Supporting Information

Metal-free dehydrosulfurization of thioamides to nitriles under visible light

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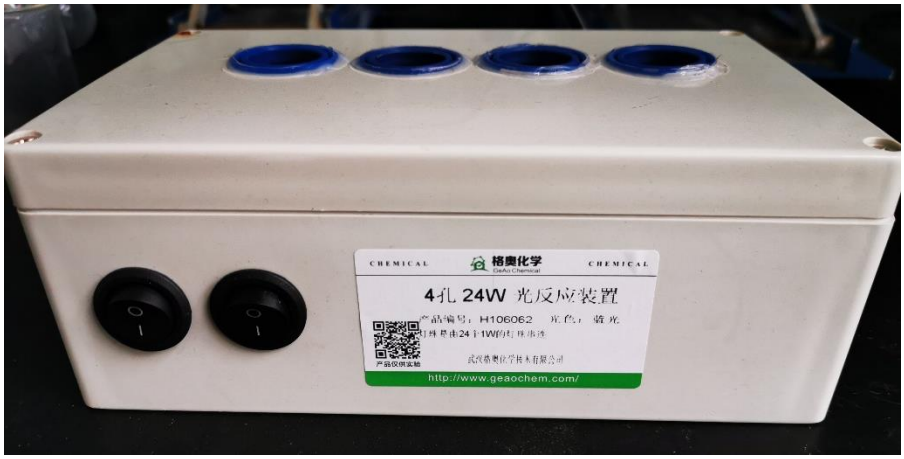
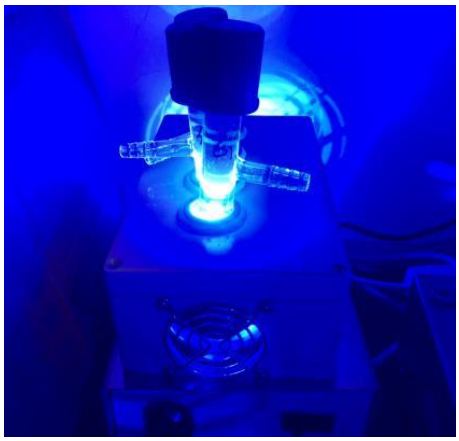
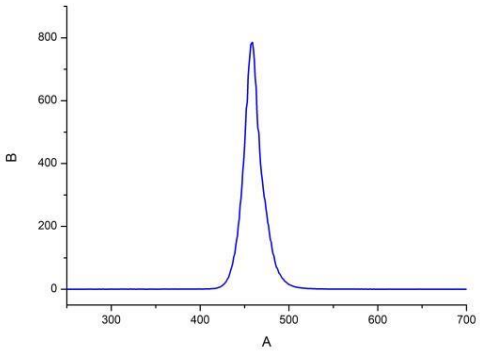
1. General information

All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on silica gel. The product spots on the thin layer chromatography (TLC) was identified/visualized by fluorescence quenching or potassium permanganate stains. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz and 100 MHz) instrument, and are internally referenced to solvent residual signals (note: $CDCl_3$ referenced at 7.26 and 77.16 ppm respectively). Data for ^{1}H NMR were reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in ppm with the internal chloroform signal at 77.16 ppm as a standard..

Photo-reactor and reaction setup: The reactions were conducted in photo-reactors (H106062:blue light, H106063: purple light, purchased from GeAo Chemical: http://www.geaochem.com/), which comprise a fan for cooling (approximately room temperature) and six 1W blue LED beads for each place. The average power output of the photo-reactor was recorded at 30 mW/cm^2. The emission spectra of the blue LEDs were recorded on an Ocean Optics HR4000CG-UVNIR spectrometer. The spectra was normalised to 1.0 at the maximum (460 nm).



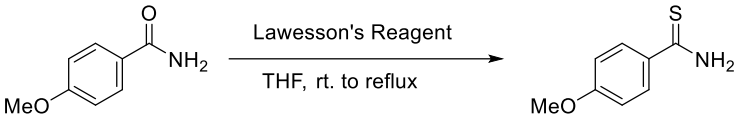




2. Synthesis of thioamides

Most of thioamides are commercially available and purchased from Energy, Adamas, TCI, Aldrich. No attempt was made to optimize for yield during the syntheses of the thioamides below.

4-Methoxybenzothioamide (1a)



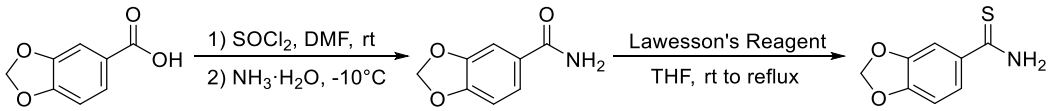
4-Methoxybenzamide (1.81 g, 12.0 mmol) in THF (80 mL) was added to the flask containing Lawesson's reagent (2.43 g, 6.0 mmol). The solution was stirred overnight at room temperature and then heated to reflux for 60 hours. Upon completion, solvent was evaporated using rotary evaporator and the crude residue was purified by flash column chromatography (SiO_2; petroleum ether/EtOAc = 3:1) to afford thioamide **1a** (1.60 g, 80%) as a pale yellow solid. The product can be recrystallized from EtOAc for further purification.

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ (ppm) 9.64 (br, 1H, N-H^a), 9.32 (br, 1H, N-H^b), 7.96 (d, J = 7.3 Hz, 2H, Ar-H), 6.95 (d, J = 7.4 Hz, 2H, Ar-H), 3.80 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ (ppm) 199.1, 162.4, 131.8, 129.9, 113.5, 55.9.

All data are in agreement with the reported values in the literature.[1]

Benzo[*d*][1,3]dioxole-5-carbothioamide (1j)



According to the reported procedure,[2] commercially available benzo[*d*][1,3]dioxole-5-carboxylic acid (1.66 g, 10 mmol), $SOCl_2$ (5.8 mL, 50 mmol) and DMF (0.10 mL) were mixed together in a flask linked to basic absorption (1.0 M NaOH). The resulting reaction mixture was stirred at room temperature for 24 hours. Then, the excess $SOCl_2$ was removed under reduce pressure, and the resulting residue was diluted with $CHCl_3$

(5 mL) at –10 °C and added dropwise to a stirred solution of aqueous ammonia (25%, 8 mL) at –10 °C. The reaction mixture was warmed up to room temperature, stirred for additional 2 hours, and then extracted with EtOAc (3×10 mL). The combined organic extracts were dried over $MgSO_4$ and filtered. The solvent was then evaporated to afford the corresponding amide (1.60 g, 80%) as a white solid, which was used in the next step without further purification.

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ (ppm) 7.83 (br, 1H, N-H^a), 7.47 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.40 (s, 1H, Ar-H), 7.24 (br, 1H, N-H^b), 6.95 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.08 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ (ppm) 167.6, 150.2, 147.8, 128.8, 123.0, 108.2, 108.1, 102.1.

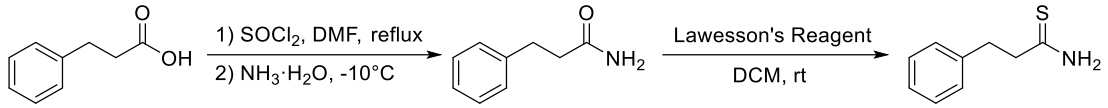
All data are in agreement with the literature values.[2]

Benzo[*d*][1,3]dioxole-5-carboxamide (0.83 g, 5.0 mmol) in THF (50 mL) was added to Lawesson's reagent (1.01 g, 2.50 mmol). The solution was stirred overnight at room temperature and then heated to reflux for 60 hours. Upon completion, solvent was evaporated using rotary evaporator and the crude residue was purified by flash column chromatography (SiO_2; pPetroleum ether/EtOAc = 3:1) to afford thioamide **1j** (0.50 g, 55%) as a pale yellow solid. The product can be recrystallized from EtOAc for further purification.

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ (ppm) 9.70 (br, 1H, N-H^a), 9.30 (br, 1H, N-H^b), 7.57 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.50 (s, 1H, Ar-H), 6.94 (d, *J* = 8.2 Hz, 1H, Ar-H), 6.10 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ (ppm) 198.8, 150.5, 147.4, 133.6, 123.3, 108.1, 107.8, 102.3.

3-Phenylpropanethioamide (1q)

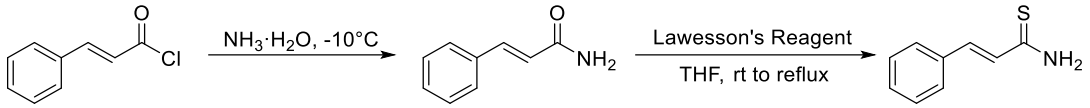


According to the reported procedure:[3,4] to the solution of 3-phenylpropionic acid (0.45 g, 3 mmol) in DMF (20 mL), was added an excess of $SOCl_2$ (5mL). The solution was then refluxed for 5 hours. The excess $SOCl_2$ was removed under reduced pressure. The crude product was dissolved in 5 mL of THF and cooled to -10°C. An excess amount of NH_4OH (26-28% NH_3, 15 mL) was added to the solution slowly, and the solution was then stirred for additional 0.5 hour at -10 °C. The solution was extracted using (1x10mL) THF and (3x10mL) EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated to give the amide as a white solid (400 mg, 2.68 mmol). Then the amide was dissolved in CH_2Cl_2 (0.50 M), added to a flask containing Lawesson's reagent (0.5 eq, 0.25 M) of dichloromethane, and stirred at room temperature for 2 hours. The mixture was concentrated and purified by column chromatography (CH_2Cl_2, then 20% ethyl acetate in petroleum ether (30−60)) to give the product as a white solid (300 mg, 1.82 mmol).

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 9.38 (s, 1H), 9.18 (s, 1H), 7.23 (ddd, J = 20.5, 14.0, 7.4 Hz, 5H), 2.97 (t, J = 7.9 Hz, 2H), 2.75 (t, J = 7.9 Hz, 2H).

^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 207.2, 140.8, 128.2(2C), 126.0, 45.7, 34.5.

2-Propenethioamide (1r)

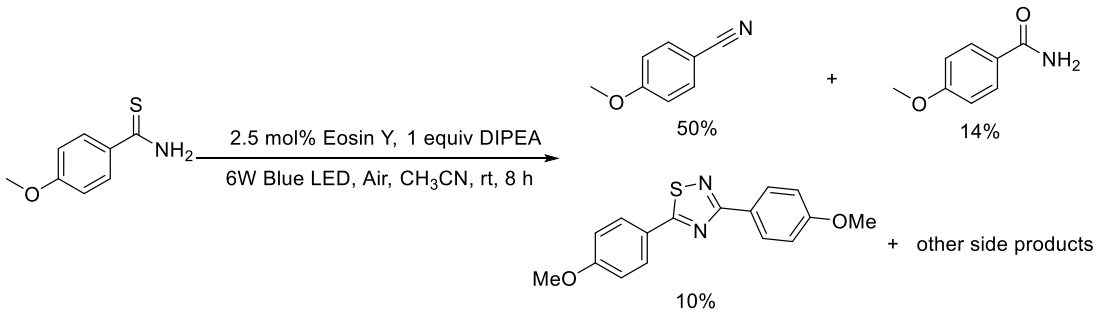


According to the reported procedure: [5] cinnamoyl chloride (10 mmol) was slowly added into 10 mL of the corresponding amine (20 mmol) aqueous solution at -10 °C within 10 minutes. After vigorously stirring at -10 °C for 1 hour, the mixture was warmed up to room temperature. The reaction solution was extracted with CH_2Cl_2, washed with water and dried over anhydrous sodium sulfate. The solvent was filtered and concentrated to give the amide as a white solid (1268 mg, 8.62 mmol). Then the amide (0.74 g, 5.0 mmol) in THF (50 mL) was added to Lawesson's reagent (1.01 g, 2.50 mmol). The solution was stirred overnight at room temperature and then heated to reflux for 6 hours. Upon completion, solvent was evaporated using rotary evaporator and the crude residue was purified by flash column chromatography to afford thioamide **1r** (0.45 g, 55%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 15.3 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.42-7.35 (m, 3H), 7.04-6.93 (m, 2H), 6.88 (d, *J* = 15.4 Hz, 1H).

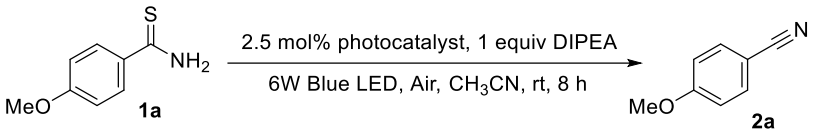
^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 143.6, 134.4, 130.3, 128.9, 128.3, 125.8.

3. Reaction optimization



Scheme S1. Product distribution for the initial test.

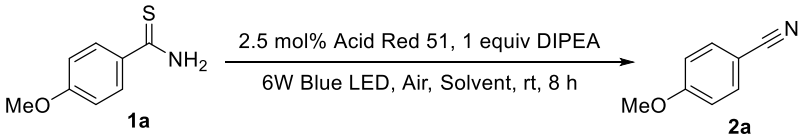
Table S1: Screening of photocatalyst. [a]



Entry	Photocatalyst	Yield (%)
1	$[Acr\text{-}Mes]^{+}(ClO_4)^{-}$	55 %
2	Rose Bengal	32 %
3	Methylene Blue	43 %
4	Rhodamine B	52 %
5	(-)-Riboflavin	41 %
6	Fluorescein	58 %
7	**Acid Red 51**	**65 %**
8	Rhodamine 6G	63 %
9	Methyl Orange	50 %
10	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$	49 %

[a]Reaction conditions: **1a** (0.05 mmol), photocatalyst (2.5 mol%), DIPEA (1.0 equiv.) and CH_3CN (0.5 mL) were irradiated with 6 W blue LEDs at room temperature under air for 8 h. Yields were determined by NMR with using benzyl ether as an internal standard.

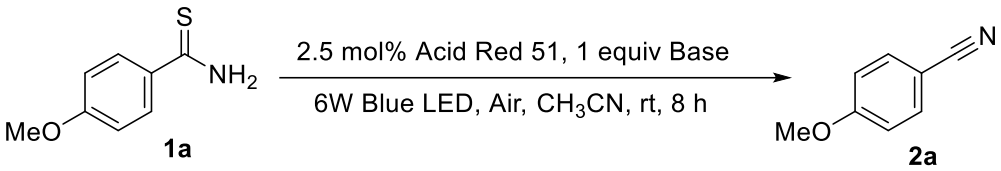
Table S2: Screening of Solvent. [a]



Entry	Solvent	Yield (%)
1	**CH_3CN**	**65 %**
2	DCM	57 %
3	1,4-Dioxane	62 %
4	DCE	49 %
5	DMSO	36 %
6	N,N-Dimethylacetamide	55 %
7	THF	53 %

[a]Reaction conditions: **1a** (0.05 mmol), Acid Red 51 (2.5 mol%), DIPEA (1.0 equiv.) and solvent (0.5 mL) were irradiated with 6 W blue LEDs at room temperature under air for 8 h. Yields were determined by NMR with using benzyl ether as an internal standard.

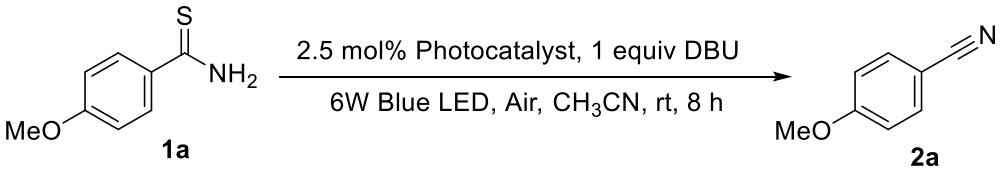
Table S3: Screening of Base. [a]



Entry	Base	Yield (%)
1	Na_2CO_3	23 %
2	K_2HPO_4	40 %
3	K_2CO_3	26 %
4	**DBU**	**93 %**
5	Et_3N	66 %
6	TMEDA	61 %

[a]Reaction conditions: **1a** (0.05 mmol), Acid Red 51 (2.5 mol%), base (1.0 equiv.) and CH_3CN (0.5 mL) were irradiated with 6 W blue LEDs at room temperature under air for 8 h. yields were determined by NMR with using benzyl ether as an internal standard.

Table S4: Further Screening of Photocatalyst. [a]



Entry	Photocatalyst	Yield (%)
1	Acid Red 51	93 %
2	Eosin Y	88 %
3	Rhodamine 6G	82 %
4	**Methylene Blue**	**96 %**

[a]Reaction conditions: 1a (0.05 mmol), Photocatalyst (2.5 mol%), DBU (1.0 equiv.) and CH_3CN (0.5 mL) were irradiated with 6 W blue LEDs at room temperature under air for 8 h. yields were determined by NMR with using benzyl ether as an internal standard.

4. Fluorescence quenching experiments

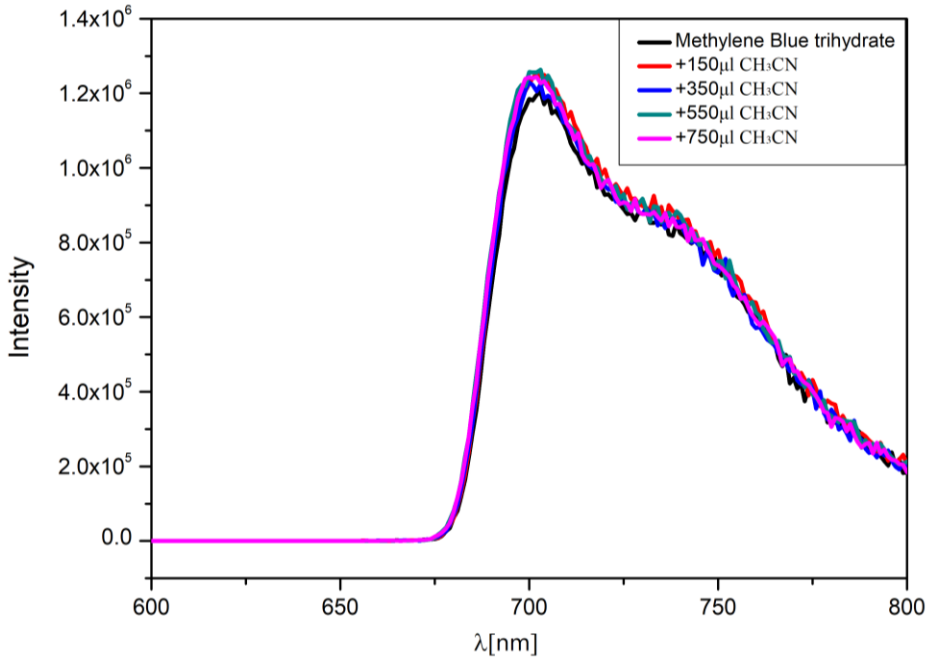


Figure S1. Fluorescence titration of Methylene Blue (250 µM in CH_3CN) with blank sample (solvent CH_3CN).

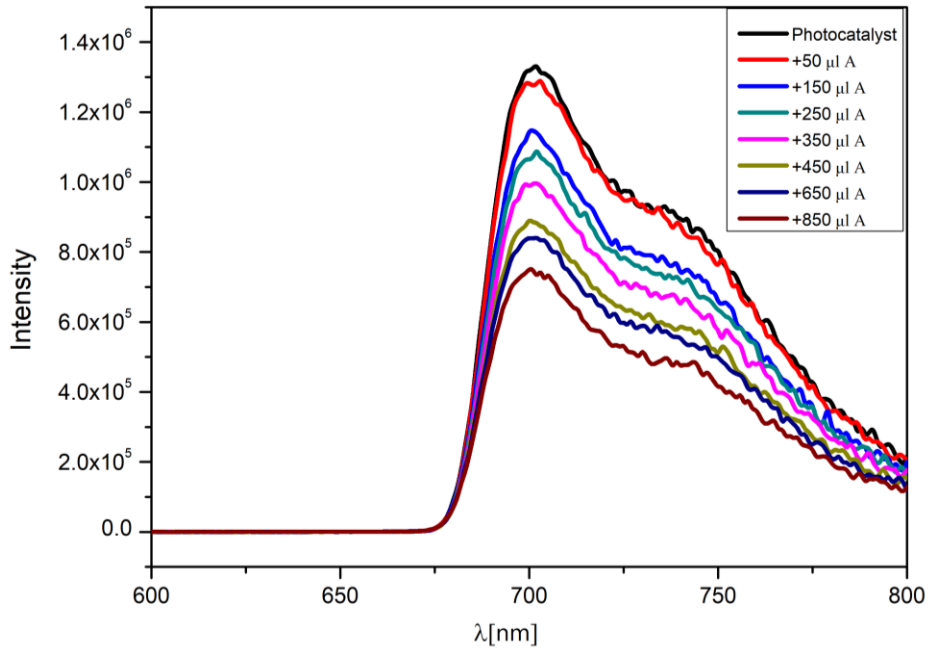


Figure S2. Fluorescence quenching of Methylene Blue (250 µM in CH_3CN) with thioamide 1a (300 mM in CH_3CN).

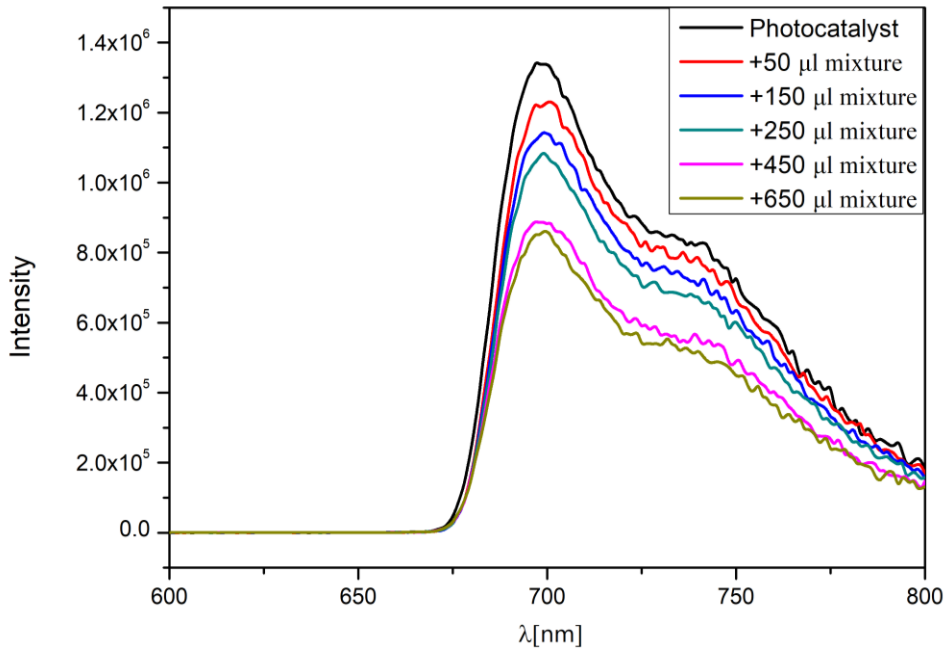


Figure S3. Fluorescence quenching of Methylene Blue (250 µM in CH_3CN) with the mixture of K_2HPO_4 and thioamide 1a (300 mM in CH_3CN).

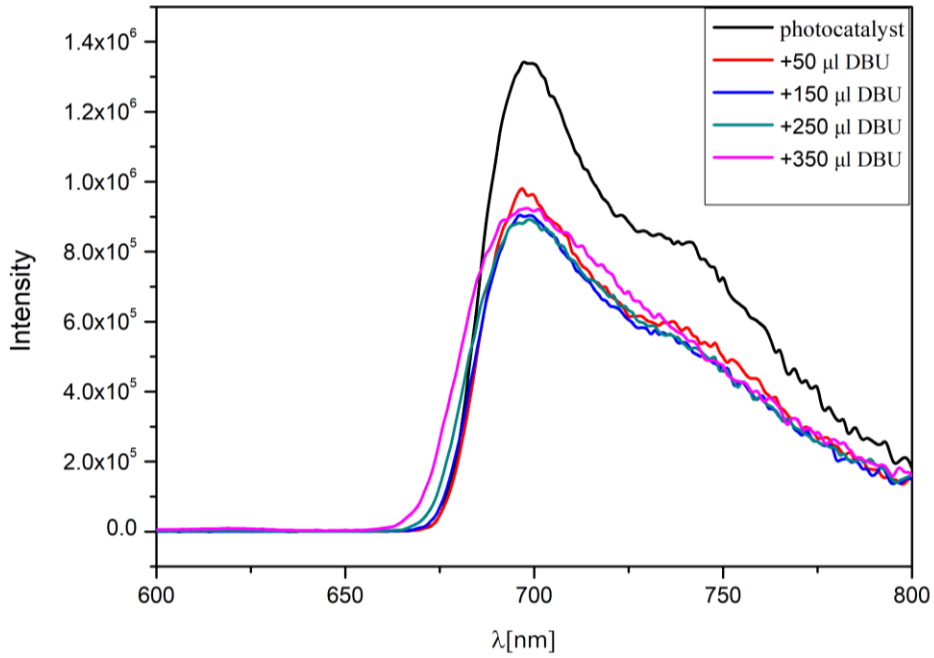
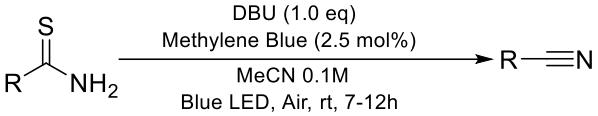


Figure S4. Changes in the fluorescence spectrum of Methylene Blue (250 µM in CH_3CN) upon titration with DBU (300 mM in CH_3CN).

5. General procedure for the dehydrosulfurization under light



To a glass bottle equipped with a stir bar, was added thioamide (0.3 mmol, 1 equiv.), Methylene Blue (2.4 mg, 2.5 mol%), and DBU (45 μL, 0.3 mmol, 1 equiv.), followed by the addition of dry MeCN (3 mL). A rubber stopper with an air-filled balloon is used to seal the glass bottle to prevent the solvent from evaporating during the reaction. The reaction was stirred for 7 to 12 hours under the irradiation of blue LEDs (6 W, at approximately 2 cm away from the LED beads, ca. 25 °C) until the thioamide was consumed (followed by TLC). The crude product residue was purified by flash chromatography on silica gel to afford the corresponding pure nitrile product.

4-Methoxybenzonitrile **(2a)**: white solid. Yield: 75.1 mg (94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 133.9, 119.2, 114.7, 103.9, 55.5.

Benzonitrile **(2b)**: yellow liquid. Yield: 49.5 mg (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.56 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.7, 132.0, 129.0, 118.8, 112.3.

2-Methoxybenzonitrile **(2c)**: colorless oil. Yield: 38.0 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 6.96 – 6.94 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 134.3, 133.7, 120.7, 116.5, 111.2, 101.8, 55.9.

4-Hydroxybenzonitrile **(2d)**: white solid. Yield: 63.1 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 6.94 (d, J = 8.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 134.3, 119.3, 116.4, 102.6.

4-Fluorobenzonitrile **(2e)**: white solid. Yield: 62.6 mg (86%). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.68 (m, 2H), 7.18 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0 (d, *J* = 256.6 Hz), 134.6 (d, *J* = 9.4 Hz), 118.0, 116.8 (d, *J* = 22.7 Hz), 108.5 (d, *J* = 3.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.4.

4-Chlorobenzonitrile **(2f)**: white solid. Yield: 72.3 mg (87%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 133.4, 129.7, 117.9, 110.8.

3-Chloro-4-fluorobenzonitrile **(2g)**: light yellow solid. Yield: 41.5 mg (89%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 6.8, 1.5 Hz, 1H), 7.61 (m, 1H), 7.30 (t, *J* = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (d, *J* = 258.9 Hz), 134.6, 132.6 (d, *J* = 8.4 Hz), 122.7 (d, *J* = 18.9 Hz), 117.8 (d, *J* = 22.5 Hz), 116.7, 109.5 (d, *J* = 4.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.8.

4-(Trifluoromethyl)benzonitrile **(2h)**: colorless oil. Yield: 45.0 mg (87%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5 (d, *J* = 33.2 Hz), 132.6, 126.2 (q, *J* = 3.7 Hz), 123.0 (d, *J* = 273.0 Hz), 117.4, 116.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5.

3-(Trifluoromethyl)benzonitrile **(2i)**: colorless oil. Yield: 43.5 mg (85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.87 (t, *J* = 6.7 Hz, 2H), 7.66 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 132.0 (q, *J* = 33.7 Hz), 129.9, 129.5 (q, *J* = 3.6 Hz), 129.0 (q, *J* = 3.8 Hz), 122.9 (d, *J* = 272.8 Hz), 117.3, 113.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2.

Piperonylonitrile **(2j)**: white solid. Yield: 84.4 mg (95%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 1H), 7.03 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 148.0, 128.2, 118.9, 111.4, 109.1, 104.9, 102.2.

2-Pyridinecarbonitrile **(2k)**: white solid. Yield: 55.1 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.73 (m, 1H), 7.85 (m, 1H), 7.71 (d, *J* = 7.8, 1H), 7.53 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 137.0, 134.1, 128.5, 126.9, 117.1.

3-Pyridinecarbonitrile **(2l)**: white solid. Yield: 60.1 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 2.0 Hz, 1H), 8.79 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.95 (dt, *J* = 8.1, 1.9 Hz, 1H), 7.42 (dd, *J* = 8.0, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 152.5, 139.2, 123.6, 116.5, 110.2.

4-Pyridinecarbonitrile **(2m)**: light yellow solid. Yield: 58.9 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 – 8.81 (m, 2H), 7.54 – 7.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 125.2, 120.4, 116.3.

2-Ethyl-4-pyridinecarbonitrile **(2n)**: colorless oil. Yield: 68.7 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.0 Hz, 1H), 7.39 (s, 1H), 7.34 (d, *J* = 4.9 Hz, 1H), 2.89 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 150.2, 123.7, 122.3, 120.6, 116.7, 31.3, 13.4.

Pyrimidine-2-carbonitrile **(2o)**: white solid. Yield: 25.7 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 5.1, 2.0 Hz, 2H), 7.55 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 145.4, 123.5, 115.5.

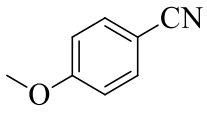
Thiophene-2-carbonitrile **(2p)**: light yellow solid. Yield: 52.9 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 132.5, 127.6, 114.2, 109.8.

3-Phenylpropanenitrile **(2q)**: yellow oil. Yield: 35.6 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.5 Hz, 2H), 7.29 (m, 3H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 128.8, 128.2, 127.2, 119.1, 31.6,

19.3.

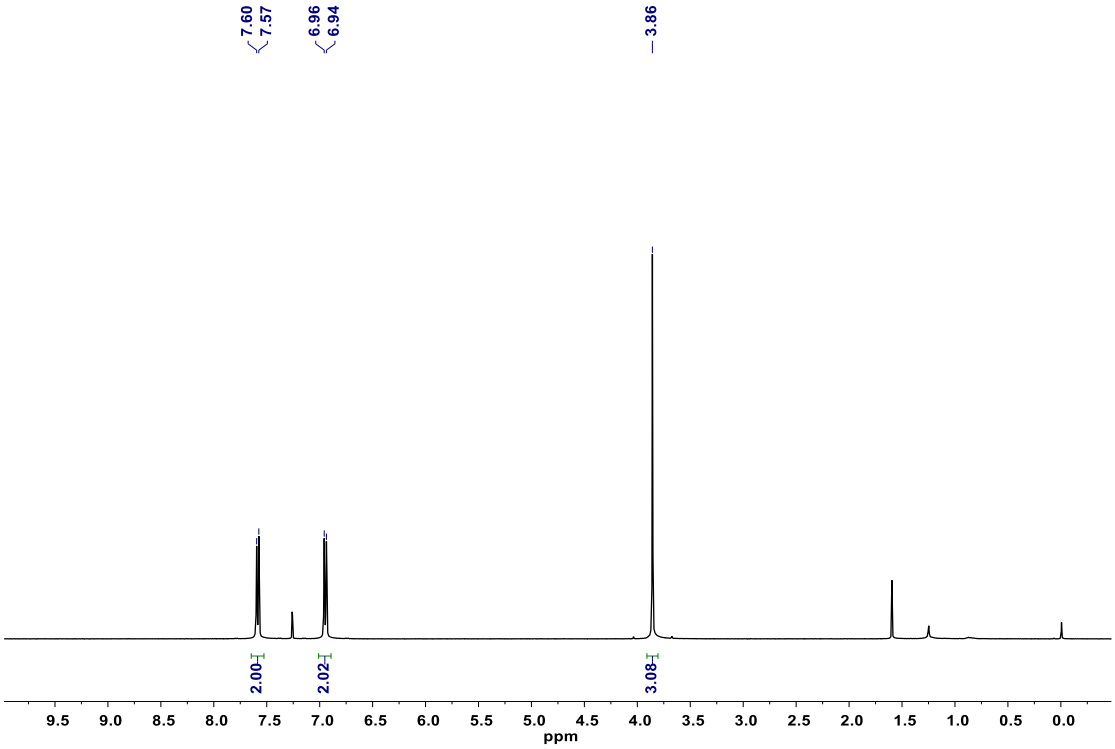
Cinnamonitrile* (2r)**: oil. Yield: 24.0 mg, 62%; (E***)**-2r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 6H), 5.86 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 133.5, 131.2, 129.1, 127.3, 118.1, 96.3; (***Z***)**-2r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.79 (m, 2H), 7.35(s, 3H), 7.11 (d, *J* = 12.0 Hz, 1H), 5.43 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 133.5, 130.9, 129.0, 128.9, 117.3, 95.0.

6. NMR spectra

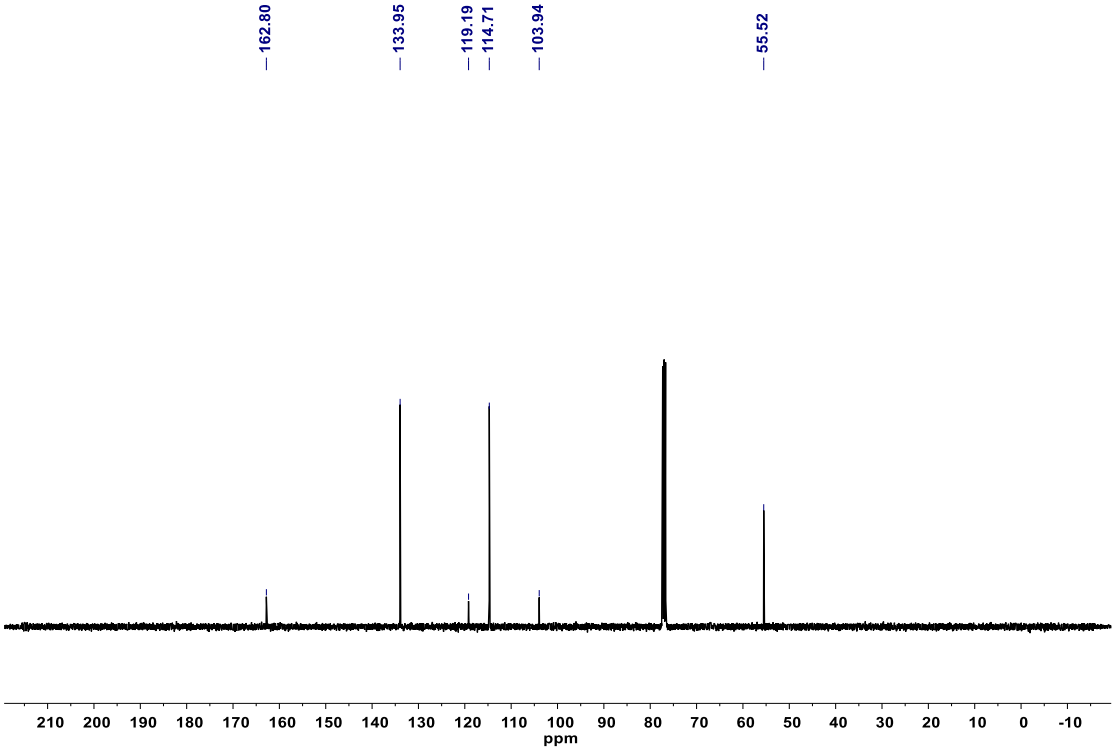


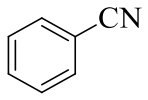
(2a)

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



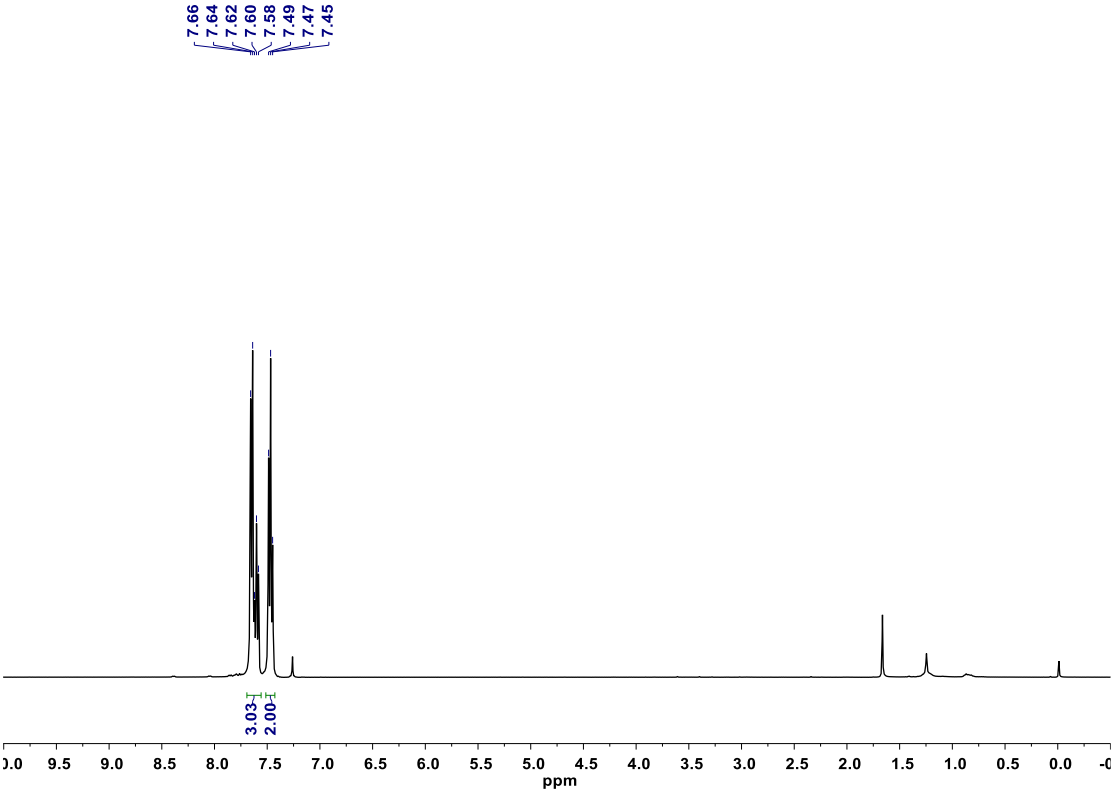
^{13}C NMR (101 MHz, $CDCl_3$):



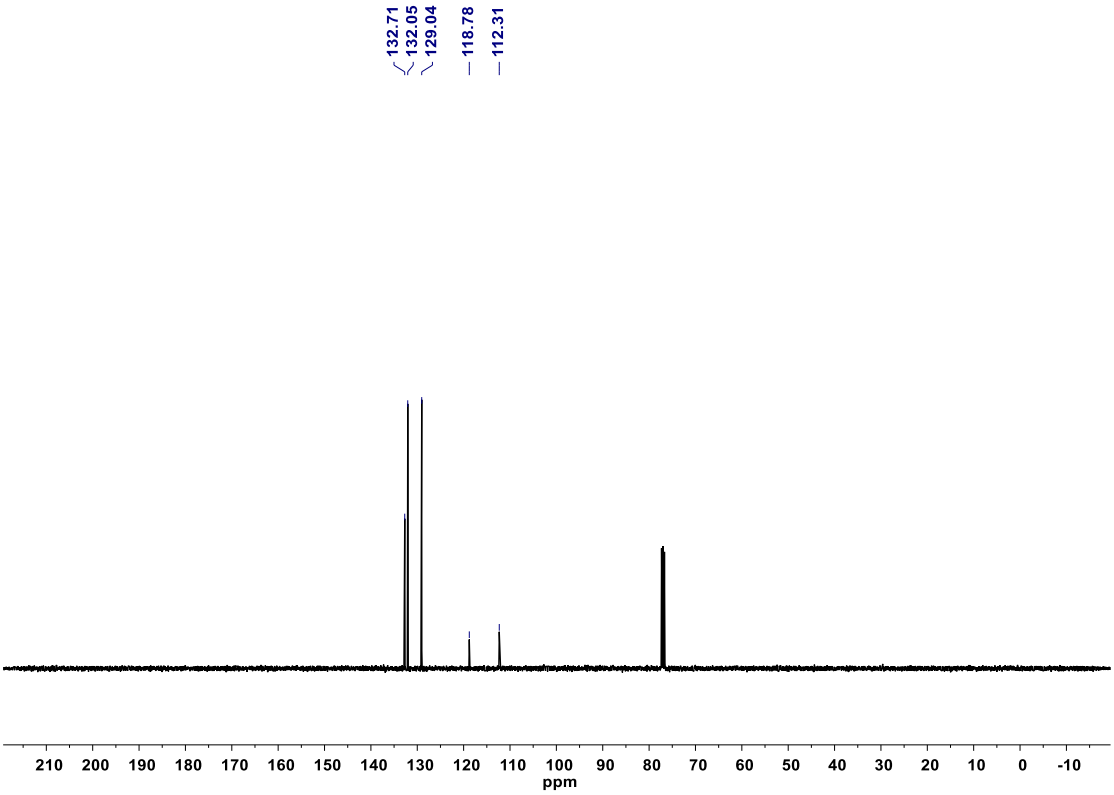


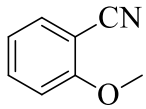
(2b)

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



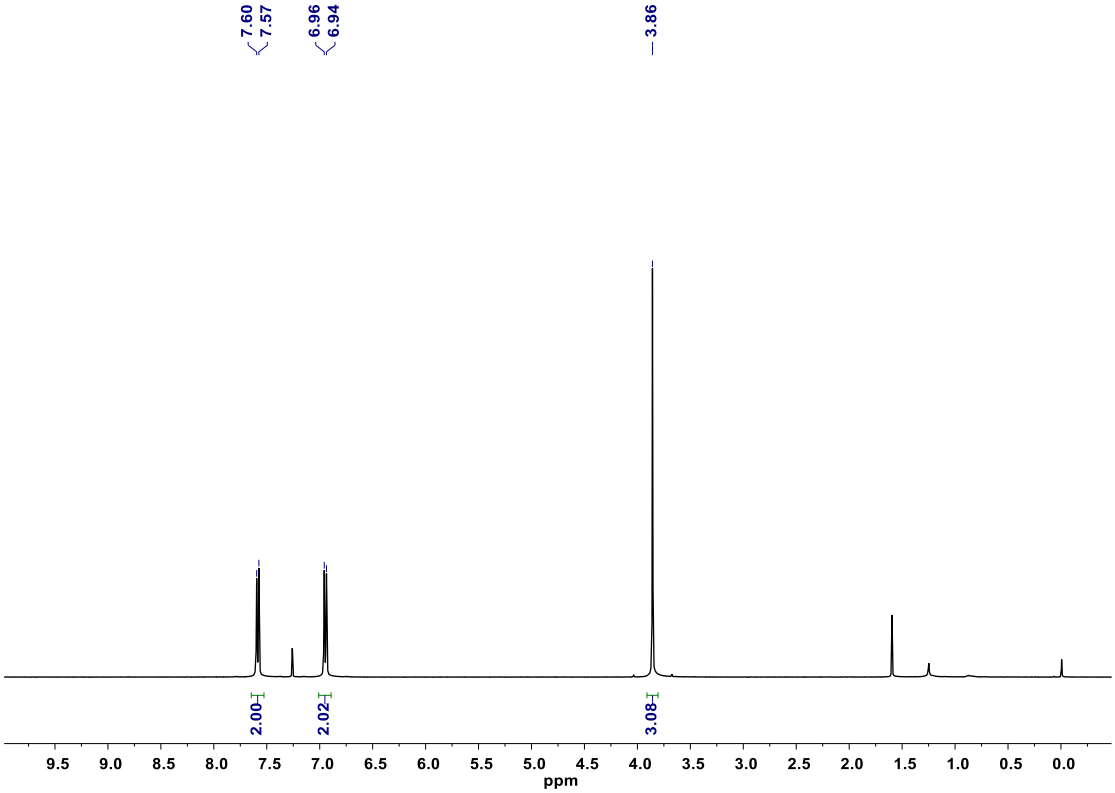
^{13}C NMR (101 MHz, $CDCl_3$):



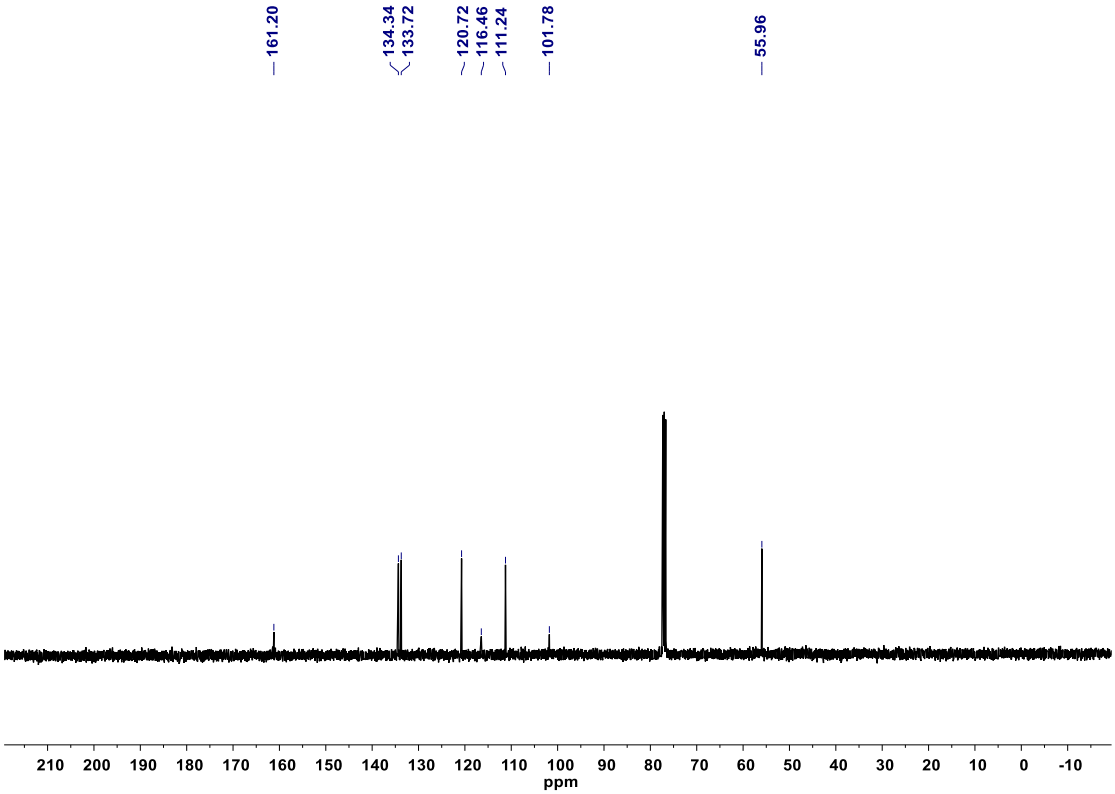


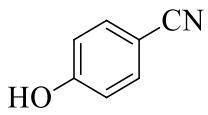
(2c)

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



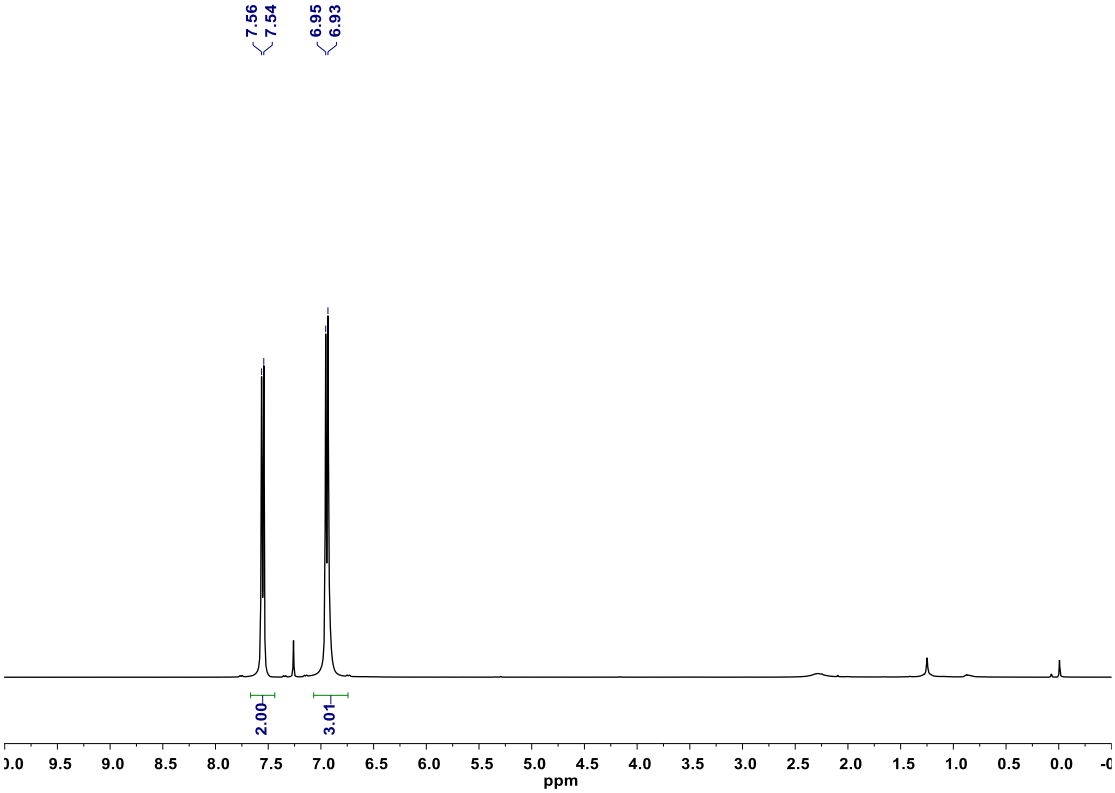
^{13}C NMR (101 MHz, $CDCl_3$):



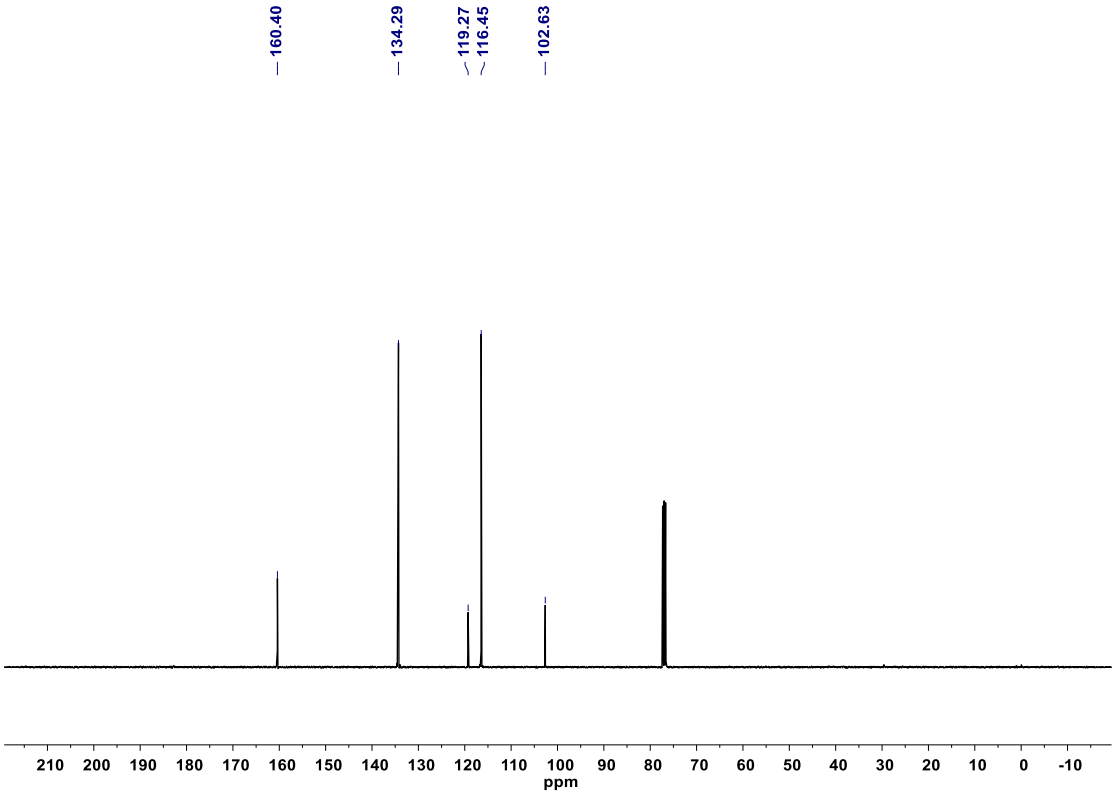


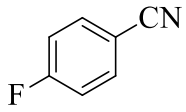
(2d)

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



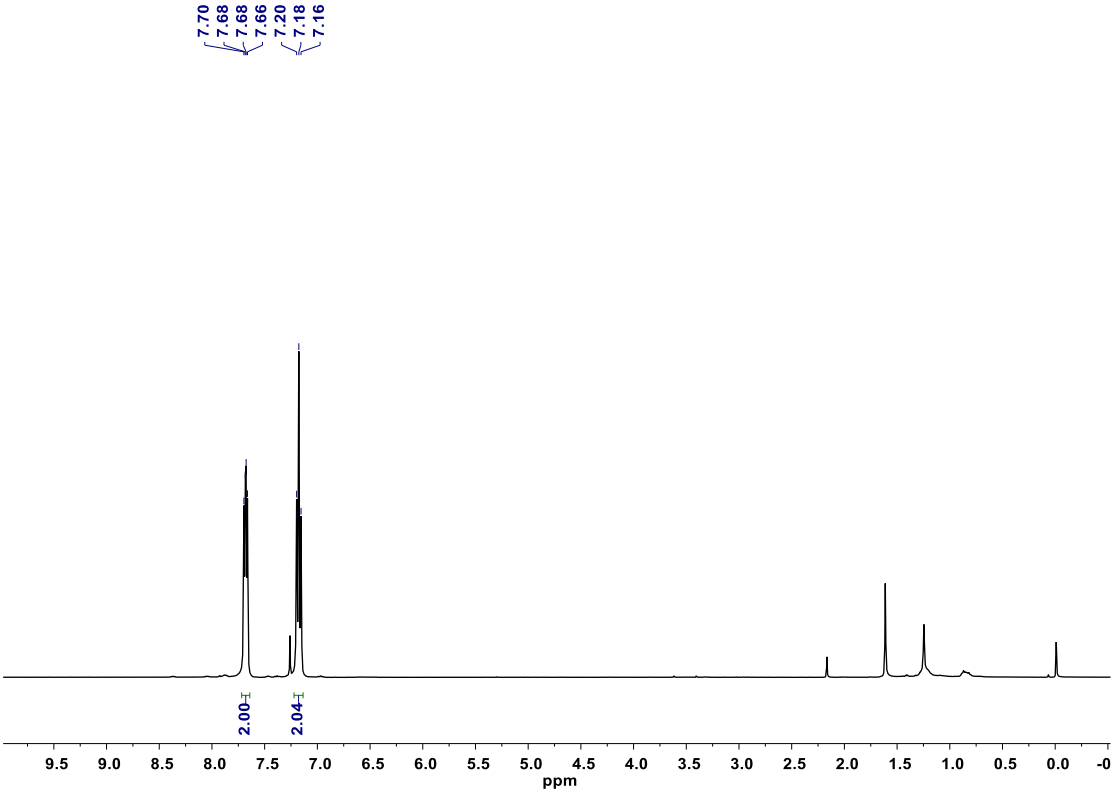
^{13}C NMR (101 MHz, $CDCl_3$):



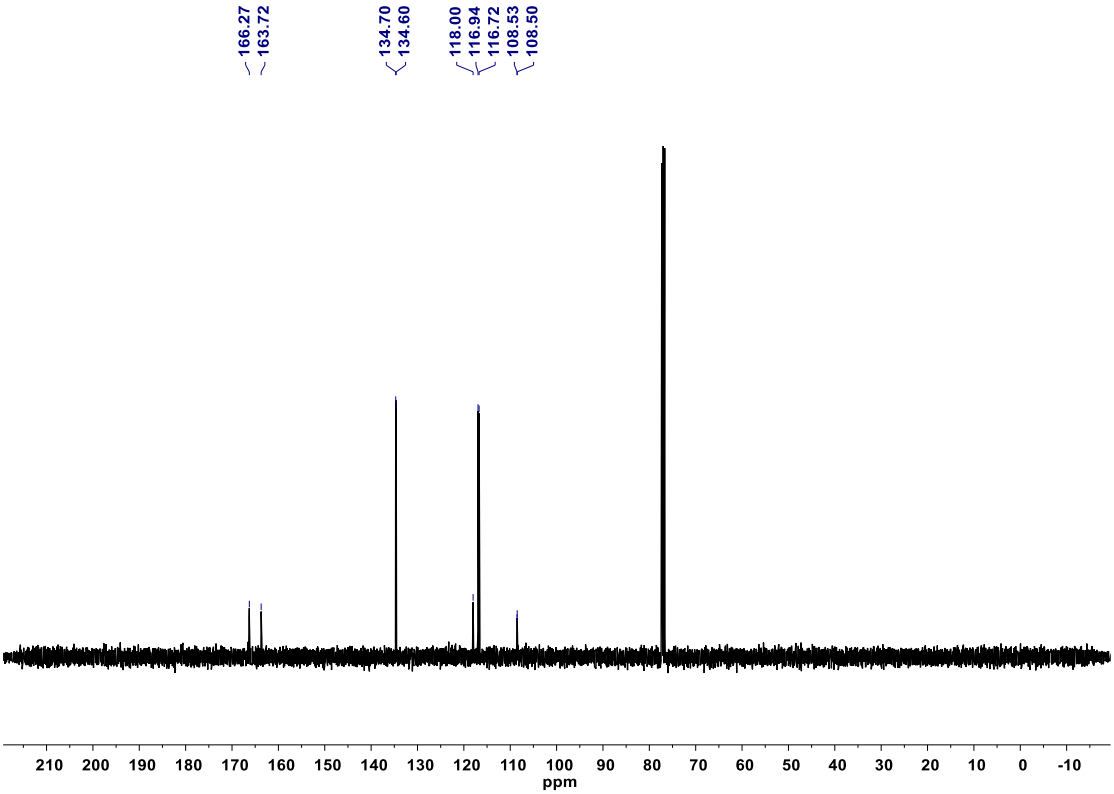


(2e)

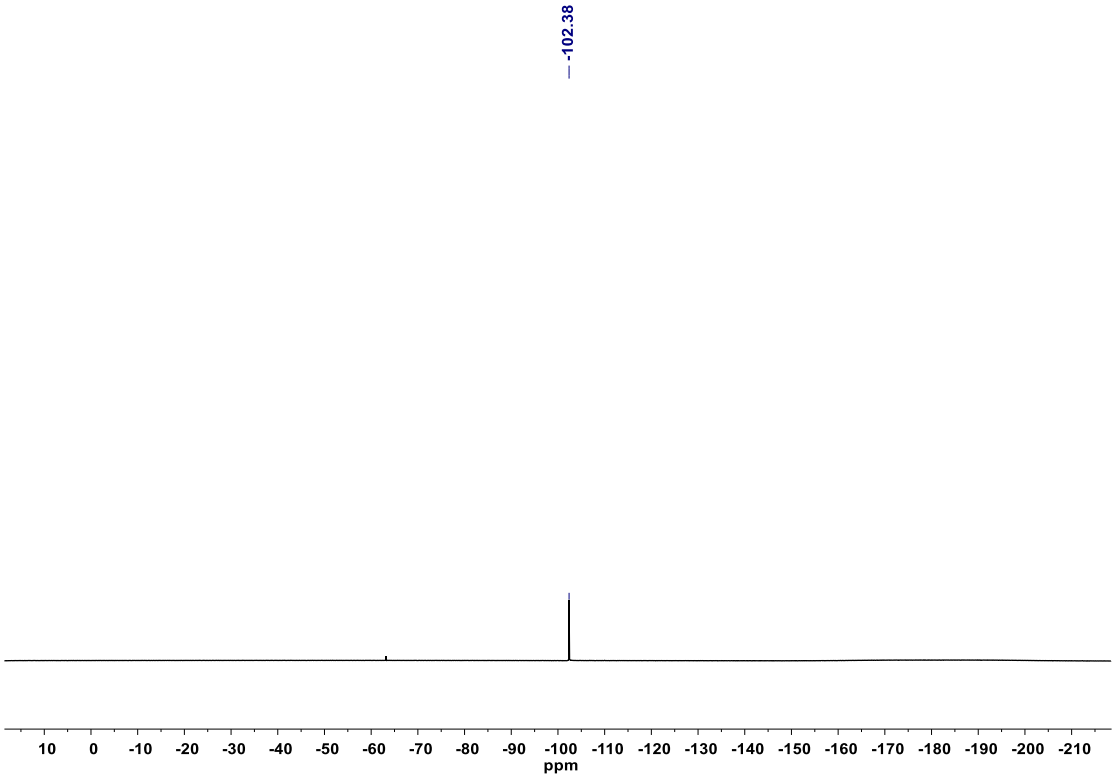
^{1}H NMR (400 MHz, $CDCl_3$):

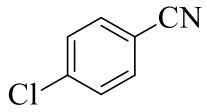


^{13}C NMR (101 MHz, $CDCl_3$):



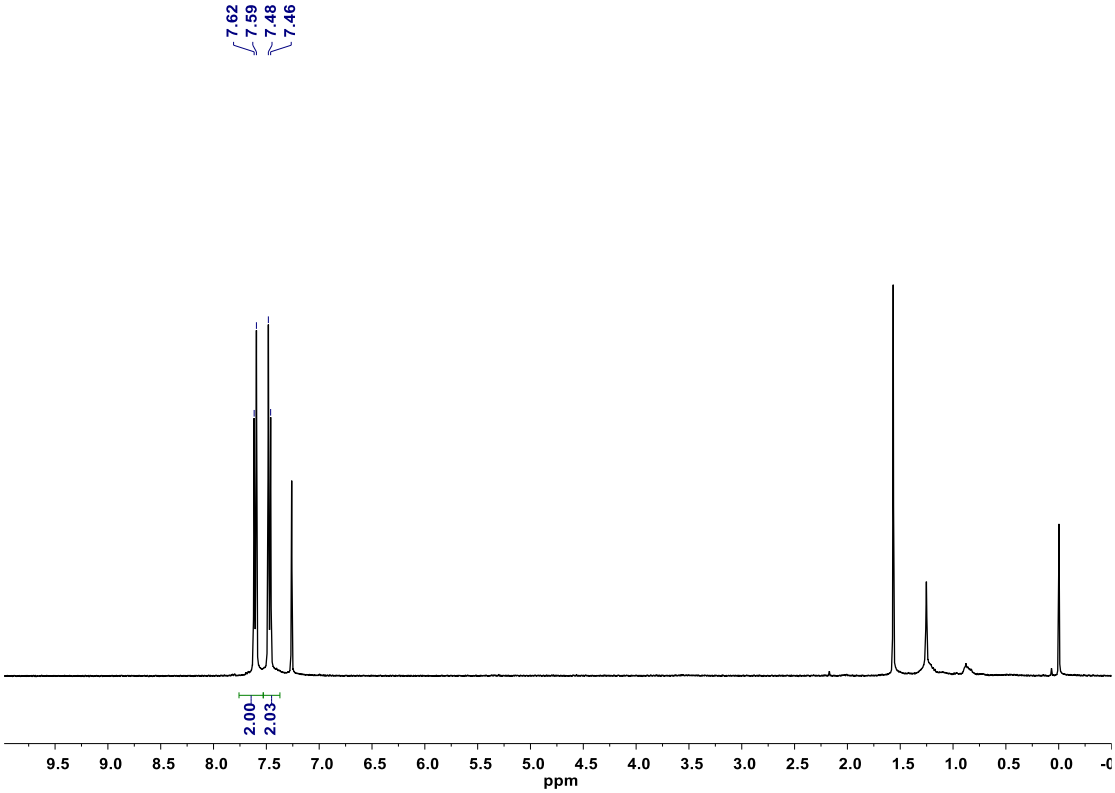
^{19}F NMR (376 MHz, $CDCl_3$):



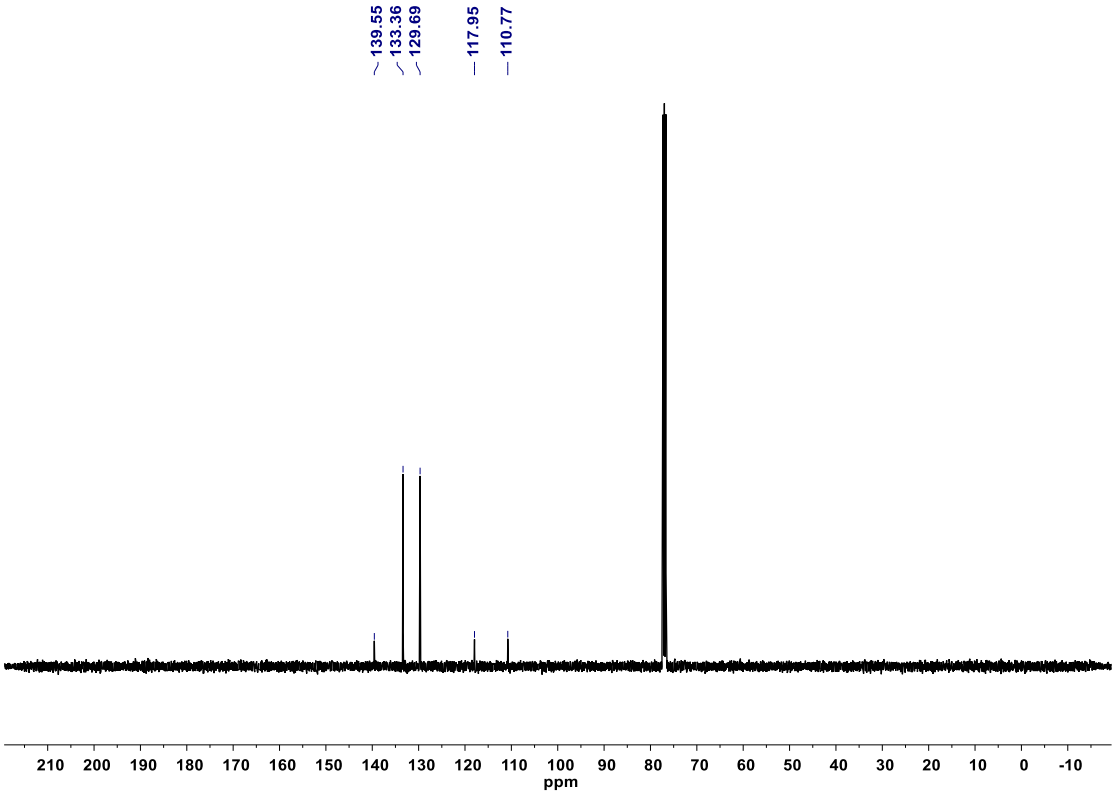


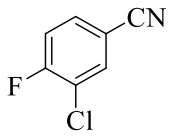
(2f)

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



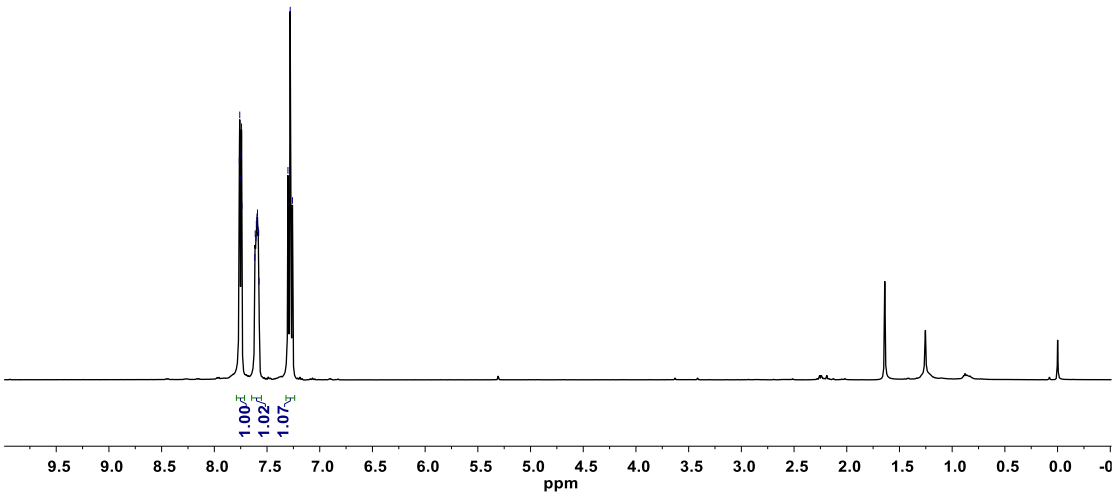
^{13}C NMR (101 MHz, $CDCl_3$):



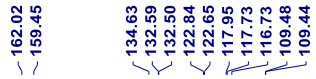


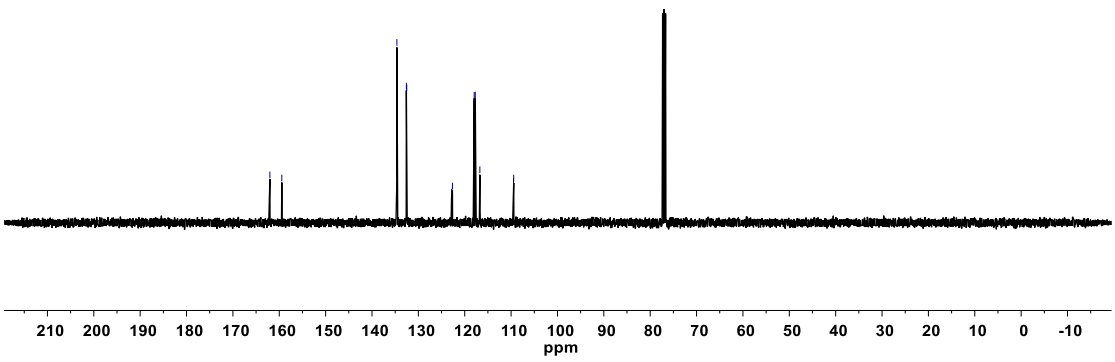
(2g)

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

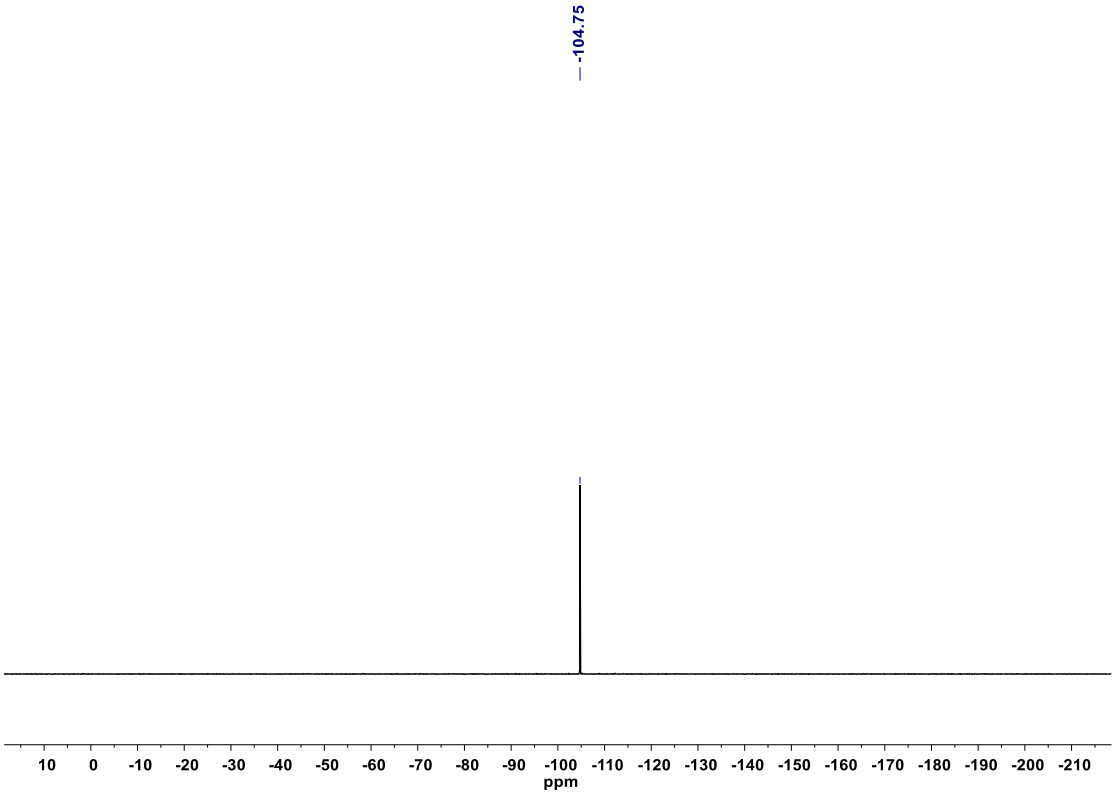


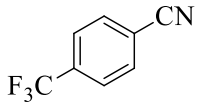
^{13}C NMR (101 MHz, $CDCl_3$):





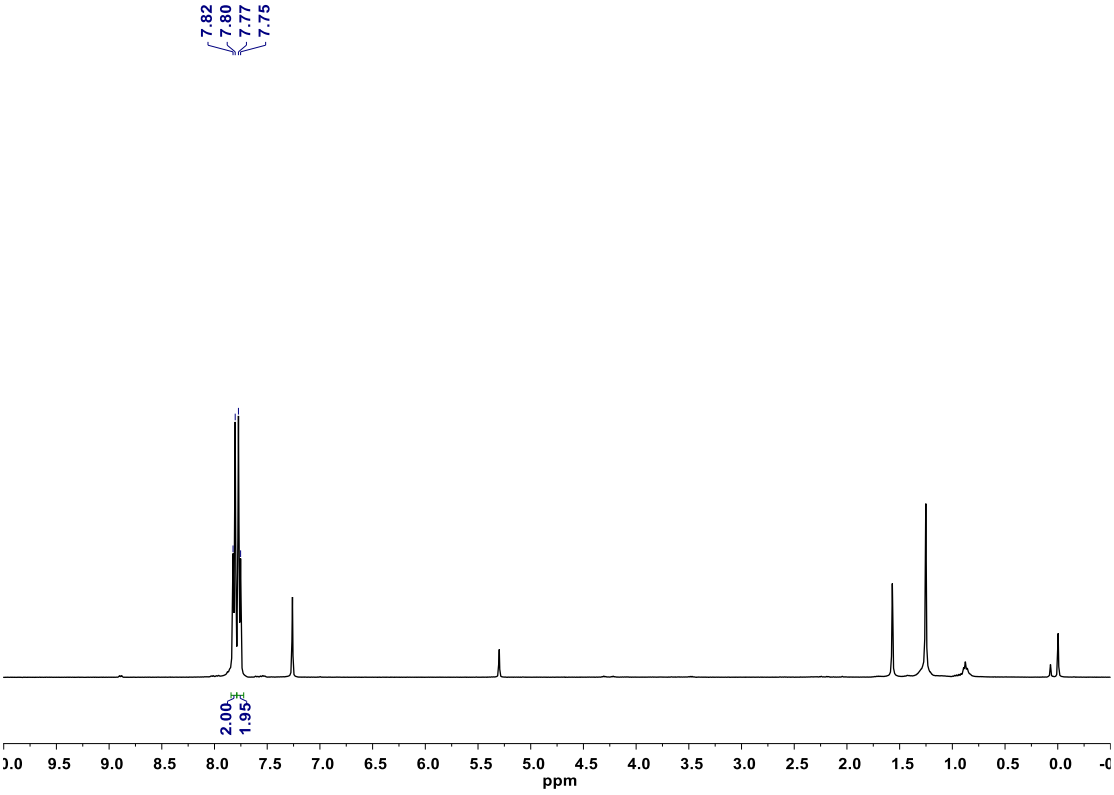
^{19}F NMR (376 MHz, $CDCl_3$):



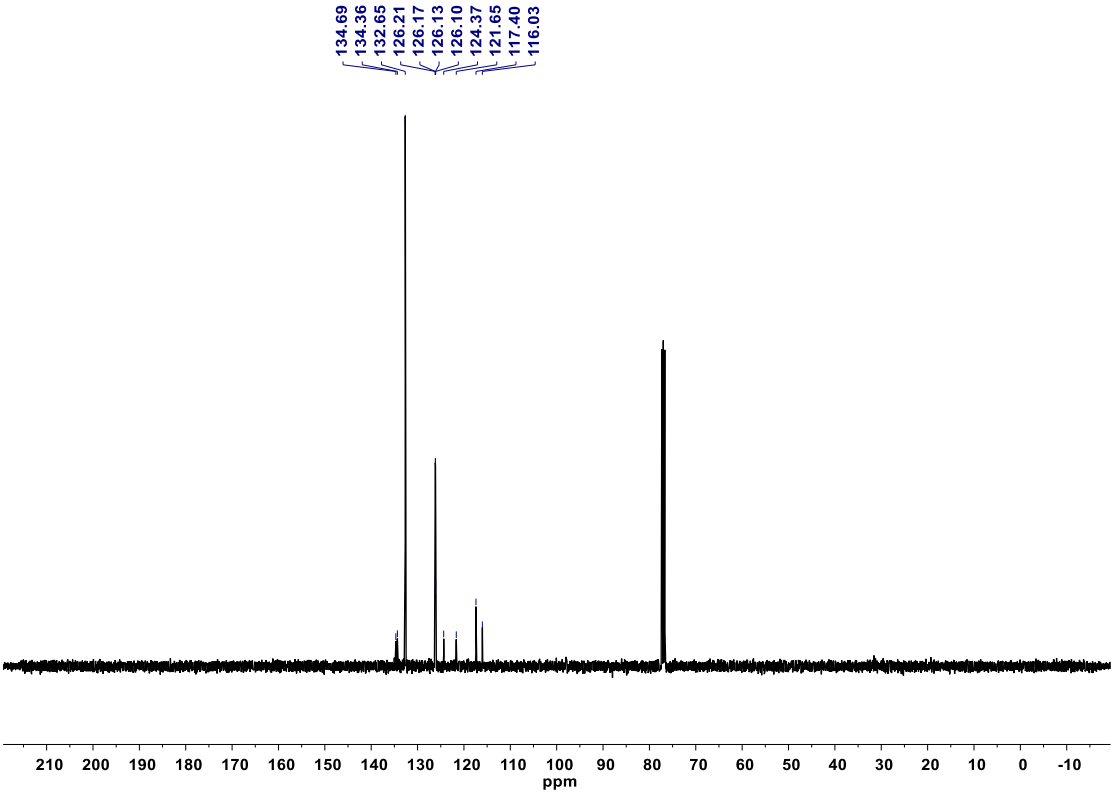


(2h)

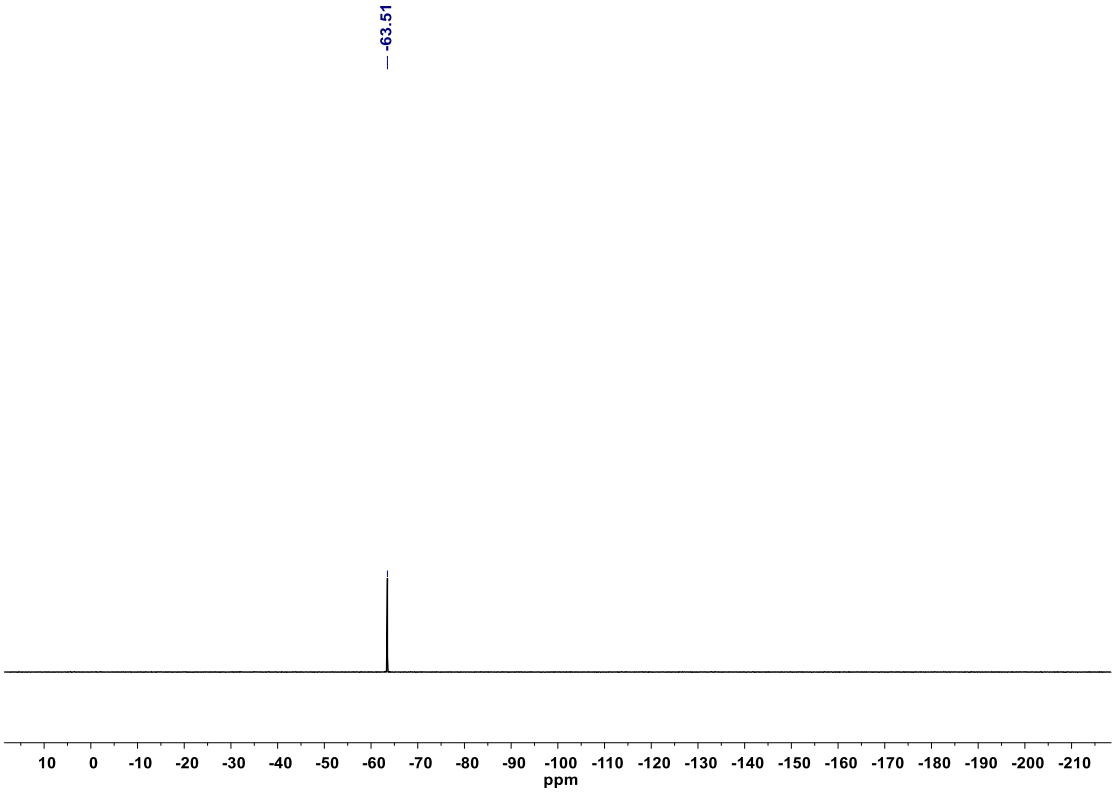
^{1}H NMR (400 MHz, $CDCl_3$):

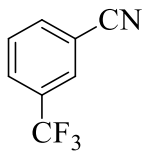


^{13}C NMR (101 MHz, $CDCl_3$):



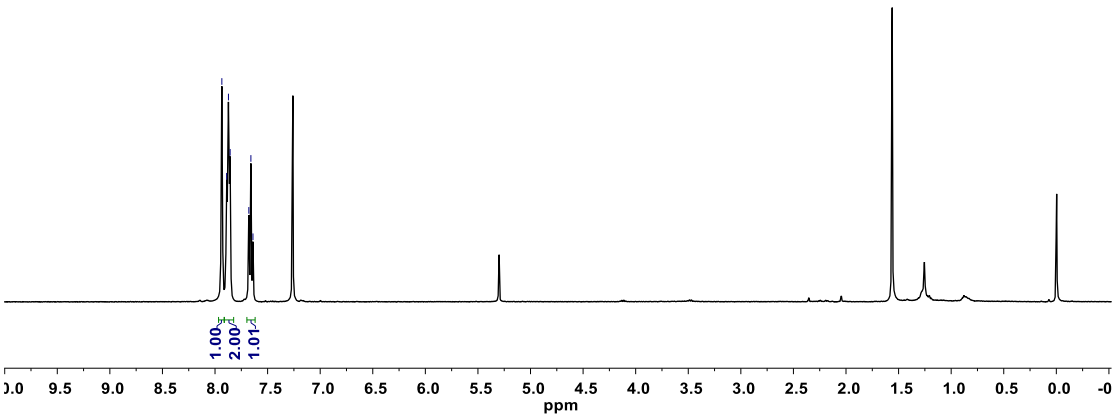
^{19}F NMR (376 MHz, $CDCl_3$):



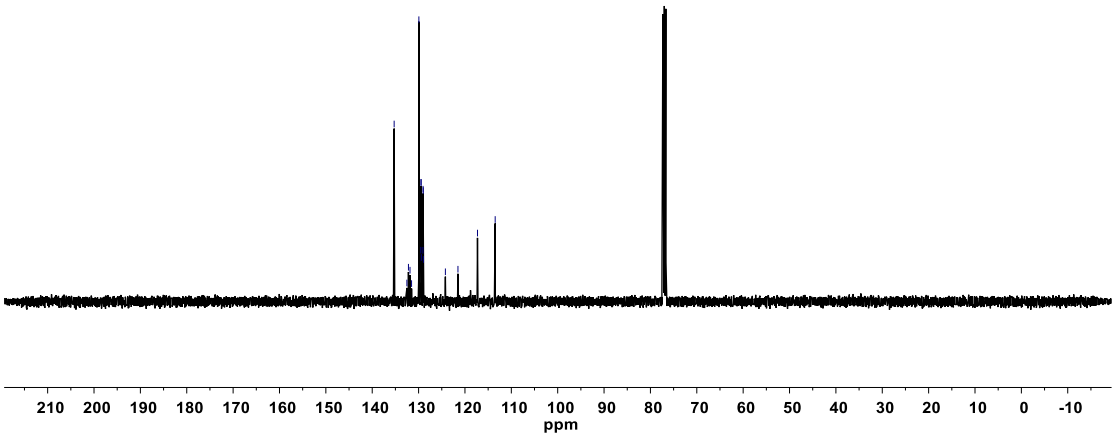


(2i)

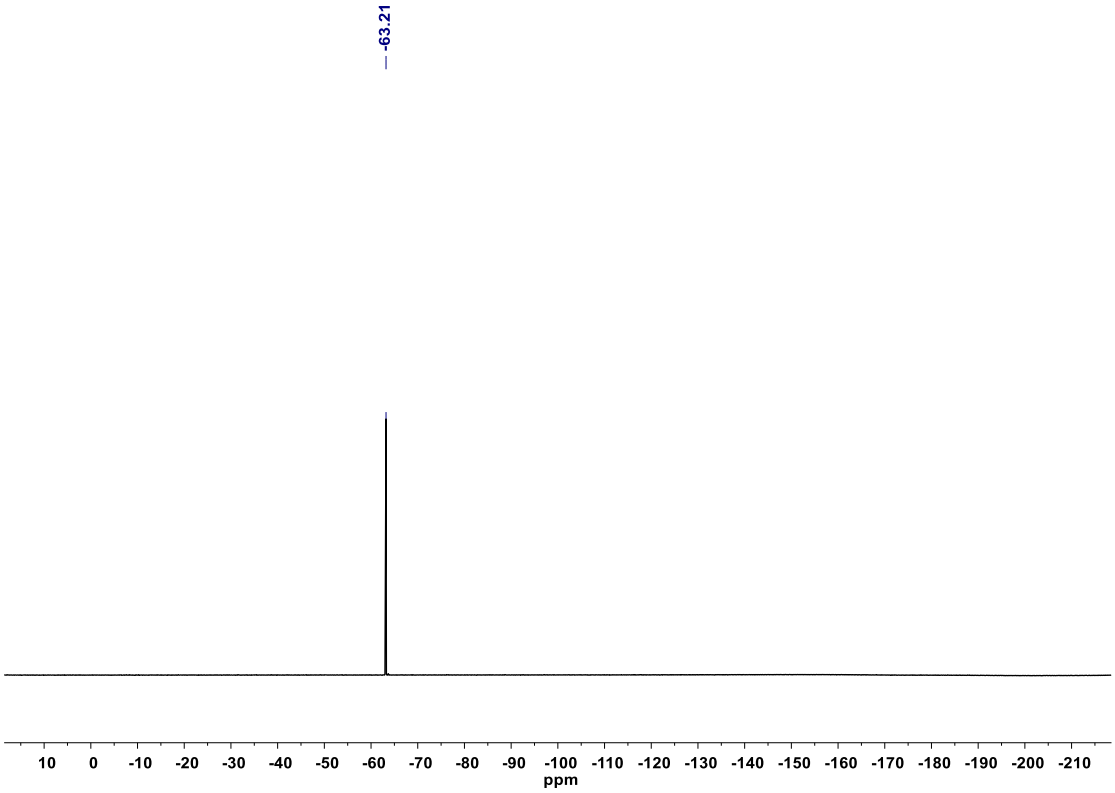
^{1}H NMR (400 MHz, $CDCl_3$):

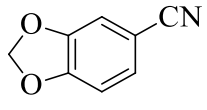


^{13}C NMR (101 MHz, $CDCl_3$):



^{19}F NMR (400 MHz, $CDCl_3$):





(2j)

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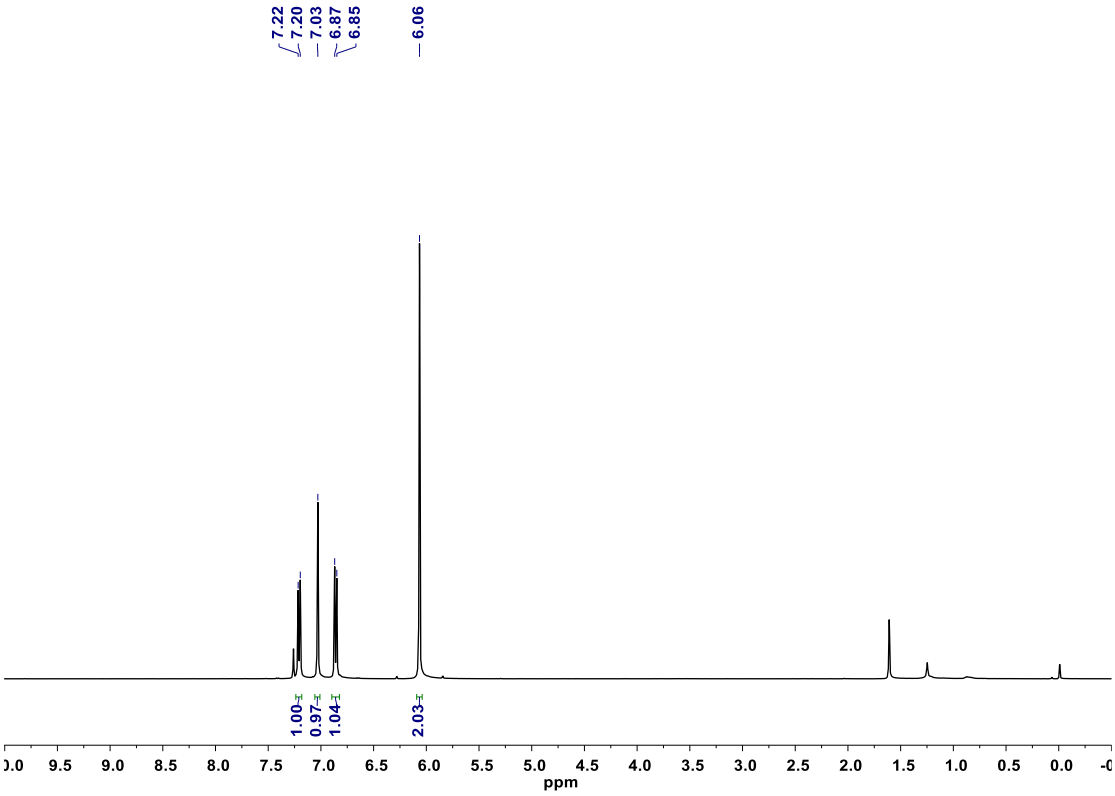

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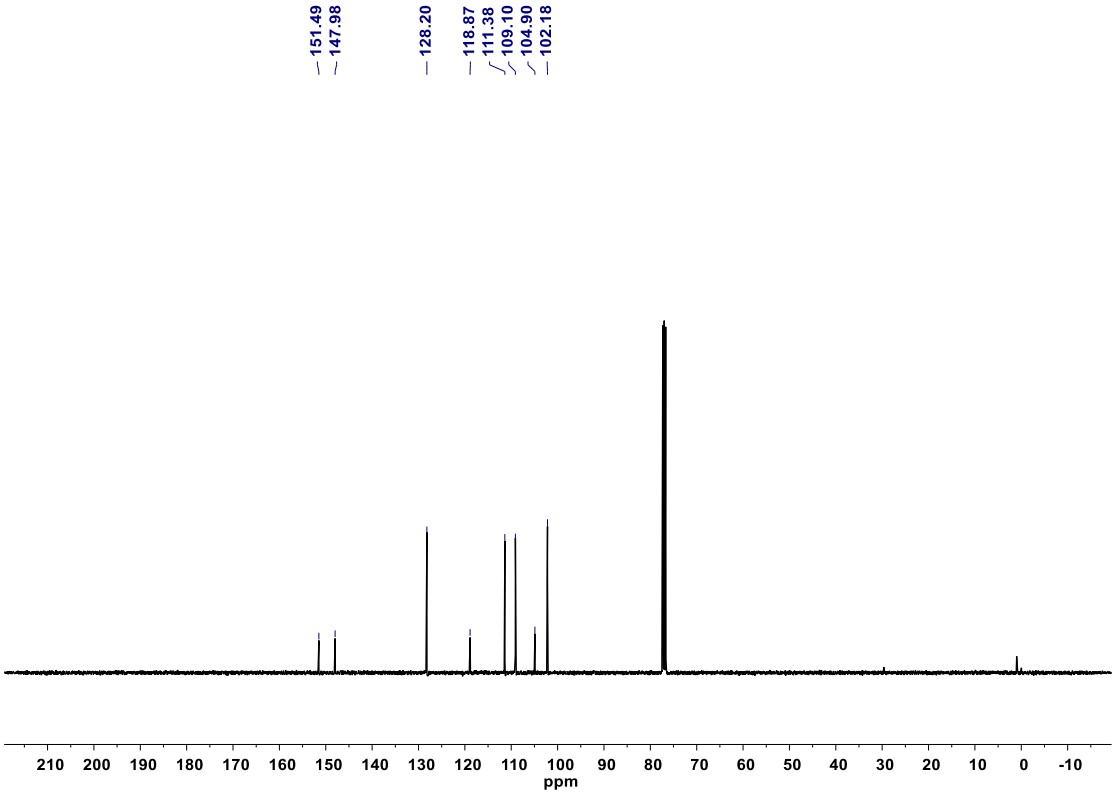
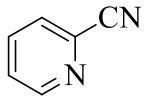
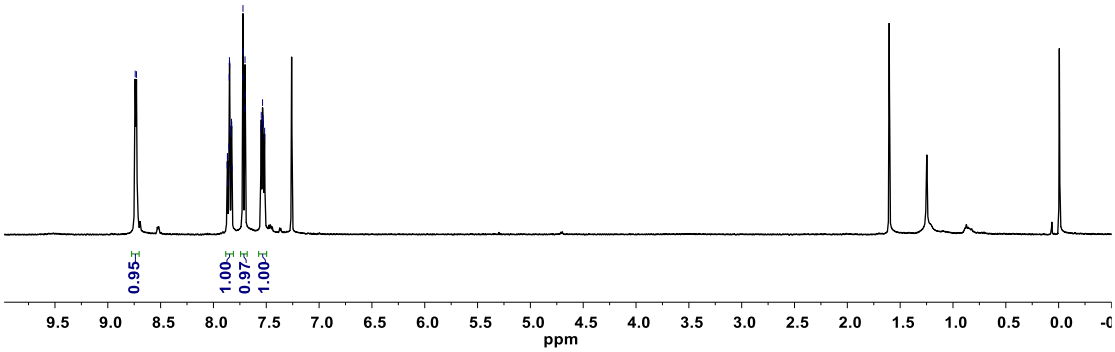


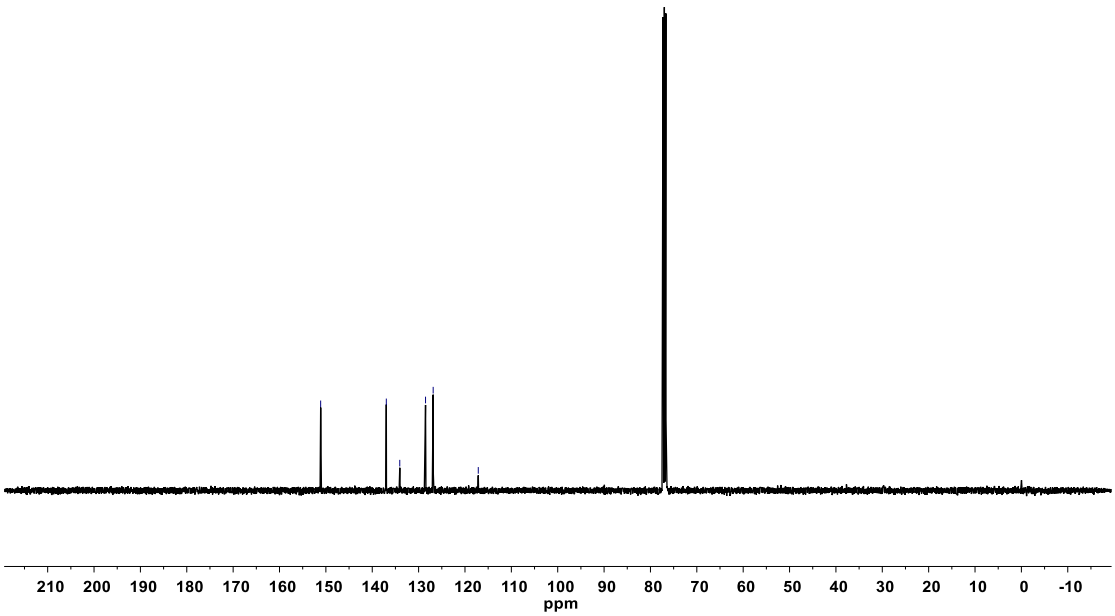


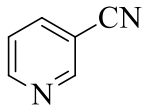
(2k)

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



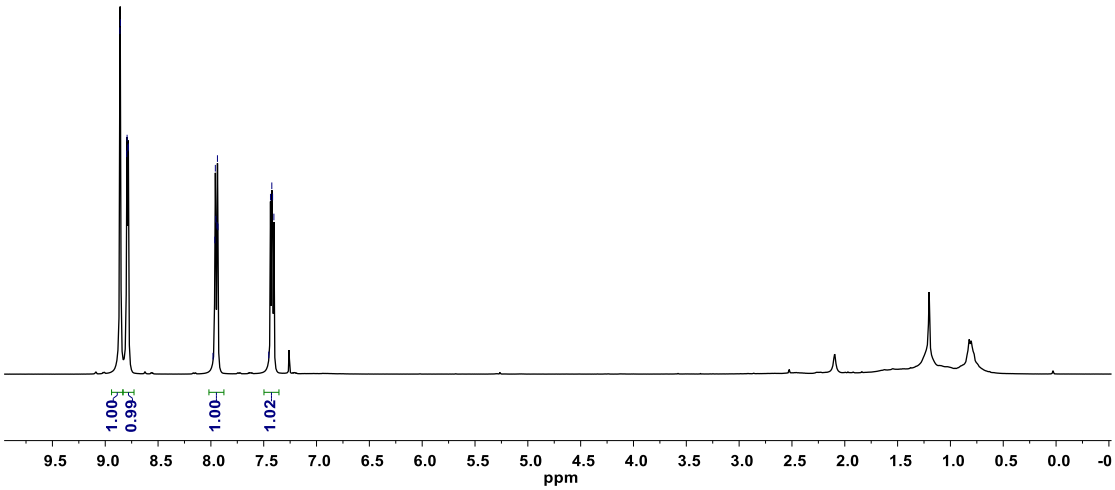
^{13}C NMR (101 MHz, $CDCl_3$):



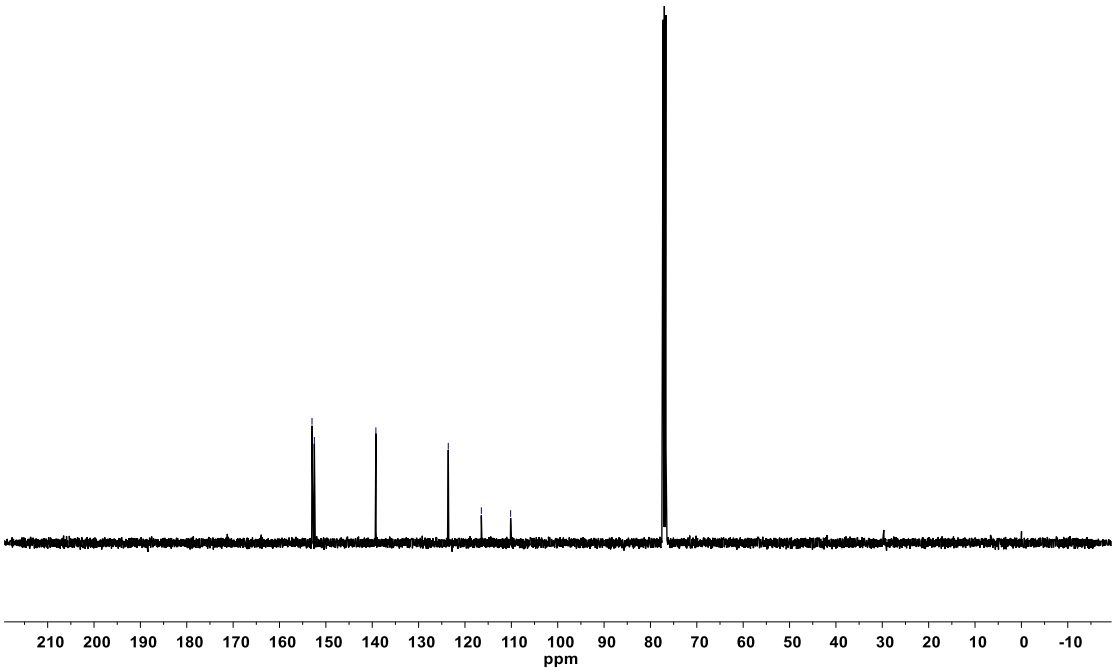


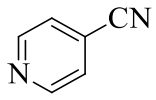
(2l)

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



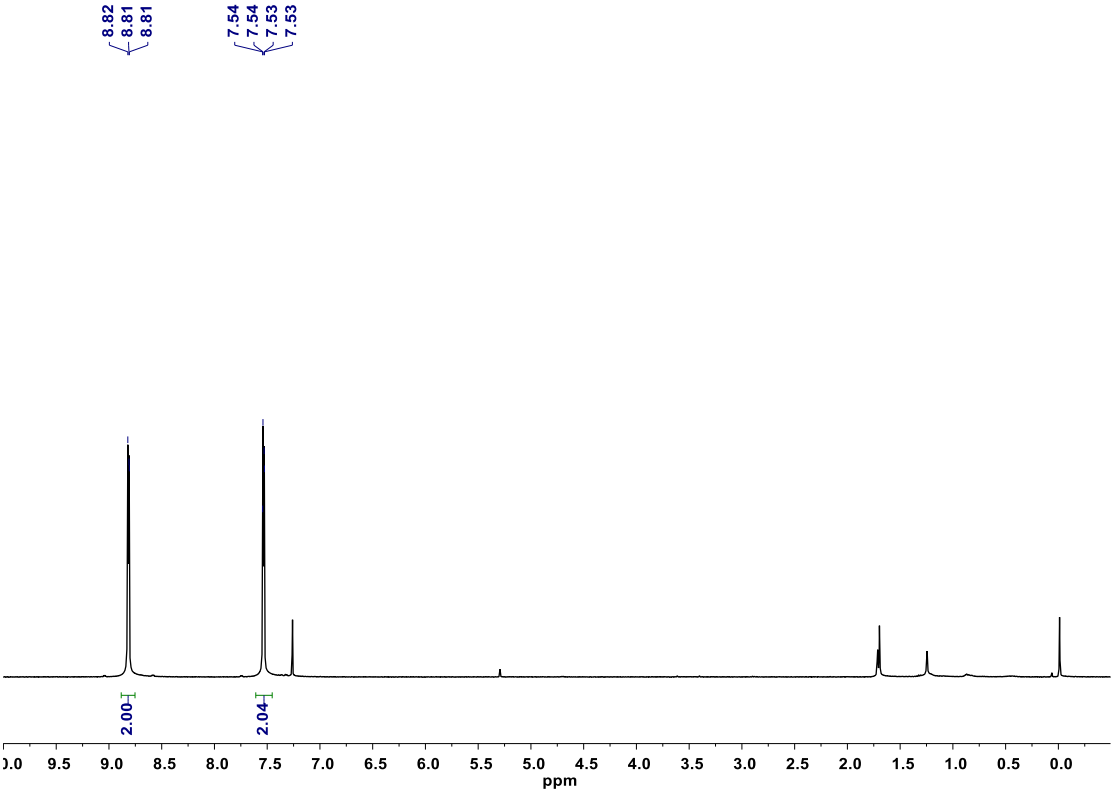
^{13}C NMR (101 MHz, $CDCl_3$):



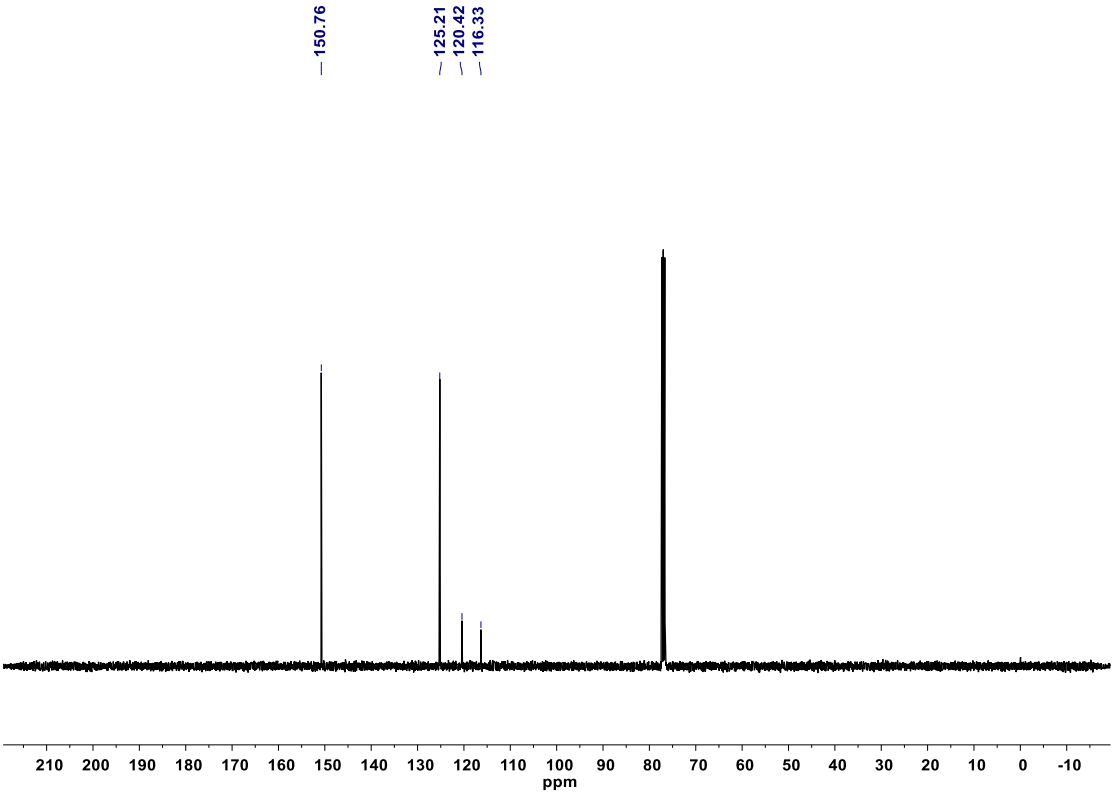


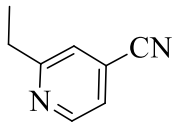
(2m)

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



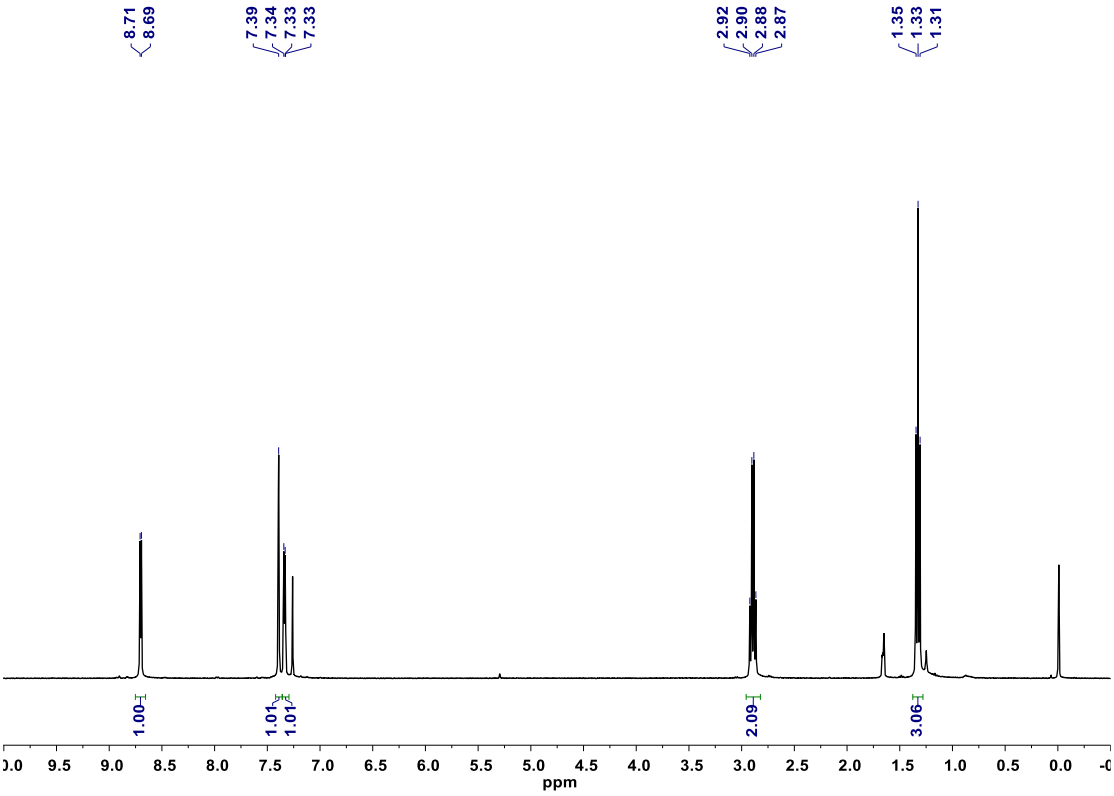
^{13}C NMR (101 MHz, $CDCl_3$):



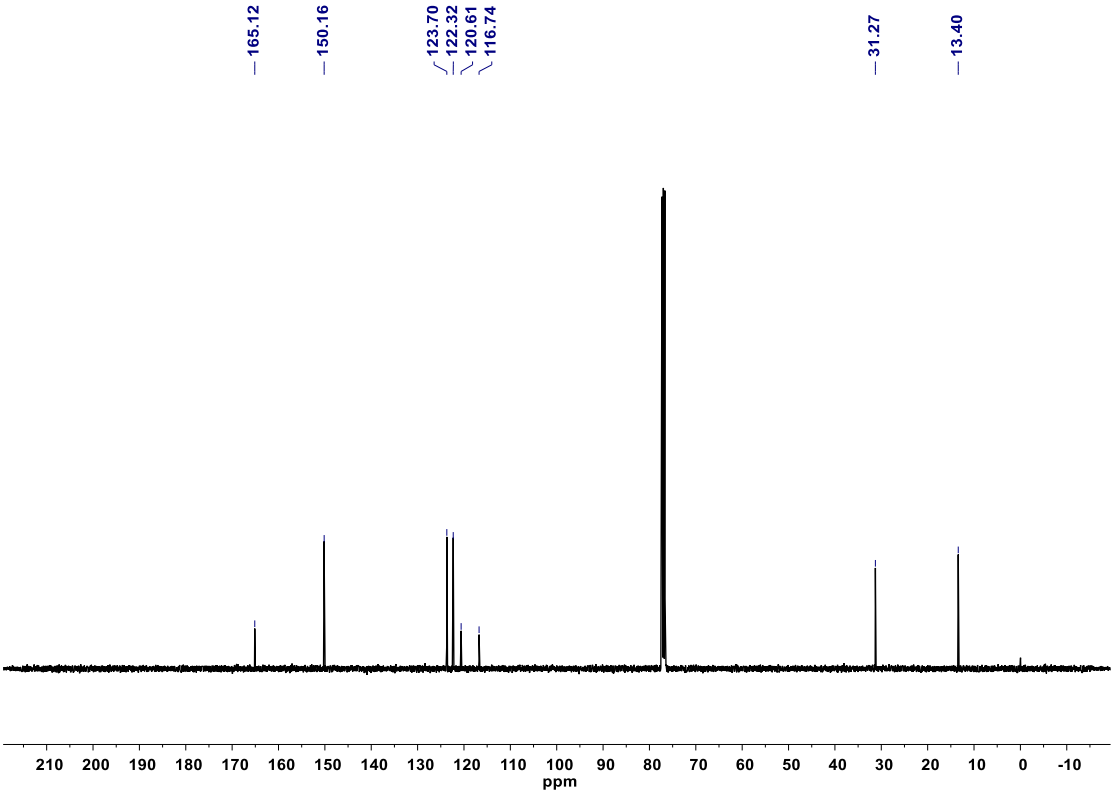


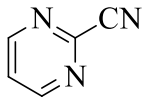
(2n)

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



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





(2o)

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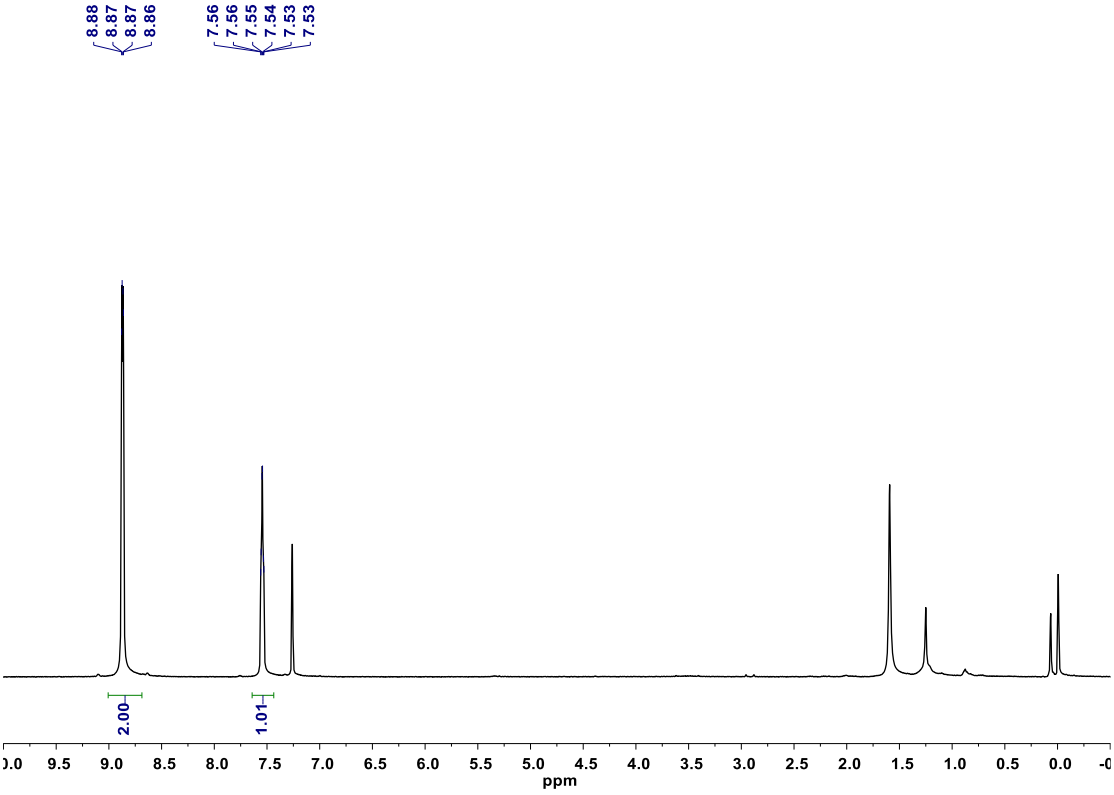
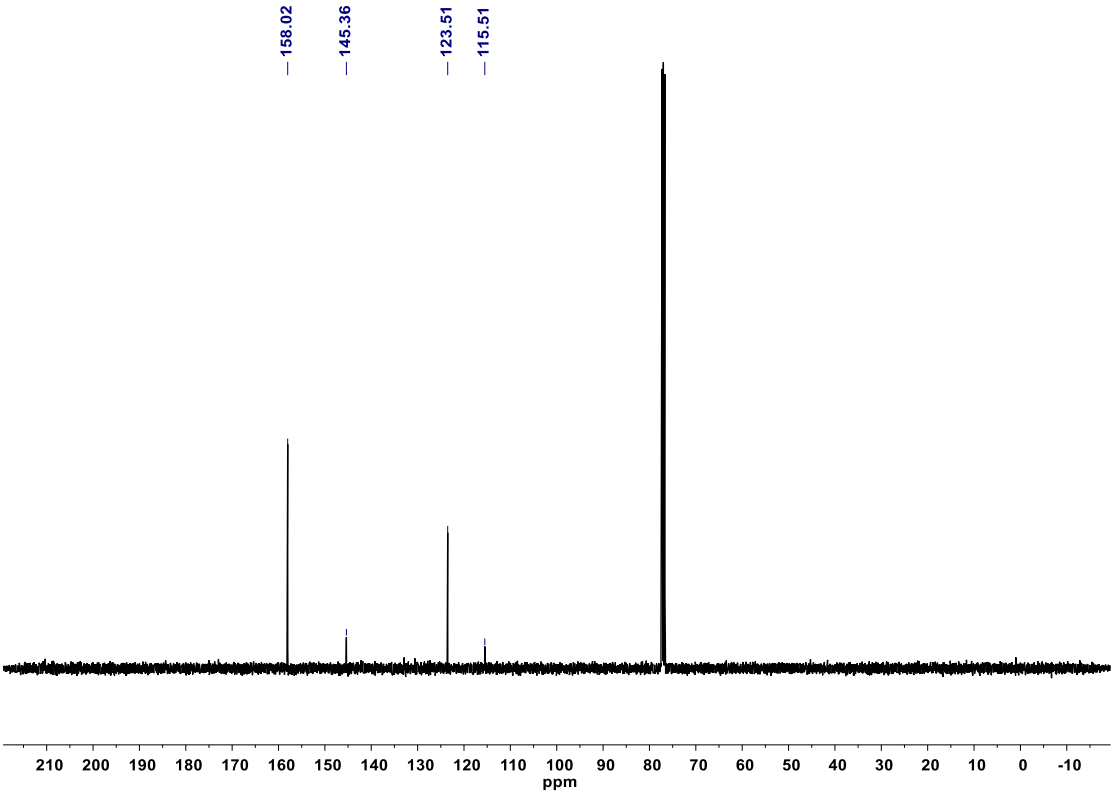
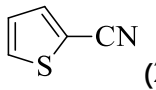


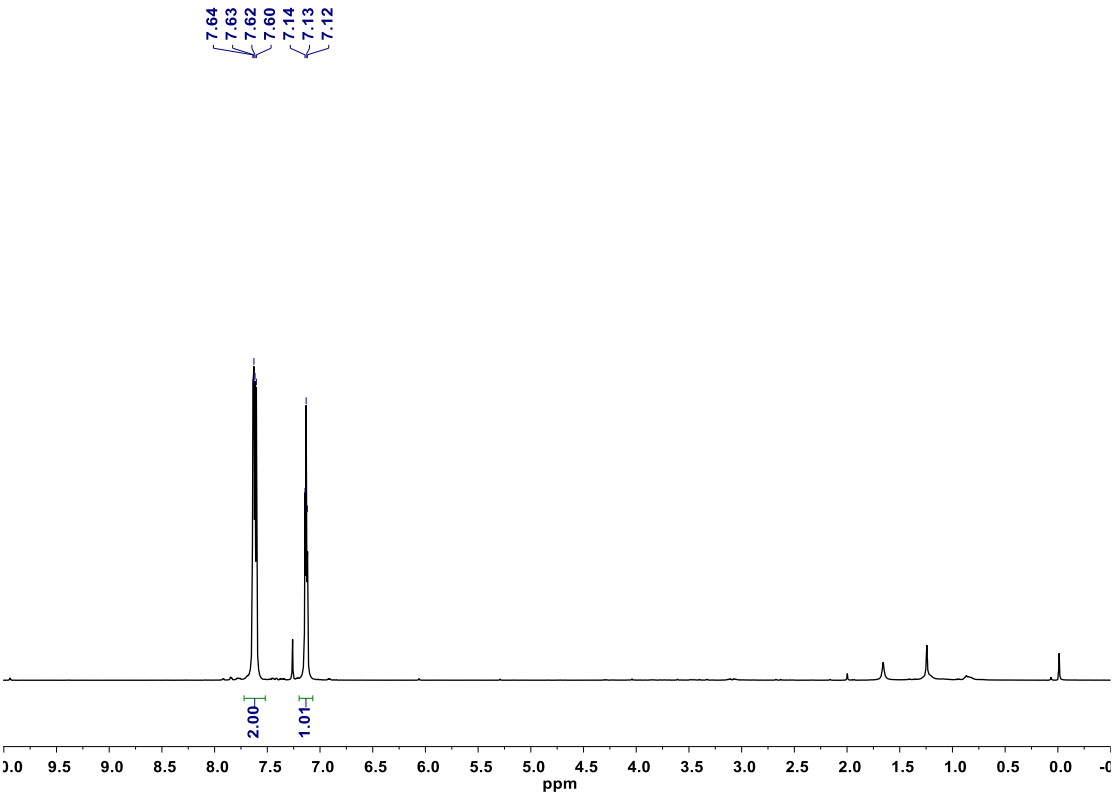
^{13}C NMR (101 MHz, $CDCl_3$):



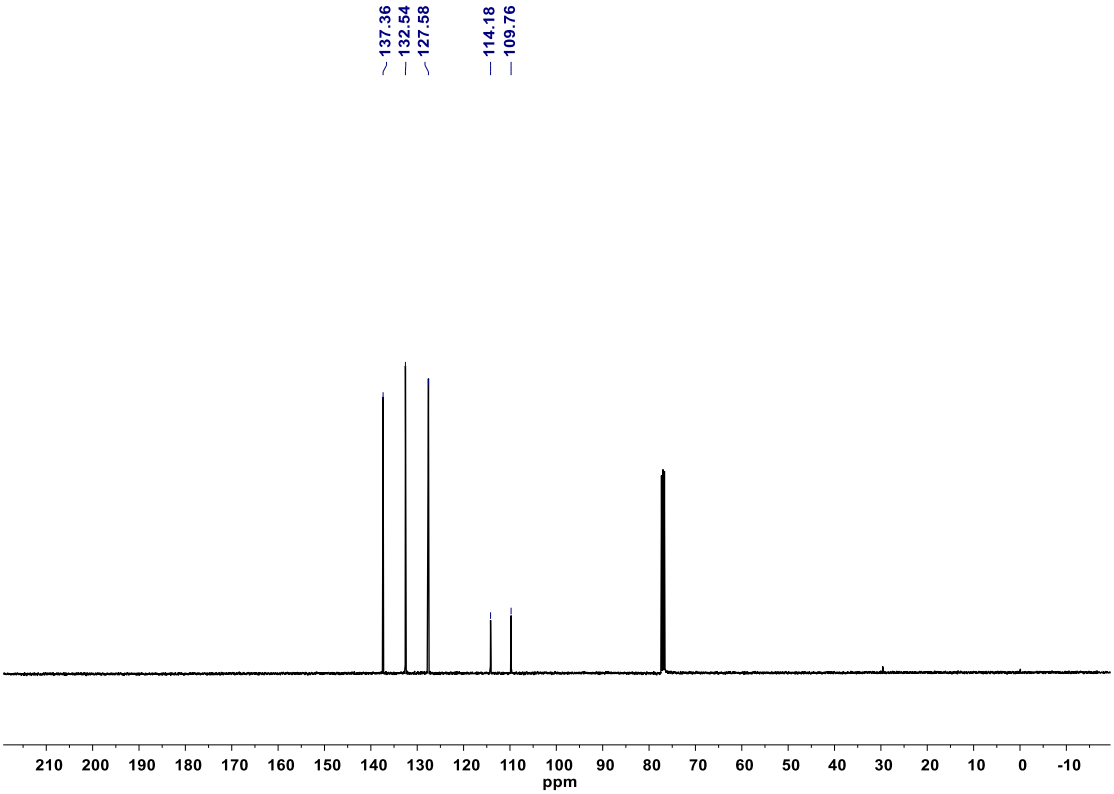


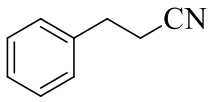
(2p)

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



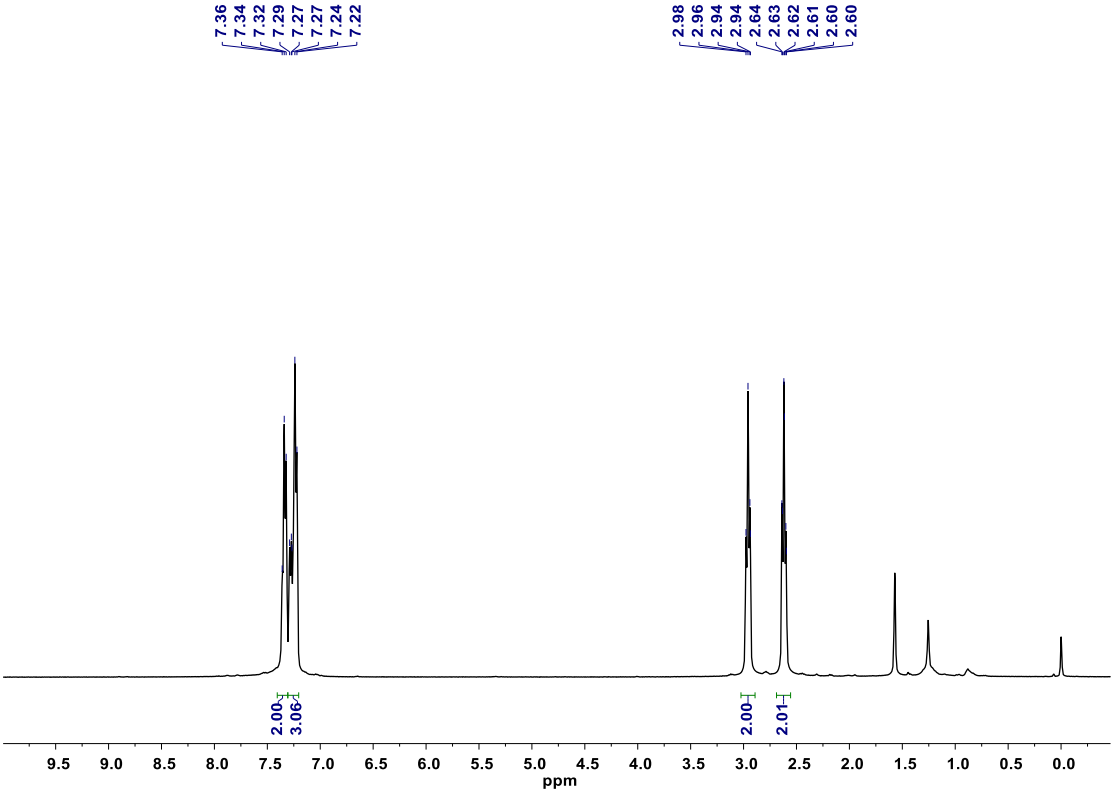
^{13}C NMR (101 MHz, $CDCl_3$):



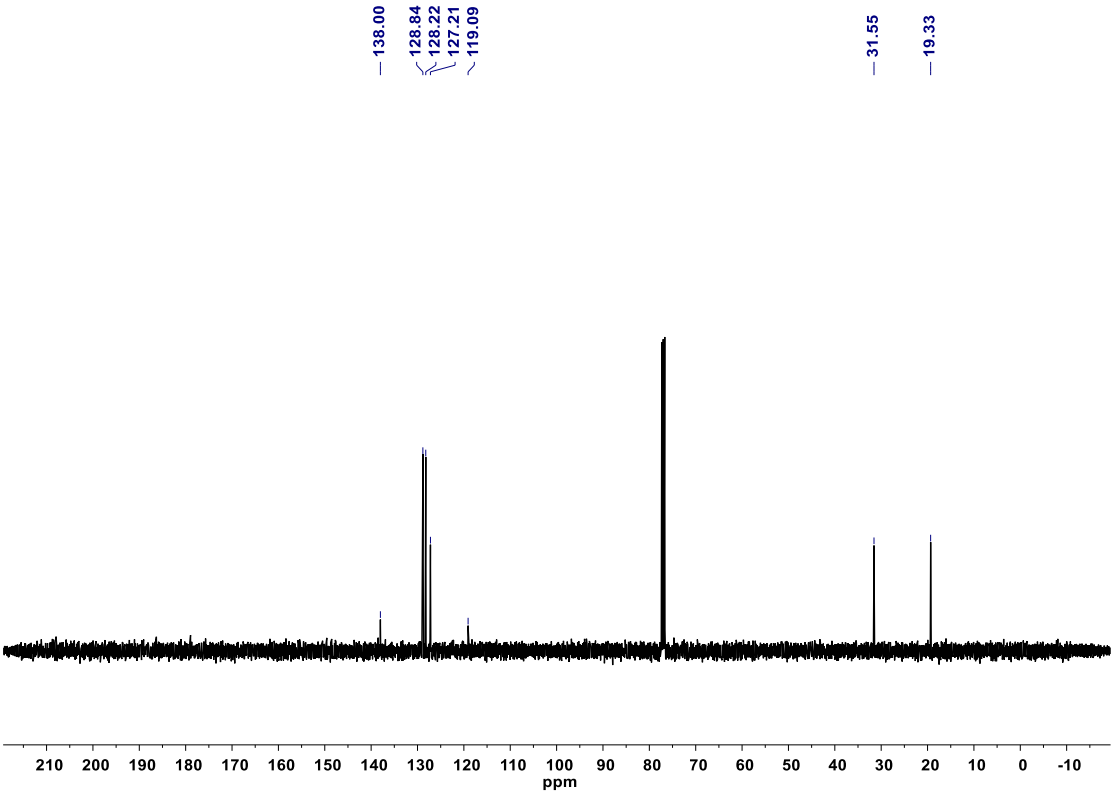


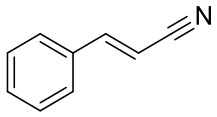
(2q)

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



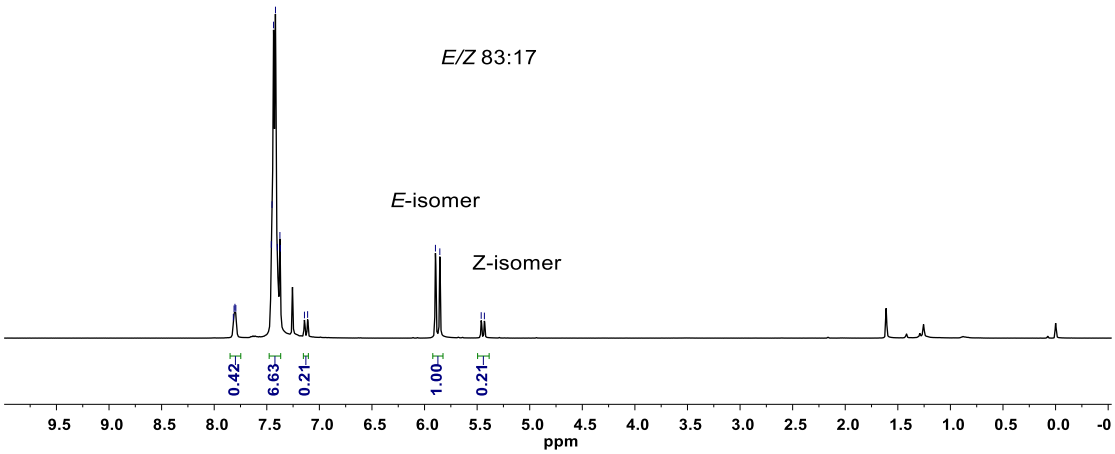
^{13}C NMR (101 MHz, $CDCl_3$):





(2r)

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



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