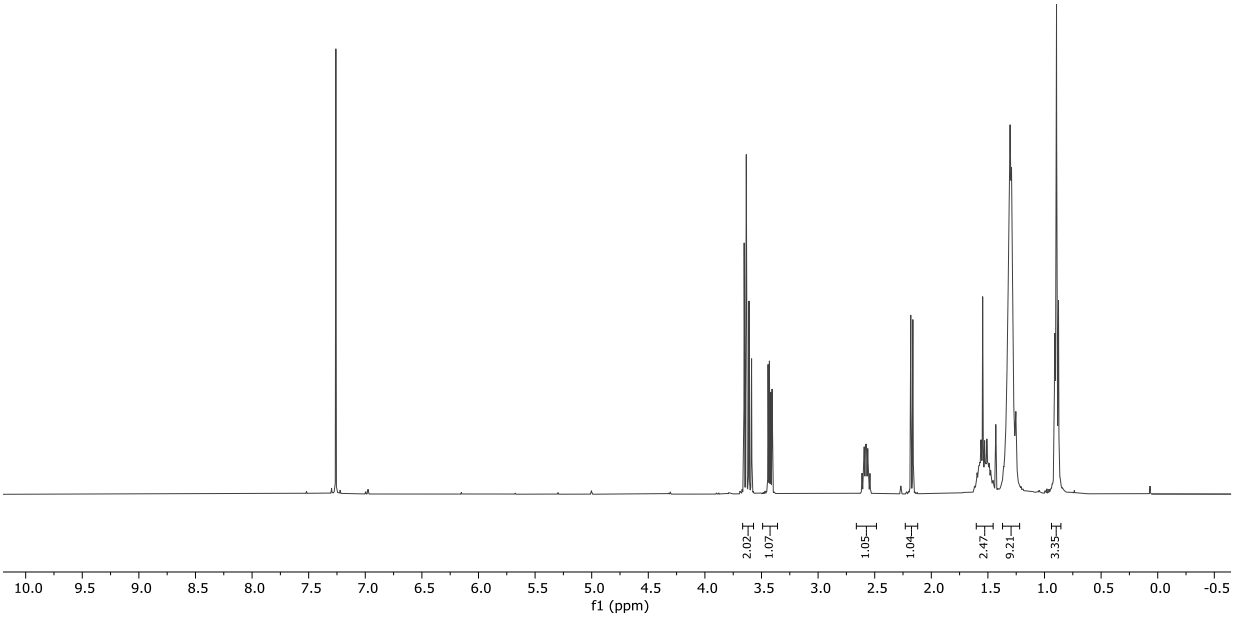
2r (55/45) **2q**

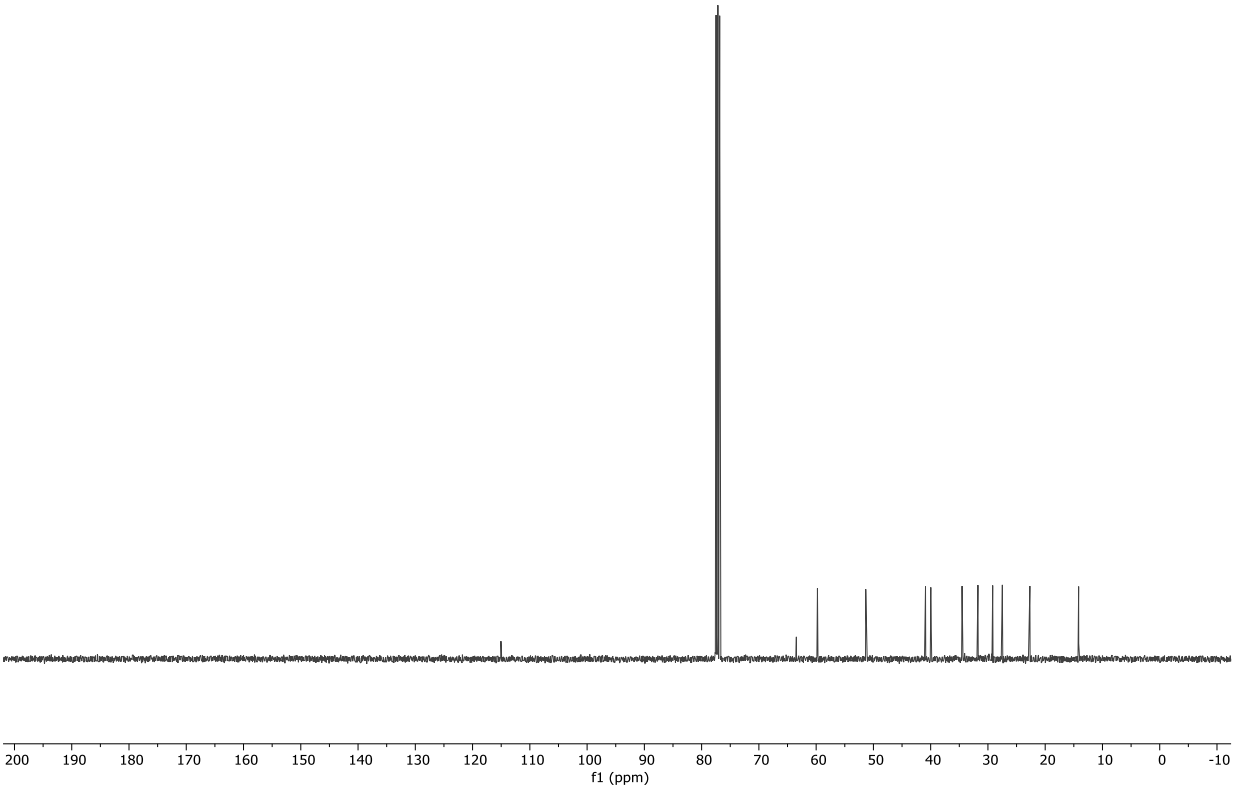

0.41
0.52
0.55
0.45
2.01
1.16
1.15
0.99
1.21
1.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

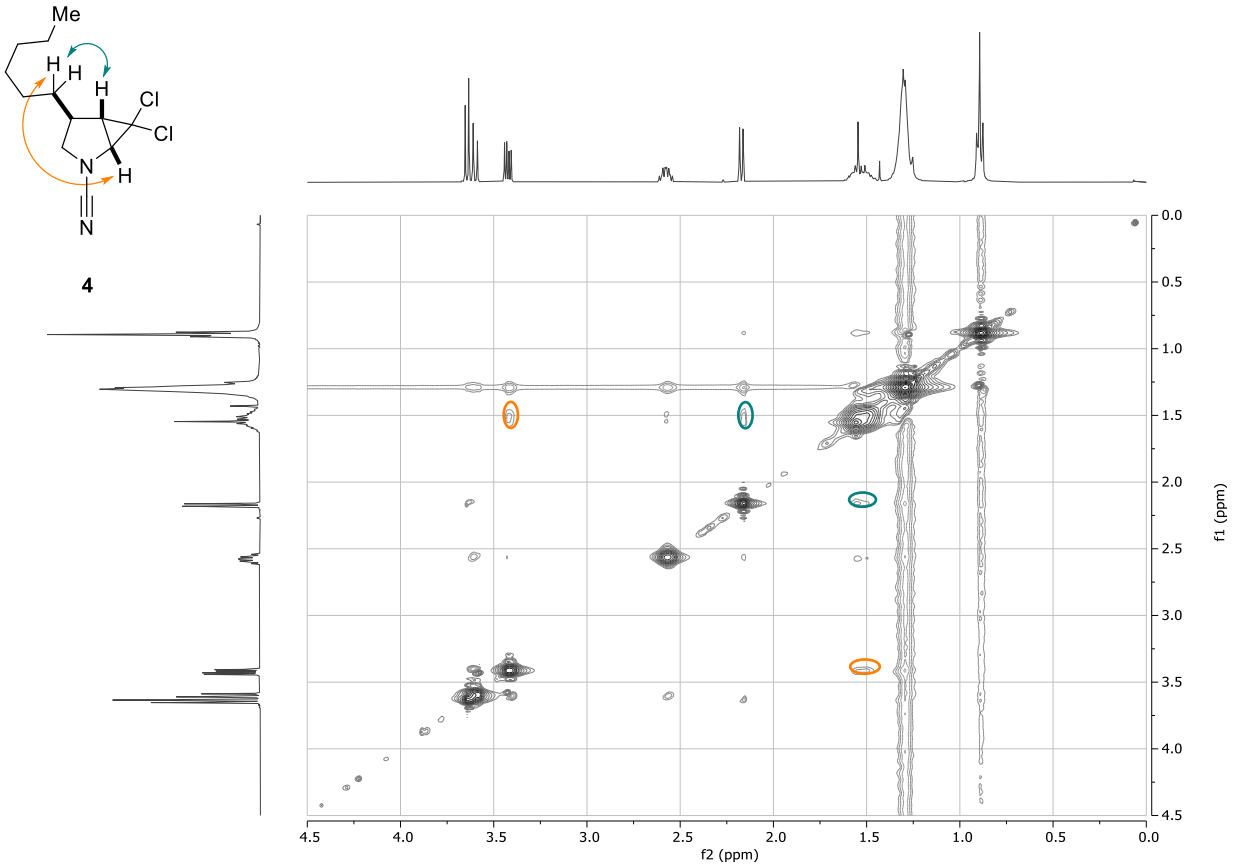

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

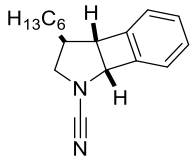

H13C6
H
Cl
Cl
N
H
N

4

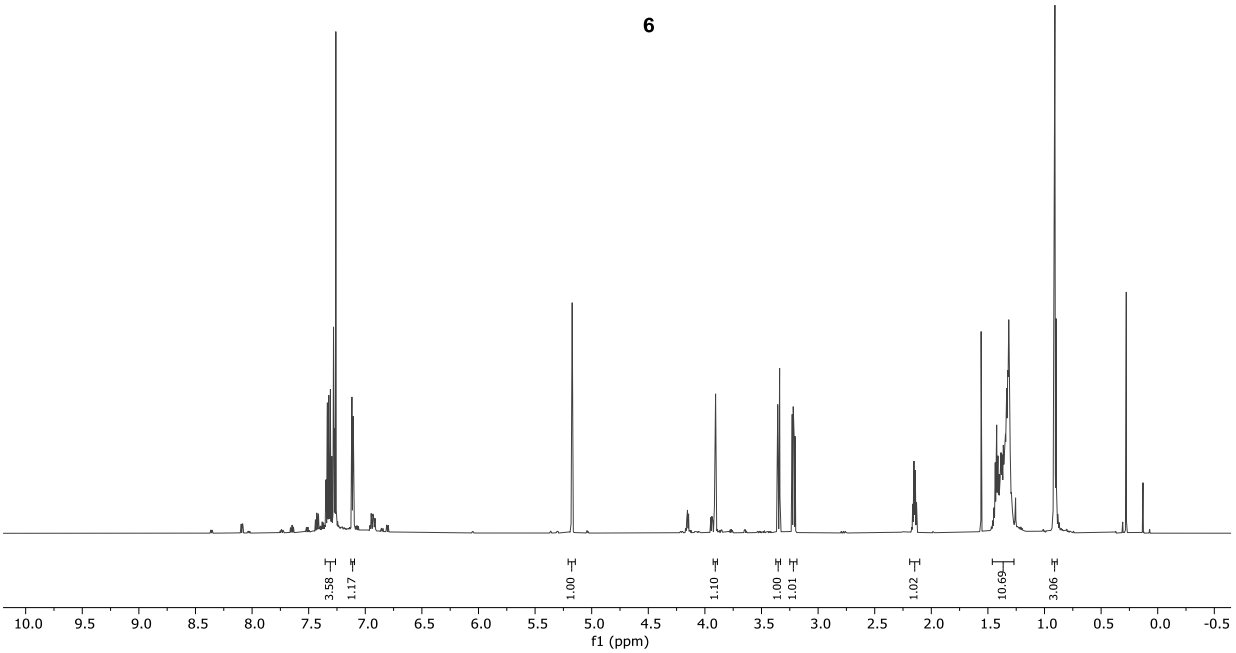

2.02
1.07
1.05
1.04
2.47
9.21
3.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

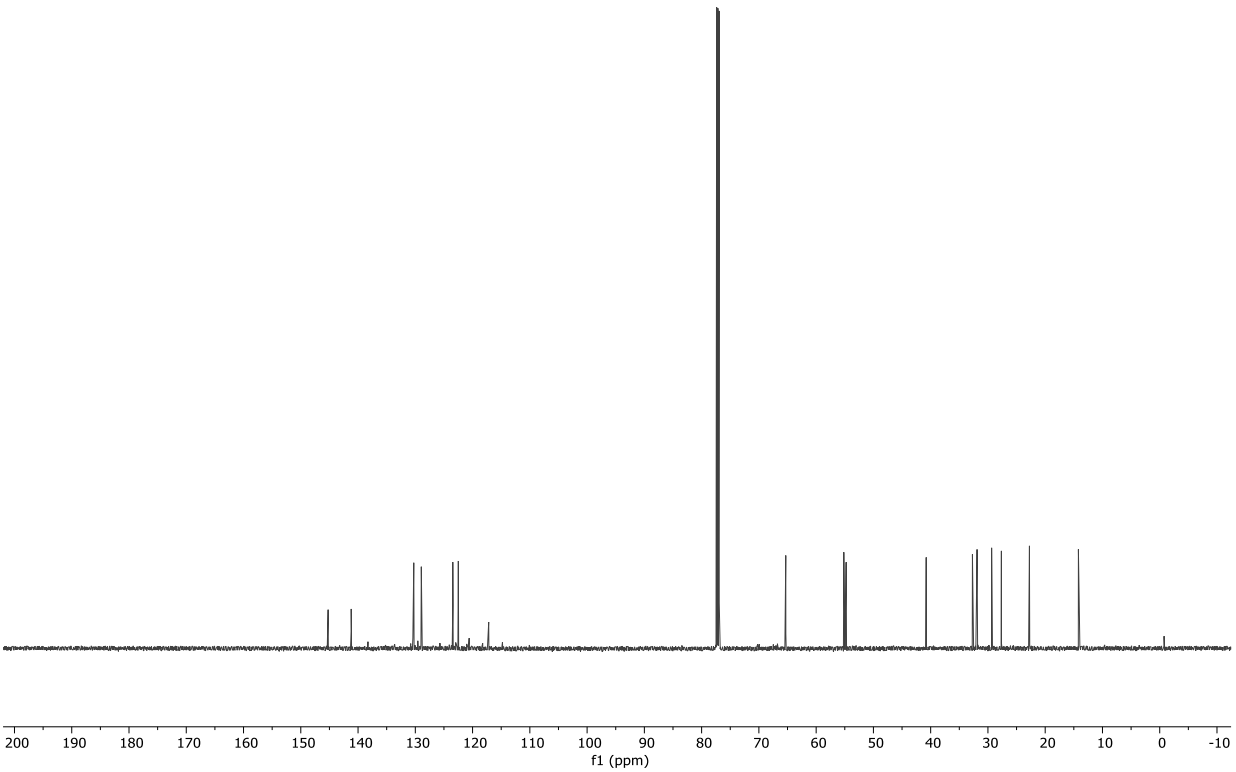

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

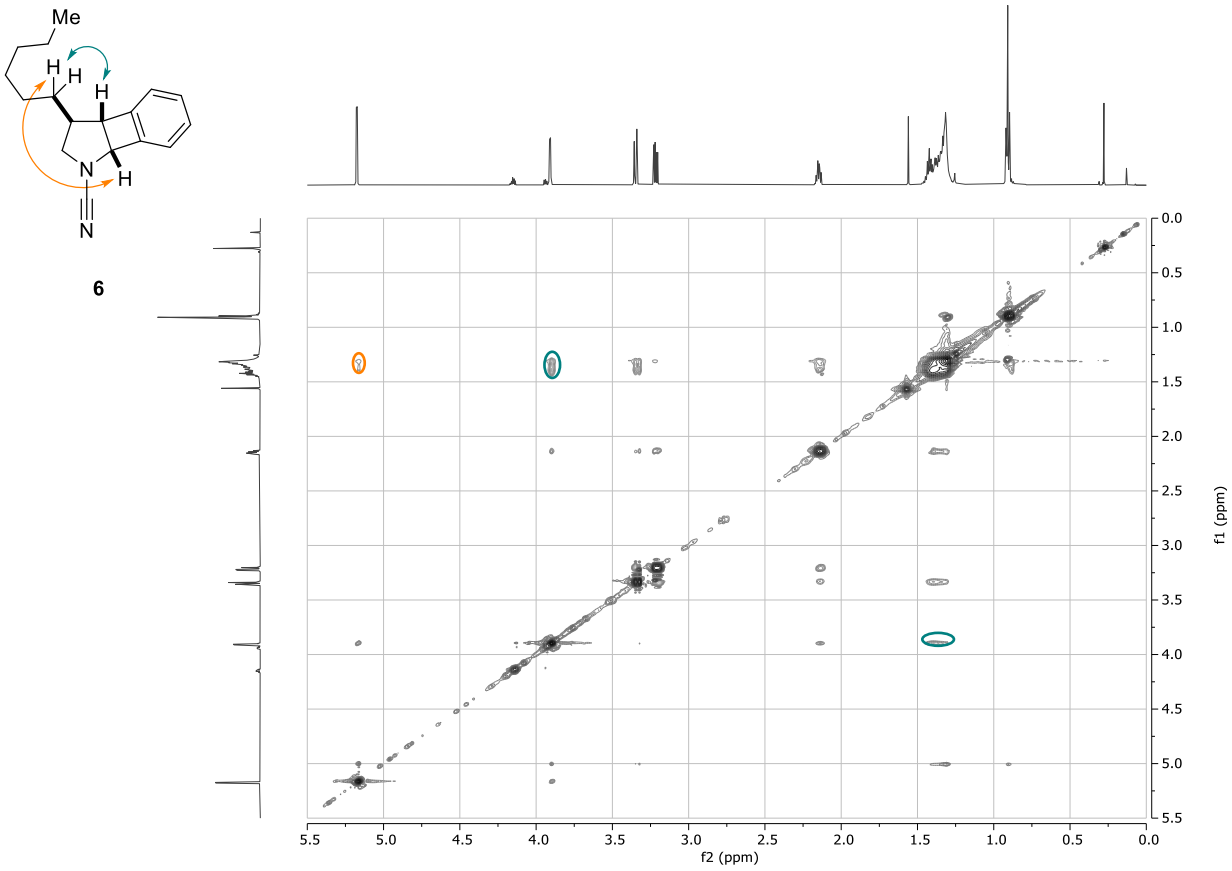

Me
H
H
H
Cl
Cl
N
H
N
4
f2 (ppm)
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


H13C6
H
N
H
N

6


3.58
1.17
1.00
1.10
1.00
1.01
1.02
10.69
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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