Supporting Information

Momentary Clicking Nitrile Synthesis by an Aminoazanium Reagent

Liangxuan Xu,[1,2] Yue Hu,[1] Xiang Zhu,[1] Lin He,[1] Qing Wu,[3] Chen Li,[3] Chungu Xia,[1] and Chao Liu[1,*]

[1] *State Key Laboratory for Oxo Synthesis and Selective Oxidation & CAS Key Laboratory of Chemistry of Northwestern Plant Resources, Suzhou Research Institute, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000*

[2] *University of Chinese Academy of Sciences, Beijing 100049*

[3] *China National Offshore Oil Corporation, Beijing, 100010*

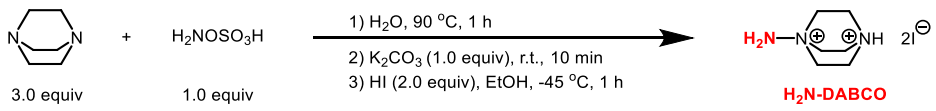
E-mail: chaoliu@licp.cas.cn

Table of Contents

General Information

All air and water sensitive reactions were carried out in oven-dried glassware under nitrogen. Toluene was purified using Pure Solv 7-SDS solvent drying system. THF (Superdry, water ⩽ 50.0 ppm) was purchased from Adamas-beta®. ^{n}BuLi (2.5 M in hexane) and ^{t}BuLi (1.3 M in pentane) were purchased from *J&K*. Unless otherwise noted, chemicals were purchased from Acros Organics, Alfa Aesar, TCI, Adamas-beta® and *J&K* without further purification. 3-([1,1'-Biphenyl]-4-yl)propiolaldehyde (**A-43**) was prepared according to the literature.[1] Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 100-200 mesh silica gel or through SepaBeamTM Machine SPB-3006012. Gas chromatographic analysis were performed on GC-2010 Plus gas chromatography instrument with FID detector and 1-cyanonaphthalene was added as an internal standard. GC-MS spectra were recorded on a GCMS-QP2010 SE. The High Resolution MS analyses were performed on Agilent 6530 Accurate-Mass Q-TOF LC/MS with ESI mode. The ^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (376 MHz) and ^{31}P NMR (162 MHz) data were recorded on 400 MHz spectrometer using $CDCl_3$, CD_2Cl_2 or DMSO-d_6 as solvent. For $CDCl_3$, ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.000 ppm) as the internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as the internal reference. For CD_2Cl_2, ^{1}H NMR spectra was recorded with CD_2Cl_2 (δ = 5.320 ppm) as the internal reference; ^{13}C NMR spectra was recorded with CD_2Cl_2 (δ = 53.84 ppm) as the internal reference. For DMSO-d_6, ^{1}H NMR spectra was recorded with DMSO (δ = 2.500 ppm) as the internal reference; ^{13}C NMR spectra was recorded with DMSO (δ = 39.52 ppm) as the internal reference.

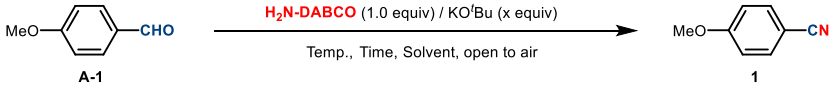
Modified Synthetic Procedure for H_2N-DABCO



H_2N-DABCO was synthesized according to our previous procedure with modifications.[2] To a 500 mL round-bottomed flask equipped with a magnetic stirring bar was added a solution of DABCO (168.3 g, 1.5 mol) in water (200 mL). Subsequently, a solution of H_2NOSO_3H (56.6 g, 0.5 mol) in water (100 mL) was added dropwise within 5 min. Then the mixture was heated at 90 °C for 1 hour. Upon completion, the mixture was cooled to room temperature, and K_2CO_3 (69.1 g, 0.5 mol) was added. The resulting

mixture was allowed to stir for 10 min. Then, the solvent was removed by vacuum-rotary evaporation, and the crude residue was washed by THF for 5 times (5 x 600 mL) to remove the excess DABCO. The residue was dissolved in 300 mL EtOH, followed by the filtration of K_2CO_3. The solution was cooled to -45 °C. Subsequently, 140 mL hydriodic acid (224.4 g, 1.0 mol, 57 wt.%) was added dropwise to the solution at -45 °C with stirring for 1 hour. Upon completion, the pale-yellow precipitate was filtrated and washed by cold EtOH to afford the desired product as a white powder (153.4 g, 80% yield).

Reaction Parameters for the Synthesis of Nitriles from Aldehydes

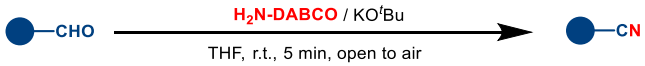


A-1 1

Entry	Solvent	Base (x equiv)	Temp.	Time (min)	Yield[a]
1	THF	none	25 °C	30	n.d.
2	THF	KO^{t}Bu (1.0)	25 °C	30	trace
3	THF	KO^{t}Bu (1.5)	25 °C	30	37%
4	**THF**	**KO^{t}Bu (2.0)**	**25 °C**	**2**	**96% (91%)[b]**
5	**THF**	**KO^{t}Bu (2.0)**	**25 °C**	**5**	**96%**
6	THF	KO^{t}Bu (2.0)	-60 °C	5	49%
7	**THF**	**KO^{t}Bu (3.0)**	**-60 °C**	**5**	**90%**
8	CH_3OH	KO^{t}Bu (2.0)	25 °C	5	7%
9	EtOH	KO^{t}Bu (2.0)	25 °C	5	52%
10	**^{i}PrOH**	**KO^{t}Bu (2.0)**	**25 °C**	**5**	**94%**
11	**^{t}BuOH**	**KO^{t}Bu (2.0)**	**25 °C**	**5**	**92%**
12	DMF	KO^{t}Bu (2.0)	25 °C	5	31%
13	DMAc	KO^{t}Bu (2.0)	25 °C	5	80%
14	Toluene	KO^{t}Bu (2.0)	25 °C	5	42%
15	CH_3CN	KO^{t}Bu (2.0)	25 °C	5	52%
16	Et_2O	KO^{t}Bu (2.0)	25 °C	5	11%
17	DCM	KO^{t}Bu (2.0)	25 °C	5	26%
18	DMSO	KO^{t}Bu (2.0)	25 °C	5	45%
19	Dioxane	KO^{t}Bu (2.0)	25 °C	5	60%
20	THF	K_2CO_3 (2.0)	25 °C	5	N.R.
21	THF	KOH (2.0)	25 °C	5	N.R.
22	THF	K_3PO_4 (2.0)	25 °C	5	N.R.
23	THF	NaOEt (2.0)	25 °C	5	60%
24	THF	NaO^{t}Bu (2.0)	25 °C	5	75%

Conditions: **A-1** (0.25 mmol), H_2N-DABCO (0.25 mmol), Solvent (2.0 mL), open to air. [a] Yield was determined by GC analysis with 1-cyanonaphthalene as the internal standard. [b] Isolated yield.

General Procedure A: Synthesis of Nitriles from Aldehydes



To a 15 mL vial equipped with a magnetic stirring bar was added H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL) in air. The reaction mixture was stirred for 5 min before adding aldehyde (0.25 mmol). Then the reaction mixture was allowed to stir for 5 min. Upon completion, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography through silica gel and eluted with petroleum ether/ethyl acetate to afford the desired nitrile. Products **2**-**66** in Fig. 2 were prepared according to this procedure.

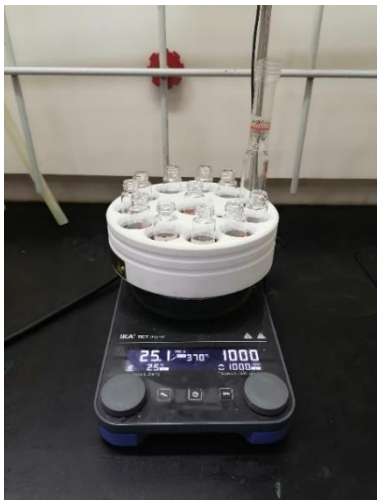
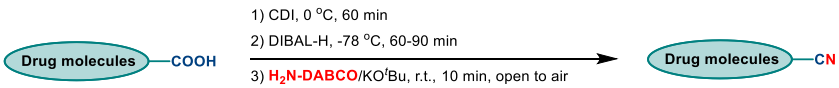


Figure S1. Reaction Setup for Procedure A

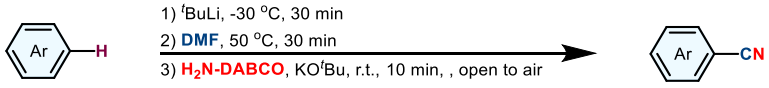
General Procedure B: Synthesis of Nitriles from Carboxylic Acids



To a 25 mL flame-dried resealable reaction tube of solvent flask equipped with a magnetic stirring bar was added carboxylic acid (0.50 mmol) and anhydrous dichloromethane (3.0 mL) under nitrogen. The solution was cooled to 0 °C. Then, 1,1'-carbonyldiimidazole (CDI, 0.75 mmol) was added. After stirring for 60 min, the reaction mixture was cooled to -78 °C for 15 min. Subsequently, DIBAL-H solution (2.0

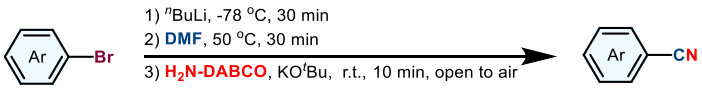
mmol, 1.0 M in hexane) was added dropwise with a syringe. The reaction mixture was stirred at -78 °C until completion with the indication by TLC (60 - 90 min). The resulting solution was added to the pre-prepared mixture (stirred for 5 min) of H_2N-DABCO (0.75 mmol), KO^{t}Bu (5.0 mmol) and THF (10 mL) in a 40 mL vial equipped with a magnetic stirring bar. The resulting mixture was allowed to stir for 10 min. Upon completion, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography through silica gel and eluted with petroleum ether/ethyl acetate to afford the desired nitriles. Products **67-72** in Fig. 3A were prepared according to this procedure.

General Procedure C: Synthesis of Nitriles from Aromatics



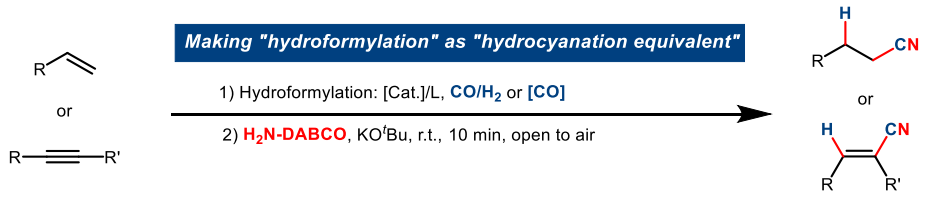
To a 25 mL flame-dried resealable reaction tube of solvent flask equipped with a magnetic stirring bar was added aromatic compound (0.50 mmol) and THF (2.0 mL) under nitrogen. The tube was sealed with Teflon screw cap and the reaction mixture was cooled to -30 °C. Subsequently, ^{t}BuLi (0.60 mmol, 1.3 M in pentane) was added to the mixture at this temperature and the resulting solution was stirred for 30 min before adding DMF (0.75 mmol). Then, the reaction mixture was stirred for 30 min at 50 °C. The resulting solution was added to the pre-prepared mixture (stirred for 5 min) of H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL) in a 25 mL vial equipped with a magnetic stirring bar. The resulting mixture was allowed to stir for 10 min. Upon completion, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 10.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography through silica gel and eluted with petroleum ether/ethyl acetate to afford the desired nitriles. Products **26, 27, 73-79** in Fig. 3B were prepared according to this procedure.

General Procedure D: Synthesis of Nitriles from Aryl Bromides



To a 25 mL flame-dried resealable reaction tube of solvent flask equipped with a magnetic stirring bar was added aryl bromide (0.50 mmol, 1.0 equiv) and THF (2.0 mL) under nitrogen. The tube was sealed with Teflon screw cap and the reaction mixture was cooled to -78 °C. Subsequently, ^{t}BuLi (1.2 equiv, 1.3 M in pentane) or ^{n}BuLi (1.1 ~ 3.3 equiv, 2.5 M in hexane) was added to the mixture at -78 °C and the resulting solution was stirred for 30 min before adding DMF (1.5 ~ 4.5 equiv). Then, the reaction mixture was stirred for 30 min at 50 °C. The resulting solution was added to the pre-prepared mixture (stirred for 5 min) of H_2N-DABCO (1.5 ~ 4.5 equiv), KO^{t}Bu (3.0 ~ 9.0 equiv) and THF (4.0 mL) in a 25 mL vial equipped with a magnetic stirring bar. The resulting mixture was allowed to stir for 10 min. Upon completion, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography through silica gel and eluted with petroleum ether/ethyl acetate to afford the desired nitriles. Products **2, 4, 33, 34, 80-93** in Fig. 3C were prepared according to this procedure.

General Procedure E: Synthesis of nitriles from alkenes and alkynes

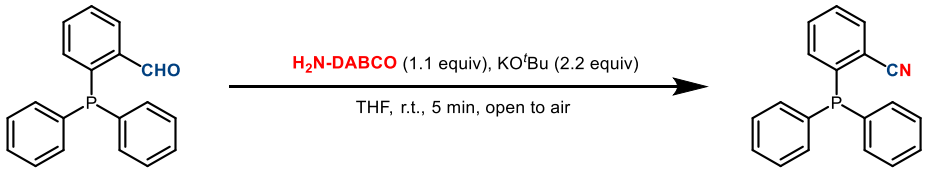


The hydroformylation of **HF-1** – **HF-9** was according to the literature,[3] the hydroformylation of **HF-10** was according to the literature,[4] the hydroformylation of **HF-11** was according to the literature[5] and the hydroformylation of **HF-12** was according to the literature.[6]

Synthesis of nitriles **44**, **94-101** by the "Hydrocyanation": In a glove box, to a glass tube equipped with a magnetic bar was added $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%) and toluene (0.5 mL). After stirring for 10 min, alkene (0.50 mmol) was charged to the reaction mixture. The glass tube was transferred into an autoclave and taken out of the glovebox. Then the autoclave was purged and charged with CO/H_2 (1:1, 10 bar). The reaction mixture was stirred at 50 °C for 12 hours. After the completion of the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. The resulting solution was added to the pre-prepared mixture (stirred for 5 min) of KO^{t}Bu (1.20 mmol), H_2N-DABCO (0.60 mmol) and THF (4.0 mL) in a 25 mL vial equipped with a magnetic stirring bar. The

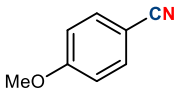
resulting mixture was allowed to stir for 10 min. Upon completion, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography through silica gel and eluted with petroleum ether/ethyl acetate to afford the desired nitriles. Products **44, 94-101** in Fig. 3D were prepared according to this procedure.

Gram-Scale Synthesis of 2-(Diphenylphosphaneyl)benzonitrile (38)

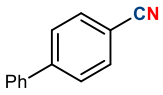


To a 250 mL round-bottomed flask equipped with a magnetic stirring bar was added H_2N-DABCO (22.0 mmol), KO^{t}Bu (44.0 mmol) and THF (100 mL) in air. The reaction mixture was stirred for 10 min before adding 2-(diphenylphosphaneyl)benzaldehyde (**A-38**, 20.0 mmol). Then the reaction mixture was allowed to stir for 5 min. Upon completion, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography (PE : EA = 10 : 1) to give 5.34 g (93% yield) of the desired product **38** as a white solid.

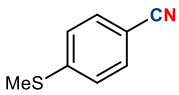
Detailed Descriptions for Products



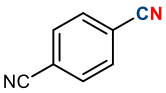
4-Methoxybenzonitrile (1).[7] Prepared according to the **General Procedure A** using 4-methoxybenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 61-62 °C, 30.1 mg, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 133.9, 119.2, 114.7, 103.9, 55.5 ppm.



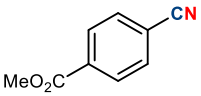
[1,1'-Biphenyl]-4-carbonitril (2).[8] Prepared according to the **General Procedure A** using [1,1'-biphenyl]-4-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 83-85 °C, 42.9 mg, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.59 – 7.57 (m, 2H), 7.50 – 7.46 (m, 2H), 7.44 – 7.40 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.7, 127.2, 118.9, 110.8 ppm.



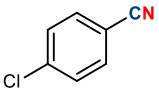
4-(Methylthio)benzonitrile (3).[7] Prepared according to the **General Procedure A** using 4-(methylthio)benzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 61-63 °C, 33.5 mg, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.28 – 7.25 (m, 2H), 2.51 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.1, 132.1, 125.4, 118.9, 107.5, 14.6 ppm.



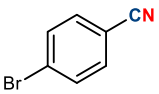
Terephthalonitrile (4).[7] Prepared according to the **General Procedure A** using 4-formylbenzonitrile (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 219-221 °C, 27.2 mg, 85% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.08 (s, 4H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 133.3, 117.6, 115.8 ppm.



Methyl-4-cyanobenzoate (5).[9] Prepared according to the **General Procedure A** using methyl-4-formylbenzoate (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.55 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 65-68 °C, 31.4 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.13 (m, 2H), 7.77 – 7.74 (m, 2H), 3.97 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 133.9, 132.2, 130.1, 117.9, 116.3, 52.7 ppm.

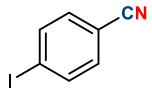


4-Chlorobenzonitrile (6).[7] Prepared according to the **General Procedure A** using 4-chlorobenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 93-95 °C, 28.2 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 133.2, 129.5, 117.8, 110.6 ppm.

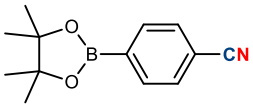


4-Bromobenzonitrile (7).[9] Prepared according to the **General Procedure A** using 4-bromobenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL).

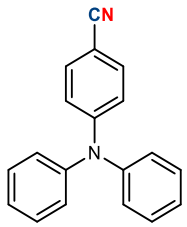
Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 112-114 °C, 38.6 mg, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.55 – 7.51 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.4, 132.6, 128.0, 118.0, 111.2 ppm.



4-Iodobenzonitrile (8).[7] Prepared according to the **General Procedure A** using 4-iodobenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 122-125 °C, 48.2 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 133.1, 118.2, 111.7, 100.3 ppm.

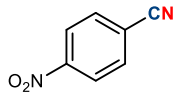


4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (9).[10] Prepared according to the **General Procedure A** using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (0.25 mmol), H_2N-DABCO (0.55 mmol), KO^{t}Bu (1.10 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 96-97 °C, 49.8 mg, 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 1.35 (s, 12H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.0, 131.0, 118.7, 114.5, 84.4, 24.8 ppm.



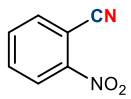
4-(Diphenylamino)benzonitrile (10).[11] Prepared according to the **General Procedure A** using 4-(diphenylamino)benzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF

(2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 125-126 °C, 64.2 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.32 (m, 4H), 7.15 (m, 6H), 6.99 – 6.92 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 145.9, 133.1, 129.7, 126.1, 125.1, 119.6, 102.4 ppm.



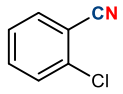
4-Nitrobenzonitrile (11).[7] Prepared according to the **General Procedure A** using 4-nitrobenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 143-146 °C, 31.2 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 – 8.35 (m, 2H), 7.92 – 7.89 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0, 133.4, 124.3, 118.3, 116.8 ppm.

3-Nitrobenzonitrile (12).[10] Prepared according to the **General Procedure A** using 3-nitrobenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a yellow solid, m.p. 113-115 °C, 29.5 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 – 8.54 (m, 1H), 8.51 – 8.48 (m, 1H), 8.03 – 8.01 (m, 1H), 7.78 – 7.74 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2, 137.6, 130.6, 127.5, 127.2, 116.5, 114.1 ppm.

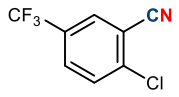


2-Nitrobenzonitrile (13).[9] Prepared according to the **General Procedure A** using 2-nitrobenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 107-109 °C, 37.1 mg, 90% yield. **^{1}H NMR** (400 MHz,

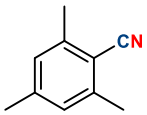
$CDCl_3$) δ 8.38 – 8.34 (m, 1H), 7.97 – 7.93 (m, 1H), 7.89 – 7.84 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.5, 135.6, 134.3, 133.7, 125.5, 114.9, 108.0 ppm.



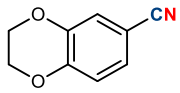
2-Chlorobenzonitrile (14).[12] Prepared according to the **General Procedure A** using 2-chlorobenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 43-44 °C, 30.0 mg, 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 1H), 7.62 – 7.46 (m, 2H), 7.40 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 133.9, 133.8, 130.0, 127.1, 115.9, 113.3 ppm.



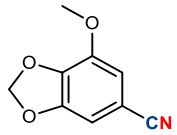
2-Chloro-5-(trifluoromethyl)benzonitrile (15).[7] Prepared according to the **General Procedure A** using 2-chloro-5-(trifluoromethyl)benzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 48.8 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5, 130.8, 130.7, 130.4 (q, J = 3.0 Hz), 129.7 (q, J = 34.3 Hz), 122.5 (q, J = 273.7 Hz), 114.4, 114.1 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.10 ppm.



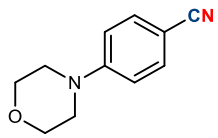
2,4,6-Trimethylbenzonitrile (16).[10] Prepared according to the **General Procedure A** using 2,4,6-trimethylbenzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 54-56 °C, 33.3 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 2.48 (s, 6H), 2.32 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.8, 142.0, 128.2, 117.6, 110.3, 21.6, 20.6 ppm.



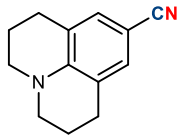
2,3-Dihydrobenzo[*b*][1,4]dioxine-6-carbonitrile (17).[7] Prepared according to the **General Procedure A** using 2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.55 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 103-105 °C, 38.2 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.13 (m, 2H), 6.93 – 6.90 (m, 1H), 4.34 – 4.31 (m, 2H), 4.30 – 4.27 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 143.7, 125.8, 121.2, 118.8, 118.2, 104.4, 64.5, 64.0 ppm.



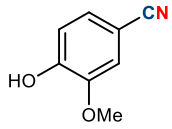
7-Methoxybenzo[*d*][1,3]dioxole-5-carbonitrile (18).[13] Prepared according to the **General Procedure A** using 7-methoxybenzo[*d*][1,3]dioxole-5-carbaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.55 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 5 : 1) to give a white solid, m.p. 115-116 °C, 93% yield. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 6.88 (d, *J* = 1.2 Hz, 1H), 6.79 (d, *J* = 1.6 Hz, 1H), 6.06 (s, 2H), 3.90 (s, 3H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 149.6, 144.4, 140.2, 119.2, 113.6, 106.4, 105.4, 103.2, 57.3 ppm.



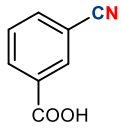
4-Morpholinobenzonitrile (19).[10] Prepared according to the **General Procedure A** using 4-morpholinobenzaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.80 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 82-83 °C, 42.1 mg, 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 6.89 – 6.85 (m, 2H), 3.86 – 3.84 (m, 4H), 3.29 – 3.27 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.4, 133.4, 119.8, 114.0, 100.8, 66.4, 47.2 ppm.



2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*i*,*j*]quinoline-9-carbonitrile (20). Prepared according to the **General Procedure A** using 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline-9-carbaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.80 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 115-117 °C, 48.5 mg, 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 (s, 2H), 3.24 (t, *J* = 5.6 Hz, 4H), 2.69 (t, *J* = 6.4 Hz, 4H), 1.96 – 1.90 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.7, 130.5, 121.2, 120.8, 95.5, 49.7, 27.4, 21.0 ppm. **HRMS** (ESI) calcd for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230; found: 199.1232.



4-Hydroxy-3-methoxybenzonitrile (21).[7] Prepared according to the **General Procedure A** using 4-hydroxy-3-methoxybenzaldehyde (0.25 mmol), H_2N-DABCO (0.63 mmol), KO^{t}Bu (1.25 mmol) and THF (5.0 mL) + DMF (1.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 2 : 1) to give a white solid, m.p. 85-87 °C, 28.0 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 1H), 7.09 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.38 (s, 1H), 3.93 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0, 146.7, 126.7, 119.1, 115.2, 113.8, 102.7, 56.0 ppm.

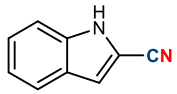


3-Cyanobenzoic acid (22).[14] Prepared according to the **General Procedure A** using 3-formylbenzoic acid (0.25 mmol), H_2N-DABCO (0.63 mmol), KO^{t}Bu (1.25 mmol) and THF (5.0 mL) + DMF (1.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 2 : 1) to give a white solid, m.p. 221-222 °C, 30.2 mg, 82% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 13.55 (s, 1H), 8.31 – 8.23 (m, 2H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.78 –

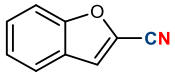
7.74 (m, 1H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.7, 136.2, 133.7, 132.8, 132.2, 130.0, 118.1, 112.0 ppm.

2-Aminonicotinonitrile (23).[15] Prepared according to the **General Procedure A** using 2-aminonicotinaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.55 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 5 : 1) to give a white solid, m.p. 127-139 °C, 28.8 mg, 97% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.19 (d, J = 4.8 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 6.87 (s, 2H), 6.63 (m, 1H). ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 153.2, 142.2, 117.0, 112.0, 89.2 ppm.

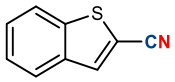
1-Methyl-1*H*-indole-3-carbonitrile (24).[16] Prepared according to the **General Procedure A** using 1-methyl-1*H*-indole-3-carbaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.80 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 35.9 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 1H), 7.52 (s, 1H), 7.39 – 7.25 (m, 3H), 3.82 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.9, 135.5, 127.7, 123.7, 122.0, 119.7, 115.9, 110.3, 85.2, 33.5 ppm.



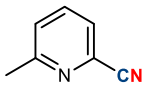
1*H*-indole-2-carbonitrile (25).[17] Prepared according to the **General Procedure A** using 1*H*-indole-2-carbaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.80 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, 33.8 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.46 – 7.30 (m, 2H), 7.26 – 7.12 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 126.2, 126.1, 122.0, 121.6, 114.4, 111.8(1), 111.8(0), 105.9 ppm.



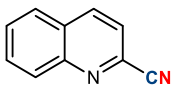
Benzofuran-2-carbonitrile (26).[10] Prepared according to the **General Procedure A** using benzofuran-2-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 35.8 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.24 (s, 1H), 7.18 – 7.16 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 128.4, 127.3, 125.5, 124.5, 122.5, 118.4, 112.1, 111.8 ppm.



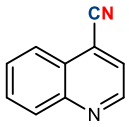
Benzo[*b*]thiophene-2-carbonitrile (27).[18] Prepared according to the **General Procedure A** using benzo[*b*]thiophene-2-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 39.8 mg, 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 3H), 7.55 – 7.51 (m, 1H), 7.49 – 7.45 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 137.4, 135.0, 127.8, 125.7, 125.2, 122.3, 114.4, 109.6 ppm.



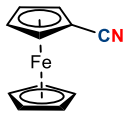
6-Methylpicolinonitrile (28).[19] Prepared according to the **General Procedure A** using 6-methylpicolinaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 70-73 °C, 23.1 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0, 1H), 2.62 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 137.0, 133.1, 126.9, 125.7, 117.4, 24.4 ppm.



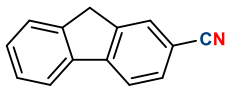
Quinoline-2-carbonitrile (29).[18] Prepared according to the **General Procedure A** using quinoline-2-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 94-96 °C, 36.9 mg, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.98 – 7.81 (m, 2H), 7.73 – 7.69 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 137.4, 133.5, 131.2, 129.9, 129.4, 128.6, 127.7, 123.2, 117.5 ppm.



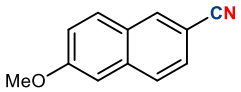
Quinoline-4-carbonitrile (30).[18] Prepared according to the **General Procedure A** using quinoline-4-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 101-103 °C, 36.1 mg, 94% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 4.0 Hz, 1H), 8.23 – 8.19 (m, 2H), 7.90 – 7.86 (m, 1H), 7.79 – 7.74 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 148.1, 131.1, 130.3, 129.2, 125.7, 124.9, 124.8, 118.6, 115.5 ppm.



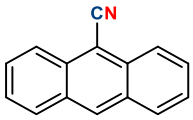
Ferrocenecarbonitrile (31).[20] Prepared according to the **General Procedure A** using ferrocenecarboxaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.55 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 5 : 1) to give a yellow solid, m.p. 106-109 °C, 48.8 mg, 93% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.66 (t, *J* = 2.0 Hz, 2H), 4.39 (t, *J* = 2.0 Hz, 2H), 4.34 (m, 5H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 120.2, 71.7, 70.7, 70.5, 51.8 ppm.



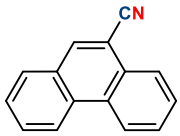
9*H*-fluorene-2-carbonitrile (32).[21] Prepared according to the **General Procedure A** using 9*H*-fluorene-2-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL), N_2 protection. Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 50 : 1) to give a white solid, m.p. 90-91 °C, 40.1 mg, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 3H), 7.59 (d, *J* =8.0 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.41 – 7.24 (m, 2H), 3.83 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.1, 143.8, 143.5, 139.8, 131.0, 128.5, 127.2, 125.2, 120.9, 120.2, 119.6, 109.5, 36.6 ppm.



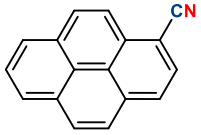
6-Methoxy-2-naphthonitrile (33).[22] Prepared according to the **General Procedure A** using 6-methoxy-2-naphthaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 105-106 °C, 42.2 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.78 – 7.75 (m, 2H), 7.56 – 7.53 (m, 1H), 7.25 – 7.22 (m, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 3.94 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 136.4, 133.7, 129.9, 127.8, 127.7, 127.0, 120.6, 119.5, 106.7, 105.9, 55.4 ppm.



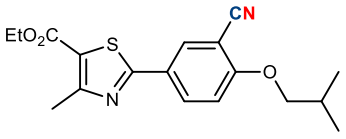
Anthracene-9-carbonitrile (34).[7] Prepared according to the **General Procedure A** using anthracene-9-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a yellow solid, m.p. 175-178 °C, 49.5 mg, 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.32 – 8.30 (m, 2H), 7.98 – 7.96 (m, 2H), 7.66 – 7.62 (m, 2H), 7.53 – 7.49 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.1, 132.6, 130.4, 128.8(3), 128.8(0), 126.2, 125.1, 117.2, 105.2 ppm.



Phenanthrene-9-carbonitrile (35).[23] Prepared according to the **General Procedure A** using phenanthrene-9-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 109-111 °C, 48.6 mg, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 – 8.58 (m, 2H), 8.25 – 8.21 (m, 1H), 8.14 (s, 1H), 7.86 – 7.83 (m, 1H), 7.77 – 7.68 (m, 3H), 7.65 – 7.61 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.5, 131.6, 129.8, 129.7, 129.6, 129.4, 128.7, 128.1, 128.0, 127.5, 125.9, 123.0, 122.7, 117.9, 109.2 ppm.

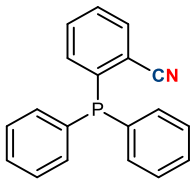


Pyrene-1-carbonitrile (36).[10] Prepared according to the **General Procedure A** using pyrene-1-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a yellow solid, m.p. 148-150 °C, 54.3 mg, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 3H), 8.00 – 7.94 (m, 4H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.7, 132.4, 130.4, 130.1(0), 130.0(8), 130.0, 129.1, 126.8, 126.6(9), 126.6(6), 126.5, 124.0, 123.4(2), 123.3(7), 123.0, 118.7, 105.1 ppm.

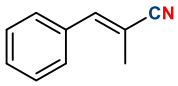


Ethyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (37).[24] Prepared according to the **General Procedure A** using ethyl 2-(3-formyl-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 5 : 1) to give a white solid, m.p. 168-170 °C, 73.2 mg, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 4.0 Hz, 1H), 8.08 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.90 (d, *J* =

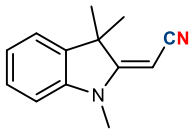
6.4 Hz, 2H), 2.76 (s, 3H), 2.24 – 2.17 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.09 (d, *J* = 6.4 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 162.5, 162.0, 161.1, 132.5, 132.0, 126.1, 121.9, 115.3, 112.6, 103.0, 75.7, 61.3, 28.1, 19.0, 17.4, 14.3 ppm.



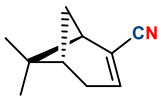
2-(Diphenylphosphaneyl)benzonitrile (38).[25] Prepared according to the **General Procedure A** using 2-(diphenylphosphaneyl)benzaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 154-155 ^{o}C, 63.9 mg, 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (m, 1H), 7.50 – 7.26 (m, 12H), 7.04 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0 (d, *J* = 20.2 Hz), 134.7 (d, *J* = 10.1 Hz), 134.0 (d, *J* = 20.2 Hz), 133.7 (d, *J* = 5.1 Hz), 133.4, 132.3, 129.4, 128.8 (d, *J* = 7.1 Hz), 118.1, 117.8, 117.5 (d, *J* = 4.0 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -8.46 ppm.



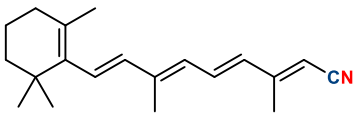
(*E*)-2-Methyl-3-phenylacrylonitrile (39).[26] Prepared according to the **General Procedure A** using (*E*)-2-methyl-3-phenylacrylaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.55 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a yellow oil, 31.8 mg, 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 3H), 7.34 – 7.32 (m, 2H), 7.22 – 7.21 (m, 1H), 2.15 (d, *J* = 1.6 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 134.1, 129.3, 129.2, 128.6, 121.3, 109.6, 16.8 ppm.



(*E*)-2-(1,3,3-Trimethylindolin-2-ylidene)acetonitrile (40).[27] Prepared according to the **General Procedure A** using (*E*)-2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.80 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1, *E*/*Z* = 98 : 2) to give a white solid, m.p. 113-116 °C, 45.7 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 7.00 – 6.95 (m, 1H), 6.79 – 6.71 (m, 1H), 4.11 – 4.03 (m, 1H), 3.11 (s, 3H), 1.67 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 143.7, 137.7, 127.8, 121.8, 121.6, 120.2, 106.8, 58.1, 46.9, 29.0, 25.7 ppm.

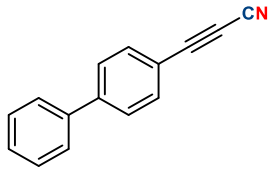


(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbonitrile (41).[28] Prepared according to the **General Procedure A** using (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.80 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 27.3 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.57 – 6.56 (m, 1H), 2.53 – 2.38 (m, 4H), 2.19 – 2.14 (m, 1H), 1.33 (s, 3H), 1.27 – 1.24 (m, 1H), 0.89 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 120.9, 118.5, 44.5, 39.7, 38.1, 32.6, 31.2, 25.6, 20.9 ppm.

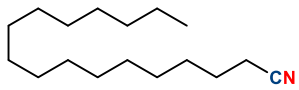


(2*E*,4*E*,6*E*,8*E*)-3,7-Dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraenenitrile (42).[29] Prepared according to the **General Procedure A** using (2*E*,4*E*,6*E*,8*E*)-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraenal (0.25 mmol, *E*/*Z* = 96 : 4), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1, *E*/*Z* = 94 : 6) to give a yellow oil, 60.3 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 – 6.79 (m, 1H), 6.35 – 6.27 (m, 2H), 6.16 – 6.10 (m, 2H), 5.18 (s, 0.94H), 5.07 (s, 0.06H), 2.22 (s, 3H), 2.04 – 2.01 (m, 5H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.65 – 1.59 (m, 2H), 1.49 – 1.46 (m, 2H), 1.03 (s, 6H) ppm; **^{13}C NMR** (101

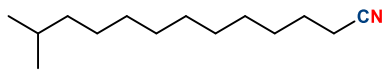
MHz, $CDCl_3$) δ 156.9, 141.3, 137.5, 136.9, 132.5, 131.2, 130.4, 129.6, 128.7, 118.2, 96.4, 39.5, 34.2, 33.1, 28.9, 21.7, 19.1, 16.6, 12.9 ppm.



3-([1,1'-biphenyl]-4-yl)propiolonitrile (43).[30] Prepared according to the **General Procedure A** using 3-([1,1'-biphenyl]-4-yl)propiolaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and ^{i}PrOH (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 98-100 °C, 39.1 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.53 (m, 6H), 7.51 – 7.37 (m, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 139.3, 133.9, 129.0, 128.5, 127.4, 127.1, 116.0, 105.5, 83.1, 63.6 ppm.

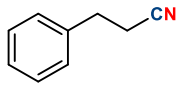


Heptadecanenitrile (44).[31] Prepared according to the **General Procedure A** using heptadecanal (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 50 : 1) to give a white solid, m.p. 34-35 °C, 46.4 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.33 (t, J = 6.8 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.33 – 1.21 (m, 26H), 0.88 (t, J = 7.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 119.8, 31.9, 29.7, 29.6(4), 29.6(3), 29.6(2), 29.6(0), 29.5(5), 29.5, 29.3(2), 29.2(6), 28.7, 28.6, 25.4, 22.7, 17.1, 14.1 ppm.

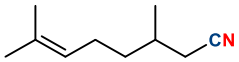


12-Methyltridecanenitrile (45).[32] Prepared according to the **General Procedure A** using 12-methyltridecanal (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE) to give a colorless oil, 42.0 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.33 (t,

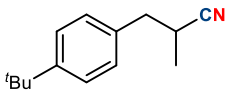
J = 7.2 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.61 – 1.49 (m, 1H), 1.49 – 1.40 (m, 2H), 1.33 – 1.23 (m, 12H), 1.15 (m, 2H), 0.86 (d, J = 6.8 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 119.8, 39.0, 29.8, 29.6, 29.5, 29.3, 28.7, 28.6, 27.9, 27.3, 25.4, 22.6, 17.1 ppm.



3-Phenylpropanenitrile (46).[9] Prepared according to the **General Procedure A** using 3-phenylpropanal (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 25.5 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.24 – 7.18 (m, 2H), 2.91 (t, J = 7.6 Hz, 2H), 2.57 (t, J = 7.2 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0, 128.7, 128.1, 127.1, 119.0, 31.4, 19.1 ppm.

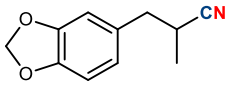


3,7-Dimethyloct-6-enenitrile (47).[10] Prepared according to the **General Procedure A** using 3,7-dimethyloct-6-enal (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 26.9 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.09 – 5.05 (m, 1H), 2.36 – 2.21 (m, 2H), 2.04 – 1.98 (m, 2H), 1.91 – 1.82 (m, 1H), 1.69 (d, J = 1.2 Hz, 3H), 1.61 (d, J = 1.6 Hz, 3H), 1.51 – 1.42 (m, 1H), 1.39 – 1.30 (m, 1H), 1.09 (d, J = 6.8 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.2, 123.4, 118.9, 35.8, 29.9, 25.7, 25.2, 24.4, 19.3, 17.7 ppm.

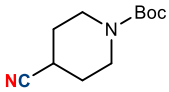


3-(4-(*tert*-Butyl)phenyl)-2-methylpropanenitrile (48).[33] Prepared according to the **General Procedure A** using 3-(4-(*tert*-butyl)phenyl)-2-methylpropanal (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 42.3 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.18 – 7.14 (m, 2H), 2.94 – 2.89 (m,

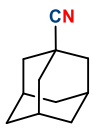
1H), 2.85 – 2.76 (m, 2H),1.33 – 1.31 (m, 12H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 133.8, 128.7, 125.6, 122.7, 39.5, 34.5, 31.3, 27.5, 17.6 ppm.



3-(Benzo[*d*][1,3]dioxol-5-yl)-2-methylpropanenitrile (49).[10] Prepared according to the **General Procedure A** using 3-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropanal (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 40.5 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.78 – 6.76 (m, 1H), 6.71 – 6.67 (m, 2H), 5.94 (s, 2H), 2.86 – 2.72 (m, 3H), 1.32 (d, *J* = 6.8 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 146.7, 130.5, 122.4, 122.2, 109.2, 108.3, 101.0, 39.6, 27.7, 17.4 ppm.

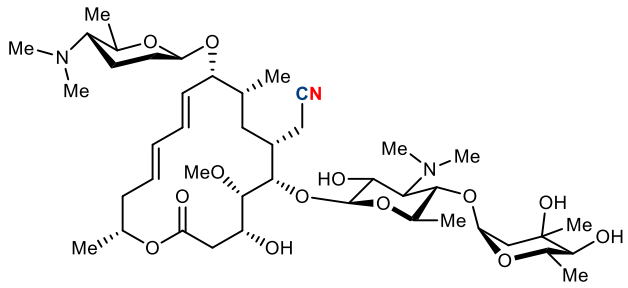


***tert*-Butyl 4-cyanopiperidine-1-carboxylate (50).**[34] Prepared according to the **General Procedure A** using *tert*-butyl-4-formylpiperidine-1-carboxylate (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 49-51 °C, 49.6 mg, 94% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.69 – 3.63 (m, 2H), 3.37 – 3.30 (m, 2H), 2.84 – 2.78 (m, 1H), 1.92 – 1.85 (m, 2H), 1.83 – 1.75 (m, 2H), 1.46 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.3, 121.0, 80.0, 41.6, 28.3(3), 28.2(7), 26.2 ppm.



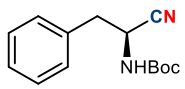
1-Adamantanecarbonitrile (51).[20] Prepared according to the **General Procedure A** using (3*r*,5*r*,7*r*)-adamantane-1-carbaldehyde (0.25 mmol), H_2N-DABCO (0.25 mmol), KO^{t}Bu (0.50 mmol) and THF (2.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 186-187 °C, 38.5 mg, 96%

yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.05 – 2.02 (m, 9H), 1.77 – 1.70 (m, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 125.2, 39.8, 35.7, 30.1, 27.0 ppm.

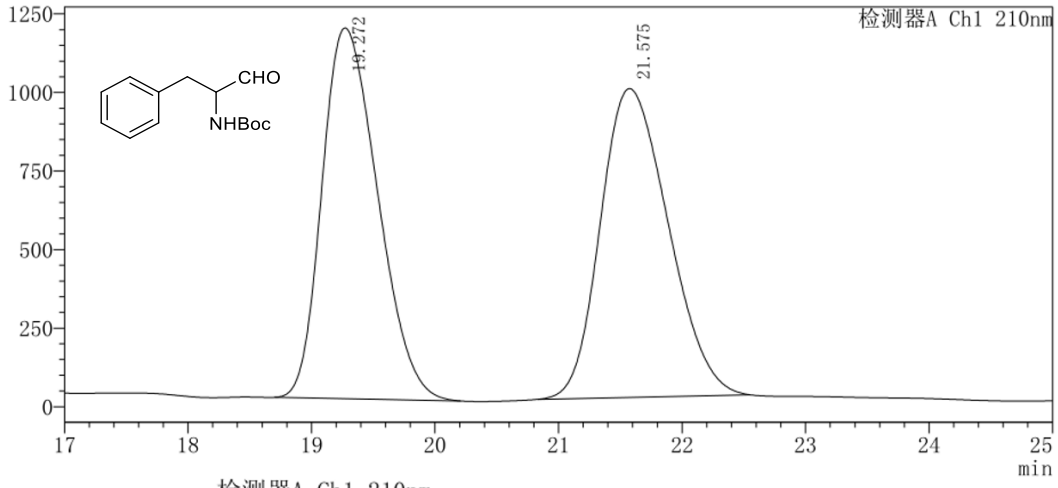


Product **A**

Product **A (52).**[35] Prepared according to the **General Procedure A** using spiramycin (0.25 mmol), H_2N-DABCO (0.28 mmol), KO^{t}Bu (0.55 mmol) and THF (5.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and the organic layer was separated and the aqueous layer was extracted with EA (2 × 10.0 mL). The combined organic layer was washed with saturated brine (10.0 mL) and dried over anhydrous Na_2SO_4. Then solvent was evaporated in vacuum. The crude product was dissolved in 1.0 mL of DCM. Then, 5.0 mL of hexane was added. After 10 min, the by-products were settled on the bottom of the flask. The milk white upper layer was filtered out and concentrated under vacuum to remove solvents to afford purified Product **A** (white solid), 199.2 mg, 95% yield，$[\alpha]_D^{25}$ = -29.8 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.21 – 6.15 (m, 1H), 6.03 – 5.89 (m, 1H), 5.66 – 5.60 (m, 1H), 5.56 – 5.48 (m, 1H), 5.23 – 5.18 (m, 1H), 5.03 – 5.01 (m, 1H), 4.53 – 4.51 (m, 1H), 4.40 – 4.37 (m, 1H), 4.14 – 4.11 (m, 1H), 4.06 – 4.00 (m, 2H), 3.67 (d, *J* = 10.8 Hz, 1H), 3.57 – 3.52 (m, 1H), 3.45 (s, 3H), 3.40 – 3.56 (m, 1H), 3.33 – 3.29 (m, 1H), 3.25 – 3.21 (m, 1H), 3.00 – 2.98 (m, 1H), 2.88 (d, *J* = 9.6 Hz, 1H), 2.78 (s, 2H), 2.66 – 2.53 (m, 2H), 2.44 (s, 9H), 2.15 (s, 8H), 2.07 – 1.89 (m, 4H), 1.83 – 1.75 (m, 2H), 1.72 – 1.67 (m, 1H), 1.56 – 1.35 (m, 3H), 1.27 – 1.16 (m, 16H), 0.99 – 0.89 (m, 4H), 0.85 – 0.78 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 134.4, 132.6, 130.9, 128.5, 119.4, 103.5, 100.3, 96.4, 84.6, 79.2, 78.7, 76.2, 75.1, 73.7, 72.9, 71.1, 69.3, 69.2, 68.7, 68.1, 65.8, 64.7, 61.6, 46.7, 41.8, 41.7, 40.8, 40.5, 37.5, 31.4, 31.1, 30.6, 29.1, 25.3, 22.4, 19.9, 18.8(3), 18.8(1), 18.7, 18.2, 18.1, 15.2, 13.9 ppm.

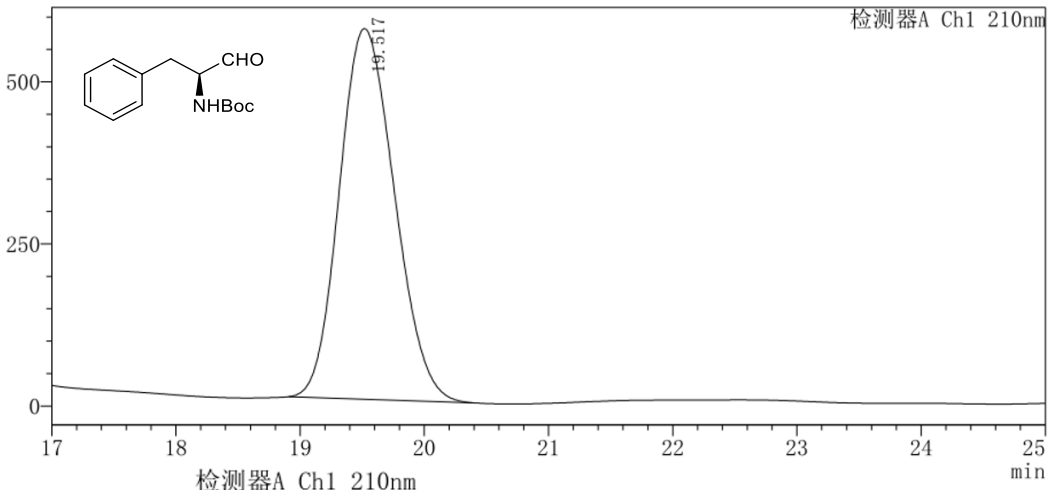


***tert*-Butyl (*S*)-(1-cyano-2-phenylethyl)carbamate (53)**.[35] To a 15 mL vial equipped with a magnetic stirring bar was added KO^{t}Bu (1.00 mmol), H_2N-DABCO (0.25 mmol) and THF (2.0 mL) in air. The reaction mixture was stirred for 5 min and then cooled to -60 °C stirring for 5 min. Subsequently, *tert*-butyl (*S*)-(1-cyano-2-phenylethyl)carbamate (0.25 mmol) was added to the mixture at -60 °C and the resulting solution was stirred for 1 hour. Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : MTBE = 10 : 1) to give a white solid, m.p. 113-115 °C, 44.3 mg, 72% yield. The ee of the product was determined by HPLC using an AD-H column (*n*-hexane/*i*-PrOH = 95:5), flow rate 0.75 mL/min, λ = 210 nm, τ_{maj} = 21.7 min, τ_{min} = 20.8 min; $[\alpha]_D^{25}$ = -9.7 (*c* 1.00, $CHCl_3$), ee > 99%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.19 (m, 5H), 4.88 (m, 2H), 3.18 – 2.99 (m, 2H), 1.44 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.1, 133.9, 129.4, 128.9, 127.8, 118.4, 81.2, 43.3, 39.1, 28.1 ppm.



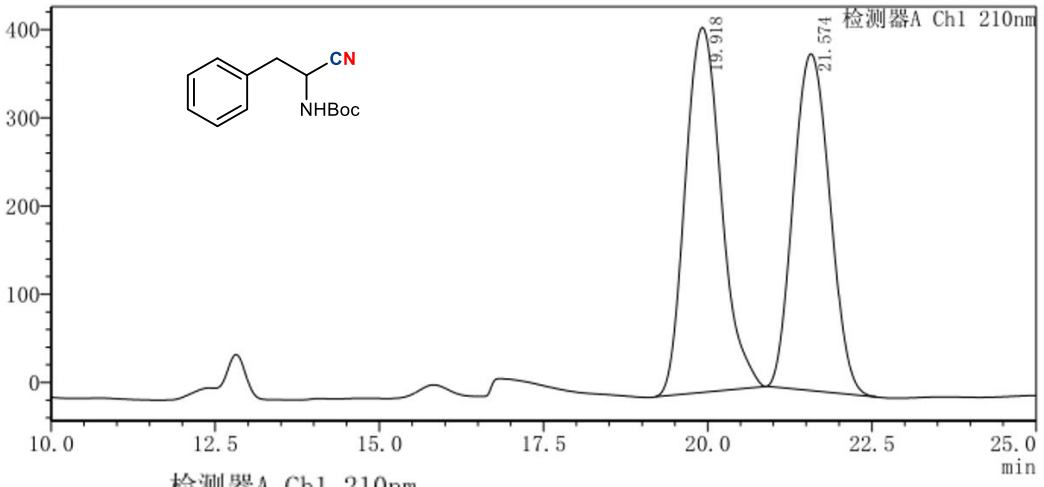
检测器A Ch1 210nm

峰号	保留时间	面积	高度	面积%
1	19.272	36978095	1180269	49.643
2	21.575	37510527	982943	50.357
总计		74488622	2163212	100.000



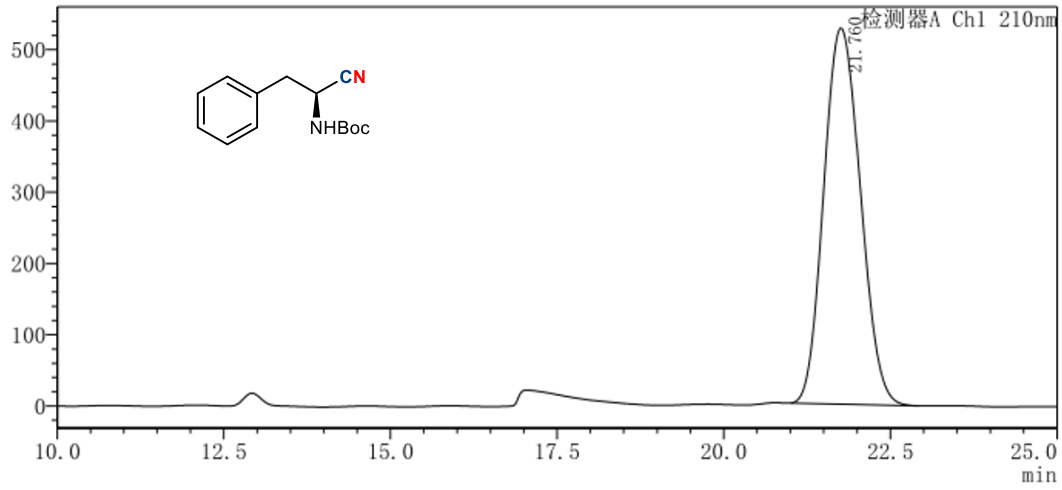
检测器A Ch1 210nm

峰号	保留时间	面积	高度	面积%
1	19.517	17661825	571774	100.000
总计		17661825	571774	100.000



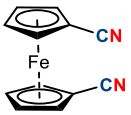
检测器A Ch1 210nm

峰号	保留时间	面积	高度	面积%
1	19.918	15765817	413427	51.699
2	21.574	14729493	381664	48.301
总计		30495310	795092	100.000

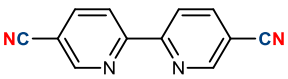


检测器A Ch1 210nm

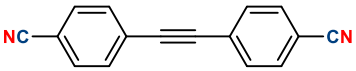
峰号	保留时间	面积	高度	面积%
1	21.760	20141576	527811	100.000
总计		20141576	527811	100.000



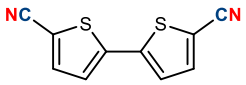
1,1'-Ferrocenedicarbonitrile (54).[36] Prepared according to the **General Procedure A** using 1,1'-Ferrocenedicarboxaldehyde (0.25 mmol), H_2N-DABCO (0.55 mmol), KO^{t}Bu (1.10 mmol) and THF (5.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 5 : 1) to give a yellow solid, m.p. 200-201 ºC, 57.2 mg, 97% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.83 (t, *J* = 2.0 Hz, 4H), 4.61 (t, *J* = 2.0 Hz, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 118.1, 73.7, 73.3, 54.6 ppm..



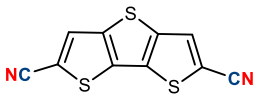
[2,2'-Dipyridine]-5,5'-dicarbonitrile (55).[37] Prepared according to the **General Procedure A** using [2,2'-bipyridine]-5,5'-dicarbaldehyde (0.25 mmol), H_2N-DABCO (0.55 mmol), KO^{t}Bu (1.10 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a white solid, m.p. 287-289 ºC, 33.0 mg, 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 2.0 Hz, 2H), 8.64 (d, *J* = 8.4 Hz, 2H), 8.15 – 8.13 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.0, 152.1, 140.5, 121.6, 116.5, 110.8 ppm.



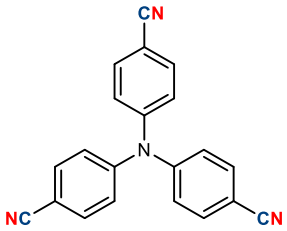
4,4'-(Ethyne-1,2-diyl)dibenzonitrile (56).[38] Prepared according to the **General Procedure A** using 4,4'-(ethyne-1,2-diyl)dibenzaldehyde (0.25 mmol), H_2N-DABCO (0.55 mmol), KO^{t}Bu (1.10 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM : PE = 3 : 1) to give a white solid, m.p. 260-261 °C, 52.5 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 4H), 7.56 (d, *J* = 8.4 Hz, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.3, 132.2, 127.1, 118.2, 112.4, 91.5 ppm.



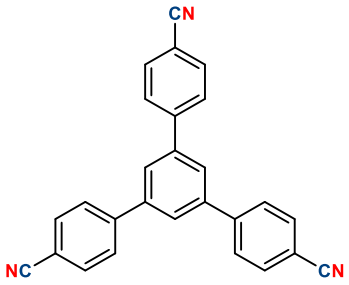
[2,2'-Bithiophene]-5,5'-dicarbonitrile (57).[39] Prepared according to the **General Procedure A** using [2,2'-bithiophene]-5,5'-dicarbaldehyde (0.25 mmol), H_2N-DABCO (0.55 mmol), KO^{t}Bu (1.10 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM : PE = 3 : 1) to give a white solid, m.p. 260-262 °C, 40.6 mg, 75% yield. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 4.0 Hz, 2H), 7.29 (d, *J* = 4.0 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 141.9, 138.9, 126.3, 113.8, 110.6 ppm.



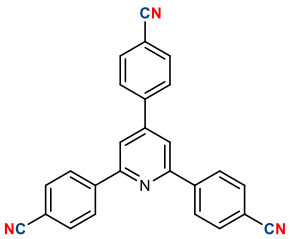
Dithieno[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarbonitrile (58). Prepared according to the **General Procedure A** using dithieno[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarbaldehyde (0.25 mmol), H_2N-DABCO (0.55 mmol), KO^{t}Bu (1.10 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a yellow solid, m.p. 328-330 °C, 50.5 mg, 82% yield. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.91 (s, 2H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 144.4, 134.4, 131.5, 114.1, 112.3 ppm. **HRMS** (ESI) calcd for $C_{10}H_3N_2S_3$ $[M+H]^+$: 246.9453; found: 246.9450.



4,4',4''-Nitrilotribenzonitrile (59).[7] Prepared according to the **General Procedure A** using 4,4',4''-nitrilotribenzaldehyde (0.25 mmol), H_2N-DABCO (0.83 mmol), KO^{t}Bu (1.65 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a white solid, m.p. 351-353 °C, 61.7 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 6H), 7.16 (d, J = 8.8 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 134.0, 124.6, 118.3, 108.1 ppm.

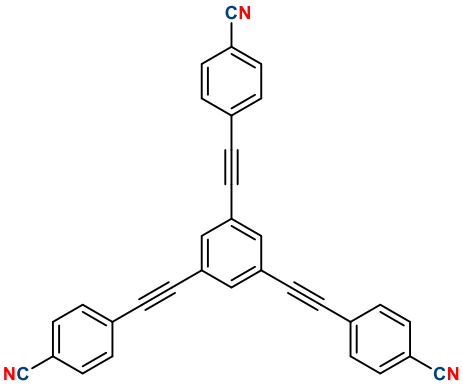


5'-(4-Cyanophenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarbonitrile (60).[40] Prepared according to the **General Procedure A** using 5'-(4-formylphenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde (0.25 mmol), H_2N-DABCO (0.83 mmol), KO^{t}Bu (1.65 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a white solid, m.p. 349-350 °C, 80.1 mg, 84% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.17 (d, J = 8.4 Hz, 6H), 8.15 (s, 3H), 7.99 (d, J = 8.4 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 143.9, 140.1, 132.8, 128.3, 126.2, 118.8, 110.6 ppm.

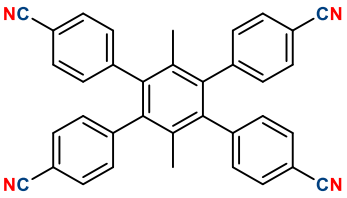


4,4',4''-(Pyridine-2,4,6-triyl)tribenzonitrile (61). Prepared according to the **General Procedure A** using 4,4',4''-(pyridine-2,4,6-triyl)tribenzaldehyde (0.25 mmol), H_2N-DABCO (0.83 mmol), KO^{t}Bu (1.65 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a yellow solid, m.p. 391-393 °C, 53.5 mg, 56% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.58 – 8.50 (m, 6H), 8.33 (s, 2H), 8.08 – 8.02 (m, 6H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 155.0, 148.3, 142.3, 141.4, 132.9, 132.7, 128.5, 127.8,

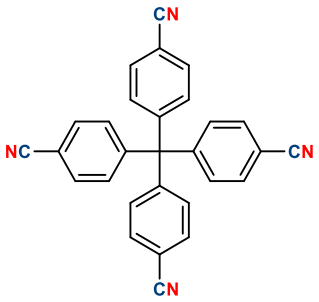
118.8, 118.7, 112.1, 111.9 ppm. **HRMS** (ESI) calcd for $C_{26}H_{15}N_4$ $[M+H]^+$: 383.1291; found: 383.1288.



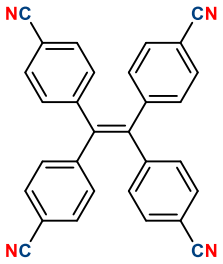
4,4',4''-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzonitrile (62).[41] Prepared according to the **General Procedure A** using 4,4',4"-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzaldehyde (0.25 mmol), H_2N-DABCO (0.83 mmol), KO^{t}Bu (1.65 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a yellow solid, m.p. 267-269 ^{o}C, 88.4 mg, 78% yield. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.72 (s, 3H), 7.67 (d, *J* = 8.4 Hz, 6H), 7.64 (d, *J* = 8.4 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 135.3, 132.6, 127.6, 123.9, 118.7, 112.6, 91.5, 89.6 ppm.



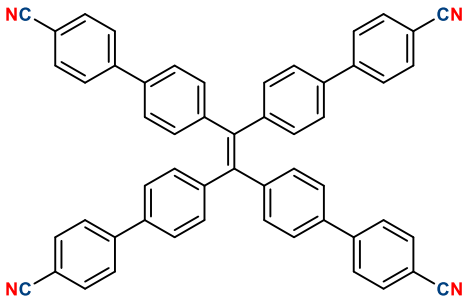
4',5'-Bis(4-cyanophenyl)-3',6'-dimethyl-[1,1':2',1''-terphenyl]-4,4''-dicarbonitrile (63).[42] Prepared according to the **General Procedure A** using 4',5'-bis(4-formylphenyl)-3',6'-dimethyl-[1,1':2',1"-terphenyl]-4,4"-dicarbaldehyde (0.25 mmol), H_2N-DABCO (1.10 mmol), KO^{t}Bu (2.20 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a white solid, m.p. > 400 ^{o}C, 125.1 mg, 98% yield. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.50 (d, *J* = 8.8 Hz, 8H), 7.15 (d, *J* = 8.0 Hz, 8H), 1.72 (s, 6H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 145.6, 140.2, 132.3, 131.6, 131.2, 119.0, 111.3, 19.3 ppm.



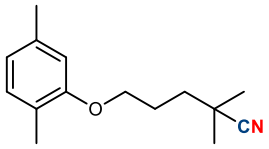
4,4',4'',4'''-Methanetetrayltetrabenzonitrile (64).[43] Prepared according to the **General Procedure A** using 4,4',4'',4'''-methanetetrayltetrabenzaldehyde (0.25 mmol), H_2N-DABCO (1.10 mmol), KO^{t}Bu (2.20 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a white solid, m.p. 316-317 °C, 88.3 mg, 84% yield. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 8.8 Hz, 8H), 7.29 (d, *J* = 8.4 Hz, 8H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 149.1, 132.7, 131.6, 118.5, 111.8, 66.1 ppm.



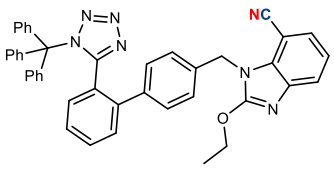
4,4',4'',4'''-(Ethene-1,1,2,2-tetrayl)tetrabenzonitrile (65).[44] Prepared according to the **General Procedure A** using 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetrabenzaldehyde (0.25 mmol), H_2N-DABCO (1.10 mmol), KO^{t}Bu (2.20 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a white solid, m.p. 365-367 °C, 100.6 mg, 93% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 8H), 7.02 (d, *J* = 8.4 Hz, 8H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 141.4, 132.1, 131.5, 117.9, 111.8 pm.



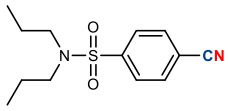
4',4''',4''''',4'''''''-(Ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-4-carbonitrile)) (66).[45] Prepared according to the **General Procedure A** using 4',4''',4''''',4'''''''-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-4-carbaldehyde)) (0.25 mmol), H_2N-DABCO (1.10 mmol), KO^{t}Bu (2.20 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (DCM) to give a green solid, m.p. 344-345 °C, 175.0 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 16H), 7.42 (d, *J* = 8.0 Hz, 8H), 7.22 (d, *J* = 8.0 Hz, 8H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 143.6, 140.7, 137.5, 132.6, 132.1, 127.4, 126.7, 118.8, 111.0 pm.



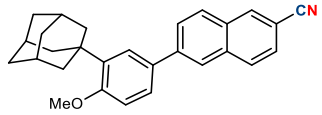
5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanenitrile (67). Prepared according to the **General Procedure B** using gemfibrozil (0.50 mmol), CDI (0.75 mmol) and anhydrous dichloromethane (3.0 mL), 0 °C, 1 hour, N_2, then DIBAL-H (2.00 mmol), -78 °C, 1 hour, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (5.00 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 95.7 mg, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 – 6.99 (m, 1H), 6.68 – 6.61 (m, 2H), 3.98 (t, *J* = 6.0 Hz, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 2.02 – 1.94 (m, 2H), 1.76 – 1.71 (m, 2H), 1.38 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.7, 136.4, 130.3, 124.8, 123.4, 120.9, 111.9, 67.1, 37.8, 32.1, 26.6, 25.5, 21.3, 15.7 ppm. **HRMS** (ESI) calcd for $C_{15}H_{21}NONa$ $[M+Na]^+$: 254.1515; found: 254.1517.



2-Ethoxy-1-((2'-(1-trityl-1*H*-tetrazol-5-yl)-[1,1'-biphenyl]-4-yl)methyl)-1*H*-benzo[*d*]imidazole-7-carbonitrile (68). Prepared according to the **General Procedure B** using N-Trityl Candesartan (0.50 mmol), CDI (0.75 mmol) and anhydrous dichloromethane (3.0 mL), 0 °C, 1 hour, N_2, then DIBAL-H (2.00 mmol), -78 °C, 1 hour, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (5.00 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 4 : 1) to give a white solid, m.p. 177 - 179 °C, 162.5 mg, 49% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.10 (m, 10H), 7.09 – 7.01 (m, 5H), 6.84 (d, *J* = 8.0 Hz, 6H), 5.32 (s, 2H), 4.53 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 158.4, 141.5, 141.2(2), 141.1(7), 140.8, 134.3, 133.2, 130.7, 130.2, 130.1, 129.8, 129.6, 128.1, 127.5(3), 127.4(8), 126.8, 126.3, 126.2, 122.6, 121.6, 117.0, 92.9, 82.8, 67.1, 45.4, 14.5 ppm. **HRMS** (ESI) calcd for $C_{43}H_{33}N_7ONa$ $[M+Na]^+$: 686.2639; found: 686.2643.

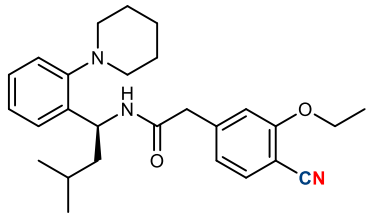


4-Cyano-N,N-dipropylbenzenesulfonamide (69).[46] Prepared according to the **General Procedure B** using probenecid (0.50 mmol), CDI (0.75 mmol) and anhydrous dichloromethane (3.0 mL), 0 °C, 1 hour, N_2, then DIBAL-H (2.00 mmol), -78 °C, 1 hour, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (5.00 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 48-49 °C, 107.9 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 4H), 1.59 – 1.53 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 132.8, 127.5, 117.3, 115.8, 49.8, 21.8, 11.0 ppm.

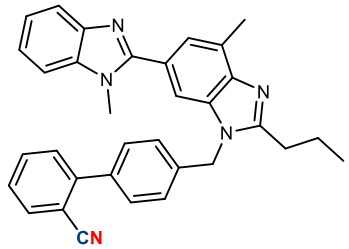


6-(3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-4-methoxyphenyl)-2-naphthonitrile (70). Prepared according to the **General Procedure B** using adapalene (0.50 mmol), CDI (0.75 mmol) and anhydrous dichloromethane (3.0 mL), 0 °C, 1 hour, N_2, then DIBAL-H (2.00 mmol), -78 °C, 1.5 hours, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (5.00 mmol) and THF (10.0 mL). Upon completion, the reaction mixture

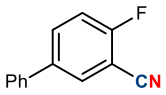
was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : DCM = 10 : 1) to give a white solid, m.p. 247-248 °C, 123.1 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.91 (s, 1H), 7.85 – 7.81 (m, 2H), 7.76 – 7.74 (m, 1H), 7.51 – 7.49 (m, 2H), 7.45 – 7.42 (m, 1H), 6.91 – 6.89 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 2.09 (s, 6H), 2.02 (s, 3H), 1.72 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 142.1, 139.1, 135.1, 133.8, 131.9, 130.9, 129.2, 128.7, 127.4, 126.6, 125.9, 125.7, 124.8, 119.4, 112.1, 108.6, 55.1, 40.5, 37.2, 37.1, 29.0 ppm. **HRMS** (ESI) calcd for $C_{28}H_{28}NO$ $[M+H]^+$: 394.2165; found: 394.2169.



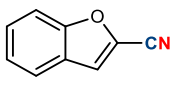
2-(4-Cyano-3-ethoxyphenyl)-*N*-(3-methyl-1-(2-(piperidin-1-yl)phenyl)butyl)acetamide (71). Prepared according to the **General Procedure B** using repaglinide (0.50 mmol), CDI (0.75 mmol) and anhydrous dichloromethane (3.0 mL), 0 °C, 1 hour, N_2, then DIBAL-H (2.00 mmol), -78 °C, 1 hour, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (5.00 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 102-104 °C, 123.7 mg, 57% yield，$[\alpha]_D^{25}$ = 3.2 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.14 – 7.12 (m, 1H), 7.09 – 7.02 (m, 2H), 6.87 – 6.84 (m, 2H), 5.40 – 5.34 (m, 1H), 4.07 – 3.97 (m, 2H), 3.57 – 3.49 (m, 2H), 2.97 – 2.92 (m, 2H), 2.66 – 2.61 (m, 2H), 1.76 – 1.47 (m, 9H), 1.41 (t, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 160.7, 152.3, 142.6, 138.5, 133.6, 127.9, 127.6, 125.0, 122.8, 121.2, 116.5, 112.8, 100.3, 64.5, 49.8, 46.6, 44.1, 26.7, 25.2, 24.0, 22.7, 22.4, 14.3 ppm. **HRMS** (ESI) calcd for $C_{27}H_{36}N_3O_2$ $[M+H]^+$: 434.2802; found: 434.2807.



4'-((1,7'-Dimethyl-2'-propyl-1*H*,3'*H*-[2,5'-bibenzo[*d*]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carbonitrile (72).[47] Prepared according to the **General Procedure B** using telmisartan (0.50 mmol), CDI (0.75 mmol) and anhydrous dichloromethane (3.0 mL), 0 °C, 1 hour, N_2, then DIBAL-H (2.00 mmol), -78 °C, 1 hour, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (5.00 mmol) and THF (10.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 1 : 1) to give a yellow solid, m.p. 176-178 °C, 118.2 mg, 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.49 – 7.37 (m, 6H), 7.30 – 7.22 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.42 (s, 2H), 3.69 (s, 3H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.77 (s, 3H), 1.91 – 1.81 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 154.3, 144.3, 143.0, 142.5, 137.6, 136.4, 136.3, 134.7, 133.5, 132.7, 129.8, 129.3, 129.2, 127.6, 126.3, 123.8, 123.6, 122.3, 122.1, 119.2, 118.4, 110.9, 109.5, 108.6, 46.7, 31.6, 29.6, 21.7, 16.7, 13.9 ppm.

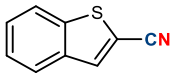


4-Fluoro-[1,1'-biphenyl]-3-carbonitrile (73).[48] Prepared according to the **General Procedure C** using 4-fluoro-1,1'-biphenyl (0.50 mmol), ^{t}BuLi (0.60 mmol, 1.3 M in pentane) and THF (2.0 mL), -30 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 71-74 °C, 79.8 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.52 – 7.44 (m, 4H), 7.43 – 7.39 (m, 1H), 7.30 – 7.25 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7 (d, $J_{C\text{-}F}$ = 260.3 Hz), 138.5 (d, $J_{C\text{-}F}$ = 3.6 Hz), 137.9, 133.6 (d, $J_{C\text{-}F}$ = 8.5 Hz), 131.8, 129.1, 128.4, 126.9, 116.9 (d, $J_{C\text{-}F}$ = 20.1 Hz), 113.9, 101.9 (d, $J_{C\text{-}F}$ = 16.0 Hz) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.50 ppm.

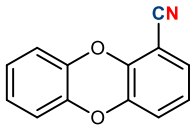


Benzofuran-2-carbonitrile (26).[10] Prepared according to the **General Procedure C** using benzofuran (0.50 mmol), ^{t}BuLi (0.60 mmol, 1.3 M in pentane) and THF (2.0 mL), -30 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL).

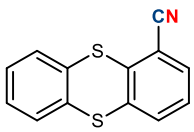
Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 53.6 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.24 (s, 1H), 7.18 – 7.16 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 128.4, 127.3, 125.5, 124.5, 122.5, 118.4, 112.1, 111.8 ppm.



Benzo[*b*]thiophene-2-carbonitrile (27).[18] Prepared according to the **General Procedure C** using benzo[*b*]thiophene (0.50 mmol), ^{t}BuLi (0.60 mmol, 1.3 M in pentane) and THF (2.0 mL), -30 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 70.0 mg, 88% yield.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 3H), 7.55 – 7.51 (m, 1H), 7.49 – 7.45 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 137.4, 135.0, 127.8, 125.7, 125.2, 122.3, 114.4, 109.6 ppm.

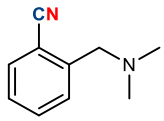


Dibenzo[*b*,*e*][1,4]dioxine-1-carbonitrile (74).[49] Prepared according to the **General Procedure C** using dibenzo[*b*,*e*][1,4]dioxine (0.50 mmol), H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 141-143 °C, 79.4 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 – 7.03 (m, 1H), 6.94 – 6.92 (m, 1H), 6.88 – 6.81 (m, 4H), 6.78 – 6.72 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 142.6, 141.2, 140.8, 127.2, 125.0, 124.6, 123.8, 120.7, 116.8, 116.4, 114.4, 101.0 ppm.

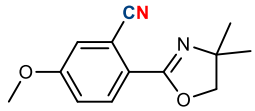


Thianthrene-1-carbonitrile (75). The in situ generated aldehyde was synthesized according to this literature.[50] Prepared according the **General Procedure C** using thianthrene (0.50 mmol), H_2N-DABCO

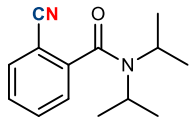
(0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p.190-191 °C, 82.0 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 -7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 7.40 – 7.34 (m, 1H), 7.22 – 7.16 (m, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 137.8, 134.4, 133.2, 132.3, 131.9, 129.1, 128.7, 128.4, 128.3, 127.6, 116.3, 112.8 ppm. **HRMS** (ESI) calcd for $C_{13}H_8NS_2$ $[M+H]^+$: 242.0093; found: 242.0092.



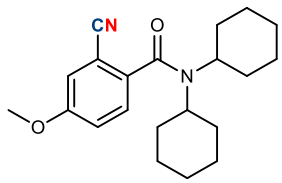
2-((Dimethylamino)methyl)benzonitrile (76).[51] The in situ generated aldehyde was synthesized according to this literature.[52] Prepared according to the **General Procedure C** using *N*,*N*-dimethyl-1-phenylmethanamine (0.50 mmol), H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a yellow oil, 76.0 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.6 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.35 (m, 1H), 3.63 (s, 2H), 2.29 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 132.7, 132.5, 130.0, 127.5, 117.7, 112.9, 61.7, 45.3 ppm.



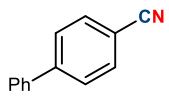
2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-5-methoxybenzonitrile (77). The in situ generated aldehyde was synthesized according to this literature.[53] Prepared according to the **General Procedure C** using 2-(4-methoxyphenyl)-4,4-dimethyl-4,5-dihydrooxazole (0.50 mmol), H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 2 : 1) to give a colorless oil, 92.0 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8, 1H), 7.21 – 7.20 (m, 1H), 7.13 – 7.10 (m, 1H), 4.17 (s, 2H), 3.88 (s, 3H), 1.40 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1, 159.5, 131.8, 122.9, 119.1, 118.3, 117.5, 112.9, 79.6, 67.9, 55.7, 28.2 ppm. **HRMS** (ESI) calcd for $C_{13}H_{15}N_2O_2$ $[M+H]^+$: 231.1128; found: 231.1123.



2-Cyano-*N*,*N*-diisopropylbenzamide (78).[54] Prepared according to the **General Procedure C** using *N*,*N*-diisopropylbenzamide (0.50 mmol), ^{t}BuLi (0.60 mmol, 1.3 M in pentane) and THF (2.0 mL), -30 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 103-105 °C, 103.6 mg, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.48 – 7.44 (m, 1H), 7.36 – 7.34 (m, 1H), 3.63 – 3.53 (m, 2H), 1.60 (d, *J* = 6.8 Hz, 6H), 1.22 – 1.17 (m, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 142.5, 133.0, 132.8, 128.6, 125.8, 116.8, 109.1, 51.4, 46.2, 20.7, 20.3 ppm.

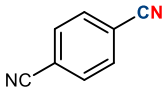


2-Cyano-*N*,*N*-dicyclohexyl-4-methoxybenzamide (79). Prepared according to the **General Procedure C** using *N*,*N*-dicyclohexyl-4-methoxybenzamide (0.50 mmol), ^{t}BuLi (0.60 mmol, 1.3 M in pentane) and THF (2.0 mL), -30 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 118-120 °C, 149.7 mg, 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (m, 1H), 7.15 – 7.10 (m, 2H), 3.85 (s, 3H), 3.14 – 3.06 (m, 2H), 1.82 – 1.43 (m, 13H), 1.30 – 0.97 (m, 7H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 159.0, 135.3, 127.1, 119.2, 117.3, 116.8, 110.1, 60.3, 56.4, 55.6, 31.1, 29.6, 26.8, 26.4, 25.6, 25.1 ppm. **HRMS** (ESI) calcd for $C_{21}H_{29}N_2O_2$ $[M+H]^+$: 341.2224; found: 341.2226.

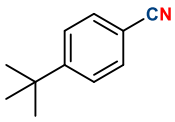


[1,1'-Biphenyl]-4-carbonitril (2).[8] Prepared according to the **General Procedure D** using 4-bromo-1,1'-biphenyl (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF

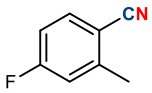
(4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 83-85 °C, 78.8 mg, 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.59 – 7.57 (m, 2H), 7.50 – 7.46 (m, 2H), 7.44 – 7.40 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.7, 127.2, 118.9, 110.8 ppm.



Terephthalonitrile (4).[7] Prepared according to the **General Procedure D** using 4-bromobenzonitrile (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.5 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 219-221 °C, 46.1 mg, 72% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.05 (s, 4H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 133.3, 117.6, 115.8 ppm.

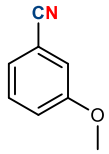


4-(*tert*-Butyl)benzonitrile (80).[22] Prepared according to the **General Procedure D** using 1-bromo-4-(*tert*-butyl)benzene (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a colorless oil, 66.1 mg, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.50 – 7.46 (m, 2H), 1.33 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 131.9, 126.1, 119.1, 109.3, 35.2, 30.9 ppm.

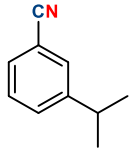


4-Fluoro-2-methylbenzonitrile (81).[55] Prepared according to the **General Procedure D** using 1-bromo-4-fluoro-2-methylbenzene (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol)

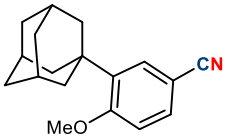
and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 101-103 ^oC, 50.7 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 1H), 7.05 – 7.02 (m, 1H), 7.01 – 6.96 (m, 1H), 2.56 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8 (d, $J_{C\text{-}F}$ = 257.6 Hz), 145.3 (d, $J_{C\text{-}F}$ = 9.1 Hz), 134.7 (d, $J_{C\text{-}F}$ =10.1 Hz), 117.5 (d, $J_{C\text{-}F}$ = 23.2 Hz), 117.3, 113.9 (d, $J_{C\text{-}F}$ = 22.2 Hz), 108.9 (d, $J_{C\text{-}F}$ = 4.0 Hz), 20.4 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.74 ppm.



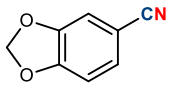
3-Methoxybenzonitrile (82).[35] Prepared according to the **General Procedure D** using 1-bromo-3-methoxybenzene (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 ^{o}C, 30 min, N_2, then DMF (0.75 mmol), 50 ^{o}C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a colorless oil, 40.0 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 2H), 7.06 – 6.95 (m, 2H), 3.93 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2, 134.3, 133.7, 120.7, 116.4, 111.3, 101.8, 56.0 ppm.



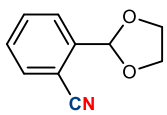
3-Isopropylbenzonitrile (83).[56] Prepared according to the **General Procedure D** using 1-bromo-3-isopropylbenzene (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 ^{o}C, 30 min, N_2, then DMF (0.75 mmol), 50 ^{o}C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 54.5 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.42 (m, 3H), 7.41 – 7.33 (m, 1H), 2.94 (m, 1H), 1.26 (d, J = 7.2 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 131.2, 130.2, 129.6, 129.1, 119.2, 112.3, 33.9, 23.6 ppm.



3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxybenzonitrile (84). Prepared according to the **General Procedure D** using (3*r*,5*r*,7*r*)-1-(5-bromo-2-methoxyphenyl)adamantane (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 177-179 °C, 127.7 mg,, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 2.07 – 2.04 (m, 9H), 1.73 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 139.5, 131.5, 130.6, 119.8, 111.6, 103.5, 55.1, 40.0, 37.1, 36.7, 28.7 ppm. **HRMS** (ESI) calcd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1696; found: 268.1698.

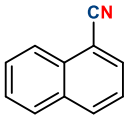


Benzo[*d*][1,3]dioxole-5-carbonitrile (85).[7] Prepared according to the **General Procedure D** using 5-bromobenzo[*d*][1,3]dioxole (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 96-98 °C, 54.5 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.22 (m, 1H), 7.03 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 148.0, 128.1, 118.8, 111.3, 109.0, 104.9, 102.2 ppm.

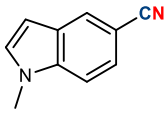


2-(1,3-Dioxolan-2-yl)benzonitrile (86).[57] Prepared according to the **General Procedure D** using 2-(2-bromophenyl)-1,3-dioxolane (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous

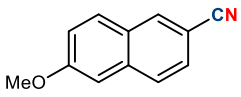
$NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a yellow oil, 49.0 mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.52 – 7.43 (m, 1H), 5.99 (s, 1H), 4.28 – 4.24 (m, 2H), 4.12 – 4.08 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 133.7, 132.6, 129.7, 127.9, 117.1, 111.4, 102.0, 66.0 ppm.



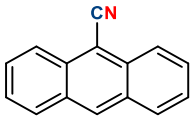
1-Naphthonitrile (87).[10] Prepared according to the **General Procedure D** using 1-bromonaphthalene (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 60.5 mg, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 – 8.20 (d, *J* = 8.4 Hz, 1H), 8.05 – 8.03 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.86 (t, *J* = 8.0 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.61 – 7.57 (m, 1H), 7.51 – 7.47 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.2, 132.8, 132.5, 132.2, 128.6, 128.5, 127.4, 125.0, 124.8, 117.7, 110.1 ppm.



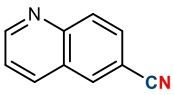
1-Methyl-1*H*-indole-5-carbonitrile (88).[58] Prepared according to the **General Procedure D** using 5-bromo-1-methyl-1*H*-indole (0.50 mmol), ^{t}BuLi (0.60 mmol, 1.3 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 76-77 °C, 62.0 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.94 (m, 1H), 7.44 –7.41 (m, 1H), 7.36 – 7.34 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.16 (d, *J* = 3.2 Hz, 1H), 6.56 – 6.55 (m, 1H), 3.82 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 131.1, 128.1, 126.4, 124.4, 120.8, 110.0, 102.3, 102.1, 33.0 ppm.



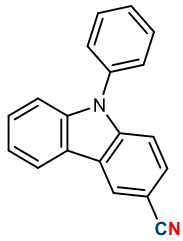
6-Methoxy-2-naphthonitrile (33).[22] Prepared according to the **General Procedure D** using 2-bromo-6-methoxynaphthalene (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 105-106 °C, 62.3 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.78 – 7.75 (m, 2H), 7.56 – 7.53 (m, 1H), 7.25 – 7.22 (m, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 3.94 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 136.4, 133.7, 129.9, 127.8, 127.7, 127.0, 120.6, 119.5, 106.7, 105.9, 55.4 ppm.



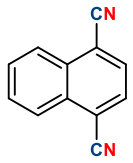
Anthracene-9-carbonitrile (34).[7] Prepared according to the **General Procedure D** using 9-bromoanthracene (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a yellow solid, m.p. 175-178 °C, 70.1 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.32 – 8.30 (m, 2H), 7.98 – 7.96 (m, 2H), 7.66 – 7.62 (m, 2H), 7.53 – 7.49 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.1, 132.6, 130.4, 128.8(3), 128.8(0), 126.2, 125.1, 117.2, 105.2 ppm.



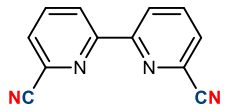
Quinoline-6-carbonitrile (89).[22] Prepared according to the **General Procedure D** using 6-bromoquinoline (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 132-135 °C, 50.2 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.09 – 9.07 (m, 1H), 8.28 – 8.15 (m, 3H), 7.89 – 7.86 (m, 1H), 7.60 – 7.56 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.9, 148.6, 136.7, 134.0, 130.6, 130.2, 127.5, 122.7, 118.3, 110.5 ppm.



9-Phenyl-9*H*-carbazole-3-carbonitrile (90).[59] Prepared according to the **General Procedure D** using 3-bromo-9-phenyl-9*H*-carbazole (0.50 mmol), ^{n}BuLi (0.55 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (0.75 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (0.75 mmol), KO^{t}Bu (1.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 201-202 °C, 115.0 mg, 86% yield. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.26 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.41 – 7.29 (m, 4H), 7.25 – 7.17 (m, 3H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 142.6, 141.7, 136.5, 130.2, 129.2, 128.4, 127.4, 127.1, 125.2, 123.5, 122.3, 121.2, 120.7, 120.3, 110.5, 110.4, 102.8, ppm.

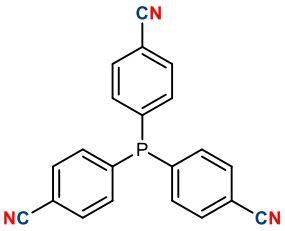


Naphthalene-1,4-dicarbonitrile (91).[60] The in situ generated aldehyde was synthesized according to this literature.[61] Then prepared according to the **General Procedure D** using H_2N-DABCO (1.50 mmol), KO^{t}Bu (3.00 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a white solid, m.p. 208-210 °C, 59.0 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 – 8.32 (m, 2H), 7.97 (s, 2H), 7.90 – 7.84 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.0, 131.1, 130.3, 126.0, 116.2, 115.2 ppm.

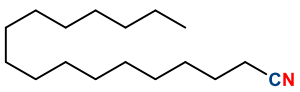


[2,2'-Bipyridine]-6,6'-dicarbonitrile (92).[62] Prepared according to the **General Procedure D** using 6,6'-dibromo-2,2'-bipyridine (0.50 mmol), ^{n}BuLi (1.10 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (1.50 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (1.50 mmol), KO^{t}Bu (3.00

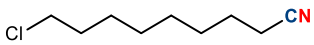
mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 3 : 1) to give a white solid, m.p. 319-320 °C, 60.0 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 – 8.71 (m, 2H), 8.04 – 8.00 (m, 2H), 7.79 – 7.77 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.6, 138.4, 133.4, 129.1, 124.7, 117.0 ppm.



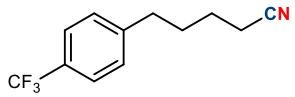
4,4',4''-Phosphanetriyltribenzonitrile (93).[63] Prepared according to the **General Procedure D** using tris(4-bromophenyl)phosphane (0.50 mmol), ^{n}BuLi (1.65 mmol, 2.5 M in hexane) and THF (2.0 mL), -78 °C, 30 min, N_2, then DMF (2.25 mmol), 50 °C, 30 min, N_2; H_2N-DABCO (2.25 mmol), KO^{t}Bu (4.50 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 5 : 1) to give a white solid, m.p. 220-221 °C, 73.8 mg, 44% yield. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.69 –7.67 (m, 6H), 7.41 – 7.37 (m, 6H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 141.4 (d, J = 16.2 Hz), 134.5 (d, J = 20.2 Hz), 132.7 (d, J = 7.1 Hz), 118.5, 113.8 ppm; **^{31}P NMR** (162 MHz, CD_2Cl_2) δ -3.96 ppm.



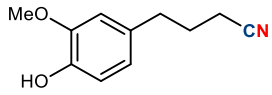
Heptadecanenitrile (44).[31] Prepared according to the **General Procedure E** using hexadec-1-ene (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar) and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.20 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a white solid, m.p. 34-35 °C, 91.8 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.33 (t, J = 6.8 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.33 – 1.21 (m, 26H), 0.88 (t, J = 7.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 119.8, 31.9, 29.7, 29.6(4), 29.6(3), 29.6(2), 29.6(0), 29.5(5), 29.5, 29.3(2), 29.2(6), 28.7, 28.6, 25.4, 22.7, 17.1, 14.1 ppm.



9-Chlorononanenitrile (94).[64] Prepared according to the **General Procedure E** using 8-chlorooct-1-ene (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar) and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.20 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a colorless oil, 54.5 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.53 (t, *J* = 6.8 Hz, 2H), 2.34 (t, *J* = 8.0 Hz, 2H), 1.82 – 1.72 (m, 2H), 1.69 – 1.62 (m, 2H), 1.52 – 1.40 (m, 4H), 1.34 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 119.7, 44.9, 32.5, 28.5(3), 28.4(9), 28.4(7), 26.6, 25.3, 17.0 ppm.

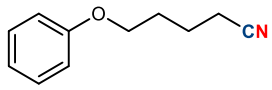


5-(4-(Trifluoromethyl)phenyl)pentanenitrile (95). Prepared according to the **General Procedure E** using 1-(but-3-en-1-yl)-4-(trifluoromethyl)benzene (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar) and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.2 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 73.8 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 6.8 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.73 – 1.64 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.3, 128.6, 128.3, 125.4 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 272.7 Hz), 119.3, 34.8, 29.9, 24.7, 17.0 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.34 ppm. **HRMS** (ESI) calcd for $C_{12}H_{12}F_3NNa$ $[M+Na]^+$: 250.0814; found: 250.0812.

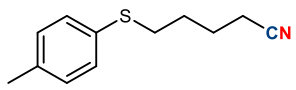


4-(4-Hydroxy-2-methoxyphenyl)butanenitrile (96).[65] Prepared according to the **General Procedure E** using 4-allyl-2-methoxyphenol (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar) and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.70 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 2 : 1) to give a yellow oil, 60.2 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 7.6 Hz, 1H), 6.70 – 6.64 (m, 2H), 5.60 (s, 1H), 3.87 (s,

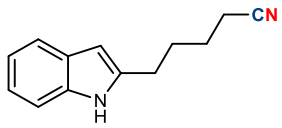
3H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.97 – 1.90 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.6, 144.2, 131.5, 121.0, 119.5, 114.4, 111.0, 55.9, 34.0, 27.1, 16.2 ppm.



5-Phenoxypentanenitrile (97).[66] Prepared according to the **General Procedure E** using (but-3-en-1-yloxy)benzene (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar) and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.20 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a colorless oil, 58.6 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 6.97 – 6.92 (m, 1H), 6.90 – 6.86 (m, 2H), 3.99 (t, *J* = 5.6 Hz, 2H), 2.42 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.82 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 129.4, 120.8, 119.4, 114.4, 66.5, 28.2, 22.4, 16.9 ppm.

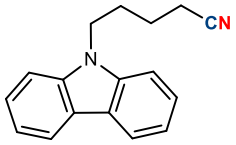


5-(*p*-Tolylthio)pentanenitrile (98). Prepared according to the **General Procedure E** using but-3-en-1-yl(*p*-tolyl)sulfane (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar) and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.20 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 10 : 1) to give a colorless oil, 58.5 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 2.32 (m, 5H), 1.83 – 1.71 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.5, 131.9, 130.4, 129.7, 119.2, 33.6, 28.0, 24.2, 20.9, 16.7 ppm. **HRMS** (ESI) calcd for $C_{12}H_{16}NS$ $[M+H]^+$: 206.0998; found: 206.0999.

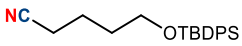


5-(1*H*-indol-2-yl)pentanenitrile (99). Prepared according to the **General Procedure E** using 2-(but-3-en-1-yl)-1*H*-indole (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar)

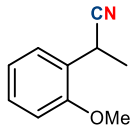
and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.70 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 5 : 1) to give a clossless oil, 64.0 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.08 – 6.96 (m, 2H), 6.14 (s, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.20 (t, *J* = 6.8 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.64 – 1.52 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.2, 135.9, 128.6, 121.1, 119.7, 119.6(2), 119.5(5), 110.4, 99.8, 27.9, 27.2, 24.6, 16.8 ppm. **HRMS** (ESI) calcd for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230; found: 199.1231.



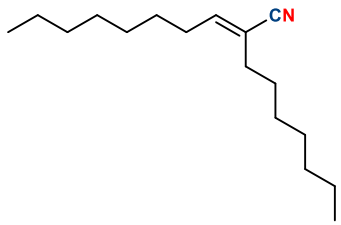
5-(9*H*-carbazol-9-yl)pentanenitrile (100). Prepared according to the **General Procedure E** using 9-(but-3-en-1-yl)-9*H*-carbazole (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar) and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.20 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 5 : 1) to give a white solid, m.p. 150-151 °C,65.8 mg, 53% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.43 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.18 (m, 2H), 4.30 – 4.23 (m, 2H), 2.17 (t, *J* = 6.8 Hz, 2H), 2.03 – 1.91 (m, 2H), 1.62 – 1.55 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.2, 125.8, 122.9, 120.4, 119.0, 108.4, 42.0, 28.1, 23.1, 16.9 ppm. **HRMS** (ESI) calcd for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1386; found: 249.1385.



5-((*tert*-Butyldiphenylsilyl)oxy)pentanenitrile (101).[67] Prepared according to the **General Procedure E** using (but-3-en-1-yloxy)(*tert*-butyl)diphenylsilane (0.50 mmol), $Rh(acac)(CO)_2$ (1.0 mol%), BISBI (2.2 mol%), CO/H_2 (5 bar : 5 bar) and toluene (0.5 mL), 50 °C, 12 hours; H_2N-DABCO (0.60 mmol), KO^{t}Bu (1.20 mmol) and THF (4.0 mL). Upon completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and purified by column chromatography (PE : EA = 20 : 1) to give a colorless oil, 80.0 mg, 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 4H), 7.45 – 7.34 (m, 6H), 3.69 (t, *J* = 6.0 Hz, 2H), 2.32 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.68 (m, 2H), 1.05 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.5, 133.6, 129.7, 127.7, 119.6, 62.6, 31.2, 26.8, 22.2, 19.1, 16.8 ppm.

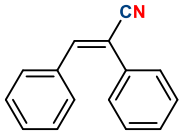


2-(2-Methoxyphenyl)propanenitrile (102).[4] In a glovebox filled with nitrogen, to a 5 mL vial equipped with a magnetic bar was added (*S*,*S*)-Ph-BPE (3 mol%) and Rh(acac)$(CO)_2$ (1 mol% in 1.0 mL THF). After stirring for 10 min, 1-methoxy-2-vinylbenzene (0.50 mmol), 1-aminopiperidine (1.50 mmol), PhCOOH (0.05 mmol) and additional solvent (1.5 mL THF) were charged to bring the total volume of the reaction mixture to 2.5 mL. The vial was transferred into an autoclave and taken out of the glovebox. H_2 (5 bar) and CO (5 bar) were charged in sequence. The reaction mixture was stirred at 60 °C for 24 h. Upon completion, the autoclave was cooled to room temperature and the pressure was carefully released. The resulting solution was added to the pre-prepared mixture (stirred for 5 min) of KO^{t}Bu (1.20 mmol), H_2N-DABCO (0.60 mmol) and THF (4.0 mL) in a 25 mL vial equipped with a magnetic stirring bar. The resulting mixture was allowed to stir for 10 min. After the reaction was completed, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 10.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography (PE : EA = 20 : 1) to give a colorless oil, 66.1 mg, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.00 – 6.96 (m, 1H), 6.90 – 6.88 (d, *J* = 8.4 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9, 129.2, 127.5, 125.3, 121.9, 120.9, 110.7, 55.4, 25.5, 19.4 ppm.

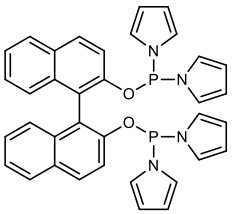


(*E*)-2-Heptyldec-2-enenitrile (103). A Schlenk tube with a magnetic stir bar was charged with [Rh(cod)OMe]$_2$ (0.01 mmol), Xantphos (0.02 mmol), 4-NO_2-$PhCO_2H$ (0.02 mmol), hexadec-8-yne (1.00 mmol), and n-butyraldehyde (0.50 mmol) in THF (0.25 mL) under nitrogen. The resulting mixture was stirred at 80 °C for 24 h. The resulting solution was added to the pre-prepared mixture (stirred for 5 min) of KO^{t}Bu (1.20 mmol), H_2N-DABCO (0.60 mmol) and THF (4.0 mL) in a 25 mL vial equipped with a

magnetic stirring bar. The resulting mixture was allowed to stir for 10 min. Upon completion, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography (PE) to give a colorless oil, 85.1 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.32 (t, *J* = 7.6 Hz, 1H), 2.21 – 2.13 (m, 4H), 1.55 – 1.28 (m, 20H), 0.89 (t, *J* = 6.8 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 120.1, 114.9, 31.6, 29.1, 28.9(2), 28.8(9), 28.8, 28.3(9), 28.3(6), 28.3(5), 27.9, 22.5, 14.0 ppm. **HRMS** (ESI) calcd for $C_{17}H_{32}N$ $[M+H]^+$: 250.2529; found: 250.2523.

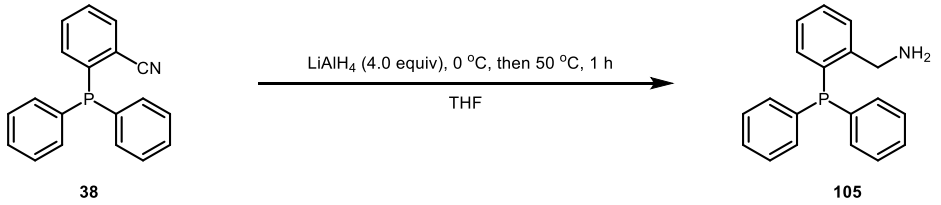


(*E*)-2,3-Diphenylacrylonitrile (104).[22] In a glove box, a Parr autoclave equipped with a magnetic stirring bar was charged with the biphenylacetylene (0.50 mmol), **L1** (1 mol%), $Rh(acac)(CO)_2$ (0.5 mol%), and toluene (1.0 mL). The vial was transferred into an autoclave and taken out of the glovebox. H_2 (10 bar) and CO (10 bar) were charged in sequence. The autoclave was then heated at 60 ℃ for 12 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The resulting solution was added to the pre-prepared mixture (stirred for 5 min) of KO^{t}Bu (1.20 mmol), H_2N-DABCO (0.60 mmol) and THF (4.0 mL) in a 25 mL vial equipped with a magnetic stirring bar. The resulting mixture was allowed to stir for 10 min. Upon completion, the crude mixture was quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 10.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography (PE) to give a colorless oil, 73.9 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 6H), 7.27 – 7.25 (m, 1H), 7.23 – 7.19 (m, 2H), 7.15 – 7.13 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 133.4, 132.5, 129.8, 129.7, 129.2, 129.0, 128.7, 128.4, 120.0, 114.2 ppm.



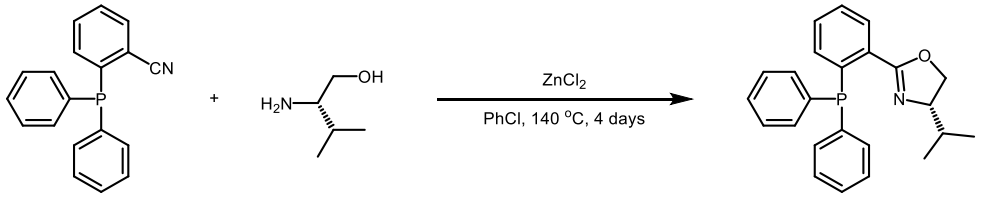
L1

Synthetic application of nitriles



38 105

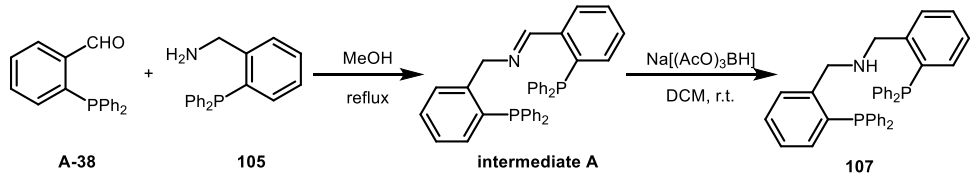
(2-(Diphenylphosphaneyl)phenyl)methanamine.[68] A round-bottomed flask was charged with **38** (71.8 mg, 0.25 mmol) and anhydrous THF (2.0 mL). The reaction flask was then cooled to 0 °C in an ice bath before $LiAlH_4$ (38.0 mg, 1.0 mmol) was added slowly. Then the reaction mixture was stirred at 50 °C for 1 hour. Upon completion, the crude mixture was quenched by H_2O and extracted by ethyl acetate (3 x 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography (PE :EA = 2 : 1) to give a white solid (**105**), m.p. 95-97 °C, 62.7 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 1H), 7.37 – 7.21 (m, 11H), 7.17 – 7.13 (m, 1H), 6.89 – 6.86 (m, 1H), 4.01 (s, 2H), 1.50 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 147.3, 136.4(4), 136.3(5), 135.0, 134.0, 133.8, 133.5, 129.3, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 127.1, 45.2, 45.0 ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -15.80 ppm.



38 L-(+)-valinol 106

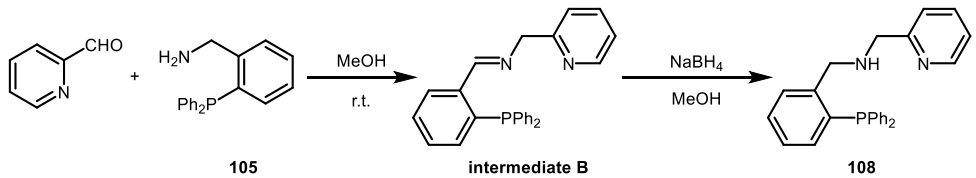
(*S*)-2-(2-(diphenylphosphaneyl)phenyl)-4-isopropyl-4,5-dihydrooxazole (106).[69] A 25 mL flask was charged with **38** (71.8 mg, 0.25 mmol), $ZnCl_2$ (51.1 mg, 0.38 mmol) and L-(+)-valinol (39.2 mg, 0.38 mmol). Degassed PhCl (2.0 mL) was added under argon. The reaction mixture was stirred at 140 °C for 4 days. After cooled to room temperature, 2,2-bipyridine (78.1 mg, 0.50 mmol) in degassed $CHCl_3$ (5.0 mL) was added to the mixture, which was stirred for 3 h at room temperature. Then, the reaction mixture was filtered by celite and evaporated most solvent under reduced pressure. The residue was further purified by silica column chromatography (PE : EA = 20 : 1) to give a white solid (**106**), m.p. 80-82 °C, 82.1 mg, 88%, $[\alpha]_D^{25}$ = -16.5 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.84 (m, 1H), 7.28 (m, 12H), 6.94 – 6.81 (m, 1H), 4.22 – 4.06 (m, 1H), 3.95 – 3.76 (m, 2H), 1.57 – 1.41 (m, 1H), 0.81 (d, *J*

= 6.8 Hz, 3H), 0.71 (d, *J* = 6.8 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 138.7 (d, *J* = 5.5 Hz), 138.3 – 138.0 (m), 134.3 – 133.5 (m), 131.9 (d, *J* = 19.6 Hz), 130.2, 129.7 (d, *J* = 3.0 Hz), 128.4 – 128.1 (m), 127.8, 73.0, 69.9, 32.6, 18.8, 18.3 ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -5.50 ppm.



A-38 **105** **intermediate A** **107**

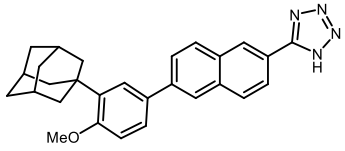
Bis(2-(diphenylphosphaneyl)benzyl)amine (107).[70] Methanol (2.0 mL) was added to a mixture of 2-(diphenylphosphino)-benzaldehyde **A-38** (72.5 mg, 0.25 mmol) and 2-(diphenylphosphino)-benzylamine **105** (72.8 mg, 0.25 mmol) and the resulting suspension was heated to reflux for 2.5 h. The reaction mixture was allowed to cool to room temperature and the precipitate was collected by filtration. After washing with methanol (2 × 1.5 mL) and drying in vacuum, the product was obtained as a slightly yellowish powder intermediate **A**. Solid sodium triacetoxy borohydride (63.3 mg, 0.30 mmol) was added to a stirred solution of intermediate **A** in CH_2Cl_2 (4.0 mL). After stirring was continued at room temperature for 12 h, the reaction mixture was filtered over Celite and water (5.0 mL) was added to the filtrate. The organic phase was separated and the aqueous one was extracted with dichloromethane (3 × 5.0 mL). The combined organic phases were washed with water (5.0 mL) and brine (5.0 mL) and then dried over magnesium sulfate. The desired product was purified by column chromatography (PE : EA = 20 : 1) to give a white solid (**107**), m.p.148-150 °C, 70.7 mg, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 24H), 7.11 (m, 2H), 6.85 (m, 2H), 3.89 (s, 4H), 1.66 (s, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5 (d, *J* = 23.2 Hz), 136.9 (d, *J* = 11.1 Hz), 135.6 (d, *J* = 14.1 Hz), 133.9 (d, *J* = 20.2 Hz), 133.4, 128.9 – 128.8 (m), 128.6 – 128.4 (m), 127.0, 51.8 (d, *J* = 22.2 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -15.73 ppm.



105 **intermediate B** **108**

***N*-(2-(Diphenylphosphaneyl)benzyl)-1-(pyridin-2-yl)methanamine (108).**[71] Picolinaldehyde (26.8 mg, 0.25 mmol) and (2-(diphenylphosphaneyl)phenyl)methanamine **105** (76.4 mg, 0.26 mmol) were stirred at room temperature in methanol (2.0 mL) in the presence of an excess of Na_2SO_4 (88.8 mg, 0.63

mmol) for 3 h. Then, after elimination of the solid by filtration, $NaBH_4$ (11.4 mg, 0.30 mmol) was added, and the mixture was gently warmed for 30 min at 45 °C. The solvent was eliminated under reduced pressure, and after the addition of water (5.0 mL), the organic material was extracted with ethyl ether (3 × 5.0 mL). The desired product was purified by column chromatography (PE : EA = 10 : 1) to give a colorless oil (**108**), 62.1 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 4.8 Hz, 1H), 7.45 – 7.33 (m, 2H), 7.21 – 7.12 (m, 11H), 7.03 – 6.98 (m, 2H), 6.95 – 6.92 (m, 1H), 6.81 – 6.78 (m, 1H), 3.94 (s, 2H), 3.70 (s, 2H), 2.14 (s, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 148.9, 144.2 (d, *J* = 24.2 Hz), 136.6 (d, *J* = 11.1 Hz), 136.0, 135.6 (d, *J* = 14.1 Hz), 133.6 (d, *J* = 19.2 Hz), 133.5, 128.9 (d, *J* = 6.1 Hz), 128.8, 128.4, 128.3 (d, *J* = 6.1 Hz), 127.1, 121.8, 121.5, 54.3, 51.8 (d, *J* = 21.2 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -15.78 ppm.



5-(6-(3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-2-benzyl-2*H*-tetrazole (109). To a 25 mL flame-dried resealable reaction tube of solvent flask equipped with a magnetic stirring bar was added 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthonitrile **70** (98.4 mg, 0.25 mmol), TBAF (0.25 mmol, 1 M in THF), TMS-N_3 (57.6 mg, 0.50 mmol) and THF (0.2 mL) under nitrogen and the resulting mixture was stirred vigorously at 85 °C for 24 h. The reaction mixture was then transferred to a separatory funnel and TBAF was removed by washing the organic phase with 1 M aqueous HCl solution (10.0 mL). After the organic phase was removed under reduced pressure, the crude product was washed with the mixed solvent (V_{DCM} : V_{PE} = 1 : 4, 3 x 5.0 mL) to give a white solid, m.p. 306-308 °C, 76.5 mg, 70% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.64 (s, 1H), 8.25 – 8.15 (m, 2H), 8.15 – 8.05 (m, 2H), 7.99 – 7.80 (m, 1H), 7.71 – 7.49 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 3H), 2.11 (s, 6H), 2.04 (s, 3H), 1.73 (s, 6H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 158.6, 155. 8, 139.7, 138.1, 134.4, 131.5, 131.4, 129.3, 129.2, 126.6, 126.3, 125.7, 125.0, 124.3, 124.0, 121.4, 112.7, 55.3, 40.1, 36.6(2), 36.5(6), 28.4 ppm. **HRMS** (ESI) calcd for $C_{28}H_{29}N_4O$ $[M+H]^+$: 437.2336; found: 437.2332.

References:

1 Feng, F.-F., Li, S., Cheung, C. W. & Ma, J.-A. Chiral β-keto propargylamine synthesis via enantioselective mannich reaction of enamides with C-alkynyl N-Boc N,O-acetals. *Org. Lett.* **21**, 8419-8423 (2019).

2 Liu, X. *et al.* Aminoazanium of DABCO: an amination reagent for alkyl and aryl pinacol boronates. *Angew. Chem. Int. Ed.* **59**, 2745-2749 (2020).

3 Kranenburg, M. *et al.* New diphosphine ligands based on heterocyclic aromatics inducing very high regioselectivity in rhodium-catalyzed hydroformylation: effect of the bite angle. *Organometallics* **14**, 3081-3089 (1995).

4 Li, X. *et al.* Asymmetric hydrocyanation of alkenes without HCN. *Angew. Chem. Int. Ed.* **58**, 10928-10931 (2019).

5 Tan, G., Wu, Y., Shi, Y. & You, J. Syngas-free highly regioselective rhodium-catalyzed transfer hydroformylation of alkynes to α,β-unsaturated aldehydes. *Angew. Chem. Int. Ed.* **58**, 7440-7444 (2019).

6 Ren, X. Y., Zhang, L., Wang, Z., Xia, C. G. & Ding, K. L. Rh-catalyzed hydroformylation of alkynes to α,β-unsaturated aldehydes. *J. Mol. Catal: China* **30**, 497-504 (2016).

7 Mudshinge, S. R., Potnis, C. S., Xu, B. & Hammond, G. B. HCl·DMPU-assisted one-pot and metal-free conversion of aldehydes to nitriles. *Green Chem.* **22**, 4161-4164 (2020).

8 Dong, Y., Yang, P., Zhao, S. & Li, Y. Reductive cyanation of organic chlorides using CO_2 and NH_3 via triphos–Ni(I) species. *Nat. Commun.* **11**, 4096 (2020).

9 Gurjar, J., Bater, J. & Fokin, V. V. Sulfuryl fluoride mediated conversion of aldehydes to nitriles. *Chem. Eur. J.* **25**, 1906-1909 (2019).

10 Zhang, W., Lin, J.-H., Zhang, P. & Xiao, J.-C. A convenient reagent for the conversion of aldoximes into nitriles and isonitriles. *Chem. Commun.* **56**, 6221-6224 (2020).

11 Easwaramoorthi, S. *et al.* Charge instability of symmetry broken dipolar states in quadrupolar and octupolar triphenylamine derivatives. *Chem. Commun.* **50**, 6902-6905 (2014).

12 Yu, C., Ma, X. & Song, Q. Palladium-catalyzed cyanation of aryl halides with in situ generated CN^- from $ClCF_2H$ and $NaNH_2$. *Org. Chem. Front.* **7**, 2950-2954 (2020).

13 Konyushkin, L. D. *et al.* Polyalkoxybenzenes from plant raw materials 4*. parsley and dill seed extracts in the synthesis of polyalkoxy-3,5-diaryl-1,2,4-oxadiazoles with antiproliferative activity. *Russ.Chem.Bull., Int.Ed.* **59**, 2268-2275 (2010).

14 Ma, C. *et al.* Nickel-catalyzed carboxylation of aryl and heteroaryl fluorosulfates using carbon dioxide. *Org. Lett.* **21**, 2464-2467 (2019).

15 Zhang, D. *et al.* An expedient Pd/DBU mediated cyanation of aryl/heteroaryl bromides with $K_4[Fe(CN)_6]$. *Chem. Commun.* **48**, 2909-2911 (2012).

16 Wu, J. *et al.* Efficient construction of diverse 3-cyanoindoles under novel tandem catalysis. *Chem. Commun.* **56**, 12660-12663 (2020).

17 Zeidan, N., Bognar, S., Lee, S. & Lautens, M. Palladium-catalyzed synthesis of 2-cyanoindoles from 2-gem-dihalovinylanilines. *Org. Lett.* **19**, 5058-5061 (2017).

18 Thakore, R. R., Takale, B. S., Singhania, V., Gallou, F. & Lipshutz, B. H. Late-stage Pd-catalyzed cyanations of aryl/heteroaryl halides in aqueous micellar media. *ChemCatChem* **13**, 212-216 (2021).

19 Yu, H., Richey, R. N., Miller, W. D., Xu, J. & May, S. A. Development of Pd/C-catalyzed cyanation of aryl halides. *J. Org. Chem.* **76**, 665-668 (2011).

20 Meng, H., Gao, S., Luo, M. & Zeng, X. Iron and phenol Co-catalysis for rapid synthesis of nitriles under mild conditions. *Eur. J. Org. Chem.* **2019**, 4617-4623 (2019).

21 Saroja, G., Pingzhu, Z., Ernsting, N. P. & Liebscher, J. Synthesis of alkylated aminofluorenes by palladium-catalyzed substitution at halofluorenes. *J. Org. Chem.* **69**, 987-990 (2004).

22 Yang, L., Liu, Y.-T., Park, Y., Park, S.-W. & Chang, S. Ni-mediated generation of "CN" unit from formamide and its catalysis in the cyanation reactions. *ACS Catal.* **9**, 3360-3365 (2019).

23 Takise, R., Itami, K. & Yamaguchi, J. Cyanation of phenol derivatives with aminoacetonitriles by nickel catalysis. *Org. Lett.* **18**, 4428-4431 (2016).

24 Kilaru, R. B. *et al.* Design, synthesis, in silico and in vitro studies of novel 4-methylthiazole-5-carboxylic acid derivatives as potent anti-cancer agents. *Bioorg. Med. Chem. Lett.* **24**, 4580-4585 (2014).

25 Reis, A. *et al.* Fluoride catalyzed P–aryl-coupling—a mild approach to functionalized arylphosphines. *New J.Chem* **35**, 2488-2495 (2011).

26 Murugesan, K. *et al.* Stable and reusable nanoscale Fe_2O_3-catalyzed aerobic oxidation process for the selective synthesis of nitriles and primary amides. *Green Chem.* **20**, 266-273 (2018).

27 Shank, N. I., Zanotti, K. J., Lanni, F., Berget, P. B. & Armitage, B. A. Enhanced photostability of genetically encodable fluoromodules based on fluorogenic cyanine dyes and a promiscuous protein partner. *J. Am. Chem. Soc.* **131**, 12960-12969 (2009).

28 Jagadeesh, R. V., Junge, H. & Beller, M. Green synthesis of nitriles using non-noble metal oxides-based nanocatalysts. *Nat. Commun.* **5**, 4123 (2014).

29 Yang, S. H. & Chang, S. Highly efficient and catalytic conversion of aldoximes to nitriles. *Org. Lett.* **3**, 4209-4211 (2001).

30 Sharma, P. K., Ram, S. & Chandak, N. Transition metal-free approach to propynenitriles and 3-chloropropenenitriles. *Adv. Synth. Catal.* **358**, 894-899 (2016).

31 King, J. F., Loosmore, S. M., Aslam, M., Lock, J. D. & McGarrity, M. J. Betylates. 3. preparative nucleophilic substitution by way of [2]-, [3]-, and [4] betylates. stoichiometric phase transfer and substrate-reagent ion-pair (SRIP) reactions of betylates. *J. Am. Chem. Soc.* **104**, 7108-7122 (1982).

32 Richardson, M. B. & Williams, S. J. A practical synthesis of long-chain Iso-fatty acids (iso-C_{12}–C_{19}) and related natural products. *Beilstein J. Org. Chem.* **9**, 1807–1812 (2013).

33 Lan, L., Huang, S., Liu, Y., Sun, B. & Tian, H. Preparation and odor characteristics of nitriles derived from aldehydes. *Flavour Fragr J.* **35**, 425-434 (2020).

34 Xia, A., Lv, P., Xie, X. & Liu, Y. Nickel-catalyzed cyanation of unactivated alkyl sulfonates with $Zn(CN)_2$. *Org. Lett.* **22**, 7842-7847 (2020).

35 An, X.-D. & Yu, S. Direct synthesis of nitriles from aldehydes using an O-benzoyl hydroxylamine (BHA) as the nitrogen source. *Org. Lett.* **17**, 5064-5067 (2015).

36 Wilkinson, L. A., Yue, T. T. C., Massey, E., White, A. J. P. & Long, N. J. Cyanoferrocenes as redox-active metalloligands for coordination-driven self-assembly. *Dalton Trans.* **48**, 72-78 (2019).

37 Vanden Bussche, F. *et al.* N-rich porous polymer with isolated Tb^{3+}-ions displays unique temperature dependent behavior through the absence of thermal quenching. *Chem. Eur. J.* **26**, 15596-15604 (2020).

38 Hillenbrand, J., Leutzsch, M. & Fürstner, A. Molybdenum alkylidyne complexes with tripodal silanolate ligands: the next generation of alkyne metathesis catalysts. *Angew. Chem. Int. Ed.* **58**, 15690-15696 (2019).

39 P, S., Sau, S. C., Vardhanapu, P. K. & Mandal, S. K. Halo-bridged abnormal NHC Palladium(II) dimer for catalytic dehydrogenative cross-coupling reactions of heteroarenes. *J. Org. Chem.* **83**, 9403-9411 (2018).

40 Klaasen, H. *et al.* Intermolecular coupling and intramolecular cyclization of aryl nitriles on Au (111). *Chem. Commun.* **55**, 11611-11614 (2019).

41 Kobayashi, N. & Kijima, M. 1,3,5-tris(Functionalised-phenylethynyl)benzene–metal complexes: synthetic survey of mesoporous coordination polymers and investigation of their carbonisation. *J. Mater. Chem.* **18**, 1037-1045 (2008).

42 Maly, K. E., Gagnon, E., Maris, T. & Wuest, J. D. Engineering hydrogen-bonded molecular crystals built from derivatives of hexaphenylbenzene and related compounds. *J. Am. Chem. Soc.* **129**, 4306-4322 (2007).

43 He, Y., Xiang, S. & Chen, B. A microporous hydrogen-bonded organic framework for highly selective C_2H_2/C_2H_4 separation at ambient temperature. *J. Am. Chem. Soc.* **133**, 14570-14573 (2011).

44 Zhang, M., Yao, Y., Stang, P. J. & Zhao, W. Divergent and stereoselective synthesis of tetraarylethylenes from vinylboronates. *Angew. Chem. Int. Ed.* **59**, 20090-20098 (2020).

45 Schultz, A., Laschat, S., Diele, S. & Nimtz, M. Tetraphenylethene-derived columnar liquid crystals and their oxidative photocyclization. *Eur. J. Org. Chem.* **2003**, 2829-2839 (2003).

46 Delcaillau, T., Boehm, P. & Morandi, B. Nickel-catalyzed reversible functional group metathesis between aryl nitriles and aryl thioethers. *J. Am. Chem. Soc.* **143**, 3723-3728 (2021).

47 Guo, X. Z. *et al.* Synthesis and biological activities of novel nonpeptide angiotensin II receptor antagonists based on benzimidazole derivatives bearing a heterocyclic ring. *Bioorg. Med. Chem.* **16**, 10301-10310 (2008).

48 Yu, P. & Morandi, B. Nickel-catalyzed cyanation of aryl chlorides and triflates using butyronitrile: merging retro-hydrocyanation with cross-coupling. *Angew. Chem. Int. Ed.* **56**, 15693-15697 (2017).

49 Eastmond, G. C., Paprotny, J., Steiner, A. & Swanson, L. Synthesis of cyanodibenzo [1,4] dioxines and their derivatives by cyano-activated fluoro displacement reactions. *New. J. Chem.* **25**, 379-384 (2001).

50 Sheikh, M. C. *et al.* Synthesis of thianthrene derivatives linked by carbon chains. *Synthesis* **46**, 42-48 (2014).

51 Sha, C.-K. & Tsou, C.-P. Reactions of diethyl [(3-bromomethyl-2-thienyl)-methylene] propanedioate with hydrazines: syntheses of dihydropyridazines, pyridazines and *o*-dimethylaminomethylarenecarbonitriles. *J. Chin. Chem. Soc* **38**, 183-186 (1991).

52 Jacobs, L. *et al.* Design, synthesis, and evaluation of novel ferroquine and phenylequine analogues as potential antiplasmodial agents. *ChemMedChem* **10**, 2099-2110 (2015).

53 Napoletano, M. *et al.* Phthalazine PDE4 inhibitors. part 3: the synthesis and in vitro evaluation of derivatives with a hydrogen bond acceptor. *Bioorg. Med. Chem. Lett.* **12**, 5-8 (2002).

54 Liu, W. & Ackermann, L. Versatile ruthenium(ii)-catalyzed C–H cyanations of benzamides. *Chem. Commun.* **50**, 1878-1881 (2014).

55 Chen, Y. *et al.* Copper catalyzed direct synthesis of nitriles from acyl azides. *ChemistrySelect* **3**, 12325-12329 (2018).

56 Çalimsiz, S. & Organ, M. G. Negishi cross-coupling of secondary alkylzinc halides with aryl/heteroaryl halides using Pd–PEPPSI–IPent. *Chem. Commun.* **47**, 5181-5183 (2011).

57 Dutta, U., Lupton, D. W. & Maiti, D. Aryl nitriles from alkynes using tert-butyl nitrite: metal-free approach to C≡C bond cleavage. *Org. Lett.* **18**, 860-863 (2016).

58 Kim, J., Kim, H. & Chang, S. Copper-mediated selective cyanation of indoles and 2-phenylpyridines with ammonium iodide and DMF. *Org. Lett.* **14**, 3924-3927 (2012).

59 Okamoto, K., Watanabe, M., Murai, M., Hatano, R. & Ohe, K. Practical synthesis of aromatic nitrilesviagallium-catalysed electrophilic cyanation of aromatic C–H bonds. *Chem. Commun* **48**, 3127-3129 (2012).

60 Gopi, E., Gravel, E. & Doris, E. Triphenylbismuth dichloride-mediated conversion of thioamides to nitriles. *Eur. J. Org. Chem.* **2019**, 4043-4045 (2019).

61 Gonzalez-Rodriguez, E. *et al.* Twofold π-extension of polyarenes via double and triple radical alkyne peri-annulations: radical cascades converging on the same aromatic core. *J. Am. Chem. Soc.* **142**, 8352-8366 (2020).

62 Lewis, F. W. *et al.* Hydrophilic sulfonated bis-1,2,4-triazine ligands are highly effective reagents for separating actinides(iii) from lanthanides(iii) via selective formation of aqueous actinide complexes. *Chem. Sci.* **6**, 4812-4821 (2015).

63 Wood, J. M., da Silva Júnior, E. N. & Bower, J. F. Rh-catalyzed [2 + 2 + 2] cycloadditions with benzoquinones: de novo access to naphthoquinones for lignan and type II polyketide synthesis. *Org. Lett.* **22**, 265-269 (2020).

64 Ezawa, M. & Togo, H. One-pot preparation of C_1-homologated aliphatic nitriles from aldehydes through a Wittig reaction under metal-cyanide-free conditions. *Eur. J. Org. Chem.* **2017**, 2379-2384 (2017).

65 Zhu, J., Wang, J. & Dong, G. Catalytic activation of unstrained C(aryl)-C(aryl) bonds in 2,2'-biphenols. *Nat. Chem.* **11**, 45-51 (2019).

66 Bhunia, A., Bergander, K. & Studer, A. Cooperative palladium/Lewis acid-catalyzed transfer hydrocyanation of alkenes and alkynes using 1-methylcyclohexa-2,5-diene-1-carbonitrile. *J. Am. Chem. Soc.* **140**, 16353-16359 (2018).

67 Wang, G., Xie, X., Xu, W. & Liu, Y. Nickel-catalyzed highly regioselective hydrocyanation of alkenes with $Zn(CN)_2$. *Org. Chem. Front.* **6**, 2037-2042 (2019).

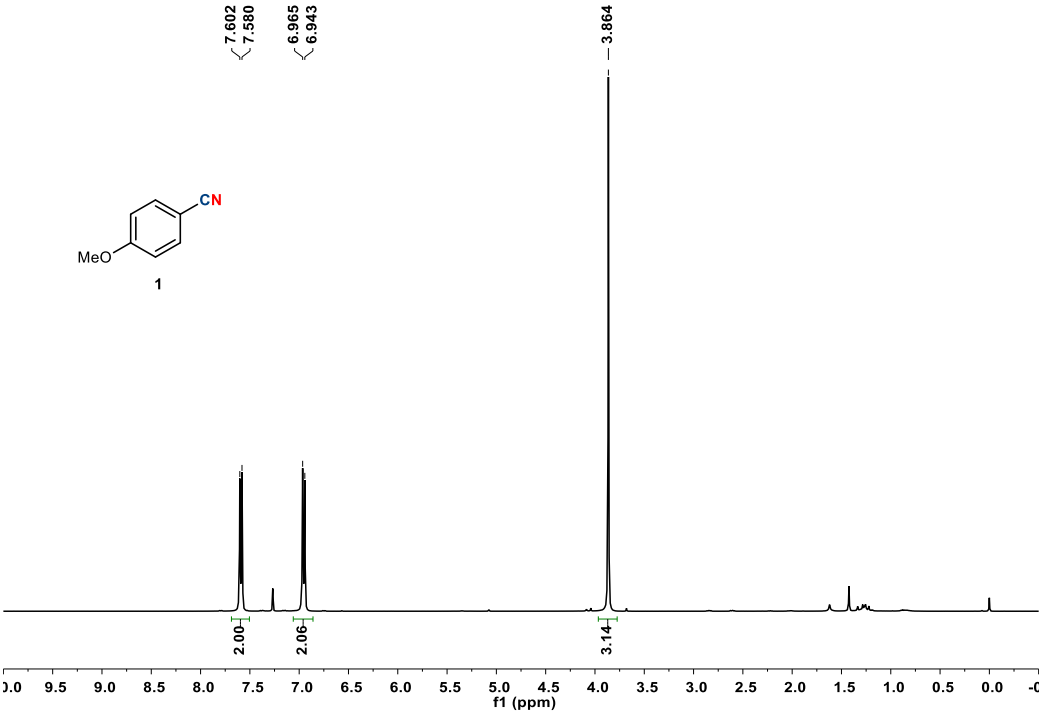
68 Li, Q. *et al.* Tridentate P,N,N-ligand promoted copper-catalyzed [3 + 2] cycloaddition of propargylic esters with β-enamino esters: synthesis of highly functionalized pyrroles. *RSC Adv.* **5**, 85879-85883 (2015).

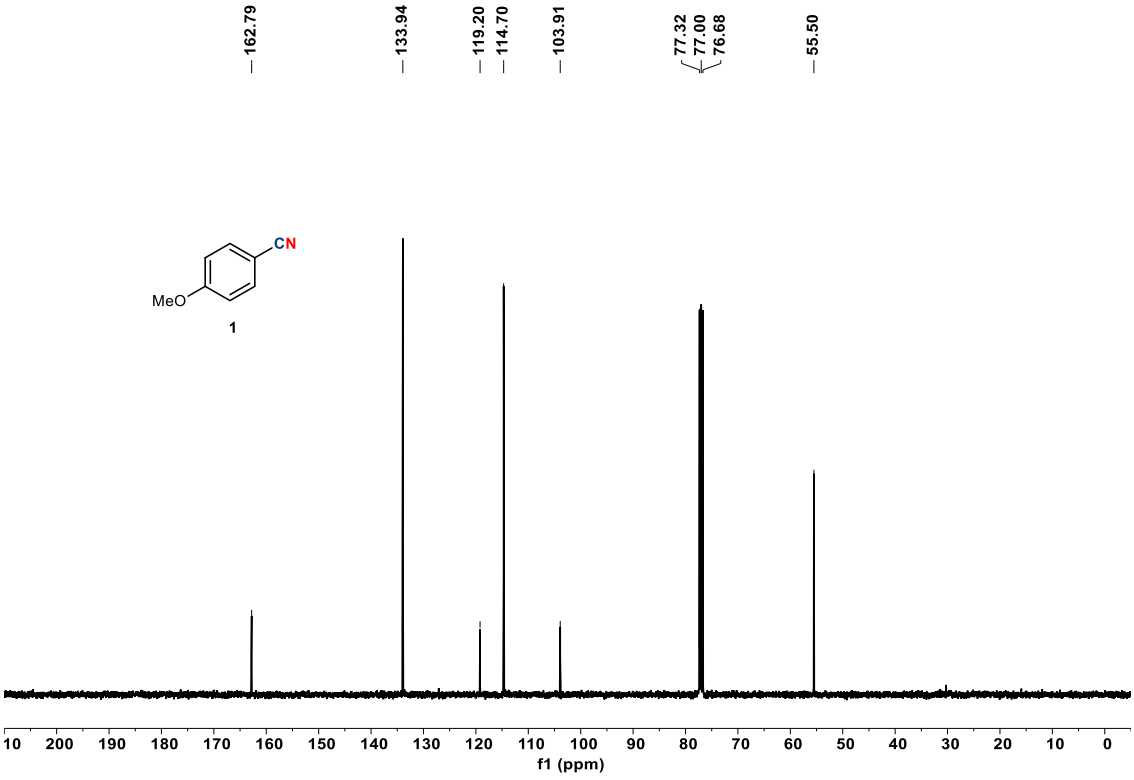
69 Koch, G. *et al.* Synthesis of chiral (phosphinoaryl) oxazolines, a versatile class of ligands for asymmetric catalysis. *Recueil des Travaux Chimiques des Pays-Bas* **114**, 206-210 (1995).

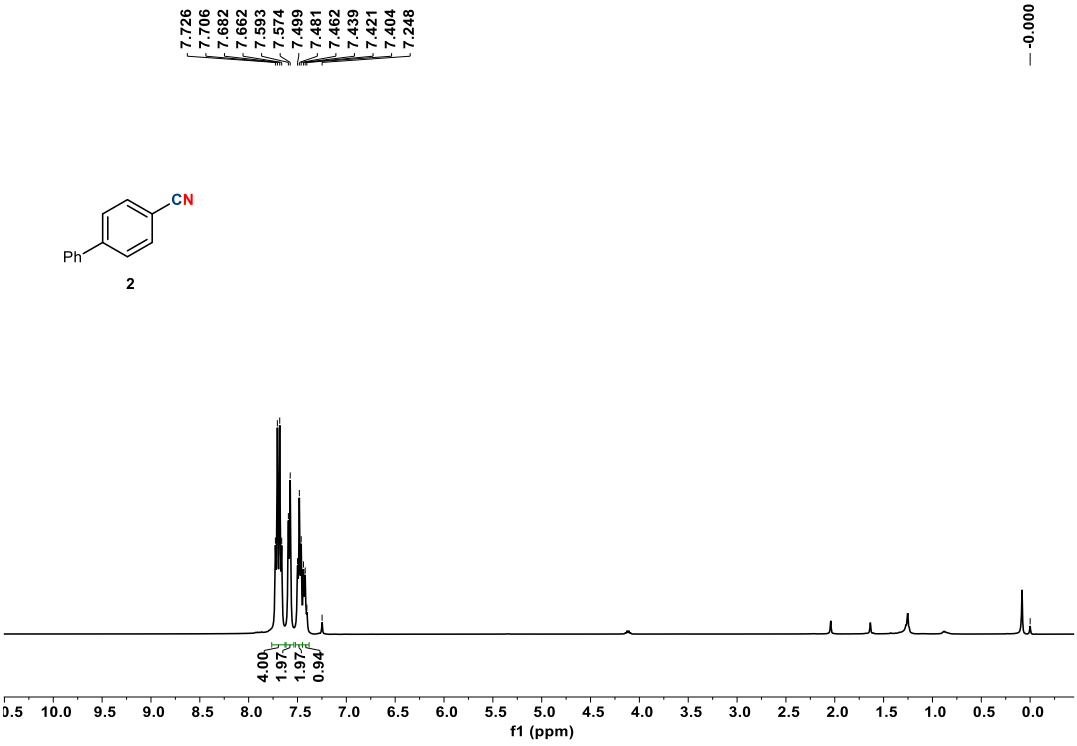
70 Liu, C., Xie, J. H., Tian, G. L., Li, W. & Zhou, Q. L. Highly efficient hydrogenation of carbon dioxide to formate catalyzed by iridium(iii) complexes of imine-diphosphine ligands. *Chem. Sci.* **6**, 2928-2931 (2015).

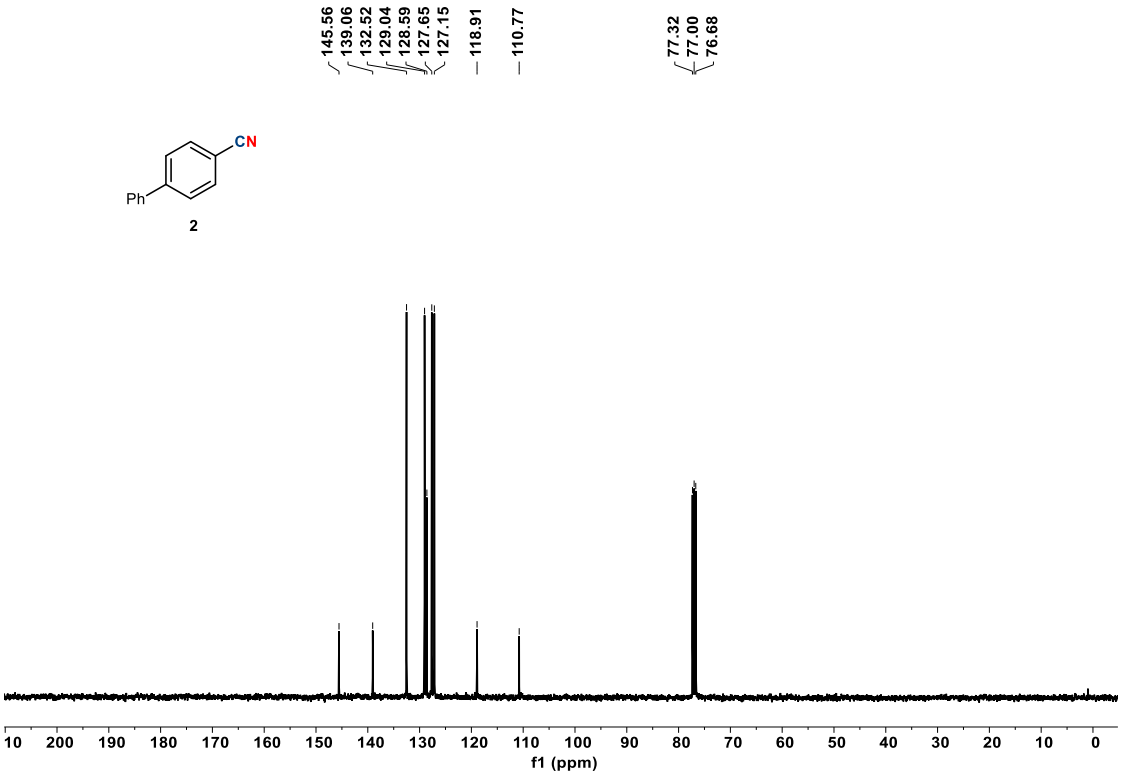
71 Del Zotto, A., Baratta, W., Ballico, M., Herdtweck, E. & Rigo, P. $[RuCl_2(PPh_3)(PNN')]$ complexes as efficient catalysts in transfer hydrogenation of ketones. *Organometallics* **26**, 5636-5642 (2007).

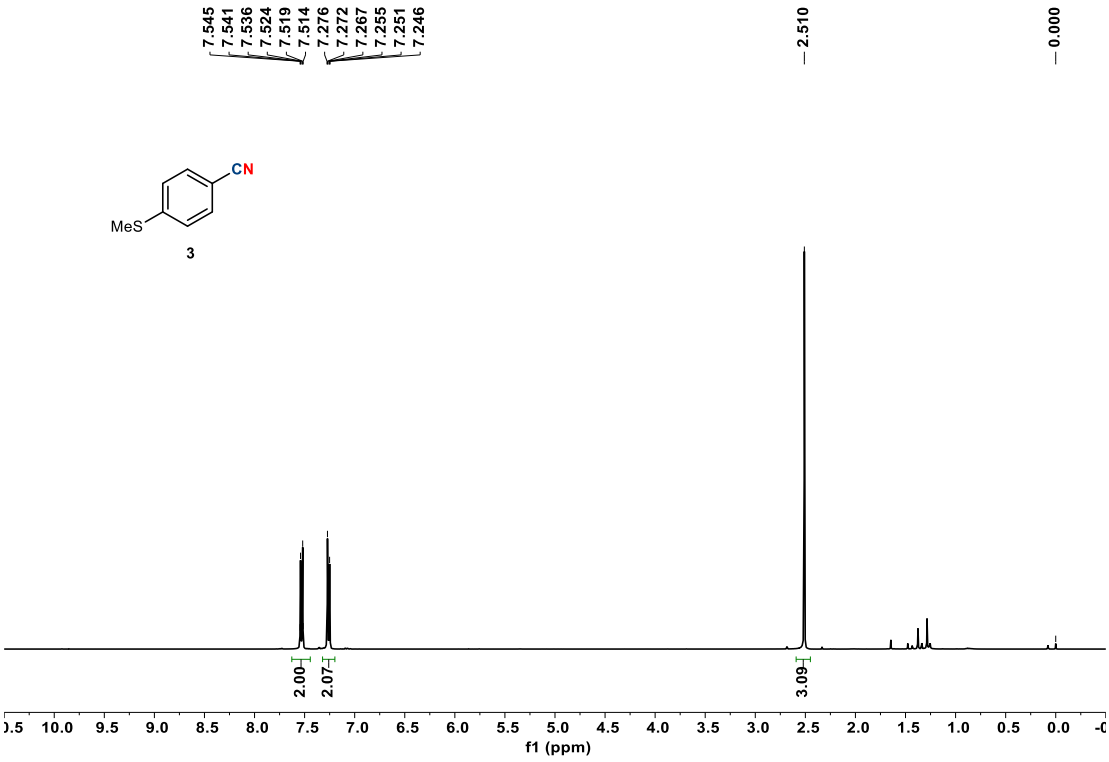
Copies of Products ^{1}H NMR and ^{13}C NMR

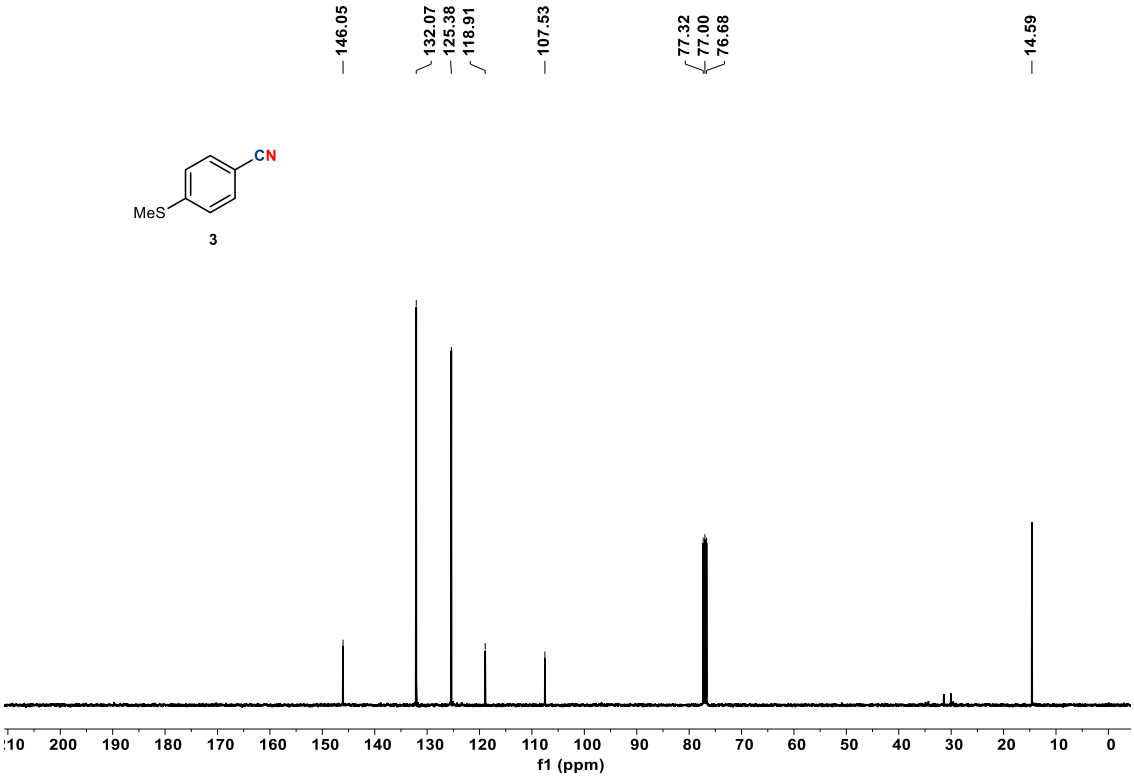


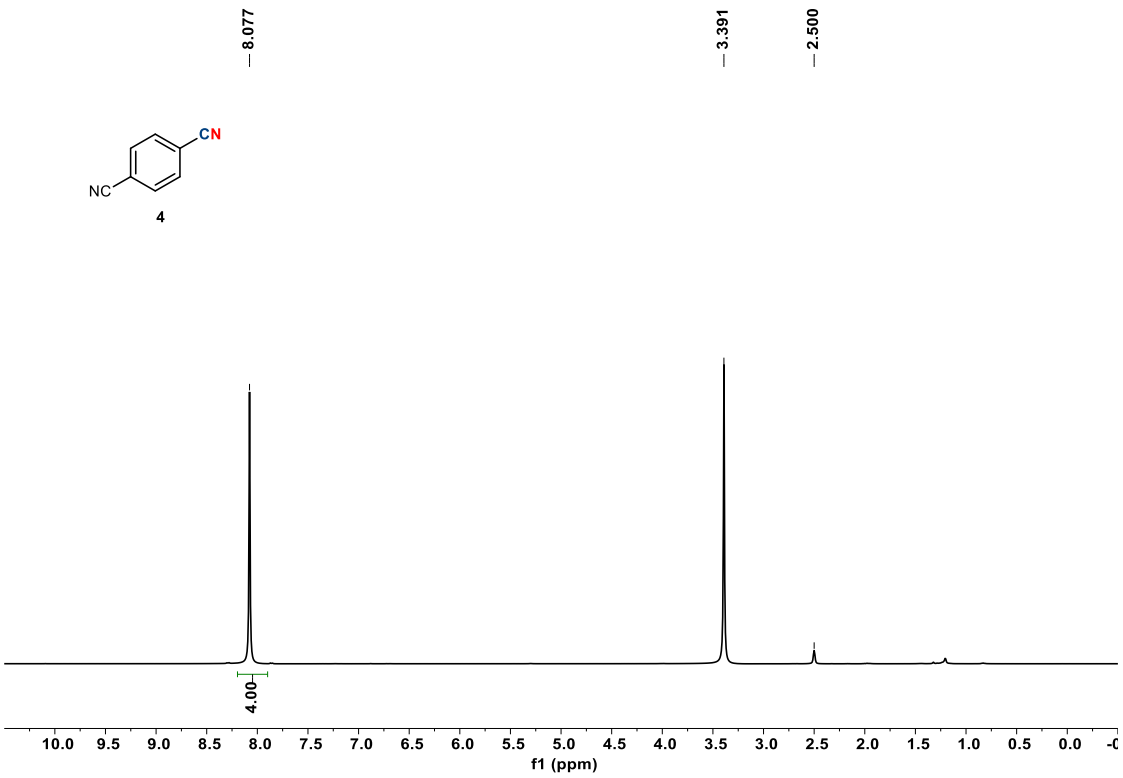


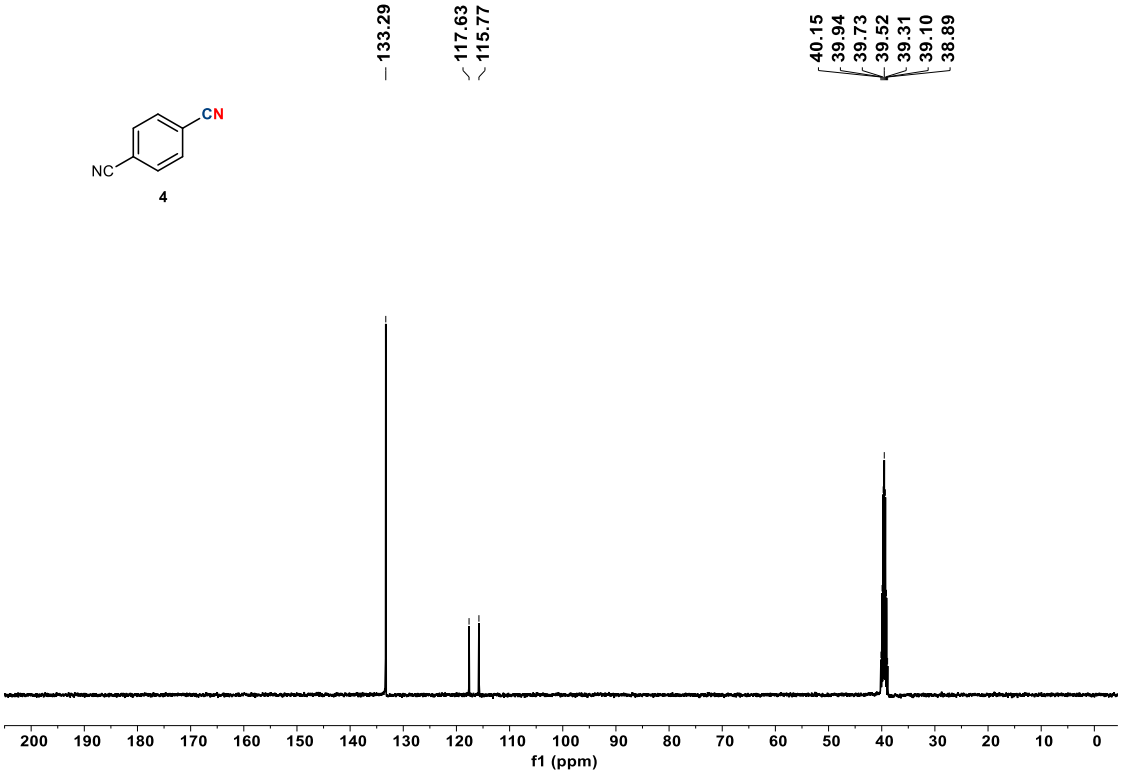

7.726
7.706
7.682
7.662
7.593
7.574
7.499
7.481
7.462
7.439
7.421
7.404
7.248
-0.000
CN
Ph
2
4.00
1.97
1.97
0.94
f1 (ppm)

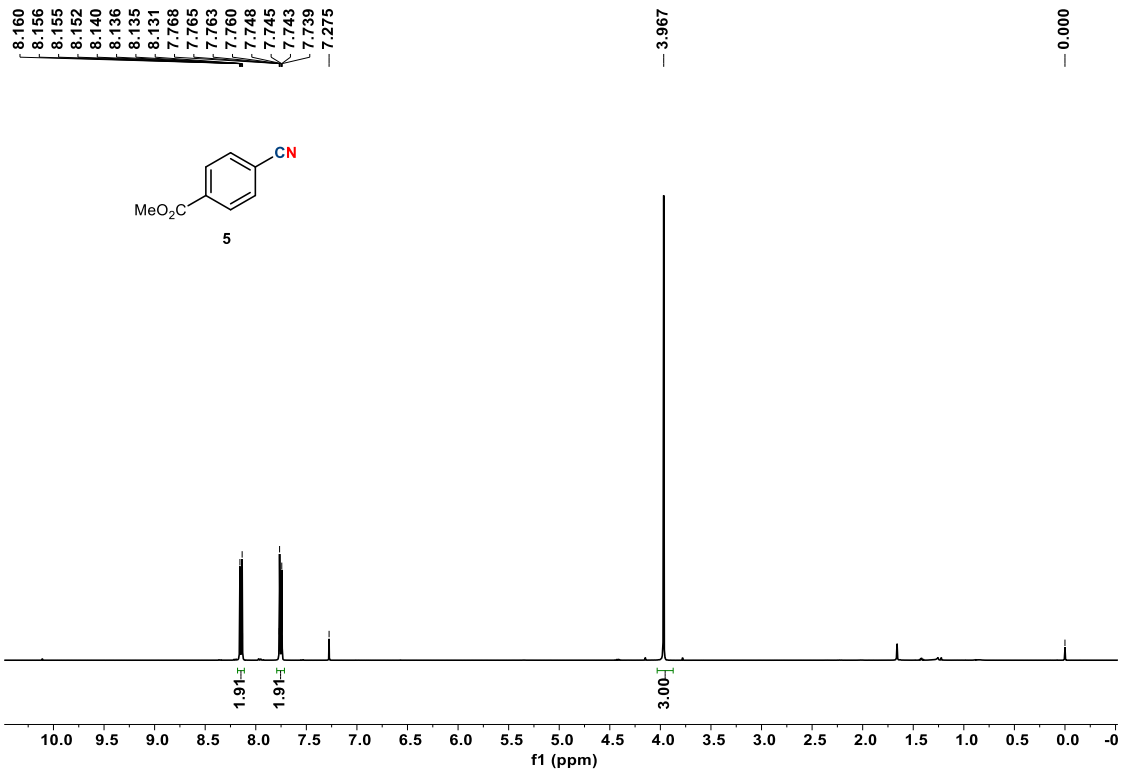

145.56
139.06
132.52
129.04
128.59
127.65
127.15
118.91
110.77
77.32
77.00
76.68
CN
Ph
2
f1 (ppm)

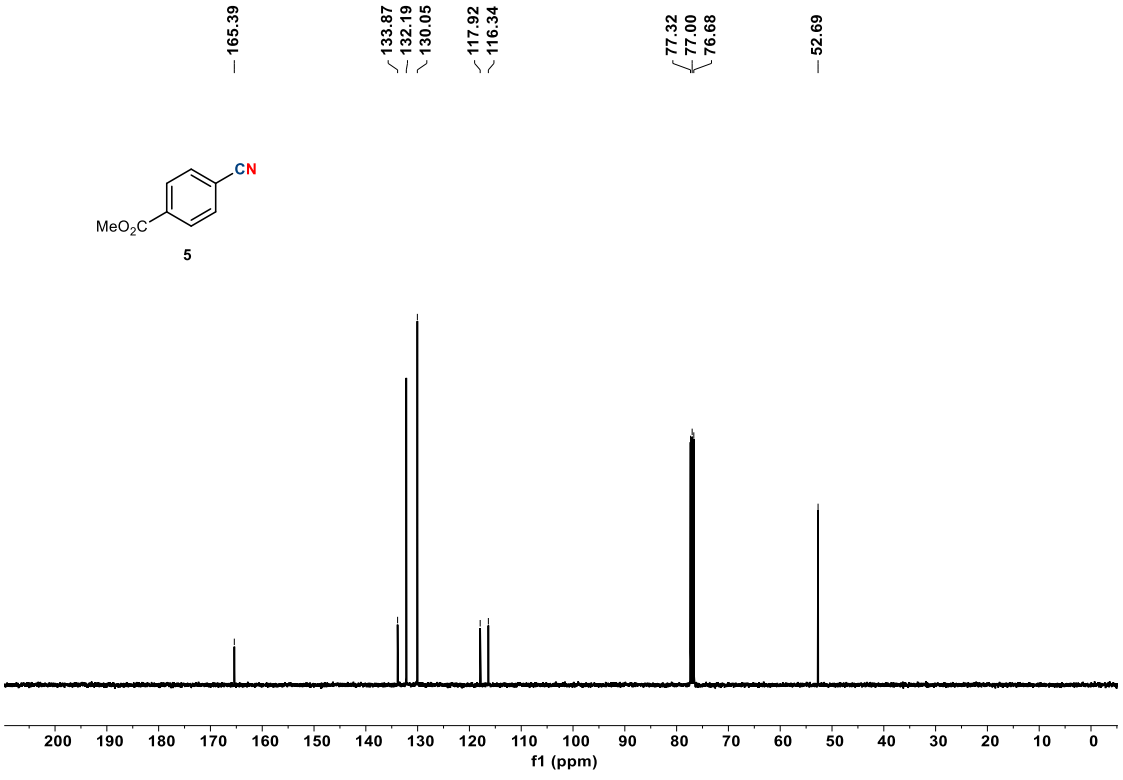

7.545
7.541
7.536
7.524
7.519
7.514
7.276
7.272
7.267
7.255
7.251
7.246
2.510
0.000
CN
MeS
3
2.00
2.07
3.09
f1 (ppm)

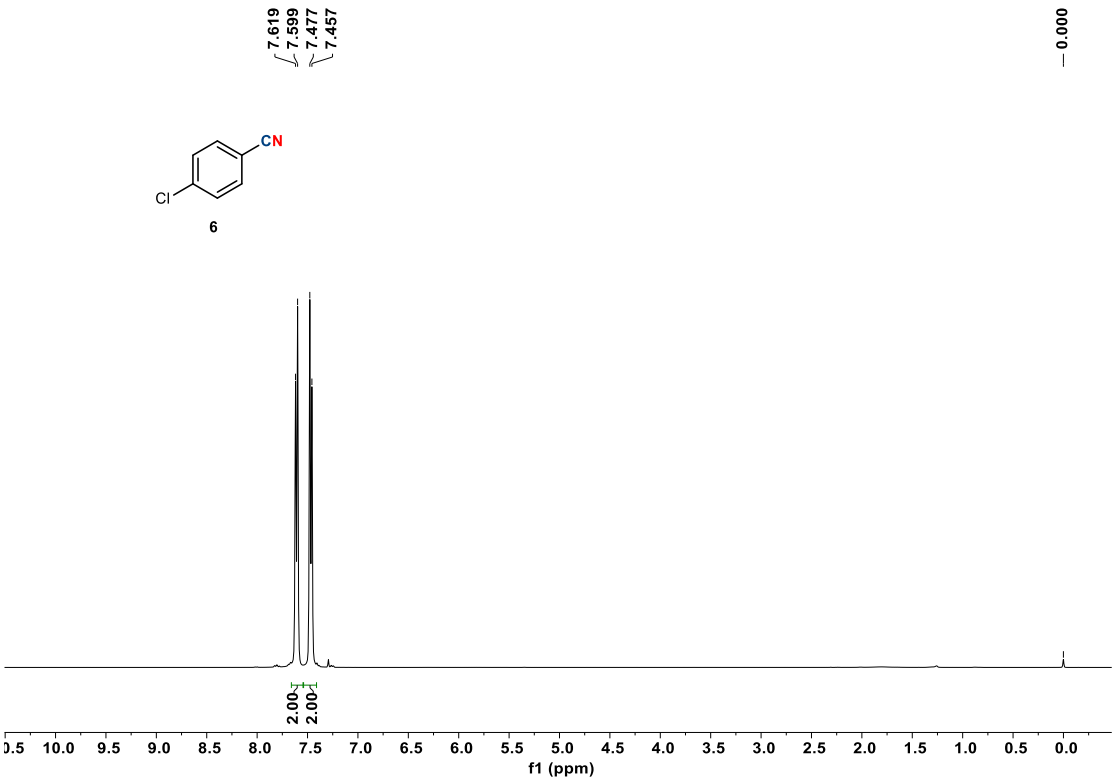

146.05
132.07
125.38
118.91
107.53
77.32
77.00
76.68
14.59
CN
MeS
3
f1 (ppm)

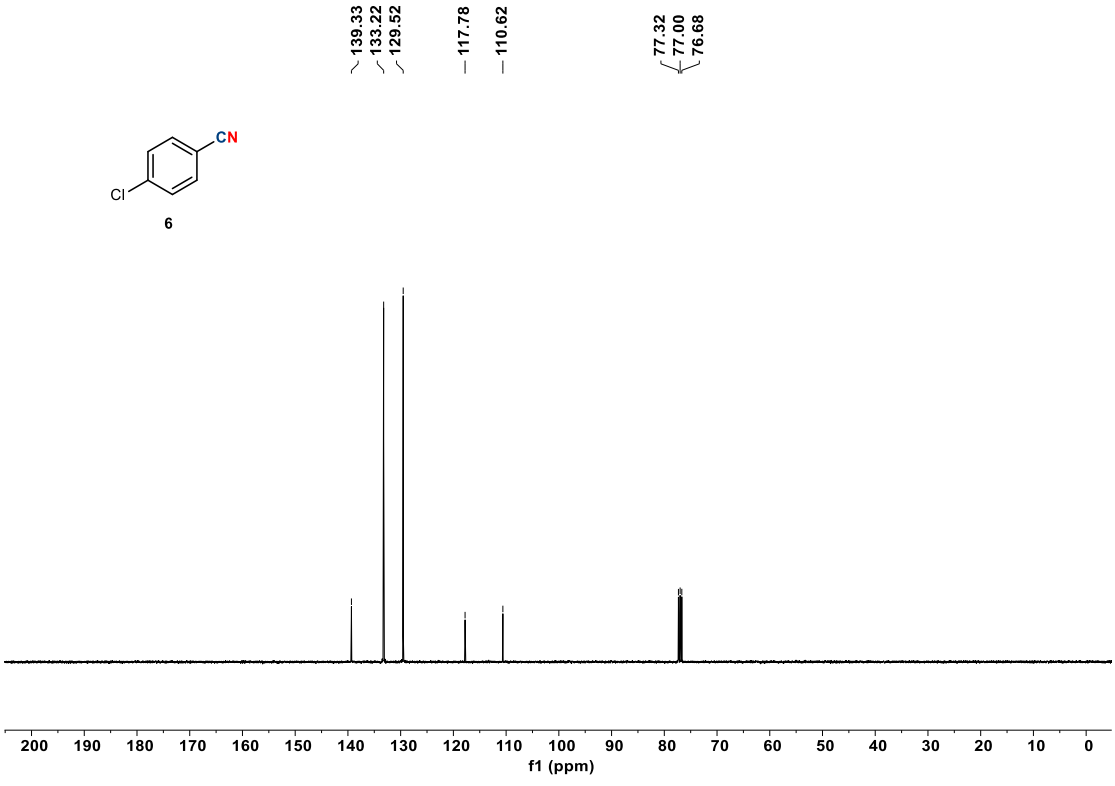

8.077
3.391
2.500
CN
NC
4
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

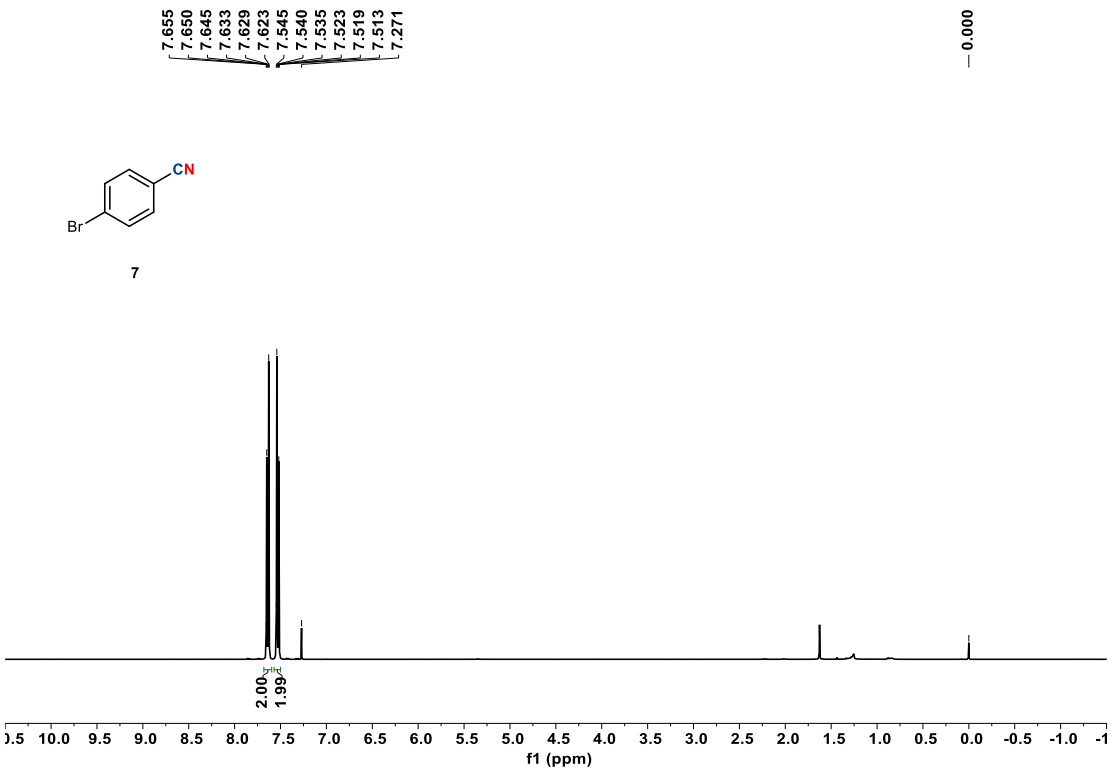

133.29
117.63
115.77
40.15
39.94
39.73
39.52
39.31
39.10
38.89
CN
NC
4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

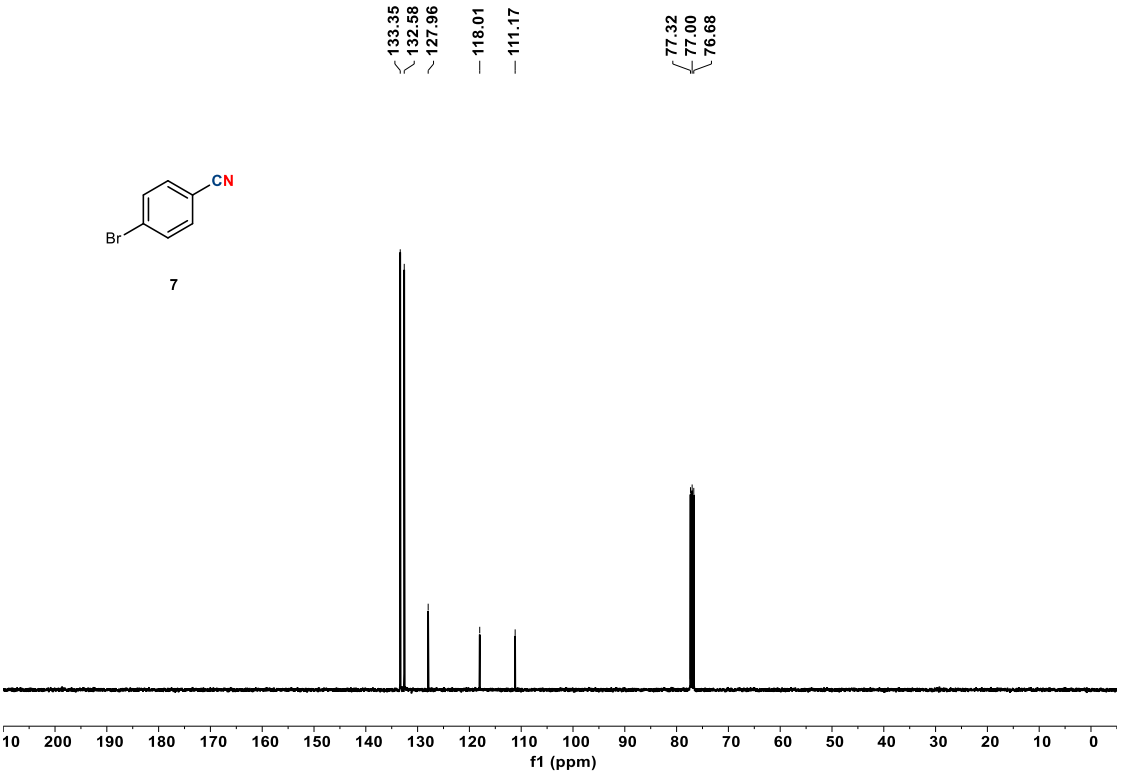

8.160
8.156
8.155
8.152
8.140
8.136
8.135
8.131
7.768
7.765
7.763
7.760
7.748
7.745
7.743
7.739
7.275
3.967
0.000
CN
MeO2C
5
1.91
1.91
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

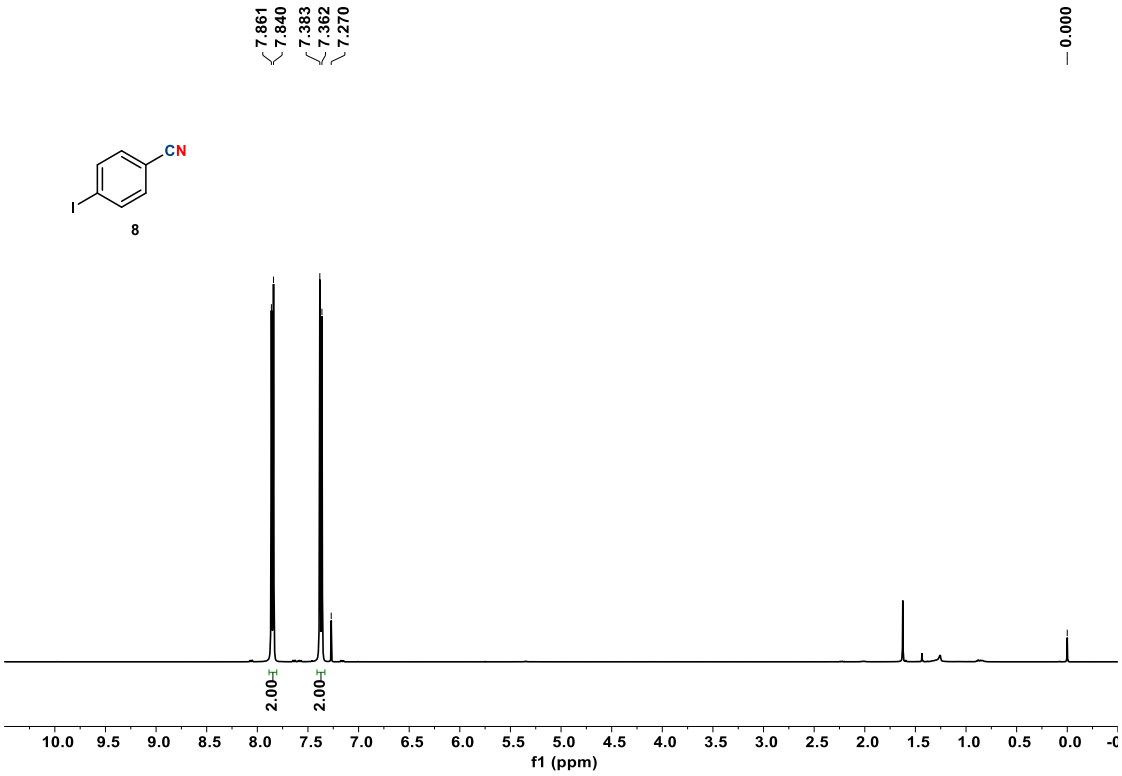

165.39
133.87
132.19
130.05
117.92
116.34
77.32
77.00
76.68
52.69
CN
MeO2C
5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

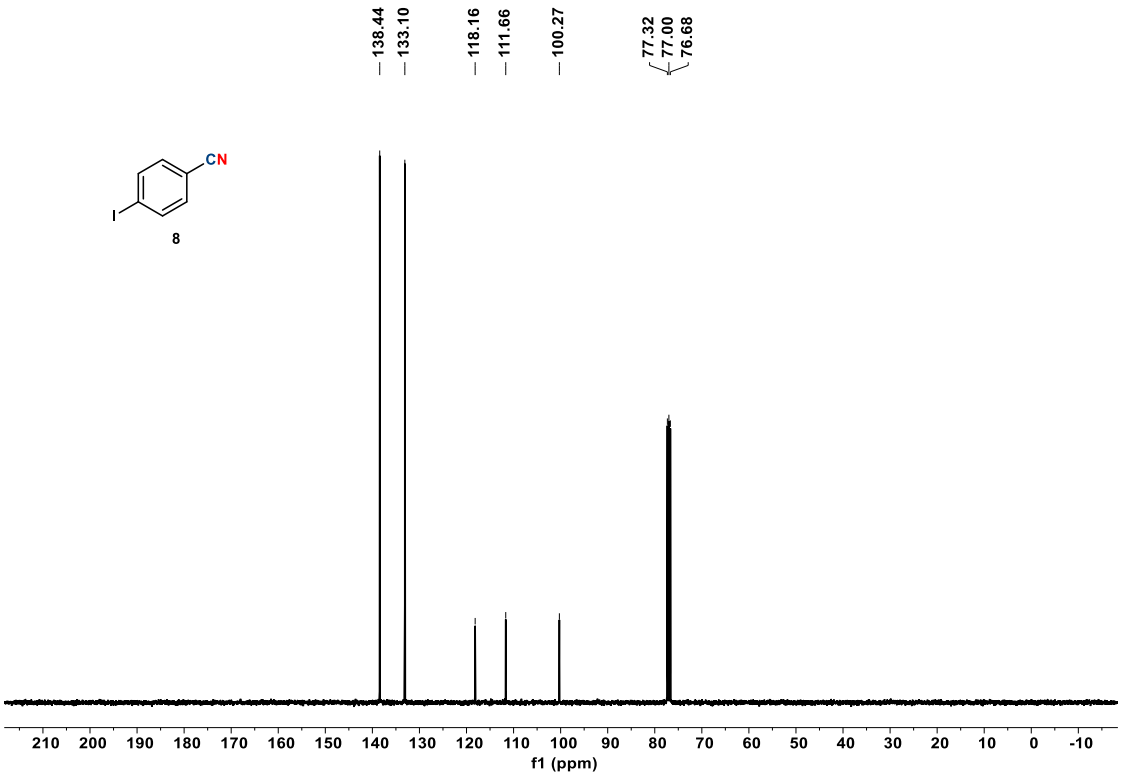

7.619
7.599
7.477
7.457
0.000
CN
Cl
6
2.00
2.00
f1 (ppm)

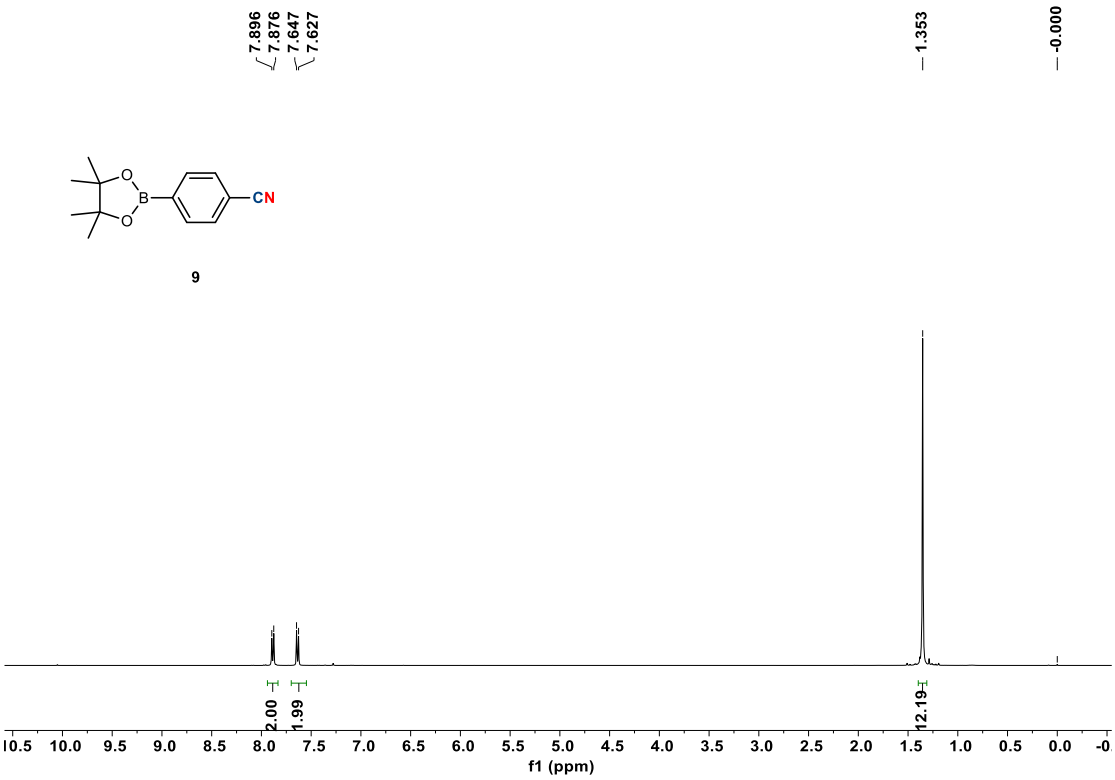

139.33
133.22
129.52
117.78
110.62
77.32
77.00
76.68
CN
Cl
6
f1 (ppm)

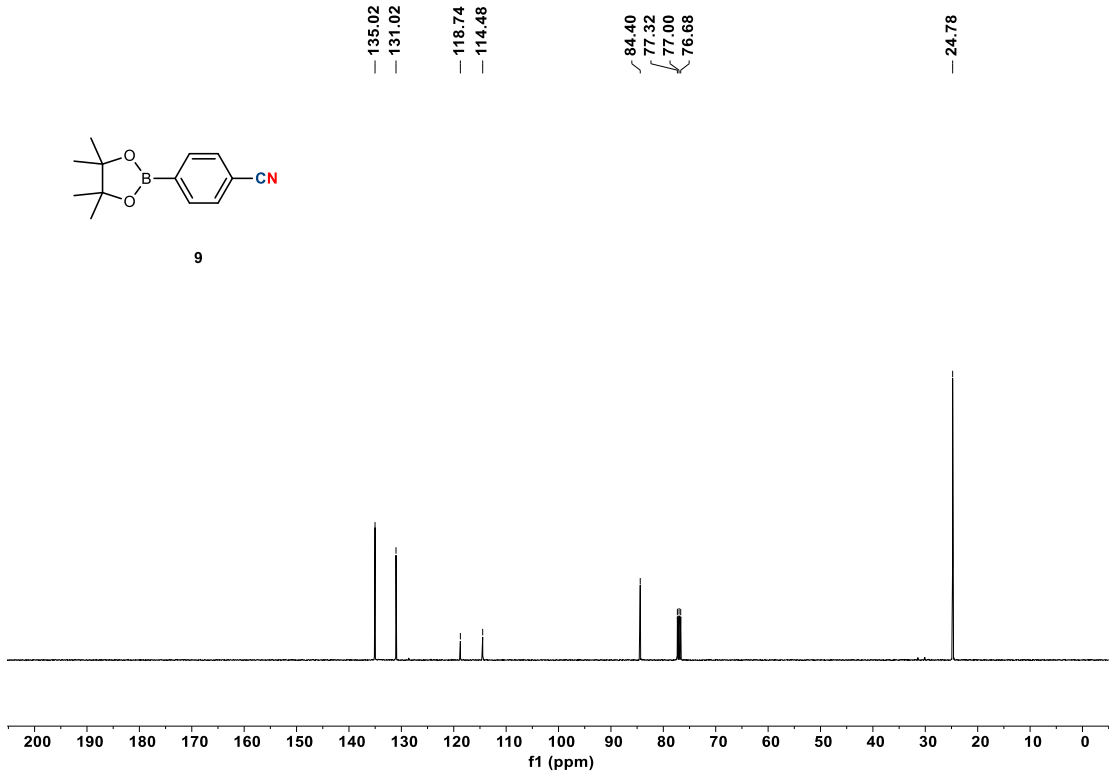

7.655
7.650
7.645
7.633
7.629
7.623
7.545
7.540
7.535
7.523
7.519
7.513
7.271
0.000
CN
Br
7
2.00
1.99
f1 (ppm)

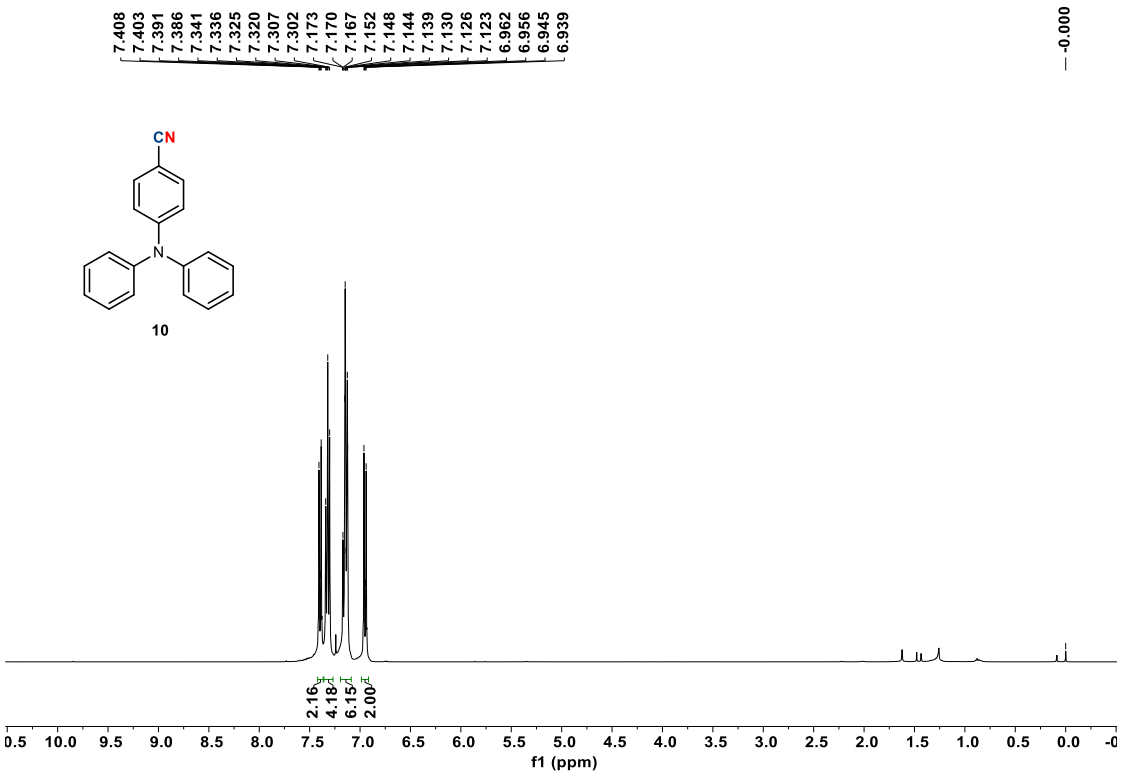

133.35
132.58
127.96
118.01
111.17
77.32
77.00
76.68
CN
Br
7
f1 (ppm)

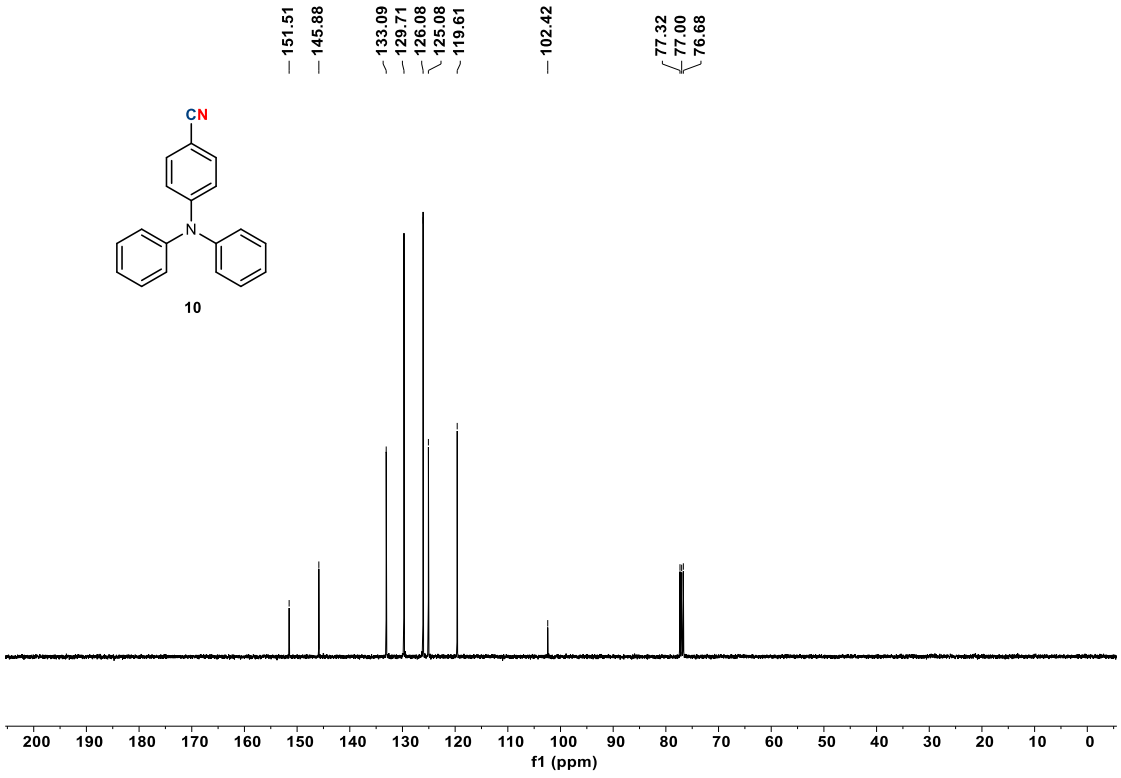

7.861
7.840
7.383
7.362
7.270
0.000
CN
I
8
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

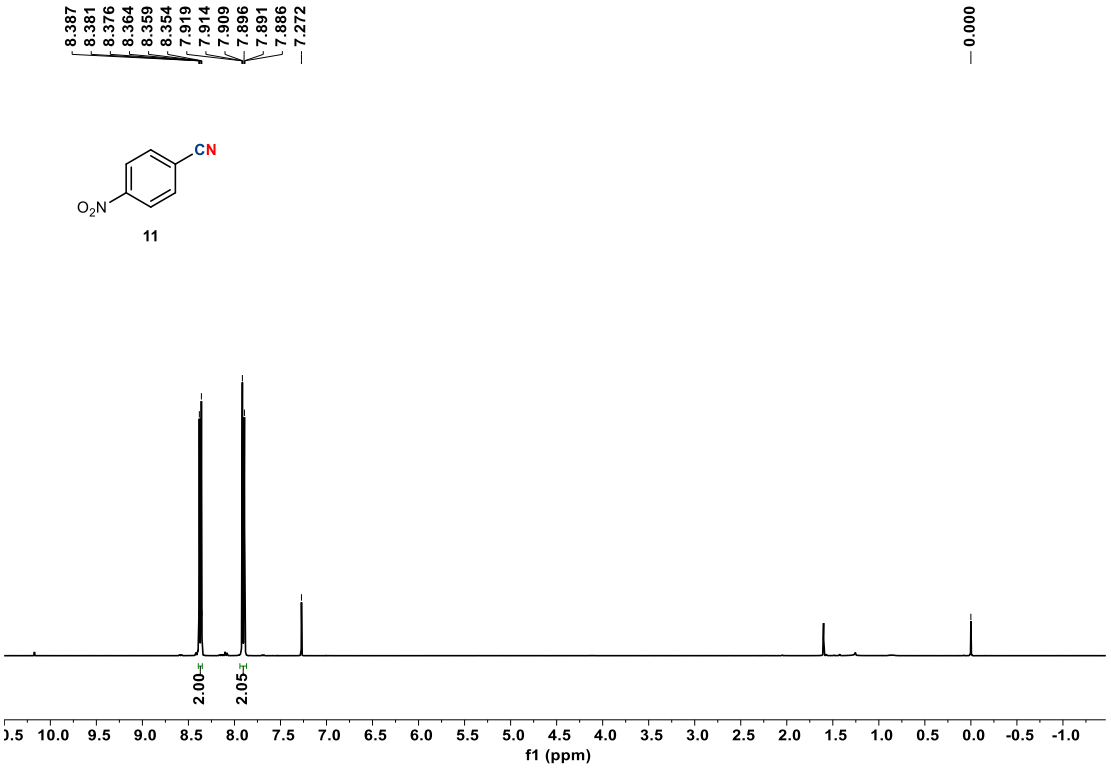

138.44
133.10
118.16
111.66
100.27
77.32
77.00
76.68
CN
I
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

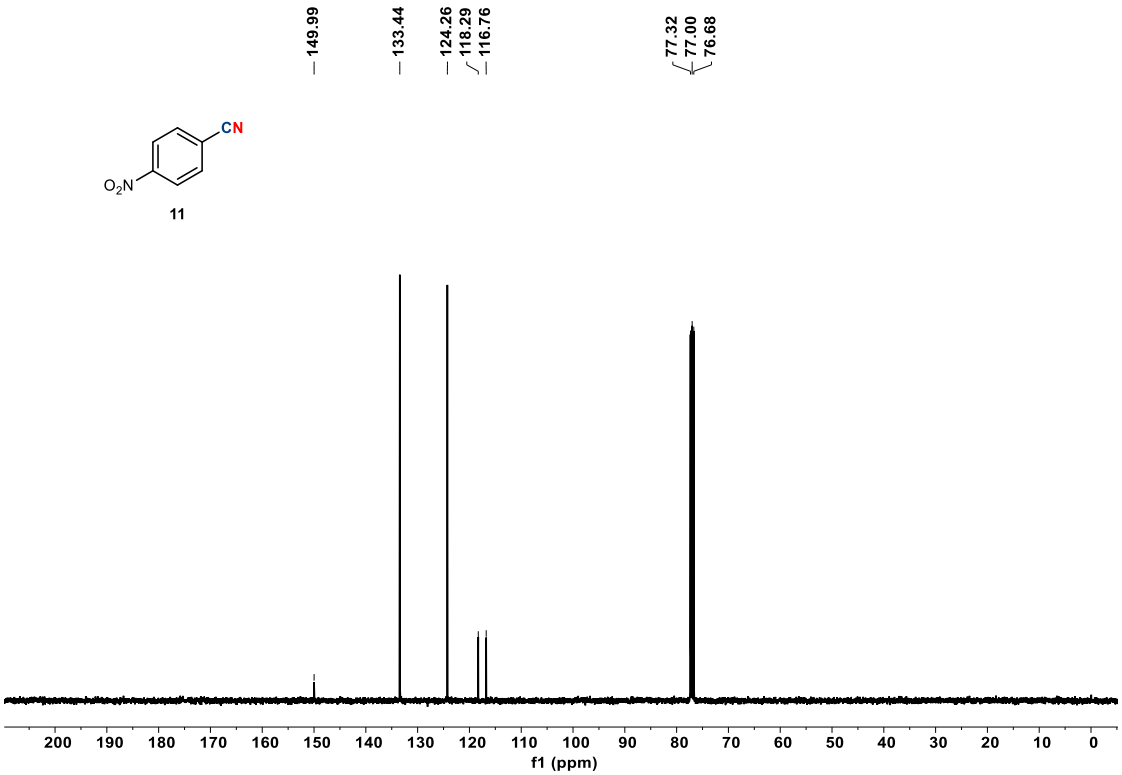

7.896
7.876
7.647
7.627
1.353
-0.000
9
2.00
1.99
12.19
f1 (ppm)

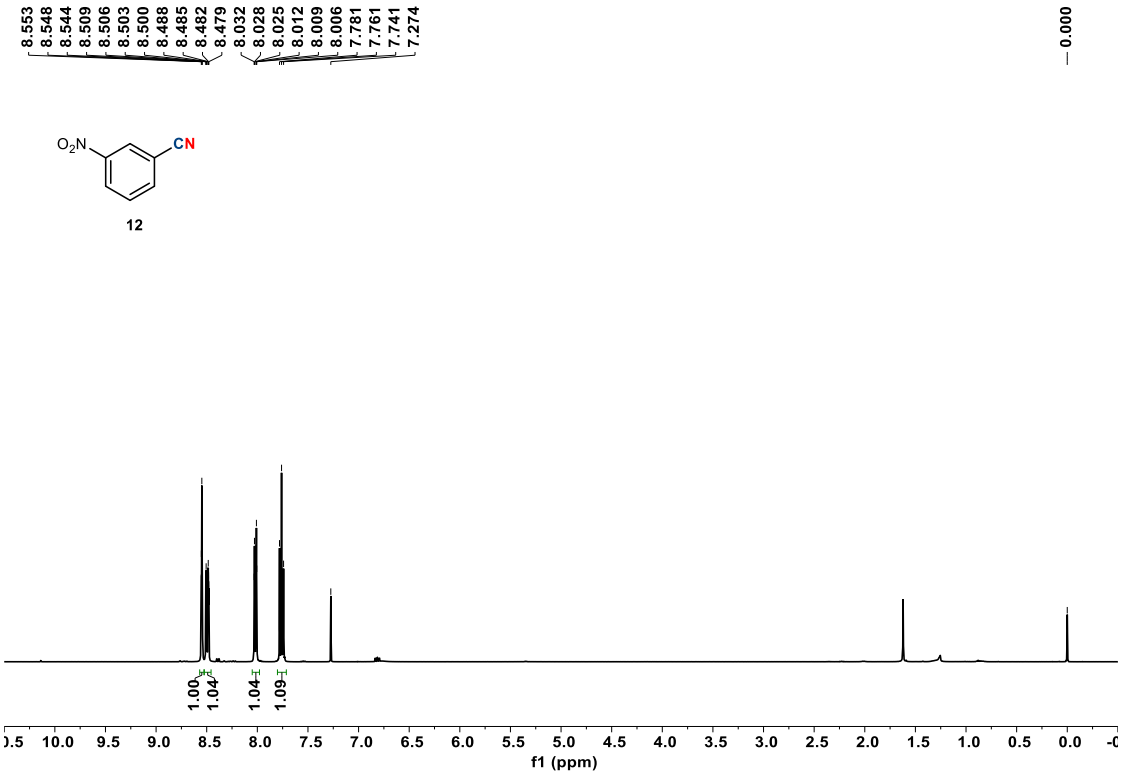

135.02
131.02
118.74
114.48
84.40
77.32
77.00
76.68
24.78
9
f1 (ppm)

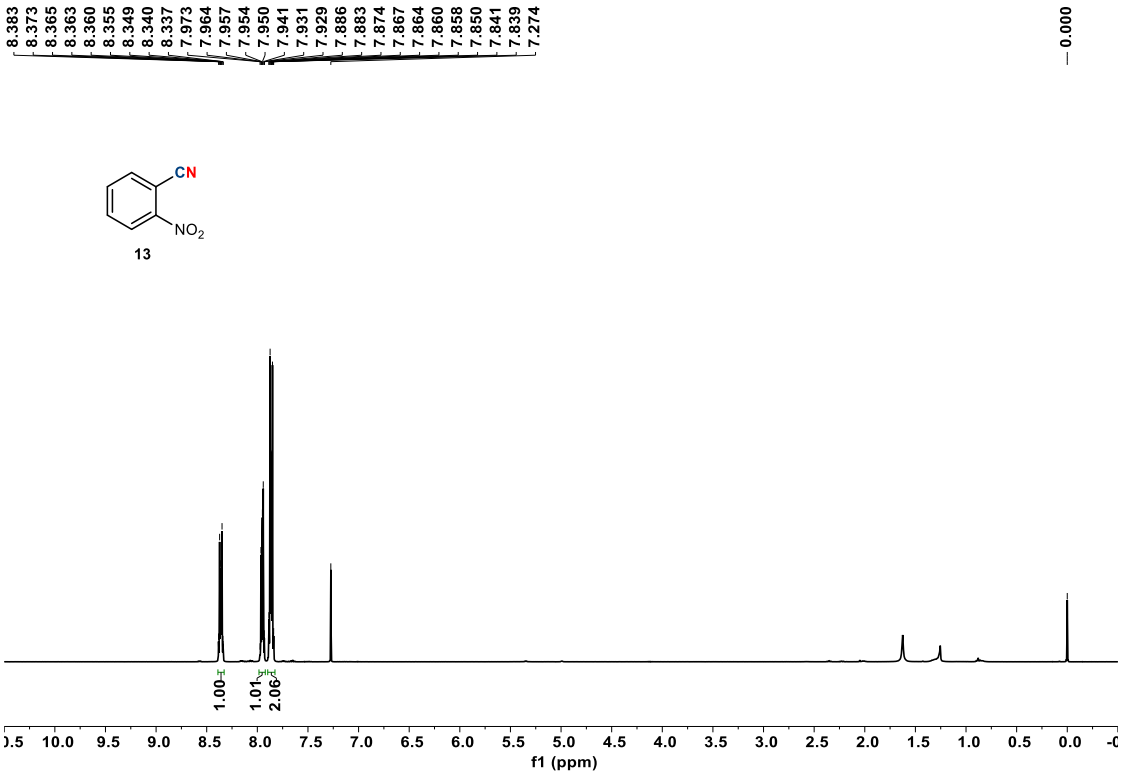

7.408
7.403
7.391
7.386
7.341
7.336
7.325
7.320
7.307
7.302
7.173
7.170
7.167
7.152
7.148
7.144
7.139
7.130
7.126
7.123
6.962
6.956
6.945
6.939
-0.000
CN
N
10
2.16
4.18
6.15
2.00
f1 (ppm)

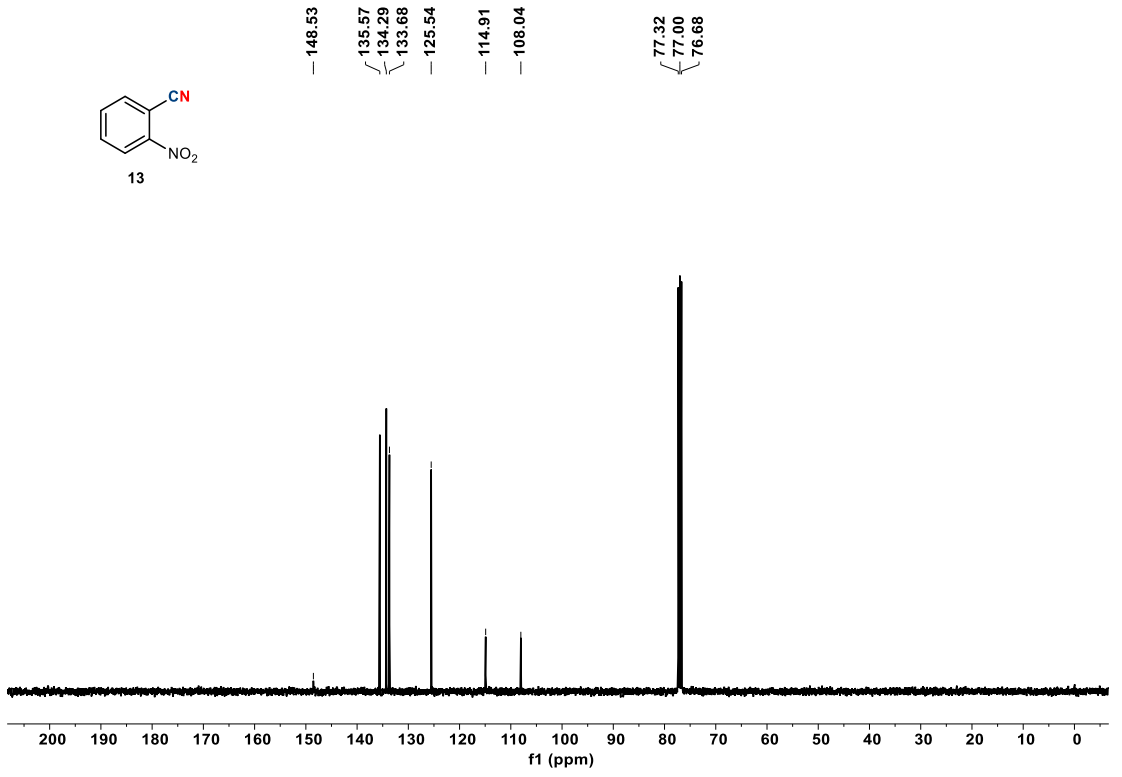

151.51
145.88
133.09
129.71
126.08
125.08
119.61
102.42
77.32
77.00
76.68
CN
N
10
f1 (ppm)

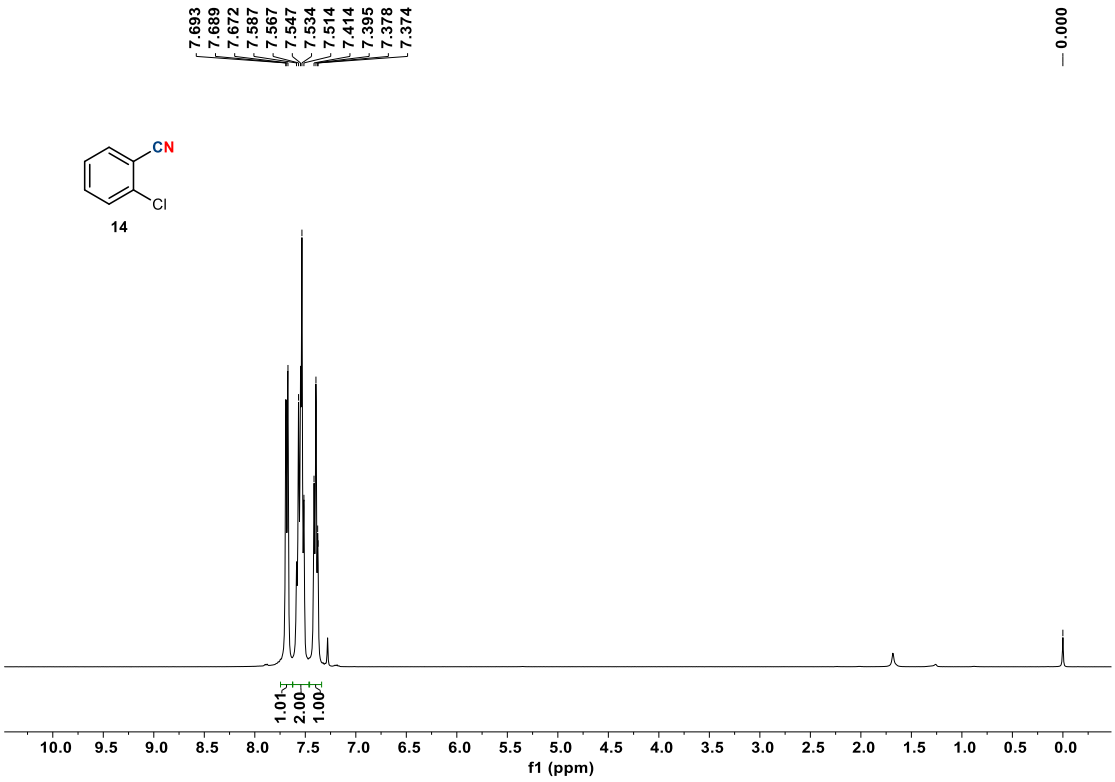

8.387
8.381
8.376
8.364
8.359
8.354
7.919
7.914
7.909
7.896
7.891
7.886
7.272
0.000
CN
O2N
11
2.00
2.05
f1 (ppm)

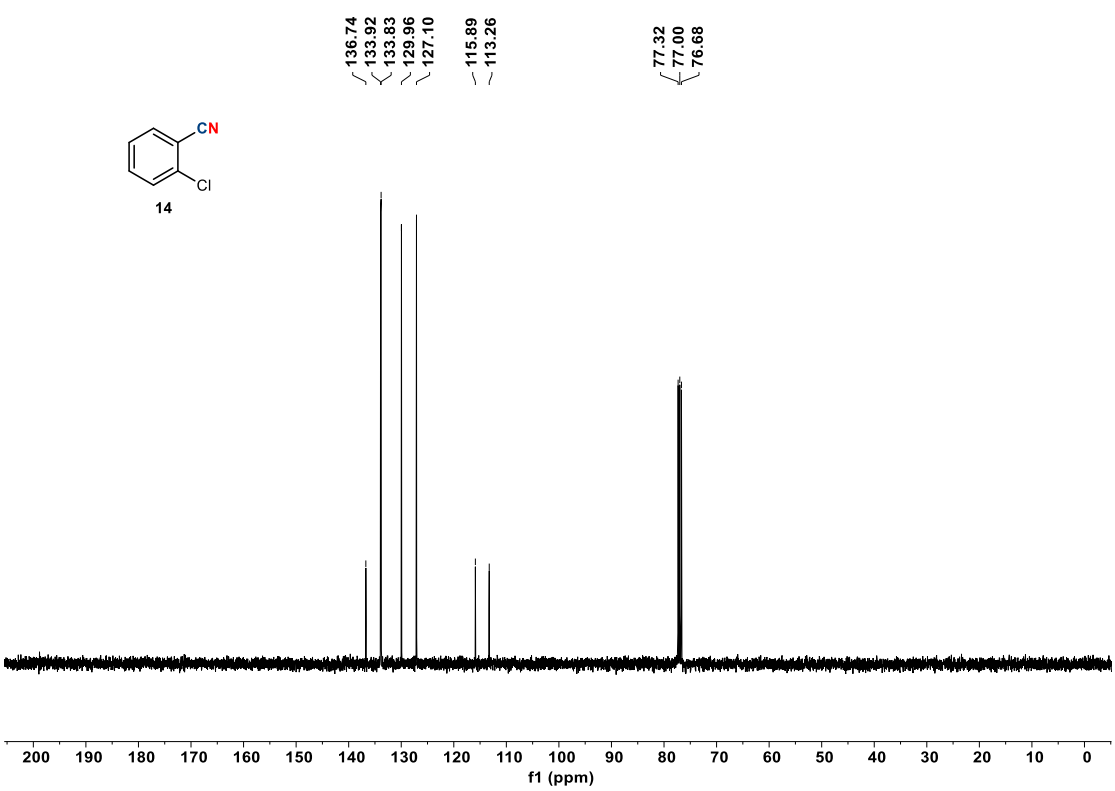

149.99
133.44
124.26
118.29
116.76
77.32
77.00
76.68
CN
O2N
11
f1 (ppm)

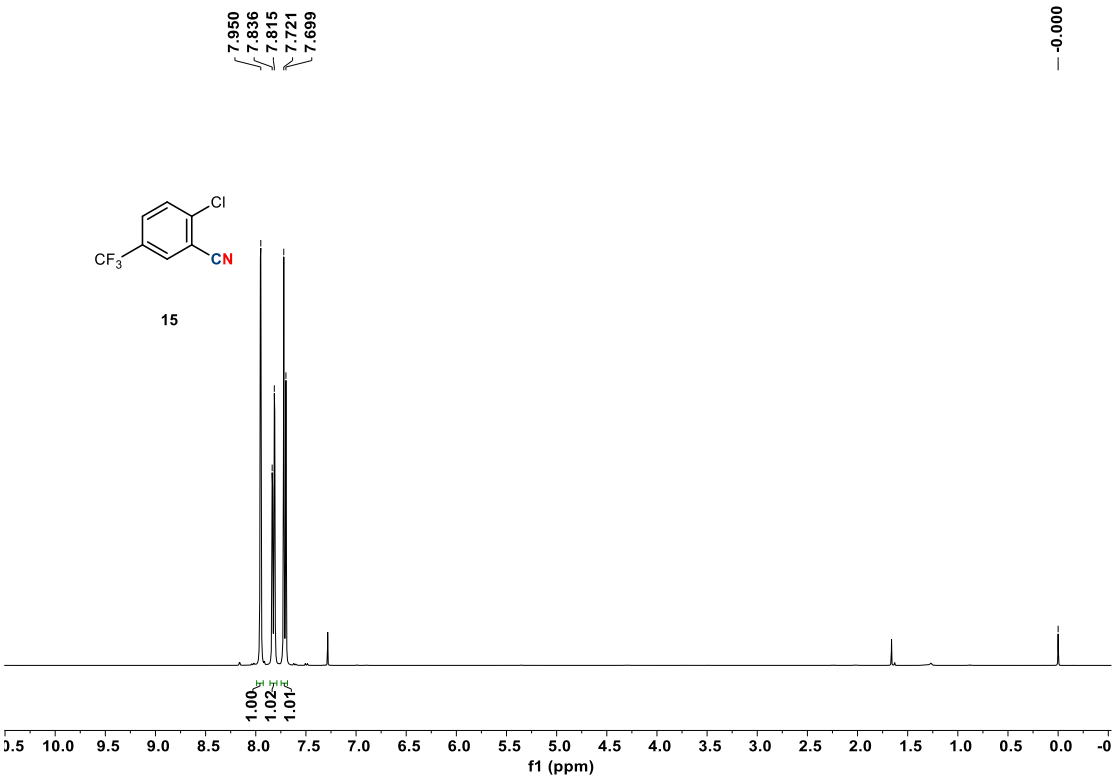

8.553
8.548
8.544
8.509
8.506
8.503
8.500
8.488
8.485
8.482
8.479
8.032
8.028
8.025
8.012
8.009
8.006
7.781
7.761
7.741
7.274
0.000
O2N
CN
12
1.00
1.04
1.04
1.09
f1 (ppm)
148.17
137.58
130.63
127.50
127.19
116.50
114.08
77.32
77.00
76.68
O2N
CN
12
f1 (ppm)

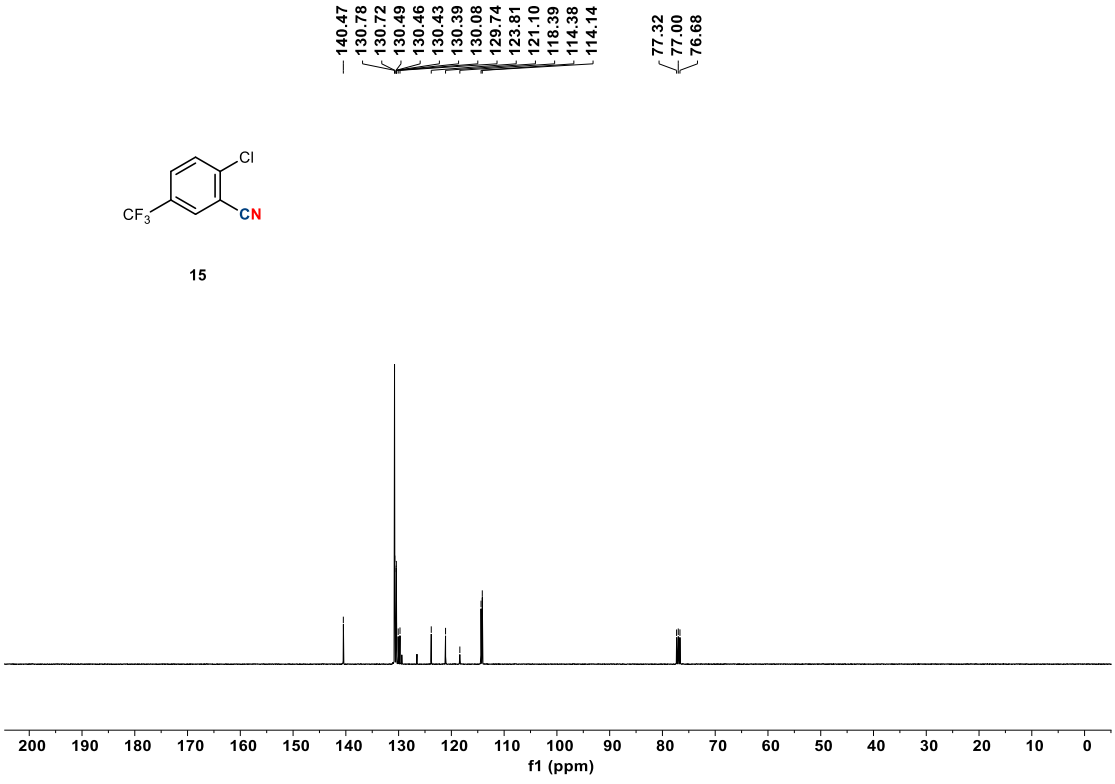

8.383
8.373
8.365
8.363
8.360
8.355
8.349
8.340
8.337
7.973
7.964
7.957
7.954
7.950
7.941
7.931
7.929
7.886
7.883
7.874
7.867
7.864
7.860
7.858
7.850
7.841
7.839
7.274
0.000
CN
NO2
13
1.00
1.01
2.06
f1 (ppm)

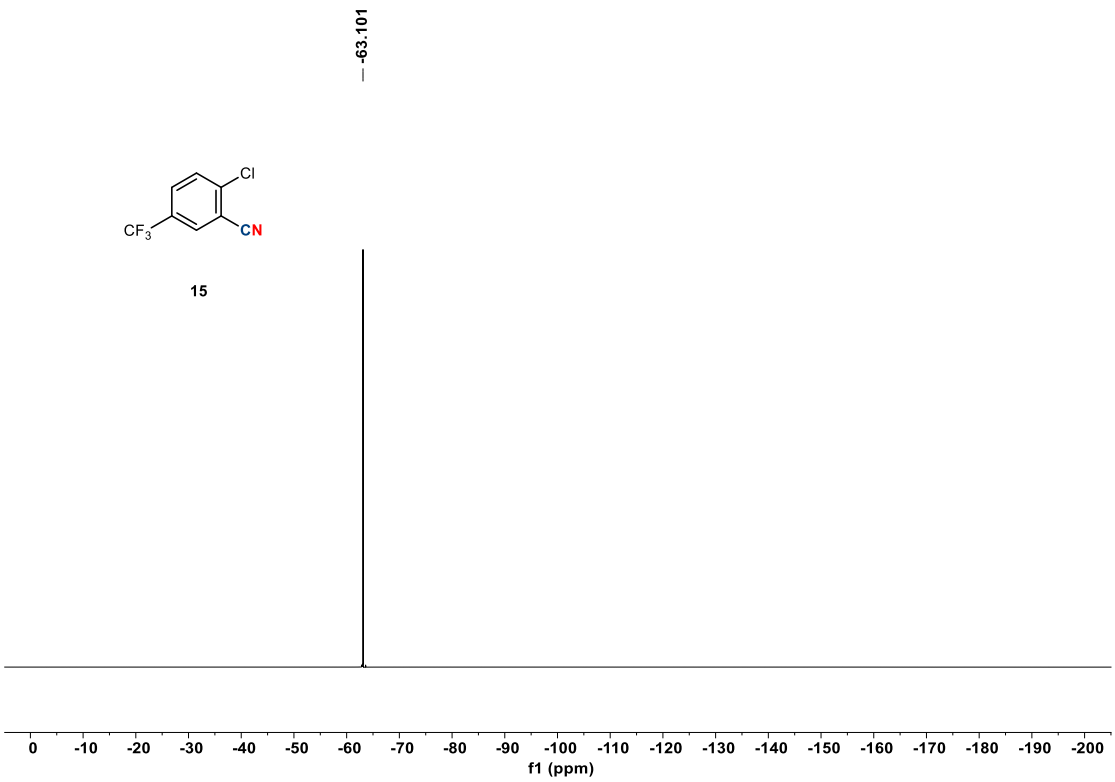

148.53
135.57
134.29
133.68
125.54
114.91
108.04
77.32
77.00
76.68
CN
NO2
13
f1 (ppm)


7.693
7.689
7.672
7.587
7.567
7.547
7.534
7.514
7.414
7.395
7.378
7.374
0.000
CN
Cl
14
1.01
2.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

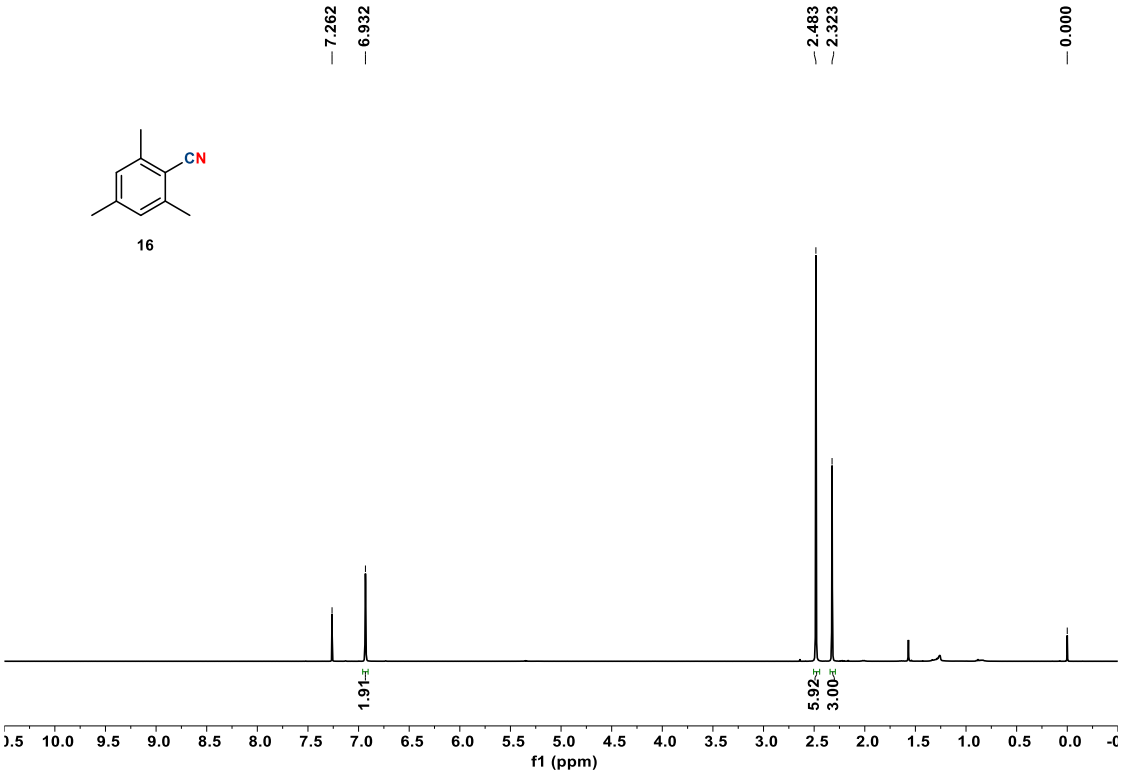

136.74
133.92
133.83
129.96
127.10
115.89
113.26
77.32
77.00
76.68
CN
Cl
14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

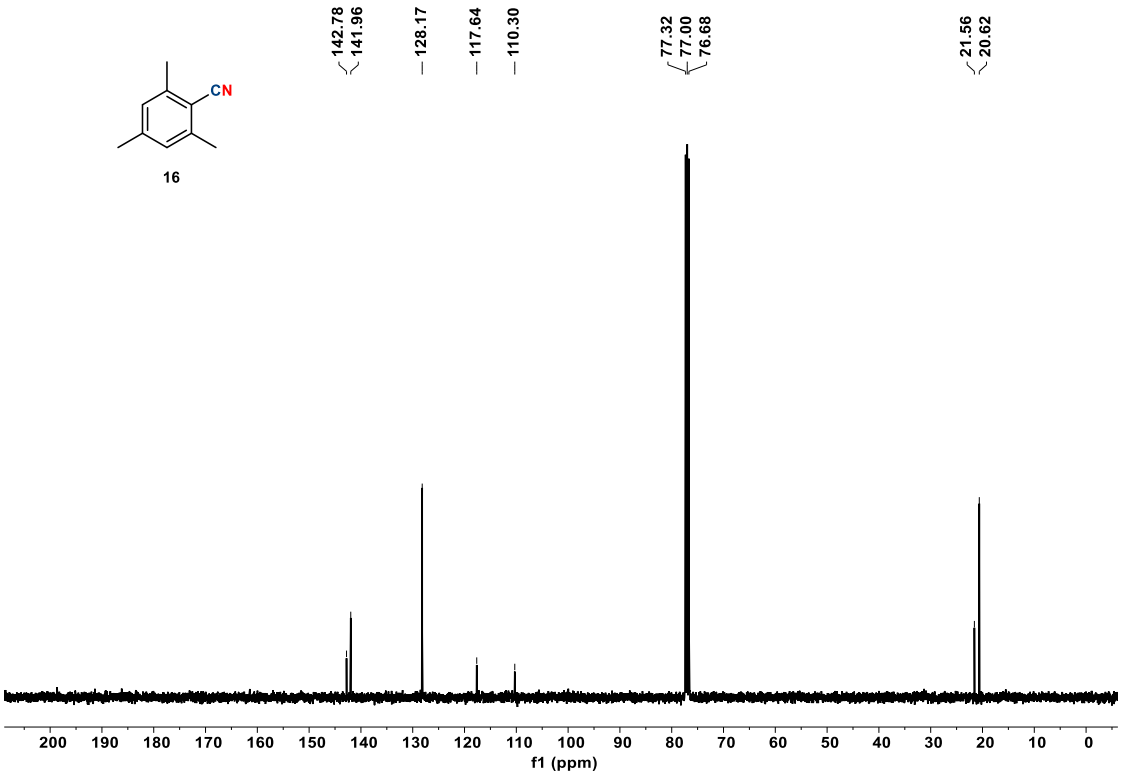

7.950
7.836
7.815
7.721
7.699
-0.000
Cl
CF3
CN
15
1.00
1.02
1.01
f1 (ppm)

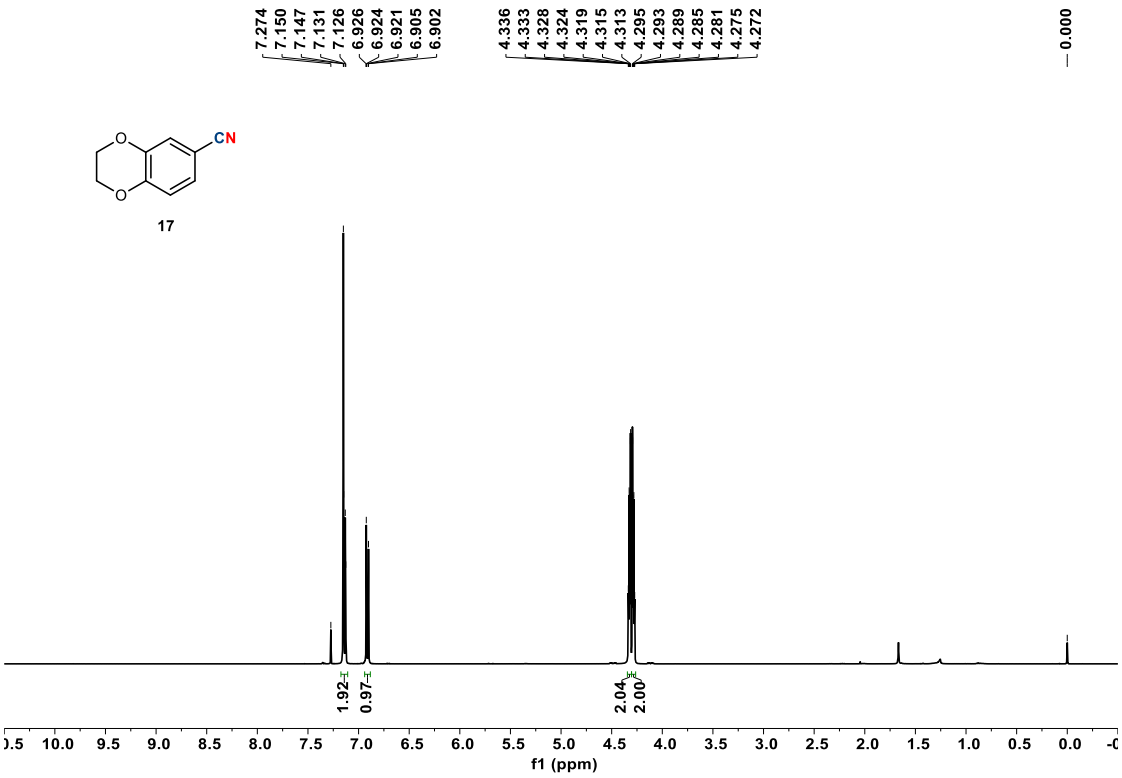

140.47
130.78
130.72
130.49
130.46
130.43
130.39
130.08
129.74
123.81
121.10
118.39
114.38
114.14
77.32
77.00
76.68
Cl
CF3
CN
15
f1 (ppm)

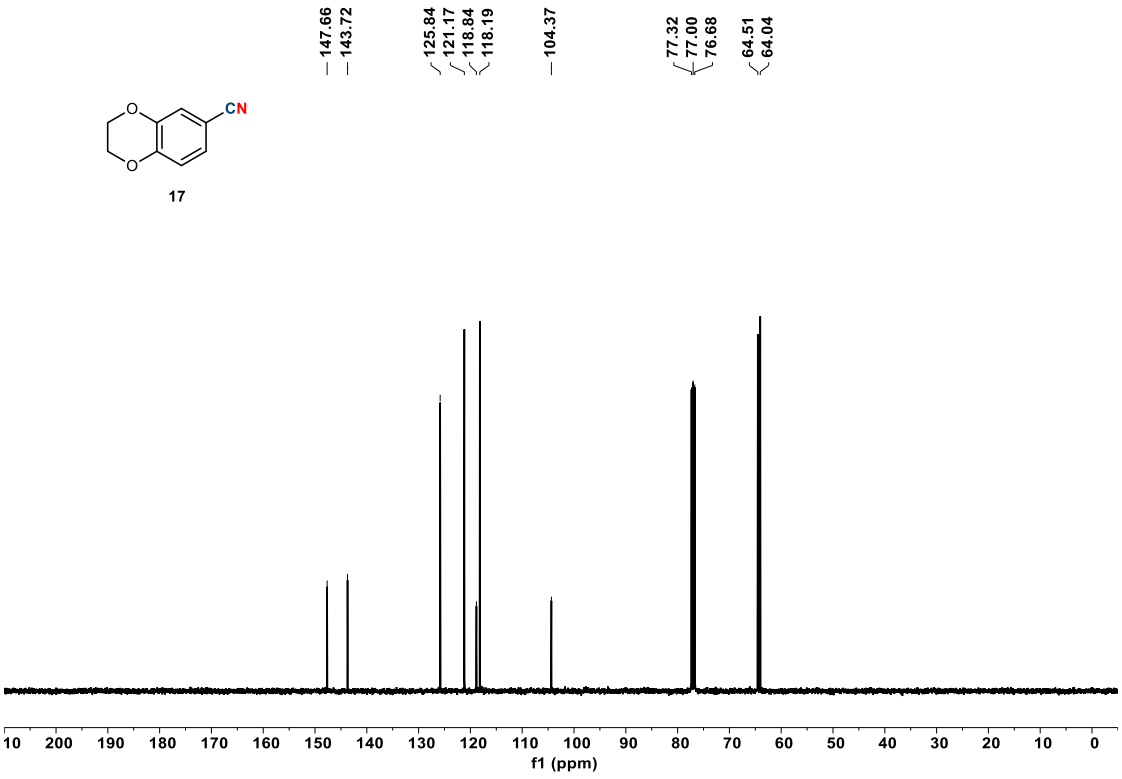


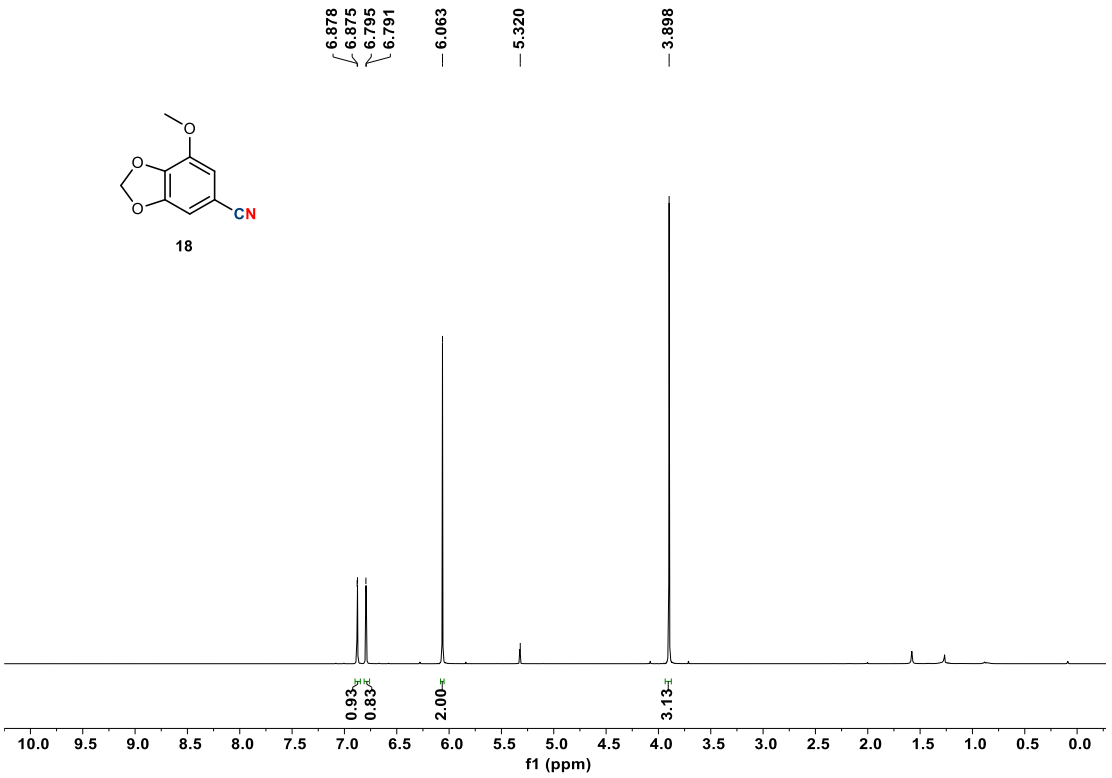
^{19}F NMR of nitrile 15

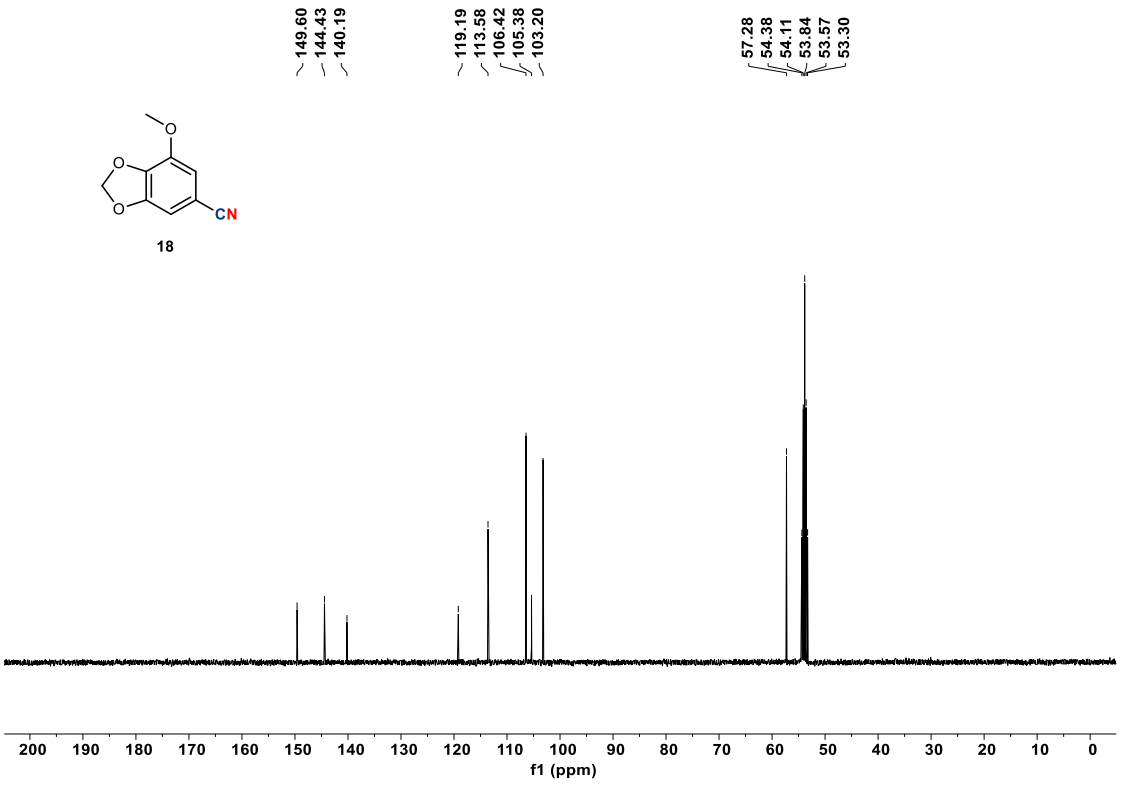

7.262
6.932
2.483
2.323
0.000
CN
16
1.91
5.92
3.00
f1 (ppm)

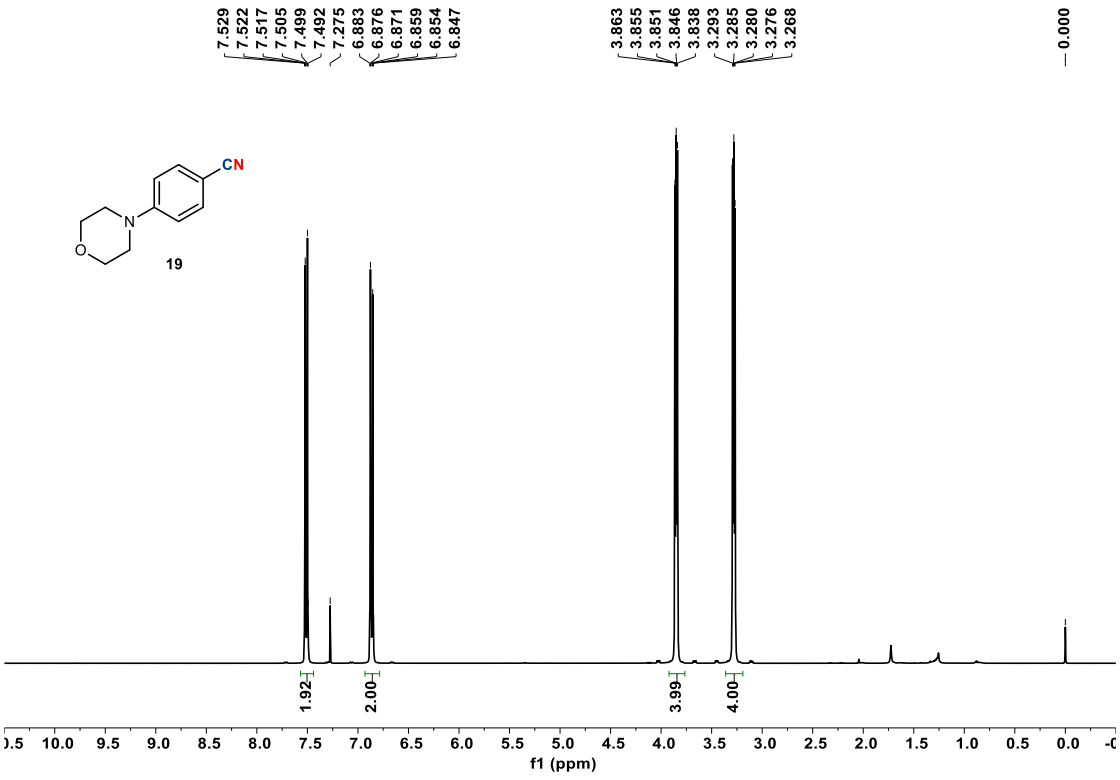

142.78
141.96
128.17
117.64
110.30
77.32
77.00
76.68
21.56
20.62
CN
16
f1 (ppm)

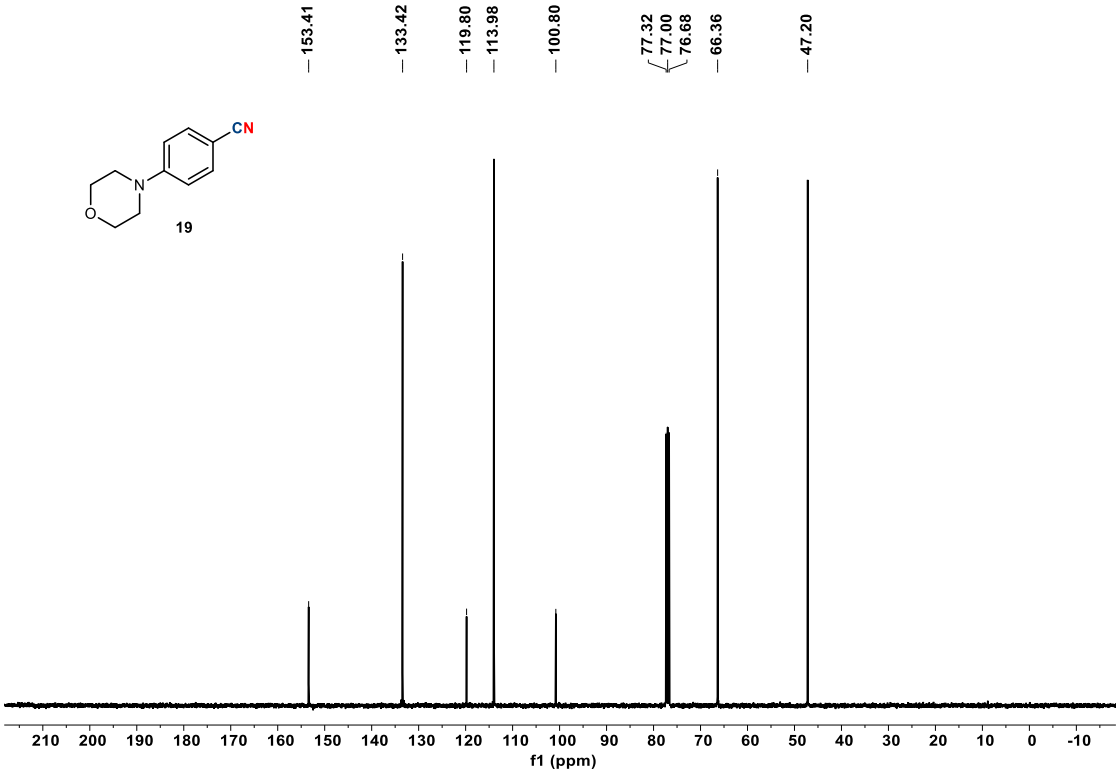

7.274
7.150
7.147
7.131
7.126
6.926
6.924
6.921
6.905
6.902
4.336
4.333
4.328
4.324
4.319
4.315
4.313
4.295
4.293
4.289
4.285
4.281
4.275
4.272
0.000
CN
17
1.92
0.97
2.04
2.00
f1 (ppm)

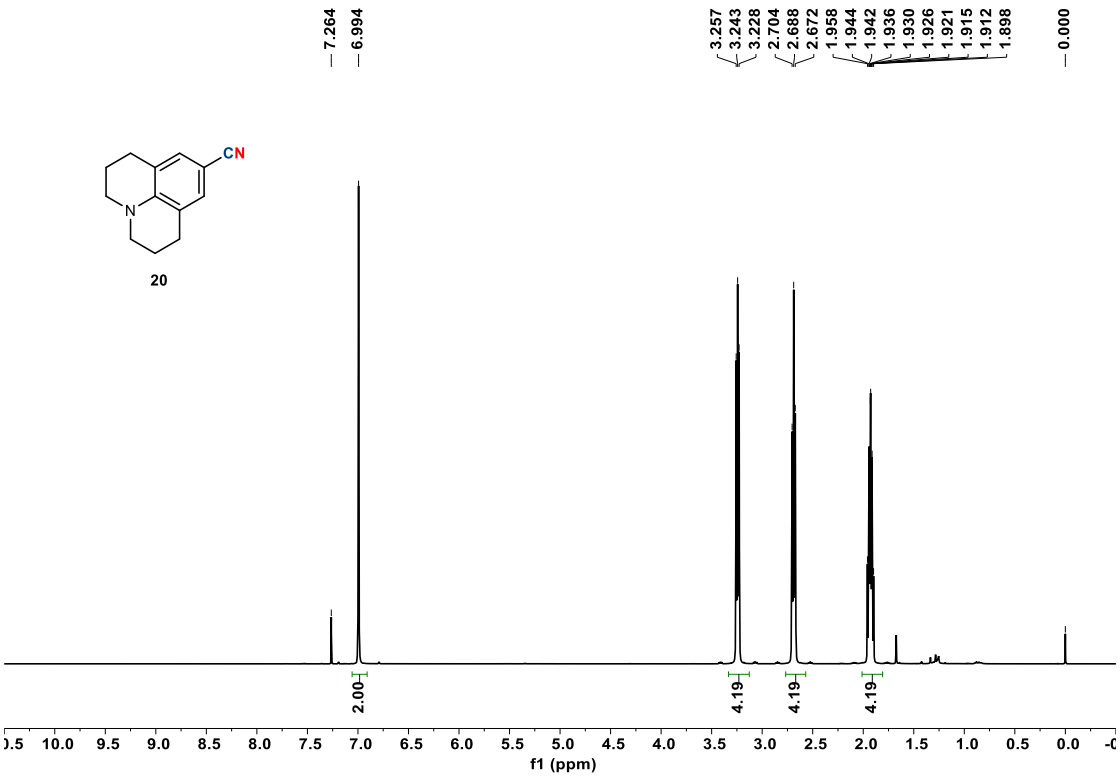

147.66
143.72
125.84
121.17
118.84
118.19
104.37
77.32
77.00
76.68
64.51
64.04
CN
17
f1 (ppm)

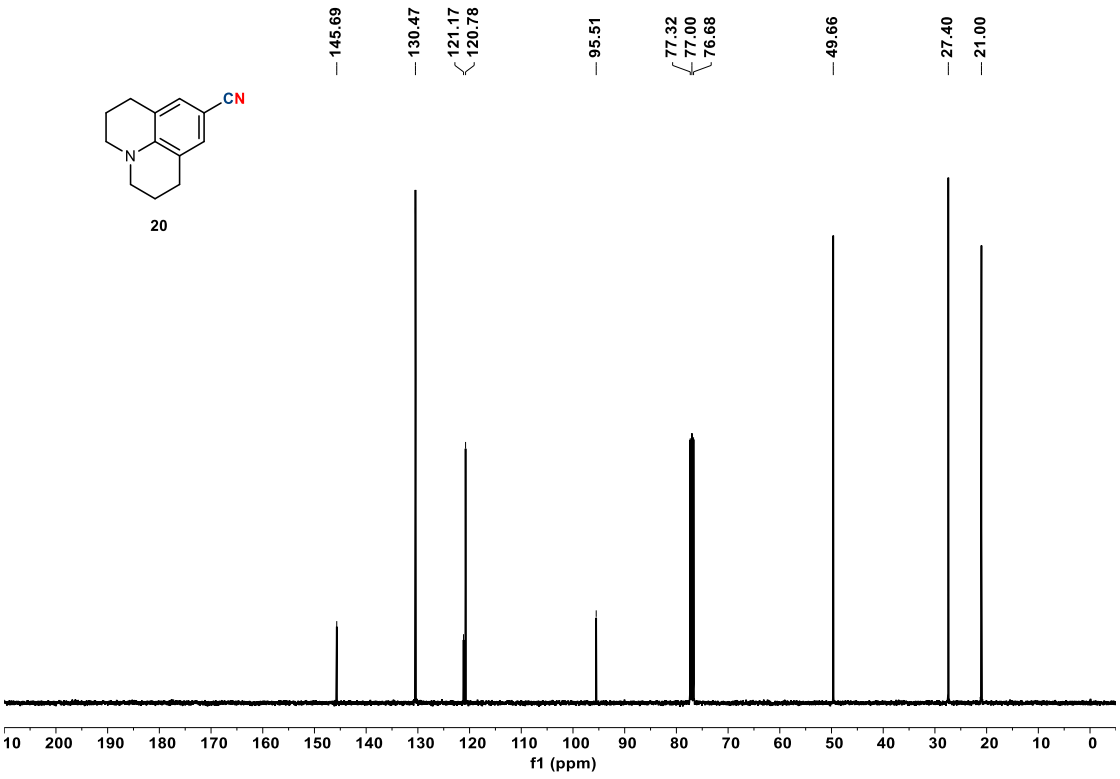

6.878
6.875
6.795
6.791
6.063
5.320
3.898
O
O
O
CN
18
0.93
0.83
2.00
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

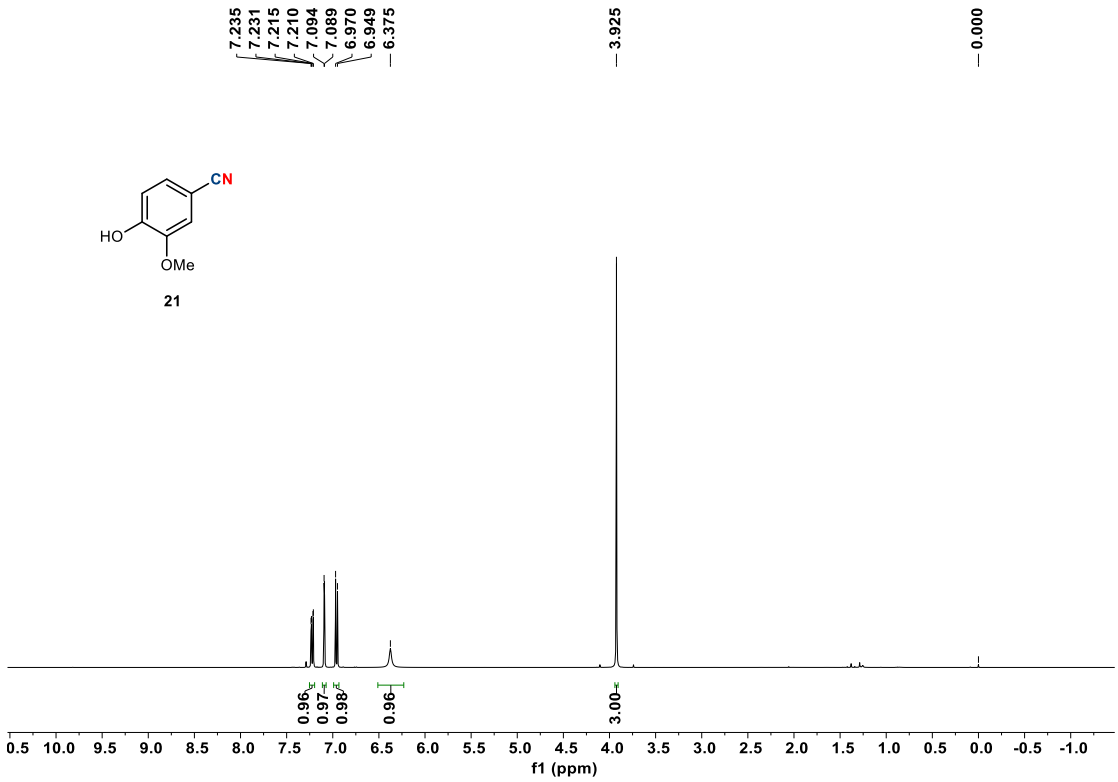

149.60
144.43
140.19
119.19
113.58
106.42
105.38
103.20
57.28
54.38
54.11
53.84
53.57
53.30
O
O
O
CN
18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

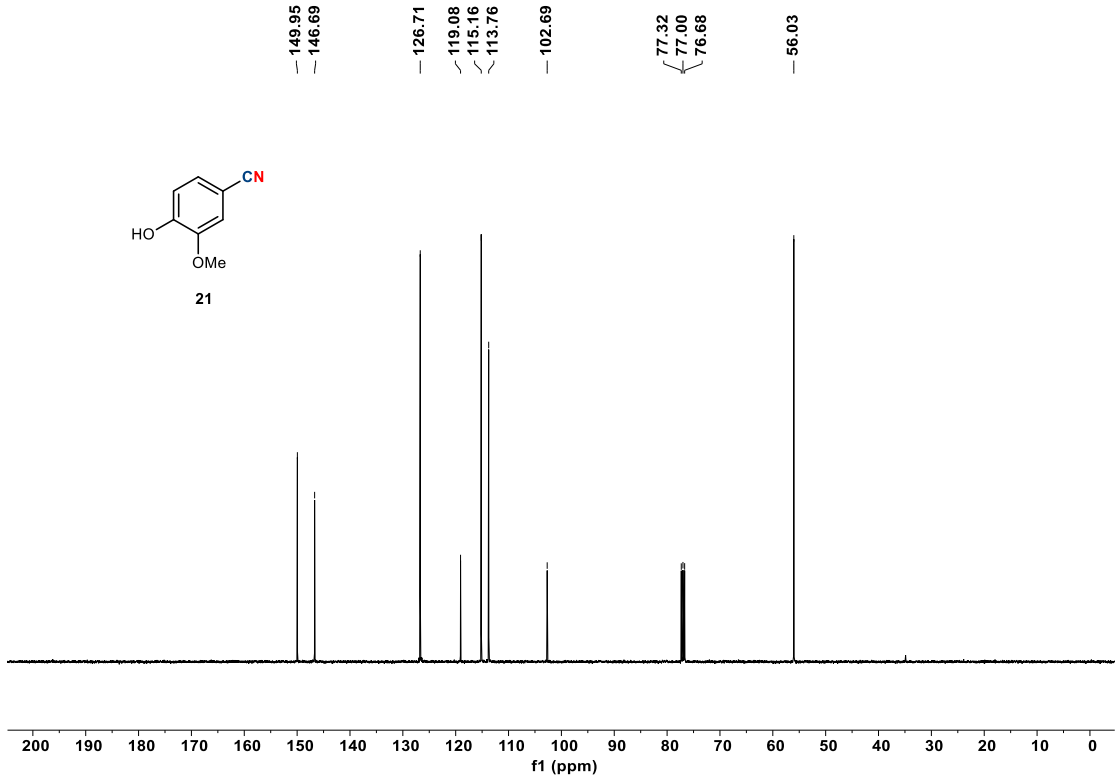

7.529
7.522
7.517
7.505
7.499
7.492
7.275
6.883
6.876
6.871
6.859
6.854
6.847
3.863
3.855
3.851
3.846
3.838
3.293
3.285
3.280
3.276
3.268
0.000
CN
N
O
19
1.92
2.00
3.99
4.00
f1 (ppm)

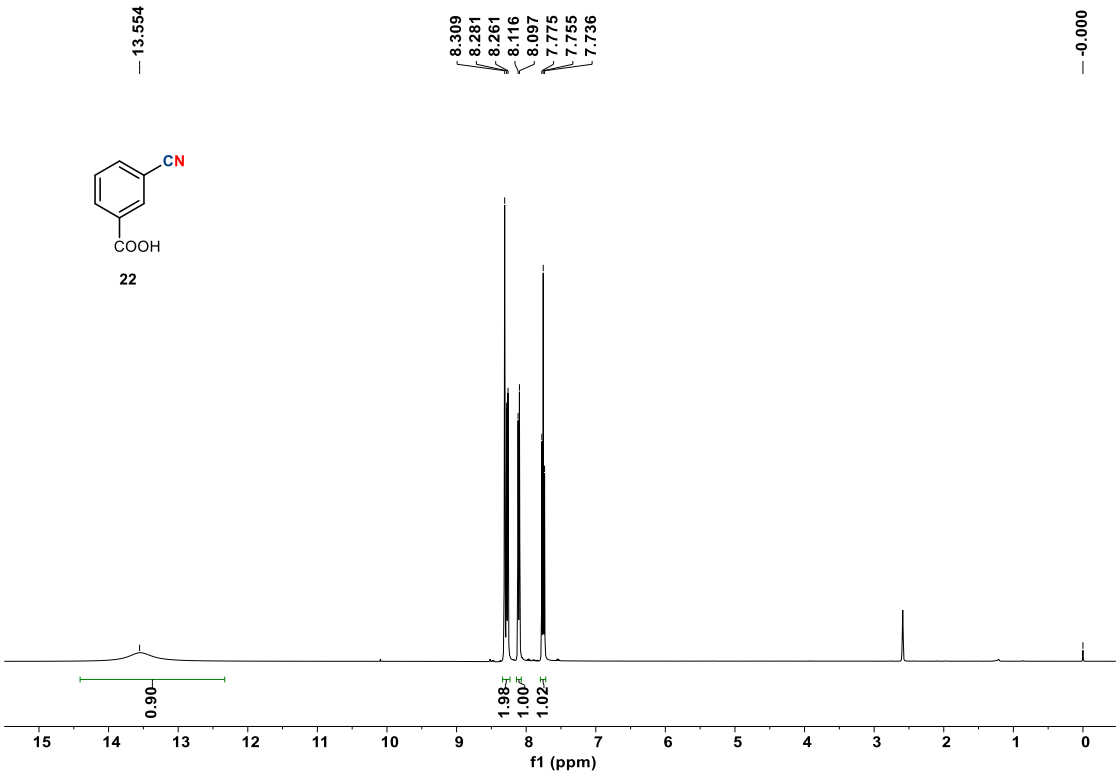

153.41
133.42
119.80
113.98
100.80
77.32
77.00
76.68
66.36
47.20
CN
N
O
19
f1 (ppm)

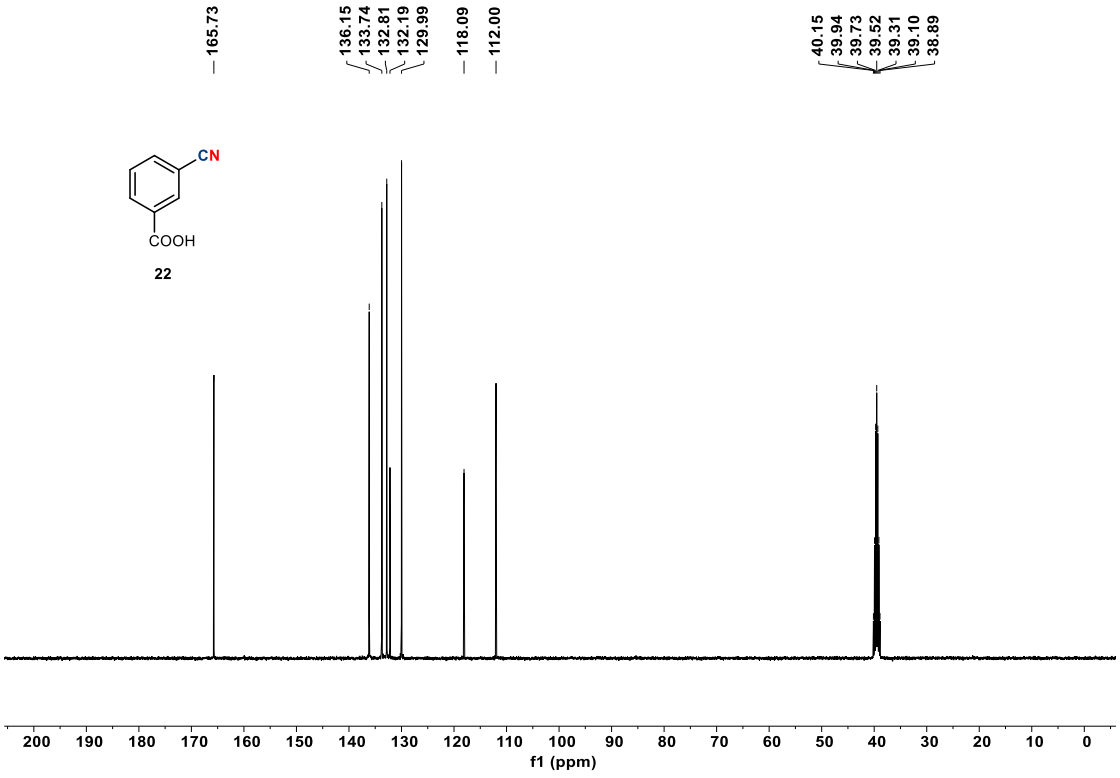

7.264
6.994
3.257
3.243
3.228
2.704
2.688
2.672
1.958
1.944
1.942
1.936
1.930
1.926
1.921
1.915
1.912
1.898
0.000
CN
N
20
2.00
4.19
4.19
4.19
f1 (ppm)

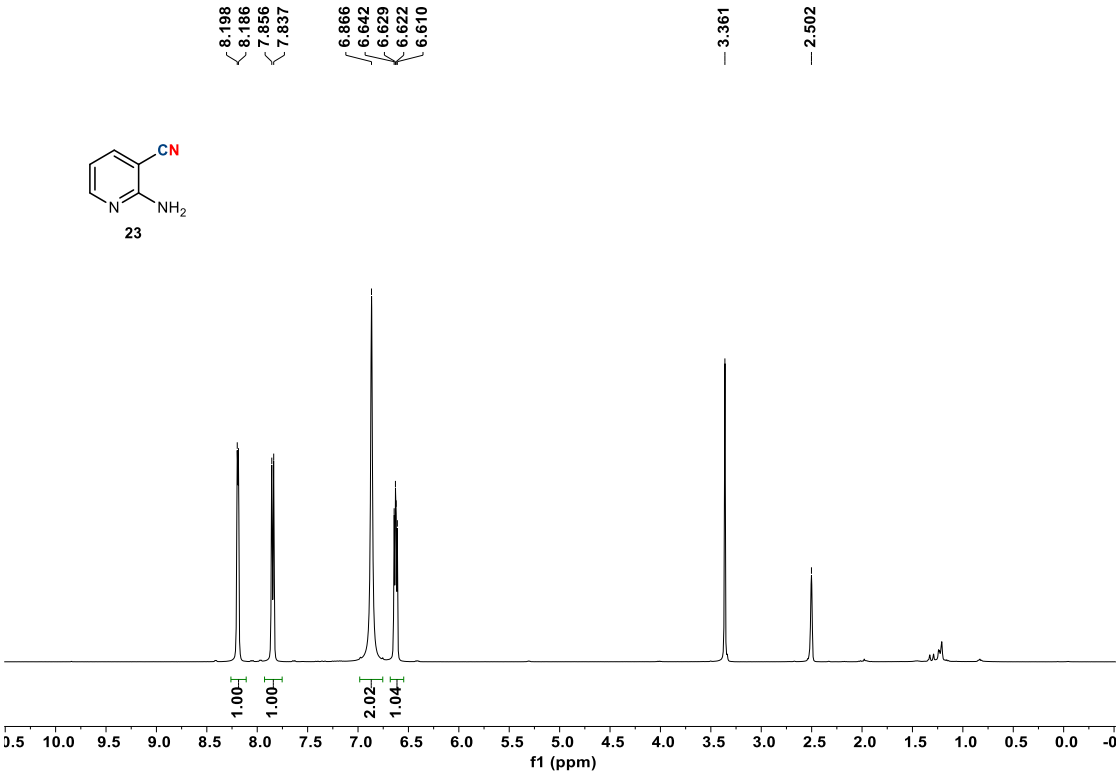

145.69
130.47
121.17
120.78
95.51
77.32
77.00
76.68
49.66
27.40
21.00
CN
N
20
f1 (ppm)

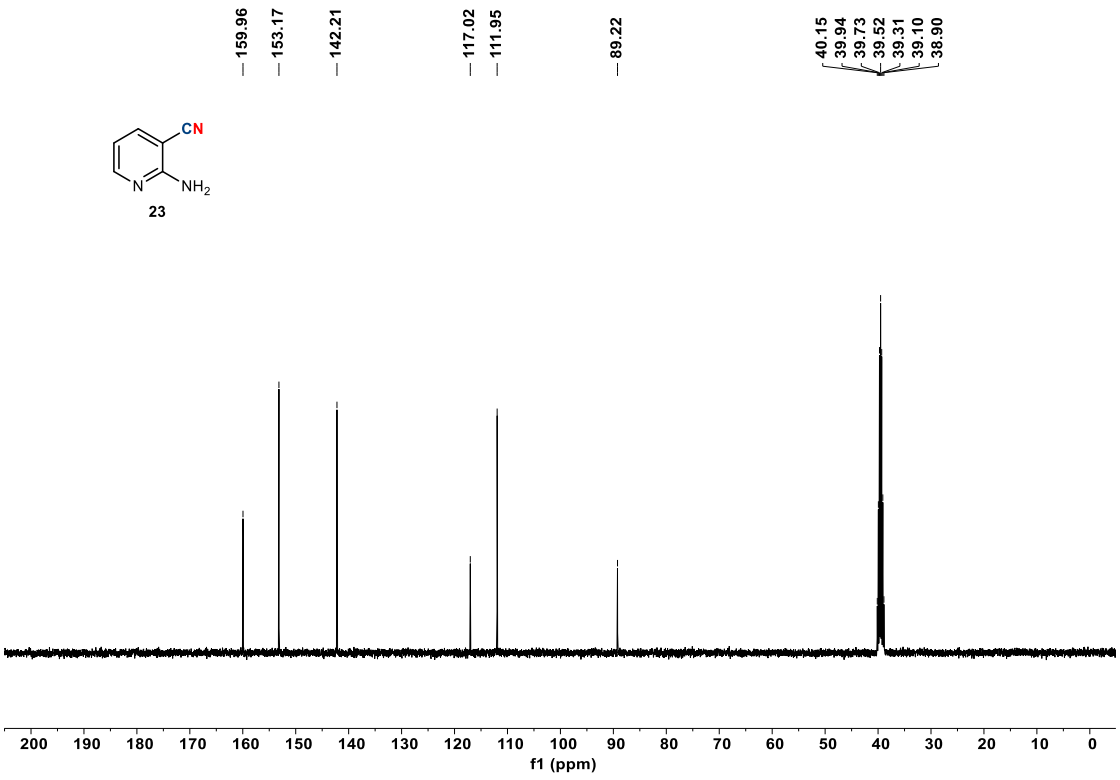

7.235
7.231
7.215
7.210
7.094
7.089
6.970
6.949
6.375
3.925
0.000
CN
HO
OMe
21
0.96
0.97
0.98
0.96
3.00
f1 (ppm)

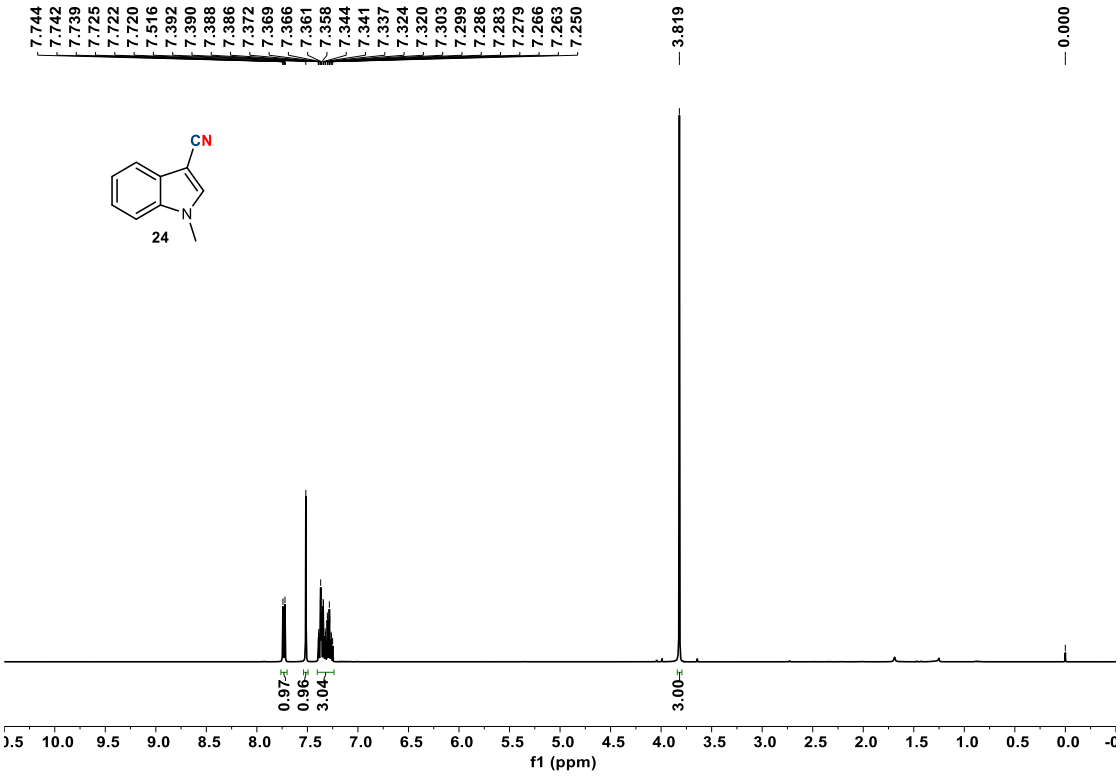

149.95
146.69
126.71
119.08
115.16
113.76
102.69
77.32
77.00
76.68
56.03
CN
HO
OMe
21
f1 (ppm)

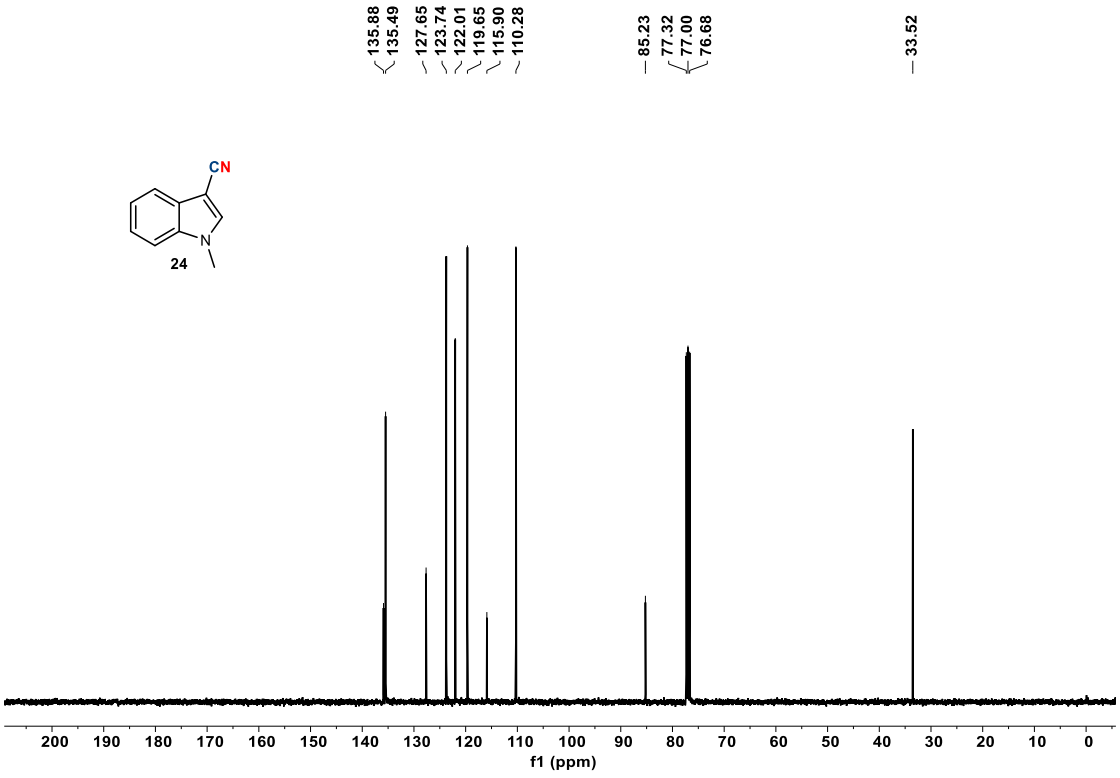

13.554
8.309
8.281
8.261
8.116
8.097
7.775
7.755
7.736
-0.000
CN
COOH
22
0.90
1.98
1.00
1.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

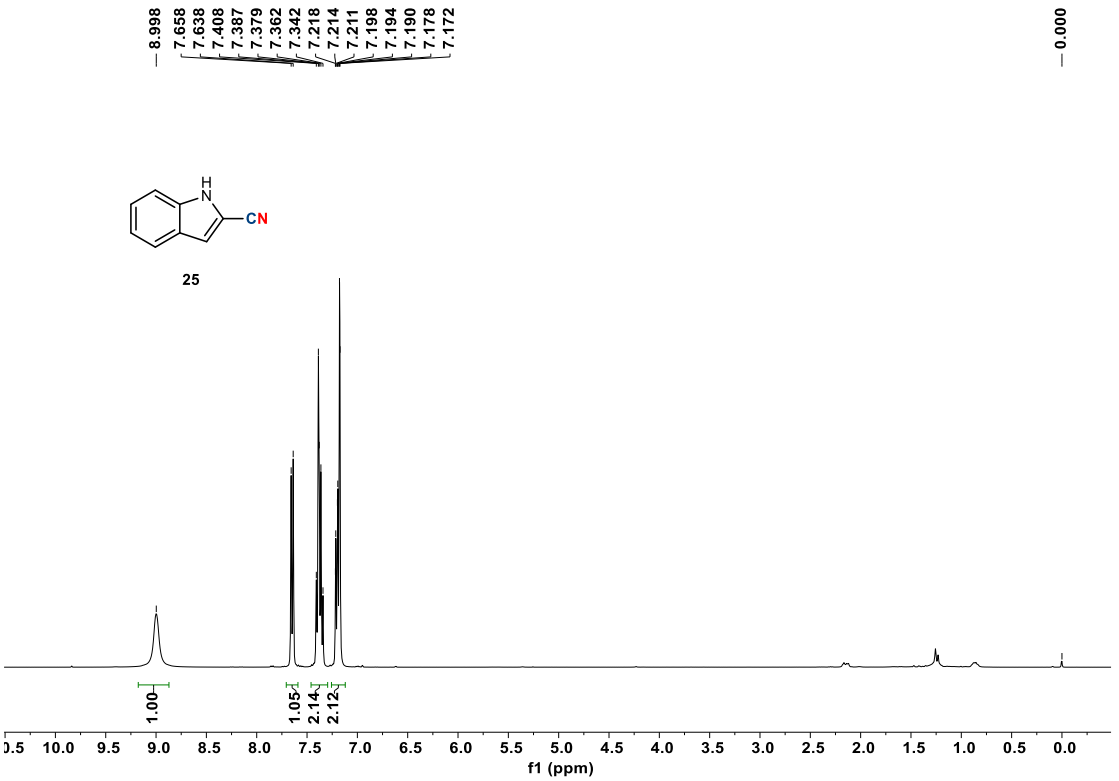

165.73
136.15
133.74
132.81
132.19
129.99
118.09
112.00
40.15
39.94
39.73
39.52
39.31
39.10
38.89
CN
COOH
22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

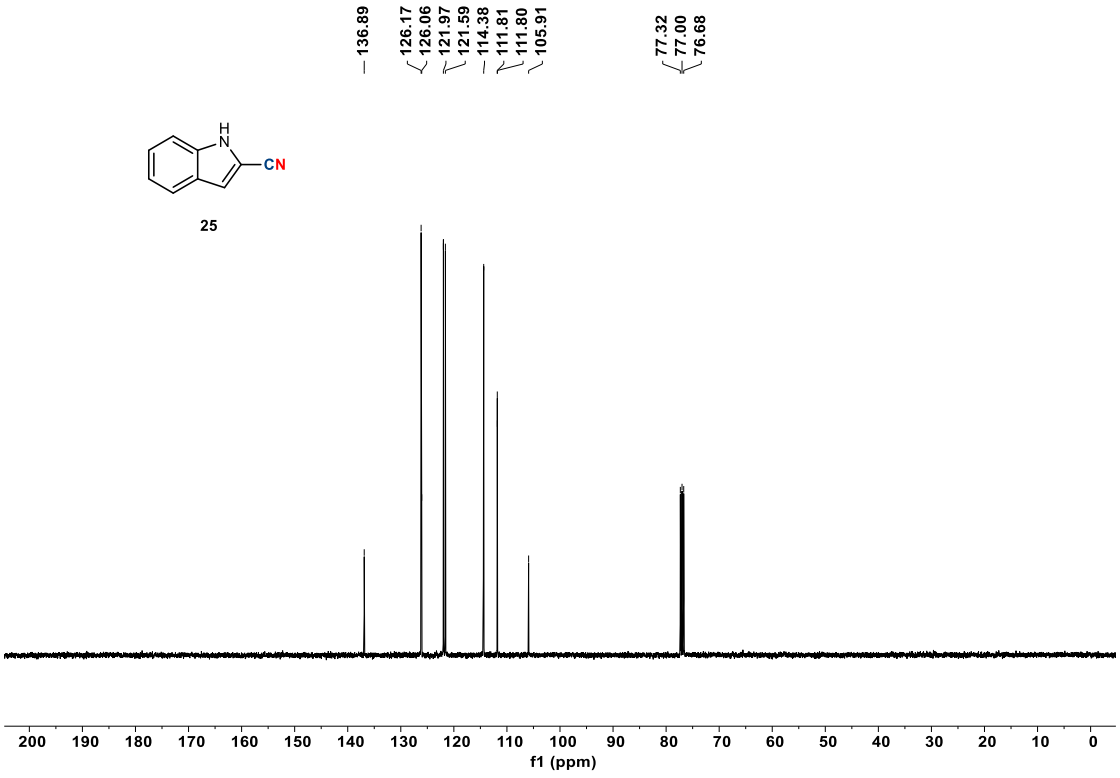

8.198
8.186
7.856
7.837
6.866
6.642
6.629
6.622
6.610
3.361
2.502
CN
N
NH2
23
1.00
1.00
2.02
1.04
f1 (ppm)

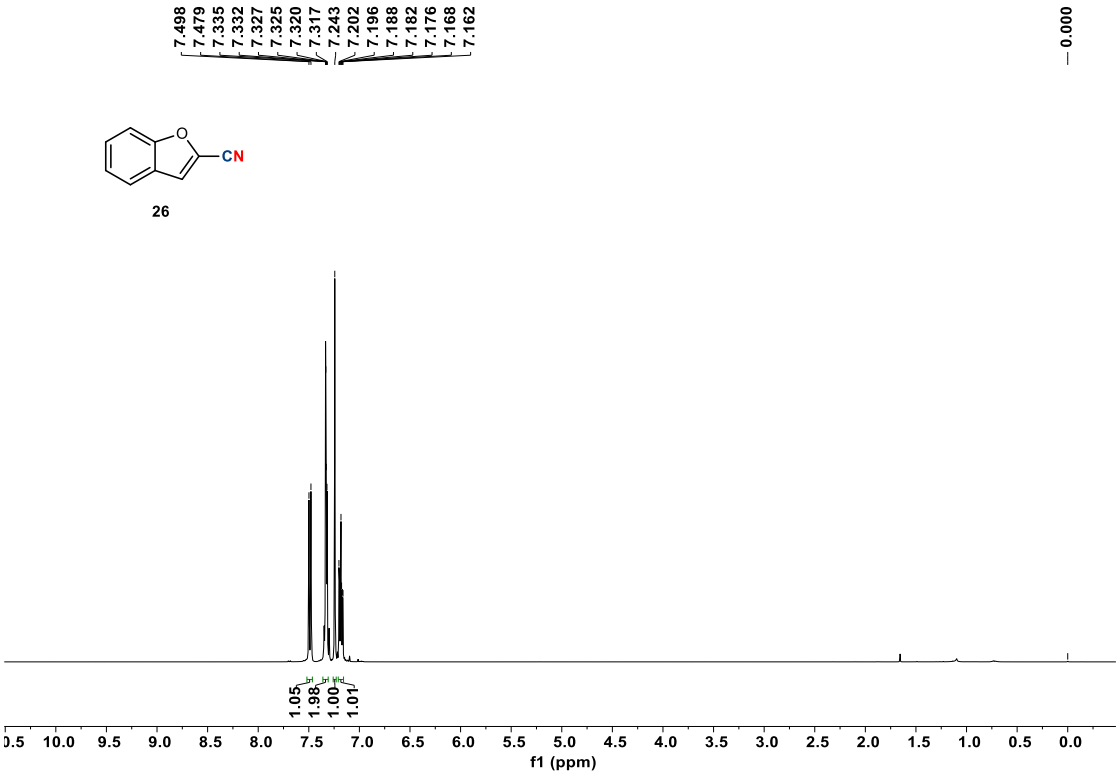

159.96
153.17
142.21
117.02
111.95
89.22
40.15
39.94
39.73
39.52
39.31
39.10
38.90
CN
N
NH2
23
f1 (ppm)

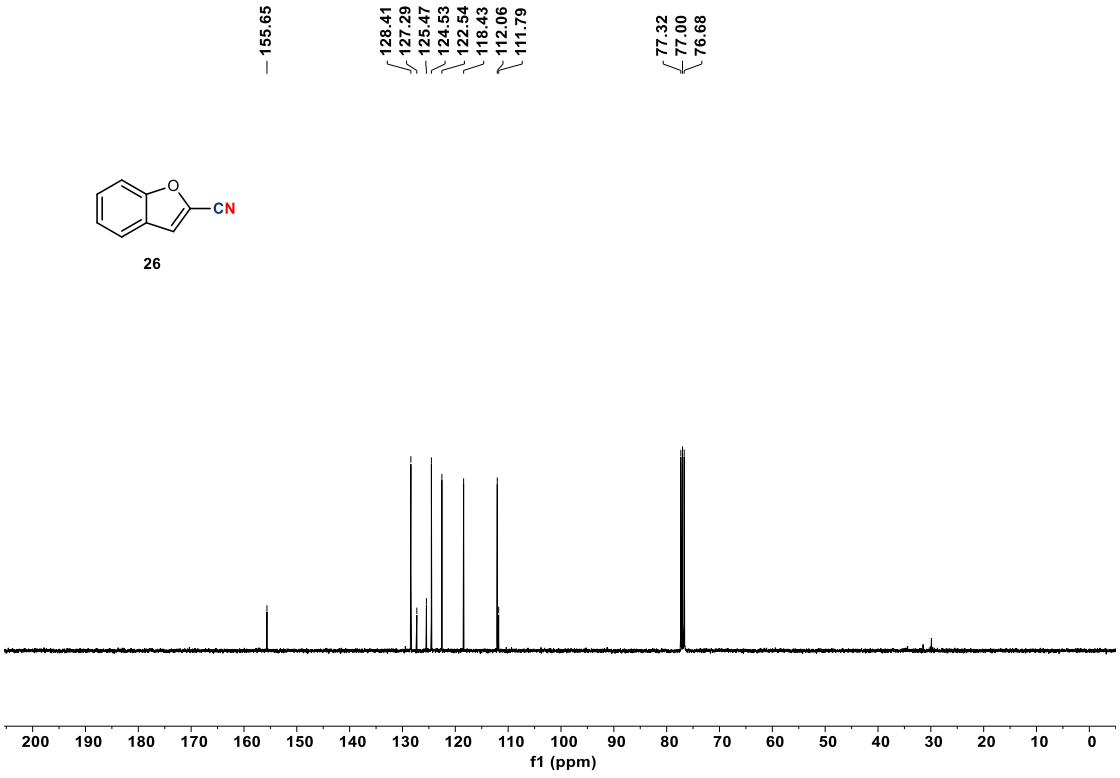

7.744
7.742
7.739
7.725
7.722
7.720
7.516
7.392
7.390
7.388
7.386
7.372
7.369
7.366
7.361
7.358
7.344
7.341
7.337
7.324
7.320
7.303
7.299
7.286
7.283
7.279
7.266
7.263
7.250
3.819
0.000
CN
N
24
0.97
0.96
3.04
3.00
f1 (ppm)

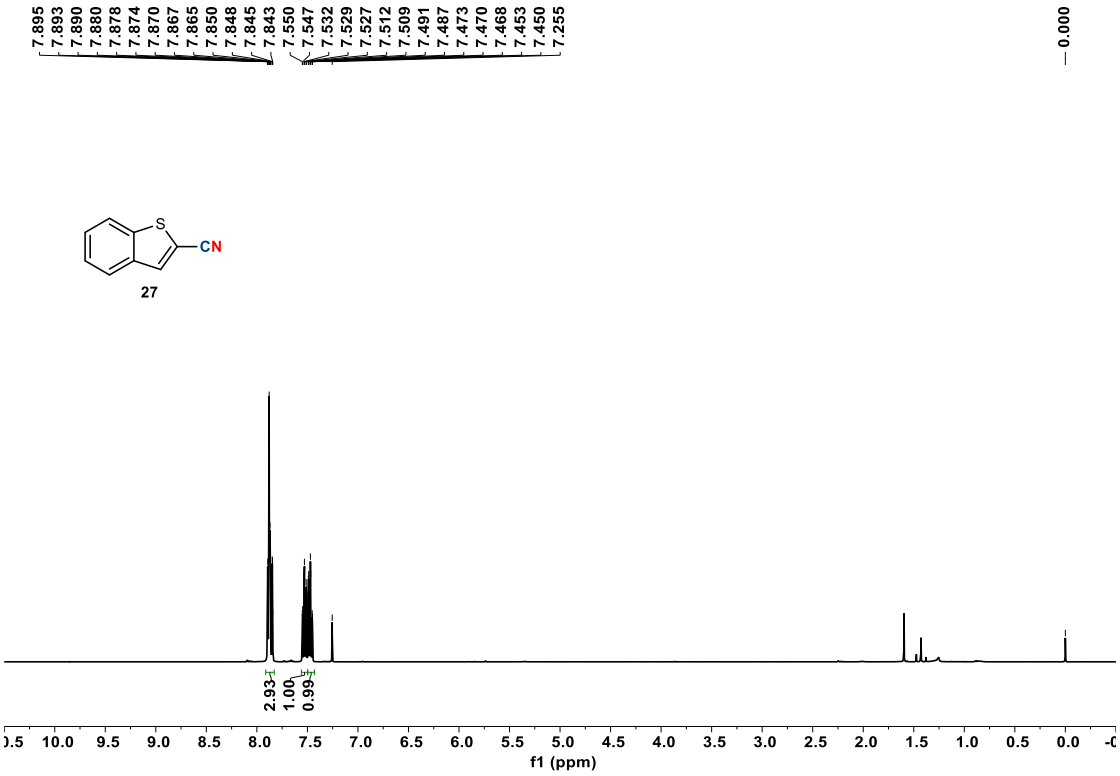

135.88
135.49
127.65
123.74
122.01
119.65
115.90
110.28
85.23
77.32
77.00
76.68
33.52
CN
N
24
f1 (ppm)

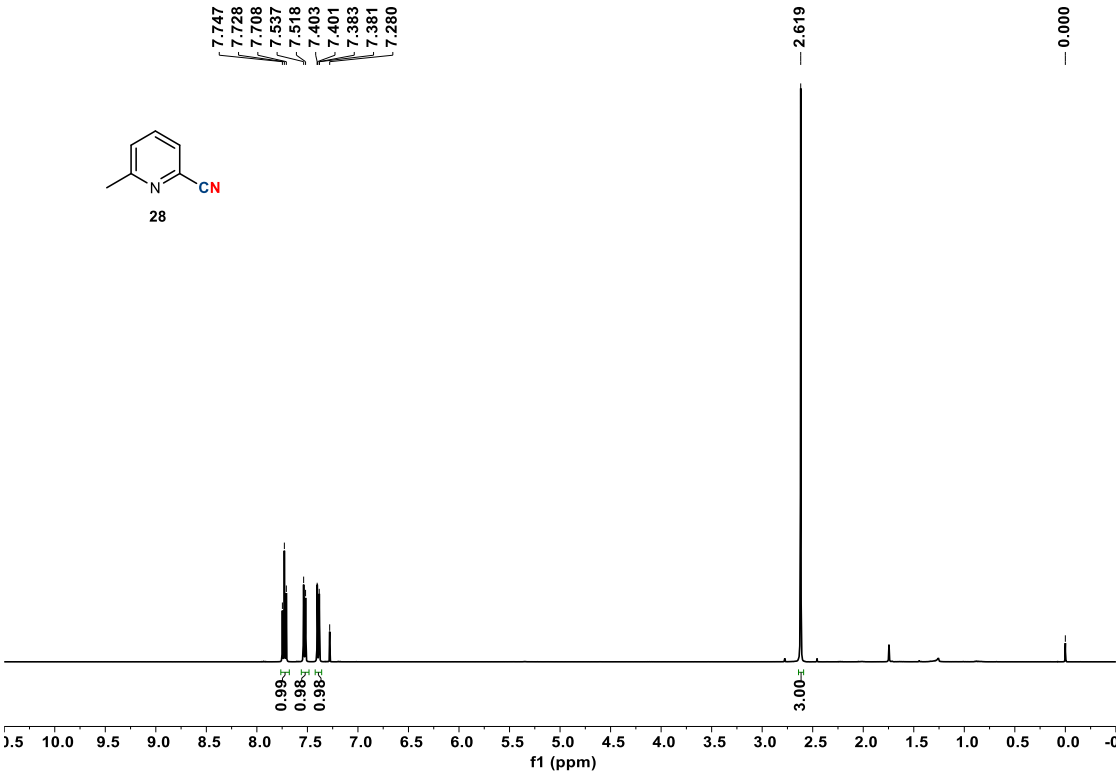

8.998
7.658
7.638
7.408
7.387
7.379
7.362
7.342
7.218
7.214
7.211
7.198
7.194
7.190
7.178
7.172
0.000
H
N
CN
25
1.00
1.05
2.14
2.12
f1 (ppm)

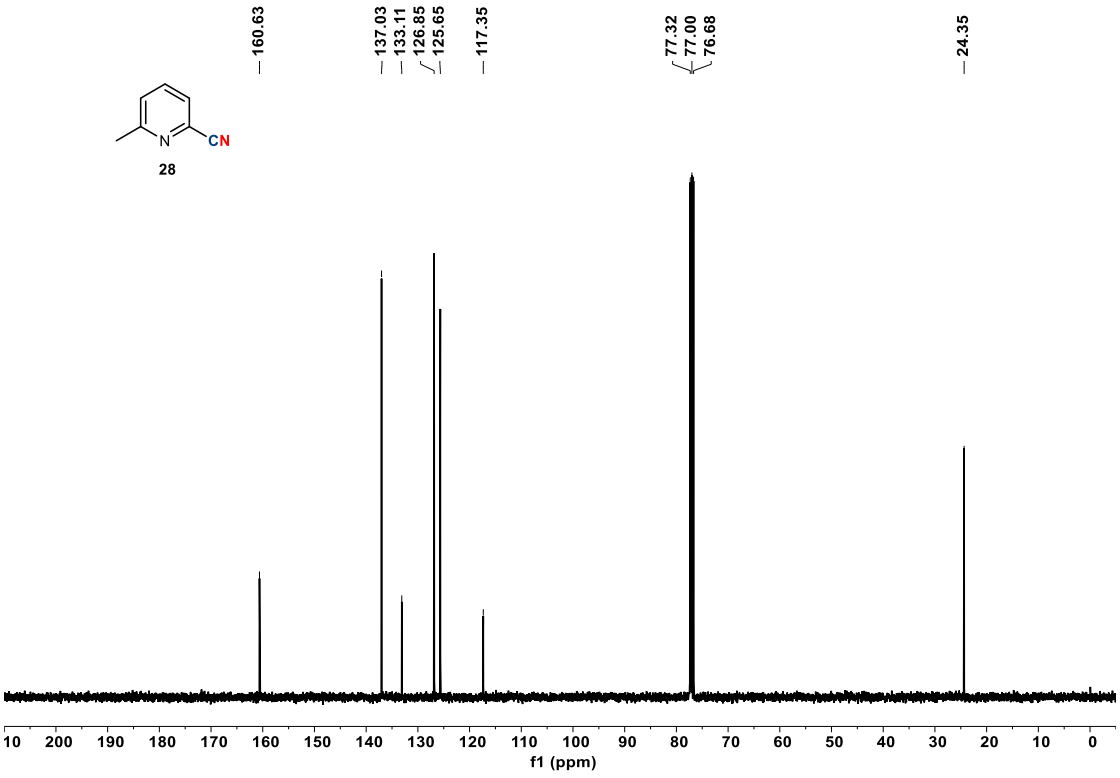

136.89
126.17
126.06
121.97
121.59
114.38
111.81
111.80
105.91
77.32
77.00
76.68
H
N
CN
25
f1 (ppm)

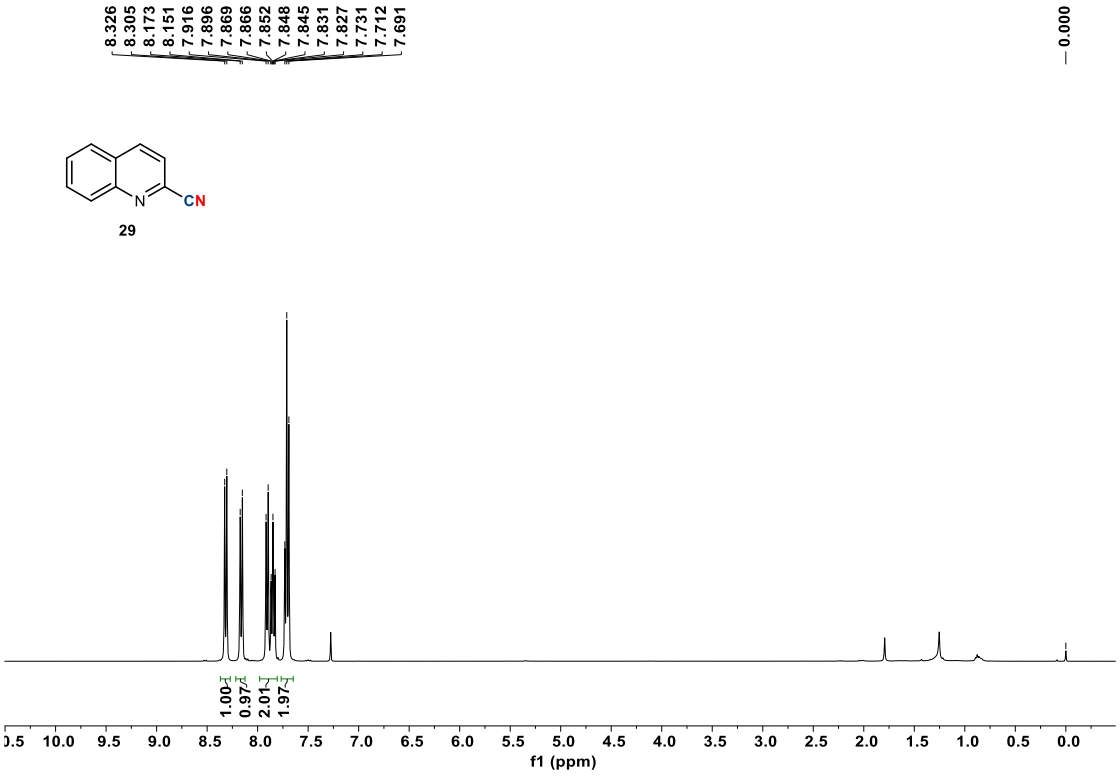

7.498
7.479
7.335
7.332
7.327
7.325
7.320
7.317
7.243
7.202
7.196
7.188
7.182
7.176
7.168
7.162
0.000
O
CN
26
1.05
1.98
1.00
1.01
f1 (ppm)

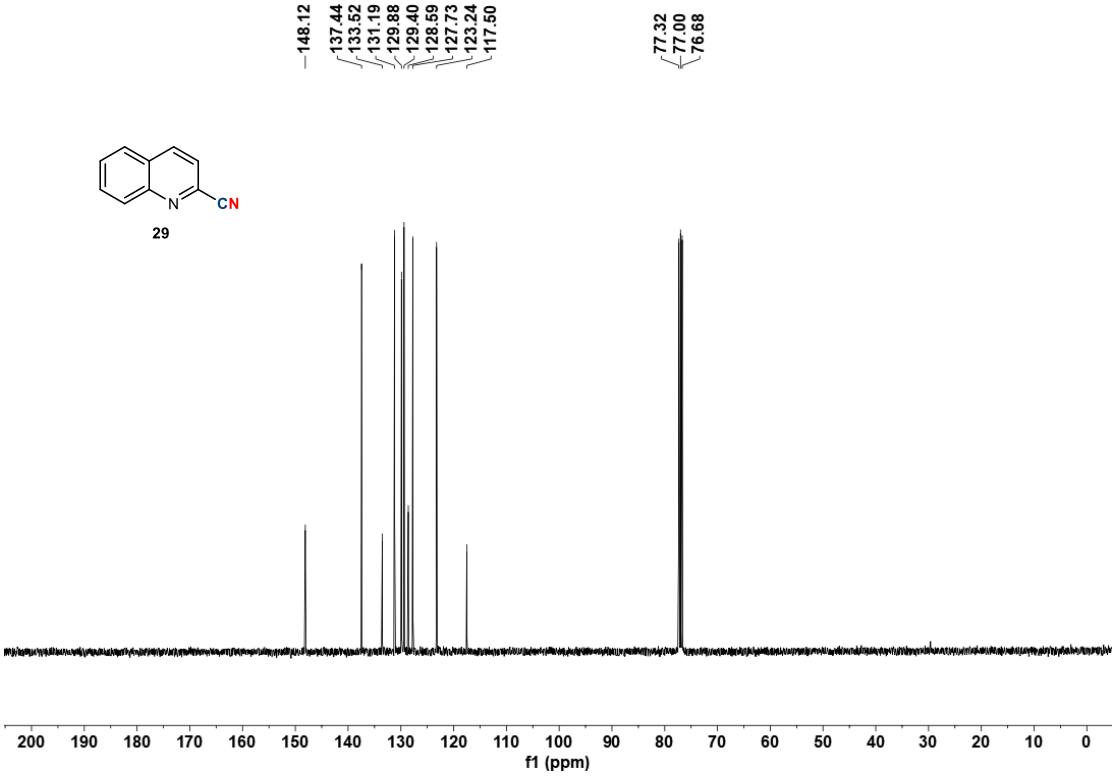

155.65
128.41
127.29
125.47
124.53
122.54
118.43
112.06
111.79
77.32
77.00
76.68
O
CN
26
f1 (ppm)

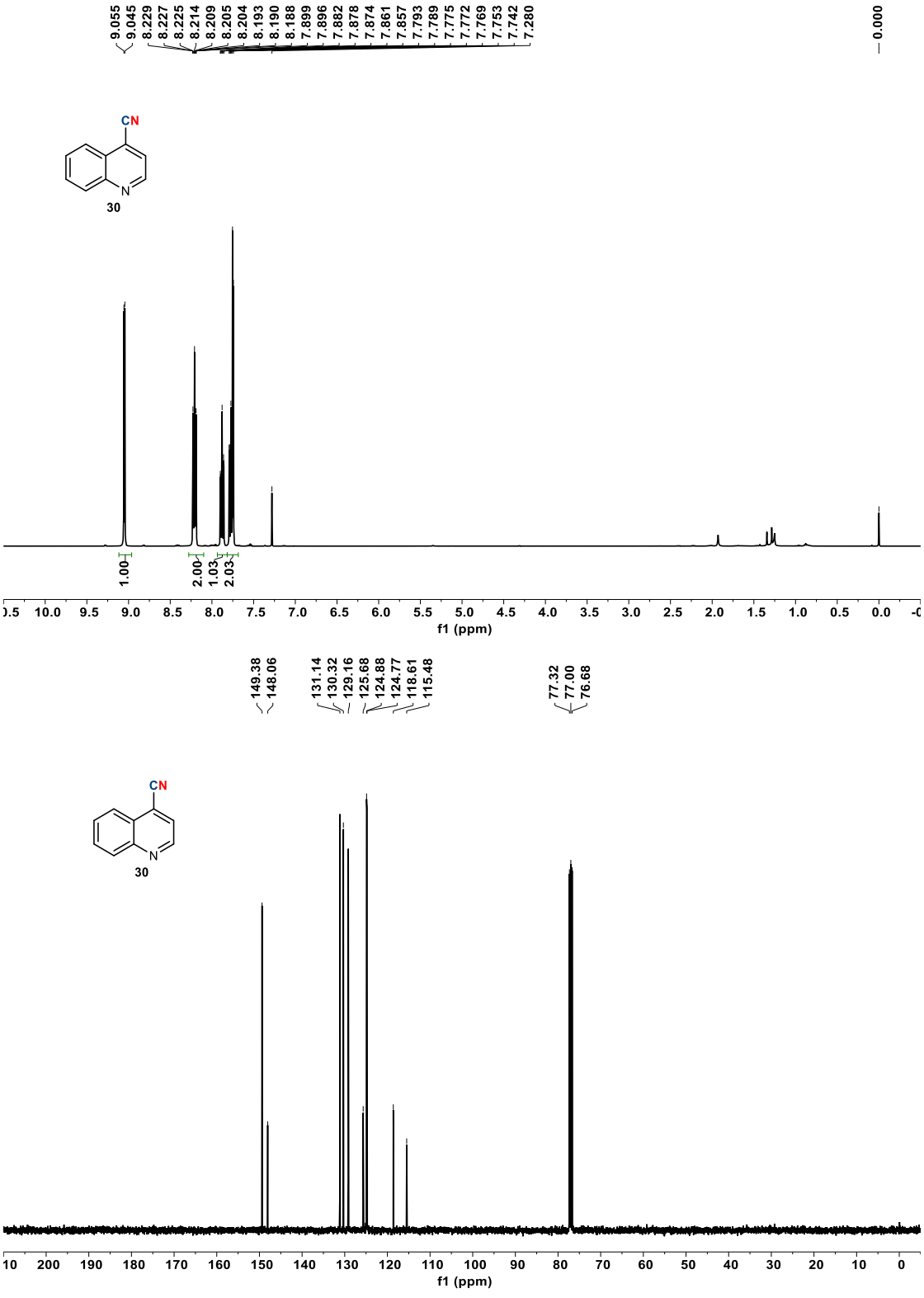

7.895
7.893
7.890
7.880
7.878
7.874
7.870
7.867
7.865
7.850
7.848
7.845
7.843
7.550
7.547
7.532
7.529
7.527
7.512
7.509
7.491
7.487
7.473
7.470
7.468
7.453
7.450
7.255
0.000
S
CN
27
2.93
1.00
0.99
f1 (ppm)
141.25
137.40
134.95
127.83
125.69
125.24
122.34
114.43
109.64
77.32
77.00
76.68
S
CN
27
f1 (ppm)

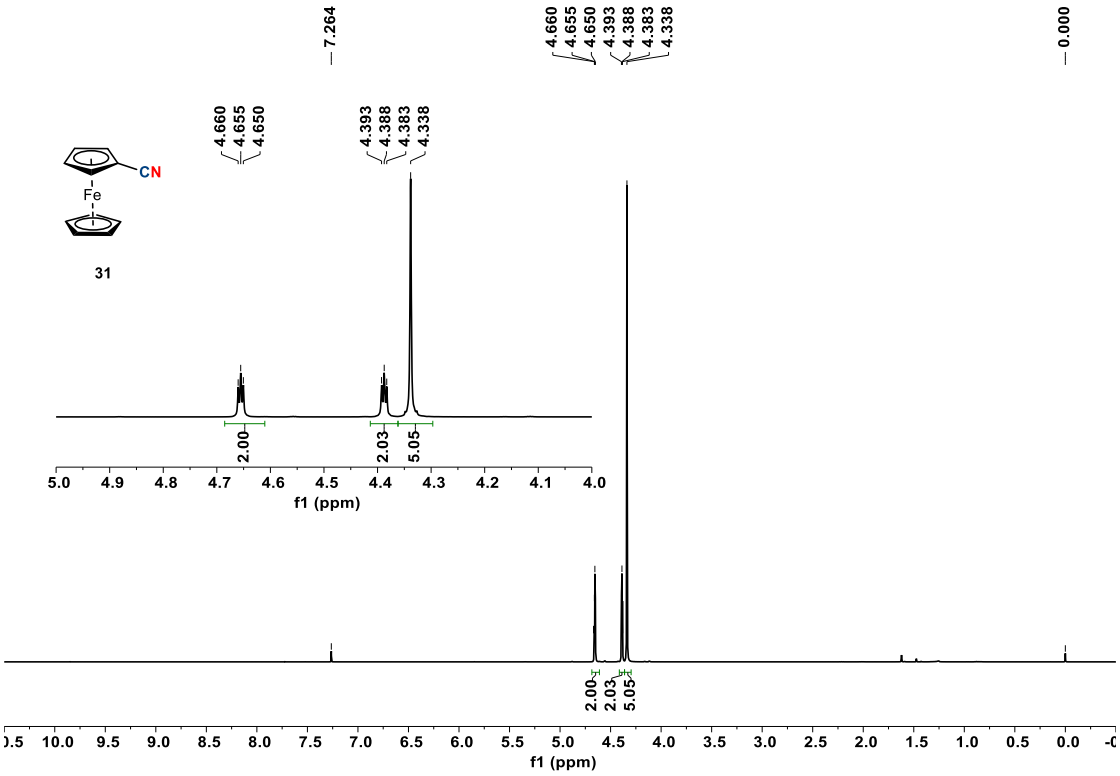

7.747
7.728
7.708
7.537
7.518
7.403
7.401
7.383
7.381
7.280
2.619
0.000
N
CN
28
0.99
0.98
0.98
3.00
f1 (ppm)

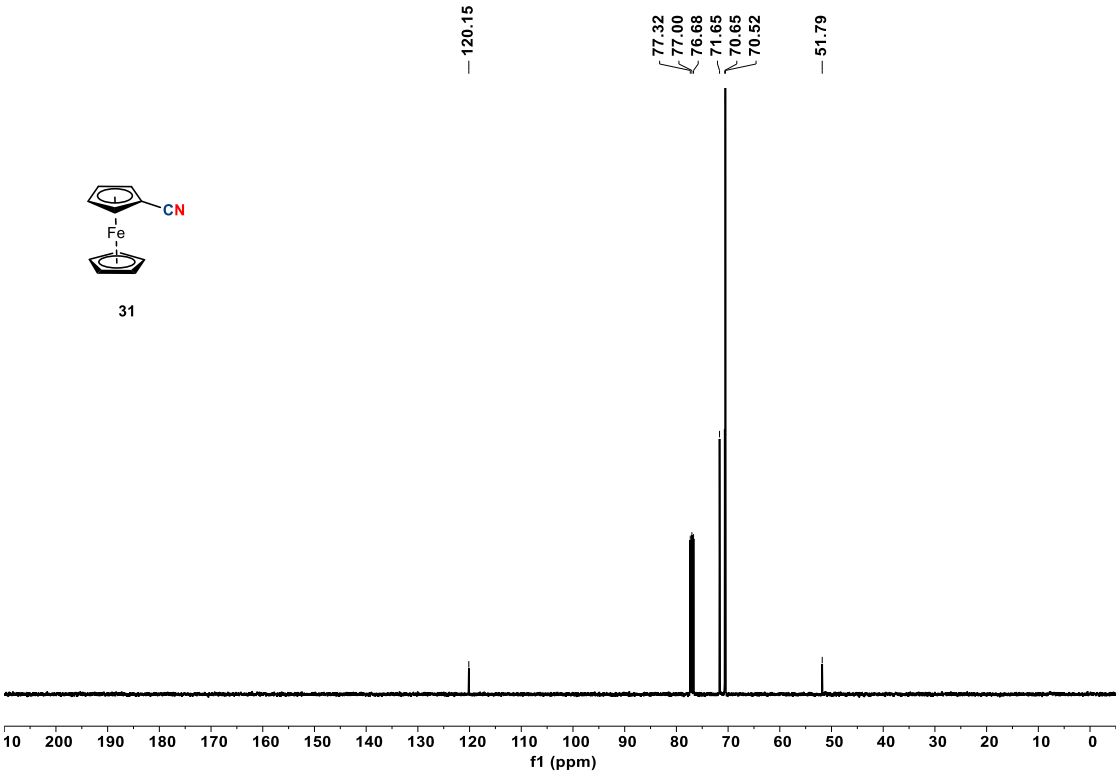

160.63
137.03
133.11
126.85
125.65
117.35
77.32
77.00
76.68
24.35
N
CN
28
f1 (ppm)

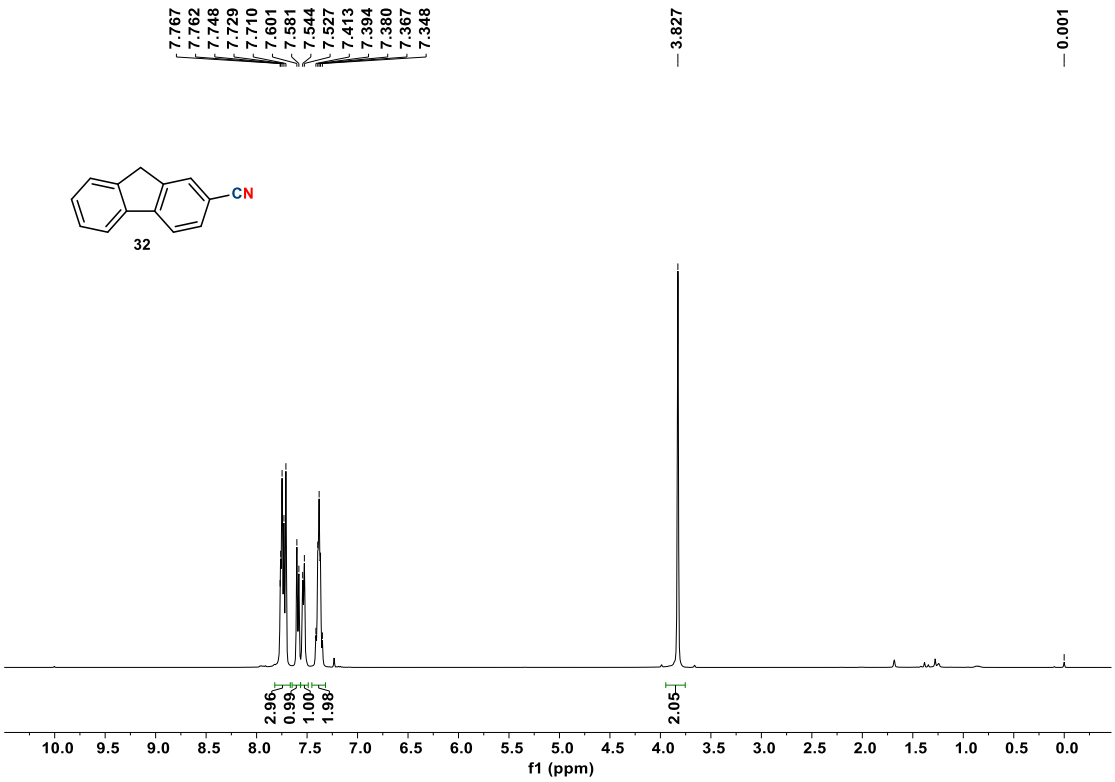

8.326
8.305
8.173
8.151
7.916
7.896
7.869
7.866
7.852
7.848
7.845
7.831
7.827
7.731
7.712
7.691
0.000
CN
29
1.00
0.97
2.01
1.97
f1 (ppm)

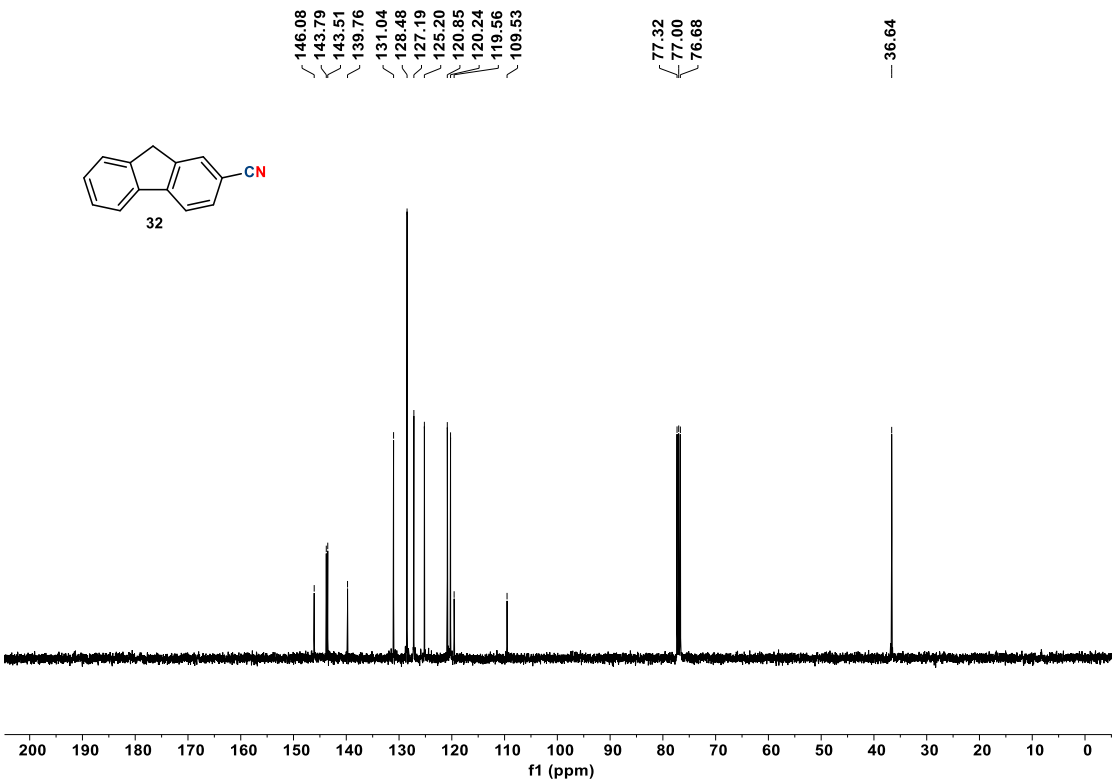

148.12
137.44
133.52
131.19
129.88
129.40
128.59
127.73
123.24
117.50
77.32
77.00
76.68
CN
29
f1 (ppm)

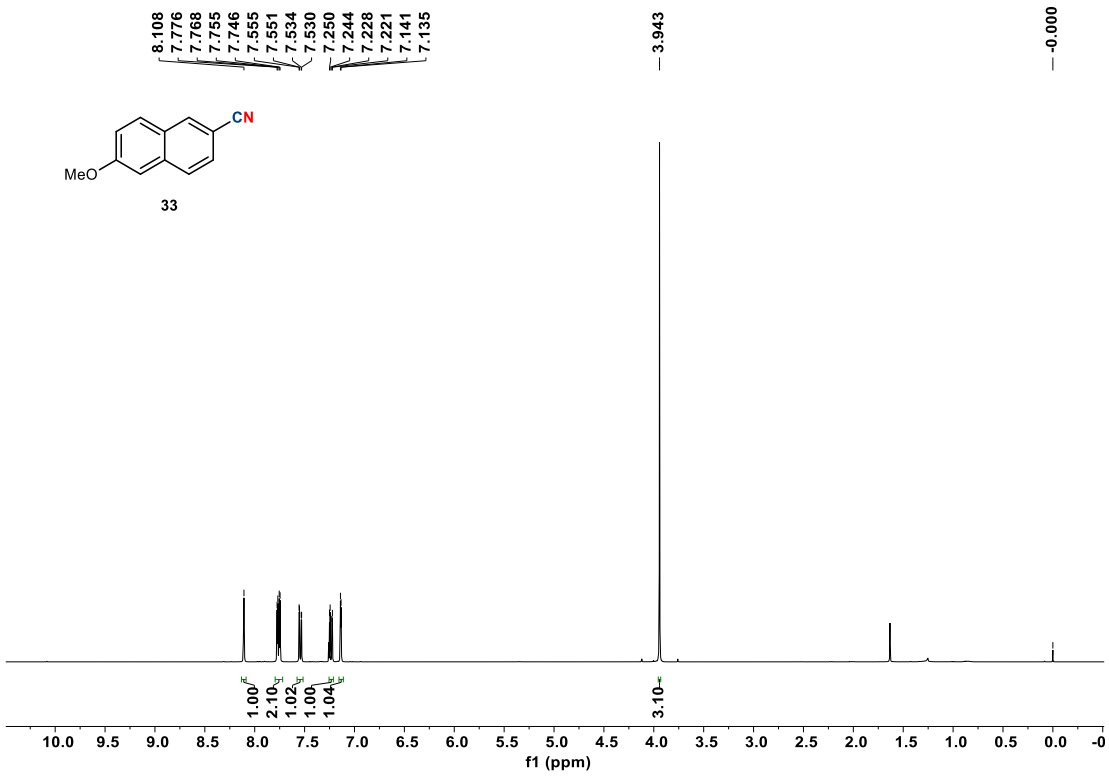

9.055
9.045
8.229
8.227
8.225
8.214
8.209
8.205
8.204
8.193
8.190
8.188
7.899
7.896
7.882
7.878
7.874
7.861
7.857
7.793
7.789
7.775
7.772
7.769
7.753
7.742
7.280
0.000
CN
N
30
1.00
2.00
1.03
2.03
f1 (ppm)
149.38
148.06
131.14
130.32
129.16
125.68
124.88
124.77
118.61
115.48
77.32
77.00
76.68
CN
N
30
f1 (ppm)

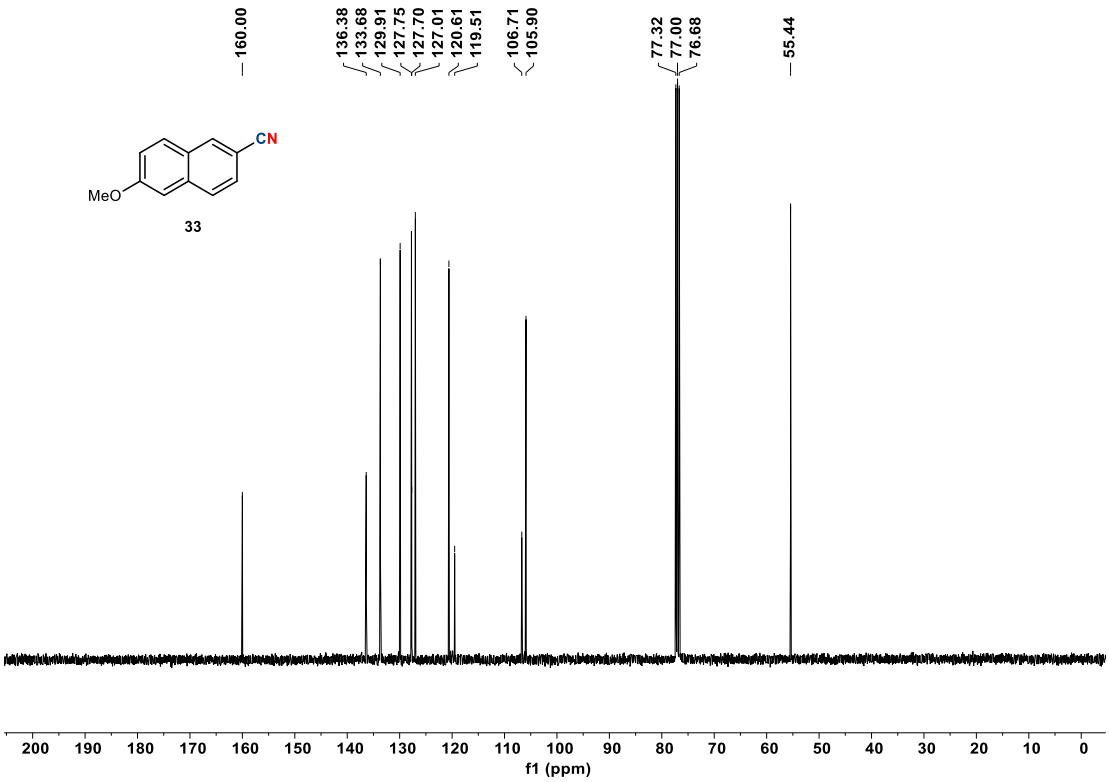

7.264
4.660
4.655
4.650
4.393
4.388
4.383
4.338
0.000
CN
Fe
31
2.00
2.03
5.05
f1 (ppm)

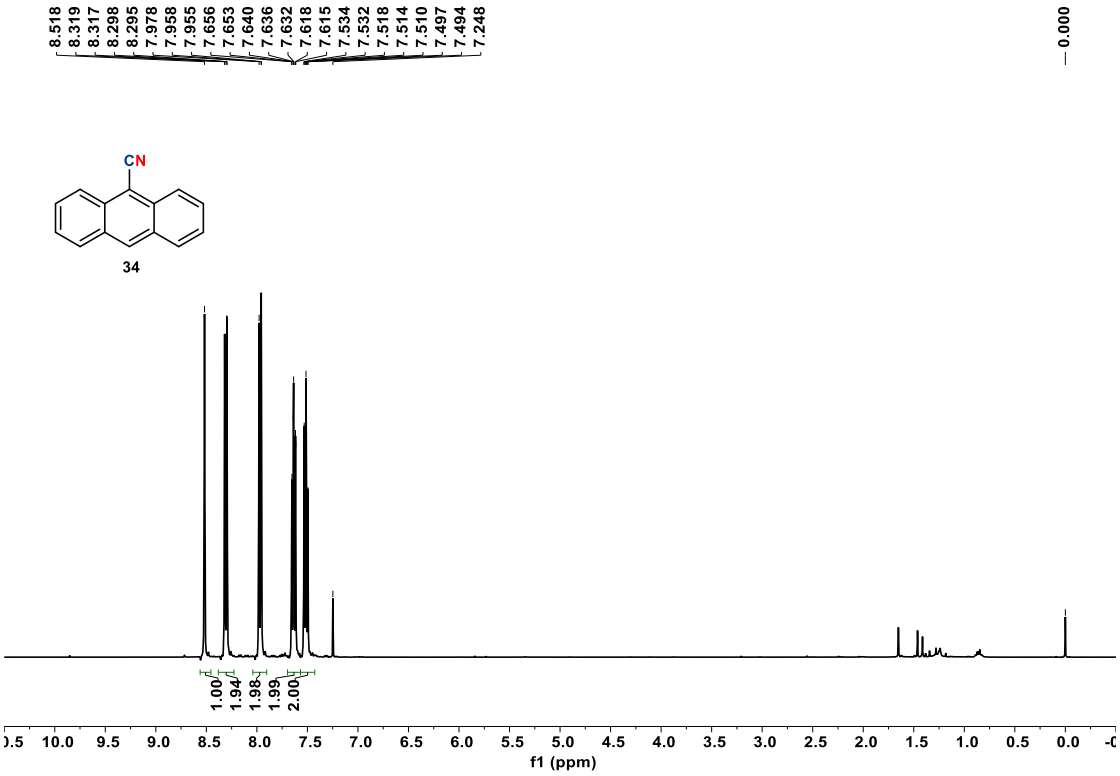

120.15
77.32
77.00
76.68
71.65
70.65
70.52
51.79
CN
Fe
31
f1 (ppm)

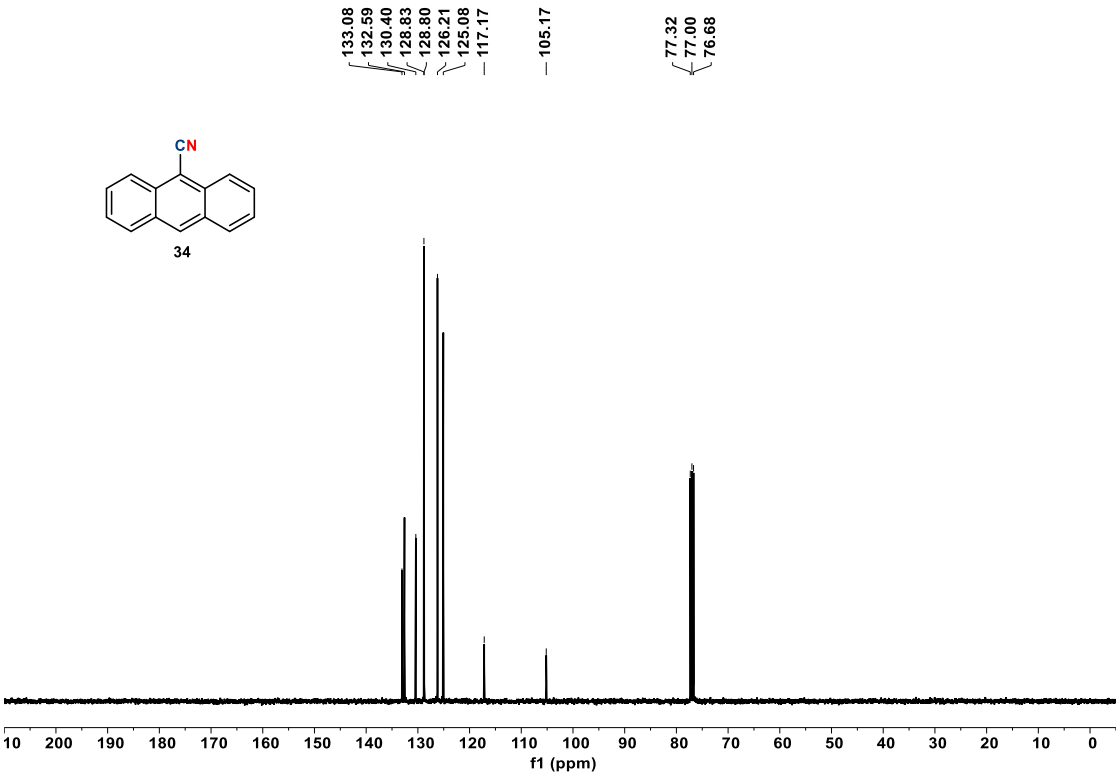

7.767
7.762
7.748
7.729
7.710
7.601
7.581
7.544
7.527
7.413
7.394
7.380
7.367
7.348
3.827
0.001
CN
32
2.96
0.99
1.00
1.98
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

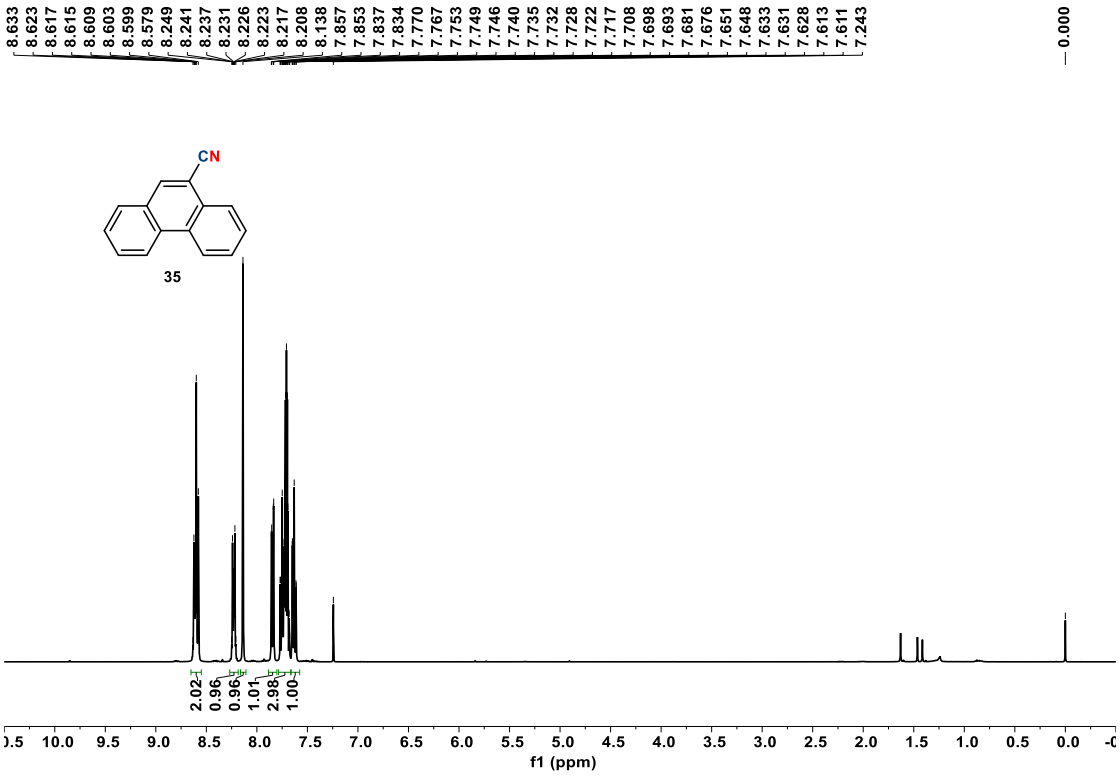

146.08
143.79
143.51
139.76
131.04
128.48
127.19
125.20
120.85
120.24
119.56
109.53
77.32
77.00
76.68
36.64
CN
32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

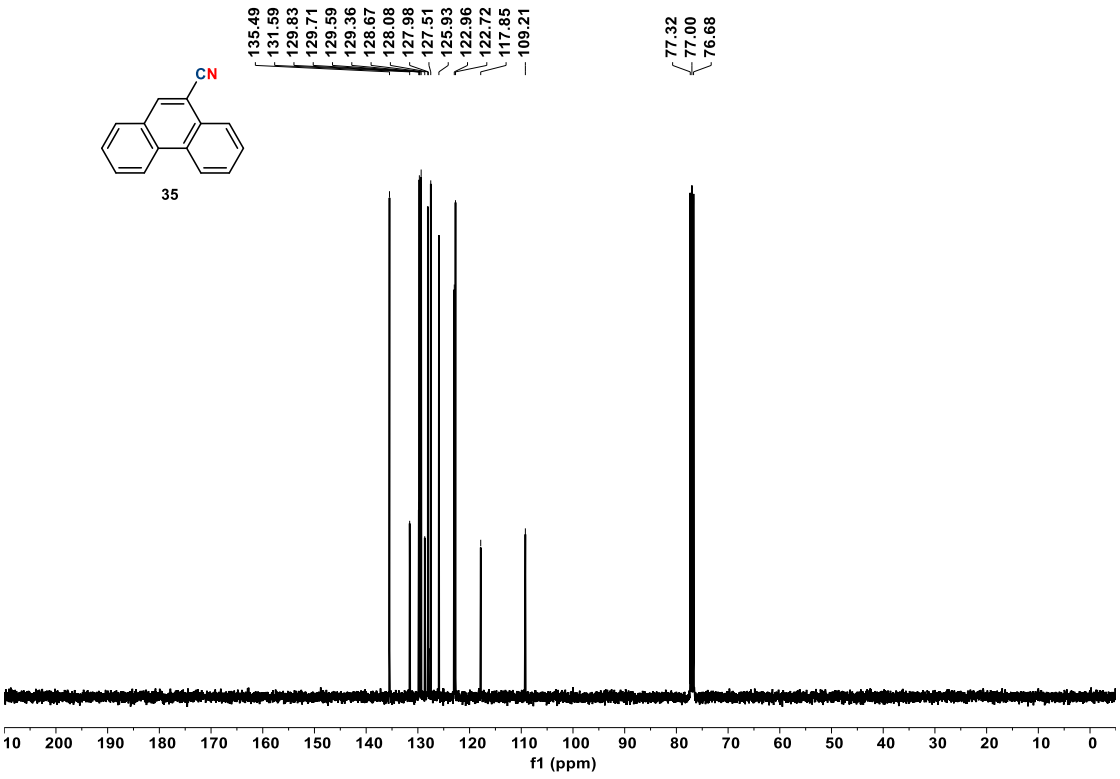

8.108
7.776
7.768
7.755
7.746
7.555
7.551
7.534
7.530
7.250
7.244
7.228
7.221
7.141
7.135
3.943
-0.000
CN
MeO
33
1.00
2.10
1.02
1.00
1.04
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

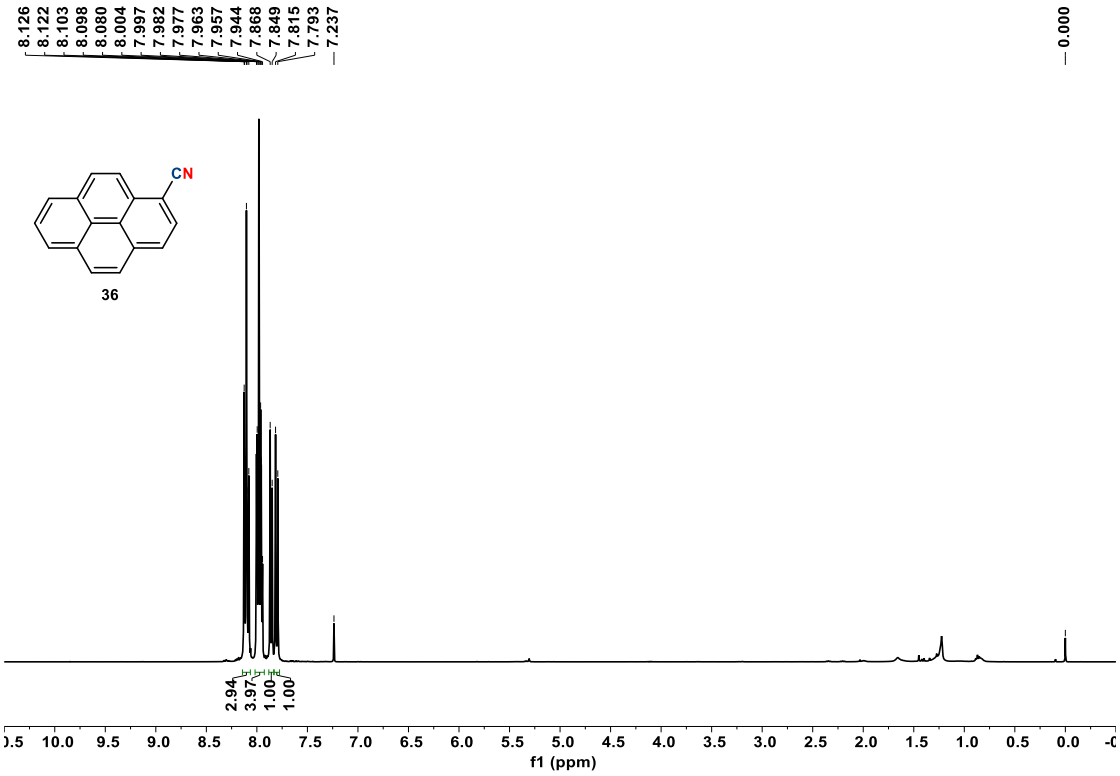

160.00
136.38
133.68
129.91
127.75
127.70
127.01
120.61
119.51
106.71
105.90
77.32
77.00
76.68
55.44
CN
MeO
33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

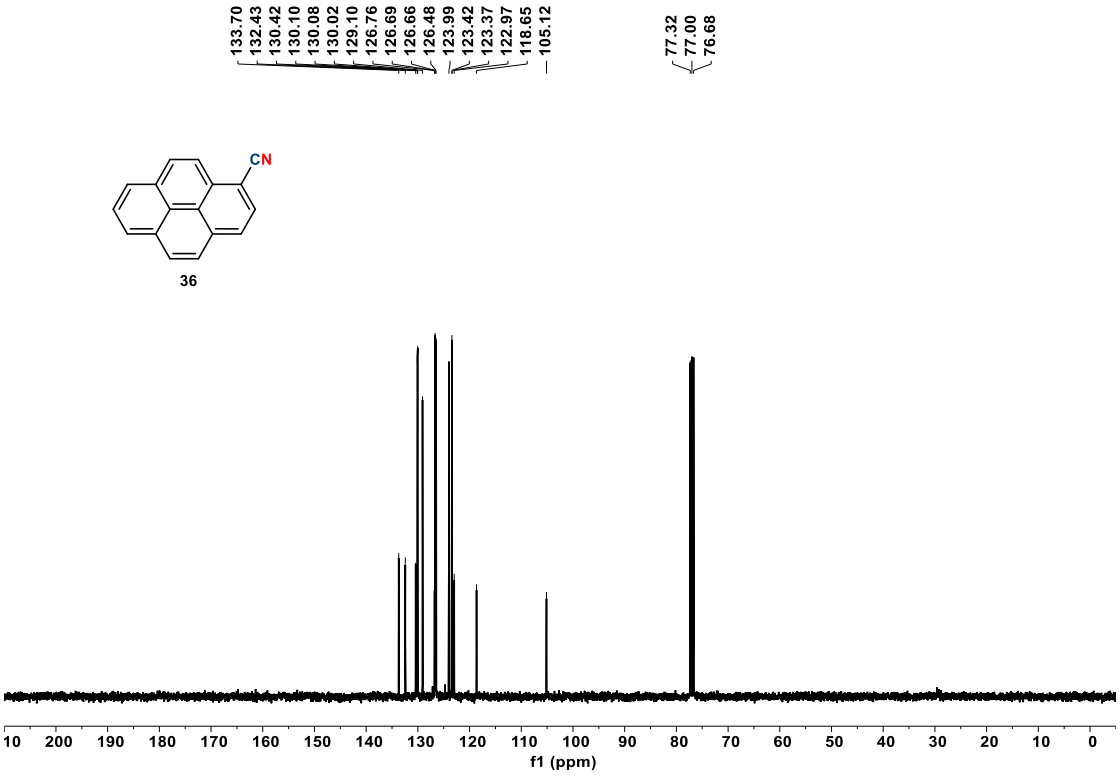

8.518
8.319
8.317
8.298
8.295
7.978
7.958
7.955
7.656
7.653
7.640
7.636
7.632
7.618
7.615
7.534
7.532
7.518
7.514
7.510
7.497
7.494
7.248
0.000
CN
34
1.00
1.94
1.98
1.99
2.00
f1 (ppm)

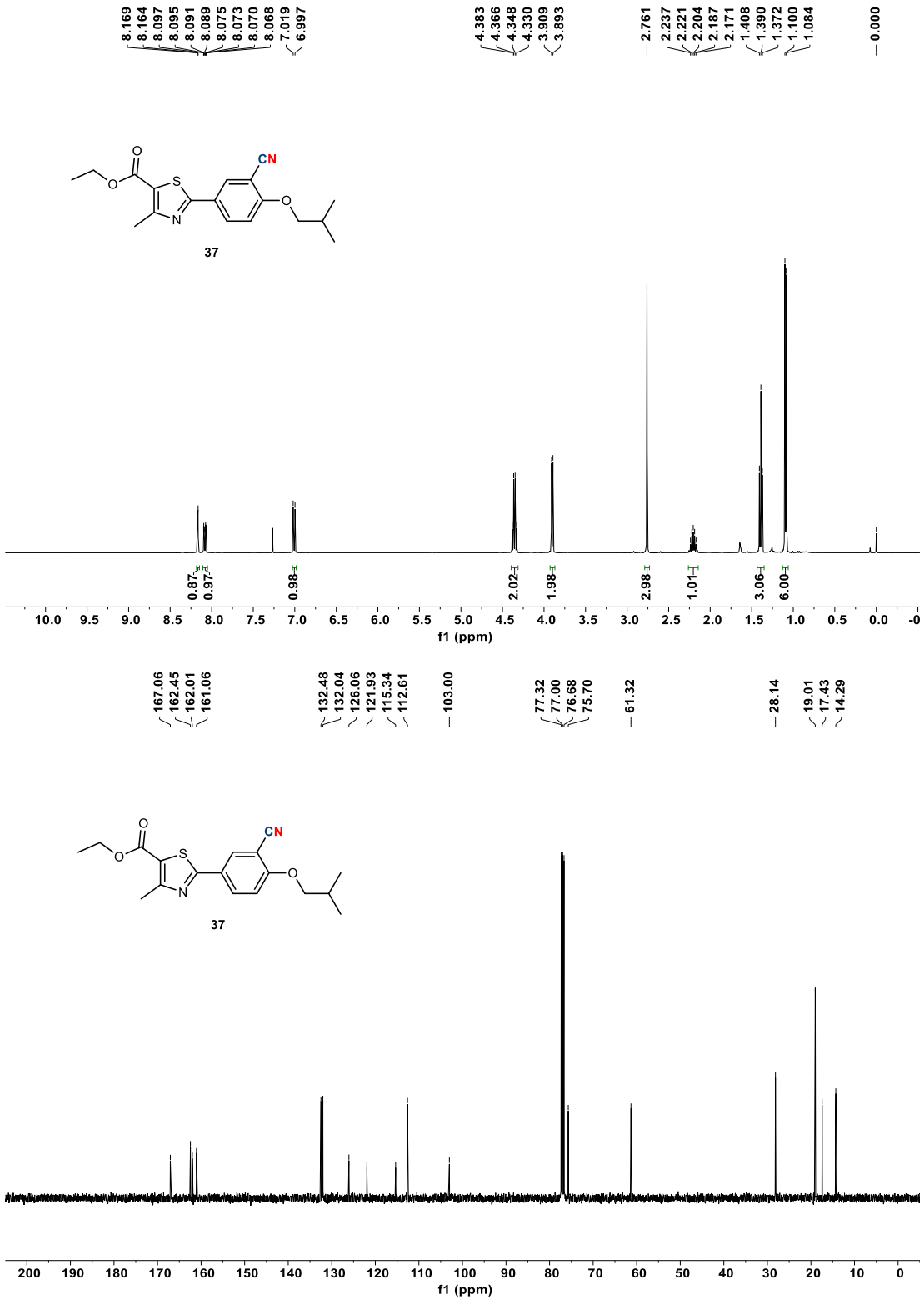

133.08
132.59
130.40
128.83
128.80
126.21
125.08
117.17
105.17
77.32
77.00
76.68
CN
34
f1 (ppm)

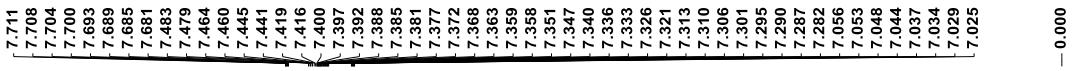

8.633
8.623
8.617
8.615
8.609
8.603
8.599
8.579
8.249
8.241
8.237
8.231
8.226
8.223
8.217
8.208
8.138
7.857
7.853
7.837
7.834
7.770
7.767
7.753
7.749
7.746
7.740
7.735
7.732
7.728
7.722
7.717
7.708
7.698
7.693
7.681
7.676
7.651
7.648
7.633
7.631
7.628
7.613
7.611
7.243
0.000
CN
35
2.02
0.96
0.96
1.01
2.98
1.00
f1 (ppm)

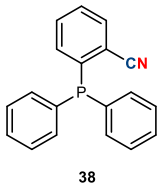

135.49
131.59
129.83
129.71
129.59
129.36
128.67
128.08
127.98
127.51
125.93
122.96
122.72
117.85
109.21
77.32
77.00
76.68
CN
35
f1 (ppm)


8.126
8.122
8.103
8.098
8.080
8.004
7.997
7.982
7.977
7.963
7.957
7.944
7.868
7.849
7.815
7.793
7.237
0.000
CN
36
2.94
3.97
1.00
1.00
f1 (ppm)

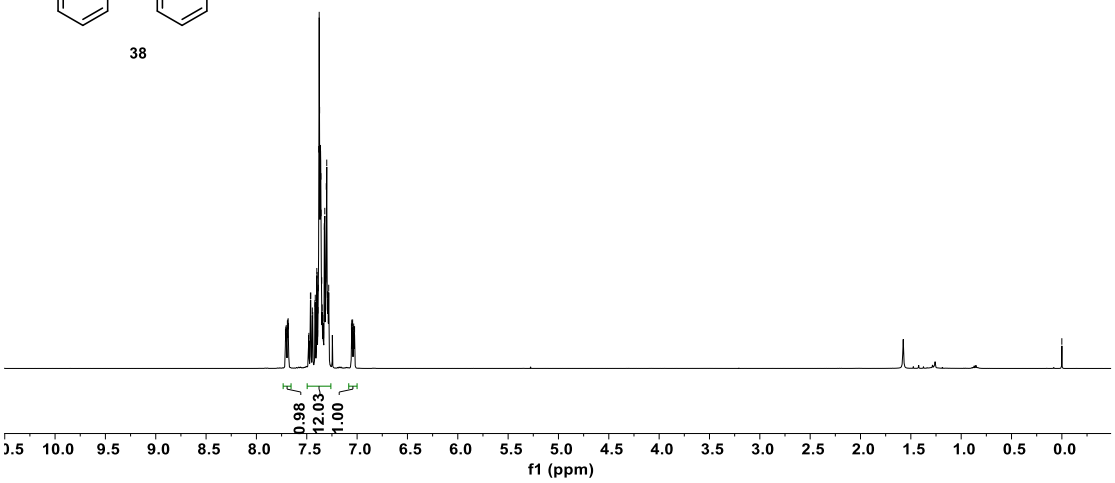

133.70
132.43
130.42
130.10
130.08
130.02
129.10
126.76
126.69
126.66
126.48
123.99
123.42
123.37
122.97
118.65
105.12
77.32
77.00
76.68
CN
36
f1 (ppm)

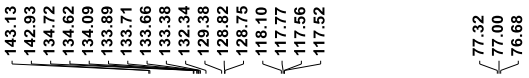

8.169
8.164
8.097
8.095
8.091
8.089
8.075
8.073
8.070
8.068
7.019
6.997
4.383
4.366
4.348
4.330
3.909
3.893
2.761
2.237
2.221
2.204
2.187
2.171
1.408
1.390
1.372
1.100
1.084
0.000
CN
O
S
N
O
O
37
0.87
0.97
0.98
2.02
1.98
2.98
1.01
3.06
6.00
f1 (ppm)
167.06
162.45
162.01
161.06
132.48
132.04
126.06
121.93
115.34
112.61
103.00
77.32
77.00
76.68
75.70
61.32
28.14
19.01
17.43
14.29
CN
O
S
N
O
O
37
f1 (ppm)

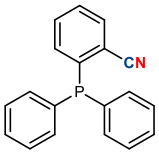

7.711
7.708
7.704
7.700
7.693
7.689
7.685
7.681
7.483
7.479
7.464
7.460
7.445
7.441
7.419
7.416
7.400
7.397
7.392
7.388
7.385
7.381
7.377
7.372
7.368
7.363
7.359
7.358
7.351
7.347
7.340
7.336
7.333
7.326
7.321
7.313
7.310
7.306
7.301
7.295
7.290
7.287
7.282
7.056
7.053
7.048
7.044
7.037
7.034
7.029
7.025
0.000


CN
P

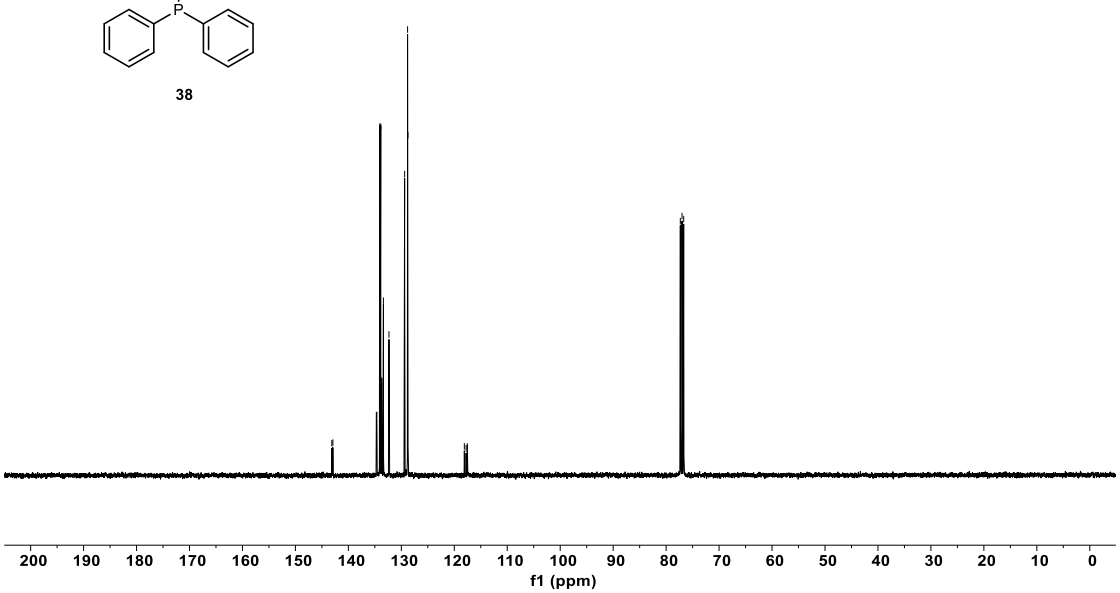
38

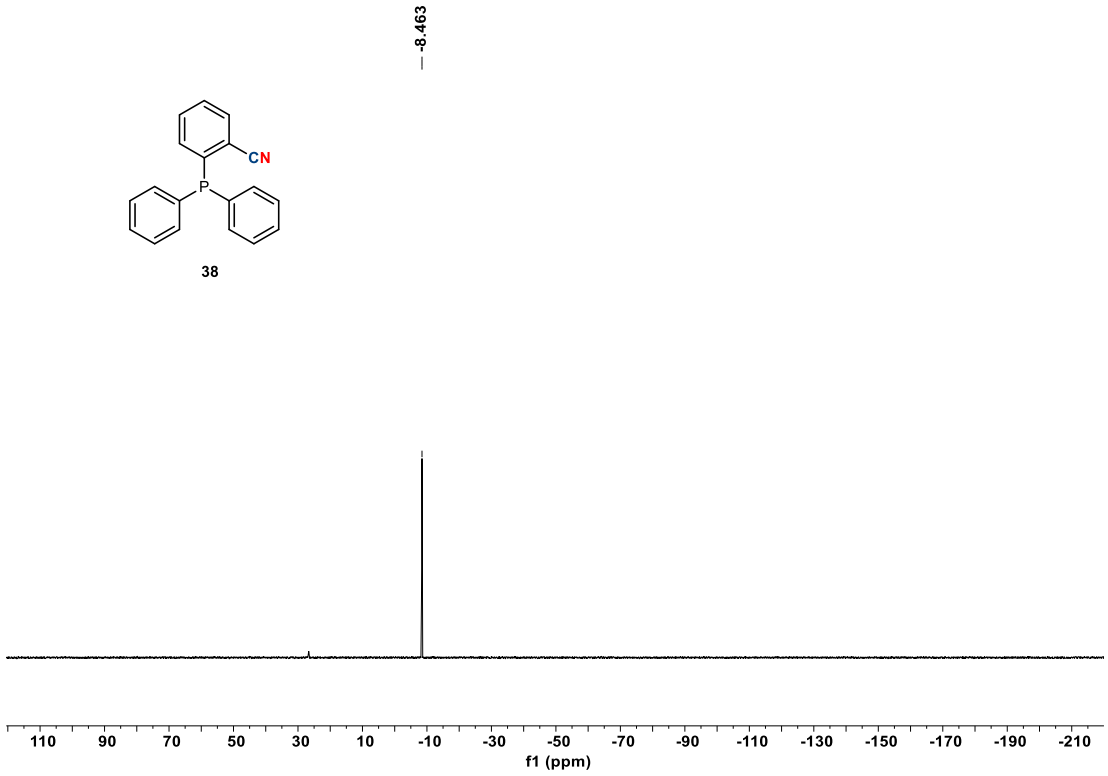

0.98
12.03
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.13
142.93
134.72
134.62
134.09
133.89
133.71
133.66
133.38
132.34
129.38
128.82
128.75
118.10
117.77
117.56
117.52
77.32
77.00
76.68

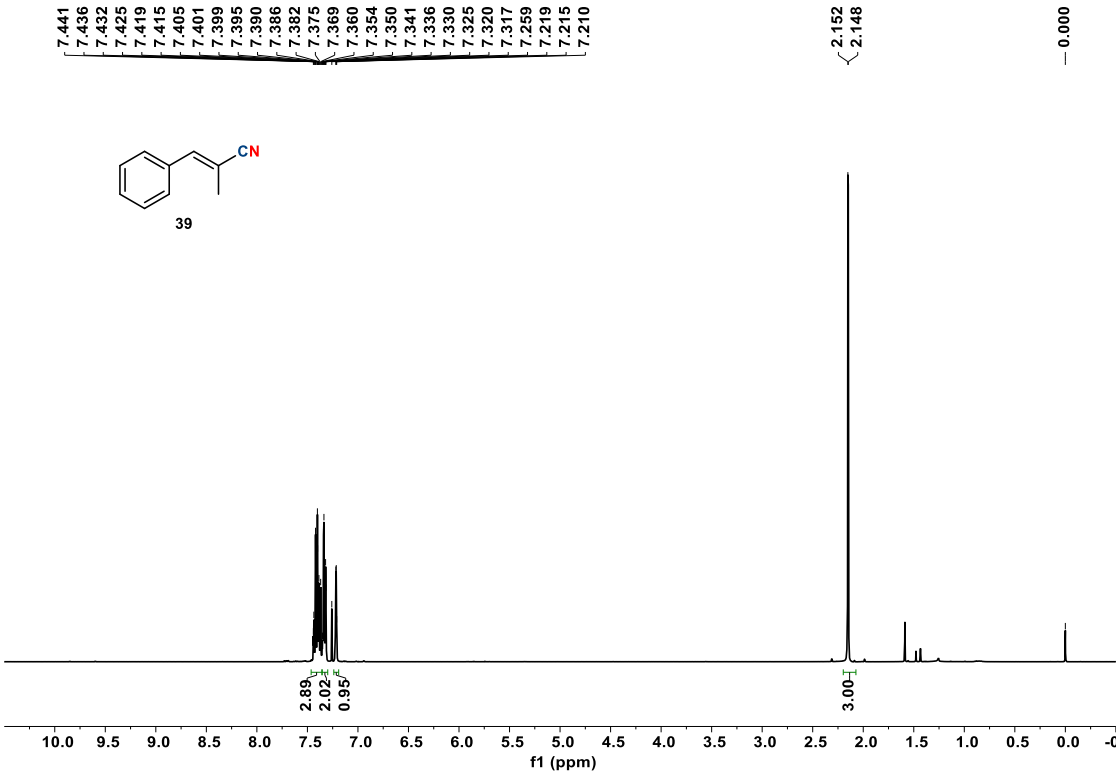

CN
P

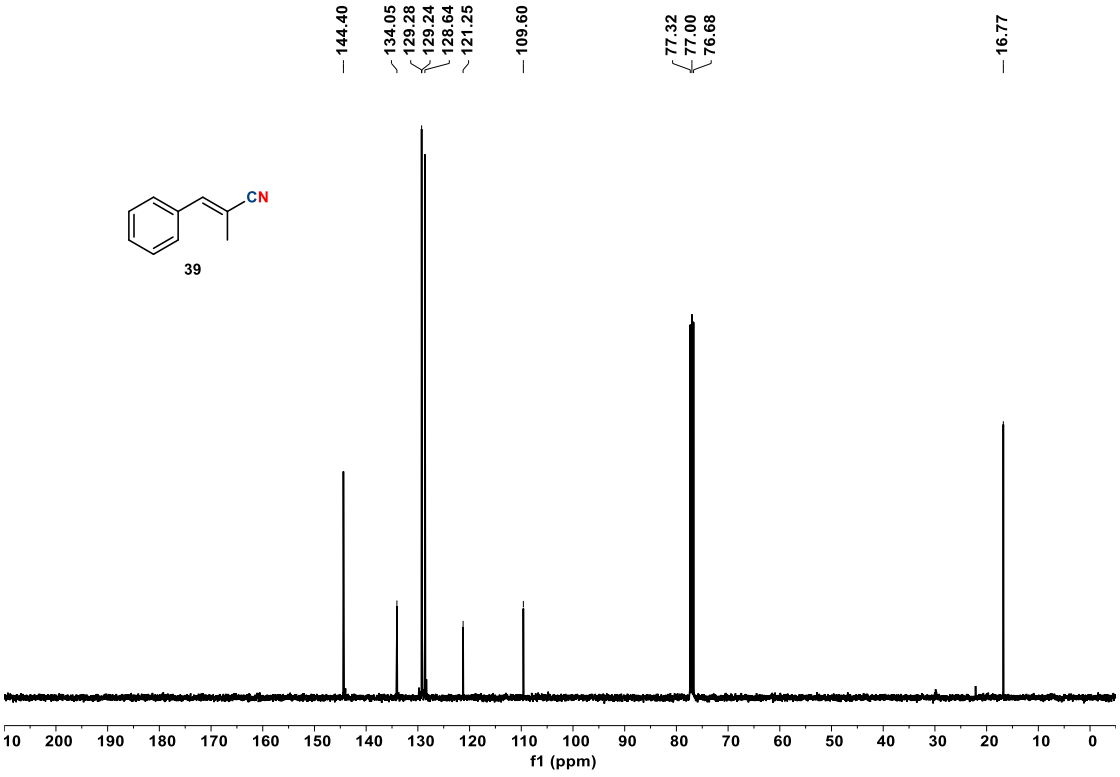
38

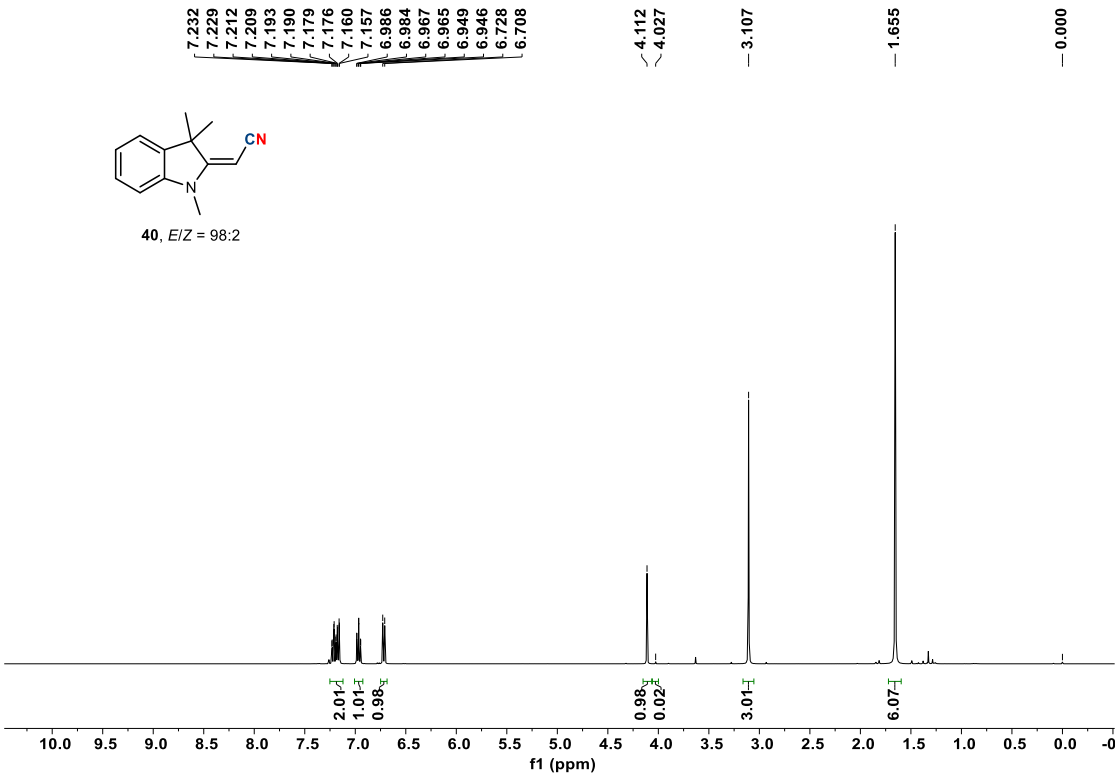

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

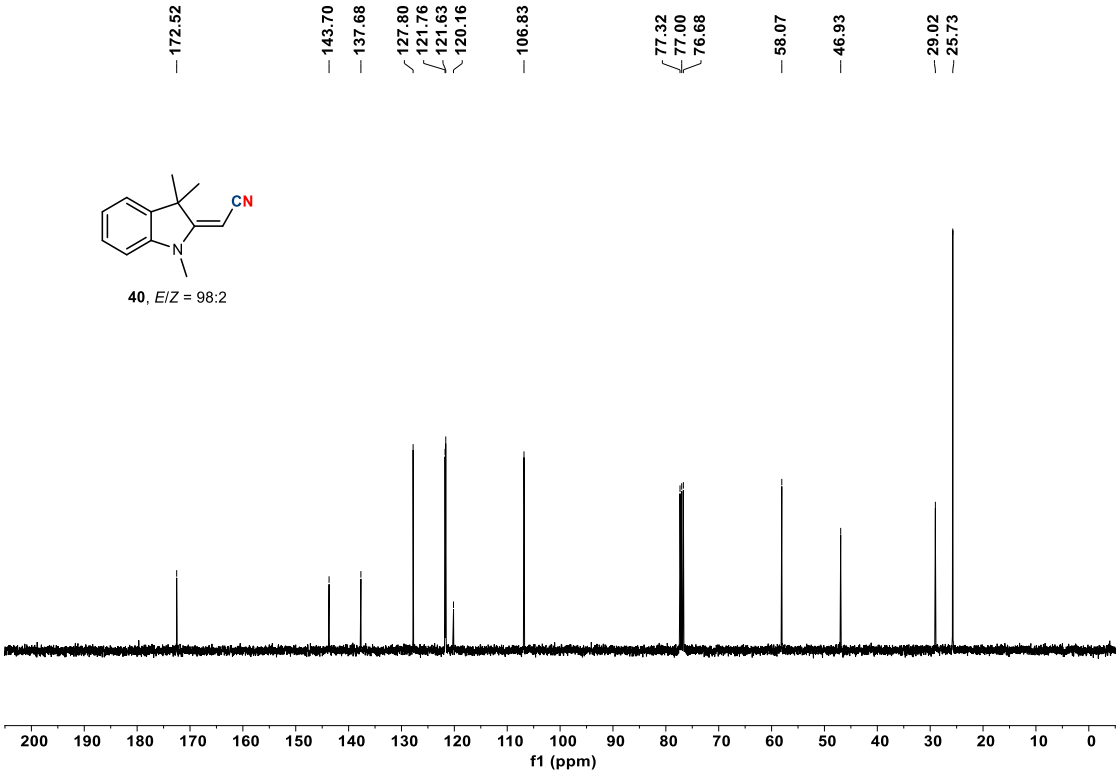


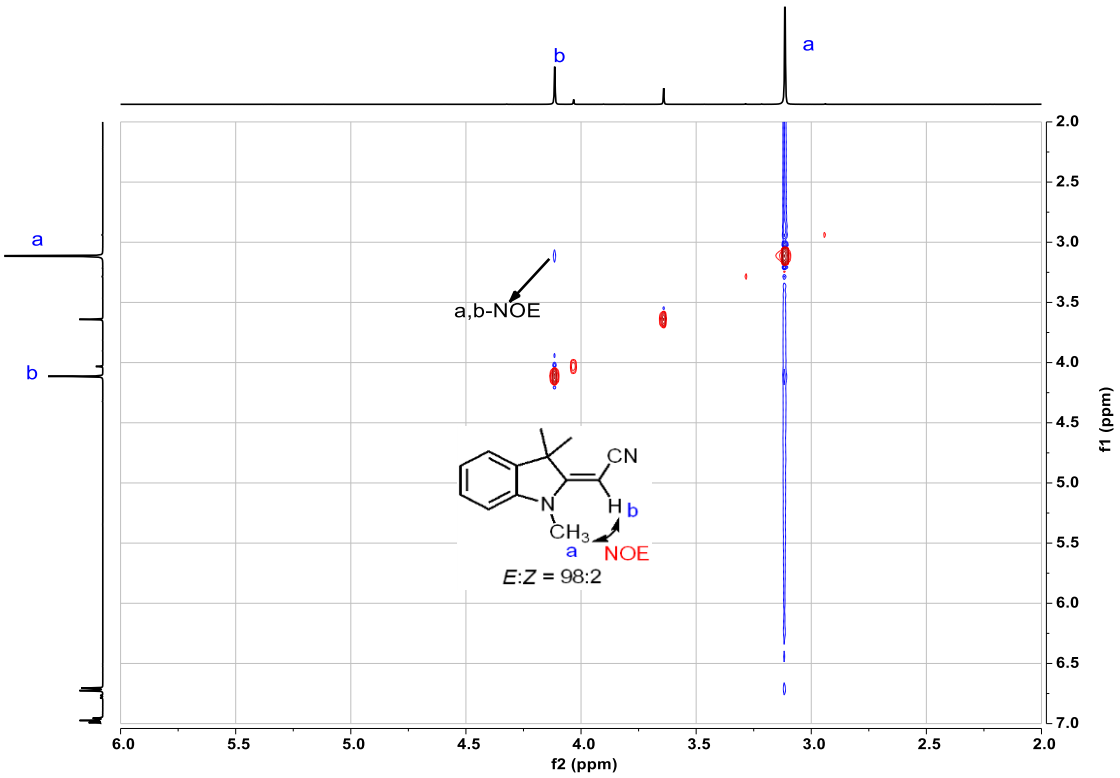
^{31}P NMR of nitrile 38

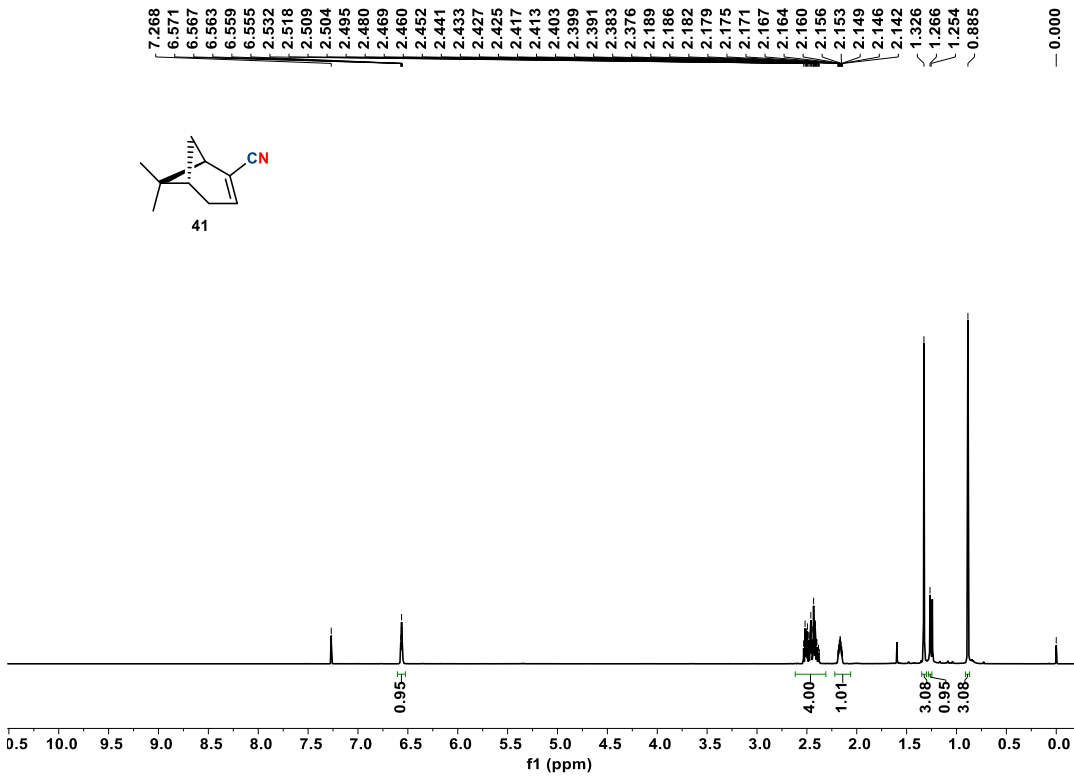

7.441
7.436
7.432
7.425
7.419
7.415
7.405
7.401
7.399
7.395
7.390
7.386
7.382
7.375
7.369
7.360
7.354
7.350
7.341
7.336
7.330
7.325
7.320
7.317
7.259
7.219
7.215
7.210
2.152
2.148
0.000
CN
39
2.89
2.02
0.95
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

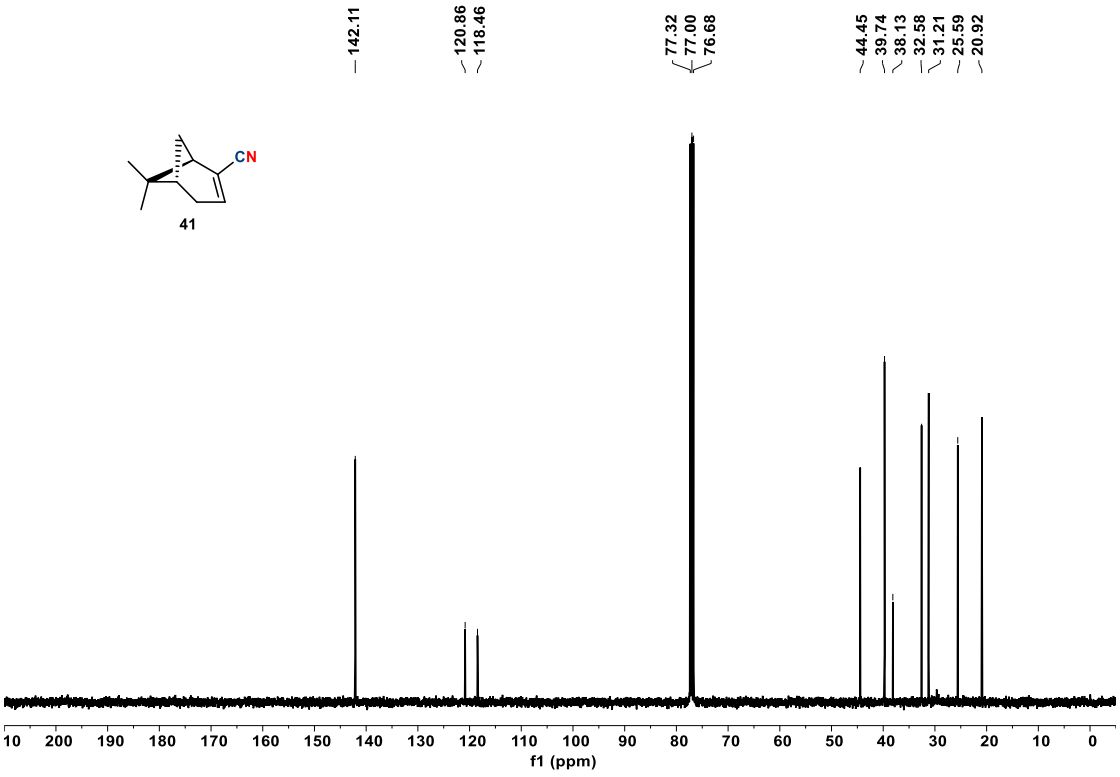

144.40
134.05
129.28
129.24
128.64
121.25
109.60
77.32
77.00
76.68
16.77
CN
39
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

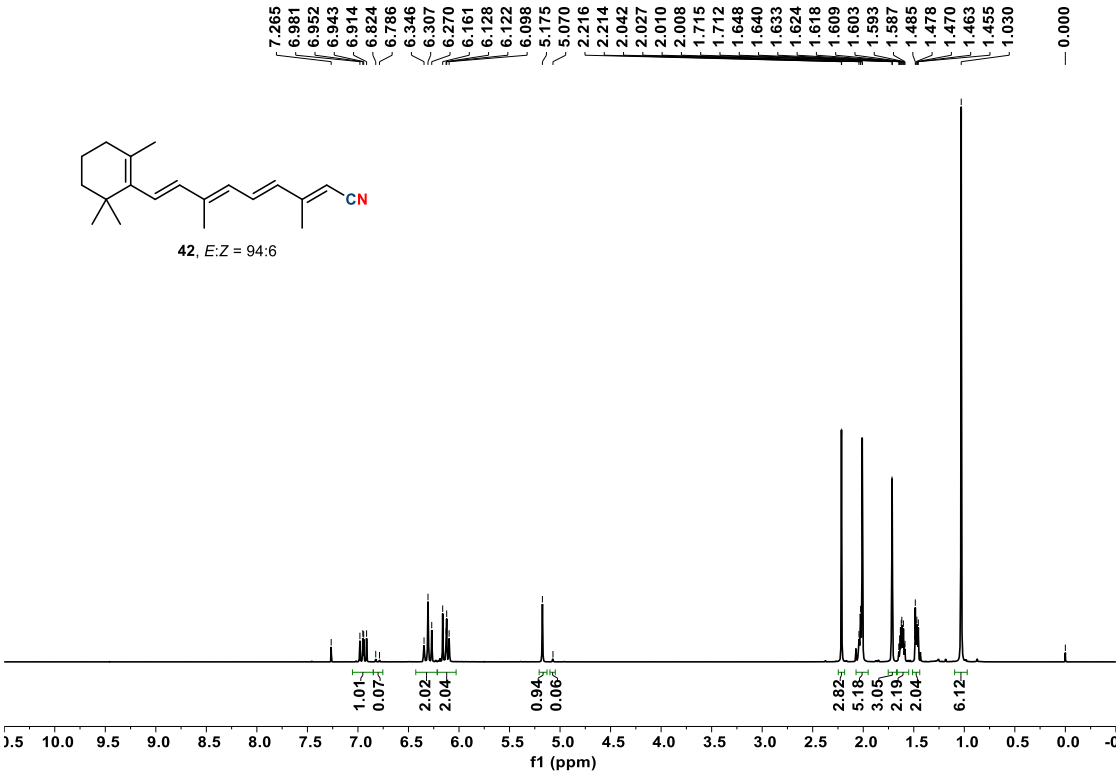

7.232
7.229
7.212
7.209
7.193
7.190
7.179
7.176
7.160
7.157
6.986
6.984
6.967
6.965
6.949
6.946
6.728
6.708
4.112
4.027
3.107
1.655
0.000
CN
N
40, E/Z = 98:2
2.01
1.01
0.98
0.98
0.02
3.01
6.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


172.52
143.70
137.68
127.80
121.76
121.63
120.16
106.83
77.32
77.00
76.68
58.07
46.93
29.02
25.73
CN
N
40, E/Z = 98:2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

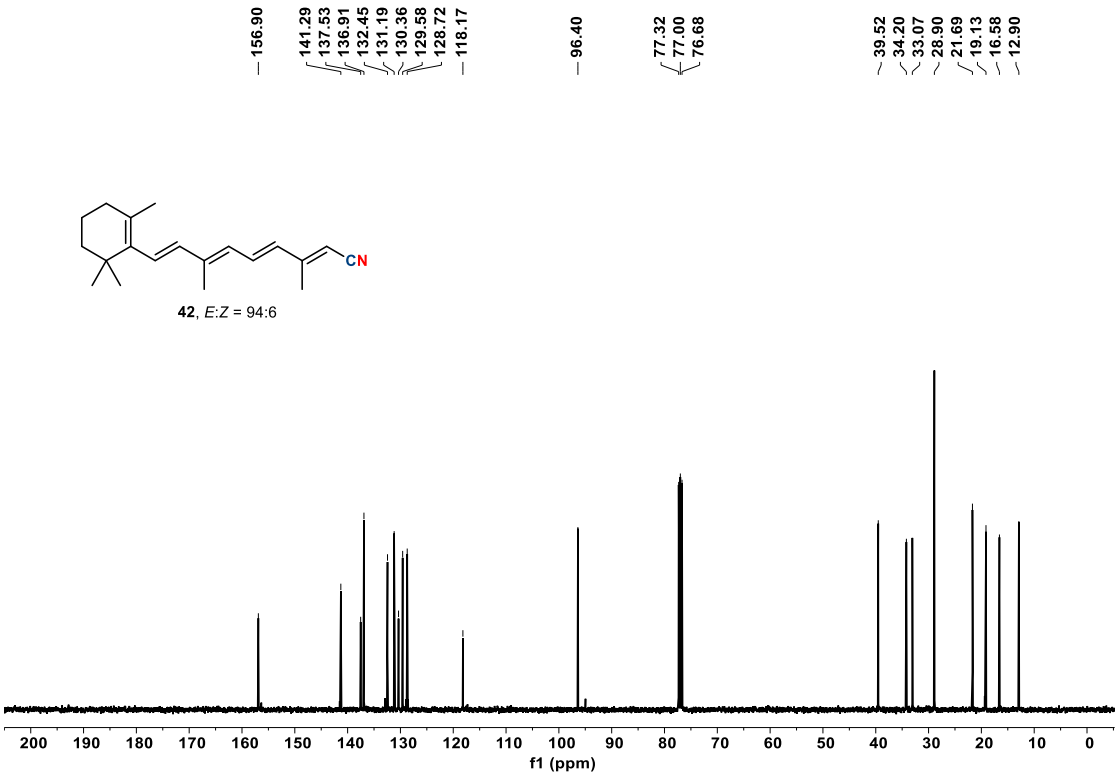

b
a
a
b
a,b-NOE
CN
H
b
N
CH3
a
NOE
E:Z = 98:2
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)


7.268
6.571
6.567
6.563
6.559
6.555
2.532
2.518
2.509
2.504
2.495
2.480
2.469
2.460
2.452
2.441
2.433
2.427
2.425
2.417
2.413
2.403
2.399
2.391
2.383
2.376
2.189
2.186
2.182
2.179
2.175
2.171
2.167
2.164
2.160
2.156
2.153
2.149
2.146
2.142
1.326
1.266
1.254
0.885
0.000
CN
41
0.95
4.00
1.01
3.08
0.95
3.08
f1 (ppm)

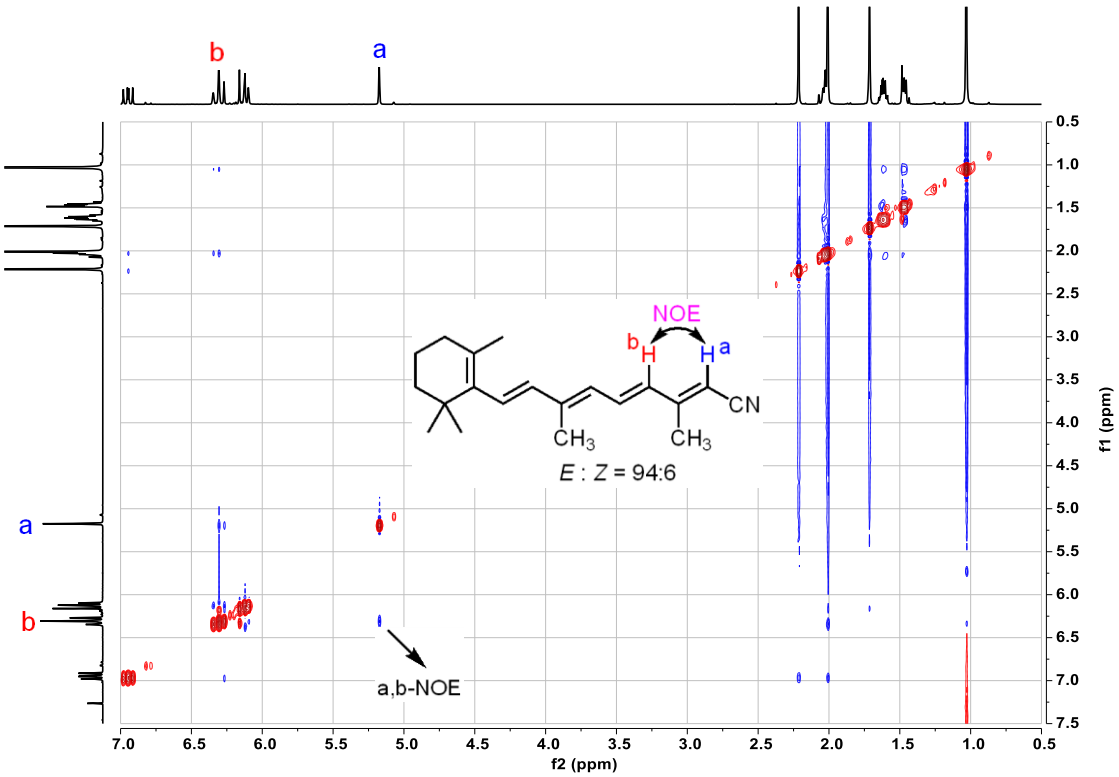

142.11
120.86
118.46
77.32
77.00
76.68
44.45
39.74
38.13
32.58
31.21
25.59
20.92
CN
41
f1 (ppm)

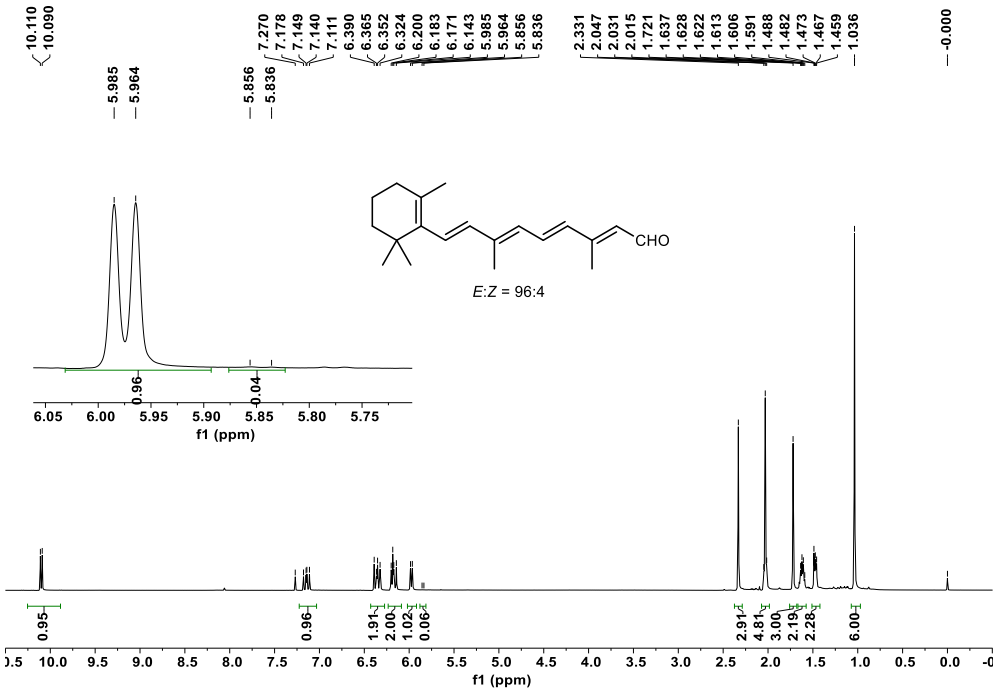


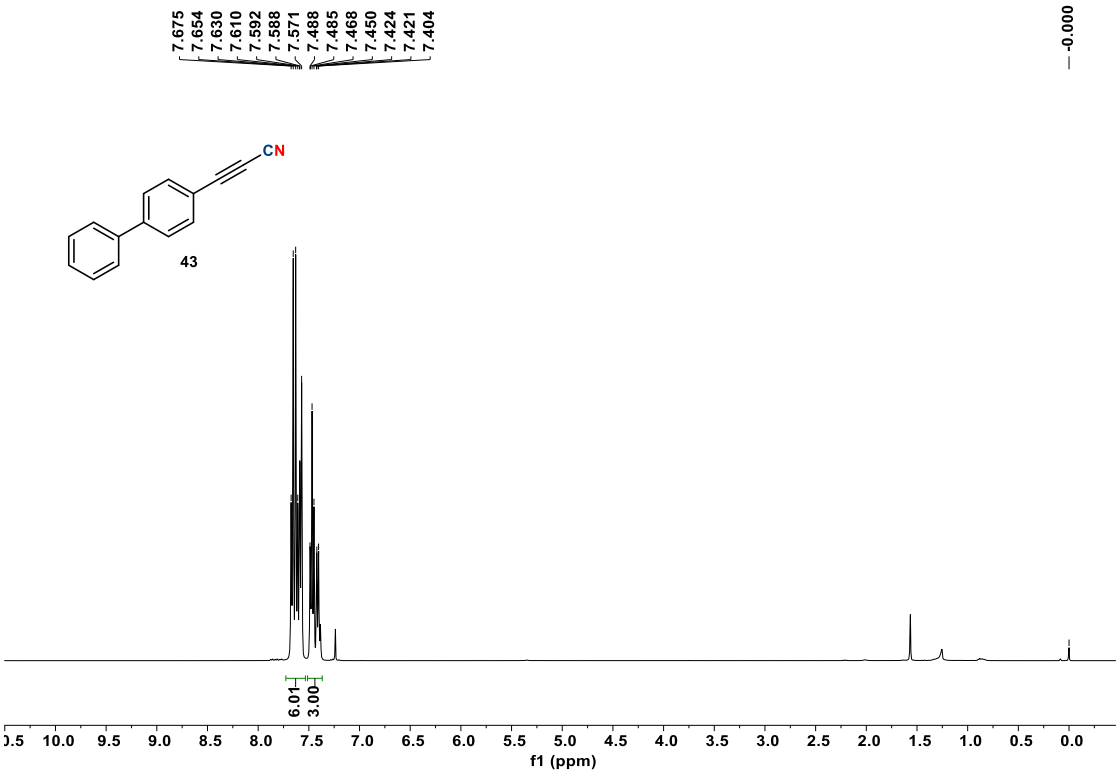
42, *E*:*Z* = 94:6

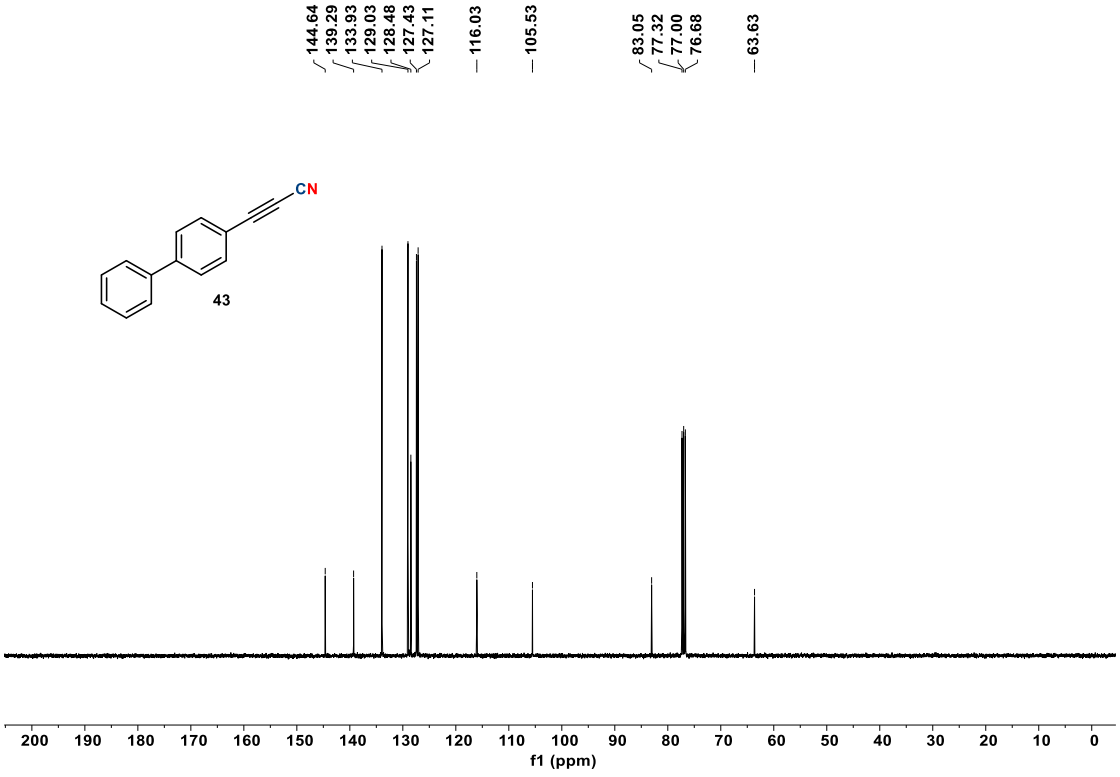


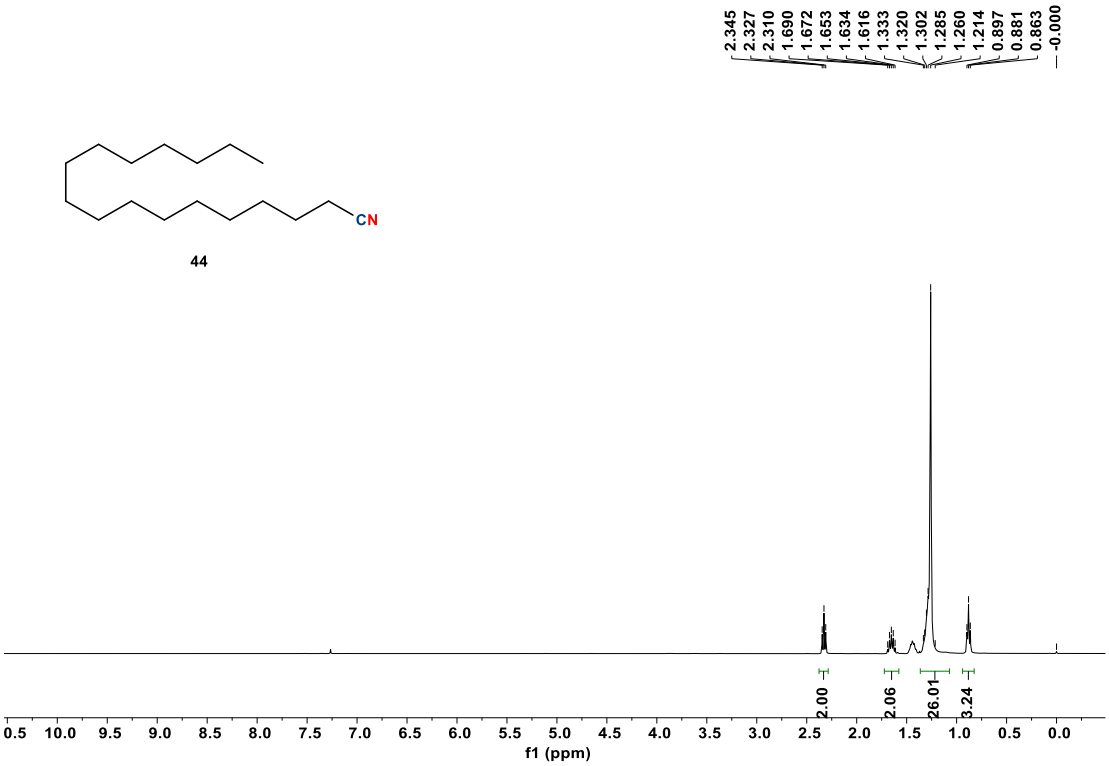
42, *E*:*Z* = 94:6

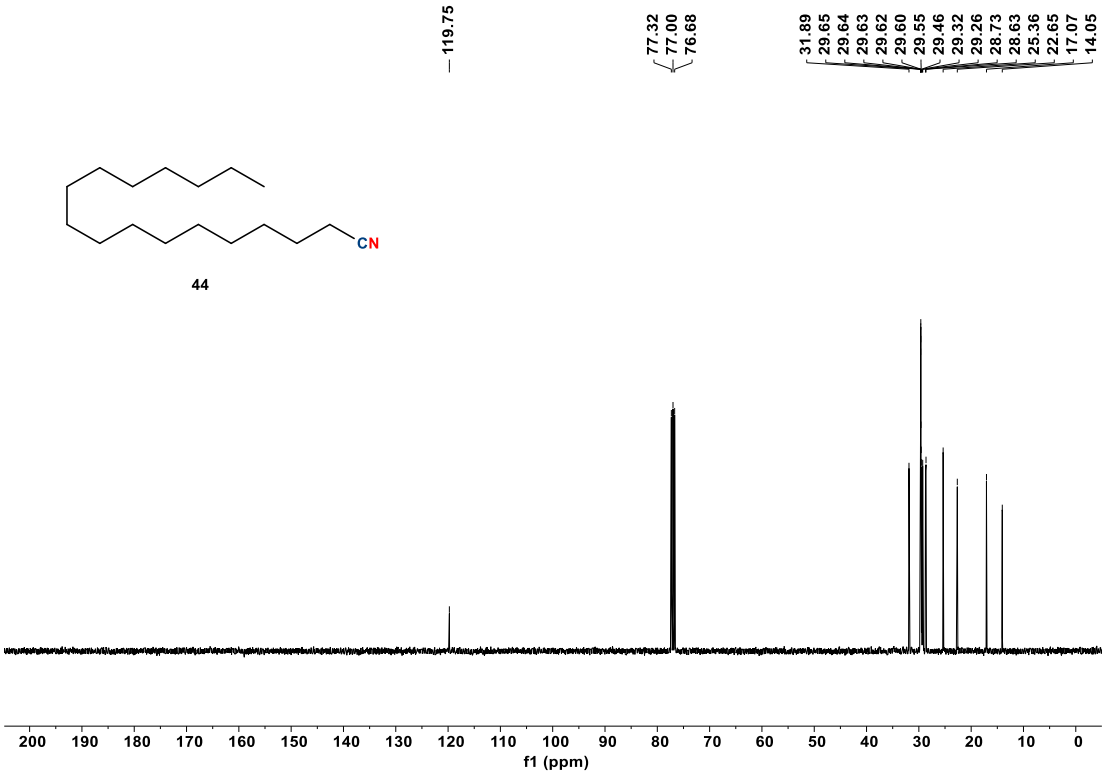

b
a
NOE
b H
H a
CN
CH3
CH3
E : Z = 94:6
a
b
a,b-NOE
f2 (ppm)
f1 (ppm)

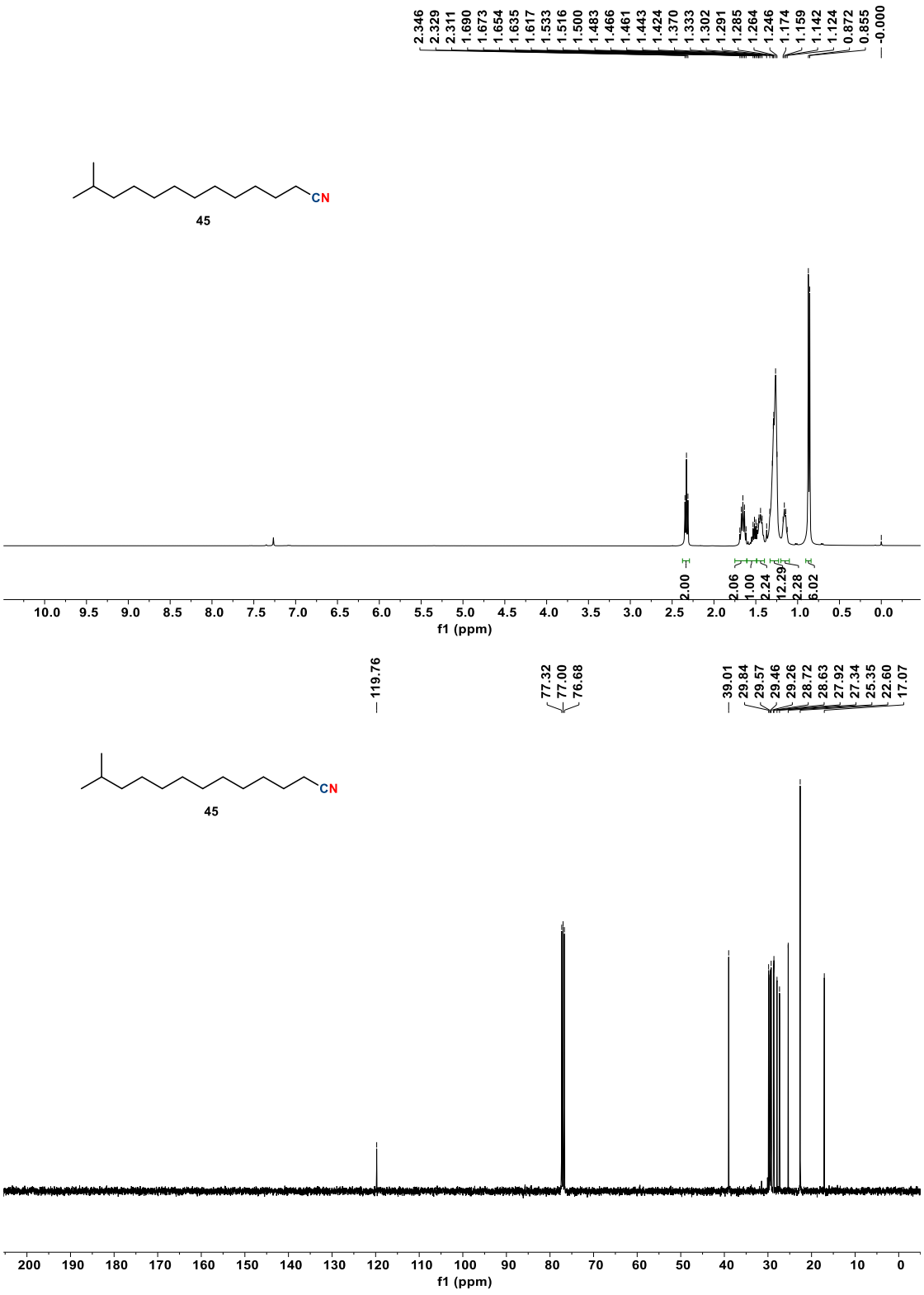

10.110
10.090
5.985
5.964
5.856
5.836
7.270
7.178
7.149
7.140
7.111
6.390
6.365
6.352
6.324
6.200
6.183
6.171
6.143
5.985
5.964
5.856
5.836
2.331
2.047
2.031
2.015
1.721
1.637
1.628
1.622
1.613
1.606
1.591
1.488
1.482
1.473
1.467
1.459
1.036
-0.000
CHO
E:Z = 96:4
0.96
0.04
f1 (ppm)
0.95
0.96
1.91
2.00
1.02
0.06
2.91
4.81
3.00
2.19
2.28
6.00
f1 (ppm)

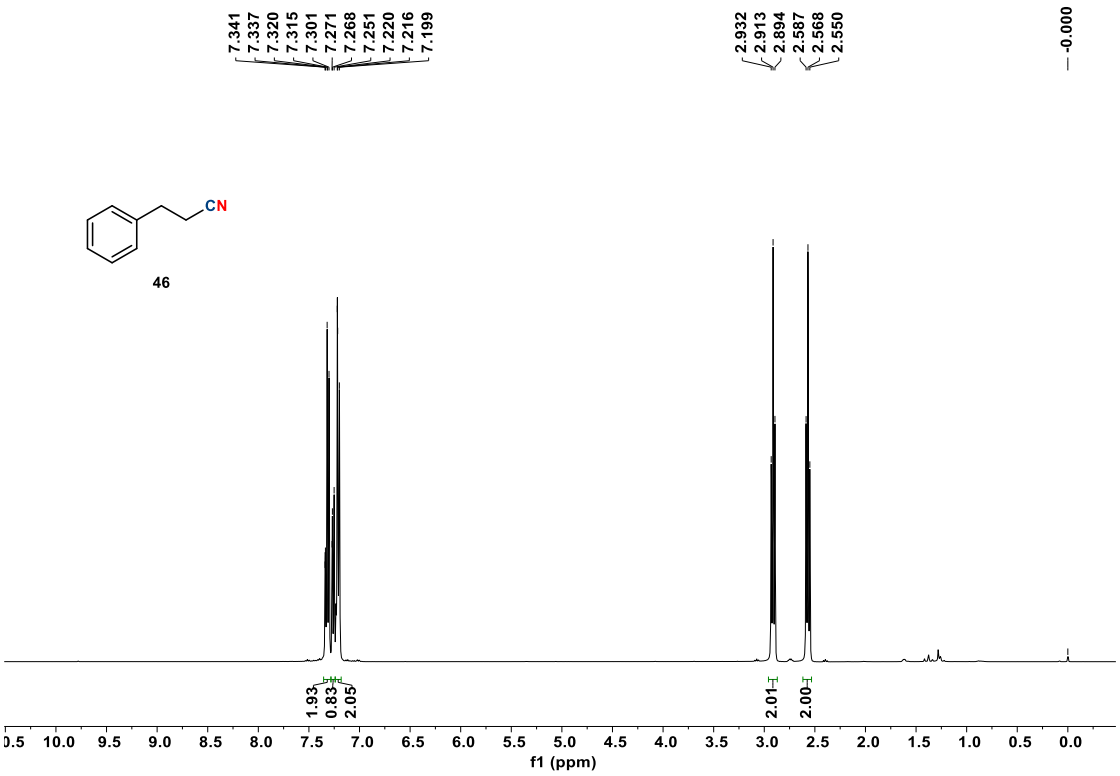

7.675
7.654
7.630
7.610
7.592
7.588
7.571
7.488
7.485
7.468
7.450
7.424
7.421
7.404
-0.000
CN
43
6.01
3.00
f1 (ppm)

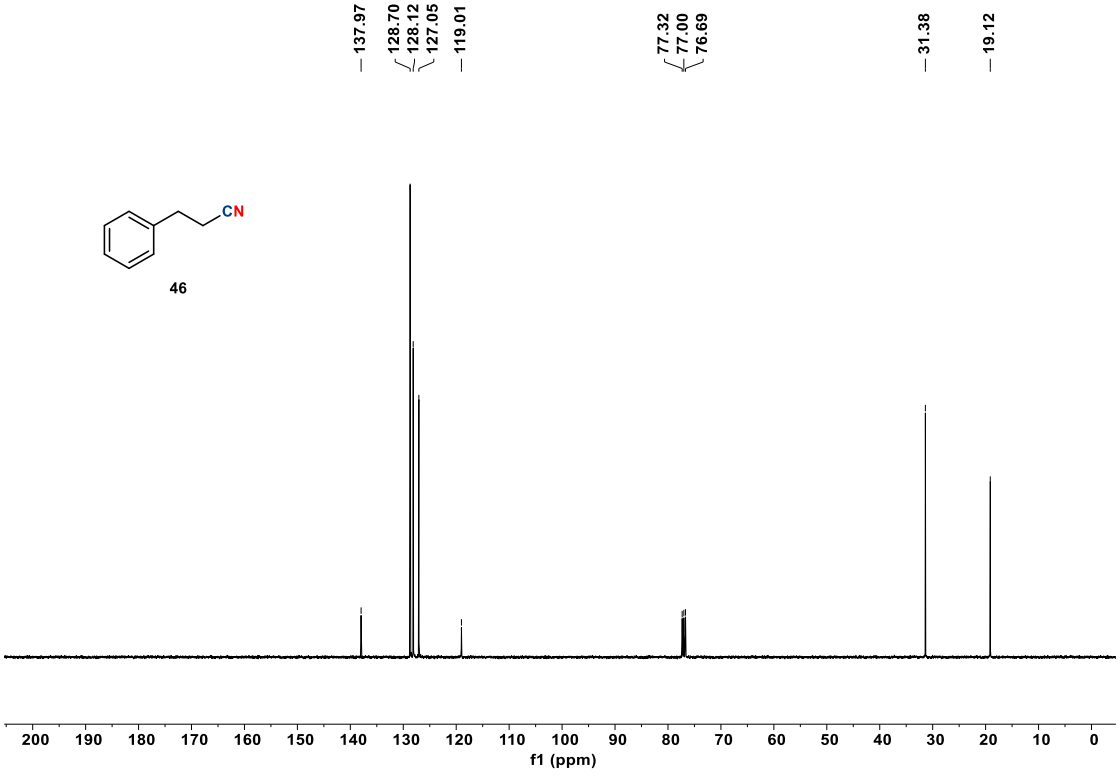

144.64
139.29
133.93
129.03
128.48
127.43
127.11
116.03
105.53
83.05
77.32
77.00
76.68
63.63
CN
43
f1 (ppm)

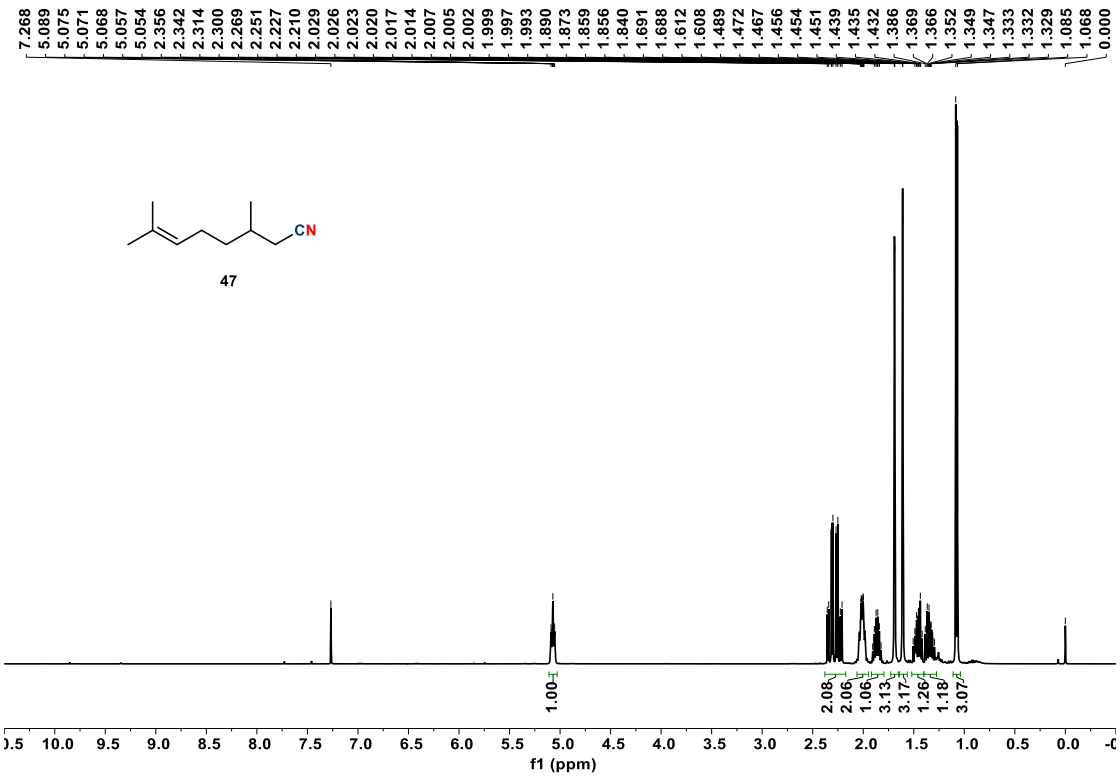

2.345
2.327
2.310
1.690
1.672
1.653
1.634
1.616
1.333
1.320
1.302
1.285
1.260
1.214
0.897
0.881
0.863
-0.000
CN
44
2.00
2.06
26.01
3.24
f1 (ppm)

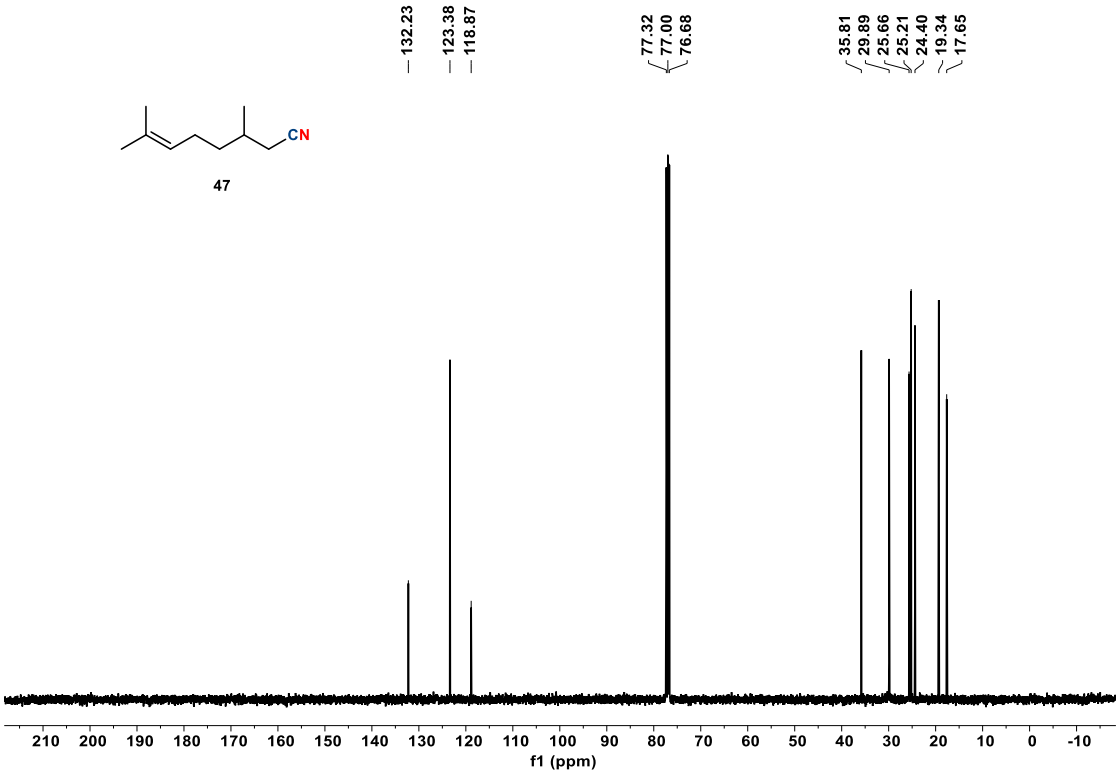

119.75
77.32
77.00
76.68
31.89
29.65
29.64
29.63
29.62
29.60
29.55
29.46
29.32
29.26
28.73
28.63
25.36
22.65
17.07
14.05
CN
44
f1 (ppm)

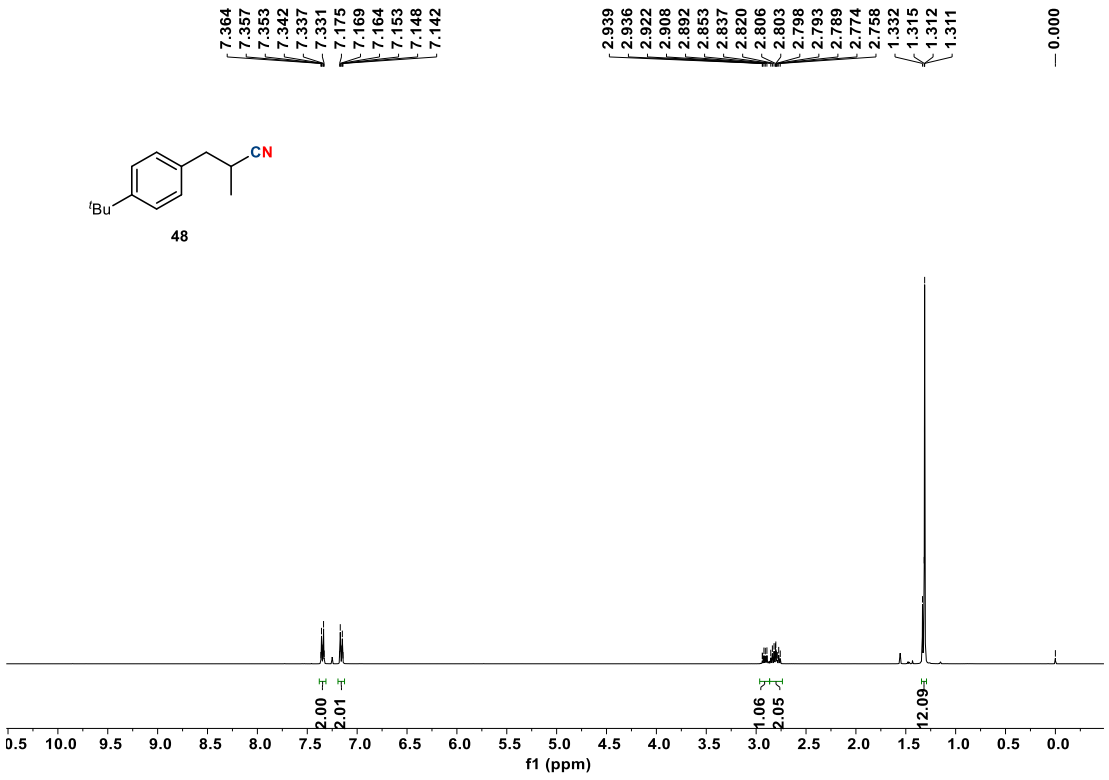

2.346
2.329
2.311
1.690
1.673
1.654
1.635
1.617
1.533
1.516
1.500
1.483
1.466
1.461
1.443
1.424
1.370
1.333
1.302
1.291
1.285
1.264
1.246
1.174
1.159
1.142
1.124
0.872
0.855
-0.000
CN
45
2.00
2.06
1.00
2.24
12.29
2.28
6.02
f1 (ppm)
119.76
77.32
77.00
76.68
39.01
29.84
29.57
29.46
29.26
28.72
28.63
27.92
27.34
25.35
22.60
17.07
CN
45
f1 (ppm)

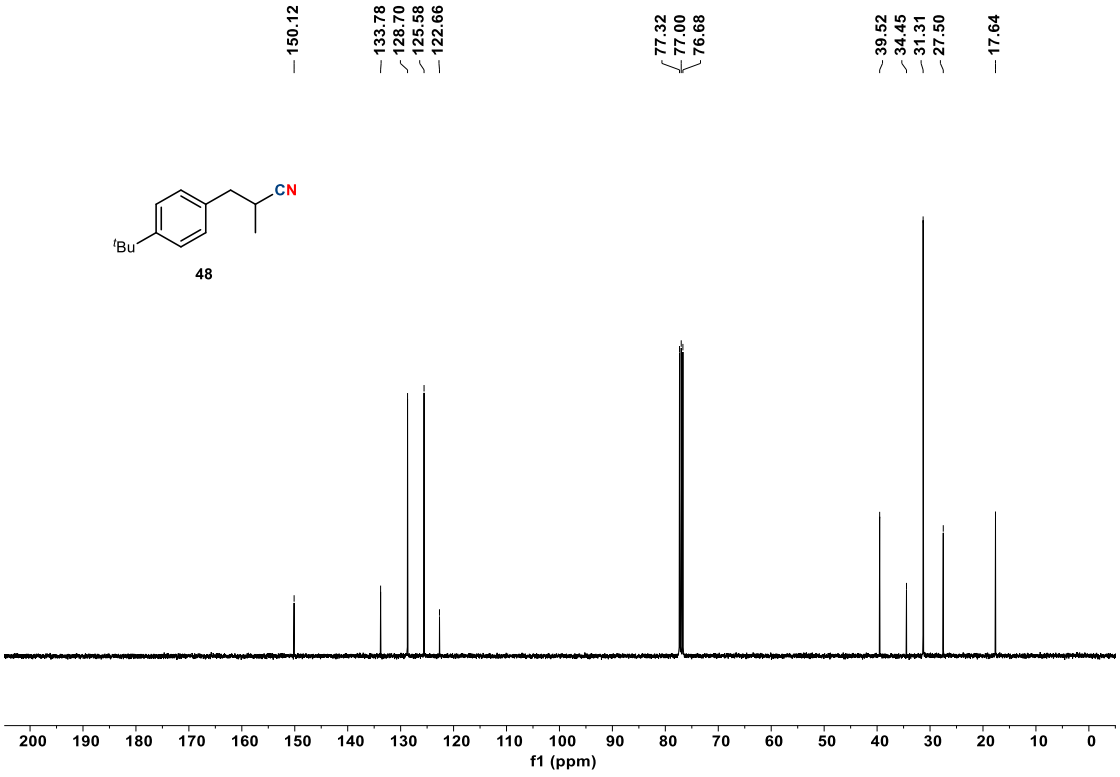

7.341
7.337
7.320
7.315
7.301
7.271
7.268
7.251
7.220
7.216
7.199
2.932
2.913
2.894
2.587
2.568
2.550
-0.000
CN
46
1.93
0.83
2.05
2.01
2.00
f1 (ppm)

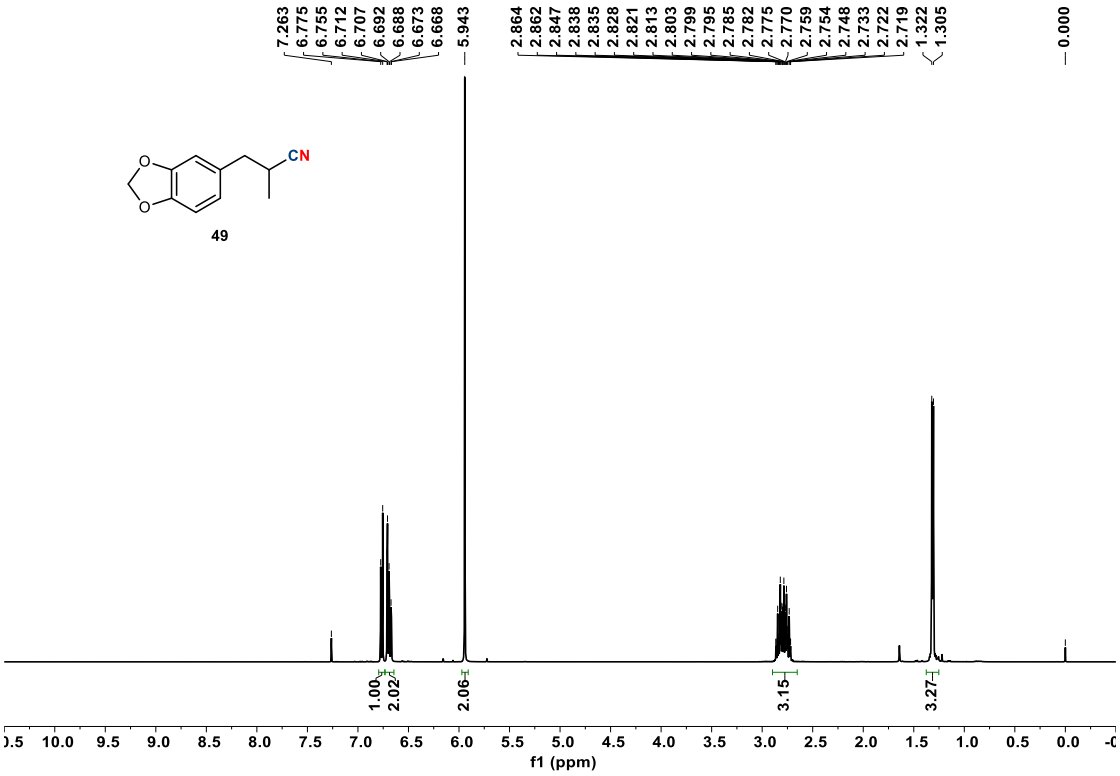

137.97
128.70
128.12
127.05
119.01
77.32
77.00
76.69
31.38
19.12
CN
46
f1 (ppm)

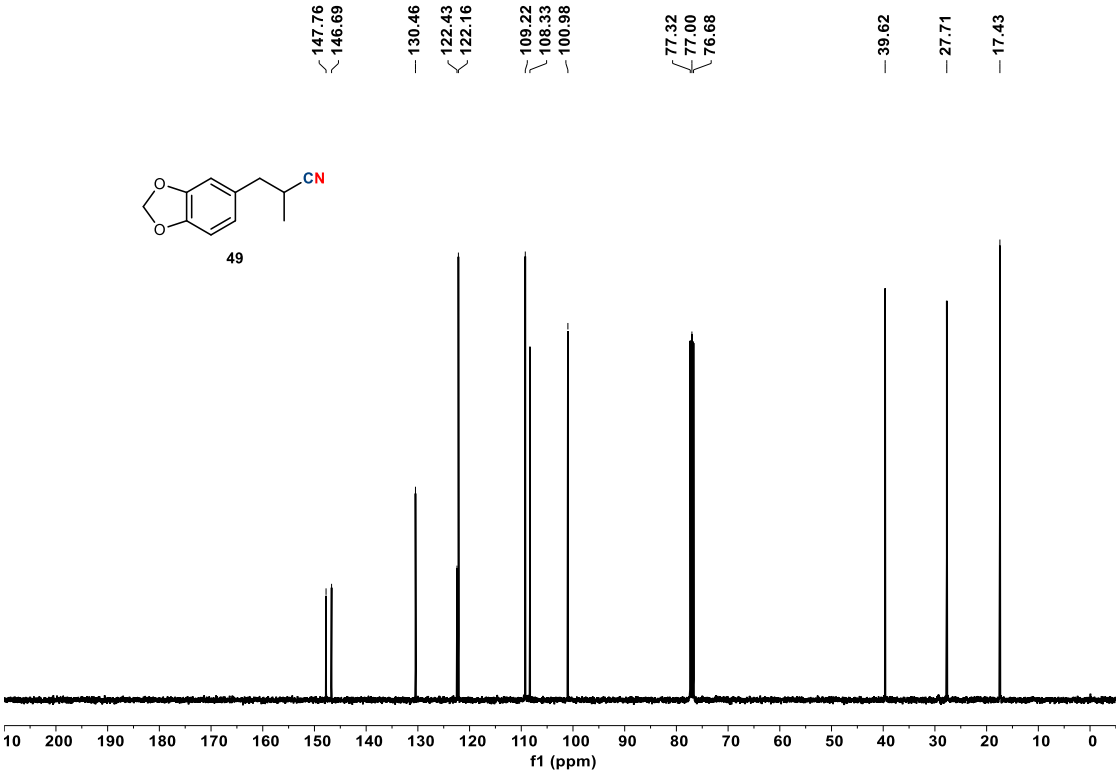

7.268
5.089
5.075
5.071
5.068
5.057
5.054
2.356
2.342
2.314
2.300
2.269
2.251
2.227
2.210
2.029
2.026
2.023
2.020
2.017
2.014
2.007
2.005
2.002
1.999
1.997
1.993
1.890
1.873
1.859
1.856
1.840
1.691
1.688
1.612
1.608
1.489
1.472
1.467
1.456
1.454
1.451
1.439
1.435
1.432
1.386
1.369
1.366
1.352
1.349
1.347
1.333
1.332
1.329
1.085
1.068
0.000
CN
47
1.00
2.08
2.06
1.06
3.13
3.17
1.26
1.18
3.07
f1 (ppm)

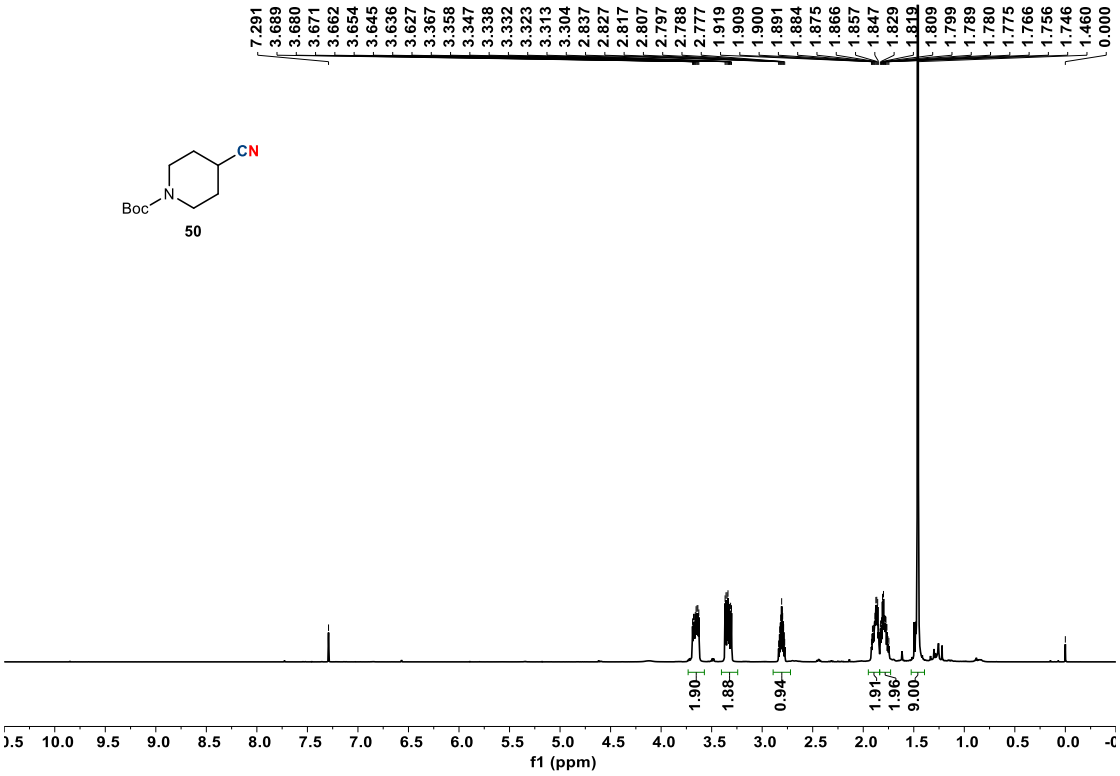

132.23
123.38
118.87
77.32
77.00
76.68
35.81
29.89
25.66
25.21
24.40
19.34
17.65
CN
47
f1 (ppm)

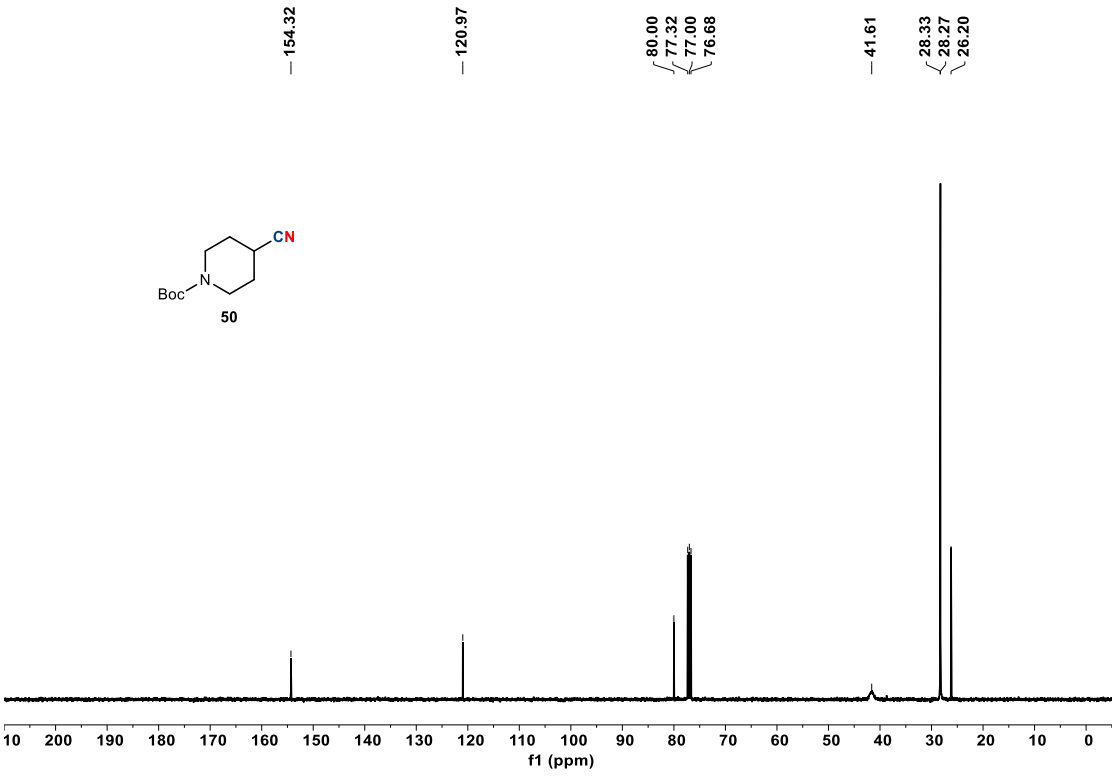

7.364
7.357
7.353
7.342
7.337
7.331
7.175
7.169
7.164
7.153
7.148
7.142
2.939
2.936
2.922
2.908
2.892
2.853
2.837
2.820
2.806
2.803
2.798
2.793
2.789
2.774
2.758
1.332
1.315
1.312
1.311
0.000
CN
tBu
48
2.00
2.01
1.06
2.05
12.09
f1 (ppm)

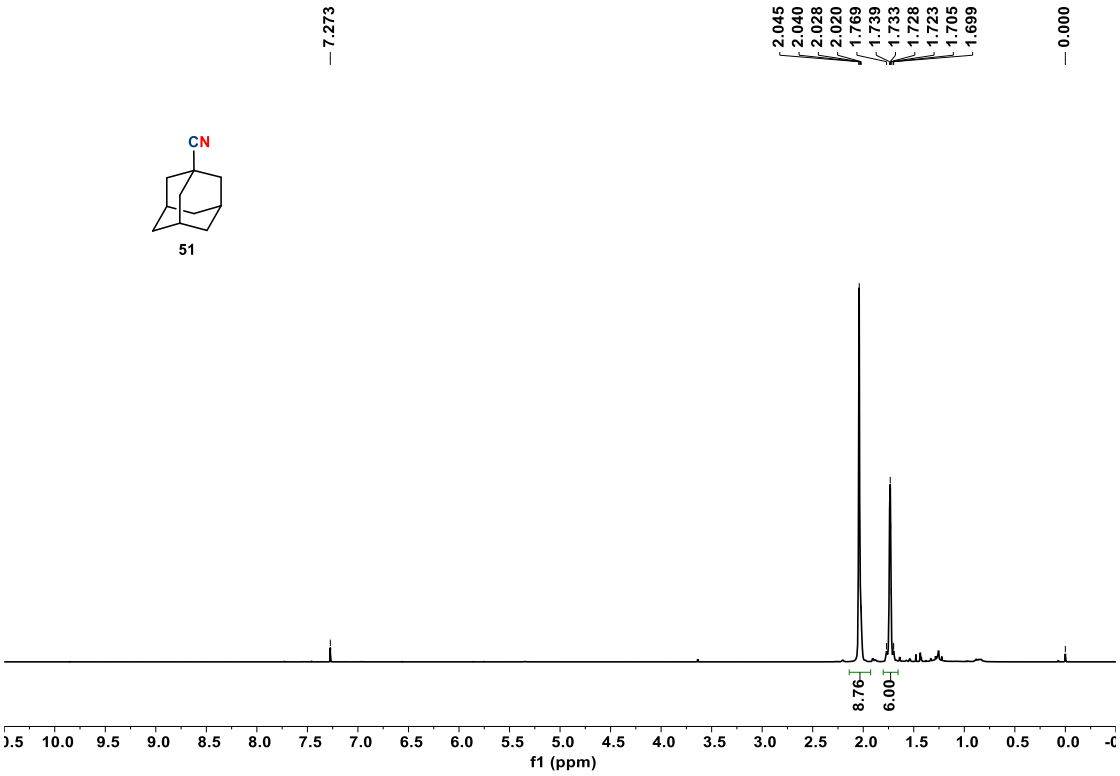

150.12
133.78
128.70
125.58
122.66
77.32
77.00
76.68
39.52
34.45
31.31
27.50
17.64
CN
tBu
48
f1 (ppm)

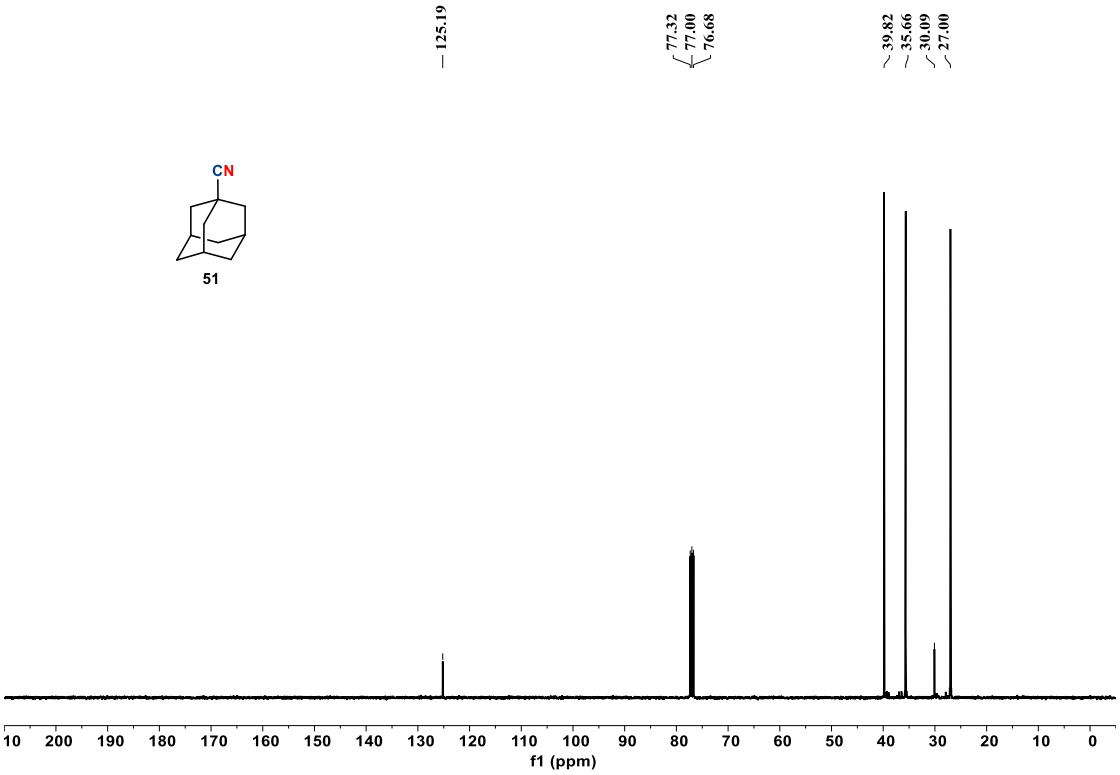

7.263
6.775
6.755
6.712
6.707
6.692
6.688
6.673
6.668
5.943
2.864
2.862
2.847
2.838
2.835
2.828
2.821
2.813
2.803
2.799
2.795
2.785
2.782
2.775
2.770
2.759
2.754
2.748
2.733
2.722
2.719
1.322
1.305
0.000
CN
O
O
49
1.00
2.02
2.06
3.15
3.27
f1 (ppm)

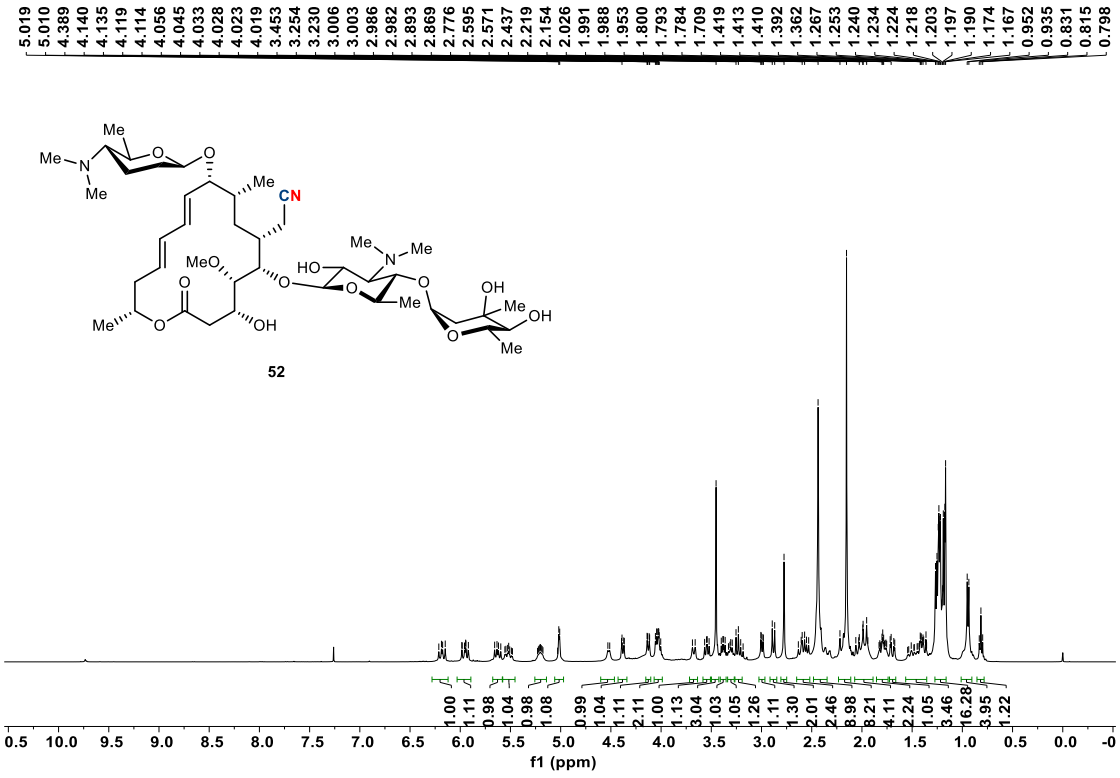

147.76
146.69
130.46
122.43
122.16
109.22
108.33
100.98
77.32
77.00
76.68
39.62
27.71
17.43
CN
O
O
49
f1 (ppm)

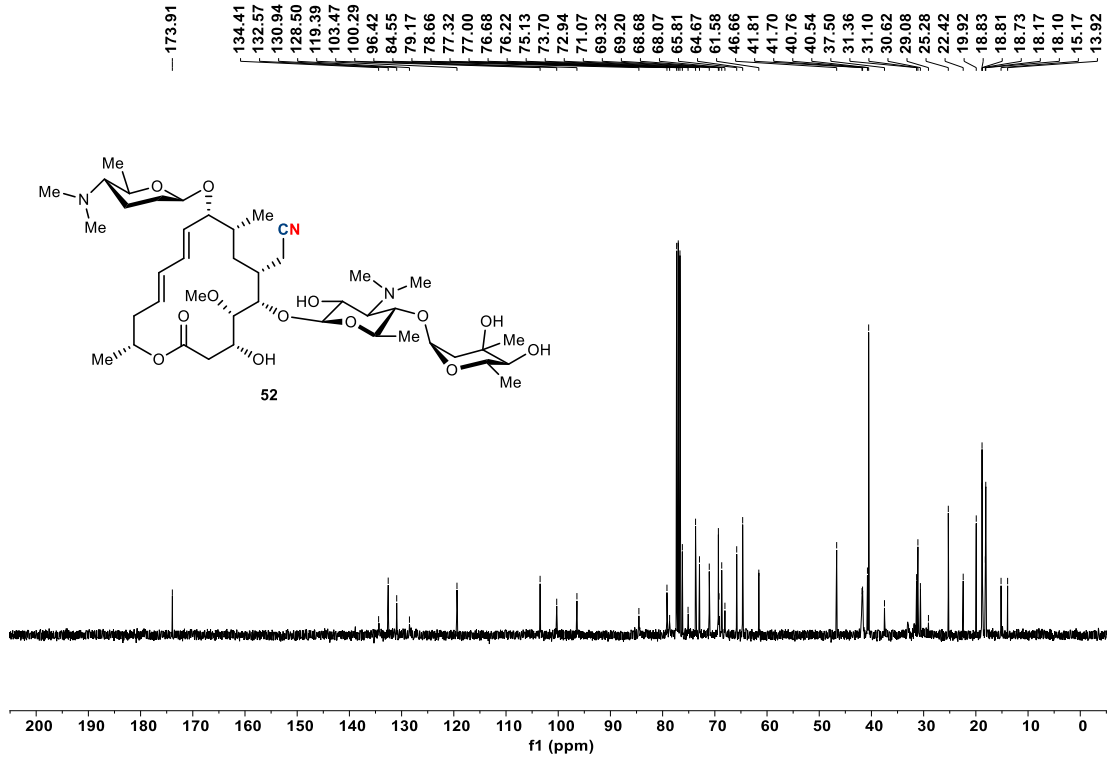

7.291
3.689
3.680
3.671
3.662
3.654
3.645
3.636
3.627
3.367
3.358
3.347
3.338
3.332
3.323
3.313
3.304
2.837
2.827
2.817
2.807
2.797
2.788
2.777
1.919
1.909
1.900
1.891
1.884
1.875
1.866
1.857
1.847
1.829
1.819
1.809
1.799
1.789
1.780
1.775
1.766
1.756
1.746
1.460
0.000
CN
Boc
N
50
1.90
1.88
0.94
1.91
1.96
9.00
f1 (ppm)

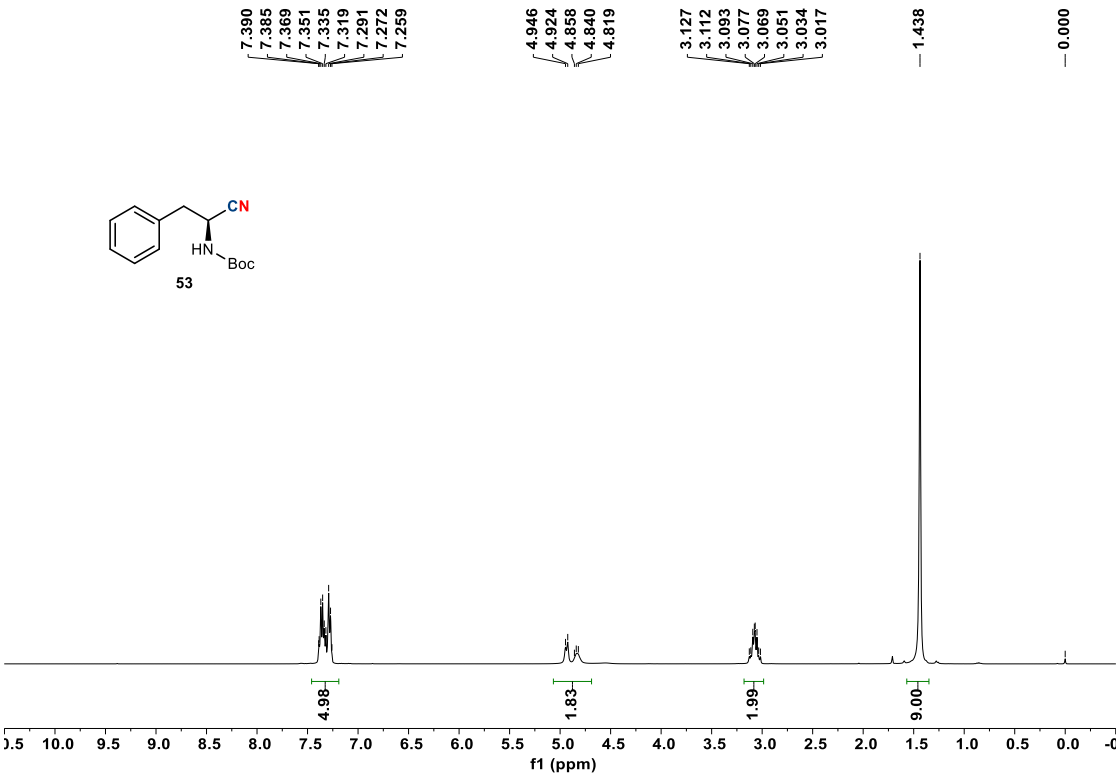

154.32
120.97
80.00
77.32
77.00
76.68
41.61
28.33
28.27
26.20
CN
Boc
N
50
f1 (ppm)

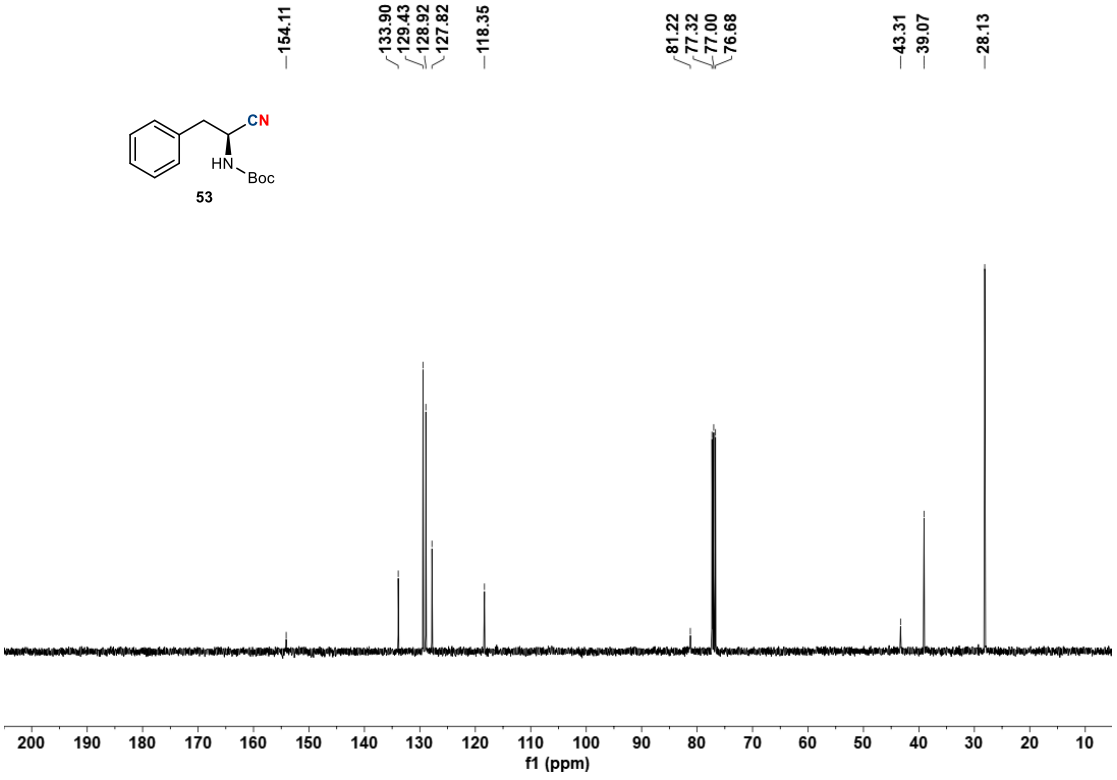

7.273
2.045
2.040
2.028
2.020
1.769
1.739
1.733
1.728
1.723
1.705
1.699
0.000
CN
51
8.76
6.00
f1 (ppm)

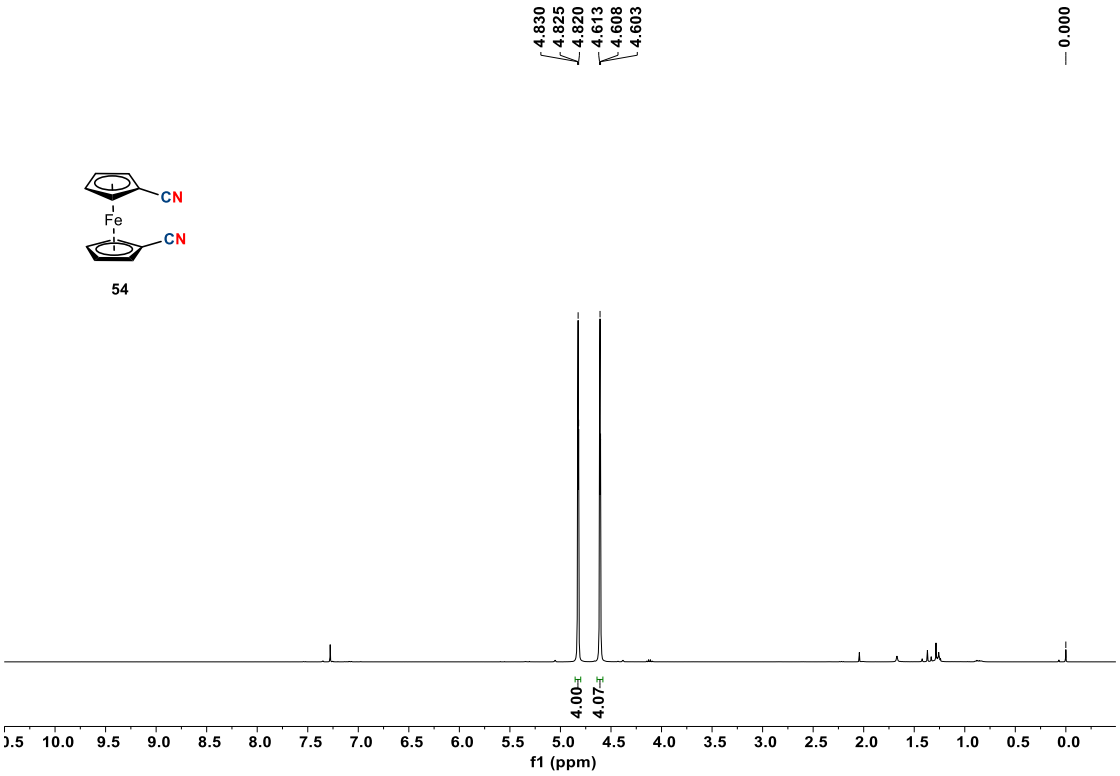

125.19
77.32
77.00
76.68
39.82
35.66
30.09
27.00
CN
51
f1 (ppm)

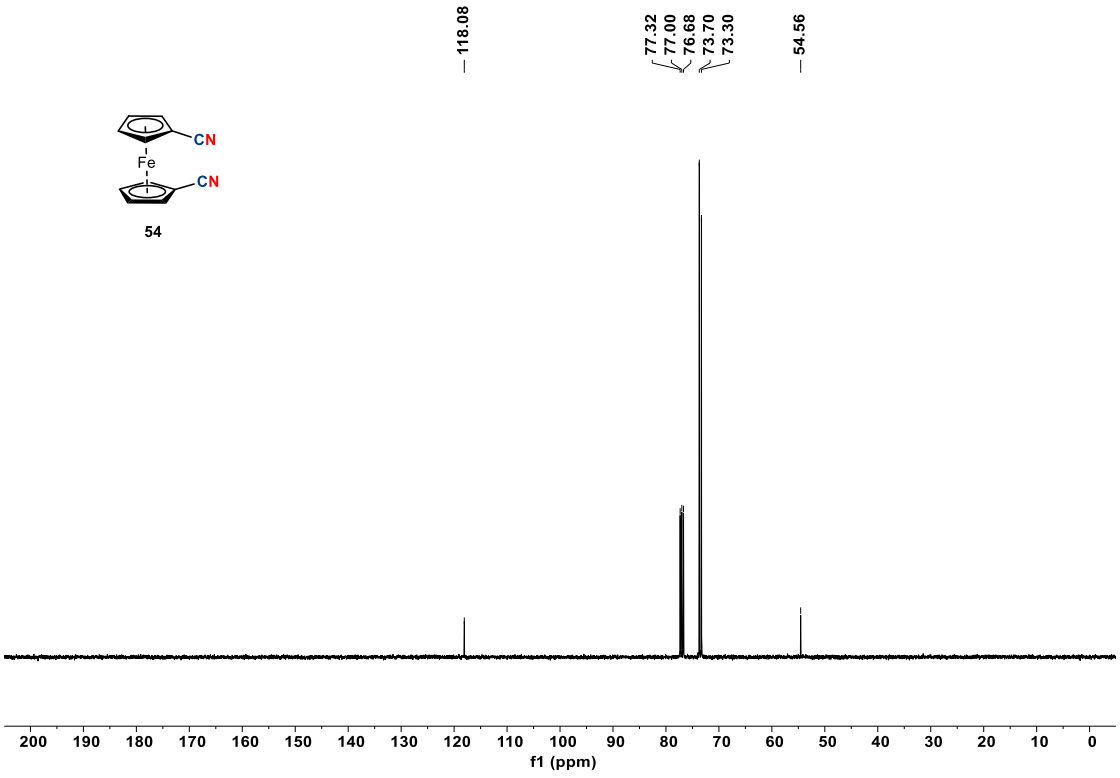

5.019 5.010 4.389 4.140 4.135 4.119 4.114 4.056 4.045 4.033 4.028 4.023 4.019 3.453 3.254 3.230 3.006 3.003 2.986 2.982 2.893 2.869 2.776 2.595 2.571 2.437 2.219 2.154 2.026 1.991 1.988 1.953 1.800 1.793 1.784 1.709 1.419 1.413 1.410 1.392 1.362 1.267 1.253 1.240 1.234 1.224 1.218 1.203 1.197 1.190 1.174 1.167 0.952 0.935 0.831 0.815 0.798
52
1.00 1.11 0.98 1.04 0.98 1.08 0.99 1.04 1.11 2.11 1.00 1.13 3.04 1.03 1.05 1.26 1.11 1.30 2.01 2.46 8.98 8.21 4.11 2.24 1.05 3.46 16.28 3.95 1.22
f1 (ppm)

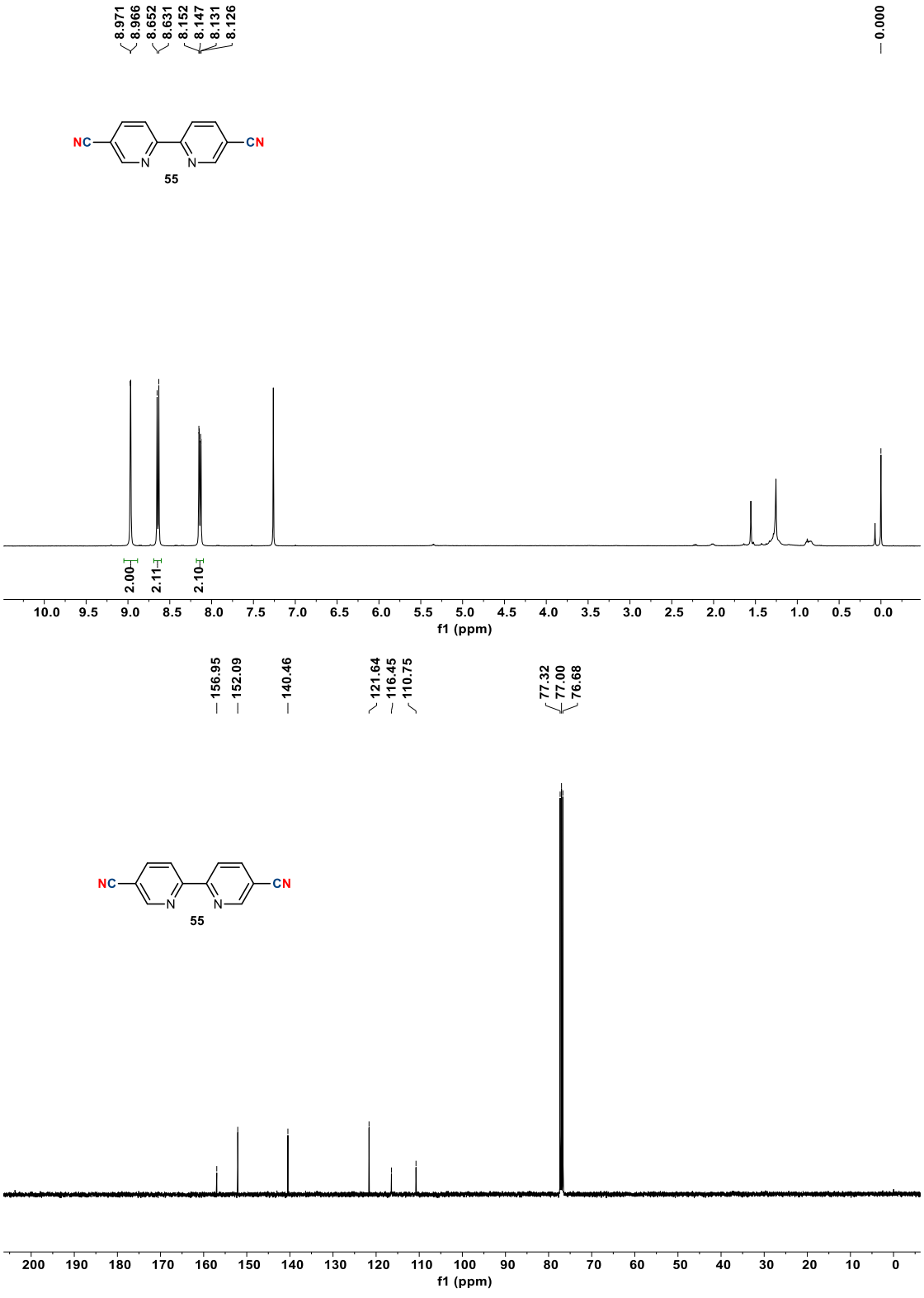

173.91
134.41 132.57 130.94 128.50 119.39 103.47 100.29 96.42 84.55 79.17 78.66 77.32 77.00 76.68 76.22 75.13 73.70 72.94 71.07 69.32 69.20 68.68 68.07 65.81 64.67 61.58 46.66 41.81 41.70 40.76 40.54 37.50 31.36 31.10 30.62 29.08 25.28 22.42 19.92 18.83 18.81 18.73 18.17 18.10 15.17 13.92
52
f1 (ppm)

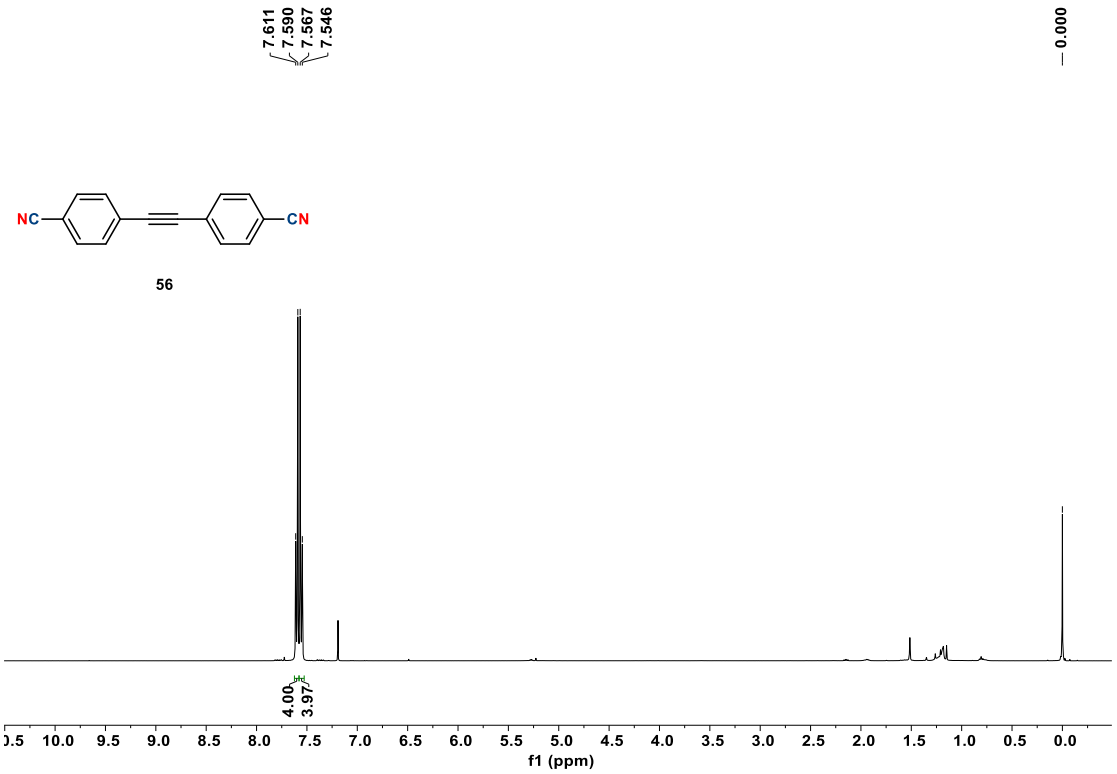

7.390
7.385
7.369
7.351
7.335
7.319
7.291
7.272
7.259
4.946
4.924
4.858
4.840
4.819
3.127
3.112
3.093
3.077
3.069
3.051
3.034
3.017
1.438
0.000
CN
HN
Boc
53
4.98
1.83
1.99
9.00
f1 (ppm)

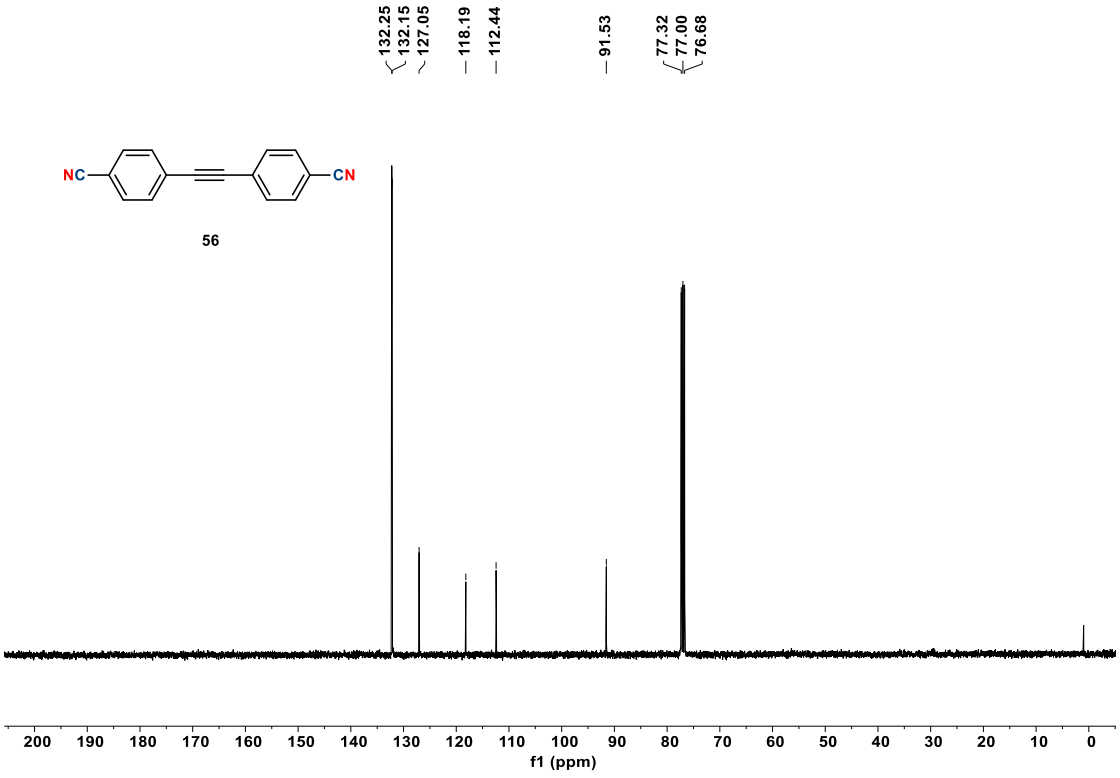

154.11
133.90
129.43
128.92
127.82
118.35
81.22
77.32
77.00
76.68
43.31
39.07
28.13
CN
HN
Boc
53
f1 (ppm)

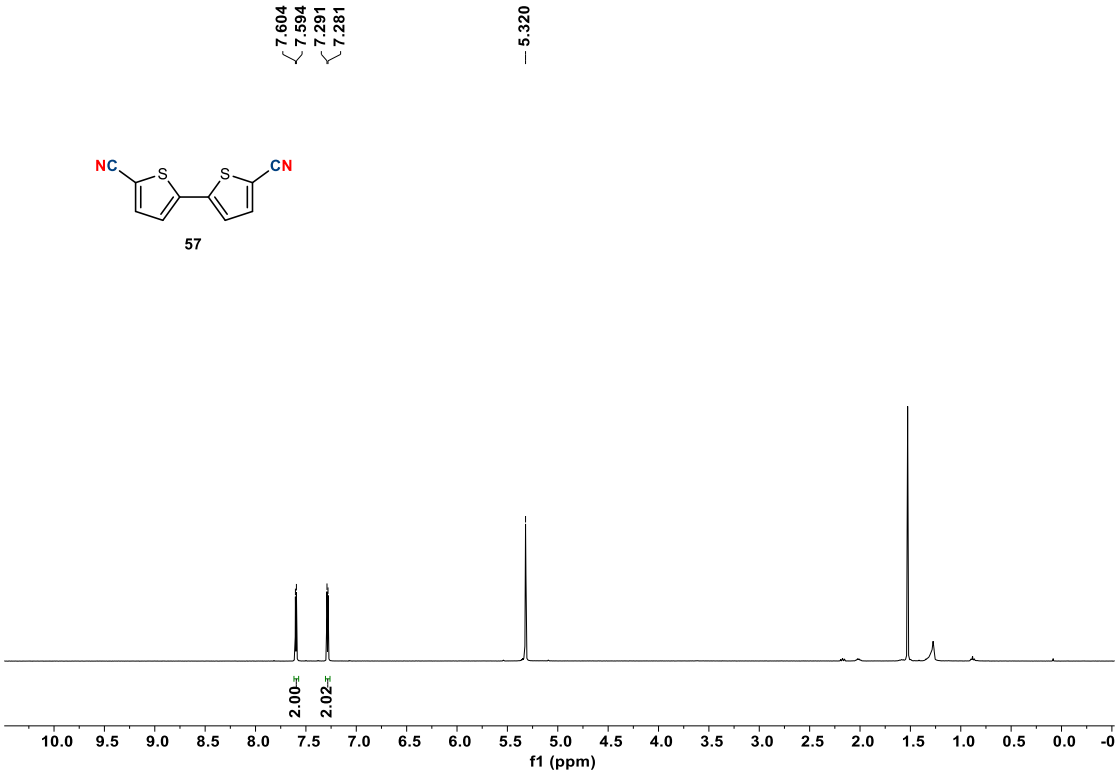

4.830
4.825
4.820
4.613
4.608
4.603
0.000
CN
Fe
CN
54
4.00
4.07
f1 (ppm)

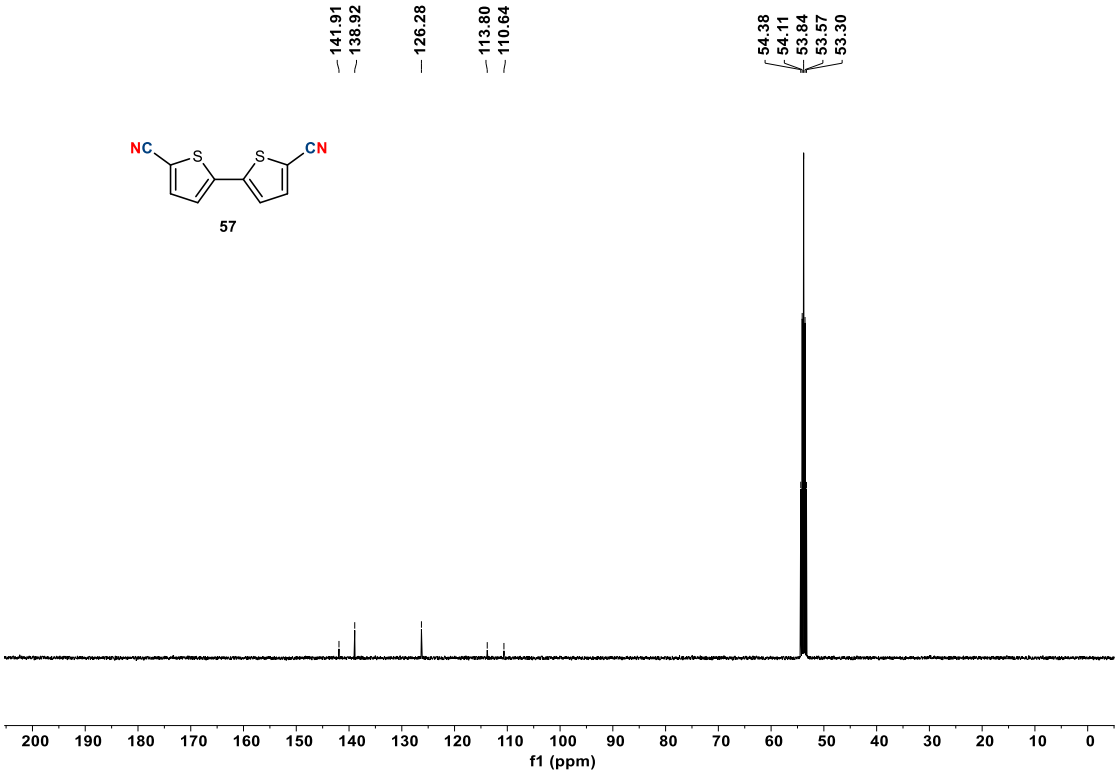

118.08
77.32
77.00
76.68
73.70
73.30
54.56
CN
Fe
CN
54
f1 (ppm)

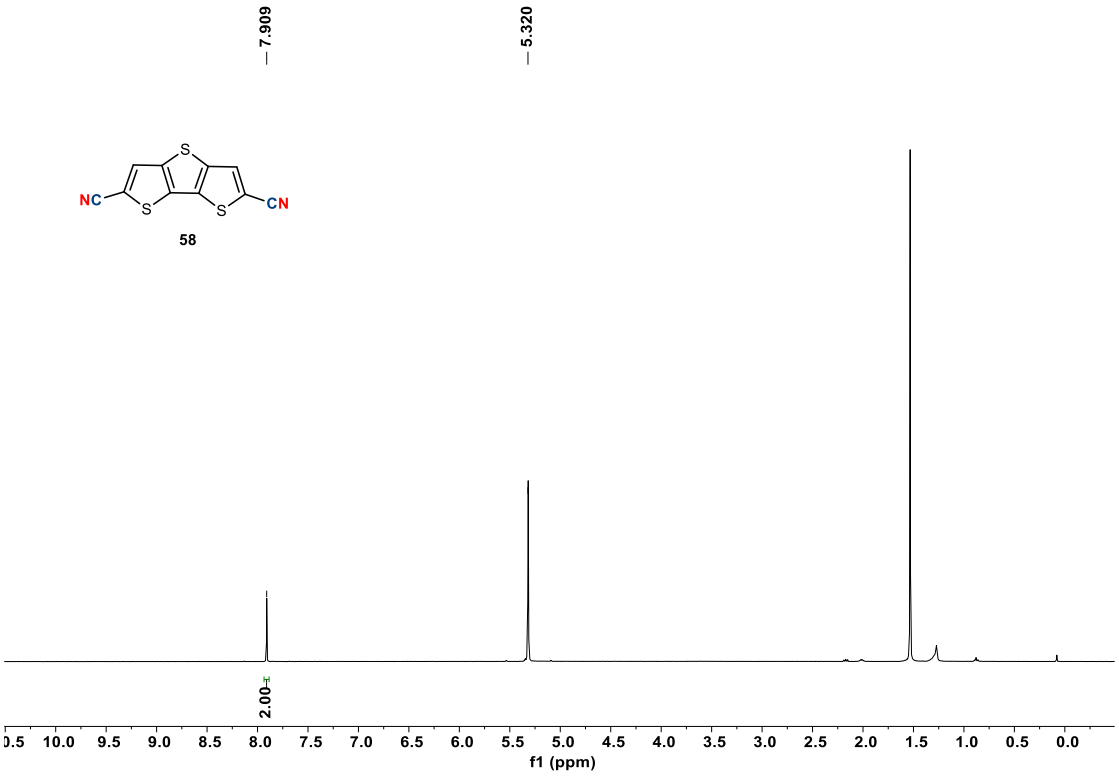

8.971
8.966
8.652
8.631
8.152
8.147
8.131
8.126
0.000
NC
CN
N
N
55
2.00
2.11
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
156.95
152.09
140.46
121.64
116.45
110.75
77.32
77.00
76.68
NC
CN
N
N
55
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

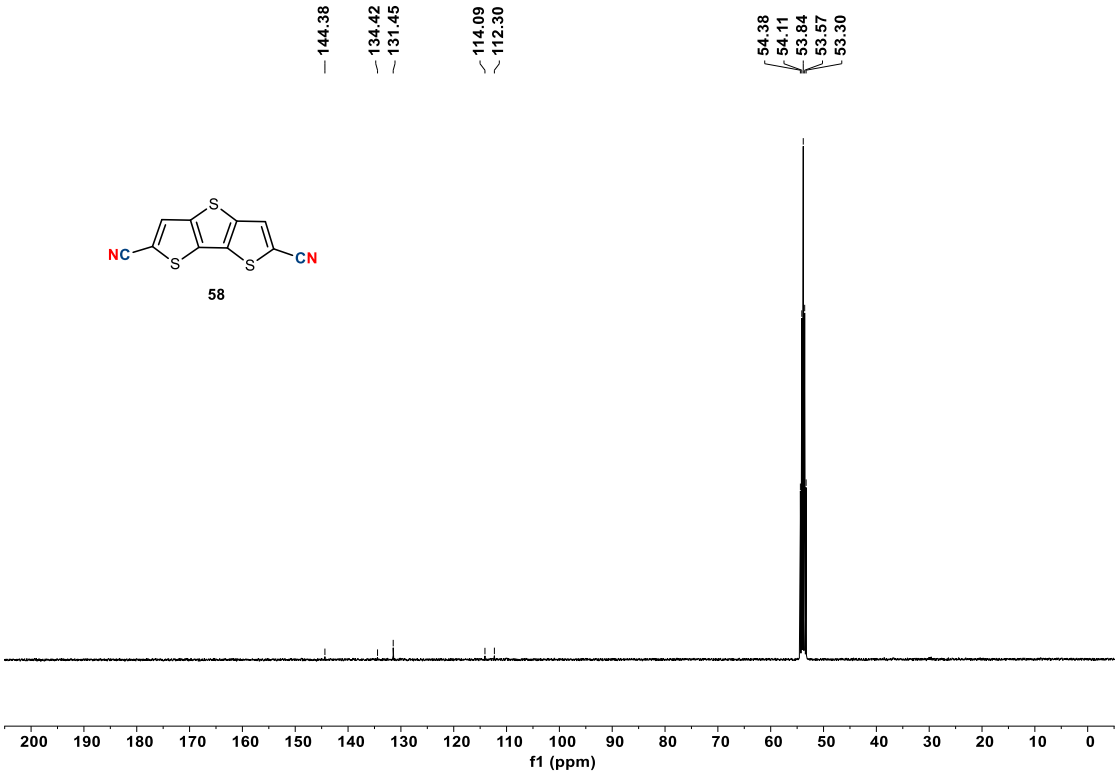

7.611
7.590
7.567
7.546
0.000
NC
CN
56
4.00
3.97
f1 (ppm)

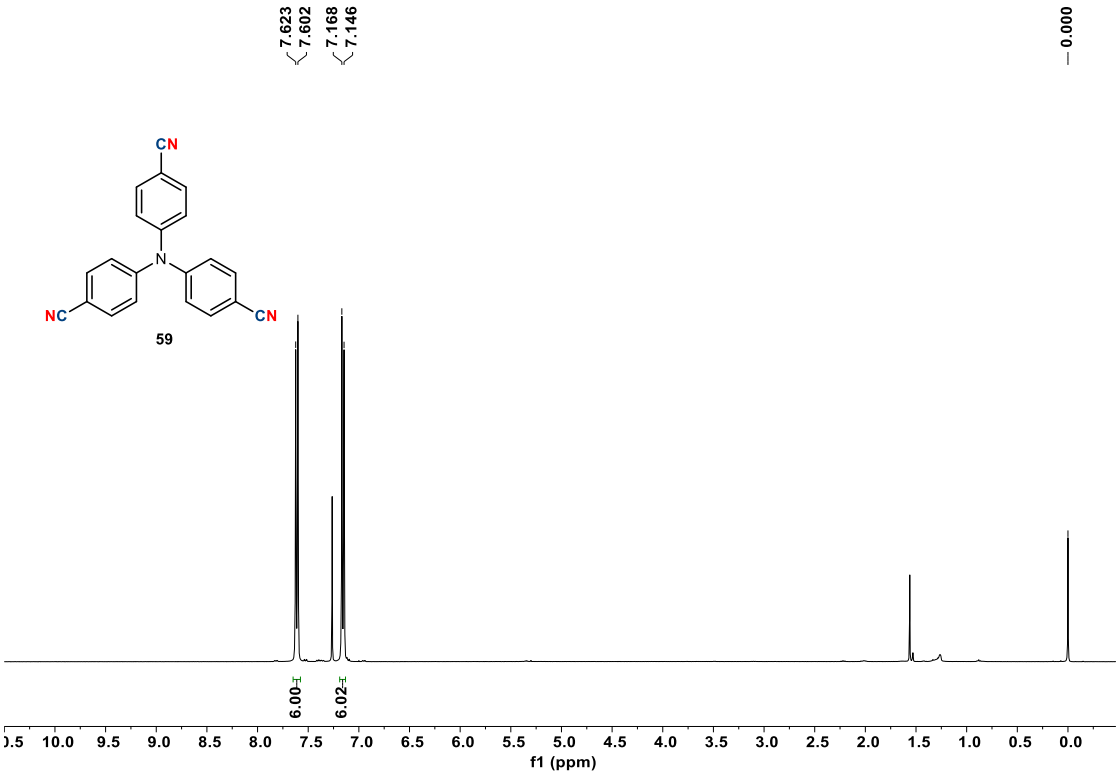

132.25
132.15
127.05
118.19
112.44
91.53
77.32
77.00
76.68
NC
CN
56
f1 (ppm)

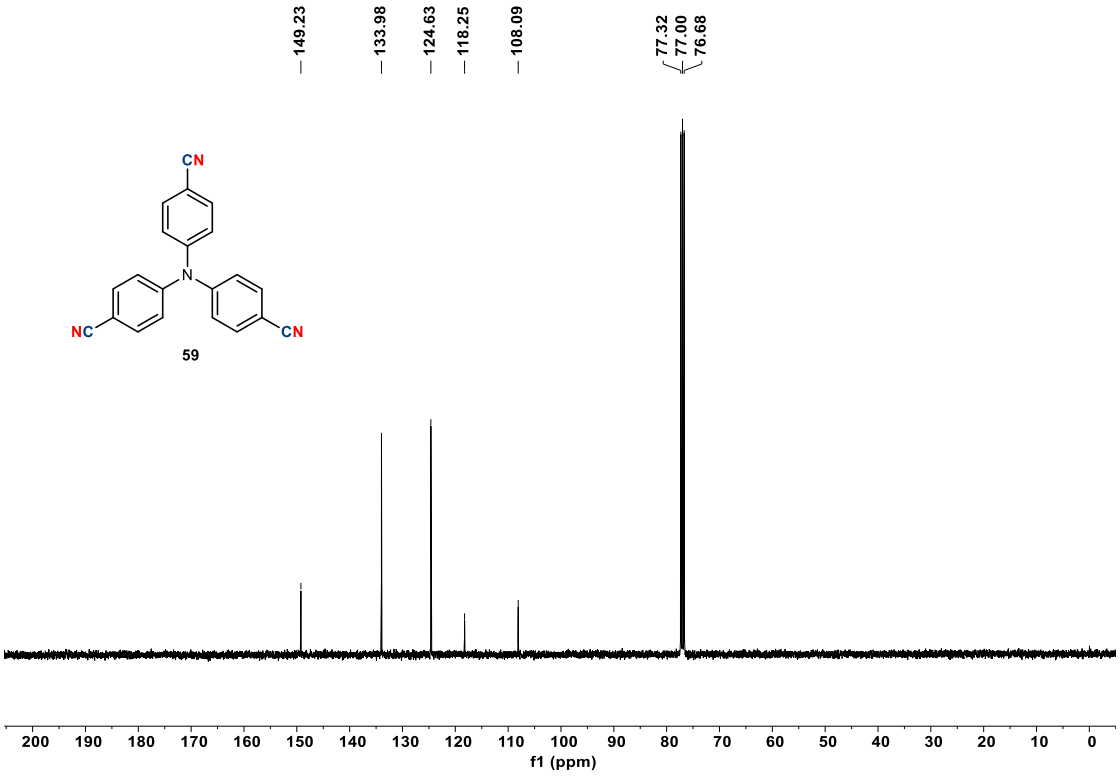

7.604
7.594
7.291
7.281
5.320
NC
S
S
CN
57
2.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

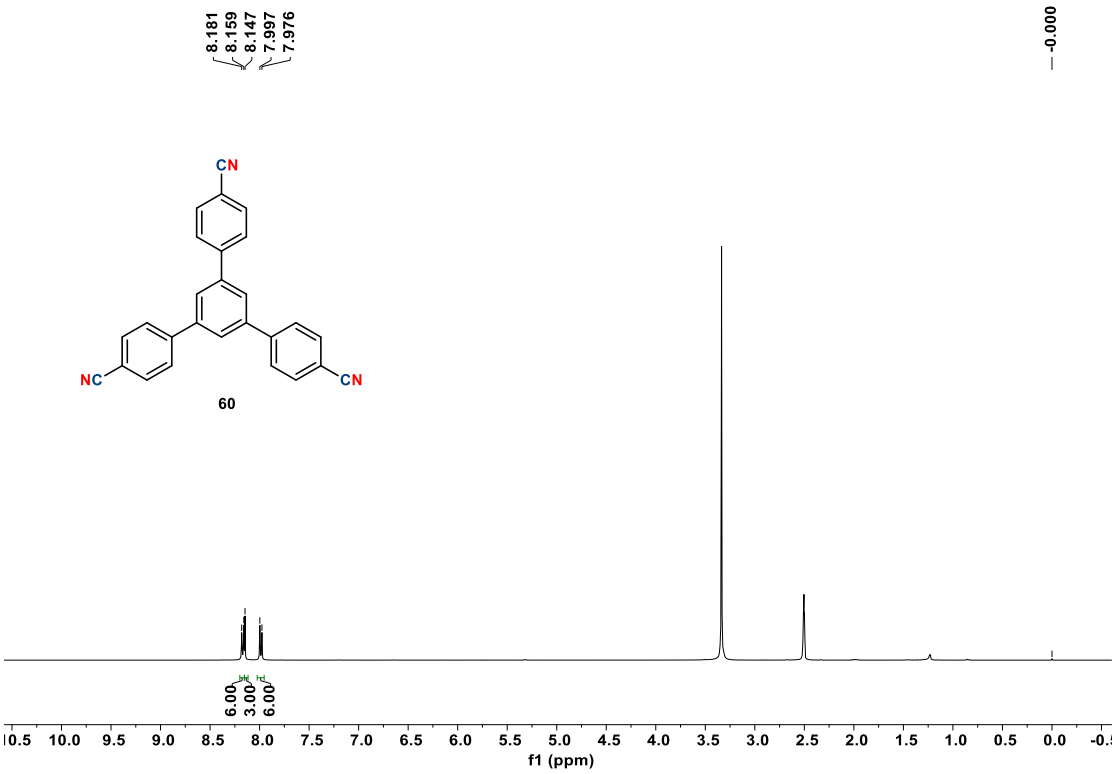

141.91
138.92
126.28
113.80
110.64
54.38
54.11
53.84
53.57
53.30
NC
S
S
CN
57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

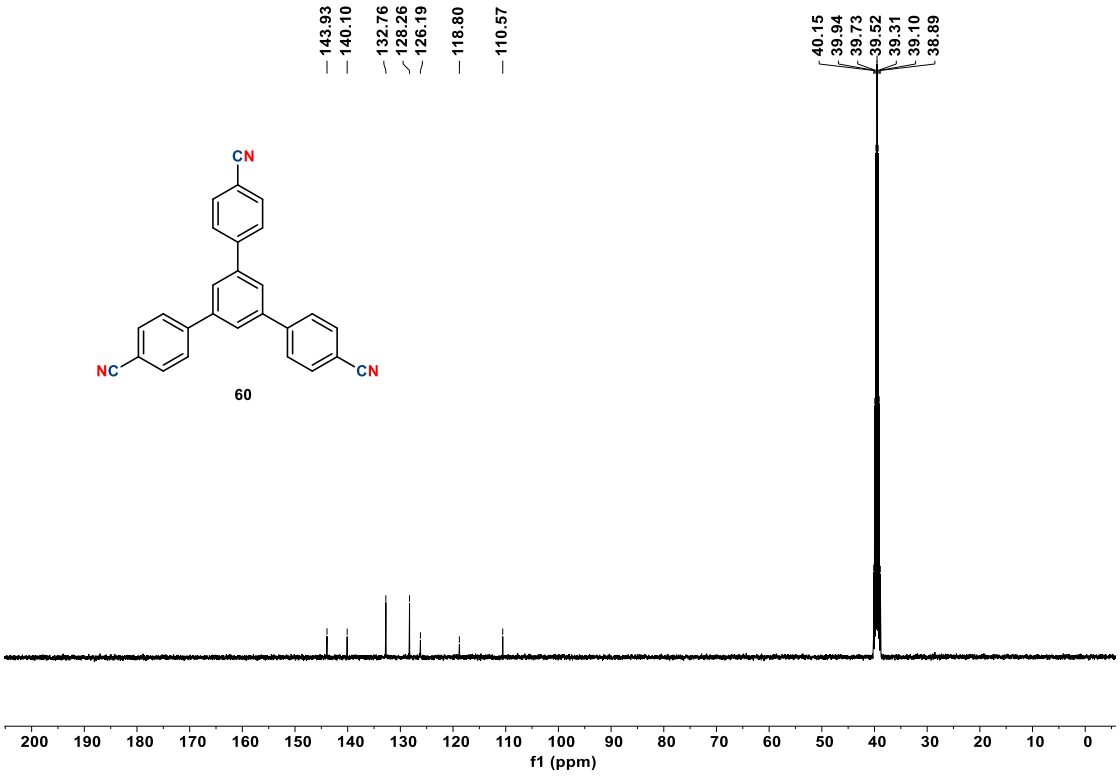

7.909
5.320
NC
CN
S
S
S
58
2.00
f1 (ppm)

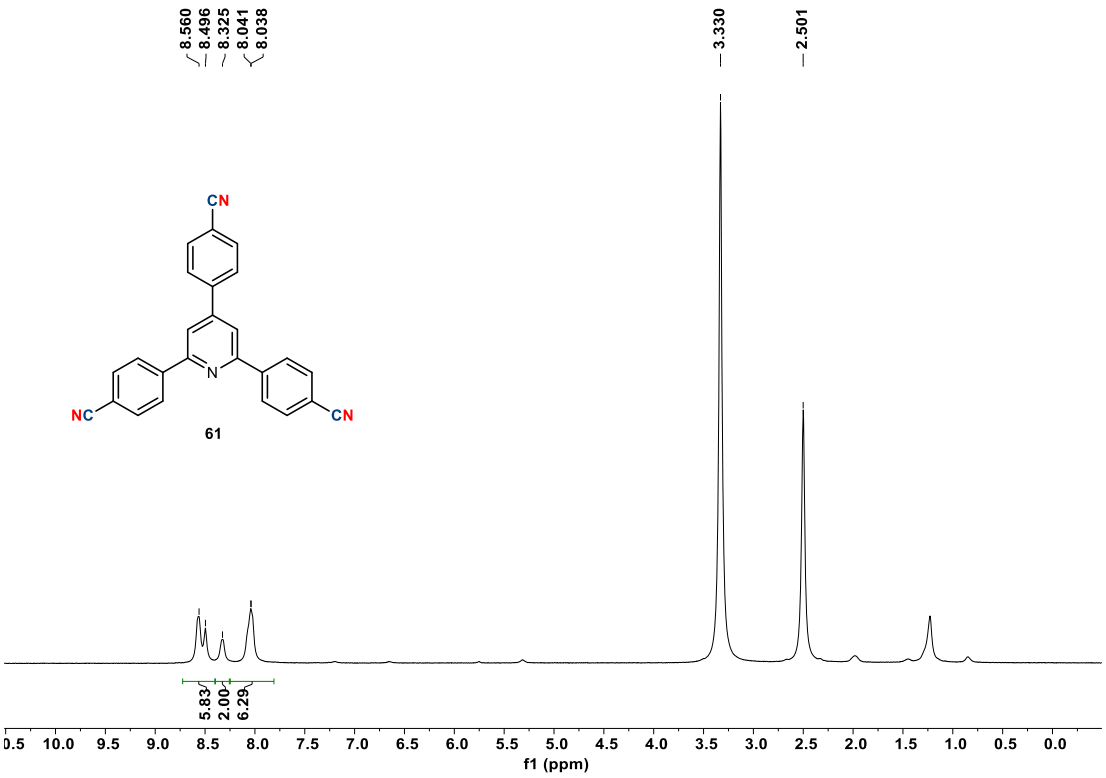

144.38
134.42
131.45
114.09
112.30
54.38
54.11
53.84
53.57
53.30
NC
CN
S
S
S
58
f1 (ppm)

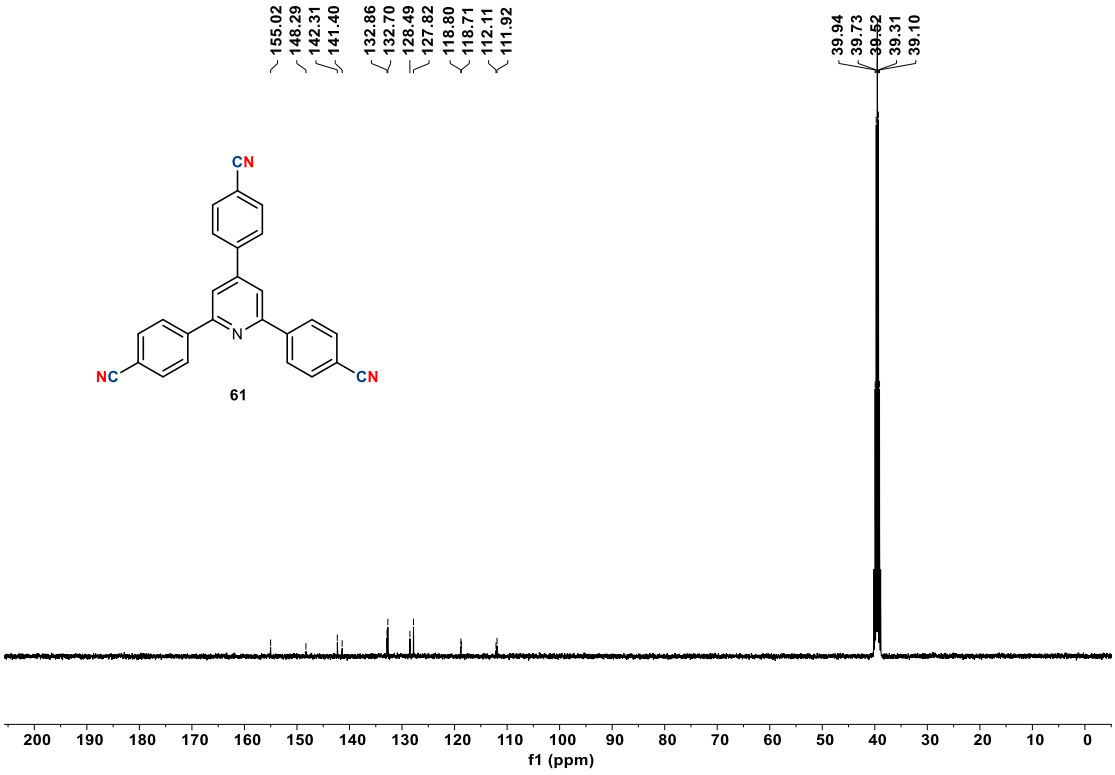

7.623
7.602
7.168
7.146
0.000
CN
N
NC
CN
59
6.00
6.02
f1 (ppm)

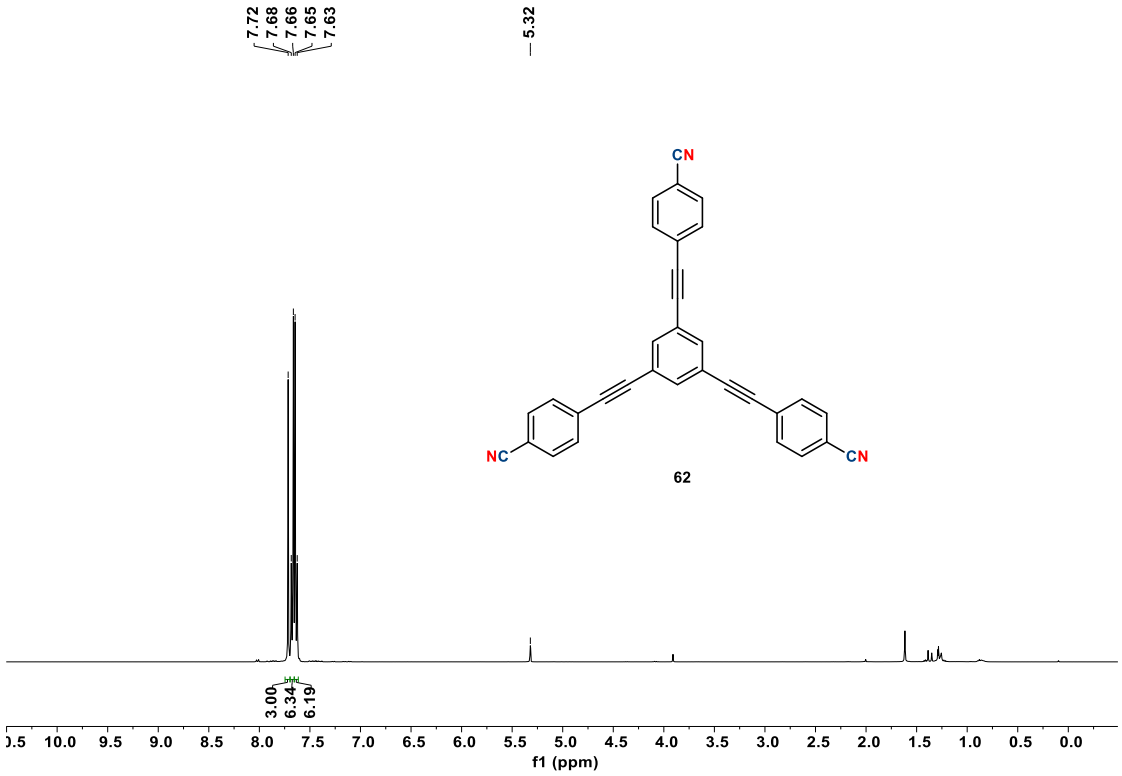

149.23
133.98
124.63
118.25
108.09
77.32
77.00
76.68
CN
N
NC
CN
59
f1 (ppm)

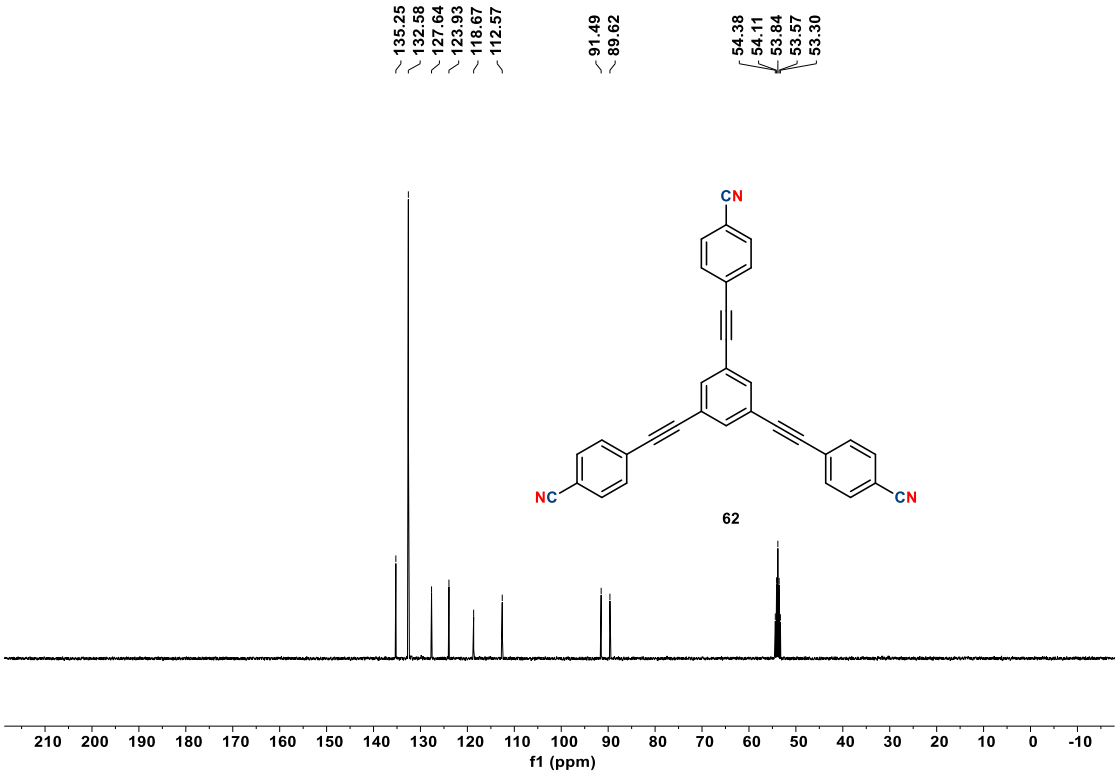

8.181
8.159
8.147
7.997
7.976
-0.000
CN
NC
CN
60
6.00
3.00
6.00
f1 (ppm)

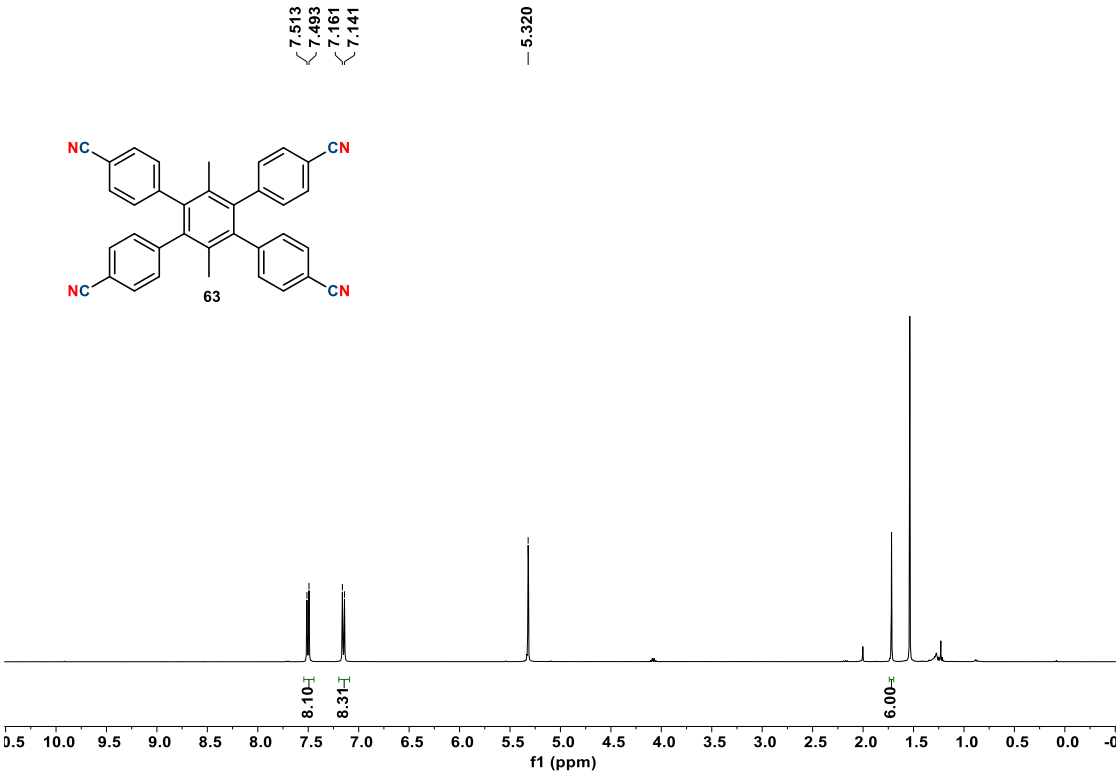

143.93
140.10
132.76
128.26
126.19
118.80
110.57
40.15
39.94
39.73
39.52
39.31
39.10
38.89
CN
NC
CN
60
f1 (ppm)

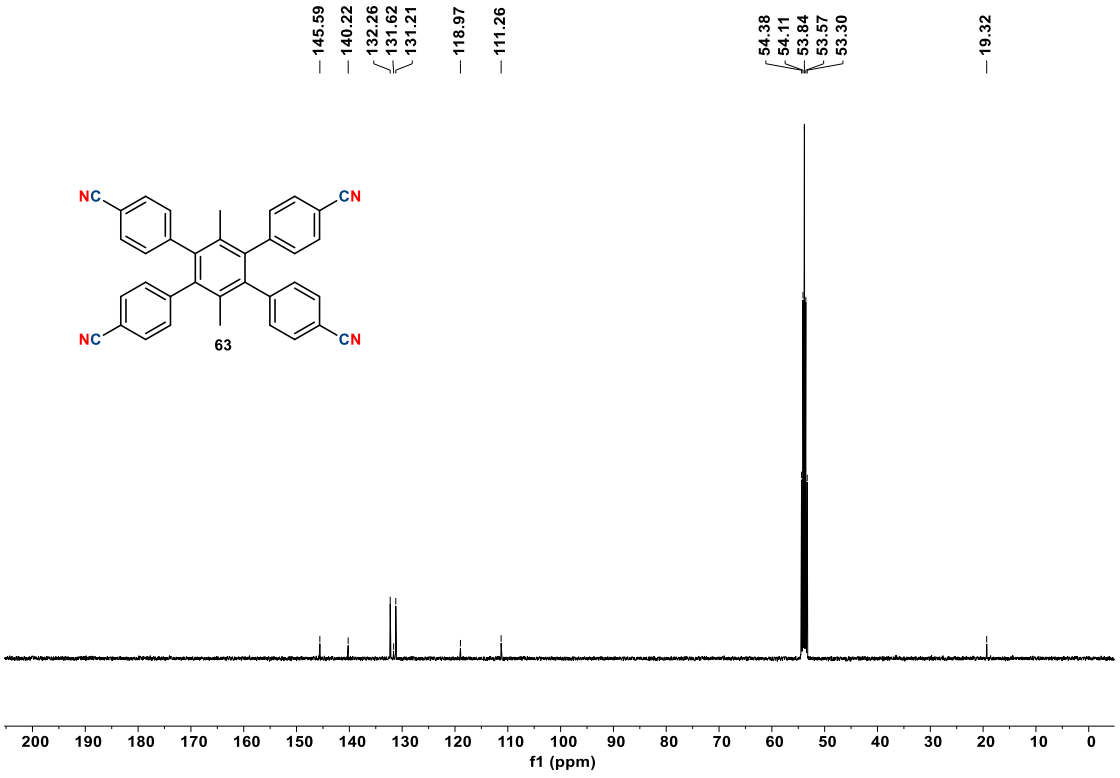

8.560
8.496
8.325
8.041
8.038
3.330
2.501
CN
NC
CN
N
61
5.83
2.00
6.29
f1 (ppm)

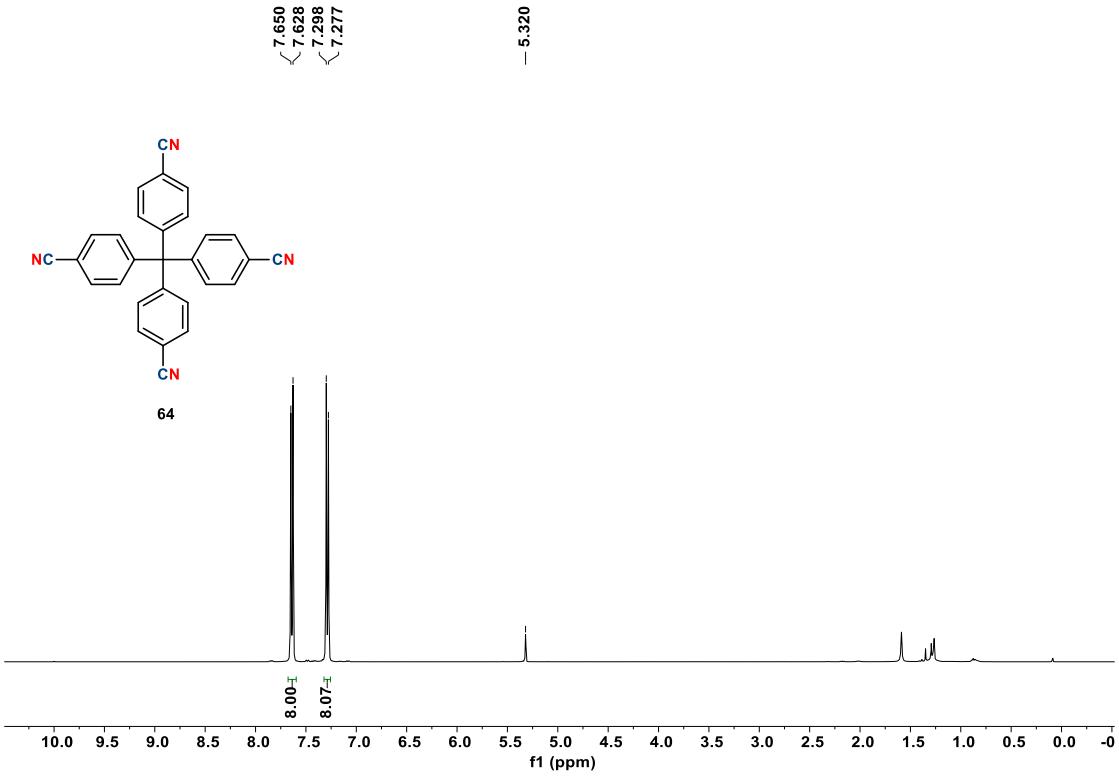

155.02
148.29
142.31
141.40
132.86
132.70
128.49
127.82
118.80
118.71
112.11
111.92
39.94
39.73
39.52
39.31
39.10
CN
NC
CN
N
61
f1 (ppm)

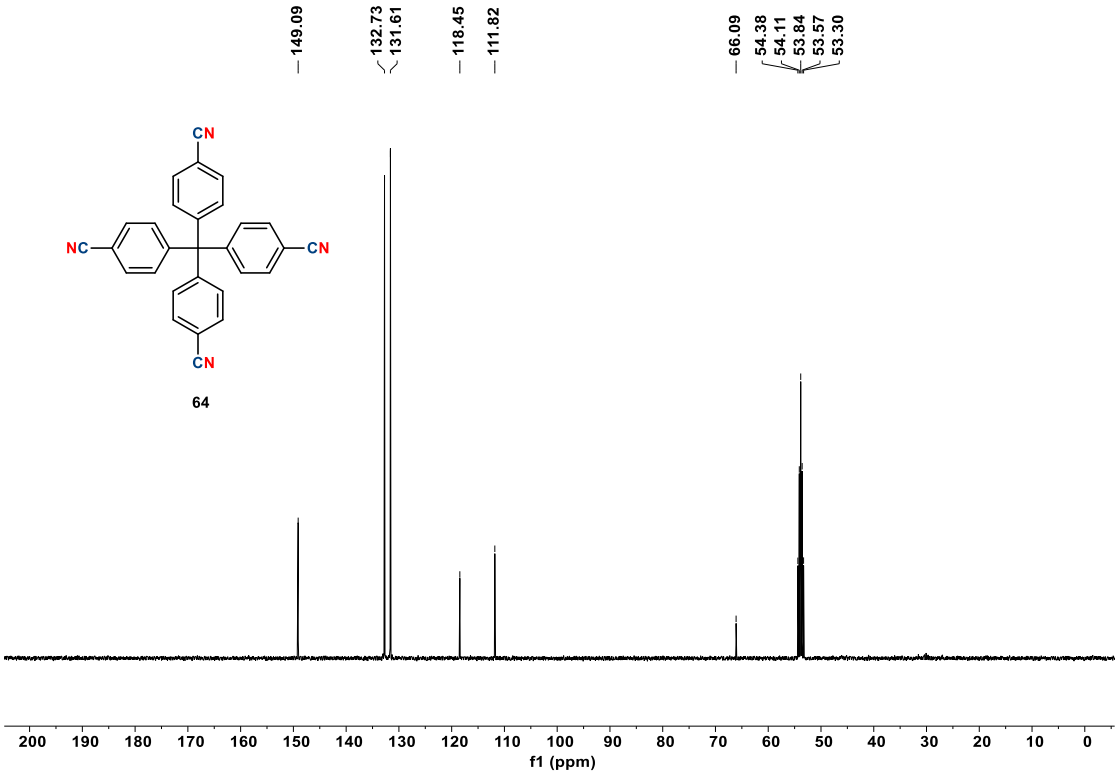

7.72
7.68
7.66
7.65
7.63
5.32
CN
NC
CN
62
3.00
6.34
6.19
f1 (ppm)

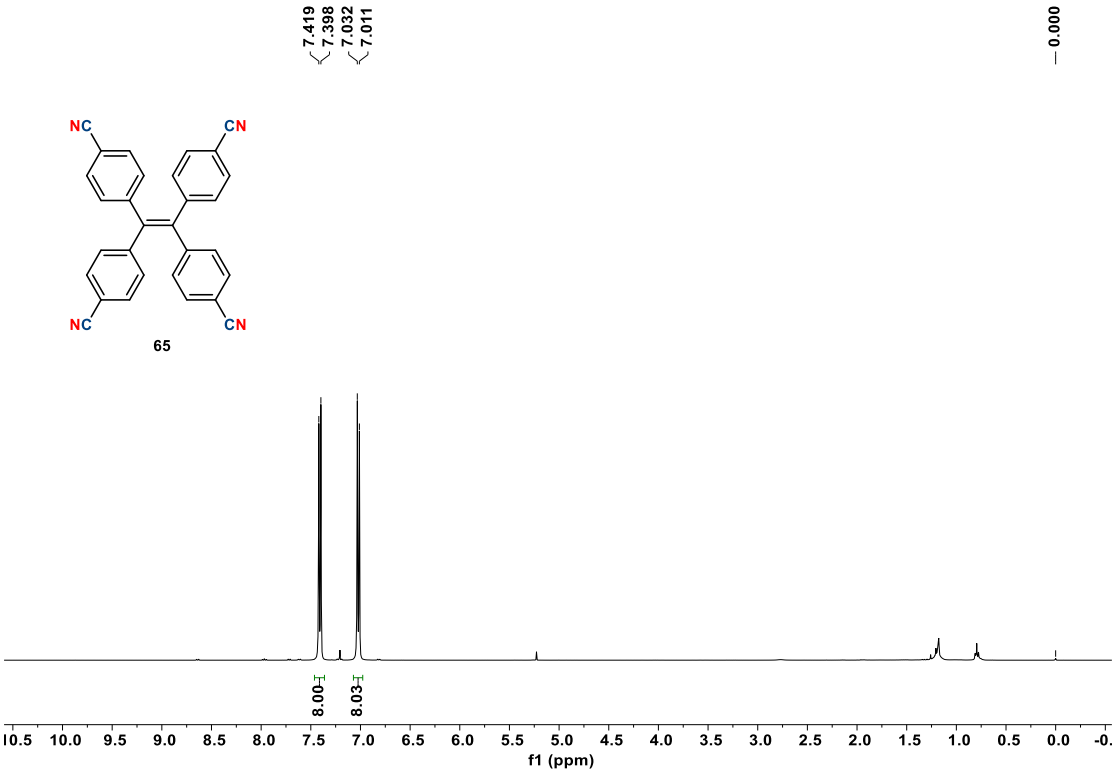

135.25
132.58
127.64
123.93
118.67
112.57
91.49
89.62
54.38
54.11
53.84
53.57
53.30
CN
NC
CN
62
f1 (ppm)

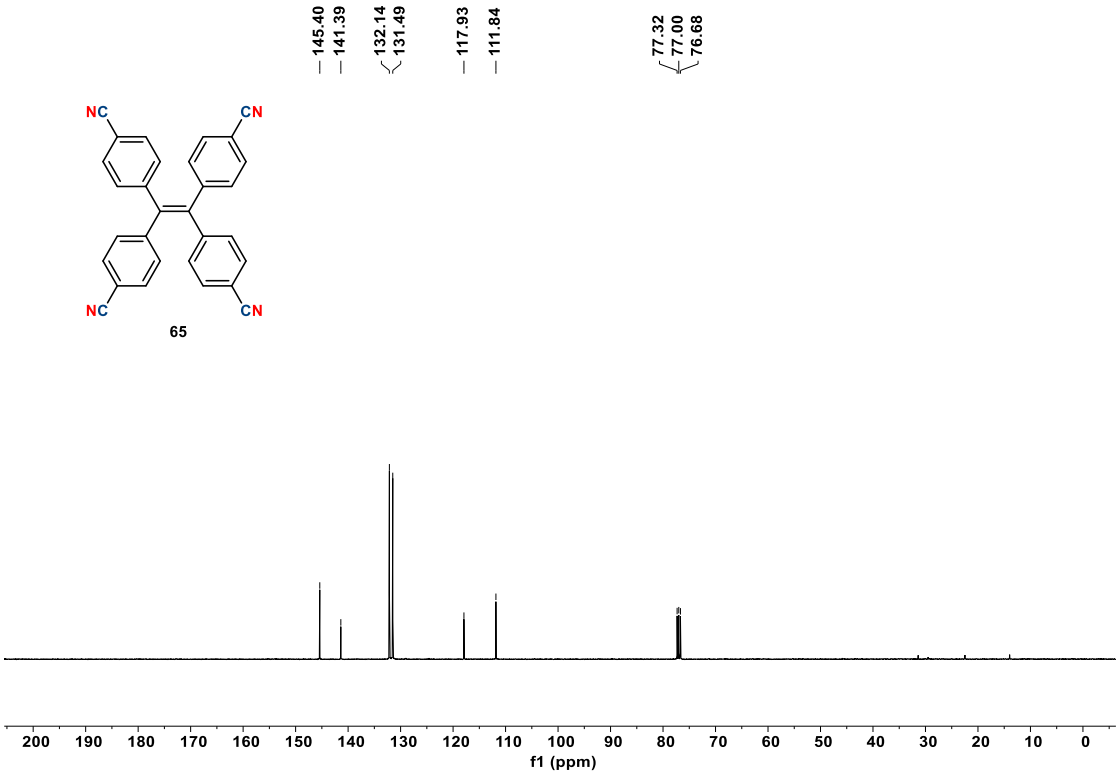

7.513
7.493
7.161
7.141
5.320
NC
CN
NC
CN
63
8.10
8.31
6.00
f1 (ppm)

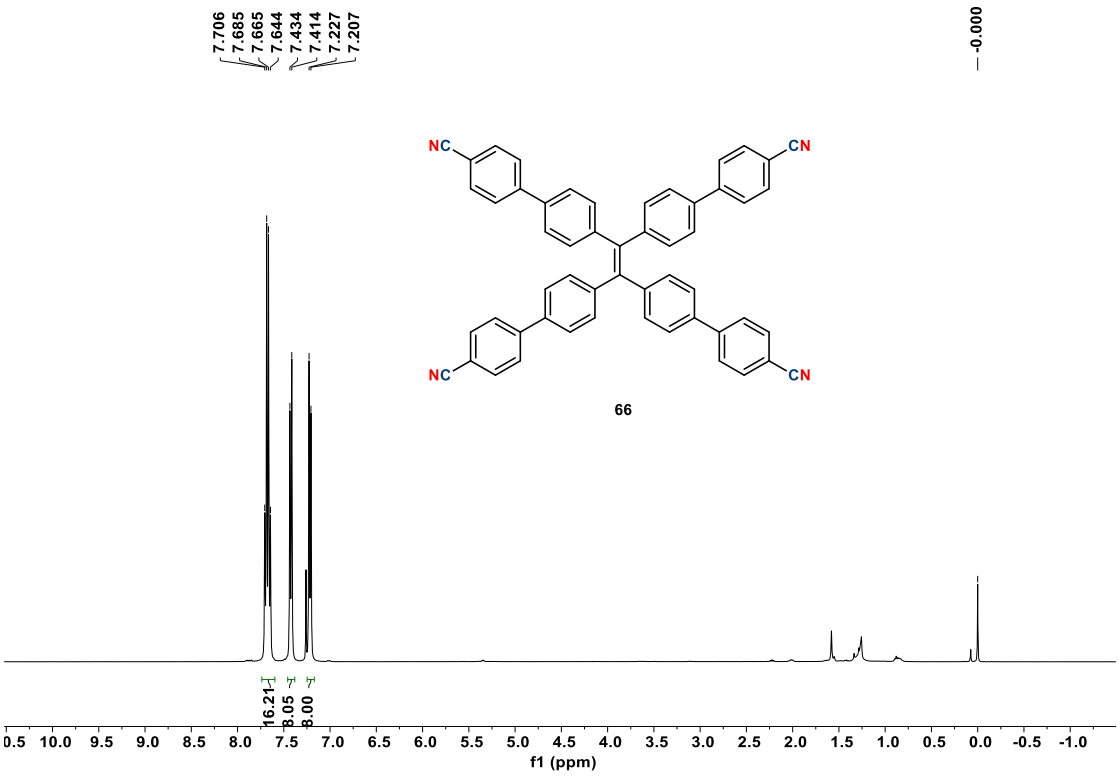

145.59
140.22
132.26
131.62
131.21
118.97
111.26
54.38
54.11
53.84
53.57
53.30
19.32
NC
CN
NC
CN
63
f1 (ppm)

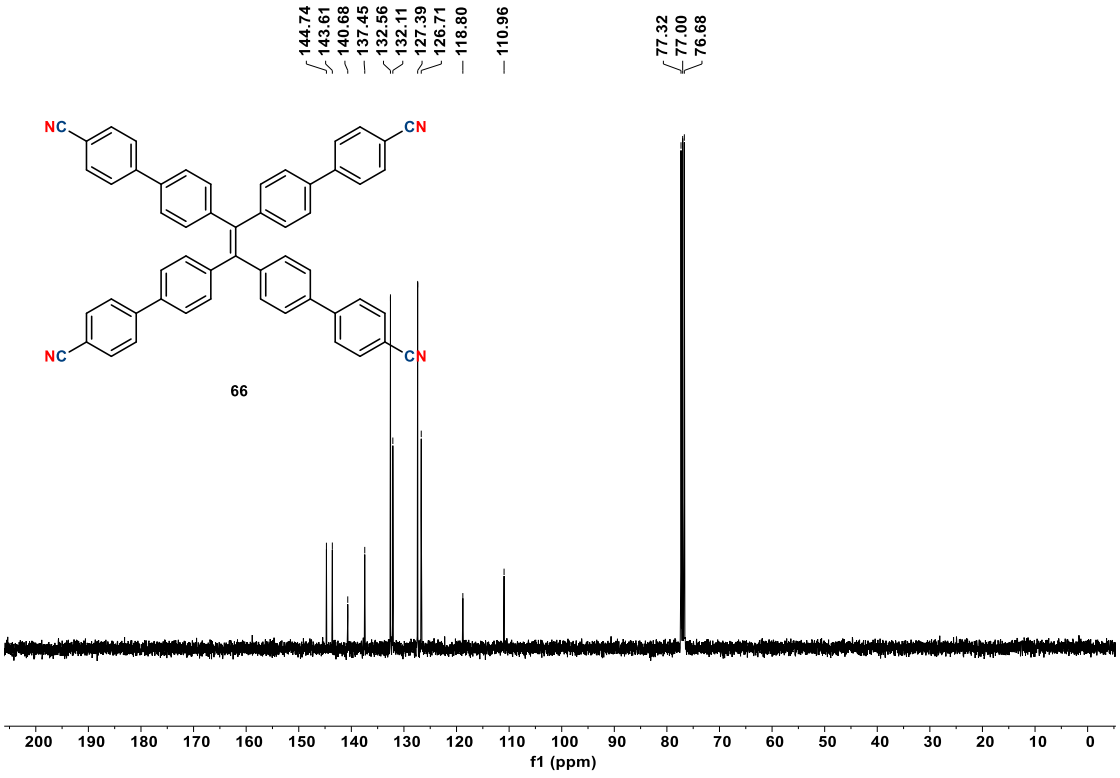

7.650
7.628
7.298
7.277
5.320
CN
NC
CN
CN
64
8.00
8.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

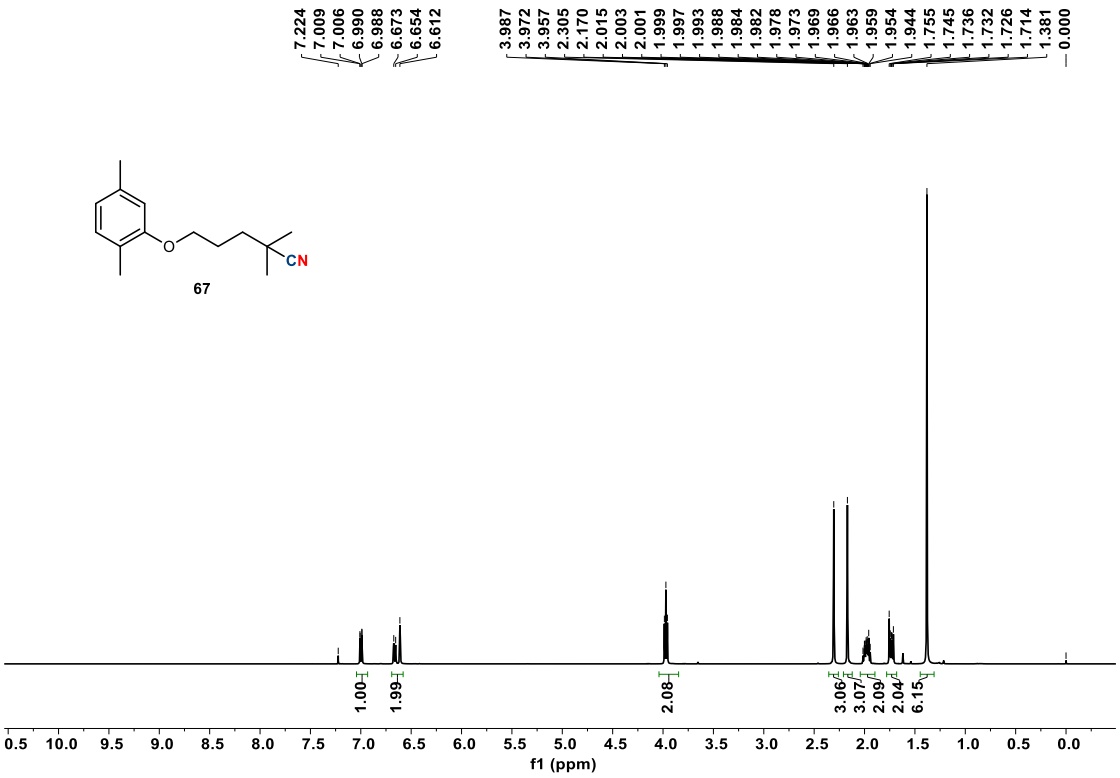

149.09
132.73
131.61
118.45
111.82
66.09
54.38
54.11
53.84
53.57
53.30
CN
NC
CN
CN
64
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

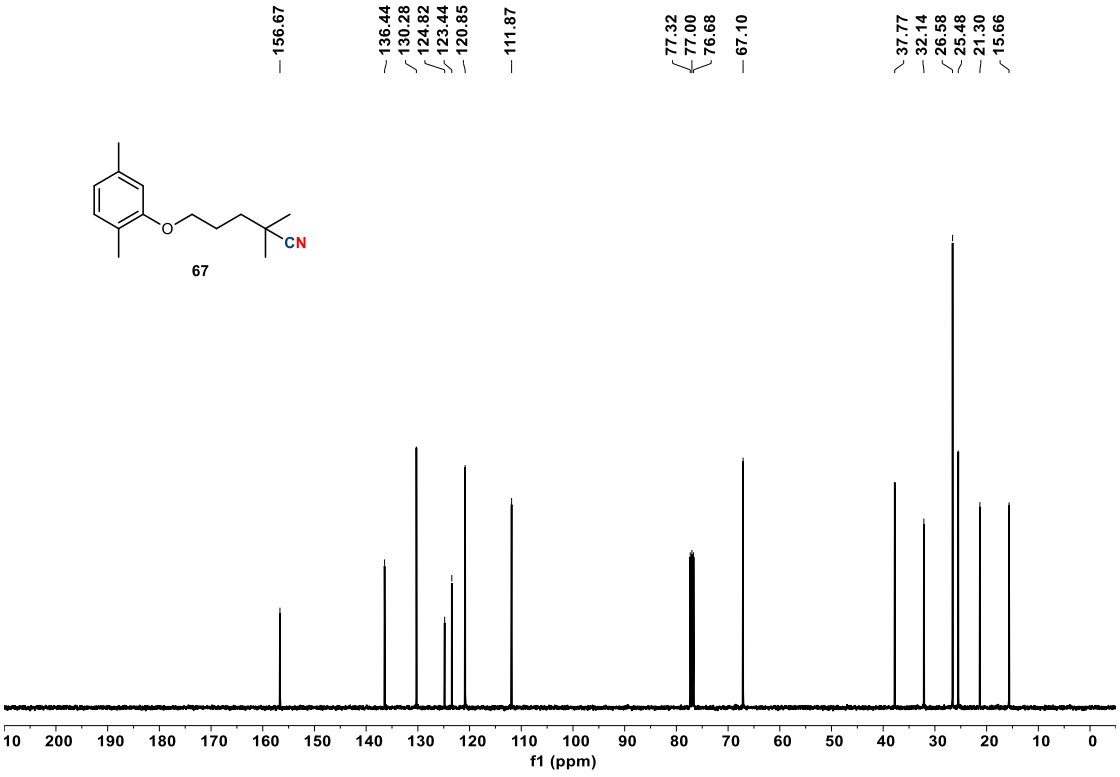

7.419
7.398
7.032
7.011
0.000
NC
CN
NC
CN
65
8.00
8.03
f1 (ppm)

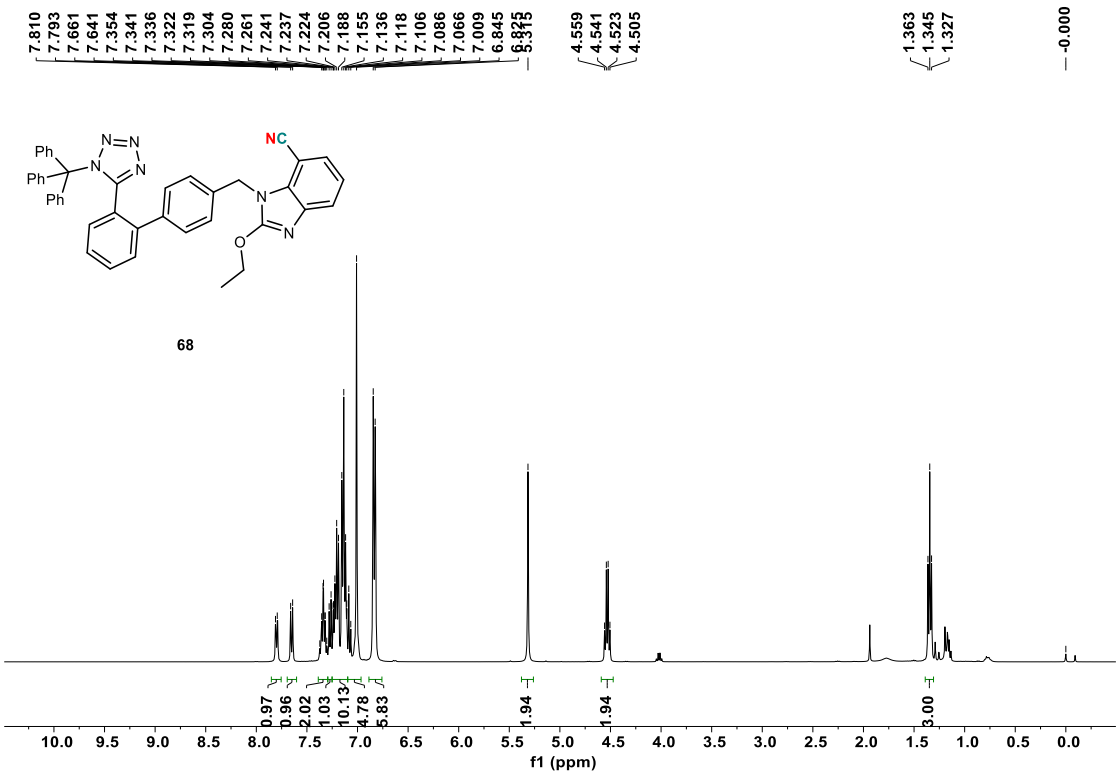

145.40
141.39
132.14
131.49
117.93
111.84
77.32
77.00
76.68
NC
CN
NC
CN
65
f1 (ppm)

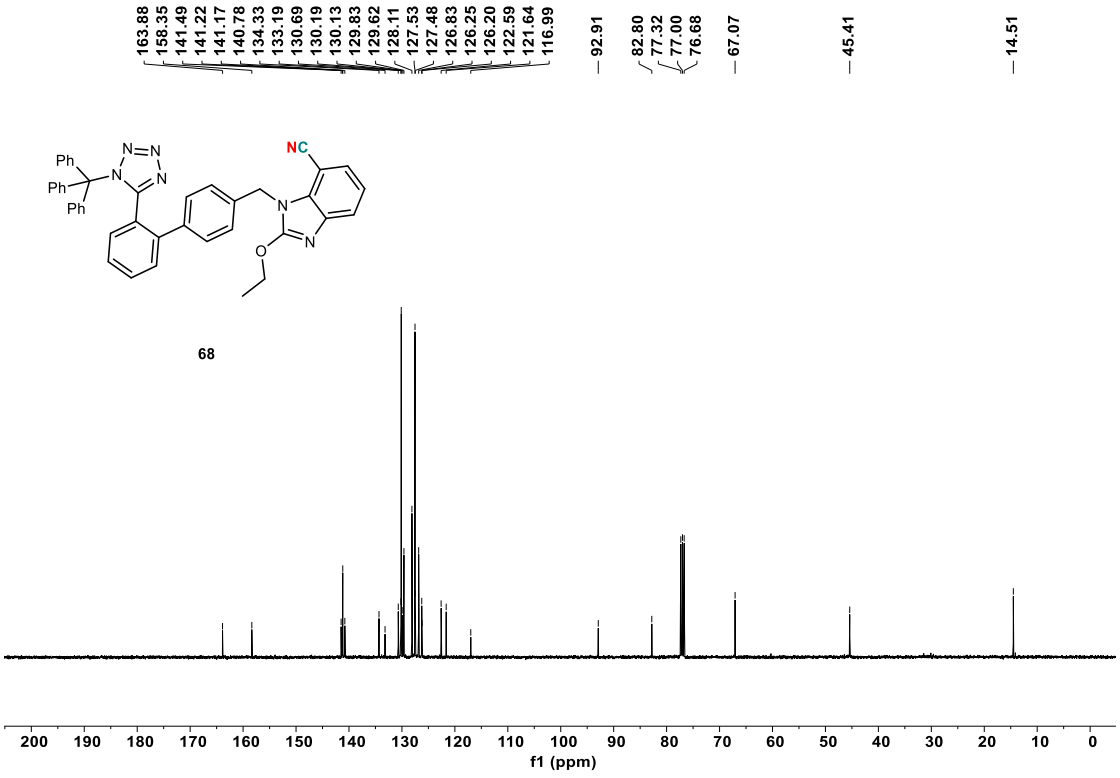

7.706
7.685
7.665
7.644
7.434
7.414
7.227
7.207
-0.000
NC
CN
NC
CN
66
16.21
8.05
8.00
f1 (ppm)

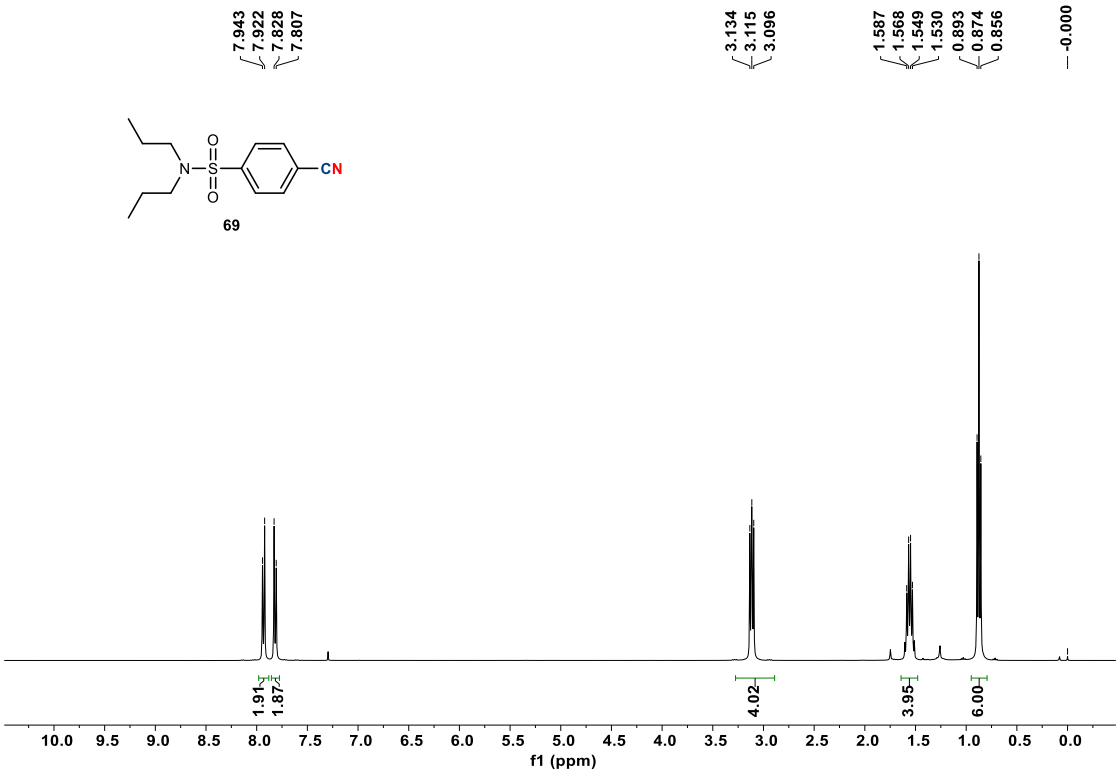

144.74
143.61
140.68
137.45
132.56
132.11
127.39
126.71
118.80
110.96
77.32
77.00
76.68
NC
CN
NC
CN
66
f1 (ppm)

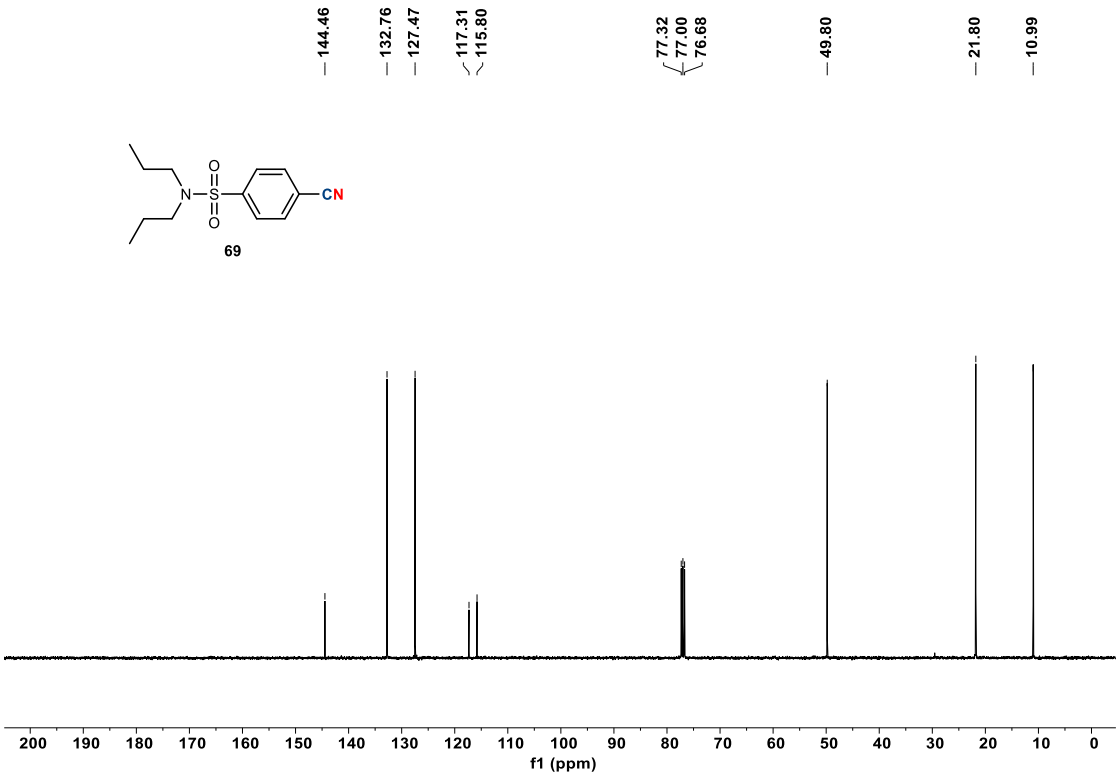

7.224
7.009
7.006
6.990
6.988
6.673
6.654
6.612
3.987
3.972
3.957
2.305
2.170
2.015
2.003
2.001
1.999
1.997
1.993
1.988
1.984
1.982
1.978
1.973
1.969
1.966
1.963
1.959
1.954
1.944
1.755
1.745
1.736
1.732
1.726
1.714
1.381
0.000
O
CN
67
1.00
1.99
2.08
3.06
3.07
2.09
2.04
6.15
f1 (ppm)

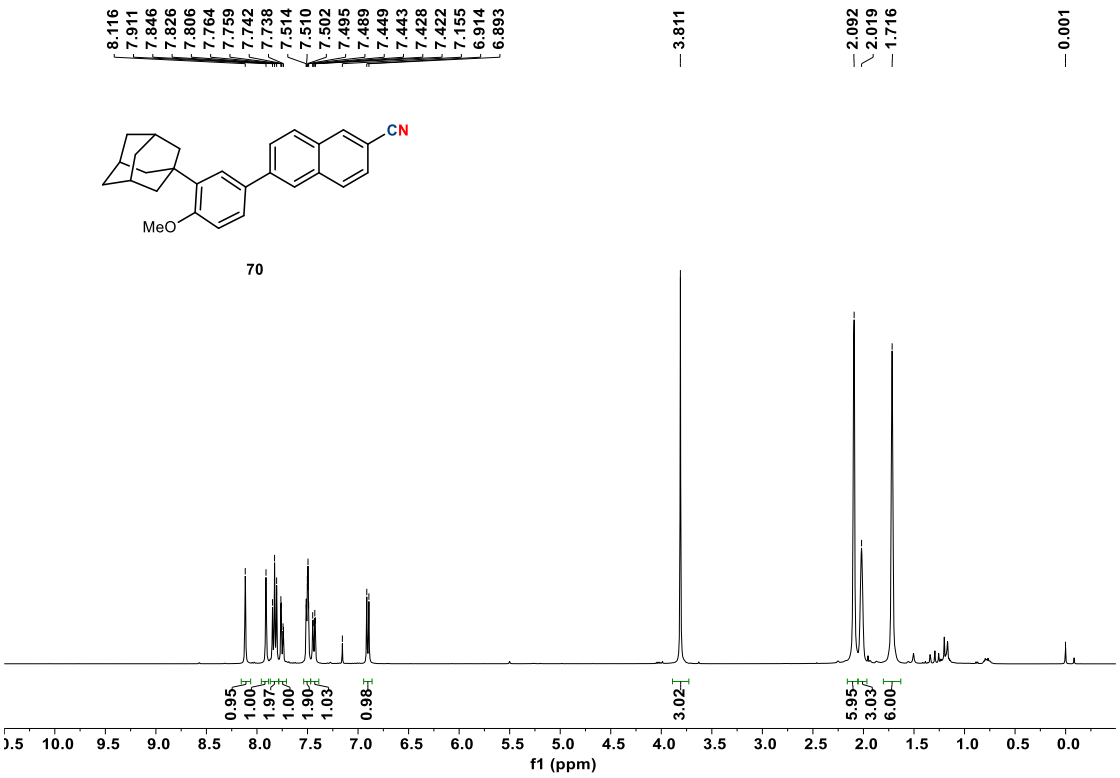

156.67
136.44
130.28
124.82
123.44
120.85
111.87
77.32
77.00
76.68
67.10
37.77
32.14
26.58
25.48
21.30
15.66
O
CN
67
f1 (ppm)

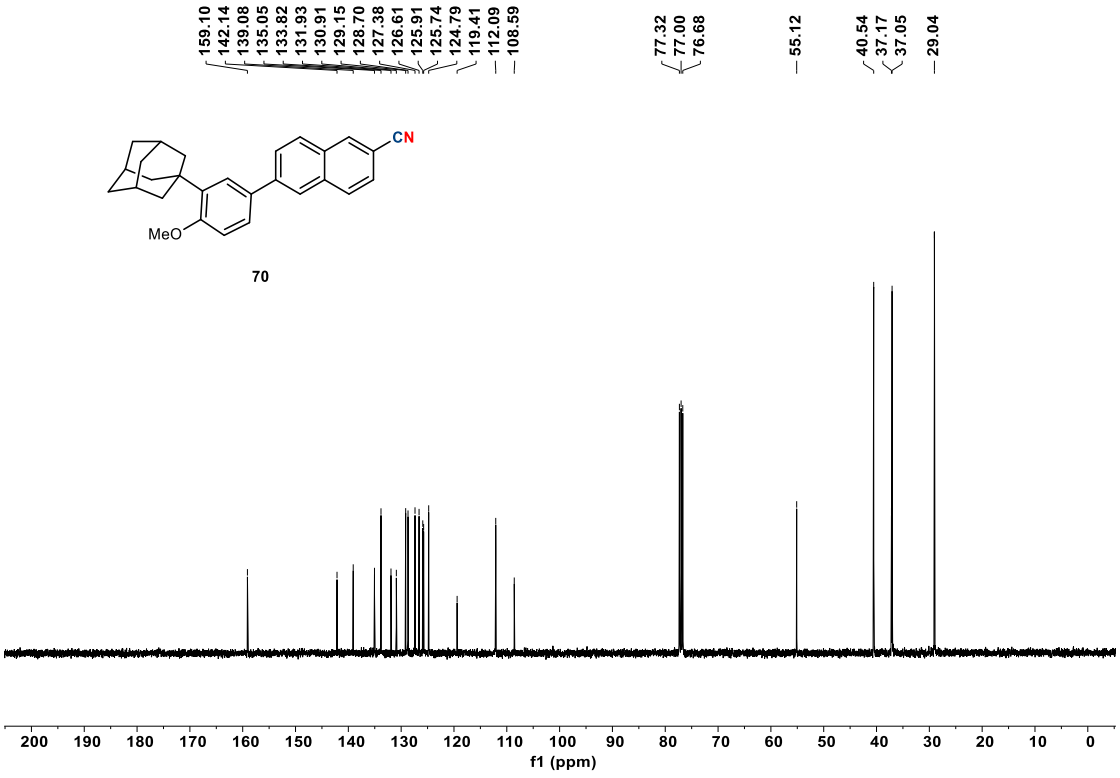

7.810
7.793
7.661
7.641
7.354
7.341
7.336
7.322
7.319
7.304
7.280
7.261
7.241
7.237
7.224
7.206
7.188
7.155
7.136
7.118
7.106
7.086
7.066
7.009
6.845
6.825
5.315
4.559
4.541
4.523
4.505
1.363
1.345
1.327
-0.000
Ph
Ph
Ph
N
N
N
N
NC
O
68
0.97
0.96
2.02
1.03
10.13
4.78
5.83
1.94
1.94
3.00
f1 (ppm)

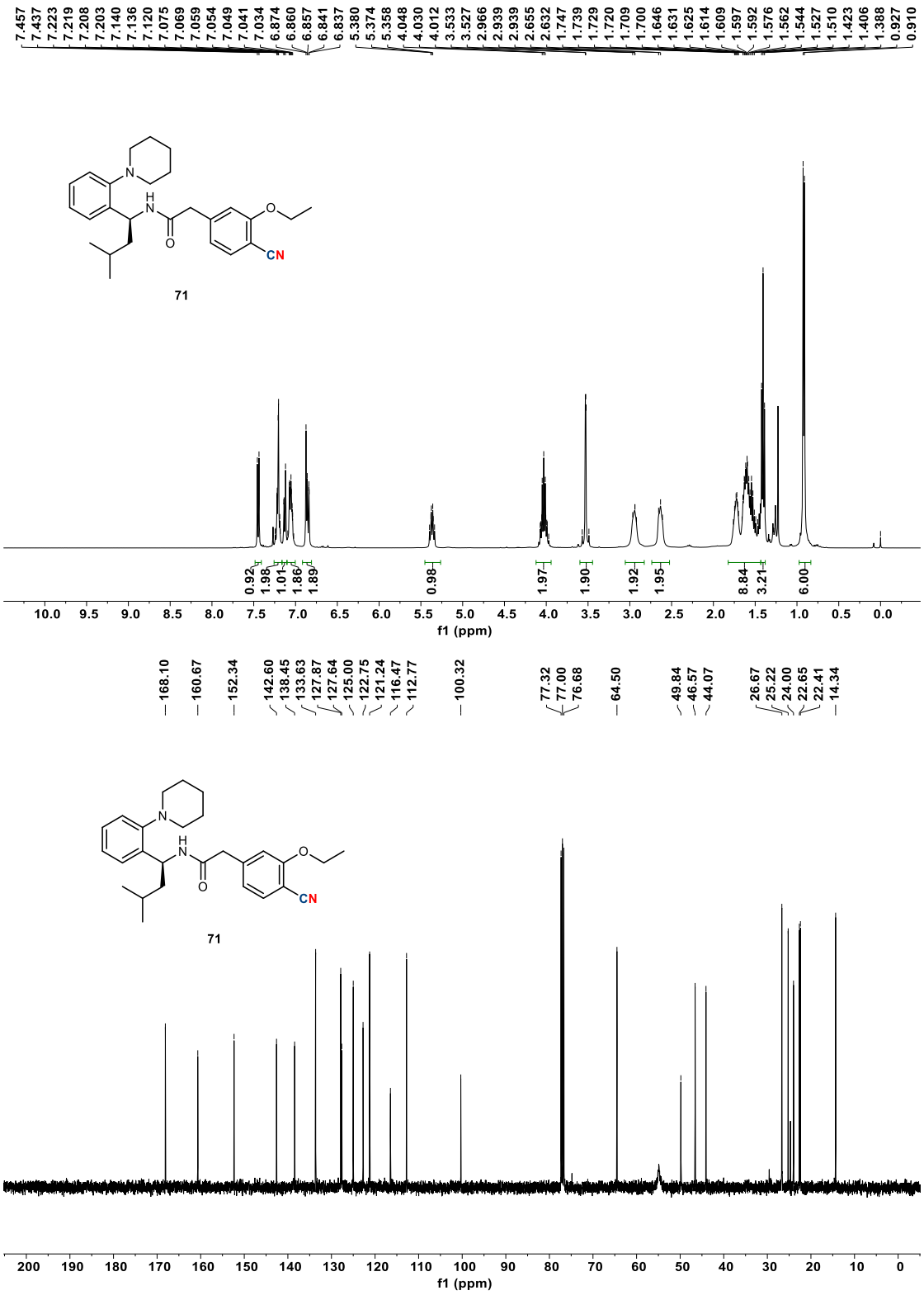

163.88
158.35
141.49
141.22
141.17
140.78
134.33
133.19
130.69
130.19
130.13
129.83
129.62
128.11
127.53
127.48
126.83
126.25
126.20
122.59
121.64
116.99
92.91
82.80
77.32
77.00
76.68
67.07
45.41
14.51
Ph
Ph
Ph
N
N
N
N
NC
O
68
f1 (ppm)

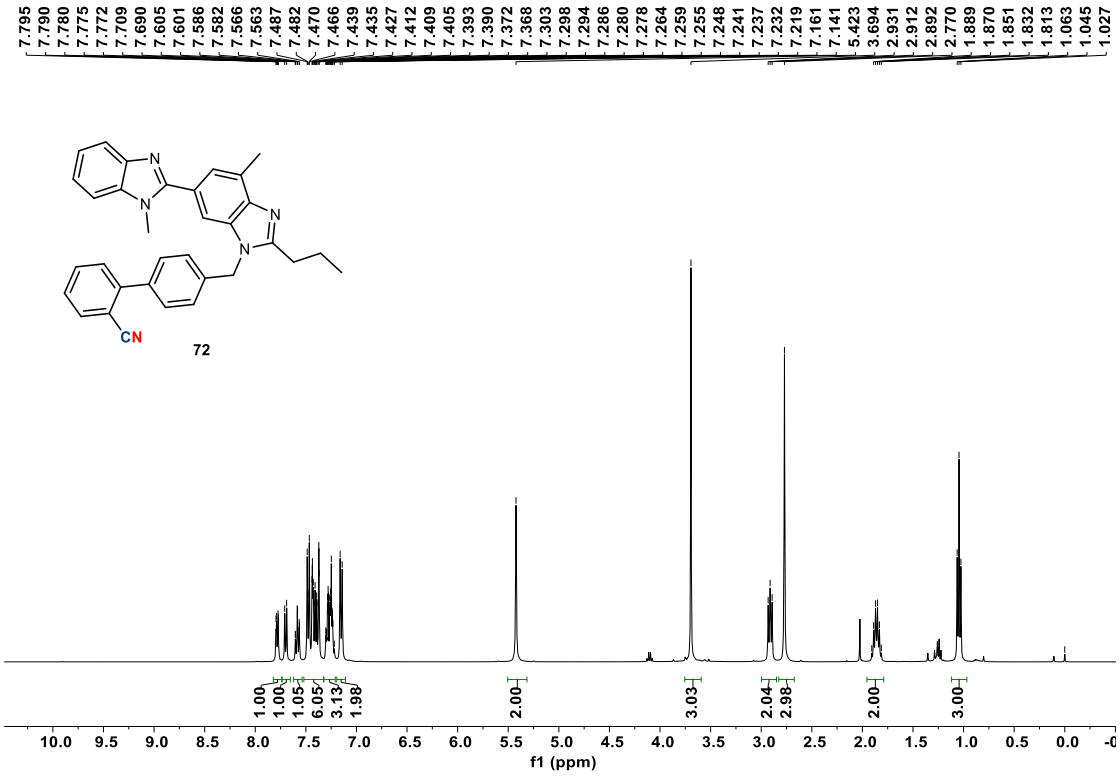

7.943
7.922
7.828
7.807
3.134
3.115
3.096
1.587
1.568
1.549
1.530
0.893
0.874
0.856
-0.000
N
S
O
O
O
CN
69
1.91
1.87
4.02
3.95
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

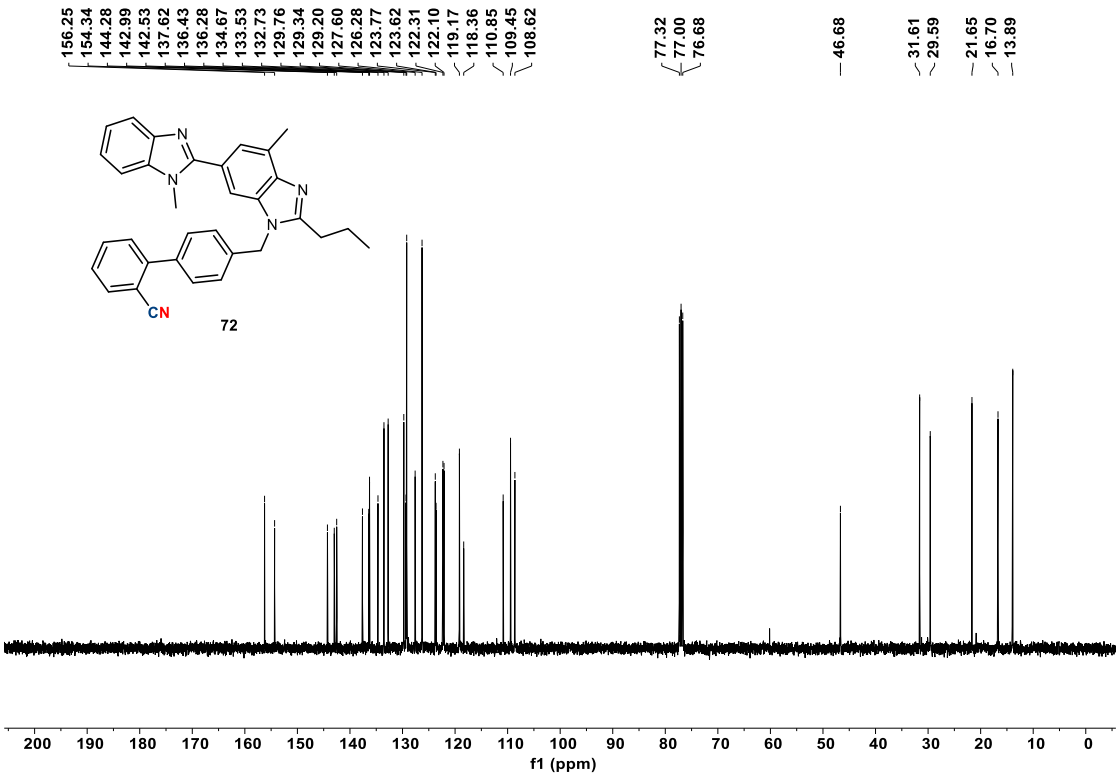

144.46
132.76
127.47
117.31
115.80
77.32
77.00
76.68
49.80
21.80
10.99
N
S
O
O
O
CN
69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

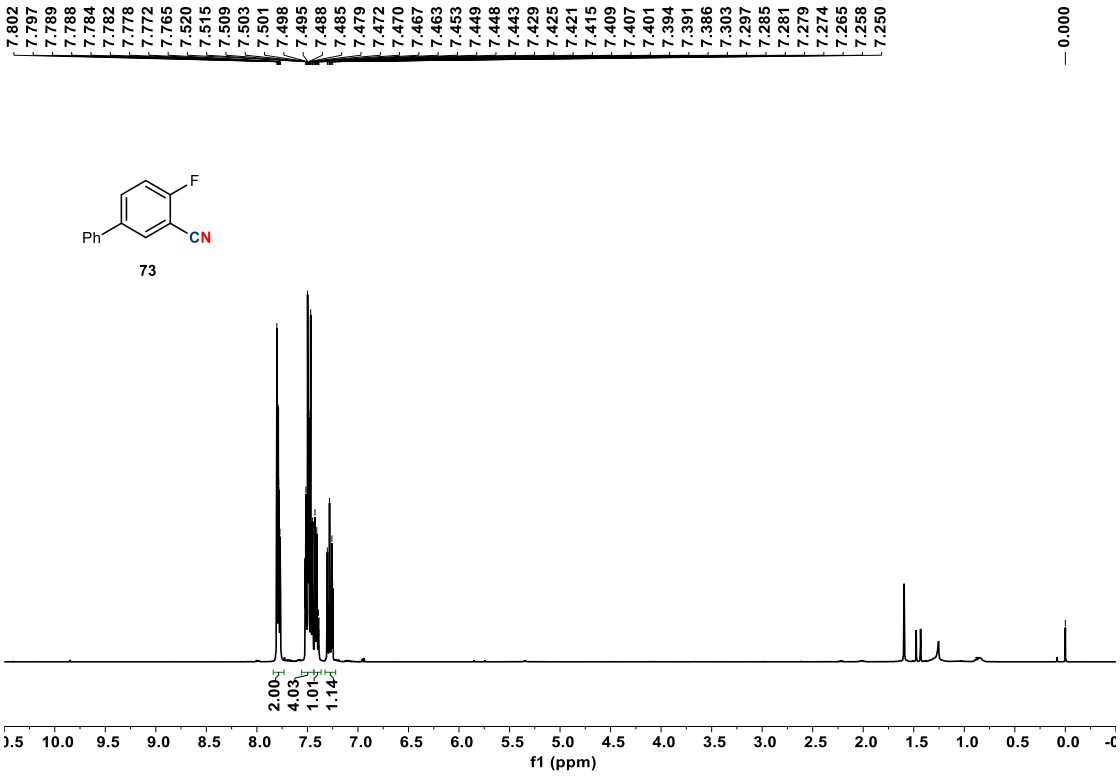

8.116
7.911
7.846
7.826
7.806
7.764
7.759
7.742
7.738
7.514
7.510
7.502
7.495
7.489
7.449
7.443
7.428
7.422
7.155
6.914
6.893
3.811
2.092
2.019
1.716
0.001
CN
MeO
70
0.95
1.00
1.97
1.00
1.90
1.03
0.98
3.02
5.95
3.03
6.00
f1 (ppm)

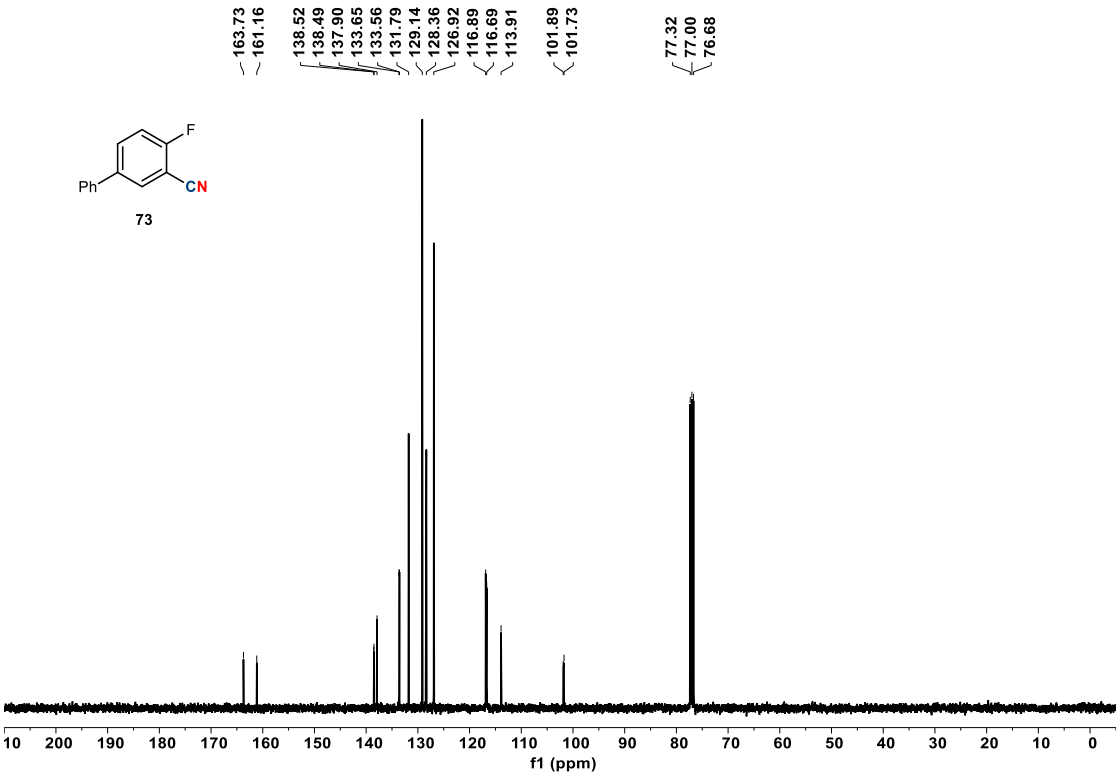

159.10
142.14
139.08
135.05
133.82
131.93
130.91
129.15
128.70
127.38
126.61
125.91
125.74
124.79
119.41
112.09
108.59
77.32
77.00
76.68
55.12
40.54
37.17
37.05
29.04
CN
MeO
70
f1 (ppm)

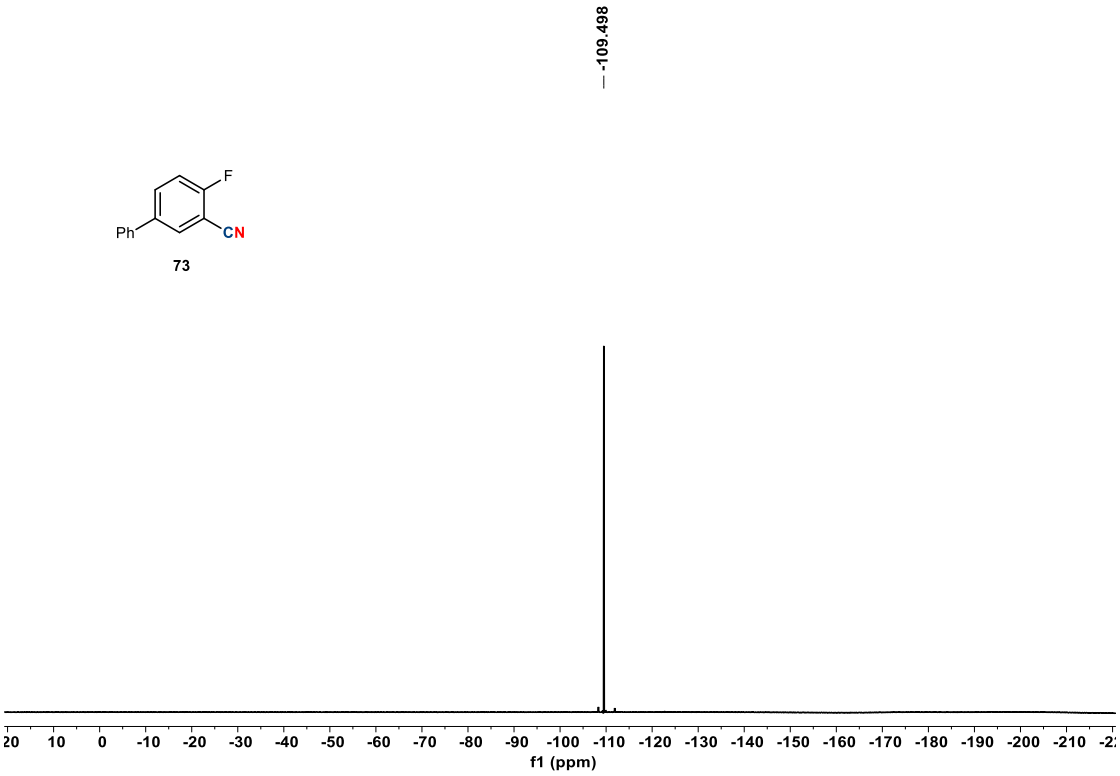

7.457
7.437
7.223
7.219
7.208
7.203
7.140
7.136
7.120
7.075
7.069
7.059
7.054
7.049
7.041
7.034
6.874
6.860
6.857
6.841
6.837
5.380
5.374
5.358
4.048
4.030
4.012
3.533
3.527
2.966
2.939
2.939
2.655
2.632
1.747
1.739
1.729
1.720
1.709
1.700
1.646
1.631
1.625
1.614
1.609
1.597
1.592
1.576
1.562
1.544
1.527
1.510
1.423
1.406
1.388
0.927
0.910
71
0.92
1.98
1.01
1.86
1.89
0.98
1.97
1.90
1.92
1.95
8.84
3.21
6.00
f1 (ppm)
168.10
160.67
152.34
142.60
138.45
133.63
127.87
127.64
125.00
122.75
121.24
116.47
112.77
100.32
77.32
77.00
76.68
64.50
49.84
46.57
44.07
26.67
25.22
24.00
22.65
22.41
14.34
71
f1 (ppm)


7.795
7.790
7.780
7.775
7.772
7.709
7.690
7.605
7.601
7.586
7.582
7.566
7.563
7.487
7.482
7.470
7.466
7.439
7.435
7.427
7.412
7.409
7.405
7.393
7.390
7.372
7.368
7.303
7.298
7.294
7.286
7.280
7.278
7.264
7.259
7.255
7.248
7.241
7.237
7.232
7.219
7.161
7.141
5.423
3.694
2.931
2.912
2.892
2.770
1.889
1.870
1.851
1.832
1.813
1.063
1.045
1.027
N
N
N
N
CN
72
1.00
1.00
1.05
6.05
3.13
1.98
2.00
3.03
2.04
2.98
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

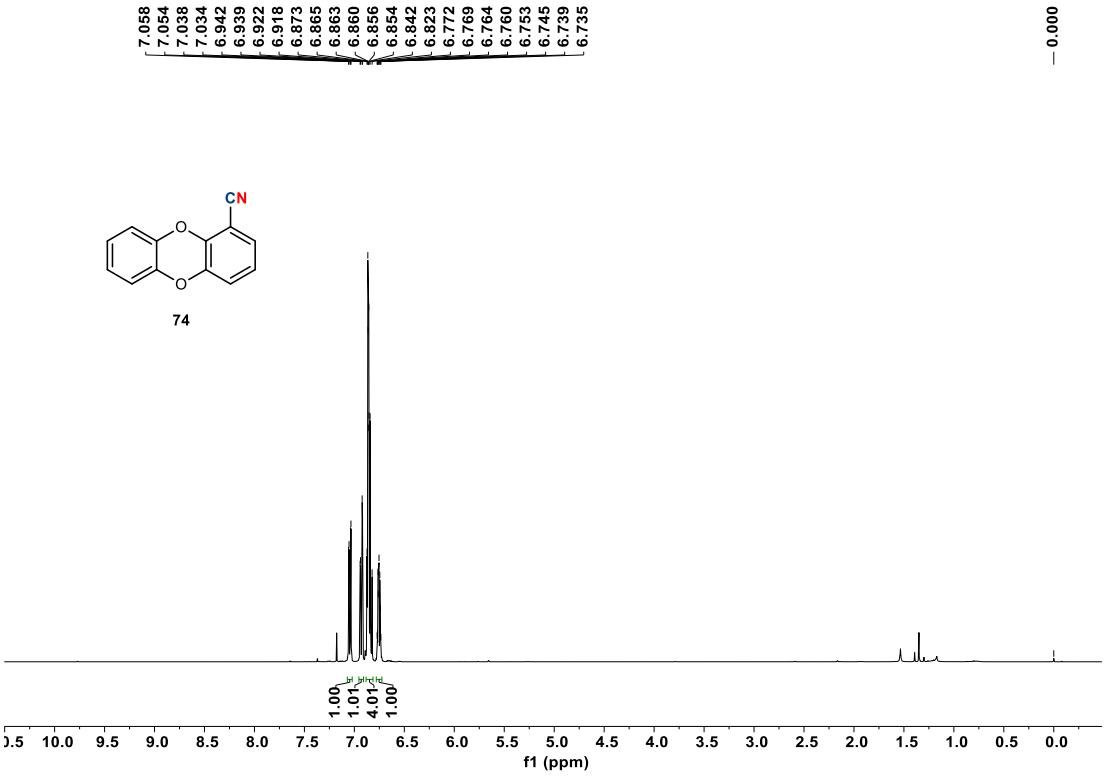

156.25
154.34
144.28
142.99
142.53
137.62
136.43
136.28
134.67
133.53
132.73
129.76
129.34
129.20
127.60
126.28
123.77
123.62
122.31
122.10
119.17
118.36
110.85
109.45
108.62
77.32
77.00
76.68
46.68
31.61
29.59
21.65
16.70
13.89
N
N
N
N
CN
72
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

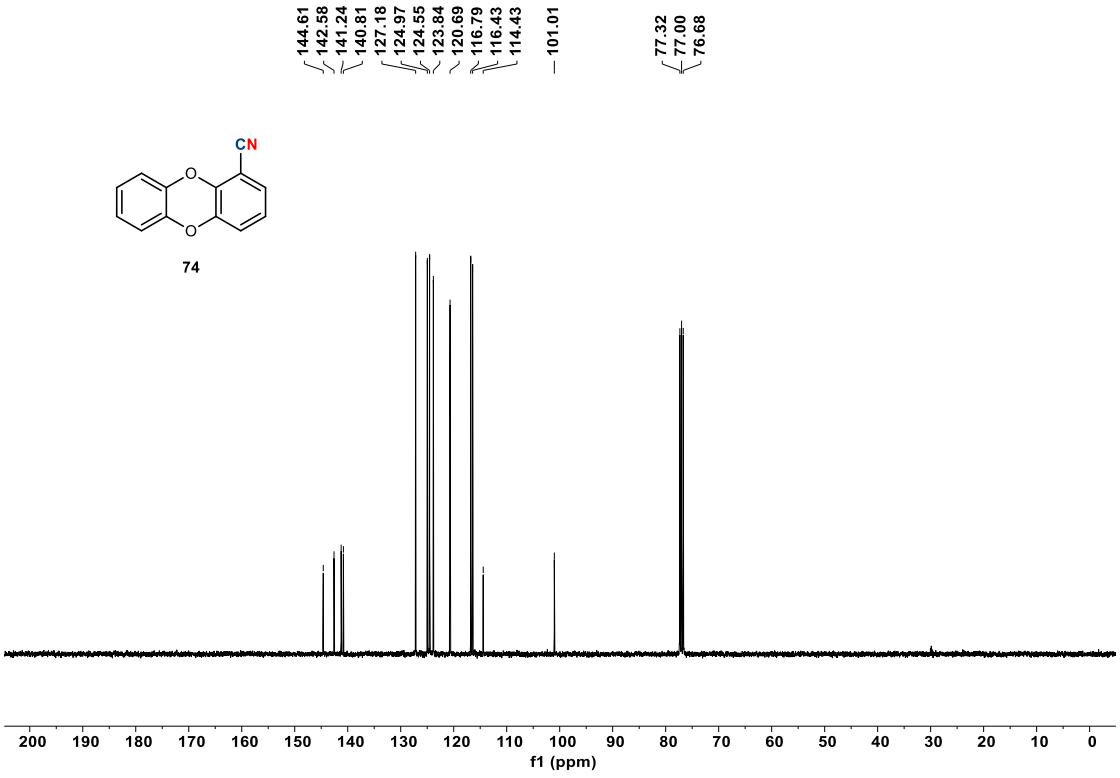

7.802
7.797
7.789
7.788
7.784
7.782
7.778
7.772
7.765
7.520
7.515
7.509
7.503
7.501
7.498
7.495
7.488
7.485
7.479
7.472
7.470
7.467
7.463
7.453
7.449
7.448
7.443
7.429
7.425
7.421
7.415
7.409
7.407
7.401
7.394
7.391
7.386
7.303
7.297
7.285
7.281
7.279
7.274
7.265
7.258
7.250
0.000
F
Ph
CN
73
2.00
4.03
1.01
1.14
f1 (ppm)


163.73
161.16
138.52
138.49
137.90
133.65
133.56
131.79
129.14
128.36
126.92
116.89
116.69
113.91
101.89
101.73
77.32
77.00
76.68
F
Ph
CN
73
f1 (ppm)



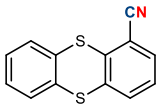
^{19}F NMR of nitrile 73


7.058
7.054
7.038
7.034
6.942
6.939
6.922
6.918
6.873
6.865
6.863
6.860
6.856
6.854
6.842
6.823
6.772
6.769
6.764
6.760
6.753
6.745
6.739
6.735
0.000
CN
O
O
74
1.00
1.01
4.01
1.00
f1 (ppm)

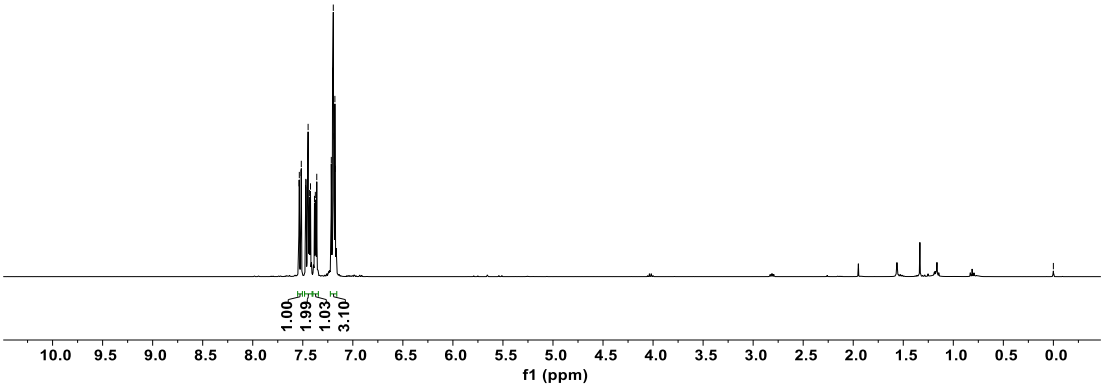

144.61
142.58
141.24
140.81
127.18
124.97
124.55
123.84
120.69
116.79
116.43
114.43
101.01
77.32
77.00
76.68
CN
O
O
74
f1 (ppm)


7.537
7.535
7.518
7.515
7.470
7.467
7.451
7.447
7.439
7.437
7.432
7.423
7.383
7.375
7.370
7.367
7.360
7.215
7.202
7.195
7.188
7.179
7.176


-0.000

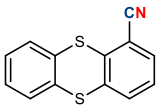

CN
S
S

75

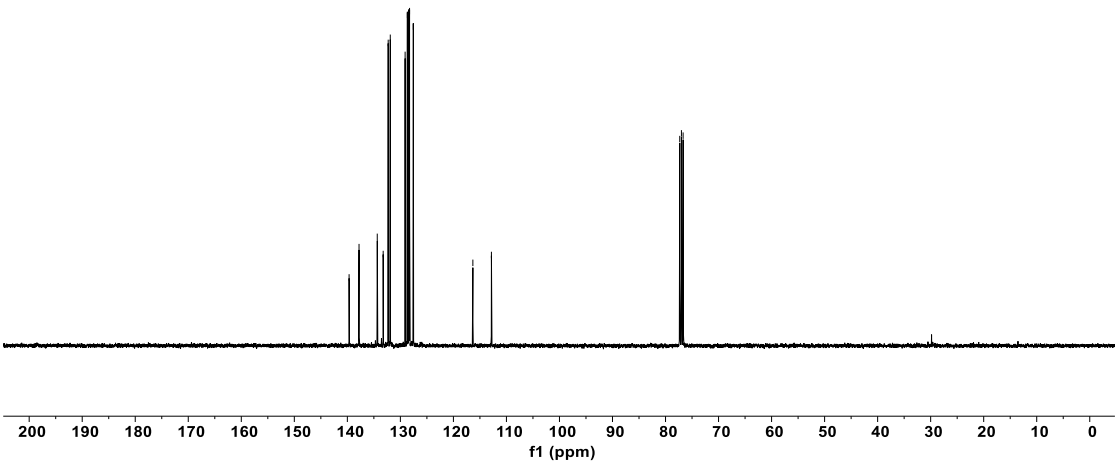

1.00
1.99
1.03
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

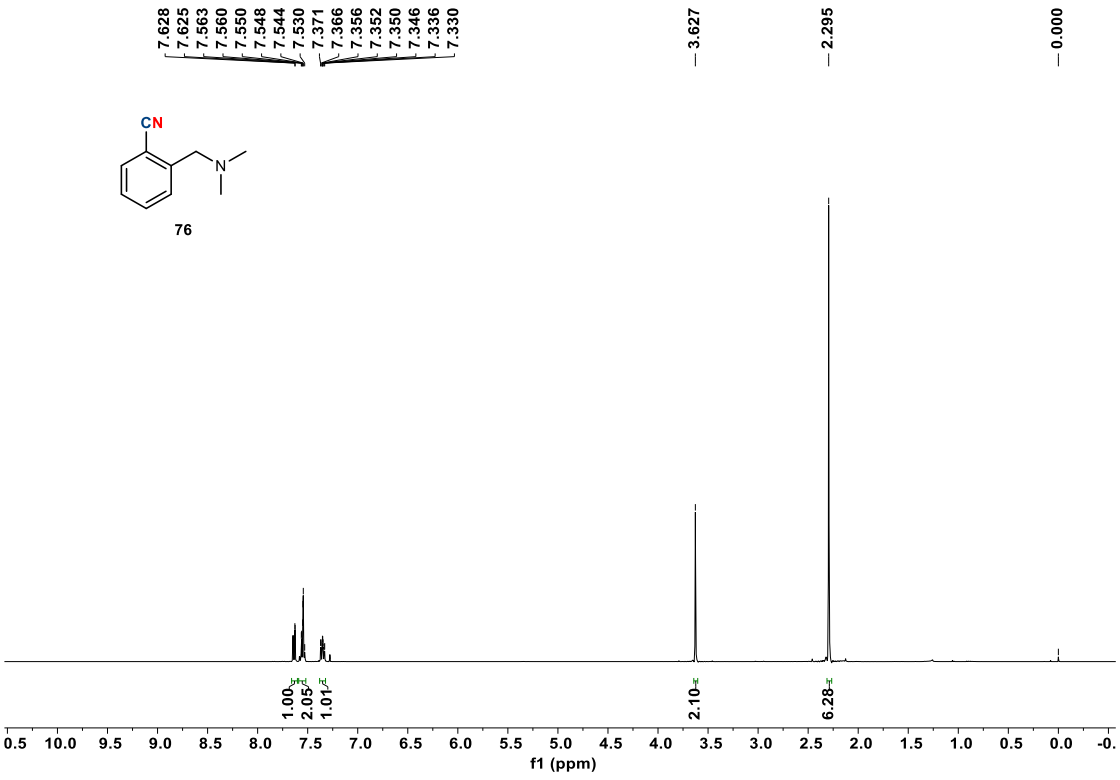

139.67
137.80
134.36
133.24
132.30
131.91
129.11
128.68
128.44
128.27
127.56
116.33
112.83

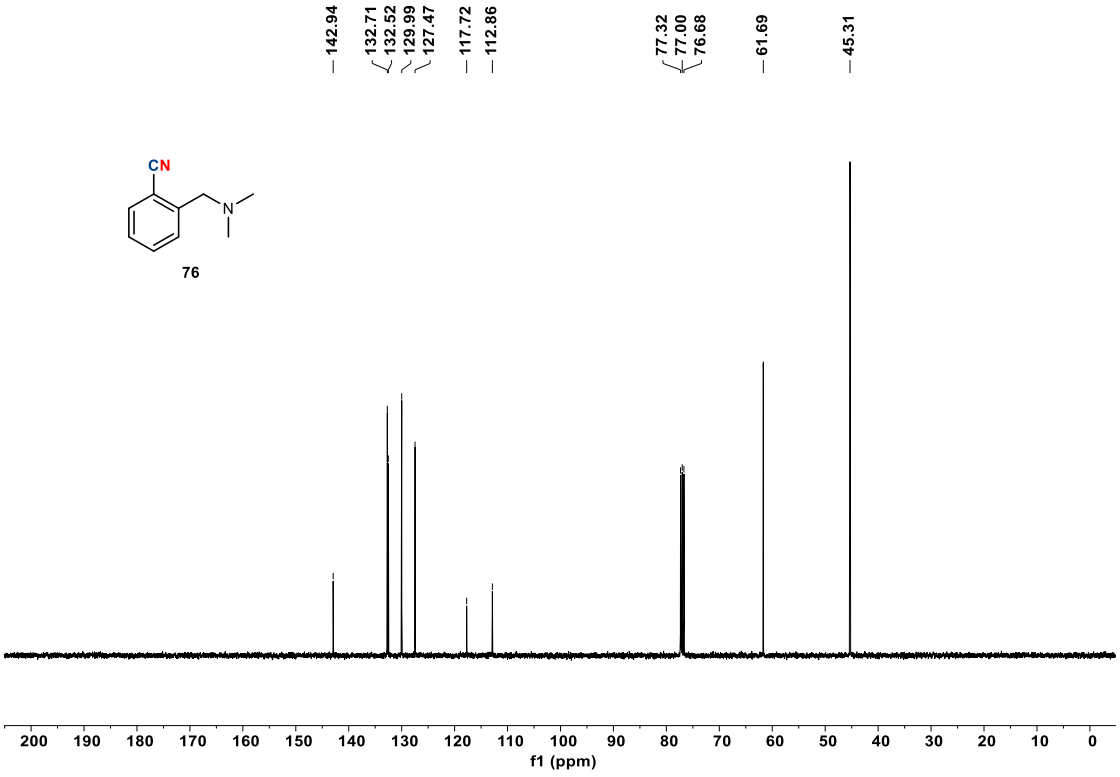

77.32
77.00
76.68

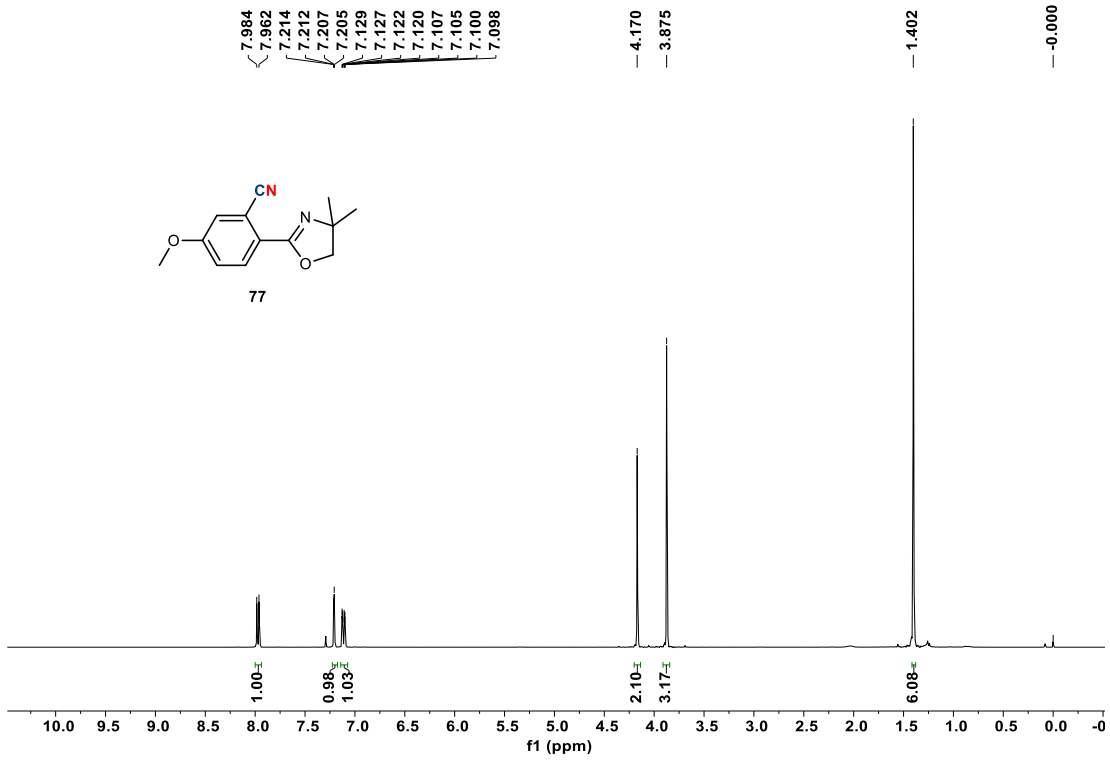

CN
S
S

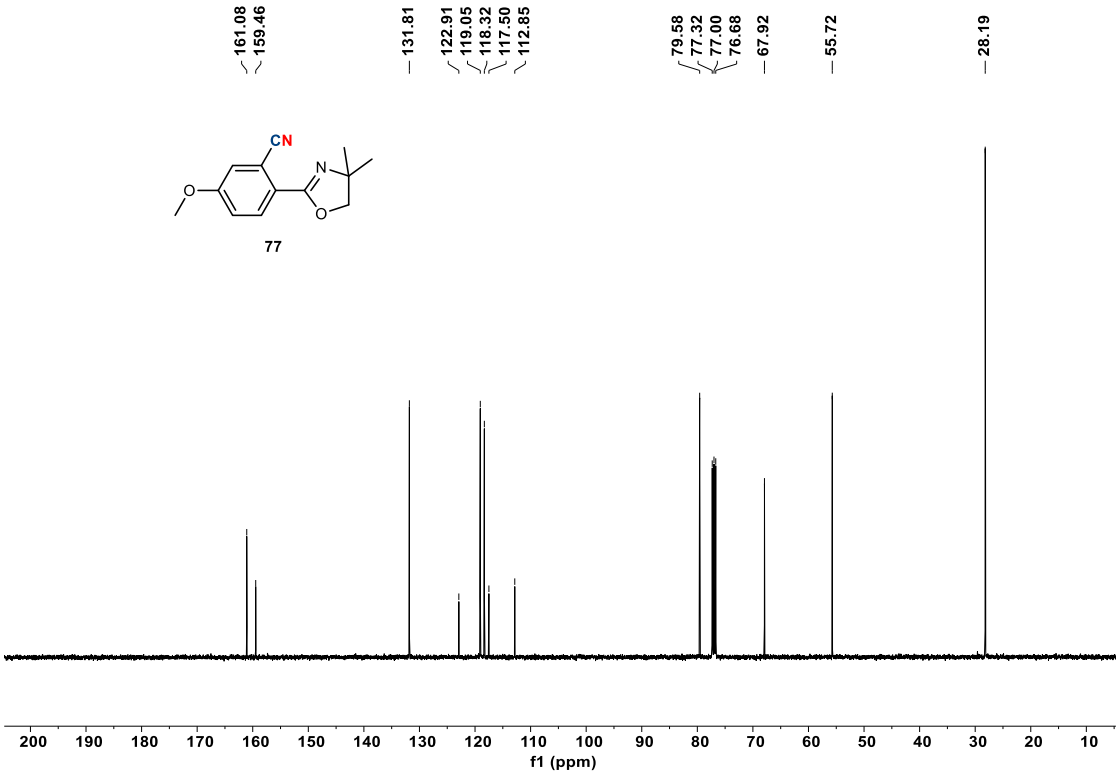
75

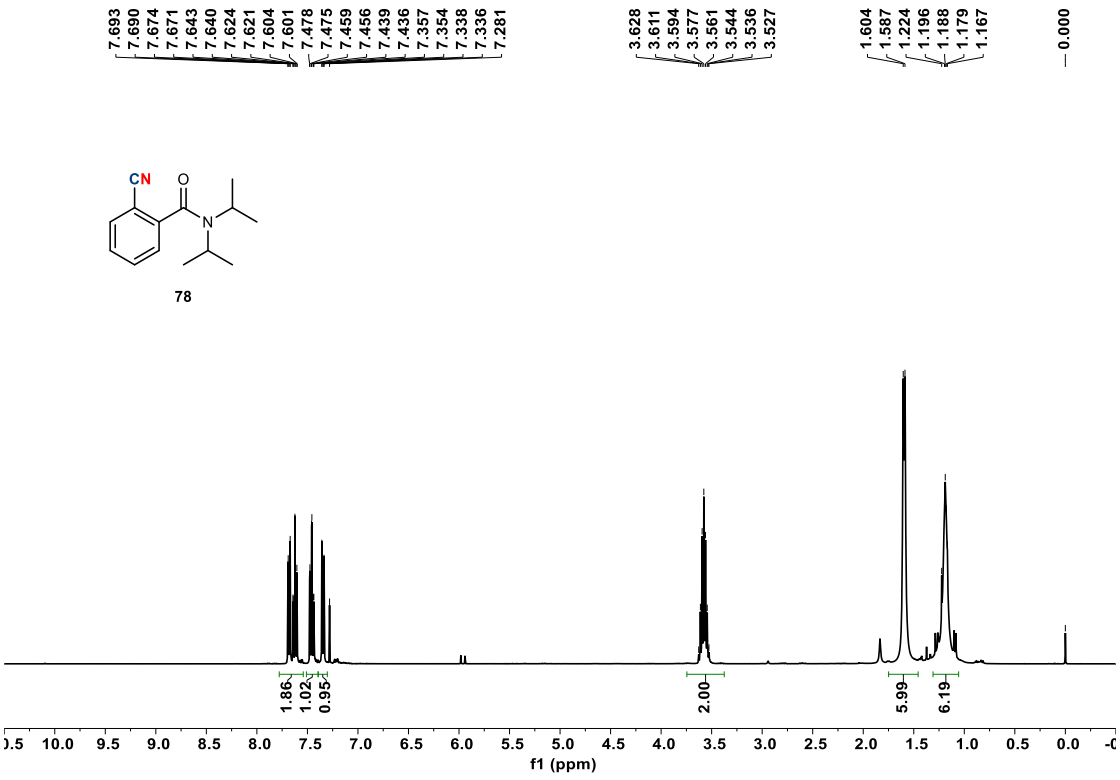

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

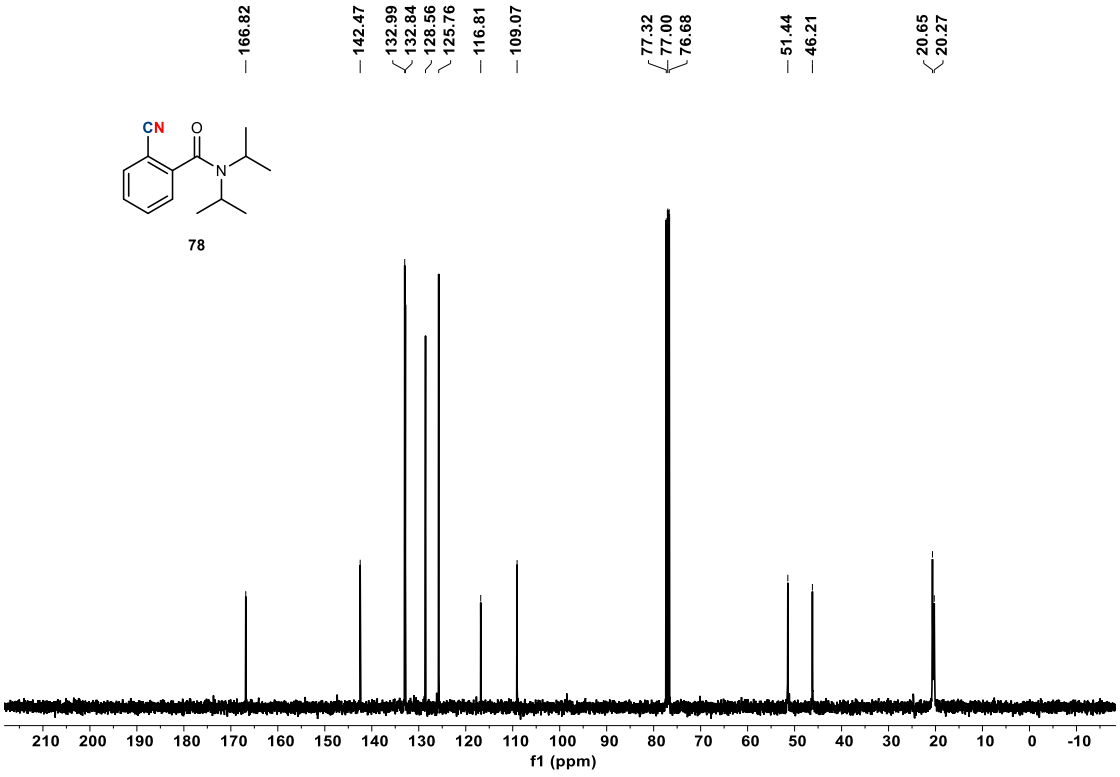

7.628
7.625
7.563
7.560
7.550
7.548
7.544
7.530
7.371
7.366
7.356
7.352
7.350
7.346
7.336
7.330
3.627
2.295
0.000
CN
N
76
1.00
2.05
1.01
2.10
6.28
f1 (ppm)

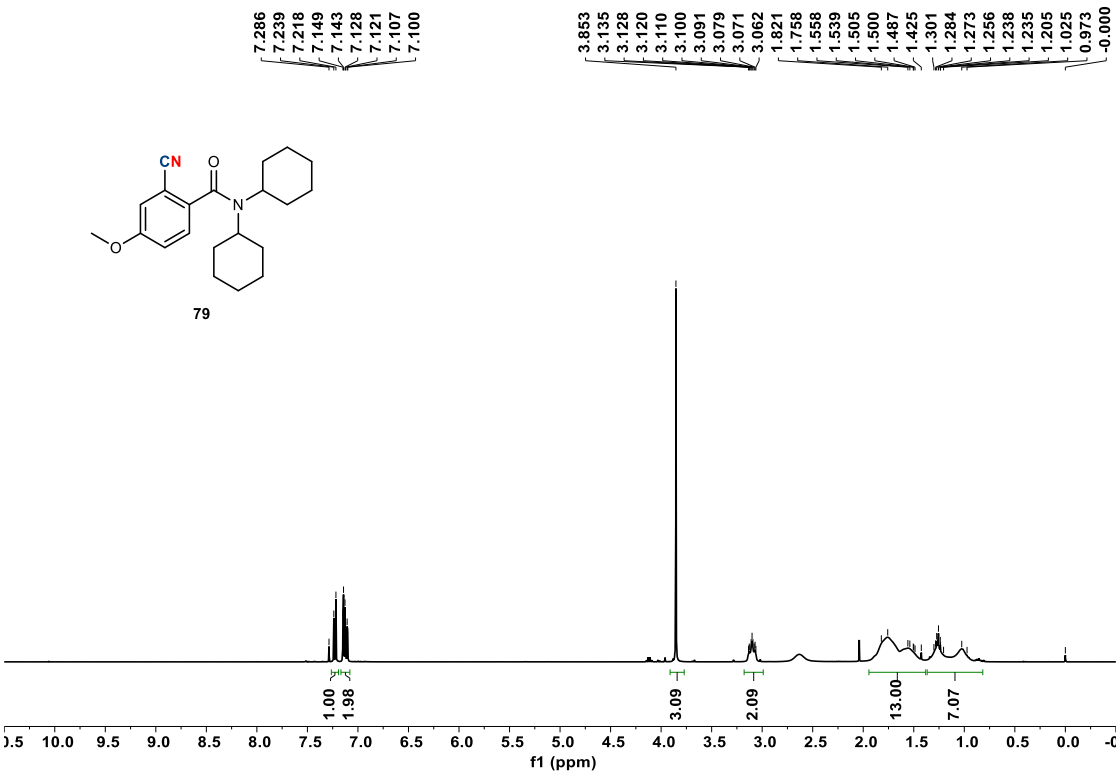

142.94
132.71
132.52
129.99
127.47
117.72
112.86
77.32
77.00
76.68
61.69
45.31
CN
N
76
f1 (ppm)

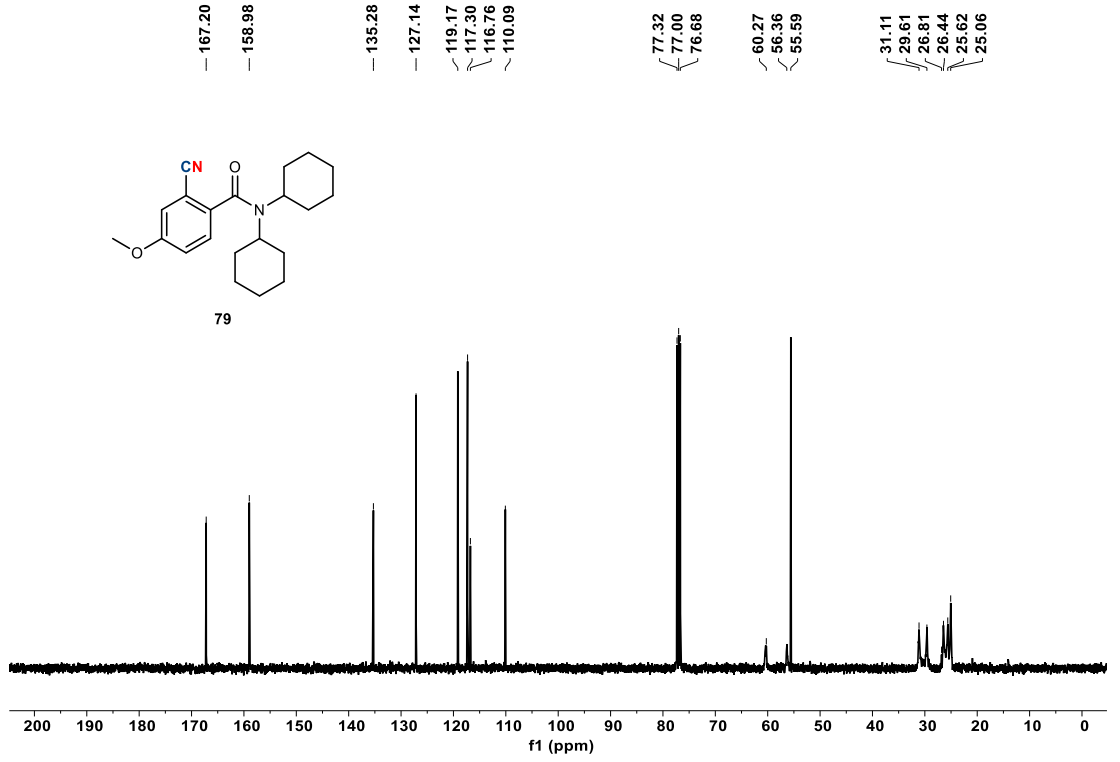

7.984
7.962
7.214
7.212
7.207
7.205
7.129
7.127
7.122
7.120
7.107
7.105
7.100
7.098
4.170
3.875
1.402
-0.000
CN
N
O
O
77
1.00
0.98
1.03
2.10
3.17
6.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

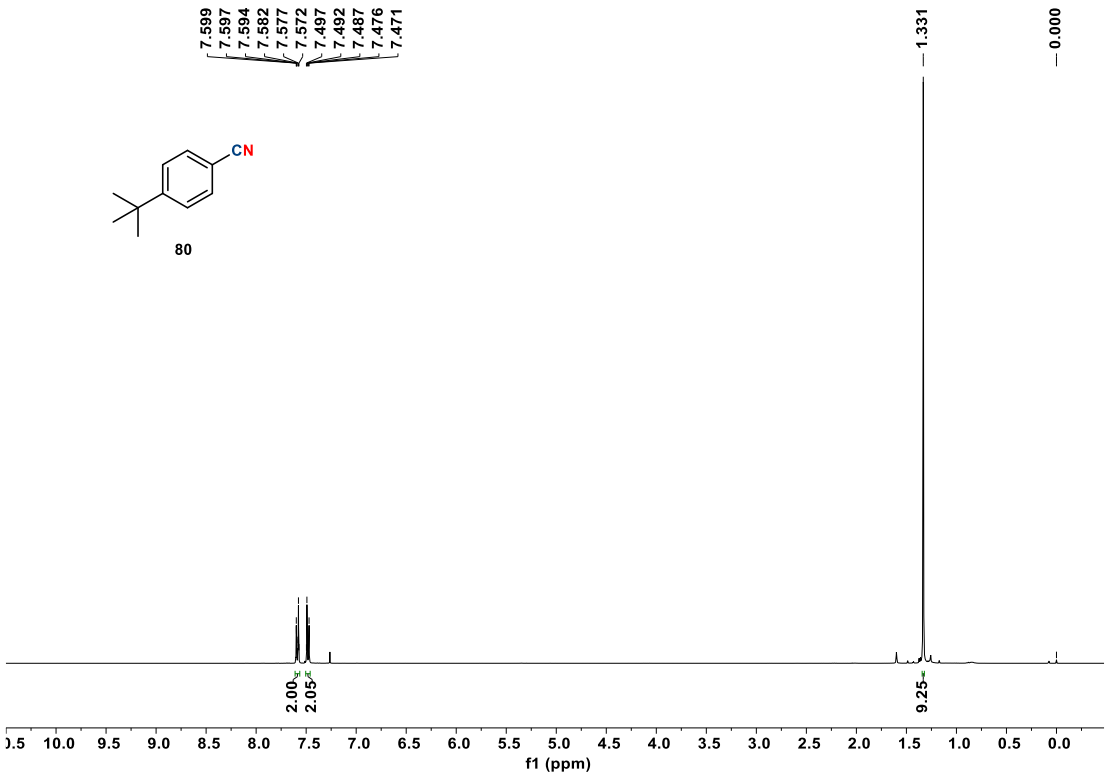

161.08
159.46
131.81
122.91
119.05
118.32
117.50
112.85
79.58
77.32
77.00
76.68
67.92
55.72
28.19
CN
N
O
O
77
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

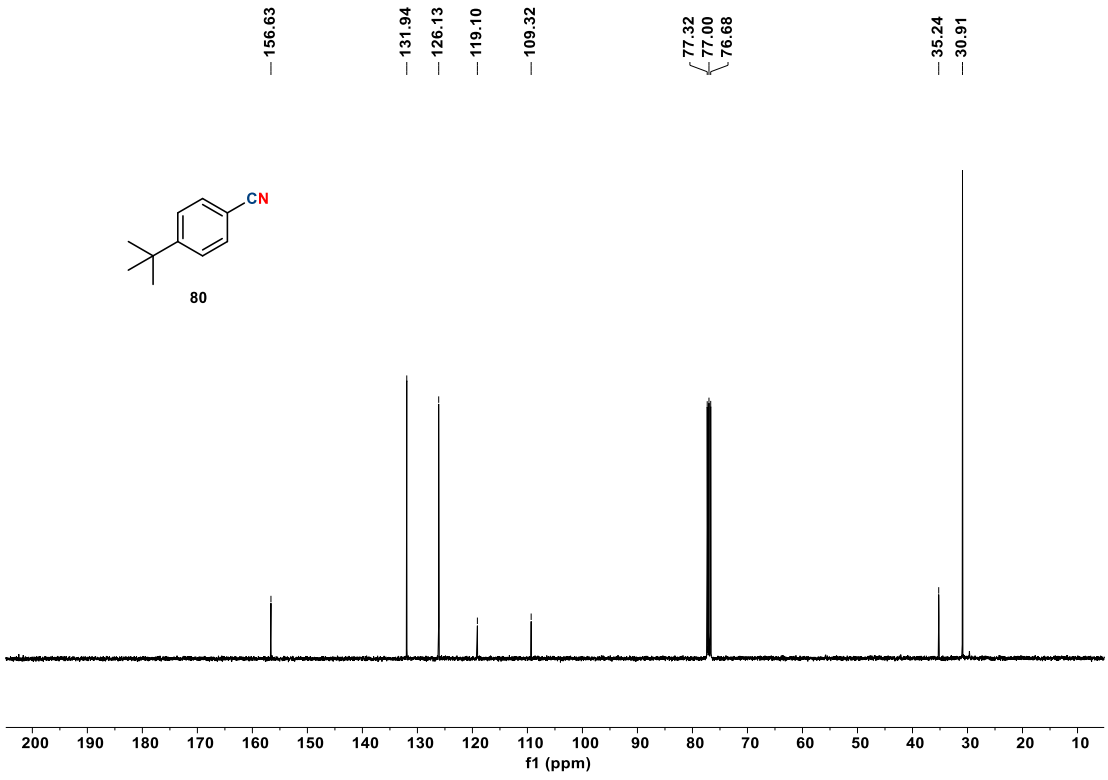

7.693
7.690
7.674
7.671
7.643
7.640
7.624
7.621
7.604
7.601
7.478
7.475
7.459
7.456
7.439
7.436
7.357
7.354
7.338
7.336
7.281
3.628
3.611
3.594
3.577
3.561
3.544
3.536
3.527
1.604
1.587
1.224
1.196
1.188
1.179
1.167
0.000
CN
O
N
78
1.86
1.02
0.95
2.00
5.99
6.19
f1 (ppm)

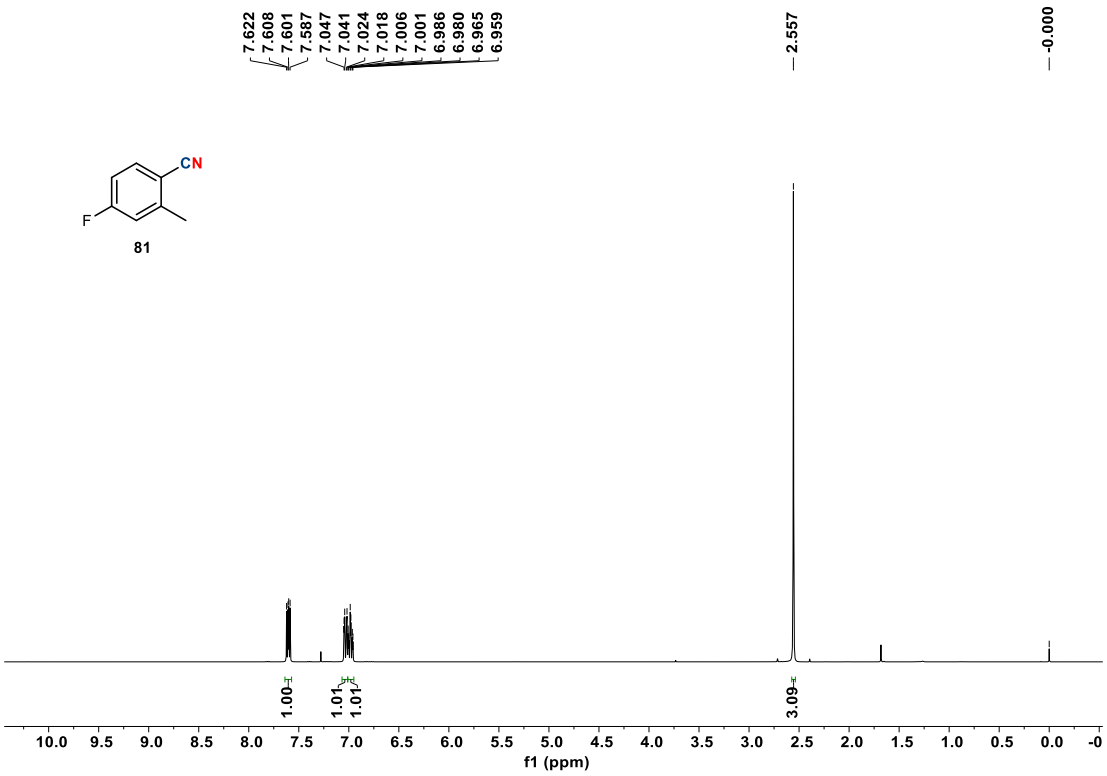

166.82
142.47
132.99
132.84
128.56
125.76
116.81
109.07
77.32
77.00
76.68
51.44
46.21
20.65
20.27
CN
O
N
78
f1 (ppm)

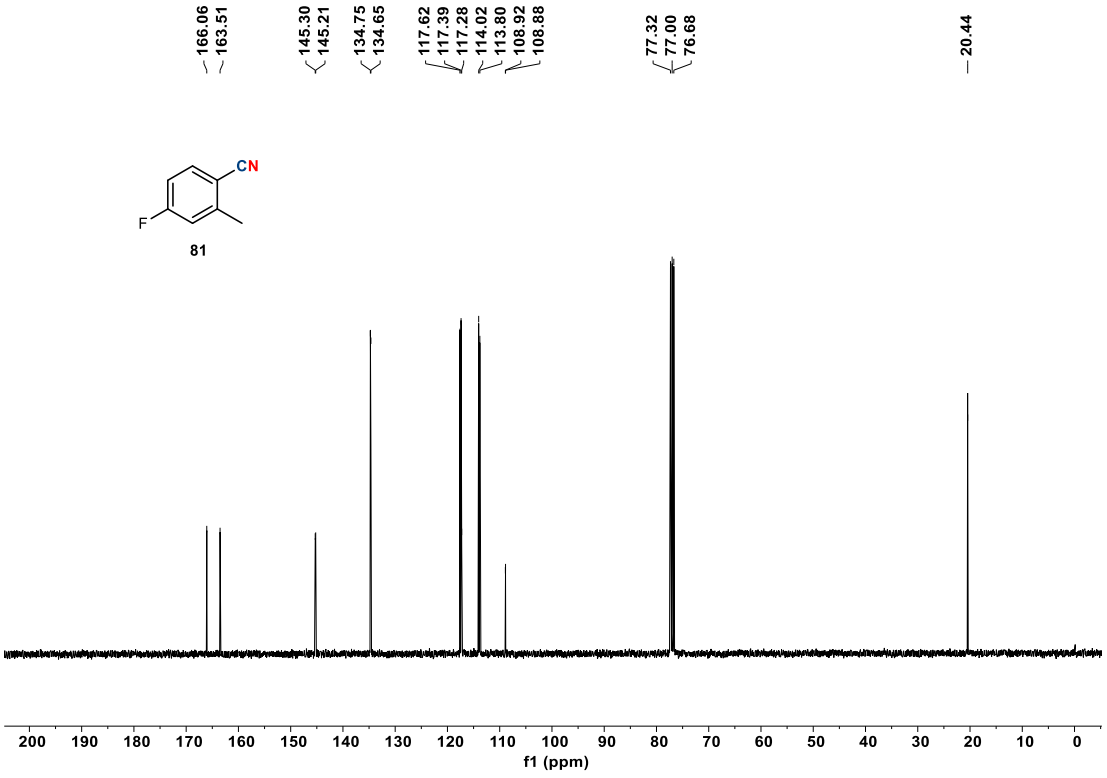

7.286
7.239
7.218
7.149
7.143
7.128
7.121
7.107
7.100
3.853
3.135
3.128
3.120
3.110
3.100
3.091
3.079
3.071
3.062
1.821
1.758
1.558
1.539
1.505
1.500
1.487
1.425
1.301
1.284
1.273
1.256
1.238
1.235
1.205
1.025
0.973
-0.000
CN
O
N
O
79
1.00
1.98
3.09
2.09
13.00
7.07
f1 (ppm)

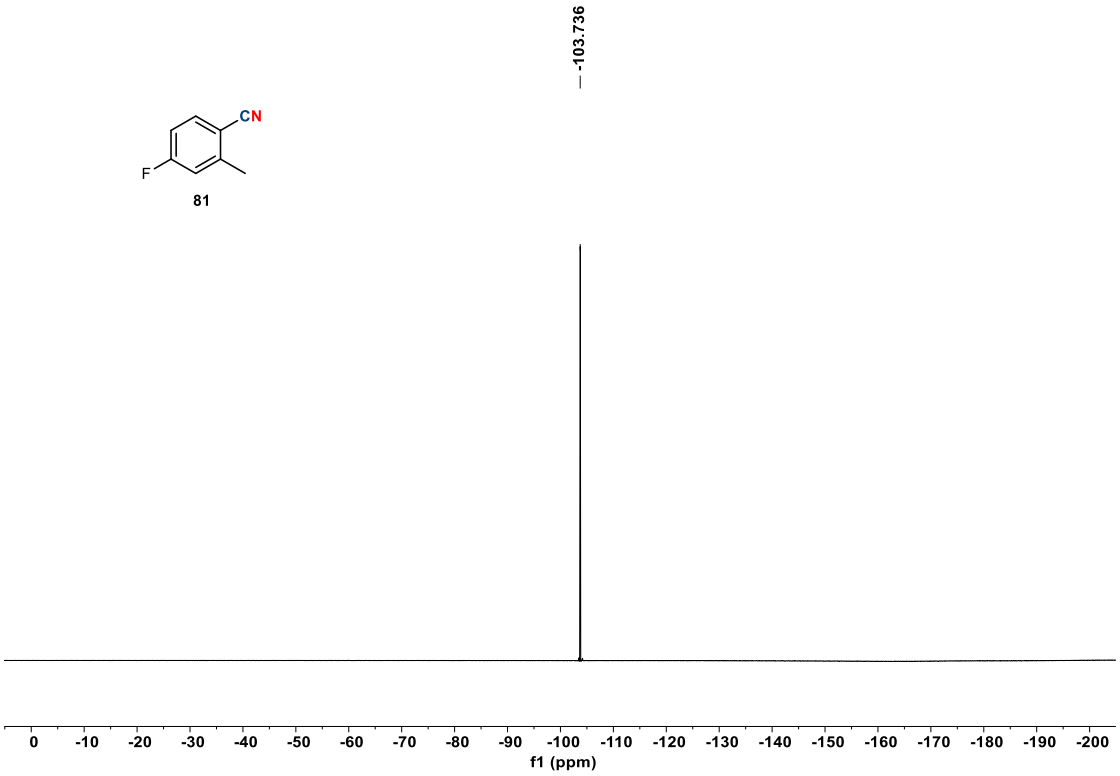

167.20
158.98
135.28
127.14
119.17
117.30
116.76
110.09
77.32
77.00
76.68
60.27
56.36
55.59
31.11
29.61
26.81
26.44
25.62
25.06
CN
O
N
O
79
f1 (ppm)


7.599
7.597
7.594
7.582
7.577
7.572
7.497
7.492
7.487
7.476
7.471
1.331
0.000
CN
80
2.00
2.05
9.25
f1 (ppm)

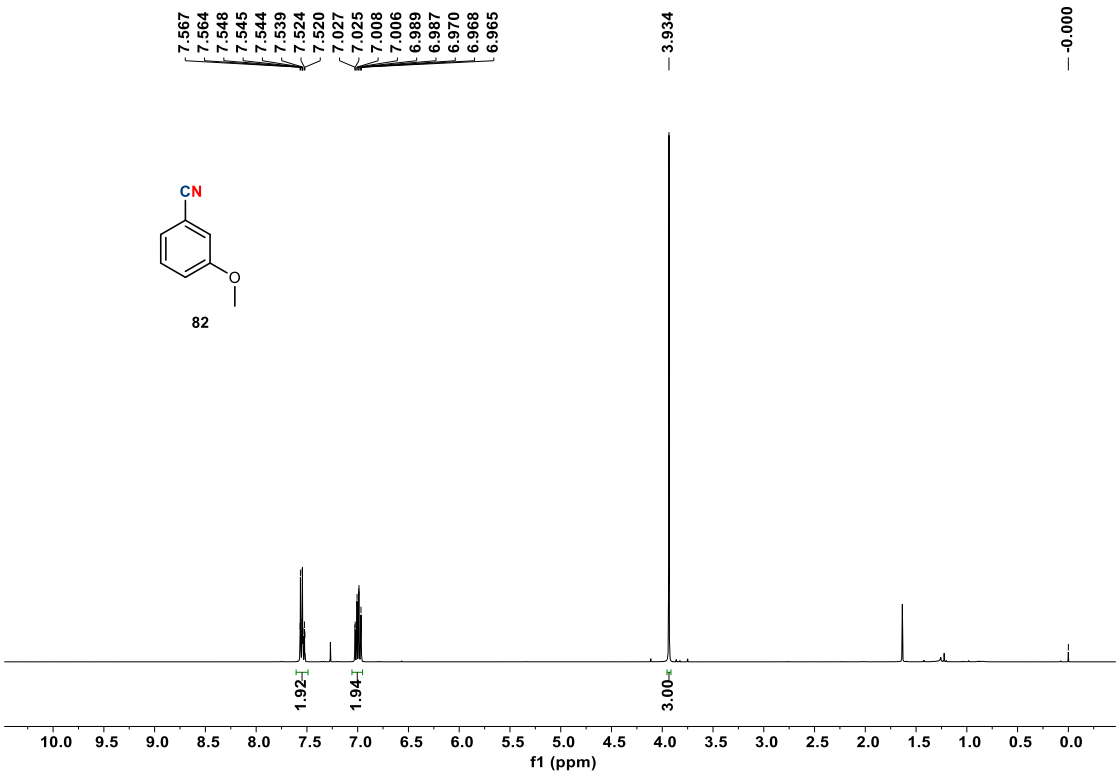

156.63
131.94
126.13
119.10
109.32
77.32
77.00
76.68
35.24
30.91
CN
80
f1 (ppm)

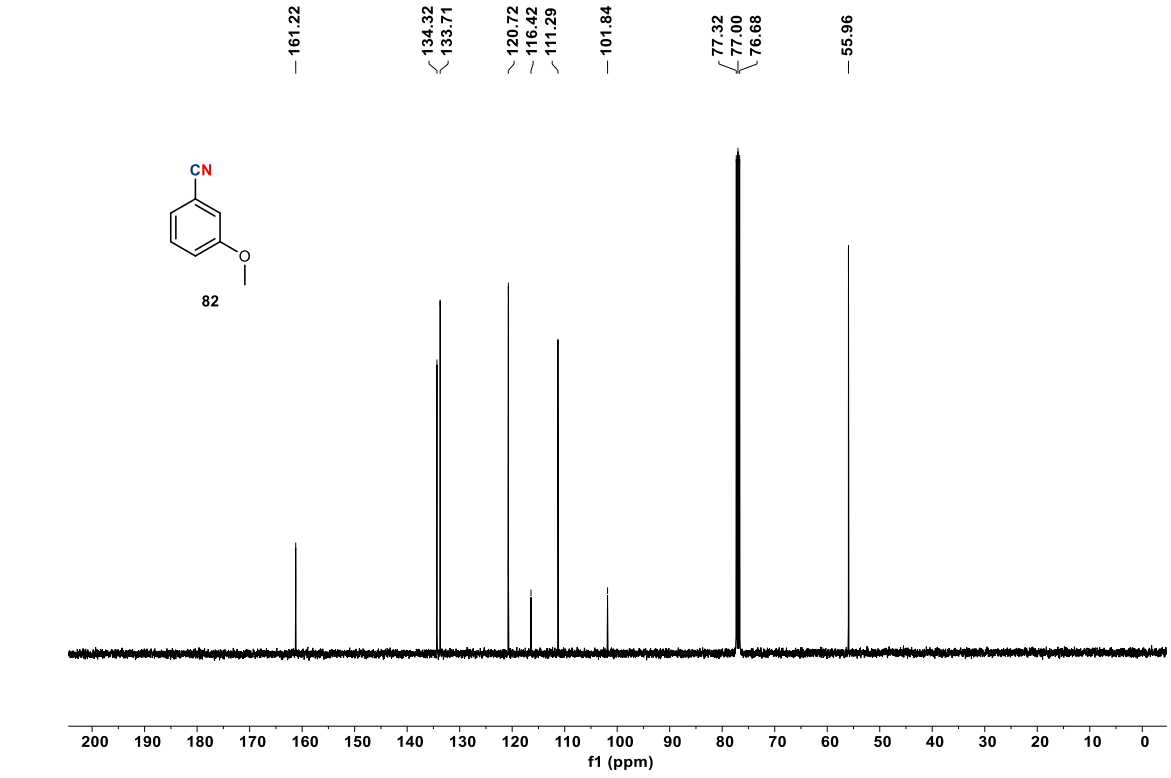

7.622
7.608
7.601
7.587
7.047
7.041
7.024
7.018
7.006
7.001
6.986
6.980
6.965
6.959
2.557
-0.000
CN
F
81
1.00
1.01
1.01
3.09
f1 (ppm)

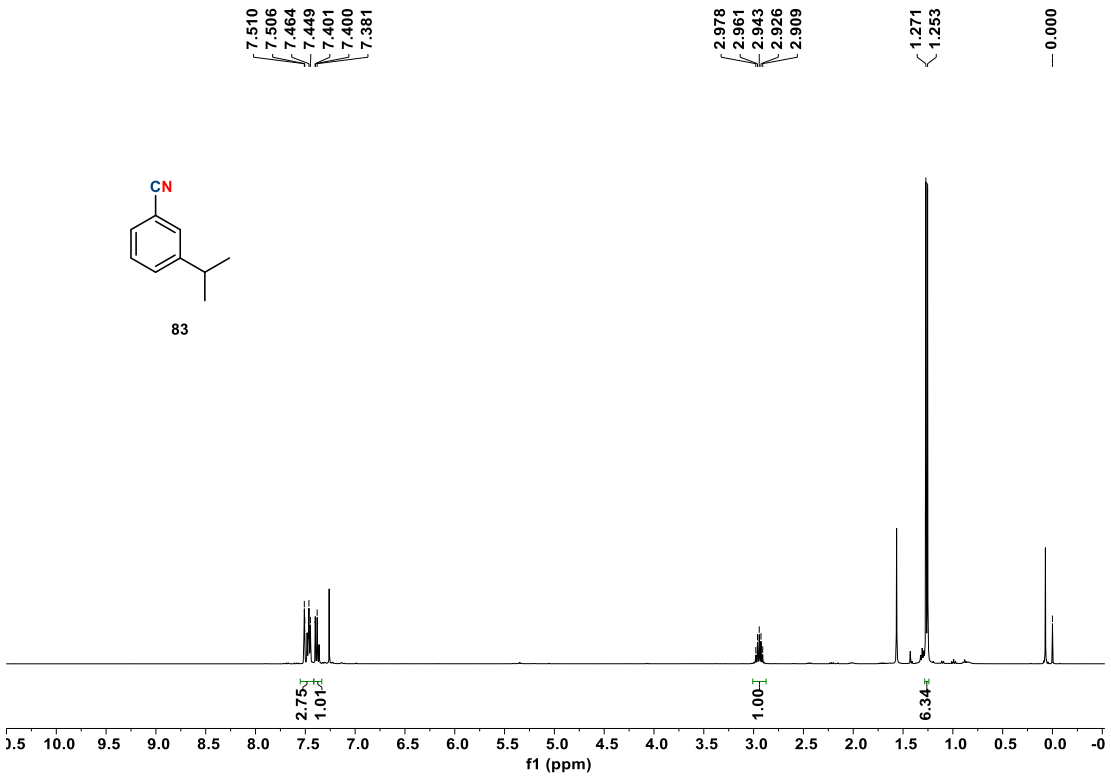

166.06
163.51
145.30
145.21
134.75
134.65
117.62
117.39
117.28
114.02
113.80
108.92
108.88
77.32
77.00
76.68
20.44
CN
F
81
f1 (ppm)

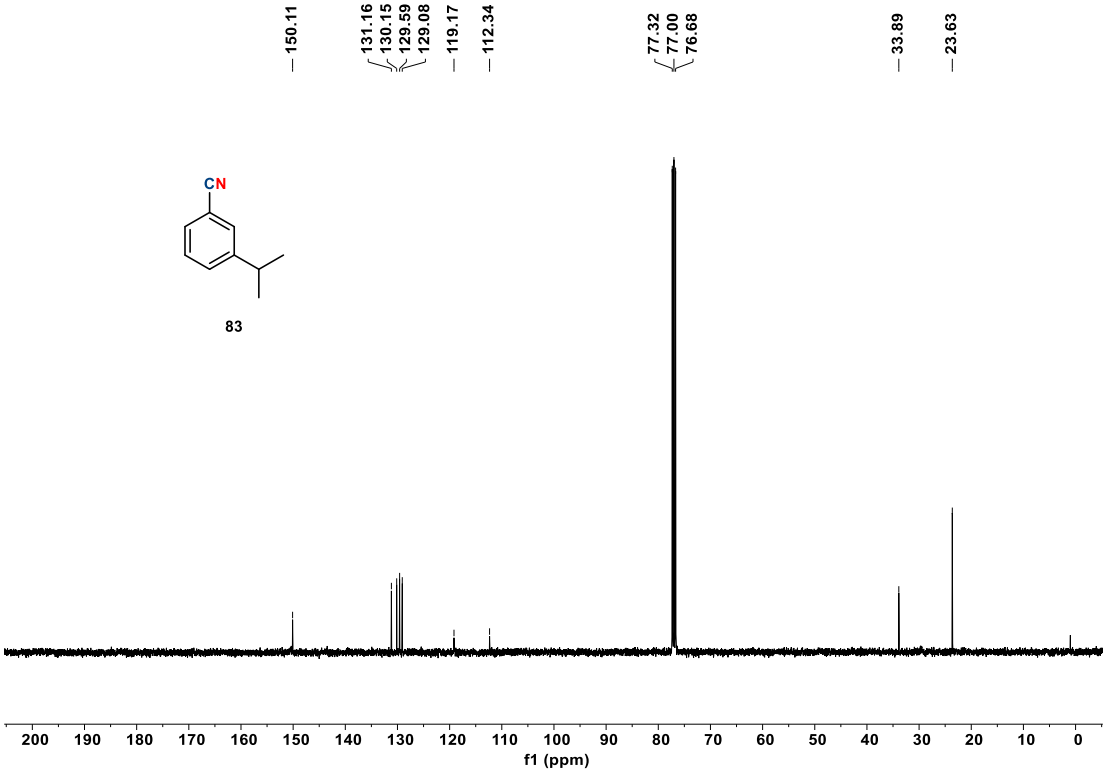


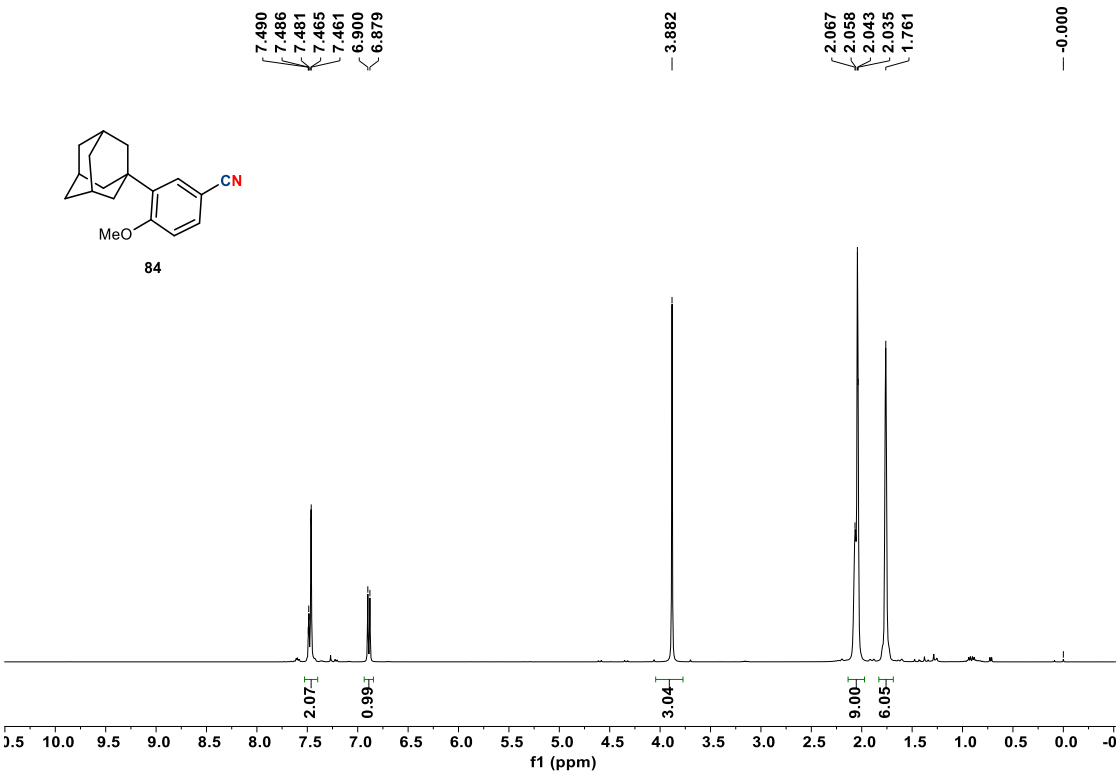
^{19}F NMR of nitrile 81

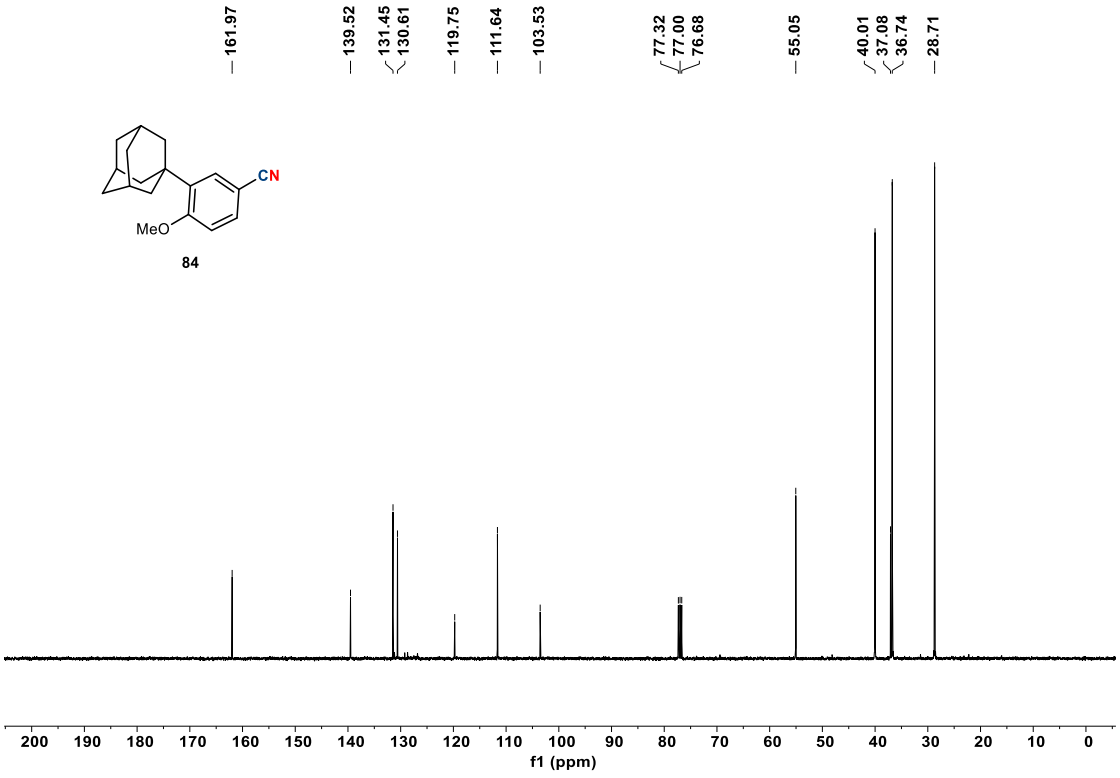

7.567
7.564
7.548
7.545
7.544
7.539
7.524
7.520
7.027
7.025
7.008
7.006
6.989
6.987
6.970
6.968
6.965
3.934
-0.000
CN
O
82
1.92
1.94
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

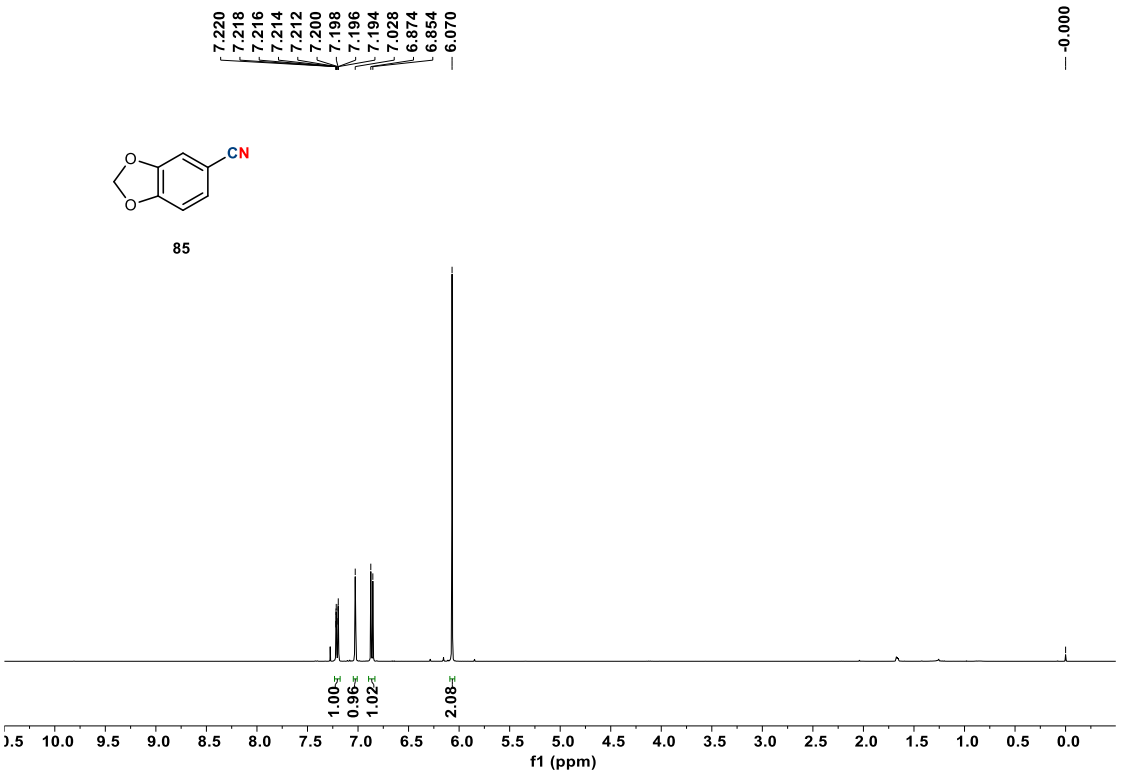

161.22
134.32
133.71
120.72
116.42
111.29
101.84
77.32
77.00
76.68
55.96
CN
O
82
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

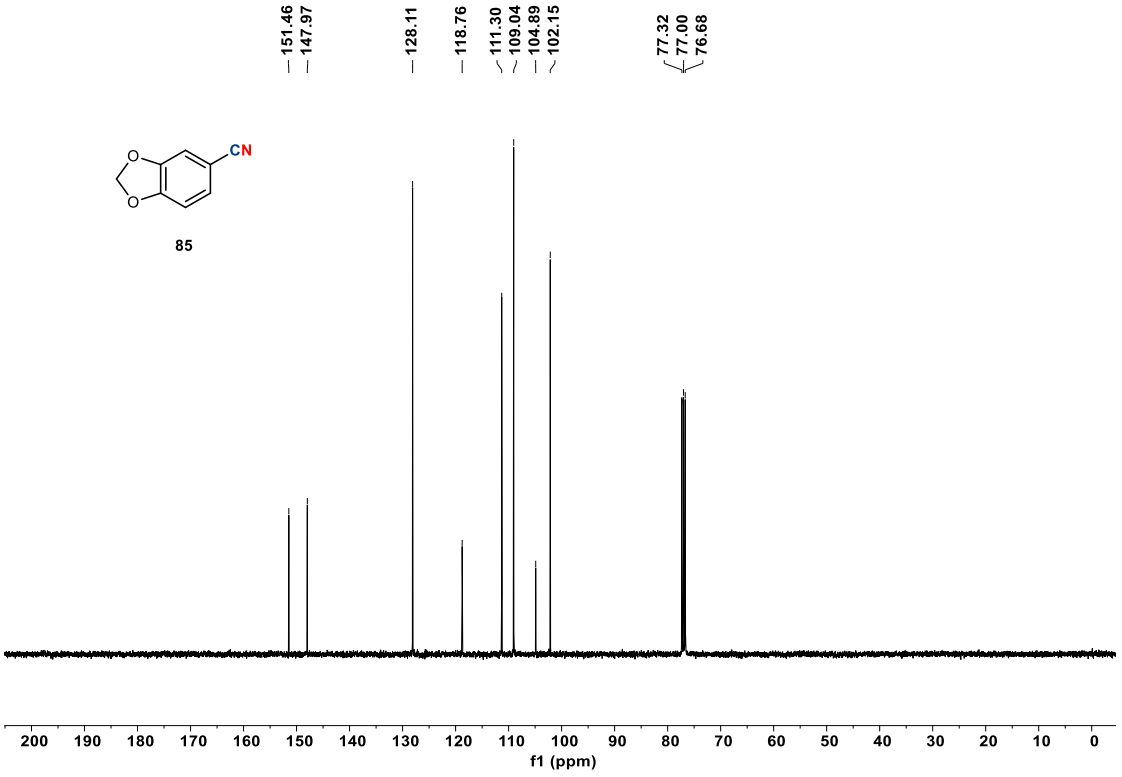

7.510
7.506
7.464
7.449
7.401
7.400
7.381
2.978
2.961
2.943
2.926
2.909
1.271
1.253
0.000
CN
83
2.75
1.01
1.00
6.34
f1 (ppm)

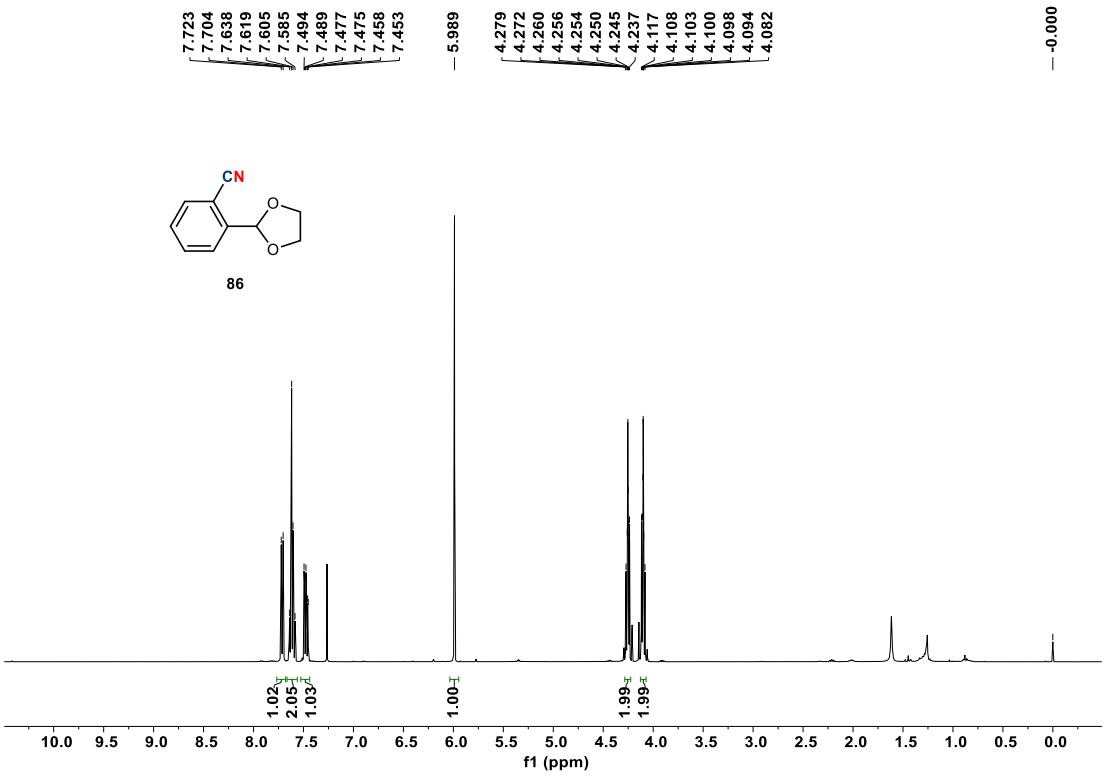

150.11
131.16
130.15
129.59
129.08
119.17
112.34
77.32
77.00
76.68
33.89
23.63
CN
83
f1 (ppm)

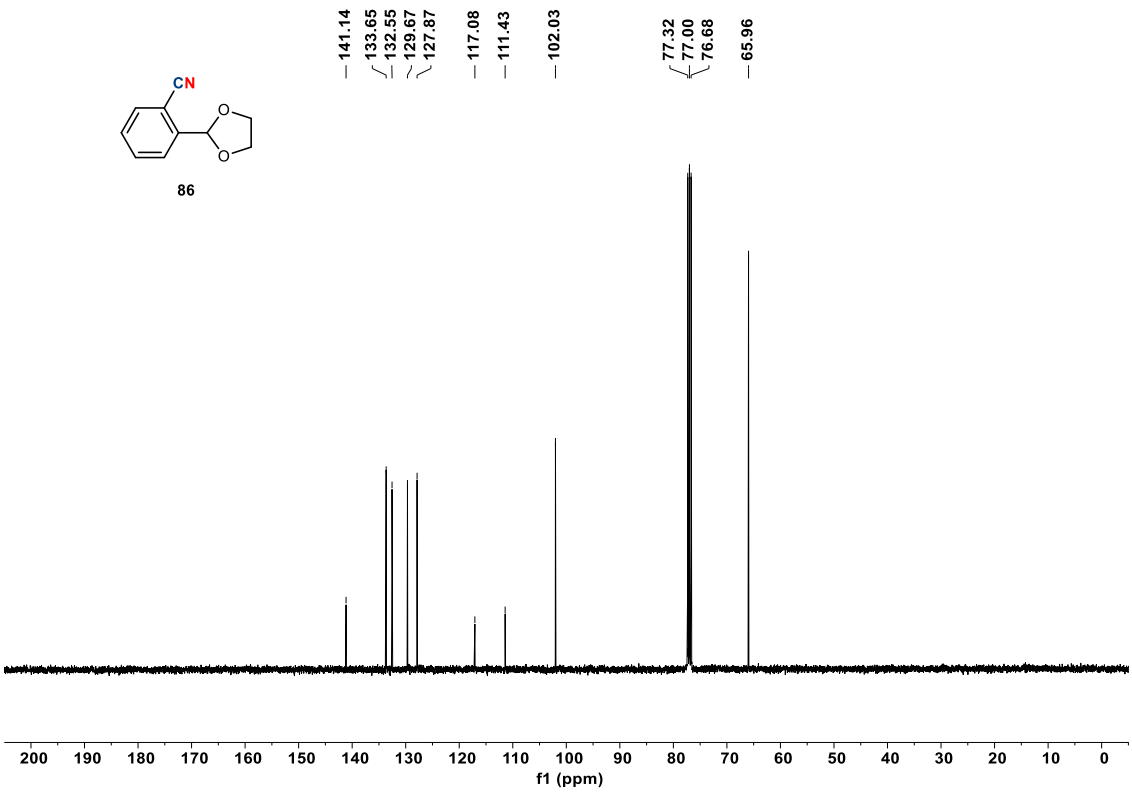

7.490
7.486
7.481
7.465
7.461
6.900
6.879
3.882
2.067
2.058
2.043
2.035
1.761
-0.000
CN
MeO
84
2.07
0.99
3.04
9.00
6.05
f1 (ppm)

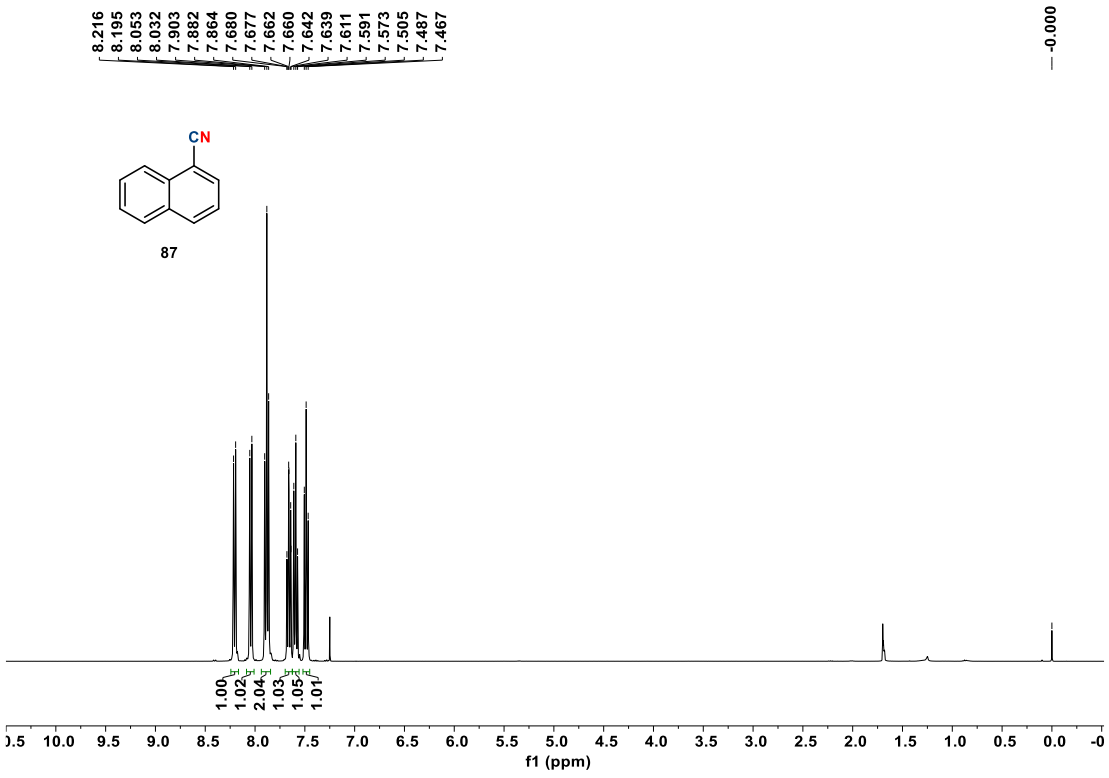

161.97
139.52
131.45
130.61
119.75
111.64
103.53
77.32
77.00
76.68
55.05
40.01
37.08
36.74
28.71
CN
MeO
84
f1 (ppm)

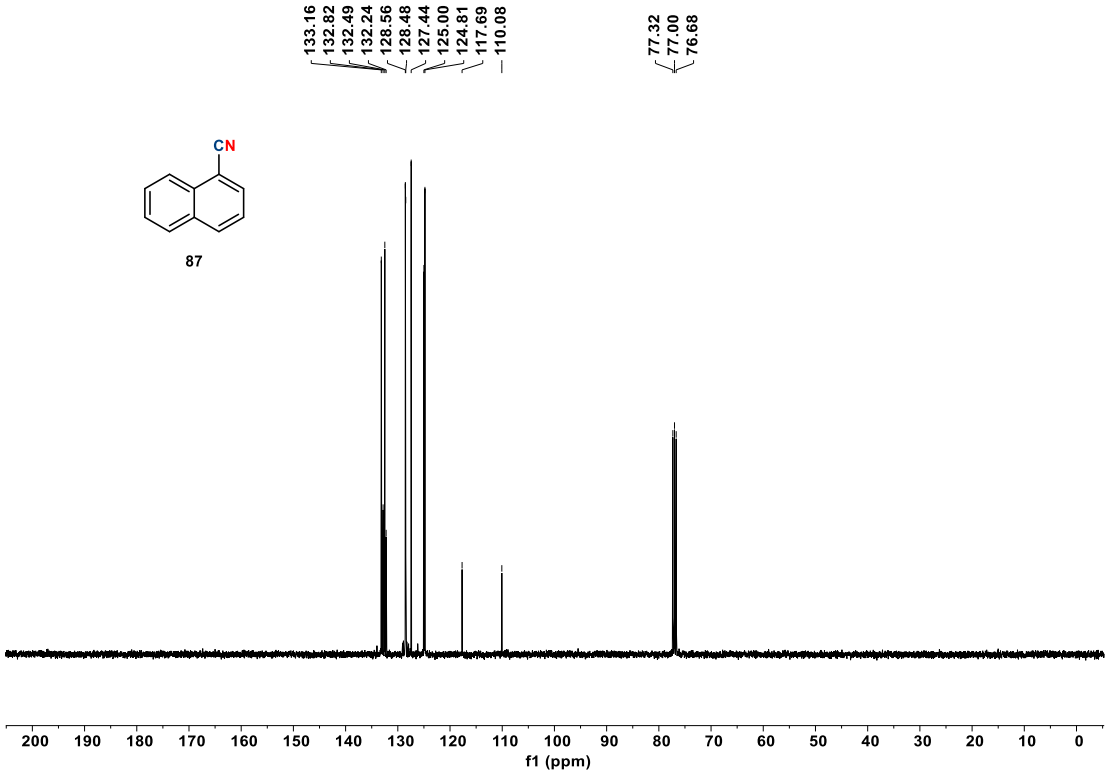

7.220
7.218
7.216
7.214
7.212
7.200
7.198
7.196
7.194
7.028
6.874
6.854
6.070
-0.000
CN
85
1.00
0.96
1.02
2.08
f1 (ppm)

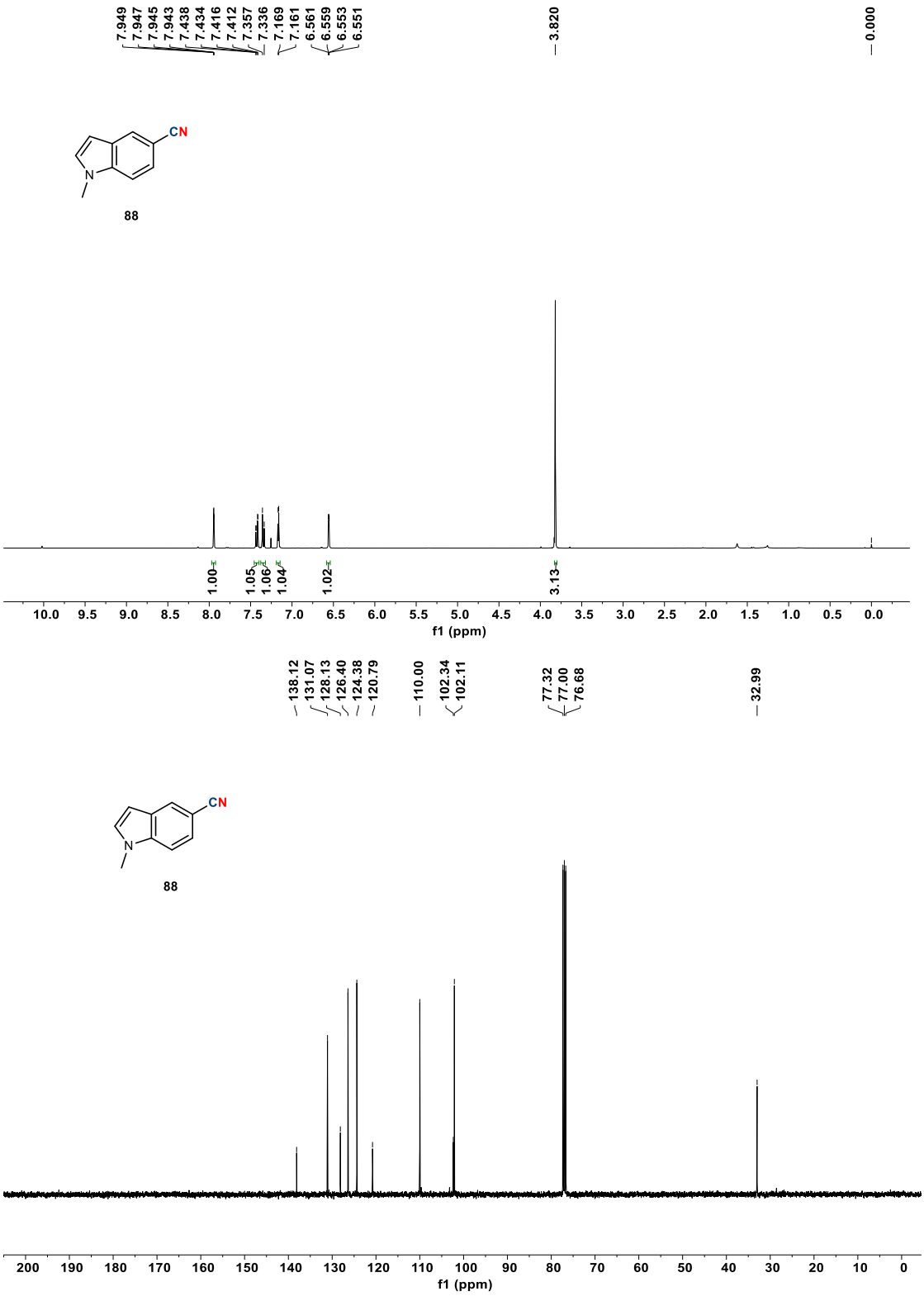

151.46
147.97
128.11
118.76
111.30
109.04
104.89
102.15
77.32
77.00
76.68
CN
85
f1 (ppm)

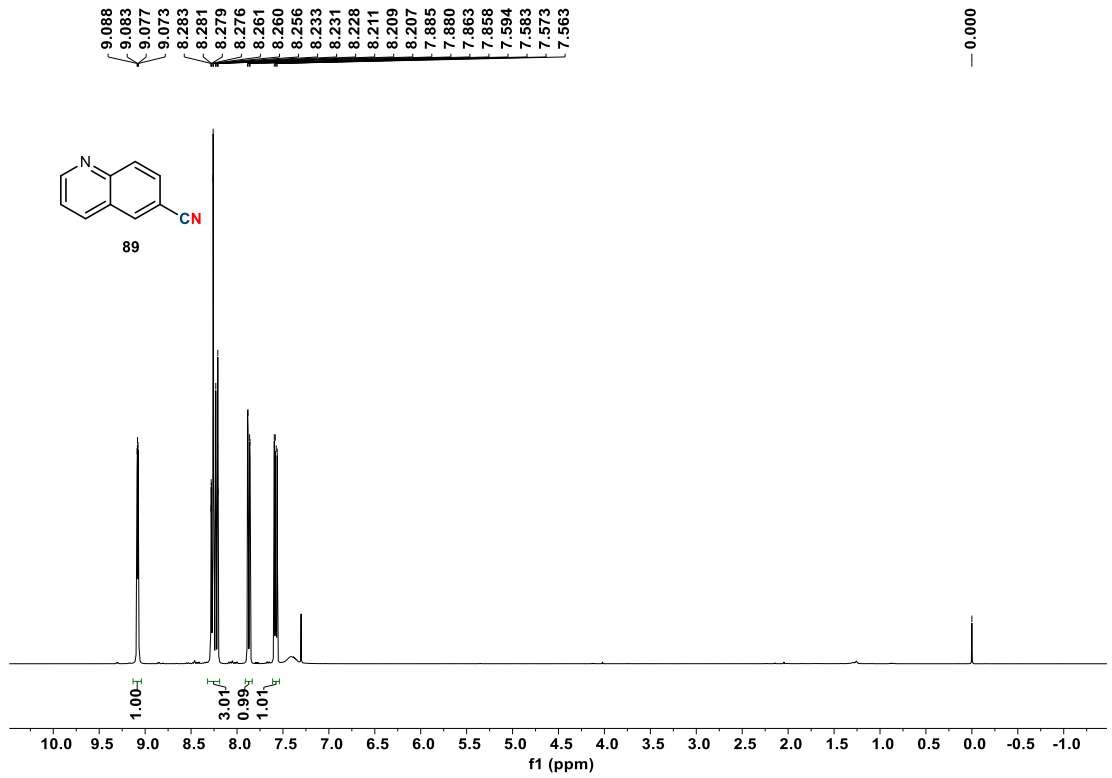

7.723
7.704
7.638
7.619
7.605
7.585
7.494
7.489
7.477
7.475
7.458
7.453
5.989
4.279
4.272
4.260
4.256
4.254
4.250
4.245
4.237
4.117
4.108
4.103
4.100
4.098
4.094
4.082
-0.000
CN
O
O
86
1.02
2.05
1.03
1.00
1.99
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

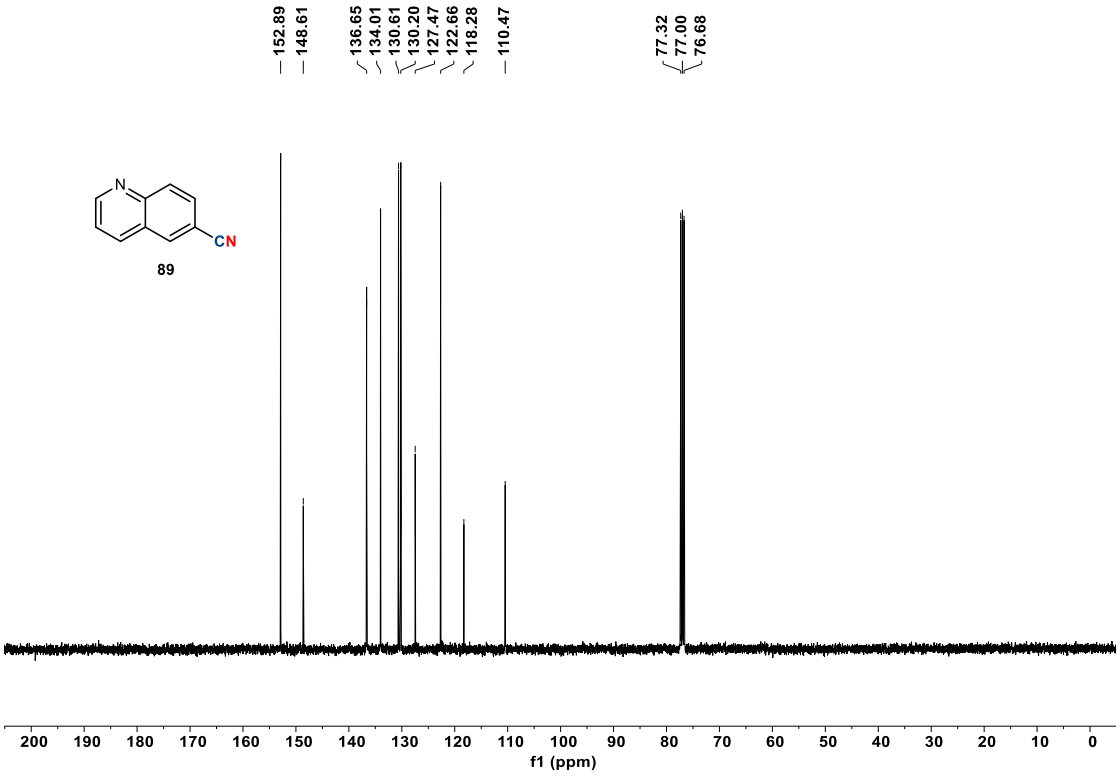

141.14
133.65
132.55
129.67
127.87
117.08
111.43
102.03
77.32
77.00
76.68
65.96
CN
O
O
86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

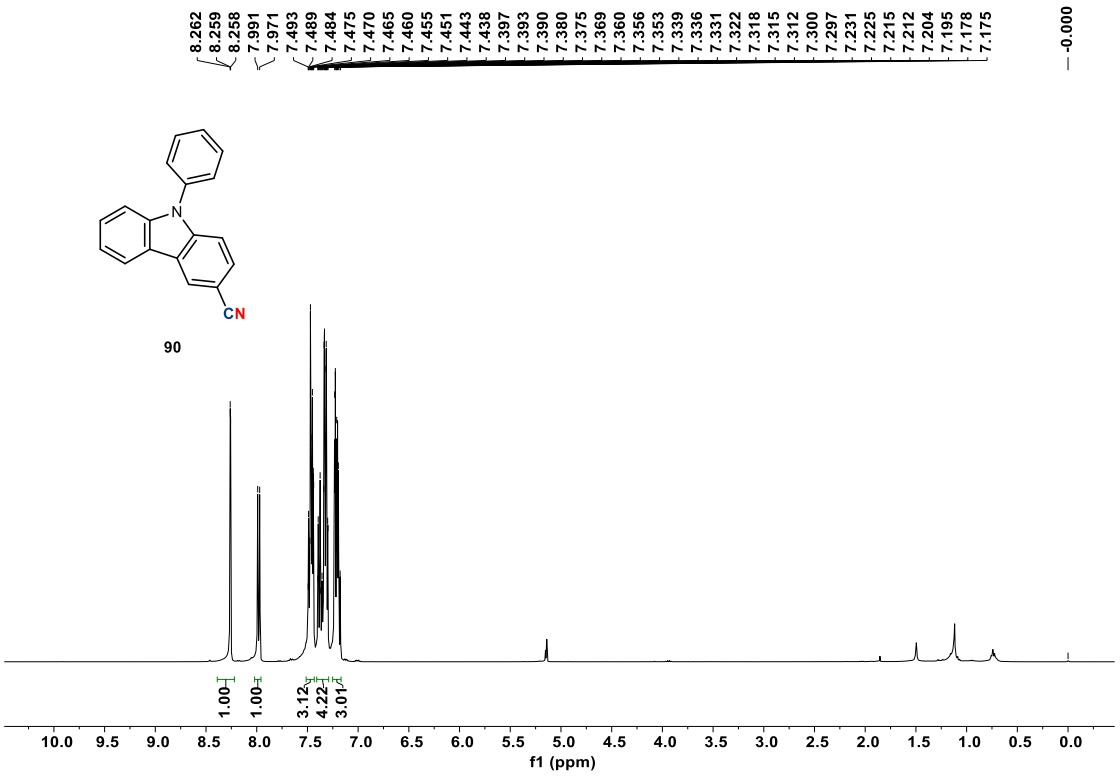

8.216
8.195
8.053
8.032
7.903
7.882
7.864
7.680
7.677
7.662
7.660
7.642
7.639
7.611
7.591
7.573
7.505
7.487
7.467
-0.000
CN
87
1.00
1.02
2.04
1.03
1.05
1.01
f1 (ppm)

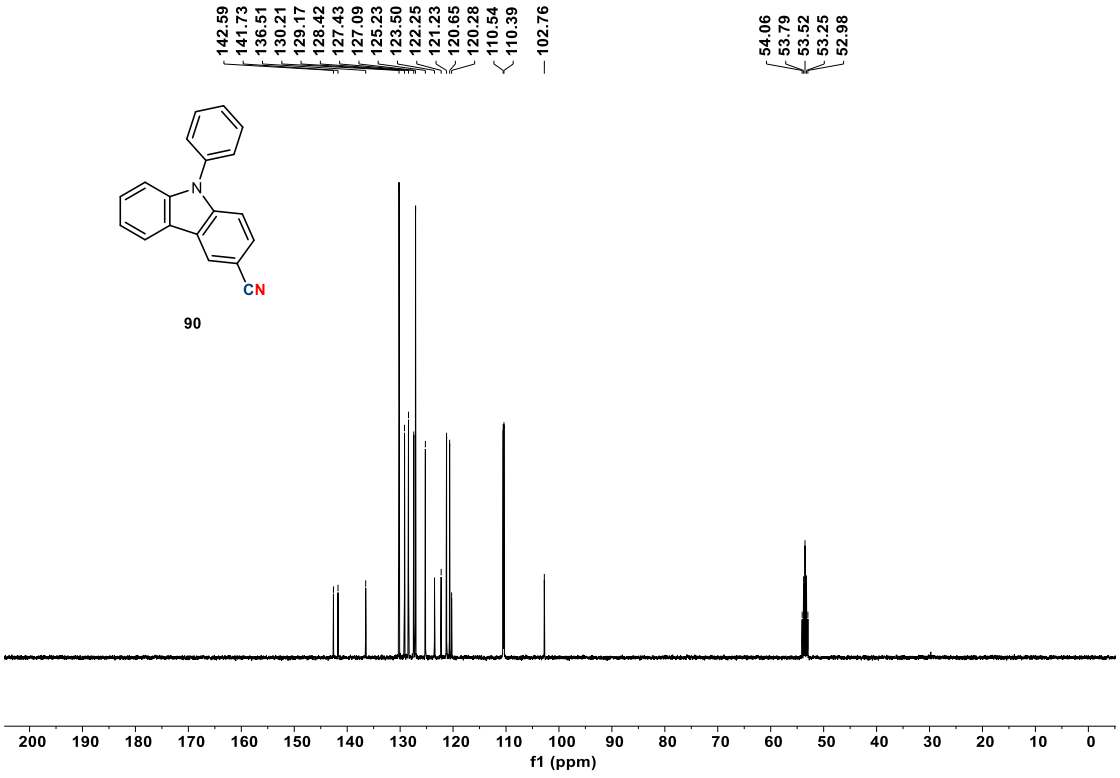

133.16
132.82
132.49
132.24
128.56
128.48
127.44
125.00
124.81
117.69
110.08
77.32
77.00
76.68
CN
87
f1 (ppm)

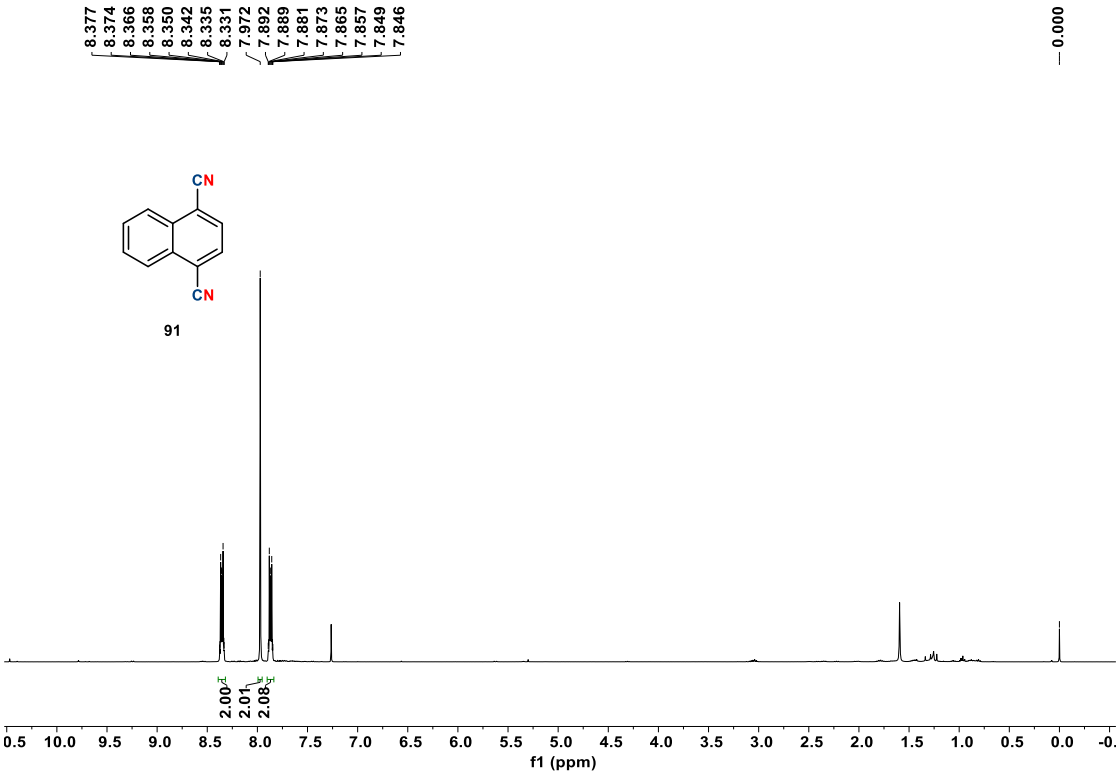

7.949
7.947
7.945
7.943
7.438
7.434
7.416
7.412
7.357
7.336
7.169
7.161
6.561
6.559
6.553
6.551
3.820
0.000
CN
N
88
1.00
1.05
1.06
1.04
1.02
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
138.12
131.07
128.13
126.40
124.38
120.79
110.00
102.34
102.11
77.32
77.00
76.68
32.99
CN
N
88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

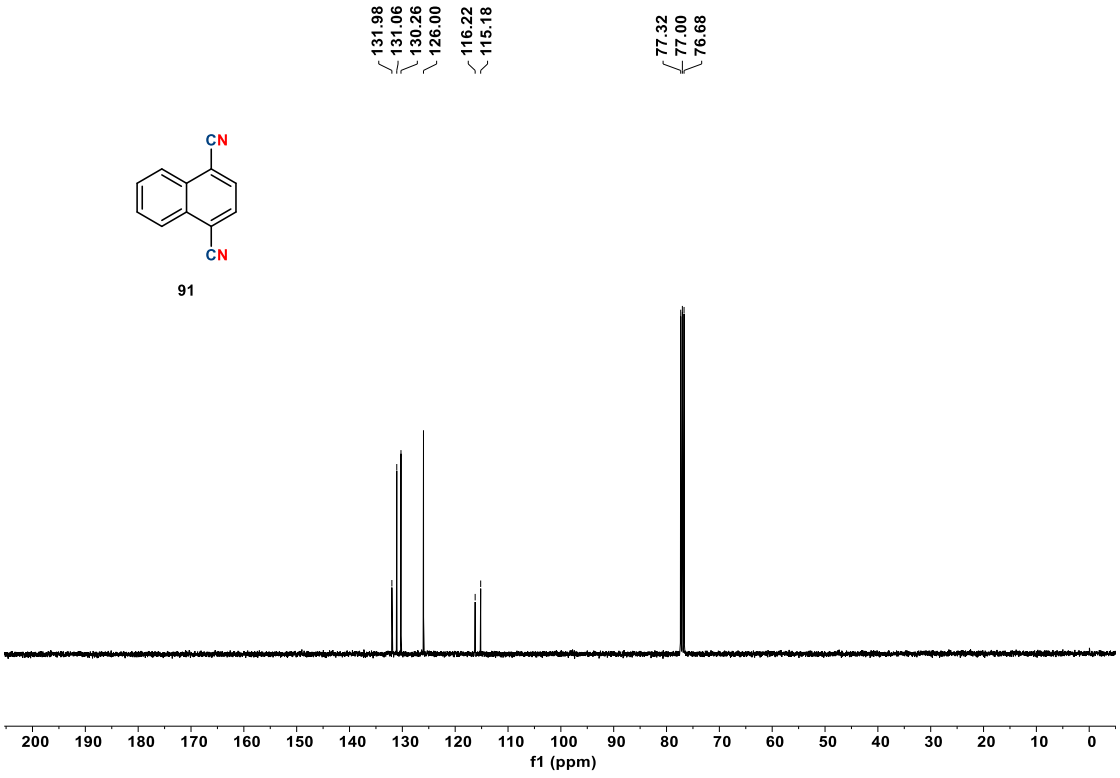

9.088
9.083
9.077
9.073
8.283
8.281
8.279
8.276
8.261
8.260
8.256
8.233
8.231
8.228
8.211
8.209
8.207
7.885
7.880
7.863
7.858
7.594
7.583
7.573
7.563
0.000
N
CN
89
1.00
3.01
0.99
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

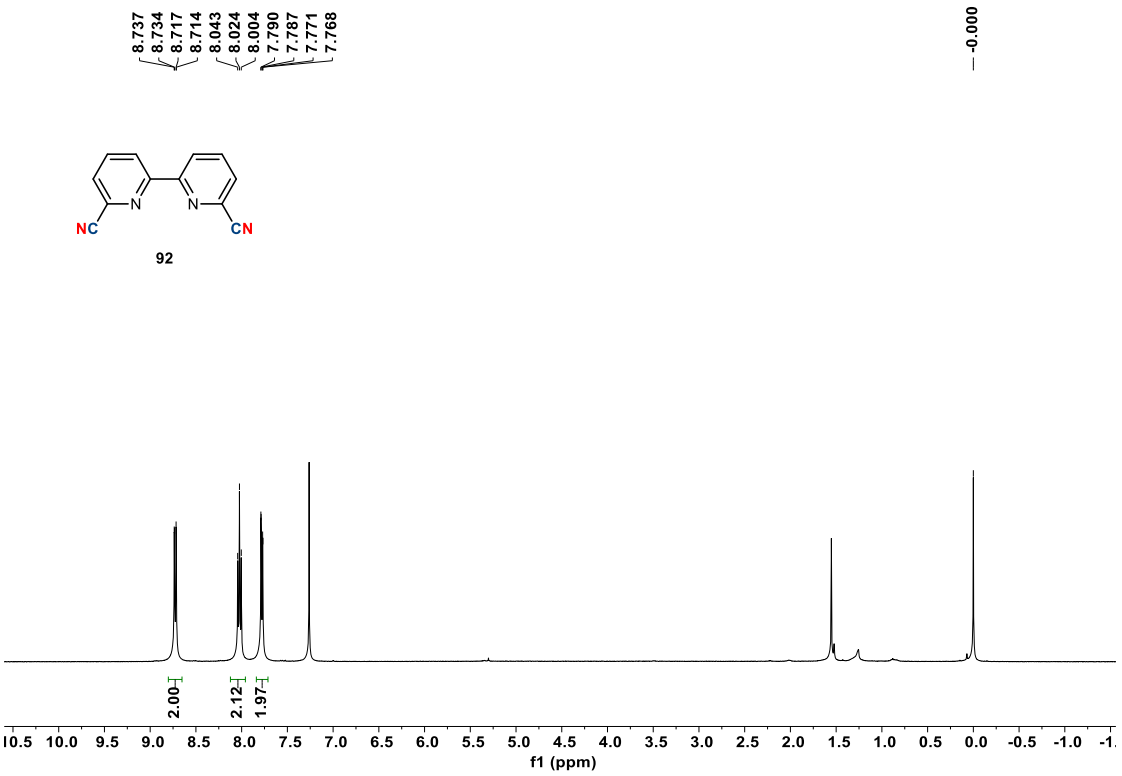

152.89
148.61
136.65
134.01
130.61
130.20
127.47
122.66
118.28
110.47
77.32
77.00
76.68
N
CN
89
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

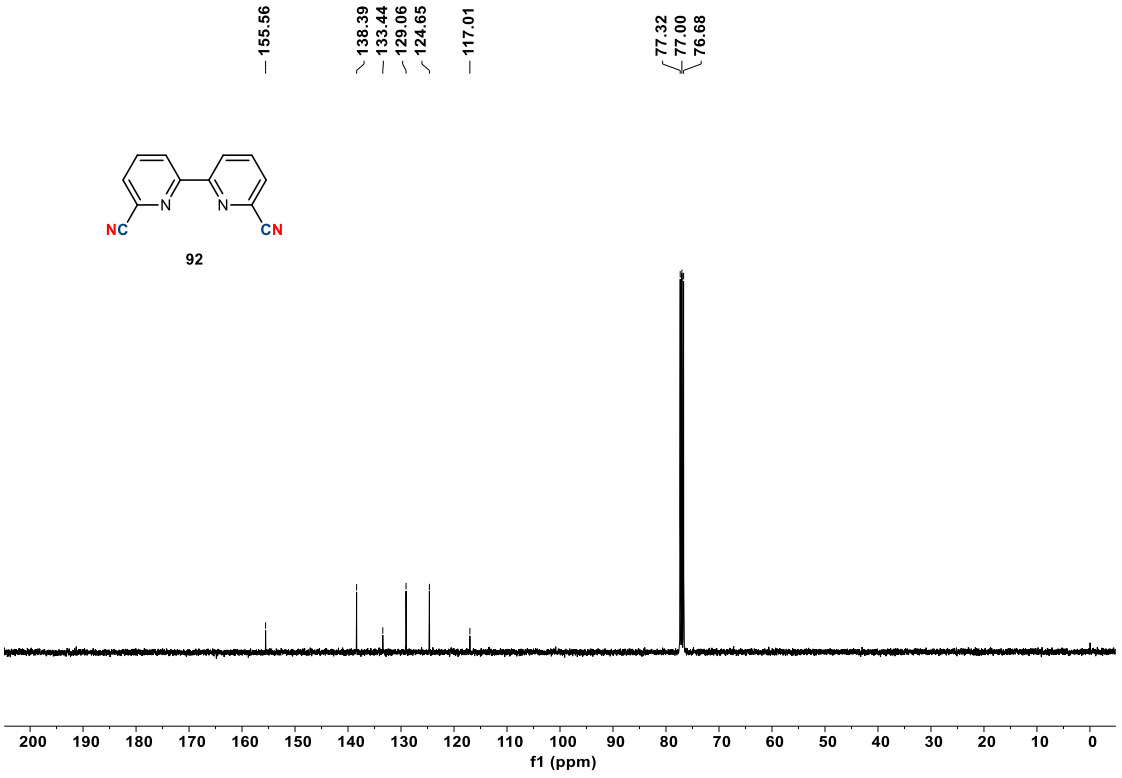

8.262
8.259
8.258
7.991
7.971
7.493
7.489
7.484
7.475
7.470
7.465
7.460
7.455
7.451
7.443
7.438
7.397
7.393
7.390
7.380
7.375
7.369
7.360
7.356
7.353
7.339
7.336
7.331
7.322
7.318
7.315
7.312
7.300
7.297
7.231
7.225
7.215
7.212
7.204
7.195
7.178
7.175
-0.000
N
CN
90
1.00
1.00
3.12
4.22
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

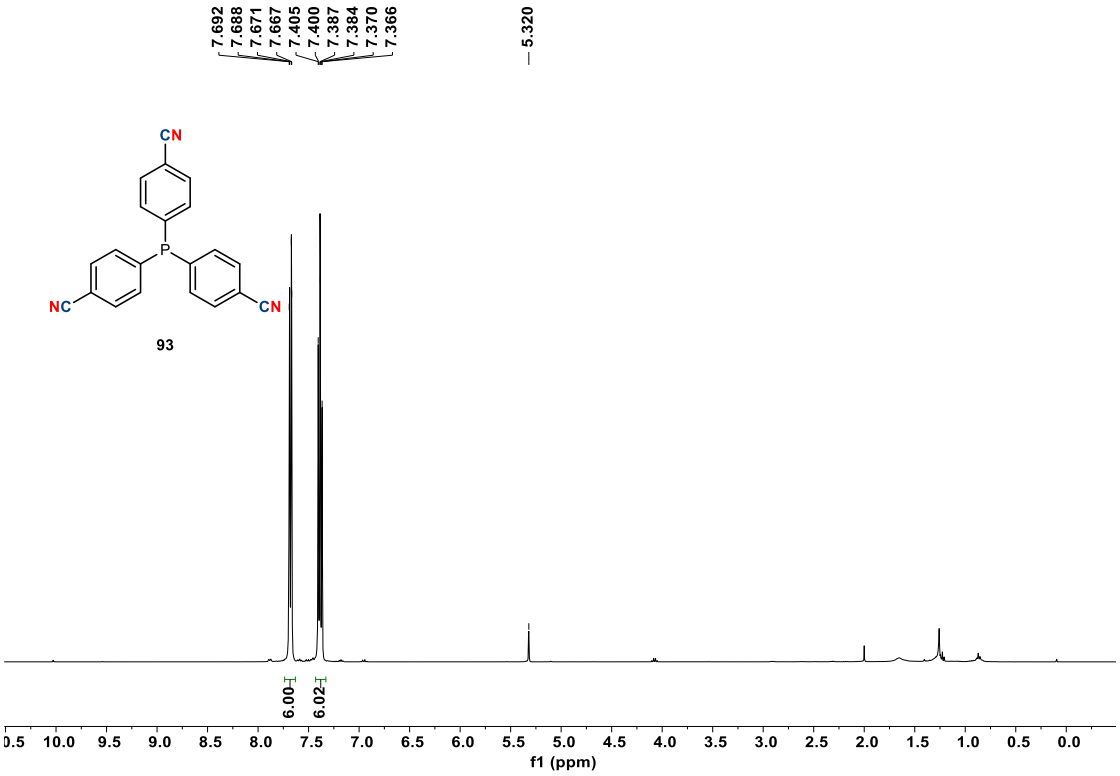

142.59
141.73
136.51
130.21
129.17
128.42
127.43
127.09
125.23
123.50
122.25
121.23
120.65
120.28
110.54
110.39
102.76
54.06
53.79
53.52
53.25
52.98
N
CN
90
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

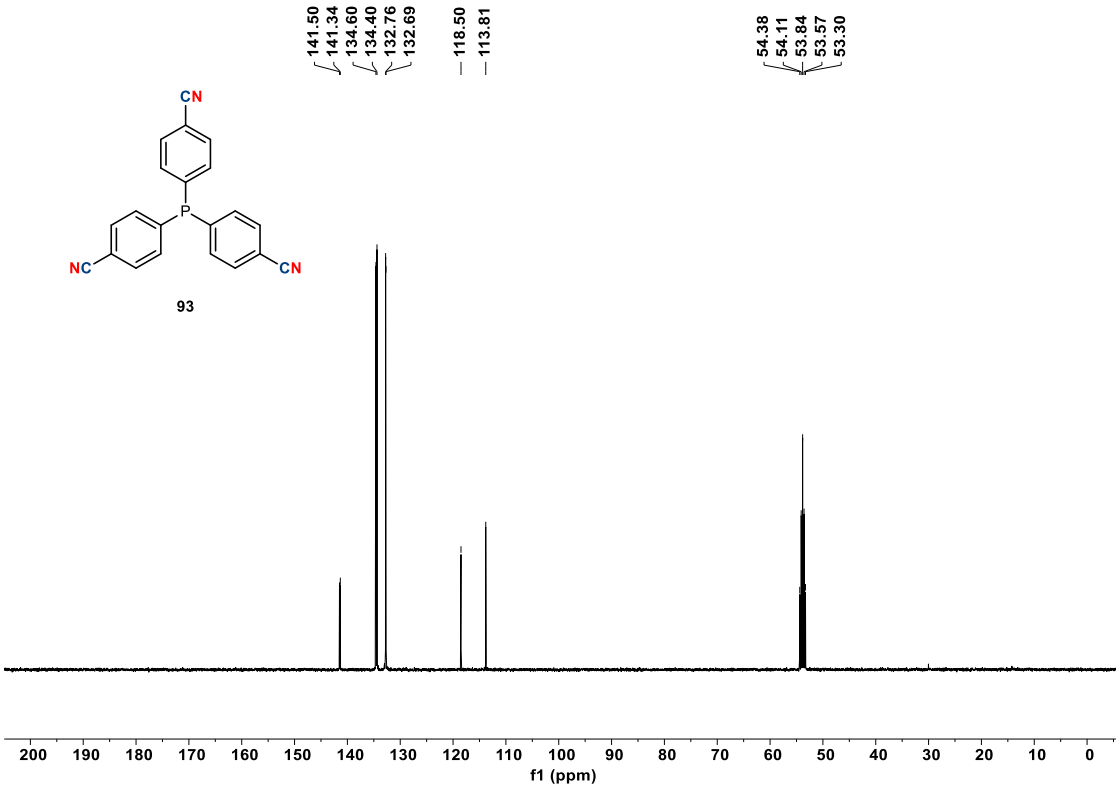

8.377
8.374
8.366
8.358
8.350
8.342
8.335
8.331
7.972
7.892
7.889
7.881
7.873
7.865
7.857
7.849
7.846
0.000
CN
CN
91
2.00
2.01
2.08
f1 (ppm)

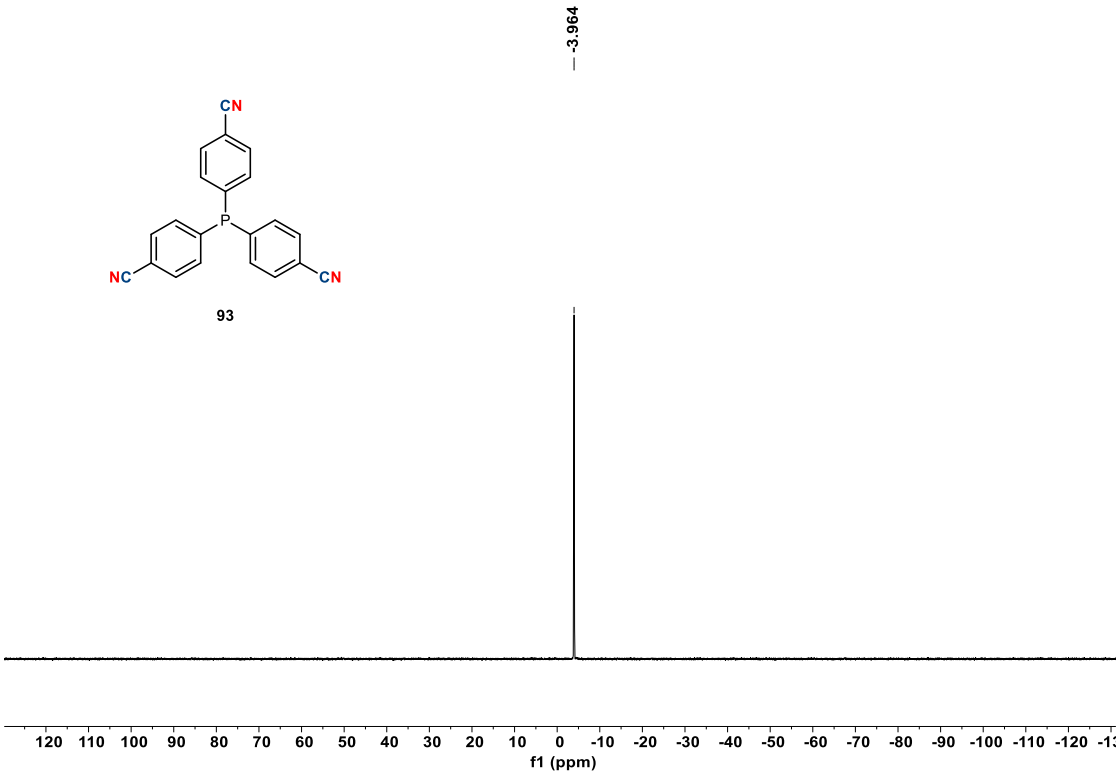

131.98
131.06
130.26
126.00
116.22
115.18
77.32
77.00
76.68
CN
CN
91
f1 (ppm)


8.737
8.734
8.717
8.714
8.043
8.024
8.004
7.790
7.787
7.771
7.768
-0.000
NC
CN
92
2.00
2.12
1.97
f1 (ppm)

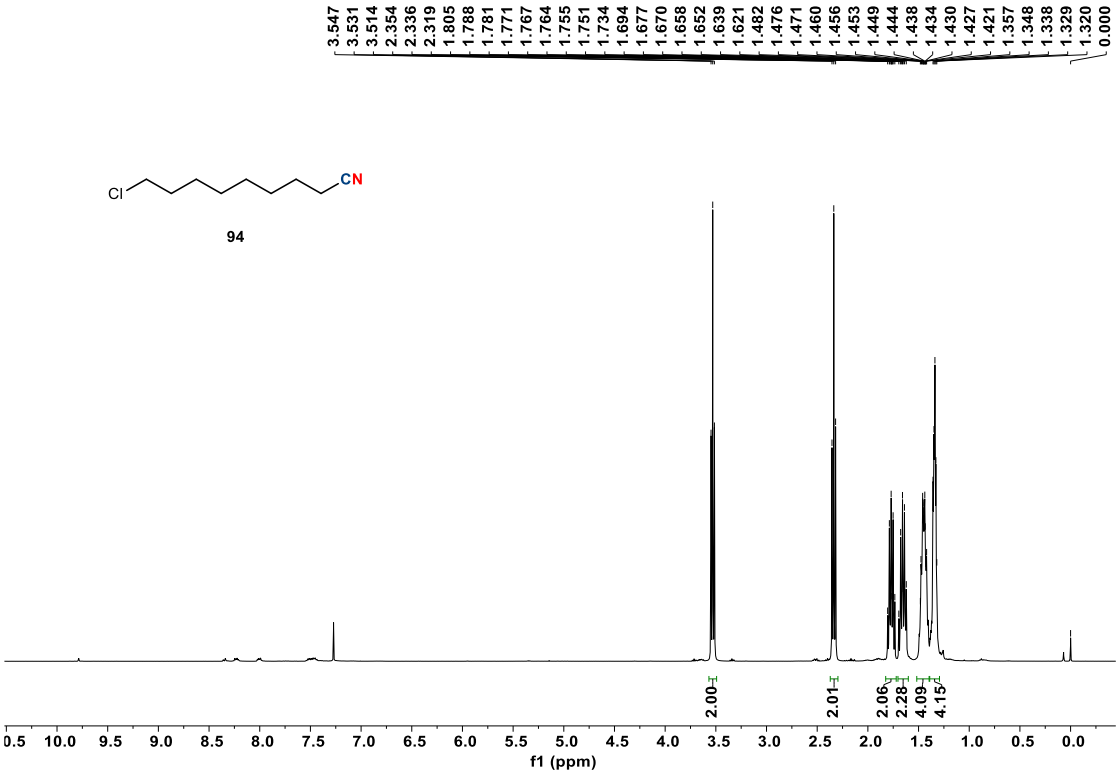

155.56
138.39
133.44
129.06
124.65
117.01
77.32
77.00
76.68
NC
CN
92
f1 (ppm)

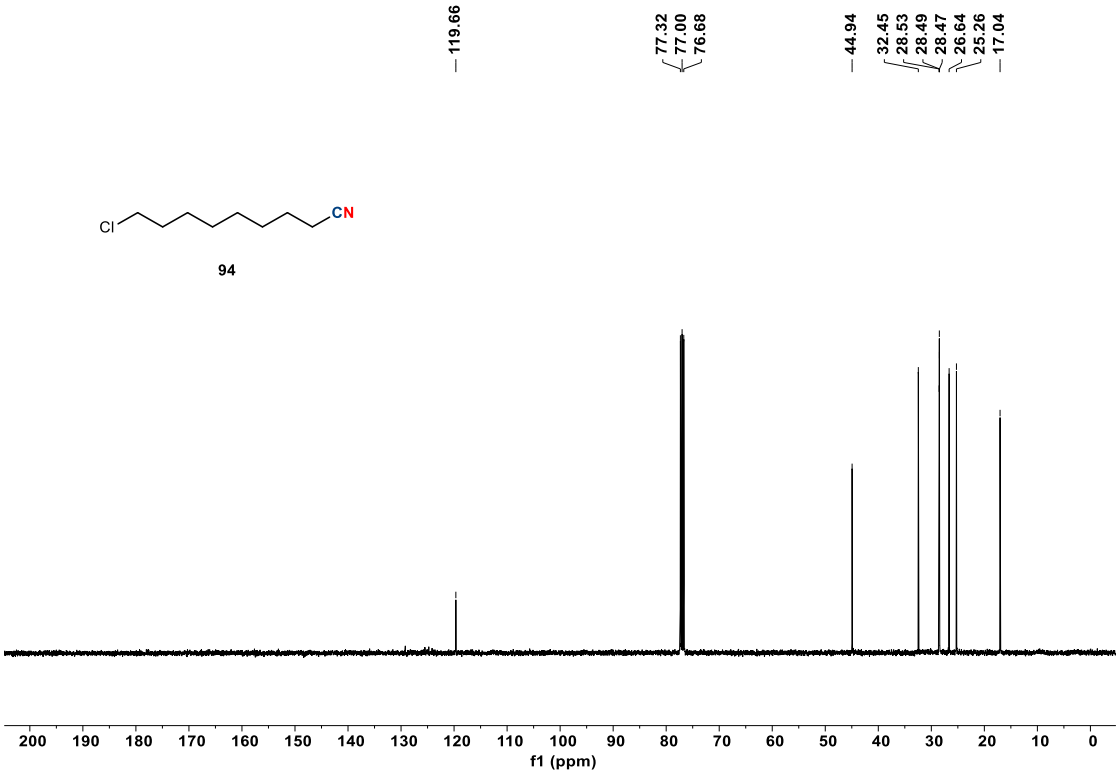

7.692
7.688
7.671
7.667
7.405
7.400
7.387
7.384
7.370
7.366
5.320
CN
NC
CN
P
93
6.00
6.02
f1 (ppm)

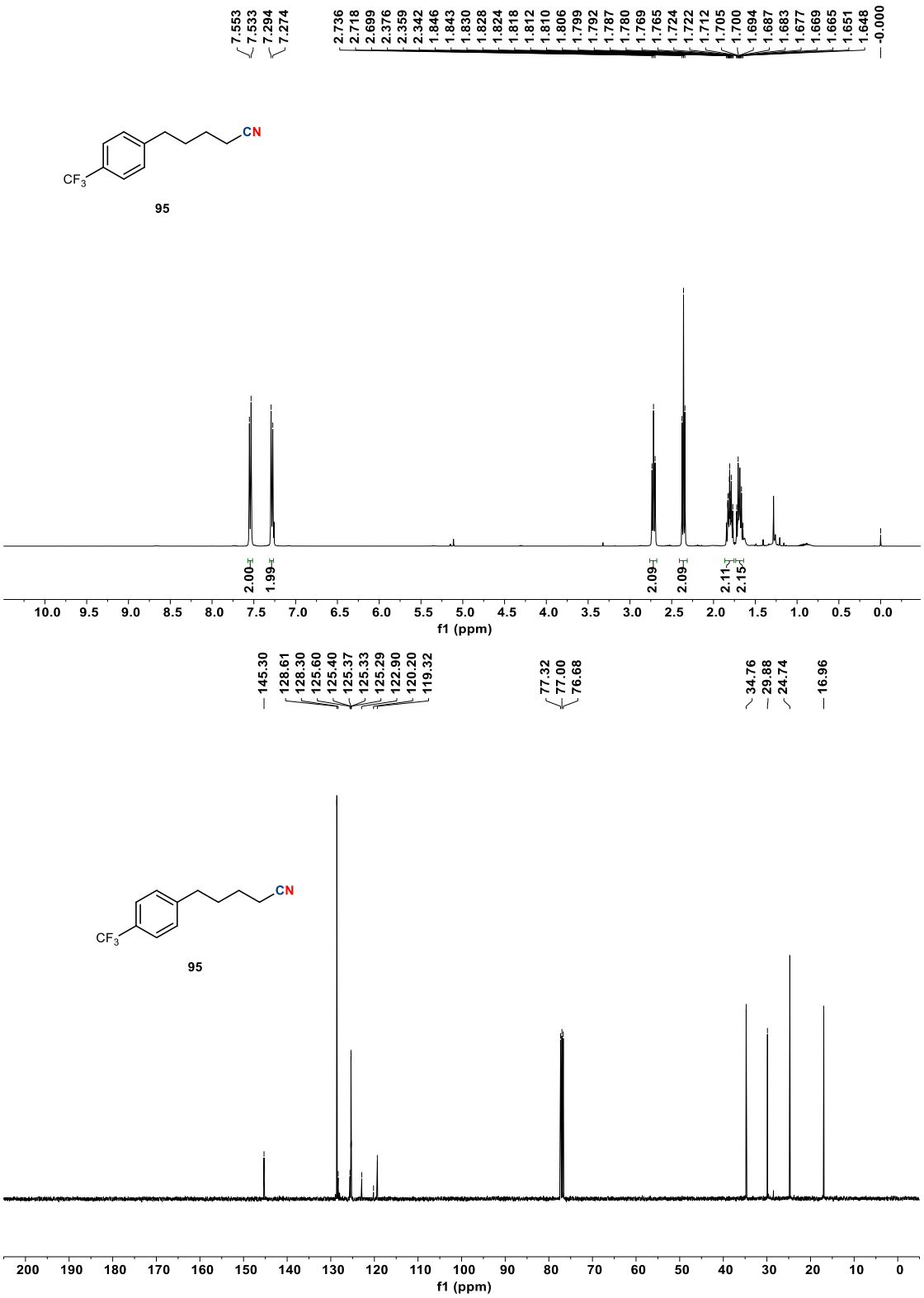

141.50
141.34
134.60
134.40
132.76
132.69
118.50
113.81
54.38
54.11
53.84
53.57
53.30
CN
NC
CN
P
93
f1 (ppm)

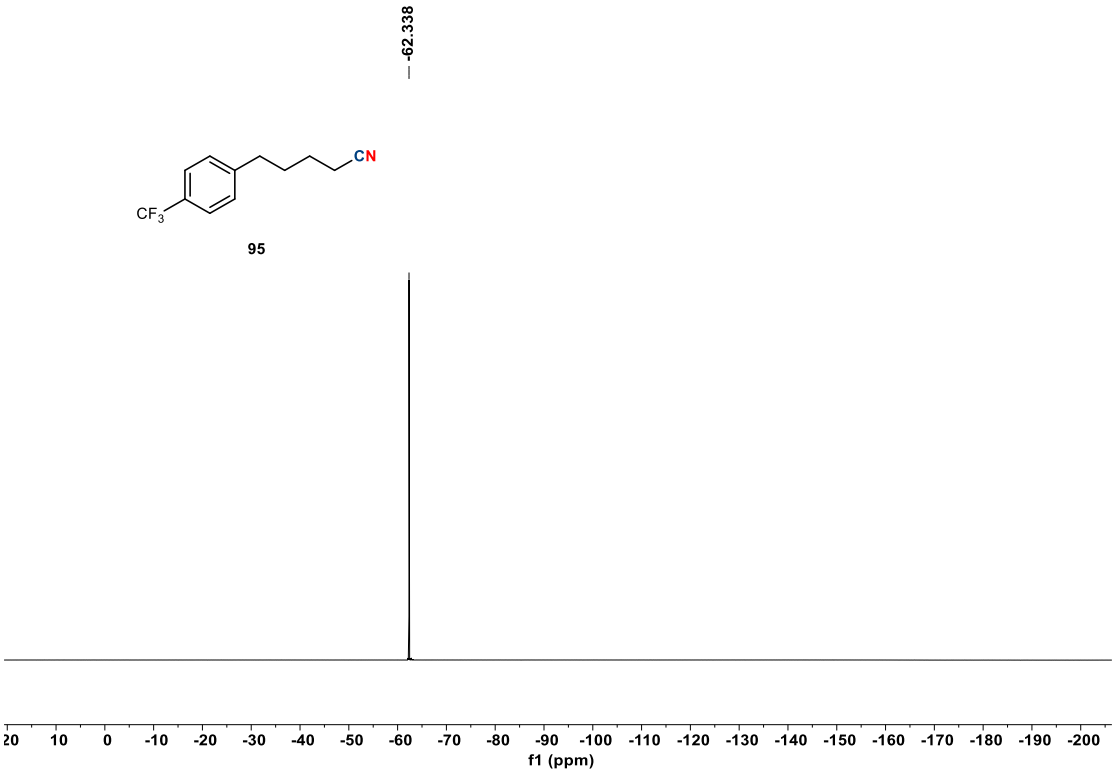


^{31}P NMR of nitrile 93

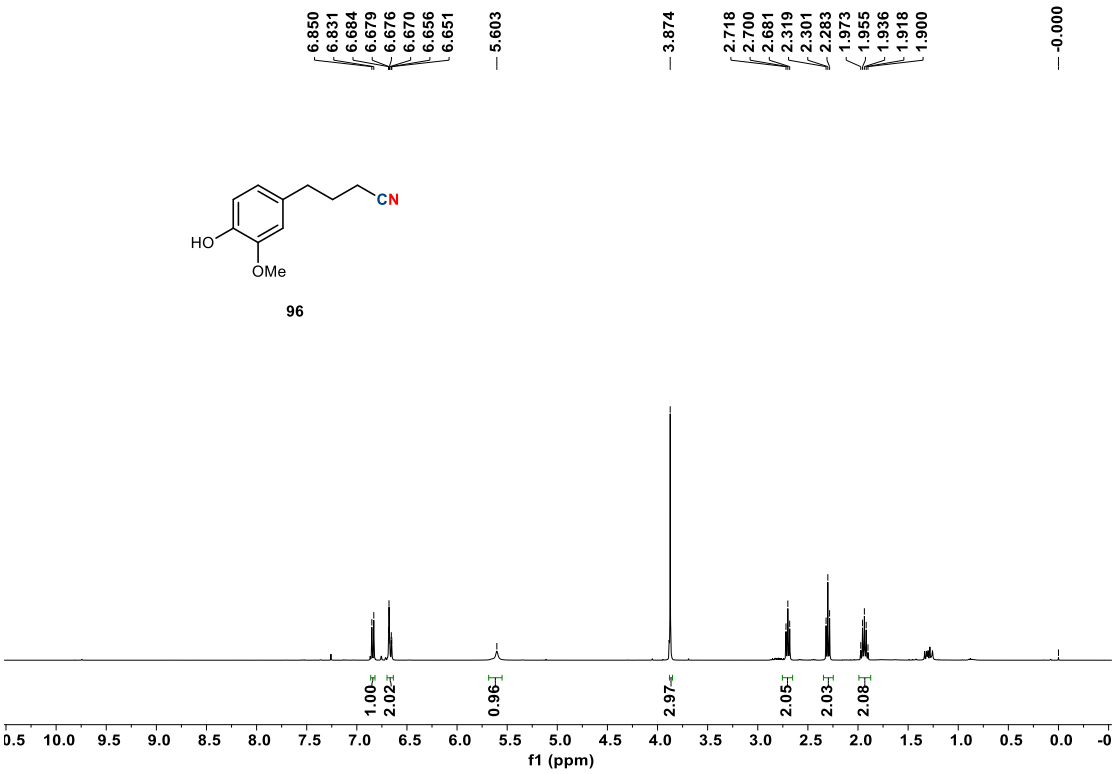

3.547
3.531
3.514
2.354
2.336
2.319
1.805
1.788
1.781
1.771
1.767
1.764
1.755
1.751
1.734
1.694
1.677
1.670
1.658
1.652
1.639
1.621
1.482
1.476
1.471
1.460
1.456
1.453
1.449
1.444
1.438
1.434
1.430
1.427
1.421
1.357
1.348
1.338
1.329
1.320
0.000
Cl
CN
94
2.00
2.01
2.06
2.28
4.09
4.15
f1 (ppm)

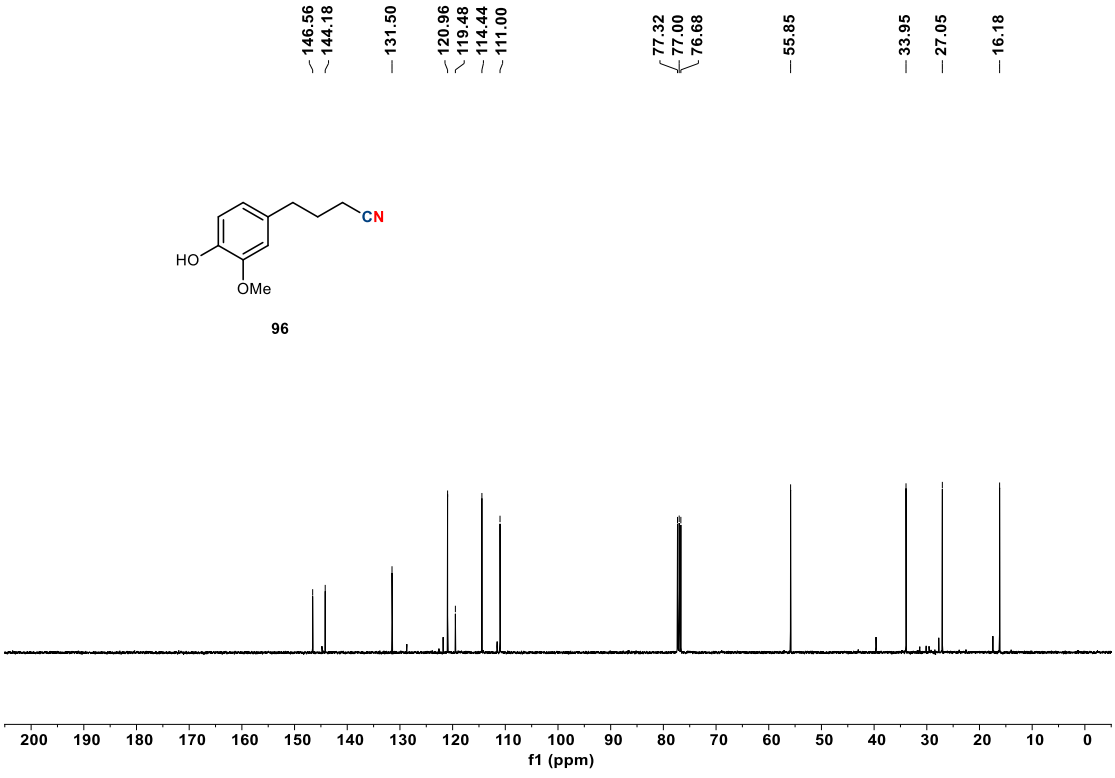

119.66
77.32
77.00
76.68
44.94
32.45
28.53
28.49
28.47
26.64
25.26
17.04
Cl
CN
94
f1 (ppm)

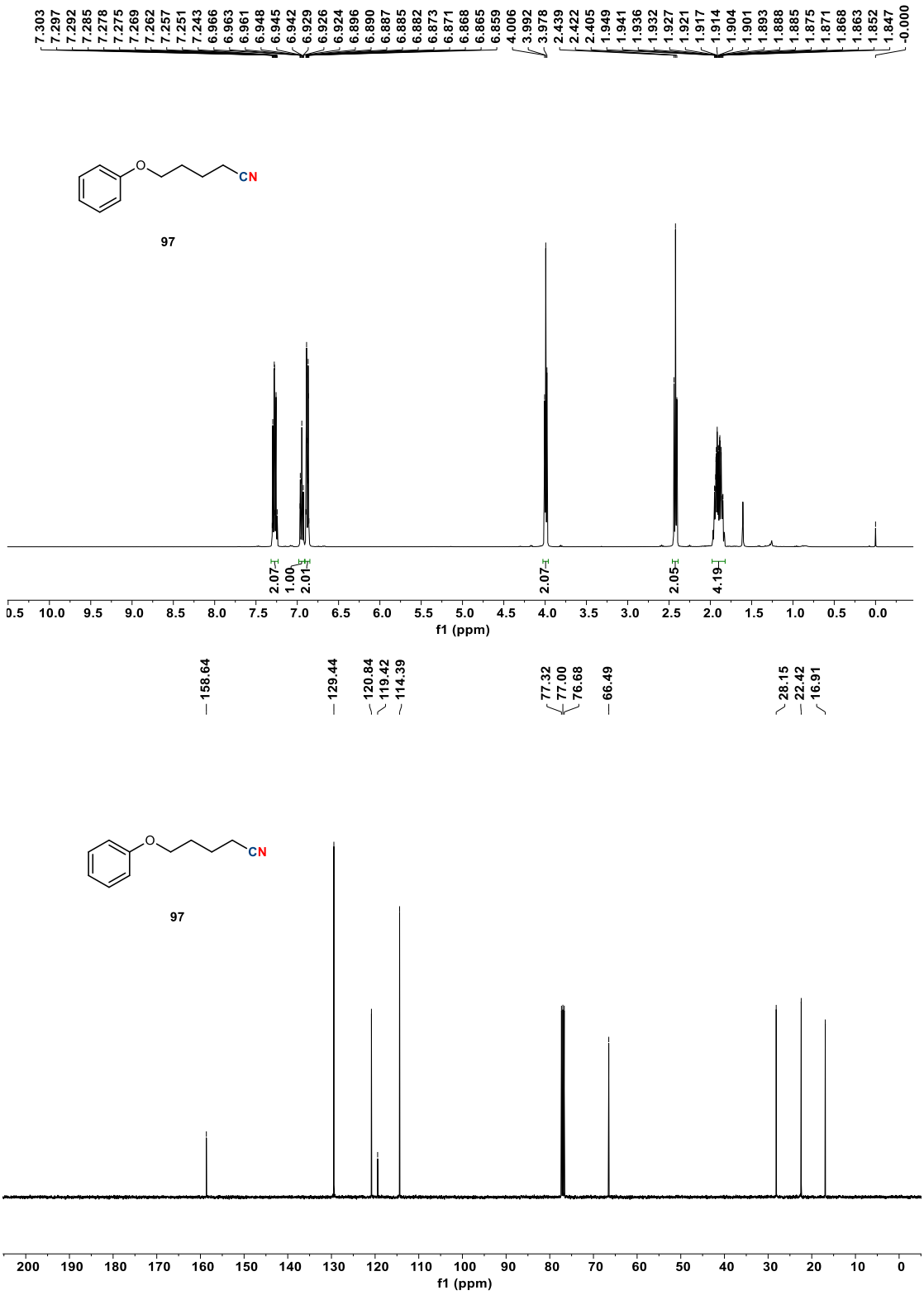

7.553
7.533
7.294
7.274
2.736
2.718
2.699
2.376
2.359
2.342
1.846
1.843
1.830
1.828
1.824
1.818
1.812
1.810
1.806
1.799
1.792
1.787
1.780
1.769
1.765
1.724
1.722
1.712
1.705
1.700
1.694
1.687
1.683
1.677
1.669
1.665
1.651
1.648
-0.000
CN
CF3
95
2.00
1.99
2.09
2.09
2.11
2.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
145.30
128.61
128.30
125.60
125.40
125.37
125.33
125.29
122.90
120.20
119.32
77.32
77.00
76.68
34.76
29.88
24.74
16.96
CN
CF3
95
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

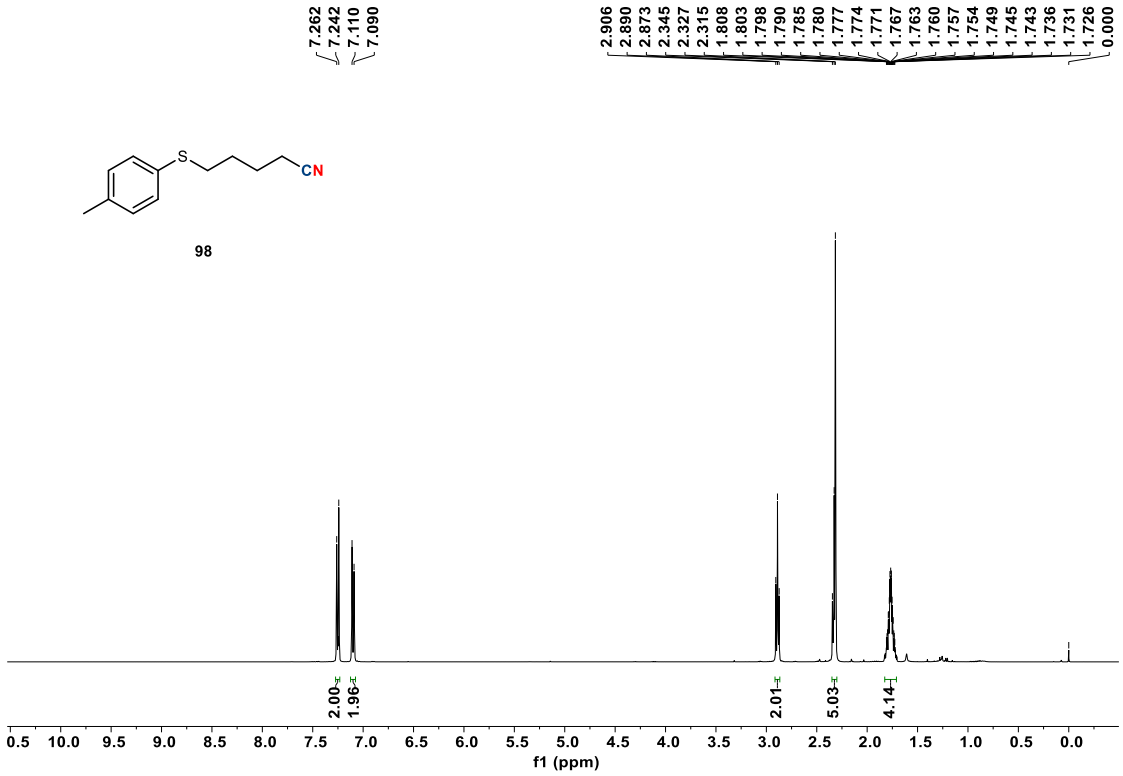


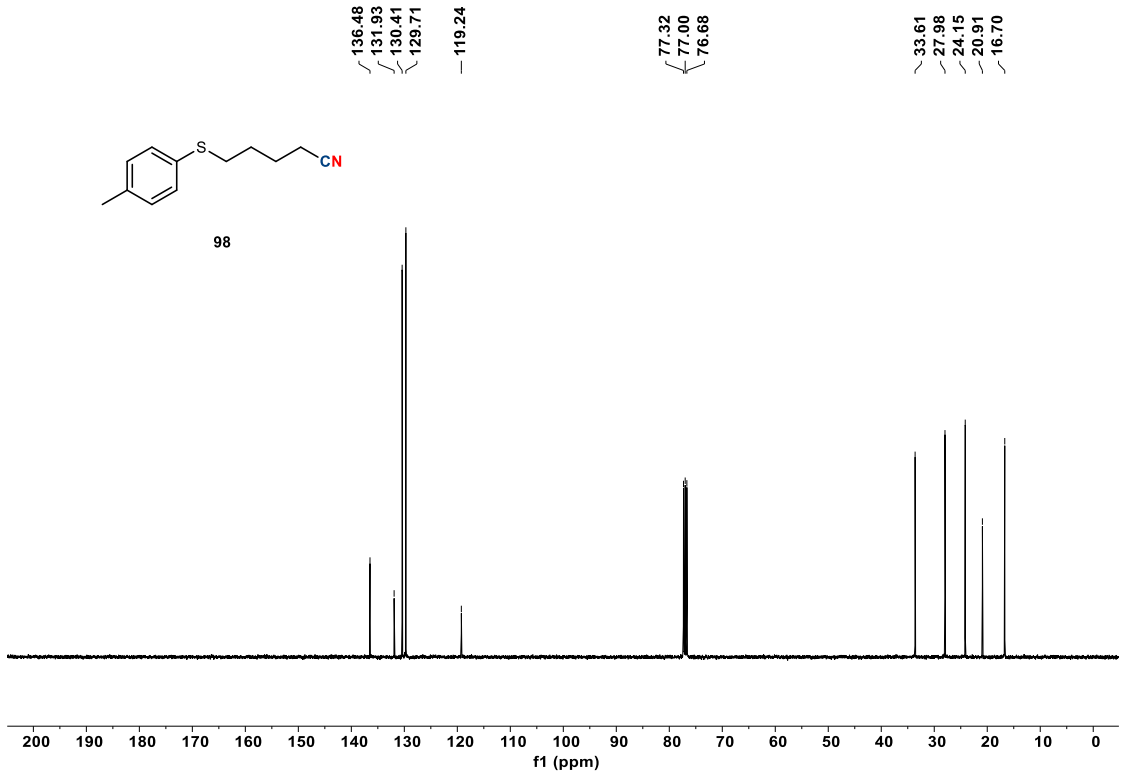
^{19}F NMR of nitrile 95

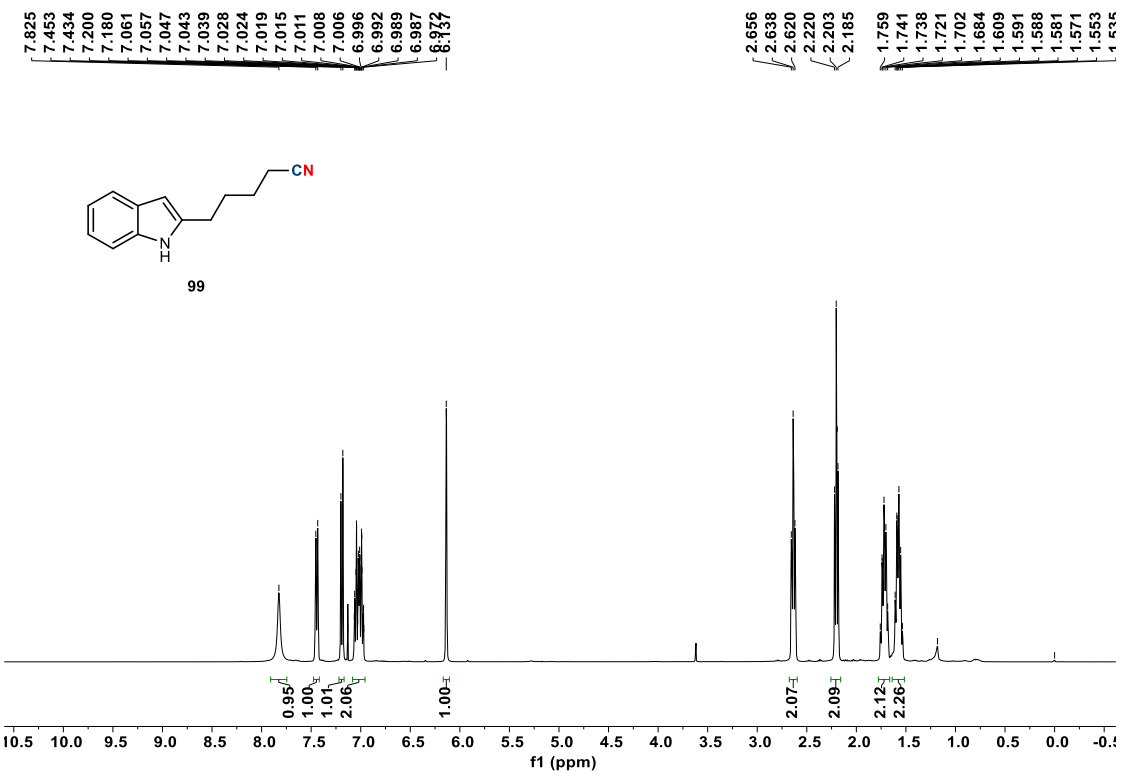

6.850
6.831
6.684
6.679
6.676
6.670
6.656
6.651
5.603
3.874
2.718
2.700
2.681
2.319
2.301
2.283
1.973
1.955
1.936
1.918
1.900
-0.000
CN
HO
OMe
96
1.00
2.02
0.96
2.97
2.05
2.03
2.08
f1 (ppm)

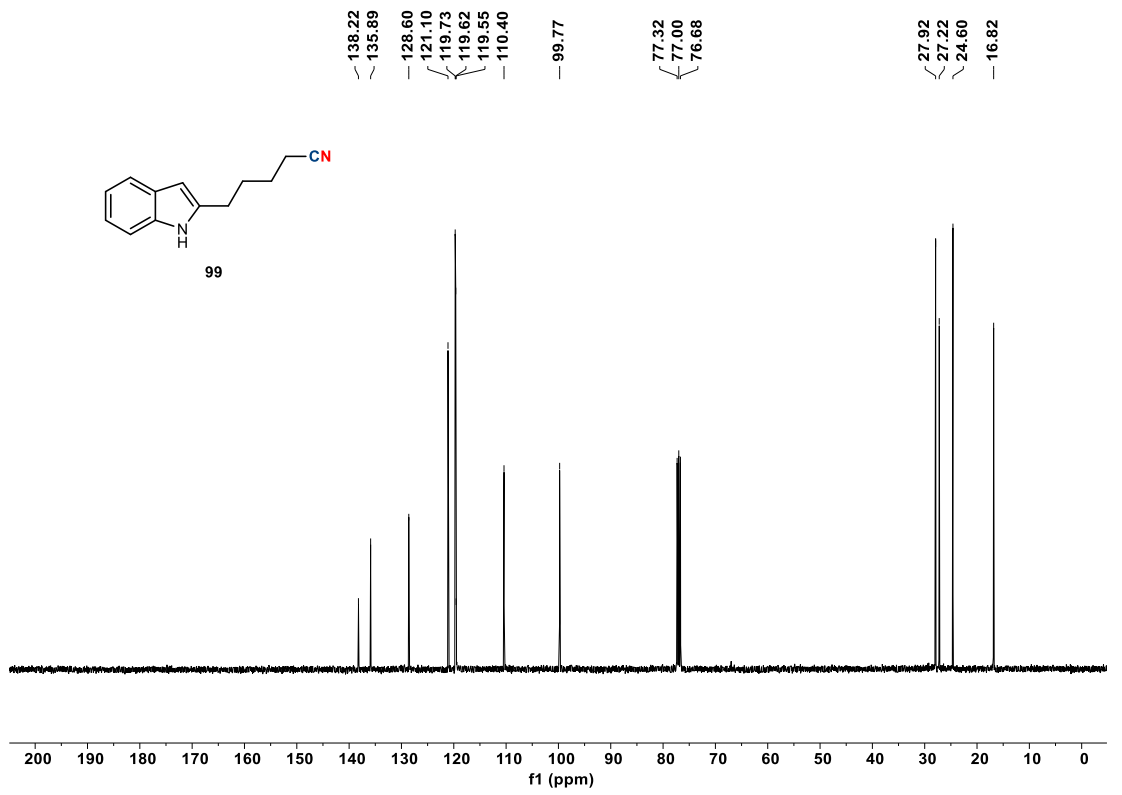

146.56
144.18
131.50
120.96
119.48
114.44
111.00
77.32
77.00
76.68
55.85
33.95
27.05
16.18
CN
HO
OMe
96
f1 (ppm)

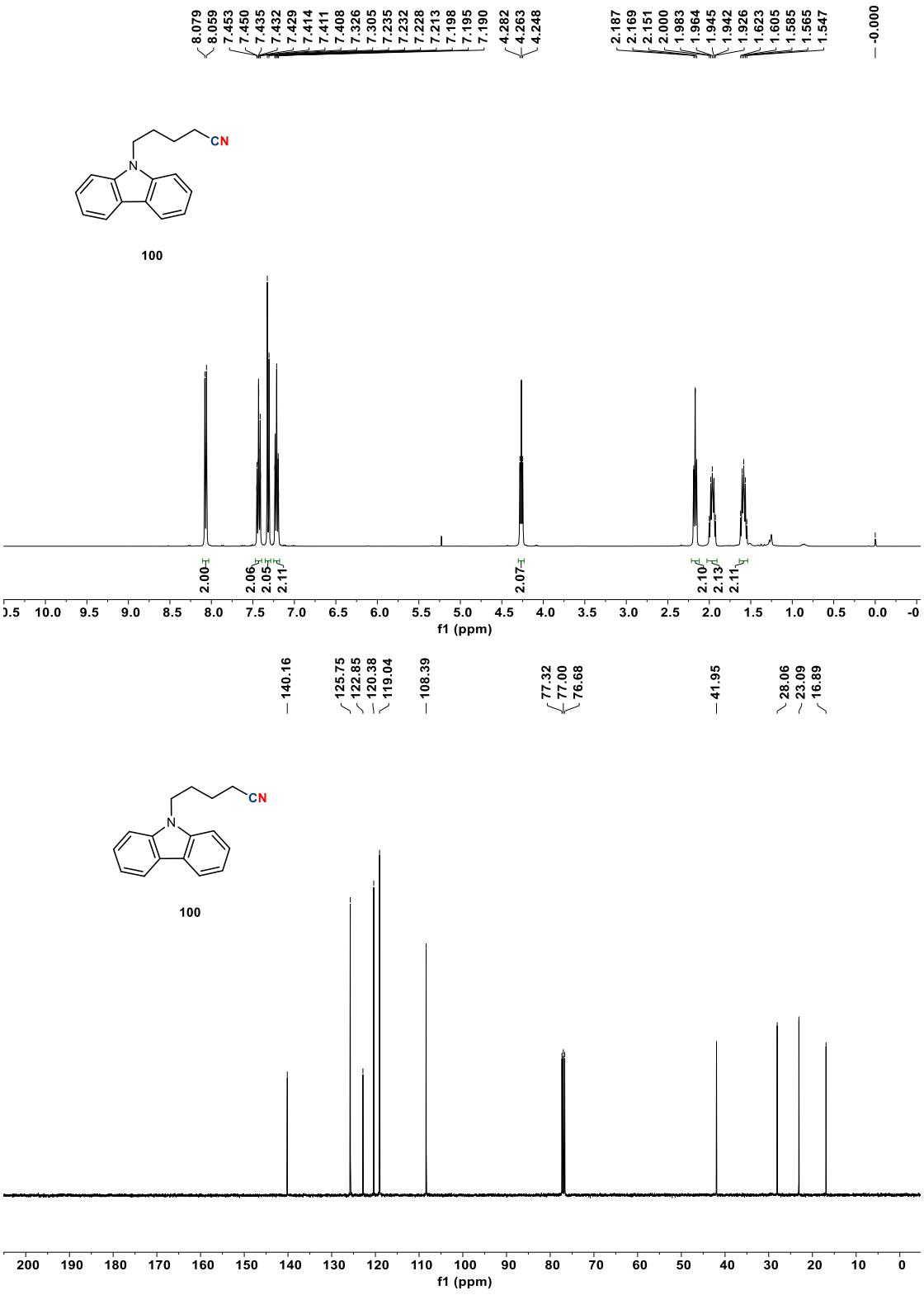

7.303
7.297
7.292
7.285
7.278
7.275
7.269
7.262
7.257
7.251
7.243
6.966
6.963
6.961
6.948
6.945
6.942
6.929
6.926
6.924
6.896
6.890
6.887
6.885
6.882
6.873
6.871
6.868
6.865
6.859
4.006
3.992
3.978
2.439
2.422
2.405
1.949
1.941
1.936
1.932
1.927
1.921
1.917
1.914
1.904
1.901
1.893
1.888
1.885
1.875
1.871
1.868
1.863
1.852
1.847
-0.000
O
CN
97
2.07
1.00
2.01
2.07
2.05
4.19
f1 (ppm)
158.64
129.44
120.84
119.42
114.39
77.32
77.00
76.68
66.49
28.15
22.42
16.91
O
CN
97
f1 (ppm)

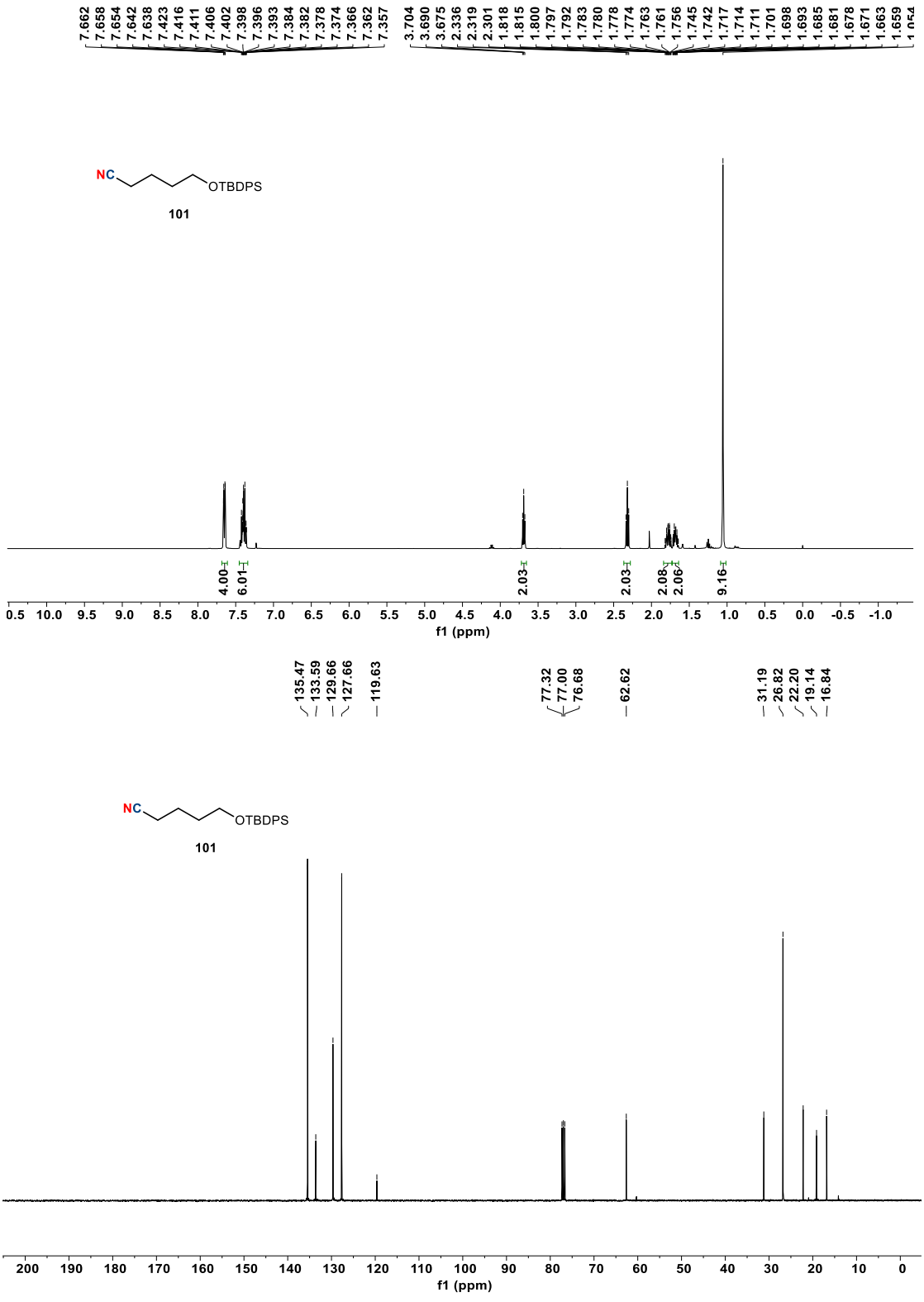

7.262
7.242
7.110
7.090
2.906
2.890
2.873
2.345
2.327
2.315
1.808
1.803
1.798
1.790
1.785
1.780
1.777
1.774
1.771
1.767
1.763
1.760
1.757
1.754
1.749
1.745
1.743
1.736
1.731
1.726
0.000
S
CN
98
2.00
1.96
2.01
5.03
4.14
f1 (ppm)

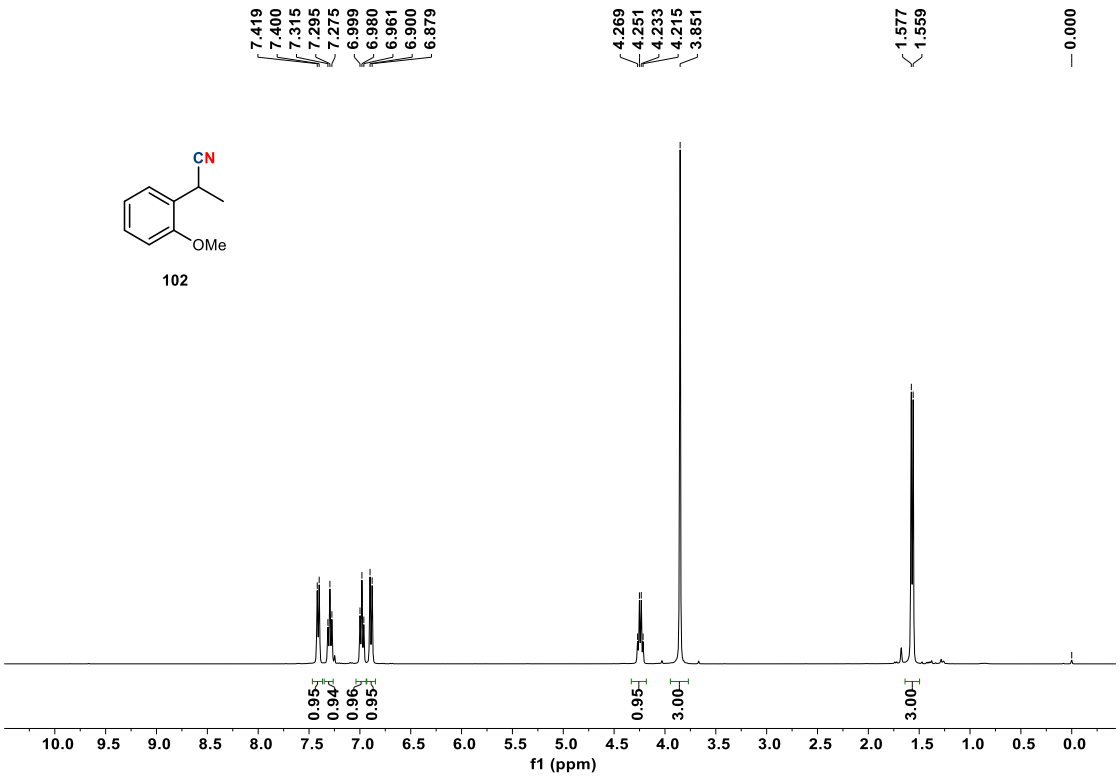

136.48
131.93
130.41
129.71
119.24
77.32
77.00
76.68
33.61
27.98
24.15
20.91
16.70
S
CN
98
f1 (ppm)

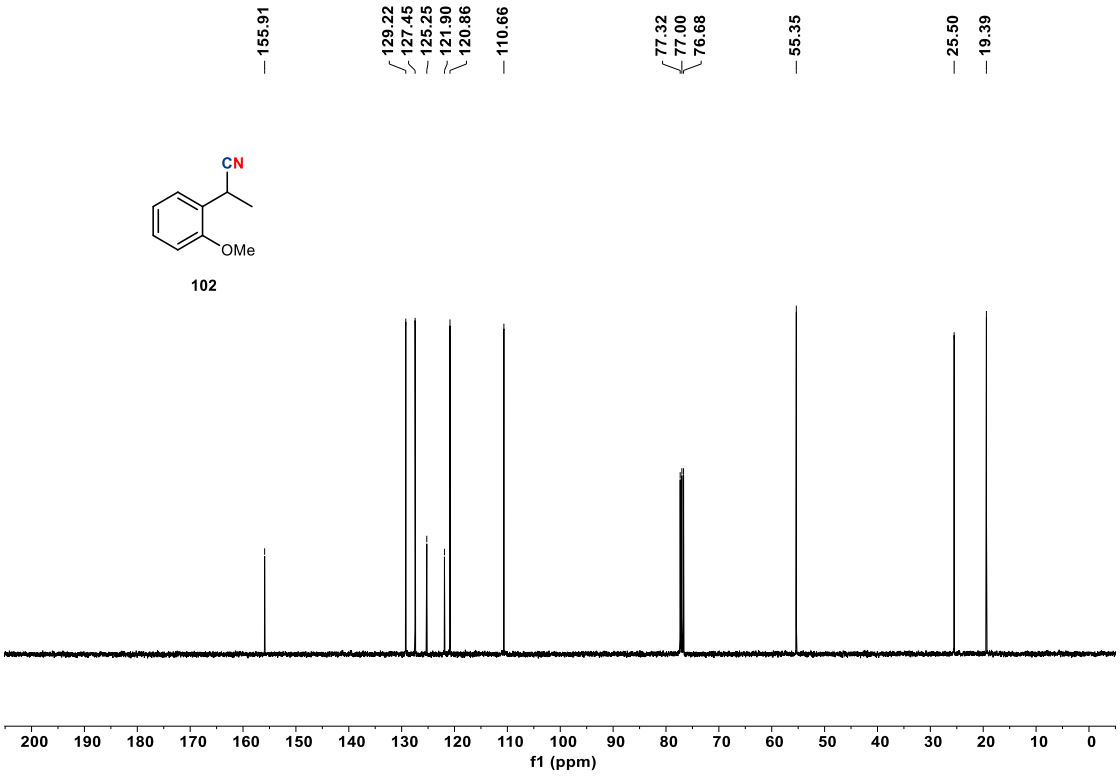

7.825
7.453
7.434
7.200
7.180
7.061
7.057
7.047
7.043
7.039
7.028
7.024
7.019
7.015
7.011
7.008
7.006
6.996
6.992
6.989
6.987
6.972
6.137
2.656
2.638
2.620
2.220
2.203
2.185
1.759
1.741
1.738
1.721
1.702
1.684
1.609
1.591
1.588
1.581
1.571
1.553
CN
N
H
99
0.95
1.00
1.01
2.06
1.00
2.07
2.09
2.12
2.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

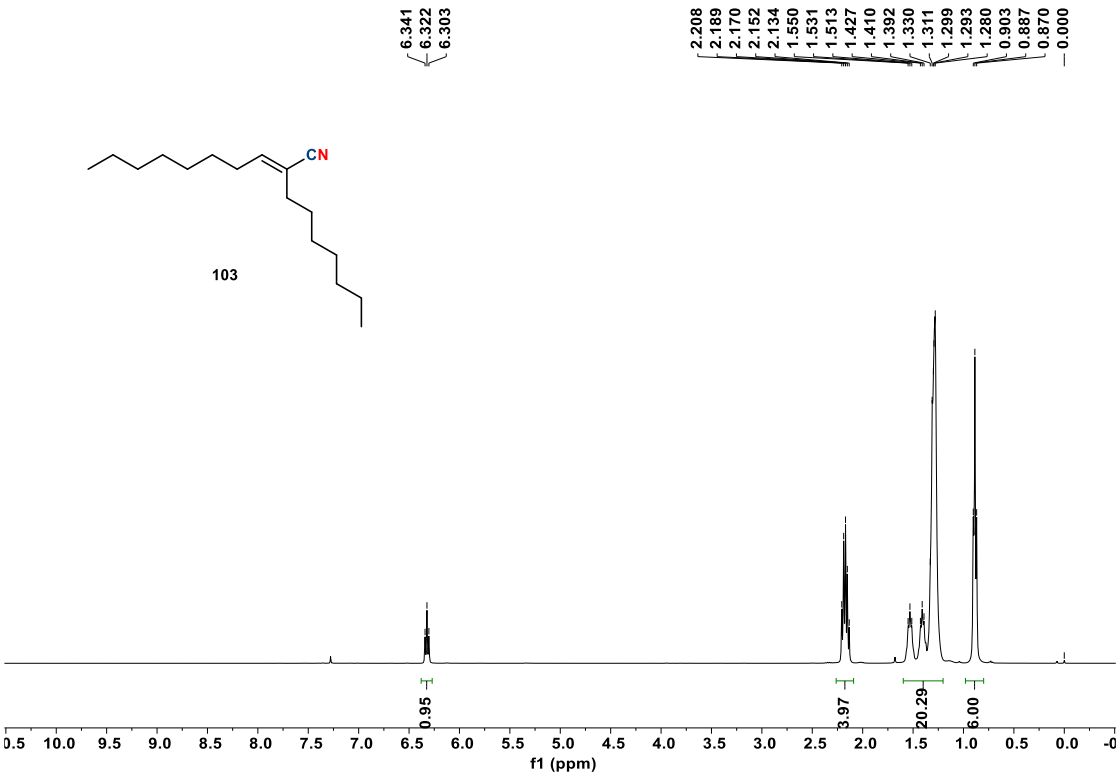

138.22
135.89
128.60
121.10
119.73
119.62
119.55
110.40
99.77
77.32
77.00
76.68
27.92
27.22
24.60
16.82
CN
N
H
99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

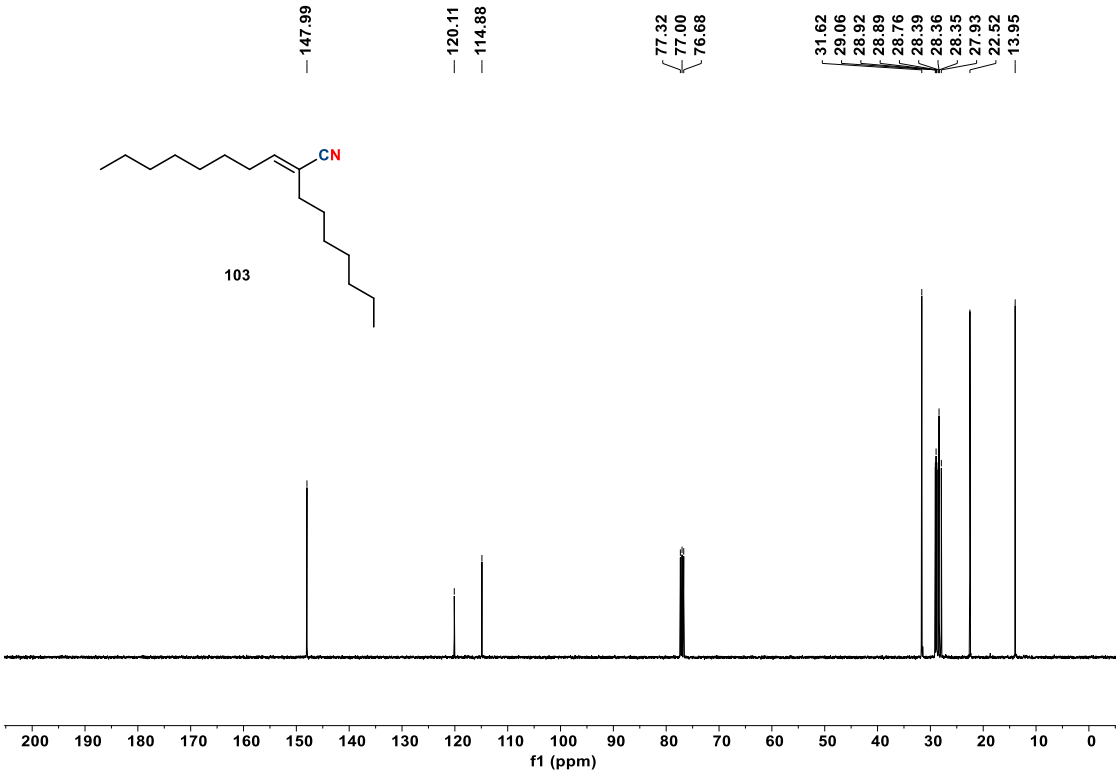

8.079
8.059
7.453
7.450
7.435
7.432
7.429
7.414
7.411
7.408
7.326
7.305
7.235
7.232
7.228
7.213
7.198
7.195
7.190
4.282
4.263
4.248
2.187
2.169
2.151
2.000
1.983
1.964
1.945
1.942
1.926
1.623
1.605
1.585
1.565
1.547
-0.000
CN
N
100
2.00
2.06
2.05
2.11
2.07
2.10
2.13
2.11
f1 (ppm)
140.16
125.75
122.85
120.38
119.04
108.39
77.32
77.00
76.68
41.95
28.06
23.09
16.89
CN
N
100
f1 (ppm)

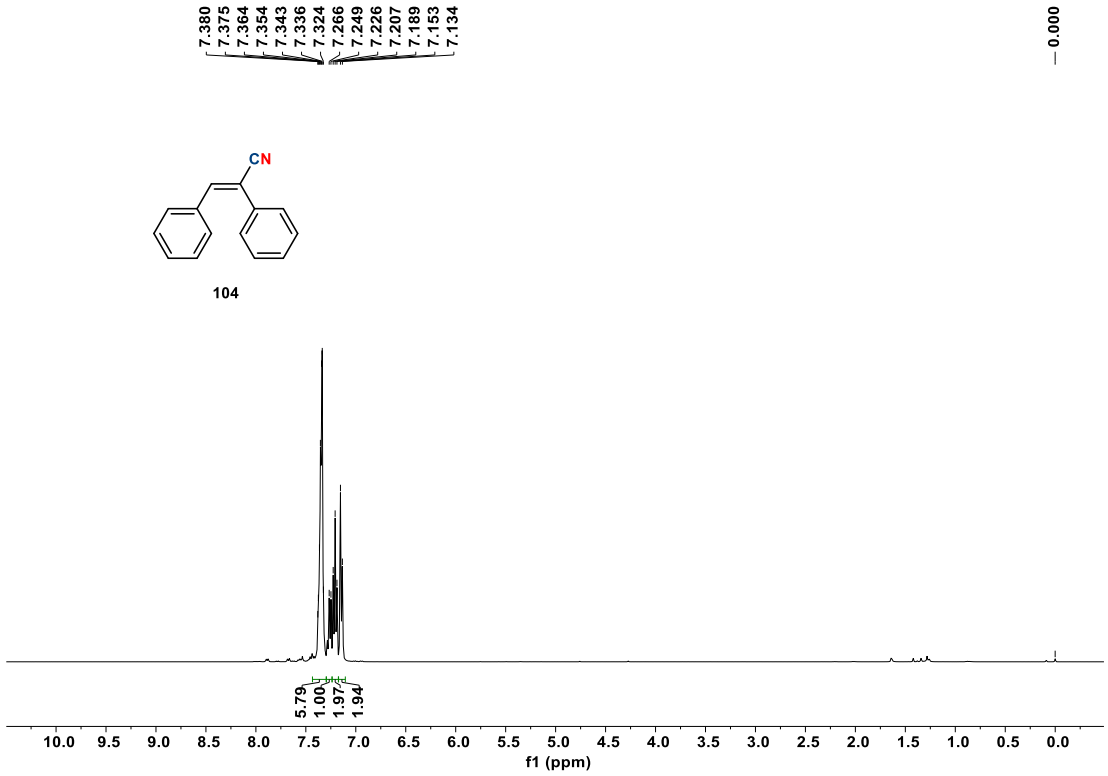

7.662
7.658
7.654
7.642
7.638
7.423
7.416
7.411
7.406
7.402
7.398
7.396
7.393
7.384
7.382
7.378
7.374
7.366
7.362
7.357
3.704
3.690
3.675
2.336
2.319
2.301
1.818
1.815
1.800
1.797
1.792
1.783
1.780
1.778
1.774
1.763
1.761
1.756
1.745
1.742
1.717
1.714
1.711
1.701
1.698
1.693
1.685
1.681
1.678
1.671
1.663
1.659
NC
OTBDPS
101
4.00
6.01
2.03
2.03
2.08
2.06
9.16
f1 (ppm)
135.47
133.59
129.66
127.66
119.63
77.32
77.00
76.68
62.62
31.19
26.82
22.20
19.14
16.84
NC
OTBDPS
101
f1 (ppm)

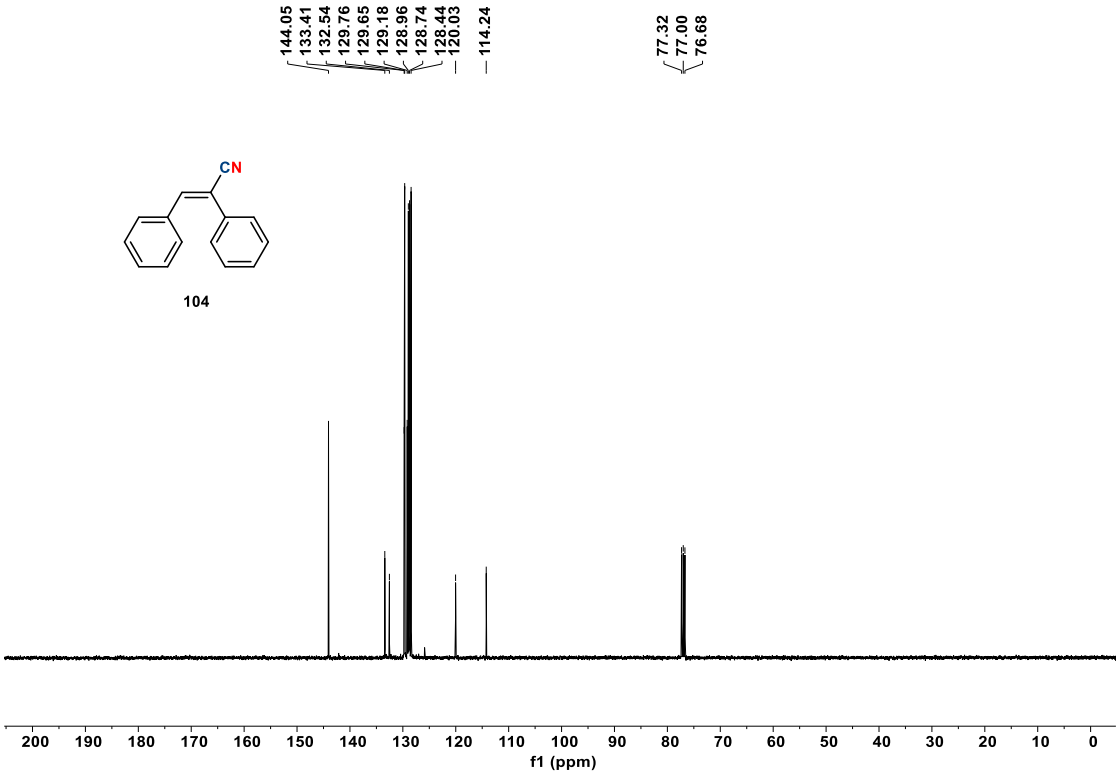

7.419
7.400
7.315
7.295
7.275
6.999
6.980
6.961
6.900
6.879
4.269
4.251
4.233
4.215
3.851
1.577
1.559
0.000
CN
OMe
102
0.95
0.94
0.96
0.95
0.95
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

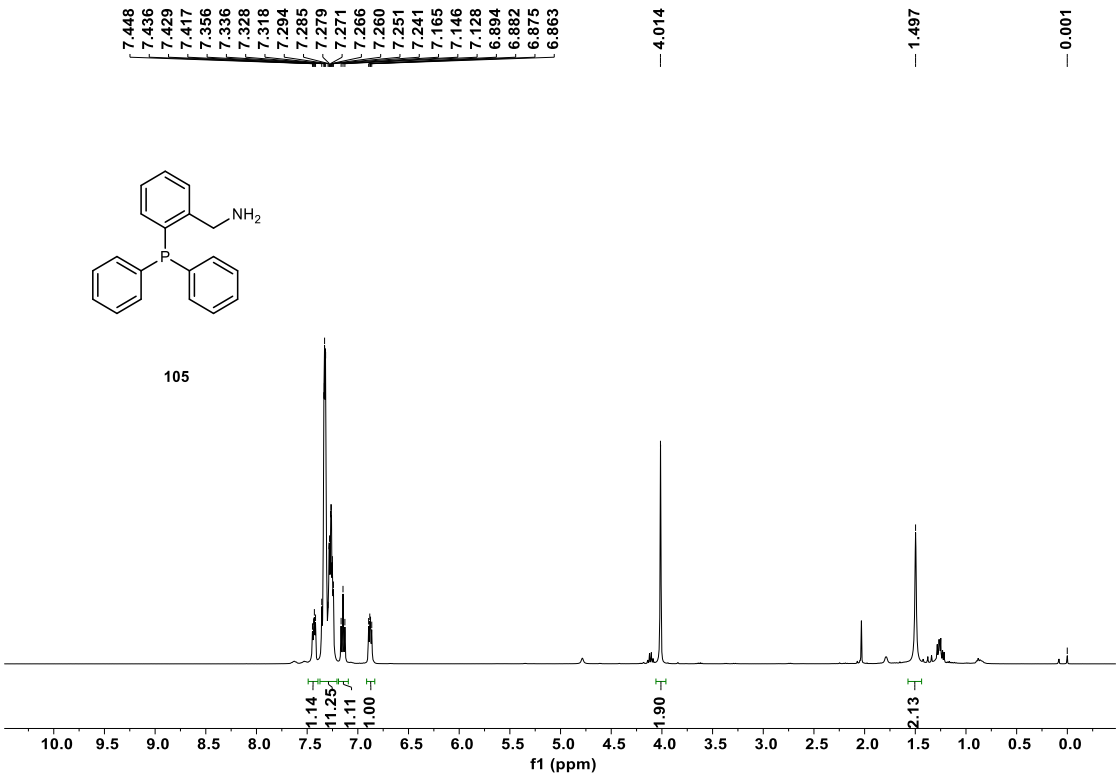

155.91
129.22
127.45
125.25
121.90
120.86
110.66
77.32
77.00
76.68
55.35
25.50
19.39
CN
OMe
102
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

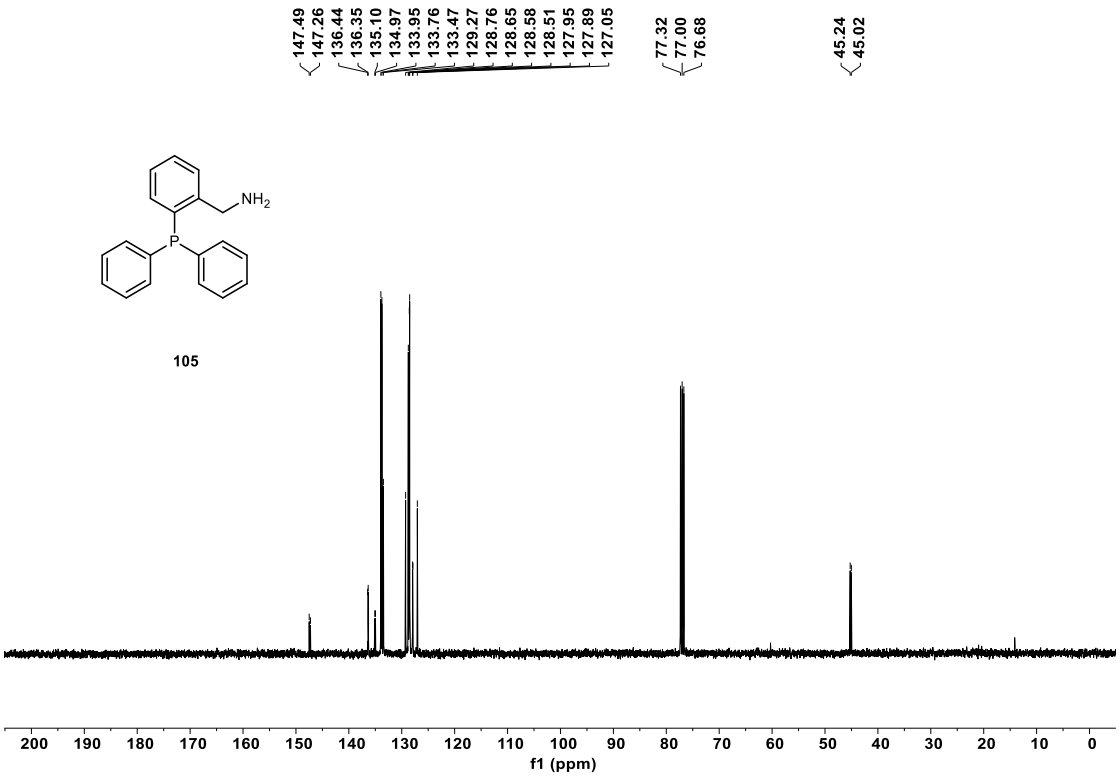

6.341
6.322
6.303
2.208
2.189
2.170
2.152
2.134
1.550
1.531
1.513
1.427
1.410
1.392
1.330
1.311
1.299
1.293
1.280
0.903
0.887
0.870
0.000
CN
103
0.95
3.97
20.29
6.00
f1 (ppm)

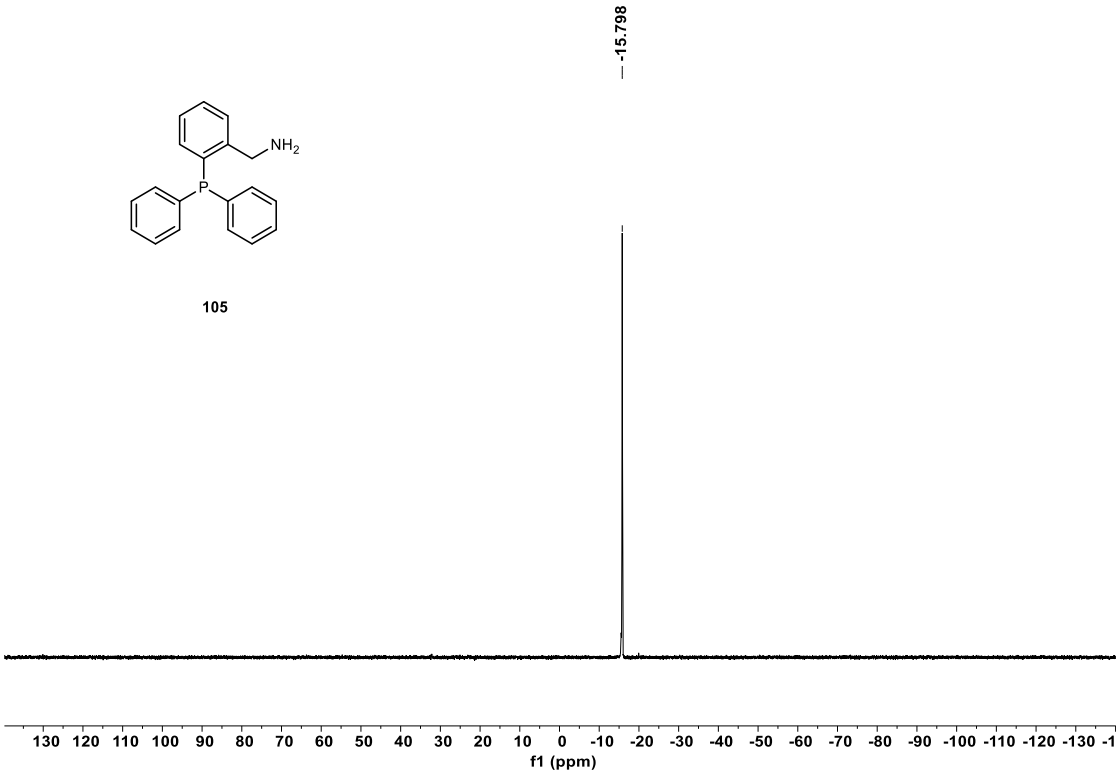

147.99
120.11
114.88
77.32
77.00
76.68
31.62
29.06
28.92
28.89
28.76
28.39
28.36
28.35
27.93
22.52
13.95
CN
103
f1 (ppm)


7.380
7.375
7.364
7.354
7.343
7.336
7.324
7.266
7.249
7.226
7.207
7.189
7.153
7.134
0.000
CN
104
5.79
1.00
1.97
1.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

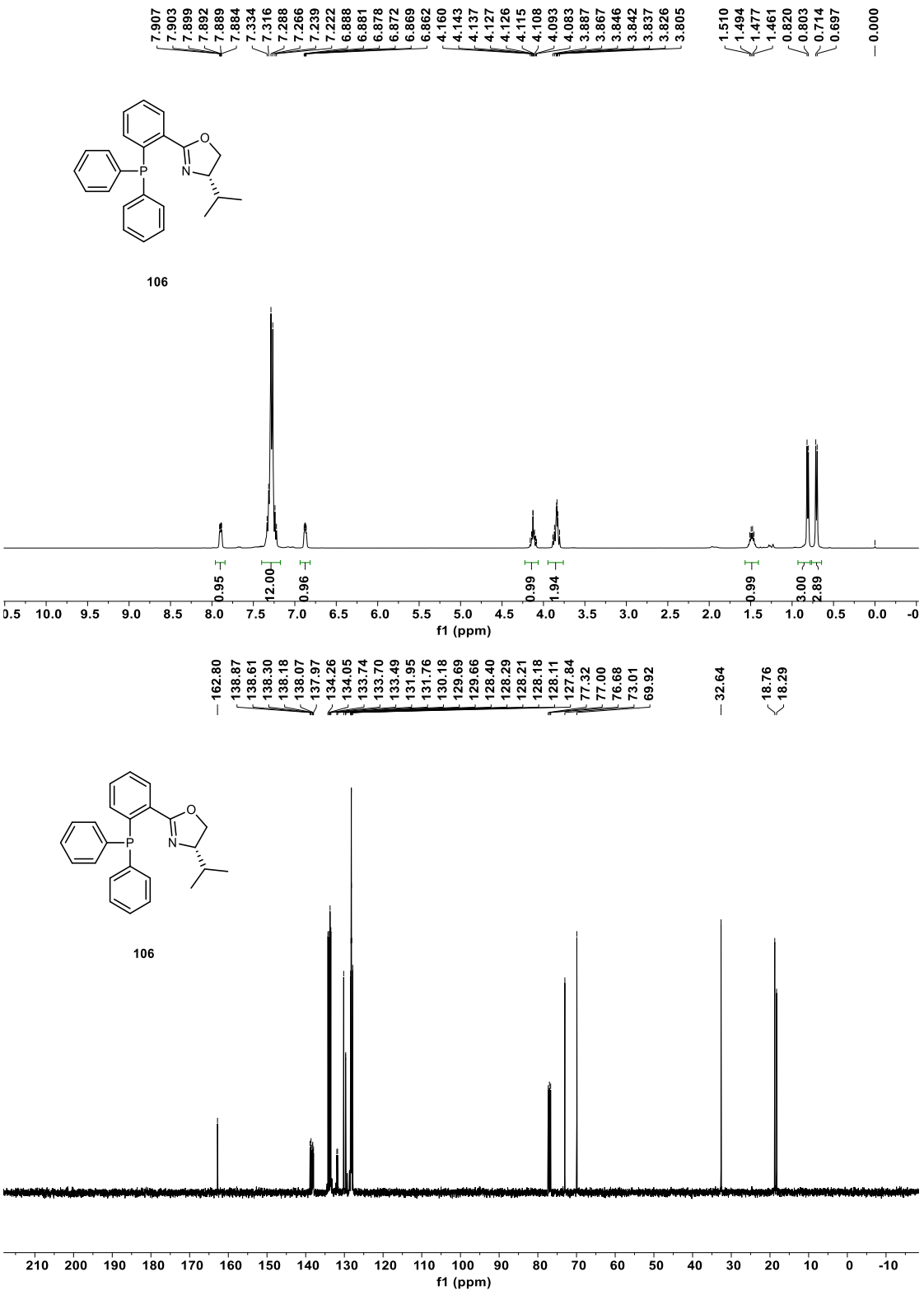

144.05
133.41
132.54
129.76
129.65
129.18
128.96
128.74
128.44
120.03
114.24
77.32
77.00
76.68
CN
104
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

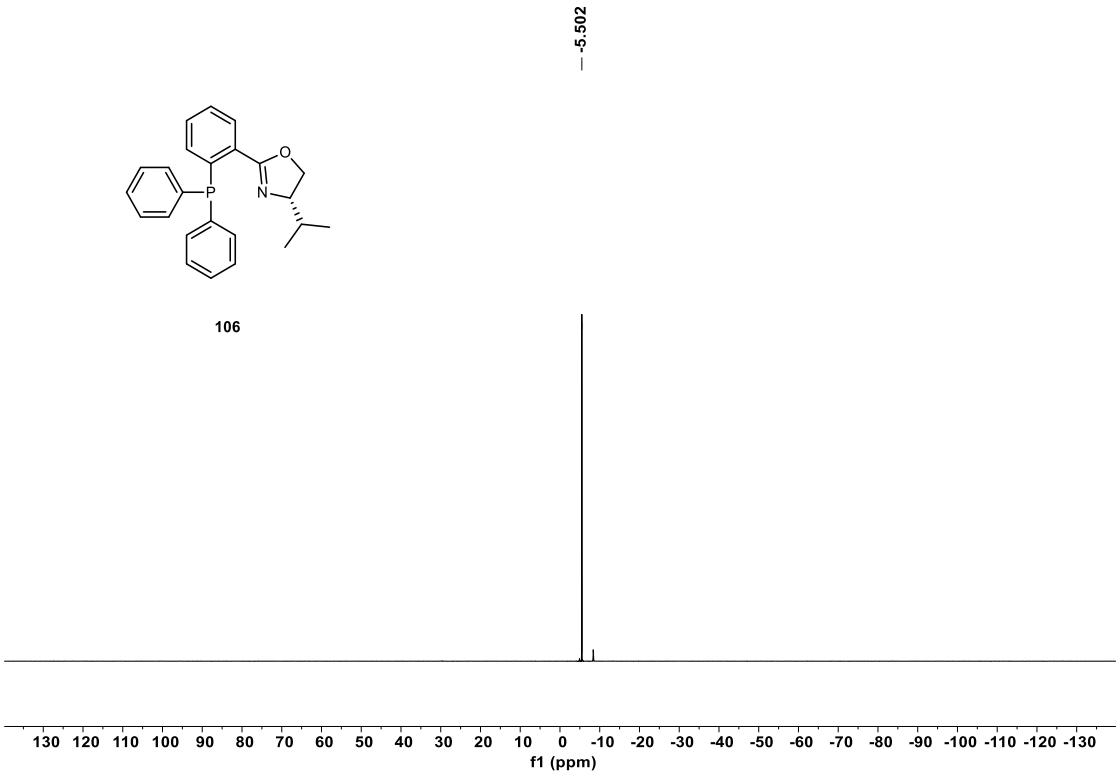

7.448
7.436
7.429
7.417
7.356
7.336
7.328
7.318
7.294
7.285
7.279
7.271
7.266
7.260
7.251
7.241
7.165
7.146
7.128
6.894
6.882
6.875
6.863
4.014
1.497
0.001
NH2
P
105
1.14
11.25
1.11
1.00
1.90
2.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.49
147.26
136.44
136.35
135.10
134.97
133.95
133.76
133.47
129.27
128.76
128.65
128.58
128.51
127.95
127.89
127.05
77.32
77.00
76.68
45.24
45.02
NH2
P
105
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

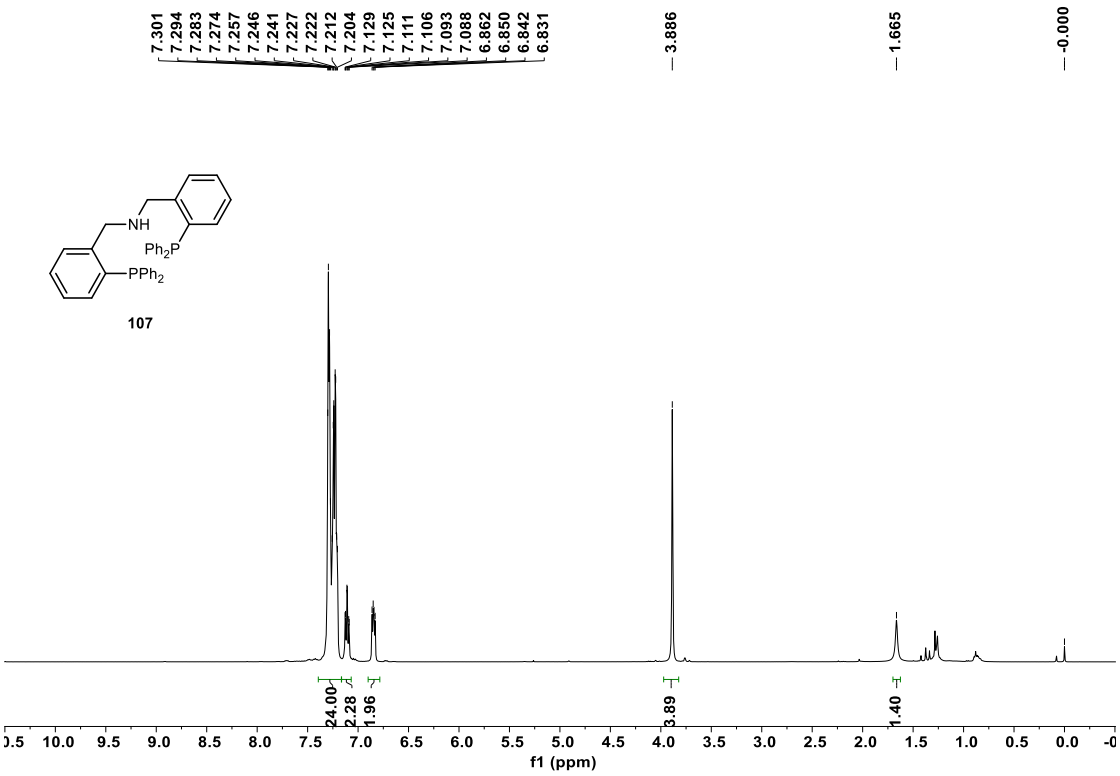


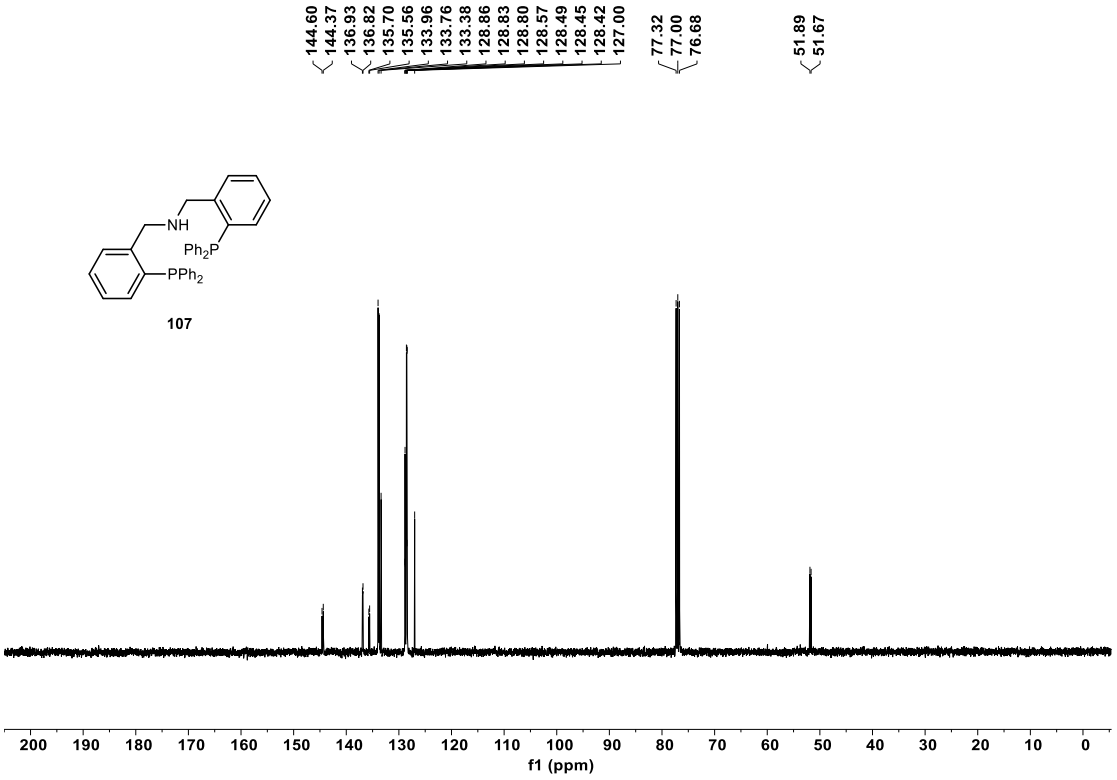
^{31}P NMR of 105

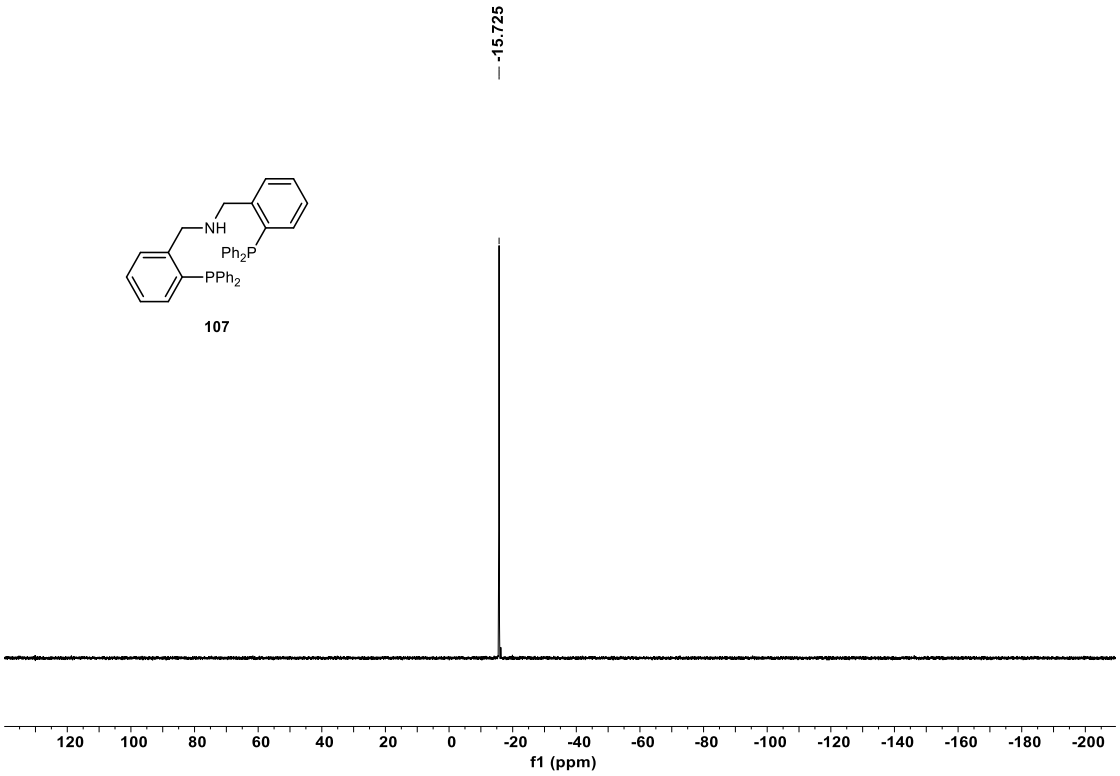

7.907
7.903
7.899
7.892
7.889
7.884
7.334
7.316
7.288
7.266
7.239
7.222
6.888
6.881
6.878
6.872
6.869
6.862
4.160
4.143
4.137
4.127
4.126
4.115
4.108
4.093
4.083
3.887
3.867
3.846
3.842
3.837
3.826
3.805
1.510
1.494
1.477
1.461
0.820
0.803
0.714
0.697
0.000
106
0.95
12.00
0.96
0.99
1.94
0.99
3.00
2.89
f1 (ppm)
162.80
138.87
138.61
138.30
138.18
138.07
137.97
134.26
134.05
133.74
133.70
133.49
131.95
131.76
130.18
129.69
129.66
128.40
128.29
128.21
128.18
128.11
127.84
77.32
77.00
76.68
73.01
69.92
32.64
18.76
18.29
106
f1 (ppm)



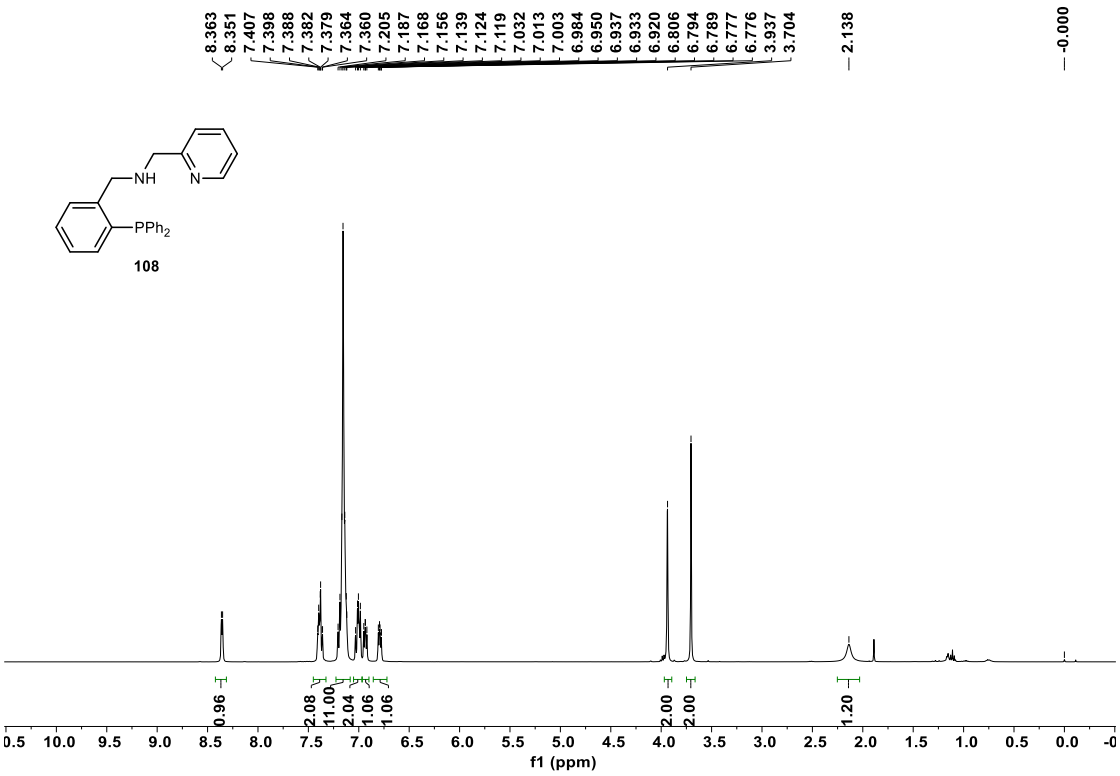
^{31}P NMR of 106

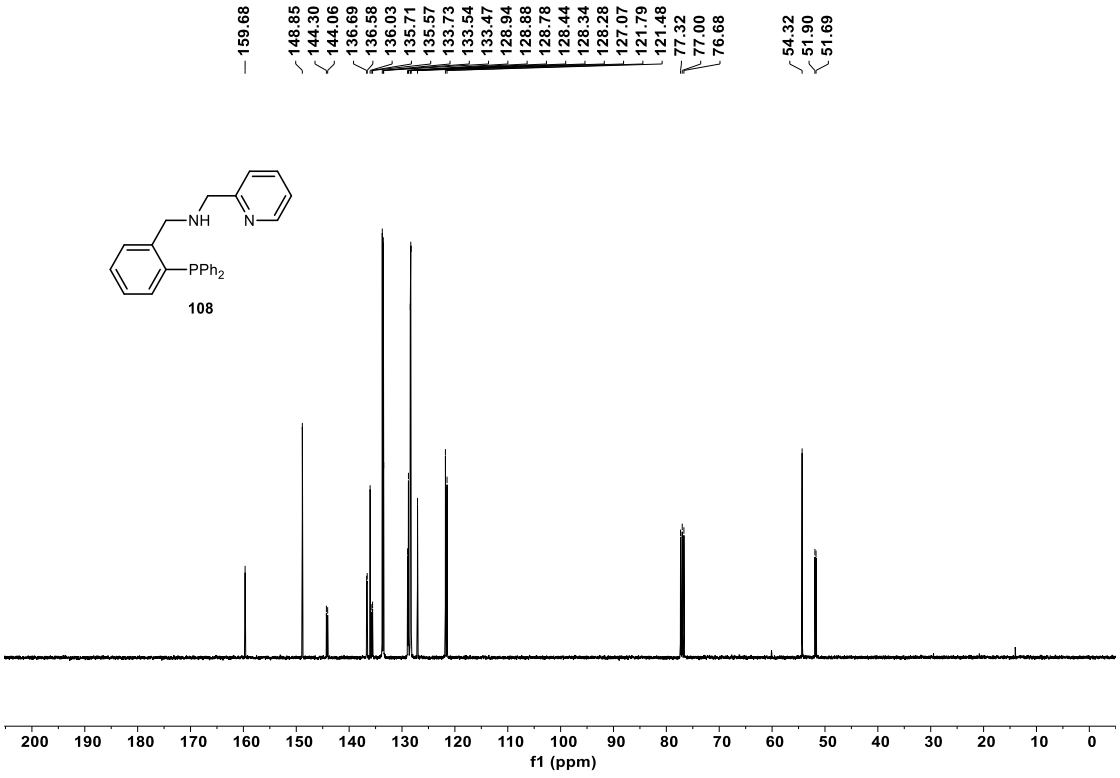

7.301
7.294
7.283
7.274
7.257
7.246
7.241
7.227
7.222
7.212
7.204
7.129
7.125
7.111
7.106
7.093
7.088
6.862
6.850
6.842
6.831
3.886
1.665
-0.000
NH
Ph2P
PPh2
107
24.00
2.28
1.96
3.89
1.40
f1 (ppm)

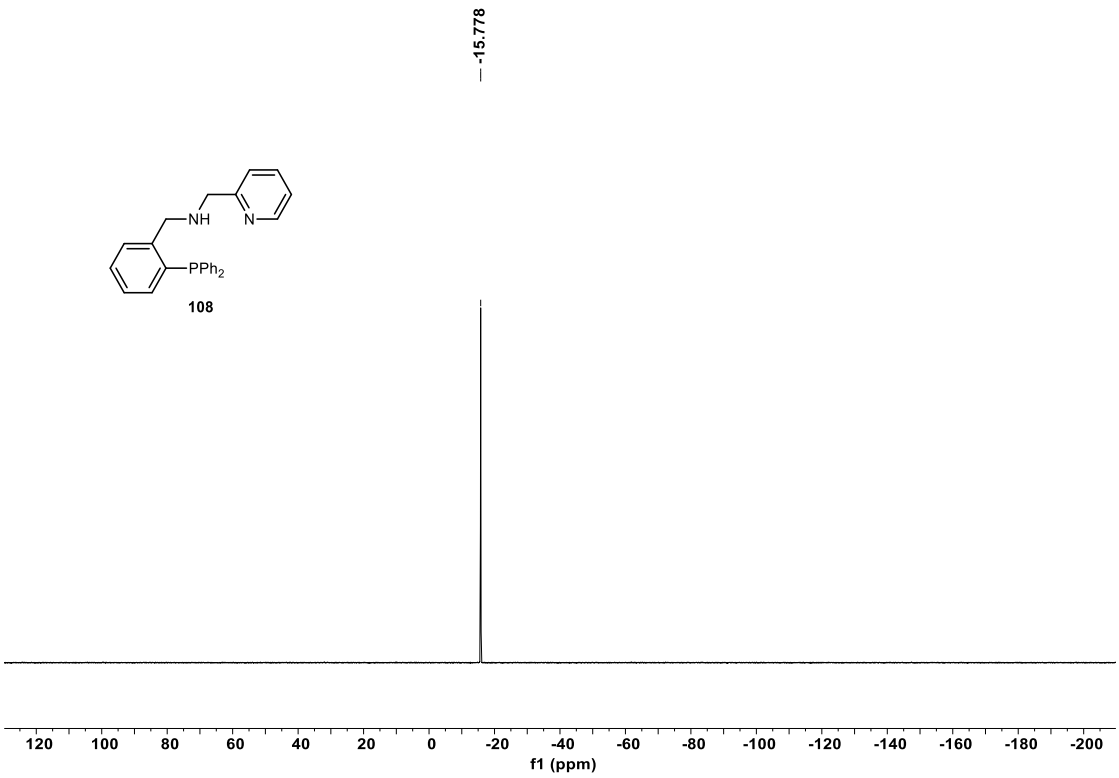

144.60
144.37
136.93
136.82
135.70
135.56
133.96
133.76
133.38
128.86
128.83
128.80
128.57
128.49
128.45
128.42
127.00
77.32
77.00
76.68
51.89
51.67
NH
Ph2P
PPh2
107
f1 (ppm)



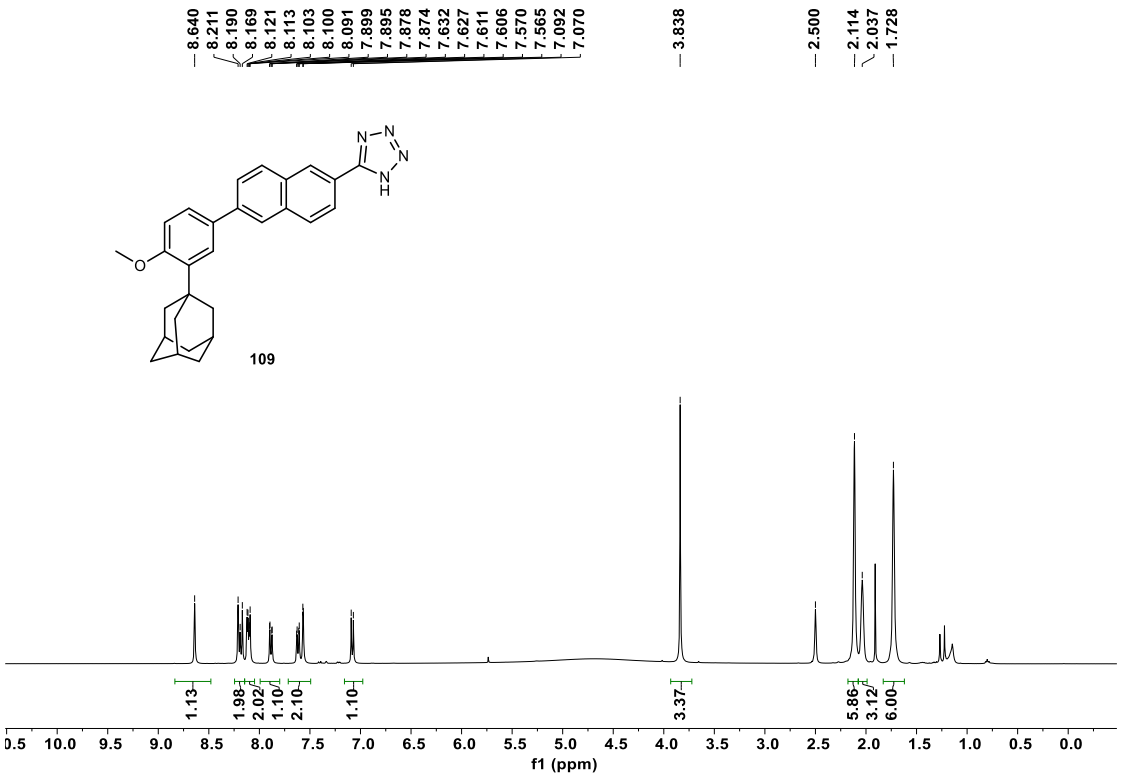
^{31}P NMR of 107

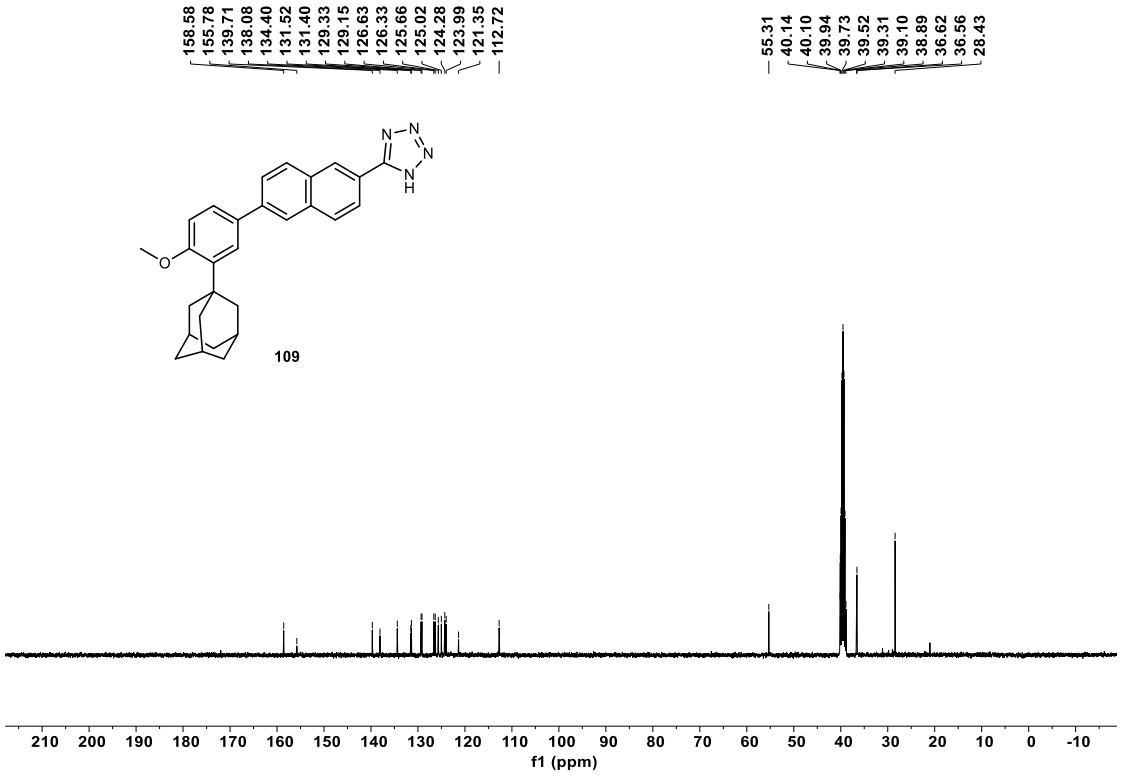

8.363
8.351
7.407
7.398
7.388
7.382
7.379
7.364
7.360
7.205
7.187
7.168
7.156
7.139
7.124
7.119
7.032
7.013
7.003
6.984
6.950
6.937
6.933
6.920
6.806
6.794
6.789
6.777
6.776
3.937
3.704
2.138
-0.000
NH
N
PPh2
108
0.96
2.08
11.00
2.04
1.06
1.06
2.00
2.00
1.20
f1 (ppm)


159.68
148.85
144.30
144.06
136.69
136.58
136.03
135.71
135.57
133.73
133.54
133.47
128.94
128.88
128.78
128.44
128.34
128.28
127.07
121.79
121.48
77.32
77.00
76.68
54.32
51.90
51.69
NH
N
PPh2
108
f1 (ppm)



^{31}P NMR of 108


8.640
8.211
8.190
8.169
8.121
8.113
8.103
8.100
8.091
7.899
7.895
7.878
7.874
7.632
7.627
7.611
7.606
7.570
7.565
7.092
7.070
3.838
2.500
2.114
2.037
1.728
109
1.13
1.98
2.02
1.10
2.10
1.10
3.37
5.86
3.12
6.00
f1 (ppm)


158.58
155.78
139.71
138.08
134.40
131.52
131.40
129.33
129.15
126.63
126.33
125.66
125.02
124.28
123.99
121.35
112.72
55.31
40.14
40.10
39.94
39.73
39.52
39.31
39.10
38.89
36.62
36.56
28.43
109
f1 (ppm)