Supporting Information

A radical approach towards polarity-reversed *para*-substitution of electron-deficient arenes

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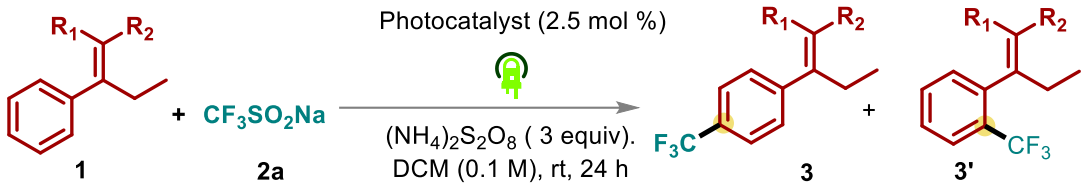
Table of Content

1. General Information.

Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents with residual protonated solvent signal as internal reference on Bruker-Ava-500. Chemical shifts are reported in parts per million using the solvent resonance internal standard (chloroform, 7.26 and 77.0 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Electrospray and electron impact high resolution mass spectrometry was performed by Bruker mass spectrometer. The data is recorded as the ionization method followed by the calculated and measured masses. The Fluorescence emission intensities were measured on Horiba-Jobin-Yvon. Solvents for starting material preparation and coupling reactions were dried before use. Green LEDs (2.50 W, λ = 535 nm) Rebel LED, mounted on a 25 mm cool base was purchased from commercial supplier Luxeon Star LEDs Quadica Developments Inc.10-3447 30 Ave N. Lethbridge, Alberta T1H 7B5 Canada.

2: Optimization studies

Table S1: Influence of the photocatalyst[a]

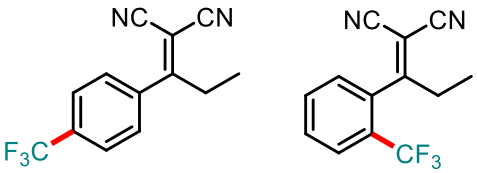


1 2a 3 3'

Entry[b]	Photocatalyst	Total Yield	p/o
1	TPT	10	83:17
2	Eosin B	56	90:10
3	Rose bengal	25	79:21
4	Fluorescein	N.R	-
5	$[Ru(bpy)_3](PF_6)_2$	N.R	-
6	Mes^-Acr^+	62	88:12
7	Eosin Y	60	92:8
8[c]	Eosin Y	50	60:4
9	none	N.R	-

[a]Reaction Conditions: **1** (0.2 mmol), **2a** (3.0 equiv), photocatalyst (2.5 mol %), $(NH_4)_2S_2O_8$, ACN (2 mL) at room temperature using irradiation with 12 W green LEDs for 24 h. Yield are isolated. (p/o) determined by ^{19}F NMR. [b]Condition R_1= CN, R_2= CN, [c]Condition R_1= CN, R_2= COOEt,

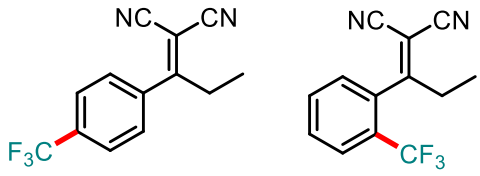
Entry 1



δ= 63.19 ppm δ= 62.91 ppm

(p:o = 83:17)

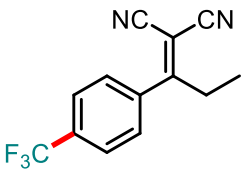
Entry 3



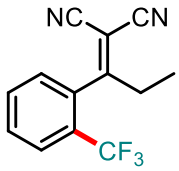
δ= 63.20 ppm δ= 62.92 ppm

(p:o = 79:21)

Entry 6



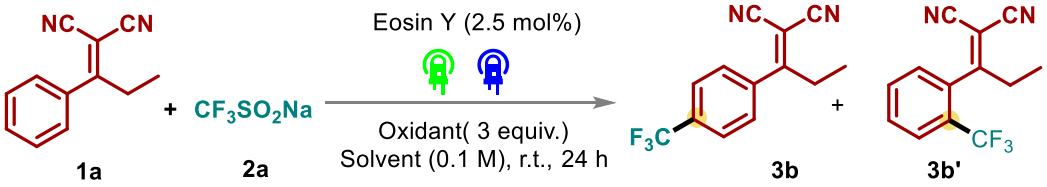
δ= 63.20 ppm



δ= 62.91 ppm

(p:o = 88:12)

Table S2: Influence of the solvent, oxidant and light source[a]

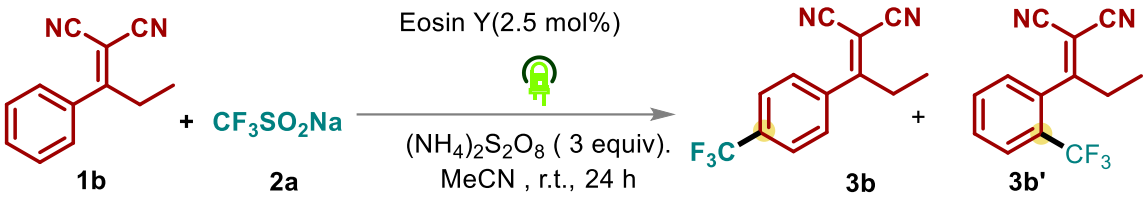


1a 2a 3b 3b'

Entry	Solvent	Oxidant	Light Source	Total Yield[b]	p/o
1	DCM	$(NH_4)_2S_2O_8$	12 W Green LEDs	60	83:17
2	MeCN	$(NH_4)_2S_2O_8$	12 W Green LEDs	70	> 20:1
3	DCE	$(NH_4)_2S_2O_8$	12 W Green LEDs	35	80:20
4	DMF	$(NH_4)_2S_2O_8$	12 W Green LEDs	Trace	-
5	THF	$(NH_4)_2S_2O_8$	12 W Green LEDs	N.D	-
6	Dioxane	$(NH_4)_2S_2O_8$	12 W Green LEDs	N.D	-
7	DMSO	$(NH_4)_2S_2O_8$	12 W Green LEDs	Trace	-
8	MeCN	$(NH_4)_2S_2O_8$	12 W Blue LEDs	50	>20:1
9	MeCN	$(NH_4)_2S_2O_8$	at 50° C	N.R	-
10	MeCN	$(NH_4)_2S_2O_8$	at 70° C	N.R	-
11	MeCN	$(NH_4)_2S_2O_8$	at 120° C	Trace	-
12	MeCN	$K_2S_2O_8$	12 W Green LEDs	66	>20:1
13	MeCN	none	12 W Green LEDs	< 5	-

[a]Reaction Conditions: **1b** (0.2 mmol), **2a** (3.0 equiv.), Eosin Y (2.5 mol%), Oxidant (3.0 equiv.), Solvent (0.1 M) at room temperature using irradiation with 12 W green LEDs for 24 h. [b]Yield are isolated.

Table S3: Effect of additive and concentration variation[a]



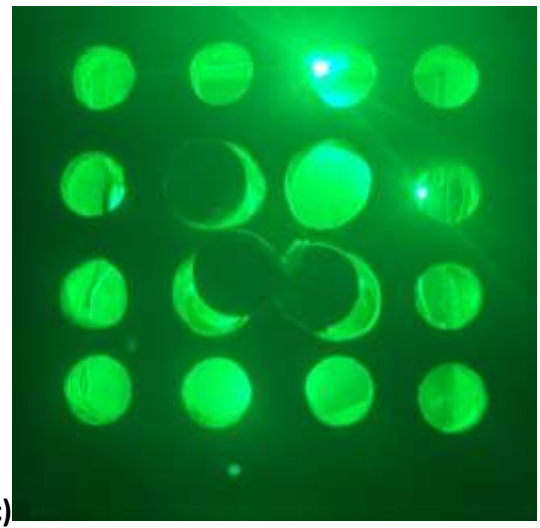
Entry	Additive	Total Yield	p/o
1	DIPEA (1 equiv)	65	>20:1
2	DIPEA (2.0 equiv)	71	>20:1
3	-	70	>20:1
4	**2a** (1 equiv.)	53	>20:1
5	**2a** (2 equiv.)	60	>20:1
6	MeCN (0.033 M)	55	>20:1
7	MeCN (0.2 M)	65	>20:1

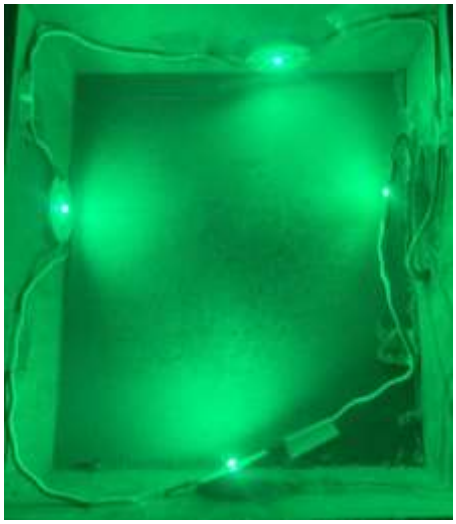
[a]Reaction Conditions: **1b** (0.2 mmol), **2a,** Eosin Y (2.5 mol%), $(NH_4)_2S_2O_8$(3.0 equiv.), MeCN using irradiation with 12 W green LEDs for 24 h. [b]Yield are isolated.

3: Photo Reaction Setup

(a) 

(b) 

(c) 

(d) 

(a) Whole Setup Setup

(b) DC Regulator controlling Current and voltage

(c) Box- cover with holes for RB and RB illuminated by Green LEDs

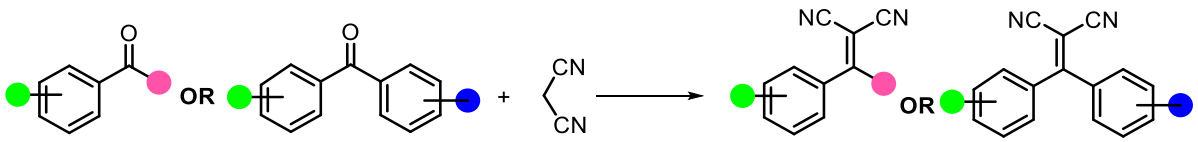
(d) Uncovered box (6' * 6') with 4 LEDs

Each RB was at 5cm distance from LEDs.

4: Preparation of Substrates

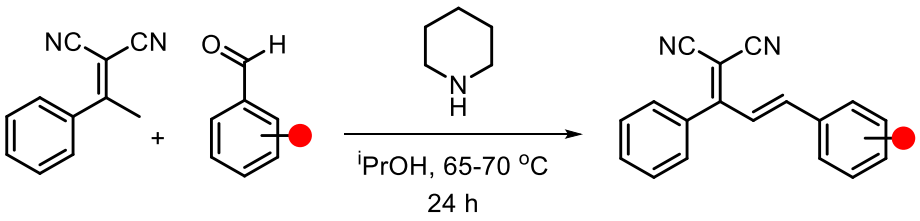
4.1: Preparation of Aryl/Alkylidene Malononitriles

Aryl/Alkylidene Malononitrile are known starting materials and synthesized accordingly using known literature procedure.[1,2]



Scheme 1: Preparation of alkylidene malononitrile

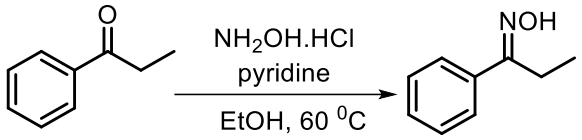
To a 25 mL round-bottom was added the corresponding ketone (3.0 mmol, 1.0 eq.), toluene (6 mL), ammonium acetate (231.2 mg, 3.0 mmol, 1.0 eq.), malononitrile (297.1mg, 4.5 mmol, 1.5 eq.) and acetic acid (0.2 mL). The round-bottom was attached to a Dean-Stark apparatus and heated to reflux until the consumption of the corresponding ketone. The reaction was removed from heat, cooled to room temperature, and then alkalified with saturation sodium carbonate solution. The aqueous layer was extracted with dichloromethane (3 × 10 mL); combined organic phase was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The products were purified by column chromatography on a silica gel (petroleum ether/ethyl acetate) to afford the desired products. **(1zh)** was performed on 1 mmol scale, (**1a-1zs**) was performed on 3 mmol scale (Scheme 1).



Scheme 2: Synthesis of (E)-2-(1,3-Diarylallylidene)malononitriles

To an oven-dried 50 mL round bottom flask was added 2-(1phenylethylidene)malononitrile (1 mmol), benzaldehyde (10 mmol), and piperidine (0.1 mmol) in $^{i}PrOH$ (1 mL). The reaction mixture was stirred at 65-70 °C in a preheated oil bath for 24 h. Completion of the reaction was monitored by TLC. Then the reaction mixture was cooled to room temperature, and mixed with ethyl acetate (50 mL) and the organic layer was washed with brine (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using

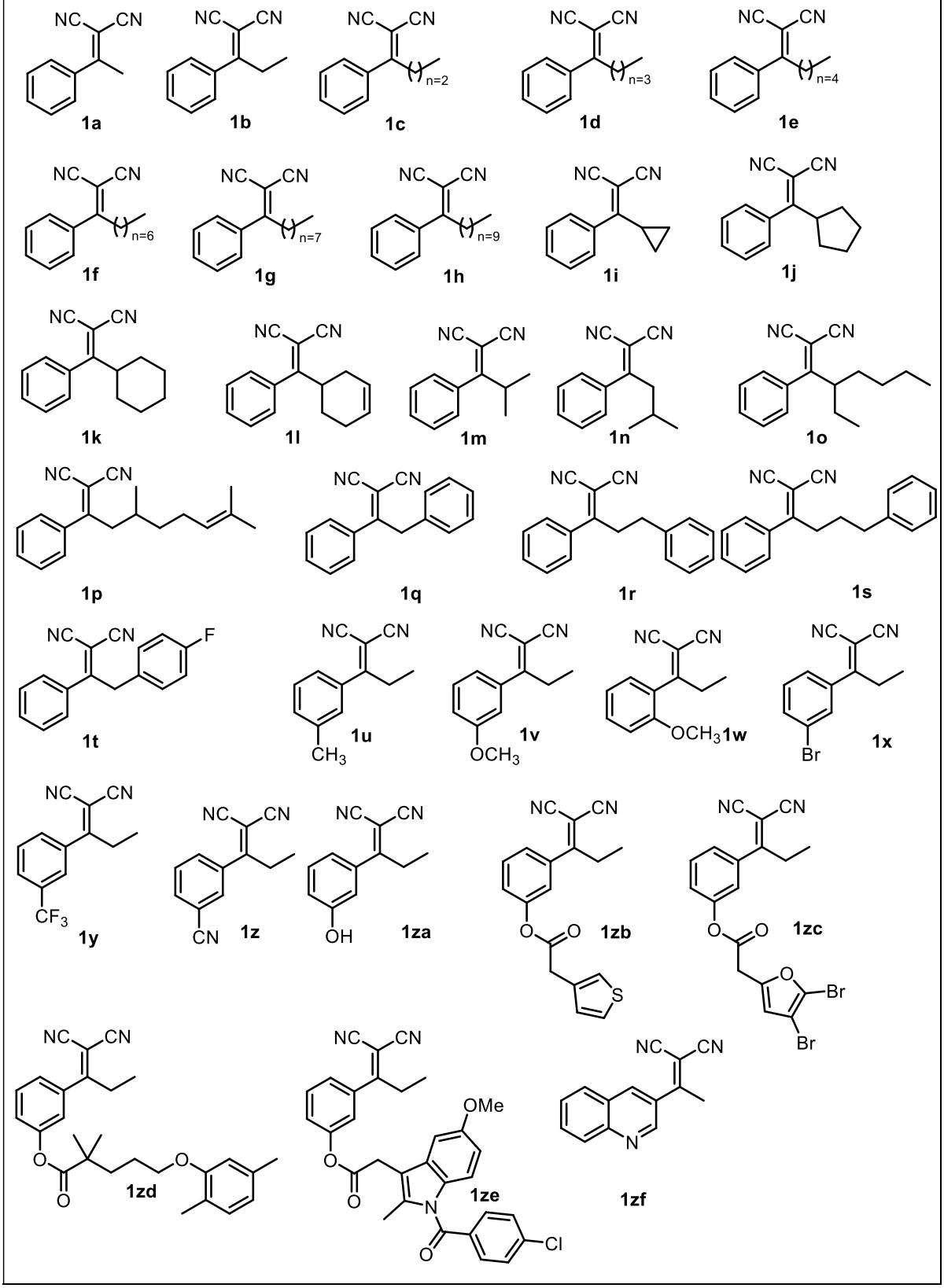
hexane/ethyl acetate = 99:1 to give pure (E)-2-(1,3diphenylallylidene)malononitrile (Scheme 2).

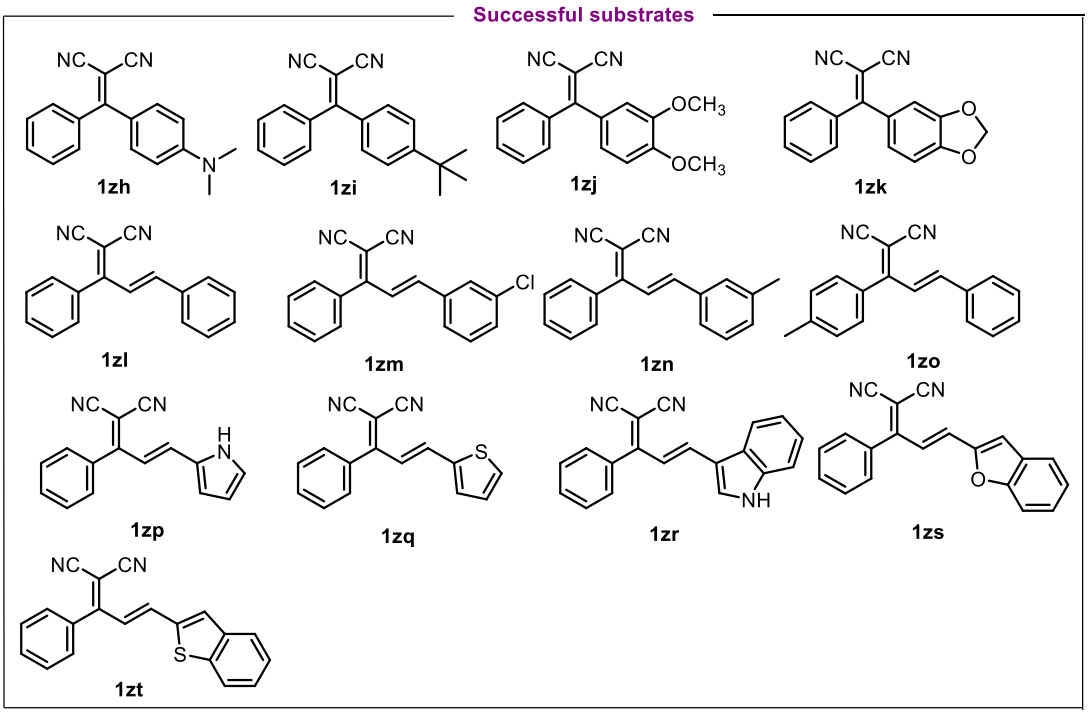


Scheme 3: Synthesis of (E)-1-phenylpropan-1-one oxime

(*E*)-1-phenylpropan-1-one oxime is a known starting material and synthesized accordingly using known literature procedure[2b]. To a solution of ketone and pyridine in EtOH (20 mL) was added $NH_2OH.HCl$ in one portion and the reaction mixture was stirred at 60 °C for 1 h. The reaction was quenched by adding water and the system was extracted twice with EtOAc. The combined organic extracts were washed with 1N aqueous HCl and brine, dried over MgSO4, filtered, and evaporated in vacuo to afford the ketoxime which was purification by column chromatography.

Successful substrates





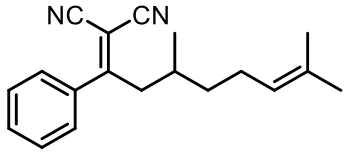
2-(1-phenylnonylidene)malononitrile (1g): Physical State: White liquid**; Yield:** 407 mg, 51 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.55-7.45 (m, 5H), 2.97 – 2.94 (m, 2H), 1.46– 1.40 (m, 2H), 1.34 – 1.31 (m, 2H), 1.27 – 1.20 (m, 8H), 0.86 (t, J = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 180.7, 135.0, 132.0, 129.2, 127.5, 112.8, 112.7, 84.7, 37.7, 31.7, 29.1, 29.0, 28.9, 28.3, 22.6, 14.1. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{18}H_{21}N_2$ 265.1705; Found 265.1706.

2-(cyclopentyl(phenyl)methylene)malononitrile (1j): Physical State: White solid; **Yield:** 300 mg, 45 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.47 (h, J = 3.7 Hz, 3H), 7.19 (dd, J = 7.5, 2.2 Hz, 2H), 3.44 (tt, J = 10.1, 7.6 Hz, 1H), 2.04 – 1.98 (m, 2H), 1.68 (td, J = 5.5, 2.8 Hz, 4H), 1.55 (tt, J = 9.6, 4.6 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 185.6, 134.5, 130.5, 128.9, 127.1, 112.2, 112.1, 87.1, 47.7, 31.9, 25.6. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{15}H_{13}N_2$ 221.1079; Found 221.1077.

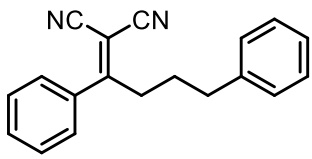
2-(cyclohex-3-en-1-yl(phenyl)methylene)malononitrile (1l): Physical state: Yellow solid**; Yield:** 393 mg, 56 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.61– 7.51 (m, 3H), 7.37 – 7.24 (m, 2H), 5.78 – 5.68 (m, 2H), 3.41 (m, 1H), 2.29 – 2.17 (m, 3H), 1.95-1.91 (m, 1H), 1.67 (tt, J = 12.2, 6.1 Hz, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 185.3, 134.3, 130.5, 128.9, 128.2, 128.0, 127.1, 126.8, 126.7,

126.6, 126.5, 126.3, 125.9, 125.5, 124.3, 112.0, 111.8, 87.2, 79.9, 42.7, 28.9, 26.8, 26.4, 24.9, 23.6. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{16}H_{13}N_2$ 233.1079; Found 233.1074.

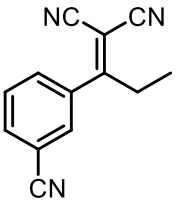
2-(3,7-dimethyl-1-phenyloct-6-en-1-ylidene)malononitrile (1p): **Physical state:** Viscous liquid; **Yield:** 467 mg, 56 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.56 – 7.47 (m, 3H), 7.47 – 7.42 (m, 2H), 4.98 – 4.90 (m, 1H), 2.99 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.81 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.96 (td, *J* = 14.9, 7.5 Hz, 1H), 1.88 (dd, *J* = 14.8, 7.5 Hz, 1H), 1.67 – 1.60 (m, 3H), 1.55 (s, 3H), 1.52 – 1.43 (m, 1H), 1.34 – 1.24 (m, 2H), 0.88 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.1, 134.9, 132.0, 131.9, 129.1, 127.4, 123.6, 112.8, 85.4, 44.6, 36.5, 32.4, 25.7, 25.2, 19.1, 17.7. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{19}H_{21}N_2$ 277.1705; Found 277.1708.



2-(1,4-diphenylbutylidene)malononitrile (1t): Physical state: White solid; **Yield:** 400 mg, 49 %. **^{1}H NMR (500 MHz, $CDCl_3$)** *δ* 7.56 – 7.53 (m, 1H), 7.48 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.17 (m, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 3.01 – 2.98 (m, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.74 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 180.1, 140.4, 134.7, 132.2, 129.3, 128.6, 128.4, 127.5, 126.5, 112.8, 112.6, 84.9, 77.4, 77.2, 76.9, 37.2, 35.3, 29.8. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{19}H_{15}N_2$ 271.1235; Found 271.1236.



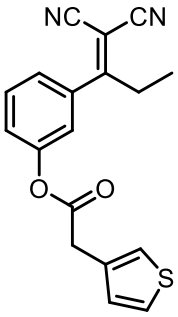
2-(1-(3-cyanophenyl)propylidene)malononitrile (1z): Physical State: White solid**; Yield:** 323 mg, 52 %. **^{1}H NMR (500 MHz, $CDCl_3$)** *δ* 7.84 (dt, *J* = 7.3, 1.6 Hz, 1H), 7.71 – 7.65 (m, 3H), 3.01-2.97 (m, 2H), 1.12 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 178.7, 136.1, 135.0, 131.7, 130.7, 130.5, 117.4, 114.1, 111.9, 111.6, 86.8, 31.3, 12.7. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{13}H_8N_3$ 206.0718; Found 206.0734.



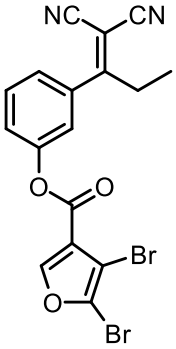
2-(1-(3-(trifluoromethyl)phenyl)propylidene)malononitrile (1y): Physical state: White solid; **Yield:** 360 mg, 48 %. **^{1}H NMR (500 MHz, $CDCl_3$)** *δ* 7.81 (tt, *J* = 5.4, 2.7 Hz, 1H), 7.71 – 7.65 (m, 3H), 3.01 (q, *J* = 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 179.85, 135.47, 132.25 (C-F, $2J_{C-F}$ = 32.76 Hz), 131.99 (C-F, $2J_{C-F}$ = 32.76 Hz), 131.73 (C-F, $2J_{C-F}$ = 32.76 Hz), 131.46 (C-F, $2J_{C-F}$ = 32.0 Hz), 130.96, 130.07, 128.86 (C-F, $1J_{C-F}$ = 273.42 Hz), 128.55 (C-F,

$^3J_{C\text{-}F}$ = 3.7 Hz), 128.52 (C-F, $^3J_{C\text{-}F}$ = 3.7 Hz), 128.49 (C-F, $^3J_{C\text{-}F}$ = 3.7 Hz), 128.46 (C-F, $^3J_{C\text{-}F}$ = 3.7 Hz), 128.24, 126.68 (C-F, $^1J_{C\text{-}F}$ = 273.42 Hz), 124.51 (C-F, $^1J_{C\text{-}F}$ = 273.42 Hz), 124.22 (C-F, $^3J_{C\text{-}F}$ = 3.9 Hz), 124.19 (C-F, $^1J_{C\text{-}F}$ = 3.9 Hz), 124.16 (C-F, $^3J_{C\text{-}F}$ = 3.9 Hz), 124.13 (C-F, $^3J_{C\text{-}F}$ = 3.9 Hz), 122.34 (C-F, $^1J_{C\text{-}F}$ = 273.42 Hz), 112.17, 111.90, 86.13, 31.24, 12.63. **^{19}F NMR (471 MHz, $CDCl_3$)** δ 62.87. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{13}H_8N_2F_3$ 249.0640; Found 249.0653.

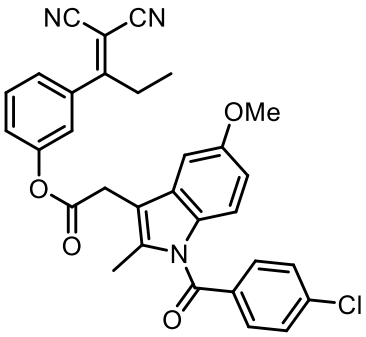
3-(1,1-dicyanobut-1-en-2-yl)phenyl 2-(thiophen-3-yl)acetate (1zb): Physical state: White solid: **Yield:** 531 mg, 55 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.56 (t, *J* = 8.0 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 (t, *J* = 2.2 Hz, 1H), 7.22 – 7.12 (m, 1H), 3.98 (s, 2H), 3.00 (q, *J* = 7.5 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.2, 169.2, 151.2, 135.9, 132.5, 130.5, 128.4, 126.4, 125.1, 123.6, 120.7, 112.5, 112.2, 85.3, 35.9, 31.3, 12.9. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{18}H_{13}N_2O_2S$ 321.0698; Found 321.0708.



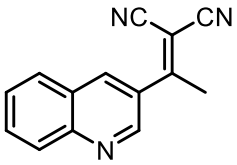
3-(1,1-dicyanobut-1-en-2-yl)phenyl 2-(4,5-dibromofuran-2-yl)acetate (1zc): Physical State: White liquid; **Yield ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 (t, *J* = 8.0 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.32 (t, *J* = 2.1 Hz, 1H), 2.97 (q, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.9, 154.7, 150.3, 144.8, 136.1, 130.7, 130.2, 125.5, 124.9, 124.0, 120.6, 112.4, 112.1, 104.5, 85.4, 77.4, 77.2, 76.9, 31.2, 12.8. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{17}H_9N_2O_3Br_2$ 446.8980; Found 446.8978.



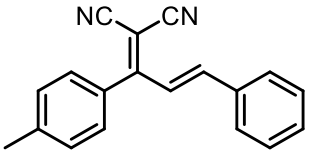
3-(1,1-dicyanobut-1-en-2-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (1ze): **Physical state:** White solid; **Yield:** 285 mg, 53 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.47 (m, 3H), 7.45 – 7.24 (m, 3H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 6.76 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.99 (s, 2H), 3.89 (d, *J* = 8.1 Hz, 3H), 3.00 (q, *J* = 7.5 Hz, 2H), 2.52 (s, 3H), 1.16 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.1, 168.9, 168.4, 156.3, 139.6, 136.5, 136.0, 133.9, 131.4, 131.0, 130.5, 129.3, 129.3, 125.1, 125.0, 120.7, 115.2, 112.4, 112.2, 111.9, 111.6, 101.4, 85.4, 55.9, 31.3, 30.7, 13.5, 12.8. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{31}H_{23}N_3O_4Cl$ 536.1377; Found 536.1375.



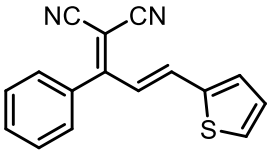
2-(1-(quinolin-3-yl)ethylidene)malononitrile (1zf): Physical state: Yellow solid; **Yield:** 335 mg, 51 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.01 (d, *J* = 2.5 Hz, 1H), 8.42 (d, *J* = 2.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.87 (t, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 2.77 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.1, 149.3, 147.1, 136.0, 132.4, 129.7, 129.0, 129.0, 128.4, 126.6, 112.6, 112.4, 86.4, 24.3. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{14}H_8N_3$ 218.0718; Found 218.0729.



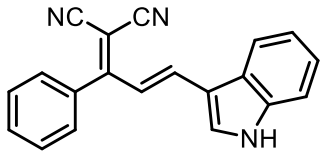
(E)-2-(3-phenyl-1-(p-tolyl)allylidene)malononitrile (1zo): Physical state: white solid; **Yield** 486 mg (60 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.53 (m, 3H), 7.43 – 7.38 (m, 5H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 15.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.0, 162.3, 149.1, 149.1, 134.5, 131.7, 131.2, 129.3, 128.8, 125.2, 124.9, 114.6, 114.1, 113.3, 81.2, 55.6. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{19}H_{13}N_2$ 269.1079; Found 269.1085.



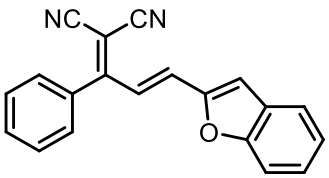
(E)-2-(1-phenyl-3-(thiophen-2-yl)allylidene)malononitrile (1zq): Physical State: Yellow solid; **Yield:** 377 mg, 48 %. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 – 7.45 (m, 4H), 7.30 – 7.26 (m, 3H), 7.18 – 7.17 (m, 1H), 7.01 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.96 – 6.90 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.9, 141.5, 141.5, 140.2, 133.4, 133.1, 131.7, 131.7, 131.3, 130.0, 129.2, 129.2, 129.1, 129.0, 128.9, 123.5, 113.7, 113.1, 81.2. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{16}H_9N_2S$ 261.0486; Found 261.0484.



(E)-2-(3-(1H-indol-3-yl)-1-phenylallylidene)malononitrile (1zr): Physical State: Red solid; **Yield:** 504 mg, 57 %. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 12.30 (s, 1H), 8.10 (d, *J* = 3.2 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.62 – 7.58 (m, 3H), 7.54 – 7.53 (m, 1H), 7.50 – 7.47 (m, 3H), 7.31 – 7.29 (m, 2H), 7.19 (d, *J* = 15.2 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.1, 144.8, 138.1, 136.9, 133.4, 130.6, 129.0, 128.8, 124.4, 123.6, 122.3, 119.9, 117.8, 115.0, 114.5, 114.0, 113.2, 73.9. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{20}H_{12}N_3$ 294.1031; Found 294.1024.

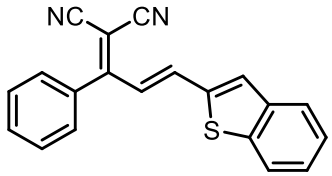


(E)-2-(3-(benzofuran-2-yl)-1-phenylallylidene)malononitrile (1zx): Physical State: Yellow solid; **Yield:** 408 mg 46 %. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 15.1 Hz, 1H), 7.61 – 7.54 (m, 5H), 7.45 – 7.38 (m, 3H), 7.29 – 7.25 (m, 1H), 6.95 (s, 1H), 6.73 (d, *J* = 15.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.3, 156.3, 152.4, 134.4, 132.9, 131.3,



129.3, 128.9, 128.4, 127.9, 124.9, 123.9, 122.3, 114.5, 113.6, 112.9, 111.9, 82.9. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{20}H_{11}N_2O$ 295.0871; Found 295.0861.

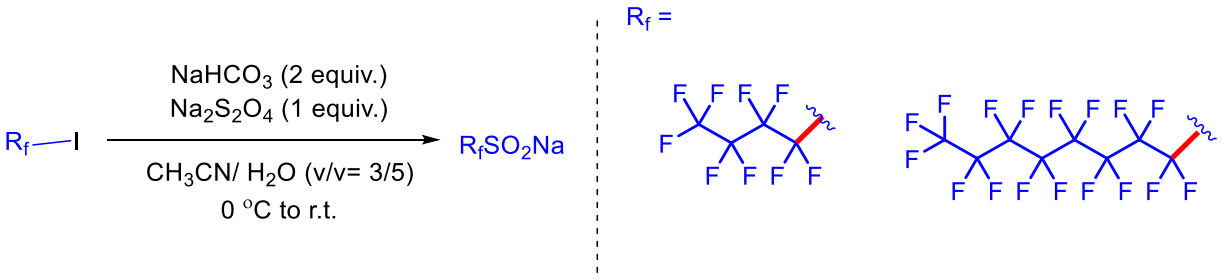
(E)-2-(3-(benzo[b]thiophen-2-yl)-1-phenylallylidene)malononitrile (1zt): Physical State:



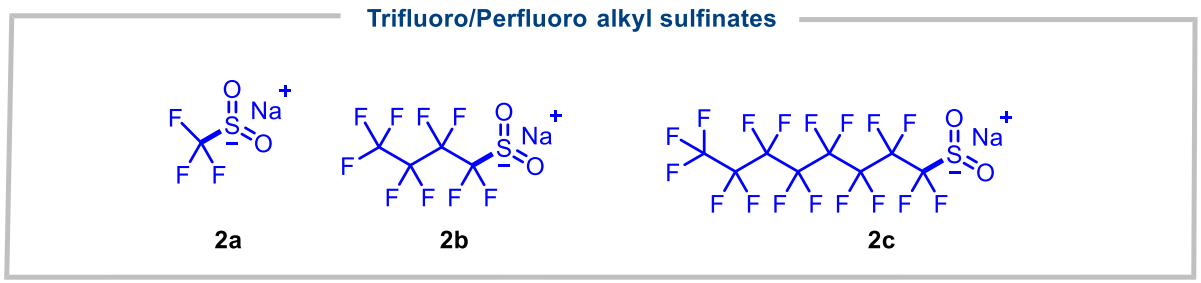
Yellow solid; **Yield:** 487 mg, 52 %. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.61 – 7.55 (m, 3H), 7.44 – 7.35 (m, 6H), 7.09 (d, *J* = 15.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 141.8, 141.4, 139.9, 139.5, 132.9, 131.4, 131.3, 129.8, 129.3, 129.2, 128.9, 128.9, 127.4, 125.8, 125.4, 125.1, 125.0, 122.8, 113.5, 112.8. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{20}H_{11}N_2S$ 311.0643; Found 311.0633.

4.2: With respect to perfluoroalkanesulfinates.

Perfluoroiodine compounds (R_f = C_4F_9, C_8F_{17}) (10 mmol) was bubbled into CH_3CN (6 mL) in a round bottom flask at 0°C. $NaHCO_3$ (1.68 g, 20 mmol, 2 equiv), $Na_2S_2O_4$ (1.58 g, 10 mmol, 2 equiv), and H_2O (10 mL) were added. The reaction mixture was stirred at room temperature overnight and then extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated to dryness. The residue was washed with diethyl ether (3 × 20 mL) and dried in vacuum to give corresponding perfluoroalkanesulfinates as a white solid (Scheme 4). The spectral data matched with those reported in the literature.[3]

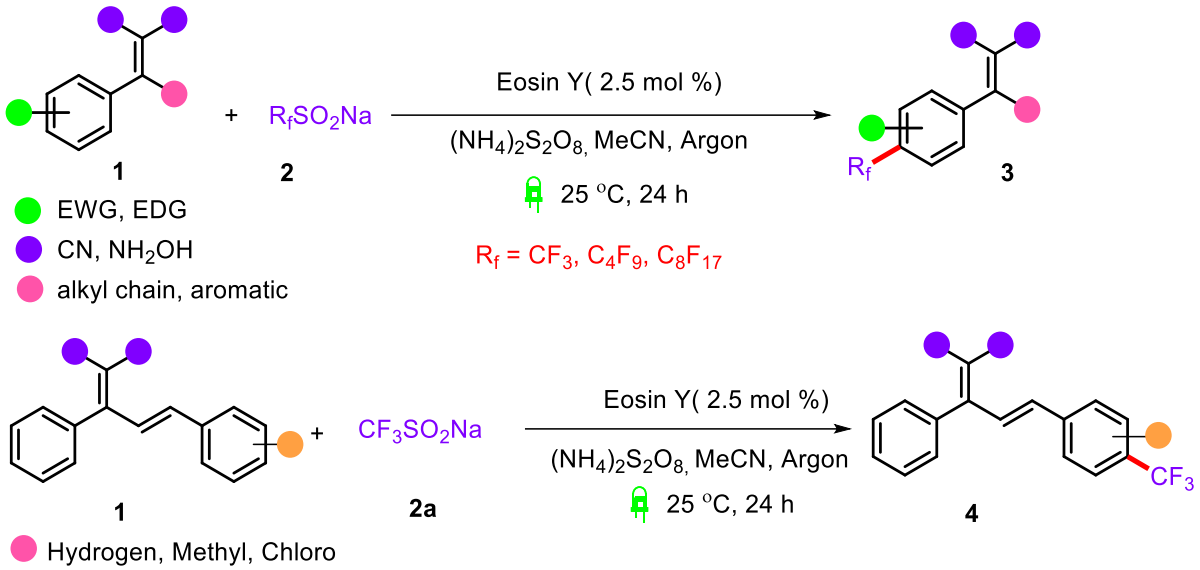


Scheme 4: Preparation of perfluoroalkanesulfinates



5: General experimental procedures and analytical data for the preparation of 3 and4.

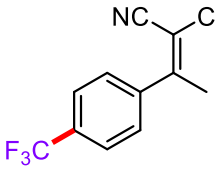
5.1: General procedures for the synthesis of 3 and 4.



Scheme 5: Preparation of trifluoromethylated alkylidene malononitrile

0.2 mmol of **1** (1.0 equiv.), Trifluoro/Perfluoro alkyl sulfinates (0.6 mmol, 3 equiv.) were taken in a long neck round bottom flask and 2.5 mol % of Eosin Y was added into it followed by ammonium peroxodisulfate, the RB was capped with septum. The mixture was degassed and filled with N_2 (three times). The reaction mixture was irradiated with green LED for 24 h. After completion (monitored through TLC), reaction was quenched with saturated $NaHCO_3$ solution and extracted with DCM (3 x 10 mL), washed with brine solution. After removal of solvent in vacuo, the product was purified by silica gel chromatography using EtOAc-hexane (3:7 to 5:5) as eluent to provide the desired product.

2-(1-(4-(trifluoromethyl)phenyl)ethylidene)malononitrile (3a): Physical State: White solid



Yield: 26 mg, 56 %**. ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 2.66 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.87, 139.40, 134.29 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 134.02 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 133.76 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 133.50 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 130.08 (C-F, $1J_{C\text{-}F}$ = 278.46 Hz), 127.87 (C-F, $1J_{C\text{-}F}$ = 278.46 Hz), 126.45 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.42 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.39 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.36 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 124.52 (C-F, $1J_{C\text{-}F}$ = 272.16 Hz), 122.36 (C-F, $1J_{C\text{-}F}$ = 272.16 Hz), 112.20, 112.16, 86.96, 24.53. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.9, -63.2. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{12}H_6N_2F_3$ 235.0483; Found 235.0492.

2-(1-(4-(trifluoromethyl)phenyl)propylidene)malononitrile (3b): Physical State: White solid **Yield:** 35 mg, 70 % . **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 3.00 (q, J = 7.6 Hz, 2H), 1.11 (t, J = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.00, 138.22, 133.96 (C-F, $2J_{C-F}$ = 32.0 Hz), 133.70 (C-F, $2J_{C-F}$ = 32.0 Hz), 133.44 (C-F, $2J_{C-F}$ = 32.0 Hz), 133.17 (C-F, $2J_{C-F}$ = 32.0 Hz),) 127.99, 126.43 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.40 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.37 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.34 (C-F, $3J_{C-F}$ = 3.7 Hz), 124.54 (C-F, $1J_{C-F}$ = 273.4 Hz), 122.37 (C-F, $1J_{C-F}$ = 273.4 Hz), 112.14, 111.86, 86.32, 31.33, 12.59. **^{19}F NMR (471 MHz, $CDCl_3$)** δ 63.17. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{13}H_8N_2F_3$ 249.0640; Found 249.0638.

2-(1-(4-(trifluoromethyl)phenyl)butylidene)malononitrile (3c): Physical State: Yellow liquid**, Yield:** 40 mg, 75, 697 mg, (66%) on 4 mmol scale. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 2.98 – 2.95 (m, 2H), 1.48 (q, J = 7.5 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.72, 138.46, 133.94 (C-F, $2J_{C-F}$ = 33.1 Hz), 133.68 (C-F, $2J_{C-F}$ = 33.1 Hz), 133.41 (C-F, $2J_{C-F}$ = 33.1 Hz), 133.15 (C-F, $2J_{C-F}$ = 33.1 Hz), 127.94, 126.42 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.39 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.36 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.33 (C-F, $3J_{C-F}$ = 3.7 Hz), 124.54 (C-F, $1J_{C-F}$ = 272.16 Hz) , 122.38 (C-F, $1J_{C-F}$ = 272.16 Hz), 112.17, 112.05, 86.84, 39.66, 21.60, 13.59. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.18. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{14}H_{10}N_2F_3$ 263.0796; Found 263.0807.

2-(1-(4-(trifluoromethyl)phenyl)pentylidene)malononitrile (3d) : Physical State: White Liquid**, Yield:** 45 mg, 80 %**. ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 2.98 (t, J = 7.3 Hz, 2H), 1.43 – 1.34 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.94, 138.57, 134.04 (C-F, $2J_{C-F}$ = 33.2 Hz), 133.78 (C-F, $2J_{C-F}$ = 33.2 Hz), 133.51 (C-F, $2J_{C-F}$ = 33.2 Hz), 133.25 (C-F, $2J_{C-F}$ = 33.2 Hz), 129.33, 127.96, 126.48 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.45 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.42 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.39 (C-F, $3J_{C-F}$ = 3.7 Hz), 124.58 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.41 (C-F, $1J_{C-F}$ = 273.42 Hz), 112.19, 112.04, 86.73, 37.75, 30.23, 22.47, 13.66. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.16. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{15}H_{12}N_2F_3$ 277.0953; Found 277.0966.

2-(1-(4-(trifluoromethyl)phenyl)pentylidene)malononitrile (3e): Physical State: white liquid; **yield:** 41 mg, 70 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 1.43 (t, J = 7.4 Hz, 2H), 1.34 – 1.25 (m, 4H), 0.86 (t, J = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.96, 138.54, 134.03 (C-F, $2J_{C\text{-}F}$ = 33.2 Hz), 133.76 (C-F, $2J_{C\text{-}F}$ = 33.2 Hz), 133.50 (C-F, $2J_{C\text{-}F}$ = 33.2 Hz), 133.23 (C-F, $2J_{C\text{-}F}$ = 33.2 Hz), 132.08, 129.32, 127.95, 127.55, 126.47 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.44 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.41(C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.38 (C-F, $2J_{C\text{-}F}$ = 3.7 Hz), 124.57 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.40 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 112.19, 112.04, 86.71, 37.94, 31.32, 27.87, 22.25, 13.86. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.15. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^+$ Calcd. $C_{16}H_{14}N_2F_3$ 291.1109; Found 291.1119.

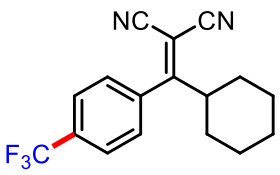
2-(1-(4-(trifluoromethyl)phenyl)octylidene)malononitrile (3f) : Physical State: white liquid. **Yield**: 44 mg, 69 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 2.98 – 2.95 (m, 2H), 1.43 – 1.39 (m, 2H), 1.34 – 1.28 (m, 2H), 1.27 – 1.20 (m, 6H), 0.86 (t, J = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.83, 138.42, 133.88 (C-F, $2J_{C\text{-}F}$ = 33.2 Hz), 133.62 (C-F, $2J_{C\text{-}F}$ = 33.2 Hz), 133.35 (C-F, $2J_{C\text{-}F}$ = 33.2 Hz), 133.09 (C-F, $2J_{C\text{-}F}$ = 33.2 Hz), 131.93, 129.17, 127.82, 127.41, 126.33 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.30 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.27 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.24 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 124.44 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.27 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 112.06, 111.90, 86.56, 37.84, 31.45, 29.05, 28.69, 28.67, 28.05, 22.49, 22.47, 13.99, 13.95. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.87, -63.15. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{18}H_{18}N_2F_3$ 319.1422; Found 319.1428.

2-(1-(4-(trifluoromethyl)phenyl)nonylidene)malononitrile (3g): Physical State: white liquid**; Yield:** 47 mg, 70 %**. ^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.78 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 2.97 (t, J = 7.5 Hz, 2H), 1.44 – 1.39 (m, 2H), 1.34 –1.28 (m, 2H), 1.27 – 1.20 (m, 6H), 0.86 (t, J = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.01, 138.53, 133.96 (C-F, $2J_{C\text{-}F}$ = 33.3 Hz), 133.69 (C-F, $2J_{C\text{-}F}$ = 33.3 Hz), 133.43 (C-F, $2J_{C\text{-}F}$ = 33.3 Hz), 133.17 (C-F, $2J_{C\text{-}F}$ = 33.3 Hz), 127.94, 126.43 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.40 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.37 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.34 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 124.56 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.39 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 112.20, 112.04, 86.63, 37.95, 31.76, 29.19, 29.07, 29.04, 28.15, 22.66, 14.12. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.17. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{19}H_{20}N_2F_3$ 333.1579; Found 333.1588.

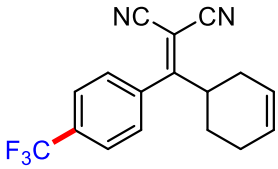
2-(1-(4-(trifluoromethyl)phenyl)undecylidene)malononitrile (3h): Physical State: white liquid**; Yield:** 47 mg, 65 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.78 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 2.97 (t, J = 7.5 Hz, 2H), 1.44 – 1.39 (m, 2H), 1.36 – 1.30 (m, 2H), 1.28 – 1.23 (m, 12H), 0.87 (t, J = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 178.98, 138.50, 133.84 (C-F, $2J_{C\text{-}F}$ = 33.5 Hz),133.57 (C-F, $2J_{C\text{-}F}$ = 33.5 Hz), 133.31 (C-F, $2J_{C\text{-}F}$ = 33.5 Hz), 133.05 (C-F, $2J_{C\text{-}F}$ = 33.5 Hz), 127.92, 126.35 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz),126.32 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 126.29 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 126.26 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 124.54 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.37 (C-F, $1J_{C\text{-}F}$ = 272.42 Hz), 112.18, 112.02, 86.55, 37.88, 31.88, 29.47, 29.32, 29.27, 29.12, 29.06, 28.07, 22.70, 14.11. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.16. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{21}H_{24}N_2F_3$ 361.1892; Found 361.1901.

2-(cyclopropyl(4-(trifluoromethyl)phenyl)methylene)malononitrile (3i): Physical State: white solid; **Yield:** 26 mg, 50 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.74 (d, J = 8.1 Hz, 2H), 7.31 – 7.21 (m, 2H), 2.53 – 2.48 (m, 1H), 1.35 – 1.30 (m, 2H), 0.83 – 0.79 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 182.05, 135.54, 133.01 (C-F, $2J_{C\text{-}F}$ = 34.0 Hz), 132.75 (C-F, $2J_{C\text{-}F}$ = 34.0 Hz), 132.48 (C-F, $2J_{C\text{-}F}$ = 34.0 Hz), 132.22 (C-F, $2J_{C\text{-}F}$ = 34.0 Hz), 128.05, 126.10 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.07 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.04 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.02 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 124.59 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.42 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 112.15, 111.85, 85.93, 19.72, 10.75. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.04. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. 261.0640; Found 261.0651.

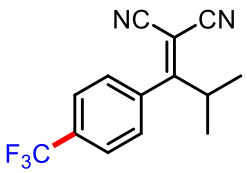
2-(cyclopentyl(4-(trifluoromethyl)phenyl)methylene)malononitrile (3j): Physical state: White solid; **Yield:** 32 mg, 56 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.75 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 3.50 – 3.43 (m, 1H), 2.07 – 2.01 (m, 2H), 1.71 – 1.66 (m, 4H), 1.52 – 1.40 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 183.65, 137.90, 132.86 (C-F, $2J_{C\text{-}F}$ = 32.7 Hz), 132.60 (C-F, $2J_{C\text{-}F}$ = 32.7 Hz), 132.33 (C-F, $2J_{C\text{-}F}$ = 32.7 Hz), 132.07 (C-F, $2J_{C\text{-}F}$ = 32.7 Hz), 127.73, 126.09 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.06 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.03 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.00 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 124.68 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.51 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 111.67, 111.55, 88.20, 47.59, 31.90, 25.44. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.04. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. 289.0953; Found 289.0963.

2-(cyclohexyl(4-(trifluoromethyl)phenyl)methylene)malononitrile (3k): Physical State: 

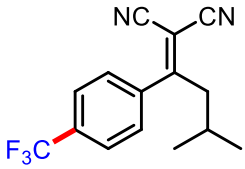
White solid**; Yield:** 35 mg, 57 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.75 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.15 – 3.09 (m, 1H), 1.84 – 1.79 (m, 4H), 1.70 (d, J = 13.7 Hz, 1H), 1.44 – 1.35 (m, 2H), 1.27 – 1.19 (m, 2H), 1.12 – 1.02 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 184.26, 138.10, 132.62 (C-F, $2J_{C-F}$ = 32.1 Hz), 132.37 (C-F, $2J_{C-F}$ = 32.1 Hz), 132.11(C-F, $2J_{C-F}$ = 32.1 Hz), 131.86 (C-F, $2J_{C-F}$ = 32.1 Hz),127.29, 125.94 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.91(C-F, $3J_{C-F}$ = 3.7 Hz), 124.69 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.52 (C-F, $1J_{C-F}$ = 273.42 Hz), 111.60, 111.36, 87.82, 46.73, 30.56, 30.54, 25.50, 25.05. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -62.98. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. 303.1109; Found 303.1122.

2-(cyclohex-3-en-1-yl(4-(trifluoromethyl)phenyl)methylene)malononitrile (3l): Physical state: 

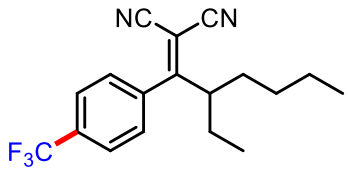
Yellow Solid**; Yield:** 32 mg, 53 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.76 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.73 – 5.64 (m, 2H), 3.42 – 3.36 (m, 1H), 2.20 – 2.15 (m, 3H), 2.07 – 2.01 (m, 1H), 1.92 – 1.88 (m, 1H), 1.57 – 1.53 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 183.45, 137.75, 132.88 (C-F, $2J_{C-F}$ = 33.3 Hz), 132.62 (C-F, $2J_{C-F}$ = 33.3 Hz), 132.35 (C-F, $2J_{C-F}$ = 33.3 Hz), 132.09 (C-F, $2J_{C-F}$ = 33.3 Hz), 127.32, 126.89, 126.07 (C-F, 3JC-F = 3.7 Hz), 126.04 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.01 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.98 (C-F, $3J_{C-F}$ = 3.7 Hz), 124.55 (C-F, $1J_{C-F}$ = 273.42 Hz), 123.97, 122.38 (C-F, $1J_{C-F}$ = 273.42 Hz), 88.35, 42.63, 28.81, 26.86, 24.74. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.05. **HRMS (ESI/QTOF), m/z:** [M-H] $^-$ Calcd. 301.0957; Found 301. 0953.

2-(2-methyl-1-(4-(trifluoromethyl)phenyl)propylidene)malononitrile (3m): Physical 

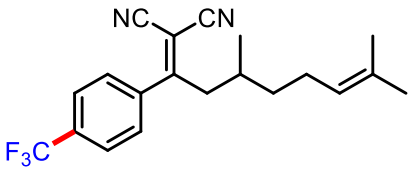
State: White liquid**; Yield:** 32mg, 60 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.76 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 3.52 – 3.46 (m, 1H), 1.19 (d, J = 6.9 Hz, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 184.89, 137.44, 132.98 (C-F, $2J_{C-F}$ = 33.0 Hz), 132.72 (C-F, $2J_{C-F}$ = 33.0 Hz), 132.45 (C-F, $2J_{C-F}$ = 33.0 Hz), 132.19 (C-F, $2J_{C-F}$ = 33.0 Hz), 127.56, 126.12(C-F, 3JC-F = 3.8 Hz), 126.09 (C-F, 3JC-F = 3.8 Hz), 126.06 (C-F, 3JC-F = 3.8 Hz), 126.03 (C-F, 3JC-F = 3.8 Hz),124.68 (C-F, 1JC-F = 272.16 Hz), 122.52 (C-F, 3JC-F = 272.16 Hz), 111.53, 111.25, 87.98, 36.30, 29.81, 20.55. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.06. **HRMS (ESI/QTOF), m/z:** [M-H] $^+$ Calcd. $C_{14}H_{10}N_2F_3$ 263.0808; Found 263.0796.

2-(3-methyl-1-(4-(trifluoromethyl)phenyl)butylidene)malononitrile (3n): Physical state: 

white liquid**; Yield:** 34 mg, 62 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79 – 7.77 (m, 2H), 7.57 – 7.56 (m, 2H), 2.89 (d, J = 7.3 Hz, 2H), 1.63 (dt, J = 13.6, 6.8 Hz, 1H), 0.95 (d, J = 6.7 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.06, 138.62, 134.00 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 133.74 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 133.48 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 133.21 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 127.95, 126.48 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 126.45 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 126.42 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 126.39 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 124.54 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.37 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 112.24, 112.21, 87.32, 46.58, 28.37, 22.23. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.16. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{15}H_{12}N_2F_3$ 277.0953; Found 277.0965.

2-(2-ethyl-1-(4-(trifluoromethyl)phenyl)hexylidene)malononitrile (3o): Physical state: 

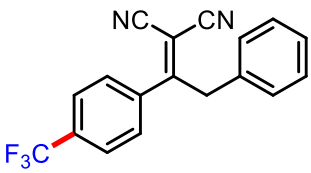
white liquid; **Yield**: 45 mg, 70 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 3.13 – 3.08 (m, 1H), 1.65 – 1.57 (m, 1H), 1.56 – 1.34 (m, 6H), 1.03 (t, J = 7.4 Hz, 3H), 0.92 (t, J = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 183.10, 137.77, 133.08 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 132.81 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 132.55 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 132.28, 128.59, 127.63, 126.83 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 126.19 (C-F, $3J_{C\text{-}F}$ = 3.5 Hz), 126.16 (C-F, $3J_{C\text{-}F}$ = 3.5 Hz), 126.13 (C-F, $3J_{C\text{-}F}$ = 3.5 Hz), 126.10 (C-F, $3J_{C\text{-}F}$ = 3.5 Hz), 124.66 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.48 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 111.67, 89.74, 50.16, 32.86, 30.01, 26.48, 22.69, 13.97, 12.42. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.09. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{18}H_{18}N_2F_3$ 319.1422; Found 319.1435.

2-(3,8-dimethyl-1-(4-(trifluoromethyl)phenyl)non-7-en-1-ylidene)malononitrile (3p): 

Physical State: yellow liquid; **Yield**: 29 mg, 40%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 4.94 – 4.91 (m, 1H), 2.99 (dd, J = 13.6, 6.2 Hz, 1H), 2.83 (dd, J = 13.6, 8.3 Hz, 1H), 1.97 (dt, J = 14.7, 7.3 Hz, 1H), 1.94 – 1.87 (m, 1H), 1.62 (d, J = 1.5 Hz, 3H), 1.55 (d, J = 1.3 Hz, 3H), 1.49 – 1.42 (m, 1H), 1.33 – 1.27 (m, 2H), 0.91 (d, J = 6.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.29, 138.54, 133.93 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 133.67 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 133.40 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 133.14 (C-F, $2J_{C\text{-}F}$ = 33.1 Hz), 132.33, 127.95, 126.38 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.35 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.33 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.30(C-F, $3J_{C\text{-}F}$ = 33.1 Hz), 124.55 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 123.50, 122.38 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 112.23, 112.20, 87.40, 44.88,

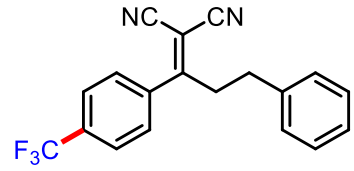
36.56, 32.35, 25.69, 25.20, 19.25, 17.76. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.16. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{18}H_{18}N_2F_3$ 319.1422; Found 319.1435.

2-(2-phenyl-1-(4-(trifluoromethyl)phenyl)ethylidene)malononitrile (3q): Physical State :



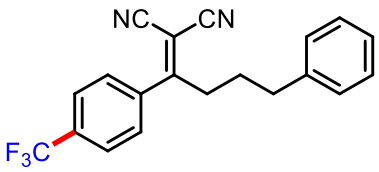
white solid; **Yield:** 32 mg, 52 %**. ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 6.9 Hz, 3H), 7.09 (dd, J = 7.4, 2.1 Hz, 2H), 4.28 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 175.98, 138.18, 133.50 (C-F, $2J_{C-F}$ = 33.0 Hz),133.45,133.24 (C-F, $2J_{C-F}$ = 33.0 Hz), 132.97 (C-F, $2J_{C-F}$ = 33.0 Hz), 132.71 (C-F, $2J_{C-F}$ = 33.0 Hz), 129.23, 128.80, 128.19, 128.02, 126.61 (C-F, $1J_{C-F}$ = 273.42 Hz), 126.06 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.03 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.00 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.97 (C-F, $3J_{C-F}$ = 3.7 Hz), 124.44 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.27 (C-F, $1J_{C-F}$ = 273.42 Hz), 120.11 (C-F, $1J_{C-F}$ = 273.42 Hz), 112.30, 112.00, 87.17, 43.36. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.01. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{20}H_{20}N_2F_3$ 345.1579; Found 345.1582.

2-(3-phenyl-1-(4-(trifluoromethyl)phenyl)propylidene)malononitrile (3r): Physical State:



white solid; **Yield:** 42 mg, 65 %, 704 mg (54). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.79 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 7.5 Hz, 2H), 3.33 (t, J = 7.6 Hz, 2H), 2.77 (t, J = 7.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 177.44, 138.22, 138.15, 133.82 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.56 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.30 (C-F, $2J_{C-F}$ = 33.0 Hz),, 133.03 (C-F, $2J_{C-F}$ = 33.0 Hz), 128.91, 128.46, 128.19, 127.18, 126.79 (C-F, $1J_{C-F}$ = 273.42 Hz),, 126.35 (C-F, $3J_{C-F}$ = 3.8 Hz), 126.32 (C-F, $3J_{C-F}$ = 3.8 Hz), 126.29 (C-F, $2J_{C-F}$ = 3.8 Hz), 126.26 (C-F, $2J_{C-F}$ = 3.8 Hz), 124.62 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.45 (C-F, $2J_{C-F}$ = 33.5 Hz), 120.29 (C-F, $1J_{C-F}$ = 273.42 Hz), 112.18, 112.01, 87.21, 39.31, 33.84. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.95. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{19}H_{12}N_2F_3$ 325.0953; Found 325.0960.

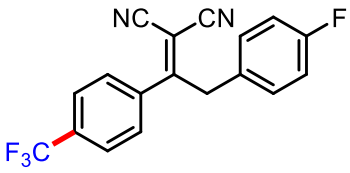
2-(4-phenyl-1-(4-(trifluoromethyl)phenyl)butylidene)malononitrile (3s): Physical state:



white solid; **Yield:** 46mg, 68 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.75 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 7.09 (d, J = 7.4 Hz, 2H), 3.01 (dd, J = 8.8, 6.7 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 1.77 (p, J = 7.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.37, 140.05, 138.19, 134.00 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.74 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.47 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.21 (C-F, $2J_{C-F}$ = 33.0 Hz), 128.75, 128.44, 127.96, 126.67, 126.41 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.38 (C-F, $3J_{C-F}$ =

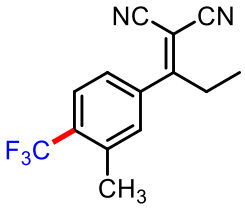
3.7 Hz), 126.35 (C-F, $2J_{C-F}$ = 3.7 Hz), 126.32 (C-F, $2J_{C-F}$ = 3.7 Hz), 124.52(C-F, $1J_{C-F}$ = 273.42), 122.35 (C-F, $1J_{C-F}$ = 273.42 Hz), 112.13, 111.99, 86.76, 37.31, 35.31, 29.55. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.13. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd.$C_{20}H_{14}N_2F_3$ 339.1109; Found 339.1118.

2-(2-(4-fluorophenyl)-1-(4-(trifluoromethyl)phenyl)ethylidene)malononitrile (3t):



Physical state: white liquid; **Yield:** 36 mg, 55 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.03 – 6.99 (m, 2H), 6.96 (t, J = 8.6 Hz, 2H), 4.23 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 175.70, 163.51, 161.54, 138.08, 134.05 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.75 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.48 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.20 (C-F, $2J_{C-F}$ = 33.0 Hz), 130.62, 130.55, 129.29 (C-F, $3J_{C-F}$ = 3.8 Hz), 129.26 (C-F, $3J_{C-F}$ = 3.8 Hz),129.23 (C-F, $3J_{C-F}$ = 3.8 Hz),129.20 (C-F, $3J_{C-F}$ = 3.8 Hz), 128.25, 126.40 (C-F, $3J_{C-F}$ = 3.9 Hz), 126.37 (C-F, $3J_{C-F}$ = 3.9 Hz), 126.34 (C-F, $3J_{C-F}$ = 3.9 Hz), 126.31 (C-F, $3J_{C-F}$ = 3.9 Hz), 124.47 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.30 (C-F, $1J_{C-F}$ = 273.42 Hz), 116.56, 116.39, 112.23, 111.87, 87.52, 42.75. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.19, -113.23. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{18}H_9N_2F_4$ 329.0702; Found 329.0713.

2-(1-(3-methyl-4-(trifluoromethyl)phenyl)propylidene)malononitrile (3u): Physical state:



white liquid; **Yield:** 42 mg, 80 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.74 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 6.6 Hz, 2H), 2.98 (q, J = 7.6 Hz, 2H), 2.56 (s, 3H), 1.11 (t, J = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.18, 138.60 (C-F, $2J_{C-F}$ = 32.76 Hz), 138.35 (C-F, $2J_{C-F}$ = 32.76 Hz), 138.09 (C-F, $2J_{C-F}$ = 32.76 Hz), 137.76 (C-F, $2J_{C-F}$ = 32.76 Hz), 132.11, 131.86, 130.63, 127.12 (C-F, $1J_{C-F}$ = 273.42 Hz), 127.00 (C-F, $3J_{C-F}$ = 5.5 Hz), 126.96 (C-F, $3J_{C-F}$ = 5.5 Hz), 126.91 (C-F, $3J_{C-F}$ = 5.5 Hz), 126.87 (C-F, $3J_{C-F}$ = 5.5 Hz), 124.97(C-F, $1J_{C-F}$ = 273.42 Hz), 122.80 (C-F, $1J_{C-F}$ = 273.42 Hz), 121.38, 120.63(C-F, $1J_{C-F}$ = 273.42 Hz), 112.22, 111.96, 86.09, 31.30, 19.56, 12.67. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.25 (major), -62.85 (minor). **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{14}H_{10}N_2F_3$ 263.0796; Found 263.0809.

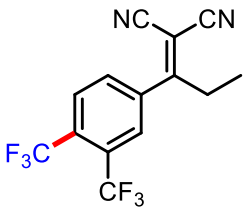
2-(1-(3-methoxy-4-(trifluoromethyl)phenyl)propylidene)malononitrile (3v): Physical state: white liquid; **Yield:** 38 mg, 68 %. **Yield**: 526 mg, (47 %) on 4 mmol scale. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.70 (d, J = 8.1 Hz, 1H), 7.06 – 7.04 (m, 2H), 3.97 (s, 3H), 2.99 (q, J = 7.6 Hz, 2H), 1.13 (t, J = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 180.08, 157.92, 139.55, 128.37 (C-F, $^{3}J_{C\text{-}F}$ = 5.04 Hz), 128.33 (C-F, $^{3}J_{C\text{-}F}$ = 5.04 Hz), 128.28 (C-F, $^{3}J_{C\text{-}F}$ = 5.04 Hz), 126.22 (C-F, $^{1}J_{C\text{-}F}$ = 273.42 Hz), 124.05 (C-F, $^{1}J_{C\text{-}F}$ = 273.42 Hz), 122.22 (C-F, $^{2}J_{C\text{-}F}$ = 31.5 Hz), 121.97 (C-F, $^{2}J_{C\text{-}F}$ = 31.5 Hz), 121.88 (C-F, $^{1}J_{C\text{-}F}$ = 273.42 Hz), 121.72 (C-F, $^{2}J_{C\text{-}F}$ = 31.5 Hz), 121.46 (C-F, $^{2}J_{C\text{-}F}$ = 31.5 Hz), 119.71 (C-F, $^{1}J_{C\text{-}F}$ = 273.42 Hz), 118.90, 112.29, 111.92, 111.16, 86.15, 56.46, 31.32, 12.73. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.05. **HRMS (ESI/QTOF), m/z:** [M-H]$^+$ Calcd. $C_{14}H_{10}N_2OF_3$ 279.0757; Found 279.0754.

2-(1-(2-methoxy-4-(trifluoromethyl)phenyl)propylidene)malononitrile (3w): Physical state: white liquid; **Yield:** 34 mg, 60 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.74 – 7.71 (m, 1H), 7.38 (d, J = 2.2 Hz, 1H), 7.10 (d, J = 8.7 Hz, 1H), 3.94 (s, 3H), 2.95 (q, J = 7.6 Hz, 2H), 1.07 (t, J = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 178.79, 170.44, 158.37, 129.70 (C-F, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 129.68 (C-F, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 129.65 (C-F, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 129.62 (C-F, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 126.94 (C-F, $^{1}J_{C\text{-}F}$ = 273.42 Hz), 125.65 (C-F, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 125.62 (C-F, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 125.59 (C-F, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 125.56 (C-F, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 124.78 (C-F, $^{1}J_{C\text{-}F}$ = 273.42 Hz), 124.50, 123.80 (C-F, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 123.54 (C-F, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 123.27 (C-F, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 123.00 (C-F, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 122.62 (C-F, $^{1}J_{C\text{-}F}$ = 273.42 Hz), 111.90, 111.84, 111.70, 88.19, 56.19, 31.00, 11.97. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -61.71. **HRMS (ESI/QTOF), m/z:** [M-H]$^+$ Calcd. $C_{14}H_{10}N_2OF_3$ 279.0757; Found 279.0752.

2-(1-(3-bromo-4-(trifluoromethyl)phenyl)propylidene)malononitrile (3x): Physical state: yellow liquid**; Yield:** 39 mg, 60 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.83 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 1.8 Hz, 1H), 7.51 – 7.47 (m, 1H), 2.97 (q, J = 7.6 Hz, 2H), 1.13 (t, J = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 178.08, 139.48, 133.38 (C-F, $^{2}J_{C\text{-}F}$ = 32.76 Hz), 133.13 (C-F, $^{2}J_{C\text{-}F}$ = 32.76 Hz), 132.87 (C-F, $^{2}J_{C\text{-}F}$ = 32.76 Hz), 132.62 (C-F, $^{2}J_{C\text{-}F}$ = 32.76 Hz), 128.84 (C-F, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 128.79 (C-F, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 128.75 (C-F, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 128.71 (C-F, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 127.82 (C-F, $^{1}J_{C\text{-}F}$ = 272.91 Hz), 126.44, 125.64 (C-F, $^{1}J_{C\text{-}F}$ = 272.91 Hz), 123.47 (C-F, $^{1}J_{C\text{-}F}$ = 272.91 Hz), 121.32 (C-F, $^{1}J_{C\text{-}F}$ = 272.91 Hz), 111.72,

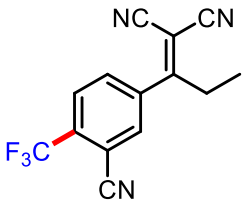
111.49, 87.27, 31.27, 12.55. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.17. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{13}H_7N_2F_3Br$ 326.9745; Found 326.9756.

2-(1-(3,4-bis(trifluoromethyl)phenyl)propylidene)malononitrile (3y): Physical state: white



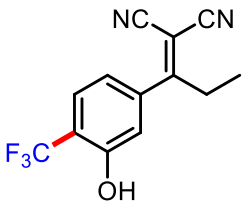
liquid**; Yield:** 38 mg, 60 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (d, J = 8.2 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.79 – 7.78 (m, 1H), 3.03 (q, J = 7.6 Hz, 2H), 1.14 (t, J = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 177.77, 138.86, 131.27, 129.38 (C-F, $3J_{C-F}$ = 5.6 Hz), 129.33 (C-F, $3J_{C-F}$ = 5.6 Hz), 129.29 (C-F, $3J_{C-F}$ = 5.6 Hz), 129.24 (C-F, $3J_{C-F}$ = 5.6 Hz), 126.87 (C-F, $3J_{C-F}$ = 5.6 Hz), 126.82(C-F, $3J_{C-F}$ = 5.6 Hz), 126.77 (C-F, $3J_{C-F}$ = 5.6 Hz), 126.73 (C-F, $3J_{C-F}$ = 5.6 Hz), 123.29 (C-F, $1J_{C-F}$ = 275.94 Hz), 121.10 (C-F, $1J_{C-F}$ = 275.94 Hz), 111.61, 111.34, 87.92, 31.27, 12.56. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -59.56 (q, J = 12.3, 11.3 Hz), -59.74 (q, J = 13.6, 12.3 Hz). **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{14}H_7N_2F_6$. 317.0513; Found 317.0522.

2-(1-(3-cyano-4-(trifluoromethyl)phenyl)propylidene)malononitrile (3z): Physical state:



white liquid**; Yield:** 36 mg, 65 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.98 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 1.8 Hz, 1H), 7.82 – 7.80 (m, 1H), 3.01 (q, J = 7.6 Hz, 2H), 1.14 (t, J = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 176.99, 139.19, 135.56 (C-F, $2J_{C-F}$ = 33.5 Hz), 135.30 (C-F, $2J_{C-F}$ = 33.0 Hz), 135.03 (C-F, $2J_{C-F}$ = 33.0 Hz), 134.76 (C-F, $2J_{C-F}$ = 33.0 Hz), 133.18, 131.93, 128.10 (C-F, $3J_{C-F}$ = 4.6 Hz), 128.07 (C-F, $3J_{C-F}$ = 4.6 Hz), 128.03 (C-F, $3J_{C-F}$ = 4.6 Hz), 127.99 (C-F, $3J_{C-F}$ = 4.6 Hz), 125.09 (C-F, $1J_{C-F}$ = 274.6 Hz), 122.91 (C-F, $1J_{C-F}$ = 274.6 Hz), 120.72 (C-F, $1J_{C-F}$ = 274.6 Hz), 114.24, 111.90, 111.45, 111.13, 88.23, 31.27, 12.45. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.24. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{14}H_7N_3F_3$ 274.0592; Found 274.0598.

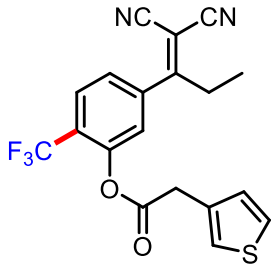
2-(1-(3-hydroxy-4-(trifluoromethyl)phenyl)propylidene)malononitrile (3za): Physical



state: white liquid**; Yield:** 27 mg, 50 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 7.9 Hz, 1H), 7.10 (s, 1H), 7.03 (d, J = 8.3 Hz, 1H), 2.98 – 2.94 (m, 2H), 1.12 (t, J = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.89, 140.10 (C-F, $2J_{C-F}$ = 31.5 Hz), 139.85 (C-F, $2J_{C-F}$ = 31.5 Hz), 139.60 (C-F, $2J_{C-F}$ = 31.5 Hz), 139.35 (C-F, $2J_{C-F}$ = 31.5 Hz), 131.76, 128.25 (C-F, $3J_{C-F}$ = 4.8 Hz), 128.22 (C-F, $3J_{C-F}$ = 4.8 Hz), 128.18 (C-F, $3J_{C-F}$ = 4.8 Hz), 128.15 (C-F, $3J_{C-F}$ = 4.8 Hz), 123.34, 61 (C-F, $1J_{C-F}$ = 274.68 Hz), 121.16 (C-F, $1J_{C-F}$ = 274.68 Hz), 119.02, 118.98 (C-F, $1J_{C-F}$ = 274.68 Hz), 116.80 (C-F, $1J_{C-F}$ = 274.68 Hz), 112.25, 111.88, 86.05, 31.31, 12.72. **^{19}F NMR (471**

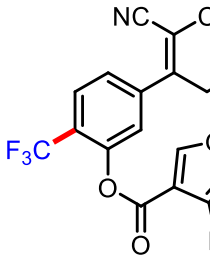
MHz, $CDCl_3$) δ -62.08. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{13}H_8N_2F_3O$ 265.0589; Found 265.0592.

5-(1,1-dicyanobut-1-en-2-yl)-2-(trifluoromethyl)phenyl 2-(thiophen-3-yl)acetate (3zb):



Physical state: white liquid**; Yield:** 46 mg, 59 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 – 7.47 (m, 2H), 7.36 (dd, *J* = 6.7, 2.1 Hz, 1H), 7.24 – 7.14 (m, 2H), 7.03 – 6.92 (m, 1H), 4.06 (s, 2H), 2.96 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.12, 167.98, 156.37, 150.98, 135.94, 130.68, 130.64, 130.53, 129.90, 127.92 (C-F, $3J_{C\text{-}F}$ = 2.02 Hz), 127.91 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 127.89 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 127.88 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 127.74 (C-F, $1J_{C\text{-}F}$ = 273.71 Hz), 125.23, 125.03 (C-F, $1J_{C\text{-}F}$ = 273.71 Hz), 124.94, 122.32 (C-F, $1J_{C\text{-}F}$ = 273.71 Hz), 120.51, 119.75, 119.60 (C-F, $1J_{C\text{-}F}$ = 273.71 Hz), 114.44, 112.37, 112.17, 85.33, 33.96, 31.23, 12.80. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -53.50. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{19}H_{12}N_2O_2SF_3$ 389.0572; Found 389.0574.

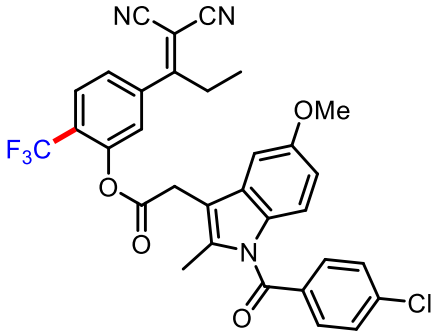
5-(1,1-dicyanobut-1-en-2-yl)-2-(trifluoromethyl)phenyl 4,5-dibromofuran-3-carboxylate (3zc): Physical state: white liquid**; Yield:** 46 mg, 45 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 (td, *J* = 8.5, 4.2 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.94 (s, 1H), 2.95 (q, *J* = 7.5, 6.7 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 181.70, 156.38, 136.07, 130.76, 130.68, 121.02 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 120.48, 119.82, 119.39, 118.88 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 116.74 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 115.18, 114.59 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 114.50, 112.89, 112.48, 84.36, 31.26, 12.93. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -61.93.



5-(1,1-dicyanobut-1-en-2-yl)-2-(trifluoromethyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3zd): **Physical state:** white liquid**; Yield:** 61 mg, 61%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.17 (t, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 26.8 Hz, 2H), 4.03 (d, *J* = 4.9 Hz, 1H), 3.92 (t, *J* = 5.9 Hz, 1H), 2.96 (q, *J* = 7.5 Hz, 2H), 2.42 (s, 2H), 2.30 (s, 2H), 2.18 (d, *J* = 6.5 Hz, 3H), 1.90 (s, 1H), 1.40 (s, 6H), 1.20 (s, 3H), 1.12 (d, *J* = 7.3 Hz, 3H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.23, 176.57, 175.94, 159.09, 157.11, 151.57, 138.61, 136.66, 136.02, 135.93, 130.73 (C-F, $1J_{C\text{-}F}$ = 273.4 Hz), 130.48, 130.46, 129.71, 128.55 (C-F, $1J_{C\text{-}F}$ = 273.4 Hz), 128.37 (C-F, $3J_{C\text{-}F}$ = 5.04 Hz), 128.33 (C-F, $3J_{C\text{-}F}$ = 5.04 Hz), 128.29 (C-F, $3J_{C\text{-}F}$ = 5.04 Hz), 128.25

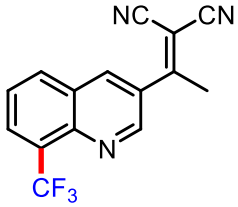
(C-F, $3J_{C-F}$ = 5.04 Hz), 126.40 (C-F, $1J_{C-F}$ = 273.4 Hz), 126.20, 125.48, 125.09, 124.90, 124.22 (C-F, $1J_{C-F}$ = 273.4 Hz), 124.03, 123.73, 121.13, 120.93, 120.71, 114.08, 112.36, 112.24, 85.40, 68.24, 68.17, 68.12, 48.19, 42.73, 41.83, 37.91, 37.11, 33.34, 32.08, 31.29, 29.84, 25.76, 25.71, 25.30, 25.28, 25.25, 25.02, 22.83, 21.52, 19.52, 15.94, 15.78, 14.24, 12.83. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -59.96. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{28}H_{28}N_2O_3F_3$ 497.2052; Found 497.2047.

5-(1,1-dicyanobut-1-en-2-yl)-2-(trifluoromethyl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (3ze):



Physical State: White liquid. **Yield:** 40 mg, 66 %. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.67 (dd, *J* = 8.6, 2.3 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.42 – 7.30 (m, 3H), 7.22 (t, *J* = 2.0 Hz, 1H), 6.86 (d, *J* = 9.2 Hz, 1H), 4.06 (q, *J* = 2.6 Hz, 2H), 3.89 (s, 3H), 2.96 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 180.31, 169.75, 168.24, 155.15, 151.40, 140.47, 139.59, 135.94, 133.33, 132.21, 131.63, 130.50, 129.84, 129.58, 125.22, 125.09, 124.52 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.36 (C-F, $1J_{C-F}$ = 273.42 Hz), 120.72, 120.13 (C-F, $1J_{C-F}$ = 273.42 Hz), 118.24, 118.02 (C-F, $1J_{C-F}$ = 273.42 Hz), 112.48, 112.30, 110.26, 109.94, 85.23, 57.85, 31.28, 13.86, 12.85. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -51.47, -52.44. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{32}H_{22}N_3O_4ClF_3$ 604.1251; Found 604.1249.

2-(1-(8-(trifluoromethyl)quinolin-3-yl)ethylidene)malononitrile (3zf): **Physical state:**



white liquid**; Yield:** 32 mg, 56 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.10 (d, *J* = 2.3 Hz, 1H), 8.67 (s, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 1H), 7.91 (t, *J* = 7.9 Hz, 1H), 2.80 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 171.43, 149.39, 147.84, 134.44, 132.34, 131.09, 130.50, 130.47, 130.41, 127.72 (C-F, $2J_{C-F}$ = 30.24 Hz), 127.48 (C-F, $2J_{C-F}$ = 30.24 Hz), 127.24 (C-F, $2J_{C-F}$ = 30.24 Hz), 127.10 (C-F, $1J_{C-F}$ = 273.42 Hz), 127.04 (C-F, $2J_{C-F}$ = 30.24 Hz), 126.91(C-F, $3J_{C-F}$ = 2.52 Hz), 126.89 (C-F, $3J_{C-F}$ = 2.52 Hz), 126.87 (C-F, $3J_{C-F}$ = 2.52 Hz), 126.85 (C-F, $3J_{C-F}$ = 2.52 Hz), 124.93 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.95, 122.75 (C-F, $1J_{C-F}$ = 273.42 Hz), 120.57 (C-F, $1J_{C-F}$ = 273.42 Hz), 112.05, 112.03, 87.89, 24.39. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -58.72. **HRMS (ESI/QTOF), m/z:** [M-H]$^+$ Calcd. $C_{15}H_7N_3F_3$ 286.0595; Found 286.0592.

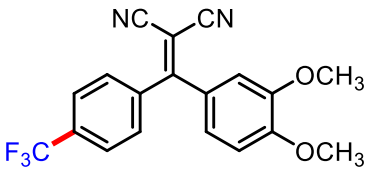
2-(1-(5,8-bis(trifluoromethyl)quinolin-3-yl)ethylidene)malononitrile (3zg): Physical state: white liquid**; Yield:** 10 mg, 14 %. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.22 (d, *J* = 2.3 Hz, 1H), 8.73 (dq, *J* = 2.9, 1.5 Hz, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 2.81 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 170.56, 148.47, 145.85, 133.17 (C-F, $2J_{C-F}$ = 31.5 Hz), 132.93 (C-F, $2J_{C-F}$ = 31.5 Hz), 132.68 (C-F, $2J_{C-F}$ = 31.5 Hz), 132.44 (C-F, $2J_{C-F}$ = 31.5 Hz), 132.31, 132.29, 131.60 (C-F, $2J_{C-F}$ = 31.5 Hz), 131.35 (C-F, $2J_{C-F}$ = 31.5 Hz), 131.15, 131.09 (C-F, $2J_{C-F}$ = 31.5 Hz), 130.84 (C-F, $2J_{C-F}$ = 31.5 Hz), 129.03 (C-F, $3J_{C-F}$ = 5.7 Hz), 128.99 (C-F, $3J_{C-F}$ = 5.7 Hz), 128.94 (C-F, $3J_{C-F}$ = 5.7 Hz), 128.90 (C-F, $3J_{C-F}$ = 5.7 Hz), 126.37 (C-F, $1J_{C-F}$ = 273.42 Hz), 126.24 (C-F, $1J_{C-F}$ = 273.42 Hz), 125.75 (C-F, $3J_{C-F}$ = 5.7 Hz), 125.71 (C-F, $3J_{C-F}$ = 5.7 Hz), 125.66 (C-F, $3J_{C-F}$ = 5.7 Hz), 125.62 (C-F, $3J_{C-F}$ = 5.7 Hz), 124.19 (C-F, $1J_{C-F}$ = 273.42 Hz), 124.06 (C-F, $1J_{C-F}$ = 273.42 Hz), 123.61, 122.01 (C-F, $1J_{C-F}$ = 273.42 Hz), 121.88 (C-F, $1J_{C-F}$ = 273.42 Hz), 119.84 (C-F, $1J_{C-F}$ = 273.42 Hz), 119.70 (C-F, $1J_{C-F}$ = 273.42 Hz), 111.79, 111.76, 88.79, 24.38. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -59.23, -60.82. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{16}H_6N_3O_4F_6$ 354.0466; Found 354.0473.

2-((4-(dimethylamino)phenyl)(4-(trifluoromethyl)phenyl)methylene)malononitrile (3zh): Physical state: red solid**; Yield:** 31 mg. **^{1}H NMR (500 MHz, CDCl$_3$)** *δ* 7.74 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.42 (m, 2H), 6.69 – 6.66 (m, 2H), 3.11 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** *δ* 171.27, 153.82, 140.74, 133.75 (C-F, $2J_{C-F}$ = 32.6 Hz), 133.50 (C-F, $2J_{C-F}$ = 32.6 Hz), 133.43, 133.23 (C-F, $2J_{C-F}$ = 32.6 Hz), 132.97 (C-F, $2J_{C-F}$ = 32.6 Hz), 130.80, 125.74 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.71 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.68 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.65 (C-F, $3J_{C-F}$ = 3.7 Hz), 124.74 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.57 (C-F, $1J_{C-F}$ = 273.42 Hz), 121.62, 115.63, 115.16, 111.32, 74.73, 40.12. **^{19}F NMR (471 MHz, CDCl$_3$)** *δ* -62.93. **HRMS (ESI/QTOF), m/z:** $[M+H]^+$ Calcd. $C_{19}H_{15}F_3N_3$ 342.1212; Found 342.1202.

2-((4-(tert-butyl)phenyl)(4-(trifluoromethyl)phenyl)methylene)malononitrile (3zi): Physical state: white solid**; Yield:** 35 mg. **^{1}H NMR (500 MHz, CDCl$_3$)** *δ* 7.76 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.43 – 7.37 (m, 2H), 1.36 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** *δ* 173.08, 157.68, 139.83, 134.32 (C-F, $2J_{C-F}$ = 33.2 Hz), 134.06 (C-F, $2J_{C-F}$ = 33.2 Hz), 133.79 (C-F, $2J_{C-F}$ = 33.2 Hz), 133.52 (C-F, $2J_{C-F}$ = 33.2 Hz), 132.46, 130.79, 130.55, 127.65, 126.26, 126.03 (C-F, $3J_{C-F}$ = 3.7 Hz), 126.00 (C-F, $3J_{C-F}$

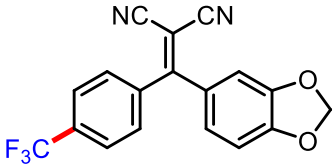
= 3.7 Hz), 125.97 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.94 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.14 , 124.60 (C-F, $1J_{C-F}$ = 272.16 Hz), 122.44 (C-F, $1J_{C-F}$ = 272.16 Hz), 113.79, 113.65, 82.33, 35.44, 31.10. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.15. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{21}H_{17}N_2F_3$ 354.1356; Found 354.1354.

2-((3,4-dimethoxyphenyl)(4-(trifluoromethyl)phenyl)methylene)malononitrile (3zj):



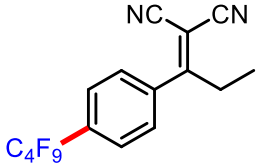
Physical state: white solid**; Yield:** 36 mg. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 2.1 Hz, 1H), 6.95 – 6.90 (m, 2H), 3.95 (s, 3H), 3.87 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.30, 153.87, 149.19, 139.85, 134.52 (C-F, $2J_{C-F}$ = 34.02 Hz), 134.25 (C-F, $2J_{C-F}$ = 34.02 Hz), 134.00 (C-F, $2J_{C-F}$ = 34.02 Hz), 133.72 (C-F, $2J_{C-F}$ = 34.02 Hz), 130.87, 127.53, 126.06, 125.97 (C-F, $3J_{C-F}$ = 3.8 Hz), 125.94 (C-F, $3J_{C-F}$ = 3.8Hz), 125.91 (C-F, $3J_{C-F}$ = 3.8 Hz), 125.88 (C-F, $3J_{C-F}$ = 3.8 Hz), 124.60 (C-F, $1J_{C-F}$ = 272.16 Hz), 122.44 (C-F, $1J_{C-F}$ = 272.16 Hz), 80.65, 56.34. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.11. **HRMS (ESI/QTOF), m/z:** $[M+H]^+$ Calcd. $C_{19}H_{14}N_2O_2F_3$ 359.1007; Found 359.1015.

2-(benzo[d][1,3]dioxol-5-yl(4-(trifluoromethyl)phenyl)methylene)malononitrile: (3zk):



Physical state: white solid**; Yield:** 36 mg. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.04 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.10 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.07, 152.23, 148.37, 139.67, 133.91 (C-F, $2J_{C-F}$ = 32.76 Hz), 133.68 (C-F, $2J_{C-F}$ = 32.76 Hz), 133.42 (C-F, $2J_{C-F}$ = 32.76 Hz), 133.13 (C-F, $2J_{C-F}$ = 32.76 Hz), 130.67, 128.82, 127.01, 126.62 (C-F, $1J_{C-F}$ = 273.42 Hz), 125.80 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.77 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.74 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.71 (C-F, $3J_{C-F}$ = 3.7 Hz), 124.46 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.29 (C-F, $1J_{C-F}$ = 273.42 Hz), 120.12 (C-F, $1J_{C-F}$ = 273.42 Hz), 113.78, 113.62, 110.01, 108.68, 81.08. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.06. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{18}H_{10}N_2O_2F_3$ 343.0694: Found 343.0706.

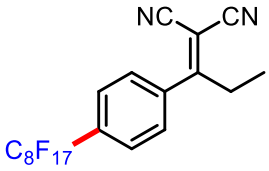
2-(1-(4-(perfluorobutyl)phenyl)propylidene)malononitrile (3zl): Physical state: white



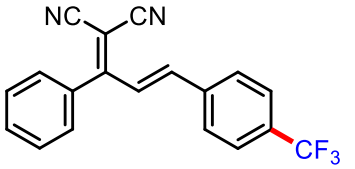
liquid**; Yield:** 52 mg. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 3.01 (q, *J* = 7.6 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -81.01 (t, *J* = 9.9 Hz), -111.46 (t, *J* = 13.6 Hz), -122.56 (q, *J* = 10.3 Hz), -125.51 – -125.62 (m). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.77, 138.48, 132.33 (C-F, $2J_{C-F}$ = 23.94 Hz) , 132.14 (C-F, $2J_{C-F}$ = 23.94 Hz), 131.94 (C-F, $2J_{C-F}$ = 23.94 Hz), 129.32 (C-F, $1J_{C-F}$ = 216.72 Hz),

128.03 (C-F, $3J_{C-F}$ = 6.3 Hz), 127.98 (C-F, $3J_{C-F}$ = 6.3 Hz), 127.93 (C-F, $3J_{C-F}$ = 6.3 Hz), 127.84, 127.60 (C-F, $1J_{C-F}$ = 216.72 Hz), 112.10, 111.86, 86.48, 31.35, 12.63. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{16}H_8N_2F_9$ 399.0544; Found 399.0553.

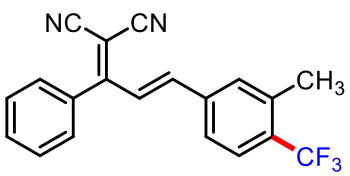
2-(1-(4-(1,1,2,2,3,3,4,4,5,5,7,7,8,8,8pentadecafluorooctyl)phenyl)propylidene)malononitrile (3zm): Physical state: white liquid**; Yield:** 17 mg. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 3.01 (q, *J* = 7.6 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 3H). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -80.71 (t, *J* = 10.0 Hz, 3H), -111.19 (t, *J* = 14.8 Hz, 2H), -121.03 –121.58 (m, 4H), -121.85 (d, *J* = 40.1 Hz, 3H), -122.73 (d, *J* = 20.4 Hz, 2H), -126.11 (td, *J* = 14.4, 6.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.80, 138.48, 132.30 (C-F, $2J_{C-F}$ = 24.7 Hz), 132.11 (C-F, $2J_{C-F}$ = 24.7 Hz), 131.91 (C-F, $2J_{C-F}$ = 24.7 Hz), 129.30 (C-F, $1J_{C-F}$ = 215.46 Hz), 128.02 (C-F, $3J_{C-F}$ = 6.3 Hz), 127.97 (C-F, $3J_{C-F}$ = 6.3 Hz), 127.91 (C-F, $3J_{C-F}$ = 6.3 Hz), 127.84, 127.59 (C-F, $1J_{C-F}$ = 215.46 Hz), 112.10, 111.86, 86.45, 77.41, 77.16, 76.91, 31.34, 12.61. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{20}H_8N_2F_{17}$ 599.0416; Found 599.0424.



(E)-2-(1-phenyl-3-(4-(trifluoromethyl)phenyl)allylidene)malononitrile (4a): Physical state: yellow solid**; Yield:** 36 mg, 55 %. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.56 (m, 8H), 7.43 – 7.36 (m, 2H), 6.91 (d, *J* = 15.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.65, 147.04, 137.62, 137.61, 133.26 (C-F, $2J_{C-F}$ = 32.32 Hz), 132.94 (C-F, $2J_{C-F}$ = 32.32 Hz), 132.74, 132.61 (C-F, $2J_{C-F}$ = 32.32 Hz), 132.28 (C-F, $2J_{C-F}$ = 32.32 Hz), 131.59, 129.31, 129.30, 128.97, 128.93, 128.92, 127.80 (C-F, $1J_{C-F}$ = 273.71 Hz), 126.85, 126.28 (C-F, $3J_{C-F}$ = 4.04 Hz), 126.24 (C-F, $3J_{C-F}$ = 4.04 Hz), 126.20 (C-F, $3J_{C-F}$ = 4.04 Hz), 126.16 (C-F, $3J_{C-F}$ = 4.04 Hz), 125.09 (C-F, $1J_{C-F}$ = 273.71 Hz), 122.38 (C-F, $1J_{C-F}$ = 273.71 Hz), 119.67 (C-F, $1J_{C-F}$ = 273.71 Hz), 116.02, 113.14, 113.14, 112.59, 77.53, 77.21, 76.89. **^{19}F NMR (376 MHz, $CDCl_3$)** *δ* -62.88. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{19}H_{10}N_2F_3$ 323.0796; Found 323.0803.

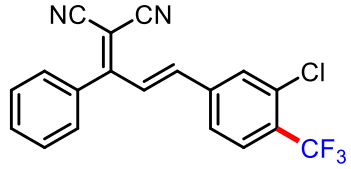


(E)-2-(3-(3-methyl-4-(trifluoromethyl)phenyl)-1-phenylallylidene)malononitrile (4b): Physical state: yellow solid**; Yield:** 41 mg, 60 %. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.57 (m, 3H), 7.53 (d, *J* = 15.4 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.29 (d, *J* = 3.0 Hz, 1H), 2.30 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.94, 145.94, 136.71, 135.81, 132.96, 131.64, 130.28, 130.26, 129.25,



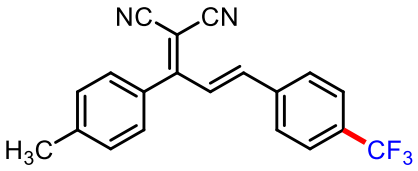
128.96, 128.48 (C-F, $3J_{C-F}$ = 6.1 Hz), 128.42 (C-F, $3J_{C-F}$ = 6.1 Hz), 128.36 (C-F, $3J_{C-F}$ = 6.1 Hz), 128.30 (C-F, $3J_{C-F}$ = 6.1 Hz), 128.23 (C-F, $1J_{C-F}$ = 273.71 Hz), 127.74, 126.58, 125.52 (C-F, $1J_{C-F}$ = 273.71 Hz), 122.81 (C-F, $1J_{C-F}$ = 273.71 Hz), 120.12 (C-F, $1J_{C-F}$ = 273.71 Hz), 113.16, 112.63, 83.80, 77.44, 77.13, 76.81, 15.39. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -60.59. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{20}H_{12}N_2F_3$ 337.0953; Found 337.0966.

(E)-2-(3-(3-chloro-4-(trifluoromethyl)phenyl)-1-phenylallylidene)malononitrile (4c):

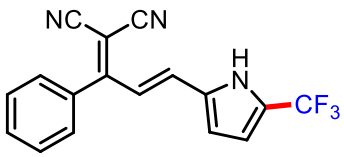


Physical state: yellow solid**; Yield:** 28 mg, 39 %. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.65 – 7.51 (m, 4H), 7.51 – 7.37 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.54, 143.73, 135.17, 132.54, 131.83, 131.05, 129.80 (C-F, J_{C-F} = 5.6 Hz), 129.74 (C-F, J_{C-F} = 5.6 Hz), 129.69 (C-F, J_{C-F} = 5.6 Hz), 129.63 (C-F, J_{C-F} = 5.6 Hz), 129.33 (C-F, $1J_{C-F}$ = 273.71 Hz), 129.29, 129.05, 129.03, 128.44, 127.33, 126.63 (C-F, $1J_{C-F}$ = 273.71 Hz), 123.92 (C-F, $1J_{C-F}$ = 273.71 Hz), 121.20 (C-F, $1J_{C-F}$ = 273.71 Hz), 112.99, 112.51, 84.74. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.64. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{19}H_{10}N_2F_3Cl$ 357.0406; Found 357.0412.

(E)-2-(1-(p-tolyl)-3-(4-(trifluoromethyl)phenyl)allylidene)malononitrile (4d): **Physical state:** yellow solid**; Yield:** 37 mg, 55 %. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.61 (m, 5H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 15.7 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.23, 162.52, 146.68, 137.70, 137.68, 131.20, 128.83, 127.23 (C-F, $1J_{C-F}$ = 273.71 Hz), 127.13, 126.28 (C-F, $3J_{C-F}$ = 3.8 Hz), 126.24 (C-F, $3J_{C-F}$ = 3.8 Hz), 126.20 (C-F, $3J_{C-F}$ = 3.8 Hz), 126.16 (C-F, $3J_{C-F}$ = 3.8 Hz), 125.07 (C-F, $1J_{C-F}$ = 273.71 Hz), 124.75, 122.36 (C-F, $1J_{C-F}$ = 273.71 Hz), 119.65 (C-F, $1J_{C-F}$ = 273.71 Hz), 114.72, 113.70, 113.00, 82.73, 55.66. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.83.



(E)-2-(1-phenyl-3-(5-(trifluoromethyl)-1H-pyrrol-2-yl)allylidene)malononitrile (4e):



Physical state: yellow liquid**; Yield:** 38 mg, 60 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.59 – 7.54 (m, 3H), 7.37 – 7.32 (m, 3H), 6.70 (d, *J* = 15.5 Hz, 1H), 6.61 (s, 1H), 6.53 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.67, 137.21, 132.89, 131.31, 130.37, 129.22, 129.09, 128.89, 127.16 (C-F, $1J_{C-F}$ = 269.67 Hz), 126.57 (C-F, J_{C-F} = 40.4 Hz), 126.17 (C-F, J_{C-F} = 40.4 Hz), 124.49 (C-F, $1J_{C-F}$ = 269.67 Hz), 121.83 (C-F, $1J_{C-F}$ = 269.67 Hz), 121.41, 119.16 (C-F, $1J_{C-F}$ = 269.67 Hz), 117.53, 113.66 (C-F, J_{C-F} = 14.14 Hz),

113.52 (C-F, J_{C-F} = 14.14 Hz), 112.26, 112.23, 112.20, 112.17, 80.39. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -60.13. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{17}H_9N_3F_3$ 312.0749; Found 312.0740.

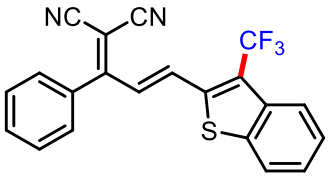
2-(1-phenyl-3-(5-(trifluoromethyl)thiophen-2-yl)allylidene)malononitrile (4f): Physical state: yellow liquid**; Yield:** 26 mg, 40 % (E/Z = 1.1). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.59 (dt, *J* = 7.8, 1.7 Hz, 2H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.38 - 7.36 (m, 3H), 7.20 (d, *J* = 5.9 Hz, 1H), 7.05 (dd, *J* = 5.3, 1.5 Hz, 1H), 6.82 - 6.79 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 170.11, 169.29, 137.07, 132.94, 132.73, 132.31, 131.80 (C-F, $1J_{C-F}$ = 260.82 Hz), 131.41, 129.84, 129.71 (C-F, $1J_{C-F}$ = 260.82 Hz), 129.32, 129.07, 128.92, 128.74, 127.64 (C-F, $1J_{C-F}$ = 260.82 Hz), 126.97, 126.91, 126.19 (C-F, J_{C-F} = 3.78 Hz), 126.16 (C-F, J_{C-F} = 3.78 Hz), 126.14 (C-F, J_{C-F} = 3.78 Hz), 126.11 (C-F, J_{C-F} = 3.78 Hz), 125.57 (C-F, $1J_{C-F}$ = 260.82 Hz), 123.64, 121.85, 113.22, 113.19, 112.82, 112.56, 85.77, 83.93. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -56.30, -56.99. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{17}H_8N_2F_3S$ 329.0360; Found 329.0352.

(E)-2-(1-phenyl-3-(2-(trifluoromethyl)-1H-indol-3-yl)allylidene)malononitrile (4g): **Physical state:** red solid**; Yield:** 47 mg, 65 %. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 13.22 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.53 (m, 5H), 7.43 – 7.33 (m, 4H), 7.04 (d, *J* = 15.5 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 171.39, 138.68, 136.45, 132.53, 131.18, 128.98, 128.86, 128.15 (C-F, $2J_{C-F}$ = 36.7 Hz), 127.86 (C-F, $2J_{C-F}$ = 36.7 Hz), 127.57 (C-F, $2J_{C-F}$ = 36.7 Hz), 127.28 (C-F, $2J_{C-F}$ = 36.7 Hz), 125.81, 124.19 (C-F, $1J_{C-F}$ = 270.9 Hz), 123.91, 123.52, 123.33, 122.04 (C-F, $1J_{C-F}$ = 270.9 Hz), 120.83, 119.89 (C-F, $1J_{C-F}$ = 270.9 Hz), 117.74 (C-F, $1J_{C-F}$ = 270.9 Hz), 114.04, 113.97, 113.56, 112.11, 112.09, 79.43. **^{19}F NMR (376 MHz, CDCl$_3$)** *δ* -57.90. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{21}H_{11}N_3F_3$ 362.0898; Found 362.0905.

(E)-2-(1-phenyl-3-(3-(trifluoromethyl)benzofuran-2-yl)allylidene)malononitrile (4h): Physical State: yellow solid; **Yield:** 44 mg, (60 %). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.74 – 7.57 (m, 8H), 7.48 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 15.3 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 168.33, 154.23, 150.20 (C-F, $3J_{C-F}$ = 3.8 Hz), 150.17 (C-F, $3J_{C-F}$ = 3.8 Hz), 150.14 (C-F, $3J_{C-F}$ = 3.8 Hz), 150.11 (C-F, $3J_{C-F}$ = 3.8 Hz), 131.98, 131.61, 129.16 (C-F, $2J_{C-F}$ = 8.1 Hz), 129.09 (C-F, $2J_{C-F}$ = 8.1 Hz), 129.02 (C-F, $2J_{C-F}$ = 8.1 Hz), 128.96 (C-F, $2J_{C-F}$ = 8.1 Hz), 125.62 (C-F, $1J_{C-F}$ = 269.64 Hz), 125.57, 123.63, 123.47 (C-F, $1J_{C-F}$ = 269.64 Hz), 121.33 (C-F, $1J_{C-F}$ = 269.64 Hz), 120.51, 119.19 (C-F, $1J_{C-F}$ = 269.64

Hz), 113.38, 112.96, 112.71, 112.67, 112.45, 85.61. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -55.88. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{21}H_{10}N_2F_3O$ 363.0745; Found 363.0735.

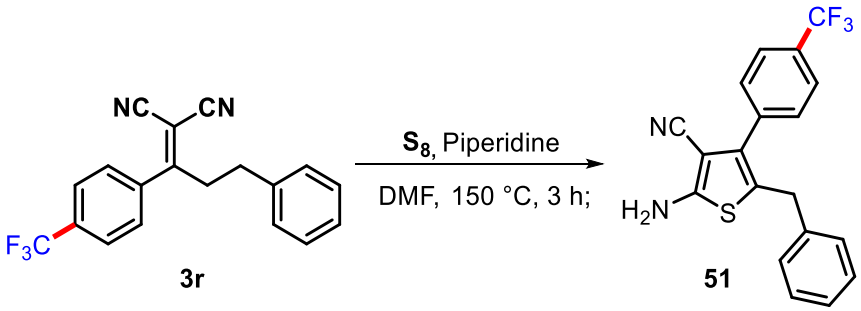
(E)-2-(1-phenyl-3-(3-(trifluoromethyl)benzo[β]thiophen-2-yl)allylidene)malononitrile



(4i): Physical state: Yellow solid; Yield: 38 mg (50 %). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.20 – 8.18 (m, 1H), 7.89 (dt, *J* = 8.0, 1.8 Hz, 1H), 7.68 – 7.55 (m, 7H), 7.46 (d, *J* = 15.3 Hz, 1H), 7.27 – 7.24 (m, 1H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 168.69, 141.16, 141.14, 138.39, 135.76 (C-F, $3J_{C-F}$ = 3.0 Hz), 135.74 (C-F, $3J_{C-F}$ = 3.0 Hz), 135.71 (C-F, $3J_{C-F}$ = 3.0 Hz), 135.68 (C-F, $3J_{C-F}$ = 3.0 Hz), 135.39, 132.11, 131.59, 130.09, 129.06, 128.98, 128.00, 126.80, 125.73 (C-F, $1J_{C-F}$ = 273.42 Hz), 124.22 (C-F, $2J_{C-F}$ = 32.76 Hz), 123.96 (C-F, $2J_{C-F}$ = 32.76 Hz), 123.70 (C-F, $2J_{C-F}$ = 32.76 Hz), 123.56 (C-F, $1J_{C-F}$ = 273.42 Hz), 123.48, 123.44 (C-F, $2J_{C-F}$ = 32.76 Hz), 123.15, 123.13, 123.11, 121.39 (C-F, $1J_{C-F}$ = 273.42 Hz), 119.22 (C-F, $1J_{C-F}$ = 273.42 Hz), 113.36, 112.63. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ – 49.54. **HRMS (ESI/QTOF), m/z:** $[M-H]^+$ Calcd. $C_{21}H_{10}N_2F_3S$ 379.0517; Found 379.0498.

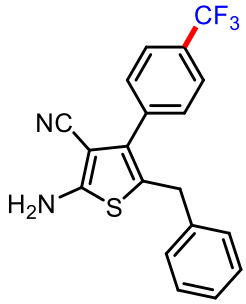
5.1. General Procedure for preparation of thiophene core[4]

In an oven- and vacuum-dried seal tube, **3r** (32.6 mg, 0.1 mmol, 1 equiv), Sulfur (**S$_8$**) (3.2 mg, 0.1 mmol, 1 equiv.) and piperidine (3μL, 0.03 mmol, 3 equiv) were taken in 150 μL of freshly distilled DMF. Next, the seal tube was purged with argon and was heated to reflux at 160 °C for 3 h. After cooling down to rt, the reaction mixture was diluted with 2 mL water and 10 mL EtOAc. Subsequently the aqueous layer was extracted with EtOAc (3 × 10 mL) and dried over Na_2SO_4. Then the solvent was removed under reduced pressure, and crude reaction mixture was purified through silica gel column chromatography (eluent: EtOAc/Petroleum ether = 20/80) (Scheme 6).

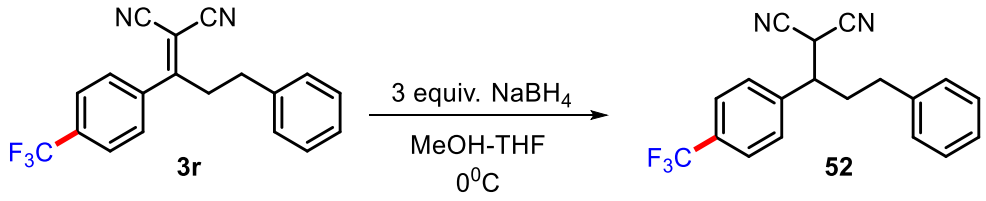


Scheme 6: Gewald synthesis for thiophene construction

2-amino-5-benzyl-4-(4-(trifluoromethyl)phenyl)thiophene-3-carbonitrile (51):Physical state: White solid; **Yield:** 35mg, 99 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.18 – 7.14 (m, 2H), 4.40 (s, 2H), 3.96 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.54, 139.48, 137.30, 134.64, 130.66 (C-F, $2J_{C\text{-}F}$ = 32.76 Hz), 130.41 (C-F, $2J_{C\text{-}F}$ = 32.76 Hz), 130.15 (C-F, $2J_{C\text{-}F}$ = 32.76 Hz), 129.89 (C-F, $2J_{C\text{-}F}$ = 32.76 Hz), 129.60, 128.88, 128.34, 127.38 (C-F, $1J_{C\text{-}F}$ = 272.16 Hz), 127.05, 125.83 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 125.80 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 125.77 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 125.74 (C-F, $3J_{C\text{-}F}$ = 3.8 Hz), 125.22 (C-F, $1J_{C\text{-}F}$ = 272.16 Hz), 124.93, 123.06 (C-F, $1J_{C\text{-}F}$ = 272.16 Hz), 115.59, 89.08, 33.77. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.97. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^+$ Calcd. $C_{19}H_{12}N_2F_3S$ 357.0674; Found 357.0670.



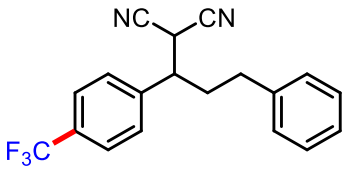
5.2. General Procedure for alkylidene reduction



Scheme 7: Reduction of alkylidene malononitrile

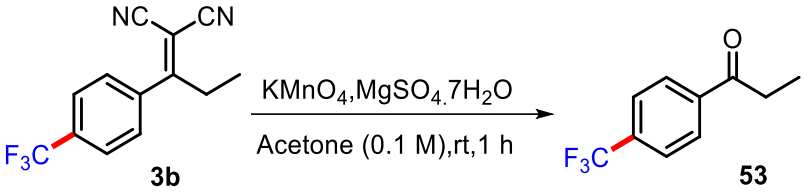
3r (32.6 mg, 0.1 mmol, 1 equiv.) was dissolved in MeOH-THF 3:1 (300 µL, 0.5M) at 0 °C. $NaBH_4$ (12 mg, 0.3 mmol, 3 equiv.) was added portion wise. Upon completion (consumption of the starting material – as indicated by TLC), the mixture was acidified using 2M HCl solution and then the solvents evaporated. The residue was partitioned between ethyl acetate (5 mL) and water (5 mL). The organic layer was washed with 2N HCl (3 mL) and brine (5 mL), dried over Na2SO4, filtered, and then the solvent was evaporated. The pure product was isolated via flash chromatography, 15 → 30% ethyl acetate hexanes (Scheme 7).

2-(3-phenyl-1-(4-(trifluoromethyl)phenyl)propyl)malononitrile (52): Physical State: White liquid; **Yield:** 31 mg, 95 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.73 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.31 (dd, J = 8.1, 6.7 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.07 (dd, J = 7.0, 1.8 Hz, 2H), 3.88 (d, J = 6.0 Hz, 1H), 3.25 (dt, J = 10.6, 5.7 Hz, 1H), 2.66 (ddd, J = 13.1, 7.9, 5.1 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.41 – 2.34 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.22, 139.44, 131.95 (C-F, $2J_{C\text{-}F}$ = 32.76 Hz), 131.69 (C-F, $2J_{C\text{-}F}$ = 32.76 Hz), 131.43 (C-F, $2J_{C\text{-}F}$ = 32.76 Hz), 131.16 (C-F, $2J_{C\text{-}F}$ = 32.76 Hz), 128.95, 128.95, 128.76, 128.41, 126.88, 126.61 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.58 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 126.55 (C-F, $3J_{C\text{-}F}$ = 3.7



Hz), 126.52 (C-F, $3J_{C-F}$ = 3.7 Hz), 124.95 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.78 (C-F, $1J_{C-F}$ = 273.42 Hz), 111.49, 111.46, 45.30, 33.44, 32.72, 30.10. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.78. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{19}H_{14}N_2F_3$ 327.1109; Found 327.1117.

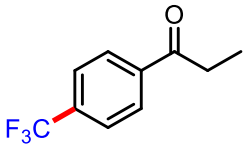
S5.3. Synthesis of 4-trifluoromethyl propiophenone



Scheme 8: Synthesis of trifluoromethylated propiophenone

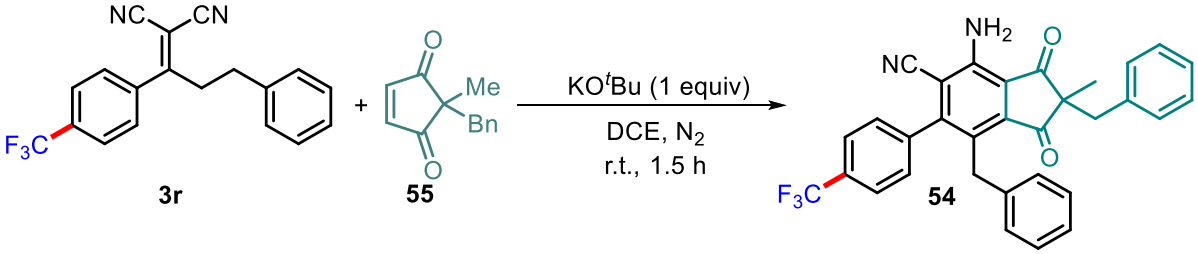
Potassium permanganate (43 mg, 0.3 mmol) and magnesium sulfate hydrate (98.4 mg, 0.4 mmol) in 2.0 mL solution of **3b** (36 mg, 0.2 mmol), 20 µL drop of water was added and stirred at room temperature for 1 hour. The reaction is quenched with sodium dithionite, water is added, the aqueous solution is extracted with ethyl acetate (3 mL * 3), the solvent is evaporated and the residue is silica gel column chromatography to obtain the desired α-trifluoromethyl ketone **53** (40.0 mg, 99 %) as a colourless liquid (Scheme 8).

1-(4-(trifluoromethyl)phenyl)propan-1-one (53): Physical State: White Liquid; **Yield:** 40



mg, 99 %. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.05 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 3.02 (q, J = 7.1 Hz, 2H), 1.24 (td, J = 7.2, 1.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 199.83, 139.68, 134.73 (C-F, $2J_{C-F}$ = 32.76 Hz), 134.47 (C-F, $2J_{C-F}$ = 32.76 Hz), 134.21 (C-F, $2J_{C-F}$ = 32.76 Hz), 133.95 (C-F, $2J_{C-F}$ = 32.76 Hz), 128.42, 127.02 (C-F, $1J_{C-F}$ = 273.42 Hz), 125.81 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.79 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.75 (C-F, $3J_{C-F}$ = 3.7 Hz), 125.72(C-F, $3J_{C-F}$ = 3.7 Hz), 124.85 (C-F, $1J_{C-F}$ = 273.42 Hz), 122.68 (C-F, $1J_{C-F}$ = 273.42 Hz), 120.52 (C-F, $1J_{C-F}$ = 273.42 Hz), 32.26, 8.10. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.15. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd.$C_{10}H_8OF_3$ 201.0527; Found 201.0532.

5.4. General procedure of vinylogous annulation cascade reaction[5]

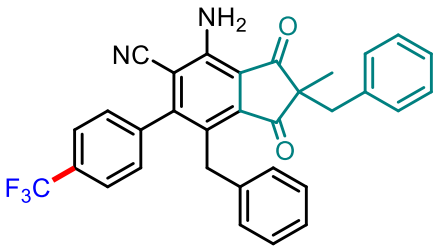


Scheme 9: (4+2) cycloaddition reaction

The alkylidene malononitriles **3r** (0.1 mmol, 1 equiv.), cyclopentene-1,3-diones **55** (0.16 mmol, 1.6 equiv.), and anhydrous potassium *tert*-butoxide (1 equiv.) were taken in a 16×100

mm oven dried reaction tube equipped with a magnetic stir. The reaction tube was capped with a rubber septum, evacuated and backfilled with nitrogen gas. Then, dry DCE (2 mL) was added via syringe. The mixture was allowed to stir at room temperature for 1–1.5 h. After completion (TLC monitored), the crude reaction mixture was loaded directly onto silica gel column and purified with a gradient eluent of hexane and ethyl acetate to provide pure 1,3-indandiones **54** (Scheme 9).

4-amino-2,7-dibenzyl-2-methyl-1,3-dioxo-6-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-indene-5-carbonitrile (54): Physical State: Yellow Liquid; **Yield:** 45 mg, 85 % . **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.59 (ddd, J = 66.2, 8.1, 2.0 Hz, 3H), 7.33 – 7.20 (m, 2H), 7.16 – 7.06 (m, 6H), 6.93 (dt, J = 8.0, 2.3 Hz, 3H), 6.47 – 6.44 (m, 2H), 4.49 (d, J = 15.3 Hz, 1H), 3.82 (d, J = 15.2 Hz, 1H), 3.14 (q, J = 13.2 Hz, 2H), 1.40 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 204.28, 204.25, 154.04, 147.32, 141.88, 139.74, 139.59, 135.84, 129.87, 129.24, 128.98, 128.94, 128.76, 128.47, 128.41, 128.29, 128.13, 127.04, 126.07, 126.04, 126.04, 125.72 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 123.55 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 114.61, 103.08, 56.35, 41.66, 32.66, 20.68. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.79. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd.$C_{32}H_{22}O_2F_3N_2$ 523.1634; Found 523.1628.

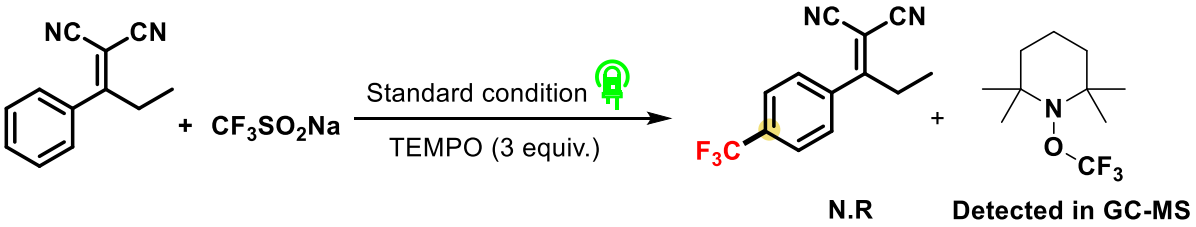


6: Mechanistic Investigation

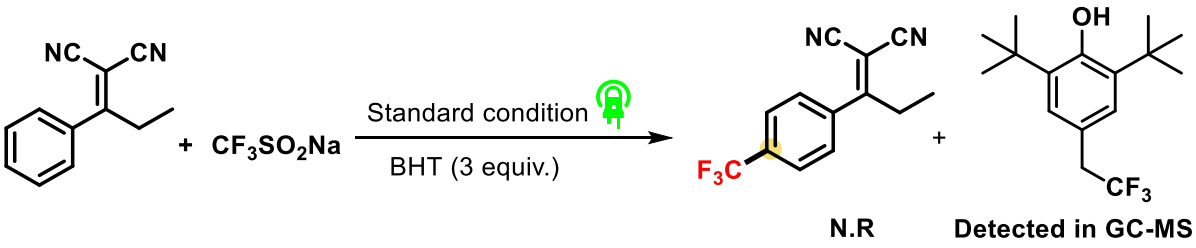
6.1: Radical trapping experiments

Corresponding adducts of a trifluoromethyl radical with the respective radical traps was observed in GC-MS analysis (Scheme 10 and Figure 1 – 3).

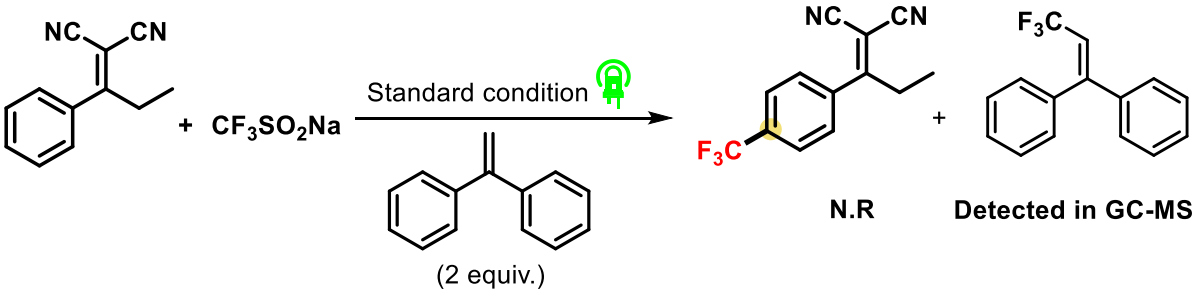
(a): Effect of TEMPO



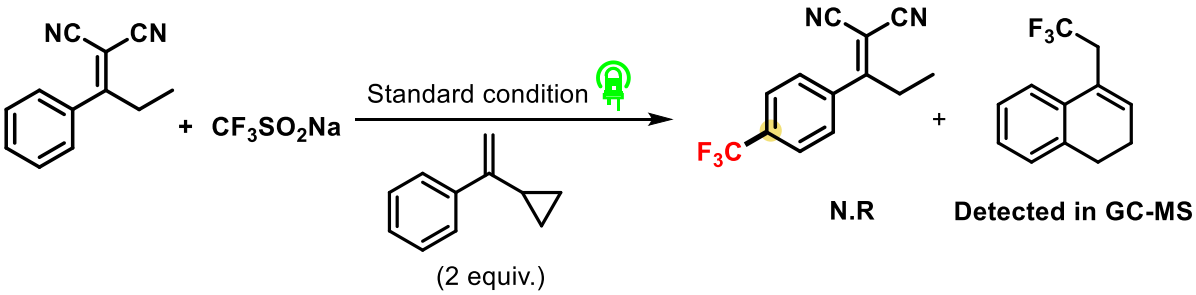
(b): Effect of BHT



(c) Effect of diphenyl ethylene



(d) Radical Clock experiment



Scheme 10: (a-d) Radical Trapping experiment

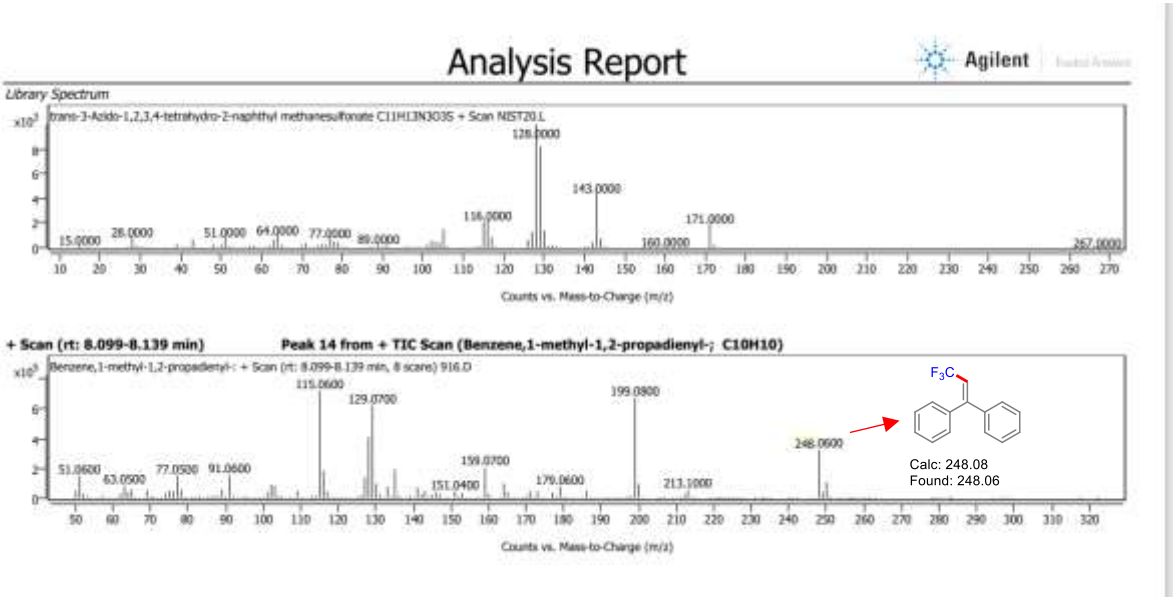


Figure 1: GC-MS Spectra for S6.1 (b)

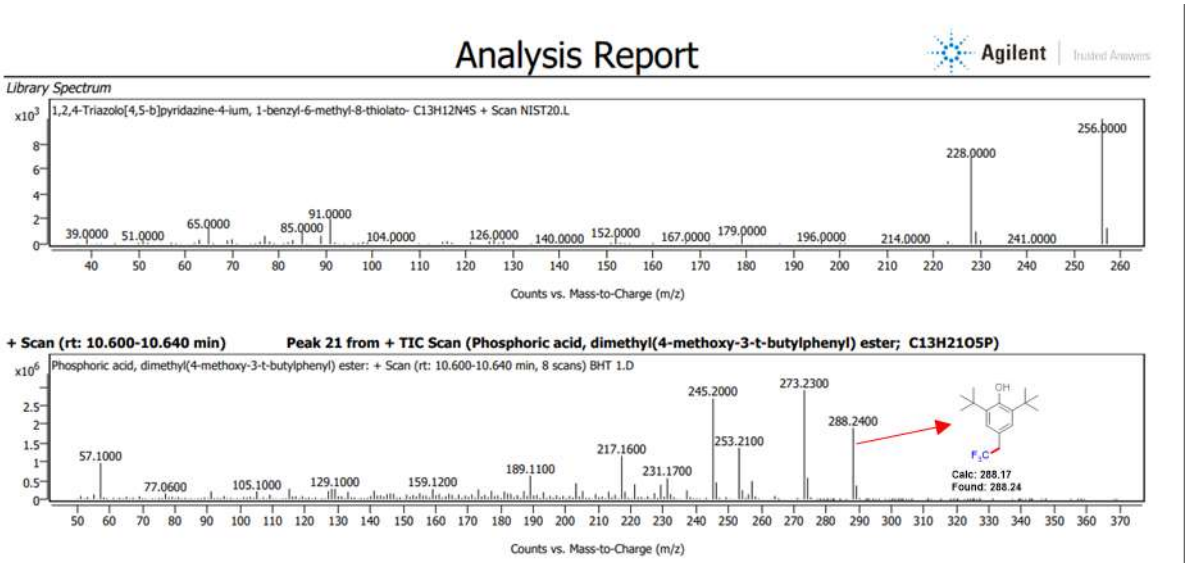


Figure 2: GC-MS Spectra for S6.1 (c)

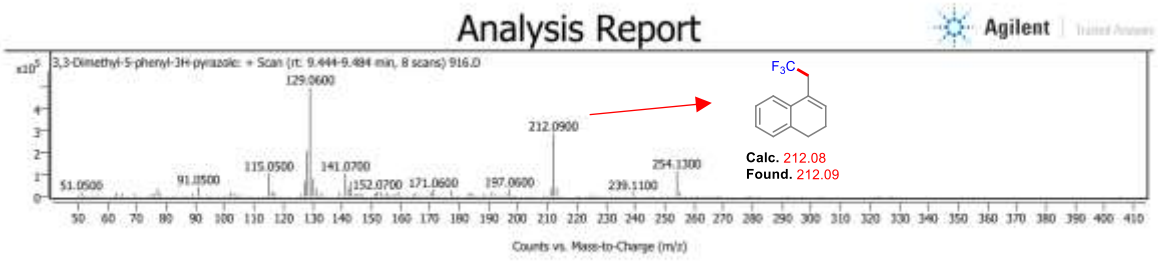
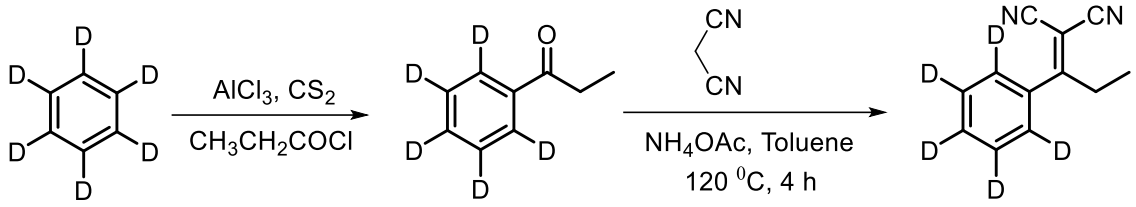


Figure 3: GC-MS Spectra for S6.1 (d)

6.2: Kinetic Isotope Effect Experiment:

6.2.1: Preparation of [D5]-1b:



Scheme 11: Synthesis of D5- alkylidene malononitrile

Step 1: Preparation of D5-propiophenone: Following the literature procedure[5], benzene-d_6 (1.2 mL, 12.8 mmol, 1.0 equiv.), $AlCl_3$ (2.14 g, 16 mmol, 1.25 equiv.), and anhydrous CS_2 (3.0 mL) were added to a 25 mL flask under N_2 atmosphere. To the mixture was dropwise added a solution of acetyl chloride (1.26 g, 16 mmol, 1.25 equiv.) in anhydrous CS_2 (5.0 mL) at 0°C. The resulting mixture was allowed to warm to ambient temperature and was stirred for 5 h. Then the mixture was heated to 50°C in oil bath for 3 h. After cooling to ambient temperature, the resulting mixture was poured into ice water and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was washed with saturated aqueous Na_2CO_3 (30 mL) and brine (20 mL), and then dried over Na_2SO_4. After concentration under reduced pressure, purification by column chromatography on silica gel (hexanes/EtOAc) afforded **1b**-d5 (1.39 g, 87%) as colorless solid (Scheme 11).

Step 2: Preparation of D5-propiophenone-derived malononitriles: To a 25 mL round-bottom was added the corresponding ketone (3.0 mmol, 1.0 eq.), toluene (6 mL), ammonium acetate (231.2 mg, 3.0 mmol, 1.0 eq.), malononitrile (297.1mg, 4.5 mmol, 1.5 eq.) and acetic acid (0.2 mL). The round-bottom was attached to a Dean-Stark apparatus and heated to reflux until the consumption of the corresponding ketone. The reaction was removed from heat, cooled to room temperature, and then alkalified with saturation sodium carbonate solution. The aqueous layer was extracted with dichloromethane (3 × 10 mL); combined organic phase was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The products were purified by column chromatography on a silica gel (petroleum ether/ethyl acetate) to afford the desired products (Figure 4).

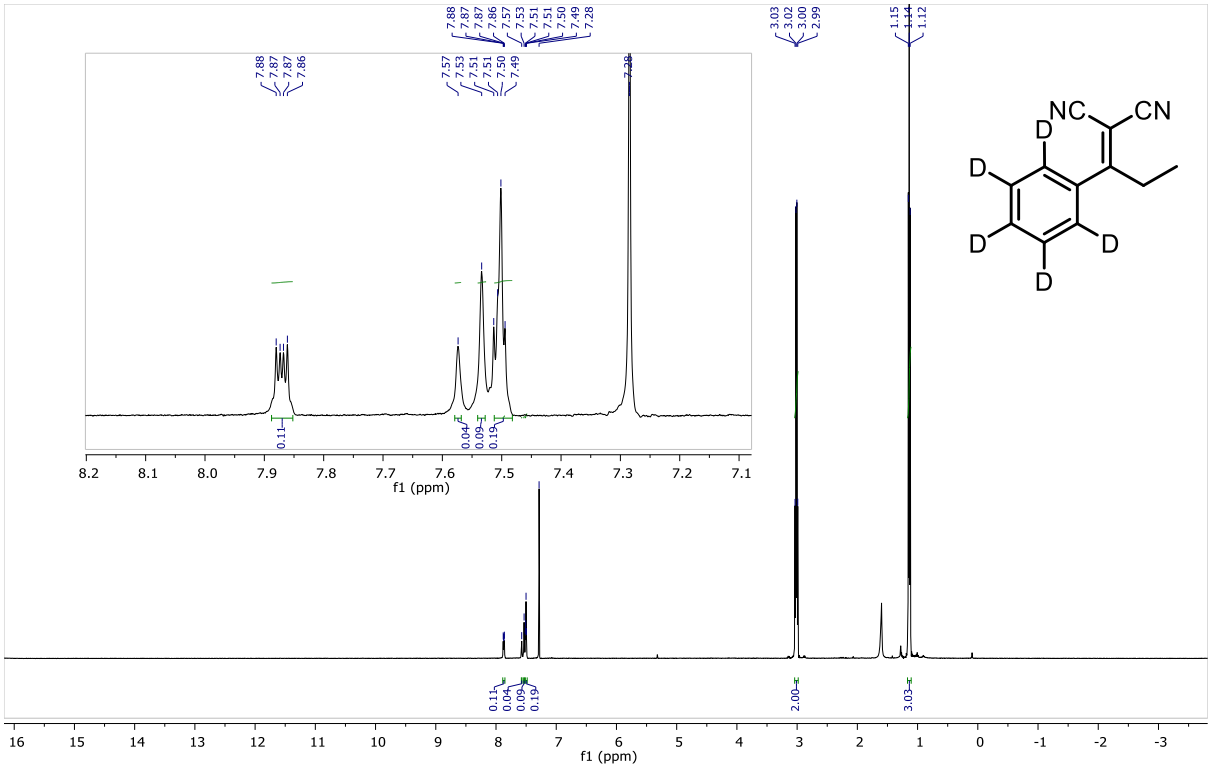
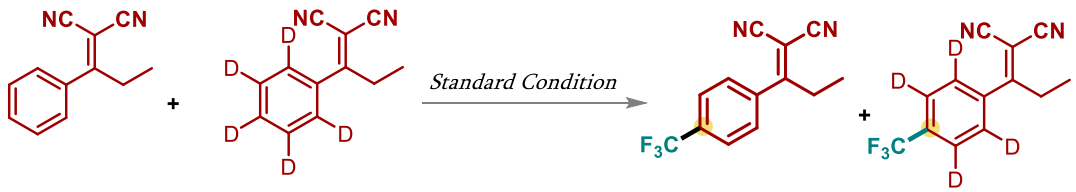


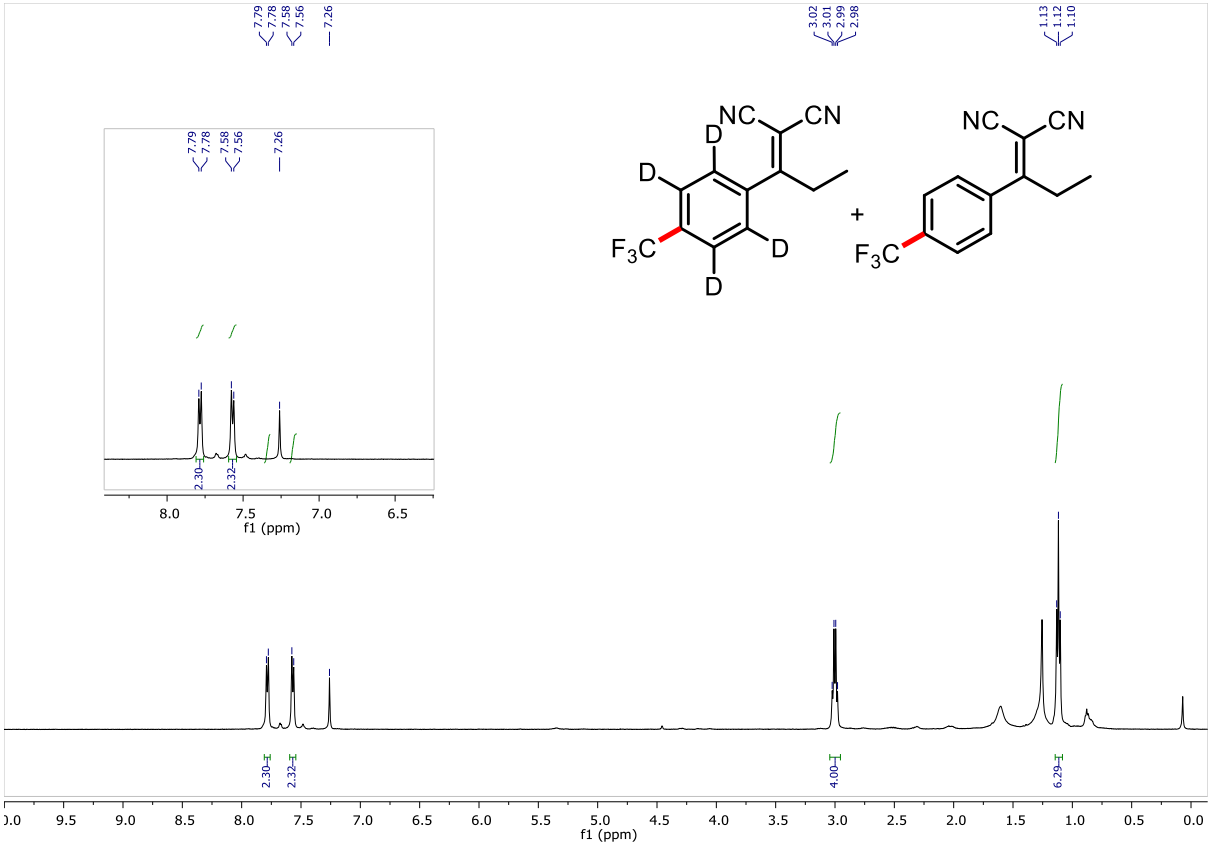
Figure 4: ^{1}H NMR of [D5]-**1b**

Procedure for Intermolecular KIE:



Scheme 12: Intermolecular kinetic isotopic experiment

0.2 mmol of **1b** and **[D5]-1b** (1.0 equiv.), trifluoromethylsulfinates (0.6 mmol, 3 equiv.) were taken in a long neck round bottom flask and 2.5 mol % of Eosin Y was added into it followed by ammonium peroxo disulfate, the RB was capped with septum. The mixture was degassed and filled with N_2 (three times). The reaction mixture was irradiated with green LED for 24 h. After completion (monitored through TLC), reaction was quenched with saturated $NaHCO_3$ solution and extracted with DCM (3 x 10 mL), washed with brine solution. After removal of solvent in vacuo, the product was purified by silica gel chromatography using EtOAc-hexane (3:7 to 5:5) as eluent to provide the desired product (Scheme 12).



- **Calculation:**

Since, 91% deuteration is occurred therefore 9 % of non-deuterated **1b** will be added to **1b**.

Now, 9 % of 0.1 mmol = 0.009 mmol.

So, actual amount of H = (0.1+0.009) mmol = 0.109 mmol responsible for 4.62 H in ^{1}H-NMR spectra.

So, for 0.1 mmol number of Hydrogen will be {(4.62 x 0.1)/0.109} = 4.23 H.

So, for 0.1 mmol number of Deuterium will be (8.00-4.23) = 3.77 D.

So, $\frac{K_H}{K_D} = \frac{4.23}{3.77} = 1.12$

Intermolecular KIE respect to **1b** is 1.12, suggesting that C−H cleavage of hydrogen of **1b** should be a fast step and might not be involved in the rate-determining step.

6.3: EPR Evidence for Free Radical Generation

Continuous wave (CW) EPR spectra were obtained using a Bruker A300-9.5/12/S/W instrument with X-band of 8.75-9.65 GHz. The spectral data was collected at 77 K with the following spectrometer settings: microwave power = 0.48 mW, center field = 3350 G, sweep width = 100 G, sweep time = 30 s, modulation frequency = 9.6 GHz, modulation amplitude = 10 G, time constant = 0.01 ms.

For all the EPR measurements, the corresponding sample solution was transferred into the EPR tube and then placed in liquid Nitrogen to freeze the sample solution prior to recording of the spectra. After that, the sample tube was inserted in the EPR cavity which was kept frozen with continuous supply of liquid nitrogen for the recording of the spectra. For experiments in which the sample was irradiated, the sample tube was kept at 5 cm distance as shown in setup in S3: Photo Reaction Setup. Shown below are the spectrum acquired from a sample which was frozen shortly after applying standard condition and irradiating for time as designated in the graph (Figure 5-12).

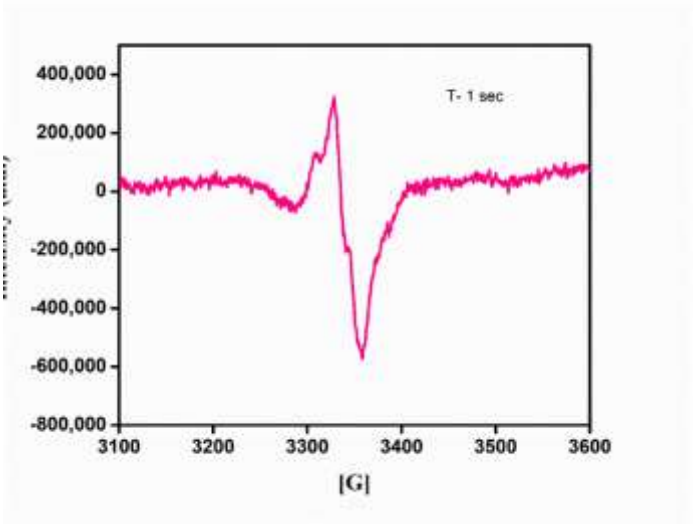


Figure 5: EPR spectra at immediately at 77 K

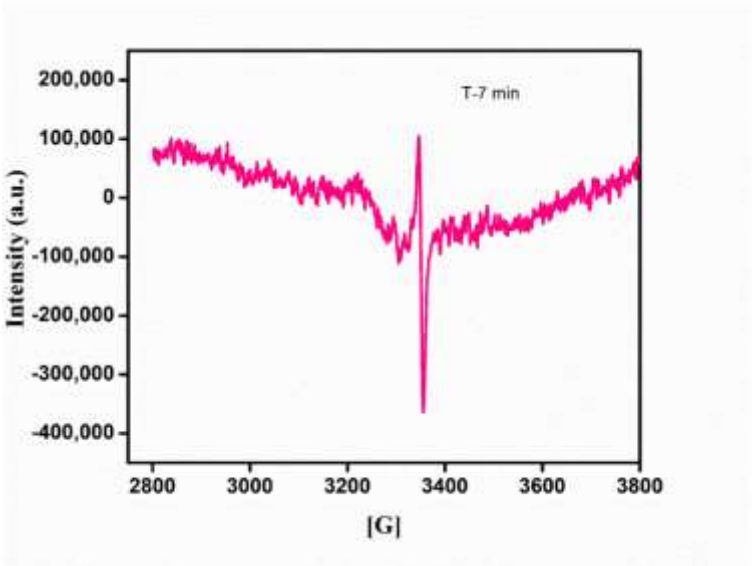


Figure 6: EPR spectra after 7 minutes at 77 K

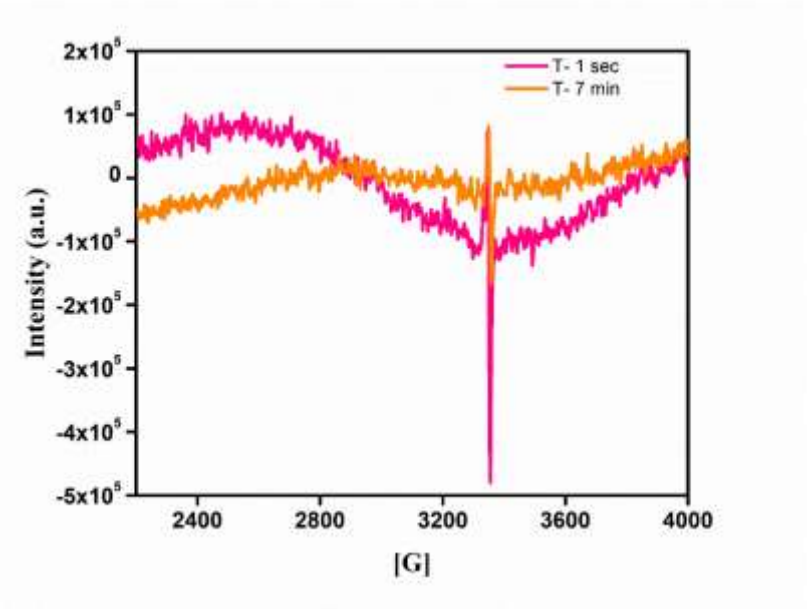


Figure 7: Comparison of EPR spectra at different interval at 77 K

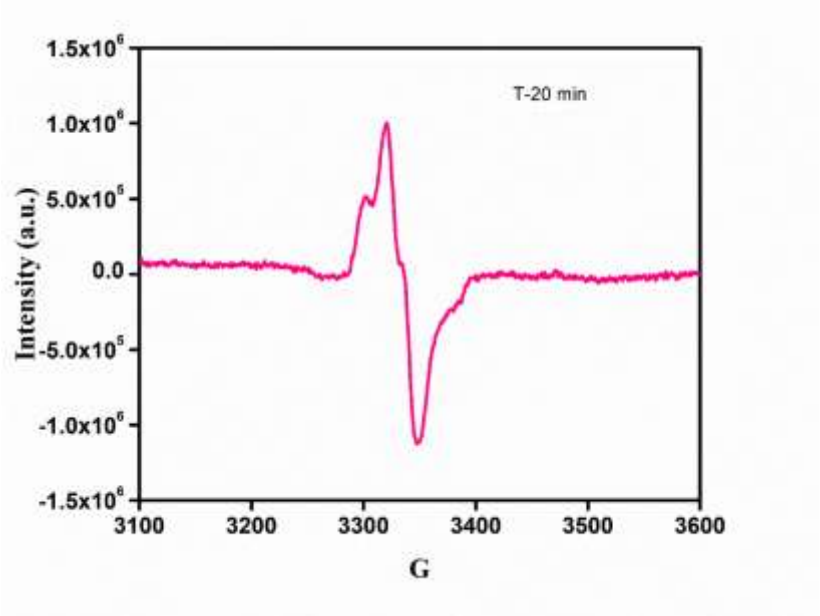


Figure 8: EPR spectra after 20 minutes at 77 K

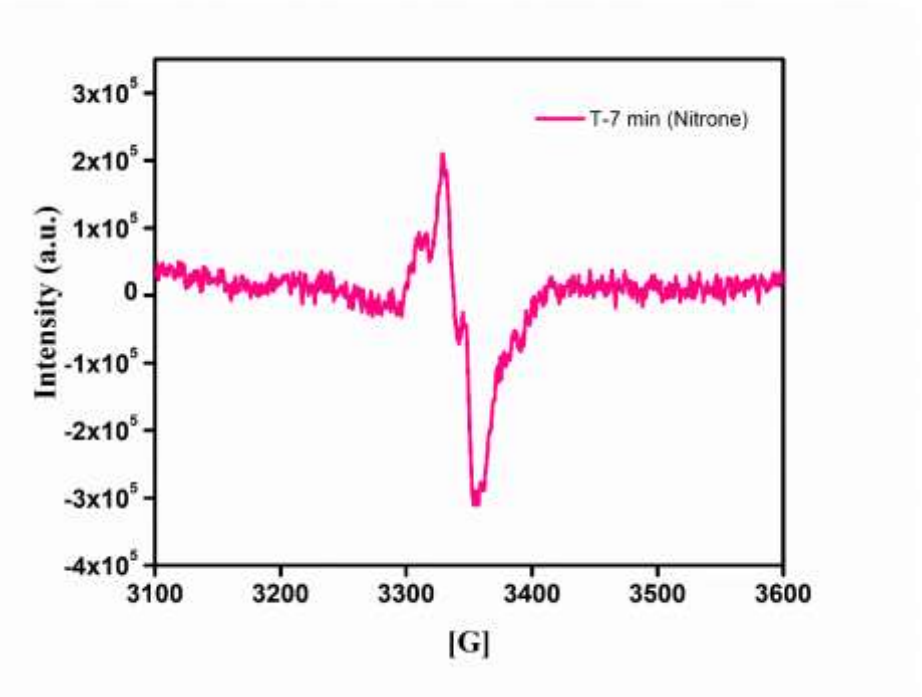


Figure 9: EPR spectra after 7 minutes with nitrone addition at 77 K

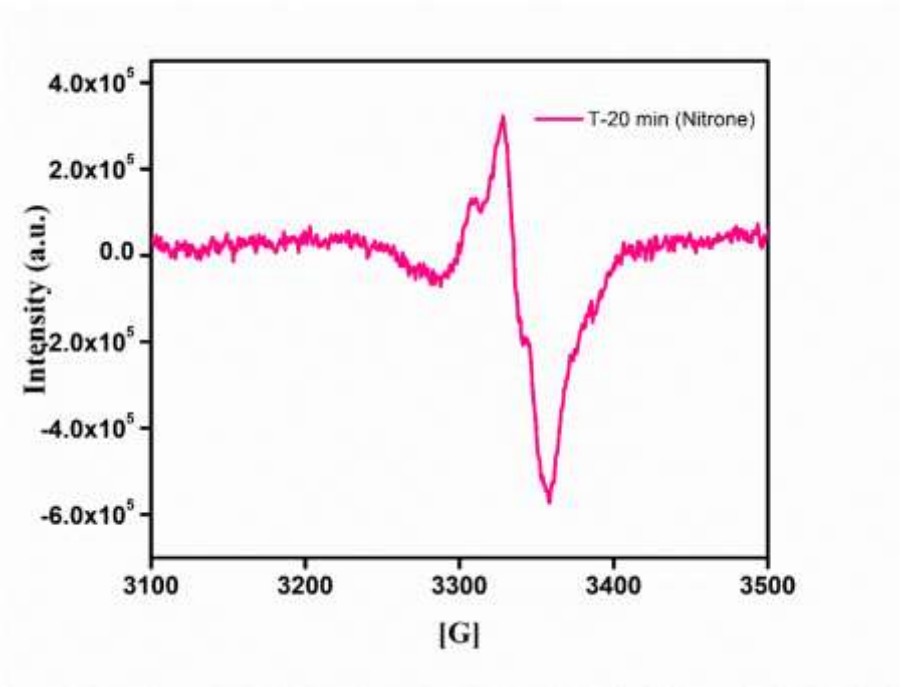


Figure 10: EPR spectra after 20 minutes with nitrone addition at 77 K

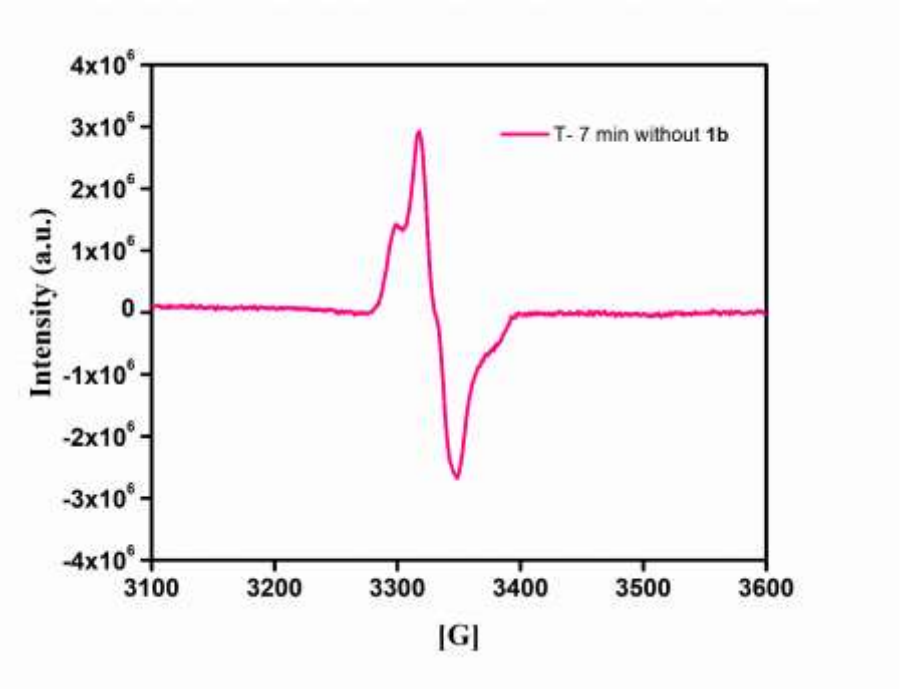


Figure 11: EPR spectra after 7 minutes without substrate addition at 77 K

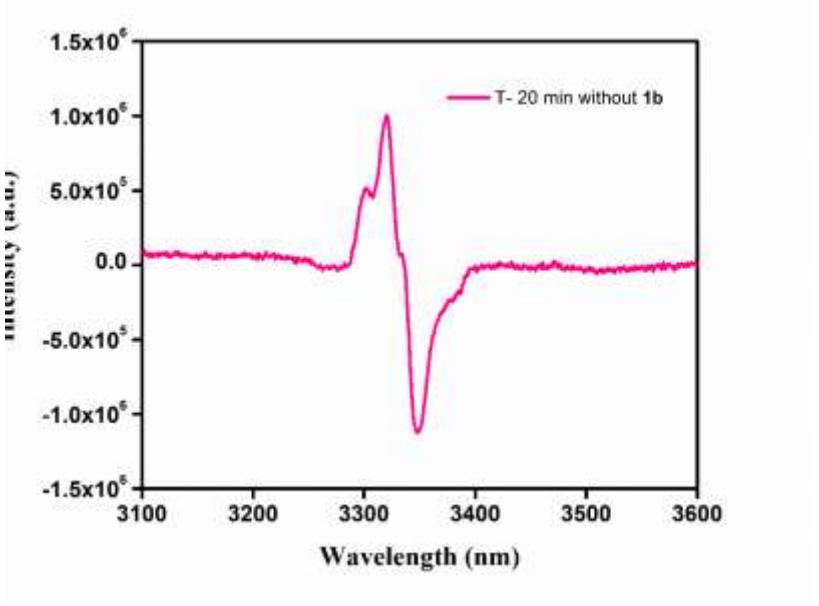


Figure 12: EPR spectra after 20 minutes without substrate addition at 77 K

6.4: Fluorescence titration of photocatalyst

Fluorescence Quenching Experiments Test conditions for quenching reaction (I_0 and I are respective fluorescence intensities in the absence and presence of the indicated concentrations of the quenchers and corresponding results were showcased in Figure 13–18.

Eosin Y: 1.3 mg dissolved in 25 mL ACN (0.00008 M)

Quencher:

9.12 mg of $(NH_4)_2S_2O_8$ dissolved in 10 mL ACN (0.004 M)

15.6 mg of CF_3SO_2Na dissolved in 10 mL ACN (0.004 M)

18.2 mg of **1b** dissolved in 25 mL ACN (0.004 M)

General procedure: 1 mL of prepared solution containing Eosin-Y was added to a cuvette, keep the total volume at 3 mL, quenchers and ACN were adjusted according to the Fluorescence graphs.

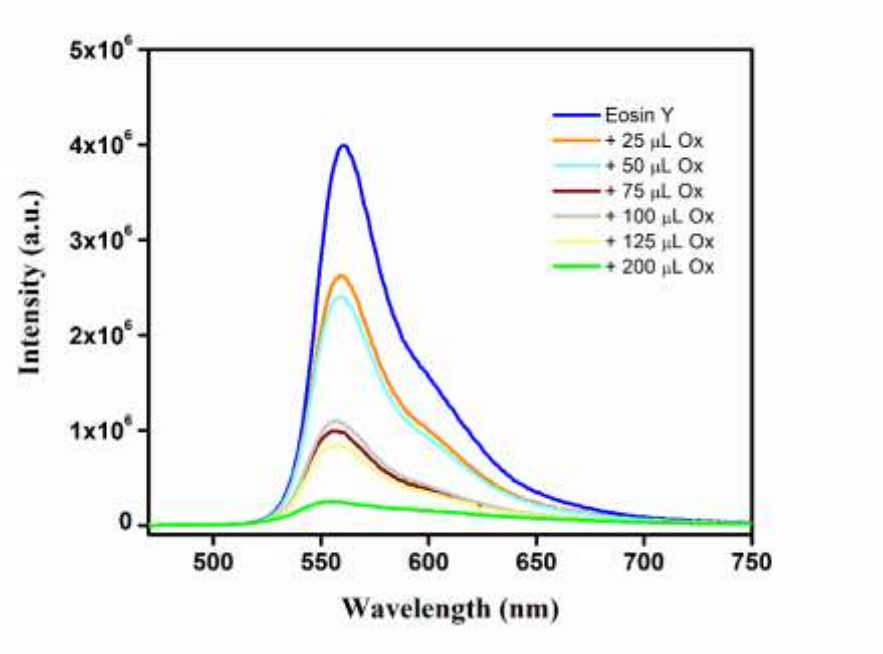


Figure 13: Fluorescence quenching experiments with $(NH_4)_2S_2O_8$

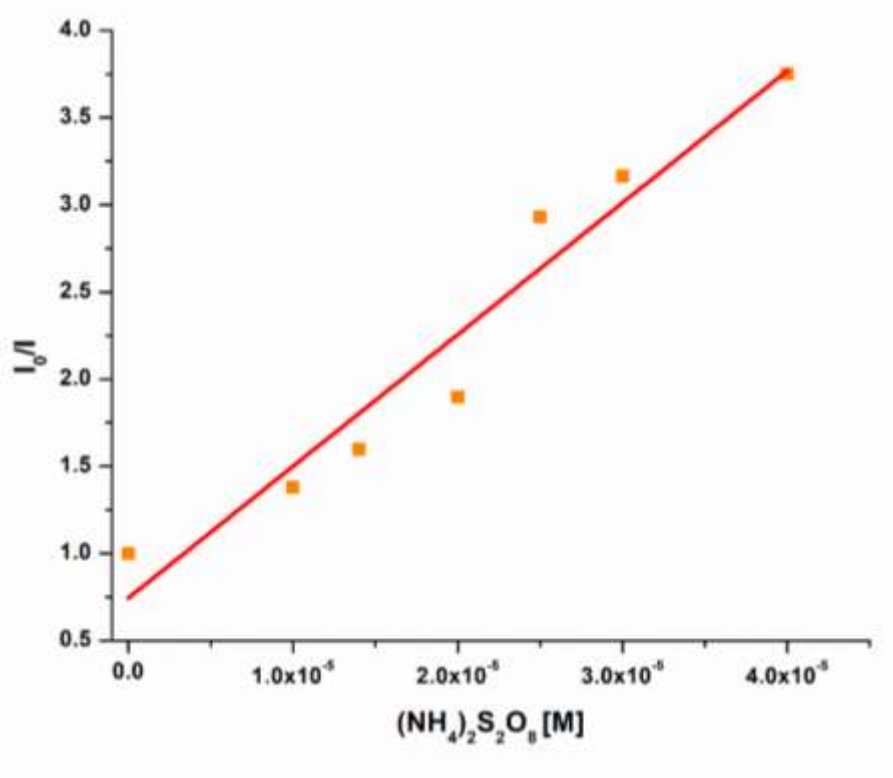


Figure 14: Stern-Volmer plots of $(NH_4)_2S_2O_8$

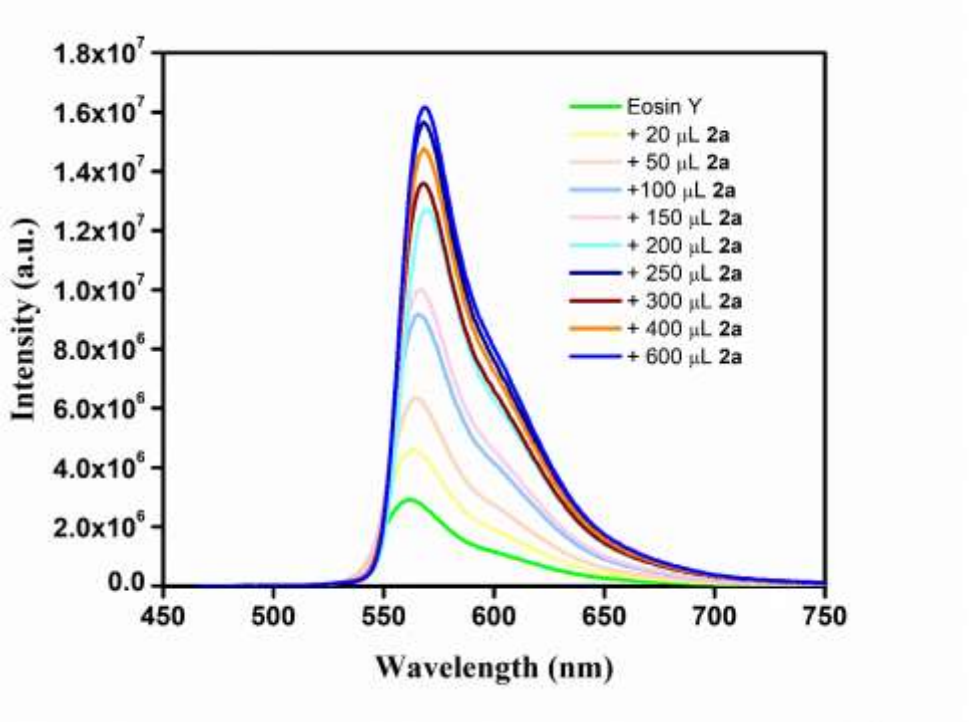


Figure 15: Fluorescence quenching experiments with CF_3SO_2Na

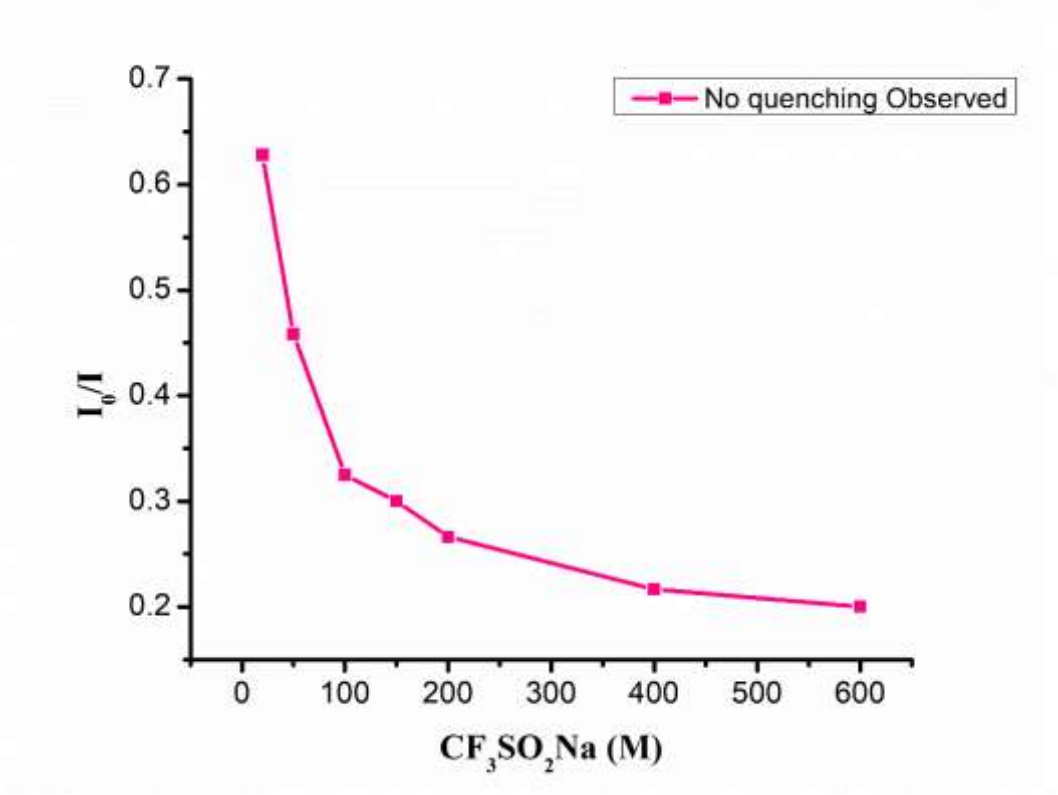


Figure 16: Stern Volmer quenching of Eosin Y- with CF_3SO_2Na

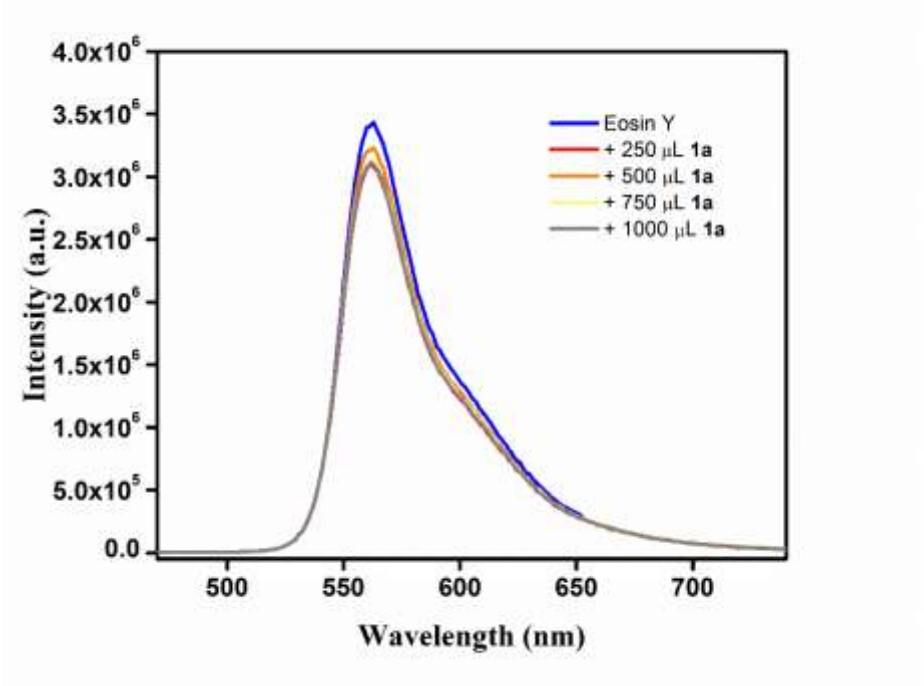


Figure 17: Fluorescence quenching experiments with **1a**

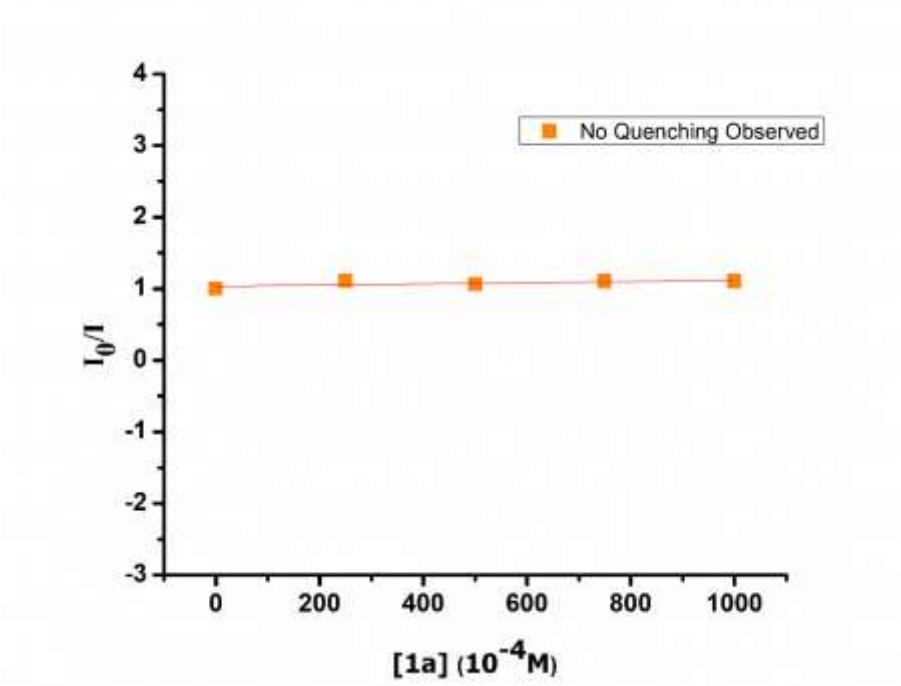


Figure 18: Stern Volmer quenching of Eosin Y- with **1a**

Conclusion

The aforementioned studies clearly show that the strongest quenching of Eosin-Y occurs in the presence of Oxidant $(NH_4)S_2O_8$, No quenching was observed with substrate **1b** and Langlois Reagent **2a** indicating that quenching of the catalytic cycle is with $(NH_4)S_2O_8$ favouring Oxidative Quenching Cycle initiated by Single electron oxidation of Eosin Y on irradiation with green light.

6.5: UV- Visible Studies

UV-Visible spectra were taken on a (UV-2450, Shimadzu, Japan) of Catalyst (Eosin -Y) solutions as well solutions of **1b**, oxidant and **2a**. To investigate the possibility of a donor-acceptor complex between **1b** and **2a**, **1a** and [Eosin Y] and **2a** and [Eosin Y] along with other combination were studied and respective spectra are shown in Figure 19.

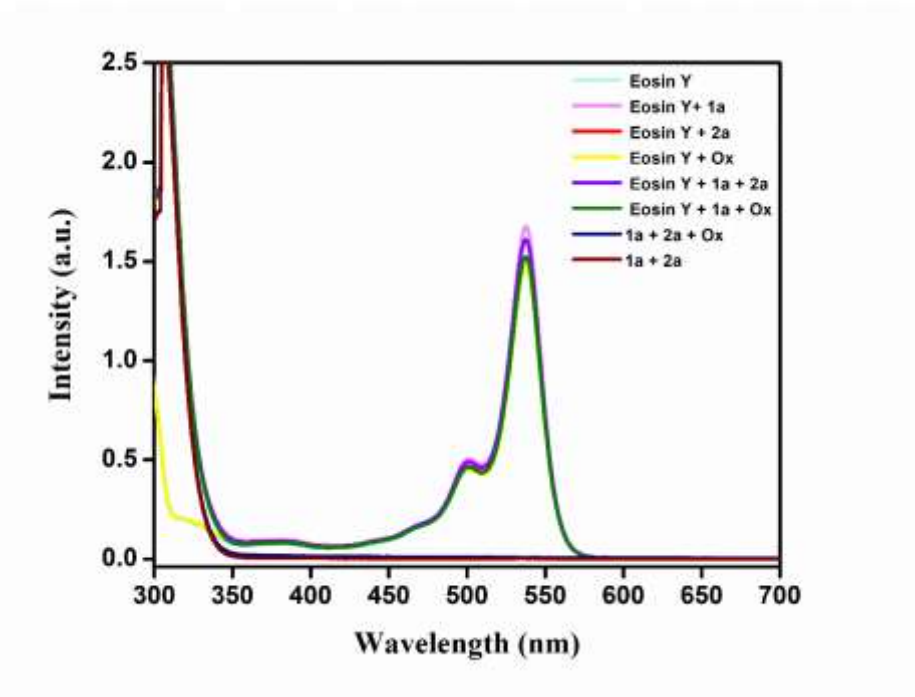


Figure 19: UV Spectra

Conclusion

*The aforementioned studies clearly show that the addition of the quencher **2a**, **1b**, Oxidant doesn't affect the stability of Eosin Y - as well as no evidence of EDA is concluding from above all spectral graphs, indicating that no possibility of EDA complex in the reaction medium.*

6.6: In-Situ IR Studies

In-situ FTIR experiments for detection of SO_2 evolution and CF_3 Stretching Frequency. For detection of SO_2 evolution in the reaction, In-situ FTIR experiments was conducted using a Mettler-Toledo ReactIR 700 (SN: C049640472) equipped with a TEMCT detector, DiComp (Dimond) probe, with a 9.5mm x 2m AgX fiber interface. Data was collected using the spectral window of 2500 to 650 cm-1 with 8 cm-1 resolution and sampled in 15 second intervals. In a glass vial, Eosin Y (2.5 mol%), **1b** (0.1 mmol), **2a** (0.3 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), with a magnetic stirring bead was taken and 1 mL of CH_3CN solvent was added. Then, diamond probe was inserted in solution containing vial and *In*-situ FTIR spectra were recorded for 8 hr at 15 second intervals. As depicted in Figure 20 (side view and top view), the signal intensity at 1361 cm-1 (corresponding to asymmetric stretching of SO_2) gradually increases with the progression of the reaction (Figure 20).

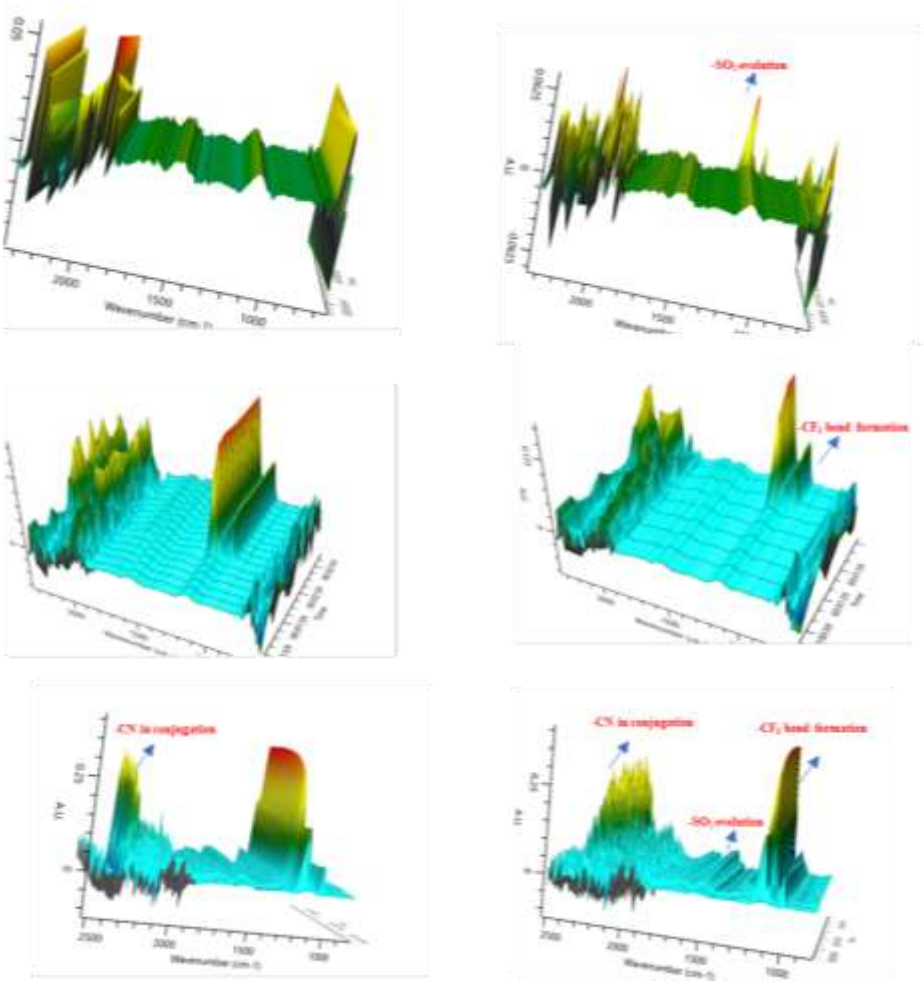


Figure 20: *In-situ* FTIR studies for the detection of SO_2 and monitoring the reaction pathway.

6.7: Cyclic voltammetry (CV) experiments

For all the Cyclic Voltammetric (CV) experiments, no extra precaution was taken to exclude air or moisture. All the measurements were carried out using a Metrohm Autolab PGSTAT204 potentiostat. A glassy carbon working electrode (disk, diameter: 3mm), a coiled platinum wire counter electrode and Ag/AgCl reference electrode were employed for the CV studies. All the voltammograms were recorded in MeCN at room temperature with 0.1M nBu_4NPF_6 as supporting electrolyte.

CV of **1b**. The individual cyclic voltammogram of 1a (using 0.1 M nBu_4NPF_6 as a supporting electrolyte in MeCN) was recorded (initial potential = 0 V, Upper vertex potential = 2.5 V, Lower vertex potential = −2.5 V, stopping potential = 0 V) with 200 mV/s scan rate (Figure 21-23).

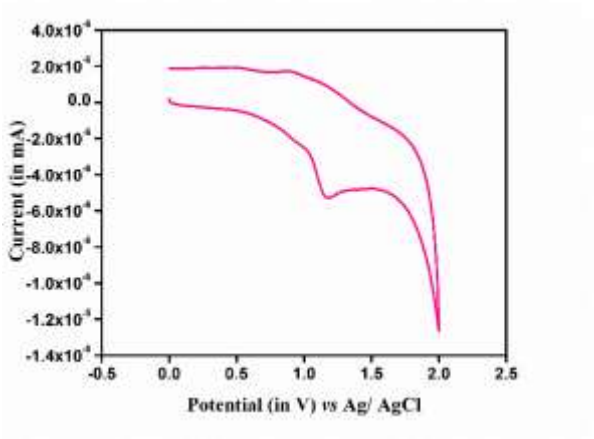


Figure 21: (a) Reduction Range for **1b**

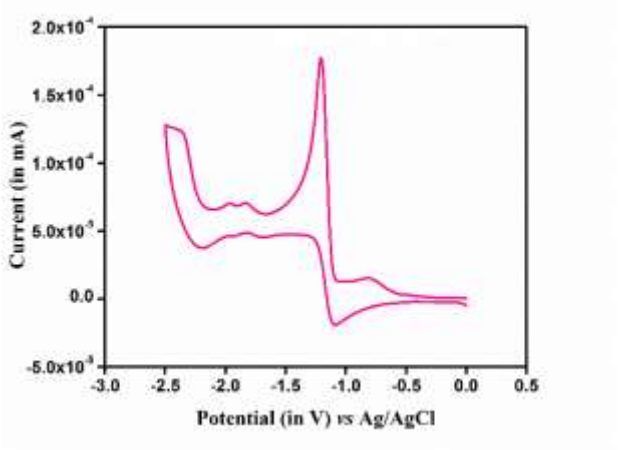


Figure 22: (b) Oxidation Range for **1b**

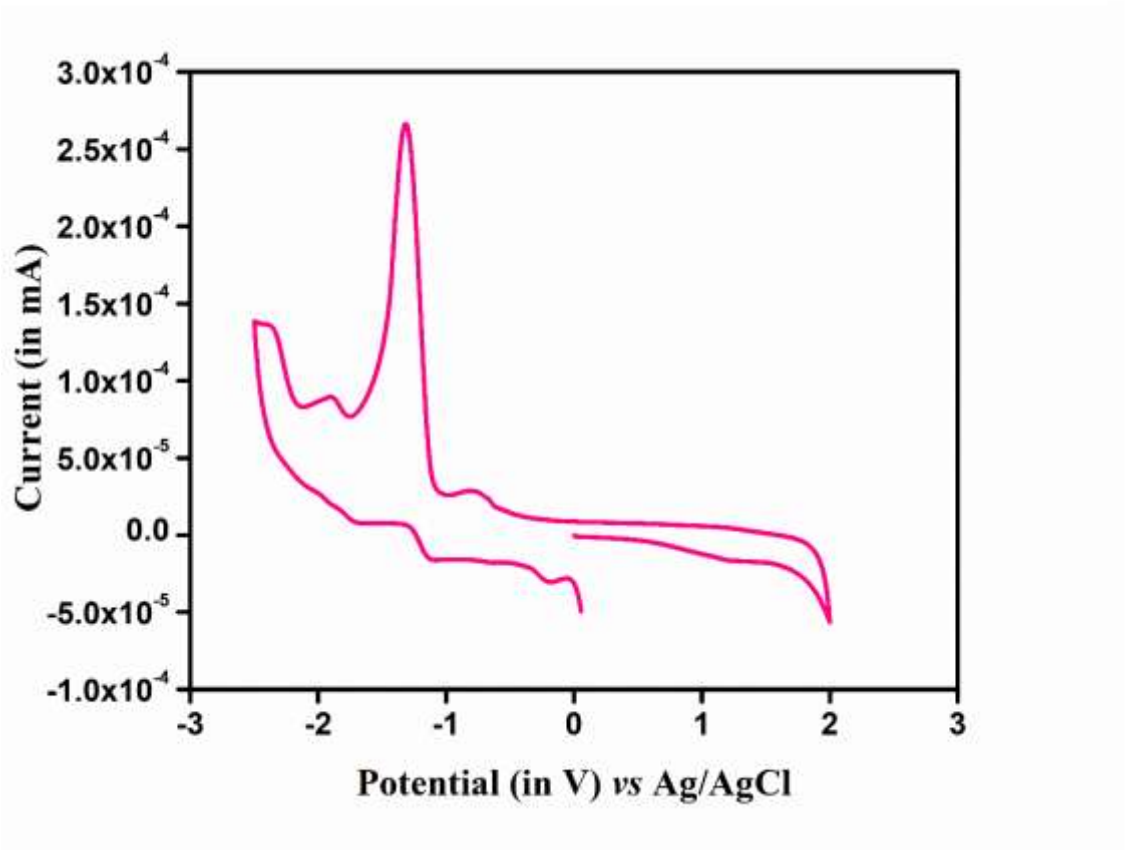
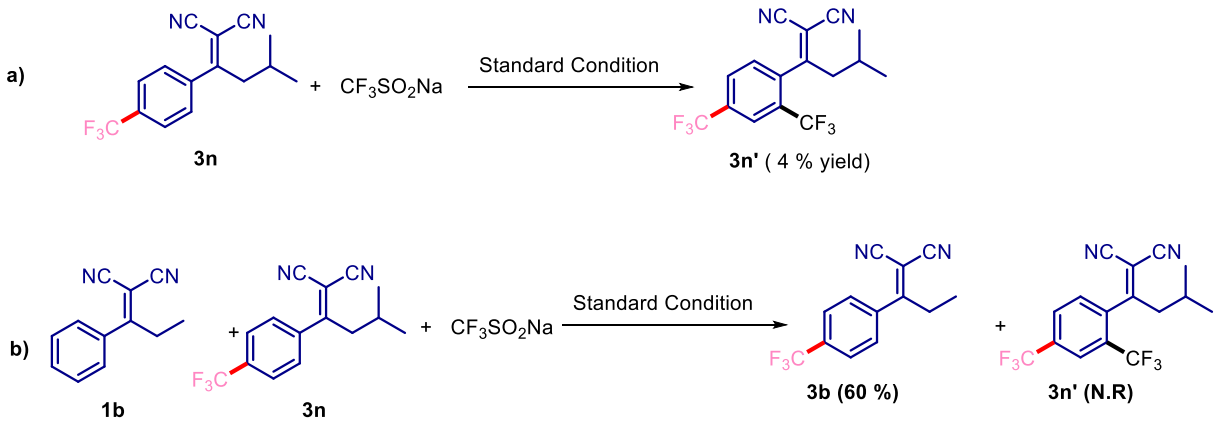


Figure 23: (c) Cyclic Voltammetry of **1b** (Full scan)

6.8: Cross over/competitive experiment



Scheme 13: (a-b) Crossover/competitive experiments with para-substituted alkylidene-malononitrile

(a) 0.2 mmol of **3n** (1.0 equiv.), Langlois reagent (0.6 mmol, 3 equiv.) were taken in a long neck round bottom flask and 2.5 mol % of Eosin Y was added into it followed by ammonium peroxo disulfate, the RB was capped with septum. The mixture was degassed and filled with N_2 (three times). The reaction mixture was irradiated with green LED for 24 h. After completion (monitored through TLC), reaction was quenched with saturated $NaHCO_3$ solution and extracted with DCM (3 x 10 mL), washed with brine solution. Analysis of Crude ^{19}F provided the percent conversion (Scheme 13a).

(b) (a) 0.2 mmol of **1b** and **3n** (1.0 equiv.), Langlois reagent (0.6 mmol, 3 equiv.) were taken in a long neck round bottom flask and 2.5 mol % of Eosin Y was added into it followed by ammonium peroxo disulfate, the RB was capped with septum. The mixture was degassed and filled with N_2 (three times). The reaction mixture was irradiated with green LED for 24 h. After completion (monitored through TLC), reaction was quenched with saturated $NaHCO_3$ solution and extracted with DCM (3 x 10 mL), washed with brine solution. After removal of solvent in vacuo, the product was purified by silica gel chromatography using EtOAc-hexane (3:7 to 5:5) as eluent to provide the desired product (Scheme 13b).

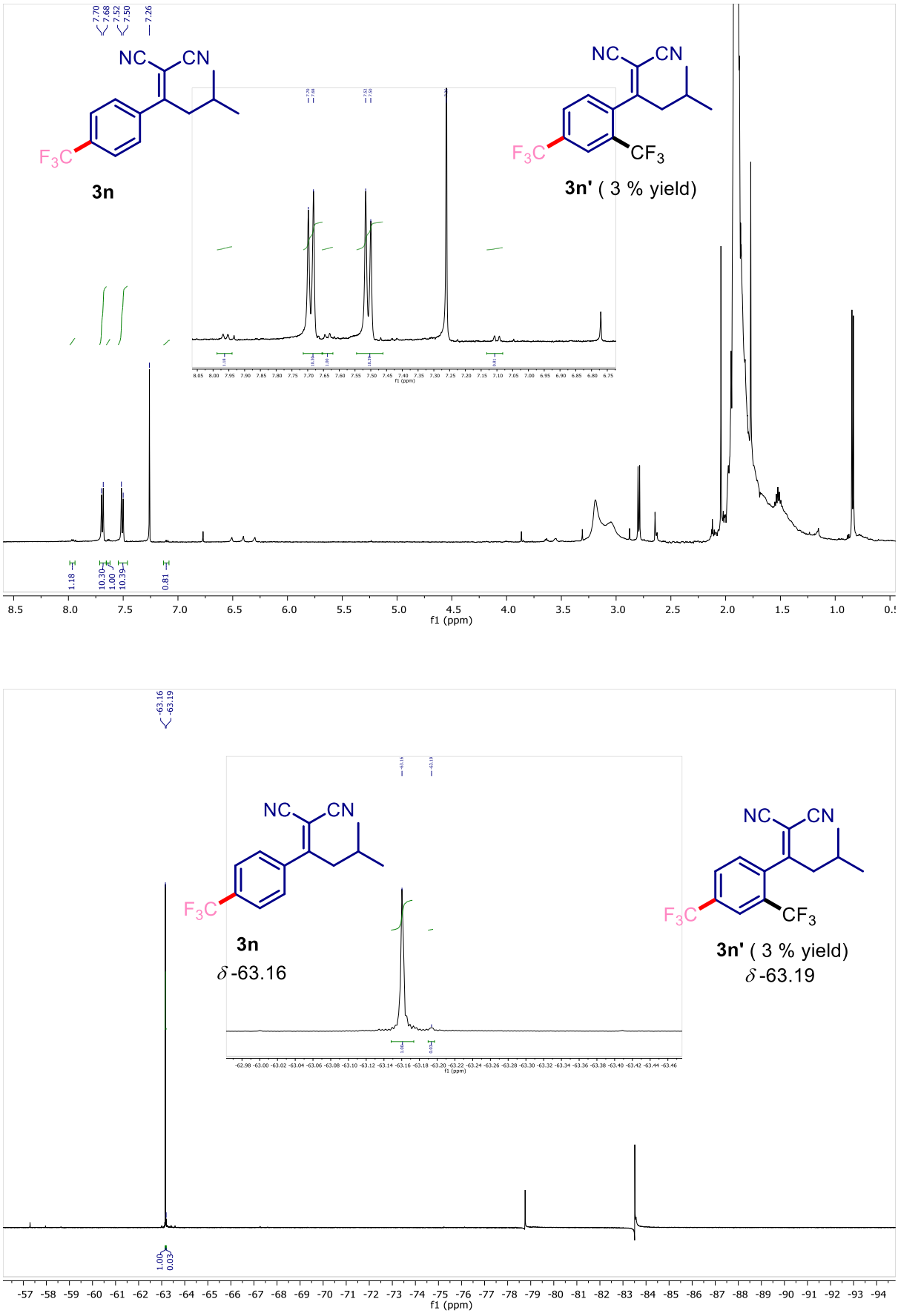


Figure 24: NMR Spectra

7.1 Computational Details

All calculations were performed with the Gaussian 16 program.[6] Structure optimization was performed using the B3LYP functional,[7] with Grimme's dispersion correction (denoted B3LYP-D3BJ)[8] and the 6-31g(d,p) basis set[9] for all atoms. Furthermore, we have also considered the solvent effects in acetonitrile (ε = 35.688) using the SMD solvation model,[10] for all structure optimizations. Harmonic vibrational frequencies were calculated at the same level for all stationary points to confirm them as a local minima or transition structures. Key transition state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations.[11] To improve the calculation accuracy, single point energy calculations were performed using the B3LYP functional,[7] with Grimme's dispersion correction (denoted B3LYP-D3BJ)[8] and the 6-311++G** basis set[12] for all atoms. Furthermore, we have also considered the solvent effects in acetonitrile (ε = 35.688) using the SMD solvation model,[10] for all single-point energy calculations. The CYL View software was employed to show the 3D structures of the studied species.[13]

7.2 Calculation of Single Electron Transfer Steps by Marcus-Hush Theory

To get more details of the singlet electron transfer (SET) process, we estimated the free energy barrier of SET process using the Marcus-Hush theory (Figure 24),[14] which can be calculated according to the following formula:

$$\Delta G_{MH}^{\ddagger} = \frac{(\Delta G_r + \lambda)^2}{4\lambda}$$

Where ΔGr is the Gibbs free energy change of the SET step, λ is the reorganization energy including inner sphere energy and outer sphere energy. However, the outer sphere energy is often much larger than the inner sphere contribution. Hence, the outer sphere reorganization energy (λouter) can be regarded as the total reorganization energy, which can be calculated according to the following formula:

$$\lambda = \lambda_{outer} = 332 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R}\right)\left(\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_s}\right)$$

Where r_1 and r_2 are the radii of electron donor and acceptor, R is the sum of r_1 and r_2, ε_{opt} and ε_s is the high frequency (optical) dielectric constant and static dielectric constant of solvent respectively (for MeCN, ε_{opt} = 1.807, ε_s = 35.688).

Table S4. Calculated Energies of SET processes.

	r_1	r_2	R	λ	ΔG_r	$\Delta G^{\ddagger}_{MH}$
SET	6.6367	7.2815	13.9182	12.58	9.66	9.83

7.3 Computed Reaction Pathways

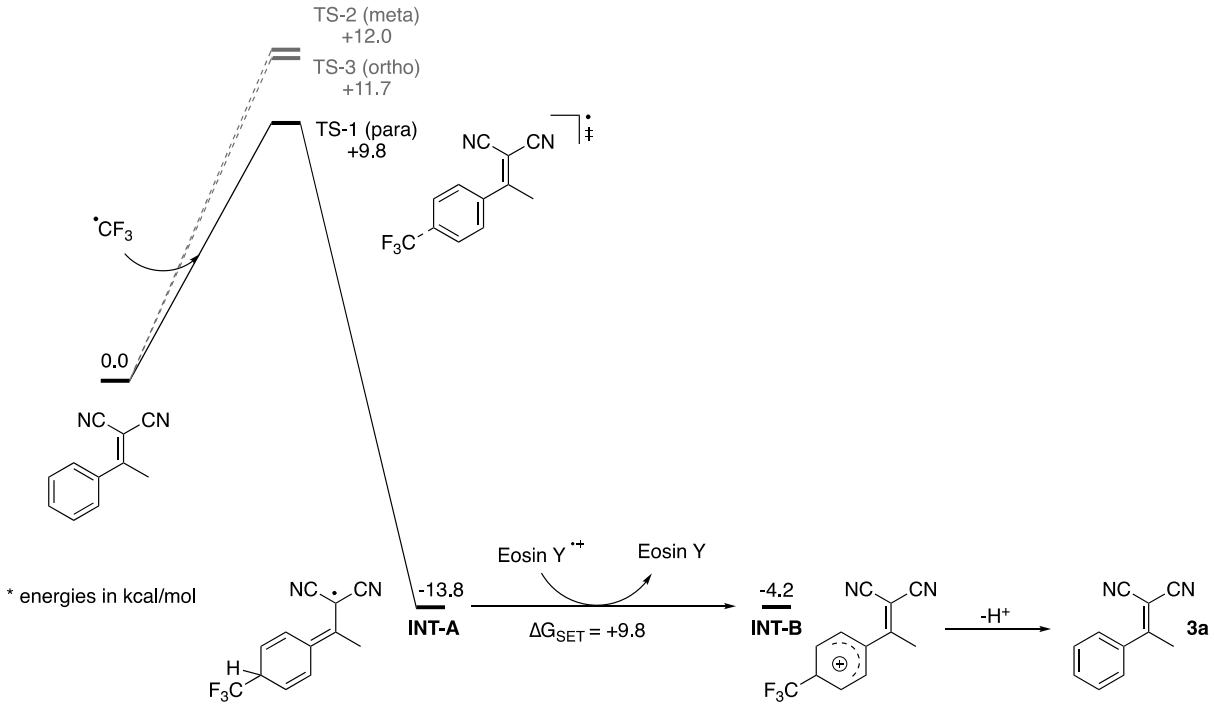


Figure 25: Calculated photocatalytic reaction pathway; energies in kcal/mol.

7.4 Computed Energies of all Stationary Points

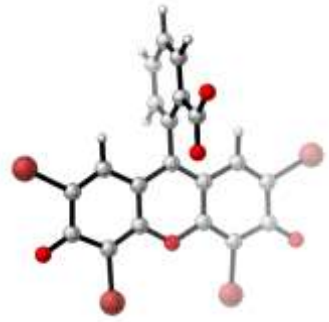
Table S5. Calculated Energies of all Stationary Points for Reaction Pathways.

Thermal correction to Gibbs Free energies (***TCG***, in Hartree), thermal correction to enthalpies (***TCH***, in Hartree), sum of electronic and thermal Free energies (***G***, in Hartree), sum of electronic and thermal enthalpies (***H***, in Hartree), at the B3LYP-D3BJ / 6-31g(d,p) level in acetonitrile, single point energies in acetonitrile computed at the B3LYP-D3BJ / 6-311++G** level (E_{sol}, in Hartree).

Name	*TCG* /Hartree	*TCH* /Hartree	*G* /Hartree	*H* /Hartree	E_{sol} /Hartree
^{1}Eosin Y	0.146929	0.233582	-11428.94381	-11428.94381	-11439.17053
^{3}Eosin Y	0.14506	0.231552	-11428.88179	-11428.7953	-11439.10534
Eosin Y$^+$	0.146057	0.233234	-11428.78358	-11428.6964	-11438.99148
CF_3	-0.014794	0.016344	-337.564612	-337.533474	-337.670293
1	0.121181	0.17193	-533.398289	-533.347541	-533.648372
TS-1 (para)	0.123788	0.188463	-870.949429	-870.884754	-871.320443
TS-2 (ortho)	0.12565	0.188407	-870.948366	-870.885609	-871.318815
TS-3 (meta)	0.124844	0.188215	-870.946154	-870.882783	-871.318452
INT-A	0.128426	0.190337	-870.990485	-870.928574	-871.362746
INT-B	0.12911	0.190879	-870.805691	-870.743922	-871.16985
Product (3a)	0.119383	0.17997	-870.44001	-870.44001	-870.80301

7.5 3D Structure and Coordinates of all Stationary Points

1Eosin Y



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C 2.49393400 1.03000000 -0.19792300

C 3.63080500 0.27841600 -0.16815600

C 0.00163300 1.14274700 -0.15338200

C -1.21834900 0.43592200 -0.14840500

C -1.20191500 -0.98596900 -0.05514100

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C -3.68730300 -1.13092900 -0.06682700

C -3.64033800 0.33216000 -0.16394700

C -2.49272500 1.06684900 -0.19942100

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H -2.53255300 2.14709600 -0.26468200

Br -5.33455500 1.22532200 -0.24189100

Br -2.26319800 -3.62654200 0.10167200

Br 2.19587900 -3.66279700 0.04827000

Br 5.33732900 1.14814000 -0.24136200

O -4.74530000 -1.78276800 -0.03373900

O -0.01898200 -1.65994400 -0.00597900

O 4.70562300 -1.85324800 -0.05730200

C 0.01390200 2.61182900 -0.41531900

C 0.06211600 3.56662200 0.61352400

C -0.01679900 3.02899700 -1.75459700

C 0.08136500 4.92382900 0.27357600

C 0.00118000 4.38561700 -2.07594800

H -0.05393600 2.28301300 -2.54320100

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H -0.02305200 4.69419400 -3.11689200

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3Eosin Y

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C 0.44896800 3.22573800 -1.51962500

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H -0.40381500 6.48444600 -1.07040900

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O -1.01612800 1.89022100 2.31454300

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Eosin Y^{+}

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CF_3

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1

Charge: 0

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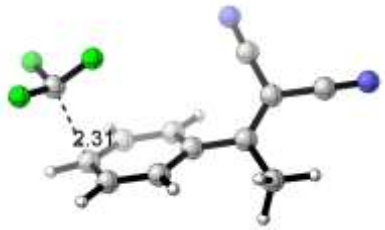

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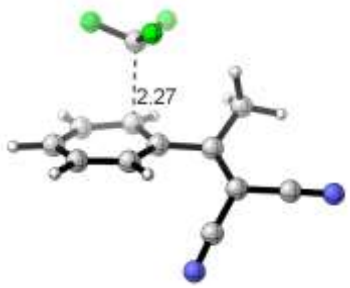

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N -4.41221600 -1.93471500 0.08584300

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H -0.19682500 -2.12195200 -1.21544900

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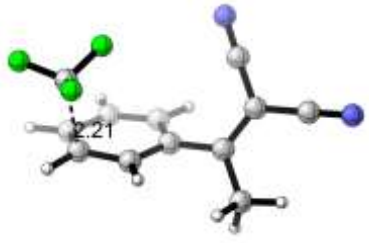

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C 2.38104800 1.68155900 -1.37021000
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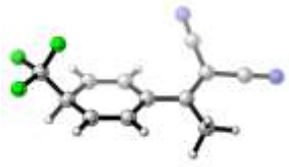
INT-A



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C 0.08943700 0.60684200 -0.89518300
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H 0.17440200 -2.57505600 0.41805600
C -1.24387800 0.74198900 -1.08238400
H 0.73656100 1.40020400 -1.24363300
C -2.22161700 -0.33028100 -0.71170500
H -2.22008300 -2.37287700 0.14936900
H -1.64026600 1.63847000 -1.54675500
H -2.79046700 -0.61478900 -1.61380100
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N 2.35538400 2.83087100 0.31936800
C 4.36411600 0.11351600 0.18805900
N 5.51487300 -0.03326900 0.30268800
C 2.62725200 -2.13642200 0.03996700
H 2.17051200 -2.81288200 -0.68507800
H 3.70809900 -2.15668300 -0.10087200
H 2.41774900 -2.52713900 1.04290000
C -3.29786400 0.20673900 0.23466400
F -3.93979900 1.26849700 -0.29944800
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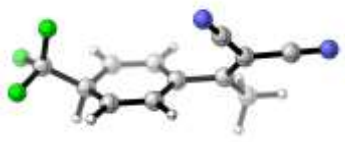
INT-B



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C -0.04587300 -1.42932300 -0.65518200

C 0.13674700 0.24025200 1.16337500

C -1.40742600 -1.33224100 -0.62663500

H 0.44076600 -2.07303800 -1.37750300

C -1.22342000 0.33919800 1.23110200

H 0.76189200 0.82026100 1.83074200

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H -2.47673100 -1.26556700 1.10895300

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H 2.10405700 -1.82476200 -1.25828400

H 1.65228600 1.62560600 1.27183700

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H -3.73108200 -2.21257700 0.45294700

H -2.32584500 -2.77348100 -0.47120500

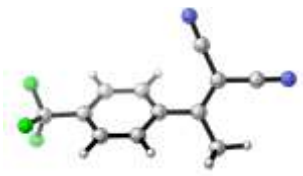
C 3.51817800 0.11936500 0.00661600

F 3.86226700 1.42460000 0.08566200

F 4.09533100 -0.49774600 1.06791400

F 4.10623600 -0.38445900 -1.1011690

Product (3a)



Charge: 0

Spin: 1

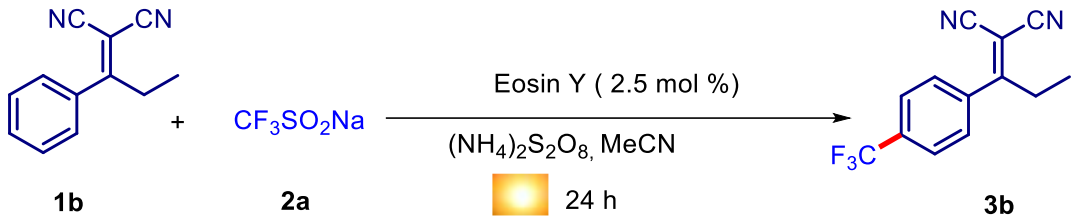
C -3.08994400 0.28885500 -0.04754800

C -2.19067700 -0.73113300 0.11906900

C -0.73497700 -0.48774200 0.06898000

C 0.09805700 -1.36731300 -0.64296600

8: Sunlight-driven experiment



Scheme 14: Preparation of trifluoromethylated alkylidene malononitrile in sunlight

0.2 mmol of **1b** (1.0 equiv.), Langlois reagent (0.6 mmol, 3 equiv.) were taken in a long neck round bottom flask and 2.5 mol % of Eosin Y was added into it followed by ammonium peroxodisulfate, the RB was capped with septum. The mixture was degassed and filled with N_2 (three times). The reaction mixture was irradiated under sunlight (Location: 28.5457° N, 77.1928° E E) for 24 h. After completion (monitored through TLC), reaction was quenched with saturated $NaHCO_3$ solution and extracted with DCM (3 x 10 mL), washed with brine solution. After removal of solvent in vacuo, the product was purified by silica gel chromatography using EtOAc-hexane (3:7 to 5:5) as eluent to provide the desired product **3b** (Scheme 14).

Yield: 19 mg, 38 %.

9. Crystallographic data

Sample preparation: Single crystal of compound **3c** suitable for the X-ray diffraction studies were grown from Ethylacetate/Heptane solution at room temperature.

Single crystal of compound **3zr** suitable for the X-ray diffraction studies were grown from Chloroform/Heptane solution at room temperature.

Molecular structure determination of compounds **3c** and **3zr**: Single crystal X-ray diffraction data for compound **3c** and **3zr** was collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer (Figure 26 and Figure 27). The crystals were covered with Paratone–*N* and mounted a glass capillary. The data were collected at room temperature. Integration of data was performed using SAINT. Empirical absorption correction was applied using SADABS. Structure solutions were accomplished by directs methods and refine by full matrix least square on F2 using OLEX2. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atoms was fixed according to a riding model and were refined isotropically.

Table S6. Crystal data and structure refinement for 3c

Bond precision:	C-C = 0.0048 A		Wavelength=0.71073
Cell:	a=7.639(17)	b=21.17(3)	c=8.402(14)
	alpha=90	beta=99.33(4)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	1341(4)	1341(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C14 H11 F3 N2	C14 H11 F3 N2
Sum formula	C14 H11 F3 N2	C14 H11 F3 N2
Mr	264.25	264.25
Dx,g cm-3	1.309	1.309
Z	4	4
Mu (mm-1)	0.108	0.108

F000	544.0	544.0
F000'	544.34	
h,k,lmax	10,28,11	10,28,11
Nref	3316	3271
Tmin,Tmax	0.999,0.999	0.648,0.746
Tmin'	0.999	

Correction method= # Reported T Limits: Tmin=0.648 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.986 Theta(max)= 28.252

R(reflections)= 0.0558(1293) wR2(reflections)= 0.1602(3271)

S = 0.990 Npar= 200

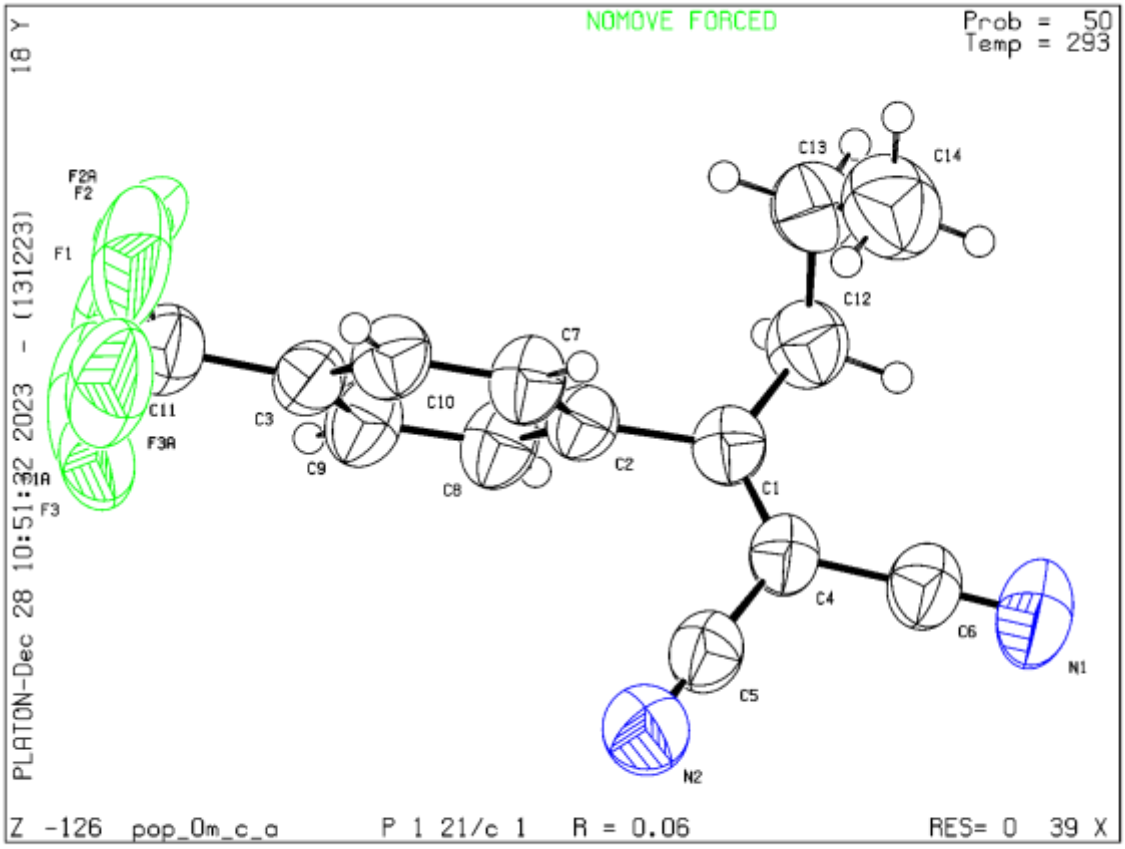


Figure 26: Single Crystal X-ray Structure of Compound **3c (CCDC Number:** 2322306)

Table S7. Crystal data and structure refinement for 4a

Bond precision: C-C = 0.0048 A Wavelength=0.71073

Cell: a=13.1854(9) b=8.7585(6) c=14.5343(11)
alpha=90 beta=101.895(3) gamma=90

Temperature: 303 K

	Calculated	Reported
Volume	1642.4(2)	1642.4(2)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C19 H11 F3 N2	C19 H11 F3 N2
Sum formula	C19 H11 F3 N2	C19 H11 F3 N2
Mr	324.30	324.30
Dx,g cm-3	1.311	1.311
Z	4	4
Mu (mm-1)	0.102	0.102
F000	664.0	664.0
F000'	664.39	
h,k,lmax	17,11,19	17,11,19
Nref	4101	4093
Tmin,Tmax	0.999,0.999	0.641,0.746
Tmin'	0.999	

Correction method= # Reported T Limits: Tmin=0.641 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 28.336

R(reflections)= 0.0826(2137) wR2(reflections)= 0.2981(4093)

S = 1.050 Npar= 214

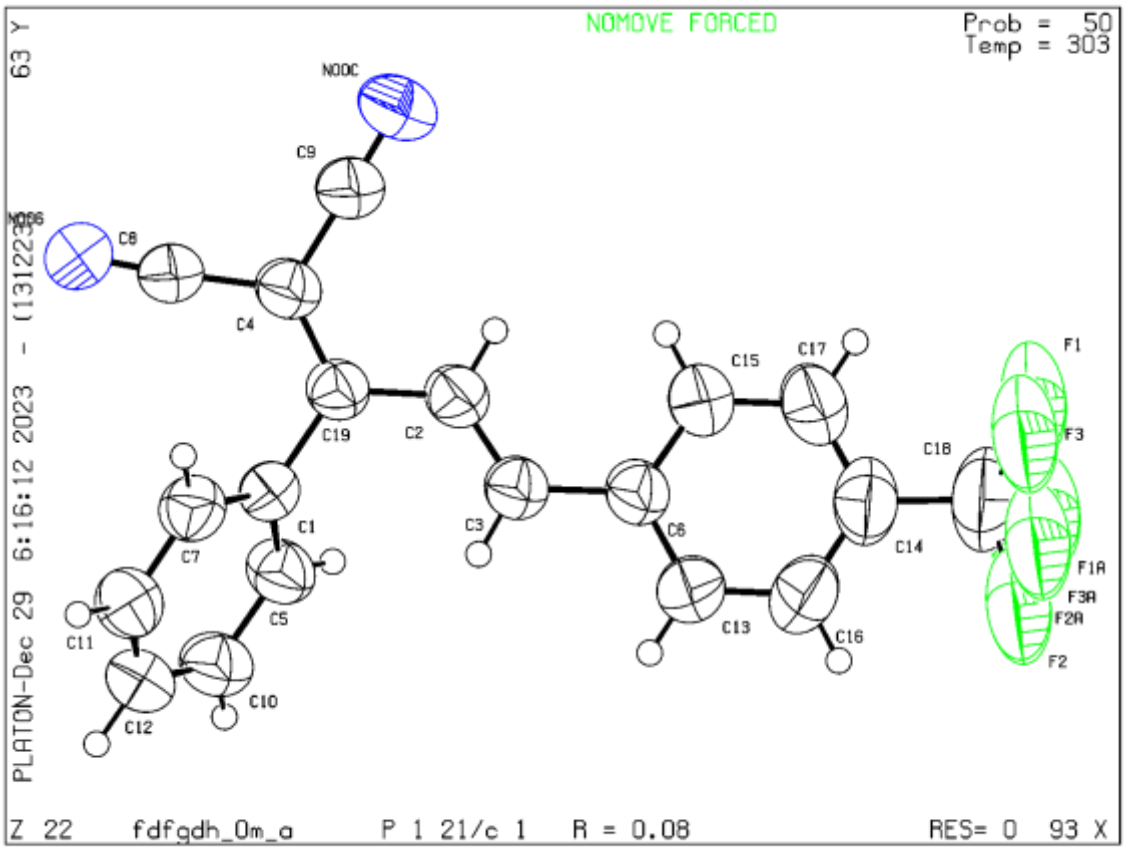


Figure 27: Single Crystal X-ray Structure of Compound **4a (CCDC Number:** 2322456**)**

10: References

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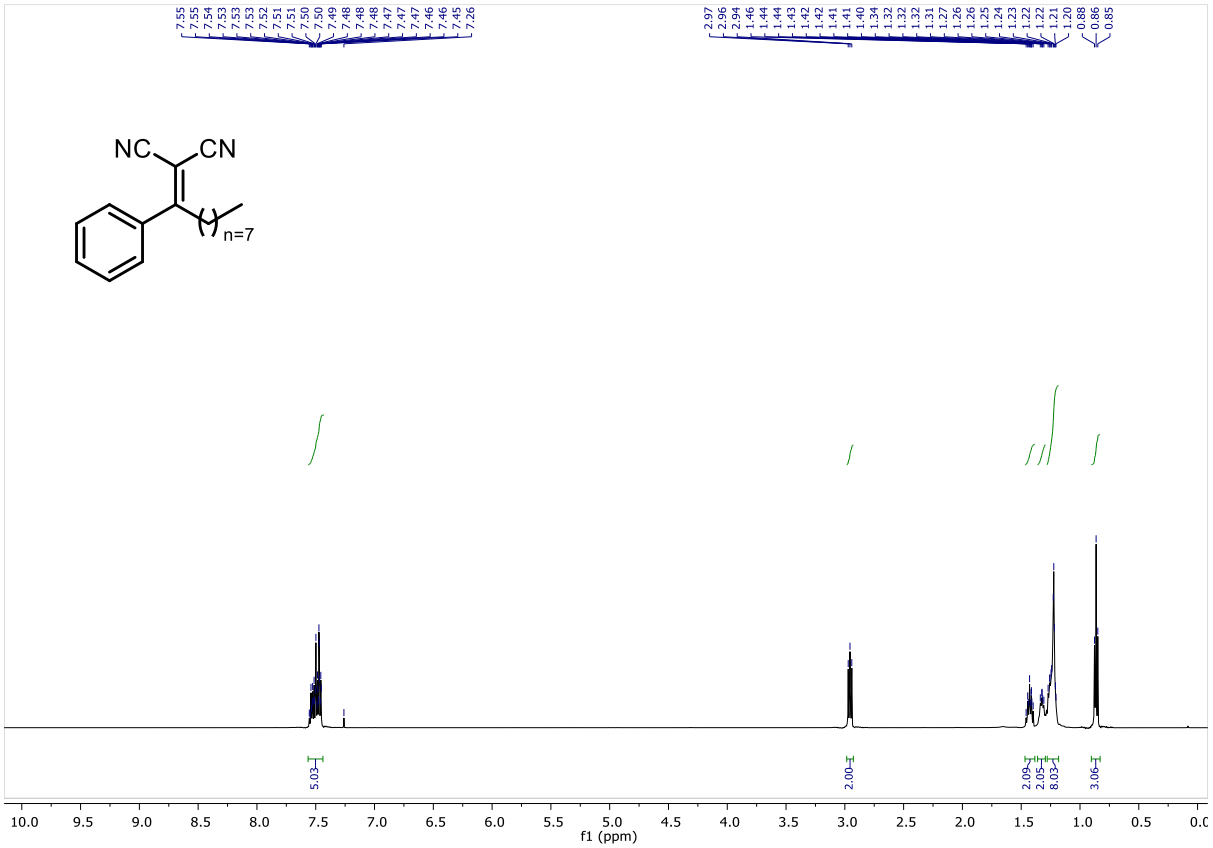
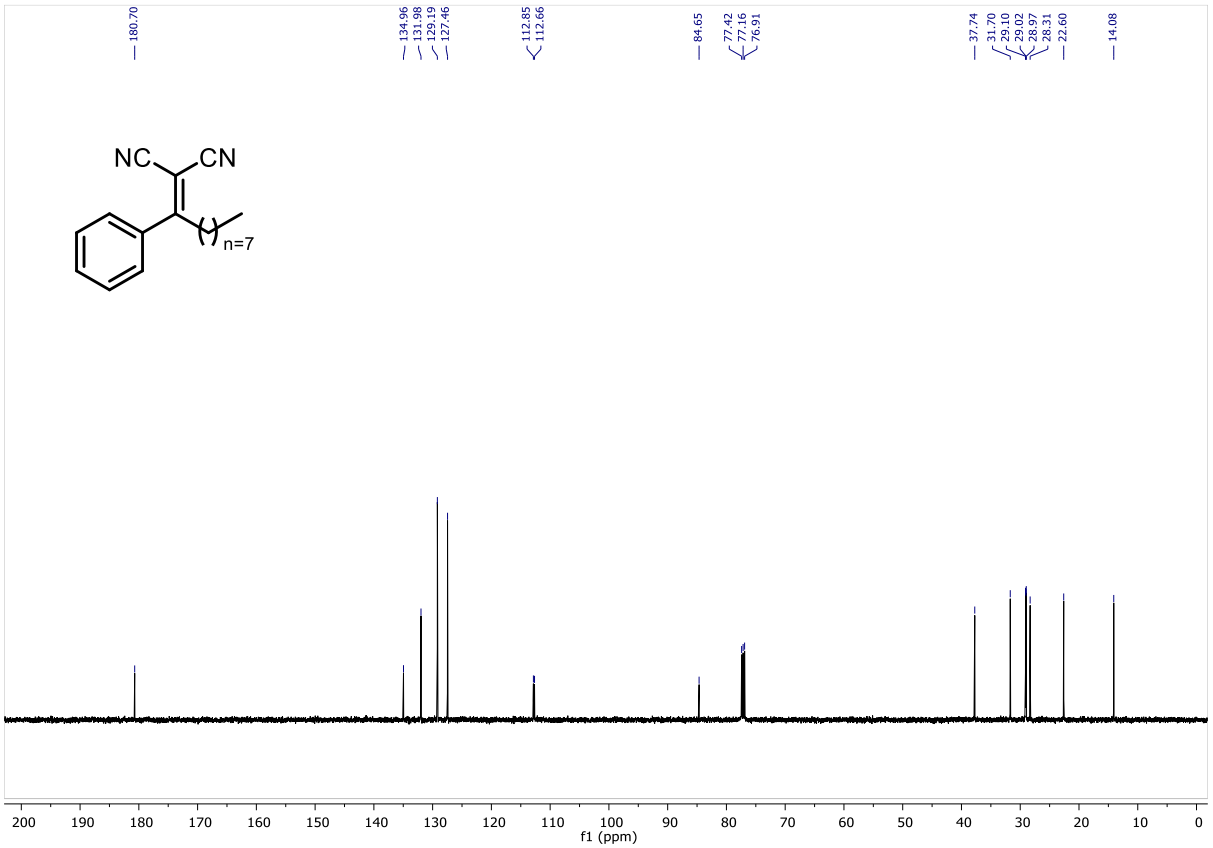
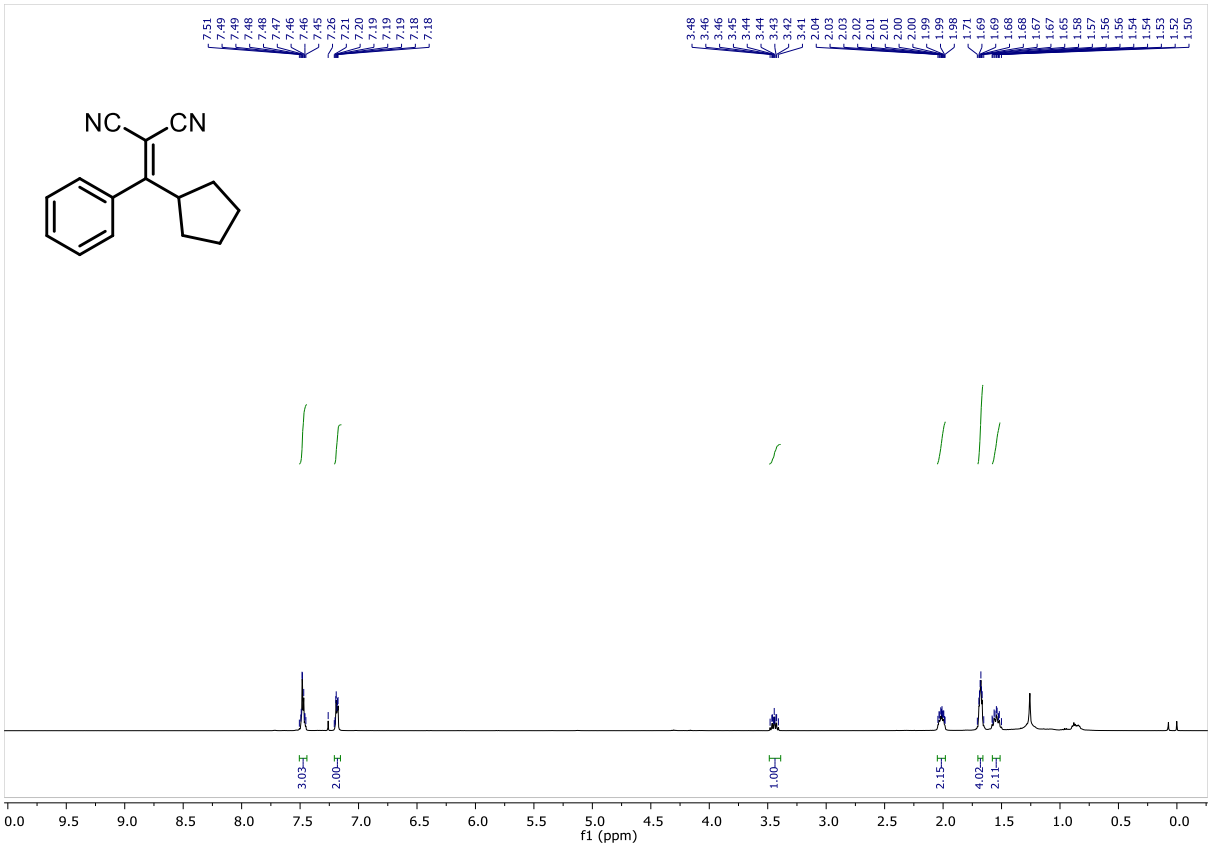
11: ^{1}H, ^{13}C and ^{19}F spectra of compounds



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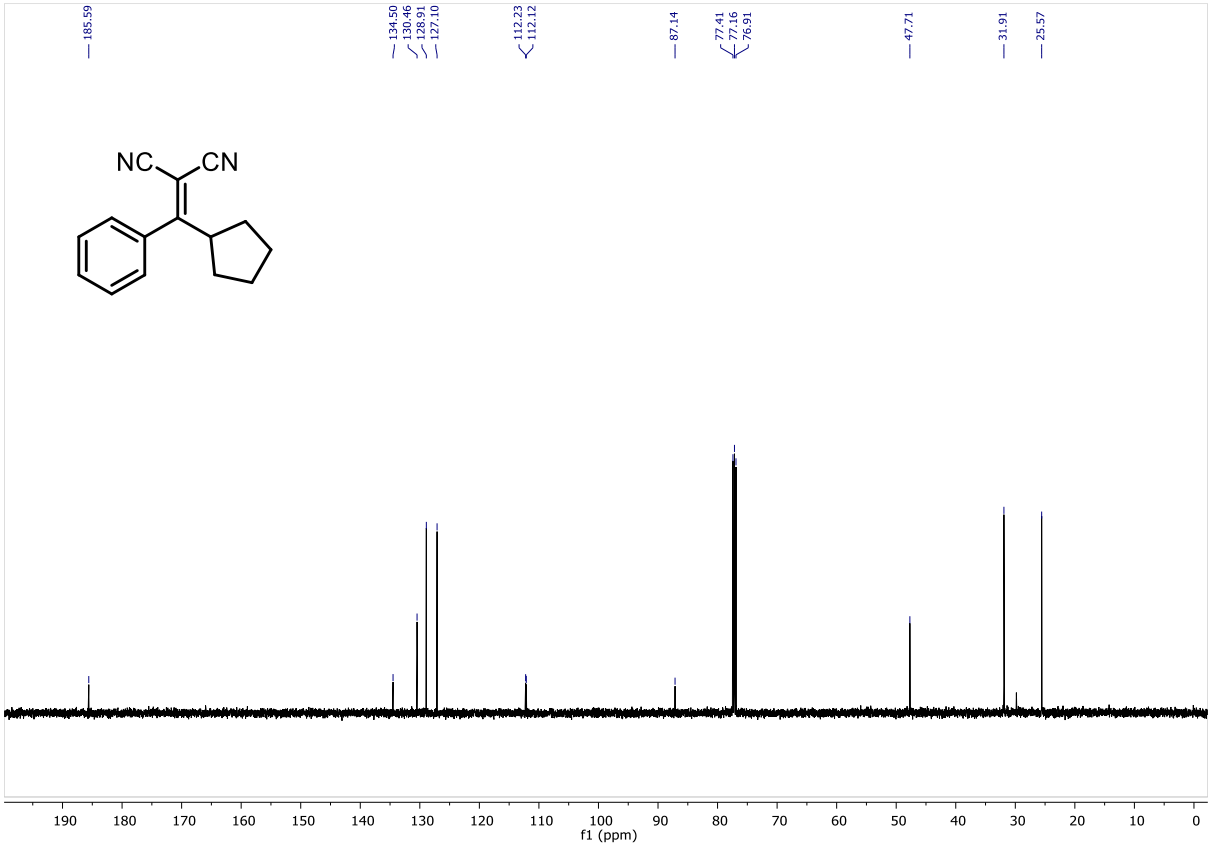
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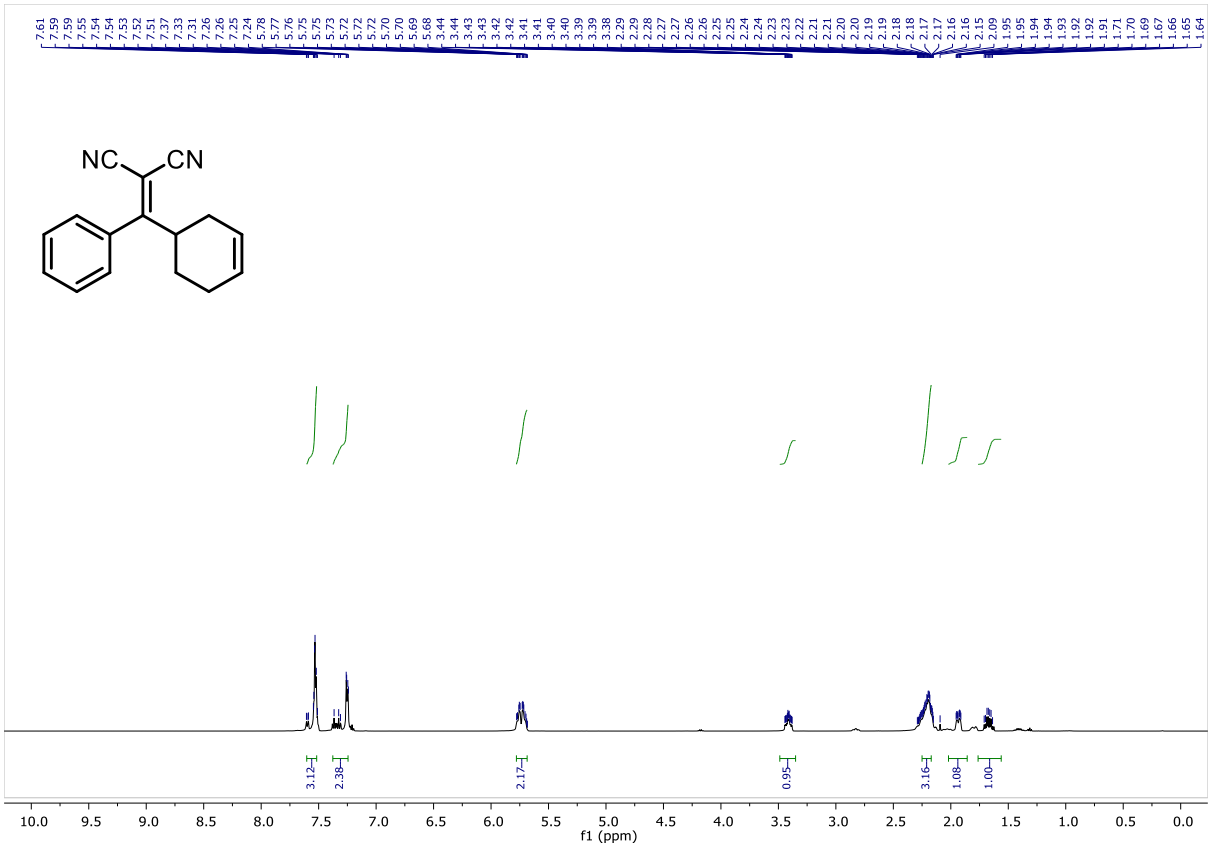
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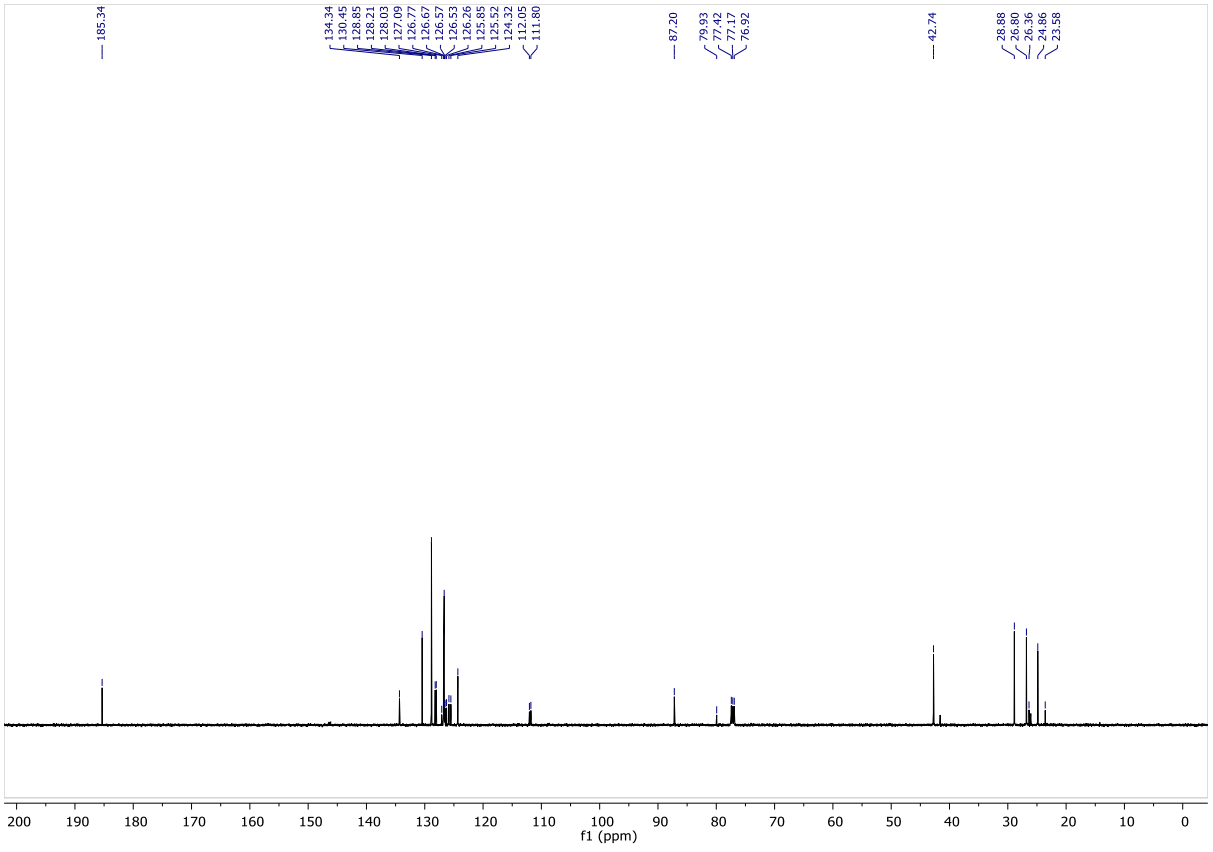
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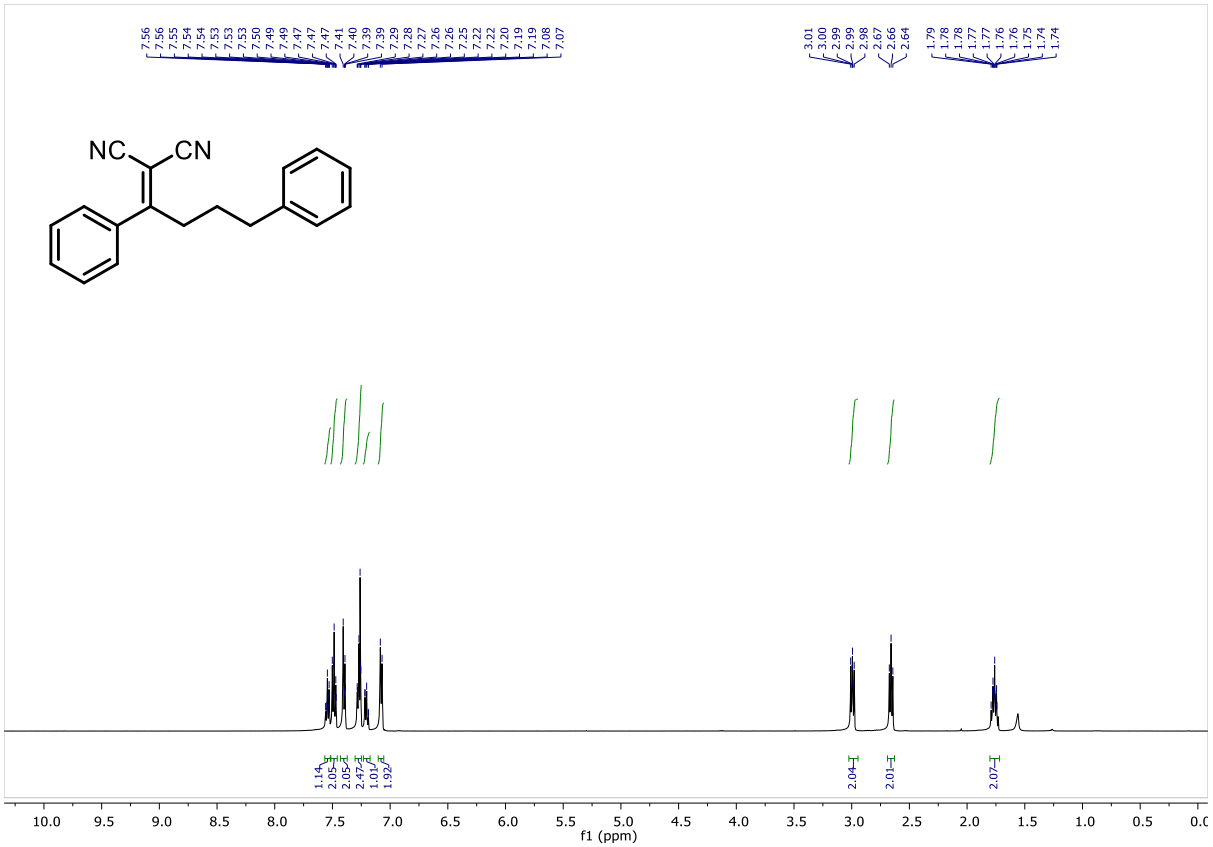
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3.01 3.00 2.99 2.99 2.98 2.67 2.66 2.64
1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.74 1.74
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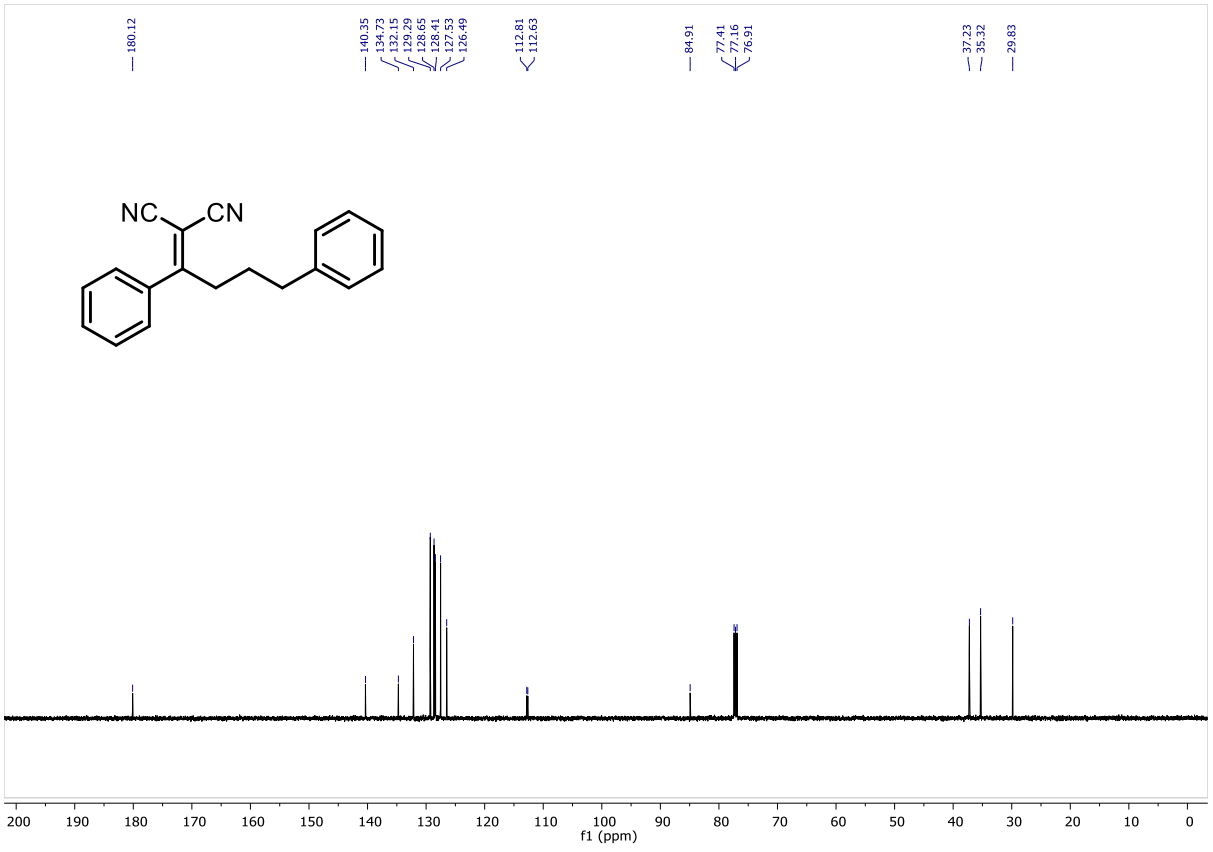
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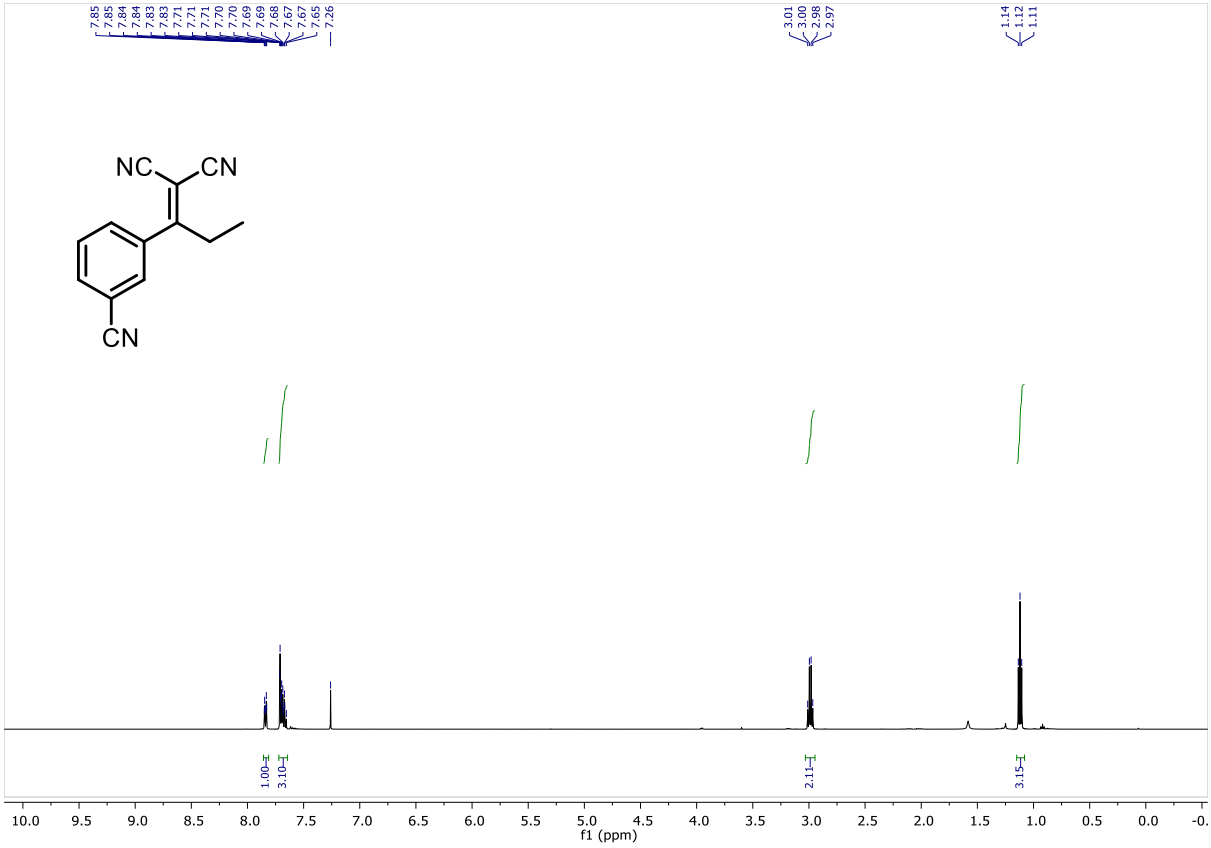
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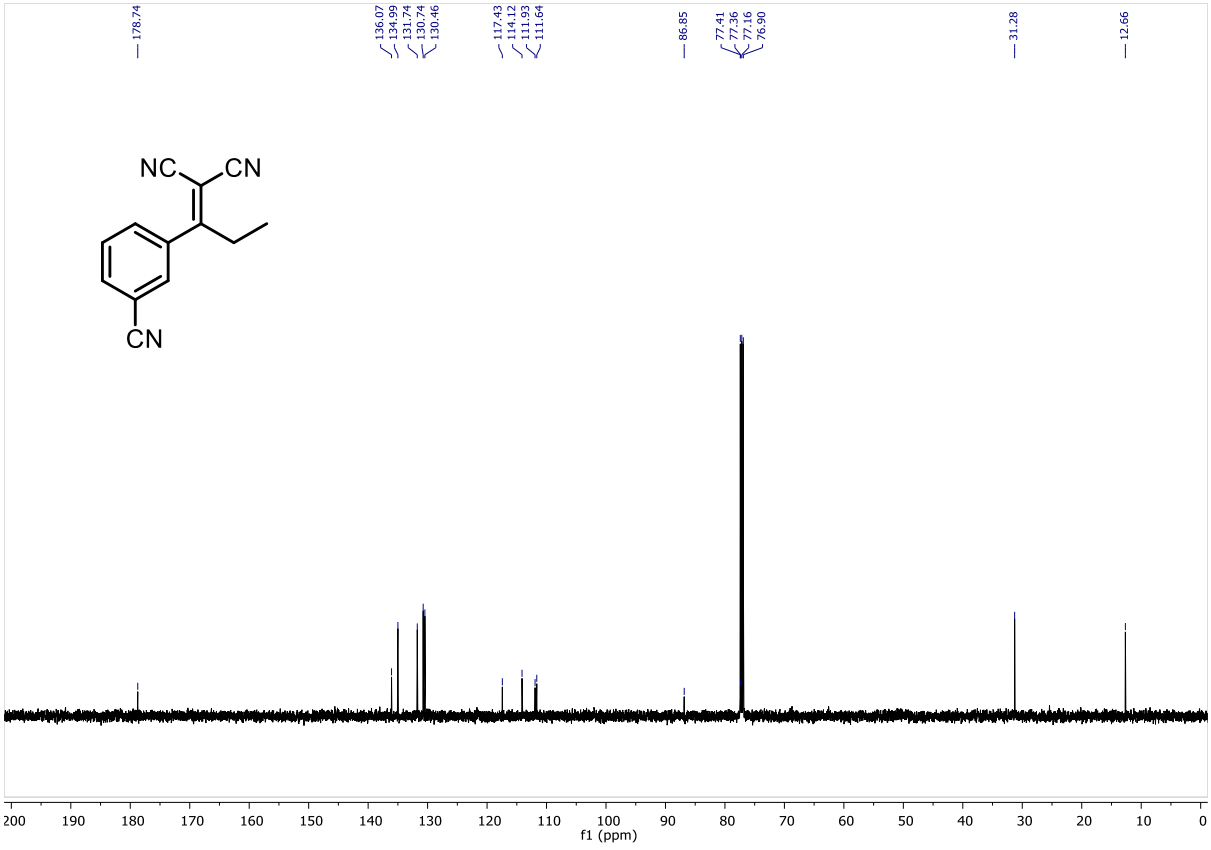
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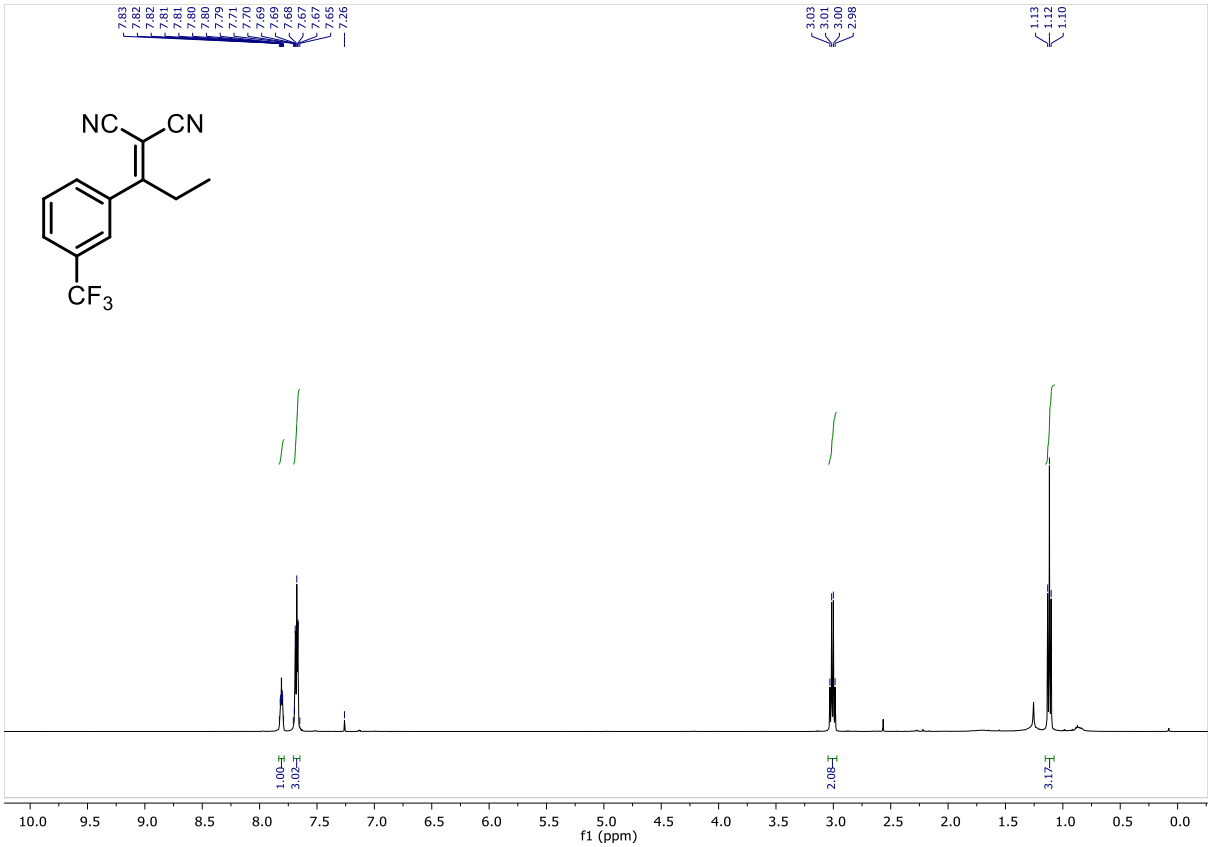
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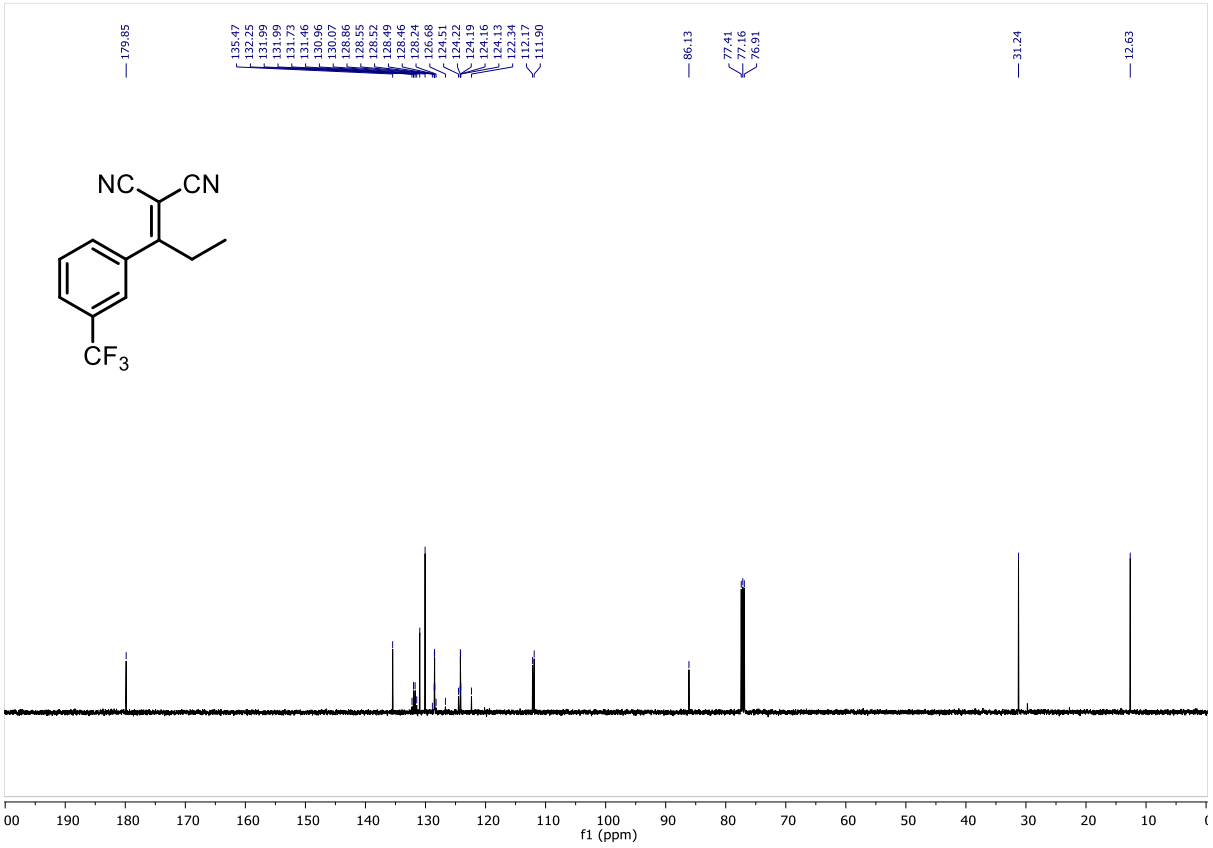
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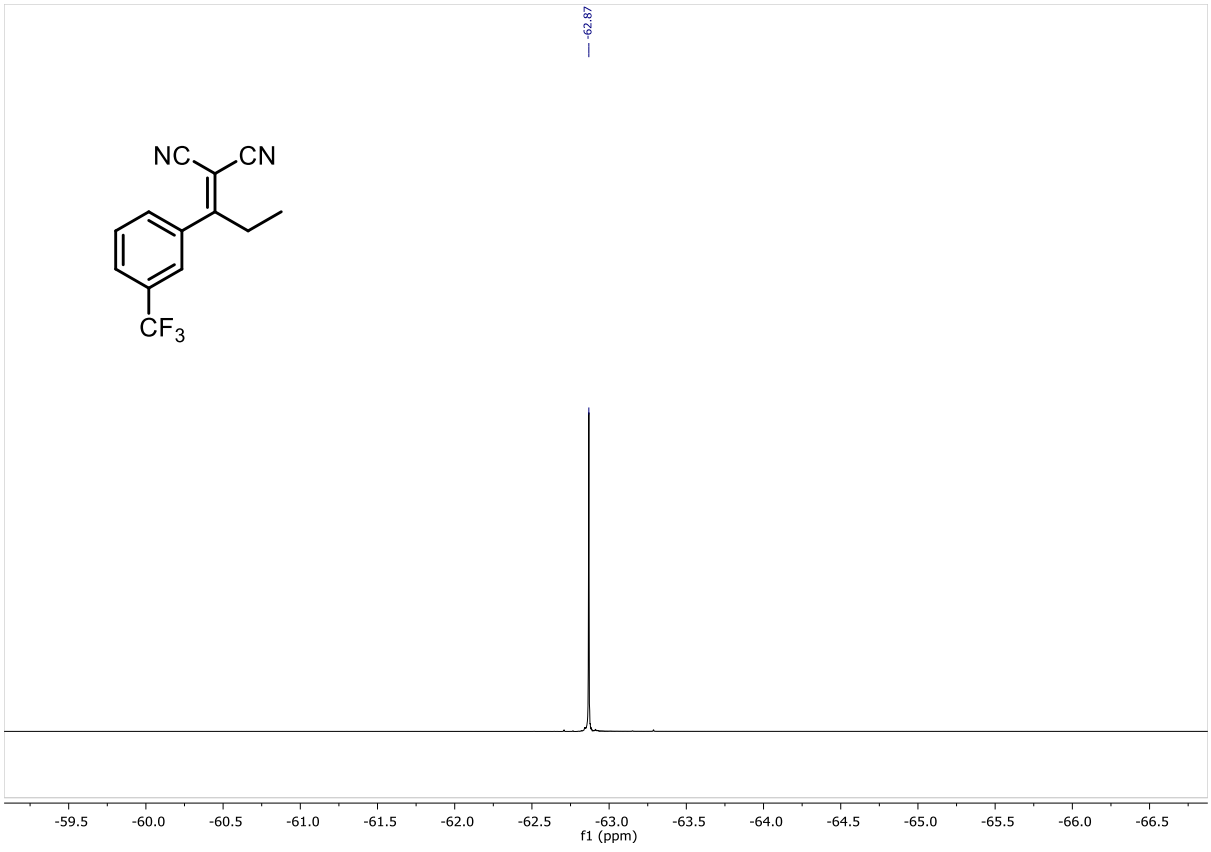
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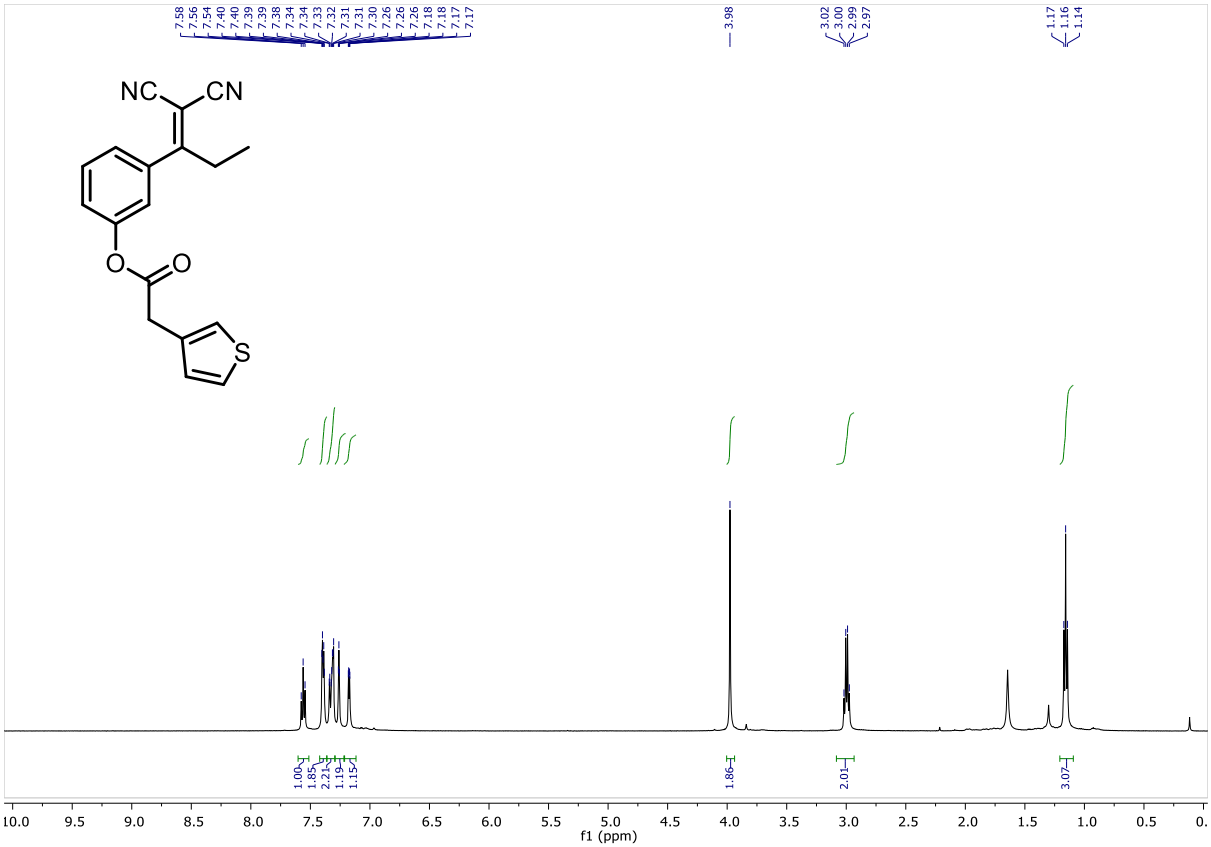
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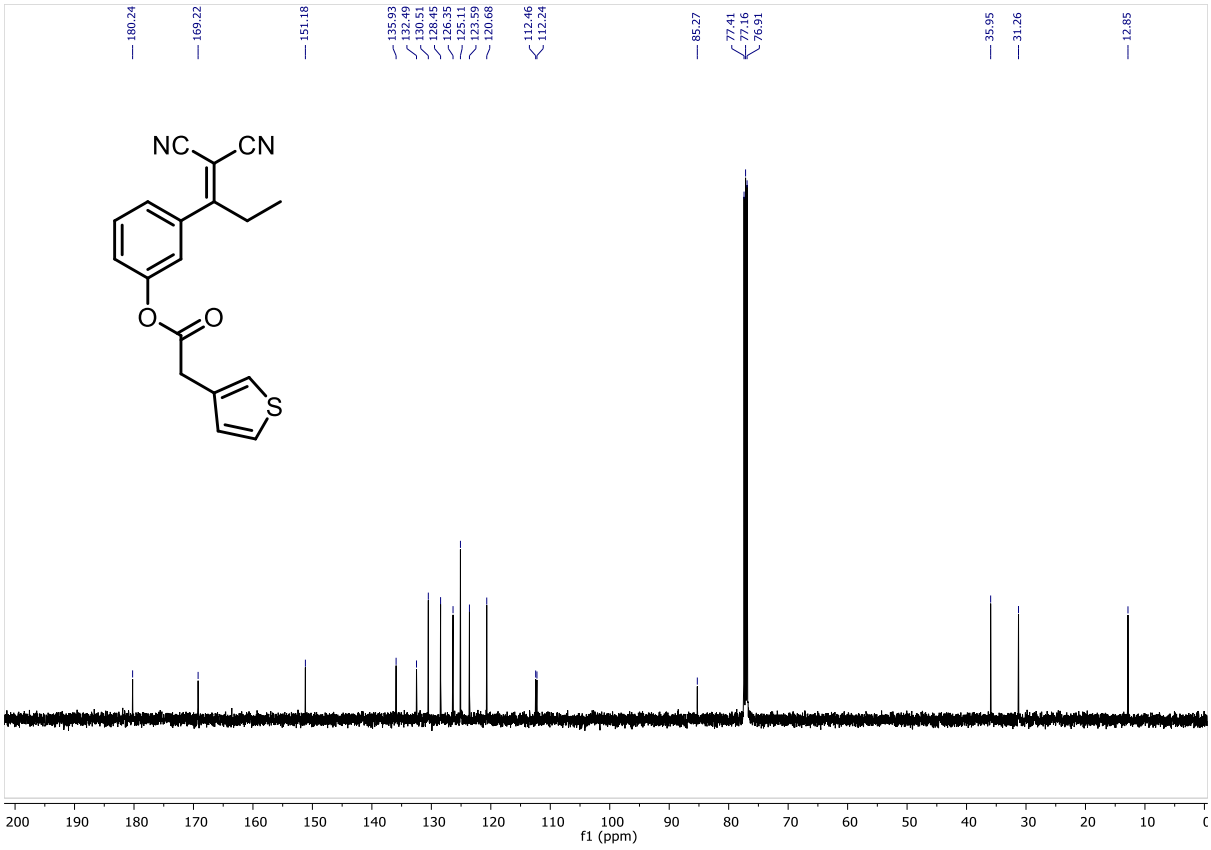
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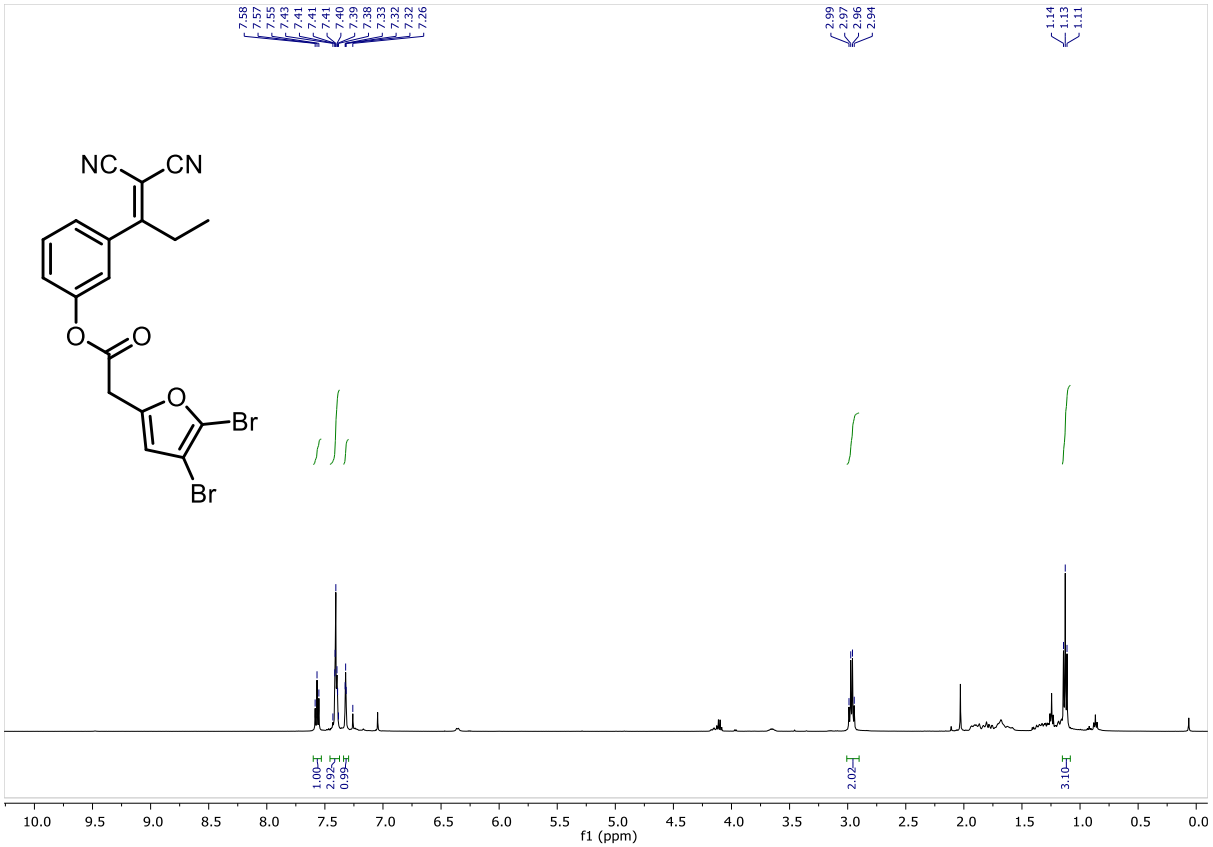
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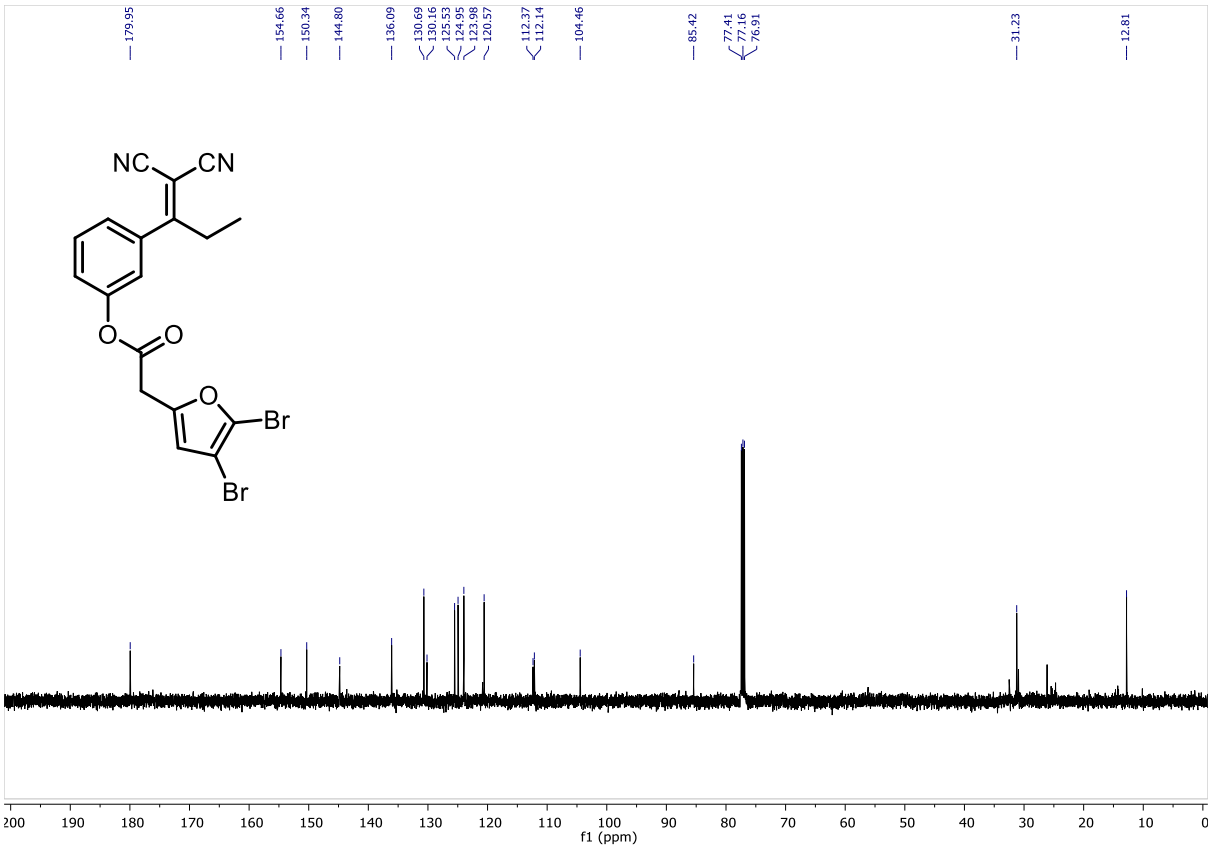
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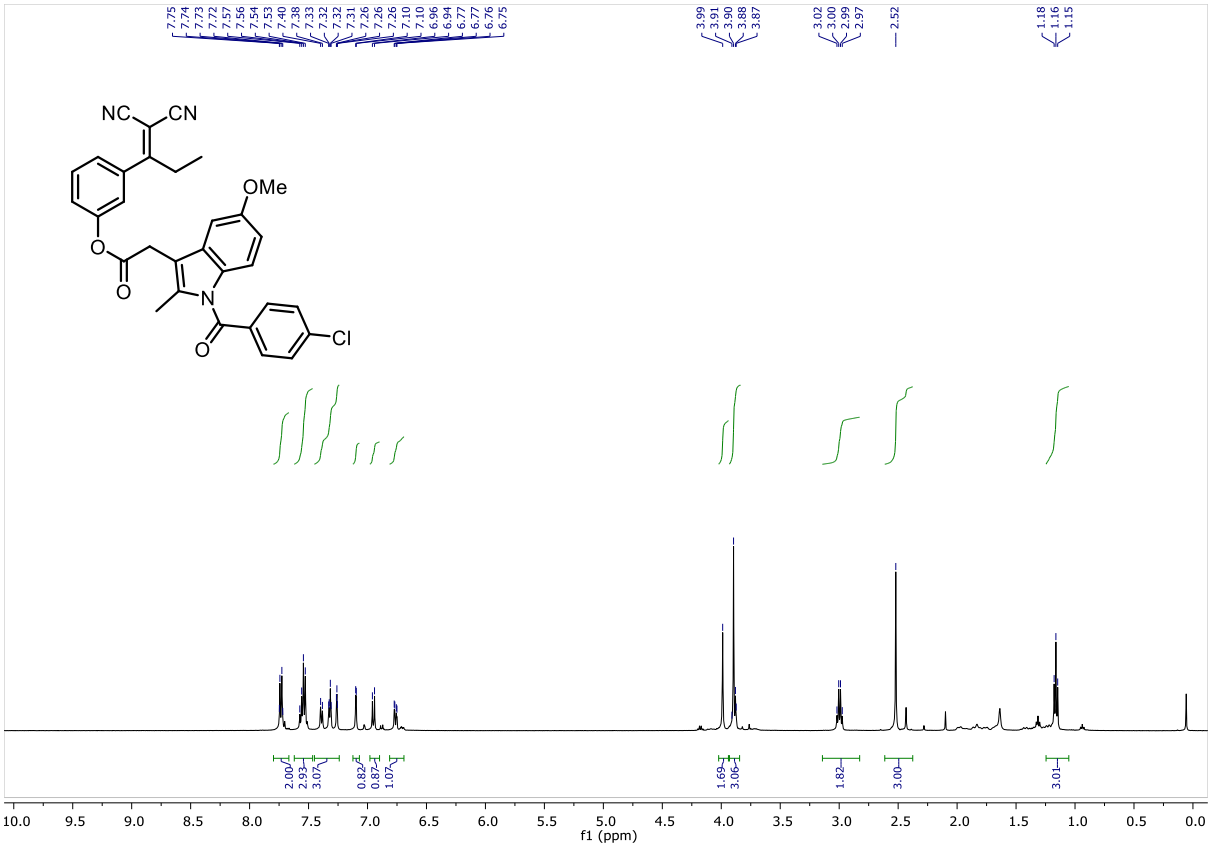
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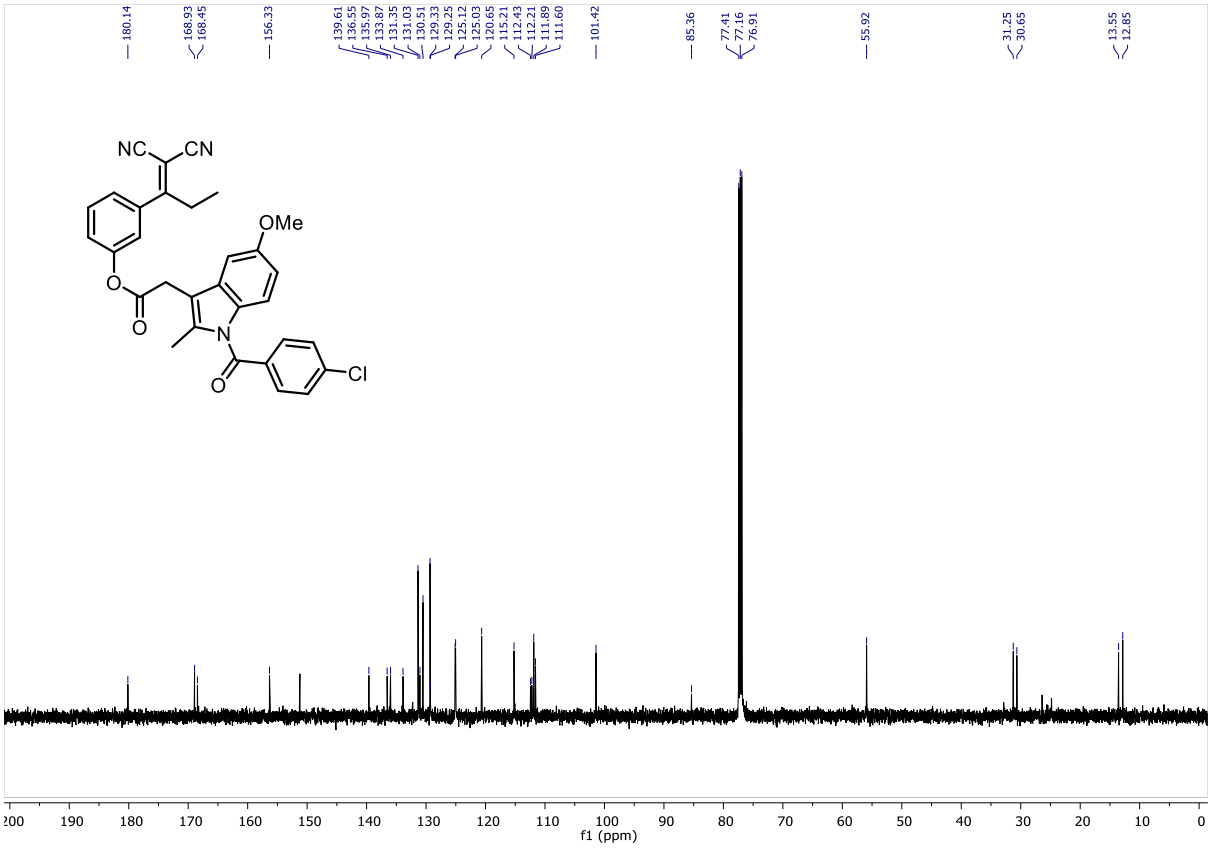
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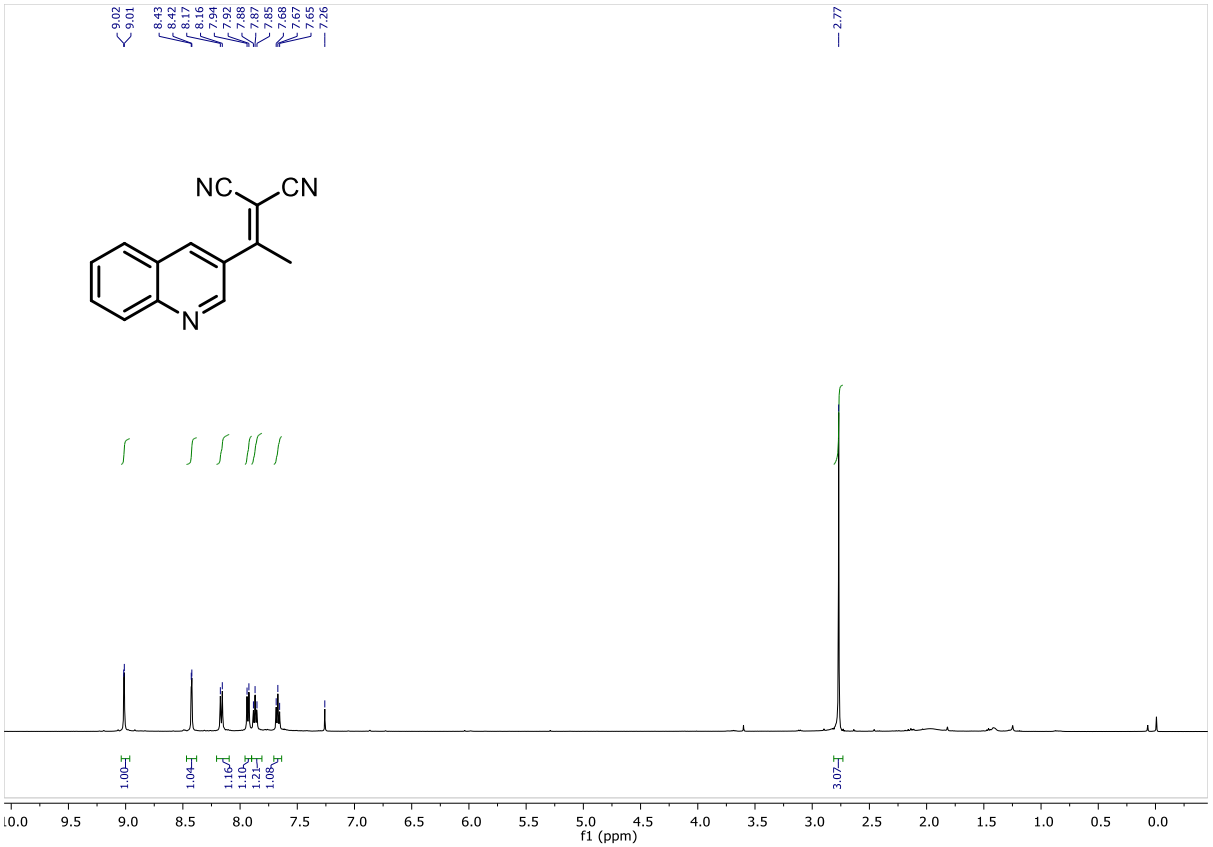
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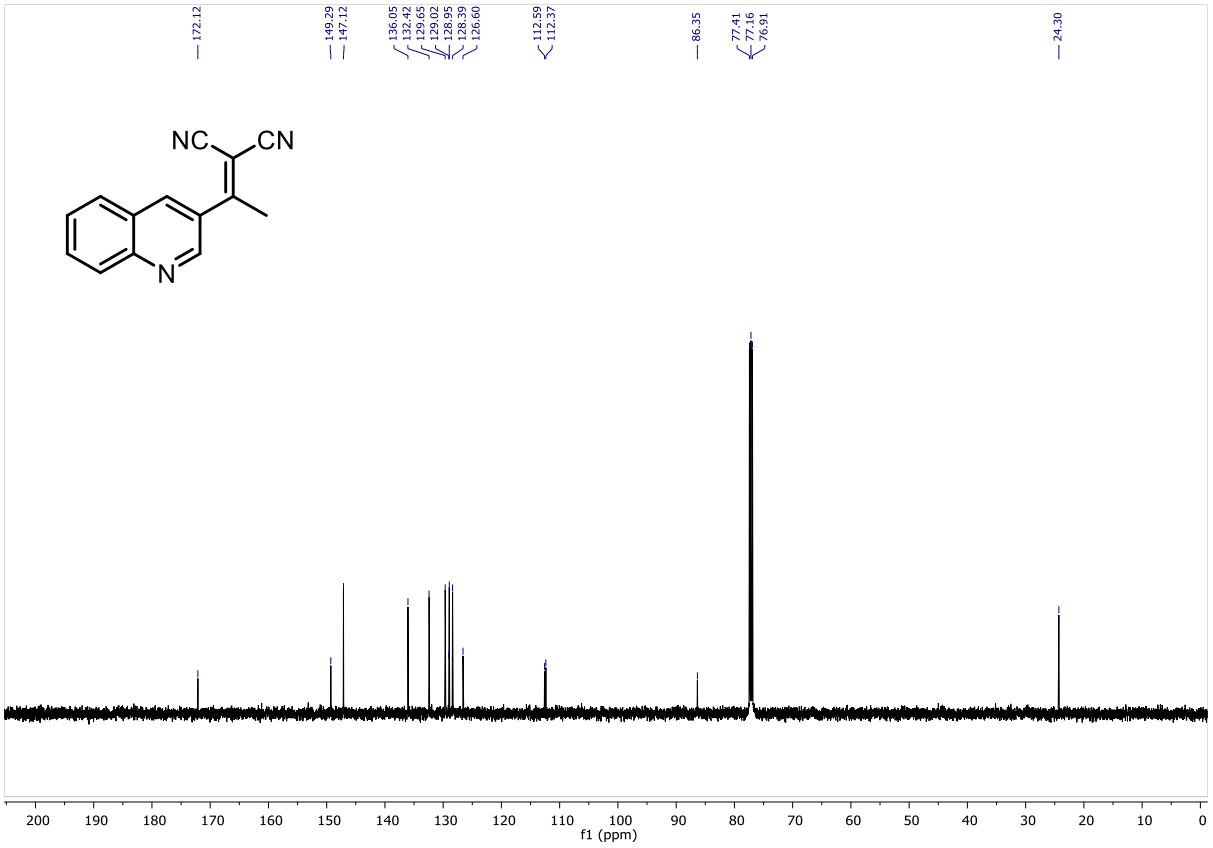
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76.91
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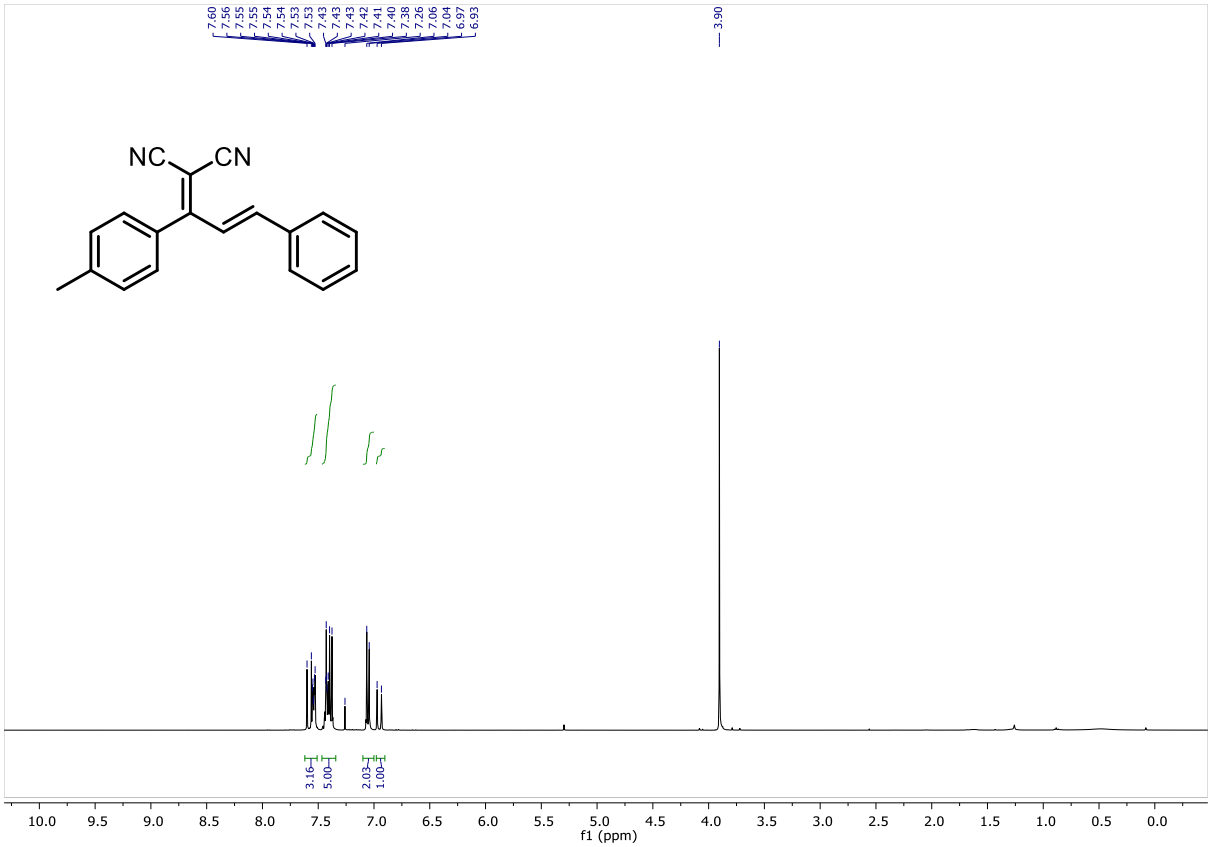
NC
CN
N
f1 (ppm)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7.54
7.53
7.53
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7.43
7.43
7.42
7.41
7.40
7.38
7.26
7.06
7.04
6.97
6.93
3.90
NC
CN
3.16
5.00
2.03
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
1.0
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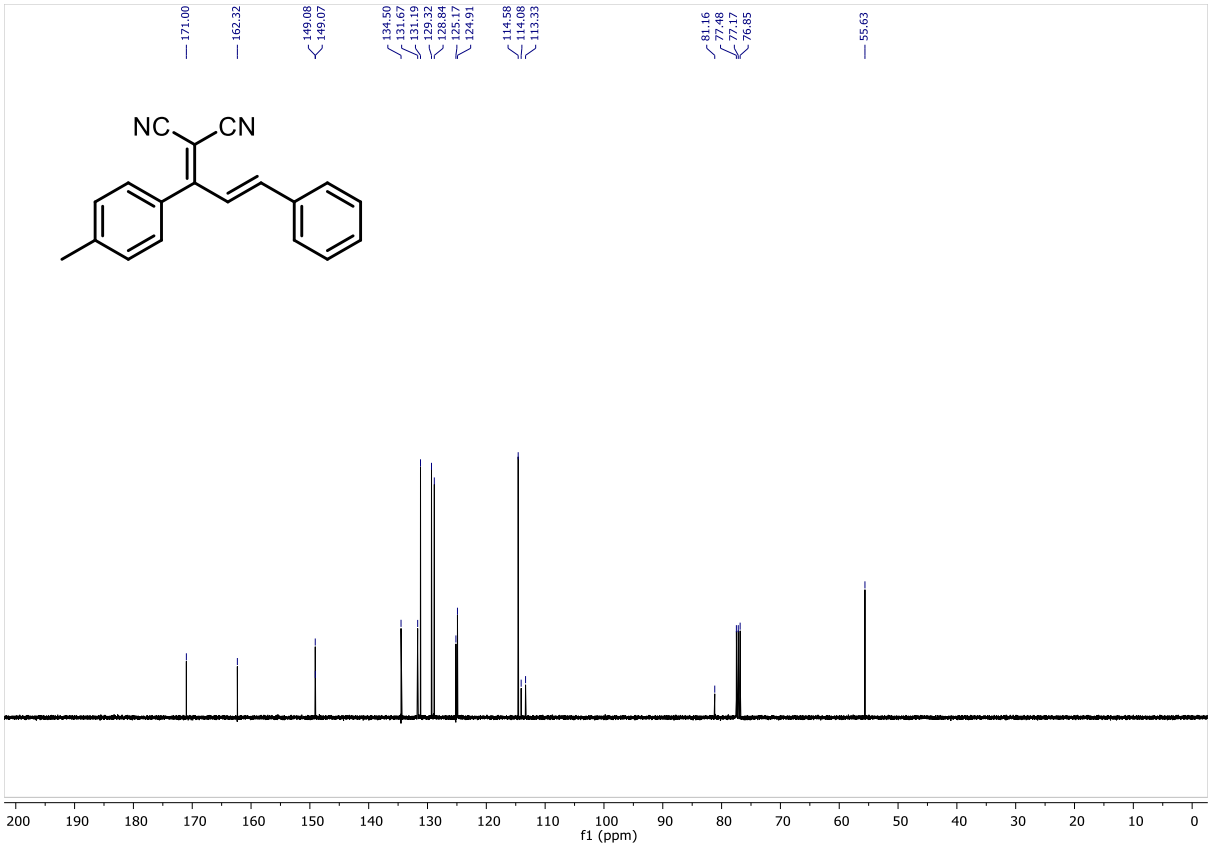
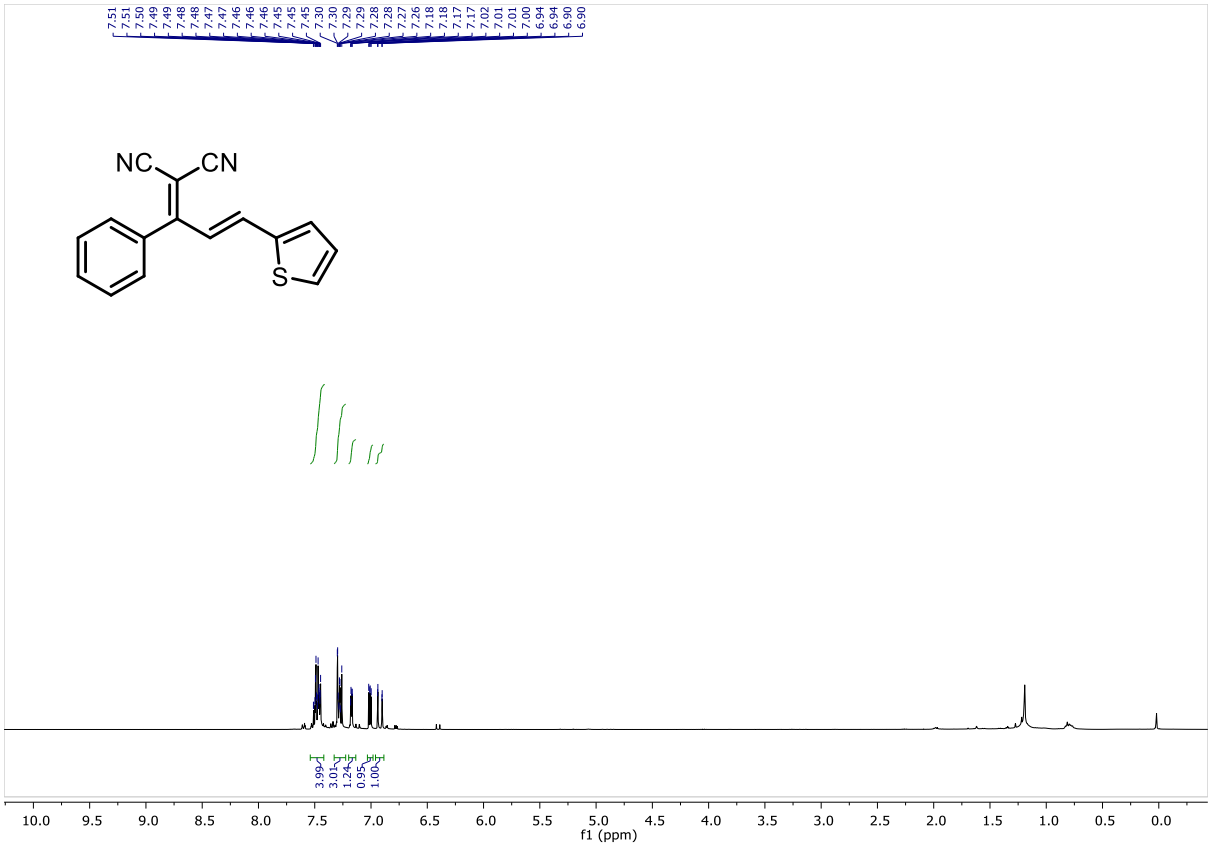
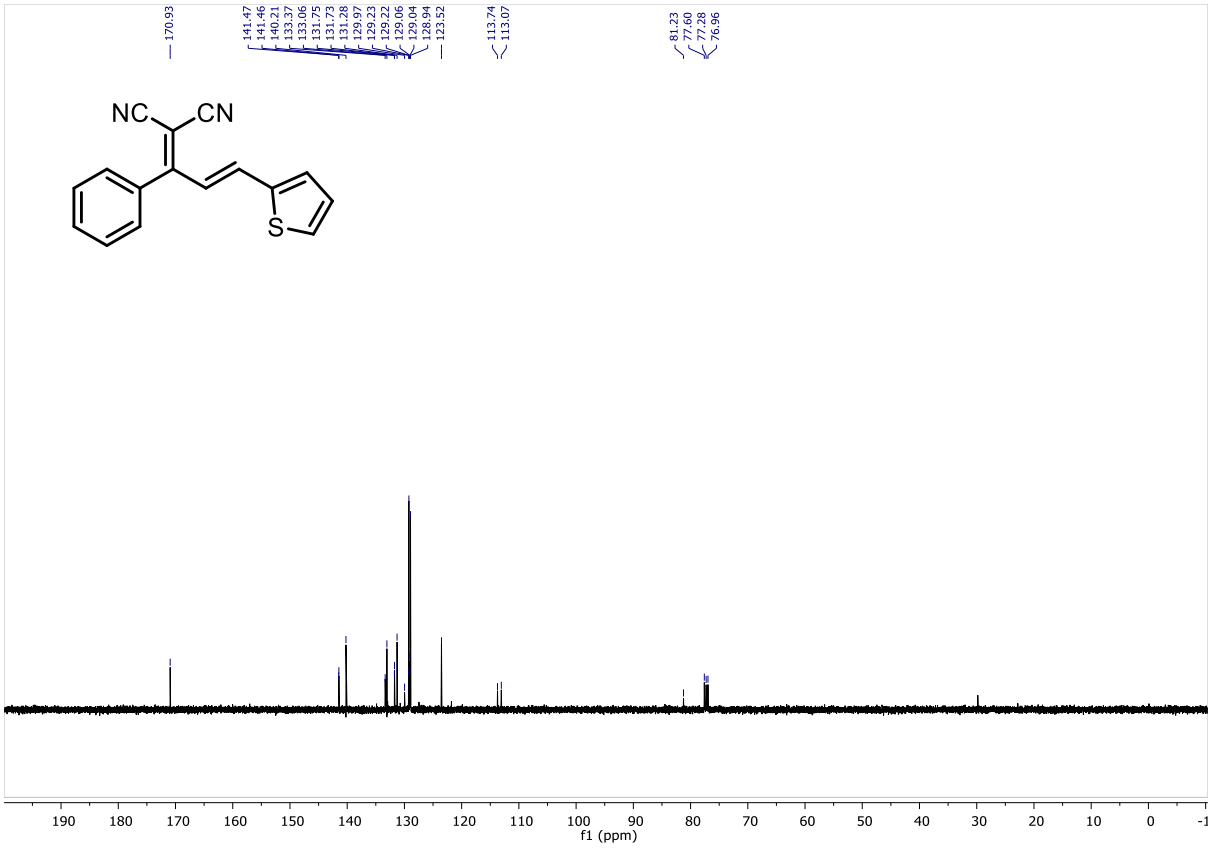
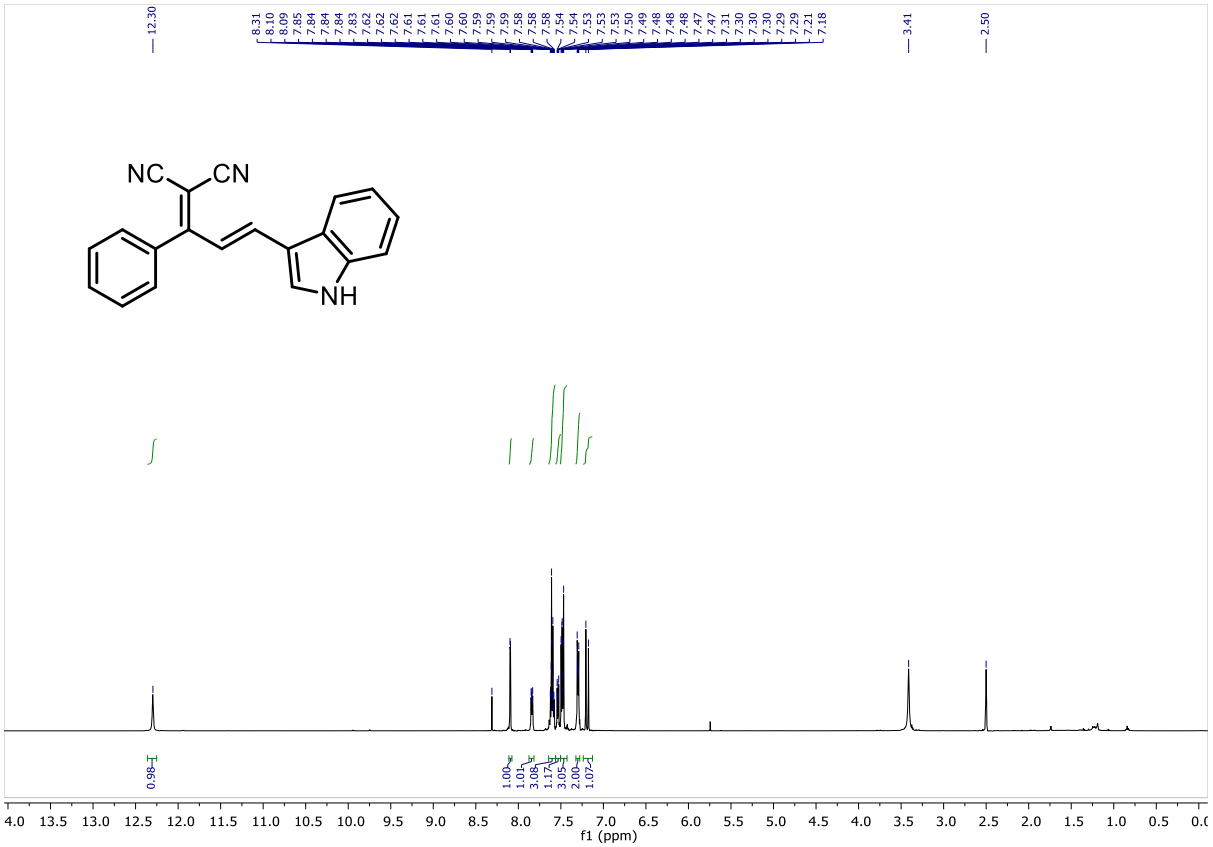
0.0
f1 (ppm)


171.00
162.32
149.08
149.07
134.50
131.67
131.19
129.32
128.84
125.17
124.91
114.58
114.08
113.33
81.16
77.48
77.17
76.85
55.63
NC
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NC
CN
S
f1 (ppm)


NC
CN
S
f1 (ppm)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8.31
8.10
8.09
7.85
7.84
7.84
7.84
7.83
7.62
7.62
7.62
7.61
7.61
7.61
7.60
7.60
7.59
7.59
7.59
7.58
7.58
7.58
7.54
7.54
7.53
7.53
7.53
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.31
7.30
7.30
7.30
7.29
7.29
7.21
7.18
3.41
2.50
NC
CN
NH
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1.00
1.01
3.08
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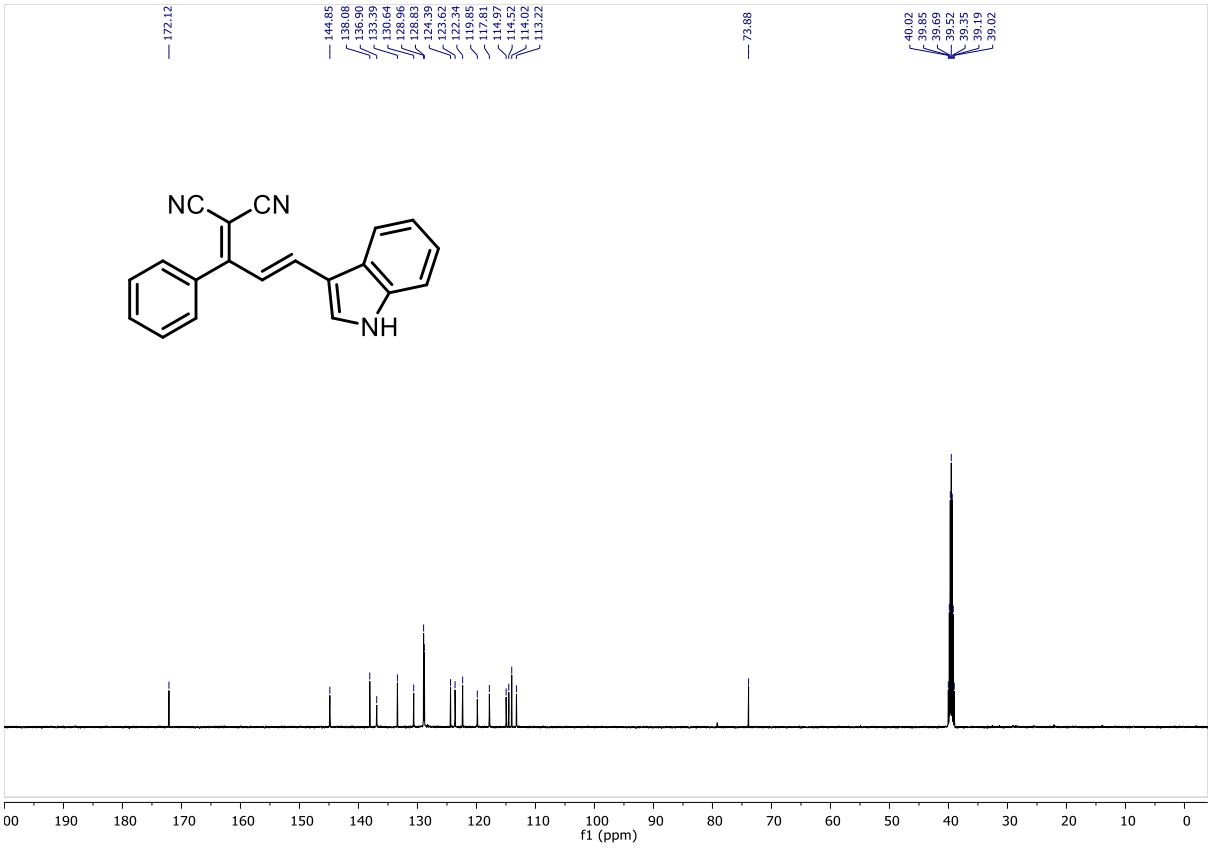
3.05
2.00
1.07
f1 (ppm)


172.12
144.85
138.08
136.90
133.39
130.64
128.96
128.83
124.39
123.62
122.24
119.85
117.81
114.97
114.52
114.02
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40.02
39.85
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39.52
39.35
39.19
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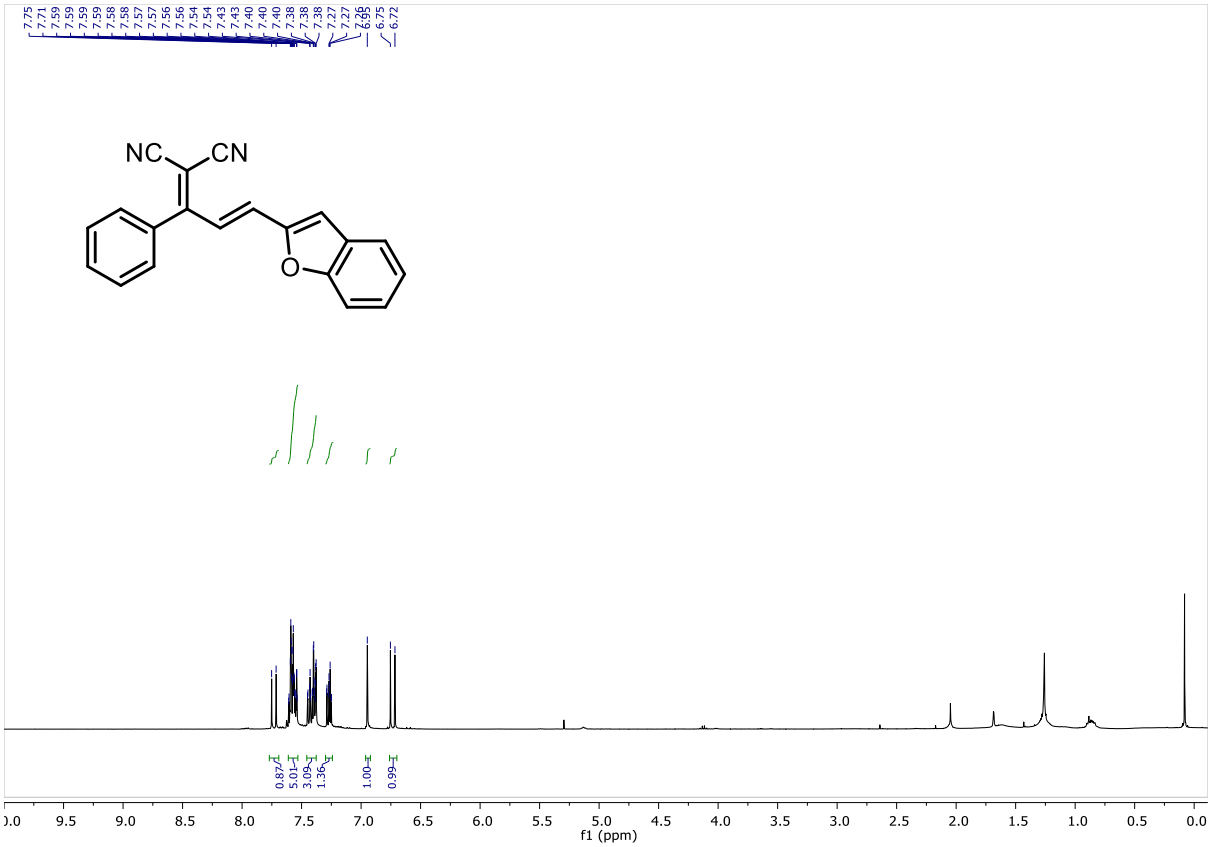
NC
CN
NH
f1 (ppm)


7.75
7.71
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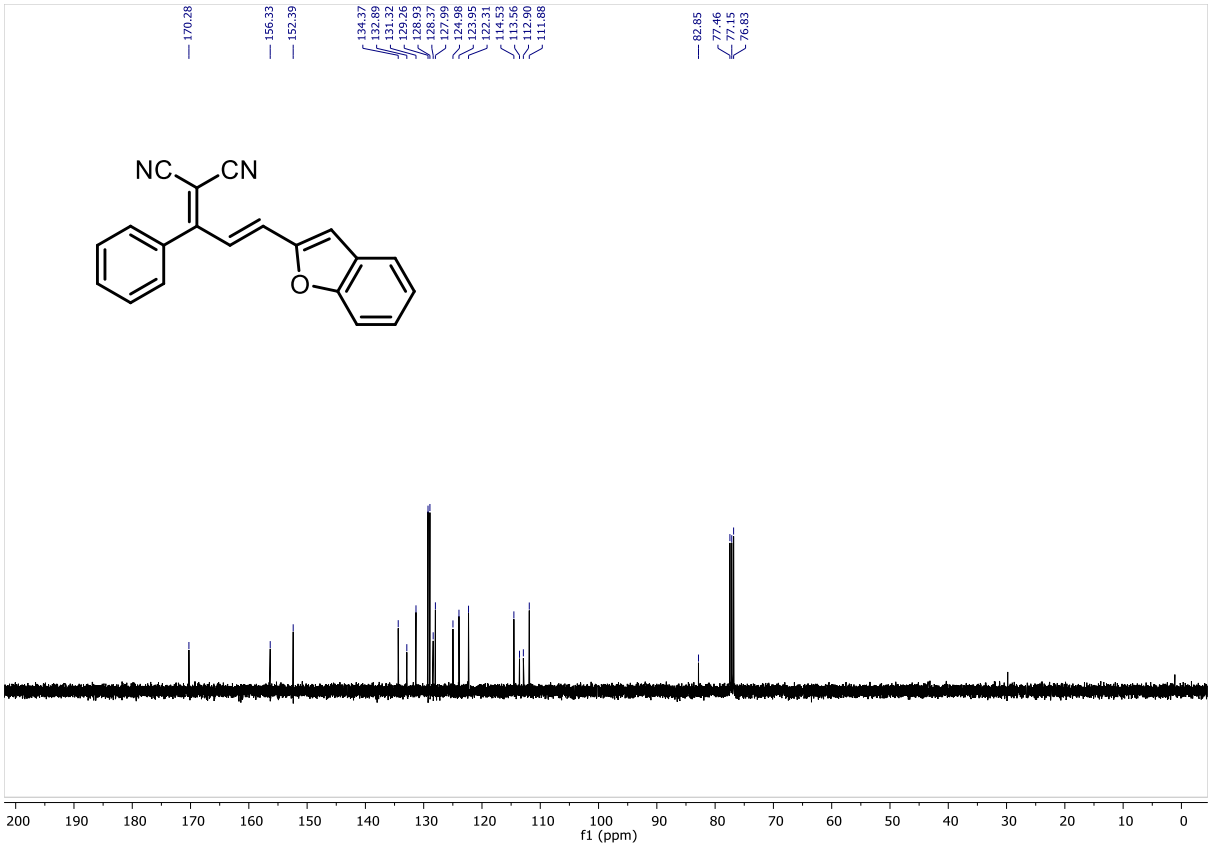
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.54
7.54
7.43
7.43
7.40
7.40
7.40
7.38
7.38
7.27
7.27
6.75
6.72
NC
CN
O
0.87
5.01
3.09
1.36
1.00
0.99
f1 (ppm)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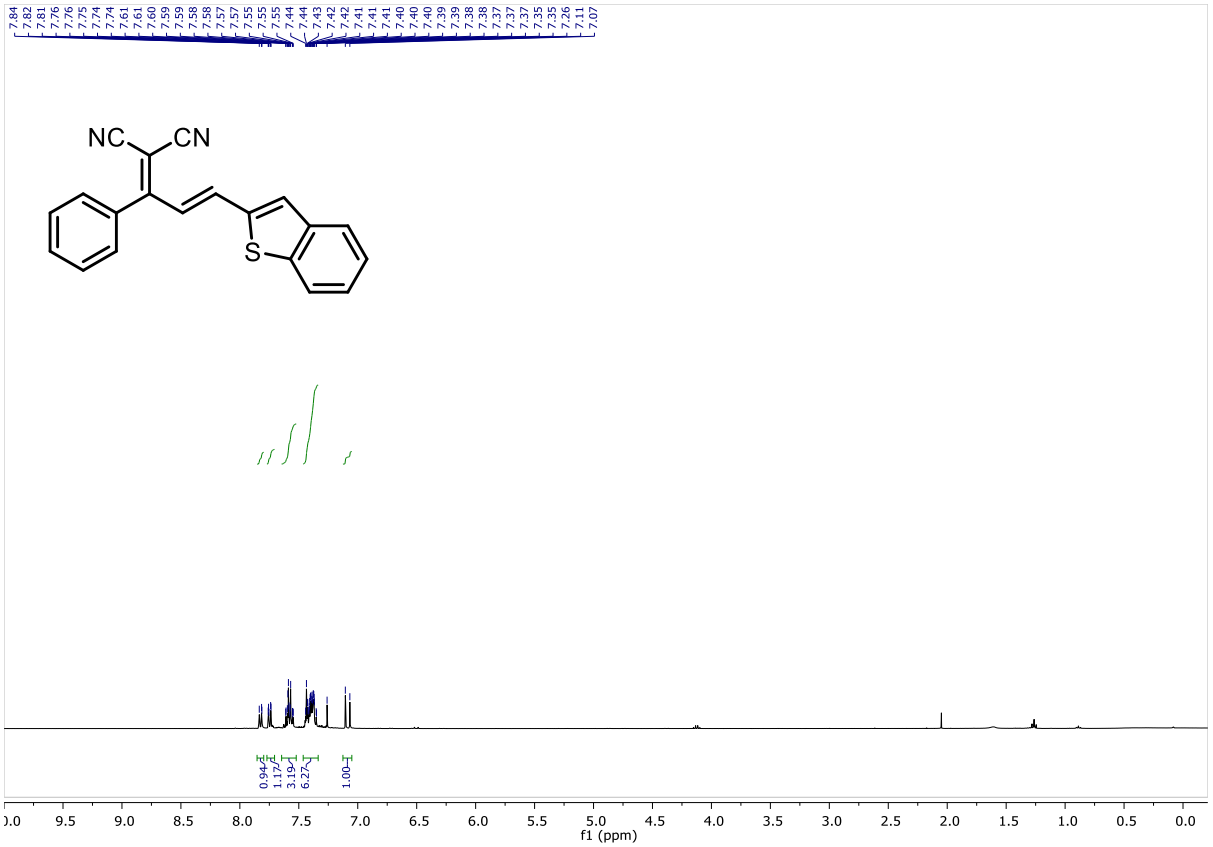
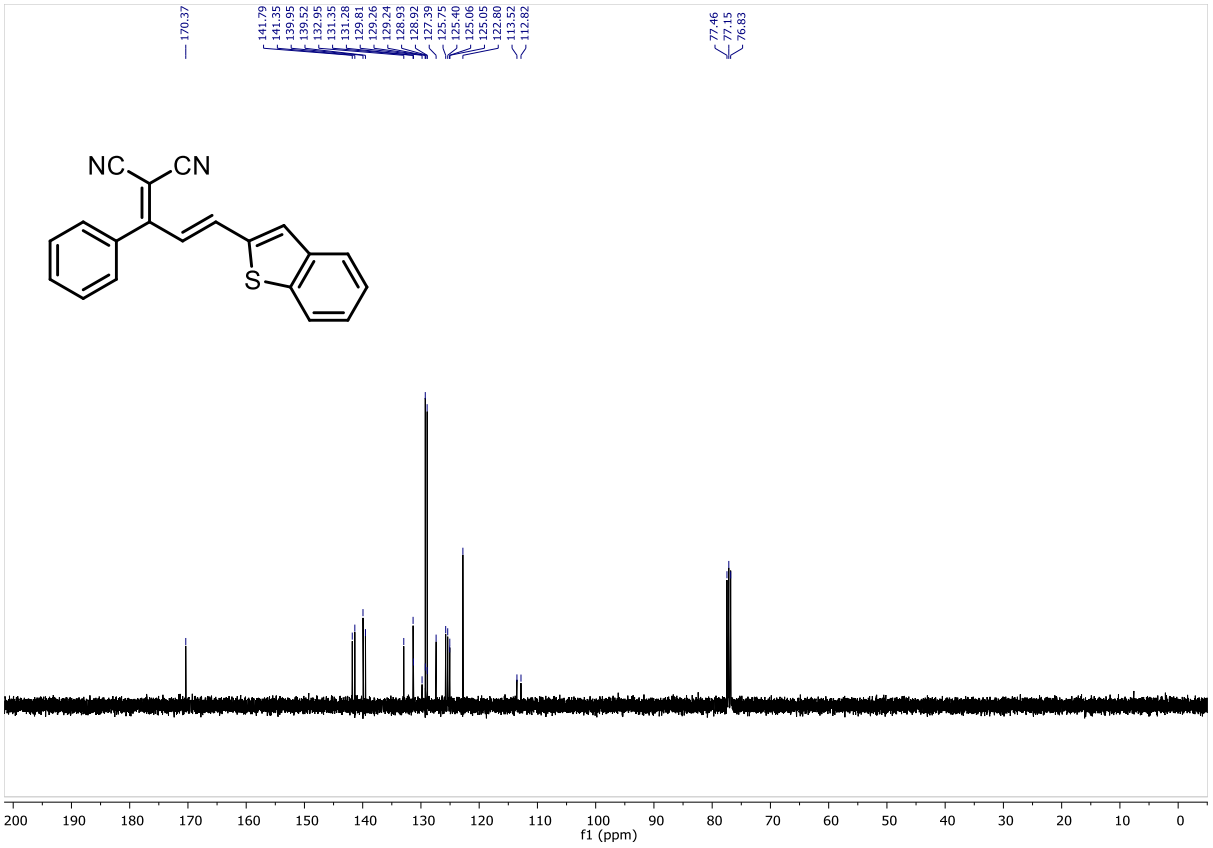
156.33
152.39
134.37
132.89
131.32
129.26
128.93
128.37
127.99
124.98
123.95
122.31
114.53
113.56
112.90
111.88
82.85
77.46
77.15
76.83
NC
CN
O
f1 (ppm)


7.84
7.82
7.81
7.76
7.76
7.75
7.74
7.74
7.61
7.61
7.60
7.59
7.59
7.58
7.58
7.57
7.57
7.55
7.55
7.44
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.35
7.26
7.11
7.07
NC
CN
S
0.94
1.12
3.19
6.27
1.00
f1 (ppm)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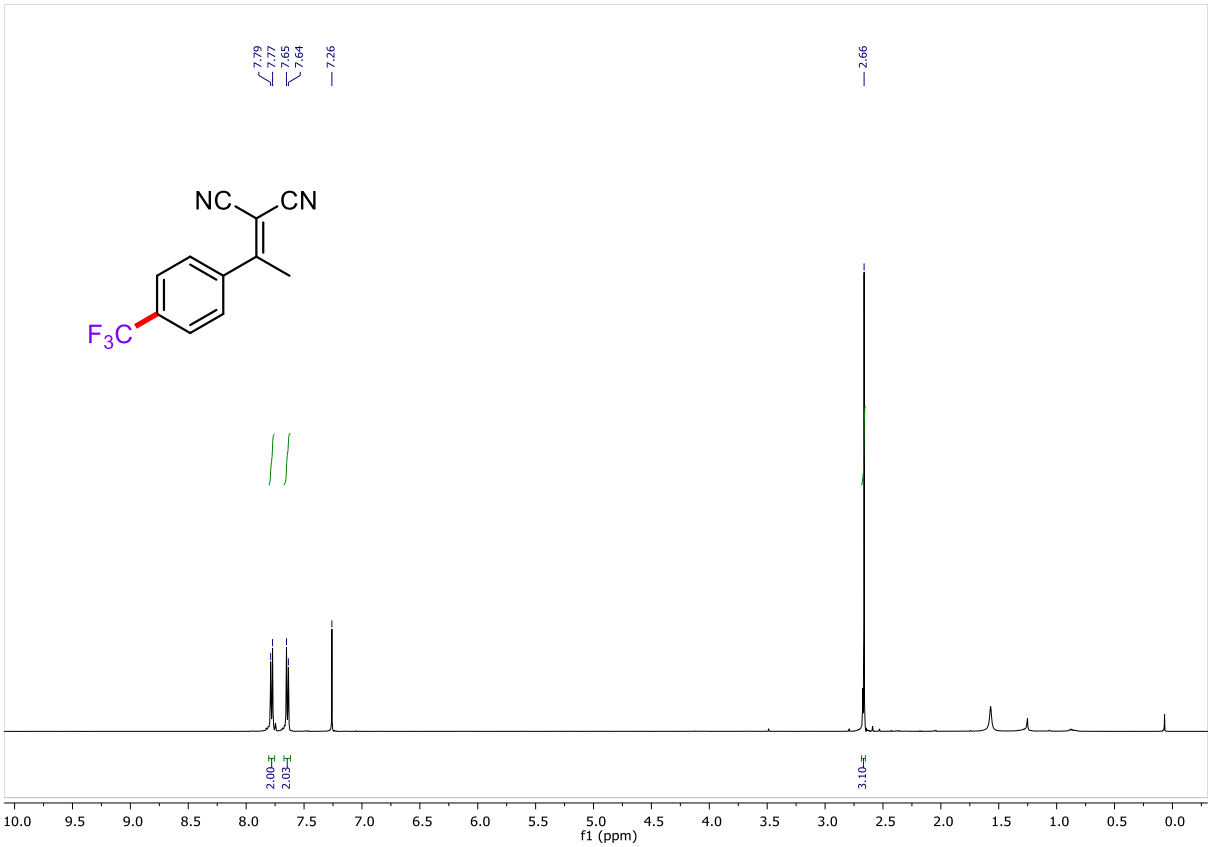
141.79
141.35
139.95
139.52
132.95
131.35
131.28
129.81
129.26
129.24
128.93
128.92
127.39
125.75
125.40
125.06
125.05
122.80
113.52
112.82
77.46
77.15
76.83
NC
CN
S
f1 (ppm)


7.79
7.77
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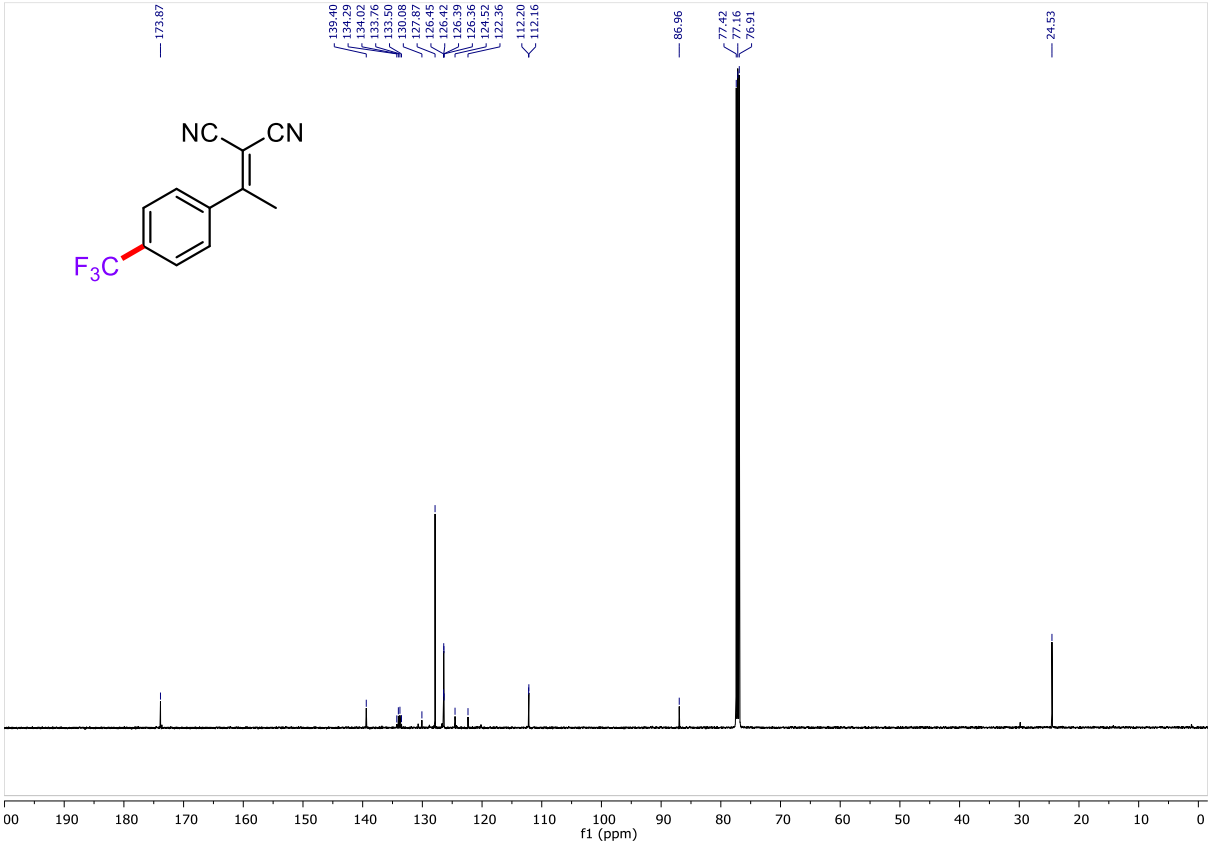
7.64
7.26
2.66
NC
CN
F3C
2.00
2.03
3.10
f1 (ppm)


173.87
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133.50
130.08
127.87
126.45
126.42
126.39
126.36
124.52
122.36
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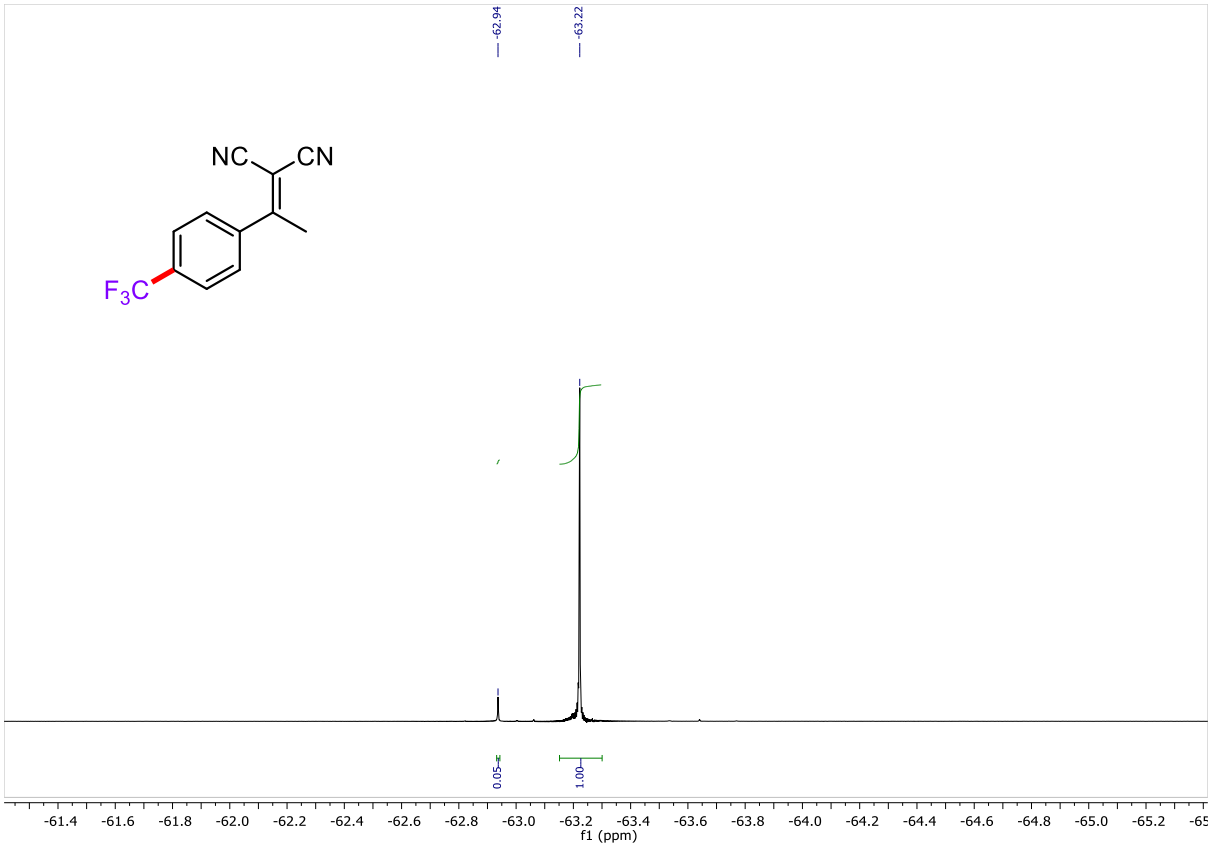
112.16
86.96
77.42
77.16
76.91
24.53
NC
CN
F3C
f1 (ppm)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NC
CN
F3C
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1.00
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-61.6
-61.8
-62.0
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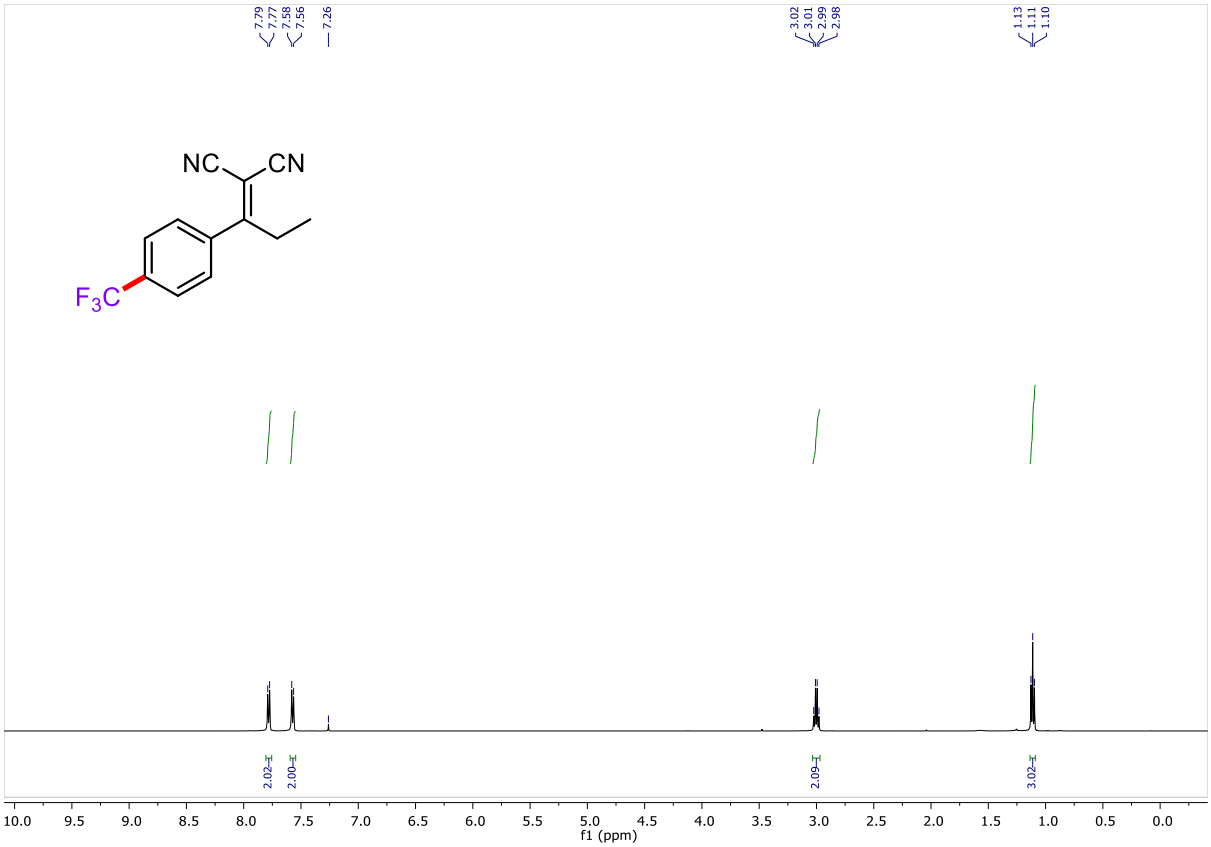
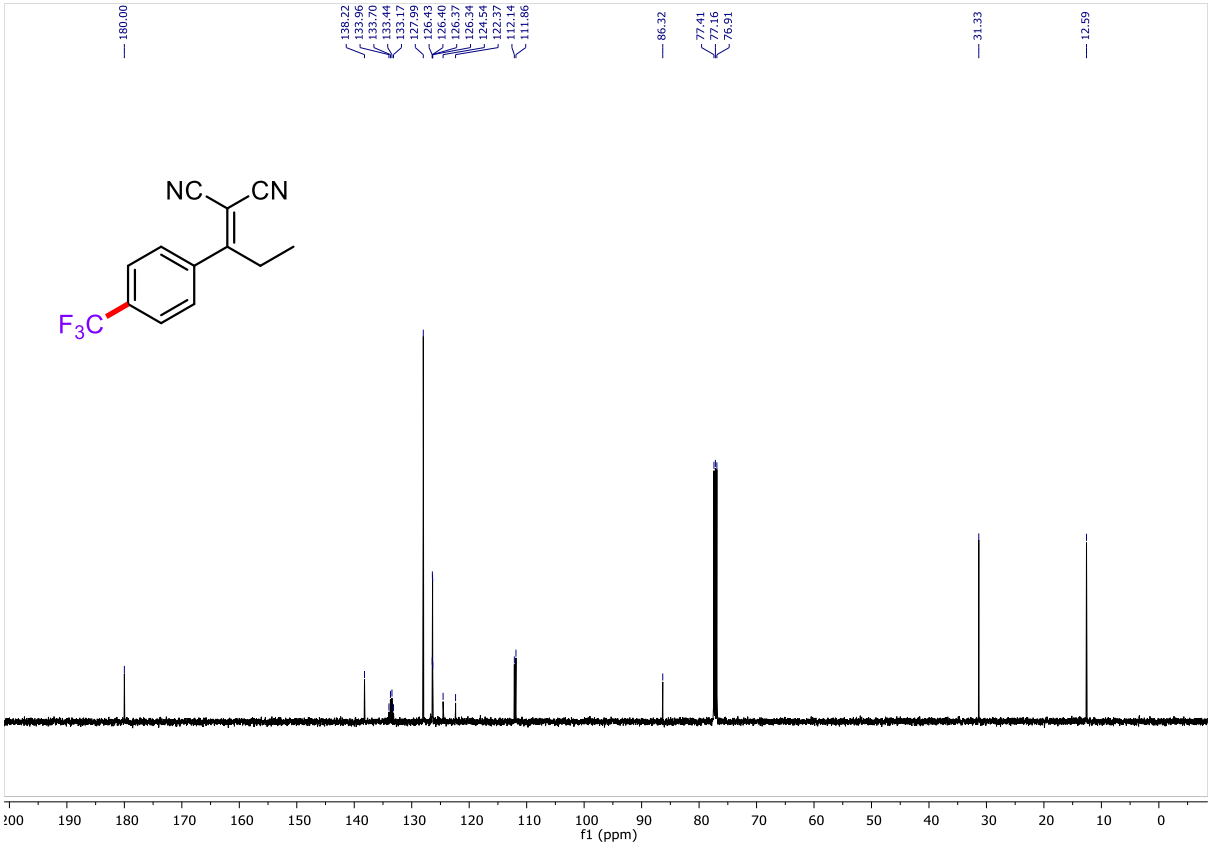
-62.4
-62.6
-62.8
-63.0
-63.2
-63.4
-63.6
-63.8
-64.0
-64.2
-64.4
-64.6
-64.8
-65.0
-65.2
f1 (ppm)


7.79
7.77
7.58
7.56
7.26
3.02
3.01
2.99
2.98
1.13
1.11
1.10
NC
CN
F3C
2.02
2.00
2.09
3.02
f1 (ppm)


180.00
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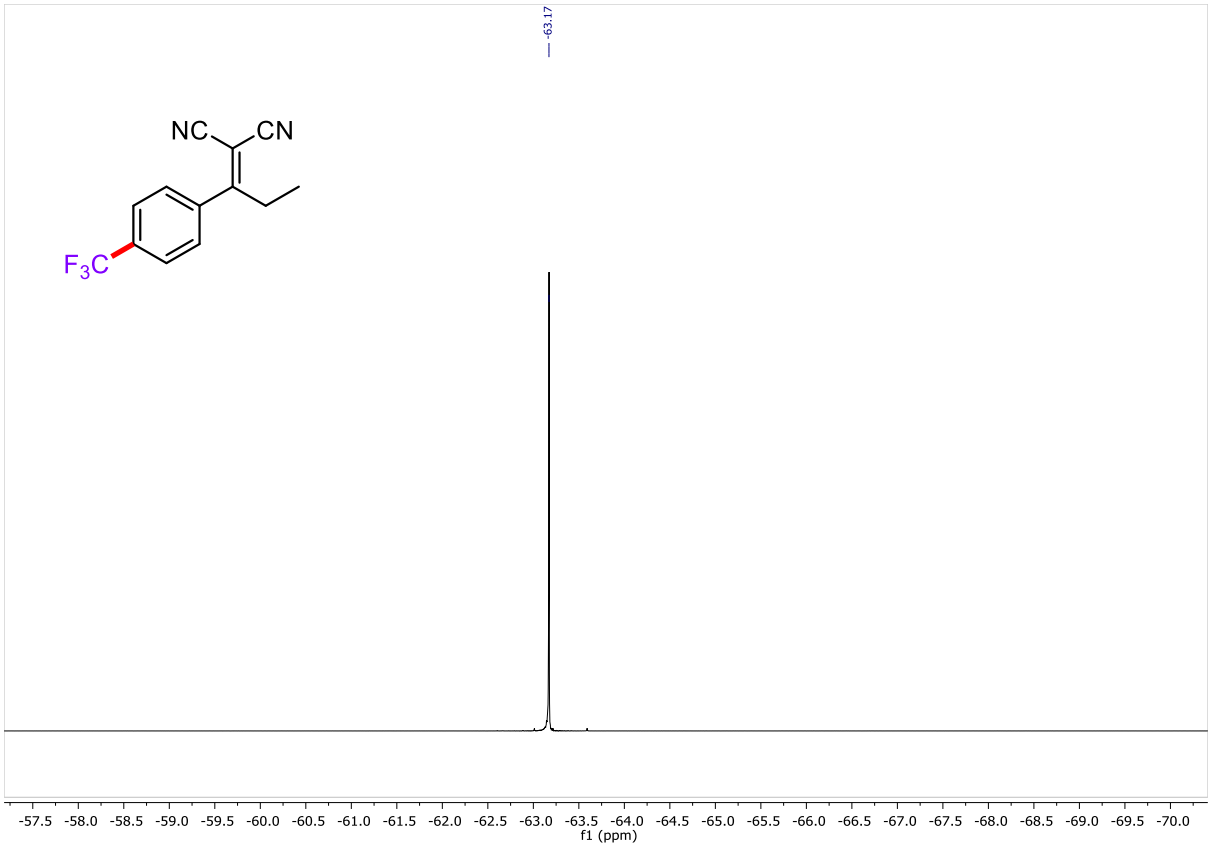
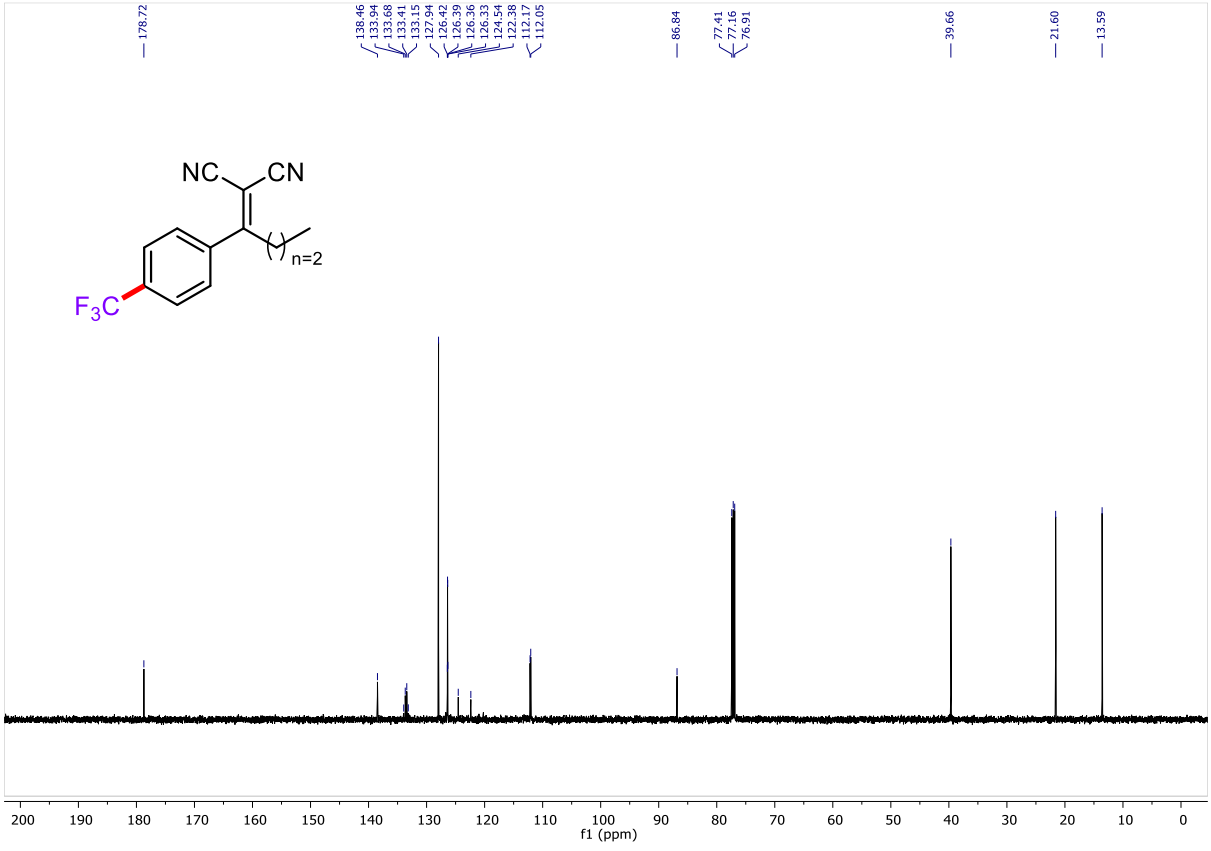
133.44
133.17
132.99
126.43
126.40
126.37
126.34
124.54
122.37
112.14
111.86
86.32
77.41
77.16
76.91
31.33
12.59
NC
CN
F3C
f1 (ppm)


-63.17
NC
CN
F3C
-57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0
f1 (ppm)


7.78
7.77
7.58
7.56
2.98
2.96
2.96
2.96
2.95
1.50
1.48
1.47
1.45
0.98
0.97
0.95
NC
CN
n=2
F3C
2.00
2.02
2.07
2.10
3.10
f1 (ppm)


178.72
138.46
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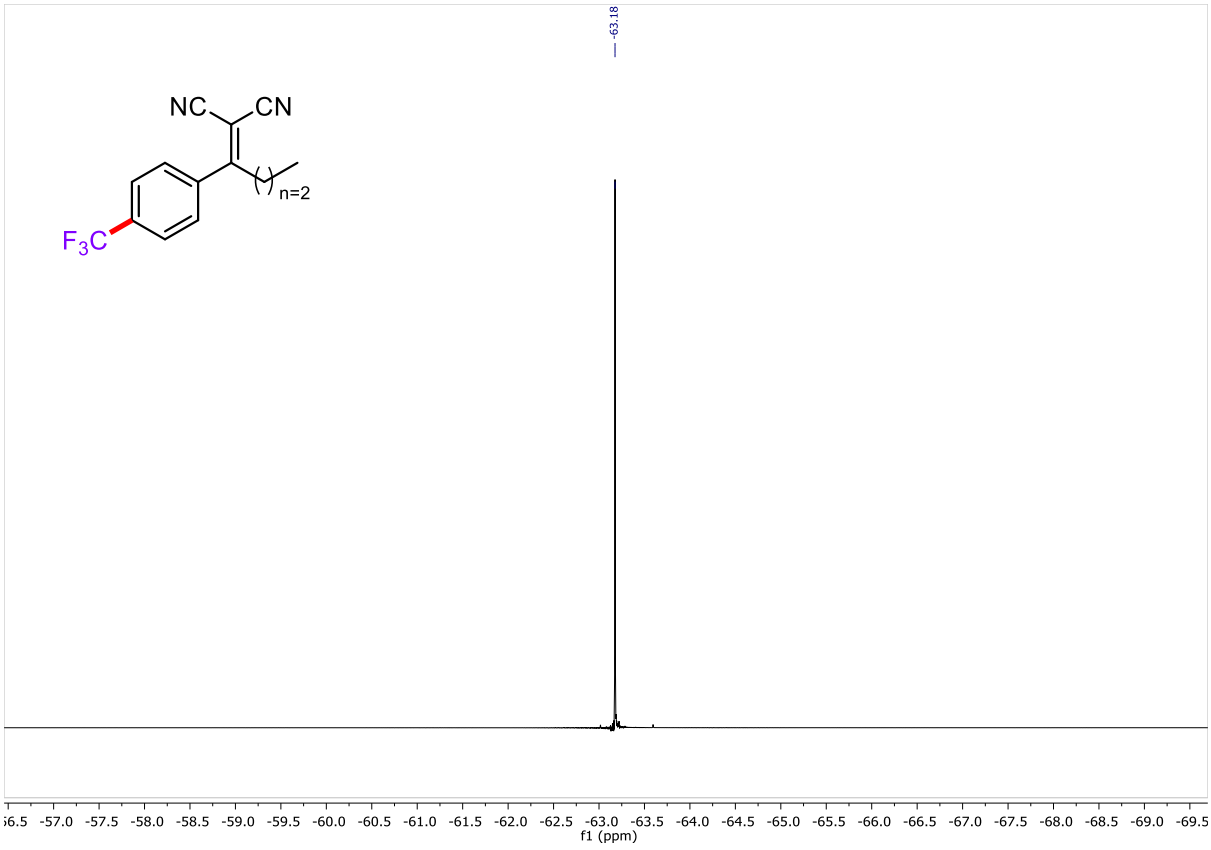
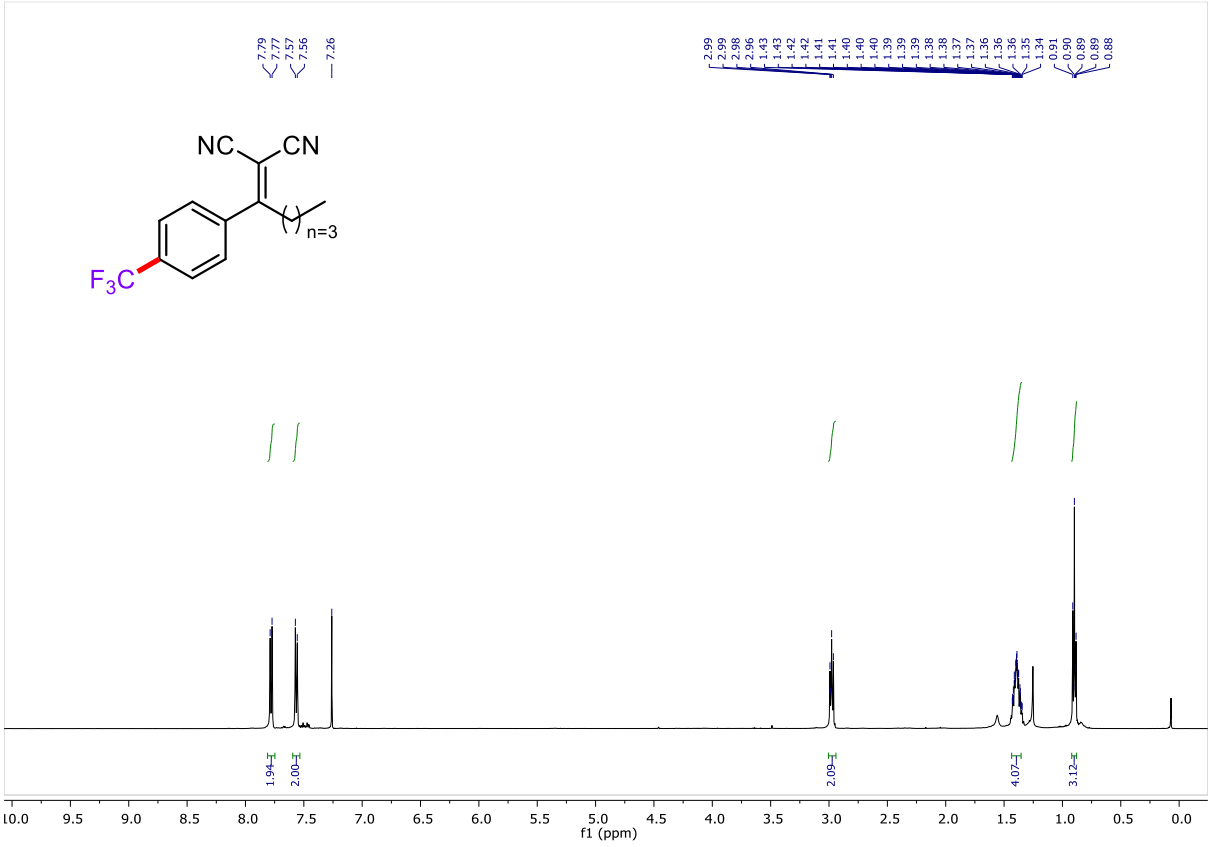
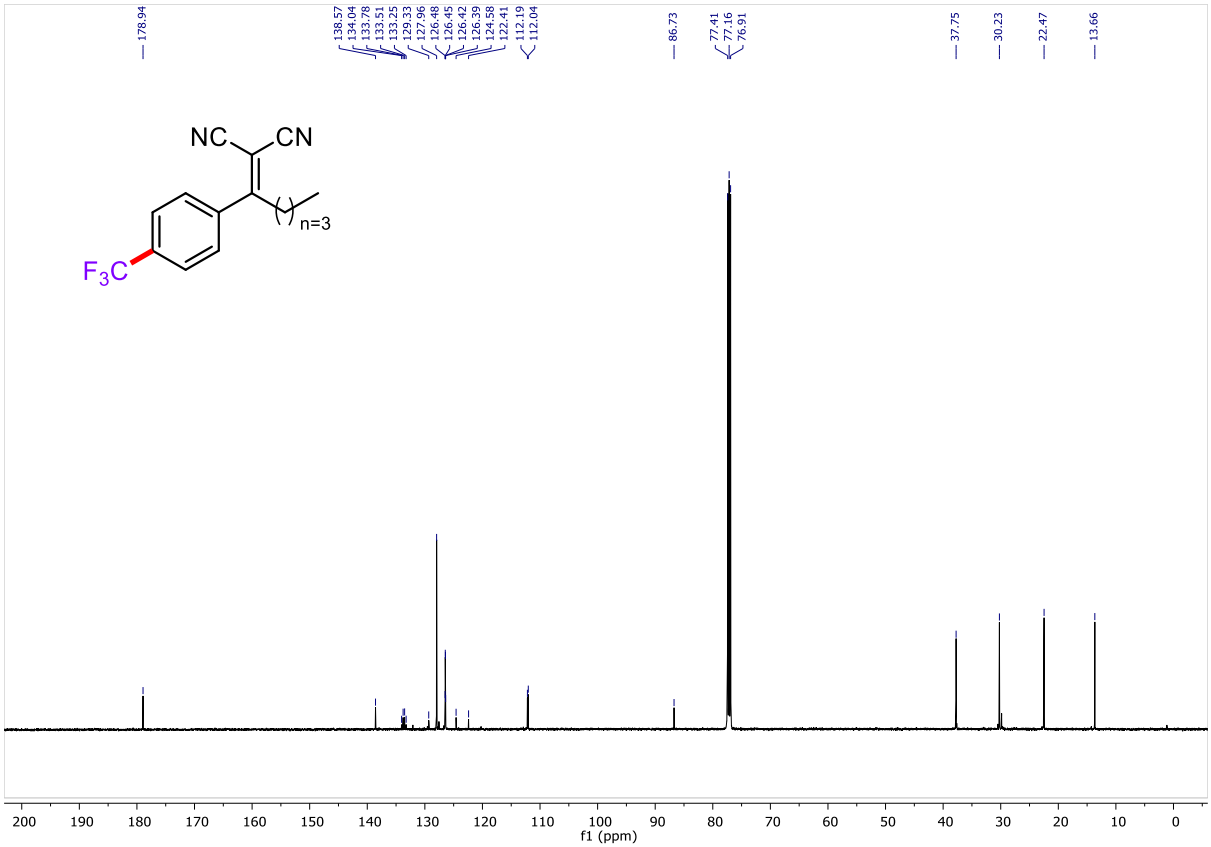
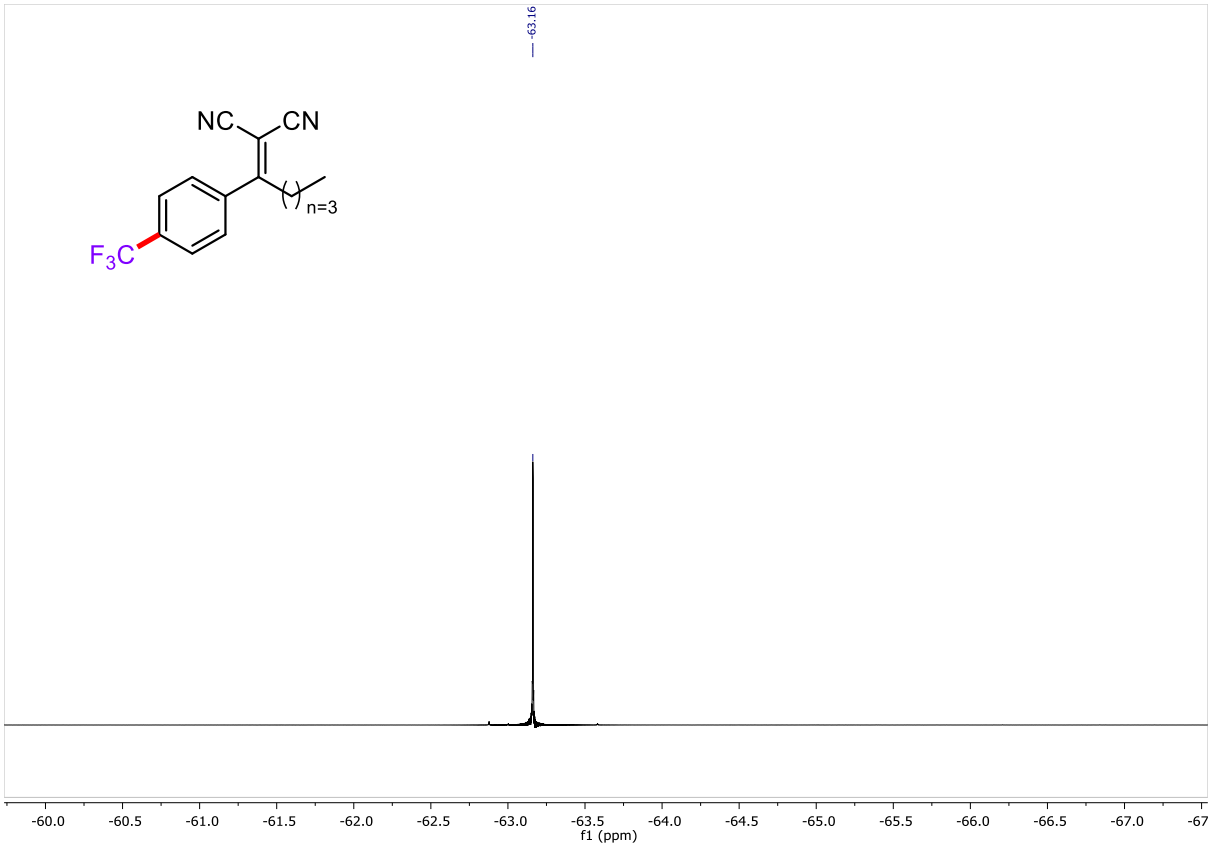
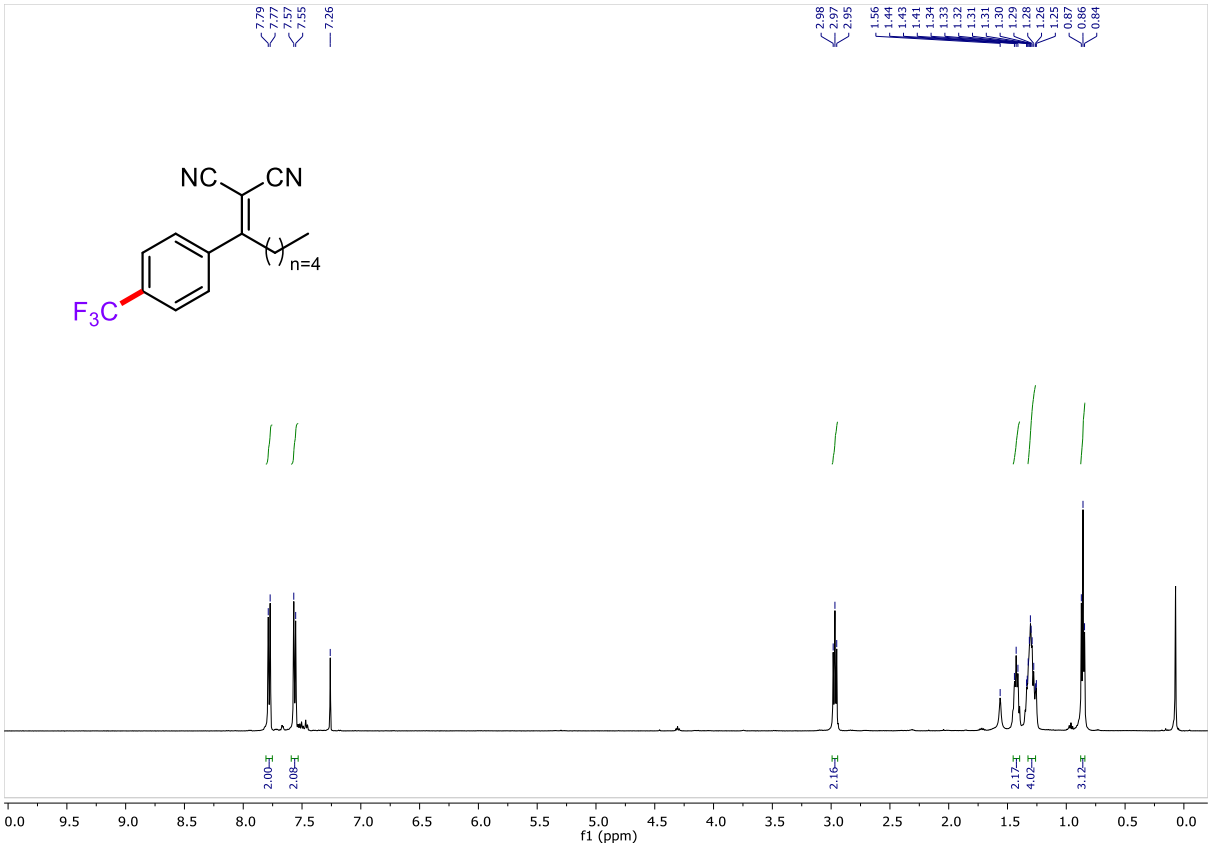
133.68
133.41
133.15
127.94
126.42
126.39
126.36
126.33
124.54
122.38
112.17
112.05
86.84
77.41
77.16
76.91
39.66
21.60
13.59
NC
CN
n=2
F3C
f1 (ppm)

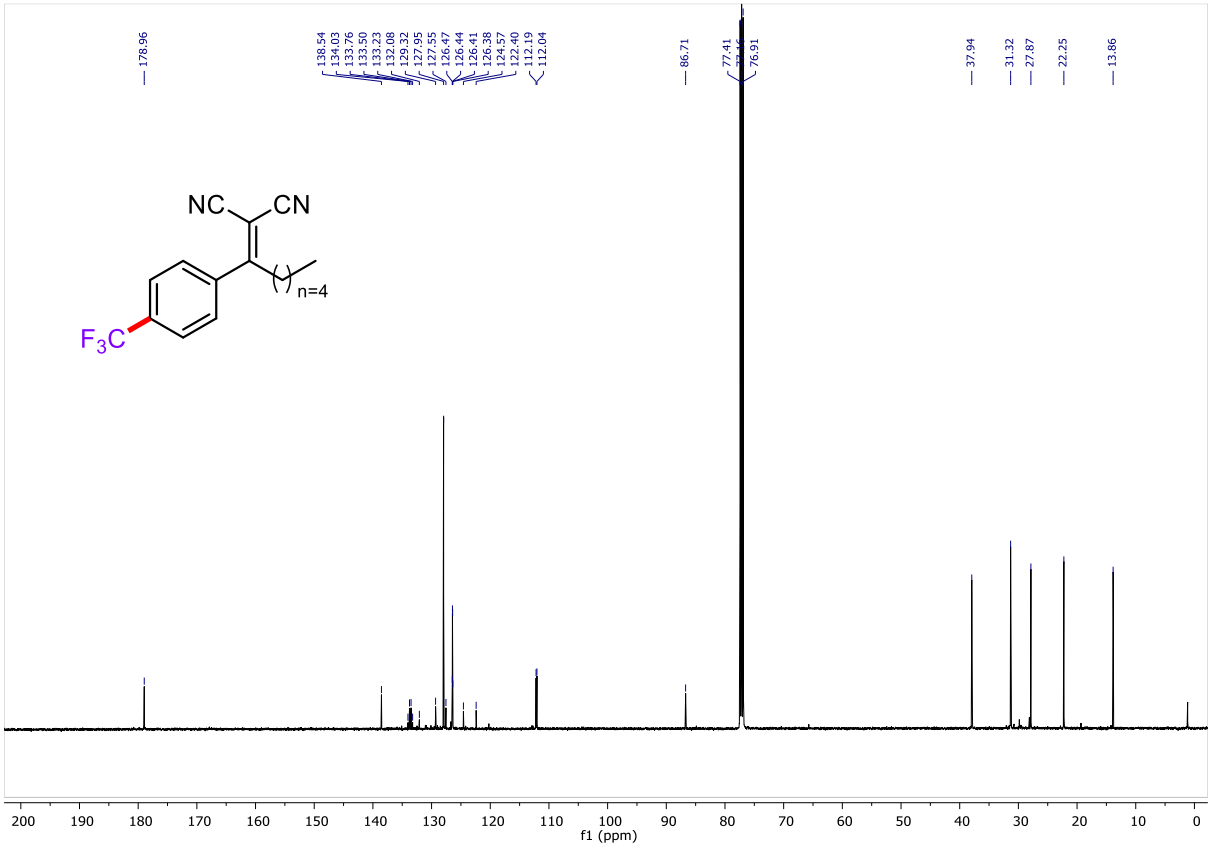

-63.18
NC
CN
n=2
F3C
-56.5 -57.0 -57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5
f1 (ppm)


7.79
7.77
7.57
7.56
7.26
2.99
2.99
2.98
2.96
2.43
1.43
1.42
1.42
1.41
1.41
1.40
1.40
1.40
1.39
1.39
1.39
1.38
1.38
1.37
1.37
1.36
1.36
1.36
1.35
1.34
0.91
0.90
0.89
0.89
0.88
NC
CN
n=3
F3C
1.94
2.00
2.09
4.07
3.12
f1 (ppm)


178.94
138.57
134.04
133.78
133.51
133.25
129.33
127.96
126.48
126.45
126.42
126.39
124.58
122.41
112.19
112.04
86.73
77.41
77.16
76.91
37.75
30.23
22.47
13.66
NC
CN
n=3
F3C
f1 (ppm)


-63.16
NC
CN
n=3
F3C
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67
f1 (ppm)


7.79
7.77
7.57
7.55
7.26
2.98
2.97
2.95
1.56
1.44
1.43
1.41
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.26
1.25
0.87
0.86
0.84
NC
CN
n=4
F3C
2.00
2.08
2.16
2.17
4.02
3.12
f1 (ppm)


178.96
138.54
134.03
133.76
133.50
133.23
132.08
129.32
127.95
127.55
126.47
126.44
126.41
126.38
124.57
122.40
112.19
112.04
86.71
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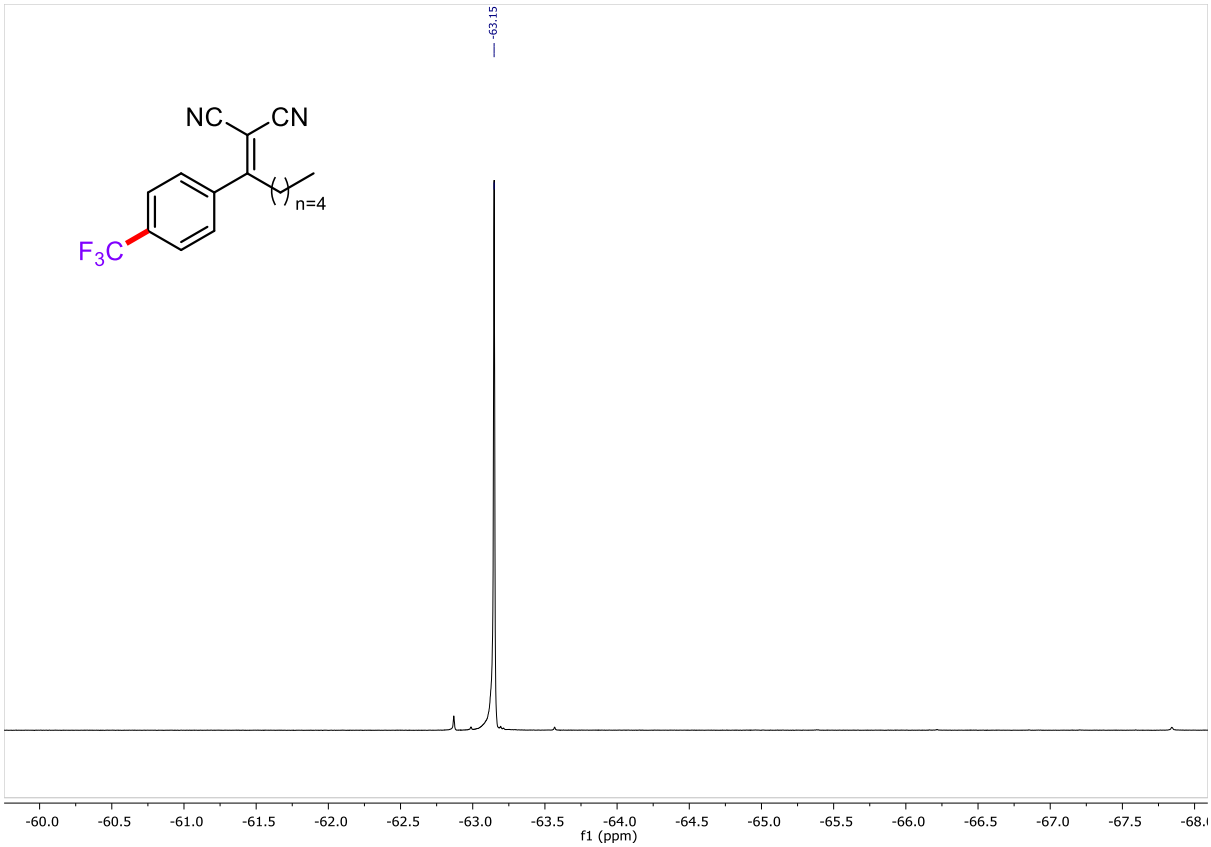
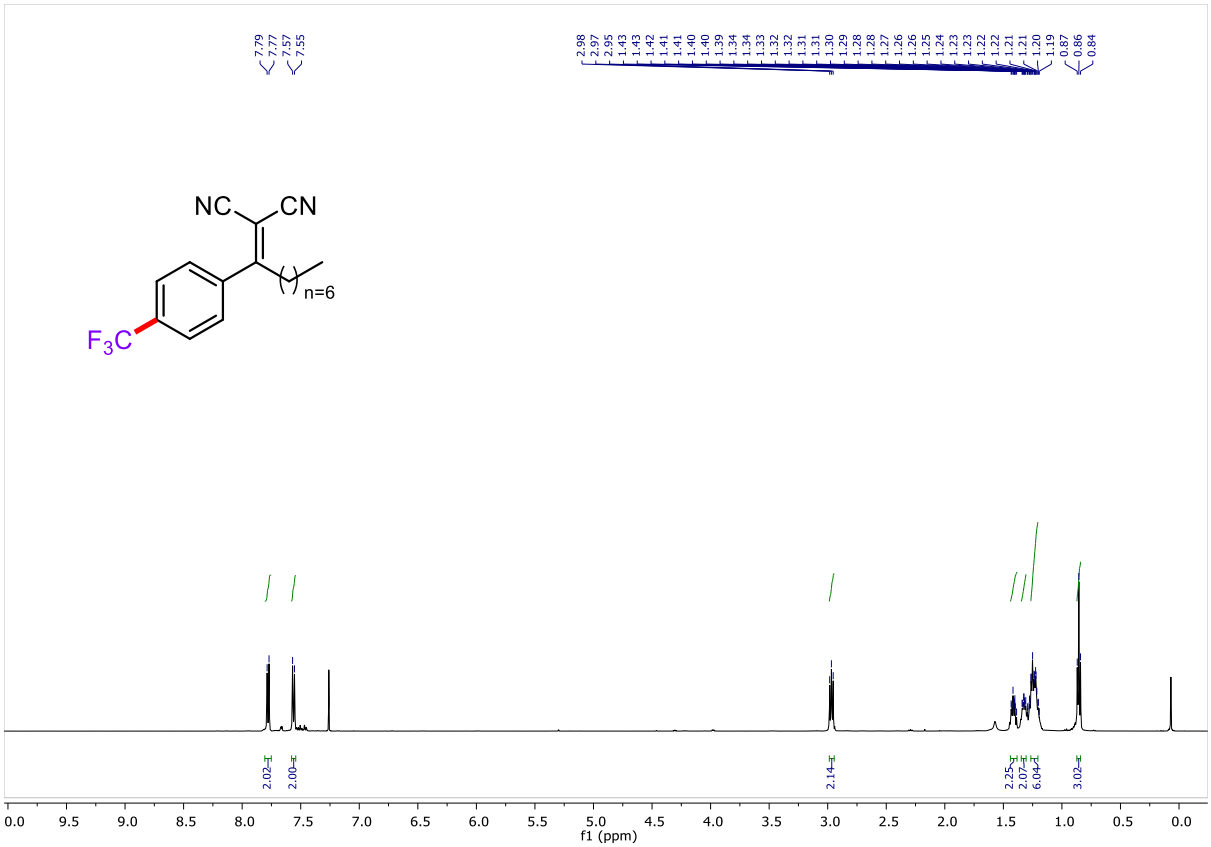
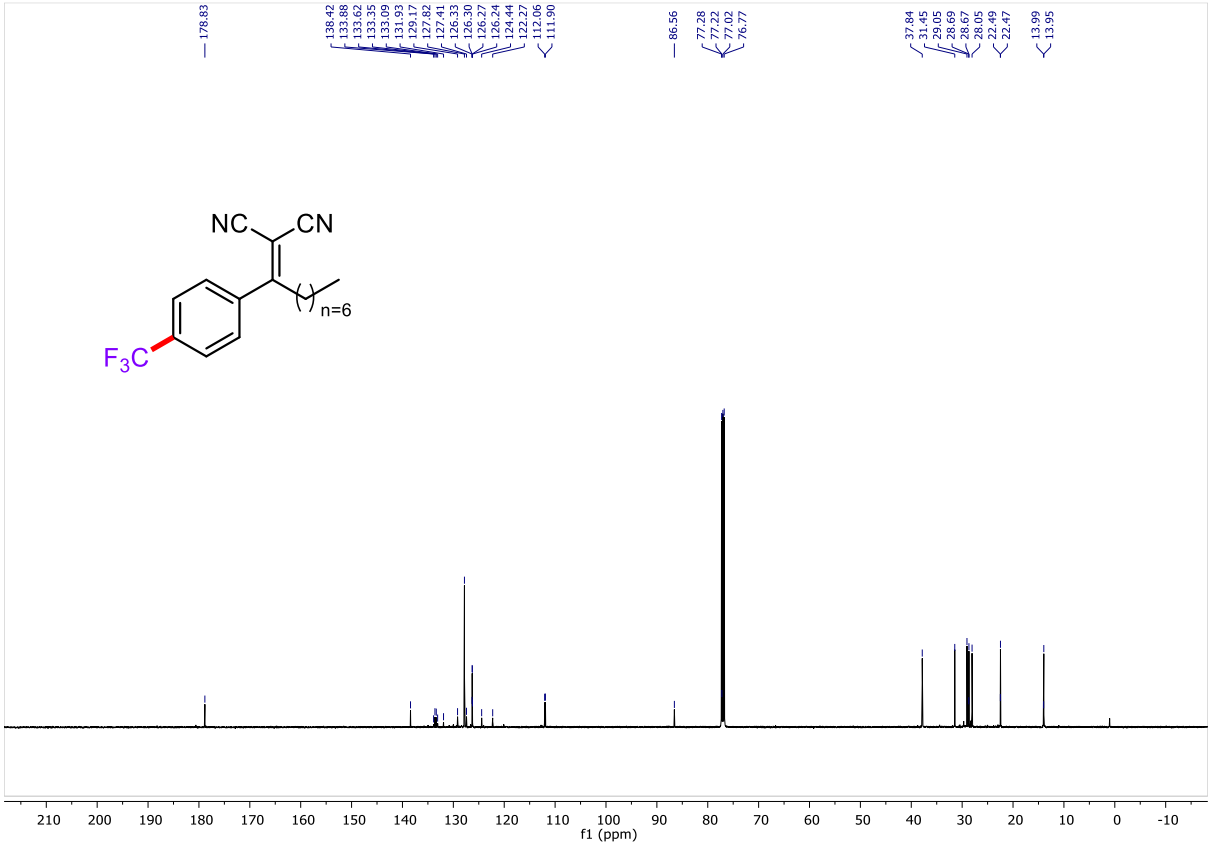
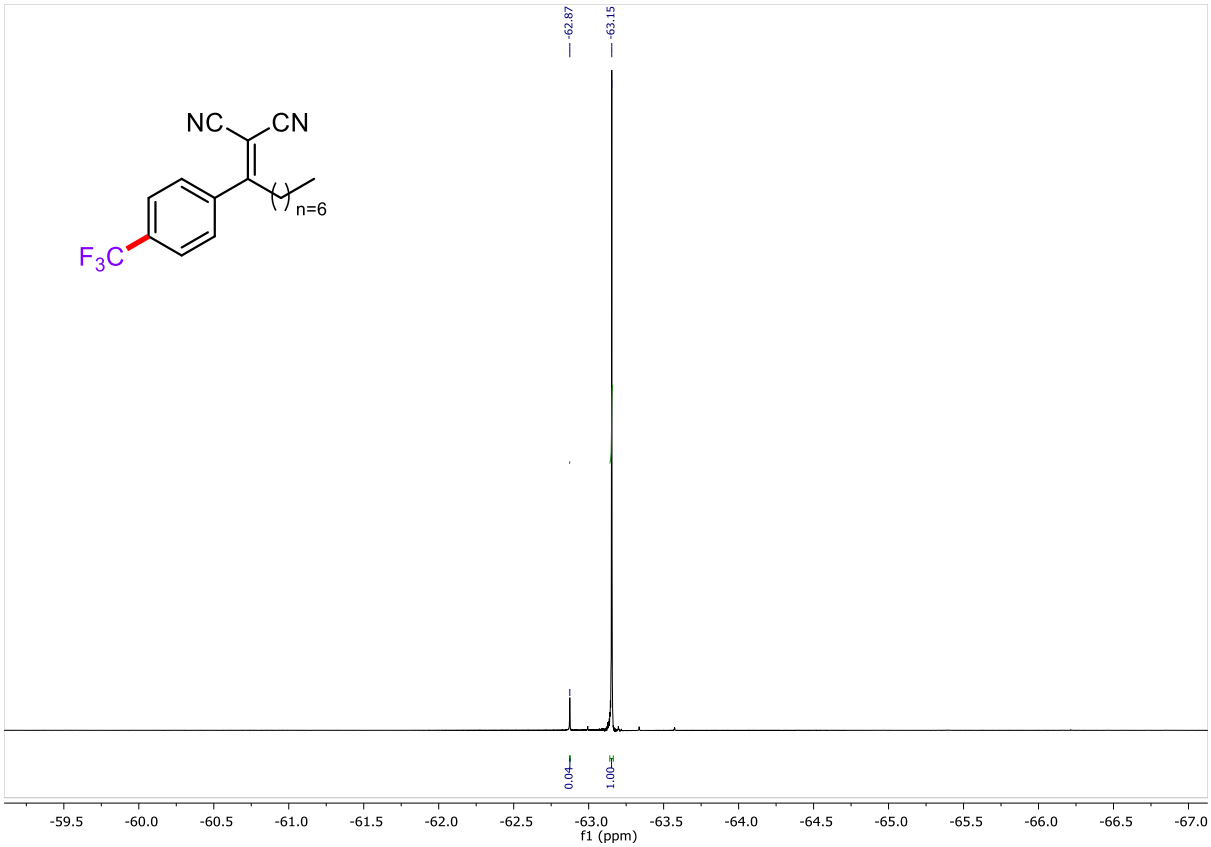
13.86
NC
CN
n=4
F3C
f1 (ppm)


-63.15
NC
CN
n=4
F3C
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
f1 (ppm)


NC
CN
n=6
F3C
f1 (ppm)


NC
CN
n=6
F3C
f1 (ppm)


NC
CN
n=6
F3C
-62.87
-63.15
0.04
1.00
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
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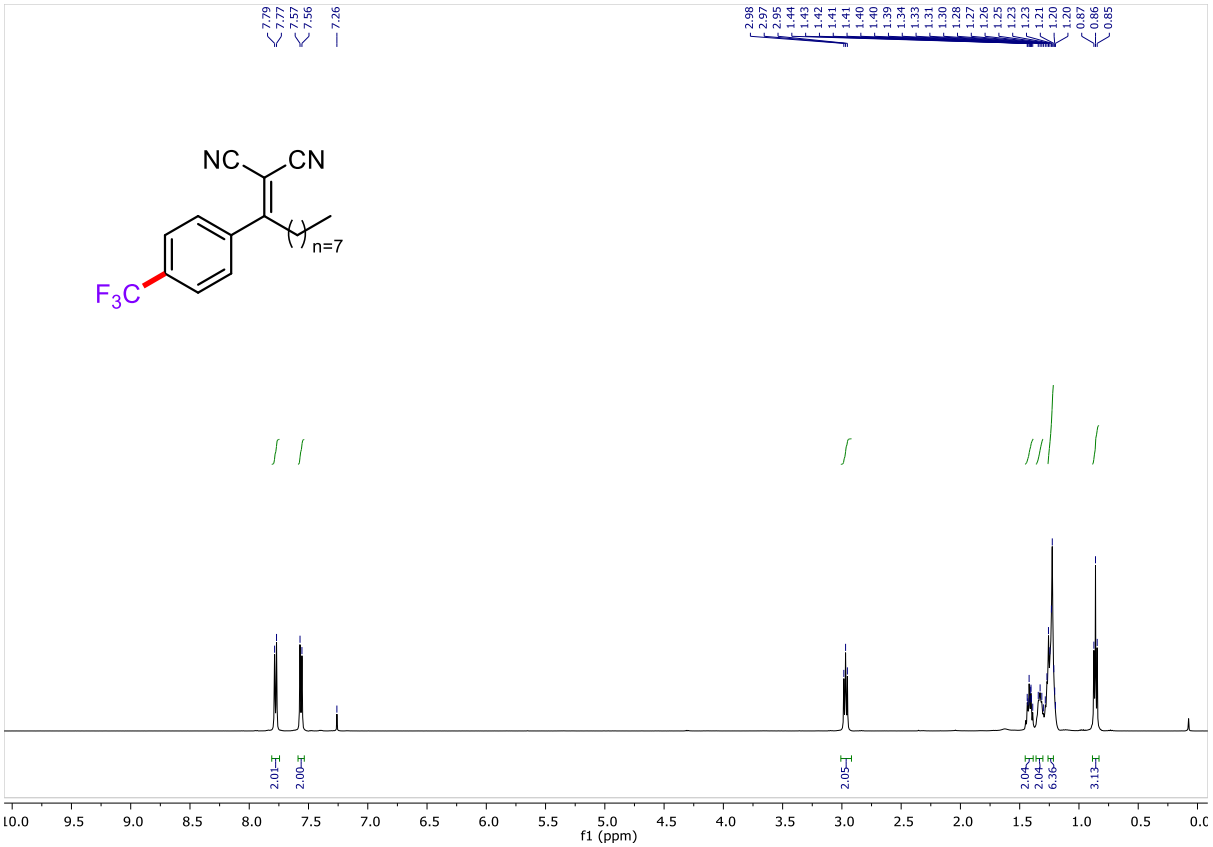
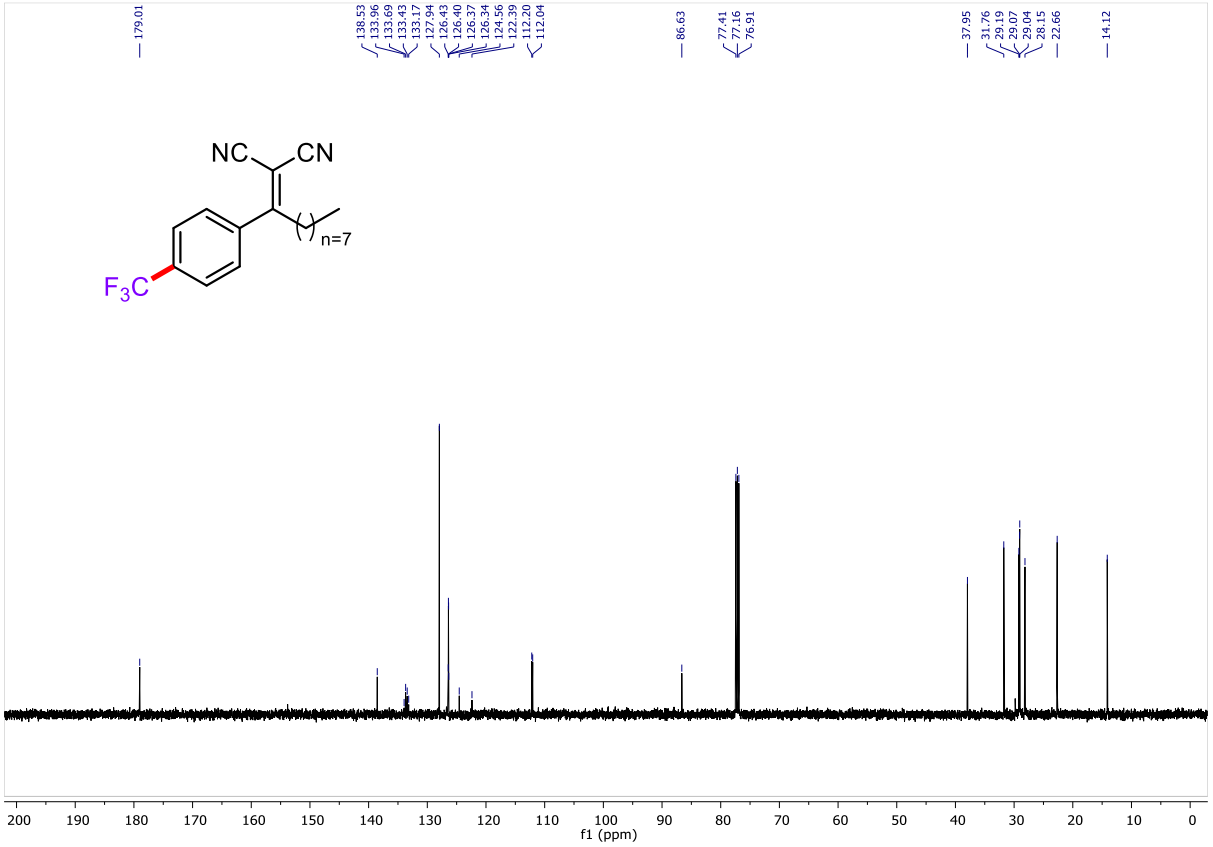
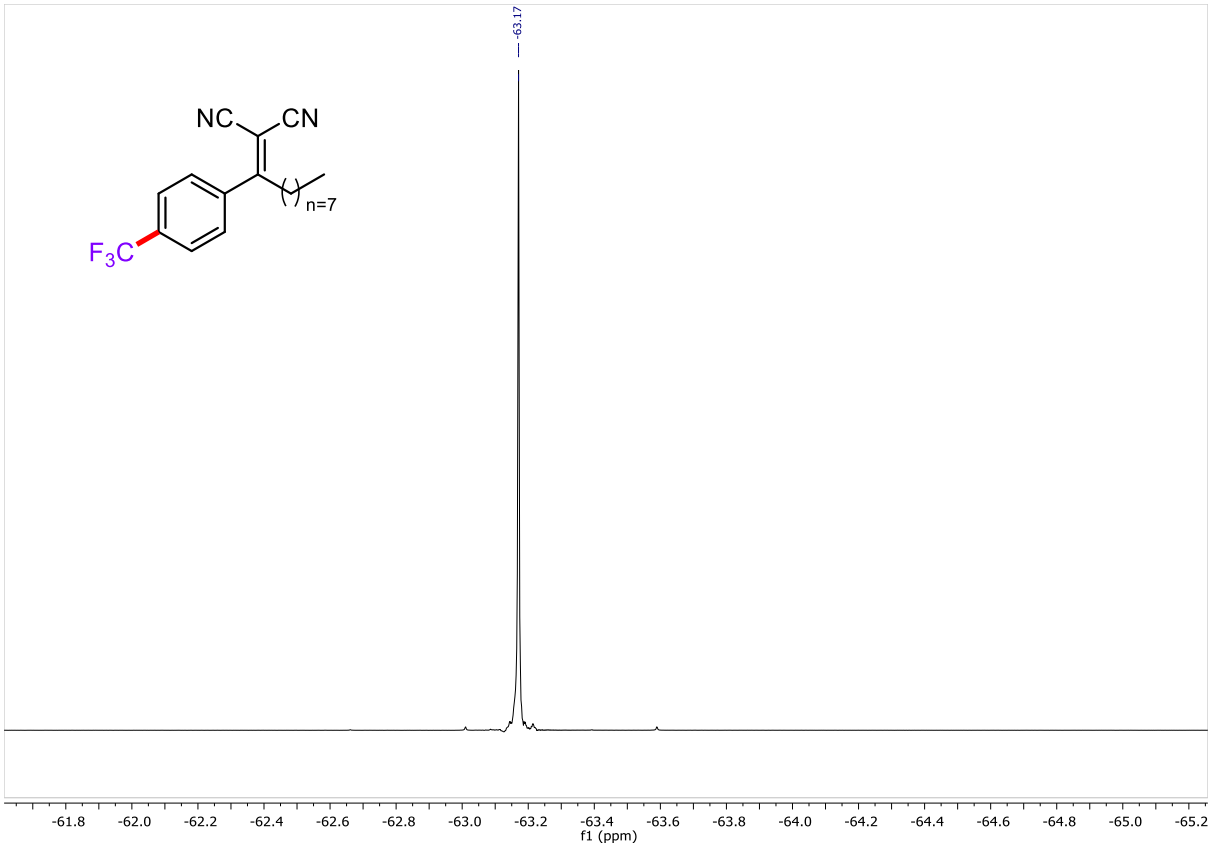
-66.0
-66.5
-67.0
f1 (ppm)


NC
CN
n=7
F3C
f1 (ppm)


NC
CN
n=7
F3C
f1 (ppm)


-63.17
NC
CN
n=7
F3C
-61.8
-62.0
-62.2
-62.4
-62.6
-62.8
-63.0
-63.2
-63.4
-63.6
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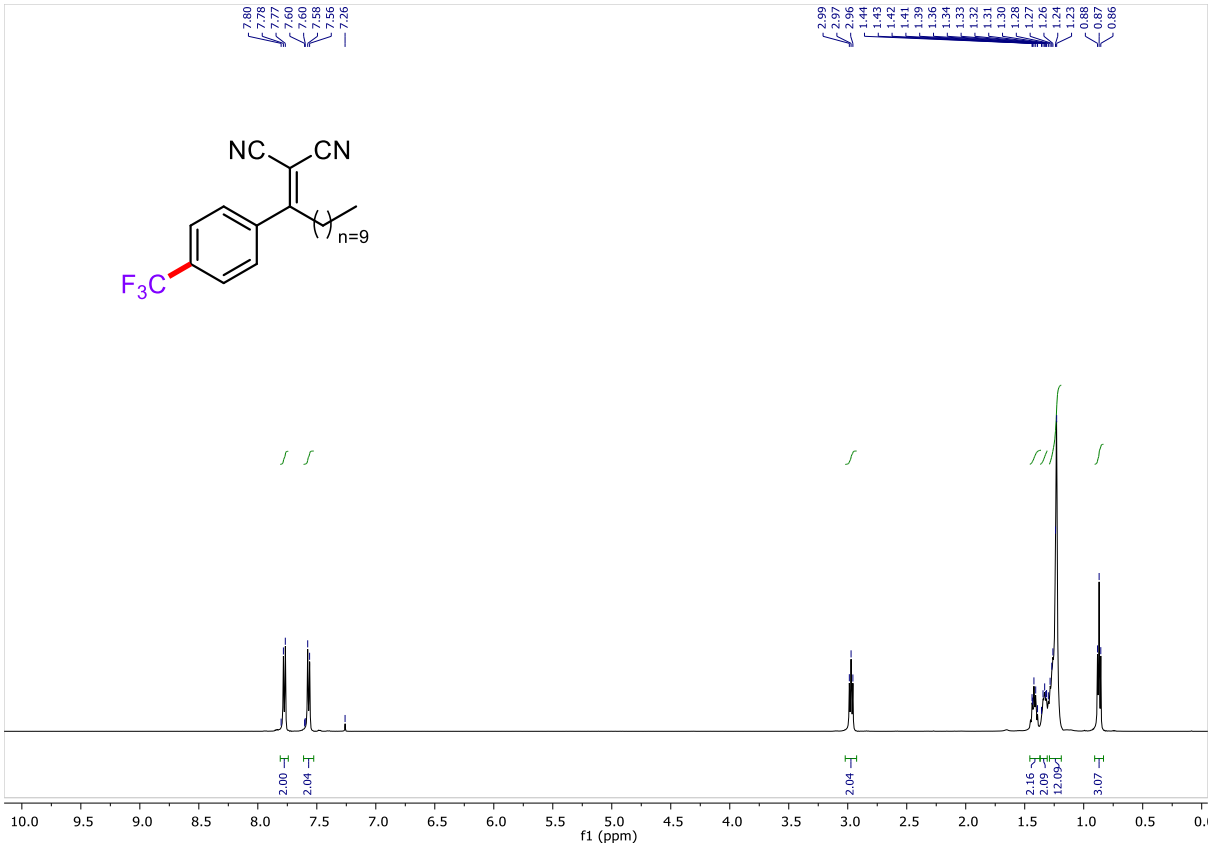
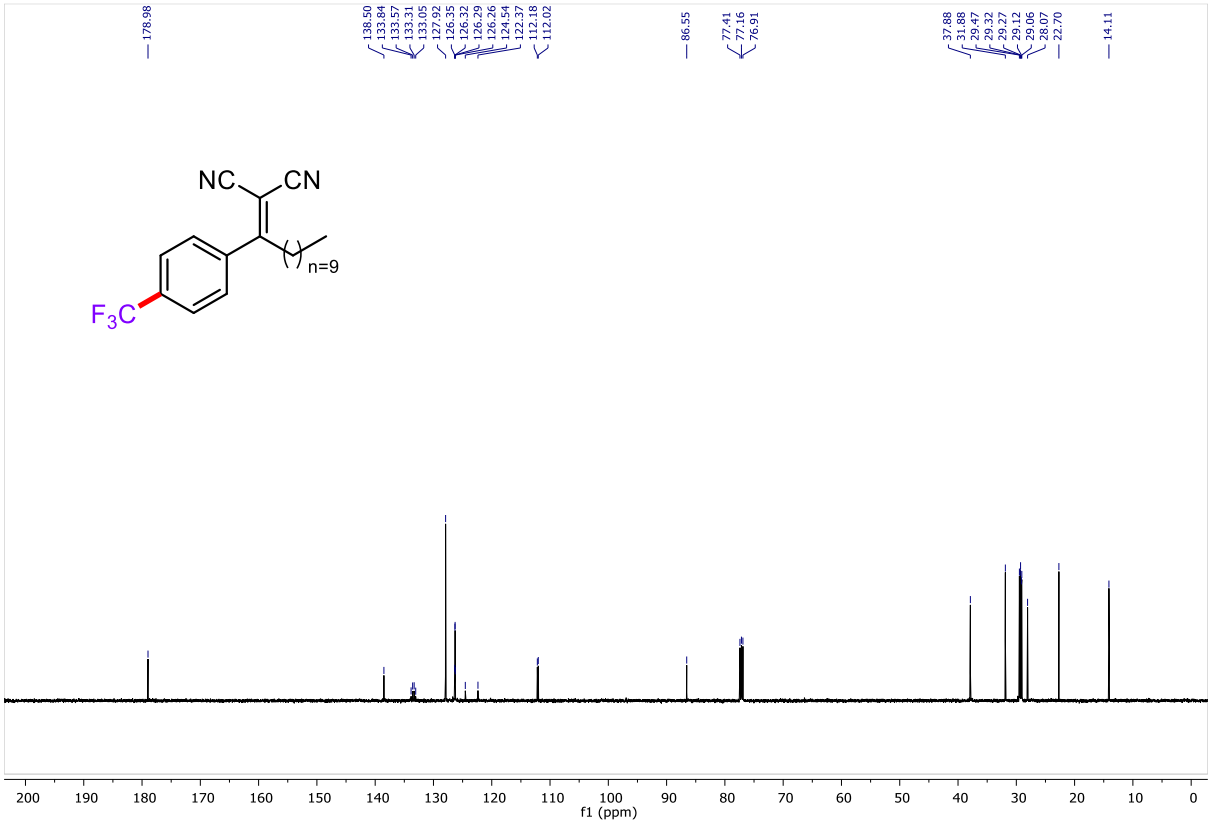
-64.0
-64.2
-64.4
-64.6
-64.8
-65.0
-65.2
f1 (ppm)


NC
CN
n=9
F3C
f1 (ppm)


NC
CN
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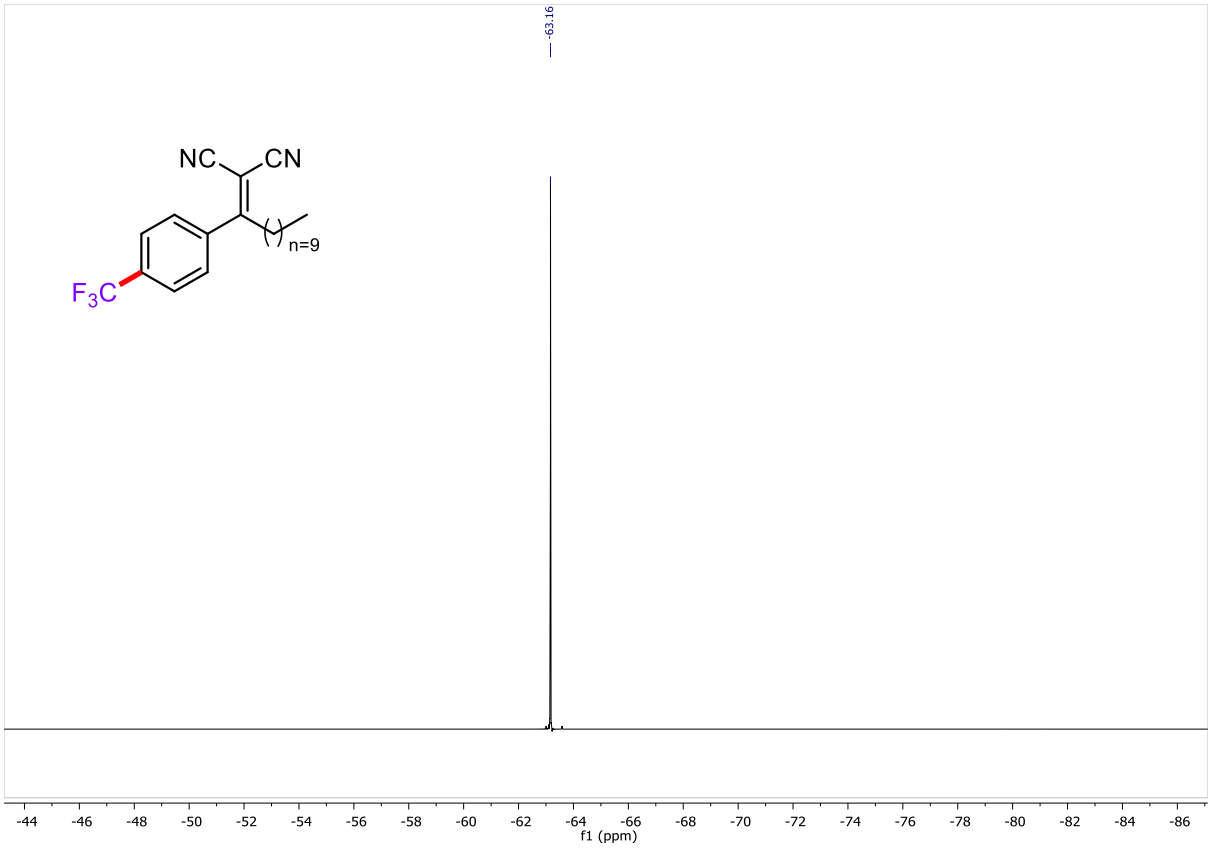
F3C
f1 (ppm)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CN
n=9
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-44
-46
-48
-50
-52
-54
-56
-58
-60
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-64
-66
-68
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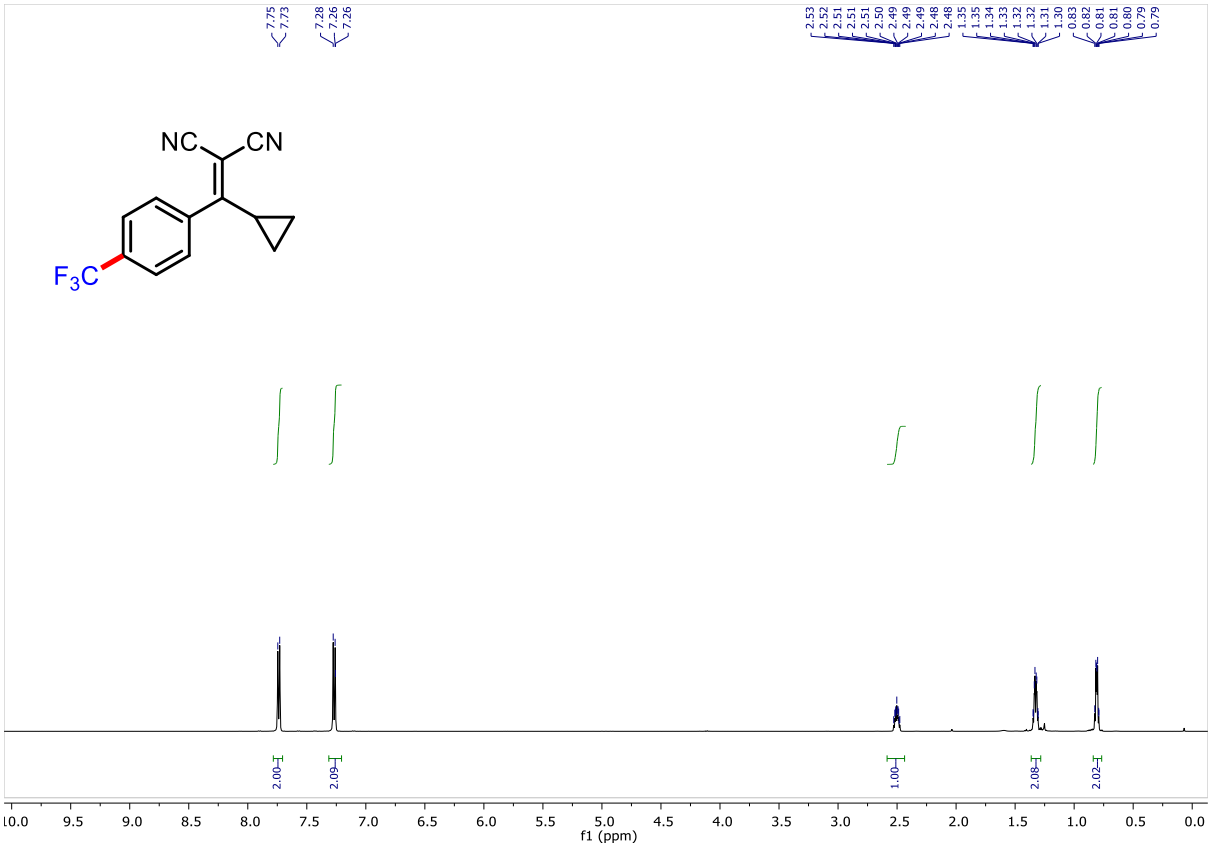
-72
-74
-76
-78
-80
-82
-84
-86
f1 (ppm)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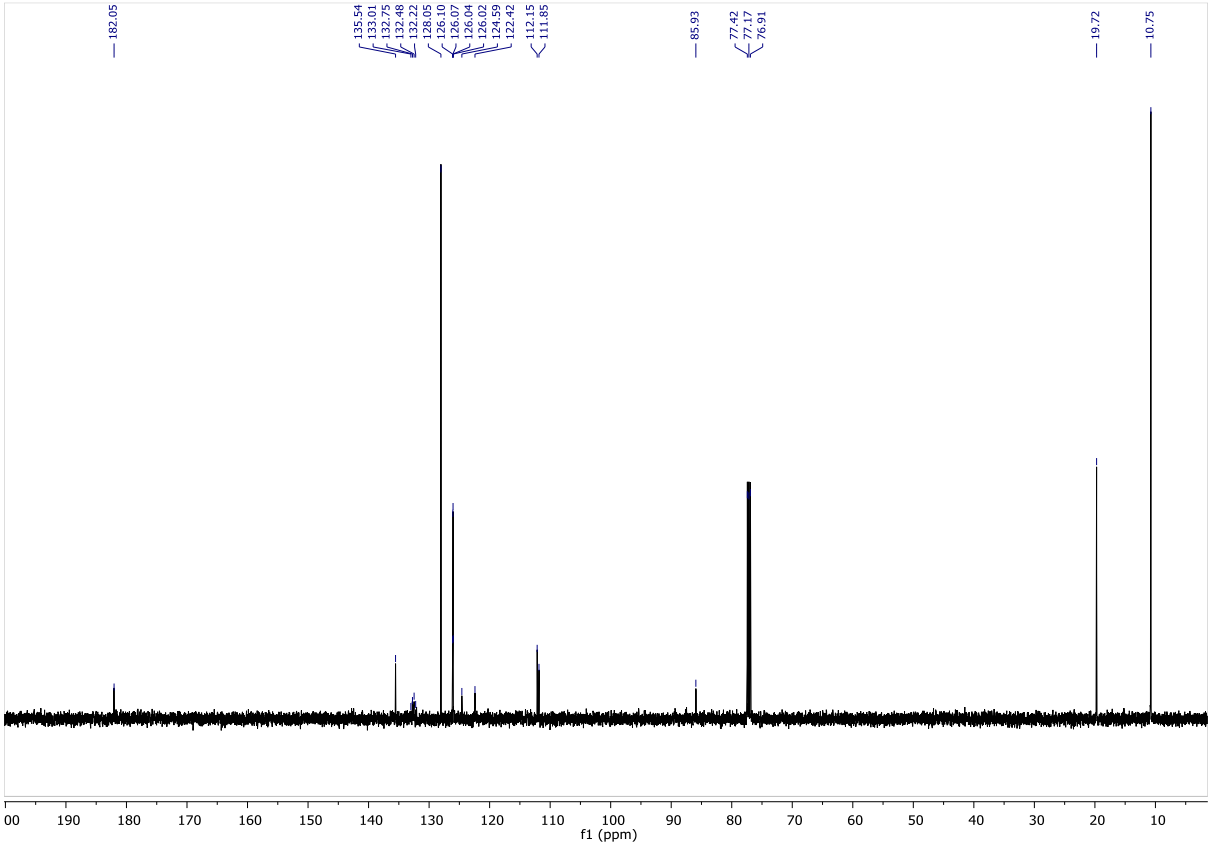
F3C
f1 (ppm)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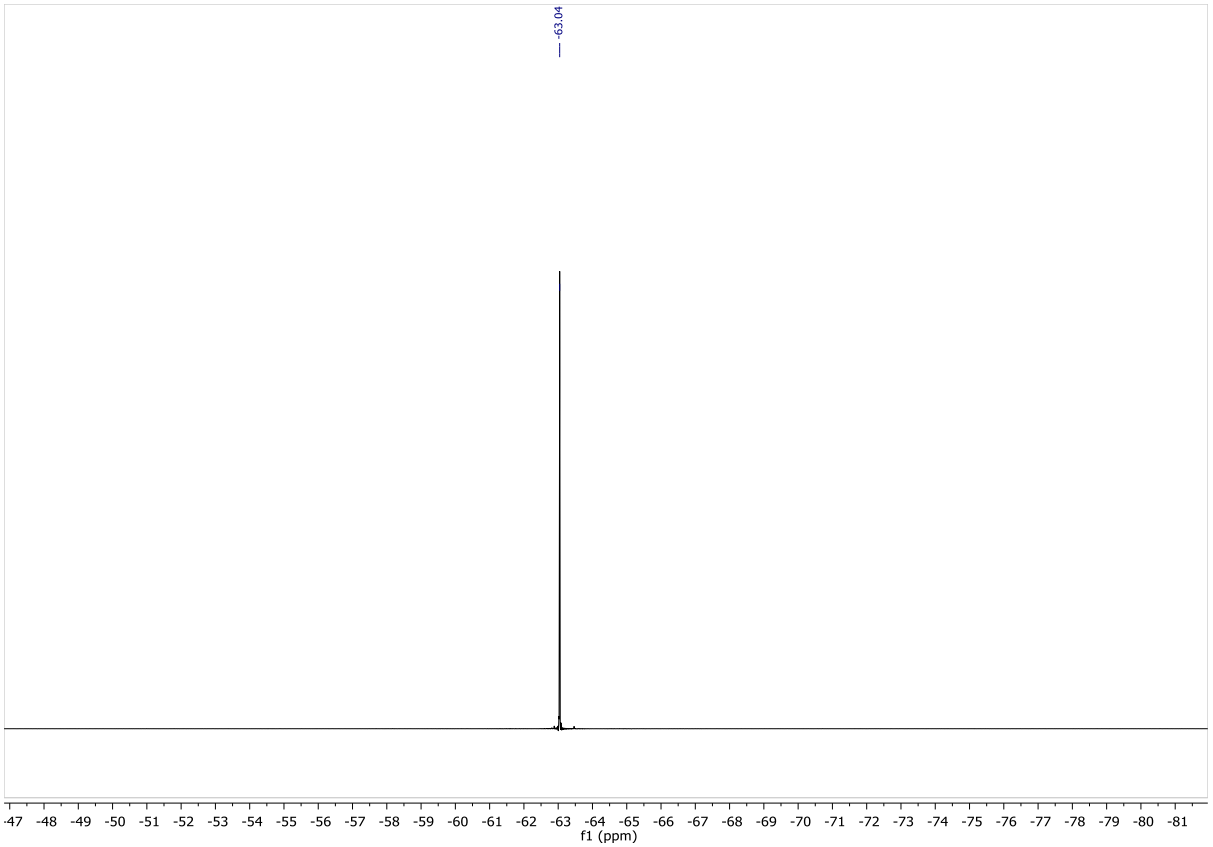
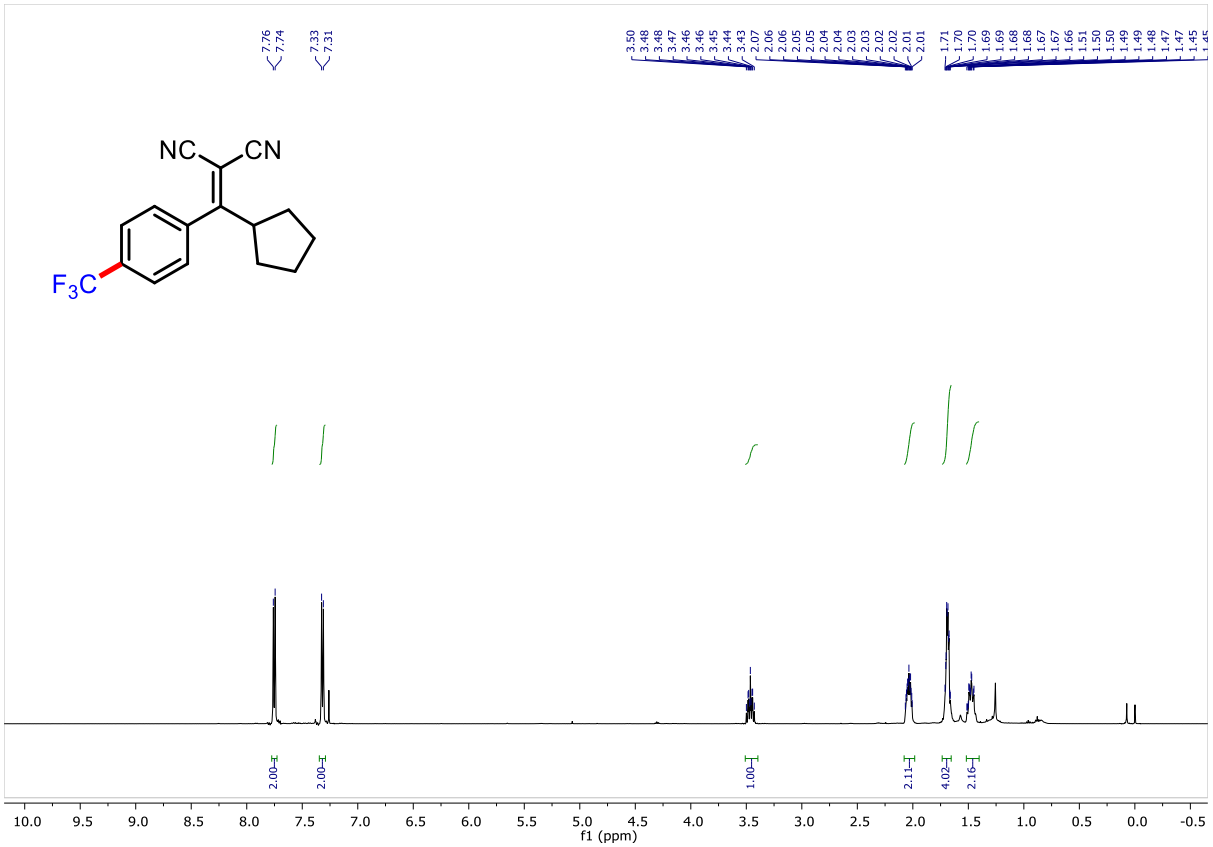

-63.04
-47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81
f1 (ppm)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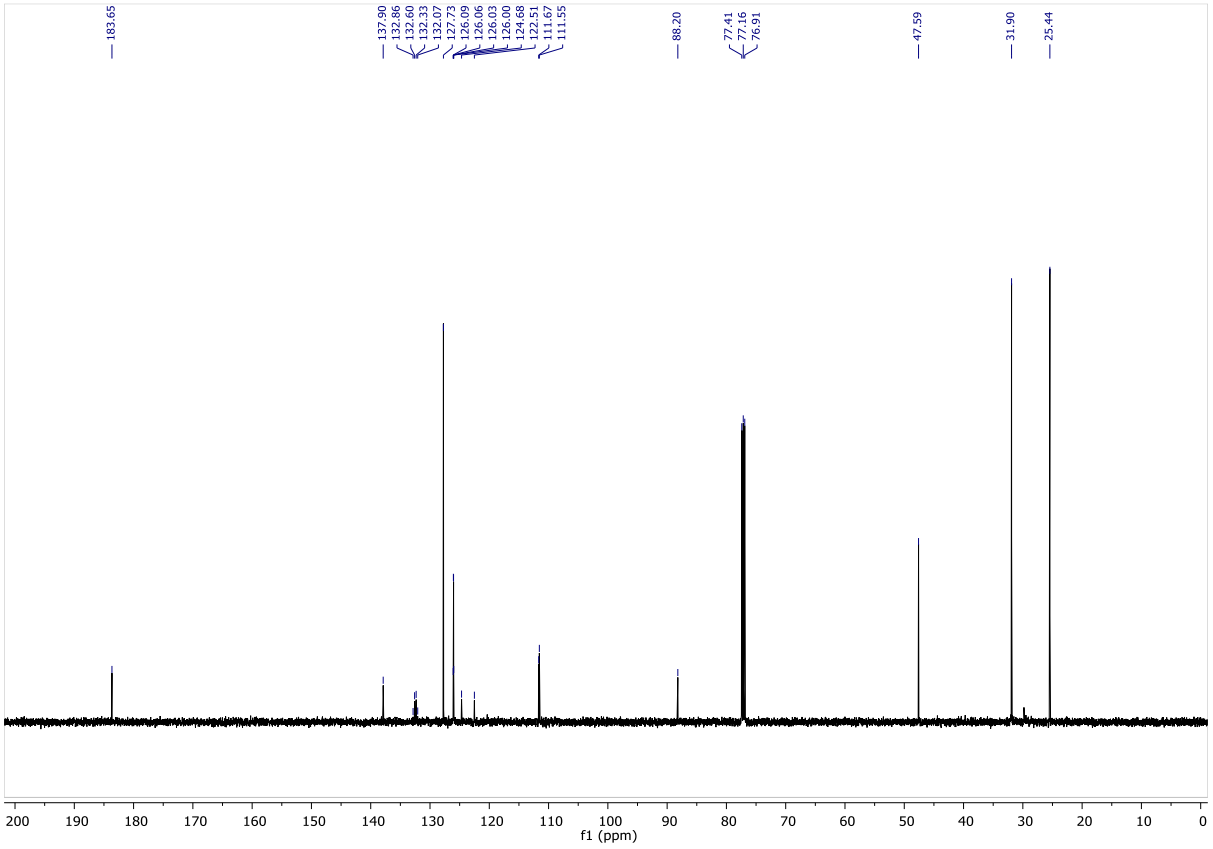
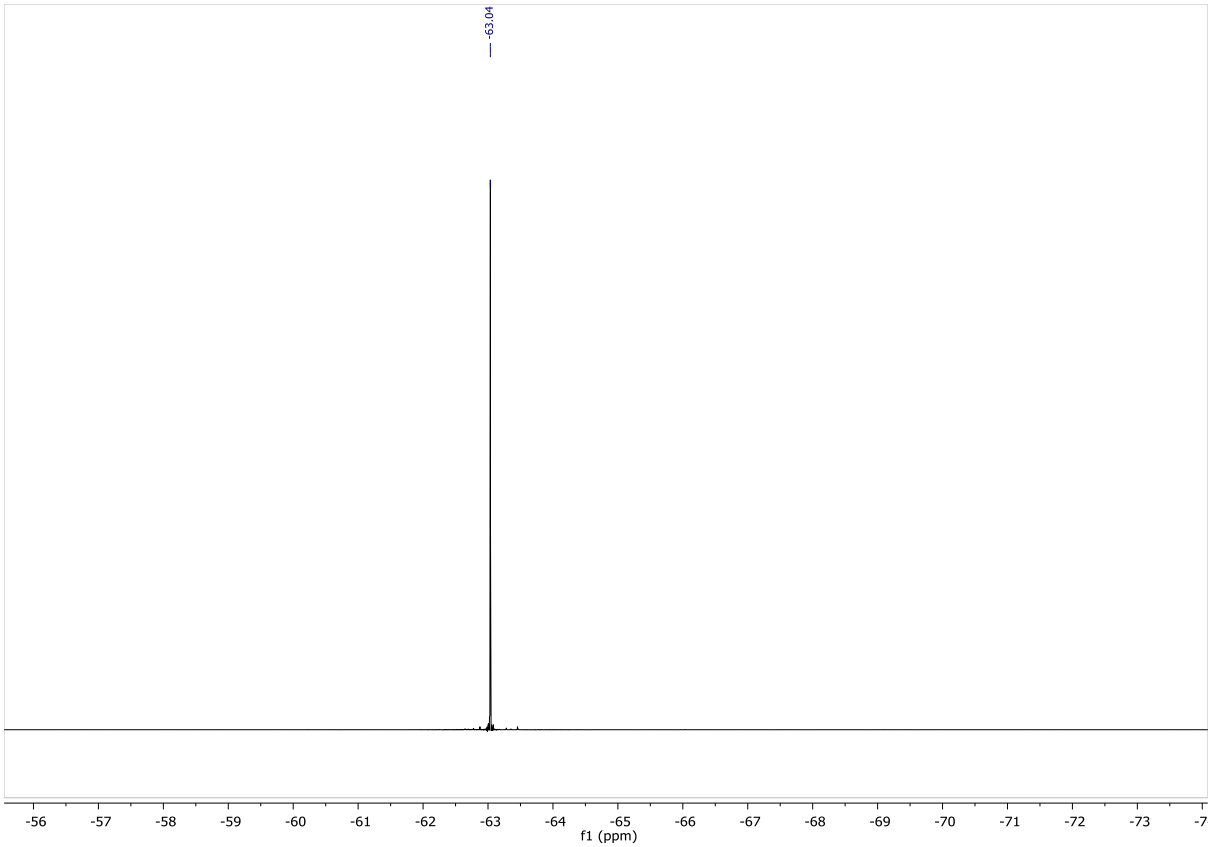
CN
F3C
f1 (ppm)


f1 (ppm)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-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
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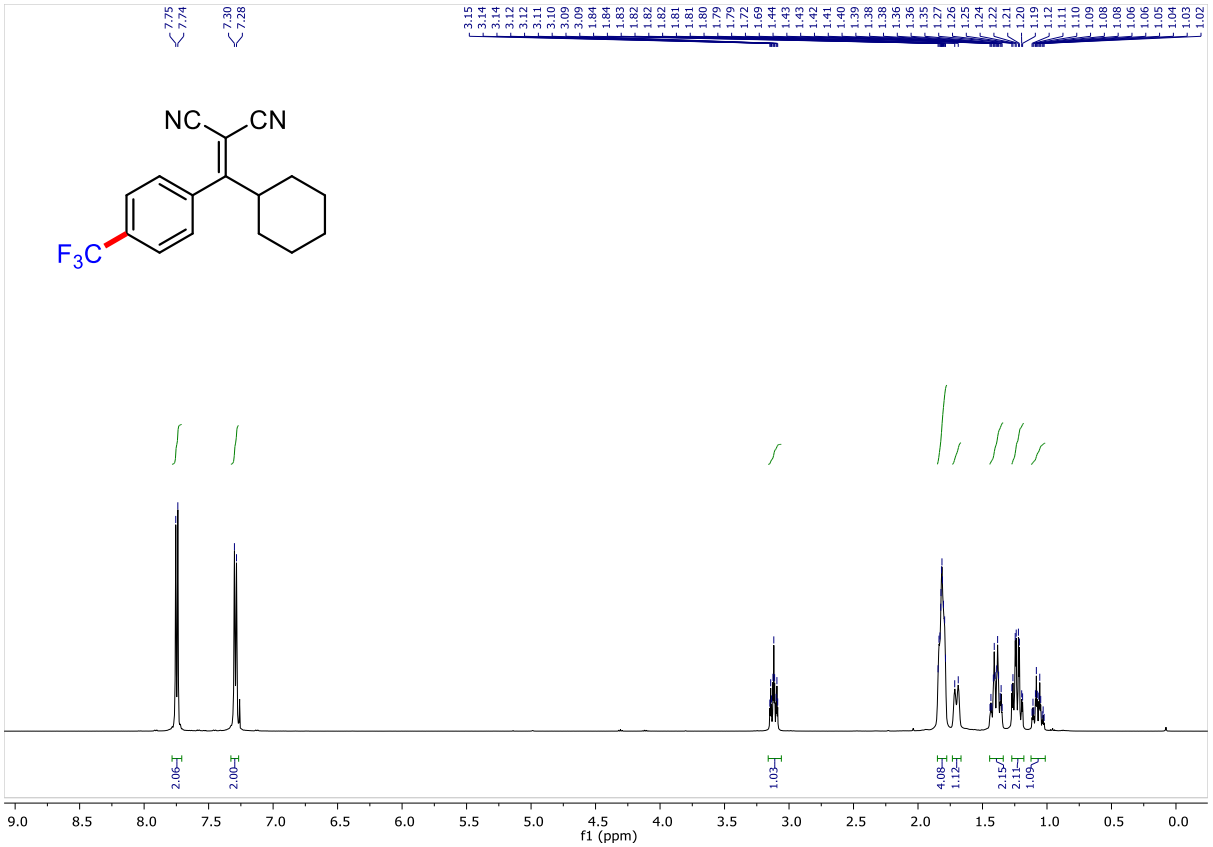
-70
-71
-72
-73
-7
f1 (ppm)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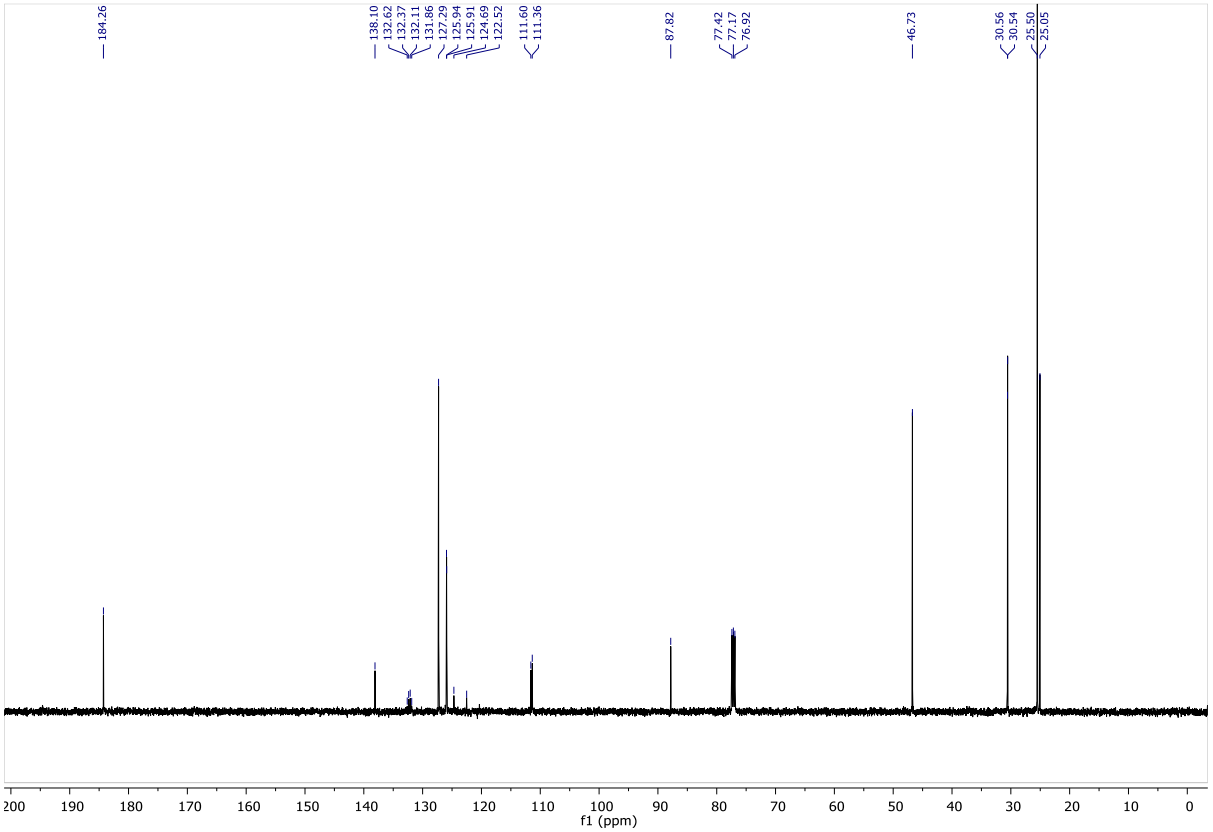
CN
F3C
f1 (ppm)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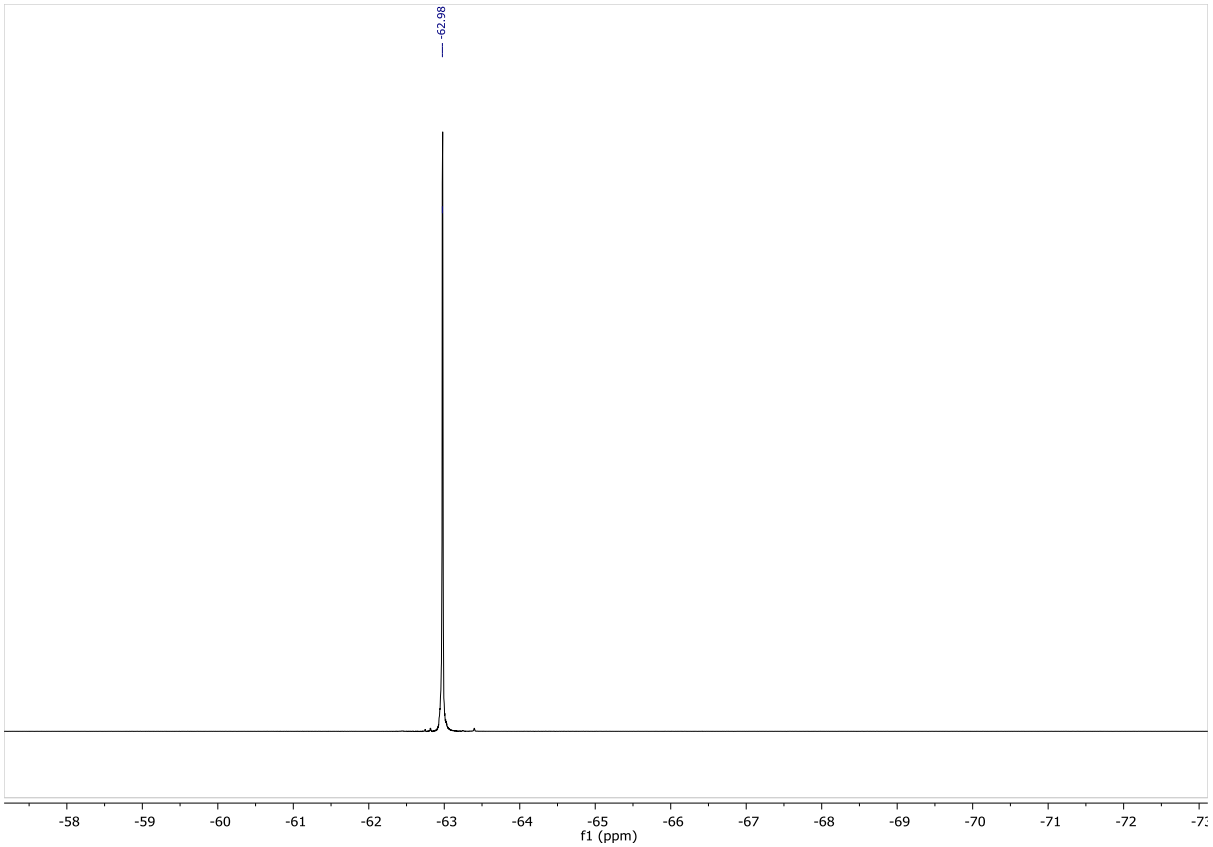
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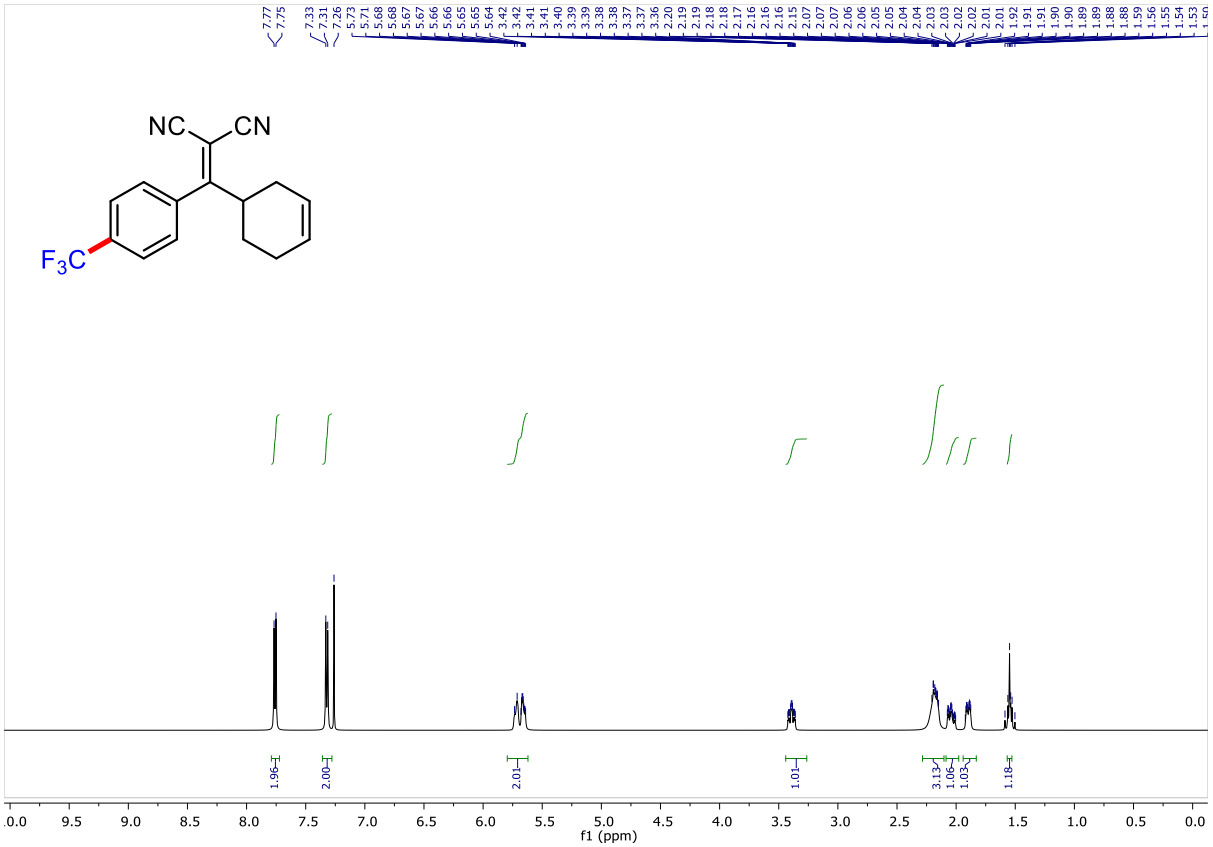
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
f1 (ppm)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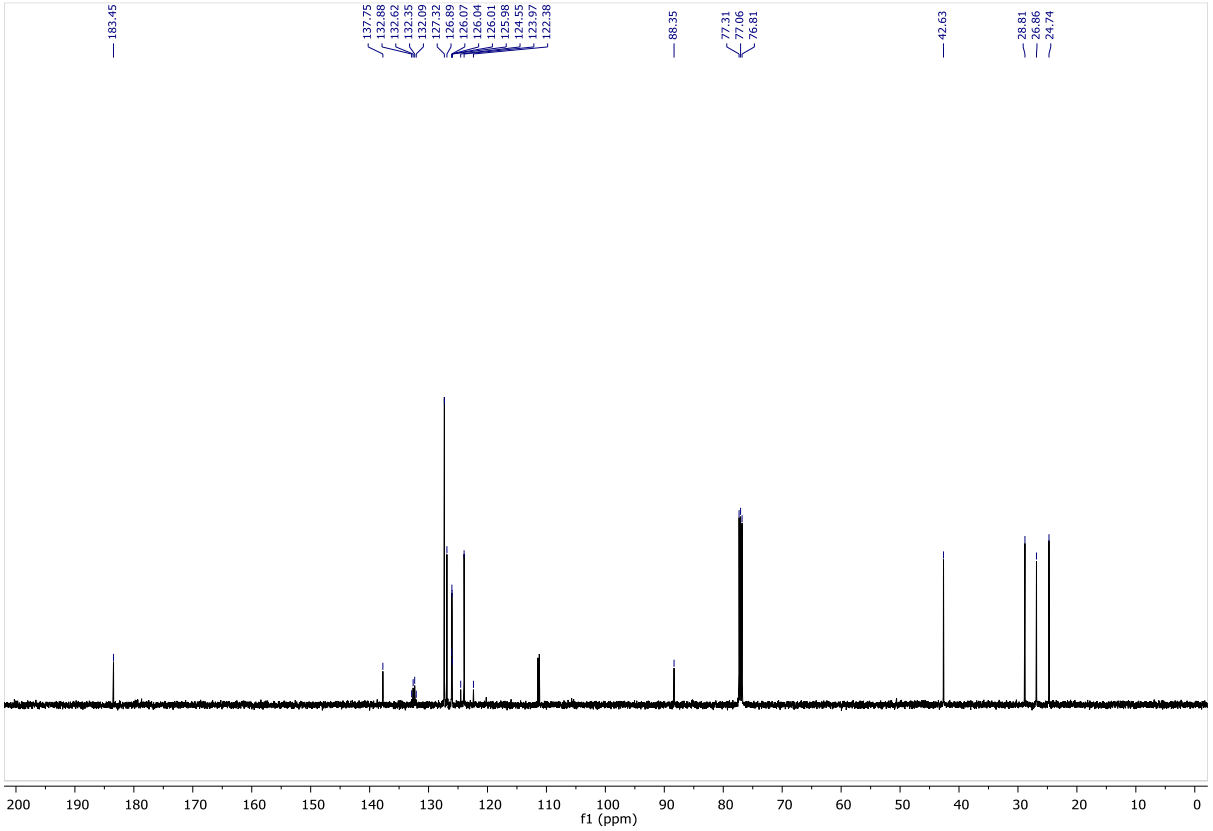
CN
F3C
f1 (ppm)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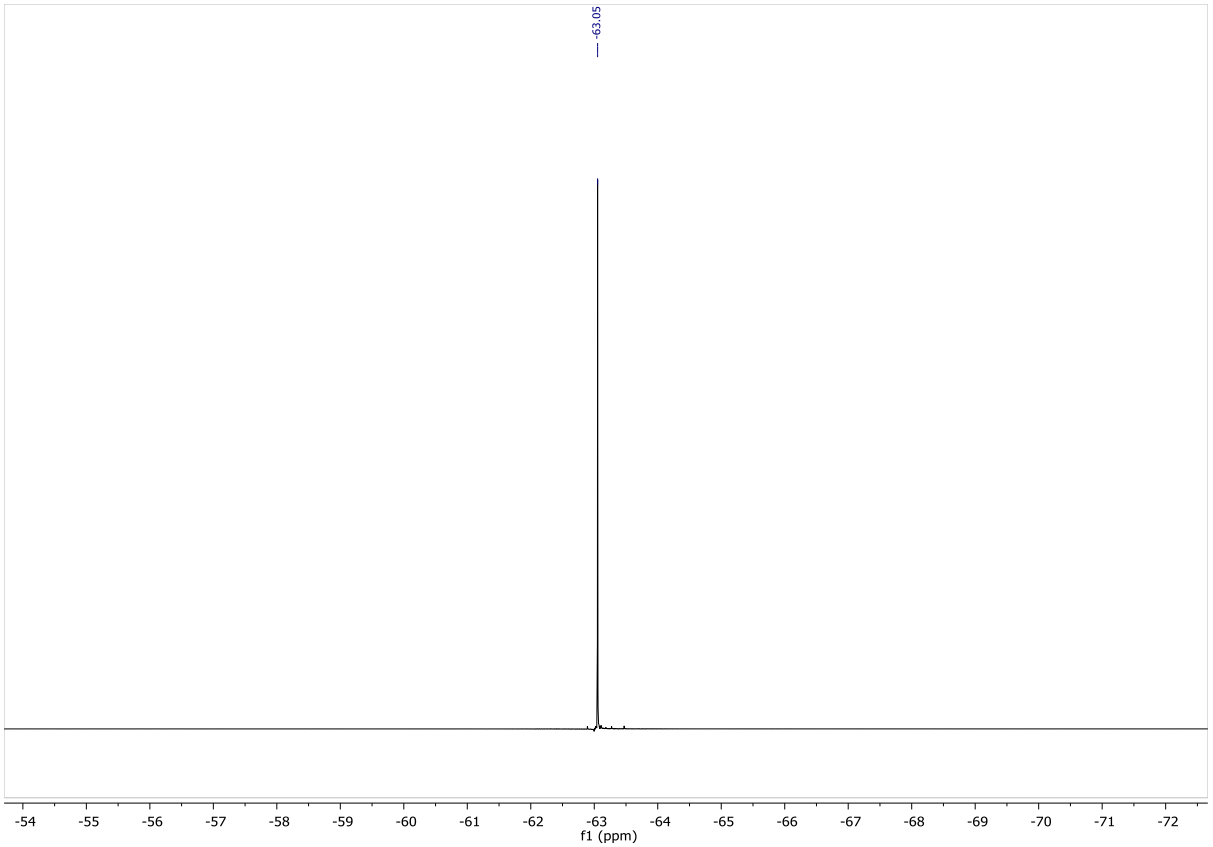
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-55
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-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
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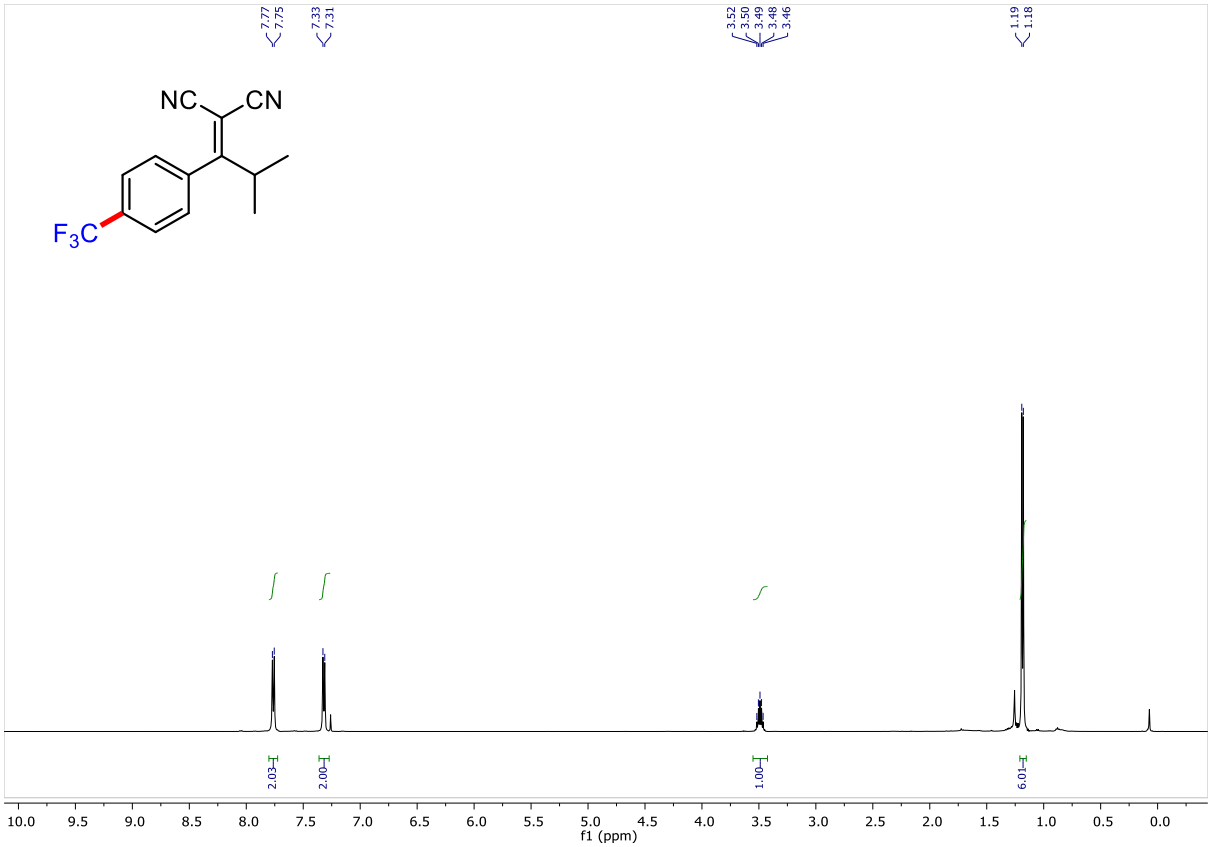
-68
-69
-70
-71
-72
f1 (ppm)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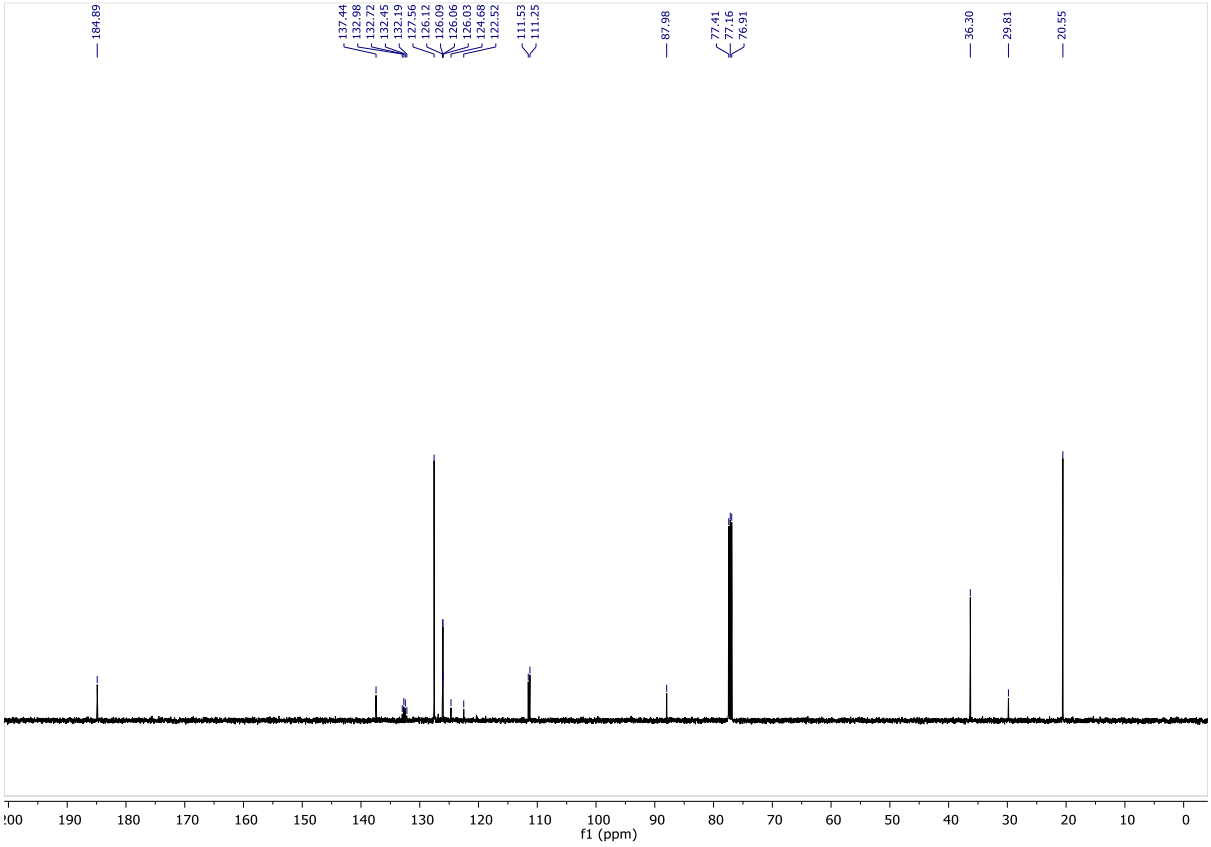
7.75
7.33
7.31
3.52
3.50
3.49
3.48
3.46
1.19
1.18
NC
CN
F3C
2.03
2.00
1.00
6.01
f1 (ppm)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132.19
127.56
126.12
126.09
126.06
126.03
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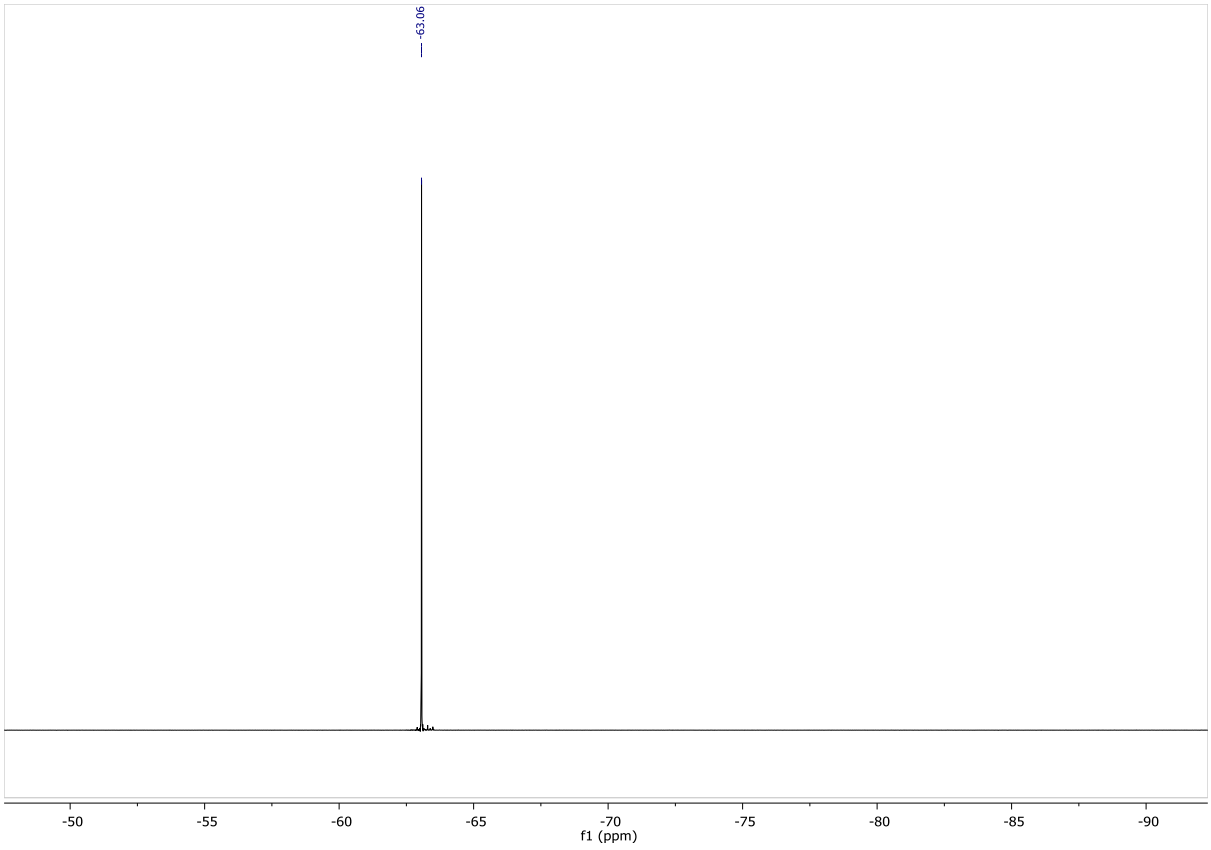
77.41
77.16
76.91
36.30
29.81
20.55
f1 (ppm)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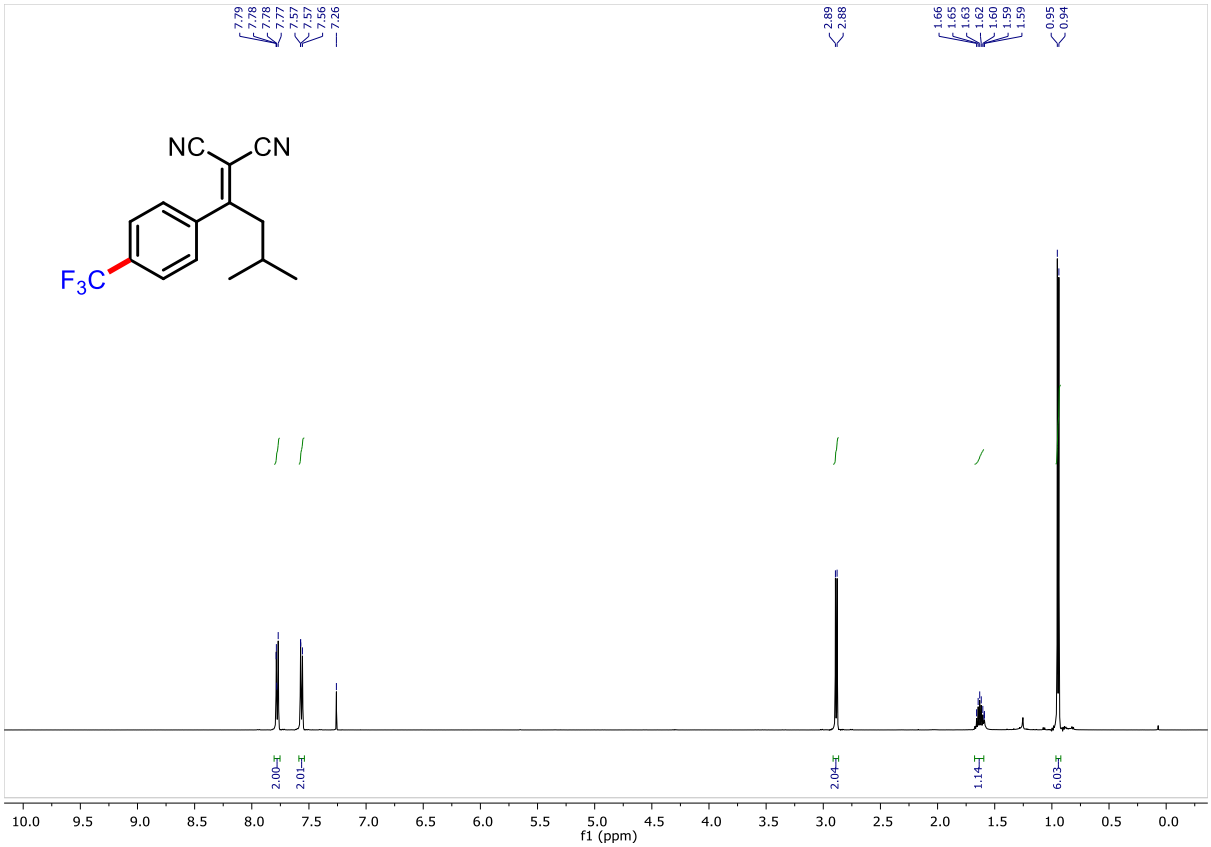
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)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7.78
7.78
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7.57
7.56
7.26
2.89
2.88
1.66
1.65
1.63
1.62
1.60
1.59
1.59
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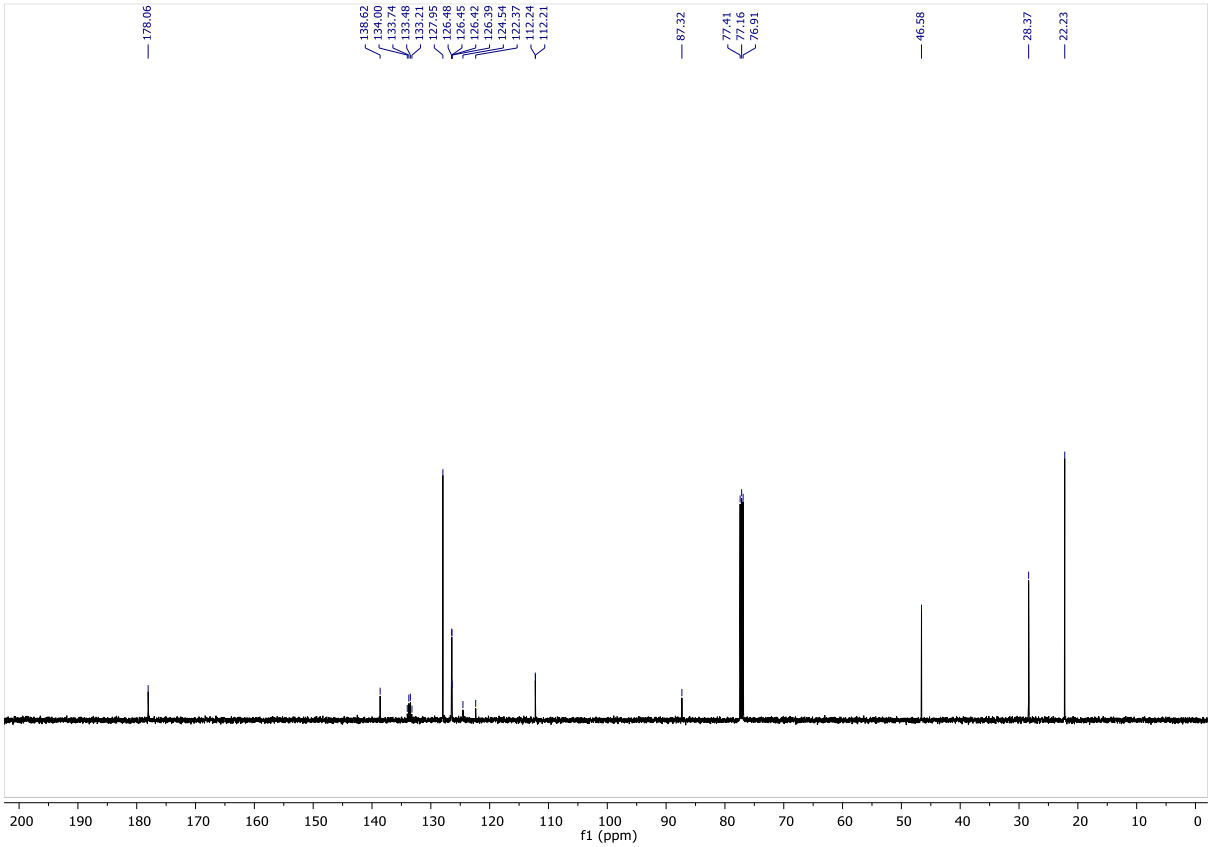
0.94
NC
CN
F3C
2.00
2.01
2.04
1.14
6.03
f1 (ppm)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126.48
126.45
126.42
126.39
124.54
122.37
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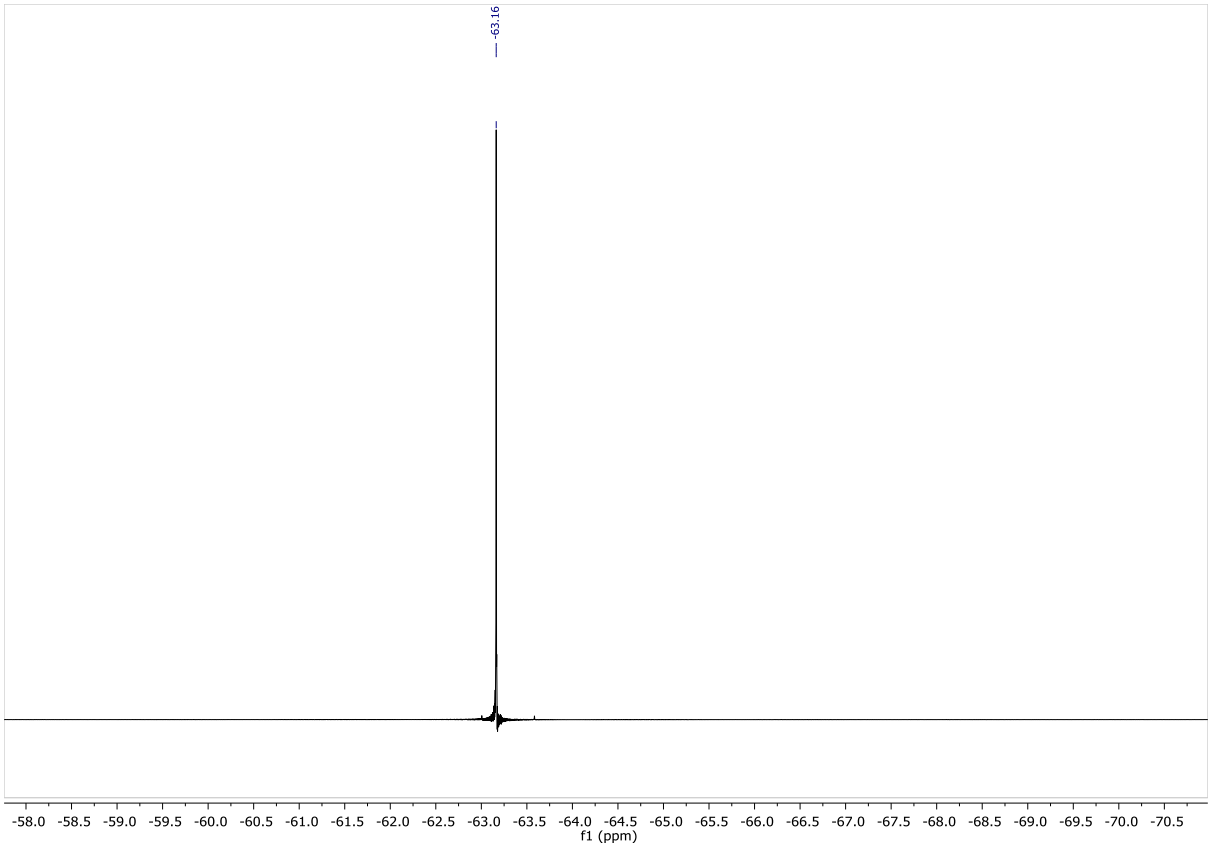
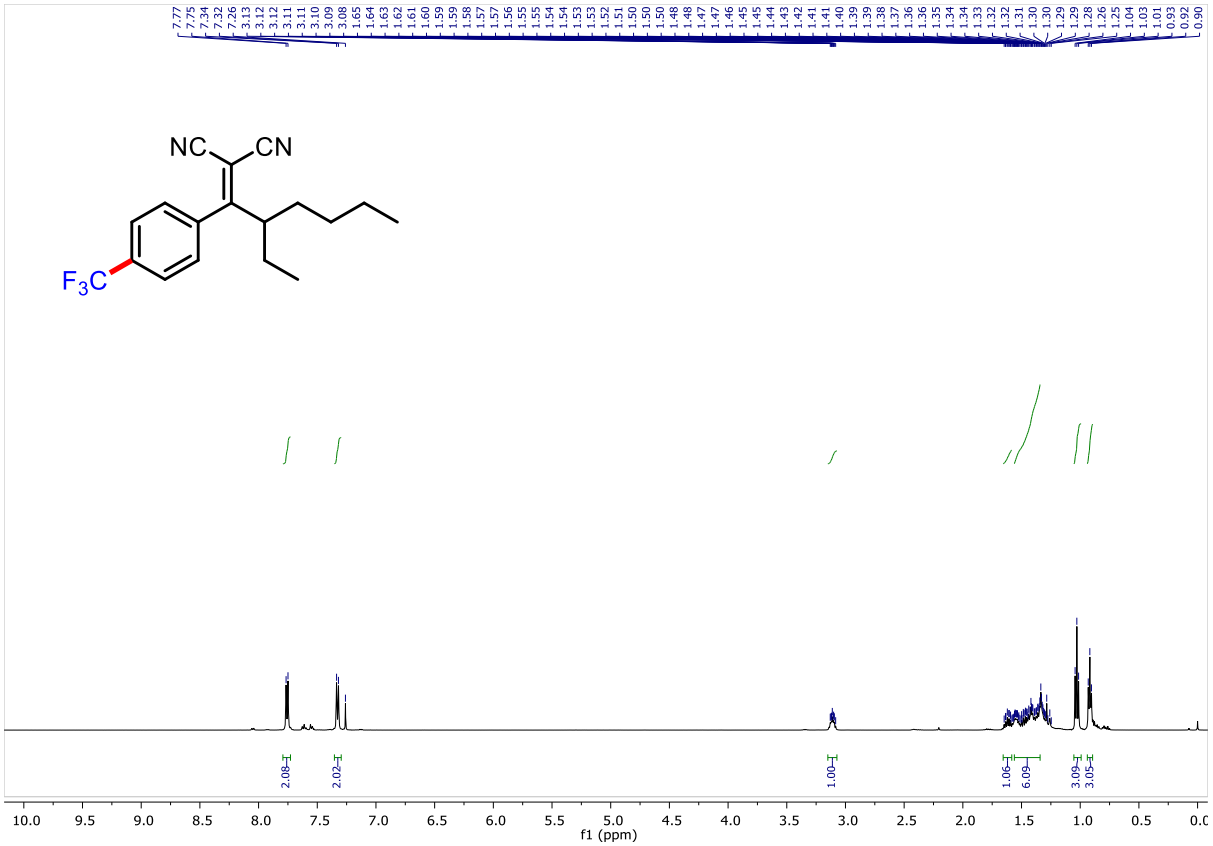
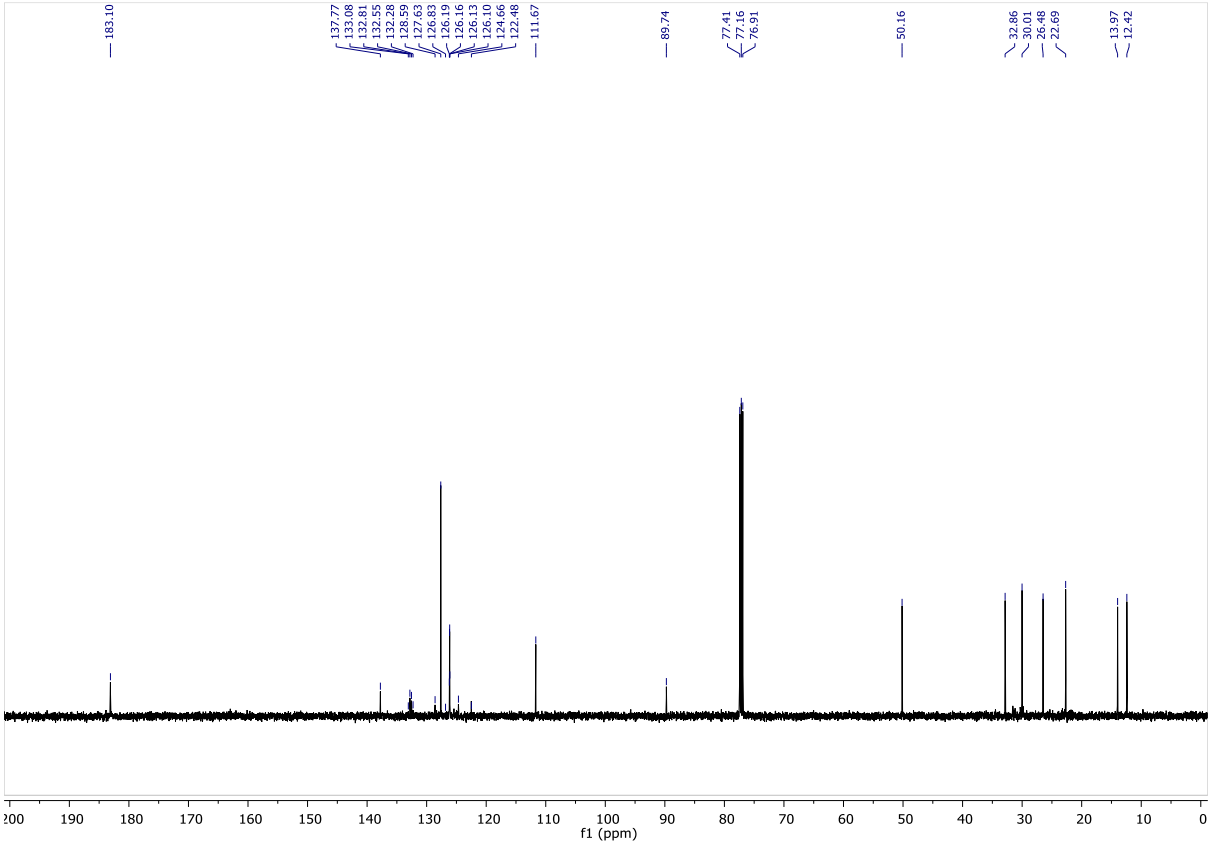
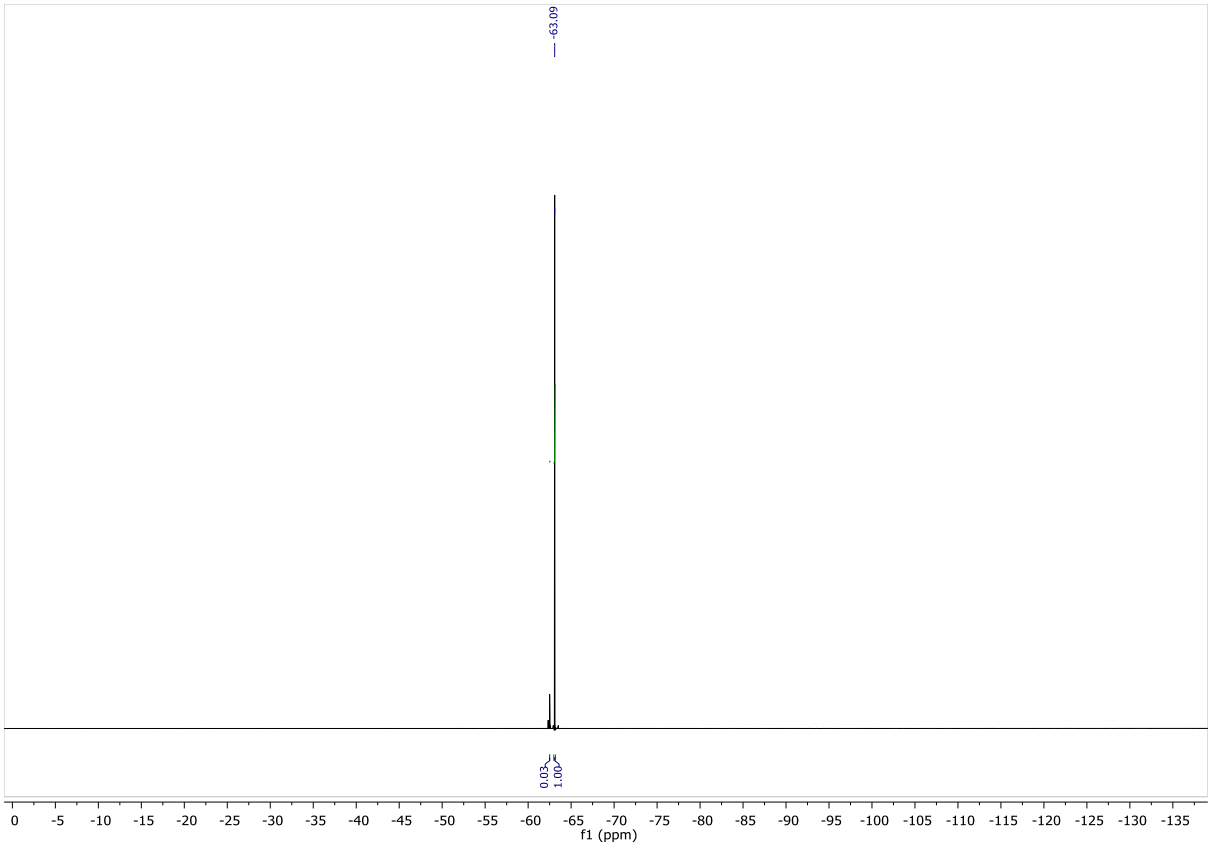
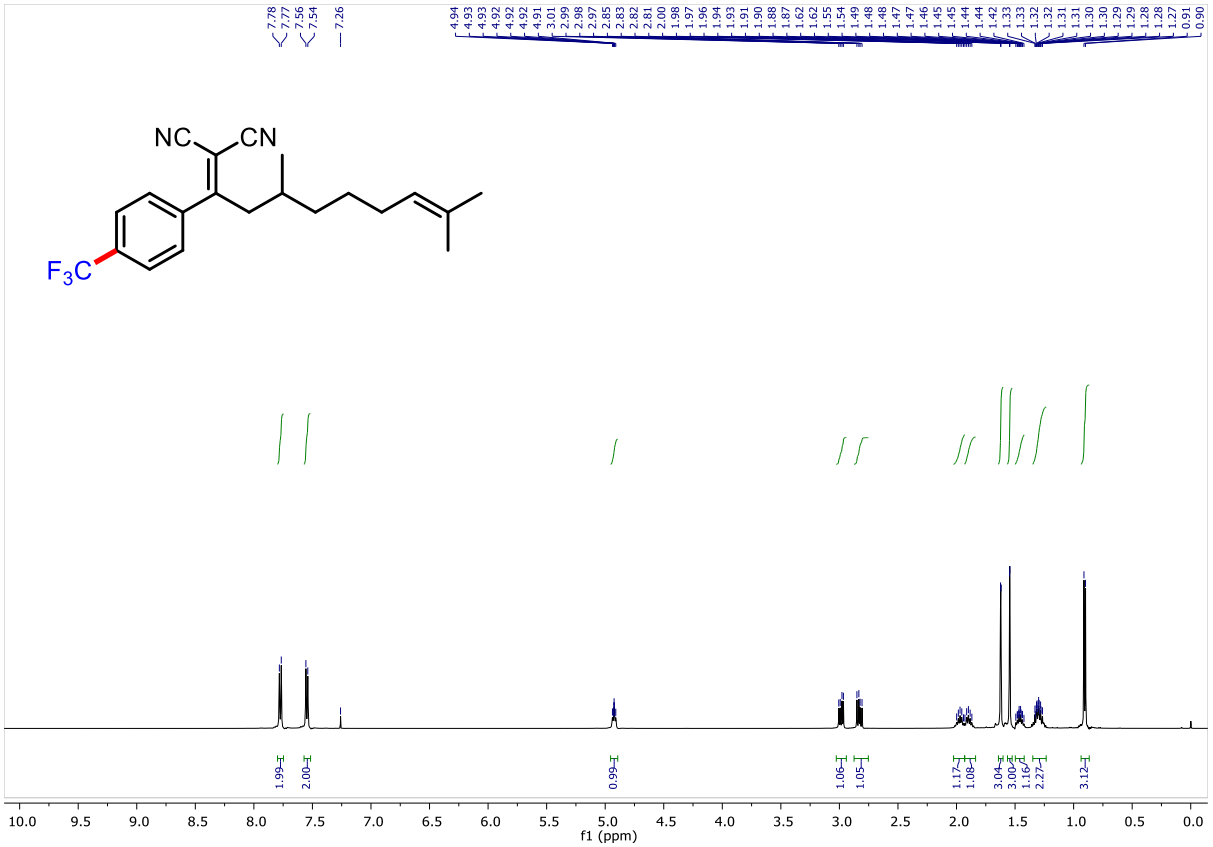
112.21
87.32
77.41
77.16
76.91
46.58
28.37
22.23
f1 (ppm)

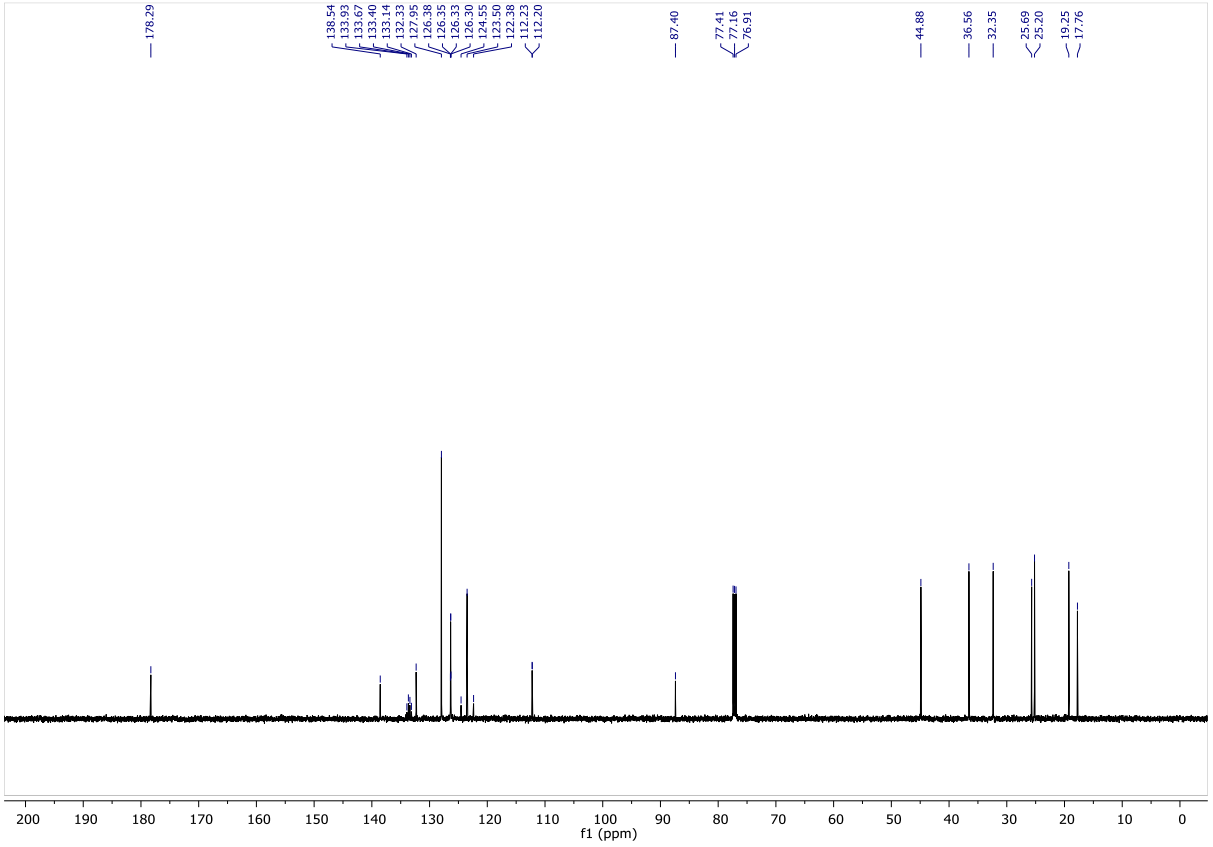

-63.16
-58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0 -70.5
f1 (ppm)

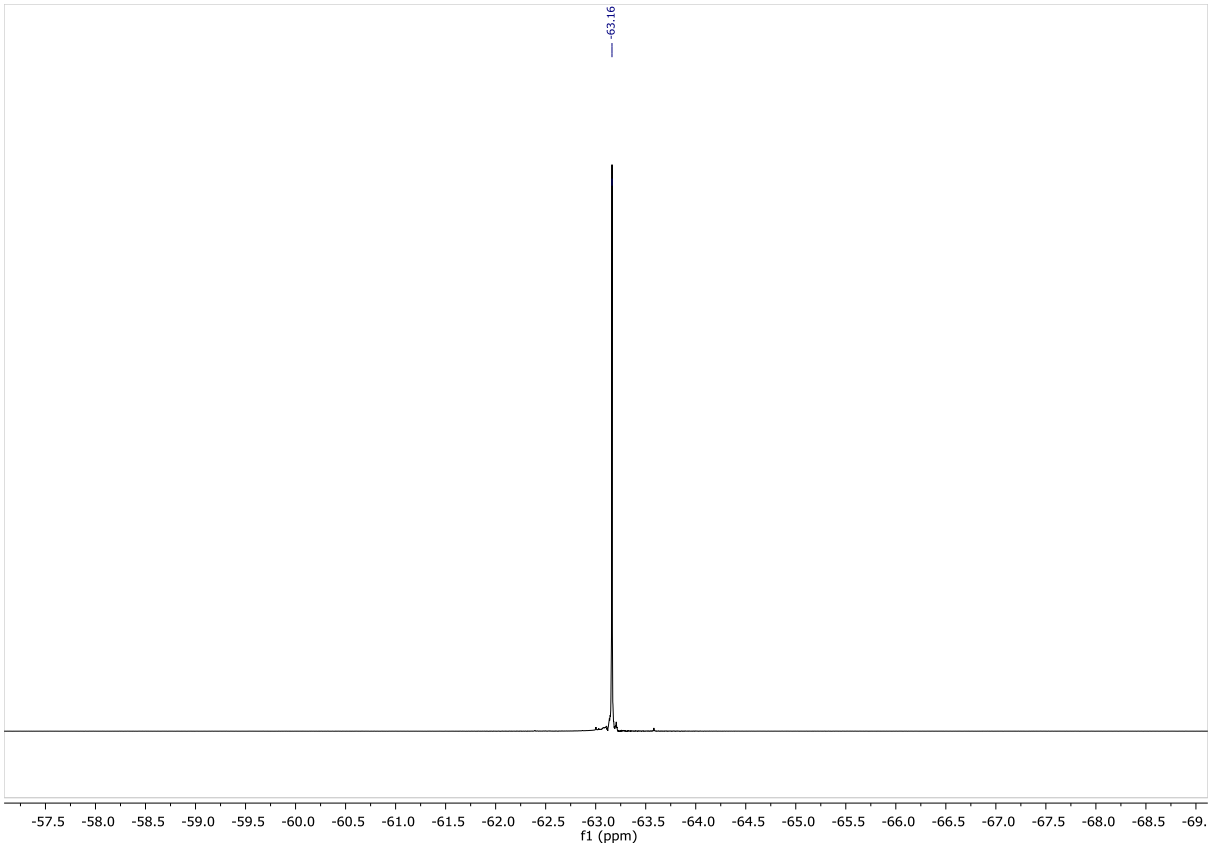

NC
CN
F3C
f1 (ppm)

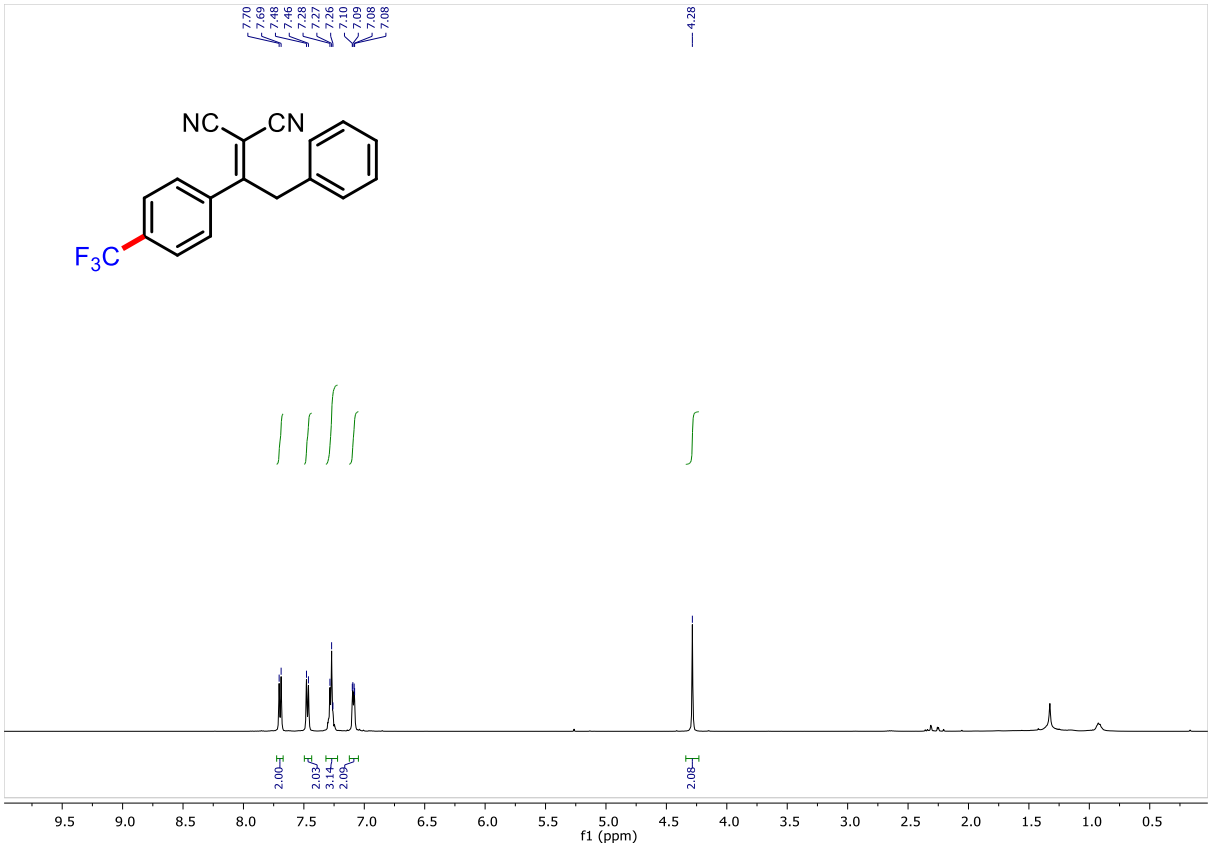

f1 (ppm)


-63.09
0.03
1.00
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)


NC
CN
F3C
f1 (ppm)


f1 (ppm)


-63.16
-57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.
f1 (ppm)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7.69
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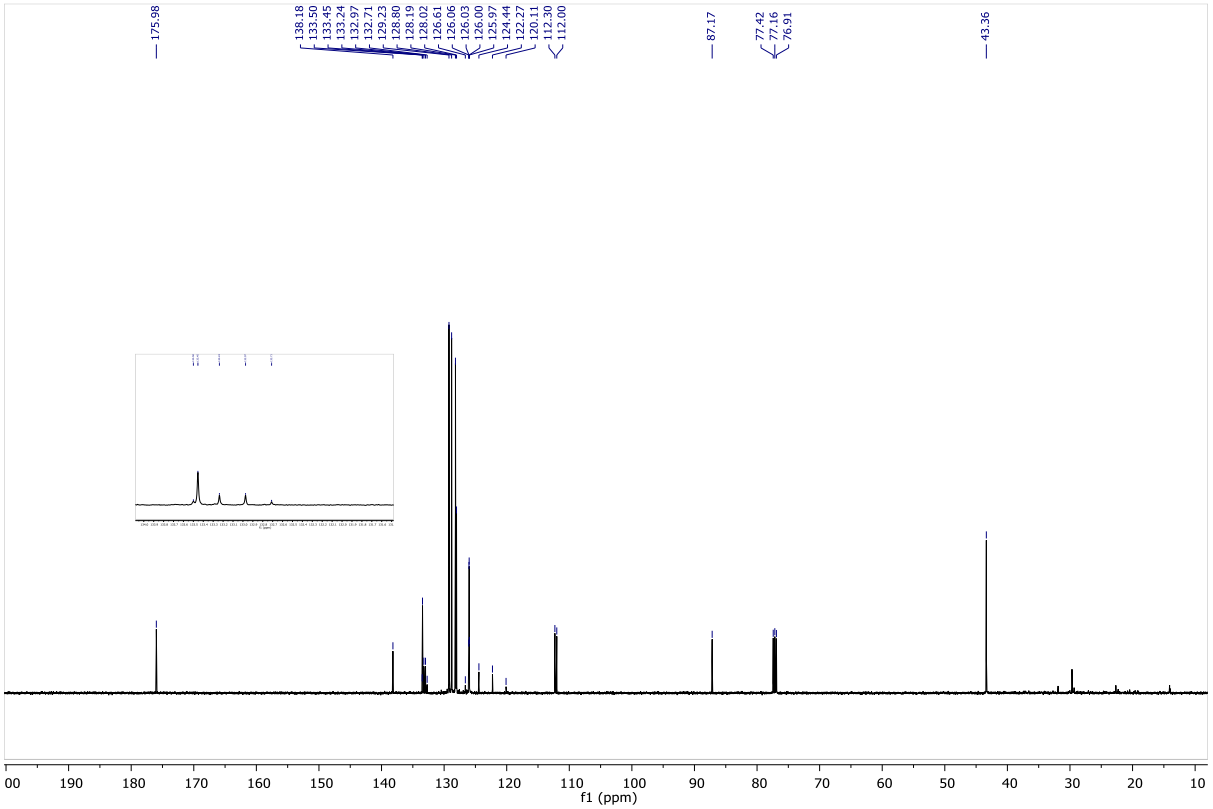
7.46
7.28
7.27
7.26
7.10
7.09
7.08
7.08
4.28
NC
CN
F3C
2.00
2.03
3.14
2.09
2.08
f1 (ppm)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129.23
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128.19
128.02
126.61
126.06
126.03
126.00
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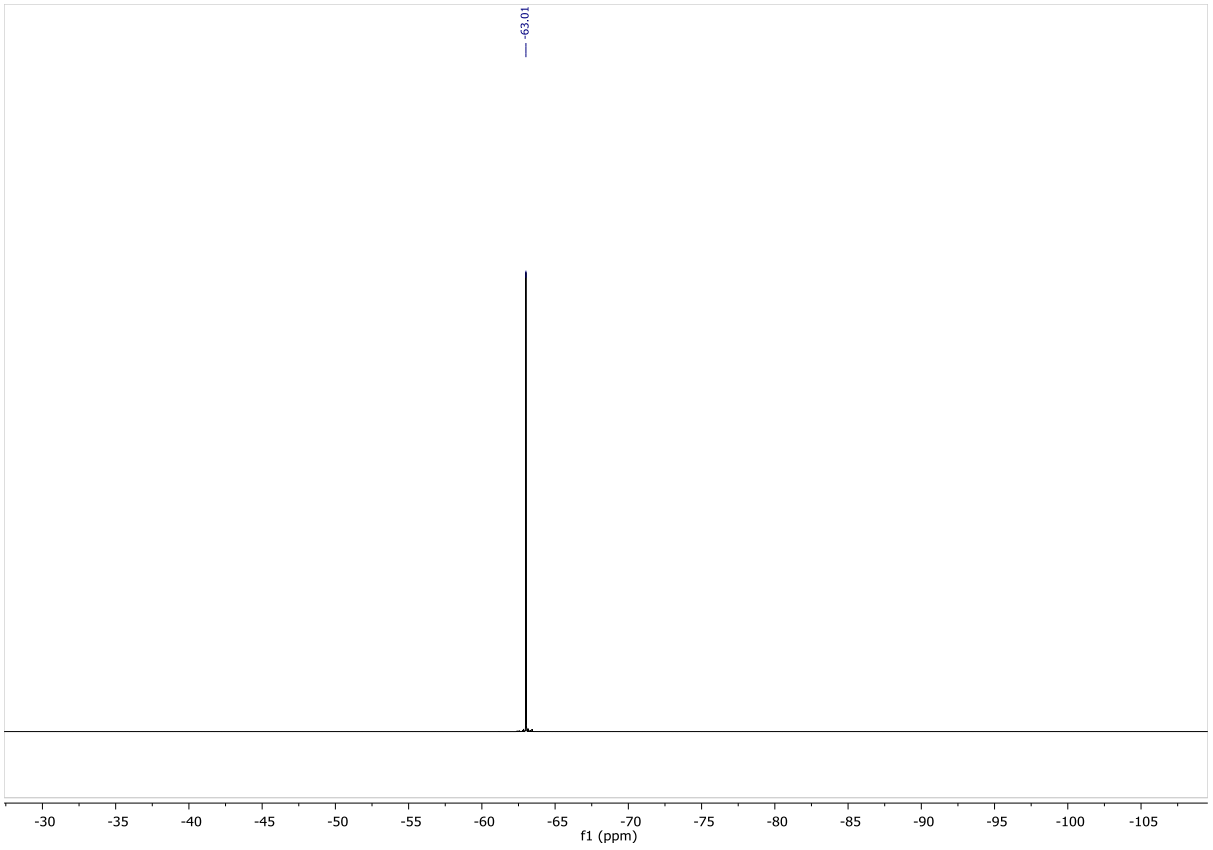
112.30
112.00
87.17
77.42
77.16
76.91
43.36
f1 (ppm)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-65
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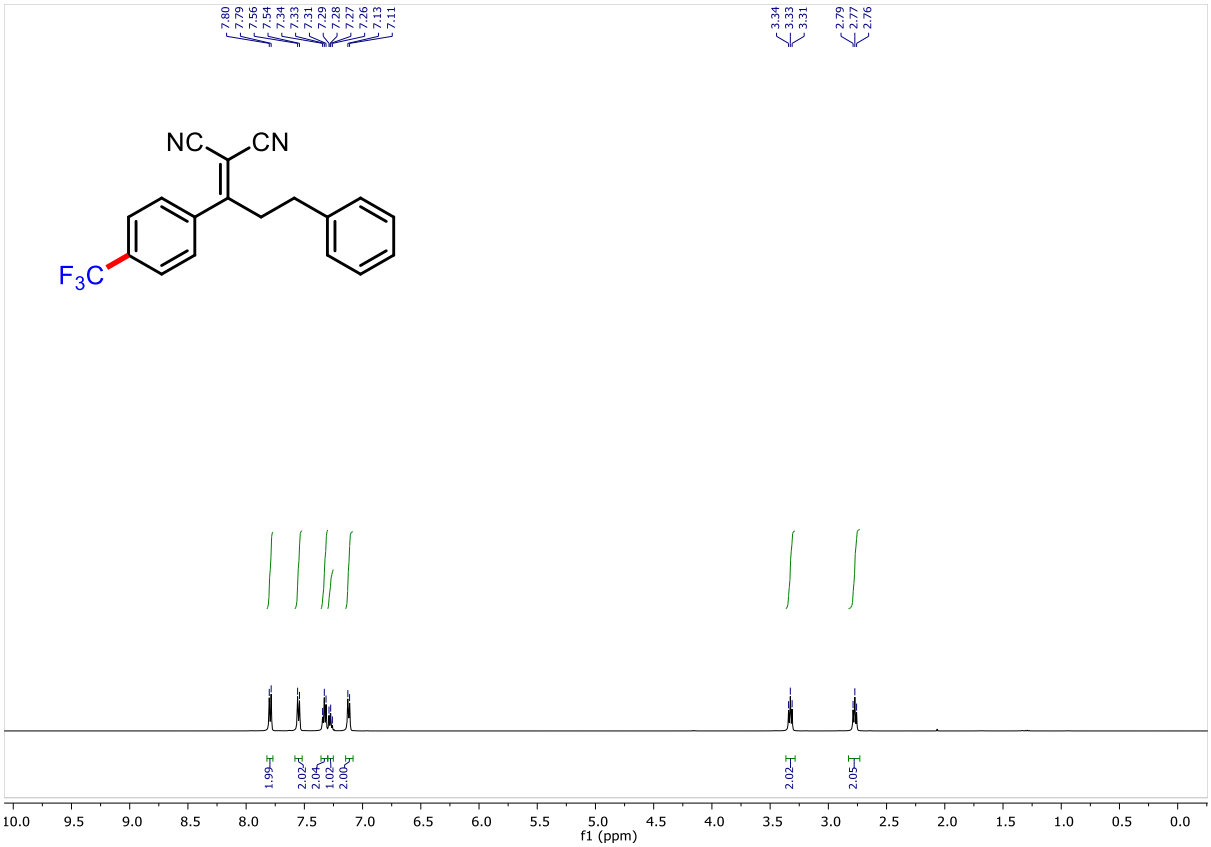
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)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7.29
7.28
7.27
7.26
7.13
7.11
3.34
3.33
3.31
2.79
2.77
2.76
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CN
F3C
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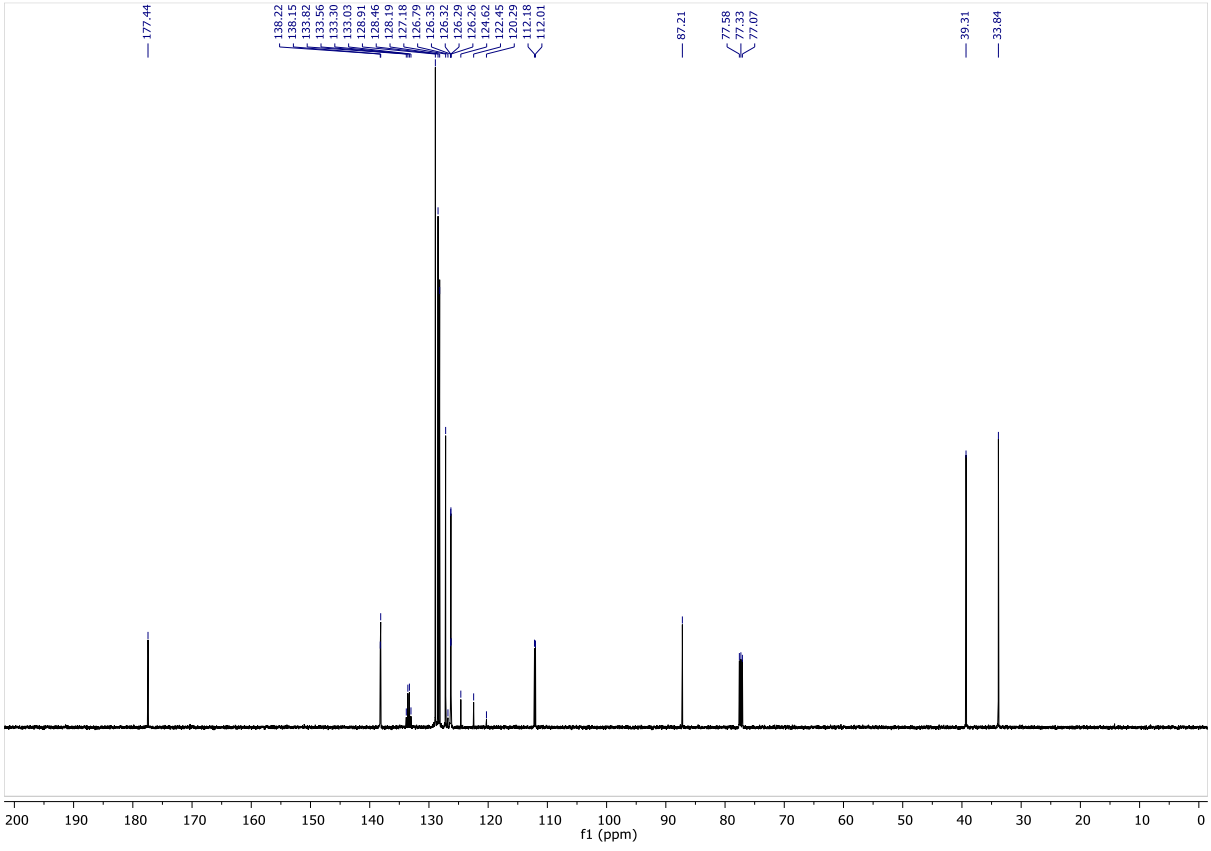
2.02
2.04
1.02
2.00
2.02
2.05
f1 (ppm)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126.79
126.35
126.32
126.29
126.26
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122.45
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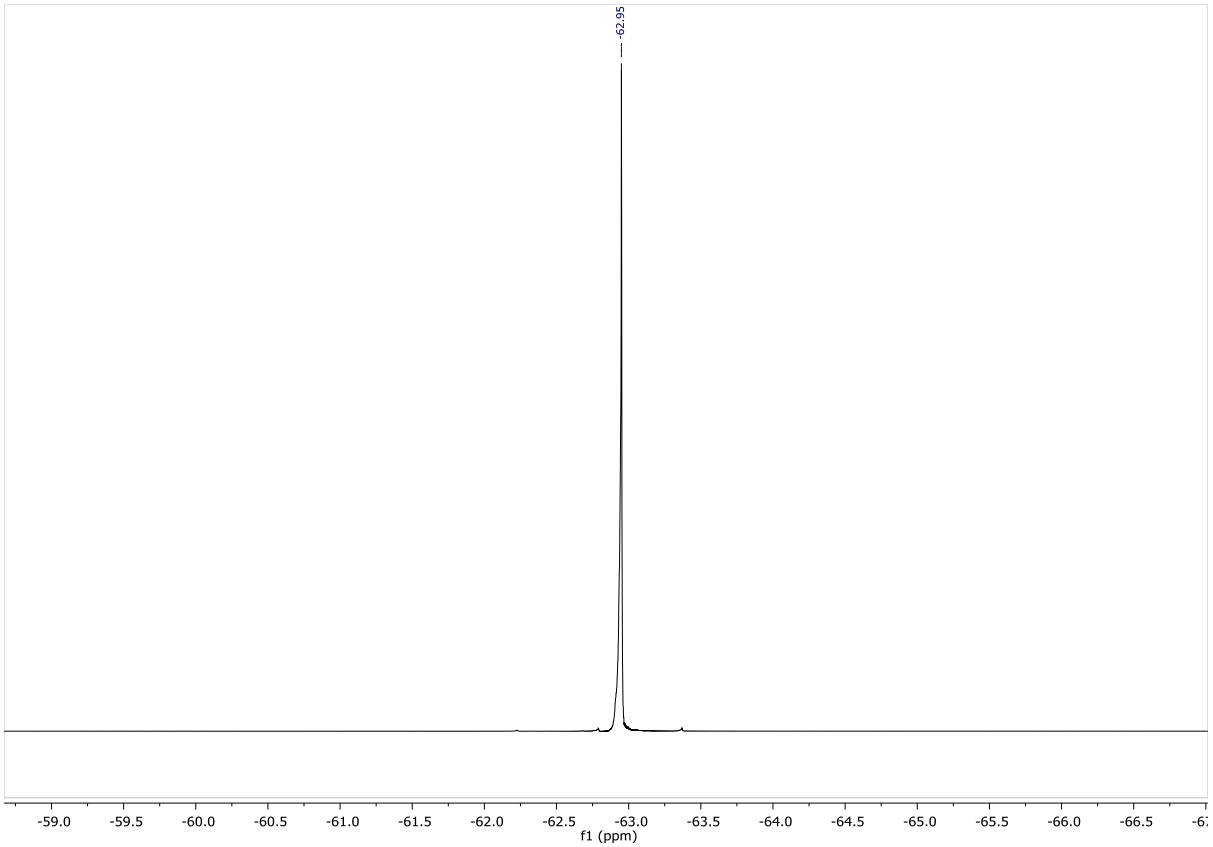
112.18
112.01
87.21
77.58
77.33
77.07
39.31
33.84
f1 (ppm)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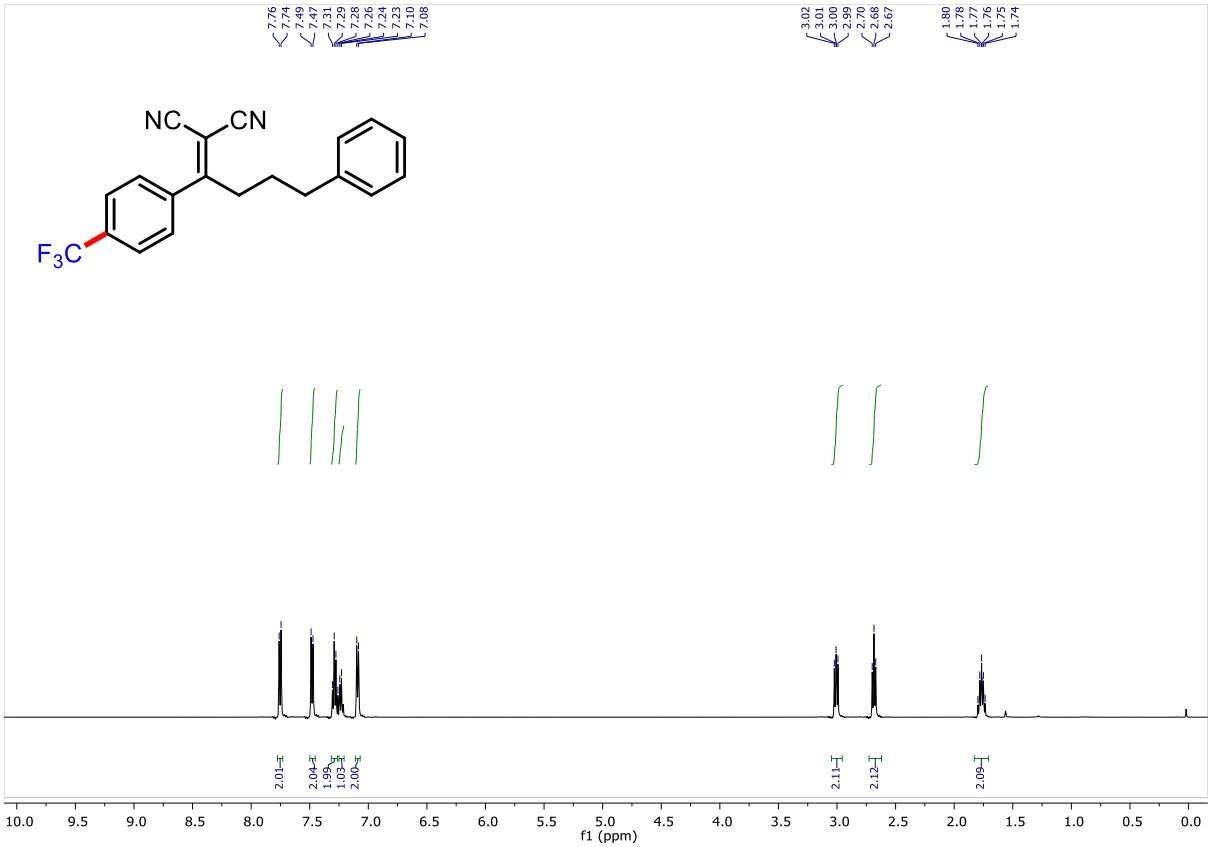
-65.5
-66.0
-66.5
f1 (ppm)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CN
F3C
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7.26
7.24
7.23
7.10
7.08
3.02
3.01
3.00
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2.68
2.67
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1.75
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1.03
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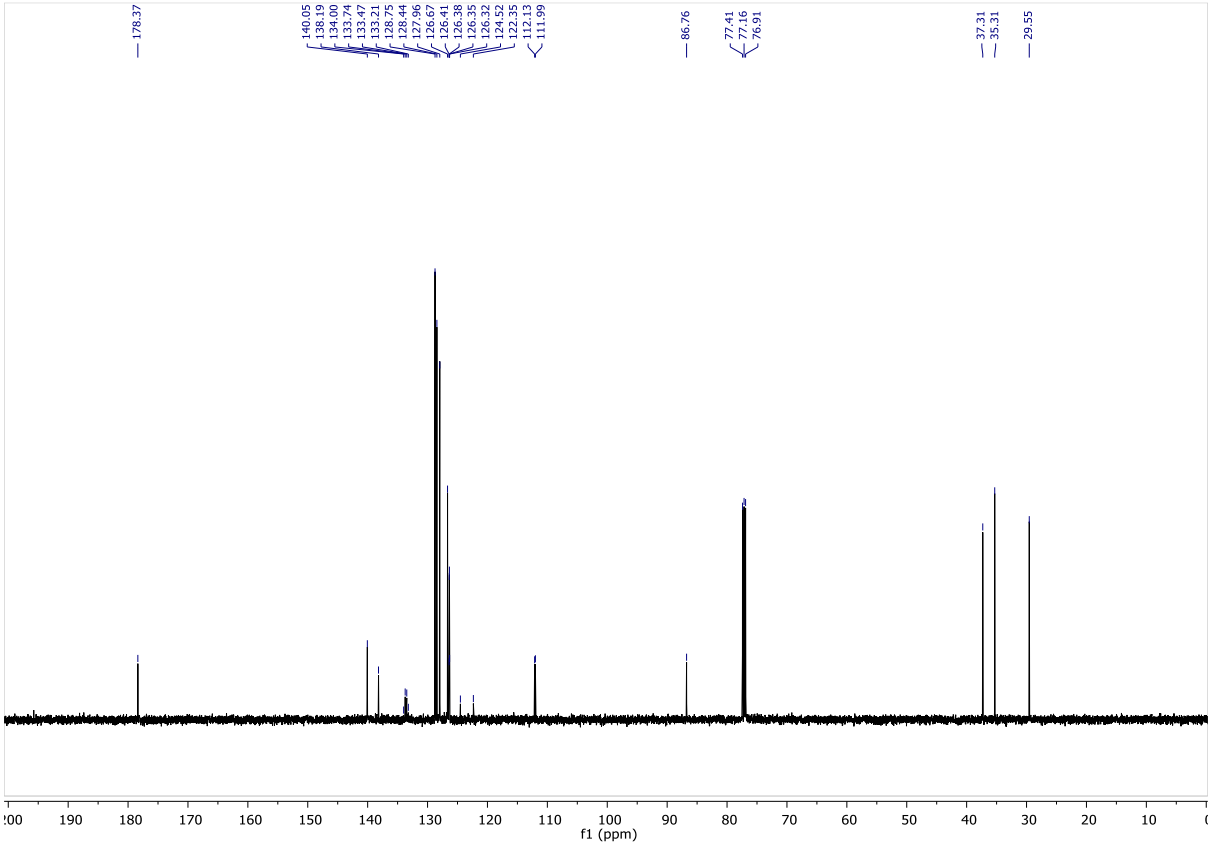
2.09
f1 (ppm)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126.35
126.32
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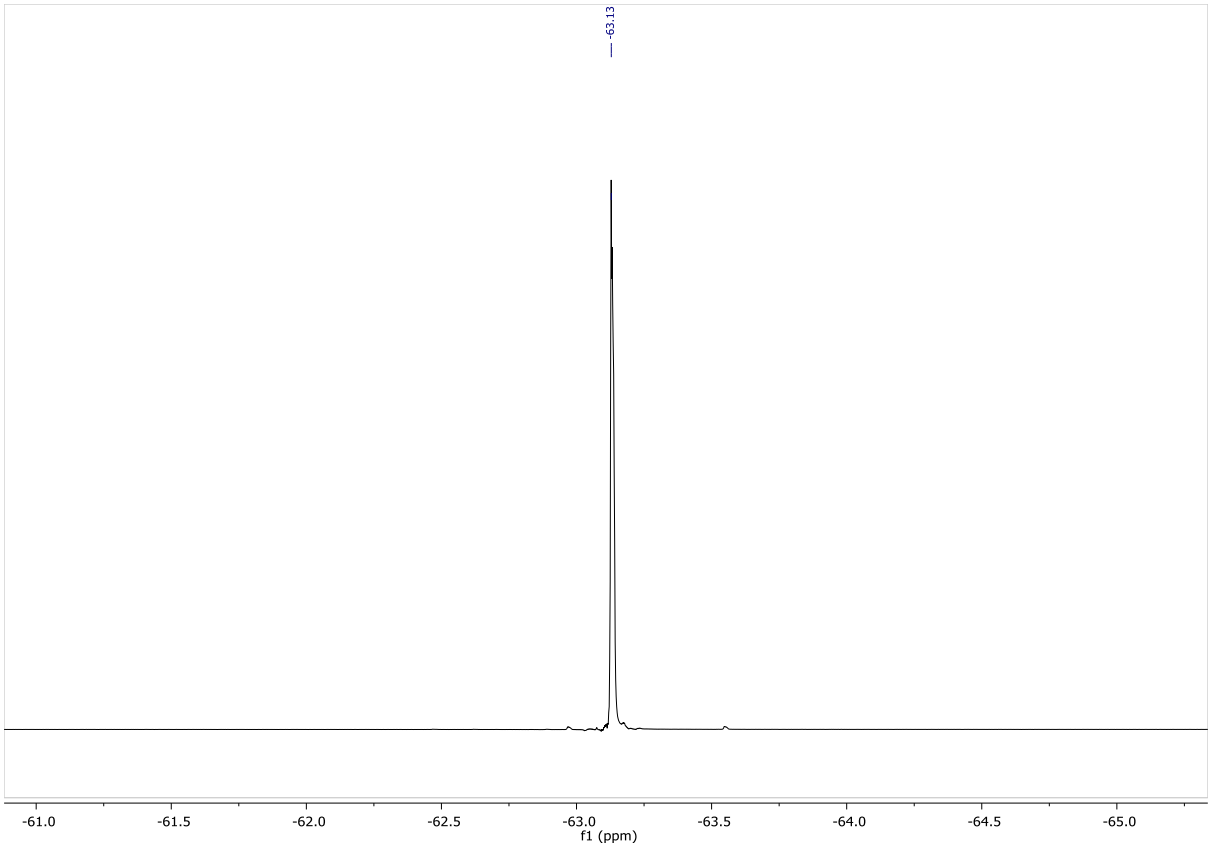
76.91
37.31
35.31
29.55
f1 (ppm)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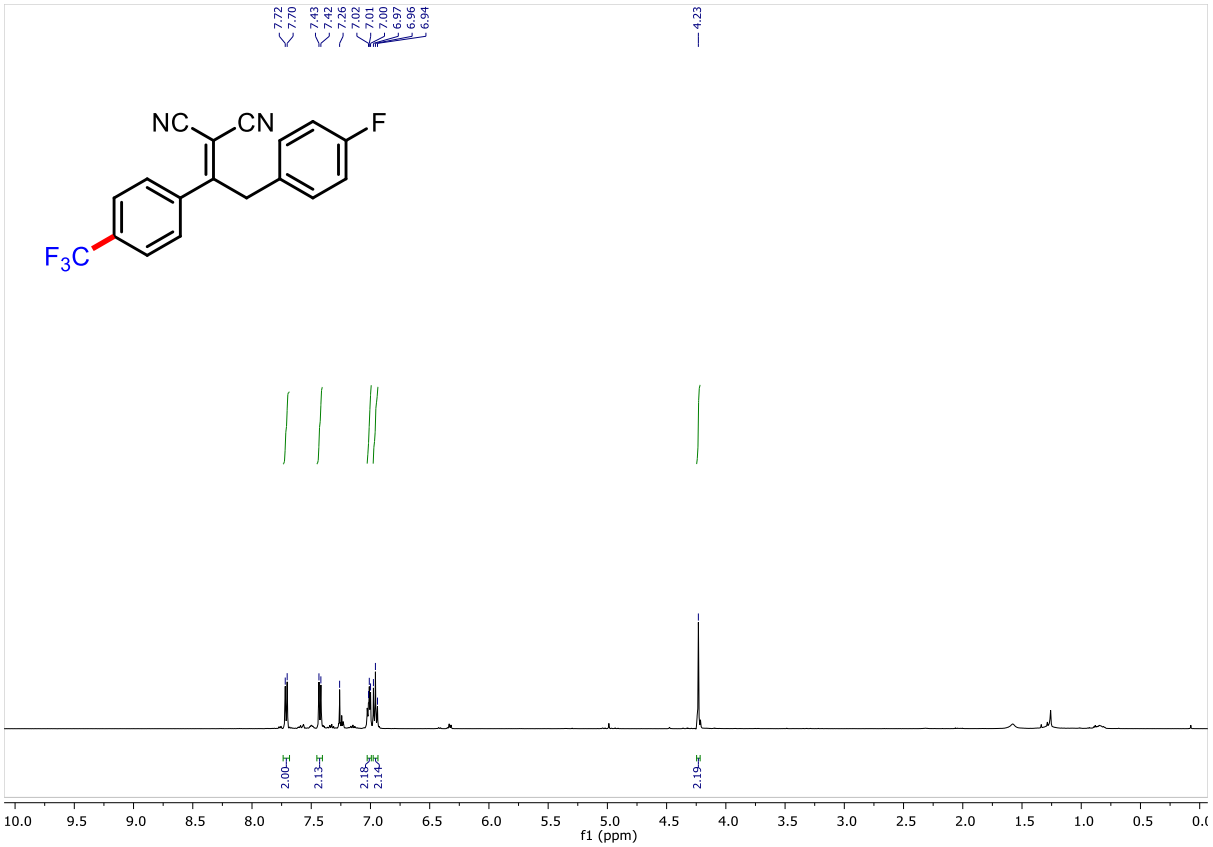
-65.0
f1 (ppm)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7.26
7.02
7.01
7.00
6.97
6.96
6.94
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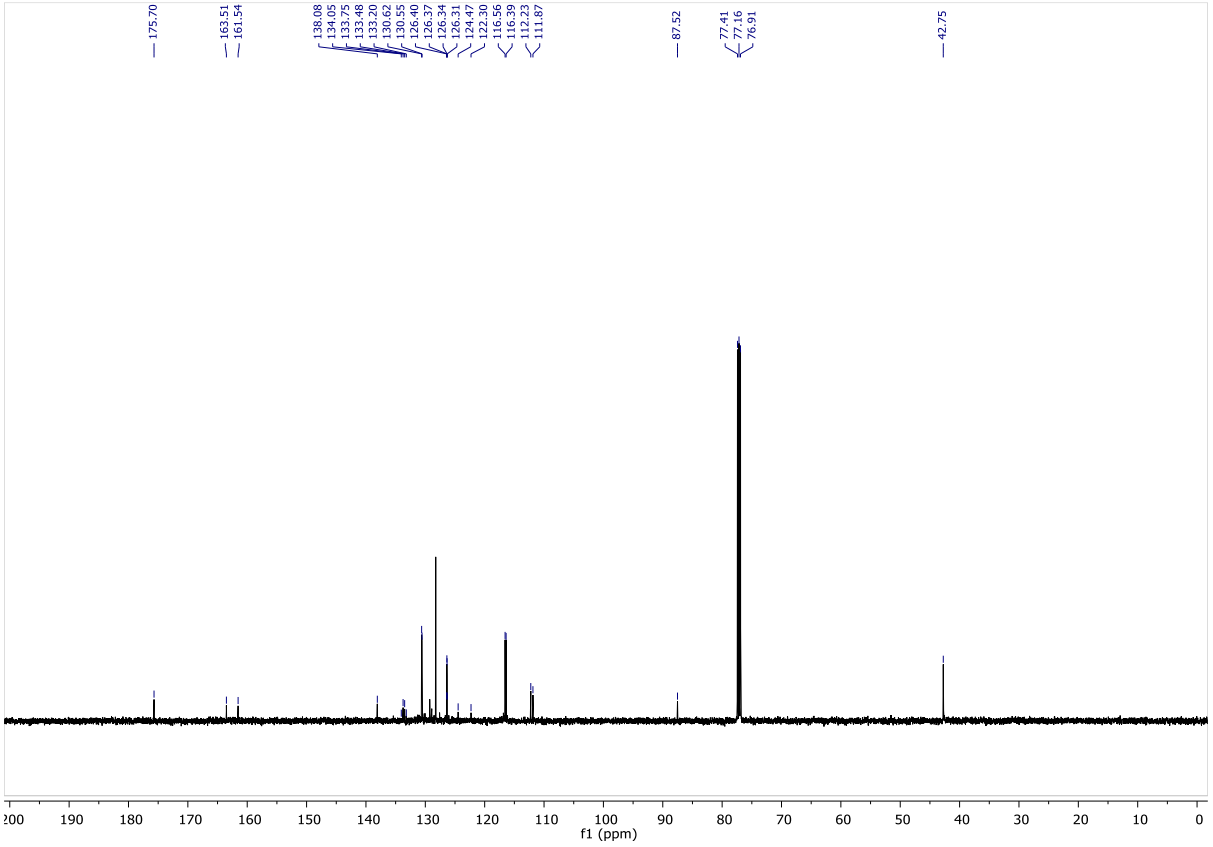
NC
CN
F
F3C
2.00
2.13
2.18
2.14
2.19
f1 (ppm)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126.31
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77.16
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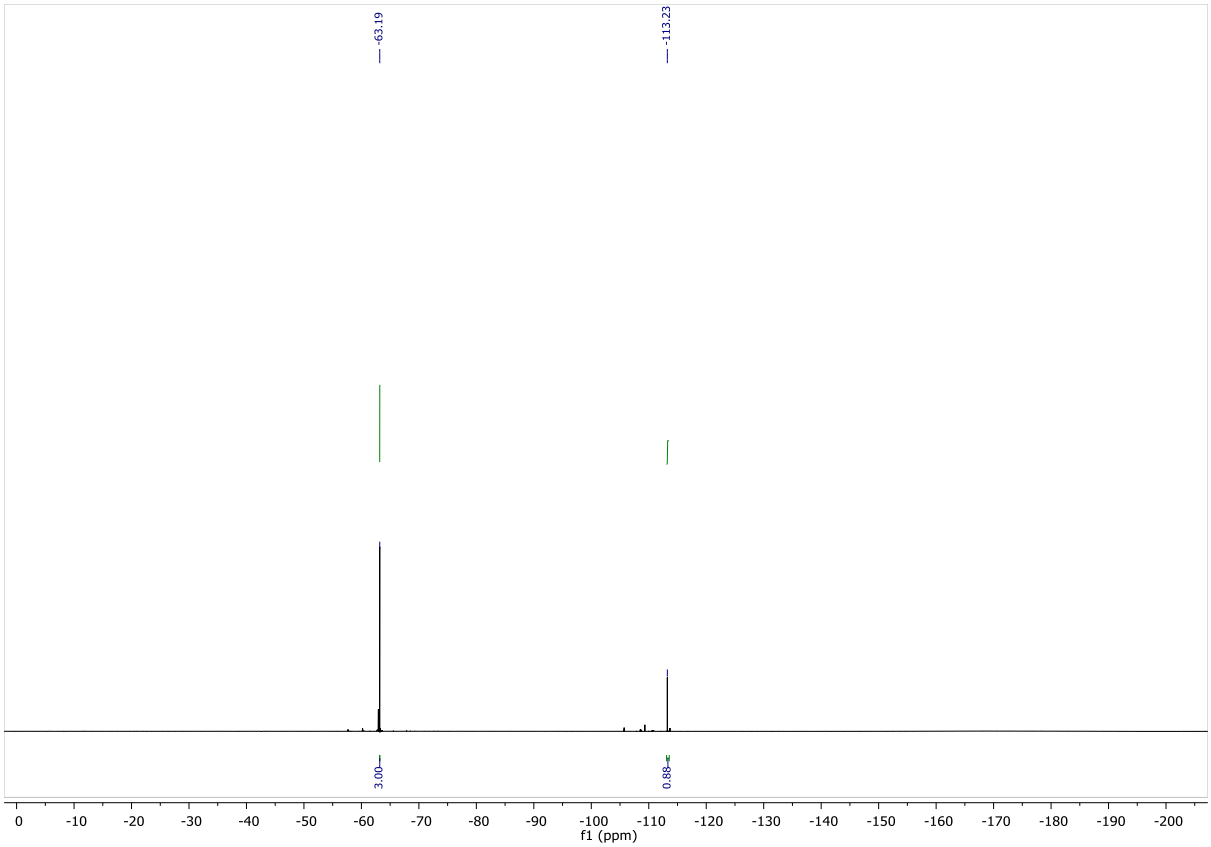
42.75
f1 (ppm)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0
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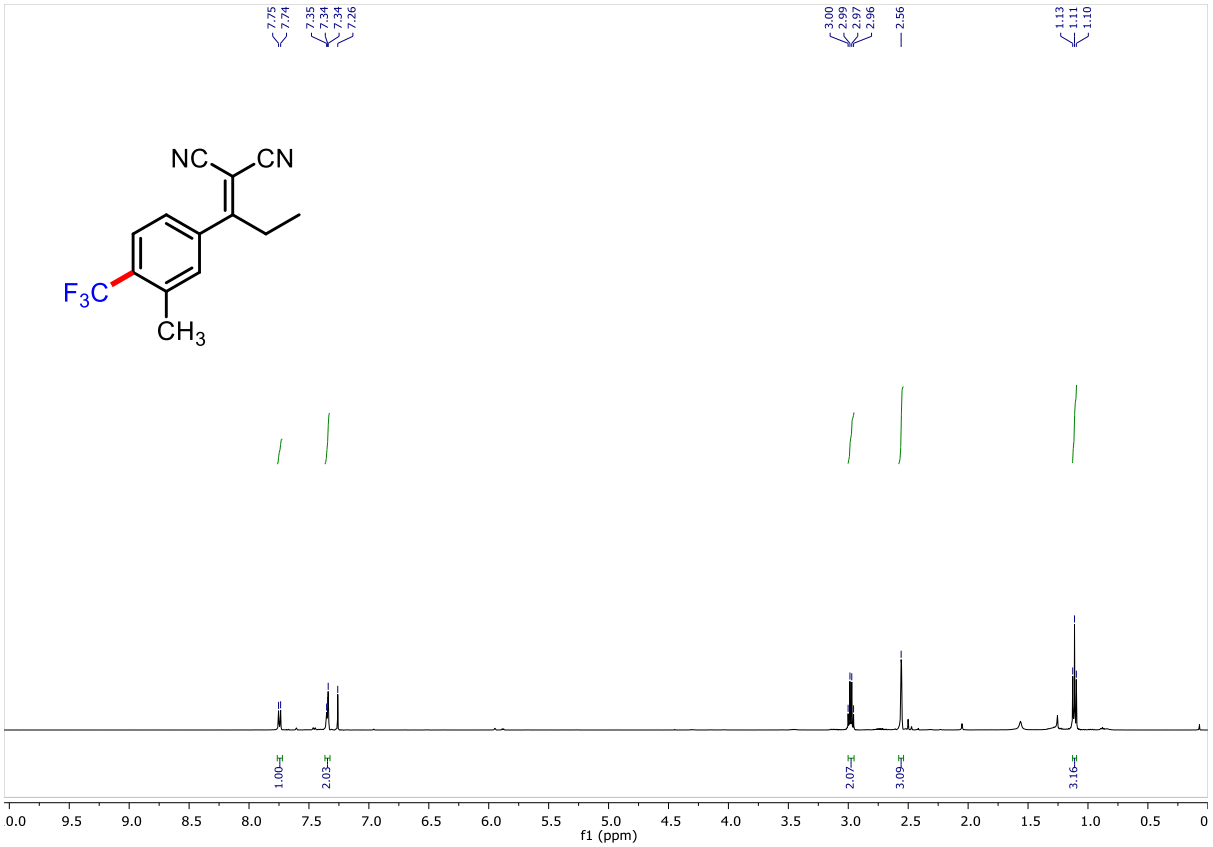
f1 (ppm)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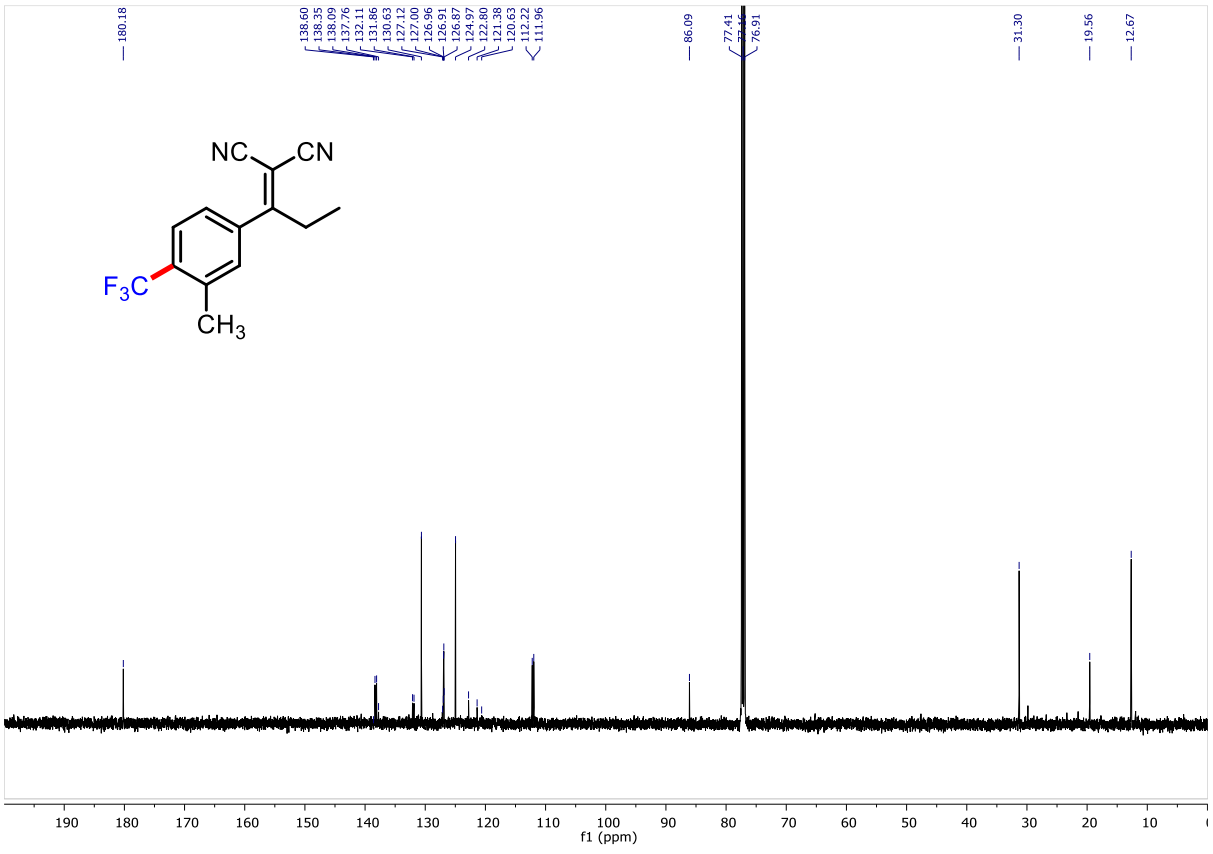
2.96
2.56
1.13
1.11
1.10
NC
CN
F3C
CH3
1.00
2.03
2.07
3.09
3.16
f1 (ppm)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130.63
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127.00
126.96
126.91
126.87
124.97
122.80
121.38
120.63
112.22
111.96
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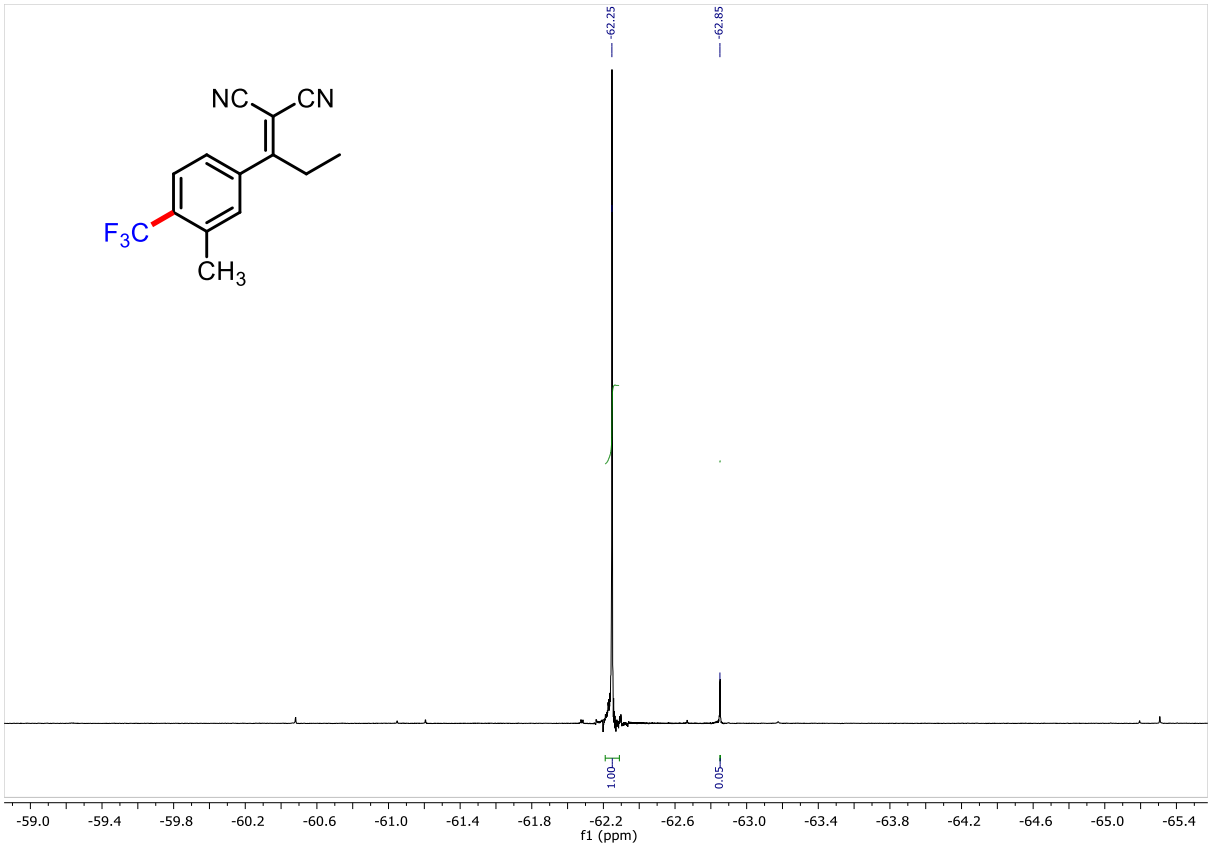
77.16
76.91
31.30
19.56
12.67
NC
CN
F3C
CH3
f1 (ppm)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-60.2
-60.6
-61.0
-61.4
-61.8
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-63.8
-64.2
-64.6
-65.0
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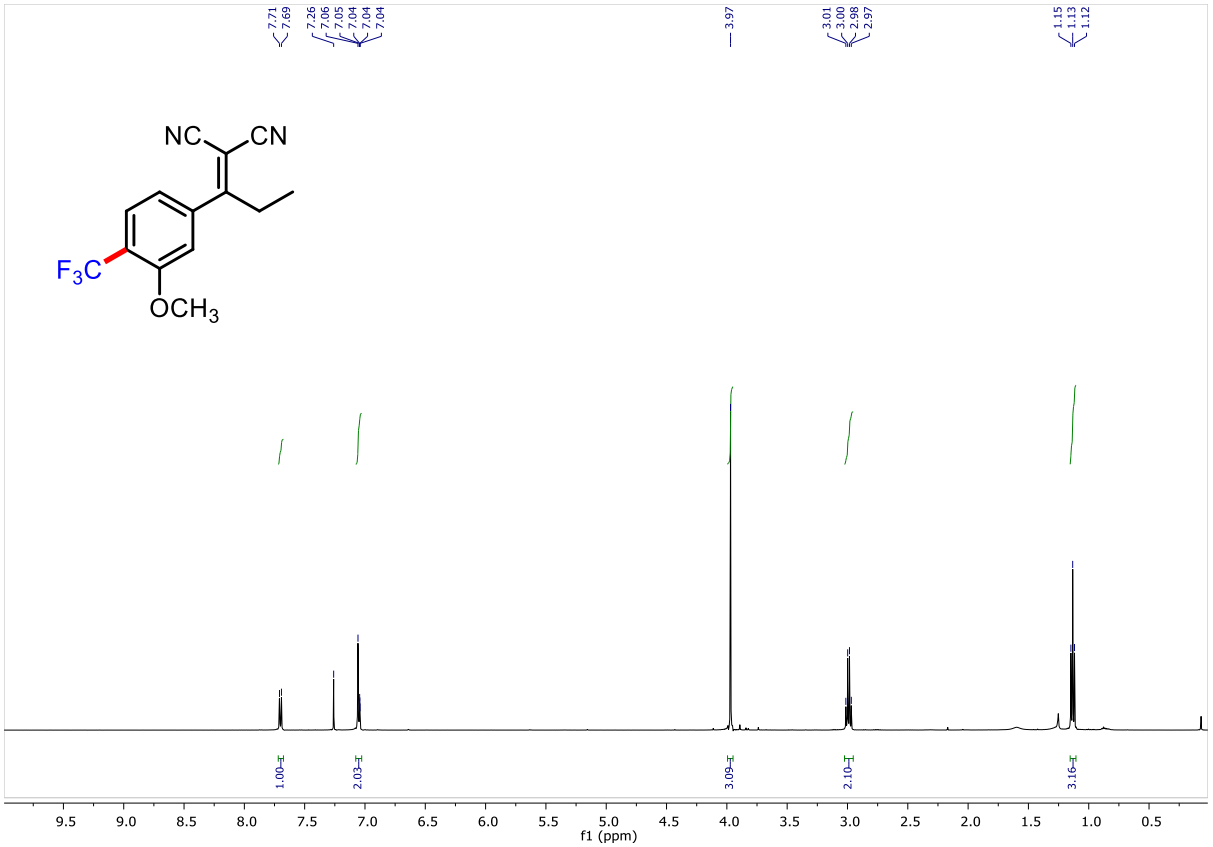
f1 (ppm)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7.04
7.04
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3.01
3.00
2.98
2.97
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CN
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OCH3
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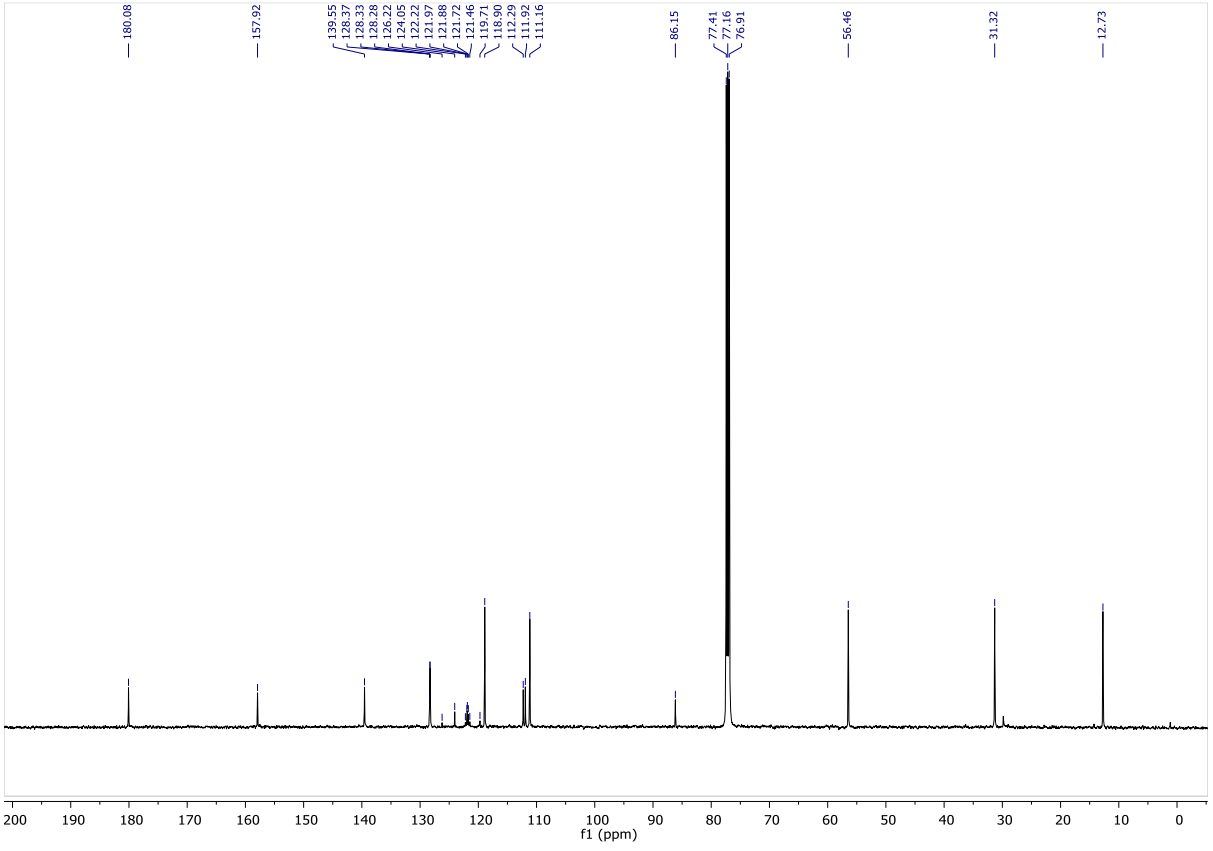
3.09
2.10
3.16
f1 (ppm)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124.05
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121.97
121.88
121.72
121.46
119.71
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112.29
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111.16
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77.16
76.91
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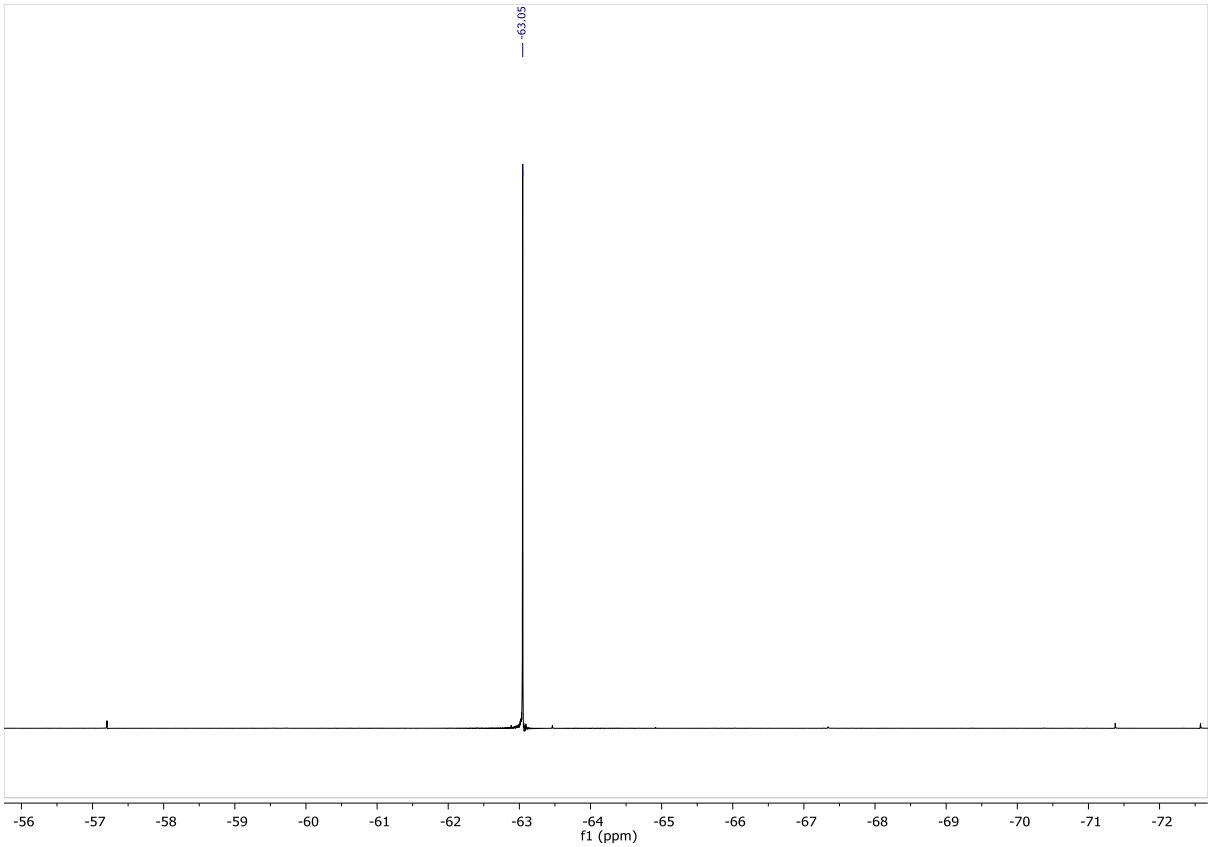
12.73
f1 (ppm)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-71
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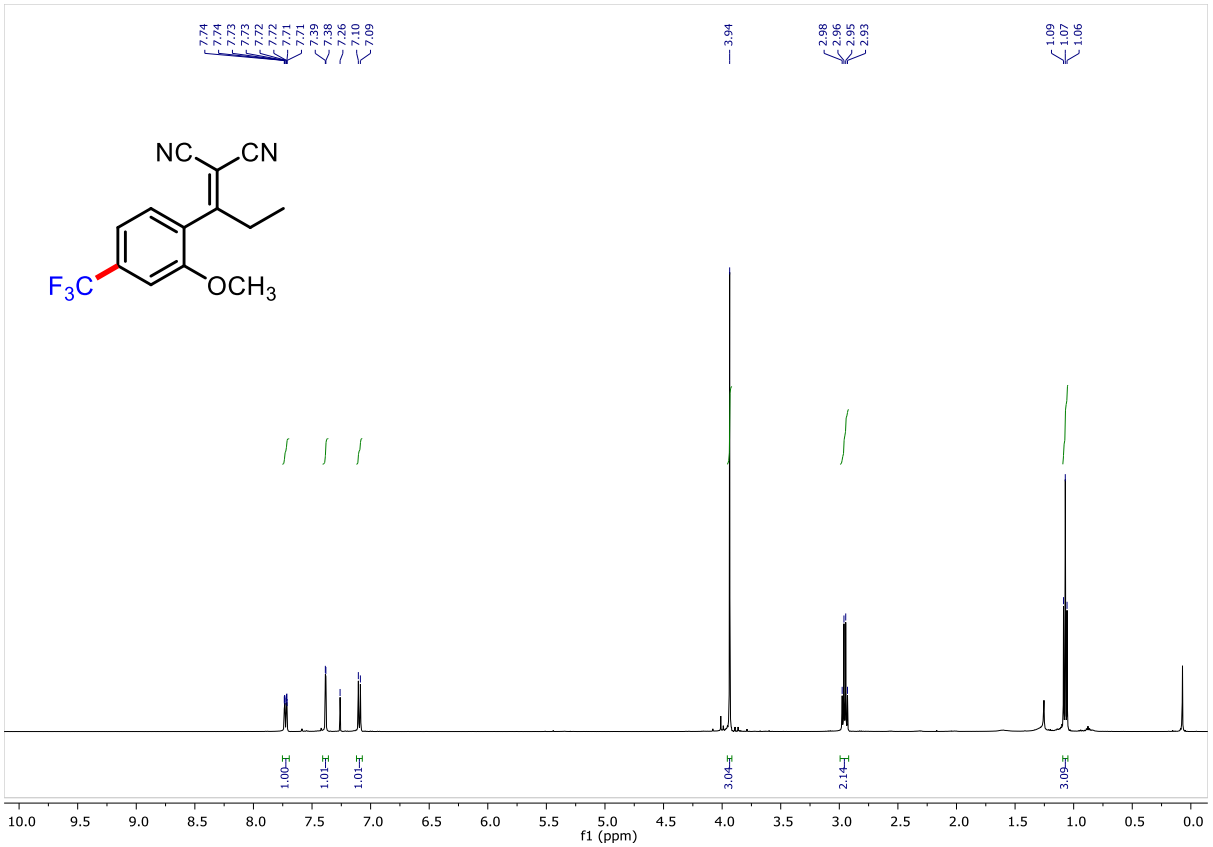
f1 (ppm)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7.71
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7.38
7.26
7.10
7.09
3.94
2.98
2.96
2.95
2.93
1.09
1.07
1.06
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CN
F3C
OCH3
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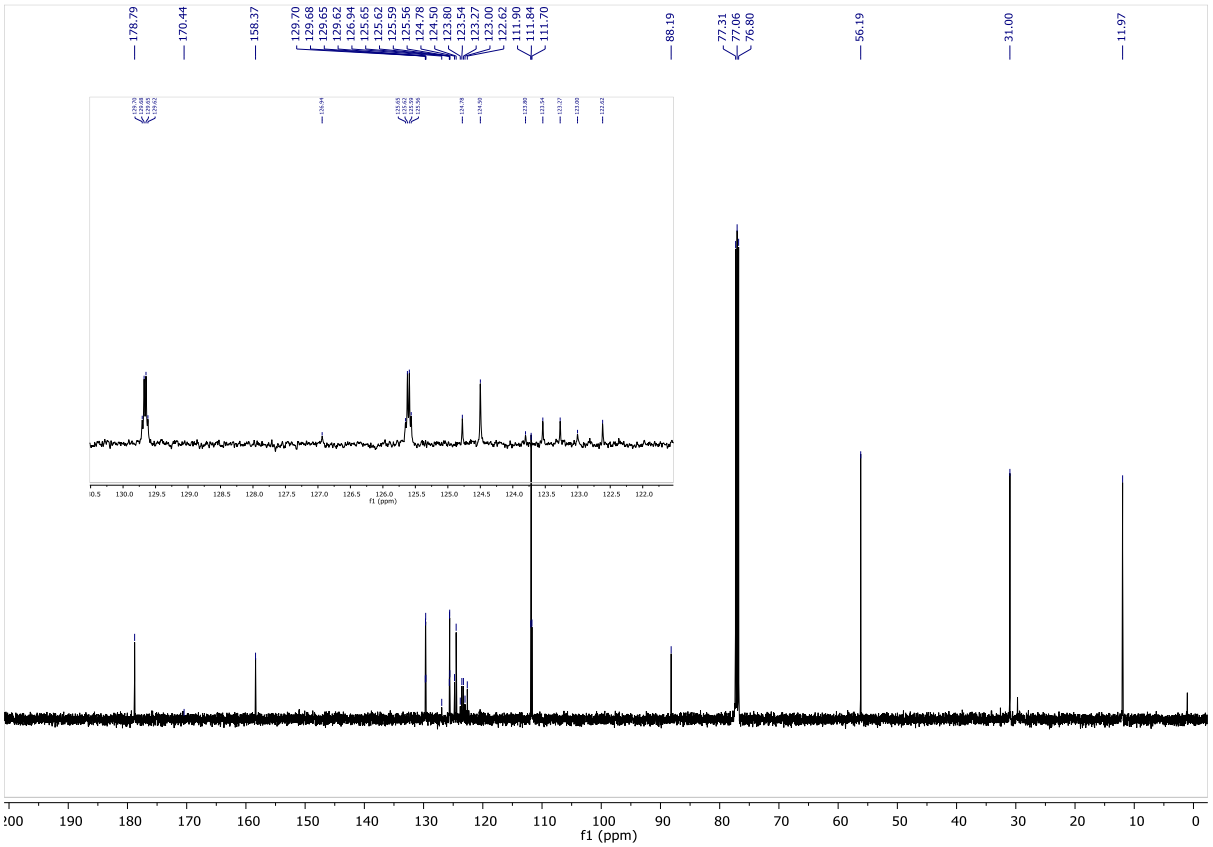
1.01
1.01
3.04
2.14
3.09
f1 (ppm)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126.94
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125.56
124.78
124.50
123.80
123.54
123.27
123.00
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111.90
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88.19
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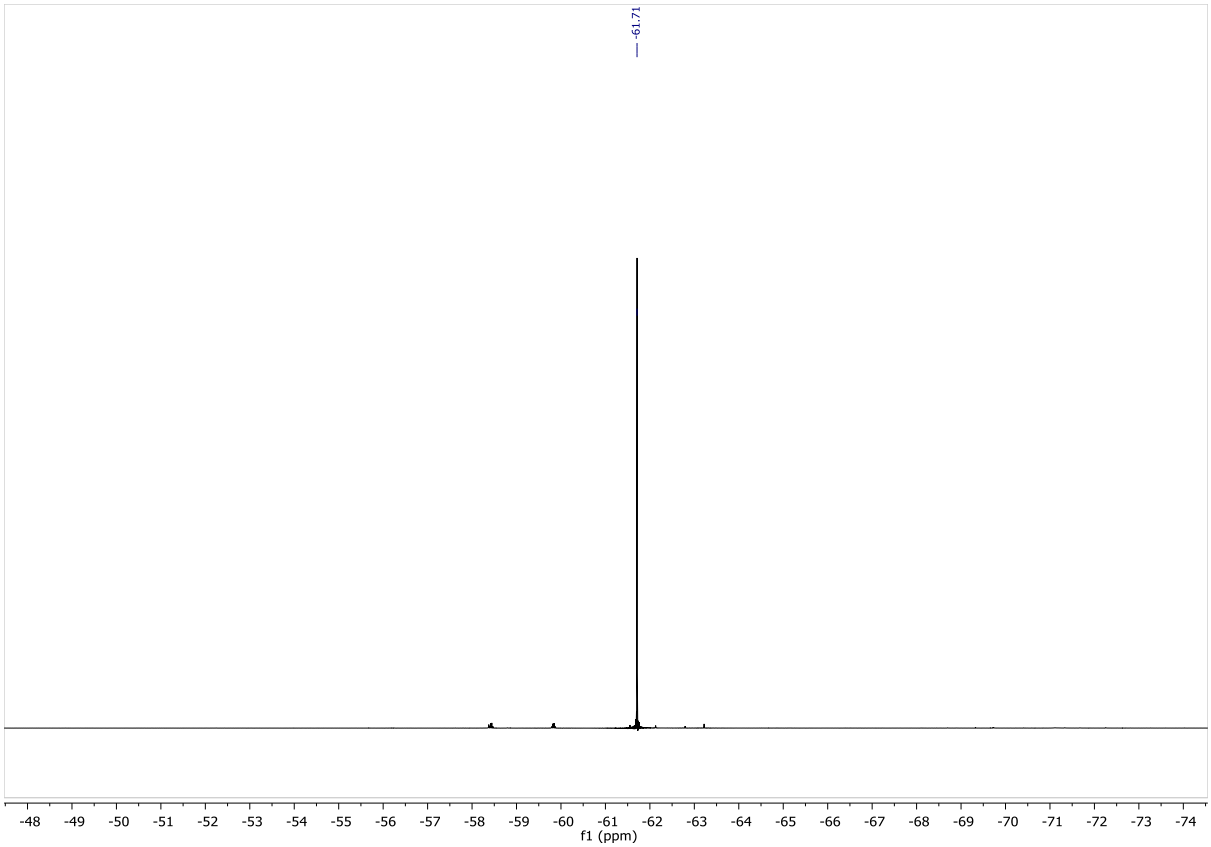
76.80
56.19
31.00
11.97
f1 (ppm)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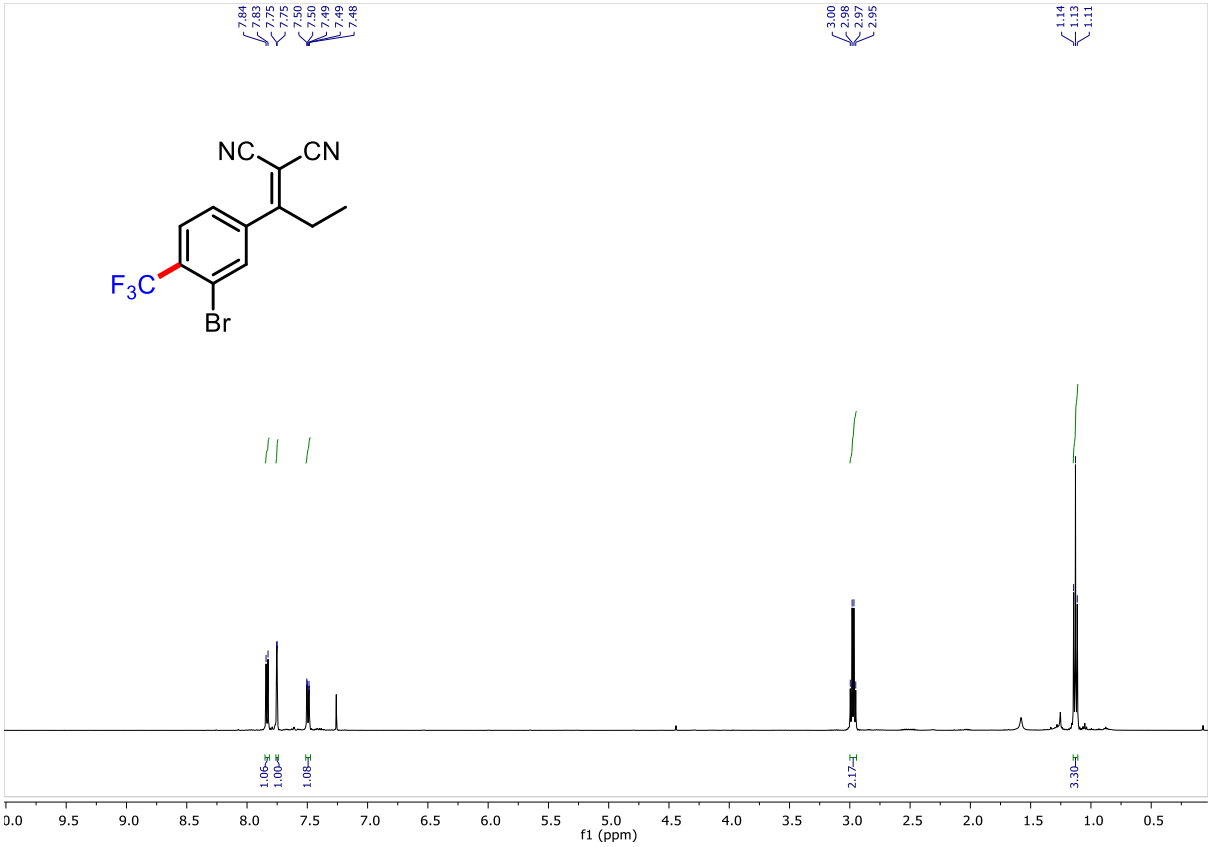
-48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74
f1 (ppm)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2.97
2.95
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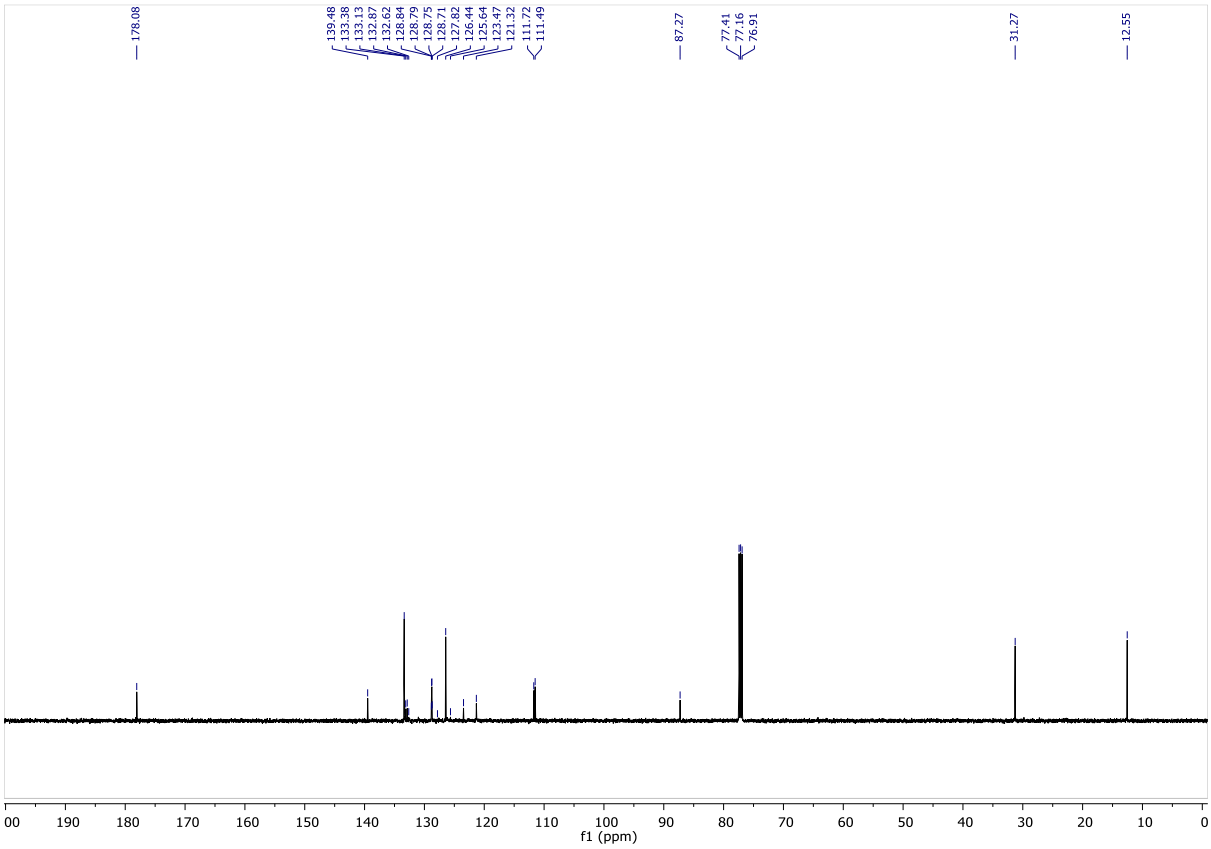
CN
F3C
Br
1.06
1.00
1.08
2.17
3.30
f1 (ppm)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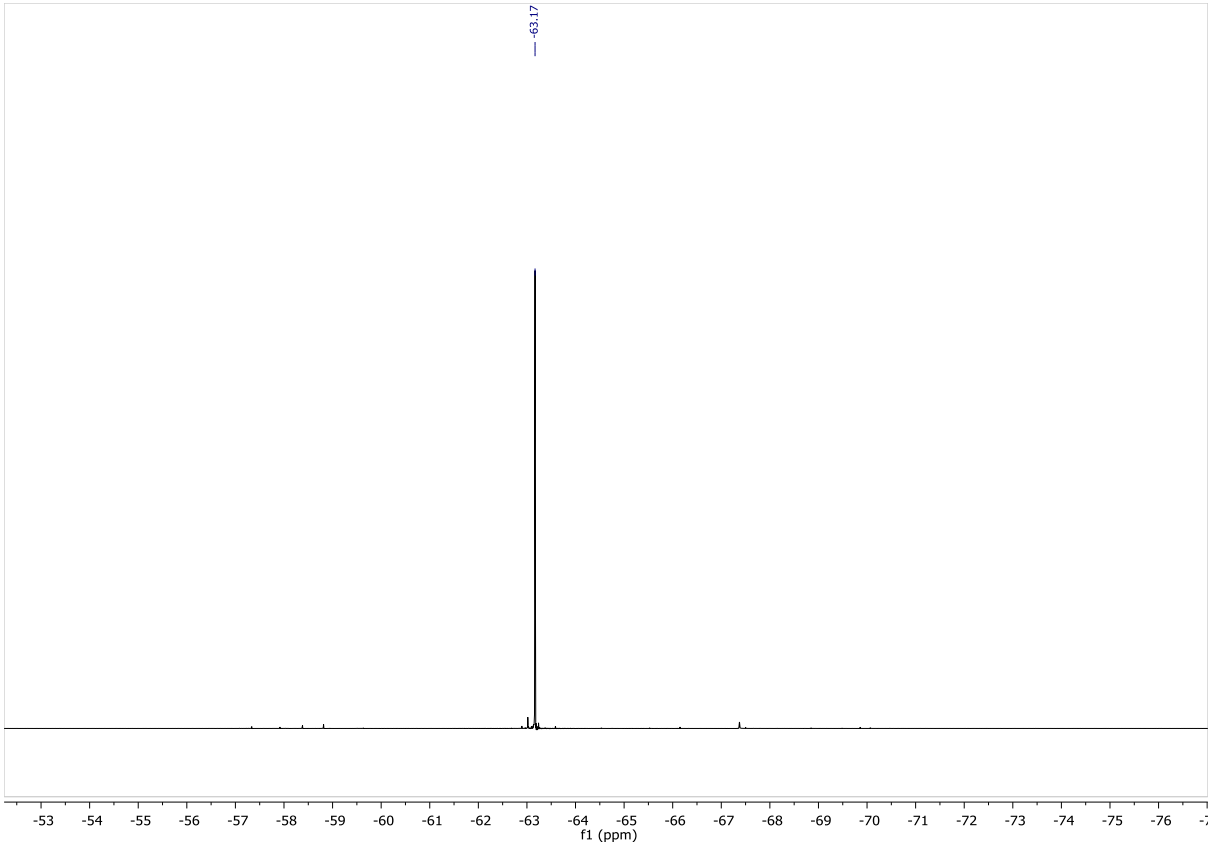
128.71
127.82
126.44
125.64
123.47
121.32
111.72
111.49
87.27
77.41
77.16
76.91
31.27
12.55
f1 (ppm)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-63
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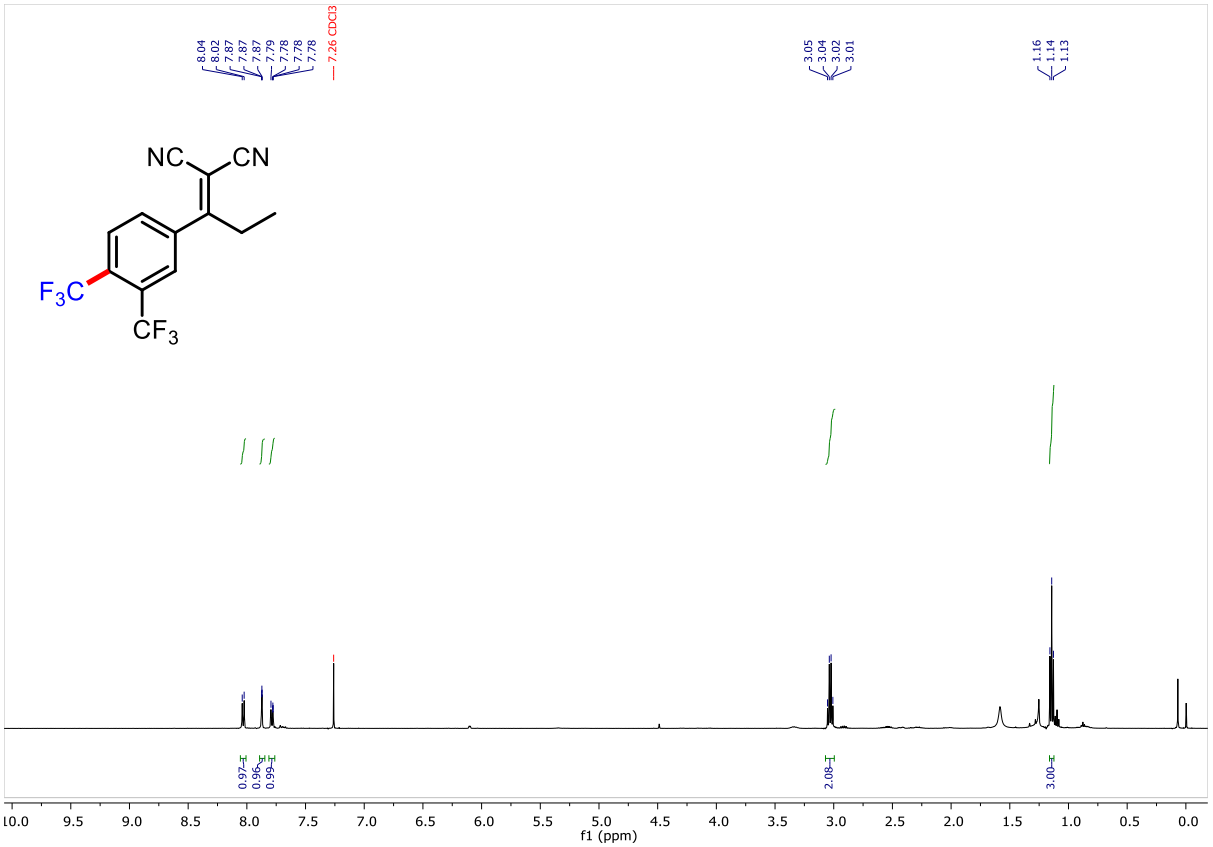
-72
-73
-74
-75
-76
f1 (ppm)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7.79
7.78
7.78
7.78
7.26 CDCl3
3.05
3.04
3.02
3.01
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1.14
1.13
NC
CN
F3C
CF3
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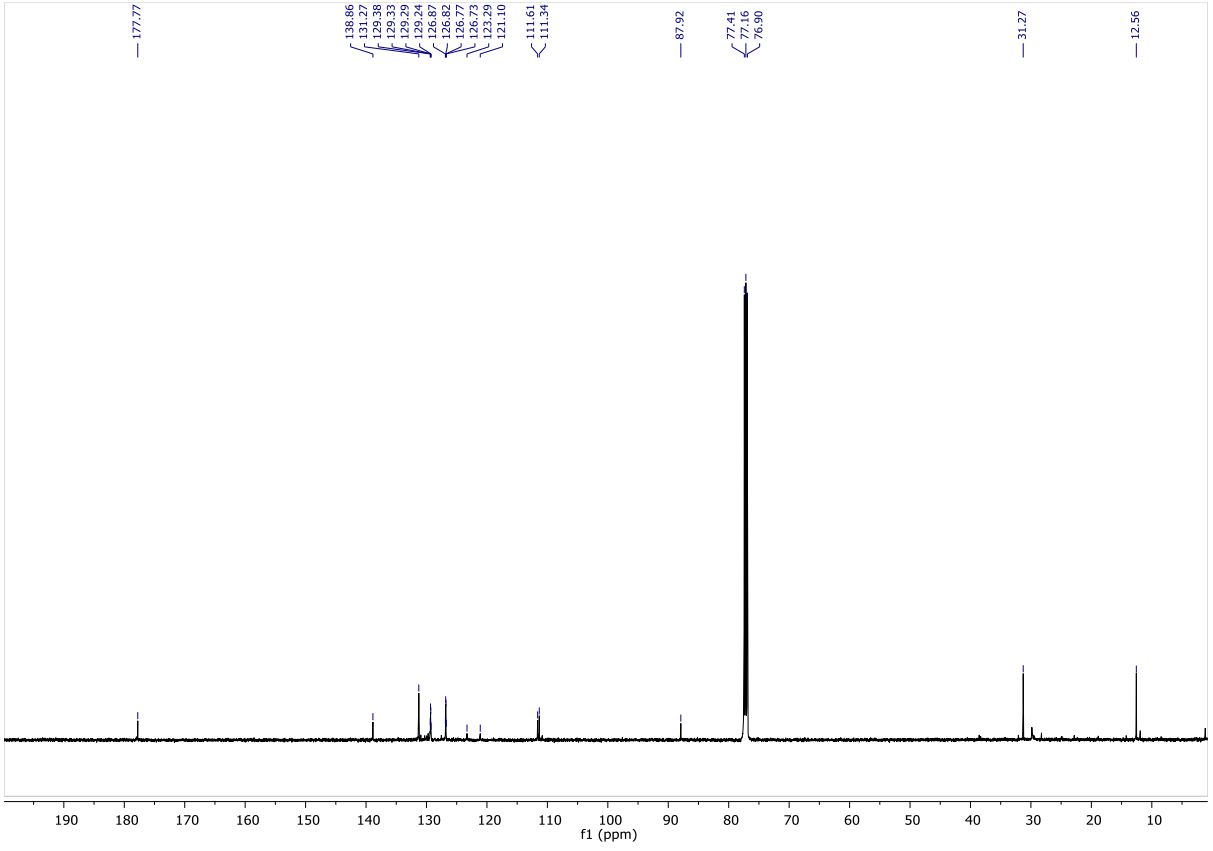
0.96
0.99
2.08
3.00
f1 (ppm)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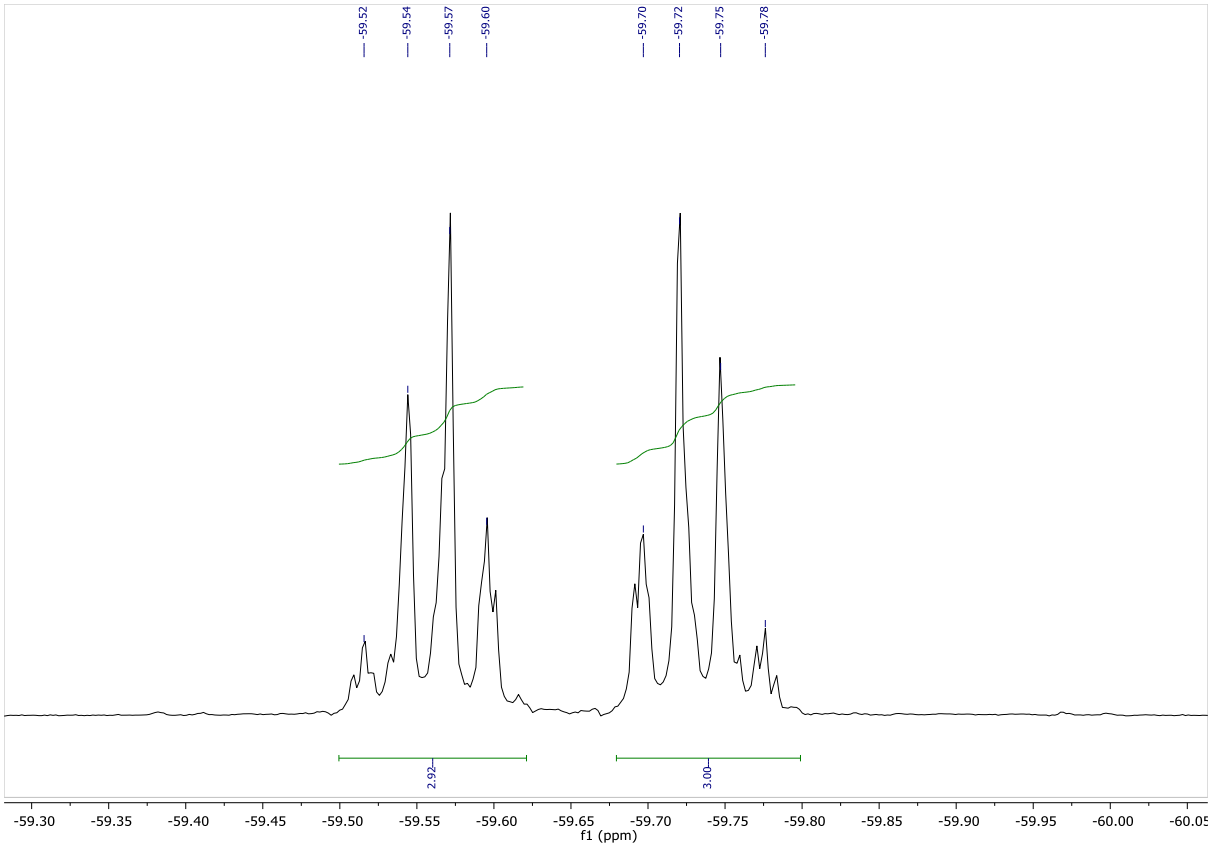
76.90
31.27
12.56
f1 (ppm)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-59.55
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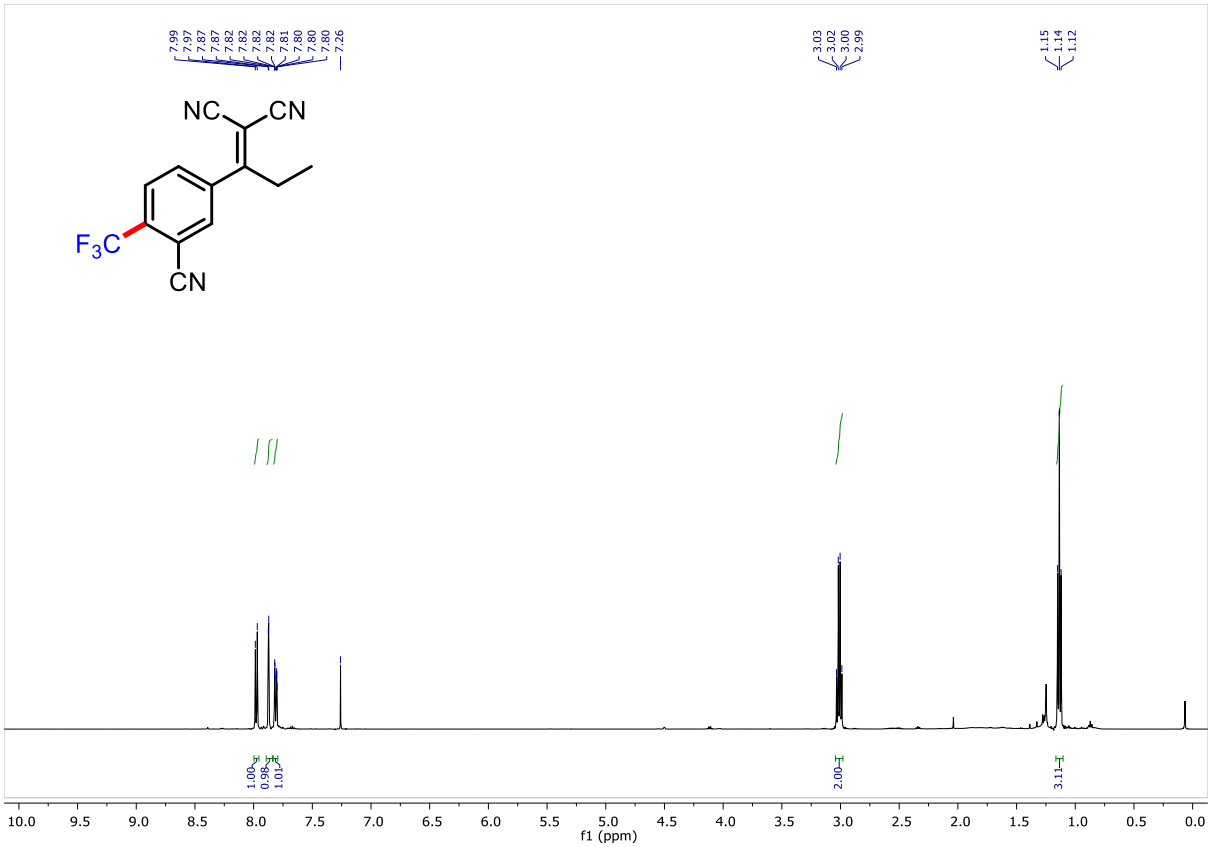
f1 (ppm)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7.80
7.80
7.26
3.03
3.02
3.00
2.99
1.15
1.14
1.12
NC
CN
F3C
CN
1.00
0.98
1.01
2.00
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
1.5
1.0
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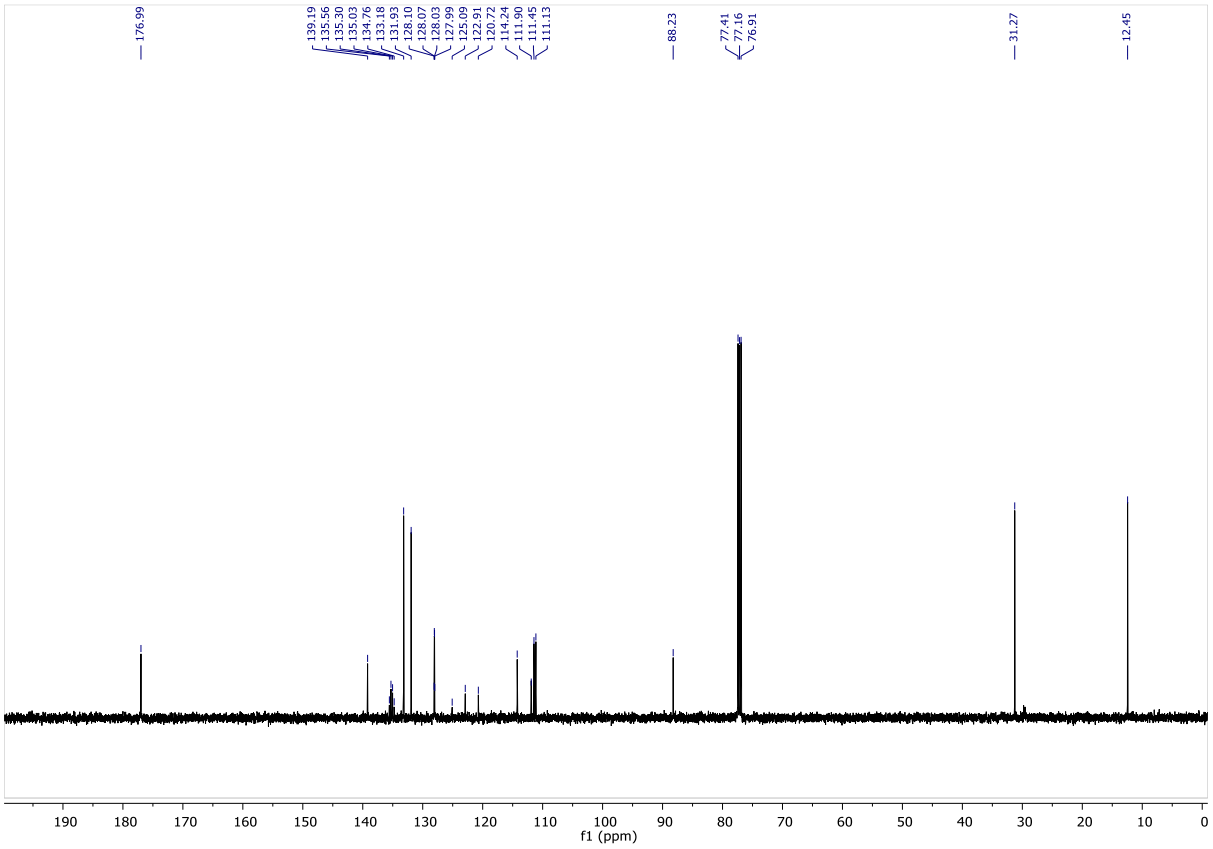
0.0
f1 (ppm)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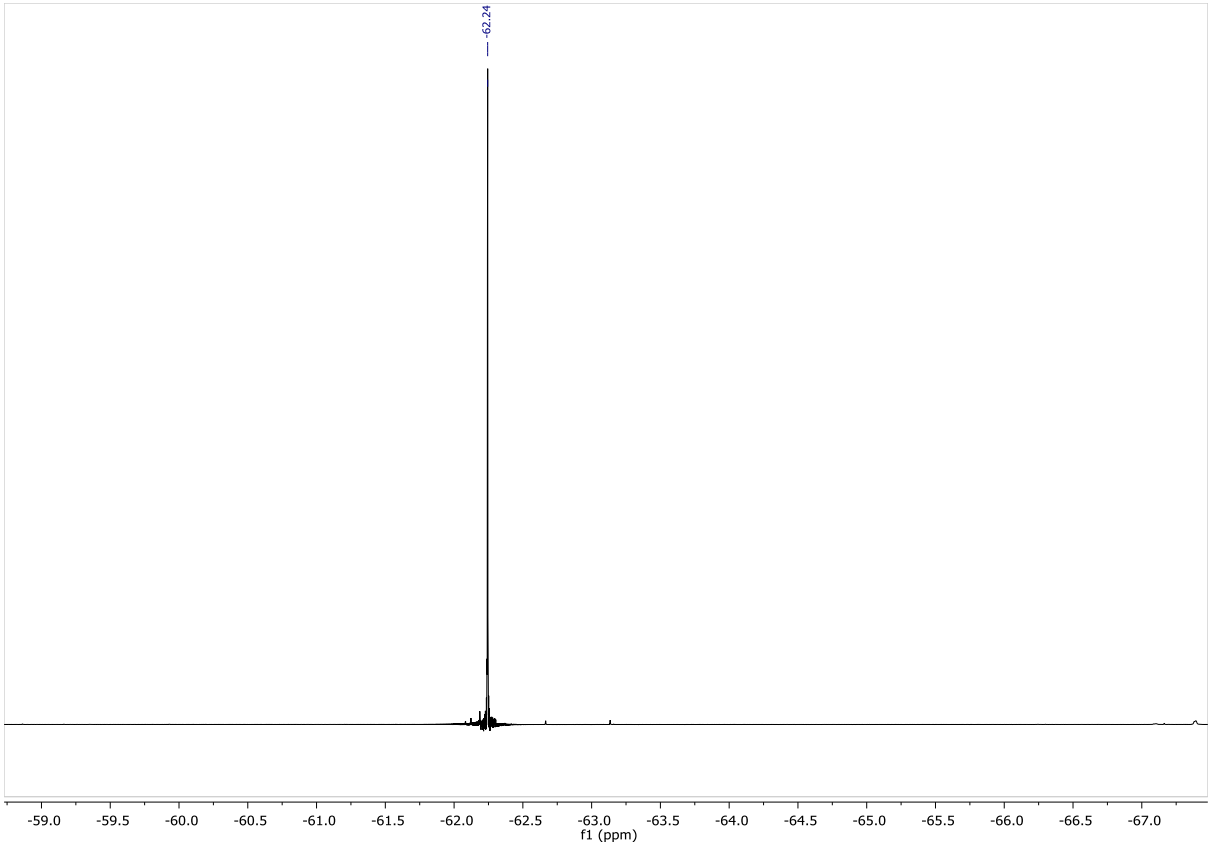
125.09
122.91
120.72
114.24
111.90
111.45
111.13
88.23
77.41
77.16
76.91
31.27
12.45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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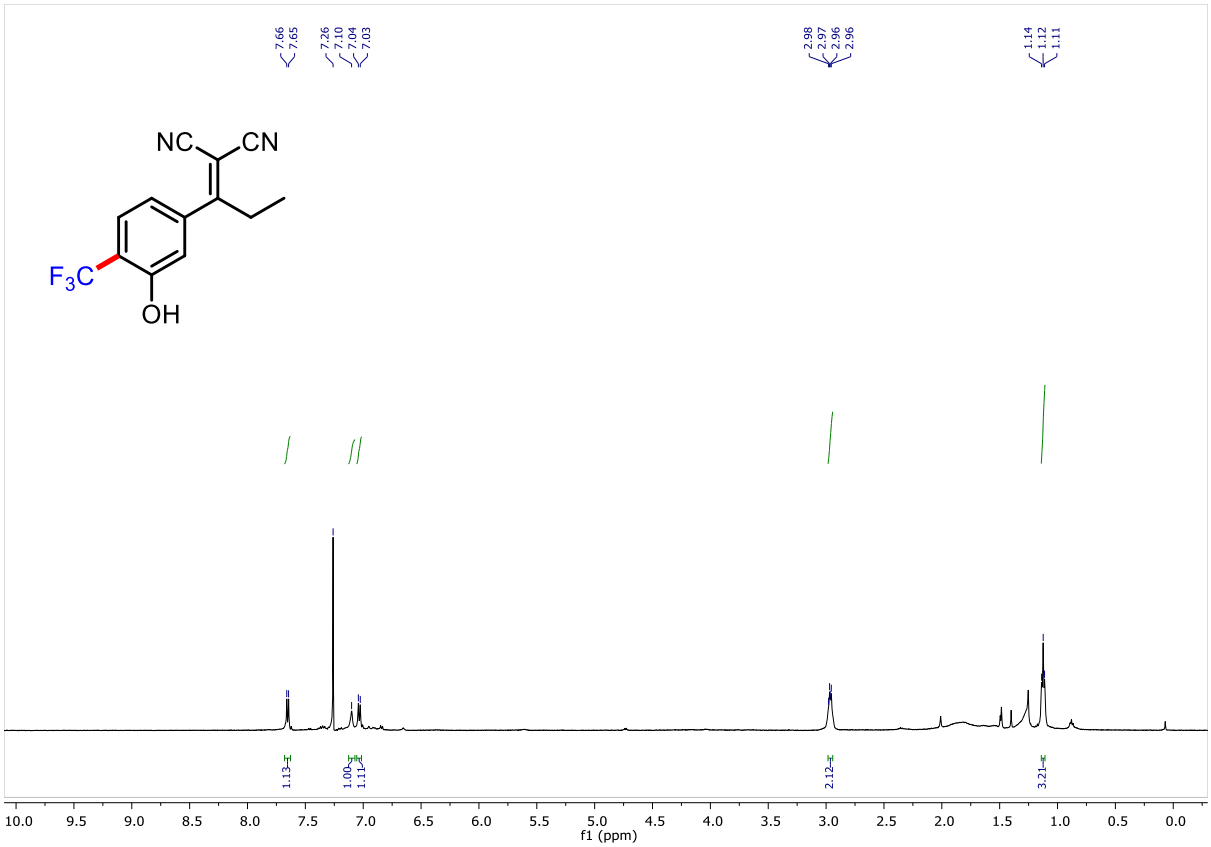
f1 (ppm)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7.65
7.26
7.10
7.04
7.03
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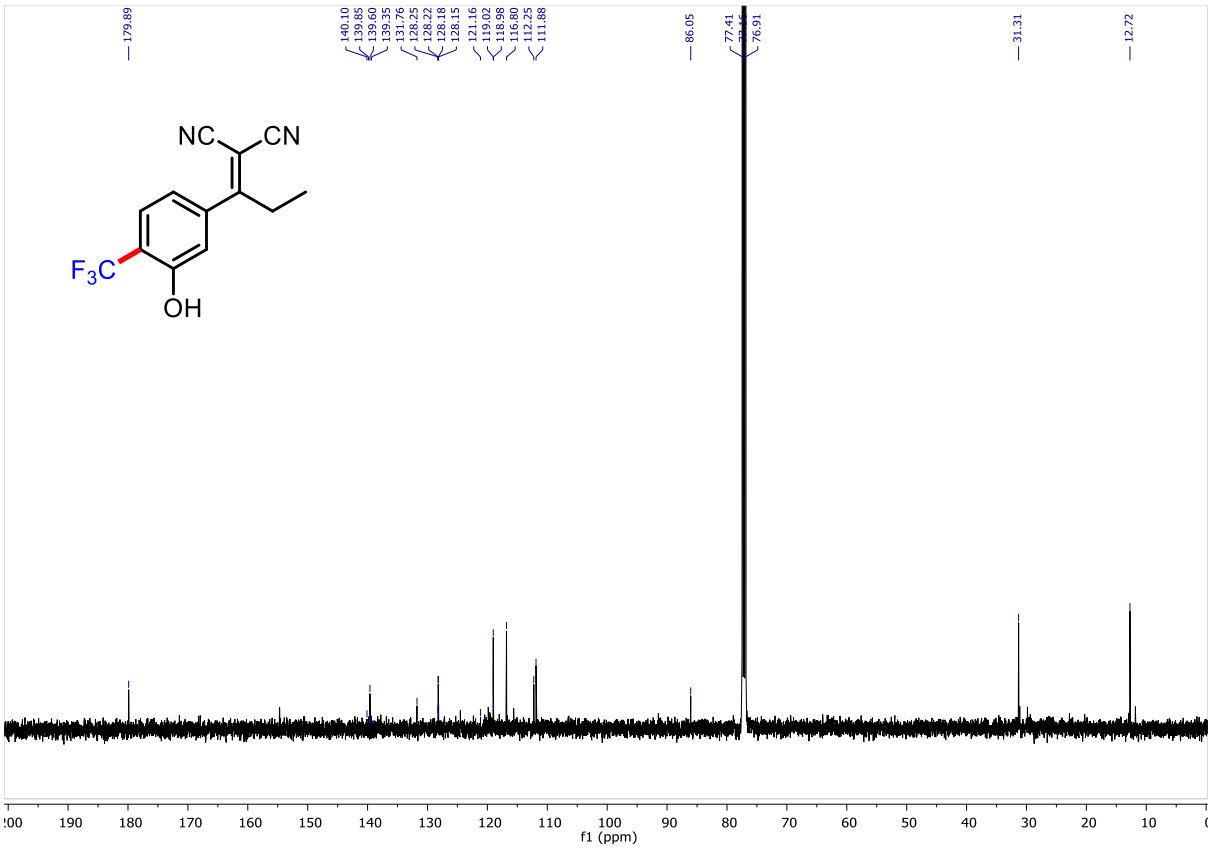
2.97
2.96
2.96
1.14
1.12
1.11
NC
CN
F3C
OH
1.13
1.00
1.11
2.12
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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119.02
118.98
116.80
112.25
111.88
86.05
77.41
77.16
76.91
31.31
12.72
NC
CN
F3C
OH
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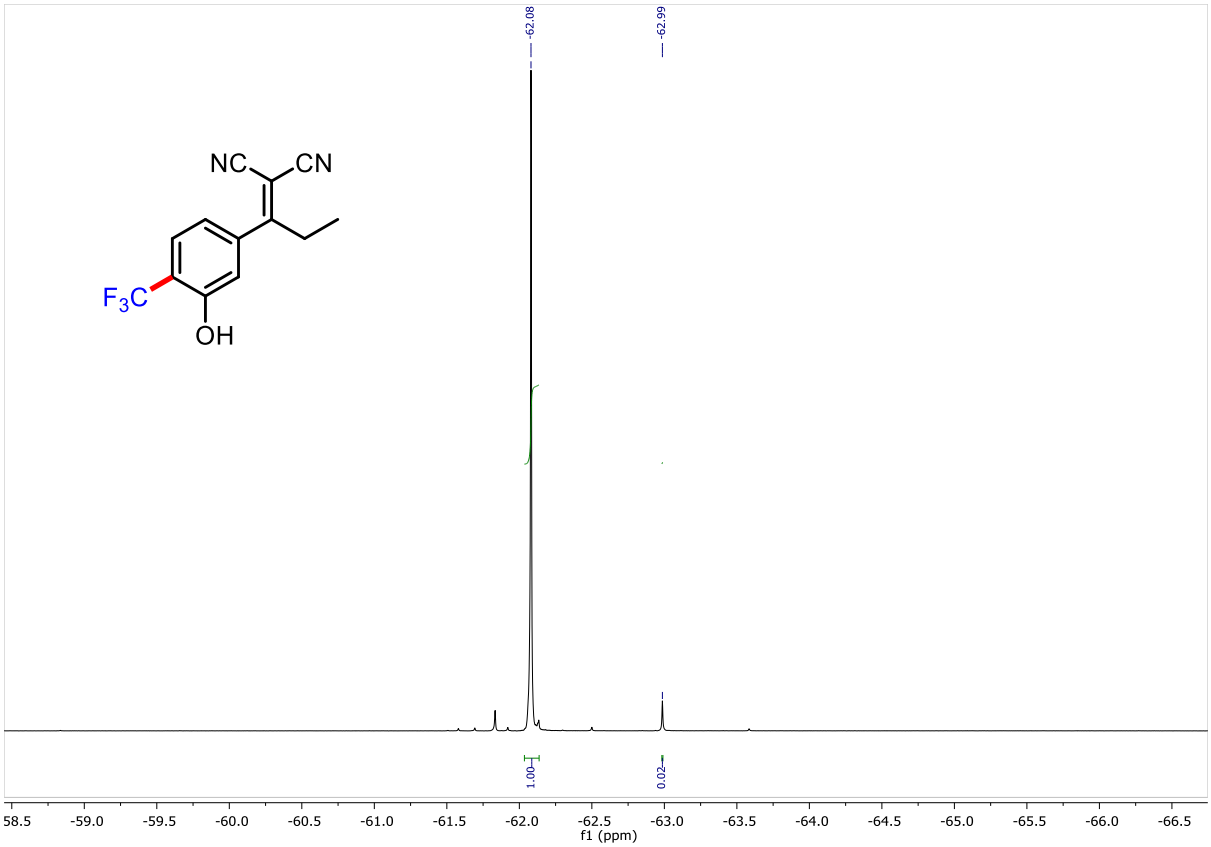
f1 (ppm)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CN
F3C
OH
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0.02
58.5
-59.0
-59.5
-60.0
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-61.5
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-63.5
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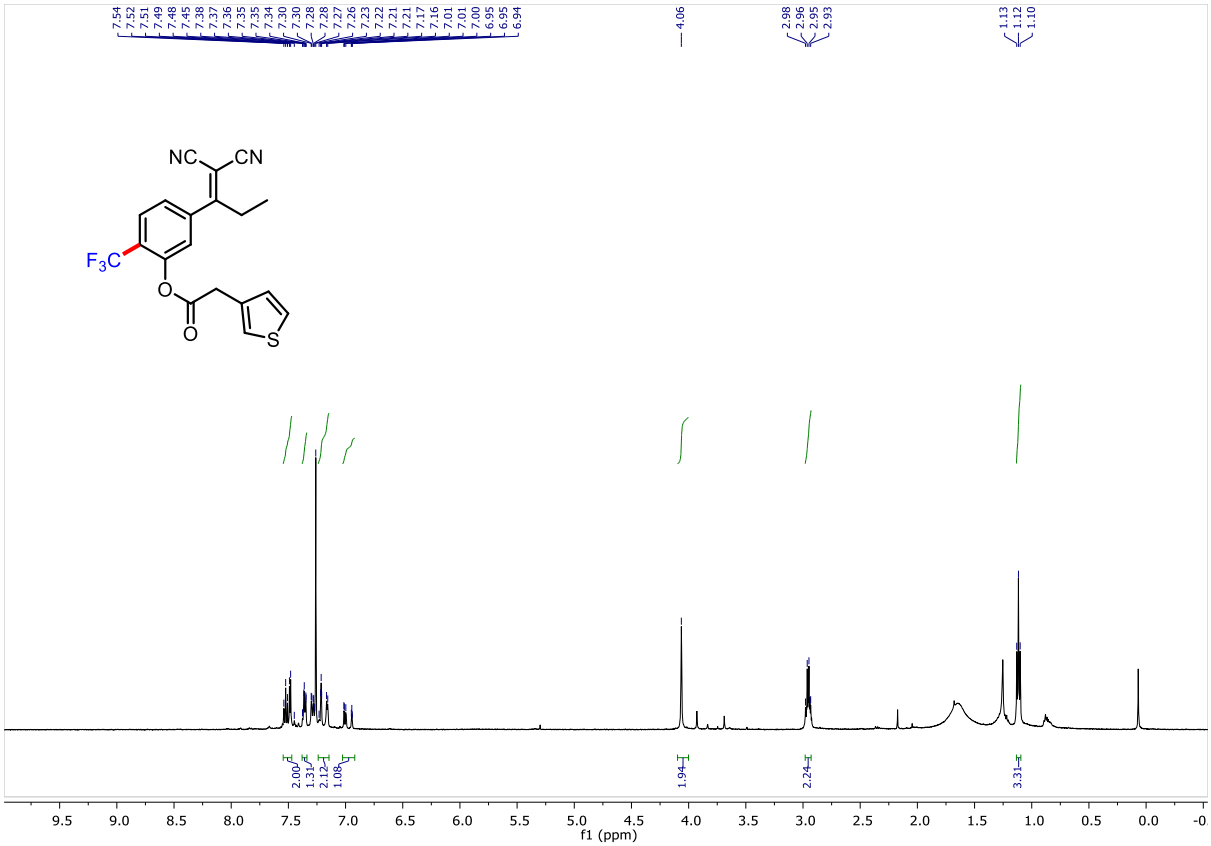
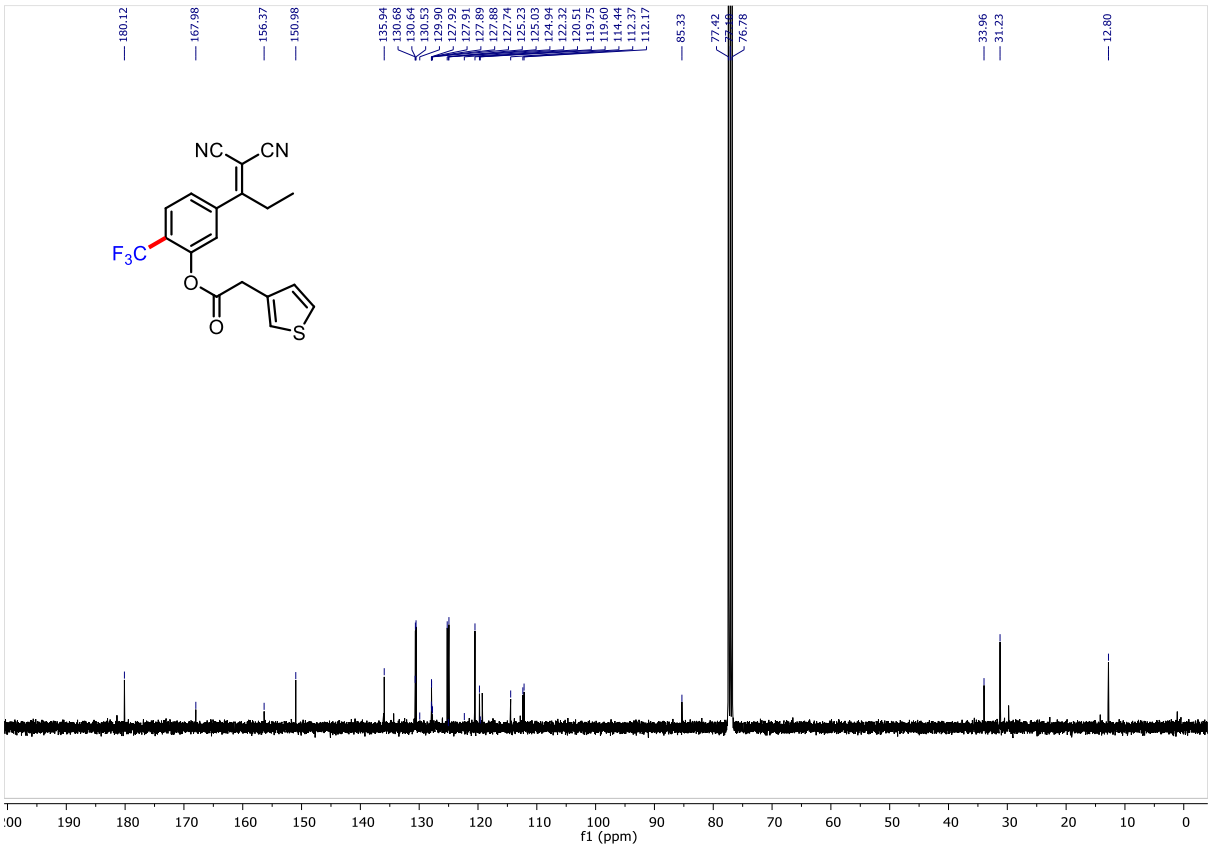
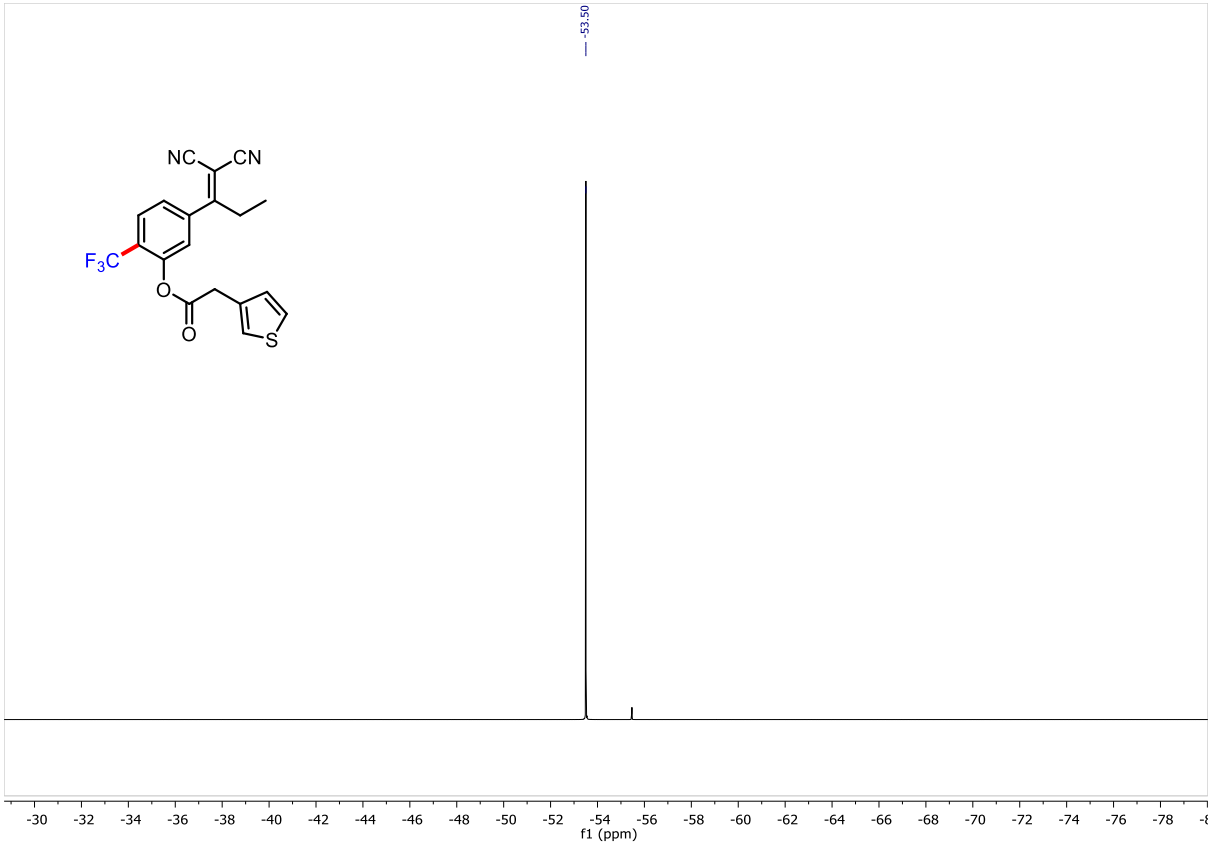
-64.5
-65.0
-65.5
-66.0
-66.5
f1 (ppm)


NC
CN
F3C
O
O
S
f1 (ppm)


NC
CN
F3C
O
O
S
f1 (ppm)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O
S
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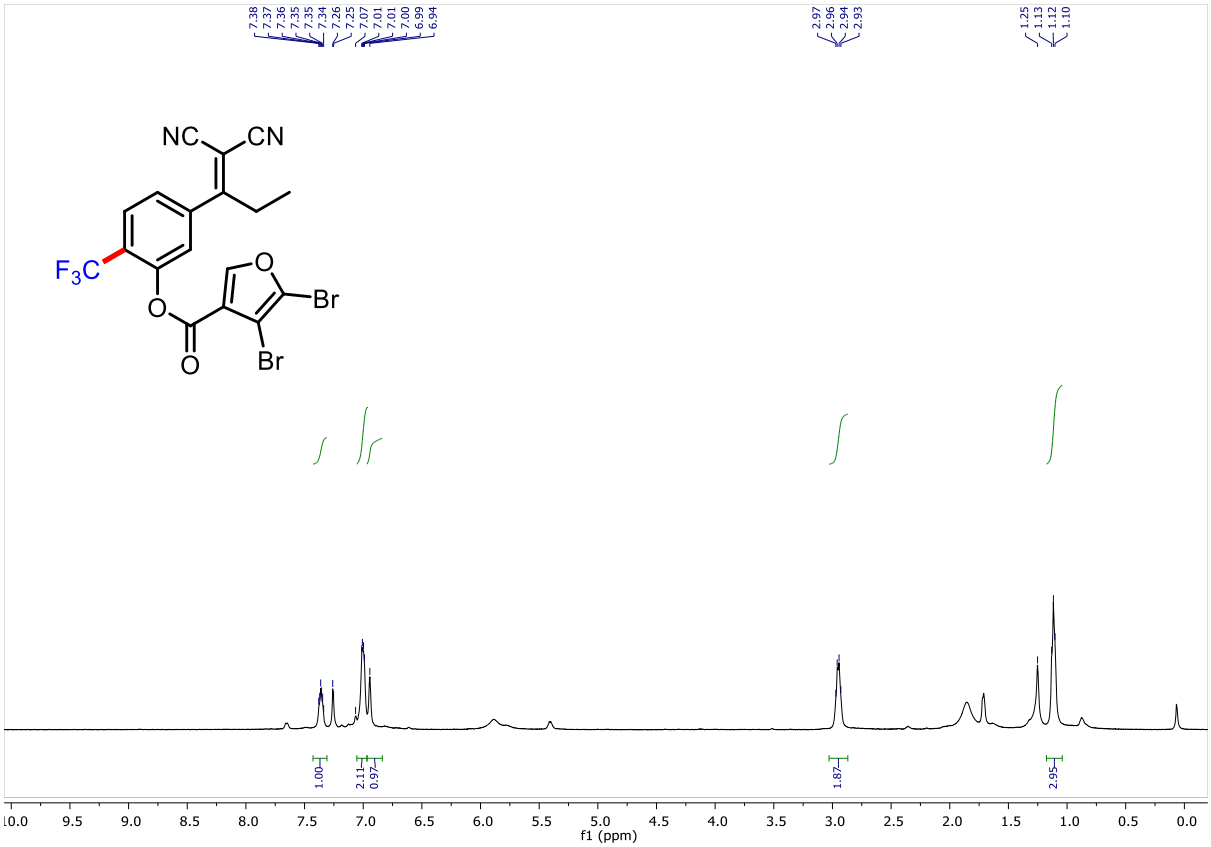
f1 (ppm)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O
Br
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7.25
7.07
7.01
7.01
7.00
6.99
6.94
2.97
2.96
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2.93
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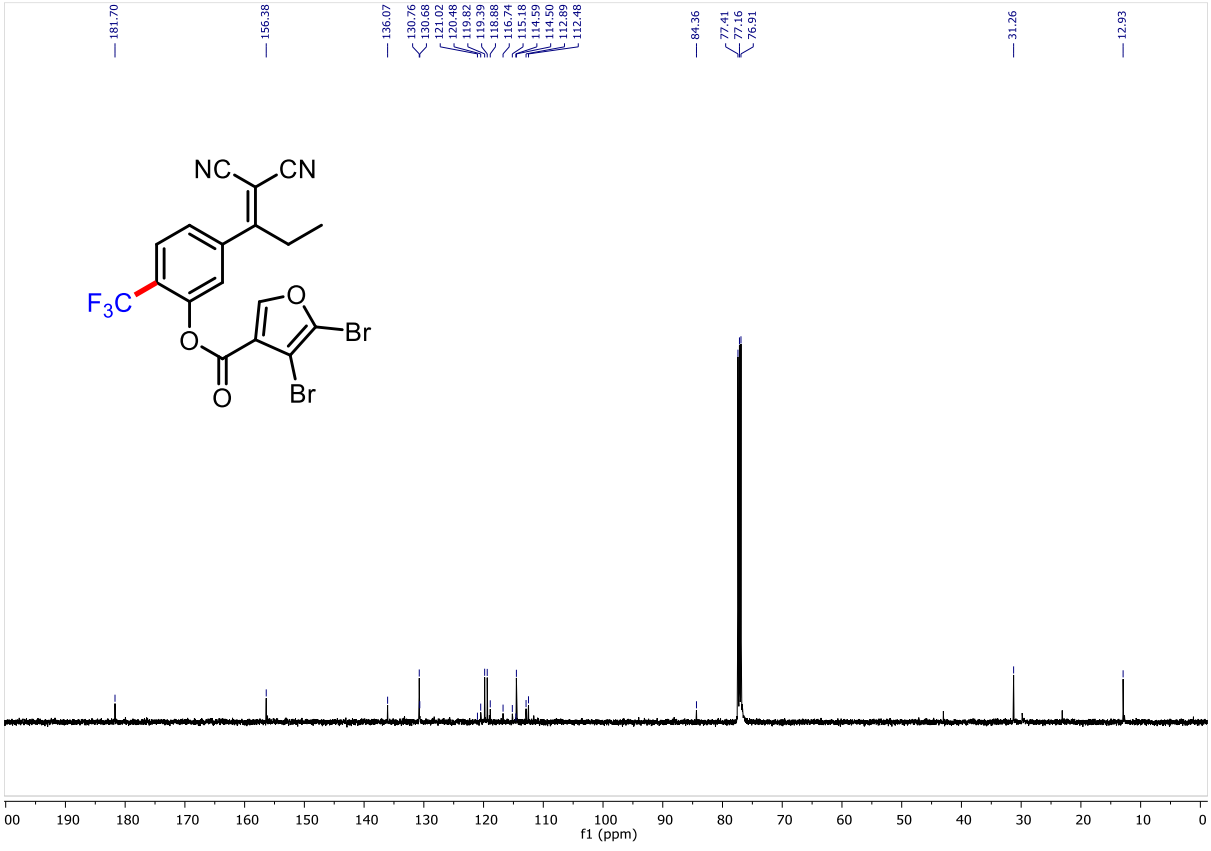
1.13
1.12
1.10
1.00
2.11
0.97
1.87
2.95
f1 (ppm)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O
Br
O
Br
O
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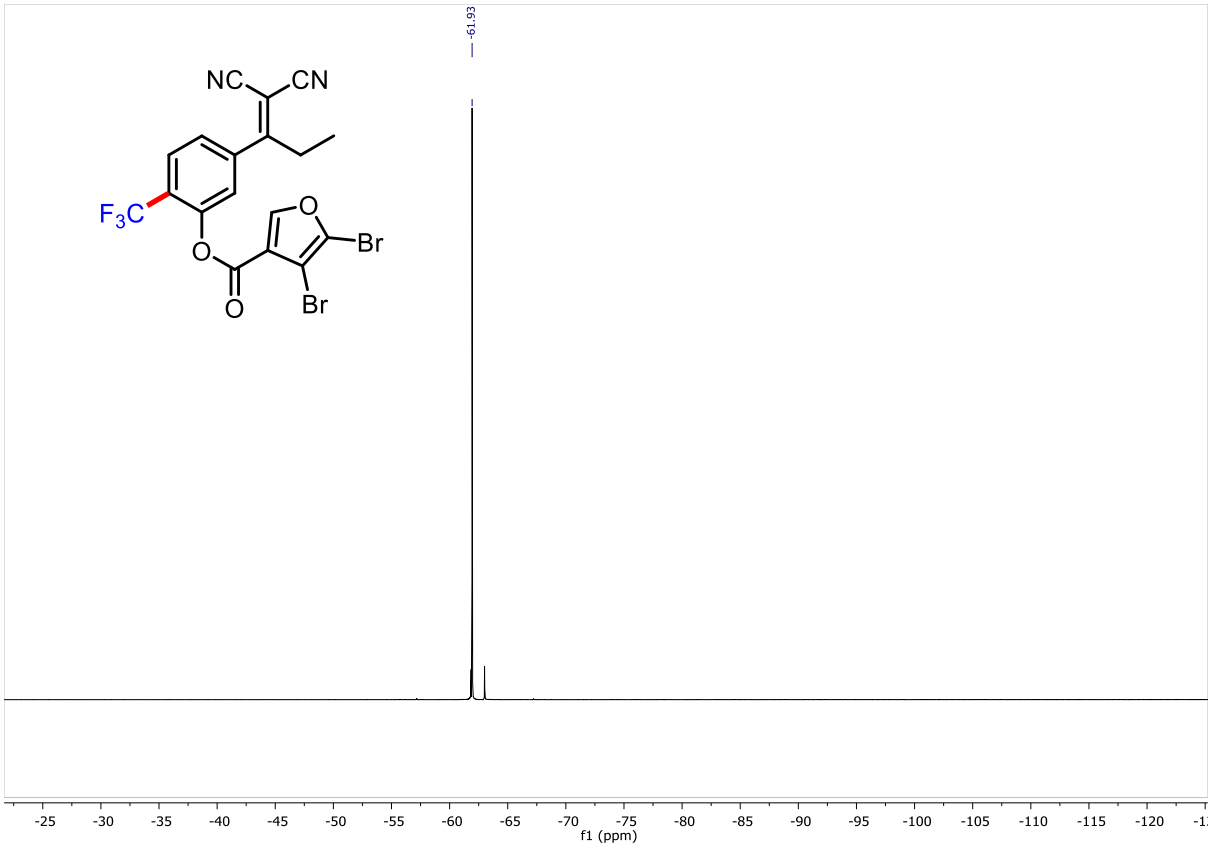
112.89
112.48
84.36
77.41
77.16
76.91
31.26
12.93
f1 (ppm)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-95
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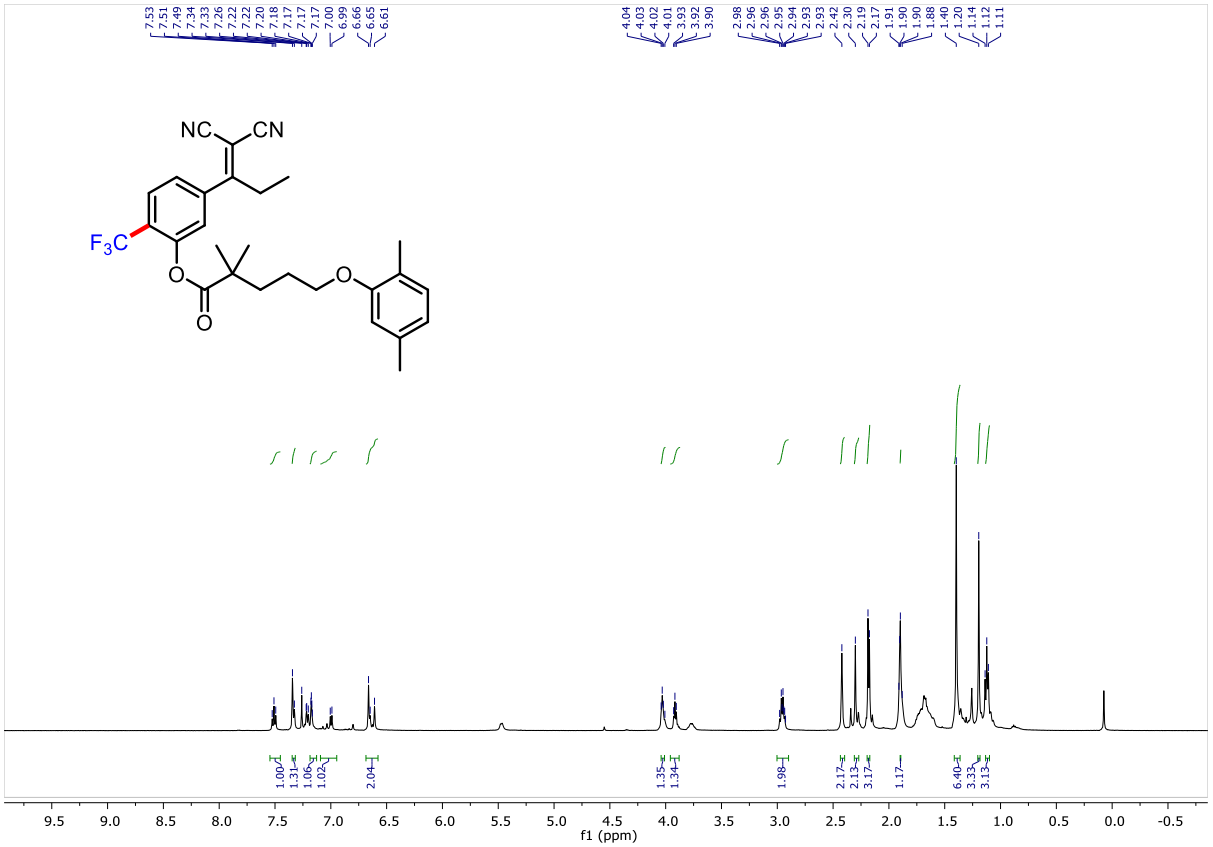
-105
-110
-115
-120
f1 (ppm)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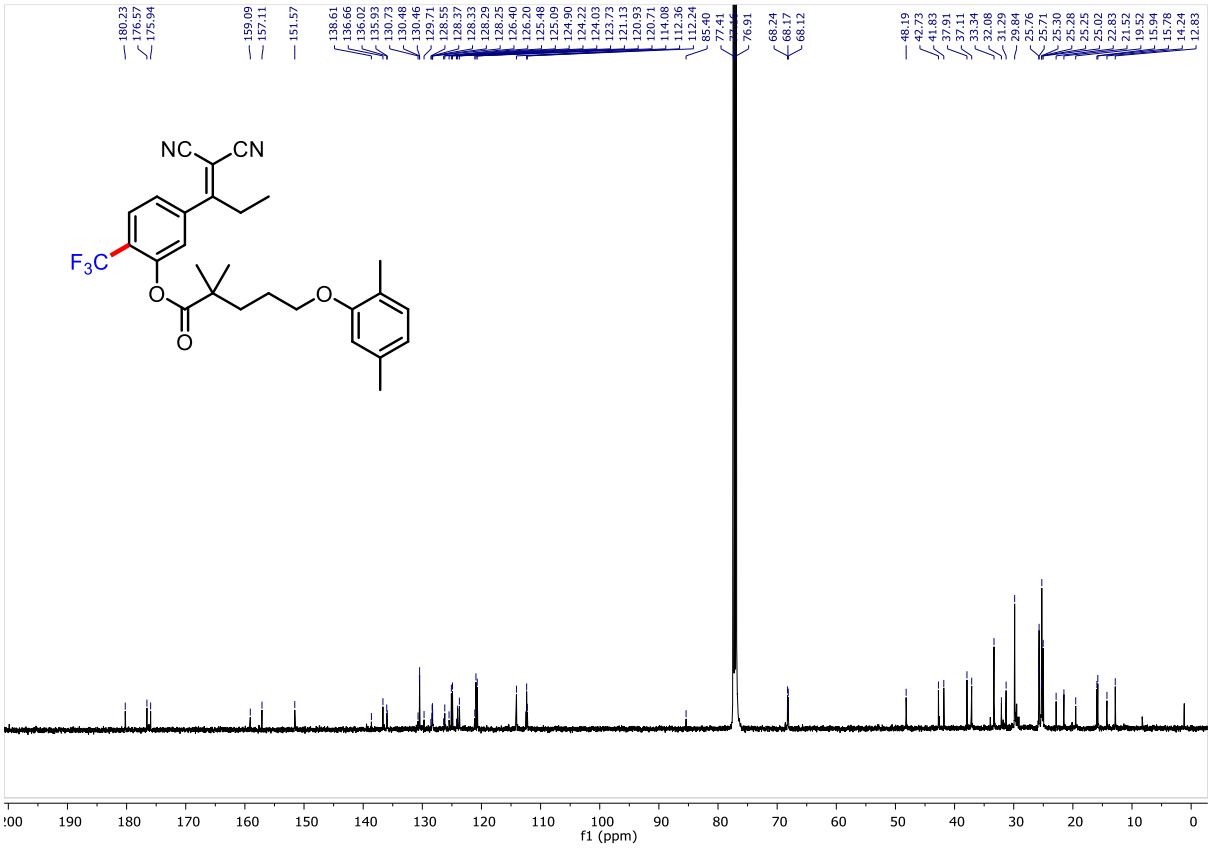
CN
F3C
O
O
O
f1 (ppm)


NC
CN
F3C
O
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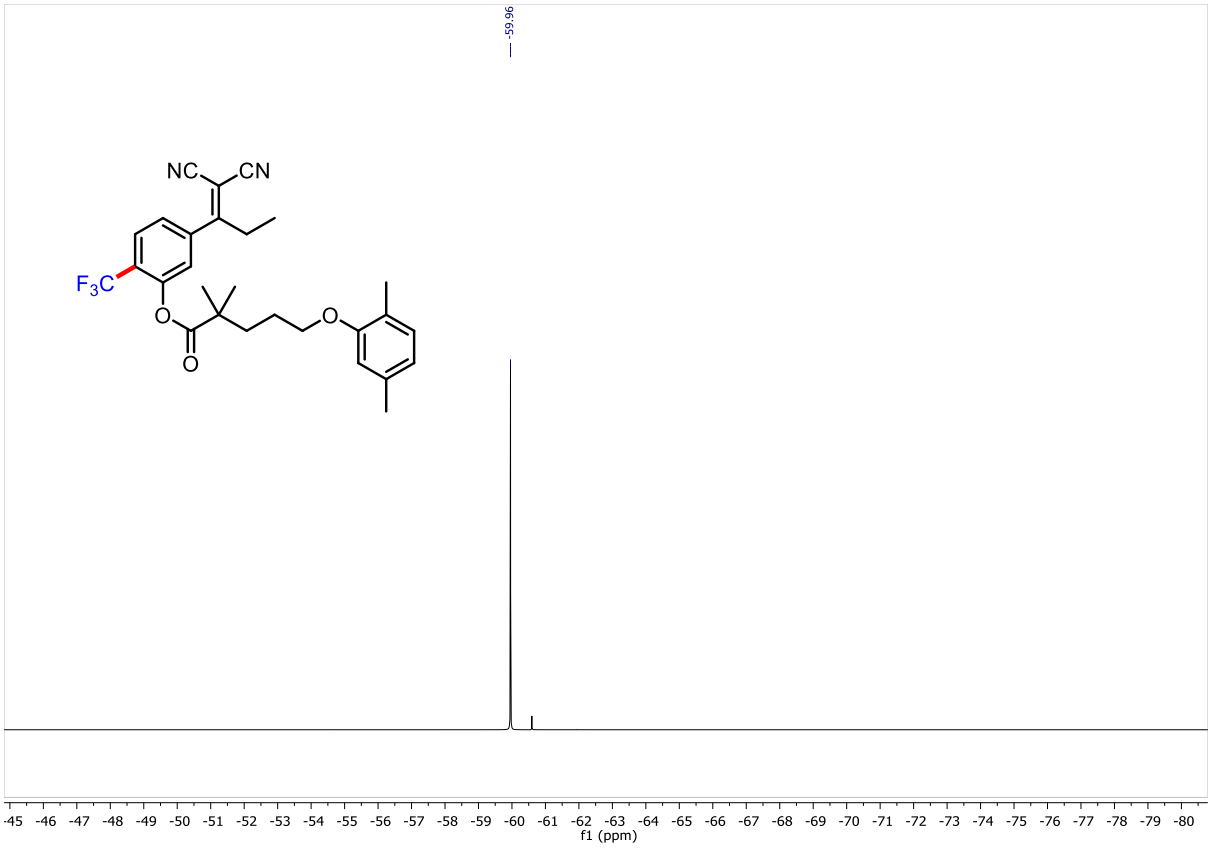
O
f1 (ppm)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F3C
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O
O
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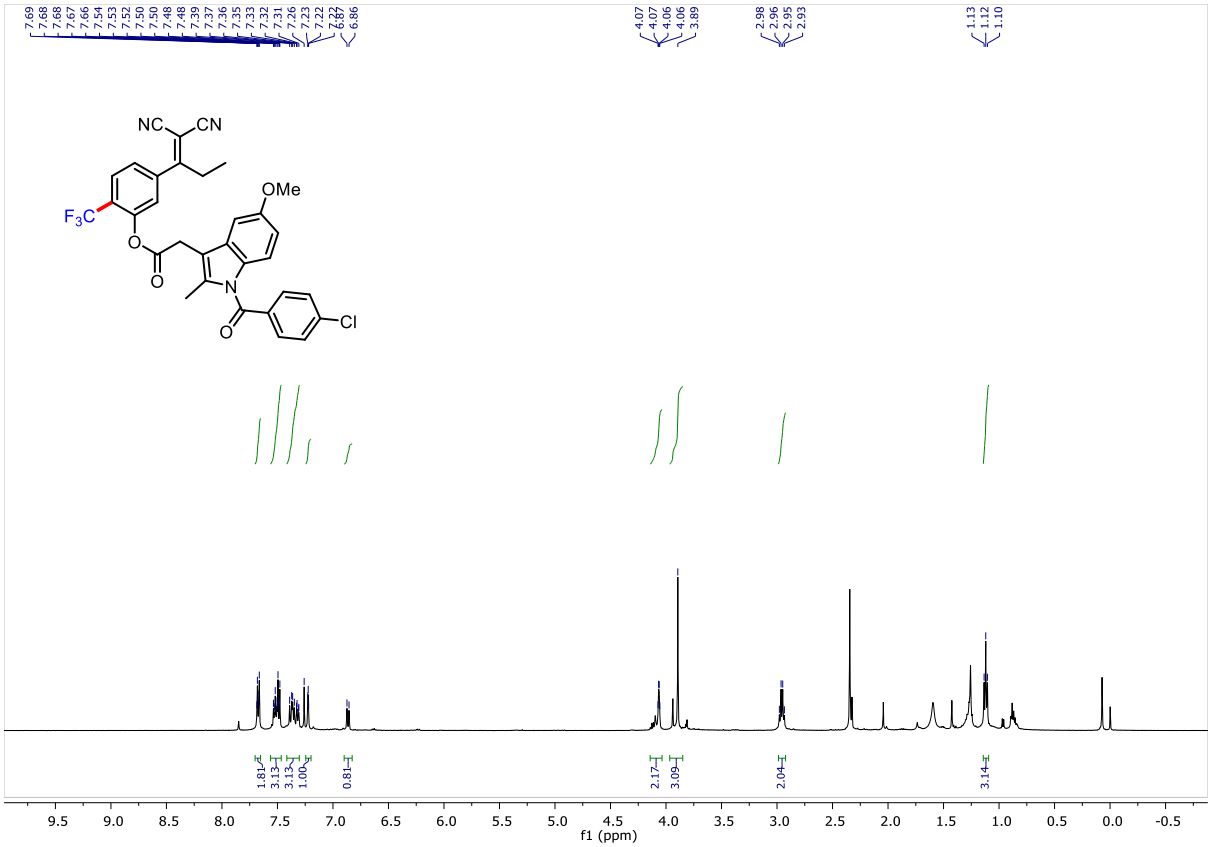
f1 (ppm)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7.23
7.22
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6.86
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4.07
4.06
4.06
3.89
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2.95
2.93
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1.12
1.10
NC
CN
OMe
F3C
O
O
N
O
Cl
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3.13
3.13
1.00
0.81
2.17
3.09
2.04
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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1.5
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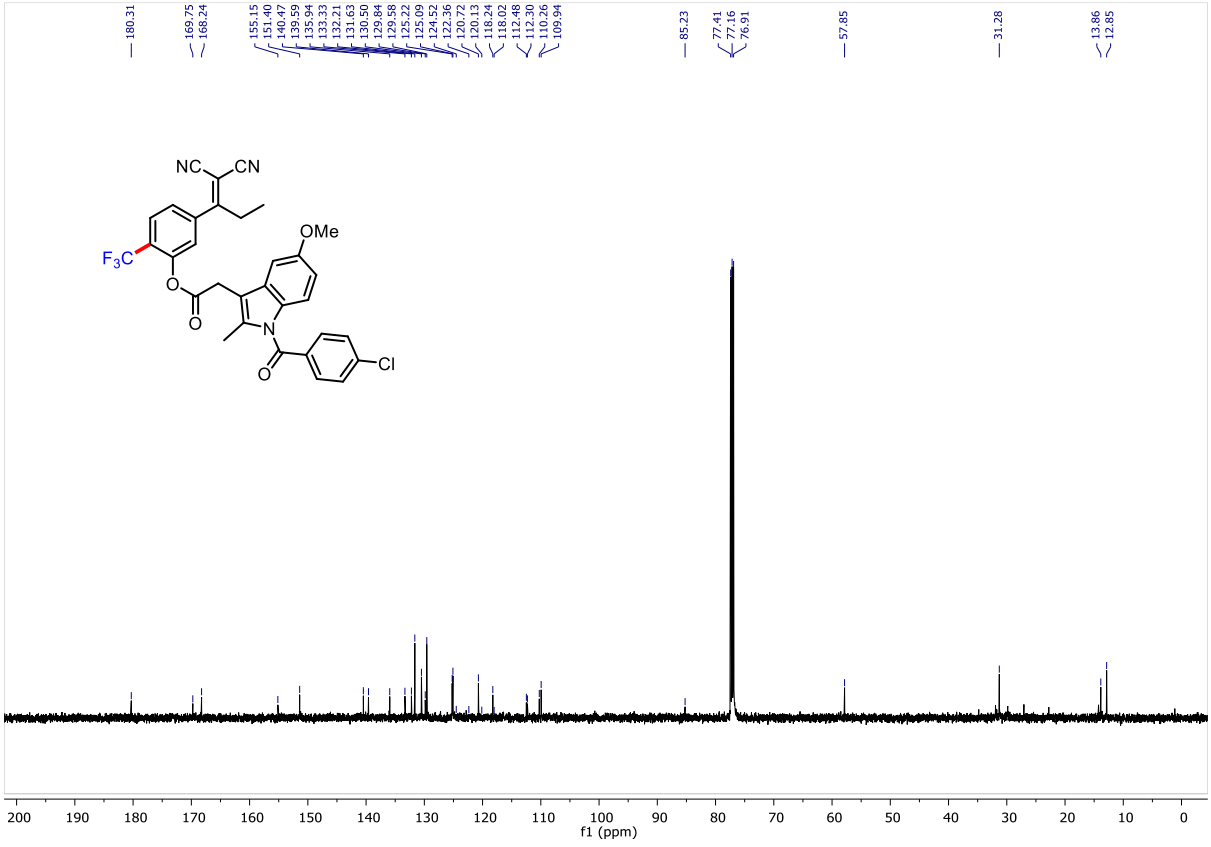
0.5
0.0
-0.5
f1 (ppm)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125.09
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122.36
120.72
120.13
118.24
118.02
112.48
112.30
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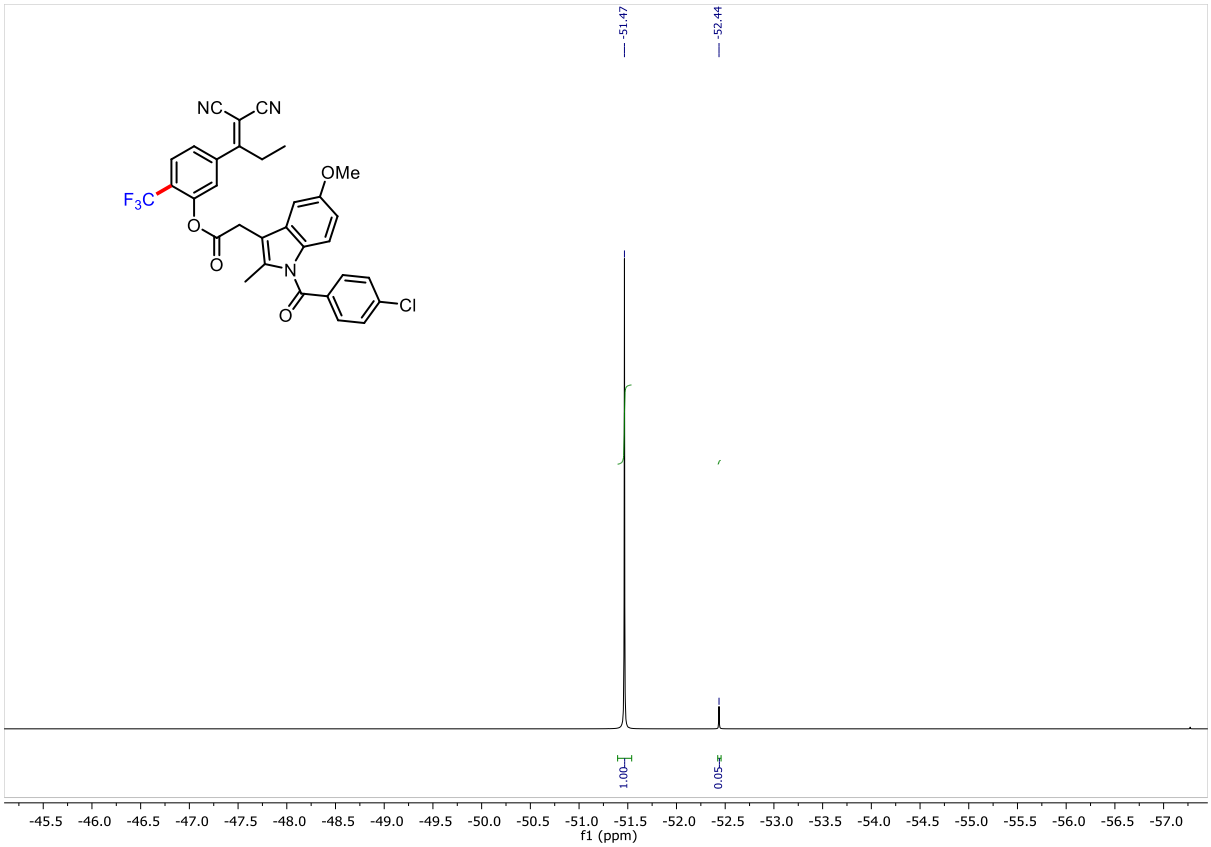
109.94
85.23
77.41
77.16
76.91
57.85
31.28
13.86
12.85
NC
CN
OMe
F3C
O
O
N
O
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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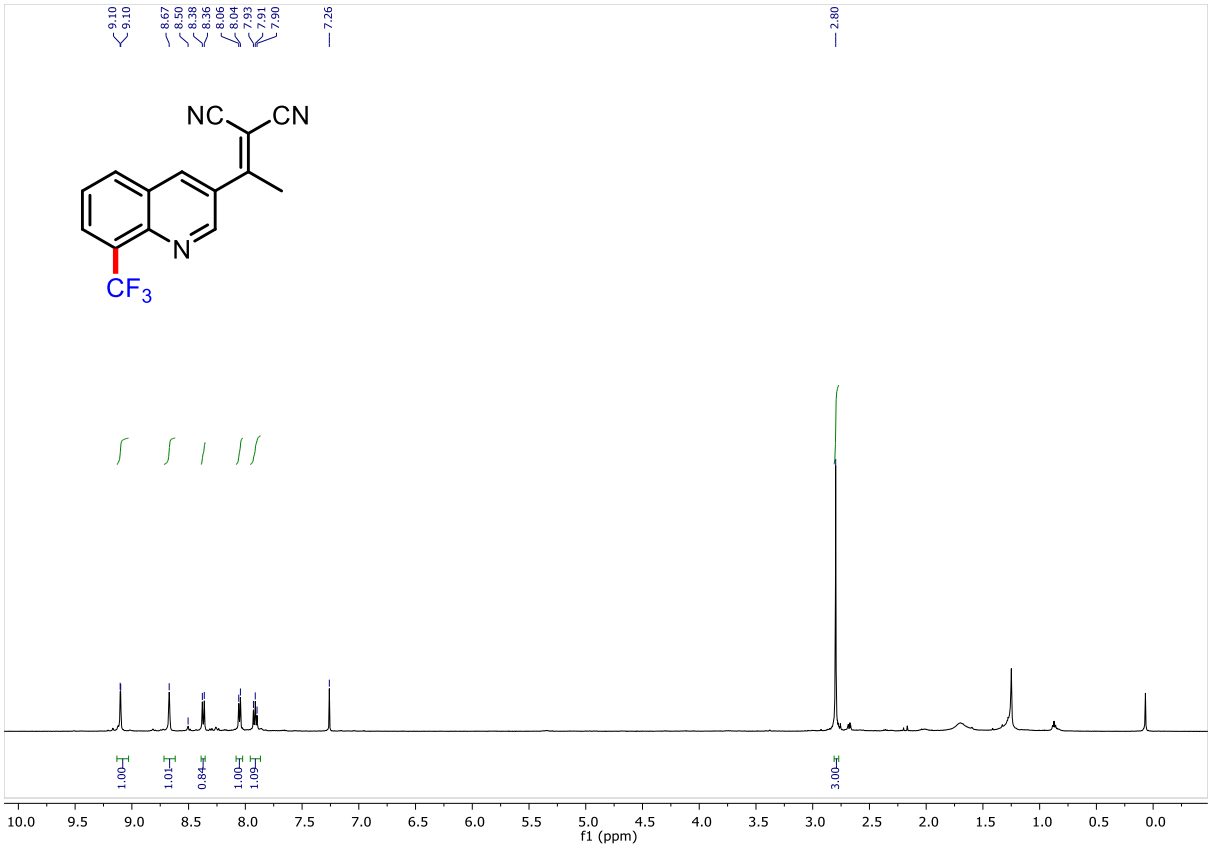
-52.44
NC
CN
OMe
F3C
O
O
N
O
Cl
1.00
0.05
-45.5 -46.0 -46.5 -47.0 -47.5 -48.0 -48.5 -49.0 -49.5 -50.0 -50.5 -51.0 -51.5 -52.0 -52.5 -53.0 -53.5 -54.0 -54.5 -55.0 -55.5 -56.0 -56.5 -57.0
f1 (ppm)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9.10
8.67
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8.36
8.06
8.04
7.93
7.91
7.90
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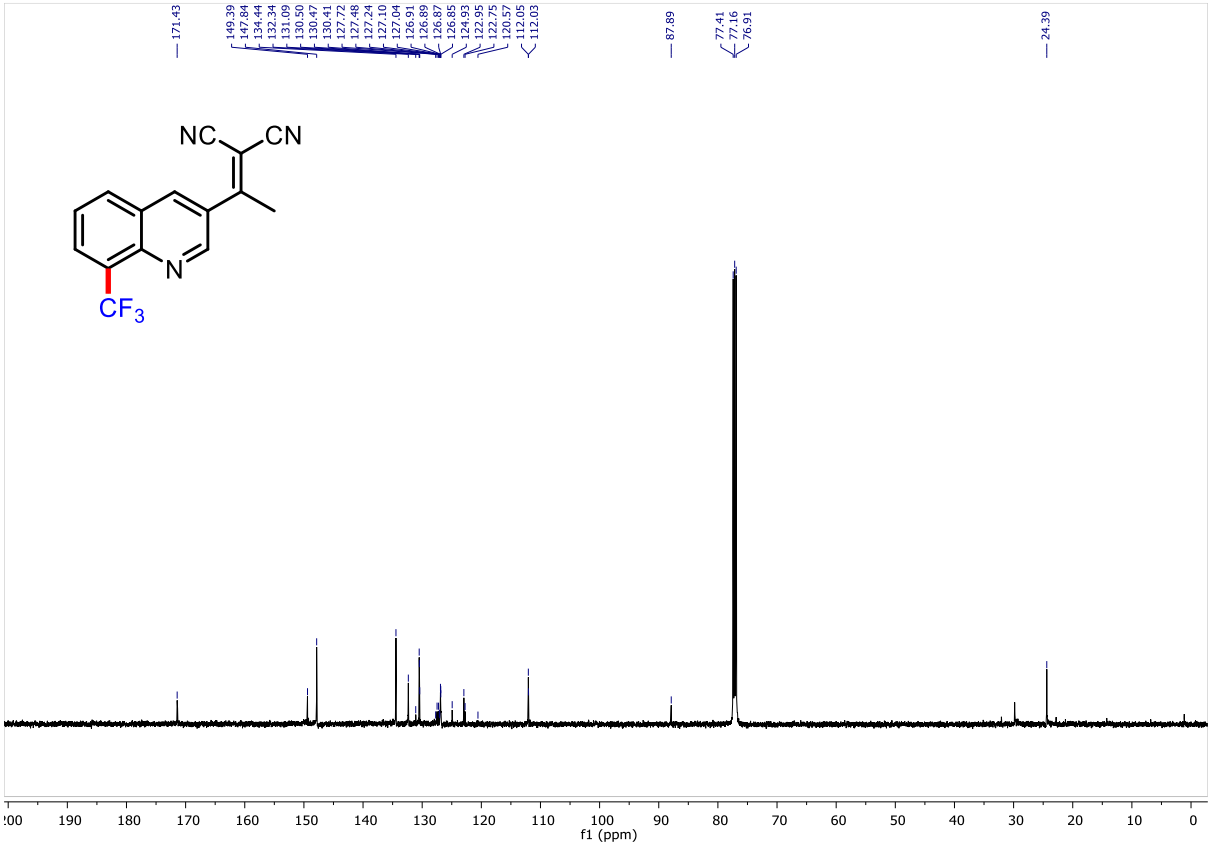
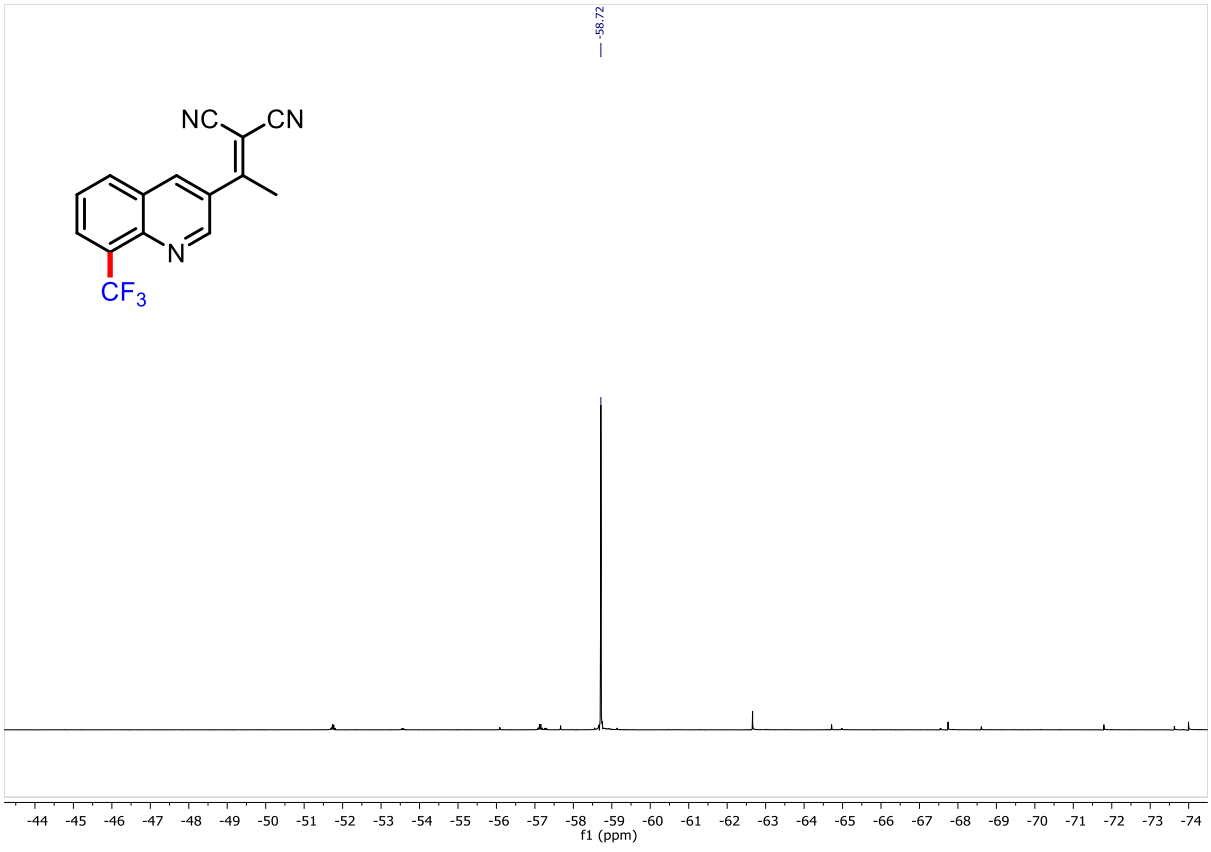
NC
CN
N
CF3
1.00
1.01
0.84
1.00
1.09
3.00
f1 (ppm)


171.43
149.39
147.84
134.44
132.34
131.09
130.50
130.47
130.41
127.72
127.48
127.24
127.10
127.04
126.91
126.89
126.87
126.85
124.93
122.95
122.75
120.57
112.05
112.03
87.89
77.41
77.16
76.91
24.39
NC
CN
N
CF3
f1 (ppm)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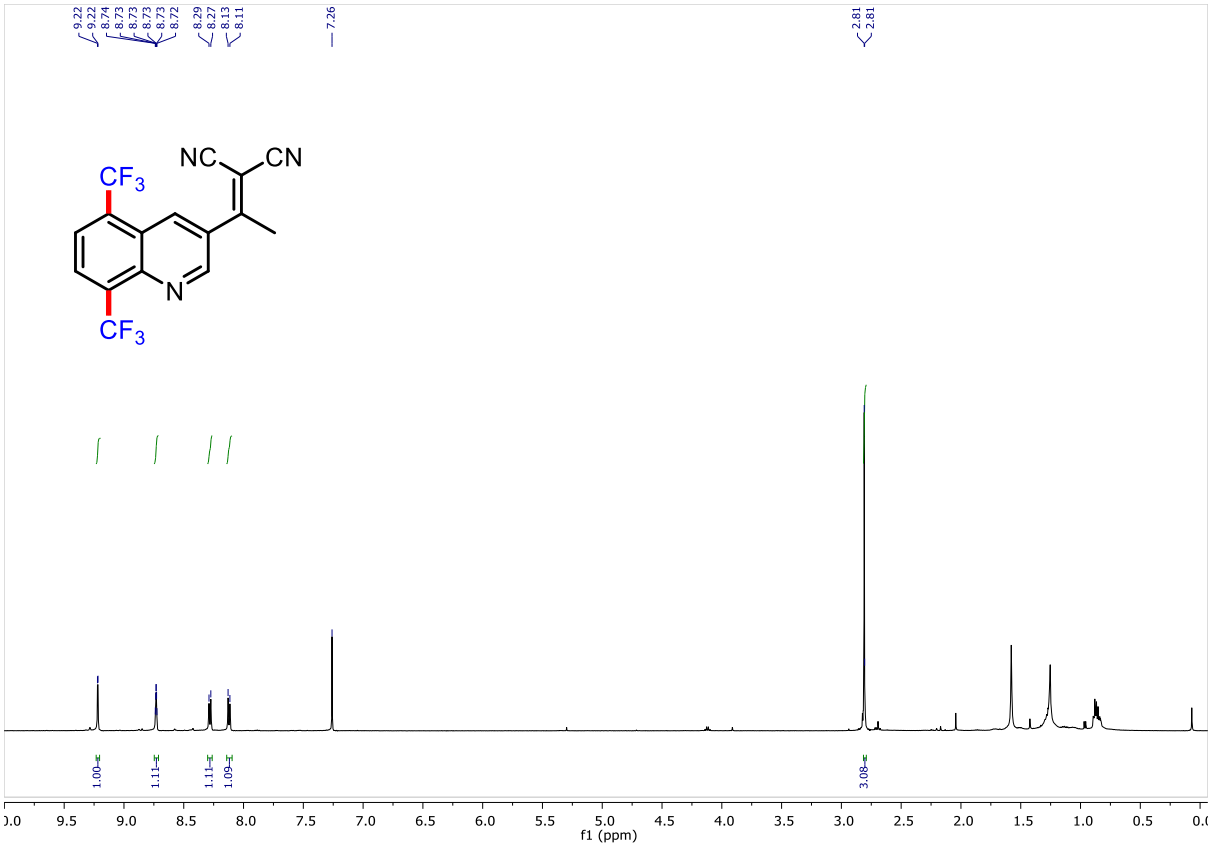
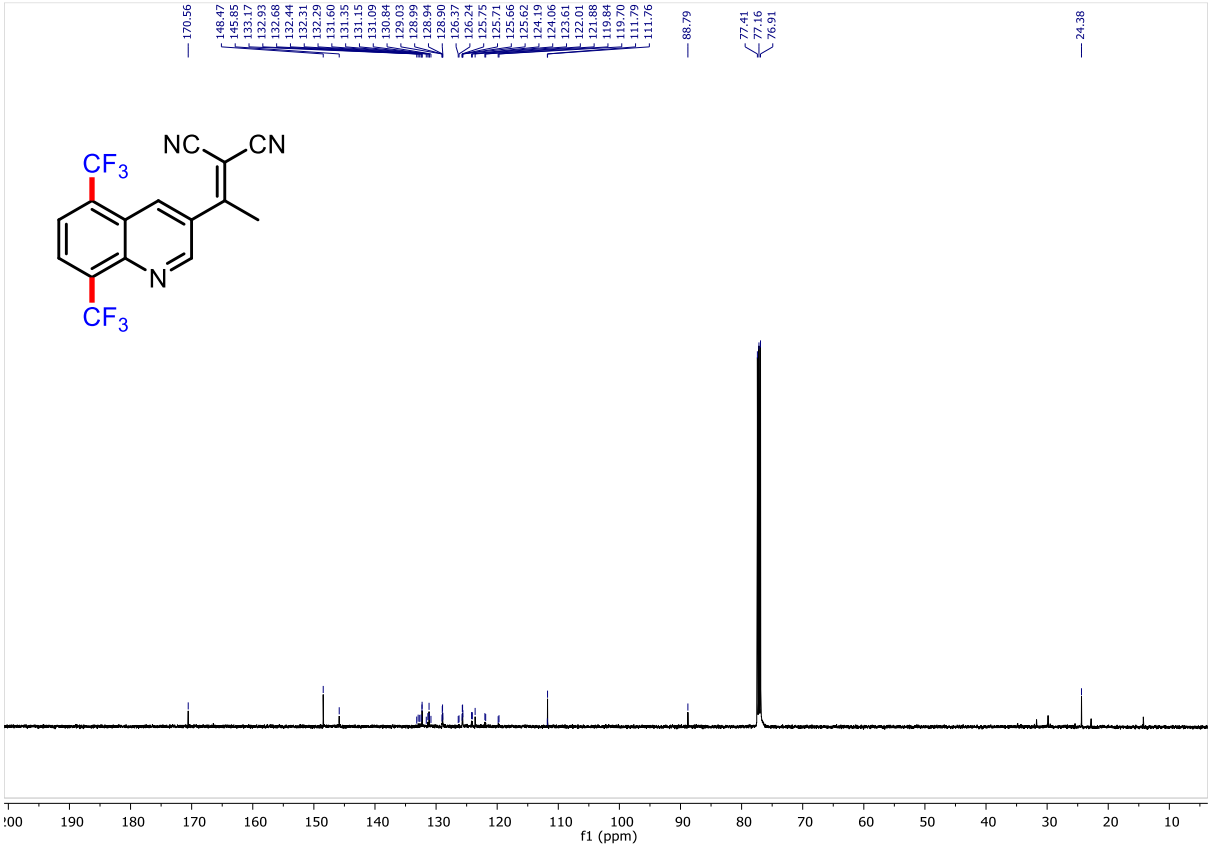
CN
N
CF3
-44 -45 -46 -47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74
f1 (ppm)


9.22
9.22
8.74
8.73
8.73
8.73
8.73
8.72
8.29
8.27
8.13
8.11
7.26
2.81
2.81
NC
CN
CF3
CF3
N
1.00
1.11
1.11
1.09
3.08
f1 (ppm)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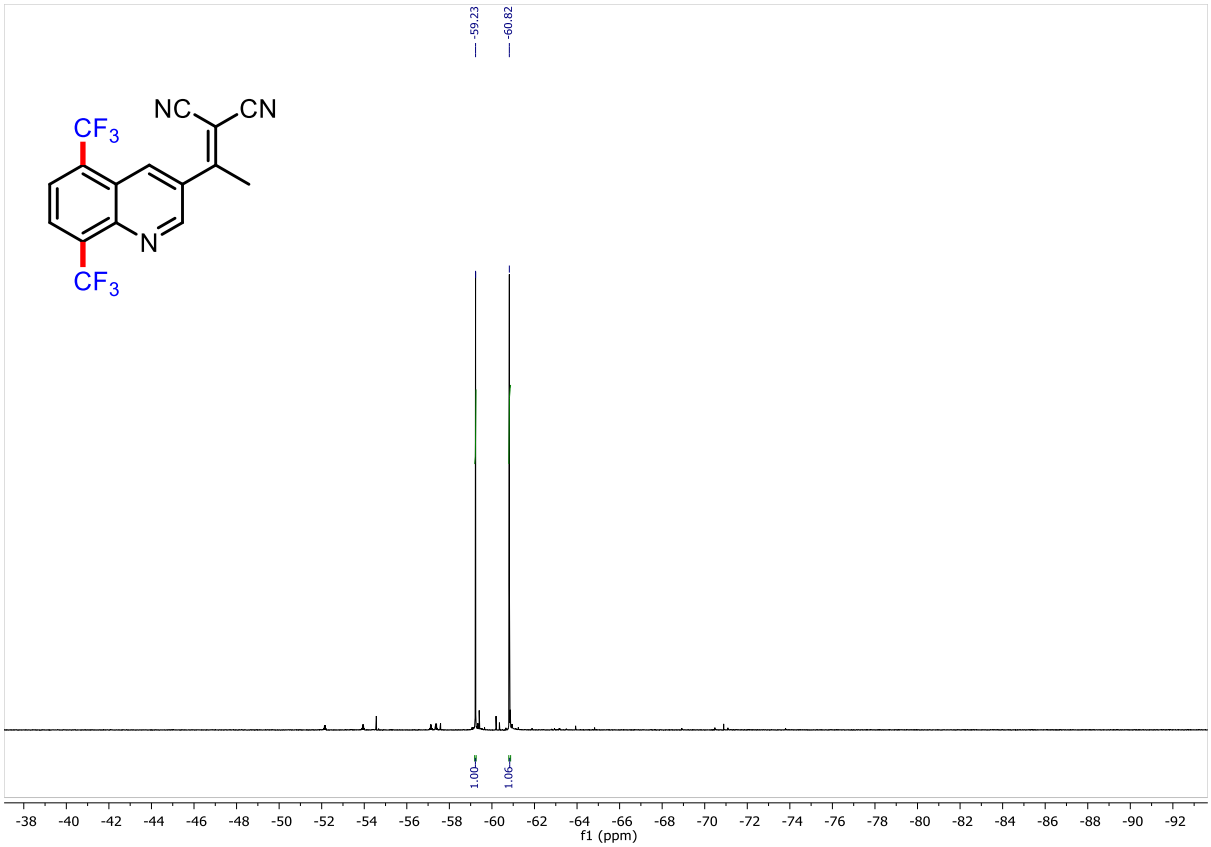
148.47
145.85
133.17
132.93
132.68
132.44
132.31
132.29
131.60
131.35
131.15
131.09
131.04
129.03
128.99
128.94
128.90
126.37
126.24
125.75
125.71
125.66
125.62
124.19
124.06
123.61
122.01
121.88
119.84
119.70
111.79
111.76
88.79
77.41
77.16
76.91
24.38
NC
CN
CF3
CF3
N
f1 (ppm)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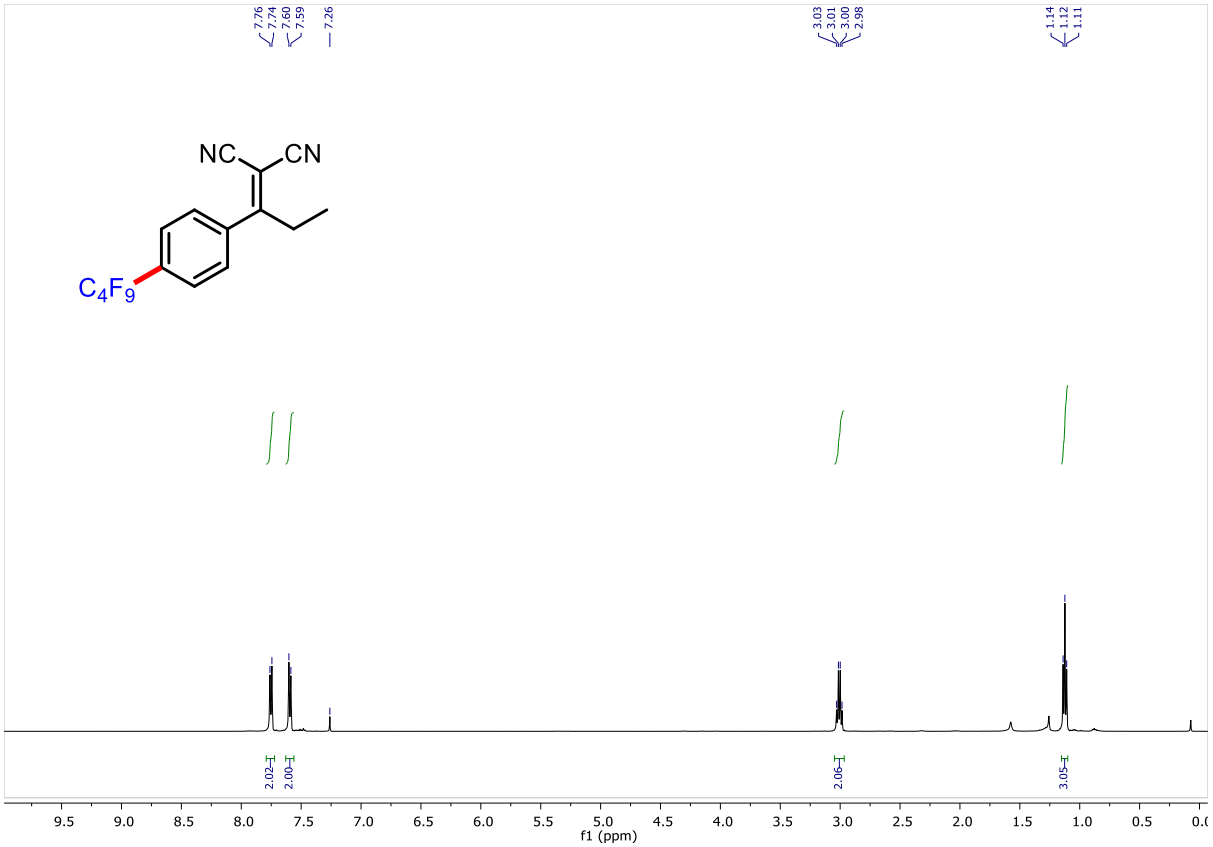
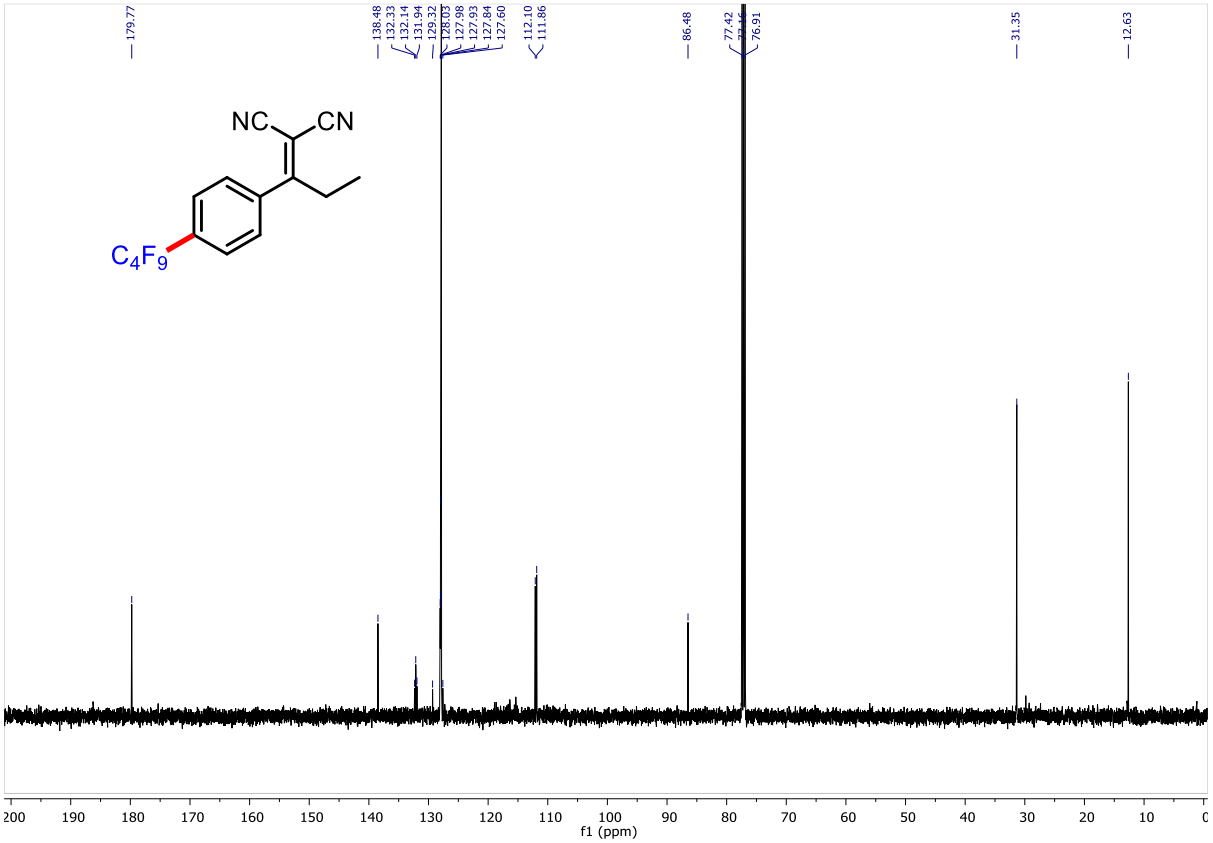
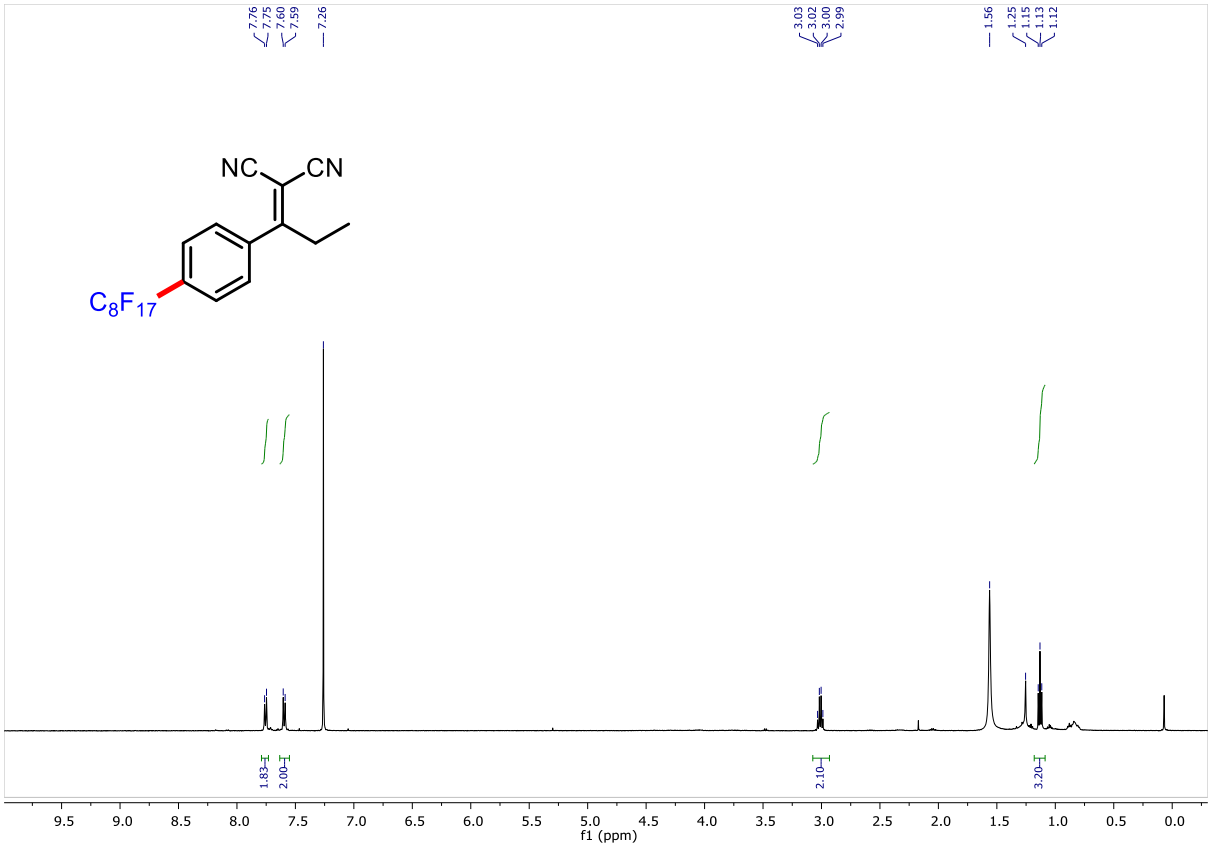
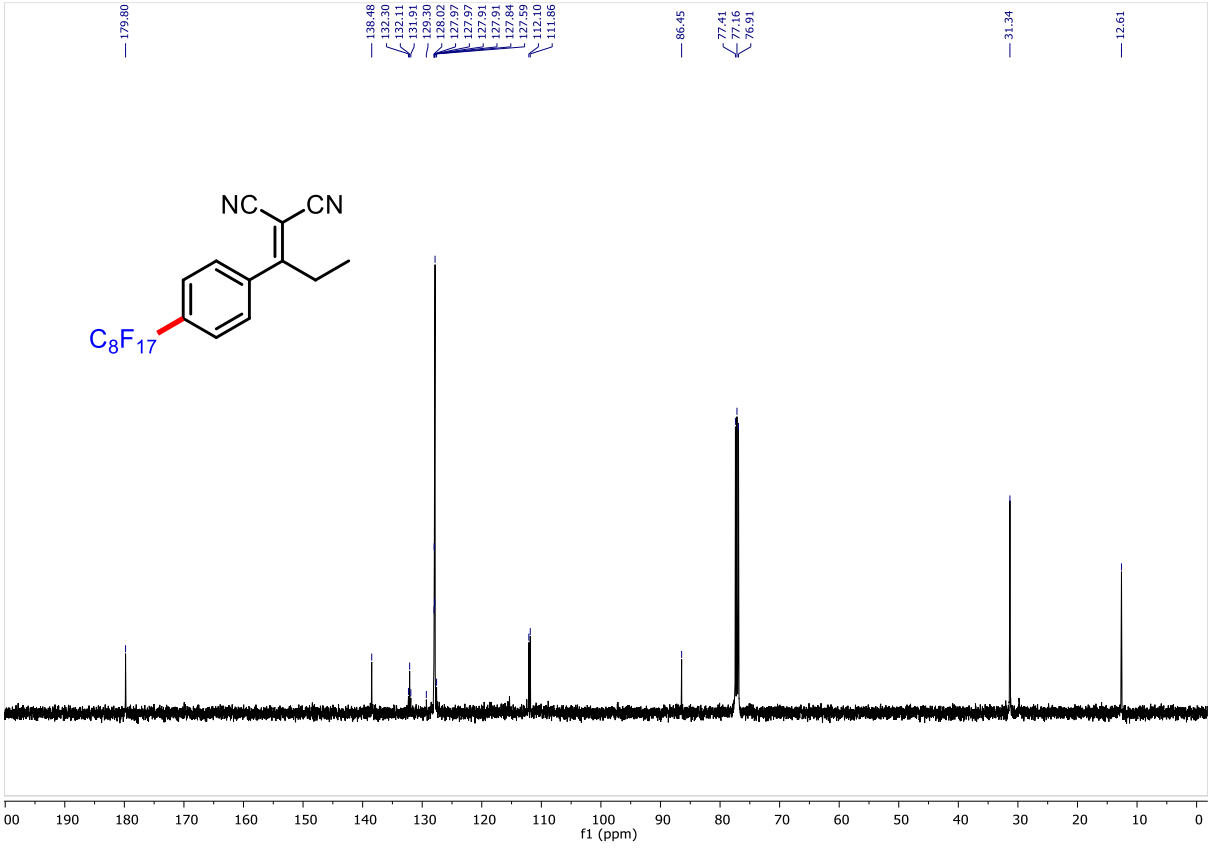
-60.82
NC
CN
CF3
CF3
N
1.00
1.06
-38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92
f1 (ppm)


7.76
7.74
7.60
7.59
7.26
3.03
3.01
3.00
2.98
1.14
1.12
1.11
NC
CN
C4F9
2.02
2.00
2.06
3.05
f1 (ppm)


179.77
138.48
132.33
132.14
131.94
129.32
128.03
127.98
127.93
127.84
127.60
112.10
111.86
86.48
77.42
76.91
31.35
12.63
NC
CN
C4F9
f1 (ppm)


-80.99
-81.01
-81.04
-111.43
-111.46
-111.49
-122.53
-122.55
-122.57
-122.60
-125.51
-125.53
-125.56
-125.57
-125.59
NC
CN
C4F9
3.00
2.29
2.12
2.24
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)


7.76
7.75
7.60
7.59
7.26
3.03
3.02
3.00
2.99
1.56
1.25
1.15
1.13
1.12
NC
CN
C8F17
1.83
2.00
2.10
3.20
f1 (ppm)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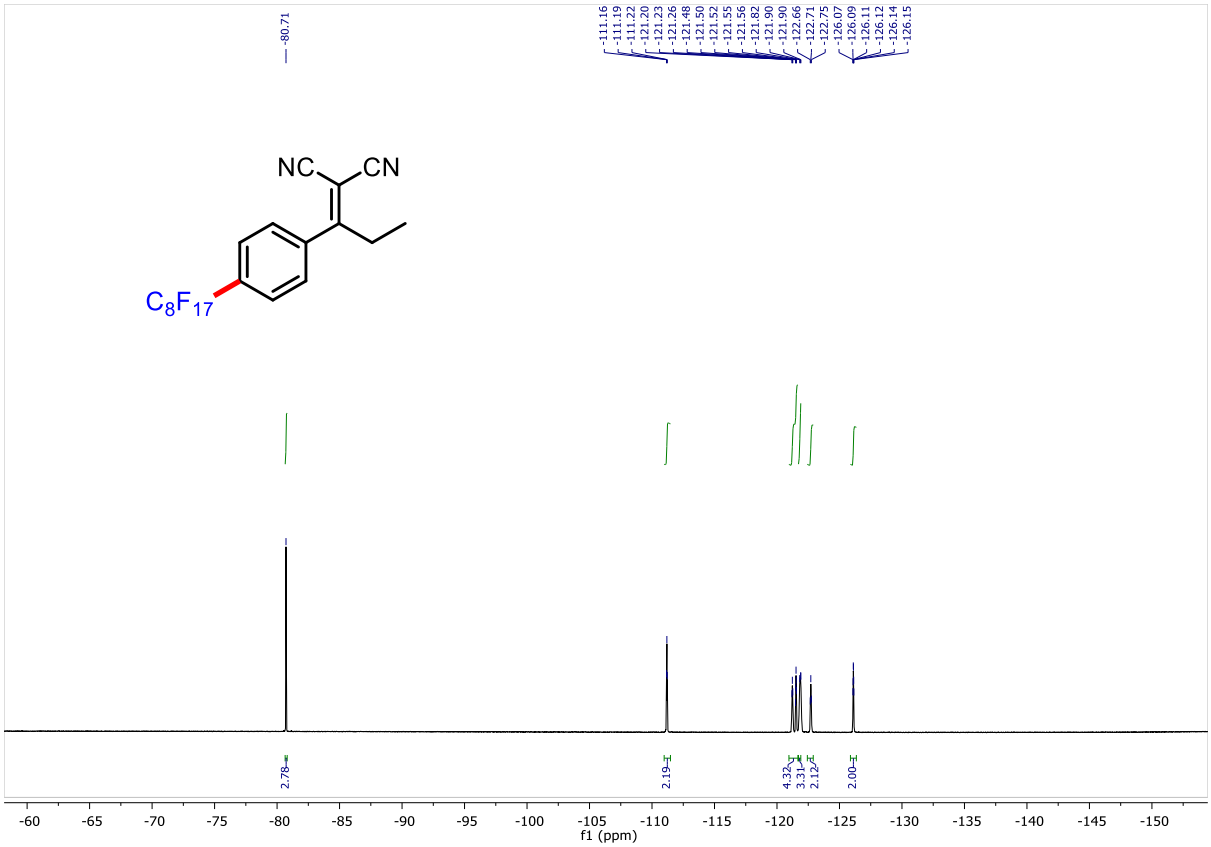
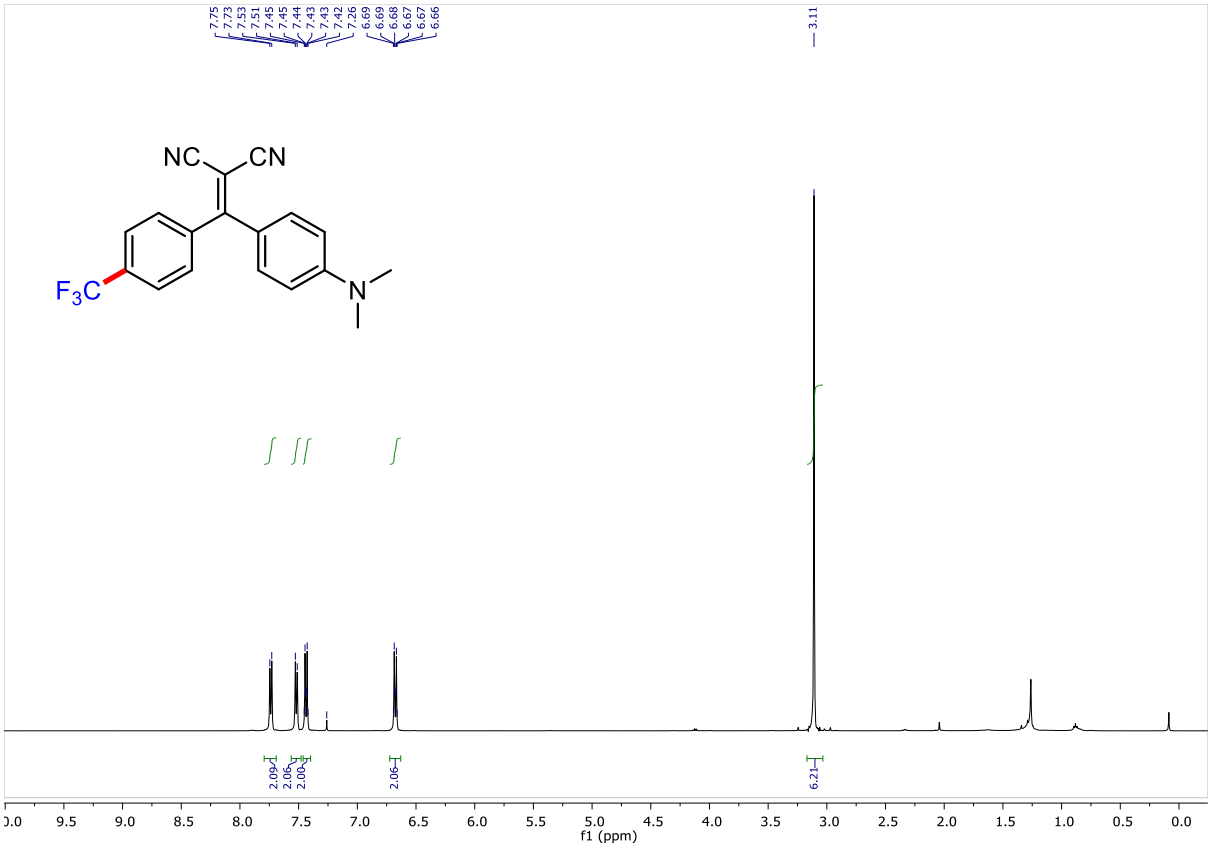
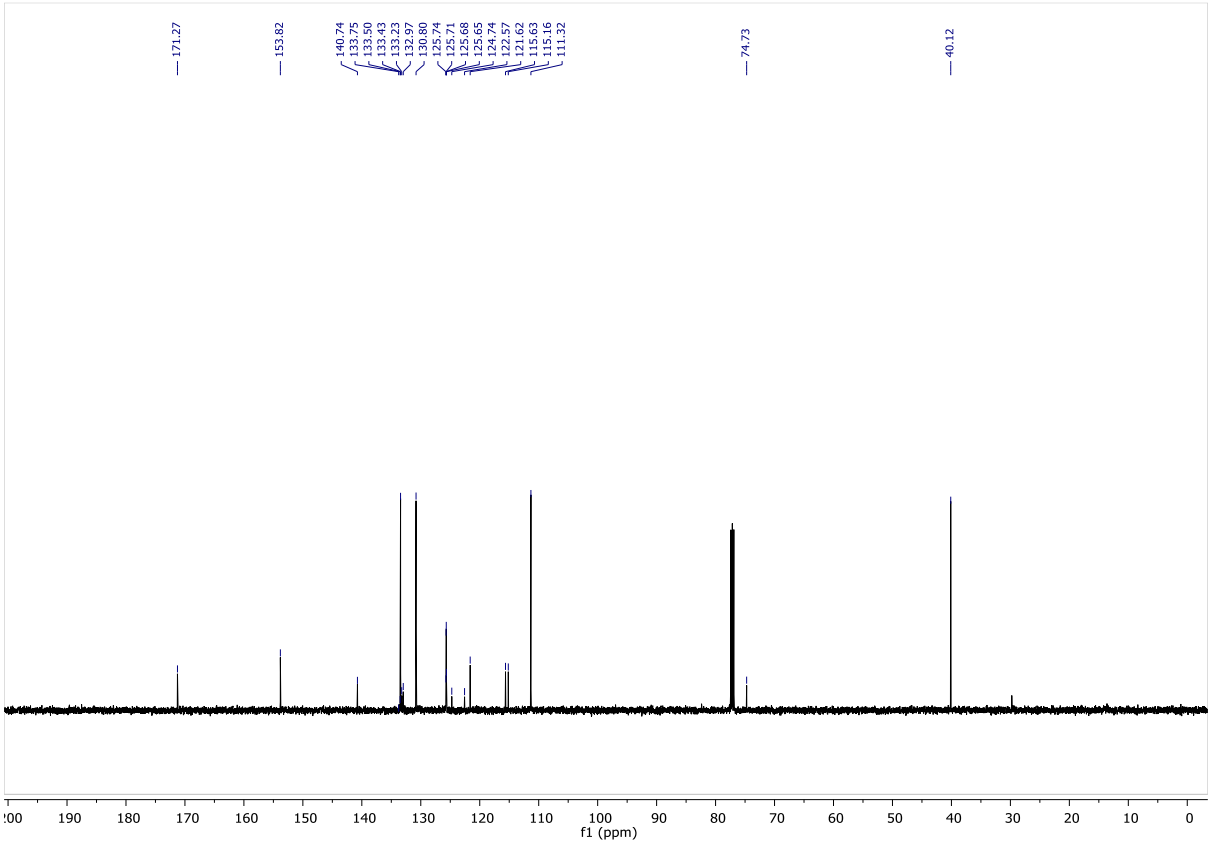
138.48
132.30
132.11
131.91
129.30
128.02
127.97
127.97
127.91
127.91
127.84
127.59
112.10
111.86
86.45
77.41
77.16
76.91
31.34
12.61
NC
CN
C8F17
f1 (ppm)


-80.71
-111.16
-111.19
-111.22
-121.20
-121.23
-121.26
-121.48
-121.50
-121.52
-121.55
-121.56
-121.82
-121.90
-121.90
-122.66
-122.71
-122.75
-126.07
-126.09
-126.11
-126.12
-126.14
-126.15
NC
CN
C8F17
2.78
2.19
4.32
3.31
2.12
2.00
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)


7.75
7.73
7.53
7.51
7.45
7.45
7.44
7.43
7.43
7.42
7.26
6.69
6.69
6.68
6.67
6.67
6.66
3.11
NC
CN
F3C
N
2.09
2.05
2.00
2.06
6.21
f1 (ppm)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153.82
140.74
133.75
133.50
133.43
133.23
132.97
130.80
125.74
125.71
125.68
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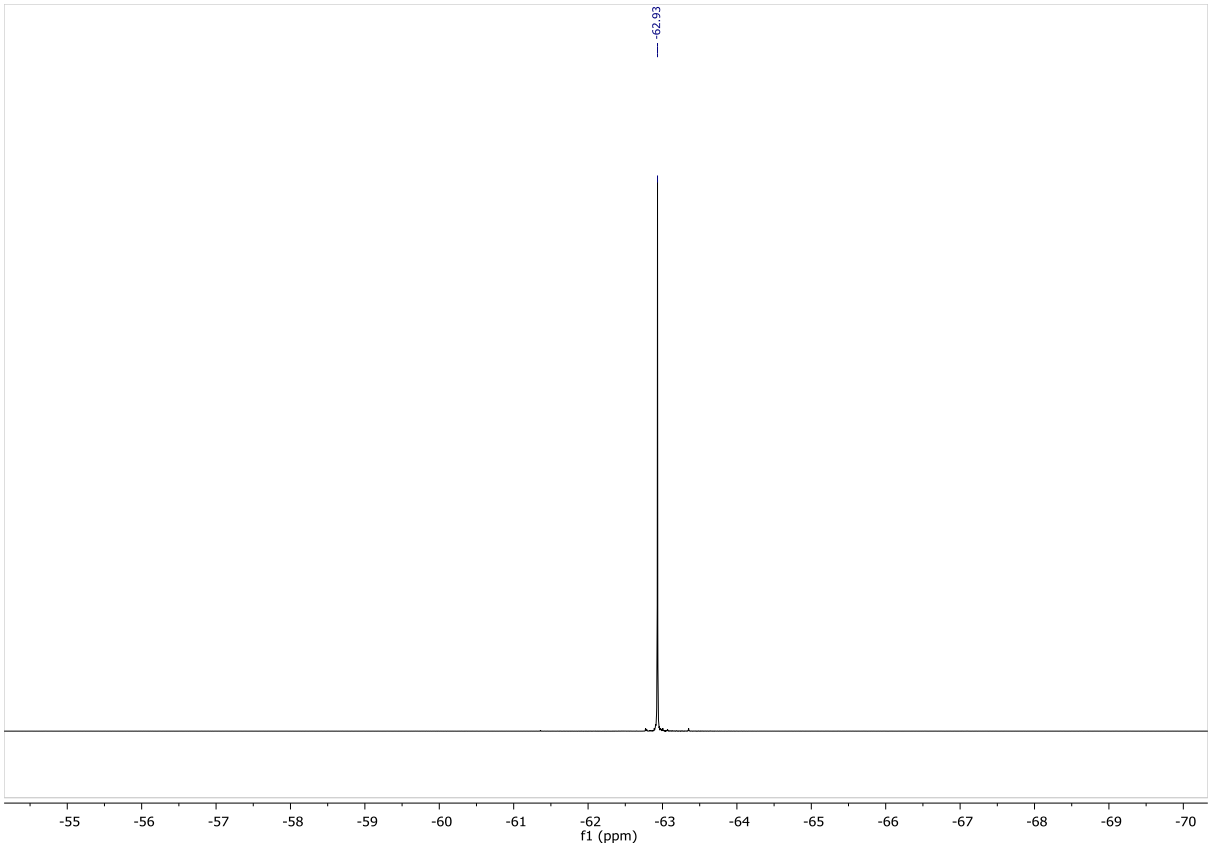
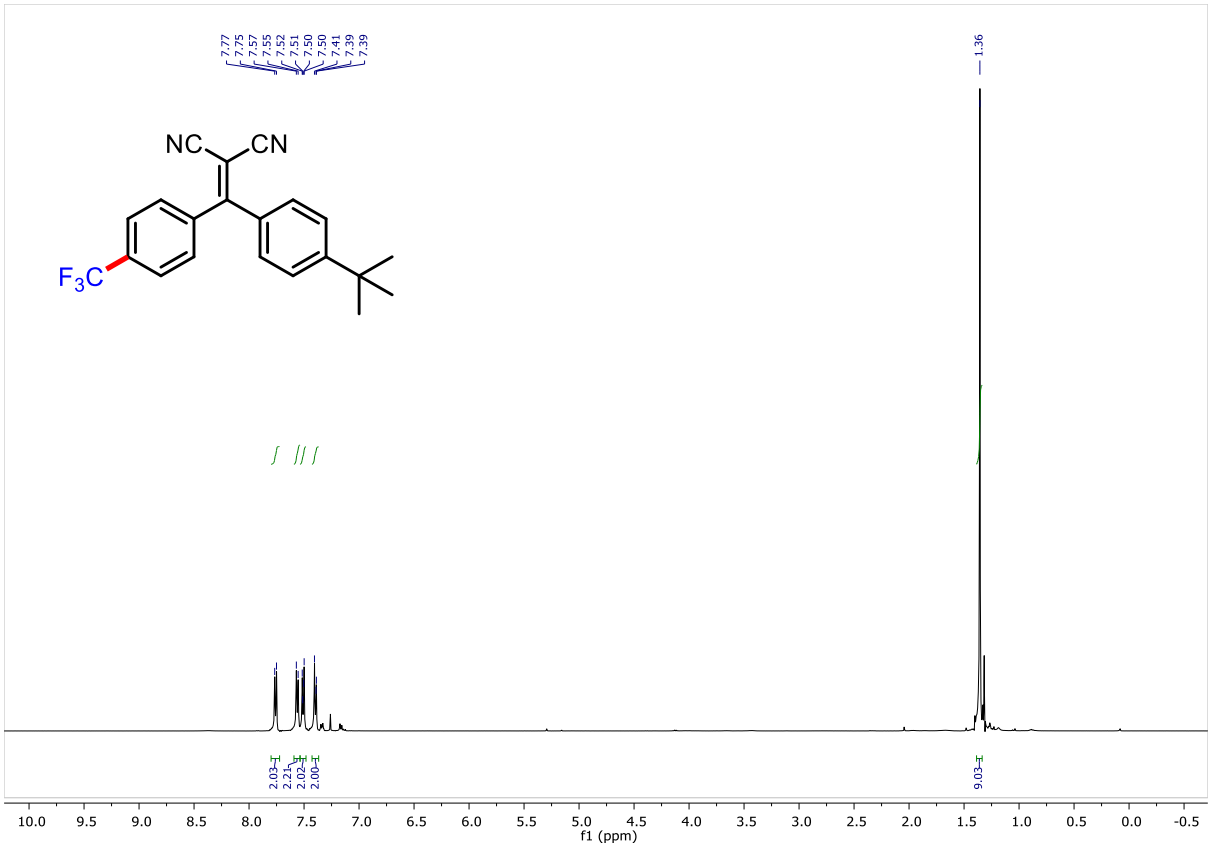
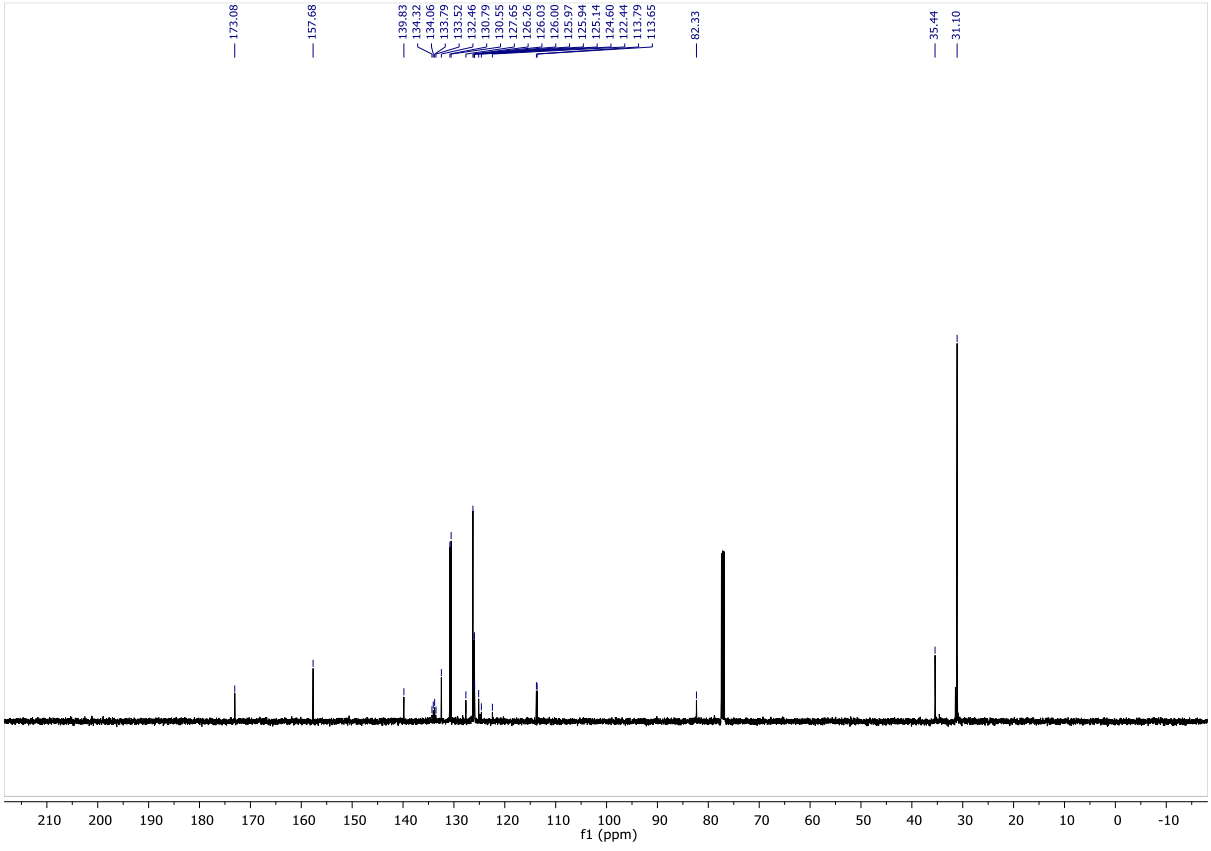
124.74
122.57
121.62
115.63
115.16
111.32
74.73
40.12
f1 (ppm)


-62.93
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
f1 (ppm)


7.77
7.75
7.57
7.55
7.52
7.51
7.50
7.50
7.41
7.39
7.39
1.36
NC
CN
F3C
2.03
2.21
2.02
2.00
9.03
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
f1 (ppm)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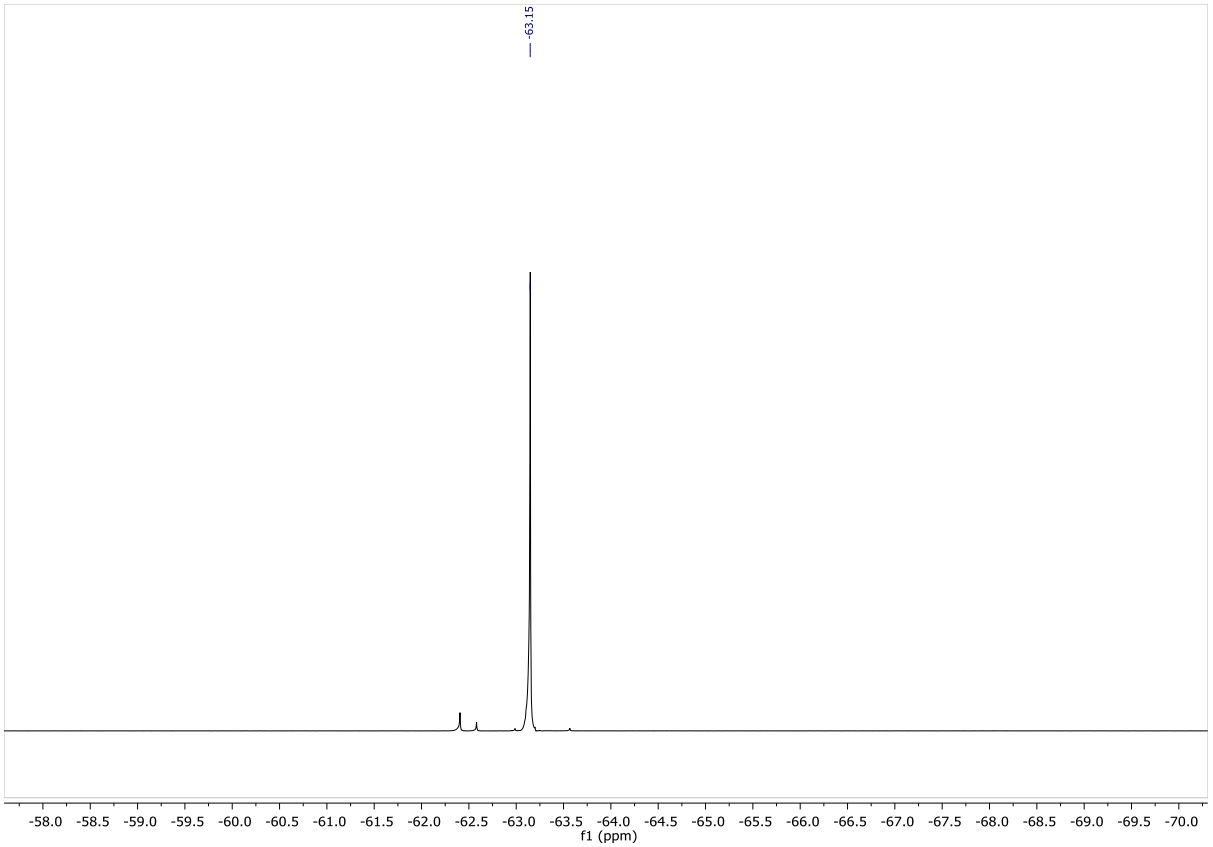
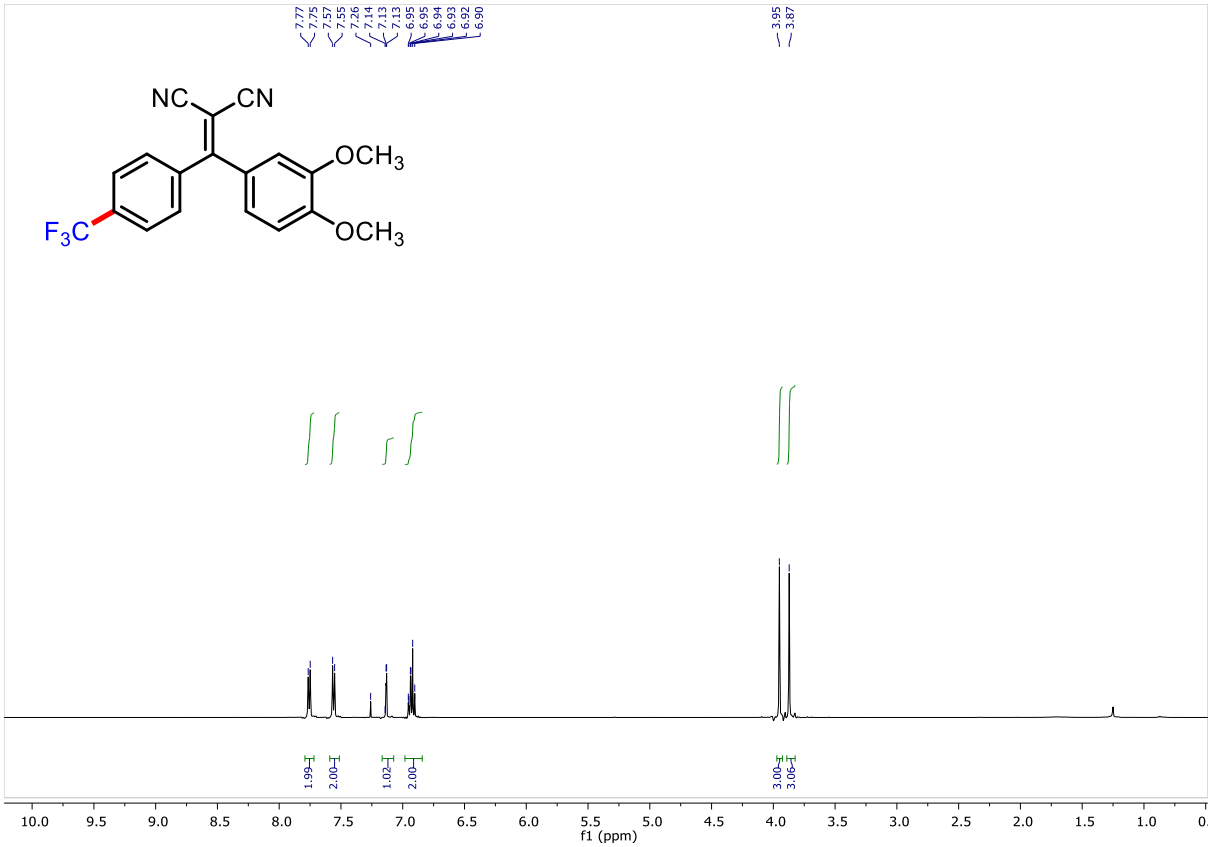
157.68
139.83
134.32
134.06
133.79
133.52
132.46
130.79
130.55
127.65
126.26
126.03
126.00
125.97
125.94
125.14
124.60
124.44
113.79
113.65
82.33
35.44
31.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-63.15
-58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0
f1 (ppm)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7.55
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7.14
7.13
6.95
6.95
6.94
6.93
6.92
6.90
3.95
3.87
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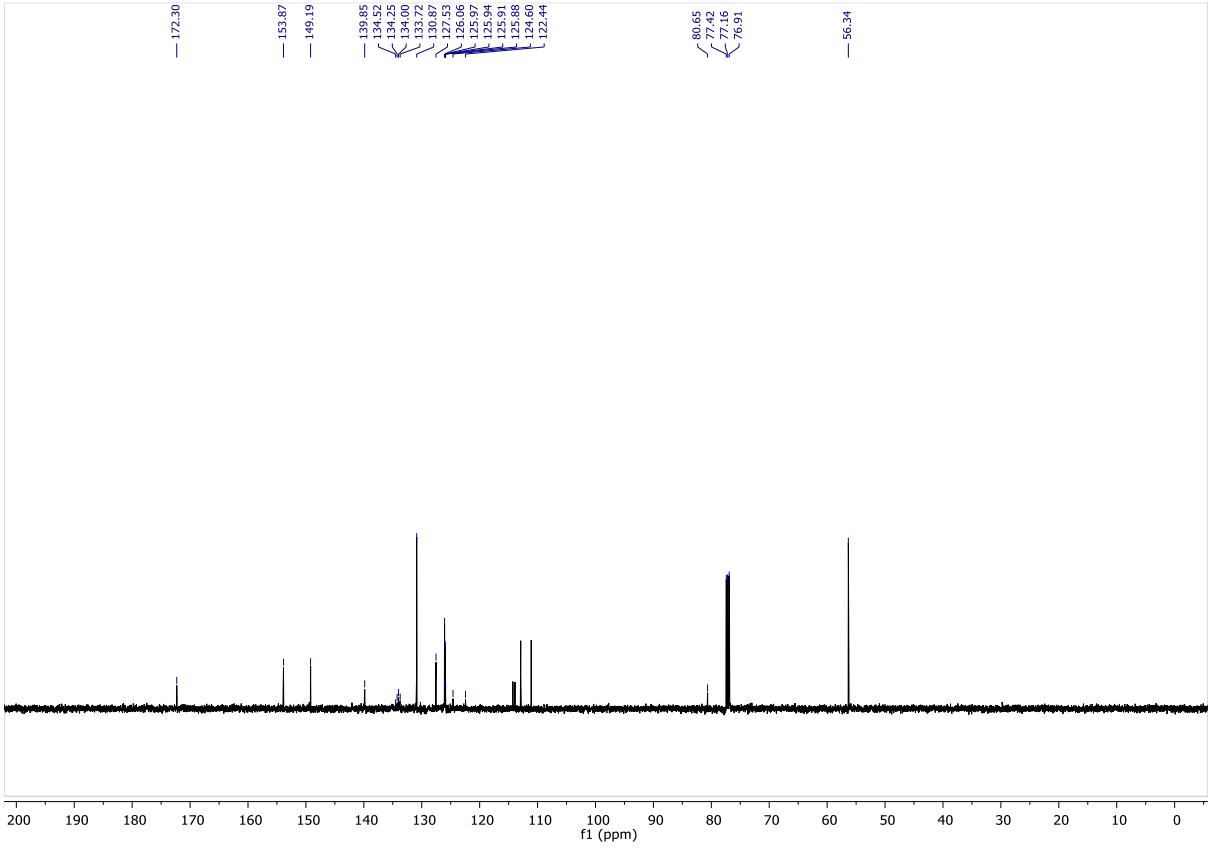
CN
OCH3
OCH3
F3C
1.99
2.00
1.02
2.00
3.00
3.06
f1 (ppm)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134.52
134.25
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133.72
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127.53
126.06
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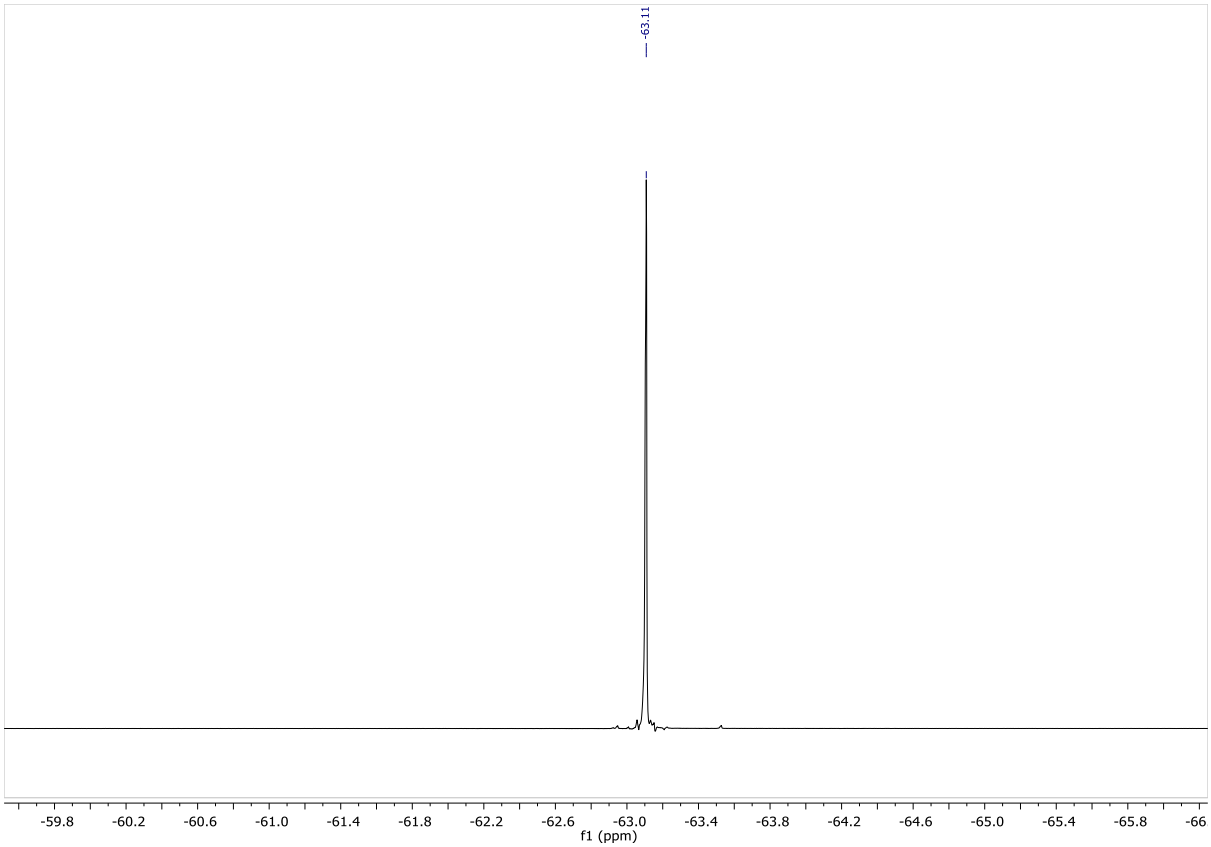
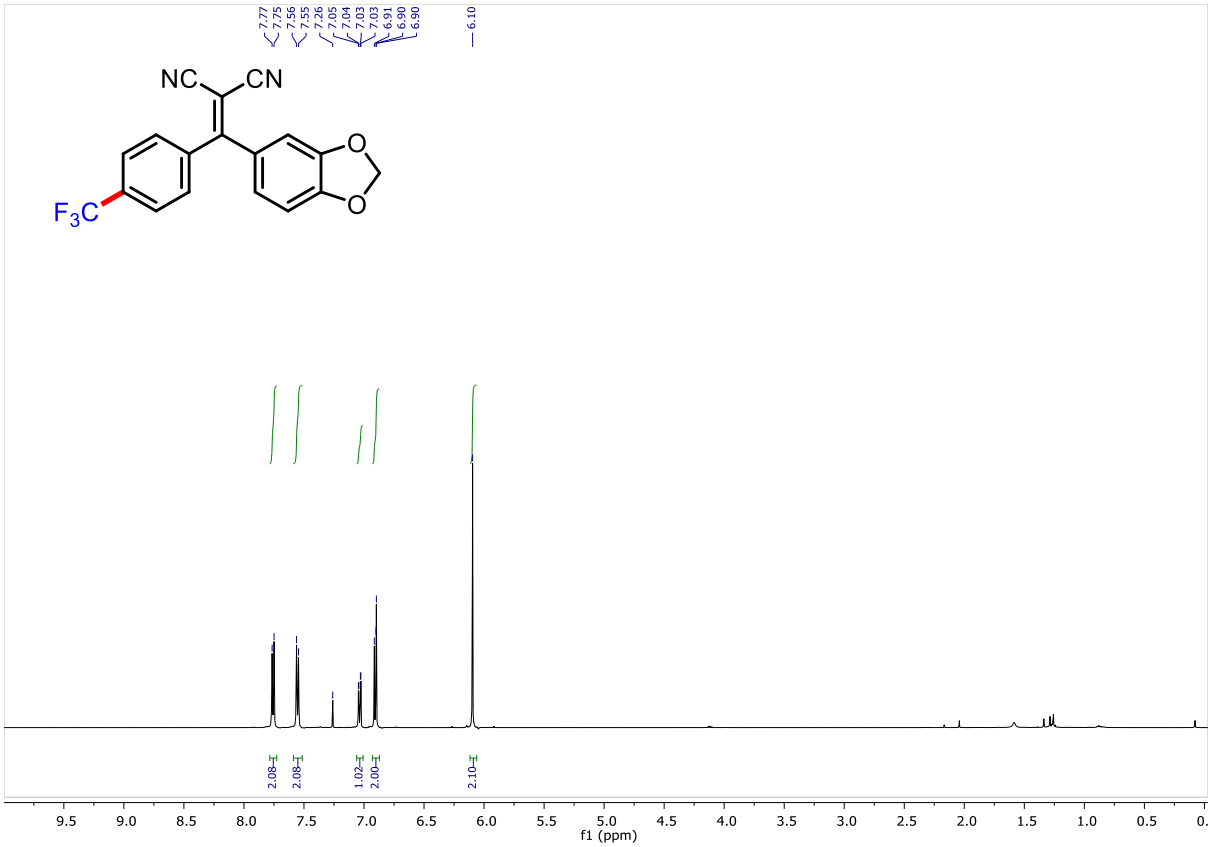
77.42
77.16
76.91
56.34
f1 (ppm)


-63.11
-59.8
-60.2
-60.6
-61.0
-61.4
-61.8
-62.2
-62.6
-63.0
-63.4
-63.8
-64.2
-64.6
-65.0
-65.4
-65.8
-66
f1 (ppm)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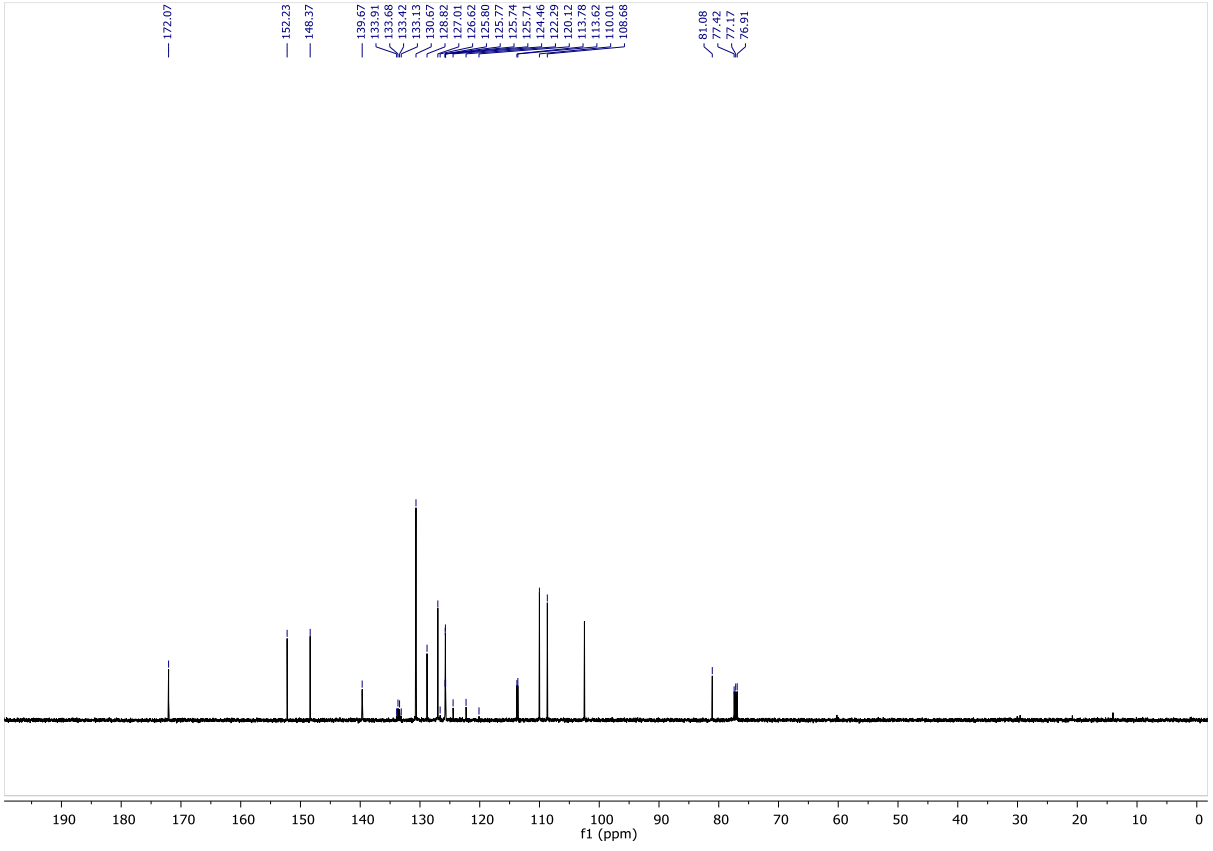
7.55
7.26
7.05
7.04
7.03
7.03
6.91
6.90
6.90
6.10
NC
CN
O
O
F3C
2.08
2.08
1.02
2.00
2.10
f1 (ppm)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127.01
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125.77
125.74
125.71
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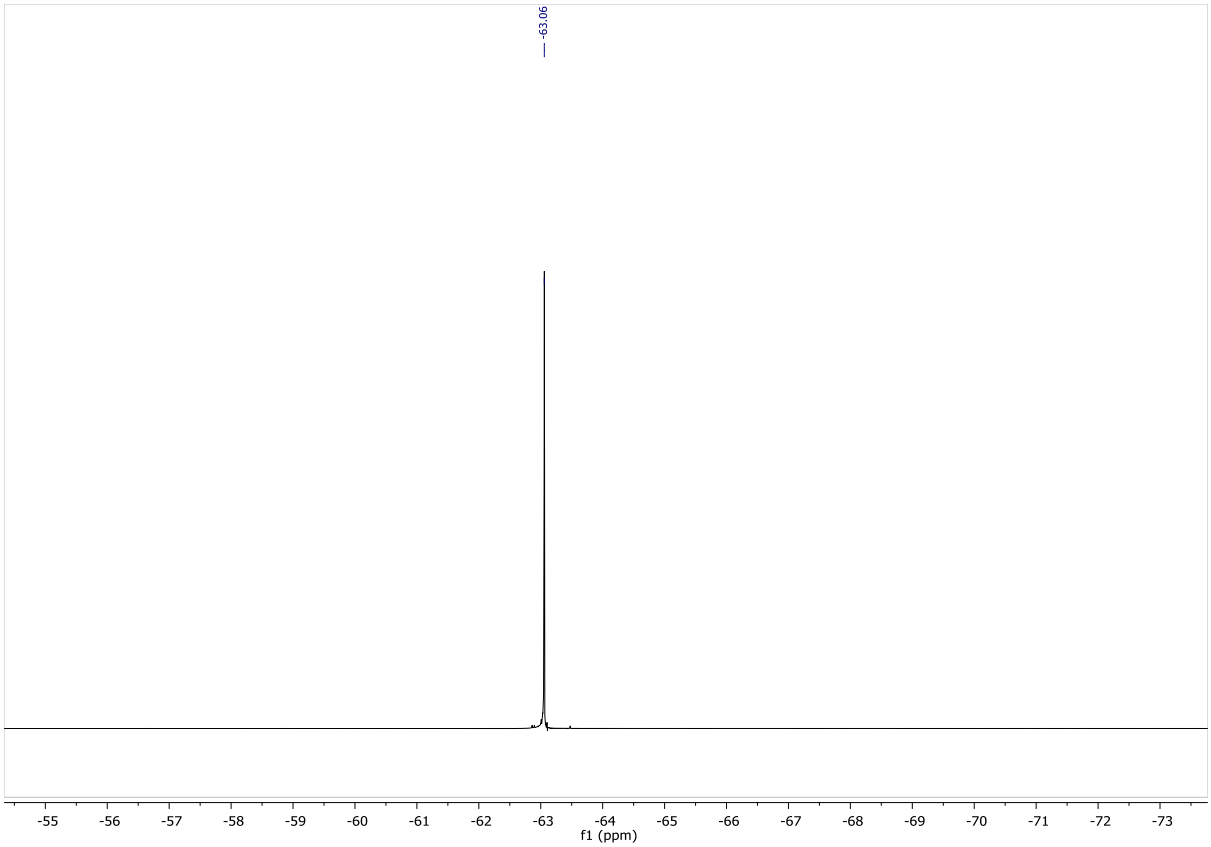
113.78
113.62
110.01
108.68
81.08
77.42
77.17
76.91
f1 (ppm)


-63.06
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
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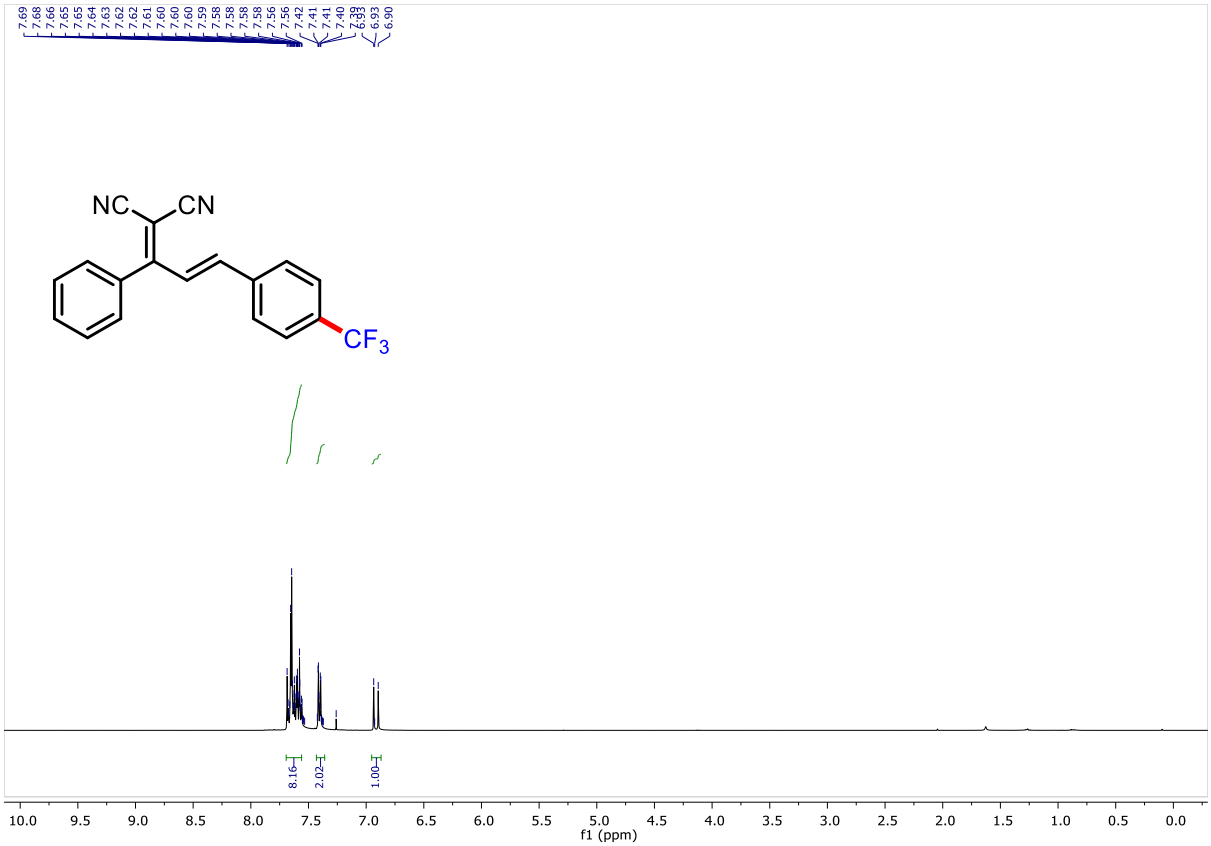
-69
-70
-71
-72
-73
f1 (ppm)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7.63
7.62
7.61
7.60
7.60
7.60
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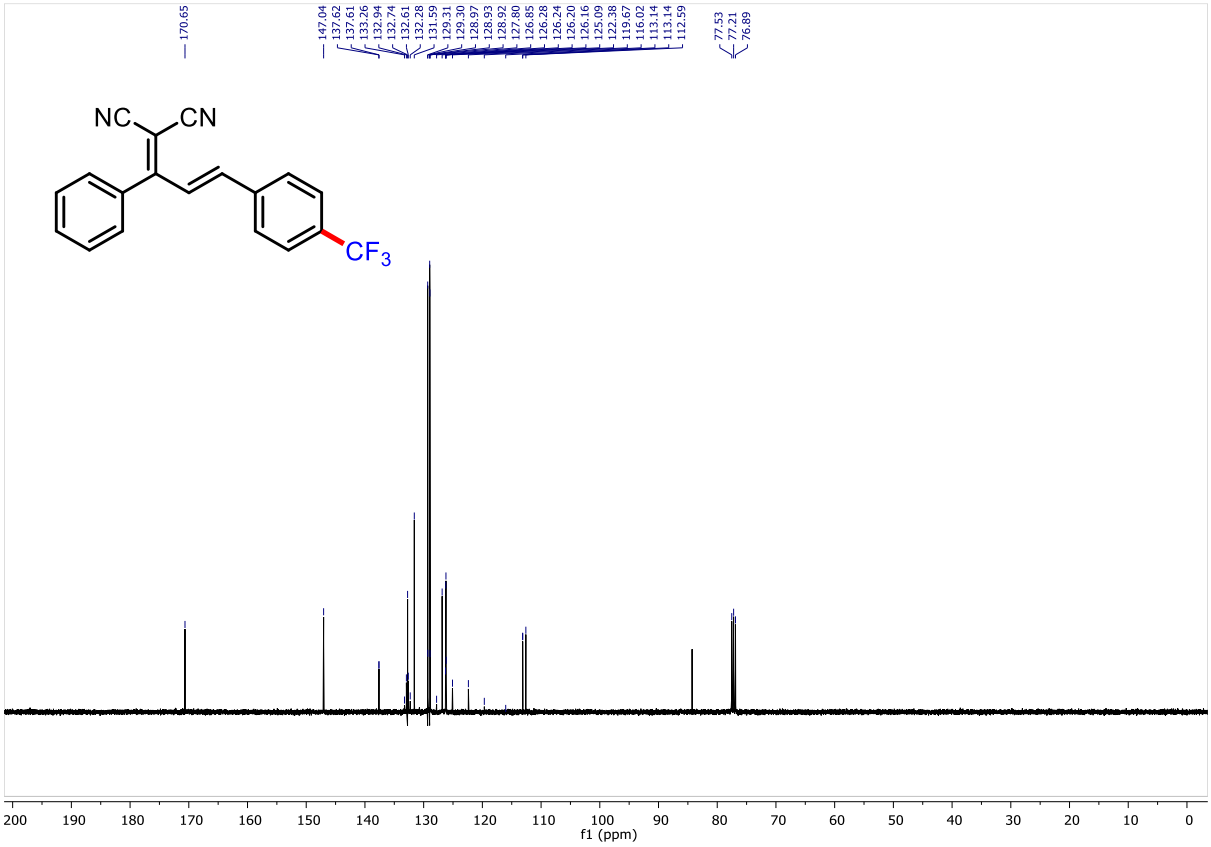
7.58
7.58
7.58
7.58
7.56
7.56
7.42
7.41
7.40
6.93
6.93
6.90
NC
CN
CF3
8.16
2.02
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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137.61
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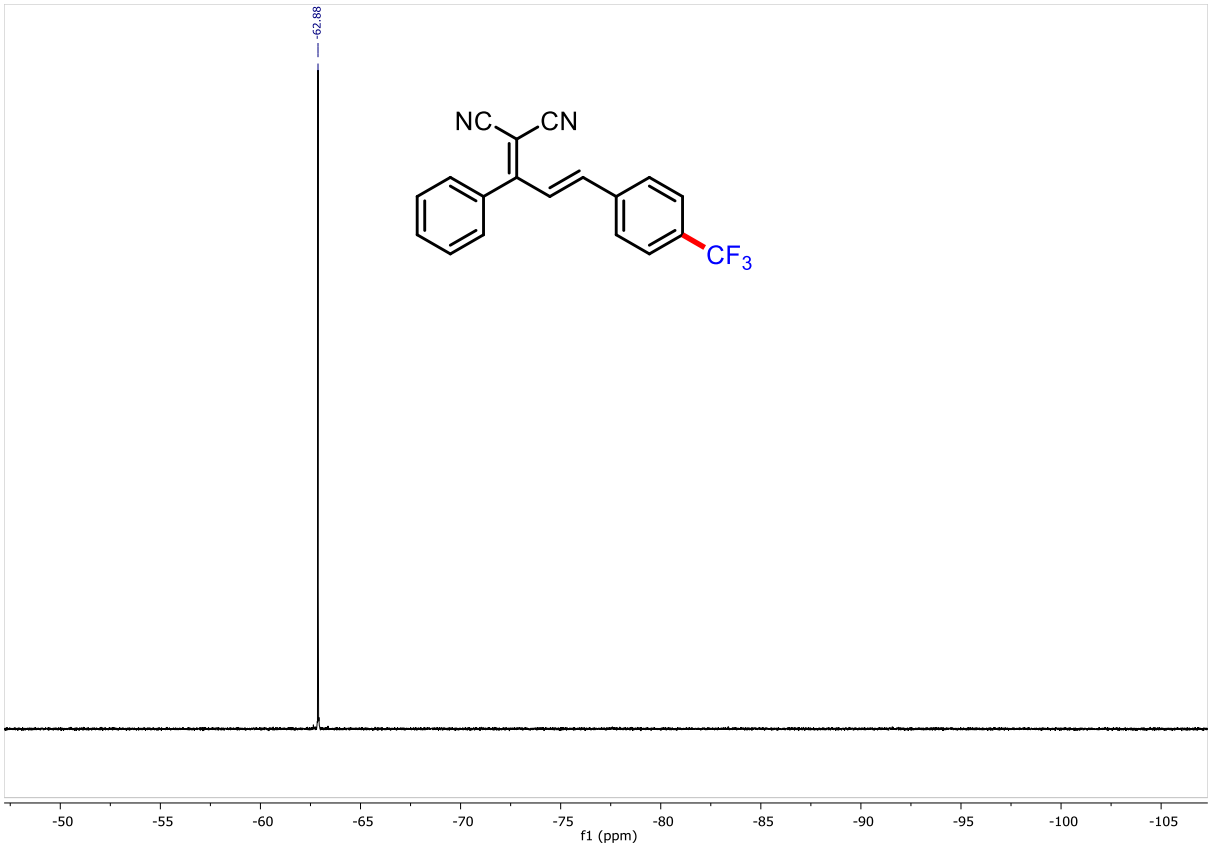
132.28
131.59
129.31
129.30
128.97
128.93
128.92
127.80
126.85
126.28
126.24
126.20
126.16
125.09
122.38
119.67
116.02
113.14
113.14
112.59
77.53
77.21
76.89
NC
CN
CF3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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-55
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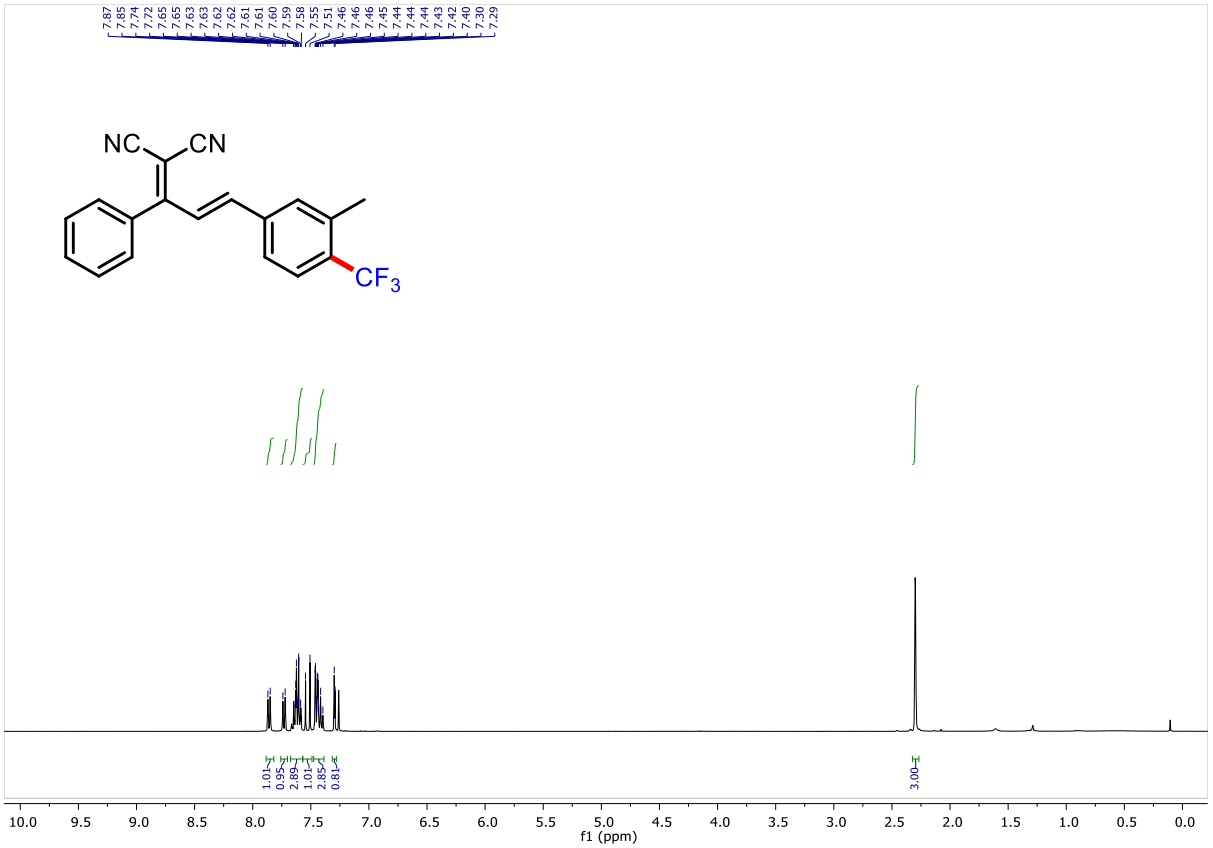
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)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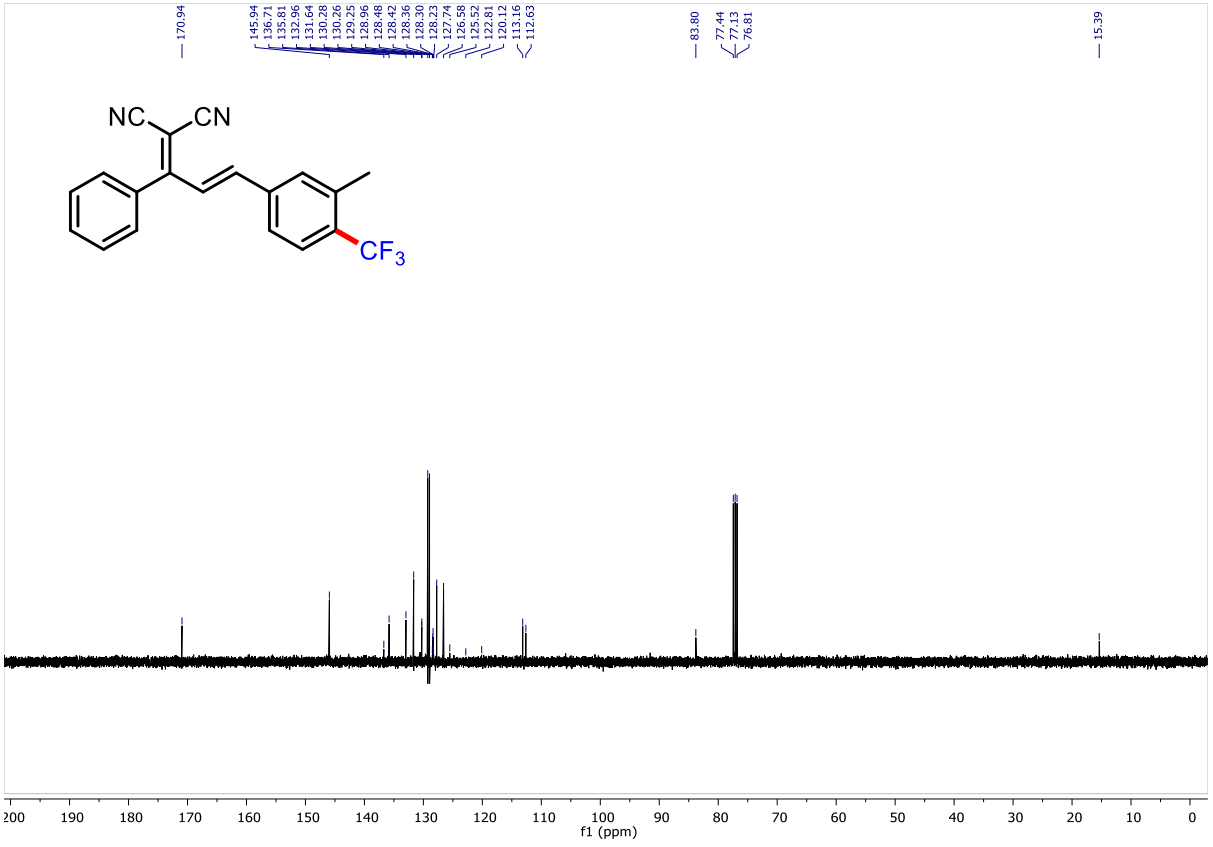
7.61
7.60
7.59
7.58
7.55
7.51
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.40
7.30
7.29
NC
CN
CF3
1.01
0.95
2.89
1.01
2.85
0.81
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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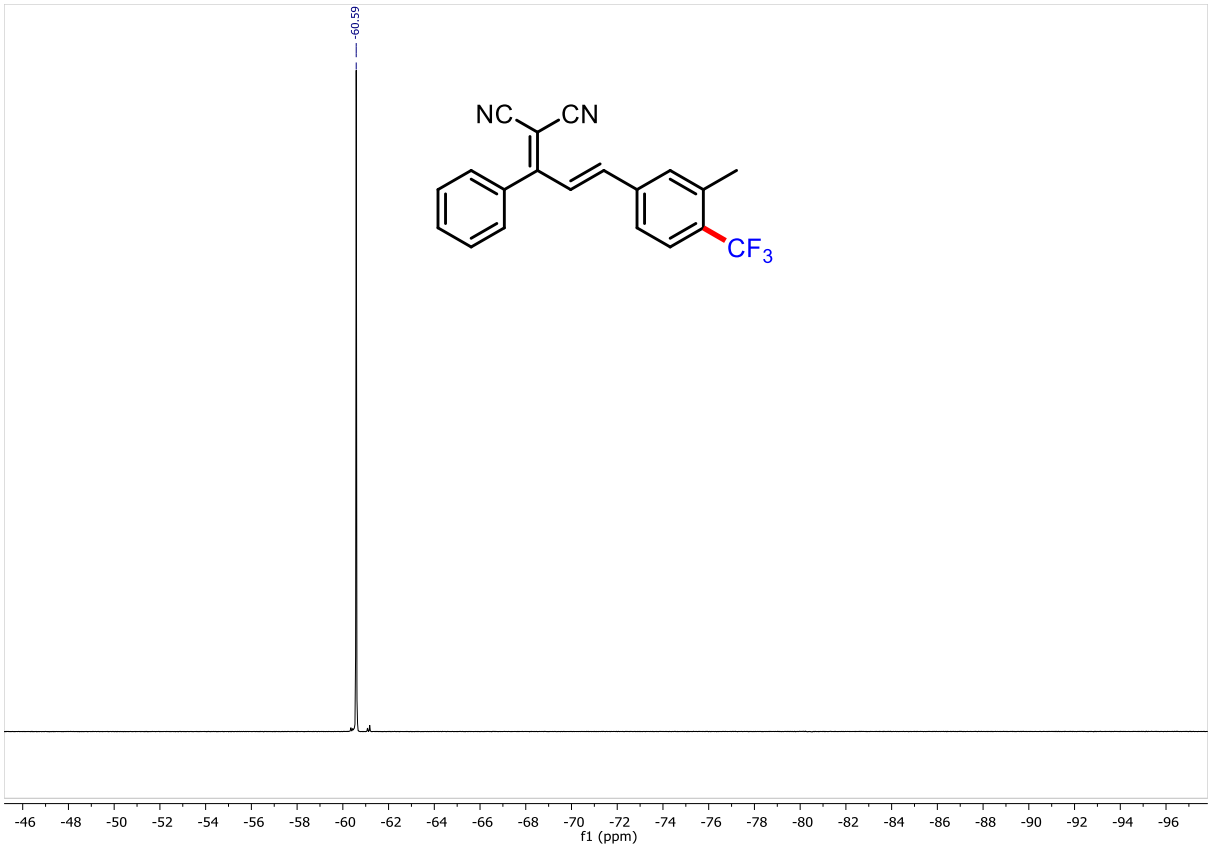
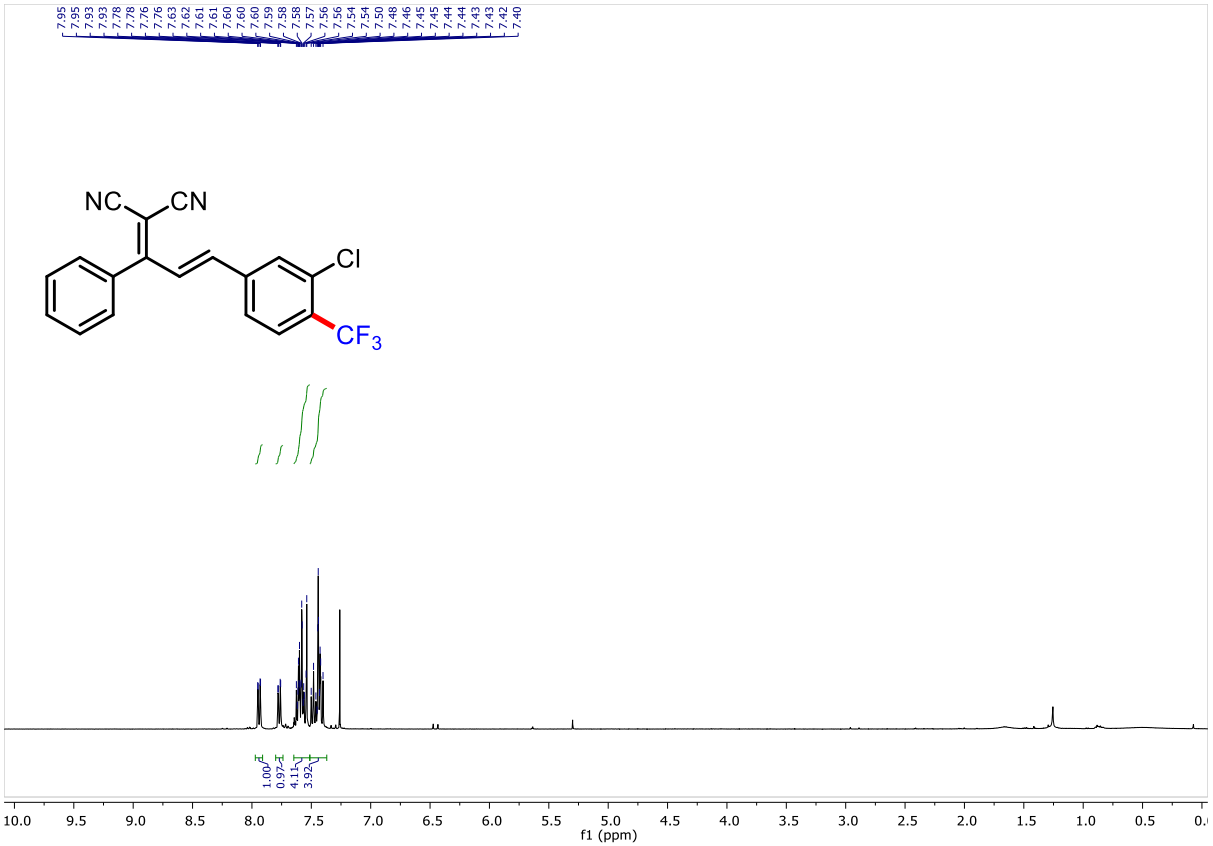
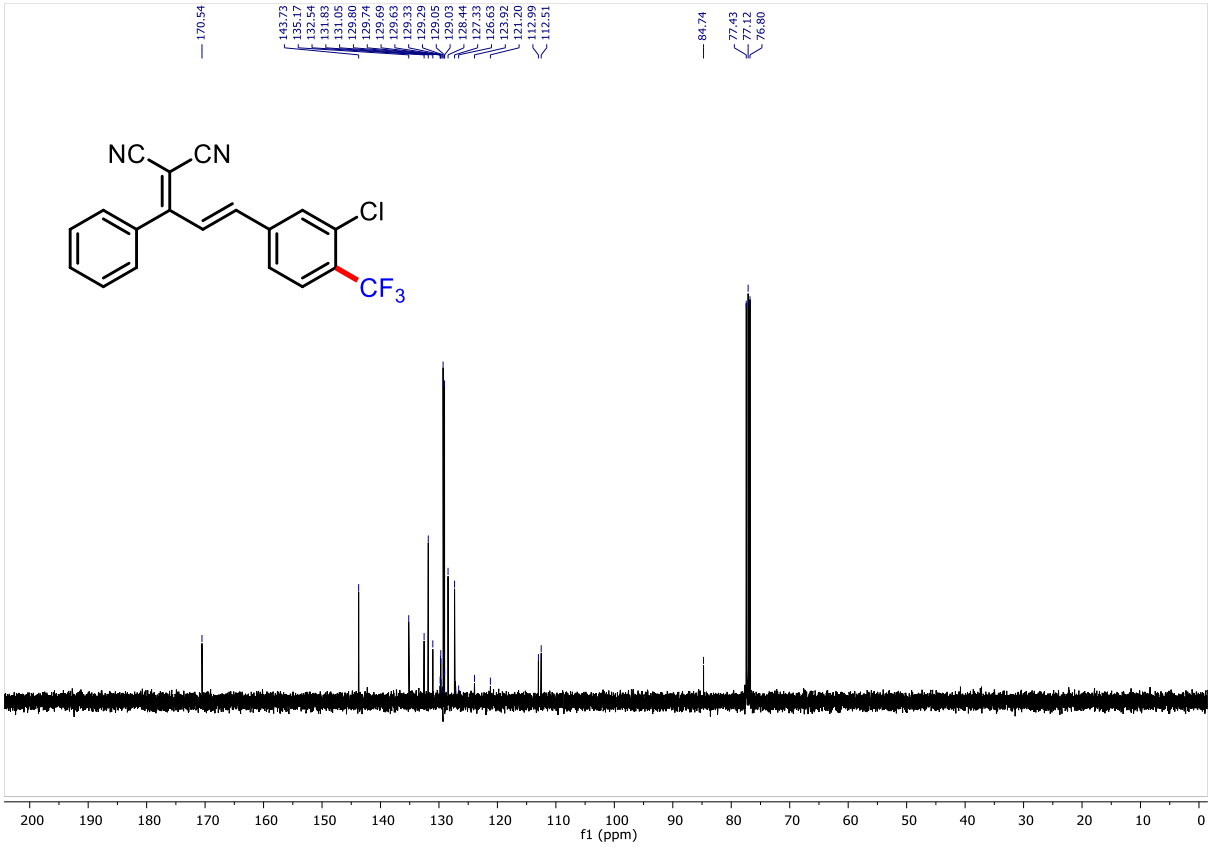
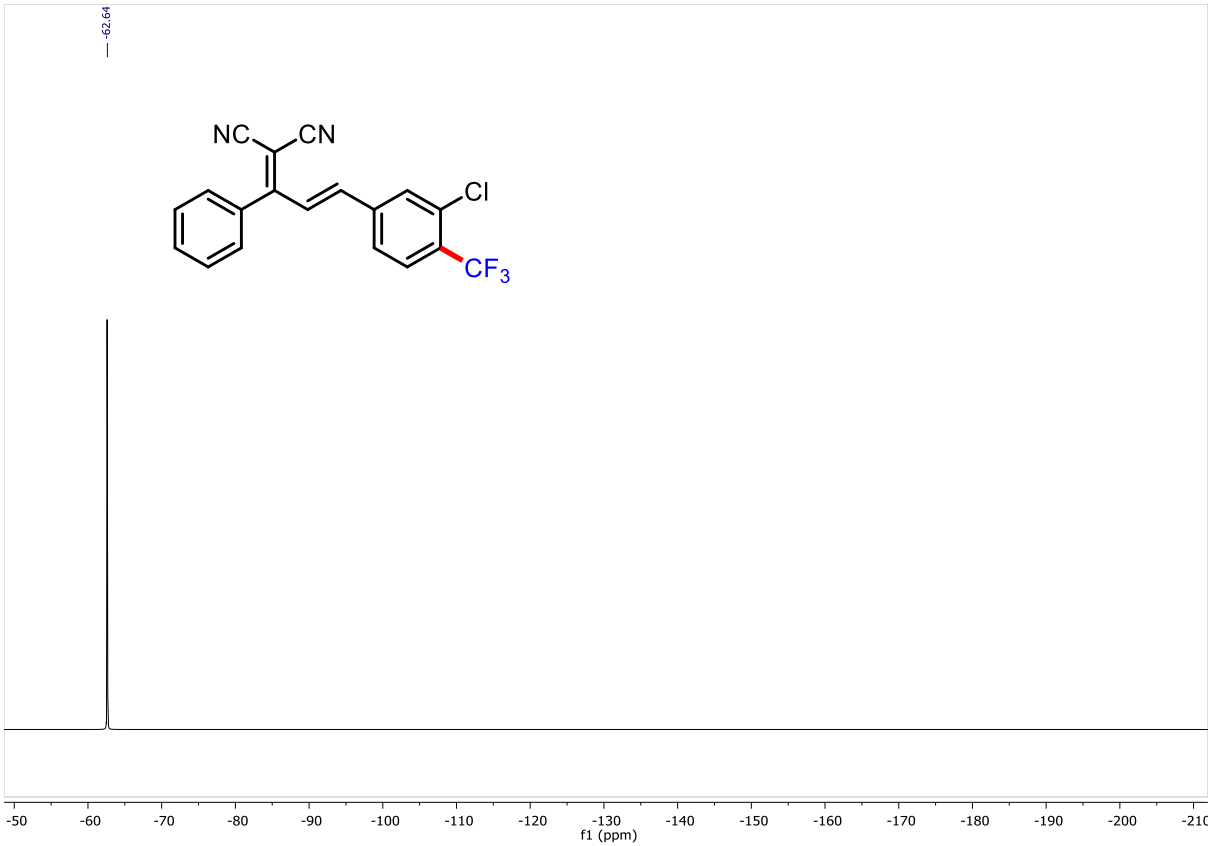
128.30
128.23
127.74
126.58
125.52
122.81
120.12
113.16
112.63
83.80
77.44
77.13
76.81
15.39
NC
CN
CF3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-60.59
NC
CN
CF3
-46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96
f1 (ppm)


NC
CN
Cl
CF3
1.00
0.97
4.11
3.92
f1 (ppm)


NC
CN
Cl
CF3
f1 (ppm)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Cl
CF3
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
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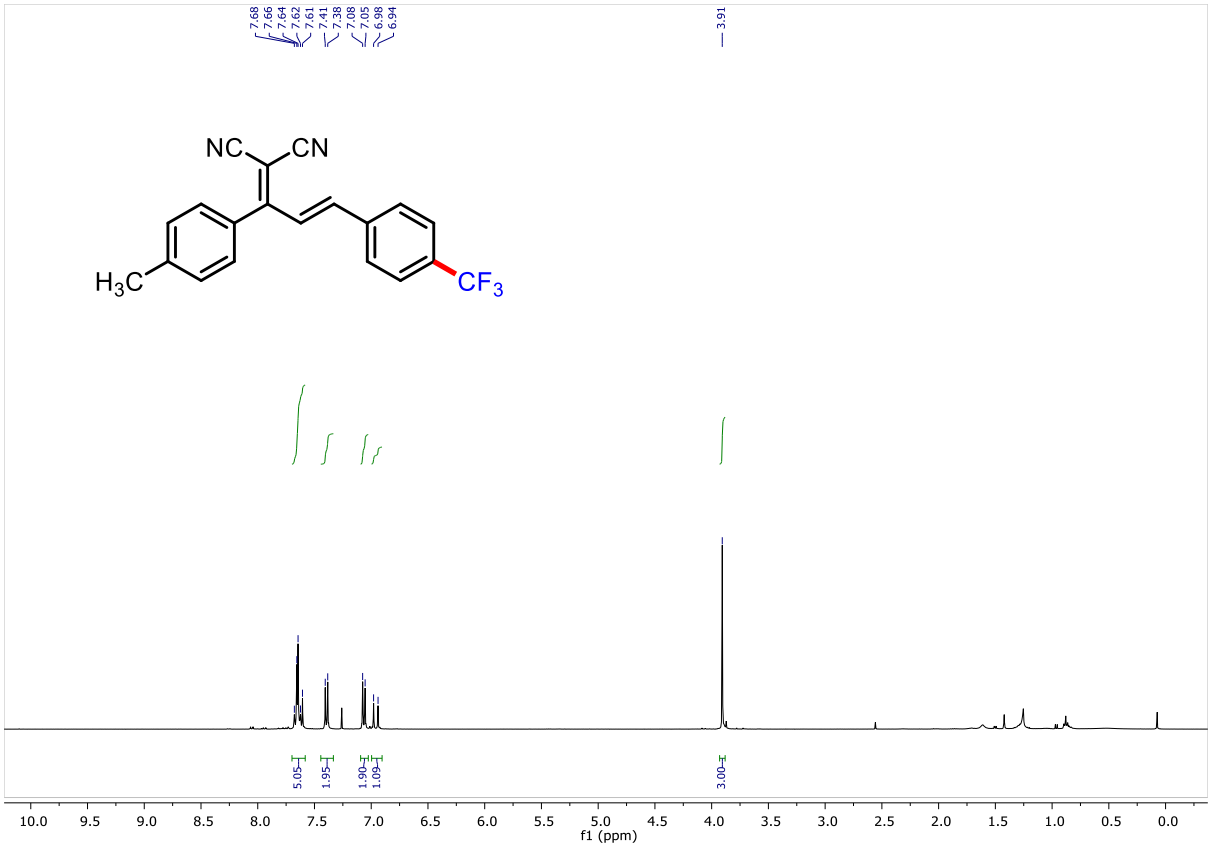
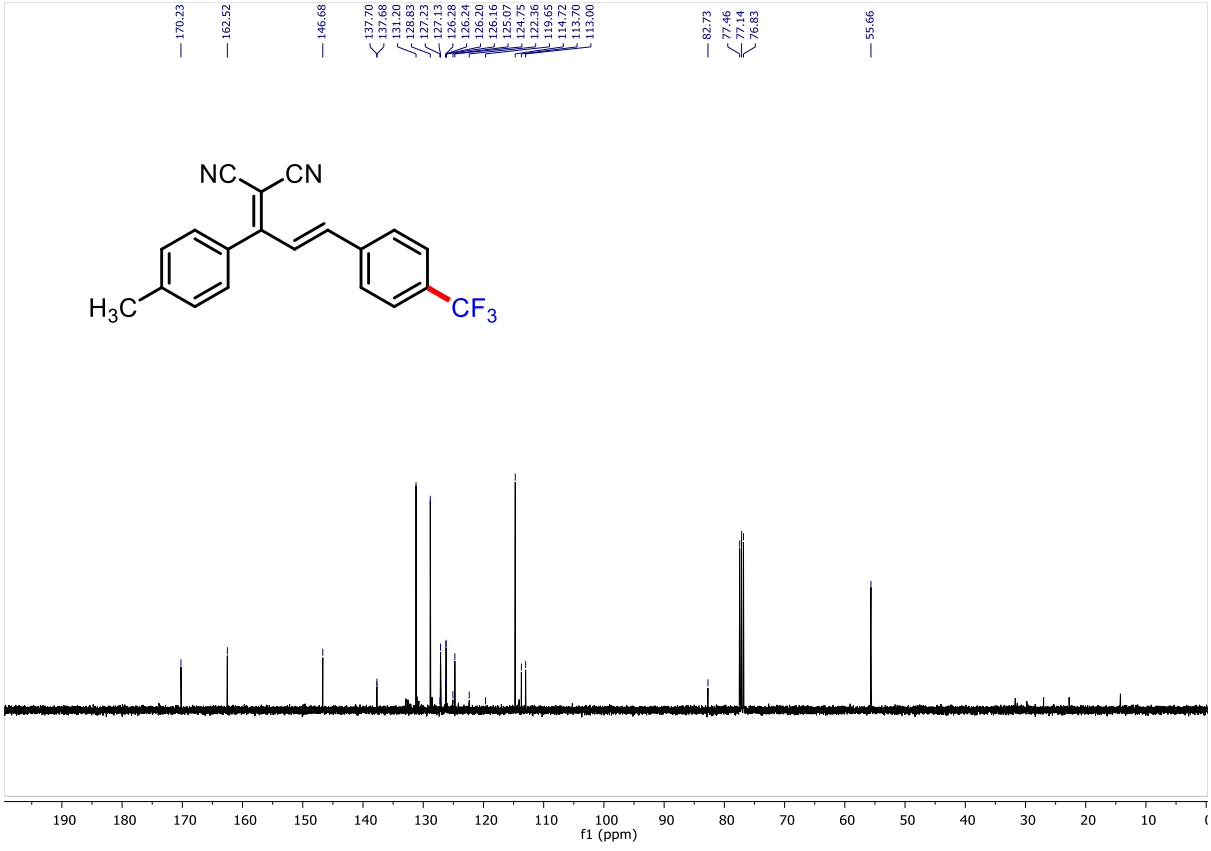
-160
-170
-180
-190
-200
f1 (ppm)


7.68
7.66
7.64
7.62
7.61
7.41
7.38
7.08
7.05
6.98
6.94
3.91
NC
CN
H3C
CF3
5.05
1.95
1.90
1.09
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)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162.52
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137.70
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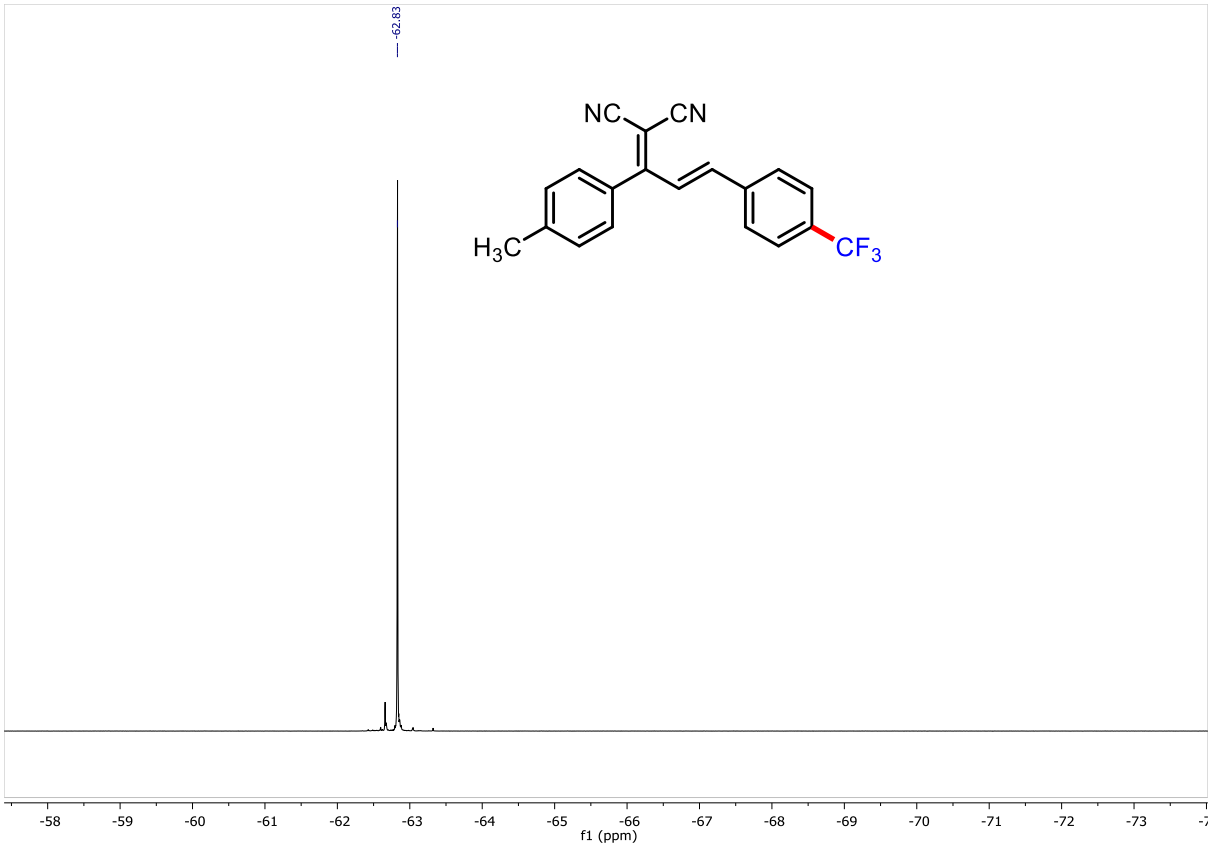
131.20
128.83
127.23
127.13
126.28
126.24
126.20
126.16
125.07
124.75
122.36
119.65
114.72
113.70
113.00
82.73
77.46
77.14
76.83
55.66
NC
CN
H3C
CF3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-62.83
NC
CN
H3C
CF3
-58
-59
-60
-61
-62
-63
-64
-65
-66
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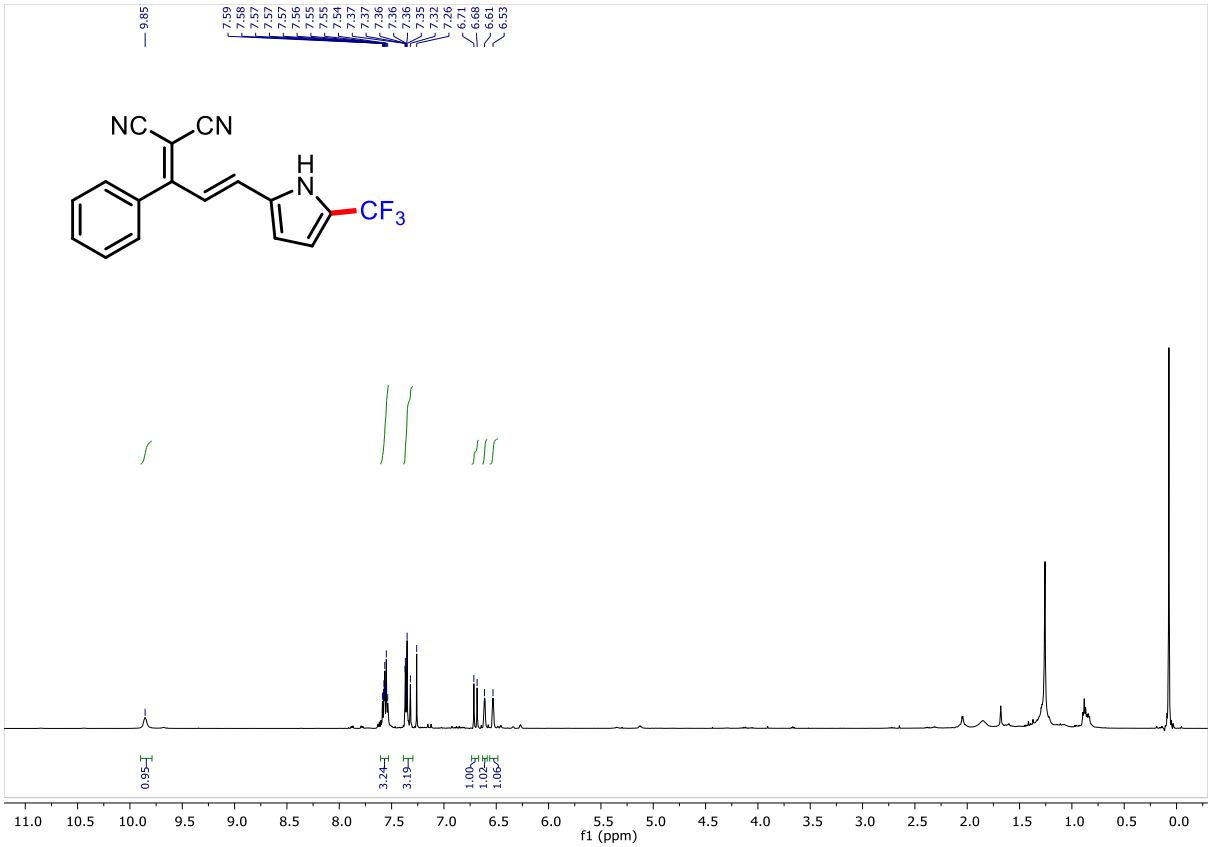
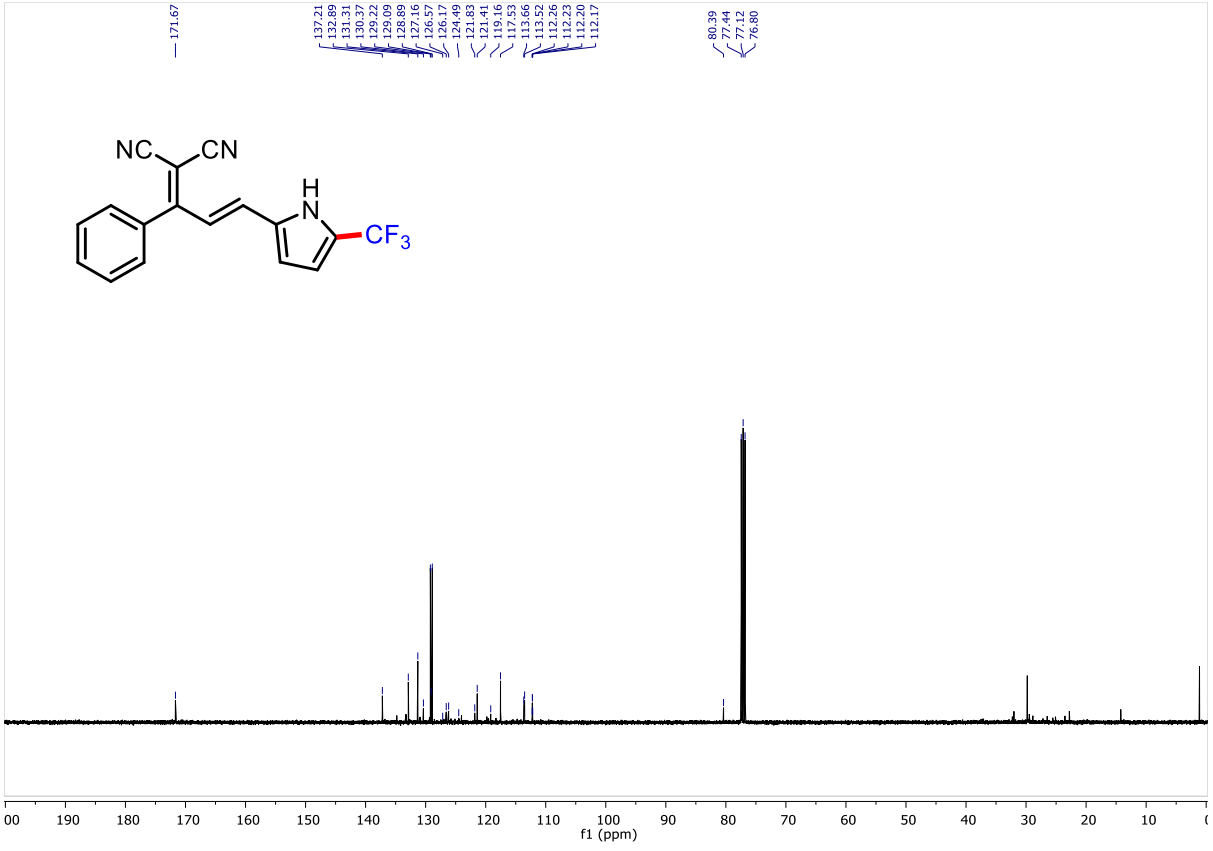
-68
-69
-70
-71
-72
-73
f1 (ppm)


9.85
7.59
7.58
7.57
7.57
7.57
7.56
7.55
7.55
7.54
7.37
7.37
7.36
7.36
7.36
7.35
7.32
7.26
6.71
6.68
6.61
6.53
NC
CN
H
N
CF3
0.95
3.24
3.19
1.00
1.02
1.06
f1 (ppm)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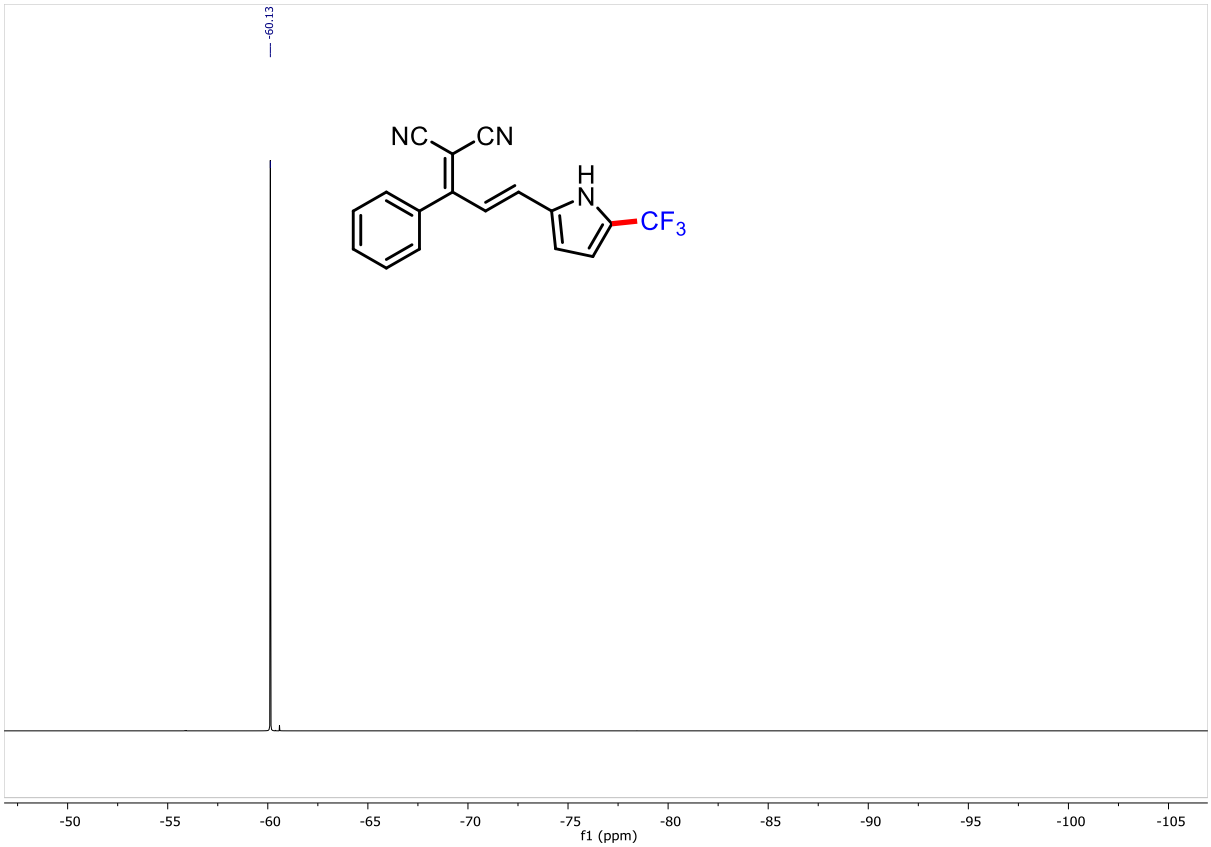
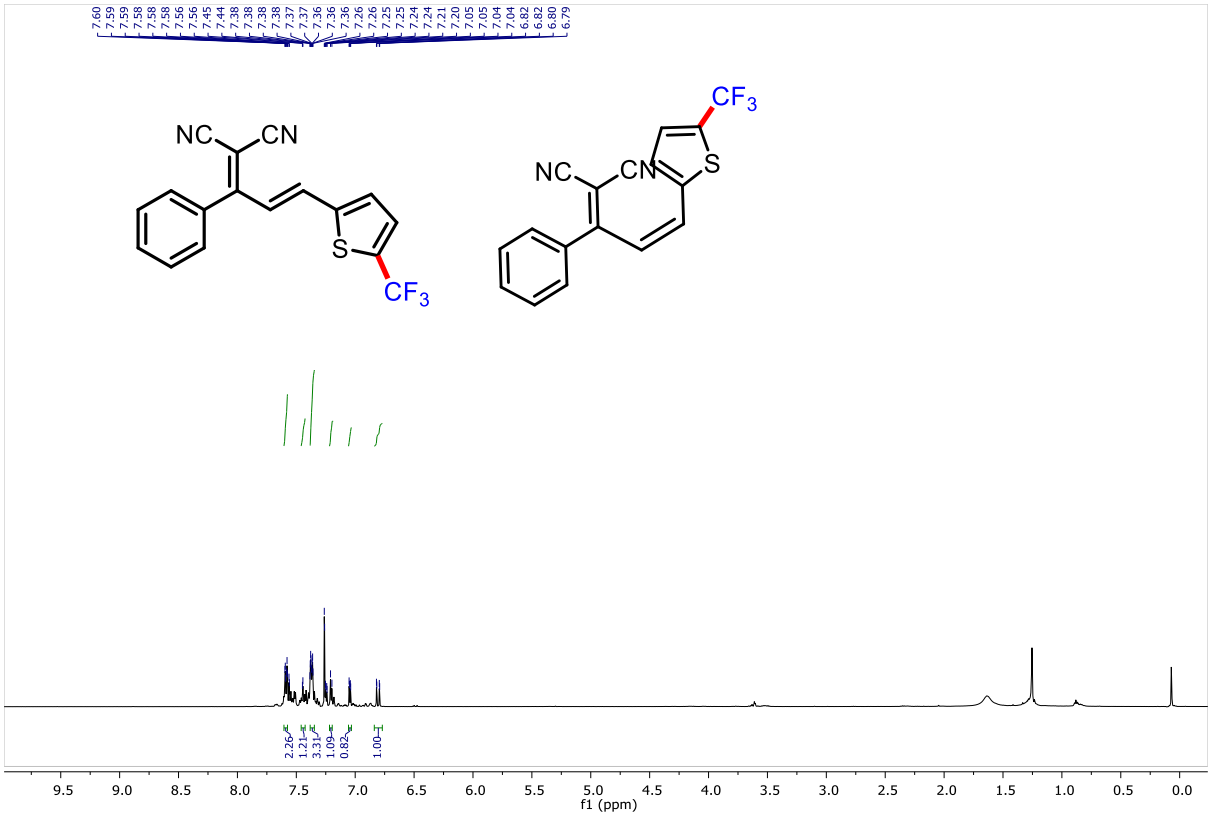
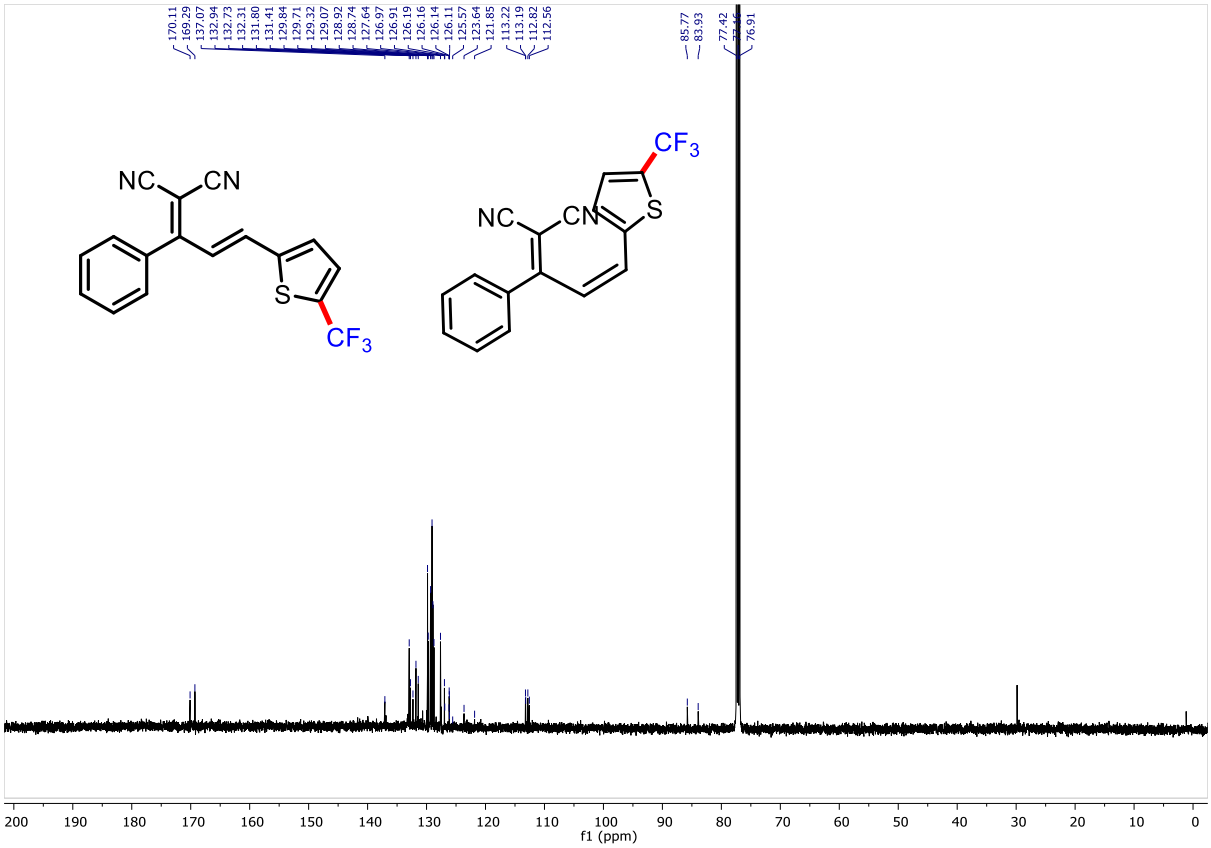
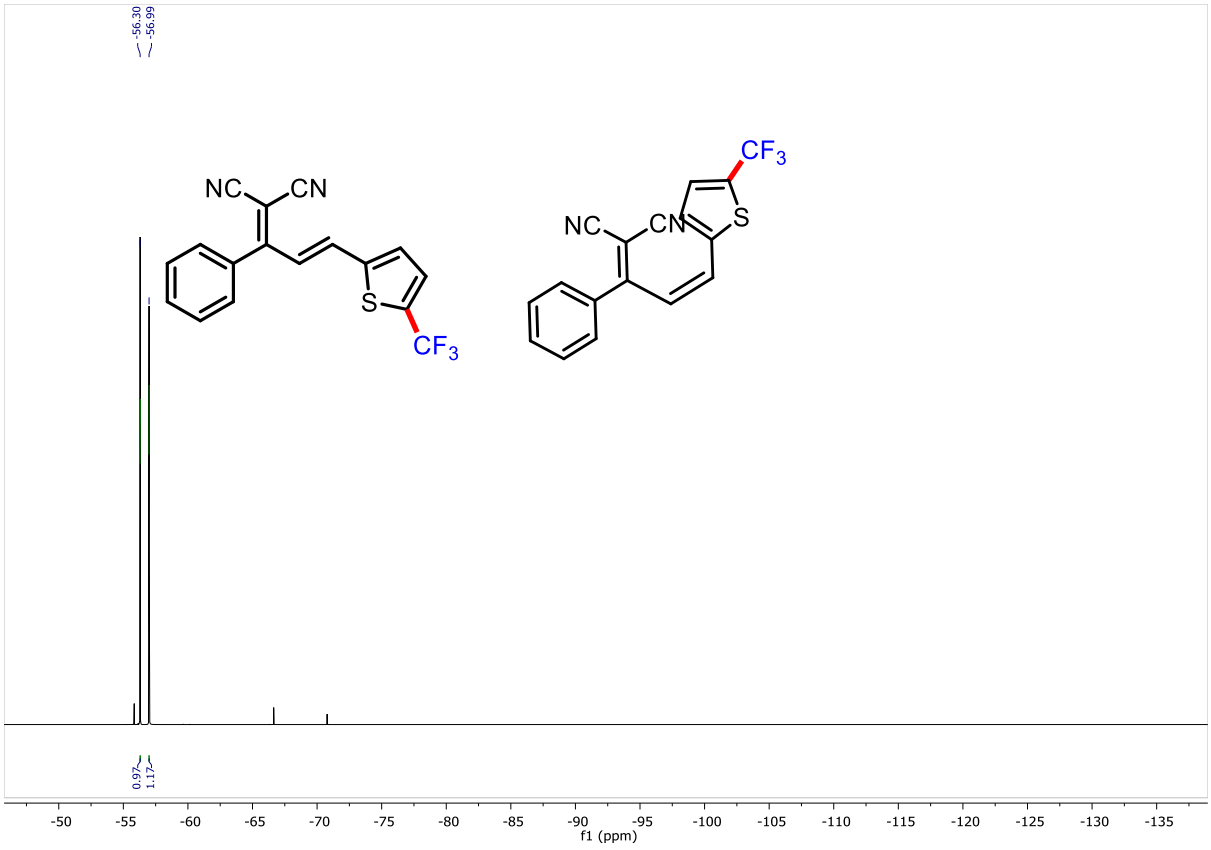
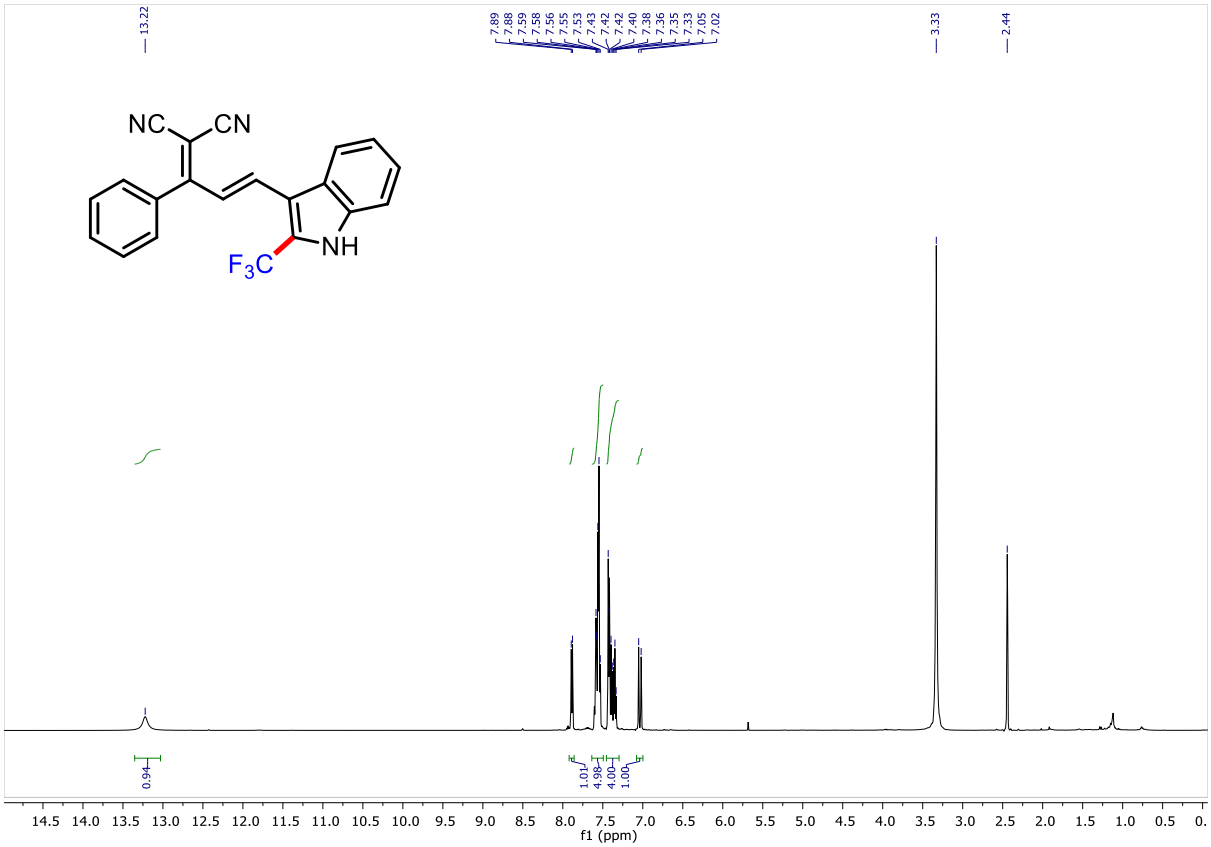
132.89
131.31
130.37
129.22
129.09
128.89
127.16
126.57
126.17
124.49
121.83
121.41
119.16
117.53
113.66
113.52
112.26
112.23
112.20
112.17
80.39
77.44
77.12
76.80
NC
CN
H
N
CF3
f1 (ppm)

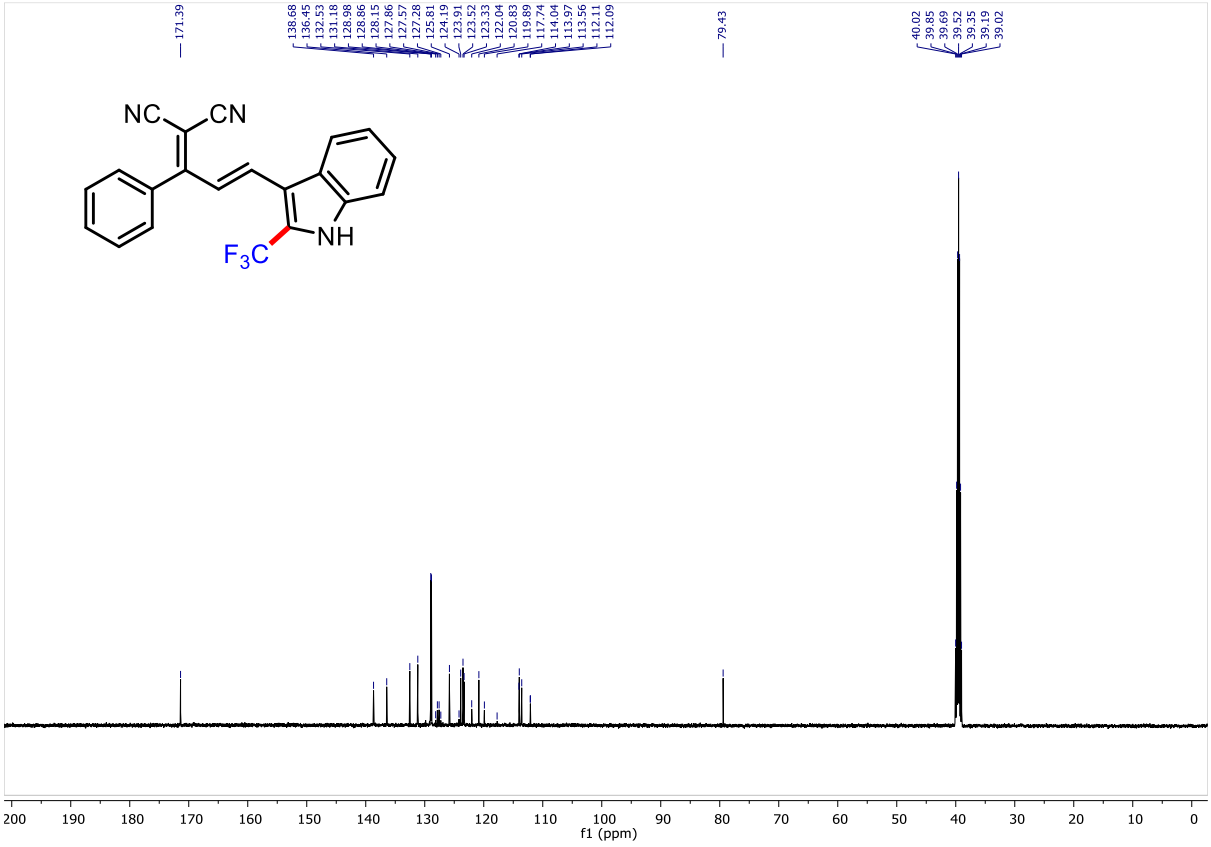

-60.13
NC
CN
H
N
CF3
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)


NC
CN
S
CF3
NC
CN
S
CF3
f1 (ppm)


NC
CN
S
CF3
NC
CN
S
CF3
f1 (ppm)


-56.30
-56.99
NC
CN
S
CF3
NC
CN
S
CF3
0.97
1.17
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
f1 (ppm)


13.22
7.89
7.88
7.59
7.58
7.56
7.55
7.53
7.43
7.42
7.42
7.40
7.38
7.36
7.35
7.33
7.05
7.02
3.33
2.44
NC
CN
NH
F3C
0.94
1.01
4.98
4.00
1.00
f1 (ppm)


171.39
138.68
136.45
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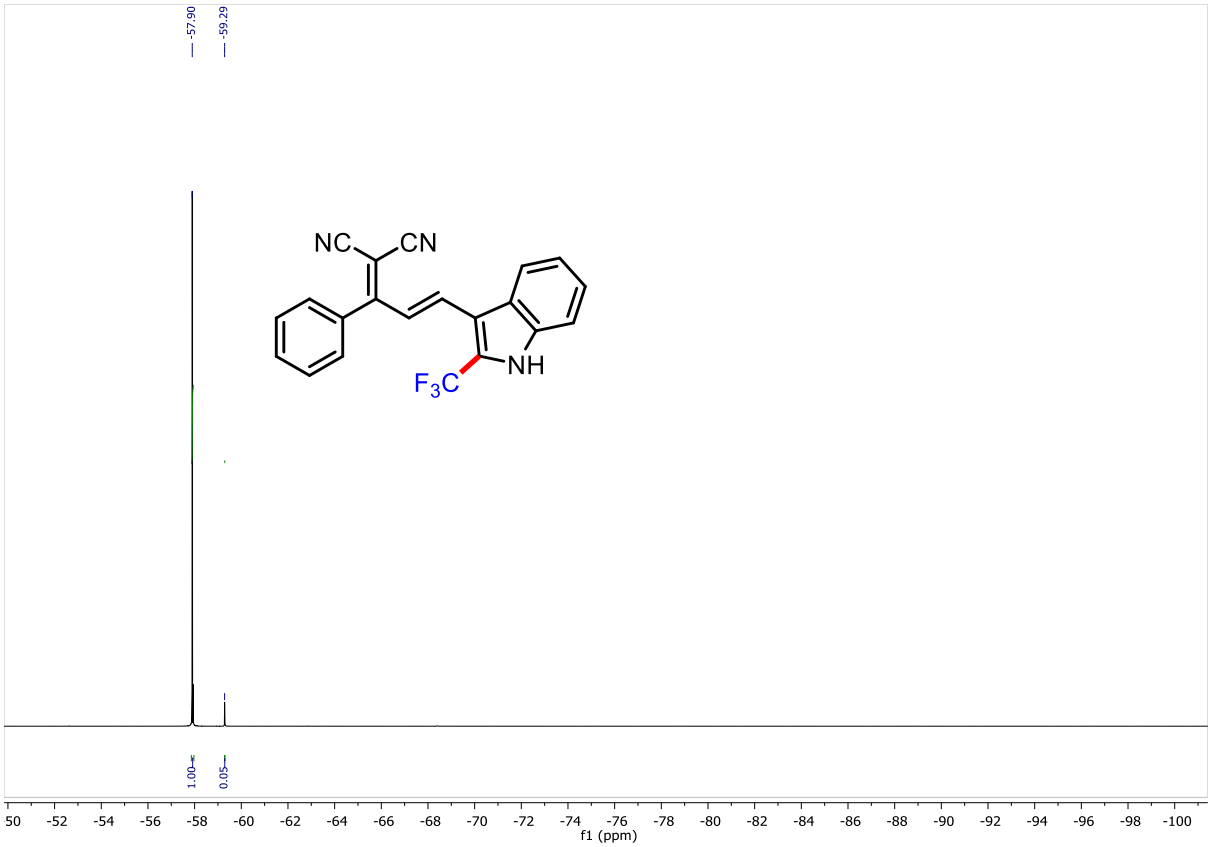
131.18
128.98
128.86
128.15
127.86
127.57
127.28
125.81
124.19
123.91
123.52
123.33
122.04
120.83
119.89
117.74
114.04
113.97
113.56
112.11
112.09
79.43
40.02
39.85
39.69
39.52
39.35
39.19
39.02
NC
CN
NH
F3C
f1 (ppm)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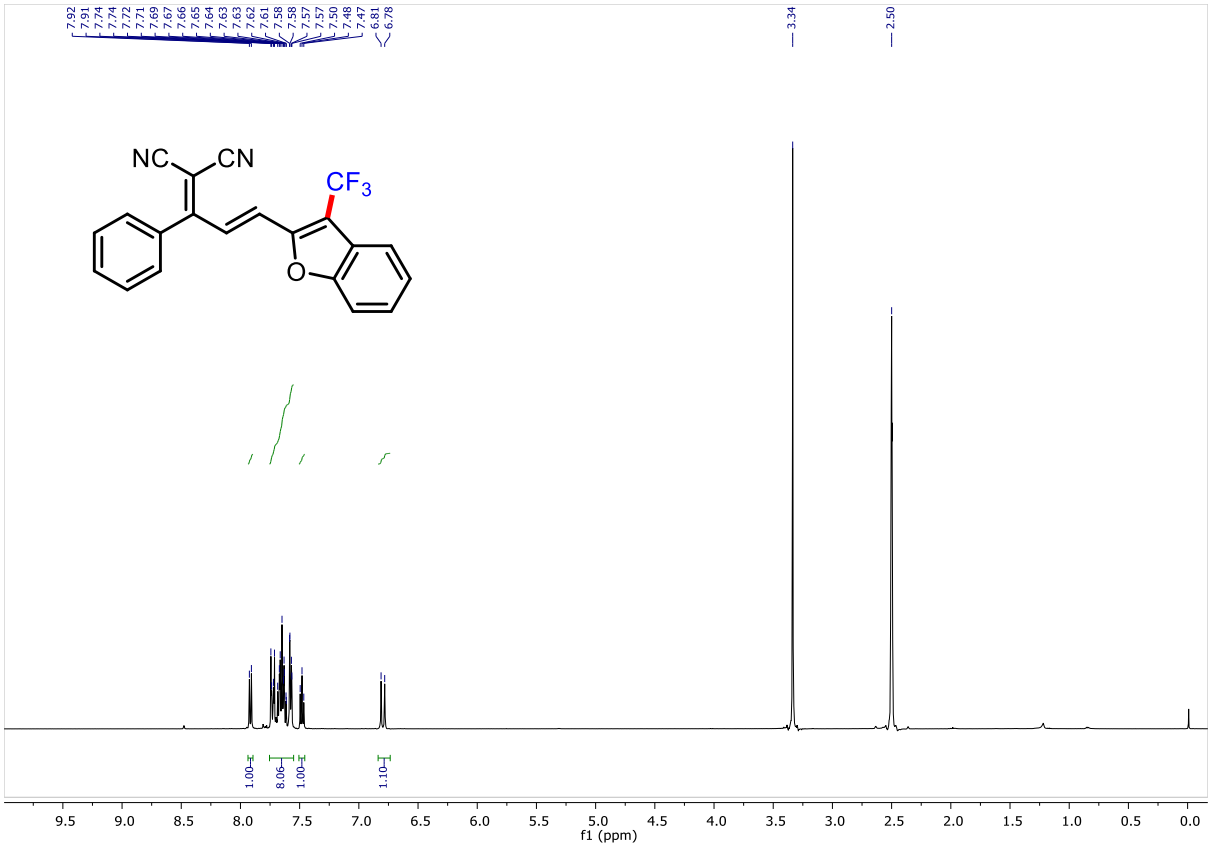
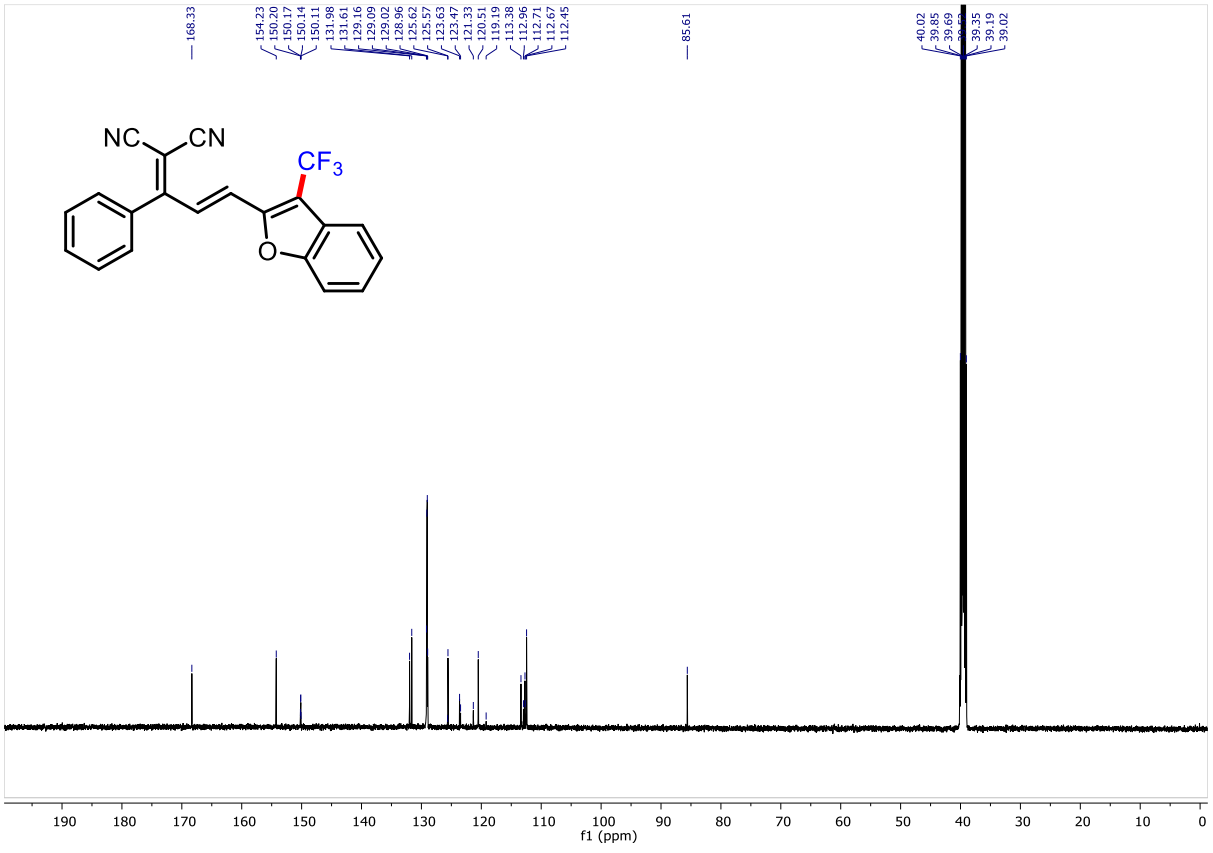
-59.29
NC
CN
NH
F3C
1.00
0.05
50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100
f1 (ppm)


7.92
7.91
7.74
7.74
7.72
7.71
7.69
7.67
7.66
7.65
7.64
7.63
7.63
7.62
7.61
7.58
7.58
7.57
7.57
7.50
7.48
7.47
6.81
6.78
3.34
2.50
NC
CN
CF3
O
1.00
8.06
1.00
1.10
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)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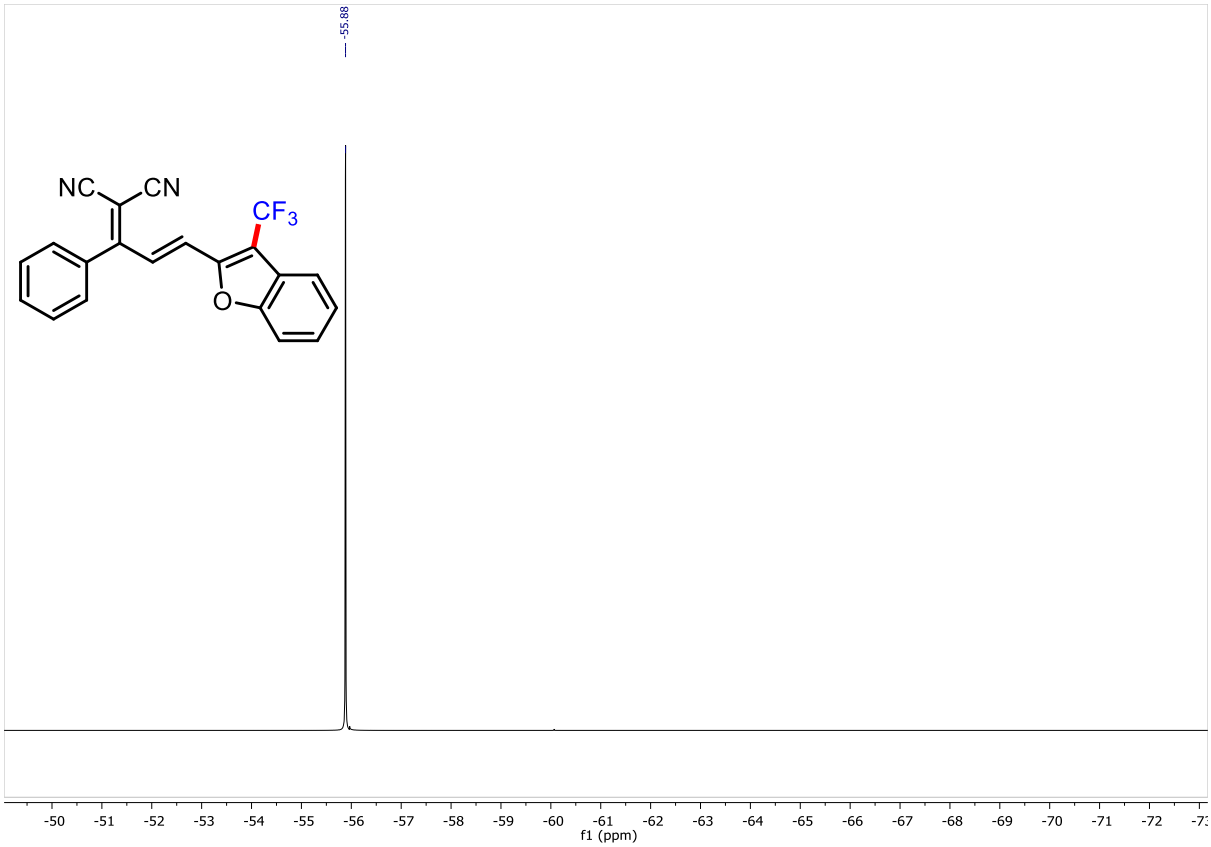
154.23
150.20
150.17
150.14
150.11
131.98
131.61
129.16
129.09
129.02
128.96
125.62
125.57
123.63
123.47
121.33
120.51
119.19
113.38
112.96
112.71
112.67
112.45
85.61
40.02
39.85
39.69
39.52
39.35
39.19
39.02
NC
CN
CF3
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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CN
CF3
O
-50
-51
-52
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-54
-55
-56
-57
-58
-59
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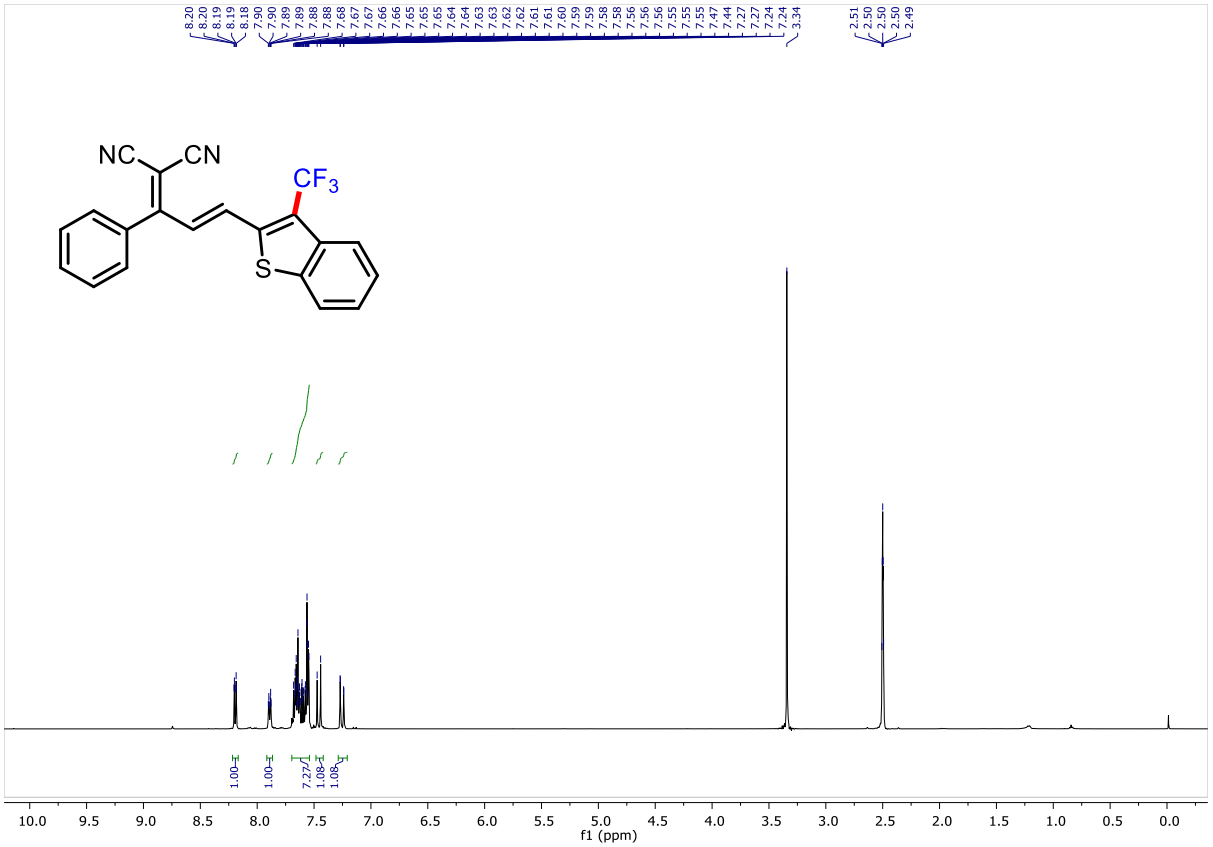
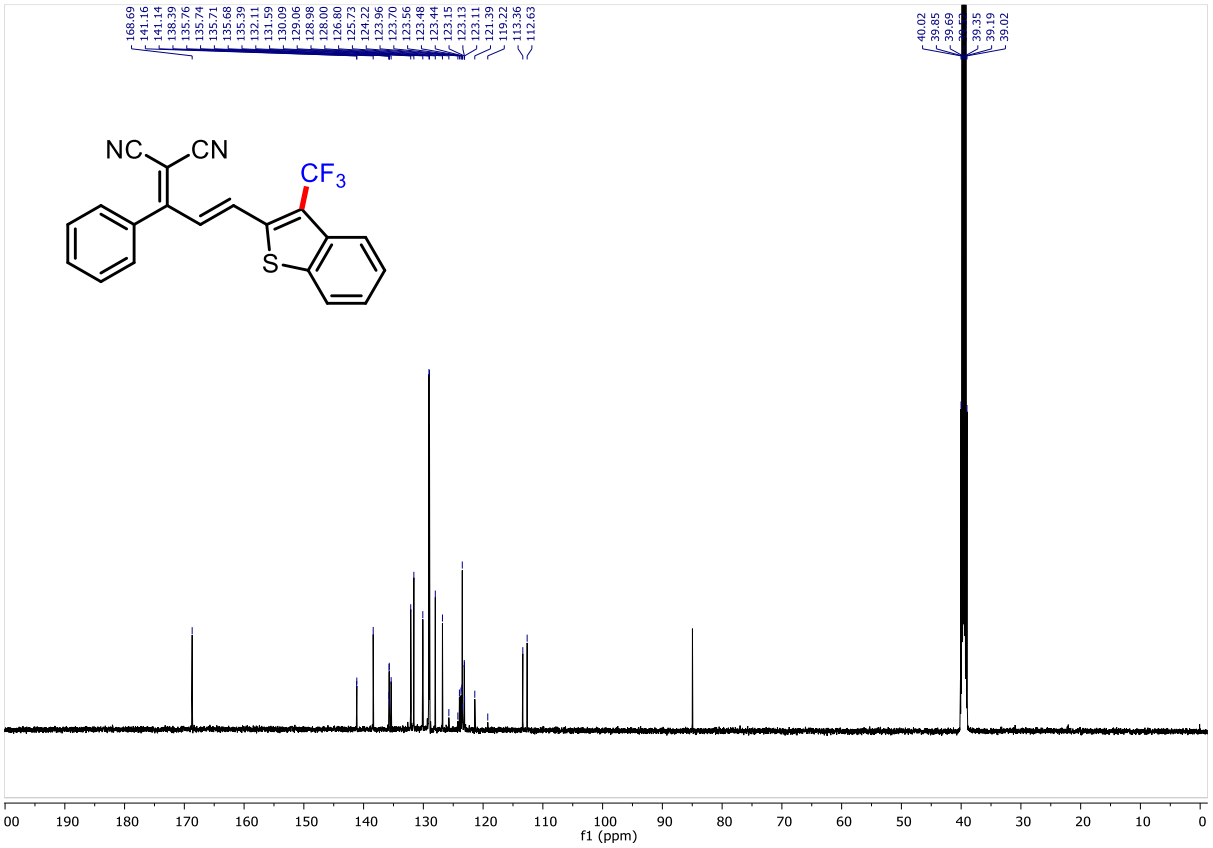
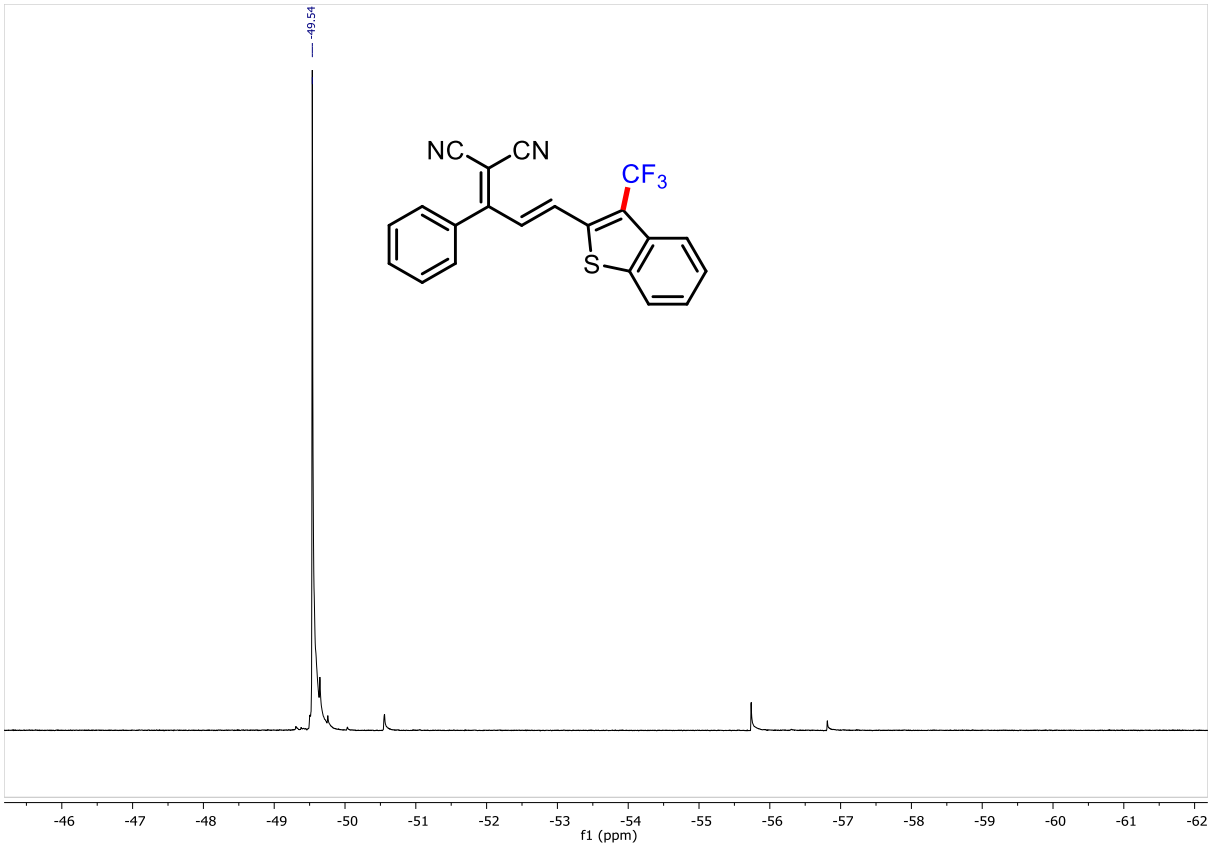
-67
-68
-69
-70
-71
-72
f1 (ppm)


NC
CN
CF3
S
f1 (ppm)


NC
CN
CF3
S
f1 (ppm)


-49.54
NC
CN
CF3
S
-46
-47
-48
-49
-50
-51
-52
-53
-54
-55
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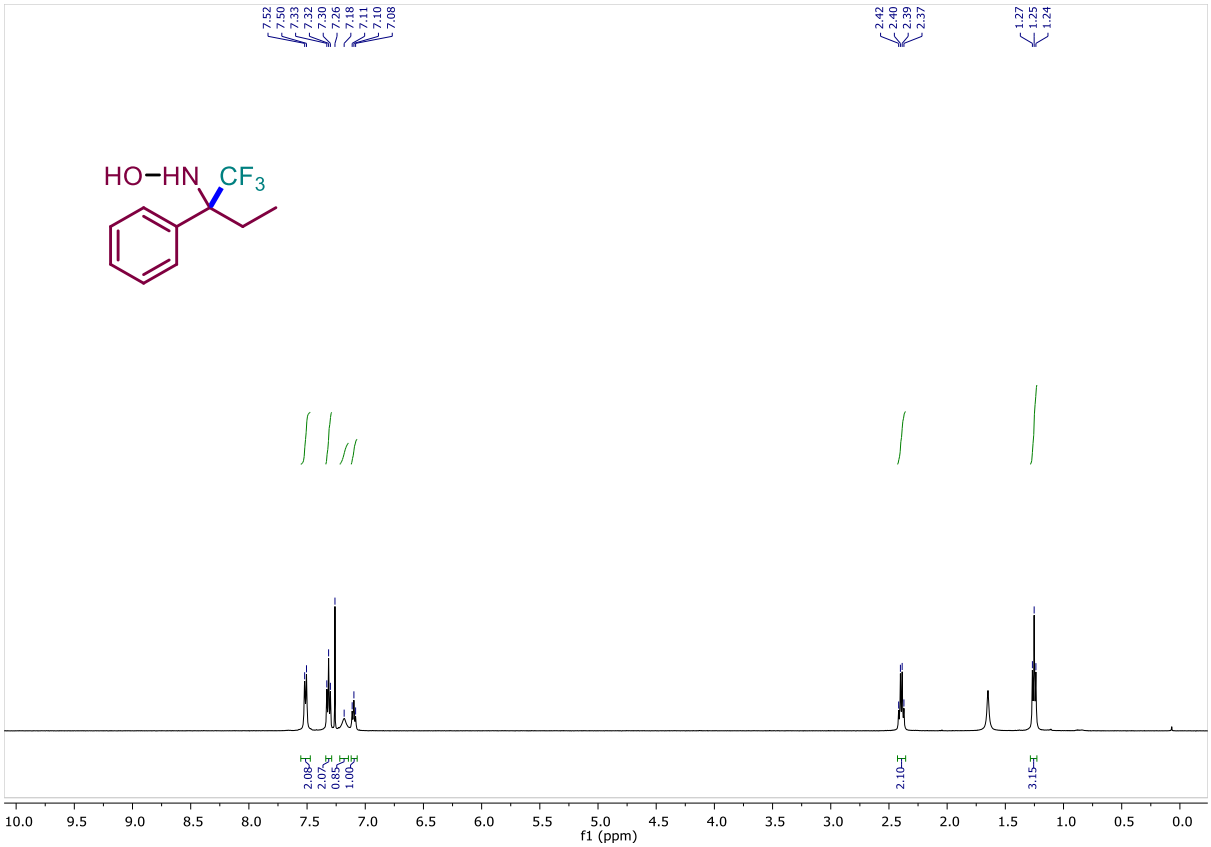
-57
-58
-59
-60
-61
-62
f1 (ppm)


7.52
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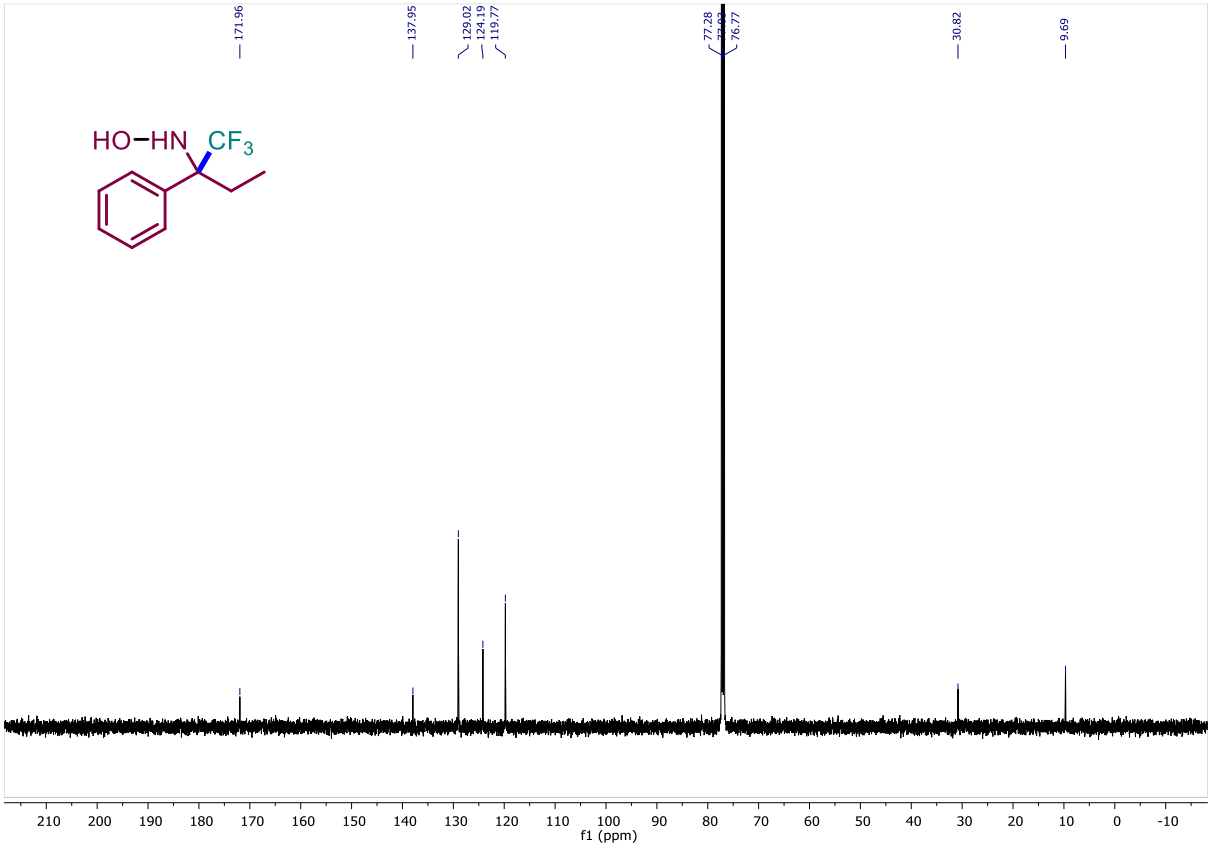
7.32
7.30
7.26
7.18
7.11
7.10
7.08
2.42
2.40
2.39
2.37
1.27
1.25
1.24
HO–HN
CF3
2.08
2.07
0.85
1.00
2.10
3.15
f1 (ppm)


171.96
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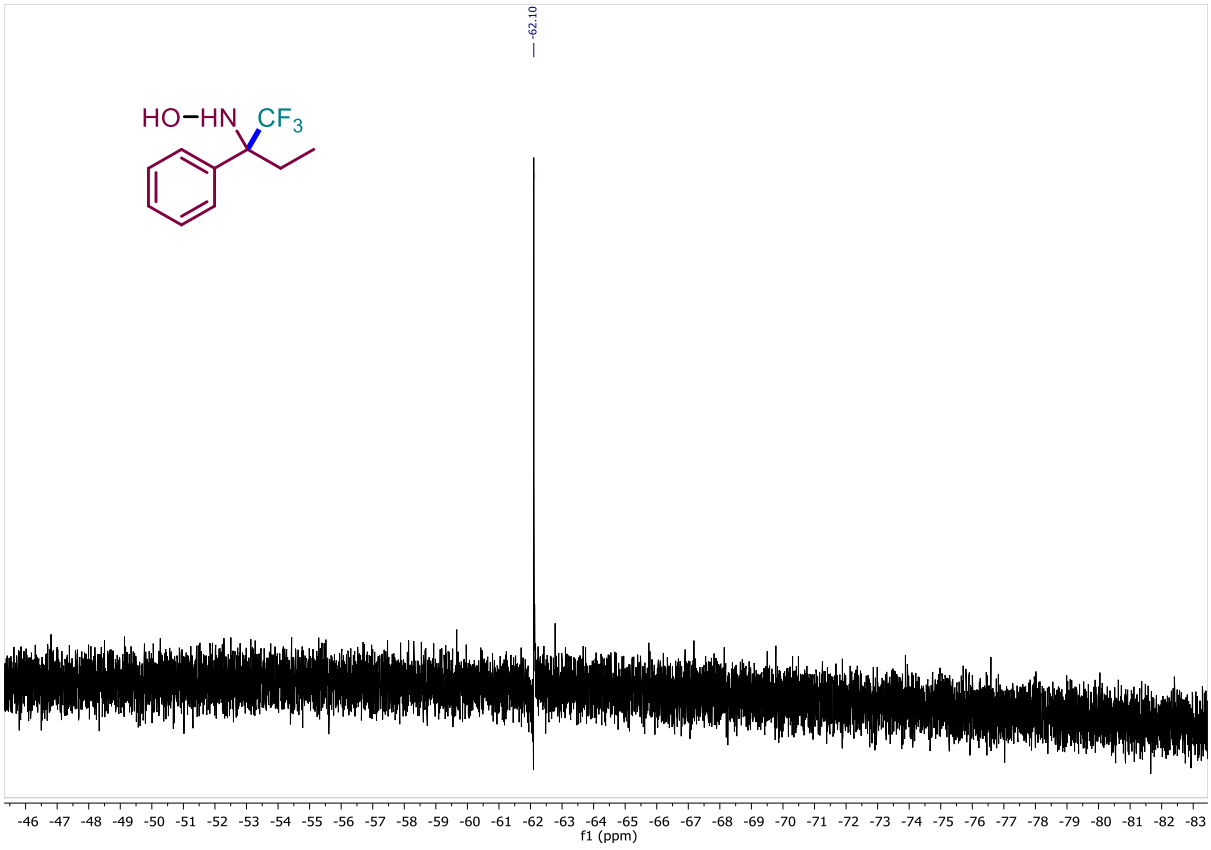
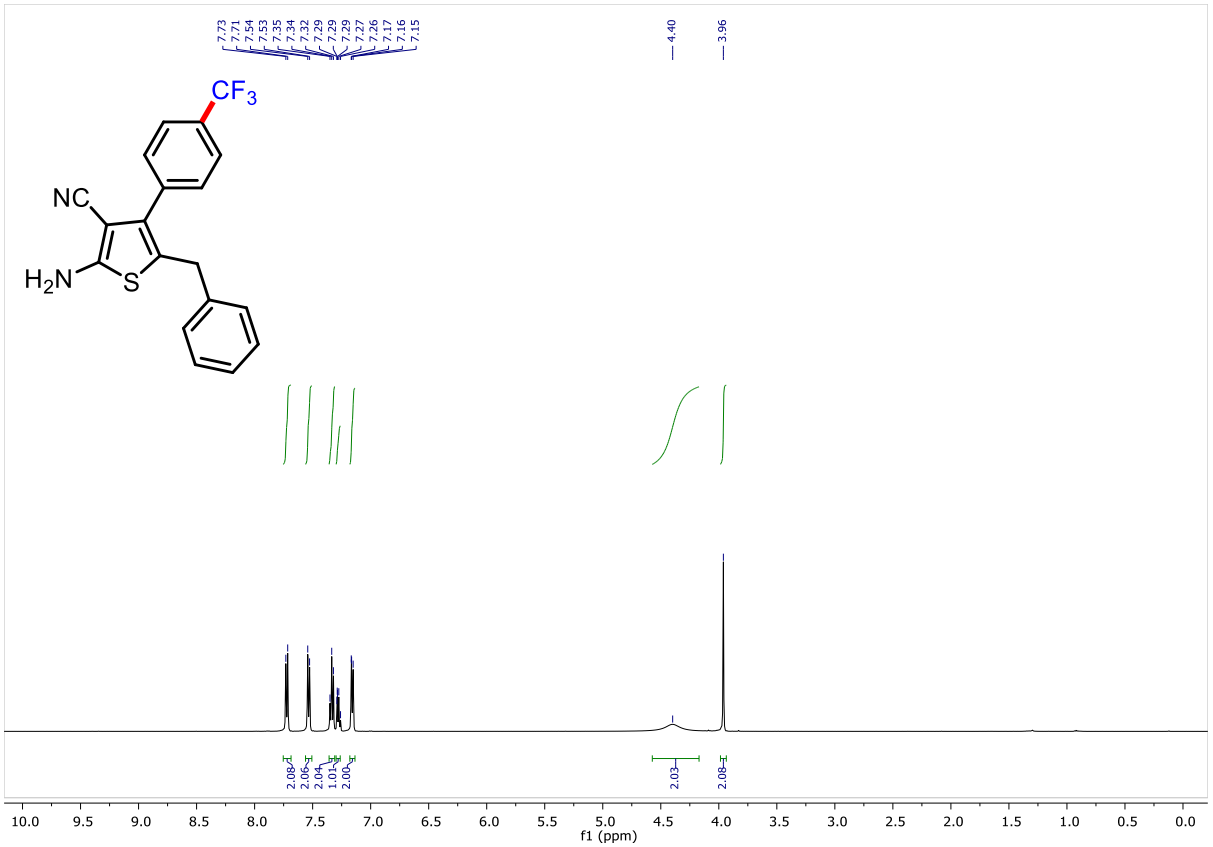
129.02
124.19
119.77
77.28
77.03
76.77
30.82
9.69
HO–HN
CF3
f1 (ppm)


-62.10
HO–HN
CF3
-46 -47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83
f1 (ppm)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7.71
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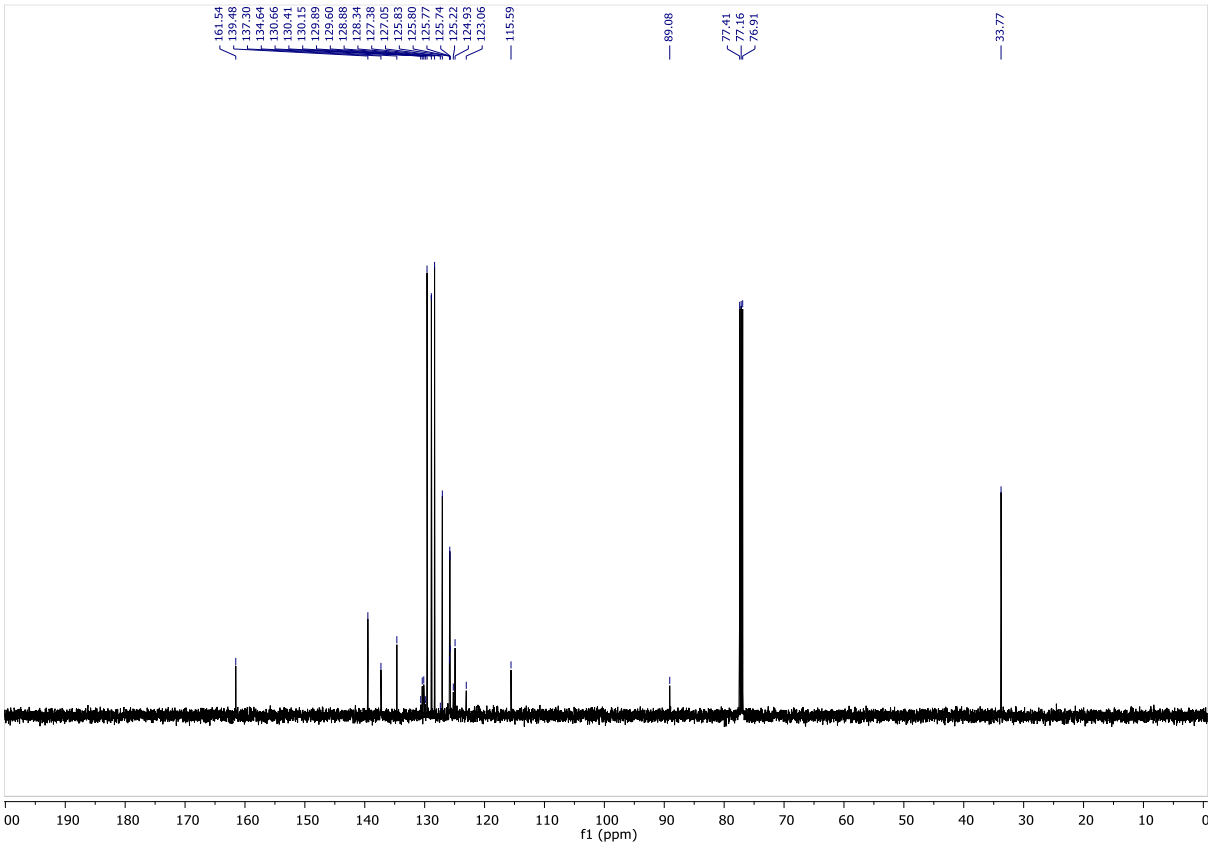
7.35
7.34
7.32
7.29
7.29
7.29
7.27
7.26
7.17
7.16
7.15
4.40
3.96
CF3
NC
H2N
S
2.08
2.06
2.04
1.01
2.00
2.03
2.08
f1 (ppm)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139.48
137.30
134.64
130.46
130.41
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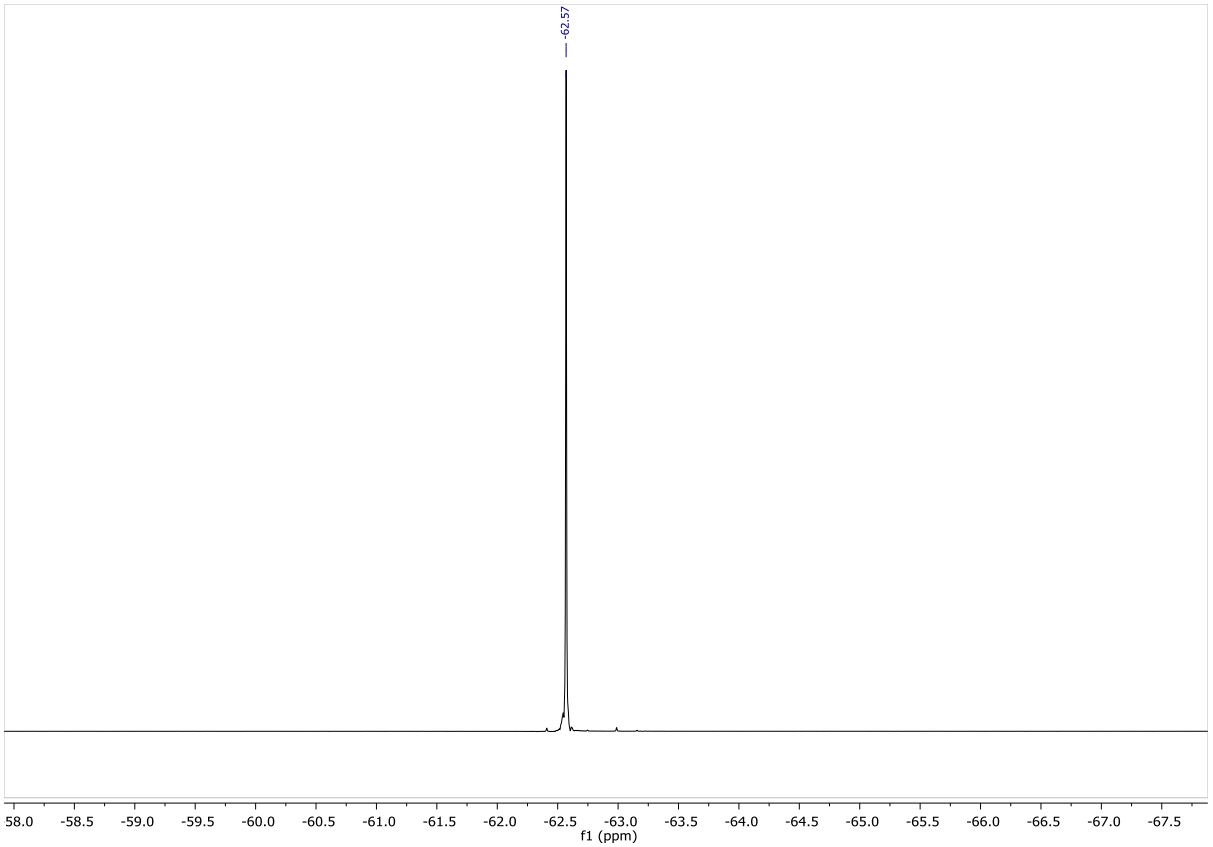
129.89
129.60
128.88
128.34
127.38
127.05
125.83
125.80
125.77
125.74
125.22
124.93
123.06
115.59
89.08
77.41
77.16
76.91
33.77
f1 (ppm)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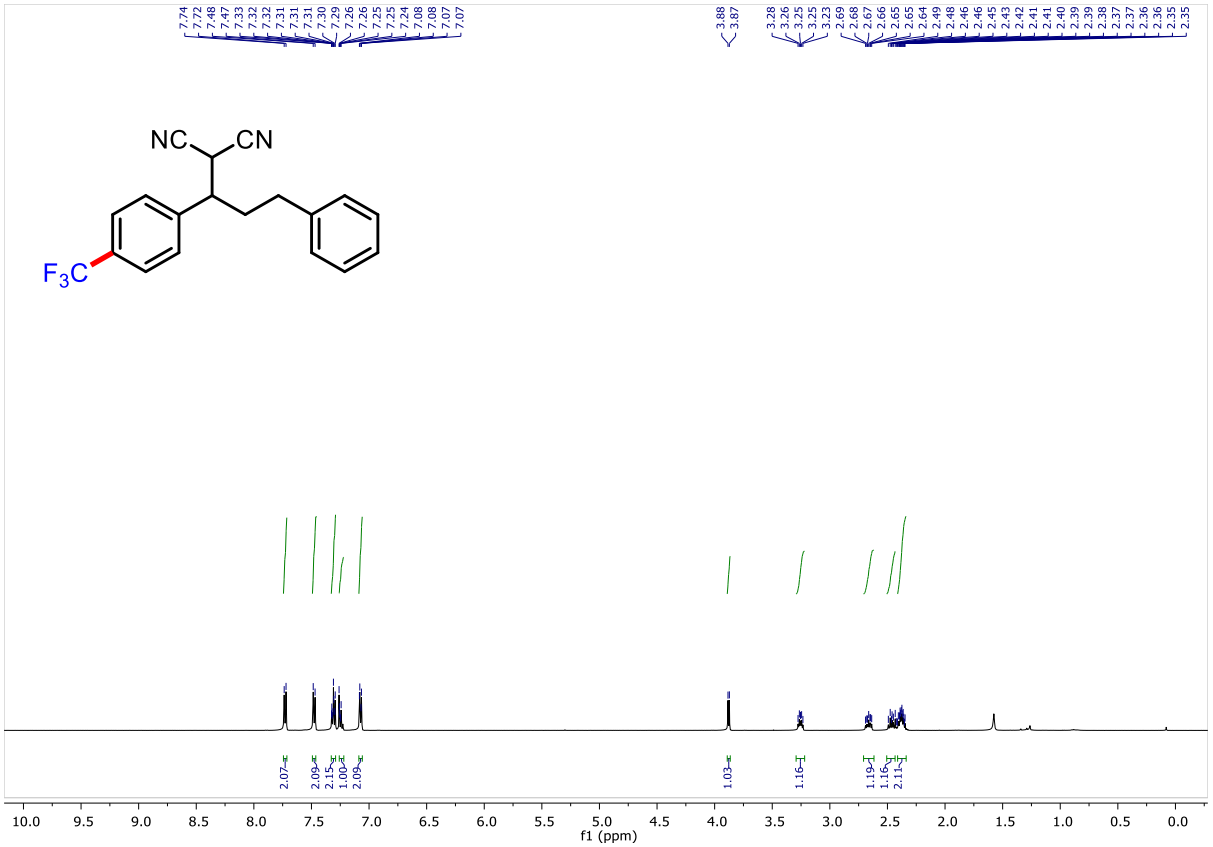
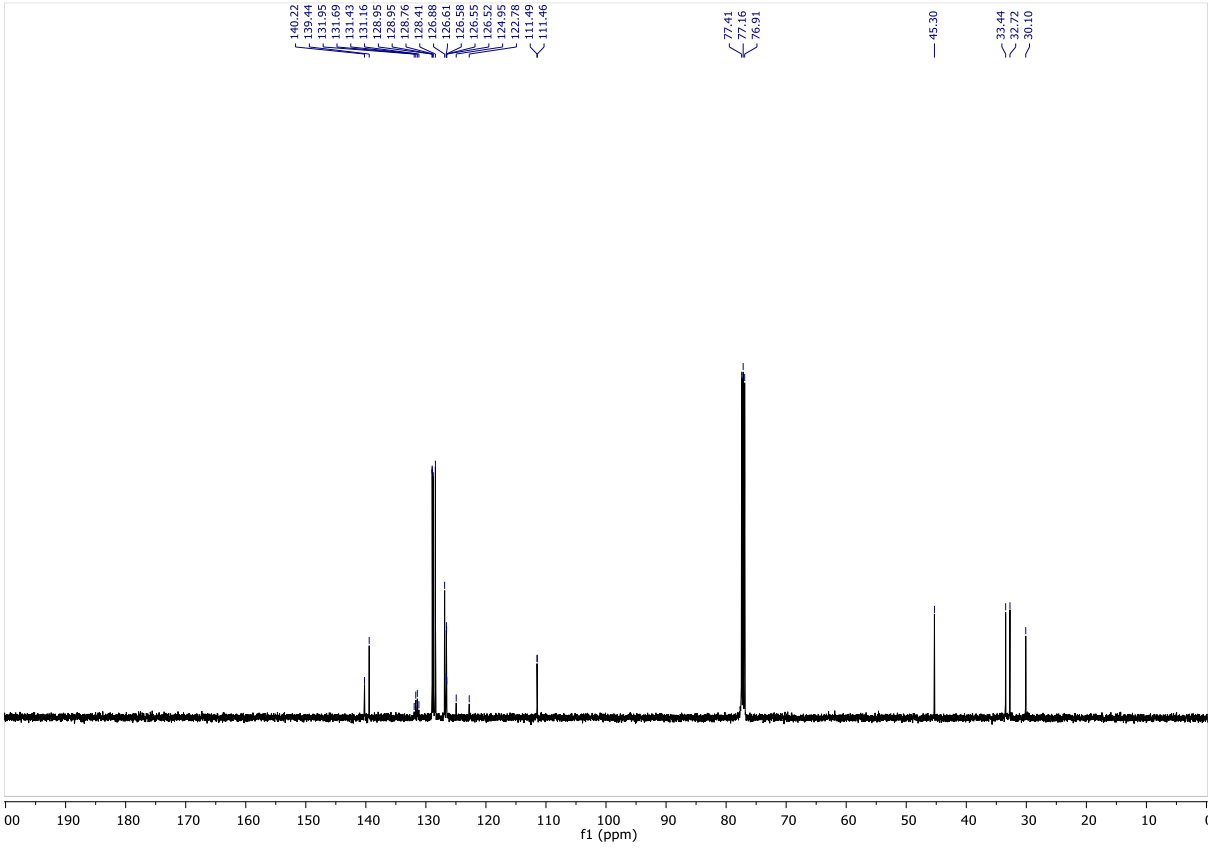
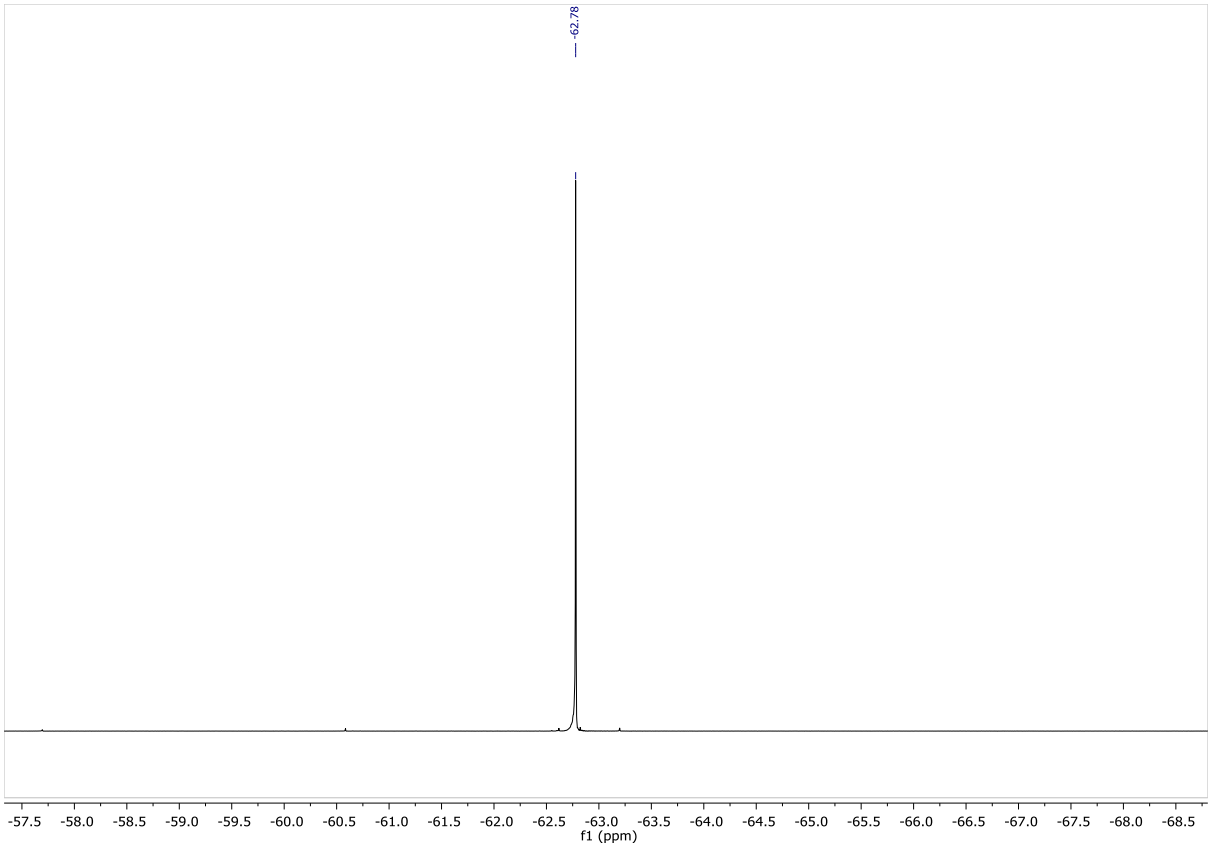
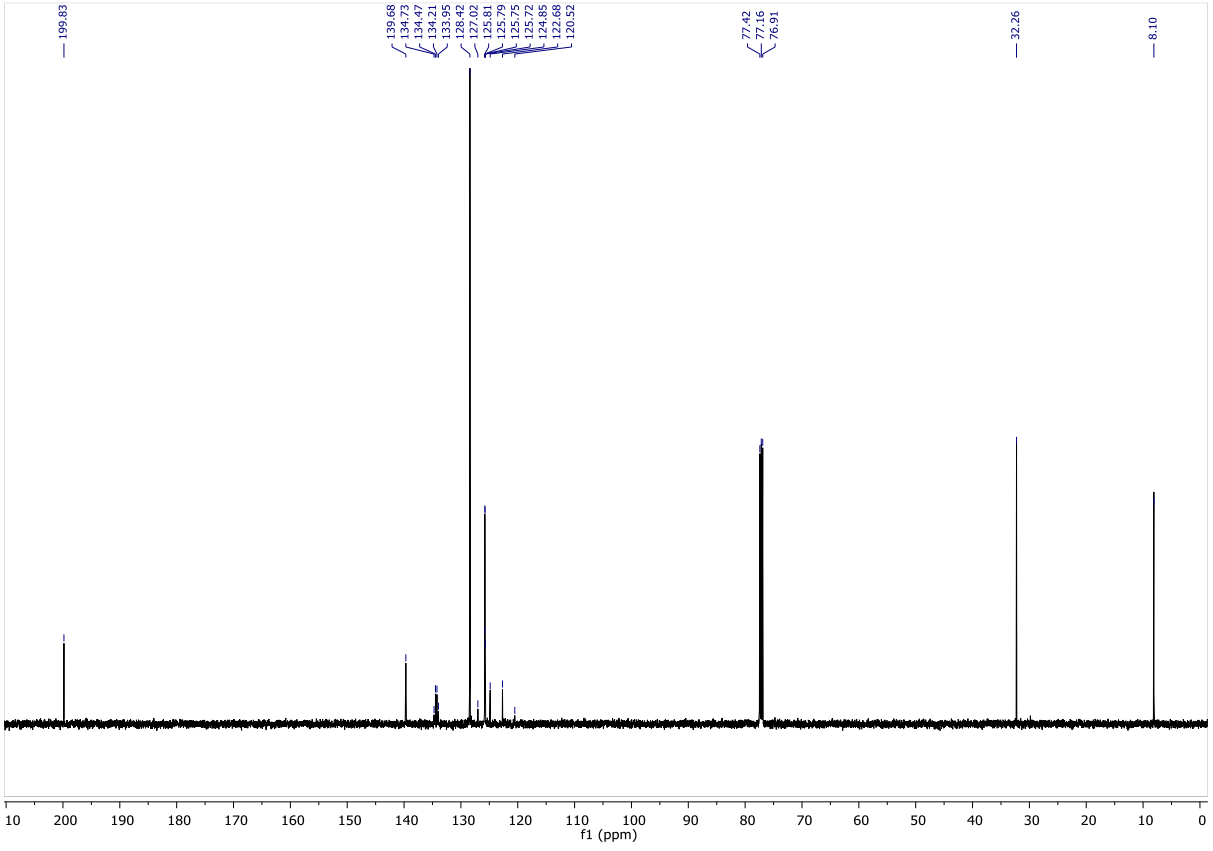
-58.5
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
f1 (ppm)


NC
CN
F3C
f1 (ppm)


f1 (ppm)


-62.78
-57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5
f1 (ppm)


8.08
8.06
8.04
7.72
7.70
7.26
3.04
3.03
3.02
3.00
1.25
1.25
1.24
1.23
1.22
1.22
O
F3C
2.00
2.02
2.09
3.09
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)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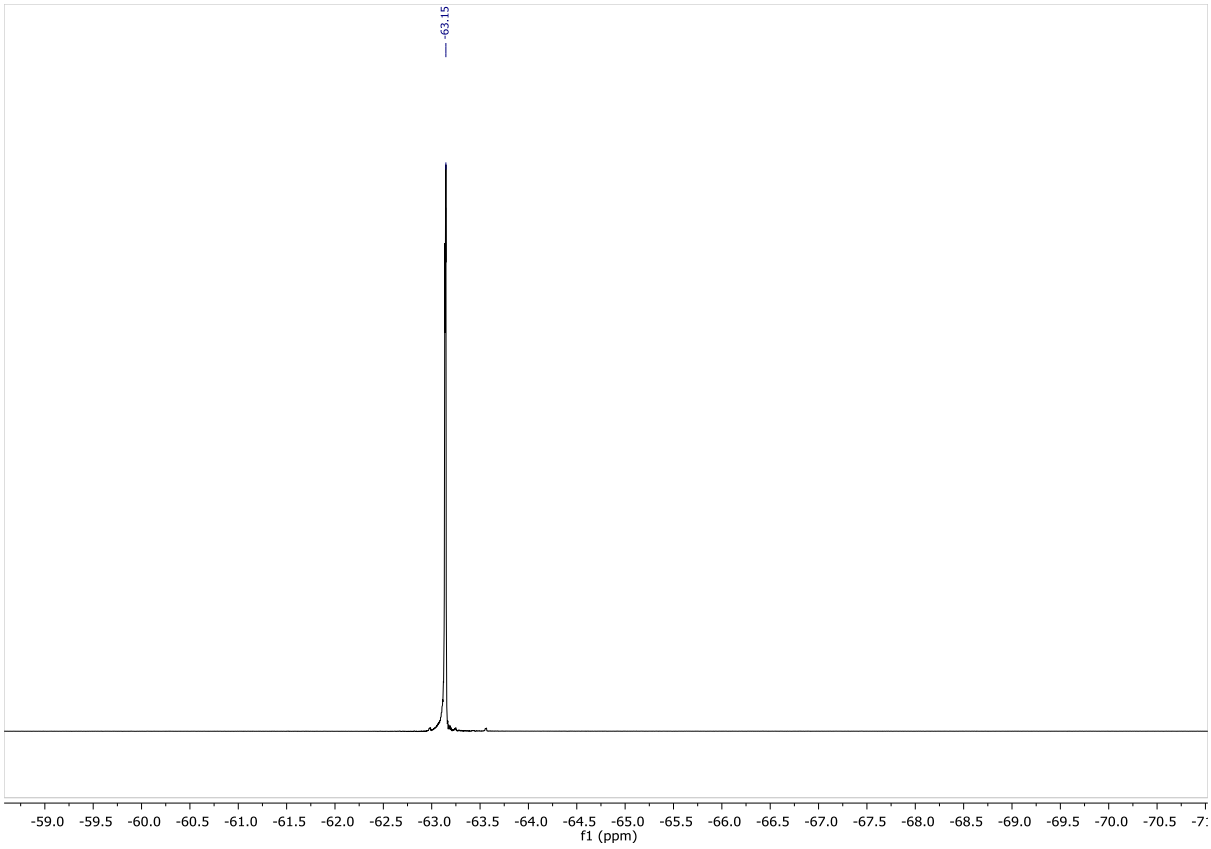
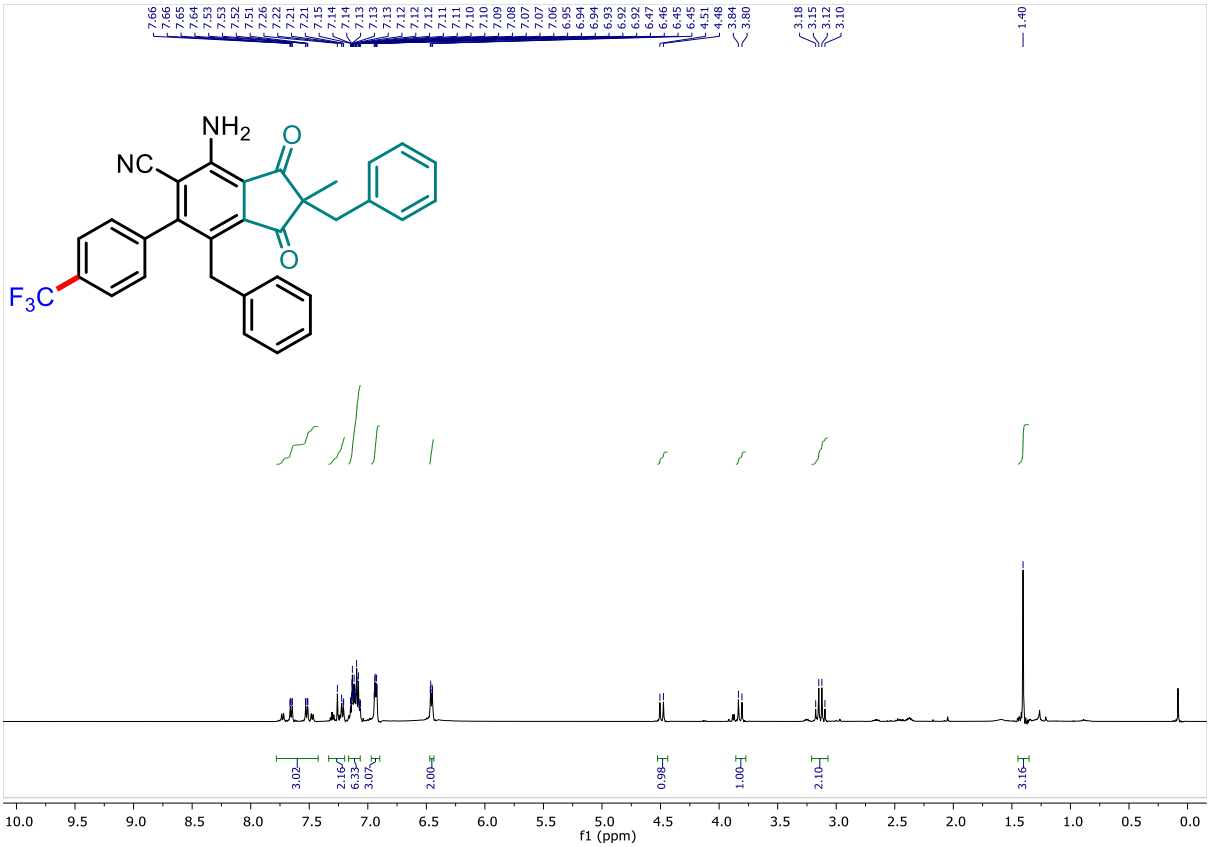
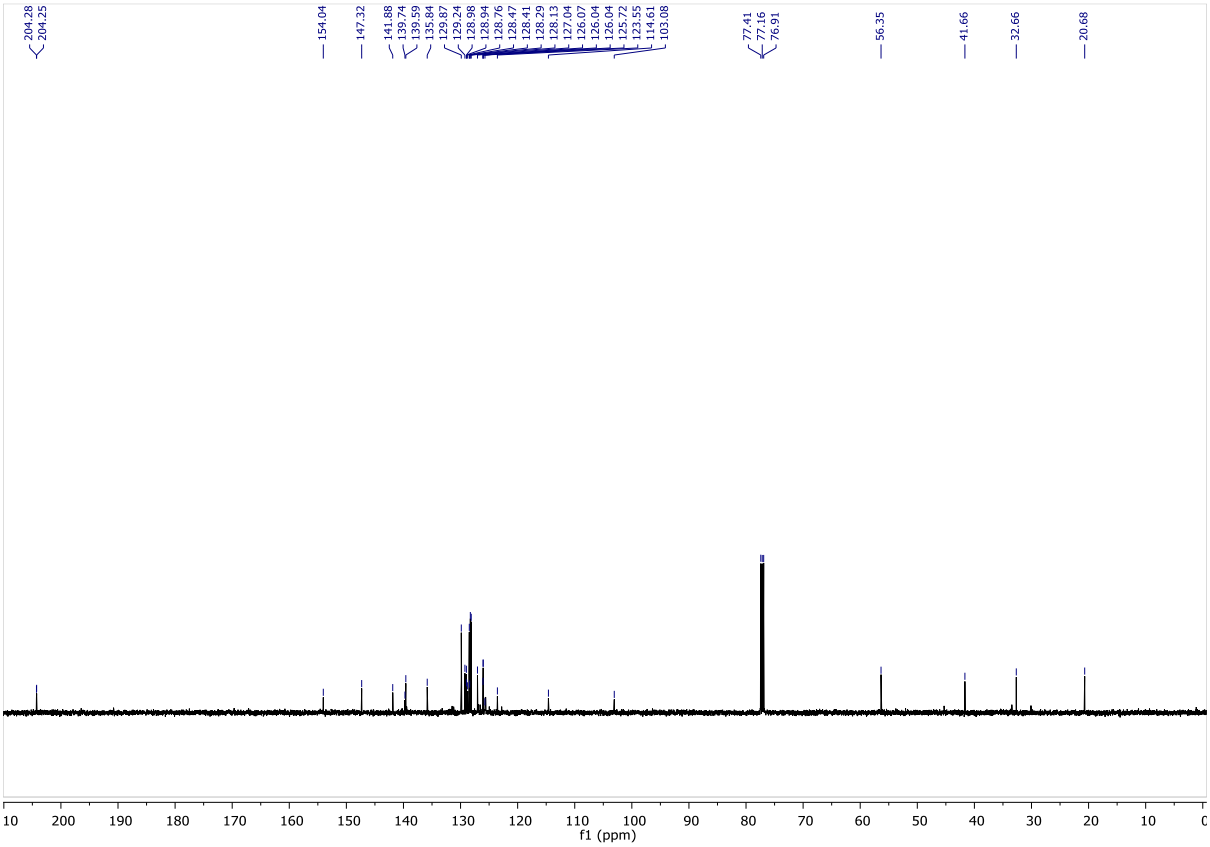
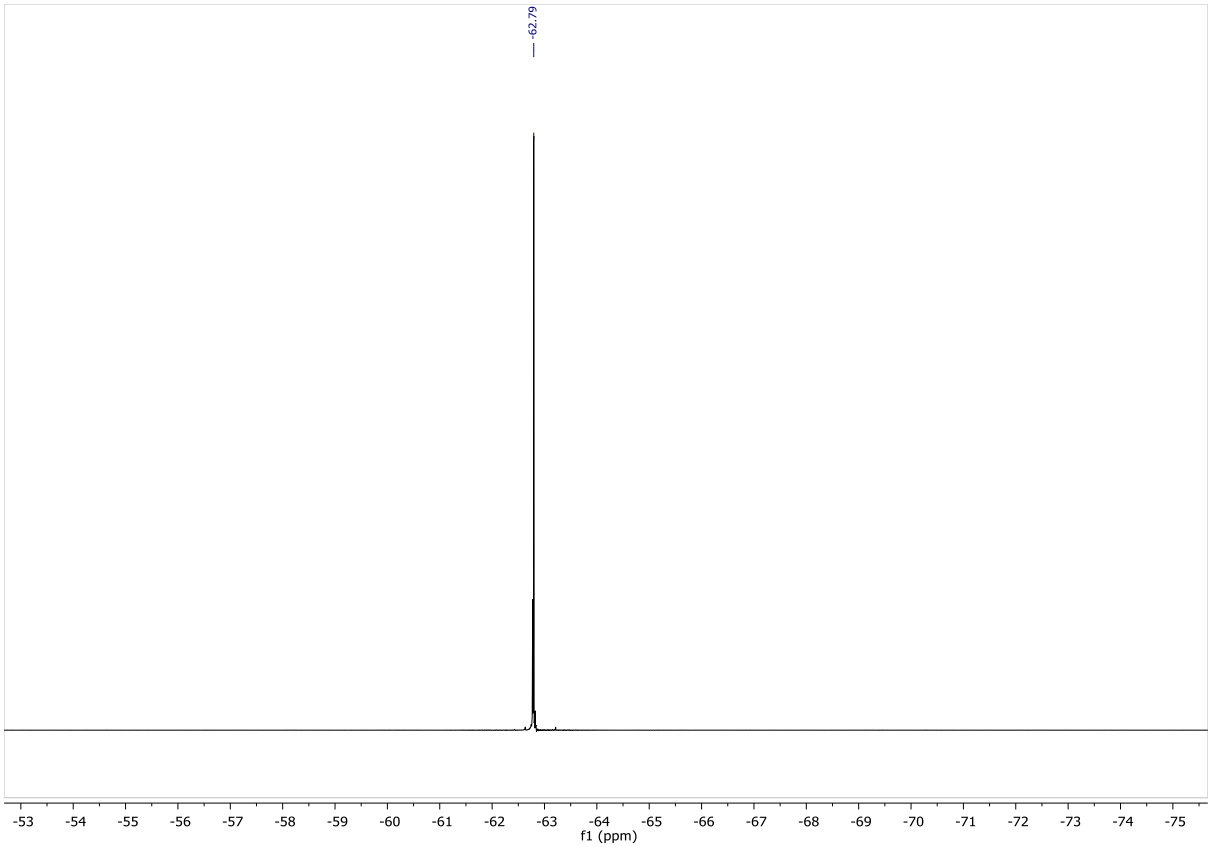
127.02
125.81
125.79
125.75
125.72
124.85
122.68
120.52
77.42
77.16
76.91
32.26
8.10
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.15
-59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0 -70.5
f1 (ppm)


NH2
NC
O
O
F3C
f1 (ppm)


f1 (ppm)


-62.79
-53
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
f1 (ppm)