Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Stereoselective synthesis of vinyl nitriles through Ramberg-Backlünd olefination reaction

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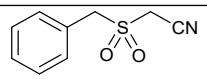
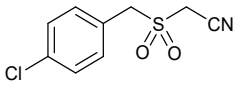
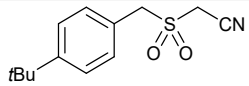
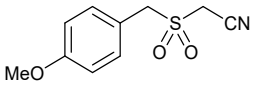
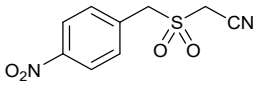
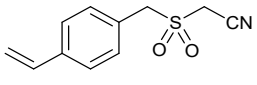
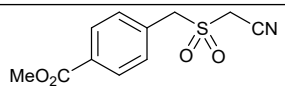
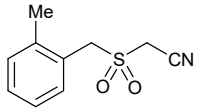
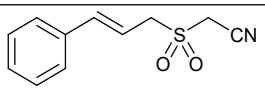
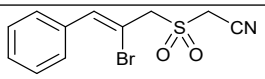
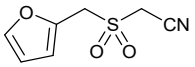
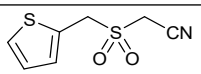
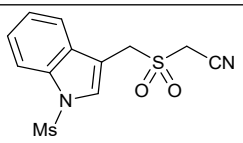
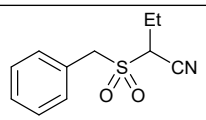
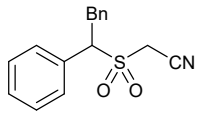
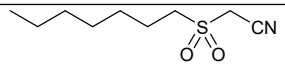
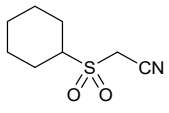
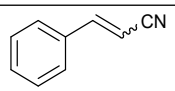
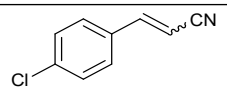
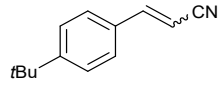
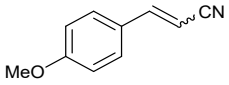
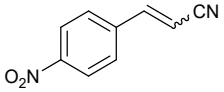
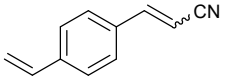
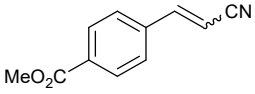
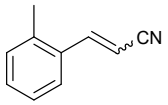
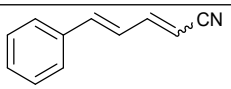
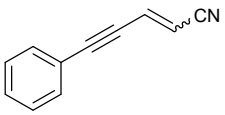
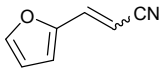
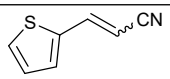
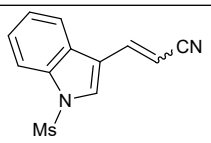
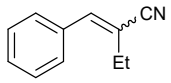
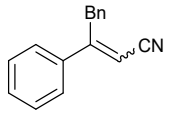
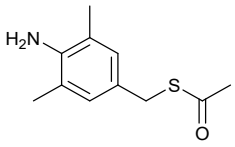
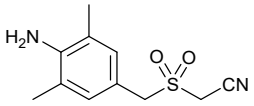
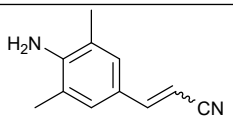
Supporting information

Compound	Experimental and spectroscopic data	^{1}H NMR	^{13}C NMR
 **1a**	S9	S18	S18
 **1b**	9	S19	S19
 **1c**	S9	S20	S20
 **1d**	S9	S21	S21
 **1e**	S10	S22	S22
 **1f**	S10	S23	S23

 **1g**	S10	S24	S24
 **1h**	S10	S25	S25
 **1i**	S11	S26	S26
 **1j**	S11	S27	S27
 **1k**	S11	S28	S28
 **1l**	S11	S29	S29
 **1m**	S12	S30	S30
 **1n**	S12	S31	S31
 **1o**	S12	S32	S32
 **1p**	S12	S33	S33
 **1q**	S13	S34	S34
 **2a**	S13	S35	S35

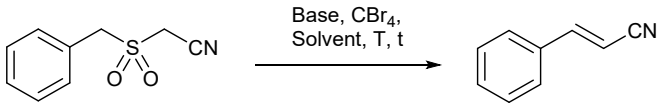
 **2b**	S13	S36	S36
 **2c**	S13	S37	S37
 **2d**	S14	S38	S38
 **2e**	S14	S39 S40	S39 S40
 **2f**	S14	S41	S41
 **2g**	S14	S42	S42
 **2h**	S15	S43	S43
 **2i**	S15	S44	S44
 **2j**	S15	S45 S46	S45 S46
 **2k**	S15	S47	S47
 **2l**	S15	S48	S48
 **2m**	S16	S49	S49

 **2n**	S16	S50	S50
 **2o**	S16	S51	S51
 **6**	S16	S52	S52
 **7**	S17	S53	S53
 **3**	S17	S54 S55	S54 S55

1. General experimental conditions

All reagents and solvents were of reagent or analytical grade and used without further purification unless otherwise stated. Qualitative thin layer chromatography (TLC) analyses and preparative runs were performed using glass or aluminum baked silica gel (F_{254}). TLC plates were visualized by exposition to UV light (254 nm), iodine and/or phosphomolybdic acid solution (20%). Purifications were performed by flash column chromatography on 230-400 mesh silica gel or using a rotary chromatography device (Chromatotron™), using 1-, 2-, or 4-mm high purity SiO_2 rotary plates, 2-25 μm particle size. ^1H and ^{13}C NMR were acquired using Bruker Advance III HD 400 and JEOL ECA 500 spectrometers. Chemical shifts of both ^1H and ^{13}C are reported in parts per million (ppm) on the δ scale, referenced with respect to residual solvent ($CDCl_3$) at 7.26 ppm or from internal standard tetramethylsilane (TMS) at 0.00 ppm. Data were reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *dd* = doublet of doublets, *t* = triplet, *m* = multiplet), coupling constants (Hz) and integration. ^{13}C NMR data were collected with complete proton decoupling. Infrared spectra were recorded on a Varian FT-IR 600IR spectrometer equipped with an ATR sampling accessory and IR Spectrum GX. Mass spectra were acquired on an Agilent G1969A ESI-TOF. Melting points were measured on an MelTemp II.

2. Initial optimization of the Ramberg-Bäcklund reaction conditions.



1a **2a**

Entry	Solvent	Base (equiv)	T (°C)	t (h)	Conv. %	Ratio *E/Z*
1	*t*-BuOH	KO*t*-Bu (2)	rt	72	-	-
2	*t*-BuOH	KO*t*-Bu (5)	rt	72	-	-
3	*t*-BuOH	KO*t*-Bu (10)	rt	96	-	-
4	*t*-BuOH	KO*t*-Bu (2)	90	6	22	50:50
5	THF:*t*-BuOH	KO*t*-Bu (2)	70	6	25	50:50
6	THF:*t*-BuOH	KO*t*-Bu (2.5)	70	6	18	50:50
7	THF:*t*-BuOH	KO*t*-Bu (2)	0	48	5	72:28
8	CH_2Cl_2:*t*-BuOH	KO*t*-Bu (2)	0	4	15	44:56
9	MeOH	DBU (2)	70	2	90	84:16
10	MeOH	DBU (3)	70	3	100	84:16
11	MeOH	DBU (5)	70	3	100	83:17
12	MeOH	DBU (5)	rt	2	100	83:17
13	MeOH	DBU (3)	rt	2.5	100	84:16
14	MeOH	DBU (3)	10	3	100	82:18
15	MeOH	DBU (3)	0	3	100	83:17
16	Et_2O	DBU (3)	rt	48	100	88:12

* 1.1 equiv of CBr_4 were used in all cases

Table S1. Evaluation of solvent, base and temperature in the RBR olefination of **1a.**

We initially employed classic or traditional conditions for the RBR reaction (entries 1-3). However, we observed little to no formation of the olefinic products and mostly recovered starting materials. A modest conversion was detected at 90 °C with no stereoselectivity (entry 4), which led us to attempt increasing the conversion by adding co-solvents like THF (entries 5-7). Unfortunately, we found no improvement in either yield or stereoselectivity. Interestingly, a decrease in temperature to 0 °C improved the stereoselectivity but resulted in lower conversion (entry 7). The use of additional binary solvent mixtures like CH_2Cl_2/t-BuOH (entry 8) did not improve either stereoselectivity or conversion. However, when we switched to a protic solvent such as methanol, there was a significant improvement in both conversion and stereoselectivity (entry 9). Although a higher base load (3 eq) was needed for complete conversion (entry 10), stereoselectivity remained unchanged. A similar result was obtained even when an excess of base was used (entry 11). Interestingly, lowering the reaction temperature to room temperature resulted in virtually the same outcome (entry 12), and 3 eq of base was optimal (entry 13). Colder conditions (entries 14 and 15) did not improve stereoselectivity, and another polar but aprotic solvent like ethyl ether yielded a comparable result (entry 16), but with longer reaction times.

3. Post-RBR isomerization trials

Control experiments were necessary to exclude the possibility of *E/Z* equilibration on the olefinic products **(2)** after the Ramberg-Bäcklund olefination on sulfones **(1)**. We first monitored the *E/Z* ratio by ^{1}H-NMR over longer reaction times and observed no change. The ratio remained constant even after 12 hours of reaction exposure **(Figure S1)**.

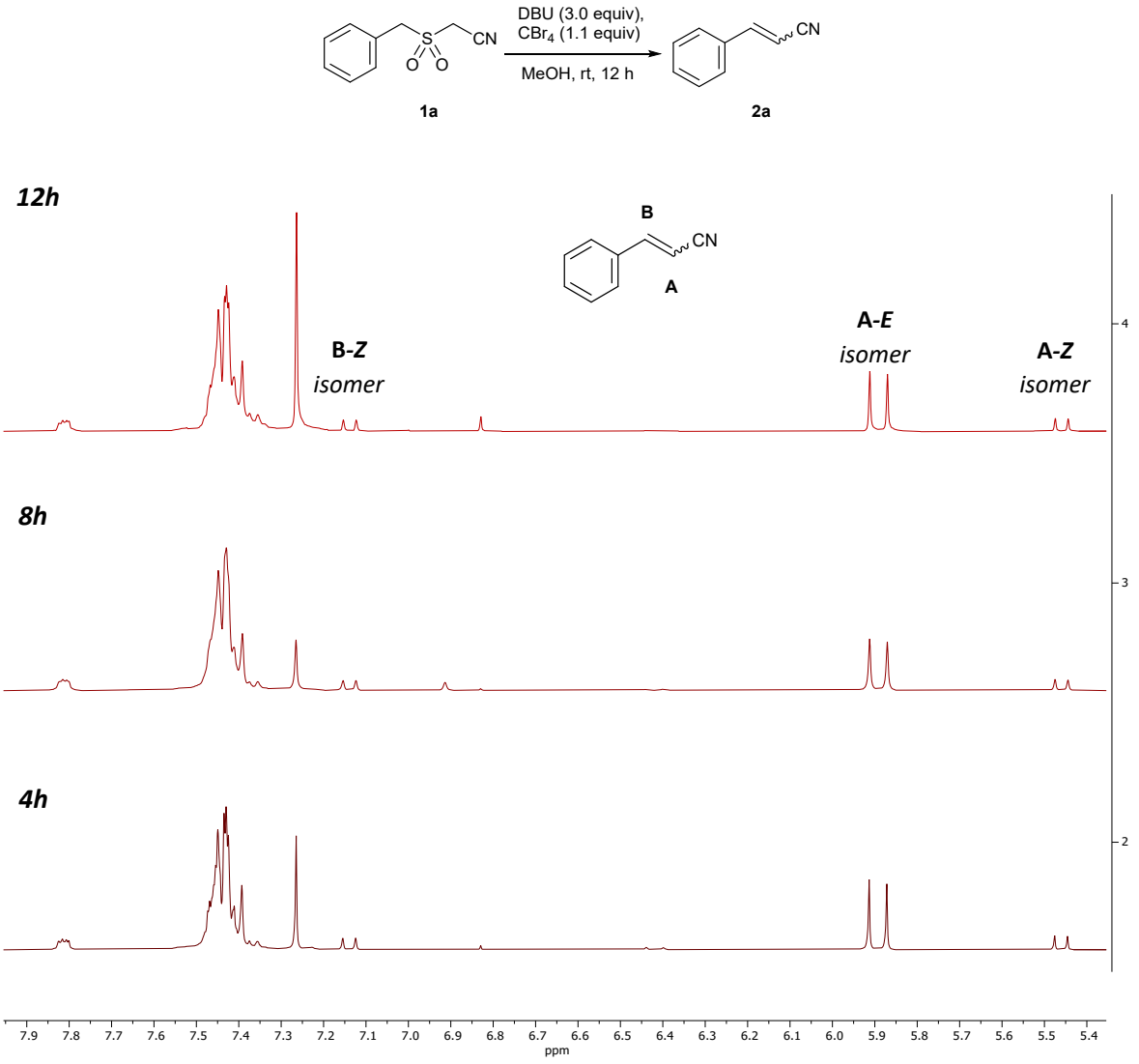


Figure S1. ^{1}H-NMR spectra of crude reaction mixtures of **1a** olefination after 4, 8 and 12 h.

A similar outcome was found when a pure, isolated mixture of 2a was exposed to DBU excess in MeOH. After 40h the *E/Z* ratio remained constant.

Secondly, a **Z-enriched** mixture of **2a** (*E/Z* ratio 14:86; obtained through a Chromatotron® "dry plate" separation method, eluent 100 µL acetone:100 mL hexanes), was exposed to the reaction conditions for up to 24 hours, without observing any significant change in the *E/Z* ratio **(Figure S2)**.

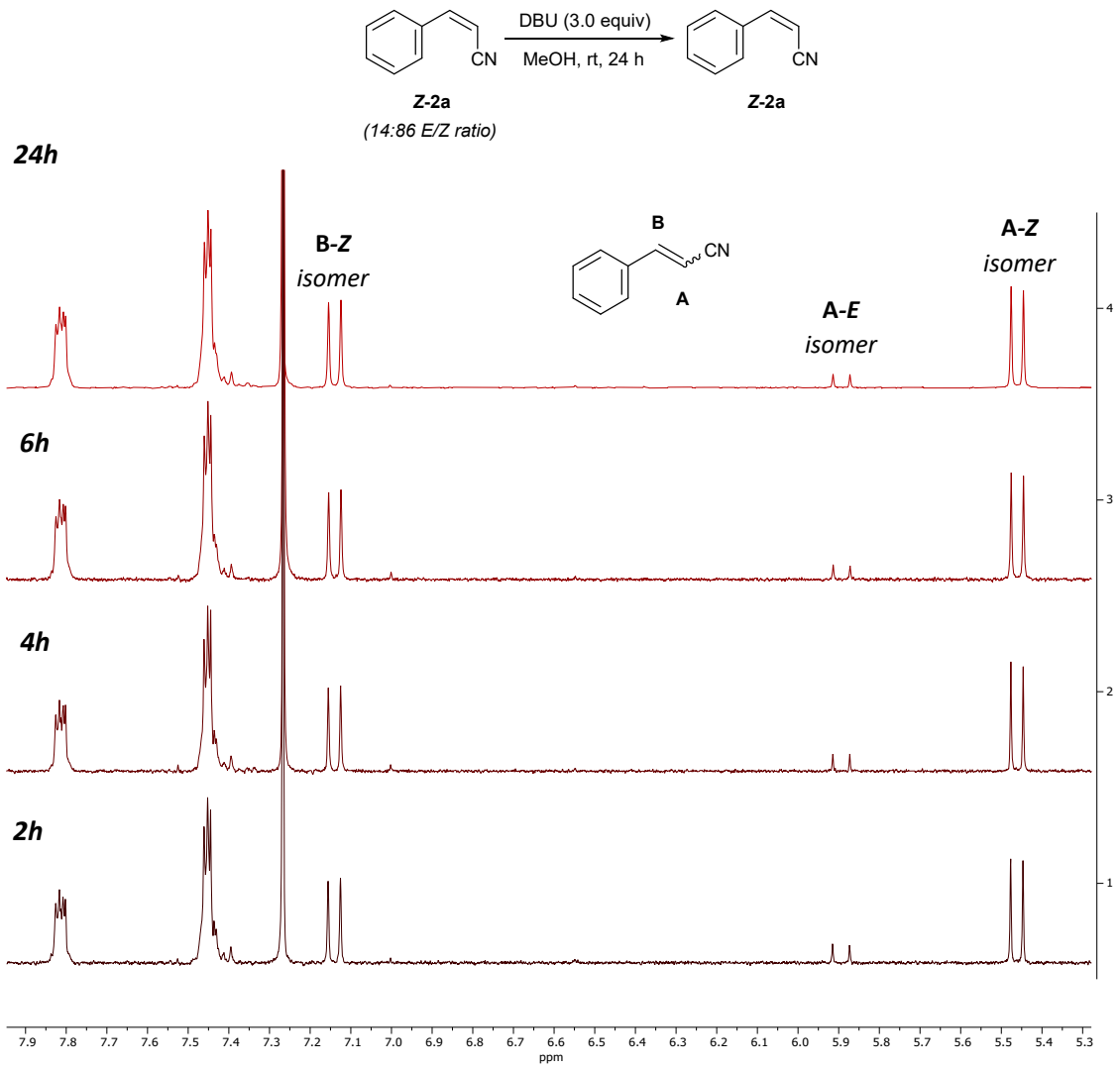


Figure S2. ^{1}H-NMR spectra of an **Z-2a** enriched mixtures with DBU in MeOH, after 2, 4, 6 and 24 h.

4. General thioacetate (S1) synthesis

To a cold solution (0 °C) of the corresponding alkyl halide (**S4**, 1.0 eq) in CH_2Cl_2 (0.3 M considering **S4**), thiolacetic acid (1.1 eq) and triethylamine (1.1 eq) were added dropwise. The mixture was allowed to warm to rt and stirred for *ca.* 2 h until starting material was consumed (monitored by TLC). Water was added, and the aqueous layer extracted with ethyl acetate (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude alkyl thioacetate (**S1**). Pure **S1** was obtained by SiO_2 chromatography using mixtures of hexanes and ethyl acetate as eluents.

5. General alkylation 1 - Thioether (S2) synthesis from thiols (S3)

To a cold slurry (0°C) of NaH (1.1 eq) in dimethylformamide(0.3 M considering **S3**), corresponding thiol (**S3**, 1.0 eq, dissolved in a minimal amount of dimethylformamide) was added dropwise and stirred at 0 °C for 30 min. Then, chloroacetonitrile (1.0 eq) was added dropwise. The mixture was allowed to warm to rt and stirred for *ca.* 1 h until starting material was consumed (monitored by TLC). Water was added, and the aqueous layer was extracted with ethyl acetate (x3). The combined organic

extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude thioether (**S2**). Pure **S2** was obtained by SiO_2 chromatography using mixtures of hexanes and ethyl acetate as eluents.

6. General alkylation 2 - Thioether (S2) synthesis B from thios (S1)

To a cold (0°C) solution of the corresponding thioacetate (**S1**, 1.0 eq) in MeOH (0.3 M with respect to **S1**) $LiOH{\cdot}H_2O$ (1.05 eq) was added, and the mixture stirred 5 min. Then chloroacetonitrile (1.05 eq) was added dropwise to the mixture. The mixture was allowed to warm to rt and stirred for *ca.* 1 h until starting material was consumed (monitored by TLC). Water was added, and the aqueous layer was extracted with CH_2Cl_2 (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford the crude thioether (**S2**). Pure **S2** was obtained by SiO_2 chromatography using mixtures of hexanes and ethyl acetate as eluents.

7. General oxidation 1 – Sulfones (1) from thioethers (S2) using Oxone®

To a solution of the corresponding thioether (**S2**, 1.0 eq) in MeOH (0.3 M with respect to **S2**), Oxone® (3.0 eq) was added portionwise and stirred at room temperature. The mixture was allowed to warm (rt) and stirred for *ca.* 12 h until starting material was consumed (monitored by TLC). The mixture was filtered and concentrated under vacuum to a quarter of the original volume, water was added, and the aqueous layer was extracted with ethyl acetate (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude sulfone **(1)**. Pure **1** was obtained by SiO_2 chromatography using mixtures of hexanes and ethyl acetate as eluents.[1]

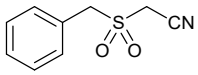
8. General oxidation 2 – Sulfones (1) from thioethers (S2) using *m*-CPBA

To a solution of corresponding thioether (**S2**, 1.0 eq) in a mixture dioaxane:buffer pH=8 (1:1, 0.3 M with respect to **S2**), *m*-CPBA (2.2 eq) was added portionwise and stirred at room temperature. The mixture was stirred and monitored by TLC chromatography until starting material was consumed (*ca.* 12 h). Solution was cooled at 0°C and solid $NaHCO_3$ was added, and the mixture stirred for 30 min. The mixture was diluted with water and the aqueous layer was extracted with CH_2Cl_2 (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude sulfone **(1)**. Pure **1** was obtained by SiO_2 chromatography using mixtures of hexanes and ethyl acetate as eluents.[1]

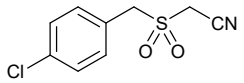
[1] Initial hexanes/ethyl acetate in a 80:20 ratio was often used, usually increasing ethyl acetate towards 60:40 or 50:50 ratio (gradient) to ensure maximum product recovery.

9. General olefination procedure (Ramberg-Bäcklund reaction)

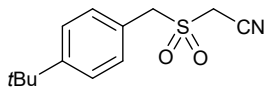
To solution of the corresponding sulfone **1** in MeOH (0.1 M with respect to **1**), CBr_4 (1.1eq) and 1,8-*di*azabicyclo[5.4.0]undec-7-ene (DBU, 3 eq) were sequentially added and stirred until starting material was consumed (monitored by TLC). Water was added, and the aqueous layer was extracted with CH_2Cl_2 (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude vinyl nitrile **(2)**. Pure **2** was obtained flash or radial SiO_2 chromatography using mixtures of hexanes and ethyl acetate as eluents.[2]



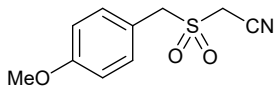
2-(Benzylsulfonyl)acetonitrile (1a) was prepared through a two-step alkylation-oxidation sequence from the corresponding thiol **(S3a**, 654 mg, 5.3 mmol**)** Alkylation of **S3a (alkylation 1)** delivered the corresponding thioether product **S2a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 2.22 (m, 5H), 3.88 (s, 2H), 3.02 (s, 2H) ppm. Oxidation of **S2a (oxidation 1)** delivered sulfonyl nitrile **1a**, which was purified by SiO_2 flash chromatography. Pure **1a** was obtained as a white solid (two-step yield: 88%). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.46 (m, 5H), 4.52 (s, 2H), 3.72 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.8, 130.2, 129.8, 126.4, 110.4, 59.7, 40.0 ppm.



2-((4-Chlorobenzyl)sulfonyl)acetonitrile (1b) was prepared through a two-step alkylation-oxidation sequence from the corresponding thiol **(S3b**, 612 mg, 3.9 mmol**)**. Alkylation of **S3b (alkylation 1)** delivered the corresponding thioether product **S2b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J*= 8.6 Hz, 2H), 7.28 (d, *J*= 8.5 Hz, 2H), 3.89 (s, 2H), 3.08 (s, 2H) ppm. Oxidation of **S2b (oxidation 1)** delivered sulfonyl nitrile **1b**, which was purified by SiO_2 flash chromatography. Pure **1b** was obtained as a solid (two-step yield 75%). mp 178-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J*= 8.6 Hz, 2H), 7.43 (d, *J*= 8.6 Hz, 2H), 4.50 (s, 2H), 3.75 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 132.2, 129.7, 124.7, 110.5, 58.7, 40.5 ppm. MS (ESI+), m/z: Calculated for $C_9H_8NO_2SCl$ 229.0; found 252.0 $[M+Na]^+$. IR-KBr ν_{max} (cm^{-1}) (2254 CN), (1306, 1134 SO_2).



2-((4-(Tert-butyl)benzyl)sulfonyl)acetonitrile (1c) was prepared through a two-step alkylation-oxidation sequence from the corresponding thiol **(S3c**, 919 mg, 5.1 mmol**)**. Alkylation of **S3c (alkylation 1)** delivered the corresponding thioether product **S2c**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J*= 8.3 Hz, 2H), 7.27 (d, *J*= 8.3 Hz, 2H), 3.88 (s, 2H), 3.07 (s, 2H), 1.31 (s, 9H) ppm. Oxidation of **S2c (oxidation 1)** delivered sulfonyl nitrile **1c**, which was purified by SiO_2 flash chromatography. Pure **1c** was obtained as a solid (two-step yield 91%). mp 106-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.48 (d, *J*= 8.5 Hz, 2H), 7.41 (d, *J*= 8.4 Hz, 2H), 4.49 (s, 2H), 3.72 (s, 2H), 1.33 (s, 9H) ppm. NMR ^{13}C (100 MHz, $CDCl_3$) δ 153.5, 130.5, 126.8, 123.3, 110.5, 59.3, 39.9, 35.0, 31.3 ppm. MS (ESI+), m/z: Calculated for $C_{13}H_{17}NO_2S$ 251.1; found 269.2 $[M+H_2O]^+$, IR-ATR ν_{max} (cm^{-1}) (2255 CN), (1330, 1128 SO_2).

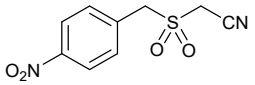


2-((4-Methoxybenzyl)sulfonyl)acetonitrile (1d) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1d**, 469 mg, 2.4 mmol**)**. Alkylation of **S1d (alkylation 2)** delivered the corresponding thioether product **S2d.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J*= 8.6 Hz, 2H), 6.88 (d, *J*= 8.7 Hz, 2H), 3.88 (s, 2H), 3.81 (s, 3H), 3.07 (s, 2H) ppm. Oxidation of **S2d (oxidation 1)** delivered sulfonyl nitrile **1d**, which was purified by SiO_2 flash chromatography. Pure **1d** was obtained as a solid

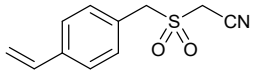
[2] Vinylnitriles eluted efficiently usually by using hexanes/ethyl acetate (95:5 ratio).

[3] Bostick, T. M.; Christie, S. D.; Connolly, T. J.; Copp, S.; Langler, R. F.; Reid, D. L.; Zaworotko, M. *Aust. J. Chem.* **1996**, *49*, 243–247. *Org. Lett.* 2011, 13, 2, 208–211

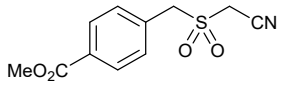
(two-step yield 89%). mp 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J*= 8.7 Hz, 2H), 6.98 (d, *J*= 8.7 Hz, 2H), 4.47 (s, 2H), 3.84 (s, 3H), 3.71 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 132.1, 118.1, 115.2, 110.5, 59.1, 55.6, 39.7 ppm. MS (ESI+), m/z: Calculated for $C_{10}H_{11}NO_3S$ 225.1; found 248.1 $[M+Na]^+$, IR-ATR ν_{max} (cm^{-1}) (2242 CN), (1301, 1174 SO_2), (1242, 1030 MeO).



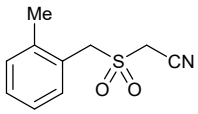
2-((4-Nitrobenzyl)sulfonyl)acetonitrile (1e) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1e**, 652 mg, 3.1 mmol**)**. Alkylation of **S1e (alkylation 2)** delivered the corresponding thioether product **S2e.** ^{1}H NMR (500 MHz, $CDCl_3$δ 8.23 (d, *J*= 8.7 Hz, 2H), 7.55 (d, *J*= 8.6 Hz, 2H), 4.02 (s, 2H), 3.14 (s, 2H) ppm. Oxidation of **S2e (oxidation 1)** delivered sulfonyl nitrile **1e**, which was purified by SiO_2 flash chromatography. Pure **1e** was obtained as a white solid (two-step yield 79%). mp 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J*= 8.4 Hz, 2H), 7.71 (d, *J*= 8.4 Hz, 2H), 4.65 (s, 2H), 3.85 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 132.8, 132.1, 124.8, 110.1, 58.7, 41.2 ppm. MS (ESI+), m/z: Calculated for $C_9H_8N_2O_4S$ 240.1; found 263.1 $[M+Na]^+$, IR-ATR ν_{max} (cm^{-1}) (2238 CN), (1508, 1344 NO_2), (1307, 1107 SO_2).



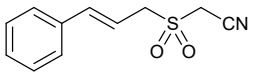
2-((4-Vinylbenzyl)sulfonyl)acetonitrile (1f) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1f**, 310 mg, 1.6 mmol**)**. Alkylation of **S1f (alkylation 2)** delivered the corresponding thioether product **S2f** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J*= 8.1 Hz, 2H), 6.71 (dd, *J*= 17.6, 10.9 Hz, 1H), 5.76 (d, *J*= 17.6 Hz, 1H), 5.27 (d, *J*= 10.9 Hz, 1H), 3.91 (s, 2H), 3.07 (s, 2H).Oxidation of **S2f (oxidation 2)** delivered sulfonyl nitrile **1f**, which was purified by SiO_2 flash chromatography. Pure **1f** was obtained as a white solid (two-step yield 77%). mp 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J*= 8.3 Hz, 2H), 7.44 (d, *J*= 8.5 Hz, 2H), 6.73 (dd, *J*= 17.6, 10.9 Hz, 1H), 5.83 (d, *J*= 17.6 Hz, 1H), 5.36 (d, *J*= 10.9 Hz, 1H), 4.51 (s, 2H), 3.74 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 135.8, 131.0, 127.4, 125.5, 116.1, 110.5, 59.4, 40.0 ppm. MS (ESI+), m/z: Calculated for $C_{11}H_{11}NO_2S$ 221.1; found 222.1 $[M+H]^+$, IR-ATR ν_{max} (cm^{-1}) (3086 C=C-H), (2265 CN), (1334, 1133 SO_2).



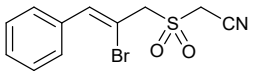
Methyl 4-(((cyanomethyl)sulfonyl)methyl)benzoate (1g) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1g**, 507 mg, 2.3 mmol**)**. Alkylation of **S1g (alkylation 2)** delivered the corresponding thioether product **S2g.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J*= 8.0 Hz, 2H), 7.44 (d, *J*= 8.0 Hz, 2H), 3.97 (s, 2H), 3.93 (s, 3H), 3.09 (s, 2H) ppm. Oxidation of **S2g (oxidation 2)** delivered sulfonyl nitrile **1g**, which was purified by SiO_2 flash chromatography. Pure **1g** was obtained as a solid (two-step yield 89%). mp 138-140°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J*= 8.4 Hz, 2H), 7.59 (d, *J*= 8.3 Hz, 3H), 4.59 (s, 2H), 3.95 (s, 3H), 3.76 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2 131.9, 131.0, 130.9, 130.8, 110.3, 59.2, 52.7, 40.5 ppm. MS (ESI+), m/z: Calculated for $C_{11}H_{11}NO_4S$ 253.0; found 254.0 $[M+H]^+$, IR-KBr ν_{max} (cm^{-1}) (2266 CN), (1726 CO_2Me), (1333, 1134 SO_2).



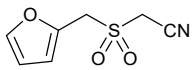
2-((2-Methylbenzyl)sulfonyl)acetonitrile (1h) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1h**, 493 mg, 2.73 mmol**)**. Alkylation of **S1h (alkylation 2)** delivered the corresponding thioether product **S2h.** Oxidation of **S2h (oxidation 1)** delivered sulfonyl nitrile **1h**, which was purified by SiO_2 flash chromatography. Pure **1h** was obtained as a solid (two-step yield 87%). mp 126-128°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 4.59 (s, 2H), 3.86 (s, 2H), 2.49 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 131.8, 131.5, 130.3, 127.1, 124.6, 110.6, 57.3, 40.6, 20.0 ppm. MS (ESI+), m/z: Calculated for $C_{10}H_{11}NO_2S$ 209.1; found 232.1 $[M+Na]^+$, IR-ATR ν_{max} (cm^{-1}) (2258 CN), (1316, 1131 SO_2)



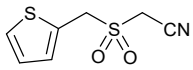
2-(Cinnamylsulfonyl)acetonitrile (1i) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1i**, 300 mg, 1.56 mmol**)**. Alkylation of **S1i (alkylation 2)** delivered the corresponding thioether product **S2i.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J*= 7.5 Hz, 2H), 7.34 (t, *J*= 7.5 Hz, 2H), 7.29 (d, *J*= 7.4 Hz, 1H), 6.58 (d, *J*= 15.7 Hz, 1H), 6.13 (dt, *J*= 15.5, 7.6 Hz, 1H), 3.53 (d, *J*= 7.6 Hz, 2H), 3.25 (s, 2H) ppm. Oxidation of **S2i (oxidation 2)** delivered sulfonyl nitrile **1i**, which was purified by SiO_2 flash chromatography. Pure **1i** was obtained as a white solid (two-step yield 38%). mp: 101°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 5H) 7.45 (d, *J*= 6.3 Hz, 2H), 7.34 (dd, *J*= 7.3, 6.2 Hz, 3H), 6.88 (d, *J*= 15.7 Hz, 1H), 6.26 (dt, *J*= 15.7, 7.7 Hz, 1H), 4.16 (d, *J*= 7.6 Hz, 2H), 3.96 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 134.9, 129.6, 129.1, 127.1, 113.5, 110.4, 57.7, 40.3 ppm. MS (ESI+), m/z: Calculated for $C_{11}H_{11}NO_2S$ 221.1; found 244.1 $[M+Na]^+$, IR-ATR ν_{max} (cm^{-1}) (2257 CN) (1325, 1123 SO_2), (3054 C=C-H)



***(Z)*-2-((2-Bromo-3-phenylallyl)sulfonyl)acetonitrile (1j)** was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1j**, 300 mg, 1.1 mmol**)**. Alkylation of **S1j (alkylation 2)** delivered the corresponding thioether product **S2j.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J*= 7.5 Hz, 2H), 7.34 (t, *J*= 7.5 Hz, 2H), 7.29 (d, *J*= 7.4 Hz, 1H), 6.58 (d, *J*= 15.7 Hz, 1H), 6.13 (dt, *J*= 15.5, 7.6 Hz, 1H), 3.53 (d, *J*= 7.6 Hz, 2H), 3.25 (s, 2H). Oxidation of **S2j (oxidation 2)** delivered sulfonyl nitrile **1j**, which was purified by SiO_2 flash chromatography. Pure **1j** was obtained as solid (two-step yield 33%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J*= 7.8, 1.9 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.27 (s, 1H), 4.53 (s, 2H), 4.15 (s, 2H) ppm.^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 133.9, 129.8, 129.3, 128.6, 110.2, 106.8, 66.1, 42.3 ppm. MS (ESI+), m/z: Calculated for $C_{11}H_{10}BrNO_2S$ 301.0; found 323.9 $[M+Na]^+$, IR-ATR ν_{max} (cm^{-1}) 2255 (CN).

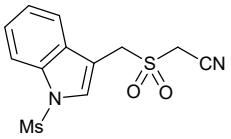


2-((Furan-2-ylmethyl)sulfonyl)acetonitrile (1k) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate[4] **(S1k**, 336 mg, 2.15 mmol**)**. Alkylation of **S1k (alkylation 2)** delivered the corresponding thioether product **S2k.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J*= 1.9, 0.9 Hz, 1H), 6.35 (d, *J*= 1.8 Hz, 1H), 6.31 (d, *J*= 3.1 Hz, 1H), 3.95 (s, 2H), 3.22 (s, 2H). Oxidation of **S2k (oxidation 2)** delivered sulfonyl nitrile **1k**, which was purified by SiO_2 flash chromatography. Pure **1k** was obtained as a white solid (two-step yield 32%). mp 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J*= 1.9 Hz, 1H), 6.64 (d, *J*= 3.4 Hz, 1H), 6.49 (dd, *J*= 3.4, 1.9 Hz, 1H), 4.61 (s, 2H), 3.96 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 140.5, 113.9, 112.0, 110.1, 53.1, 41.3 ppm. MS (ESI+), m/z: Calculated for $C_7H_7NO_3S$ 185.0; found 184.0 $[M-H]^-$, IR-ATR ν_{max} (cm^{-1}) (2260 CN), (1330, 1144 SO_2).

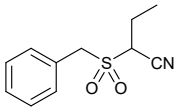


2-((Thiophen-2-ylmethyl)sulfonyl)acetonitrile (1l) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1l** 600 mg, 3.48 mmol**)**. Alkylation of **S1l (alkylation 2)** delivered the corresponding thioether product **S2l**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J*= 5.1, 1.3 Hz, 1H), 7.04 (dd, *J*= 3.5, 1.1 Hz, 1H), 6.95 (dd, *J*= 5.1, 3.4 Hz, 1H), 4.16 (s, 2H), 3.18 (s, 2H) ppm. Oxidation of **S2l (oxidation 2)** delivered sulfonyl nitrile **1l**, which was purified by SiO_2 flash chromatography. Pure **1l** was obtained as a white solid with (two-step yield 78%). mp 92-94°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J*= 5.2, 1.2 Hz, 1H), 7.30 (dd, *J*= 3.6, 1.1 Hz, 1H), 7.12 (dd, *J*= 5.2, 3.6 Hz, 1H), 4.74 (s, 2H), 3.82 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 129.3, 128.2, 126.6, 110.2, 54.3, 39.8 ppm. MS (ESI+), m/z: Calculated for $C_7H_7NO_2S_2$ 201.0; found 200.0 $[M-H]^-$, IR-ATR ν_{max} (cm^{-1}) (2254 CN), (1319, 1145 SO_2).

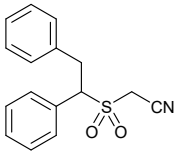
[4] **S1k**, **S1l** and **S1m** were prepared through aldehyde reduction with $NaBH_4$ (D'Alessandro, S.; Alfano, G.; Di Cerbo, L.; Brogi, S.; Chemi, G.; Relitti, N.; Brindisi, M.; Lamponi, S.; Novellino, E.; Campiani, G.; et al. *Bioorg. Chem.* **2019**, *89*, 103020), followed by displacement using thiolacetic acid (Mitsunobu) (Schulze, O.; Voss, J.; Adiwidjaja, G.; Olbrich, F. *Carbohydr. Res.* **2004**, *339*, 1787–1802.)



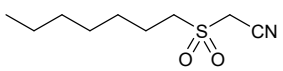
2-(((1-(Methylsulfonyl)-1*H*-indol-3-yl)methyl)sulfonyl)acetonitrile (1m) was prepared through a two-step alkylation-oxidation sequence from the corresponding thioacetate **(S1m**, 580 mg, 2.1 mmol**)**. Alkylation of **S1m (alkylation 2)** delivered the corresponding thioether product **S2m**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J*= 8.2 Hz, 1H), 7.73 (d, *J*= 7.7 Hz, 1H), 7.49 (s, 1H), 7.43 (t, *J*= 7.7 Hz, 1H), 7.37 (t, *J*= 7.6 Hz, 1H), 4.09 (s, 2H), 3.20 (s, 2H), 3.14 (s, 3H) ppm. Oxidation of **S2m (oxidation 2)** delivered sulfonyl nitrile **1m**, which was purified by SiO_2 flash chromatography. Pure **1m** was obtained as a solid with (two-step yield 45%). mp 178-180°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J*= 5.2, 1.2 Hz, 1H), 7.30 (dd, *J*= 3.6, 1.1 Hz, 1H), 7.12 (dd, *J*= 5.2, 3.6 Hz, 1H), 4.74 (s, 2H), 3.83 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 129.3, 128.2, 126.6, 110.2, 54.3, 39.8 ppm. MS (ESI+), m/z: Calculated for $C_{12}H_{12}N_2O_4S_2$ 312.0; found 335.0 $[M+Na]^+$, IR-ATR ν_{max} (cm^{-1}) 2244 (CN), (1359, 1172, 1124 SO_2).



2-(Benzylsulfonyl)butanenitrile (1n). To a cold slurry (0°C) of NaH (1.1 eq) in dimethylformamide (0.3 M with respect to **1a**) under inert atmosphere (Ar), sulfone **1a** (1 eq, dissolved in a minimal amount of dimethylformamide) was added and stirred for 1 h at 0°C. The corresponding alkyl halide (1.0 eq) was added, and the mixture allowed to warm (rt) and stirred for *ca.* 1 h until starting material was consumed (monitored by TLC). The reaction was diluted with half-saturated NH_4Cl solution (twice the volume of the reaction mixture), and the aqueous layer extracted with ethyl acetate (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford the crude sulfone **(1n).** Pure **1n** was obtained by SiO_2 chromatography (plug) using a mixture of hexanes and ethyl acetate 80:20 as eluent. Pure **1n** was obtained as a white solid (yield 95%). mp 82-84°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 - 7.45 (m, 5H), 4.64 (d, *J*= 14.3 Hz, 1H), 4.45 (d, *J*= 14.3 Hz, 1H), 3.58 (dd, *J*= 10.0, 5.0 Hz, 1H), 2.14 – 2.01 (m, 2H), 1.19 (t, *J*= 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.0, 129.9, 129.6, 126.3, 114.1, 58.7, 52.9, 18.7, 11.3 ppm. MS (ESI+), m/z: Calculated for $C_{11}H_{13}NO_2S$ 223.1; found 224.1 $[M+H]^+$, IR-ATR ν_{max} (cm-1) (2248 CN), (1304, 1133 SO_2).

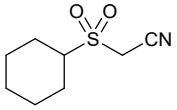


2-((1,2-Diphenylethyl)sulfonyl)acetonitrile (1o). To a cold (0°C) solution of sulfone **1a** in tetrahydrofuran (0.3 M) under inert atmosphere (Ar), lithium bis(trimethylsilyl)amide (2.5 eq) was added dropwise, and the mixture stirred for 1 h. Alkyl halide (2.5 eq) was added to the mixture and stirred for 3 h. The reaction mixture was diluted with half-saturated NH_4Cl solution (twice the volume of the reaction mixture), and the aqueous layer extracted with ethyl acetate (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford the crude sulfone **(1o)**. Pure **1o** was obtained by SiO_2 chromatography using a mixture of hexanes and ethyl acetate 80:20 as eluent. Pure **1o** was obtained as a white solid (yield 85%). mp 102-104°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 - 7.37 (m, 5H), 7.22 - 7.16 (m, 3H), 7.03 (dd, *J*= 7.4, 1.8 Hz, 2H), 4.66 (dd, *J*= 13.8, 3.9 Hz, 1H), 3.79 (dd, *J*= 13.7, 3.9 Hz, 1H), 3.59 (d, *J*= 16.7 Hz, 1H), 3.50 (d, *J*= 16.7 Hz, 1H), 3.37 (dd, J= 13.7, 10.9 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 130.8, 130.2, 129.9, 129.7, 129.3, 128.8, 127.4, 110.3, 70.8, 40.5, 33.5 ppm. MS (ESI+), m/z: Calculated for $C_{16}H_{15}NO_2S$ 285.1; found 308.1 $[M+Na]^+$, IR-ATR ν_{max} (cm^{-1}) (2258 CN), (1336, 1133 SO_2).



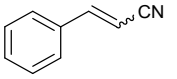
2-(Heptylsulfonyl)acetonitrile (1p) was prepared through a two-step alkylation-oxidation sequence from the corresponding thiol **(S3p**, 876 mg, 6.6 mmol**)**. Alkylation of thiol **S3p (alkylation 1)** delivered the corresponding thioether product **S2p**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.27 (s, 2H), 2.71 (t, *J*= 7.4 Hz, 2H), 1.62 (q, *J*= 7.4 Hz, 2H), 1.38 (q, *J*= 6.7 Hz, 2H), 1.32-1.21 (m, 6H), 0.86 (t, *J*= 6.9 Hz, 3H) ppm. Oxidation of **S2n (oxidation 1)** delivered sulfonyl nitrile **1p**, which was purified by SiO_2 flash chromatography. Pure **1p** was obtained as a solid with (two-step yield 80%). mp 65-67°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (s, 2H), 3.30 - 3.25 (m,

2H), 1.92 (m, 2H), 1.49 (q, *J*= 7.7, 7.3 Hz, 2H), 1.39 - 1.28 (m, 6H), 0.90 (t, *J*= 6.9 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.5, 53.6, 42.2, 31.5, 28.7, 28.3, 22.6, 22.1, 14.1 ppm. MS (ESI+), m/z: Calculated for $C_9H_{17}NO_2S$; 203.1 found 204.1 $[M+H]^+$, IR-ATR ν_{max} (cm^{-1}) (2260 CN) (1330, 1133 SO_2).

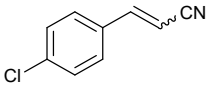


2-(Cyclohexylsulfonyl)acetonitrile (1q) was prepared through a two-step alkylation-oxidation sequence from the corresponding thiol **(S3q**, 658 mg, 5.7 mmol**)**. Alkylation of thiol **S3q (alkylation 1)** delivered the corresponding thioether product **S2q**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.27 (s, 2H), 2.71 (t, *J*= 7.4 Hz, 2H), 1.62 (q, *J*= 7.4 Hz, 2H), 1.38 (q, *J*= 6.7 Hz, 2H), 1.32 - 1.21 (m, 6H), 0.86 (t, *J*= 6.9 Hz, 3H). Oxidation of **S2q (oxidation 1)** delivered sulfonyl nitrile **1q**, which was purified by SiO_2 flash chromatography. Pure **1r** was obtained as a solid (two-step yield 80%). mp 68-70°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95 (s, 2H), 3.28 (tt, *J*= 12.2, 3.5 Hz, 1H), 2.27 – 2.17 (m, 2H), 1.99 (dp, *J*= 10.4, 3.7 Hz, 2H), 1.89 – 1.69 (m, 1H), 1.64 (ddd, *J*= 25.0, 12.5, 3.3 Hz, 2H), 1.38 (qt, *J*= 13.1, 3.4 Hz, 2H), 1.26 (qt, *J*= 13.1, 3.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.6, 62.4, 39.6, 25.2, 24.9, 24.9. MS (ESI+), m/z: Calculated for $C_8H_{13}NO_2S$; 187.1 found 147.1 $[M-CH_2CN]^+$, IR-ATR ν_{max} (cm^{-1}) (2261 CN), (1297, 1134 SO_2).

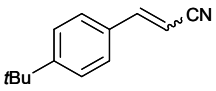
Vinyl nitriles



Cinnamonitrile (2a) was prepared from **1a** (100 mg, 0.5 mmol) following the general olefination procedure. **2a** was purified by flash chromatography. Pure **2a** was obtained as an oil (yield 84%), as a mixture of isomers (86:14 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[5] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) 7.47 - 7.37 (m, 6H), 5.88 (d, *J*= 16.7 Hz, 1H). ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) 7.82 – 7.80 (m, 2H), 7.47 - 7.38 (m, 3H), 7.13 (d, *J*= 12.1 Hz, 1H), 5.45 (d, *J*= 12.1 Hz, 1H) ppm. ***E*-isomer** ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 133.7, 131.3, 129.3, 127.5, 118.3, 96.5. ***Z*-isomer** ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 133.7, 131.1, 129.1, 129.1, 118.3, 95.2.



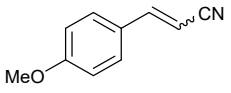
3-(4-Chlorophenyl)acrylonitrile (2b) was prepared from **1b** (150 mg, 0.65 mmol) following general olefination procedure. **2b** was purified by radial chromatography. Pure **2b** was obtained as a solid (yield 76%), as a mixture of isomers (83:17 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[5] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 4H), 7.36 (d, *J*= 16.7 Hz, 1H), 5.86 (d, *J*= 16.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 137.5, 132.1, 130.4, 129.6, 128.7, 118.0, 97.1 ppm. ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J*= 8.5 Hz, 2H), 7.42 (d, *J*= 8.6 Hz, 2H), 7.09 (d, *J*= 12.1 Hz, 1H), 5.48 (d, *J*= 12.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 137.1, 132.1, 130.4, 129.4, 118.0, 95.8 ppm.



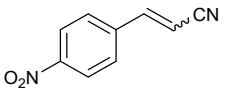
3-(4-(Tert-butyl)phenyl)acrylonitrile (2c) was prepared from **1c** (116 mg, 0.46 mmol) following the general olefination procedure. **2c** was purified by radial chromatography. Pure **2c** was obtained as an oil (yield 78 %), as a mixture of isomers (82:18 *E:Z*). The ^{1}H and ^{13}C spectroscopy results were consistent with the data reported in the literature.[6] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.35 (m, 5H), 5.84 (d, *J*= 16.6 Hz, 1H), 1.32 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 150.5, 130.9, 127.3, 126.2, 118.6, 95.3, 35.1, 31.2 ppm. ***Z*-isomer** (resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J*= 8.4 Hz, 2H), 7.10 (d, *J*= 12.1 Hz, 1H), 5.38 (d, *J*= 12.1 Hz, 1H), 1.33 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 148.6, 131.0, 129.0, 126.0, 117.8, 94.0, 35.1, 31.2 ppm.

[5] a) Peppe, C.; de Azevedo Mello, P.; das Chagas, R. P. *J. Organomet. Chem.* **2006**, *691*, 2335–2339. b) Zhang, Q.; Zheng, M.; Song, G.; Hou, J.; Li, B. *Asian J. Org. Chem.* **2019**, *8*, 1824-1826.

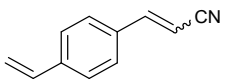
[6] Wang, Z.; Chang, S. *Org. Lett.* **2013**, *15*, 1990–1993.



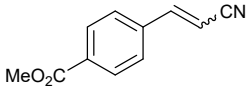
3-(4-Methoxyphenyl)acrylonitrile (2d) was prepared **1d** (151 mg, 0.67 mmol) following the general olefination procedure. **2d** was purified by radial chromatography. Pure **2d** was obtained as an oil (yield 61%), as a mixture of isomers (83:17 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[7] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J*= 8.8 Hz, 2H), 7.31 (d, *J*= 16.6 Hz, 1H), 6.91 (d, *J*= 8.8 Hz, 2H), 5.70 (d, *J*= 16.6 Hz, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 150.1, 131.0, 129.1, 126.3, 118.8, 114.5, 93.3, 55.5 ppm. ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J*= 8.8 Hz, 2H), 7.03 (d, *J*= 12.1 Hz, 1H), 6.94 (d, *J*= 9.6 Hz, 2H), 5.28 (d, *J*= 12.1 Hz, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 148.1, 131.0, 126.6, 118.1, 114.3, 91.9, 55.4 ppm.



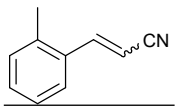
3-(4-Nitrophenyl)acrylonitrile (2e) was prepared from **1e** (152 mg, 0.63 mmol) following the general olefination procedure. **2e** was purified by radial chromatography. Pure **2e** was obtained as an oil (yield 49%), as a mixture of isomers (82:18 1 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[6] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 16.7 Hz, 1H), 6.08 (d, *J* = 16.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 139.3, 128.3, 124.6, 117.1, 101.2 ppm. ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J*= 8.9 Hz, 2H), 7.96 (d, *J*= 8.8 Hz, 2H), 7.23 (d, *J*= 12.1 Hz, 1H), 5.70 (d, *J*= 12.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 139.2, 129.9, 124.3, 116.4, 99.8 ppm.



3-(4-Vinylphenyl)acrylonitrile (2f) was prepared **1f** (162 mg, 0.73 mmol) following the general olefination procedure. **2f** was purified by radial chromatography. Pure **2f** was obtained as an oil (yield 76%), as a mixture of isomers (85:15 *E:Z*). ***E*-isomer** (resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 16.6 Hz, 1H), 5.83 (d, *J* = 17.6 Hz, 1H), 5.36 (d, *J* = 10.9 Hz, 1H) pmm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 140.6, 136.1, 133.0, 127.8, 127.0, 118.4, 116.2, 96.0 ppm. ***Z*-isomer** (resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 12.1 Hz, 1H), 5.84 (d, *J* = 17.6 Hz, 1H), 5.42 (d, *J* = 12.1 Hz, 1H), 5.36 (d, *J* = 10.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 140.3, 136.2, 133.1, 129.5, 126.8, 117.6, 115.5, 94.7 ppm. MS (ESI+), m/z: Calculated for $C_{11}H_9N$; 155.1, found 156.1 $[M+H]^+$, IR-KBr ν_{max} (cm^{-1}) (2217 CN)



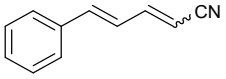
Methyl 4-(2-cyanovinyl)benzoate (2g) was prepared **1g** (163 mg, 0.64 mmol) the general olefination procedure. **2e** was purified by radial chromatography. Pure **2e** was obtained as an oil (yield 49%), as a mixture of isomers (83:17 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[7] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J*= 8.1 Hz, 2H), 7.53 (d, *J*= 8.2 Hz, 2H), 7.44 (d, *J*= 16.7 Hz, 1H), 6.00 (d, *J*= 16.7 Hz, 1H), 3.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 149.4, 137.5, 132.4, 130.4, 127.4, 117.7, 99.0, 52.6 ppm. ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J*= 8.2 Hz, 2H), 7.87 (d, *J*= 8.2 Hz, 2H), 7.19 (d, *J*= 12.1 Hz, 1H), 5.59 (d, *J*= 12.1 Hz, 1H), 3.95 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 147.6, 137.5, 132.1, 130.2, 129.0, 117.0, 97.7, 52.5 ppm.



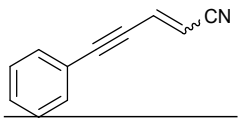
3-(o-Tolyl)acrylonitrile (2h) was prepared **1h** (163 mg, 0.79 mmol) the general olefination procedure. **2h** was purified by radial chromatography. Pure **2h** was obtained as an oil (yield 22%), as a mixture of isomers (73:27 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[7,8,9] ***E*-isomer (**resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.6 Hz, 1H), 5.78 (d, *J* = 16.6 Hz, 1H), 2.38 (s, 3H) ppm.

[7] Mu, Y.; Nguyen, T. T.; Koh, M. J.; Schrock, R. R.; Hoveyda, A. H. *Nat. Chem.* **2019**, *11*, 478–487.
[8] Qin, C.; Jiao, N. *J. Am. Chem. Soc.* **2010**, *132*, 15893-15895.
[9] Grübel, M.; Jandl, C.; Bach, T. *Synlett* **2019**, *30*, 1825-1829.

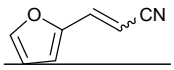
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 137.3, 132.6, 131.1, 131.0, 126.6, 125.6, 118.4, 97.3, 19.6.***Z*-isomer** (only resolved signals) ^{1}H NMR (400 MHz, $CDCl_3$) 7.91 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 12.0 Hz, 1H), 5.51 (d, *J* = 12.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 137.2, 132.8, 130.62, 130.60, 127.7, 126.5, 117.2, 97.0, 19.7.



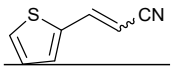
5-Phenylpenta-2,4-dienenitrile (2i) was prepared from **1i** (148 mg, 0.67 mmol) following the general olefination procedure. **2i** was purified by radial chromatography. Pure **2i** was obtained as an oil (yield 60%), as a mixture of isomers (58:42 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[7] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J*= 7.9, 1.7 Hz, 2H), 7.37 (tdd, *J*= 7.0, 5.3, 3.2 Hz, 3H), 7.15 (dd, *J*= 15.8, 10.0 Hz, 1H), 6.89 (d, *J*= 17.4 Hz, 1H), 6.81 (dd, *J*= 15.5, 9.9 Hz, 1H), 5.43 (d, *J*= 15.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 141.5, 135.3, 129.8, 129.0, 127.5, 125.5, 118.5, 98.3 ppm. ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J*= 7.9, 1.7 Hz, 1H), 7.37 (tdd, *J*= 7.0, 5.3, 3.2 Hz, 3H), 7.23 (d, *J*= 4.3 Hz, 1H), 7.19 (d, *J*= 5.3 Hz, 1H), 6.98 (m, 1H), 5.25 (d, *J*= 10.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 141.8, 135.4, 129.8, 129.0, 127.7, 124.2, 116.8, 96.6 ppm.



5-phenylpent-2-en-4-ynenitrile (2j) was prepared from **1j** (150 mg, 0.5 mmol) the general olefination procedure. **2j** was purified by radial chromatography with a system a hexanes:ethyl acetate system (99: 1). Pure **2j** was obtained as an oil (yield 48%), as a mixture of isomers (31:69 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[10] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.42 – 7.36 (m, 3H), 6.70 (d, *J*= 16.3 Hz, 1H), 5.80 (d, *J*= 16.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 131.2, 130.1, 128.8, 121.5, 117.3, 108.2, 100.9, 85.5 ppm. ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.42 – 7.35 (m, 4H), 6.53 (d, *J*= 10.9 Hz, 1H), 5.67 (d, *J*= 10.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 130.1, 129.6, 128.7, 121.5, 116.1, 107.3, 102.5, 84.8 ppm. **2j-*Z*** isomer was obtained as an inseparable mixture with



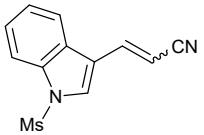
3-(Furan-2-yl)acrylonitrile (2k) was prepared from **1k** (145 mg, 0.79 mmol) following the general olefination procedure. **2k** was purified by radial chromatography. Pure **2k** was obtained as an oil (yield 55%), as a mixture of isomers (80:20 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[11] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J*= 1.8 Hz, 1H), 7.11 (d, *J*= 16.2 Hz, 1H), 6.63 (d, *J*= 3.5 Hz, 1H), 6.50 (dd, *J*= 3.5, 1.8 Hz, 1H), 5.76 (d, *J*= 16.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 145.6, 136.2, 118.4, 115.6, 112.8, 93.5 ppm. ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J*= 1.8 Hz, 1H), 7.03 (d, *J*= 3.6 Hz, 1H), 6.95 (d, *J*= 12.0 Hz, 1H), 6.54 (dd, *J*= 3.5, 1.7 Hz, 5.23 (d, *J*= 12.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 145.1, 135.0, 117.5, 115.7, 112.6, 91.3 ppm.



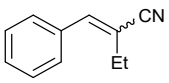
3-(Thiophen-2-yl)acrylonitrile (2l) was prepared from **1l** (152 mg, 0.75 mmol) following the general olefination procedure. **2l** was purified by radial chromatography. Pure **2l** was obtained as an oil (yield 58%), as a mixture of isomers (75:25 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[9] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ, 7.58 (d, *J*= 16.3 Hz, 1H), 7.42 (d, *J*= 5.1 Hz, 1H), 7.24 (m, 1H), 7.08 (dd, *J*= 5.1, 3.7 Hz, 1H), 5.65 (d, *J*= 16.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.5, 131.4, 129.4, 128.5, 118.1, 94.5 ppm. ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J*= 3.8 Hz, 1H), 7.54 (d, *J*= 5.1 Hz, 1H), 7.24 (m, 1H) 7.12 (dd, *J*= 5.1, 3.7 Hz, 1H), 5.26 (d, *J*= 11.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 137.8, 132.5, 130.4, 127.8, 117.7, 91.9 ppm.

[10] Li, B.; Li, Z.; You, K.; Qin, A.; Tang, B. Z. *Sci. China Chem.* **2022**, *65*, 771–777.

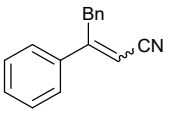
[11] Wu, H.; Yang, P.; Du, Z.; Fu, Y. *ChemistrySelect* **2017**, *2*, 2183–2186.



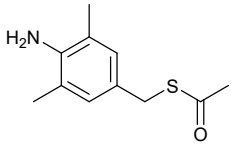
3-(1-(Methylsulfonyl)-*1H*-indol-3-yl)acrylonitrile (2m) was prepared from **1m** (148 mg, 0.47 mmol) following the general olefination procedure. **2m** was purified by radial chromatography using hexanes:ethyl acetate (80:20) as eluent. Pure **2m** was obtained as an oil (yield 60%), as a mixture of isomers (54:46 *E:Z*). ***E*-isomer** (resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J*= 7.8 Hz, 1H), 7.73 (s, 1H), 7.70 (d, *J*= 7.8 Hz, 1H), 5.98 (d, *J*= 16.7 Hz, 1H), 3.22 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 134.4, 129.0, 128.1, 126.2, 124.7, 120.5, 117.4, 116.1, 113.5, 96.5, 41.5 ppm. ***Z*-isomer** (resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.95 (dd, *J*= 8.2, 5.5 Hz, 2H), 7.38 (d, *J*= 11.6 Hz, 1H), 5.52 (d, *J*= 11.8 Hz, 1H), 3.24 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 135.5, 127.3, 126.6, 126.0, 124.2, 119.00, 118.3, 117.8, 113.3, 95.1, 41.6 ppm. IR-KBr ν_{max} (cm^{-1}) (2213 CN), (1363, 1167 SO_2).



2-Benzylidenebutanenitrile (2n) was prepared from **1n** (100 mg, 0.45 mmol) following the general olefination procedure. **2n** was purified by radial chromatography. Pure **2n** was obtained as an oil (yield 88%), as a mixture of isomers (72:28 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[11] ***E*-isomer** (resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.27 (m, 2H), 7.19 (s, 1H) , 2.50 (qd, *J*= 7.5 Hz, 1.3 Hz, 2H), 1.25 (t, *J*= 7.5 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 134.2, 129.3, 129.2, 128.8, 120.3, 117.3, 23.1, 12.9 ppm. ***Z*-isomer** (resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J*= 7.6, 1.6 Hz, 2H), 6.94 (s, 1H), 2.44 (qd, *J*= 7.5, 1.2 Hz, 2H), 1.26 (t, *J*= 7.5 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 134.2, 129.9, 128.9, 128.6, 118.8, 113.1, 29.7, 13.1 ppm.



3,4-Diphenylbut-2-enenitrile (2o) was prepared from **1o** (100 mg, 0.35 mmol) following the general olefination procedure. **2o** was purified by radial chromatography. Pure **2o** was obtained as an oil (yield 70%), as a mixture of isomers (72:28 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data for the *E*-isomer.[12] *Z*-isomer spectroscopic data was not found in the literature; however, we were able to assign *Z*-isomer related signals from the pure mixture of isomers. ***E*-isomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 - 7.38 (m, 2H), 7.37 - 7.31 (m, 3H), 7.23 (d, *J*= 6.3 Hz, 2H), 7.19 (d, *J*= 6.9 Hz, 3H), 5.71 (s, 1H), 4.22 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 137.5, 136.9, 130.3, 129.0, 128.9, 128.8, 127.0, 126.8, 117.7, 97.27, 39.9. ***Z*-isomer** (resolved signals only) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (t, *J* = 1.6 Hz, 1H), 3.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 137.6, 136.4, 129.9, 129.4, 129.0, 128.8, 127.5, 127.3, 126.3, 117.6, 97.31, 44.1.

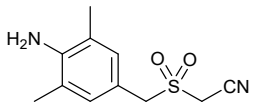


***S*-(4-Amino-3,5-*d*imethylbenzyl) ethanethioate (6)** was prepared from (4-amino-3,5-*d*imethylphenyl)methanol **(5)**[13] (750 mg, 0.36 mmol) and thioacetic acid (0.713 mg, 0.94 mmol) dissolved in dry tetrahydrofuran at 0°C, this solution was added slowly to a stirred solution of triphenylphosphine (PPh_3, 2.66 g, 1.01 mmol) and diisopropyl azodicarboxylate (DIAD, 1.89 g, 0.94 mmol) in dry tetrahydrofuran at 0°C, and stirred overnight at room temperature. The reaction was monitored by TLC until starting material was consumed. The mixture was poured in cooled $NaHCO_3$ saturated solution and stirred until 10 pH was reached. The aqueous layer was extracted with ethyl acetate (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude thioacetate **(6)** Pure **6** was obtained by SiO_2 chromatography using a mixture of hexanes and ethyl acetate 70:30 as eluent (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 4.01 (s, 2H),

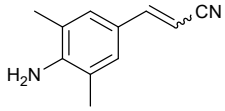
[12] Yu, X. Y.; Wang, P. Z.; Yan, D. M.; Lu, B.; Chen, J. R.; Xiao, W. J. *Adv. Synth. Catal.* **2018**, *360*, 3601–3606.

[13] Kimiyuki, S.; Katsumi, K.; Yukihiro, S.; Toru, M.; Chiyoka, O.; Toshiyuki, E.; Mitsuteru, H.; Taddaki, O. *Novel Cyclic Diamine Compounds and Medicine Containing the Same*. US2004038987A1, 2004.

3.55 (bs, 1H), 2.32 (s, 3H), 2.13 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 142.1, 128.8, 126.4, 122.0, 33.4, 30.5, 17.7. MS (ESI+), m/z: Calculated for $C_{11}H_{15}NOS$ 209.1; found 210.1 $[M+H]^+$, IR-KBr ν_{max} (cm-1) 3472, 3389 (NH), 1683 (NH).



2-((4-Amino-3,5-dimethylbenzyl)sulfonyl)acetonitrile (7) was prepared from 2-((4-amino-3,5-*d*imethylbenzyl)thio)acetonitrile **(S7)**, (139.0 mg, 0.89 mmol**)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 3.80 (s, 2H), 3.62 (s, 2H), 3.07 (s, 2H), 2.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 129.2, 129.1, 124.4, 122.1, 116.8, 36.0, 17.7, 15.9. Oxidation of **S7 (oxidation 1)**, delivered sulfonyl nitrile **7**, which was purified by SiO_2 flash chromatography using hexanes:ethyl acetate (60:40) as eluent. Pure **7** was obtained as a solid with (two-step yield 75%), mp: 68-70°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 2H), 4.37 (s, 2H), 3.78 (bs, 2H), 3.70 (s, 2H), 2.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 130.6, 122.6, 114.6, 110.7, 59.6, 39.4, 17.7. MS (ESI+), m/z: Calculated for $C_{11}H_{14}N_2O_2S$; 238.1 found 239.1 $[M+H]^+$, IR-KBrν_{max} (cm^{-1}) 1304, 1131 (SO_2) 2254 (CN), 2854, 2934, 2990 (NH).



3-(4-Amino-3,5-dimethylphenyl)acrylonitrile (3) was prepared from **7** (163.0 mg, 1.2 mmol) following the general olefination procedure. **3** was purified by radial chromatography using hexanes:ethyl acetate (80:20). Pure **3** was obtained as a solid (yield 68%), as a mixture of isomers (84:16 *E:Z*). ^{1}H and ^{13}C NMR spectroscopy matched literature reported data.[14] ***E*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 16.5 Hz, 1H), 7.05 (s, 2H), 5.59 (d, *J* = 16.5 Hz, 1H), 3.96 (bs, 2H), 2.18 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 146.3, 128.1, 123.3z, 121.6, 119.7, 90.3, 17.6 ***Z*-isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 2H), 6.90 (d, *J* = 12.0 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 3.96 (s, 6H), 2.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 146.0, 129.9, 123.7, 121.3, 118.9, 88.8, 17.6

[14] Schils, D.; Stappers, F.; Solberghe, G.; Van Heck, R.; Coppens, M.; Van Den Heuvel, D.; Van Der Donck, P.; Callewaert, T.; Meeussen, F.; De Bie, E.; et al. *Org. Process Res. Dev.* **2008**, *12*, 530–536.

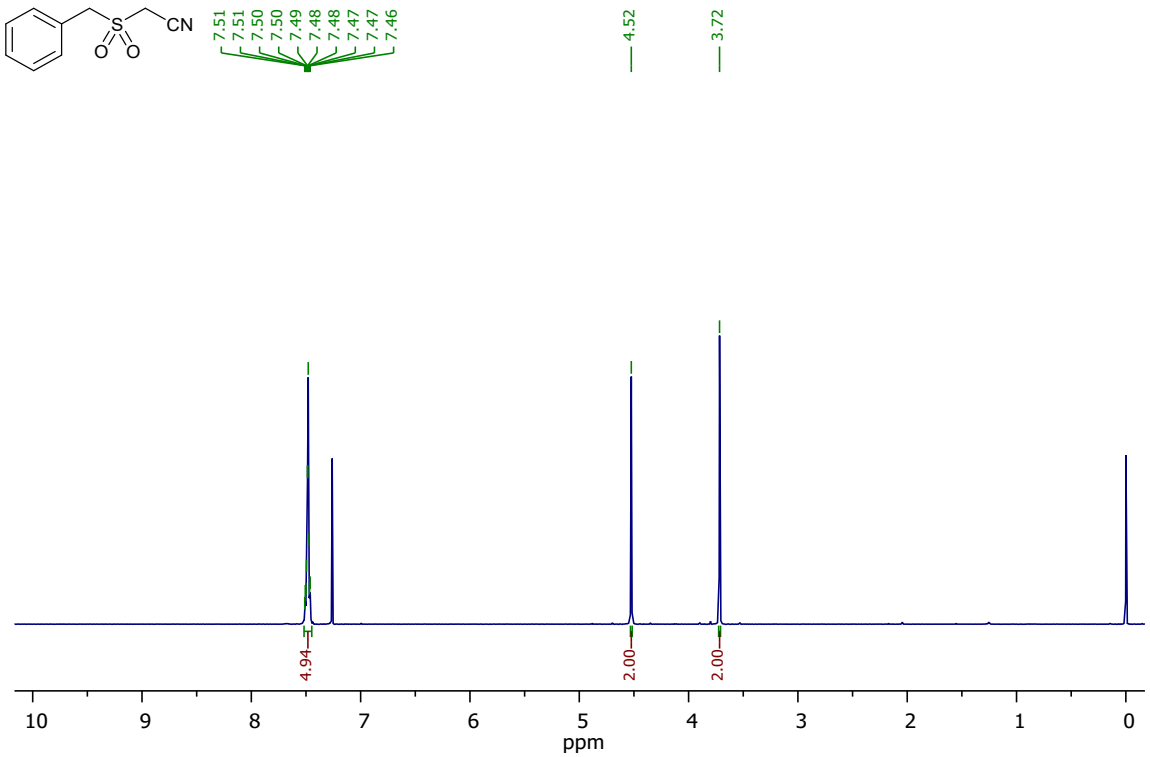


Figure 1. ^{1}H NMR spectra of compound **1a**

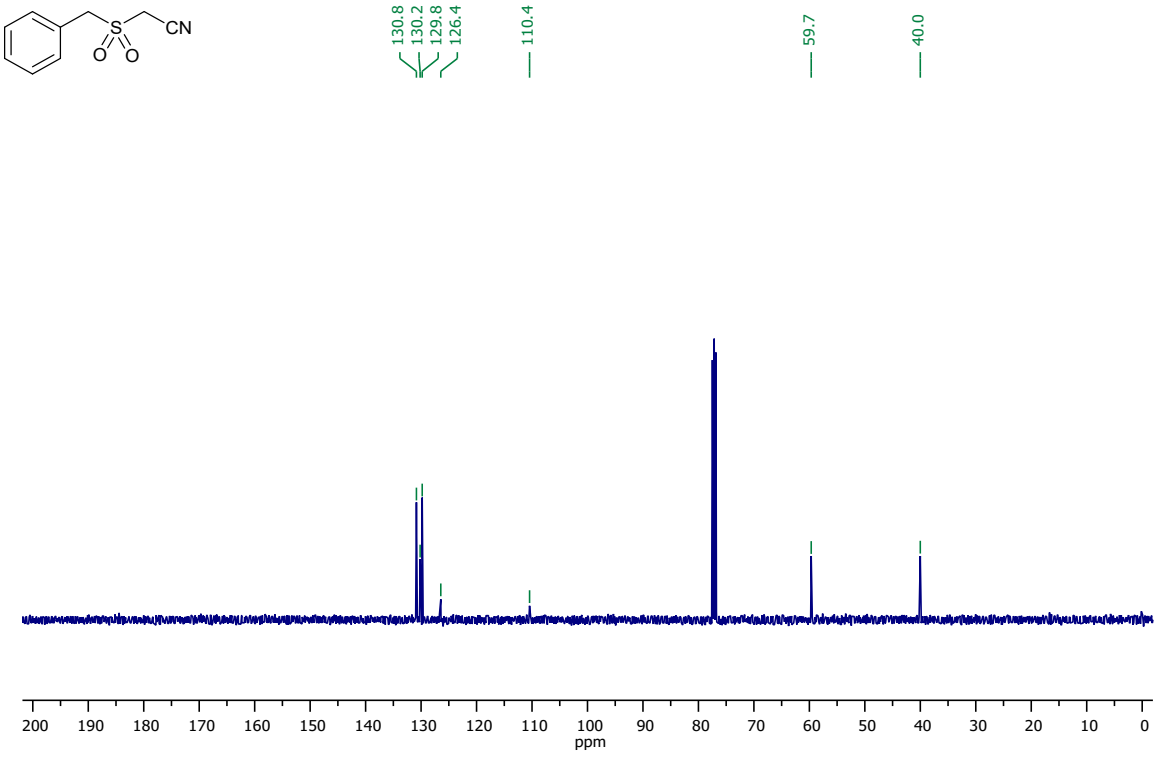


Figure 2. ^{13}C NMR spectra of compound **1a**

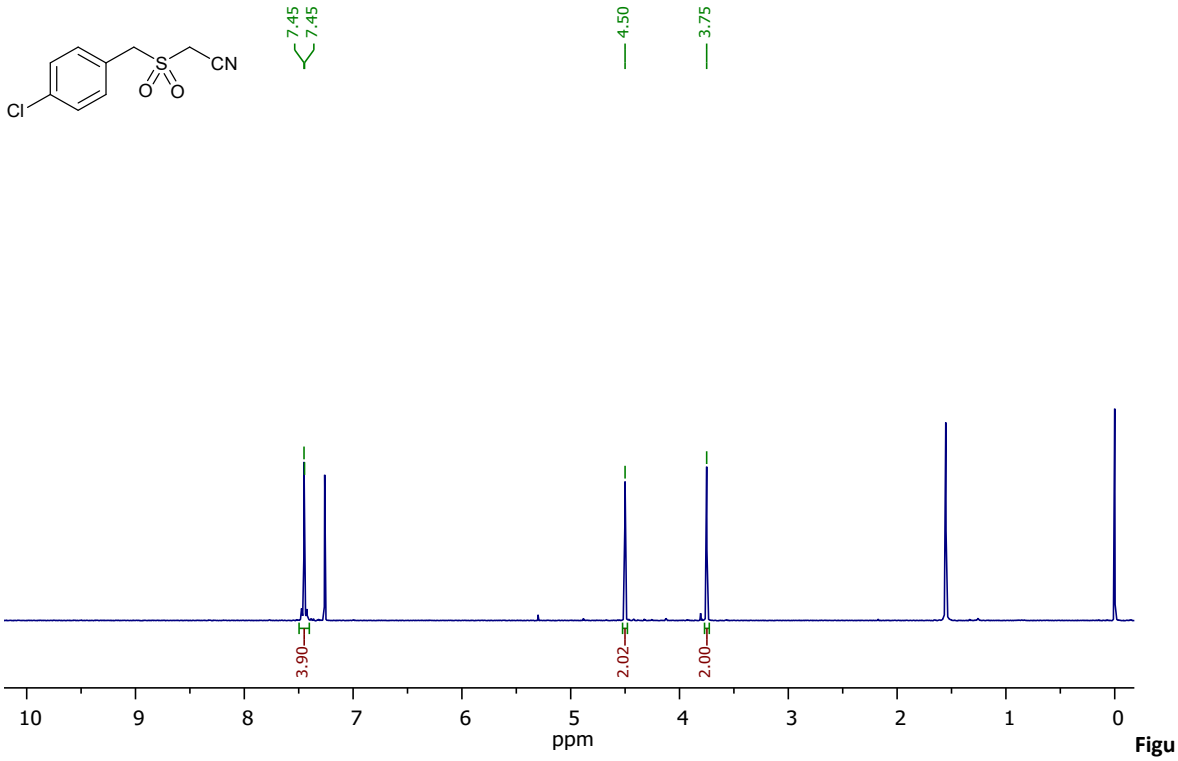


Figure 3. ^{1}H NMR spectra of compound **1b**

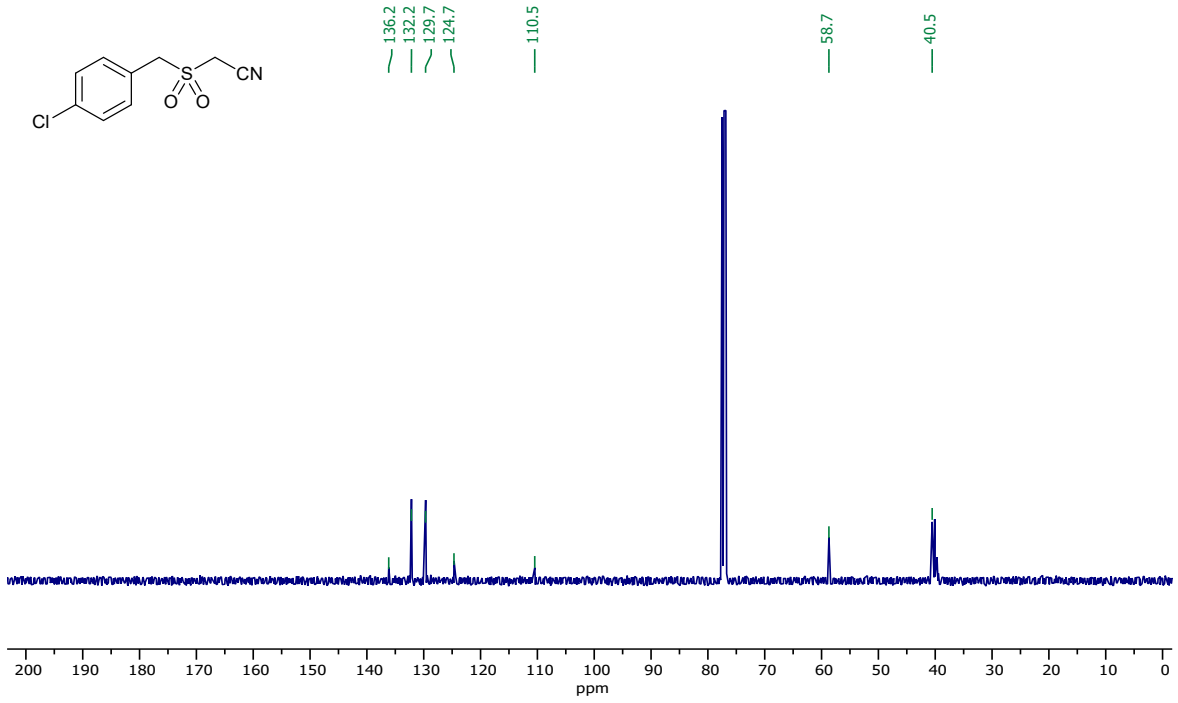


Figure 4. ^{13}C NMR spectra of compound **1b**

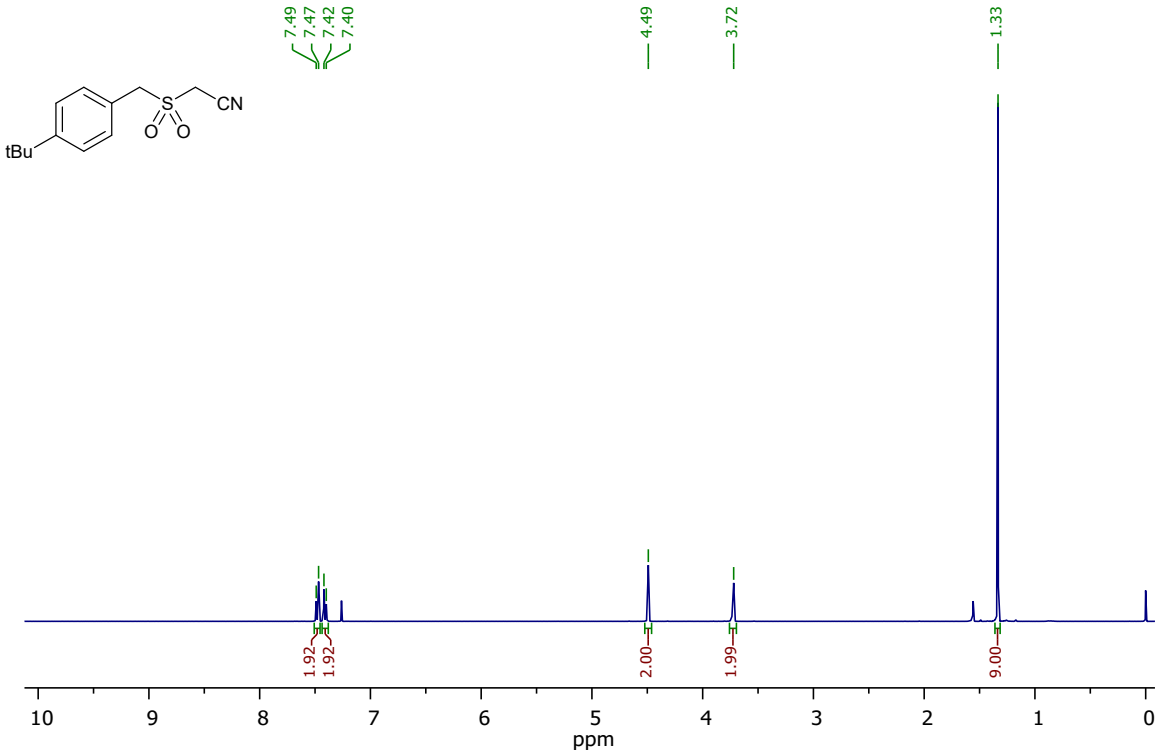


Figure 5. ^{1}H NMR spectra of compound **1c**

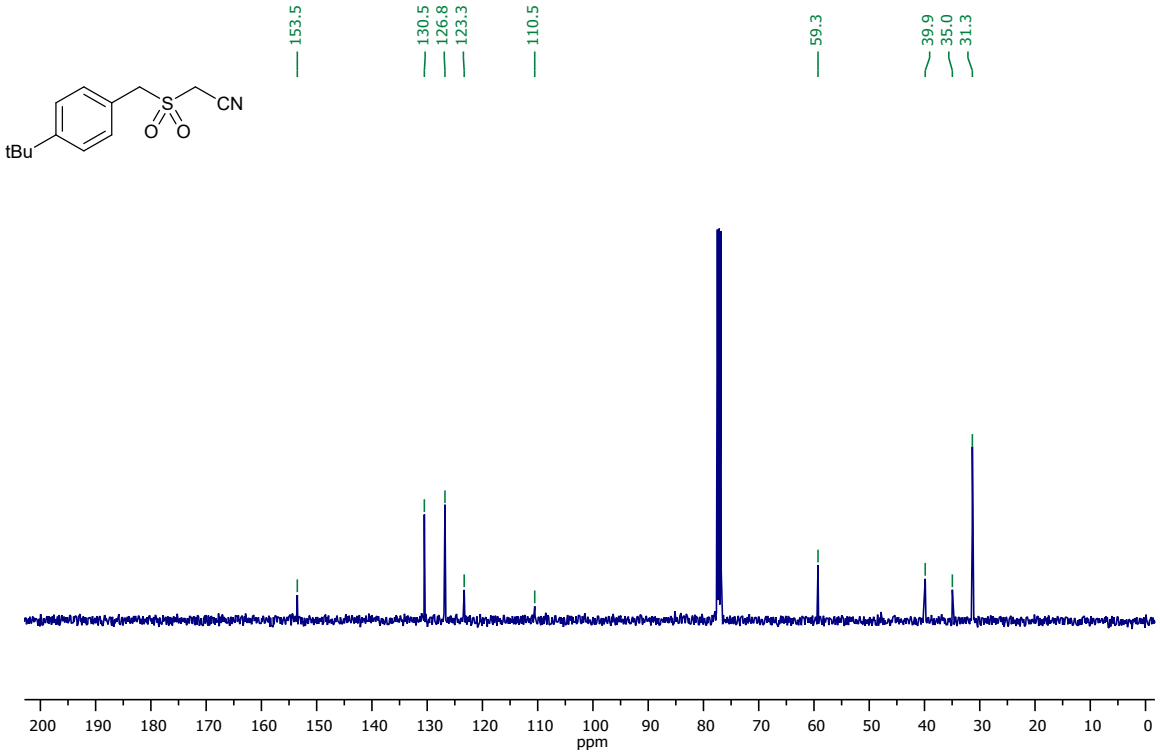


Figure 6. ^{13}C NMR spectra of compound **1c**

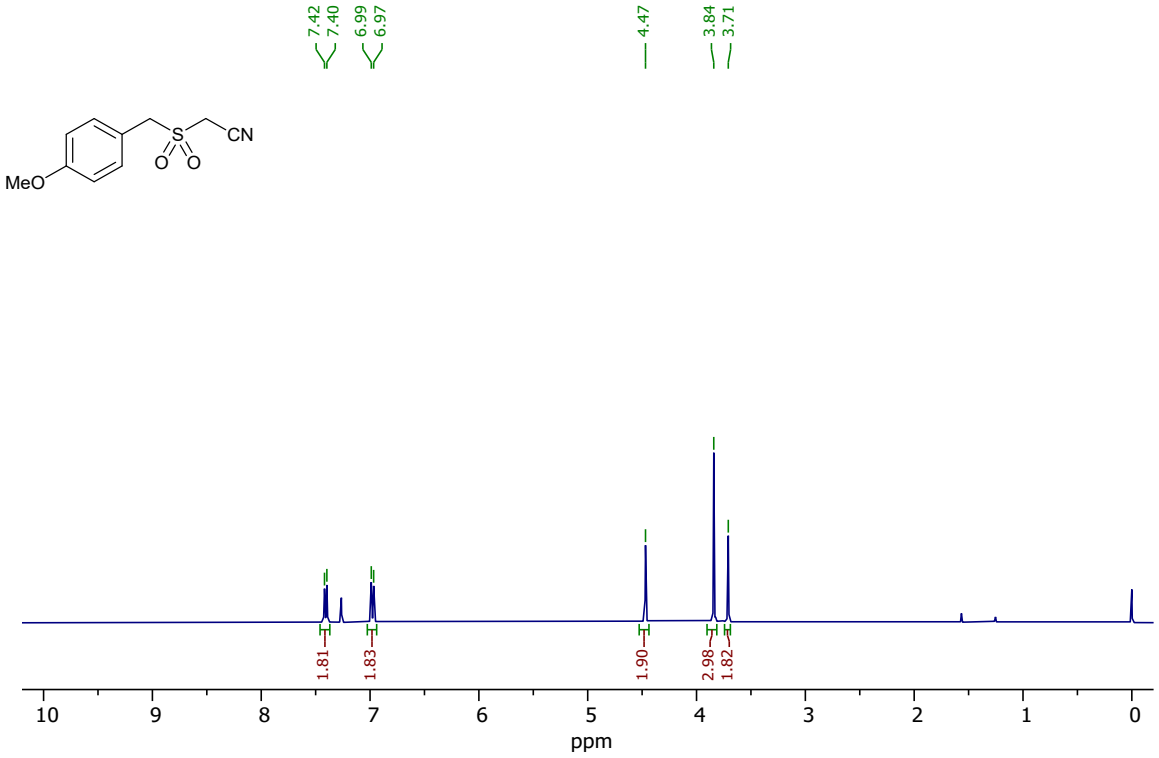


Figure 7. ^{1}H NMR spectra of compound **1d**

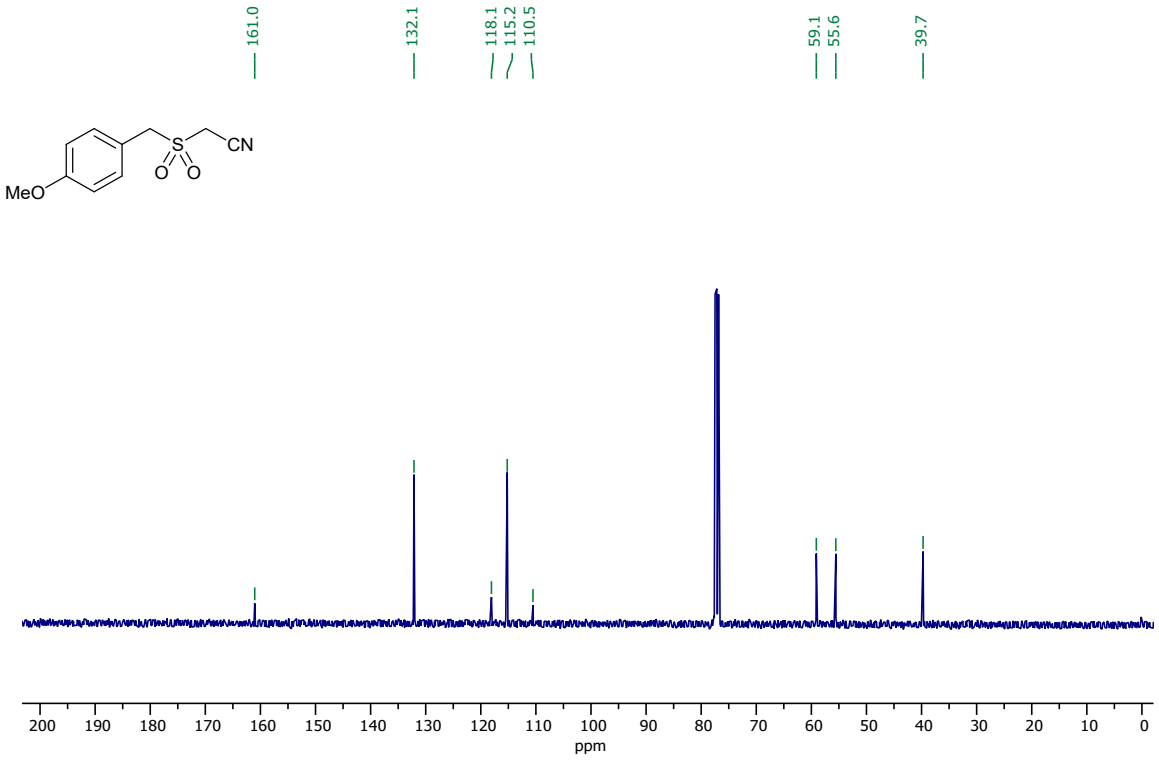


Figure 8. ^{13}C NMR spectra of compound **1d**

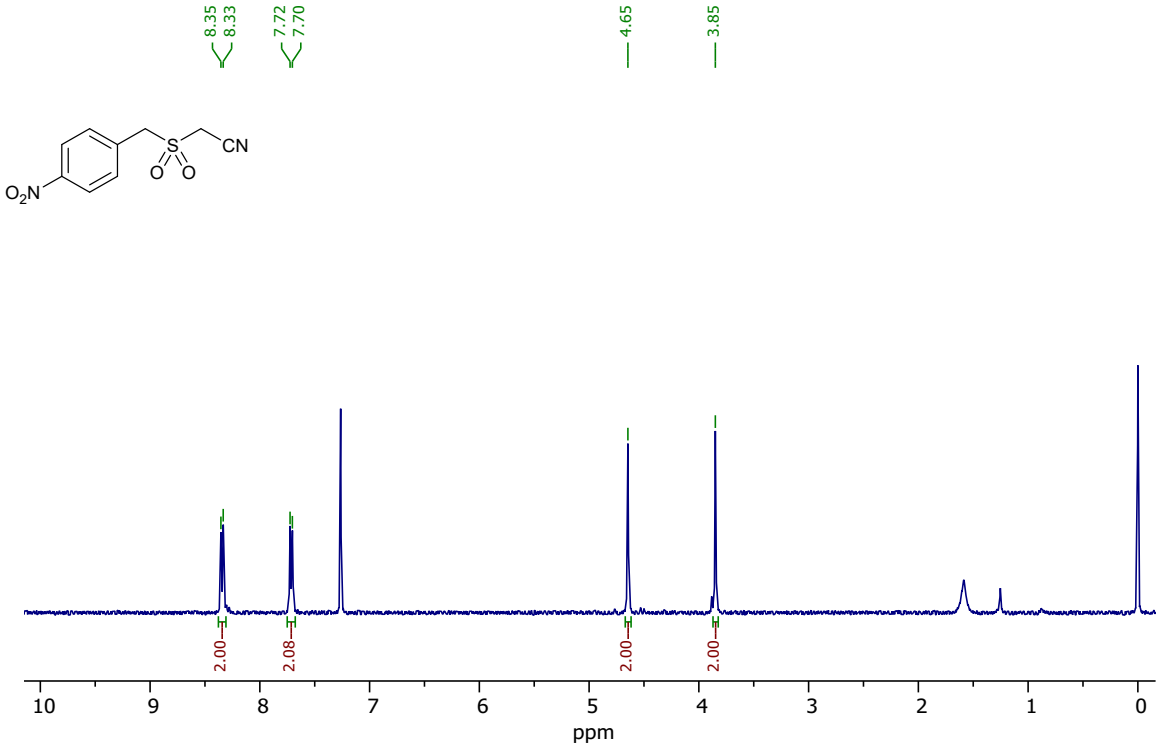


Figure 9. ^{1}H NMR spectra of compound **1e**

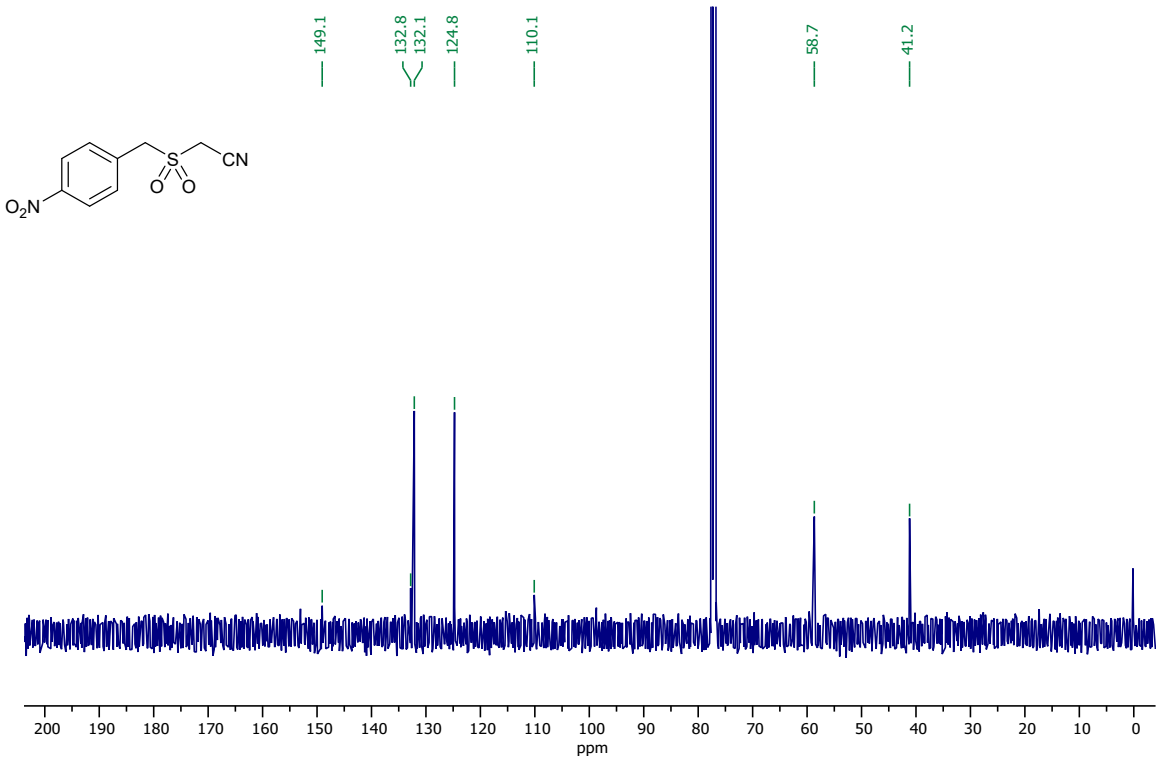


Figure 10. ^{13}C NMR spectra of compound **1e**

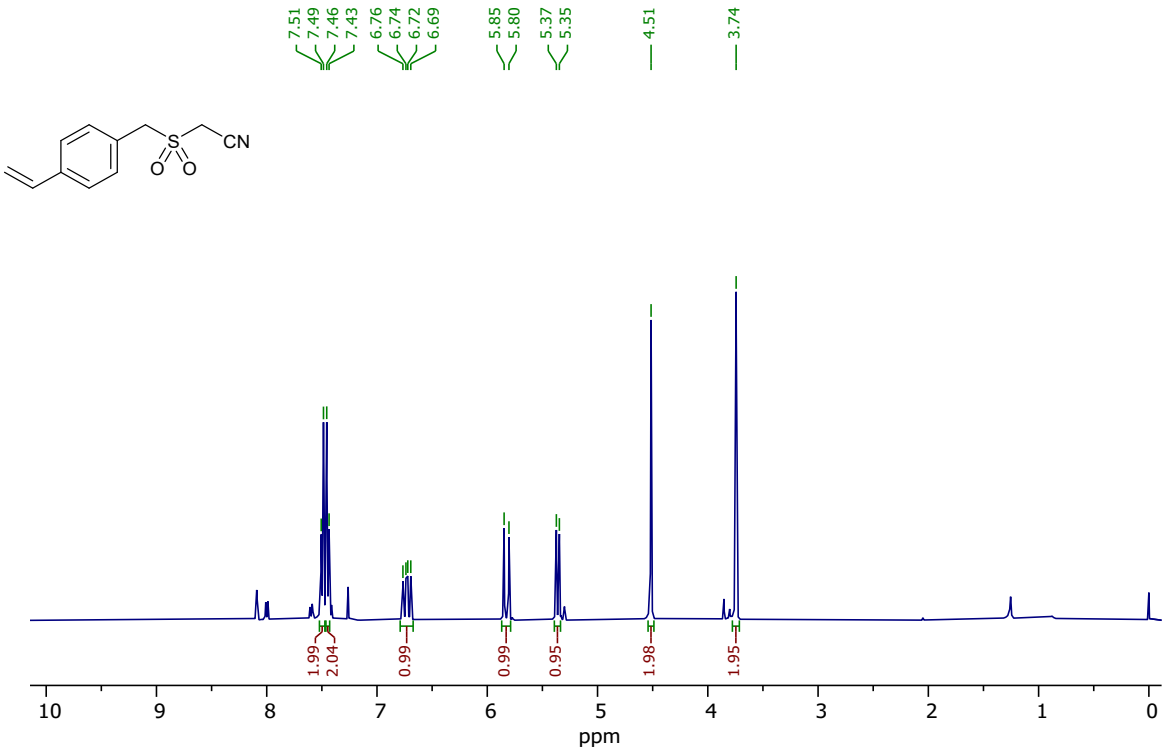


Figure 11. ^{1}H NMR spectra of compound **1f**

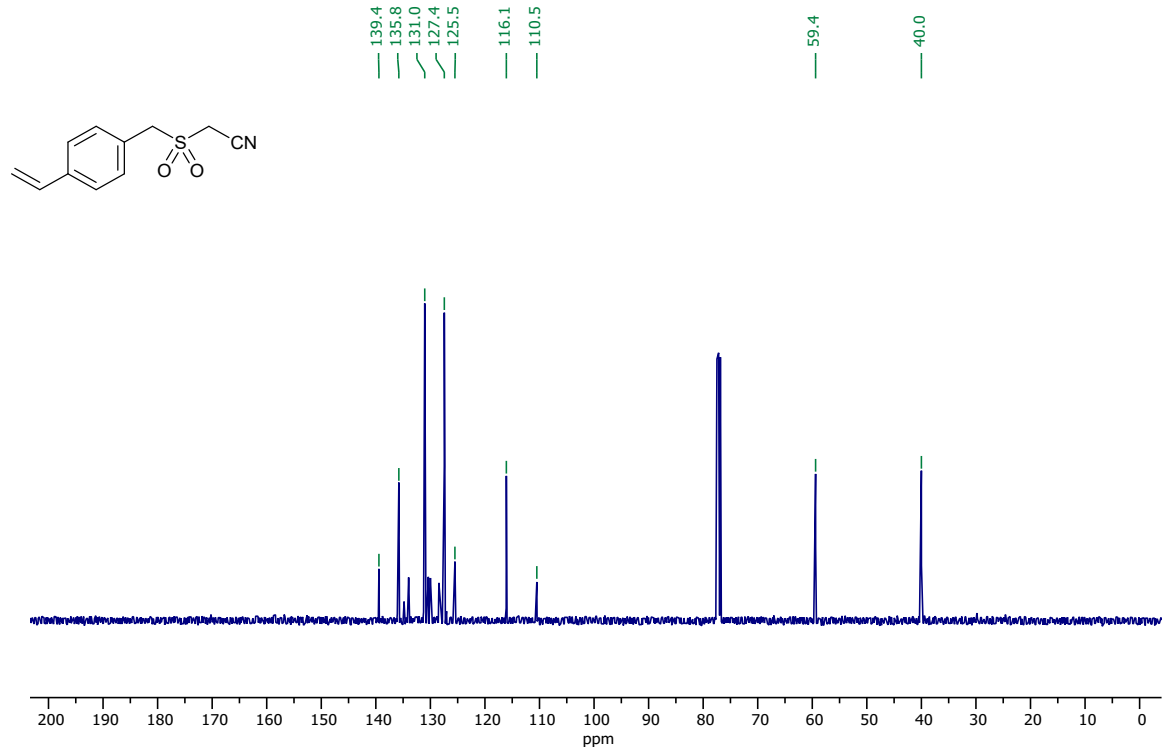


Figure 12. ^{13}C NMR spectra of compound **1f**

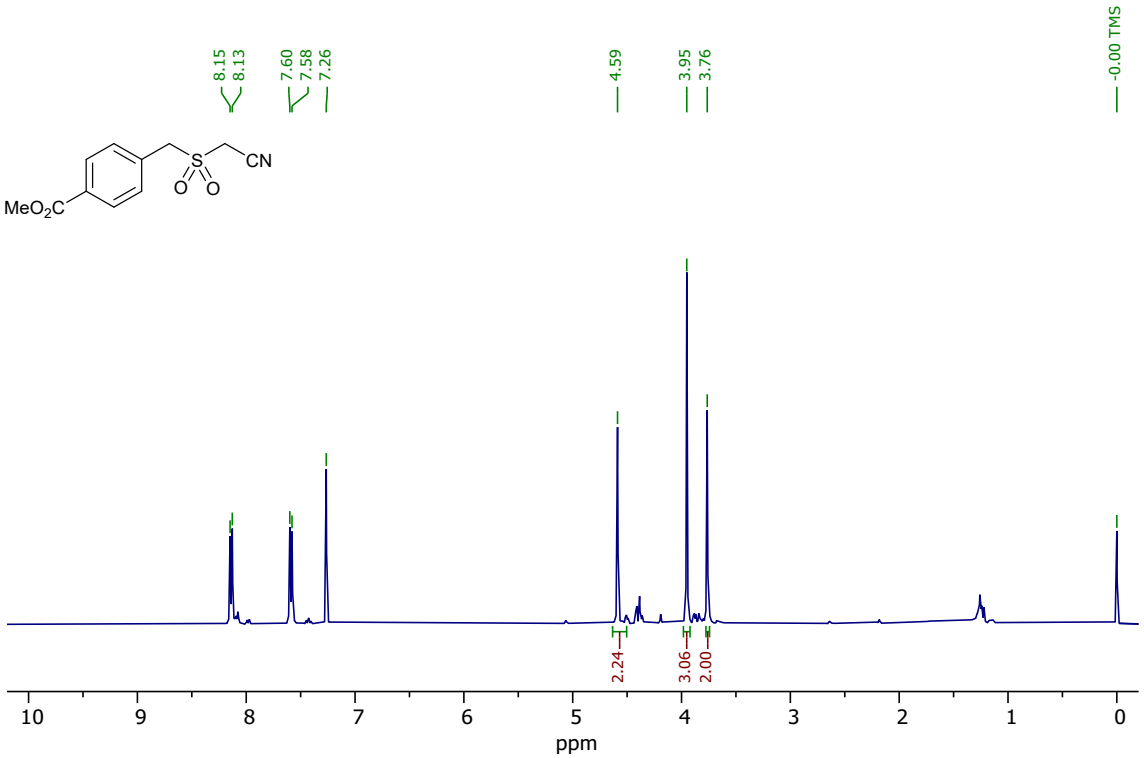


Figure 13. ^{1}H NMR spectra of compound **1g**

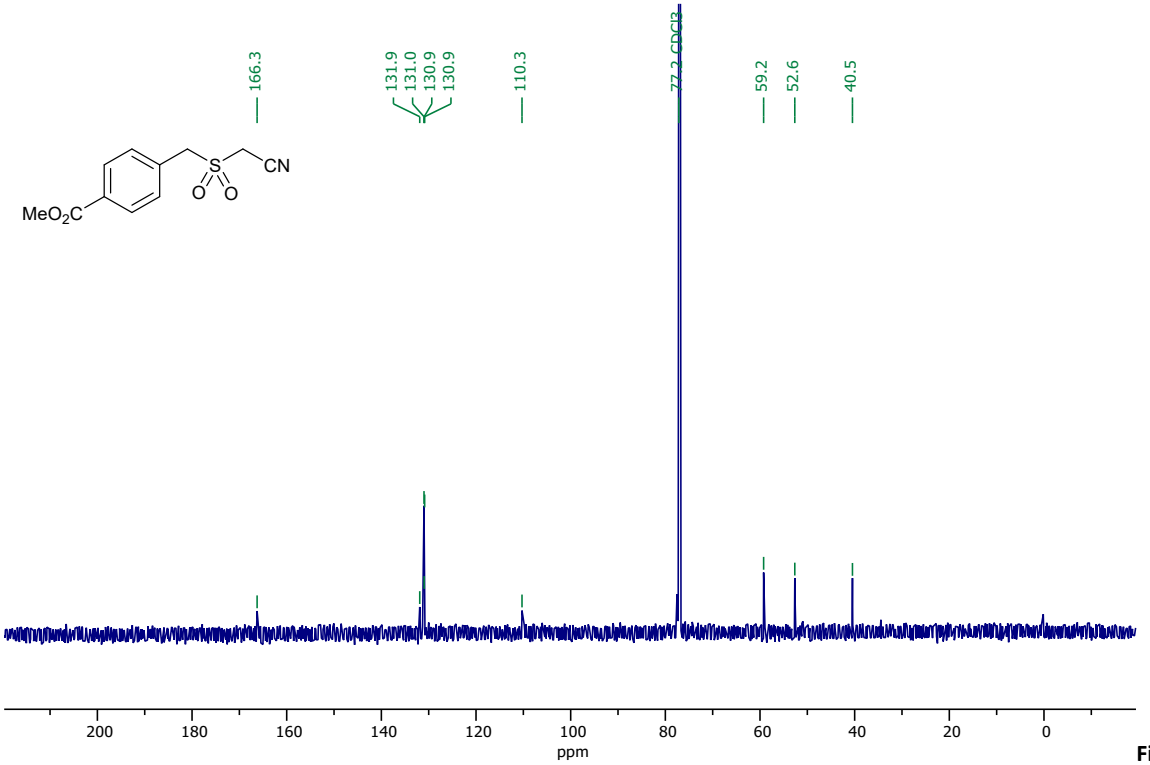


Figure 14. ^{13}C NMR spectra of compound **1g**

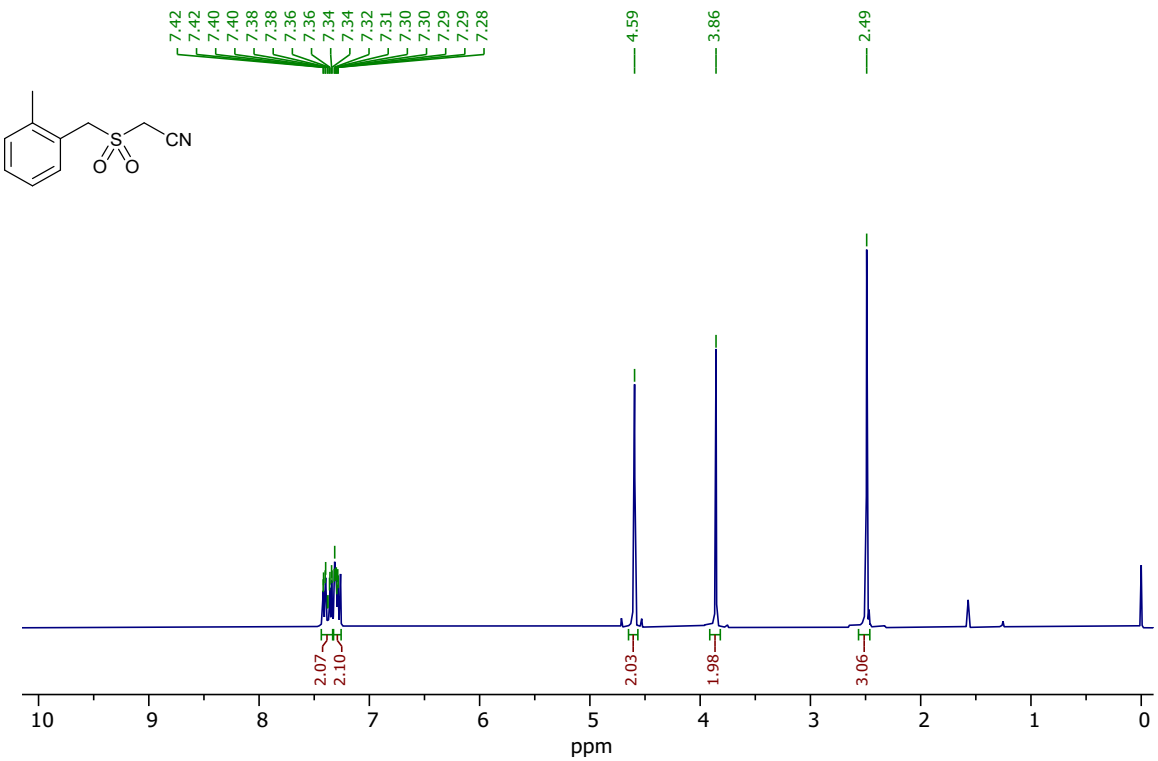


Figure 15. ^{1}H NMR spectra of compound **1h**

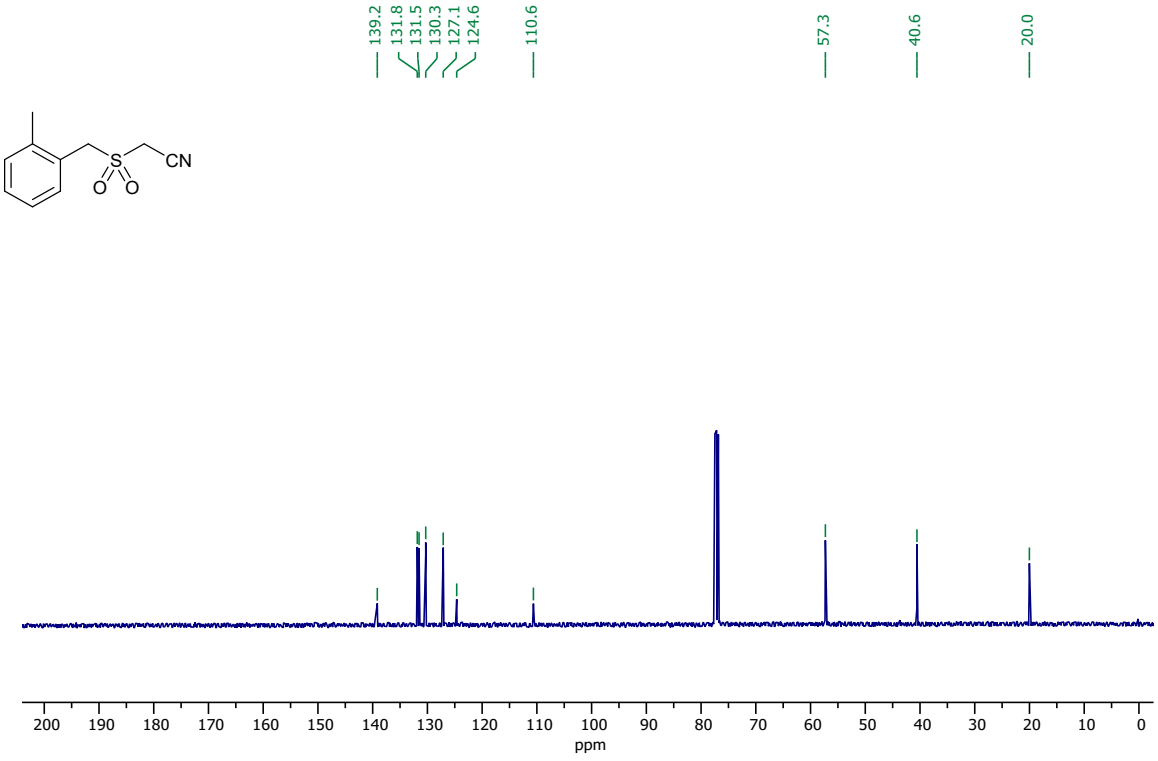


Figure 16. ^{13}C NMR spectra of compound **1h**

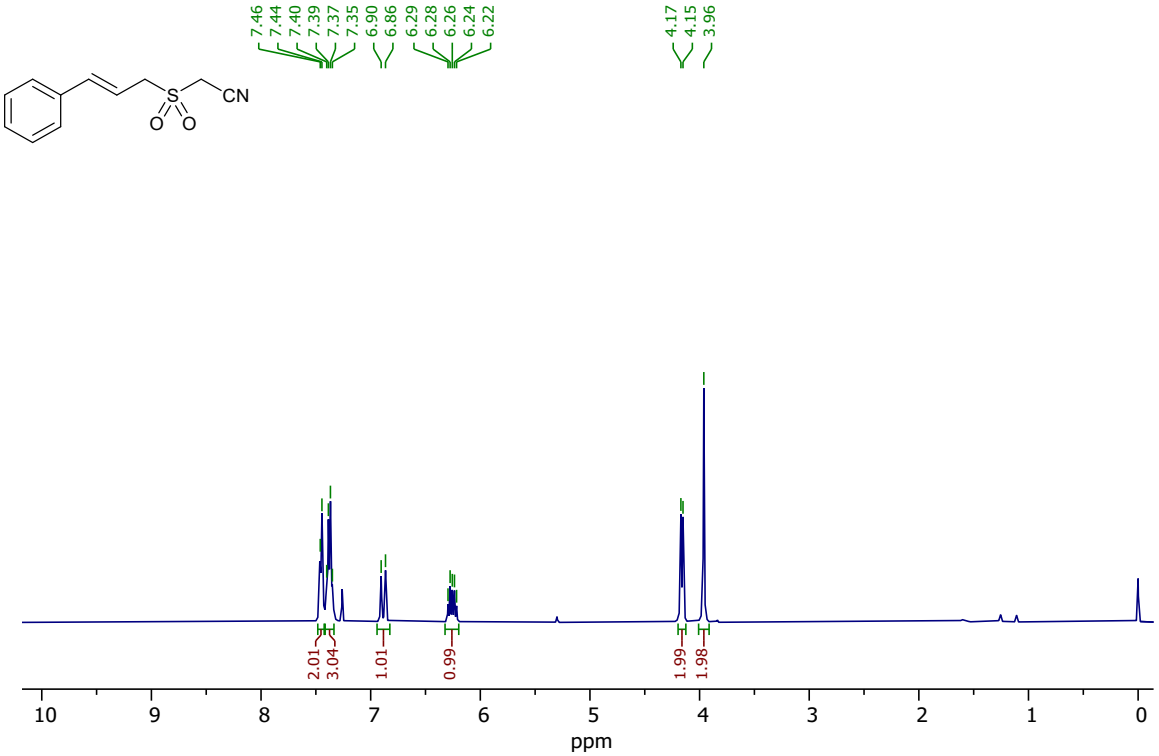


Figure 17. ^{1}H NMR spectra of compound **1i**

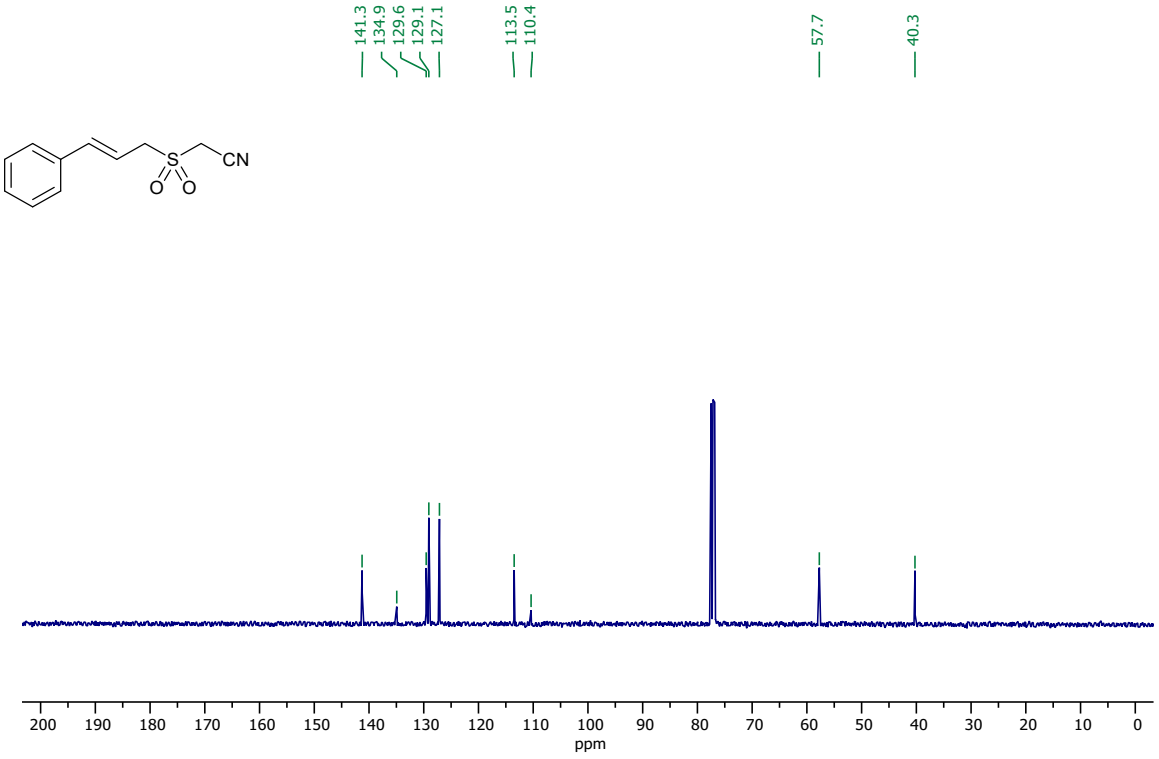


Figure 18. ^{13}C NMR spectra of compound **1i**

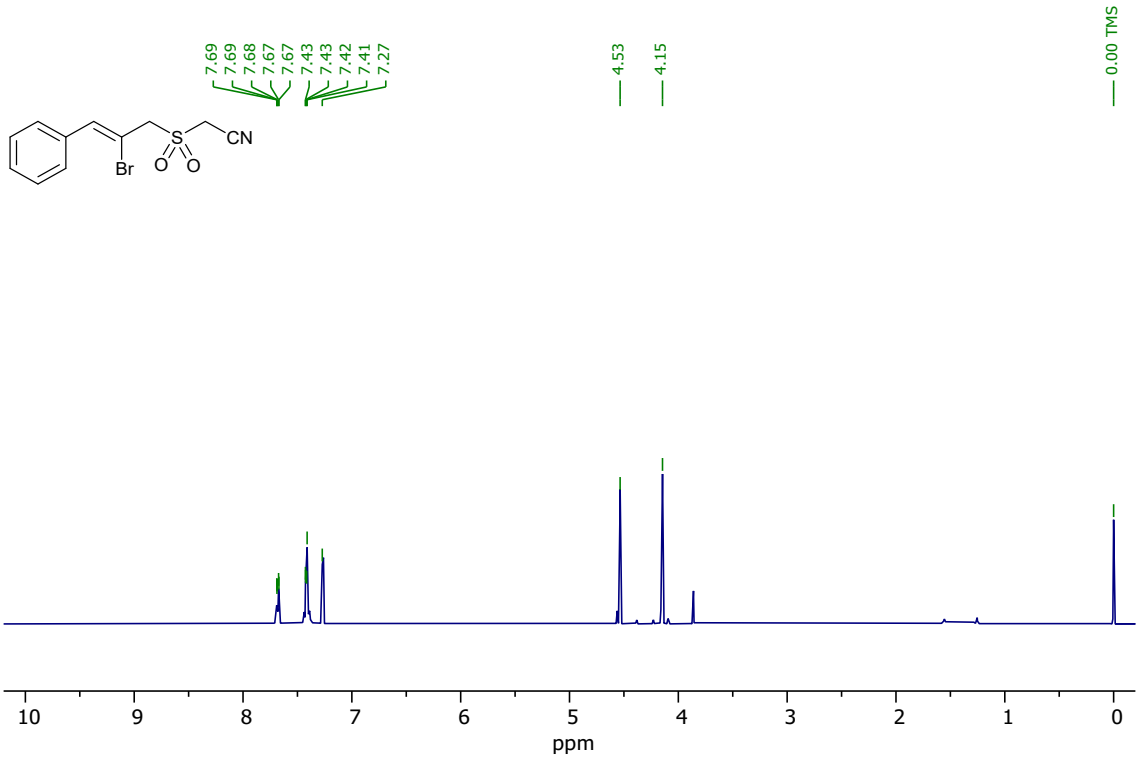


Figure 19. ^{1}H NMR spectra of compound **1j**

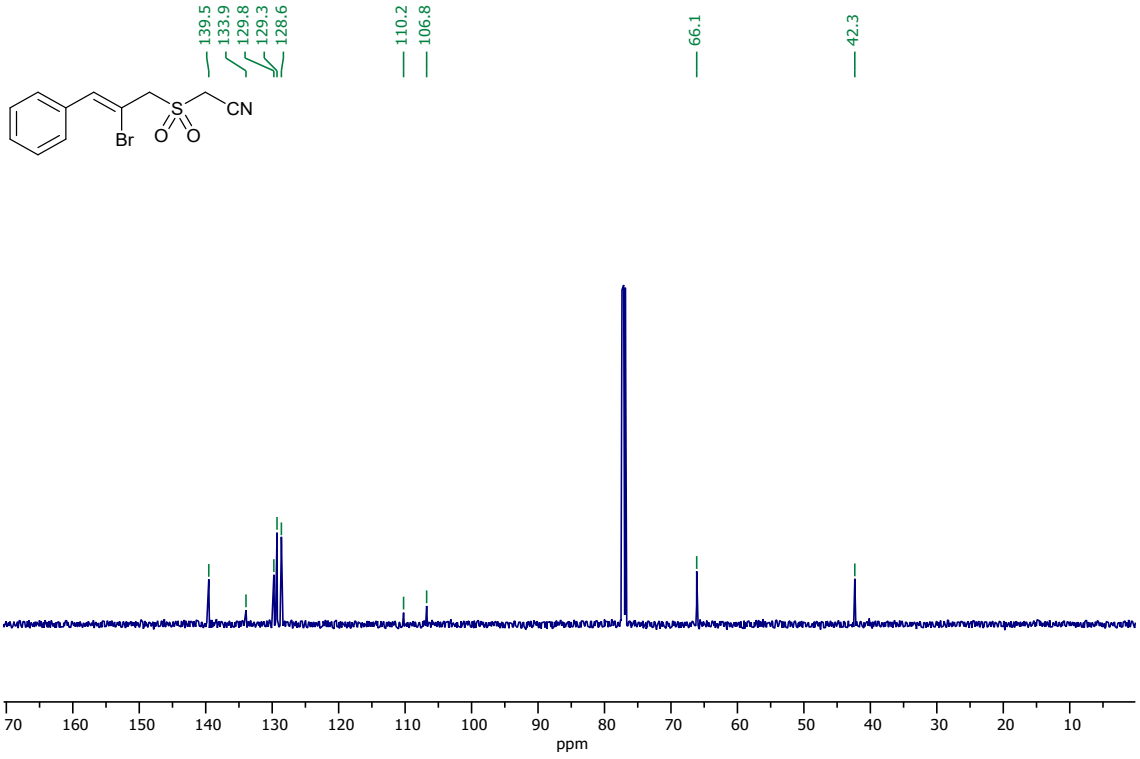


Figure 20. ^{13}C NMR spectra of compound **1j**

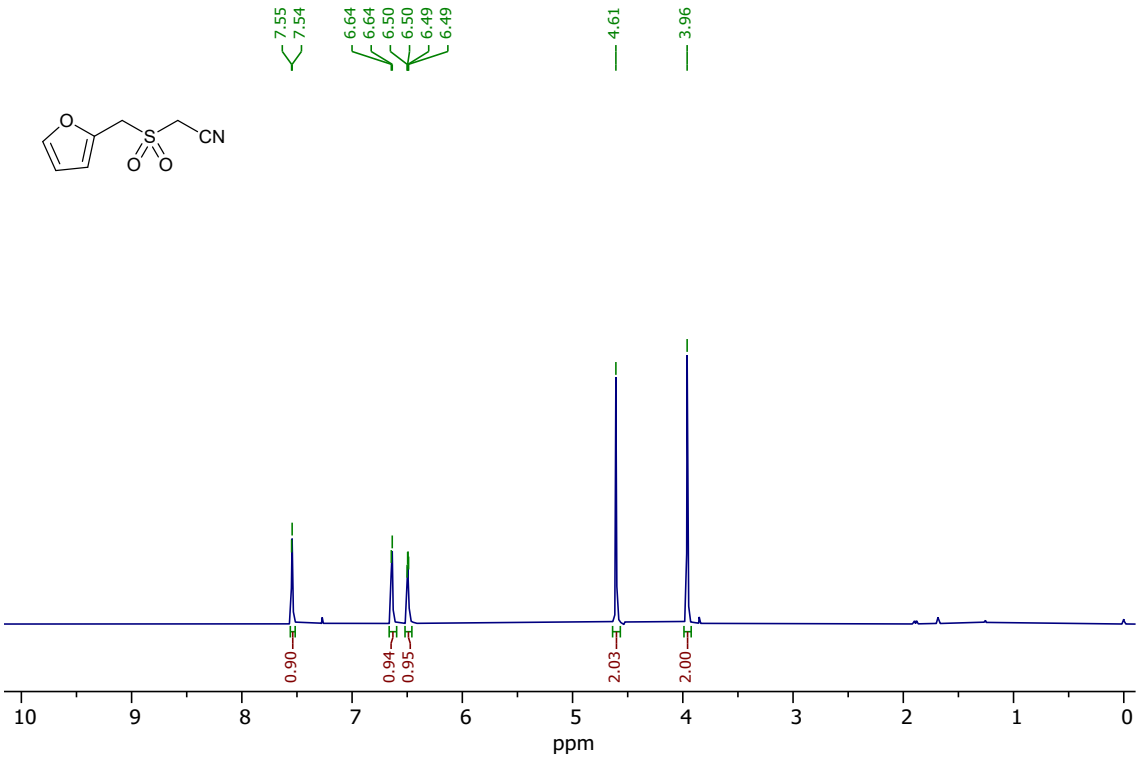


Figure 21. ^{1}H NMR spectra of compound **1k**

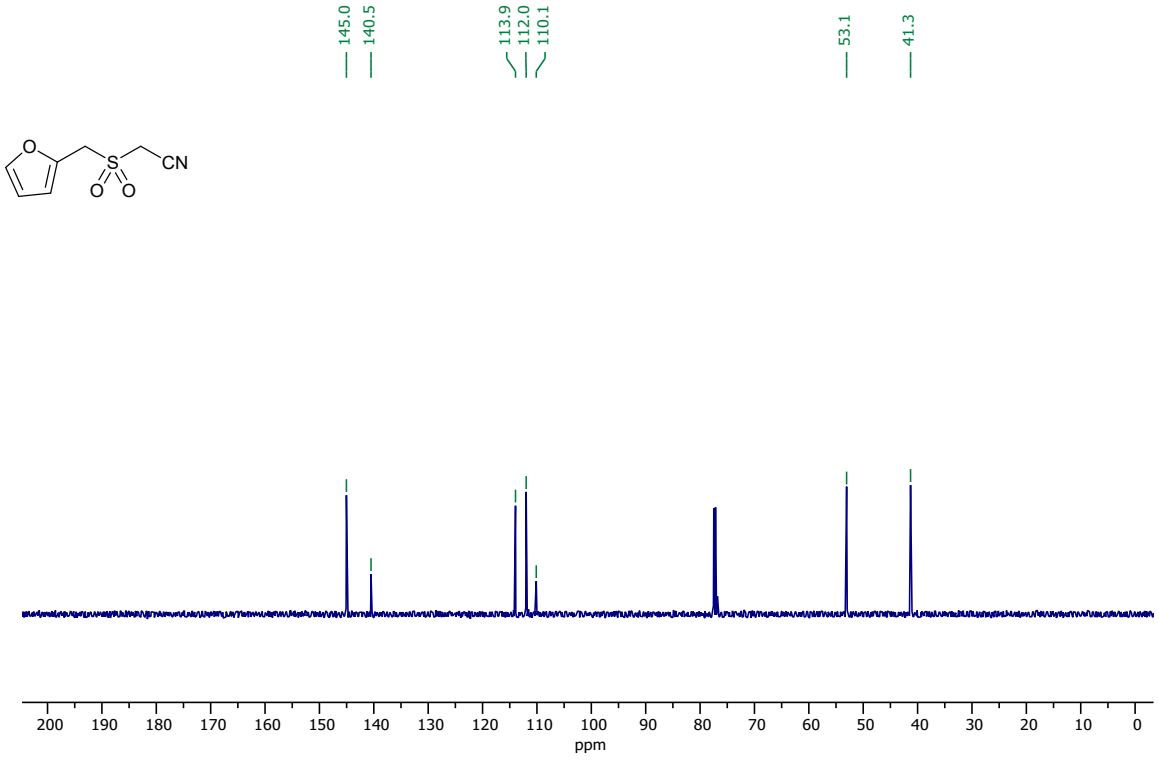


Figure 22. ^{13}C NMR spectra of compound **1k**

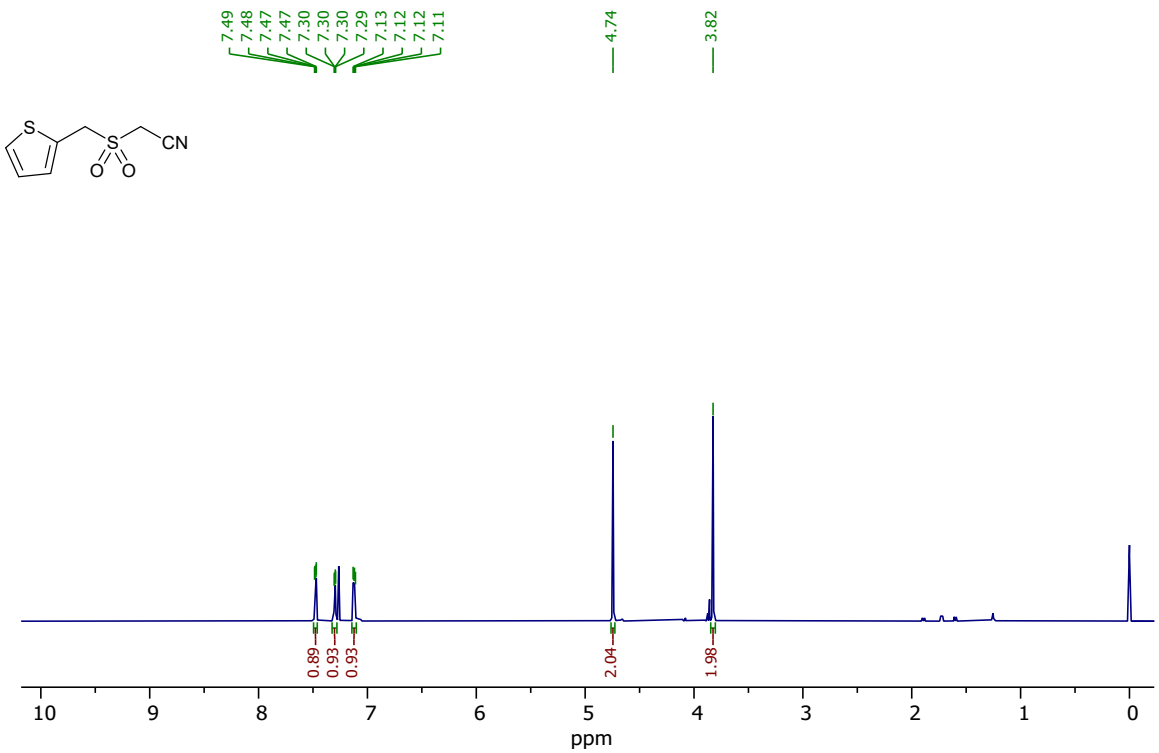


Figure 23. ^{1}H NMR spectra of compound **1l**

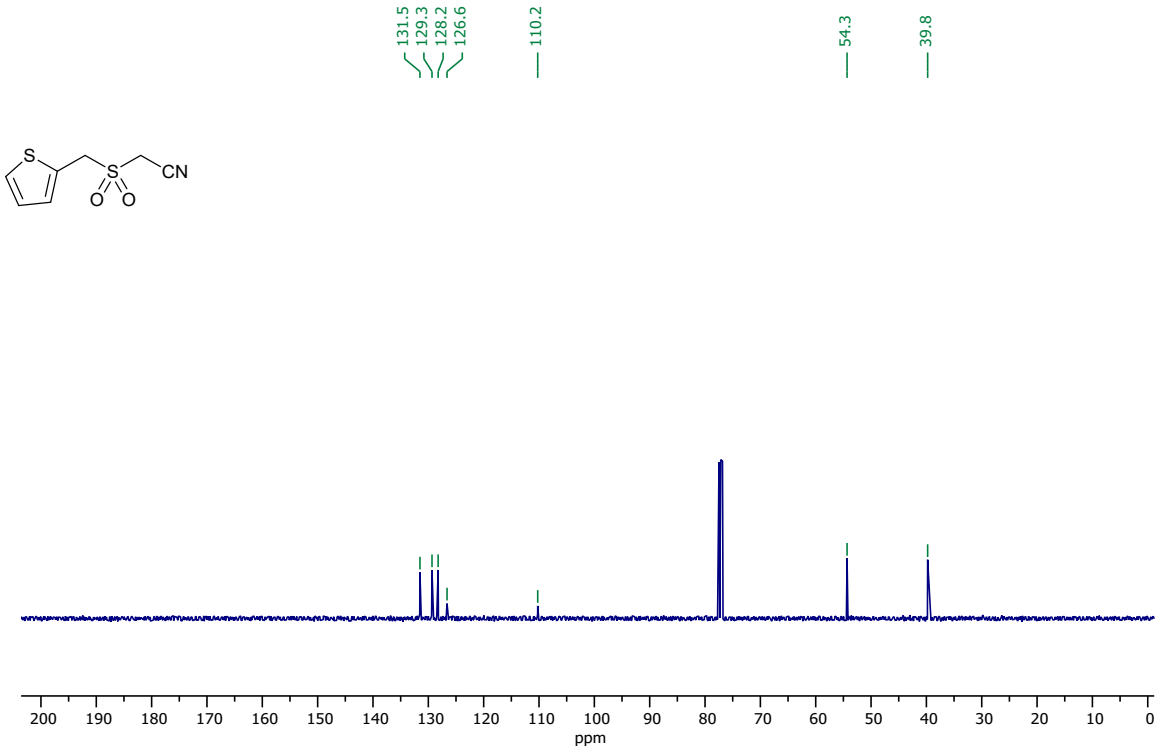


Figure 24. ^{13}C NMR spectra of compound **1l**

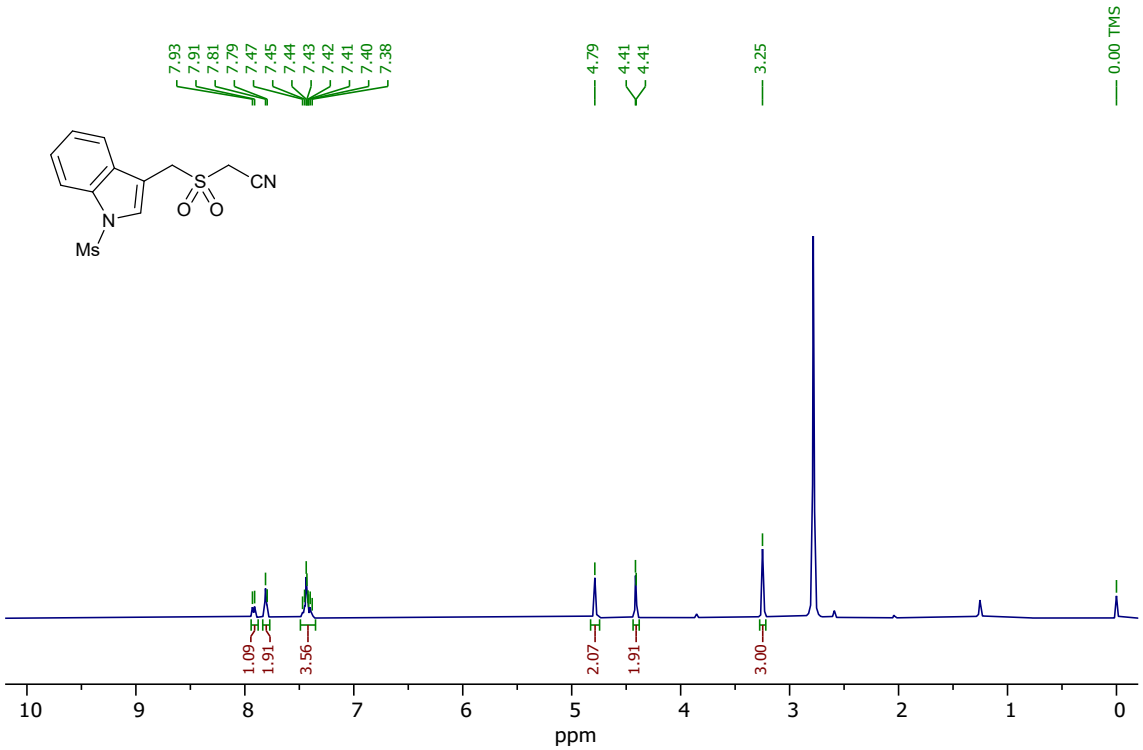


Figure 25. ^{1}H NMR spectra of compound **1m**

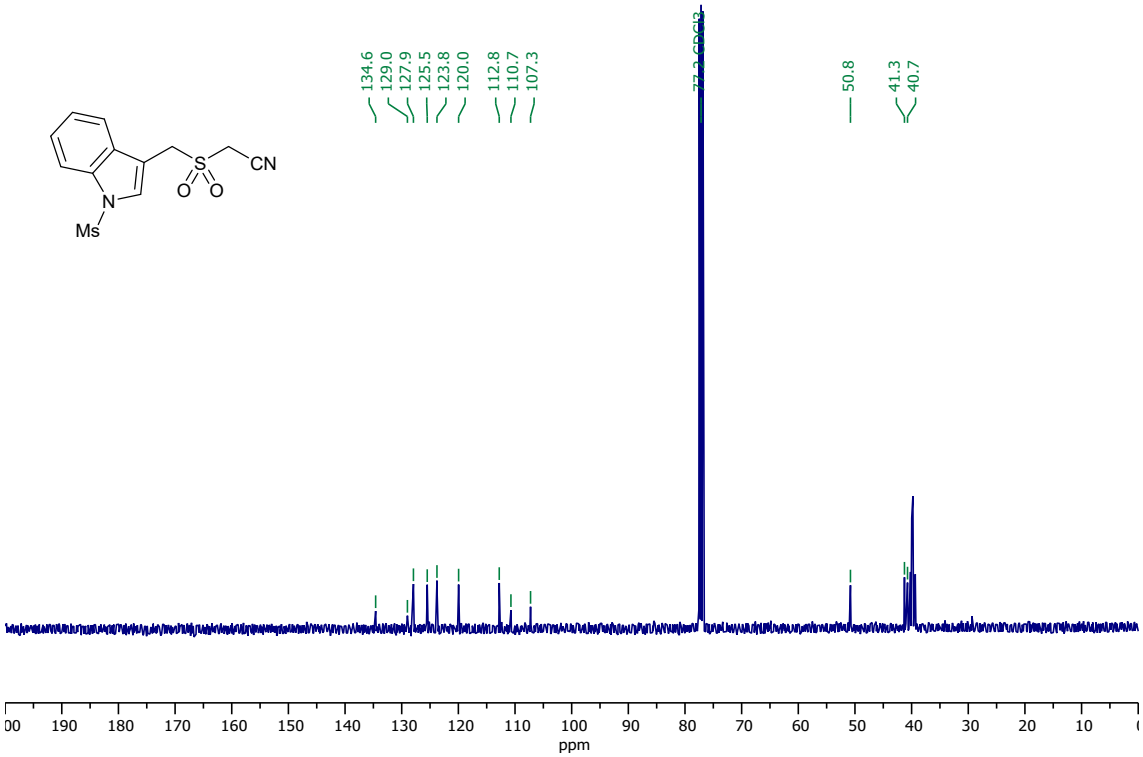


Figure 26. ^{13}C NMR spectra of compound **1m**

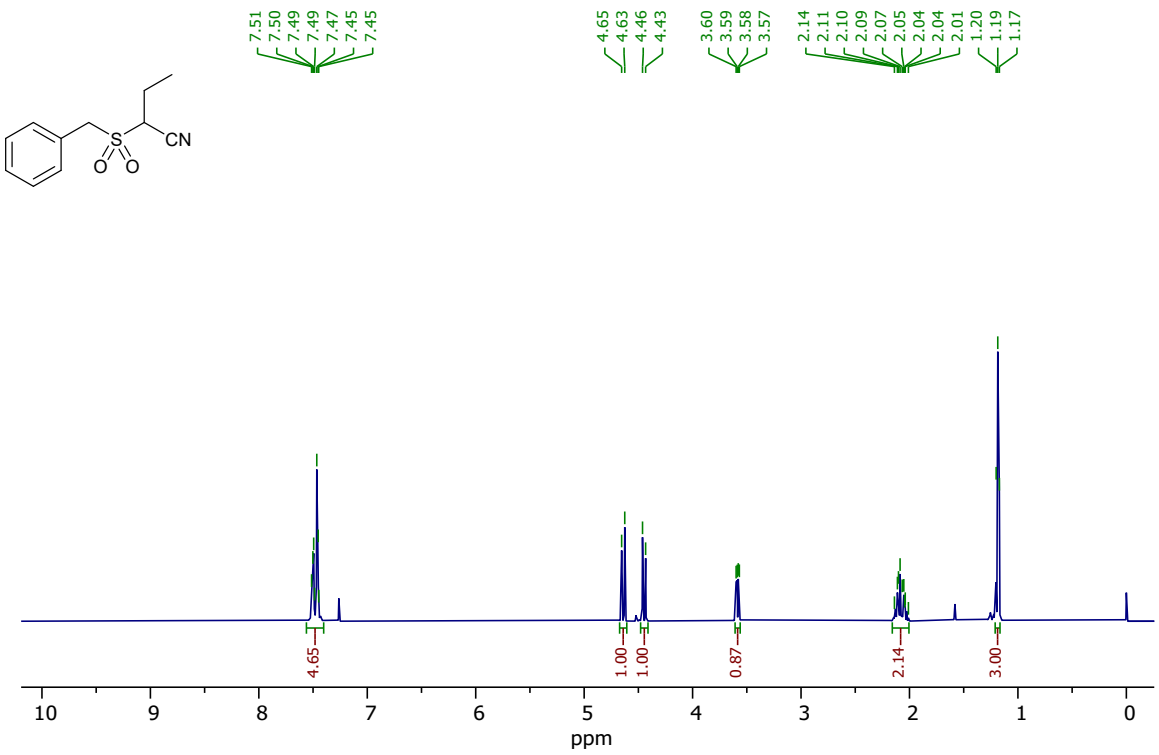


Figure 27. ^{1}H NMR spectra of compound **1n**

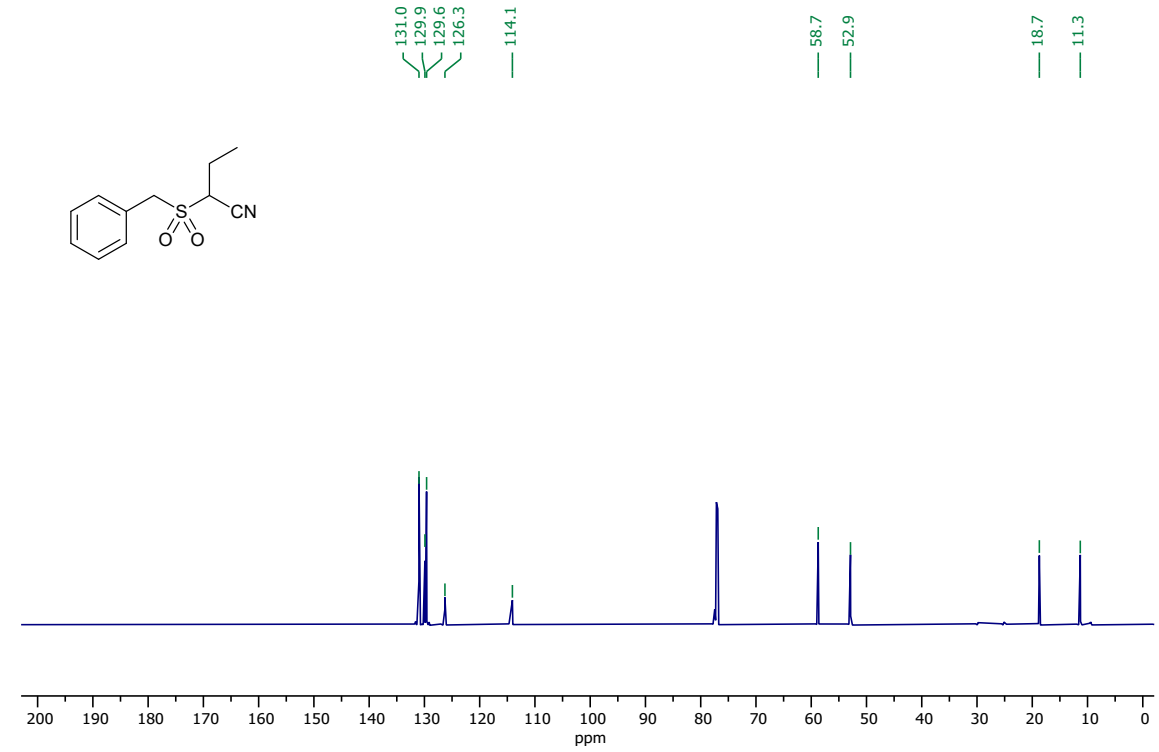


Figure 28. ^{13}C NMR spectra of compound **1n**

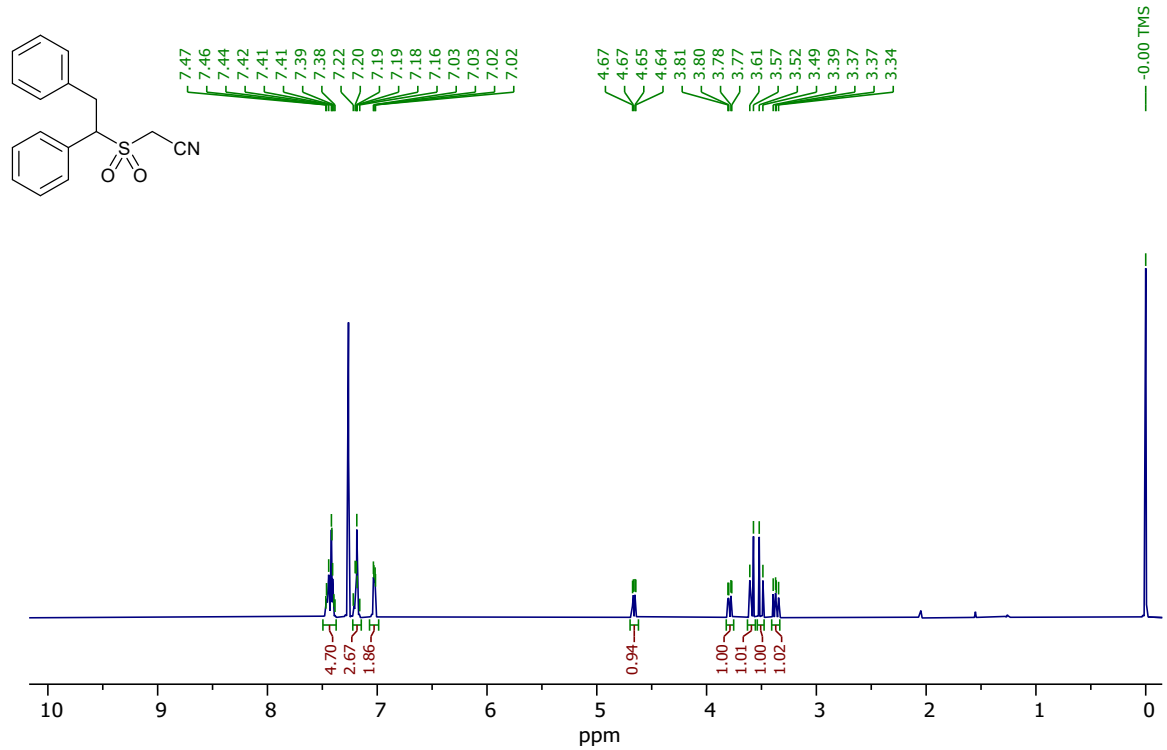


Figure 29. ^{1}H NMR spectra of compound **1o**

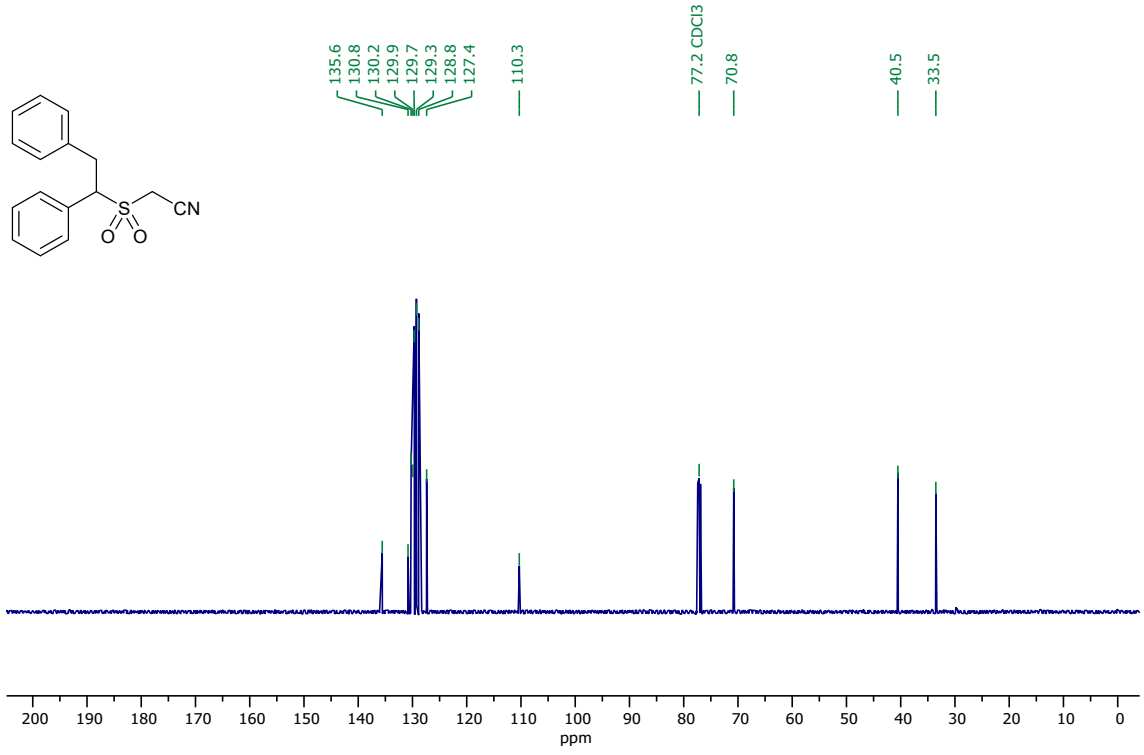


Figure 30. ^{13}C NMR spectra of compound **1o**

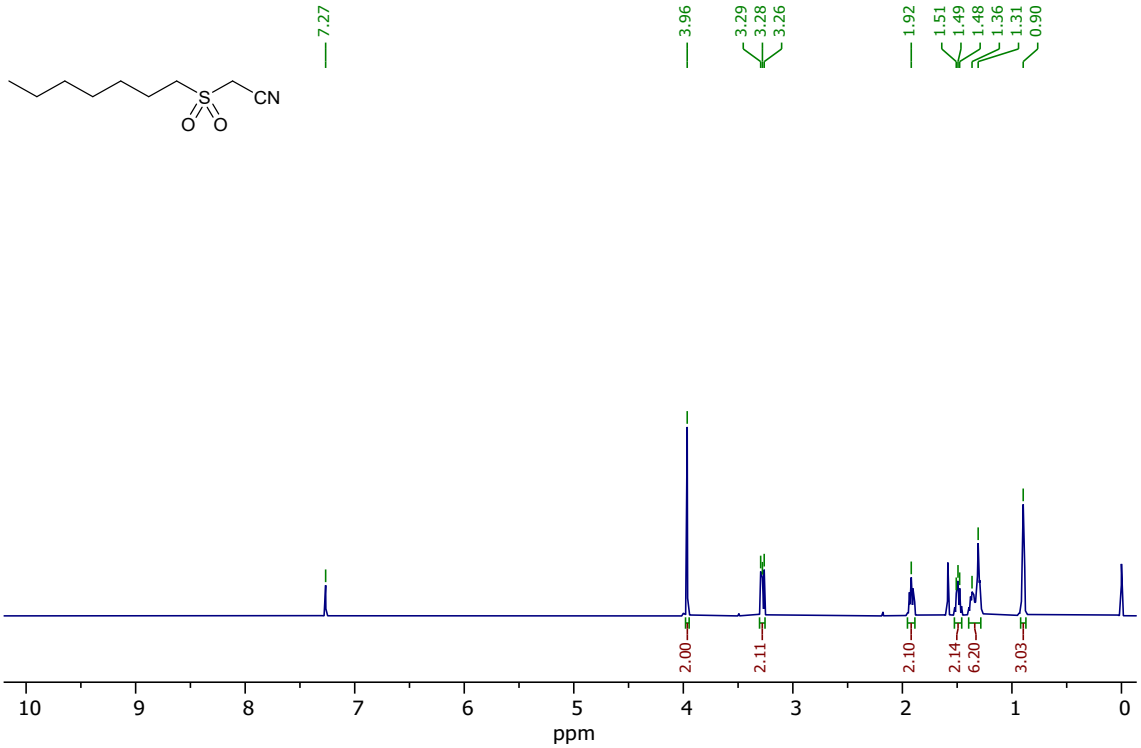


Figure 31. ^{1}H NMR spectra of compound **1p**

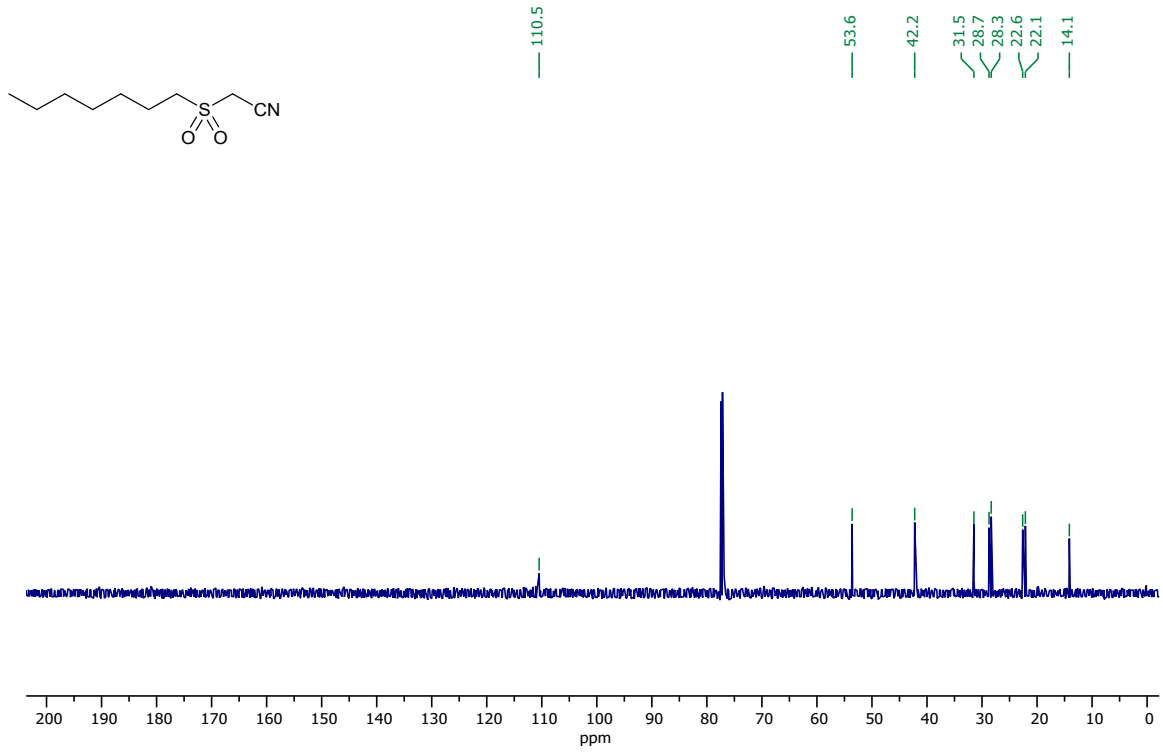


Figure 32. ^{13}C NMR spectra of compound **1p**

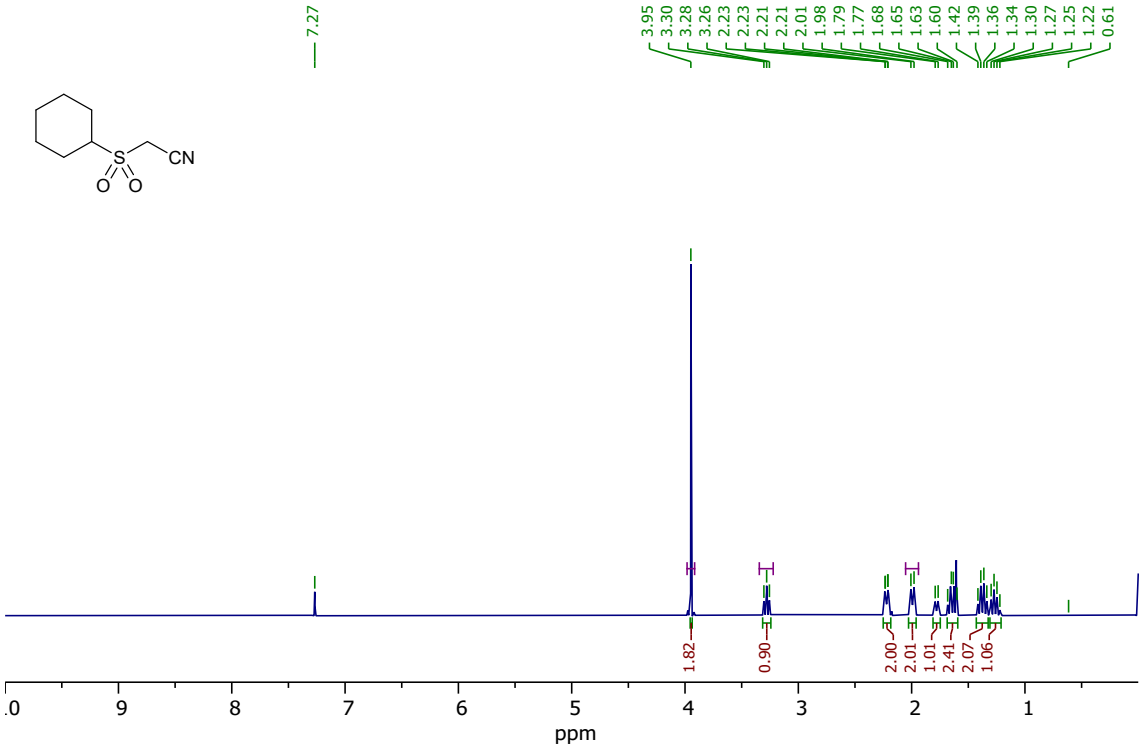


Figure 33. ^{1}H NMR spectra of compound **1q**

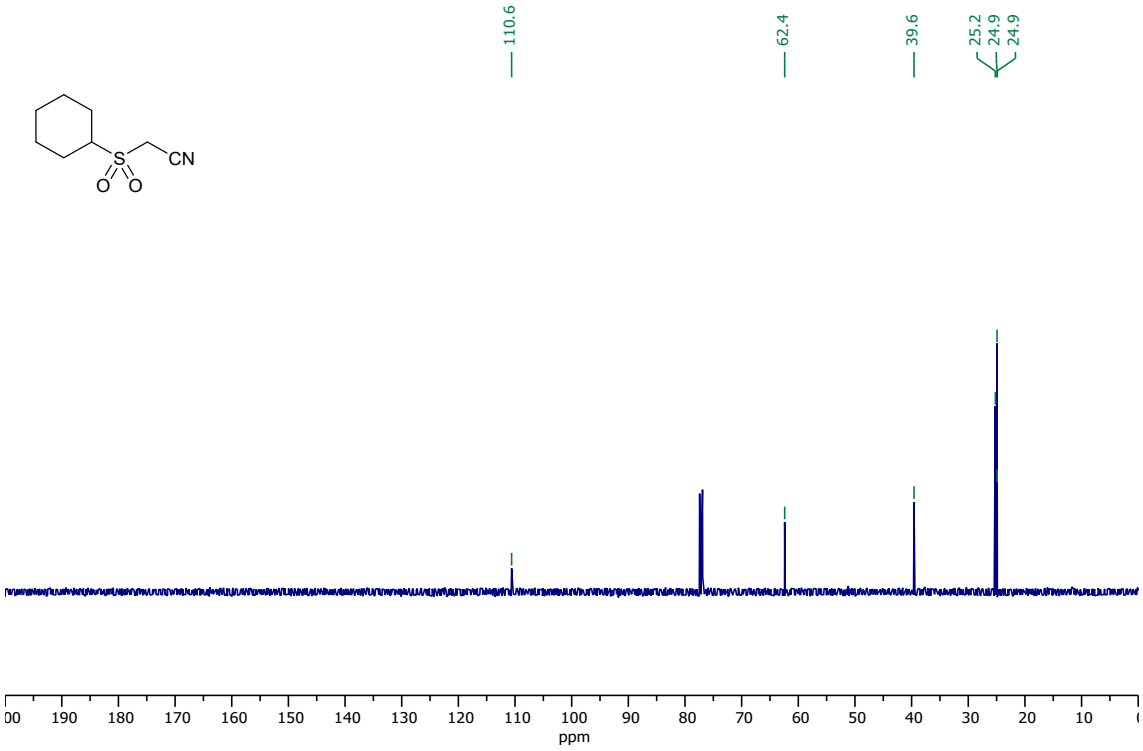


Figure 34. ^{13}C NMR spectra of compound **1q**

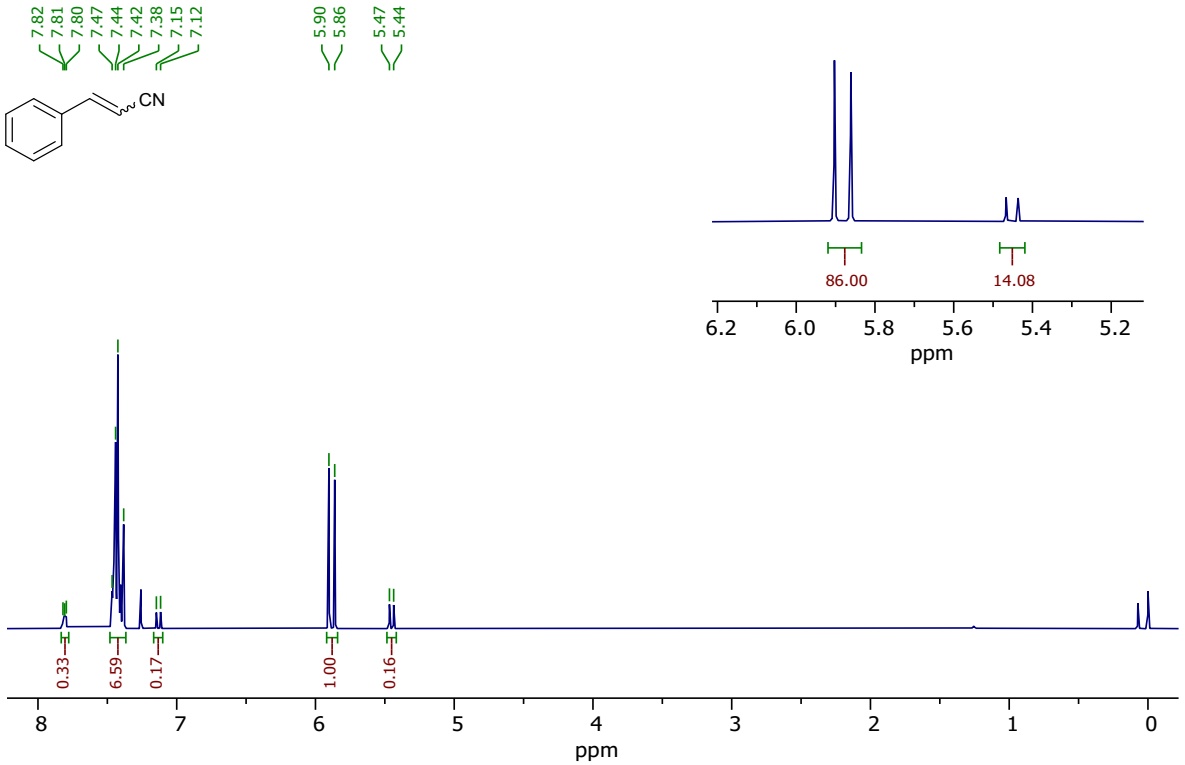


Figure 35. ^{1}H NMR spectra of compound **2a**

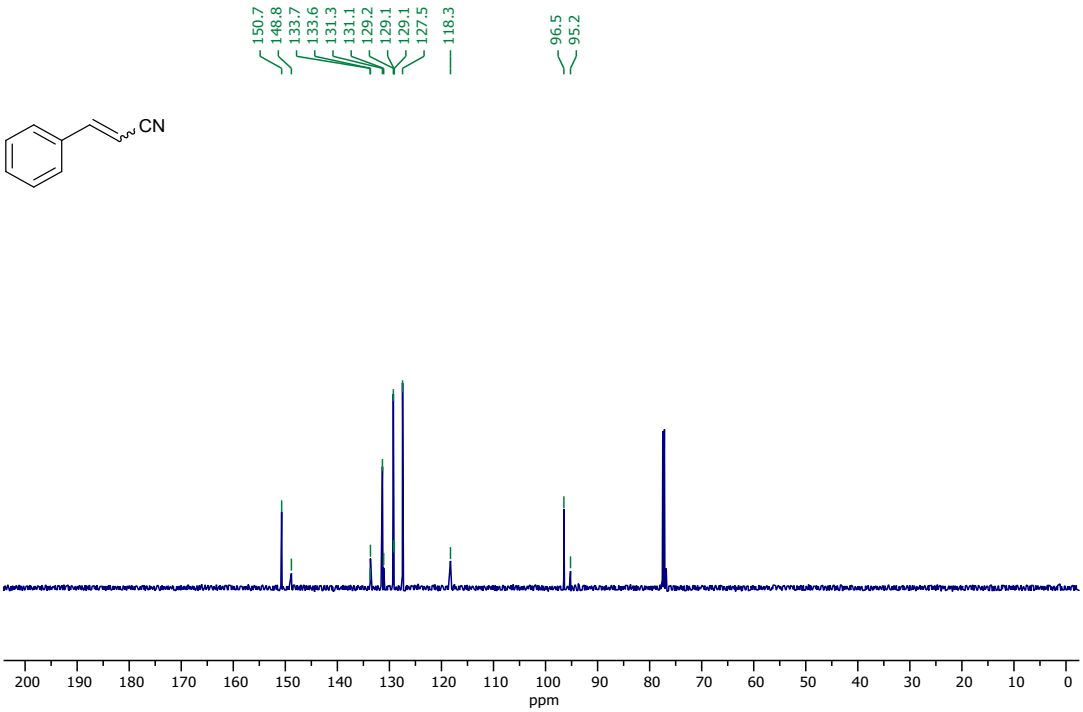


Figure 36. ^{13}C NMR spectra of compound **2a**

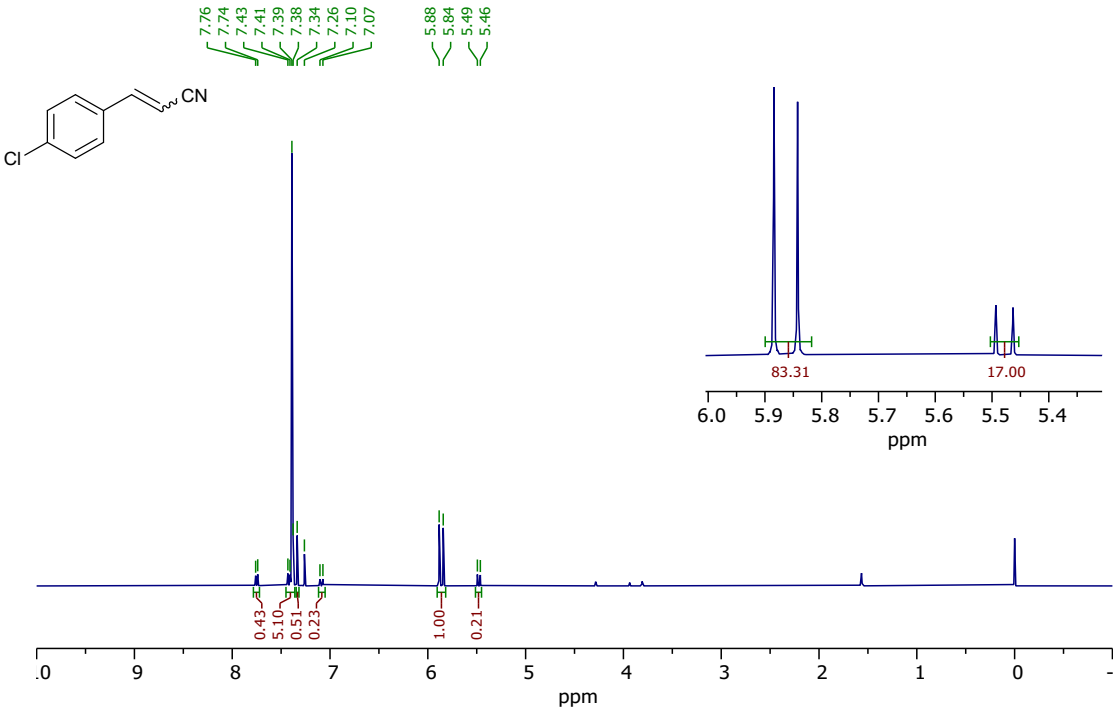


Figure 37. ^{1}H NMR spectra of compound **2b**

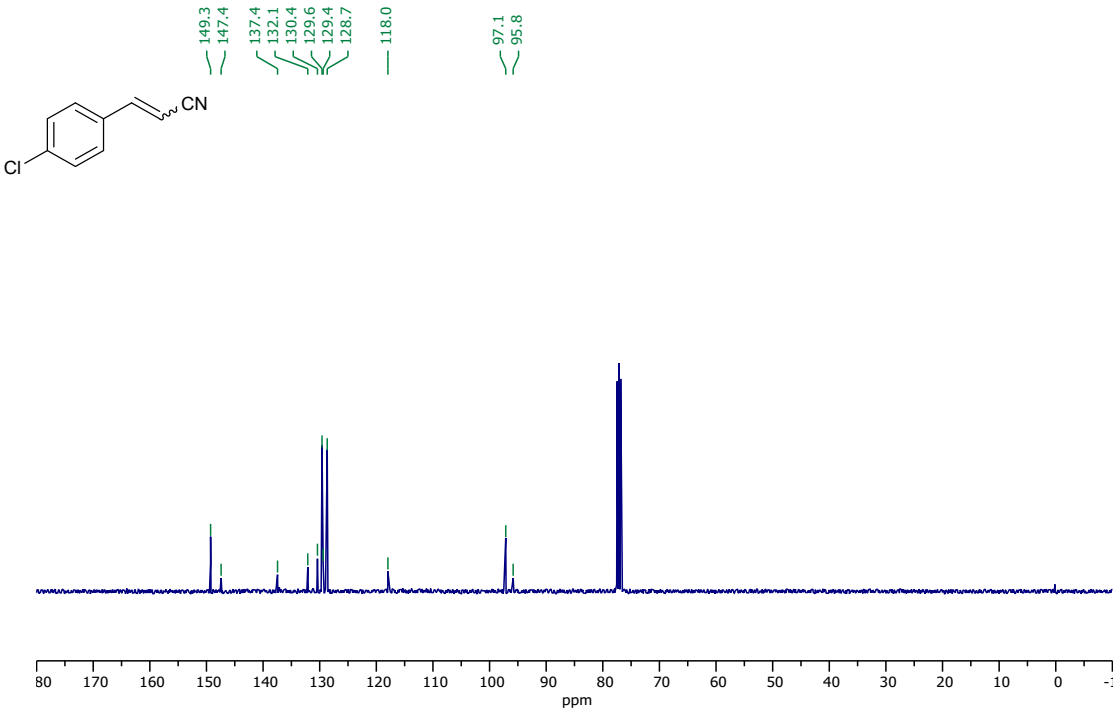


Figure 38. ^{13}C NMR spectra of compound **2b**

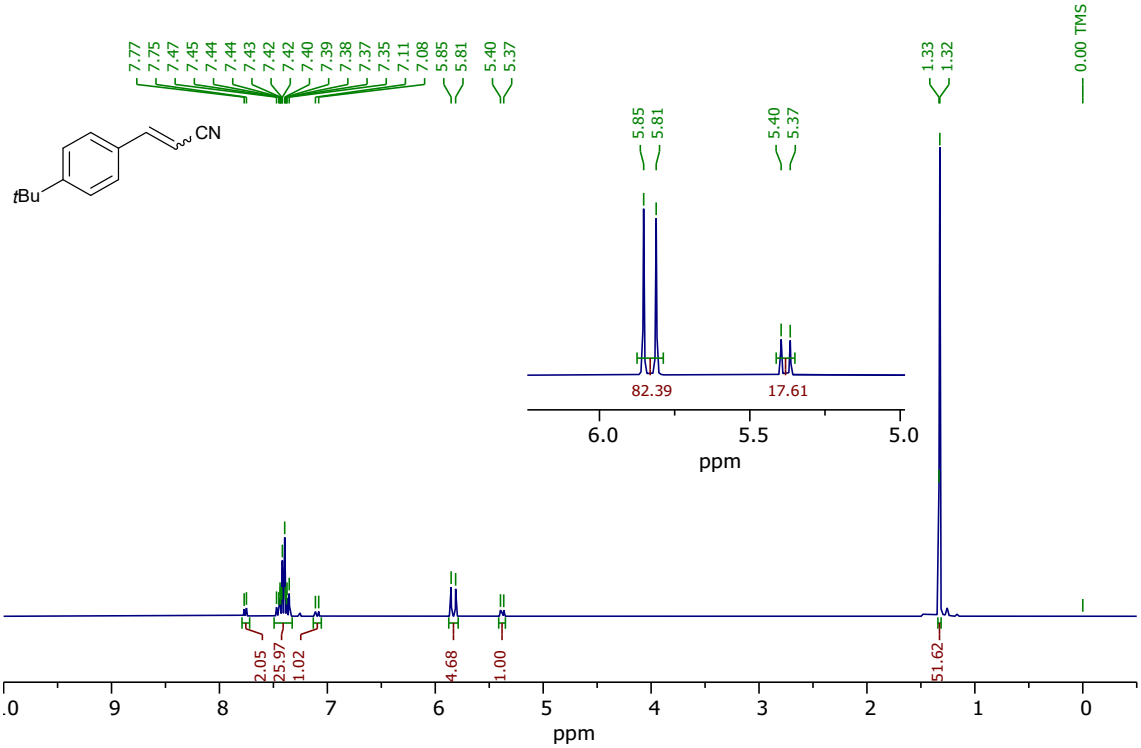


Figure 39. ^{1}H NMR spectra of compound **2c**

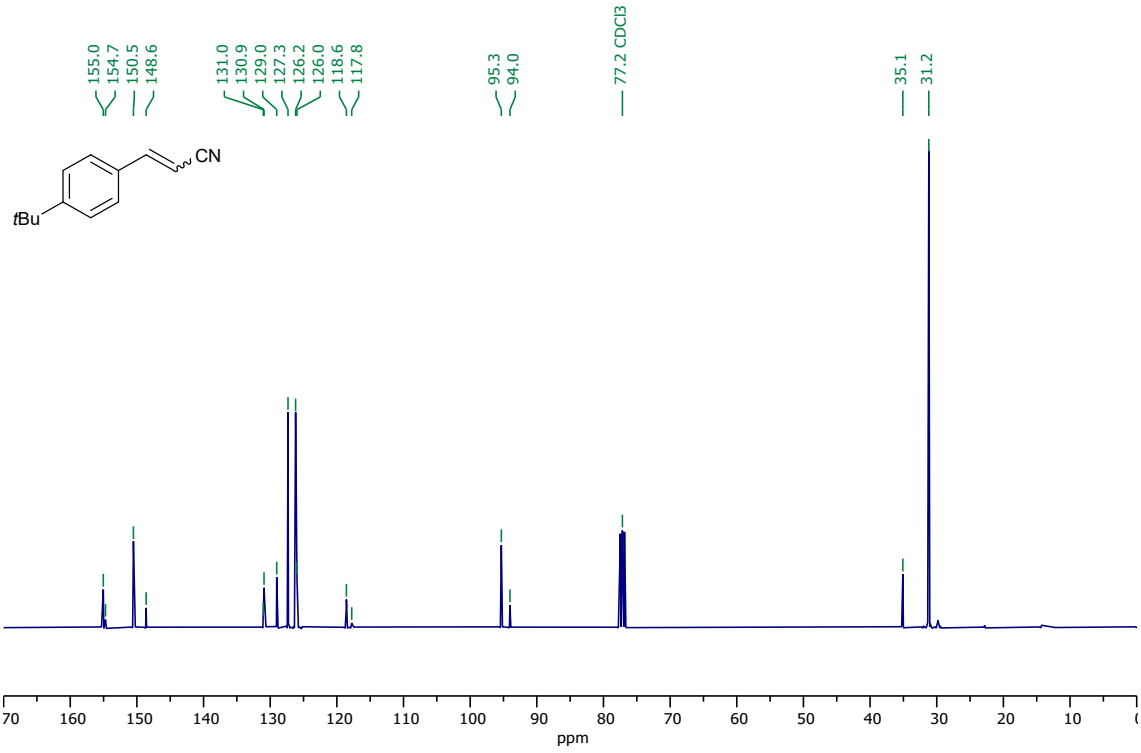


Figure 40. ^{13}C NMR spectra of compound **2c**

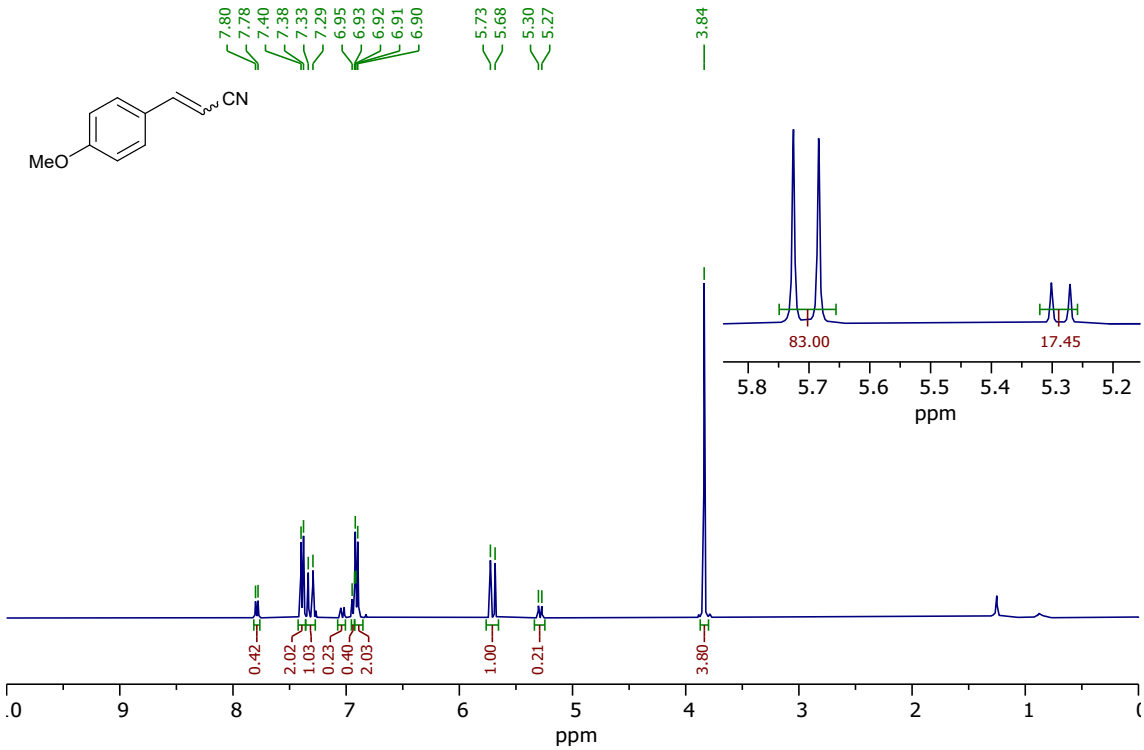


Figure 41. ^{1}H NMR spectra of compound **2d**

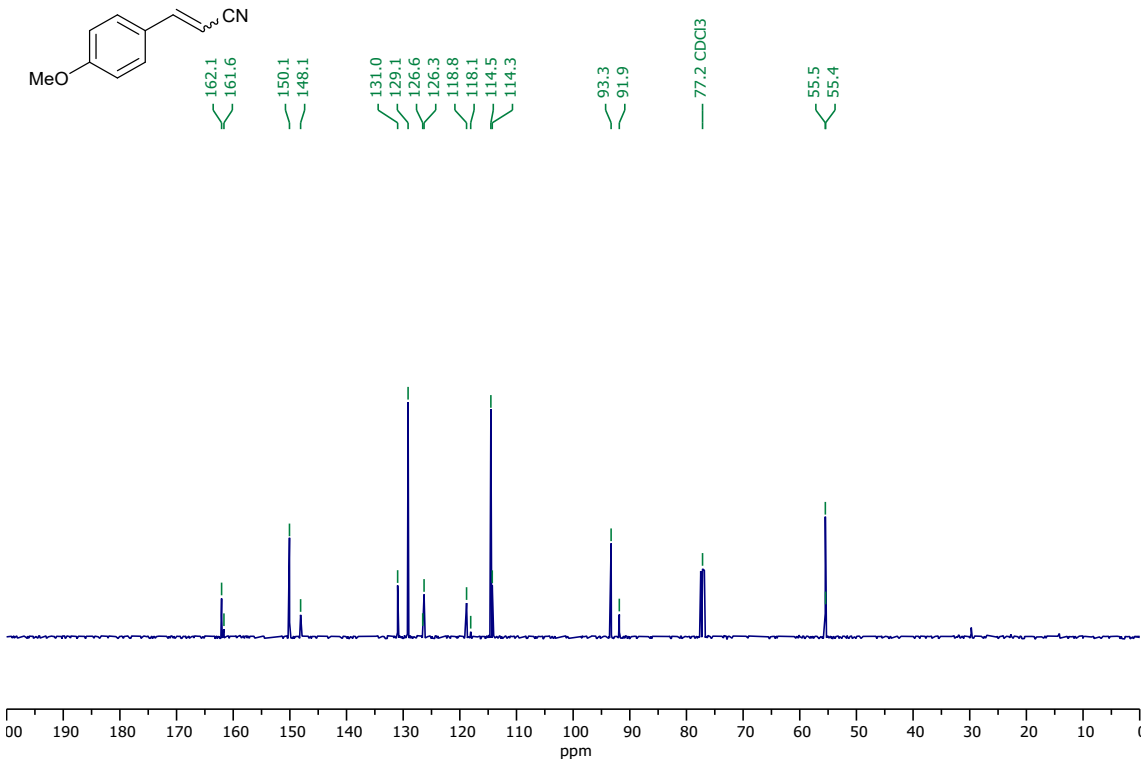


Figure 42. ^{13}C NMR spectra of compound **2d**

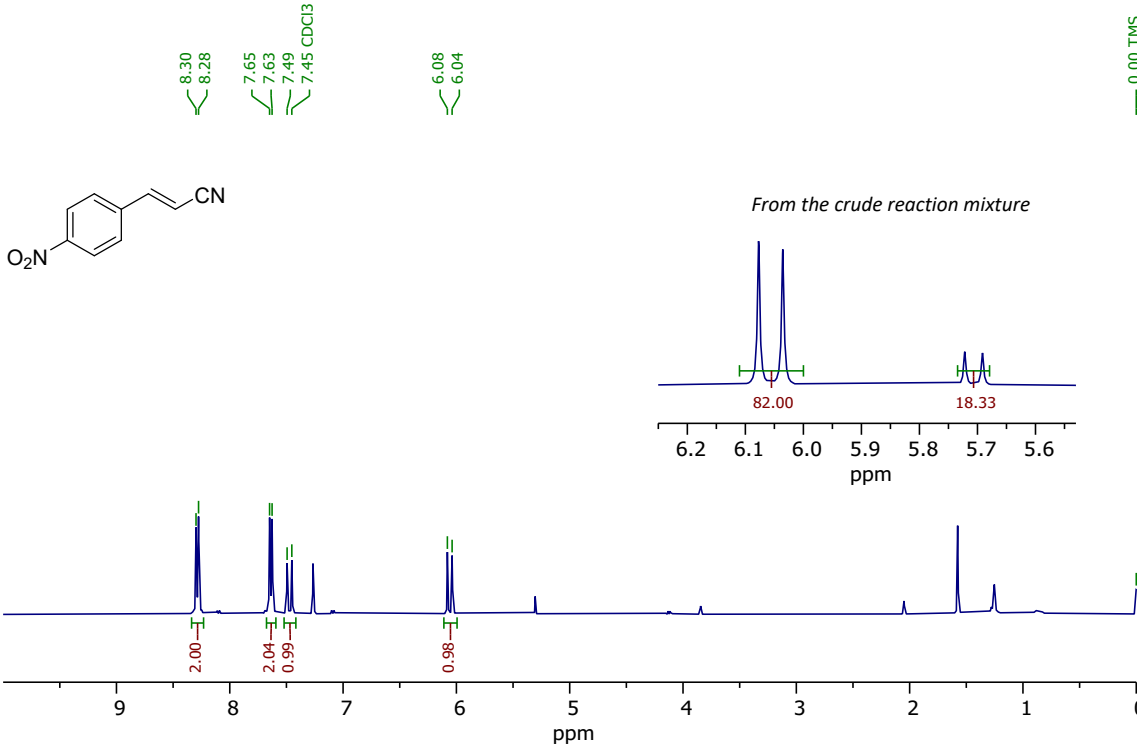


Figure 43. ^{1}H NMR spectra of compound ***E*-2e**

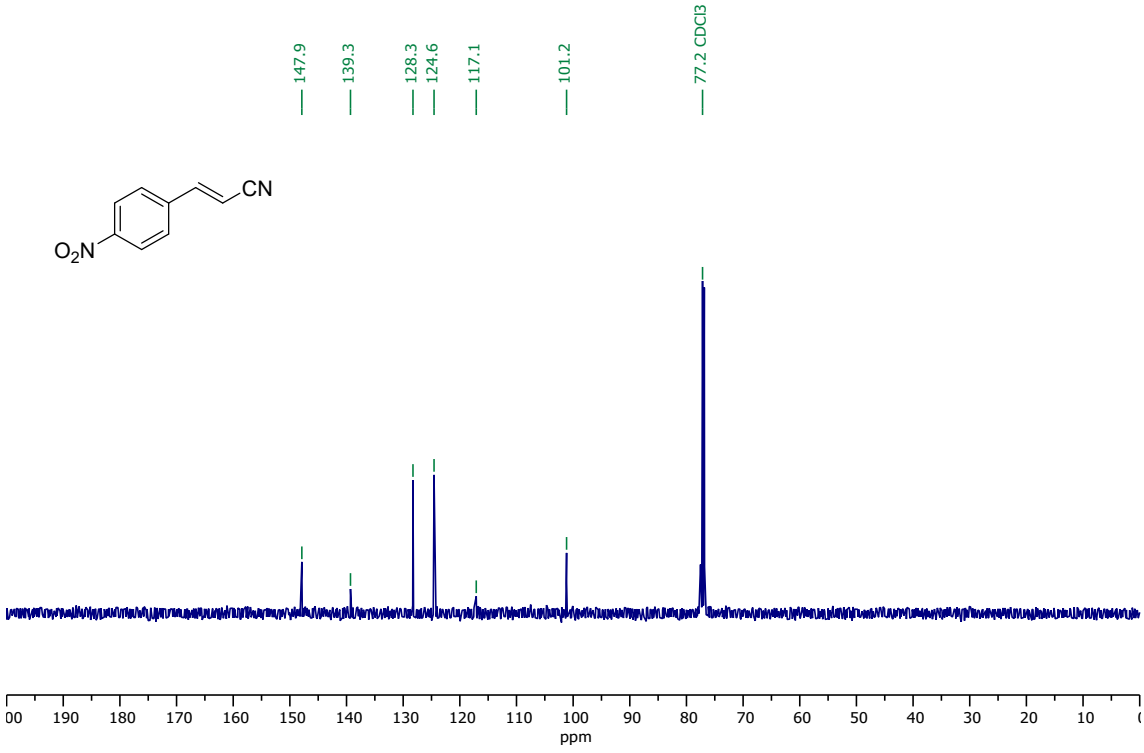


Figure 44. ^{13}C NMR spectra of compound ***E*-2e**

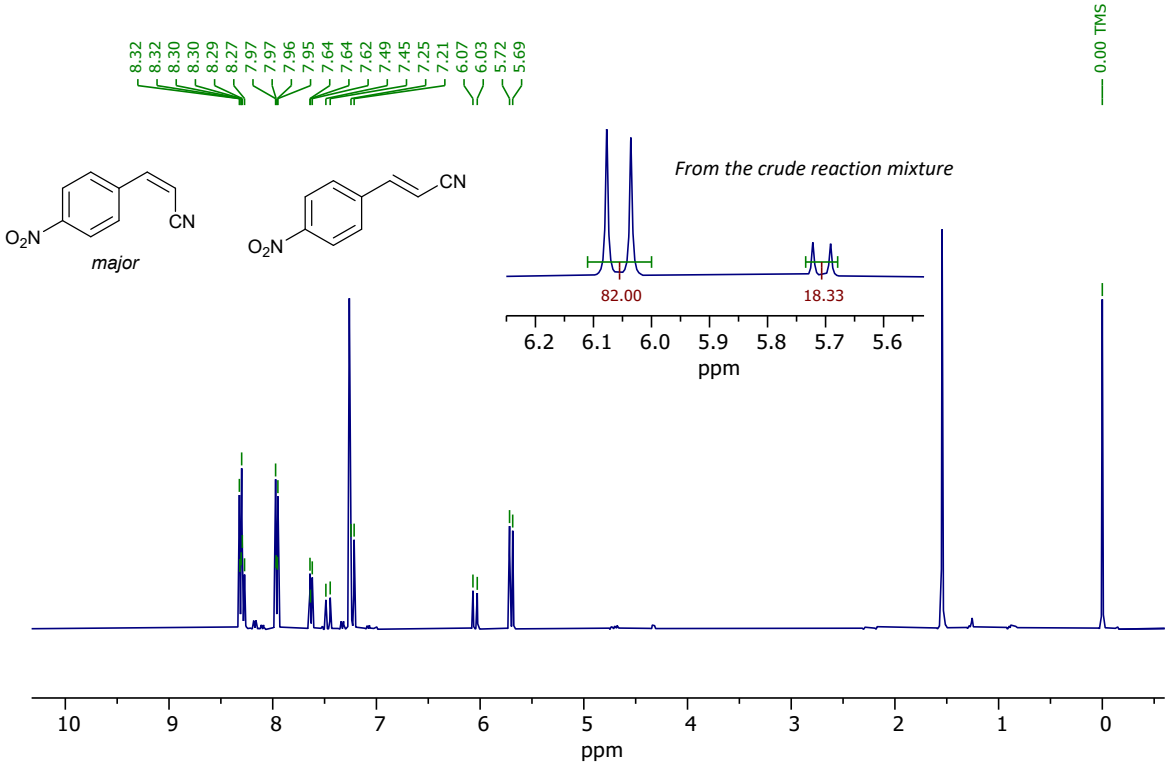


Figure 45. ^{1}H NMR spectra of compound ***Z*-2e** (major) and ***E*-2e**

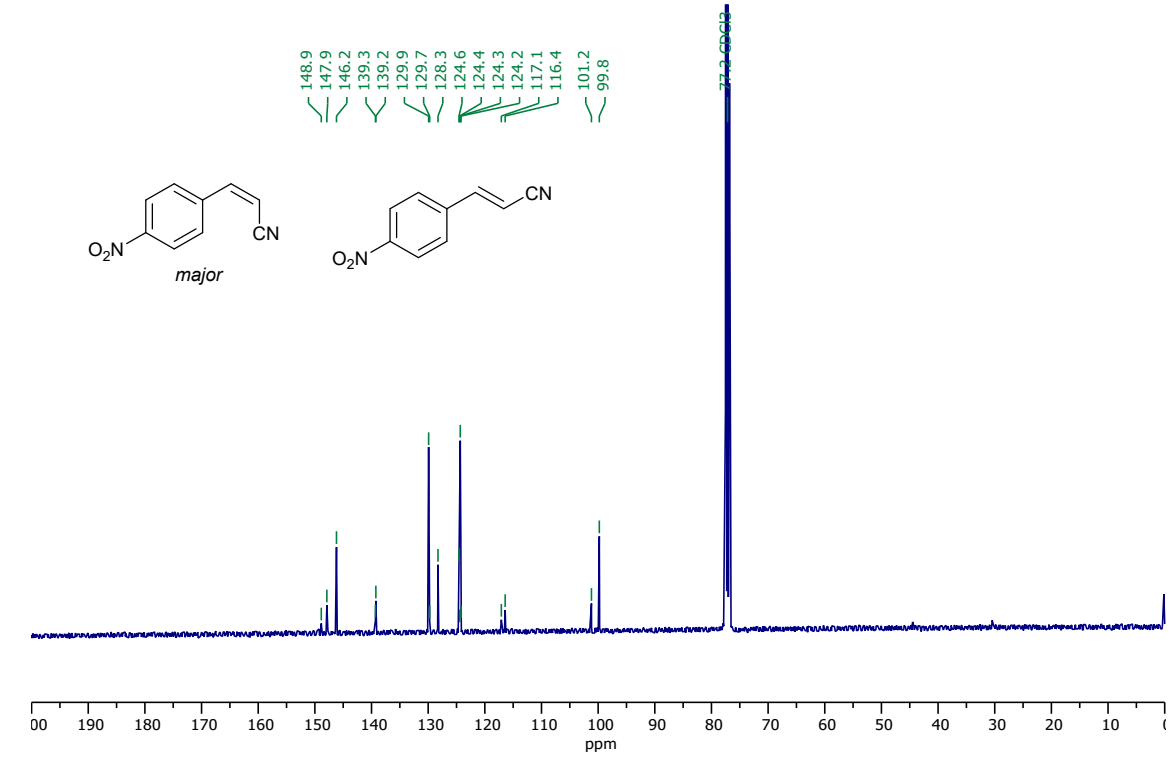


Figure 46. ^{13}C NMR spectra of compound ***Z*-2e** (major) and ***E*-2e.**

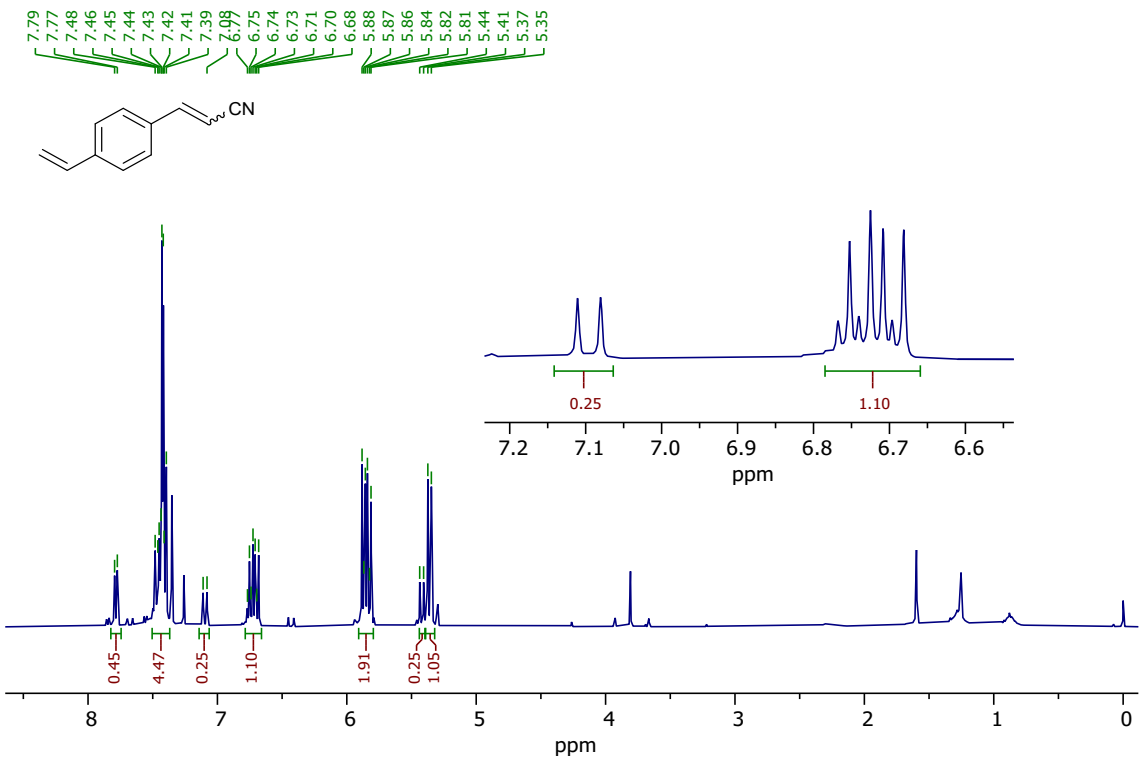


Figure 47. ^{1}H NMR spectra of compound **2f**

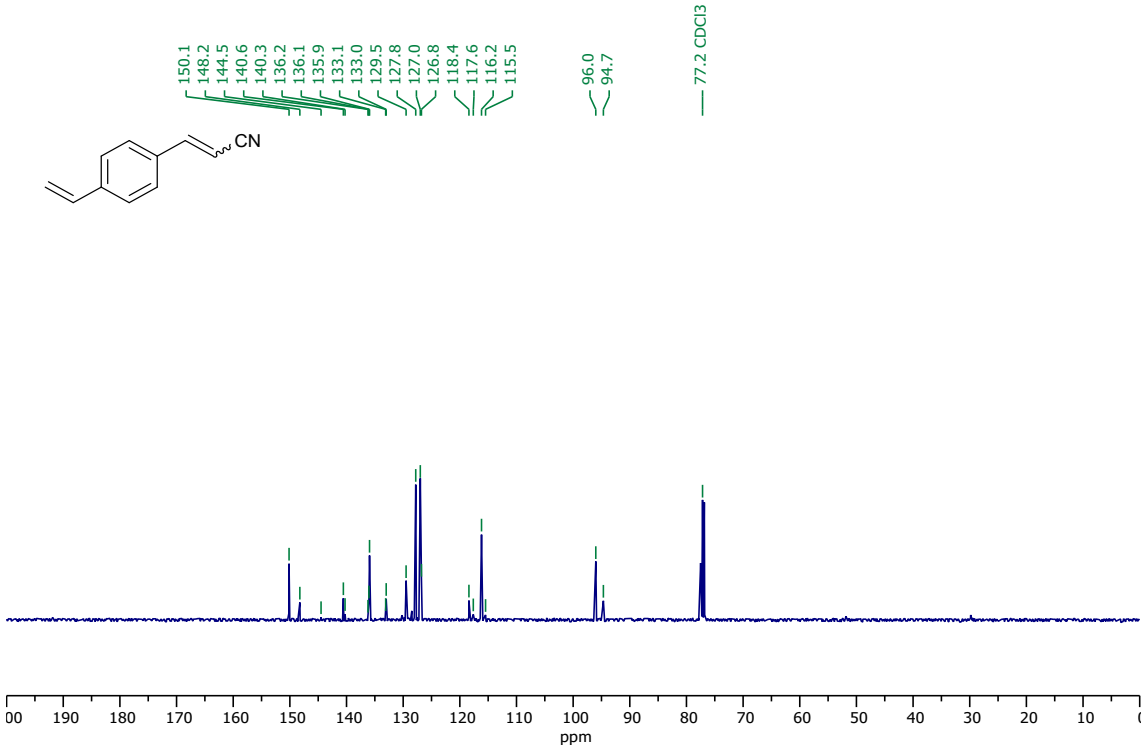


Figure 48. ^{13}C NMR spectra of compound **2f**

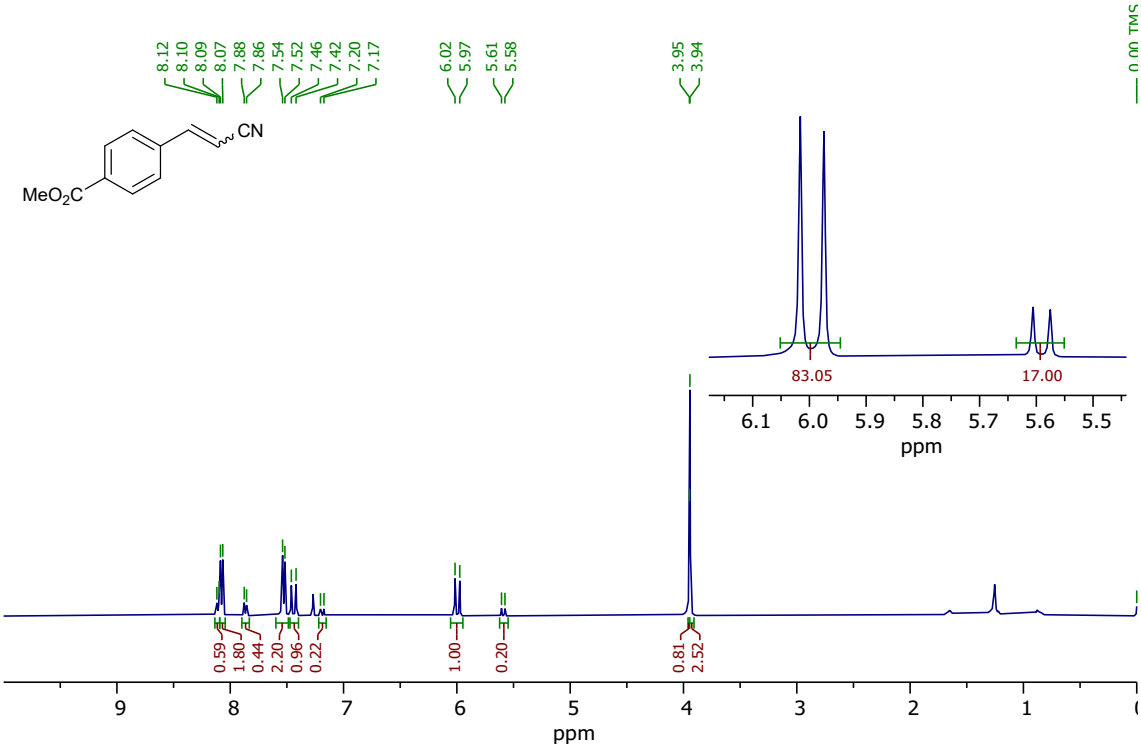


Figure 49. ^{1}H NMR spectra of compound **2g**

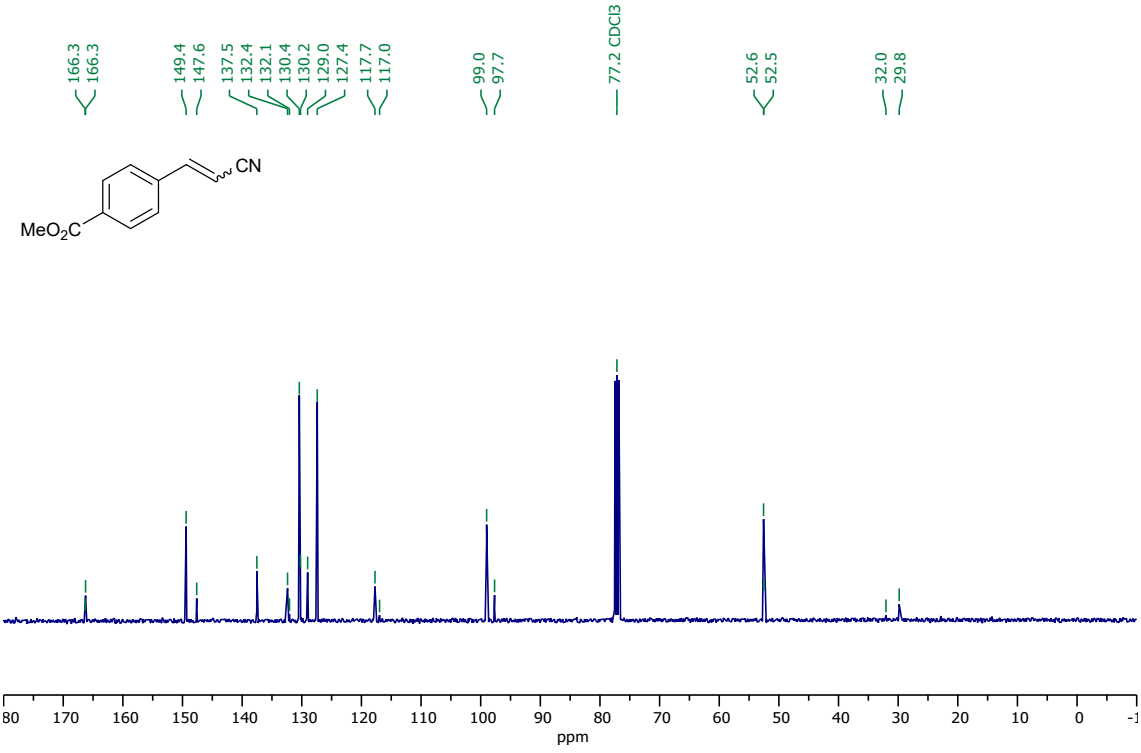


Figure 50. ^{13}C NMR spectra of compound **2g**

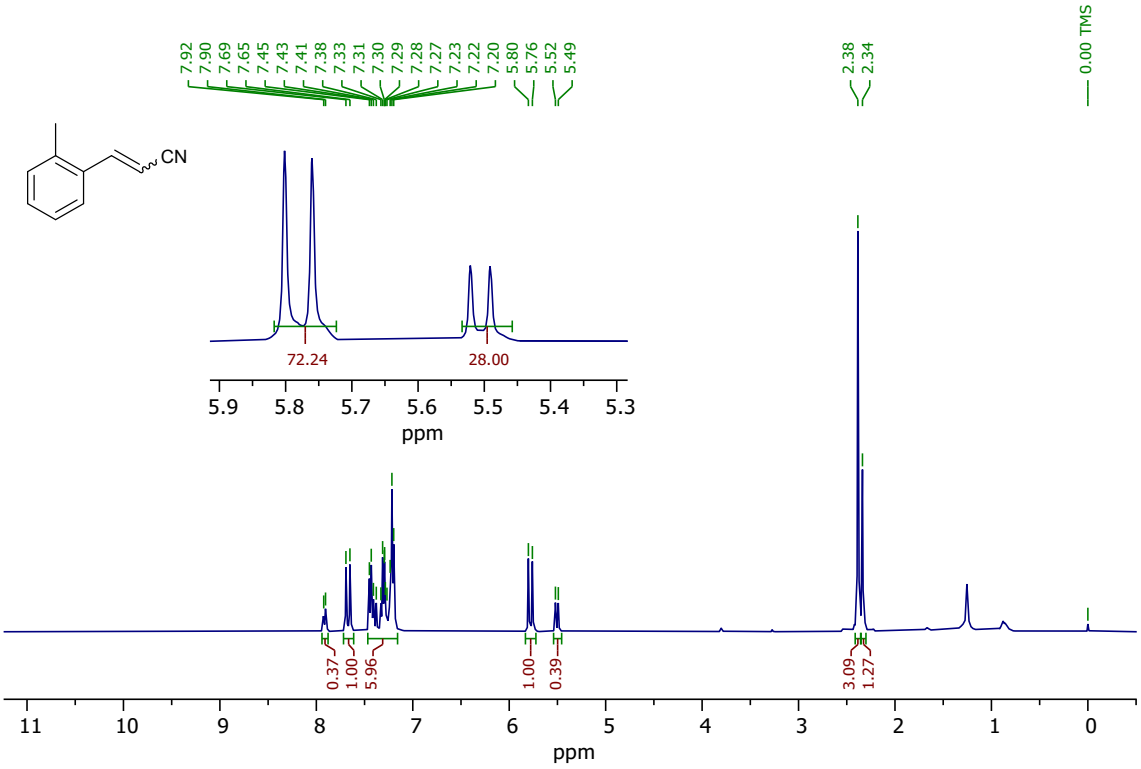


Figure 51. ^{1}H NMR spectra of compound **2h**

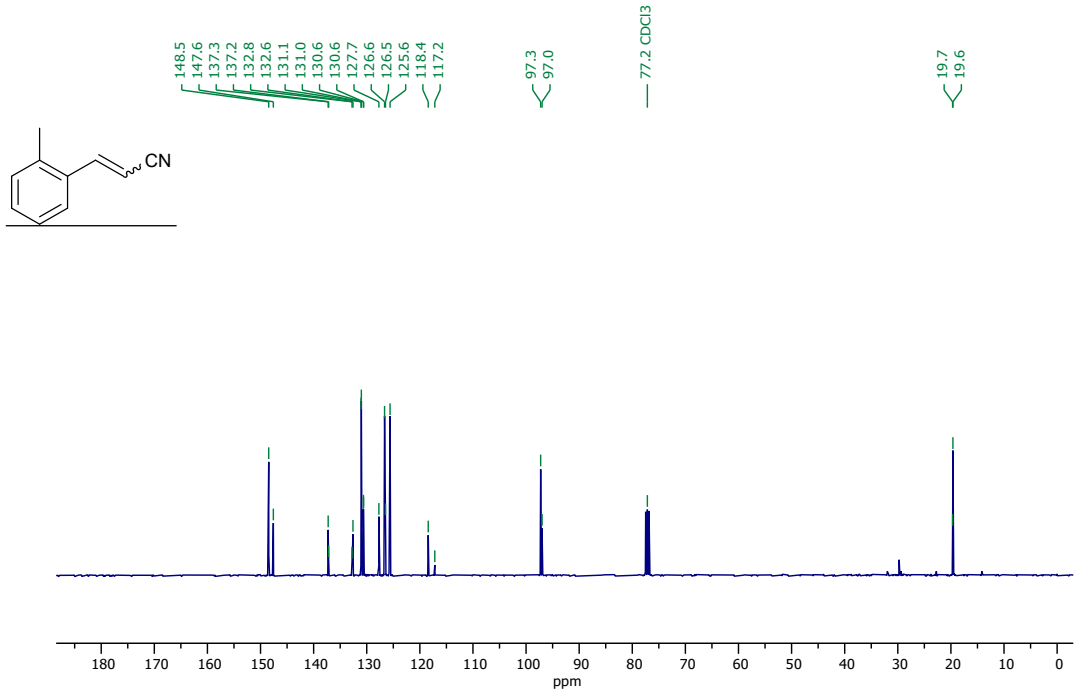


Figure 52. ^{13}C NMR spectra of compound **2h**

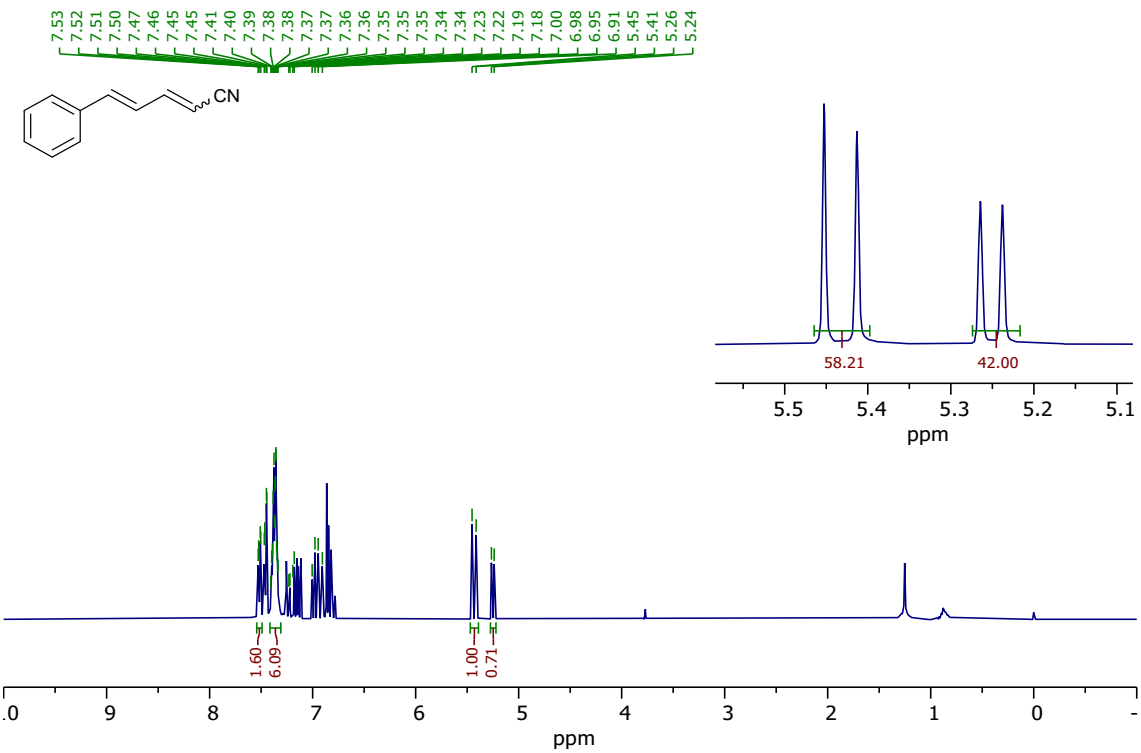


Figure 53. ^{1}H NMR spectra of compound **2i**

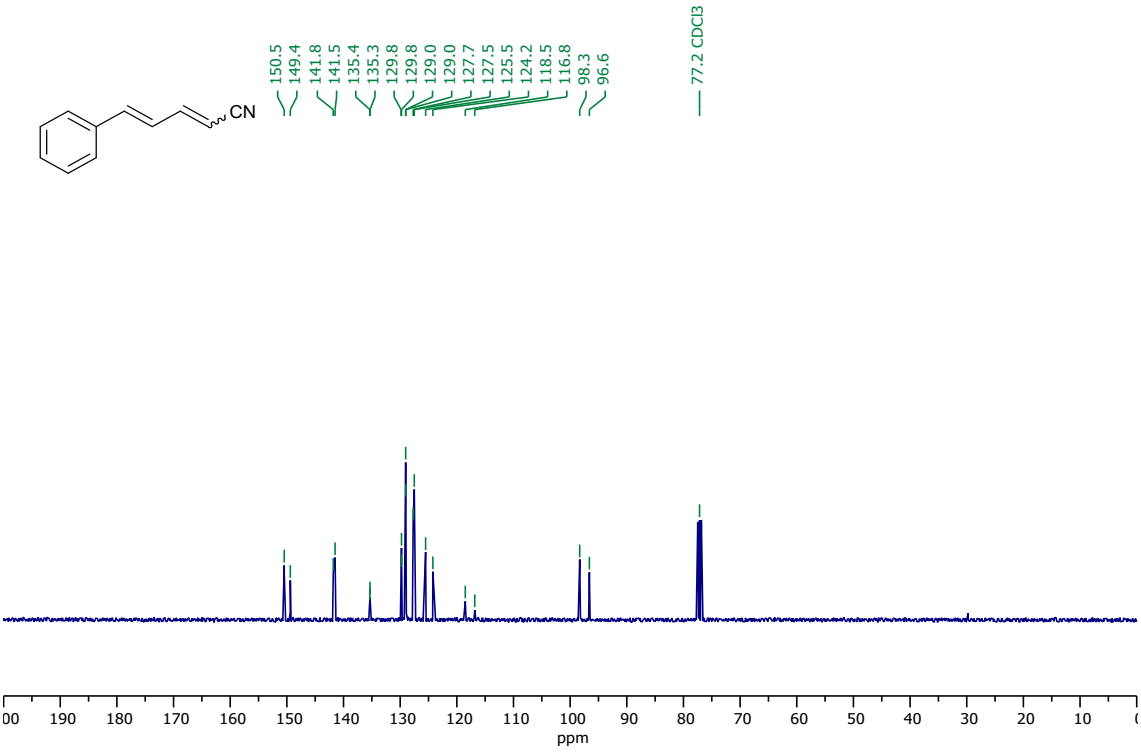


Figure 54. ^{13}C NMR spectra of compound **2i**

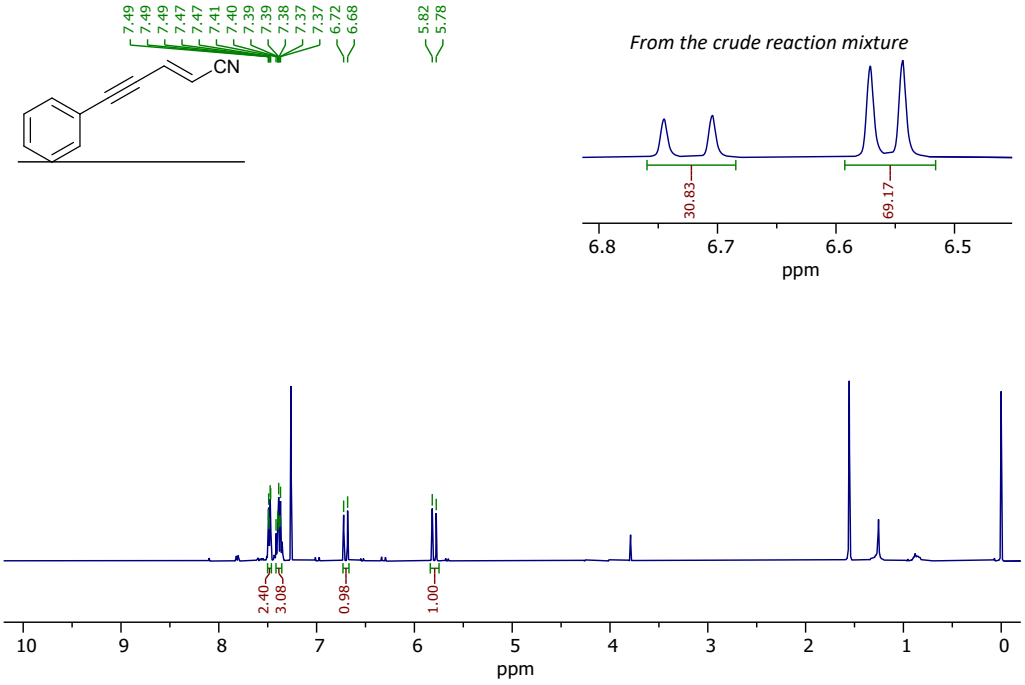


Figure 55. ^{1}H NMR spectra of compound ***E*-2j**

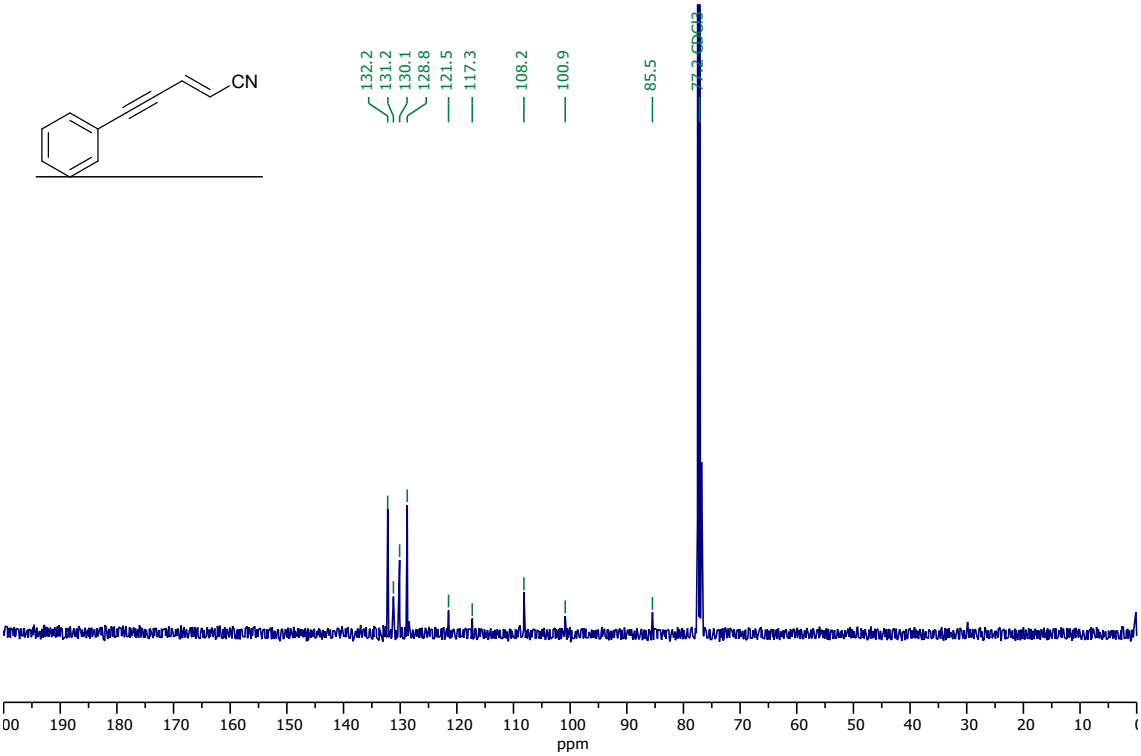


Figure 56. ^{13}C NMR spectra of compound ***E*-2j**

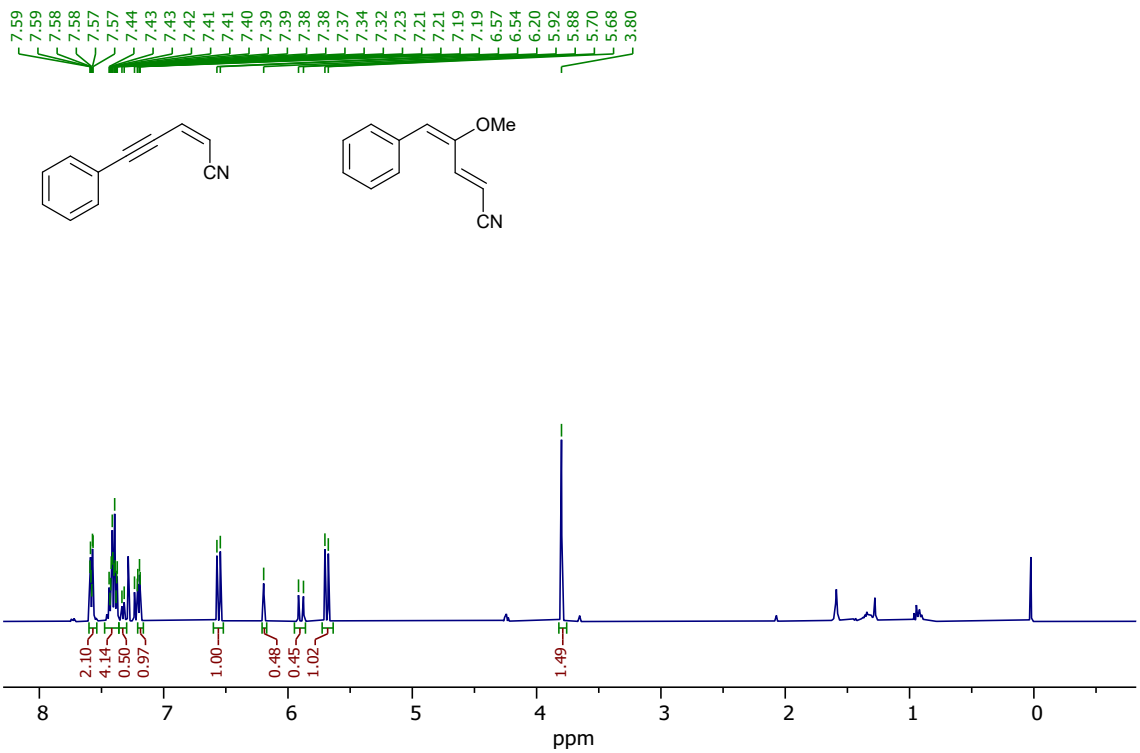


Figure 57. ^{1}H NMR spectra of compound ***Z*-2j** and *(2E,4E)*-4-methoxy-5-phenylpenta-2,4-dienenitrile

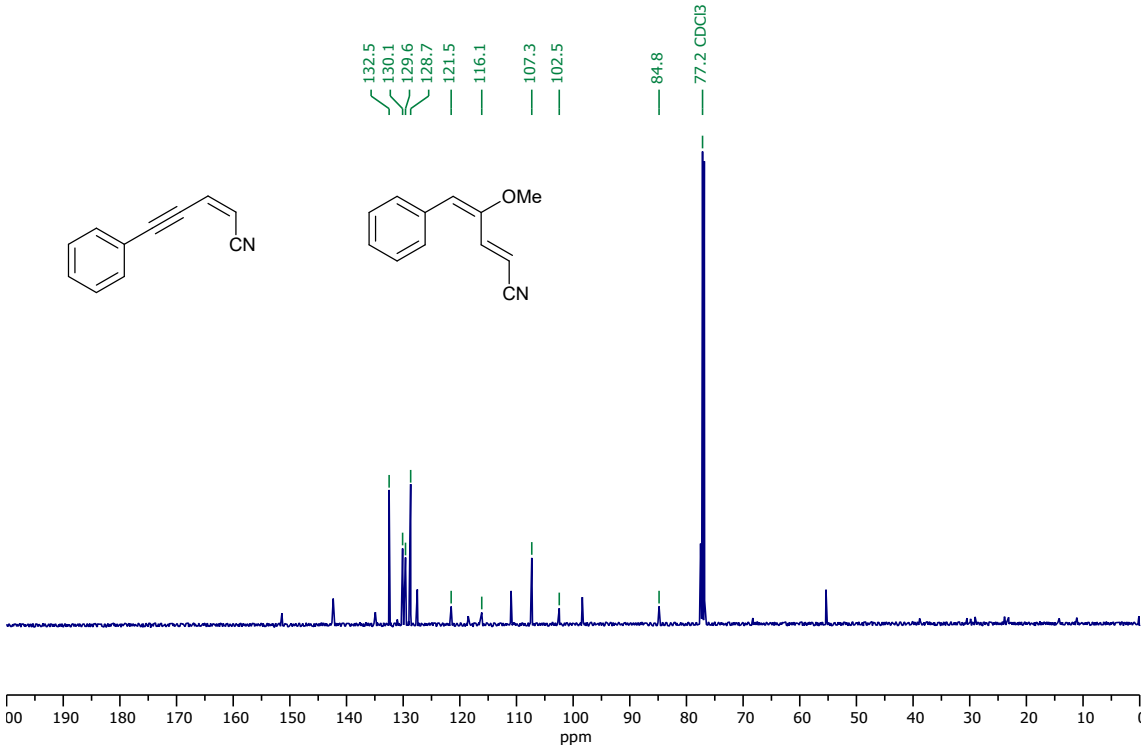


Figure 58. ^{13}C NMR spectra of compound ***Z*-2j** and *(2E,4E)*-4-methoxy-5-phenylpenta-2,4-dienenitrile

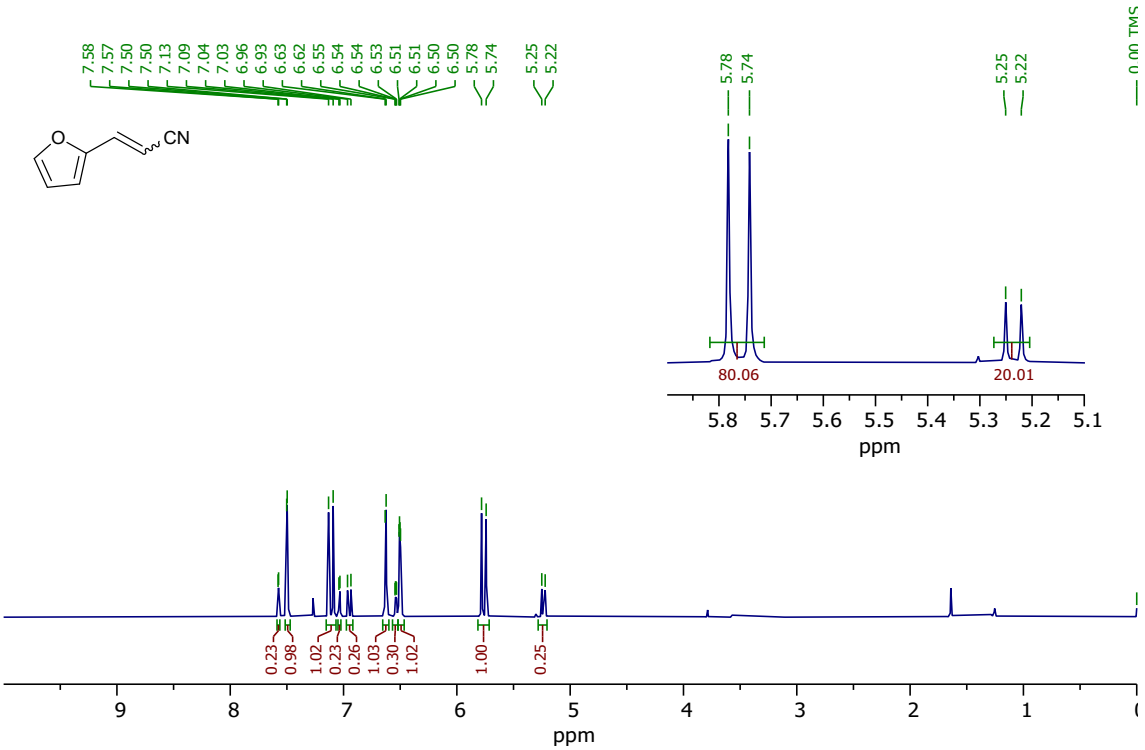


Figure 59. ^{1}H NMR spectra of compound **2k**

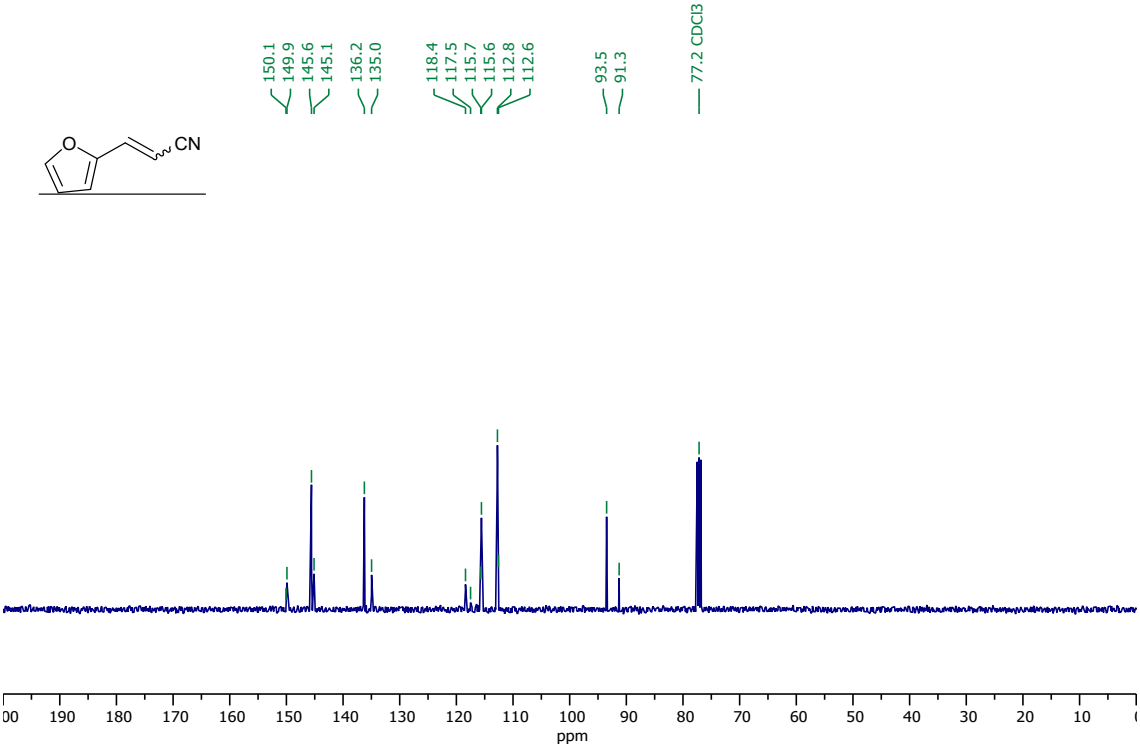


Figure 60. ^{13}C NMR spectra of compound **2k**

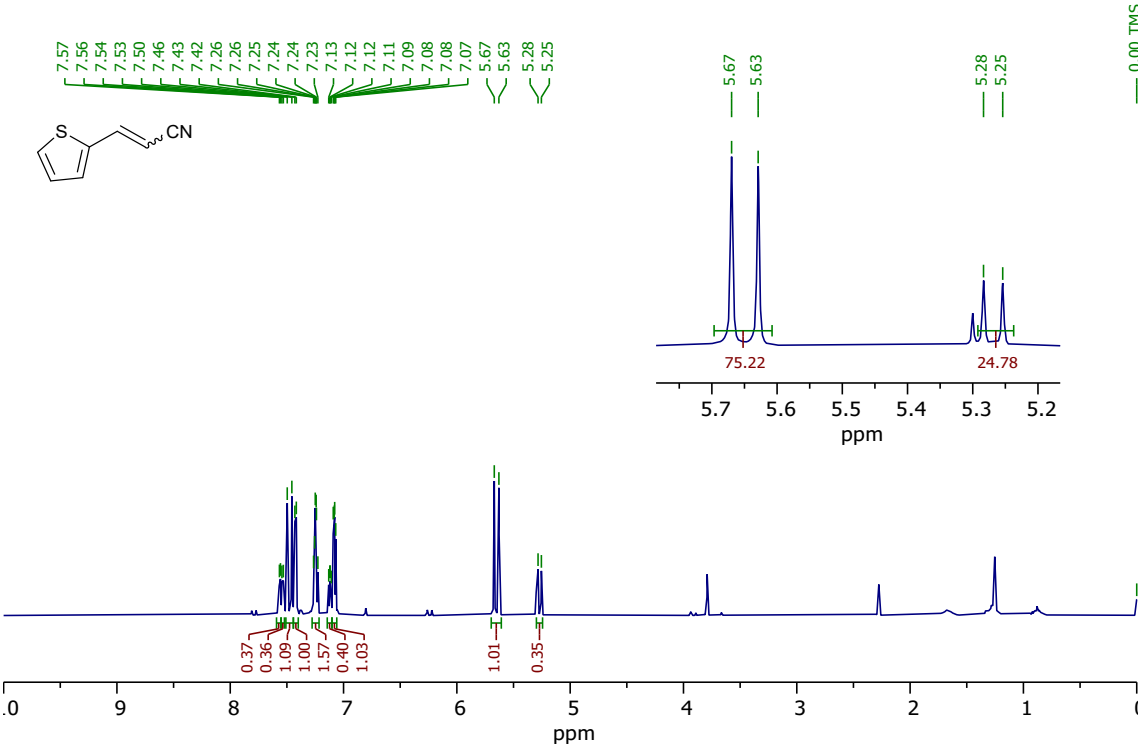


Figure 61. ^{1}H NMR spectra of compound **2l**

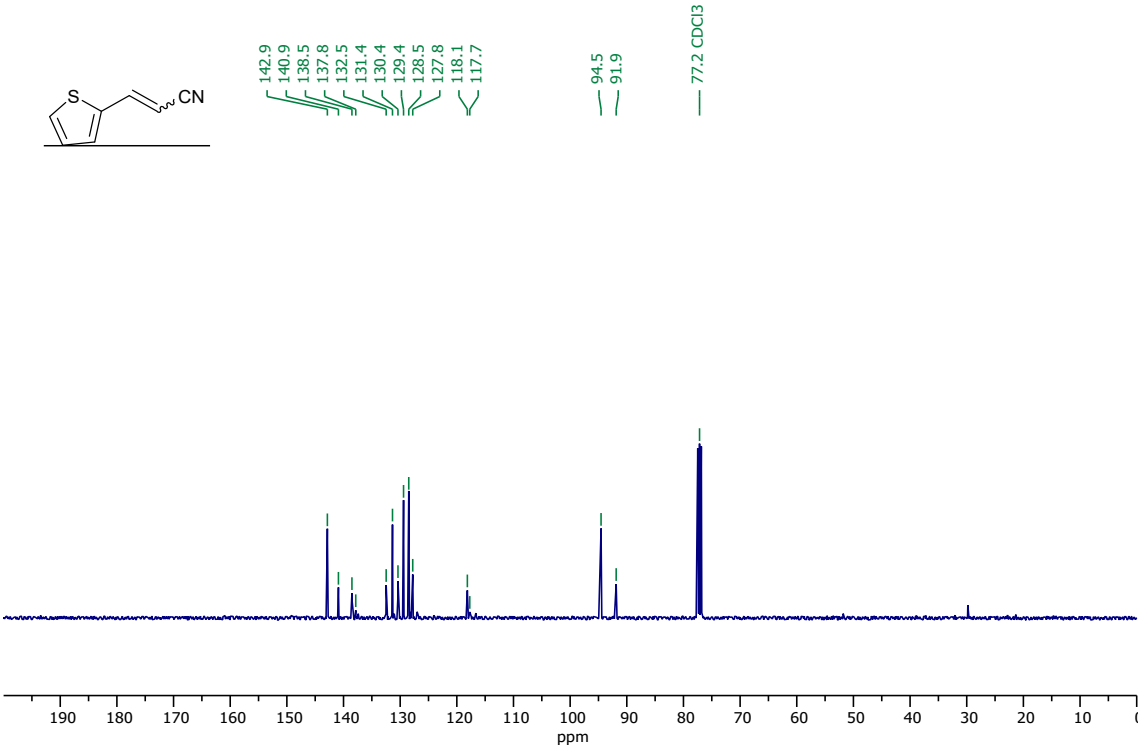


Figure 62. ^{13}C NMR spectra of compound **2l**

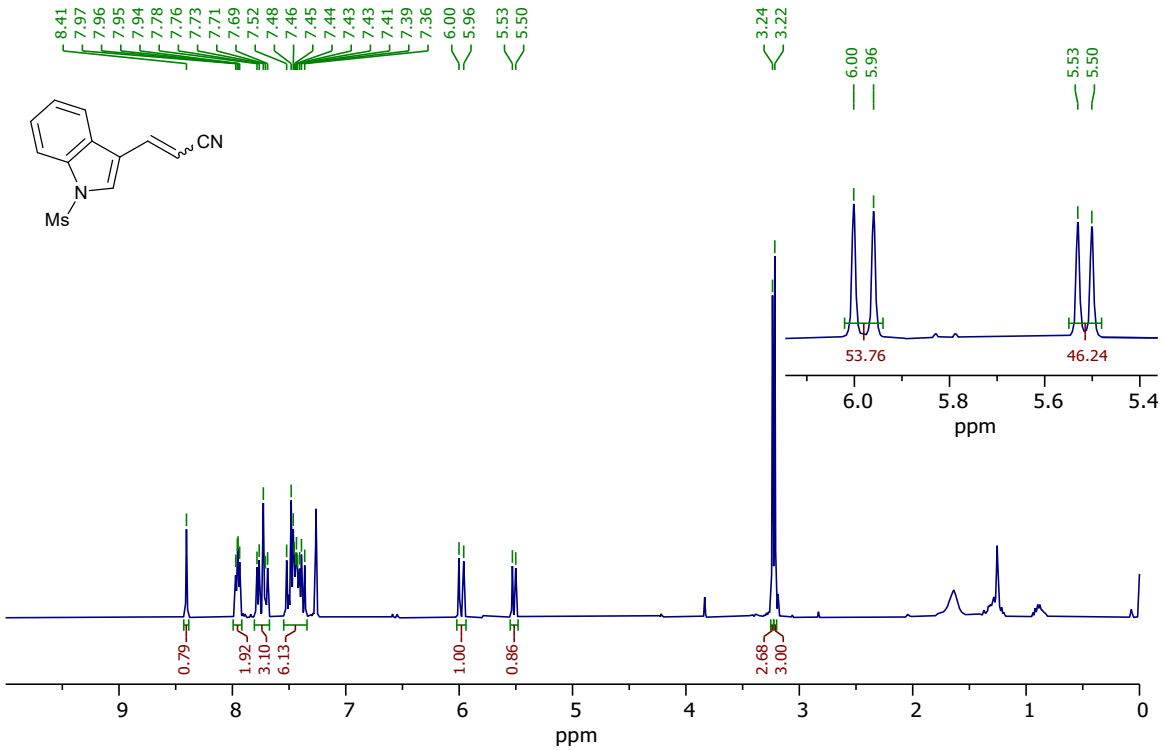


Figure 63. ^{1}H NMR spectra of compound **2m**

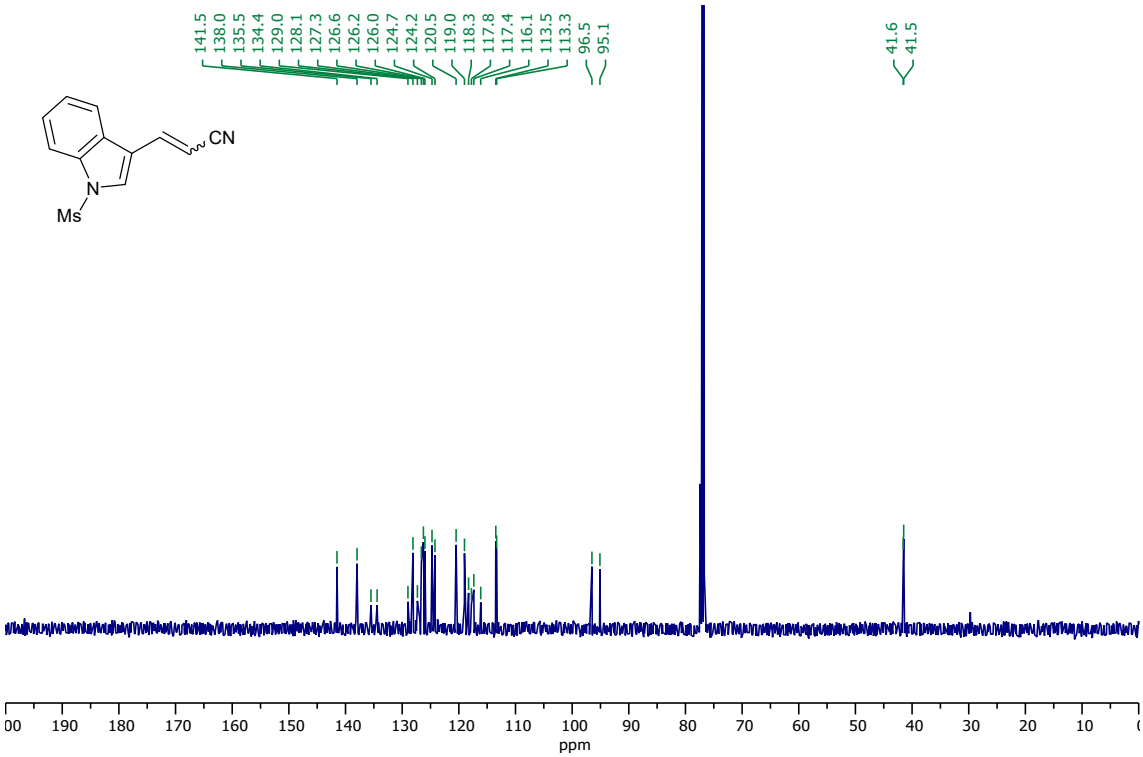


Figure 64. ^{13}C NMR spectra of compound **2m**

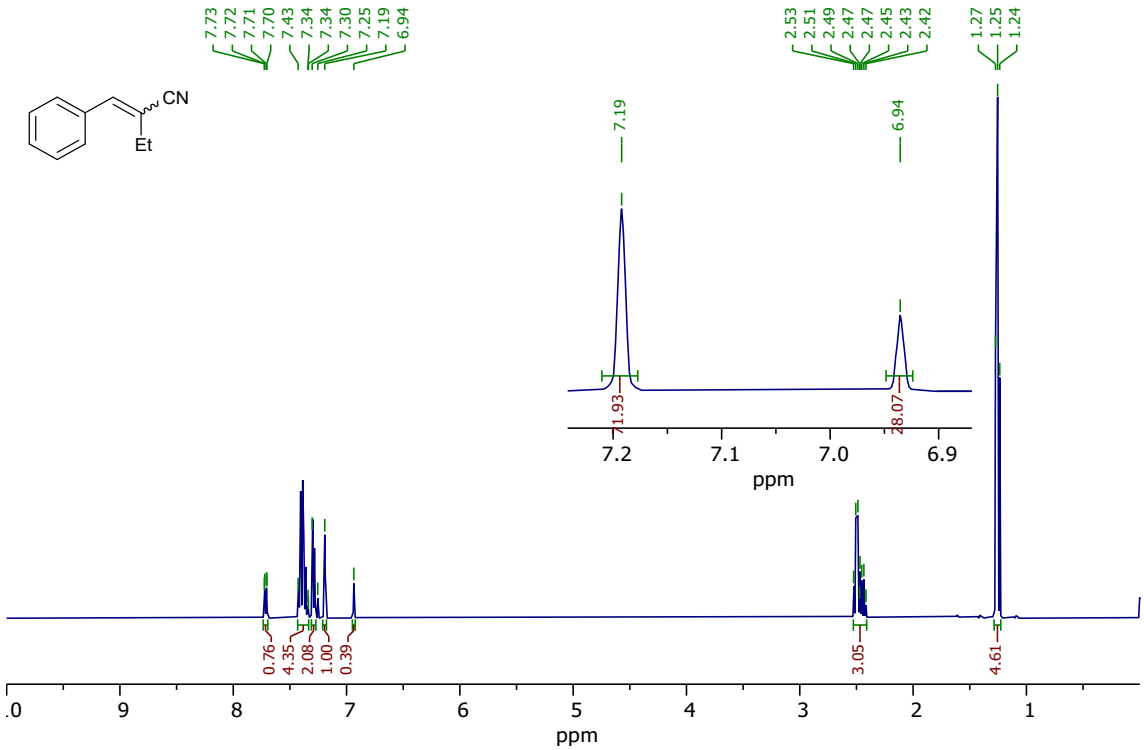


Figure 65. ^{1}H NMR spectra of compound **2n**

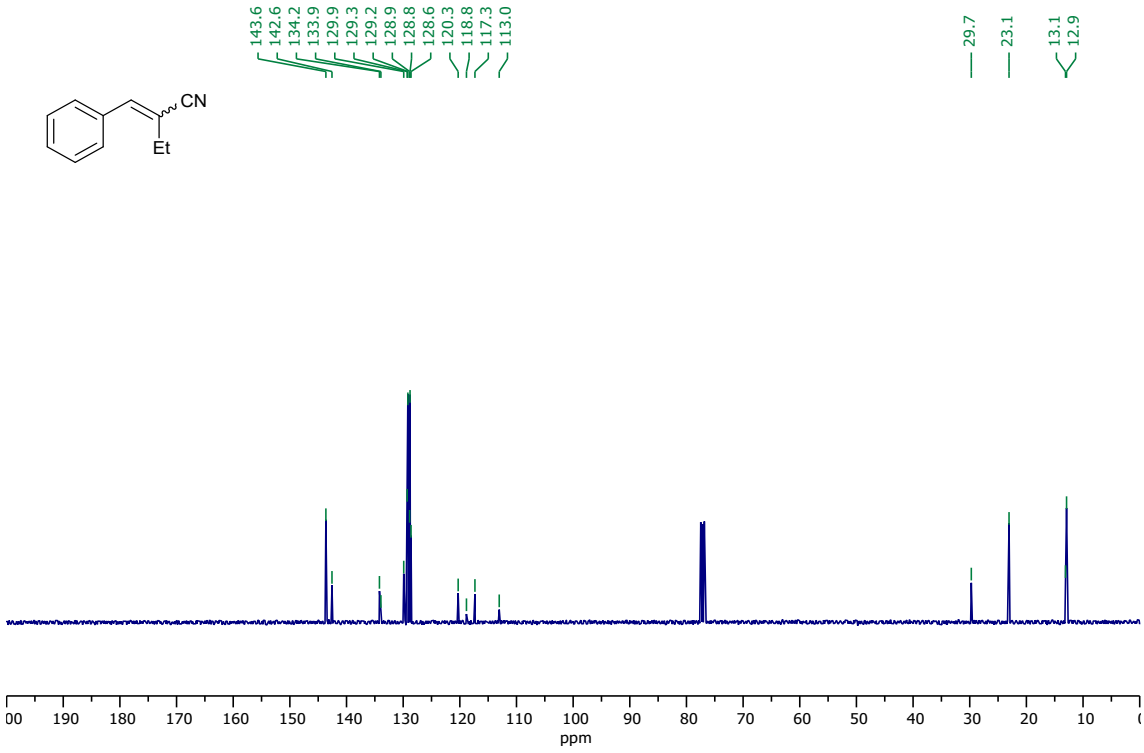


Figure 66. ^{13}C NMR spectra of compound **2n**

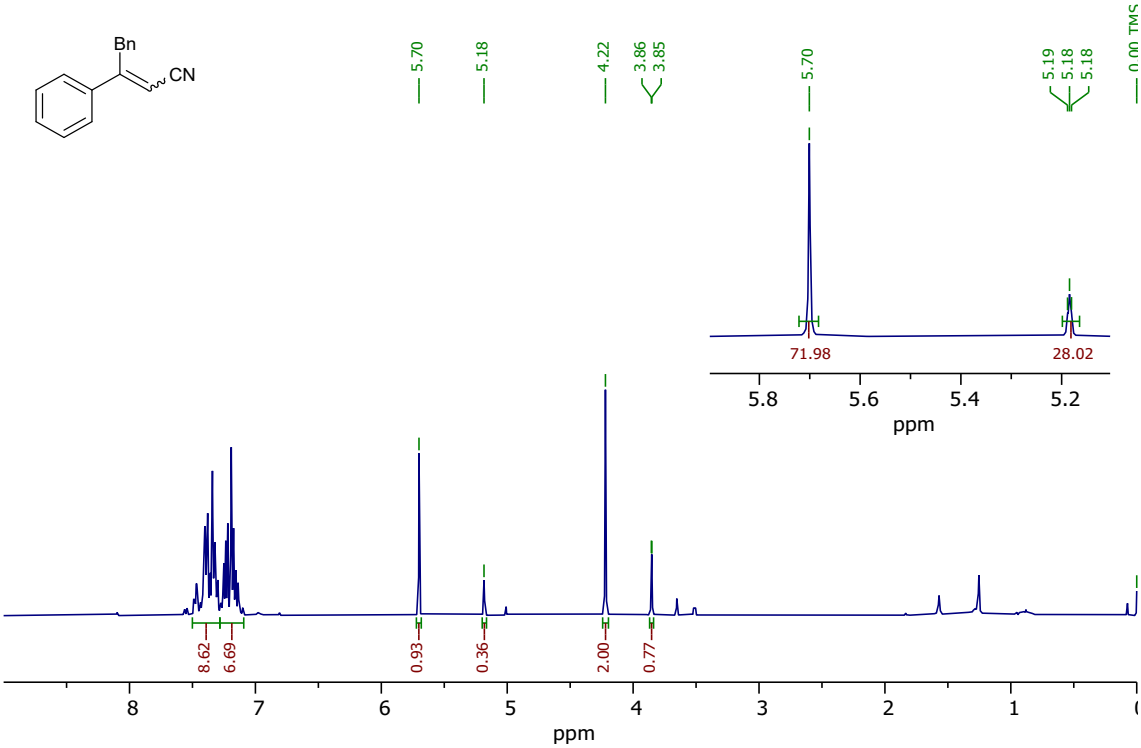


Figure 67. ^{1}H NMR spectra of compound **2o**

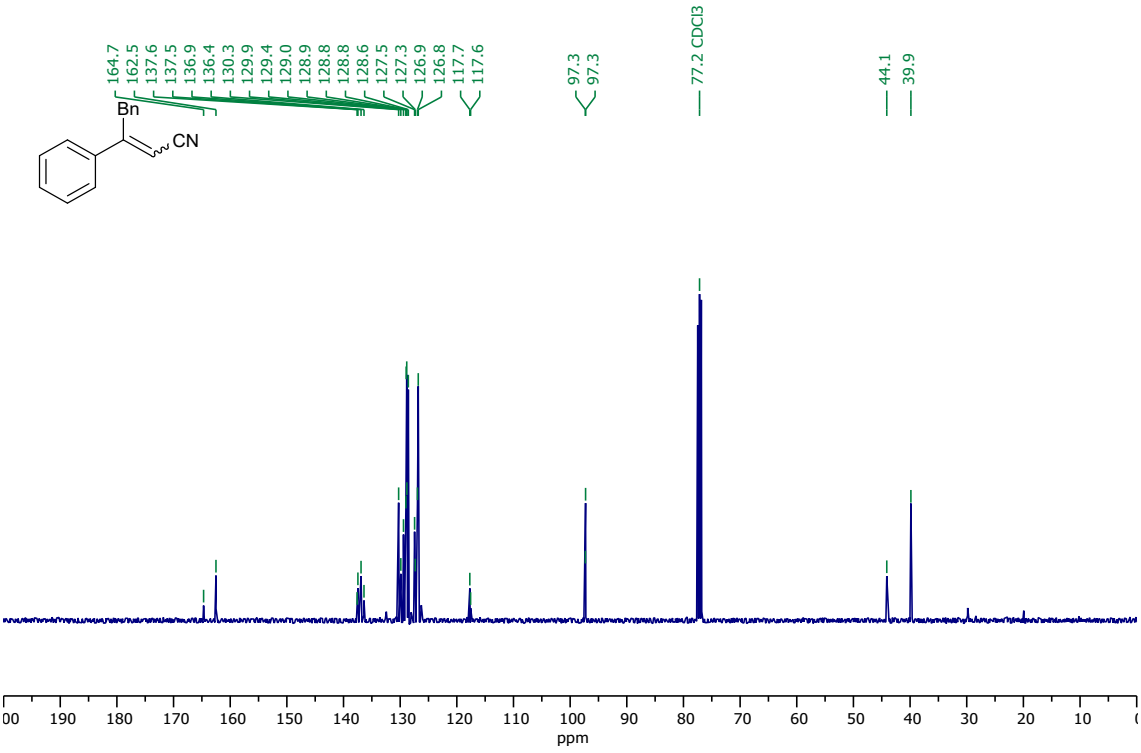


Figure 68. ^{13}C NMR spectra of compound **2o**

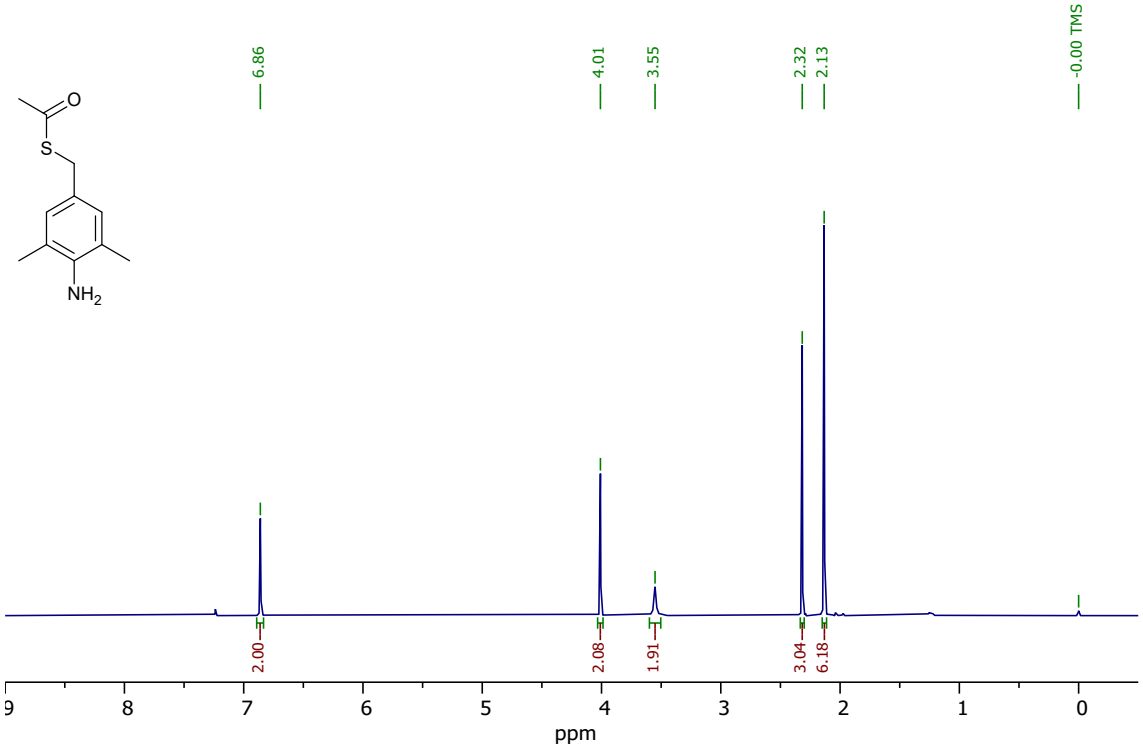


Figure 69. ^{1}H NMR spectra of compound **6**

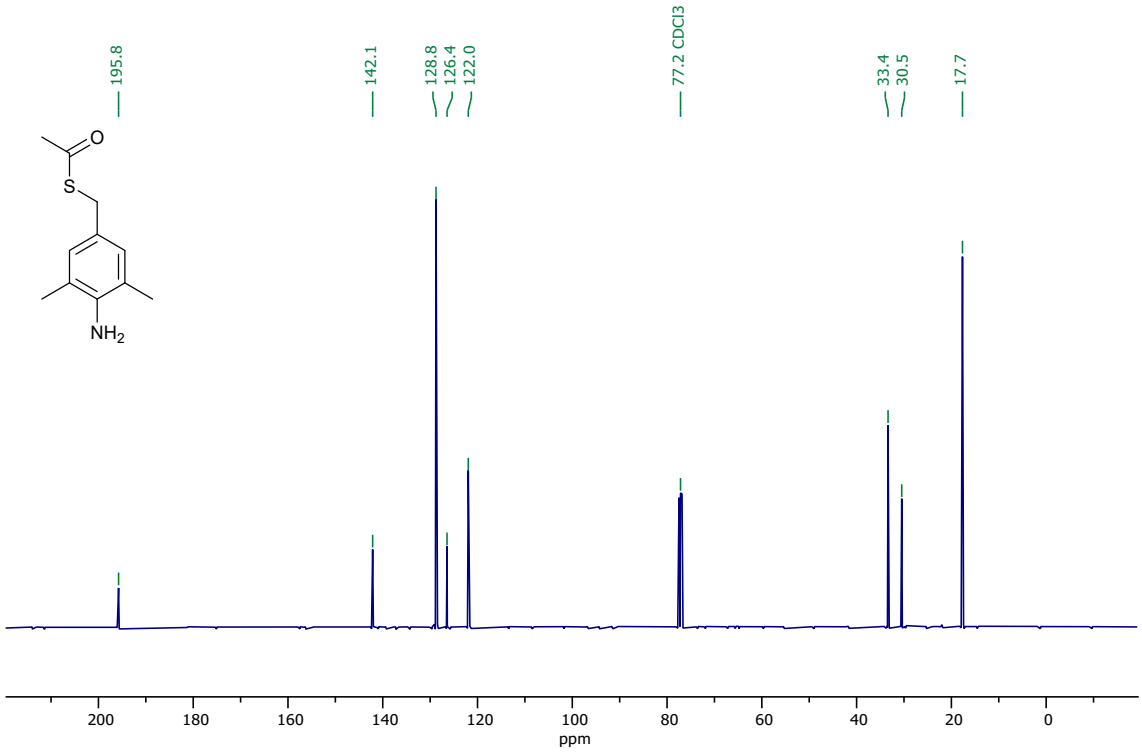


Figure 70. ^{1}H NMR spectra of compound **6**

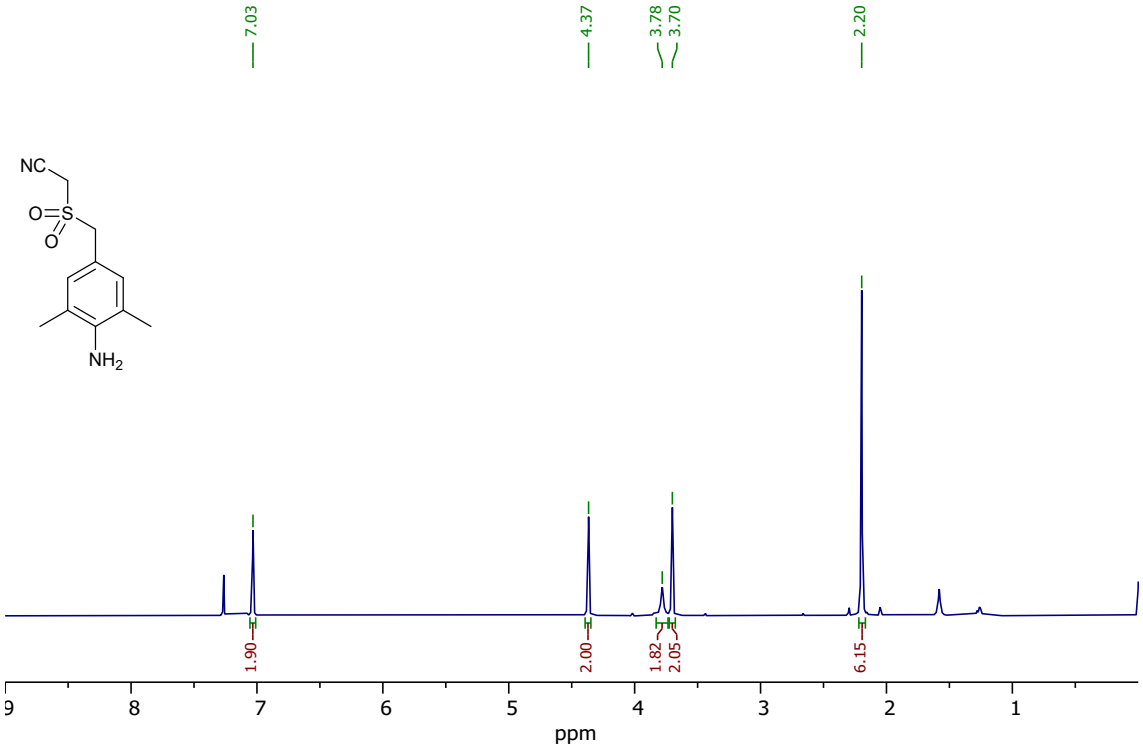


Figure 71. ^{1}H NMR spectra of compound **7**

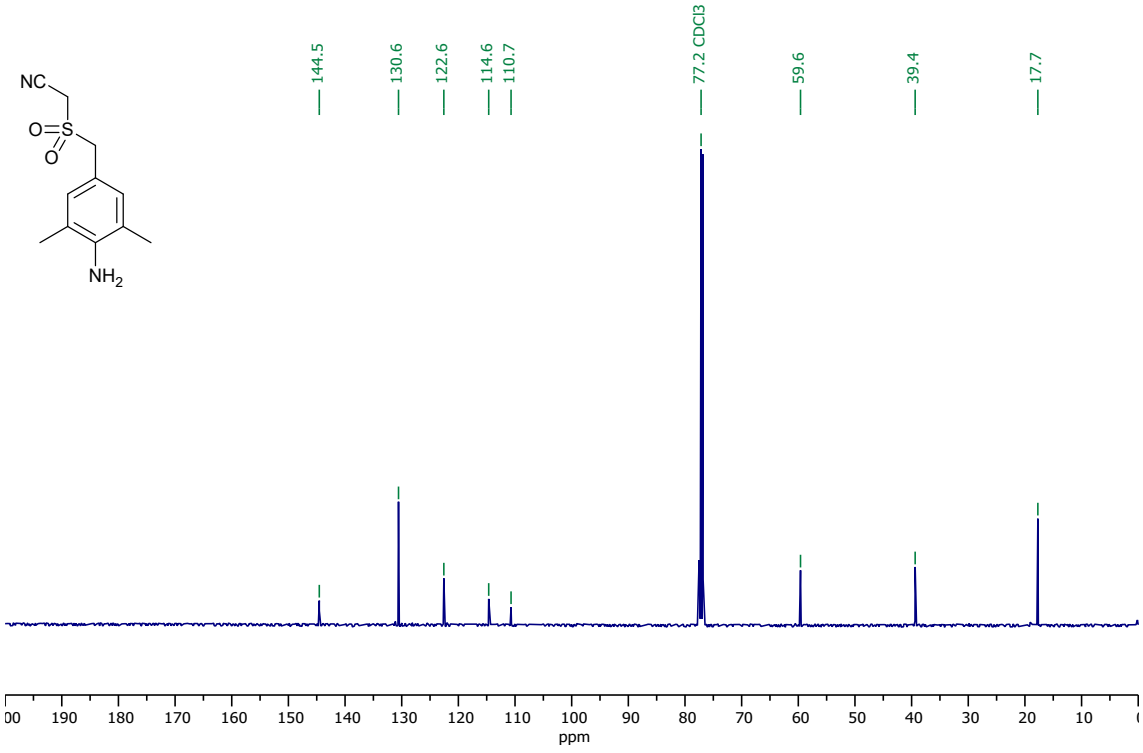


Figure 72. ^{13}C NMR spectra of compound **7**

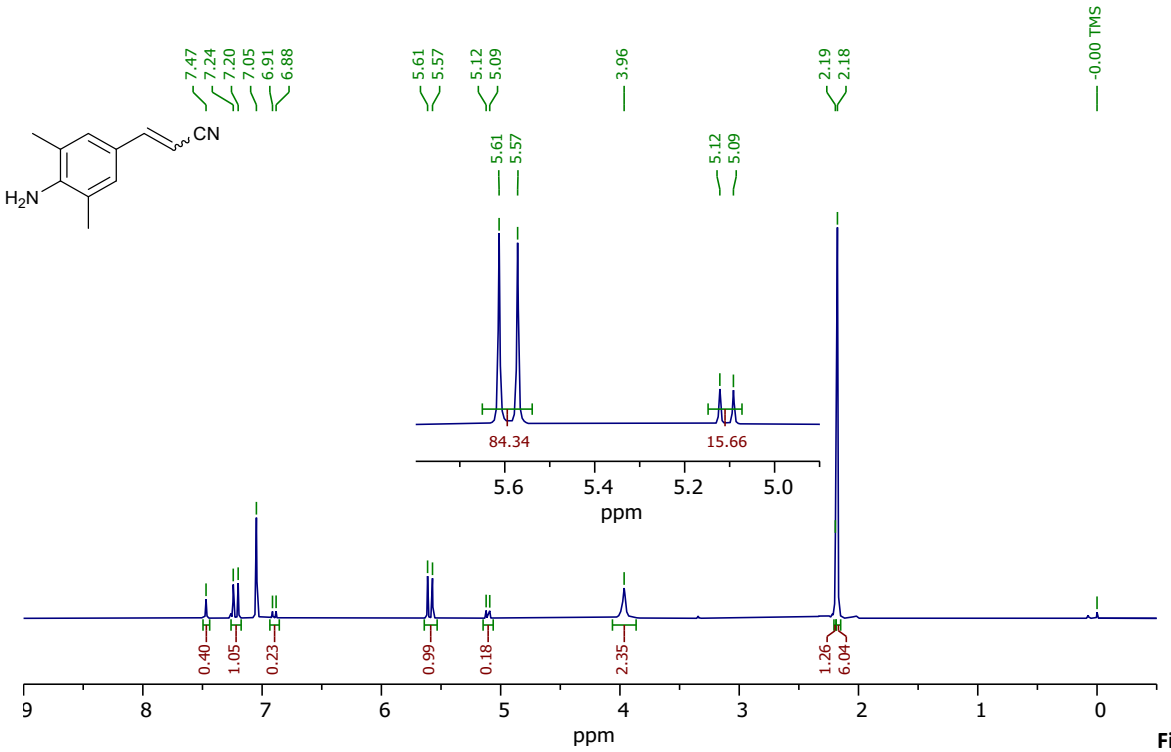


Figure 73. ^{1}H NMR spectra of compound **3**

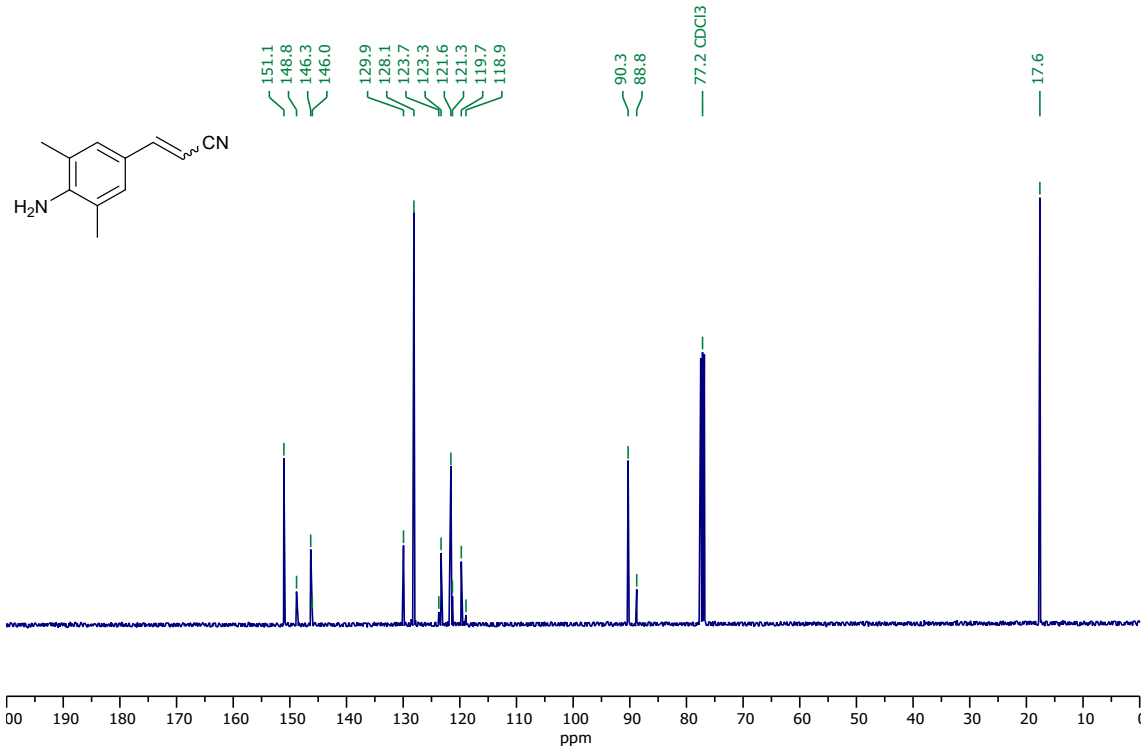


Figure 74. ^{13}C NMR spectra of compound **3**

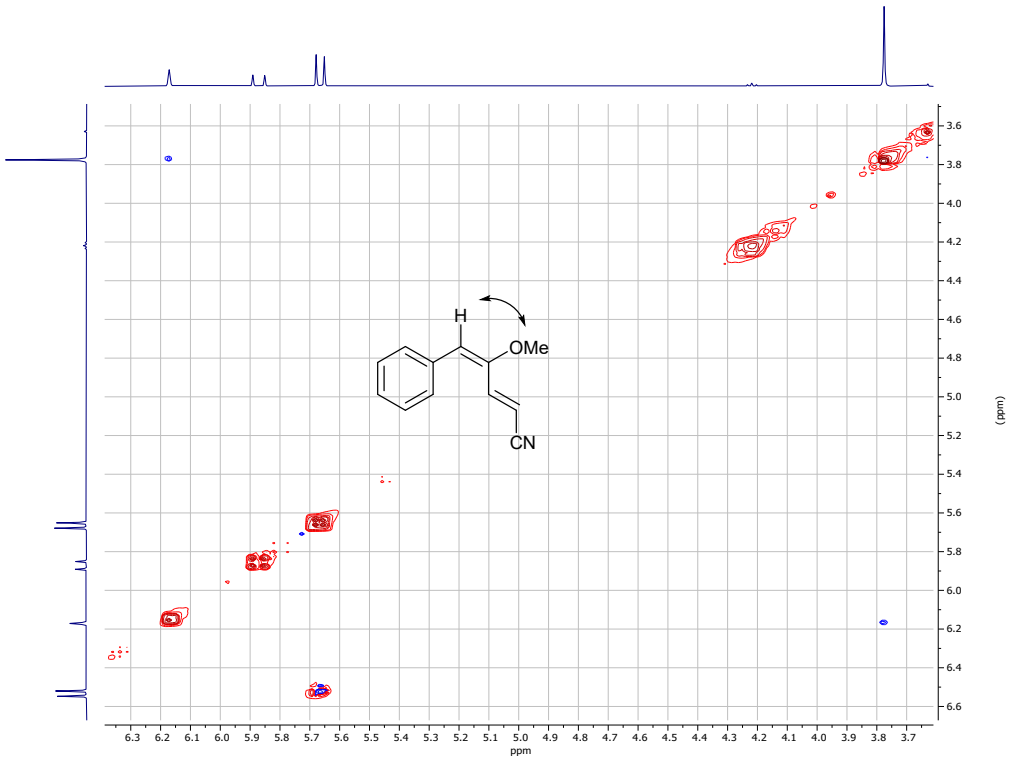


Figure 75. NOESY spectra of compound **S1j**

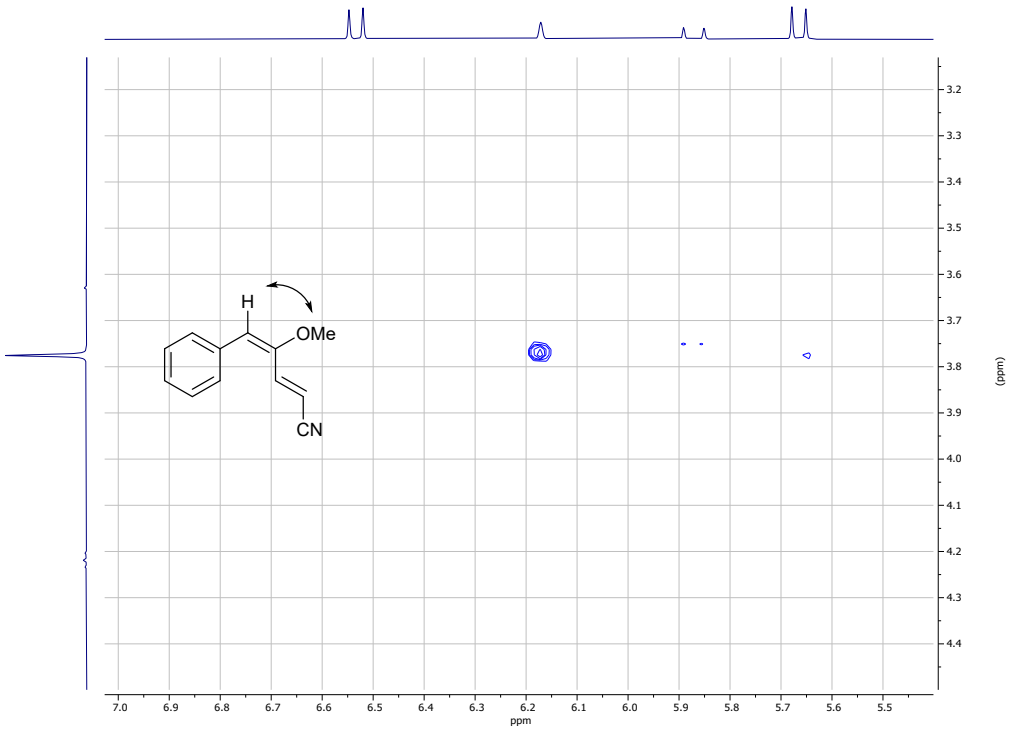


Figure 76. NOESY spectra of compound **S1j**