

Supporting Information

Room Temperature Synthesis of α,β -Unsaturated Nitriles by Manganese-Catalysed Base-Free Coupling of α -Saturated Nitriles with Aldehydes

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1. General Considerations

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in an MBraun glovebox or using standard Schlenk techniques. All glassware was oven-dried before use. All solvents, including deuterated ones, were of HPLC or equivalent grade, and were degassed with nitrogen and stored in the glovebox over 4Å molecular sieves. Complexes **Mn-1**,¹ **Mn-2**,² and **Mn-3**³ were synthesized according to literature procedures. All ¹H, ¹³C and ³¹P NMR spectra were recorded using Bruker Avance III 300 MHz, Avance III 400 MHz, or Avance III HD 500 MHz spectrometers at 293 K. ¹H and ¹³C chemical shifts are reported in ppm relative to tetramethylsilane (0 ppm), and were referenced to the corresponding residual solvent peaks. ³¹P chemical shifts are reported in ppm

relative to 85% H₃PO₄ in D₂O (0 ppm), and were referenced to an external standard of this concentrated acid. 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 N₂ as carrier gas (Column: HP-5, 30 m, 320 μm, Inlets: 280 °C; Detector: FID 280 °C; Flow: 1 mL/min; Oven: 50 °C, hold 8 min; 15 °C/min to 280 °C, 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 Procedure for the Optimization of Catalytic Conditions:

Inside an N₂-filled glovebox, a 7 mL glass vial was equipped with a Teflon-coated magnetic stirring bar and loaded with the catalyst candidate (**Mn-1**, **Mn-2** or **Mn-3**; 3.8-4.6 mg, 0.009 mmol), 3,4-dimethoxybenzaldehyde (0.3 mmol) and CH₃CN (1 mL). 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 as an internal standard. The resulting mixture was 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 3,4-dimethoxybenzaldehyde was determined by GC-FID. The E/Z ratio of the product **2a** was determined by ¹H NMR analysis of the crude reaction mixture. The solvent was then evaporated under reduced pressure, and the resulting residue was subjected to column chromatography over silica gel (100-200 mesh), using an ethyl acetate/hexane mixture (1:50) as the eluent. Yields were calculated for the pure isolated product **2a**.

General Experimental Procedure for Coupling Aliphatic Nitriles with Aldehydes:

Inside an N₂-filled glovebox, a 7 mL glass vial was equipped with a Teflon-coated magnetic stirring bar and loaded with **Mn-1** (4.6 mg, 0.009 mmol), aldehyde (0.3 mmol) and aliphatic nitrile (1 mL). 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 as an internal standard. The resulting mixture was 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 aldehyde was determined by GC-FID. The E/Z ratio of the products was determined by ¹H NMR analysis or GC analysis of the crude reaction mixtures. The solvent was then evaporated under reduced pressure, and the resulting residue was subjected to column chromatography over silica gel (100-200 mesh), using an ethyl acetate/hexane mixture (1:50-1:20) as the eluent. Yields were calculated for the pure isolated products.

General Experimental Procedure for Coupling Benzylic Nitriles with Aldehydes:

Inside an N₂-filled glovebox, a 7 mL glass vial was equipped with a Teflon-coated magnetic stirring bar and loaded with **Mn-1** (4.6 mg, 0.009 mmol), aldehyde (0.3 mmol), benzylic nitrile (0.3 mmol) and THF (1 mL). 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 as an internal standard. The resulting mixture was 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 benzylic nitriles was determined using GC-FID or ¹H NMR analysis. The E/Z ratio of the products was determined by ¹H NMR analysis of the crude reaction mixture. The solvent was then evaporated under reduced pressure, and the

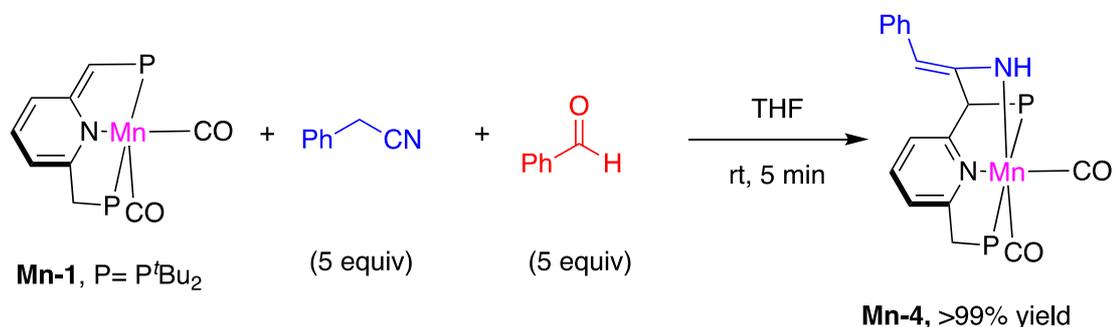
resulting residue was subjected to column chromatography over silica gel (100-200 mesh), using an ethyl acetate/hexane mixture (1:50-1:20) as the eluent. Yields were calculated for the pure isolated products.

Procedure for the Synthesis of α -Deuterated Vinyl Nitriles:

Inside an N₂-filled glovebox, a 7 mL glass vial was equipped with a Teflon-coated magnetic stirring bar and loaded with **Mn-1** (4.6 mg, 0.009 mmol), aldehyde (0.3 mmol) and CD₃CN (1 mL). 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 as an internal standard. The resulting mixture was 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 aldehyde was determined by GC-FID analysis. The E/Z ratio of the products was determined by ¹H NMR analysis of the crude reaction mixture. The solvent was then evaporated under reduced pressure, and the resulting residue was subjected to column chromatography over silica gel (100-200 mesh), using an ethyl acetate/hexane mixture (1:50-1:20) as the eluent. Yields were calculated for the pure isolated products.

Mechanistic Studies

Competition Experiment with Complex Mn-1, Benzyl Nitrile and Benzaldehyde:



Procedure: In an N₂-filled glovebox, an 8 mL glass vial was equipped with a Teflon-coated magnetic stirring bar and loaded with **Mn-1** (10 mg, 0.02 mmol) and THF (1 mL). Benzyl nitrile (5 equiv) and benzaldehyde (5 equiv) were then added to the mixture, and it was stirred for 5 min at room temperature. The resulting solution was directly analyzed by ³¹P NMR spectroscopy.

The complex **Mn-4** was synthesized using our previously reported procedure.¹

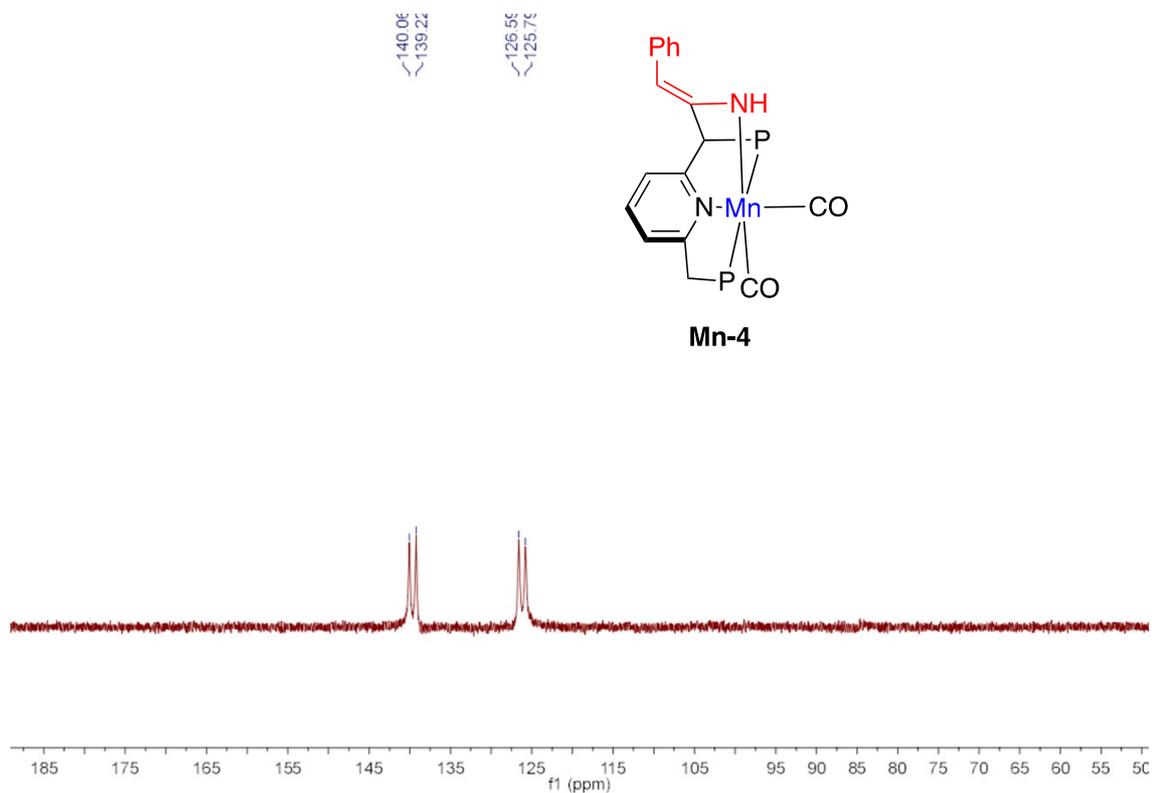


Figure S1. ³¹P{¹H} NMR Spectrum of **Mn-4** (121 MHz, THF, 298 K)

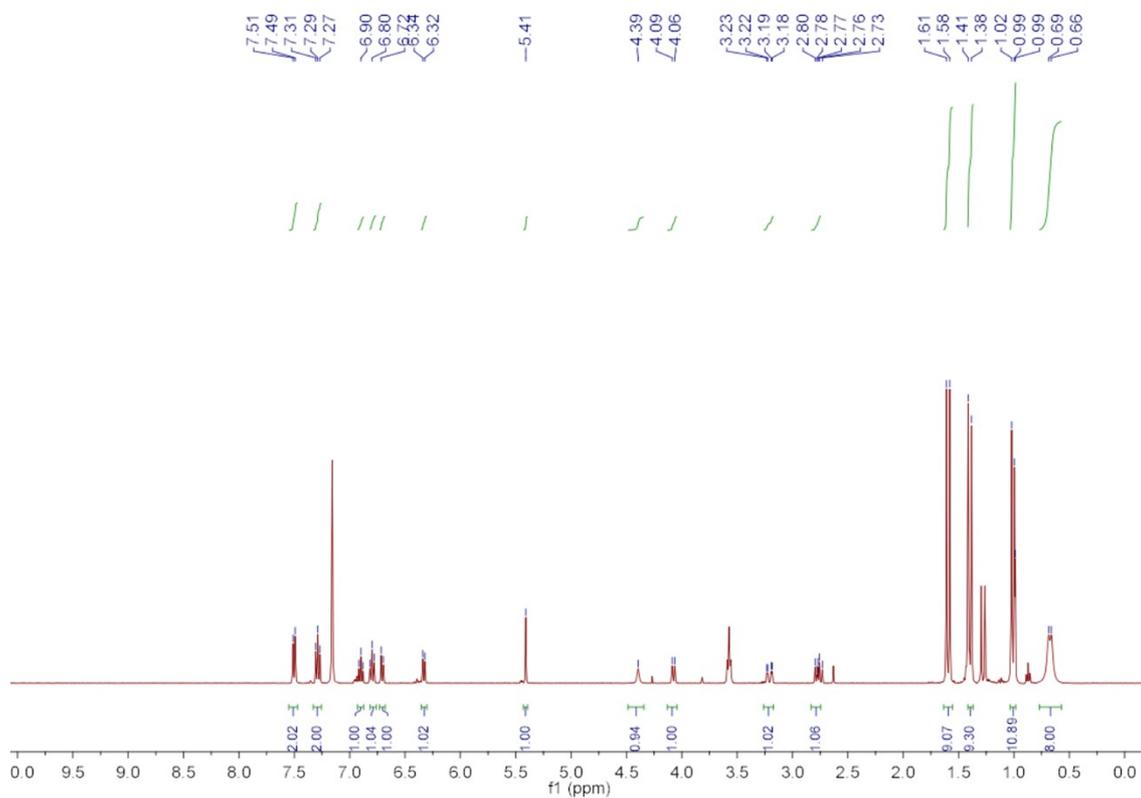


Figure S2. ^1H NMR Spectrum of **Mn-4** (400 MHz, C_6D_6 , 298 K)

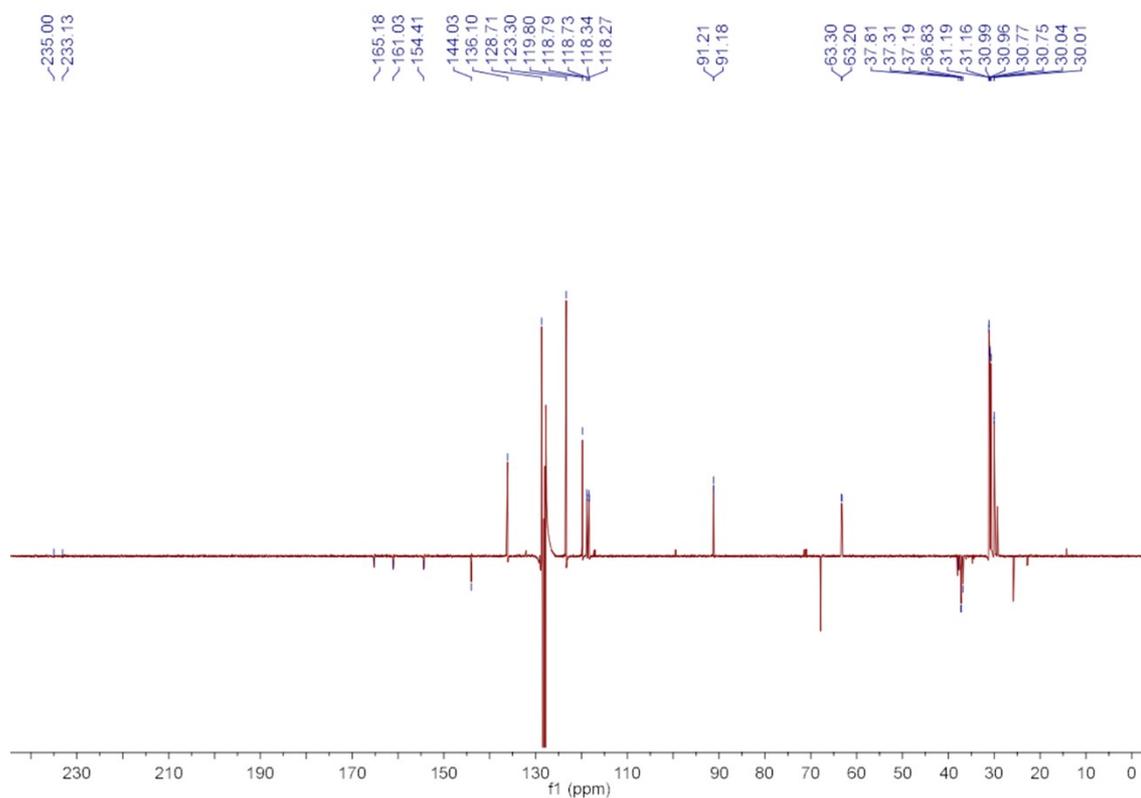
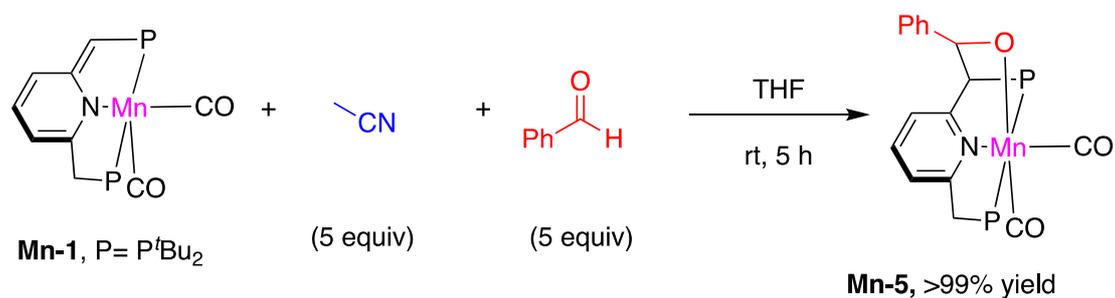


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **Mn-4** (100 MHz, C_6D_6 , 298 K)

Competition Experiment with Complex Mn-1, Benzaldehyde and Acetonitrile in THF:



Procedure: In an N₂-filled glovebox, an 8 mL glass vial was equipped with a Teflon-coated magnetic stirring bar and loaded with **Mn-1** (10 mg, 0.02 mmol) and THF (1 mL). Subsequently, 1 mL of a THF solution containing benzaldehyde (5 equiv) and acetonitrile (5 equiv) was added to the same vial and the mixture was stirred for 5 h at room temperature. The resulting solution was directly analyzed by ³¹P NMR spectroscopy. Complex **Mn-5** was originally reported in our previous publication.⁴

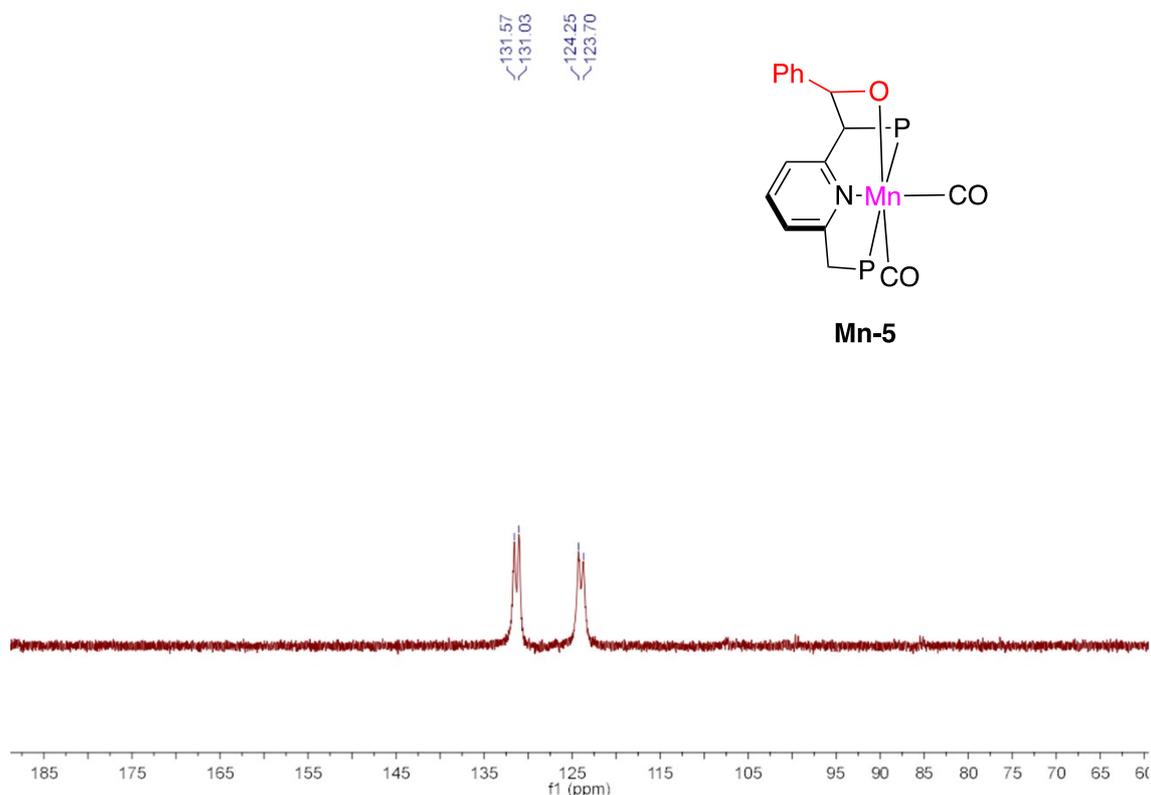
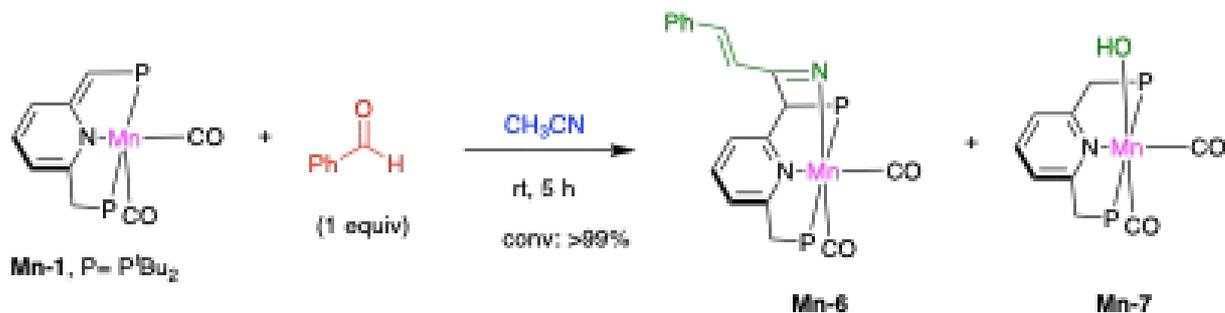


Figure S4. ³¹P{¹H} NMR Spectrum of **Mn-5** (121 MHz, THF, 298 K)

Competition Experiment with Complex Mn-1 and Benzaldehyde in Acetonitrile:



Procedure: In an N_2 -filled glovebox, an 8 mL glass vial was equipped with a Teflon-coated magnetic stirring bar, and loaded with **Mn-1** (10 mg, 0.02 mmol) and acetonitrile (1 mL). Benzaldehyde (2 equiv) was then added to the mixture, and it was stirred for 5 h at room temperature. The resulting solution was directly analyzed by ^{31}P NMR spectroscopy.

Note: In solution, at room temperature, complexes **Mn-6**⁵ and **Mn-7**⁶ are in equilibrium with **Mn-1**, cinnamoyl and H_2O . Thus, the ratio of **Mn-6** to **Mn-7** could not be determined.

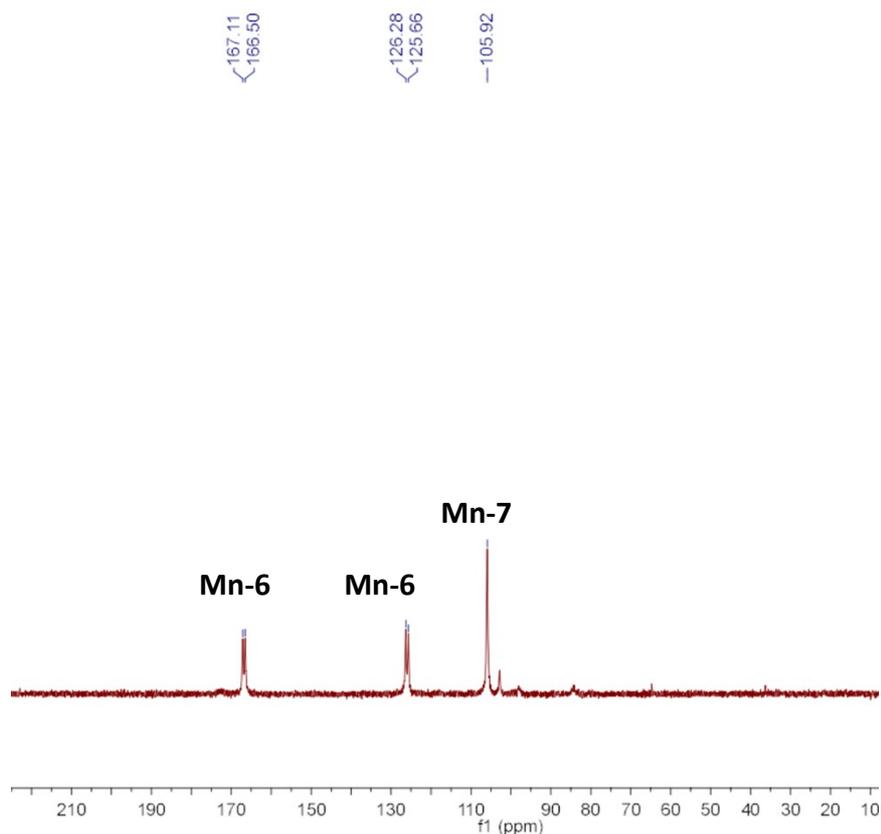
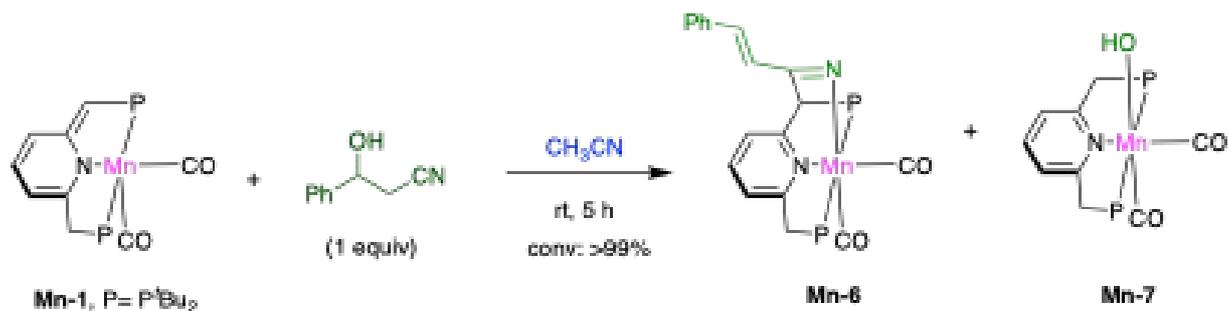


Figure S5. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of **Mn-6** and **Mn-7** Obtained *in situ* from **Mn-1** and Benzaldehyde in Acetonitrile (121 MHz, CH_3CN , 298 K)

Competition Experiment with Complex Mn-1 and 3-Hydroxy-3-phenylpropanenitrile in Acetonitrile:



Procedure: In an N_2 -filled glovebox, an 8 mL glass vial was equipped with a Teflon-coated magnetic stirring bar and loaded with **Mn-1** (10 mg, 0.02 mmol) and CH_3CN (1 mL). 3-Hydroxy-3-phenylpropanenitrile (2 equiv) was then added to the mixture, and it was stirred for 5 h at room temperature. The resulting solution was directly analyzed by ^{31}P NMR spectroscopy, indicating the formation of **Mn-6** and **Mn-7**.

Note: In solution, at room temperature, complexes **Mn-6**⁵ and **Mn-7**⁶ are in equilibrium with **Mn-1**, cinnamitrile and H_2O . Thus, the ratio of **Mn-6** to **Mn-7** could not be determined.

Spectroscopic Data for the Products of Nitrile-Aldehyde Coupling:

3-(3,4-Dimethoxyphenyl)acrylonitrile (2a).⁷ Purified by column chromatography using



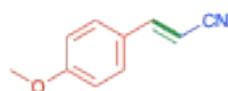
silica gel (eluent: hexane/EtOAc = 97:3) to afford **2a** as a colorless liquid (56 mg, 99% yield). The product **2a** was isolated as an unseparable mixture of cis/trans isomers (E/Z=95:5). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (m, 1.16 H), 6.95 (dd, *J* = 8.3, 1.8 Hz, 1.13 H), 6.86 (d, *J* = 1.7 Hz, 1.07 H), 6.79 (d, *J* = 8.3 Hz, 1.12 H), 5.65 (d, *J* = 16.6 Hz, 1 H, *trans* isomer), 5.22 (d, *J* = 12.1 Hz, 0.03 H, *cis* isomer), 3.83 (d, *J* = 3.2 Hz, 6.65 H). ¹³C NMR (100.6 MHz, CDCl₃): δ 151.85, 150.28, 149.38, 148.37, 126.60, 122.11, 118.67, 111.11, 108.90, 93.61, 56.04, 55.99. Exact mass calculated for C₁₁H₁₁NO₂: *m/z* 189.07; GC-MS, *m/z* 189.07.

3-Phenylacrylonitrile (2b).⁸ Purified by column chromatography using silica gel (eluent:



hexane/EtOAc = 97:3) to afford **2b** as a colorless oil (38 mg, 99% yield). The product **2b** was isolated as an unseparable mixture of cis/trans isomers (E/Z=70:30). ¹H NMR (400 MHz, CDCl₃) δ 7.81-7.69 (m, 0.92 H), 7.39-7.26 (m, 7.38 H), 7.04 (d, *J* = 12.1 Hz, 0.46 H), 5.79 (d, *J* = 16.7 Hz, 1 H *trans* isomer), 5.36 (d, *J* = 12.1 Hz, 0.44 H *cis* isomer). ¹³C NMR (100.6 MHz, CDCl₃): δ 150.64, 148.78, 133.66, 133.58, 131.29, 131.04, 129.19, 129.08, 129.00, 127.43, 118.23, 117.44, 96.41, 95.14. Exact mass calculated for C₉H₇N, *m/z* 129.05; GC-MS, *m/z* 129.05.

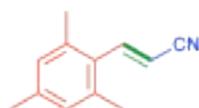
3-(4-Methoxyphenyl)acrylonitrile (2c).⁸ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 97:3) to afford **2c** as a colorless oil (46 mg, 96% yield). The product **2c** was isolated as an unseparable mixture of cis/trans isomers (E/Z=51:49). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, *J* = 6.8, 4.8 Hz, 2.49 H), 7.45-7.38 (m, 2.30 H), 7.34 (d, *J* = 16.6 Hz, 0.76 H), 7.05 (d, *J* = 12.1 Hz, 1.47 H), 6.99-6.90 (m, 4.50 H), 5.73 (d, *J* = 16.6 Hz, 1 H *trans* isomer), 5.31 (d, *J* = 12.1 Hz, 0.99 H *cis* isomer), 3.86

(d, $J = 3.5$ Hz, 6.77 H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 162.15, 161.75, 150.12, 148.14, 131.04, 129.18, 126.65, 126.44, 118.82, 118.09, 114.61, 114.37, 93.44, 91.98, 55.54, 55.51. Exact mass calculated for $\text{C}_{10}\text{H}_9\text{NO}$, m/z 159.06; GC-MS, m/z 159.06.

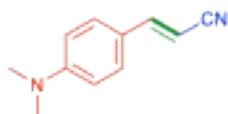
3-Mesitylacrylonitrile (2d).⁸ Purified by column chromatography using silica gel (eluent:



hexane/EtOAc = 97:3) to afford **2d** as a colorless oil (50 mg, 98% yield).

The product **2d** was isolated as an unseparable mixture of *cis/trans* isomers ($E/Z=95:5$). ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 17.0$ Hz, 1.06 H), 6.81 (s, 2.30 H), 5.63 (d, $J = 11.5$ Hz, 0.05 H *cis* isomer), 5.43 (d, $J = 17.0$ Hz, 1 H *trans* isomer), 2.21 (d, $J = 7.9$ Hz, 9.61 H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 149.63, 139.48, 136.67, 130.12, 129.54, 118.24, 101.57, 21.14, 21.04. Exact mass calculated for $\text{C}_{12}\text{H}_{13}\text{N}$, m/z 171.10; GC-MS, m/z 171.10.

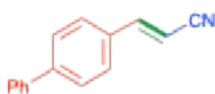
3-(4-(Dimethylamino)phenyl)acrylonitrile (2e).⁹ Purified by column chromatography using



silica gel (eluent: hexane/EtOAc = 95:5) to afford **2e** as a colorless oil (48 mg, 93% yield). The product **2e** was isolated as an unseparable mixture of

cis/trans isomers ($E/Z=93:7$). ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 9.0$ Hz, 0.07 H), 7.20 (dd, $J = 19.4, 12.7$ Hz, 3.06 H), 6.85 (d, $J = 12.0$ Hz, 0.03 H), 6.56 (d, $J = 8.9$ Hz, 2.06 H), 5.47 (d, $J = 16.5$ Hz, 1 H *trans* isomer), 4.99 (d, $J = 12.0$ Hz, 0.03 H *cis* isomer), 2.94 (s, 6.21 H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 152.25, 150.62, 129.10, 121.43, 119.85, 111.75, 89.39, 40.13. Exact mass calculated for $\text{C}_{11}\text{H}_{12}\text{N}_2$, m/z 172.10; GC-MS, m/z 172.10.

3-([1,1'-Biphenyl]-4-yl)acrylonitrile (2f).¹⁰ Purified by column chromatography using silica

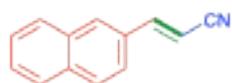


gel (eluent: hexane/EtOAc = 97:3) to afford **2f** as a colorless solid (61 mg, 99% yield). The product **2f** was isolated as an unseparable mixture of

cis/trans isomers ($E/Z=85:15$). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.3$ Hz, 0.29 H), 7.60-7.47 (m, 4.74 H), 7.43-7.26 (m, 6.51 H), 7.04 (d, $J = 12.1$ Hz, 0.21 H), 5.78 (d, $J = 16.6$

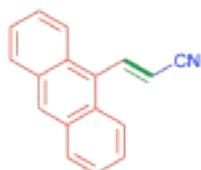
Hz, 1 H *trans* isomer), 5.34 (d, $J = 12.1$ Hz, 0.12 H *cis* isomer). ^{13}C NMR (100.6 MHz, CDCl_3): δ 150.11, 148.24, 144.01, 139.79, 132.50, 129.64, 129.06, 129.03, 128.22, 128.15, 127.95, 127.75, 127.55, 127.17, 127.11, 118.35, 96.09, 94.79. Exact mass calculated for $\text{C}_{15}\text{H}_{11}\text{N}$, m/z 205.08; GC-MS, m/z 205.08.

3-(Naphthalen-2-yl)acrylonitrile (2g).¹⁰ Purified by column chromatography using silica gel



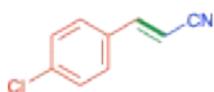
(eluent: hexane/EtOAc = 97:3) to afford **2g** as a colorless solid (47 mg, 88% yield). The product **2g** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=90:10). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (dd, $J = 9.1, 6.1$ Hz, 4.24 H), 7.55-7.31 (m, 4.18 H), 5.87 (d, $J = 16.6$ Hz, 1 H *trans* isomer), 5.41 (d, $J = 12.1$ Hz, 0.04 H *cis* isomer). ^{13}C NMR (100.6 MHz, CDCl_3): δ 150.64, 134.61, 133.16, 131.06, 129.77, 129.15, 128.81, 127.96, 127.92, 127.20, 122.30, 118.43, 96.38. Exact mass calculated for $\text{C}_{13}\text{H}_9\text{N}$, m/z 179.07; GC-MS, m/z 179.07.

3-(Anthracen-9-yl)acrylonitrile (2h).¹¹ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 97:3) to afford **2h** as a pale yellow solid (67 mg, 98% yield). The product **2h** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=98:2). ^1H NMR (400 MHz, CDCl_3) δ 8.32 (s, 1.13 H), 8.17 (d, $J = 16.8$ Hz, 1.12 H), 7.98 (d, $J = 8.4$ Hz, 2.10 H), 7.89 (d, $J = 7.9$ Hz, 2.29 H), 7.51-7.32 (m, 4.28 H), 6.07 (d, $J = 11.6$ Hz, 0.2 H *cis* isomer), 5.74 (d, $J = 16.9$ Hz, 1 H *trans* isomer). ^{13}C NMR (100.6 MHz, CDCl_3): δ 148.56, 134.11, 131.16, 129.39, 129.15, 129.12, 127.77, 127.08, 125.63, 124.46, 117.69, 105.62. Exact mass calculated for $\text{C}_{17}\text{H}_{11}\text{N}$, m/z 229.08; GC-MS, m/z 229.08.

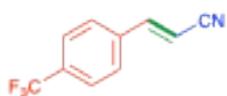
3-(4-Chlorophenyl)acrylonitrile (2i).⁸ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 97:3) to afford **2i** as a pale colorless oil (33 mg, 68% yield). The product **2i** was isolated as an unseparable mixture of

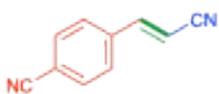
cis/trans isomers (E/Z=88:12). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.6 Hz, 0.12 H), 7.38-7.23 (m, 5.25 H), 7.01 (d, *J* = 12.1 Hz, 0.07 H), 5.79 (d, *J* = 16.7 Hz, 1 H *trans* isomer), 5.40 (d, *J* = 12.1 Hz, 0.06 H *cis* isomer). ¹³C NMR (100.6 MHz, CDCl₃): δ 149.24, 147.39, 137.39, 132.09, 130.37, 129.55, 129.35, 128.66, 117.94, 97.11, 95.81. Exact mass calculated for C₉H₆NCl, *m/z* 163.01; GC-MS, *m/z* 163.01

3-(4-(Trifluoromethyl)phenyl)acrylonitrile (2j).¹⁰ Purified by column chromatography



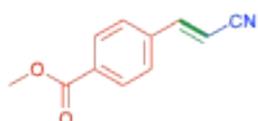
using silica gel (eluent: hexane/EtOAc = 95:5) to afford **2j** as a colorless oil (37 mg, 62% yield). The product **2j** was isolated as *trans* isomers (E/Z=99:1). ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 16.7 Hz, 1H), 5.92 (d, *J* = 16.7 Hz, 1H). ¹³C NMR (100.6 MHz, CDCl₃): δ 148.93, 136.84, 133.02, 132.69, 127.73, 126.28 (q, *J* = 3.8 Hz), 125.07, 122.36, 117.50, 99.39. Exact mass calculated for C₁₀H₆F₃N, *m/z* 197.04; GC-MS, *m/z* 197.04

4-(2-Cyanovinyl)benzotrile (2k).⁸ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 70:30) to afford **2k** as a pale colorless solid (40 mg, 87% yield). The product **2k** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=96:4). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 0.11 H), 7.81 (d, *J* = 8.3 Hz, 2.10 H), 7.66 (d, *J* = 8.3 Hz, 2.17 H), 7.51 (d, *J* = 16.7 Hz, 1.05 H), 7.27 (d, *J* = 12.1 Hz, 0.03 H), 6.10 (d, *J* = 16.7 Hz, 1 H *trans* isomer), 5.75 (d, *J* = 12.1 Hz, 0.03 H *cis* isomer). ¹³C NMR (100.6 MHz, CDCl₃): δ 148.36, 137.58, 133.01, 127.93, 118.08, 117.21, 114.62, 100.46. Exact mass calculated for C₁₀H₆N₂, *m/z* 154.05; GC-MS, *m/z* 154.05

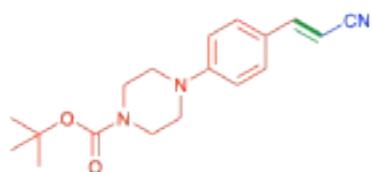
Methyl 4-(2-cyanovinyl)benzoate (2l).¹² Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 70:30) to afford **2l** as a colorless solid (34 mg, 60% yield). The product **2l** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=96:4). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.4 Hz, 2.06 H), 7.79

(d, $J = 8.4$ Hz, 0.14 H), 7.45 (d, $J = 8.3$ Hz, 2.05 H), 7.36 (d, $J = 16.7$ Hz, 1.04 H), 7.11 (d, $J = 12.2$ Hz, 0.06 H), 5.92 (d, $J = 16.7$ Hz, 1 H *trans* isomer), 5.51 (d, $J = 12.1$ Hz, 0.03 H *cis* isomer). ^{13}C NMR (100.6 MHz, CDCl_3): δ 166.27, 149.40, 137.57, 132.44, 130.44, 130.25, 129.03, 127.41, 117.71, 99.04, 52.57. Exact mass calculated for $\text{C}_{11}\text{H}_9\text{NO}_2$, m/z 187.06; GC-MS, m/z 187.06

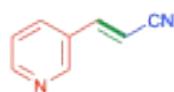
tert-Butyl 4-(4-(2-cyanovinyl)phenyl)piperazine-1-carboxylate (2m). Purified by column



chromatography using silica gel (eluent: hexane/EtOAc = 70:30) to afford **2m** as a colorless solid (85 mg, 90% yield).

The product **2m** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=82:18). ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.4$ Hz, 0.27 H), 7.27 (d, $J = 8.4$ Hz, 2 H), 7.21 (d, $J = 16.5$ Hz, 1.10 H), 6.90 (d, $J = 12.1$ Hz, 0.14 H), 6.78 (d, $J = 8.4$ Hz, 2.24 H), 5.58 (d, $J = 16.5$ Hz, 1 H *trans* isomer), 5.12 (d, $J = 12.0$ Hz, 0.13 H *cis* isomer), 3.50 (s, 4.54 H), 3.20 (d, $J = 4.1$ Hz, 4.53 H), 1.41 (s, 10.22 H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 154.71, 152.88, 150.13, 148.09, 130.87, 129.01, 124.47, 119.23, 115.13, 114.81, 91.87, 90.34, 80.22, 47.78, 47.70, 28.49. Exact mass calculated for $\text{C}_{18}\text{H}_{23}\text{N}_3\text{O}_2$, m/z 313.17; GC-MS, m/z 313.17.

3-(Pyridin-3-yl)acrylonitrile (2n).¹³ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 90:10) to afford **2n** as a colorless solid (37 mg, 96% yield). The product **2n** was isolated as a *trans* isomer (E/Z=99:1). ^1H NMR

(400 MHz, CDCl_3) δ 8.71-8.50 (m, 2H), 7.72 (d, $J = 7.9$ Hz, 1H), 7.48-7.20 (m, 2H), 5.92 (d, $J = 16.7$ Hz, 1H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 152.06, 149.13, 147.15, 133.63, 129.43, 124.01, 117.45, 98.96. Exact mass calculated for $\text{C}_8\text{H}_6\text{N}_2$, m/z 130.05; GC-MS, m/z 130.05.

3-(Furan-2-yl)acrylonitrile (2o).⁸ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 97:3) to afford **2o** as a colorless solid (35 mg, 99%

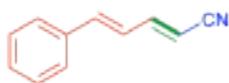
yield). The product **2o** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=87:13). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 19.5 Hz, 1.25 H), 7.18-7.06 (m, 1.01 H), 7.05-6.89 (m, 0.44 H), 6.77-6.40 (m, 2.33 H), 5.75 (d, *J* = 16.2 Hz, 1 H *trans* isomer), 5.23 (d, *J* = 12.0 Hz, 0.21 H *cis* isomer). ¹³C NMR (100.6 MHz, CDCl₃): δ 149.75, 145.50, 145.01, 136.14, 134.84, 118.30, 115.61, 115.54, 112.67, 112.45, 93.24, 91.11. Exact mass calculated for C₇H₅NO, *m/z* 119.03; GC-MS, *m/z* 119.03.

3-Cyclopentylacrylonitrile (2p).⁸ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 95:5) to afford **2s** as a colorless oil (22 mg, 60% yield). The product **2s** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=95:5). ¹H NMR (400 MHz, CDCl₃) δ 6.62 (dd, *J* = 16.3, 8.0 Hz, 1.19 H), 6.33 (dd, *J* = 27.1, 16.6 Hz, 0.08 H), 5.23 (dd, *J* = 16.3, 0.9 Hz, 1H *trans* isomer), 5.14 (d, *J* = 10.8 Hz, 0.05 H *cis* isomer), 2.64-2.45 (m, 1.24 H), 1.86-1.73 (m, 2.41 H), 1.70-1.51 (m, 4.62 H), 1.31 (dq, *J* = 13.5, 7.4 Hz, 2.36 H). ¹³C NMR (100.6 MHz, CDCl₃): δ 160.20, 159.93, 117.82, 97.80, 97.47, 43.99, 42.70, 32.95, 32.18, 25.60, 25.22. Exact mass calculated for C₈H₁₁N, *m/z* 121.08; GC-MS, *m/z* 121.08.

5-Phenylpenta-2,4-dienitrile (2q).⁸ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 90:10) to afford **2p** as a colorless oil (46 mg, 98% yield). The product **2p** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=82:18). ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.22 (m, 6.24 H), 7.20-6.99 (m, 1.30 H), 6.94-6.66 (m, 2.53 H), 5.34 (d, *J* = 15.9 Hz, 1 H, *trans* isomer), 5.16 (d, *J* = 10.6 Hz, 0.21 H, *cis* isomer). ¹³C NMR (100.6 MHz, CDCl₃): δ 150.41, 149.33, 141.78, 141.44, 135.35, 129.82, 129.74, 129.02, 127.69, 127.50, 125.52, 124.23, 118.45, 116.78, 98.33, 96.62. Exact mass calculated for C₁₁H₉N, *m/z* 155.07; GC-MS, *m/z* 155.07.

4-Methyl-5-phenylpenta-2,4-dienenitrile (2r). Purified by column chromatography using



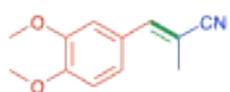
silica gel (eluent: hexane/EtOAc = 90:10) to afford **2q** as a colorless oil (50 mg, 98% yield). The product **2q** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=92:8). ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.17 (m, 5.58 H), 7.12 (d, *J* = 16.2 Hz, 1.17 H), 6.75 (d, *J* = 19.4 Hz, 1.16 H), 5.37 (d, *J* = 12.8 Hz, 0.08 H *cis* isomer), 5.32 (d, *J* = 16.2 Hz, 1 H *trans* isomer), 1.93 (d, *J* = 0.8 Hz, 3.41 H). ¹³C NMR (100.6 MHz, CDCl₃): δ 155.43, 148.64, 139.88, 138.20, 136.04, 133.53, 129.64, 129.48, 128.55, 128.35, 118.78, 97.63, 95.22, 19.80, 13.13. Exact mass calculated for C₁₂H₁₁N, *m/z* 169.08; GC-MS, *m/z* 169.08.

5-(Furan-2-yl)penta-2,4-dienenitrile (2s). Purified by column chromatography using silica



gel (eluent: hexane/EtOAc = 90:10) to afford **2r** as a colorless oil (37 mg, 84% yield). The product **2r** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=83:17). ¹H NMR (400 MHz, CDCl₃) δ 7.52-7.35 (m, 1.14 H), 7.12-6.93 (m, 1.21 H), 6.82 (t, *J* = 11.1 Hz, 0.24 H), 6.62 (ddd, *J* = 29.3, 18.1, 13.0 Hz, 2.25 H), 6.49-6.36 (m, 2.40 H), 5.33 (d, *J* = 15.8 Hz, 1 H *trans* isomer), 5.13 (d, *J* = 10.6 Hz, 0.20 H *cis* isomer). ¹³C NMR (100.6 MHz, CDCl₃): δ 151.63, 149.85, 148.73, 144.52, 144.36, 127.96, 127.64, 123.78, 122.61, 118.61, 113.28, 113.22, 112.48, 112.43, 98.02, 96.33. Exact mass calculated for C₉H₇NO, *m/z* 145.05; GC-MS, *m/z* 145.05.

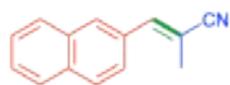
3-(3,4-Dimethoxyphenyl)-2-methylacrylonitrile (2t). Purified by column chromatography



using silica gel (eluent: hexane/EtOAc = 97:3) to afford **2t** as a colorless oil (49 mg, 80% yield). The product **2t** was isolated as an unseparable mixture of *cis/trans* isomers (E/Z=80:20). ¹H NMR (400 MHz, CDCl₃): δ 7.43 (s, 0.56 H), 7.19 (s, 0.79 H), 7.12-7.05 (m, 1.42 H), 6.89 (d, *J* = 8.3 Hz, 1.07 H), 6.84-6.80 (m, 1.43 H), 6.79 (d, *J* = 6.0 Hz, 1.94 H), 3.85 (d, *J* = 5.4 Hz, 6 H), 3.82 (s, 3 H), 2.10 (s, 3 H *trans* isomer), 2.07 (s, 1.93 H *cis* isomer). ¹³C NMR (100.6 MHz, CDCl₃): δ 150.60, 150.20, 149.10, 149.03,

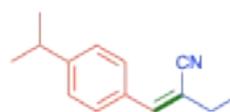
144.37, 144.00, 127.27, 126.99, 123.15, 123.01, 121.90, 120.01, 112.56, 111.16, 110.99, 110.36, 107.46, 103.24, 56.11, 56.08, 22.18, 17.07. Exact mass calculated for C₁₂H₁₃NO₂, m/z 203.09; GC-MS, m/z 203.09.

2-Methyl-3-(naphthalen-2-yl)acrylonitrile (2u). Purified by column chromatography using



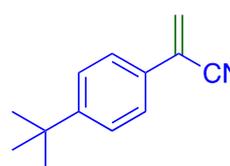
silica gel (eluent: hexane/EtOAc = 97:3) to afford **2u** as a colorless oil (34 mg, 57% yield). The product **2u** was isolated as an unseparable mixture of cis/trans isomers (E/Z=75:25). ¹H NMR (400 MHz, CDCl₃): δ 7.84-7.74 (m, 3.77 H), 7.72 (s, 1.06 H), 7.51-7.41 (m, 2.43 H), 7.35 (dd, J = 8.5, 1.6 Hz, 1.07 H), 7.29 (s, 1 H *trans* isomer), 7.18 (s, 0.25 H *cis* isomer), 2.16 (d, J = 1.5 Hz, 3 H), 2.14 (d, J = 1.5 Hz, 0.39 H). ¹³C NMR (100.6 MHz, CDCl₃): δ 144.64, 144.19, 133.38, 133.08, 131.74, 129.61, 129.19, 128.71, 128.69, 128.55, 127.87, 127.84, 127.45, 127.37, 126.95, 126.79, 126.31, 124.98, 121.53, 109.90, 22.50, 17.11. Exact mass calculated for C₁₄H₁₁N, m/z 193.08; GC-MS, m/z 193.08.

2-(4-Isopropylbenzylidene)butanenitrile (2v). Purified by column chromatography using



silica gel (eluent: hexane/EtOAc = 97:3) to afford **2v** as a colorless oil (51 mg, 86% yield). The product **2v** was isolated as an unseparable mixture of cis/trans isomers (E/Z=70:30). ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, J = 8.2 Hz, 1.75 H), 7.23-7.11 (m, 4.50 H), 7.08 (s, 0.43 H *cis* isomer), 6.83 (s, 1 H *trans* isomer), 2.85 (dt, J = 13.8, 6.9 Hz, 1.47 H), 2.38 (dtd, J = 22.5, 7.5, 0.9 Hz, 2.99 H), 1.26-1.07 (m, 13.31 H). ¹³C NMR (100.6 MHz, CDCl₃): δ 151.14, 150.53, 143.68, 142.59, 142.18, 131.83, 131.59, 130.12, 129.42, 128.75, 127.26, 126.98, 126.91, 125.19, 120.60, 119.12, 116.31, 111.85, 34.59, 34.16, 34.11, 29.70, 29.19, 23.89, 23.87, 23.75, 23.43, 23.10, 13.19, 12.93. Exact mass calculated for C₁₄H₁₇N, m/z 199.13; GC-MS, m/z 199.13.

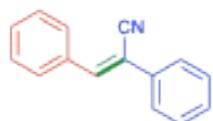
2-(4-(tert-Butyl)phenyl)acrylonitrile (2w). Purified by column chromatography using silica



gel (eluent: hexane/EtOAc = 97:3) to afford **2w** as a colorless oil (50 mg,

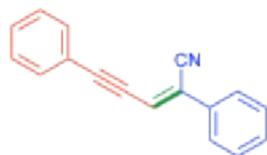
90% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, $J = 8.5$ Hz, 2H), 7.37 (d, $J = 8.5$ Hz, 2H), 6.22 (s, 1H), 5.98 (s, 1H), 1.26 (s, 9H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 153.50, 129.73, 127.19, 126.12, 125.65, 122.90, 118.01, 34.94, 31.30. Exact mass calculated for $\text{C}_{13}\text{H}_{15}\text{N}$, m/z 185.12; GC-MS, m/z 185.12.

2,3-Diphenylacrylonitrile (2x).¹⁴ Purified by column chromatography using silica gel



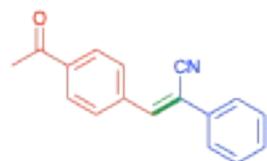
(eluent: hexane/EtOAc = 97:3) to afford **2x** as a colorless oil (61 mg, 99% yield). The product **2x** was isolated as a trans isomer (E/Z=99:1). ^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, $J = 7.4$ Hz, 2H), 7.78 (d, $J = 7.8$ Hz, 2H), 7.64 (s, 1H), 7.60-7.33 (m, 6H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 142.40, 134.62, 133.87, 130.68, 129.41, 129.35, 129.21, 129.10, 126.15, 118.14, 111.86. Exact mass calculated for $\text{C}_{15}\text{H}_{11}\text{N}$, m/z 205.08; GC-MS, m/z 205.08.

2,5-Diphenylpent-2-en-4-ynenitrile (2y). Purified by column chromatography using silica



gel (eluent: hexane/EtOAc = 90:10) to afford **2y** as a colorless oil (62 mg, 90% yield). The product **2y** was isolated as an unseparable mixture of cis/trans isomers (E/Z=70:30). ^1H NMR (400 MHz, CDCl_3): δ 7.53 (ddd, $J = 9.5, 7.9, 2.2$ Hz, 4.15 H), 7.42-7.28 (m, 6.48 H), 6.80 (s, 1 H *trans* isomer), 6.60 (s, 0.08 H *cis* isomer). ^{13}C NMR (100.6 MHz, CDCl_3): δ 132.46, 132.40, 132.08, 130.33, 130.27, 130.03, 129.87, 129.33, 128.79, 128.74, 128.68, 128.16, 125.80, 123.76, 122.05, 121.58, 121.31, 116.64, 102.72, 86.50. Exact mass calculated for $\text{C}_{17}\text{H}_{11}\text{N}$, m/z 229.08; GC-MS, m/z 229.08.

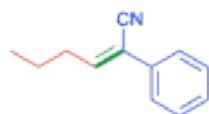
3-(4-Acetylphenyl)-2-phenylacrylonitrile (2z). Purified by column chromatography using



silica gel (eluent: hexane/EtOAc = 80:20) to afford **2z** as a colorless solid (72 mg, 97% yield). The product **2z** was isolated as a trans isomer (E/Z=99:1). ^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, $J = 30.9, 8.4$ Hz,

4H), 7.62 (dd, $J = 7.9, 1.2$ Hz, 2H), 7.49 (s, 1H), 7.43-7.33 (m, 3H), 2.56 (s, 3H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 197.30, 140.60, 138.04, 138.00, 134.03, 129.88, 129.46, 129.30, 128.93, 126.26, 117.64, 114.28, 26.83. Exact mass calculated for $\text{C}_{17}\text{H}_{13}\text{NO}$, m/z 247.09; GC-MS, m/z 247.09.

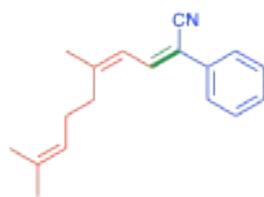
2-Phenylhex-2-enenitrile (2ab).¹⁵ Purified by column chromatography using silica gel



(eluent: hexane/EtOAc = 97:3) to afford **2ab** as a colorless oil (44 mg, 85% yield). The product **2ab** was isolated as an unseparable mixture of cis/trans

isomers (E/Z=90:10). ^1H NMR (400 MHz, CDCl_3): δ 7.53-7.41 (m, 2.04 H), 7.39-7.21 (m, 3.49 H), 6.75 (t, $J = 7.8$ Hz, 1 H *trans* isomer), 6.55 (t, $J = 7.6$ Hz, 0.09 H *cis* isomer), 2.49 (dd, $J = 15.0, 7.5$ Hz, 2.11 H), 2.24 (dd, $J = 14.9, 7.5$ Hz, 0.21 H), 1.64-1.47 (m, 2.21 H), 1.41-1.35 (m, 0.28 H), 0.94 (t, $J = 7.4$ Hz, 3.16 H), 0.85 (t, $J = 7.4$ Hz, 0.32 H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 149.72, 147.08, 133.41, 129.60, 129.25, 129.03, 128.95, 128.91, 128.82, 128.75, 125.73, 116.78, 116.20, 34.21, 31.71, 22.24, 22.13, 13.80. Exact mass calculated for $\text{C}_{12}\text{H}_{13}\text{N}$, m/z 171.10; GC-MS, m/z 171.10.

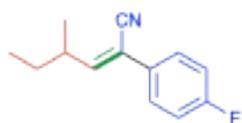
(4E)-5,9-Dimethyl-2-phenyldeca-2,4,8-trienenitrile (2ac). Purified by column



chromatography using silica gel (eluent: hexane/EtOAc = 97:3) to afford **2ac** as a pale yellow oil (67 mg, 89% yield). The product **2ac** was isolated as an unseparable mixture of cis/trans isomers

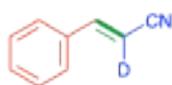
(E/Z=98:2). ^1H NMR (400 MHz, CDCl_3): δ 7.50 (dd, $J = 12.2, 4.4$ Hz, 2H), 7.40 (dd, $J = 11.7, 6.8$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.26-7.16 (m, 1H), 6.46 (d, $J = 11.7$ Hz, 1H), 5.05 (dd, $J = 9.7, 3.9$ Hz, 1H), 2.33-2.01 (m, 4H), 1.90 (dd, $J = 11.6, 0.8$ Hz, 3H), 1.57 (dd, $J = 23.9, 11.5$ Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 151.74, 151.65, 138.21, 138.06, 134.01, 133.16, 132.62, 129.05, 128.69, 128.66, 125.59, 125.55, 123.64, 123.23, 123.12, 122.85, 117.37, 110.93, 110.58, 40.70, 33.47, 26.96, 26.55, 25.80, 24.91, 17.93, 17.87, 17.86. Exact mass calculated for $\text{C}_{18}\text{H}_{21}\text{N}$, m/z 251.16; GC-MS, m/z 251.16.

2-(4-Fluorophenyl)-4-methylhex-2-enenitrile (2ad). Purified by column chromatography



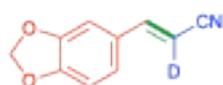
using silica gel (eluent: hexane/EtOAc = 97:3) to afford **2ad** as a colorless oil (53 mg, 87% yield). The product **2ac** was isolated as an unseparable mixture of cis/trans isomers (E/Z=90:10). ¹H NMR (400 MHz, CDCl₃): δ 7.44 (ddd, J = 7.0, 5.0, 2.5 Hz, 1.94 H), 7.31-7.20 (m, 0.26 H), 7.02 (q, J = 8.6 Hz, 2.18 H), 6.45 (d, J = 10.3 Hz, 1 H *trans* isomer), 6.33 (d, J = 10.9 Hz, 0.10 H *cis* isomer), 2.75 (ddd, J = 14.3, 10.3, 6.6 Hz, 0.97 H), 2.43 (dt, J = 17.8, 6.8 Hz, 0.11 H), 1.64-1.29 (m, 2.12 H), 1.08 (d, J = 6.6 Hz, 3.23 H), 0.98 (d, J = 6.6 Hz, 0.39 H), 0.88 (t, J = 7.4 Hz, 3.11 H), 0.76 (t, J = 7.5 Hz, 0.32 H). ¹³C NMR (100.6 MHz, CDCl₃): δ 164.35, 161.88, 155.70, 152.54, 152.52, 130.62, 130.53, 129.61, 129.58, 127.66, 127.58, 116.77, 116.19, 115.97, 113.88, 39.07, 35.45, 29.80, 29.59, 20.06, 19.73, 11.95, 11.80. Exact mass calculated for C₁₃H₁₄FN, m/z 203.11; GC-MS, m/z 203.11.

3-Phenylacrylonitrile-2-D (2ae).¹⁶ Purified by column chromatography using silica gel



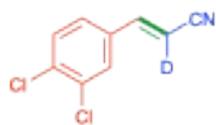
(eluent: hexane/EtOAc = 97:3) to afford **2ae** as a colorless oil (39 mg, 99% yield). The product **2ae** was isolated as a mixture of cis/trans isomers with an E/Z ratio of 80:20. ¹H NMR (400 MHz, CDCl₃): δ 7.58-7.13 (m, 6H). ¹³C NMR (100.6 MHz, CDCl₃): δ 150.57, 148.68, 133.59, 131.30, 131.06, 129.21, 129.10, 129.02, 127.45, 118.23, 96.47, 96.21, 95.95.

3-(Benzo[d][1,3]dioxol-5-yl)acrylonitrile-2-D (2af). Purified by column chromatography



using silica gel (eluent: hexane/EtOAc = 97:3) to afford **2af** as a colorless solid (51 mg, 97% yield). The product **2af** was isolated as a mixture of cis/trans isomers with an E/Z ratio was not determined. ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.21 (m, 1H), 6.94 (dd, J = 6.6, 1.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 1H), 6.04 (s, 2H). ¹³C NMR (100.6 MHz, CDCl₃): δ 150.48, 150.05, 148.70, 148.00, 128.08, 125.63, 124.20, 118.57, 108.78, 108.62, 108.05, 105.69, 101.94, 101.88, 94.04, 93.78, 93.52.

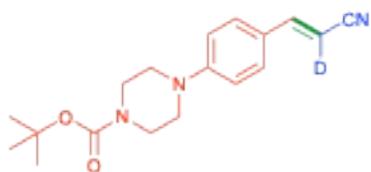
3-(3,4-Dichlorophenyl)acrylonitrile-2-D (2ag). Purified by column chromatography using



silica gel (eluent: hexane/EtOAc = 97:3) to afford **2ag** as a colorless solid (30 mg, 50% yield). The product **2ag** was isolated as a mixture of cis/trans

isomers with an E/Z ratio of 99:1. ^1H NMR (400 MHz, CDCl_3): δ 7.55-7.37 (m, 2H), 7.32-7.13 (m, 2H), 5.82 (d, J = 16.6 Hz, 1H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 147.99, 147.89, 135.52, 133.81, 133.48, 131.31, 129.13, 126.43, 117.47, 98.63, 98.59, 98.36, 98.11.

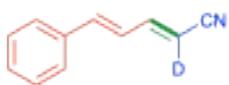
tert-Butyl 4-(4-(2-cyanovinyl-2-D)phenyl)piperazine-1-carboxylate (2ah). Purified by



column chromatography using silica gel (eluent: hexane/EtOAc = 70:30) to afford **2ah** as a colorless solid (91 mg, 97% yield). The product **2ah** was isolated as a mixture of

cis/trans isomers with an E/Z ratio of 96:4. ^1H NMR (400 MHz, CDCl_3): δ 7.27 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 3.3 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 3.63-3.41 (m, 4H), 3.31-3.11 (m, 4H), 1.41 (s, 9H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 154.74, 152.89, 150.06, 148.00, 130.89, 129.03, 124.49, 119.23, 115.16, 114.84, 91.94, 91.69, 91.43, 80.26, 47.81, 28.51.

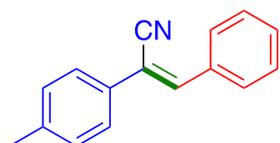
(4E)-5-Phenylpenta-2,4-dienitrile-2-D (2ai). Purified by column chromatography using



silica gel (eluent: hexane/EtOAc = 90:10) to afford **2ai** as a colorless solid (45 mg, 96% yield). The product **2ai** was isolated as a mixture of cis/trans

isomers with an E/Z ratio of 90:10. ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.35 (m, 2H), 7.34-7.24 (m, 3H), 7.09 (ddd, J = 21.5, 13.2, 10.0 Hz, 1H), 6.96-6.63 (m, 2H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 150.34, 150.28, 149.24, 141.82, 141.47, 141.37, 135.40, 129.86, 129.78, 129.06, 129.05, 127.73, 127.53, 125.52, 124.27, 118.46, 116.80, 98.40, 98.14, 97.88.

3-Phenyl-2-(p-tolyl)acrylonitrile (2aj).¹⁴ Purified by column chromatography using silica



gel (eluent: hexane/EtOAc = 98:2) to afford **2aj** as a colorless solid (53 mg, 80% yield). The product **2aj** was isolated as a single Z-

isomer. ^1H NMR (500 MHz, CDCl_3): δ 7.79 (d, $J = 7.3$ Hz, 2H), 7.48 (d, $J = 7.7$ Hz, 2H), 7.43-7.31 (m, 4H), 7.16 (d, $J = 7.3$ Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (125.7 MHz, CDCl_3): δ 141.33, 139.53, 133.98, 131.77, 130.44, 129.87, 129.30, 129.03, 125.98, 118.22, 111.76, 21.33. Exact mass calculated for $\text{C}_{16}\text{H}_{13}\text{N}$, m/z 219.10; GC-MS, m/z 219.10.

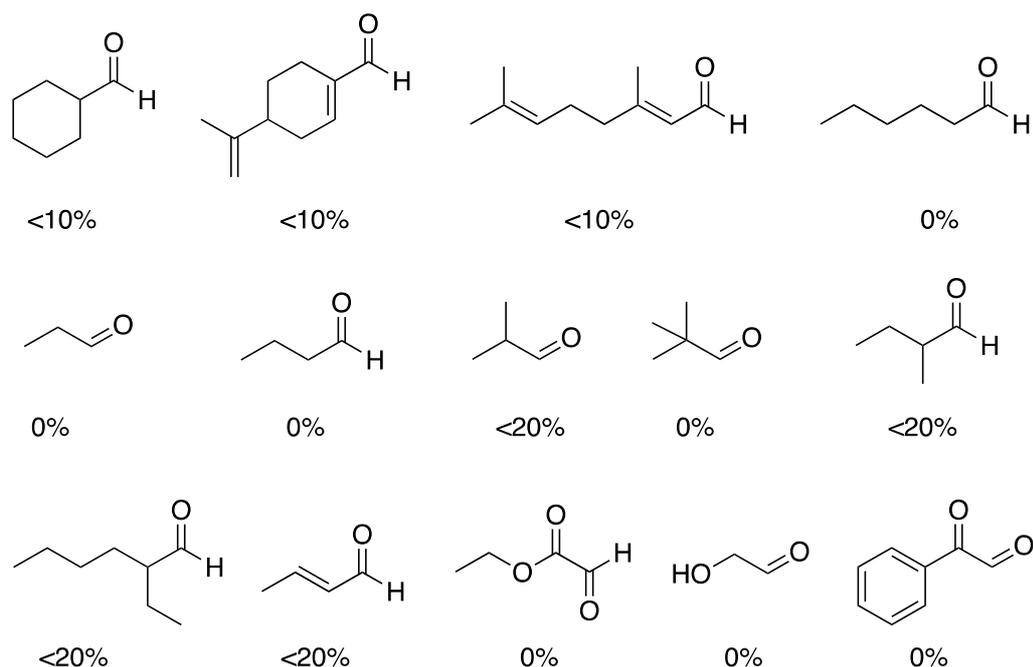
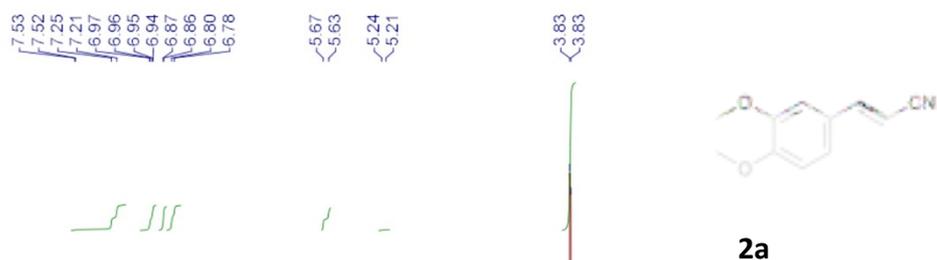


Figure S6. Aldehyde Substrates that Gave Poor Results in Reactions with Acetonitrile

Reaction Conditions: Aliphatic aldehydes were reacted with acetonitrile, both at room temperature and at elevated temperatures (60-100 $^{\circ}\text{C}$); only aldehyde self-condensation was observed, and formation of the desired vinyl nitriles was minimal.

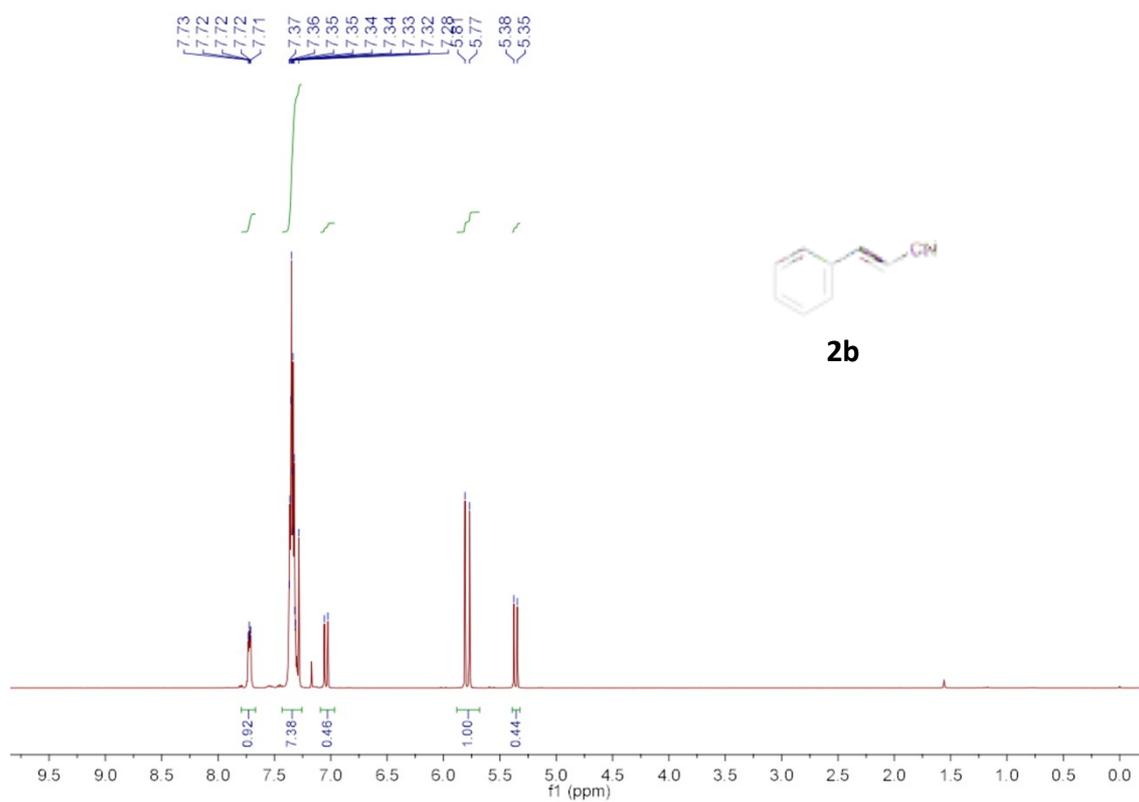
NMR Spectra of the Products

^1H NMR (400 MHz, CDCl_3)

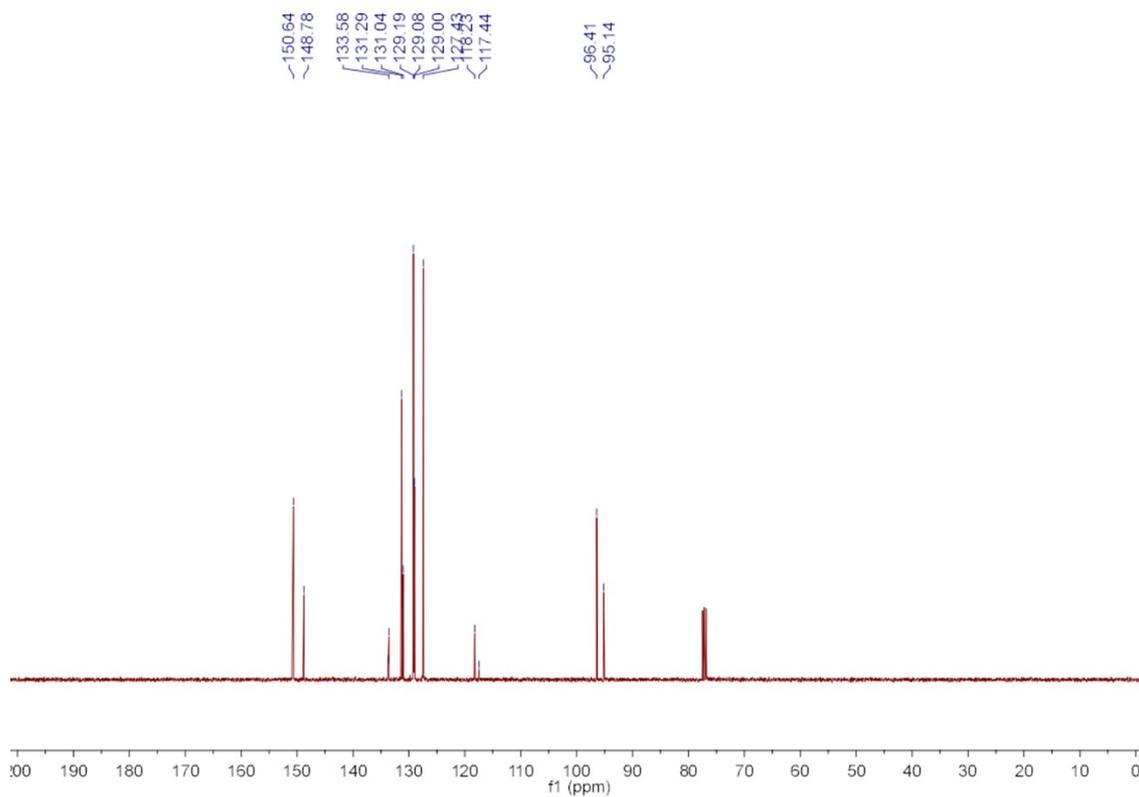


^{13}C NMR (100.6 MHz, CDCl_3)

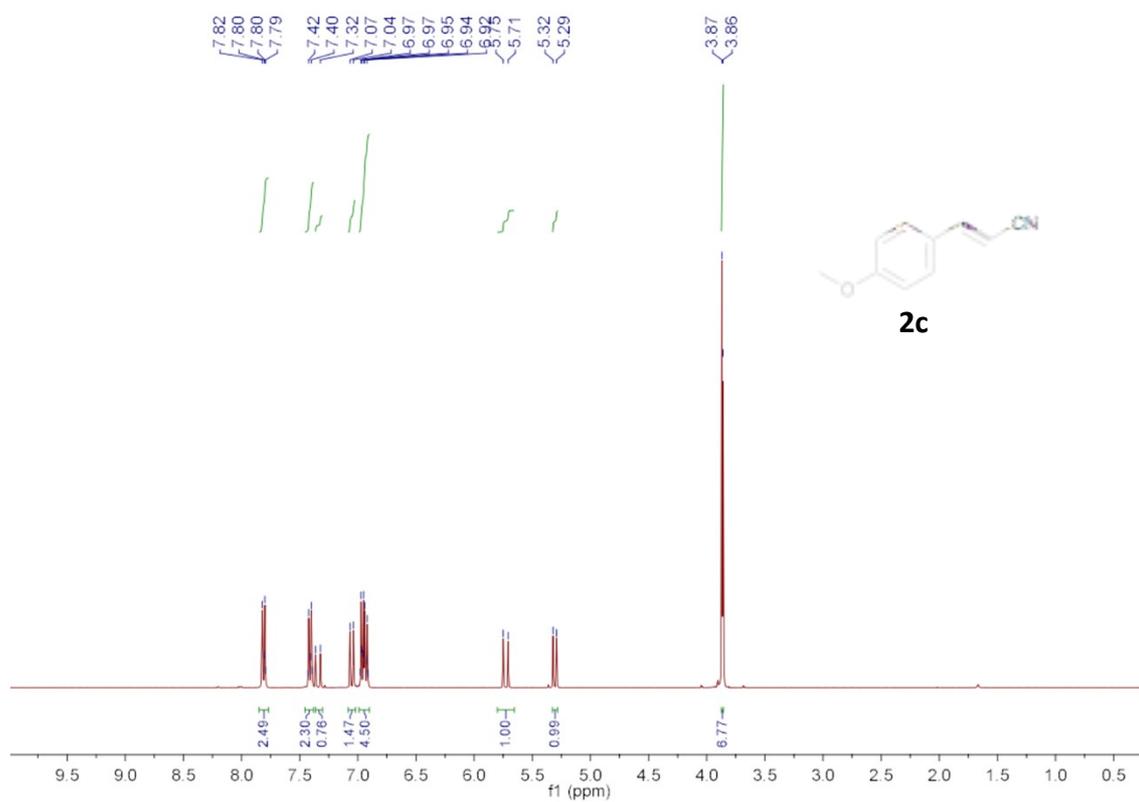
¹H NMR (400 MHz, CDCl₃)



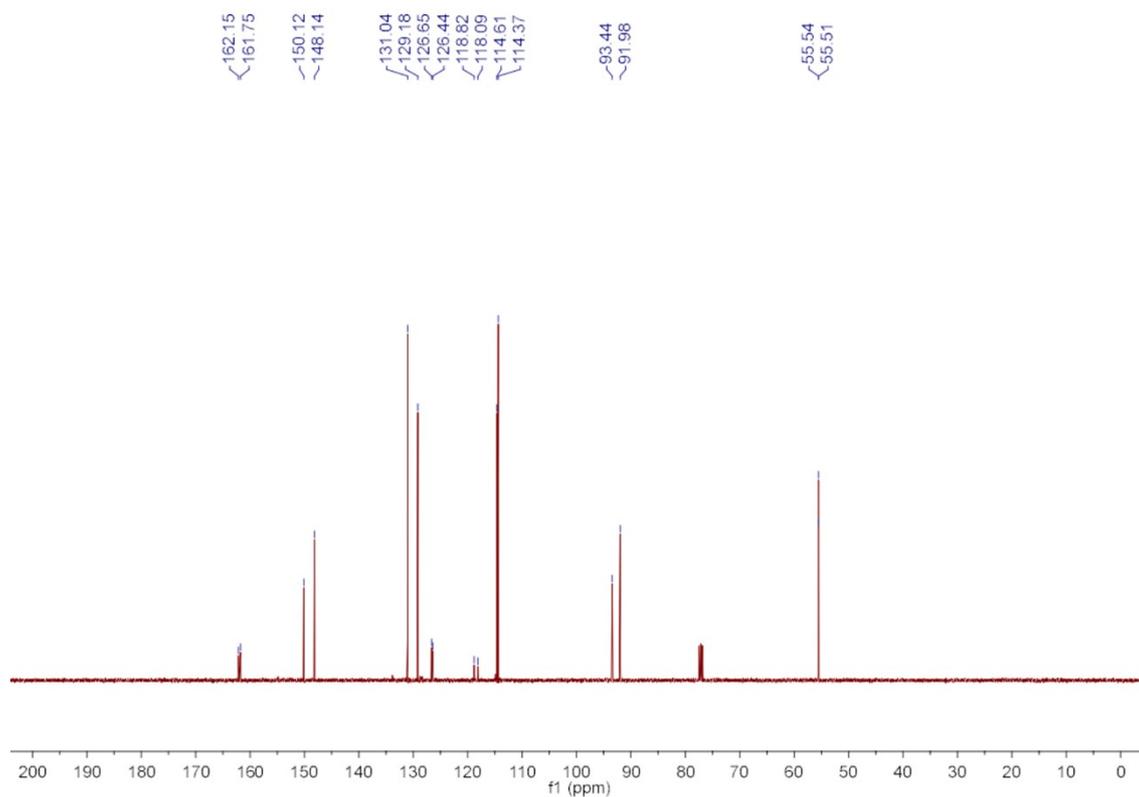
¹³C NMR (100.6 MHz, CDCl₃)



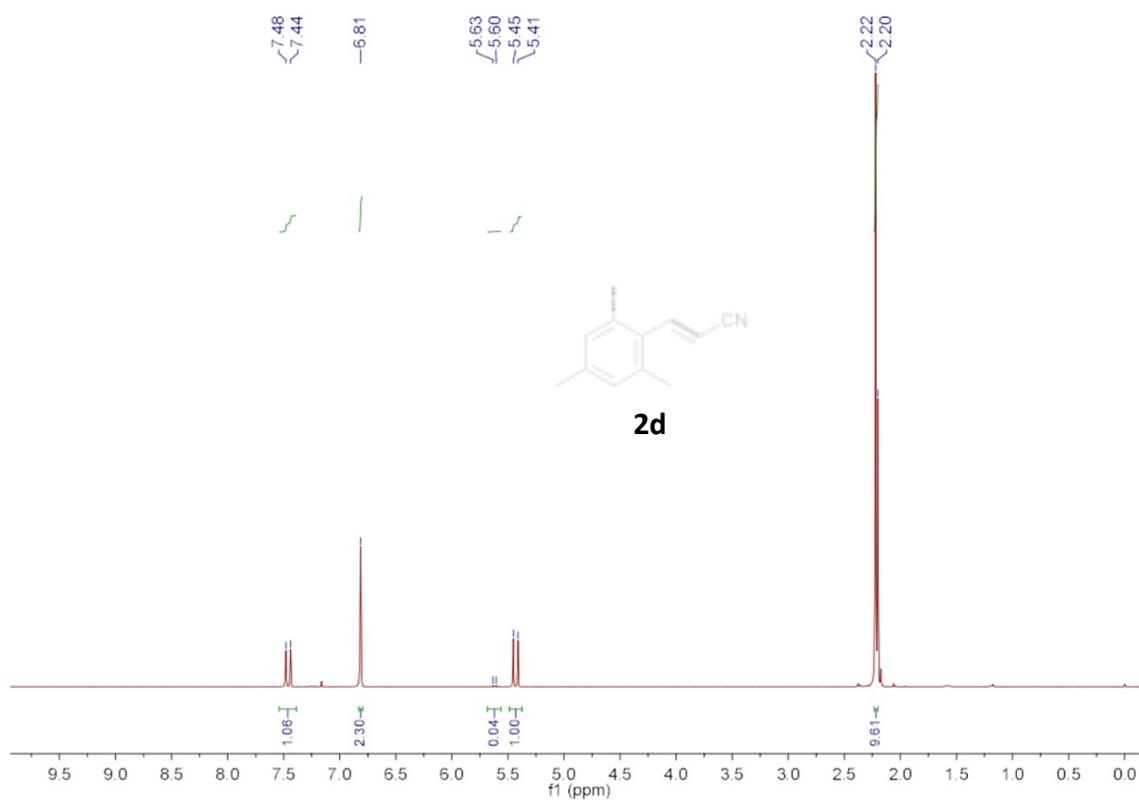
¹H NMR (400 MHz, CDCl₃)



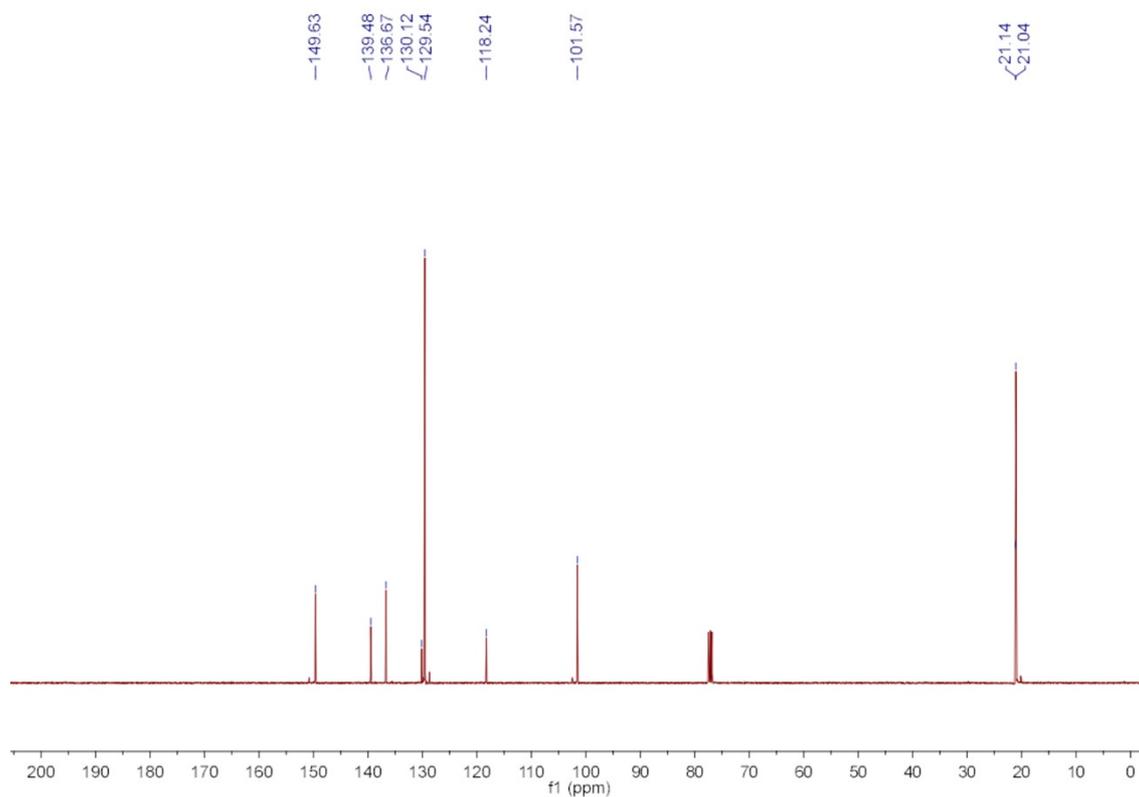
¹³C NMR (100.6 MHz, CDCl₃)



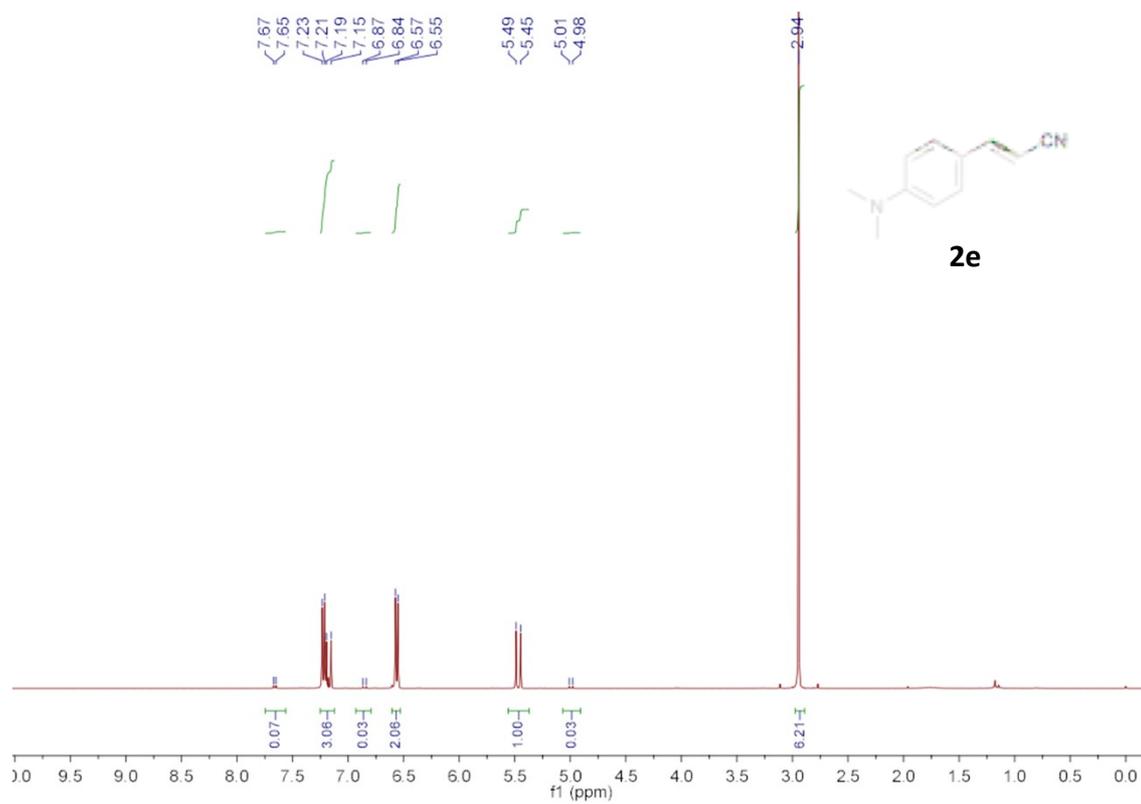
¹H NMR (400 MHz, CDCl₃)



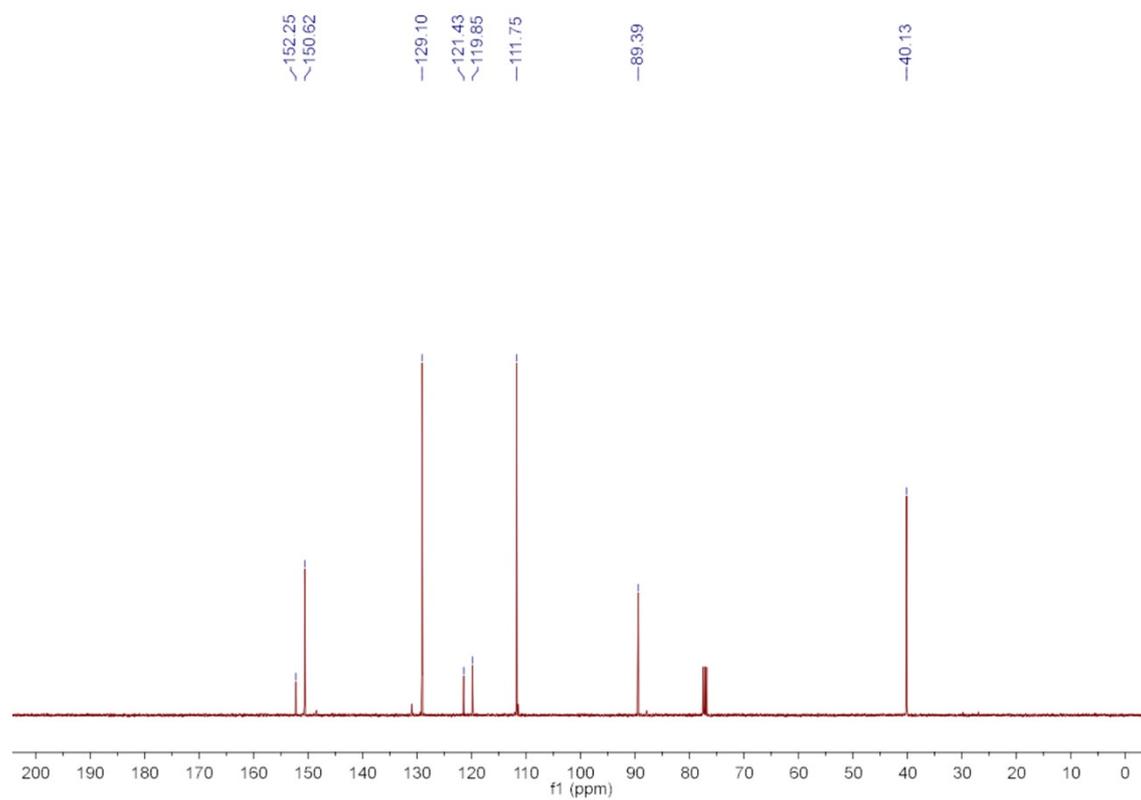
¹³C NMR (100.6 MHz, CDCl₃)



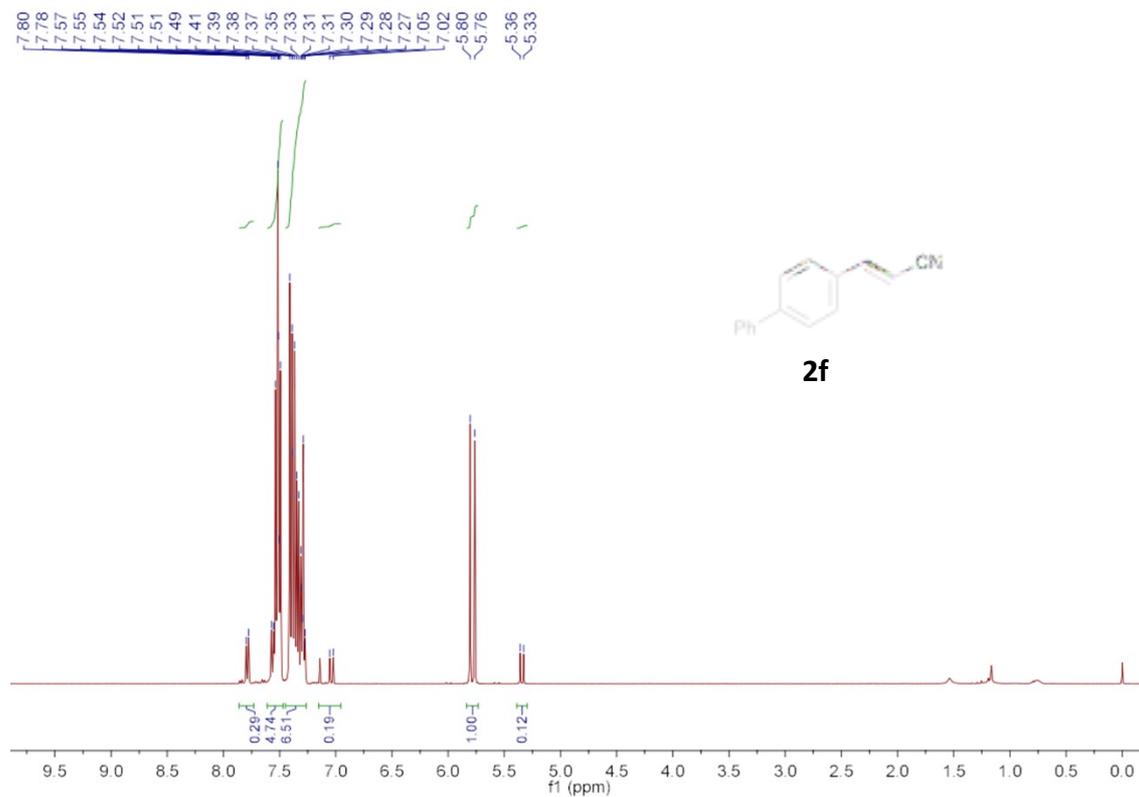
¹H NMR (400 MHz, CDCl₃)



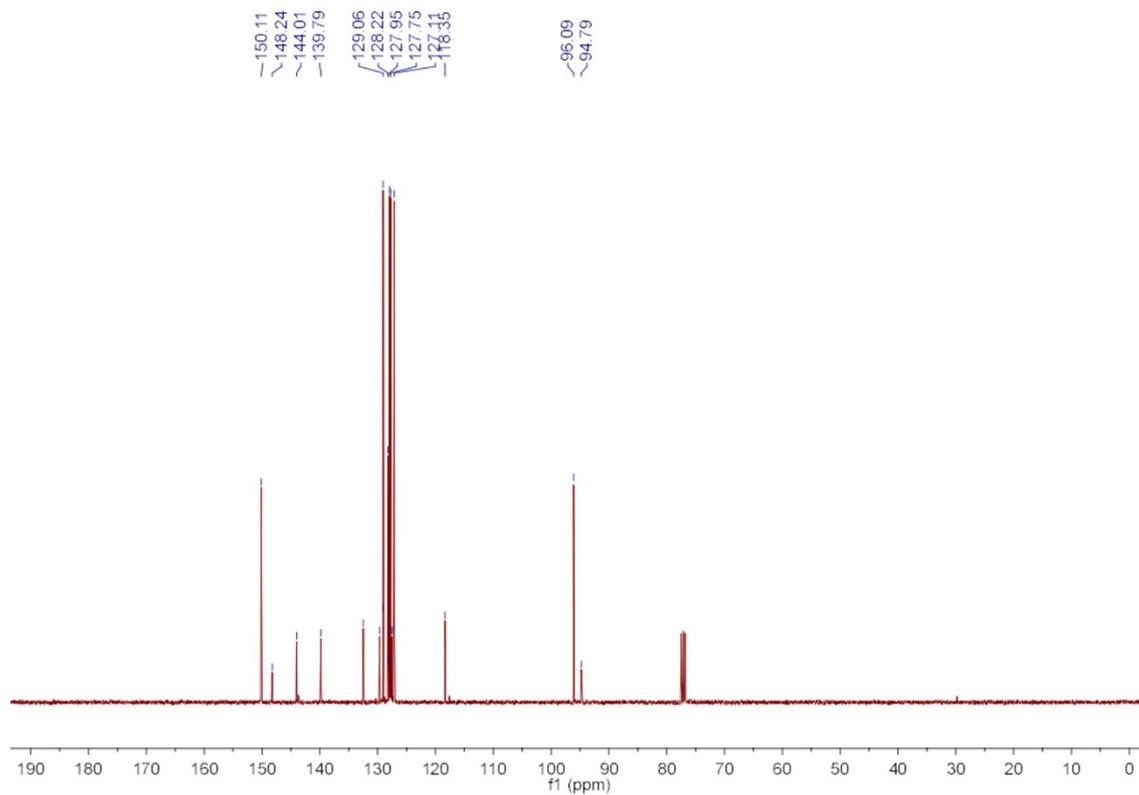
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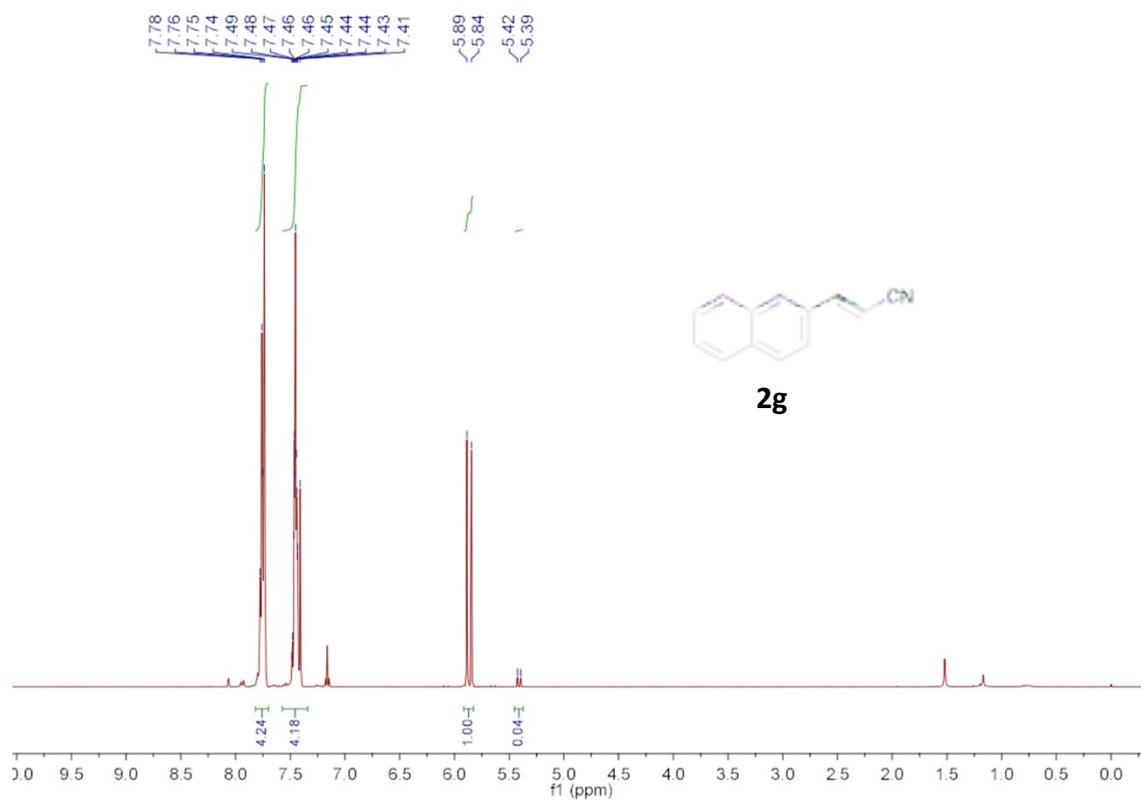
¹H NMR (400 MHz, CDCl₃)



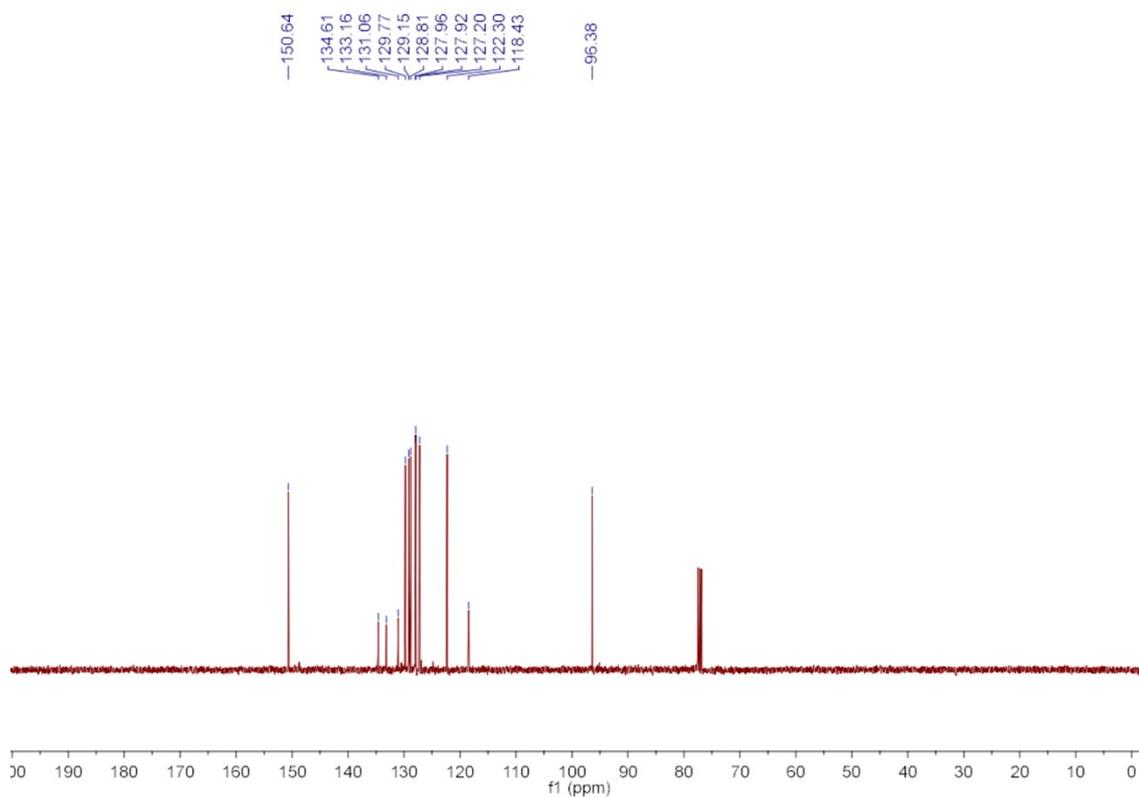
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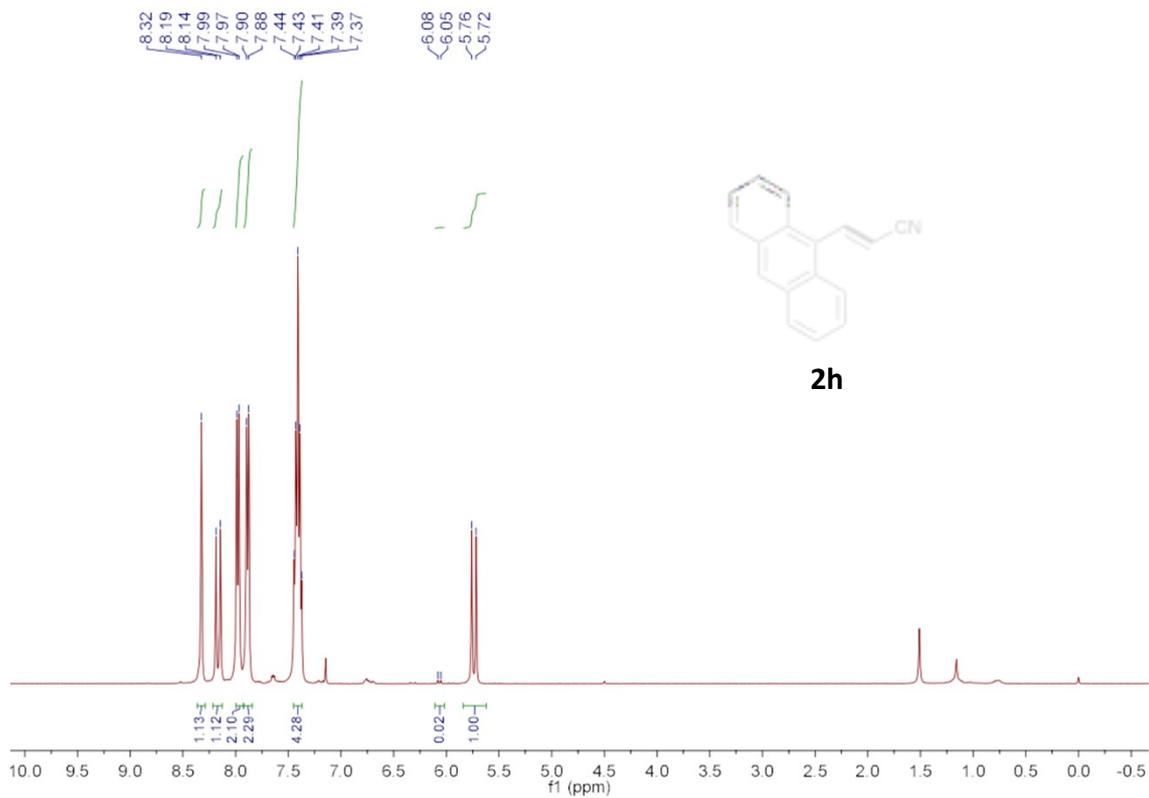
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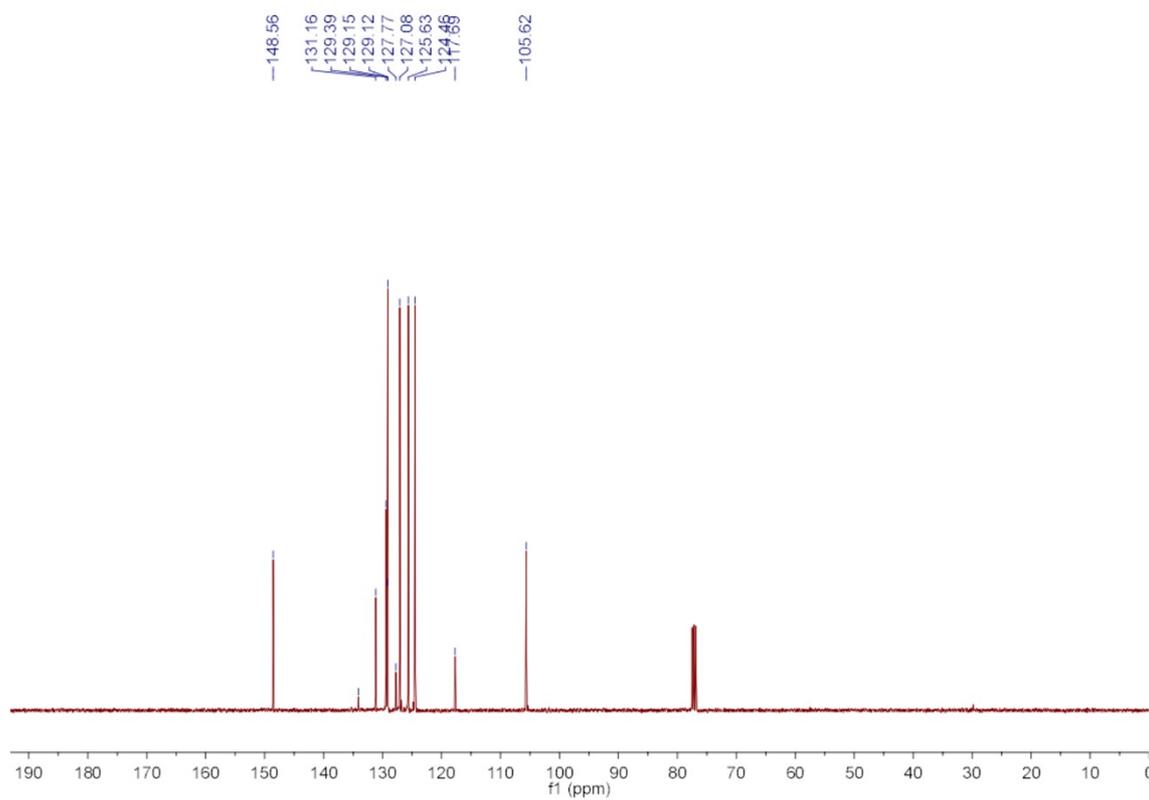
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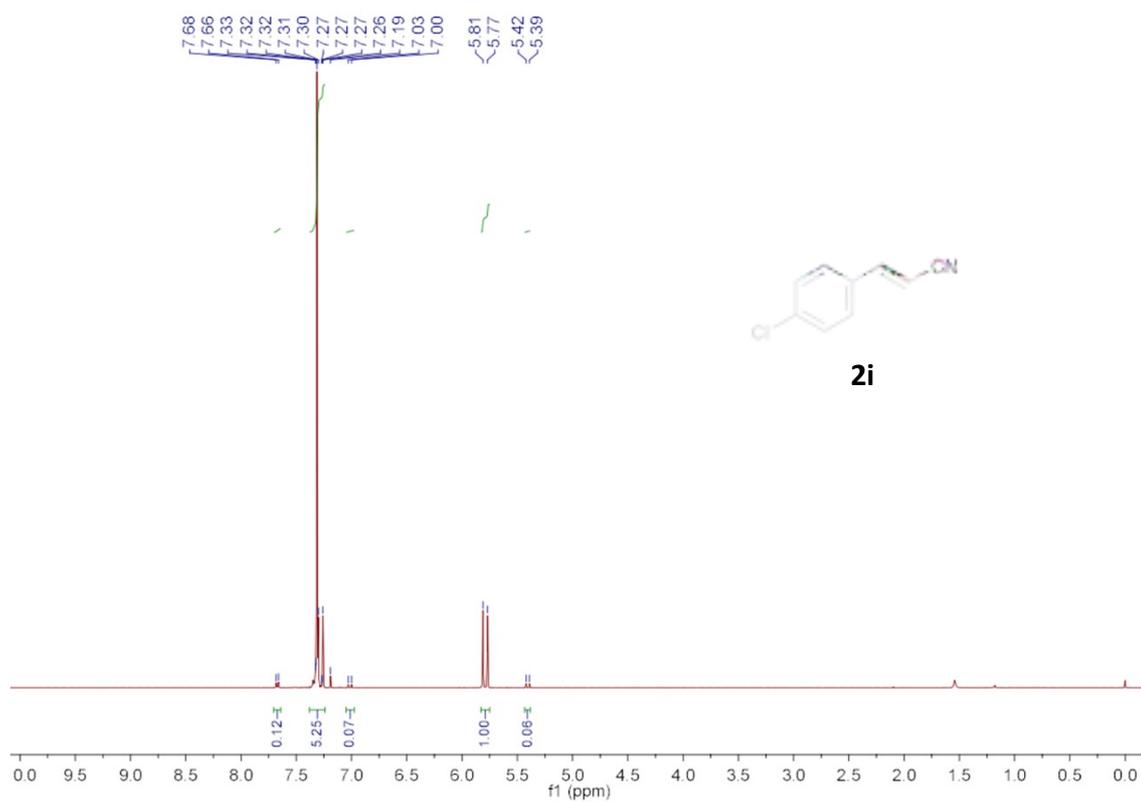
¹H NMR (400 MHz, CDCl₃)



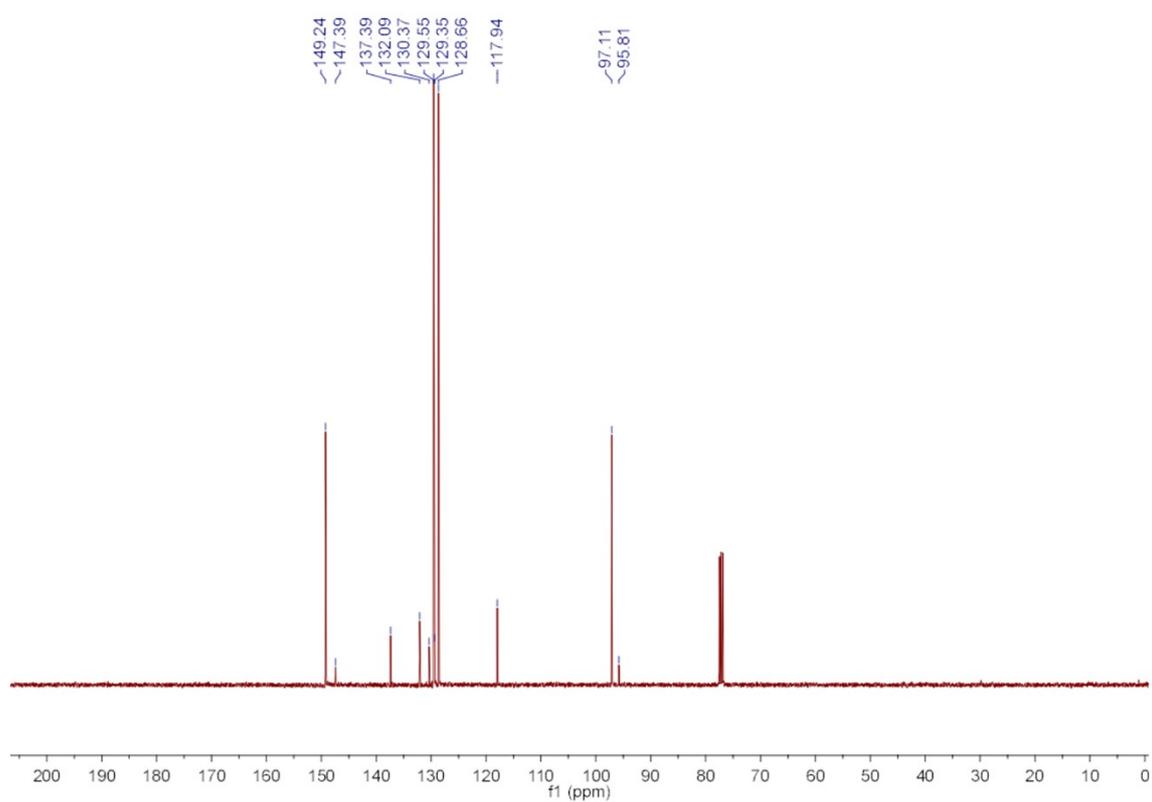
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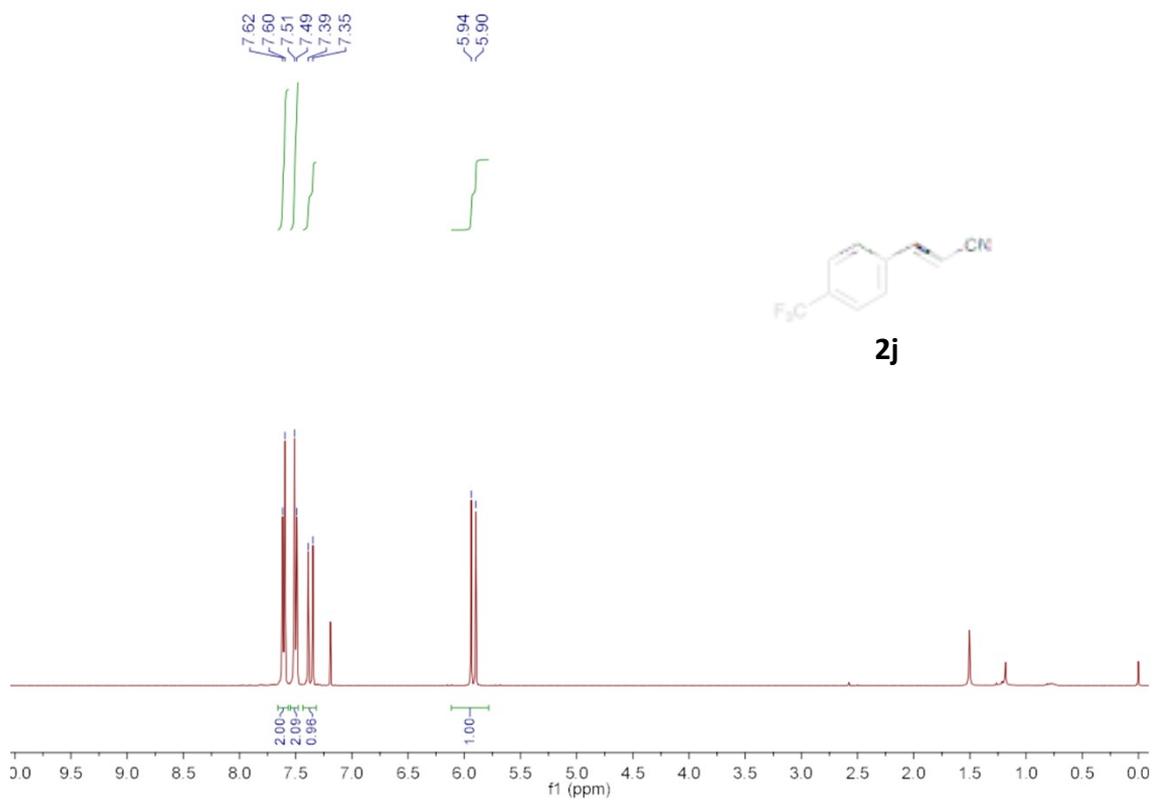
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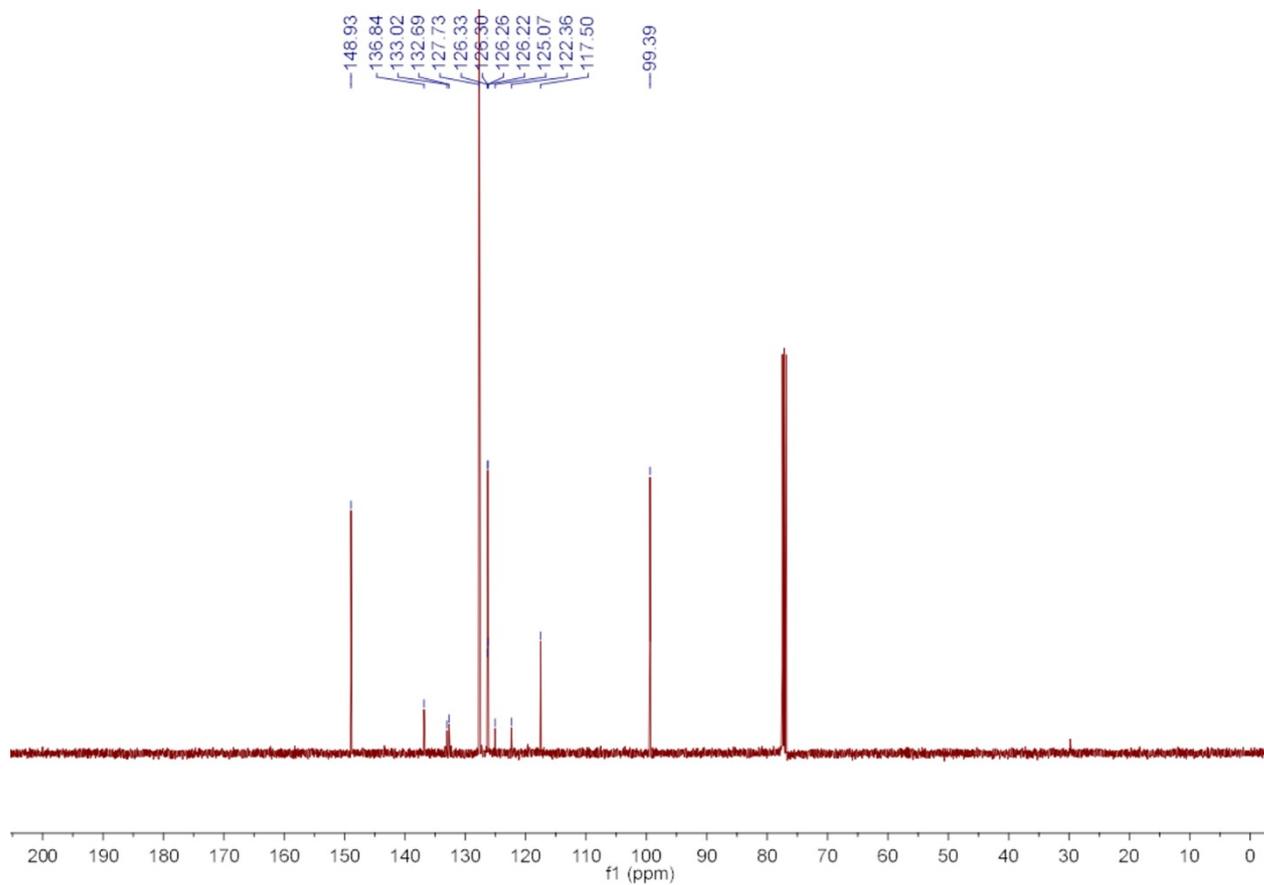
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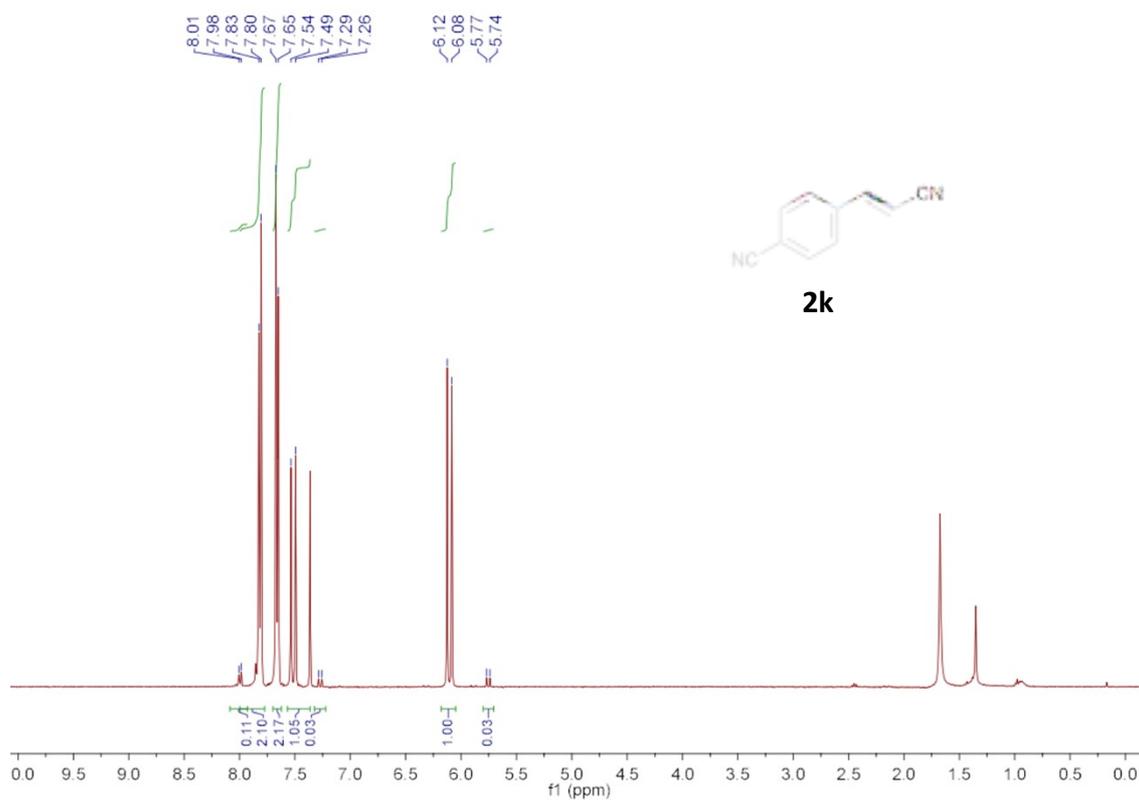
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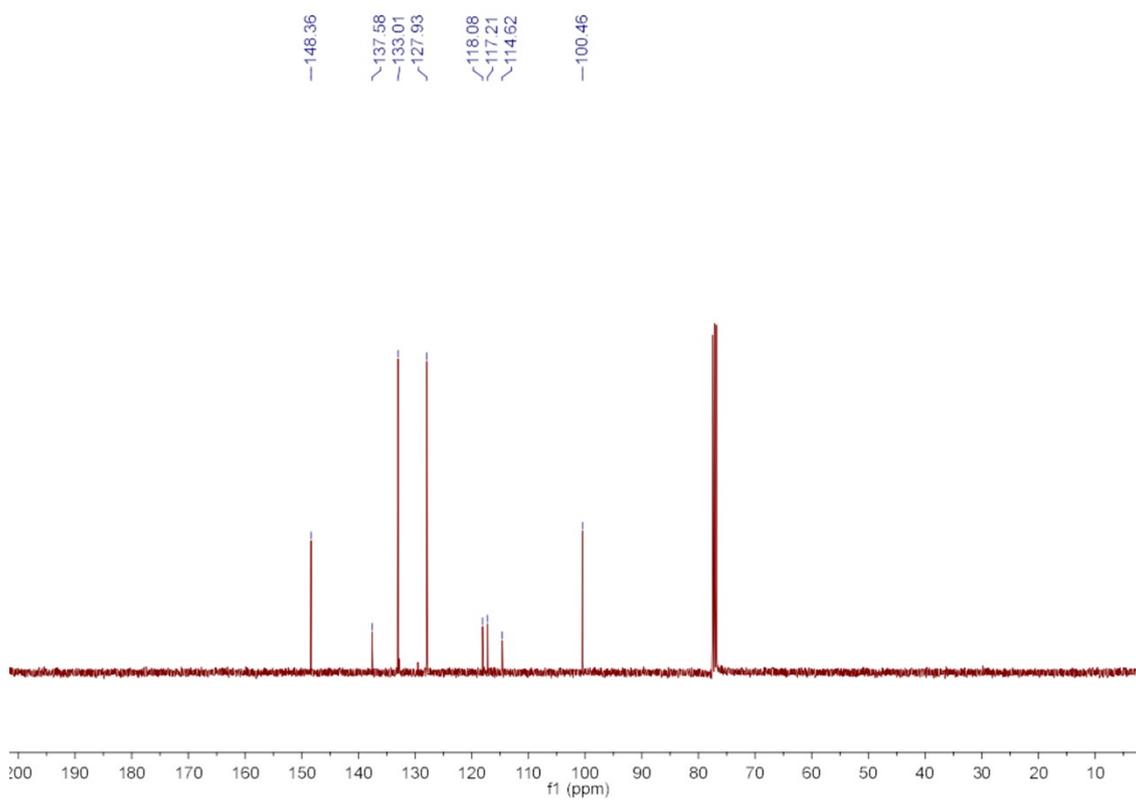
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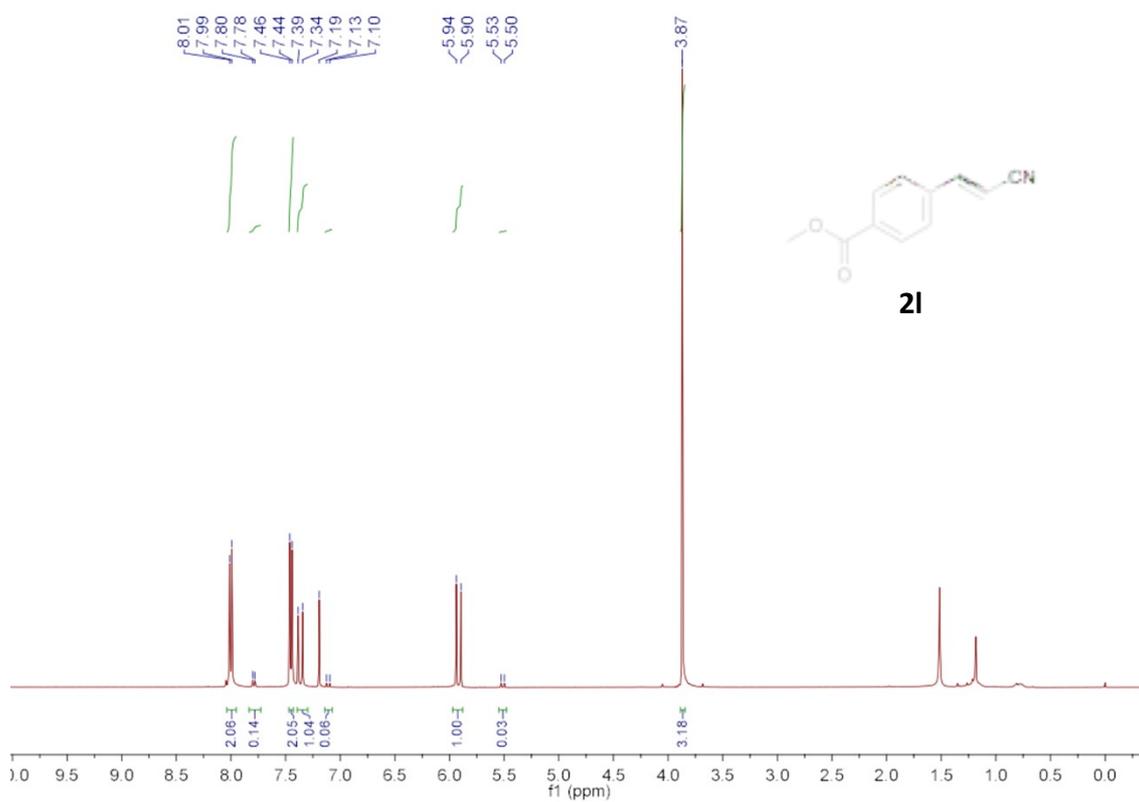
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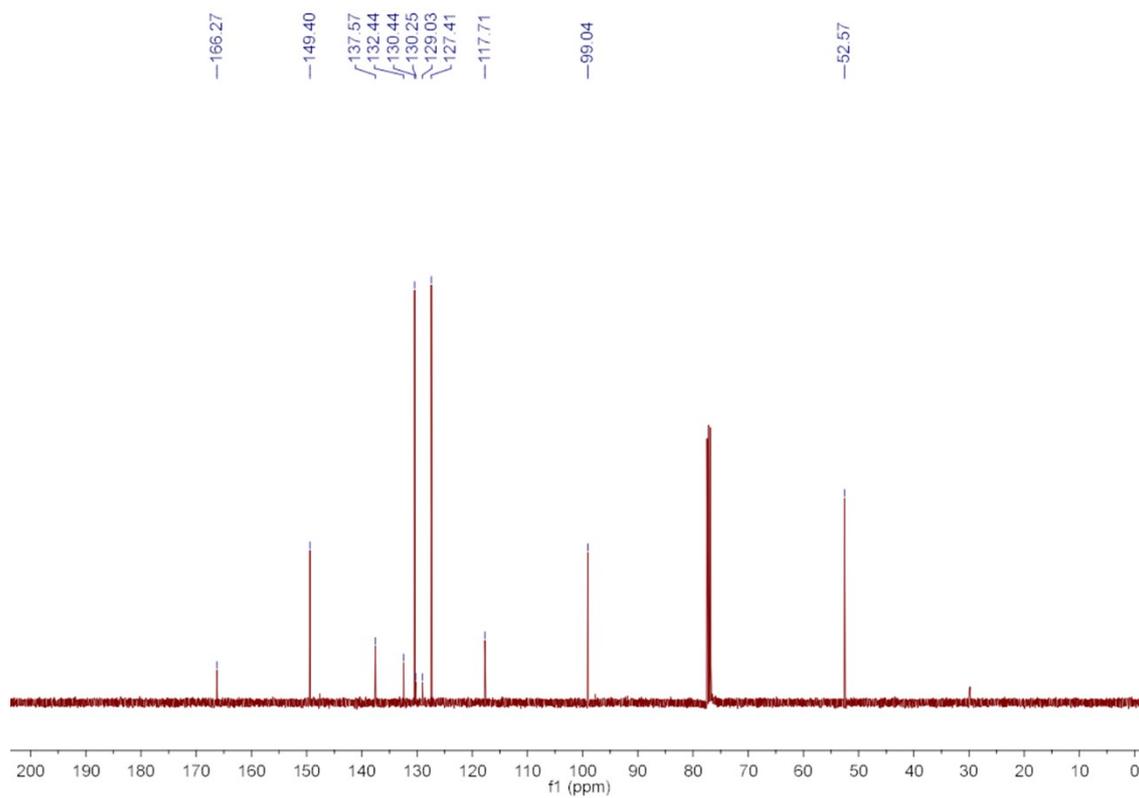
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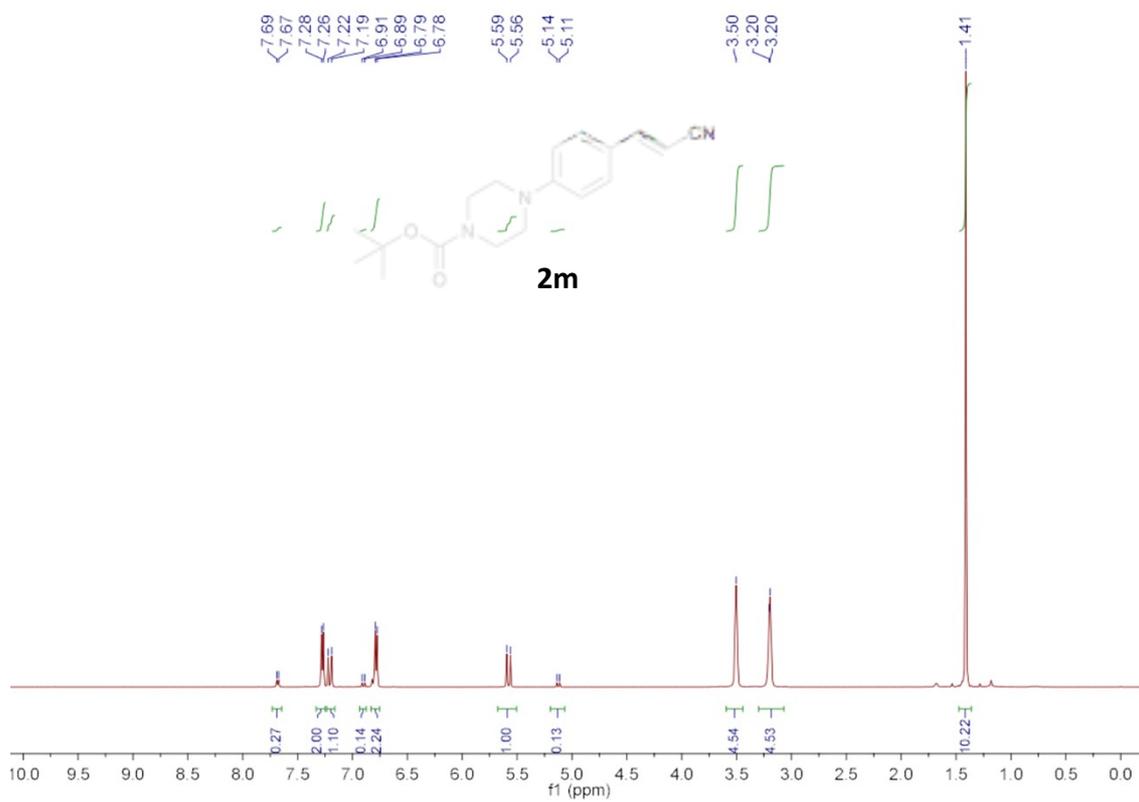
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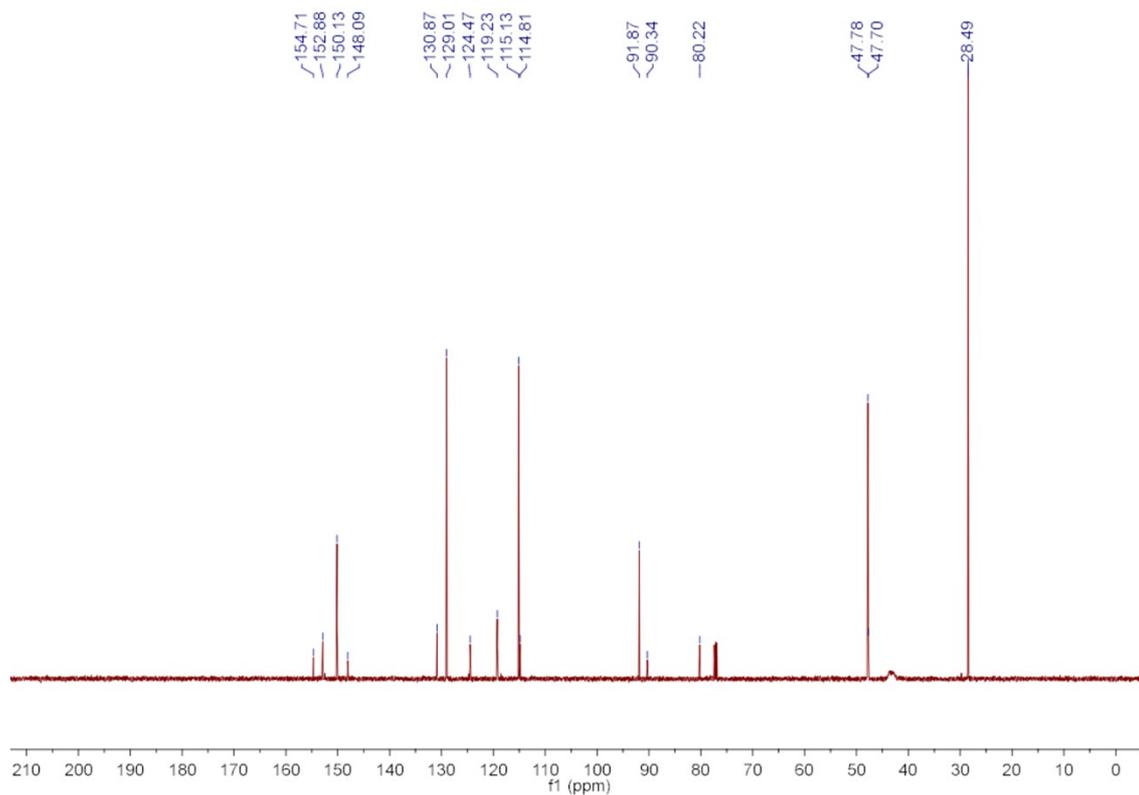
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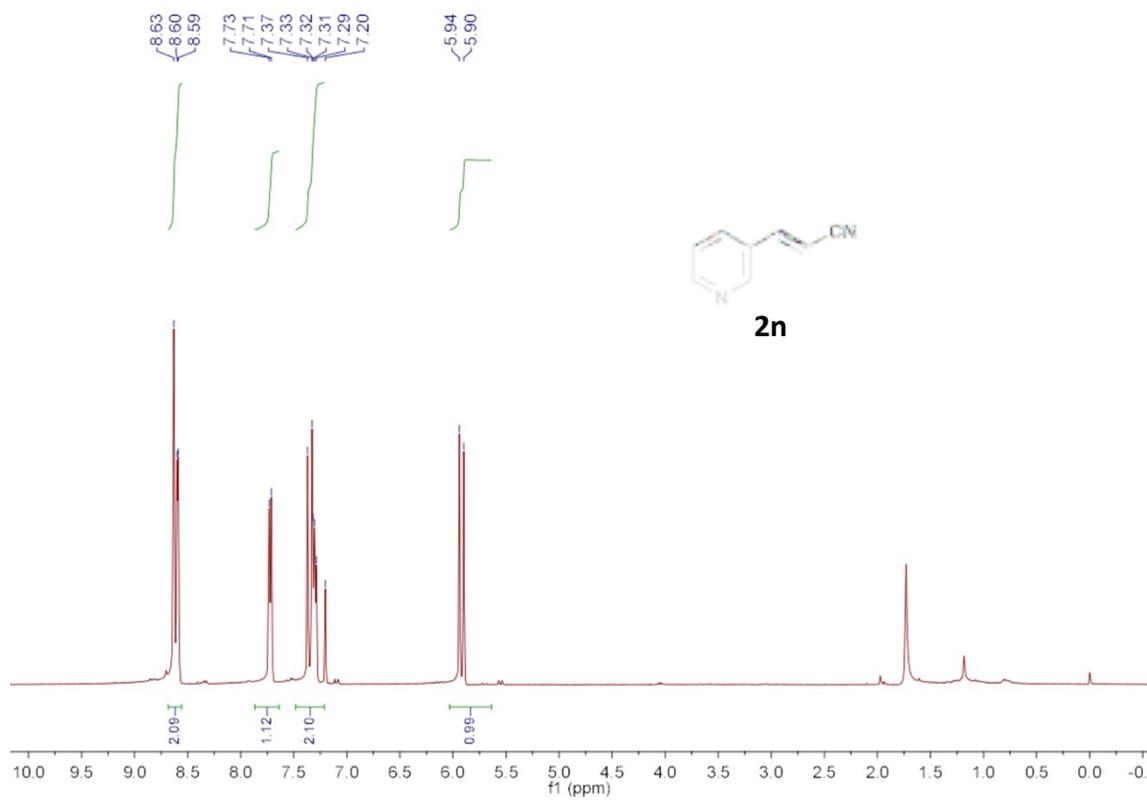
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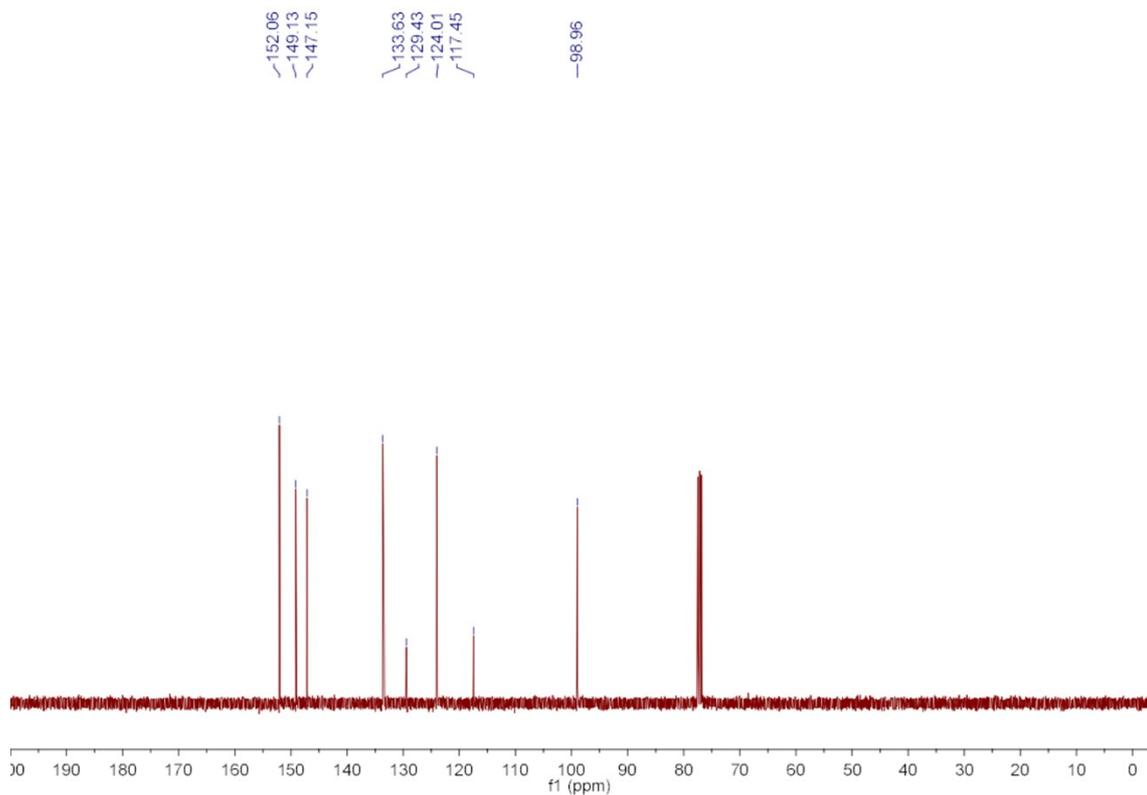
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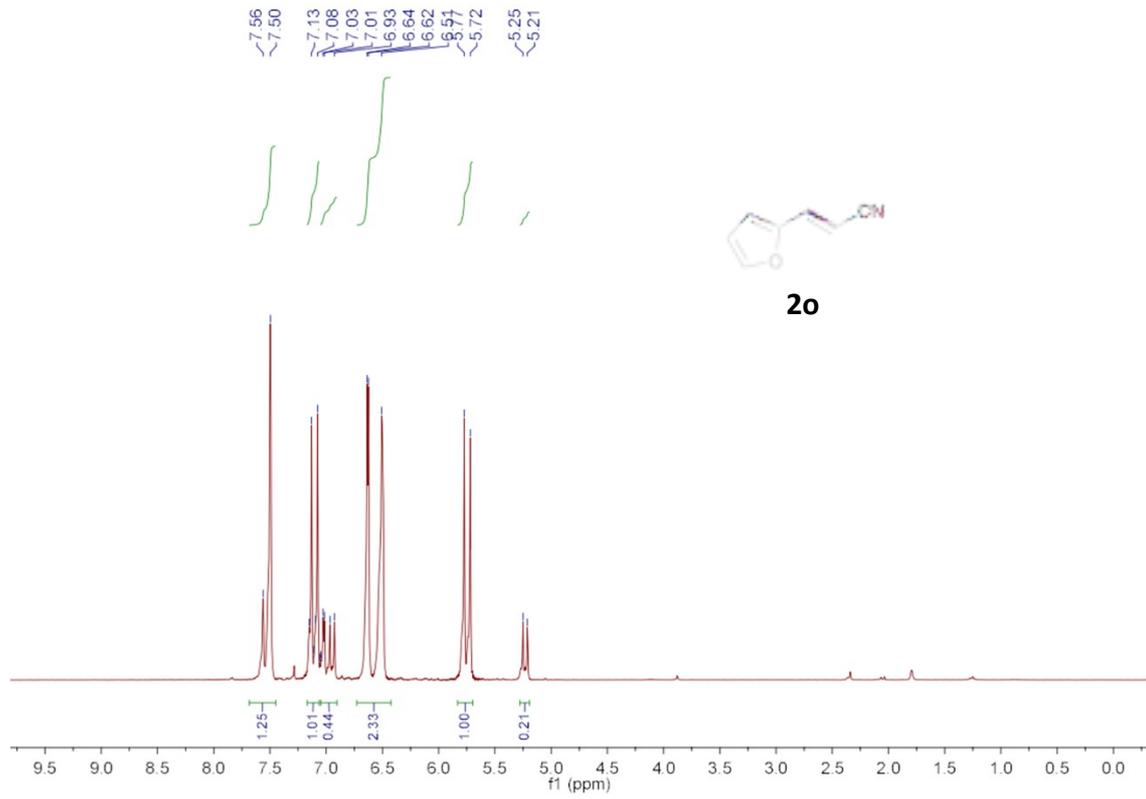
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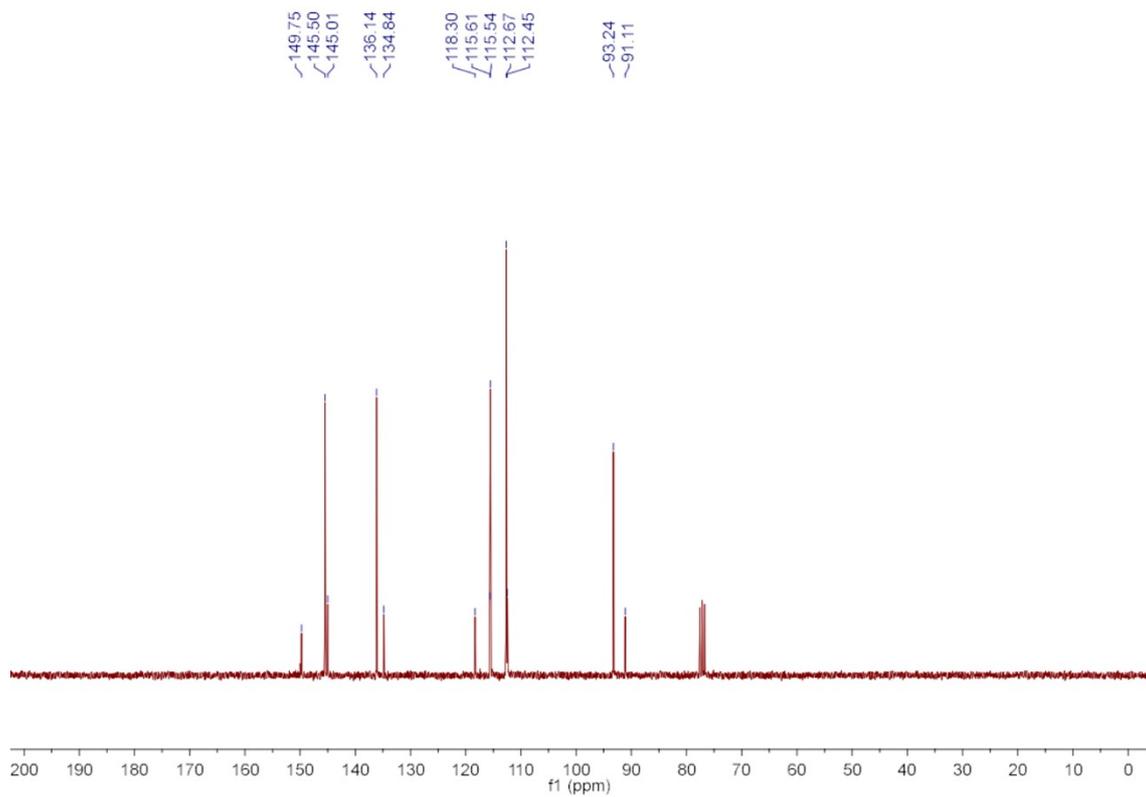
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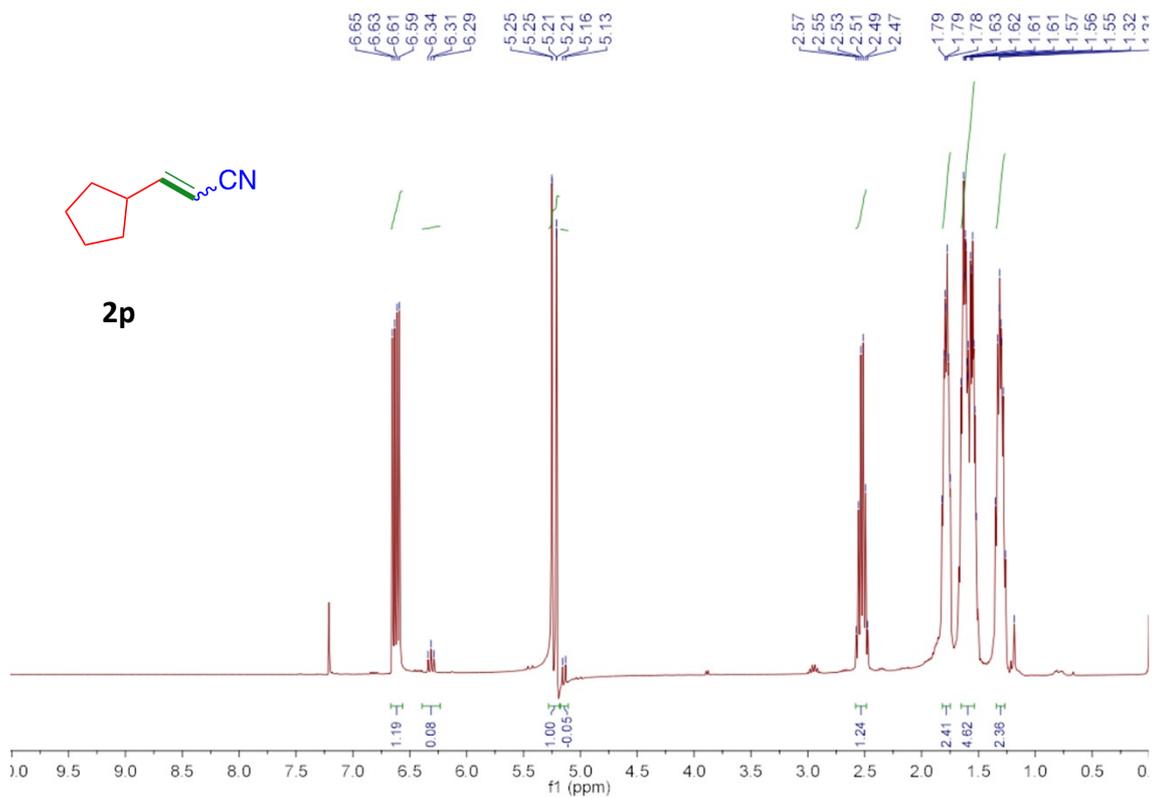
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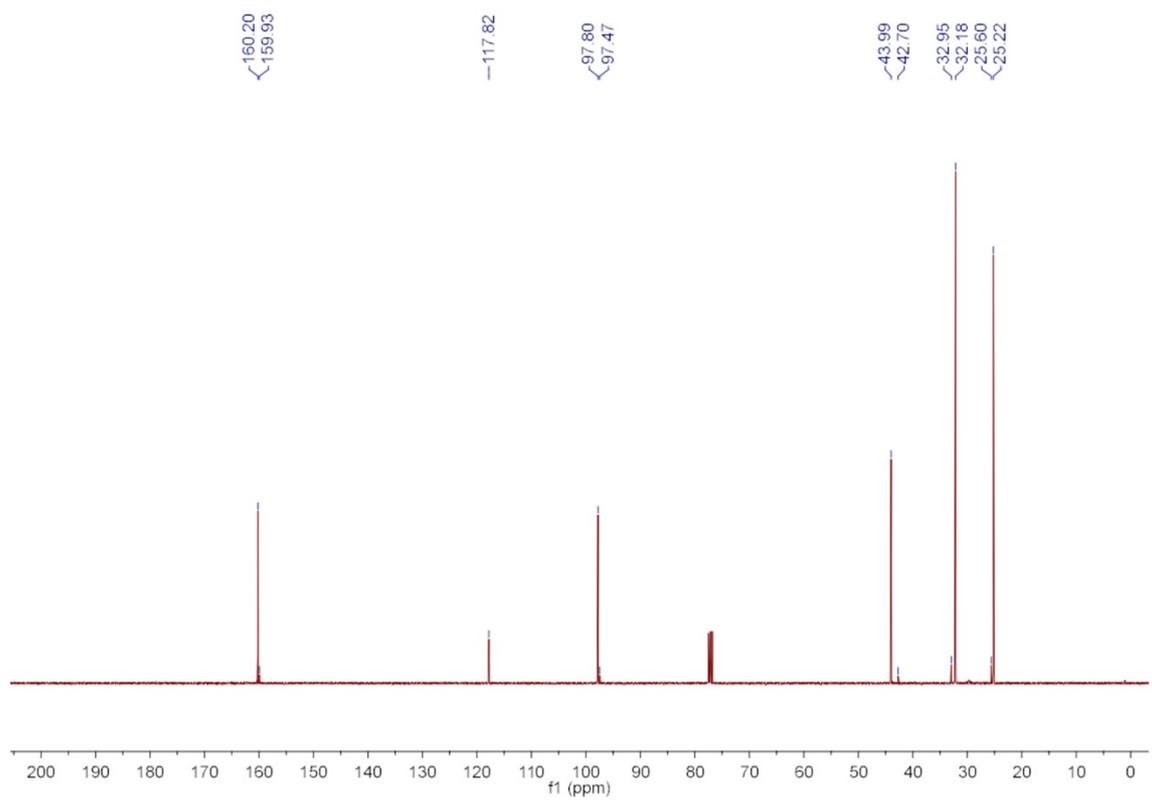
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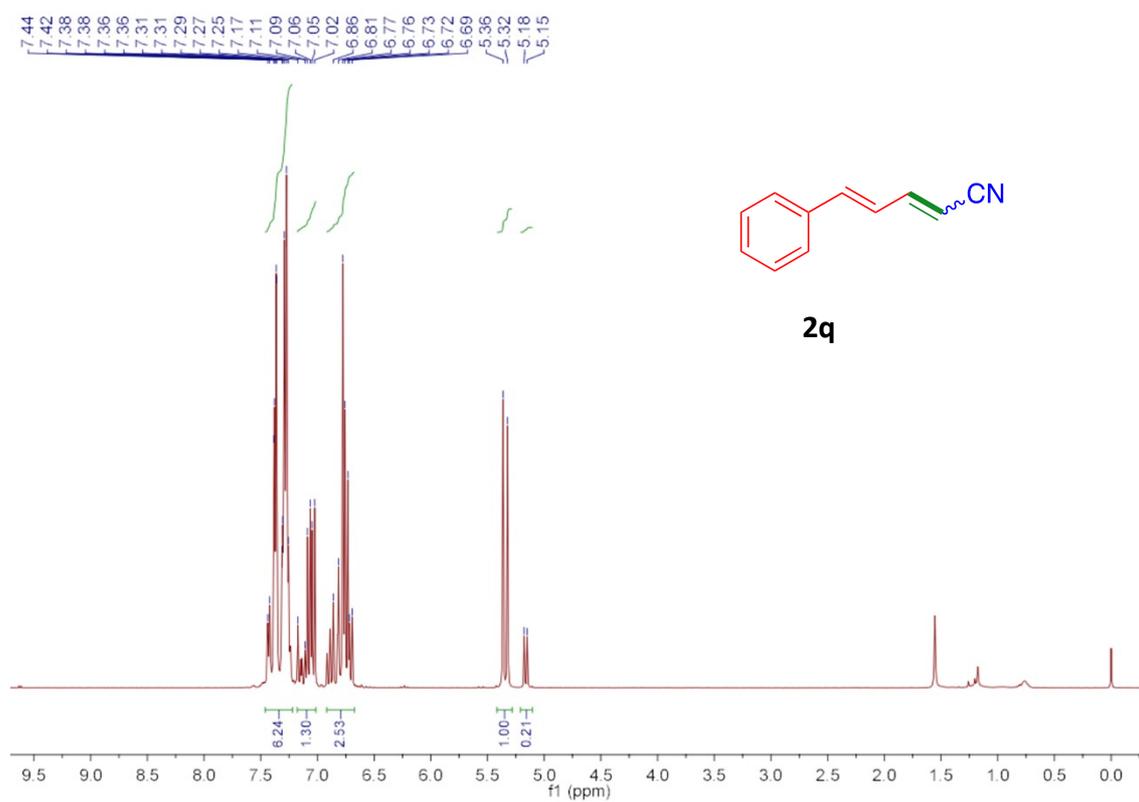
^1H NMR (400 MHz, CDCl_3)



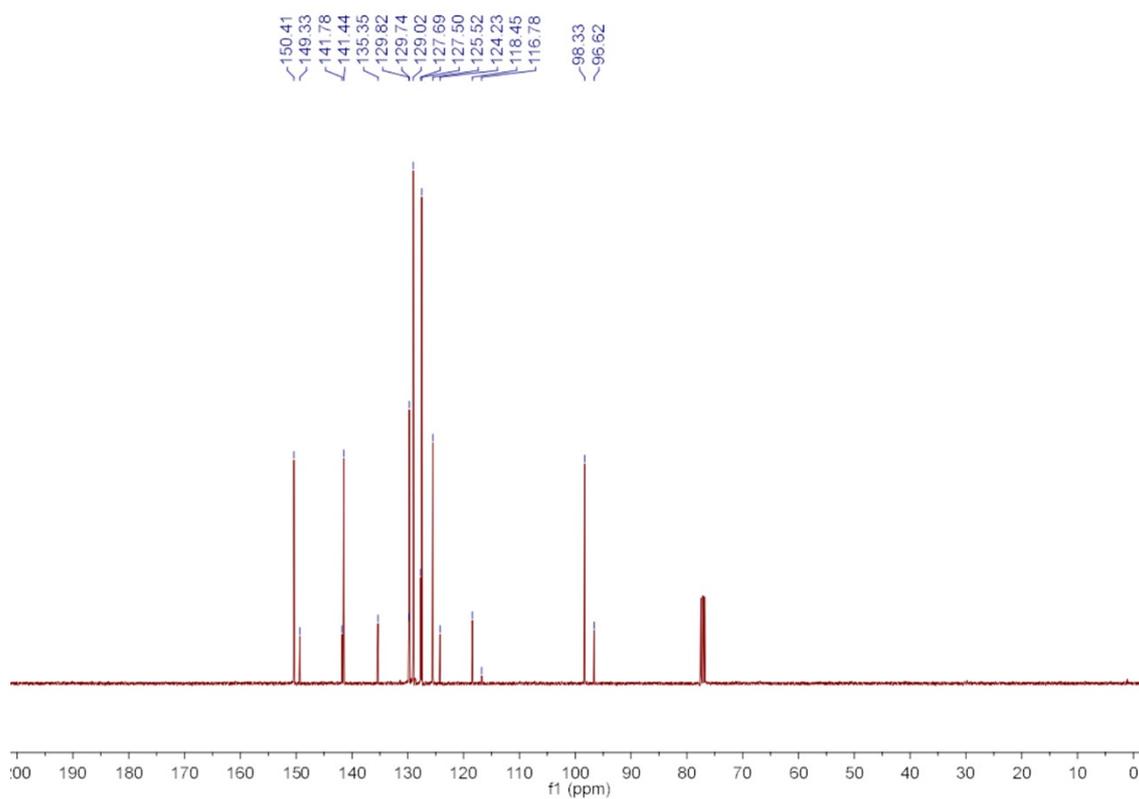
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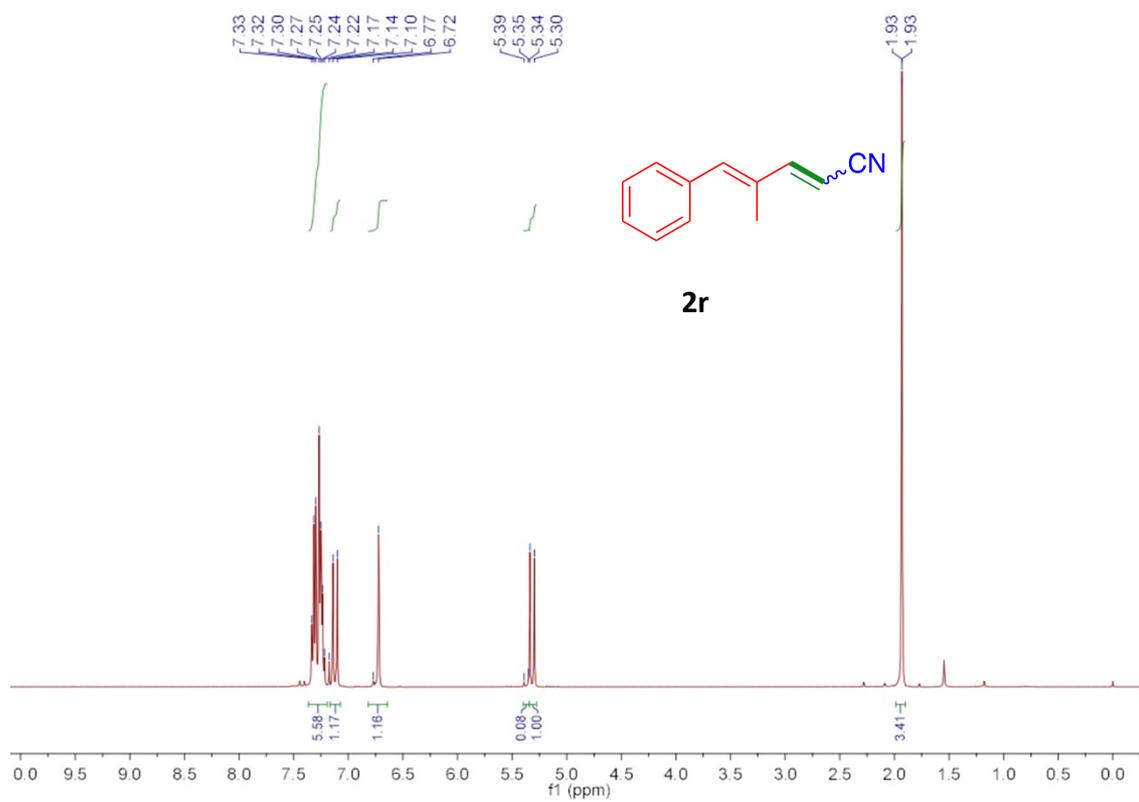
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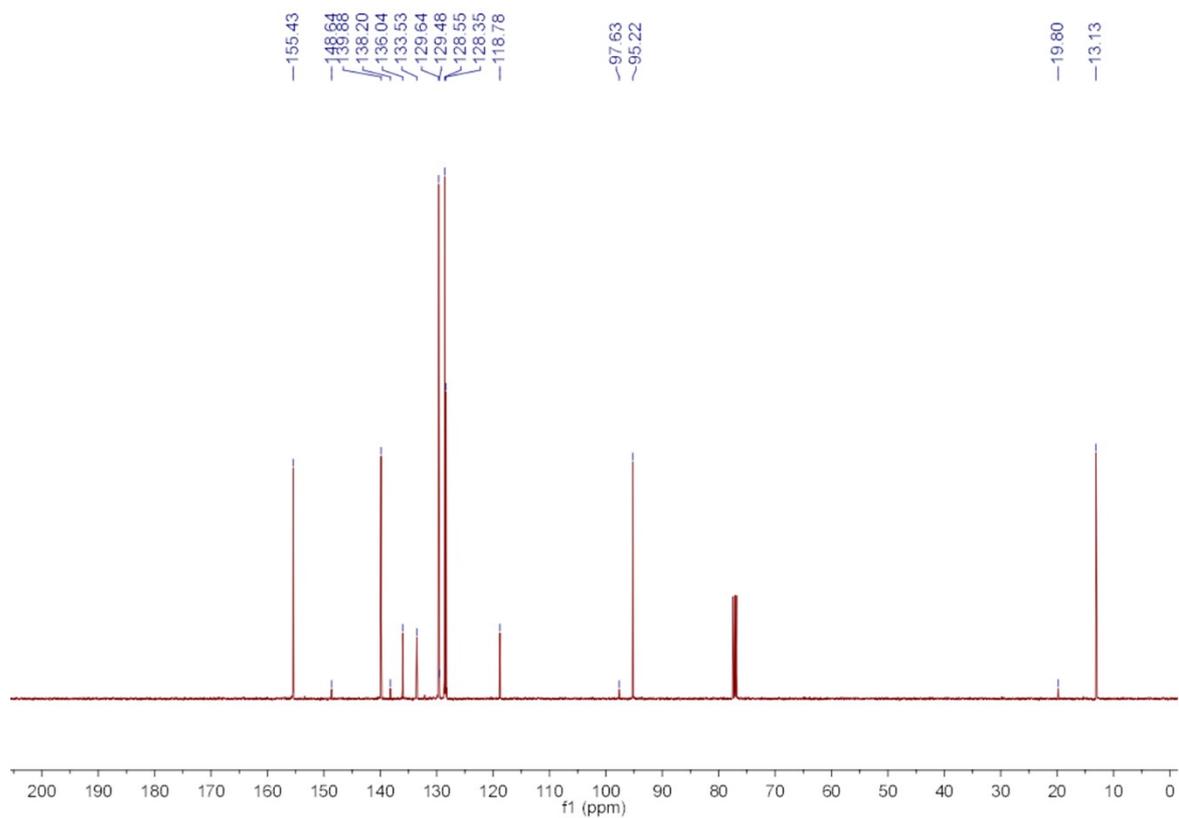
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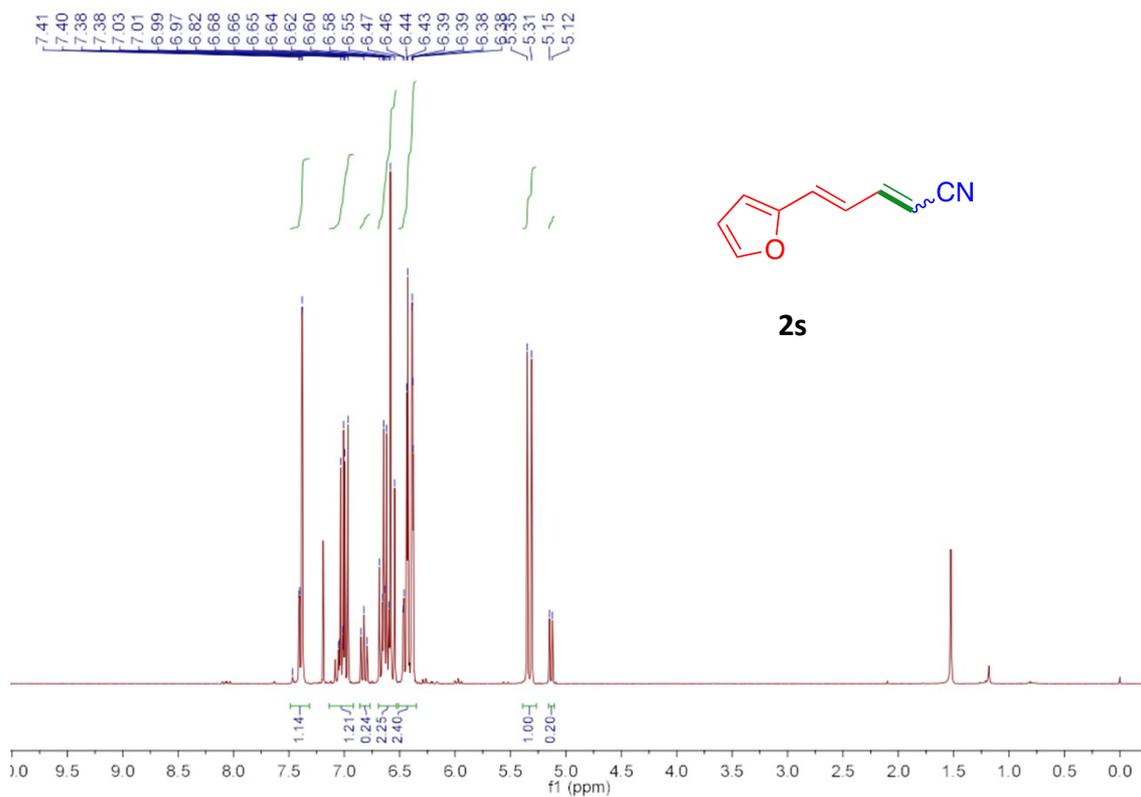
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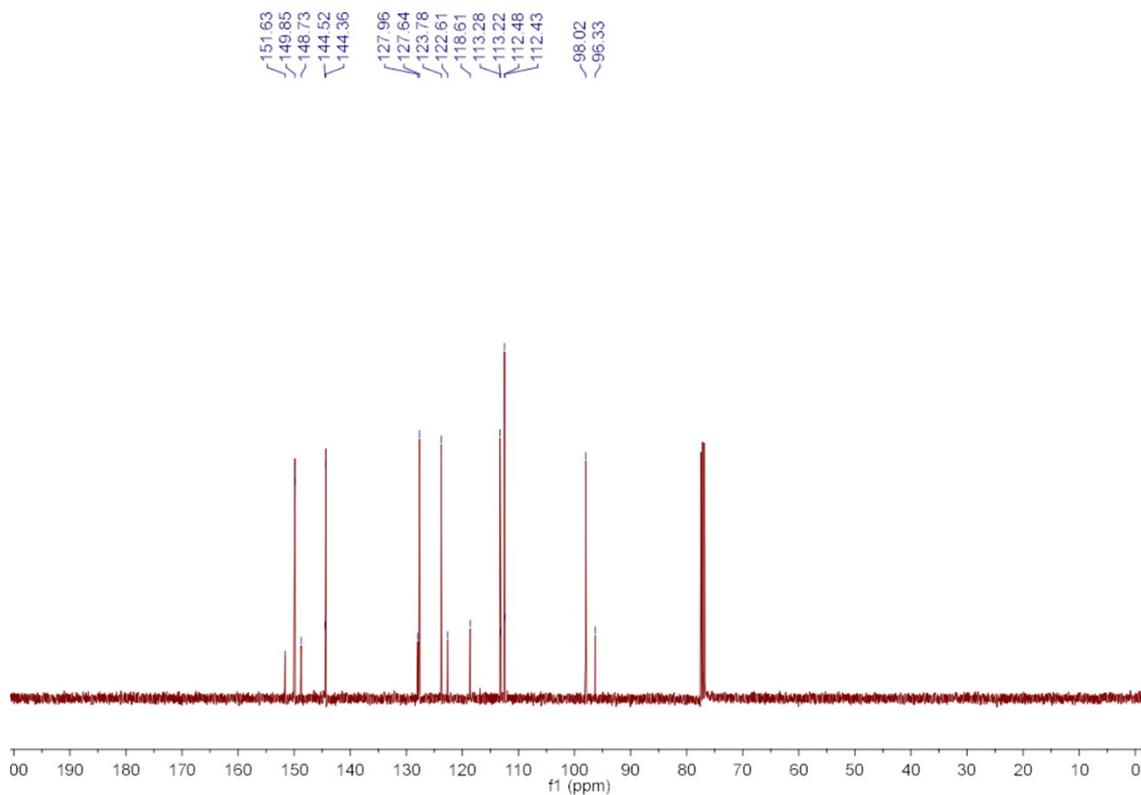
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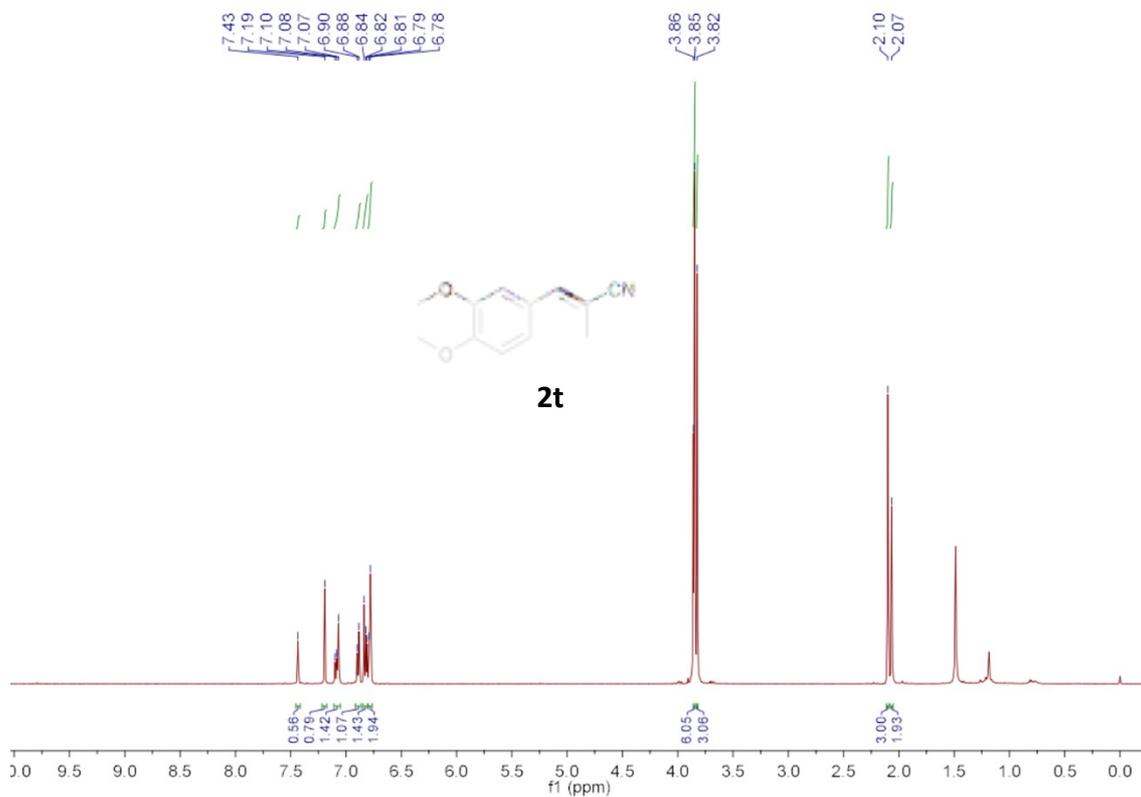
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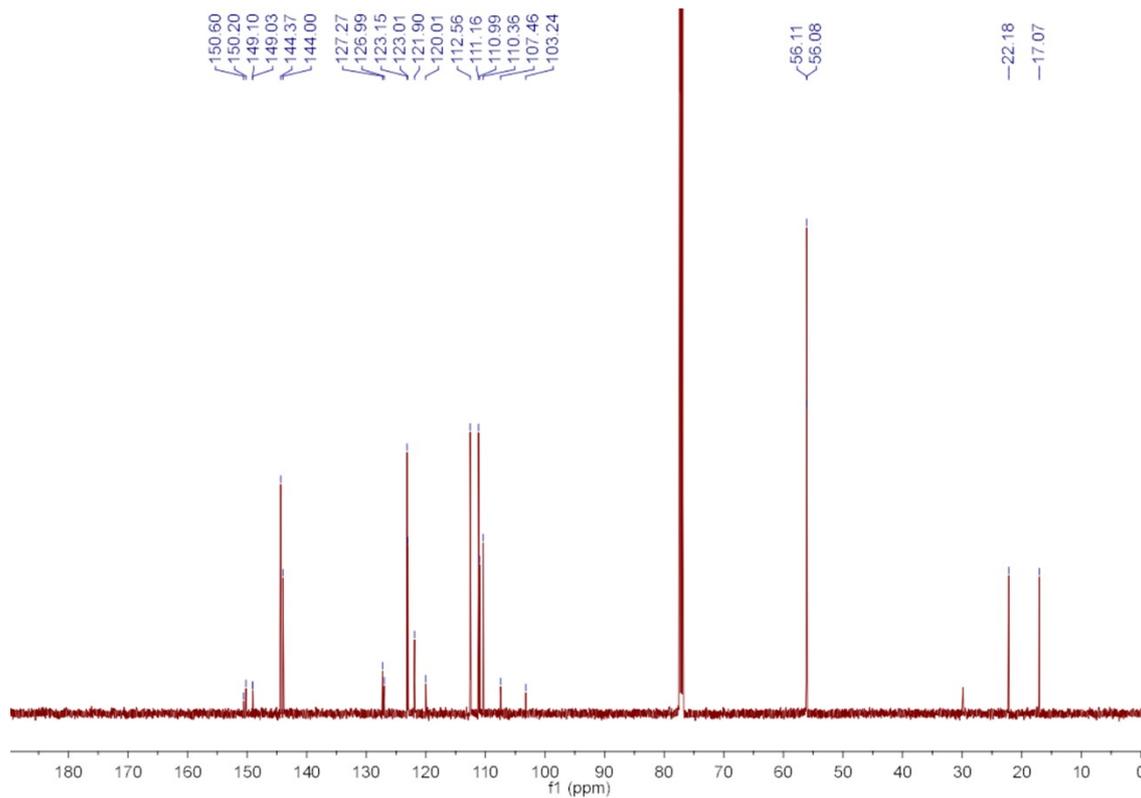
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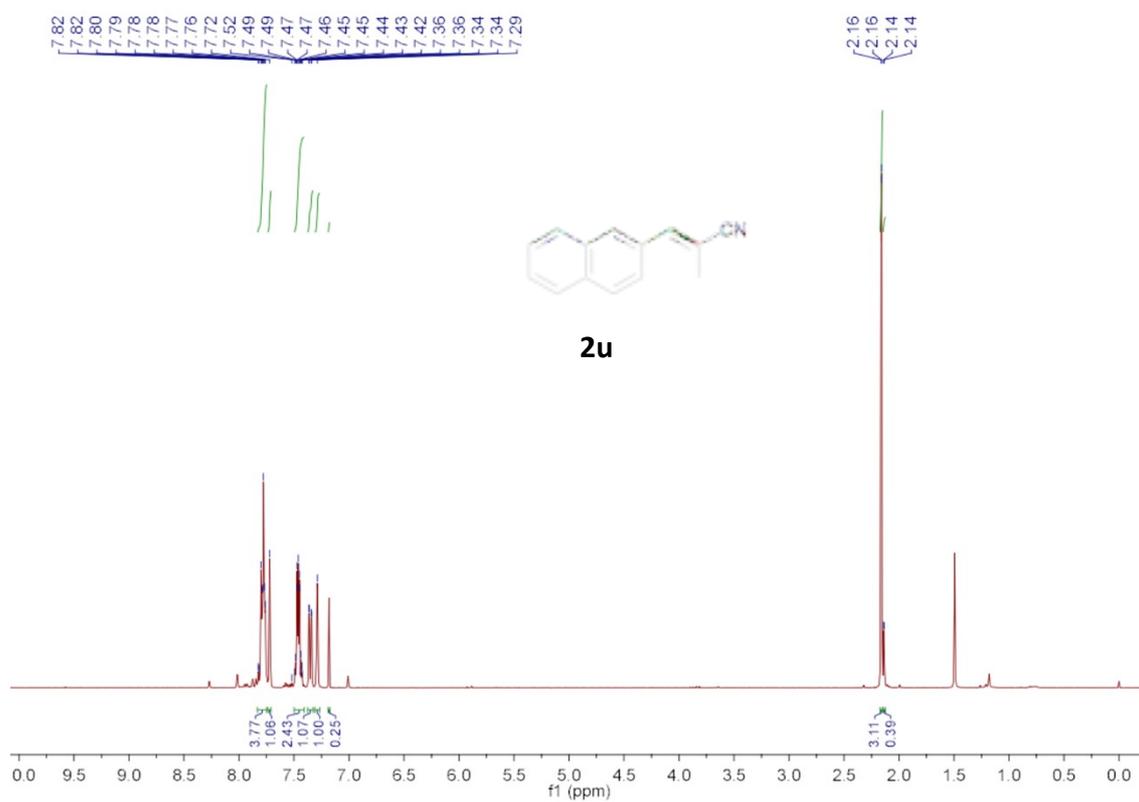
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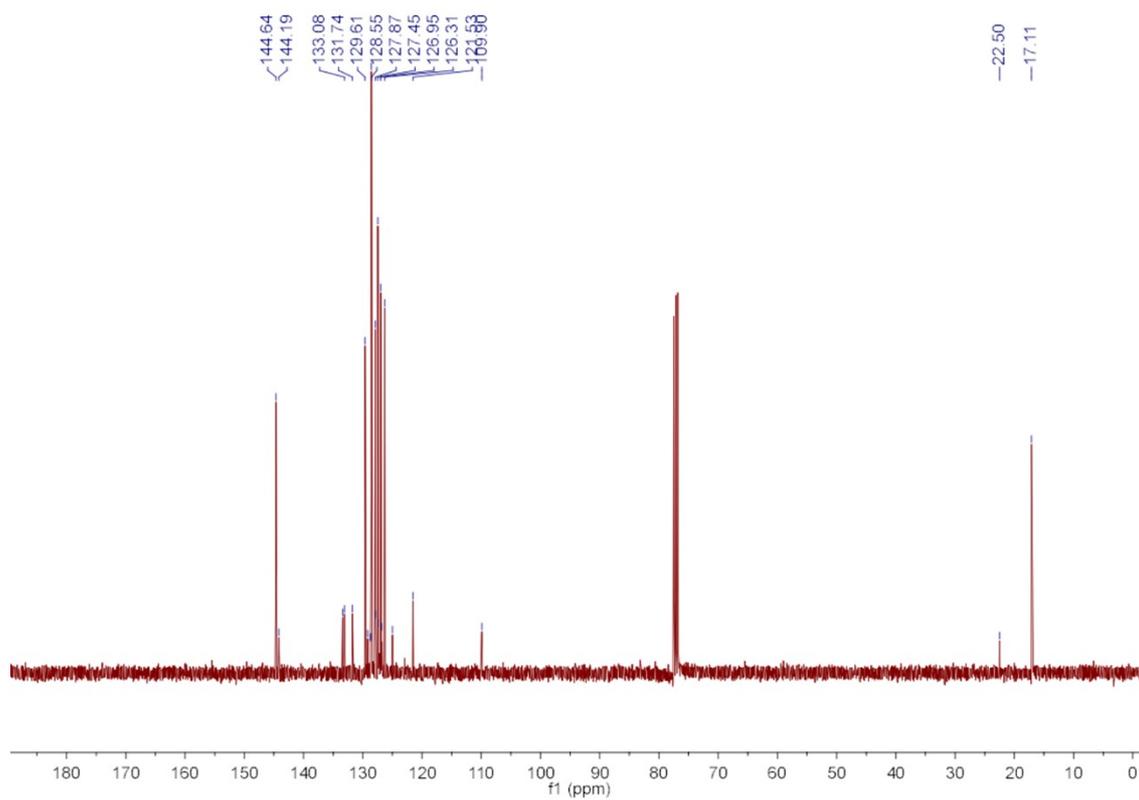
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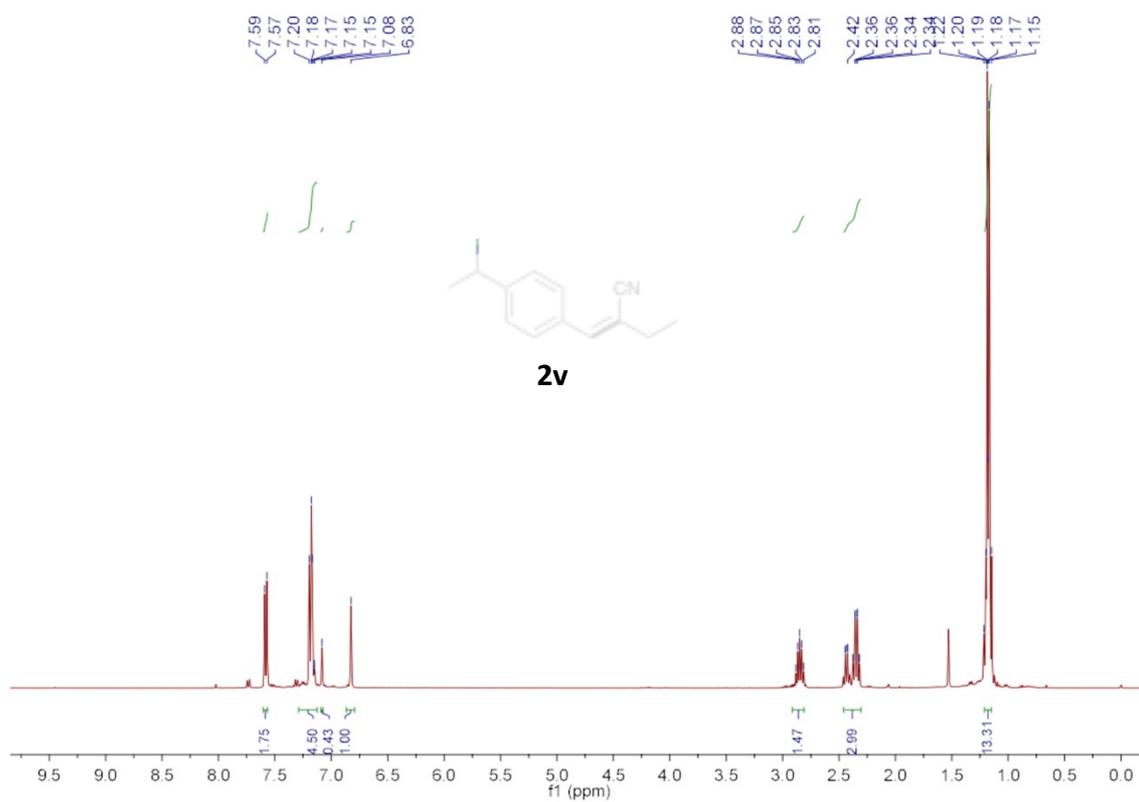
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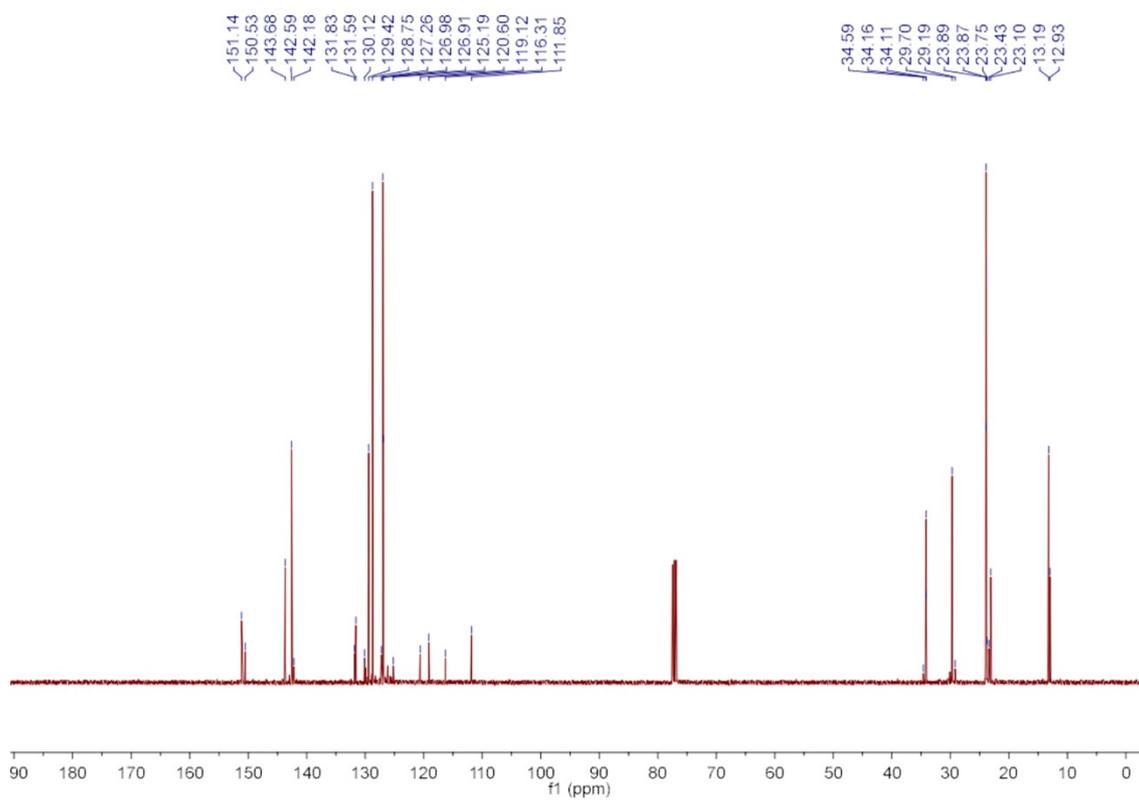
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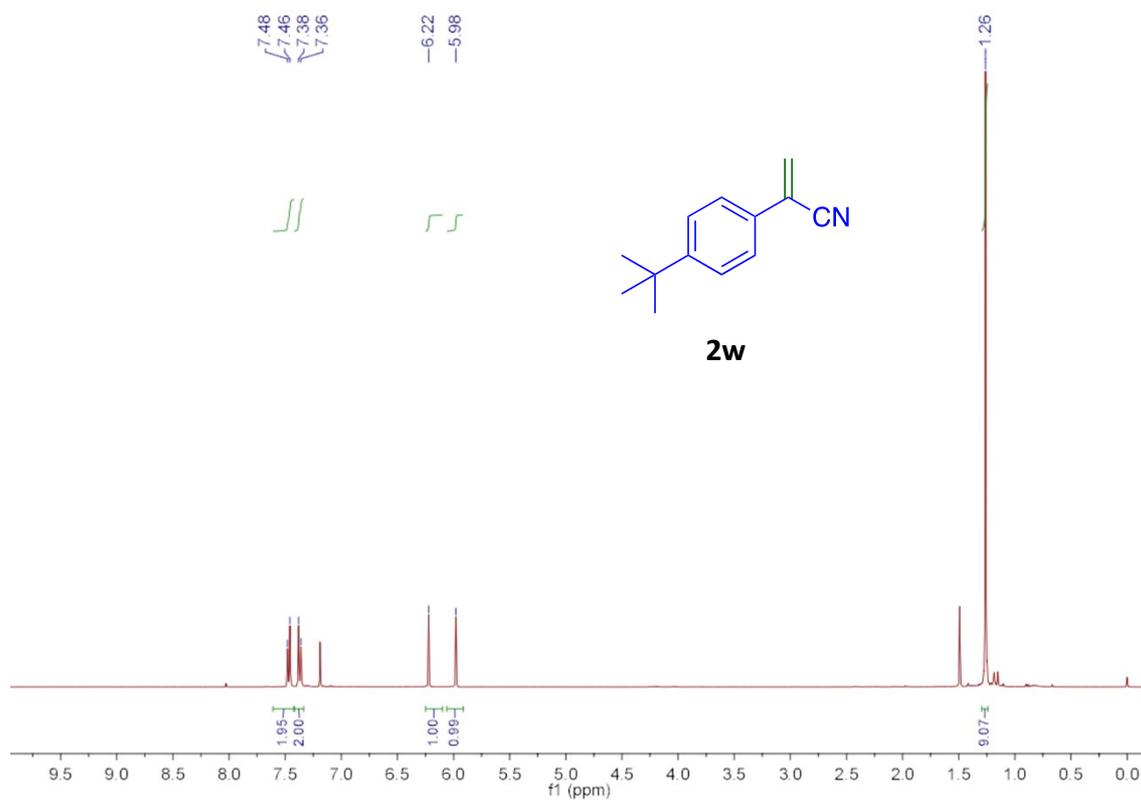
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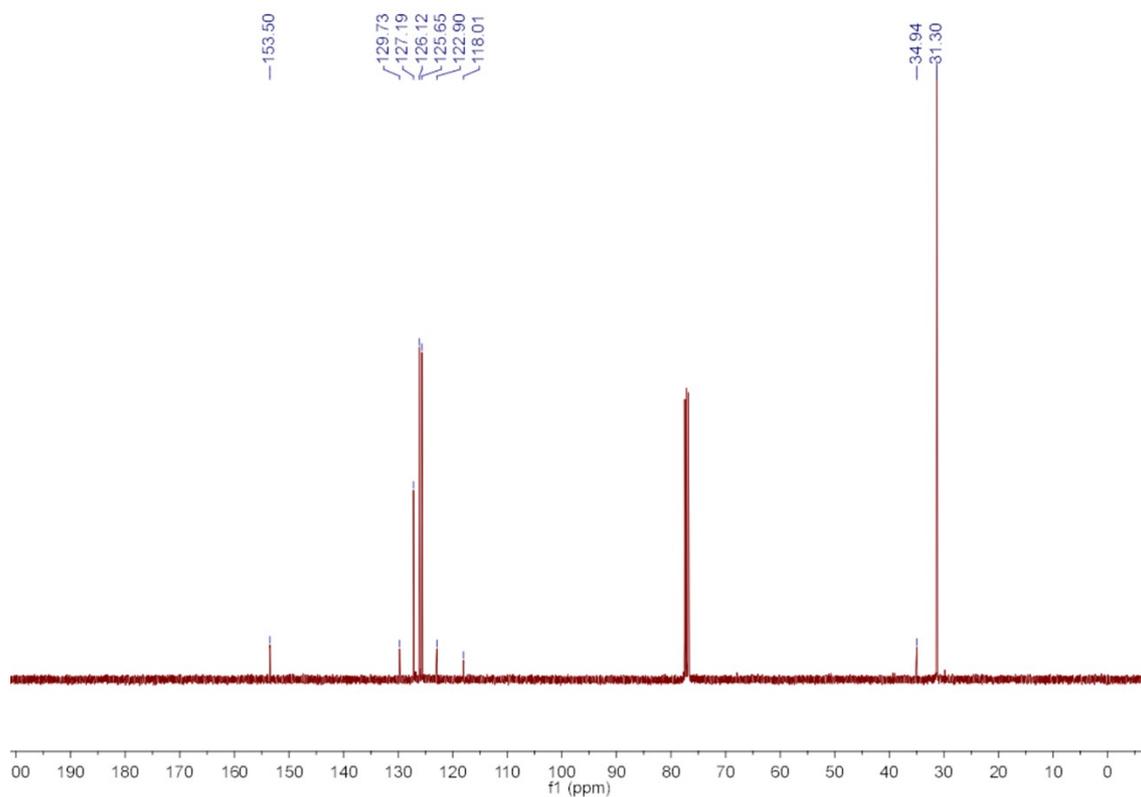
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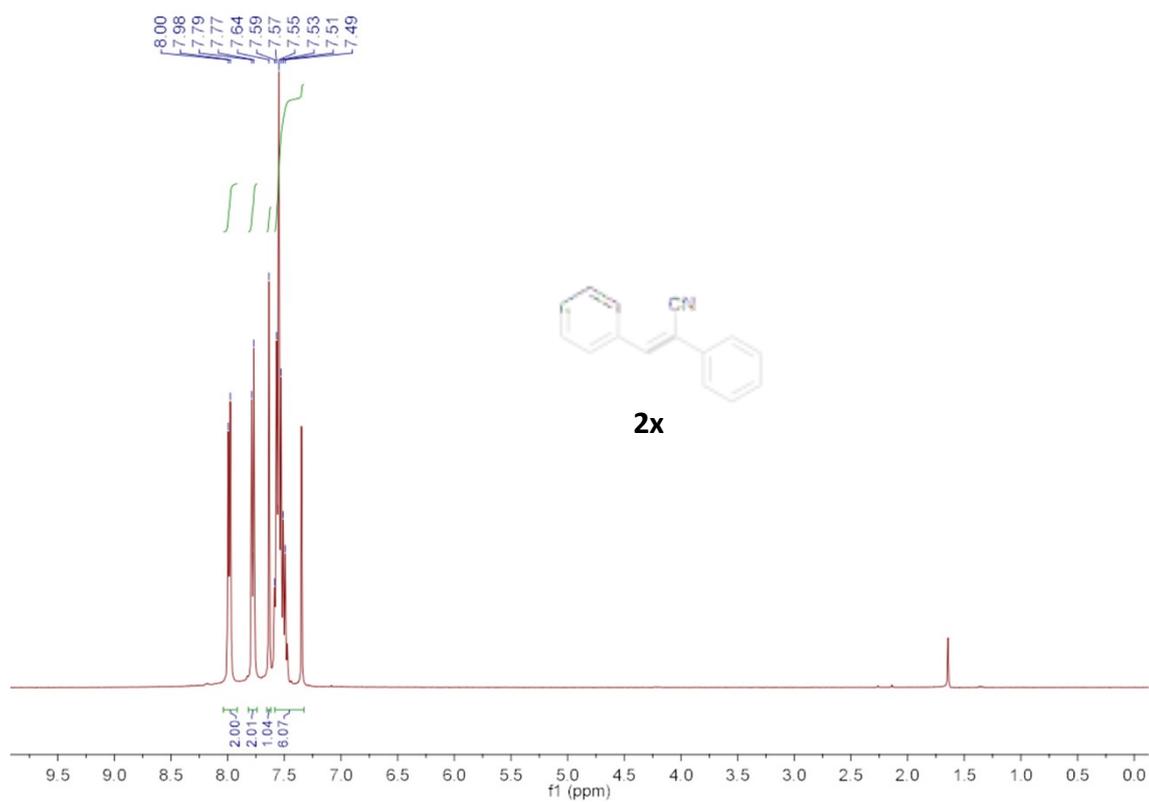
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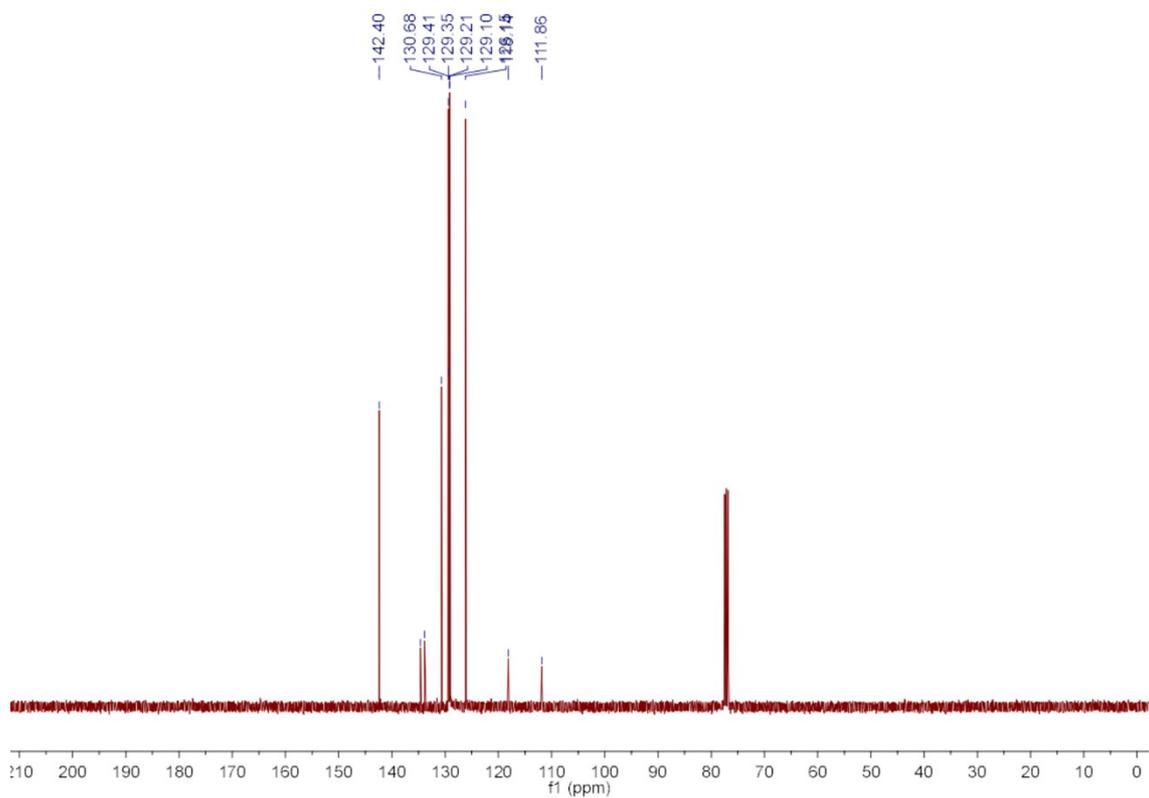
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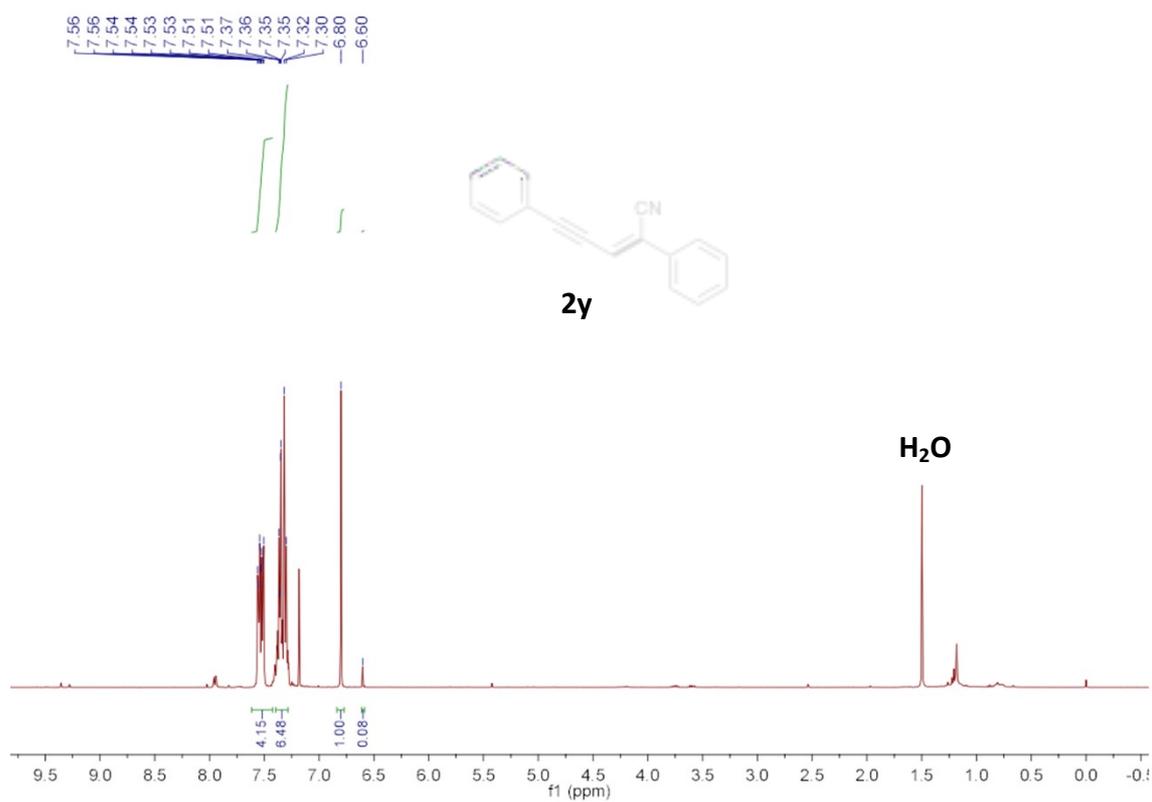
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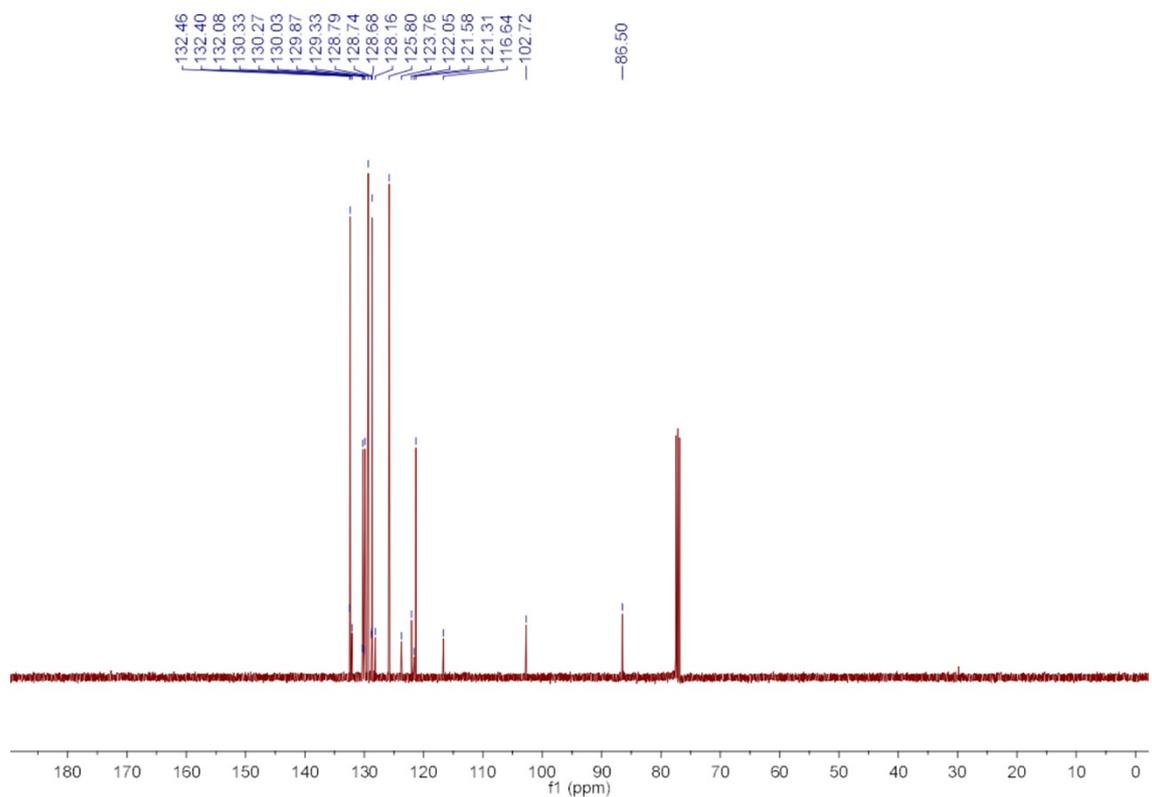
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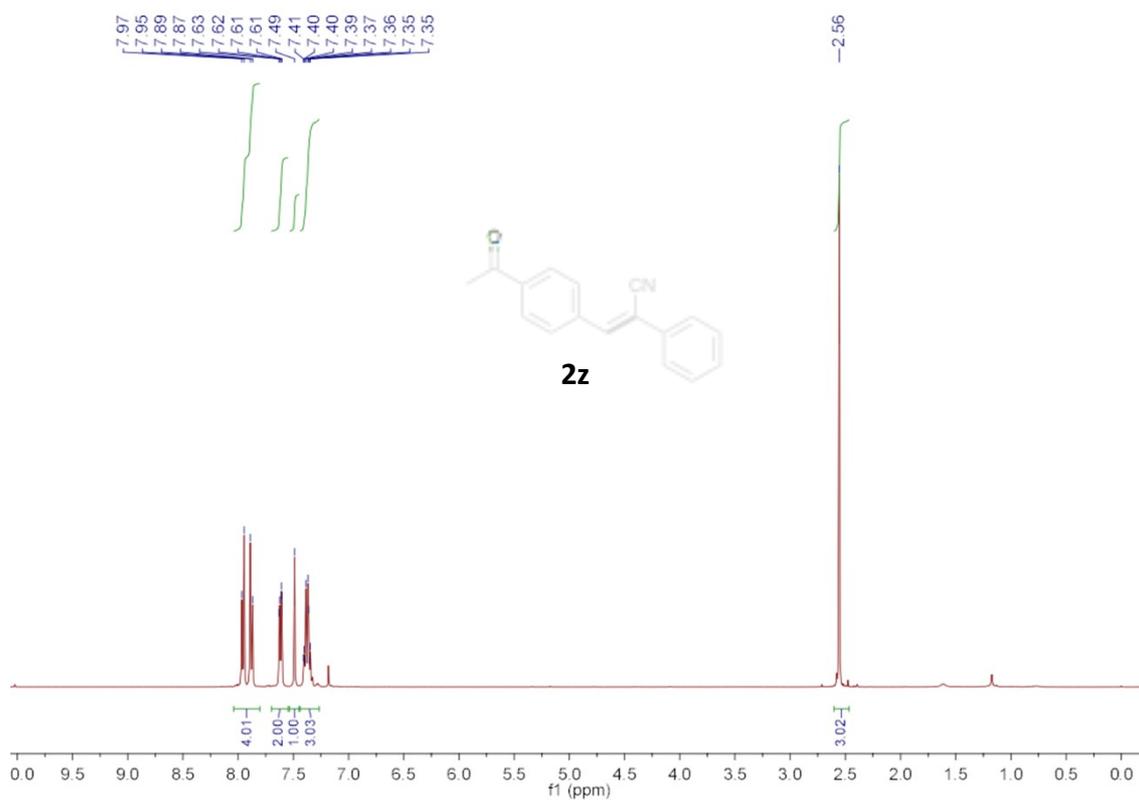
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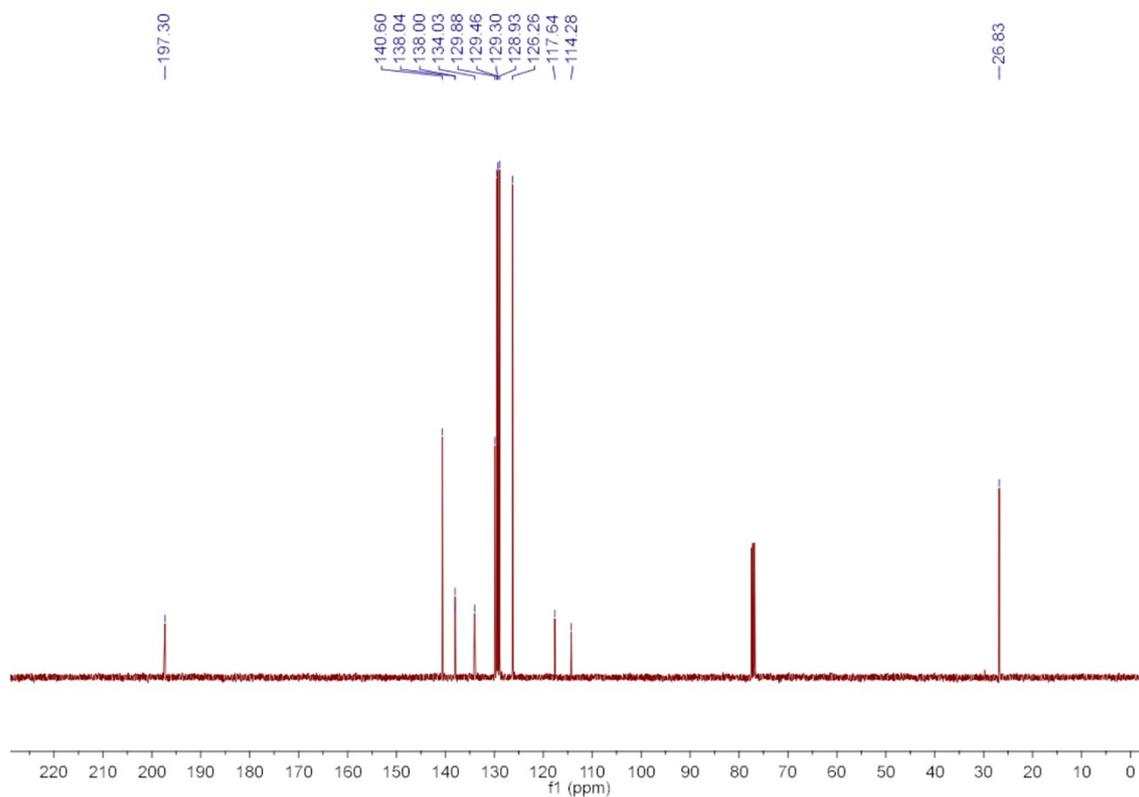
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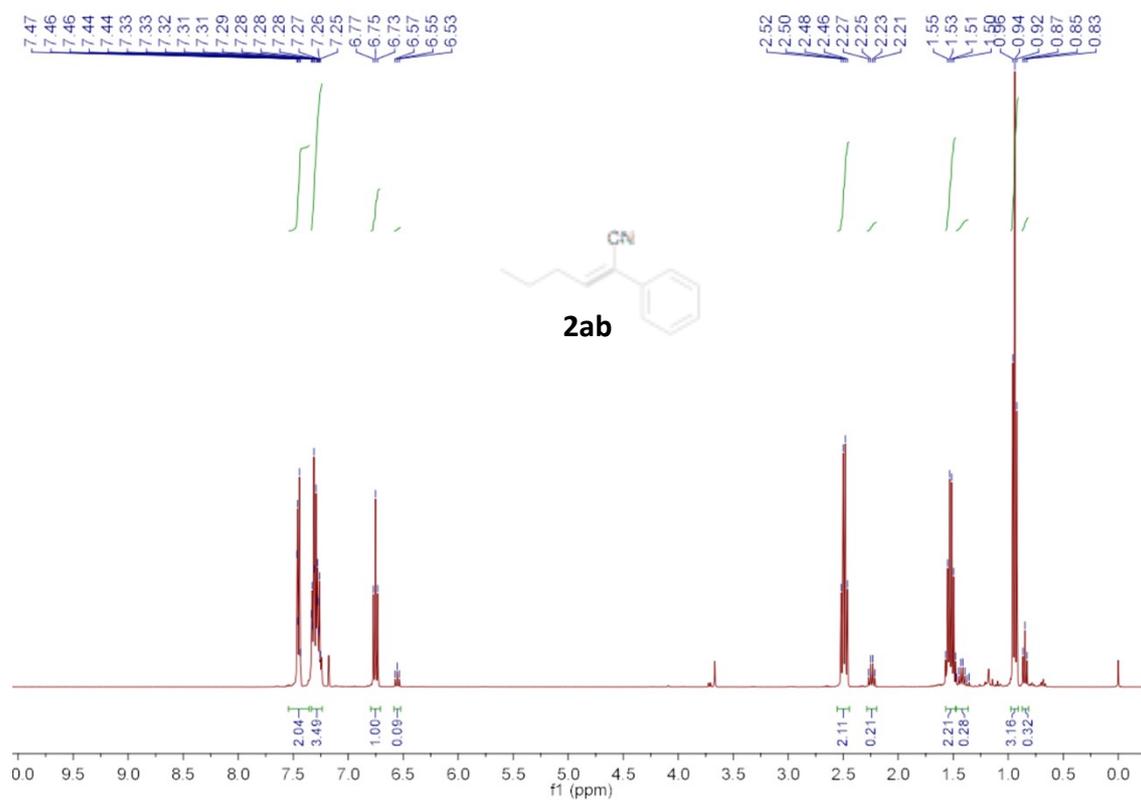
¹H NMR (400 MHz, CDCl₃)



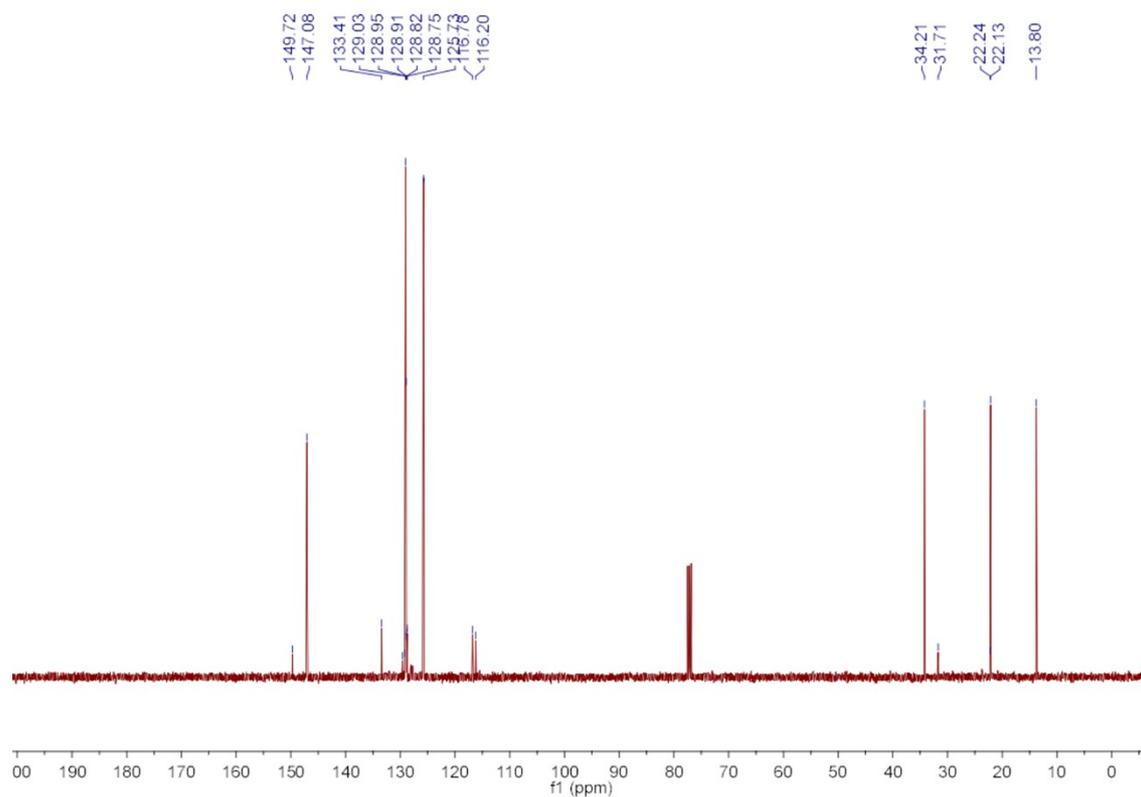
¹³C NMR (100.6 MHz, CDCl₃)



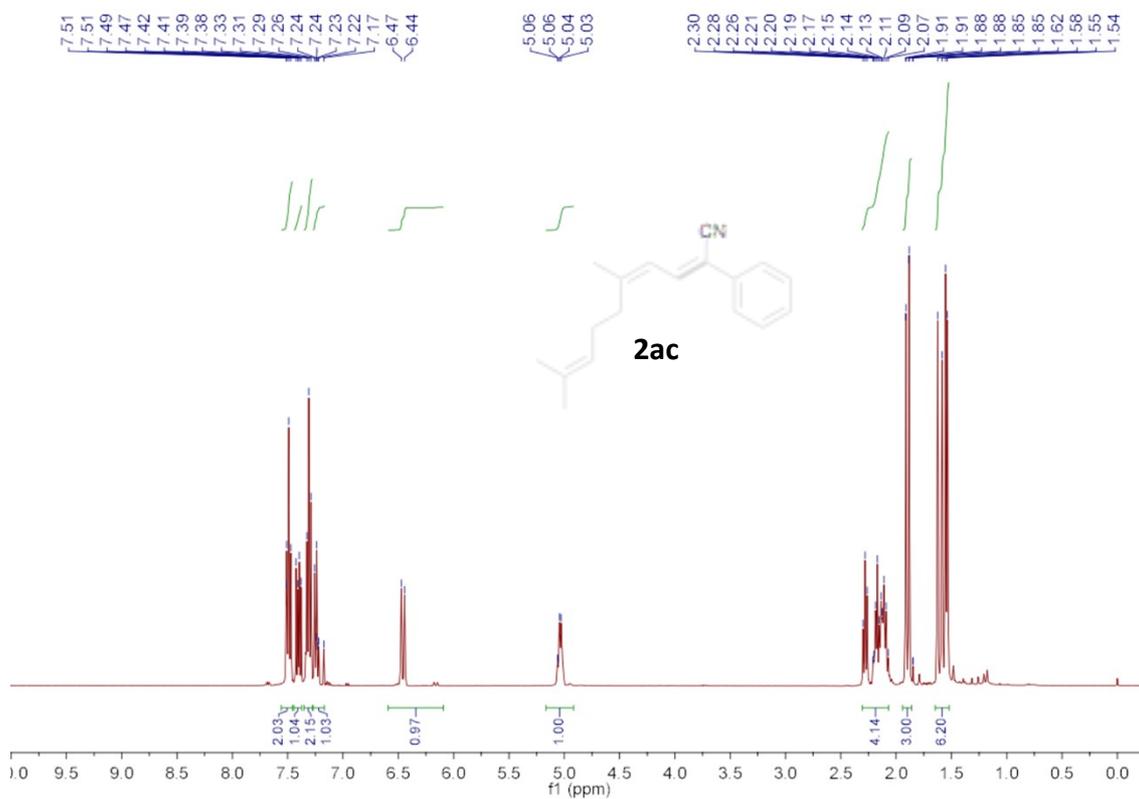
^1H NMR (400 MHz, CDCl_3)



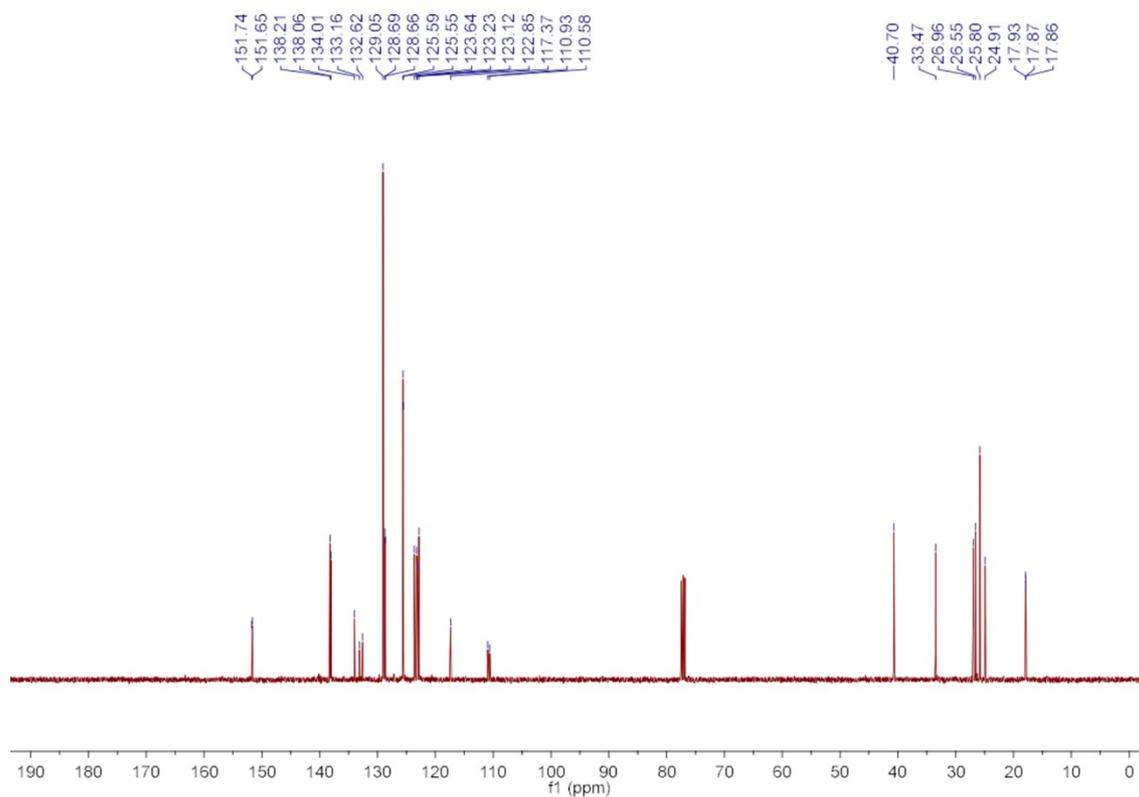
^{13}C NMR (100.6 MHz, CDCl_3)



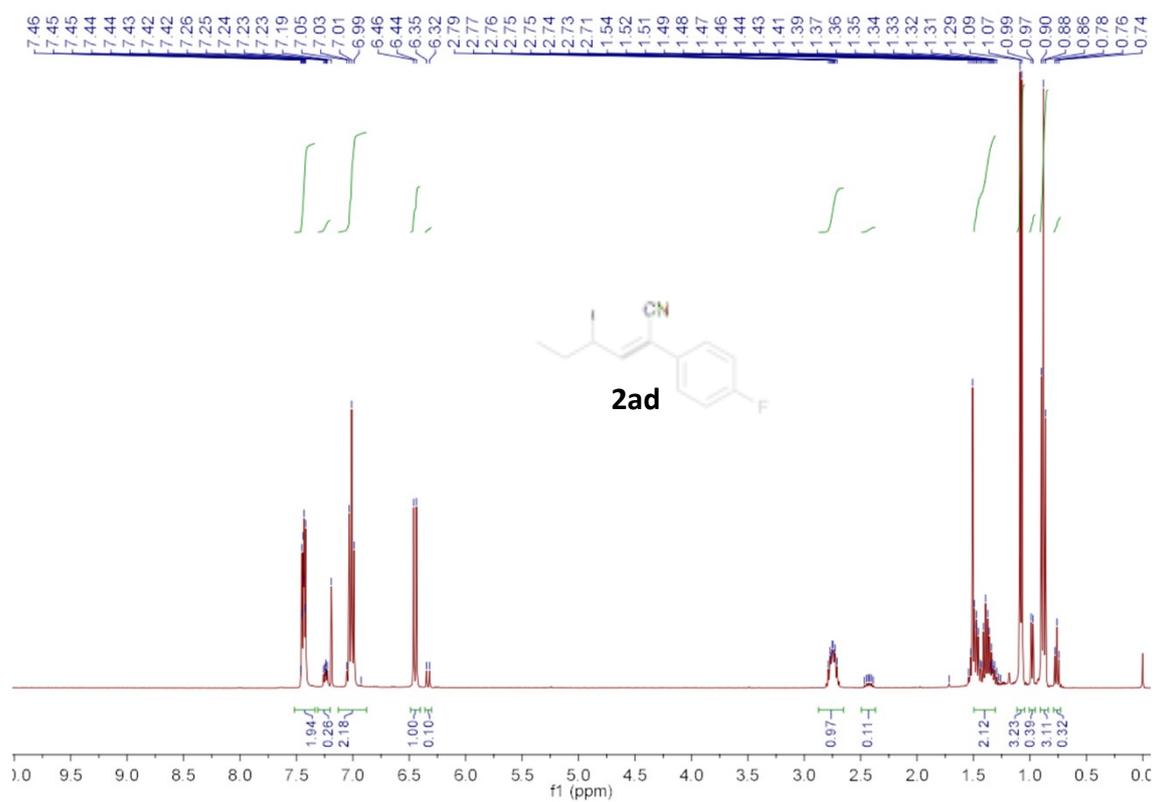
¹H NMR (400 MHz, CDCl₃)



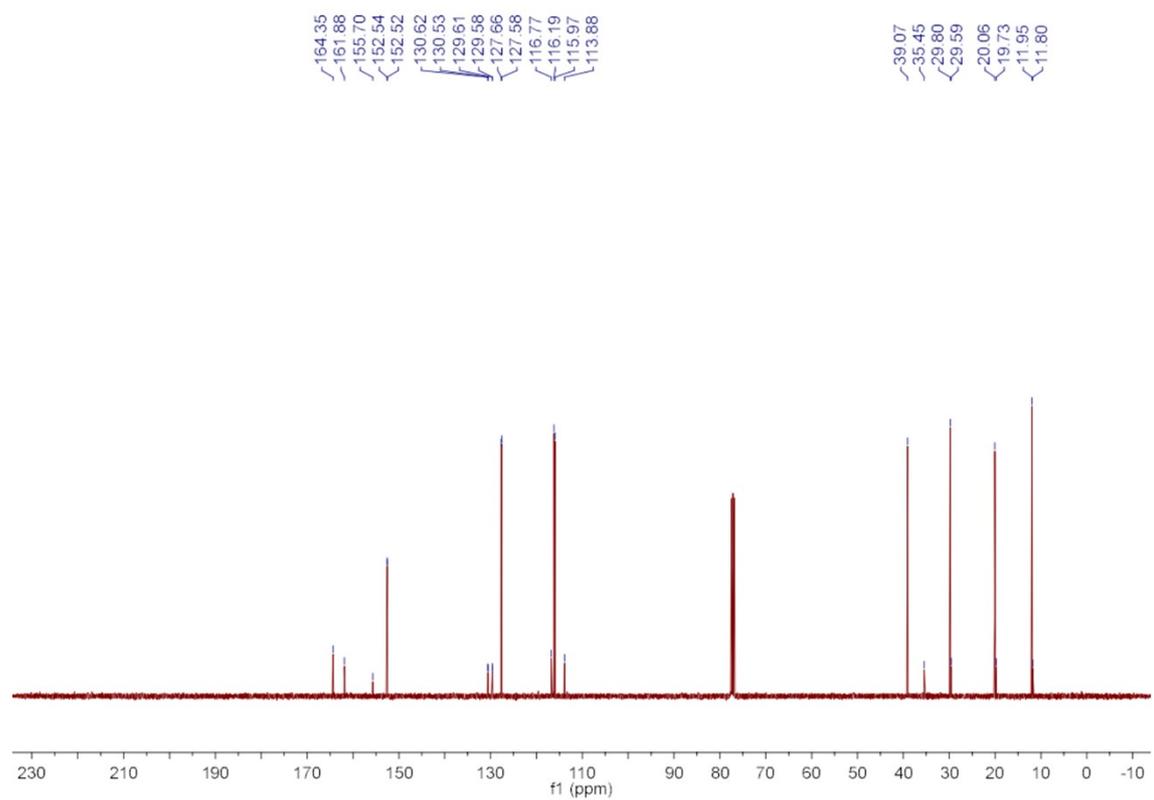
¹³C NMR (100.6 MHz, CDCl₃)



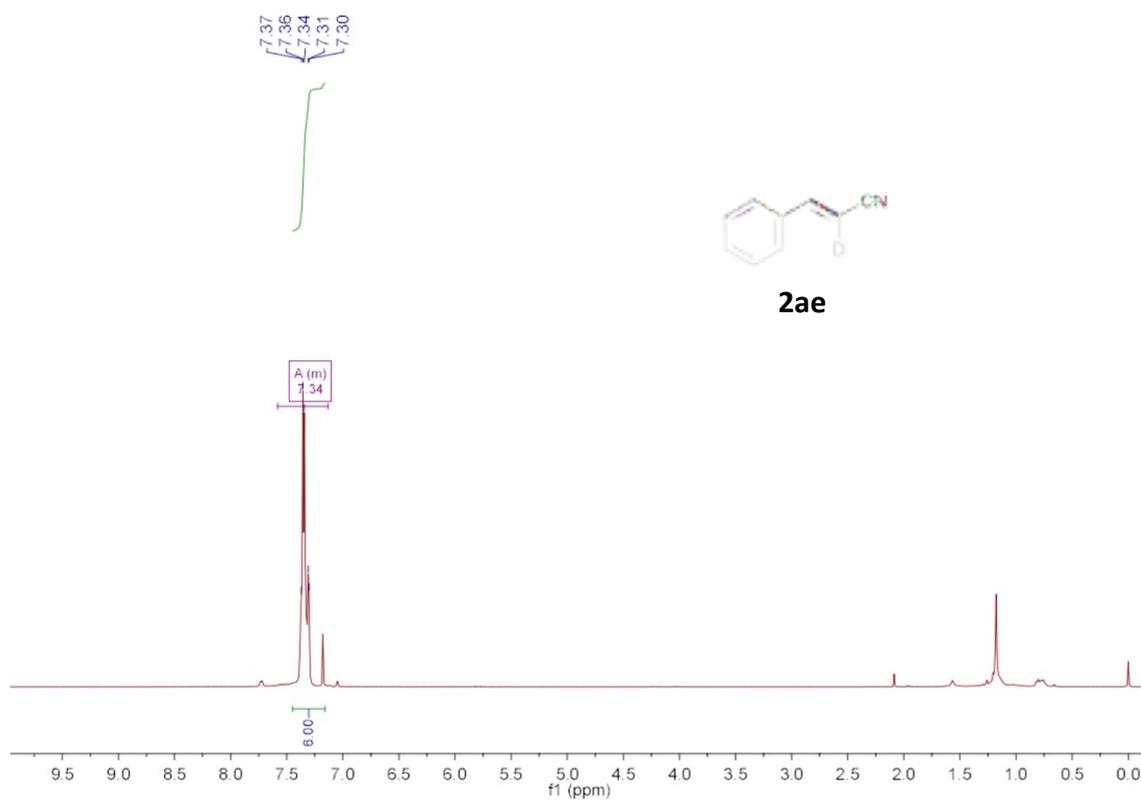
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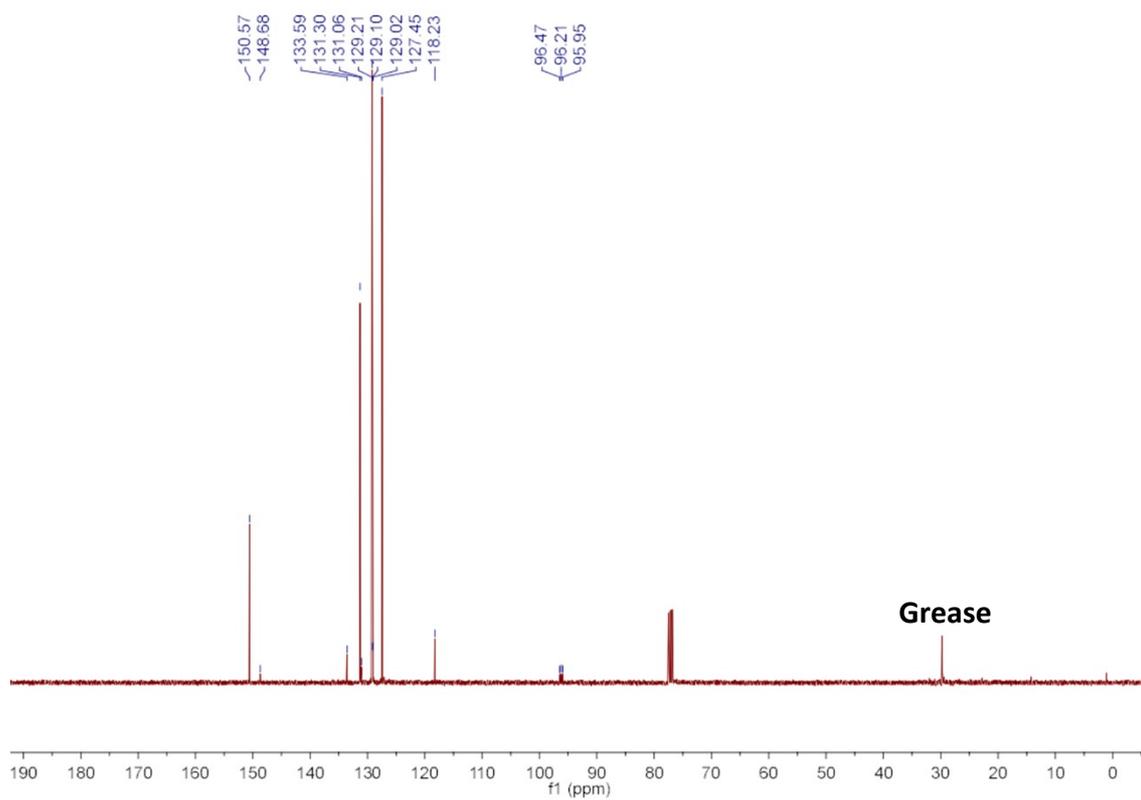
¹³C NMR (100.6 MHz, CDCl₃)



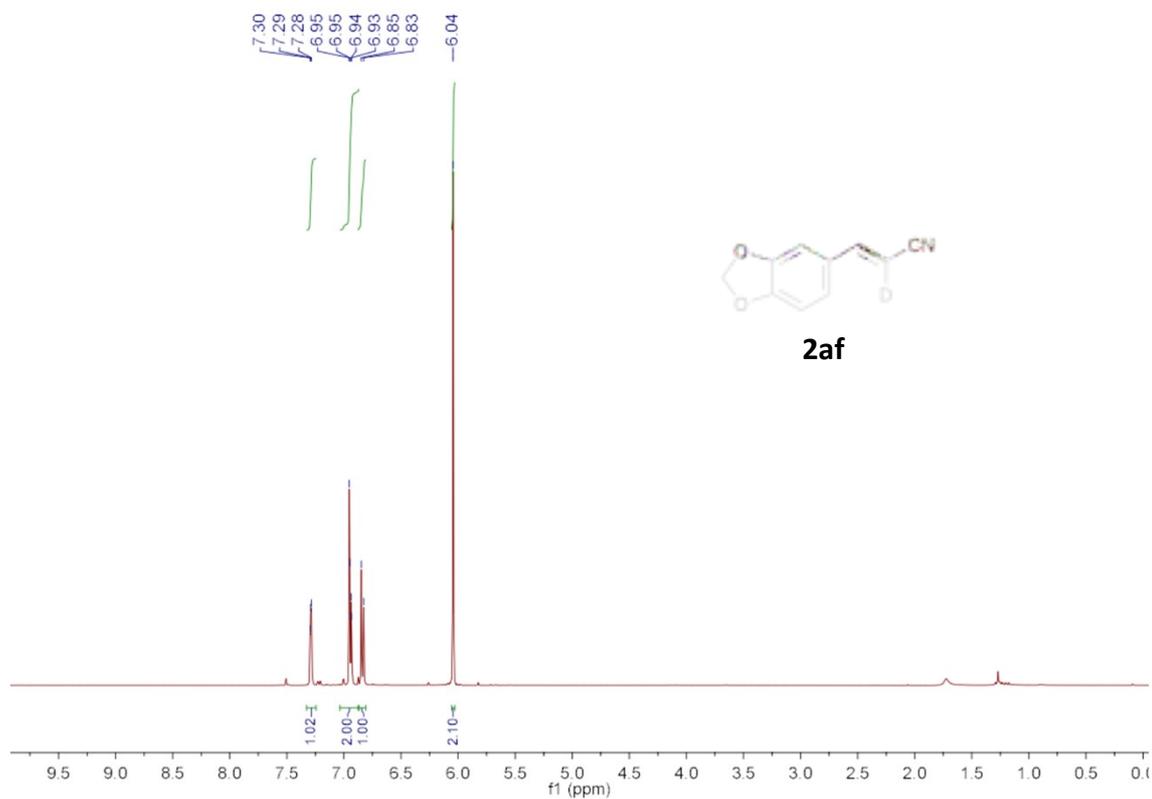
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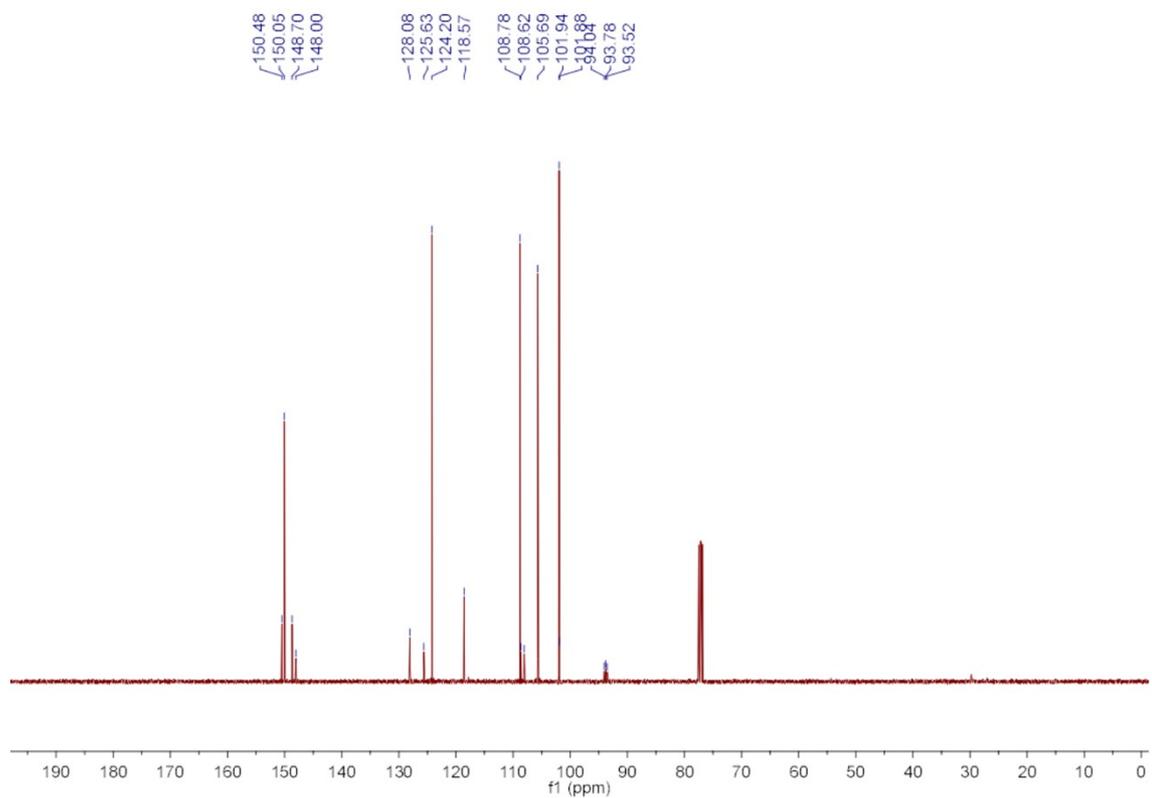
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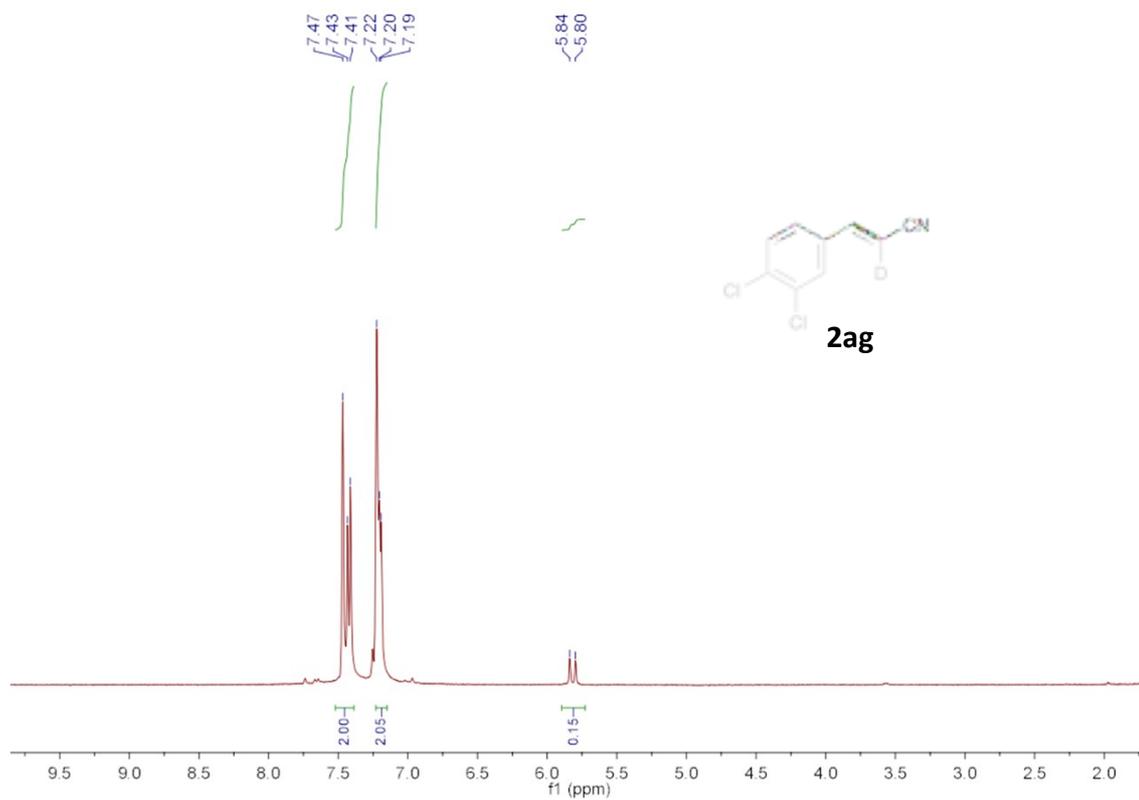
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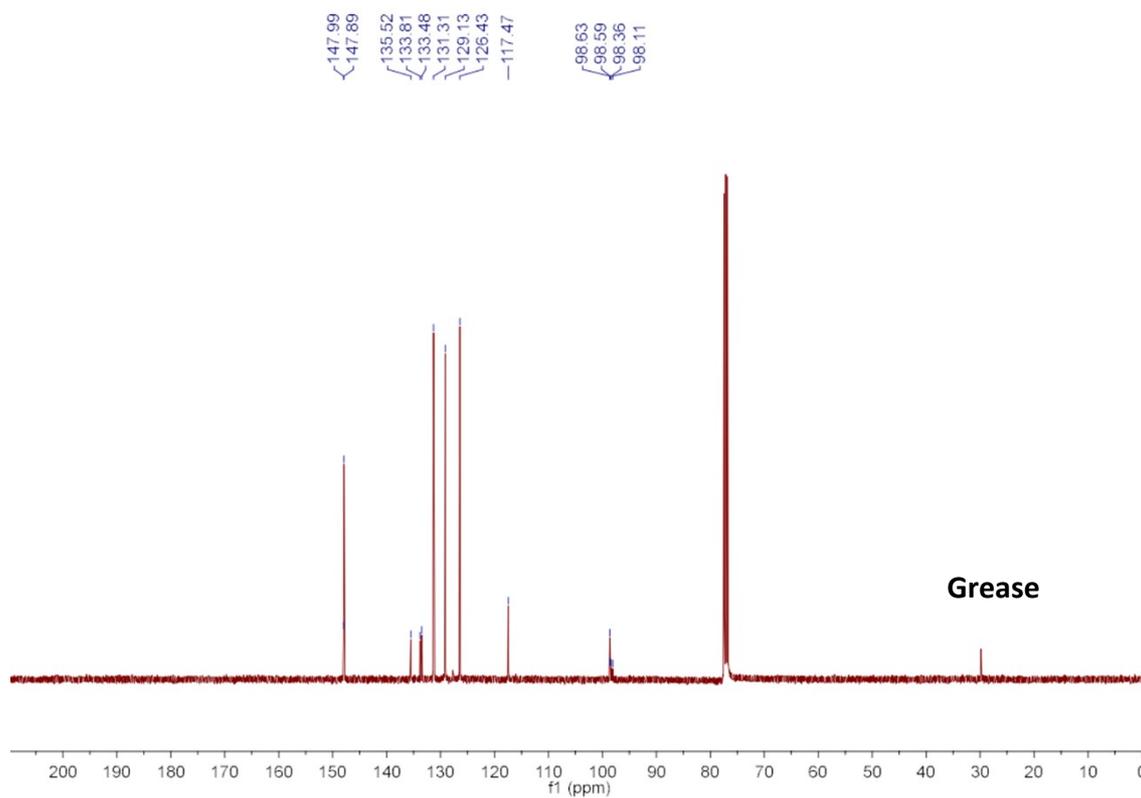
¹³C NMR (100.6 MHz, CDCl₃)



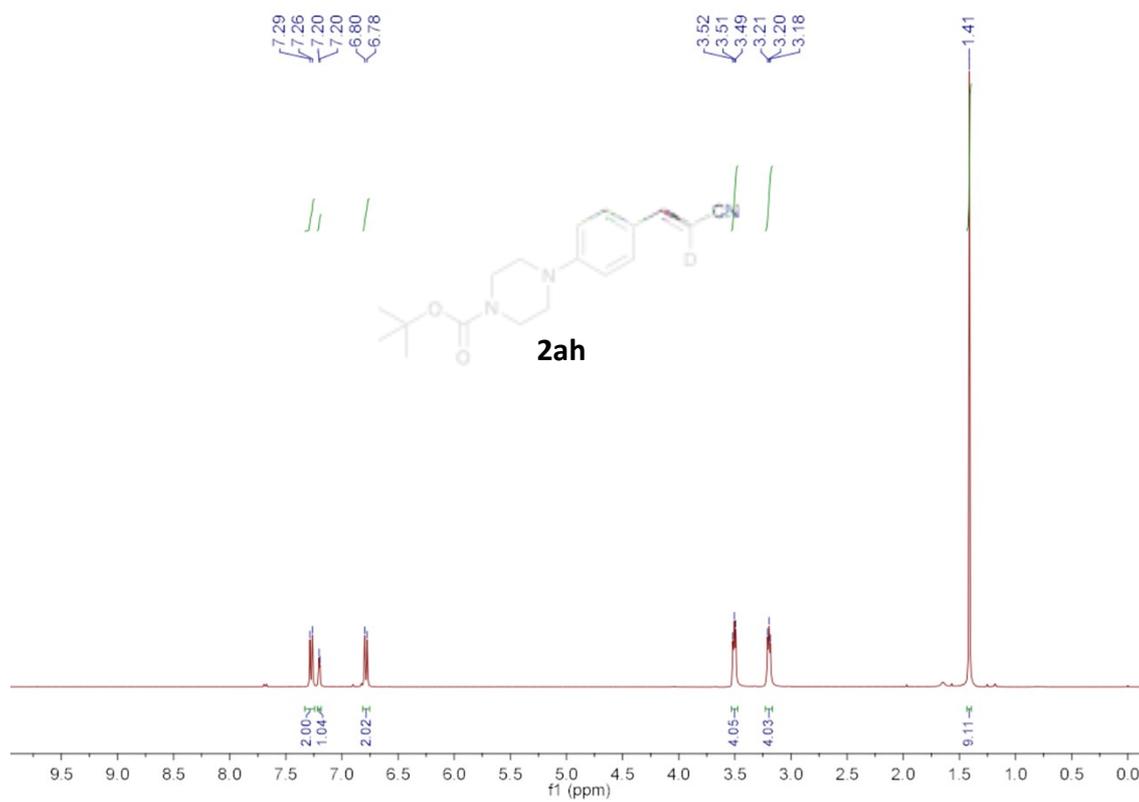
^1H NMR (400 MHz, CDCl_3)



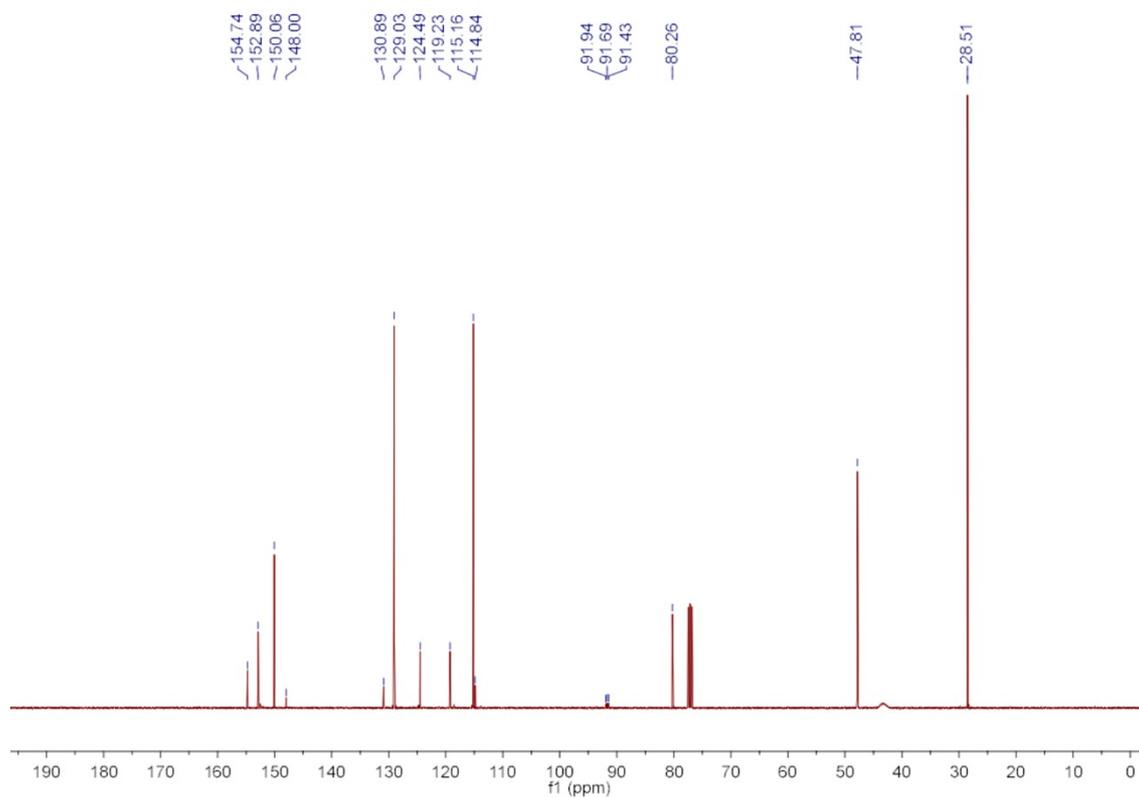
^{13}C NMR (100.6 MHz, CDCl_3)



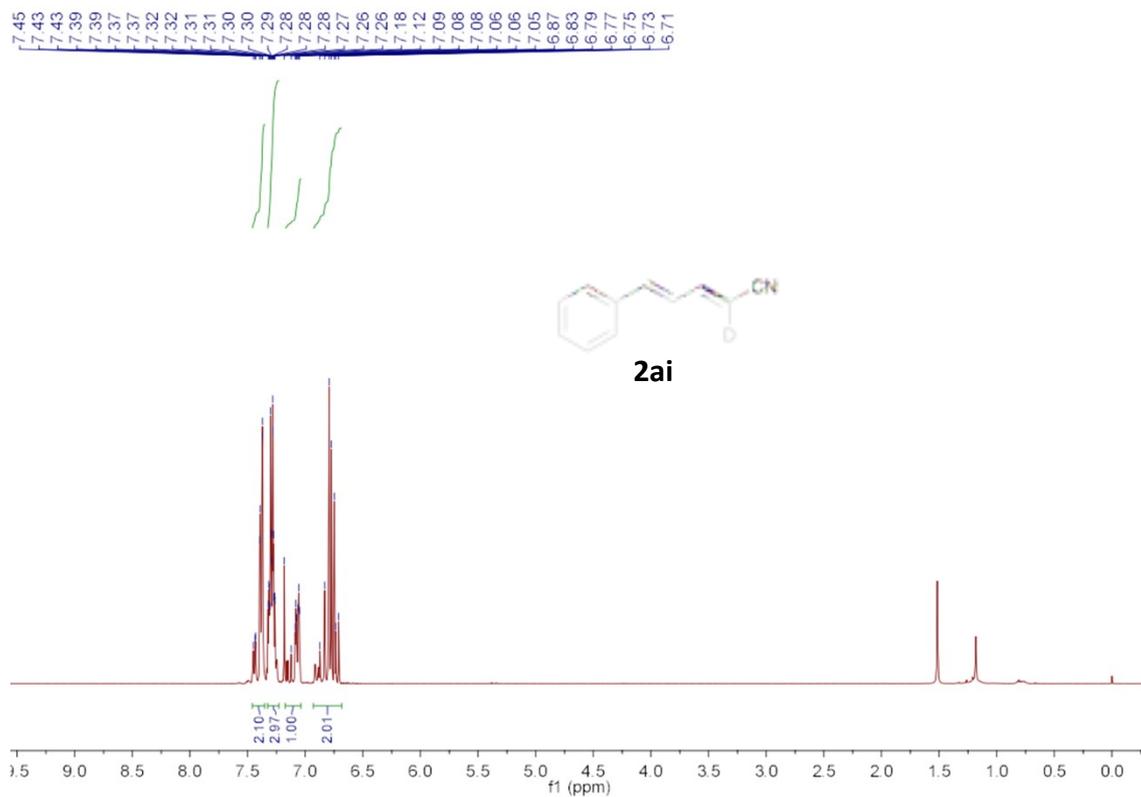
^1H NMR (400 MHz, CDCl_3)



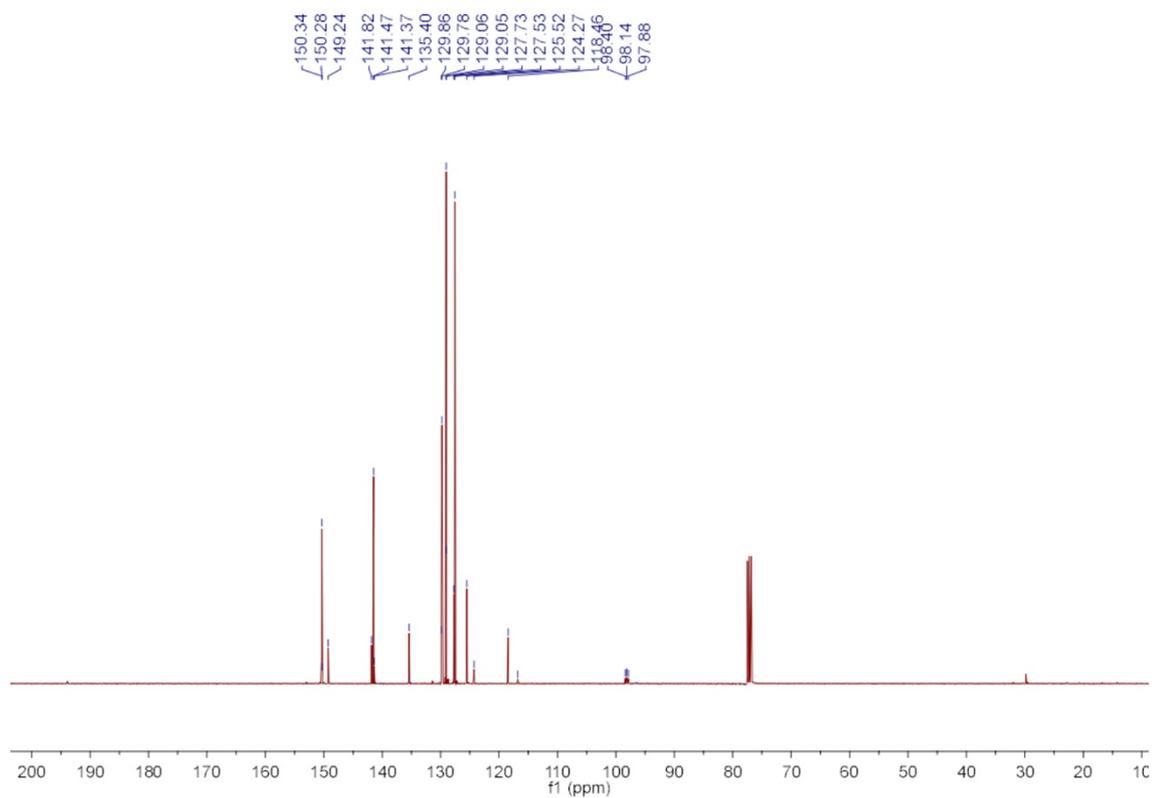
^{13}C NMR (100.6 MHz, CDCl_3)



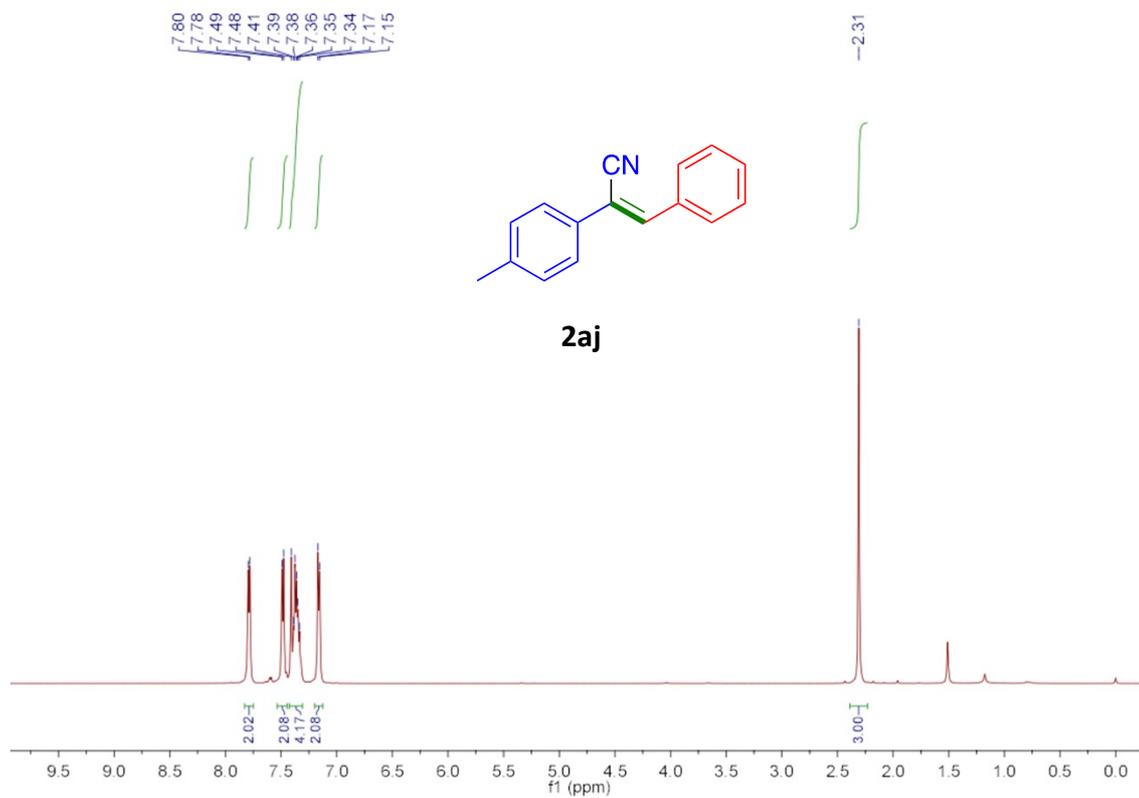
¹H NMR (400 MHz, CDCl₃)



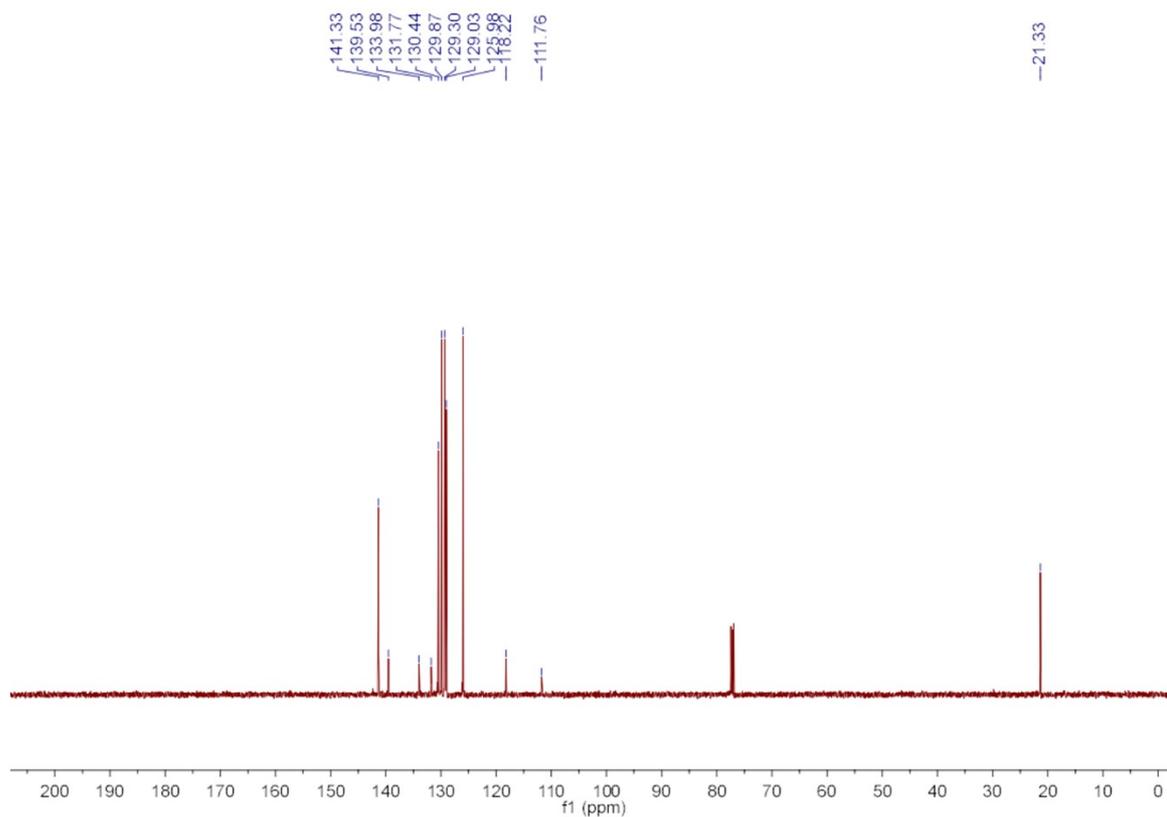
¹³C NMR (100.6 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100.6 MHz, CDCl₃)



Computational Details

Geometry optimizations were performed in the gas phase with Gaussian 16 (C.01 revision),¹⁷ using Truhlar's M06-L functional,¹⁸ the triple- ξ def2-TZVP basis set,¹⁹ W06 density fitting,²⁰ and Grimme's D3(0) empirical dispersion correction.²¹ Frequency calculations at the same level of theory were run to confirm stationary points and transition states, as well as obtain thermodynamic corrections. Single point energies of the optimized structures were computed with ORCA (6.0),²² using the range-separated meta-GGA hybrid functional ω B97M-V of the Head-Gordon group,²³ including VV10 dispersion correction,^{24,25} together with the triple- ξ def2-TZVPP basis set and the corresponding auxiliary basis sets, def2/J²⁰ and def2-TZVPP/C²⁶. The functional and basis set selections are based on recent benchmark studies.¹⁸ The Conductor-like Continuum Polarization Model (CPCM) was used in these calculations to account for acetonitrile solvation effects.²⁷ Gibbs free energies were computed by adding the free energy correction term from the frequency calculation to the single point energy in acetonitrile, according to the following equation:

$$\mathbf{G}^{\omega\text{B97M-V}} = \mathbf{E}^{\omega\text{B97M-V}} + \mathbf{corr}^{\text{M06-L}}_{freq}$$

where $\mathbf{E}^{\omega\text{B97M-V}}$ is the single point energy in acetonitrile, and $\mathbf{corr}^{\text{M06-L}}_{freq}$ is the thermal correction to the Gibbs free energy from the frequency calculation (at $T = 298.15$ K and $P = 1$ atm).

NBO analysis was performed at the ω B97M-V/def2-TZVPP level of theory, employing the NBO 7.0 software.²⁸

Computational Results

Table S7. Relative free energies (ΔG_{298} , kcal/mol) of select complexes in the gas phase and in acetonitrile, referenced to **Mn-1** and the free reactants.

| | Gas phase | Acetonitrile |
|-----------------|-----------|--------------|
| P1 | 4.24 | 5.97 |
| P2 | 3.98 | 2.26 |
| II-MeCN | 3.66 | 7.02 |
| II-EtCN | 1.71 | 5.97 |
| II-BnCN | -1.40 | 1.94 |
| III-MeCN | 0.43 | 5.57 |
| III-EtCN | 0.83 | 6.76 |
| III-BnCN | -4.44 | -0.79 |
| IV-MeCN | -1.84 | 4.78 |
| V-MeCN | 12.43 | 9.69 |
| IVb-MeCN | -0.32 | 6.60 |

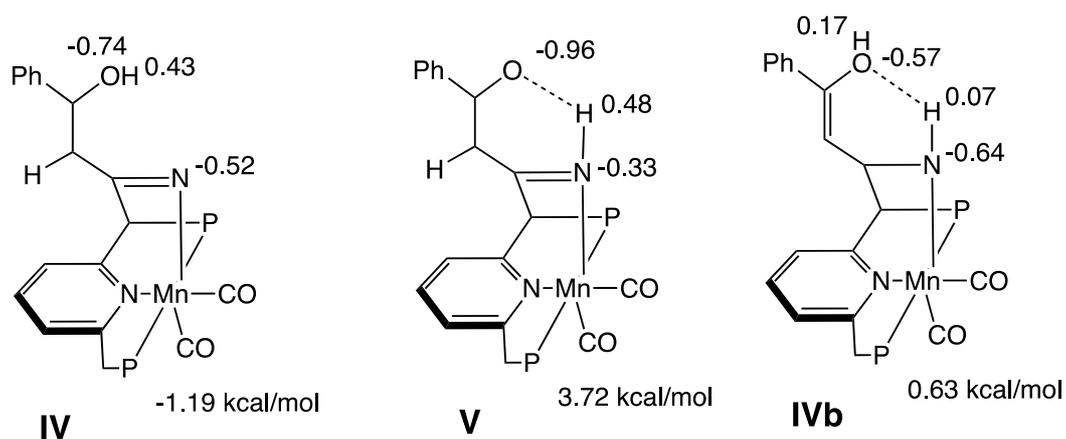
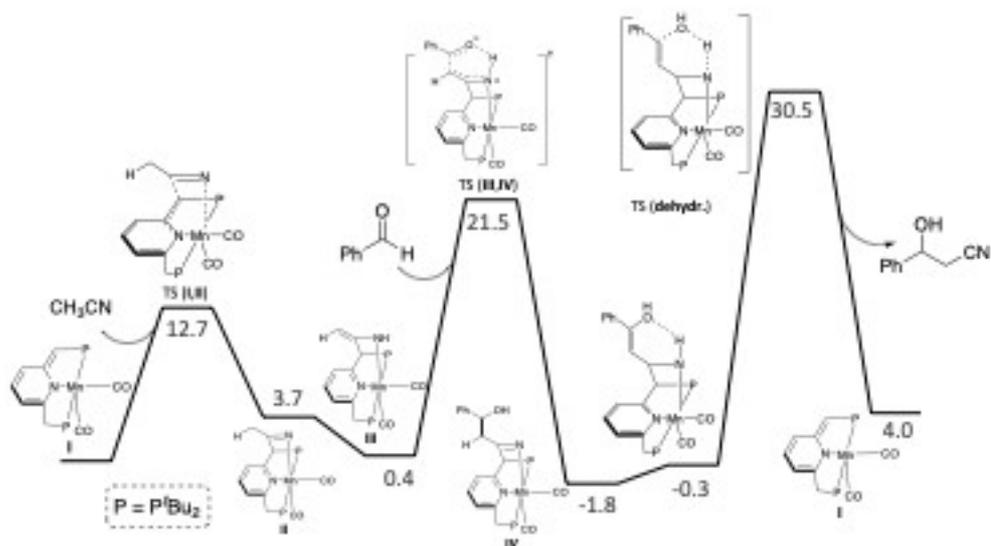


Figure S7. Relative free energies of complex **IV** and two of its isomers in acetonitrile, referenced to **Mn-1** and 3-hydroxy-3-phenylpropanenitrile, and select atomic APT charges.

a)



b)

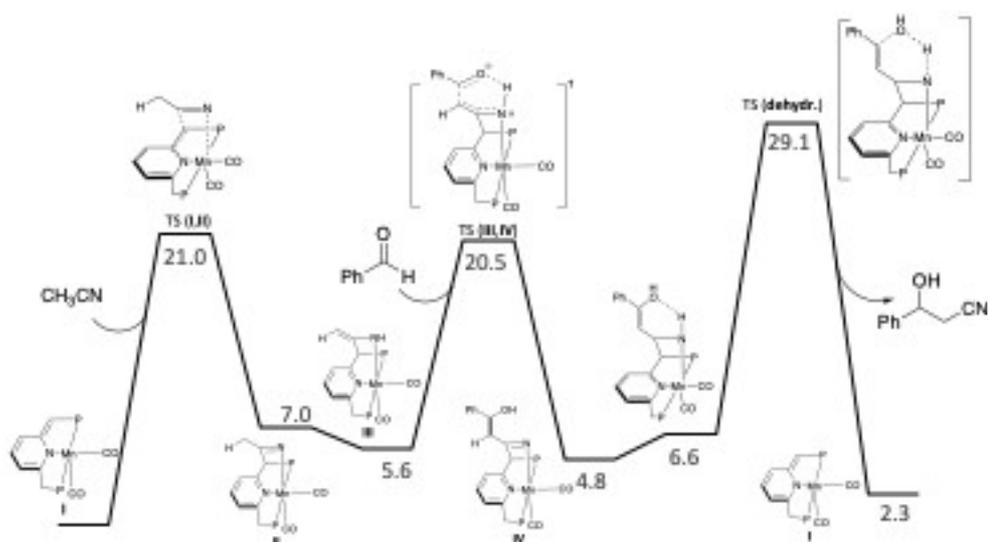
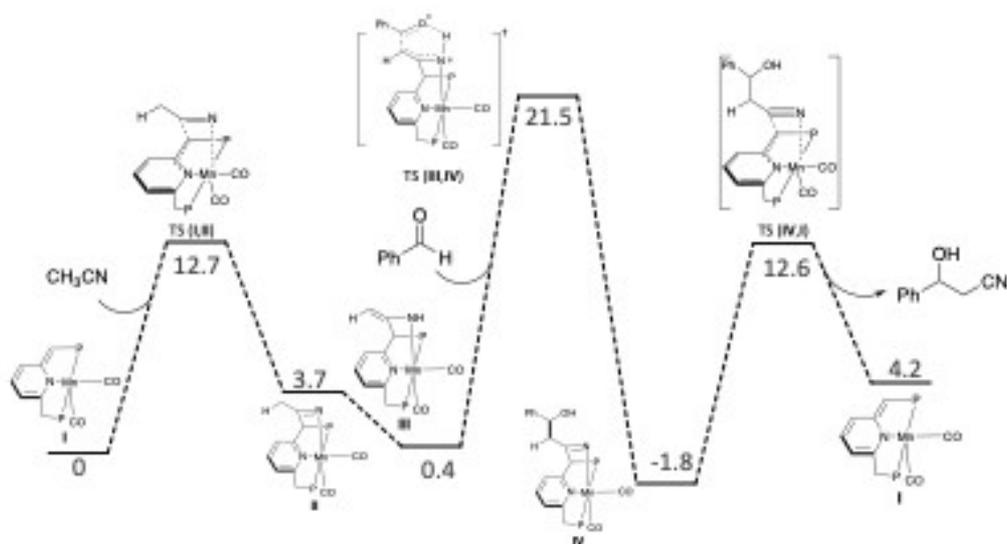


Figure S8. Reaction pathway for the formation of cinnamionitrile directly from CH₃CN and benzaldehyde catalysed by **Mn-1** in the gas phase (a) and in acetonitrile (b). All energies are in kcal/mol and are referenced to complex **Mn-1** and the free reactants.

a)



b)

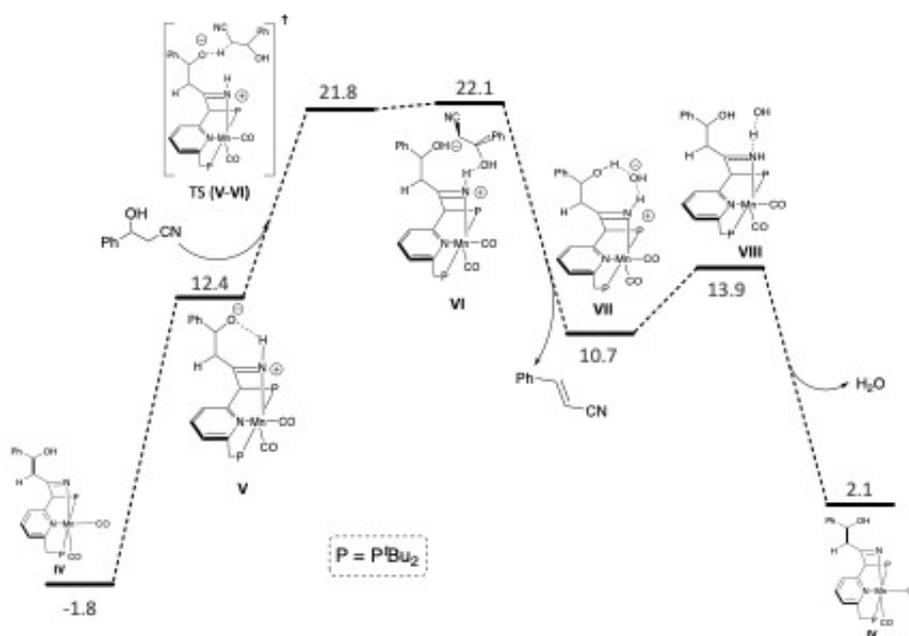


Figure S9. Reaction profiles for the stepwise formation of cinnamionitrile from CH_3CN and benzaldehyde in the gas phase, involving C–C coupling between CH_3CN and benzaldehyde promoted by complex **Mn-1** (a), and dehydration of the resulting β -hydroxynitrile intermediate promoted by the in-situ-generated complex **IV** (b). All energies are in kcal/mol and are referenced to complex **Mn-1** and the free reactants.

Effect of Electronic Structure on the Catalytic Activity of Complexes **Mn-1**, **Mn-2** and **Mn-3**

The PNP pincer ligand in complex **Mn-1** features two strongly electron-donating P^tBu₂ groups. By contrast, complexes **Mn-2** and **Mn-3** are based on PNN-type pincer ligands bearing weakly donating NEt₂ or pyridyl groups, which are situated away from the reactive site of each complex. NBO analysis shows that the side-arm nitrogen atoms in **Mn-2** and **Mn-3** carry negative charges of -0.410 and -0.436, respectively, in sharp contrast to the high positive charge (+1.170) on the corresponding phosphorus atom in **Mn-1**. This difference translates into an overall lower electron density across the structures of complexes **Mn-2** and **Mn-3**.

The reduced electron density at the Mn centers of **Mn-2** and **Mn-3**, relative to **Mn-1**, favors the initial coordination of the nitrile, with concomitant formation of the Mn–N bond in **TS(I,II)**, along a reaction pathway that is analogous to the one shown in Figure 4a. However, the reduced electron density also weakens the interaction of the nitrile with the pincer ligand arm. This is reflected in the NBO charge on the bridging C atom of the unsaturated arm, which decreases in absolute value from -0.870 in **Mn-1** to -0.859 in **Mn-2**, and even further to -0.846 in **Mn-3**. Thus, the activation of the coordinated nitrile is less efficient in **Mn-2** and **Mn-3**.

Furthermore, the diminished electron density on the abovementioned C atom destabilizes complex IV, which serves as the catalytically active species in the dehydration of the β-hydroxynitrile intermediate. The relative free energy of species IV increases from +4.8 kcal/mol, in the case of **Mn-1**, to +7.6 and +12.1 kcal/mol, in the case of **Mn-2** and **Mn-3**, respectively. In addition, the basicity of complex IV decreases upon going from **Mn-1** to **Mn-2** and **Mn-3**, as reflected in a gradual decrease in the NBO charge on the oxygen atom of the coordinated β-hydroxynitrile (from -0.785 to -0.779 and -0.773), and this hampers the final dehydrogenation step.

Overall, the relative electron deficiency of the PNN complexes **Mn-2** and **Mn-3** leads to weaker metal-ligand cooperation and diminished ability to activate the coordinated β-hydroxynitrile, as compared with the PNP complex **Mn-1**. Nevertheless, these electronic effects are quite modest, and all three complexes are catalytically active.

Cartesian Coordinates for Calculated Structures, Å

I (Mn-1)

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N 0.0111650000 1.6272130000 -0.4571630000
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H -5.0073970000 2.2700360000 -1.4290530000
P 2.1202480000 -0.2419600000 0.0587580000
C 3.8792040000 -1.9879450000 -1.2557100000
H 4.3865190000 -2.2707800000 -2.1795860000
H 4.6253470000 -2.0009270000 -0.4657220000
H 3.1375350000 -2.7598770000 -1.0449700000
C 2.4187660000 -0.7044490000 -2.7478300000
H 3.0675460000 -1.1264880000 -3.5188410000
H 1.5488710000 -1.3481100000 -2.6550630000
H 2.0731310000 0.2614100000 -3.1002110000
C 2.4126680000 0.0651410000 2.8144690000
H 2.5257080000 1.1474180000 2.7927560000
H 1.3524000000 -0.1709240000 2.8702210000
H 2.8728360000 -0.2885380000 3.7392030000
C 4.5537440000 -0.0888200000 1.6212740000
H 4.9914430000 -0.2288180000 2.6126310000

H 5.1941990000 -0.6131830000 0.9159980000
H 4.5994710000 0.9779400000 1.3979260000
C 1.0427270000 1.6939460000 -1.3131590000
C -0.2861930000 -1.9557390000 -1.0982870000
O -0.4036840000 -2.8898250000 -1.7779500000
Mn -0.1669860000 -0.5445020000 -0.0033270000
C -0.2300940000 -1.5779960000 1.4429450000
O -0.2123090000 -2.2071910000 2.4255980000
N 0.1518710000 0.8380190000 -1.5198440000
C 1.3363300000 2.8939040000 -2.1794750000
H 2.3977630000 2.8917940000 -2.4553240000
H 1.2156410000 3.7940500000 -1.5628000000
C 0.4642670000 2.9700070000 -3.4119810000
H 0.7079420000 3.8411040000 -4.0186800000
H 0.5802290000 2.0788300000 -4.0272860000
H -0.5890260000 3.0234680000 -3.1407560000

II-BnCN

P -2.4509520000 -0.3084130000 0.0319610000
N -0.1747920000 1.0213520000 1.0519370000
C 0.8925680000 1.8416150000 0.9606970000
C 0.9550160000 3.0252540000 1.6874670000
H 1.8121800000 3.6765160000 1.5750560000
C -0.0939840000 3.3517100000 2.5227330000
H -0.0637610000 4.2643710000 3.1038980000
C -1.2036870000 2.5175770000 2.5849650000
H -2.0578260000 2.7692810000 3.1987010000
C -1.2282080000 1.3645430000 1.8193160000

C -2.4284540000 0.4783550000 1.7148990000
H -3.3379210000 1.0237950000 1.9755820000
H -2.3457750000 -0.3575730000 2.4173640000
C 1.8834720000 1.4348530000 -0.0652040000
H 2.7860530000 2.0484810000 -0.0171090000
C 3.1061910000 -0.7945340000 1.5413160000
C 3.2400630000 -0.7715890000 -1.5444690000
C 3.1148590000 -2.3030860000 1.8090870000
H 2.1146060000 -2.7277400000 1.7948490000
H 3.5261260000 -2.4781100000 2.8055790000
H 3.7287990000 -2.8596810000 1.1085940000
C 4.3252750000 0.2872170000 -1.7375470000
H 3.8988290000 1.2688010000 -1.9408570000
H 4.9301620000 0.0188460000 -2.6068240000
H 4.9998990000 0.3836240000 -0.8918090000
C -3.6920350000 -1.7274530000 0.2441780000
C -4.1458840000 -2.2236150000 -1.1282680000
H -3.2991350000 -2.4639480000 -1.7716300000
H -4.7800310000 -1.5115680000 -1.6512600000
H -4.7267890000 -3.1391430000 -0.9997110000
C -4.9024940000 -1.3537060000 1.1013850000
H -5.4993360000 -0.5448700000 0.6934820000
H -4.6106240000 -1.0814810000 2.1155900000
H -5.5547260000 -2.2258270000 1.1854710000
C -2.9984530000 -2.8953330000 0.9428970000
H -3.7175040000 -3.7107530000 1.0473730000
H -2.6522800000 -2.6401000000 1.9424980000
H -2.1495010000 -3.2723040000 0.3770070000

C -3.2391210000 0.9996150000 -1.0935000000
C -2.9521570000 0.6055420000 -2.5449330000
H -3.4493760000 -0.3163450000 -2.8379440000
H -1.8795690000 0.4975030000 -2.7073100000
H -3.3199200000 1.3949550000 -3.2052530000
C -2.5329090000 2.3287750000 -0.8171590000
H -2.8612160000 3.0554680000 -1.5645620000
H -1.4524900000 2.2373370000 -0.8950470000
H -2.7852120000 2.7391630000 0.1616640000
C -4.7331470000 1.2400750000 -0.9001450000
H -4.9825420000 1.5118840000 0.1265180000
H -5.3480020000 0.3911430000 -1.1898960000
H -5.0332920000 2.0790900000 -1.5327890000
P 2.1174680000 -0.4089160000 -0.0388100000
C 3.8842300000 -2.1461040000 -1.3564610000
H 4.3951400000 -2.4225060000 -2.2803370000
H 4.6268820000 -2.1662020000 -0.5633340000
H 3.1405390000 -2.9185500000 -1.1550290000
C 2.4334030000 -0.8495750000 -2.8454240000
H 3.0885130000 -1.2581710000 -3.6182900000
H 1.5689020000 -1.5018950000 -2.7633820000
H 2.0802100000 0.1161930000 -3.1900160000
C 2.3916050000 -0.1263300000 2.7217700000
H 2.5046320000 0.9560130000 2.7098320000
H 1.3310740000 -0.3625250000 2.7698420000
H 2.8467390000 -0.4879750000 3.6459000000
C 4.5392200000 -0.2669480000 1.5395550000
H 4.9700660000 -0.4115630000 2.5332140000

H 5.1854750000 -0.7869180000 0.8362640000
H 4.5848030000 0.8011490000 1.3224810000
C 1.0685150000 1.5474270000 -1.4005630000
C -0.2935300000 -2.0946140000 -1.2376580000
O -0.4143250000 -3.0190970000 -1.9298250000
Mn -0.1724470000 -0.6991170000 -0.1226820000
C -0.2329360000 -1.7514330000 1.3091830000
O -0.2110800000 -2.3913890000 2.2846160000
N 0.1600230000 0.7138320000 -1.6233480000
C 1.4168990000 2.7218220000 -2.3069750000
H 0.6678290000 2.7364580000 -3.0994370000
H 2.3844600000 2.5323920000 -2.7839560000
C 1.4689880000 4.0357430000 -1.5840460000
C 0.2979870000 4.7397050000 -1.3071200000
C 2.6743780000 4.5577840000 -1.1181570000
C 0.3280400000 5.9144240000 -0.5734540000
C 2.7105120000 5.7338520000 -0.3838100000
C 1.5343000000 6.4133140000 -0.1022220000
H -0.6460920000 4.3552950000 -1.6736280000
H 3.5979350000 4.0327610000 -1.3401930000
H -0.5940200000 6.4445880000 -0.3702470000
H 3.6592140000 6.1234470000 -0.0364610000
H 1.5591380000 7.3326790000 0.4683490000

III-MeCN

P -2.3279350000 -0.0133450000 -0.0186780000
N -0.0093800000 1.0484660000 1.2024650000
C 1.1110850000 1.7909060000 1.2139210000

C 1.2228770000 2.9111380000 2.0266860000
H 2.1296830000 3.4998420000 2.0015550000
C 0.1648240000 3.2497330000 2.8485480000
H 0.2338000000 4.1089600000 3.5029620000
C -0.9993230000 2.4983120000 2.8033850000
H -1.8595850000 2.7647280000 3.4022570000
C -1.0704470000 1.4104620000 1.9480240000
C -2.3266030000 0.6325690000 1.7223690000
H -3.2038660000 1.2279850000 1.9841290000
H -2.3454980000 -0.2580960000 2.3586340000
C 2.1388110000 1.3921240000 0.2094740000
H 3.0835970000 1.9088880000 0.3807660000
C 3.0948160000 -1.0349850000 1.7100200000
C 3.4250090000 -0.8003440000 -1.3536080000
C 2.9778120000 -2.5557250000 1.8565930000
H 1.9512280000 -2.8991340000 1.7585480000
H 3.3195850000 -2.8377710000 2.8548190000
H 3.5867730000 -3.1023500000 1.1441620000
C 4.5828140000 0.1976960000 -1.4034020000
H 4.2206080000 1.2101370000 -1.5816420000
H 5.2295690000 -0.0626930000 -2.2445080000
H 5.2013930000 0.1971190000 -0.5105150000
C -3.6925160000 -1.3293580000 0.0250010000
C -4.1416470000 -1.6498570000 -1.4000280000
H -3.2965880000 -1.8695560000 -2.0534290000
H -4.7245390000 -0.8497790000 -1.8504570000
H -4.7767920000 -2.5375150000 -1.3813280000
C -4.8947520000 -0.9307450000 0.8826790000

H -5.3937820000 -0.0264400000 0.5499990000
H -4.6183320000 -0.7994040000 1.9285940000
H -5.6310770000 -1.7368270000 0.8510900000
C -3.1243370000 -2.6138180000 0.6252020000
H -3.9117010000 -3.3705500000 0.6289400000
H -2.7952850000 -2.4853640000 1.6542750000
H -2.2892430000 -3.0072910000 0.0497590000
C -2.9556900000 1.4510840000 -1.0547160000
C -2.7251370000 1.1231010000 -2.5338970000
H -3.4829110000 0.4530380000 -2.9325240000
H -1.7571990000 0.6563080000 -2.7052230000
H -2.7638610000 2.0420050000 -3.1219810000
C -2.1164640000 2.6786400000 -0.6819450000
H -2.3644390000 3.4887850000 -1.3709080000
H -1.0471840000 2.4937020000 -0.7552130000
H -2.3466070000 3.0359000000 0.3219970000
C -4.4180760000 1.8352670000 -0.8491900000
H -4.6465570000 2.0544010000 0.1945090000
H -5.1149050000 1.0782740000 -1.2020480000
H -4.6235680000 2.7462090000 -1.4167030000
P 2.2409190000 -0.4692390000 0.1067280000
C 3.9633150000 -2.2274140000 -1.2413440000
H 4.5139560000 -2.4633850000 -2.1535020000
H 4.6514660000 -2.3627250000 -0.4110230000
H 3.1601700000 -2.9605240000 -1.1495590000
C 2.6937580000 -0.7150130000 -2.6979540000
H 3.3708350000 -1.1002240000 -3.4643270000
H 1.7902580000 -1.3179060000 -2.7217850000

H 2.441840000 0.306603000 -2.964615000
C 2.355842000 -0.407256000 2.896813000
H 2.536904000 0.663222000 2.975156000
H 1.281672000 -0.576044000 2.869362000
H 2.732212000 -0.863728000 3.814361000
C 4.559314000 -0.620764000 1.832327000
H 4.915774000 -0.875144000 2.833422000
H 5.208171000 -1.132085000 1.125354000
H 4.696315000 0.453780000 1.705839000
C 1.527806000 1.761543000 -1.140009000
C -0.235689000 -1.880812000 -1.331752000
O -0.381271000 -2.738197000 -2.100718000
Mn -0.080253000 -0.581103000 -0.115121000
C -0.298834000 -1.728062000 1.215898000
O -0.384215000 -2.450776000 2.128156000
N 0.525161000 0.914340000 -1.438835000
H 0.127031000 1.097331000 -2.349588000
C 2.003955000 2.832426000 -1.825746000
H 1.574779000 3.127218000 -2.774336000
H 2.830509000 3.414946000 -1.447493000

III-EtCN

P -2.318524000 -0.009408000 -0.023280000
N 0.001970000 1.052588000 1.194816000
C 1.126040000 1.789752000 1.200168000
C 1.240830000 2.921062000 1.997340000
H 2.151782000 3.503767000 1.969181000
C 0.181034000 3.277699000 2.809577000

H 0.2521090000 4.1456480000 3.4521490000
C -0.9872240000 2.5322500000 2.7694540000
H -1.8488150000 2.8121330000 3.3602480000
C -1.0602460000 1.4320320000 1.9300740000
C -2.3195480000 0.6578970000 1.7099360000
H -3.1947240000 1.2605760000 1.9619150000
H -2.3445580000 -0.2251620000 2.3564950000
C 2.1542170000 1.3751320000 0.2025850000
H 3.1072740000 1.8665920000 0.3915470000
C 3.1057290000 -1.0422550000 1.7017520000
C 3.4197010000 -0.8199280000 -1.3635250000
C 2.9857670000 -2.5616260000 1.8582530000
H 1.9566570000 -2.9011830000 1.7721600000
H 3.3364160000 -2.8399060000 2.8544990000
H 3.5851740000 -3.1145280000 1.1424050000
C 4.5684880000 0.1883520000 -1.4253430000
H 4.1979640000 1.1954970000 -1.6134430000
H 5.2180720000 -0.0745660000 -2.2634880000
H 5.1870250000 0.2048650000 -0.5324120000
C -3.6921060000 -1.3154480000 0.0331300000
C -4.1387310000 -1.6520230000 -1.3889530000
H -3.2929490000 -1.8855020000 -2.0365890000
H -4.7151500000 -0.8542420000 -1.8517180000
H -4.7795290000 -2.5353790000 -1.3606740000
C -4.8946420000 -0.8976000000 0.8811690000
H -5.3857340000 0.0061200000 0.5352300000
H -4.6211250000 -0.7551190000 1.9263910000
H -5.6367890000 -1.6986100000 0.8568830000

C -3.1337660000 -2.5951970000 0.6523000000
H -3.9267230000 -3.3459740000 0.6669840000
H -2.8034400000 -2.4542600000 1.6793980000
H -2.3015220000 -3.0030920000 0.0828030000
C -2.9335580000 1.4458430000 -1.0799170000
C -2.6996010000 1.0963440000 -2.5537410000
H -3.4628760000 0.4293700000 -2.9471350000
H -1.7359860000 0.6167660000 -2.7143050000
H -2.7256790000 2.0078470000 -3.1540290000
C -2.0866830000 2.6721020000 -0.7203030000
H -2.3250650000 3.4743700000 -1.4219210000
H -1.0186220000 2.4762810000 -0.7855550000
H -2.3189550000 3.0452470000 0.2773870000
C -4.3938610000 1.8428410000 -0.8849980000
H -4.6245480000 2.0772520000 0.1549050000
H -5.0945400000 1.0859130000 -1.2303390000
H -4.5911940000 2.7475980000 -1.4652530000
P 2.2410980000 -0.4858050000 0.1006780000
C 3.9719040000 -2.2412470000 -1.2435570000
H 4.5255190000 -2.4768760000 -2.1540260000
H 4.6599390000 -2.3673920000 -0.4118640000
H 3.1749640000 -2.9806540000 -1.1492850000
C 2.6838580000 -0.7525490000 -2.7061670000
H 3.3607510000 -1.1411460000 -3.4711830000
H 1.7838240000 -1.3608220000 -2.7208310000
H 2.4232100000 0.2645400000 -2.9814730000
C 2.3725740000 -0.4058200000 2.8876460000
H 2.5555500000 0.6649730000 2.9582800000

H 1.2979740000 -0.5729680000 2.8650660000
H 2.7515490000 -0.8567460000 3.8069080000
C 4.5712040000 -0.6288540000 1.8162100000
H 4.9326360000 -0.8818050000 2.8159350000
H 5.2173260000 -1.1404020000 1.1069320000
H 4.7079890000 0.4456170000 1.6883200000
C 1.5466140000 1.7491210000 -1.1460310000
C -0.2383150000 -1.9020340000 -1.3128320000
O -0.3886350000 -2.7657160000 -2.0741490000
Mn -0.0753080000 -0.5927280000 -0.1086640000
C -0.2997120000 -1.7273190000 1.2317420000
O -0.3853790000 -2.4434110000 2.1495300000
N 0.5460080000 0.8852810000 -1.4397570000
H 0.1411270000 1.0670450000 -2.3478820000
C 1.9758180000 2.8174890000 -1.8694240000
H 1.4603490000 2.9920930000 -2.8108470000
C 3.0620940000 3.7764580000 -1.5292480000
H 3.5527890000 3.5418820000 -0.5838640000
H 3.8523510000 3.8076620000 -2.2876680000
H 2.6990600000 4.8059350000 -1.4370280000

III-BnCN

P -2.4655400000 -0.1168390000 -0.0451010000
N -0.1514350000 0.9496950000 1.1812260000
C 0.9731710000 1.6869980000 1.2143490000
C 1.0958990000 2.7609240000 2.0861690000
H 2.0151140000 3.3291770000 2.1122520000
C 0.0391680000 3.0745890000 2.9199040000

H 0.1202950000 3.8984770000 3.6168230000
C -1.1340680000 2.3422400000 2.8365030000
H -1.9929550000 2.5906670000 3.4449050000
C -1.2100790000 1.2876670000 1.9409410000
C -2.4669560000 0.5151950000 1.7000890000
H -3.3434870000 1.1104490000 1.9649870000
H -2.4905820000 -0.3800720000 2.3297070000
C 1.9991850000 1.3078030000 0.1958270000
H 2.9512370000 1.8042950000 0.3753860000
C 2.9604850000 -1.1238430000 1.6974590000
C 3.2881370000 -0.8978430000 -1.3665350000
C 2.8447080000 -2.6449550000 1.8445840000
H 1.8177970000 -2.9891280000 1.7528510000
H 3.1918190000 -2.9251240000 2.8413930000
H 3.4500480000 -3.1925460000 1.1302100000
C 4.4507890000 0.0951580000 -1.4195890000
H 4.1055380000 1.1151510000 -1.5813500000
H 5.0866870000 -0.1623580000 -2.2697060000
H 5.0792960000 0.0797830000 -0.5340920000
C -3.8247050000 -1.4382250000 -0.0121110000
C -4.2692910000 -1.7515050000 -1.4401580000
H -3.4220780000 -1.9648120000 -2.0929220000
H -4.8536380000 -0.9504540000 -1.8870310000
H -4.9017480000 -2.6411200000 -1.4284270000
C -5.0304510000 -1.0500430000 0.8455150000
H -5.5348790000 -0.1478060000 0.5156250000
H -4.7566090000 -0.9212400000 1.8924090000
H -5.7614880000 -1.8606490000 0.8096190000

C -3.2522230000 -2.7236570000 0.5822200000
H -4.0358470000 -3.4841450000 0.5781460000
H -2.9286330000 -2.5999480000 1.6136220000
H -2.4129990000 -3.1098620000 0.0079680000
C -3.0961010000 1.3548470000 -1.0689480000
C -2.8622400000 1.0437790000 -2.5508120000
H -3.6055400000 0.3604120000 -2.9538180000
H -1.8844360000 0.6004400000 -2.7274760000
H -2.9219740000 1.9664470000 -3.1311030000
C -2.2619240000 2.5820270000 -0.6846410000
H -2.5217380000 3.4013650000 -1.3579720000
H -1.1927360000 2.4044970000 -0.7721220000
H -2.4825040000 2.9222660000 0.3273820000
C -4.5603720000 1.7304840000 -0.8612460000
H -4.7913700000 1.9381930000 0.1841850000
H -5.2529520000 0.9736870000 -1.2226270000
H -4.7693040000 2.6458900000 -1.4200660000
P 2.1032760000 -0.5630540000 0.0937930000
C 3.8250220000 -2.3254810000 -1.2480420000
H 4.3750170000 -2.5644250000 -2.1596910000
H 4.5145280000 -2.4566130000 -0.4184330000
H 3.0224550000 -3.0587310000 -1.1530250000
C 2.5563490000 -0.8231210000 -2.7114940000
H 3.2325540000 -1.2150300000 -3.4747360000
H 1.6530110000 -1.4264720000 -2.7312020000
H 2.3068980000 0.1956710000 -2.9905500000
C 2.2241600000 -0.4988640000 2.8873710000
H 2.4174340000 0.5682920000 2.9754650000

H 1.1481200000 -0.6563920000 2.8574560000
H 2.5941240000 -0.9670230000 3.8014740000
C 4.4246860000 -0.7070050000 1.8160240000
H 4.7809350000 -0.9538650000 2.8189760000
H 5.0736860000 -1.2235930000 1.1132850000
H 4.5619230000 0.3664470000 1.6810210000
C 1.4049680000 1.6539400000 -1.1646540000
C -0.3632910000 -1.9820920000 -1.3476240000
O -0.5072990000 -2.8412430000 -2.1144840000
Mn -0.2130640000 -0.6785190000 -0.1335110000
C -0.4339520000 -1.8246400000 1.1995240000
O -0.5201870000 -2.5450850000 2.1126010000
N 0.3903730000 0.8195590000 -1.4443370000
H 0.0236220000 0.9687550000 -2.3754150000
C 1.9042150000 2.6228190000 -2.0026280000
H 1.4760860000 2.6090040000 -3.0031030000
C 2.9935980000 3.5491440000 -1.8290710000
C 3.3965980000 4.1089600000 -0.6020150000
C 3.7159260000 3.9673420000 -2.9654440000
C 4.4762920000 4.9710400000 -0.5124810000
C 4.7843690000 4.8370750000 -2.8762310000
C 5.1887460000 5.3389910000 -1.6444450000
H 2.8136960000 3.9095050000 0.2860090000
H 3.4228600000 3.5759410000 -3.9333260000
H 4.7479170000 5.3814480000 0.4530360000
H 5.3138530000 5.1238640000 -3.7768350000
H 6.0280970000 6.0175480000 -1.5724400000

IV

P -2.547600000 -0.4109690000 0.4768850000
N -0.3104680000 1.0496720000 1.4016450000
C 0.6532810000 1.9880020000 1.2967190000
C 0.6700920000 3.1000330000 2.1311780000
H 1.4485800000 3.8424870000 2.0161700000
C -0.3084320000 3.2267530000 3.0970800000
H -0.3071340000 4.0753000000 3.7686790000
C -1.3102000000 2.2694170000 3.1815410000
H -2.1118530000 2.3620380000 3.9012450000
C -1.3014500000 1.1994170000 2.3021060000
C -2.4095070000 0.2005840000 2.2247320000
H -3.3331620000 0.6114430000 2.6374430000
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H 2.4023200000 2.4963030000 0.1662340000
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H 2.5414470000 -2.4707930000 1.4841990000
H 3.9805930000 -2.0851840000 2.4100910000
H 4.0878860000 -2.2497400000 0.6709660000
C 3.7258000000 1.1834310000 -1.9665940000
H 3.0464550000 2.0065720000 -2.1851360000
H 4.3548450000 1.0475690000 -2.8491660000
H 4.3755110000 1.4897120000 -1.1486270000
C -3.6076730000 -1.9712700000 0.6633610000
C -4.1824760000 -2.3691300000 -0.6955420000

H -3.4106940000 -2.4243670000 -1.4635380000
H -4.9604450000 -1.6925080000 -1.0409720000
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H 5.107631000 0.121595000 0.468966000
H 4.304616000 1.480898000 1.253638000
C 0.614465000 1.976938000 -1.081062000
C -0.412303000 -1.783718000 -1.229244000
O -0.561616000 -2.621733000 -2.017550000
Mn -0.270839000 -0.526505000 0.037486000
C -0.043886000 -1.749301000 1.309633000
O 0.184698000 -2.513841000 2.159614000
N -0.224946000 1.070647000 -1.321938000
C 0.697972000 3.308938000 -1.791182000
H 1.727553000 3.678157000 -1.805879000
H 0.128670000 4.047696000 -1.211307000
C 0.136930000 3.264299000 -3.214178000
H 0.750628000 2.541775000 -3.781745000
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H -1.190882000 2.032637000 -2.662628000
C 0.260334000 4.604054000 -3.884944000

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C -0.8467000000 5.4248470000 -4.0612670000
C 1.6483970000 6.3032880000 -4.8941290000
C -0.7071440000 6.6743370000 -4.6485610000
C 0.5381670000 7.1190320000 -5.0642220000
H 2.3739560000 4.4129380000 -4.1905170000
H -1.8150630000 5.0640200000 -3.7419420000
H 2.6237560000 6.6375900000 -5.2246840000
H -1.5782380000 7.3031000000 -4.7852460000
H 0.6443340000 8.0927860000 -5.5249380000

V

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N -0.1012788885 1.26679437 1.1237759722
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H 1.7735137121 3.9572820767 1.8354376509
C -0.0807936828 3.4480147444 2.8085415951
H -0.0741460206 4.3001131292 3.4753479183
C -1.1399032151 2.5532806465 2.828828735
H -1.9814272394 2.70097834 3.491498702
C -1.141762631 1.4798091942 1.9517105799
C -2.3044265675 0.5563575133 1.7918136705
H -3.2232910819 1.0253285035 2.1488563471
H -2.1557686497 -0.3505856339 2.387143813
C 1.9064629614 1.8826372501 -0.0095543512
H 2.7832656509 2.5261887469 0.0759281294
C 3.2050235339 -0.3535047417 1.4914119717

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H 3.6227328049 1.938530209 -2.1332406369
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H -4.737311287 -1.1017043798 -1.6832182153
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C -4.7225576069 -1.2934559042 1.0565118142
H -5.3483541507 -0.4469537941 0.7942429162
H -4.3939876555 -1.1651899703 2.0878718115
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C -2.7788753166 -2.7301952783 0.6229525092
H -3.4661650728 -3.5780253857 0.6557971955
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H 2.8950061622 -0.3223952627 3.606296131
C 4.5416198371 0.3830333481 1.5613900218
H 5.0096104131 0.18078421 2.5274269922
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C 1.1002105688 2.1543620909 -1.2743066605
C -0.2054082245 -1.5389382571 -1.5414371425
O -0.3534927825 -2.3422880527 -2.3615217339
Mn -0.0723573308 -0.3092171561 -0.2404601296

C -0.0356342461 -1.5607014601 1.0236236366
O 0.0667847657 -2.3551350988 1.8680571688
N 0.2014707014 1.2907323198 -1.5471547341
C 1.239066791 3.4505104088 -2.0005489884
H 2.2958000857 3.7262373911 -2.0813497377
H 0.782206343 4.2171212526 -1.3600935982
C 0.481331344 3.4407819467 -3.3670172193
O -0.7743867949 2.9830446751 -3.2102420245
H 0.5208389231 4.4988966348 -3.717504143
H -0.3835324047 1.7112847796 -2.3554274034
C 1.3022234676 2.6500247196 -4.3971769512
C 2.6463201964 2.9125515004 -4.6571155845
C 0.6804808539 1.6340262408 -5.1148395432
C 3.356162223 2.1661276925 -5.5858199571
C 1.3830806488 0.8869803418 -6.0495585849
C 2.7256262021 1.1449267122 -6.2847959758
H 3.1469848705 3.7217400621 -4.1331987903
H -0.3691729624 1.4579603938 -4.9080510129
H 4.4013756596 2.3847839571 -5.771376937
H 0.8814168002 0.0982673278 -6.5977419213
H 3.276353617 0.5624523979 -7.01287294

IVb

P 2.571704 -1.431820 -0.195861
N 1.101295 0.228175 1.554014
C -0.037101 0.652654 2.128736
C -0.262436 0.486212 3.488108
H -1.196125 0.820102 3.919685

| | | | |
|---|-----------|-----------|-----------|
| C | 0.716358 | -0.111451 | 4.259363 |
| H | 0.571345 | -0.239140 | 5.324191 |
| C | 1.871244 | -0.578227 | 3.651427 |
| H | 2.633871 | -1.091317 | 4.221306 |
| C | 2.028882 | -0.419212 | 2.283756 |
| C | 3.161245 | -1.023028 | 1.517244 |
| H | 3.590795 | -1.867175 | 2.060788 |
| H | 3.964170 | -0.291954 | 1.378337 |
| C | -1.058721 | 1.181352 | 1.178659 |
| H | -1.882855 | 1.665081 | 1.704195 |
| C | 0.320446 | 3.820329 | 0.716540 |
| C | -1.629209 | 2.631737 | -1.367420 |
| C | 1.252806 | 4.612131 | -0.206522 |
| H | 2.075720 | 4.005354 | -0.575621 |
| H | 1.688371 | 5.436650 | 0.361909 |
| H | 0.743280 | 5.046894 | -1.060097 |
| C | -2.957807 | 2.915690 | -0.664972 |
| H | -3.320541 | 2.034347 | -0.135630 |
| H | -3.705269 | 3.162669 | -1.422914 |
| H | -2.917230 | 3.750134 | 0.029175 |
| C | 4.188043 | -1.718134 | -1.142070 |
| C | 3.892629 | -2.481231 | -2.432729 |
| H | 3.087062 | -2.017697 | -3.003385 |
| H | 3.632999 | -3.522911 | -2.259199 |
| H | 4.783713 | -2.473066 | -3.063270 |
| C | 5.252326 | -2.449301 | -0.321729 |
| H | 4.952222 | -3.437258 | 0.011855 |
| H | 5.551666 | -1.873296 | 0.553692 |

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|---|-----------|-----------|-----------|
| H | 6.146030 | -2.573264 | -0.937223 |
| C | 4.781351 | -0.366443 | -1.534311 |
| H | 5.704466 | -0.543100 | -2.090404 |
| H | 5.036754 | 0.245086 | -0.671315 |
| H | 4.115548 | 0.209832 | -2.172855 |
| C | 1.694862 | -3.106249 | -0.001433 |
| C | 0.917796 | -3.394537 | -1.292685 |
| H | 1.550125 | -3.831206 | -2.062380 |
| H | 0.466740 | -2.499622 | -1.717595 |
| H | 0.115406 | -4.104493 | -1.085776 |
| C | 0.707773 | -2.988431 | 1.165749 |
| H | 0.106227 | -3.897985 | 1.203762 |
| H | 0.019215 | -2.154644 | 1.059272 |
| H | 1.224894 | -2.906591 | 2.122117 |
| C | 2.599544 | -4.295589 | 0.310026 |
| H | 3.193732 | -4.140000 | 1.211347 |
| H | 3.271798 | -4.550698 | -0.506173 |
| H | 1.972143 | -5.171492 | 0.491654 |
| P | -0.225987 | 2.213059 | -0.140132 |
| C | -1.208608 | 3.838245 | -2.207596 |
| H | -1.939404 | 3.977048 | -3.006100 |
| H | -1.177051 | 4.765364 | -1.641368 |
| H | -0.236984 | 3.687282 | -2.680874 |
| C | -1.870448 | 1.481799 | -2.351368 |
| H | -2.544387 | 1.849806 | -3.129095 |
| H | -0.957862 | 1.145965 | -2.835915 |
| H | -2.346387 | 0.627674 | -1.879715 |
| C | 1.127527 | 3.451726 | 1.966106 |

| | | | |
|----|-----------|-----------|-----------|
| H | 0.500342 | 3.041668 | 2.755392 |
| H | 1.933138 | 2.749634 | 1.763226 |
| H | 1.582824 | 4.362678 | 2.359341 |
| C | -0.826535 | 4.715986 | 1.178780 |
| H | -0.415855 | 5.539767 | 1.767411 |
| H | -1.380658 | 5.159977 | 0.355377 |
| H | -1.532567 | 4.184990 | 1.818364 |
| C | -1.528299 | -0.027129 | 0.380868 |
| C | 1.426316 | 0.535797 | -2.301485 |
| O | 1.558712 | 0.556083 | -3.454512 |
| Mn | 1.293576 | 0.479780 | -0.520403 |
| C | 2.729125 | 1.499756 | -0.329901 |
| O | 3.636657 | 2.212001 | -0.156237 |
| N | -0.567524 | -0.453784 | -0.447991 |
| C | -2.786358 | -0.525109 | 0.563317 |
| H | -3.435424 | -0.092165 | 1.311671 |
| C | -3.298625 | -1.637293 | -0.272792 |
| O | -2.700136 | -2.887060 | 0.142623 |
| H | -3.032522 | -3.571135 | -0.451994 |
| H | -2.985037 | -1.462354 | -1.319303 |
| C | -4.804613 | -1.692668 | -0.257954 |
| C | -5.532469 | -0.828984 | -1.073040 |
| C | -5.492569 | -2.551800 | 0.590455 |
| C | -6.916610 | -0.825449 | -1.044550 |
| C | -6.880706 | -2.550078 | 0.620736 |
| C | -7.596803 | -1.688804 | -0.195363 |
| H | -4.997712 | -0.153085 | -1.733040 |
| H | -4.925812 | -3.218737 | 1.228407 |

H -7.468290 -0.151437 -1.687940
H -7.404568 -3.224293 1.287020
H -8.679032 -1.690355 -0.173646
H -0.838573 -1.285135 -0.955539

TS(I,II)

P 2.365334 -0.219562 -0.042319
N 0.062427 1.305175 -0.793209
C -1.035504 2.100953 -0.592674
C -1.016876 3.425965 -1.076088
H -1.882025 4.053798 -0.906779
C 0.067933 3.888146 -1.776580
H 0.072239 4.898396 -2.166698
C 1.166730 3.054953 -1.983586
H 2.041284 3.396467 -2.518862
C 1.134447 1.776773 -1.458858
C 2.317993 0.860613 -1.543471
H 3.234918 1.426971 -1.718922
H 2.201806 0.173917 -2.388585
C -2.113172 1.557673 0.164782
H -3.005263 2.179113 0.215836
C -3.201737 -0.521011 -1.602396
C -3.382413 -0.803239 1.461500
C -3.164074 -1.993719 -2.021363
H -2.177019 -2.435003 -1.915645
H -3.440920 -2.072388 -3.074845
H -3.864813 -2.606969 -1.463071
C -4.503526 0.193264 1.752395

| | | | |
|---|-----------|-----------|-----------|
| H | -4.103830 | 1.166322 | 2.038298 |
| H | -5.098630 | -0.171307 | 2.593284 |
| H | -5.180994 | 0.343710 | 0.916587 |
| C | 3.578629 | -1.598677 | -0.518775 |
| C | 4.042603 | -2.330444 | 0.739961 |
| H | 3.199497 | -2.654856 | 1.350991 |
| H | 4.705529 | -1.733725 | 1.362004 |
| H | 4.595073 | -3.225580 | 0.447507 |
| C | 4.780391 | -1.106149 | -1.326995 |
| H | 5.416264 | -0.407934 | -0.793627 |
| H | 4.472714 | -0.638238 | -2.262008 |
| H | 5.398592 | -1.966181 | -1.593762 |
| C | 2.849949 | -2.619133 | -1.390835 |
| H | 3.549753 | -3.418769 | -1.642630 |
| H | 2.495103 | -2.193605 | -2.327010 |
| H | 2.001995 | -3.070409 | -0.880328 |
| C | 3.203015 | 0.868753 | 1.274784 |
| C | 2.964852 | 0.245540 | 2.651806 |
| H | 3.472249 | -0.708793 | 2.773163 |
| H | 1.903509 | 0.097317 | 2.839876 |
| H | 3.355058 | 0.918529 | 3.419110 |
| C | 2.543069 | 2.251015 | 1.238393 |
| H | 2.893458 | 2.824025 | 2.099867 |
| H | 1.459593 | 2.203968 | 1.288534 |
| H | 2.819966 | 2.810678 | 0.344927 |
| C | 4.698681 | 1.102203 | 1.075990 |
| H | 4.927057 | 1.527518 | 0.098209 |
| H | 5.297058 | 0.204265 | 1.209786 |

| | | | |
|----|-----------|-----------|-----------|
| H | 5.037941 | 1.823597 | 1.823401 |
| P | -2.257807 | -0.225133 | 0.032990 |
| C | -3.969198 | -2.171622 | 1.114581 |
| H | -4.485979 | -2.568537 | 1.990211 |
| H | -4.695046 | -2.131153 | 0.307633 |
| H | -3.192163 | -2.888192 | 0.843869 |
| C | -2.594330 | -0.992840 | 2.762279 |
| H | -3.223391 | -1.549995 | 3.459877 |
| H | -1.672119 | -1.551493 | 2.623029 |
| H | -2.343093 | -0.053320 | 3.244665 |
| C | -2.490792 | 0.309693 | -2.678471 |
| H | -2.649036 | 1.376718 | -2.531748 |
| H | -1.420171 | 0.131540 | -2.727012 |
| H | -2.909276 | 0.046028 | -3.651716 |
| C | -4.650117 | -0.037326 | -1.576740 |
| H | -5.058949 | -0.088214 | -2.588913 |
| H | -5.294598 | -0.644952 | -0.945164 |
| H | -4.726514 | 1.000938 | -1.250801 |
| C | -0.907135 | 1.438781 | 1.970682 |
| C | 0.125707 | -2.191374 | 0.913049 |
| O | 0.174551 | -3.237748 | 1.414046 |
| Mn | 0.076287 | -0.607453 | 0.084538 |
| C | 0.097152 | -1.395464 | -1.496315 |
| O | 0.089168 | -1.874216 | -2.558461 |
| N | -0.141821 | 0.544564 | 1.822229 |
| C | -1.345826 | 2.577444 | 2.773801 |
| H | -0.745527 | 2.653213 | 3.681643 |
| H | -2.395924 | 2.483521 | 3.048484 |

H -1.238146 3.498704 2.200865

TS(III,IV)

P -2.4675690000 0.0906980000 0.0853030000

N -0.2071000000 1.3901240000 1.1866240000

C 0.7802630000 2.3029770000 1.1575340000

C 0.8081830000 3.3648860000 2.0496330000

H 1.6039560000 4.0947510000 1.9894510000

C -0.1912920000 3.4619210000 3.0003330000

H -0.1851940000 4.2711770000 3.7187290000

C -1.2208800000 2.5340810000 3.0038460000

H -2.0402700000 2.6128510000 3.7051220000

C -1.2216740000 1.5165620000 2.0614260000

C -2.3637700000 0.5705780000 1.8789180000

H -3.2839800000 0.9896960000 2.2908980000

H -2.1737520000 -0.3661060000 2.4128710000

C 1.7346610000 2.1453530000 0.0158670000

H 2.5925500000 2.8096850000 0.1220740000

C 3.1639480000 -0.1494040000 1.3118920000

C 3.2311200000 0.2761640000 -1.7546380000

C 3.4090330000 -1.6623210000 1.3224370000

H 2.4828640000 -2.2251420000 1.2271090000

H 3.8551300000 -1.9358130000 2.2806870000

H 4.0904310000 -1.9936620000 0.5471090000

C 4.0535340000 1.5582000000 -1.8826900000

H 3.4233860000 2.4310810000 -2.0505200000

H 4.7070480000 1.4703640000 -2.7531550000

H 4.6864080000 1.7520960000 -1.0185160000

C -3.6041720000 -1.4248730000 0.1163760000
C -4.1458900000 -1.6840720000 -1.2889460000
H -3.3509250000 -1.7086350000 -2.0347980000
H -4.8836780000 -0.9488760000 -1.6008190000
H -4.6369480000 -2.6587260000 -1.3053980000
C -4.7542300000 -1.2973110000 1.1168150000
H -5.4131580000 -0.4562550000 0.9283380000
H -4.3908070000 -1.2197950000 2.1413420000
H -5.3630820000 -2.2024920000 1.0671790000
C -2.7908370000 -2.6501380000 0.5279310000
H -3.4537670000 -3.5177100000 0.5331690000
H -2.3724160000 -2.5591700000 1.5283760000
H -1.9775990000 -2.8608250000 -0.1630310000
C -3.4094470000 1.5206530000 -0.7380580000
C -3.2832480000 1.3719490000 -2.2591980000
H -3.9765880000 0.6356640000 -2.6579180000
H -2.2847570000 1.0807010000 -2.5763550000
H -3.5122230000 2.3250450000 -2.7391570000
C -2.7422730000 2.8307440000 -0.3049140000
H -3.1746740000 3.6478160000 -0.8855190000
H -1.6700370000 2.8362930000 -0.4773510000
H -2.9284800000 3.0529180000 0.7462800000
C -4.8856270000 1.6418880000 -0.3683560000
H -5.0401080000 1.7330120000 0.7075480000
H -5.4892500000 0.8148740000 -0.7344110000
H -5.2840290000 2.5512440000 -0.8242780000
P 2.1195250000 0.3246280000 -0.2037120000
C 4.1703410000 -0.9298910000 -1.7283440000

H 4.6699910000 -0.9855770000 -2.6970230000
H 4.9486400000 -0.8683720000 -0.9720790000
H 3.6275790000 -1.8658030000 -1.5961500000
C 2.3672880000 0.1034610000 -3.0071660000
H 3.0309110000 0.1324120000 -3.8747710000
H 1.8764010000 -0.8676690000 -3.0123390000
H 1.6070970000 0.8647460000 -3.1589950000
C 2.3936330000 0.1828910000 2.5952610000
H 2.3361080000 1.2526940000 2.7819170000
H 1.3868480000 -0.2270890000 2.6094220000
H 2.9338030000 -0.2571840000 3.4355480000
C 4.4924440000 0.6014540000 1.3856420000
H 4.9894230000 0.3531400000 2.3262710000
H 5.1788900000 0.3423490000 0.5840910000
H 4.3511200000 1.6832480000 1.3743660000
C 0.8780470000 2.5010050000 -1.1929540000
C -0.3017360000 -1.2762780000 -1.6295790000
O -0.4370060000 -2.0555960000 -2.4742940000
Mn -0.1808880000 -0.1039930000 -0.2766000000
C -0.0638090000 -1.4188130000 0.9127650000
O 0.0829340000 -2.2572910000 1.7076170000
N 0.0010550000 1.5781580000 -1.4799640000
C 1.0019650000 3.7347110000 -1.8840680000
H 1.7723330000 4.4128040000 -1.5265590000
H 0.0622120000 4.2413230000 -2.0719920000
C 1.1936410000 3.2823400000 -3.7945610000
O 0.3042570000 2.4317970000 -4.0748630000
H -0.4516490000 1.7859700000 -2.3718580000

H 2.2583080000 2.9538510000 -3.7620040000
C 1.1013190000 4.6786050000 -4.3405780000
C 2.1994500000 5.5321620000 -4.3189420000
C -0.0929350000 5.1310990000 -4.8905160000
C 2.1076980000 6.8176220000 -4.8269780000
C -0.1895910000 6.4170680000 -5.3978690000
C 0.9088980000 7.2656670000 -5.3664940000
H 3.1351750000 5.1735150000 -3.8994150000
H -0.9290990000 4.4419280000 -4.9193430000
H 2.9708640000 7.4718300000 -4.8083400000
H -1.1227350000 6.7599210000 -5.8286040000
H 0.8348130000 8.2683630000 -5.7681370000

TS(IV,I)

P -2.5239080000 -0.4136930000 0.4346230000
N -0.2877500000 1.1760800000 1.2726960000
C 0.7135630000 2.1095790000 1.1587540000
C 0.6202680000 3.3018890000 1.9117590000
H 1.4005560000 4.0440790000 1.8054230000
C -0.4205130000 3.4894130000 2.7820870000
H -0.4764930000 4.3944880000 3.3741750000
C -1.4094780000 2.5121630000 2.9046670000
H -2.2472690000 2.6369890000 3.5757220000
C -1.3175000000 1.3806270000 2.1184100000
C -2.3954040000 0.3377160000 2.1177010000
H -3.3330890000 0.7477390000 2.4982320000
H -2.1178840000 -0.4885560000 2.7808160000
C 1.7694300000 1.8488040000 0.2474000000

H 2.5950430000 2.5561370000 0.2634420000
C 3.1806800000 -0.4525870000 1.3869490000
C 3.0735210000 -0.0288870000 -1.6621710000
C 3.3038950000 -1.9786080000 1.4520090000
H 2.3629320000 -2.4880400000 1.2630910000
H 3.6323460000 -2.2710260000 2.4514320000
H 4.0372400000 -2.3671090000 0.7514360000
C 4.0781920000 1.1129150000 -1.8092070000
H 3.5757250000 2.0802820000 -1.8328070000
H 4.6125920000 1.0020520000 -2.7560120000
H 4.8222660000 1.1434260000 -1.0183710000
C -3.5477090000 -1.9857390000 0.7109350000
C -4.0895330000 -2.4818120000 -0.6291380000
H -3.2997650000 -2.5660380000 -1.3768550000
H -4.8764330000 -1.8489460000 -1.0325600000
H -4.5161130000 -3.4775570000 -0.4940190000
C -4.6842940000 -1.8054240000 1.7182210000
H -5.4266660000 -1.0726320000 1.4211720000
H -4.3086230000 -1.5268040000 2.7026120000
H -5.2019520000 -2.7597640000 1.8371800000
C -2.6378700000 -3.0807500000 1.2634170000
H -3.2323100000 -3.9867470000 1.3984330000
H -2.2144960000 -2.8244810000 2.2320750000
H -1.8195290000 -3.3200190000 0.5877930000
C -3.6017550000 0.8219100000 -0.5330480000
C -3.4820460000 0.5140950000 -2.0281090000
H -4.0066070000 -0.3960280000 -2.3094950000
H -2.4426450000 0.4010730000 -2.3345050000

H -3.9266590000 1.3305250000 -2.6029930000
C -3.0621770000 2.2307130000 -0.2623320000
H -3.5455780000 2.9299410000 -0.9478310000
H -1.9889650000 2.3168330000 -0.4053060000
H -3.2900710000 2.5609100000 0.7508710000
C -5.0792340000 0.8531790000 -0.1486880000
H -5.2271360000 1.0513210000 0.9131980000
H -5.6120710000 -0.0584860000 -0.4074740000
H -5.5607830000 1.6685580000 -0.6938390000
P 2.0570280000 0.1131230000 -0.0540960000
C 3.7961930000 -1.3757440000 -1.6826550000
H 4.2534990000 -1.5195560000 -2.6632300000
H 4.5925670000 -1.4406570000 -0.9474030000
H 3.1088140000 -2.2072030000 -1.5197160000
C 2.1776590000 -0.0044450000 -2.9055280000
H 2.7705230000 -0.3429560000 -3.7578480000
H 1.3107680000 -0.6555150000 -2.8204690000
H 1.8246490000 0.9941400000 -3.1483410000
C 2.5178770000 0.0472880000 2.6774330000
H 2.5742650000 1.1311530000 2.7617640000
H 1.4755190000 -0.2424620000 2.7728200000
H 3.0532140000 -0.3779400000 3.5284970000
C 4.5759560000 0.1684950000 1.3602470000
H 5.0864000000 -0.0661430000 2.2975800000
H 5.2016180000 -0.2137250000 0.5565130000
H 4.5354040000 1.2557110000 1.2801320000
C 0.3223330000 1.9814300000 -1.5334960000
C -0.2271260000 -1.8812000000 -1.1379600000

O -0.2262900000 -2.7994570000 -1.8484880000
Mn -0.2373080000 -0.5069750000 0.0059630000
C -0.0089360000 -1.6062840000 1.3686910000
O 0.1562220000 -2.2991620000 2.2896680000
N -0.3222640000 0.9947990000 -1.4627920000
C 0.5764770000 3.2822050000 -2.1408980000
H 1.6419820000 3.4065440000 -2.3420330000
H 0.2968690000 4.0634740000 -1.4275760000
C -0.2428370000 3.4399030000 -3.4404110000
H 0.1208380000 2.6804570000 -4.1491760000
O -1.6161060000 3.2578510000 -3.1937770000
H -1.7236500000 2.3802240000 -2.8004940000
C -0.0141860000 4.8026740000 -4.0287070000
C 1.1751530000 5.0711870000 -4.6999190000
C -0.9497520000 5.8189210000 -3.8768400000
C 1.4287800000 6.3338070000 -5.2089570000
C -0.6969620000 7.0825820000 -4.3899610000
C 0.4911050000 7.3449500000 -5.0540870000
H 1.9039860000 4.2780050000 -4.8325410000
H -1.8778910000 5.6047560000 -3.3647190000
H 2.3555110000 6.5273820000 -5.7336660000
H -1.4348090000 7.8659690000 -4.2717780000
H 0.6847330000 8.3312590000 -5.4553250000

TS(dehydration)

P 2.178847 -1.826036 -0.117259
N 1.042176 0.198982 1.524028
C 0.015699 0.875542 2.068322

| | | | |
|---|-----------|-----------|-----------|
| C | -0.242231 | 0.822388 | 3.430588 |
| H | -1.087270 | 1.361010 | 3.837768 |
| C | 0.598880 | 0.081797 | 4.239882 |
| H | 0.431006 | 0.038310 | 5.308016 |
| C | 1.643684 | -0.626749 | 3.668029 |
| H | 2.295678 | -1.243227 | 4.271479 |
| C | 1.829370 | -0.574738 | 2.295418 |
| C | 2.834143 | -1.407939 | 1.572364 |
| H | 3.122901 | -2.274542 | 2.169973 |
| H | 3.744733 | -0.827855 | 1.390960 |
| C | -0.854882 | 1.583048 | 1.084888 |
| H | -1.564971 | 2.247504 | 1.577907 |
| C | 1.111449 | 3.810448 | 0.620566 |
| C | -1.040605 | 3.081754 | -1.480064 |
| C | 2.170539 | 4.401012 | -0.317376 |
| H | 2.846195 | 3.640800 | -0.701475 |
| H | 2.775083 | 5.112994 | 0.248188 |
| H | 1.749358 | 4.938824 | -1.159384 |
| C | -2.304296 | 3.594916 | -0.788458 |
| H | -2.879342 | 2.776651 | -0.354338 |
| H | -2.942151 | 4.072421 | -1.535593 |
| H | -2.110020 | 4.331923 | -0.013325 |
| C | 3.735103 | -2.439205 | -1.020514 |
| C | 3.334079 | -3.273884 | -2.236464 |
| H | 2.563569 | -2.785345 | -2.833192 |
| H | 2.978484 | -4.265696 | -1.966962 |
| H | 4.206923 | -3.405550 | -2.878540 |
| C | 4.674796 | -3.243215 | -0.119162 |

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|---|-----------|-----------|-----------|
| H | 4.224520 | -4.136123 | 0.301657 |
| H | 5.064996 | -2.639897 | 0.700228 |
| H | 5.535375 | -3.563634 | -0.710574 |
| C | 4.533620 | -1.241336 | -1.530081 |
| H | 5.396341 | -1.614956 | -2.085393 |
| H | 4.915177 | -0.620504 | -0.722428 |
| H | 3.957501 | -0.609006 | -2.201918 |
| C | 1.047623 | -3.314660 | 0.196589 |
| C | 0.262156 | -3.637888 | -1.073143 |
| H | 0.884912 | -4.037586 | -1.868573 |
| H | -0.316008 | -2.789939 | -1.434591 |
| H | -0.490690 | -4.390133 | -0.830140 |
| C | 0.049820 | -2.924671 | 1.292396 |
| H | -0.722780 | -3.692432 | 1.342692 |
| H | -0.462788 | -1.989911 | 1.081663 |
| H | 0.524028 | -2.865421 | 2.273250 |
| C | 1.772497 | -4.571131 | 0.673440 |
| H | 2.407871 | -4.391563 | 1.541983 |
| H | 2.374686 | -5.035960 | -0.104632 |
| H | 1.022282 | -5.305112 | 0.975366 |
| P | 0.222451 | 2.363645 | -0.235800 |
| C | -0.391275 | 4.205772 | -2.287866 |
| H | -1.071187 | 4.485804 | -3.094125 |
| H | -0.203172 | 5.103257 | -1.704689 |
| H | 0.544350 | 3.889381 | -2.750935 |
| C | -1.462507 | 2.016568 | -2.496437 |
| H | -2.083804 | 2.505402 | -3.250101 |
| H | -0.613506 | 1.572112 | -3.008991 |

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|----|-----------|-----------|-----------|
| H | -2.053465 | 1.220804 | -2.056725 |
| C | 1.852373 | 3.286337 | 1.855727 |
| H | 1.175050 | 2.998730 | 2.656571 |
| H | 2.509306 | 2.448054 | 1.637822 |
| H | 2.476627 | 4.094550 | 2.241419 |
| C | 0.170030 | 4.912850 | 1.100237 |
| H | 0.745397 | 5.645645 | 1.670569 |
| H | -0.311391 | 5.449682 | 0.286749 |
| H | -0.607415 | 4.529772 | 1.762667 |
| C | -1.558243 | 0.478944 | 0.302602 |
| C | 1.420971 | 0.215429 | -2.330456 |
| O | 1.552864 | 0.132125 | -3.478593 |
| Mn | 1.287803 | 0.300108 | -0.545069 |
| C | 2.904209 | 1.016731 | -0.411878 |
| O | 3.933070 | 1.549647 | -0.285989 |
| N | -0.768881 | -0.221702 | -0.463992 |
| C | -2.931794 | 0.249034 | 0.486667 |
| H | -3.384330 | 0.559132 | 1.421110 |
| C | -3.636633 | -0.519932 | -0.422308 |
| O | -2.598074 | -2.399038 | -0.538251 |
| H | -3.104332 | -2.783087 | -1.264816 |
| H | -3.290369 | -0.520970 | -1.446902 |
| C | -5.009424 | -0.950968 | -0.223131 |
| C | -5.802294 | -1.273018 | -1.328174 |
| C | -5.572748 | -1.071850 | 1.050134 |
| C | -7.117063 | -1.673639 | -1.172188 |
| C | -6.885520 | -1.476639 | 1.207868 |
| C | -7.665947 | -1.774043 | 0.098292 |

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|---|-----------|-----------|-----------|
| H | -5.370656 | -1.195912 | -2.319843 |
| H | -4.957510 | -0.880048 | 1.920218 |
| H | -7.715727 | -1.912102 | -2.042107 |
| H | -7.302143 | -1.574495 | 2.202472 |
| H | -8.692341 | -2.093570 | 0.224645 |
| H | -1.278924 | -1.070258 | -0.817910 |

TS(V-VI)

| | | | |
|---|-----------|-----------|-----------|
| P | 3.295307 | 1.059540 | -0.325148 |
| N | 2.073279 | -1.492132 | -0.631327 |
| C | 1.091125 | -2.322338 | -1.025601 |
| C | 1.285937 | -3.249510 | -2.038371 |
| H | 0.470135 | -3.893010 | -2.340124 |
| C | 2.533280 | -3.330814 | -2.630613 |
| H | 2.719870 | -4.053883 | -3.413605 |
| C | 3.533776 | -2.457557 | -2.234362 |
| H | 4.504599 | -2.470496 | -2.710189 |
| C | 3.271344 | -1.523640 | -1.243208 |
| C | 4.236112 | -0.455288 | -0.849516 |
| H | 4.963630 | -0.277462 | -1.643625 |
| H | 4.800702 | -0.763593 | 0.036608 |
| C | -0.233387 | -2.045407 | -0.381320 |
| H | -0.972529 | -2.810788 | -0.622439 |
| C | 0.585383 | -3.392895 | 2.157287 |
| C | -1.642264 | -1.252267 | 2.177536 |
| C | 1.010013 | -3.242845 | 3.623552 |
| H | 1.486650 | -4.172448 | 3.939668 |
| H | 0.180621 | -3.066559 | 4.297453 |

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|---|-----------|-----------|-----------|
| H | 1.738577 | -2.447372 | 3.761807 |
| C | -2.760907 | -1.935994 | 1.400557 |
| H | -2.862516 | -1.479769 | 0.419144 |
| H | -3.709326 | -1.763547 | 1.914602 |
| H | -2.645294 | -3.012342 | 1.282232 |
| C | 4.617306 | 2.072840 | 0.583995 |
| C | 4.166597 | 3.528603 | 0.697535 |
| H | 3.159275 | 3.614862 | 1.105377 |
| H | 4.196525 | 4.056118 | -0.252320 |
| H | 4.839413 | 4.053019 | 1.378486 |
| C | 5.990735 | 1.995946 | -0.086339 |
| H | 6.001632 | 2.350099 | -1.111706 |
| H | 6.391133 | 0.982487 | -0.072937 |
| H | 6.689157 | 2.616911 | 0.478410 |
| C | 4.786190 | 1.534176 | 2.002258 |
| H | 5.538999 | 2.138575 | 2.512114 |
| H | 5.136590 | 0.504390 | 2.020161 |
| H | 3.868495 | 1.593920 | 2.583496 |
| C | 2.867086 | 1.944351 | -1.943307 |
| C | 1.862181 | 3.058926 | -1.638958 |
| H | 2.332211 | 3.917004 | -1.165118 |
| H | 1.045171 | 2.738006 | -0.993463 |
| H | 1.404921 | 3.395443 | -2.569332 |
| C | 2.216421 | 0.920220 | -2.880207 |
| H | 1.780045 | 1.449072 | -3.727952 |
| H | 1.407282 | 0.366594 | -2.413001 |
| H | 2.945481 | 0.205612 | -3.265334 |
| C | 4.054609 | 2.533905 | -2.699584 |

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|----|-----------|-----------|-----------|
| H | 4.822235 | 1.790562 | -2.919990 |
| H | 4.520103 | 3.368704 | -2.180824 |
| H | 3.694980 | 2.915171 | -3.657386 |
| P | 0.059050 | -1.707334 | 1.451880 |
| C | -1.726075 | -1.597586 | 3.663584 |
| H | -2.652407 | -1.168025 | 4.048045 |
| H | -1.765316 | -2.664936 | 3.864916 |
| H | -0.909159 | -1.160671 | 4.238280 |
| C | -1.865120 | 0.257441 | 2.073126 |
| H | -2.853043 | 0.473677 | 2.485591 |
| H | -1.141776 | 0.820338 | 2.658801 |
| H | -1.864601 | 0.626014 | 1.051761 |
| C | 1.807995 | -3.928498 | 1.402855 |
| H | 1.565443 | -4.268238 | 0.399485 |
| H | 2.623773 | -3.211795 | 1.341585 |
| H | 2.182609 | -4.796812 | 1.947482 |
| C | -0.516493 | -4.444897 | 2.034667 |
| H | -0.127257 | -5.406671 | 2.376035 |
| H | -1.391794 | -4.219601 | 2.637979 |
| H | -0.845591 | -4.579607 | 1.002750 |
| C | -0.588663 | -0.703812 | -0.994271 |
| C | 1.230933 | 1.297220 | 1.926576 |
| O | 1.038557 | 2.228538 | 2.587983 |
| Mn | 1.616387 | -0.080991 | 0.848405 |
| C | 2.820336 | -0.734153 | 1.983976 |
| O | 3.555070 | -1.231203 | 2.735314 |
| N | 0.039849 | 0.281859 | -0.471970 |
| C | -1.370495 | -0.626117 | -2.258415 |

H -1.053609 -1.451254 -2.903308
H -1.072249 0.292226 -2.765592
C -2.914982 -0.580937 -2.115349
O -3.273416 0.301875 -1.127389
H -3.257990 -0.234175 -3.112458
H -0.209705 1.192414 -0.861846
C -3.572203 -1.936782 -1.907601
C -3.035823 -3.138499 -2.364860
C -4.797577 -1.981514 -1.243761
C -3.678402 -4.348084 -2.132862
C -5.447559 -3.183122 -1.020551
C -4.885924 -4.376555 -1.454046
H -2.102695 -3.143767 -2.916887
H -5.205055 -1.047163 -0.879414
H -3.234698 -5.269337 -2.490649
H -6.396380 -3.191208 -0.498086
H -5.387886 -5.317901 -1.271045
H -2.988013 1.429005 -1.468738
C -2.678168 2.777490 -1.855135
C -2.303633 3.582380 -0.627011
C -1.638841 2.707244 -2.808739
H -3.601530 3.144260 -2.301731
O -1.240143 2.849899 0.026773
C -3.457460 3.791904 0.317362
H -1.901045 4.573895 -0.888977
N -0.753725 2.537541 -3.551172
H -1.017266 3.310688 0.843813
C -3.769549 5.070160 0.767248

| | | | |
|---|-----------|----------|----------|
| C | -4.208251 | 2.712740 | 0.783274 |
| C | -4.808878 | 5.277304 | 1.663385 |
| H | -3.189767 | 5.912196 | 0.404186 |
| C | -5.242420 | 2.918464 | 1.681272 |
| H | -3.980526 | 1.713706 | 0.430533 |
| C | -5.546593 | 4.199074 | 2.124849 |
| H | -5.040477 | 6.279717 | 2.000855 |
| H | -5.820852 | 2.073169 | 2.034477 |
| H | -6.357463 | 4.354835 | 2.825231 |

VI

| | | | |
|---|-----------|-----------|-----------|
| P | -3.220857 | 1.126238 | 0.356359 |
| N | -2.068741 | -1.460384 | 0.647272 |
| C | -1.105788 | -2.317843 | 1.030329 |
| C | -1.313177 | -3.236189 | 2.048438 |
| H | -0.513338 | -3.904018 | 2.339944 |
| C | -2.554552 | -3.280318 | 2.657451 |
| H | -2.751304 | -3.995888 | 3.444816 |
| C | -3.534977 | -2.380561 | 2.271358 |
| H | -4.499479 | -2.364945 | 2.759737 |
| C | -3.259284 | -1.456261 | 1.274622 |
| C | -4.198440 | -0.362062 | 0.890718 |
| H | -4.910967 | -0.163242 | 1.693401 |
| H | -4.782048 | -0.655432 | 0.011821 |
| C | 0.215376 | -2.085555 | 0.361883 |
| H | 0.931439 | -2.876066 | 0.590339 |
| C | -0.703041 | -3.414471 | -2.156311 |
| C | 1.601222 | -1.357419 | -2.223807 |

C -1.144654 -3.252220 -3.616453
H -1.837485 -2.424370 -3.747761
H -1.669119 -4.160093 -3.919521
H -0.318896 -3.118322 -4.304534
C 2.704743 -2.085329 -1.466020
H 2.830995 -1.647648 -0.480296
H 3.653441 -1.940200 -1.987568
H 2.552807 -3.158007 -1.356074
C -4.521698 2.179127 -0.537759
C -4.027769 3.620818 -0.652410
H -3.022151 3.677512 -1.069705
H -4.031950 4.146056 0.299127
H -4.690872 4.167342 -1.325444
C -5.888994 2.142443 0.148343
H -5.876805 2.494477 1.174375
H -6.320173 1.141604 0.137677
H -6.574686 2.785616 -0.407070
C -4.723410 1.650002 -1.955264
H -5.461802 2.279864 -2.455296
H -5.107217 0.632166 -1.972060
H -3.810868 1.681956 -2.546732
C -2.748630 1.993056 1.971301
C -1.716171 3.080491 1.660657
H -2.168515 3.954843 1.199150
H -0.916851 2.740325 1.002464
H -1.236557 3.395906 2.587321
C -2.119354 0.945798 2.897132
H -1.648050 1.457297 3.736423

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|----|-----------|-----------|-----------|
| H | -1.335100 | 0.366729 | 2.418047 |
| H | -2.867631 | 0.256487 | 3.291663 |
| C | -3.910931 | 2.613051 | 2.742502 |
| H | -4.698238 | 1.891751 | 2.966872 |
| H | -4.356278 | 3.464861 | 2.233610 |
| H | -3.529592 | 2.977208 | 3.698471 |
| P | -0.103318 | -1.746214 | -1.467081 |
| C | 1.647583 | -1.710375 | -3.709494 |
| H | 2.582200 | -1.316895 | -4.112225 |
| H | 1.643423 | -2.779307 | -3.905655 |
| H | 0.837245 | -1.246119 | -4.271673 |
| C | 1.881208 | 0.143484 | -2.129431 |
| H | 2.875622 | 0.320971 | -2.544829 |
| H | 1.177692 | 0.728566 | -2.717382 |
| H | 1.889896 | 0.527069 | -1.114239 |
| C | -1.932694 | -3.901691 | -1.380408 |
| H | -1.687031 | -4.246217 | -0.379430 |
| H | -2.720587 | -3.155520 | -1.309292 |
| H | -2.347185 | -4.757681 | -1.915512 |
| C | 0.358945 | -4.508275 | -2.048306 |
| H | -0.073791 | -5.455255 | -2.378387 |
| H | 1.231243 | -4.320424 | -2.668635 |
| H | 0.700541 | -4.652307 | -1.021633 |
| C | 0.630430 | -0.751760 | 0.956361 |
| C | -1.180810 | 1.294070 | -1.931118 |
| O | -0.972848 | 2.212591 | -2.604840 |
| Mn | -1.592449 | -0.068177 | -0.840566 |
| C | -2.835448 | -0.681965 | -1.956277 |

| | | | |
|---|-----------|-----------|-----------|
| O | -3.598063 | -1.155116 | -2.695052 |
| N | 0.012364 | 0.249374 | 0.453580 |
| C | 1.446240 | -0.684042 | 2.204864 |
| H | 1.093563 | -1.474930 | 2.873789 |
| H | 1.200543 | 0.258326 | 2.699673 |
| C | 2.978094 | -0.746782 | 2.063884 |
| O | 3.411099 | 0.103244 | 1.040909 |
| H | 3.359634 | -0.394115 | 3.037567 |
| H | 0.299464 | 1.158527 | 0.825074 |
| C | 3.564208 | -2.125918 | 1.844291 |
| C | 2.967212 | -3.288093 | 2.327331 |
| C | 4.774573 | -2.246911 | 1.162695 |
| C | 3.536726 | -4.534244 | 2.103695 |
| C | 5.348366 | -3.487761 | 0.943266 |
| C | 4.727714 | -4.640419 | 1.403581 |
| H | 2.044693 | -3.231229 | 2.893041 |
| H | 5.239195 | -1.347086 | 0.782519 |
| H | 3.048831 | -5.423066 | 2.484397 |
| H | 6.285276 | -3.556394 | 0.404607 |
| H | 5.172235 | -5.611063 | 1.225952 |
| H | 3.131610 | 1.051292 | 1.276937 |
| C | 2.637328 | 2.795967 | 1.782429 |
| C | 2.207406 | 3.583393 | 0.580819 |
| C | 1.675388 | 2.609591 | 2.770806 |
| H | 3.617012 | 3.071289 | 2.161797 |
| O | 1.257418 | 2.759479 | -0.160070 |
| C | 3.368564 | 3.949107 | -0.302142 |
| H | 1.668420 | 4.512020 | 0.836747 |

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|---|----------|----------|-----------|
| N | 0.838944 | 2.341202 | 3.551123 |
| H | 0.939068 | 3.277152 | -0.910577 |
| C | 3.681411 | 5.277513 | -0.563430 |
| C | 4.149077 | 2.949698 | -0.881562 |
| C | 4.752845 | 5.609037 | -1.381252 |
| H | 3.077020 | 6.058641 | -0.114958 |
| C | 5.215471 | 3.277197 | -1.701899 |
| H | 3.910231 | 1.912961 | -0.677815 |
| C | 5.521442 | 4.608360 | -1.954674 |
| H | 4.985111 | 6.649253 | -1.572539 |
| H | 5.815212 | 2.491386 | -2.144988 |
| H | 6.355448 | 4.863114 | -2.596373 |

VII

| | | | |
|---|-----------|-----------|-----------|
| P | 2.334033 | -2.463668 | -0.227750 |
| N | 1.716392 | -0.248541 | 1.474931 |
| C | 0.943318 | 0.721452 | 1.995978 |
| C | 0.567760 | 0.712469 | 3.328661 |
| H | -0.077301 | 1.492104 | 3.711495 |
| C | 1.012703 | -0.318029 | 4.135884 |
| H | 0.720905 | -0.360223 | 5.176274 |
| C | 1.792729 | -1.322574 | 3.589444 |
| H | 2.115859 | -2.163028 | 4.187815 |
| C | 2.122138 | -1.275136 | 2.243423 |
| C | 2.870298 | -2.365819 | 1.547378 |
| H | 2.776834 | -3.307724 | 2.091018 |
| H | 3.937903 | -2.124792 | 1.514616 |
| C | 0.410654 | 1.685874 | 0.975938 |

| | | | |
|---|-----------|-----------|-----------|
| H | -0.118471 | 2.517910 | 1.445480 |
| C | 3.022289 | 3.184517 | 0.742851 |
| C | 0.972865 | 3.209375 | -1.571046 |
| C | 4.317797 | 3.349666 | -0.059917 |
| H | 4.199349 | 3.986712 | -0.929605 |
| H | 4.734011 | 2.402285 | -0.387145 |
| H | 5.061368 | 3.823419 | 0.584170 |
| C | 0.117068 | 4.349376 | -1.019048 |
| H | -0.608931 | 4.012368 | -0.280686 |
| H | -0.458709 | 4.775345 | -1.842331 |
| H | 0.696092 | 5.157098 | -0.585336 |
| C | 3.728169 | -3.471936 | -1.034795 |
| C | 3.241993 | -4.048310 | -2.364057 |
| H | 2.793509 | -3.285192 | -3.000894 |
| H | 2.523720 | -4.854128 | -2.238400 |
| H | 4.097174 | -4.460575 | -2.902712 |
| C | 4.249296 | -4.592903 | -0.132863 |
| H | 3.492696 | -5.314878 | 0.155472 |
| H | 4.706997 | -4.201114 | 0.775152 |
| H | 5.029758 | -5.137559 | -0.668498 |
| C | 4.917169 | -2.565470 | -1.342698 |
| H | 5.683238 | -3.163201 | -1.840778 |
| H | 5.368759 | -2.148254 | -0.445893 |
| H | 4.656017 | -1.745103 | -2.008195 |
| C | 0.779972 | -3.544290 | -0.191285 |
| C | 0.114513 | -3.479350 | -1.568382 |
| H | -0.926981 | -3.789482 | -1.479199 |
| H | 0.599317 | -4.131498 | -2.290250 |

| | | | |
|---|-----------|-----------|-----------|
| H | 0.099475 | -2.469163 | -1.973235 |
| C | -0.161711 | -2.947986 | 0.857972 |
| H | -1.127979 | -3.449988 | 0.784725 |
| H | -0.349487 | -1.888184 | 0.715705 |
| H | 0.201202 | -3.098867 | 1.874984 |
| C | 0.997638 | -5.004445 | 0.196236 |
| H | 1.500277 | -5.112014 | 1.158366 |
| H | 1.552482 | -5.569075 | -0.549695 |
| H | 0.020569 | -5.482558 | 0.294580 |
| P | 1.776357 | 2.125419 | -0.231180 |
| C | 2.090154 | 3.785247 | -2.443885 |
| H | 1.640806 | 4.227669 | -3.334054 |
| H | 2.645345 | 4.575100 | -1.942965 |
| H | 2.793992 | 3.022462 | -2.780886 |
| C | 0.072366 | 2.362258 | -2.477060 |
| H | -0.179448 | 2.973321 | -3.346483 |
| H | 0.559302 | 1.459314 | -2.837433 |
| H | -0.869000 | 2.075387 | -2.013096 |
| C | 3.378243 | 2.469304 | 2.050330 |
| H | 2.562596 | 2.501014 | 2.769677 |
| H | 3.676808 | 1.433337 | 1.910653 |
| H | 4.223574 | 2.991691 | 2.501557 |
| C | 2.500923 | 4.569941 | 1.120606 |
| H | 3.186742 | 5.015578 | 1.844437 |
| H | 2.460539 | 5.242999 | 0.267942 |
| H | 1.513540 | 4.541325 | 1.583008 |
| C | -0.523296 | 0.778906 | 0.187209 |
| C | 2.427693 | -0.181432 | -2.342316 |

| | | | |
|----|-----------|-----------|-----------|
| O | 2.641571 | -0.238966 | -3.478865 |
| Mn | 2.150630 | -0.146244 | -0.569762 |
| C | 3.882269 | 0.002975 | -0.217823 |
| O | 4.995426 | 0.155711 | 0.086338 |
| N | 0.044823 | -0.021054 | -0.630700 |
| C | -1.955502 | 0.668900 | 0.612668 |
| H | -2.033001 | 0.961143 | 1.661906 |
| H | -2.204113 | -0.389302 | 0.562408 |
| C | -3.033365 | 1.406904 | -0.211583 |
| O | -2.957841 | 1.100503 | -1.560111 |
| H | -3.986903 | 1.044035 | 0.222623 |
| H | -0.673371 | -0.647433 | -1.103878 |
| C | -3.032519 | 2.908230 | -0.026167 |
| C | -2.857420 | 3.496417 | 1.226324 |
| C | -3.264806 | 3.739073 | -1.118605 |
| C | -2.881230 | 4.874429 | 1.378196 |
| C | -3.305165 | 5.116917 | -0.965781 |
| C | -3.103331 | 5.692312 | 0.279177 |
| H | -2.706141 | 2.872983 | 2.100978 |
| H | -3.400953 | 3.279694 | -2.088137 |
| H | -2.734685 | 5.310192 | 2.358757 |
| H | -3.487046 | 5.746388 | -1.828364 |
| H | -3.126097 | 6.768159 | 0.396210 |
| H | -2.709996 | 0.109025 | -1.649954 |
| C | -4.139309 | -2.067544 | 2.119531 |
| C | -4.247607 | -2.110614 | 0.777749 |
| C | -2.909394 | -1.920793 | 2.789972 |
| H | -5.012899 | -2.106824 | 2.761542 |

O -2.158187 -1.326548 -1.514675
C -5.487416 -2.195685 0.033014
H -3.353339 -2.033002 0.151851
N -1.914316 -1.776407 3.369756
H -2.124601 -1.802771 -2.348460
C -5.434482 -1.938727 -1.342374
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H -4.466306 -1.698159 -1.773168
C -7.869758 -2.539884 -0.153964
H -6.783244 -2.723109 1.673789
C -7.806316 -2.270943 -1.516955
H -6.536438 -1.758839 -3.167037
H -8.819296 -2.783004 0.305405
H -8.708275 -2.299869 -2.114991

VIII

P 3.129123 -0.449852 -0.011474
N 0.871946 0.324313 1.546615
C -0.382184 0.209492 2.024420
C -0.624031 -0.020326 3.371329
H -1.642493 -0.119694 3.723280
C 0.452050 -0.106909 4.235364
H 0.291655 -0.272031 5.292690
C 1.739928 -0.005289 3.732345
H 2.600484 -0.105369 4.379332
C 1.926289 0.191305 2.372198
C 3.272647 0.194764 1.725504

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| H | 4.000394 | -0.336764 | 2.341722 |
| H | 3.636476 | 1.222214 | 1.621913 |
| C | -1.436643 | 0.201496 | 0.965000 |
| H | -2.441359 | 0.223573 | 1.392626 |
| C | -1.296734 | 3.191091 | 0.556609 |
| C | -2.316567 | 1.341324 | -1.698841 |
| C | -0.727783 | 4.329505 | -0.298239 |
| H | -1.312584 | 4.522709 | -1.190808 |
| H | 0.301337 | 4.157203 | -0.597723 |
| H | -0.741691 | 5.245108 | 0.296466 |
| C | -3.761519 | 1.286362 | -1.201836 |
| H | -3.898796 | 0.585533 | -0.379960 |
| H | -4.393193 | 0.930631 | -2.017313 |
| H | -4.151678 | 2.251146 | -0.896401 |
| C | 4.764146 | 0.110078 | -0.799346 |
| C | 5.034923 | -0.714247 | -2.057192 |
| H | 4.173431 | -0.735595 | -2.725294 |
| H | 5.321952 | -1.739209 | -1.837016 |
| H | 5.861654 | -0.259255 | -2.605731 |
| C | 5.952208 | 0.015383 | 0.160145 |
| H | 6.134921 | -0.984569 | 0.539561 |
| H | 5.837657 | 0.685183 | 1.012100 |
| H | 6.854266 | 0.330966 | -0.368390 |
| C | 4.657150 | 1.571536 | -1.227603 |
| H | 5.594691 | 1.856941 | -1.709103 |
| H | 4.510269 | 2.244958 | -0.386508 |
| H | 3.855153 | 1.739140 | -1.943522 |
| C | 3.189510 | -2.334107 | 0.180175 |

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| C | 2.838175 | -2.961827 | -1.172114 |
| H | 2.480845 | -3.980645 | -1.022135 |
| H | 3.696232 | -3.001496 | -1.838126 |
| H | 2.034289 | -2.429629 | -1.676392 |
| C | 2.120202 | -2.718083 | 1.208112 |
| H | 2.011022 | -3.803592 | 1.208763 |
| H | 1.145640 | -2.301234 | 0.974191 |
| H | 2.401162 | -2.416090 | 2.218227 |
| C | 4.511228 | -2.909524 | 0.680074 |
| H | 4.829577 | -2.470542 | 1.626964 |
| H | 5.320972 | -2.804961 | -0.038425 |
| H | 4.378619 | -3.979699 | 0.854372 |
| P | -1.029309 | 1.516460 | -0.310231 |
| C | -2.147443 | 2.527435 | -2.650888 |
| H | -2.718937 | 2.326986 | -3.558204 |
| H | -2.531772 | 3.454844 | -2.232480 |
| H | -1.109091 | 2.681738 | -2.948937 |
| C | -2.063904 | 0.063331 | -2.506192 |
| H | -2.672116 | 0.127995 | -3.411024 |
| H | -1.027091 | -0.051975 | -2.812168 |
| H | -2.366813 | -0.844896 | -1.989622 |
| C | -0.538317 | 3.198688 | 1.888287 |
| H | -1.014997 | 2.568668 | 2.636275 |
| H | 0.503587 | 2.902038 | 1.795436 |
| H | -0.549989 | 4.218538 | 2.276799 |
| C | -2.759344 | 3.498220 | 0.874176 |
| H | -2.799027 | 4.349160 | 1.557785 |
| H | -3.322387 | 3.778794 | -0.012043 |

| | | | |
|----|-----------|-----------|-----------|
| H | -3.274328 | 2.666943 | 1.358040 |
| C | -1.122694 | -1.114322 | 0.244456 |
| C | 1.339460 | 0.698044 | -2.286822 |
| O | 1.544347 | 0.761553 | -3.424675 |
| Mn | 1.097753 | 0.612013 | -0.510322 |
| C | 1.889537 | 2.178479 | -0.243906 |
| O | 2.347508 | 3.222609 | -0.006124 |
| N | -0.115319 | -1.102691 | -0.532886 |
| C | -1.812786 | -2.372420 | 0.706187 |
| H | -2.061435 | -2.254443 | 1.764555 |
| H | -1.080534 | -3.178009 | 0.634442 |
| C | -3.060265 | -2.868289 | -0.051803 |
| O | -2.810186 | -3.047748 | -1.404170 |
| H | -3.294446 | -3.836878 | 0.432306 |
| H | -0.021304 | -2.133111 | -1.054714 |
| C | -4.293735 | -2.010346 | 0.128323 |
| C | -4.637231 | -1.457894 | 1.362019 |
| C | -5.154461 | -1.806012 | -0.946647 |
| C | -5.784728 | -0.693353 | 1.509431 |
| C | -6.312312 | -1.057614 | -0.797138 |
| C | -6.627841 | -0.487459 | 0.426407 |
| H | -4.003544 | -1.627851 | 2.226044 |
| H | -4.886384 | -2.234774 | -1.902597 |
| H | -6.026079 | -0.265180 | 2.474572 |
| H | -6.967997 | -0.910075 | -1.646621 |
| H | -7.526288 | 0.105395 | 0.540117 |
| H | -1.833639 | -3.308644 | -1.524458 |
| O | -0.261674 | -3.435649 | -1.479138 |

H 0.134744 -3.658173 -2.324455

H₂O

O -8.2252490000 -1.6361840000 6.2517500000

H -7.2660960000 -1.5914940000 6.2470080000

H -8.5025920000 -0.7220360000 6.1547470000

MeCN

C 1.0015550000 -0.0799970000 -0.0379780000

C 2.4444130000 -0.0807270000 -0.0383180000

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H 0.6193030000 -1.0005870000 -0.4750060000

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EtCN

C 0.9603120000 0.0171650000 0.1366640000

C 2.4817140000 0.0097530000 0.0722090000

C 0.4497880000 0.1865450000 1.4836360000

N 0.0602580000 0.3225420000 2.5612640000

H 0.5516220000 0.8176190000 -0.4834460000

H 0.5524470000 -0.9124740000 -0.2654540000

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H 2.8127560000 -0.1194950000 -0.9555140000

H 2.8968460000 -0.8011070000 0.6662910000

BnCN

C 1.0180330000 0.0161380000 -0.0550170000

C 0.4549200000 -1.3169150000 0.0039120000
N 0.0145150000 -2.3821710000 0.0503330000
C 2.5267260000 0.0667790000 -0.1332710000
C 3.3071980000 -1.0809560000 -0.1642140000
C 4.6897270000 -0.9861510000 -0.2379670000
C 5.3040460000 0.2540940000 -0.2813530000
C 4.5288180000 1.4048360000 -0.2505830000
C 3.1500650000 1.3110620000 -0.1770530000
H 0.6689640000 0.5700630000 0.8209290000
H 0.5802930000 0.5304020000 -0.9153110000
H 2.8313180000 -2.0536100000 -0.1299960000
H 5.2859260000 -1.8890300000 -0.2612140000
H 6.3821520000 0.3265330000 -0.3386730000
H 4.9997360000 2.3787300000 -0.2838300000
H 2.5481420000 2.2125500000 -0.1530430000

PhCHO

C 0.9544640000 0.1262080000 -0.0058330000
O 1.7539800000 0.2862770000 0.8825570000
C 0.3572500000 1.2030230000 -0.8088970000
C 0.6998810000 2.5355180000 -0.5774660000
C 0.1305430000 3.5361410000 -1.3401700000
C -0.7838390000 3.2149680000 -2.3380720000
C -1.1295370000 1.8922740000 -2.5741830000
C -0.5588470000 0.8891250000 -1.8095480000
H 0.6006640000 -0.8946170000 -0.2841310000
H 1.4145150000 2.7550760000 0.2060140000
H 0.3942430000 4.5707560000 -1.1631380000

H -1.2283700000 4.0017990000 -2.9341540000
H -1.8413280000 1.6478250000 -3.3516450000
H -0.8172690000 -0.1504420000 -1.9799720000

Hydroxy nitrile

C 1.0384030000 0.0355620000 0.1393450000
C 2.5622840000 0.0271850000 -0.0104510000
O 2.8460490000 0.9559890000 -1.0370810000
C 0.5181690000 1.3184090000 0.5669630000
N 0.1093700000 2.3345060000 0.9291800000
C 3.0599650000 -1.3634500000 -0.3163270000
C 3.4841790000 -2.1998550000 0.7104340000
C 3.9077380000 -3.4912230000 0.4383320000
C 3.9128120000 -3.9582640000 -0.8674940000
C 3.4930270000 -3.1291860000 -1.8974560000
C 3.0664540000 -1.8392510000 -1.6237120000
H 0.5924880000 -0.2341080000 -0.8208010000
H 0.7363470000 -0.7286430000 0.8569740000
H 2.9997660000 0.3576550000 0.9418110000
H 3.8013480000 1.0112770000 -1.1369600000
H 3.4882680000 -1.8307600000 1.7305170000
H 4.2407490000 -4.1310130000 1.2452950000
H 4.2482520000 -4.9643920000 -1.0826460000
H 3.4979690000 -3.4889640000 -2.9183470000
H 2.7434350000 -1.1833360000 -2.4233110000

cinnamotrile

C 1.0414780000 -0.1914510000 -0.1748970000

C 2.2290030000 0.1286310000 0.3653650000
C 0.3037900000 0.6949850000 -0.9845630000
N -0.3189390000 1.4080960000 -1.6526230000
C 3.0561850000 -0.7118220000 1.2063350000
C 2.7001530000 -2.0161600000 1.5713710000
C 3.5268180000 -2.7737940000 2.3763460000
C 4.7291290000 -2.2504740000 2.8376010000
C 5.0979480000 -0.9613500000 2.4862980000
C 4.2697100000 -0.2016010000 1.6795040000
H 0.5895340000 -1.1627820000 -0.0094430000
H 2.6252250000 1.1181000000 0.1601320000
H 1.7673470000 -2.4395580000 1.2211480000
H 3.2357800000 -3.7799240000 2.6484730000
H 5.3740100000 -2.8480900000 3.4683950000
H 6.0324070000 -0.5471360000 2.8412900000
H 4.5562930000 0.8063960000 1.4038800000

References

- 1) A. Nerush, M. Vogt, U. Gellrich, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* 2016, **138**, 6985-6997.
- 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.
- 4) A. Mukherjee, A. Nerush, G. Leitus, L. J. W. Shimon, Y. Ben David, N. A. Espinosa Jalapa, D. Milstein, *J. Am. Chem. Soc.* 2016, **138**, 4298-4301.
- 5) S. Thiyagarajan, Y. Diskin-Posner, M. Montag, D. Milstein, *Chem. Sci.* 2024, **15**, 2571-2577.
- 6) Q. Q. Zhou, Y. Q. Zou, S. Kar, Y. Diskin-Posner, Y. Ben-David, D. Milstein, *ACS Catal.*, 2021, **11**, 10239-102455.
- 7) W. Song, Q. Du, X. Li, S. Wang, G. Song, *ChemSusChem* 2022, **15**, e202200646.
- 8) G. Wang, R. Zhou, S.-H. Peng, X.-K. Chen, H.-B. Zou, *ACS Omega* 2024, **9**, 3317-3323.
- 9) V. Sharma, K. A. Chavan, G. Mali, D. Sarkar, P. Lama, M. Majumder, R. D. Erande, R. K. Metre, *J. Org. Chem.* 2023, **88**, 7448-7453.
- 10) Y. Zhang, S. Shi, Z. Yang, *J. Org. Chem.* 2024, **89**, 2748-2758.
- 11) Y. M. McNamara, S. A. Bright, A. J. Byrne, S. M. Cloonan, T. McCabe, D. C. Williams, M. J. Meegan, *Eur. J. Med. Chem.* 2014, **71**, 333-353.
- 12) J. M. Pérez, R. Postolache, M. C. Reis, E. G. Sinnema, D. Vargová, F. Vries, E. Otten, L. Ge, S. Harutyunyan, *J. Am. Chem. Soc.* 2021, **143**, 20071-20076.
- 13) S. A. DiBiase, B. A. Lipisko, A. Haag, R. A. Wolak, G. W. Gokel, *J. Org. Chem.* 1979, **44**, 4640-4649.
- 14) A. K. Bains, Y. Ankit, D. Adhikari, *Org. Lett.* 2021, **23**, 2019-2023.

- 15) S.-I. Murahashi, T. Naota, H. Taki, M. Mizuno, H. Takaya, S. Komiya, Y. Mizuho, N. Oyasato, M. Hiraoka, *J. Am. Chem. Soc.* 1995, **117**, 12436-12451.
- 16) B. Guo, J. G. de Vries, E. Otten, *Adv. Synth. Catal.* 2022, **364**, 179-186.
- 17) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.
- 18) Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* 2006, **125**, 194101-194118.
- 19) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297-3305.
- 20) F. Weigend, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057-1065.
- 21) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104-154123.
- 22) F. Neese, *Computational Molecular Science* 2022, **12**, e1606.
- 23) N. Mardirossian, M. Head-Gordon, *Phys. Chem. Chem. Phys.* 2014, **16**, 9904-9924.
- 24) O. A. Vydrova, T. V. Voorhis, *J. Chem. Phys.* 2010, **133**, 244103-244112.
- 25) W. Hujo, S. Grimme, *J. Chem. Theory Comput.* 2011, **7**, 3866-3871.
- 26) A. Hellweg, C. Hattig, S. Hoefener, W. Klopper, *Theor. Chem. Acc.* 2007, **117**, 587-597.
- 27) M. Garcia-Rates, F. Neese, F., *J. Comput. Chem.* 2020, 922-939.

28) NBO7.0. E. D. Glendening, J. K. Badenhop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI (2018).