Supporting Information for

Manganese-Catalyzed Base-Free Addition of Saturated Nitriles to Unsaturated Nitriles by Template Catalysis

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General Considerations

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmosphere Glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were stored in molecular sieves and used as received. All solvents were purchased as HPLC grade, degassed with argon, and kept in the glove box over 4Å molecular sieves. Complexes **Mn-1**[1], **Mn-2**[2], **Mn-3**[3] **Mn-4**[1] were prepared according to literature procedures. All ^{1}H NMR, ^{13}C NMR or ^{31}P NMR spectra were recorded on a Bruker AVANCE III 300MHz, 400MHz and AVANCE III HD 500MHz NMR spectrometer and reported in ppm (δ). Chemical shifts were referenced to the residual solvent peaks ($CHCl_3$, ^{1}H NMR at 7.26 ppm, ^{13}C NMR at 77.16 ppm; TMS, ^{1}H NMR at 0.00 ppm;) or an external standard of phosphoric acid (85% solution in D_2O) at 0.0 ppm (^{31}P NMR). NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

GC analysis was performed on HP 6890 series GC system with Hp-5 column and SUPELCO 1-2382 column, flame ionization detector, and N_2 as carrier gas (Column: HP-5, 30 m, 320 μm, Inlets: 280 ºC; Detector: FID 280 ºC; Flow: 1 mL/min; Oven:50 ºC, hold 8 min; 15 ºC/min to 280 ºC, hold 2 min.).

GC-MS was carried out on HP 6890 / HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas.

General Optimization Procedure:

A 7 mL scintillation vial was equipped with a stirring bar, and loaded with **Mn**-(**1-3**) (0.75 mg, 0.005 mmol), benzyl cyanide (0.3 mmol), cinnamonitrile (0.3 mmol), and THF (1 mL), inside an N_2-filled glovebox. The reaction mixture was then stirred for 24 h at room

temperature, inside the glovebox, after which the vial was taken out of the glovebox, and 0.3 mmol of mesitylene was added to the reaction mixture as an internal standard. The resulting mixture was then filtered through a plug of Celite, and the plug itself was subsequently washed with ethyl acetate (2 mL). The liquid phases were combined and analyzed by GC-MS to determine the identity of the generated products. The conversion of benzyl cyanide was determined by GC-FID. The solvent was then evaporated under reduced pressure, and the resulting residue was subjected to column chromatography over silica gel (100-200 mesh), using a 1:4 ethyl acetate/hexane mixture as the eluent. Yields were calculated for the pure isolated product of **2a**.

General Experimental Procedure

For Benzyl Nitriles Compounds:

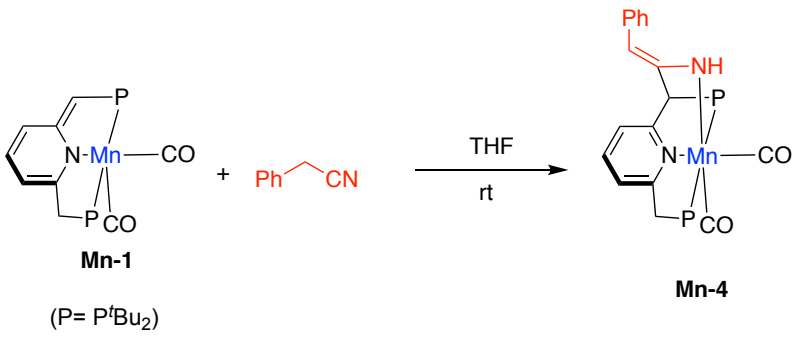
A 7 mL scintillation vial was equipped with a stirring bar, and loaded with **Mn-1** (0.75 mg, 0.005 mmol), benzyl nitrile (0.3 mmol), vinyl nitrile (0.3 mmol), and THF (1 mL), inside an N_2-filled glovebox. The reaction mixture was then stirred for 24 h at room temperature, inside the glovebox, after which the vial was taken out of the glovebox, and 0.3 mmol of mesitylene was added to the reaction mixture as an internal standard. The resulting mixture was then filtered through a plug of Celite, and the plug itself was subsequently washed with ethyl acetate (2 mL). The liquid phases were combined and analyzed by GC-MS to determine the identity of the generated products. The conversion of benzyl nitrile was determined by GC-FID. The solvent was then evaporated under reduced pressure, and the resulting residue was subjected to column chromatography over silica gel (100-200 mesh), using a 1:4 ethyl acetate/hexane mixture as the eluent. Yields were calculated for the pure isolated products.

For Aliphatic Nitriles Compounds:

A 7 mL scintillation vial was equipped with a stirring bar, and loaded with **Mn-1** (7.5 mg, 0.05 mmol), vinyl nitrile (0.3 mmol), alkyl nitrile (1 mL), inside an N_2-filled glovebox. The reaction mixture was then stirred for 48 h at room temperature, inside the glovebox, after which the vial was taken out of the glovebox, and 0.3 mmol of mesitylene was added to the reaction mixture as an internal standard. The resulting mixture was then filtered through a plug of Celite, and the plug itself was subsequently washed with ethyl acetate (2 mL). The liquid phases were combined and analyzed by GC-MS to determine the identity of the generated products. The conversion of vinyl nitrile was determined by GC-FID. The solvent was then evaporated under reduced pressure, and the resulting residue was subjected to column chromatography over silica gel (100-200 mesh), using a 1:4 ethyl acetate/hexane mixture as the eluent. Yields were calculated for the pure isolated products.

Mechanistic Studies

Synthesis of Mn-4 Complex



The reaction of complex **Mn-1** with benzyl nitrile to form complex **Mn-4** was performed according to our previous reported procedure.[1]

General procedure: In a glovebox, **Mn-1** (20.2 mg, 0.04 mmol) was suspended in toluene (1.0 mL) in a 20.0 mL vial charged with a stirring bar. Benzyl nitrile 1a (0.2 mmol, 23.4 mg, 5.0 eq.) was added to the stirred solution. After stirring at room temperature for 15 min, the

system color turned from dark blue to brownish red. $^{31}P\{^{1}H\}$ NMR of the resulting solution was recorded, indicating he complete formation **Mn-4** complex (Figure S1).

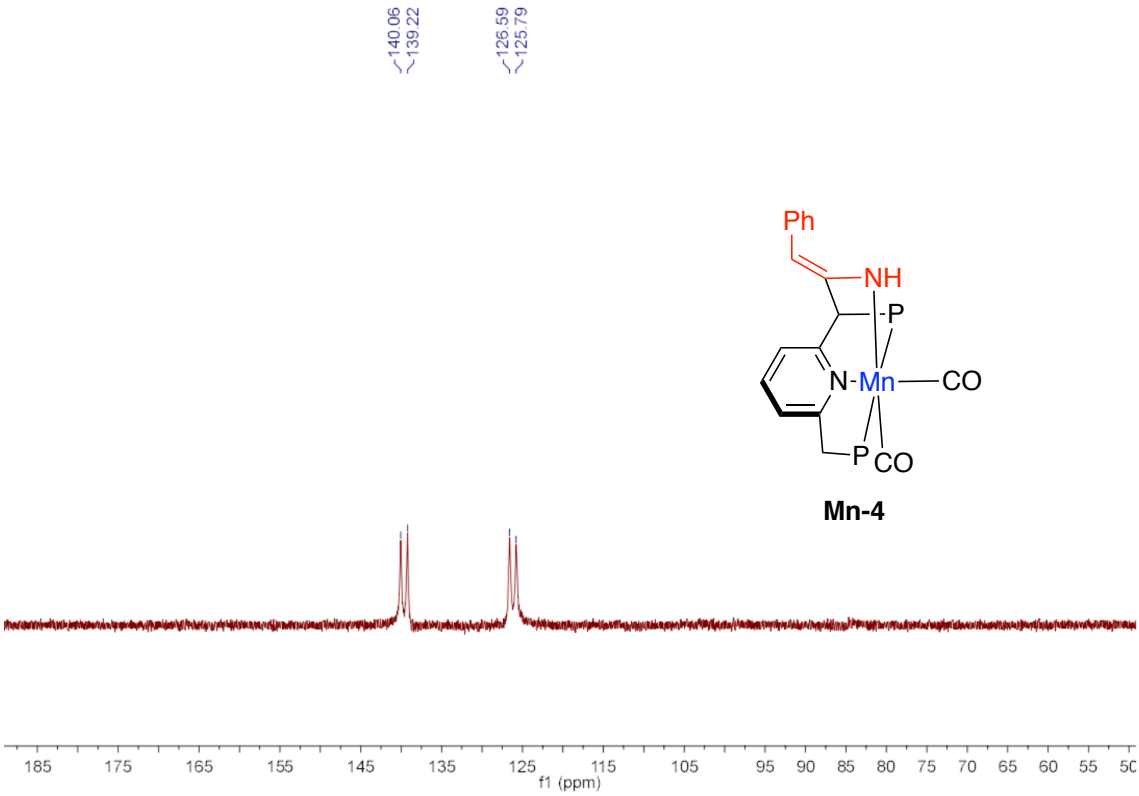


Figure S1. $^{31}P\{^{1}H\}$ NMR Spectrum (121 MHz, THF, 298 K, **Mn-1** in THF solvent)

Synthesis of Mn-5 Complex

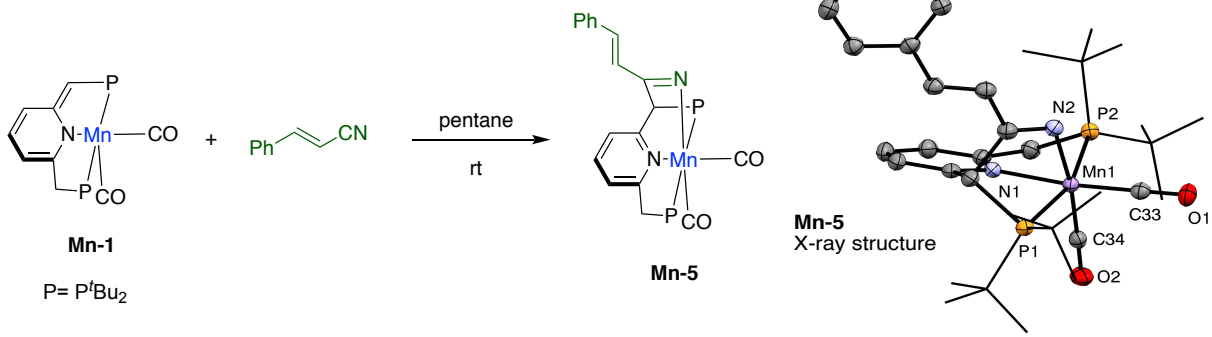
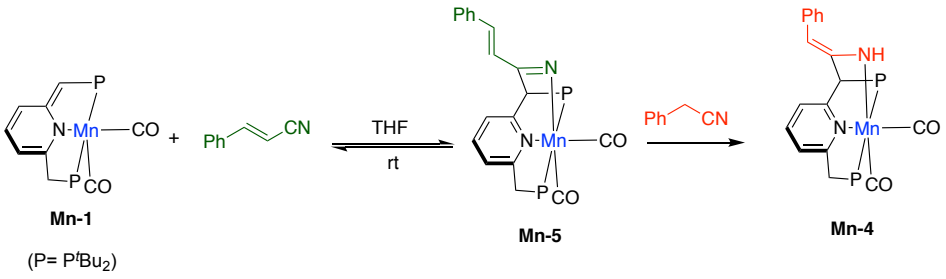


Figure S2. X-ray Crystal Structure of **Mn-5**. Most atoms are presented as thermal ellipsoids with 50% probability, but hydrogens are omitted and the ^{t}Bu side chains are presented in wire frame.

General procedure : In a glovebox, **Mn-1** (20.2 mg, 0.04 mmol) was suspended in pentane (5 mL) in a 20.0 mL vial charged with a stirring bar. Two drops of cinnamonitrile (20.6 mg, 0.20 mmol) were added to the pentane solution and it was kept at −38 °C for 24 hours, resulting in formation of complex **Mn-5** as orange crystals, and the crystals were decanted and dried under vacuum with a 66% yield. **Mn-5** exists In THF solution in equilibrium with **Mn-1** and free cinnamonitrile.

Competitive Experiment with Mn-1 Complex, Benzyl Cyanide and Cinnamonitrile



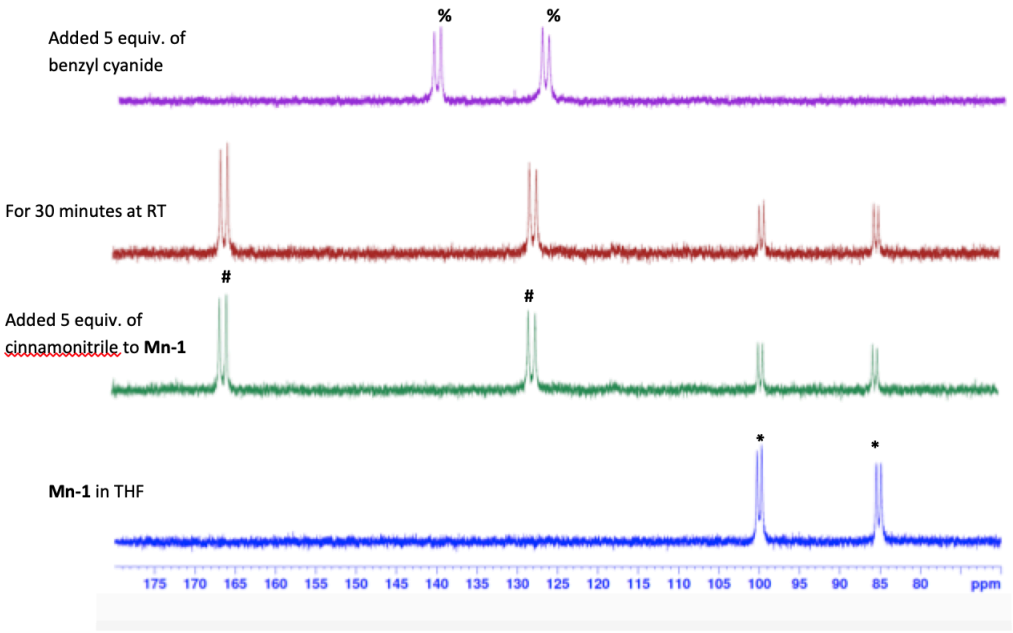


Figure S3. $^{31}P\{1H\}$ NMR spectra, monitoring the reaction conversion process of **Mn-4** and **Mn-5** complexes. Assignment: (*) = **Mn-1** complex; (#) = **Mn-5** complex; (%) = **Mn-4** complex.

General procedure: In a glovebox, **Mn-1** (10.1 mg, 0.02 mmol) was suspended in THF (0.5 mL) in a 5.0 mL via l (blue line, Figure S3). Then, 5.0 equivalent of cinnamonitrile (13 mg, 0.1 mmol) was added to the THF solution. After stirring at room temperature for 10 min, the color changed from dark blue to brownish red, and the $^{31}P\{^{1}H\}$ NMR indicated the formation of two doublets at δ = 129.7 ($^{2}J_{pp}$ = 103.4 Hz) and 168.0 ppm ($^{2}J_{pp}$ = 103.2 Hz) (Figure S3, green line). The reaction was also analyzed after 30 minutes, indicating that **Mn-5** existed in equilibrium with **Mn-1** and free cinnamonitrile. Further, 5.0 equivalents of benzyl cyanide (12 mg, 0.1 mmol) were added to the THF solution resulting in the immediate formation of the **Mn-4** complex (two doublets at δ = 139.64 (d, $^{2}J_{pp}$ = 101.7 Hz), 126.19 (d, ($^{2}J_{pp}$ = 97.2 Hz), Figure S3, purple line).

Spectral Data of the Products:

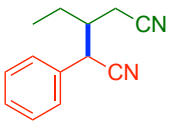
2,3-Diphenylpentanedinitrile (**2a**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2a** as a white solid (73 mg, 99% yield). Product **2a** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 50:50, as determined by comparison of the following signals: δ 4.32 (d, J =7.9 Hz, 1H, C*H*), 4.22 (d, J =6.7 Hz, 1H, C*H*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 6H), 7.12 (ddd, *J* = 7.5, 5.9, 3.1 Hz, 4H), 4.17 (dd, *J* = 40.4, 7.3 Hz, 1H), 3.46-3.25 (m, 1H), 2.76 (dddd, *J* = 61.8, 24.2, 16.9, 8.4 Hz, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.37, 136.27, 132.79, 132.38, 129.37, 129.20, 129.11, 128.93, 128.81, 128.10, 127.85, 127.78, 118.56, 117.27, 46.94, 46.89, 43.29, 42.63, 22.28, 20.90. Exact mass calculated for $C_{17}H_{14}N_2$, m/z 246.11; GC-MS obtained, 246.11.[4]

3-Cyclopentyl-2-phenylpentanedinitrile (**2b**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2b** as white solid (41 mg, 58% yield). Product **2b** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 68:32, as determined by comparison of the following signals: δ 4.26 (d, J =4.3 Hz, 1H, C*H*)-major, 4.11 (d, J =6.5 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.27 (m, 5H), 4.09 (dd, *J* = 58.3, 5.4 Hz, 1H), 2.46-1.90 (m, 5H), 1.85-1.47 (m, 5H), 1.35-1.13 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 133.17, 133.10, 129.61, 129.52, 129.00, 128.93, 128.14, 127.66, 119.64, 117.89, 46.35, 44.82, 43.83, 42.04, 41.02, 40.95, 31.56, 31.26, 29.78, 25.24, 25.09, 24.96, 24.87, 18.91, 18.00. HRMS (ESI) m/z calculated for $C_{16}H_{18}N_2Na$, $(M+Na)^+$: m/z 261.1368; found, 261.1365.

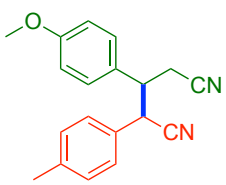
3-Methyl-2-phenylpentanedinitrile (**2c**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2c** as

colorless oil (39 mg, 70% yield). Product **2c** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 55:45, as determined by comparison of the following signals: δ 1.30 (d, J =6.6 Hz, 3H, C*H*$_3$)-major, 1.26 (d, J =6.2 Hz, 3H, C*H*$_3$)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.30 (m, 3H), 7.29-7.21 (m, 2H), 3.82 (t, *J* = 6.9 Hz, 1H), 2.56-2.15 (m, 3H), 1.18 (dd, *J* = 15.9, 6.4 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 133.17, 132.52, 129.54, 129.50, 129.05, 129.00, 127.98, 127.83, 118.59, 118.57, 117.50, 117.26, 42.63, 42.56, 36.20, 36.11, 35.84, 35.76, 22.78, 22.76, 21.72, 17.60, 17.56, 16.74, 16.72. HRMS (ESI) m/z calculated for $C_{12}H_{12}N_2Na$, $(M+Na)^+$: m/z 207.0898; found, 207.0897.

3-Ethyl-2-phenylpentanedinitrile (**2d**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2d** as colorless oil (51 mg, 86% yield). Product **2d** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 56:44, as determined by comparison of the following signals: δ 4.07 (d, J =6.3 Hz, 1H, C*H*)-minor, 3.94 (d, J =8.1 Hz, 1H, C*H*)-major. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.23 (m, 5H), 3.91 (dd, *J* = 50.0, 7.2 Hz, 1H), 2.53-2.00 (m, 3H), 1.66 (tdd, *J* = 20.7, 10.2, 6.8 Hz, 2H), 0.96 (dt, *J* = 18.6, 7.4 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 133.23, 132.76, 129.61, 129.55, 129.05, 128.98, 127.99, 127.91, 119.10, 118.33, 117.51, 117.16, 42.30 , 42.29, 41.43, 40.43, 24.40, 23.76, 19.18, 19.02, 11.28, 11.20. HRMS (ESI) m/z calculated for $C_{13}H_{14}N_2Na$, $(M+Na)^+$: m/z 221.1055; found, 221.1056.

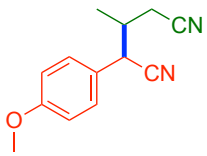


3-(4-Methoxyphenyl)-2-(*p*-tolyl)pentanedinitrile (**2e**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2e** as white solid (83 mg, 95% yield). Product **2e** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 58:42, as determined by comparison of the following



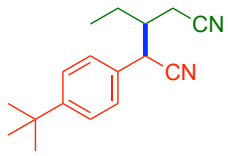
signals: δ 4.10 (d, J =8.0 Hz, 1H, C*H*)-major, 4.04 (d, J =6.6 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-6.96 (m, 6H), 6.87-6.74 (m, 2H), 4.07 (dd, *J* = 23.8, 7.3 Hz, 1H), 3.72 (d, *J* = 4.2 Hz, 3H), 3.40-3.20 (m, 1H), 2.89-2.44 (m, 2H), 2.26 (d, *J* = 7.7 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.89, 159.79, 139.02, 138.89, 130.06, 129.90, 129.36, 129.01, 128.97, 128.42, 128.03, 128.02, 118.89, 118.87, 117.56, 117.44, 114.50, 55.38, 46.35, 46.21, 43.18, 42.61, 22.47, 21.23, 21.19, 20.99. HRMS (ESI) m/z calculated for $C_{19}H_{18}N_2ONa$, $(M+Na)^+$: m/z 313.1317; found, 313.1309.

2-(4-Methoxyphenyl)-3-methylpentanedinitrile (**2f**). Purified by column chromatography



using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2f** as colorless oil (58 mg, 90% yield). Product **2f** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 60:40, as determined by comparison of the following signals: δ 1.29 (d, J = 6.5 Hz, 3H, C*H*$_3$)-major, 1.23 (d, J =6.6 Hz, 3H, C*H*$_3$)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (dd, *J* = 15.1, 6.3 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.76 (d, *J* = 5.4 Hz, 4H), 2.41-2.12 (m, 3H), 1.25-1.08 (m, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 160.03, 160.00, 129.16, 129.01, 125.02, 124.30, 118.90, 118.87, 117.58, 117.31, 114.87, 114.82, 55.49, 41.82, 36.23, 35.88, 22.63, 21.71, 17.45, 16.81. HRMS (ESI) m/z calculated for $C_{13}H_{14}N_2ONa$, $(M+Na)^+$: m/z 237.1004; found, 237.1004.

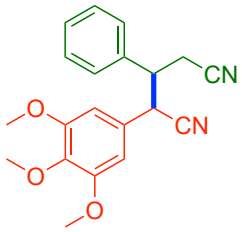
2-(4-(*tert*-Butyl)phenyl)-3-ethylpentanedinitrile (**2g**). Purified by column chromatography



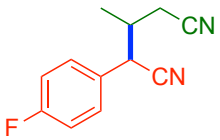
using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2g** as colorless oil (61 mg, 80% yield). Product **2g** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 53:47, as determined by comparison of the following signals: δ 3.95 (d, J = 6.2 Hz, 1H, C*H*)-major, 3.80 (d, J =8.3 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.22-7.14 (m, 2H), 3.88 (dd, *J* = 58.9, 7.2 Hz, 1H), 2.51-2.13 (m,

2H), 1.78 (ddd, *J* = 38.5, 21.2, 16.3 Hz, 3H), 1.25 (d, *J* = 1.1 Hz, 9H), 0.97 (dt, *J* = 17.2, 7.4 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 152.24, 152.17, 130.11, 129.62, 127.70, 127.62, 126.55, 126.48, 119.35, 118.49, 117.70, 117.26, 42.30, 42.24, 40.99, 39.96, 34.80, 31.35, 24.41, 23.81, 19.21, 18.99, 11.32, 11.21. HRMS (ESI) m/z calculated for $C_{17}H_{22}N_2Na$, $(M+Na)^+$: m/z 277.1681; found, 277.1678.

3-Phenyl-2-(3,4,5-trimethoxyphenyl)pentanedinitrile (**2h**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2h** as white solid (90 mg, 89% yield). Product **2h** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 60:40, as determined by comparison of the following signals: δ 4.17 (d, J = 7.5 Hz, 1H, C*H*)-major, 4.07 (d, J =6.9 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 3H), 7.13 (dd, *J* = 6.4, 2.7 Hz, 2H), 6.24 (d, *J* = 28.1 Hz, 2H), 4.11 (dd, *J* = 42.4, 7.3 Hz, 1H), 3.76 (d, *J* = 7.5 Hz, 3H), 3.69 (d, *J* = 11.4 Hz, 6H), 3.31 (d, *J* = 7.3 Hz, 1H), 2.70 (ddd, *J* = 61.4, 16.9, 6.8 Hz, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 153.75, 153.55, 138.39, 136.35, 129.17, 129.13, 128.99, 128.88, 128.13, 128.00, 127.94, 118.69, 118.54, 117.41, 117.38, 105.41, 105.20, 61.01, 56.30, 56.27, 46.91, 46.74, 43.28, 42.75, 22.25, 21.13. HRMS (ESI) m/z calculated for $C_{20}H_{20}N_2O_3Na$, $(M+Na)^+$: m/z 359.1372; found, 359.1358.

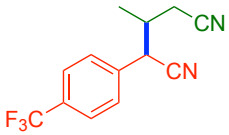


2-(4-Fluorophenyl)-3-methylpentanedinitrile (**2i**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2i** as colorless oil (48 mg, 80% yield). Product **2i** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 59:41, as determined by comparison of the following signals: δ 1.19 (d, J = 6.5 Hz, 3H, CH_3)-major, 1.14 (d, J =6.6 Hz, 3H, CH_3)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.16 (m, 2H), 7.06 (t, *J* = 8.5 Hz, 2H), 3.82 (dd, *J* = 21.3, 6.7 Hz, 1H), 2.48-2.13 (m,



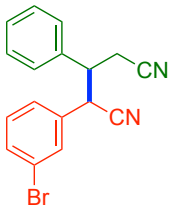
3H), 1.17 (dd, *J* = 20.5, 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.96, 163.91, 161.97, 161.93, 129.86, 129.79, 129.68, 129.61, 129.02, 129.00, 128.37, 128.34, 118.50, 118.35, 117.31, 117.13, 116.75, 116.72, 116.57, 116.54, 41.89, 41.84, 36.31, 35.89, 22.79, 21.85, 17.50, 16.66. HRMS (ESI) m/z calculated for $C_{12}H_{11}FN_2Na$, $(M+Na)^+$: m/z 225.0804; found, 225.0808.

3-Methyl-2-(4-(trifluoromethyl)phenyl)pentanedinitrile (**2j**). Purified by column



chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2j** as colorless oil (73 mg, 97% yield). Product **2j** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 57:43, as determined by comparison of the following signals: δ 3.98 (d, J = 6.4 Hz, 1H, C*H*)-major, 3.88 (d, J =6.4 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.46-7.38 (m, 2H), 3.93 (dd, *J* = 40.5, 6.4 Hz, 1H), 2.51-2.22 (m, 3H), 1.22-1.11 (m, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.17, 136.58, 131.67, 131.58, 131.34, 131.25, 128.57, 128.36, 126.68-126.43 (multiplets), 125.06, 125.05, 122.36, 122.34, 117.97, 117.66, 117.09, 117.02, 42.36, 42.27, 36.19, 35.73, 22.93, 21.90, 17.53, 16.43. HRMS (ESI) m/z calculated for $C_{13}H_{10}F_3N_2$, $(M-H)^+$: m/z 251.0796; found, 251.0783.

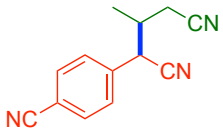
2-(3-Bromophenyl)-3-phenylpentanedinitrile (**2k**). Purified by column chromatography



using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2k** as pale yellow oil (86 mg, 88% yield). Product **2k** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 58:42, as determined by comparison of the following signals: δ 4.24 (d, J = 7.4 Hz, 1H, C*H*)-major, 4.10 (d, J =7.2 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 13.5, 8.1 Hz, 1H), 7.32-7.20 (m, 4H), 7.19-7.05 (m, 3H), 7.01 (t, *J* = 7.6 Hz, 1H), 4.13 (dd, *J* = 55.0, 7.3 Hz, 1H), 3.42-3.22 (m, 1H), 2.77 (dddd, *J* = 57.4, 24.3, 16.9, 8.3 Hz,

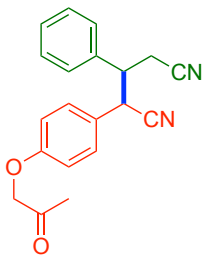
2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 135.94, 135.67, 134.93, 134.55, 132.29, 132.20, 131.17, 131.13, 130.81, 130.69, 129.31, 129.21, 129.17, 129.08, 127.86, 127.74, 126.83, 126.80, 123.29, 123.19, 118.09, 117.88, 117.10, 46.83, 46.80, 42.79, 42.19, 22.24, 21.13. HRMS (ESI) m/z calculated for $C_{17}H_{13}BrN_2Na$, $(M+Na)^+$: m/z 347.0160; found, 347.0150.

2-(4-Cyanophenyl)-3-methylpentanedinitrile (**2l**). Purified by column chromatography



using silica gel column chromatography (eluent: hexane/EtOAc = 60:40) to afford **2l** as colorless oil (38 mg, 60% yield). Product **2l** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 56:44, as determined by comparison of the following signals: δ 4.01 (d, J = 6.1 Hz, 1H, C*H*)-major, 3.87 (d, J = 6.7 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 10.1, 8.4 Hz, 2H), 3.94 (dd, *J* = 54.6, 6.4 Hz, 1H), 2.56-2.15 (m, 3H), 1.16 (dd, *J* = 6.6, 1.9 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.31, 137.74, 133.31, 133.30, 128.97, 128.74, 117.89, 117.85, 117.61, 117.19, 116.90, 113.48, 113.36, 42.57, 42.43, 36.23, 35.73, 23.04, 21.98, 17.61, 16.36. HRMS (ESI) m/z calculated for $C_{13}H_{11}N_3Na$, $(M+Na)^+$: m/z 232.0851; found, 232.0850.

2-(4-(2-Oxopropoxy)phenyl)-3-phenylpentanedinitrile (**2m**). Purified by column



chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 50:50) to afford **2m** as colorless oil (81 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.24 (m, 3H), 7.08 (ddd, *J* = 17.6, 7.1, 2.6 Hz, 4H), 6.82-6.72 (m, 2H), 4.47 (d, *J* = 9.4 Hz, 2H), 4.18 (d, *J* = 7.8 Hz, 1H), 3.29 (dd, *J* = 14.4, 7.1 Hz, 1H), 2.67 (ddd, *J* = 61.2, 16.9, 6.9 Hz, 2H), 2.20 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 204.83, 158.23, 136.28, 129.63, 129.23, 129.06, 127.92, 125.92, 118.60, 117.26, 115.41, 73.10, 47.13, 41.95, 26.74, 22.29. HRMS (ESI) m/z calculated for $C_{20}H_{18}N_2O_2Na$, $(M+Na)^+$: m/z 341.1266; found, 341.1267.

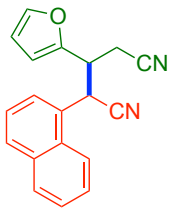
Methyl-1,3-dicyano-2-phenylpropyl)benzoate (**2n**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 60:40) to afford **2n** as white solid (74 mg, 81% yield). Product **2n** was isolated as diastereoisomers and the diastereoisomeric ratio was determined by GC analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 13.3, 8.3 Hz, 2H), 7.33-7.20 (m, 3H), 7.15 (t, *J* = 8.8 Hz, 2H), 7.10-7.01 (m, 2H), 4.24 (dd, *J* = 70.0, 7.3 Hz, 1H), 3.83 (d, *J* = 6.0 Hz, 3H), 3.46-3.27 (m, 1H), 3.02-2.58 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.24, 166.20, 137.57, 137.24, 135.89, 135.54, 130.85, 130.79, 130.46, 130.35, 129.27, 129.16, 129.11, 129.02, 128.30, 128.21, 127.85, 127.73, 118.22, 117.82, 117.13, 117.08, 52.44, 52.43, 46.79, 46.75, 43.00, 42.53, 22.25, 21.43. HRMS (ESI) m/z calculated for $C_{19}H_{16}N_2O_2Na$, $(M+Na)^+$: m/z 327.1109; found, 327.1109.

***tert*-Butyl (4-(1,3-dicyano-2-phenylpropyl)phenyl)carbamate** (**2o**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 20:80) to afford **2o** as white solid (83 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.24 (m, 5H), 7.11 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 4.16 (d, *J* = 7.9 Hz, 1H), 3.37-3.23 (m, 1H), 2.65 (ddd, *J* = 24.3, 16.9, 6.9 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 152.60, 139.26, 136.34, 129.20, 128.99, 128.85, 127.91, 126.87, 126.84, 118.95, 118.64, 117.28, 81.15, 47.04, 46.95, 42.10, 28.42, 22.24. HRMS (ESI) m/z calculated for $C_{22}H_{23}N_3O_2Na$, $(M+Na)^+$: m/z 384.1688; found, 384.1671.

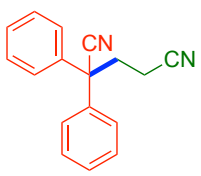
3-Methyl-2-(pyridin-3-yl)pentanedinitrile (**2p**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2p** as colorless oil (39 mg, 70% yield). Product **2p** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 56:44, as determined by comparison of the following signals: δ 3.96 (d, J = 4.5 Hz, 1H, C*H*)-major,

3.84 (d, J =6.4 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (broad, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 5.6 Hz, 1H), 3.90 (dd, *J* = 49.4, 5.5 Hz, 1H), 2.66-2.13 (m, 3H), 1.18 (dd, *J* = 11.9, 6.2 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 150.59, 149.35, 149.18, 135.69, 135.58, 135.46, 129.31, 128.80, 124.26, 117.78, 117.35, 116.97, 116.94, 40.24, 40.19, 36.07, 35.62, 22.91, 21.98, 17.42, 16.34. HRMS (ESI) m/z calculated for $C_{11}H_{12}N_3$, $(M+H)^+$: m/z 186.1031; found, 186.1032.

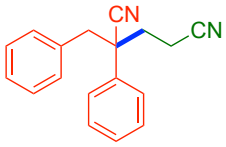
3-(Furan-2-yl)-2-(naphthalen-1-yl)pentanedinitrile (**2q**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2q** as colorless oil (77 mg, 90% yield). Product **2q** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 63:37, as determined by comparison of the following signals: δ 5.07 (d, J = 4.8 Hz, 1H, C*H*)-major, 4.97 (d, J =6.8 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.76 (m, 3H), 7.63-7.25 (m, 5H), 6.33-6.01 (m, 2H), 5.02 (dd, *J* = 41.1, 5.8 Hz, 1H), 3.75 (ddd, *J* = 11.7, 10.8, 5.8 Hz, 1H), 3.07-2.54 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 150.09, 149.02, 143.26, 143.21, 134.26, 134.15, 130.33, 130.13, 129.91, 129.73, 127.91, 127.84, 127.78, 127.72, 127.31, 126.70, 126.58, 125.38, 125.34, 121.63, 118.31, 117.89, 117.03, 117.00, 110.96, 110.74, 109.67, 108.75, 39.80, 39.43, 39.21, 38.40, 21.03, 18.43. HRMS (ESI) m/z calculated for $C_{19}H_{14}ON_2Na$, $(M+Na)^+$: m/z 309.1004; found, 309.0999.



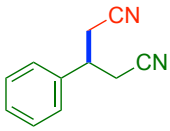
2,2-Diphenylpentanedinitrile (**2r**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2r** as colorless oil (73 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 77.72-7.14 (m, 10H), 2.86-2.60 (m, 2H), 2.59-2.26 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.20, 129.44, 128.76, 126.70, 120.86, 118.19, 50.96, 35.45, 14.20. HRMS (ESI) m/z calculated for $C_{17}H_{14}N_2Na$, $(M+Na)^+$: m/z 269.1055; found, 269.1054.



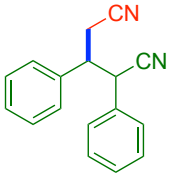
2-Benzyl-2-phenylpentanedinitrile (**2s**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2s** as white solid (53 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.22 (m, 5H), 7.22-7.09 (m, 3H), 6.94 (dd, *J* = 7.2, 1.8 Hz, 2H), 3.12 (s, 2H), 2.47-1.96 (m, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 135.52, 133.95, 130.36, 129.47, 128.88, 128.43, 127.84, 126.22, 120.43, 118.28, 49.10, 47.63, 35.05, 13.78. HRMS (ESI) m/z calculated for $C_{18}H_{16}N_2Na$, $(M+Na)^+$: m/z 283.1211; found, 283.1209.



3-Phenylpentanedinitrile (**2t**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2t** as colorless oil (51 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.34 (m, 3H), 7.28 (d, *J* = 7.0 Hz, 2H), 3.36 (p, *J* = 6.8 Hz, 1H), 2.77 (d, *J* = 7.2 Hz, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.97, 129.12, 128.45, 126.66, 117.15, 38.18, 23.21. HRMS (ESI) m/z calculated for $C_{11}H_{10}N_2Na$, $(M+Na)^+$: m/z 193.0742; found, 193.0742.



2,3-Diphenylpentanedinitrile (**2u**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2u** as colorless oil (59 mg, 80% yield). Product **2u** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 61:39, as determined by comparison of the following signals: δ 4.22 (d, J = 8.2 Hz, 1H, C*H*)-major, 4.13 (d, J =7.2 Hz, 1H, C*H*)-minor. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.21 (m, 6H), 7.17-7.02 (m, 4H), 4.15 (dd, *J* = 39.4, 7.4 Hz, 1H), 3.45-3.20 (m, 1H), 2.74 (dddd, *J* = 57.9, 24.3, 16.9, 8.5 Hz, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.41, 136.29, 132.82, 132.42, 129.42, 129.27, 129.21, 129.17, 129.11, 128.99, 128.88, 128.13, 127.89, 127.81, 118.60, 118.56, 117.34, 117.27, 47.02, 46.97, 43.36, 42.68, 22.32, 20.92. HRMS (ESI) m/z calculated for $C_{17}H_{14}N_2Na$, $(M+Na)^+$: m/z 269.1055; found, 269.1053.



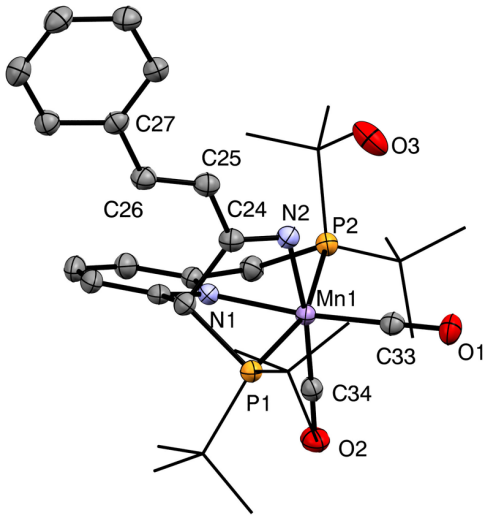
3-(4-Methoxyphenyl)-2-methylpentanedinitrile (**2v**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2v** as colorless oil (30 mg, 47% yield). Product **2v** was isolated as diastereoisomers and ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 65:35, as determined by comparison of the following signals: δ 3.80 (s, 3H, OC*H*$_3$)-minor, 3.75 (s, 3H, OC*H*$_3$)-major. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.00 (m, 2H), 6.99-6.79 (m, 2H), 3.77 (d, *J* = 23.9 Hz, 3H), 2.92 (ddd, *J* = 61.6, 52.0, 11.3 Hz, 4H), 1.16 (d, *J* = 4.5 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.99, 159.89, 129.05, 128.89, 128.61, 128.18, 121.02, 120.24, 117.53, 117.34, 114.91, 114.69, 55.45, 44.81, 44.12, 30.82, 30.62, 23.35, 22.74, 16.57, 16.42. HRMS (ESI) m/z calculated for $C_{13}H_{14}ON_2Na$, $(M+Na)^+$: m/z 237.1004; found, 237.1004.

3-Phenyl-2-propylpentanedinitrile (**2w**). Purified by column chromatography using silica gel column chromatography (eluent: hexane/EtOAc = 80:20) to afford **2w** as pale yellow oil (31 mg, 49% yield). Product **2w** was isolated as diastereoisomers and the diastereoisomeric ratio was determined by GC analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.07 (m, 5H), 3.24-2.58 (m, 4H), 1.66-1.06 (m, 4H), 0.82 (dt, *J* = 17.1, 6.9 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.42, 136.61, 129.49, 129.25, 128.85, 128.76, 127.86, 127.37, 120.13, 119.47, 117.47, 117.25, 44.01, 43.45, 36.75, 36.34, 32.52, 32.36, 23.27, 22.69, 20.58, 20.35, 13.47, 13.42. HRMS (ESI) m/z calculated for $C_{14}H_{16}N_2Na$, $(M+Na)^+$: m/z 235.1211; found, 235.1211.

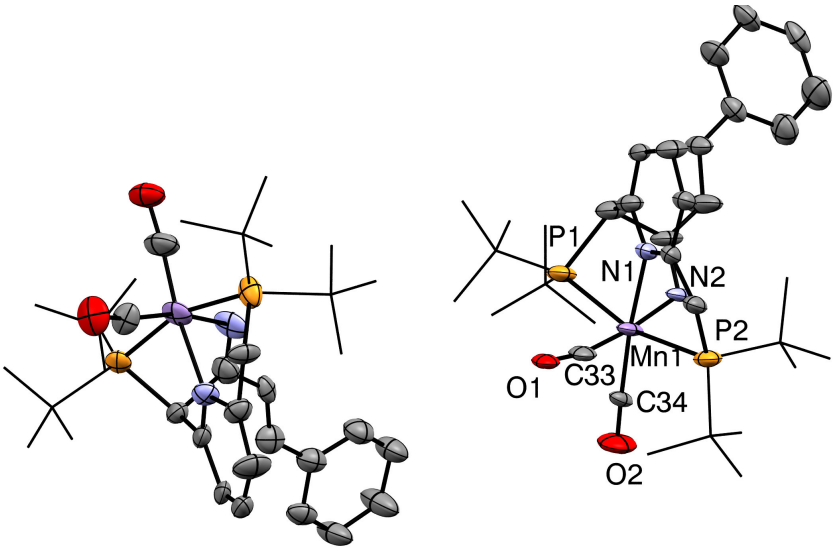
X-ray Crystal Structure Data of the Mn-5 and Mn-5' Complexes

Crystallographic data

The diffraction data from single crystals were collected on: Rigaku Synergy-S diffractometer dual source equipped with hybrid pixel CdTe Dectris 3R 300K detector with MoKα (λ=0.71073 Å) for structure **Mn-5**, and Rigaku Synergy-R diffractometer equipped with HyPix-Arc 150° detector with CuKα (λ=1.54184 Å) for structure **Mn-5'**. The data were processed with CrysAlis^{PRO}.[5] The structures were solved with SHELXT[6] Structures were refined with full matrix least-squares based on F^2 with SHELXL.[7] All structure solution and refinement programs are implemented in Olex-2 GUI.[8] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogens were placed in calculated positions and refined in a riding mode. Structure **Mn-5'** was refined as twin with Flack parameter 0.481.



Mn-5



Mn-5'

Figure S4. X-ray Crystal Structure Data of the **Mn-5** and **Mn-5'**. Atoms are presented as thermal ellipsoids with 50% probability. Hydrogen atoms are omitted for clarity. The ^{t}Bu side chains groups are displayed as wireframes for clarity. [**Note: Mn-5 and Mn-5'** are the same structure as two molecules in the asymmetric unit cell and are refined separately]

Table S1. Crystallographic data of complexes **Mn-5** and **Mn-5'**

	Mn-5	**Mn-5'**
CCDC	2224607	2224950
Empirical formula	$4C_{34}H_{49}MnN_2O_2P_2$, H_2O	$C_{34}H_{49}MnN_2O_2P_2$
Crystal description	Orange block	Orange plate
Crystal size (mm^3)	0.161×0.122×0.078	0.130x0.070x0.030
Formula weight (g/mol)	2556.53	634.63
T (K)	100.0(2)	100.0(2)
Wavelength (Å)	0.71073	1.54184

Crystal system	Monoclinic	Monoclinic
Space group	*P 2$_1$/c*	*P 2$_1$*
a (Å)	10.4236(3)	9.5026(5)
b (Å)	17.9728(5)	16.9110(6)
c (Å)	17.9093(5)	21.3649(10)
α (°)	90	90
β (°)	90.648(2)	100.110(4)
γ (°)	90	90
Volume (Å^3)	3354.92 (17)	3380.0(3)
Z	1	4
ρ_{cal} (mg/m^3)	1.265	1.247
μ (mm^{-1})	0.522	4.308
No. of reflection collected (Unique)	43438(9616)	12804(12804)
R_{int}	0.0499	
Completeness to θ (%)	100.0	99.6
Limiting indices	-14<=h<=13, -25<=k<=18, -24<=l<=23	-11<=h<=11 -19<=k<=19, -25<=l<=25
Data\restraints\ parameters	9616 / 0 / 391	12804 / 657 / 683

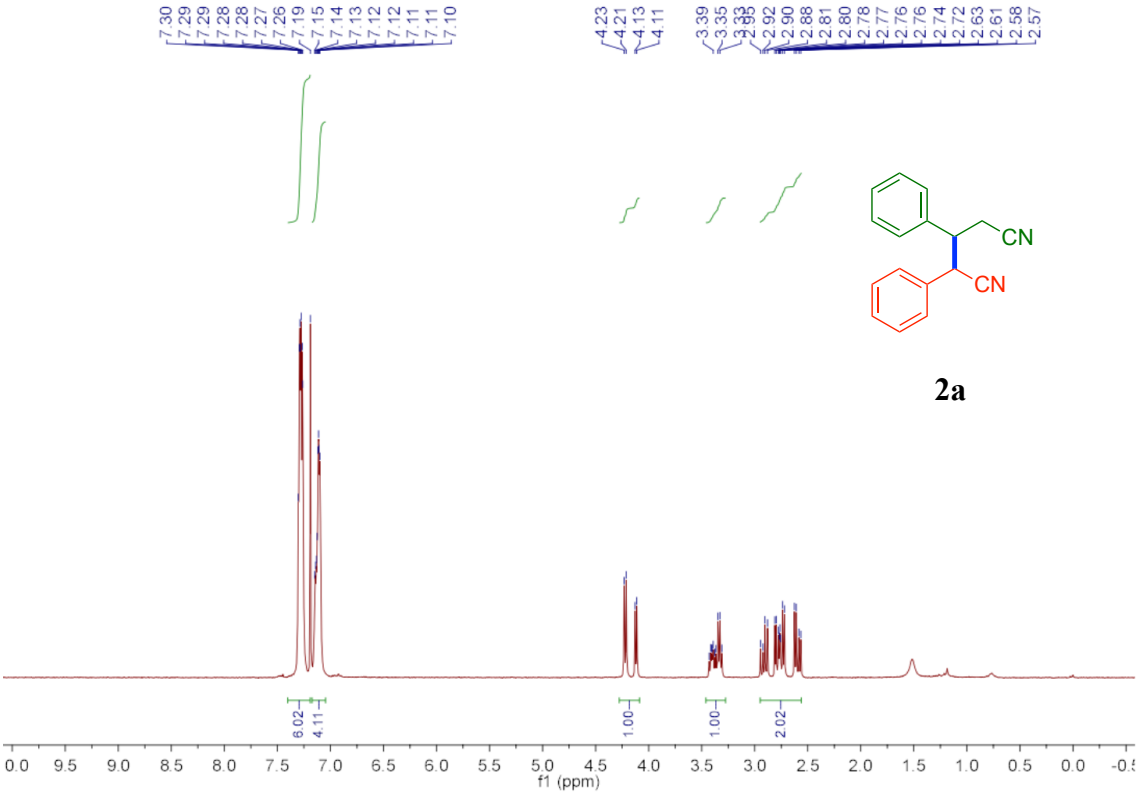
Goodness-of-fit on F^2	1.072	1.041
Final R_1 and wR_2 indices [$I>2\sigma(I)$]	R1 = 0.0434, wR2 = 0.0999	R1 = 0.0888, wR2 = 0.2071
R_1 and wR_2 indices (all data)	R1 = 0.0585, wR2 = 0.1057	R1 = 0.0978, wR2 = 0.2140
Largest diff. peak and hole ($e/Å^3$)	0.426 and -0.299	0.809 and -0.408

Table S2. Selected bond lengths [Å] and bond angles [°] of complex **Mn-5**

Bond Lengths [Å]		Bond Angles [°]	
Mn(1)-P(1)	2.3107(5)	P(1)-Mn(1)-P(2)	162.265(18)
Mn(1)-P(2)	2.3127(5)	N(1)-Mn(1)-P(1)	83.16(4)
Mn(1)-N(1)	2.0496(13)	N(1)-Mn(1)-P(2)	79.66(4)
Mn(1)-N(2)	2.0490(14)	N(2)-Mn(1)-P(1)	78.57(4)
Mn(1)-C(33)	1.7748(16)	N(2)-Mn(1)-P(2)	95.00(4)
Mn(1)-C(34)	1.7874(17)	N(2)-Mn(1)-N(1)	83.39(5)
P(1)-C(1)	1.8656(17)	C(33)-Mn(1)-P(1)	102.09(5)
P(1)-C(8)	1.8990(17)	C(33)-Mn(1)-P(2)	94.82(5)
P(1)-C(12)	1.9120(17)	C(33)-Mn(1)-N(1)	173.79(6)
P(2)-C(7)	1.8545(17)	C(33)-Mn(1)-N(2)	94.35(6)
P(2)-C(16)	1.8934(18)	C(33)-Mn(1)-C(34)	89.71(7)
P(2)-C(20)	1.8965(18)	C(34)-Mn(1)-P(1)	93.27(5)
O(1)-C(33)	1.168(2)	C(34)-Mn(1)-P(2)	92.10(5)
O(2)-C(34)	1.162(2)	C(34)-Mn(1)-N(1)	93.31(6)
O(3)-H(3A)	0.8549	C(34)-Mn(1)-N(2)	171.49(6)
O(3)-H(3B)	0.8365	C(1)-P(1)-Mn(1)	89.14(5)
N(1)-C(2)	1.349(2)	C(1)-P(1)-C(8)	104.77(7)
N(1)-C(6)	1.358(2)	C(1)-P(1)-C(12)	105.21(8)
N(2)-C(24)	1.280(2)	C(8)-P(1)-Mn(1)	122.92(6)

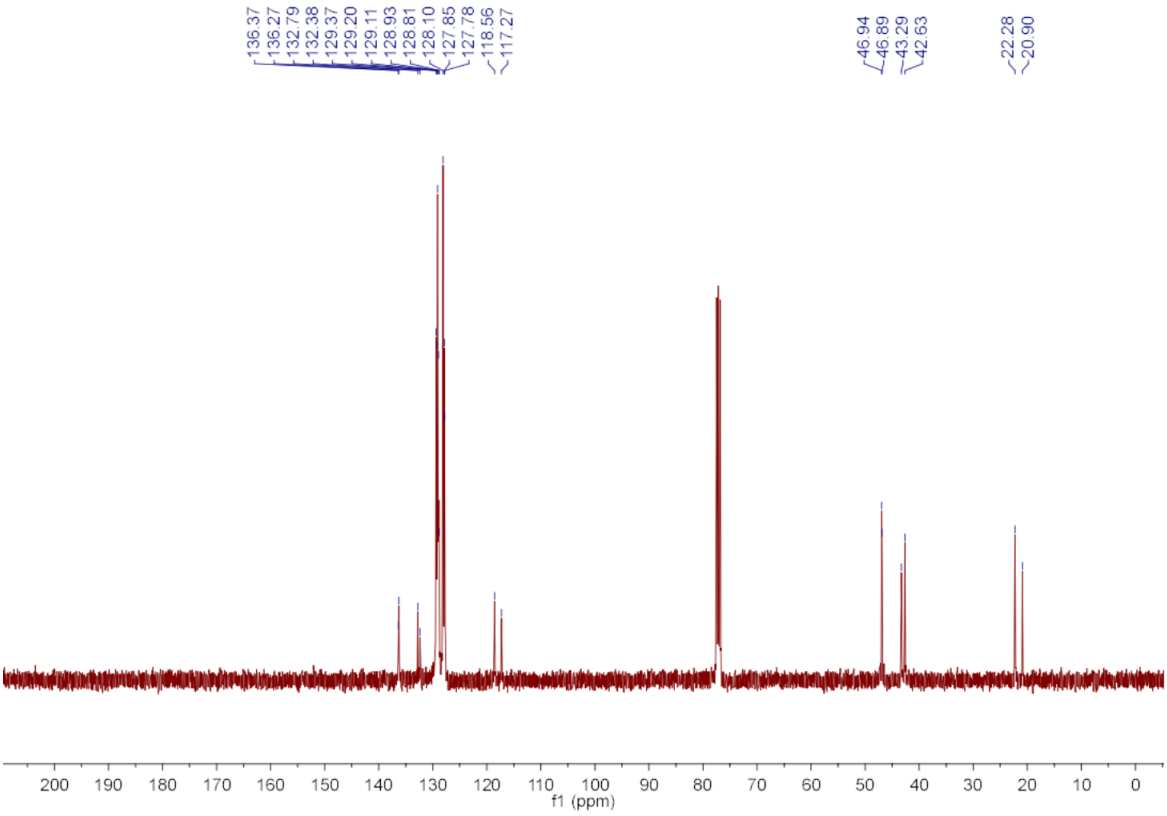
NMR Spectra of the Products

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

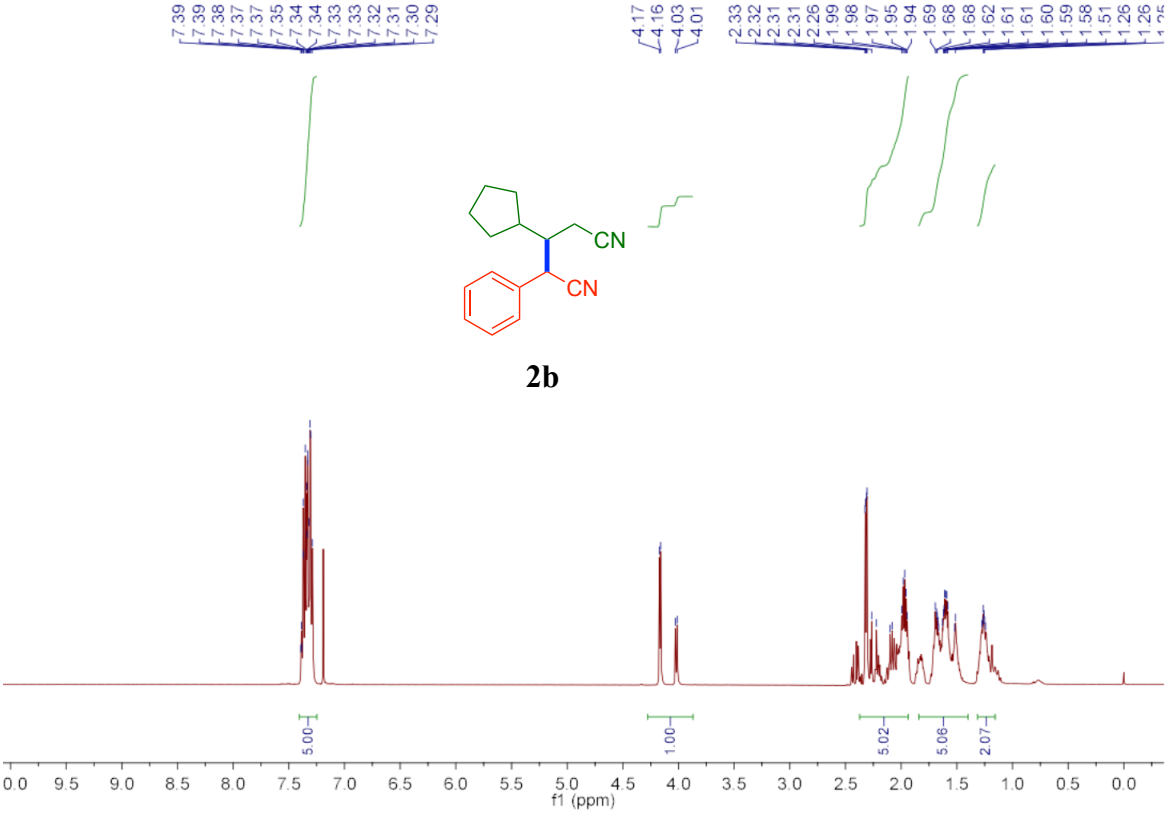


2a

^{13}C NMR (100.6 MHz, $CDCl_3$)

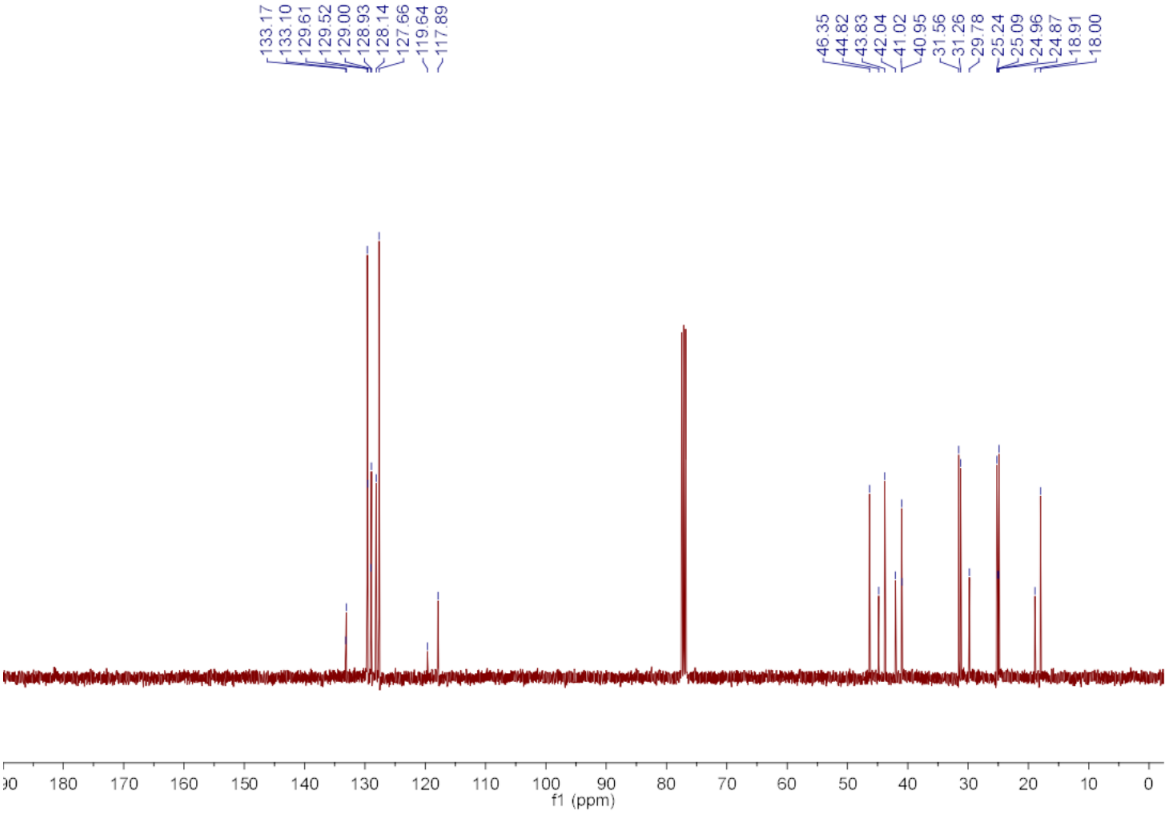


^{1}H NMR (400 MHz, $CDCl_3$)

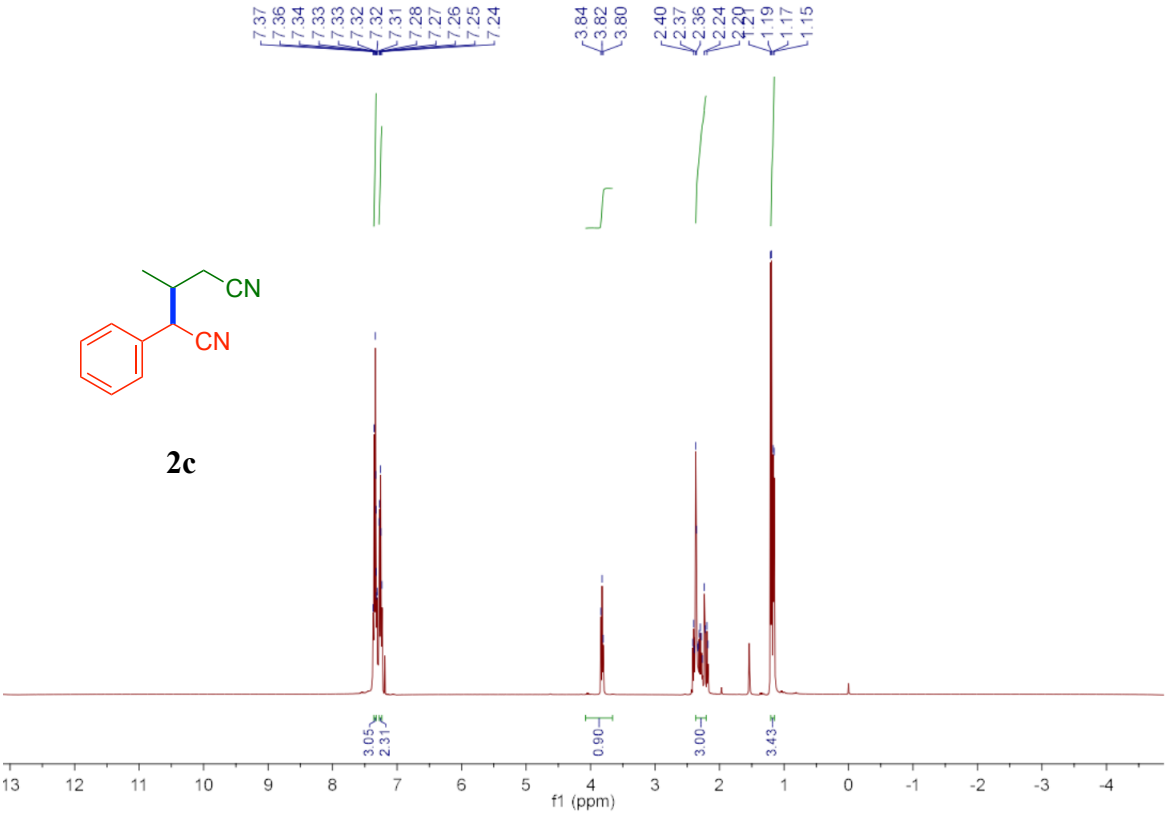


2b

^{13}C NMR (100.6 MHz, $CDCl_3$)

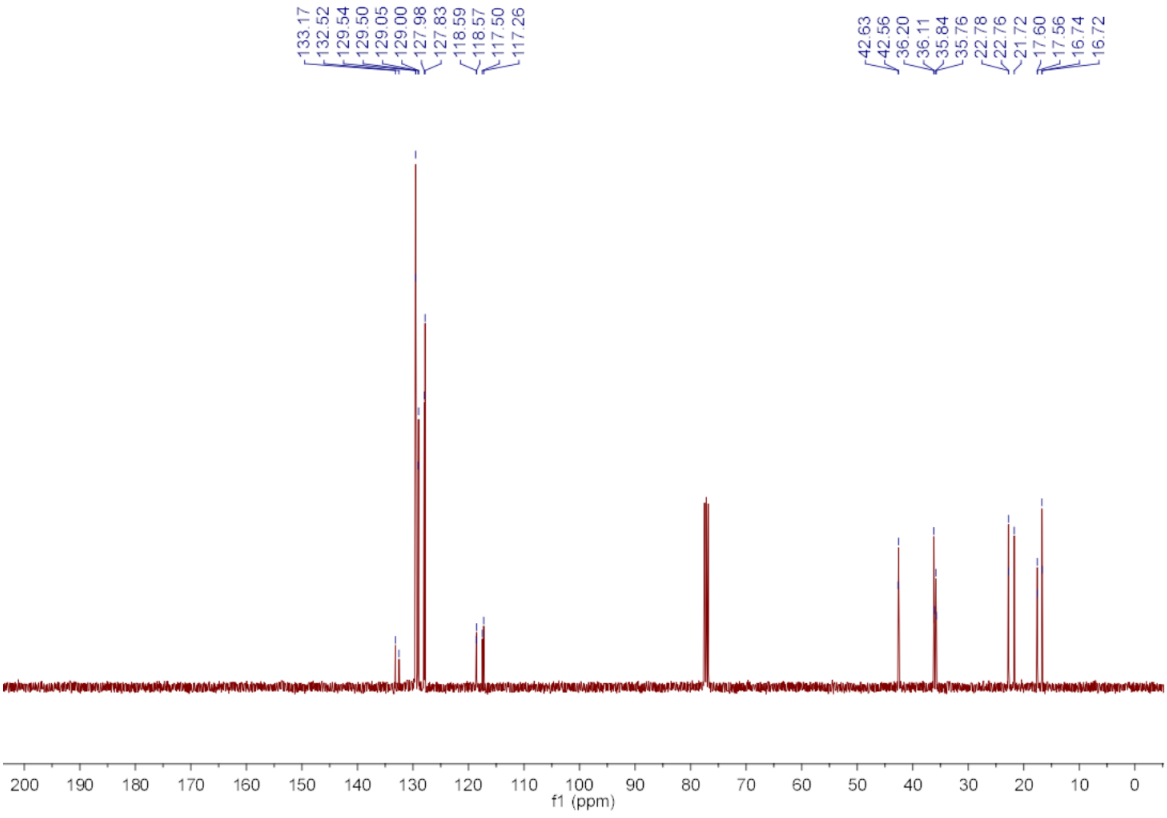


^{1}H NMR (400 MHz, $CDCl_3$)

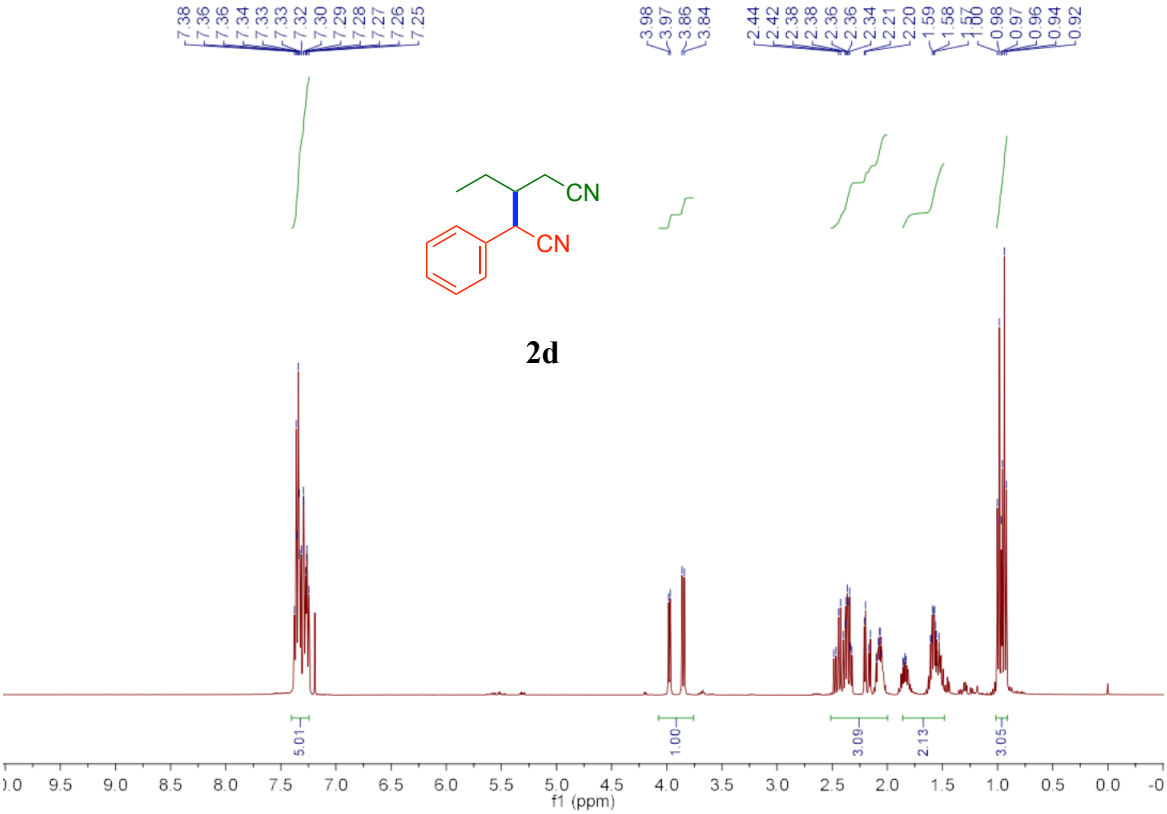


2c

^{13}C NMR (100.6 MHz, $CDCl_3$)

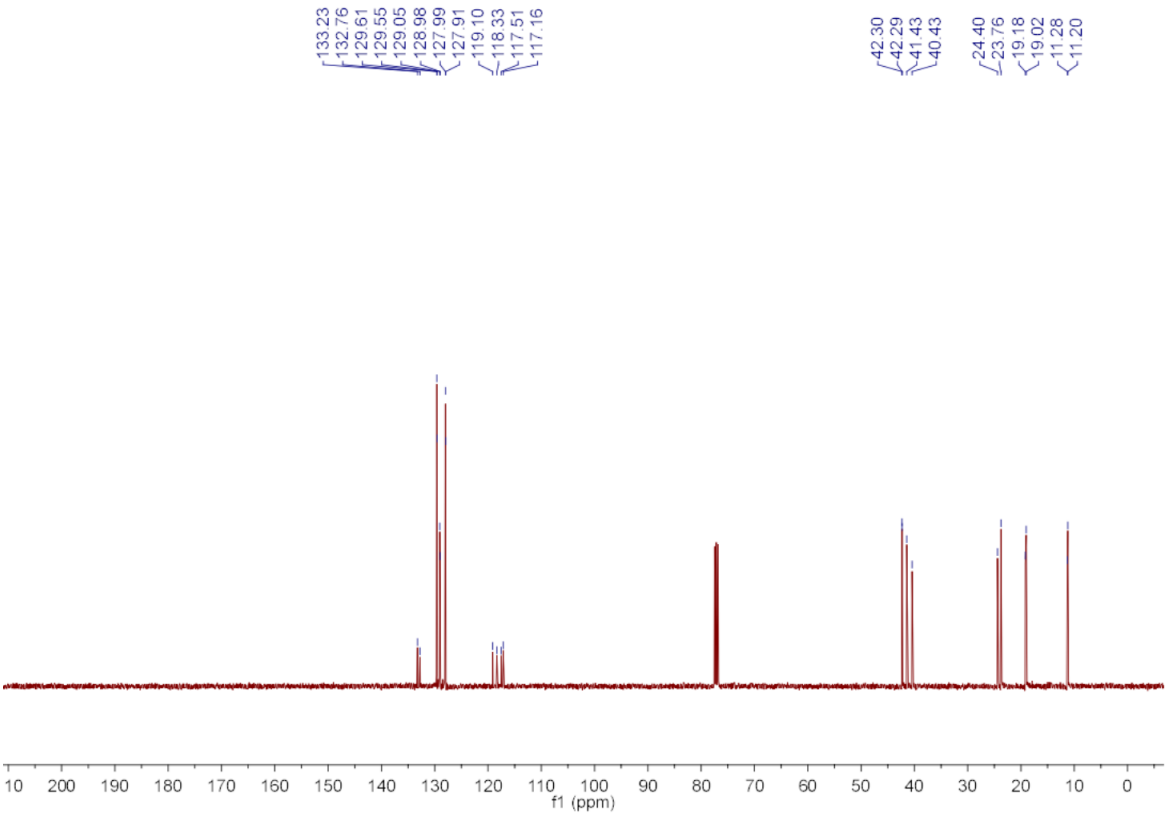


^{1}H NMR (400 MHz, $CDCl_3$)

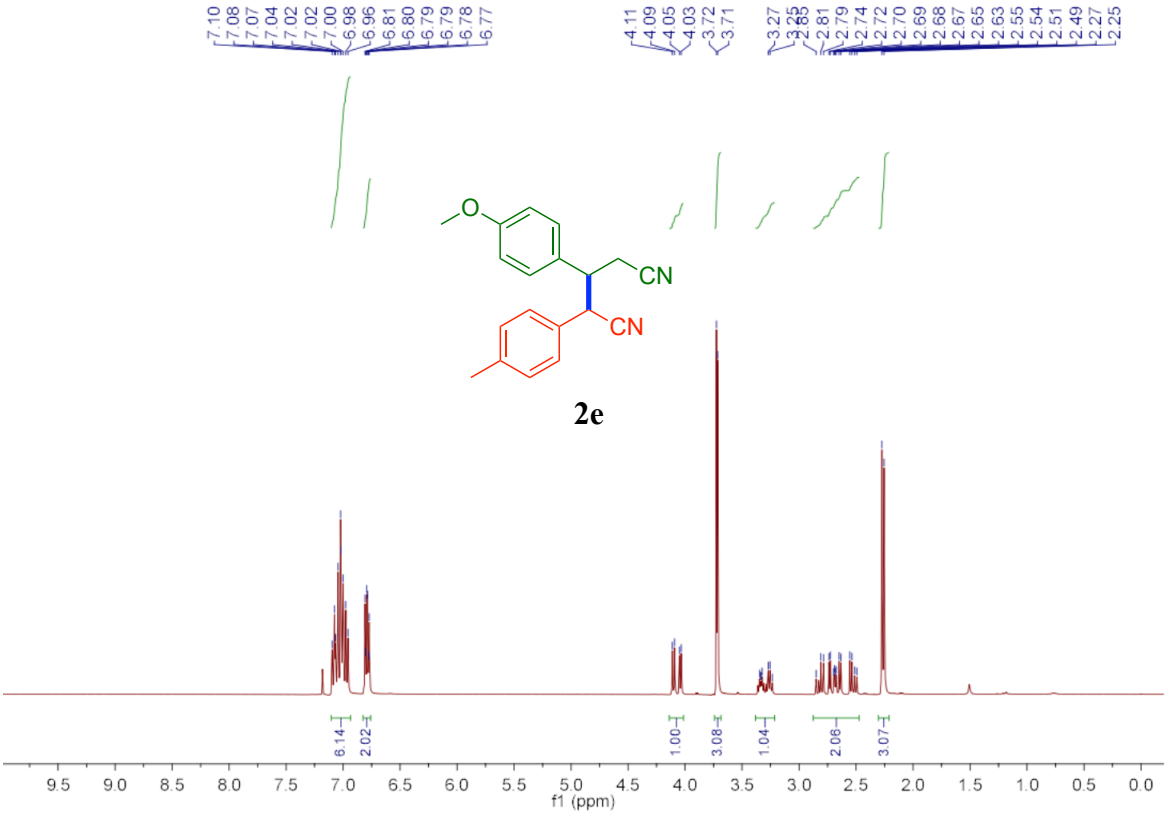


2d

^{13}C NMR (100.6 MHz, $CDCl_3$)

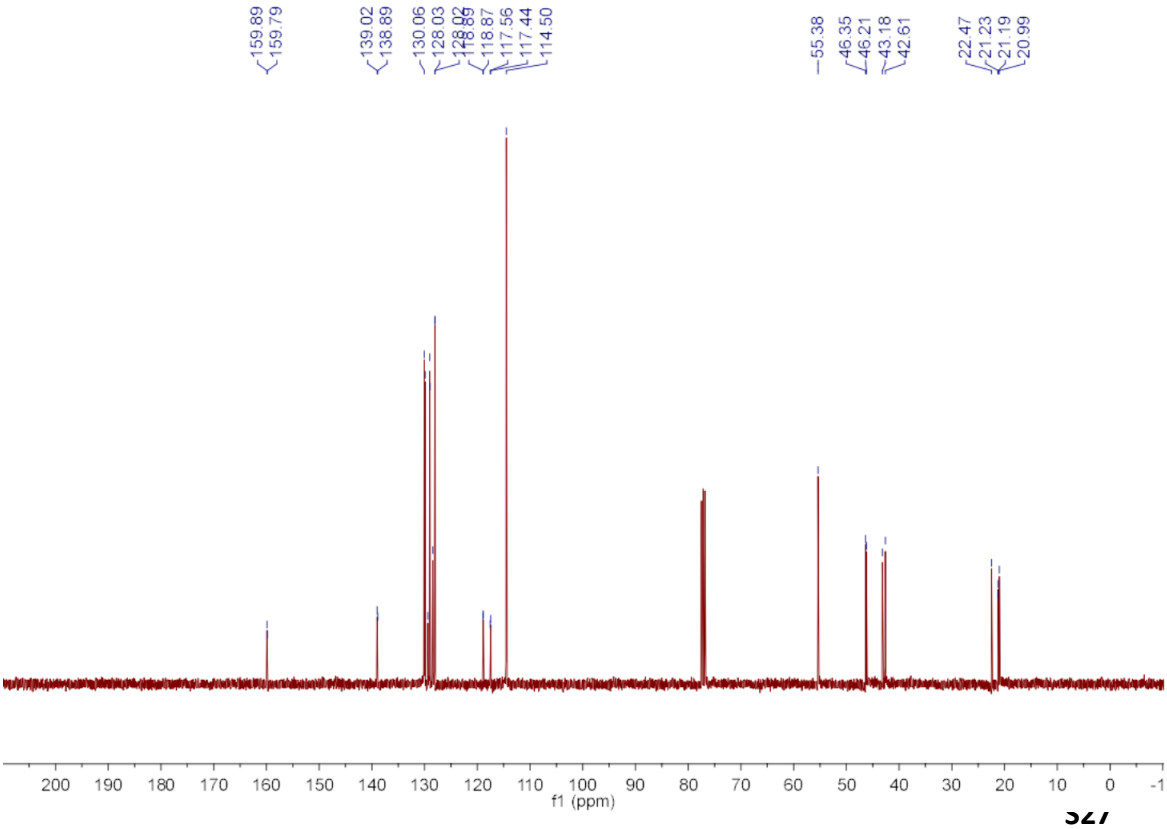


^{1}H NMR (400 MHz, $CDCl_3$)

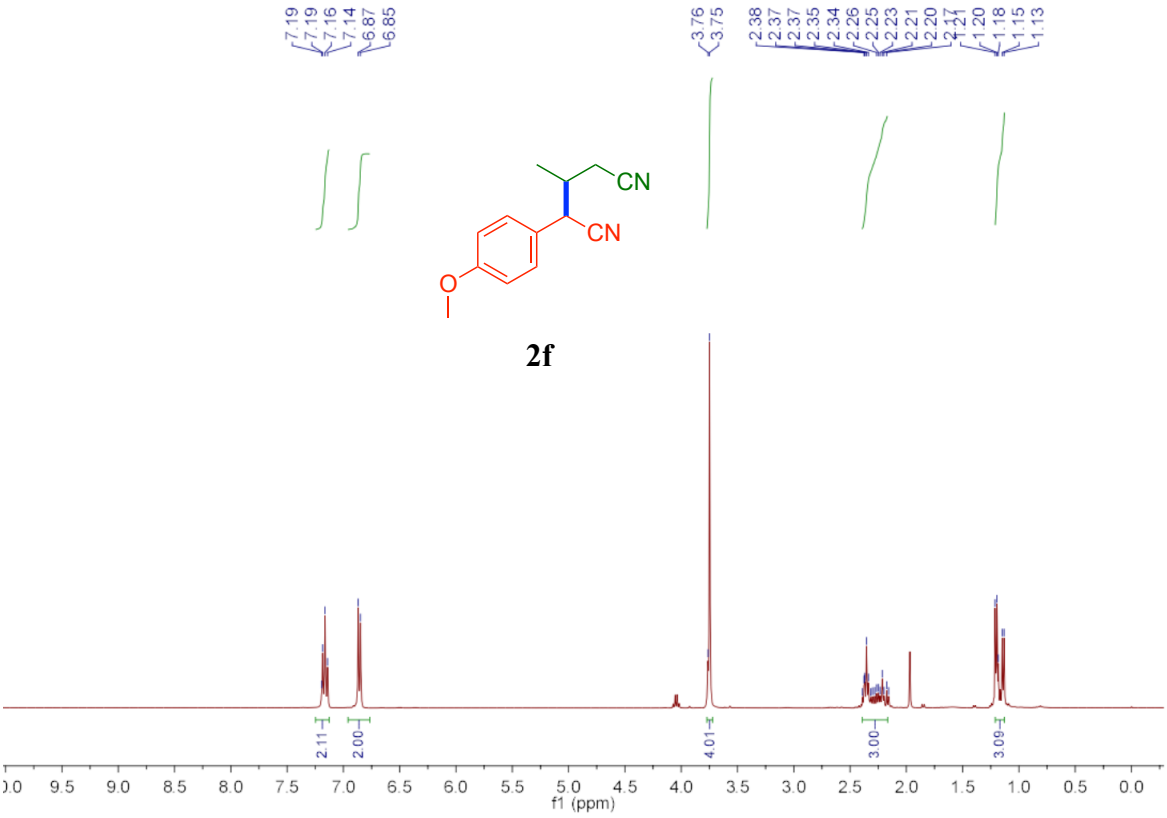


2e

^{13}C NMR (100.6 MHz, $CDCl_3$)

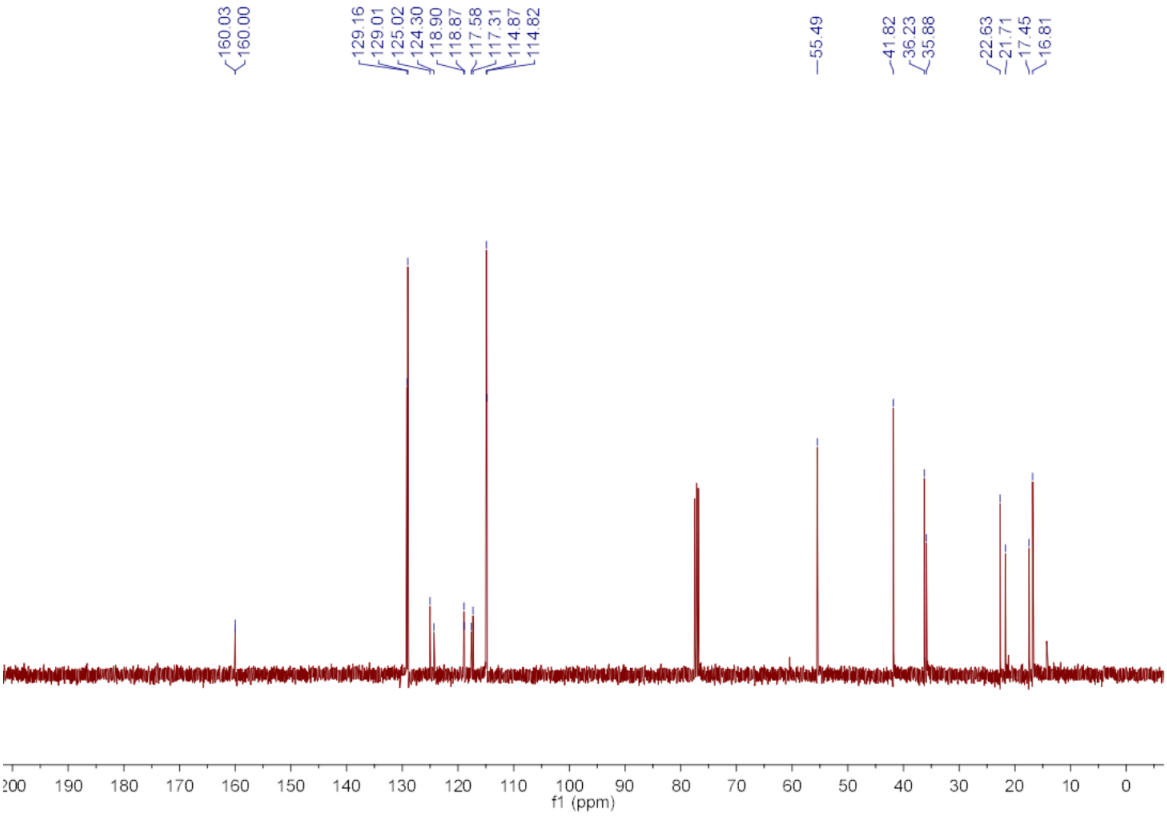


^{1}H NMR (400 MHz, $CDCl_3$)

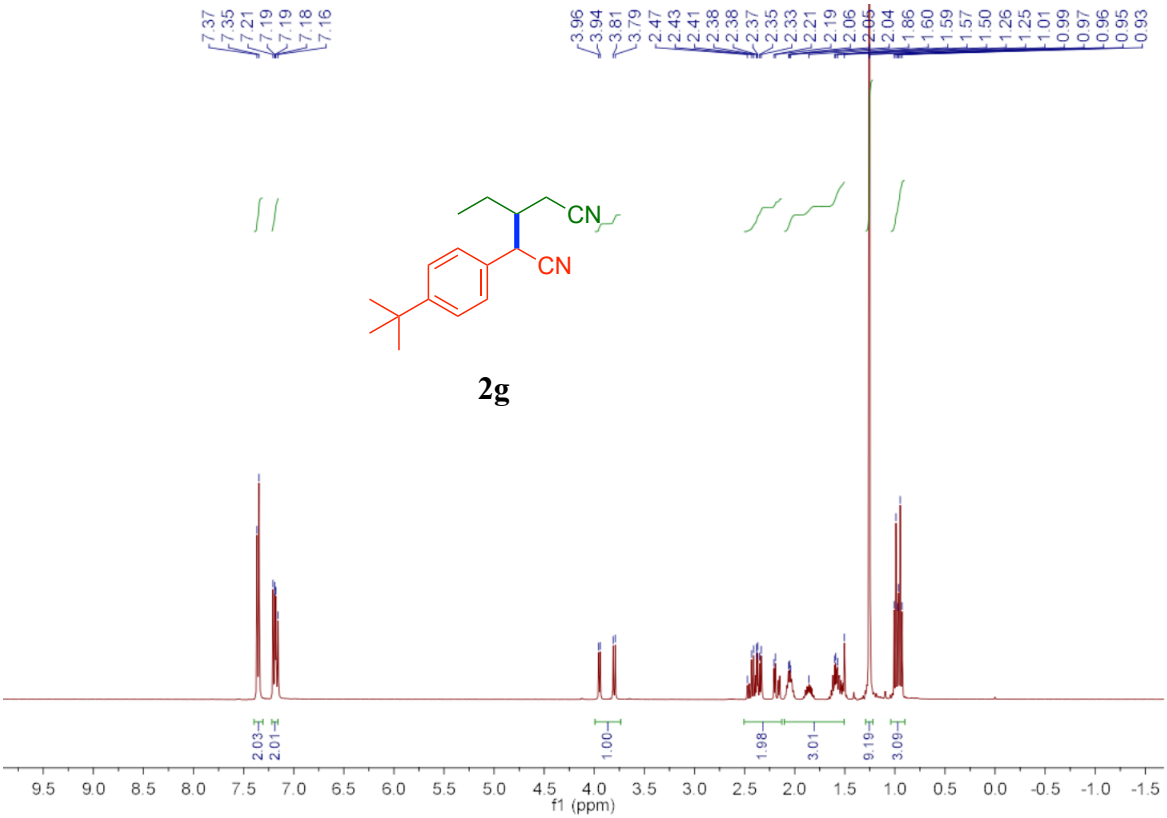


2f

^{13}C NMR (100.6 MHz, $CDCl_3$)

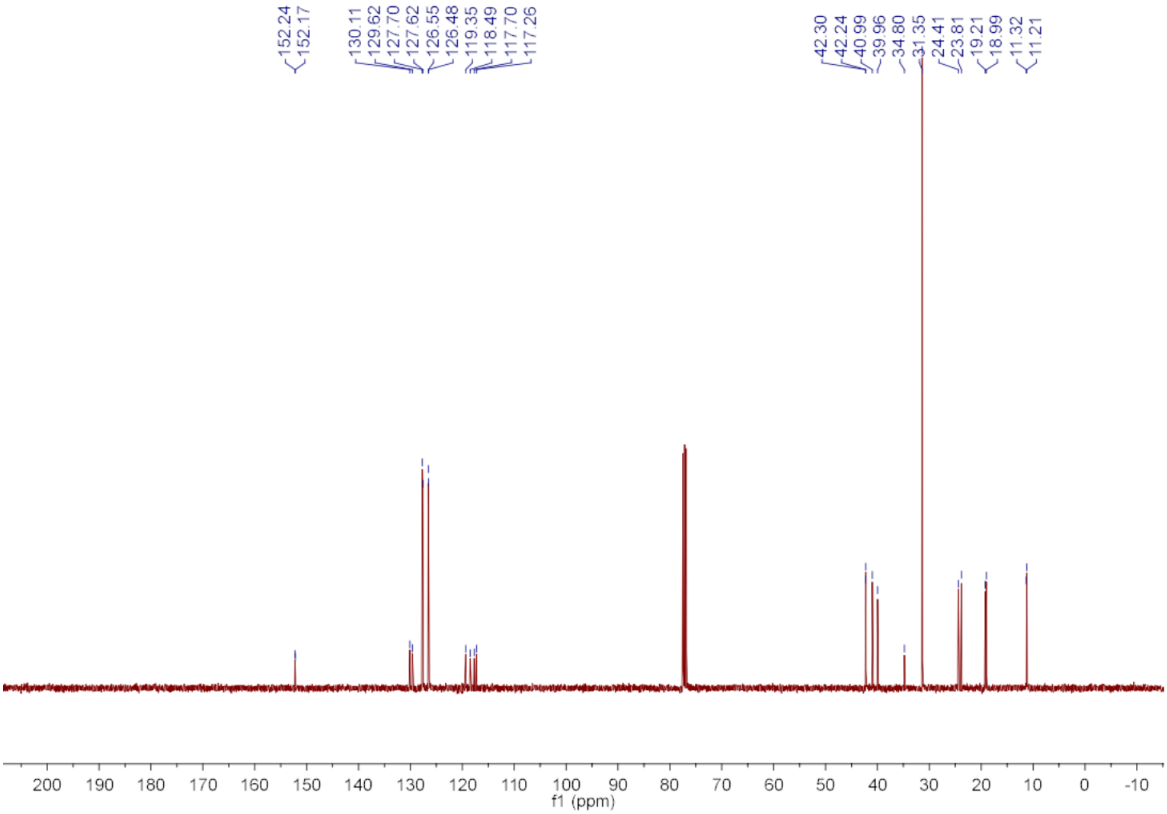


^{1}H NMR (400 MHz, $CDCl_3$)

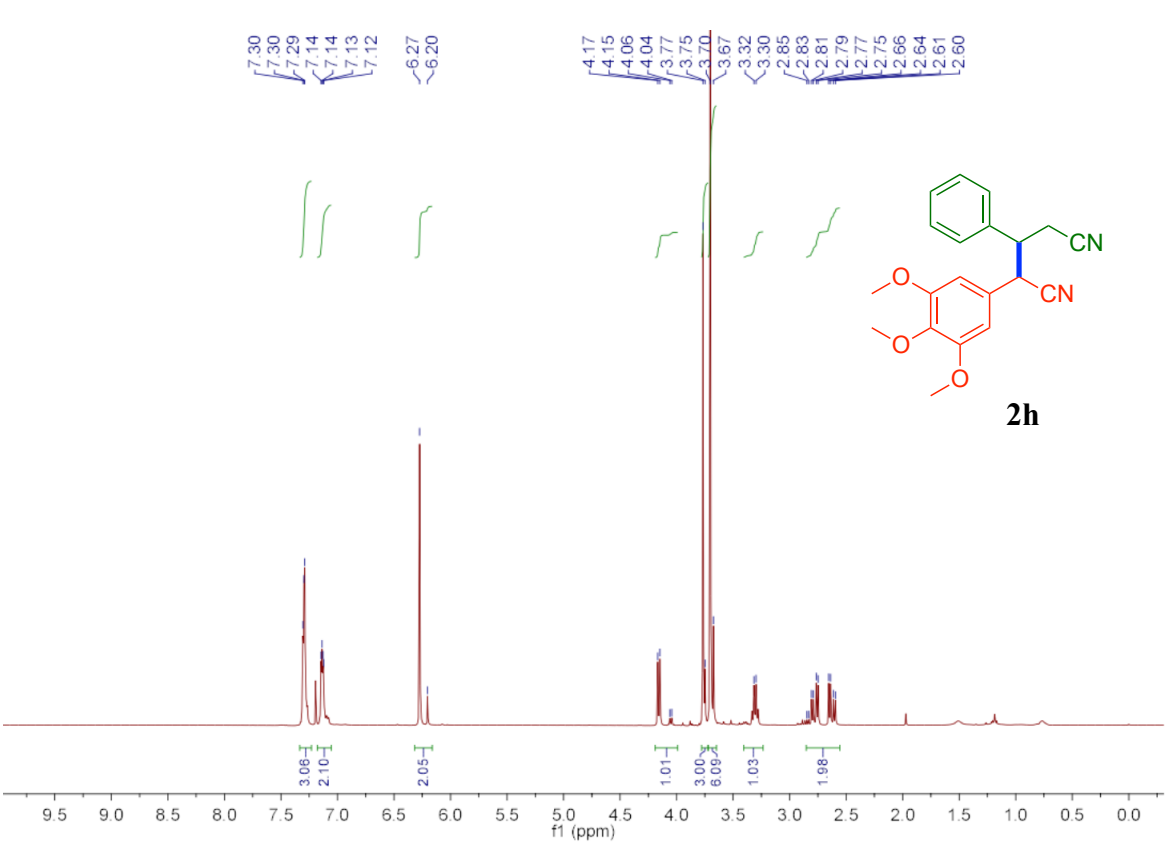


2g

^{13}C NMR (100.6 MHz, $CDCl_3$)

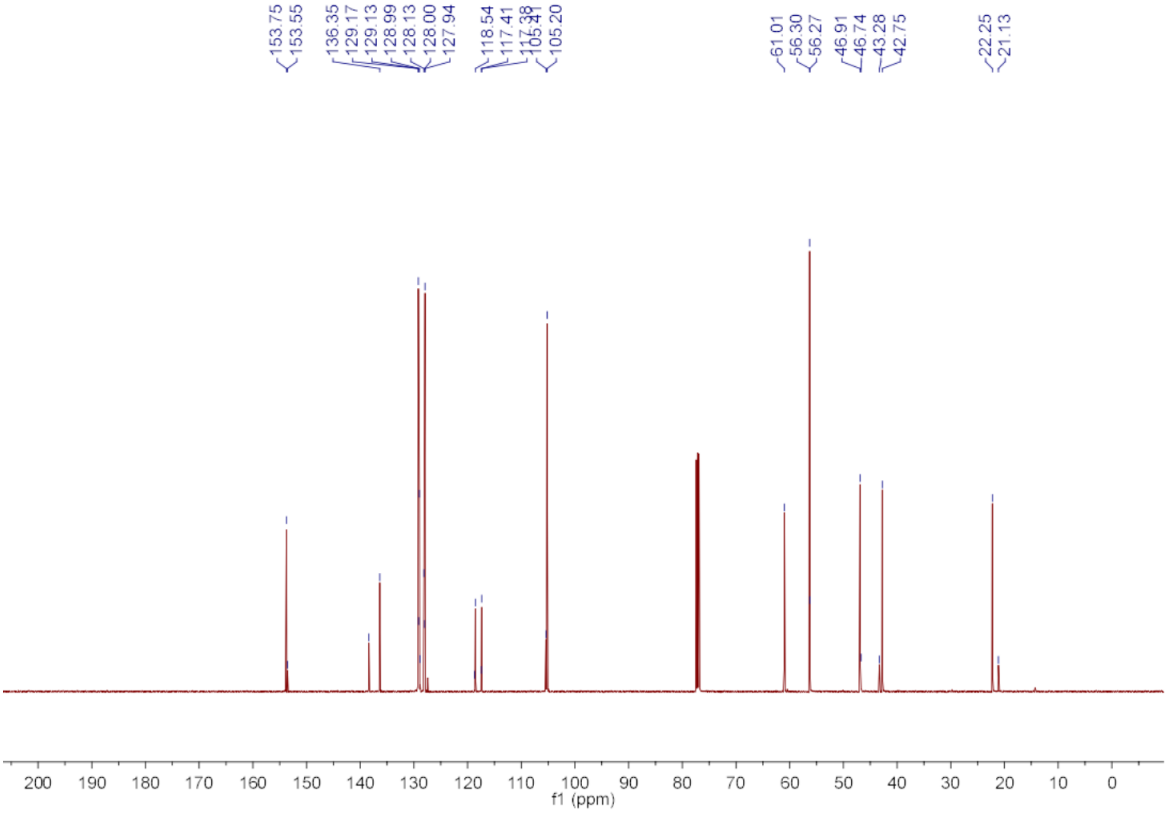


^{1}H NMR (400 MHz, $CDCl_3$)

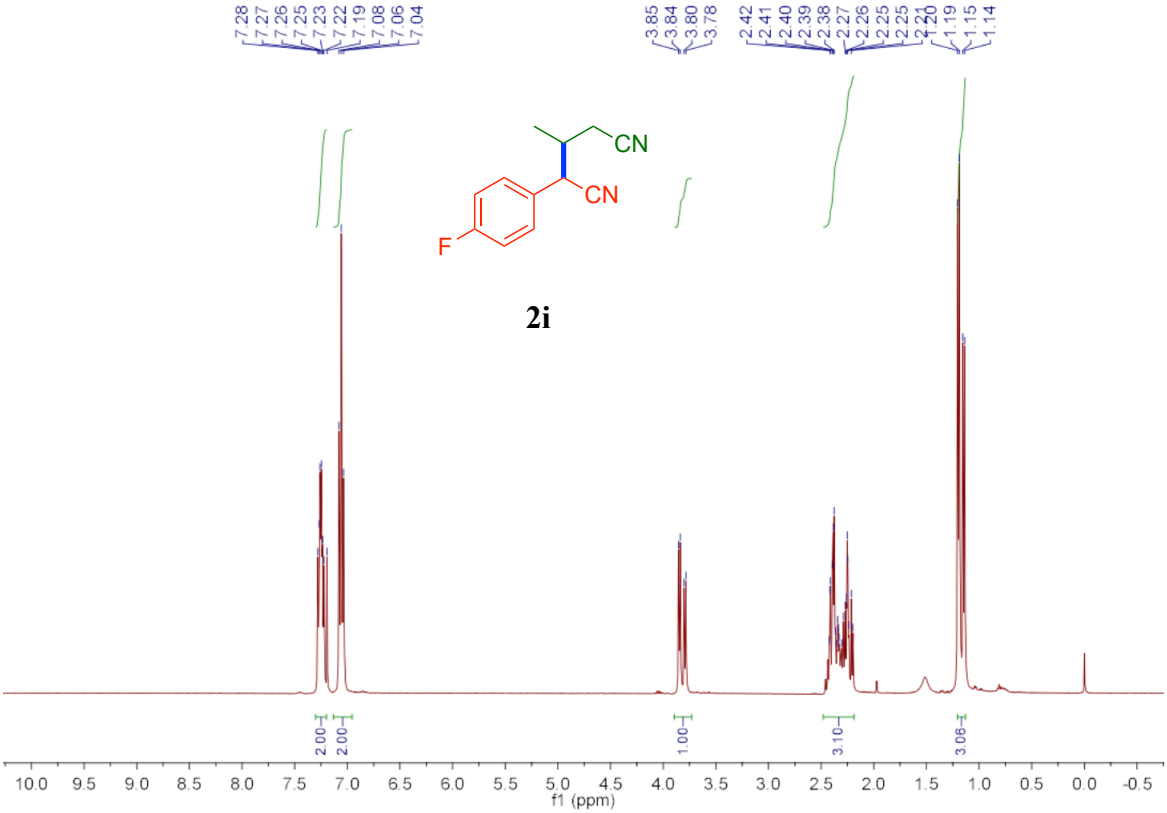


2h

^{13}C NMR (100.6 MHz, $CDCl_3$)

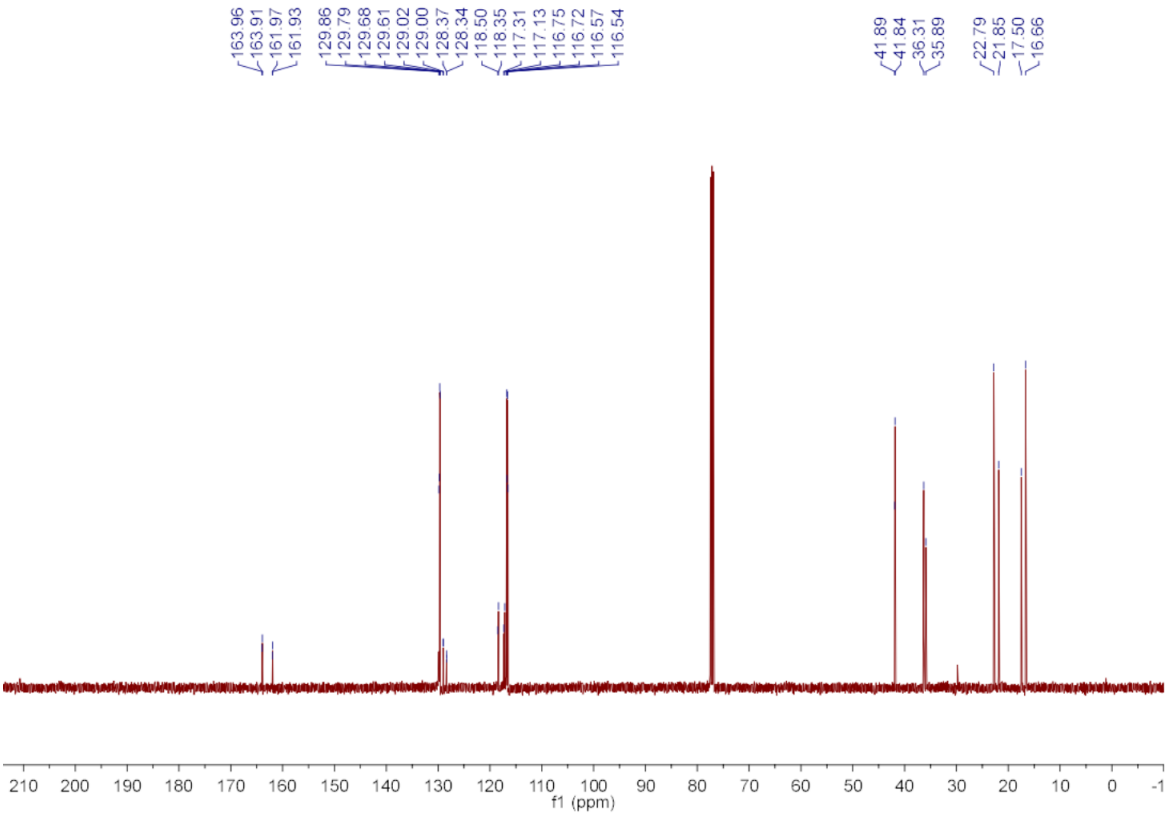


^{1}H NMR (400 MHz, $CDCl_3$)

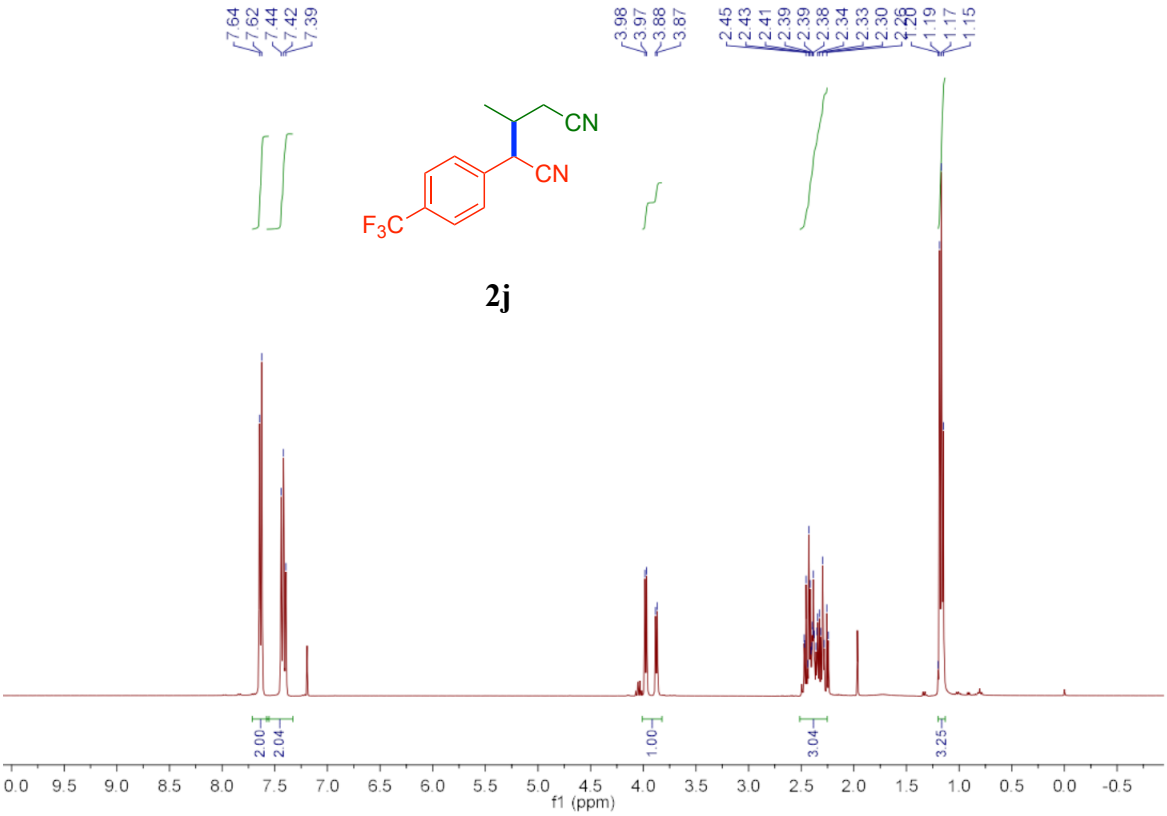


2i

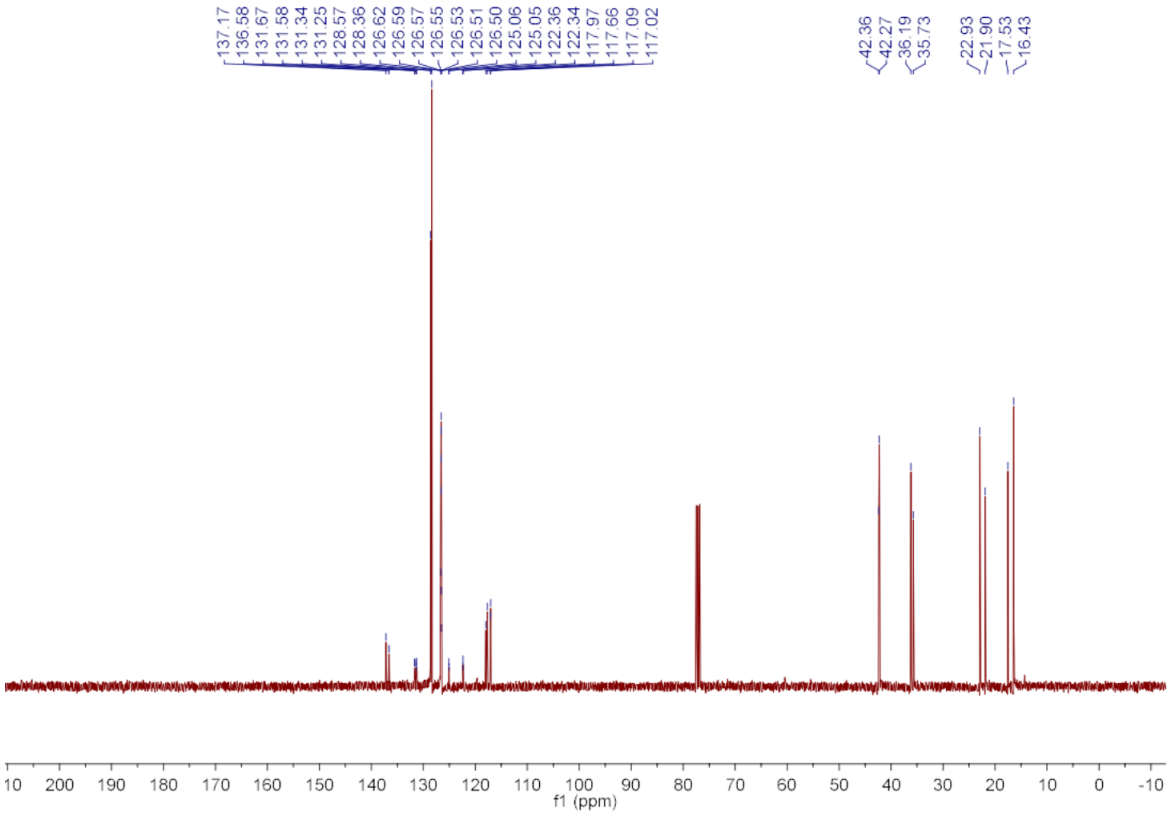
^{13}C NMR (125 MHz, $CDCl_3$)



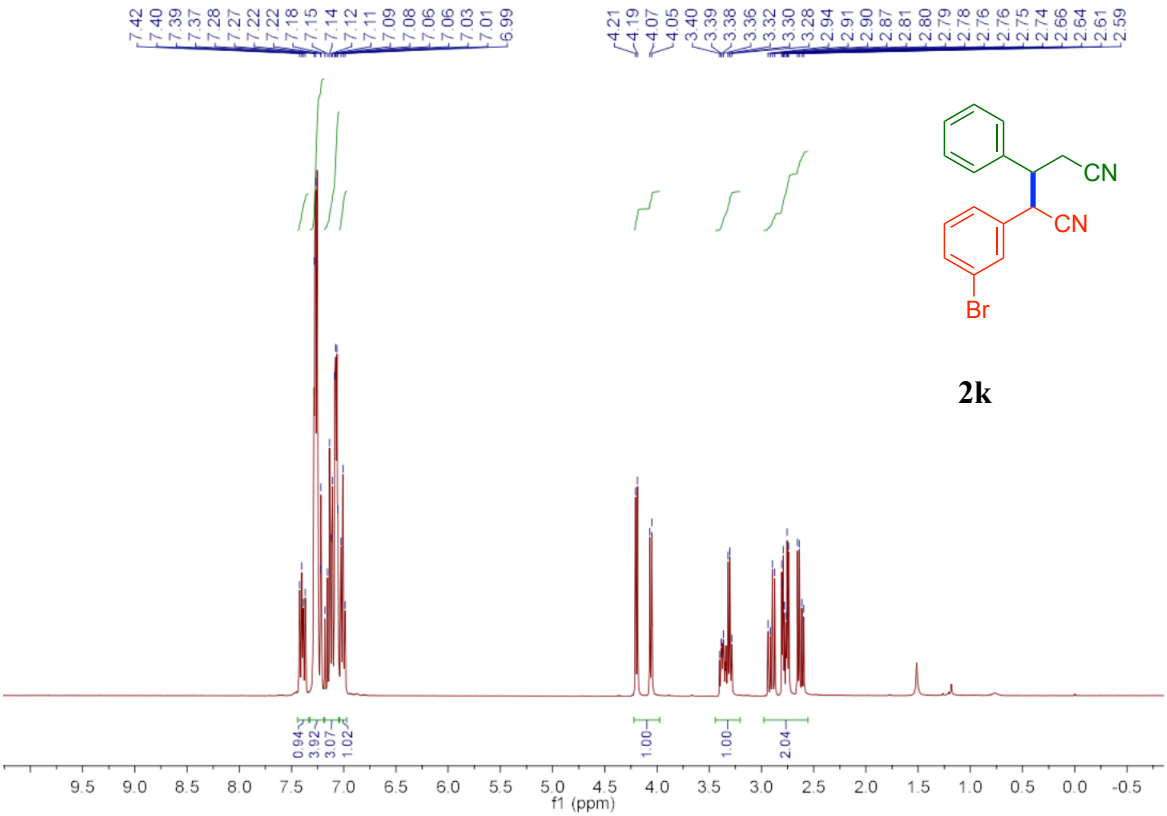
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100.6 MHz, $CDCl_3$)

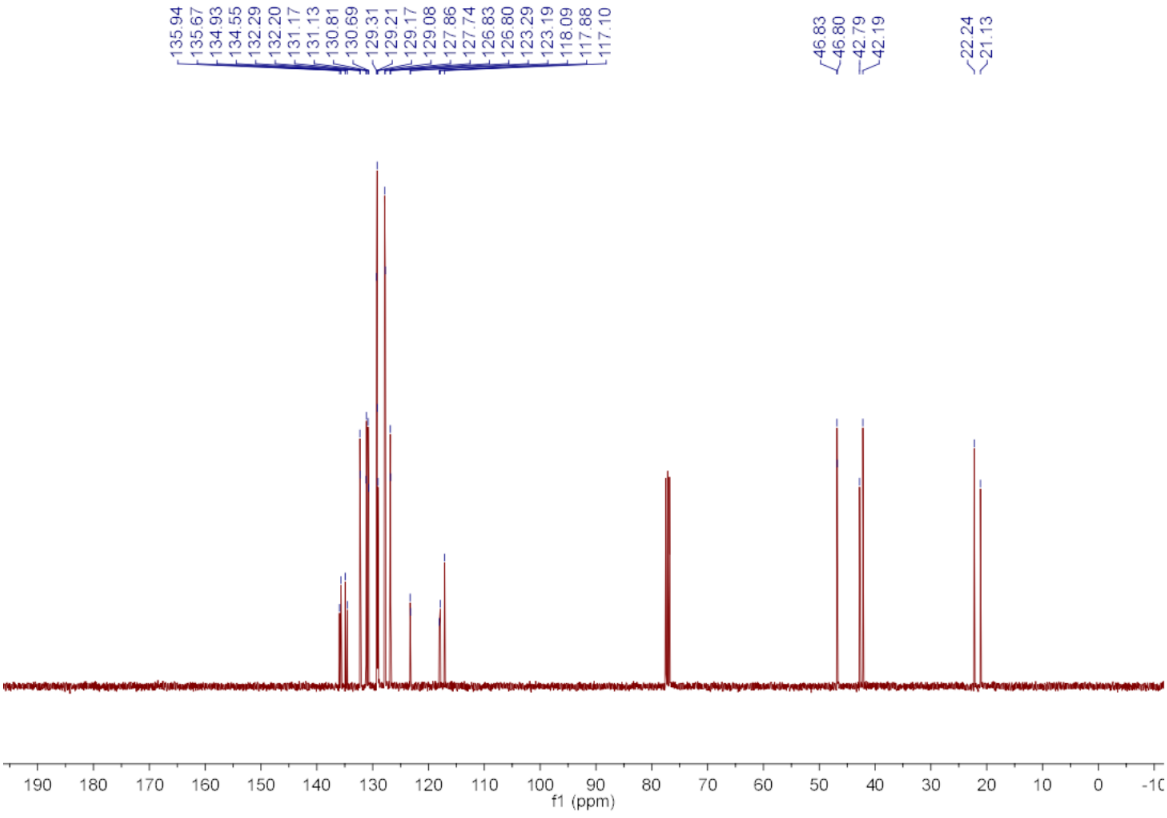


^{1}H NMR (400 MHz, $CDCl_3$)

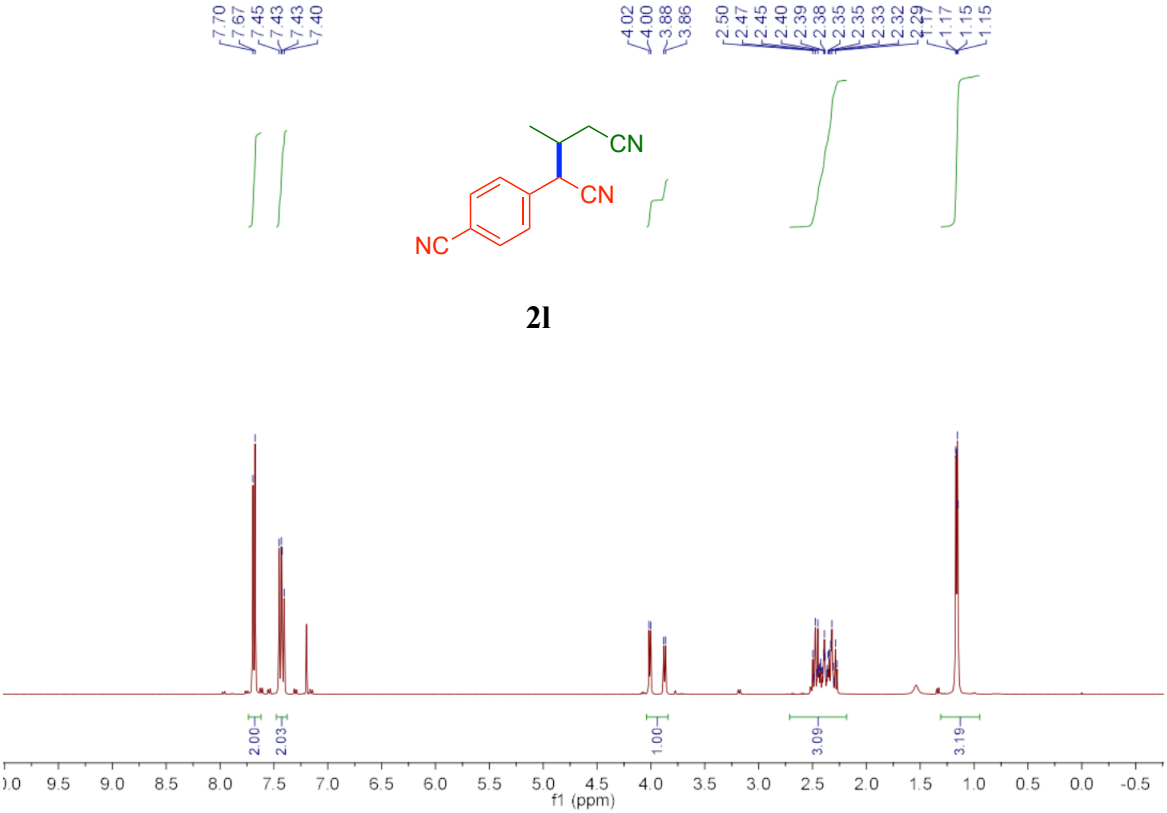


2k

^{13}C NMR (100.6 MHz, $CDCl_3$)

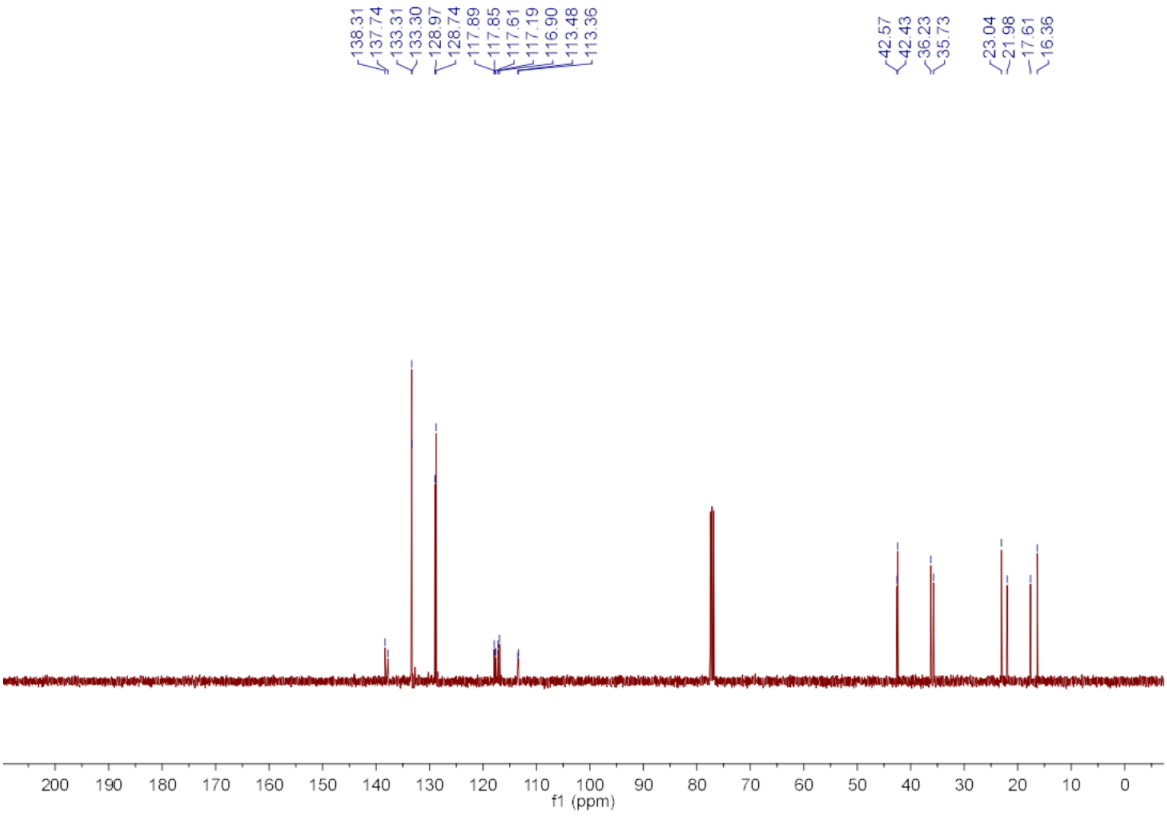


^{1}H NMR (400 MHz, $CDCl_3$)

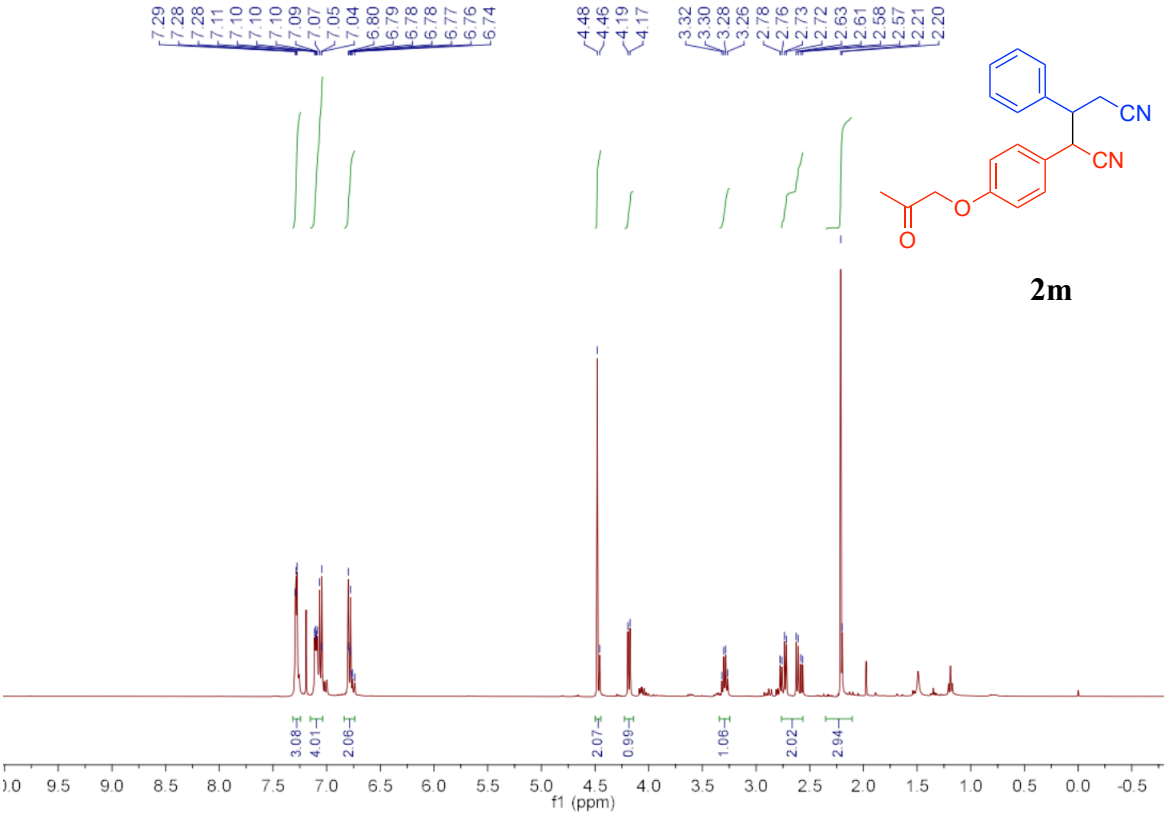


21

^{13}C NMR (100.6 MHz, $CDCl_3$)

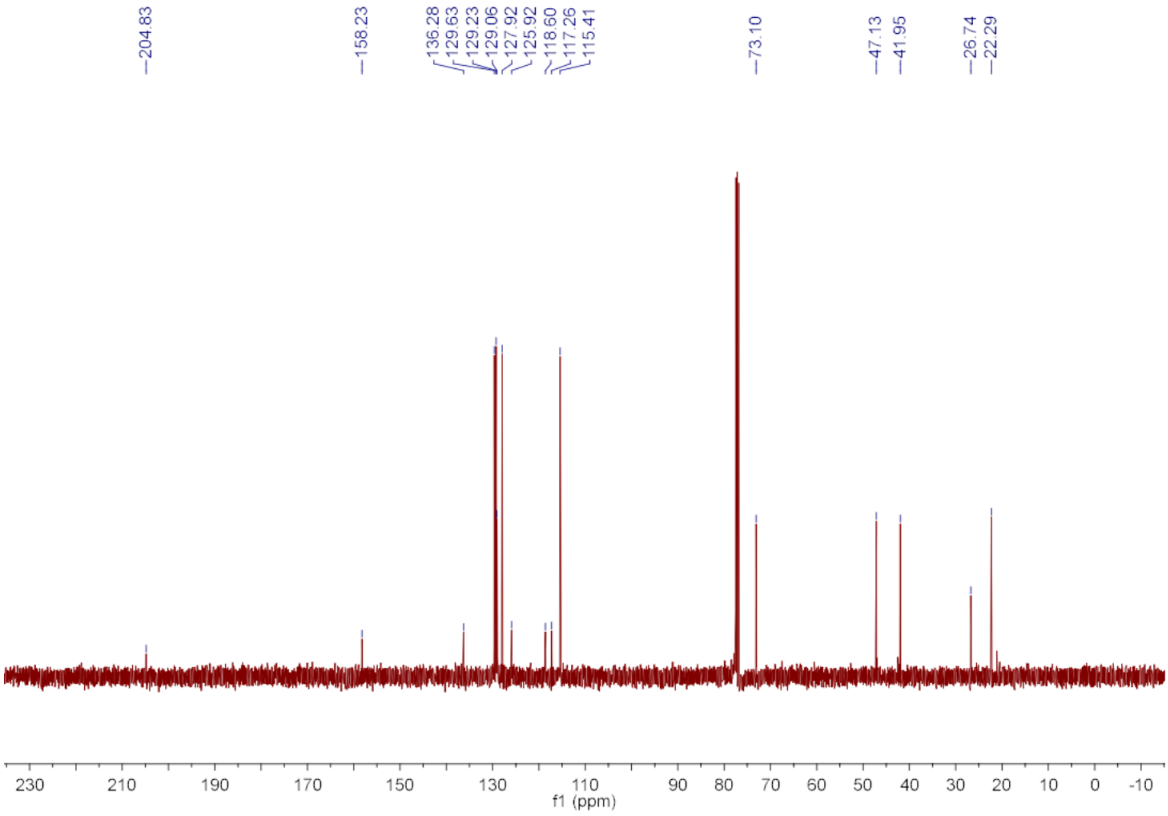


^{1}H NMR (400 MHz, $CDCl_3$)

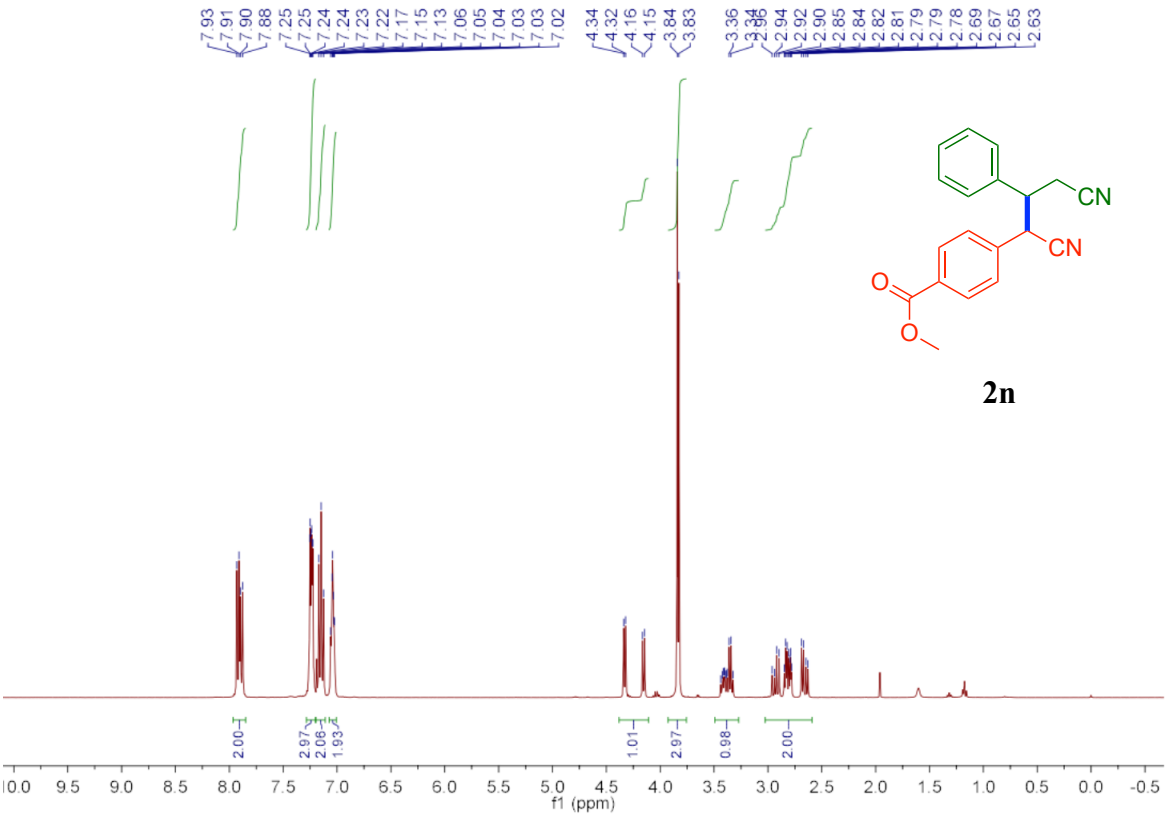


2m

^{13}C NMR (100.6 MHz, $CDCl_3$)

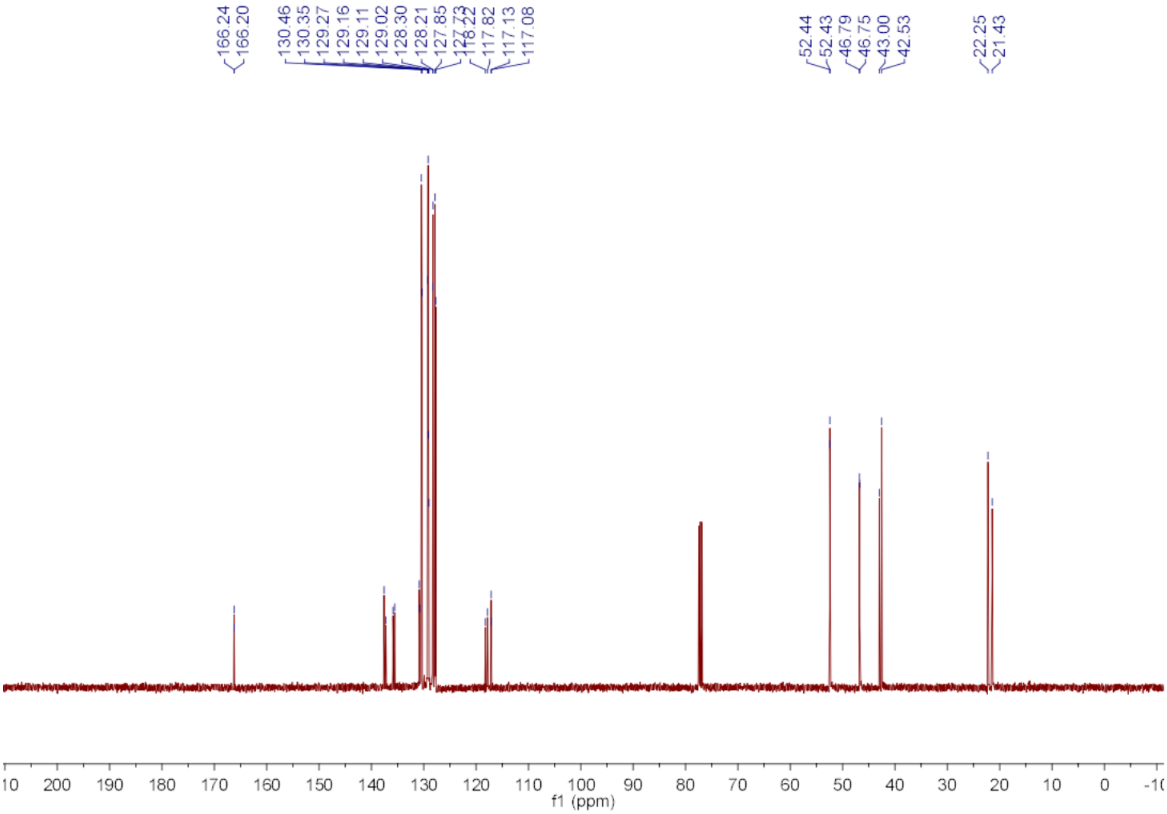


^{1}H NMR (400 MHz, $CDCl_3$)

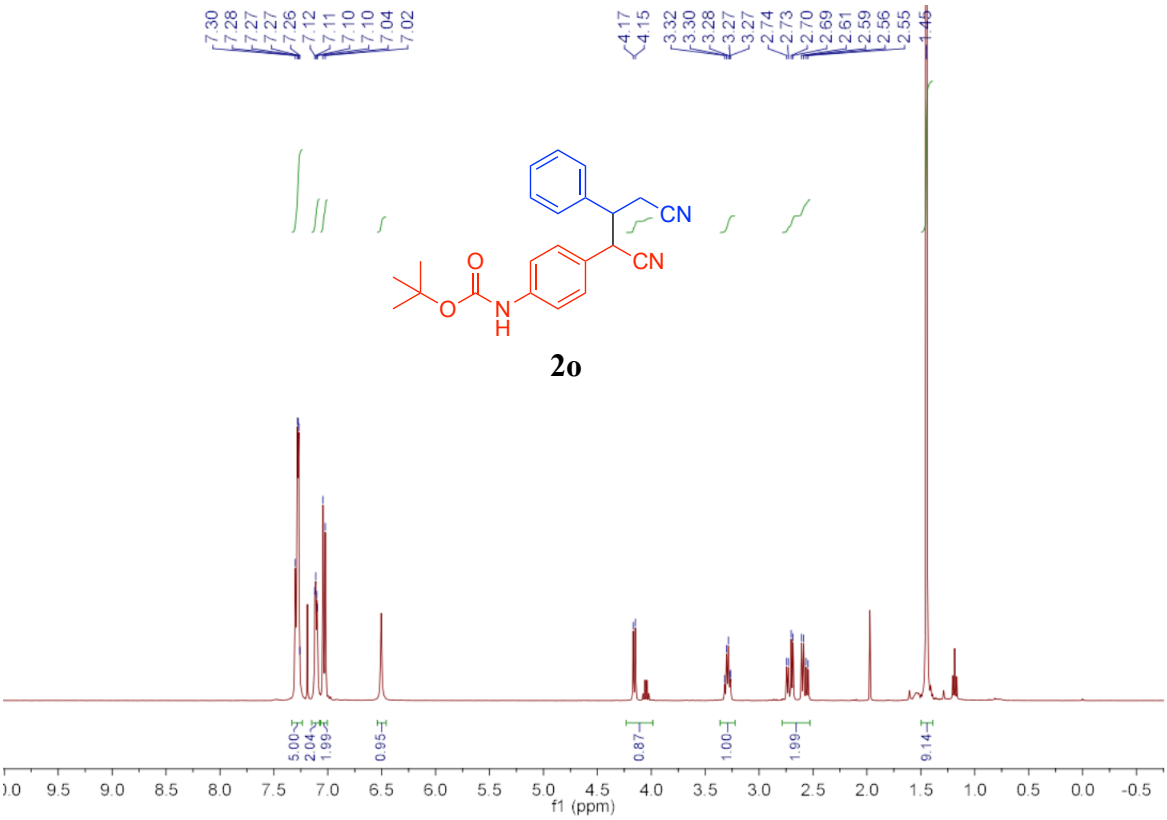


2n

^{13}C NMR (100.6 MHz, $CDCl_3$)

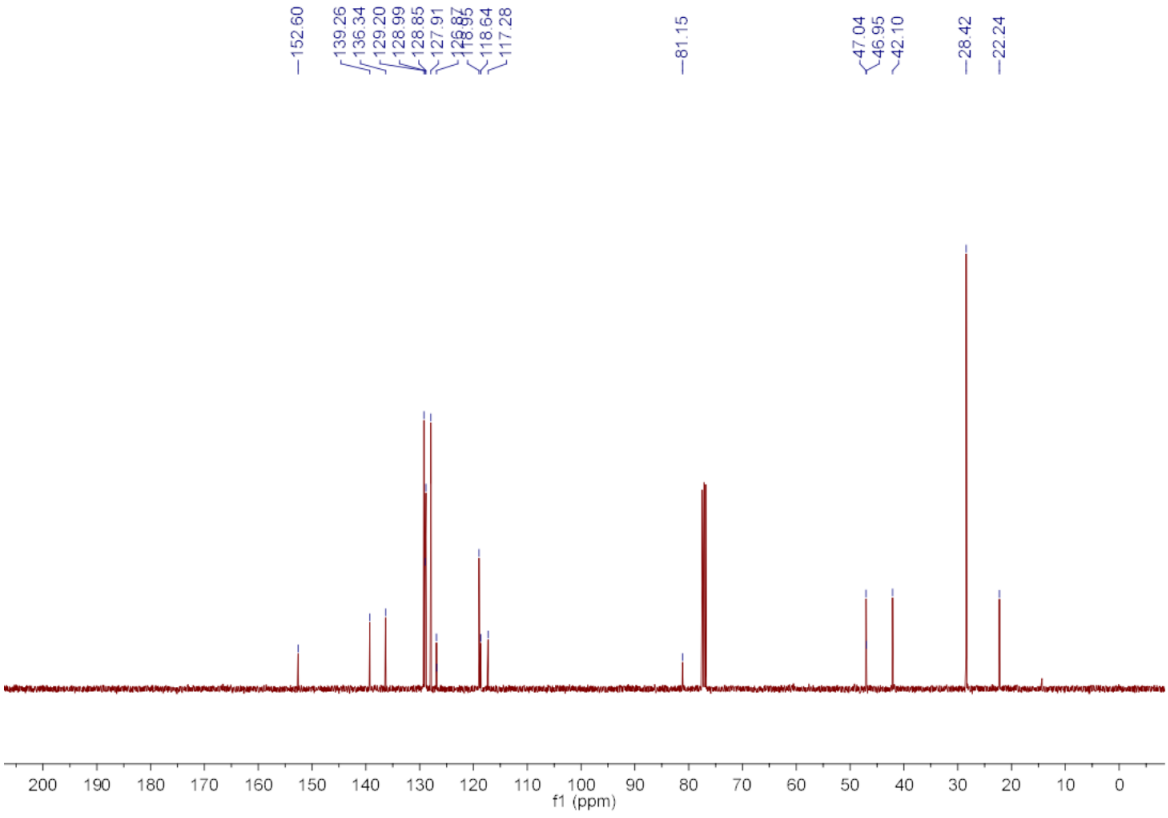


^{1}H NMR (400 MHz, $CDCl_3$)

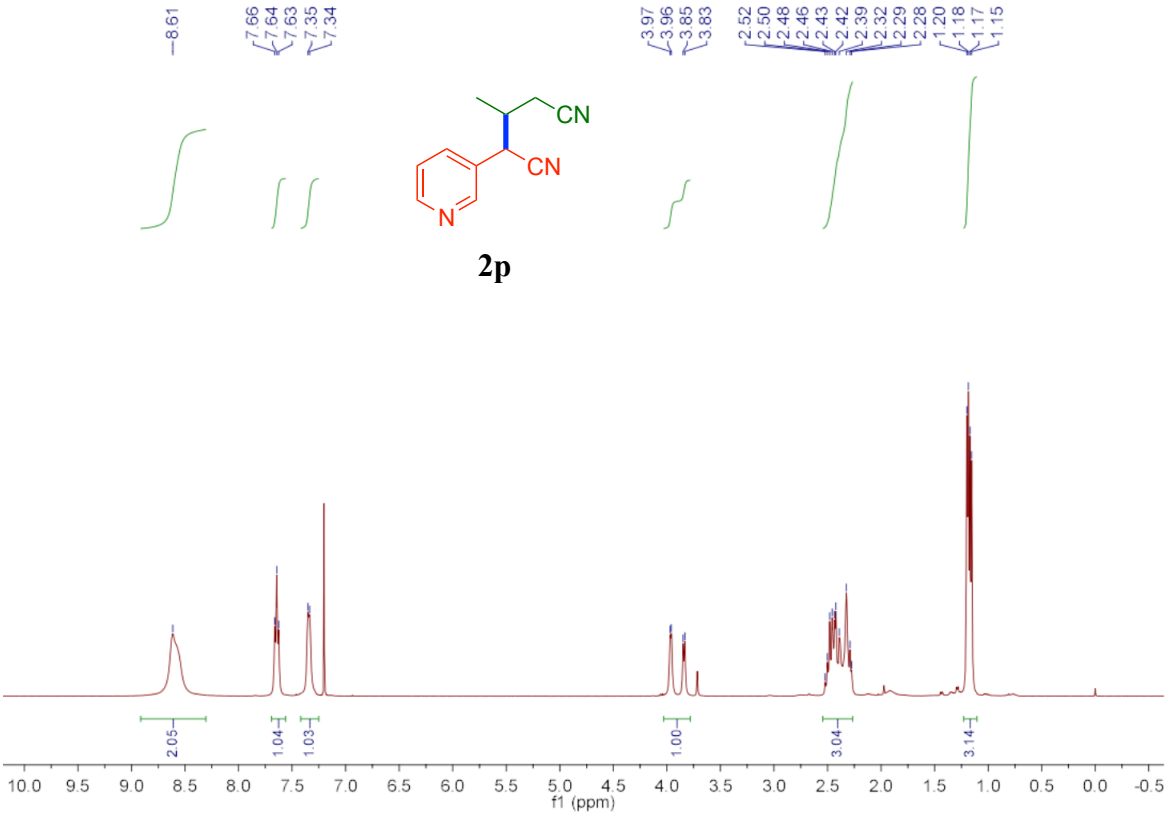


2o

^{13}C NMR (100.6 MHz, $CDCl_3$)

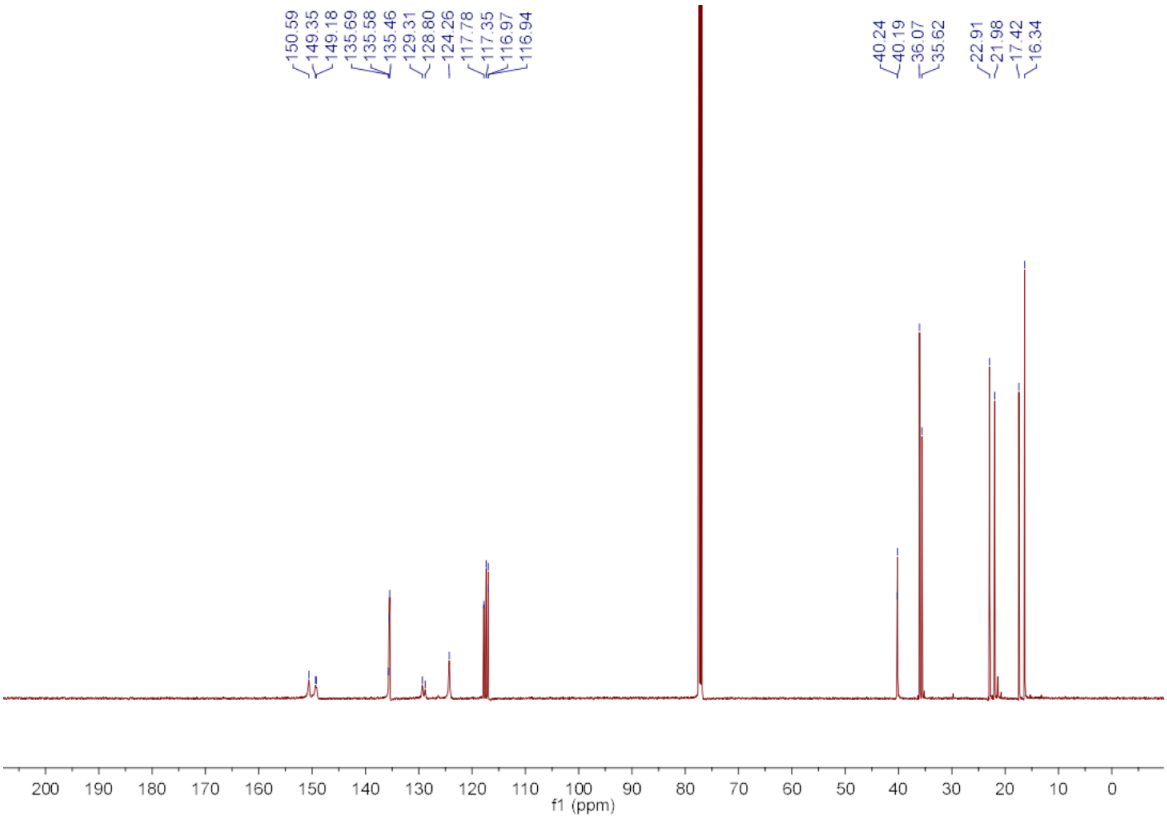


^{1}H NMR (400 MHz, $CDCl_3$)

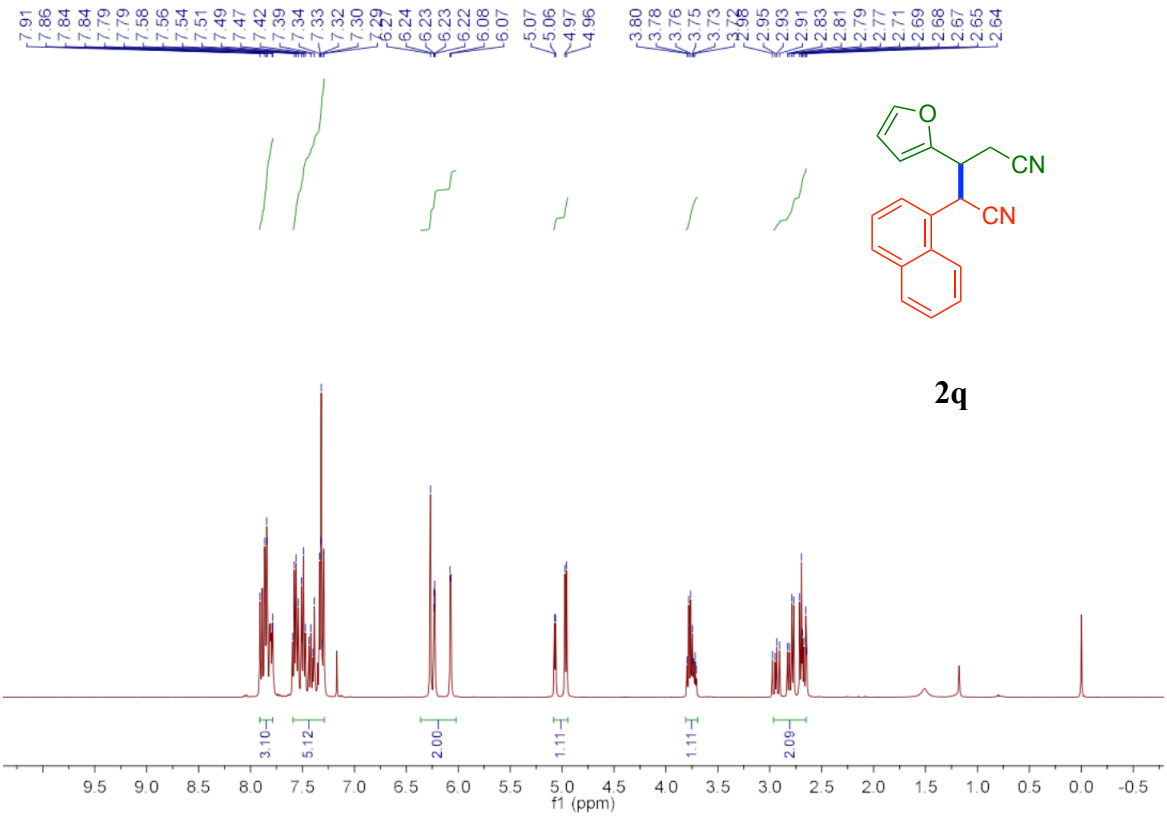


2p

^{13}C NMR (100.6 MHz, $CDCl_3$)

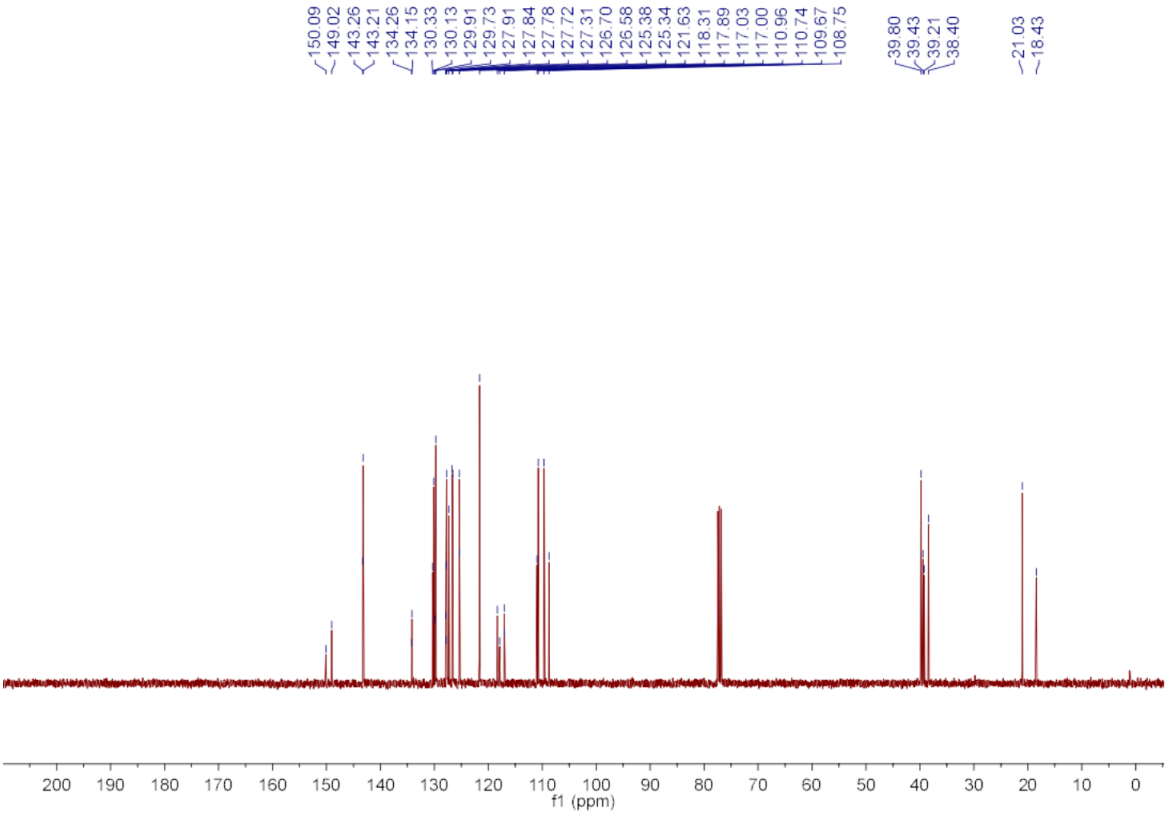


^{1}H NMR (400 MHz, $CDCl_3$)

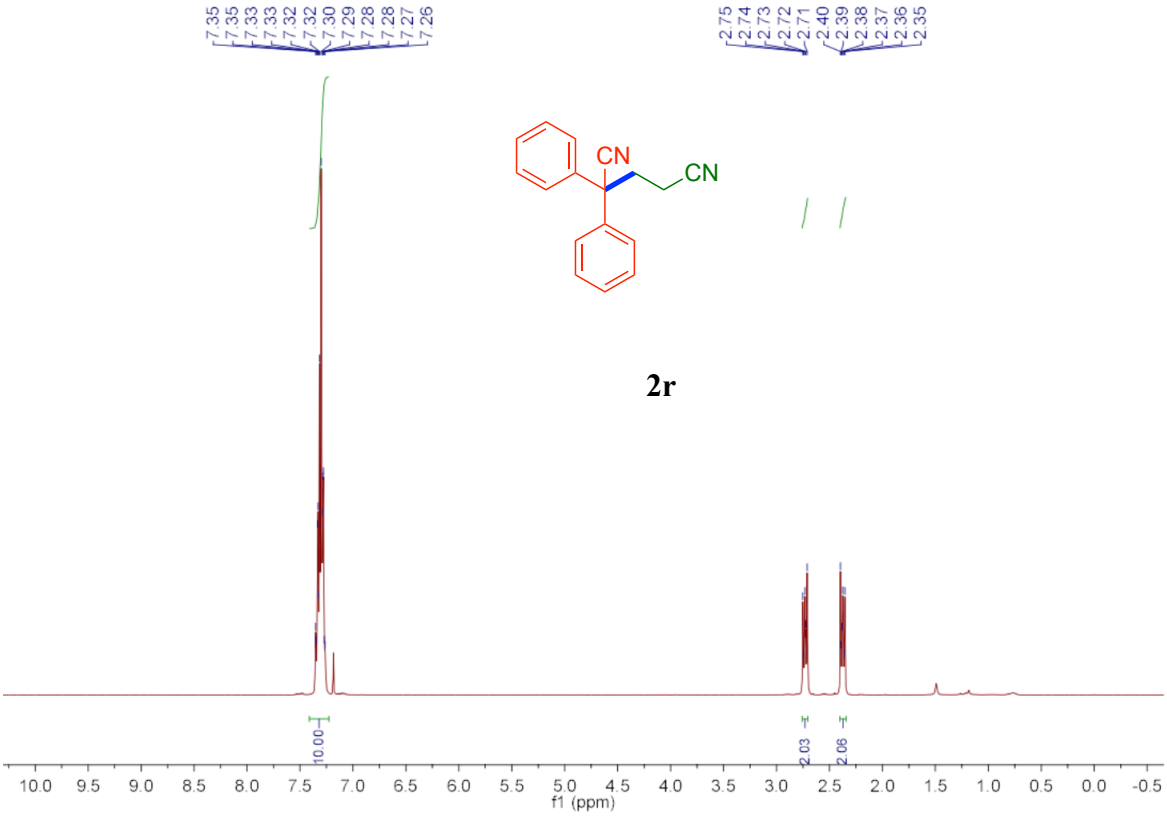


2q

^{13}C NMR (100.6 MHz, $CDCl_3$)

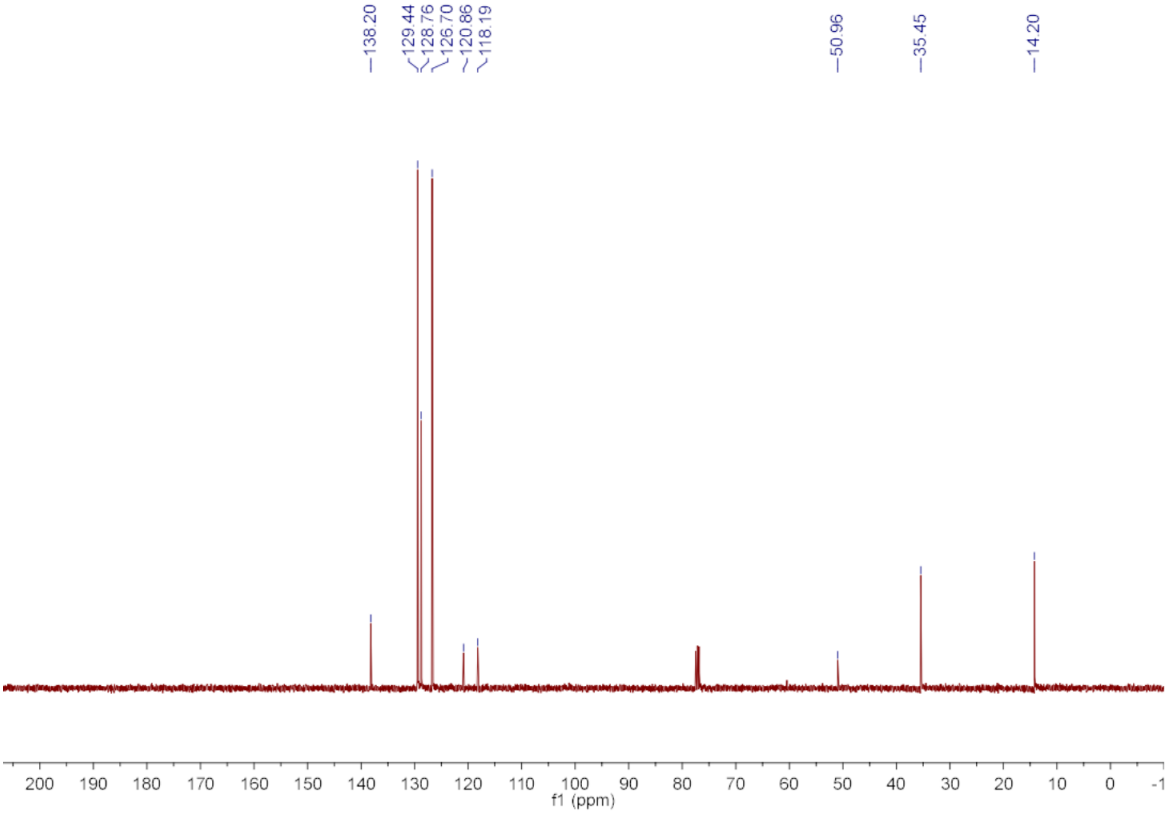


^{1}H NMR (400 MHz, $CDCl_3$)

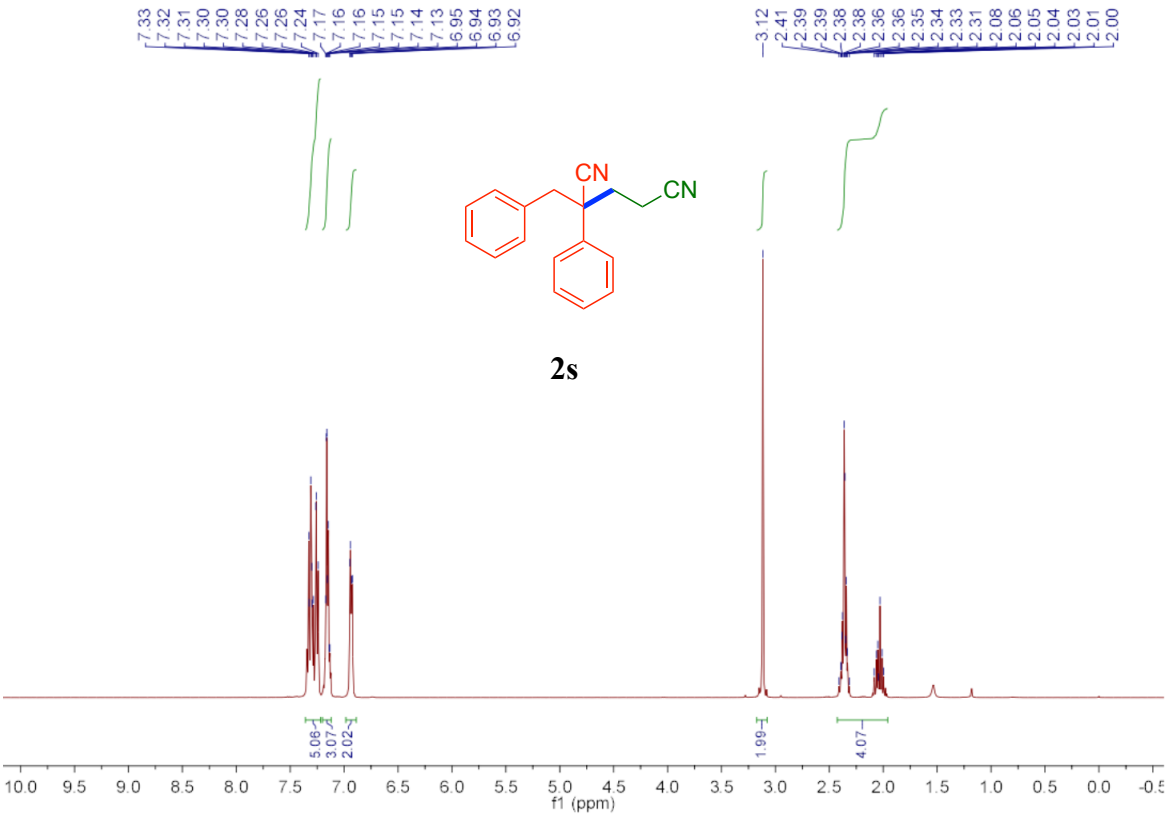


2r

^{13}C NMR (100.6 MHz, $CDCl_3$)

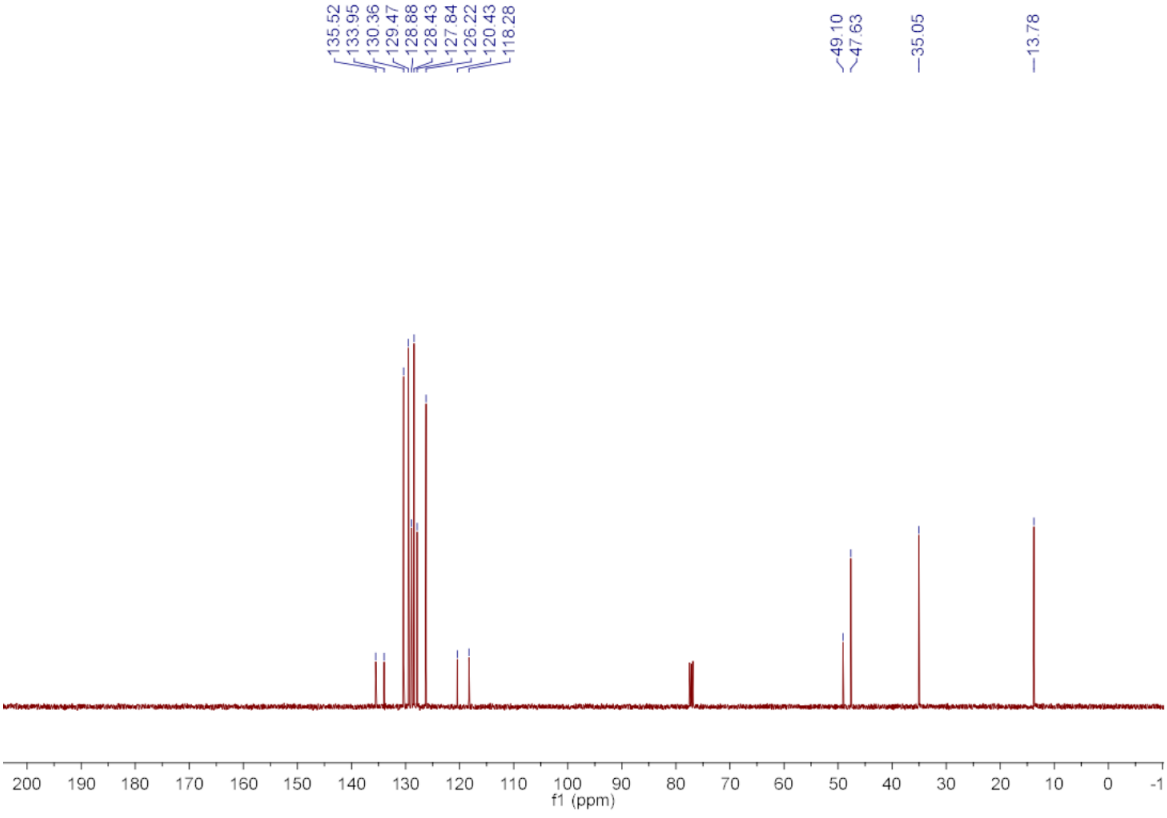


^{1}H NMR (400 MHz, $CDCl_3$)

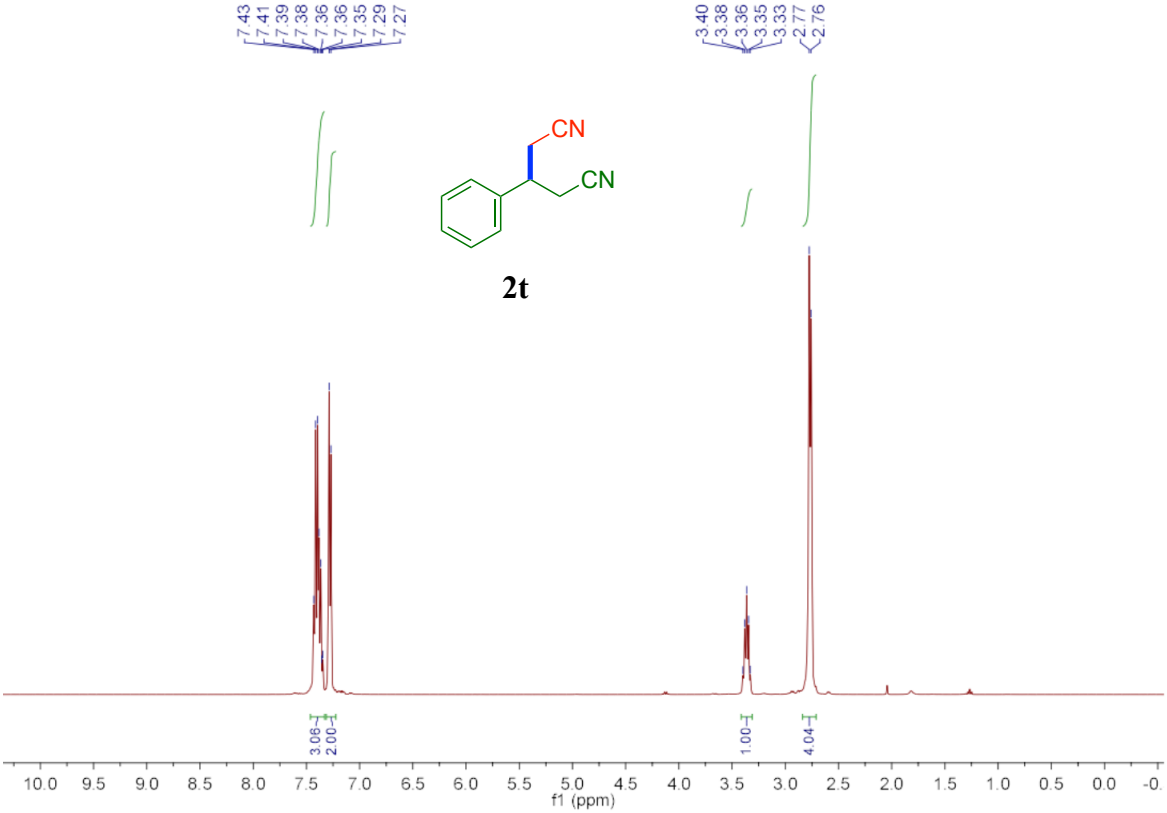


2s

^{13}C NMR (100.6 MHz, $CDCl_3$)

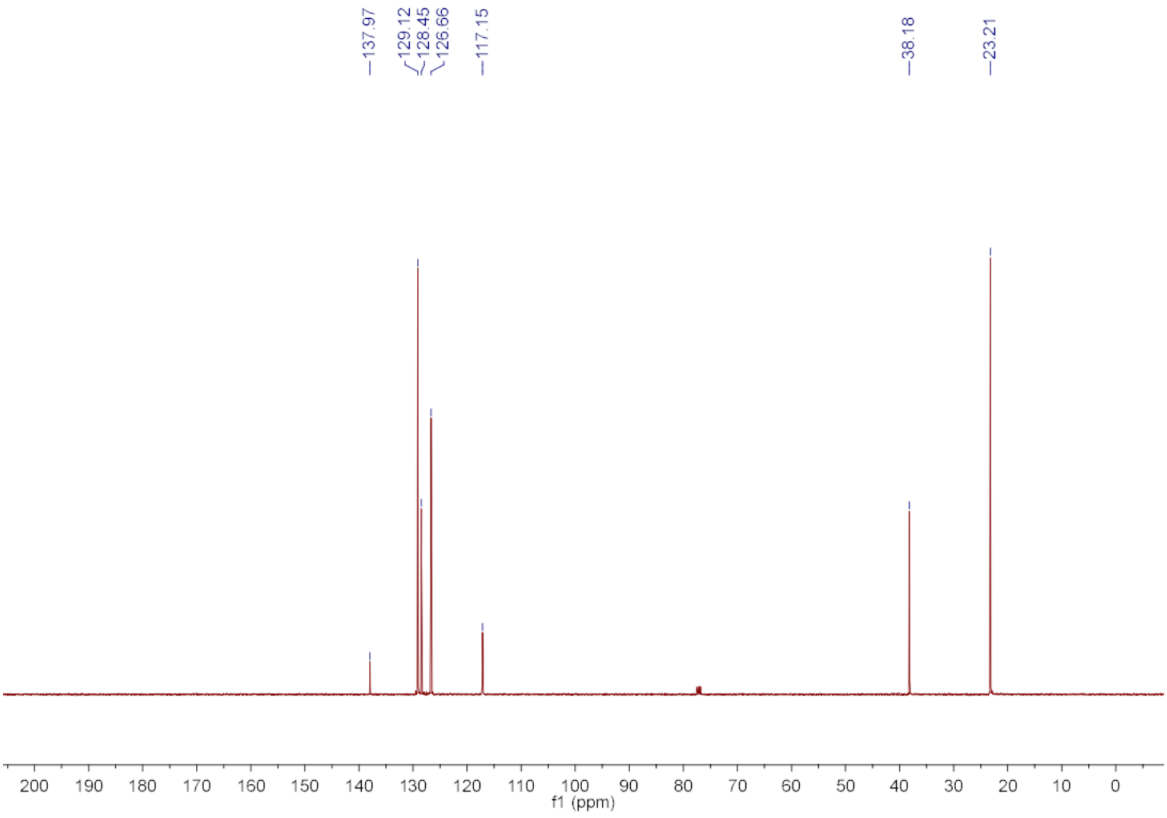


^{1}H NMR (400 MHz, $CDCl_3$)

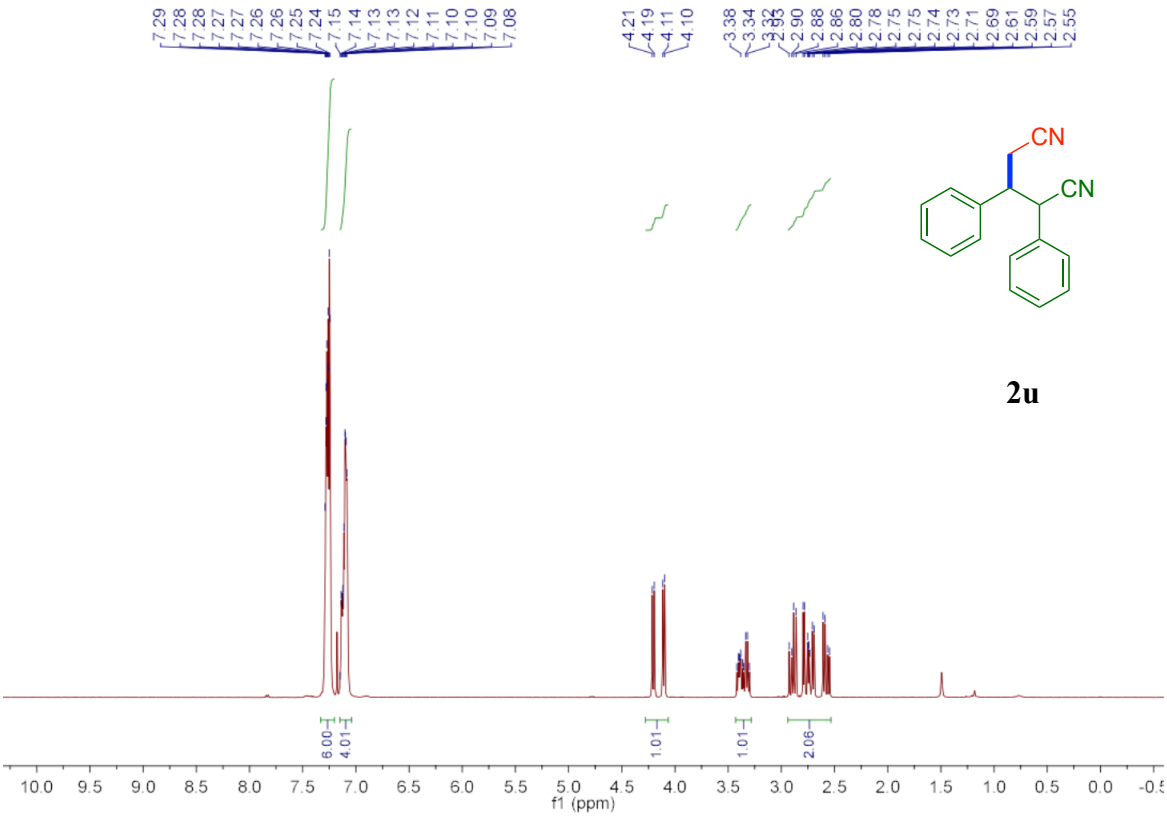


2t

^{13}C NMR (100.6 MHz, $CDCl_3$)

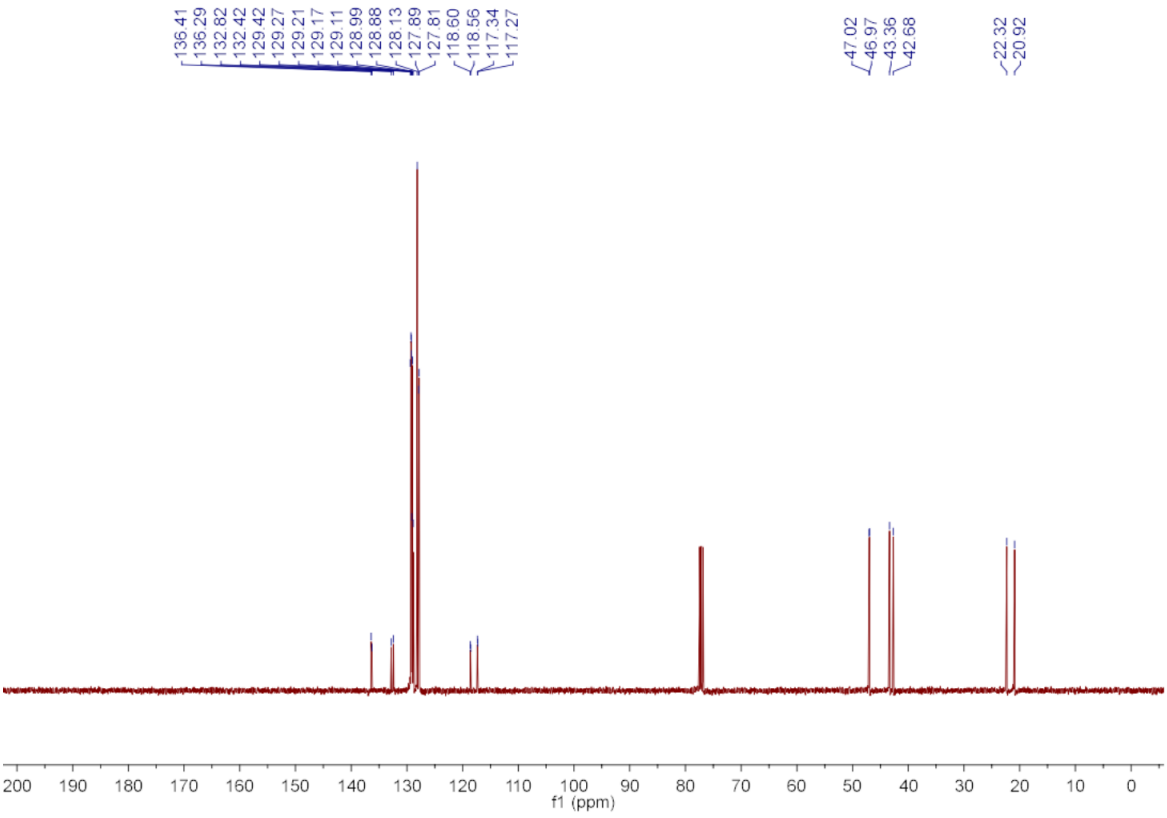


^{1}H NMR (400 MHz, $CDCl_3$)

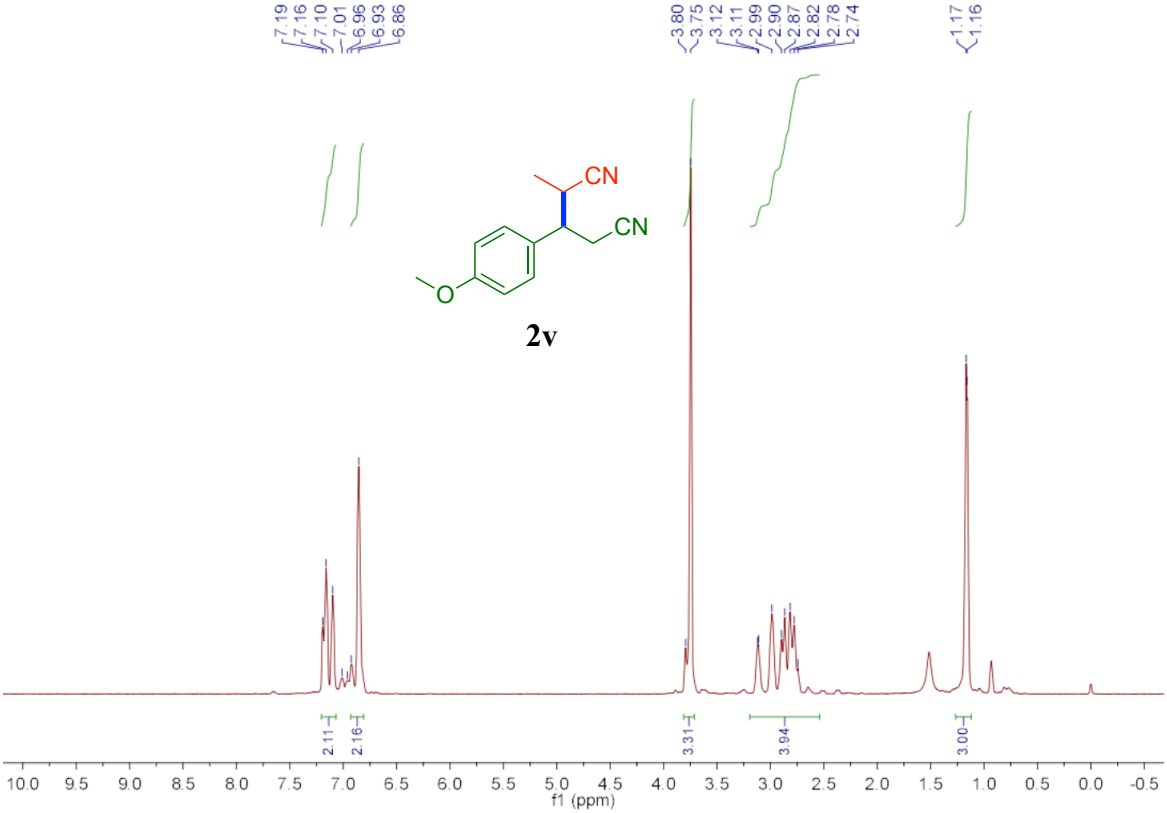


2u

^{13}C NMR (100.6 MHz, $CDCl_3$)

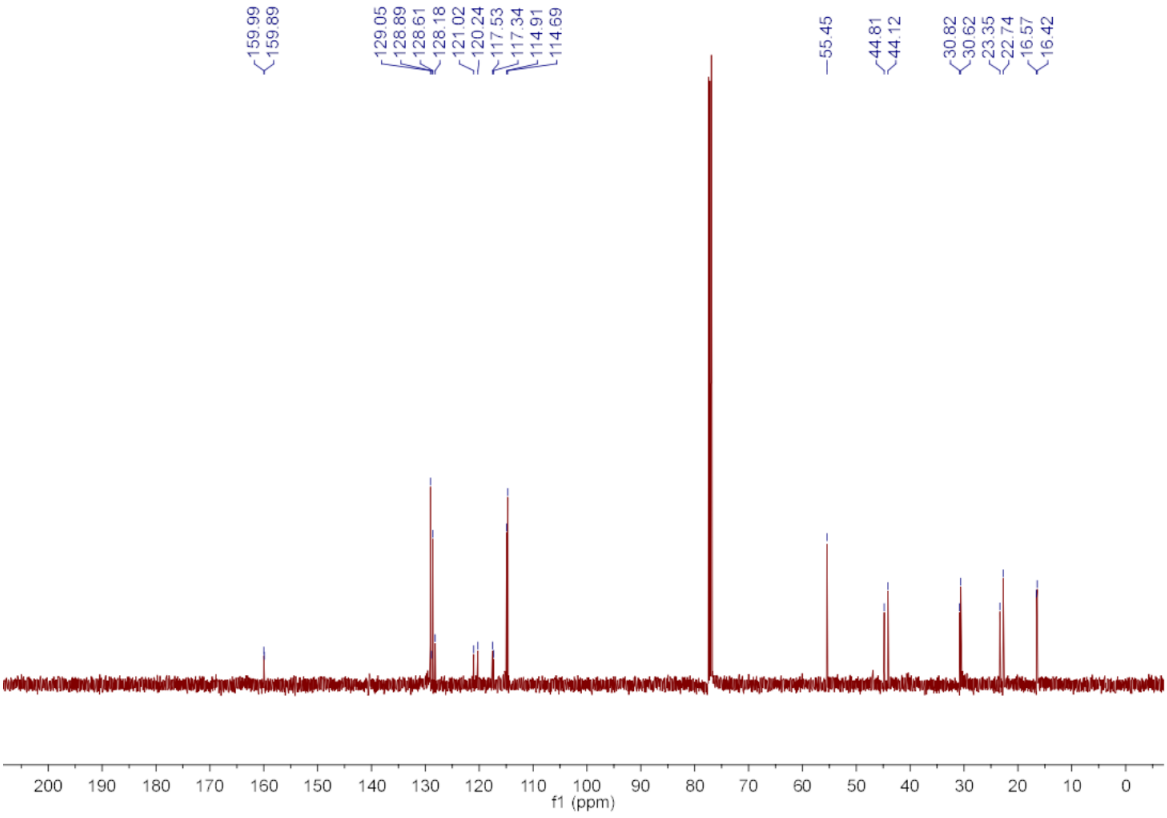


^{1}H NMR (400 MHz, $CDCl_3$)

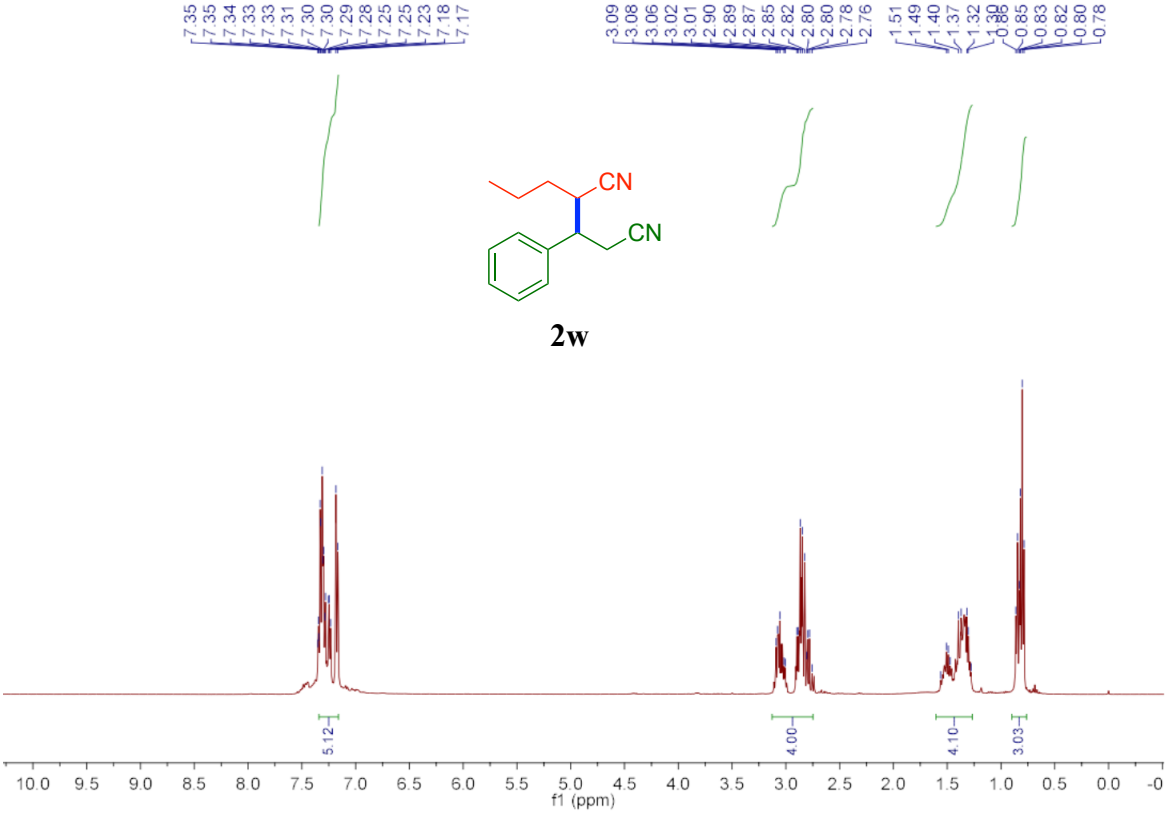


2v

^{13}C NMR (100.6 MHz, $CDCl_3$)

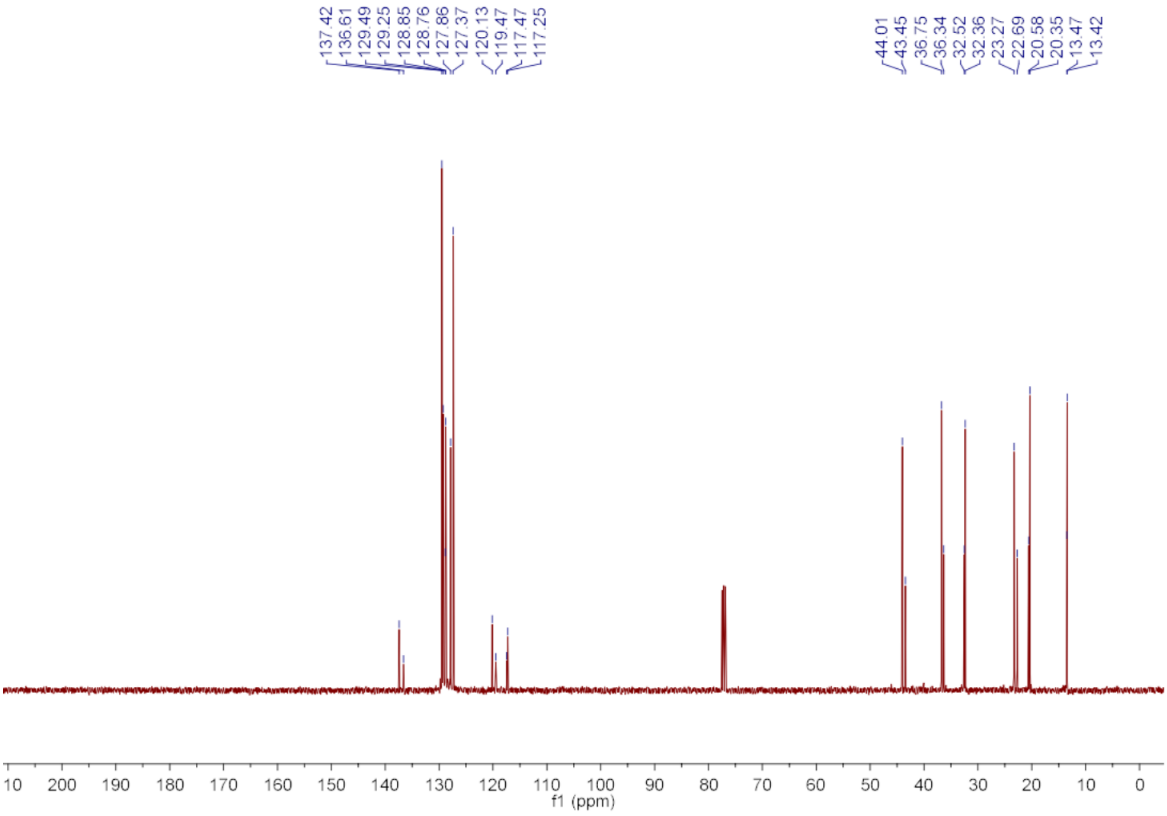


^{1}H NMR (400 MHz, $CDCl_3$)



2w

^{13}C NMR (100.6 MHz, $CDCl_3$)



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2) N. A. Espinosa-Jalapa, A. Kumar, G. Leitus, Y. Diskin-Posner, D. Milstein, *J. Am. Chem. Soc.* 2017, **139**, 11722-11725.

3) U. K. Das, Y. Ben-David, Y. Diskin-Posner, D. Milstein, *Angew. Chem. Int. Ed.* 2018, **130**, 2201-2204.

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5) Rigaku

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8) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*. 2009, **42**, 339-341.