Regioselective Synthsis of Difluoroalkyl/Perfluoroalkyl Enones via Pd-Catalyzed Four-component Carbonylative Coupling Reactions

Qiang Wang, Lan Zheng, Yu-Tao He, and Yong-Min Liang*

State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China
State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P.R. China
*E-mail: liangym@lzu.edu.cn.

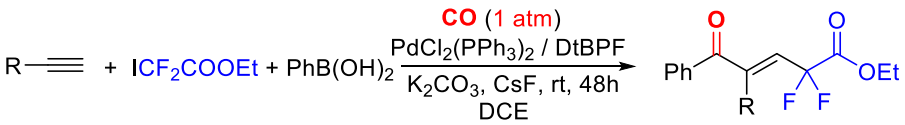
Table of Contents

1. General Remarks

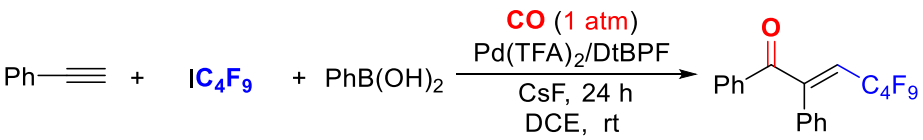
All commercially available organic compounds were purchased from adamas-beta, Alfa Asar, and accelachem in China. Unless otherwise noted, reactions were carried out under an carbon monoxide atmosphere. DMF was distilled from Mg_2SO_4 under reduced pressure before used.

For Column chromatography, 200-300 mesh silica gel was employed. Analytical TLC was performed with silica gel GF254 plates. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) were recorded in $CDCl_3$ using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. All new products were further characterized by high resolution mass spectra (HRMS); copies of their ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra are provided. All solvents were dried under standard method.

2. General experimental procedure



An oven-dried tube was charged with K_2CO_3 (0.30 mmol, 1.5 equiv), DtBPF (10 mol %), $PdCl_2(PPh_3)_2$ (10 mol %), arylboronic acid (0.22 mmol, 1.1 equiv), alkynes (0.20 mmol, 1.0equiv) and CsF (0.20 mmol, 1.0equiv). The tube was evacuated and backfilled with CO (repeated six times per 10 seconds). Then, DCE (1.5 mL) was injected after ethyl difluoroiodoacetate (0.38 mmol, 1.9 equiv) were added into the tube. The reaction mixture was stirring at rt for 48 h. The balloon was then removed. Water (3 mL) was added, and the product was extracted with DCM (3×10 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4, concentrated in vacuum and purified by flash column chromatography (silica gel) to afford the product.

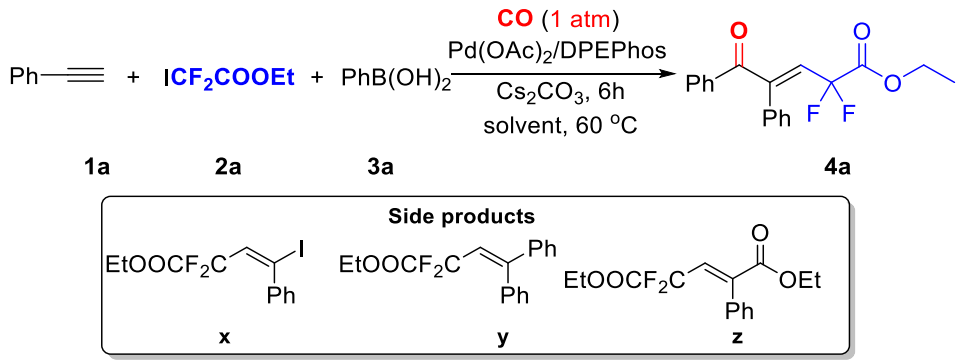


An oven-dried tube was charged with DtBPF (10 mol %), $Pd(TFA)_2$ (10 mol %), arylboronic acid (0.22 mmol, 1.1 equiv), alkynes (0.20 mmol, 1.0 equiv) and CsF (0.40 mmol, 2.0 equiv). The tube was evacuated and backfilled with CO (repeated six times per 10 seconds). Then, DCE (1.5 mL) was injected after ethyl difluoroiodoacetate (0.40 mmol, 2.0 equiv) were added into the tube. The reaction mixture was stirring at rt for 24 h. The balloon was then removed. Water (3 mL) was added, and the product was extracted with DCM (3×10 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4, concentrated in vacuum and purified by flash column chromatography (silica gel) to afford the product.

3. Optimization of Difluoroalkylation Reaction Conditions

A: Optimization with Phenylacetylene as Substrate

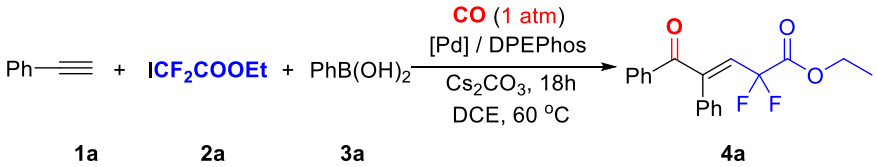
A.1. Solvent Effect



Solvent Effect		
Entry[a]	**Solvent**	**Yield (%)**[b] **4a/x/y/z**
1	toluene	12/12/30/3
2	DMF	trace
3	DCE	17/6/40/7
4	THF	trace
5	NMP	trace
6	1,4-dioxane	10/5/20/0
8	MeCN	trace

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.15 mmol, 1.5 equiv), $PhB(OH)_2$ (1.5 mmol, 1.5 equiv), Cs_2CO_3 (0.1mmol, 1.0 equiv), $Pd(OAc)_2$ (5 mol %), DPEPhos (10 mol%), solvent (1.5 mL), 60 °C, 6 h, CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).

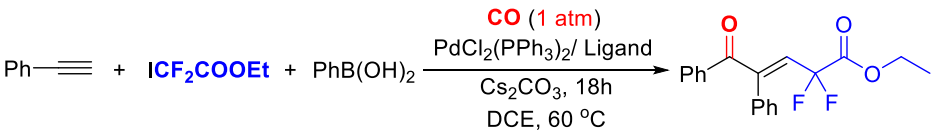
A.2. Catalyst Effect at 60 °C



Catalyst Effect at 60 °C		
Entry[a]	**Catalyst**	**Yield (%)**[b] **4a/x/y/z**
1	$Pd(TFA)_2$	trace
2	$PdCl_2(PPh_3)_2$	20/26/3/7
3	$PdCl_2(dppp)_2$	trace
4	$PdCl_2(dppf)_2$	16/12/2/0
5	$PdCl_2(PCy_3)_2$	trace
6	K_2PdCl_4	trace
7	$PdCl_2(MeCN)_2$	18/14/8/0

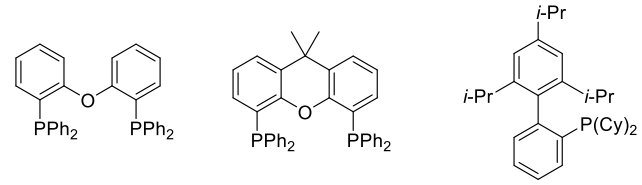
[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.15 mmol, 1.5 equiv), $PhB(OH)_2$ (0.15 mmol, 1.5 equiv), Cs_2CO_3 (0.10 mmol, 1.0 equiv), Pd-catalyst (5 mol %), DPEPhos (10 mol %), DCE (1.5 mL), 60 °C, 18 h, CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).

A.3. Ligand Effect



1a **2a** **3a** **4a**

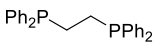
Ligand Effect		
Entry[a]	**Ligand**	**Yield (%)**[b] **4a/x/y/z**
1	DPEPhos	17/40/0/0
2	XantPhos	5/10/20/0
3	X-Phos	17/15/13/0
4	dppe	0/30/0/0
5	dppb	10/32/0/0
6	dppf	20/20/10/0
7	SPhos	15/10/8/0
8	Phen	0/30/30/0
9	L1	10/20/0/0
10	L2	0/0/0/0
11	L3	17/10/8/0
12[c]	DtBPF	79/0/10/6



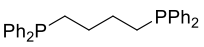
DPEPhos

XantPhos

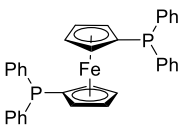
X-Phos



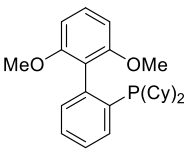
dppe



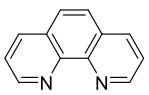
dppb



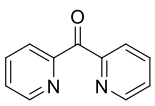
dppf



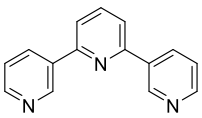
S-Phos



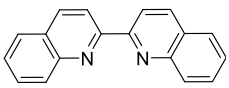
Phen



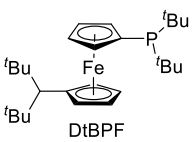
L1



L2



L3



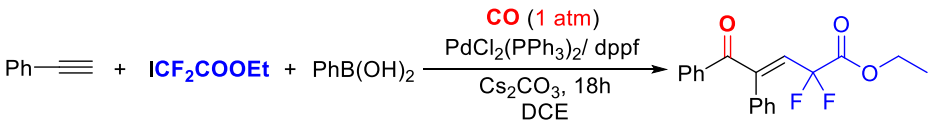
DtBPF

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.15 mmol, 1.5 equiv), $PhB(OH)_2$ (0.15 mmol, 1.5 equiv), Cs_2CO_3 (0.10 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), Ligand (5 mol %), DCE (1.5 mL), 60 °C, 18 h, under CO (1 atm).

[b] Determined by GC (phenylate was used as internal standard).

[c] The reaction was performed 1a/2a/3a=1.0/1.9/1.1, K_2CO_3 (1.5 equiv), rt, 48 h, under CO (1 atm).

A.4. Temperature Effect



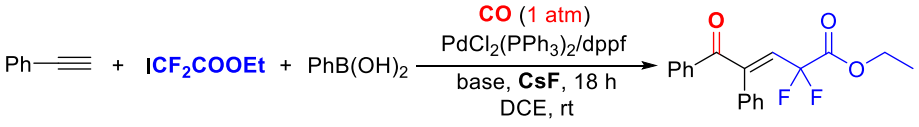
1a 2a 3a 4a

Temperature Effect		
Entry[a]	**Temperature (℃)**	**Yield (%)**[b] **4a/x/y/z**
1	100	0/0/76/0
2	80	20/0/45/0
3	60	25/0/20/0
4	40	29/0/15/0
5	RT	31/0/8/0

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.15 mmol, 1.5 equiv), $PhB(OH)_2$ (0.15 mmol, 1.5 equiv), Cs_2CO_3 (0.10 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), Ligand (5 mol %), DCE (1.5 mL), 18 h, under CO (1 atm).

[b] Determined by GC (phenylate was used as internal standard).

A.5. Base Effect



1a 2a 3a 4a

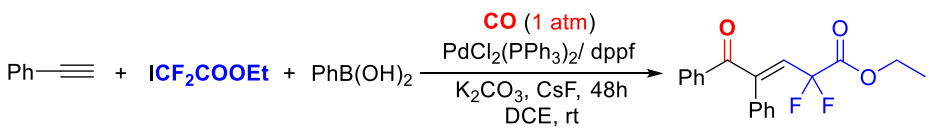
Base Effect		
Entry[a]	**Base**（equiv）	**Yield (%)**[b] **4a/x/y/z**
1	Cs_2CO_3 (1.5)	43/0/20/10
2	K_2CO_3 (1.5)	47/0/13/6
3	K_3PO_4 (1.5)	45/0/11/8
4	KOAc (1.5)	21/15/12/0
5	KO^tBu (1.5)	19/21/13/0
6	CsOAc (1.5)	trace

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.15 mmol, 1.5 equiv), $PhB(OH)_2$ (0.15 mmol, 1.5 equiv), base (x equiv), $PdCl_2(PPh_3)_2$ (5 mol %), dppf (5 mol %), CsF (0.1 mmol, 1.0 equiv), DCE (1.5 mL), 18 h, under CO (1 atm).

[b] Determined by GC (phenylate was used as internal standard).

[c] CsF was no used.

A.6. Catalyst Effect at Room Temperature



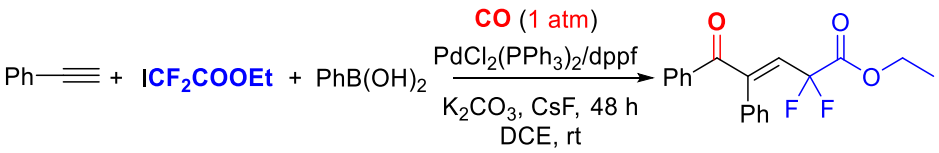
1a 2a 3a 4a

The effects of the amount of $Pd(PPh_3)_4$		
Entry[a]	**Catalyst (10 mol %)**	**Yield (%)**[b] **4a/x/y/z**

1[c]	$PdCl_2(PPh_3)_2$	51/0/18/6
2	$PdCl_2(PPh_3)_2$	59/0/16/9
3	$PdCl_2$	38/3/15/6
4	$PdCl_2(dppf)_2$	40/2/12/3
5	$Pd(PPh_3)_4$	47/5/12/3
6	$Pd(TFA)_2$	20/25/10/3
7	$PdCl_2(MeCN)_2$	23/10/17/6

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.15 mmol, 1.5 equiv), $PhB(OH)_2$ (0.15 mmol, 1.5 equiv), base (0.15 mmol, 1.5 equiv), Pd-catalyst (x mol %), dppf (10 mol %), CsF (0.1 mmol, 1.0 equiv), DCE (1.5 mL), 18 h, under CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).
[c] without CsF.

A.7. The Ratio of 1a/2a/3a Effect

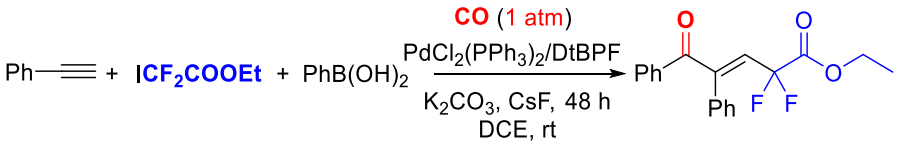


1a **2a** **3a** **4a**

The ratio of 1a/2a/3a effects.		
Entry[a]	**1a/2a/3a (equiv)**	**Yield (%)**[b] **4a/x/y/z**
1	1/1.1/1.9	54/0/12/3
2	1/1.1/1.5	53/0/10/4
3	1/1.1/1.1	55/0/13/6
4	1/1.5/1.5	59/0/12/3
5	1/1.5/1.1	63/0/17/6
6	1/1.9/1.1	70/0/13/5
7[c]	1/1.9/1.1	79 (75)[d]/0/10/6

[a] Reaction conditions: **1a** (x equive), ICF_2COOEt (y equiv), $PhB(OH)_2$ (z equiv), K_2CO_3 (0.15 mmol, 1.5 equiv), $PdCl_2(PPh_3)_2$ (10 mol %), dppf (10 mol %), CsF (0.1 mmol, 1.0 equiv), DCE (1.5 mL), rt, 48 h, under CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).
[c] DtBPF was used instead of dppf.
[d] Isolated yield.

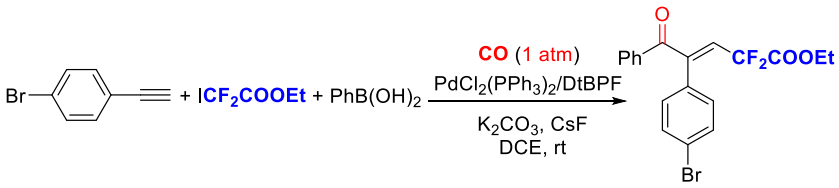
A.8. The effects of CsF



1a **2a** **3a** **4a**

CsF effects		
Entry[a]	**CsF (equiv)**	**Yield (%)**[b]
1	0	13
2[c]	0	69
3	0.5	62
4	1.0	79
5	2.0	60

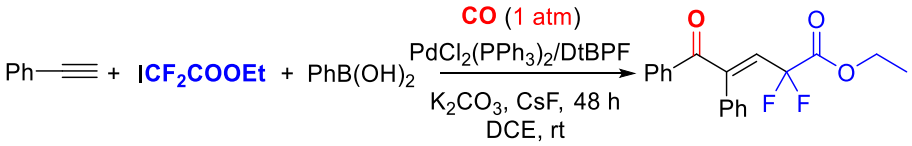
[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.19 mmol, 1.9 equiv), $PhB(OH)_2$ (0.11 mmol, 1.1 equiv), K_2CO_3 (0.15 mmol, 1.5 equiv), $PdCl_2(PPh_3)_2$ (10 mol %), DtBPF (10 mol %), DCE (1.5 mL), 48 h, under CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).
[c] The reaction was carred out for 6 days.



CsF effects			
Entry[a]	**CsF (equiv)**	Time (h)	**Yield (%)**[b]
1	1.0	48	47
2	0	48	30
3	0	72	45

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.19 mmol, 1.9 equiv), $PhB(OH)_2$ (0.11 mmol, 1.1 equiv), K_2CO_3 (0.15 mmol, 1.5 equiv), $PdCl_2(PPh_3)_2$ (10 mol %), DtBPF (10 mol %), DCE (1.5 mL), under CO (1 atm).
[b] Isolated yield.

A.9. Control reactions



1a **2a** **3a** **4a**

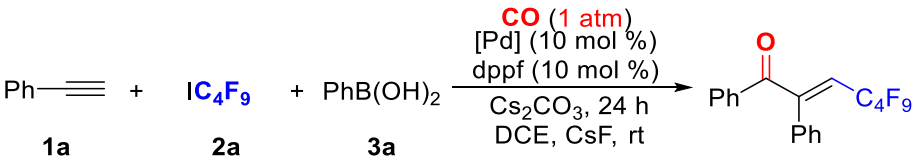
Control reactions		
Entry[a]	**remarks**	**Yield (%)**[b] **4a/x/y/z**
1	No Pd-catalyst	NR
2	No base	<10/40/12/0
3	No base and no CsF	NR

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), ICF_2COOEt (0.19 mmol, 1.9 equiv), $PhB(OH)_2$ (0.11 mmol, 1.1 equiv), K_2CO_3 (0.15 mmol, 1.5 equiv), $PdCl_2(PPh_3)_2$ (10 mol %), DtBPF (10 mol %), CsF (0.1 mmol, 1.0 equiv), DCE (1.5 mL), 48 h, under CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).

4. Optimization of Perfluoroalkylation Reaction Conditions

A: Optimization with Phenylacetylene as Substrate

A.1. Pd-catalyst Effect

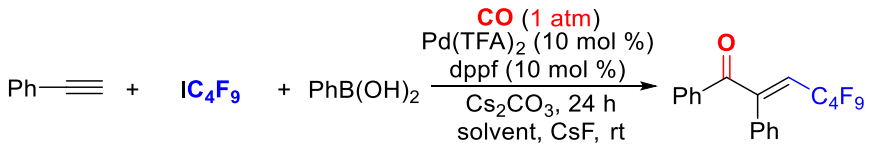


1a **2a** **3a**

Pd-catalyst Effect		
Entry[a]	**Solvent**	**Yield (%)**[b]
1	$Pd(TFA)_2$	15
2	$PdCl_2(PPh_3)_2$	<10
3	$PdCl_2(dppf)_2$	trace
4	$PdCl_2(MeCN)_2$	trace
5	$Pd(OAc)_2$	0
6	$Pd(PPh_3)_4$	trace
7	$PdCl_2(PCy_3)_2$	trace

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), **2a** (0.13 mmol, 1.3 equiv), $PhB(OH)_2$ (1.1 mmol, 1.1 equiv), Cs_2CO_3 (0.15mmol, 1.5 equiv), Pd-catalyst (10 mol %), dppf (10 mol%),CsF (0.10mmol, 1.0 equiv), DCE (1.5 mL), rt, 24 h, CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).

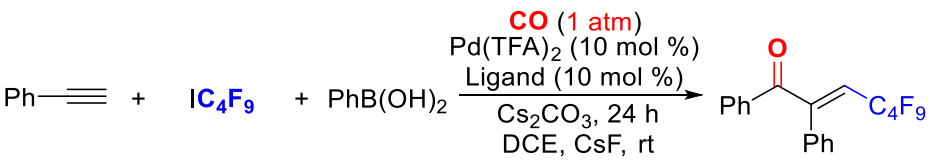
A.2. Solvent Effect



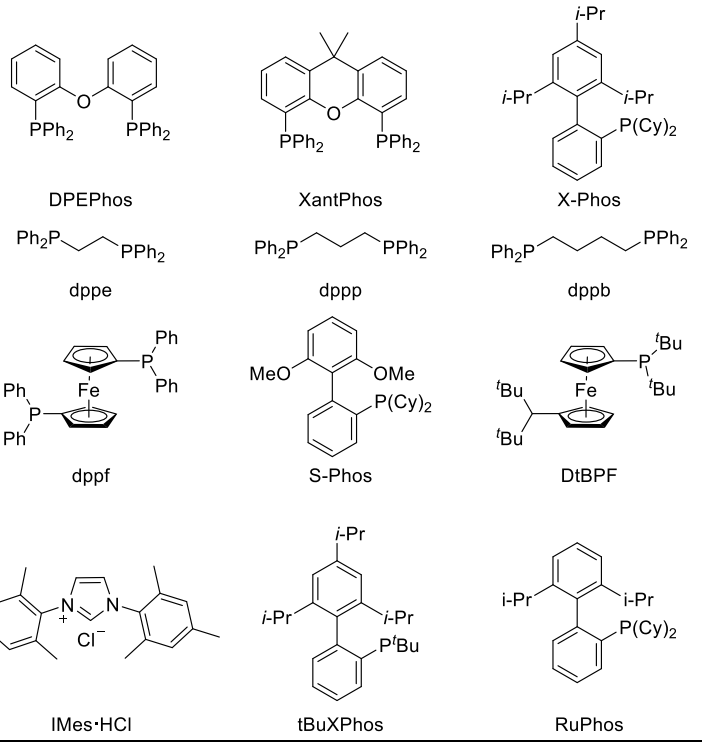
Solvent Effect		
Entry[a]	**Solvent**	**Yield (%)**[b]
1	1,4-dioxane	<10
2	THF	<10
3	toluence	<10
4	MeCN	0
5	DCE	15

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), **2a** (0.13 mmol, 1.3 equiv), $PhB(OH)_2$ (1.1 mmol, 1.1 equiv), Cs_2CO_3 (0.15mmol, 1.5 equiv), $Pd(TFA)_2$ (10 mol %), dppf (10 mol%),CsF (0.10mmol, 1.0 equiv), solvent (1.5 mL), rt, 24 h, CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).

A.3. Ligand Effect



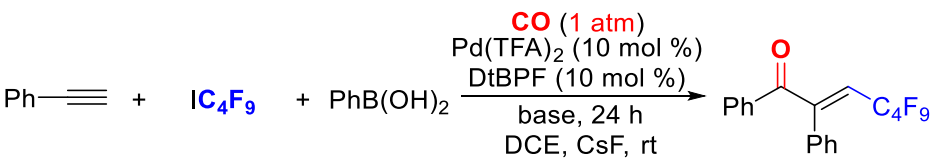
Ligand Effect		
Entry[a]	**Ligand**	**Yield (%)**[b]
1	DPEPhos	trace
2	XantPhos	trace
3	X-Phos	<10
4	dppe	trace
5	dppb	trace
6	dppp	trace
7	dppf	15
8	DtBPF	20
9	IMes·HCl	trace
10	SPhos	trace
11	tBuXPhos	<10
12	RuPhos	trace



[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), **2a** (0.13 mmol, 1.3 equiv), $PhB(OH)_2$ (1.1 mmol, 1.1 equiv), Cs_2CO_3 (0.15mmol, 1.5 equiv), $Pd(TFA)_2$ (10 mol %), ligand (10 mol%),CsF (0.10mmol, 1.0 equiv), DCE (1.5 mL), rt, 24 h, CO (1 atm).

[b] Determined by GC (phenylate was used as internal standard).

A.4. Base Effect

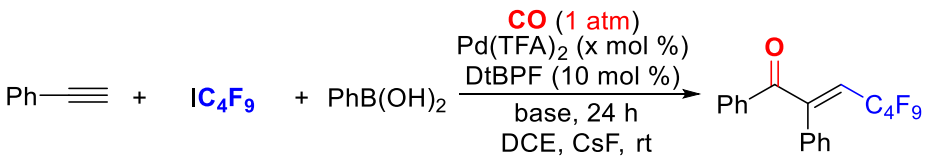


Base Effect			
Entry[a]	**Base** （equiv）		**Yield (%)**[b]
1	Cs_2CO_3 (1.5)	CsF (1.0)	20
2	CsOAc (1.5)	CsF (1.0)	13
3	K_2CO_3 (2.0)	CsF (1.0)	23
4	KOAc (1.5)	CsF (1.0)	<10
5	K_3PO_4 (1.5)	CsF (1.0)	25
6	$NaHCO_3$ (1.5)	CsF (1.0)	trace
7	CsOAc (1.5)	CsF (1.0)	17
8	KO^{t}Bu (1.5)	CsF (1.0)	27
9	NaO^{t}Bu (1.5)	CsF (1.0)	27
10	LiO^{t}Bu (1.5)	CsF (1.0)	17
11	KO^{t}Bu (1.9)	CsF (1.0)	21
12	KO^{t}Bu (1.1)	CsF (1.0)	33
13	KO^{t}Bu (0.5)	CsF (1.0)	40
14	KO^{t}Bu (1.1)	-	<10
15	-	CsF (1.0)	43
16	-	CsF (1.5)	50
17	-	CsF (2.0)	58

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equive), **2a** (0.13 mmol, 1.3 equiv), $PhB(OH)_2$ (1.1

mmol, 1.1 equiv), base (x equiv), $Pd(TFA)_2$ (10 mol %), DtBPF (10 mol%), CsF (y equiv), DCE (1.5 mL), rt, 24 h, CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).

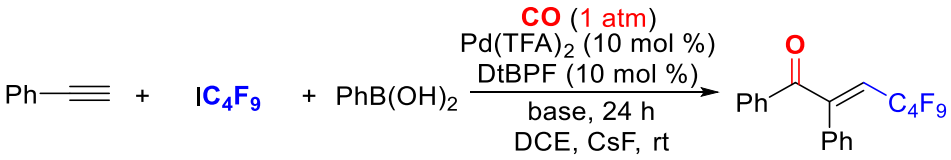
A.5. The Amount of Pd-Catalyst Effect



The effects of the amount of $Pd(PPh_3)_4$		
Entry[a]	**Catalyst (mol %)**	**Yield (%)**[b]
1	$Pd(TFA)_2$ (2.5)	23
2	$Pd(TFA)_2$ (5.0)	45
3	$Pd(TFA)_2$ (10.0)	58

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive), **2a** (0.13 mmol, 1.3 equiv), $PhB(OH)_2$ (1.1 mmol, 1.1 equiv), $Pd(TFA)_2$ (x mol %), DtBPF (10 mol%), CsF (0.20 mmol, 2.0 equiv), DCE (1.5 mL), rt, 24 h, CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).

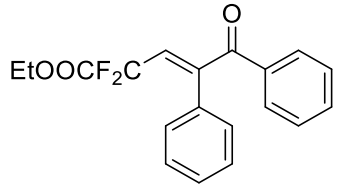
A.6. The Amount of IC_4F_9 Effect



The ratio of 1a/2a/3a effects.		
Entry[a]	**IC_4F_9 (equiv)**	**Yield (%)**[b]
1	1.1	58
2	1.5	62
3	2.0	70(65)[c]

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equive),**2a** (x, equiv), $PhB(OH)_2$ (1.1 mmol, 1.1 equiv), $Pd(TFA)_2$ (10 mol %), DtBPF (10 mol%), CsF (0.20 mmol, 2.0 equiv), DCE (1.5 mL), rt, 24 h, CO (1 atm).
[b] Determined by GC (phenylate was used as internal standard).
[c] Isolated yield.

5. Characterization Data of 4a-4q, 5a-5s and 6a-6j.



ethyl (E)-2,2-difluoro-5-oxo-4,5-diphenylpent-3-enoate (4a)

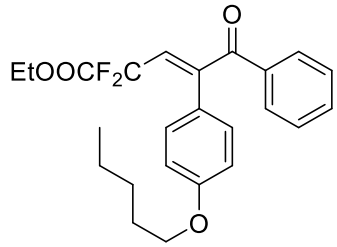
Yellow oil, 75% yield (49.5 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.61 – 7.57 (m, 1H), 7.49 – 7.45 (m, 2H), 7.36 (s, 5H), 6.25 (t, *J* = 11.2 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.7 , 162.6 (t, *J* = 33.2 Hz), 148.7 (t, *J* = 8.4 Hz), 135.6 , 133.7 , 133.0 , 130.1 , 129.1 , 128.9 , 128.7 , 128.3 , 126.5 (t, *J* = 28.6 Hz), 111.8 (t, *J* = 247.5 Hz), 63.1 , 13.6 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.4.

HRMS: m/z (ESI) calculated $[M+H]^+$: 331.1140, measured: 331.1141.



ethyl (E)-2,2-difluoro-5-oxo-4-(4-(pentyloxy)phenyl)-5-phenylpent-3-enoate (4b)

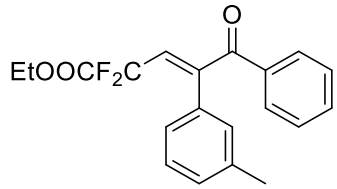
Brown oil, 73% yield (60.7 mg), E/Z=17:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.16 (t, *J* = 11.2 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.93 (t, *J* = 6.4 Hz, 2H), 1.78 – 1.73 (m, 2H), 1.44 – 1.34 (m, 4H),1.18 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.2 , 162.8 (t, *J* = 33.4 Hz), 160.0 , 148.7 (t, *J* = 8.5 Hz), 135.8 , 133.5 , 130.4 , 130.1 , 128.6 , 125.2 (t, *J* = 28.6 Hz), 125.0 , 114.3 , 112.0 (t, *J* = 246.9 Hz), 68.0 , 63.1 , 28.8 , 28.1 , 22.4 , 13.9 , 13.6 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -92.8.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 434.2137, measured: 434.2136.



ethyl (E)-2,2-difluoro-5-oxo-5-phenyl-4-(m-tolyl)pent-3-enoate (4c)

Yellow oil, 65% yield (44.7 mg), E/Z=10:1.

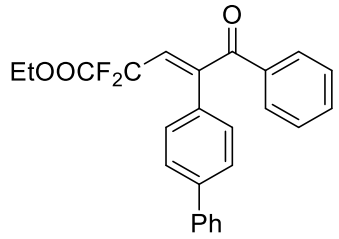
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.45 (m, 2H), 7.25 – 7.22 (m, 1H), 7.16 (s, 3H), 6.21 (t, *J* = 11.2 Hz, 1H), 3.96 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.17 (t, *J* = 7.2 Hz,

3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.8 , 162.6 (t, *J* = 33.2 Hz), 148.8 (t, *J* = 8.5 Hz), 138.0 , 135.6 , 133.6 , 132.9 , 130.1 , 129.9 , 129.4 , 128.7 , 128.2 , 126.2 (t, *J* = 28.8 Hz), 126.0 , 111.9 (t, *J* = 247.2 Hz), 63.0 , 21.3 , 13.6 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.2.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 362.1562, measured: 362.1564.



ethyl (E)-4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-5-oxo-5-phenylpent-3-enoate (4d)

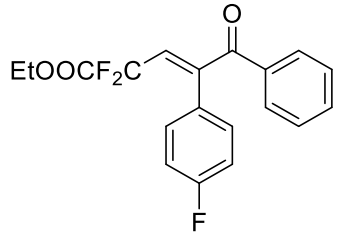
Colourless oil, 65% yield (52.8 mg), E/Z=7:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.55 (m, 5H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.40 (m, 4H),, 7.36 – 7.34 (m, 1H), 6.27 (t, *J* = 11.2 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.5 , 163.4 (t, *J* = 32.8 Hz), 149.1 (t, *J* = 8.3 Hz), 142.7 , 140.8 , 136.4 , 134.4 , 132.6 , 130.9 , 130.1 , 129.5 , 129.4 , 128.4 , 127.7 , 127.6 , 119.8 (t, *J* = 25.4 Hz), 112.6 (t, *J* = 247.8 Hz), 63.9 , 14.4 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.4.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 424.1719, measured: 424.1717.



ethyl (E)-2,2-difluoro-4-(4-fluorophenyl)-5-oxo-5-phenylpent-3-enoate (4e)

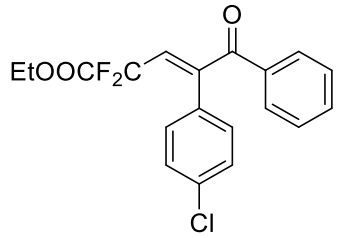
Yellow oil, 72% yield (50.1 mg), E/Z=15:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.61 – 7.58 (m, 1H), 7.50 – 7.46 (m, 2H), 7.38 – 7.34 (m, 2H), 7.05 (t, *J* = 8.4 Hz, 2H), 6.27 (t, *J* = 11.6 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.5 , 163.1 (d, *J* = 248.1 Hz), 162.6 (t, *J* = 33.2 Hz), 147.5 (t, *J* = 8.0 Hz), 135.4 , 133.7 , 130.9 (d, *J* = 8.3 Hz), 130.0 , 129.2 (d, *J* = 51.1 Hz), 128.7 , 127.0 (t, *J* = 28.2 Hz), 115.3 (d, *J* = 21.7 Hz), 111.8 (t, *J* = 248.3 Hz), 63.2 , 13.6 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.1, -111.5.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 366.1312, measured: 366.1311.



ethyl (E)-4-(4-chlorophenyl)-2,2-difluoro-5-oxo-5-phenylpent-3-enoate (4f)

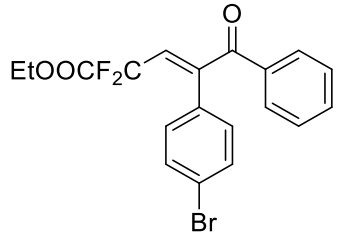
Brown oil, 51% yield (37.1 mg), E/Z=4:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.90 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 – 7.47 (m, 2H), 7.36 – 7.32 (m, 4H), 6.27 (t, *J* = 11.4 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.4 , 162.6 (t, *J* = 33.2 Hz), 147.4 (t, *J* = 7.7 Hz), 135.4 , 135.4 , 133.8 , 131.4 , 130.3 , 130.1 , 128.8 , 128.5 , 127.3 (t, *J* = 28.2 Hz), 111.7 (t, *J* = 248.8 Hz), 63.3 , 13.7 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.4.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 382.1006, measured: 382.1005.



ethyl (E)-4-(4-bromophenyl)-2,2-difluoro-5-oxo-5-phenylpent-3-enoate (4g)

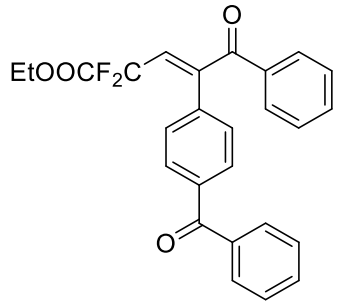
Yellow oil, 47% yield (38.4 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.90 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 – 7.47 (m, 4H), 7.26 – 7.23 (m, 2H), 6.27 (t, *J* = 11.6 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 194.3 , 162.6 (t, J = 33.1 Hz), 147.4 (t, J = 7.7 Hz), 135.4 , 133.8 , 131.9 , 131.5 , 130.5 , 130.1 , 128.8 , 127.2 (t, J = 28.1 Hz), 123.6 , 111.7 (t, J = 248.9 Hz), 63.4 , 13.7 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.5.

HRMS: m/z (ESI) calculated $[M+H]^+$: 409.0245, measured: 409.0246.



ethyl (E)-4-(4-benzoylphenyl)-2,2-difluoro-5-oxo-5-phenylpent-3-enoate (4h)

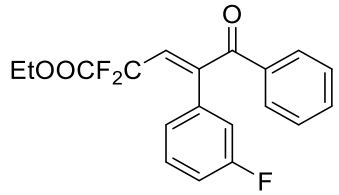
Brown oil, 45% yield (39.1 mg), E/Z=10:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.81 (m, 4H), 7.63 – 7.59 (m, 1H), 7.52 – 7.49 (m, 2H), 7.36 – 7.33 (m, 5H), 7.28 – 7.26 (m, 2H), 6.33 (t, *J* = 12.4 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.1 , 163.4 (t, *J* = 33.8 Hz), 150.0 (t, *J* = 8.5 Hz), 141.4 , 139.8 , 137.4 , 137.3 , 132.6 , 130.0 , 129.6 , 129.4 , 128.5 , 128.3 (d, *J* = 3.5 Hz), 128.3, 127.8 , 119.8 (t, *J* = 27.4 Hz), 115.3 , 112.3 (t, *J* = 247.1 Hz), 63.0 , 13.8 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -92.5.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$:452.1668, measured: 452.1664.



ethyl (E)-2,2-difluoro-4-(3-fluorophenyl)-5-oxo-5-phenylpent-3-enoate (4i)

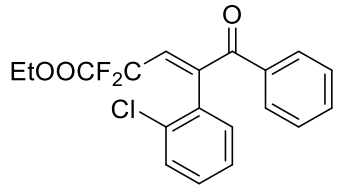
Colourless oil, 40% yield (27.8 mg), E/Z=12:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 – 7.47 (m, 2H), 7.36 – 7.31 (m, 1H), 7.16 – 7.04 (m, 3H), 6.28 (t, *J* = 11.6 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.2 , 162.6 (t, *J* = 32.9 Hz), 162.3 (d, *J* = 247.5 Hz), 147.2 (t, *J* = 7.9 Hz), 135.4 , 134.9 (d, *J* = 8.2 Hz), 133.9 , 130.1 , 129.9 (d, *J* = 8.3 Hz), 128.8 , 127.4 (t, *J* = 28.3 Hz), 124.8 , 116.1 (d, *J* = 21.0 Hz), 116.1 (d, *J* = 22.7 Hz),, 111.7 (t, *J* = 247.2 Hz), 63.3 , 13.7 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.5, -112.3.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 366.1312, measured: 366.1311.



ethyl (E)-4-(2-chlorophenyl)-2,2-difluoro-5-oxo-5-phenylpent-3-enoate (4j)

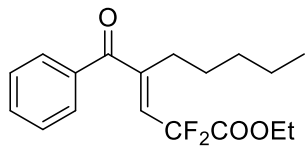
Colourless oil, 32% yield (23.3 mg), E/Z=3:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.96 (m, 2H), 7.63 – 7.59 (m, 1H), 7.52 – 7.48 (m, 2H), 7.38 – 7.34 (m, 4H), 6.53 (t, *J* = 11.2 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.9 , 162.3 (t, *J* = 33.2 Hz), 145.7 (t, *J* = 7.7 Hz), 136.1 , 133.2 , 132.6 , 132.1 (t, *J* = 28.2 Hz), 130.6 , 130.2 , 129.5 , 129.1 , 128.5 , 128.5 , 126.5 , 111.5 (t, *J* = 248.8 Hz), 63.4 , 13.7 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -98.5.

HRMS: m/z (ESI) calculated $[M+H]^+$: 365.0751, measured: 365.0752.



ethyl (E)-4-benzoyl-2,2-difluorononon-3-enoate (4k)

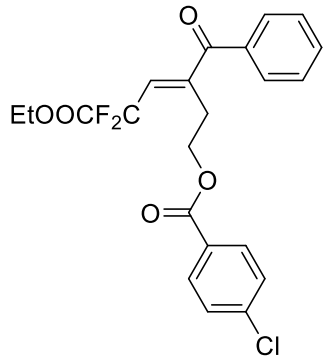
Yellow oil, 47% yield (30.5 mg), E/Z=13:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.81 (m, 1H), 7.62 – 7.58 (m, 0H), 7.50 – 7.46 (m, 1H), 5.98 (t, *J* = 13.2 Hz, 0H), 4.36 (q, *J* = 7.2 Hz, 1H), 2.68 – 2.64 (m, 1H), 1.44 – 1.41 (m, 1H), 1.37 (t, *J* = 7.2 Hz, 2H), 1.33 – 1.28 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.9 , 163.4 (t, *J* = 34.0 Hz), 150.7 (t, *J* = 6.1 Hz), 136.3 , 133.3 , 129.8 , 128.5 , 126.8 (t, *J* = 27.2 Hz), 112.3 (t, *J* = 248.3 Hz), 63.3 , 31.8 , 28.8 , 27.9 , 22.2 , 13.9 , 13.8 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.0.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 342.1875, measured: 342.1874.



(E)-3-benzoyl-6-ethoxy-5,5-difluoro-6-oxohex-3-en-1-yl 4-chlorobenzoate (4l)

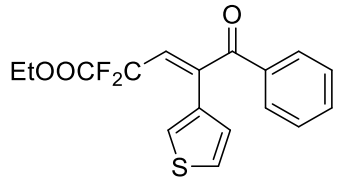
Brown oil, 40% yield (34.9 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.78 (m, 2H), 7.74 – 7.72 (m, 2H), 7.58 – 7.54 (m, 1H), 7.43 – 7.40 (m, 2H), 7.28 – 7.25 (m, 2H), 6.17 (t, *J* = 13.6 Hz, 1H), 4.48 (t, *J* = 6.0 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.24 – 3.21 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.0 , 165.2 , 163.0 (t, *J* = 33.7 Hz), 146.4 (t, *J* = 5.6 Hz), 139.3 , 135.7 , 133.4 , 130.8 , 129.9 , 129.3 (t, *J* = 27.0 Hz), 128.6 , 128.5 , 128.1 , 112.2 (t, *J* = 249.4 Hz), 63.6 , 63.4 , 28.1 , 13.8 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.15.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 454.1227, measured: 454.1230.



ethyl (E)-2,2-difluoro-5-oxo-5-phenyl-4-(thiophen-3-yl)pent-3-enoate (4m)

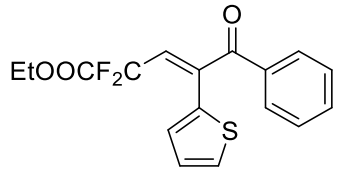
Yellow oil, 68% yield (45.7 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.45 (m, 3H), 7.31 – 7.29 (m, 1H), 7.12 – 7.11 (m, 1H), 6.16 (t, *J* = 11.4 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.4 , 162.6 (t, *J* = 33.3 Hz), 143.9 (t, *J* = 8.7 Hz), 135.5 , 133.8 , 132.7 , 130.1 , 128.7 , 127.9 , 127.3 , 126.0 , 125.4 (t, *J* = 29.1 Hz), 112.0 (t, *J* = 247.0 Hz), 63.2 , 13.6 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.0.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 354.0970, measured: 354.0972.



ethyl (Z)-2,2-difluoro-5-oxo-5-phenyl-4-(thiophen-2-yl)pent-3-enoate (4n)

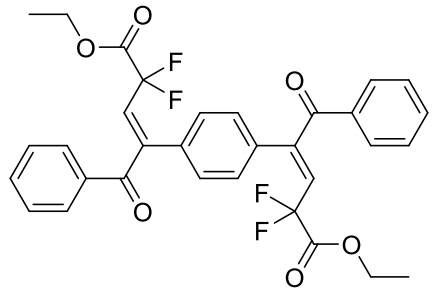
Brown oil, 43% yield (28.9 mg), E/Z=6:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.95 (m, 2H), 7.64 – 7.60 (m, 1H), 7.51 – 7.44 (m, 3H), 7.30 – 7.29 (m, 1H), 7.05 – 7.02 (m, 1H), 6.17 (t, *J* = 11.4 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.1 , 162.4 (t, *J* = 33.0 Hz), 142.1 (t, *J* = 8.9 Hz), 135.1 , 134.0 , 132.9 , 131.0 , 130.3 , 129.9 , 128.7 , 127.1 , 125.5 (t, *J* = 29.5 Hz), 111.9 (t, *J* = 244.7 Hz), 63.3 , 13.7 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.8.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 354.0970, measured: 354.0974.



diethyl 4,4'-(1,4-phenylene)(3E,3'E)-bis(2,2-difluoro-5-oxo-5-phenylpent-3-enoate) (4o)

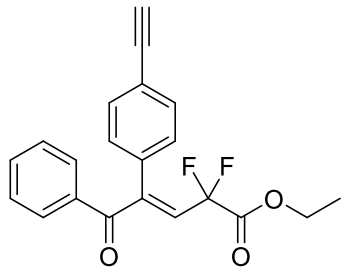
Brown oil, 29% yield (33.8 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.90 (m, 4H), 7.61 – 7.58 (m, 2H), 7.49 – 7.46 (m, 4H), 7.38 (s, 4H), 6.25 (t, *J* = 11.6 Hz, 2H), 3.96 (q, *J* = 7.2 Hz, 4H), 1.16 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3, 162.5 (t, *J* = 32.8 Hz), 147.7 (t, *J* = 7.9 Hz), 135.4 , 133.9 , 133.8 , 130.1 , 128.8 , 128.7 , 126.9 (t, *J* = 28.2 Hz), 111.7 (t, *J* = 246.6 Hz), 63.3 , 13.6 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.1.

HRMS: m/z (ESI) calculated $[M+H]^+$: 600.2004, measured: 600.1989.



ethyl (E)-4-(4-ethynylphenyl)-2,2-difluoro-5-oxo-5-phenylpent-3-enoate (4oo)

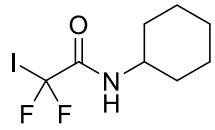
Brown oil, 37% yield (26.2 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.90 (m, 2H) , 7.61 – 7.58 (m, 1H), 7.49 – 7.48 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.27 (t, *J* = 11.6 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.12 (s, 1H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3 , 162.6 (t, *J* = 33.1 Hz), 147.8 (t, *J* = 8.0 Hz), 135.4 , 133.8 , 133.4 , 131.9 , 130.1 , 128.9 , 128.7 , 127.0 (t, *J* = 28.1 Hz), 123.1 , 111.7 (t, *J* = 247.0 Hz), 82.9 , 78.6 , 63.3 , 13.6

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.2.

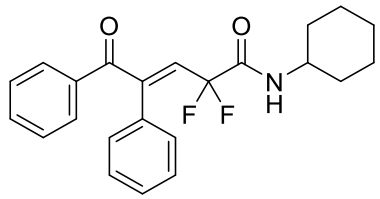
HRMS: m/z (ESI) calculated $[M+H]^+$: 355.1140, measured: 355.1131.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.16 (s, 1H), 3.82 – 3.75 (m, 1H), 1.99 – 1.95 (m, 2H), 1.79 – 1.74 (m, 3H), 1.68 – 1.63 (m, 2H), 1.45 – 1.34 (m, 3H), 1.30 – 1.19 (m, 5H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.4 (t, *J* = 24.2 Hz), 91.6 (t, *J* = 322.1 Hz), 49.3 , 32.2 , 25.2 , 24.6 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.6.



(E)-N-cyclohexyl-2,2-difluoro-5-oxo-4,5-diphenylpent-3-enamide (4p)

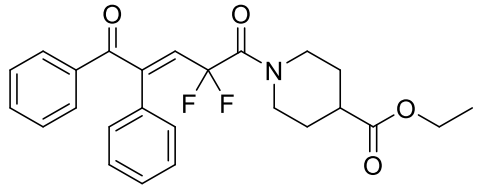
Brown oil, 42% yield (32.2 mg), E/Z=10:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.49 – 7.45 (m, 2H), 7.39 – 7.37 (m, 2H), 7.35 – 7.33 (m, 3H), 6.31 (t, *J* = 12.6 Hz, 1H), 5.96 (s, 1H), 3.61 – 3.56 (m, 1H), 1.78 – 1.75 (m, 2H), 1.69 – 1.65 (m, 2H), 1.61 – 1.58 (m, 1H), 1.33 – 1.30 (m, 2H), 1.17 – 1.11 (m, 1H), 1.08 – 1.00 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.8 , 162.2 (t, *J* = 28.6 Hz), 148.2 (t, *J* = 7.2 Hz), 135.6 , 133.5 , 130.2 , 128.8 , 128.7 , 128.6 , 128.1 , 127.3 (t, *J* = 27.1 Hz), 121.2 , 113.4 (t, *J* = 250.8 Hz), 48.6 , 32.3 , 25.2 , 24.5 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -95.5.

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 401.2035, measured: 401.2034.



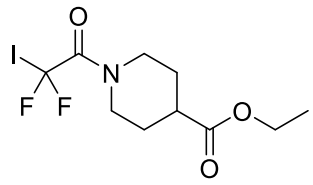
ethyl (E)-1-(2,2-difluoro-5-oxo-4,5-diphenylpent-3-enoyl)piperidine-4-carboxylate (4q)

Brown oil, 50% yield (33.8 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.95 (m, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.40 (m, 4H), 7.35 – 7.33 (m, 3H), 6.32 (t, *J* = 12.0 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.05 (d, *J* = 13.6 Hz, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 3.12 – 3.05 (m, 1H), 2.76 – 2.70 (m, 1H), 2.54 – 2.46 (m, 1H), 1.91 – 1.81 (m, 2H), 1.73 – 1.67 (m, 1H), 1.58 – 1.48 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.9 , 173.7 , 160.6 (t, *J* = 29.1 Hz), 147.3 (t, *J* = 7.6 Hz), 135.4 , 133.6 , 132.9 , 130.2 , 129.0 , 128.7 , 128.6 , 128.1 , 126.6 (t, *J* = 27.2 Hz), 114.4 (t, *J* = 248.4 Hz), 60.6 , 45.1 , 42.3 , 40.6 , 28.0 , 27.4 , 14.1 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.6 (d, *J* = 22.6 Hz).

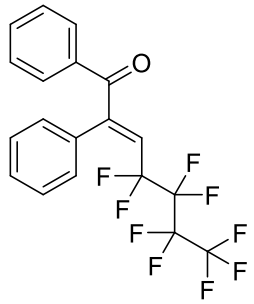


ethyl 1-(2,2-difluoro-2-iodoacetyl)piperidine-4-carboxylate

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.27 (d, *J* = 13.2 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.10 (d, *J* = 16.0 Hz, 1H), 3.30 – 3.23 (m, 1H), 3.11 – 3.04 (m, 1H), 2.67 – 2.60 (m, 1H), 2.03 – 2.00 (m, 2H), 1.90 – 1.70 (m, 2H),1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 158.2 (t, *J* = 23.5 Hz), 89.4 (t, *J* = 319.7 Hz), 60.5 , 45.9 , 42.9 , 40.0 , 27.3 , 27.2 , 13.9 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -50.39 (d, *J* = 14.3 Hz).



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-1,2-diphenylhept-2-en-1-one (5a)

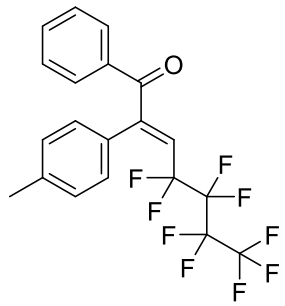
Brown oil, 63% yield (53.7 mg), E/Z=8:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.92 (m, 2H), 7.62 – 7.56 (m, 1H), 7.50 – 7.44 (m, 2H), 7.40 – 7.36 (m, 5H), 6.05 (t, *J* = 14.4 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.1, 152.4 (t, *J* = 4.6 Hz), 134.9 , 134.0 , 132.8 , 130.1 , 129.5 , 129.1 , 128.8 , 128.2 , 118.8 (t, *J* = 21.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.99 – -81.05 (m), -105.78 – -107.88 (m), -123.61 – -123.68 (m), -125.69 – -125.77 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 427.0739, measured: 427.0740.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenyl-2-(p-tolyl)hept-2-en-1-one (5b)

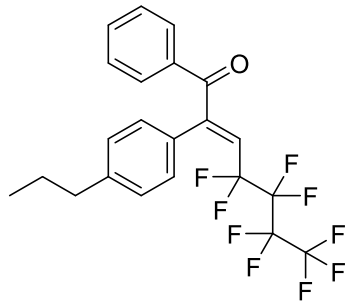
Brown oil, 47% yield (41.4 mg), E/Z=9:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.60 – 7.57 (m, 1H), 7.49 – 7.45 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.00 (t, *J* = 14.4 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3 , 152.6 (t, *J* = 4.5 Hz), 139.2 , 135.0 , 133.9 , 130.1 , 129.9 , 129.0 , 128.8 , 128.2 , 118.2 (t, *J* = 21.7 Hz), 21.3 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.99 – -81.04 (m), -105.62 – -105.69 (m), -123.62 – -123.69 (m), -125.65 – -125.73 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 441.0895, measured: 441.0893.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenyl-2-(4-propylphenyl)hept-2-en-1-one (5c)

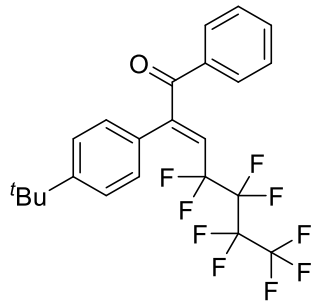
Yellow oil, 61% yield (57.1 mg), E/Z=6:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 2H), 7.60 – 7.56 (m, 1H), 7.48 – 7.45 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.99 (t, *J* = 14.4 Hz, 1H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.65 – 1.58 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3 , 152.7 (t, *J* = 4.0 Hz), 143.9 , 135.0 , 133.9 , 130.1 , 128.8 , 128.3 , 128.2 , 126.6 , 118.0 (t, *J* = 21.6 Hz), 37.8 , 24.2 , 13.7

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.01 – -81.06 (m), -105.61 – -105.67 (m), -123.64 – -123.71 (m), -125.66 – -125.74 (m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 469.1208, measured: 469.1193.



(E)-2-(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylhept-2-en-1-one (5d)

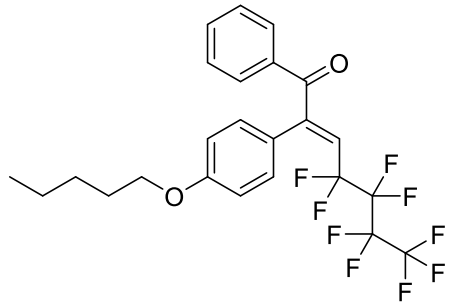
Yellow oil, 70% yield (67.5 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.60 – 7.56 (m, 1H), 7.48 – 7.44 (m, 2H), 7.39 – 7.33 (m, 4H), 5.98 (t, *J* = 14.0 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3 , 152.7 (t, *J* = 4.3 Hz), 152.3 , 135.0 , 134.0 , 130.1 , 129.7 , 128.8 , 128.0 , 125.2 , 117.8 (t, *J* = 21.9 Hz), 34.7 , 31.1 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.03 – -81.08 (m), -105.58 – -105.67 (m), -123.66 – -123.74 (m), -125.63 – -125.75 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 483.1365, measured: 483.1363.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-(pentyloxy)phenyl)-1-phenylhept-2-en-1-one (5e)

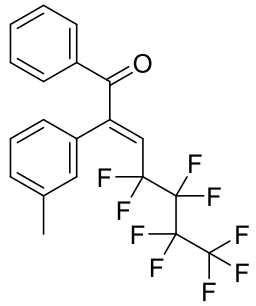
Yellow oil, 69% yield (70.7 mg), E/Z=7:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.90 (m, 2H), 7.59 – 7.55 (m, 1H), 7.47 – 7.43 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.88 – 6.86 (m, 2H), 5.96 (t, *J* = 14.4 Hz, 1H), 3.93 (t, *J* = 6.8 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.44 – 1.34 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.5 , 160.0 , 152.5 (t, *J* = 4.4 Hz), 135.1 , 133.9 , 130.1 , 129.9 , 128.7 , 124.7 , 117.3 (t, *J* = 21.5 Hz), 114.3 , 68.0 , 28.9 , 28.2 , 22.4 , 13.9 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.03 – -81.09 (m), -105.37 – -105.39 (m), -123.66 – -123.74 (m), -125.65 – -125.74 (m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 530.1736, measured: 530.1732.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenyl-2-(m-tolyl)hept-2-en-1-one (5f)

Yellow oil, 49% yield (43.2 mg), E/Z>20:1.

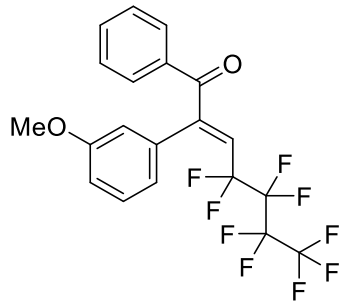
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.50 – 7.47 (m, 2H), 7.24 (s, 1H), 7.20 – 7.16 (m, 3H), 6.00 (t, *J* = 14.2 Hz, 1H), 2.34 (s, 3H).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.51 – 7.46 (m, 1H), 7.25 (s, 1H), 7.21 – 7.16 (m, 2H), 6.00 (t, *J* = 14.2 Hz, 0H), 2.34 (s, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.2 , 152.6 (t, *J* = 4.3 Hz), 137.9 , 135.0 , 134.0 , 132.7 , 130.1 , 129.9 , 128.8 , 128.1 , 125.4 , 118.4 (t, *J* = 22.0 Hz), 29.7 , 21.4 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.98 – -81.03 (m), -105.76 – -105.83 (m), -123.60 – -123.67 (m), -125.66 – -125.73 (m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 458.1161, measured: 458.1160.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-2-(3-methoxyphenyl)-1-phenylhept-2-en-1-one (5g)

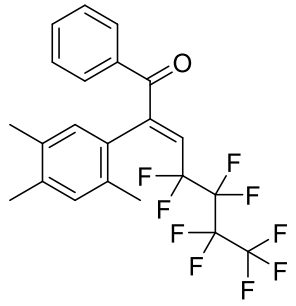
Brown oil, 33% yield (30.1 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 6.98 – 6.89 (m, 3H), 6.03 (t, *J* = 14.0 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.9 , 159.3 , 152.3 (t, *J* = 4.0 Hz), 134.9 , 134.0 , 133.9 , 130.1 , 129.3 , 128.8 , 120.6 , 118.7 (t, *J* = 22.1 Hz), 114.7 , 113.9 , 55.3 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.97 – -81.03 (m), -105.87 – -105.96 (m), -123.57 – -123.65 (m), -125.65 – -125.73 (m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 474.1110, measured: 474.1107.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenyl-2-(2,4,5-trimethylphenyl)hept-2-en-1-one (5h)

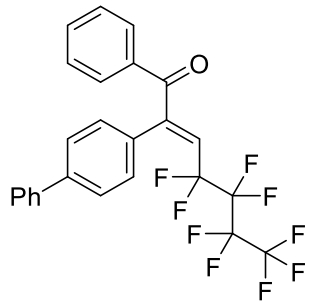
Yellow oil, 47% yield (44.0 mg), E/Z=7:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.89 (m, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 3.6 Hz, 2H), 6.25 (t, *J* = 14.0 Hz, 1H), 2.22 (s, 6H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3 , 151.6 (t, *J* = 4.6 Hz), 137.3 , 135.7 , 133.5 , 133.4 , 132.7 , 131.4 , 130.3 , 130.0 , 129.9 , 128.7 , 122.8 (t, *J* = 21.1 Hz), 19.5 , 19.5 , 19.2 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.98 – -81.04 (m), -108.22, -123.71 – -123.78 (m), -125.65 – -125.73 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 469.1208, measured: 469.1204.



(E)-2-([1,1'-biphenyl]-4-yl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylhept-2-en-1-one (5i)

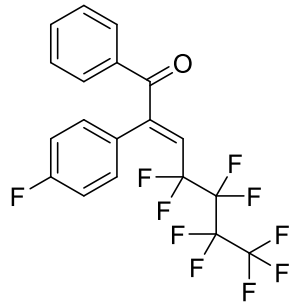
Yellow oil, 65% yield (65.3 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.95 (m, 2H), 7.60 – 7.56 (m, 5H), 7.49 – 7.45 (m, 4H), 7.43 – 7.39 (m, 2H), 7.34 – 7.31 (m, 1H), 6.07 (t, *J* = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.1 , 152.2 (t, *J* = 4.6 Hz), 142.0 , 140.1 , 134.93 134.0 , 131.7 , 130.1 , 128.8 , 128.8 , 128.8 , 128.7 , 127.7 , 127.1 , 126.9 , 118.7 (t, *J* = 22.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.97 – -81.02 (m), -105.57 – -105.67 (m), -123.53 – -123.60 (m), -125.60 – -125.68 (m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 520.1317, measured: 520.1315.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-fluorophenyl)-1-phenylhept-2-en-1-one (5j)

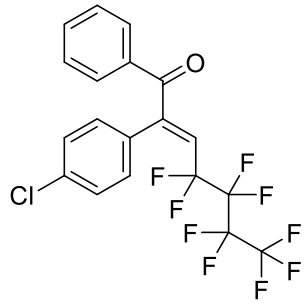
Brown oil, 47% yield (41.7 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.90 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 – 7.47 (m, 3H), 7.40 – 7.37 (m, 3H), 7.08 – 7.04 (m, 2H), 6.07 (t, *J* = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.9, 164.4 , 161.9 , 151.3 , 134.8 , 134.1 , 130.3 (d, *J* = 8.3 Hz), 129.5 (d, *J* = 115.4 Hz), 128.8 (d, *J* = 3.5 Hz),119.5 (t, *J* = 21.9 Hz), 115.4 (d, *J* = 21.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.05 – -81.10 (m), -105.82 – -105.91 (m), -111.82, -123.63 – -123.70 (m), -125.71 – -125.79 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 445.0645, measured: 445.0630.



(E)-2-(4-chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylhept-2-en-1-one (5k)

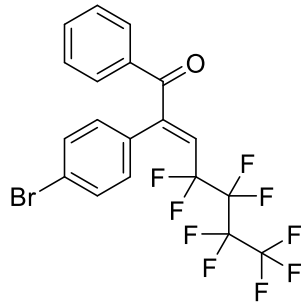
Yellow oil, 57% yield (52.4 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35 (s, 4H), 6.08 (t, *J* = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.7 , 151.1 , 135.4 , 134.7 , 134.2 , 131.2 , 130.0 , 129.6 , 128.9 , 128.5 , 119.8 (t, *J* = 22.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.01 – -81.06 (m), -105.87 – -105.98 (m), -123.59 – -124.67 (m), -125.70 – -125.79 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 461.0349, measured: 461.0335.



(E)-2-(4-bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylhept-2-en-1-one (5l)

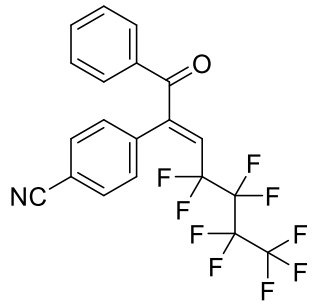
Brown oil, 52% yield (52.4 mg), E/Z=8:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.89 (m, 2H), 7.64 – 7.60 (m, 1H), 7.52 – 7.50 (m, 4H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.08 (t, *J* = 14.4 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.6, 151.1 (t, *J* = 4.2 Hz), 134.7 , 134.2 , 132.6 , 131.7 , 131.5 , 129.8 , 128.9 , 123.6 , 119.8 (t, *J* = 22.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.98 – -81.04 (m), -105.85 – -105.95 (m), -123.56 – -123.64 (m), -125.66 – -125.74 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$:506.9824, measured: 506.9809.



(E)-4-(4,4,5,5,6,6,7,7,7-nonafluoro-1-oxo-1-phenylhept-2-en-2-yl)benzonitrile (5m)

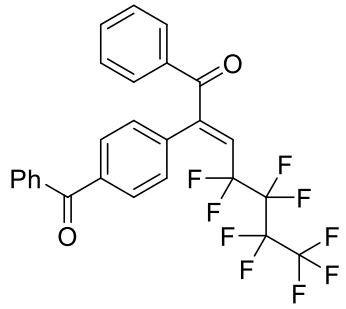
Yellow oil, 33% yield (29.8 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 3H), 7.70 – 7.65 (m, 3H), 7.55 – 7.50 (m, 5H), 6.17 (t, *J* = 13.6 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.9 , 150.0 (t, *J* = 4.6 Hz), 137.5 , 134.5 , 133.0 , 131.9 , 130.0 , 129.1 , 129.0 , 121.3 (t, *J* = 22.5 Hz), 118.1 , 113.1 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.94 – -80.99 (m), -106.18 – -106.24 (m), -123.49 – -123.56 (m), -125.68– -125.76(m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 469.0954, measured: 469.0959.



(E)-2-(4-benzoylphenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylhept-2-en-1-one (5n)

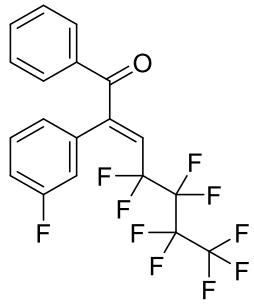
Brown oil, 39% yield (41.3 mg), E/Z=8:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.95 (m, 2H), 7.84 – 7.78 (m, 4H), 7.66 – 7.62 (m, 1H), 7.61 – 7.57 (m, 2H), 7.54 – 7.48 (m, 5H), 6.15 (t, *J* = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.9 , 193.4 , 151.2 , 137.9 , 137.2 , 136.8 , 134.7 , 134.3 , 132.6 , 130.1 , 130.0 , 129.8 , 129.0 , 128.3 , 128.2 , 126.7 , 120.2 (t, *J* = 22.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.95 – -81.00 (m), -105.96 – -106.06 (m), -123.51 – -123.59(m), -125.66 – -125.75 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 531.1001, measured: 531.0999.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-2-(3-fluorophenyl)-1-phenylhept-2-en-1-one (5o)

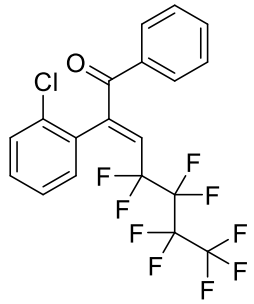
Brown oil, 51% yield (45.3 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.65 – 7.61 (m, 1H), 7.52 – 7.49 (m, 2H), 7.37 – 7.32 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 9.2 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.08 (t, *J* = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.5, 163.5 , 161.0 , 150.9 , 134.7 , 134.7 (d, *J* = 8.5 Hz), 134.2 , 129.9 (d, *J* = 8.2 Hz), 129.5 (d, *J* = 110.9 Hz), 124.1 (d, *J* = 3.2 Hz), 119.9 (t, *J* = 22.2 Hz), 116.1 (d, *J* = 20.9 Hz), 115.5 (d, *J* = 23.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.00 – -81.05 (m), -106.05 – -106.14 (m), -112.44, -123.58 – -123.66 (m), -125.68 – -125.76 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$:445.0645, measured:445.0628.



(E)-2-(2-chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylhept-2-en-1-one (5p)

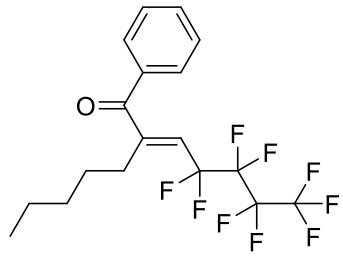
Yellow oil, 35% yield (32.2 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.96 (m, 2H), 7.64 – 7.60 (m, 1H), 7.53 – 7.49 (m, 3H), 7.40 – 7.33 (m, 4H), 6.37 (t, *J* = 13.6 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.4 , 148.7 (t, *J* = 3.8 Hz), 135.7 , 133.5 , 132.7 , 131.6 , 130.4 , 130.2 , 129.2 , 128.7 , 128.3 , 126.3 , 125.0 (t, *J* = 21.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.98 – -81.03 (m), -107.32 – -108.93 (m), -123.65, -125.70 – -125.77 (m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 478.0615, measured: 478.0611.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-2-pentyl-1-phenylhept-2-en-1-one (5q)

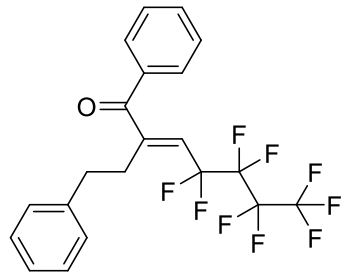
Brown oil, 29% yield (24.4 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.81 (m, 2H), 7.64 – 7.60 (m, 1H), 7.52 – 7.48 (m, 2H), 5.80 (t, *J* = 14.8 Hz, 1H), 2.73 – 2.67 (m, 2H), 1.47 – 1.41 (m, 2H), 1.35 – 1.28 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.5 , 154.4 (t, *J* = 3.9 Hz), 135.8 , 133.7 , 129.8 , 128.7 , 120.2 (t, *J* = 23.8 Hz), 31.8 , 29.3 , 28.0 , 22.2 , 13.8 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.98 – -81.03 (m), -107.08 – -107.18 (m), -124.00 – -124.08 (m), -125.68 – -125.76 (m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 421.1208, measured: 421.1194.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-2-phenethyl-1-phenylhept-2-en-1-one (5r)

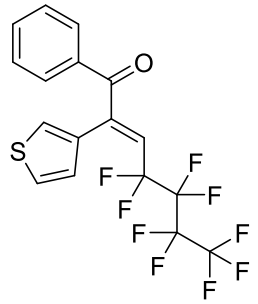
Yellow oil, 27% yield (24.5 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.73 (m, 2H), 7.63 – 7.60 (m, 1H), 7.50 – 7.46 (m, 2H), 7.26 – 7.24 (m, 2H), 7.18 – 7.15 (m, 3H), 5.88 (t, *J* = 15.2 Hz, 1H), 3.06 – 3.02 (m, 2H), 2.81 – 2.77 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.2 , 153.0 (t, *J* = 4.2 Hz), 140.2 , 135.7 , 133.7 , 129.8 , 128.7 , 128.5 , 128.4 , 126.4 , 121.6 (t, *J* = 23.6 Hz), 34.5 , 31.1 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.94 – -80.99 (m), -107.35 – -107.46 (m), -123.93 – -124.00 (m), -125.64 – -125.71 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 455.1052, measured: 455.1049.



(E)-4,4,5,5,6,6,7,7,7-nonafluoro-1-phenyl-2-(thiophen-3-yl)hept-2-en-1-one (5s)

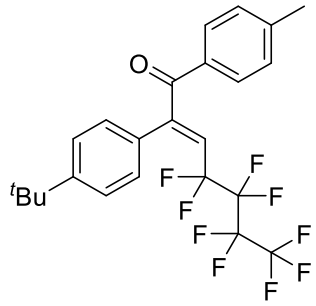
Yellow oil, 35% yield (30.2 mg), E/Z=7:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.89 (m, 2H), 7.62 – 7.58 (m, 1H), 7.49 – 7.45 (m, 3H), 7.33 – 7.31 (m, 1H), 7.18 (d, *J* = 4.0 Hz, 1H), 5.94 (t, *J* = 14.8 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.8, 147.7 (t, *J* = 4.4 Hz), 134.8 , 134.1 , 132.1 , 130.1 , 128.8 , 127.9 , 126.9 , 125.9 , 117.1 (t, *J* = 22.4 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.97 – -81.03 (m), -105.93 – -106.03 (m), -123.68 – -123.76 (m), -125.62 – -125.71 (m).

HRMS: m/z (ESI) calculated $[M+NH_4]^+$: 450.0569, measured: 450.0567.



(E)-2-(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(p-tolyl)hept-2-en-1-one (6a)

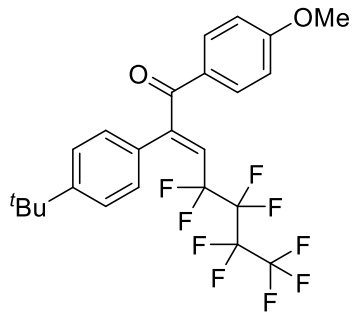
Brown oil, 60% yield (59.8 mg), E/Z=11:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.94 (t, *J* = 14.3 Hz, 1H), 2.40 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.0 , 152.9 (t, *J* = 4.0 Hz), 152.2 , 145.2 , 132.4 , 130.3 , 129.9 , 129.5 , 128.0 , 125.1 , 117.2 (t, *J* = 22.0 Hz), 34.6 , 31.1 , 21.7 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.02 – -81.08 (m), -105.53 – -105.62 (m), -123.68 – -123.76 (m), -125.64 – -125.72 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 497.1521, measured: 497.1519.



(E)-2-(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)hept-2-en-1-one (6b)

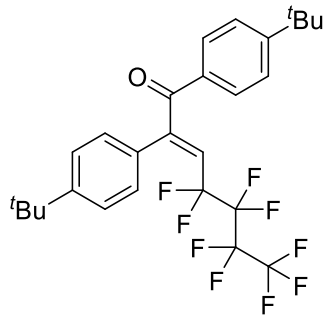
Brown oil, 65% yield (66.6 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 3.6 Hz, 4H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.92 (t, *J* = 14.4 Hz, 1H), 3.85 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.9 , 164.4 , 153.0 (t, *J* = 4.2 Hz), 152.2 , 132.6 , 130.0 , 127.9 , 127.7 , 125.2 , 116.6 (t, *J* = 21.6 Hz), 114.1 , 55.5 , 34.6 , 31.1 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.02 – -81.07 (m), -105.44 – -105.54 (m), -123.67 – -123.74 (m), -125.64 – -125.72 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 513.1471, measured: 513.1469.



(E)-1,2-bis(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-one (6c)

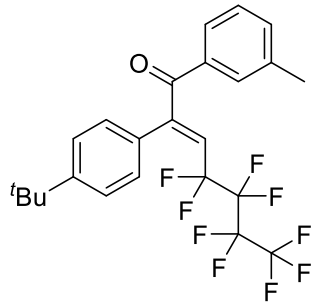
Yellow oil, 49% yield (52.7 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.33 (m, 4H), 5.93 (t, *J* = 14.4 Hz, 1H), 1.34 (s, 9H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.9 , 158.1 , 152.8 (t, *J* = 4.4 Hz), 152.2 , 132.2 , 130.2 , 129.9 , 127.9 , 125.8 , 125.2 , 117.0 (t, *J* = 21.8 Hz), 35.3 , 34.7 , 31.2 , 31.0 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.98 – -81.05 (m), -105.51 – -105.61 (m), -123.60 – -123.68 (m), -125.62 – -125.73 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 539.1991, measured: 539.1988.



(E)-2-(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(m-tolyl)hept-2-en-1-one (6d)

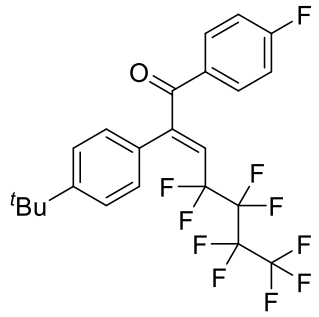
Brown oil, 67% yield (66.5 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.62 (m, 2H), 7.41 – 7.32 (m, 6H), 5.97 (t, *J* = 14.4 Hz, 1H), 2.39 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.5 , 152.7 (t, *J* = 4.5 Hz), 152.2 , 138.8 , 135.1 , 134.8 , 130.5 , 129.9 , 128.6 , 128.0 , 127.5 , 125.2 , 117.7 (t, *J* = 21.8 Hz), 34.7 , 31.1 , 21.2 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.01 – -81.08 (m), -105.59 – -105.69 (m), -123.73 – -123.80 (m), -125.62 – -125.73 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 497.1521, measured: 497.1519.



(E)-2-(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-fluorophenyl)hept-2-en-1-one (6e)

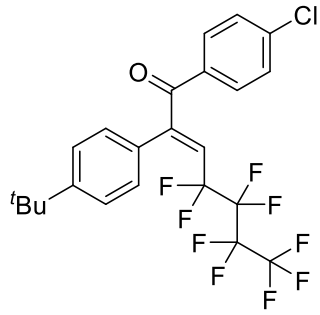
Yellow oil, 71% yield (71.0 mg), E/Z=11:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.95 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2H), 5.98 (t, *J* = 14.4 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.7, 166.2 (d, *J* = 255.5 Hz), 152.6 (t, *J* = 4.0 Hz), 152.5 , 132.8 (d, *J* = 9.5 Hz), 131.4 (d, *J* = 2.9 Hz), 129.6 , 128.0 , 125.3 , 117.6 (t, *J* = 22.0 Hz), 116.1 (d, *J* = 22.0 Hz), 34.7 , 31.1 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.06 – -81.11 (m), -103.00, -105.60 – -105.70 (m), -123.69 – -123.77 (m), -125.68 – -125.76 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 501.1271, measured: 501.1259.



(E)-2-(4-(tert-butyl)phenyl)-1-(4-chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-one (6f)

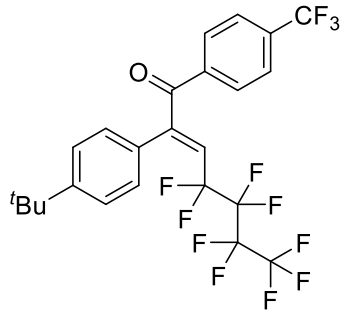
Yellow oil, 63% yield (65.0 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.99 (t, *J* = 14.4 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.1 , 152.6 , 152.4 (t, *J* = 3.9 Hz), 140.6 , 133.3 , 131.4 , 129.5 , 129.2 , 128.0 , 125.3 , 118.0 (t, *J* = 22.1 Hz), 34.7 , 31.1 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.03 – -81.08 (m), -105.63 – -105.70 (m), -123.67 – -123.74 (m), -125.64 – -125.75 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 517.0975, measured: 517.0961.



(E)-2-(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-(trifluoromethyl)phenyl)hept-2-en-1-one (6g)

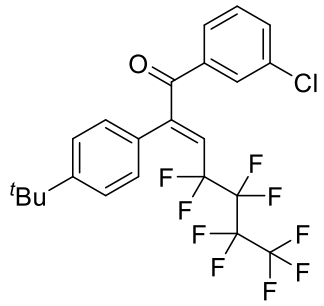
Yellow oil, 50% yield (55.0 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 12H), 6.08 (t, *J* = 14.4 Hz, 1H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.25, 77 , 152.10 (t, *J* = 4.5 Hz), 137.91 , 135.09 (q, *J* = 32.7 Hz), 130.30 , 129.17 , 128.08 , 125.82 (q, *J* = 3.7 Hz), 125.41 , 123.39 (q, *J* = 271.2 Hz), 118.99 (q, *J* = 22.1 Hz), 34.73 , 31.12 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.39 -81.02 – -81.09 (m), -105.76 – -105.84 (m), -123.64 – -123.72 (m), -125.67 – -125.75 (m).

HRMS: m/z (ESI) calculated $[M+Na]^+$: 573.1058, measured: 573.1034.



(E)-2-(4-(tert-butyl)phenyl)-1-(3-chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-one (6h)

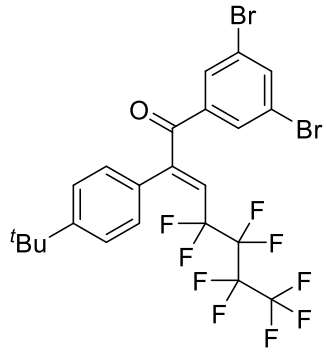
Yellow oil, 58% yield (59.9 mg), E/Z=8:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (t, *J* = 2.0 Hz, 1H), 7.77 – 7.75 (m, 1H), 7.56 – 7.53 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.01 (t, *J* = 14.0 Hz, 1H), 1.30 (s, 9H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.0 , 152.6 , 152.1 (t, *J* = 4.1 Hz), 136.7 , 135.2 , 133.8 , 130.0 , 129.9 , 129.3 , 128.2 , 128.1 , 125.3 , 118.5 (t, *J* = 21.8 Hz), 34.7 , 31.1 ..

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.99 – -81.05 (m), -105.67 – -105.77 (m), -123.69 – -123.76 (m), -125.63 – -125.71 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 517.0975, measured: 517.0961.



(E)-2-(4-(tert-butyl)phenyl)-1-(3,5-dibromophenyl)-4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-one (6i)

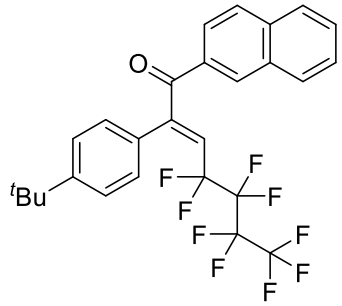
Yellow oil, 61% yield (77.8 mg), E/Z>20:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 2.0 Hz, 2H), 7.84 (t, *J* = 1.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.06 (t, *J* = 14.0 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.5 , 152.9 , 151.4 (t, *J* = 3.7 Hz), 138.9 , 138.0 , 131.6 , 129.0 , 128.1 , 125.5 , 123.5 , 119.4 (t, *J* = 21.8 Hz), 34.8 , 31.1 .

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.97 – -81.03 (m), -105.77 – -105.86 (m), -123.74 – -123.81 (m), -125.59 – -125.70 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$:638.9575, measured:638.9557.



(E)-2-(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)hept-2-en-1-one (6j)

Brown oil, 63% yield (67.0 mg), E/Z=9:1.

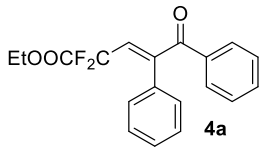
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.02 – 7.99 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.63 – 7.56 (m, 2H), 7.44 – 7.42 (m, 1H), 7.39 (m, 3H), 6.06 (t, *J* = 14.4 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3 , 152.8 (t, *J* = 4.1 Hz), 152.3 , 135.9 , 133.0 , 132.3 , 132.3 , 129.9 , 129.8 , 129.2 , 128.8 , 128.1 , 127.8 , 127.1 , 125.2 , 124.8 , 117.7 (t, *J* = 21.9 Hz), 34.7 , 31.1 .

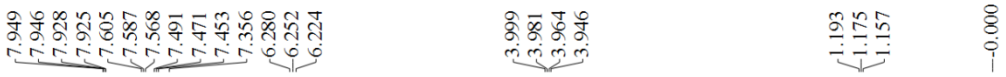
^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.96 – -81.01 (m), -105.49 – -105.55 (m), -123.63 – -123.71 (m), -125.56 – -125.63 (m).

HRMS: m/z (ESI) calculated $[M+H]^+$: 533.1521, measured: 533.1518.

6. ^{1}H NMR、^{13}C NMR、^{19}F NMR Spectra for Substrates 4a-4q, 5a-5s, 6a-6j. and 1D-NOESY for Product 4k.


O
EtOOCF2C

4a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7.928
7.925
7.605
7.587
7.568
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7.471
7.453
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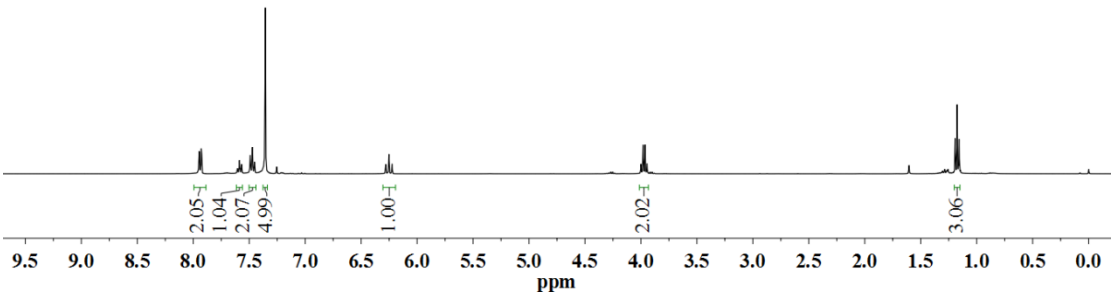
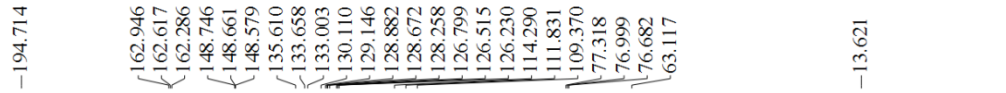
6.224
3.999
3.981
3.964
3.946
1.193
1.175
1.157
0.000


2.05
1.04
2.07
4.99
1.00
2.02
3.06
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
ppm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162.617
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148.661
148.579
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133.658
133.003
130.110
129.146
128.882
128.672
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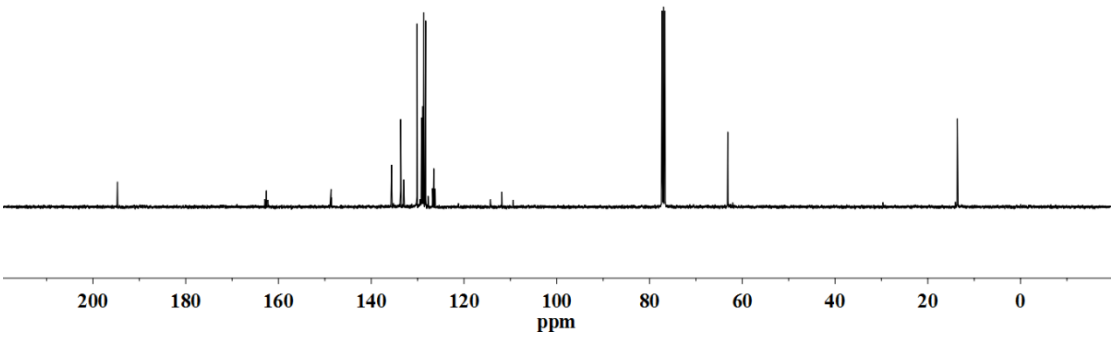
76.999
76.682
63.117
13.621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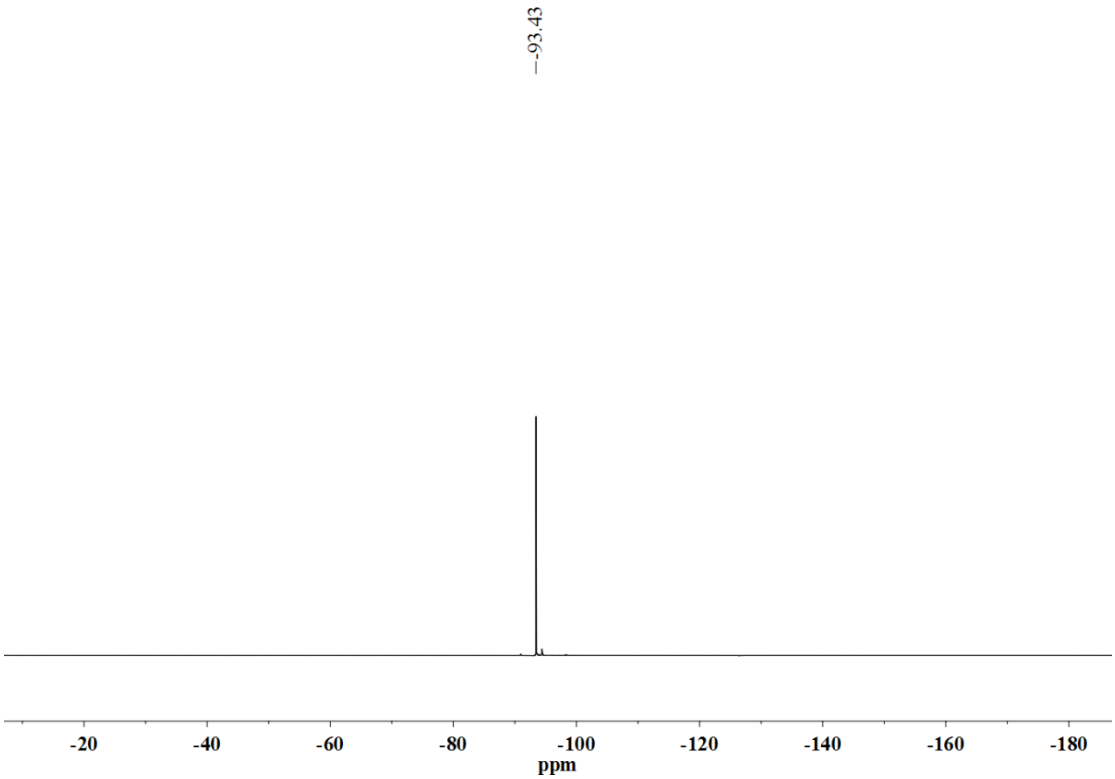
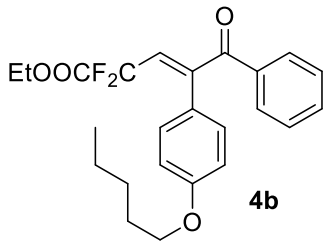
ppm

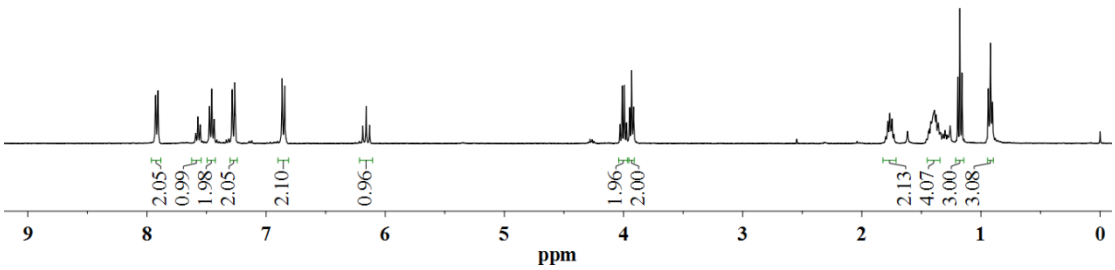


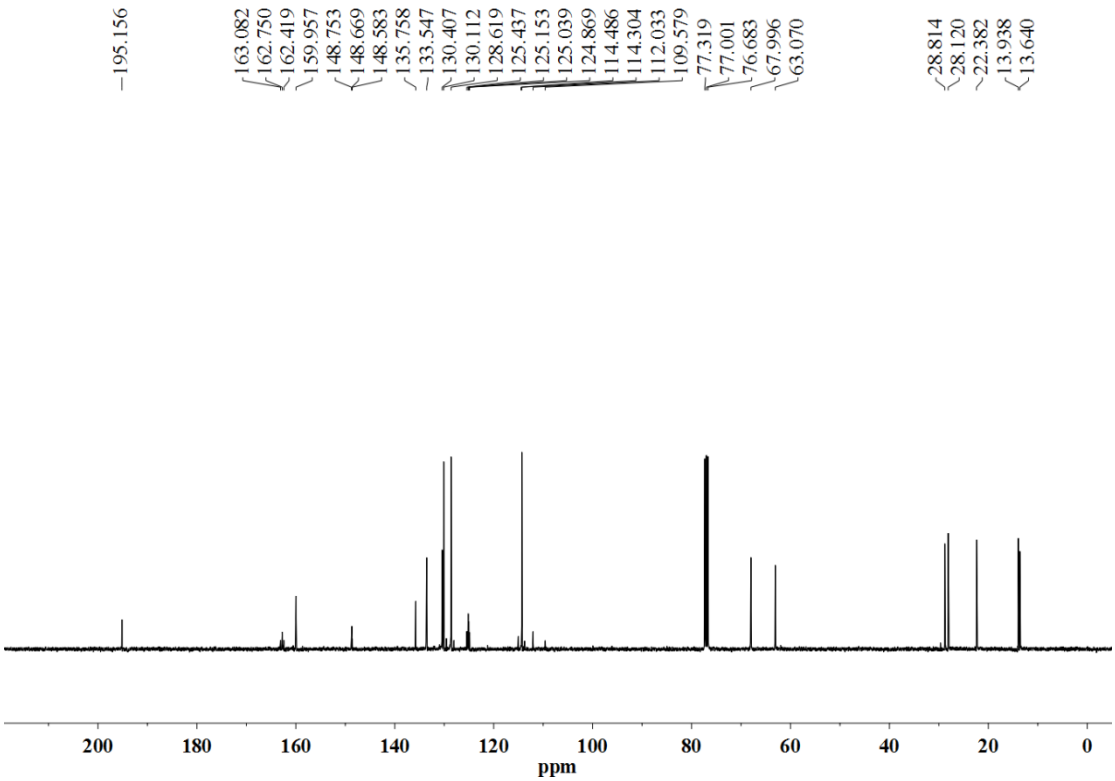


4b

7.926 7.909 7.590 7.572 7.553 7.475 7.456 7.437 7.284 7.263 6.866 6.844 6.188 6.160 6.132

4.029 4.011 3.993 3.975 3.949 3.932 3.916 1.799 1.783 1.765 1.746 1.730 1.439 1.418 1.390 1.375 1.359 1.336 1.195 1.177 1.159 0.938 0.920 0.903 -0.000

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159.957
148.753
148.669
148.583
135.758
133.547
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130.112
128.619
125.437
125.153
125.039
124.869
114.486
114.304
112.033
109.579
77.319
77.001
76.683
67.996
63.070
28.814
28.120
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13.938
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120
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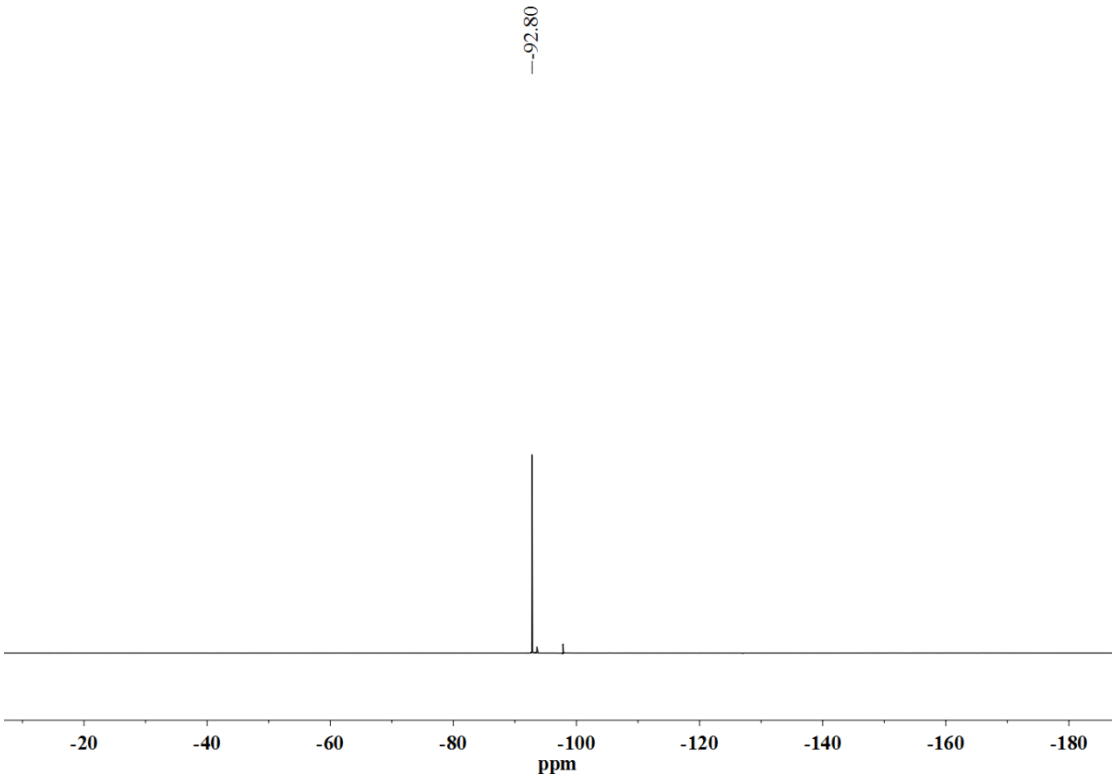
80
60
40
20
0
ppm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-140
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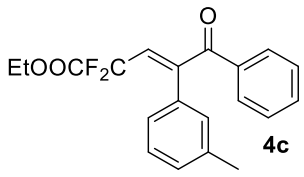
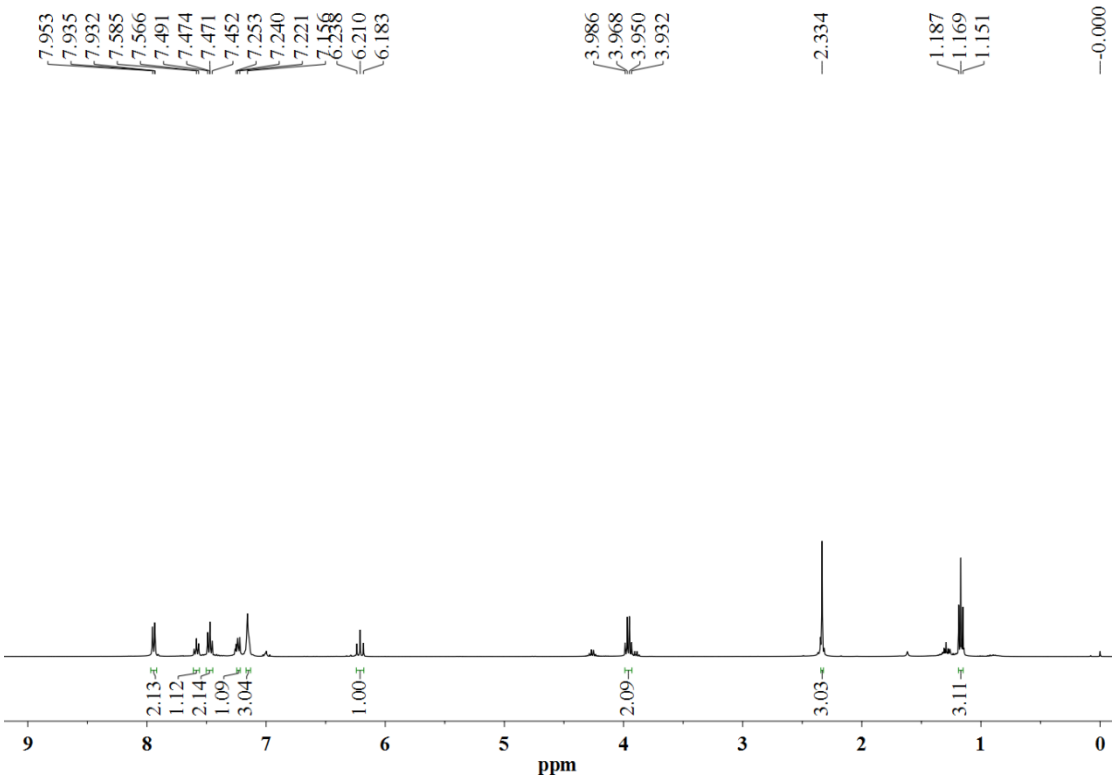
-180
ppm


O
EtOOCF2C

4c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7.138
6.210
6.183
3.986
3.968
3.950
3.932
2.334
1.187
1.169
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1.12
2.14
1.09
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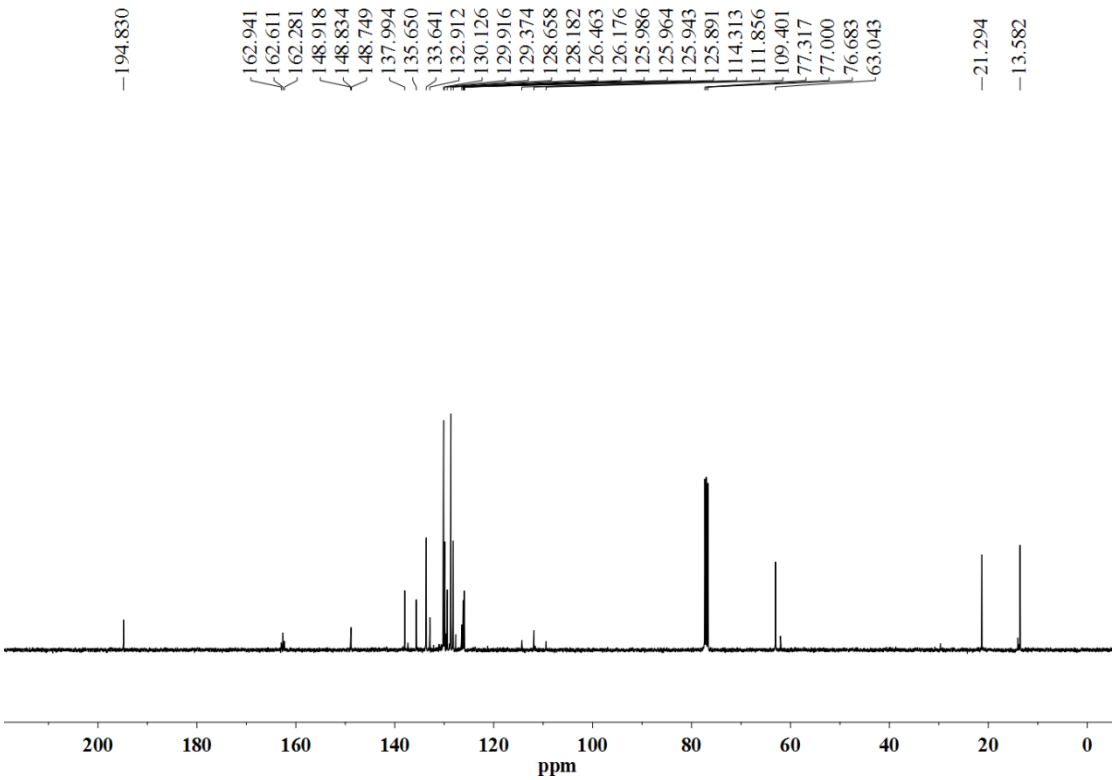
1.00
2.09
3.03
3.11
ppm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148.834
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130.126
129.916
129.374
128.658
128.182
126.463
126.176
125.986
125.964
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76.683
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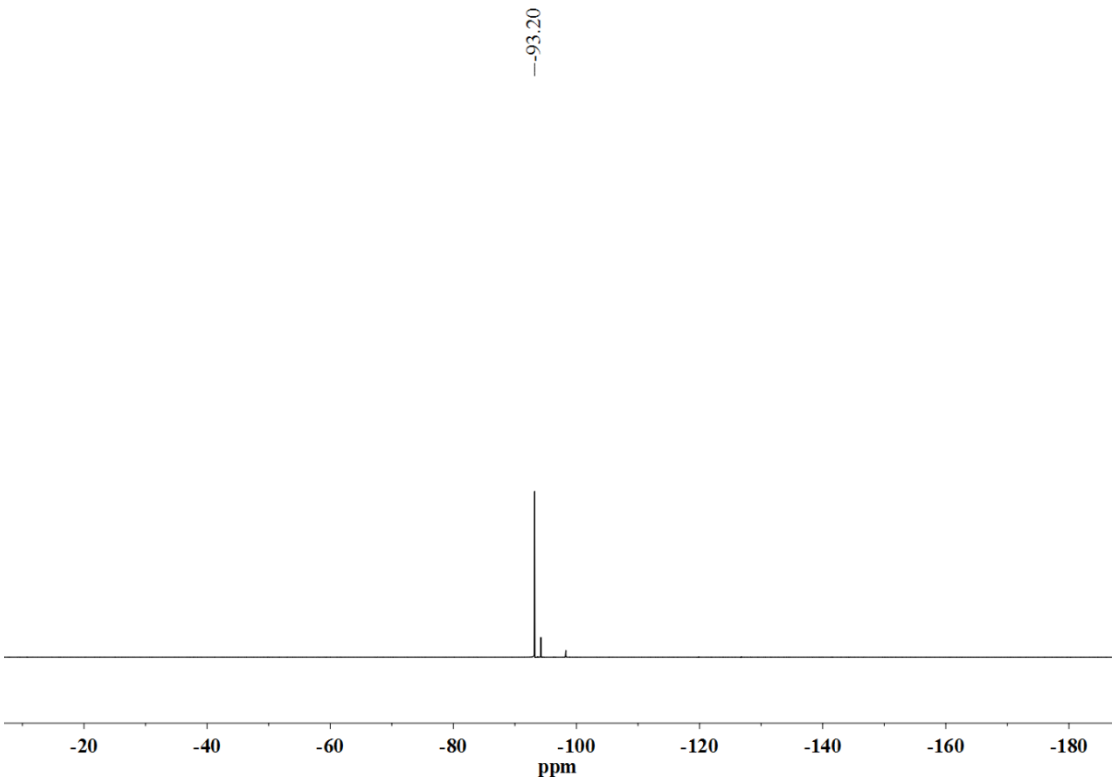
ppm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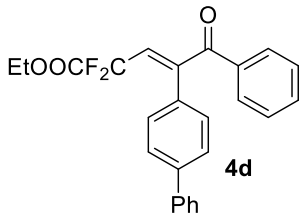
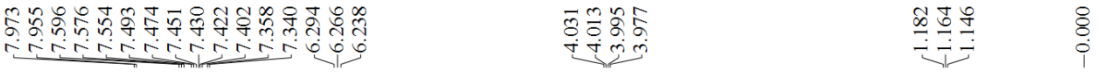
-40
-60
-80
-100
-120
-140
-160
-180
ppm


O
EtOOCF2C
4d
Ph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7.493
7.474
7.451
7.430
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7.402
7.358
7.340
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3.977
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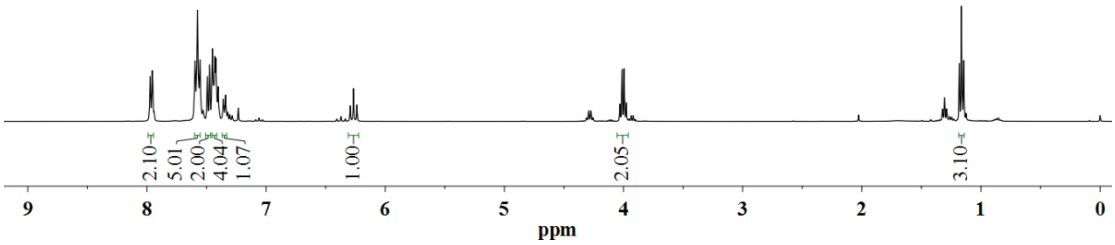
0.000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6
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2
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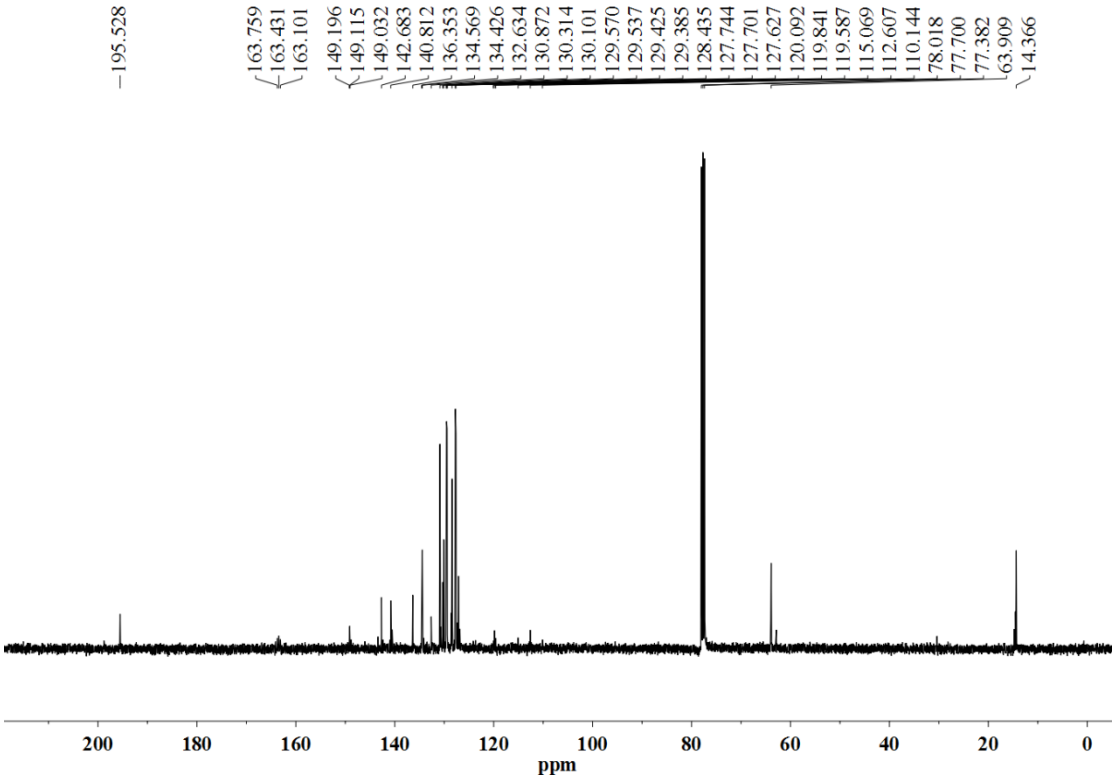
0
ppm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149.115
149.032
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134.426
132.634
130.872
130.314
130.101
129.570
129.537
129.425
129.385
128.435
127.744
127.701
127.627
120.092
119.841
119.587
115.069
112.607
110.144
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120
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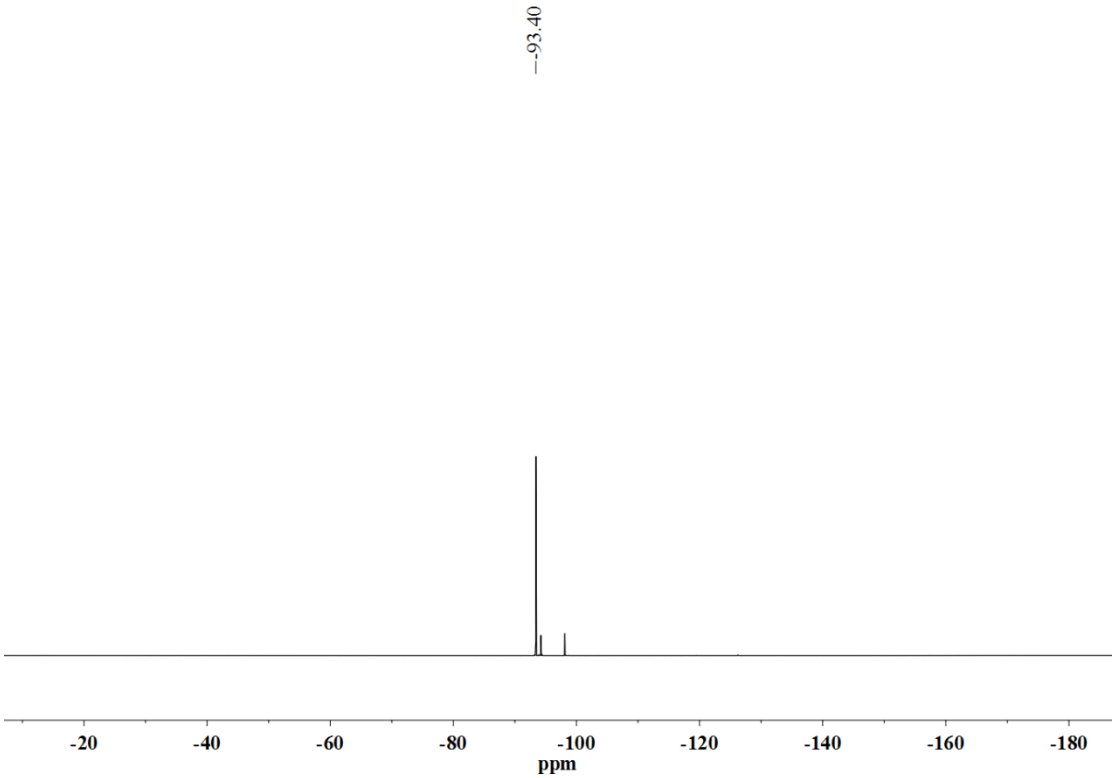
40
20
0
ppm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-180
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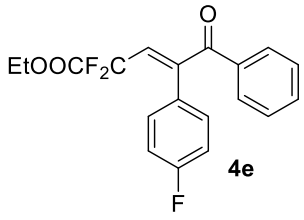
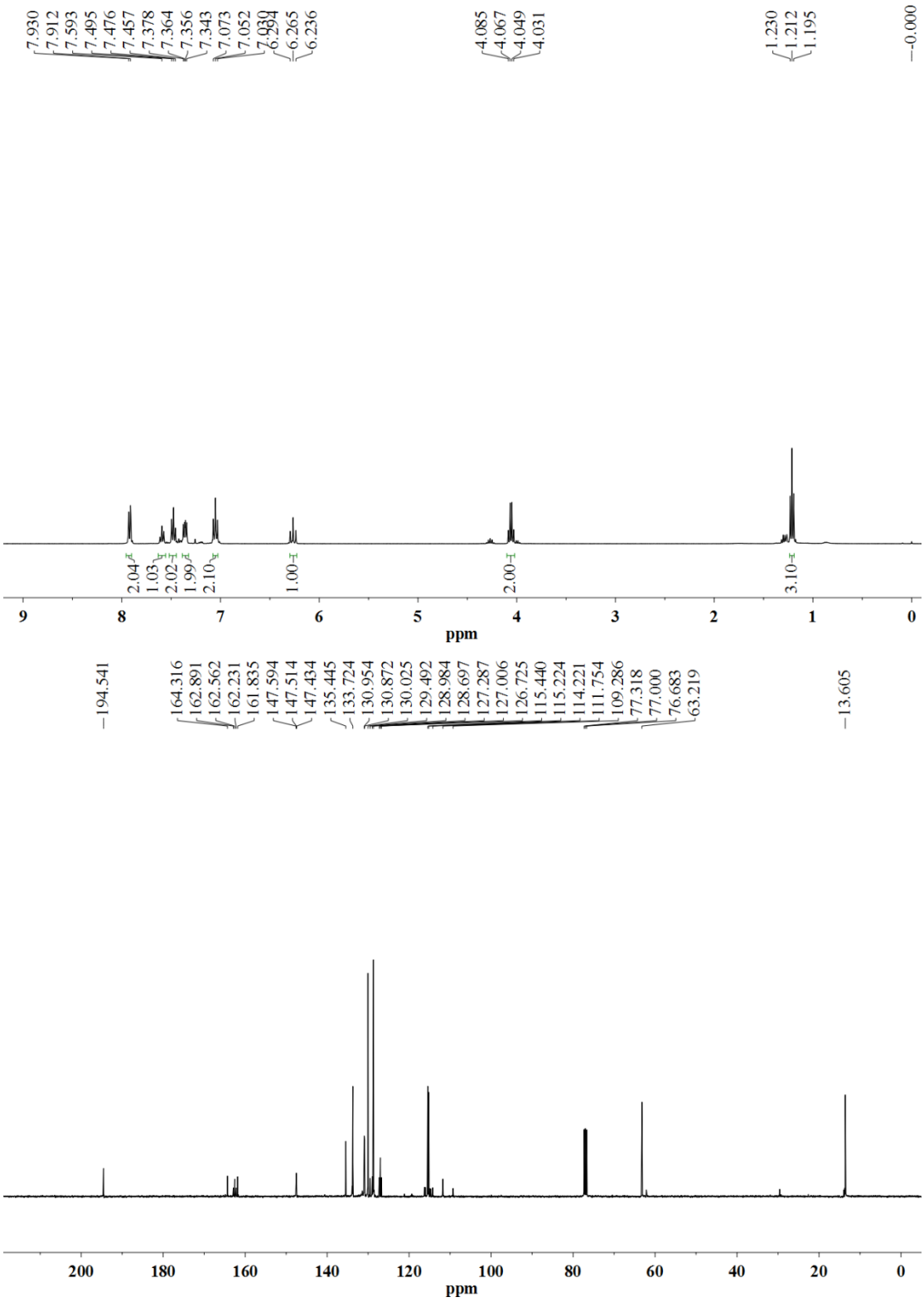

O
EtOOCF2C
F

4e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7.457
7.378
7.364
7.356
7.343
7.073
7.052
6.265
6.236
4.085
4.067
4.049
4.031
1.230
1.212
1.195
0.000
2.04
1.03
2.02
1.99
2.10
1.00
2.00
3.10
ppm
194.541
164.316
162.891
162.562
162.231
161.835
147.594
147.514
147.434
135.445
133.724
130.954
130.872
130.025
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128.697
127.287
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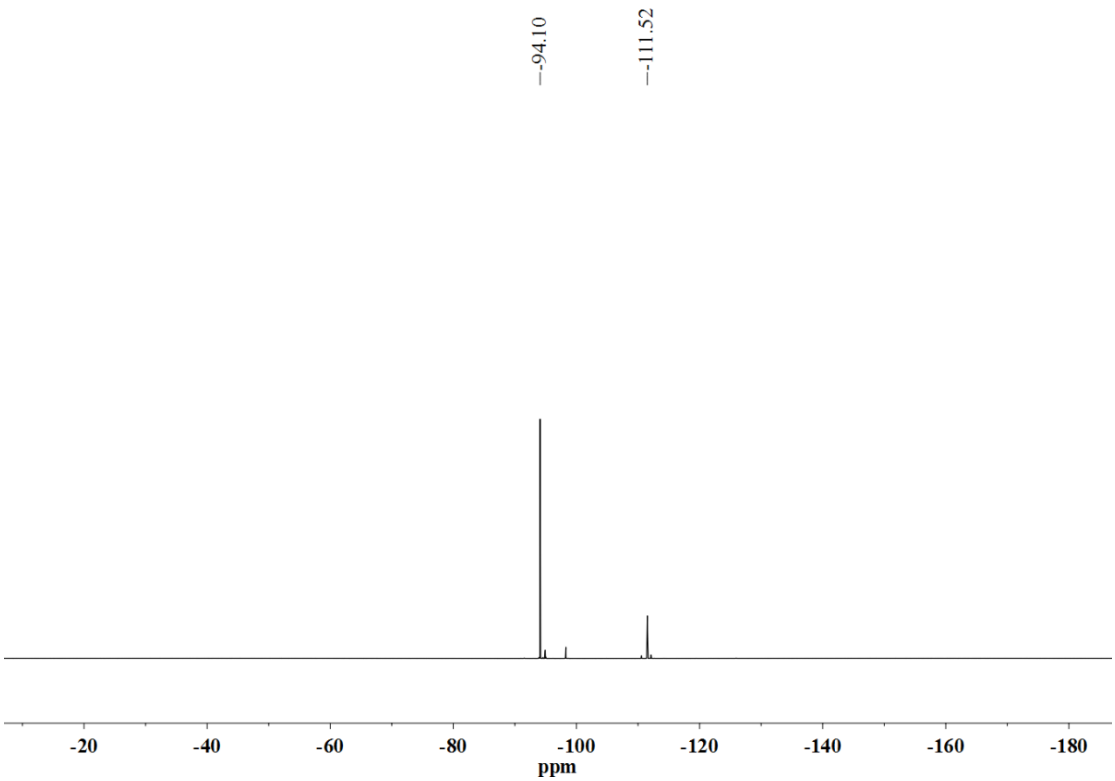
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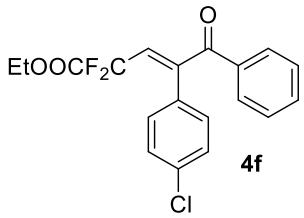
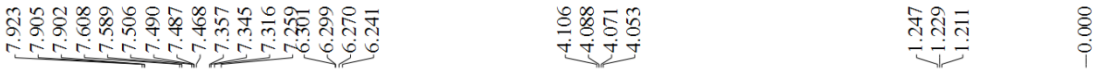
ppm


O
EtOOCF2C
Cl

4f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7.487
7.468
7.357
7.345
7.316
7.259
6.301
6.299
6.270
6.241
4.106
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4.071
4.053
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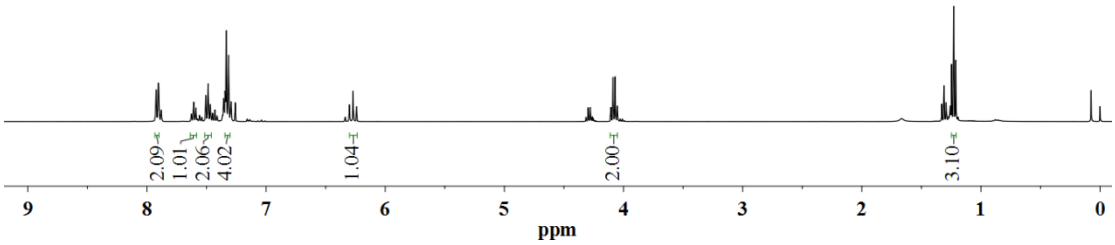
1.229
1.211
0.000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9
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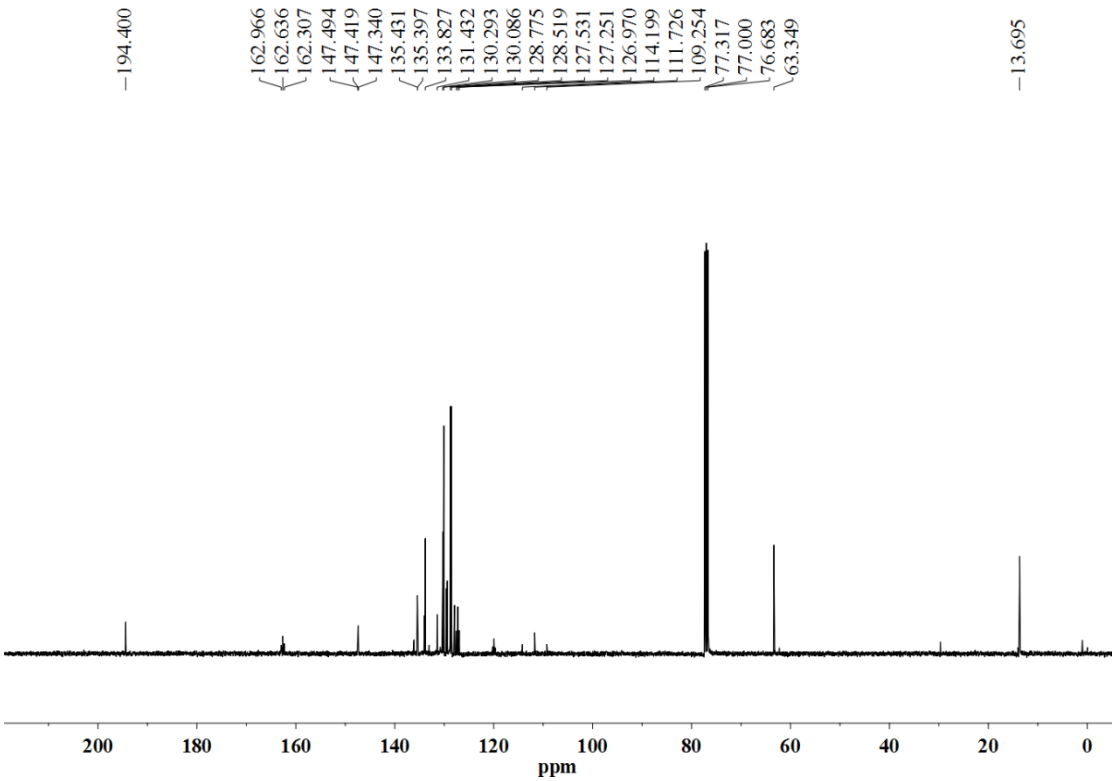
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135.431
135.397
133.827
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130.086
128.775
128.519
127.531
127.251
126.970
114.199
111.726
109.254
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77.000
76.683
63.349
13.695
200
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120
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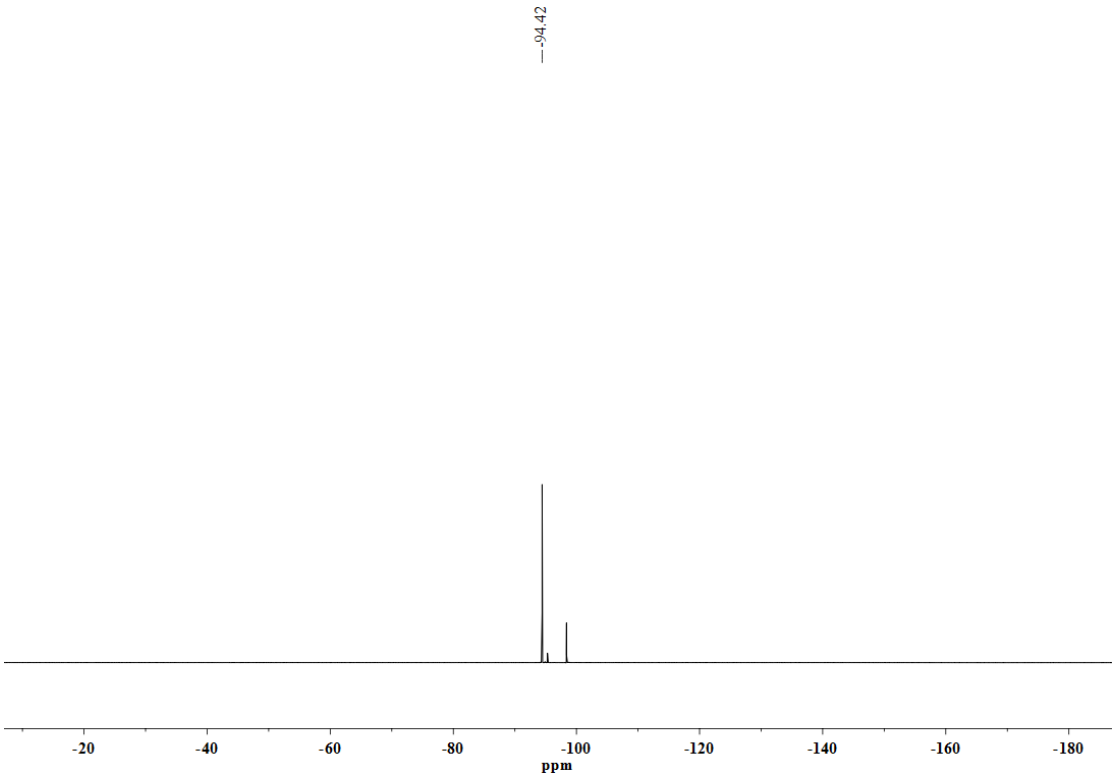
0
ppm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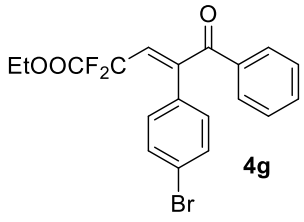
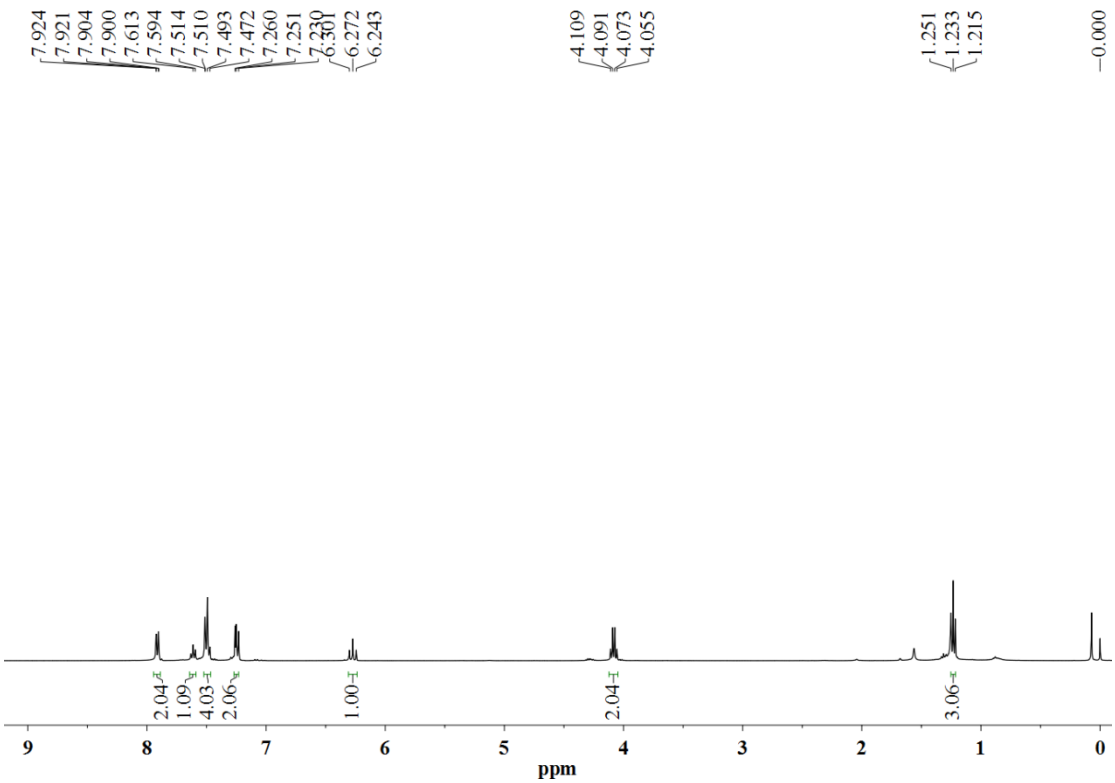

O
EtOOCF2C
Br

4g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7.510
7.493
7.472
7.260
7.251
6.301
6.272
6.243
4.109
4.091
4.073
4.055
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1.215
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1.09
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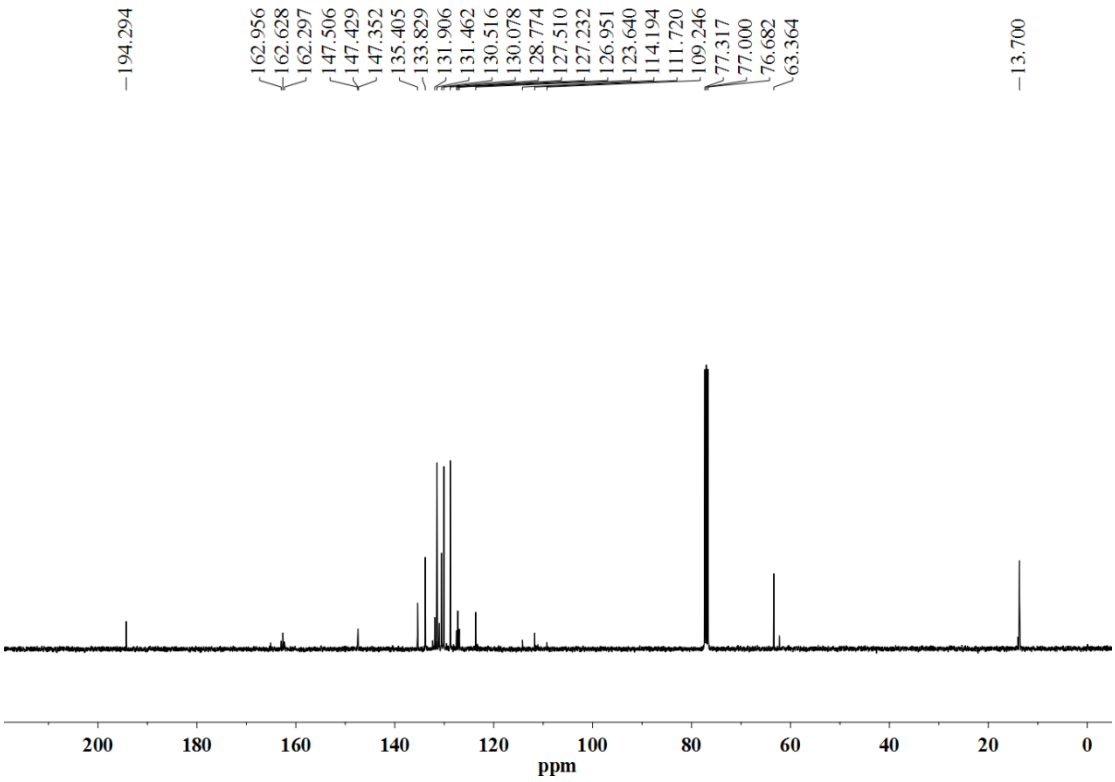
2.06
1.00
2.04
3.06
ppm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130.078
128.774
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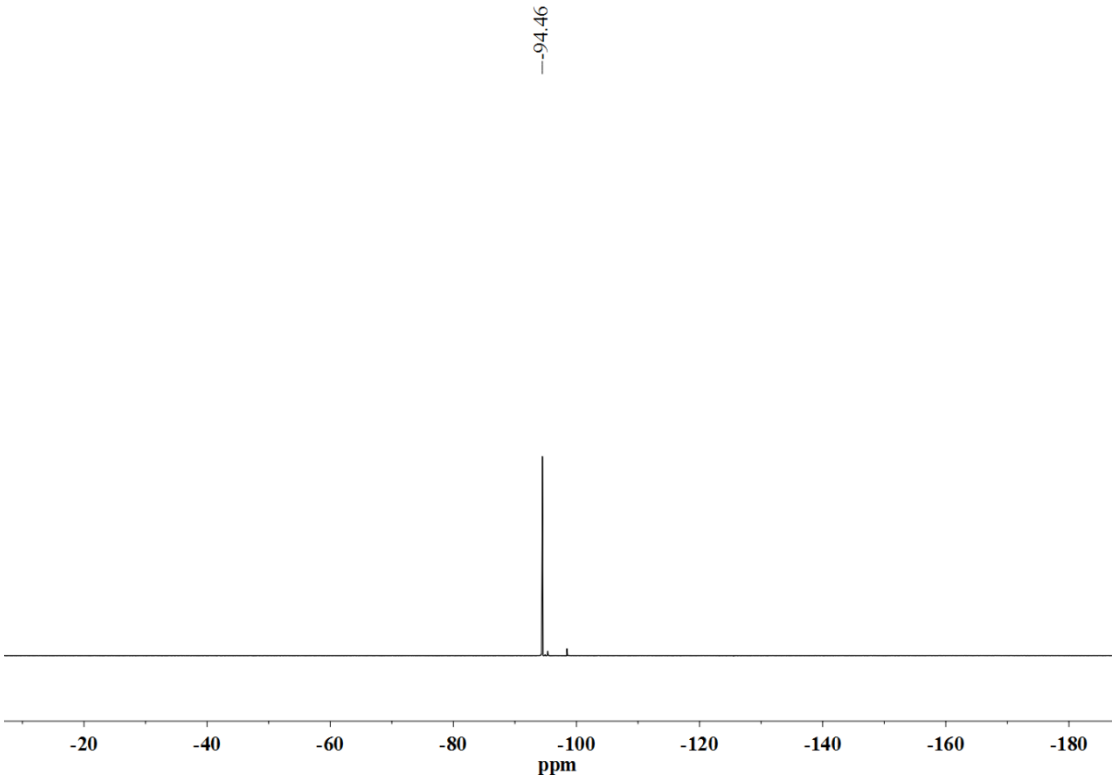

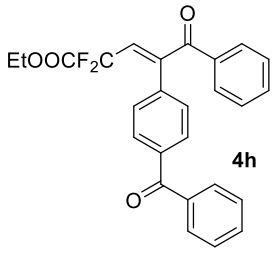

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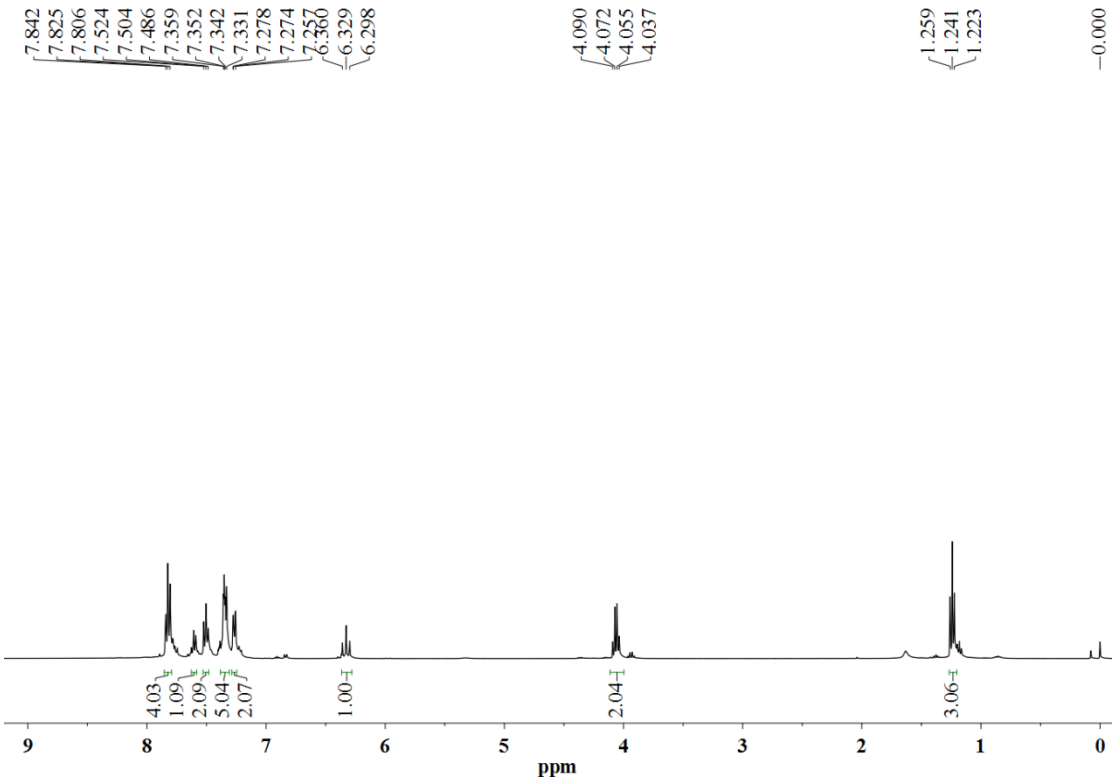
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7.486
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7.352
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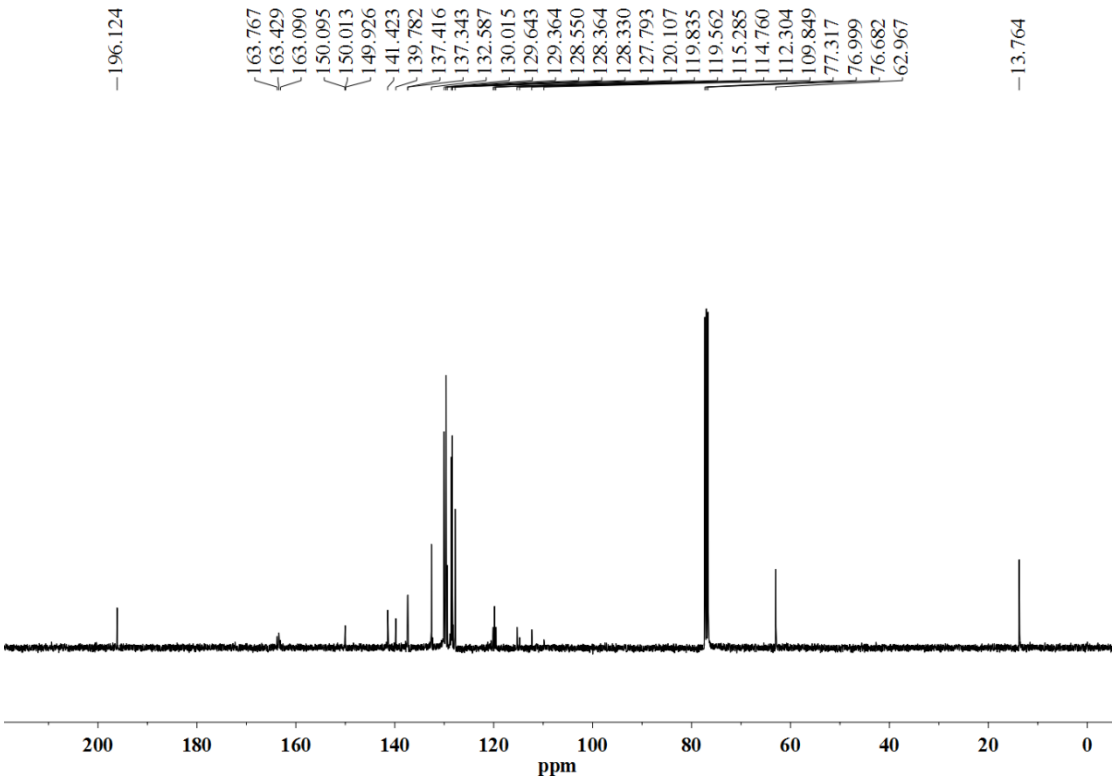
7.331
7.278
7.274
7.257
6.360
6.329
6.298
4.090
4.072
4.055
4.037
1.259
1.241
1.223
0.000
4.03
1.09
2.09
5.04
2.07
1.00
2.04
3.06
ppm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150.013
149.926
141.423
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137.416
137.343
132.587
130.015
129.643
129.364
128.550
128.364
128.330
127.793
120.107
119.835
119.562
115.285
114.760
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109.849
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76.999
76.682
62.967
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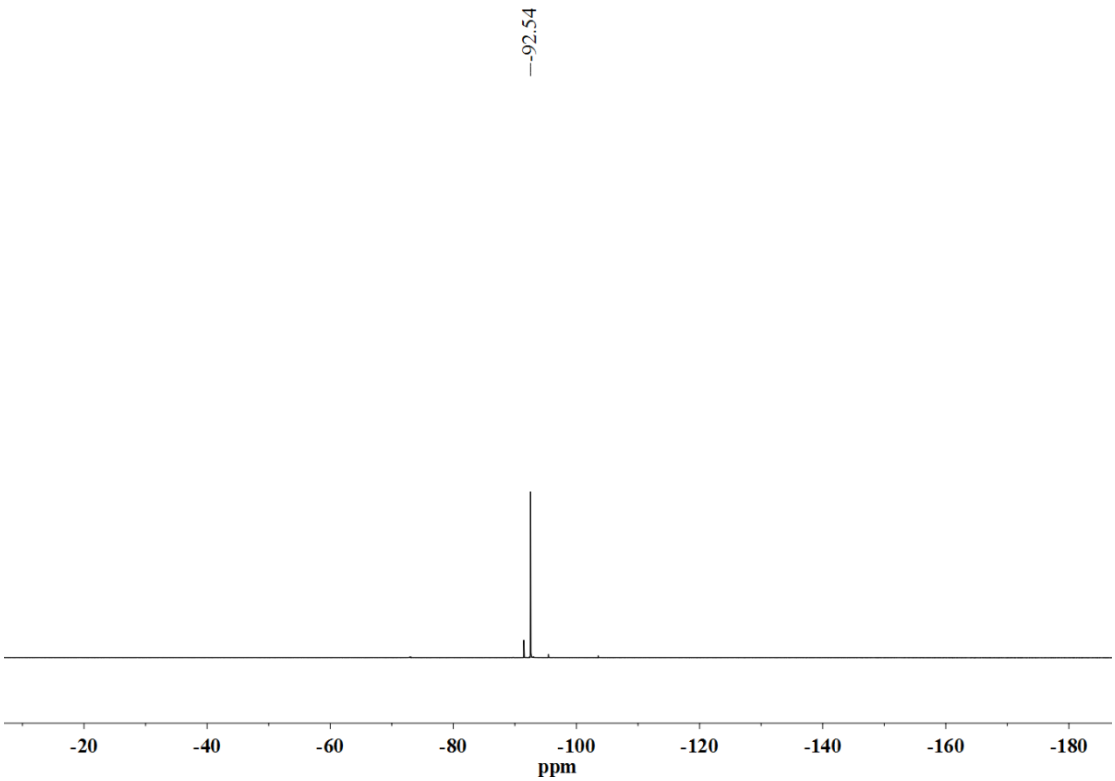
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-180
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O
EtOOCF2C
F
4i
7.940
7.922
7.918
7.628
7.610
7.591
7.510
7.491
7.472
7.363
7.343
7.329
7.309
7.258
7.157
7.138
7.117
7.094
7.062
7.057
7.041
6.308
6.279
6.250
4.113
4.096
4.078
4.060
1.254
1.236
1.218
0.000
2.07
1.07
2.07
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1.00
2.05
3.09
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8
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6
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4
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2
1
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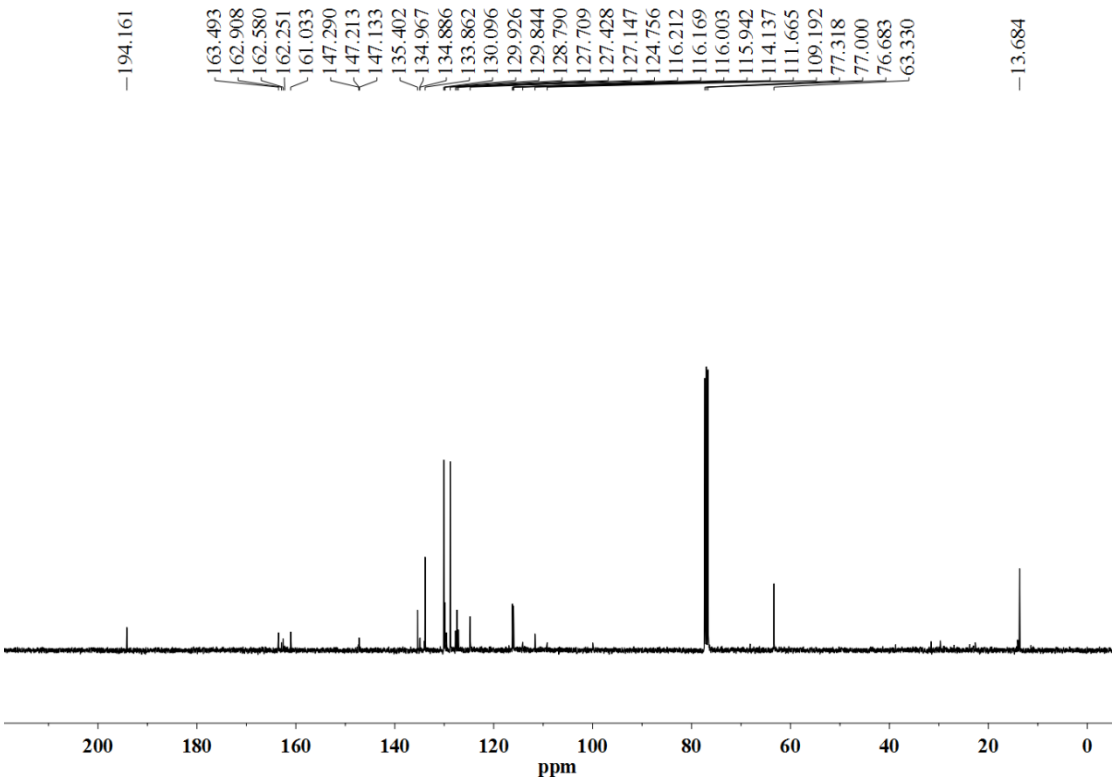
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147.290
147.213
147.133
135.402
134.967
134.886
133.862
130.096
129.926
129.844
128.790
127.709
127.428
127.147
124.756
116.212
116.169
116.003
115.942
114.137
111.665
109.192
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77.000
76.683
63.330
13.684
200
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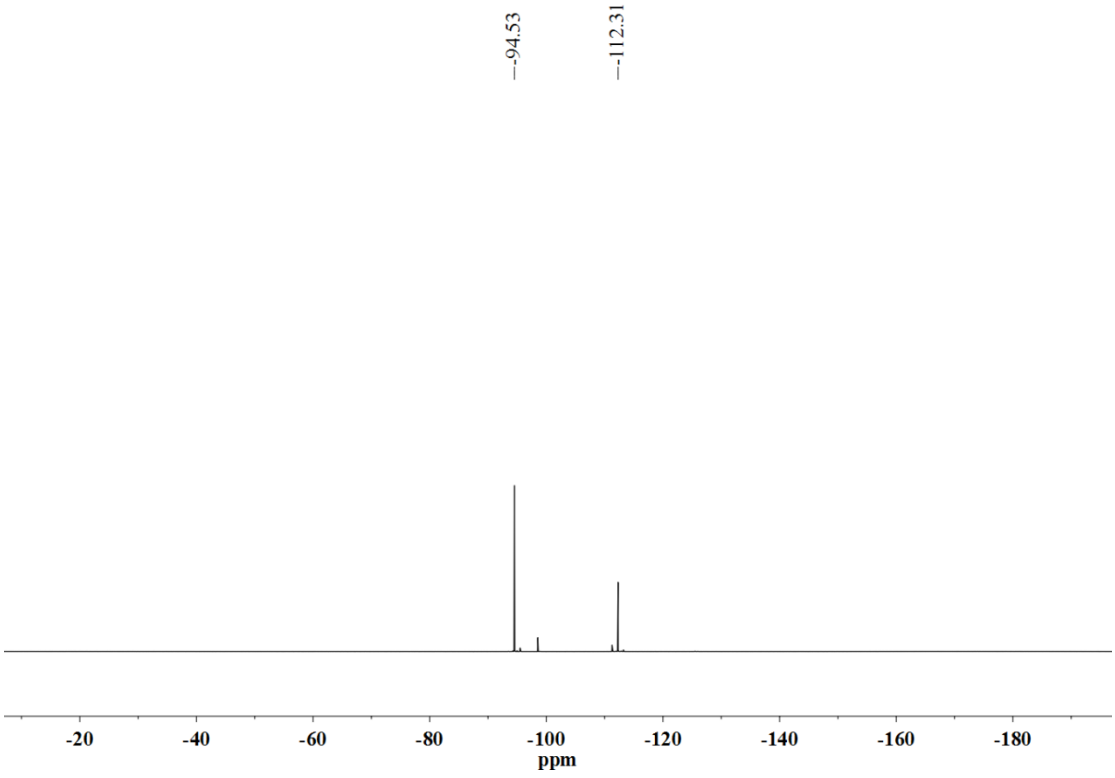
140
120
100
80
60
40
20
0
ppm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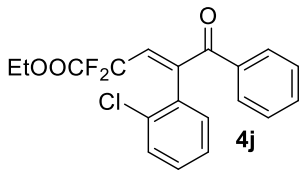
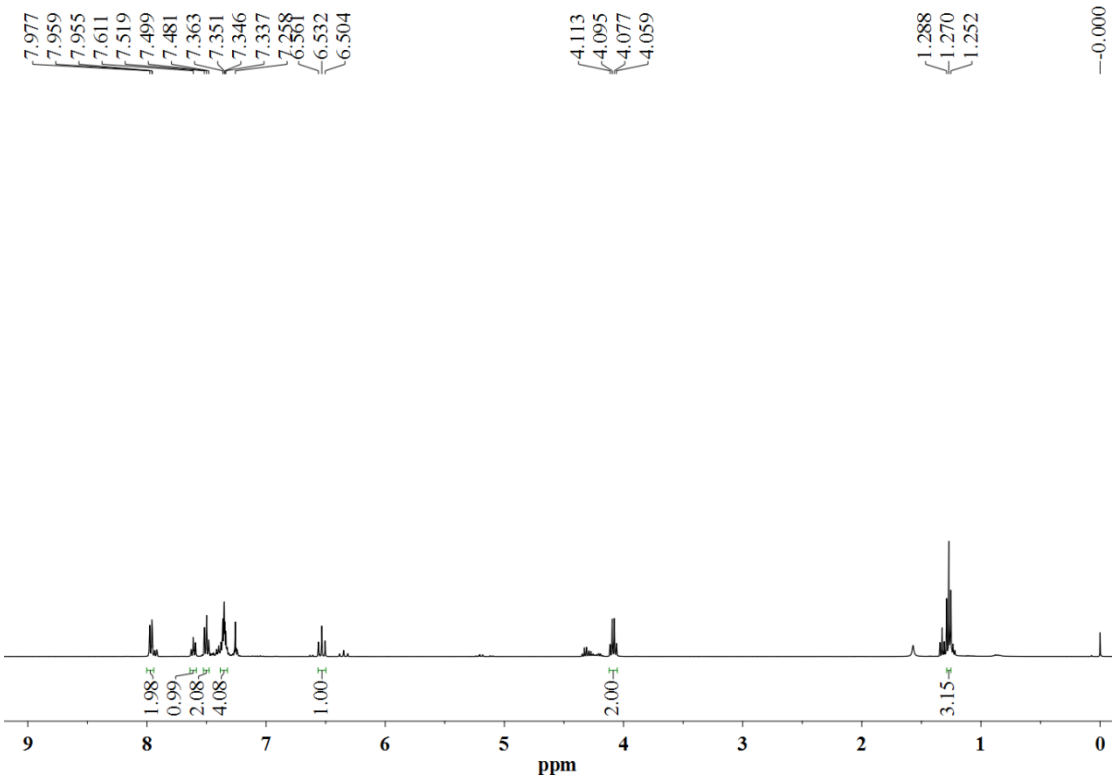
-140
-160
-180
ppm


O
EtOOCF2C
Cl

4j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7.363
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7.346
7.337
6.532
6.504
4.113
4.095
4.077
4.059
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1.270
1.252
0.000
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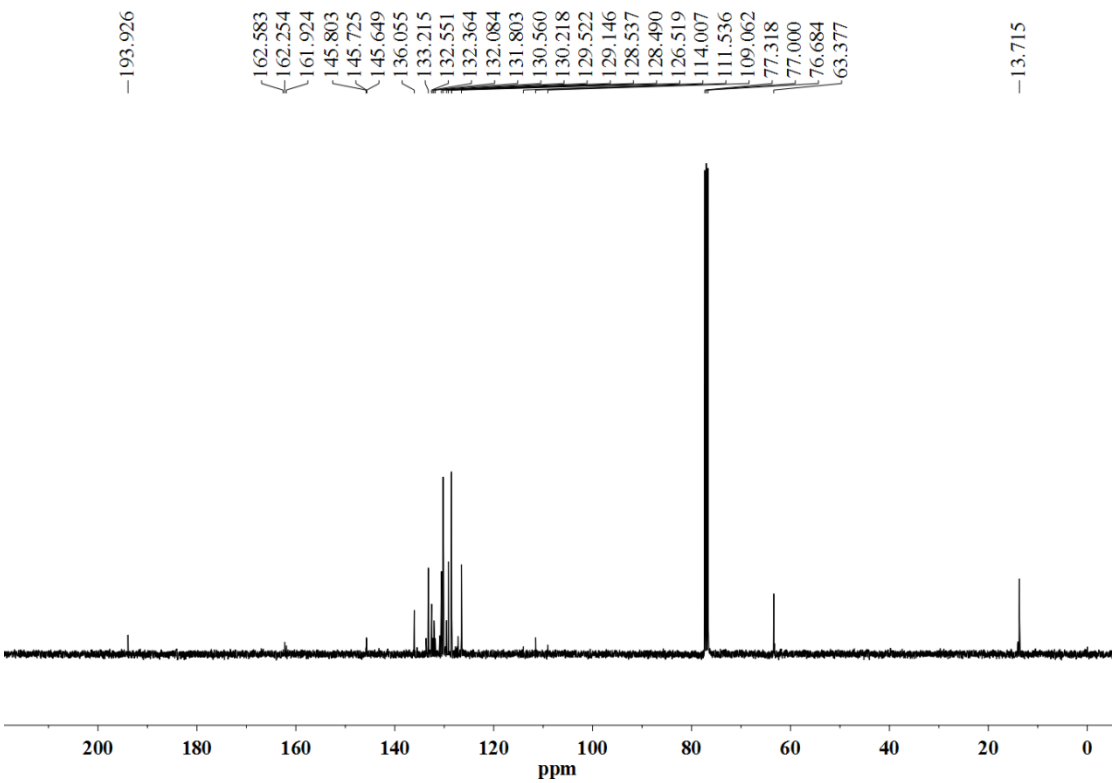
4.08
1.00
2.00
3.15
ppm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133.215
132.551
132.364
132.084
131.803
130.560
130.218
129.522
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126.519
114.007
111.536
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77.000
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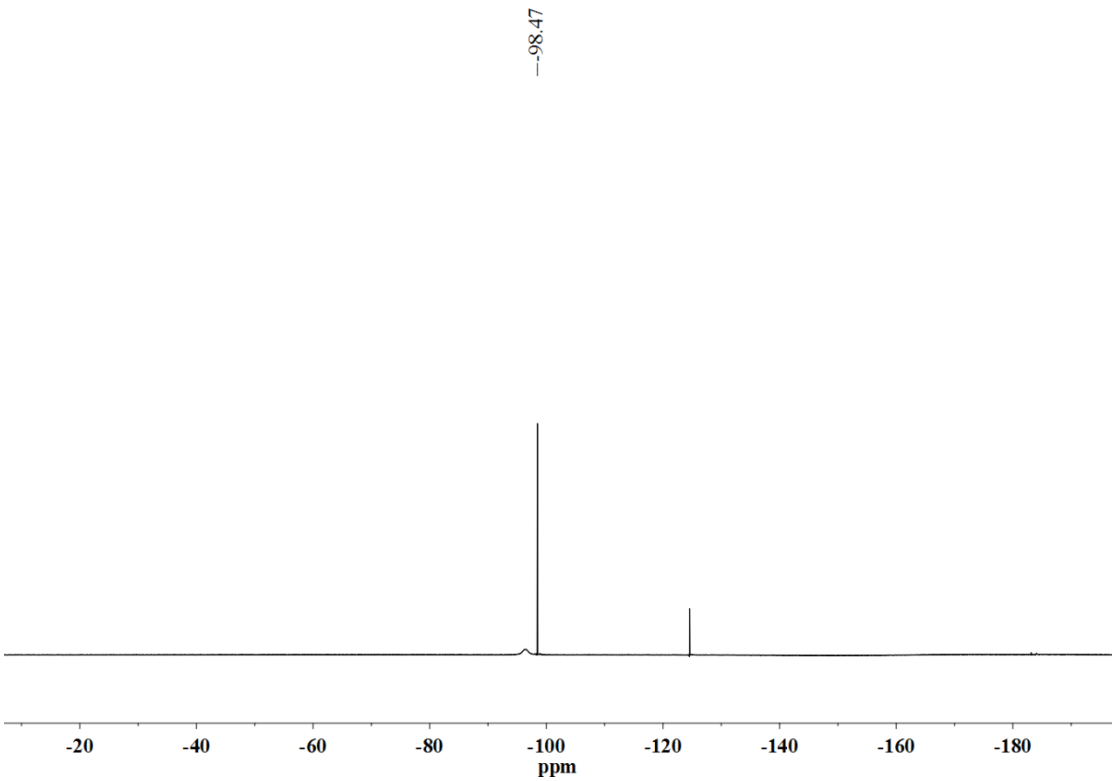
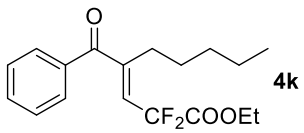
ppm





4k

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7.599
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7.500
7.481
7.462
6.012
5.978
5.944
4.387
4.369
4.351
4.334
2.680
2.661
2.642
1.444
1.426
1.413
1.406
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1.306
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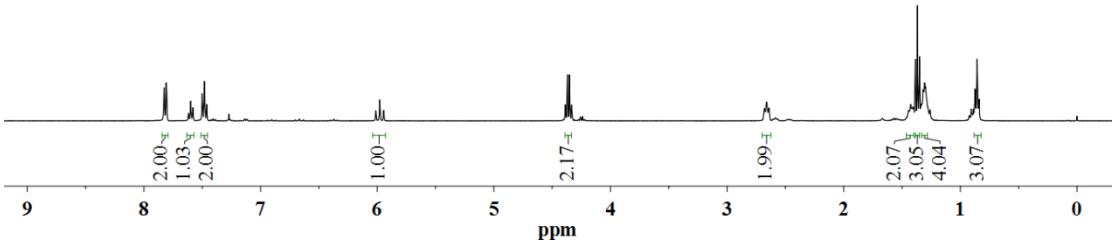

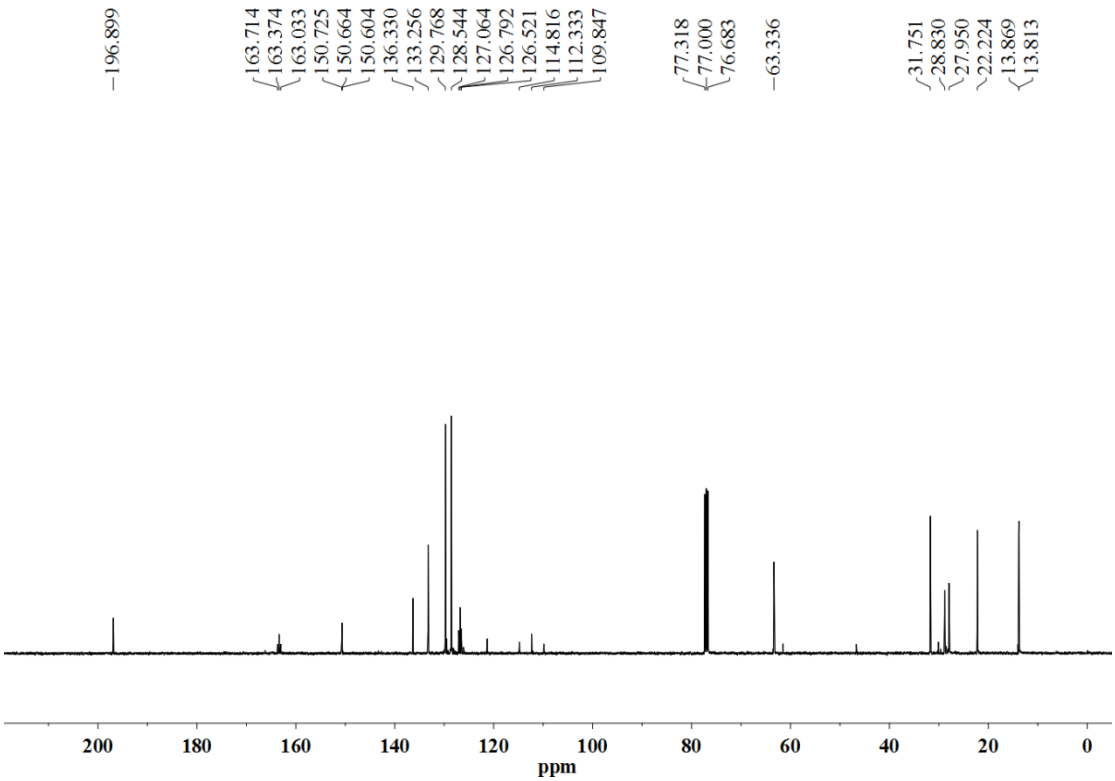
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126.521
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112.333
109.847
77.318
77.000
76.683
63.336
31.751
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13.869
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120
100
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40
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0
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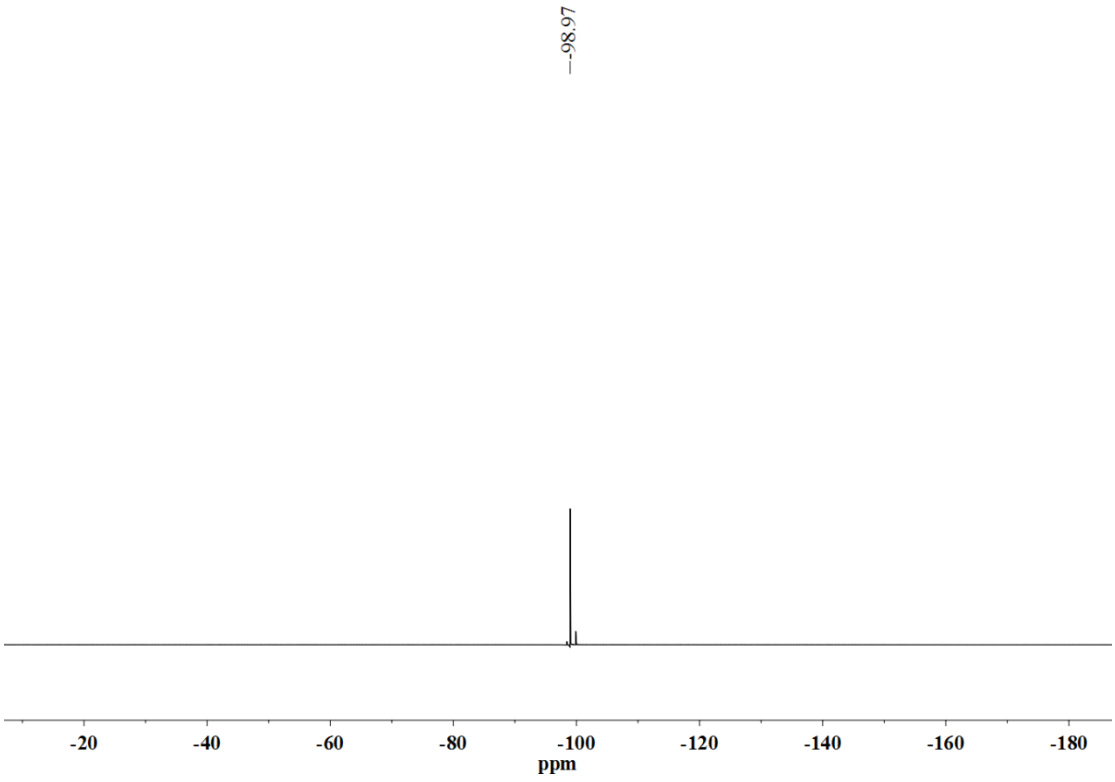
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-180
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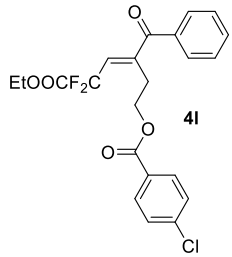
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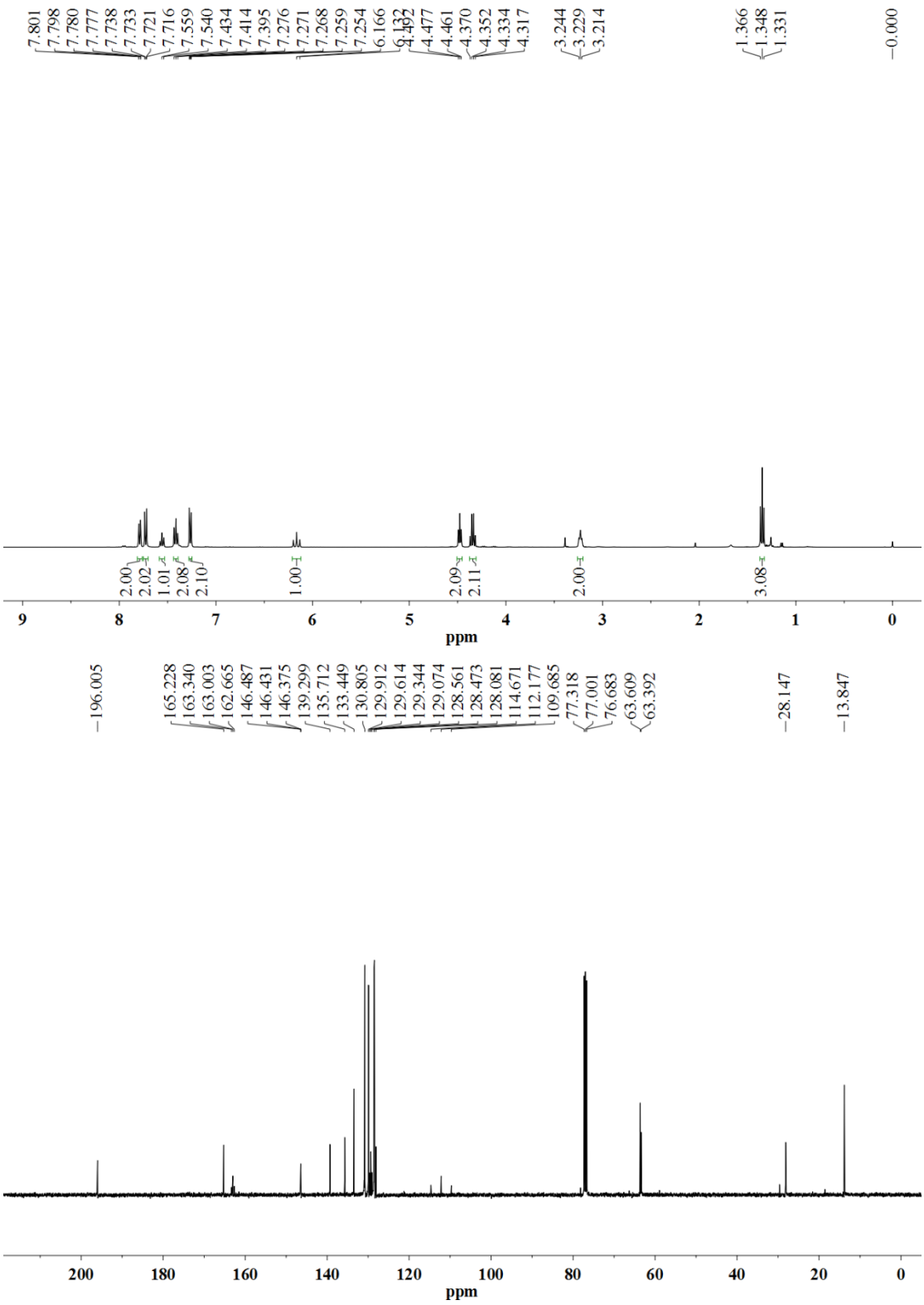
EtOOCF2C
O
O
Cl

4l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7.276
7.271
7.268
7.259
7.254
6.166
4.492
4.477
4.461
4.370
4.352
4.334
4.317
3.244
3.229
3.214
1.366
1.348
1.331
0.000
2.00
2.02
1.01
2.08
2.10
1.00
2.09
2.11
2.00
3.08
9
8
7
6
5
4
3
2
1
0
ppm
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163.003
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146.431
146.375
139.299
135.712
133.449
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129.614
129.344
129.074
128.561
128.473
128.081
114.671
112.177
109.685
77.318
77.001
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120
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60
40
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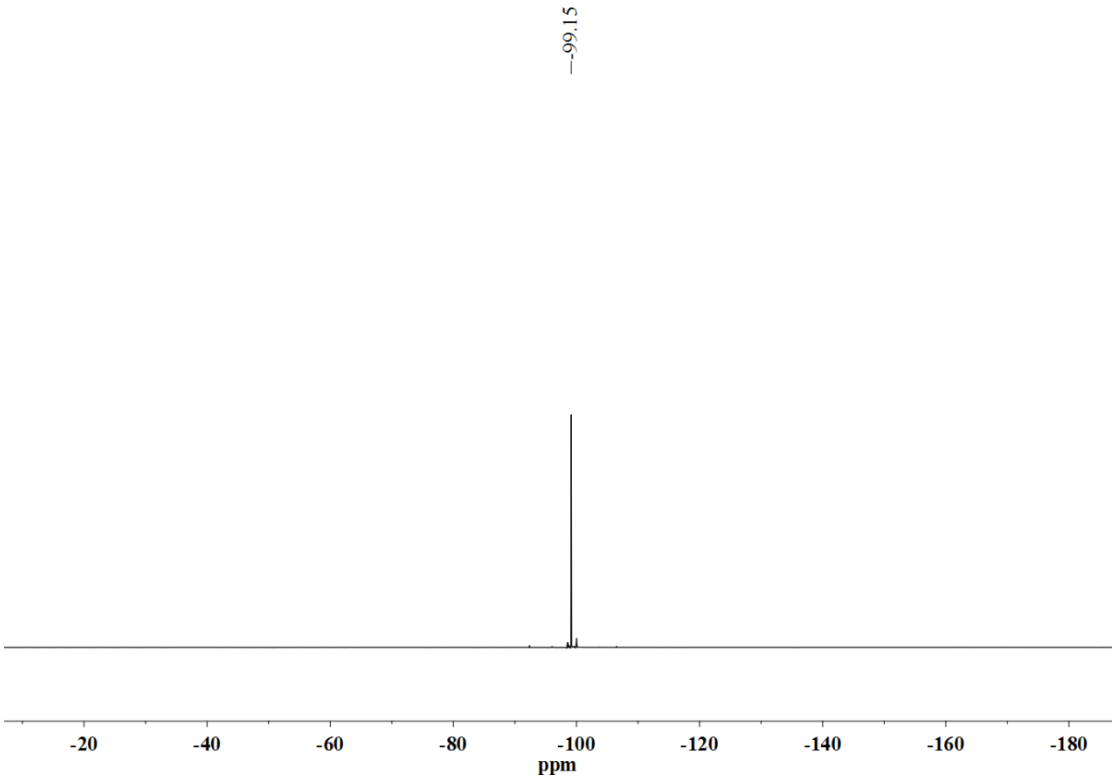
0
ppm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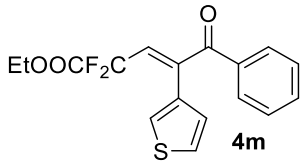
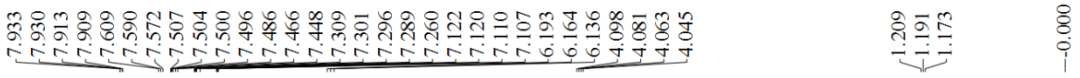

EtOOCF2C
O
S

4m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7.466
7.448
7.309
7.301
7.296
7.289
7.260
7.122
7.120
7.110
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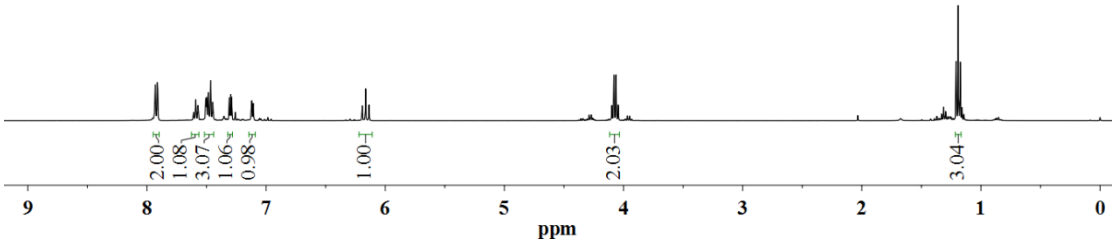
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3.04
9
8
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6
5
4
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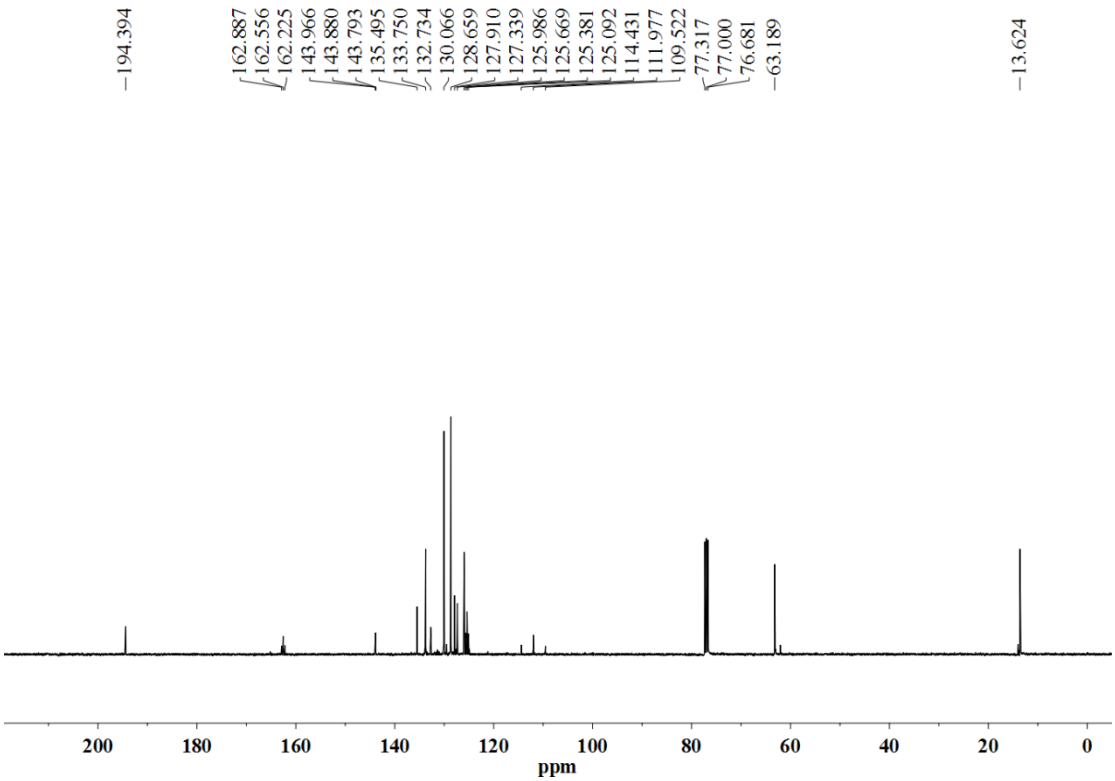
2
1
0
ppm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127.339
125.986
125.669
125.381
125.092
114.431
111.977
109.522
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120
100
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40
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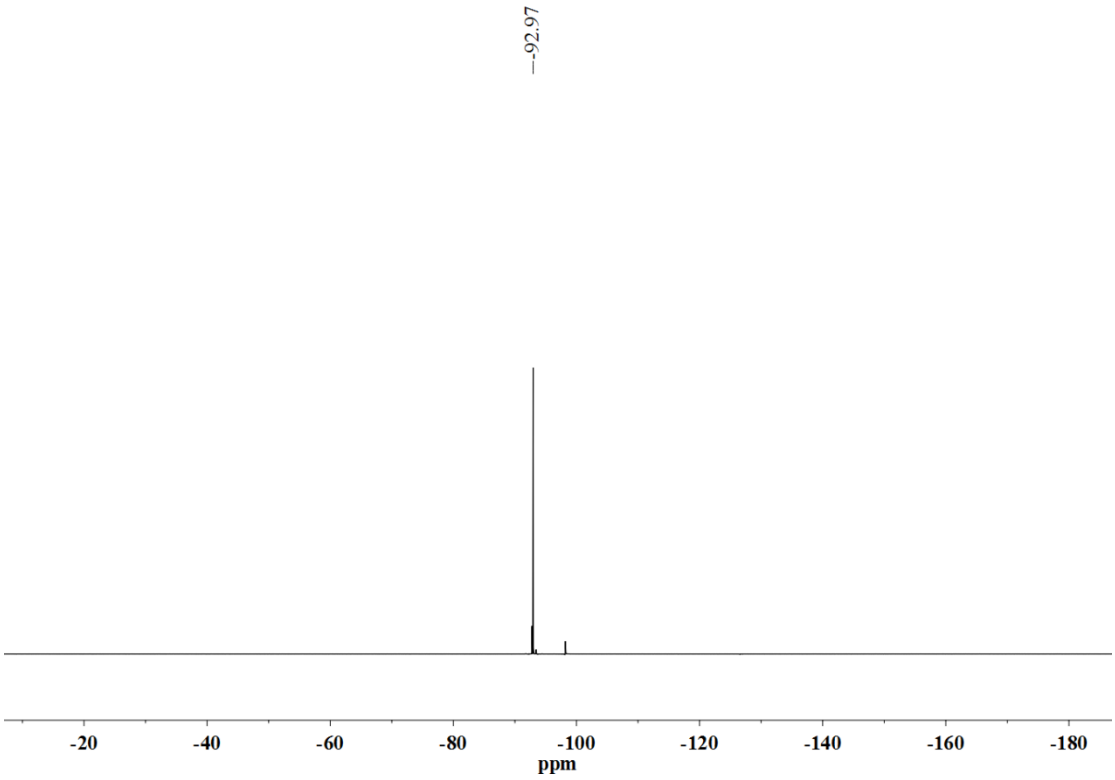
0
ppm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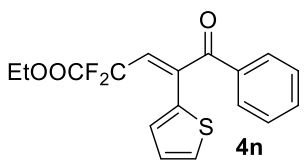
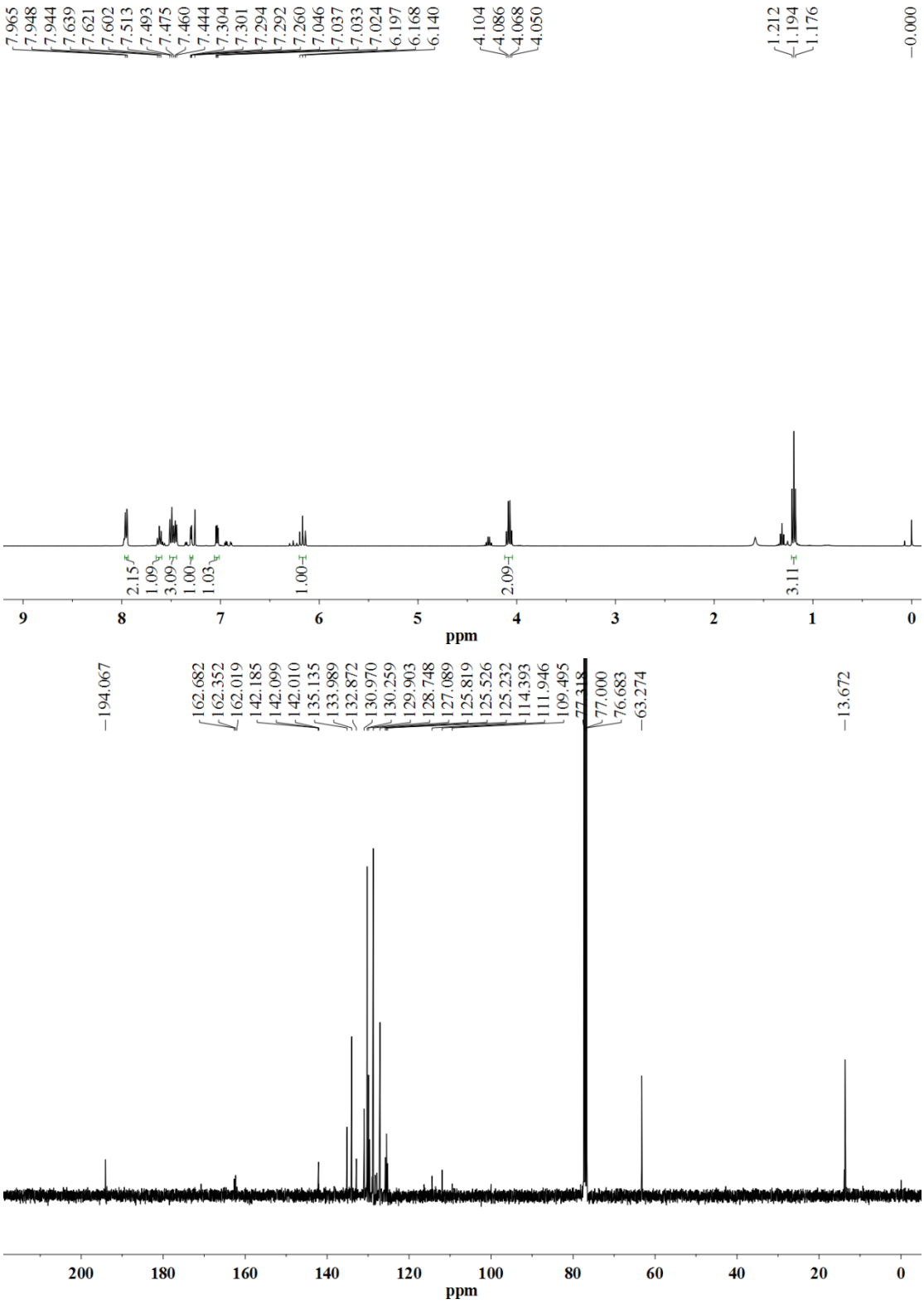

O
EtOOCF2C
S

4n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7.301
7.294
7.292
7.260
7.046
7.037
7.033
7.024
6.197
6.168
6.140
4.104
4.086
4.068
4.050
1.212
1.194
1.176
0.000
2.15
1.09
3.09
1.00
1.03
1.00
2.09
3.11
ppm
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162.352
162.019
142.185
142.099
142.010
135.135
133.989
132.872
130.970
130.259
129.903
128.748
127.089
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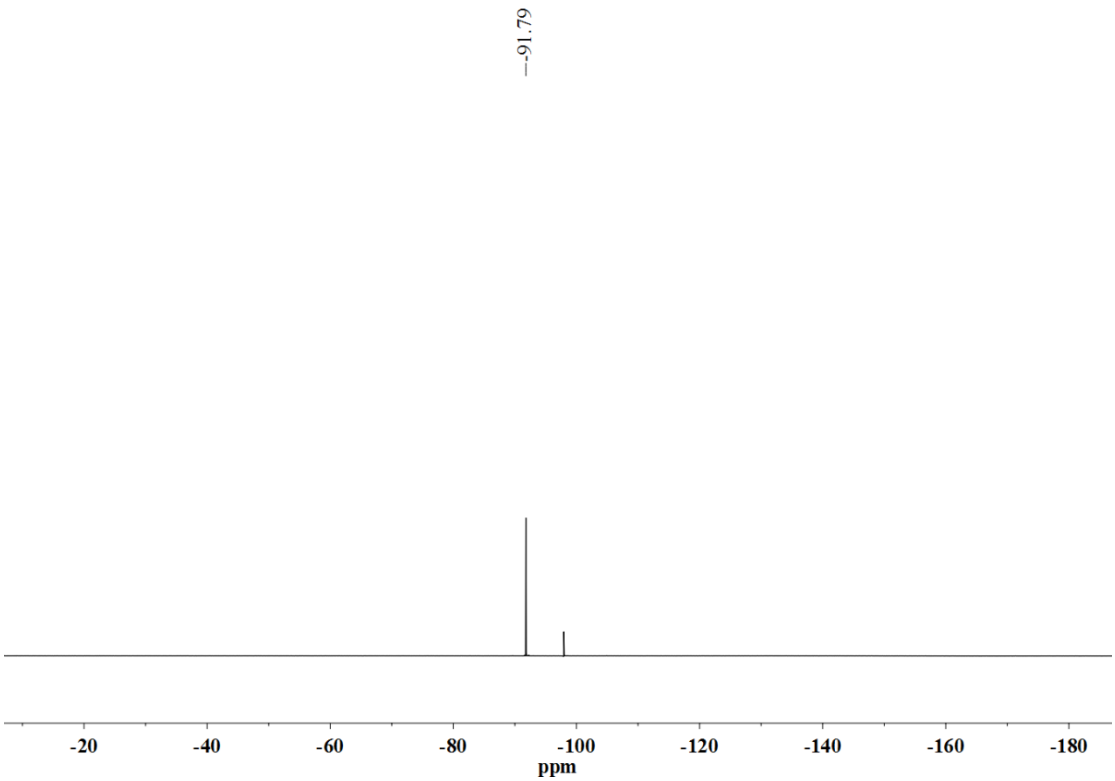
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7.612
7.593
7.575
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7.262
6.281
6.252
6.223
3.986
3.968
3.950
3.933
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1.159
1.141
0.000
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2.08
4.04
4.02
2.00
4.05
6.02
9
8
7
6
5
4
3
2
1
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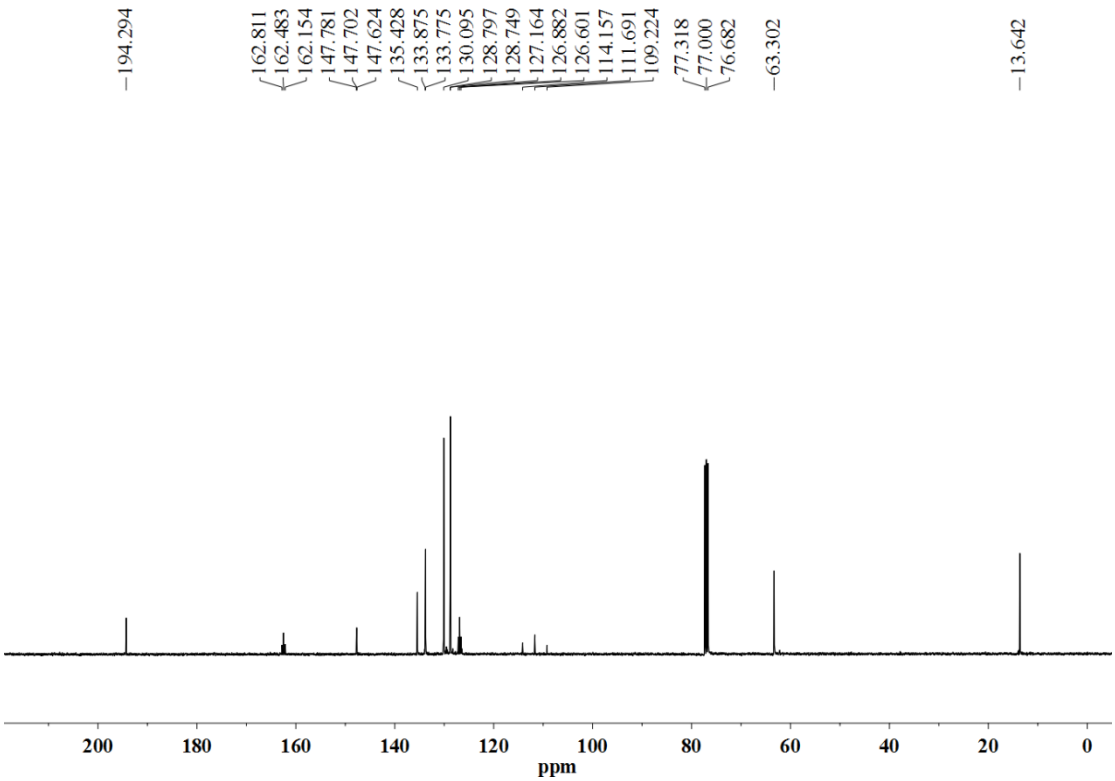
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128.749
127.164
126.882
126.601
114.157
111.691
109.224
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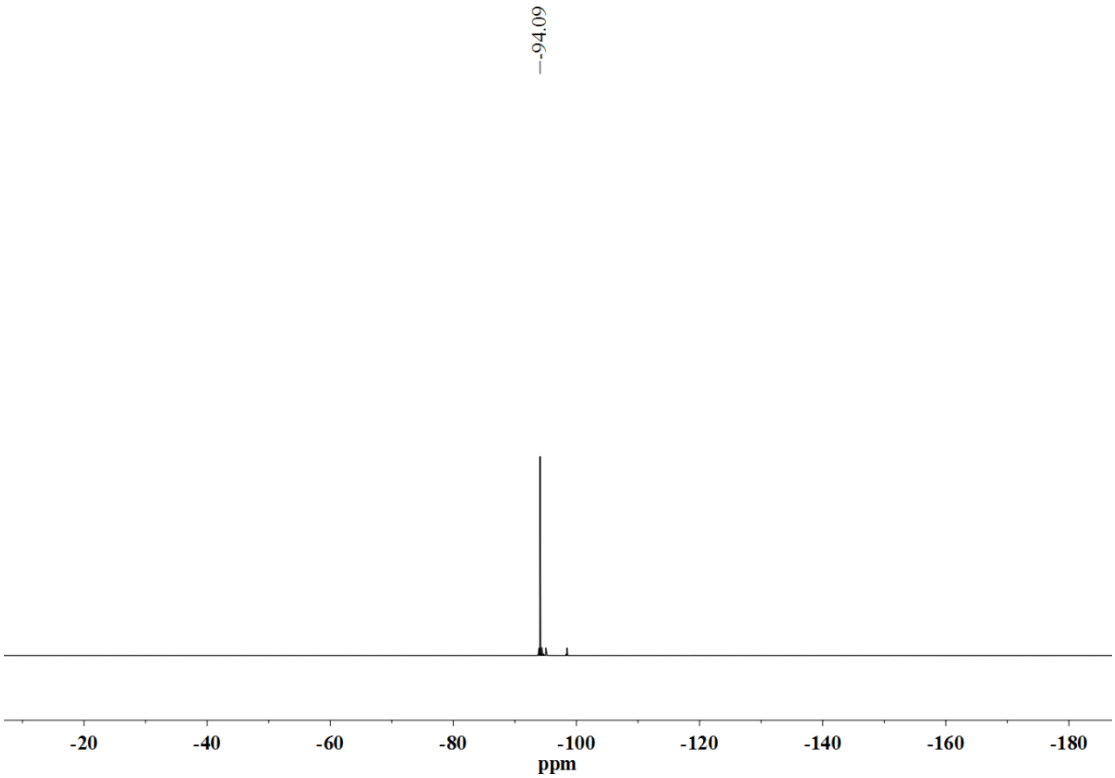
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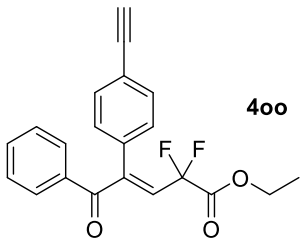
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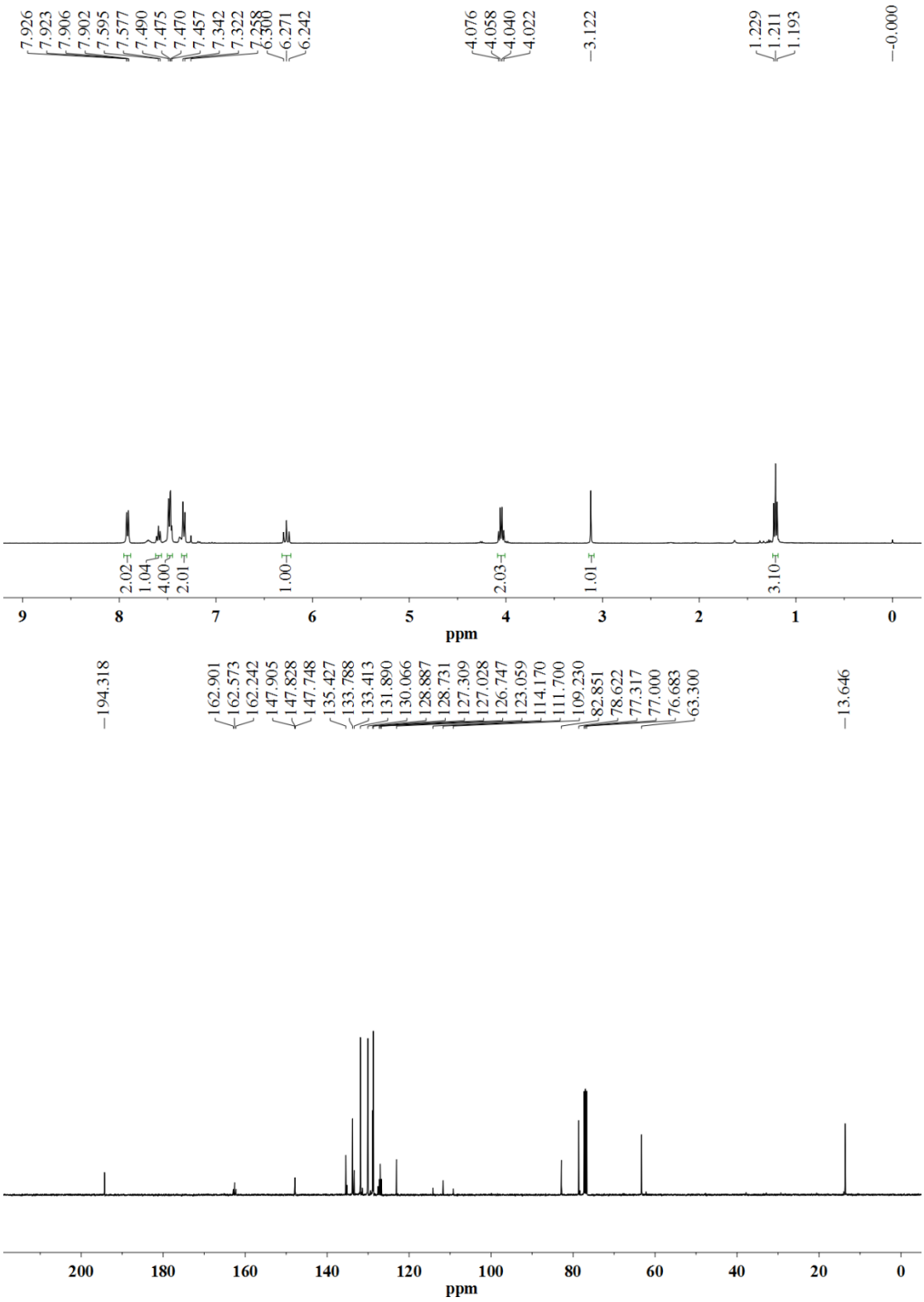
O
O
O

4oo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7.475
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7.457
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7.322
7.258
6.300
6.271
6.242
4.076
4.058
4.040
4.022
3.122
1.229
1.211
1.193
0.000
2.02
1.04
4.00
2.01
1.00
2.03
1.01
3.10
ppm
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162.573
162.242
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128.731
127.309
127.028
126.747
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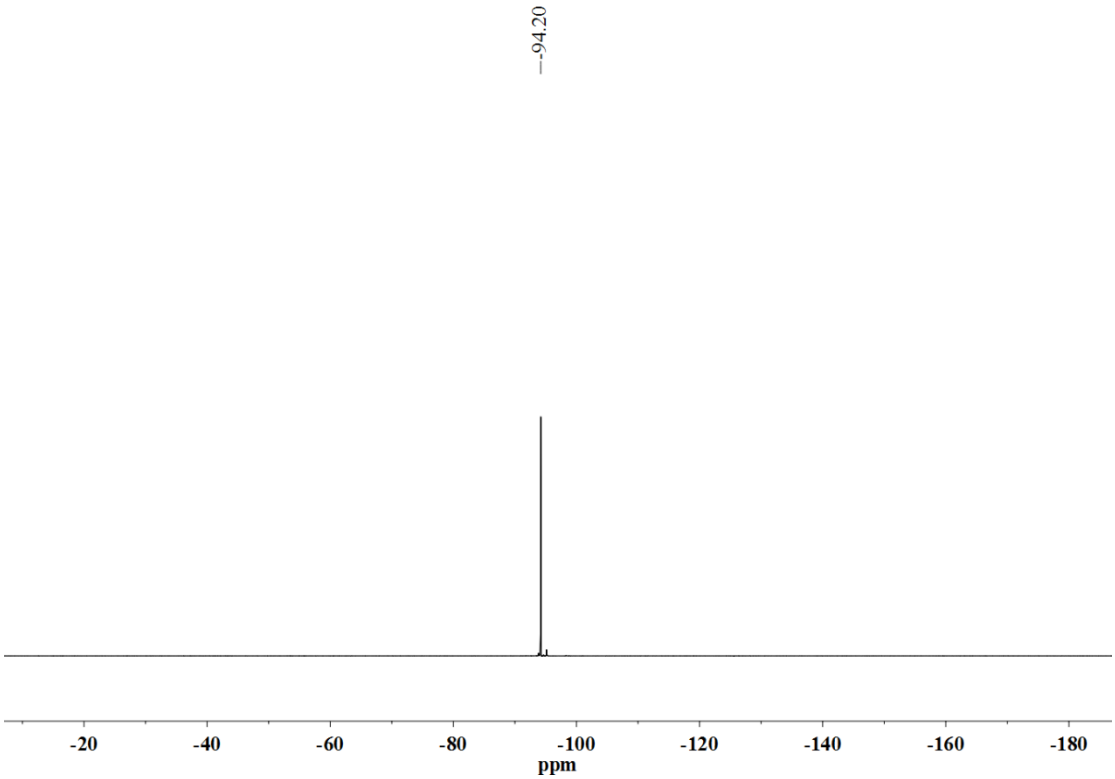
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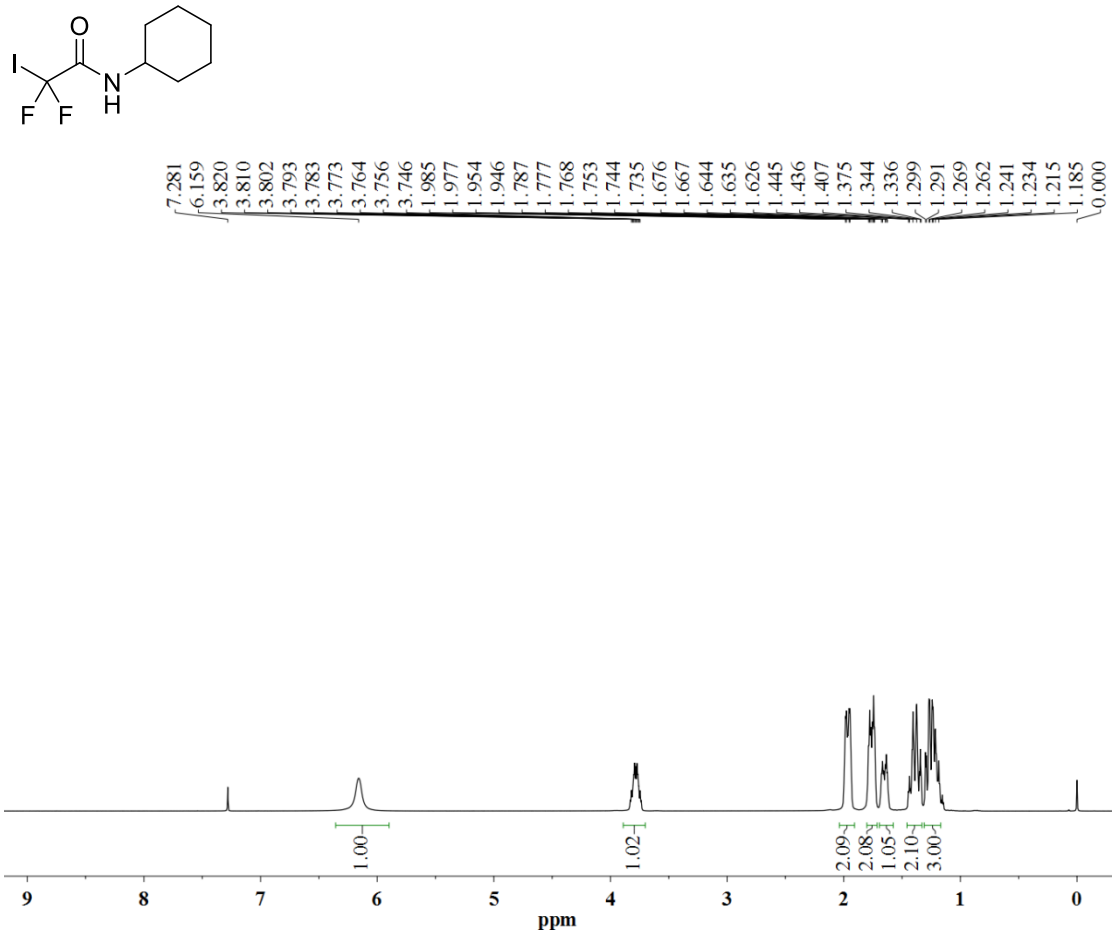
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I
N
H
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3.756
3.746
1.985
1.977
1.954
1.946
1.787
1.777
1.768
1.753
1.744
1.735
1.676
1.667
1.644
1.635
1.626
1.445
1.436
1.407
1.375
1.344
1.336
1.299
1.291
1.269
1.262
1.241
1.234
1.215
1.185
0.000
1.00
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1.05
2.10
3.00
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6
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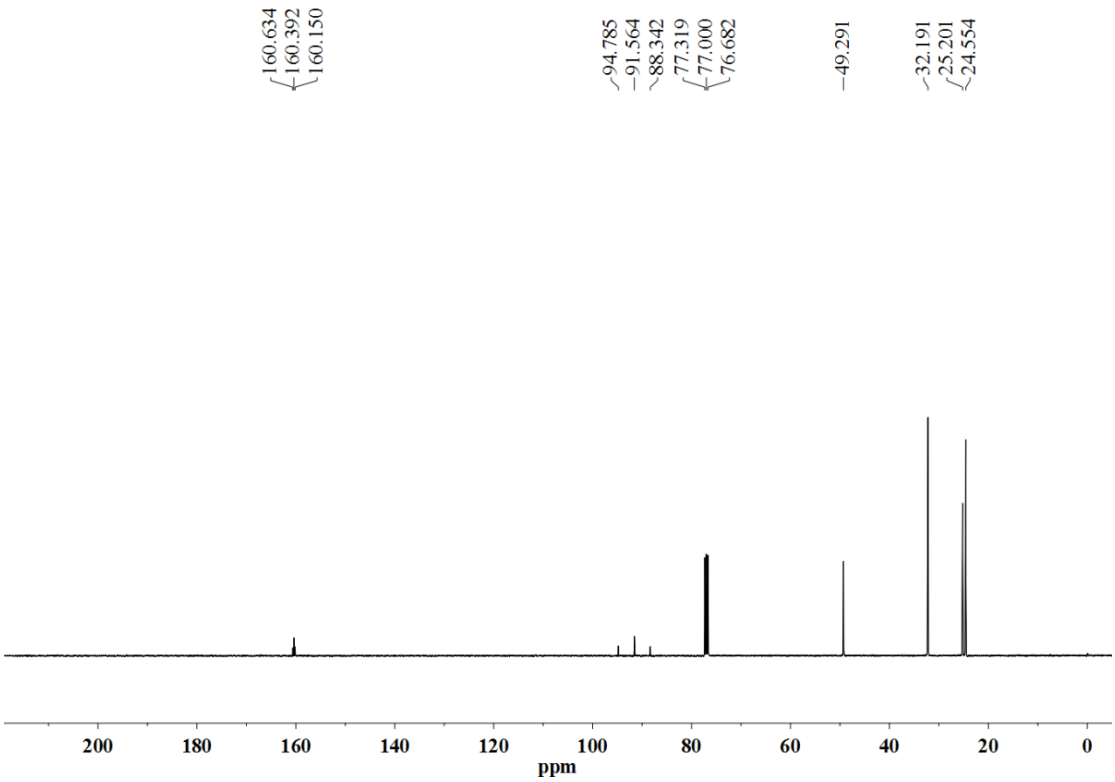
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91.564
88.342
77.319
77.000
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25.201
24.554
200
180
160
140
120
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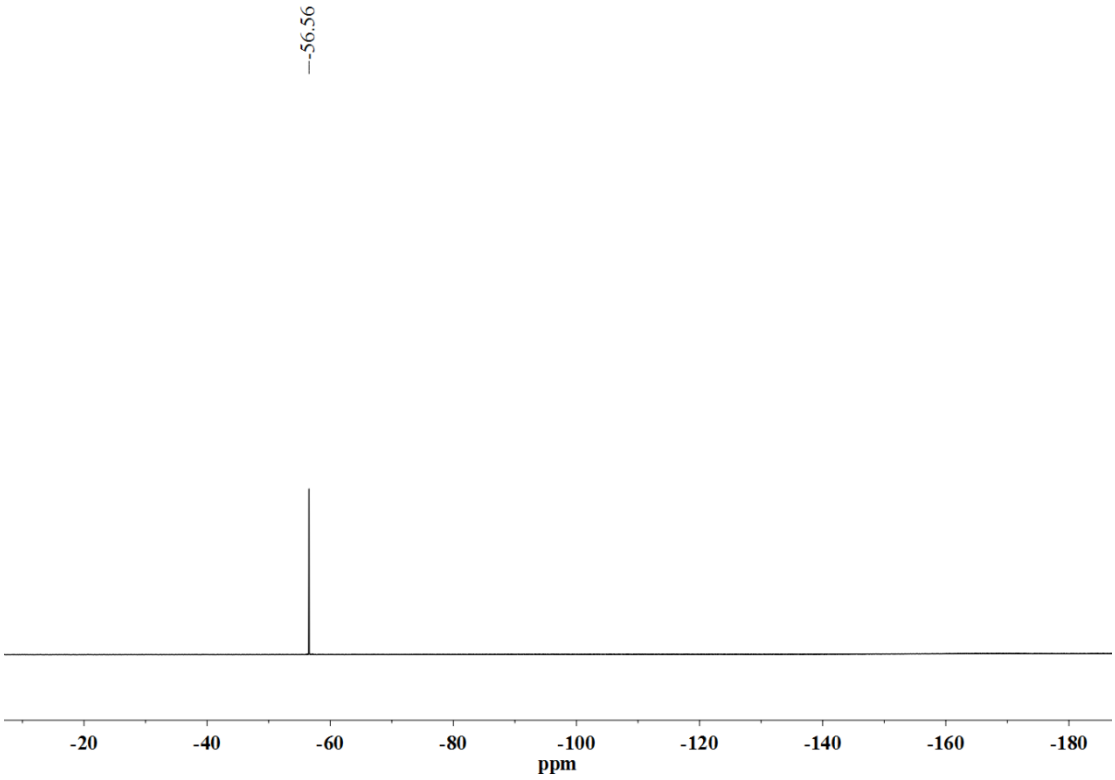
60
40
20
0
ppm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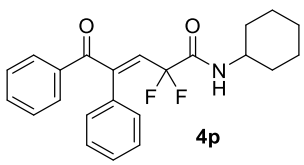
-180
ppm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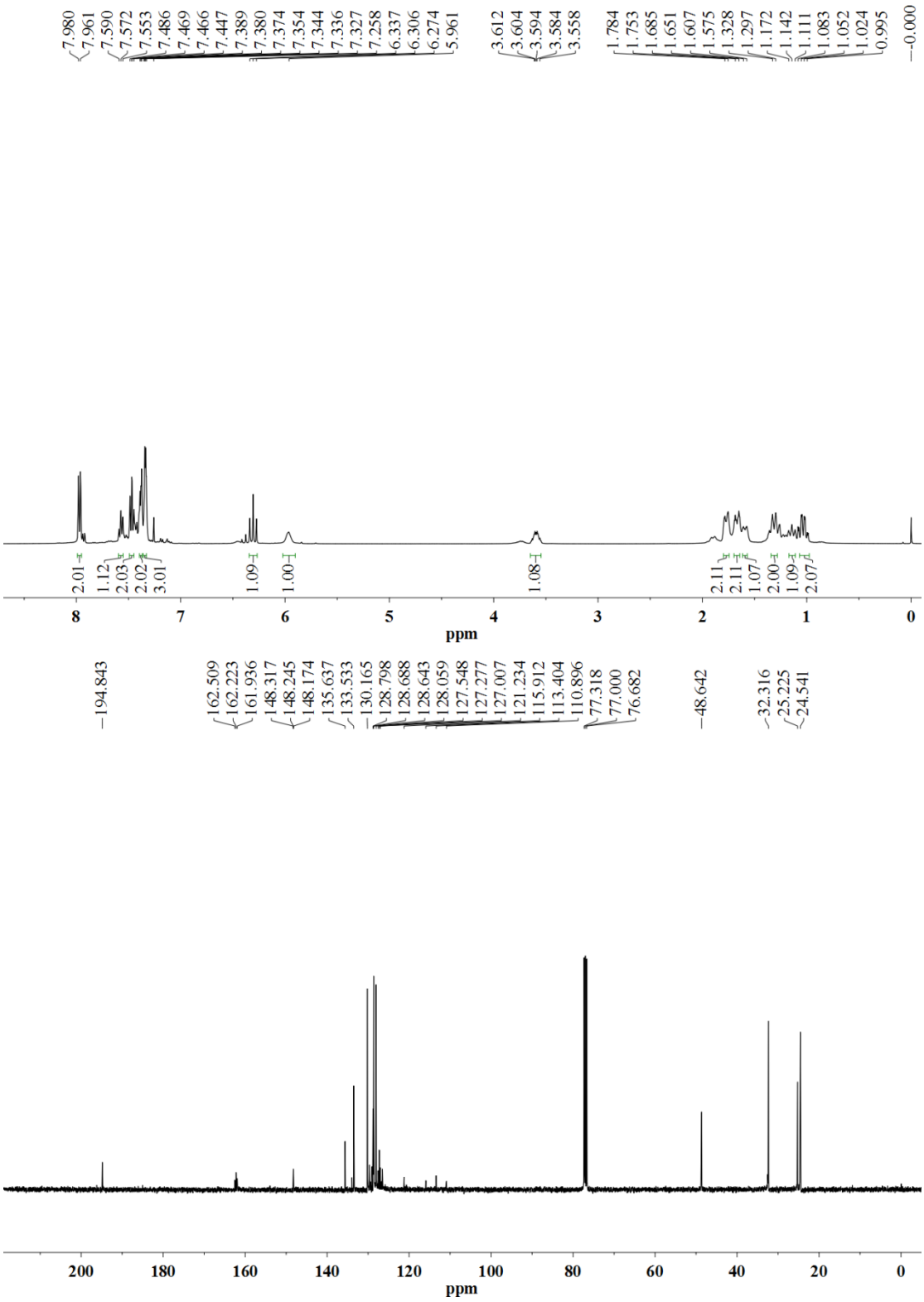
O
N
H
F
F

4p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7.466
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7.389
7.380
7.374
7.354
7.344
7.336
7.327
7.258
6.337
6.306
6.274
5.961
3.612
3.604
3.594
3.584
3.558
1.784
1.753
1.685
1.651
1.607
1.575
1.328
1.297
1.172
1.142
1.111
1.083
1.052
1.024
0.995
-0.000
2.01
1.12
2.03
2.02
3.01
1.09
1.00
1.08
2.11
2.11
1.07
2.00
1.09
2.07
8
7
6
5
4
3
2
1
0
ppm
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162.223
161.936
148.317
148.245
148.174
135.637
133.533
130.165
128.798
128.688
128.643
128.059
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127.277
127.007
121.234
115.912
113.404
110.896
77.318
77.000
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200
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120
100
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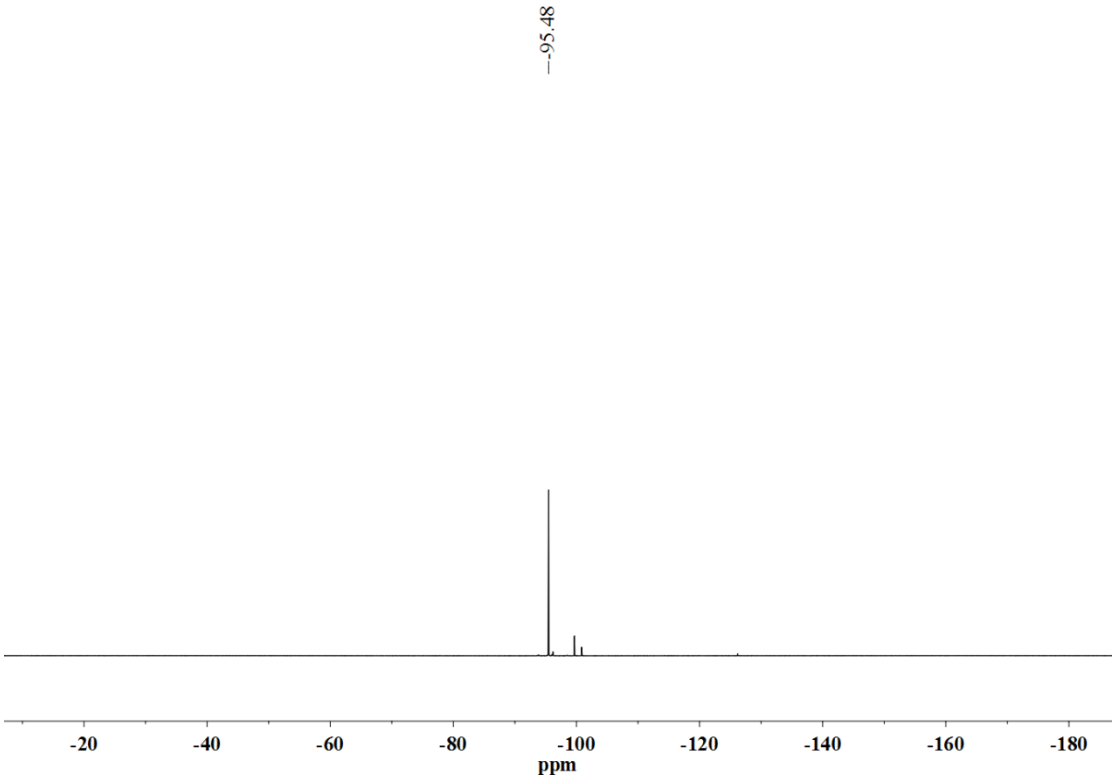
60
40
20
0
ppm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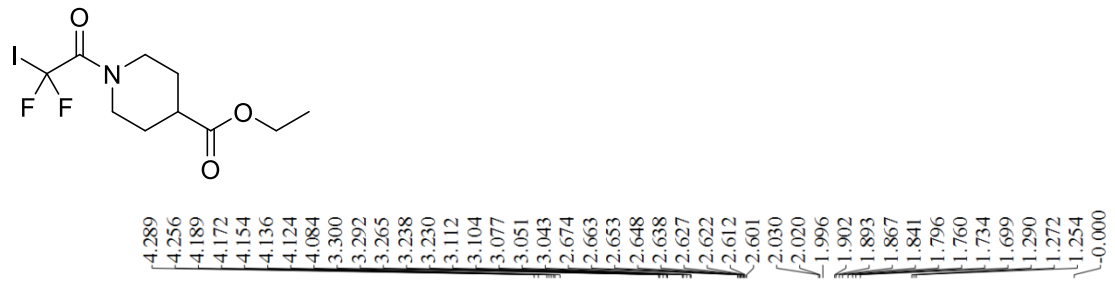
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I
N
F F
O
O
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4.189
4.172
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4.136
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3.300
3.292
3.265
3.238
3.230
3.112
3.104
3.077
3.051
3.043
2.674
2.663
2.653
2.648
2.638
2.627
2.622
2.612
2.601
2.030
2.020
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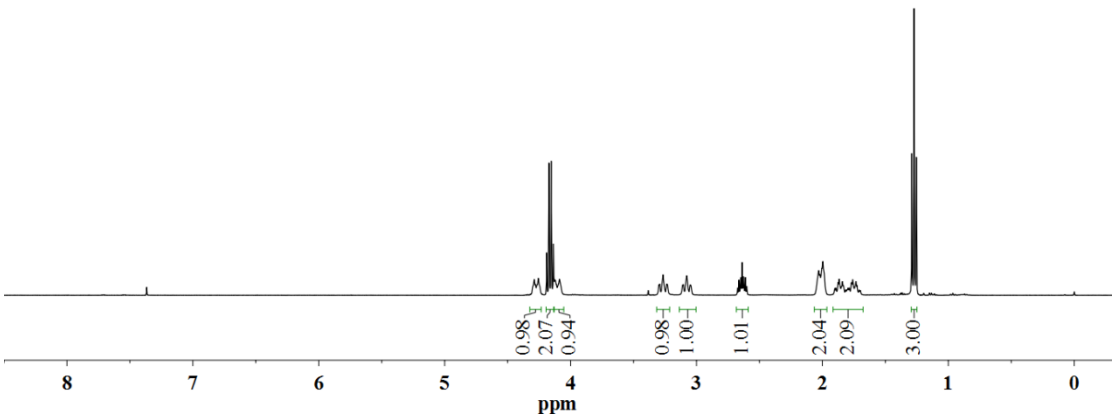
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2.04
2.09
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6
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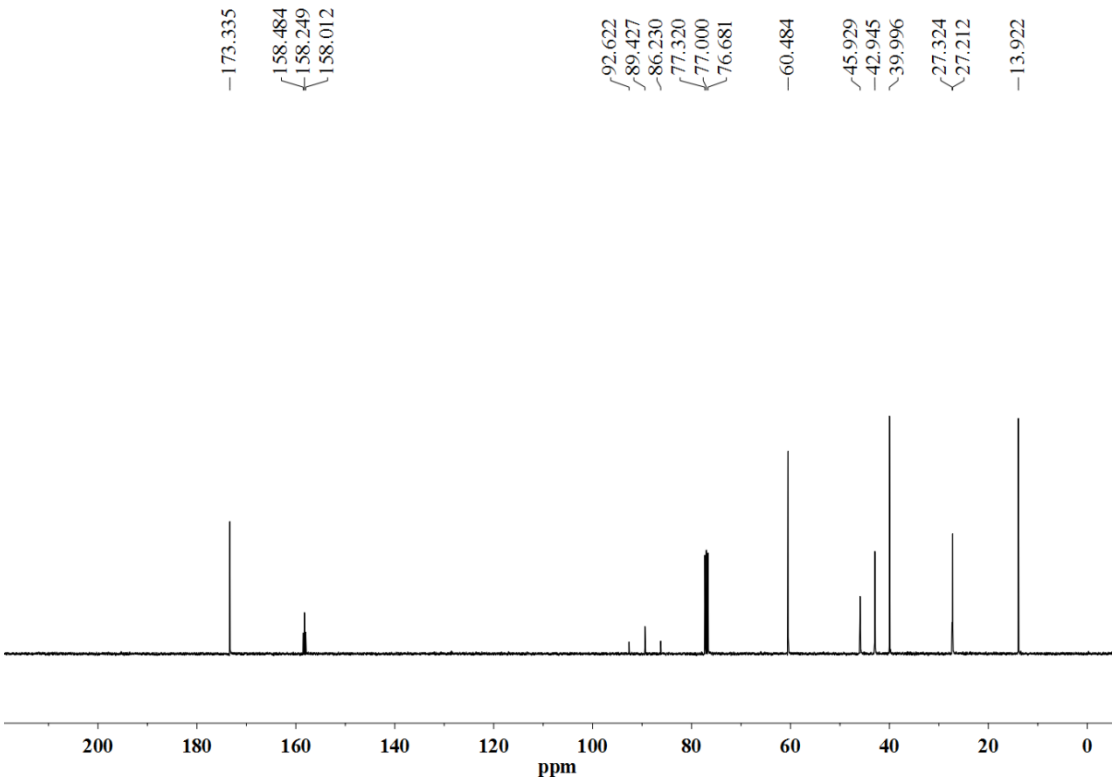
ppm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86.230
77.320
77.000
76.681
60.484
45.929
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39.996
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27.212
13.922
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120
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60
40
20
0
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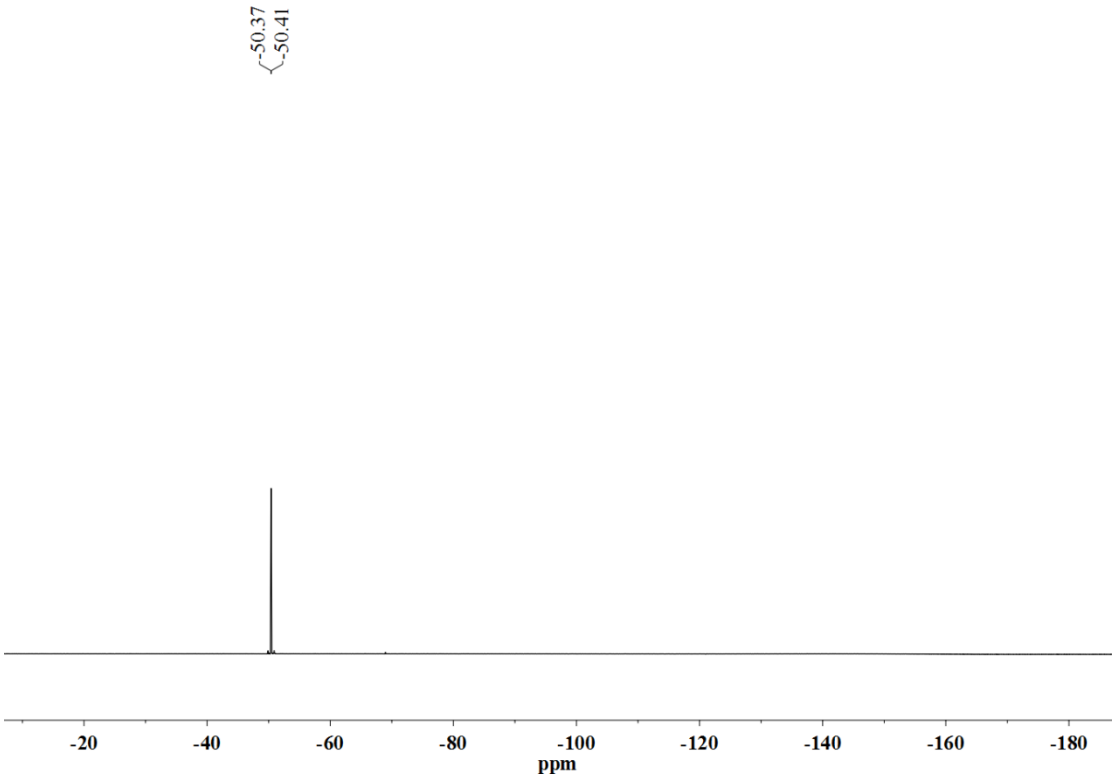
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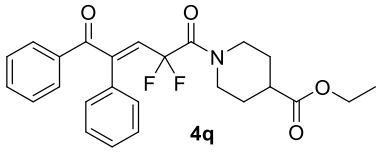
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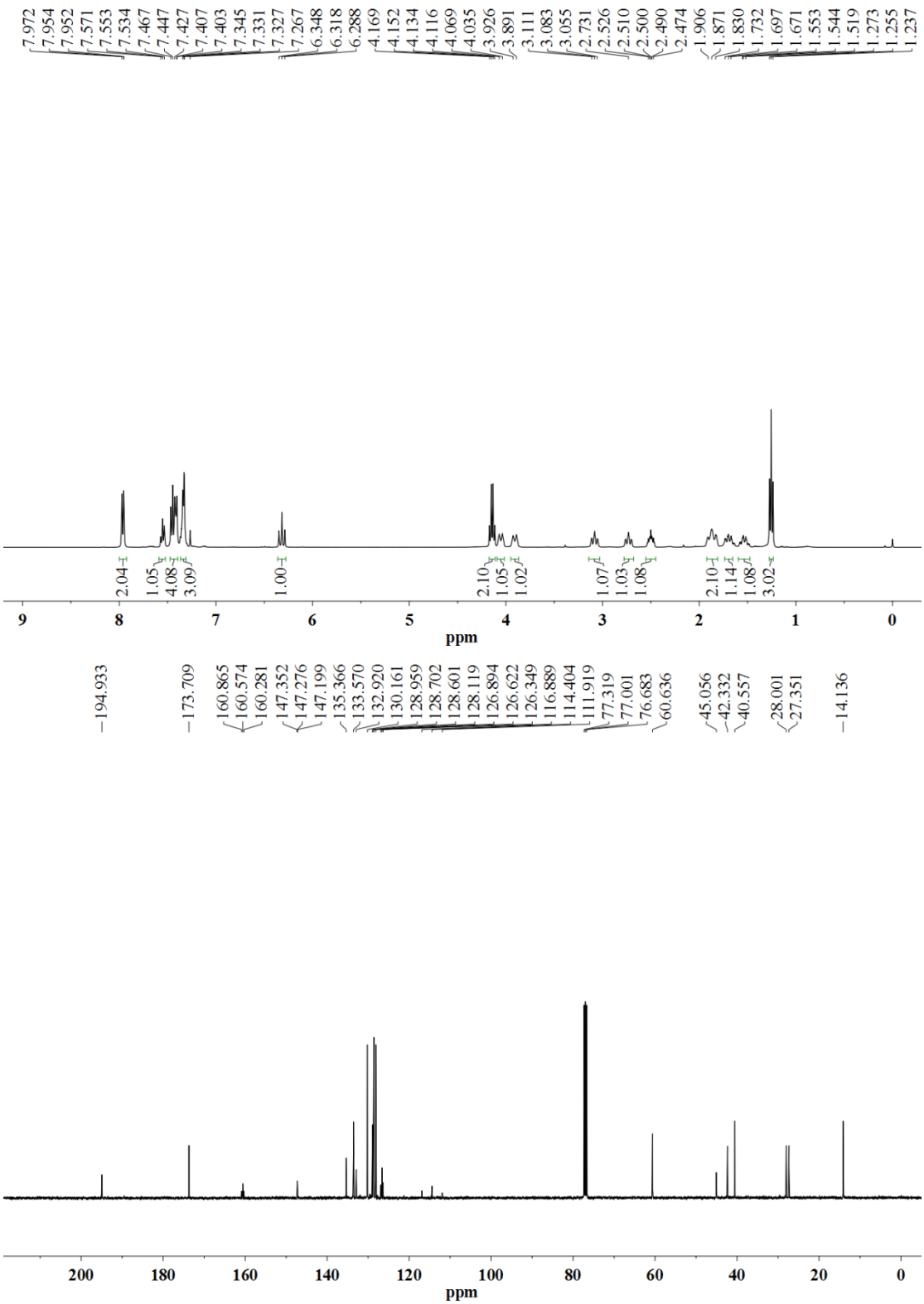
O
N
F
F
O
O

4q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7.331
7.327
7.267
6.348
6.318
6.288
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4.152
4.134
4.116
4.069
4.035
3.926
3.891
3.111
3.083
3.055
2.731
2.526
2.510
2.500
2.490
2.474
1.906
1.871
1.830
1.732
1.697
1.671
1.553
1.544
1.519
1.273
1.255
1.237
2.04
1.05
4.08
3.09
1.00
2.10
1.05
1.02
1.07
1.03
1.08
2.10
1.14
1.08
3.02
9
8
7
6
5
4
3
2
1
0
ppm
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160.865
160.574
160.281
147.352
147.276
147.199
135.366
133.570
132.920
130.161
128.959
128.702
128.601
128.119
126.894
126.622
126.349
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114.404
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77.001
76.683
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40
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0
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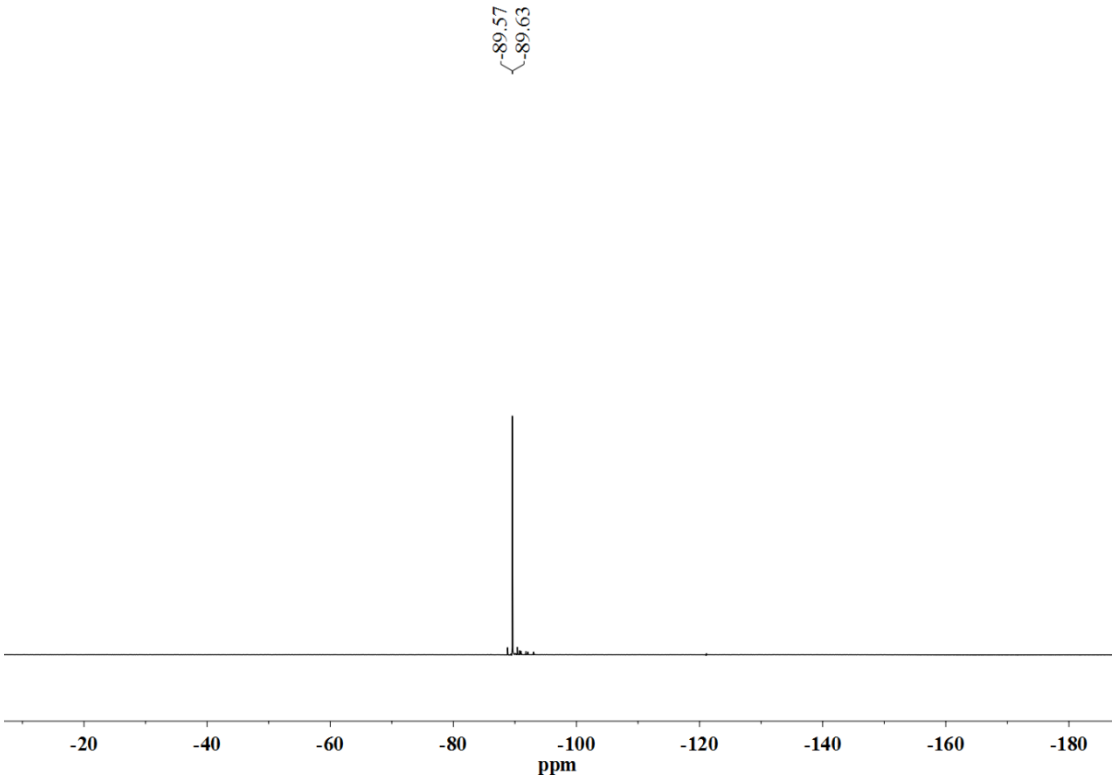
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-140
-160
-180
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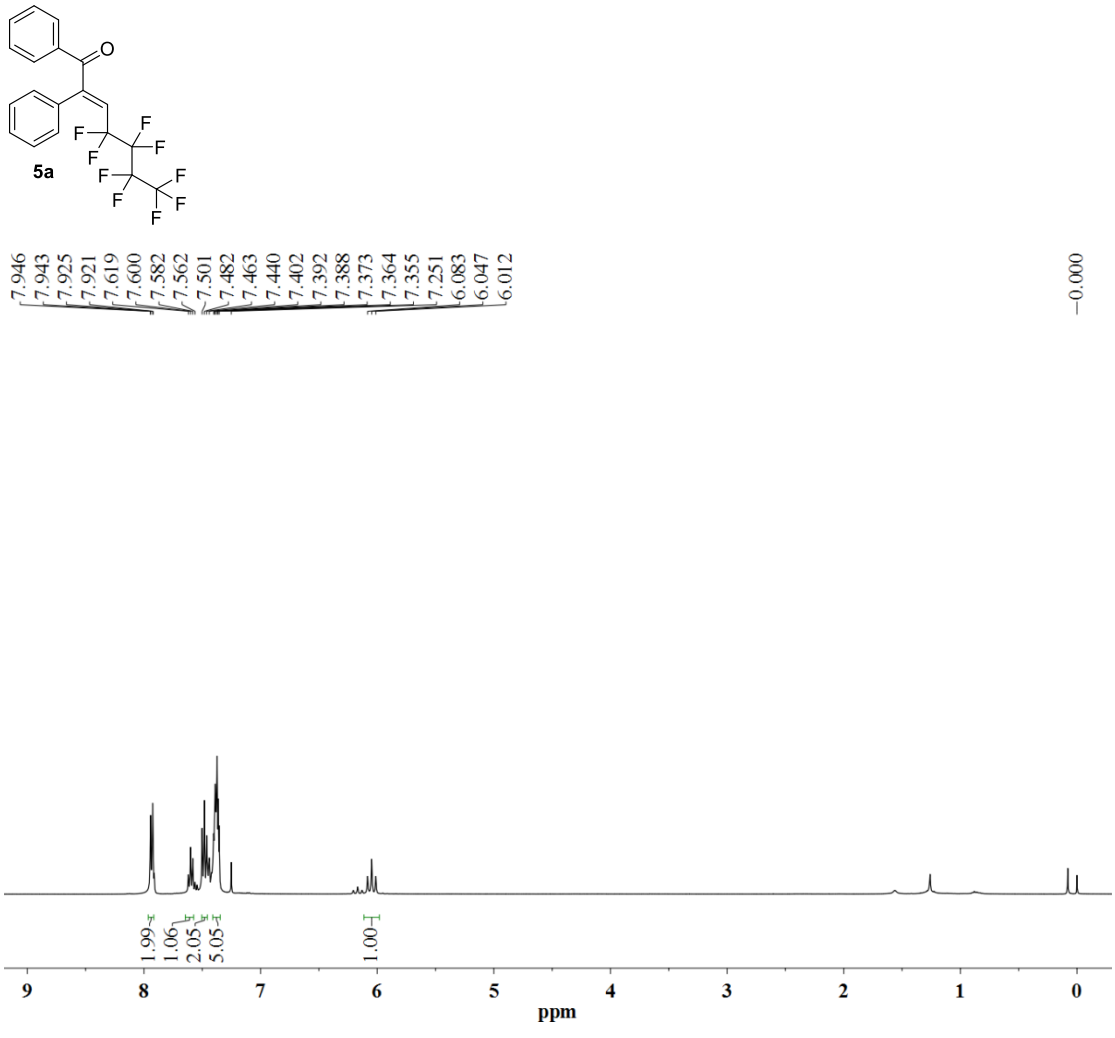
O
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F
F
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F
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7.600
7.582
7.562
7.501
7.482
7.463
7.440
7.402
7.392
7.388
7.373
7.364
7.355
7.251
6.083
6.047
6.012
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5.05
1.00
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6
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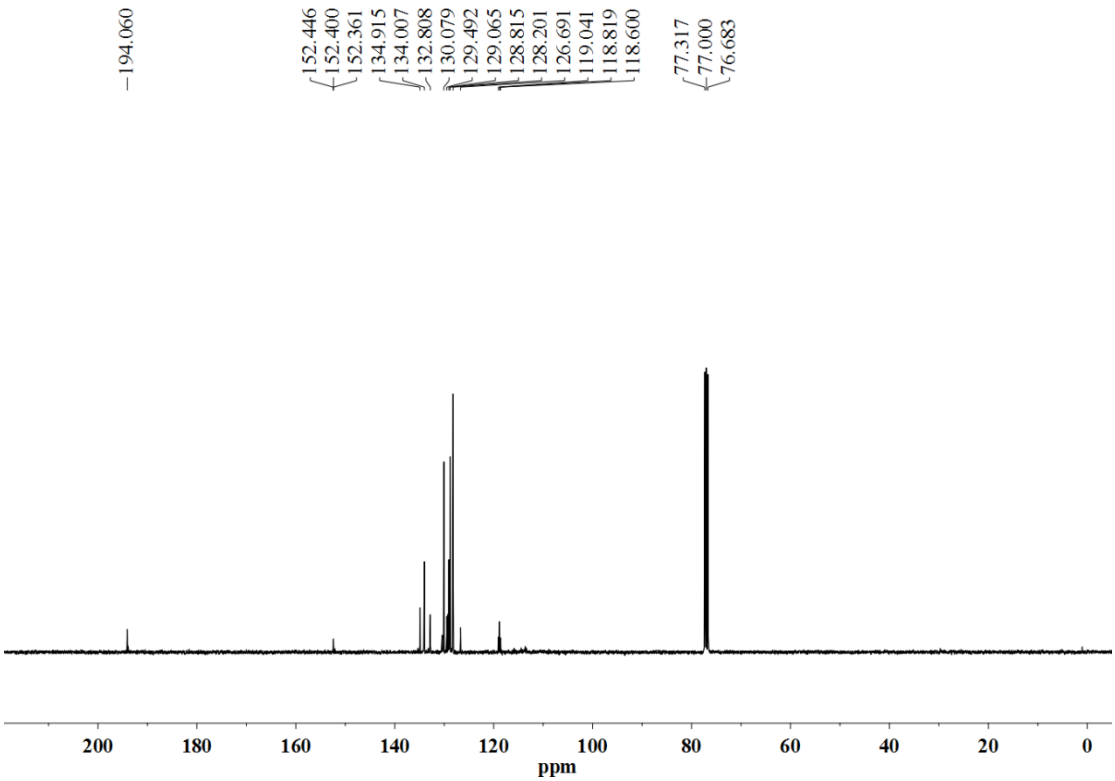
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129.065
128.815
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126.691
119.041
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77.000
76.683
200
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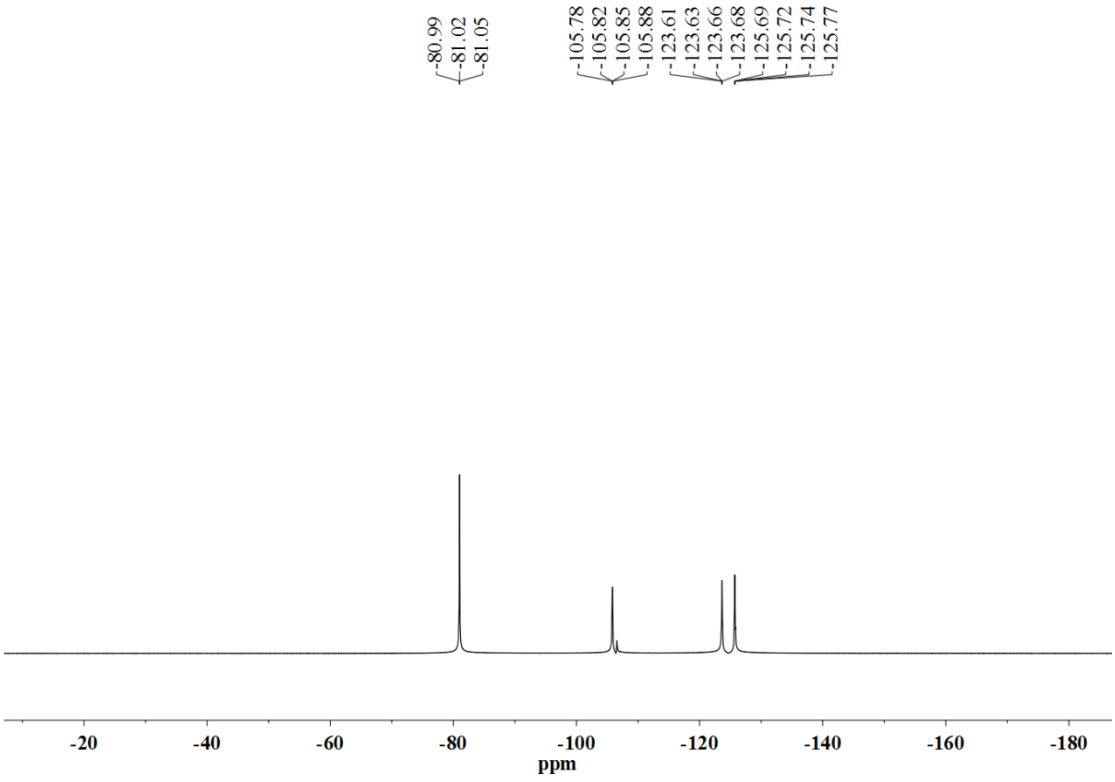
120
100
80
60
40
20
0
ppm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-105.88
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-123.63
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-125.77
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-60
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-100
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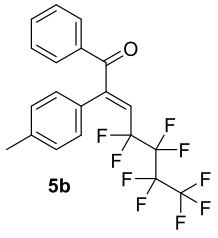
-160
-180
ppm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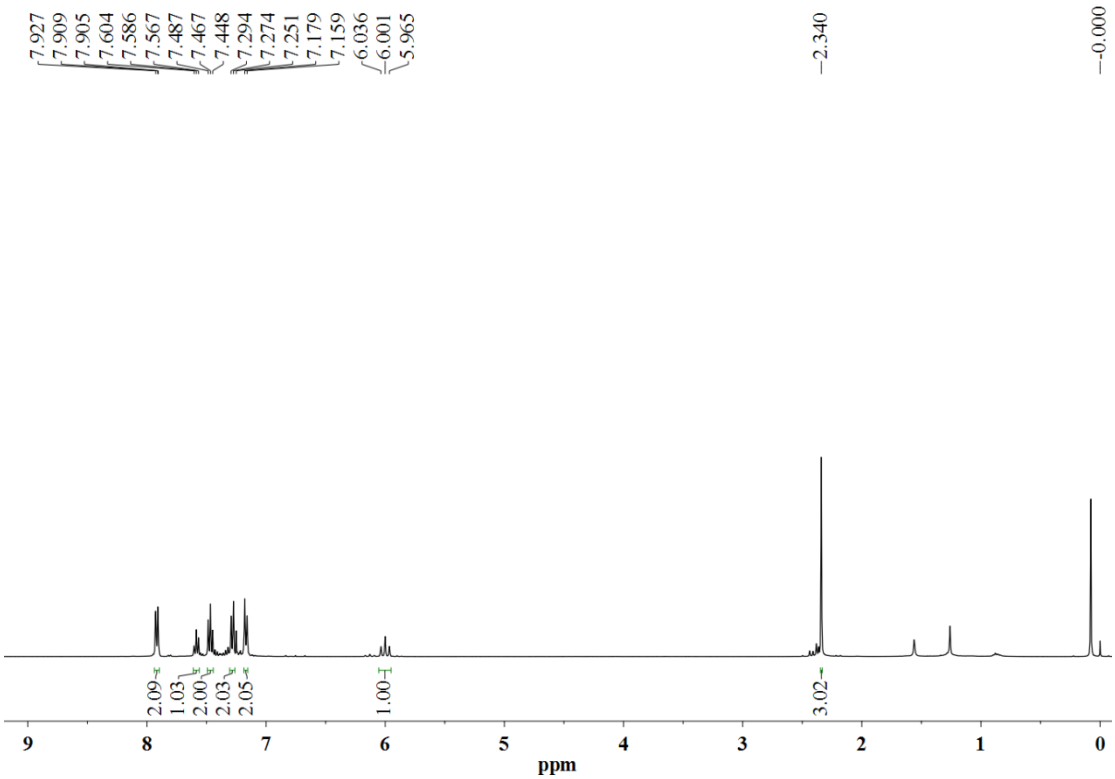
F
F
F
F
F
F
F
F

5b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7.467
7.448
7.294
7.274
7.251
7.179
7.159
6.036
6.001
5.965
2.340
0.000
2.09
1.03
2.00
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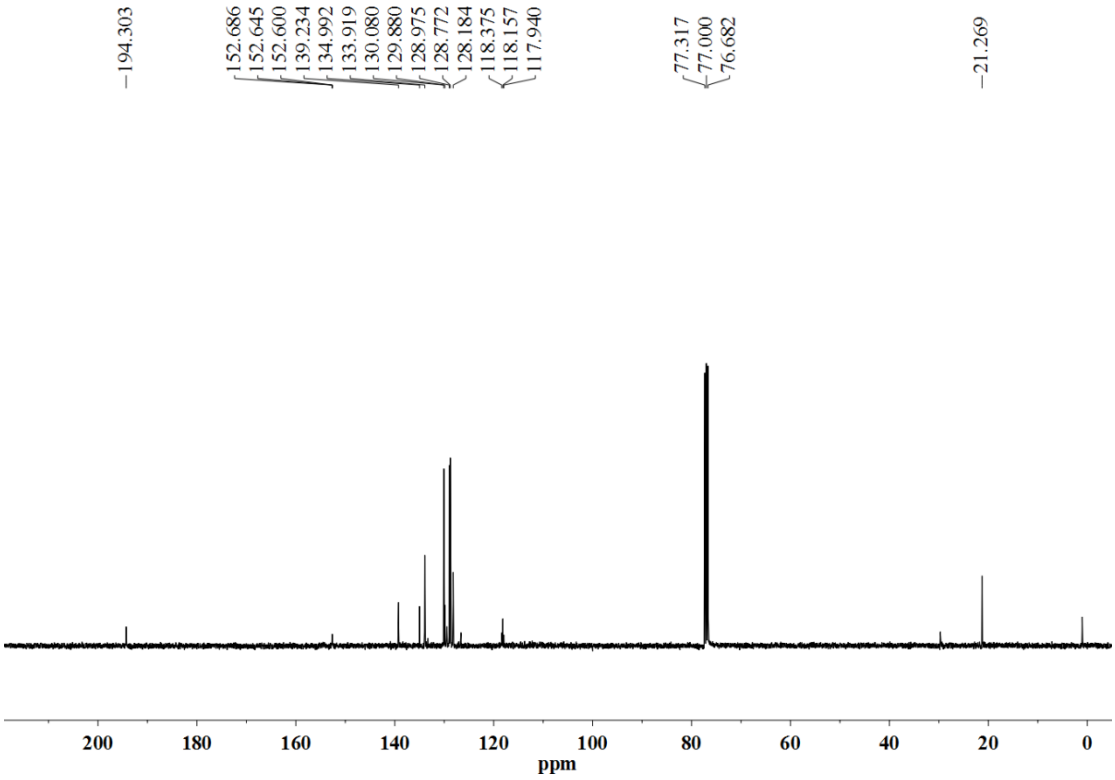
2.05
1.00
3.02
9
8
7
6
5
4
3
2
1
0
ppm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130.080
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128.975
128.772
128.184
118.375
118.157
117.940
77.317
77.000
76.682
21.269
200
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120
100
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40
20
0
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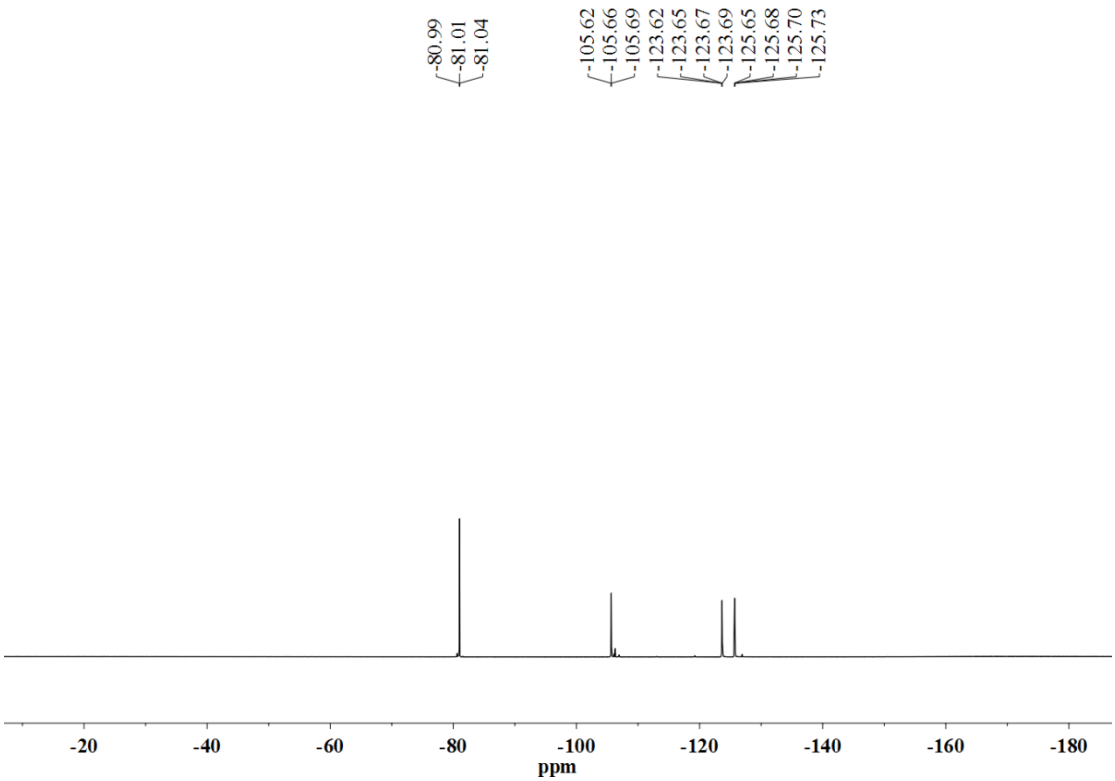
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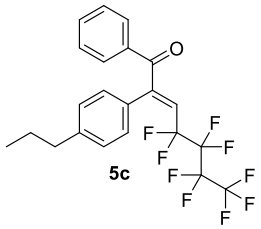
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F
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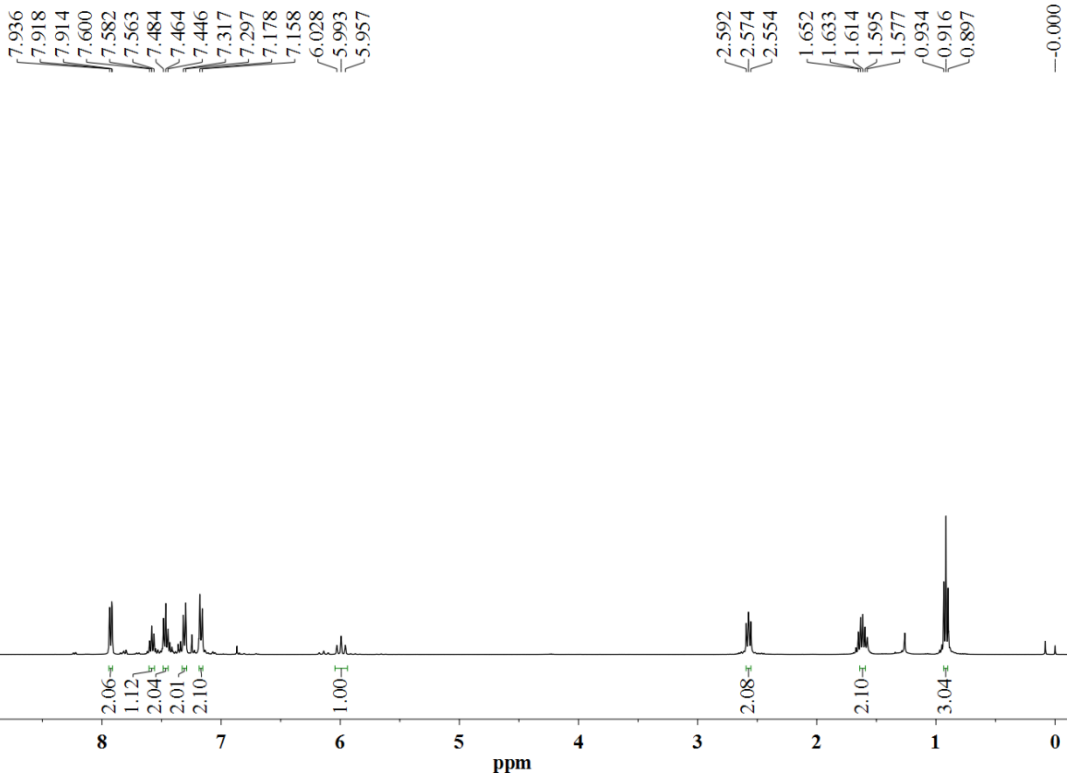
F
F
F
5c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5.957
2.592
2.574
2.554
1.652
1.633
1.614
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1.577
0.934
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0.897
0.000
2.06
1.12
2.04
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2.08
2.10
3.04
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8
7
6
5
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2
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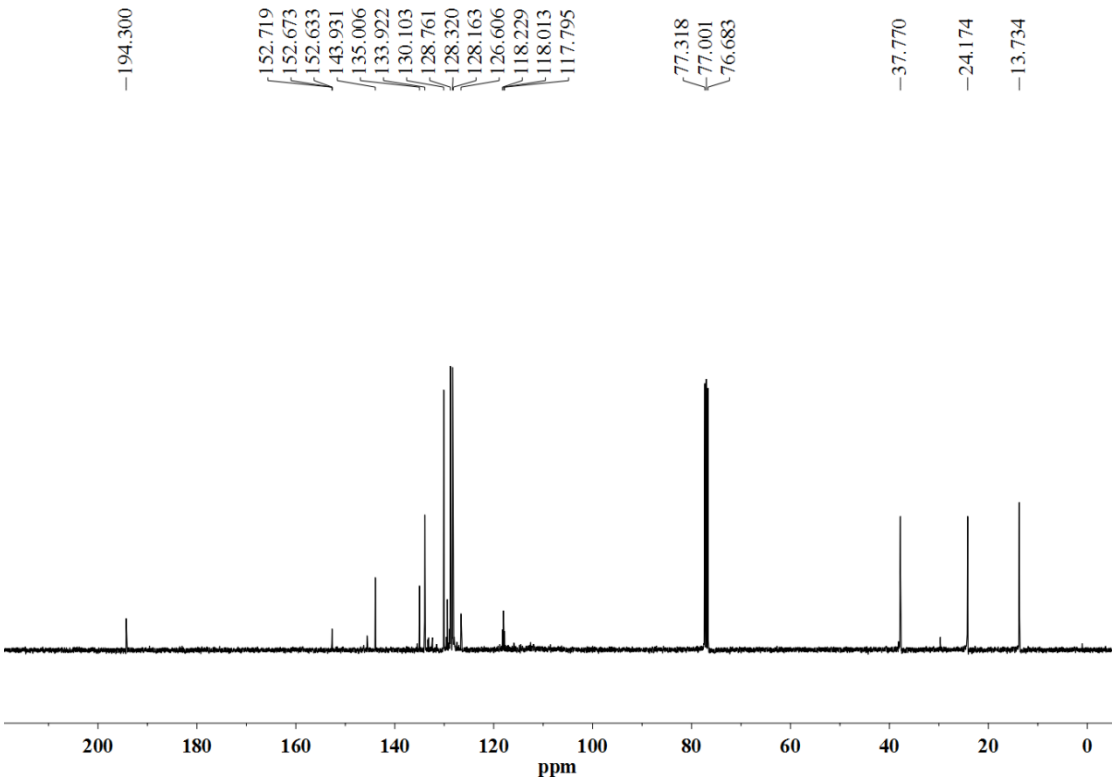
ppm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126.606
118.229
118.013
117.795
77.318
77.001
76.683
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24.174
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200
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140
120
100
80
60
40
20
0
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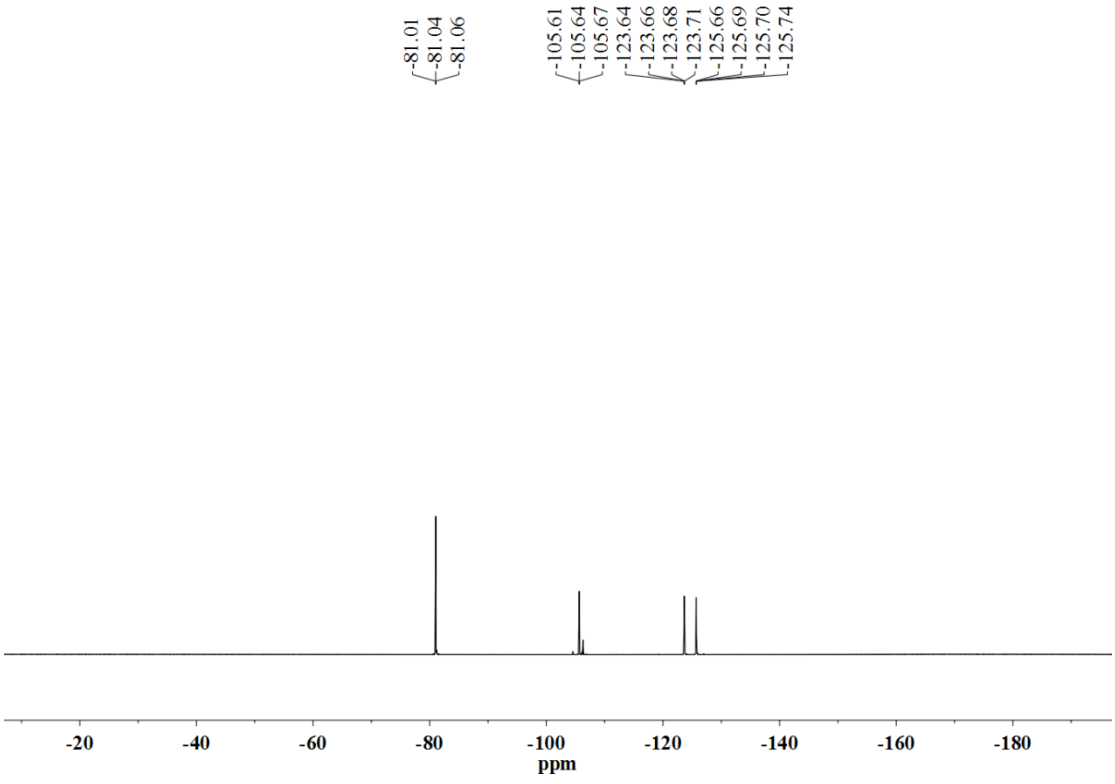
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-105.64
-105.67
-123.64
-123.66
-123.68
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-125.74
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-60
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-100
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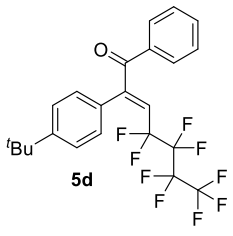
-180
ppm


O
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F

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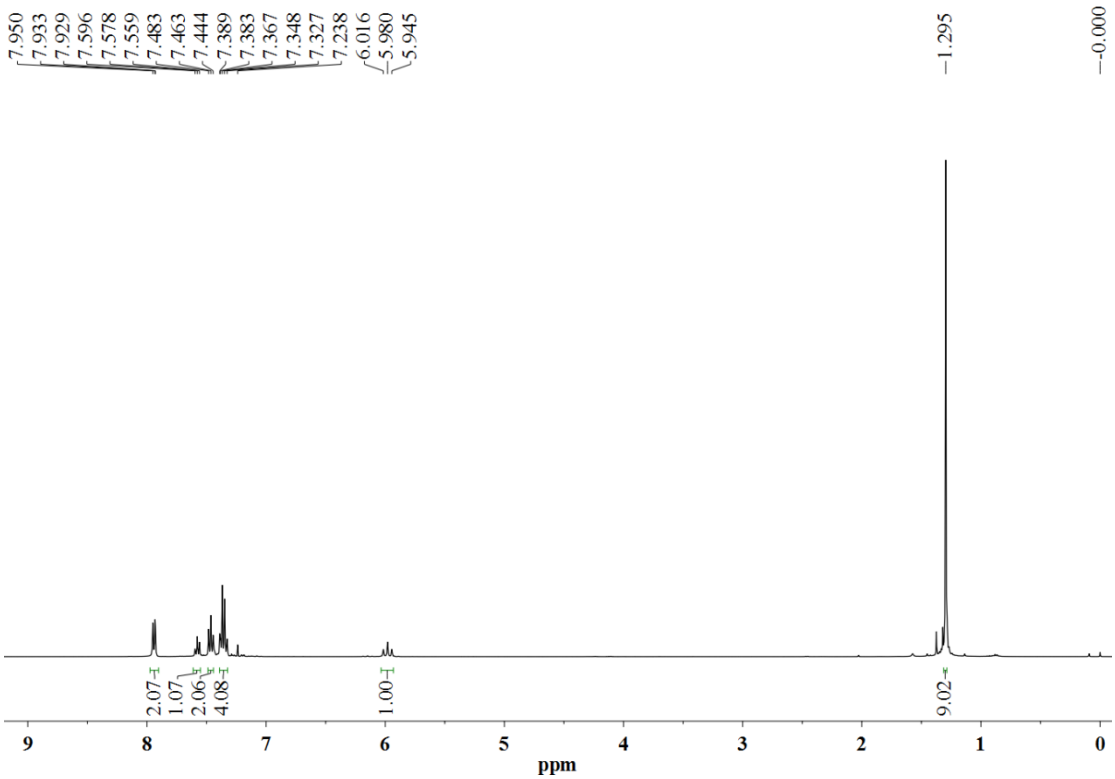
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7.327
7.238
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2.06
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1.00
9.02
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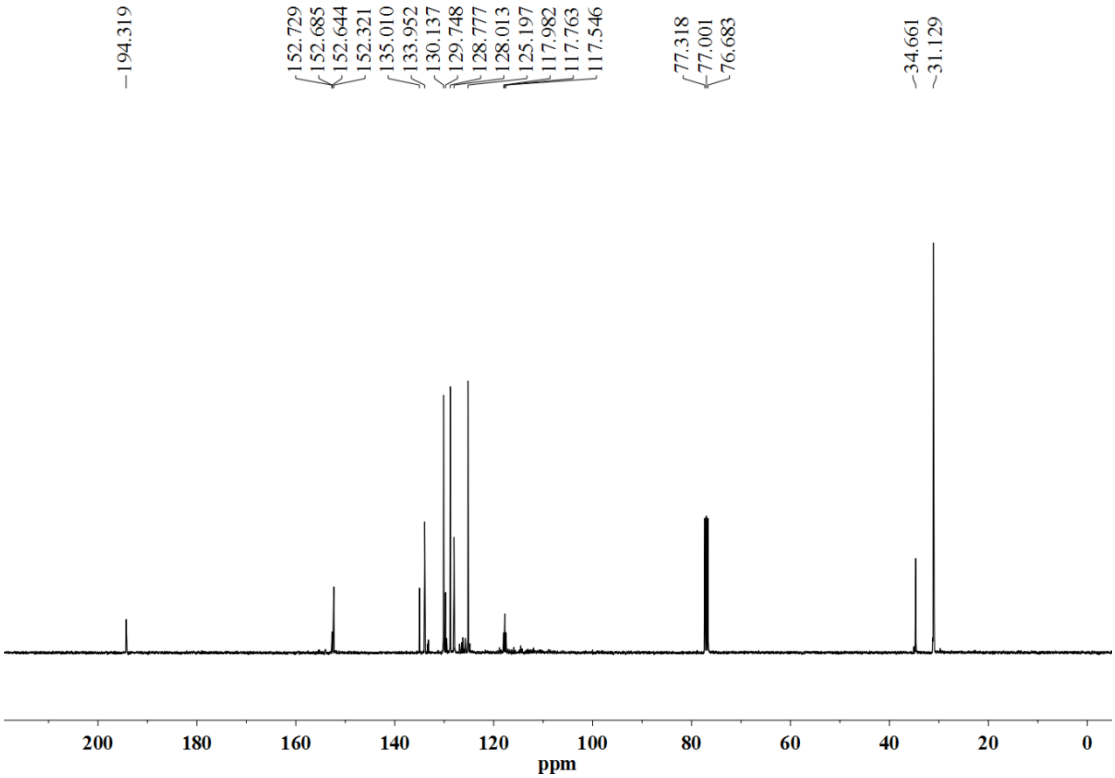
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130.137
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76.683
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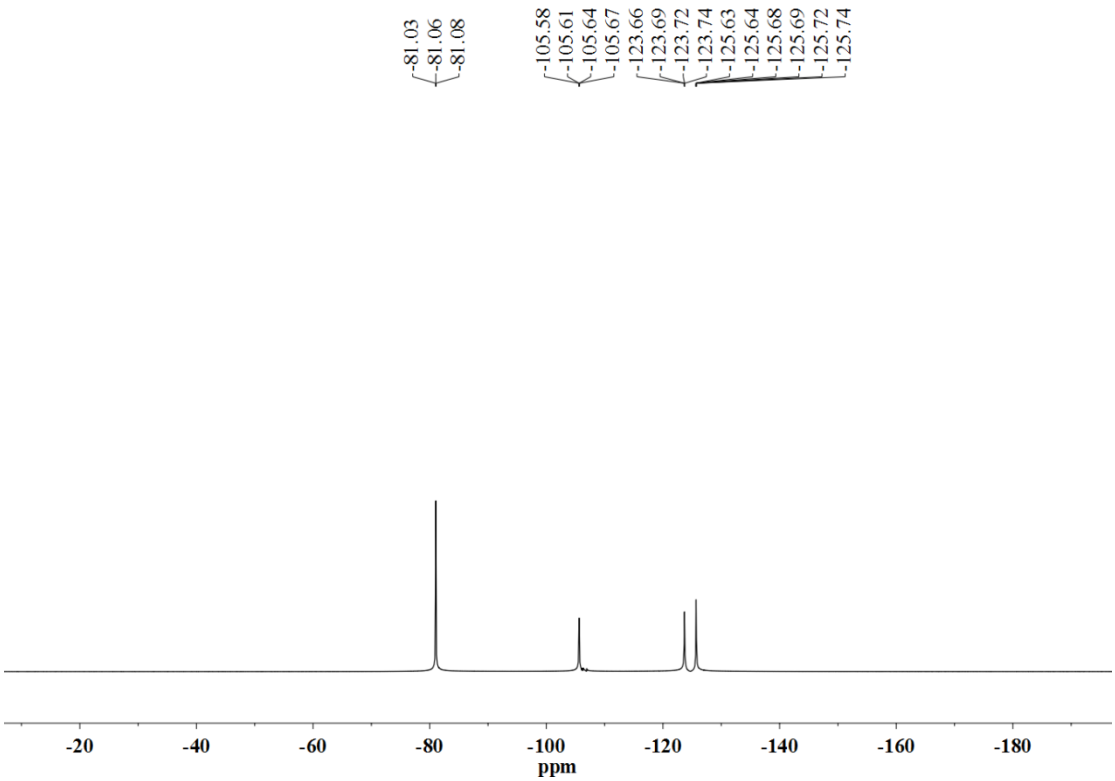
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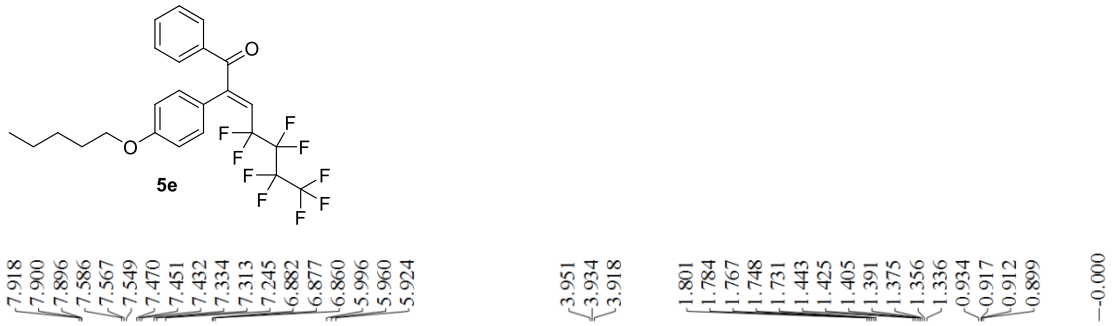
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7.334
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7.245
6.882
6.877
6.860
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5.960
5.924
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3.934
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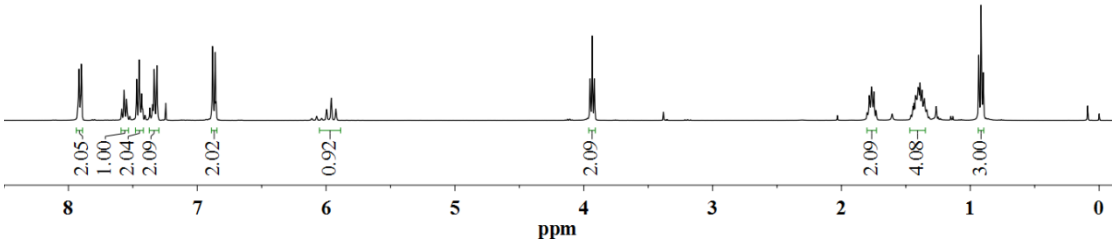
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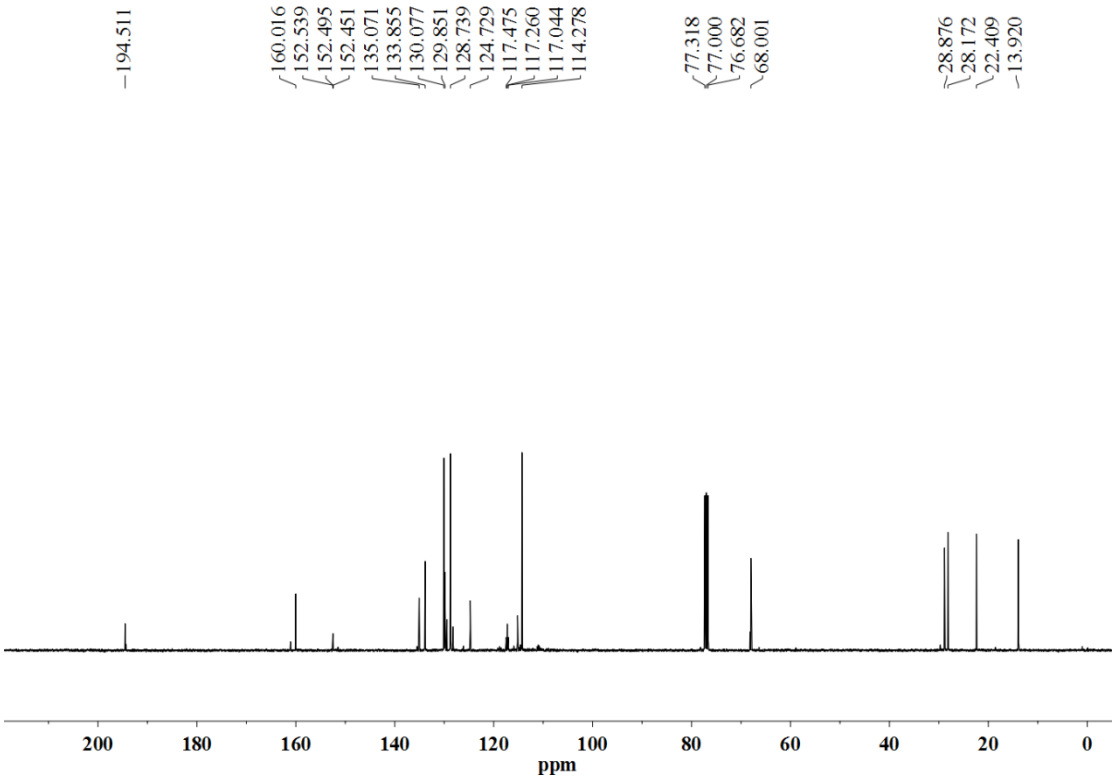
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76.682
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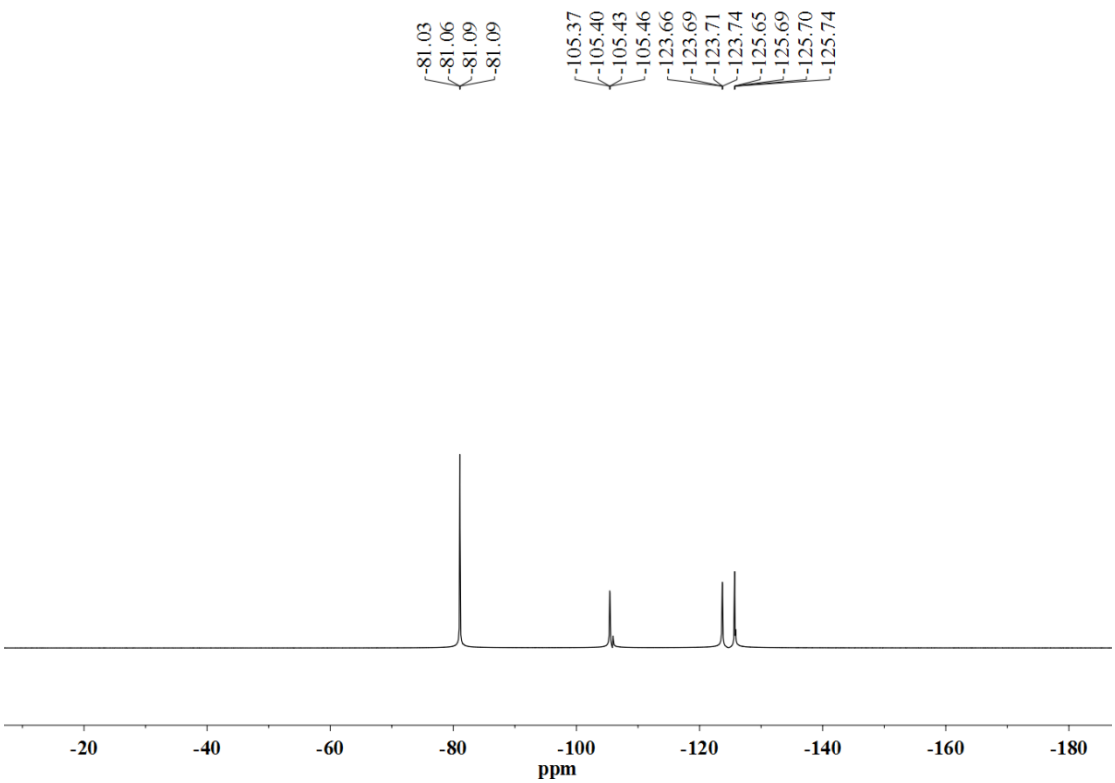
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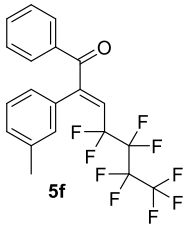
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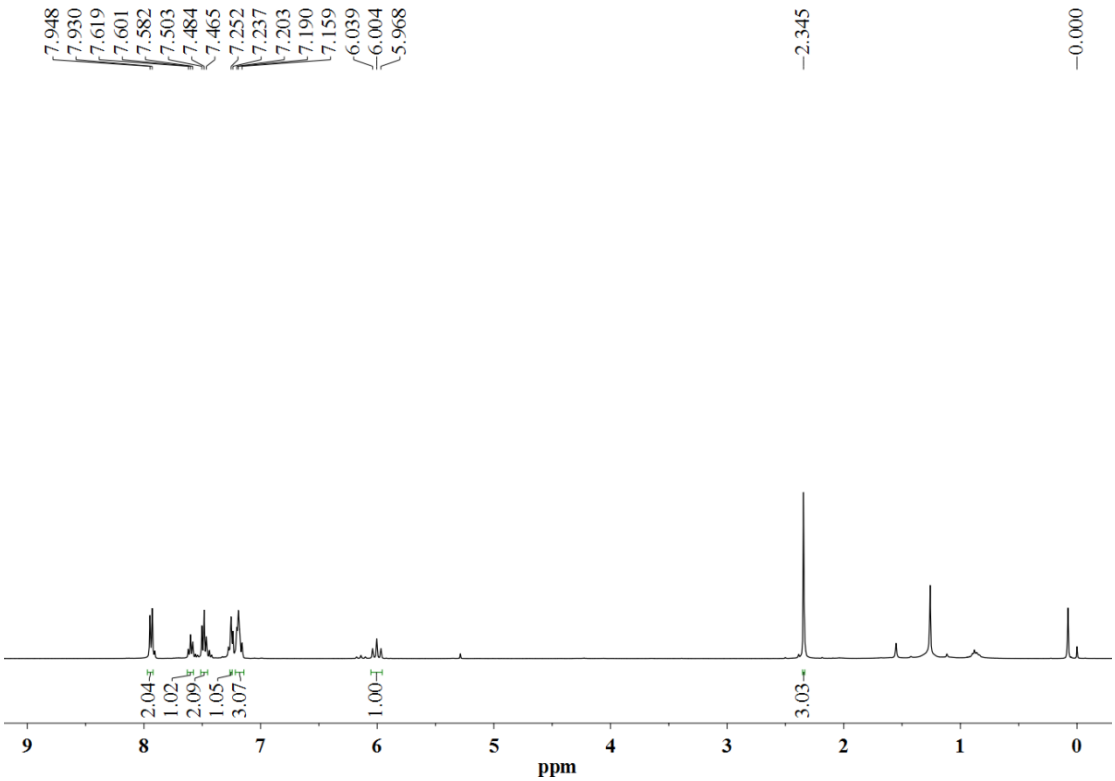
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7.252
7.237
7.203
7.190
7.159
6.039
6.004
5.968
2.345
0.000
2.04
1.02
2.09
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3.07
1.00
3.03
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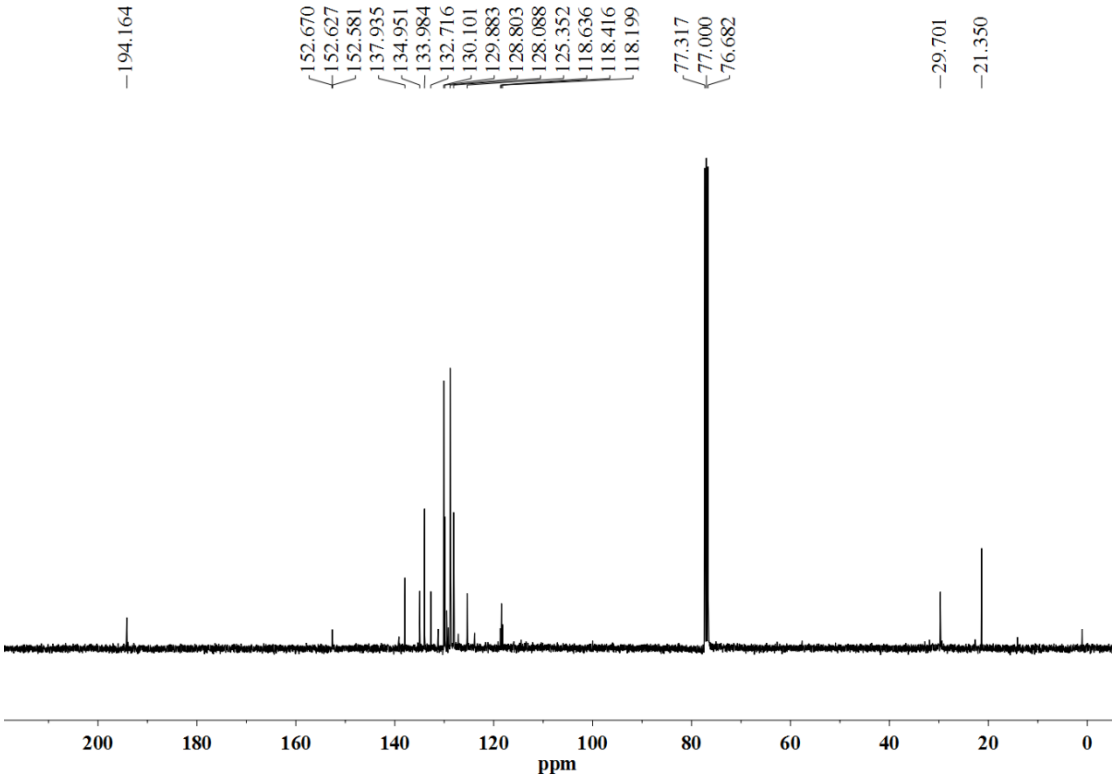
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118.416
118.199
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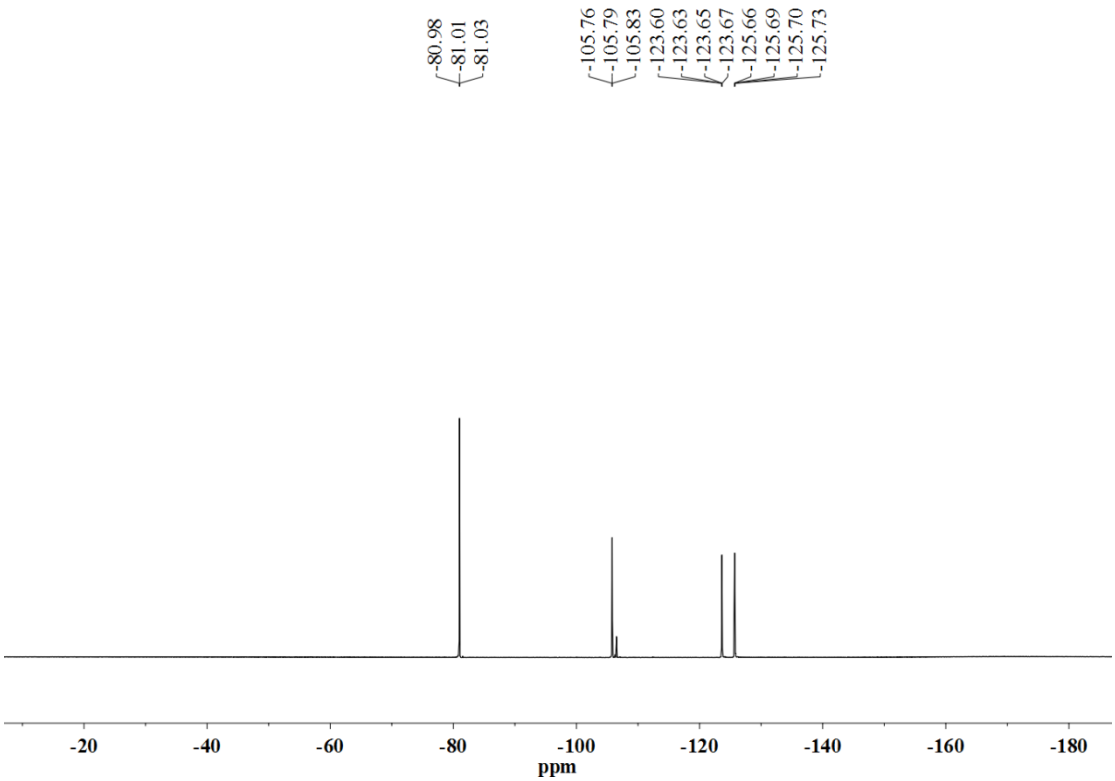
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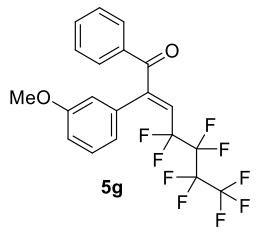
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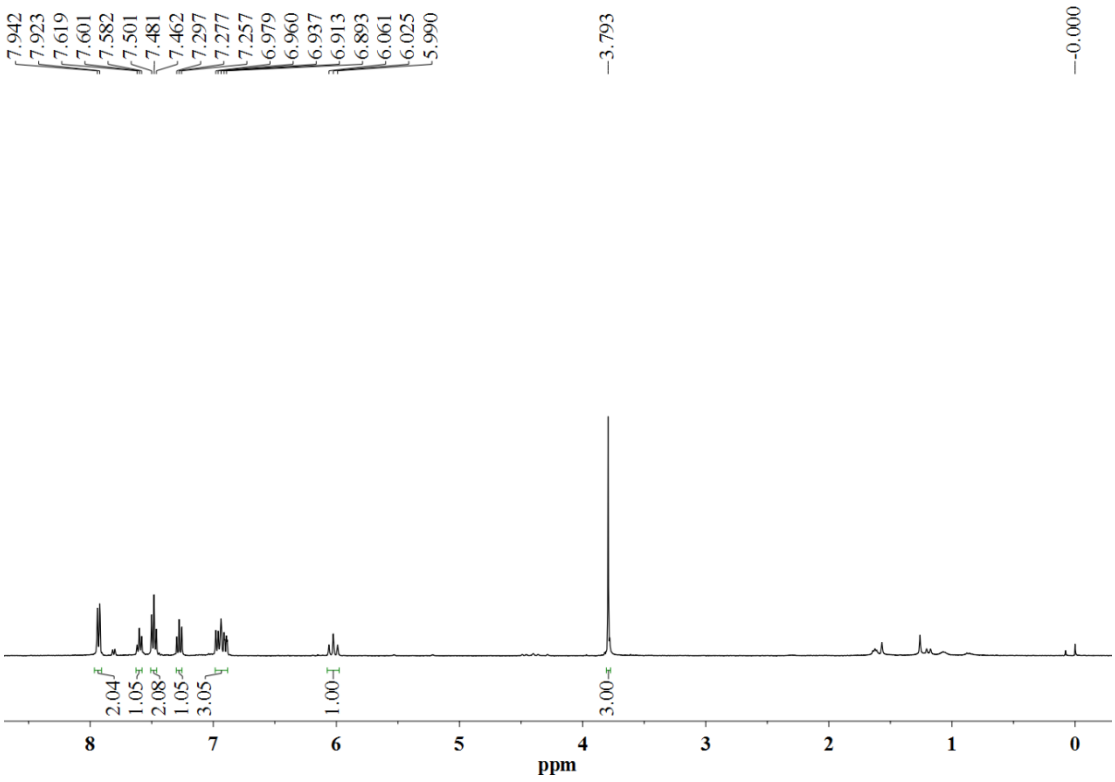
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7.257
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6.937
6.913
6.893
6.061
6.025
5.990
3.793
0.000
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3.05
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3.00
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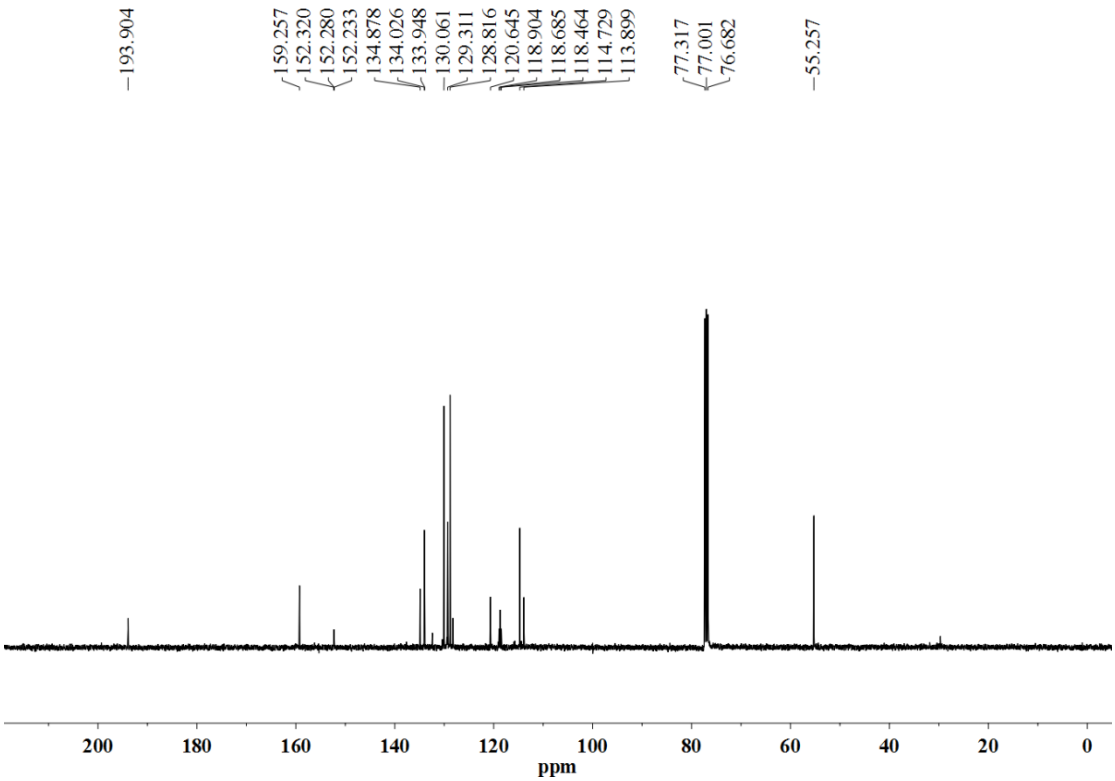
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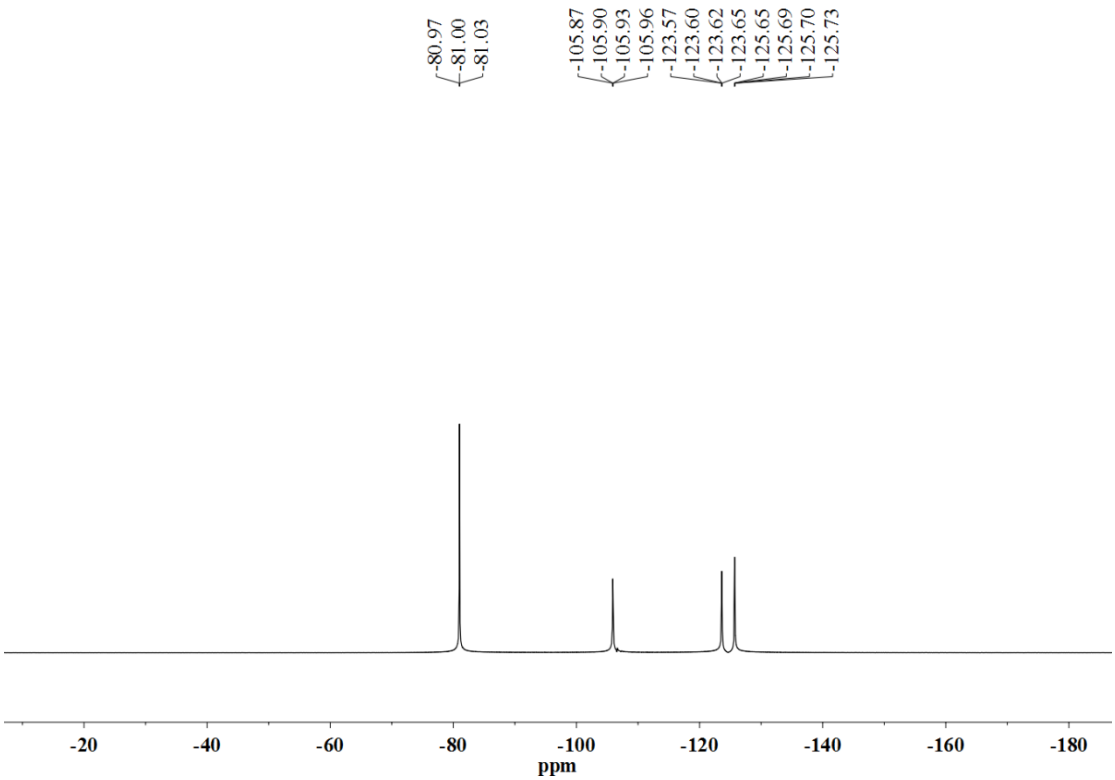
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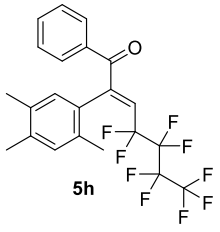
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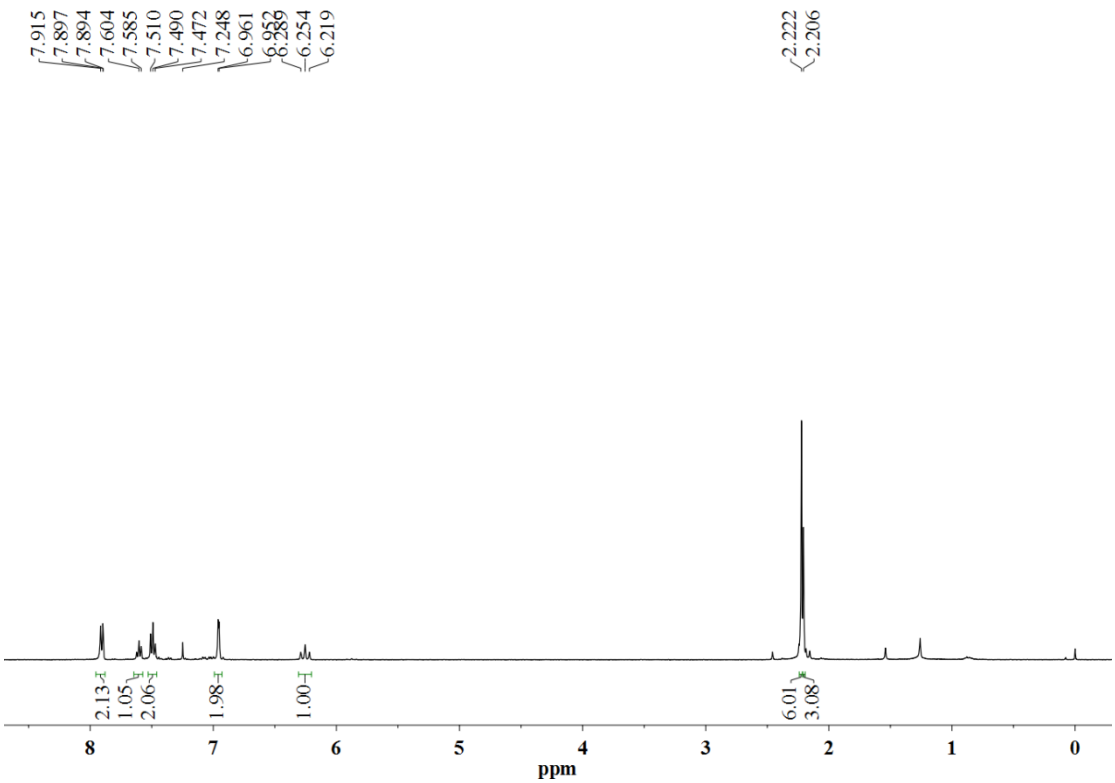
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2.13
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1.00
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3.08
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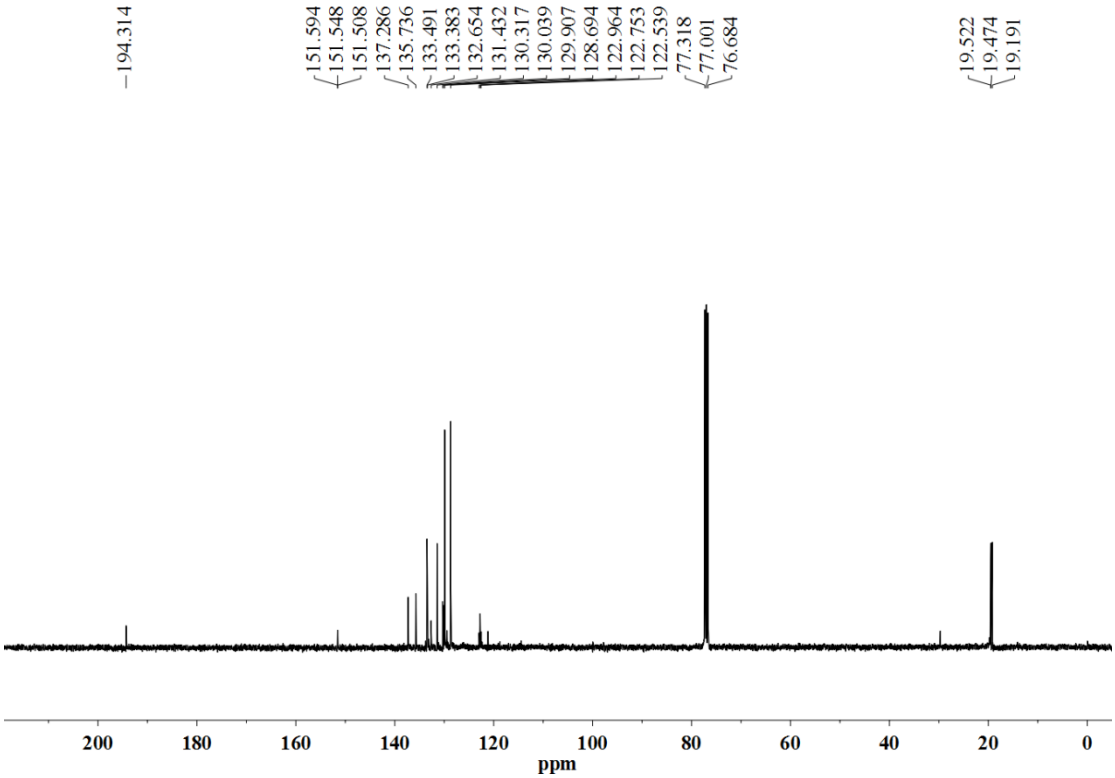
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122.753
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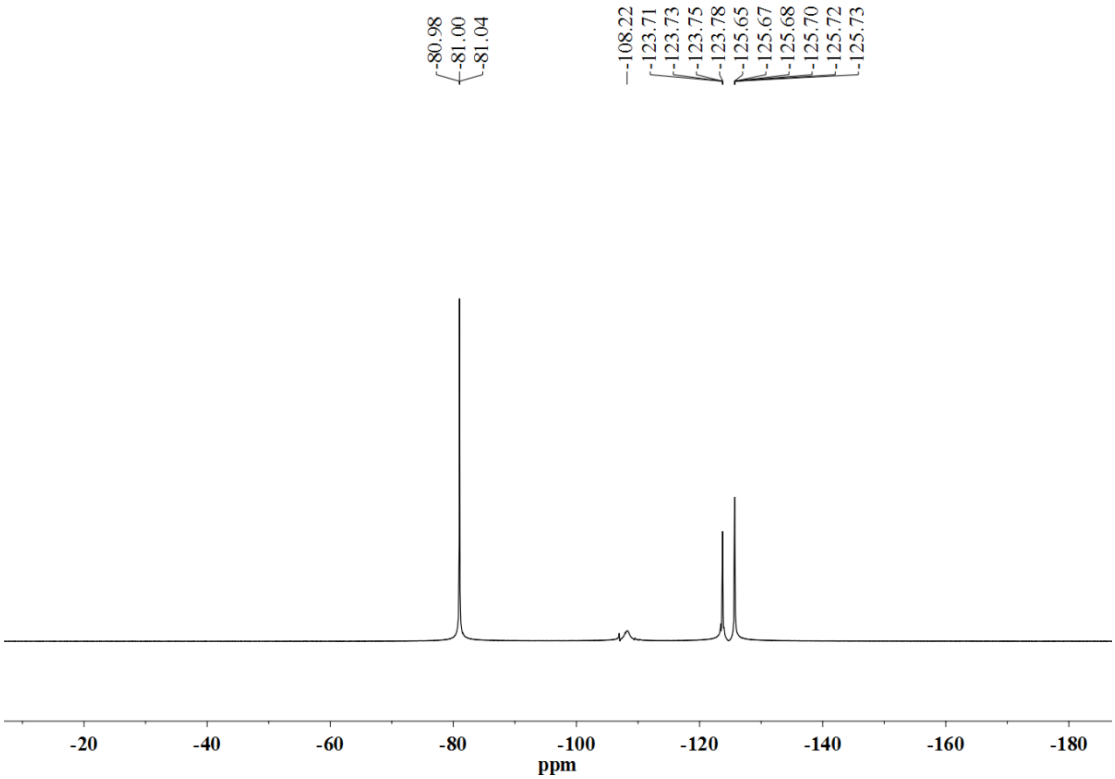
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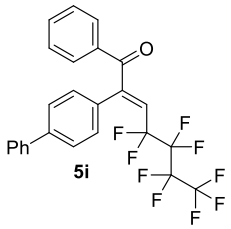
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F
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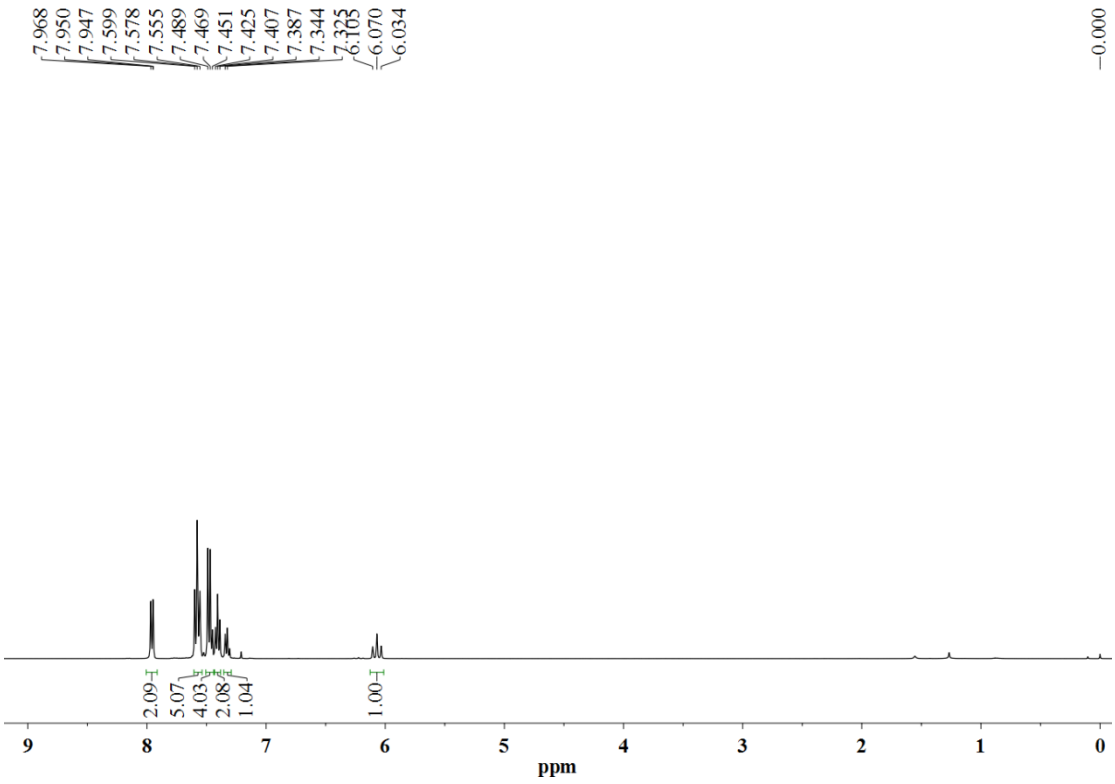
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6.070
6.034
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2.08
1.04
1.00
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8
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6
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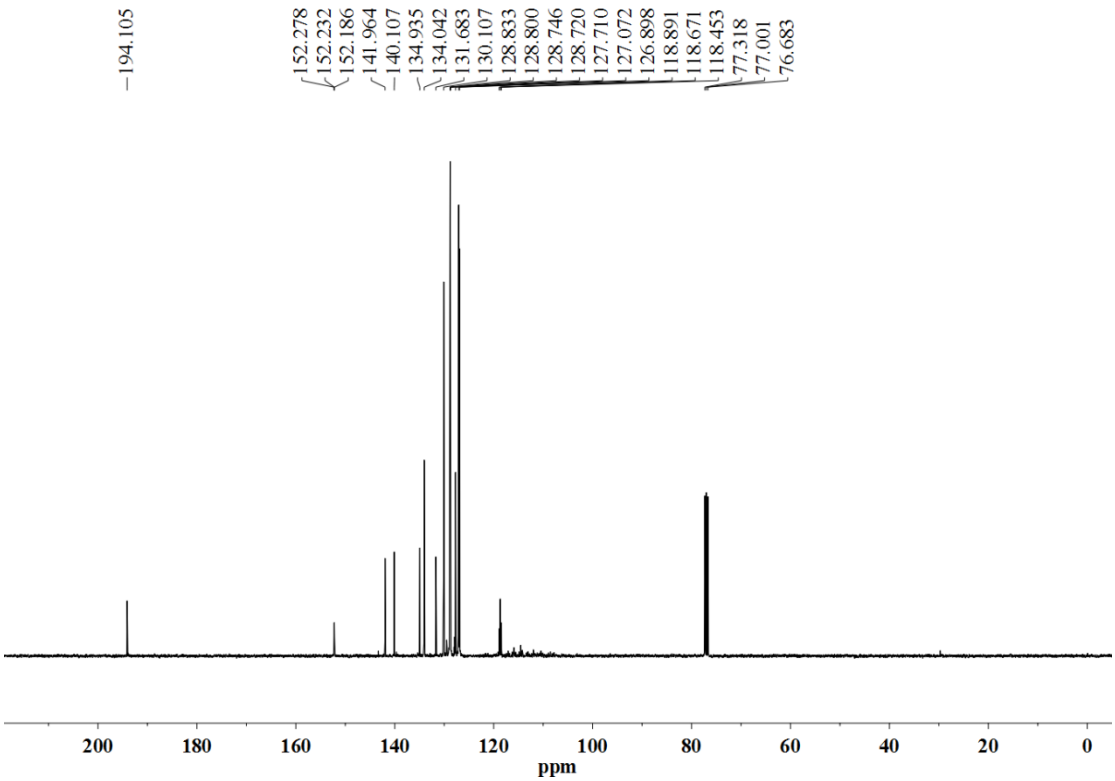
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76.683
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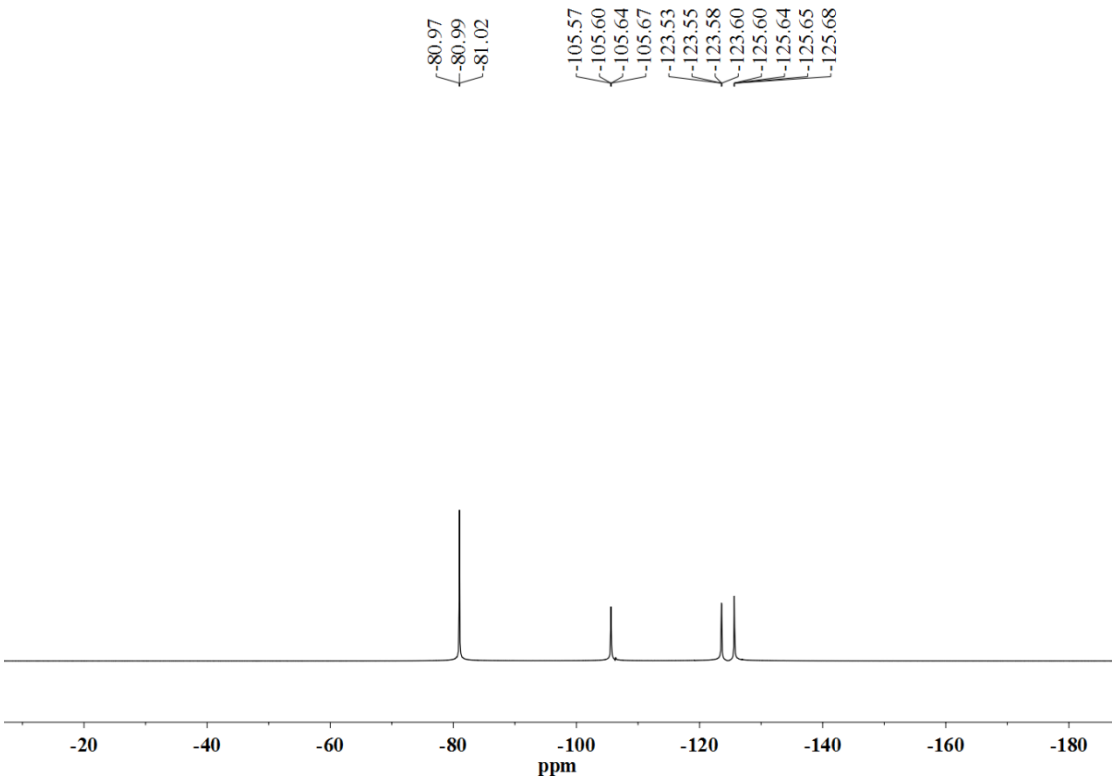
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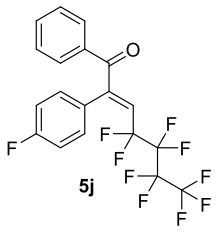
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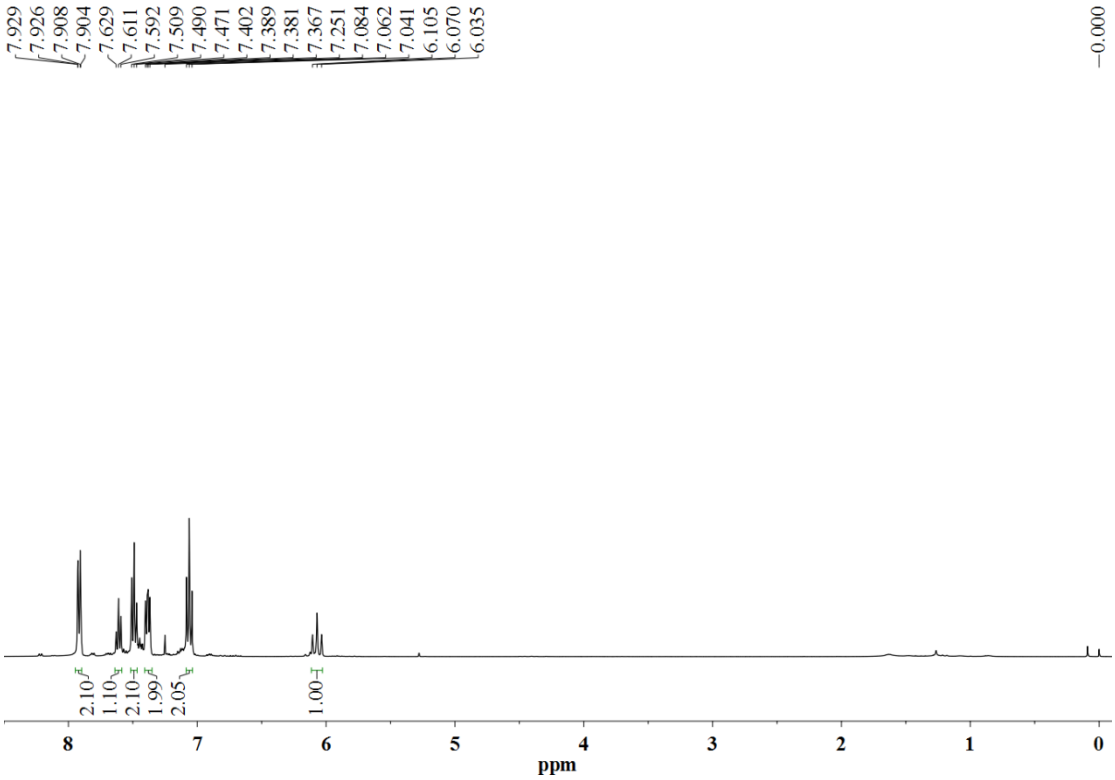
5j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7.367
7.251
7.084
7.062
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6.070
6.035
0.000
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1.00
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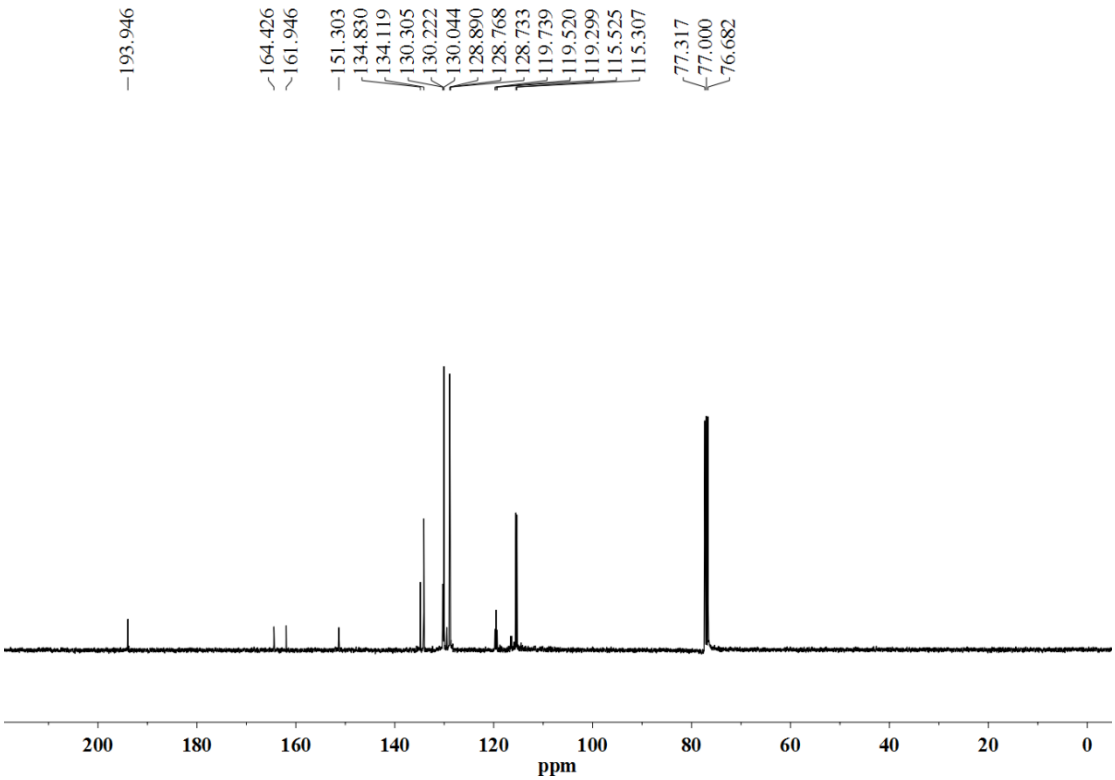
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119.299
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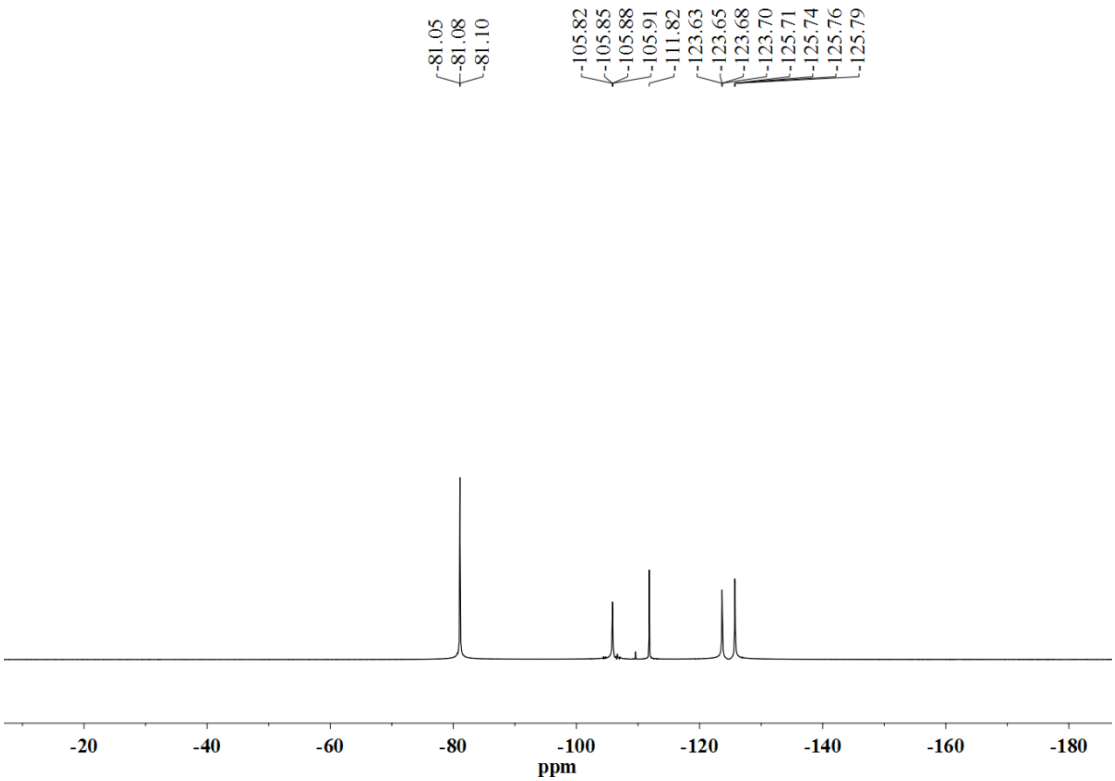
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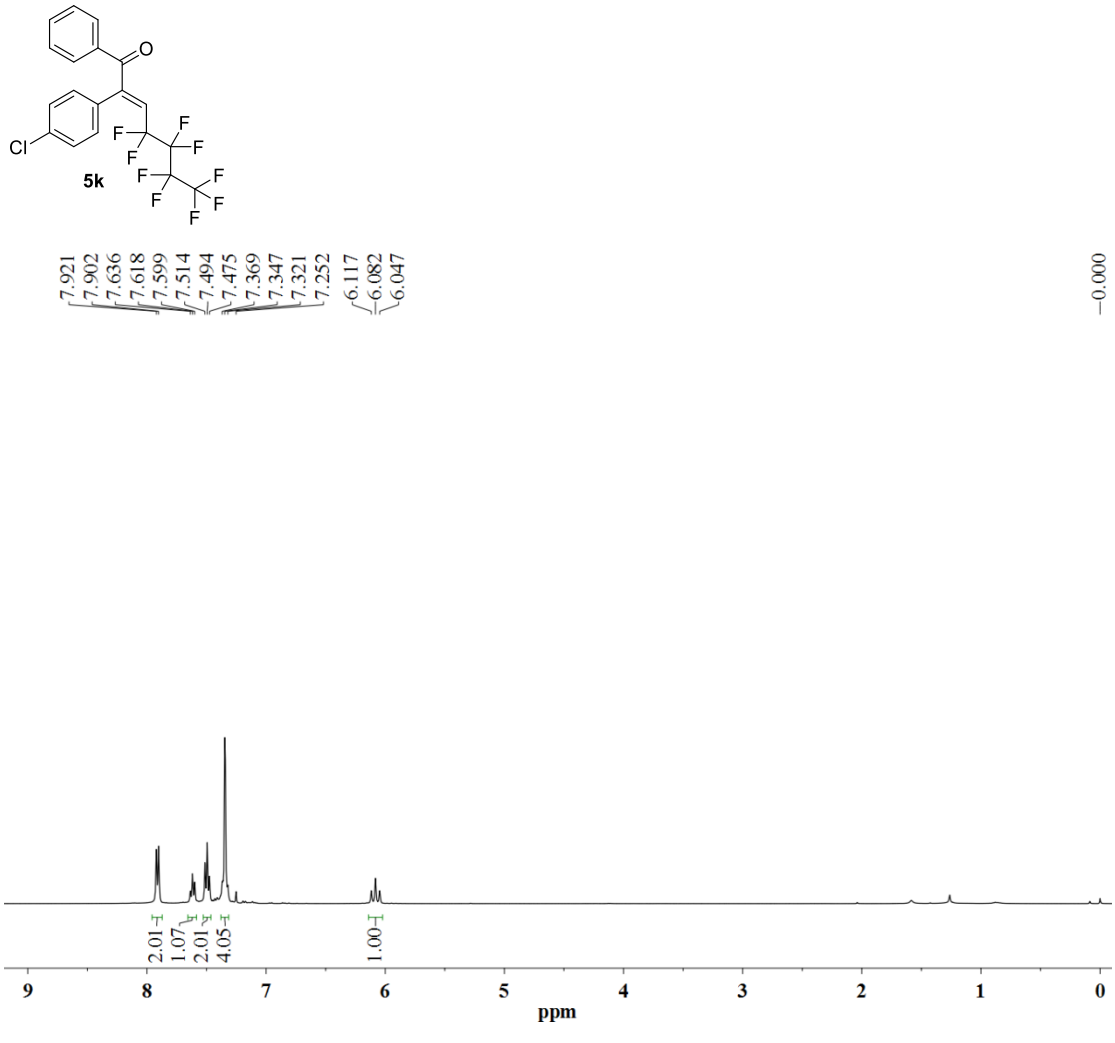
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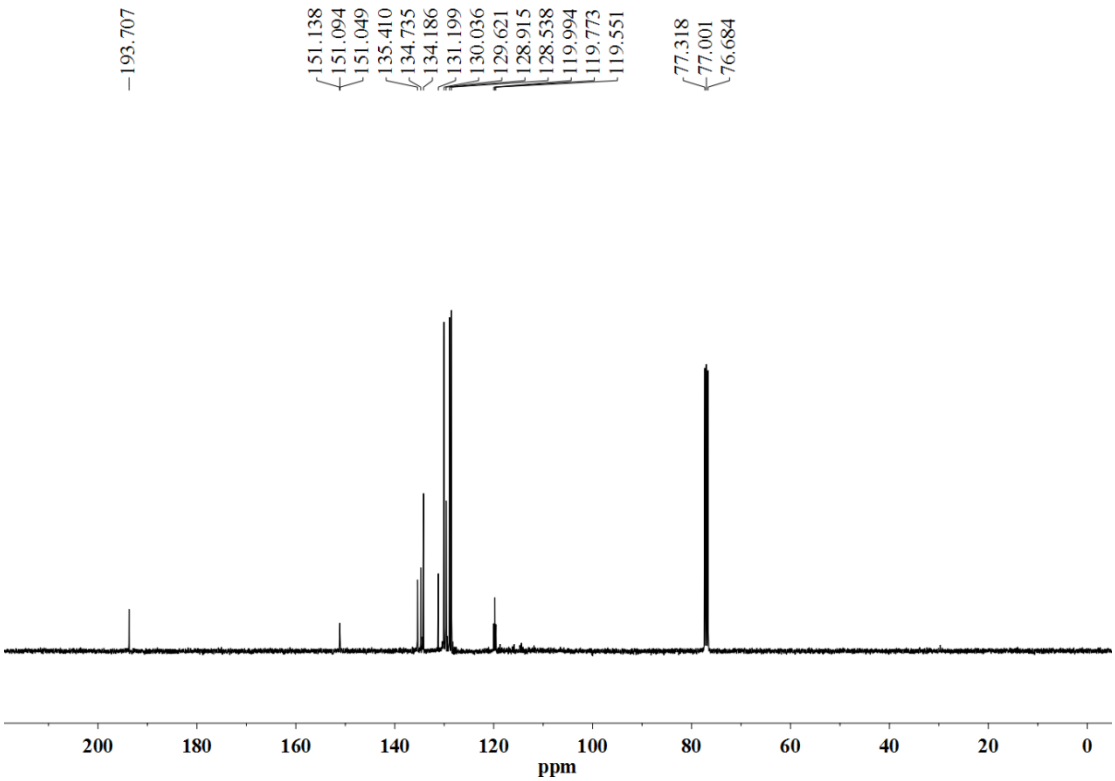
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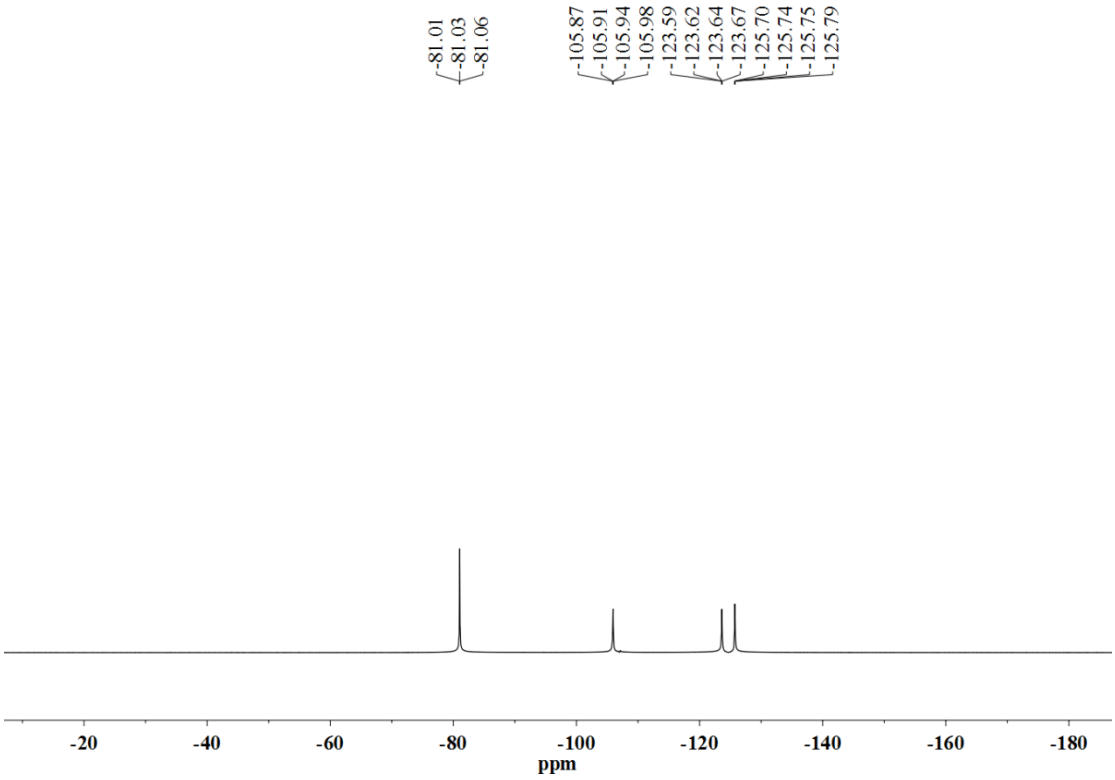
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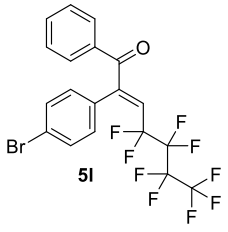
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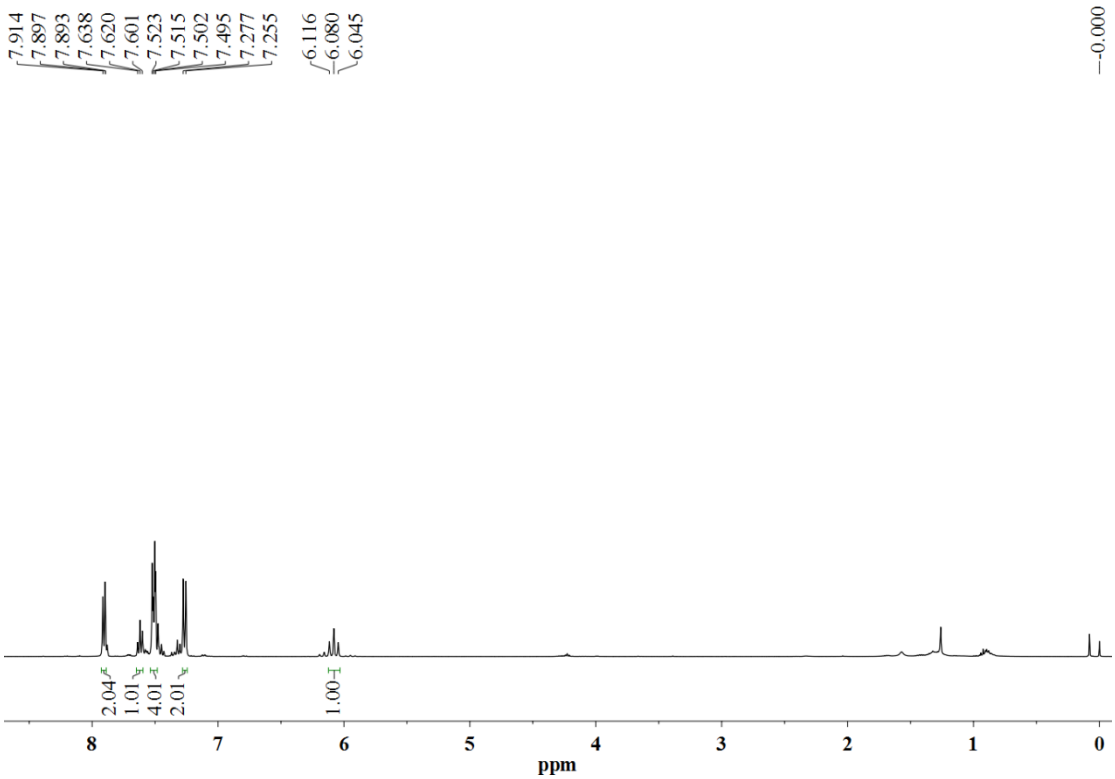
5l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2.01
1.00
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7
6
5
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3
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1
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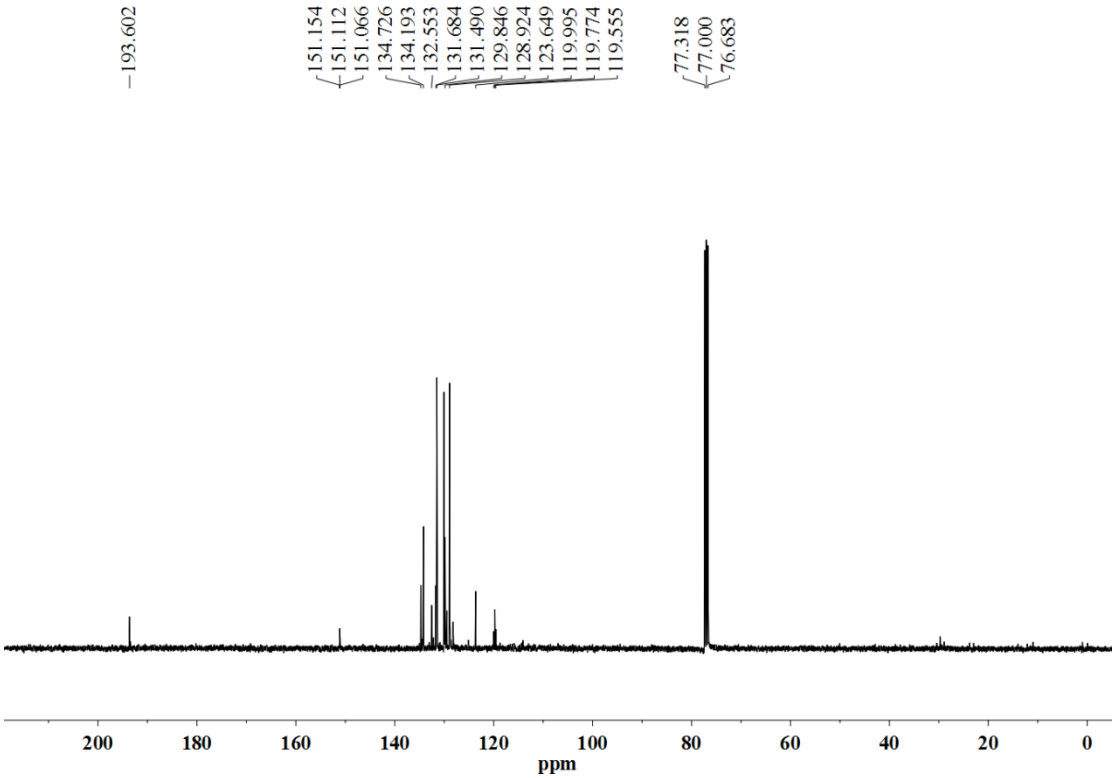
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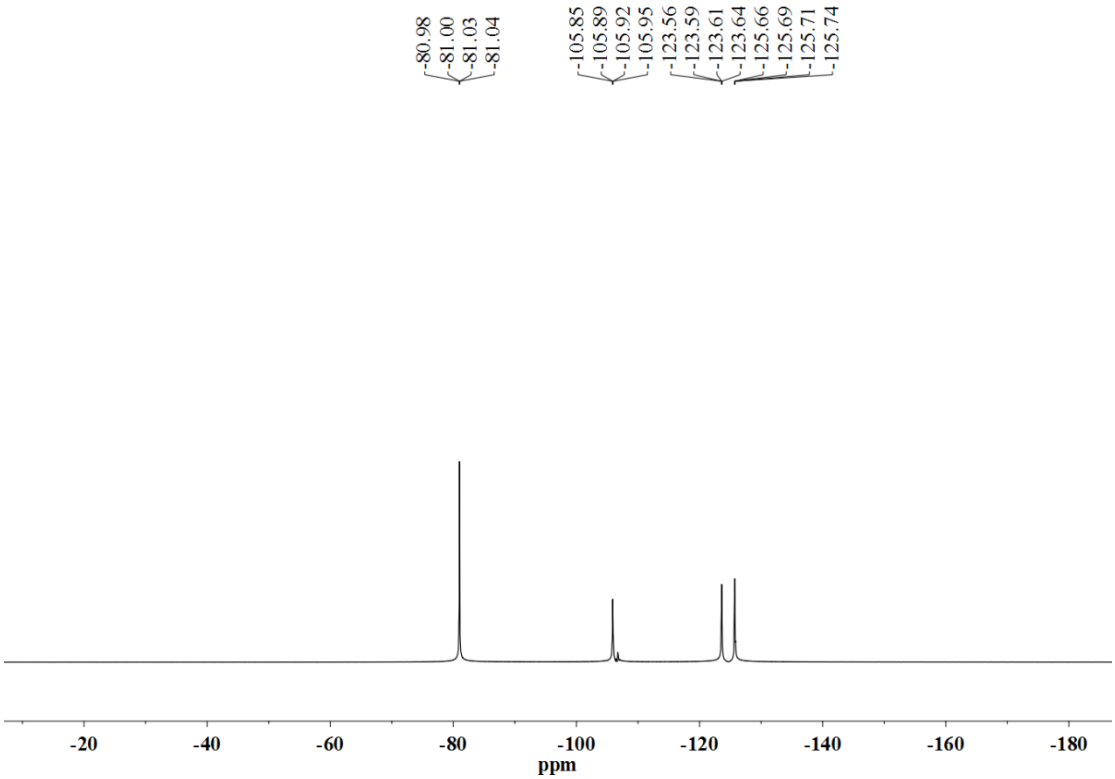
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-180
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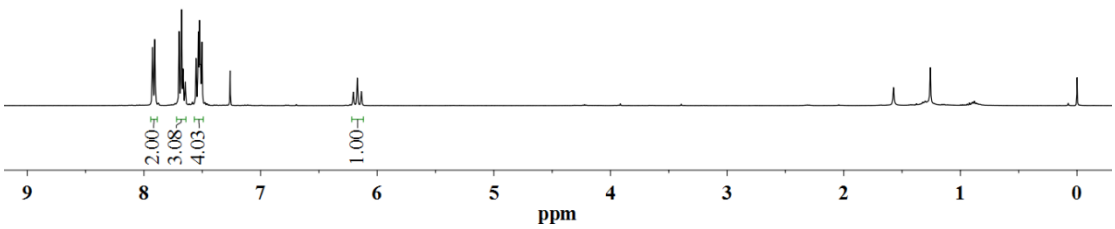
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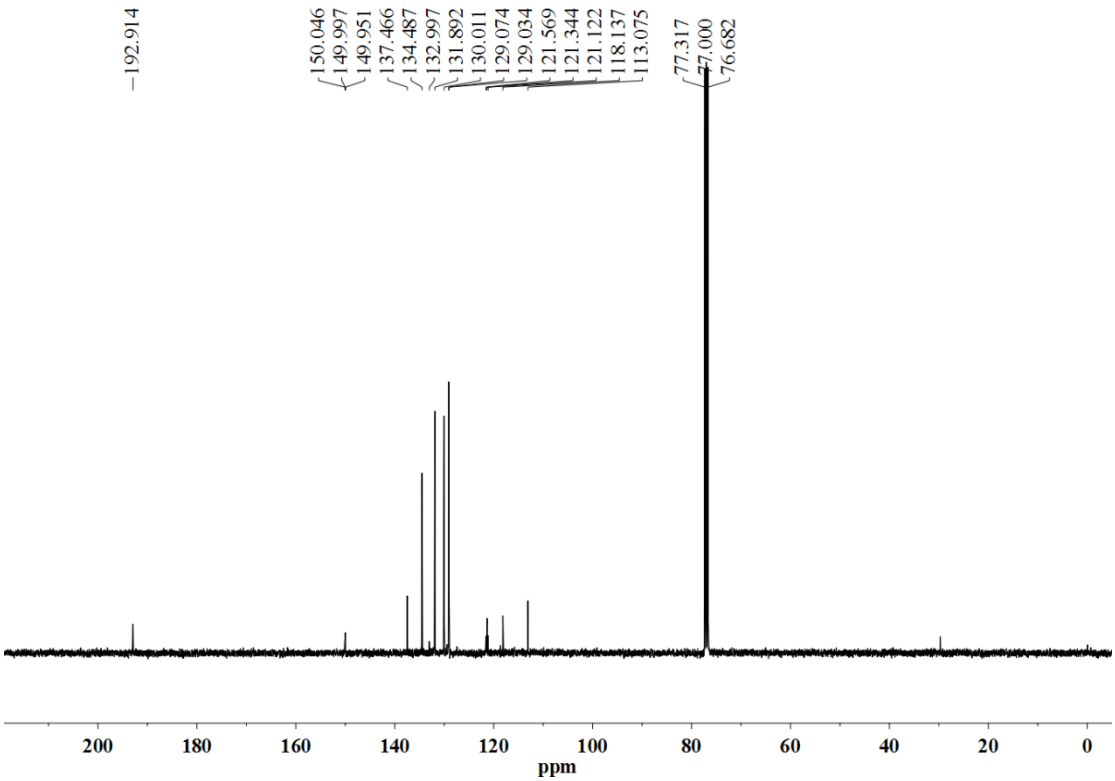
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121.122
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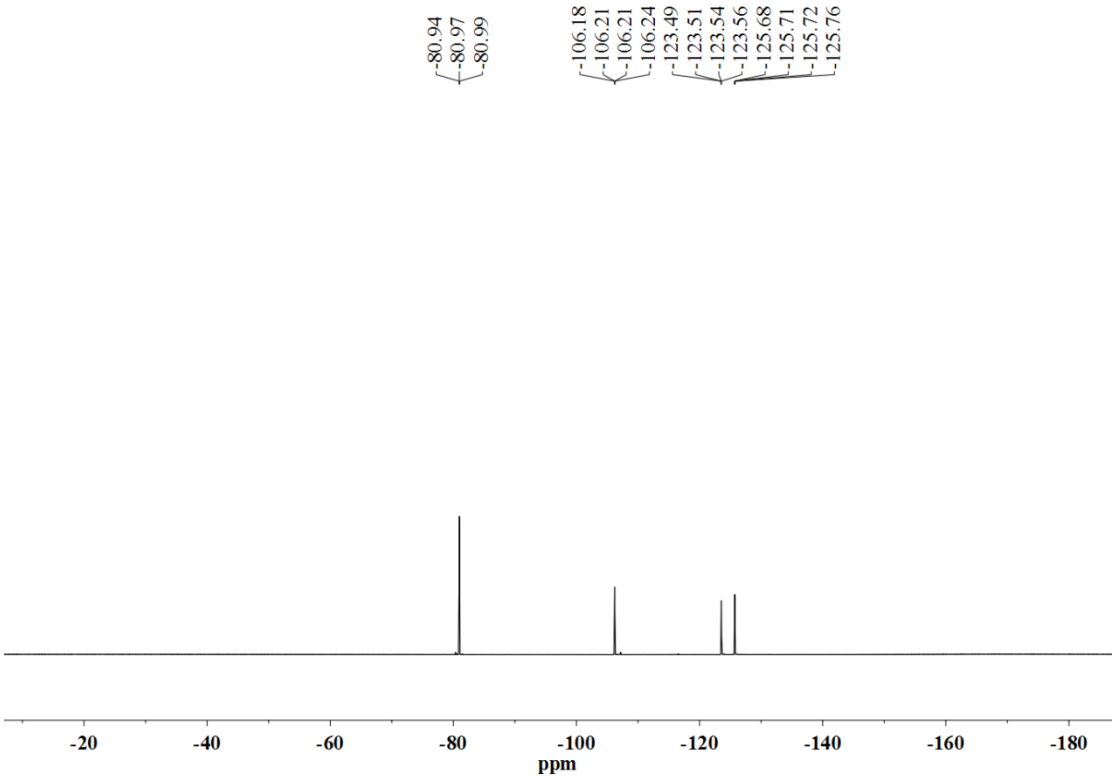
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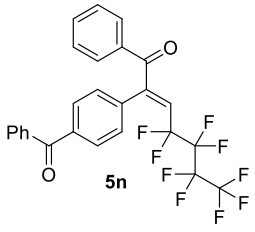
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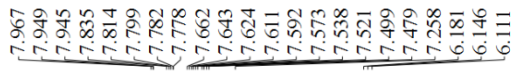
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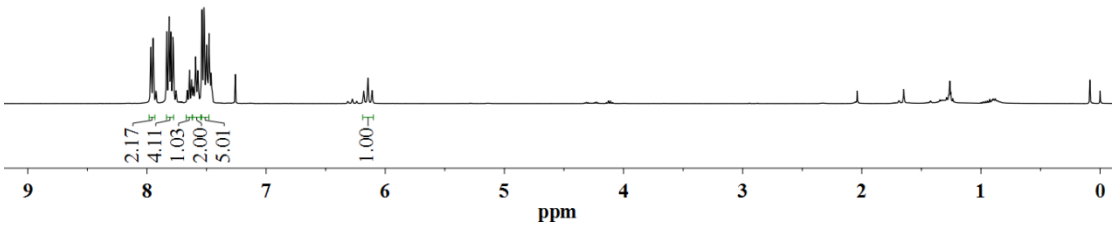
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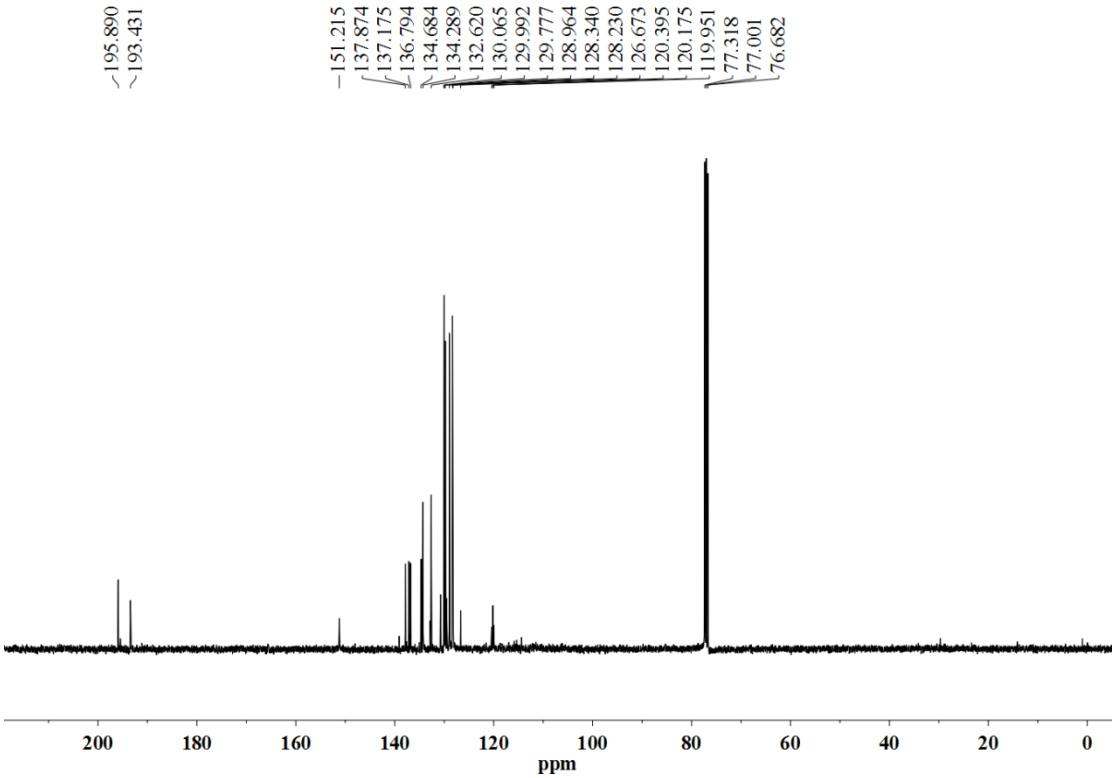
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134.289
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120.395
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77.001
76.682
200
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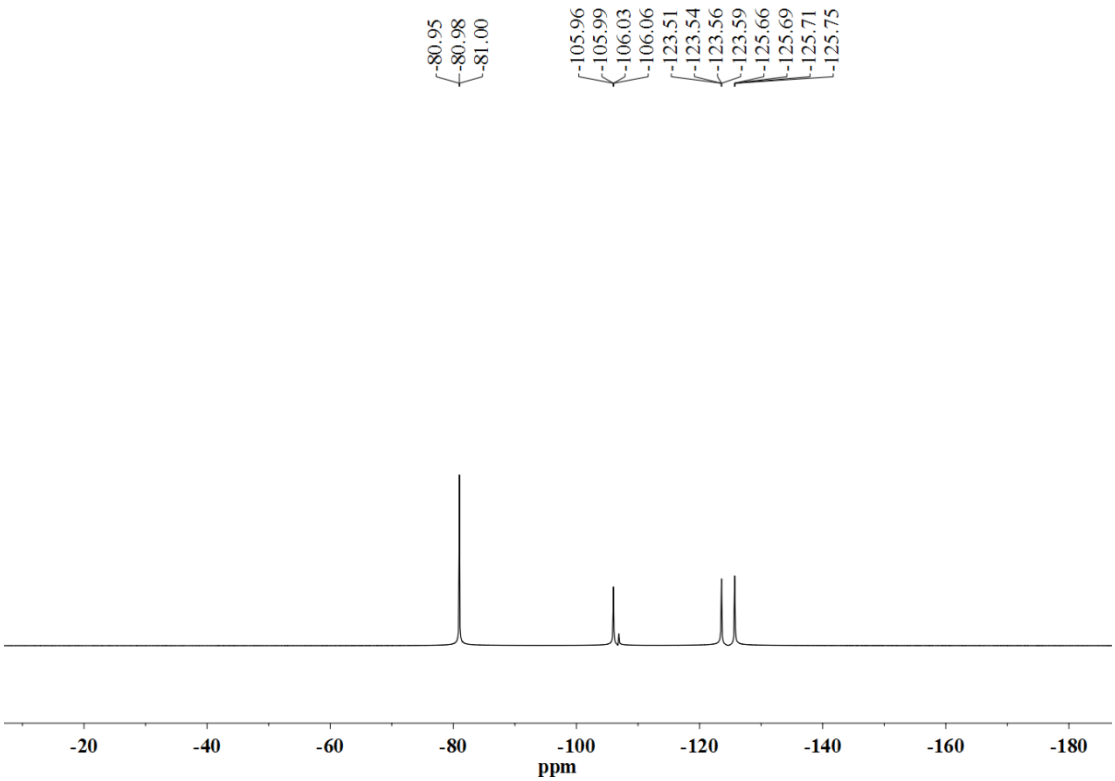
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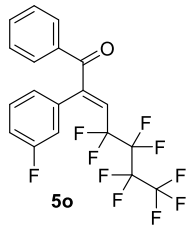
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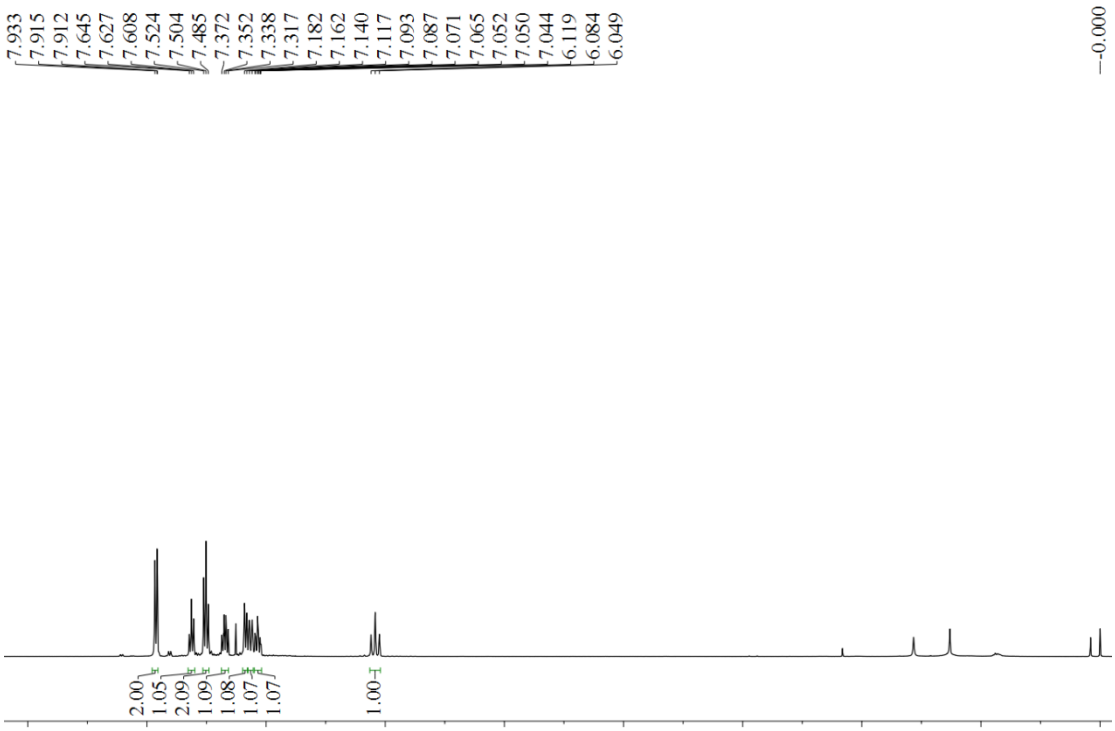
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7.162
7.140
7.117
7.093
7.087
7.071
7.065
7.052
7.050
7.044
6.119
6.084
6.049
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1.05
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1.07
1.07
1.00
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6
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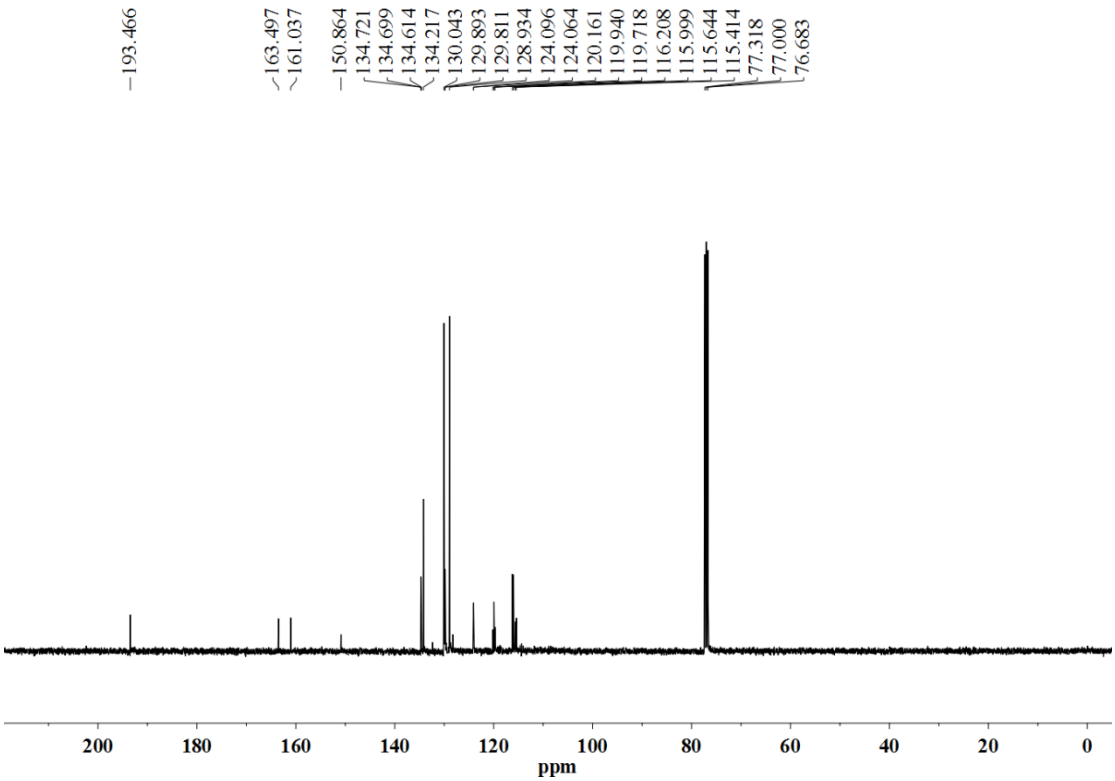
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124.064
120.161
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119.718
116.208
115.999
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120
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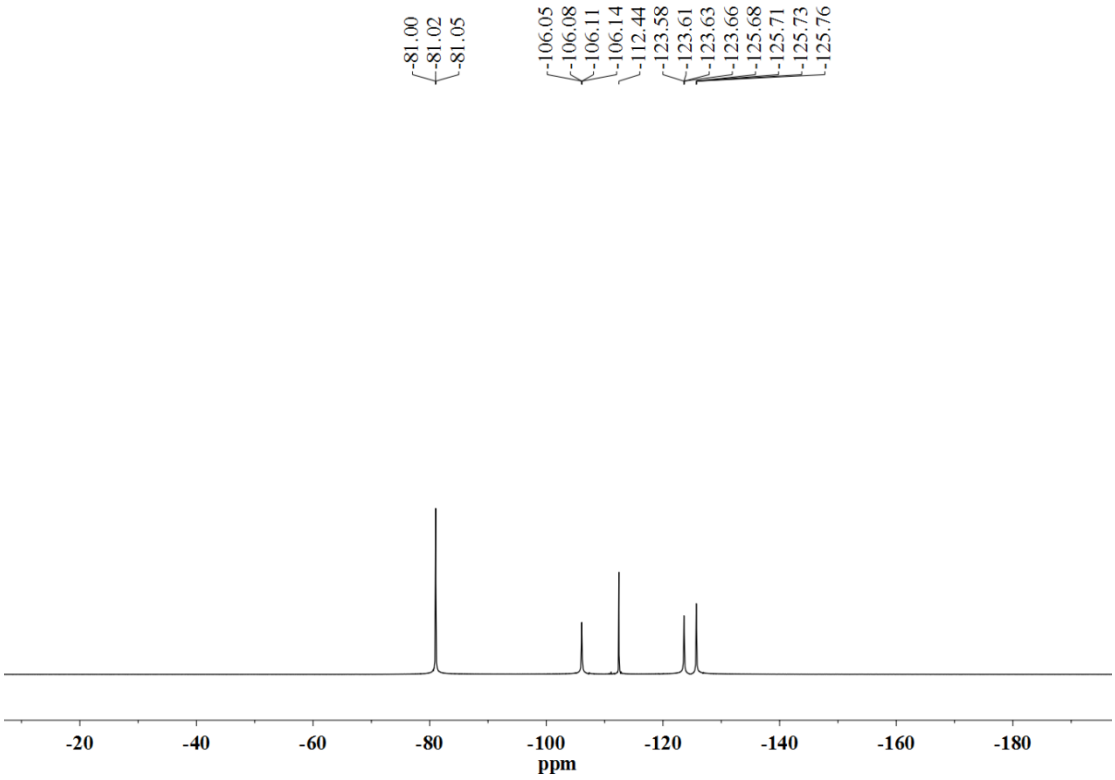
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-180
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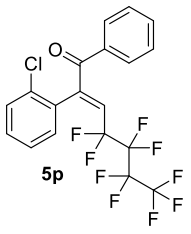
Cl
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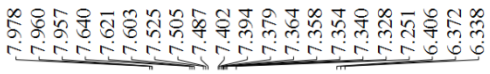
F
F
F

5p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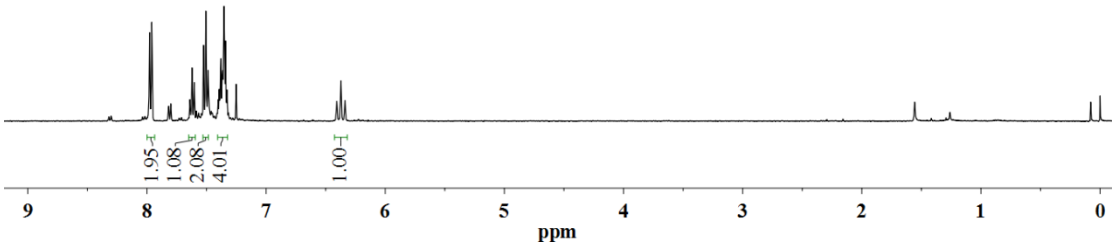
6.372
6.338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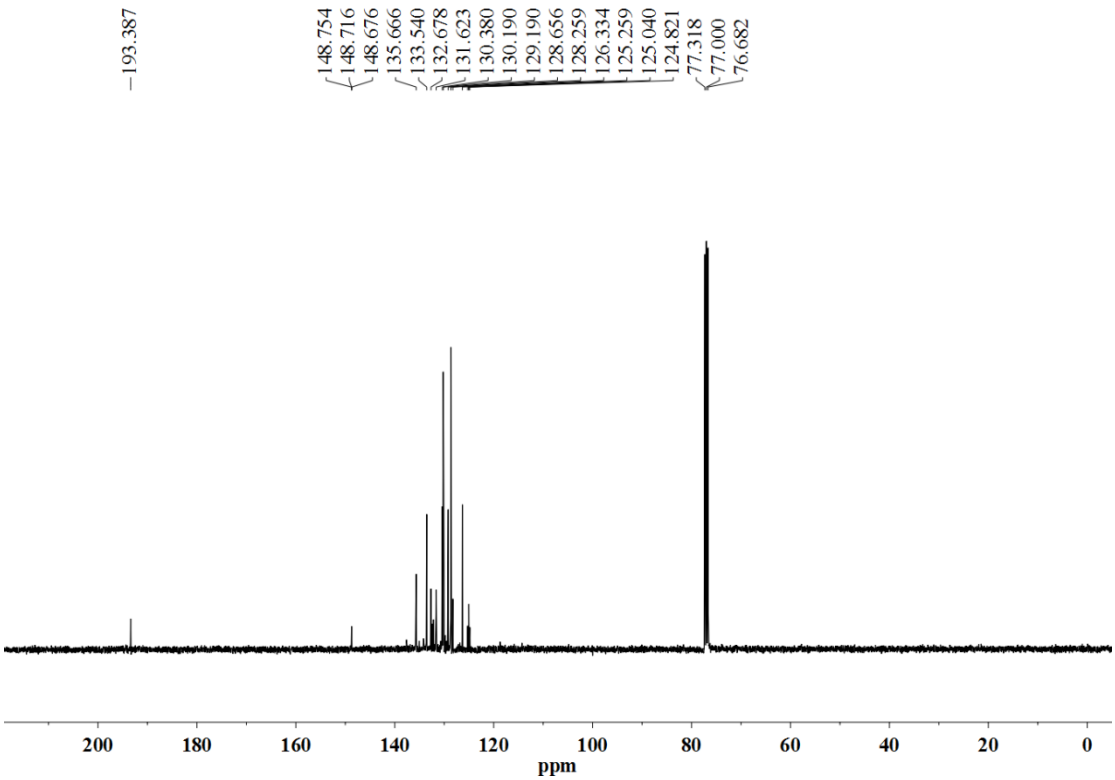
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130.380
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125.259
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77.000
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120
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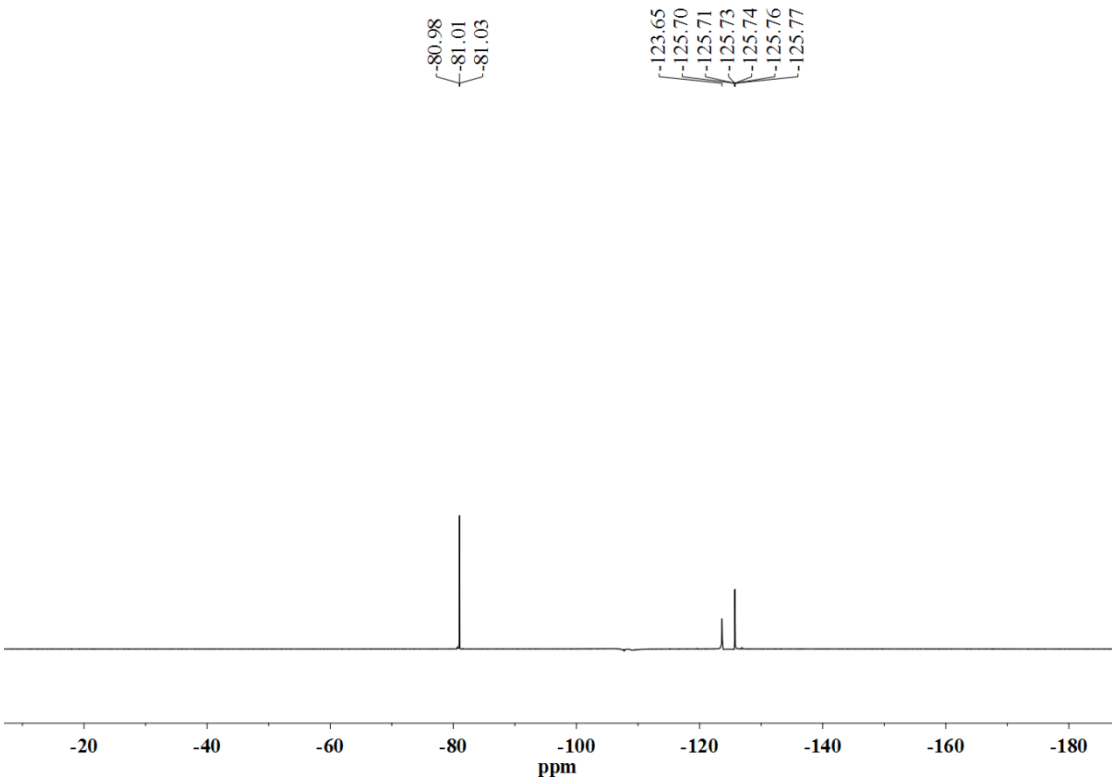
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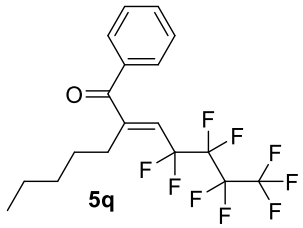
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F
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F
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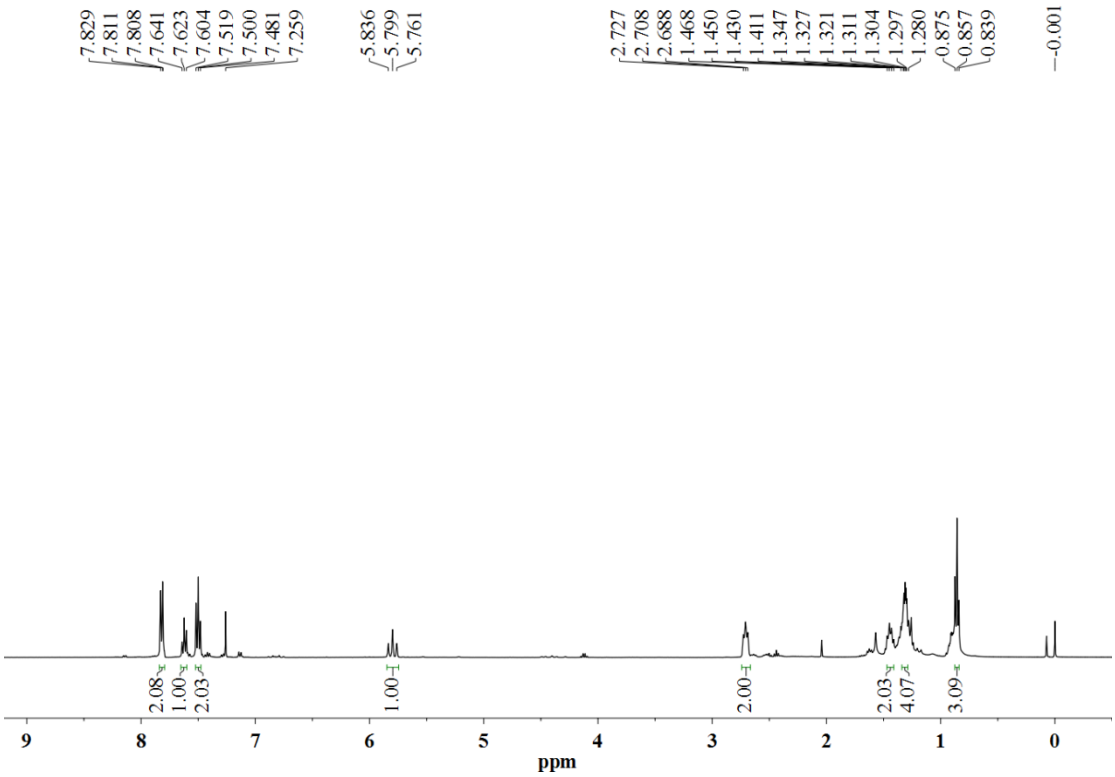
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1.430
1.411
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1.327
1.321
1.311
1.304
1.297
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0.857
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1.00
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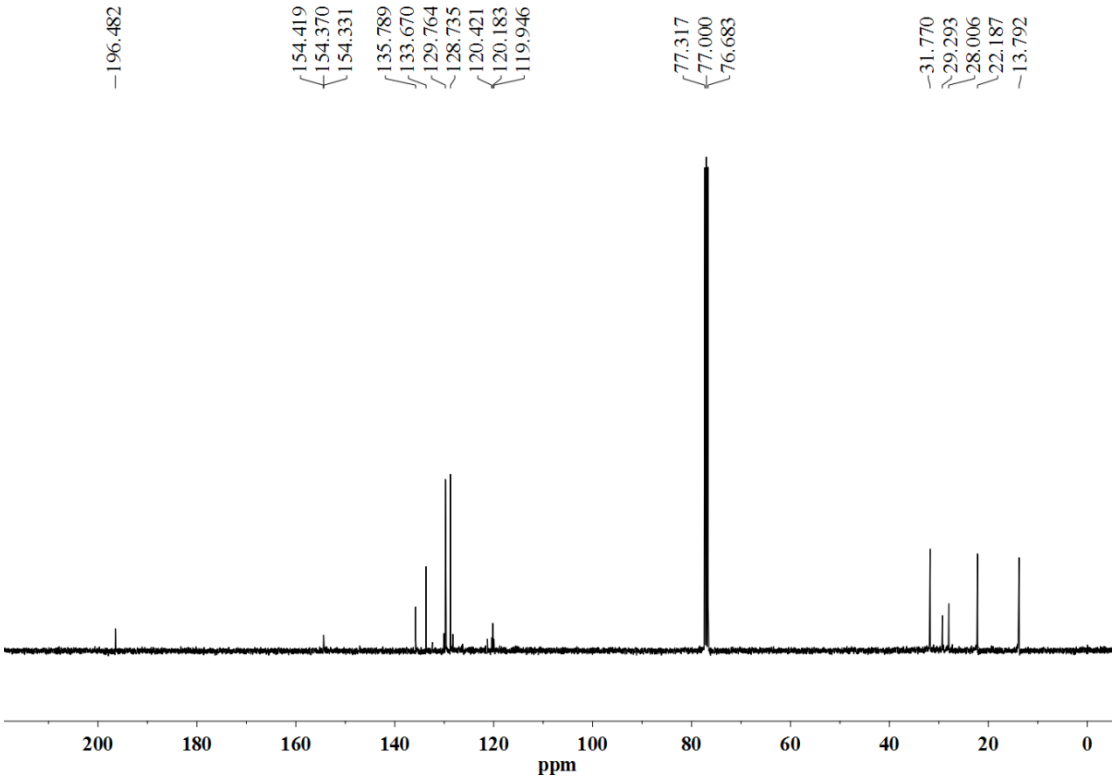
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76.683
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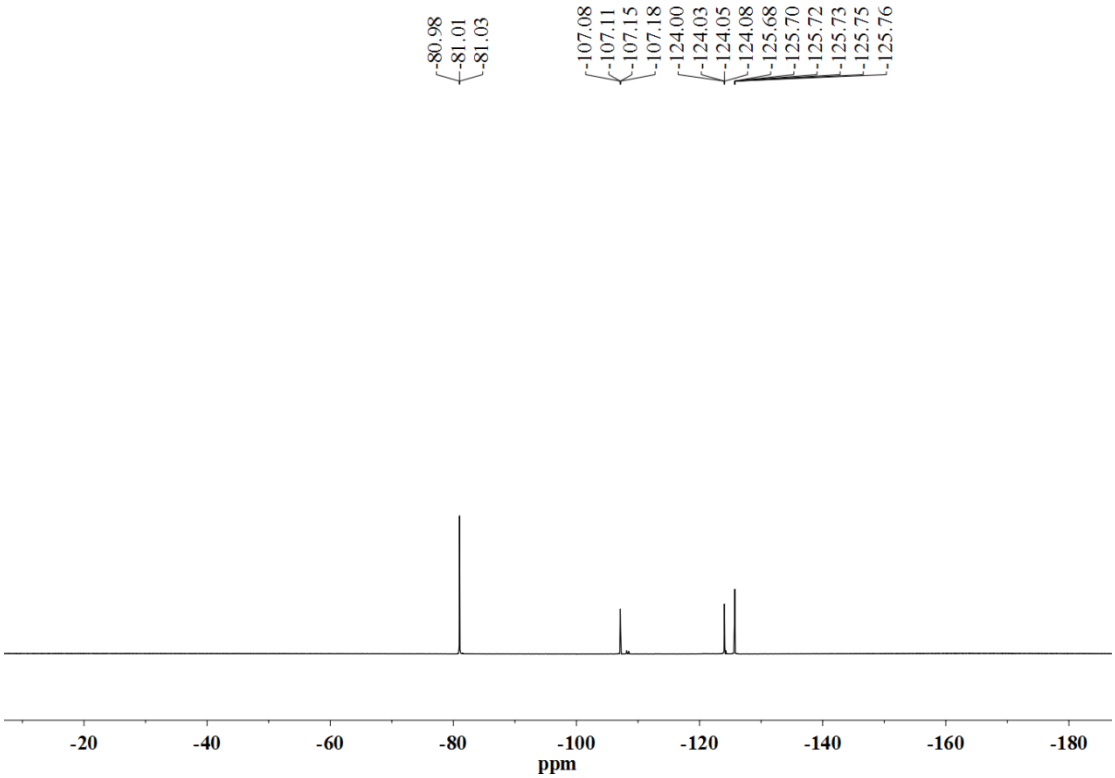
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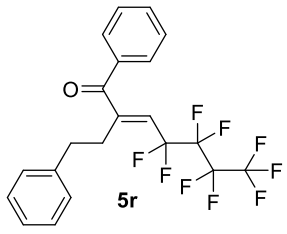
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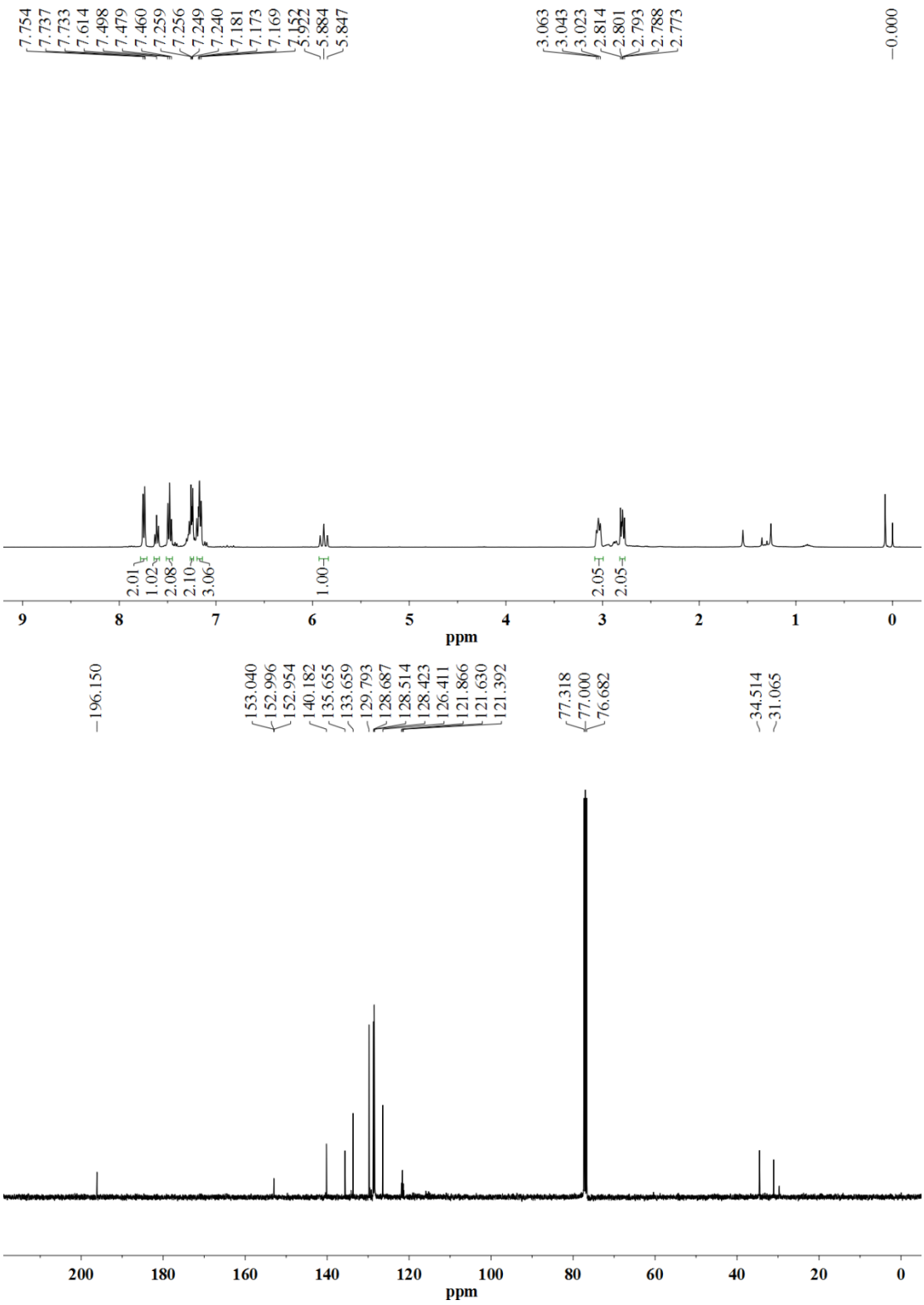
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7.173
7.169
7.152
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5.884
5.847
3.063
3.043
3.023
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2.801
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1.02
2.08
2.10
3.06
1.00
2.05
2.05
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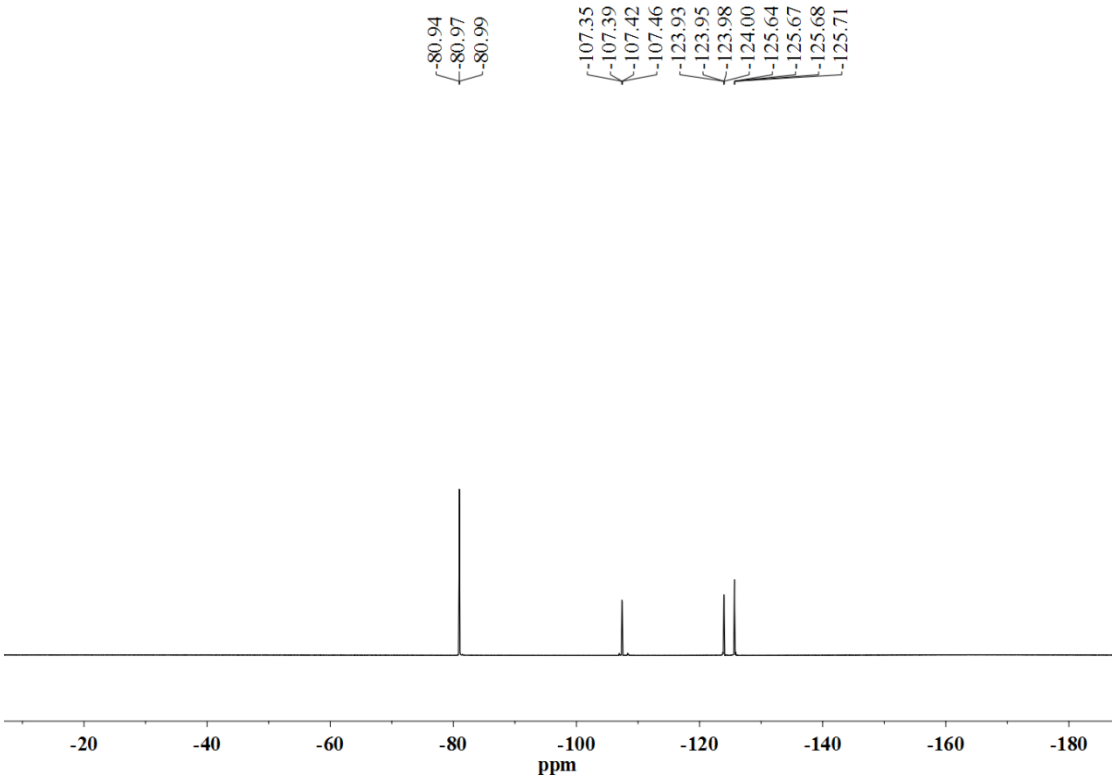
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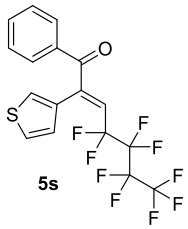
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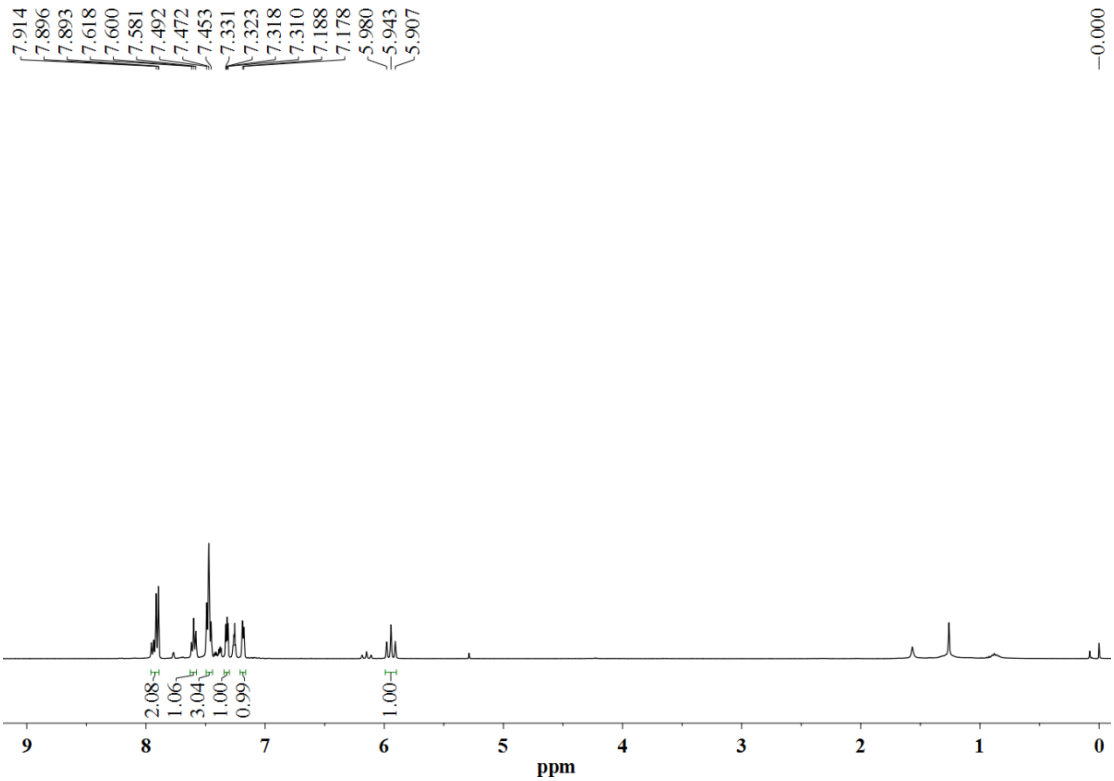
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7.188
7.178
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5.943
5.907
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1.00
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6
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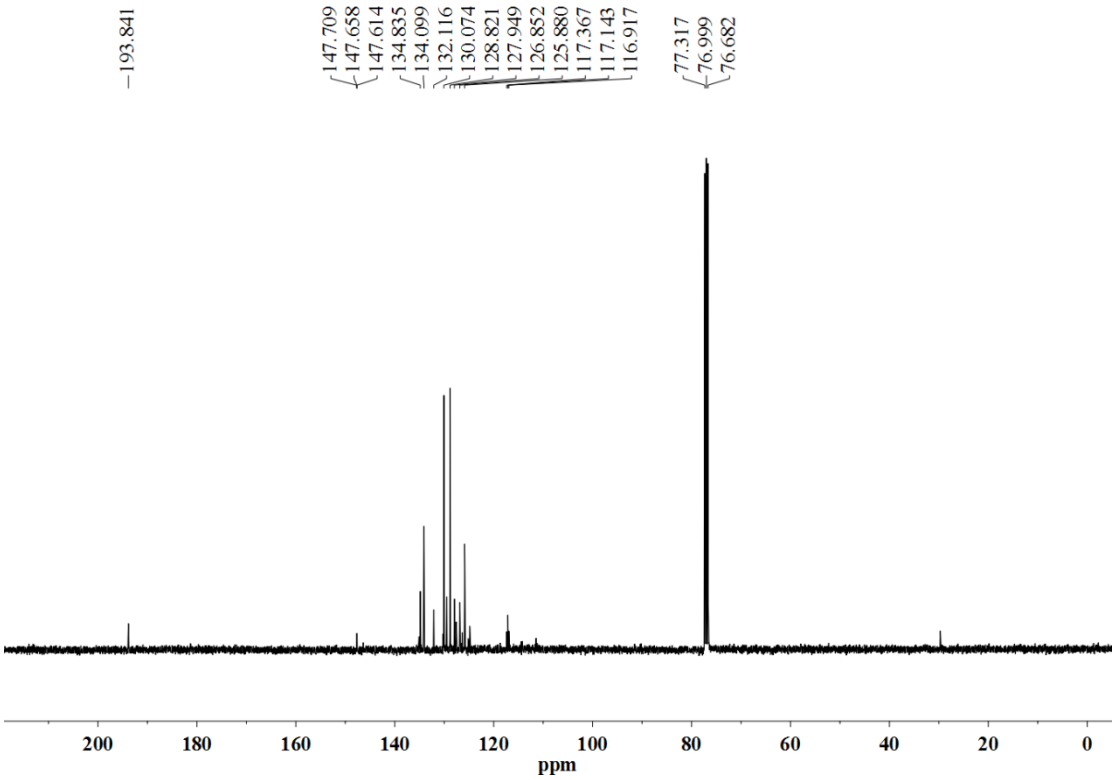
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117.367
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76.999
76.682
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120
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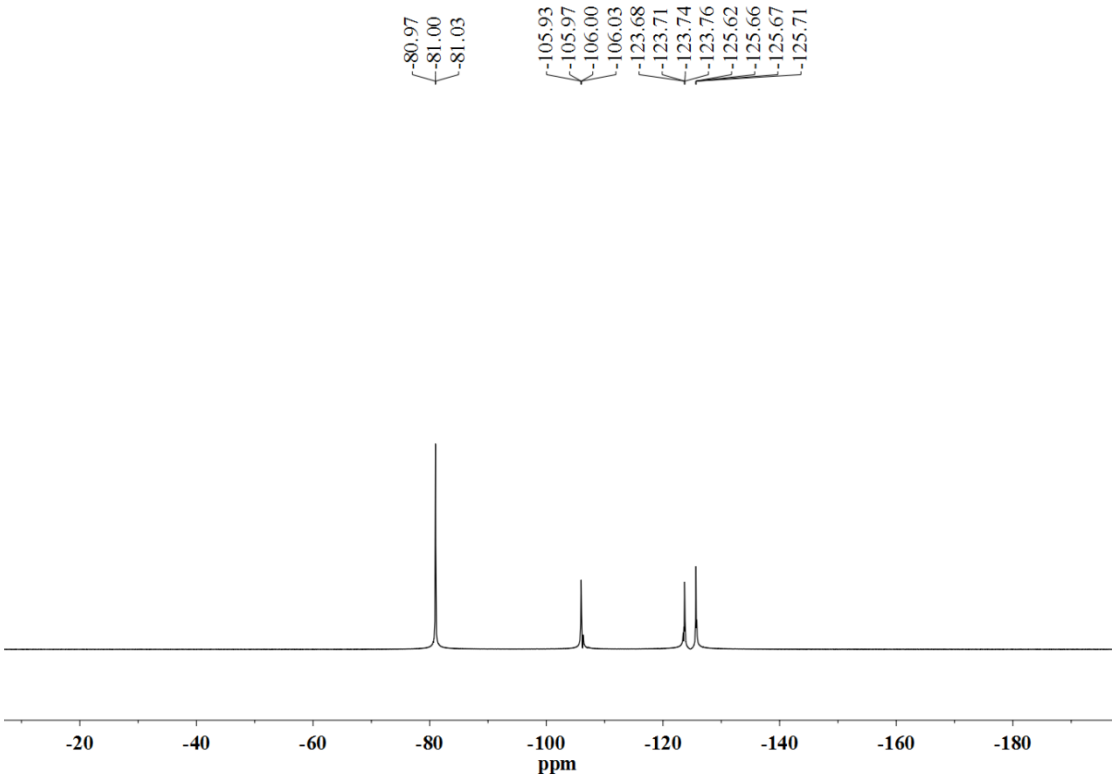
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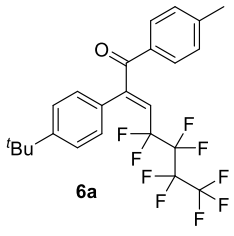
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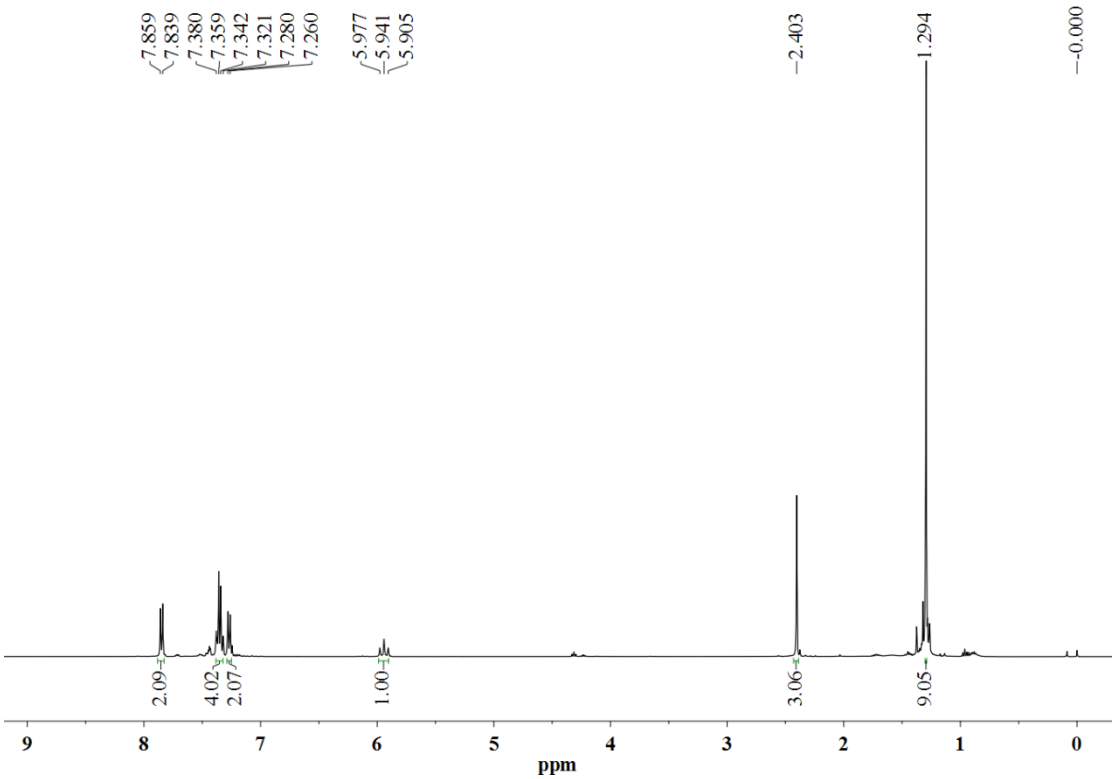
6a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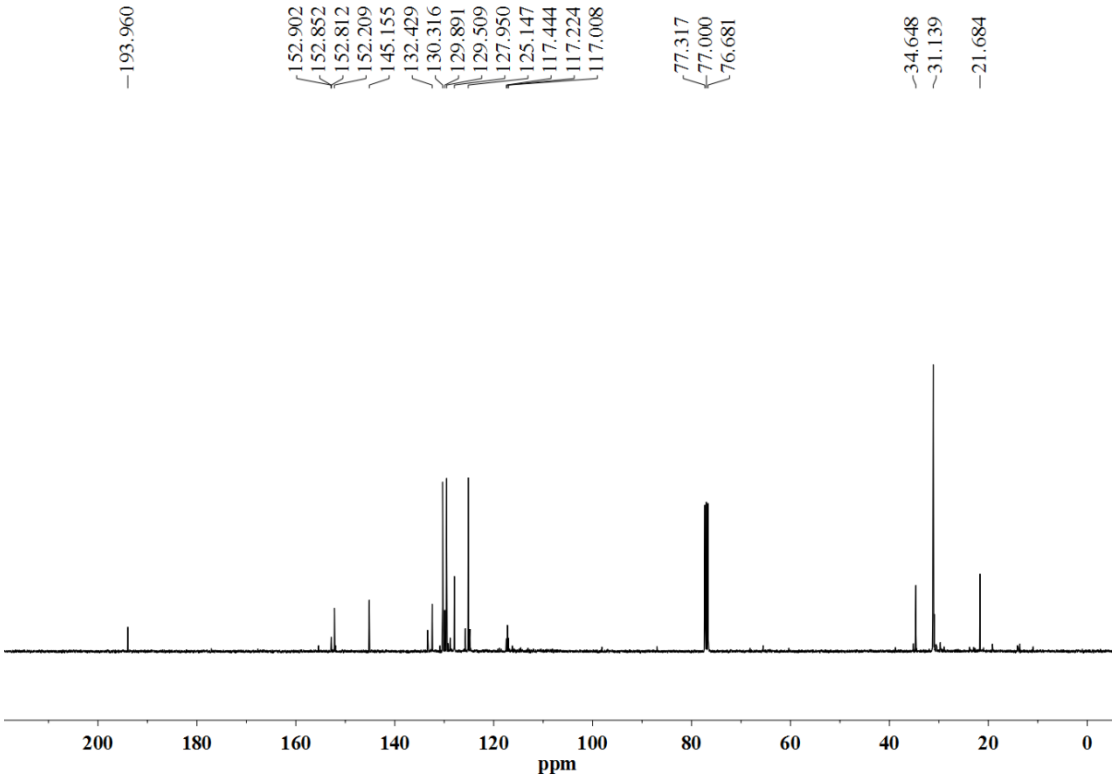
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152.852
152.812
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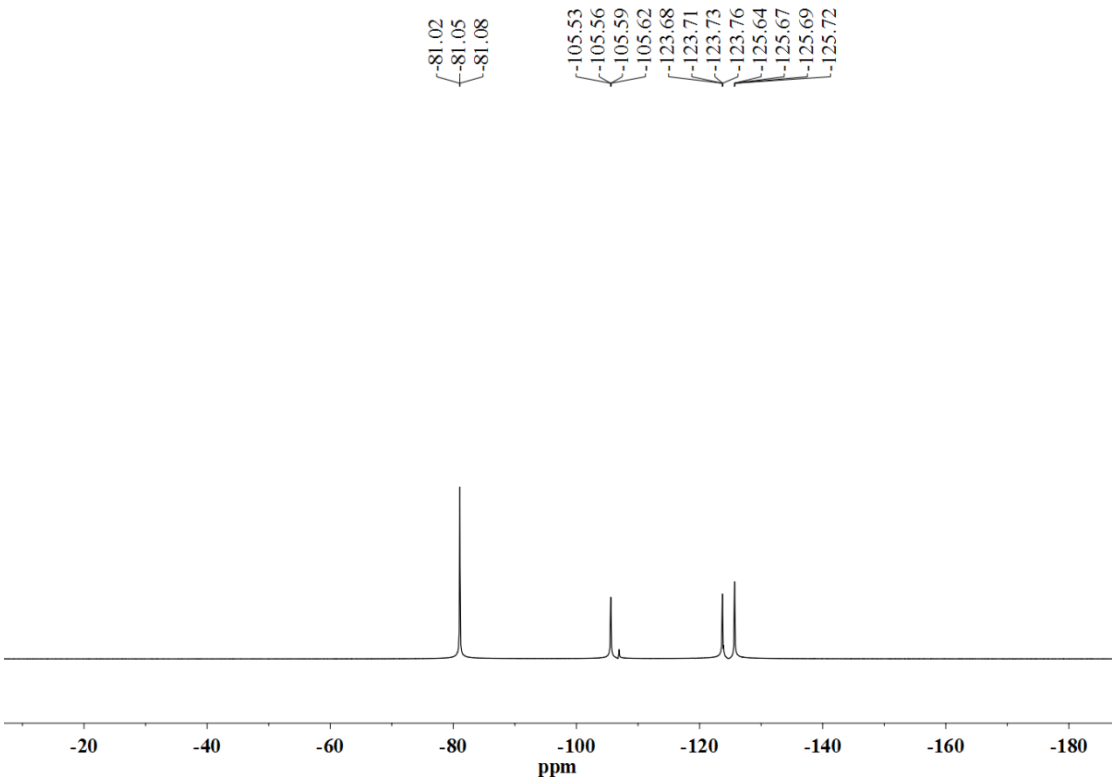
129.891
129.509
127.950
125.147
117.444
117.224
117.008
77.317
77.000
76.681
34.648
31.139
21.684
ppm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-81.08
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-105.56
-105.59
-105.62
-123.68
-123.71
-123.73
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-125.64
-125.67
-125.69
-125.72
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-40
-60
-80
-100
-120
-140
-160
-180
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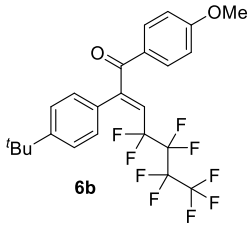
OMe
O
tBu
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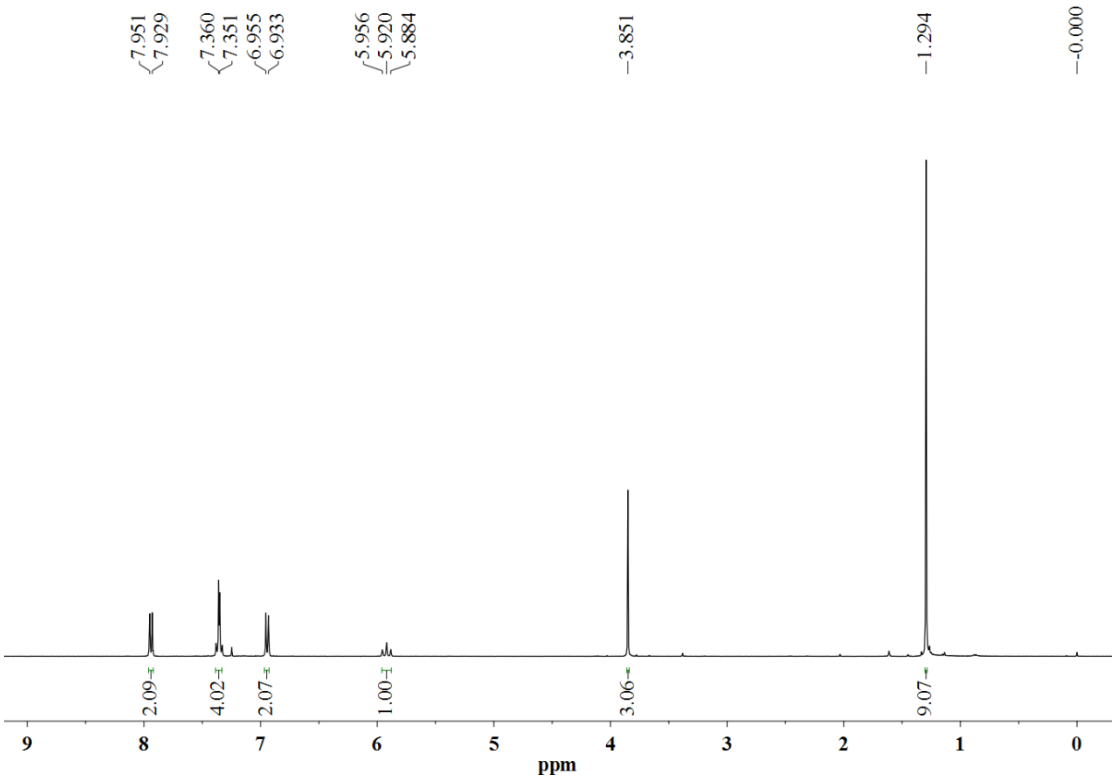
F
F
F

6b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5.920
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3.851
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0.000
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1.00
3.06
9.07
9
8
7
6
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0
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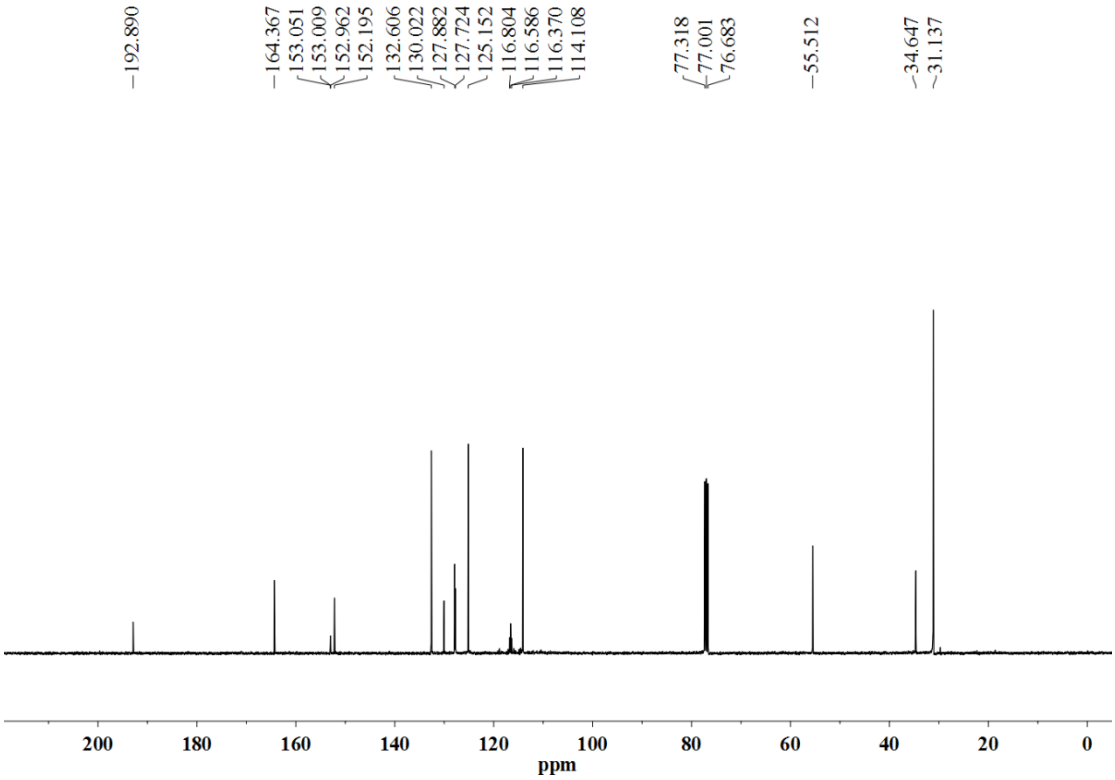
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130.022
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127.724
125.152
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116.586
116.370
114.108
77.318
77.001
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34.647
31.137
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120
100
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40
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0
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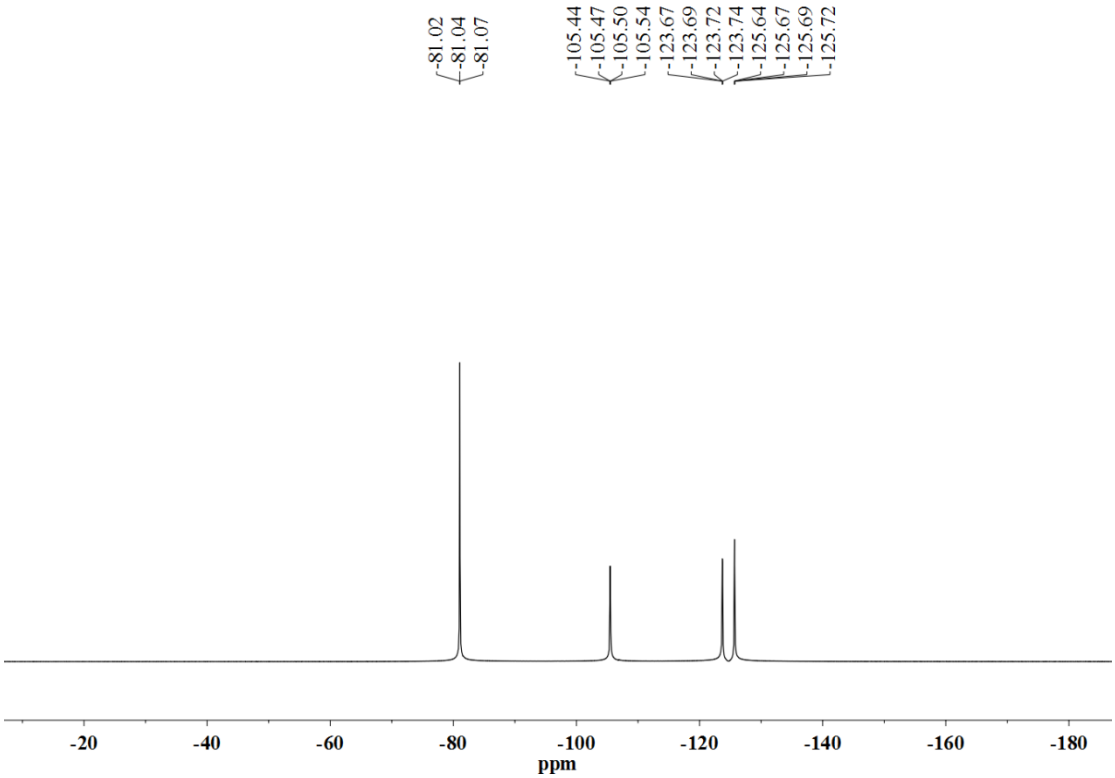
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-105.50
-105.54
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-123.69
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-160
-180
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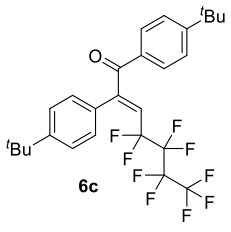
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tBu
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F
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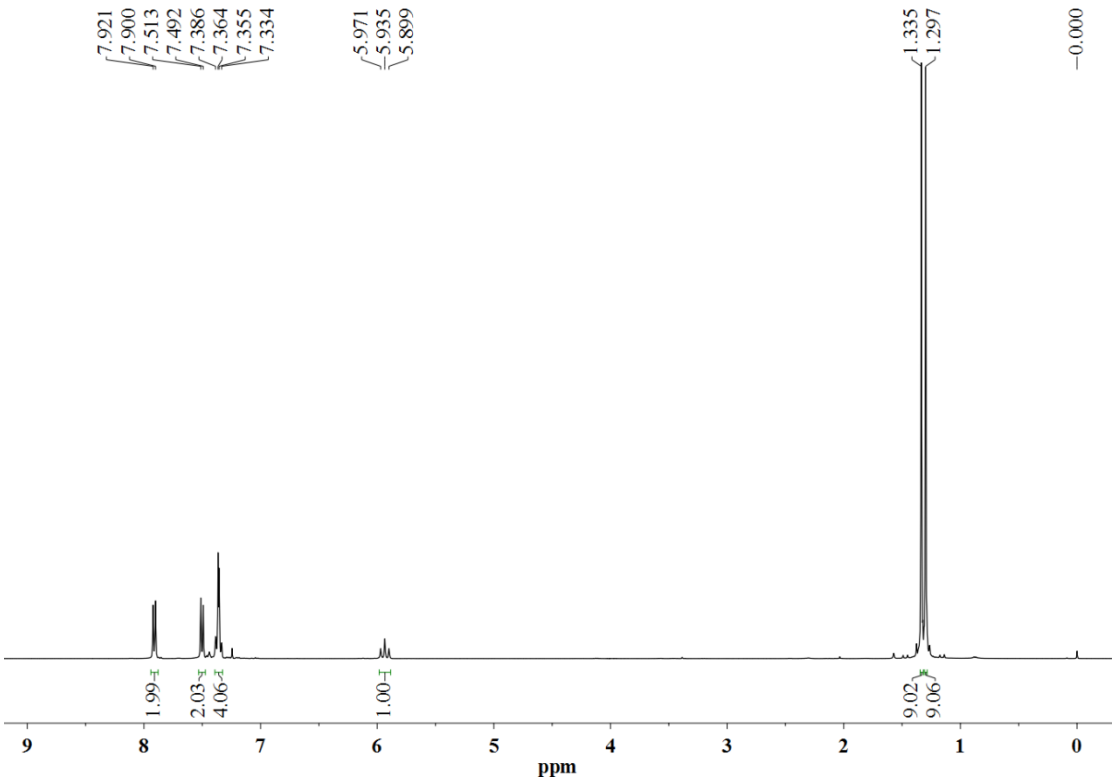
F
F
F

6c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7.900
7.513
7.492
7.386
7.364
7.355
7.334
5.971
5.935
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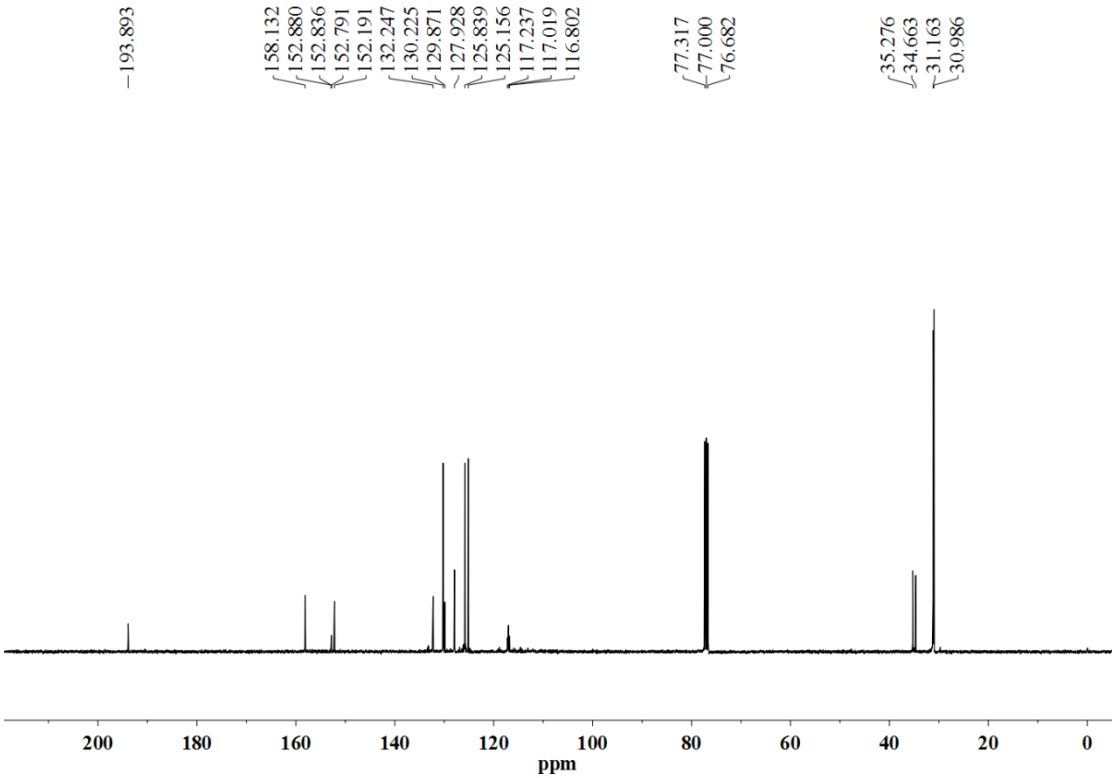
1.335
1.297
0.000
1.99
2.03
4.06
1.00
9.02
9.06
ppm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158.132
152.880
152.836
152.791
152.191
132.247
130.225
129.871
127.928
125.839
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117.019
116.802
77.317
77.000
76.682
35.276
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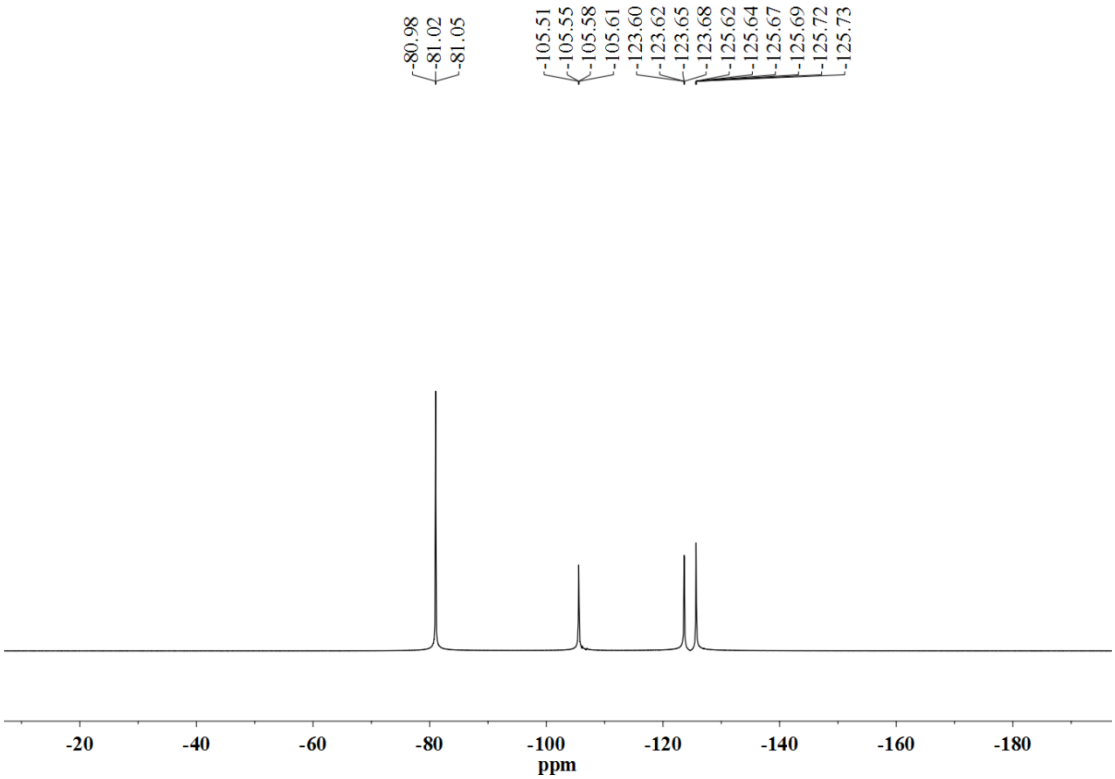
31.163
30.986
ppm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-105.51
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-105.58
-105.61
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-123.62
-123.65
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-125.64
-125.67
-125.69
-125.72
-125.73
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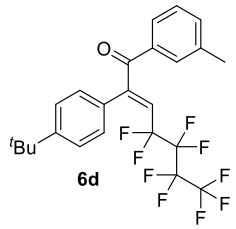
-40
-60
-80
-100
-120
-140
-160
-180
ppm


O
tBu
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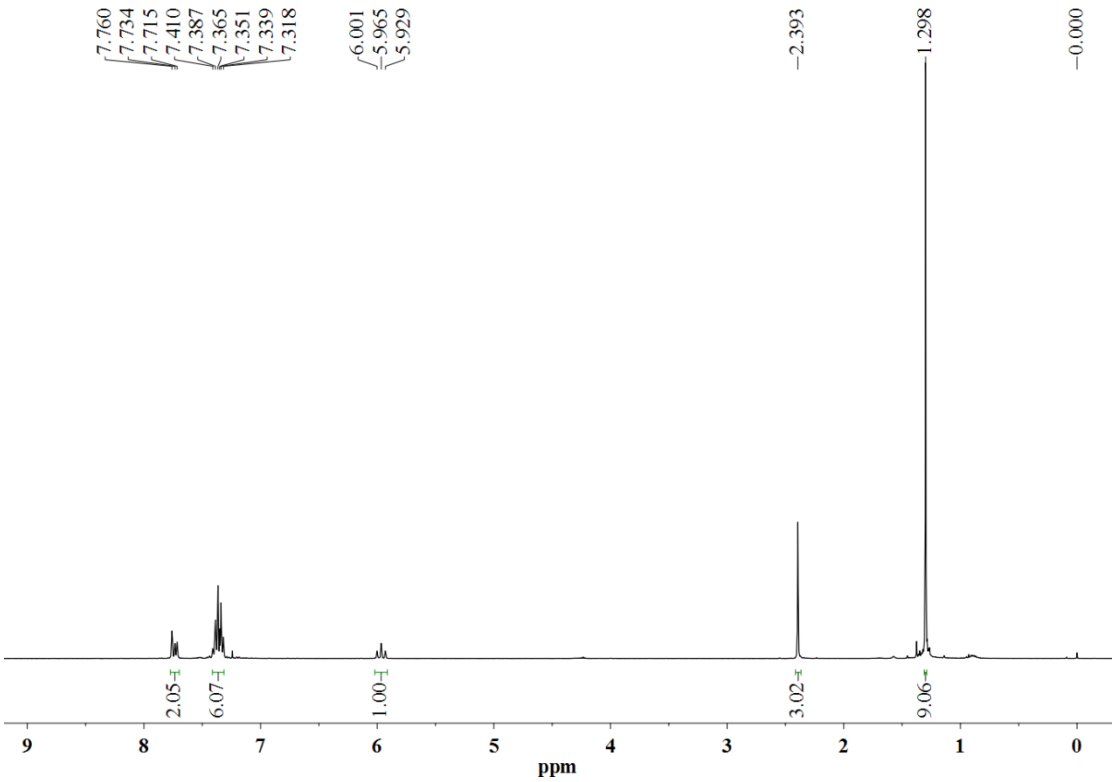
F
F
F
F
F
F
F
F

6d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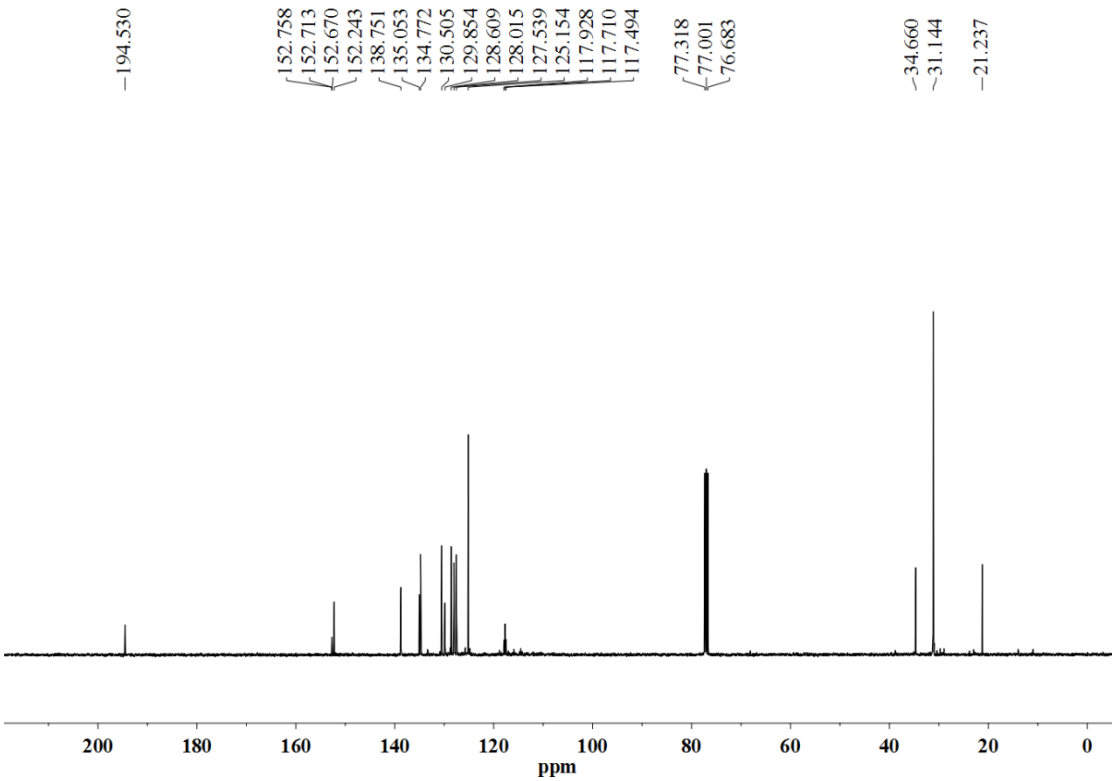
7.715
7.410
7.387
7.365
7.351
7.339
7.318
6.001
5.965
5.929
2.393
1.298
0.000
2.05
6.07
1.00
3.02
9.06
9
8
7
6
5
4
3
2
1
0
ppm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152.713
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138.751
135.053
134.772
130.505
129.854
128.609
128.015
127.539
125.154
117.928
117.710
117.494
77.318
77.001
76.683
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31.144
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200
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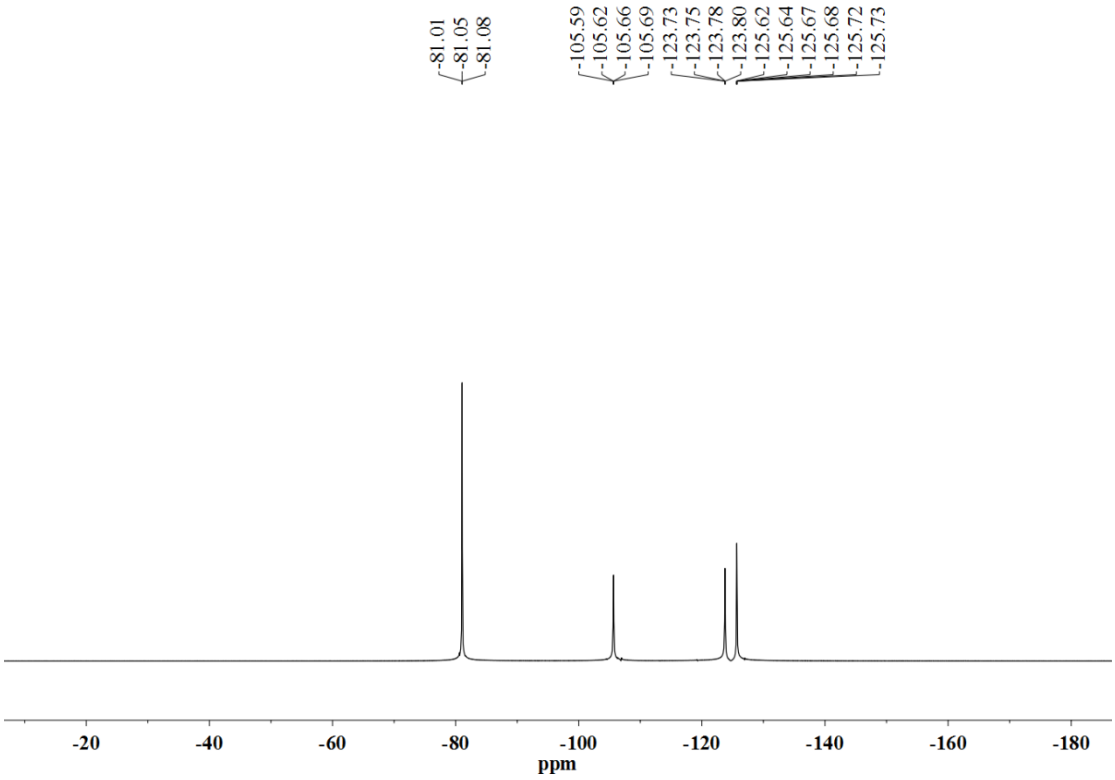
160
140
120
100
80
60
40
20
0
ppm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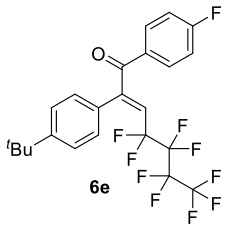
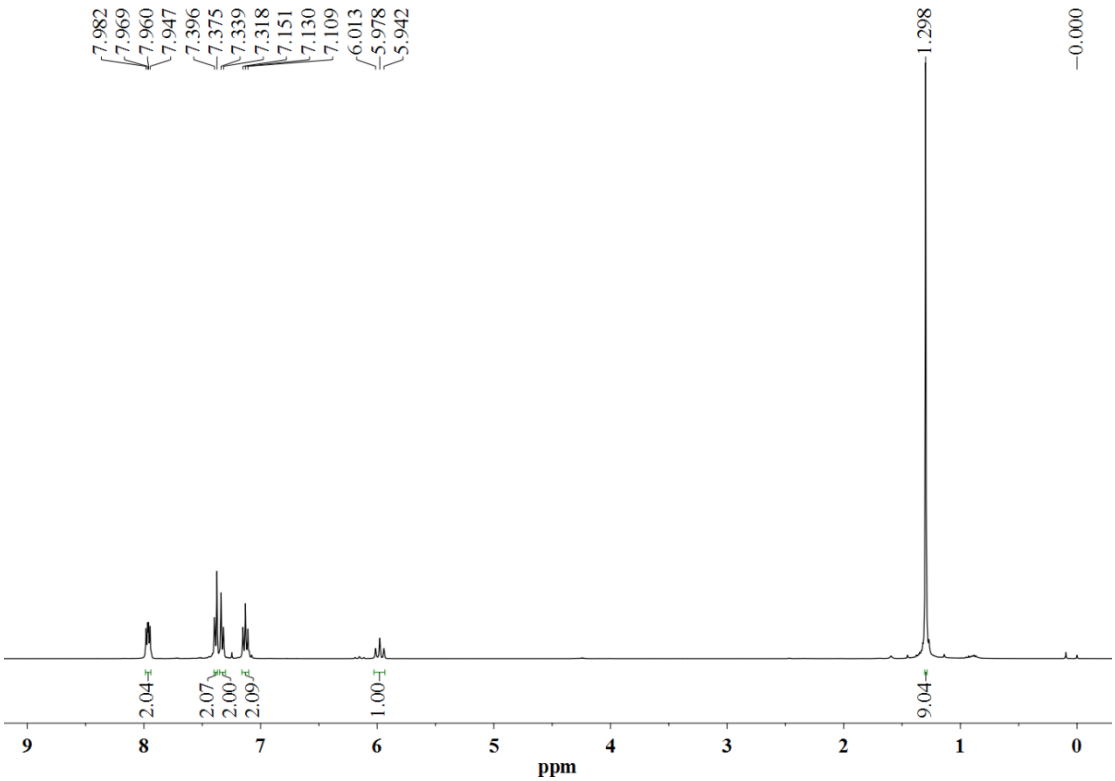
-81.05
-81.08
-105.59
-105.62
-105.66
-105.69
-123.73
-123.75
-123.78
-123.80
-125.62
-125.64
-125.67
-125.68
-125.72
-125.73
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


O
F
F
F
F
F
F
F
F
F
F
tBu

6e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7.969
7.960
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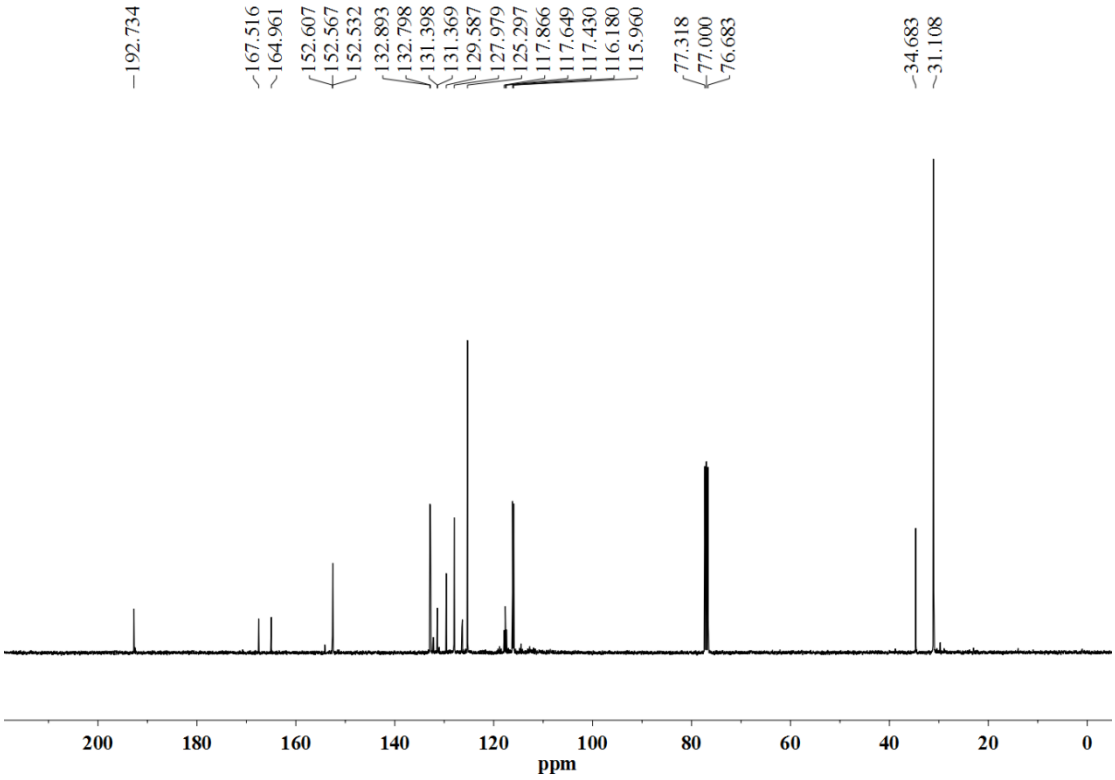
7.375
7.339
7.318
7.151
7.130
7.109
6.013
5.978
5.942
1.298
0.000
2.04
2.07
2.00
2.09
1.00
9.04
9
8
7
6
5
4
3
2
1
0
ppm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152.567
152.532
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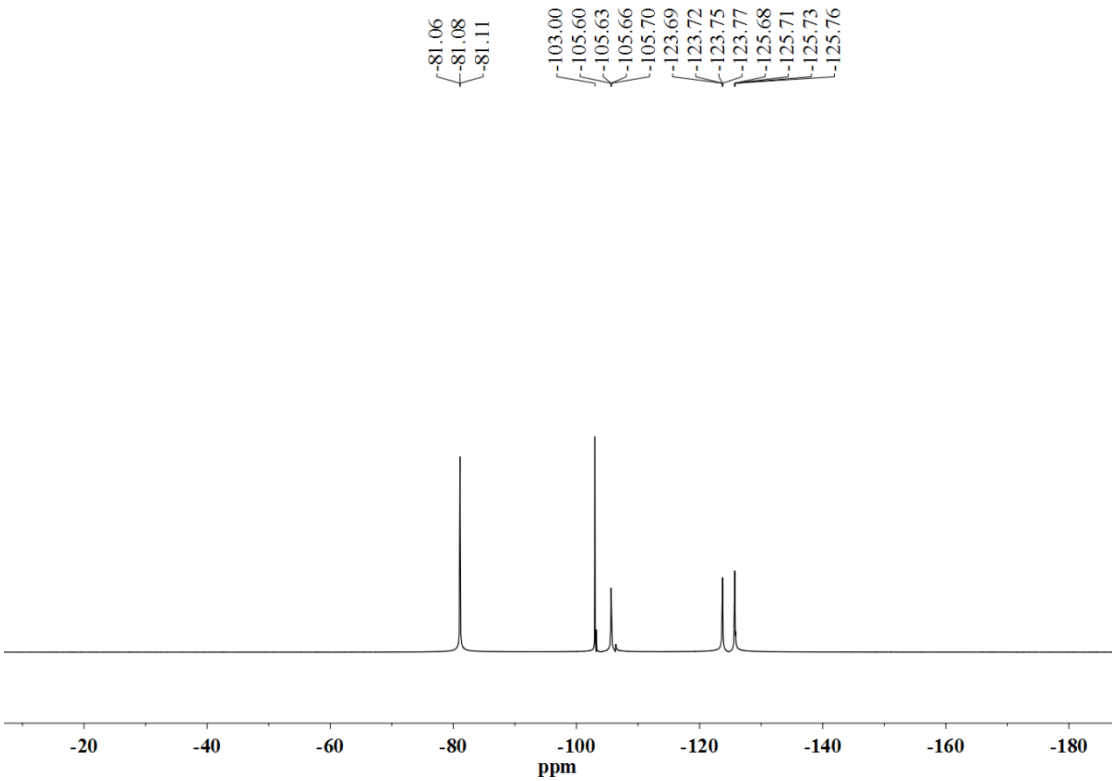
132.798
131.398
131.369
129.587
127.979
125.297
117.866
117.649
117.430
116.180
115.960
77.318
77.000
76.683
34.683
31.108
200
180
160
140
120
100
80
60
40
20
0
ppm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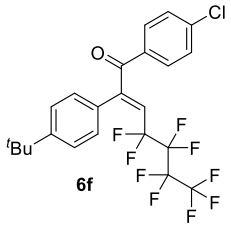
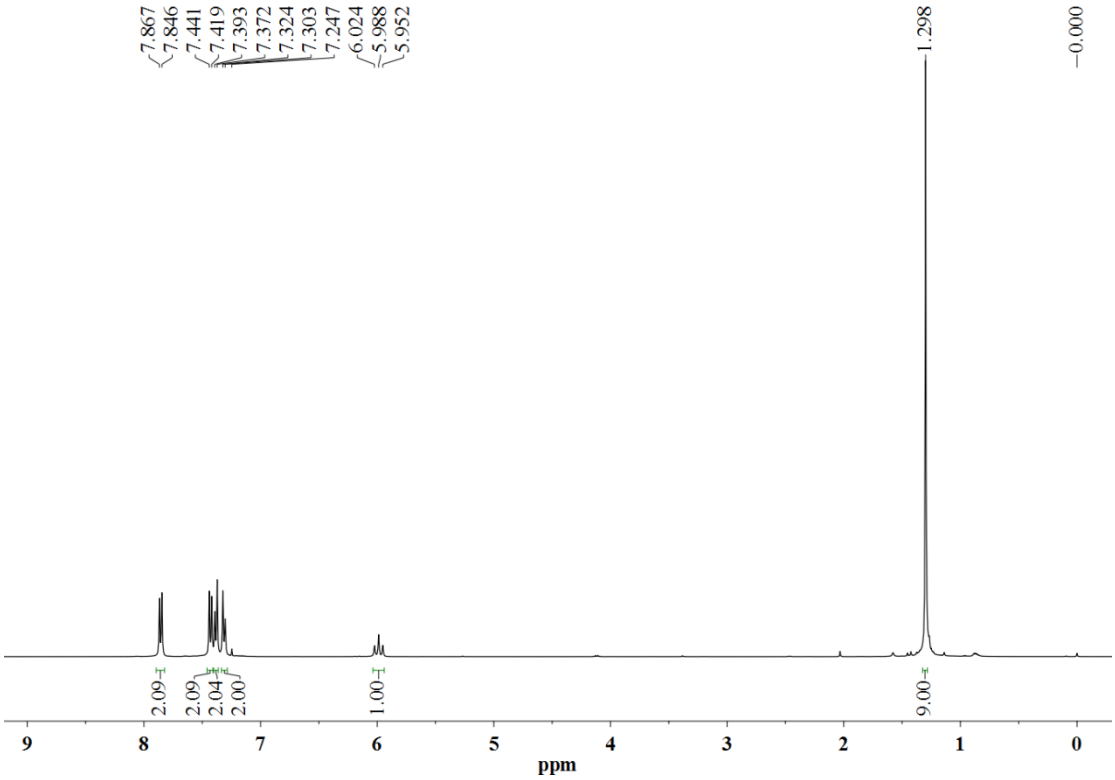
-81.08
-81.11
-103.00
-105.60
-105.63
-105.66
-105.70
-123.69
-123.72
-123.75
-123.77
-125.68
-125.71
-125.73
-125.76
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


Cl
O
tBu
F
F
F
F
F
F
F
F
F

6f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7.372
7.324
7.303
7.247
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5.988
5.952
1.298
0.000
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2.09
2.04
2.00
1.00
9.00
9
8
7
6
5
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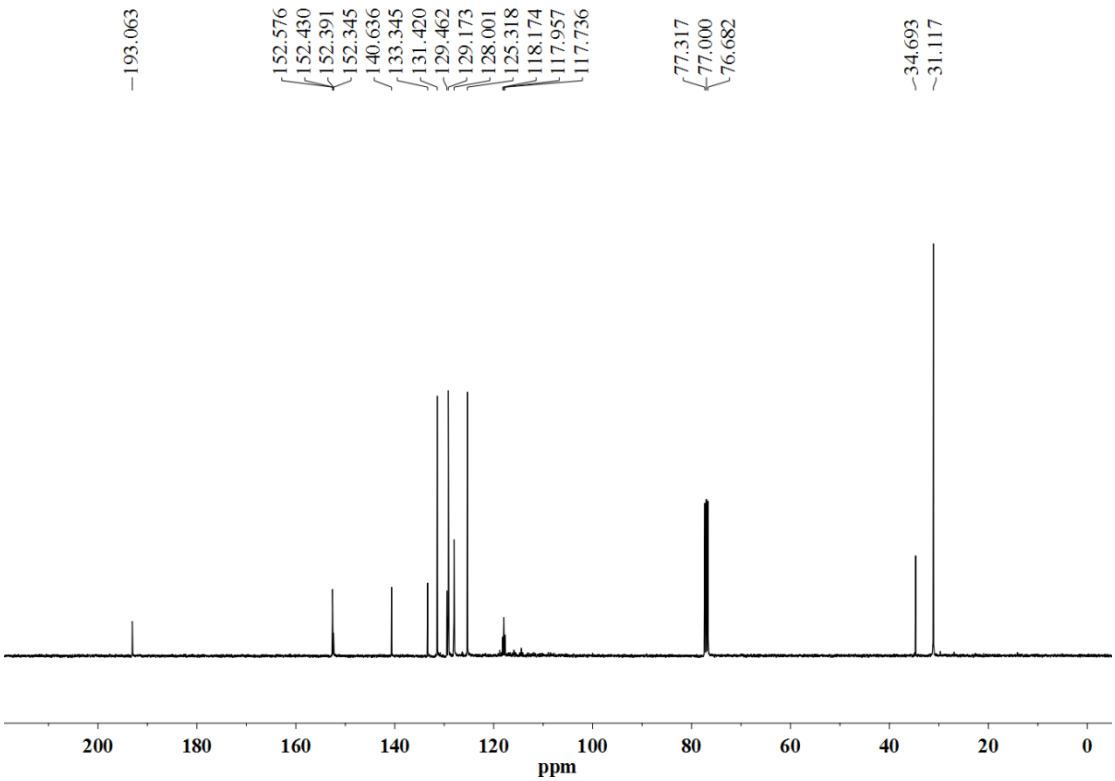
3
2
1
0
ppm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131.420
129.462
129.173
128.001
125.318
118.174
117.957
117.736
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77.000
76.682
34.693
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200
180
160
140
120
100
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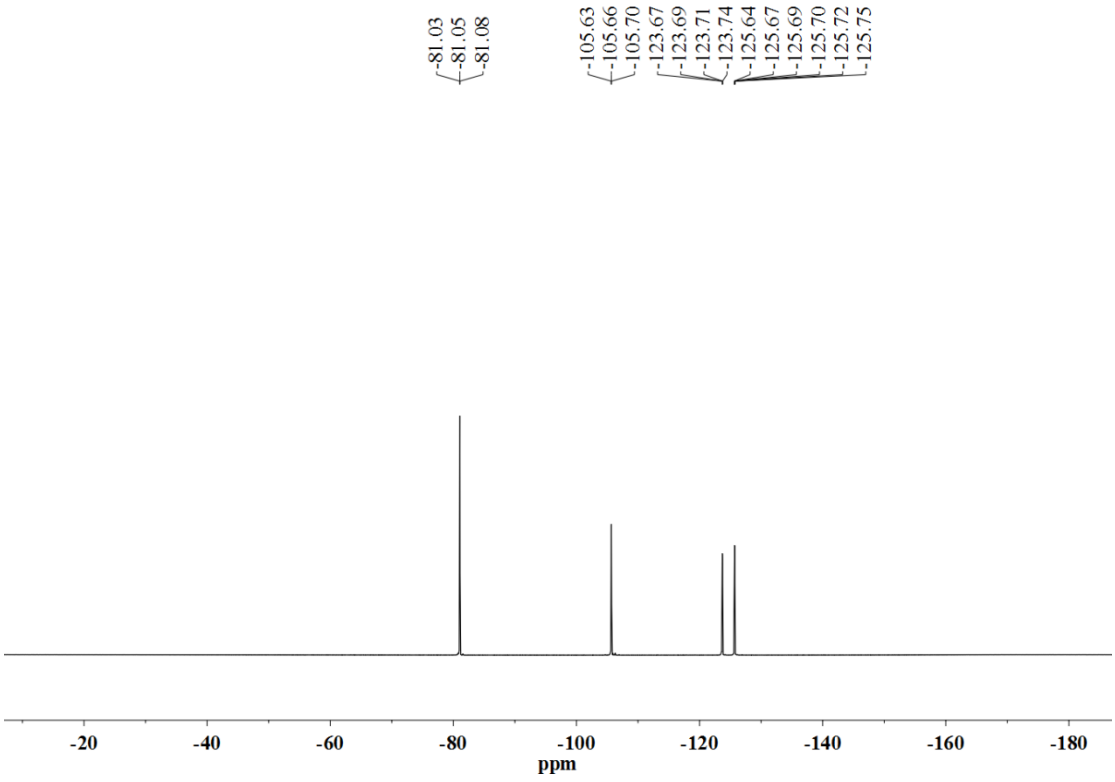
60
40
20
0
ppm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-81.08
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-105.66
-105.70
-123.67
-123.69
-123.71
-123.74
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-125.67
-125.69
-125.70
-125.72
-125.75
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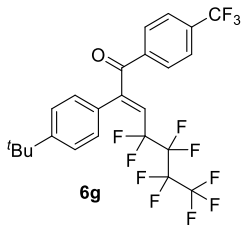
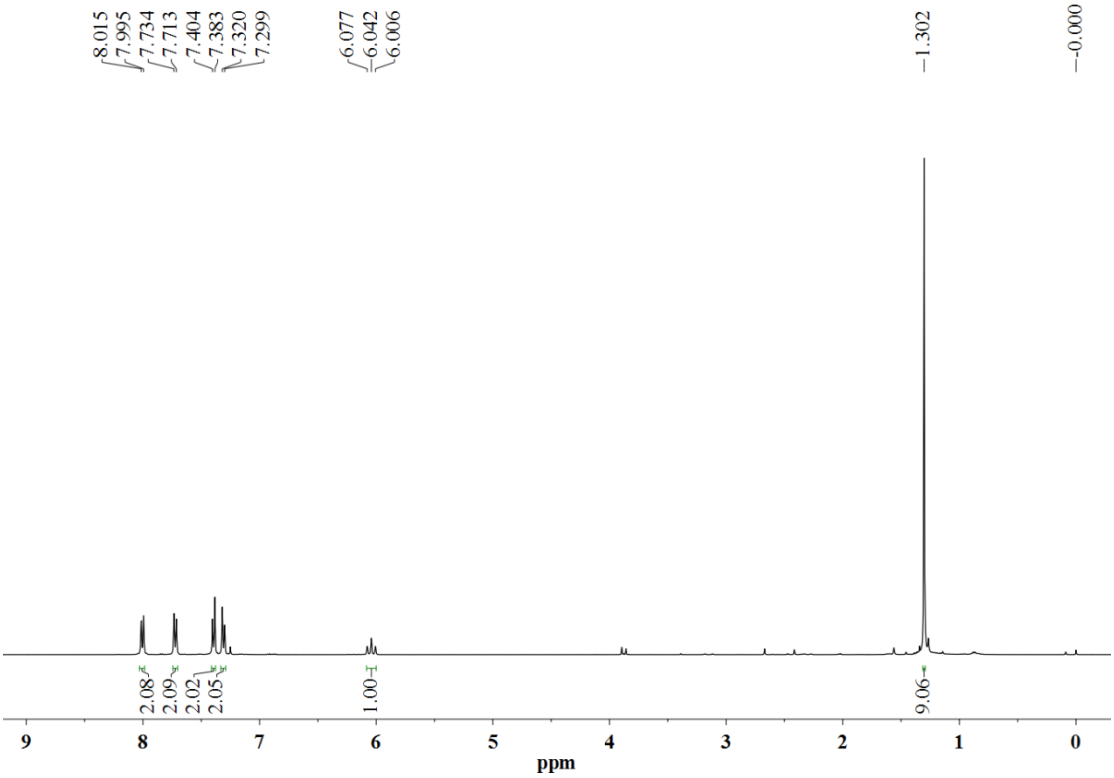
-40
-60
-80
-100
-120
-140
-160
-180
ppm


CF3
O
tBu
F
F
F
F
F
F
F
F
F

6g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7.734
7.713
7.404
7.383
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6.006
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0.000
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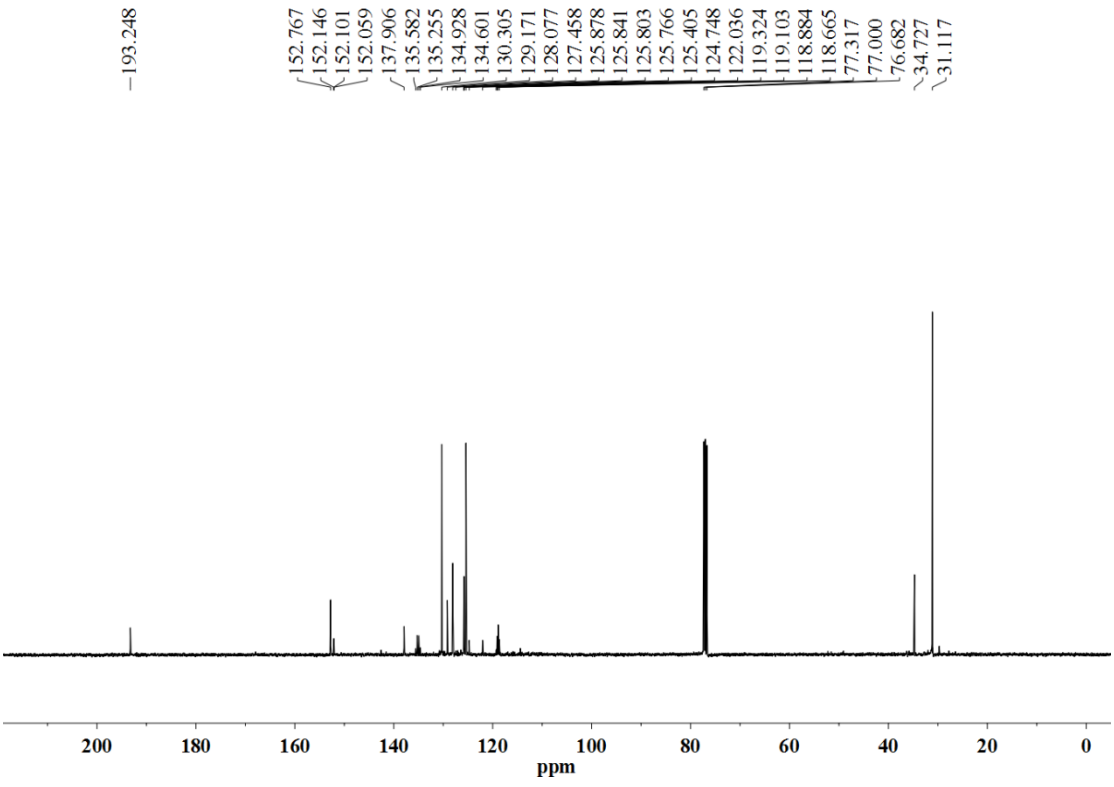
2.09
2.02
2.05
1.00
9.06
ppm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135.255
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134.601
130.305
129.171
128.077
127.458
125.878
125.841
125.803
125.766
125.405
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34.727
31.117
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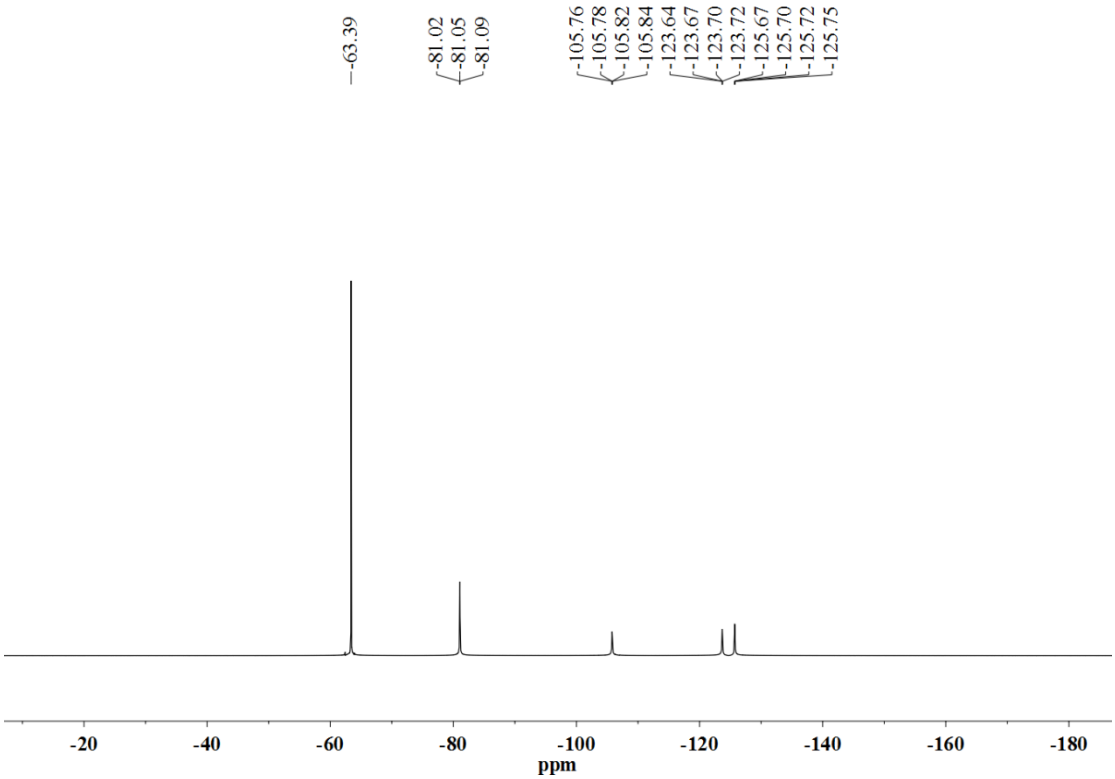
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-105.82
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-125.67
-125.70
-125.72
-125.75
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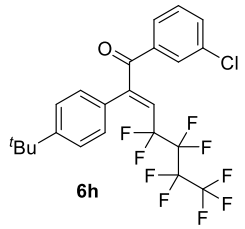
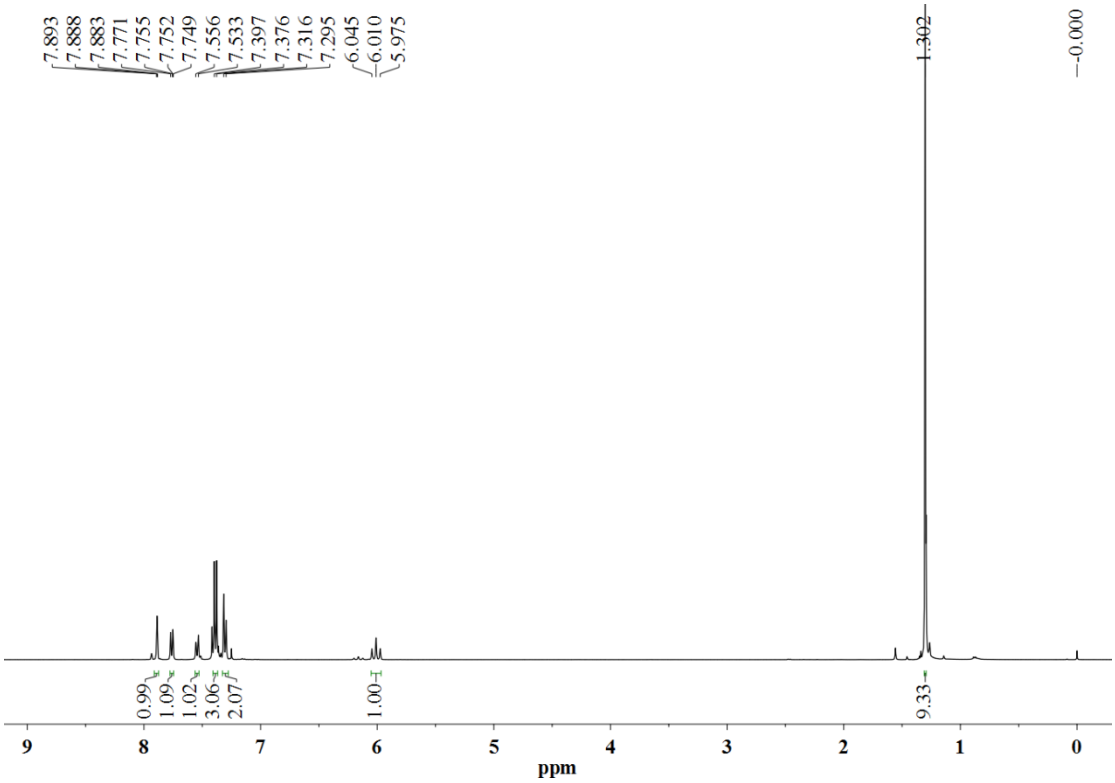
-60
-80
-100
-120
-140
-160
-180
ppm


O
Cl
tBu
F
F
F
F
F
F
F
F
F

6h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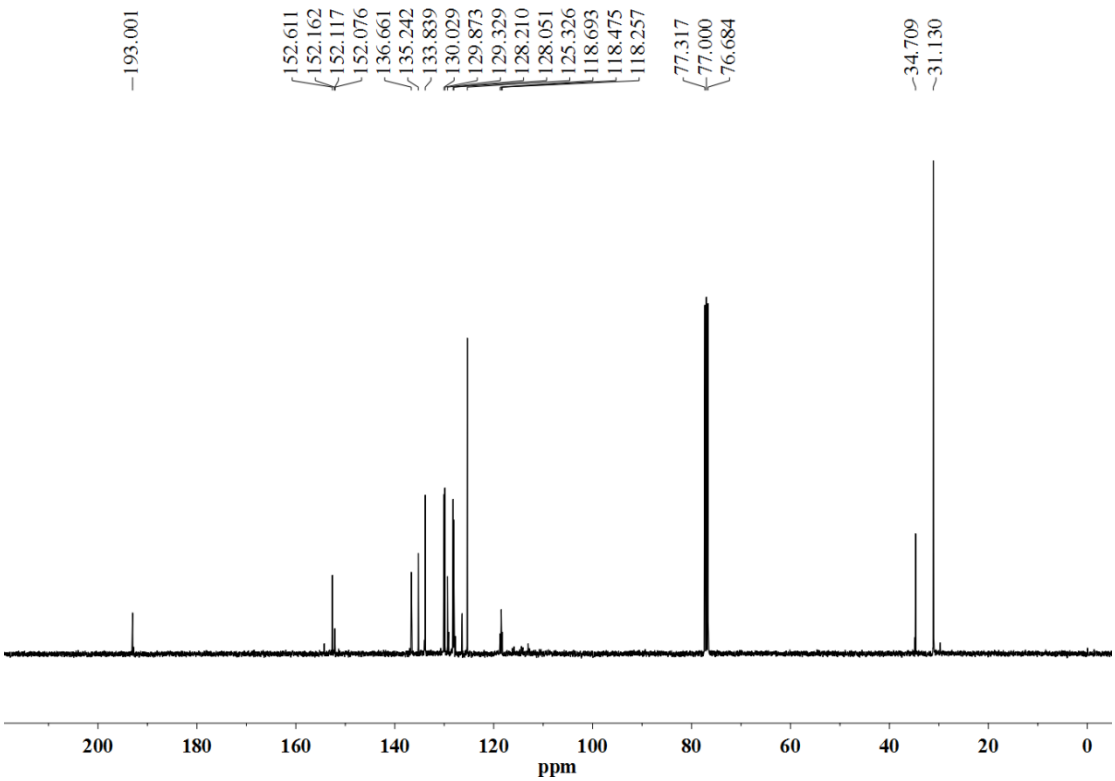
7.752
7.749
7.556
7.533
7.397
7.376
7.316
7.295
6.045
6.010
5.975
1.302
-0.000
0.99
1.09
1.02
3.06
2.07
1.00
9.33
9
8
7
6
5
4
3
2
1
0
ppm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130.029
129.873
129.329
128.210
128.051
125.326
118.693
118.475
118.257
77.317
77.000
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34.709
31.130
200
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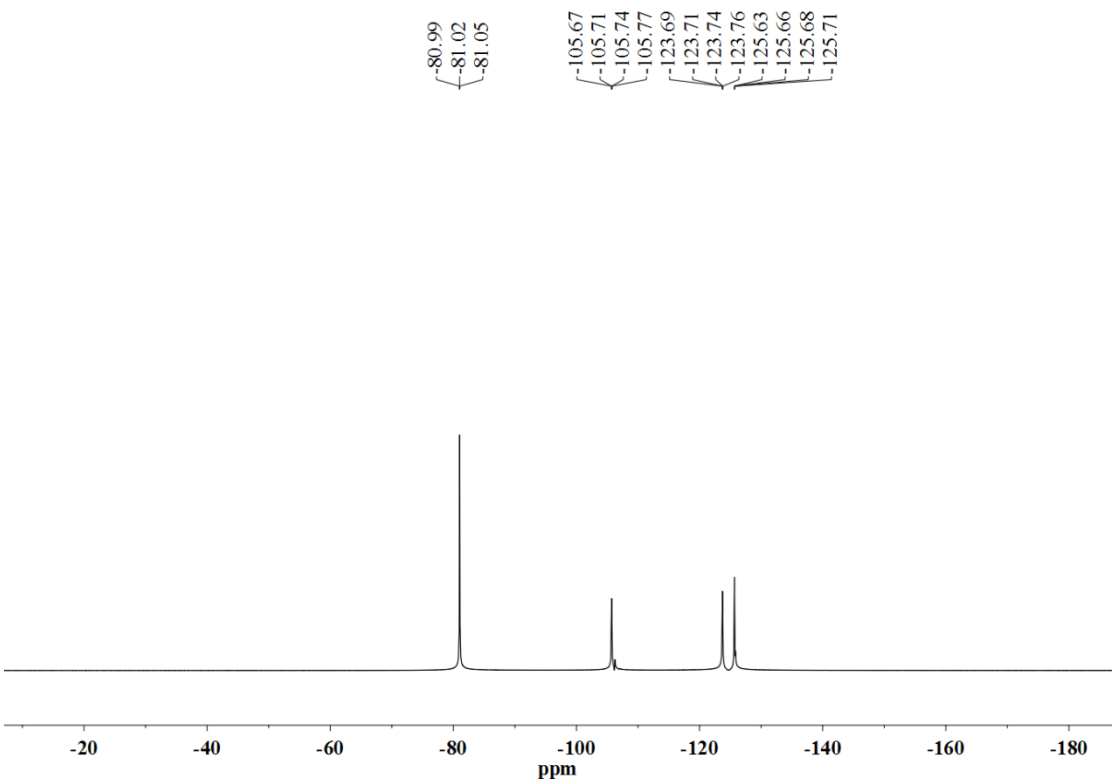
140
120
100
80
60
40
20
0
ppm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-125.71
-20
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-60
-80
-100
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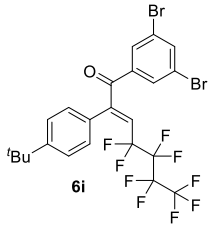
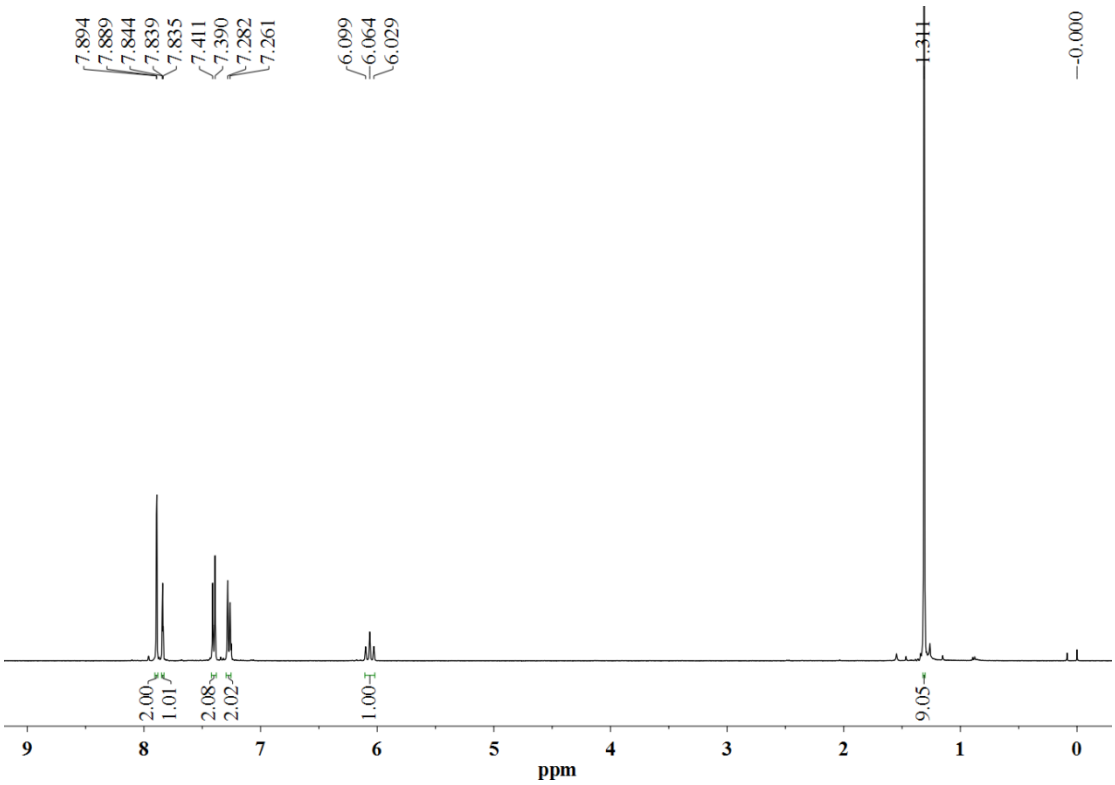
-160
-180
ppm


Br
O
Br
tBu
F
F
F
F
F
F
F
F
F

6i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7.835
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7.390
7.282
7.261
6.099
6.064
6.029
1.311
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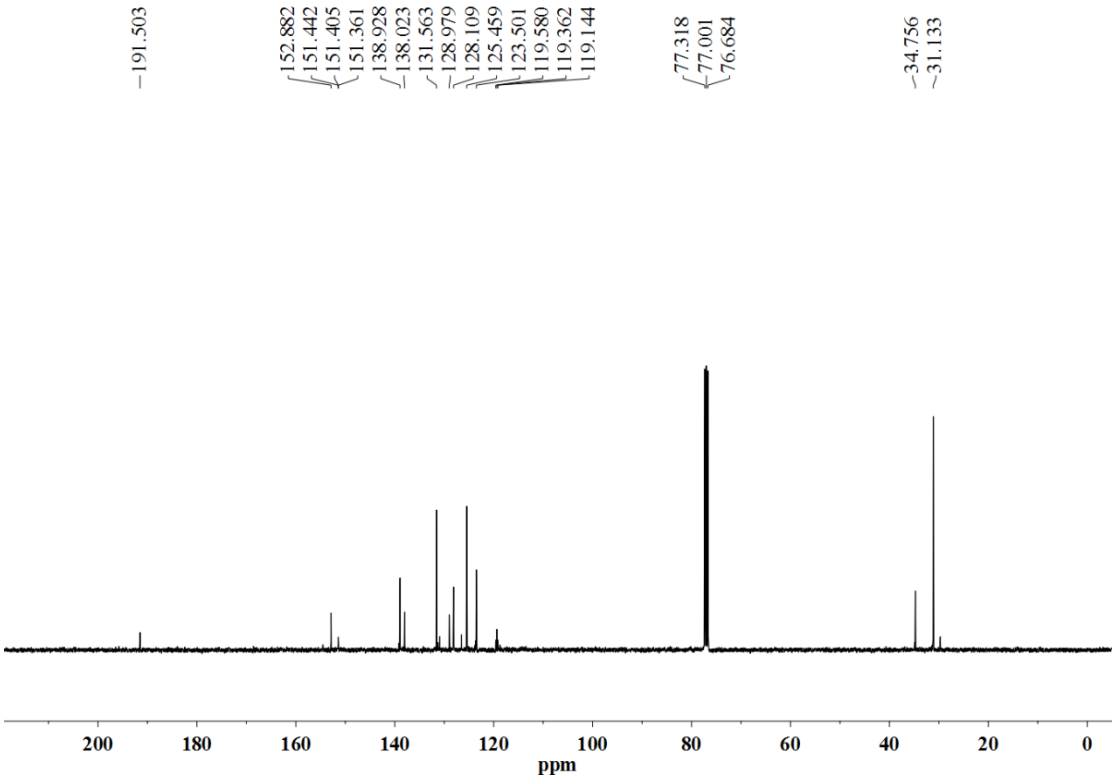
1.01
2.08
2.02
1.00
9.05
9
8
7
6
5
4
3
2
1
0
ppm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151.405
151.361
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138.023
131.563
128.979
128.109
125.459
123.501
119.580
119.362
119.144
77.318
77.001
76.684
34.756
31.133
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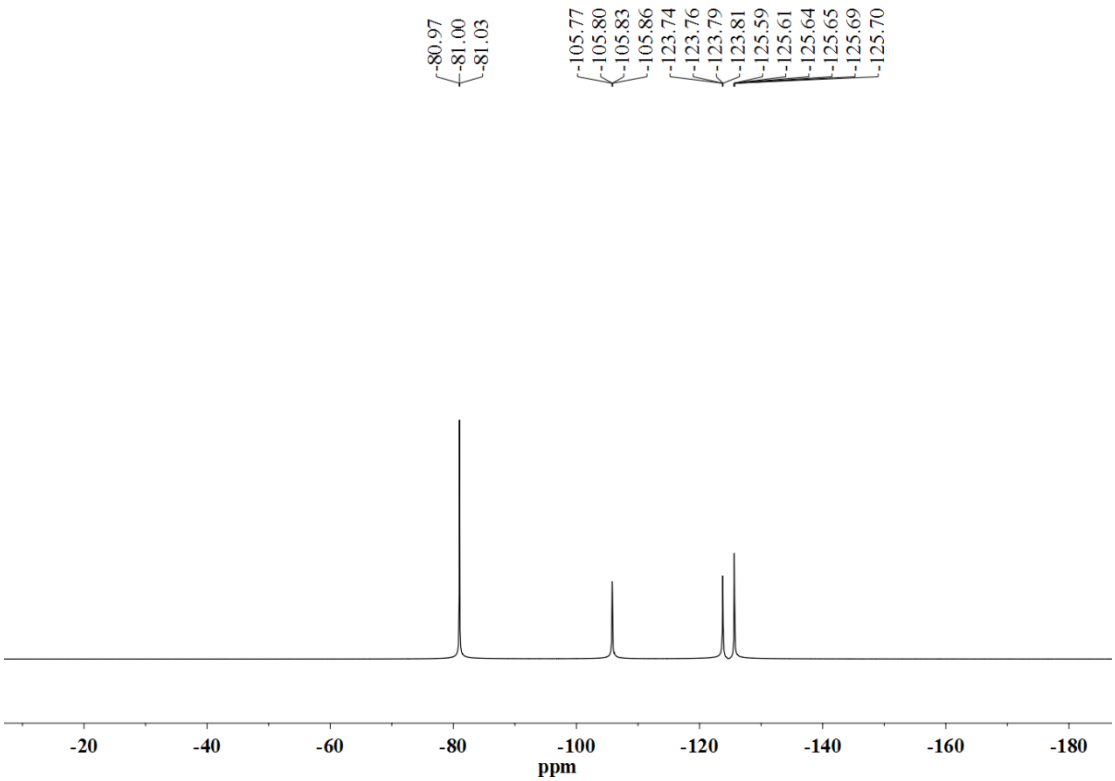
120
100
80
60
40
20
0
ppm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-80
-100
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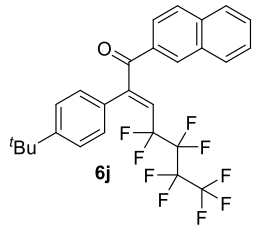
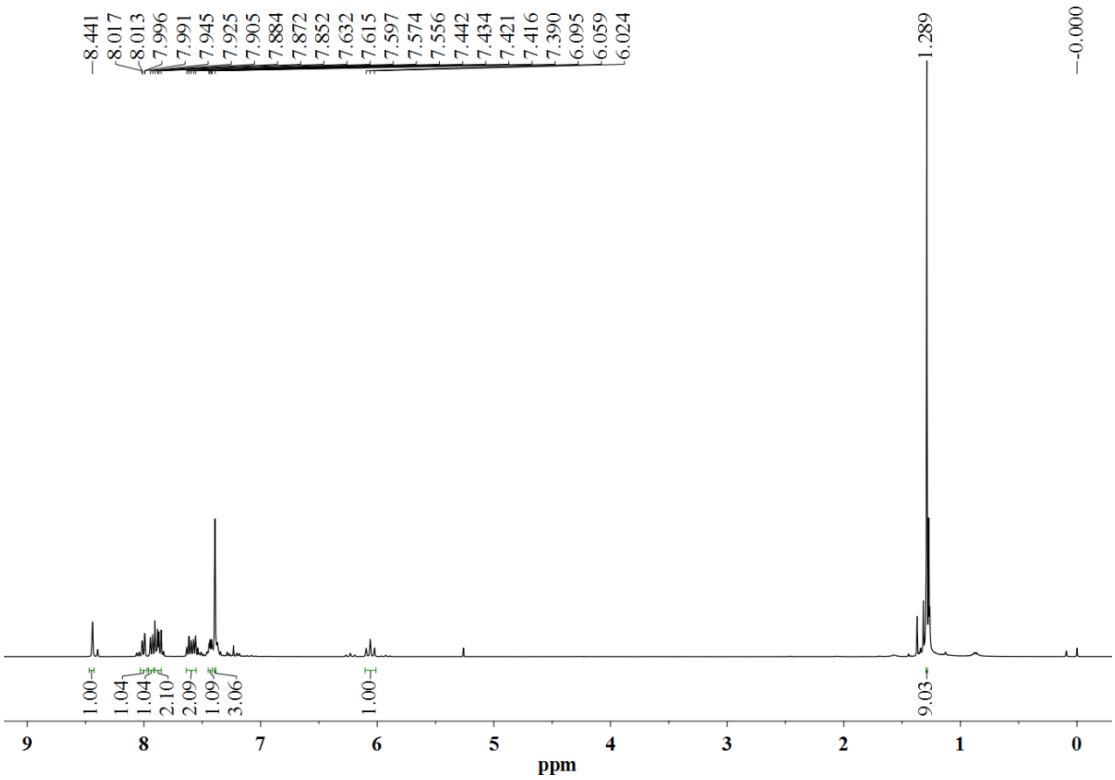
-140
-160
-180
ppm


O
tBu
F
F
F
F
F
F
F
F
F

6j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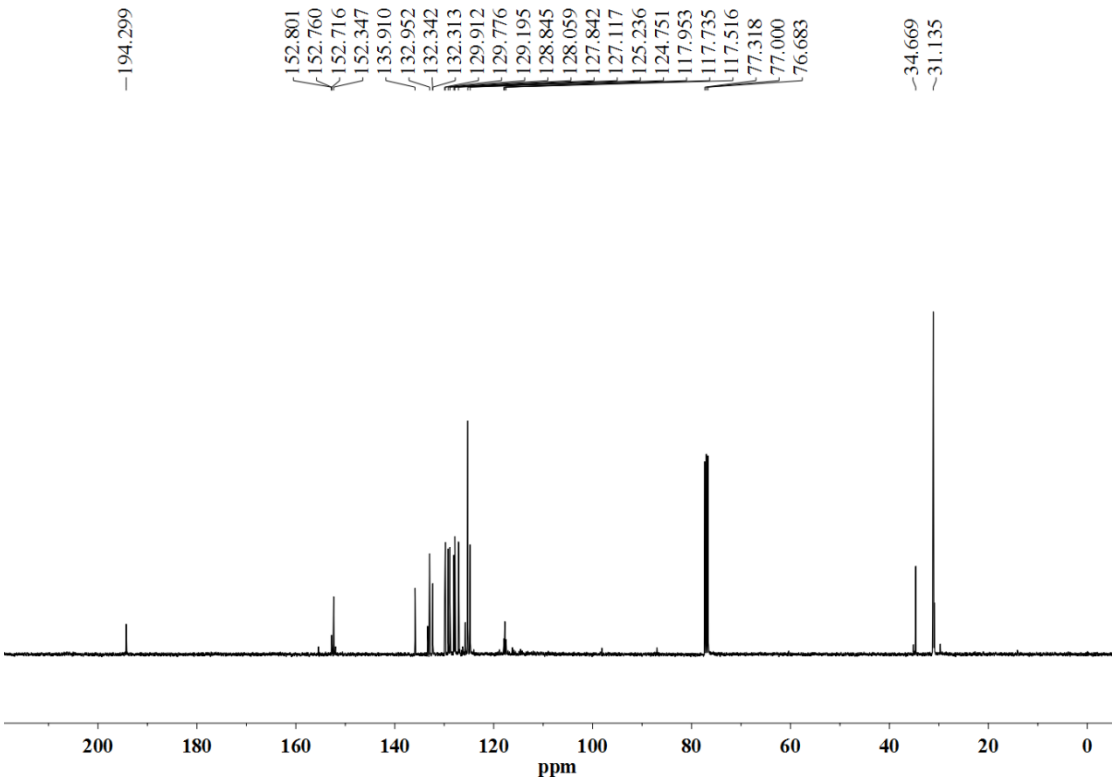
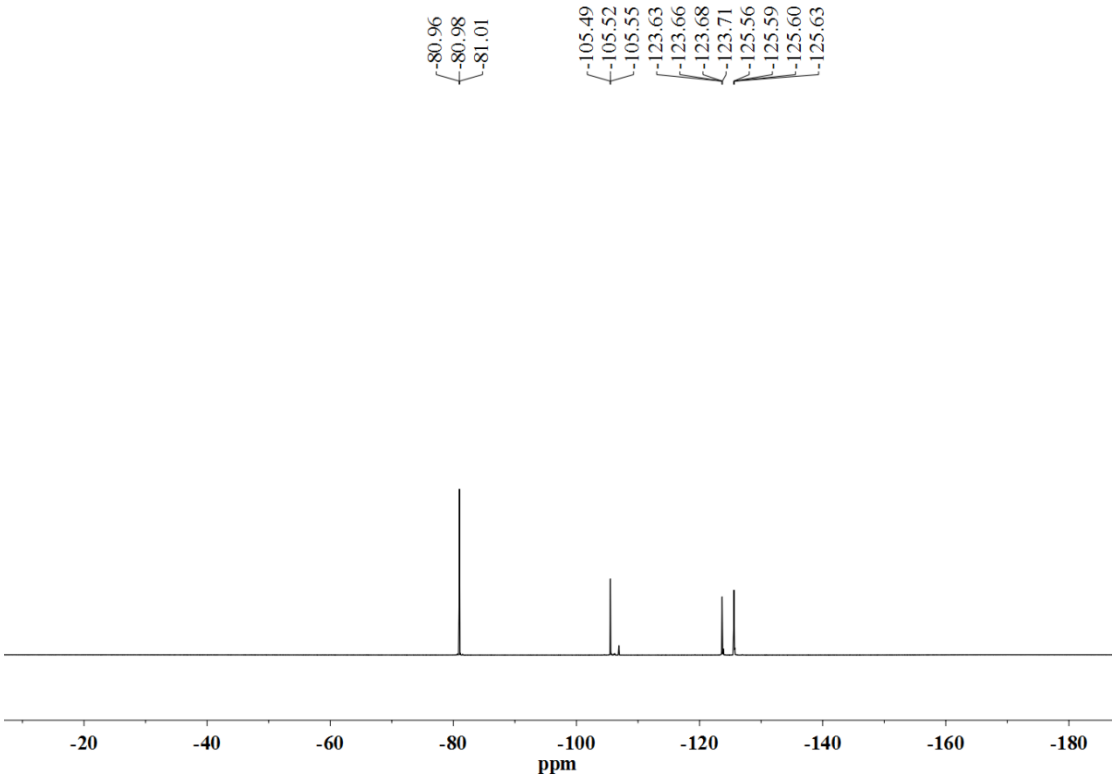
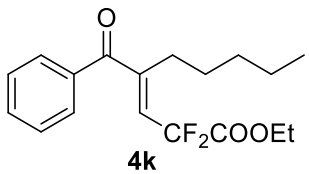
8.017
8.013
7.996
7.991
7.945
7.925
7.905
7.884
7.872
7.852
7.632
7.615
7.597
7.574
7.556
7.442
7.434
7.421
7.416
7.390
6.095
6.059
6.024
1.289
-0.000
1.00
1.04
1.04
2.10
2.09
1.09
3.06
1.00
9.03
9
8
7
6
5
4
3
2
1
0
ppm

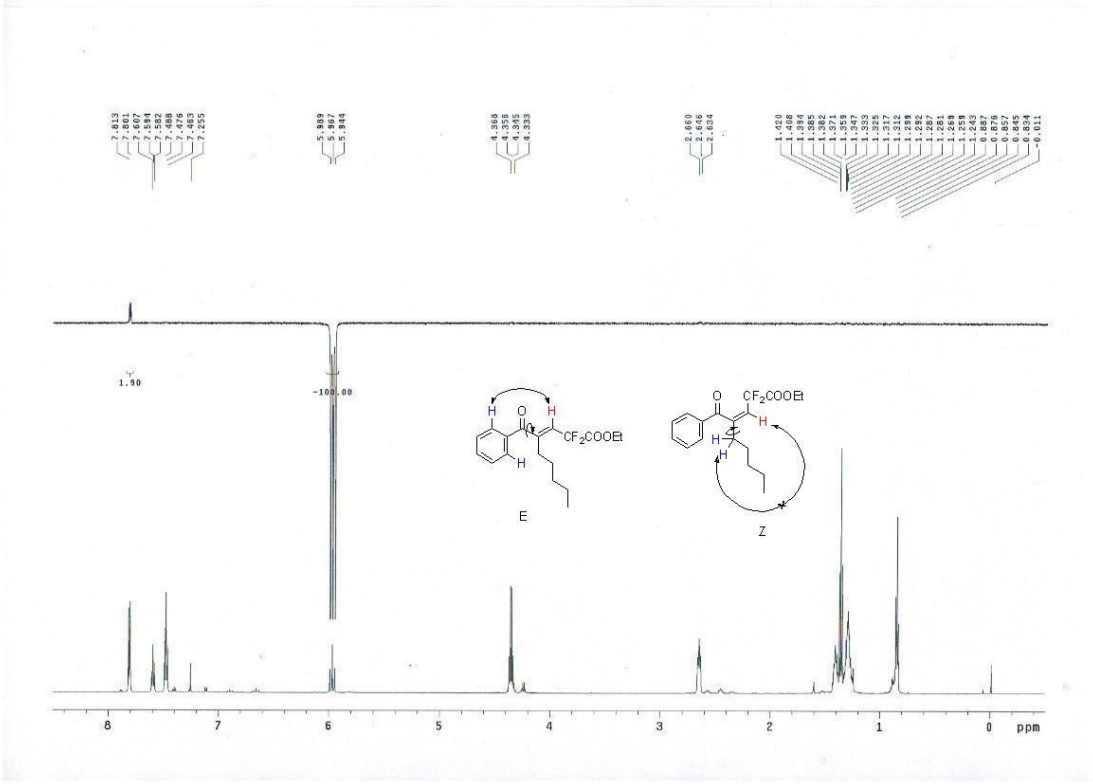




1D-NOESY for Product 4k



4k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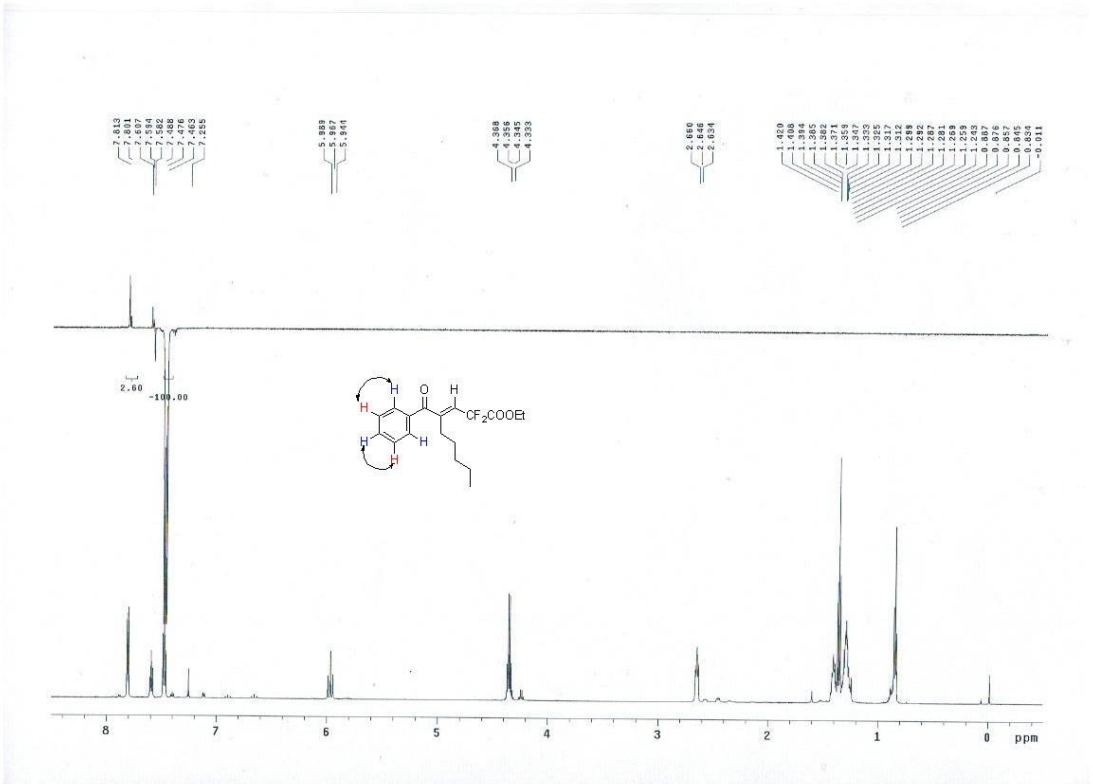
-100.00
E
Z
ppm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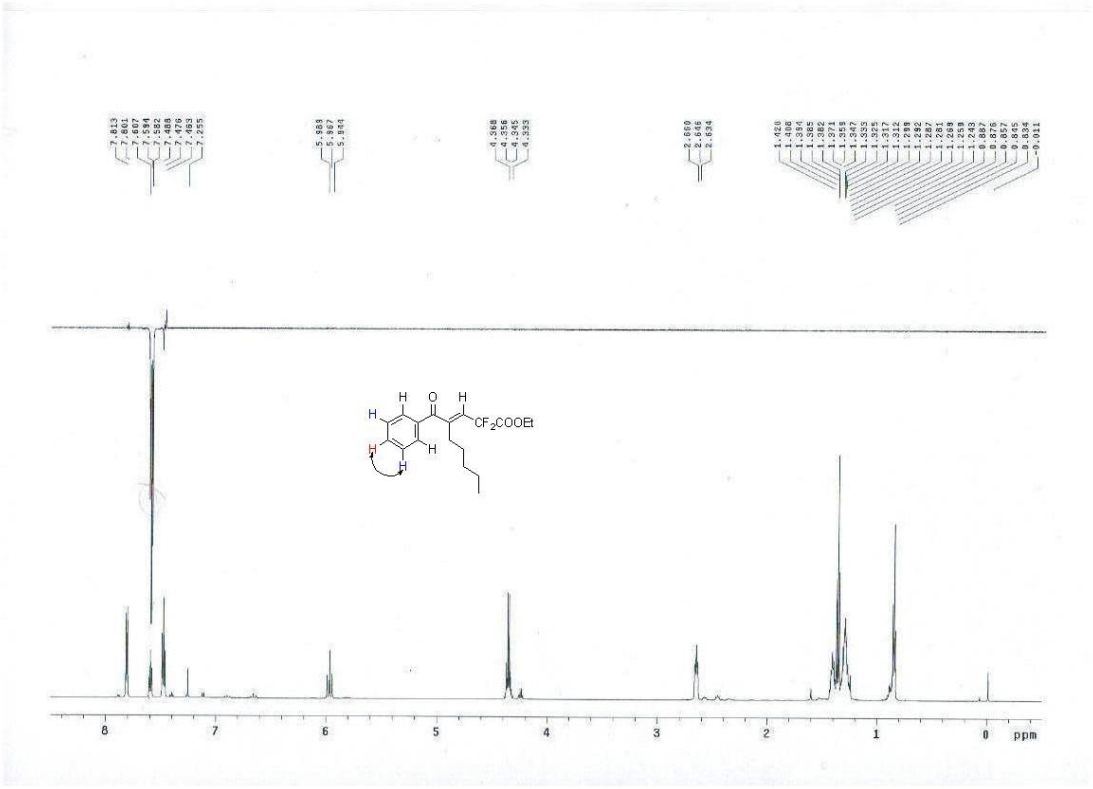
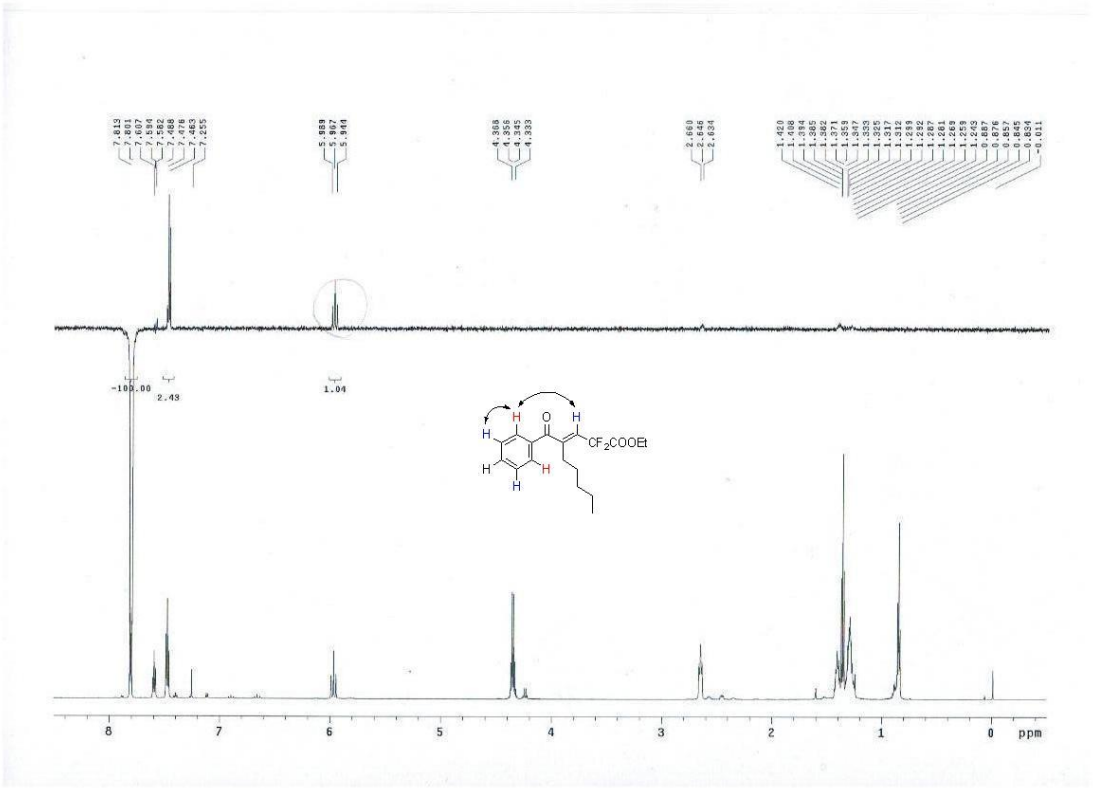
-100.00
ppm


CF2COOEt
8
7
6
5
4
3
2
1
0
ppm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2.49
1.04
CF2COOEt
8
7
6
5
4
3
2
1
0
ppm