

Supporting Information

Photoinduced Allylic Defluorinative Alkylation of Trifluoromethyl Alkenes with Katritzky Salts under Catalyst- and Metal-Free Conditions

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1. General Information.

All new compounds were fully characterized. NMR spectra were recorded on JNM-ECZ400S/L1 and calibrated using residual undeuterated solvent ($\text{CDCl}_3 = 7.26 \text{ ppm } ^1\text{H NMR}$, $77.00 \text{ ppm } ^{13}\text{C NMR}$; $\text{CD}_3\text{CN} = 1.94 \text{ ppm } ^1\text{H NMR}$, $1.32 \text{ ppm } ^{13}\text{C NMR}$; $\text{DMSO-d}_6 = 2.50 \text{ ppm } ^1\text{H NMR}$, $39.52 \text{ ppm } ^{13}\text{C NMR}$) or TMS as an internal reference. Mass spectra were conducted at Bruker MTQ III q-TOF (ESI) and Thermo Scientific Q Exactive (APCI) Mass Spectrometer. Anhydrous solvents, such as Dichloromethane (DCM), *N,N*-Dimethylacetamide (DMA), *N,N*-Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), Acetonitrile (MeCN), Tetrahydrofuran (THF), Ethyl acetate (EA), *N*-Methyl-2-pyrrolidone (NMP) were purchased from Adamas. Flash column chromatography was carried out using silica gel (General-Reagent, AR, 200-300 mesh, for column chromatography). All reactions were carried out in dried 8 mL vial under Nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. PE is the abbreviation of petroleum ether.

Photoreaction setup:

Photoredox reactions of secondary alkyl pyridinium salts and trifluoromethyl alkenes were subjected to irradiation from double 40W Kessil PR160L blue LED bulbs (456 nm), with the reaction tube placed approximately $\sim 5 \text{ cm}$ from the bulbs and using a fan to keep at room temperature (Figure S1).

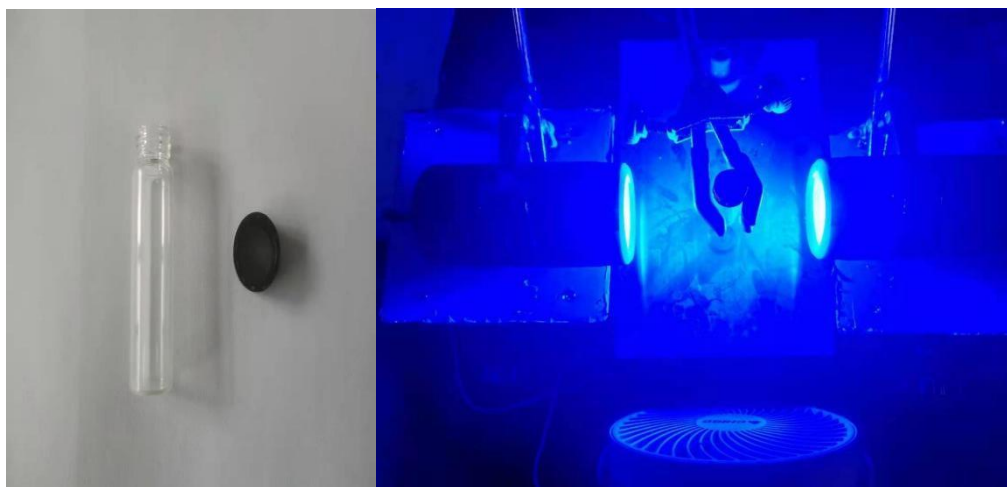


Figure S1. An over-dried 8 mL vial (left). Photoreaction setup (right).

Photoredox reactions of primary alkyl pyridinium salts and trifluoromethyl alkenes were subjected to irradiation from single 40W Kessil PR160L blue LED bulbs (456 nm), and the reaction tubes were placed in an oil bath set at 100 °C approximately 1 cm from the bulbs (Figure S2).

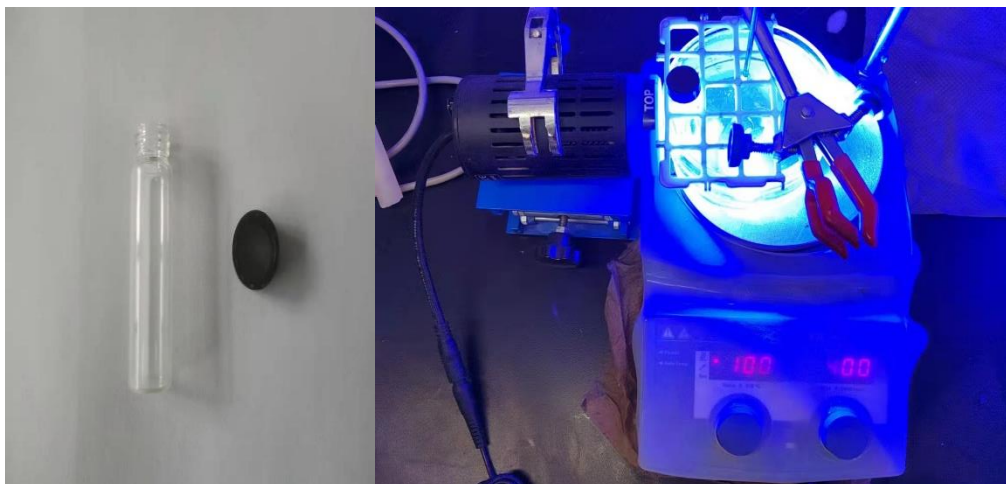


Figure S2. An over-dried 8 mL vial (left). Photoreaction setup (right)

2.Optimization of reaction conditions of 1a and 2a

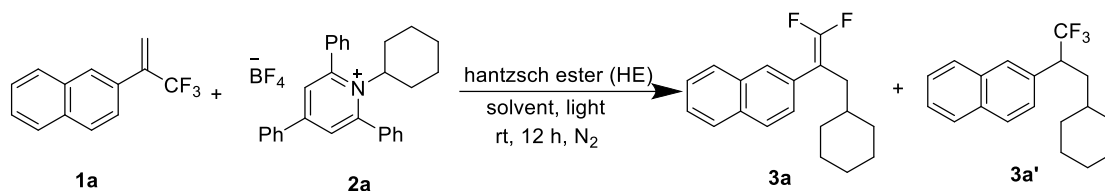


Table S1. Exploration of wavelength λ (nm)^a

Entry	Light (nm)	Remaining of 1a (%)	Yield of 3a (%)	Yield of 3a' (%)
1	390	0	43	2
2	427	0	62	1
3	440	0	85	1
4	456	0	98	<1

^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2a** (0.15 mmol, 1.5 eq), hantzsch ester (0.20 mmol, 2.0 eq), DMA (1 mL), Kessil PR160L, rt, 12 h, N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μ L, 0.10 mmol) as an internal standard.

Table S2. Exploration of solvent (1 mL)^a

Entry	Solvent	Remaining of 1a (%)	Yield of 3a (%)	Yield of 3a' (%)
5	DMA	2	98	<1
6	MeCN	18	5	<1
7	DMF	1	82	3
8	DMSO	1	80	1
9	NMP	0	82	2
10	DCE	47	32	<1
11	EtOH	90	4	0

^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2a** (0.15 mmol, 1.5 eq), hantzsch ester (0.20 mmol, 2.0 eq), Kessil PR160L (456 nm), rt, 12 h, N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μ L, 0.10 mmol) as an internal standard.

Table S3. Exploration of hantzsch ester content^a

Entry	HE content (mmol)	Remaining of 1a (%)	Yield of 3a (%)	Yield of 3a' (%)
12	0.12	9	65	<1
13	0.15	0	66	<1
14	0.20	1	98	<1

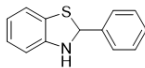
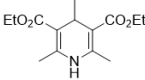
^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2a** (0.15 mmol, 1.5 eq), DMA (1 mL), Kessil PR160L (456 nm), rt, 12 h, N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μL, 0.10 mmol) as an internal standard.

Table S4. Optimization of reaction concentration^a

Entry	DMA (ml)	Remaining of 1a (%)	Yield of 3a (%)	Yield of 3a' (%)
15	1	1	98	<1
16	0.5	<1	78	<1
17	0.25	<1	64	1

^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2a** (0.15 mmol, 1.5 eq), hantzsch ester (0.20 mmol, 2.0 eq), Kessil PR160L (456 nm), rt, 12 h, N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μL, 0.10 mmol) as an internal standard.

Table S5. Optimization of reductant (0.2 mmol)^a

Entry	reductant	Remaining of 1a (%)	Yield of 3a (%)	Yield of 3a' (%)
18	HE	1	98	<1
19	Et ₃ N	57	21	2
20	DIPEA	92	8	0
21	NaOAc	100	0	0
22		66	0	0
23		26	74	0

^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2a** (0.15 mmol, 1.5 eq), DMA (1 mL), Kessil PR160L (456 nm), rt, 12 h, N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μL, 0.10 mmol) as an internal standard.

3.Optimization of reaction conditions of **1a** and **2h**

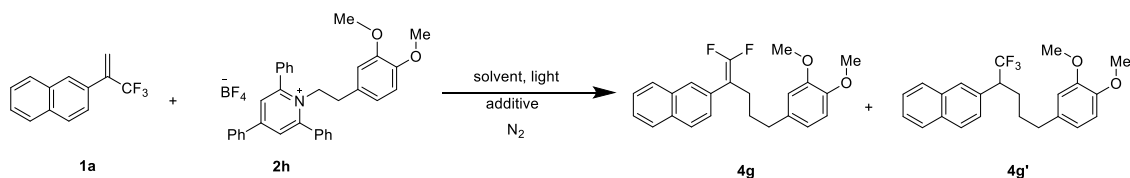


Table S6. Exploration of wavelength λ (nm)^a

Entry	Light (nm)	Remaining of 1a (%)	Remaining of 2h (%)	Yield of 4g (%)	Yield of 4g' (%)
24	390	68	68	4	<1
25	427	72	23	4	1
26	440	61	50	3	<1
27	456	57	67	6	0

^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2h** (0.15 mmol, 1.5 eq), hantzsch ester (0.20 mmol, 2.0 eq), DMA (1 mL), Kessil PR160L, rt, 12 h, N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μ L, 0.10 mmol) as an internal standard.

Table S7. Exploration of solvent (1 mL)^a

Entry	Solvent	Remaining of 1a (%)	Remaining of 2h (%)	Yield of 4g (%)	Yield of 4g' (%)
28	DMA	57	68	6	0
29	DMSO	92	16	9	0
30	NMP	89	5	8	<1
31	CH ₃ OH	52	99	0	1
32	MeCN	48	99	0	<1
33	EA	73	99	0	<1
34	DCE	53	99	0	<1

^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2h** (0.15 mmol, 1.5 eq), hantzsch ester (0.20 mmol, 2.0 eq), Kessil PR160L (456 nm), rt, 12 h, N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μ L, 0.10 mmol) as an internal standard.

Table S8. Exploration of additive (0.3 mmol)^a

Entry	Additive	Remaining of 1a (%)	Remaining of 2h (%)	Yield of 4g (%)	Yield of 4g' (%)
35	TEA	60	0	24	<1
36	DIPEA	70	2	15	0
37	<i>N</i> -Methylpiperidine	77	0	11	<1
38	4-Hydroxypiperidine	61	0	9	<1
39	Pyridine	50	22	8	<1
40	DMAP	52	0	11	1
41 ^b	TEA	78	29	21	0

^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2h** (0.15 mmol, 1.5 eq), hantzsch ester (0.20 mmol, 2.0 eq), DMSO (1 mL), Kessil PR160L (456 nm), rt, 12 h, N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μL, 0.10 mmol) as an internal standard.

^bHantzsch ester was not used.

Table S9. Exploration of parameters without HE^a

Entry	Additive	Temperature (°C)	Duration (hours)	Remaining of 1a (%)	Remaining of 2h (%)	Yield of 4g (%)	Yield of 4g' (%)
42	TEA	rt	12	78	29	21	0
43	DIPEA	rt	12	36	75	3	<1
44	DMEDA ^b	rt	12	61	37	3	<1
45	TEA	60	12	81	62	24	0
46	TEA	90	12	46	48	43	0
47	TEA	110	12	26	23	59	<1
48	TEA	110	12	0	4	71	1
49 ^c	TEA	110	24	0	0	77	1
50 ^c	TEA	100	24	0	1	80	<1

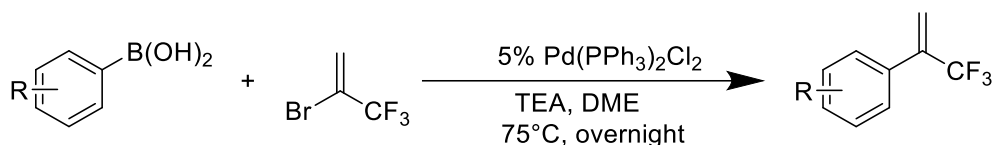
^aReaction conditions: **1a** (0.10 mmol, 1.0 eq), **2h** (0.15 mmol, 1.5 eq), Kessil PR160L (456 nm), additive (0.30 mmol, 3.0 eq), DMSO (1 mL), N₂ atmosphere. Yields determined by ¹⁹F NMR with 1,4-Difluorobenzene (9.8 μL, 0.10 mmol) as an internal standard.

^bDMEDA = *N,N*-Dimethylethylenediamine.

^cTEA (0.50 mmol, 5.0 eq) was used.

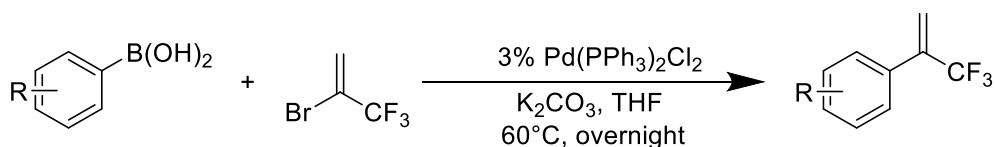
4.Preparation of Trifluoromethyl Alkenes

Method A:



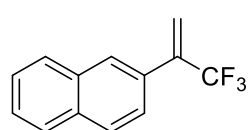
In a Schlenk tube equipped with stir bar, arylboronic acids (1.5 equiv.), Pd(PPh₃)₂Cl₂ (5 mol%) were added. The vessel was evacuated and filled with nitrogen, then TEA (8.0 equiv.), DME (0.33 M) and H₂O (0.67 M) were added. After the addition of 2-bromo-3,3,3-trifluoropropene (1.0 equiv.), the solution was stirred at 75 °C overnight (TLC tracking detection). The mixture was purified by column chromatography to afford the corresponding trifluoromethyl alkenes.

Method B:¹



In a Schlenk tube equipped with stir bar, arylboronic acids (1.0 equiv.), Pd(PPh₃)₂Cl₂ (3 mol%) and K₂CO₃ (4.0 equiv.) were added. The vessel was evacuated and filled with nitrogen, then THF (0.33 M) and H₂O (0.5 M) were added. After the addition of 2-bromo-3,3,3-trifluoropropene (2.0 equiv.), the solution was stirred at 60 °C overnight (TLC tracking detection). The mixture was purified by column chromatography to afford the corresponding trifluoromethyl alkenes.

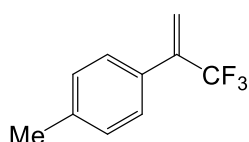
2-(3,3,3-Trifluoroprop-1-en-2-yl)naphthalene(1a)



According to Method A, the reaction was carried out with the corresponding arylboronic acid (5.16 g, 30.00 mmol), Pd(PPh₃)₂Cl₂ (701.9 mg, 1.02 mmol), TEA (8 mL, 142.50 mmol), DME (60 mL) and H₂O (30 mL), 2-bromo-3,3,3-trifluoropropene (2.08 mL, 20.00

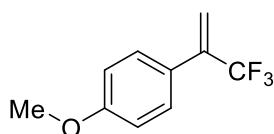
mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford 3.26 g (92%) of **1a** as a white solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.94-7.85 (m, 4H), 7.58-7.51 (m, 3H), 6.05 (s, 1H), 5.91 (s, 1H). All data are in accordance with the literature.¹

Methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1b**)



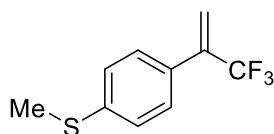
According to Method A, the reaction was carried out with the corresponding arylboronic acid (1.63 g, 12.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H_2O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford 0.49 g (33%) of **1b** as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.36 (d, $J = 7.0$ Hz, 2H), 7.20 (d, $J = 6.5$ Hz, 2H), 5.91 (s, 1H), 5.74 (s, 1H), 2.38 (s, 3H). All data are in accordance with the literature.¹

Methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1c**)



According to Method A, the reaction was carried out with the corresponding arylboronic acid (1.82 g, 12.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H_2O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford 0.67 g (42%) of **1c** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.40 (d, $J = 9.0$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 5.87 (s, 1H), 5.70 (s, 1H). All data are in accordance with the literature.²

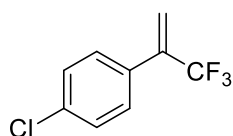
Methyl(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)sulfane (**1d**)



According to Method A, the reaction was carried out with the corresponding arylboronic acid (2.02 g, 12.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H_2O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford 1.32 g (86%) of **1d** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.38

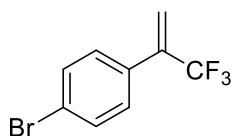
(d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.6$ Hz, 2H), 5.92 (s, 1H), 5.75 (s, 1H), 2.50 (s, 3H). All data are in accordance with the literature.³

1-Chloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1e)



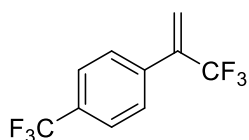
According to Method A, the reaction was carried out with the corresponding arylboronic acid (1.88 g, 12.00 mmol), Pd(PPh₃)₂Cl₂ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford 0.64 g (39%) of **1e** as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ : 7.40-7.35 (m, 4H), 5.98 (s, 1H), 5.77 (s, 1H). All data are in accordance with the literature.¹

1-Bromo-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1f)



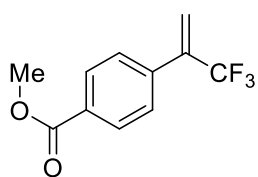
According to Method A, the reaction was carried out with the corresponding arylboronic acid (2.41 g, 12.00 mmol), Pd(PPh₃)₂Cl₂ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford 0.81 g (40%) of **1f** as a white solid: ¹H NMR (400 MHz, CDCl₃) δ : 7.52 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.6$ Hz, 2H), 5.98 (s, 1H), 5.78 (s, 1H). All data are in accordance with the literature.²

1-(Trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1g)



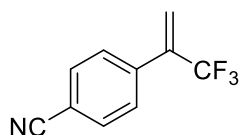
According to Method A, the reaction was carried out with the corresponding arylboronic acid (2.28 g, 12.00 mmol), Pd(PPh₃)₂Cl₂ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford 0.49 g (25%) of **1g** as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ : 7.66 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 8.8$ Hz, 2H), 6.07 (s, 1H), 5.85 (s, 1H). All data are in accordance with the literature.⁴

Methyl 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (**1h**)



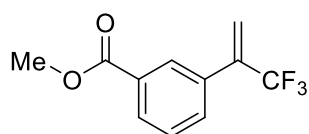
According to Method A, the reaction was carried out with the corresponding arylboronic acid (2.16 g, 12.00 mmol), Pd(PPh₃)₂Cl₂ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE: DCM=3:1) to afford 1.04 g (57%) of **1h** as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ: 8.05 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 6.05 (s, 1H), 5.87 (s, 1H), 3.94 (s, 1H). All data are in accordance with the literature.²

4-(3,3,3-Trifluoroprop-1-en-2-yl)benzotrile (**1i**)



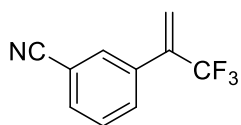
According to Method A, the reaction was carried out with the corresponding arylboronic acid (1.76 g, 12.00 mmol), Pd(PPh₃)₂Cl₂ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE: DCM=3:1) to afford 1.01 g (64%) of **1i** as an orange oil: ¹H NMR (400 MHz, CDCl₃) δ: 7.69 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 1H), 6.11(s, 1H), 5.88 (m, 1H). All data are in accordance with the literature.¹

Methyl 3-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (**1j**)



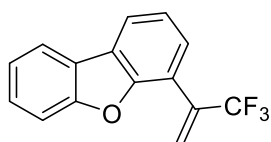
According to Method A, the reaction was carried out with the corresponding arylboronic acid (2.16 g, 12.00 mmol), Pd(PPh₃)₂Cl₂ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE: DCM=2:1) to afford 1.34 g (59%) of **1j** as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ: 8.13 (s, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 8.6 Hz, 1H), 6.03 (s, 1H), 5.84 (s, 1H), 3.94 (s, 3H). All data are in accordance with the literature.⁵

3-(3,3,3-Trifluoroprop-1-en-2-yl)benzonitrile (**1k**)



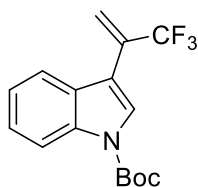
According to Method B, the reaction was carried out with the corresponding arylboronic acid (1.18 g, 8.00 mmol), Pd(PPh₃)₂Cl₂ (168.5 mg, 0.24 mmol), K₂CO₃ (4.42 g, 32.00 mmol), THF (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (1.66 mL, 16.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE: DCM=5:1) to afford 1.35 g (86%) of **1k** as a brown oil: ¹H NMR (400 MHz, CDCl₃) δ: 7.75-7.53 (m, 4H), 6.09 (s, 1H), 5.85 (s, 1H). All data are in accordance with the literature.⁶

4-(3,3,3-Trifluoroprop-1-en-2-yl)dibenzo[b,d]furan (**1l**)



According to Method B, the reaction was carried out with the corresponding arylboronic acid (1.70 g, 8.00 mmol), Pd(PPh₃)₂Cl₂ (168.5 mg, 0.24 mmol), K₂CO₃ (4.42 g, 32.00 mmol), THF (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (1.66 mL, 16.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford 1.6 g (77%) of **1l** as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ: 7.98 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.54-7.47 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 6.37 (t, *J* = 1.25 Hz, 2H). All data are in accordance with the literature.¹

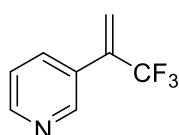
1-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (**1m**)



According to Method B, the reaction was carried out with the corresponding arylboronic acid (2.09 g, 8.00 mmol), Pd(PPh₃)₂Cl₂ (168.5 mg, 0.24 mmol), K₂CO₃ (4.42 g, 32.00 mmol), THF (24 mL) and H₂O (16 mL), 2-bromo-3,3,3-trifluoropropene (1.66 mL, 16.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE: DCM=10:1) to afford 1.33 g (54%) of **1m** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ: 8.33 (d, *J* = 8.2 Hz, 1H), 7.87 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 6.18 (s, 1H), 6.03 (s, 1H), 1.76 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ: 149.27, 135.42, 131.41 (dd, *J* = 62.4 Hz, *J* = 31.2 Hz), 128.48, 125.02, 124.90, 123.19, 123.12 (dd, *J* = 544.6 Hz, *J*

= 27.2 Hz), 119.85 (dd, $J = 11.3$ Hz, $J = 5.6$ Hz), 119.61, 115.45, 113.10, 84.30, 27.94. ^{19}F NMR (376 MHz, CDCl_3) δ : -66.43. HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 312.1211, found 312.1211.

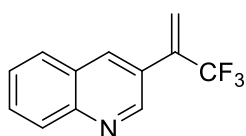
3-(3,3,3-Trifluoroprop-1-en-2-yl)pyridine (1n)



According to Method A, the reaction was carried out with the corresponding arylboronic acid (1.48 g, 12.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H_2O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol).

The crude product was purified by flash column chromatography on silica gel (PE: DCM=5:1) to afford 0.82 g (59%) of **1n** as a brown oil: ^1H NMR (400 MHz, CDCl_3) δ : 8.71 (s, 1H), 8.64 (d, $J = 4.7$ Hz, 1H), 7.78 (d, $J = 8.7$ Hz, 1H), 7.34 (t, $J = 7.0$ Hz, 1H), 6.07 (s, 1H), 5.85 (s, 1H). All data are in accordance with the literature.²

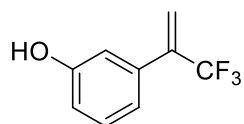
3-(3,3,3-Trifluoroprop-1-en-2-yl)quinoline (1o)



According to Method B, the reaction was carried out with the corresponding arylboronic acid (1.39 g, 8.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (168.5 mg, 0.24 mmol), K_2CO_3 (4.42 g, 32.00 mmol), THF (24 mL) and H_2O (16 mL), 2-bromo-3,3,3-trifluoropropene (1.66 mL, 16.00 mmol). The

crude product was purified by flash column chromatography on silica gel (PE: EA=10:1) to afford 1.03 g (58%) of **1o** as a yellow solid: ^1H NMR (400 MHz, CDCl_3) δ : 8.99 (s, 1H), 8.25 (s, 1H), 8.13 (d, $J = 8.6$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.77 (t, $J = 7.0$ Hz, 1H), 7.61 (t, $J = 7.0$ Hz, 1H), 6.17 (s, 1H), 6.00 (s, 1H). All data are in accordance with the literature.²

3-(3,3,3-Trifluoroprop-1-en-2-yl)phenol (1p)

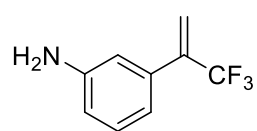


According to Method A, the reaction was carried out with the corresponding arylboronic acid (1.66 g, 12.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol),

DME (24 mL) and H_2O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (DCM) to afford 0.48 g (32%) of **1p** as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ :

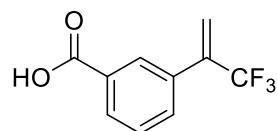
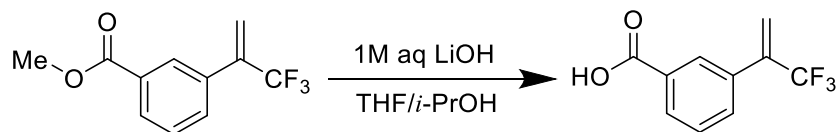
7.24 (s, 1H), 7.04 (d, $J = 7.8$ Hz, 1H), 6.94 (s, 1H), 6.86 (d, $J = 8.1$ Hz, 1H), 5.95 (s, 1H), 5.78 (s, 1H), 4.81 (s, 1H). All data are in accordance with the literature.³

3-(3,3,3-Trifluoroprop-1-en-2-yl)aniline (**1q**)



According to Method A, the reaction was carried out with the corresponding arylboronic acid (1.64 g, 12.00 mmol), Pd(PPh₃)₂Cl₂ (285.7 mg, 0.41 mmol), TEA (8 mL, 57.00 mmol), DME (24 mL) and H₂O (12 mL), 2-bromo-3,3,3-trifluoropropene (0.83 mL, 8.00 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA=5:1) to afford 0.72 g (50%) of **1q** as a brown oil: ¹H NMR (400 MHz, CDCl₃) δ : 7.16 (t, $J = 7.8$ Hz, 1H), 6.84 (d, $J = 7.7$ Hz, 1H), 6.76 (s, 1H), 6.70 (d, $J = 8.0$ Hz, 1H), 5.91 (s, 1H), 5.74 (s, 1H), 3.72 (s, 2H). All data are in accordance with the literature.¹

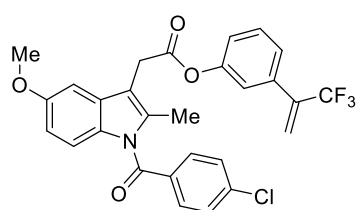
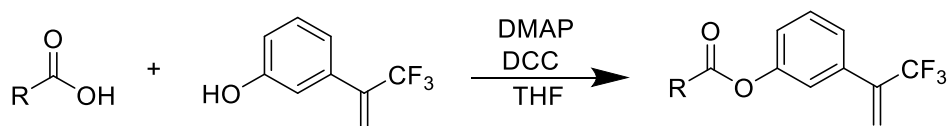
3-(3,3,3-Trifluoroprop-1-en-2-yl)benzoic acid (**1r**)



To a 50 mL round bottom flask equipped with a stir bar was added methyl 3-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (0.85 g, 3.71 mmol, 1.0 equiv.) followed by THF (10.2 mL). The reaction mixture was cooled to 0 °C in an ice-water bath. After stirring for approximately 10 min, an aq 1 M solution of LiOH (5.56 mL, 5.56 mmol, 1.5 equiv.) was added, followed by *i*-PrOH (2.04 mL, 26.64 mmol, 7.18 equiv.). After stirring for 10 min, the ice-bath was removed, and the solution was allowed to stir for approximately 5 hours at rt, at which time it was judged to be complete by HPLC. The crude reaction was concentrated in vacuo by rotary evaporation, and the resulting residue was dissolved in H₂O (5 mL). This aq solution was transferred to a separatory funnel and washed with Et₂O (2*3 mL). The aq layer was then acidified with 1 M aq HCl to a pH of ~1 and extracted with EtOAc (4*5 mL). The combined EtOAc layers were then dried (Na₂SO₄) and filtered. The solvent was removed in vacuo by rotary evaporation to give the desired carboxylic acid as a white solid (0.67 g, 85% yield): ¹H NMR (400 MHz, CDCl₃) δ : 8.20 (s, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 7.71 (d, $J = 7.8$ Hz,

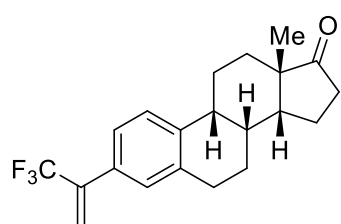
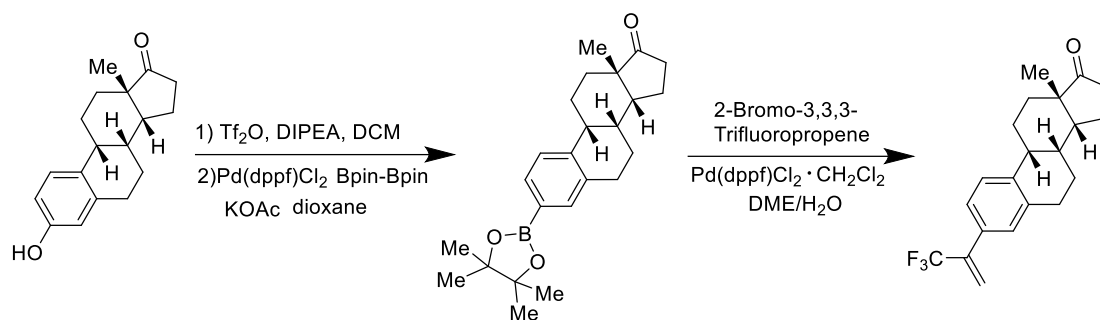
1H), 7.52 (t, $J = 7.8$ Hz, 1H), 6.05 (s, 1H), 5.87 (s, 1H). All data are in accordance with the literature.⁷

3-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**1s**)



To a solution of carboxylic acid (3.26 g, 9.10 mmol, 1.0 equiv.), 4-dimethylaminopyridine (DMAP) (111.2 mg, 0.90 mmol, 0.1 equiv.) and **1p** (1.88 g, 10.00 mmol, 1.1 equiv.) in DMF (22.75 mL), *N,N*-dicyclohexylcarbodiimide (DCC) (2.06 g, 10.00 mmol, 1.1 equiv.) was added. The reaction mixture was stirred at room temperature for 5 hours (TLC tracking detection). The mixture was purified by flash column chromatography on silica gel (PE: DCM=1:5) to afford 3.2 g (67%) of **1s** as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ : 7.68 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.40-7.30 (m, 2H), 7.20 (s, 1H), 7.14-7.11 (m, 1H), 7.09 (d, $J = 2.5$ Hz, 1H), 6.93 (d, $J = 9.0$ Hz, 1H), 6.73 (dd, $J = 9.0$ Hz, $J = 2.5$ Hz, 1H), 5.99 (s, 1H), 5.79 (s, 1H), 3.94 (s, 2H), 3.85 (s, 3H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 169.06, 168.19, 156.08, 150.66, 139.25, 137.84 (dd, $J = 60.4$ Hz, $J = 30.2$ Hz), 136.16, 134.88, 133.73, 131.11, 130.78, 130.38, 129.52, 129.05, 124.88, 123.01 (dd, $J = 506.6$ Hz, $J = 272.5$ Hz), 122.03, 121.38, 121.27 (dd, $J = 11.4$ Hz, $J = 5.7$ Hz), 120.41, 114.97, 111.74, 101.11, 55.59, 30.40, 13.34. ¹⁹F NMR (376 MHz, CDCl₃) δ : -64.58. HRMS *m/z* (ESI) calcd for C₂₇H₂₂ClF₃NO₄ (M + H)⁺ 528.1189, found 528.1189.

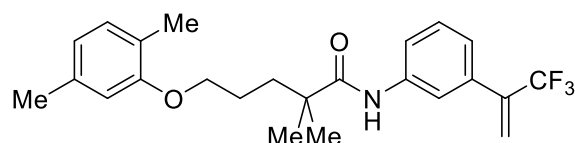
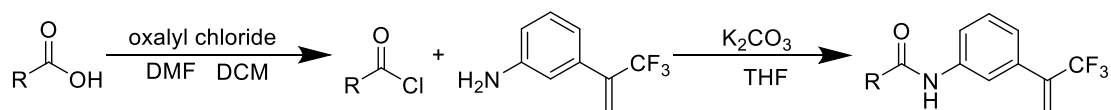
(8R,9R,13S,14R)-13-Methyl-3-(3,3,3-trifluoroprop-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1t)



To a mixture of Estrone (2.71 g, 16.00 mmol, 1.0equiv.) and DIPEA (1.89 mL, 17.60 mmol, 1.1 equiv.) in DCM (40 mL) were added Tf_2O (1.85 mL, 17.60 mmol, 1.1 equiv.) under an argon at 0 °C. The reaction mixture was stirred at room temperature for 0.5 hours. Then, the reaction mixture was extracted with EtOAc, and the organic phase was washed with brine, and dried over anhydrous Na_2SO_4 . After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected column chromatography on silica gel (PE: EA=5:1) to give estrone trifluoromethanesulfonic ester (1.85 g, yield: 28%). To a 50 mL of sealed tube were added estrone trifluoromethanesulfonic ester (1.84 g, 4.53 mmol, 1.0 equiv.), bis(pinacolato)diboron (2.30 g, 9.06 mmol, 2.0 equiv.), KOAc (1.34 g, 13.59 mmol, 3.0 equiv.), and $\text{Pd}(\text{dppf})\text{Cl}_2$ (148mg, 0.18 mmol, 4 mol%) under argon, followed by dioxane (18.12 mL) with stirring. The sealed tube was screw capped and heated to 120 °C (oil bath). After stirring for 8 hours, the reaction mixture was cooled to room temperature and diluted with THF, dried (Na_2SO_4), then filtered and concentrated. The crude product was purified by column chromatography on silica gel (PE: EA=20:1) to give the desired boronate pinacol (1.23 g, yield: 71.39%) which was used in the next step. To a 50 mL Schlenk tube was added (8R,9R,13S,14R)-13-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1.14 g, 3.00 mmol, 1.0 equiv), Cs_2CO_3 (1.18 g, 3.60 mmol, 1.2 equiv.), and $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ (0.25 g, 0.30 mmol, 0.1 equiv.). The tube was sealed with a rubber septum and evacuated three times via branch, then purged with N_2 . A mixture of degassed DME (11.7 mL) and degassed, deionized H_2O (3.5 mL) were added via syringe, followed by 2-bromo-3,3,3-trifluoroprop-1-ene (0.62 mL, 6.00 mmol, 2.0 equiv.). The tube was heated to 80 °C

(oil bath). The reaction mixture was allowed to stir at this temperature for 24 hours. Reaction progress was monitored by TLC. Once completed, the reaction was cooled to rt and diluted in EtOAc (25 mL). The resultant crude product was purified by column chromatography on silica gel (PE: DCM=10:1) to give the desired trifluoromethyl alkene as a white solid (0.92 g, 89% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.31 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.19 (s, 1H), 5.91 (s, 1H), 5.74 (s, 1H), 2.96-2.93 (m, 2H), 2.55-2.41 (m, 2H), 2.36-2.29 (m, 1H), 2.20-2.05 (m, 4H), 1.69-1.85 (m, 3H), 1.55-1.44 (m, 3H), 0.92 (s, 3H). All data are in accordance with the literature.⁸

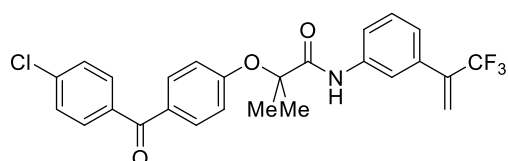
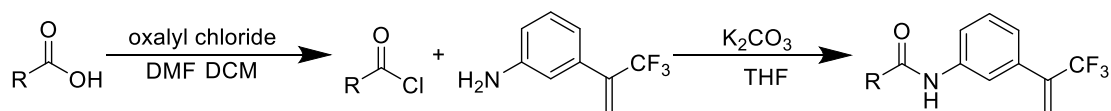
5-(2,5-Dimethylphenoxy)-2,2-dimethyl-N-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)pentanamide (1u)



To a mixture of Gemfibrozil (0.75 g, 3.00 mmol, 1.0 equiv.) and oxalylchloride (0.51 mL, 6.00 mmol, 2.0 equiv.) in dry CH₂Cl₂ (12 mL) was added dropwise DMF (23.4 μL, 0.30 mmol, 0.1 equiv.). The reaction mixture was stirred at room temperature for 6 hours. Removal of the solvent in vacuo afforded the desired acid chloride which was used in the next step without further purification. To a mixture of 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (0.57 g, 3.00 mmol, 1.0 equiv.) and K₂CO₃ (0.42 g, 3.00 mmol, 1.0 equiv.) in dry THF (6 mL) was added dropwise a solution of the freshly prepared acid chloride (3.00 mmol, 1.0 equiv.) in dry THF (6 mL). This mixture was stirred at room temperature for 6 hours before water was added to quench the reaction. The resultant mixture was extracted with EtOAc (3*20 mL). The combined organic phases were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resultant crude product was purified by column chromatography on silica gel (PE: EA=10:1) to give the desired trifluoromethyl alkene as a yellow solid (1.02 g, 82% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.64 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.39 (s, 1H), 7.33 (t, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 5.96 (s, 1H), 5.79 (s, 1H), 3.95 (s, 2H), 2.29 (s, 3H), 2.17 (s, 3H), 1.83 (s, 4H), 1.35 (s, 6H). All data are

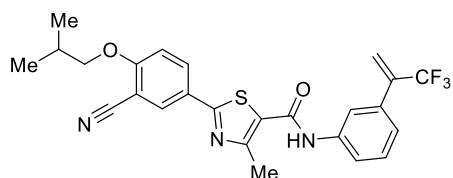
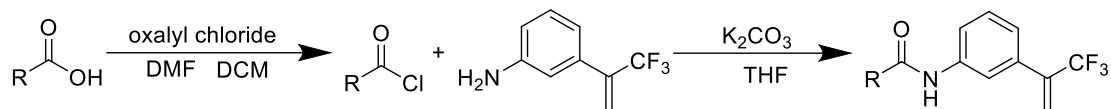
in accordance with the literature.⁹

2-(4-(4-Chlorobenzoyl)phenoxy)-2-methyl-N-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)propanamide (1v)



To a mixture of Fenofibric acid (1.09 g, 3.00 mmol, 1.0 equiv.) and oxalylchloride (0.51 mL, 6.00 mmol, 2.0 equiv.) in dry CH_2Cl_2 (12 mL) was added dropwise DMF (23.4 μL , 0.30 mmol, 0.1 equiv.). The reaction mixture was stirred at room temperature for 6 hours. Removal of the solvent in vacuo afforded the desired acid chloride which was used in the next step without further purification. To a mixture of 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (0.57 g, 3.00 mmol, 1.0 equiv.) and K_2CO_3 (0.42 g, 3.00 mmol, 1.0 equiv.) in dry THF (6 mL) was added dropwise a solution of the freshly prepared acid chloride (3.00 mmol, 1.0 equiv.) in dry THF (6 mL). This mixture was stirred at room temperature for 6 hours before water was added to quench the reaction. The resultant mixture was extracted with EtOAc (3*20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The resultant crude product was purified by column chromatography on silica gel (PE:EA=10:1) to give the desired trifluoromethyl alkene as a white solid (1.10 g, 75% yield). **^1H NMR (400 MHz, CDCl_3)** δ : 8.41 (s, 1H), 7.77 (d, J = 8.8 Hz, 2H), 7.72-7.70 (m, 3H), 7.59-7.56 (m, 1H), 7.45 (d, J = 8.6 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.24-7.22 (m, 1H), 7.05 (d, J = 8.8 Hz, 2H), 5.97 (s, 1H), 5.80 (s, 1H), 1.68 (s, 6H). **^{13}C NMR (100 MHz, CDCl_3)** δ : 194.12, 172.38, 158.01, 138.71, 138.39 (dd, J = 60.1 Hz, J = 30.1 Hz), 137.53, 135.91, 134.55, 132.22, 131.95, 131.19, 129.29, 128.61, 123.63, 123.11 (dd, J = 545.0 Hz, J = 272.5 Hz), 121.11 (dd, J = 11.3 Hz, J = 5.7 Hz), 120.35, 120.18, 118.84, 82.40, 25.03. **^{19}F NMR (376 MHz, CDCl_3)** δ : -64.64. **HRMS m/z (ESI)** calcd for $\text{C}_{26}\text{H}_{22}\text{ClF}_3\text{NO}_3$ ($M + \text{H}$)⁺ 488.1240, found 488.1239.

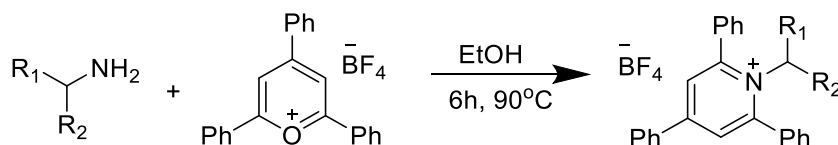
2-(3-Cyano-4-isobutoxyphenyl)-4-methyl-N-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)thiazole-5-carboxamide (1w)



To a mixture of Febuxostat (0.95 g, 3.00 mmol, 1.0 equiv.) and oxalylchloride (0.51 mL, 6.00 mmol, 2.0 equiv.) in dry CH_2Cl_2 (12 mL) was added dropwise DMF (23.4 μL , 0.30 mmol, 0.1 equiv.). The reaction mixture was stirred at room temperature for 6 hours. Removal of the solvent in vacuo afforded the desired acid chloride which was used in the next step without further purification. To a mixture of 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (0.57 g, 3.00 mmol, 1.0 equiv.) and K_2CO_3 (0.42 g, 3.00 mmol, 1.0 equiv.) in dry THF (6 mL) was added dropwise a solution of the freshly prepared acid chloride (3.00 mmol, 1.0 equiv.) in dry THF (6 mL). This mixture was stirred at room temperature for 6 hours before water was added to quench the reaction. The resultant mixture was extracted with EtOAc (3*20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The resultant crude product was purified by column chromatography on silica gel (PE: EA=5:1) to give the desired trifluoromethyl alkene as a white solid (1.09 g, 75% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.16 (d, $J = 2.2$ Hz, 1H), 8.08 (dd, $J = 8.9$ Hz, $J = 2.3$ Hz, 1H), 7.67-7.62 (m, 2H), 7.54 (s, 1H), 7.40 (t, $J = 7.9$ Hz, 1H), 7.02 (d, $J = 8.9$ Hz, 1H), 6.01-6.00 (m, 1H), 5.84-5.82 (m, 1H), 3.91 (d, $J = 6.5$ Hz, 2H), 2.80 (s, 3H), 2.24-2.17 (m, 1H), 1.09 (d, $J = 6.7$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 165.00, 162.49, 157.24, 138.48, 138.18, 134.62, 132.53, 131.96, 129.39, 125.63, 125.50, 124.53, 123.96, 121.81, 121.23, 121.17, 120.96, 120.91, 119.36, 115.49, 115.40, 112.65, 102.89, 75.70, 28.11, 18.97, 17.50. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -64.63. HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{23}\text{F}_3\text{N}_3\text{O}_2\text{S}$ ($\text{M} + \text{H}$) $^+$ 486.1463, found 486.1463.

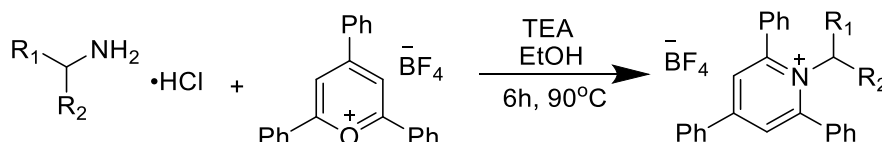
5.Preparation of Katritzky Salts

Method C: ¹⁰



An oven dried equipped with a stir bar was charged with the amine (1.2 equiv), 2,4,6-triphenylpyryliumtetrafluoroborate (1.0 equiv) and EtOH (2 M) was added. The mixture was stirred and heated at reflux in an oil bath at 90 °C for 6 hours. The mixture was then allowed to cool to room temperature. If product precipitation occurred during reflux, the solid was filtered, washed with EtOH (3*5 mL) and then Et₂O (3*20 mL), and dried under high vacuum. If product precipitation did not occur during reflux, the solution was diluted with Et₂O (3*volume of EtOH was used) and vigorously stirred for 1 h to induce trituration. The resulting solid pyridinium salt was filtered and washed with Et₂O (3*10 mL). If the salt still did not precipitate, it was subjected to silica gel chromatography with acetone/DCM.

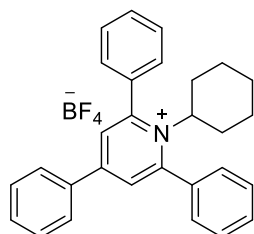
Method D: ¹¹



An oven dried equipped with a stir bar was charged with the amine hydrochloride (1.2 equiv.), 2,4,6-triphenylpyryliumtetrafluoroborate (1.0 equiv.), TEA (1.2 equiv.) and EtOH (1 M) was added. The mixture was stirred and heated at reflux in an oil bath at 90 °C for 6 hours. The mixture was then allowed to cool to room temperature. If product precipitation occurred during reflux, the solid was filtered, washed with EtOH (3*5 mL) and then Et₂O (3*20 mL), and dried under high vacuum. If product precipitation did not occur during reflux, the solution was diluted with Et₂O (3*volume of EtOH was used) and vigorously stirred for 1 hour to induce trituration. The resulting solid pyridinium salt was filtered and washed with Et₂O (3*10 mL). If the salt still did not

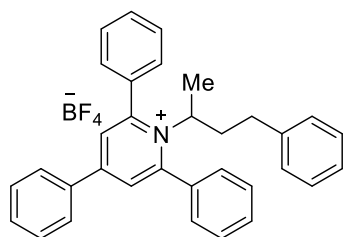
precipitate, it was subjected to silica gel chromatography with acetone/DCM.

1-Cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**2a**)



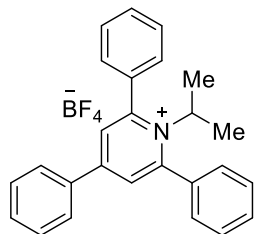
According to Method C, the reaction was carried out with the corresponding amine (2.75 mL, 24.00 mmol), triphenylpyryliumtetrafluoroborate (7.92 g, 20.00 mmol), EtOH (10 mL). Et₂O was used to wash thrice to obtain the precipitate **2a** as a white solid (6.27 g, 66% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.86-7.74 (m, 8H), 7.61-7.50 (m, 9H), 4.61-4.67 (m, 1H), 2.16-2.13 (m, 2H), 1.61-1.34 (m, 5H), 0.80-0.60 (m, 3H). All data are in accordance with the literature.¹⁰

2,4,6-Triphenyl-1-(4-phenylbutan-2-yl)pyridin-1-ium tetrafluoroborate (**2b**)



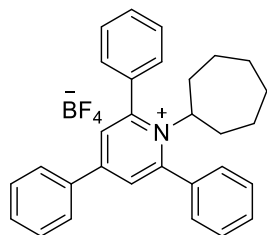
According to Method C, the reaction was carried out with the corresponding amine (3.89 mL, 24.00 mmol), triphenylpyryliumtetrafluoroborate (7.92 g, 20.00 mmol), EtOH (10 mL). The crude product was purified by flash column chromatography on silica gel (DCM: acetone=10:1) to afford **2b** as a yellow solid (7.06 g, 67% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.81-7.46 (m, 17H), 7.18-7.16 (m, 3H), 6.89-6.86 (m, 2H), 4.94-4.87 (m, 1H), 2.43-2.36 (m, 1H), 2.23-2.12 (m, 2H), 1.81-1.72 (m, 1H), 1.46 (d, *J* = 7.0 Hz, 3H). All data are in accordance with the literature.¹²

1-Isopropyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**2c**)



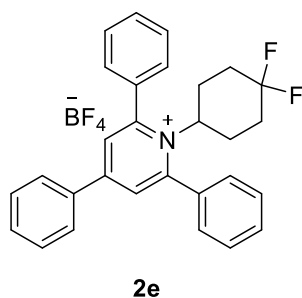
According to Method C, the reaction was carried out with the corresponding amine (0.41 mL, 4.80 mmol), triphenylpyryliumtetrafluoroborate (1.58 g, 4.00 mmol), EtOH (2 mL). Et₂O was used to wash thrice to obtain the precipitate **2c** as a white solid (1.04 g, 60% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.83-7.75 (m, 8H), 7.59-7.49 (m, 9H), 5.17-5.10 (m, 1H), 1.37 (d, *J* = 7.0 Hz, 6H). All data are in accordance with the literature.¹³

1-Cycloheptyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2d)



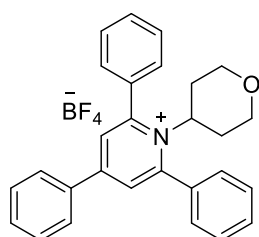
According to Method C, the reaction was carried out with the corresponding amine (0.76 mL, 6.00 mmol), triphenylpyryliumtetrafluoroborate (1.98 g, 5.00 mmol), EtOH (2.5 mL). The crude product was purified by flash column chromatography on silica gel (DCM: acetone=5:1) to afford **2d** as a yellow solid (0.72 g, 34% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.76-7.72 (m, 7H), 7.59-7.48 (m, 10H), 4.83-4.76 (m, 1H), 2.24-2.20 (m, 2H), 1.64-1.54 (m, 2H), 1.44-1.39 (m, 2H), 1.11-1.00 (m, 6H). All data are in accordance with the literature.¹³

1-(4,4-Difluorocyclohexyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2e)



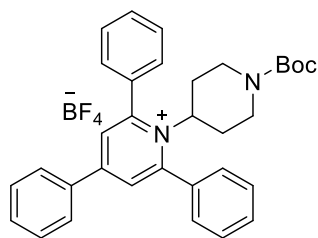
According to Method D, the reaction was carried out with the corresponding amine hydrochloride (0.82 g, 4.80 mmol), triphenylpyryliumtetrafluoroborate (1.58 g, 4.00 mmol), TEA (0.64 mL, 4.80 mmol), EtOH (4 mL). Et₂O was used to wash thrice to obtain the precipitate **2e** as a white solid (1.3 g, 64% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.87-7.76 (m, 8H), 7.62-7.48 (m, 9H), 4.74-4.70 (m, 1H), 2.29-2.26 (m, 2H), 1.96-1.79 (m, 4H), 1.30-1.15 (m, 2H). All data are in accordance with the literature.¹⁴

2,4,6-Triphenyl-1-(tetrahydro-2H-pyran-4-yl)pyridin-1-ium tetrafluoroborate (2f)



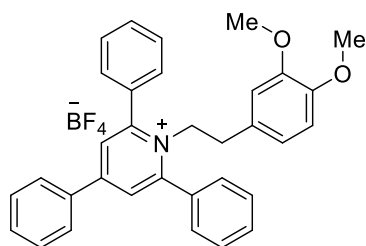
According to Method C, the reaction was carried out with the corresponding amine (0.63 mL, 6.00 mmol), triphenylpyryliumtetrafluoroborate (1.98 g, 5.00 mmol), EtOH (2.5 mL). Et₂O was used to wash thrice to obtain the precipitate **2f** as a white solid (1.96 g, 82% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.82 (s, 2H), 7.77-7.72 (m, 6H), 7.63-7.57 (m, 6H), 7.53-7.45 (m, 3H), 4.93-4.85 (m, 1H), 3.73 (dd, J = 7.5 Hz, 3.8 Hz, 2H), 2.82 (t, J = 10.4 Hz, 2H), 2.08-2.05 (m, 2H), 1.94-1.84 (m, 2H). All data are in accordance with the literature.¹⁴

1-(1-(Tert-butoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2g)



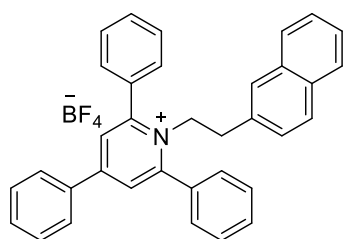
According to Method C, the reaction was carried out with the corresponding amine (1.20 g, 6.00 mmol), triphenylpyryliumtetrafluoroborate (1.98 g, 5.00 mmol), EtOH (2.5 mL). The crude product was purified by flash column chromatography on silica gel (DCM: acetone=5:1) to afford **2g** as a white solid (1.84 g, 64% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.86 (s, 2H), 7.78-7.74 (m, 6H), 7.61-7.48 (m, 9H), 4.79 (t, $J = 12.1$ Hz, 1H), 4.08-3.81 (m, 2H), 2.14-1.72 (m, 6H), 1.31 (s, 9H). All data are in accordance with the literature.¹⁴

1-(3,4-Dimethoxyphenethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2h)



According to Method C, the reaction was carried out with the corresponding amine (2.03 mL, 12.00 mmol), triphenylpyryliumtetrafluoroborate (3.96 g, 10.00 mmol), EtOH (5 mL). Et_2O was used to wash thrice to obtain the precipitate **2h** as a brown solid (5.04 g, 91% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.94 (s, 2H), 7.82-7.79 (m, 6H), 7.65-7.53 (m, 9H), 6.55 (d, $J = 8.2$ Hz, 1H), 5.92 (dd, $J = 8.1$ Hz, 1.9 Hz, 1H), 5.73 (d, $J = 1.9$ Hz, 1H), 4.66 (t, $J = 8.2$ Hz, 2H), 3.78 (s, 3H), 3.58 (s, 3H), 2.65 (t, $J = 7.7$ Hz, 2H). All data are in accordance with the literature.¹⁰

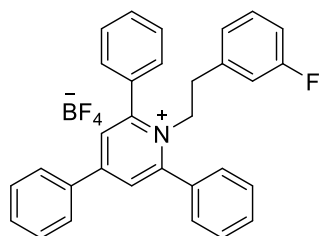
1-(2-(Naphthalen-2-yl)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2i)



According to Method C, the reaction was carried out with the corresponding amine (1.62 g, 9.40 mmol), triphenylpyryliumtetrafluoroborate (3.10 g, 7.80 mmol), EtOH (3.9 mL). Et_2O was used to wash thrice to obtain the precipitate **2i** as a white solid (3.46 g, 79% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.90-7.23 (m, 20H), 7.12-6.97 (m, 2H), 6.45-6.35 (m, 2H), 4.81-4.77 (m, 2H), 3.15-3.08 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 156.46, 156.02, 134.02, 133.60, 132.77, 132.03, 131.41, 131.32, 130.97, 129.61, 129.45, 129.30, 128.66, 128.14, 126.79, 126.54, 126.30, 125.69, 125.36, 125.24, 121.90, 54.95, 32.87.

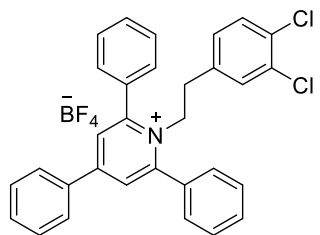
^{19}F NMR (376 MHz, CDCl_3) δ : -152.97 . HRMS m/z (ESI) calculated for $\text{C}_{35}\text{H}_{28}\text{N}[\text{M}-\text{BF}_4]^+$ 462.2216, found 462.2212.

1-(3-Fluorophenethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2j)



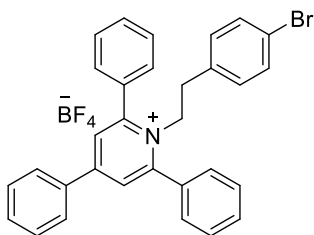
According to Method C, the reaction was carried out with the corresponding amine (0.63 mL, 4.80 mmol), triphenylpyryliumtetrafluoroborate (1.58 g, 4.00 mmol), EtOH (2 mL). Et₂O was used to wash thrice to obtain the precipitate **2j** as a white solid (1.24 g, 60% yield): ^1H NMR (400 MHz, CDCl_3) δ : 7.94-7.90 (m, 8H), 7.67-7.52 (m, 9H), 7.03 (dd, J = 13.9 Hz, 7.9 Hz, 1H), 6.84-6.79 (m, 1H), 6.08 (d, J = 7.6 Hz, 1H), 5.96 (m, J = 9.2 Hz, 1H), 4.64 (t, J = 8.2 Hz, 2H), 2.72 (t, J = 8.3 Hz, 1H). All data are in accordance with the literature.¹⁵

1-(3,4-Dichlorophenethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2k)



According to Method C, the reaction was carried out with the corresponding amine (0.36 mL, 2.40 mmol), triphenylpyryliumtetrafluoroborate (0.79 g, 2.00 mmol), EtOH (1 mL). Et₂O was used to wash thrice to obtain the precipitate **2k** as a white solid (1.01 g, 89% yield): ^1H NMR (400 MHz, CDCl_3) δ : 7.93-7.63 (m, 14H), 7.58-7.52 (m, 3H), 7.12 (d, J = 8.2 Hz, 1H), 6.30 (d, J = 2.0 Hz, 1H), 6.16 (dd, J = 8.2 Hz, 2.1 Hz, 1H), 4.64-4.60 (m, 2H), 2.72-2.68 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 156.32, 156.18, 135.63, 133.99, 132.60, 132.53, 132.04, 131.30, 131.18, 130.58, 130.09, 129.59, 129.36, 129.07, 128.14, 127.55, 126.75, 55.09, 34.49. ^{19}F NMR (376 MHz, CDCl_3) δ : -152.72 . HRMS m/z (ESI) calculated for $\text{C}_{31}\text{H}_{24}\text{Cl}_2\text{N}[\text{M}-\text{BF}_4]^+$ 480.1280, found 480.1275.

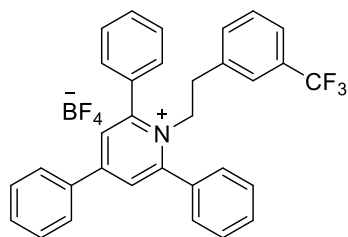
1-(4-Bromophenethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2l)



According to Method C, the reaction was carried out with the corresponding amine (0.37 mL, 2.40 mmol), triphenylpyryliumtetrafluoroborate (0.79 g, 2.00 mmol), EtOH (1 mL). Et₂O was used to wash thrice to obtain the precipitate **2l** as a white solid (1.02 g, 87% yield): ^1H NMR

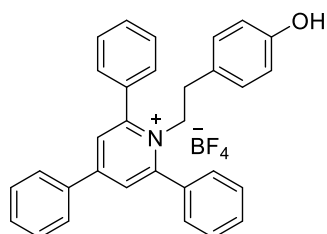
(400 MHz, CDCl₃) δ : 7.89 (s, 2H), 7.81-7.76 (m, 6H), 7.64-7.51 (m, 9H), 7.16 (d, J = 8.4 Hz, 2H), 6.15 (d, J = 8.4 Hz, 2H), 4.60 (t, J = 8.2 Hz, 2H), 2.67 (t, J = 8.3 Hz, 2H). All data are in accordance with the literature.¹⁰

2,4,6-Triphenyl-1-(3-(trifluoromethyl)phenethyl)pyridin-1-ium tetrafluoroborate (2m)



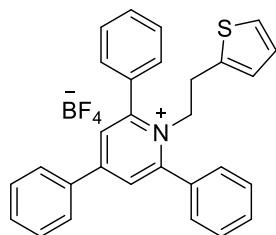
According to Method C, the reaction was carried out with the corresponding amine (0.77 mL, 4.80 mmol), triphenylpyryliumtetrafluoroborate (1.58 g, 4.00 mmol), EtOH (2 mL). Et₂O was used to wash thrice to obtain the precipitate **2m** as a white solid (2.97 g, 96% yield): ¹H NMR (400 MHz, CDCl₃) δ : 7.93-7.77 (m, 8H), 7.66-7.51 (m, 9H), 7.38 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.41 (s, 1H), 4.63 (t, J = 8.0 Hz, 2H), 2.78 (d, J = 8.7 Hz, 2H). All data are in accordance with the literature.¹⁰

1-(4-Hydroxyphenethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2n)



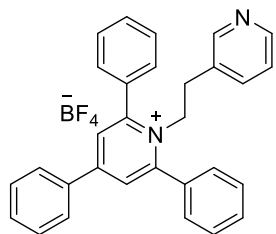
According to Method C, the reaction was carried out with the corresponding amine (0.99 g, 7.20 mmol), triphenylpyryliumtetrafluoroborate (2.38 g, 6.00 mmol), EtOH (3 mL). Et₂O was used to wash thrice to obtain the precipitate **2n** as a white solid (2.97 g, 96% yield): ¹H NMR (400 MHz, CD₃CN) δ : 8.19, (s, 2H), 8.01-7.99 (m, 2H), 7.74-7.60 (m, 13H), 6.54 (d, J = 8.5 Hz, 2H), 6.24 (d, J = 8.5 Hz, 2H), 4.48-4.51 (m, 2H), 2.60-2.56 (m, 2H). ¹³C NMR (100 MHz, DMSO-d₆) δ : 156.49, 156.06n 154.31, 133.15, 132.97, 132.43, 131.02, 129.61, 129.27, 129.07, 128.73, 126.00, 125.51, 115.44, 56.05, 33.94. ¹⁹F NMR (376 MHz, CDCl₃) δ : -148.19. HRMS m/z (ESI) calculated for C₃₁H₂₆NO [M-BF₄]⁺ 428.2009, found 428.2005.

2,4,6-Triphenyl-1-(2-(thiophen-2-yl)ethyl)pyridin-1-ium tetrafluoroborate (2o)



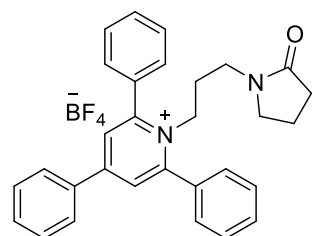
According to Method C, the reaction was carried out with the corresponding amine (0.56 mL, 4.80 mmol), triphenylpyryliumtetrafluoroborate (1.58 g, 4.00 mmol), EtOH (2 mL). Et₂O was used to wash thrice to obtain the precipitate **2o** as a white solid (1.42 g, 70% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.90 (s, 2H), 7.80-7.51 (m, 15H), 7.02 (d, *J* = 5.1 Hz, 1H), 6.76 (t, *J* = 3.8 Hz, 1H), 6.18 (d, *J* = 3.4 Hz, 1H), 4.74 (t, *J* = 7.6 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H). All data are in accordance with the literature.¹⁰

2,4,6-Triphenyl-1-(2-(pyridin-3-yl)ethyl)pyridin-1-ium tetrafluoroborate (2p)



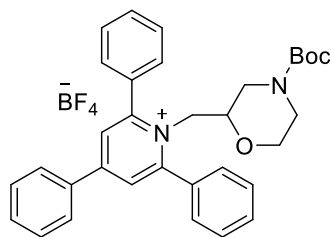
According to Method C, the reaction was carried out with the corresponding amine (0.56 mL, 4.80 mmol), triphenylpyryliumtetrafluoroborate (1.58 g, 4.00 mmol), EtOH (2 mL). Et₂O was used to wash thrice to obtain the precipitate **2p** as a white solid (1.4 g, 70% yield): ¹H NMR (400 MHz, CDCl₃) δ: 8.35 (dd, *J* = 4.8 Hz, 1H), 7.93 (s, 2H), 7.82-7.78 (m, 6H), 7.66-7.62 (m, 6H), 7.58-7.50 (m, 4H), 7.00 (dd, *J* = 8.3 Hz, 5.2 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 4.61 (t, *J* = 8.3 Hz, 2H), 2.75 (t, *J* = 8.4 Hz, 2H). All data are in accordance with the literature.¹²

1-(3-(2-Oxopyrrolidin-1-yl)propyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2q)



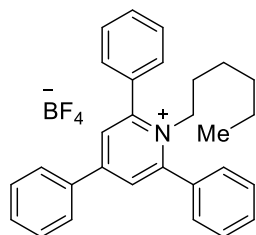
According to Method C, the reaction was carried out with the corresponding amine (0.84 mL, 6.00 mmol), triphenylpyryliumtetrafluoroborate (1.98 g, 5.00 mmol), EtOH (2.5 mL). Et₂O was used to wash thrice to obtain the precipitate **2q** as a yellow solid (2.36 g, 90% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.90 (s, 2H), 7.81-7.77 (m, 6H), 7.65-7.63 (m, 6H), 7.57-7.50 (m, 3H), 4.41 (t, *J* = 8.6 Hz, 2H), 2.87-2.79 (m, 4H), 2.05 (t, *J* = 7.9 Hz, 2H), 1.87-1.81 (m, 2H), 1.72-1.68 (m, 2H). All data are in accordance with the literature.¹⁰

1-((4-(Tert-butoxycarbonyl)morpholin-2-yl)methyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2r)



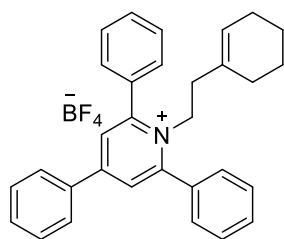
According to Method C, the reaction was carried out with the corresponding amine (1.04 g, 4.80 mmol), triphenylpyryliumtetrafluoroborate (1.58 g, 4.00 mmol), EtOH (2 mL). Et₂O was used to wash thrice to obtain the precipitate **2r** as a white solid (1.98 g, 83% yield): **¹H NMR (400 MHz, CDCl₃)** δ: 7.87-7.77 (m, 7H), 7.60-7.50 (m, 10H), 4.81-4.77 (m, 1H), 4.54-4.48 (m, 1H), 3.72-3.69 (m, 2H), 3.33-3.13 (m, 2H), 3.04-2.99 (m, 1H), 2.67-2.60 (m, 1H), 2.01 (s, 1H), 1.34 (s, 9H). **¹³C NMR (100 MHz, CDCl₃)** δ: 157.39, 155.76, 154.02, 133.56, 132.87, 132.26, 131.04, 129.66, 129.33, 129.19, 128.02, 126.06, 80.44, 71.68, 66.37, 55.44, 28.13, 28.08. **¹⁹F NMR (376 MHz, CDCl₃)** δ: -152.96. **HRMS m/z (ESI)** calculated for C₃₃H₃₅N₂O₃ [M-BF₄]⁺ 507.2642, found 507.2638.

1-Hexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2s)



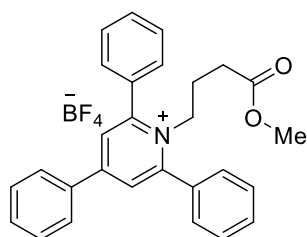
According to Method C, the reaction was carried out with the corresponding amine (0.63 mL, 4.80 mmol), triphenylpyryliumtetrafluoroborate (1.58 g, 4.00 mmol), EtOH (2 mL). Et₂O was used to wash thrice to obtain the precipitate **2s** as a white solid (1.72 g, 90% yield): **¹H NMR (400 MHz, CDCl₃)** δ: 7.85-7.68 (m, 8H), 7.58-7.44 (m, 9H), 4.42-4.35 (m, 2H), 1.42 (s, 2H), 0.95-0.88 (m, 2H), 0.73-0.62 (m, 7H). **¹³C NMR (100 MHz, CDCl₃)** δ: 156.26, 155.43, 133.92, 132.69, 131.81, 130.84, 129.52, 129.11, 128.95, 127.98, 126.52, 54.58, 29.85, 29.28, 25.50, 21.74, 13.54. **¹⁹F NMR (376 MHz, CDCl₃)** δ: -153.26. **HRMS m/z (ESI)** calculated for C₂₉H₃₀N [M-BF₄]⁺ 392.2373, found 392.2370.

1-(2-(Cyclohex-1-en-1-yl)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2t)



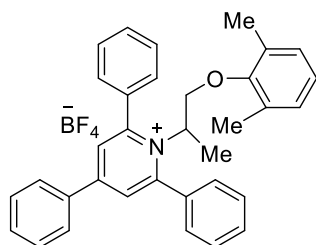
According to Method C, the reaction was carried out with the corresponding amine (0.84 mL, 6.00 mmol), triphenylpyryliumtetrafluoroborate (1.98 g, 5.00 mmol), EtOH (2.5 mL). Et₂O was used to wash thrice to obtain the precipitate **2t** as a white solid (2.29 g, 91% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.90 (s, 2H), 7.83-7.78 (6H), 7.63-7.61 (m, 6H), 7.57-7.51 (m, 3H), 4.82 (t, *J* = 2.8 Hz, 1H), 4.45 (t, *J* = 8.5 Hz, 2H), 2.02 (t, *J* = 8.5 Hz, 2H), 1.72 (s, 2H), 1.33-1.30 (m, 4H), 1.11 (s, 2H). All data are in accordance with the literature.¹⁰

1-(4-Methoxy-4-oxobutyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2u)



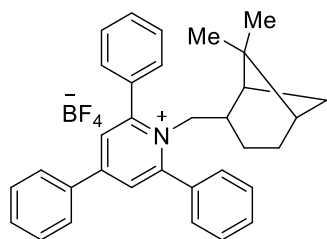
According to Method D, the reaction was carried out with the corresponding amine hydrochloride (0.92 g, 6.00 mmol), triphenylpyryliumtetrafluoroborate (1.98 g, 5.00 mmol), TEA (0.8 mL, 6.00 mmol), EtOH (5 mL). Et₂O was used to wash thrice to obtain the precipitate **2u** as a white solid (1.92 g, 78% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.90 (s, 2H), 7.82-7.78 (m, 6H), 7.63-7.51 (m, 9H), 4.53 (t, *J* = 8.4 Hz, 2H), 3.44 (s, 3H), 1.83-1.75 (m, 4H). All data are in accordance with the literature.¹⁰

1-(1-(2,6-Dimethylphenoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2v)



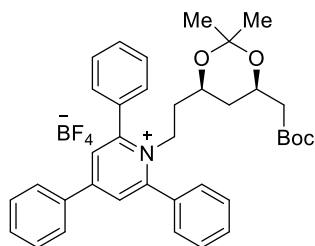
According to Method D, the reaction was carried out with the corresponding amine hydrochloride (1.30 g, 6.00 mmol), triphenylpyryliumtetrafluoroborate (1.98 g, 5.00 mmol), TEA (0.8 mL, 6.00 mmol), EtOH (5 mL). Et₂O was used to wash thrice to obtain the precipitate **2v** as a yellow solid (1.93 g, 70% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.81-7.46 (m, 17H), 7.18-7.16 (m, 3H), 6.89-6.86 (m, 2H), 4.94-4.87 (m, 1H), 2.43-2.36 (m, 1H), 2.23-2.12 (m, 2H), 1.81-1.72 (m, 1H), 1.46 (d, *J* = 7.0 Hz, 3H). All data are in accordance with the literature.¹⁴

1-(2-((1S,2S,5S)-6,6-Timethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2w)



According to Method C, the reaction was carried out with the corresponding amine (0.42 mL, 2.40 mmol), triphenylpyryliumtetrafluoroborate (0.79 g, 2.00 mmol), EtOH (1 mL). Et₂O was used to wash thrice to obtain the precipitate **2w** as a brown solid (0.93 g, 85% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.90-7.77 (m, 8H), 7.64-7.52 (m, 9H), 4.92-4.73 (m, 2H), 2.14-1.89 (m, 3H), 1.65-1.38 (m, 5H), 1.16-1.03 (m, 2H), 0.85 (s, 3H), 0.51 (d, *J* = 10.0 Hz, 1H), 0.07 (s, 3H). All data are in accordance with the literature.¹⁴

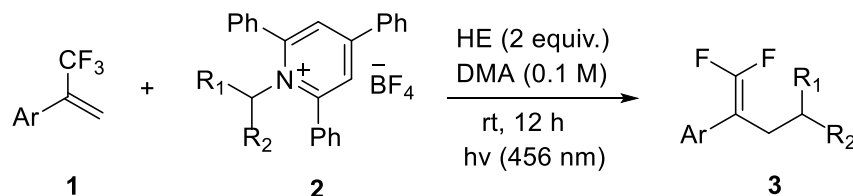
1-(2-(6-(2-(Tert-butoxy)-2-oxoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2x)



According to Method C, the reaction was carried out with the corresponding amine (0.66 mL, 2.40 mmol), triphenylpyryliumtetrafluoroborate (0.79 g, 2.00 mmol), EtOH (1 mL). Et₂O was used to wash thrice to obtain the precipitate **2x** as a white solid (0.99 g, 76% yield): ¹H NMR (400 MHz, CDCl₃) δ: 7.88-7.78 (m, 8H), 7.61-7.50 (m, 9H), 4.65-4.47 (m, 2H), 4.00-3.94 (m, 1H), 3.27 (s, 1H), 2.26-2.09 (m, 2H), 1.63-1.55 (m, 3H), 1.40 (s, 9H), 1.14 (s, 3H), 1.00 (s, 3H), 0.69 (q, *J* = 11.6 Hz, 1H). All data are in accordance with the literature.¹²

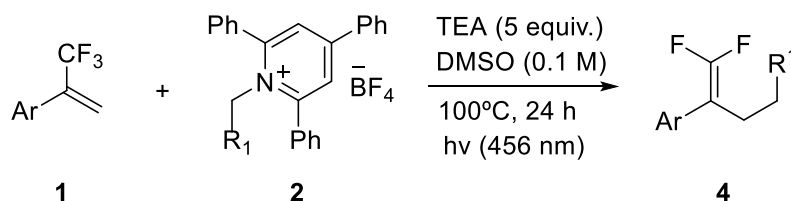
6. Experimental Procedures and Characterization of Products

Procedure A



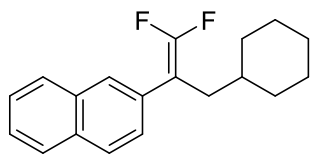
In a nitrogen-filled glovebox, an oven-dried 8.0 mL vial with a stirring bar was added with Katritzky salt (**2**) (1.5 equiv.), HE (hantzsch ester) (2.0 equiv.) and Trifluoromethyl Alkenes (**1**) (1.0 equiv.). DMA (*N,N*-Dimethylacetamide) (0.1 M) were then added. The resulting mixture was stirred at room temperature under blue LED (456 nm) irradiation for 12 hours. After this time, the reaction mixture was diluted with DCM and washed with a saturated brine for 3 times. The organic layer was separated, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography.

Procedure B



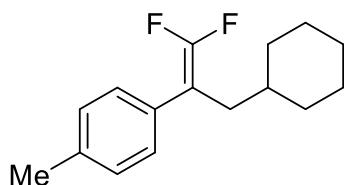
In a nitrogen-filled glovebox, an oven-dried 8.0 mL vial with a stirring bar was added with Katritzky salt (**2**) (1.5 equiv.) and Trifluoromethyl Alkenes (**1**) (1.0 equiv.). TEA (Triethylamine) (5.0 equiv.) and DMSO (Dimethyl sulfoxide) (0.1 M) were then added. The resulting mixture was stirred at room temperature under blue LED (456 nm) irradiation for 24 hours. After this time, the reaction mixture was diluted with DCM and washed with a saturated brine for 3 times. The organic layer was separated, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography.

2-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)naphthalene (**3a**)



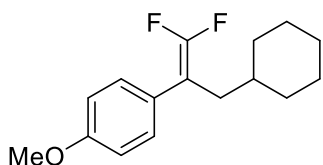
According to Procedure A, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 75.9 mg (88%) of **3a** as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.84-7.82 (m, 3H), 7.76 (s, 1H), 7.50-7.43 (m, 3H), 2.38 (dt, $J = 7.2$ Hz, 2.4 Hz, 2H), 1.73-1.63 (m, 5H), 1.32-1.22(m, 1H), 1.12-1.04 (m, 3H), 0.99-0.90 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.20 (dd, $J = 288.9\text{Hz}$, 284.9 Hz), 133.27, 132.41, 131.58 (dd, $J = 3.6$ Hz, 3.1 Hz), 127.94, 127.90, 127.58, 127.29 (t, $J = 3.3$ Hz), 126.24(t, $J = 3.1$ Hz), 126.18, 126.00, 91.22 (dd, $J = 22.2$ Hz, 12.4 Hz), 35.74 (t, $J = 2.3$ Hz), 35.30, 32.88, 26.39, 26.03. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.44 (d, $J = 9.2$ Hz), -90.76 (d, $J = 43.4$ Hz), -91.45 (d, $J = 43.4$ Hz). All data are in accordance with the literature.¹

1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (**3b**)



According to Procedure A, the reaction was carried out with **1b** (0.30 mmol, 55.9 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 63.8 mg (78%) of **3b** as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.22-7.13 (m, 4H), 2.35 (s, 3H), 2.25 (dt, $J = 7.2$ Hz, 2.5 Hz, 2H), 1.69-1.59 (m, 5H), 1.25-1.20 (m, 1H), 1.15-1.09 (m, 3H), 0.96-0.87 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 153.92 (dd, $J = 288.0$ Hz, 284.2 Hz), 136.79, 131.12 (t, $J = 3.7$ Hz), 129.07, 128.12 (t, $J = 3.3$ Hz), 90.82 (dd, $J = 21.9$ Hz, 12.9 Hz), 35.63, 35.25, 33.86, 26.42, 26.05, 21.10; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -91.77 (d, $J = 45.95$ Hz), -92.13 (d, $J = 45.95$ Hz). All data are in accordance with the literature.¹⁶

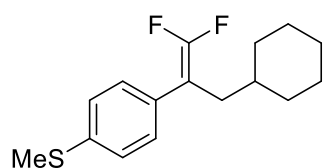
1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methoxybenzene (**3c**)



According to Procedure A, the reaction was carried out with **1c** (0.30 mmol, 60.6 mg), **2a** (0.60 mmol, 286.2 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on

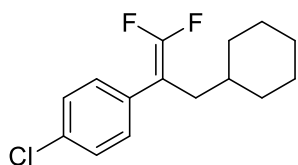
silica gel (PE) to afford 69.3 mg (86%) of **3c** as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.22 (d, $J = 7.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H), 2.23 (dt, $J = 7.1$ Hz, 2.2 Hz, 2H), 1.71-1.56 (m, 5H), 1.32-1.20 (m, 1H), 1.17-1.06 (m, 2H), 0.95-0.84 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 158.52, 153.85 (dd, $J = 287.3$ Hz, 283.8 Hz), 129.34 (t, $J = 3.3$ Hz), 126.21 ($J = 4.1$ Hz), 113.78, 90.45 (dd, $J = 21.9$ Hz, 12.8 Hz), 55.16, 35.60, 35.29, 32.83, 26.41, 26.05; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -92.25 (d, $J = 46.5$ Hz), -92.66 ($J = 46.5$ Hz). All data are in accordance with the literature.⁴

(4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)(methyl)sulfane (**3d**)



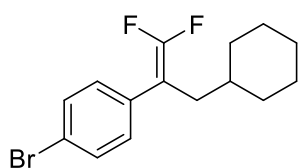
According to Procedure A, the reaction was carried out with **1d** (0.30 mmol, 65.4 mg), **2a** (0.60 mmol, 286.2 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 68.2 mg (80%) of **3d** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.27-7.25 (m, 1H), 7.23-7.22 (m, 3H), 2.49 (s, 3H), 2.24 (dt, $J = 7.2$ Hz, 2.4 Hz, 2H), 1.70-1.57 (m, 5H), 1.30-1.17 (m, 1H), 1.16-1.05 (m, 3H), 0.96-0.83 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 153.92 (dd, $J = 288.8$ Hz, 284.7 Hz, 285.3 Hz), 137.26, 130.70 (t, $J = 3.1$ Hz), 128.59 (t, $J = 3.5$ Hz), 126.61, 90.54 (dd, $J = 22.1$ Hz, 12.4 Hz), 35.64, 35.02, 32.81, 26.36, 26.02, 15.58; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -90.99 (d, $J = 44.2$ Hz), -91.46 (d, $J = 44.2$ Hz). All data are in accordance with the literature.¹⁷

1-Chloro-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (**3e**)



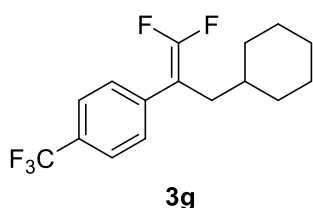
According to Procedure A, the reaction was carried out with **1e** (0.30 mmol, 61.8 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 70.2 mg (86%) of **3e** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.32 (d, $J = 8.6$ Hz, 2H), 7.23 (dd, $J = 8.6$ Hz, 1.1 Hz, 2H), 2.25 (dt, $J = 7.2$ Hz, 2.6 Hz, 2H), 1.70-1.58 (m, 5H), 1.26-1.18 (m, 1H), 1.17-1.06 (m, 3H), 0.97-0.85 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.98 (dd, $J = 289.1$ Hz, 283.8 Hz), 133.91, 132.56 (dd, $J = 4.8$ Hz, 3.2 Hz), 129.56 (t, $J = 3.3$ Hz), 128.59, 90.32 (dd, $J = 22.8$ Hz, 12.4 Hz), 35.67 (t, $J = 2.3$ Hz), 35.07, 32.81, 26.35, 26.02. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -90.70 (d, $J = 42.8$ Hz), -90.97 (d, $J = 42.8$ Hz). All data are in accordance with the literature.¹⁶

1-Bromo-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (**3f**)

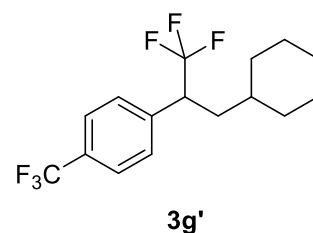


According to Procedure A, the reaction was carried out with **1f** (0.30 mmol, 75.0 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 82.1 mg (86%) of **3f** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.47 (d, $J = 8.5$ Hz, 2H), 7.17 (dd, $J = 8.5$ Hz, 1.2 Hz, 2H), 2.25 (dt, $J = 7.2$ Hz, 2.4 Hz, 2H), 1.72-1.56 (m, 5H), 1.29-1.18 (m, 1H), 1.15-1.05 (m, 3H), 0.98-0.85 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 153.90 (dd, $J = 289.3$ Hz, 285.3 Hz), 133.04 (dd, $J = 4.7$ Hz, 3.2 Hz), 131.54, 129.88 (t, $J = 3.3$ Hz), 121.01, 90.36 (dd, $J = 22.8$ Hz, 12.4 Hz), 35.66 (t, $J = 2.2$ Hz), 35.00, 32.80, 26.34, 26.01. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -90.27 (d, $J = 42.3$ Hz), -90.84 (d, $J = 42.3$ Hz). All data are in accordance with the literature.¹⁶

1-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-(trifluoromethyl)benzene (**3g**) and 1-(3-cyclohexyl-1,1,1-trifluoropropan-2-yl)-4-(trifluoromethyl)benzene (**3g'**)



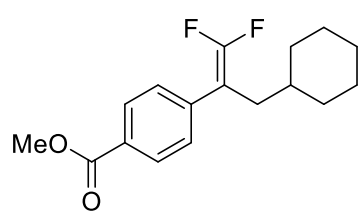
3g



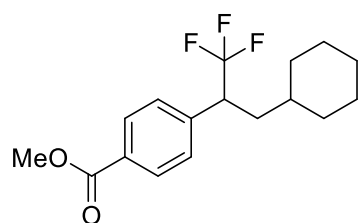
3g'

According to Procedure A, the reaction was carried out with **1g** (0.30 mmol, 93.4 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg), DIPEA (1.50 mmol, 261 μL) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 77.9 mg of a mixture of **3g** (82%) and **3g'** (3%) as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.60 (d, $J = 8.2$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 2.30 (dt, $J = 7.2$ Hz, 2.6 Hz, 2H), 1.67-1.60 (m, 5H), 1.25-1.17 (m, 1H), 1.14-1.06 (m, 3H), 0.96-0.88 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.28 (dd, $J = 290.3$ Hz, 285.5 Hz), 137.99, 129.24 (d, $J = 33.1$ Hz), 128.56, 125.36, 122.75, 90.56 (dd, $J = 22.6$ Hz, 11.4 Hz), 35.75, 34.96, 32.83, 26.32, 26.00. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -62.49, -69.59 (d, $J = 9.1$ Hz), -89.08 (d, $J = 39.9$ Hz), -89.94 (d, $J = 39.9$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{F}_5$ ($\text{M} + \text{H}$)⁺ 305.1329, found 305.1329.

Methyl 4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzoate (3h) and methyl 4-(3-cyclohexyl-1,1,1-trifluoropropan-2-yl)benzoate (3h')



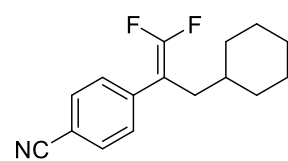
3h



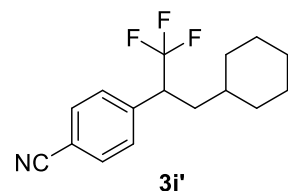
3h'

According to Procedure A, the reaction was carried out with **1h** (0.30 mmol, 69.1 mg), **2a** (0.45 mmol, 214.7mg), HE (0.60 mmol, 152.0 mg), DIPEA (1.50 mmol, 261 μ L) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE:DCM=7:1) to afford 78.8 mg of a mixture of **3h** (72%) and **3h'** (16%) as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.02 (d, $J = 8.6$ Hz, 2H), 7.38 (d, $J = 7.4$ Hz, 2H), 3.91 (s, 3H), 2.30 (dt, $J = 7.2$ Hz, 2.3 Hz, 2H), 1.66-1.59 (m, 5H), 1.23-1.19 (m, 1H), 1.12-1.05 (m, 3H), 0.95-0.87 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 166.70, 154.14 (dd, $J = 290.8$ Hz, 286.0 Hz), 138.99 (t, $J = 4.1$ Hz), 129.83, 129.60, 129.11, 128.74, 128.14 (t, $J = 3.2$ Hz), 90.83 (dd, $J = 22.7$ Hz, 11.8 Hz), 52.03, 47.20 (d, $J = 26.4$ Hz), 35.79, 34.81, 33.96 (d, $J = 13.6$ Hz), 32.77, 31.67, 29.66, 26.27, 25.96. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.51 (d, $J = 9.3$ Hz), -88.94 (d, $J = 39.1$ Hz), -89.61 (d, $J = 39.1$ Hz). All data are in accordance with the literature.¹⁸

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzonitrile (3i) and 4-(3-cyclohexyl-1,1,1-trifluoropropan-2-yl)benzonitrile (3i')



3i

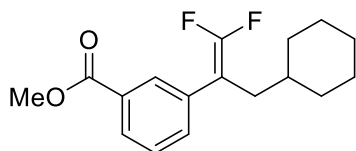


3i'

According to Procedure A, the reaction was carried out with **1i** (0.30 mmol, 59.1 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg), DIPEA (1.50 mmol, 261 μ L) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=5:1) to afford 67.5 mg of a mixture of **3i** (70%) and **3i'** (15%) as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.64 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 1H), 2.30 (dt, $J = 7.2$ Hz, 2.0 Hz, 2H), 1.66-1.60 (m, 5H), 1.23-1.17 (m, 1H), 1.14-1.10 (m, 3H), 0.95-0.93 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.31 (dd, $J = 291.9$ Hz, 287.1 Hz), 139.18 (t, $J = 4.6$ Hz), 132.44, 132.19, 129.88, 128.84 (t, $J = 3.4$ Hz), 118.67, 112.24, 110.80, 90.58 (dd, $J = 23.4$ Hz, 11.3 Hz), 35.85, 34.65, 33.99 (d, $J = 7.0$ Hz), 32.79, 26.24, 25.95. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.46 (d, $J = 9.1$ Hz), -87.49 (d, $J = 36.4$ Hz),

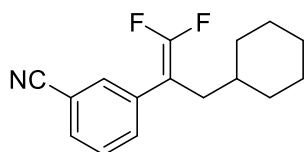
-88.54 (d, $J = 36.4$ Hz). All data are in accordance with the literature.¹

Methyl 3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzoate (**3j**)



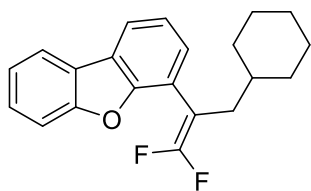
According to Procedure A, the reaction was carried out with **1j** (0.30 mmol, 69.0 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=1:1) to afford 65.9 mg (74%) of **3j** as a colorless oil: **¹H NMR (400 MHz, CDCl₃)** δ : 7.99 (s, 1H), 7.94 (dt, $J = 7.7$ Hz, 1.4 Hz, 1H), 7.49 (dd, $J = 7.8$ Hz, 1.6 Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 3.93 (s, 3H), 2.30 (dt, $J = 7.2$ Hz, 2.3 Hz, 2H), 1.71-1.57 (m, 5H), 1.26-1.17 (m, 1H), 1.15-1.04 (m, 3H), 0.98-0.87 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 166.88, 154.12 (dd, $J = 289.2$ Hz, 285.2 Hz), 134.57 (dd, $J = 4.9$ Hz, 3.0 Hz), 132.79 (t, $J = 3.1$ Hz), 130.41, 129.37 (t, $J = 3.1$ Hz), 128.49, 128.29, 90.61 (dd, $J = 22.8$ Hz, 12.4 Hz), 52.19, 35.69 (t, $J = 2.3$ Hz), 35.09, 32.81, 26.33, 26.00. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -90.33 (d, $J = 42.0$ Hz), -91.02 (d, $J = 42.0$ Hz); **HRMS m/z (ESI)** calcd for C₁₇H₂₁F₂O₂ (M + H)⁺ 295.1510, found 295.1510.

3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzotrile (**3k**)



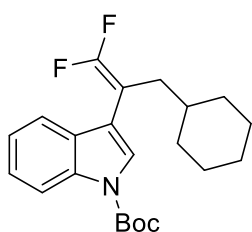
According to Procedure A, the reaction was carried out with **1k** (0.30 mmol, 59.1 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=1:1) to afford 68.4 mg (86%) of **3k** as a yellow solid: **¹H NMR (400 MHz, CDCl₃)** δ : 7.59 (s, 1H), 7.57-7.53 (m, 2H), 7.46 (t, $J = 7.6$ Hz, 1H), 2.28 (dt, $J = 7.2$ Hz, 2.5 Hz, 2H), 1.71-1.58 (m, 5H), 1.24-1.18 (m, 1H), 1.16-1.06 (m, 3H), 0.99-0.86 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 154.18 (dd, $J = 290.6$ Hz, 286.5 Hz), 135.48 (dd, $J = 5.0$ Hz, 3.3 Hz), 132.54 (t, $J = 3.3$ Hz), 131.65 (t, $J = 3.5$ Hz), 130.57, 129.22, 118.51, 112.68, 89.89 (dd, $J = 23.6$ Hz, 11.7 Hz), 35.61 (t, $J = 2.3$ Hz), 34.70, 32.67, 26.16, 28.86. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -69.73 (d, $J = 8.6$ Hz), -88.56 (d, $J = 38.8$ Hz), -89.67 (d, $J = 42.0$ Hz). All data are in accordance with the literature.¹⁹

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)dibenzo[b,d]furan (3l)



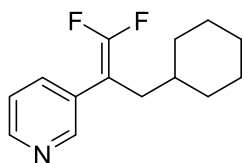
According to Procedure A, the reaction was carried out with **1l** (0.30 mmol, 78.6 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 69.5 mg (70%) of **3b** as a white solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.97 (d, $J = 7.7$ Hz, 1H), 7.92-7.89 (m, 1H), 7.60 (d, $J = 8.3$ Hz, 1H), 7.48 (t, $J = 7.3$ Hz, 1H), 7.38-7.33 (m, 3H), 2.48 (dt, $J = 7.2$ Hz, 1.8 Hz, 2H), 1.75-1.58 (m, 5H), 1.22-1.17 (m, 1H), 1.10-1.02 (m, 3H), 1.00-0.90 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 156.05, 152.85 (dd, $J = 294.4$ Hz, 288.2 Hz), 127.75 (t, $J = 2.2$ Hz), 127.24, 124.53, 124.14, 122.75, 122.68, 120.63, 119.90, 118.72 (dd, $J = 5.2$ Hz, 2.0 Hz), 111.78, 86.99 (dd, $J = 25.2$ Hz, 14.7 Hz), 35.89 (t, $J = 2.0$ Hz), 35.22, 32.82, 26.28, 26.01. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -87.93 (d, $J = 39.3$ Hz), -91.36 (d, $J = 39.3$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{11}\text{H}_{21}\text{F}_2\text{O}$ ($\text{M} + \text{H}$) $^+$ 327.1560, found 327.1560.

Tert-butyl 3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1H-indole-1-carboxylate (3m)



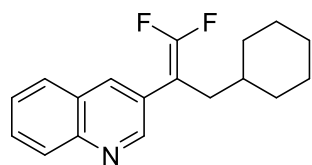
According to Procedure A, the reaction was carried out with **1m** (0.30 mmol, 93.4 mg), **2a** (0.60 mmol, 286.2 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=10:1) to afford 96.4 mg (84%) of **3m** as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.16 (d, $J = 8.0$ Hz, 1H), 7.54-7.52 (m, 2H), 7.37-7.33 (m, 1H), 7.29-7.27 (m, 1H), 2.31 (dt, $J = 7.2$ Hz, 2.2 Hz, 2H), 1.70-1.61 (m, 14H), 1.35-1.29 (m, 1H), 1.19-1.07 (m, 3H), 0.99-0.94 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 153.94 (dd, $J = 288.1$ Hz, 285.2 Hz), 149.61, 135.14, 129.31, 124.47, 122.69, 120.08 (d, $J = 3.6$ Hz), 115.27, 114.21 (dd, $J = 5.3$ Hz, 2.1 Hz), 83.98, 83.52 (dd, $J = 25.8$ Hz, 14.8 Hz), 35.87, 32.85, 28.18, 26.38, 26.01. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.97, -87.18 (d, $J = 41.4$ Hz), -91.23 (d, $J = 41.4$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{28}\text{F}_2\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 376.2088, found 376.2087.

3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)pyridine (3n)



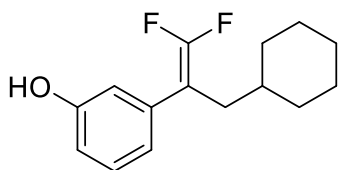
According to Procedure A, the reaction was carried out with **1i** (0.30 mmol, 51.9 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg), DIPEA (1.50 mmol, 261 μ L) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=3:1) to afford 50.5 mg (70%) of **3n** as a yellow oil: **¹H NMR (400 MHz, CDCl₃)** δ : 8.58-8.51 (m, 2H), 7.62, (d, $J = 7.4$ Hz, 1H), 7.30-7.27 (m, 1H), 2.28 (dt, $J = 7.2$ Hz, 2.2 Hz, 2H), 1.67-1.60 (m, 5H), 1.29-1.21 (m, 1H), 1.17-1.05 (m, 3H), 0.95-0.87 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 154.26 (dd, $J = 290.3$ Hz, 286.4 Hz), 149.32, 148.21, 135.57 (t, $J = 3.7$ Hz), 124.81, 123.28, 88.47 (dd, $J = 23.6$ Hz, 12.5 Hz), 35.69 (t, $J = 2.4$ Hz), 34.71, 32.78, 26.28, 25.97. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -69.80 (d, $J = 9.2$ Hz), -88.94 (d, $J = 40.3$ Hz), -90.11 (d, $J = 40.3$ Hz). **HRMS m/z (ESI)** calcd for C₁₄H₁₈F₂N (M + H)⁺ 238.1407, found 238.1406.

3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)quinoline (3o)



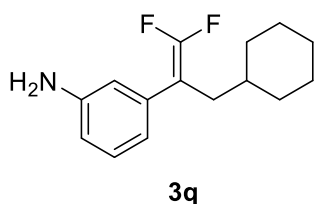
According to Procedure A, the reaction was carried out with **1o** (0.30 mmol, 66.9 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg), DIPEA (1.50 mmol, 261 μ L) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=1:1) to afford 75.7 mg (86%) of **3o** as a white solid: **¹H NMR (400 MHz, CDCl₃)** δ : 8.89 (s, 1H), 8.11-8.06 (m, 2H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.72 (t, $J = 8.0$ Hz, 1H), 7.57 (t, $J = 7.8$ Hz, 1H), 2.40 (d, $J = 7.2$ Hz, 2H), 1.71-1.58 (m, 5H), 1.32-1.28 (m, 1H), 1.12-1.07 (m, 3H), 1.00-0.94 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 154.37 (dd, $J = 289.9$ Hz, 286.9 Hz), 150.18, 146.89, 134.56, 129.35, 129.07, 127.58, 127.18, 126.78, 88.58 (dd, $J = 23.7$ Hz, 12.5 Hz), 35.60, 34.73, 32.66, 26.11, 25.81. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -69.61 (d, $J = 8.9$ Hz), -88.69 (d, $J = 39.5$ Hz), -89.96 (d, $J = 39.5$ Hz). All data are in accordance with the literature.²⁰

3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenol (**3p**)

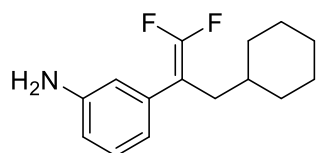


According to Procedure A, the reaction was carried out with **1p** (0.30 mmol, 56.4 mg), **2a** (0.60 mmol, 286.2 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=1:1) to afford 67.5 mg (88%) of **3p** as a yellow solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.22 (t, $J = 7.9$ Hz, 1H), 6.88 (d, $J = 7.8$, 1H), 6.80-6.79 (m, 1H), 6.76-6.76 (m, 1H), 4.80 (s, 1H), 2.24 (dt, $J = 7.2$ Hz, 2.4 Hz, 2H), 1.69-1.60 (m, 5H), 1.30-1.20 (m, 1H), 1.17-1.07 (m, 3H), 0.96-0.83 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 155.25, 153.96 (dd, $J = 288.3$ Hz, 285.3 Hz), 135.79 (dd, $J = 1.98$ Hz), 129.54, 120.90 (t, $J = 3.22$ Hz), 115.28 (t, $J = 3.33$ Hz), 114.13, 90.78 (dd, $J = 20.8$ Hz, 13.9 Hz), 35.63, 35.10, 32.97, 26.35, 26.00; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -90.61 (d, $J = 43.4$ Hz), -90.87 (d, $J = 43.4$ Hz). All data are in accordance with the literature.⁴

3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)aniline (**3q**)



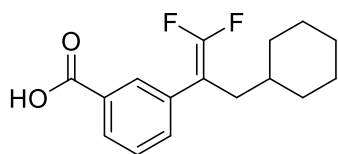
3q



3q'

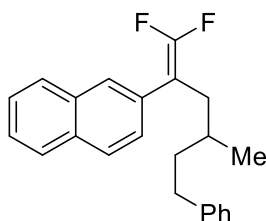
According to Procedure A, the reaction was carried out with **1q** (0.30 mmol, 56.1 mg), **2a** (0.45 mmol, 214.7 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 58.7 mg of a mixture of **3q** (72%) and **3q'** (5%) as a yellow solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.13 (t, $J = 7.8$ Hz, 1H), 6.70 (d, $J = 7.7$ Hz, 1H), 6.63-6.59 (m, 2H), 3.66 (s, 2H), 2.22 (dt, $J = 7.1$ Hz, 2.3 Hz, 2H), 1.69-1.61 (m, 5H), 1.29-1.23 (m, 1H), 1.19-1.06 (m, 3H), 0.97-0.86 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 153.81 (dd, $J = 287.9$ Hz, 284.3 Hz), 146.24, 135.08 (dd, $J = 3.8$ Hz, 2.1 Hz), 129.14, 118.59 (t, $J = 3.1$ Hz), 115.00 (t, $J = 3.2$ Hz), 113.96, 91.06 (dd, $J = 20.9$ Hz, 13.3 Hz), 35.51 (t, $J = 2.3$ Hz), 35.19, 32.78, 26.36, 26.98. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.58 (d, $J = 9.4$ Hz), -91.35 (d, $J = 44.4$ Hz), -91.54 (d, $J = 44.4$ Hz); All data are in accordance with the literature.¹

3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzoic acid (**3r**)



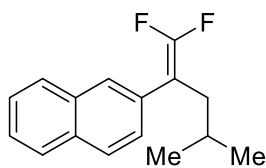
According to Procedure A, the reaction was carried out with **1r** (0.30 mmol, 64.8 mg), **2a** (0.60 mmol, 286.2 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA=2:1) to afford 73.2 mg (86%) of **3r** as a white solid: **¹H NMR (400 MHz, CDCl₃)** δ : 8.07 (s, 1H), 8.03 (d, $J = 7.7$ Hz, 1H), 7.57 (dd, $J = 7.8$ Hz, 1.3 Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 1H), 2.32 (dt, $J = 7.2$ Hz, 2.3 Hz, 2H), 1.70-1.61 (m, 5H), 1.30-1.21 (m, 1H), 1.18-1.06 (m, 3H), 0.98-0.88 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 171.88, 154.18 (dd, $J = 289.7$ Hz, 285.4 Hz), 134.76 (dd, $J = 4.9$ Hz, 3.1 Hz), 133.69 (t, $J = 3.2$ Hz), 129.93 (t, $J = 3.3$ Hz), 129.60, 128.92, 128.65, 90.53 (dd, $J = 22.8$ Hz, 12.1 Hz), 35.73 (t, $J = 2.3$ Hz), 35.06, 32.83, 26.33, 26.00. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -90.00 (d, $J = 41.6$ Hz), -90.78 (d, $J = 41.6$ Hz). **HRMS m/z (ESI)** calcd for C₁₆H₁₉F₂O₂ (M + H)⁺ 281.1353, found 281.1353.

2-(1,1-Difluoro-4-methyl-6-phenylhex-1-en-2-yl)naphthalene (**4a**)



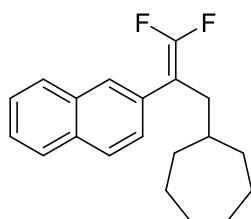
According to Procedure A, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2b** (0.45 mmol, 237.3 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 90.4 mg (89%) of **4a** as a colorless oil: **¹H NMR (400 MHz, CDCl₃)** δ : 7.93-7.89 (m, 3H), 7.84 (s, 1H), 7.59-7.57 (m, 2H), 7.52-7.49 (m, 1H), 7.33-7.29 (m, 2H), 7.26-7.24 (m, 1H), 7.20-7.18 (m, 2H), 2.76-2.57 (m, 3H), 2.49-2.43 (m, 1H), 1.83-1.76 (m, 1H), 1.67-1.55 (m, 2H), 1.05 (d, $J = 6.4$ Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ : 154.21 (dd, $J = 288.6$ Hz, 285.1 Hz), 142.50, 133.25, 132.44, 131.24 (dd, $J = 4.4$ Hz, 2.8 Hz), 128.24, 128.00, 127.89, 127.56, 127.40 (t, $J = 3.1$ Hz), 126.20, 126.17, 126.14, 126.05, 125.61, 91.52 (dd, $J = 21.6$ Hz, 13.0 Hz), 38.19, 34.83, 33.18, 30.81 (t, $J = 2.3$ Hz), 19.17. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -90.89 (d, $J = 43.1$ Hz), -91.28 (d, $J = 43.1$ Hz), **HRMS m/z (ESI)** calcd for C₂₃H₂₃F₂ (M + H)⁺ 337.1768, found 337.1767.

2-(1,1-Difluoro-4-methylpent-1-en-2-yl)naphthalene (4b)



According to Procedure A, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2c** (0.45 mmol, 196.7mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 61.6 mg (83%) of **4b** as a white solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.84-7.82 (m, 3H), 7.76 (s, 1H), 7.51-7.47 (m, 2H), 7.45-7.42 (m, 1H), 2.38 (dt, $J = 7.4$ Hz, 2.1 Hz, 2H), 1.67-1.56 (m, 1H), 0.91 (d, $J = 6.6$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.24 (dd, $J = 288.9$ Hz, 285.2 Hz), 133.26, 132.44, 131.44 (dd, $J = 4.3$ Hz, 3.0 Hz), 127.96, 127.87, 127.56, 127.34 (t, $J = 3.2$ Hz), 126.25, 126.21, 126.03, 91.79 (dd, $J = 22.0$ Hz, 12.6 Hz), 36.69, 26.48 (t, $J = 2.4$ Hz), 22.07. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -68.93 (d, $J = 9.7$ Hz), -90.51 (d, $J = 43.4$ Hz), -91.15 (d, $J = 43.4$ Hz). All data are in accordance with the literature.²¹

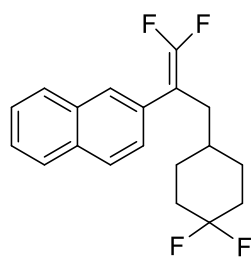
2-(3-Cycloheptyl-1,1-difluoroprop-1-en-2-yl)naphthalene (4c)



According to Procedure A, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2d** (0.45 mmol, 221.1 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 83.2 mg (91%) of **4c** as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.84-7.82 (m, 3H), 7.75 (s, 1H), 7.51-7.47 (m, 2H), 7.43 (dt, $J = 8.6$ Hz, 1.6 Hz, 1H), 2.40 (dt, $J = 7.5$ Hz, 2.2 Hz, 2H), 1.73-1.67 (m, 5H), 1.50-1.42 (m, 4H), 1.33-1.16 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.28 (dd, $J = 288.6$ Hz, 284.7 Hz), 133.27, 132.42, 131.41 (dd, $J = 4.5$ Hz, 2.9 Hz), 127.95, 127.89, 127.58, 127.35 (t, $J = 3.2$ Hz), 126.25 (t, $J = 3.0$ Hz), 126.17, 126.00, 91.79 (dd, $J = 21.9$ Hz, 12.5 Hz), 37.08 (t, $J = 2.2$ Hz), 35.70, 34.01, 28.40, 26.05. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.33 (d, $J = 9.2$ Hz), -91.09 (d, $J = 43.5$ Hz), -91.63 (d, $J = 43.5$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{23}\text{F}_2$ ($\text{M} + \text{H}$)⁺ 301.1768, found 301.1768.

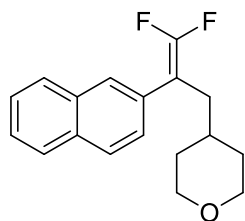
2-(3-(4,4-Difluorocyclohexyl)-1,1-difluoroprop-1-en-2-yl)naphthalene (4d)

According to Procedure A, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2e** (0.45 mmol, 231.0 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude

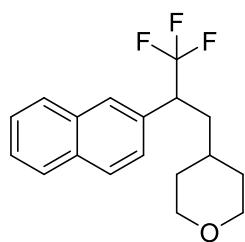


product was purified by flash column chromatography on silica gel (PE: DCM=5:1) to afford 71.7 mg (73%) of **4d** as a white solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.85-7.82 (m, 3H), 7.76 (s, 1H), 7.52-7.49 (m, 2H), 7.43 (dt, $J = 8.6$ Hz, 1.7 Hz, 1H), 2.47 (dt, $J = 6.2$ Hz, 2.6 Hz, 2H), 2.07-1.98 (m, 2H), 1.79-1.75 (m, 2H), 1.65-1.50 (m, 2H), 1.38-1.29 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.23 (dd, $J = 289.5$ Hz, 285.6 Hz), 133.22, 132.48, 132.90 (dd, $J = 4.5$ Hz, 3.1 Hz), 128.20, 127.87, 127.61, 127.27 (t, $J = 3.3$ Hz), 126.38, 126.23, 125.96 (t, $J = 3.0$ Hz), 123.48 (d, $J = 238.4$ Hz), 90.94 (dd, $J = 21.6$ Hz, 13.3 Hz), 33.87, 33.72, 33.17 (dd, $J = 22.6$ Hz, $J = 25.2$ Hz), 28.50 (d, $J = 9.5$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -90.10 (d, $J = 41.5$ Hz), -90.72 (d, $J = 41.5$ Hz), -92.01 (d, $J = 235.0$ Hz), -101.84 (d, $J = 237.0$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{F}_4(\text{M} + \text{H})^+$ 323.1423, found 323.1421.

4-(3,3-Difluoro-2-(naphthalen-2-yl)allyl)tetrahydro-2H-pyran (**4e**) and 4-(3,3,3-trifluoro-2-(naphthalen-2-yl)propyl)tetrahydro-2H-pyran (**4e'**)



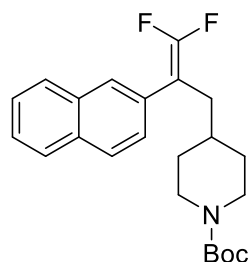
4e



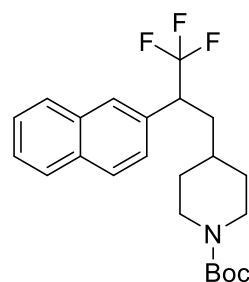
4e'

According to Procedure A, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2f** (0.45 mmol, 215.6 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL), DIPEA (1.50 mmol, 261 μL) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=1:1) to afford 79.1 mg of a mixture of **4e** (87%) and **4e'** (4%) as a yellow solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.87-7.82 (m, 3H), 7.78-7.74 (m, 1H), 7.53-7.47 (m, 2H), 7.44-7.40 (m, 1H), 3.92-3.88 (m, 2H), 3.26-3.20 (m, 2H), 2.46 (dt, $J = 7.0$ Hz, 2.1 Hz, 2H), 1.55-1.49 (m, 2H), 1.38-1.26 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.25 (dd, $J = 289.5$ Hz, 285.5 Hz), 133.20, 132.42, 131.05 (dd, $J = 4.5$ Hz, 3.1 Hz), 128.10, 127.83, 127.56, 127.23 (t, $J = 3.2$ Hz), 126.29, 126.14, 125.98 (t, $J = 3.1$ Hz), 90.46 (dd, $J = 22.0$ Hz, 13.1 Hz), 67.69, 34.73 (d, $J = 1.4$ Hz), 33.20 (t, $J = 2.5$ Hz), 32.57. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.52 (d, $J = 9.4$ Hz), -90.20 (d, $J = 42.0$ Hz), -90.77 (d, $J = 42.0$ Hz). All data are in accordance with the literature.²²

Tert-butyl 4-(3,3-difluoro-2-(naphthalen-2-yl)allyl)piperidine-1-carboxylate (4f) and tert-butyl 4-(3,3,3-trifluoro-2-(naphthalen-2-yl)propyl)piperidine-1-carboxylate (4f')



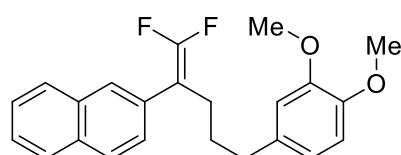
4f



4f'

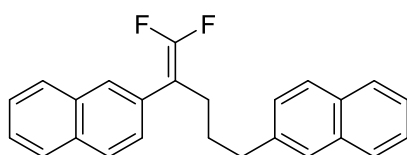
According to Procedure A, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2g** (0.45 mmol, 260.2 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (DCM) to afford 82.7 mg of a mixture of **4f** (68%) and **4f'** (3%) as a white solid: ^1H NMR (400 MHz, CDCl_3) δ : 7.85-7.82 (m, 3H), 7.76 (s, 1H), 7.52-7.48 (m, 2H), 7.44-7.42 (m, 1H), 4.0 (s, 1H), 2.57-2.44 (m, 4H), 1.66-1.59 (m, 2H), 1.44 (s, 9H), 1.20-1.10 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 154.62, 154.15 (dd, $J = 289.5$ Hz, 285.5 Hz), 133.14, 132.37, 130.92 (dd, $J = 4.5$ Hz, 3.2 Hz), 128.07, 127.78, 127.51, 127.17 (t, $J = 3.3$ Hz), 126.25, 126.10, 125.91 (t, $J = 3.0$ Hz), 90.57 (dd, $J = 21.9$ Hz, 13.0 Hz), 79.12, 34.33, 34.17 (t, $J = 2.4$ Hz), 31.61, 28.32. ^{19}F NMR (376 MHz, CDCl_3) δ : -69.55 (d, $J = 9.3$ Hz), -90.13 (d, $J = 41.8$ Hz), -90.76 (d, $J = 41.8$ Hz). All data are in accordance with the literature.²²

2-(5-(3,4-Dimethoxyphenyl)-1,1-difluoropent-1-en-2-yl)naphthalene (4g)



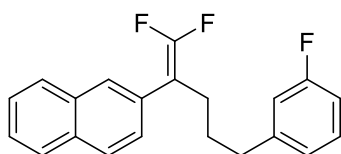
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2h** (0.45 mmol, 251.7 mg), TEA (1.50 mmol, 209 μL) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=5:1) to afford 81.7 mg (74%) of **4g** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ : 7.83-7.78 (m, 3H), 7.71 (s, 1H), 7.50-7.47 (m, 2H), 7.41 (dt, $J = 8.6$ Hz, 1.6 Hz, 2H), 6.75 (d, $J = 8.1$ Hz, 1H), 6.65 (dd, $J = 8.1$ Hz, 2.0 Hz, 1H), 6.59 (d, $J = 2.0$ Hz, 1H), 3.84 (s, 1H), 3.77 (s, 1H), 2.60-2.51 (m, 4H), 1.74-1.67 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 153.63 (dd, $J = 289.1$ Hz, 285.5 Hz), 148.62, 147.00, 134.21, 133.09, 132.28, 130.80 (dd, $J = 4.3$ Hz, 3.1 Hz), 127.87, 127.71, 127.41, 127.14 (t, $J = 3.3$ Hz), 126.12, 125.96 (t, $J = 3.4$ Hz), 120.04, 111.41, 110.97, 92.21 (dd, $J = 21.6$ Hz, 12.9 Hz), 55.67, 55.48, 34.53, 29.32 (t, $J = 2.4$ Hz), 26.90. ^{19}F NMR (376 MHz, CDCl_3) δ : -90.82 (d, $J = 43.2$ Hz), -91.14 (d, $J = 43.2$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{F}_2\text{O}_2$ ($M + \text{H}$)⁺ 369.1666, found 369.1665.

2,2'-(5,5-Difluoropent-4-ene-1,4-diyl)dinaphthalene (4h)



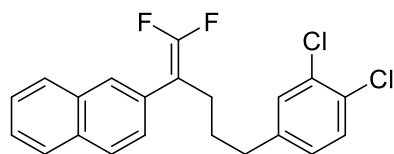
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2i** (0.45 mmol, 247.2 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 74.3 mg (69%) of **4h** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ : 7.83-7.74 (m, 6H), 7.68 (d, J = 8.1 Hz, 1H), 7.49-7.47 (m, 2H), 7.45-7.29 (m, 5H), 3.10-3.06 (m, 2H), 2.69-2.64 (m, 2H), 1.90-1.82 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 153.84 (dd, J = 289.1 Hz, 285.3 Hz), 137.87, 133.79, 133.23, 132.42, 131.69, 130.80 (dd, J = 4.3 Hz, 3.0 Hz), 128.68, 128.07, 127.88, 127.55, 127.36 (t, J = 3.3 Hz), 126.62, 126.25, 126.07, 126.07 (dd, J = 3.7 Hz, 2.9 Hz), 125.91, 125.64, 125.44, 125.35, 123.58, 92.16 (dd, J = 21.6 Hz, 12.8 Hz), 32.30, 28.55 (t, J = 2.6 Hz), 27.49. ^{19}F NMR (376 MHz, CDCl_3) δ : -90.58 (d, J = 45.4 Hz), -90.95 (d, J = 45.4 Hz). HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{21}\text{F}_2$ ($\text{M} + \text{H}$) $^+$ 359.1611, found 359.1611.

2-(1,1-Difluoro-5-(3-fluorophenyl)pent-1-en-2-yl)naphthalene (4i)



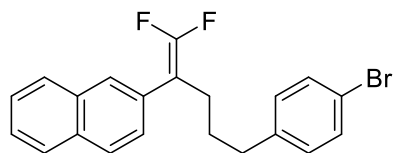
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2j** (0.45 mmol, 232.7 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 60.5 mg (62%) of **4i** as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ : 7.88-7.84 (m, 3H), 7.78 (s, 1H), 7.54-7.45 (m, 3H), 7.26-7.21 (m, 1H), 6.93-6.85 (m, 3H), 2.67 (t, J = 7.6 Hz, 2H), 2.61-2.56 (m, 2H), 1.81-1.73 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 164.09, 161.56, 153.81 (dd, J = 289.3 Hz, 285.8 Hz), 144.32 (d, J = 7.1 Hz), 133.25, 132.46, 130.83 (dd, J = 4.2 Hz, 2.9 Hz), 129.65 (d, J = 8.2 Hz), 128.09, 127.87, 127.58, 127.25 (t, J = 33.4 Hz), 126.29, 126.13, 126.02 (dd, J = 3.5 Hz, 2.8 Hz), 123.99 (d, J = 2.7 Hz), 113.94 (dd, J = 246.0 Hz, 20.8 Hz), 92.16 (dd, J = 21.5 Hz, 13.3 Hz), 34.87 (d, J = 1.6 Hz), 29.05 (t, J = 2.5 Hz), 27.13. ^{19}F NMR (376 MHz, CDCl_3) δ : -90.71 (d, J = 42.9 Hz), -90.98 (d, J = 42.9 Hz), -113.75 (d, J = 9.1 Hz), -113.79 (d, J = 9.1 Hz). HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{17}\text{F}_3\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 349.1180, found 349.1181.

2-(5-(3,4-Dichlorophenyl)-1,1-difluoropent-1-en-2-yl)naphthalene (4j)



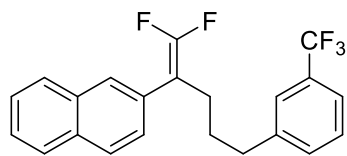
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2k** (0.45 mmol, 255.7 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 69.3mg (60%) of **4j** as a yellow oil: **¹H NMR (400 MHz, CDCl₃)** δ : 7.84-7.79 (m, 3H), 7.71 (s, 1H), 7.52-7.46 (m, 2H), 7.41-7.38 (m, 1H), 7.29 (d, $J = 8.2$ Hz, 1H), 7.18 (d, $J = 2.0$ Hz, 1H), 6.91 (dd, $J = 7.2$ Hz, 1H), 2.60-2.51 (m, 4H), 1.74-1.66 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 153.80 (dd, $J = 289.3$ Hz, 286.1 Hz), 141.94, 133.23, 132.47, 132.14, 130.69 (dd, $J = 3.6$ Hz, 2.8 Hz), 130.25, 130.16, 129.73, 128.16, 127.87, 127.80, 127.59, 127.25 (t, $J = 3.3$ Hz), 126.35, 126.19, 125.96 (t, $J = 3.2$ Hz), 92.02 (dd, $J = 21.4$ Hz, 13.4 Hz), 34.21, 28.94 (t, $J = 2.6$ Hz), 27.04. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -69.38 (d, $J = 9.2$ Hz), -90.95 (d, $J = 42.6$ Hz), -90.85 (d, $J = 42.6$ Hz). **HRMS m/z (ESI)** calcd for C₂₁H₁₆Cl₂F₂Na (M + Na)⁺ 399.0495, found 399.0495.

2-(5-(4-Bromophenyl)-1,1-difluoropent-1-en-2-yl)naphthalene (4k)



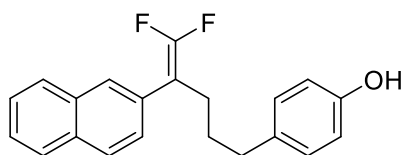
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2l** (0.45 mmol, 260.2 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 63.4 mg (55%) of **4k** as a white solid: **¹H NMR (400 MHz, CDCl₃)** δ : 7.84-7.79 (m, 3H), 7.70 (s, 1H), 7.51-7.48 (m, 2H), 7.42-7.39 (m, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 8.5$ Hz, 2H), 2.61-2.51 (m, 4H), 1.74-1.67 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 153.77 (dd, $J = 289.3$ Hz, 285.8 Hz), 140.66, 133.22, 132.43, 131.31, 130.80 (dd, $J = 4.2$ Hz, 2.9 Hz), 130.10, 128.07, 127.87, 127.57, 127.24 (t, $J = 3.3$ Hz), 126.30, 126.14, 126.02 (dd, $J = 3.5$ Hz, 3.0 Hz), 119.54, 92.13 (dd, $J = 21.5$ Hz, 13.3 Hz), 34.53, 29.15 (t, $J = 2.6$ Hz), 27.10. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -90.71 (d, $J = 43.0$ Hz), -90.97 (d, $J = 43.0$ Hz). **HRMS m/z (ESI)** calcd for C₂₁H₁₈BrF₂ (M + H)⁺ 387.0560, found 387.0560.

2-(1,1-Difluoro-5-(3-(trifluoromethyl)phenyl)pent-1-en-2-yl)naphthalene (**4l**)



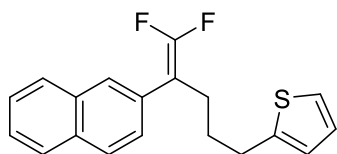
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2m** (0.45 mmol, 255.2 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 69.4 mg (61%) of **4l** as a colorless oil: **¹H NMR (400 MHz, CDCl₃)** δ : 7.88-7.83 (m, 3H), 7.77 (s, 1H), 7.54-7.51 (m, 2H), 7.46-7.42 (m, 3H), 7.37 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 2.72 (t, J = 7.6 Hz, 2H), 2.61-2.57 (m, 2H), 1.83-1.75 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 153.84 (dd, J = 289.3 Hz, 285.8 Hz), 142.61, 133.26, 132.49, 131.75 (dd, J = 2.6 Hz, 1.3 Hz), 130.78 (t, J = 3.7 Hz), 130.46, 128.70, 128.15, 127.88, 127.60, 127.27 (t, J = 3.3 Hz), 126.33, 126.18, 125.99 (dd, J = 3.4 Hz, 2.8 Hz), 125.01 (q, J = 3.8 Hz), 122.75 (q, J = 3.9 Hz), 92.09 (dd, J = 21.5 Hz, 13.4 Hz), 34.92, 29.08 (t, J = 2.7 Hz), 27.14. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -62.48, -90.63 (d, J = 42.6 Hz), -90.92 (d, J = 42.6 Hz). **HRMS m/z (ESI)** calcd for C₂₂H₁₈F₅ (M + H)⁺ 377.1329, found 377.1328.

4-(5,5-Difluoro-4-(naphthalen-2-yl)pent-4-en-1-yl)phenol (**4m**)



According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2n** (0.45 mmol, 213.8 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=1:1) to afford 61.3 mg (61%) of **4m** as a red solid: **¹H NMR (400 MHz, CDCl₃)** δ : 7.83-7.78 (m, 3H), 7.71 (s, 1H), 7.51-7.46 (m, 2H), 7.41 (dt, J = 8.6 Hz, 1.6 Hz, 1H), 6.97 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 8.5 Hz, 2H), 4.58 (s, 1H), 2.58-2.50 (m, 4H), 1.72-1.65 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 153.73 (dd, J = 289.0 Hz, 285.5 Hz), 153.52, 133.95, 133.21, 132.39, 130.97 (dd, J = 4.4 Hz, 3.1 Hz), 129.41, 127.99, 127.87, 127.54, 127.22 (t, J = 3.4 Hz), 126.22, 126.09 (dd, J = 3.7 Hz, 2.9 Hz), 126.06, 115.10, 92.29 (dd, J = 21.6 Hz, 12.9 Hz), 34.24, 29.55 (t, J = 2.6 Hz), 27.12. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -69.37 (d, J = 8.9 Hz), -90.86 (d, J = 42.8 Hz), -91.18 (d, J = 42.8 Hz). **HRMS m/z (ESI)** calcd for C₂₁H₁₉F₂O (M + H)⁺ 325.1404, found 325.1402.

2-(5,5-Difluoro-4-(naphthalen-2-yl)pent-4-en-1-yl)thiophene (4n)



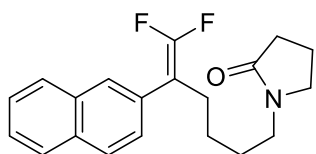
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2o** (0.45 mmol, 227.3 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA=5:1) to afford 63.7 mg (67%) of **4n** as a yellow solid: **¹H NMR (400 MHz, CDCl₃)** δ : 7.84-7.80 (m, 3H), 7.74 (s, 1H), 7.50-7.47 (m, 2H), 7.44-7.41 (m, 1H), 7.10 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 6.89 (dd, J = 5.1 Hz, 3.4 Hz, 1H), 6.74-6.73 (m, 1H), 2.85 (t, J = 7.6 Hz, 2H), 2.60-2.55 (m, 2H), 1.83-1.76 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 153.81 (dd, J = 289.3 Hz, 285.7 Hz), 144.50, 133.22, 132.42, 130.80 (dd, J = 4.3 Hz, 3.0 Hz), 128.05, 127.88, 127.55, 127.24 (t, J = 3.4 Hz), 126.67, 126.25, 126.10, 126.03 (dd, J = 3.7 Hz, 2.8 Hz), 124.27, 123.02, 92.04 (dd, J = 21.5 Hz, 13.1 Hz), 29.69 (t, J = 2.6 Hz), 29.14, 26.98. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -69.38 (d, J = 9.2 Hz), -90.54 (d, J = 42.2 Hz), -90.86 (d, J = 42.2 Hz). **HRMS m/z (ESI)** calcd for C₁₉H₁₇F₂S (M + H)⁺ 315.1019, found 315.1019.

3-(5,5-Difluoro-4-(naphthalen-2-yl)pent-4-en-1-yl)pyridine (4o)



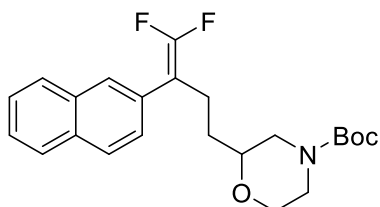
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2p** (0.45 mmol, 225.1 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA=3:1) to afford 65.1 mg (69%) of **4o** as a yellow oil: **¹H NMR (400 MHz, CDCl₃)** δ : 8.45-8.42 (m, 2H), 7.85-7.74 (m, 4H), 7.50-7.39 (m, 4H), 7.17-7.12 (1H), 2.65-2.57 (m, 4H), 1.77-1.70 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 153.75 (dd, J = 289.1 Hz, 285.8 Hz), 149.81, 147.36, 136.84, 135.61, 133.17, 132.41, 130.63 (dd, J = 4.1 Hz, 3.1 Hz), 128.09, 127.80, 127.52, 127.20 (t, J = 3.2 Hz), 126.28, 126.13, 125.91 (t, J = 3.0 Hz), 123.16, 91.96 (dd, J = 21.1 Hz, 13.6 Hz), 32.14, 28.94 (t, J = 2.4 Hz), 27.07. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -69.38 (d, J = 9.2 Hz), -90.61 (d, J = 42.8 Hz), -90.85 (d, J = 42.8 Hz). **HRMS m/z (ESI)** calcd for C₂₀H₁₈F₂N (M + H)⁺ 310.1407, found 310.1407.

1-(6,6-Difluoro-5-(naphthalen-2-yl)hex-5-en-1-yl)pyrrolidin-2-one (**4p**)



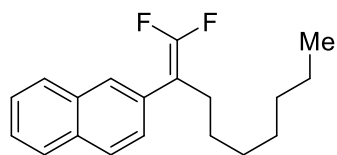
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2q** (0.45 mmol, 238.6 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (EA) to afford 71.1 mg (70%) of **4p** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.83-7.81 (m, 3H), 7.75 (s, 1H), 7.50-7.47 (m, 2H), 7.44-7.41 (m, 1H), 3.26-3.20 (m, 4H), 2.57-2.52 (m, 2H), 2.29 (t, $J = 7.9$ Hz, 2H), 1.92-1.84 (m, 2H), 1.57-1.50 (m, 2H), 1.42-1.35 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 174.80, 153.75 (dd, $J = 289.1$ Hz, 285.4 Hz), 133.14, 132.34, 130.70 (dd, $J = 4.2$ Hz, 3.1 Hz), 127.99, 127.80, 127.49, 127.21 (t, $J = 3.3$ Hz), 126.23, 126.07, 125.99 (dd, $J = 3.6$ Hz, 2.9 Hz), 92.04 (dd, $J = 21.6$ Hz, 12.9 Hz), 46.85, 41.88, 30.90, 27.02, 26.36, 24.70 (t, $J = 2.3$ Hz), 17.69. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.42 (d, $J = 9.2$ Hz), -90.80 (d, $J = 43.1$ Hz), -91.09 (d, $J = 43.1$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{F}_2\text{NO}$ ($\text{M} + \text{H}$) $^+$ 330.1669, found 330.1668.

Tert-butyl 2-(4,4-difluoro-3-(naphthalen-2-yl)but-3-en-1-yl)morpholine-4-carboxylate (**4q**)



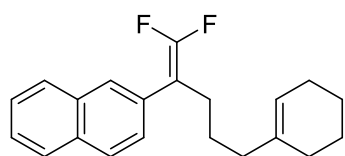
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2r** (0.45 mmol, 267.4 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (DCM) to afford 87.2 mg (71%) of **4q** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.84-7.81 (m, 3H), 7.77 (s, 1H), 7.50-7.47 (m, 2H), 7.45-7.43 (m, 1H), 3.85-3.77 (m, 3H), 3.45-3.40 (m, 1H), 3.36-3.28 (m, 1H), 2.94-2.83 (m, 1H), 2.70-2.56 (m, 3H), 1.64-1.56 (m, 2H), 1.44 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.59, 153.74 (dd, $J = 289.5$ Hz, 286.2 Hz), 133.19, 132.40, 130.70 (dd, $J = 4.1$ Hz, 3.2 Hz), 128.06, 127.86, 127.52, 127.23 (t, $J = 3.4$ Hz), 126.24, 126.10, 125.96 (dd, $J = 3.8$ Hz, 2.7 Hz), 91.99 (dd, $J = 21.5$ Hz, 13.3 Hz), 79.90, 66.35, 31.28, 29.65, 28.31, 23.50. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -90.33 (d, $J = 41.5$ Hz), -90.68 (d, $J = 41.5$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{28}\text{F}_2\text{NO}_3$ ($\text{M} + \text{H}$) $^+$ 404.2037, found 404.2036.

2-(1,1-Difluoronon-1-en-2-yl)naphthalene (**4r**)



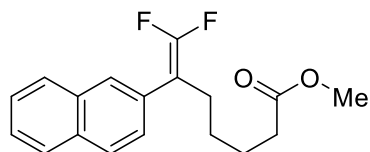
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2s** (0.45 mmol, 215.7 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 60.4 mg (69%) of **4r** as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.84-7.76 (m, 4H), 7.49-7.42 (m, 3H), 2.50-2.46 (m, 2H), 1.41-1.23 (m, 10H), 0.87-0.83 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 153.77 (dd, $J = 288.6$ Hz, 285.1 Hz), 133.27, 132.41, 131.29 (dd, $J = 4.4$ Hz, 3.0 Hz), 127.95, 127.88, 127.57, 127.26 (t, $J = 3.4$ Hz), 126.19, 126.15, 126.01, 92.58 (dd, $J = 21.6$ Hz, 12.6 Hz), 31.76, 28.99, 28.96, 27.77 (t, $J = 2.5$ Hz), 27.68, 22.61, 14.04. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.37 (d, $J = 9.1$ Hz), -91.39 (d, $J = 44.3$ Hz), -91.69 (d, $J = 44.3$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{F}_2$ ($\text{M} + \text{H}$) $^+$ 289.1768, found 289.1768.

2-(5-(Cyclohex-1-en-1-yl)-1,1-difluoropent-1-en-2-yl)naphthalene (**4s**)



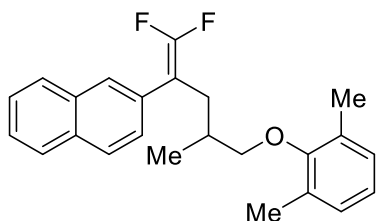
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2t** (0.45 mmol, 225.1 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA=20:1) to afford 62.9 mg (66%) of **4s** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.87-7.81 (m, 4H), 7.53-7.47 (m, 3H), 5.41 (s, 1H), 2.54-2.49 (m, 2H), 2.00 (t, $J = 7.3$ Hz, 4H), 1.89-1.87 (m, 2H), 1.64-1.51 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 153.75 (dd, $J = 289.0$ Hz, 285.4 Hz), 136.97, 133.27, 132.42, 131.23 (dd, $J = 4.5$ Hz, 3.1 Hz), 127.95, 127.87, 127.56, 127.23 (t, $J = 3.4$ Hz), 126.19, 126.15 (dd, $J = 3.7$ Hz, 3.0 Hz), 126.01, 121.35, 92.51 (dd, $J = 21.7$ Hz, 12.5 Hz), 37.35, 28.15, 27.30, 25.76 (t, $J = 2.7$ Hz), 25.21, 22.97, 22.54. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.38 (d, $J = 9.6$ Hz), -91.09 (d, $J = 43.4$ Hz), -91.47 (d, $J = 43.4$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{F}_2$ ($\text{M} + \text{H}$) $^+$ 313.1768, found 313.1768.

Methyl 7,7-difluoro-6-(naphthalen-2-yl)hept-6-enoate (**4t**)



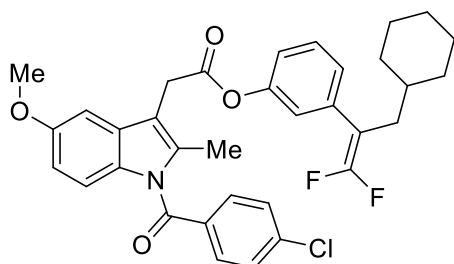
According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2u** (0.45 mmol, 222.8 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=3:1) to afford 63.9 mg (69%) of **4t** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.84-7.82 (m, 3H), 7.76 (s, 1H), 7.50-7.47 (m, 2H), 7.44-7.41 (m, 1H), 3.62 (s, 3H), 2.55-2.50 (m, 2H), 2.27 (t, $J = 7.4$ Hz, 2H), 1.70-1.62 (m, 2H), 1.46-1.38 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 173.82, 153.76 (dd, $J = 289.0$ Hz, 285.5 Hz), 133.19, 132.39, 130.82 (dd, $J = 4.2$ Hz, 2.8 Hz), 128.01, 127.84, 127.53, 127.24 (t, $J = 3.3$ Hz), 126.22, 126.06, 126.02 (t, $J = 3.0$ Hz), 92.05 (dd, $J = 21.4$ Hz, 12.7 Hz), 51.41, 33.61, 27.24, 27.09 (t, $J = 2.3$ Hz), 24.16. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.42 (d, $J = 9.4$ Hz), -90.92 (d, $J = 43.1$ Hz), -91.18 (d, $J = 43.1$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{19}\text{F}_2\text{O}_2$ ($M + \text{H}$) $^+$ 305.1353, found 305.1354.

2-(5-(2,6-Dimethylphenoxy)-1,1-difluoro-4-methylpent-1-en-2-yl)naphthalene (**5a**)



According to Procedure A, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2v** (0.45 mmol, 250.8 mg), HE (0.60 mmol, 152.0 mg) in DMA (3 mL). The crude product was purified by flash column chromatography on silica gel (PE: DCM=10:1) to afford 69.5 mg (63%) of **5a** as a colorless oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.86-7.82 (m, 4H), 7.51-7.48 (m, 3H), 6.90 (d, $J = 7.6$ Hz, 2H), 6.91 (dd, $J = 8.2$ Hz, 6.6 Hz, 1H), 3.65-3.56 (m, 2H), 2.91-2.85 (m, 1H), 2.54-2.48 (m, 1H), 2.22 (s, 6H), 2.06-1.98 (m, 1H), 1.08 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 155.70, 154.18 (dd, $J = 288.9$ Hz, 285.5 Hz), 133.26, 132.47, 130.87, 130.81 (d, $J = 2.9$ Hz), 128.81, 128.12, 127.89, 127.58, 127.46 (t, $J = 3.3$ Hz), 126.28, 126.11 (t, $J = 3.5$ Hz), 123.70, 91.13 (dd, $J = 21.4$ Hz, 13.4 Hz), 76.25, 32.57 (t, $J = 2.3$ Hz), 31.57 (d, $J = 1.3$ Hz), 16.54 16.23. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -90.28 (d, $J = 42.4$ Hz), -90.61 (d, $J = 42.4$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{25}\text{F}_2\text{O}$ ($M + \text{H}$) $^+$ 367.1873, found 367.1873.

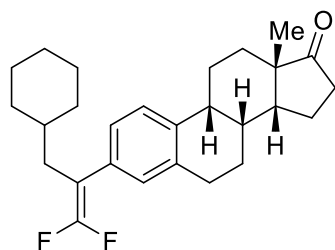
3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (5b)



According to Procedure A, the reaction was carried out with **1s** (0.20 mmol, 105.6 mg), **2a** (0.30 mmol, 143.2 mg), HE (0.40 mmol, 101.3 mg), DIPEA (1.00 mmol, 174 μ L) in DMA (2 mL). The crude product was purified by flash column chromatography on silica gel (PE:

EA=10:1) to afford 92.2 mg (75%) of **5b** as a yellow solid: **¹H NMR (400 MHz, CDCl₃)** δ : 7.68 (d, J = 8.6 Hz, 2H), 7.48(d, J = 8.6 Hz, 2H), 7.33 (t, J = 7.9 Hz, 1H), 7.18-7.15 (m, 1H), 7.07 (d, J = 2.5 Hz, 1H), 7.03 (s, 1H), 7.00-6.97(m, 1H), 6.91 (d, J = 9.2 Hz, 1H), 6.70 (dd, J = 9.0 Hz, J = 2.5 Hz, 1H), 3.92 (s, 2H), 3.84 (s, 3H), 2.46 (s, 3H), 2.26-2.23 (m, 2H), 1.67-1.58 (m, 6H), 1.17-1.04 (m, 3H), 0.94-0.87 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ : 169.13, 168.28, 156.12, 154.06 (dd, J = 289.8 Hz, J = 285.2 Hz), 150.69, 139.34, 136.21, 135.66 (dd, J = 4.8 Hz, J = 3.3 Hz), 133.80, 131.18, 130.84, 130.47, 129.25, 129.13, 125.78 (t, J = 3.3 Hz), 121.12 (t, J = 3.7 Hz), 120.11, 115.01, 111.92, 111.79, 101.19, 90.49 (dd, J = 22.6 Hz, J = 12.0 Hz), 55.69, 35.65 (t, J = 2.2 Hz), 35.01, 32.79, 30.56, 26.33, 25.79, 13.42. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -69.59 (d, J = 9.0 Hz)-89.93 (d, J = 41.5 Hz), -90.33 (d, J = 41.5 Hz). **HRMS m/z (ESI)** calcd for C₃₄H₃₃ClF₂NO₄ (M + H)⁺ 592.2066, found 592.2066.

(8R,9R,13S,14R)-3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5c)

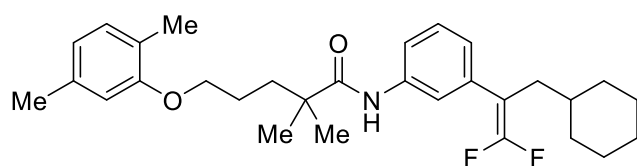


According to Procedure A, the reaction was carried out with **1t** (0.20 mmol, 69.7 mg), **2a** (0.3 mmol, 143.2 mg), HE (0.40 mmol, 101.3 mg), DIPEA (1.00 mmol, 174 μ L) in DMA (2 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA=20:1) to afford 73.8 mg (87%) of **5c** as a yellow oil: **¹H NMR (400**

MHz, CDCl₃) δ : 7.30-7.25 (m, 1H), 7.08 (d, J = 8.2 Hz, 1H), 7.03 (s, 1H), 2.94-2.90 (m, 2H), 2.55-2.48 (m, 1H), 2.44-2.40 (m, 1H), 2.34-2.28 (m, 1H), 2.26-2.23 (m, 2H), 2.20-1.96 (m, 4H), 1.70-1.49 (m, 14H), 1.16-1.09 (m, 3H), 0.92 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ : 220.73, 153.93 (dd, J = 288.3 Hz, J = 284.4 Hz), 138.63, 136.37,

131.46 (dd, $J = 4.2$ Hz, $J = 3.0$ Hz), 128.69 (t, $J = 3.2$ Hz), 125.58 (t, $J = 3.2$ Hz), 125.26, 90.67 (dd, $J = 21.6$ Hz, $J = 12.5$ Hz), 50.50, 47.94, 44.33, 38.02, 35.80, 35.55 (t, $J = 2.4$ Hz), 35.15, 32.82, 31.57, 29.38, 26.46, 26.39, 26.00, 25.55, 21.54, 13.81. ^{19}F NMR (376 MHz, CDCl_3) δ : -69.62 (d, $J = 8.2$ Hz), -91.37 (d, $J = 44.9$ Hz), -91.75 (d, $J = 44.9$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{27}\text{H}_{35}\text{F}_2\text{O}$ ($\text{M} + \text{H}$) $^+$ 413.2656, found 413.2657.

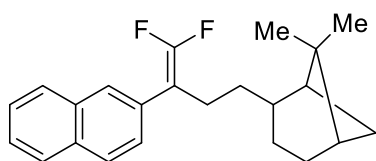
N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanamide (5d)



According to Procedure A, the reaction was carried out with **1u** (0.20 mmol, 83.9 mg), **2a** (0.30 mmol, 143.2 mg), HE (0.40 mmol,

101.3 mg), DIPEA (1.00 mmol, 174 μL) in DMA (2 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA=20:1) to afford 88.6 mg (90%) of **5d** as a yellow solid: ^1H NMR (400 MHz, CDCl_3) δ : 7.50-7.45 (m, 2H), 7.38 (s, 1H), 7.30 (t, $J = 7.9$ Hz, 1H), 7.06-7.00 (m, 2H), 6.67 (d, $J = 7.6$ Hz, 1H), 6.62 (s, 1H), 3.96 (t, $J = 5.4$ Hz, 2H), 2.30 (s, 3H), 2.28-2.25 (m, 2H), 2.18 (s, 3H), 1.86-1.82 (m, 4H), 1.70-1.64 (m, 4H), 1.36 (s, 6H), 1.32-1.30 (m, 1H), 1.16-1.09 (m, 3H), 0.96-0.88 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 175.70, 156.81, 153.94 (dd, $J = 288.3$ Hz, $J = 285.1$ Hz), 137.99, 136.50, 135.00 (dd, $J = 2.0$ Hz, $J = 5.4$ Hz), 130.29, 128.89, 124.25 (t, $J = 2.9$ Hz), 123.47, 120.84, 119.86 (t, $J = 3.4$ Hz), 118.97, 112.15, 90.91 (dd, $J = 21.3$ Hz, $J = 13.7$ Hz), 67.85, 42.82, 37.64, 35.62 ($J = 2.2$ Hz), 35.19, 32.79, 26.35, 25.99, 25.59, 25.12, 21.32, 15.77. ^{19}F NMR (376 MHz, CDCl_3) δ : -69.50 (d, $J = 9.4$ Hz), -91.00 (d, $J = 43.4$ Hz), -91.18 (d, $J = 43.4$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{30}\text{H}_{40}\text{F}_2\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 484.3027, found 484.3026.

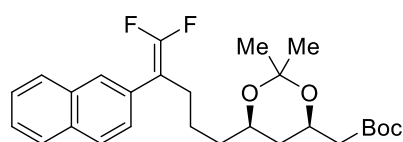
(1S,2S,5S)-2-(4,4-difluoro-3-(naphthalen-2-yl)but-3-en-1-yl)-6,6-dimethylbicyclo[3.1.1]heptane (5e)



According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2w** (0.45 mmol, 246.4 mg), TEA (1.50 mmol, 209 μL) in DMSO (3 mL). The crude product was purified by flash column chromatography on silica gel (PE) to afford 50.7 mg (48%) of **5e** as a yellow oil: ^1H

NMR (400 MHz, CDCl₃) δ : 7.84-7.82 (m, 3H), 7.77 (s, 1H), 7.50-7.47 (m, 2H), 7.46-7.43 (m, 1H), 2.51-2.46(m, 2H), 2.34-2.31 (m, 1H), 2.01-1.84 (m, 6H), .1.54-1.41 (m, 3H), 1.15 (s, 3H), 0.92 (s, 3H), 0.88 (d, $J = 2.4$ Hz, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ : 153.68 (dd, $J = 288.8$ Hz, 285.4 Hz), 133.26, 132.39, 131.28 (dd, $J = 3.9$ Hz, 2.5Hz), 127.34, 127.89, 127.56, 127.18 (t, $J = 3.5$ Hz), 126.19, 126.11 (t, $J = 3.0$ Hz), 126.00, 92.66 (dd, $J = 21.0$ Hz, 13.0 Hz), 46.16, 41.46, 40.89, 38.65, 35.59 (t, $J = 2.2$ Hz), 33.61, 28.15, 26.41, 26.11, 23.22, 22.23. **¹⁹F NMR (376 MHz, CDCl₃)** δ : -91.25 (d, $J = 43.6$ Hz), -91.44 (d, $J = 43.6$ Hz). **HRMS m/z (APCI)** calcd for C₂₃H₂₆F₂ (M)⁺ 340.2003, found 340.1997.

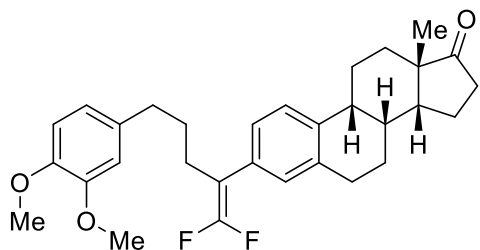
Tert-butyl 2-(6-(5,5-difluoro-4-(naphthalen-2-yl)pent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (5f)



According to Procedure B, the reaction was carried out with **1a** (0.30 mmol, 66.6 mg), **2x** (0.45 mmol, 293.2 mg), TEA (1.50 mmol, 209 μ L) in DMSO (3 mL). The crude product was purified by flash column

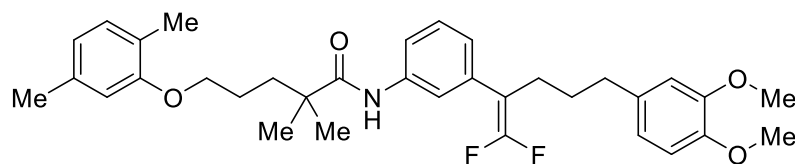
chromatography on silica gel (PE: EA=20:1) to afford 70.5 mg (71%) of **5f** as a yellow oil: **¹H NMR (400 MHz, CDCl₃)** δ : 7.84-7.81 (m, 3H), 7.76 (s, 1H), 7.50-7.47 (m, 2H), 7.45-7.42 (m, 1H), 4.23-4.16 (m, 1H), 3.81-3.75 (m, 1H), 2.53-2.50 (m, 2H), 2.43-2.37 (m, 1H), 2.28-2.23 (m, 1H), 1.53-1.49 (m, 2H), 1.48-1.45 (m, 2H), 1.43 (s, 9H), 1.40 (s, 3H), 1.35 (s, 3H), 1.27 (s, 1H), 1.16-1.07 (m, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ : 170.25, 153.78 (dd, $J = 289.0$ Hz, 285.5 Hz), 133.21, 132.40, 130.97 (dd, $J = 4.3$ Hz, 2.9 Hz), 127.97, 127.84, 127.54, 127.23 (t, $J = 3.3$ Hz), 126.21, 126.08 (t, $J = 3.2$ Hz), 126.04, 98.56, 92.24 (dd, $J = 21.6$ Hz, 12.9 Hz), 80.47, 68.44, 66.17, 42.65, 36.43, 35.46, 30.06, 28.02, 27.47, 23.15 (t, $J = 2.5$ Hz), 19.61. **¹⁹F NMR (376 MHz, CDCl₃)** δ : 69.40 (t, $J = 8.9$ Hz), -90.94 (d, $J = 43.2$ Hz), -91.22 (d, $J = 43.2$ Hz). **HRMS m/z (ESI)** calcd for C₂₇H₃₄F₂O₄Na (M + Na)⁺ 483.2323, found 483.2322.

(8R,9R,13S,14R)-3-(5-(3,4-dimethoxyphenyl)-1,1-difluoropent-1-en-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5g)



According to Procedure B, the reaction was carried out with **1t** (0.20 mmol, 69.7 mg), **2h** (0.30 mmol, 167.8 mg), TEA (1.00 mmol, 139 μ L) in DMSO (2 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA=10:1) to afford 85.3 mg (86%) of **5g** as yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.27-7.25 (m, 1H), 7.07 (d, $J = 8.2$ Hz, 1H), 7.00 (s, 1H), 6.77 (d, $J = 8.1$ Hz, 1H), 6.69-6.65 (m, 2H), 3.84 (s, 6H), 2.90-2.88 (m, 2H), 2.58-1.96 (m, 11H), 1.72-1.43 (m, 8H), 0.92 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 220.87, 153.65, 148.45, 147.25, 138.93, 136.60, 134.61, 131.11, 125.68 (t, $J = 3.1$ Hz), 125.48, 120.27, 111.78, 111.23, 91.96 (dd, $J = 18.5$ Hz, 16.0 Hz), 56.01, 55.87, 50.60, 48.06, 44.44, 38.16, 35.93, 34.85, 31.67, 29.62, 29.49, 27.19, 26.57, 25.70, 21.67, 13.93. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -91.51 HRMS m/z (ESI) calcd for $\text{C}_{31}\text{H}_{37}\text{F}_2\text{O}_3$ ($M + \text{H}$) $^+$ 495.2711, found 495.2712.

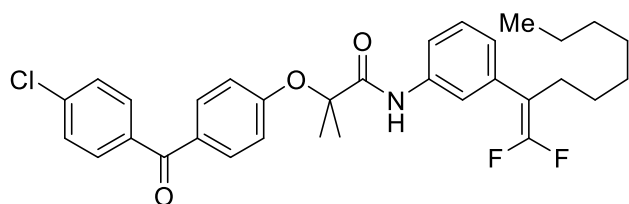
N-(3-(5-(3,4-dimethoxyphenyl)-1,1-difluoropent-1-en-2-yl)phenyl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanamide (5h)



According to Procedure B, the reaction was carried out with **1u** (0.20 mmol, 82.5 mg), **2h** (0.30 mmol, 167.8 mg), TEA (1.00 mmol, 139 μ L) in DMSO (2 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA=5:1) to afford 91.2 mg (81%) of **5h** as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.49-7.38 (m, 3H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.02-6.98 (m, 2H), 6.77 (d, $J = 8.1$ Hz, 1H), 6.68-6.61 (m, 4H), 3.97-3.94 (m, 2H), 3.84 (d, $J = 2.6$ Hz, 6H), 2.56 (t, $J = 7.6$ Hz, 2H), 2.44-2.41 (m, 2H), 2.29 (s, 3H), 2.17 (s, 3H), 1.87-1.79 (m, 4H), 1.72-1.64 (m, 2H), 1.35 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 175.72, 156.79, 153.52 (dd, $J = 288.8$ Hz, $J = 285.2$ Hz), 148.73, 147.11, 138.05, 136.51, 134.49 (dd, $J = 4.5$ Hz, $J = 2.7$ Hz), 134.44, 130.29, 128.92, 124.20 (t, $J = 3.0$ Hz), 123.46, 120.85, 120.14, 119.95

(t, $J = 3.3$ Hz), 119.02, 112.14, 111.65, 111.14, 92.03 (dd, $J = 21.9$ Hz, $J = 13.1$ Hz), 67.83, 55.86, 55.74, 42.82, 37.64, 34.68, 29.38 (t, $J = 2.3$ Hz), 27.17, 25.58, 25.12, 21.32, 15.77. ^{19}F NMR (376 MHz, CDCl_3) δ : -69.31 (d, $J = 9.4$ Hz), -90.83 (d, $J = 43.2$ Hz), -91.19 (d, $J = 43.2$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{34}\text{H}_{41}\text{F}_2\text{NO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 588.2901, found 588.2901.

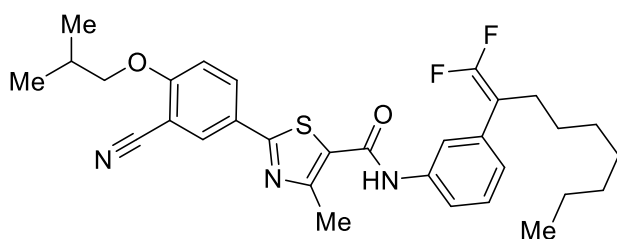
2-(4-(4-Chlorobenzoyl)phenoxy)-N-(3-(1,1-difluoronon-1-en-2-yl)phenyl)-2-methylpropanamide (5i)



According to Procedure B, the reaction was carried out with **1v** (0.20 mmol, 97.6 mg), **2s** (0.30 mmol, 143.8 mg), TEA (1.00 mmol, 139 μL) in DMSO (2 mL). The

crude product was purified by flash column chromatography on silica gel (PE: EA=10:1) to afford 78.0 mg (70%) of **5i** as a white solid: ^1H NMR (400 MHz, CDCl_3) δ : 8.32 (s, 1H), 7.78 (d, $J = 8.8$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.52 (s, 1H), 7.47-7.44 (m, 3H), 7.32 (t, $J = 7.9$ Hz, 1H), 7.09-7.05 (m, 3H), 2.39-2.35 (m, 3H), 1.68 (s, 6H), 1.37-1.23 (m, 10H), 0.87-0.84 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 194.09, 172.21, 156.42, 153.54 (dd, $J = 288.7$ Hz, $J = 285.4$ Hz), 138.69, 137.36, 136.93, 134.93 (dd, $J = 4.2$ Hz, $J = 2.6$ Hz), 132.16, 131.93, 131.18, 129.02, 128.59, 124.61 (t, $J = 3.2$ Hz), 120.17, 119.72 (t, $J = 3.2$ Hz), 118.71, 92.22 (dd, $J = 21.7$ Hz, $J = 12.8$ Hz), 82.43, 31.70, 28.89, 28.86, 27.66 (t, $J = 2.5$ Hz), 27.55, 25.04, 22.54, 14.02. ^{19}F NMR (376 MHz, CDCl_3) δ : -69.41 (d, $J = 9.2$ Hz), -91.15 (d, $J = 43.5$ Hz), -91.38 (d, $J = 43.5$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{32}\text{H}_{35}\text{ClF}_2\text{NO}_3$ ($\text{M} + \text{H}$) $^+$ 554.2274, found 554.2273.

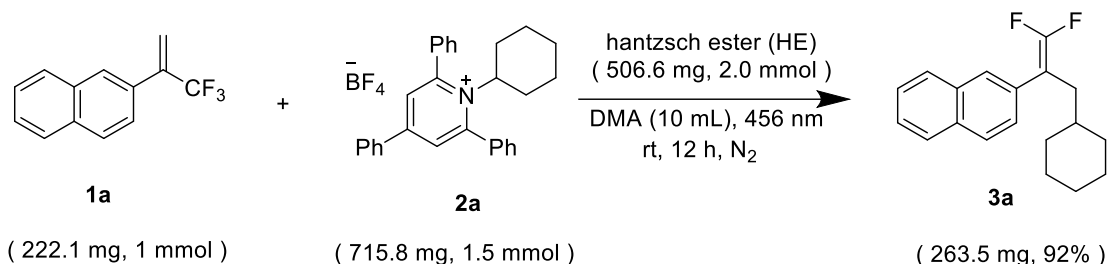
2-(3-Cyano-4-isobutoxyphenyl)-N-(3-(1,1-difluoronon-1-en-2-yl)phenyl)-4-methylthiazole-5-carboxamide (5j)



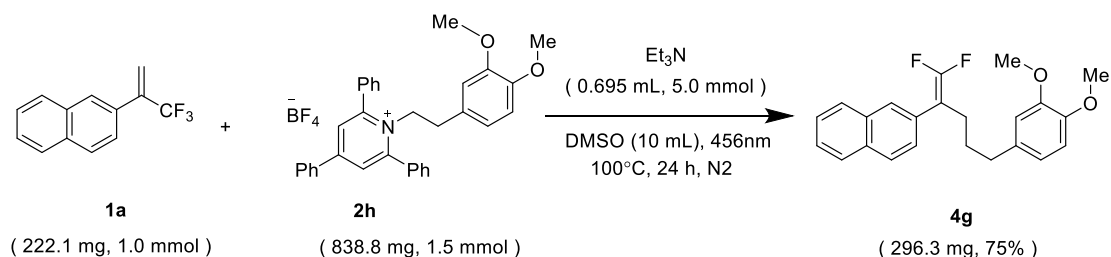
According to Procedure B, the reaction was carried out with **1w** (0.20 mmol, 97.1 mg), **2s** (0.30 mmol, 143.8 mg), TEA (1.00 mmol, 139 μL) in DMSO (2 mL). The crude product was purified by flash

column chromatography on silica gel (PE: EA=10:1) to afford 77.2 mg (74%) of **5j** as a yellow solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.12 (d, $J = 2.2$ Hz, 1H), 8.06 (dd, $J = 8.8$ Hz, 2.3 Hz, 1H), 7.59-7.57 (m, 1H), 7.53-7.51 (m, 2H), 7.35 (t, $J = 7.9$ Hz, 1H), 7.12-7.10 (m, 1H), 7.01 (t, $J = 8.9$ Hz, 1H), 3.90 (d, $J = 6.5$ Hz, 2H), 2.78 (s, 3H), 2.40-2.37 (m, 2H), 2.25-2.15 (m, 1H), 1.40-1.35 (m, 2H), 1.29-1.24 (m, 8H), 1.09 (d, $J = 6.7$ Hz, 6H), 0.86 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 164.90, 162.46, 159.73, 157.07, 153.61 (dd, $J = 288.8$ Hz, $J = 285.5$ Hz), 137.49, 135.04 (dd, $J = 4.3$ Hz, $J = 2.4$ Hz), 132.50, 131.96, 129.15, 125.74, 124.91 (t, $J = 3.2$ Hz), 124.80, 120.13 (t, $J = 3.4$ Hz), 119.19, 115.40, 112.65, 102.93, 92.22 (dd, $J = 21.6$ Hz, $J = 12.9$ Hz), 75.71, 31.74, 28.94, 28.92, 28.13, 27.70 (t, $J = 2.5$ Hz), 27.59, 22.58, 19.01, 17.49, 14.04. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ : -69.44 (d, $J = 8.9$ Hz), -91.02 (d, $J = 43.4$ Hz), -91.25 (d, $J = 43.4$ Hz), HRMS m/z (ESI) calcd for $\text{C}_{31}\text{H}_{36}\text{F}_2\text{N}_3\text{O}_2\text{S}$ (M + H) $^+$ 552.2496, found 552.2498.

7. One mmol reactions for synthesis of **3a** and **4g**



In a nitrogen-filled glovebox, an oven-dried 20.0 mL vial with a stirring bar was added with **1a** (222.1 mg, 1.0 mmol), **2a** (715.8 mg, 1.5 mmol), hantzsch ester (**HE**) (506.6 mg, 2.0 mmol). *N,N*-Dimethylacetamide (**DMA**) (10 mL) were then added. The resulting mixture was stirred at room temperature under blue LEDs (456 nm) irradiation for 12 h. After this time, the reaction mixture was diluted with DCM and washed with a saturated brine for 6 times. The organic layer was separated, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE) to afford 263.5 mg (92% yield) of **3a** as a colorless oil.



In a nitrogen-filled glovebox, an oven-dried 20.0 mL vial with a stirring bar was added with **1a** (222.1 mg, 1.0 mmol), **2h** (838.8 mg, 1.5 mmol). A mixture of dimethyl sulfoxide (**DMSO**) (10 mL) and Et₃N (0.695 mL, 5.0 mmol) were then added. The resulting mixture was stirred at 100°C under blue LEDs (456 nm) irradiation for 24 h. After this time, the cooled reaction mixture was diluted with DCM and washed with a saturated brine for 6 times. The organic layer was separated, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE: DCM=5:1) to afford 296.3 mg (75% yield) of **4g** as a colorless oil.

8. UV/Vis absorption spectra

The UV/Vis absorption spectra of *N, N*-Dimethylacetamide (**DMA**) (path length = 1 cm) solutions of **2a** (0.15 M), **HE** (0.20 M) and a mixture of **2a** (0.15 M) and **HE** (0.20 M) are shown in **Figure S4**. A bathochromic shift of the mixture observed on the **Figure S4** indicated that an EDA complex is formed between **2a** and **HE**.

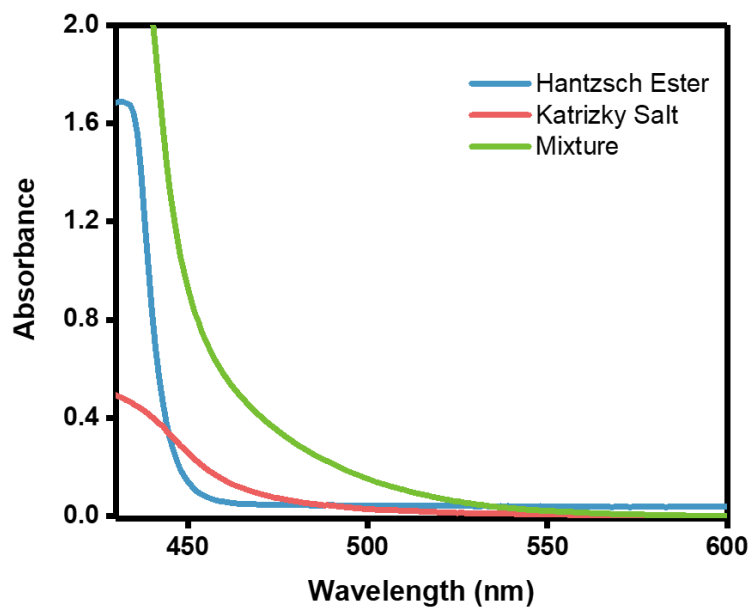


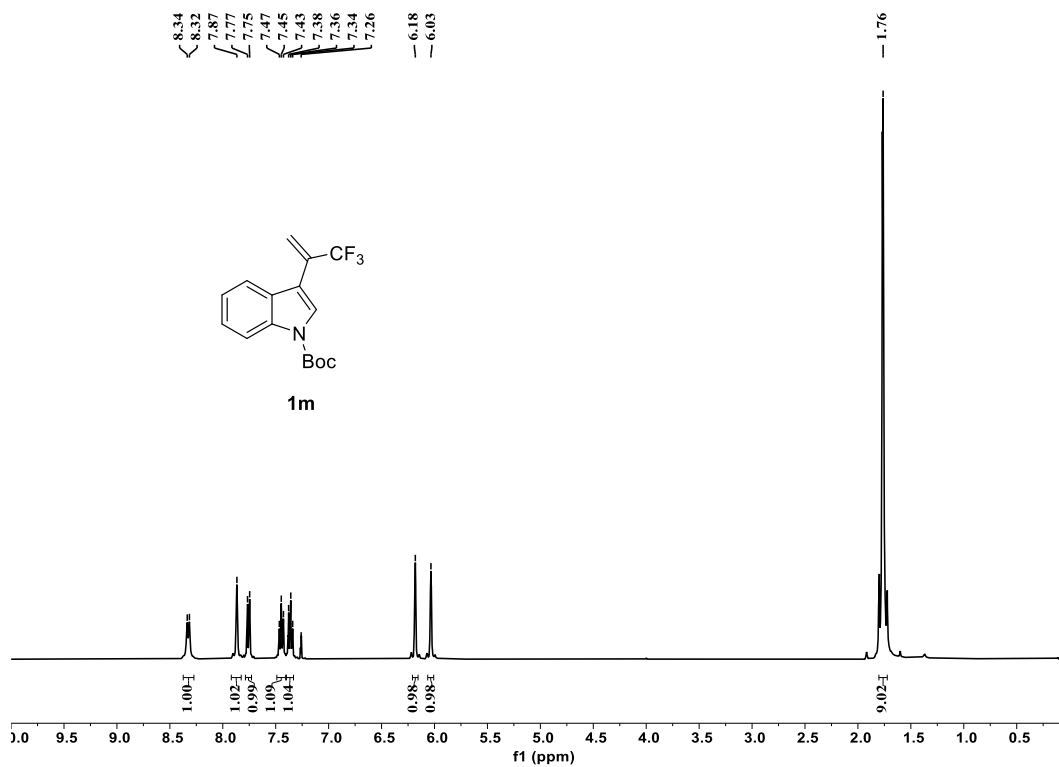
Figure S3. UV/Vis absorption spectra

9. References

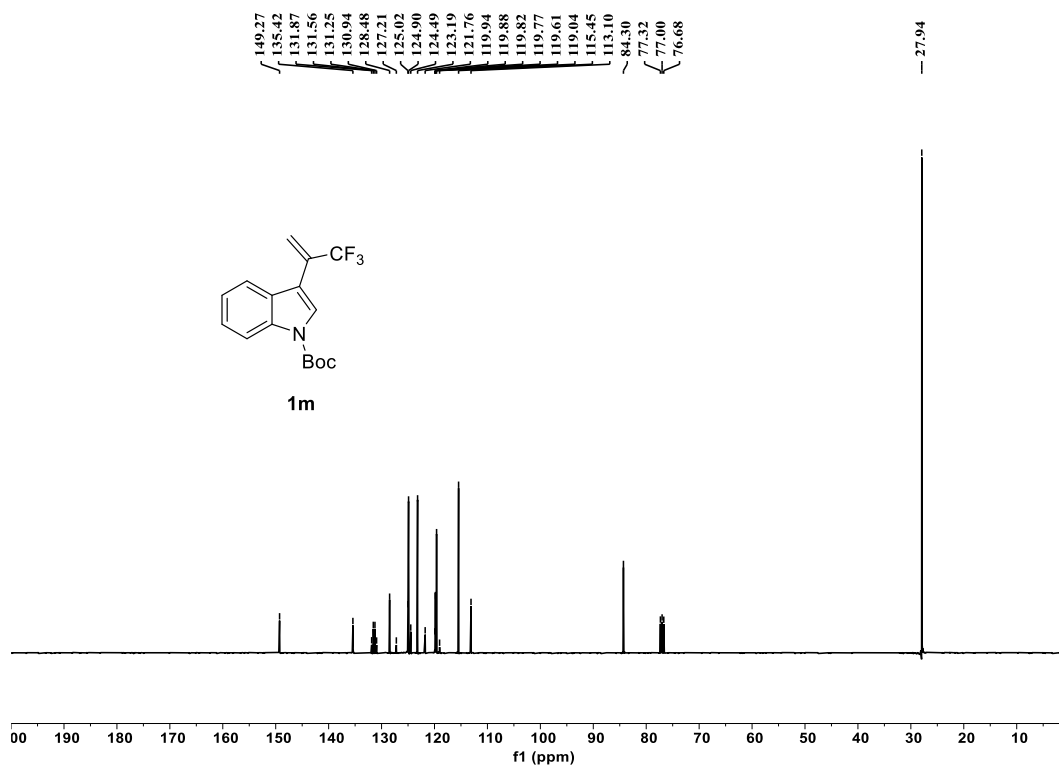
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10.Copies of NMR Spectra

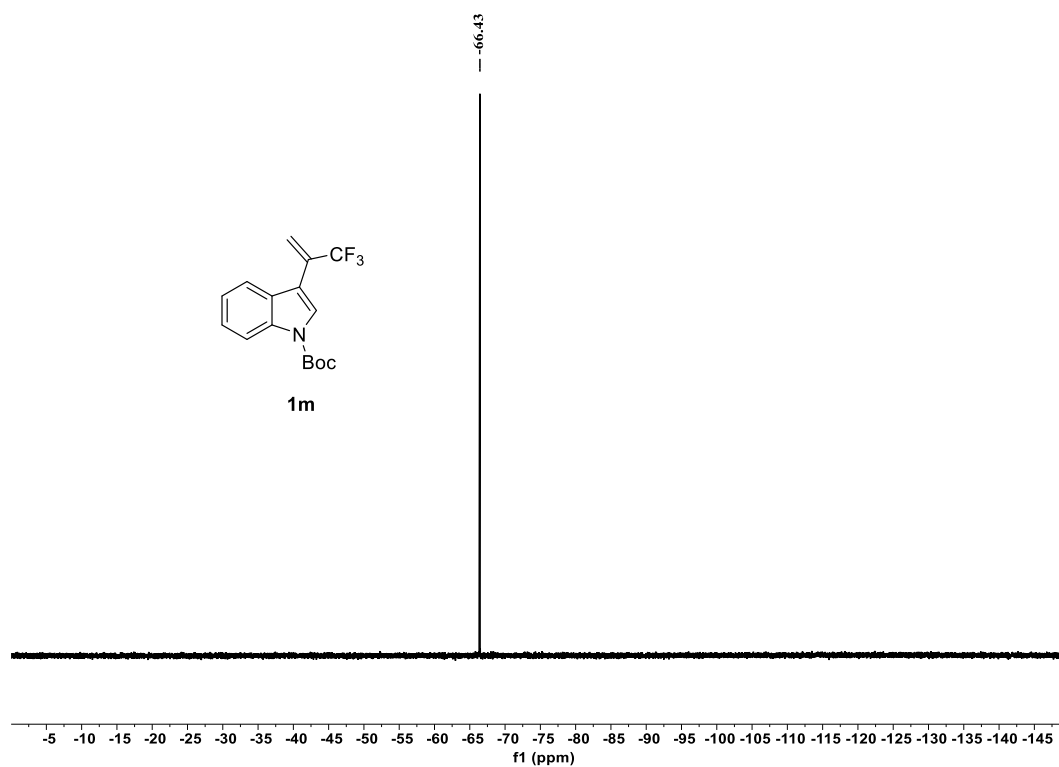
^1H NMR (400 MHz, CDCl_3)



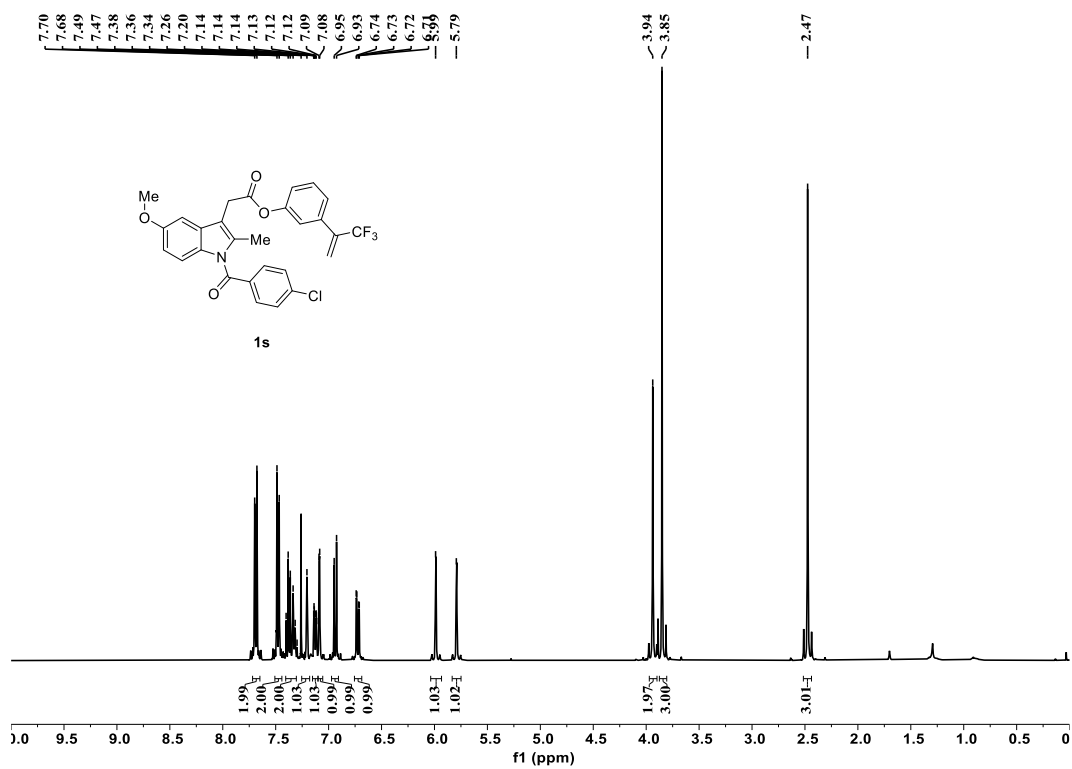
^{13}C NMR (100 MHz, CDCl_3)



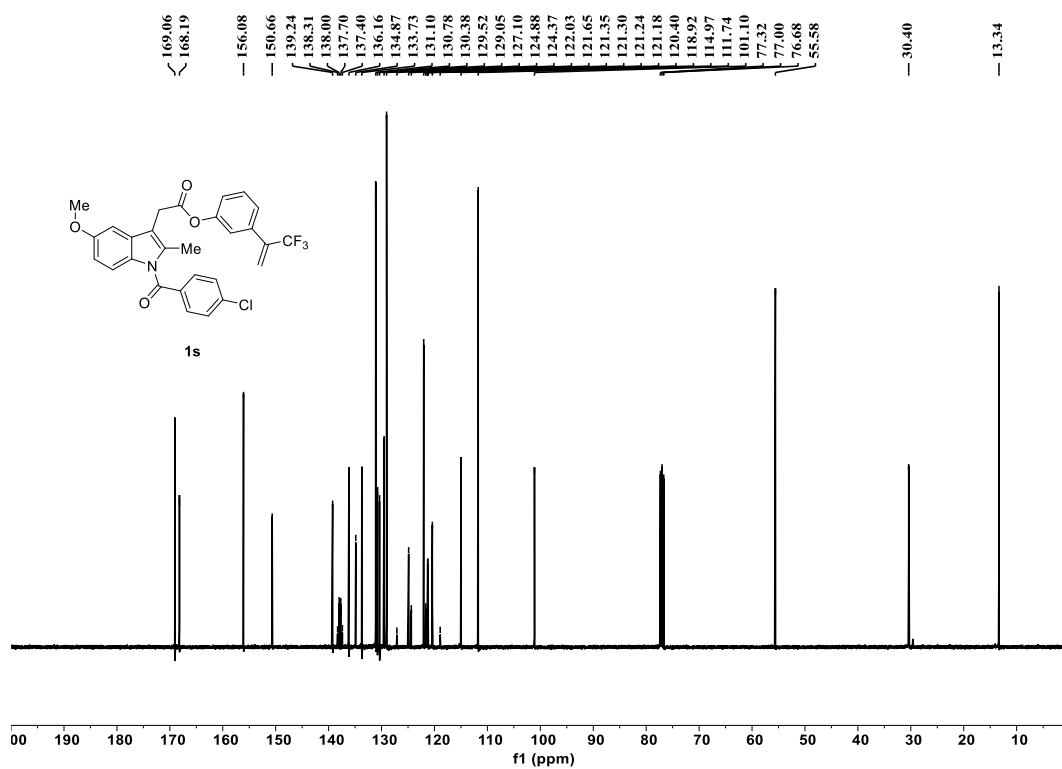
^{19}F NMR (376 MHz, CDCl_3)



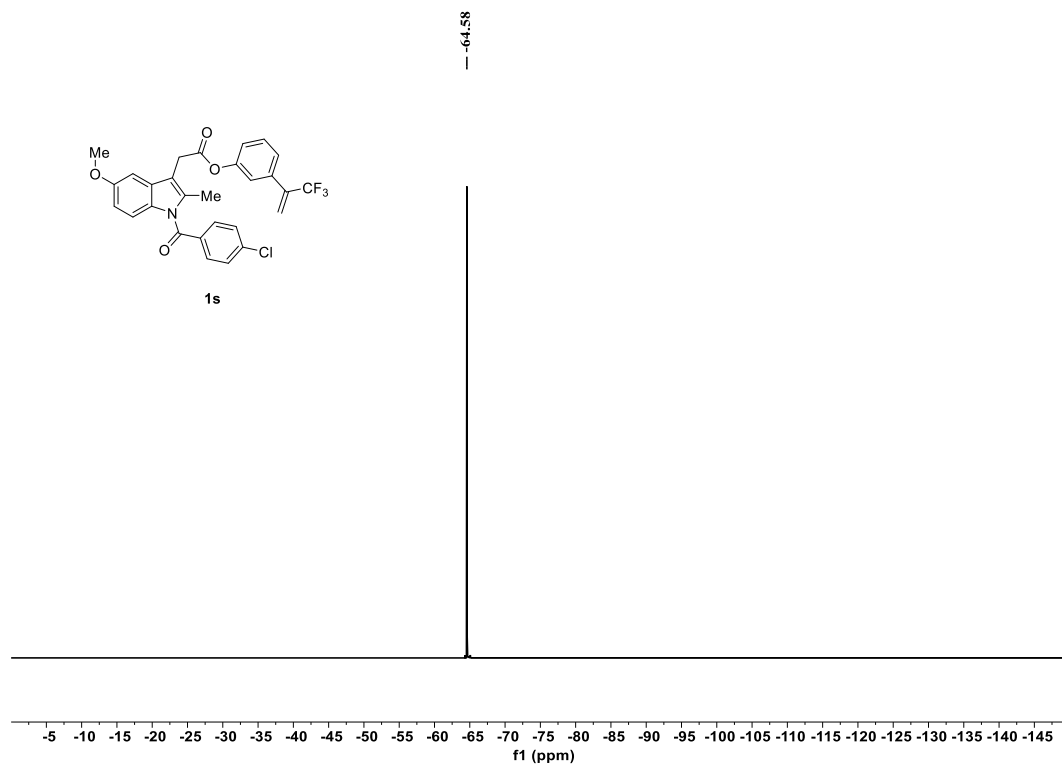
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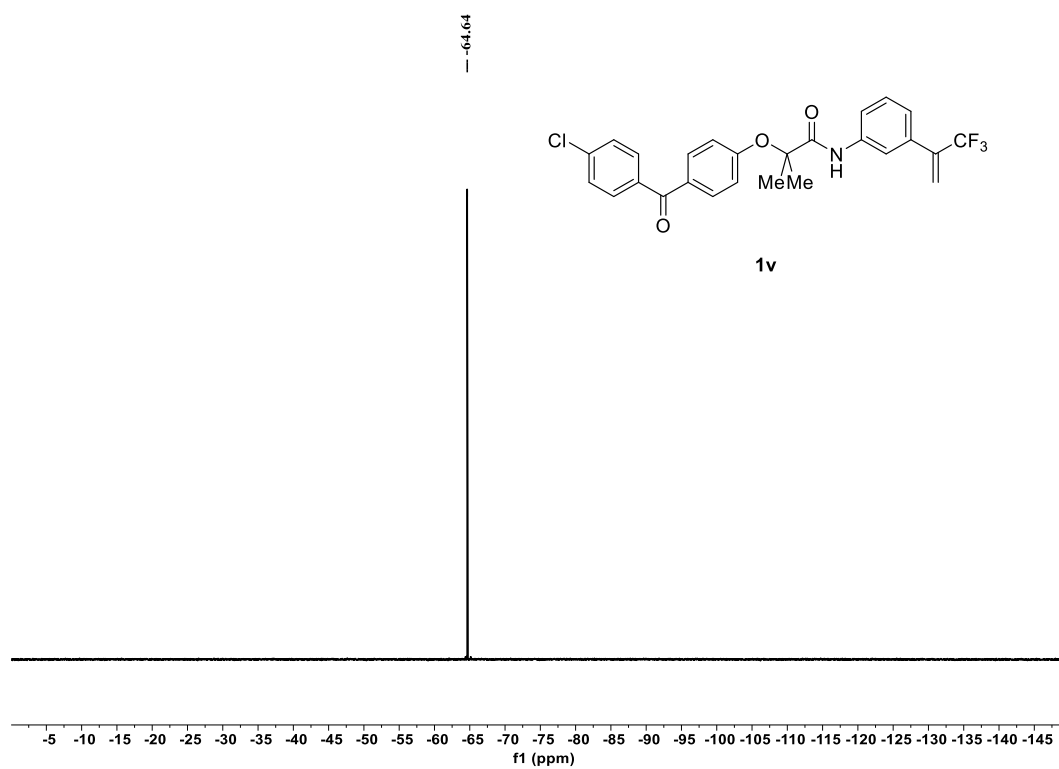
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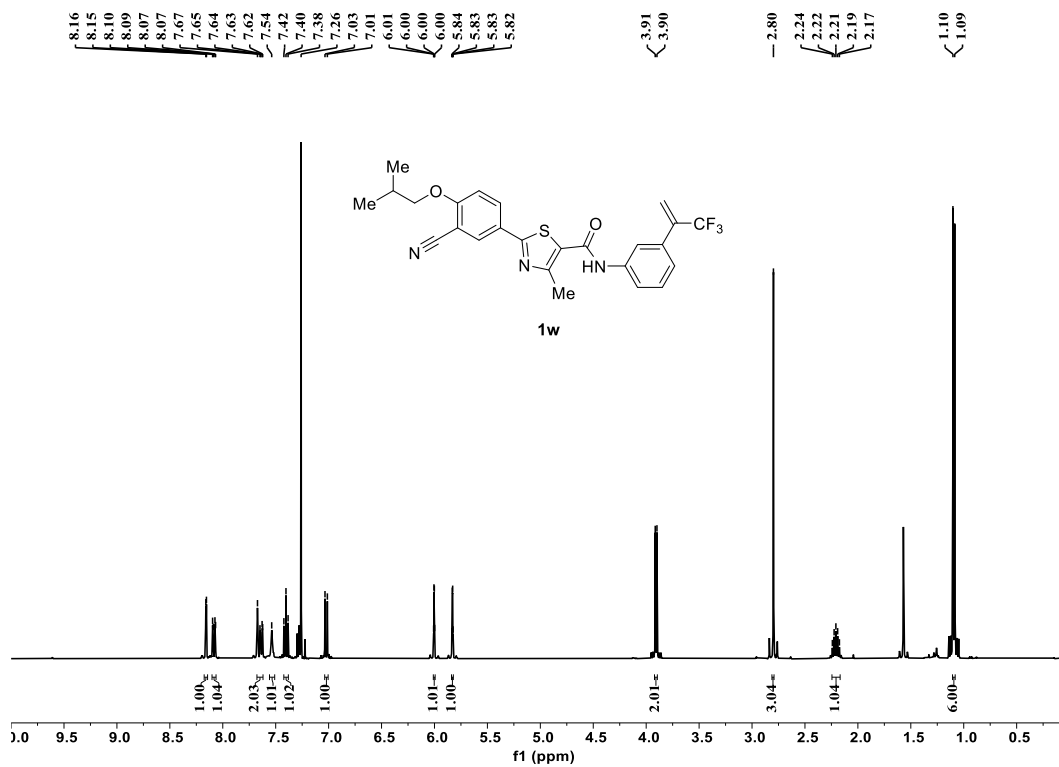
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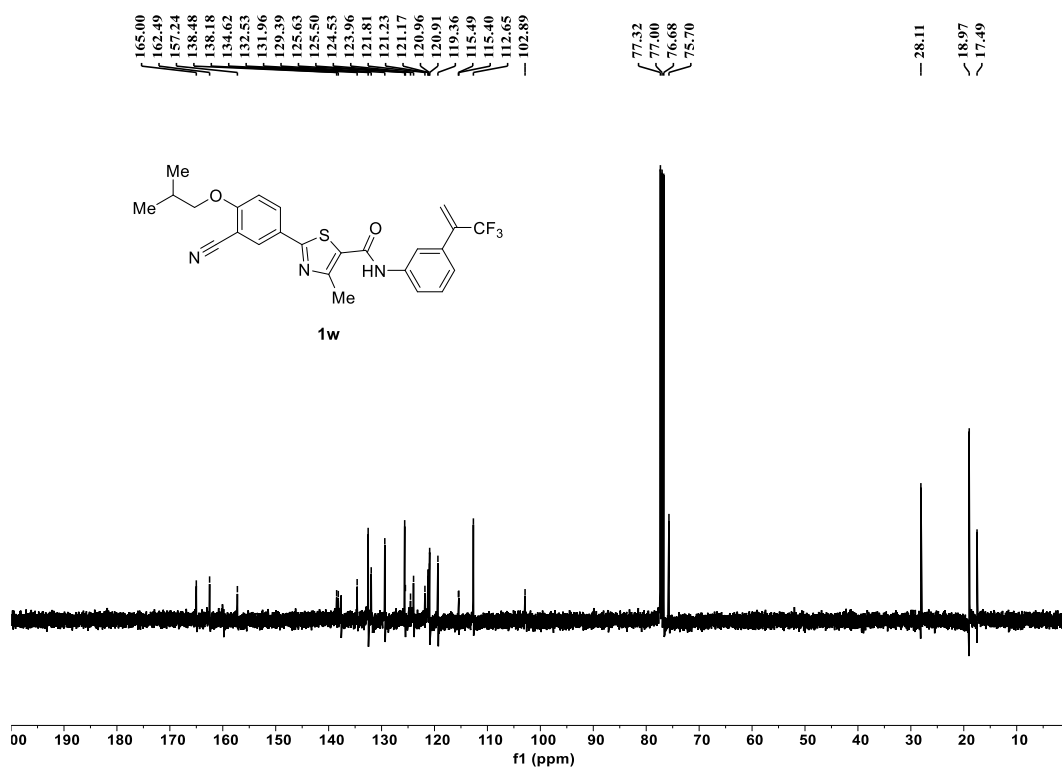
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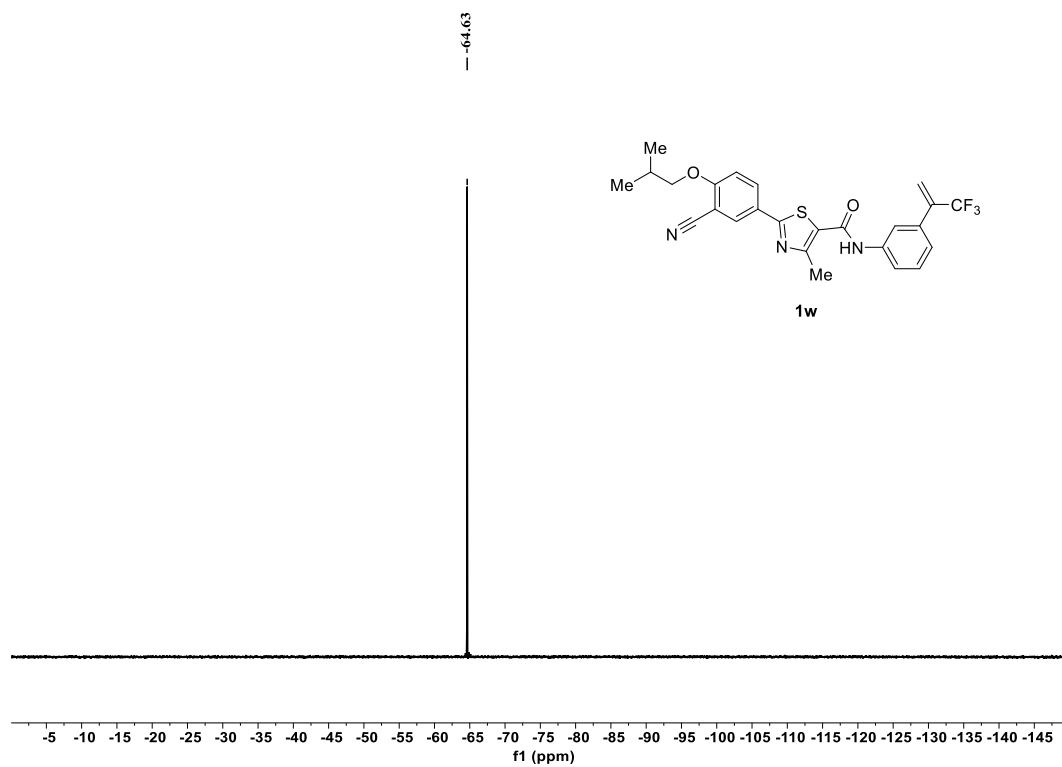
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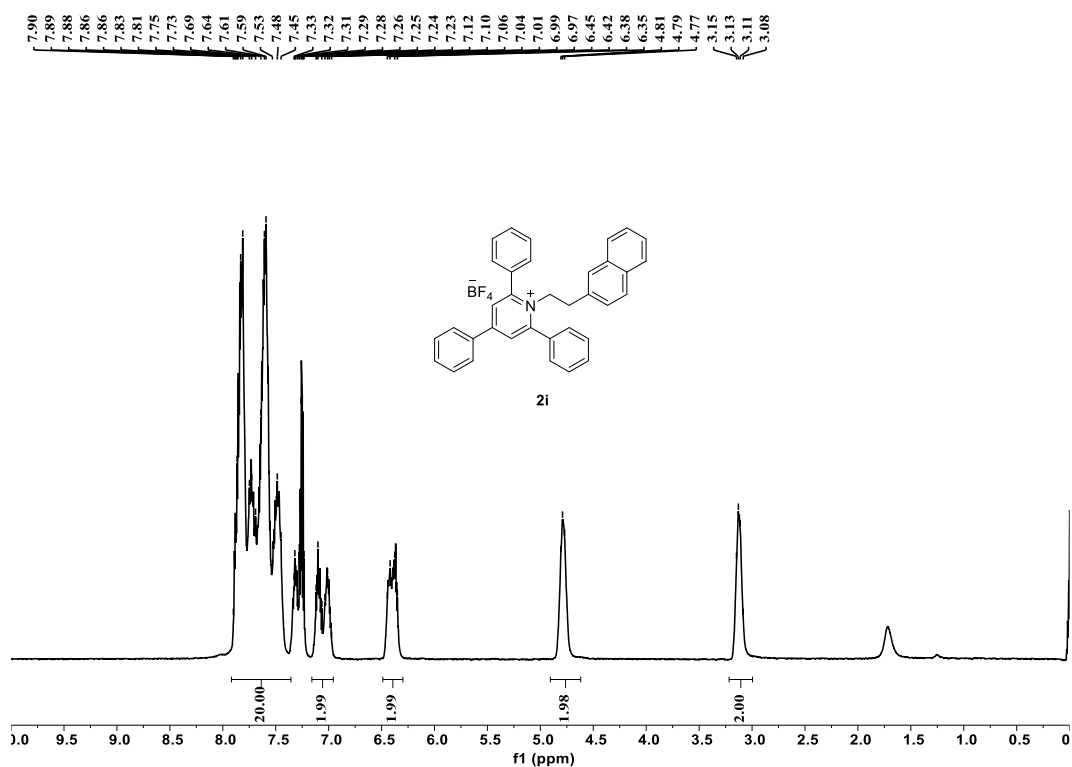
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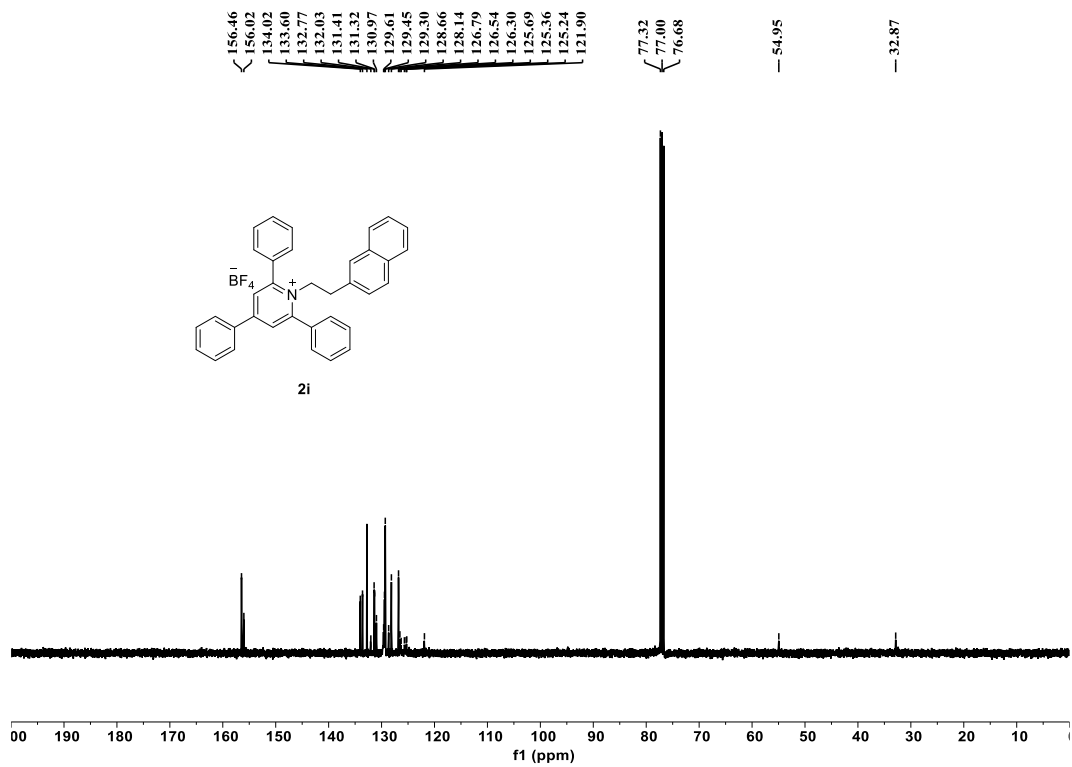
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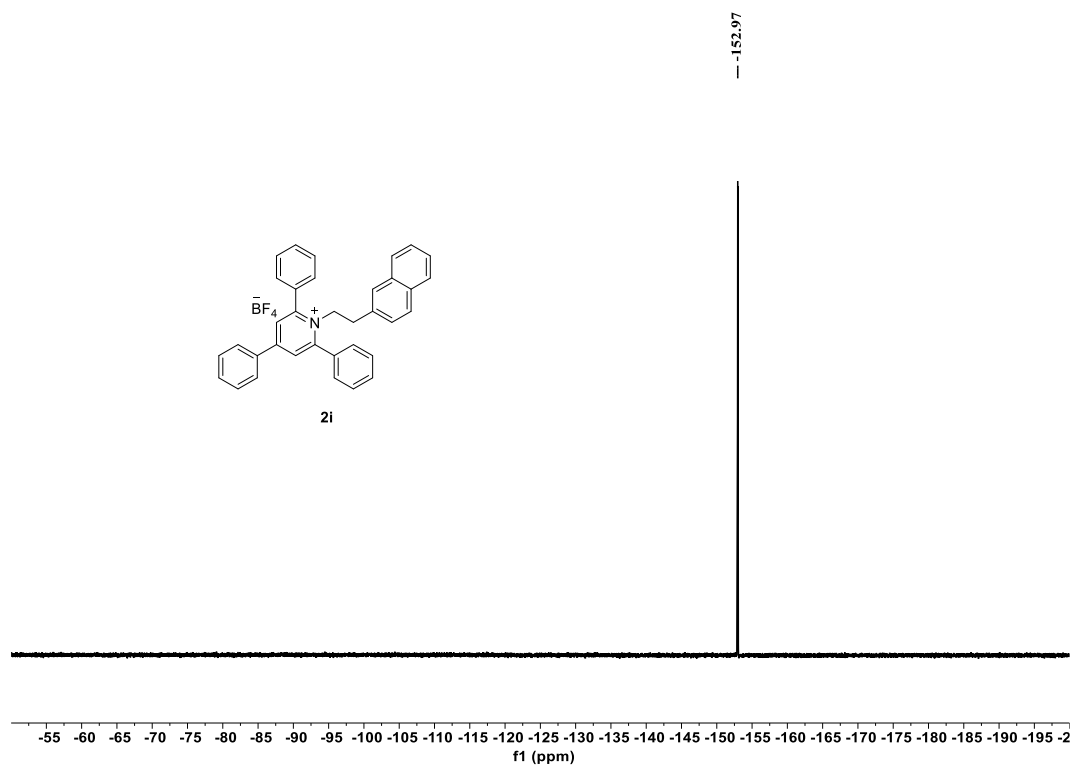
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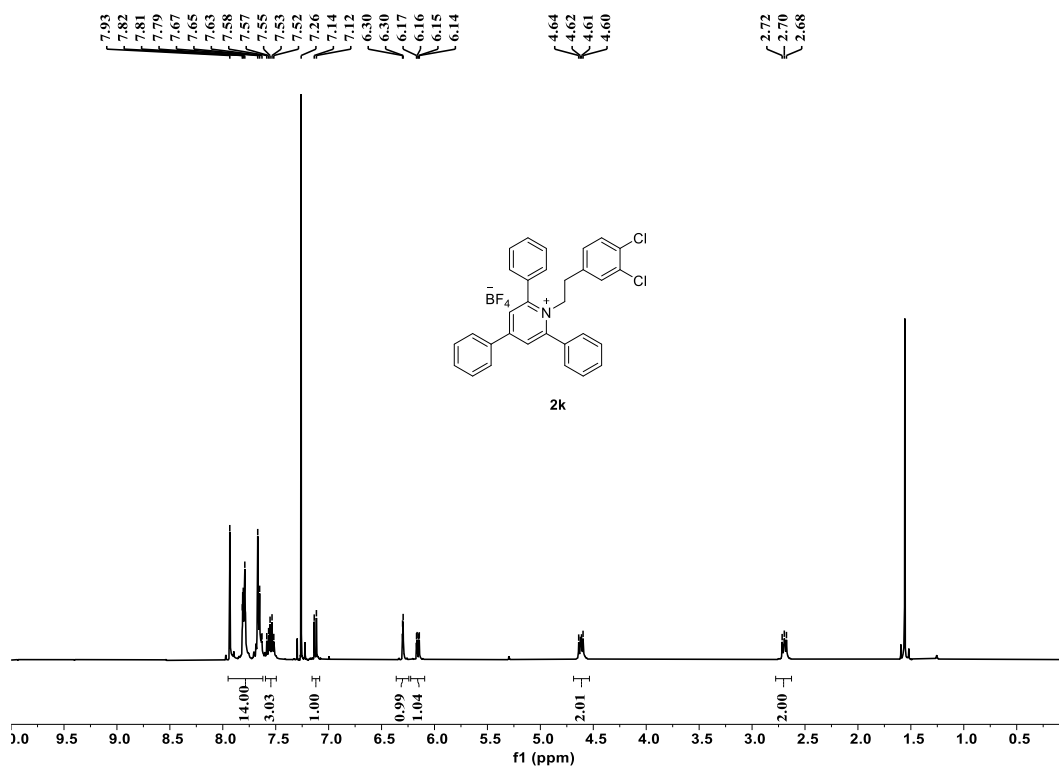
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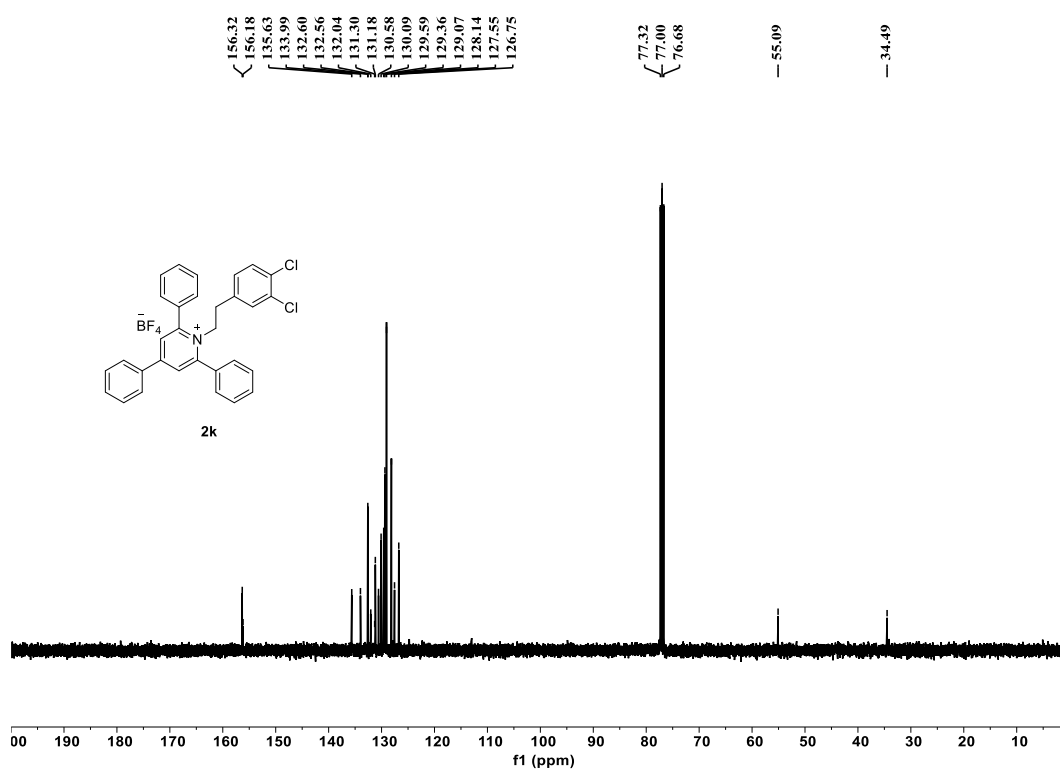
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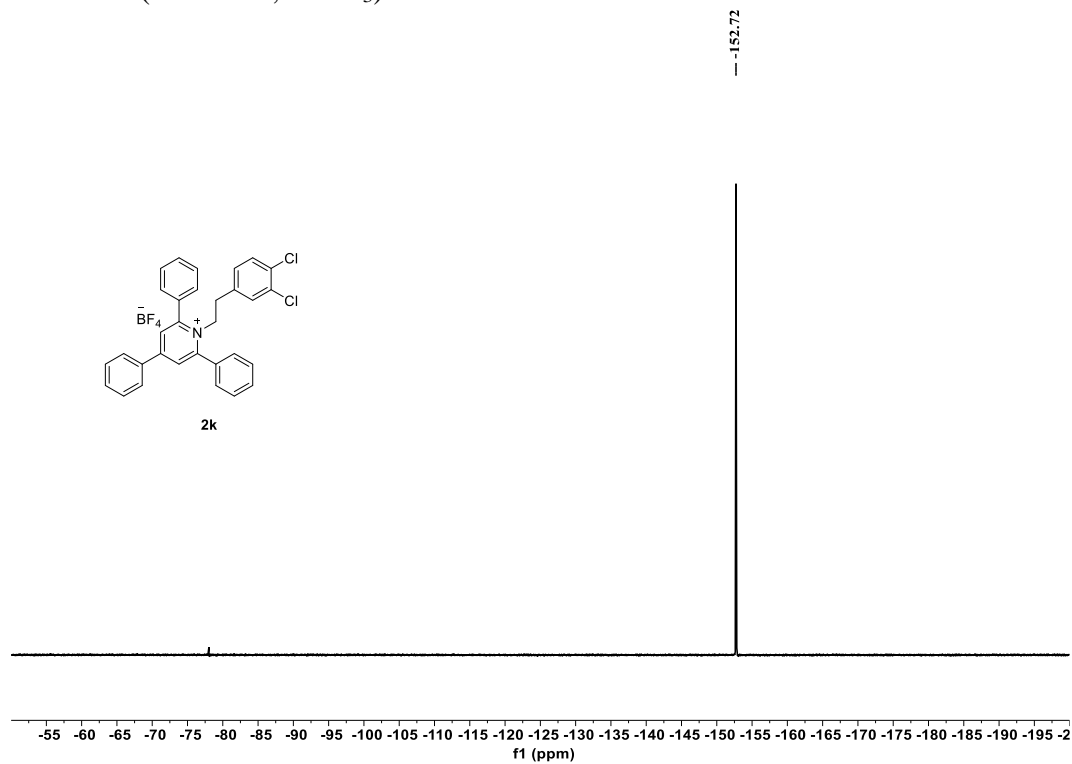
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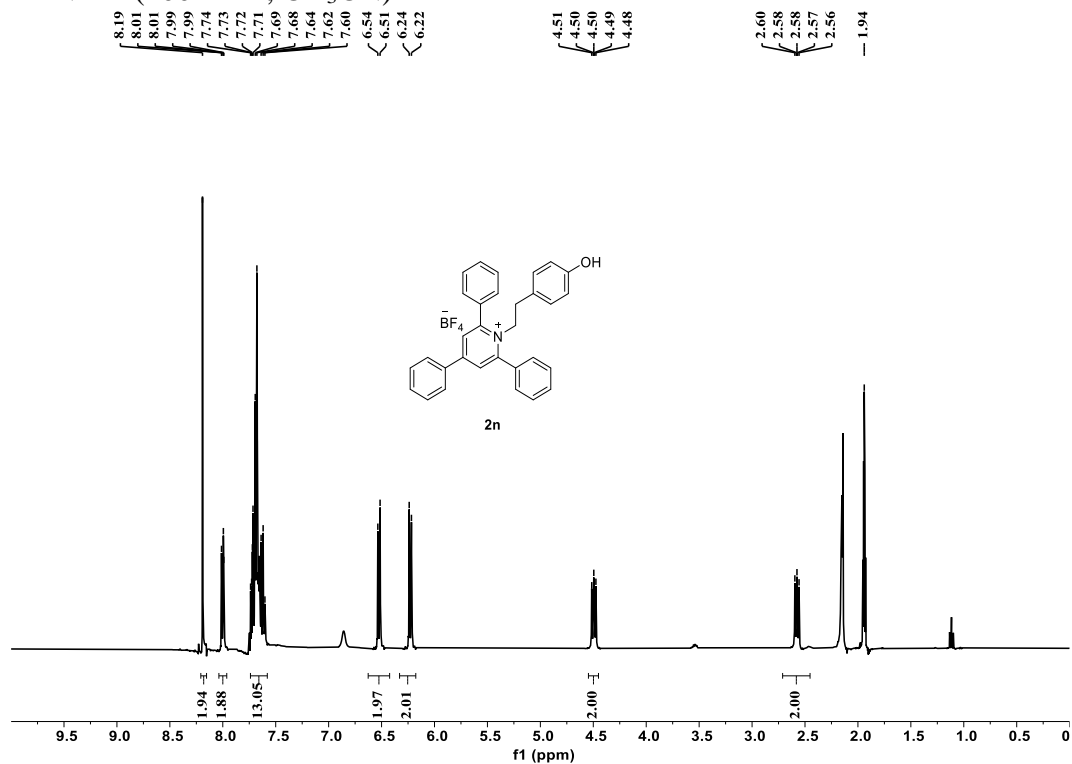
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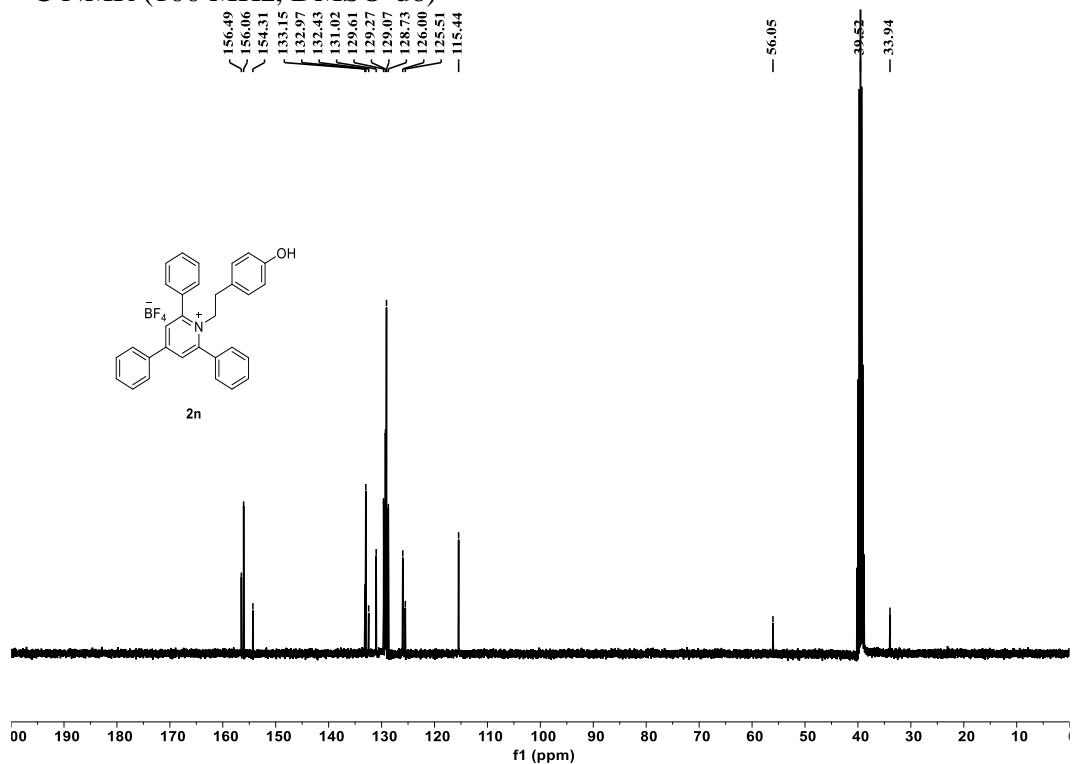
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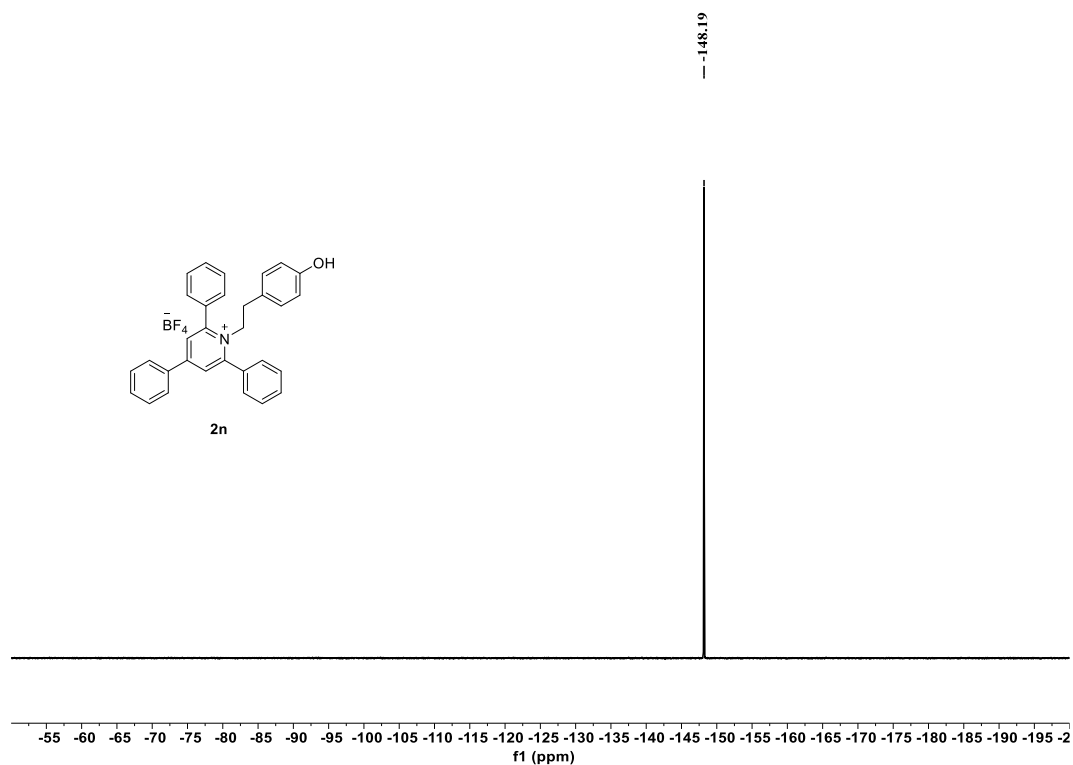
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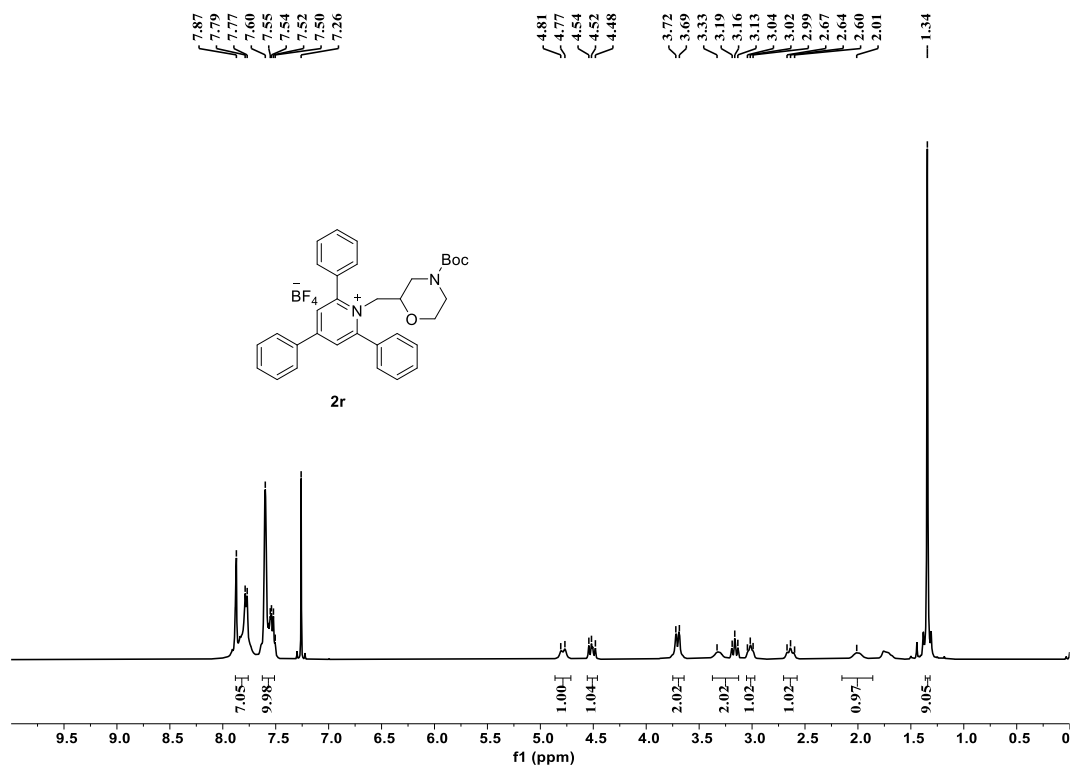
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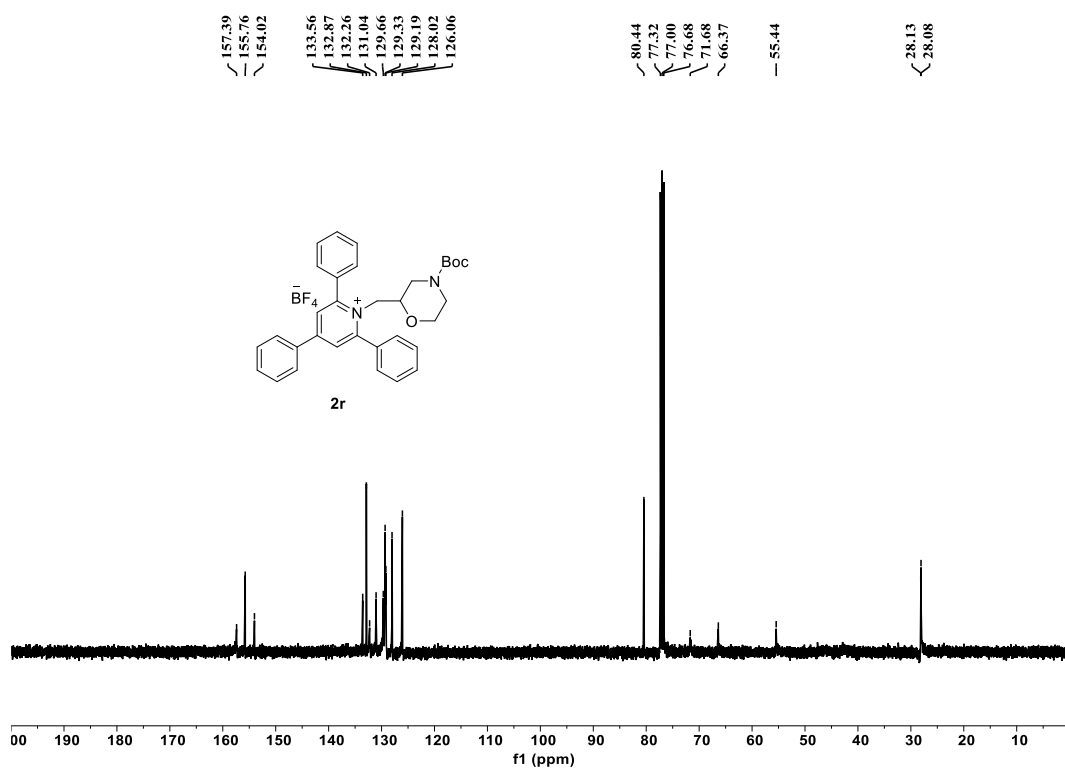
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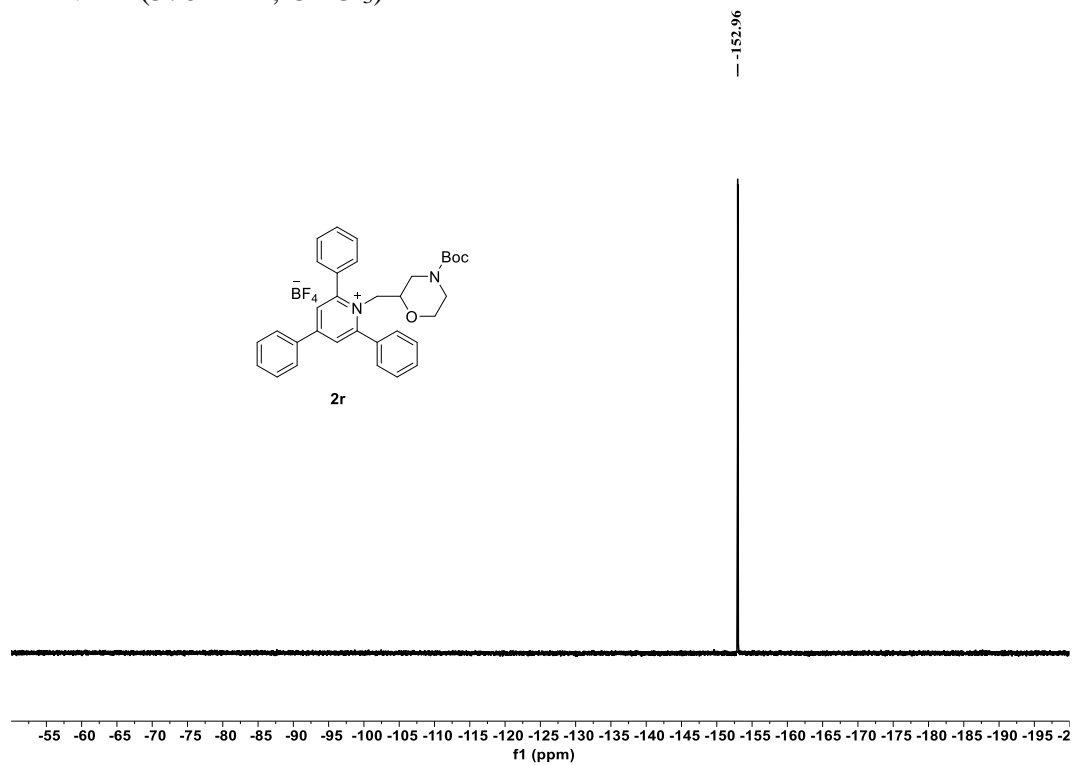
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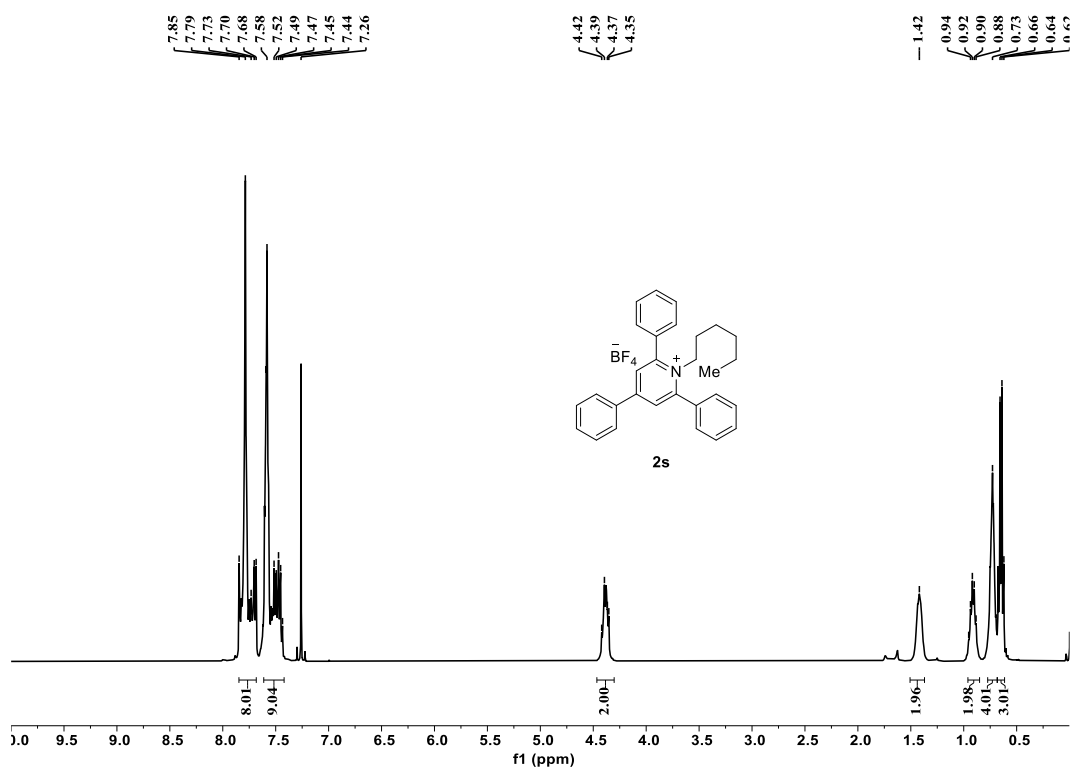
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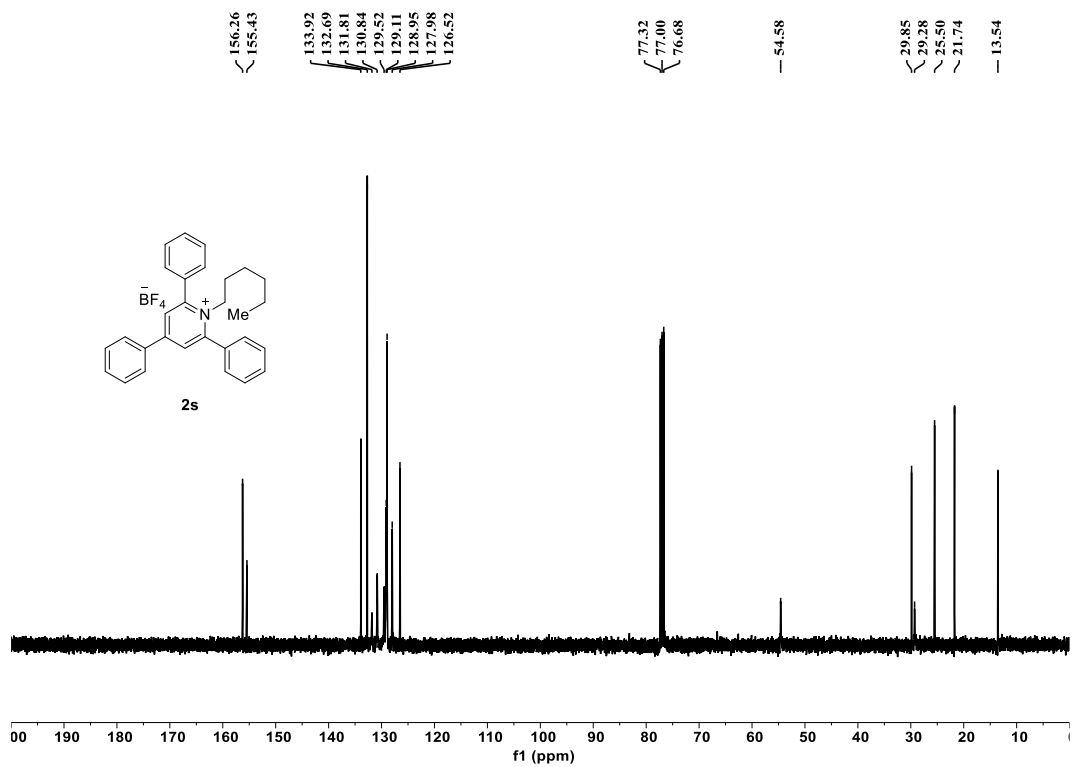
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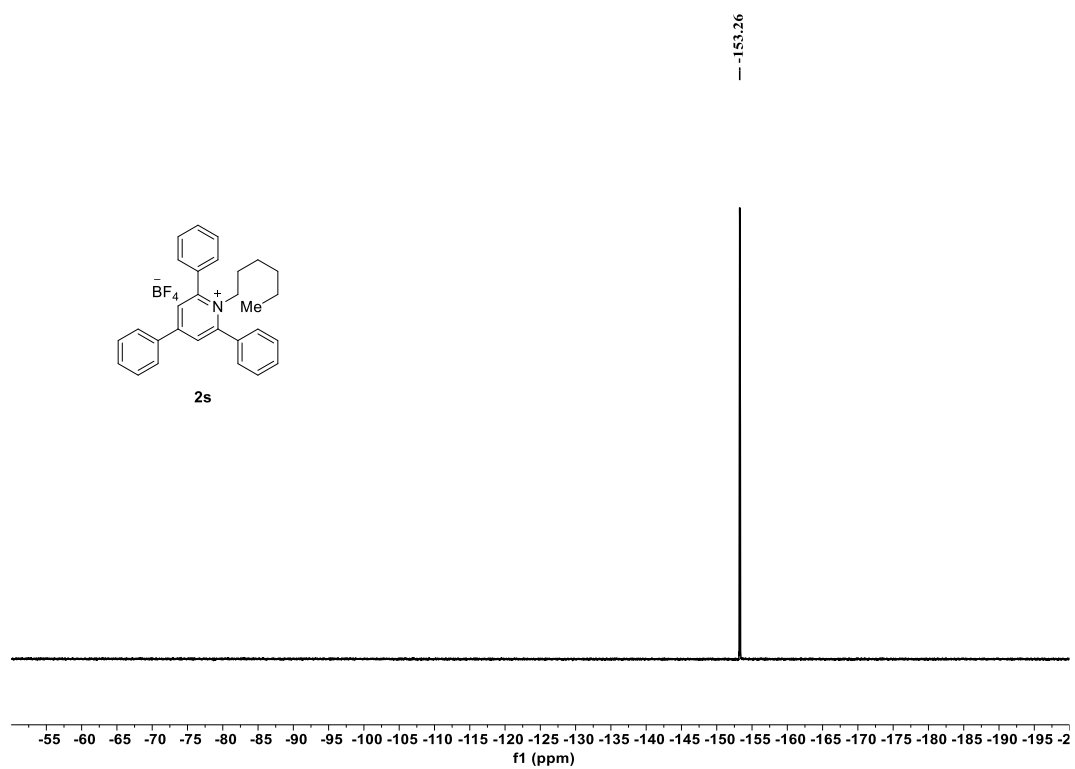
^1H NMR (400 MHz, CDCl_3)



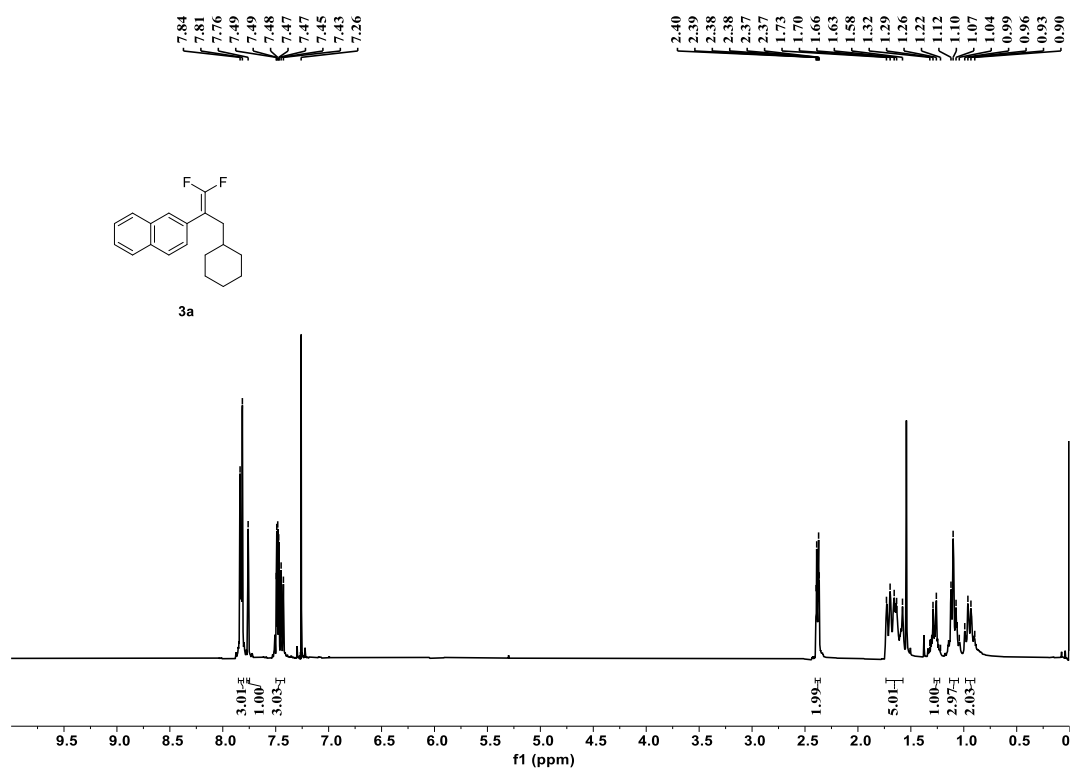
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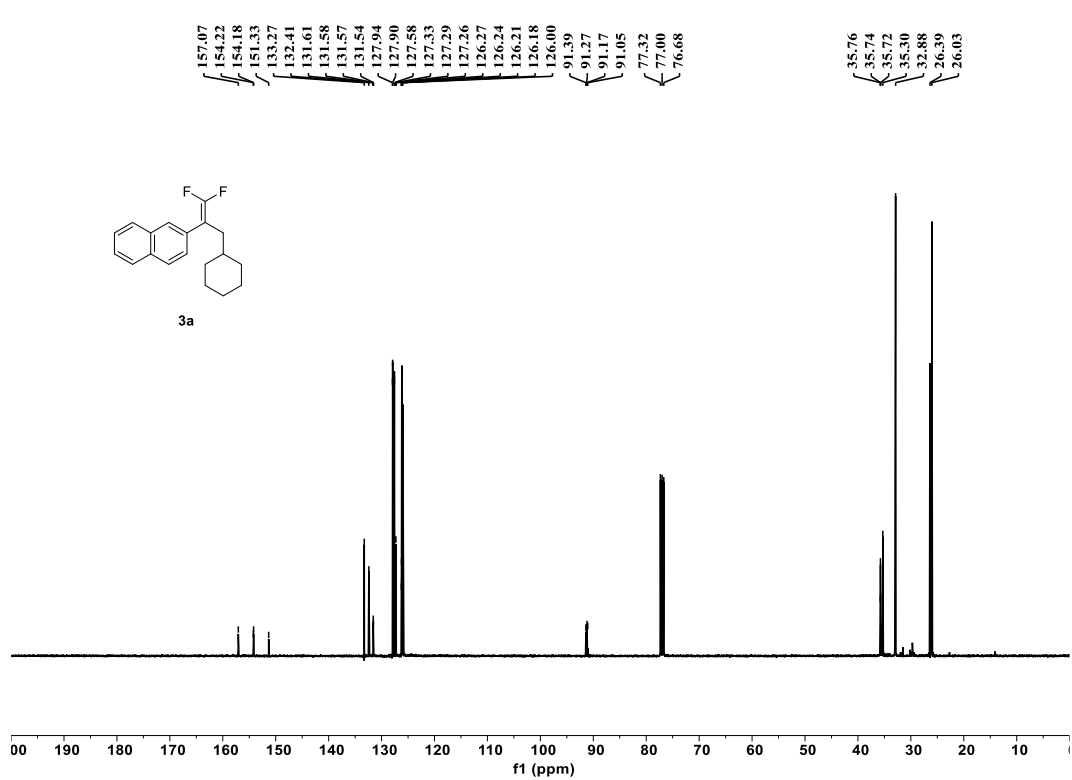
^{19}F NMR (376 MHz, CDCl_3)



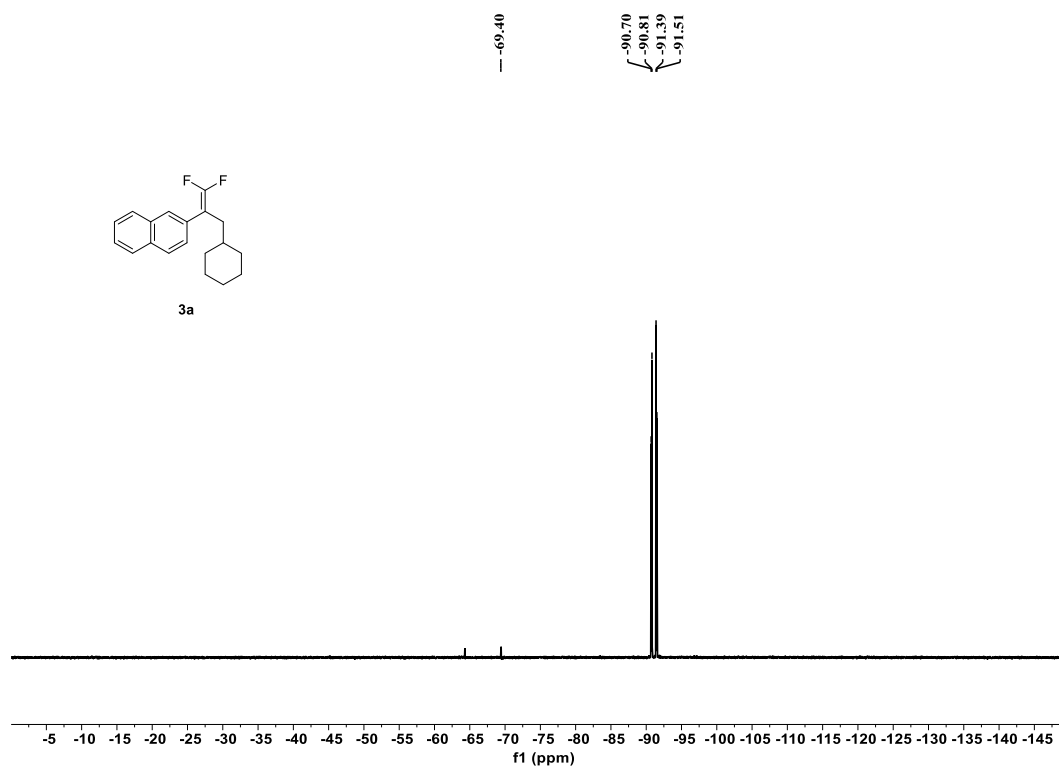
^1H NMR (400 MHz, CDCl_3)



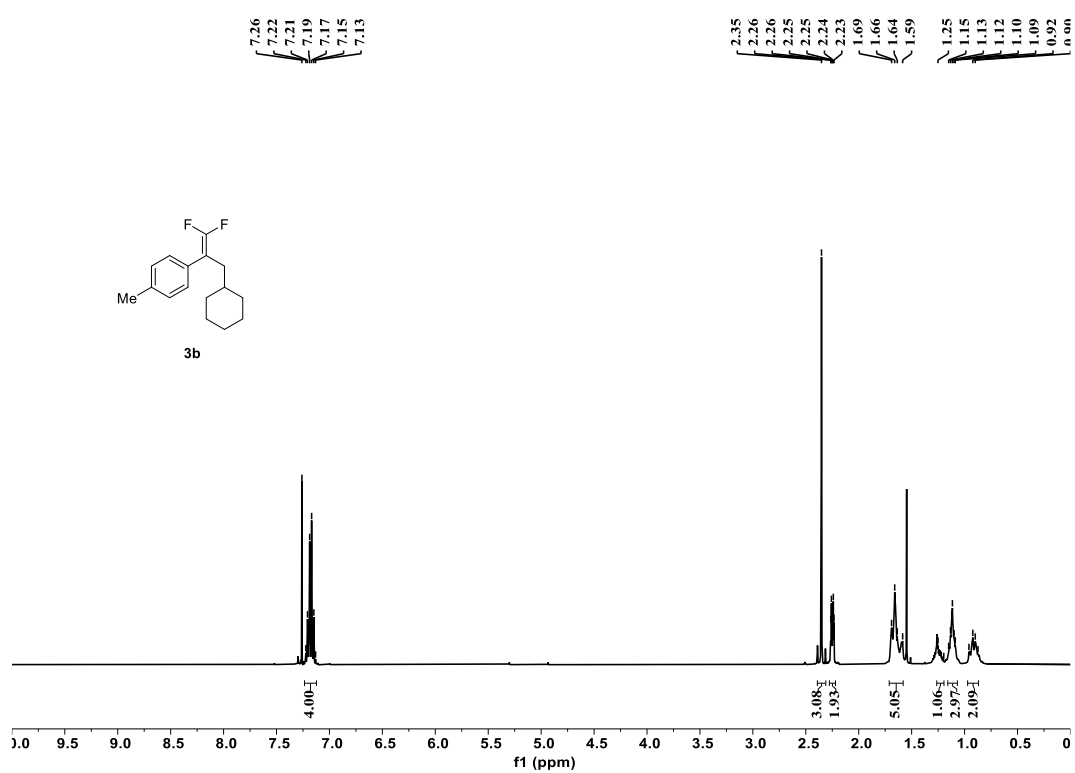
^{13}C NMR (100 MHz, CDCl_3)



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



^1H NMR (400 MHz, CDCl_3)

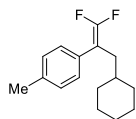


^{13}C NMR (100 MHz, CDCl_3)

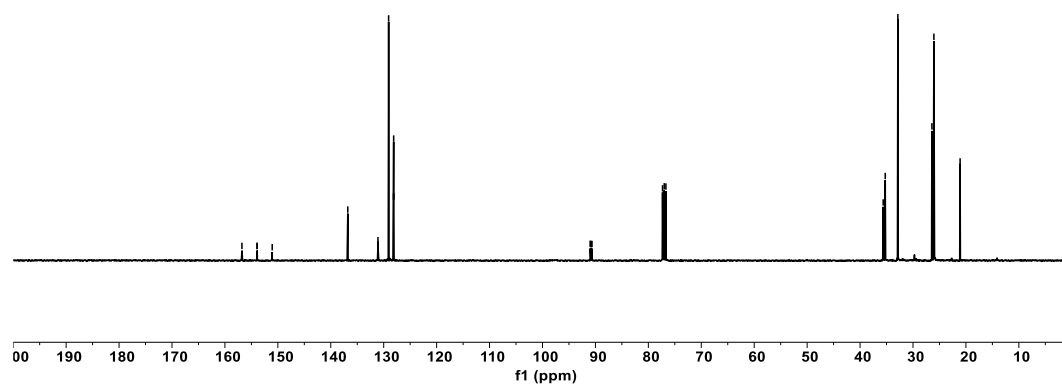
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153.94
153.90
151.06
136.79
131.12
131.09
131.05
129.07
128.15
128.12
128.09

90.09
90.87
90.78
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35.63
35.61
35.25
32.86
26.43
26.05
21.10

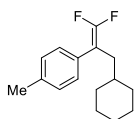


3b

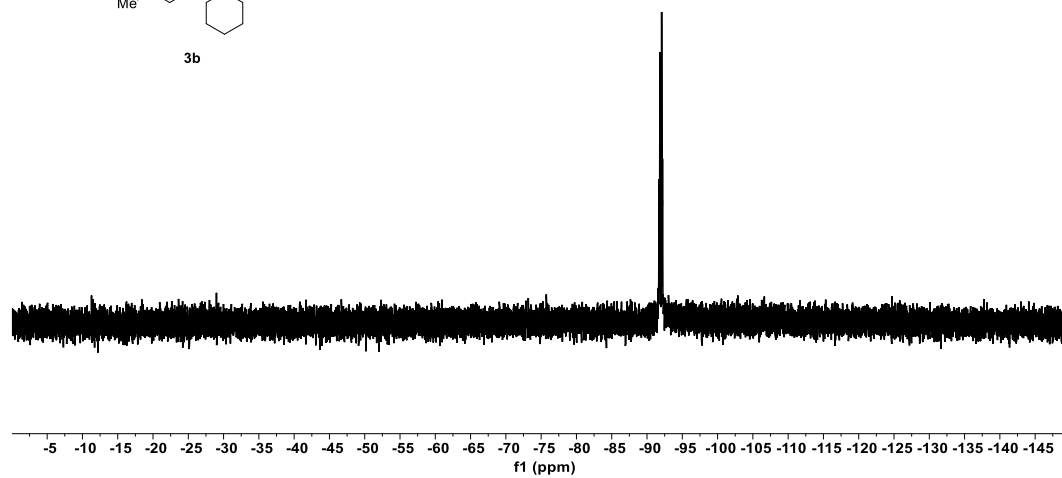


^{19}F NMR (376 MHz, CDCl_3)

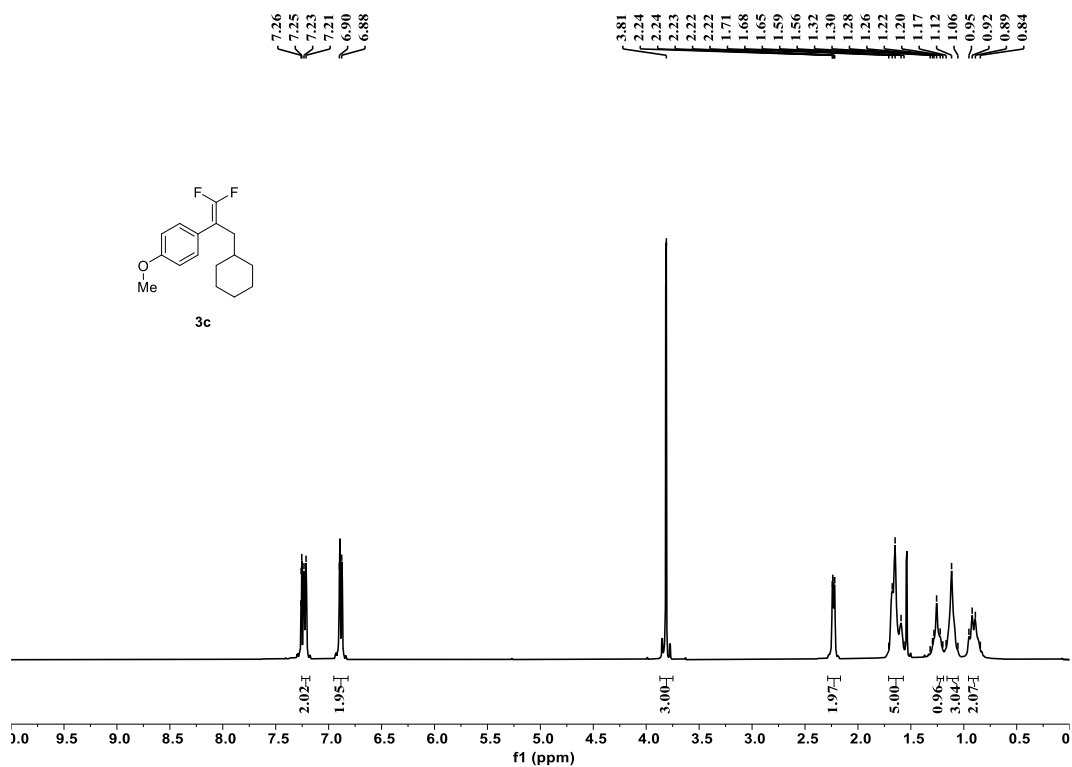
-91.71
-91.83
-92.06
-92.18



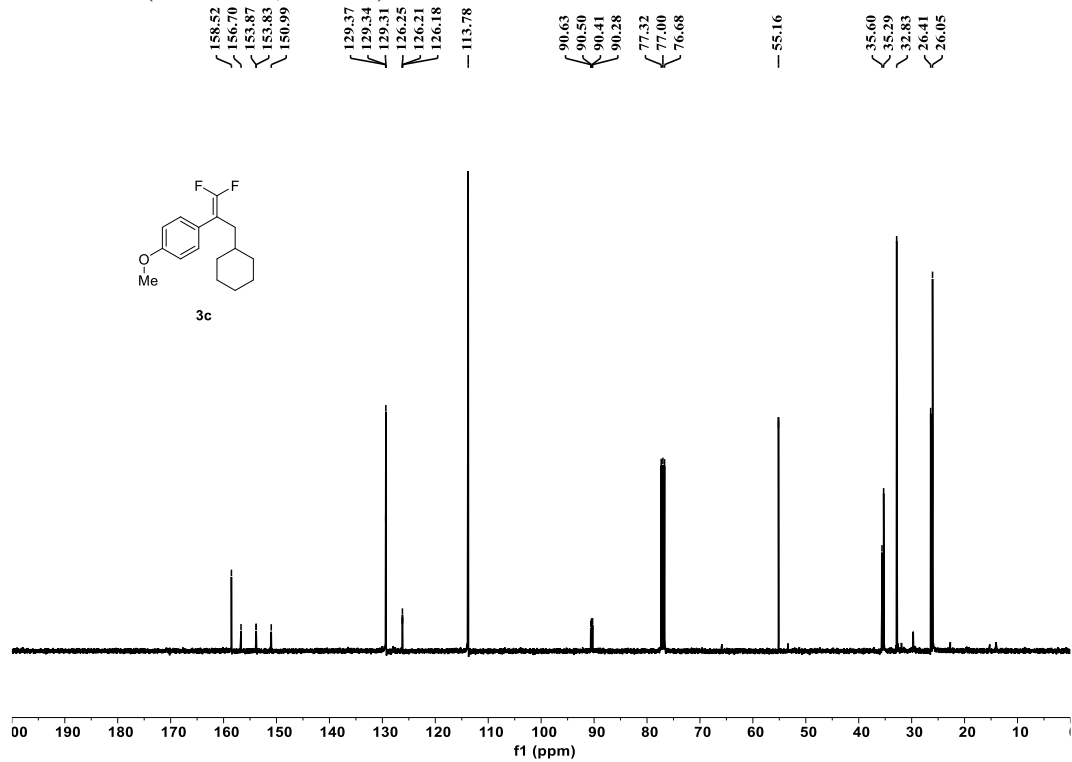
3b



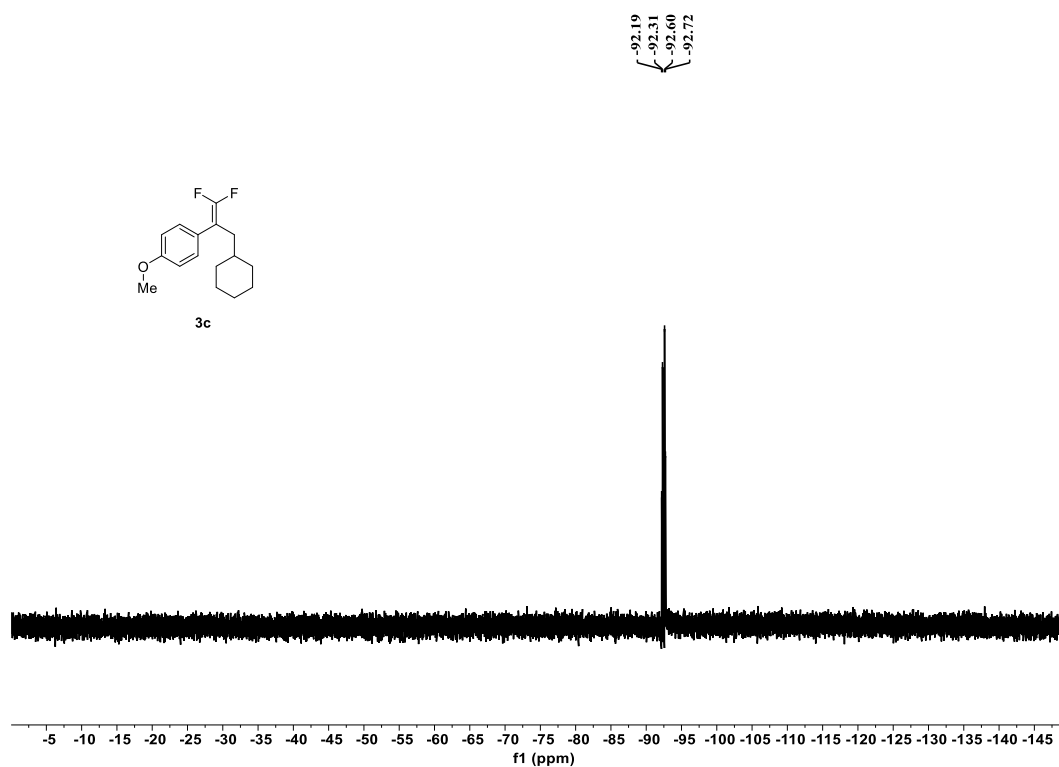
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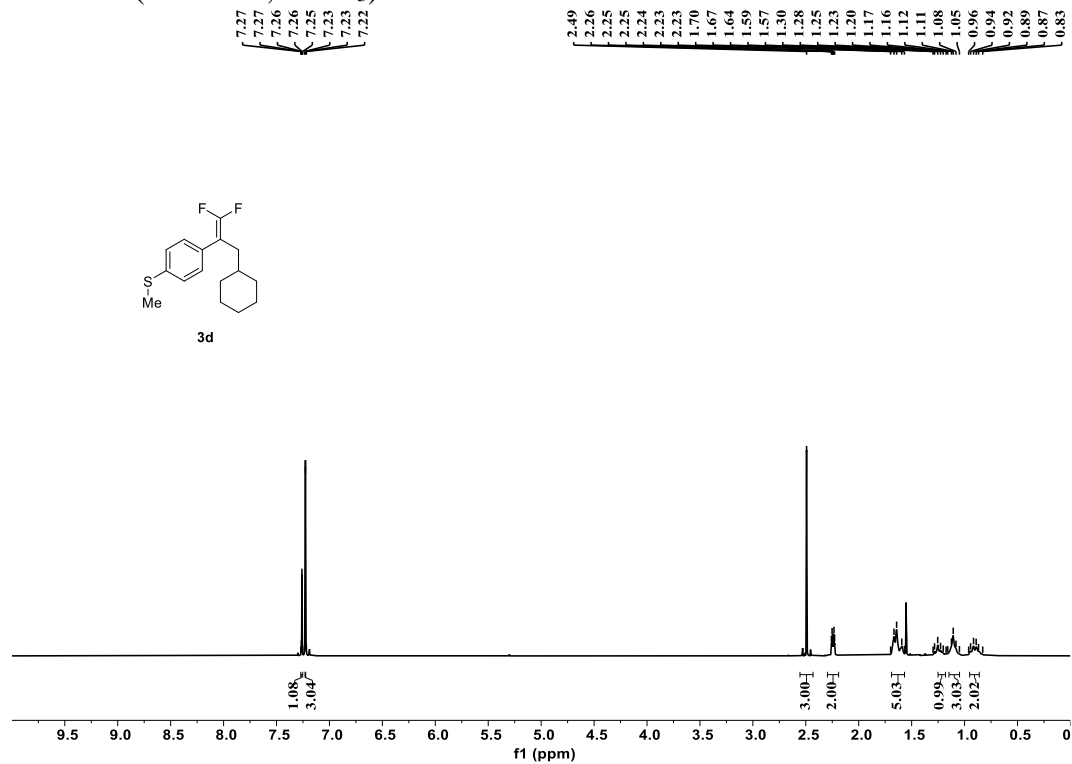
^{13}C NMR (100 MHz, CDCl_3)



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



^1H NMR (400 MHz, CDCl_3)

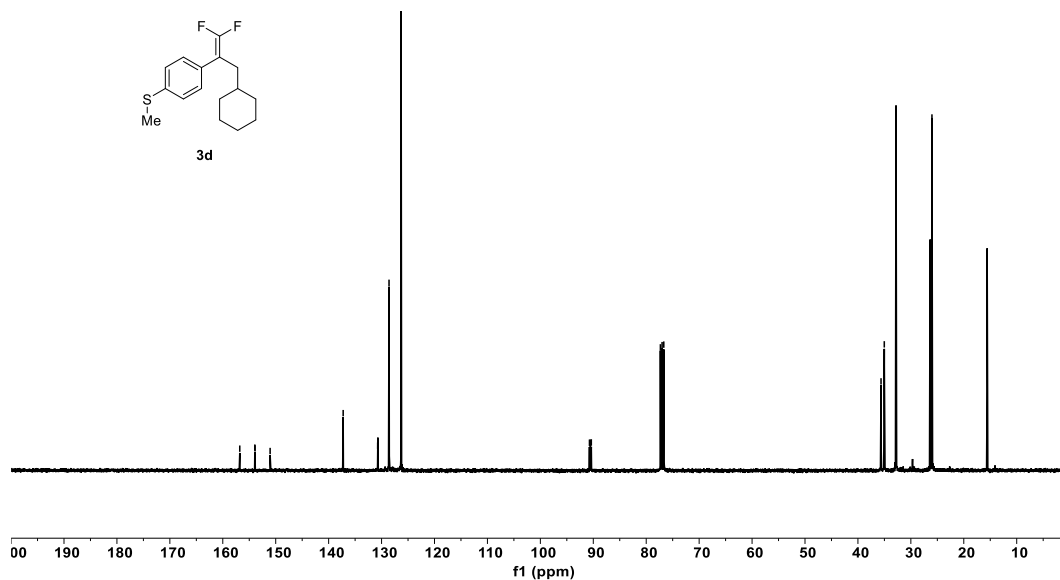
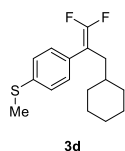


¹³C NMR (100 MHz, CDCl₃)

156.79
153.94
153.90
151.06
137.26
130.73
130.69
130.66
128.62
128.59
128.56
126.31

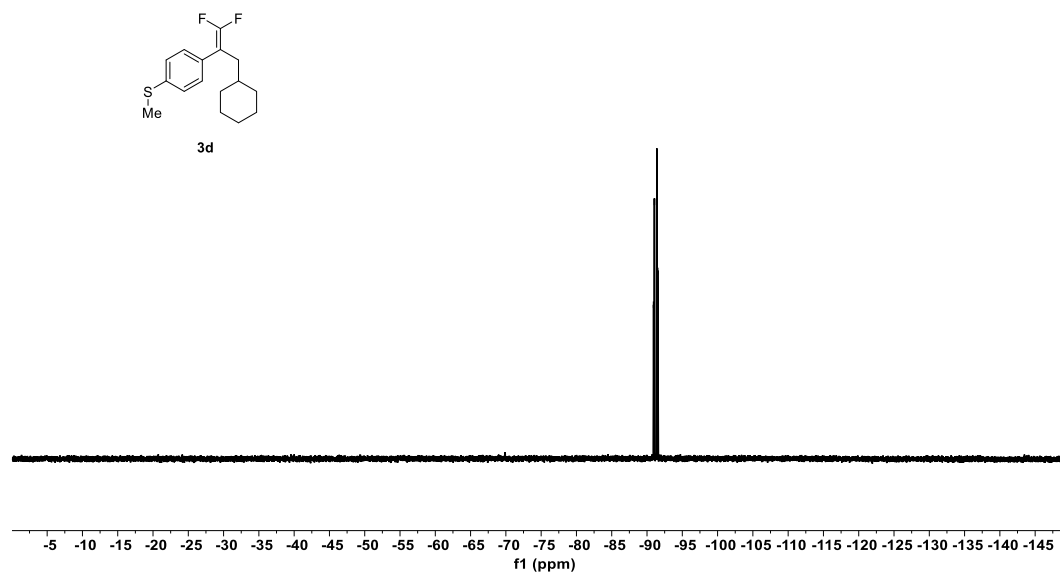
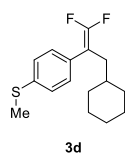
90.72
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90.37
77.32
77.00
76.68

35.64
35.02
32.81
26.36
26.02
15.58

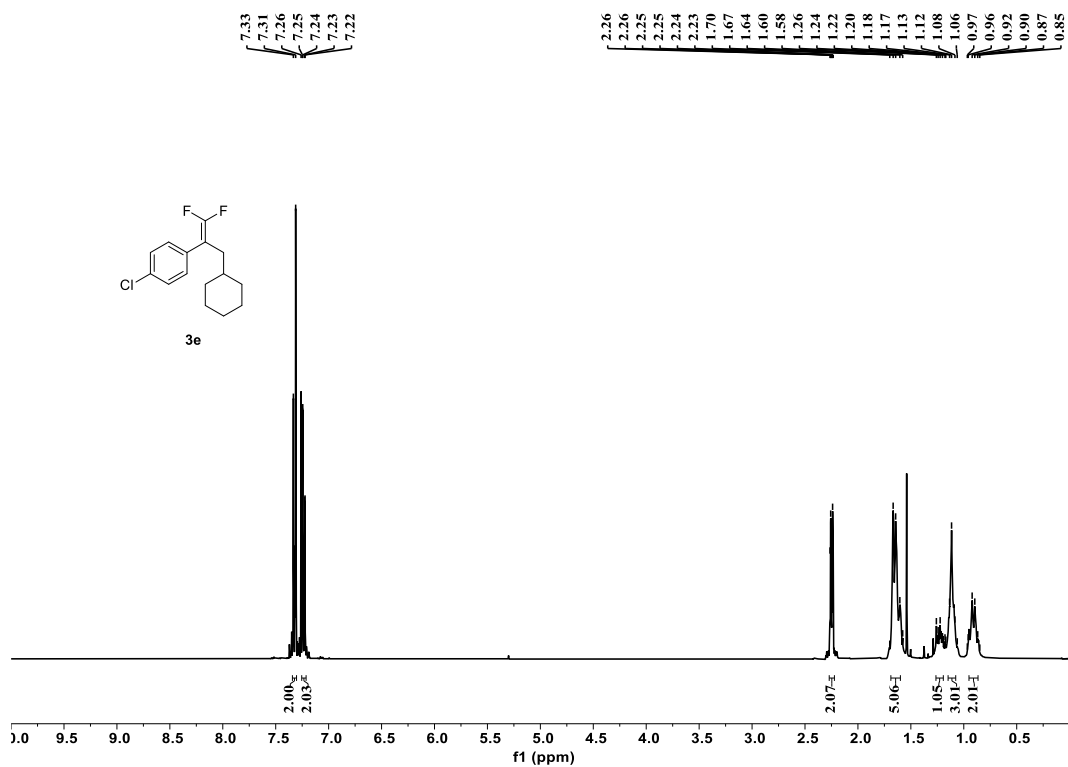


¹⁹F NMR (376 MHz, CDCl₃)

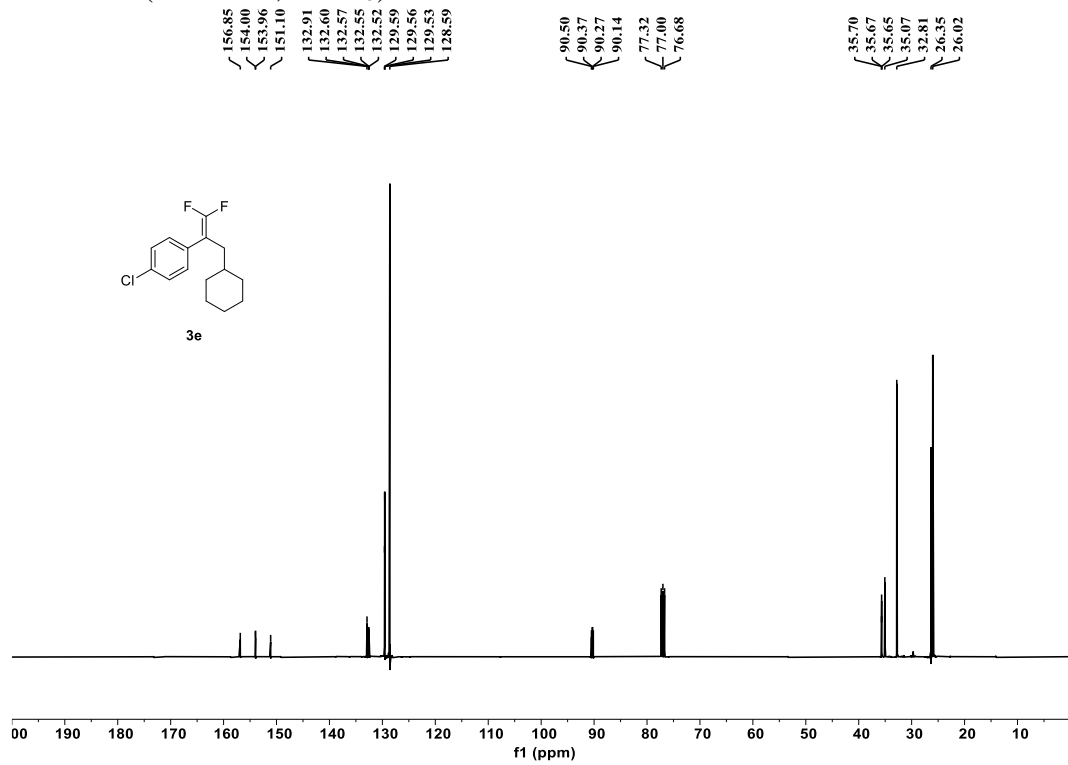
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-91.40
-91.52



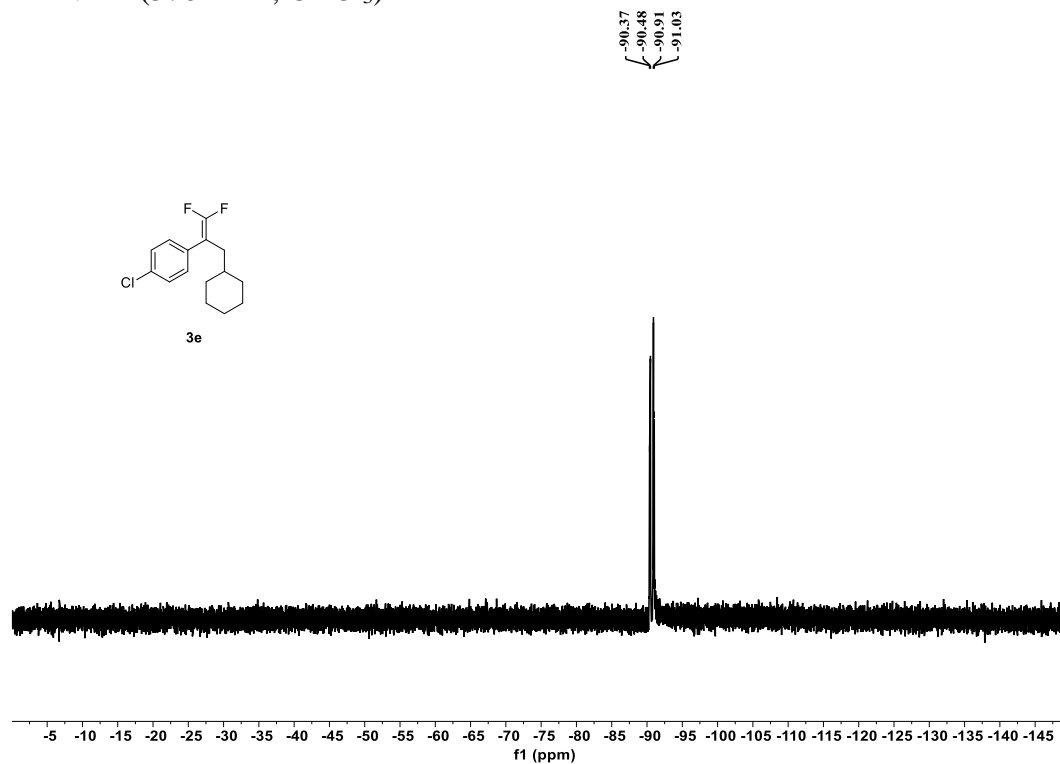
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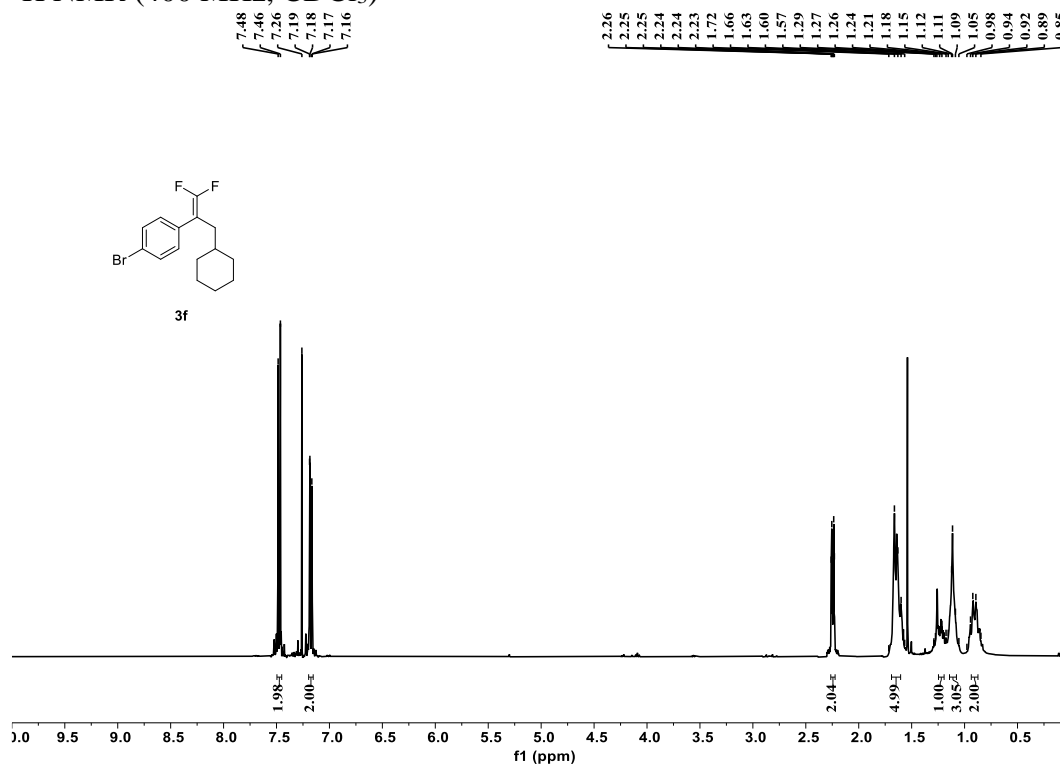
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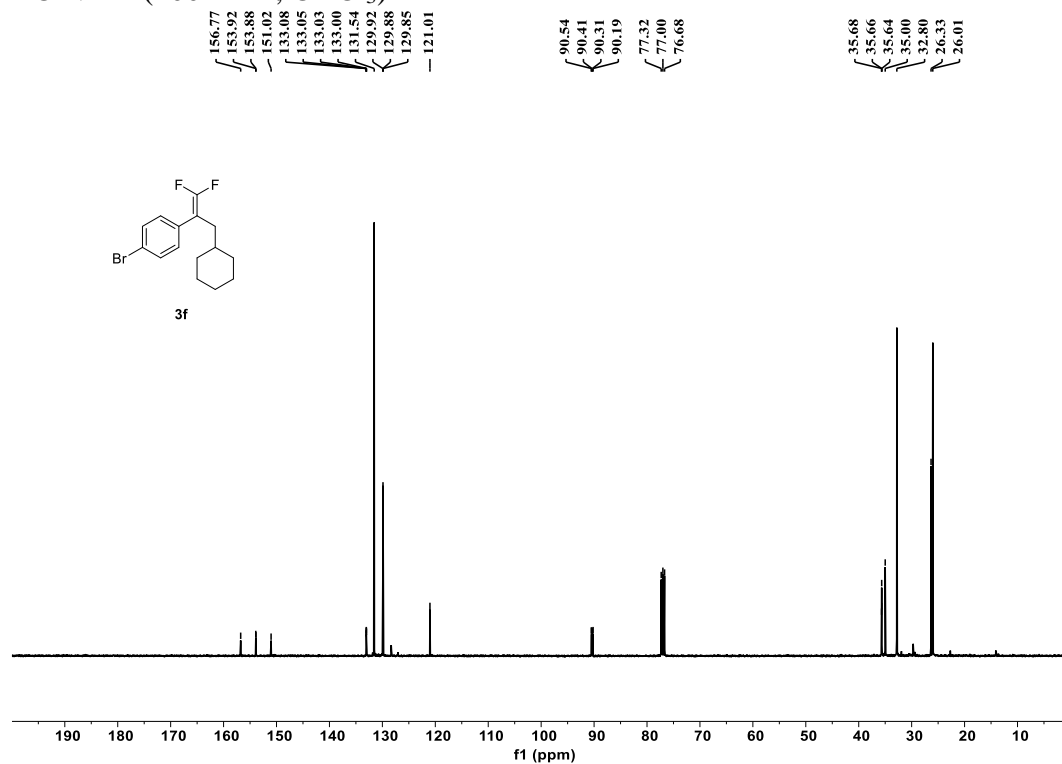
^{19}F NMR (376 MHz, CDCl_3)



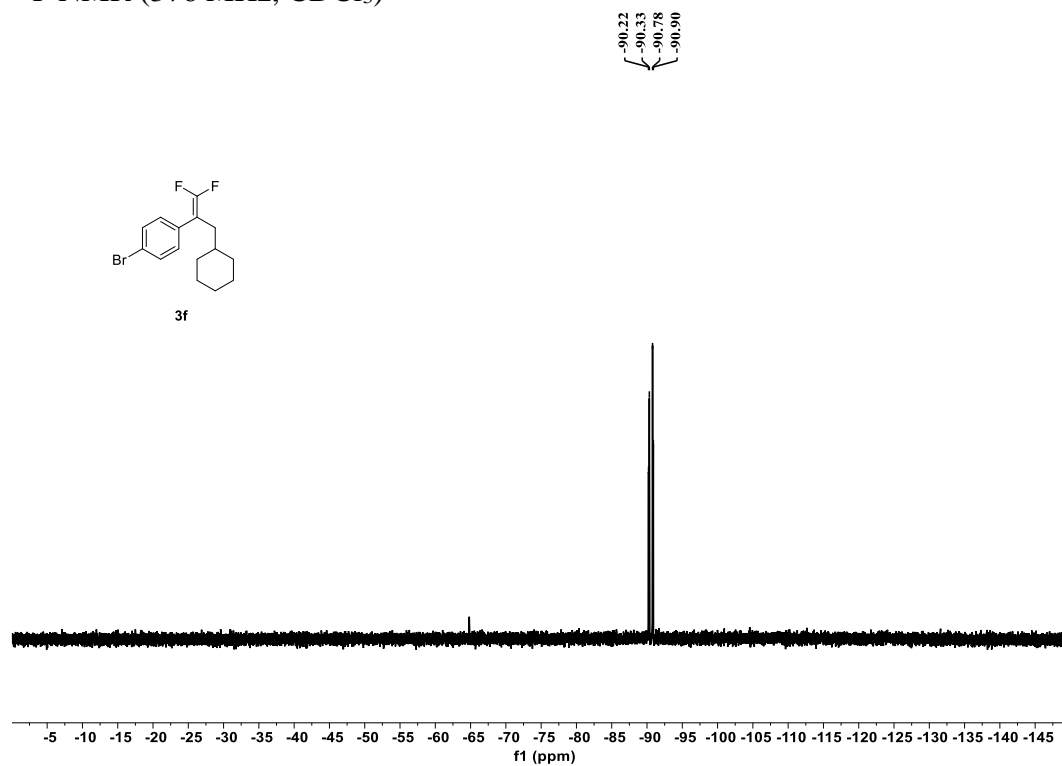
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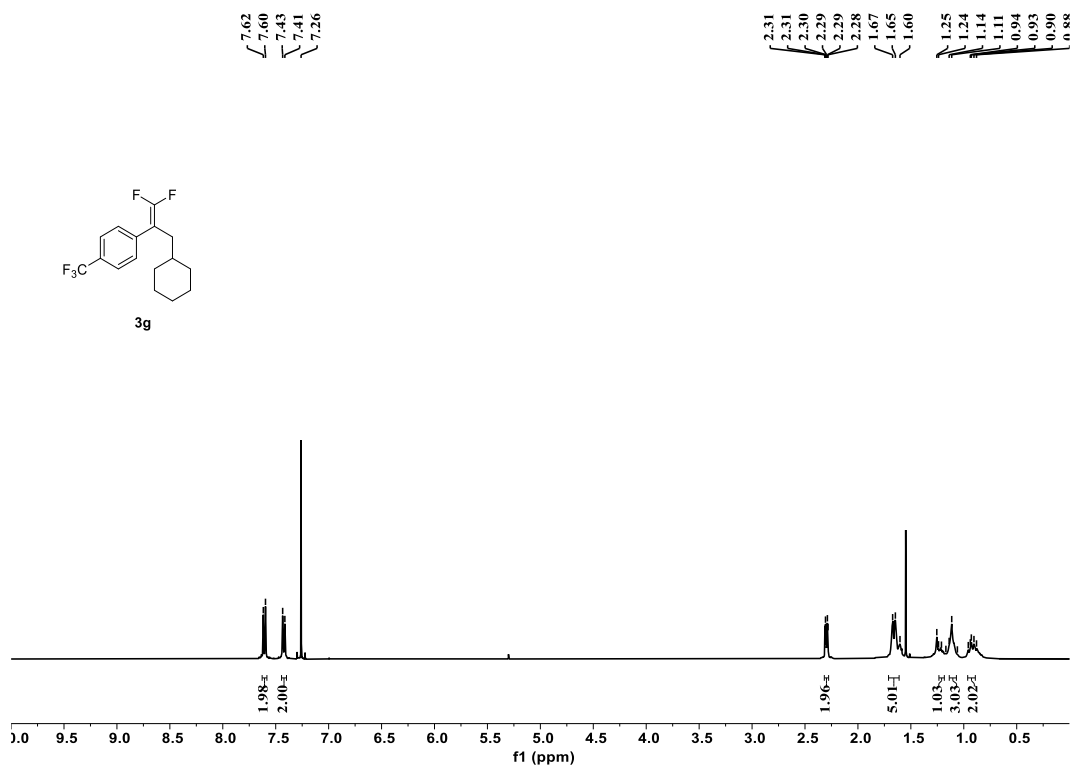
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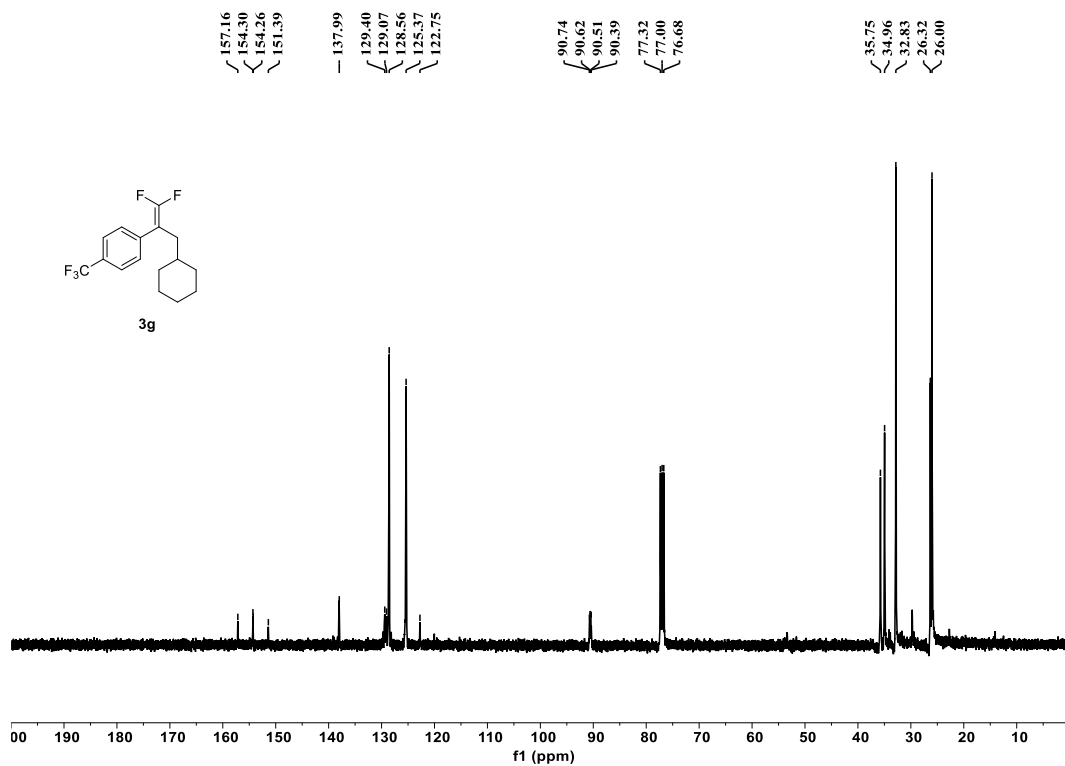
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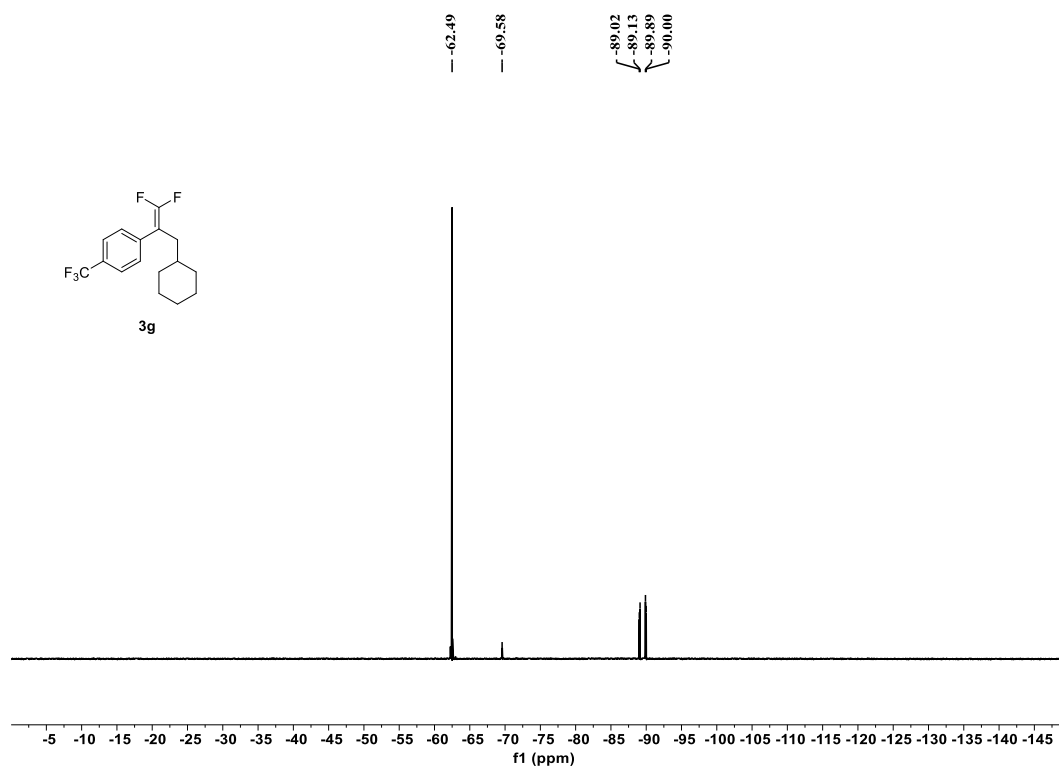
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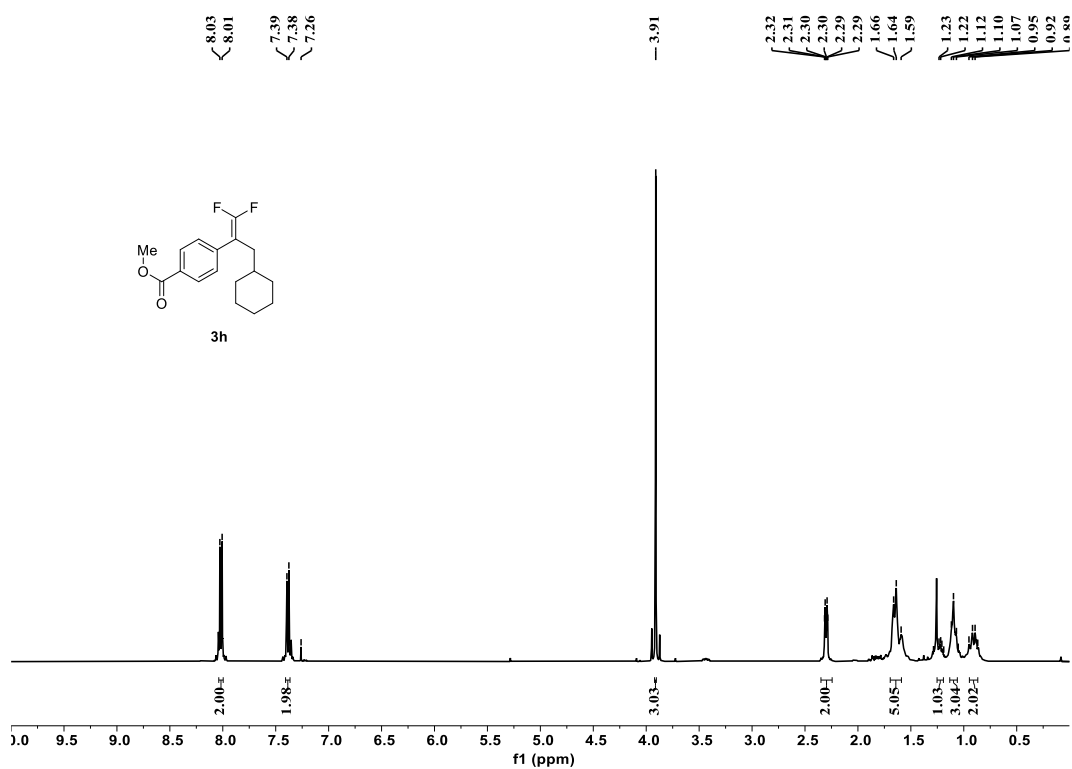
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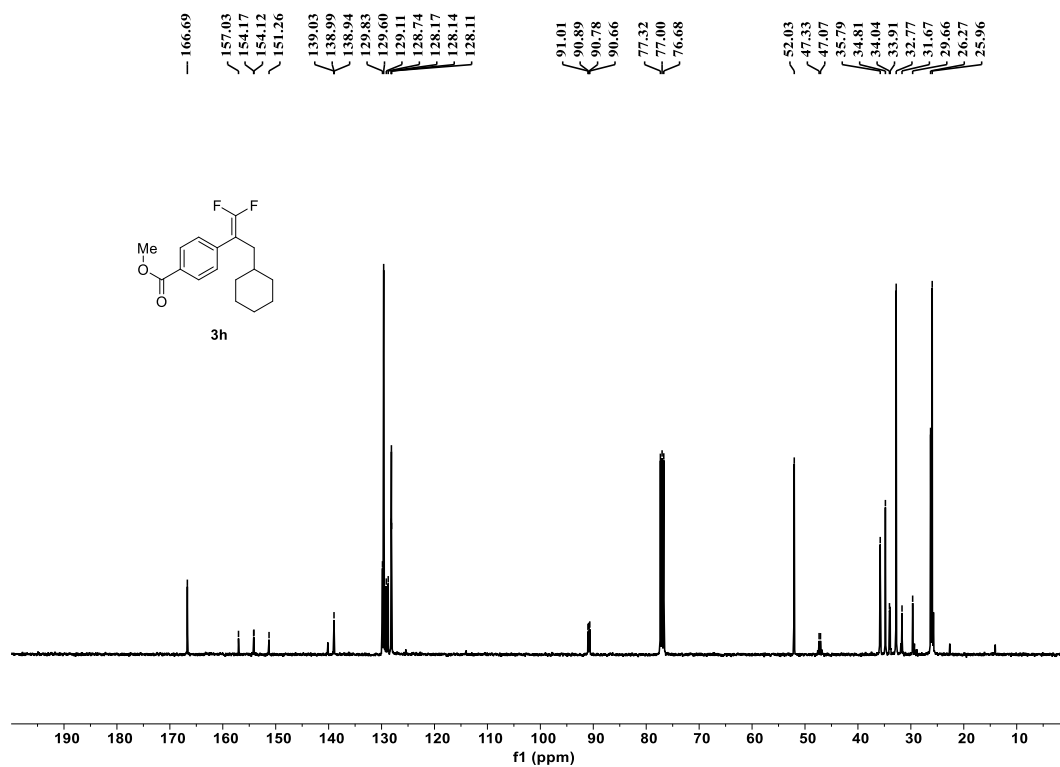
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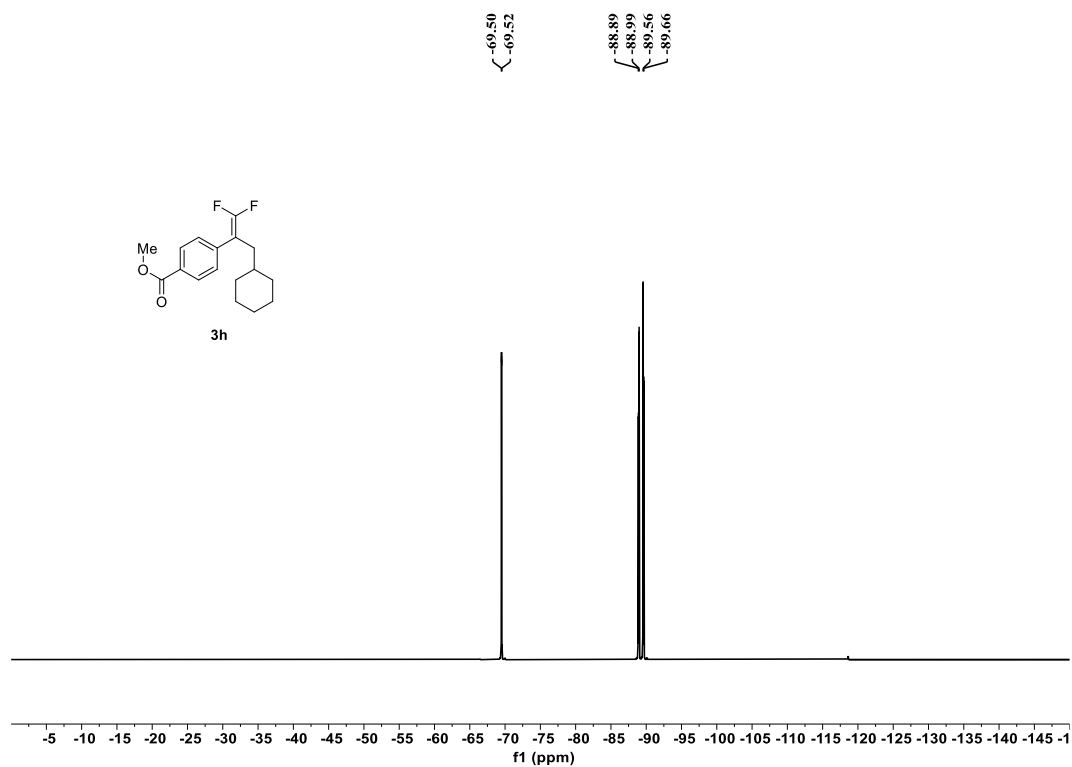
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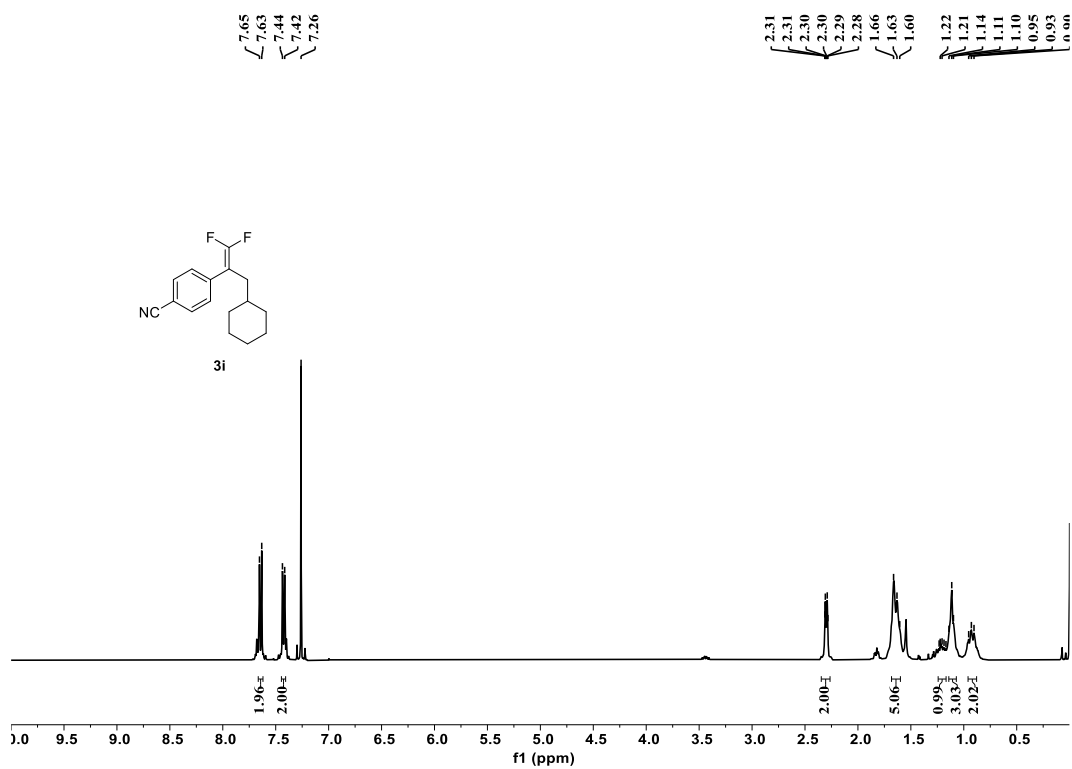
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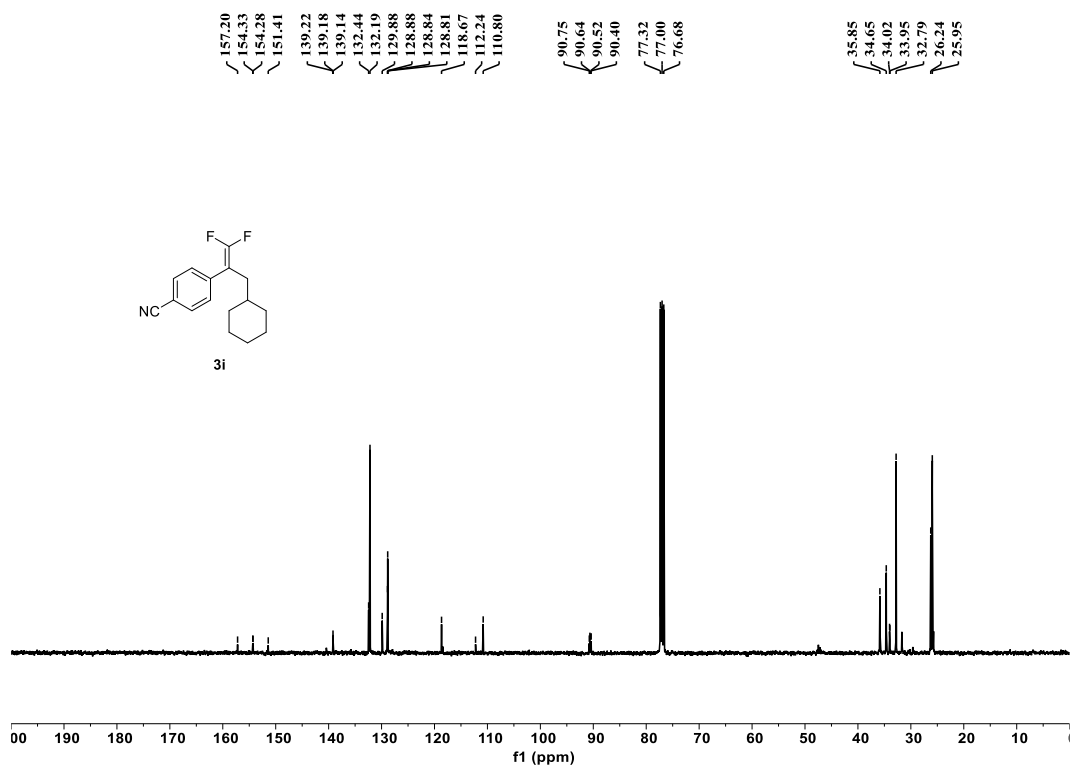
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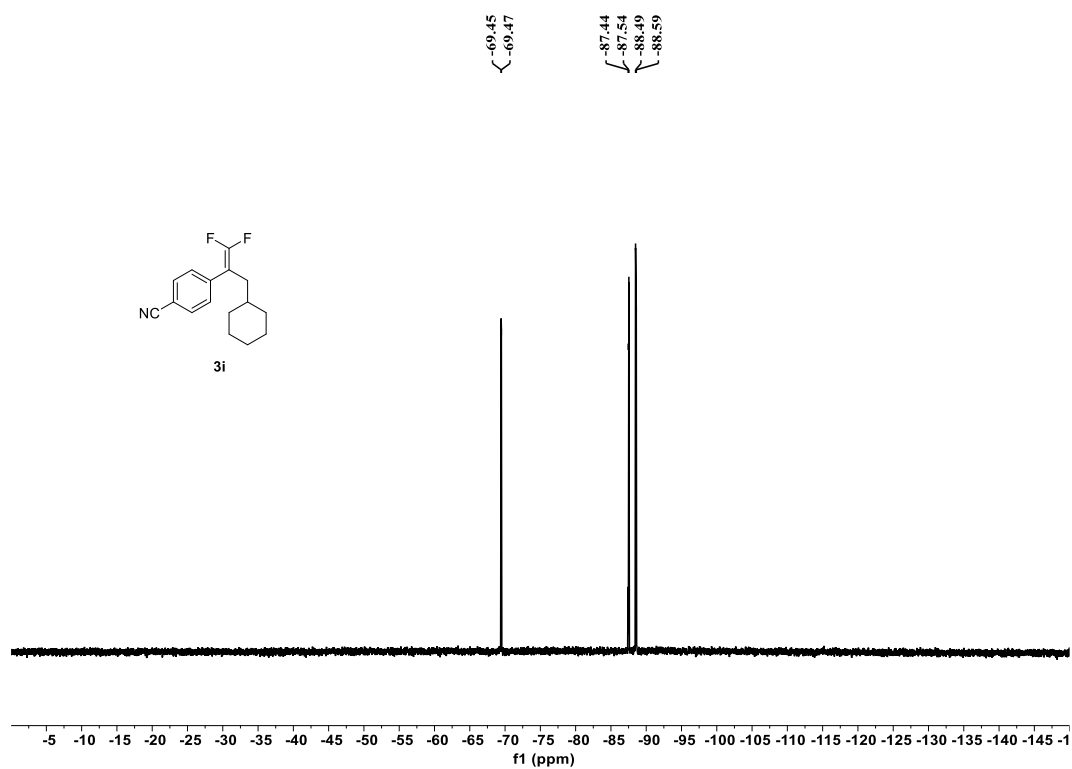
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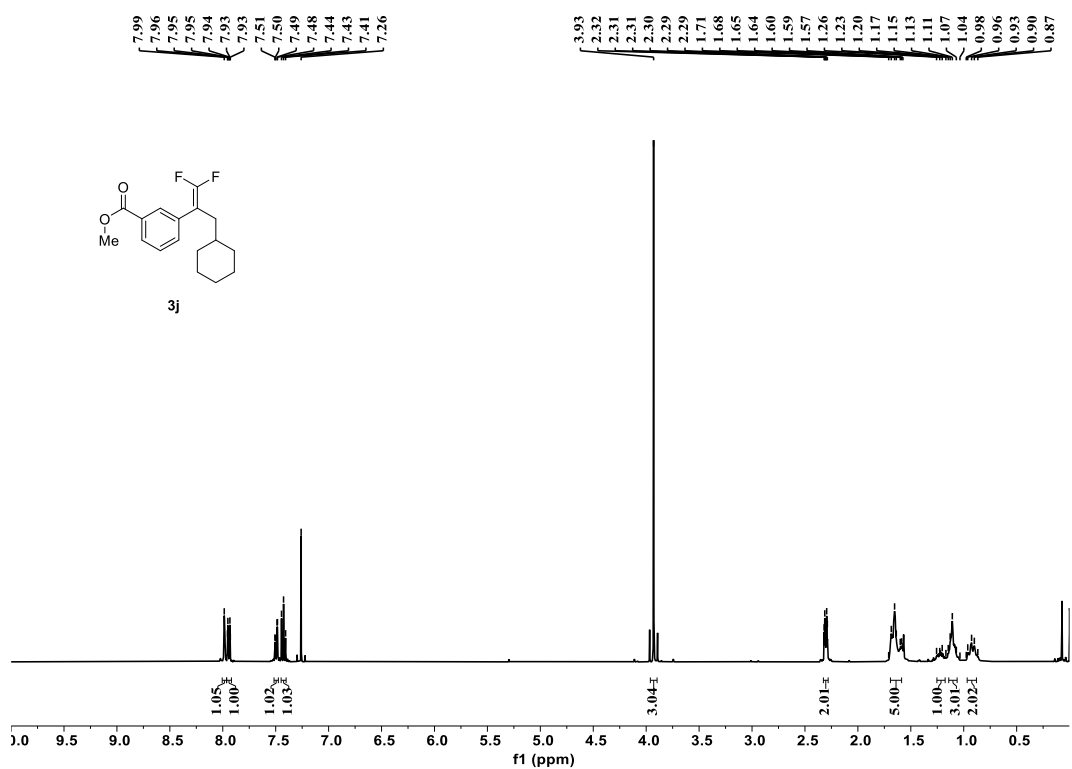
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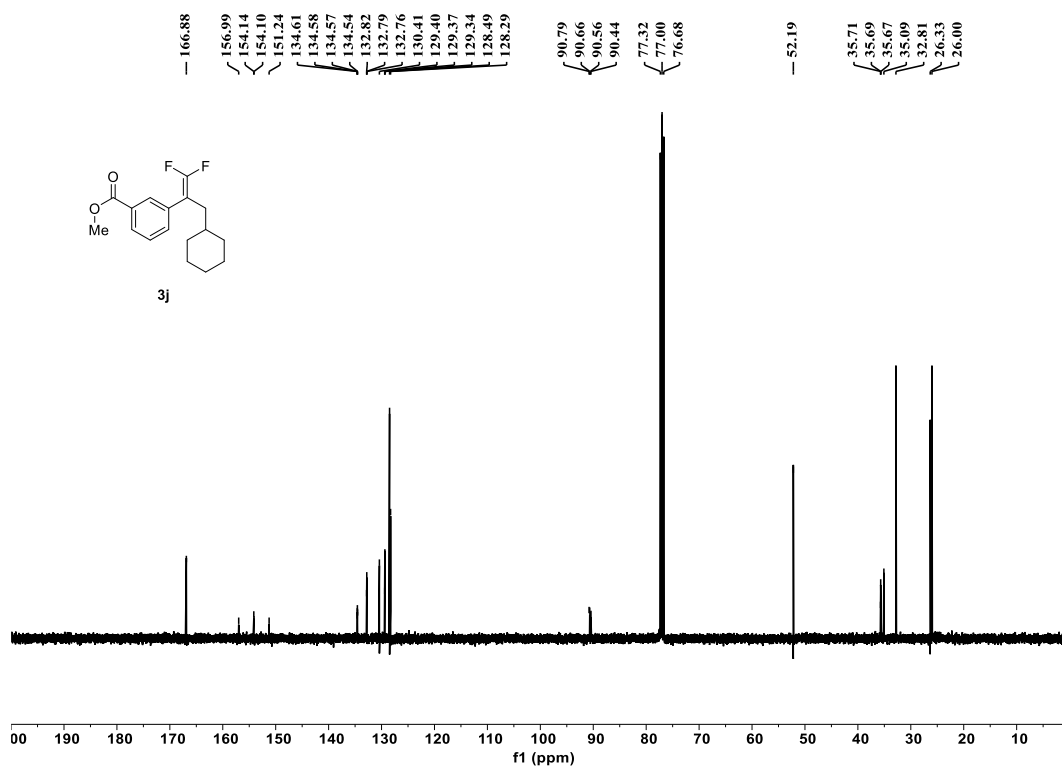
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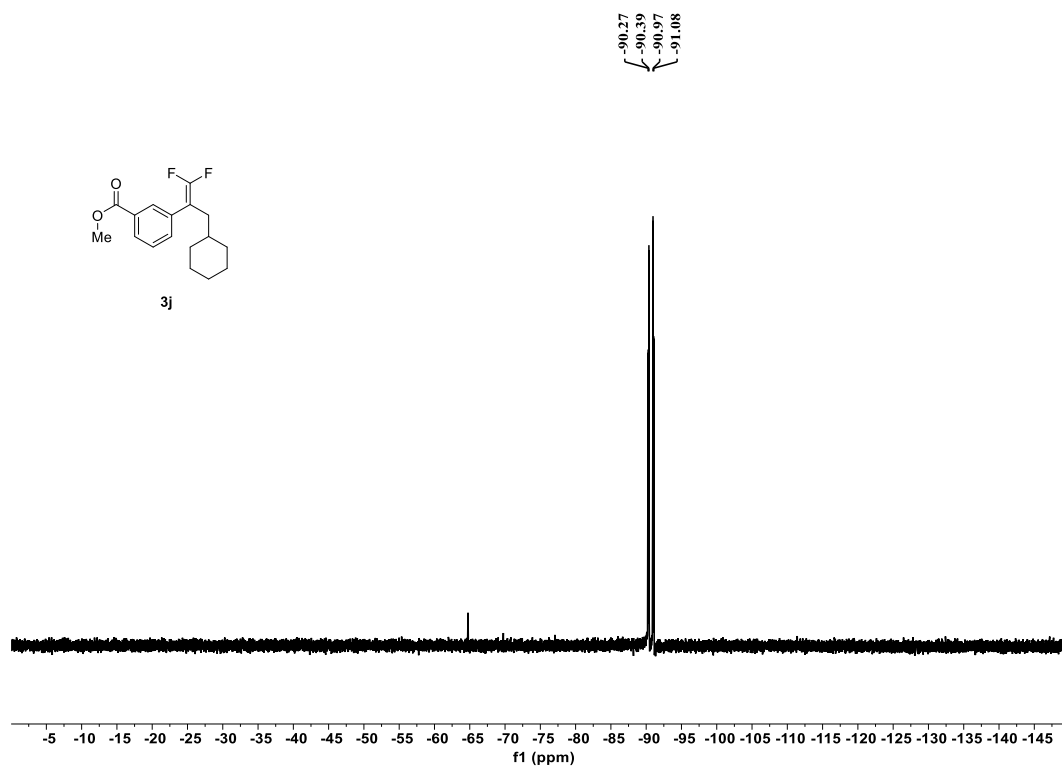
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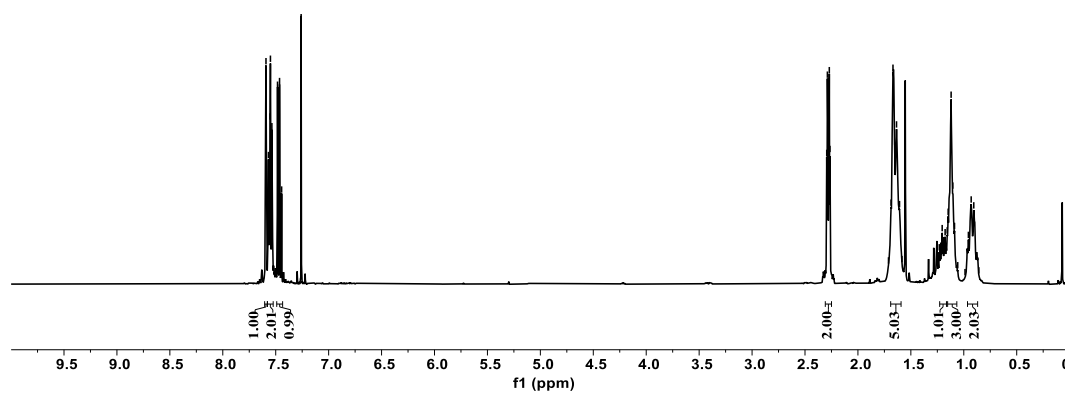
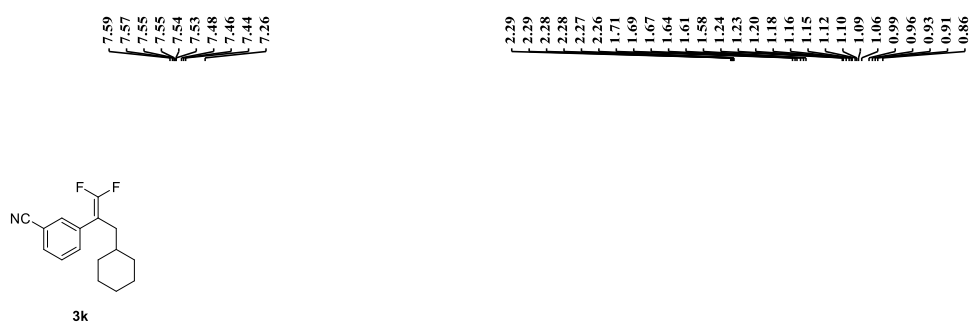
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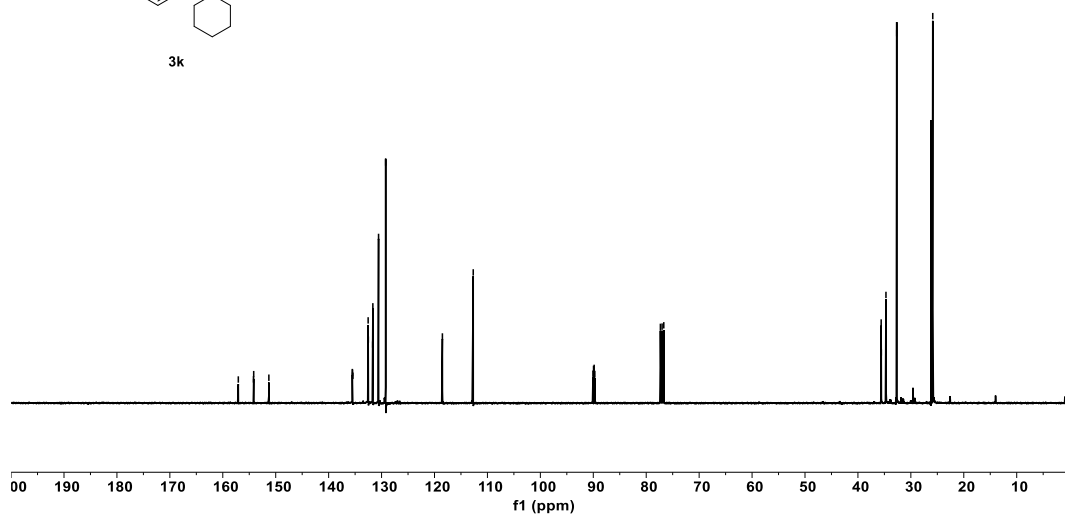
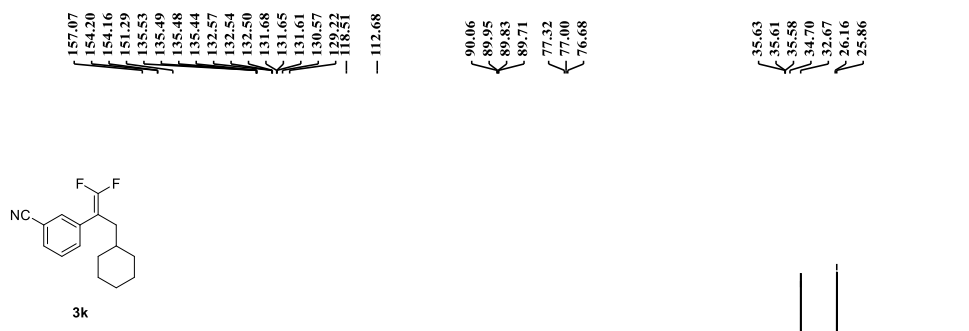
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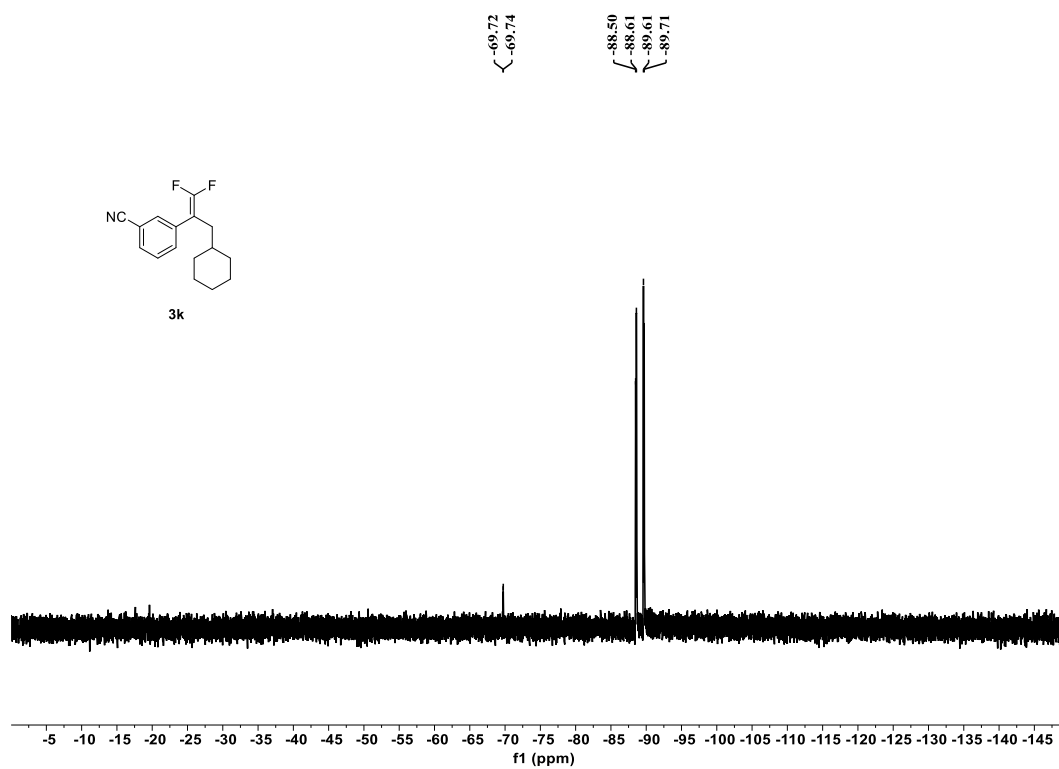
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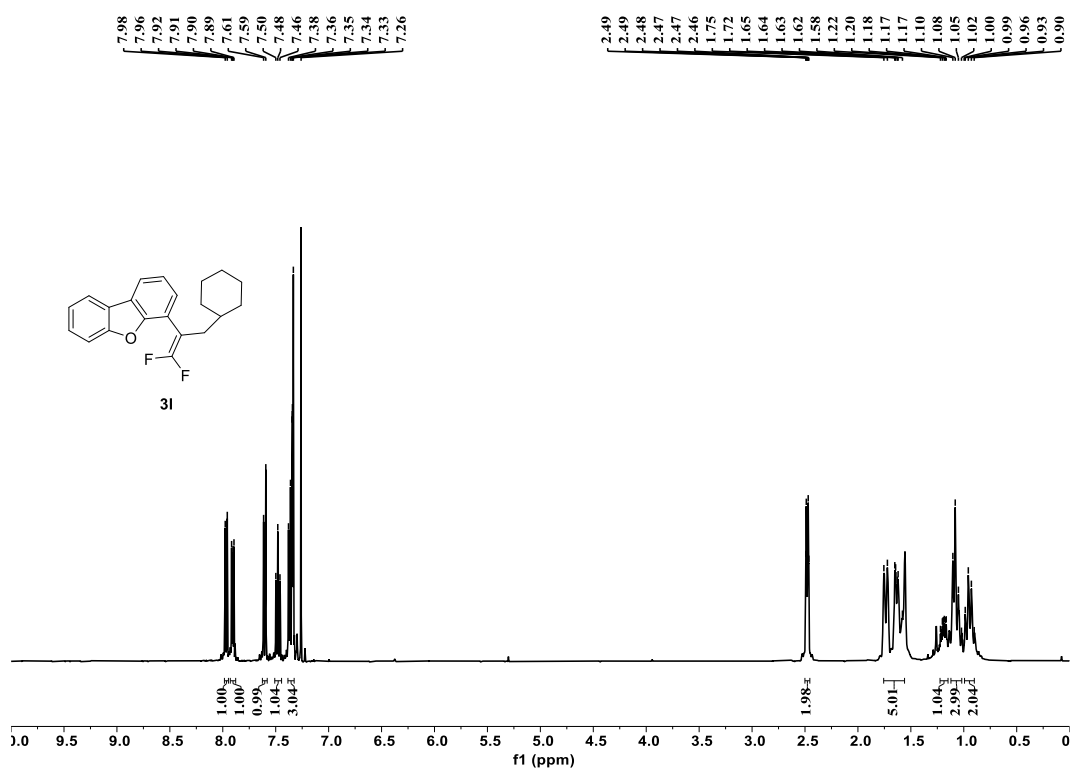
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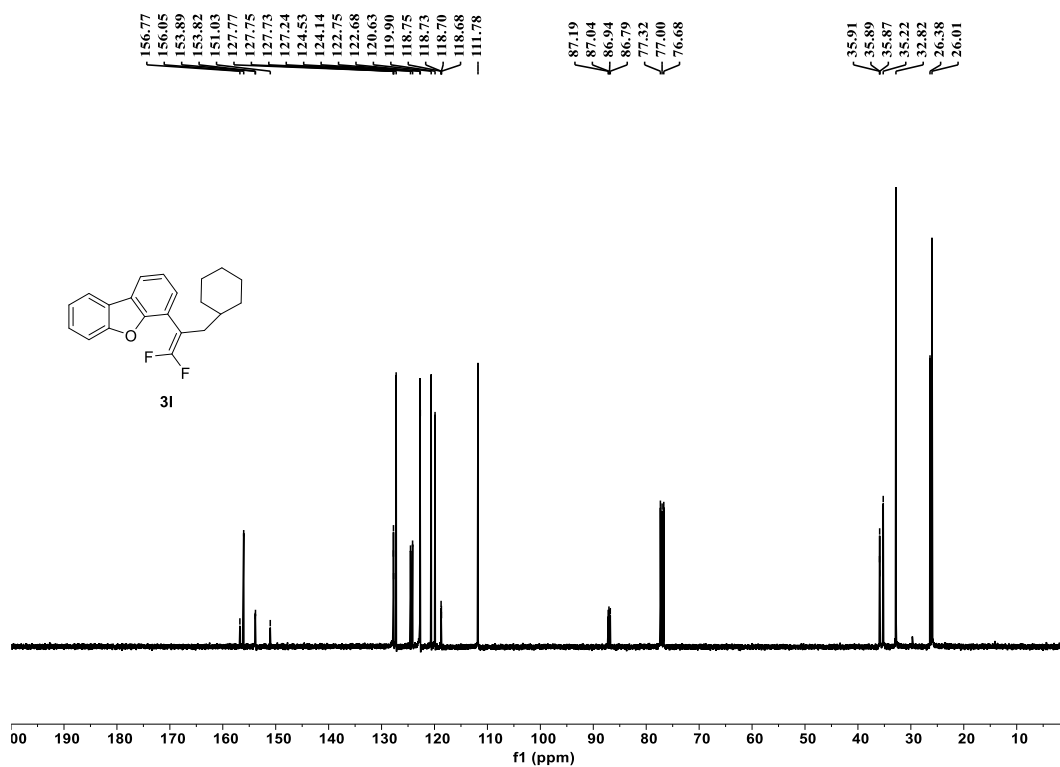
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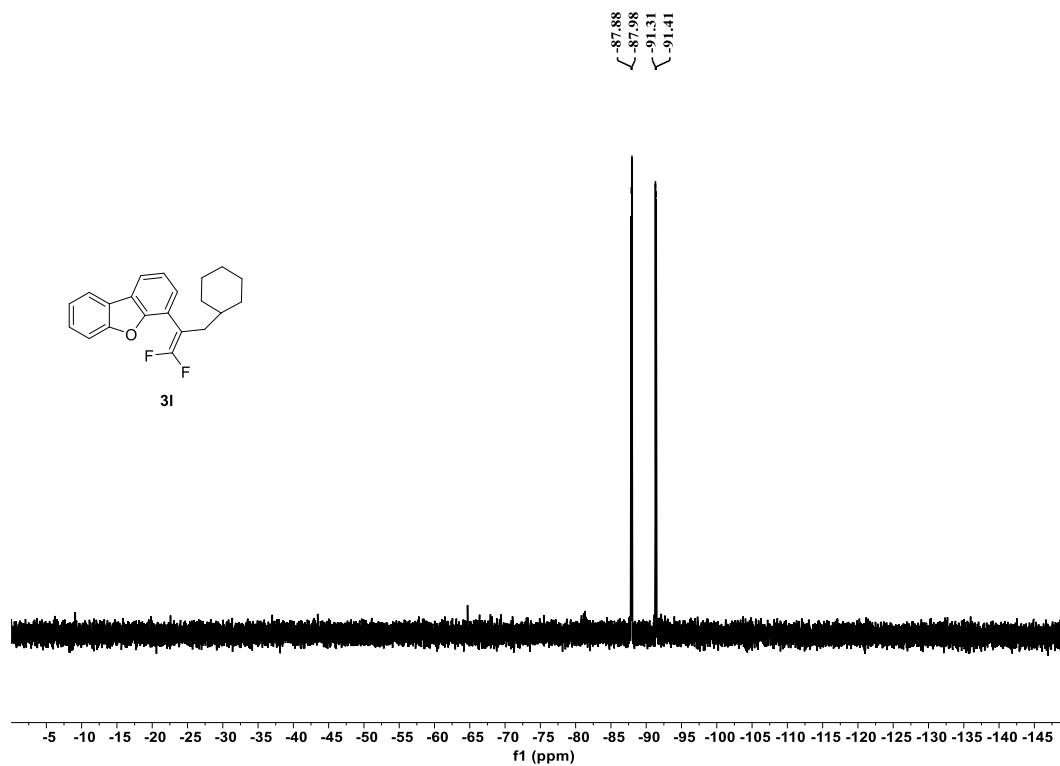
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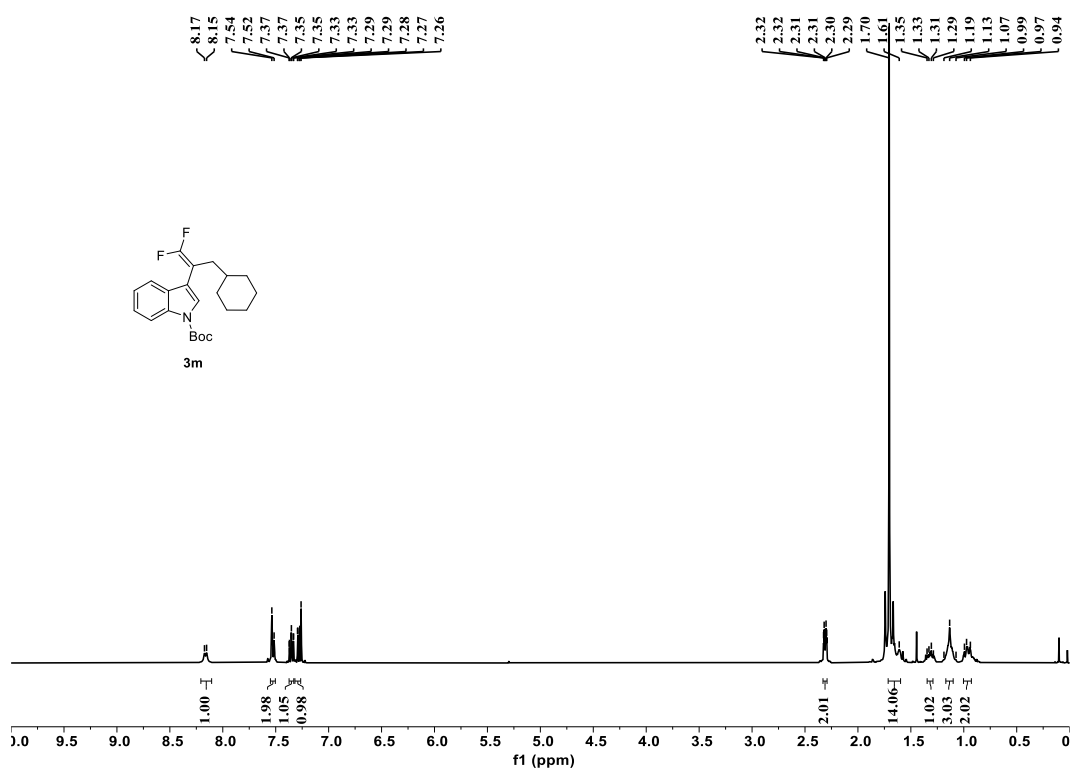
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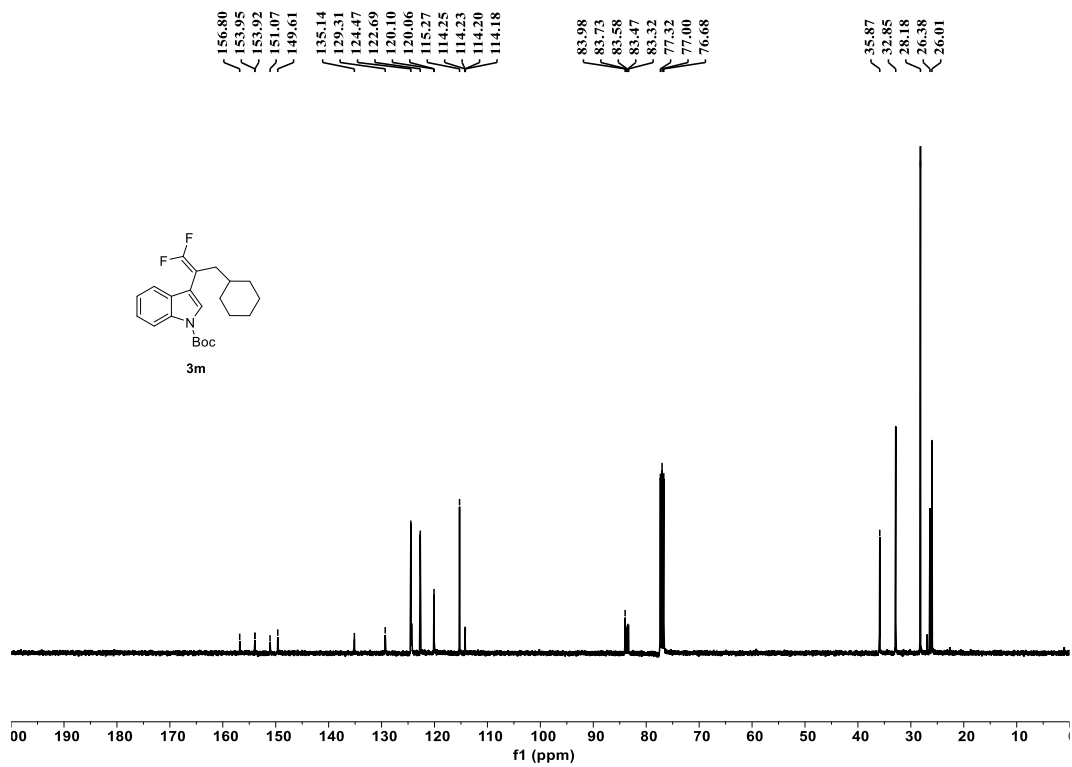
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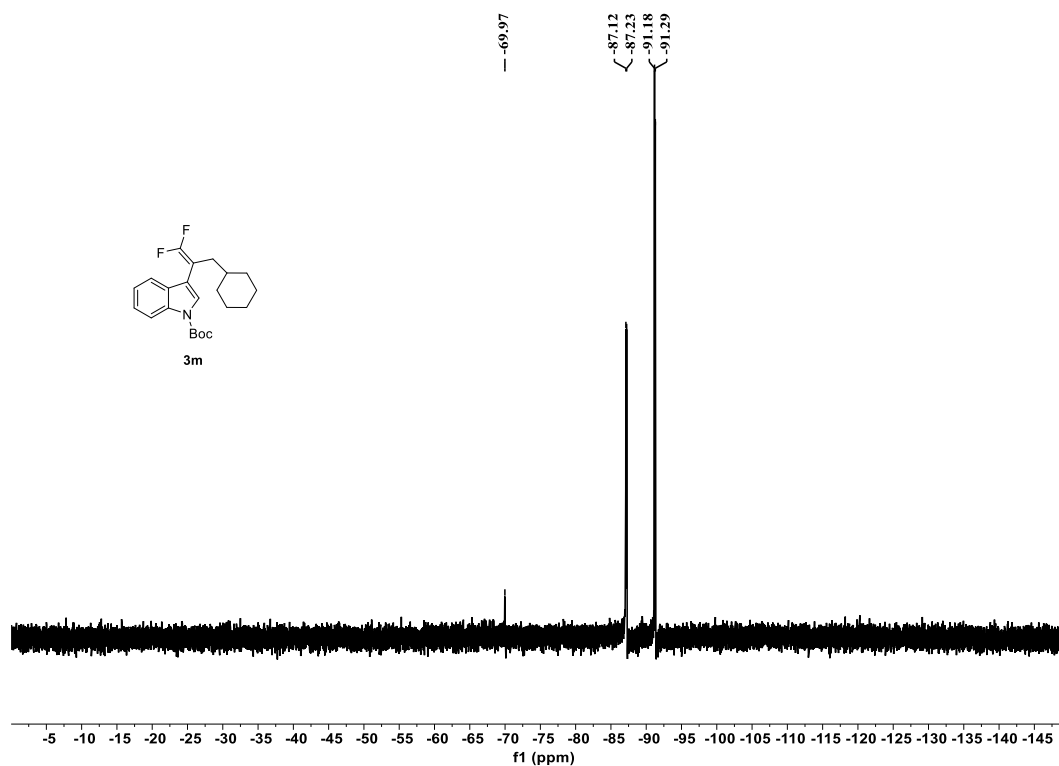
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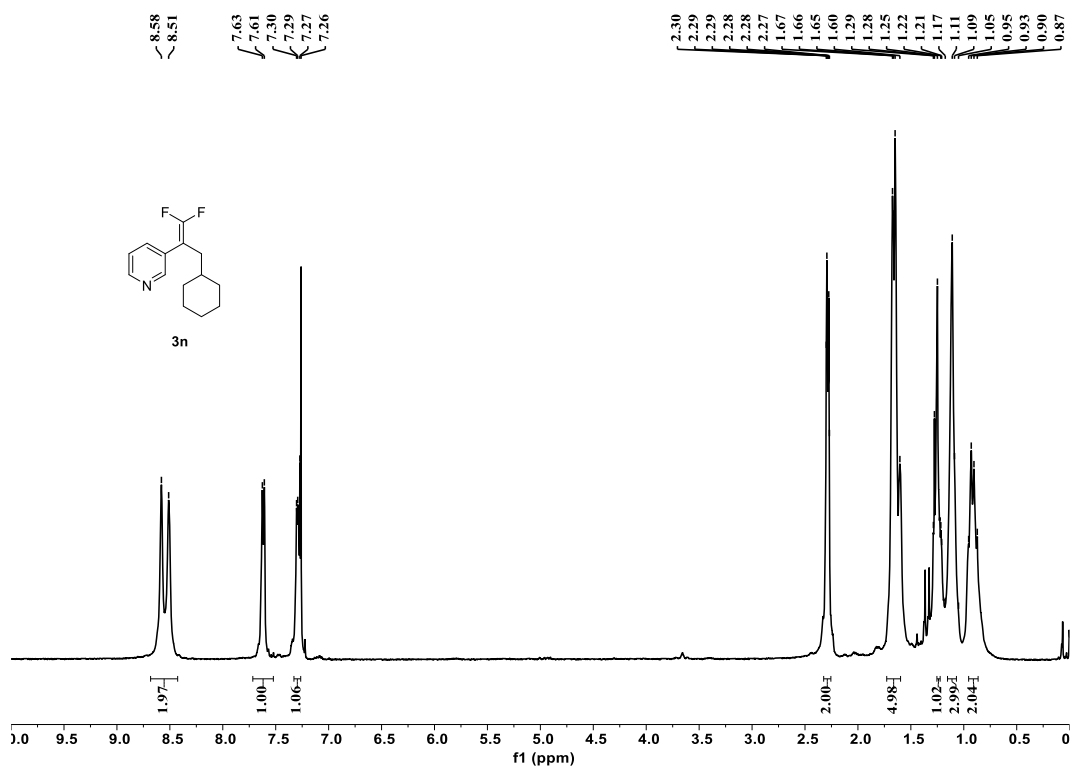
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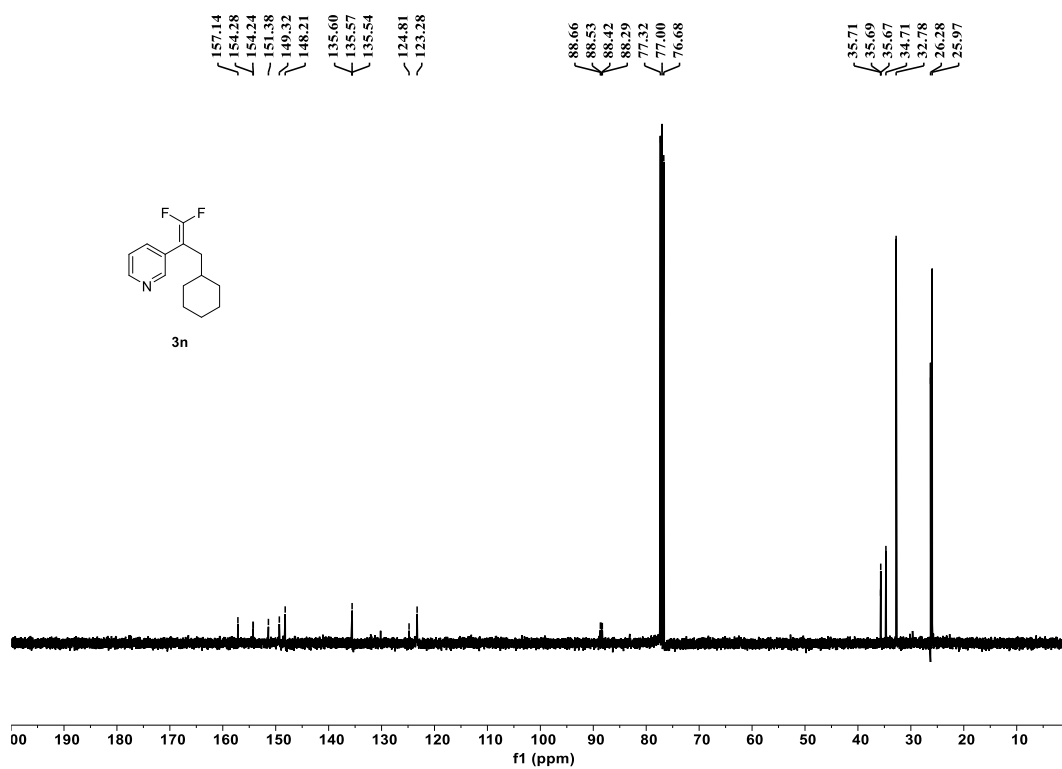
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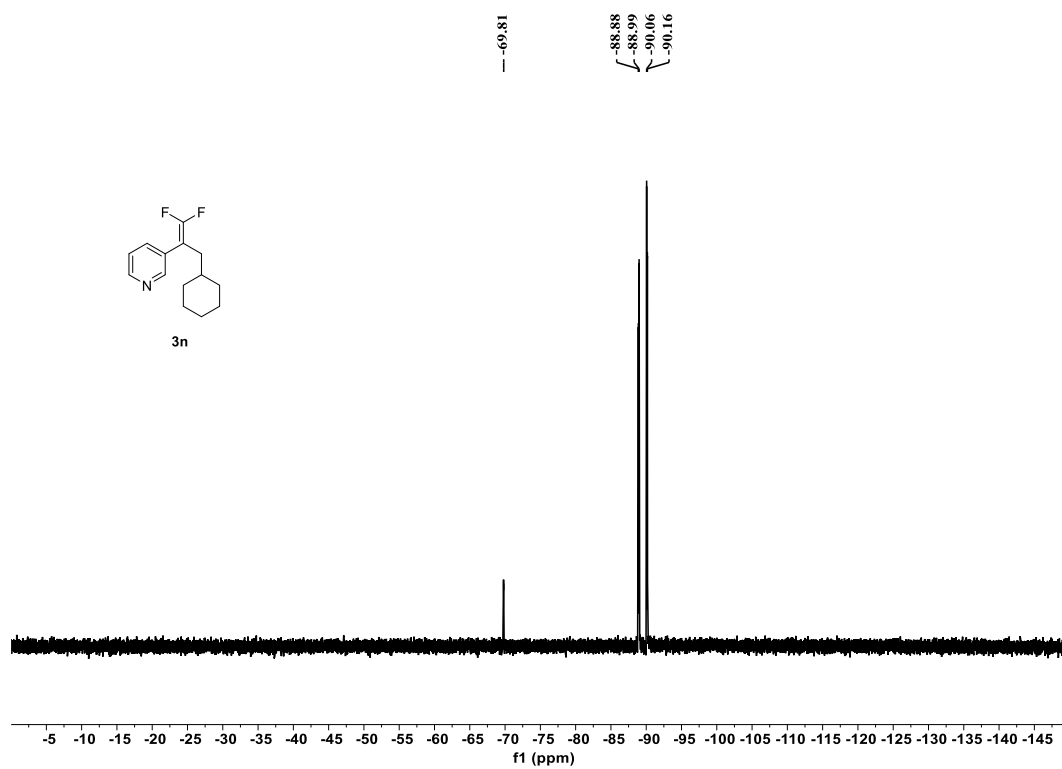
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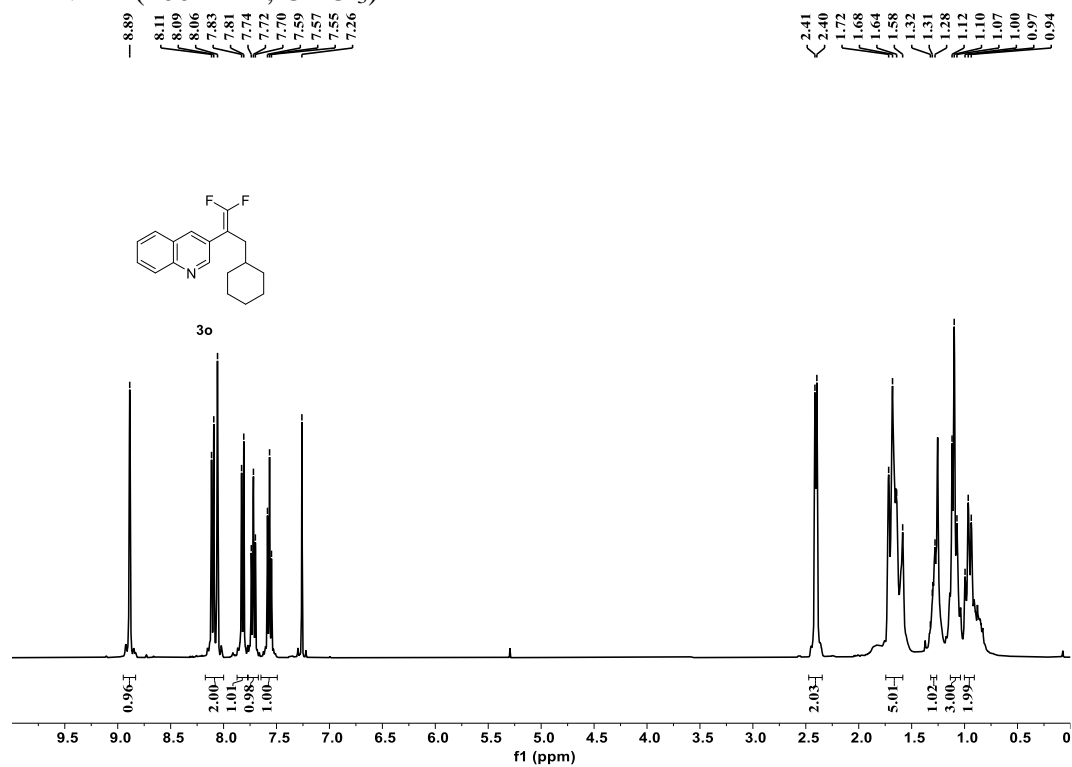
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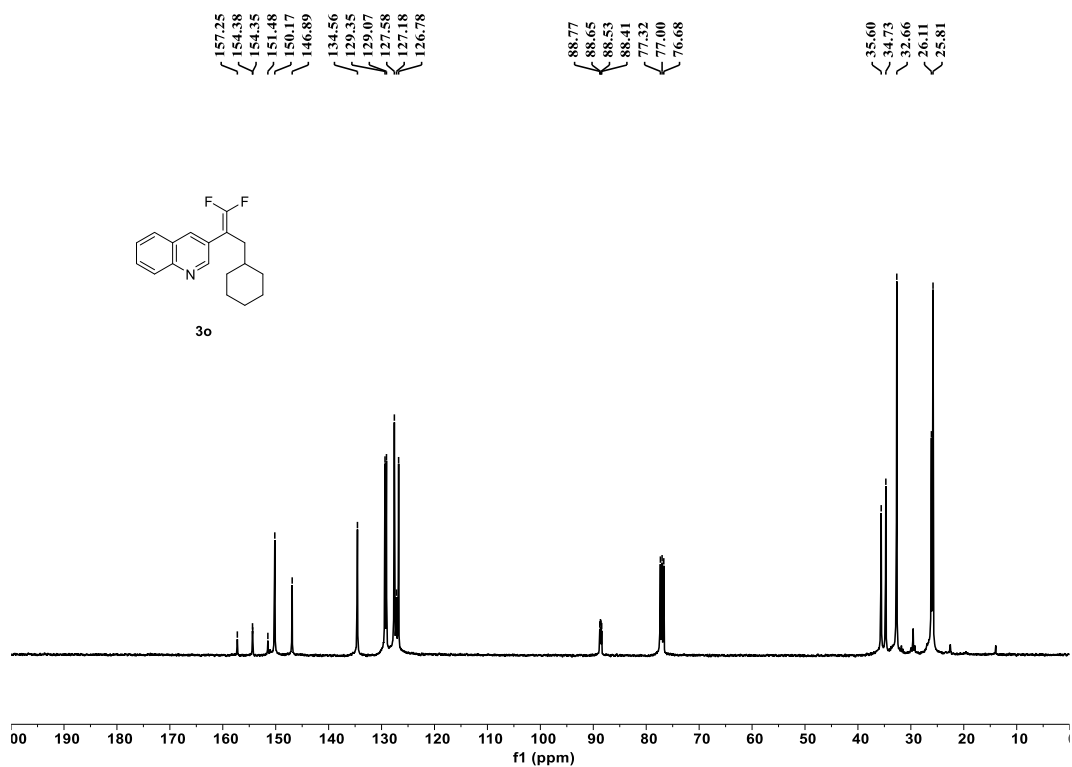
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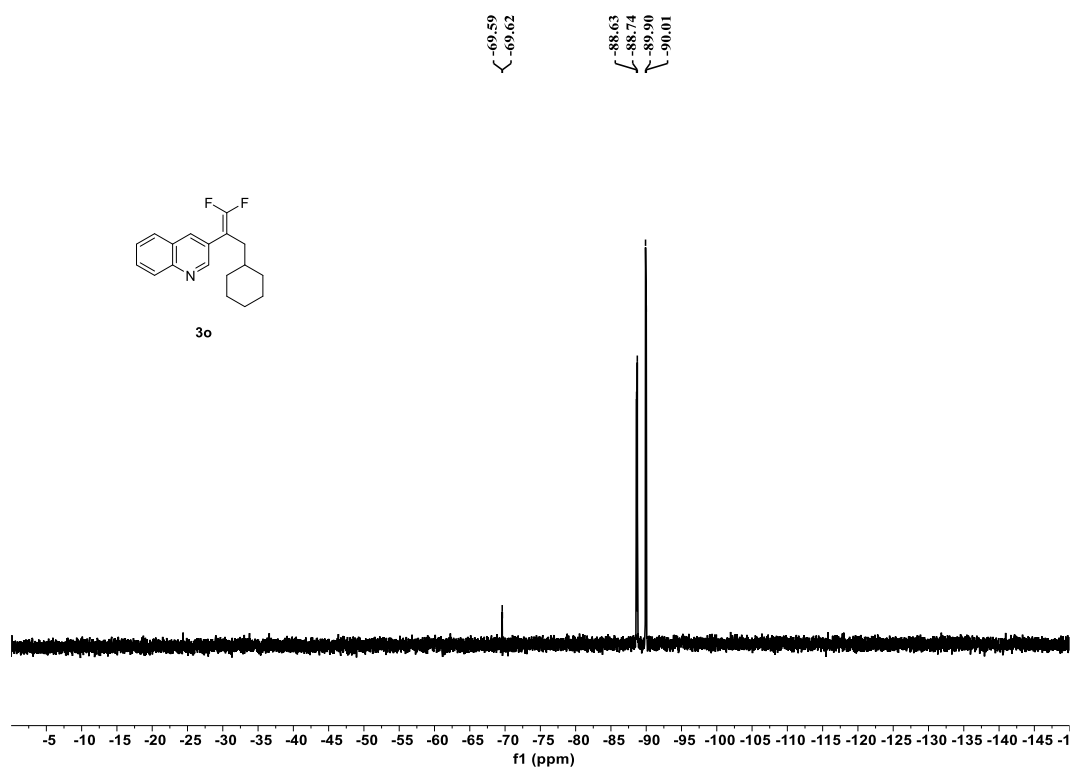
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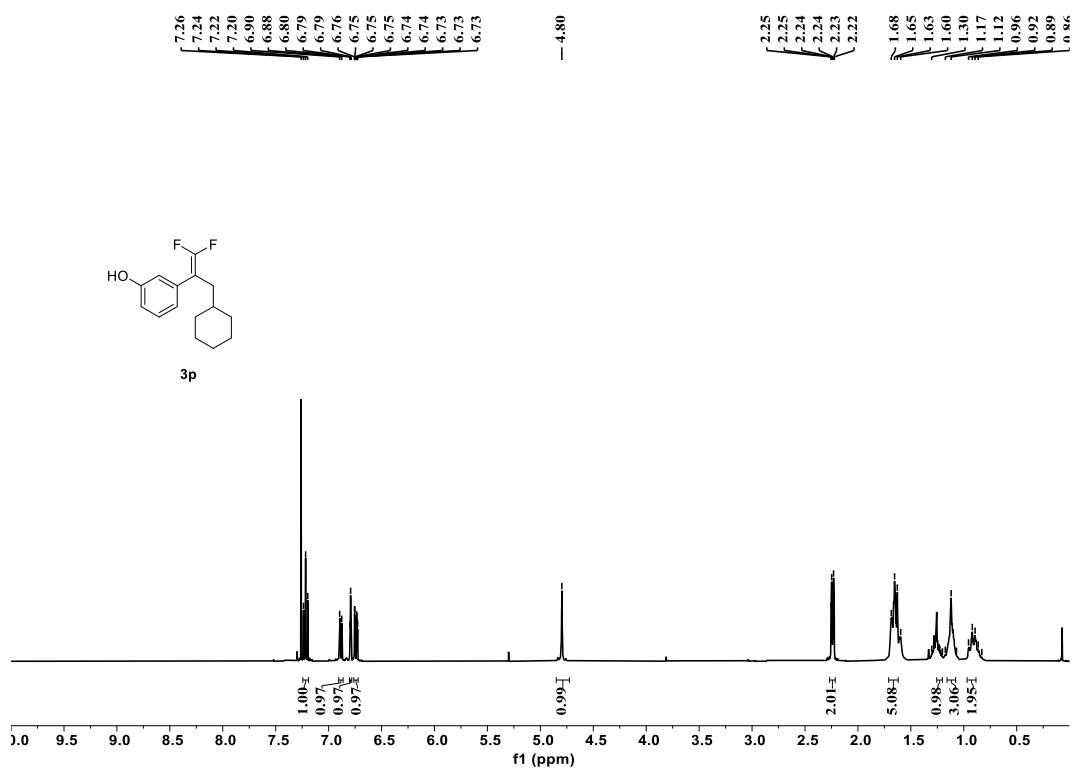
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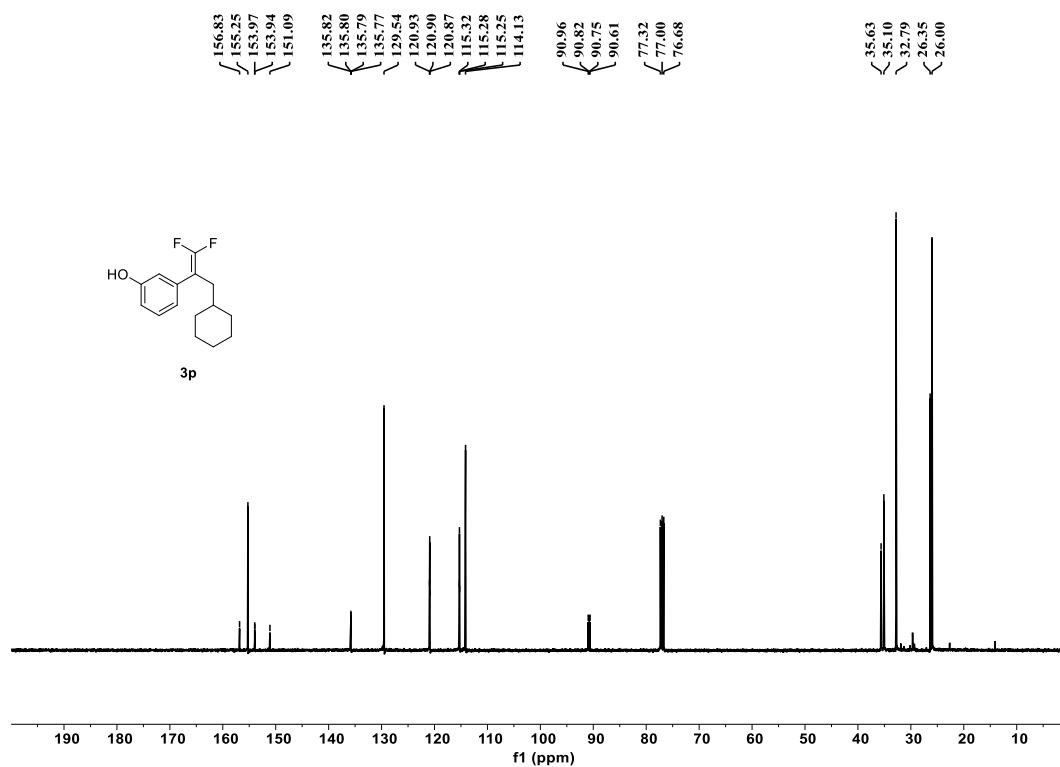
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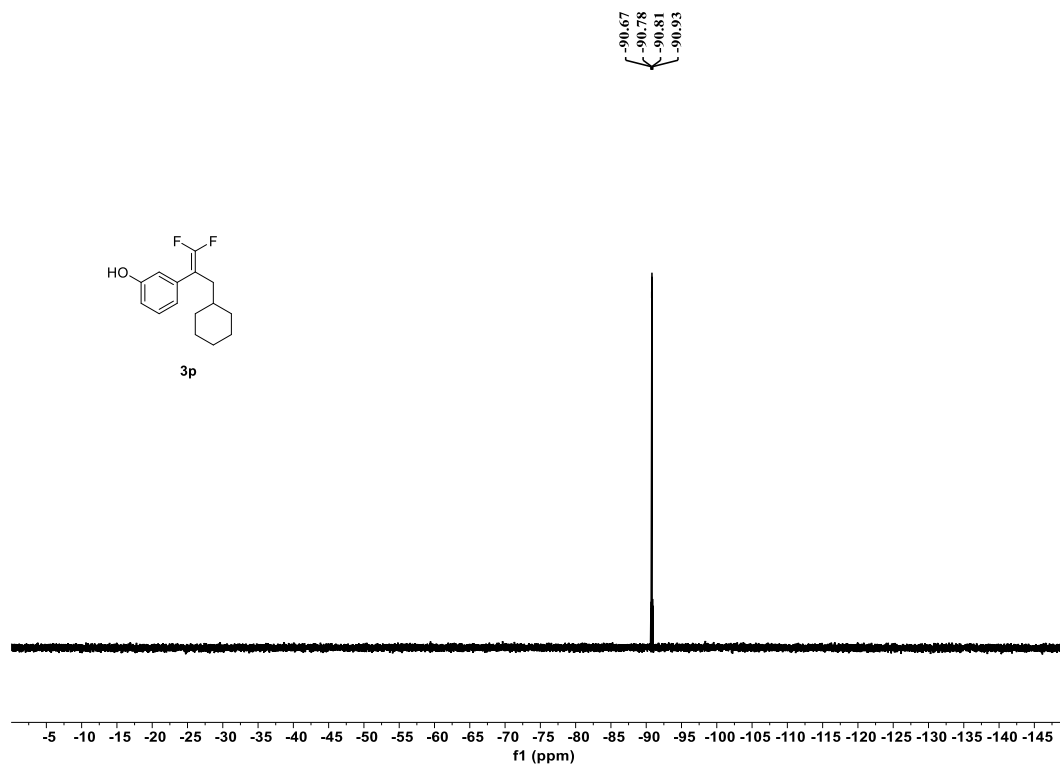
^1H NMR (400 MHz, CDCl_3)



¹³C NMR (100 MHz, CDCl₃)



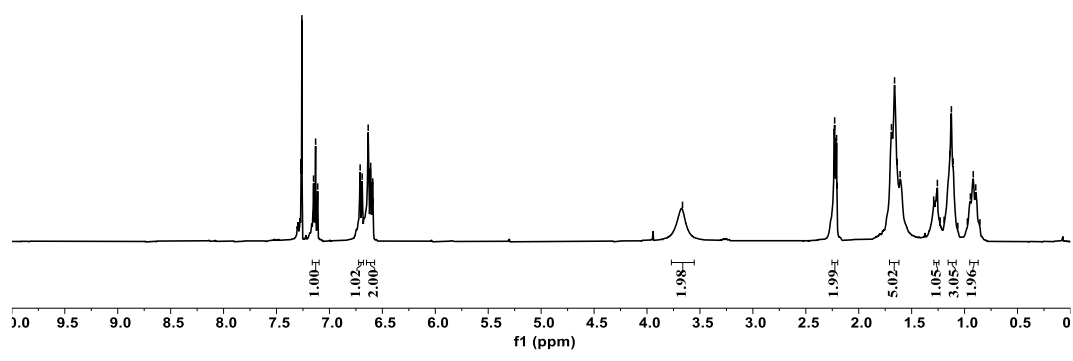
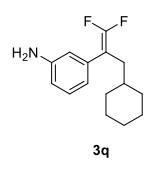
¹⁹F NMR (376 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)

7.26
7.15
7.11
6.71
6.69
6.63
6.61
6.59
6.59

3.66
2.23
2.23
2.22
2.22
2.21
2.20
1.69
1.66
1.64
1.61
1.29
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0.85

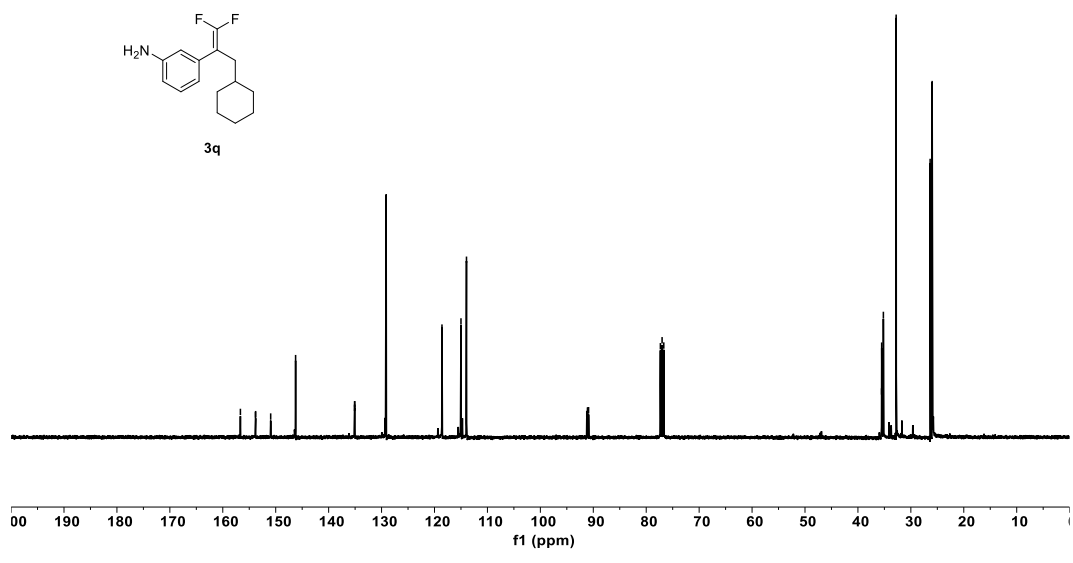
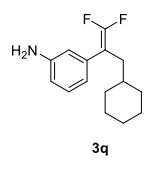


¹³C NMR (100 MHz, CDCl₃)

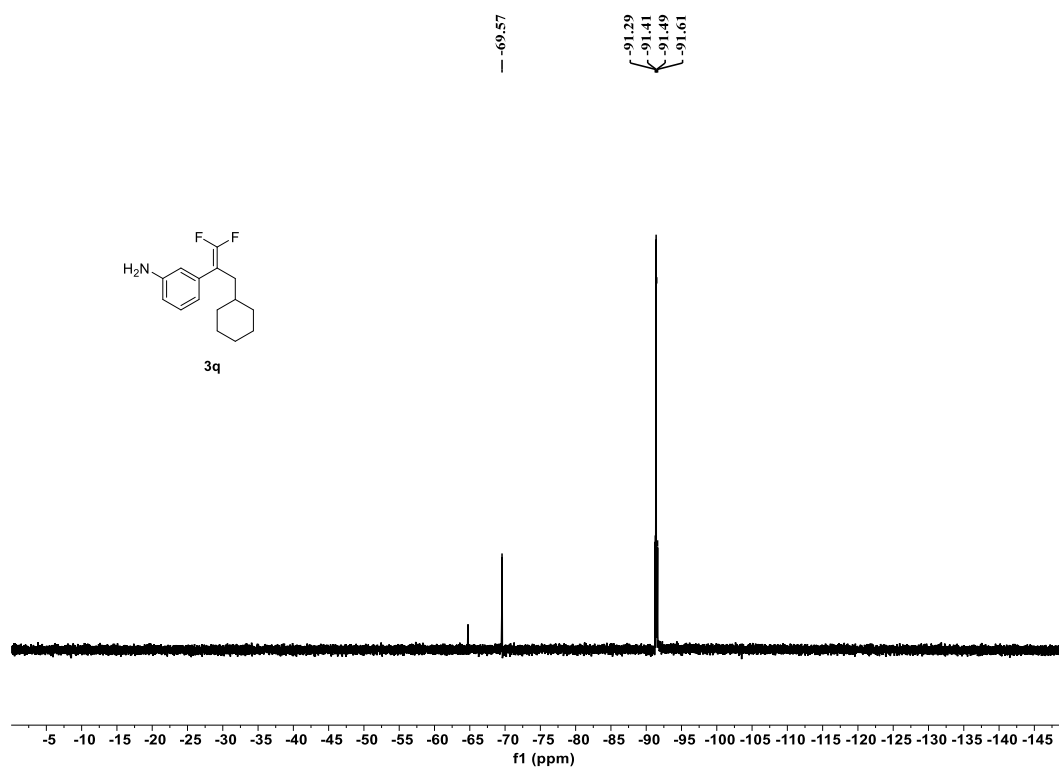
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114.97
113.96

91.23
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77.32
77.00
76.68

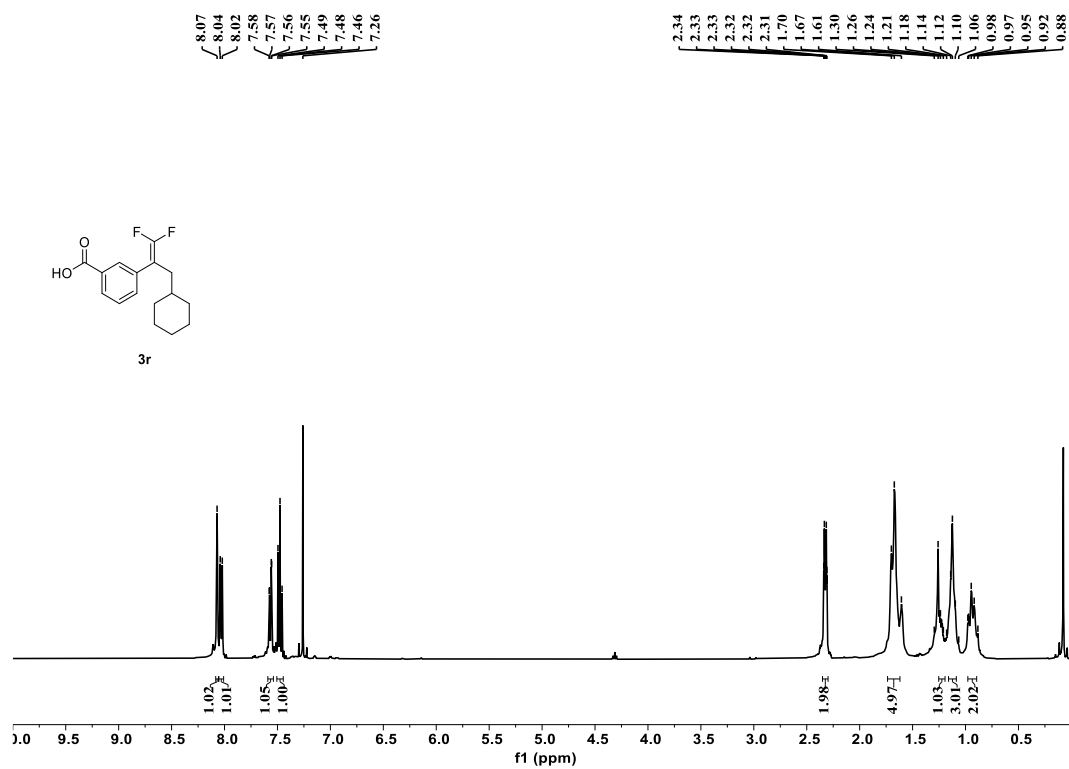
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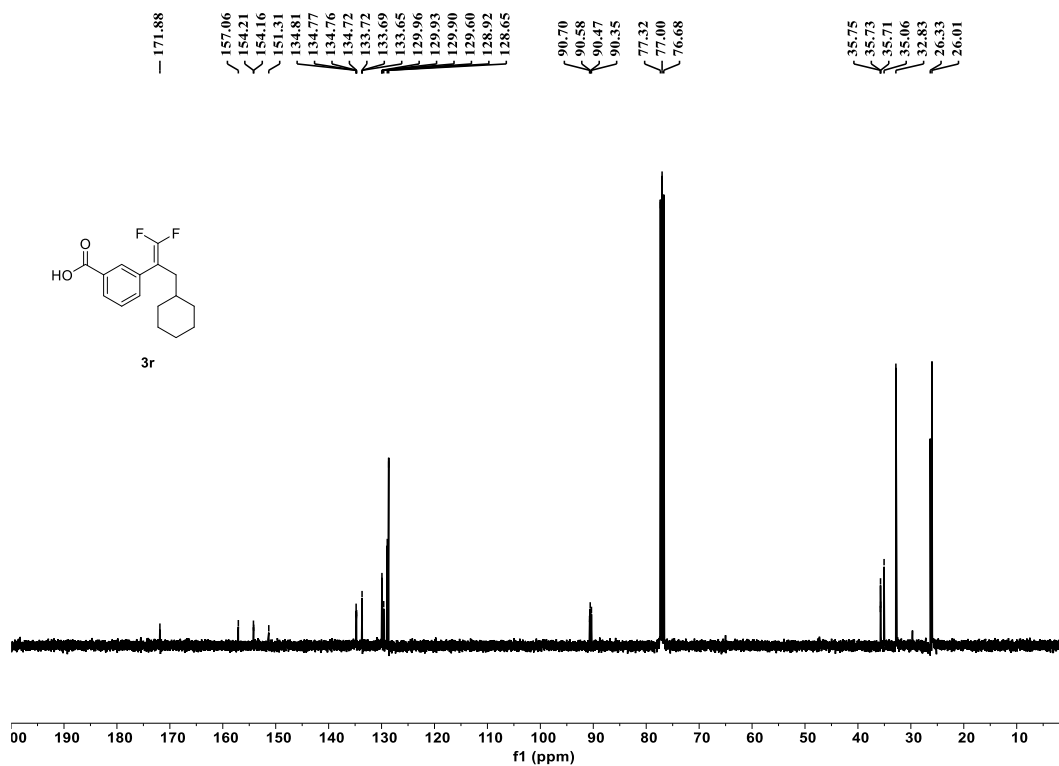
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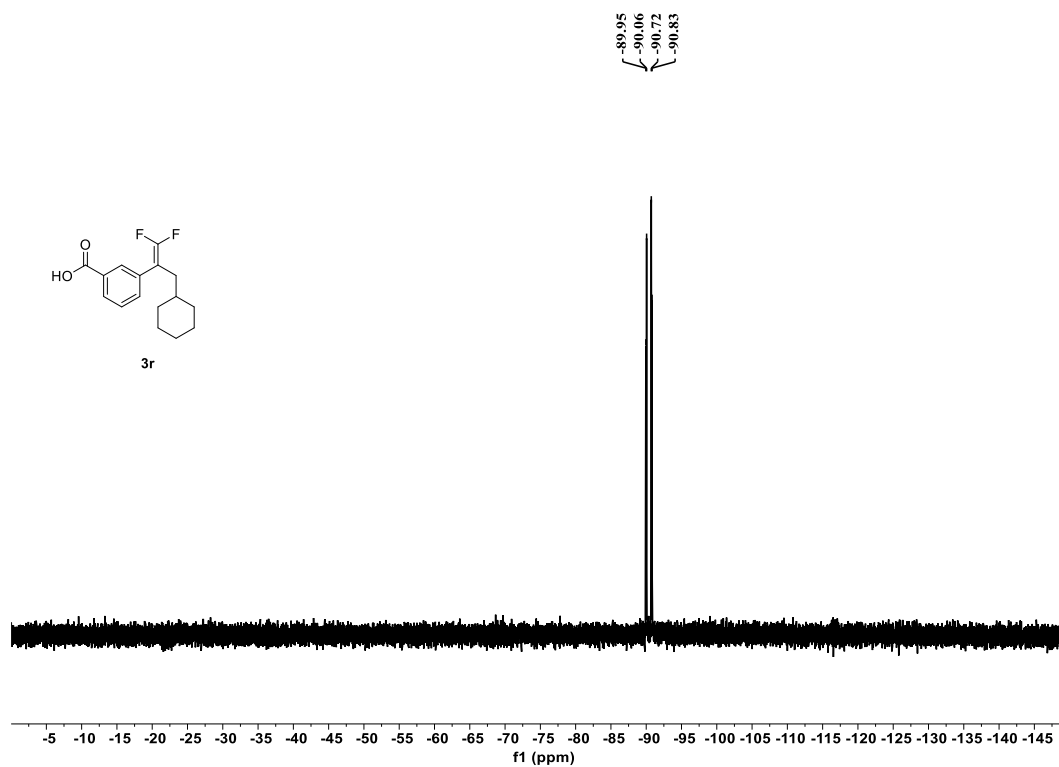
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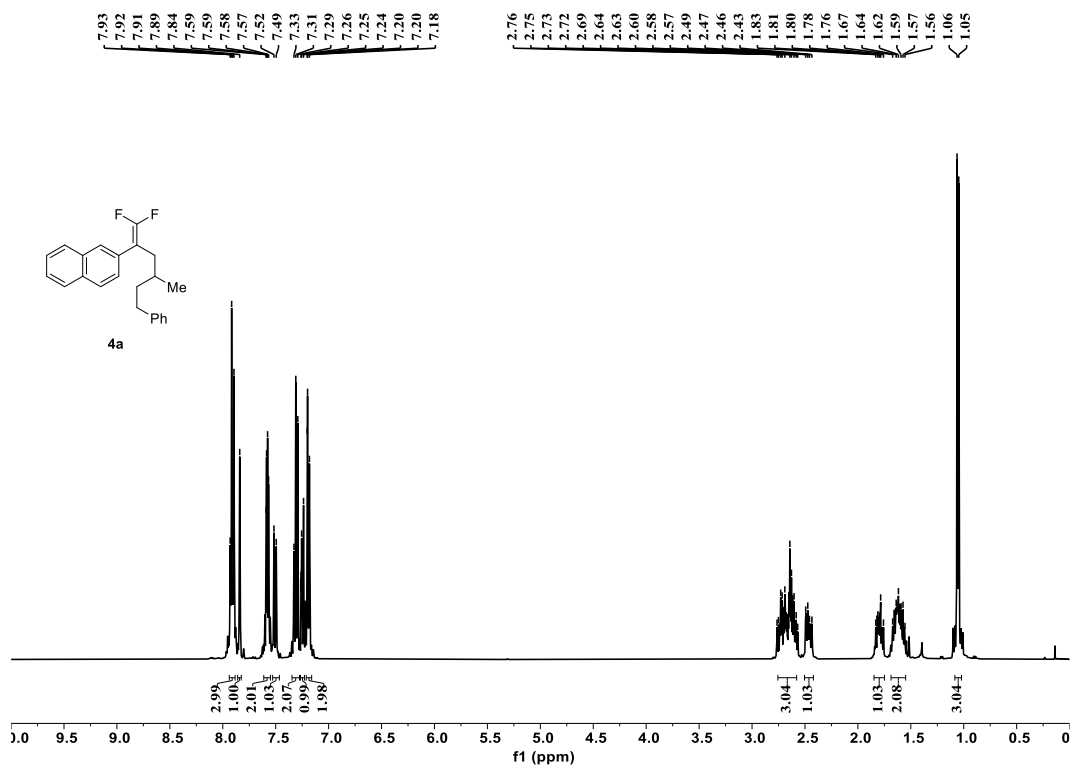
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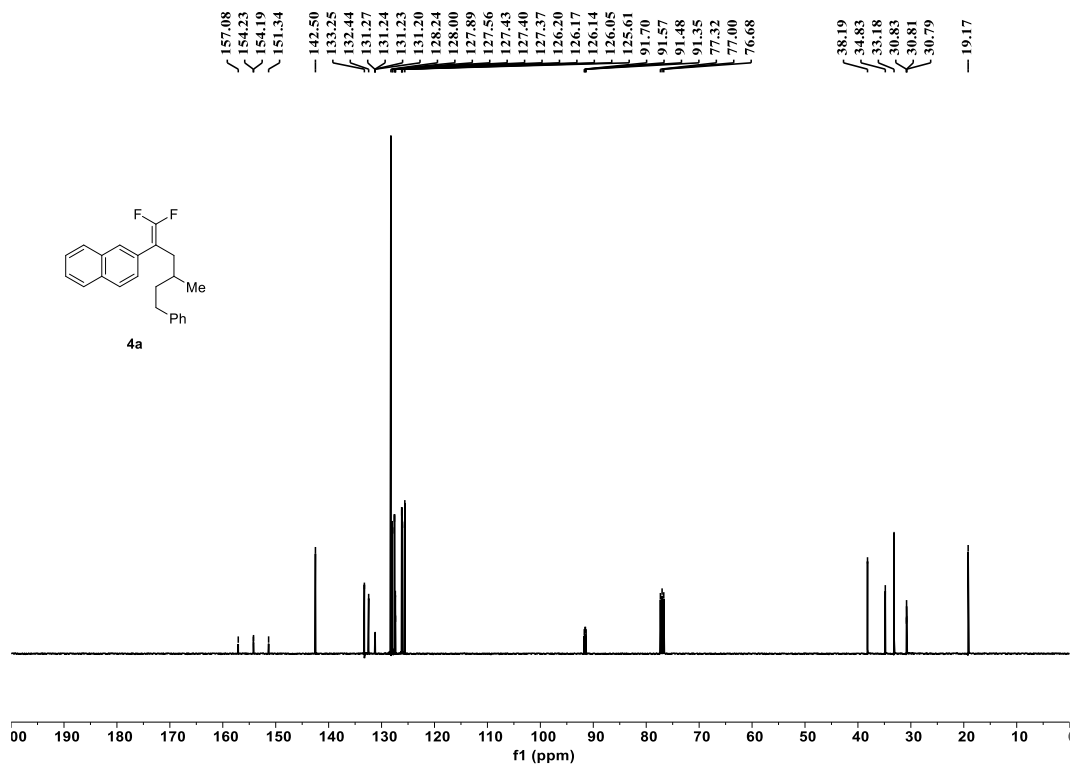
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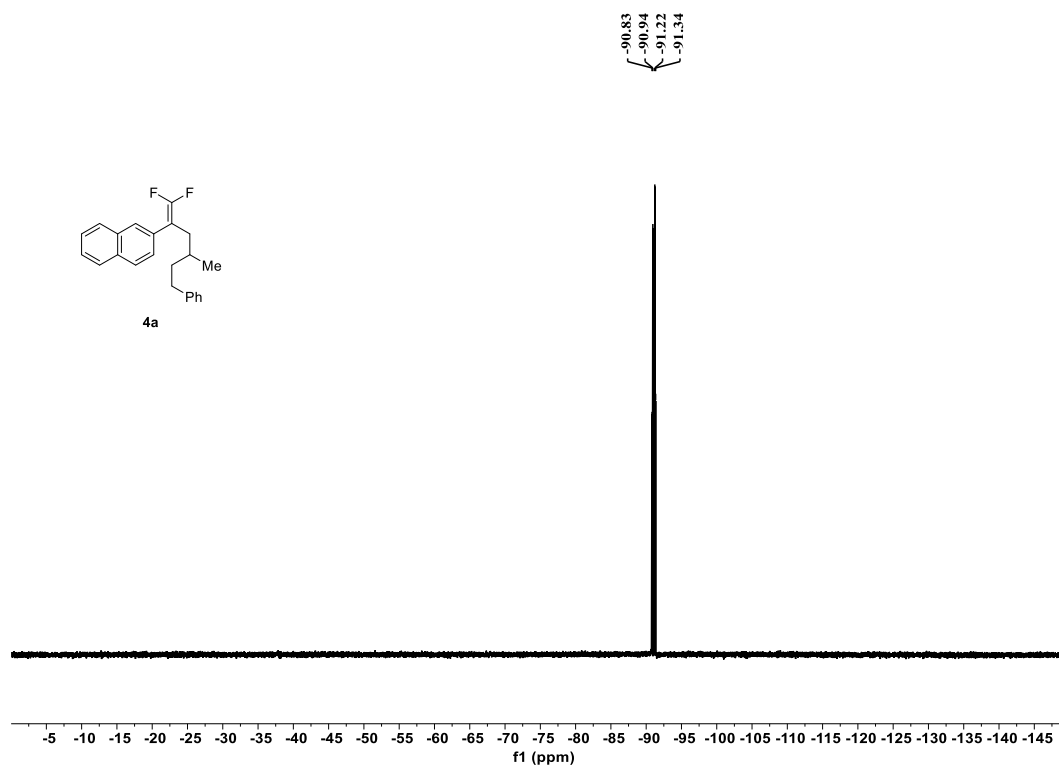
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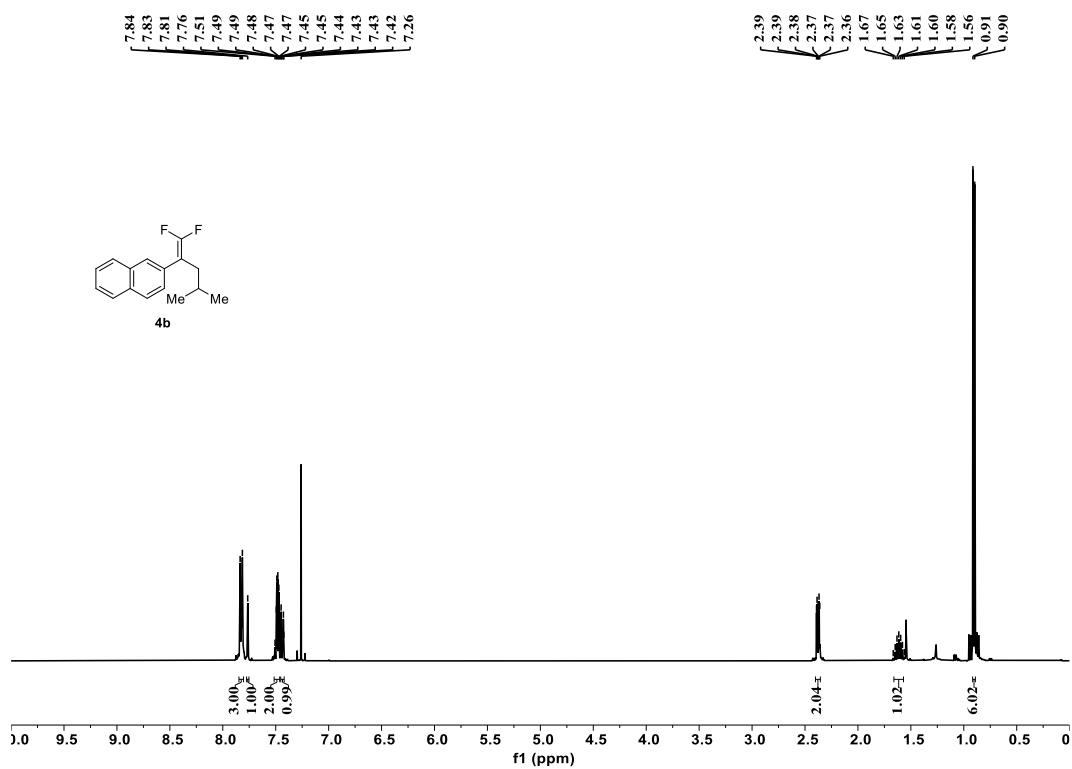
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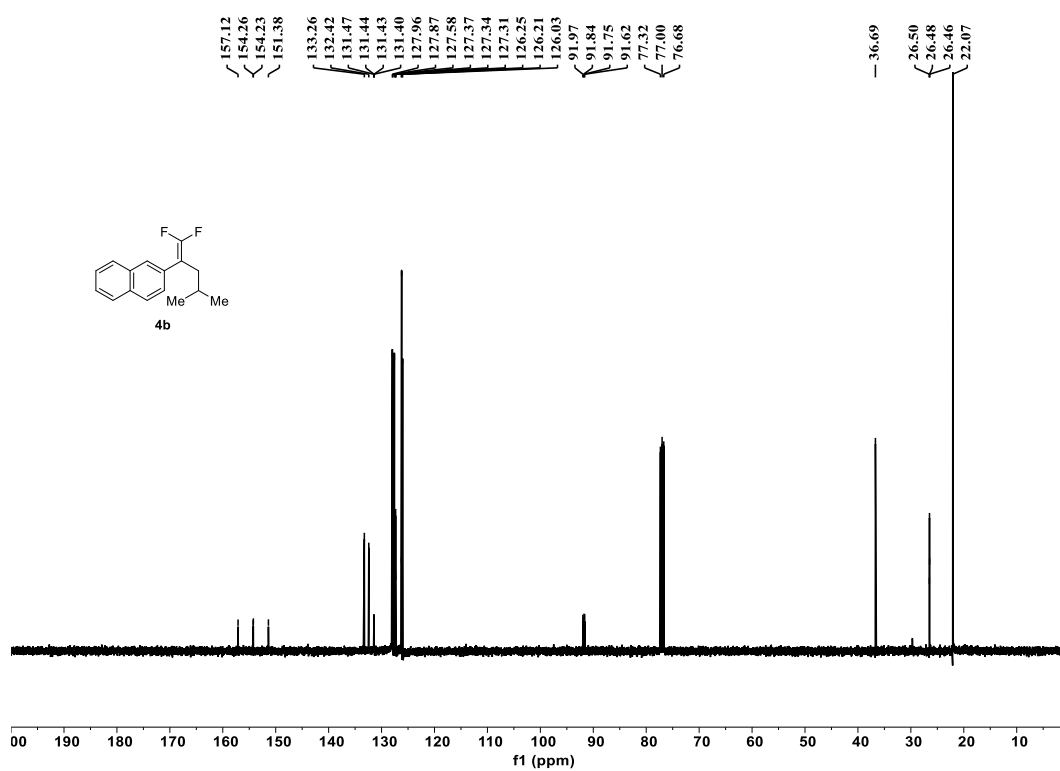
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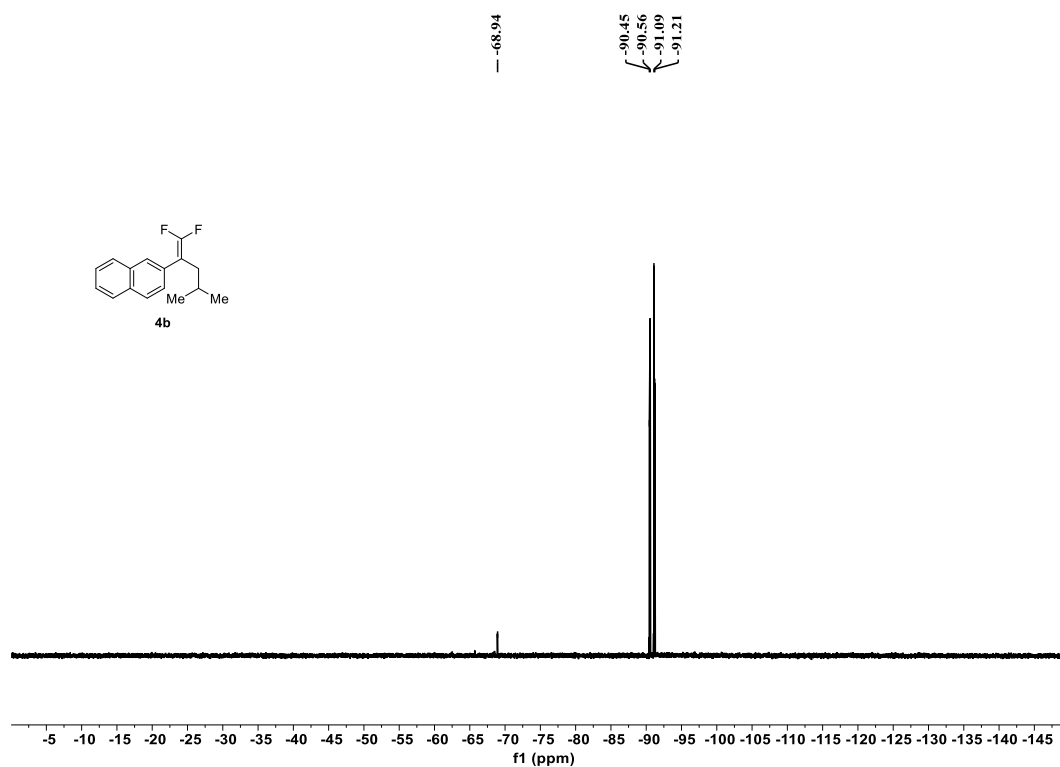
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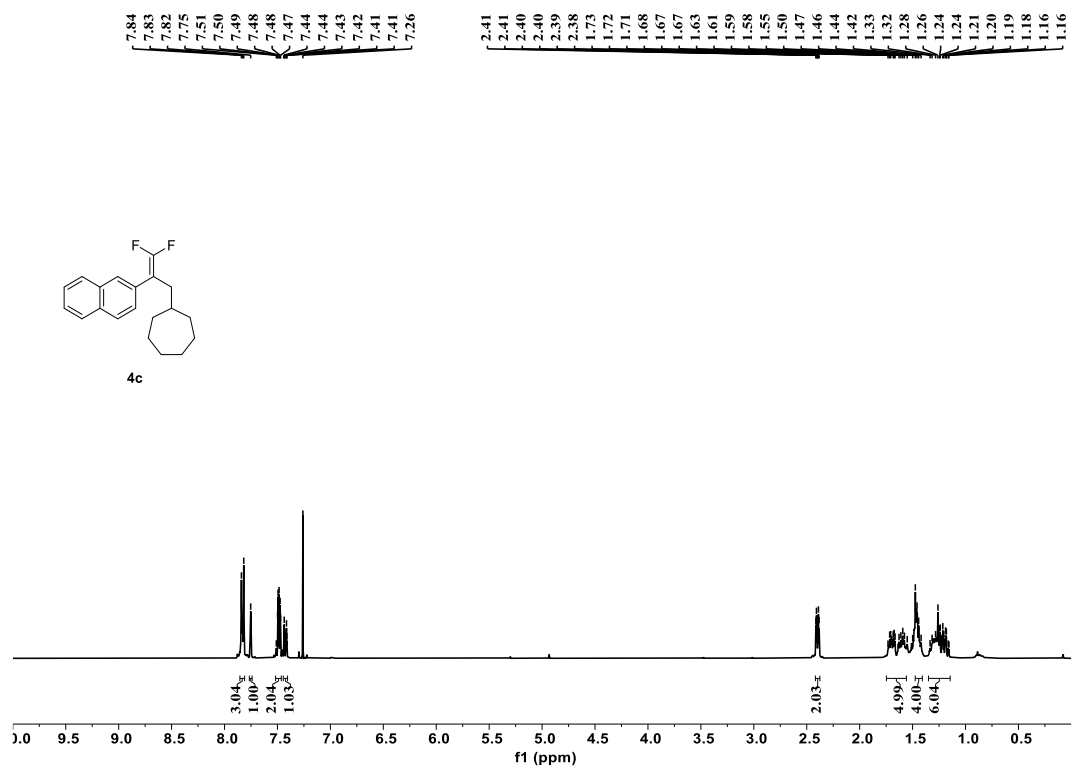
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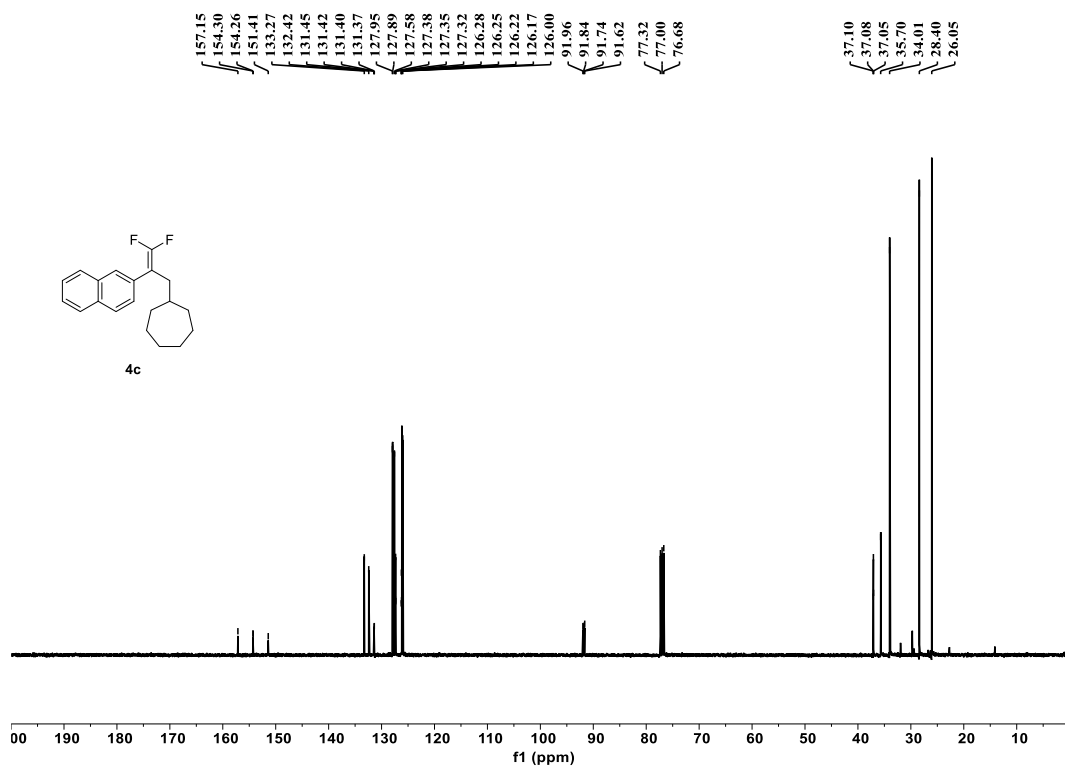
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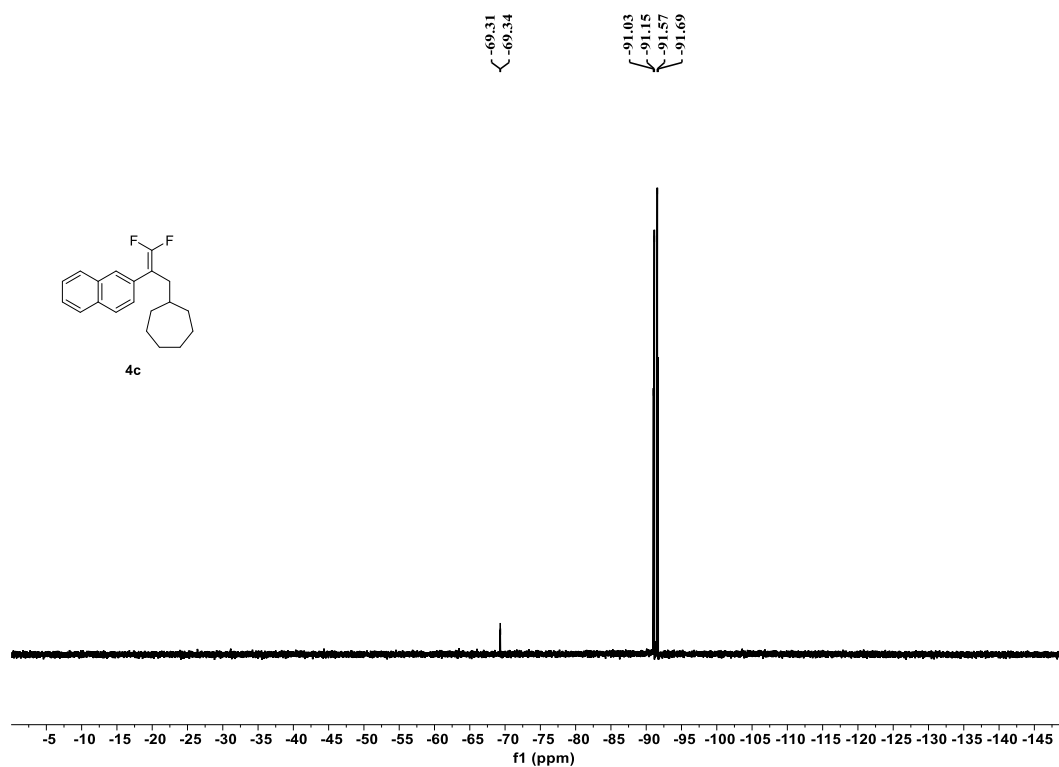
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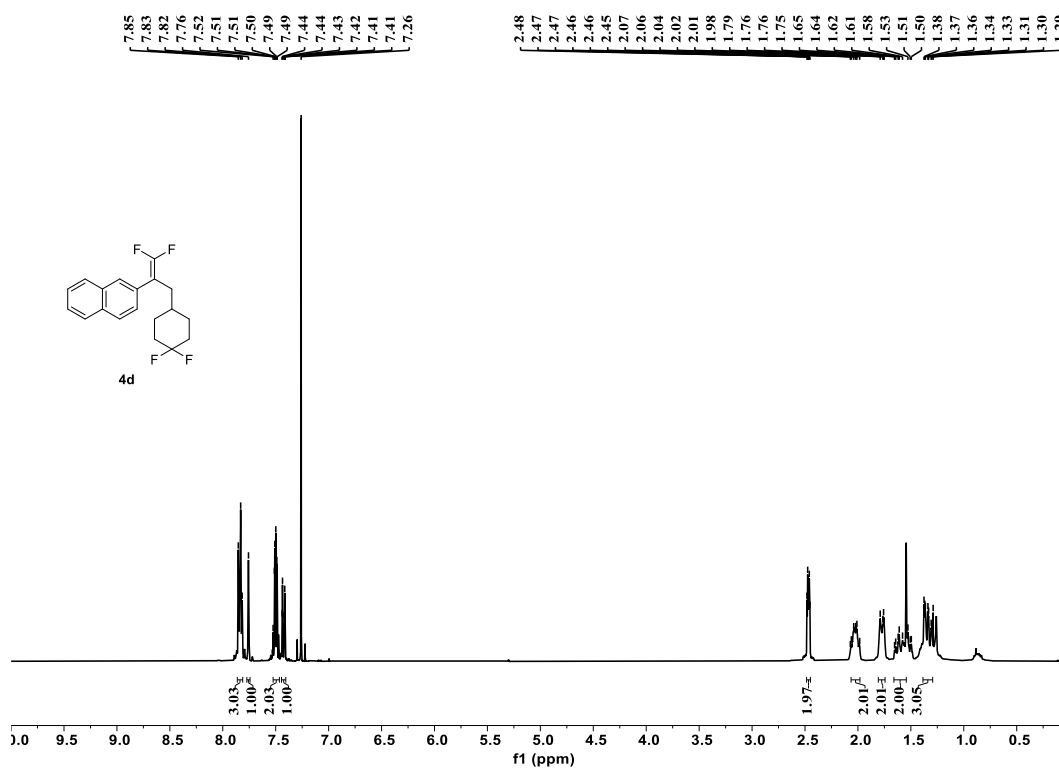
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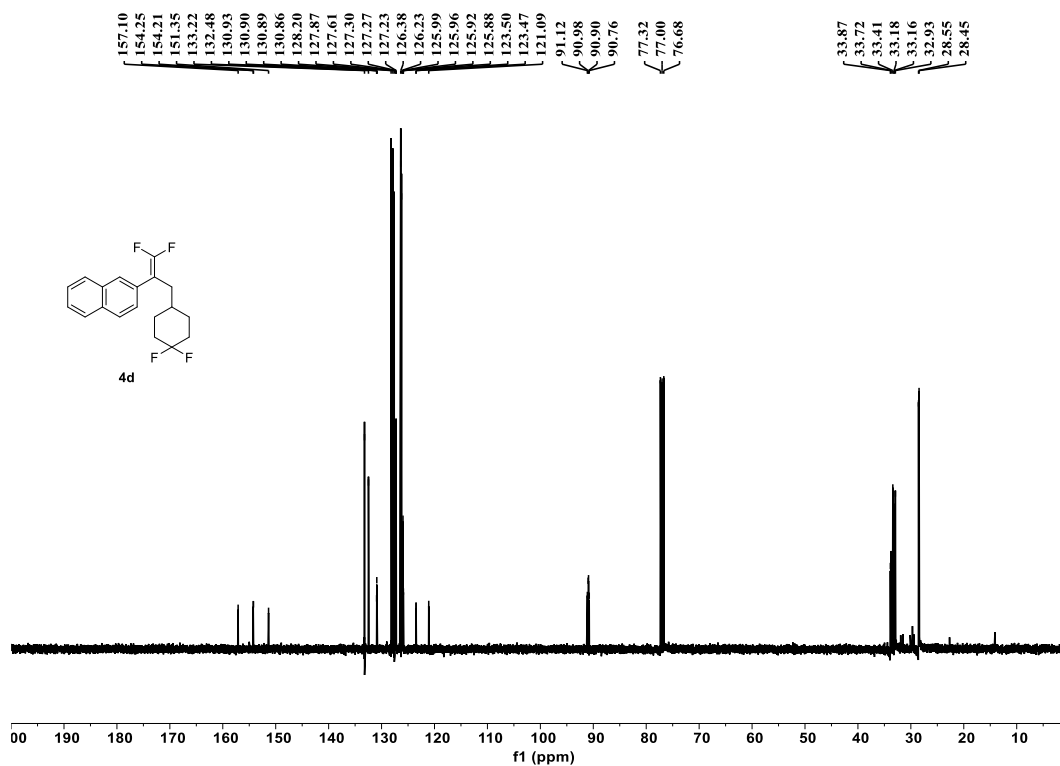
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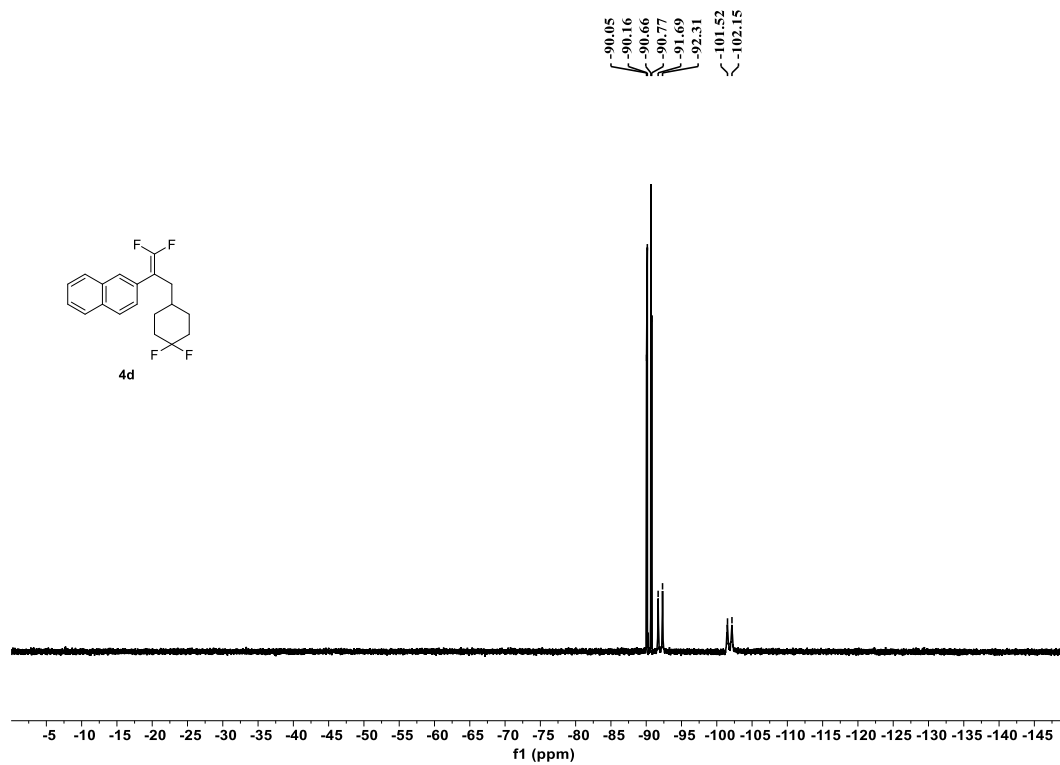
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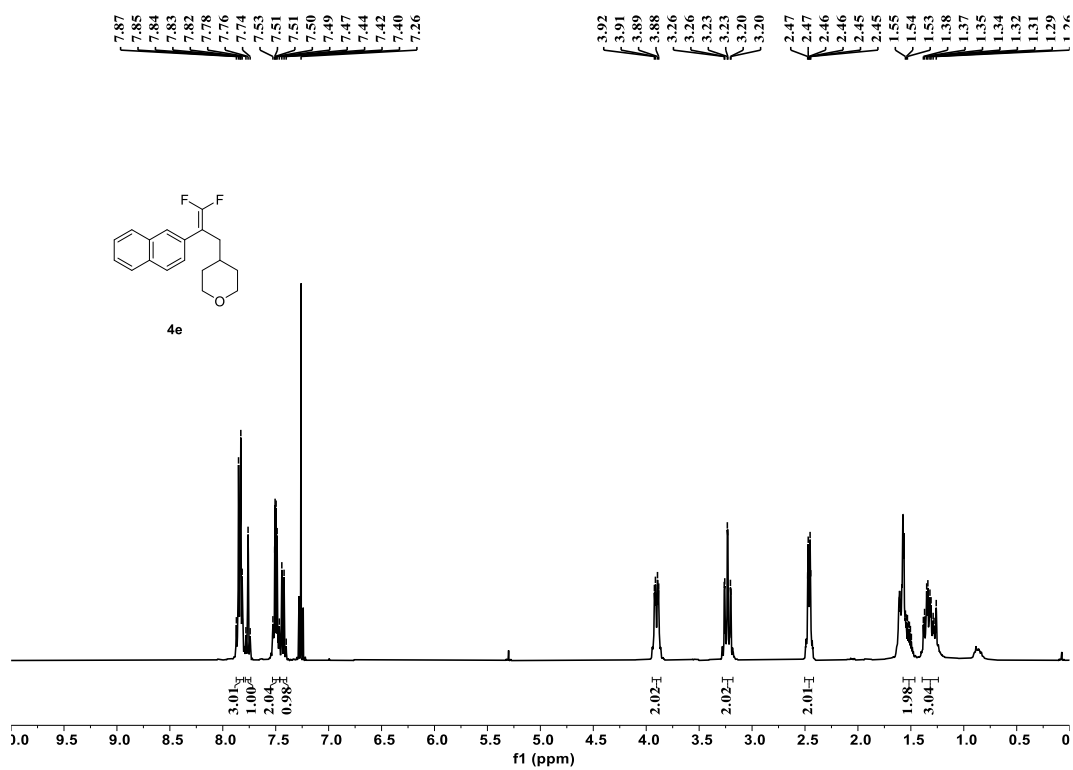
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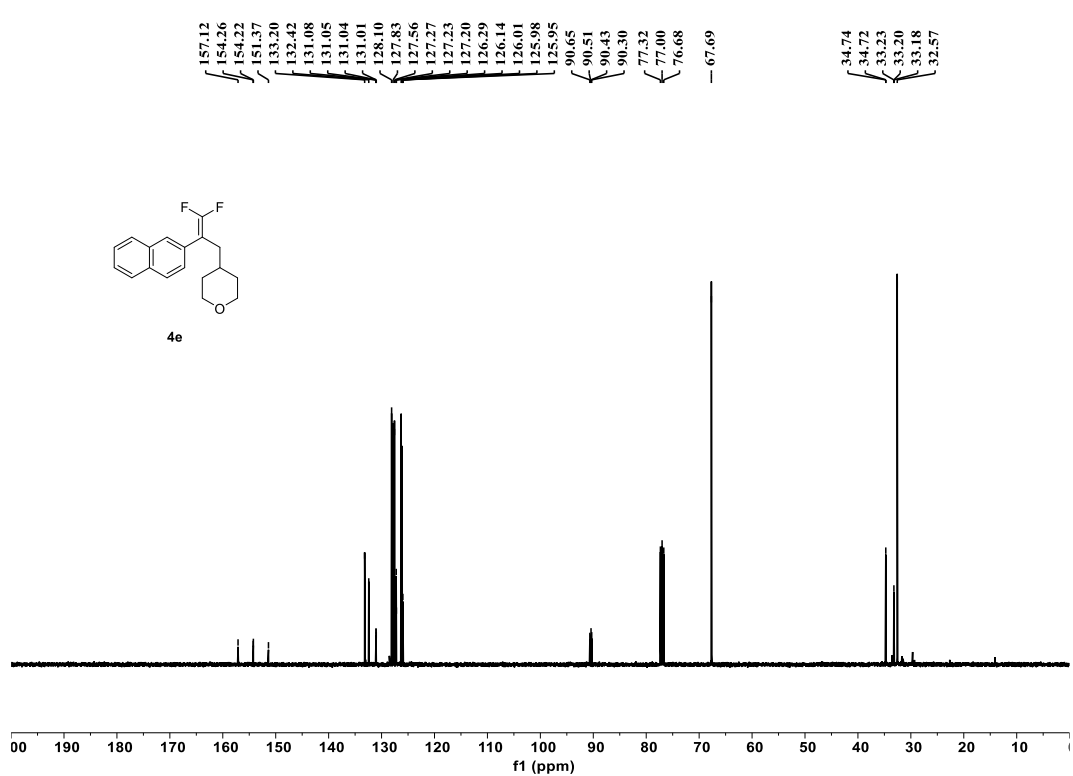
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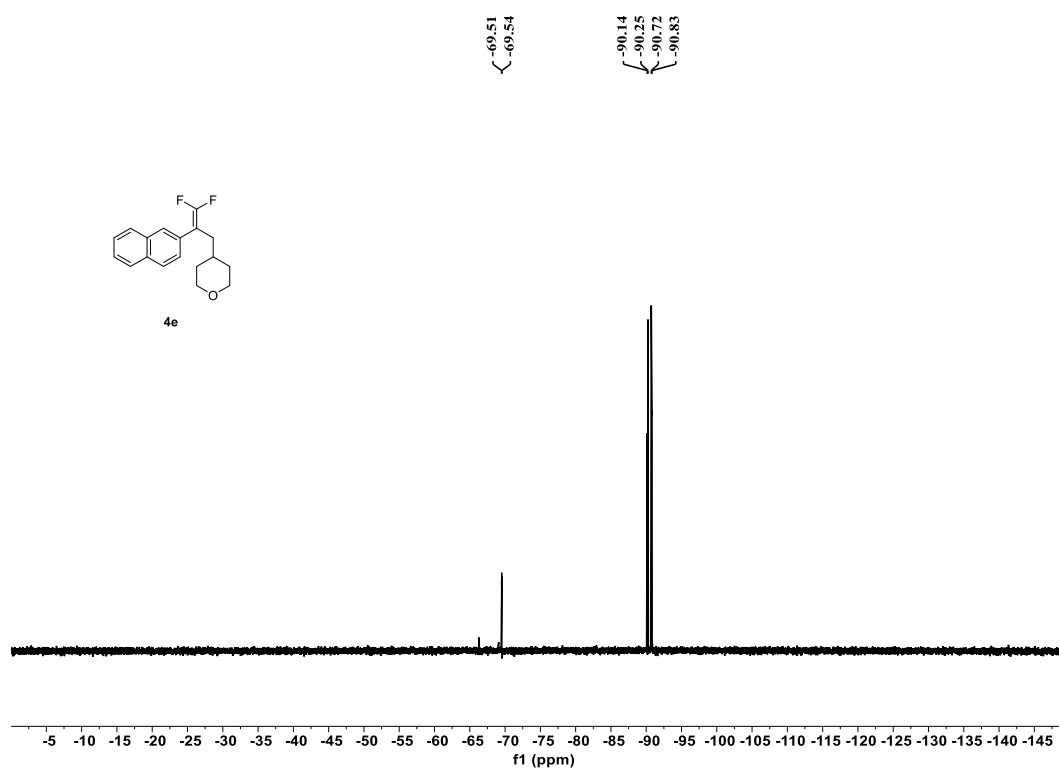
¹H NMR (400 MHz, CDCl₃)



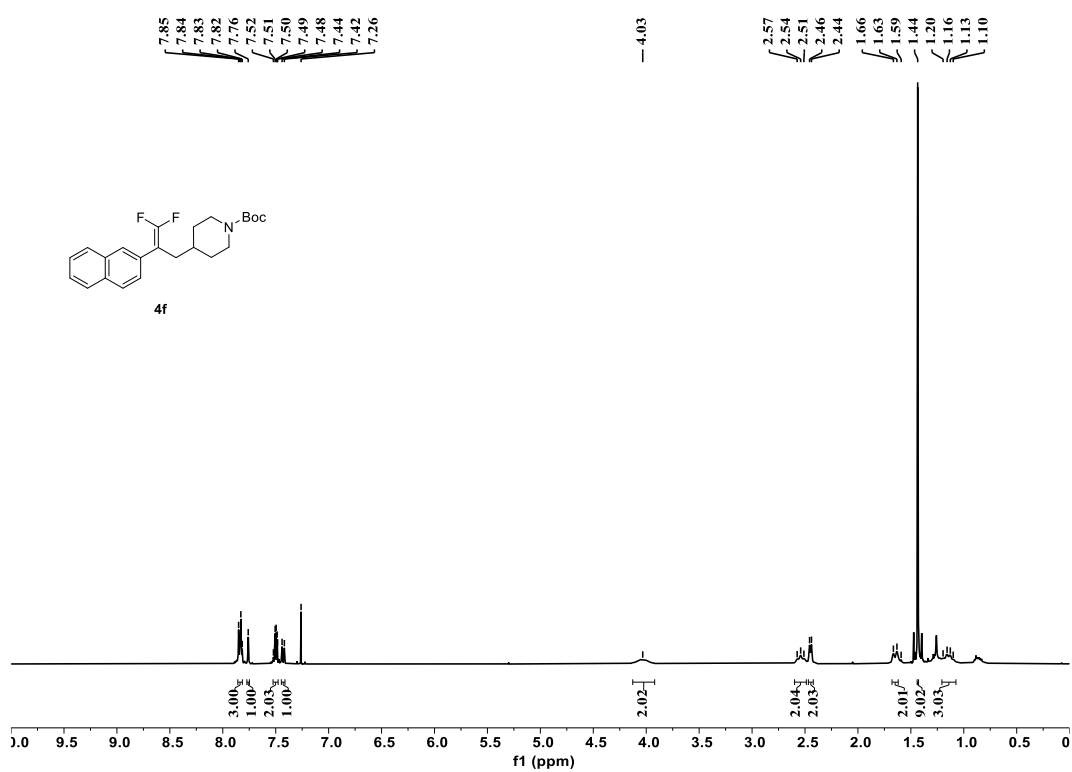
¹³C NMR (100 MHz, CDCl₃)



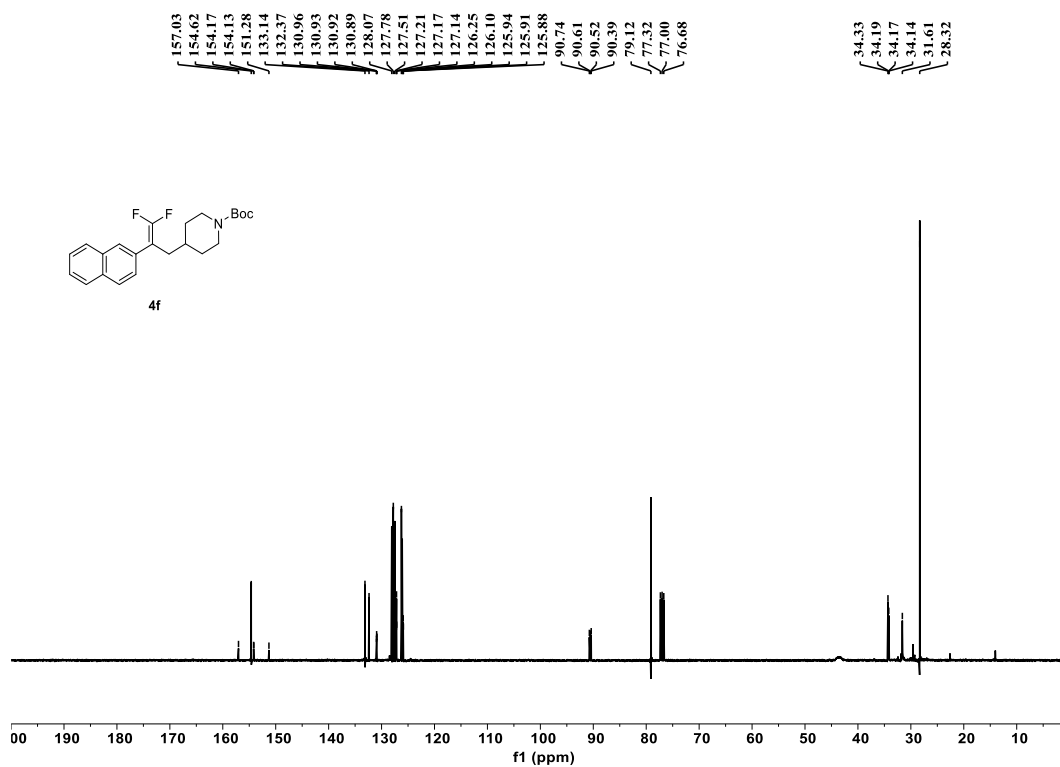
^{19}F NMR (376 MHz, CDCl_3)



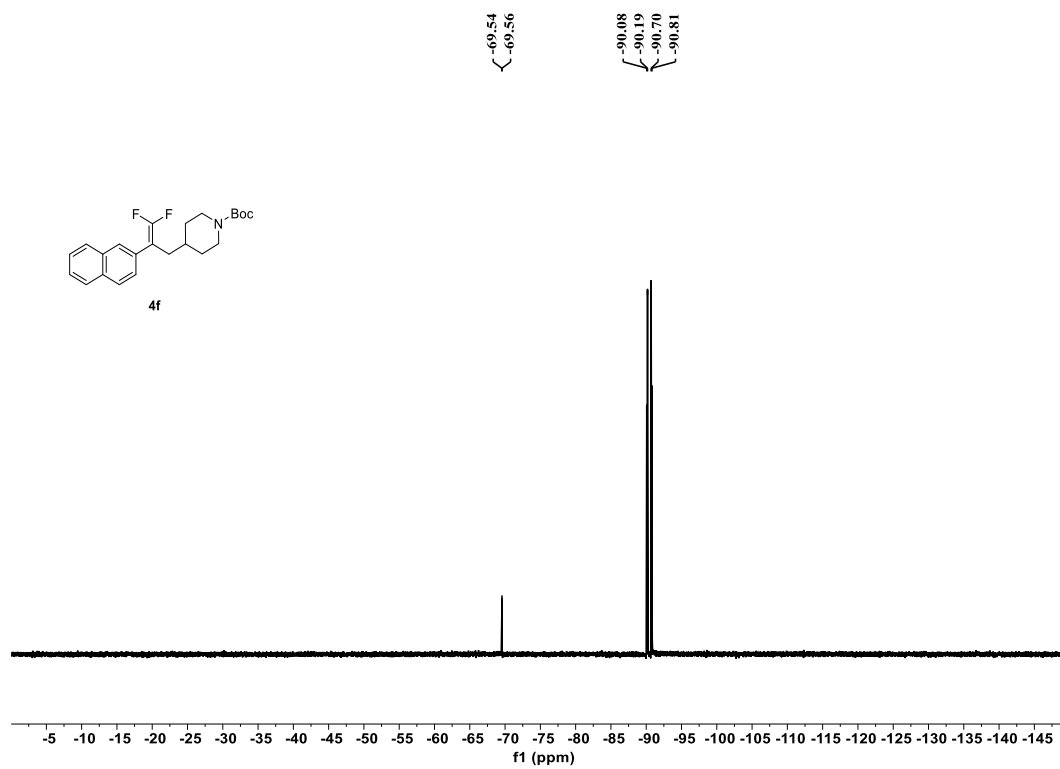
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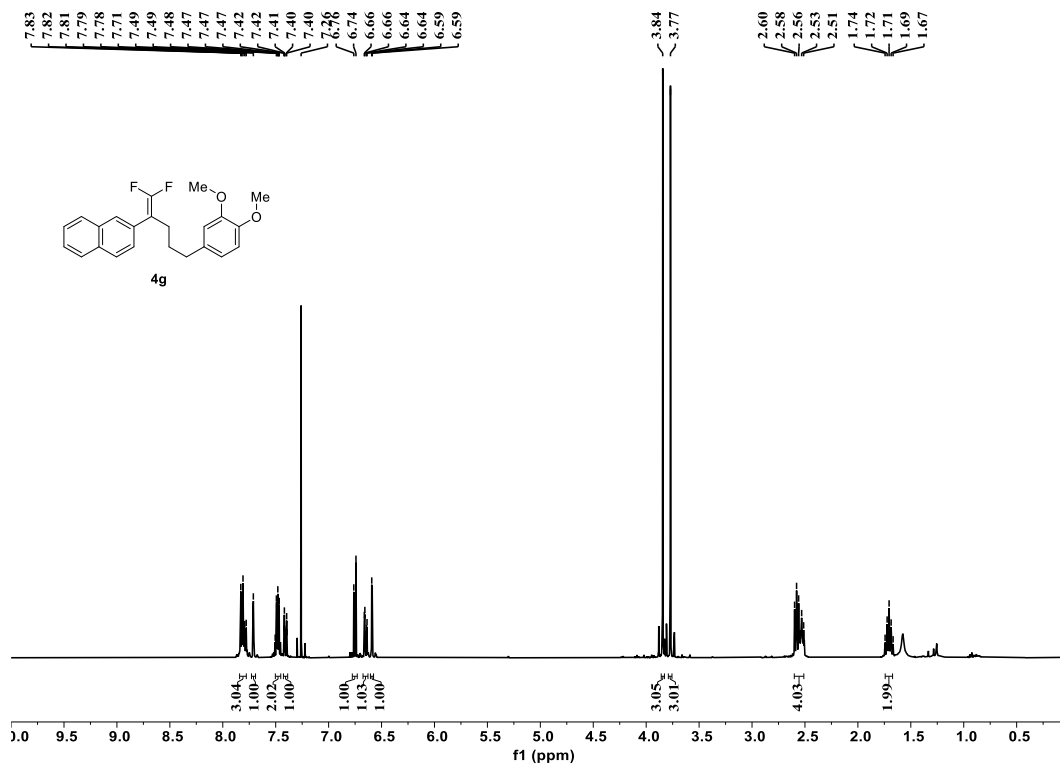
^{13}C NMR (100 MHz, CDCl_3)



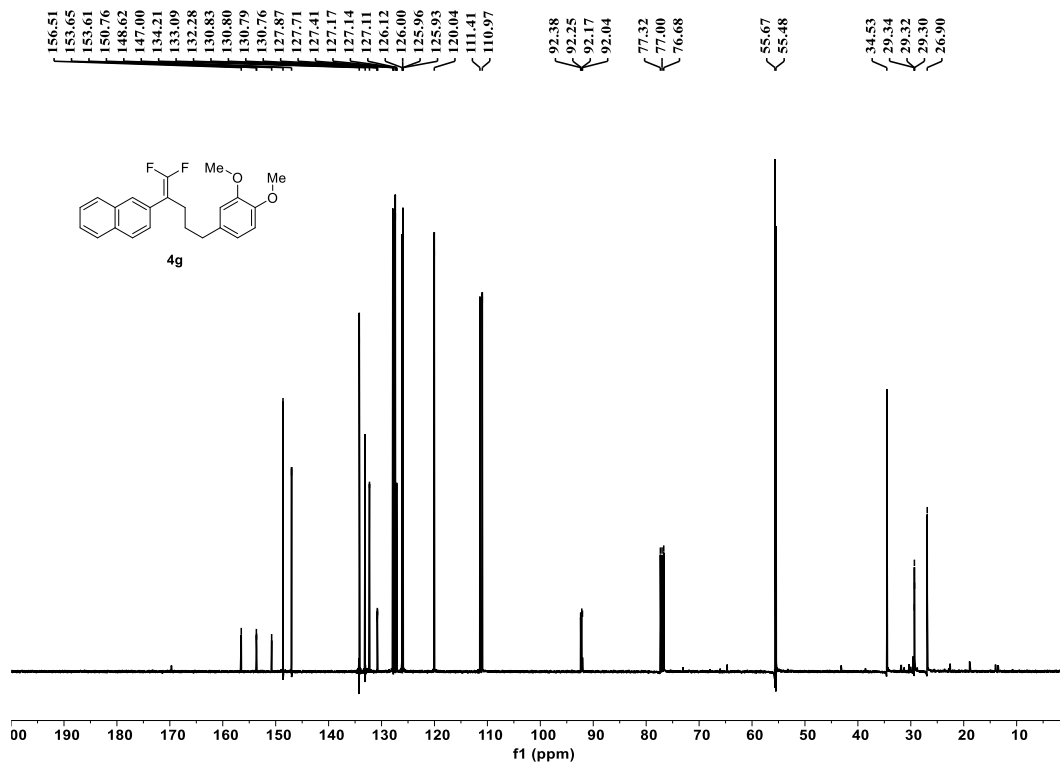
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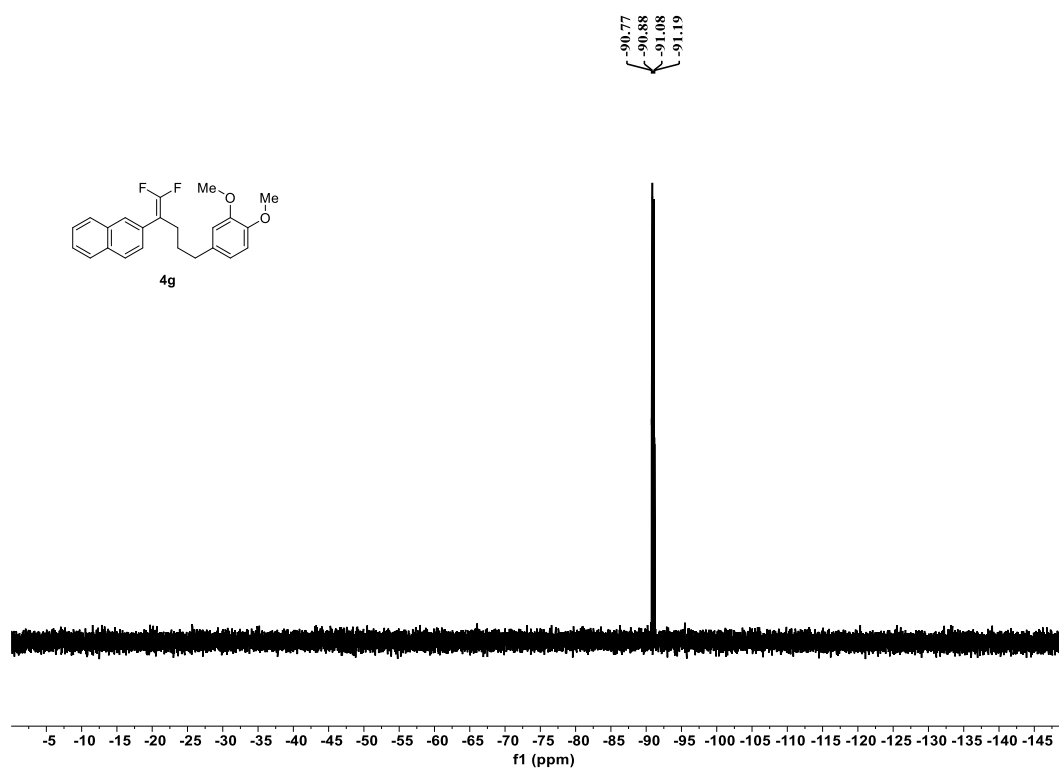
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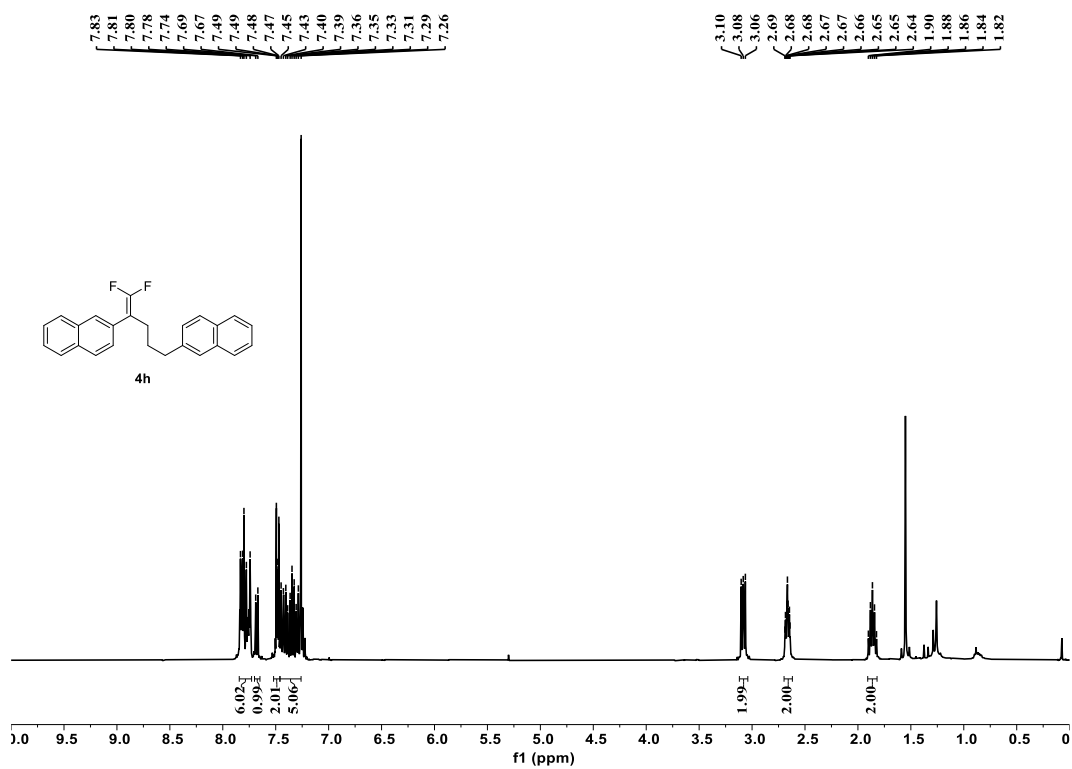
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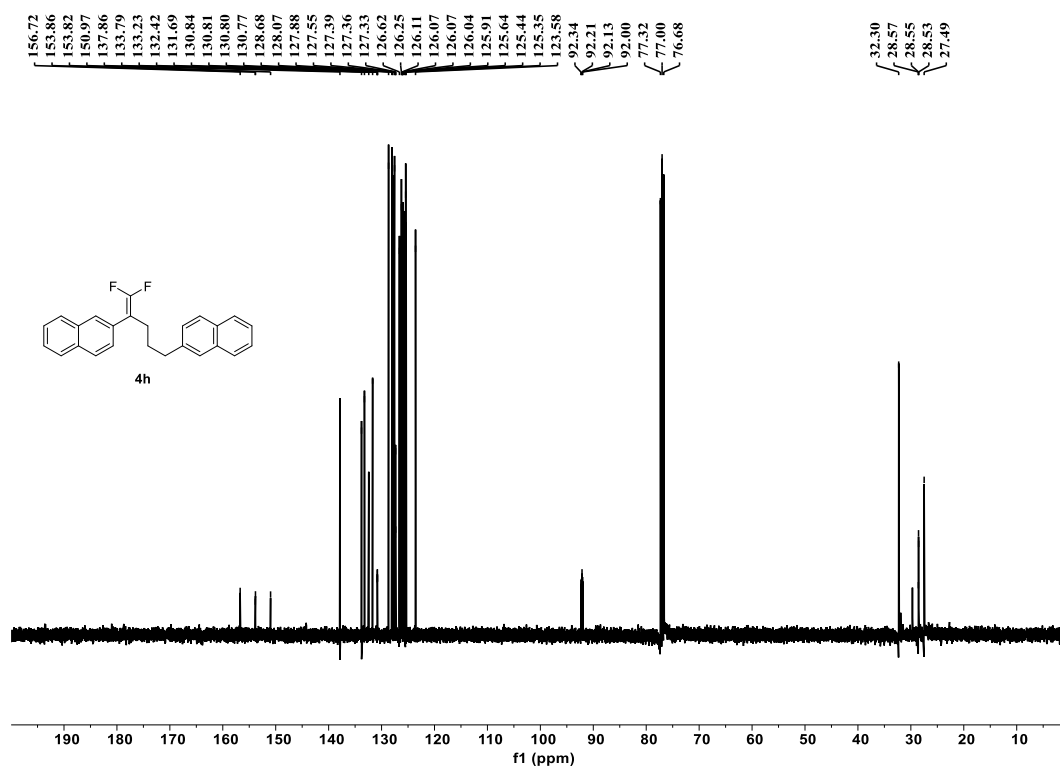
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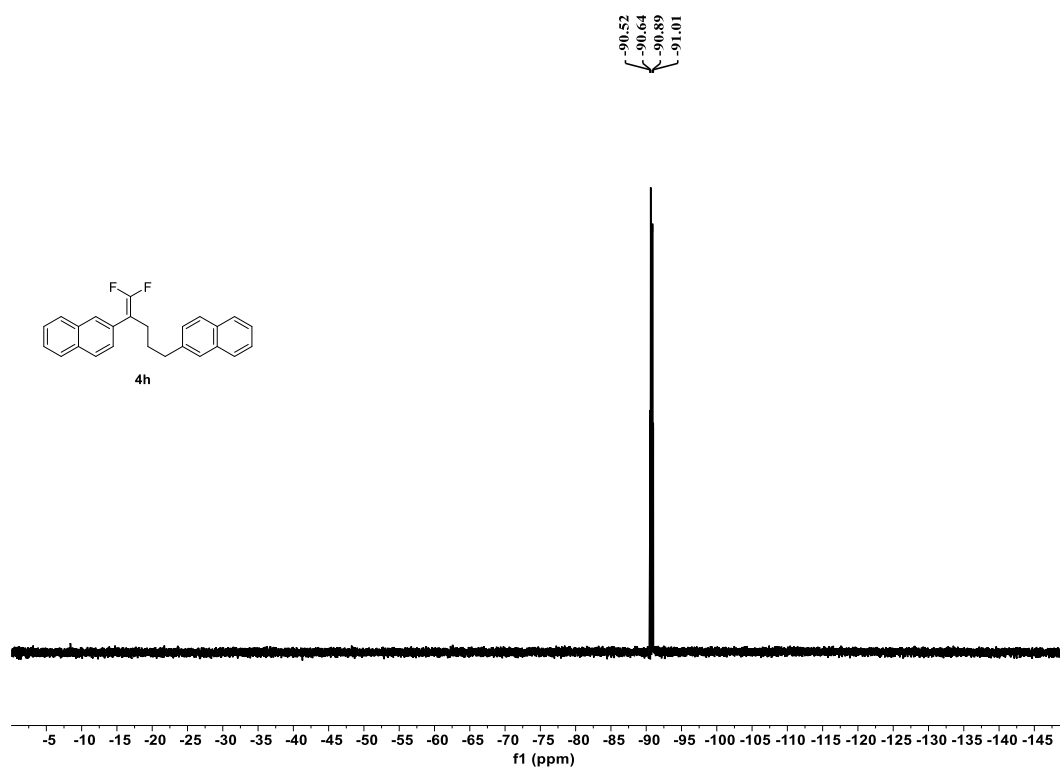
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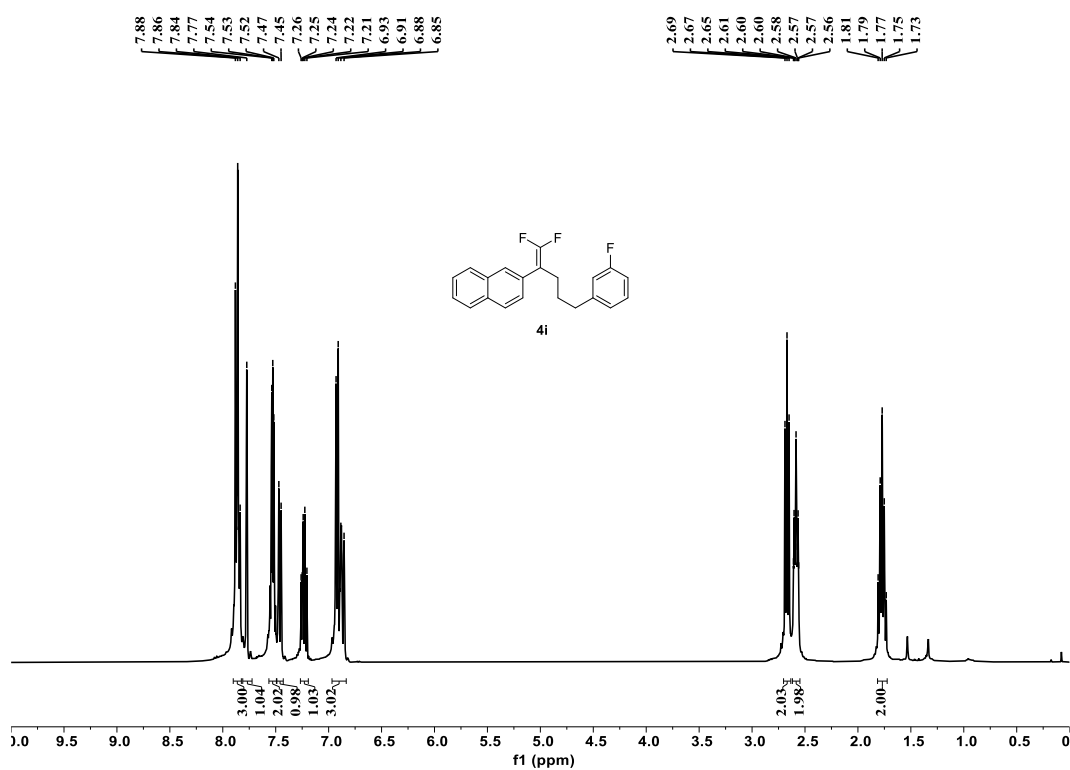
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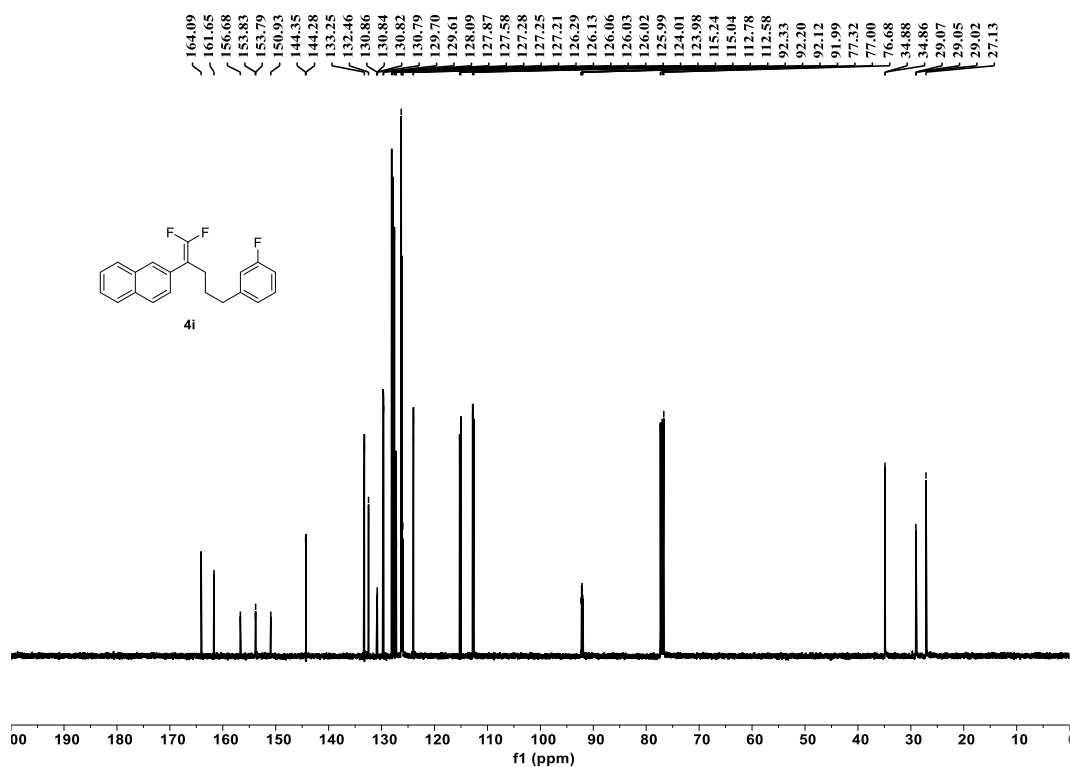
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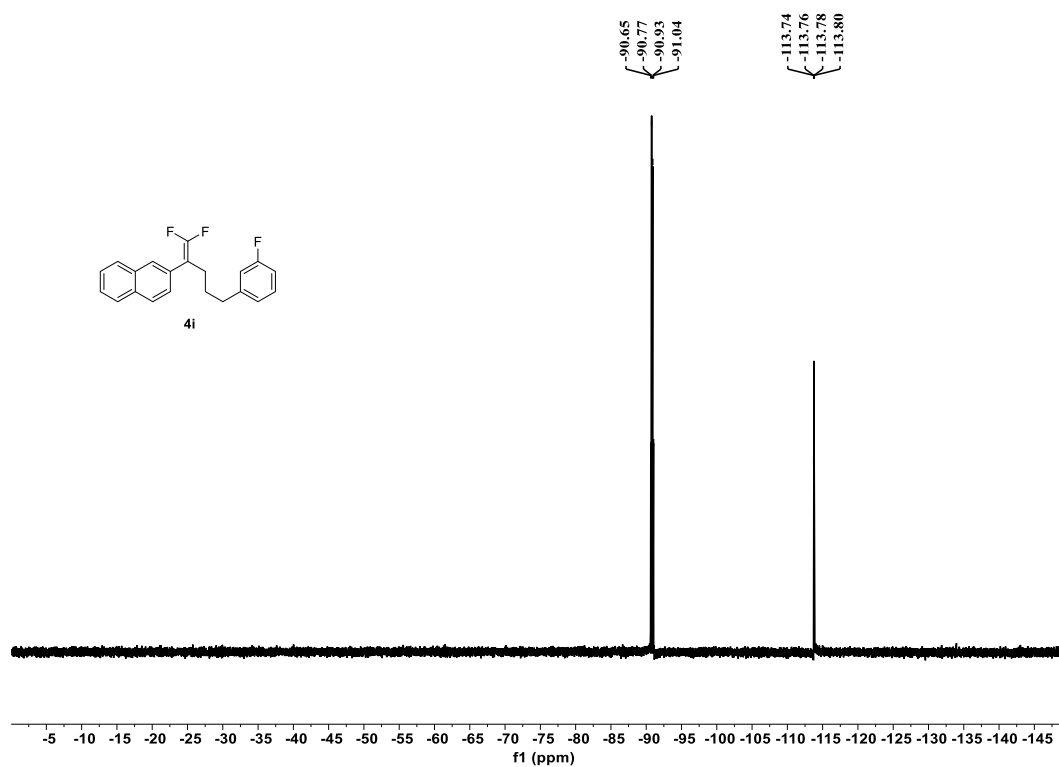
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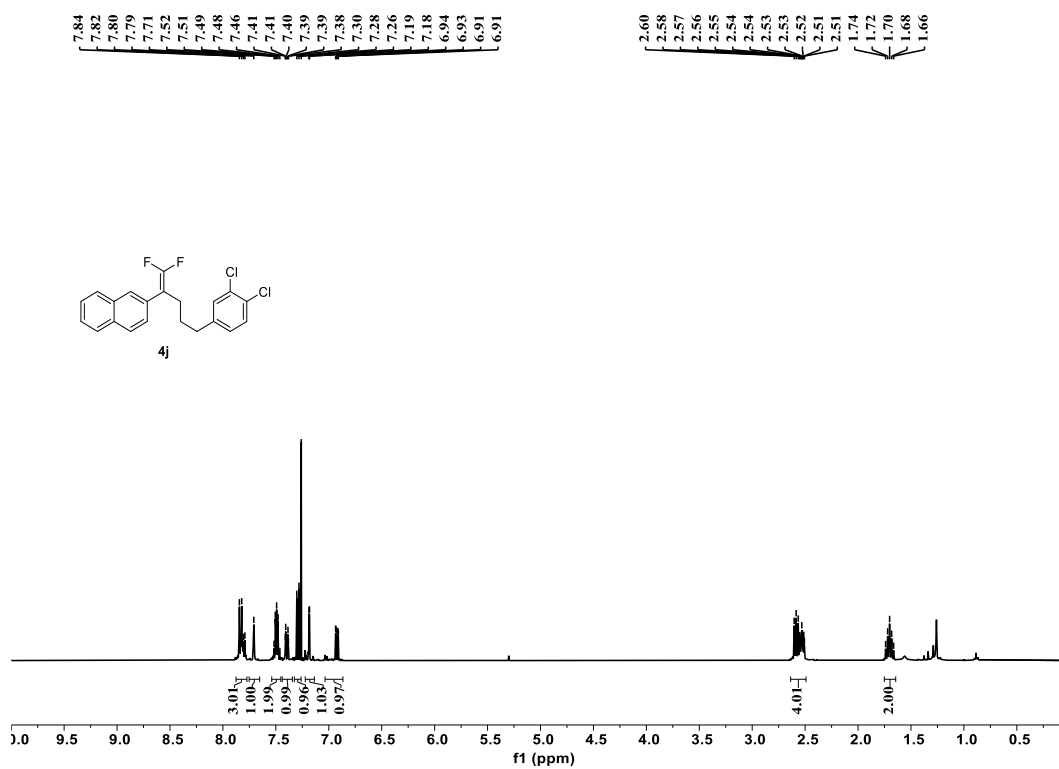
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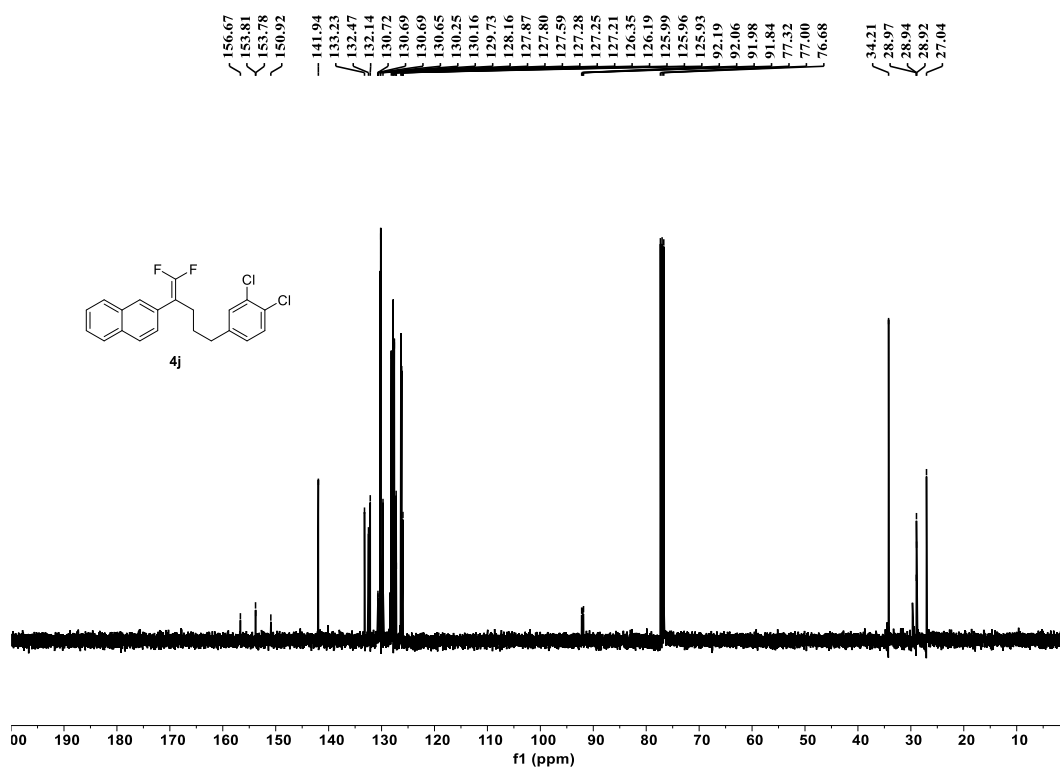
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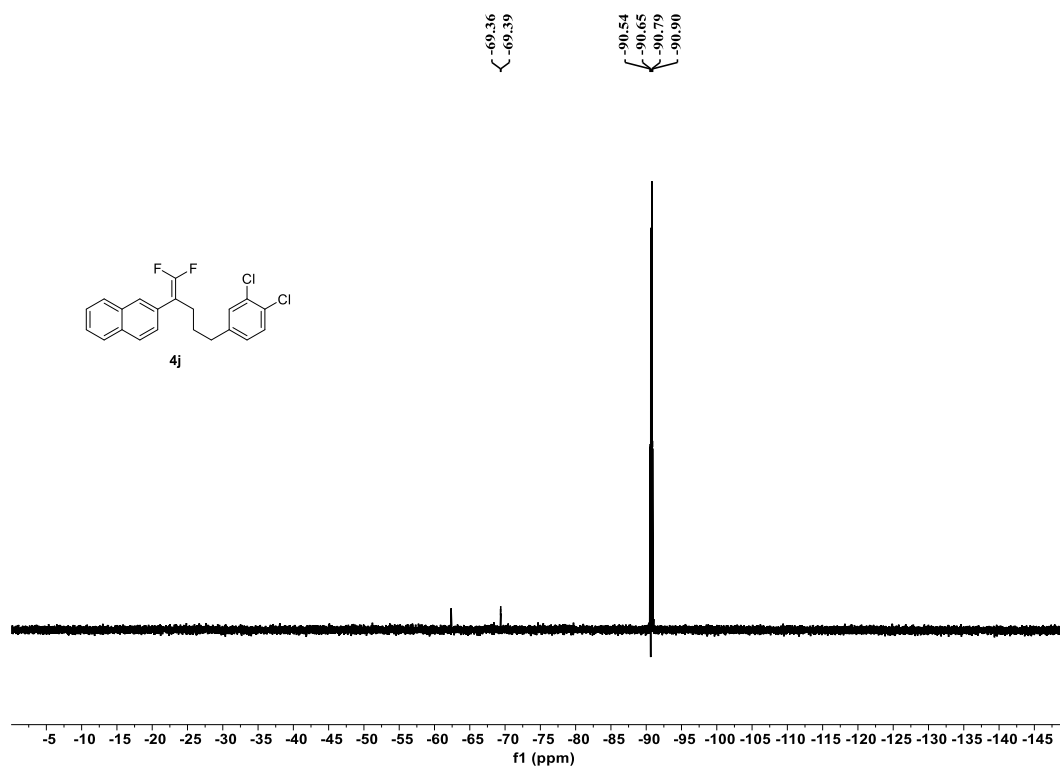
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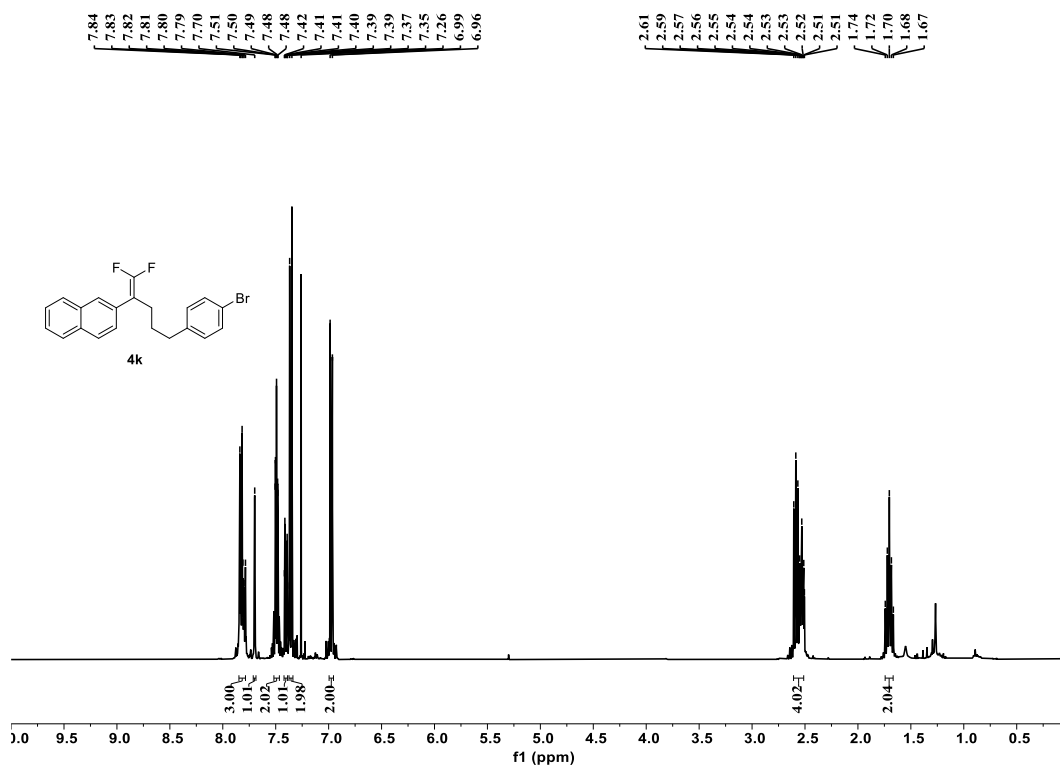
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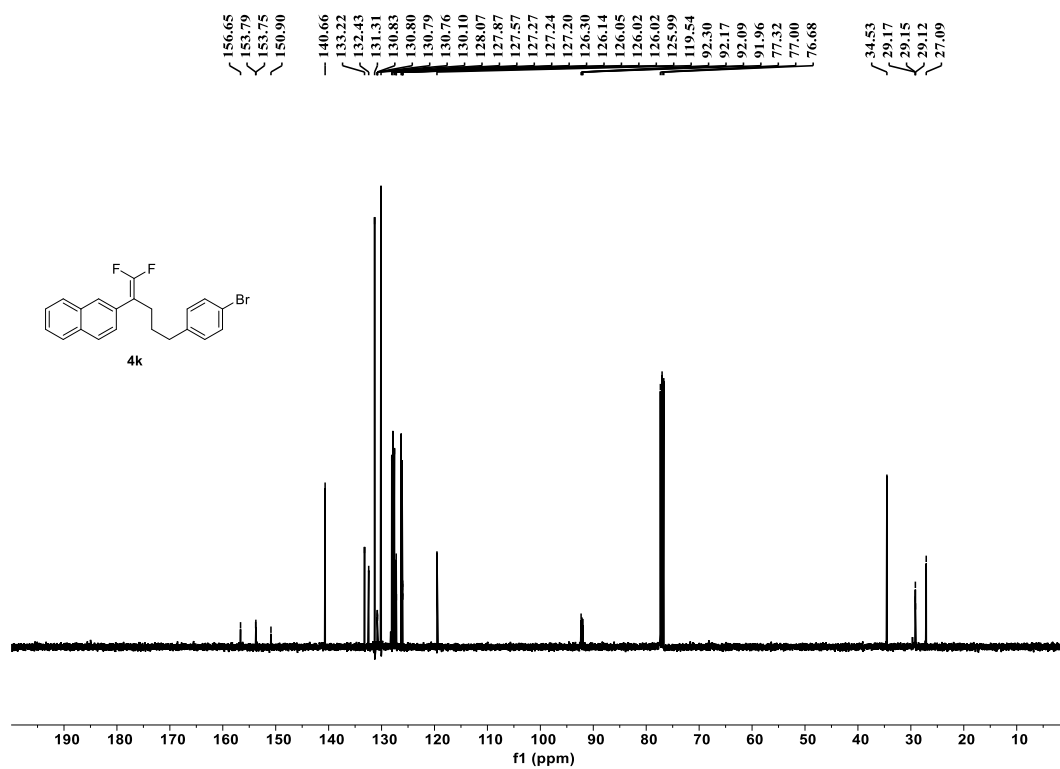
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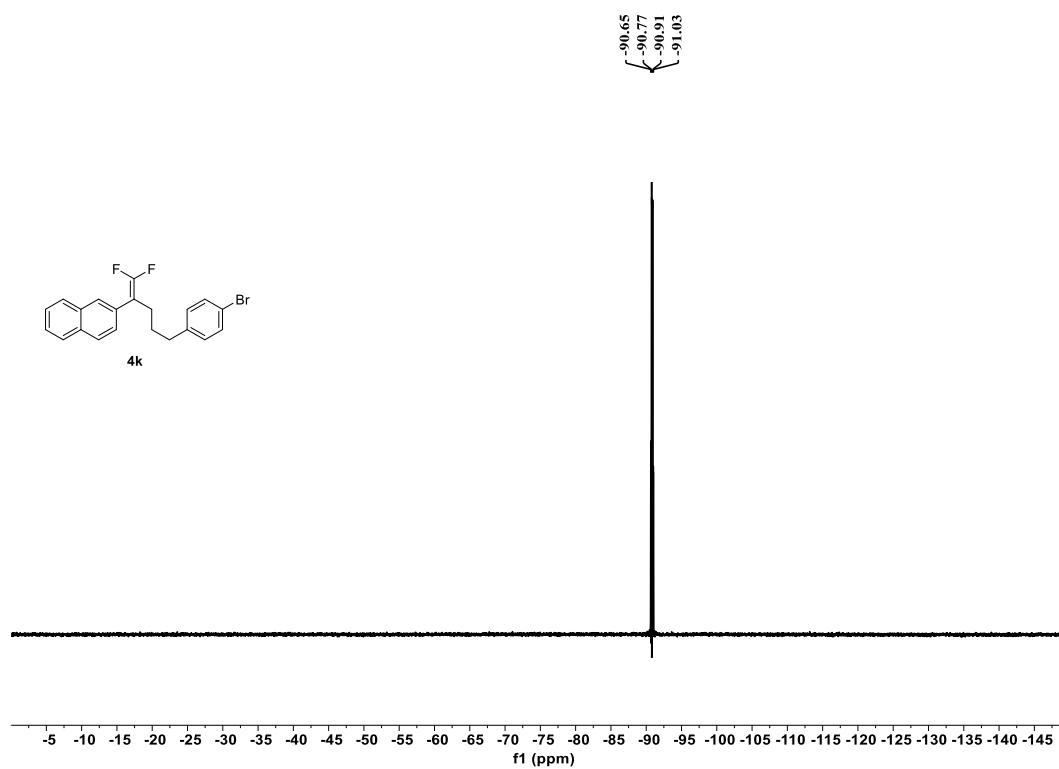
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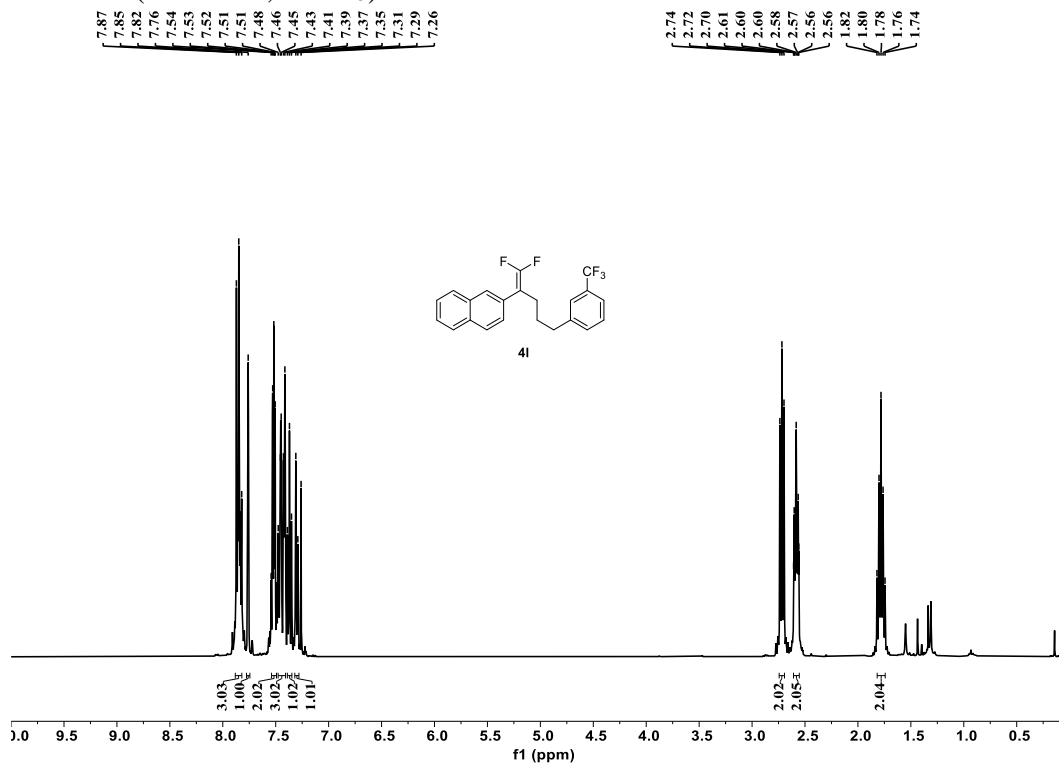
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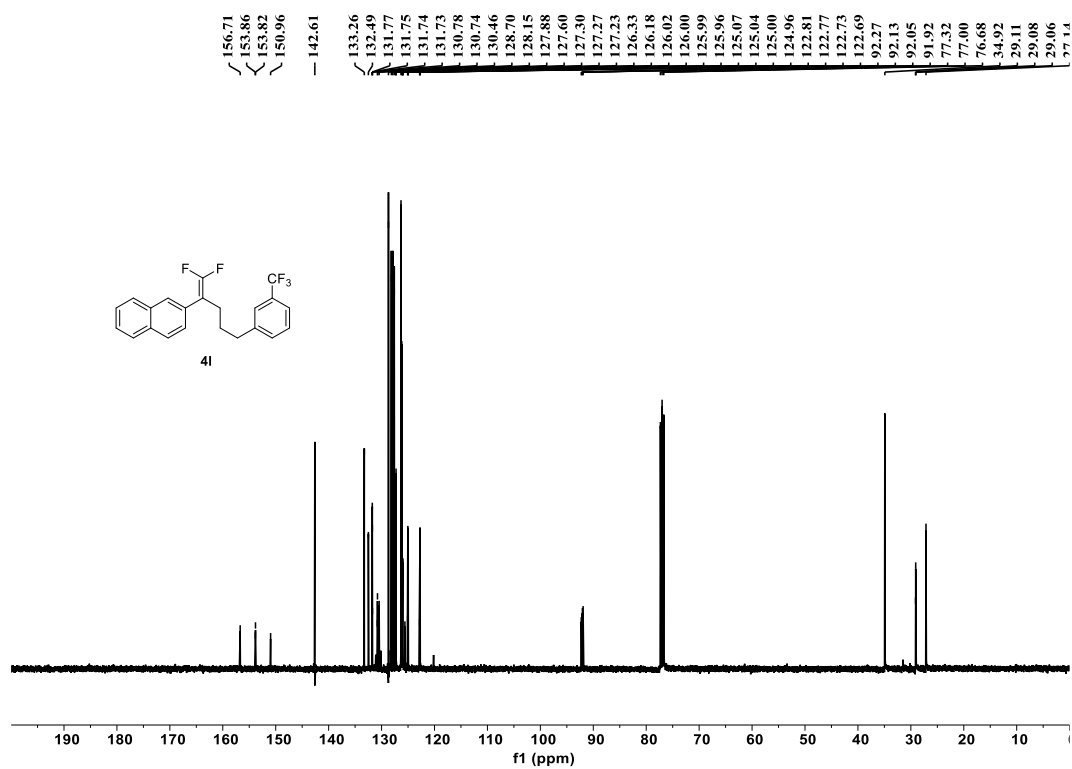
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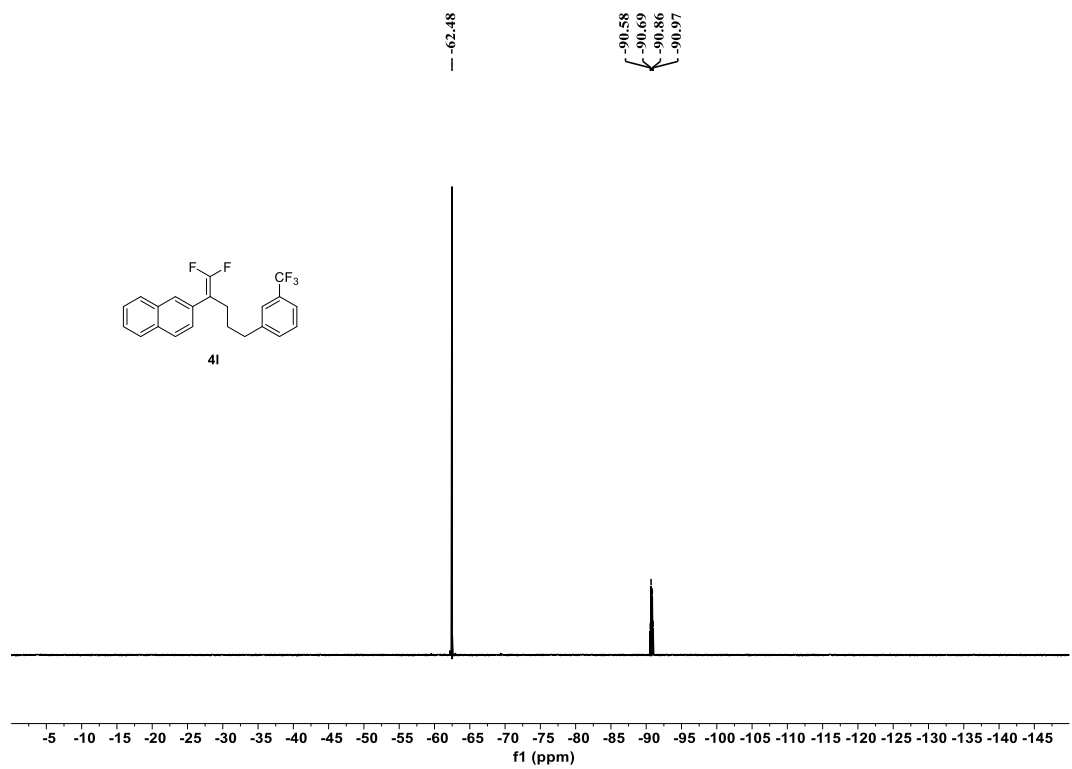
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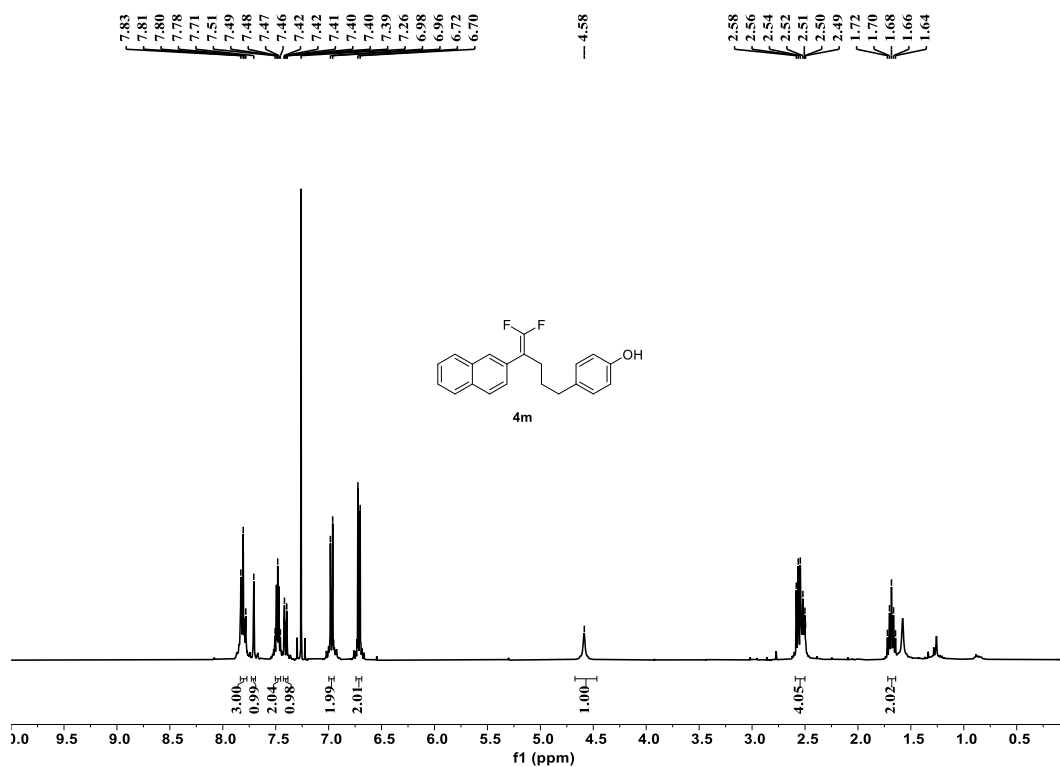
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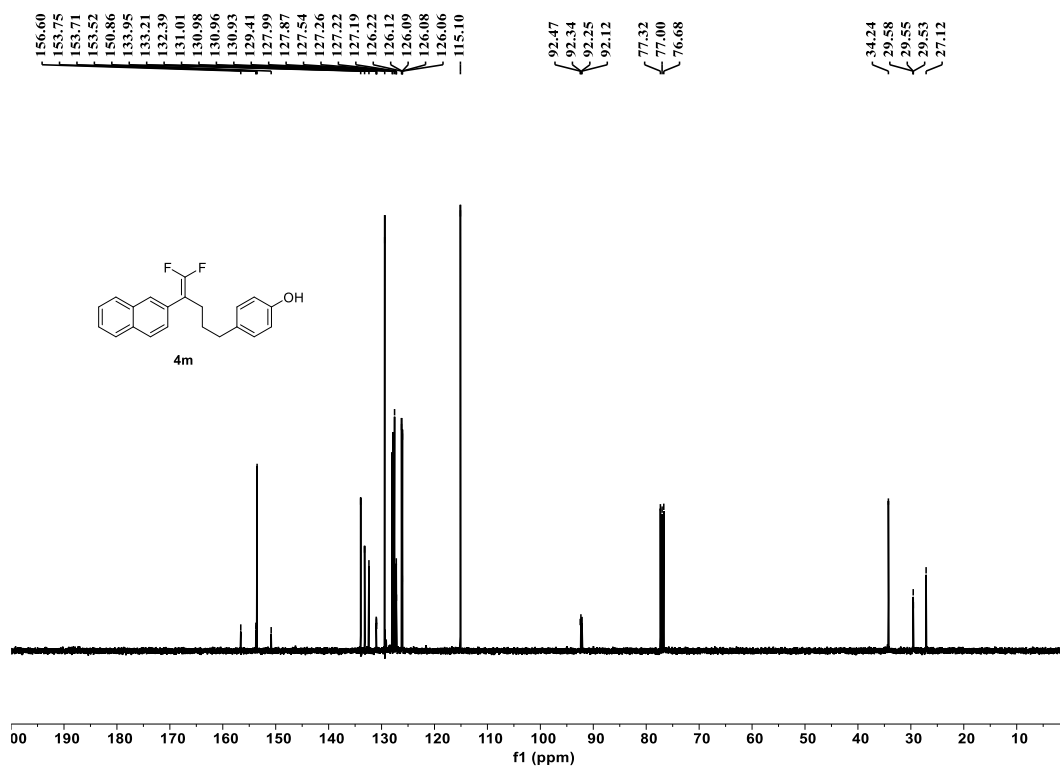
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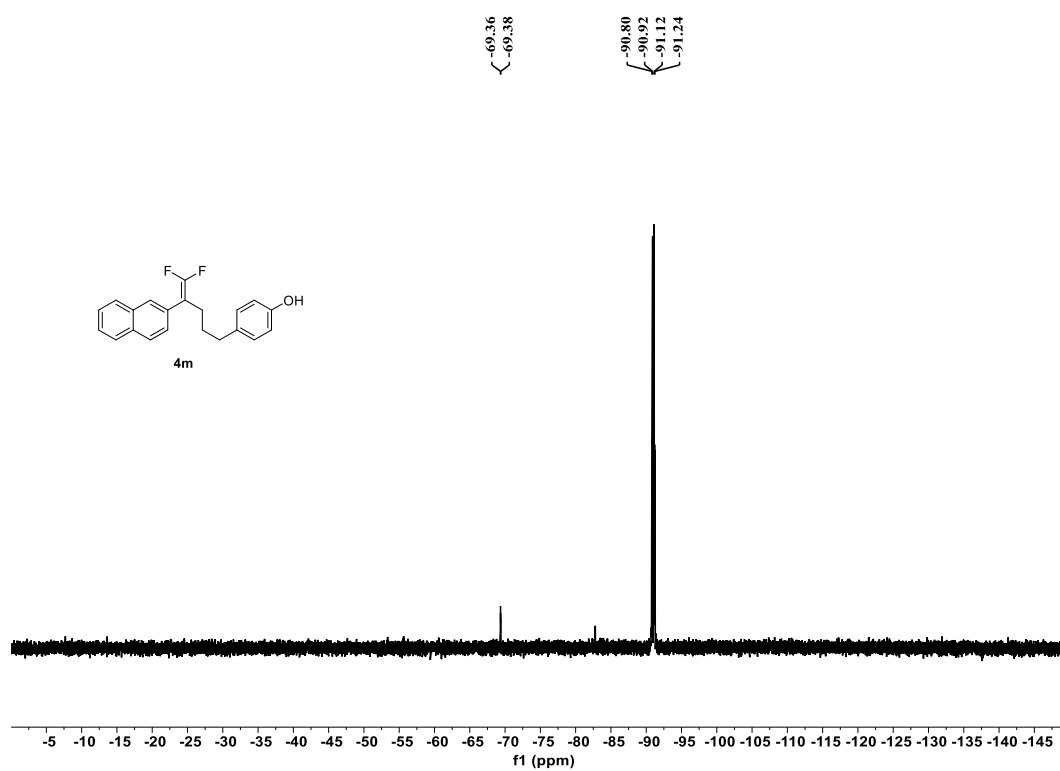
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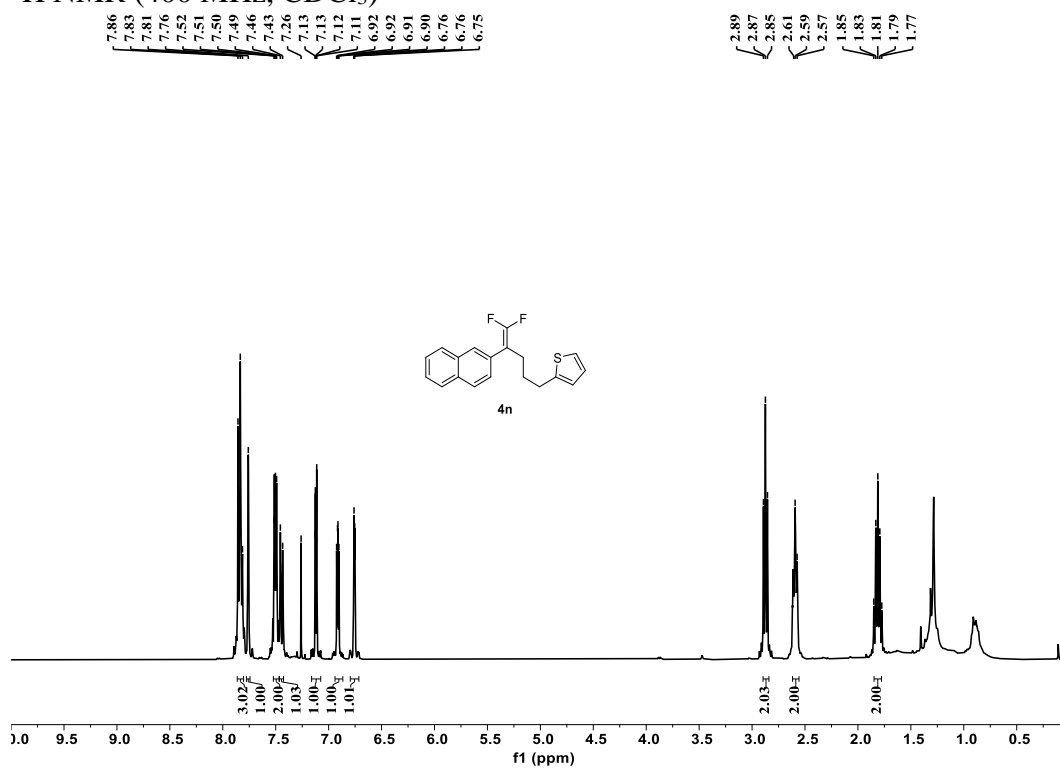
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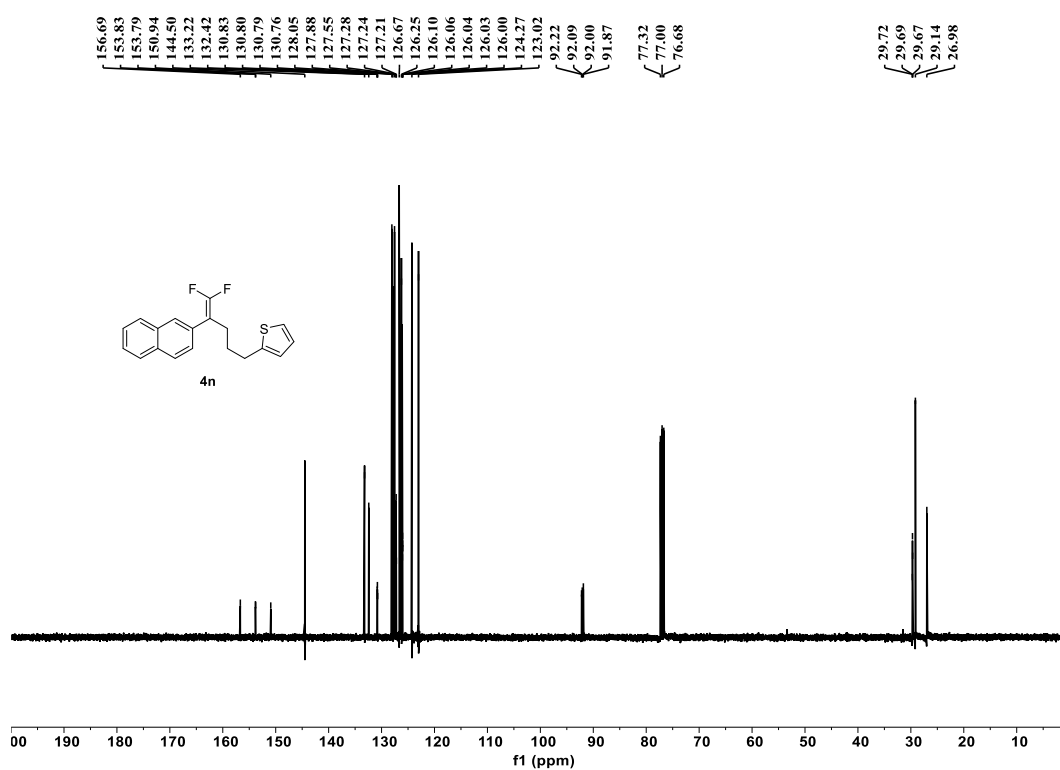
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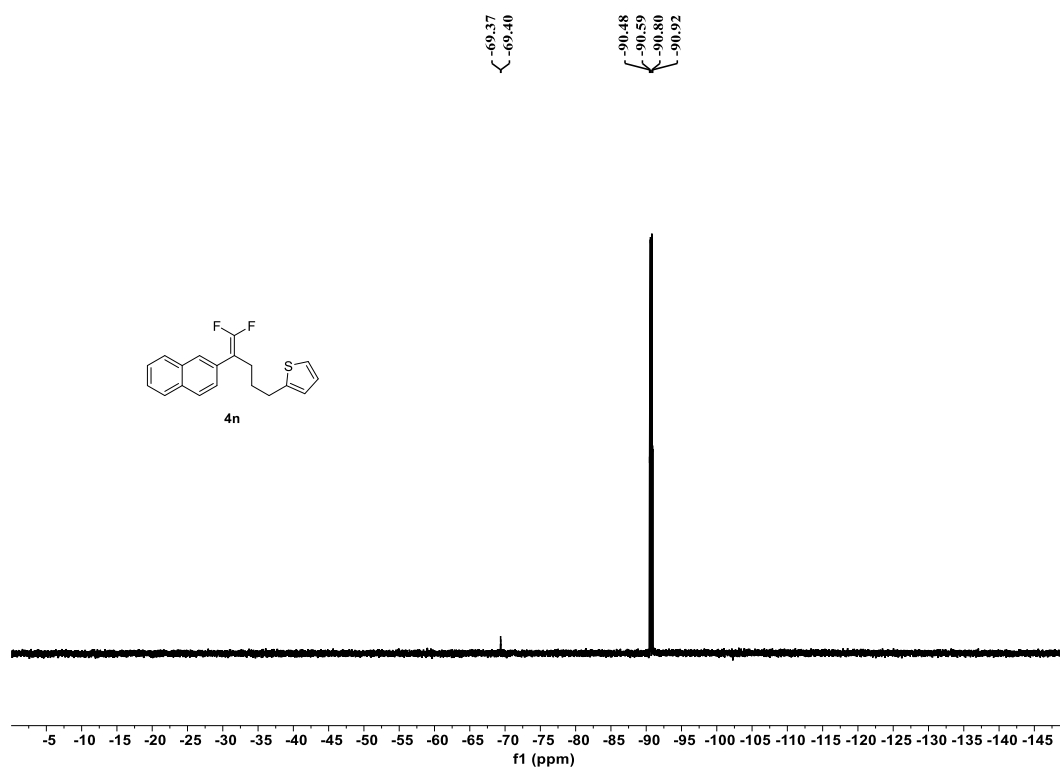
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¹³C NMR (100 MHz, CDCl₃)



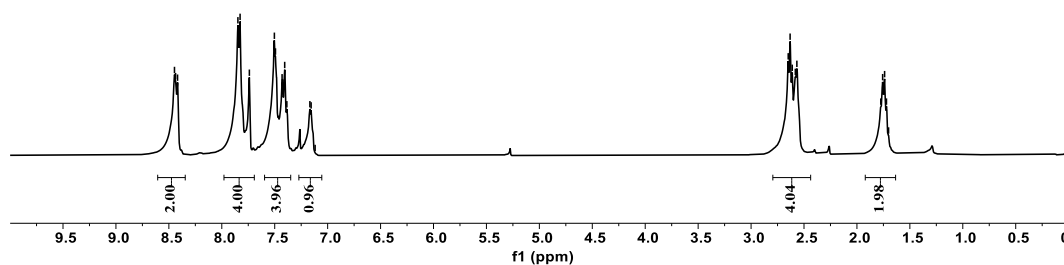
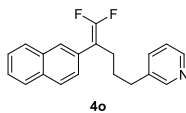
¹⁹F NMR (376 MHz, CDCl₃)



^1H NMR (400 MHz, CDCl_3)

8.45
8.44
8.42
7.85
7.83
7.74
7.50
7.49
7.43
7.41
7.39
7.26
7.17
7.16
7.12

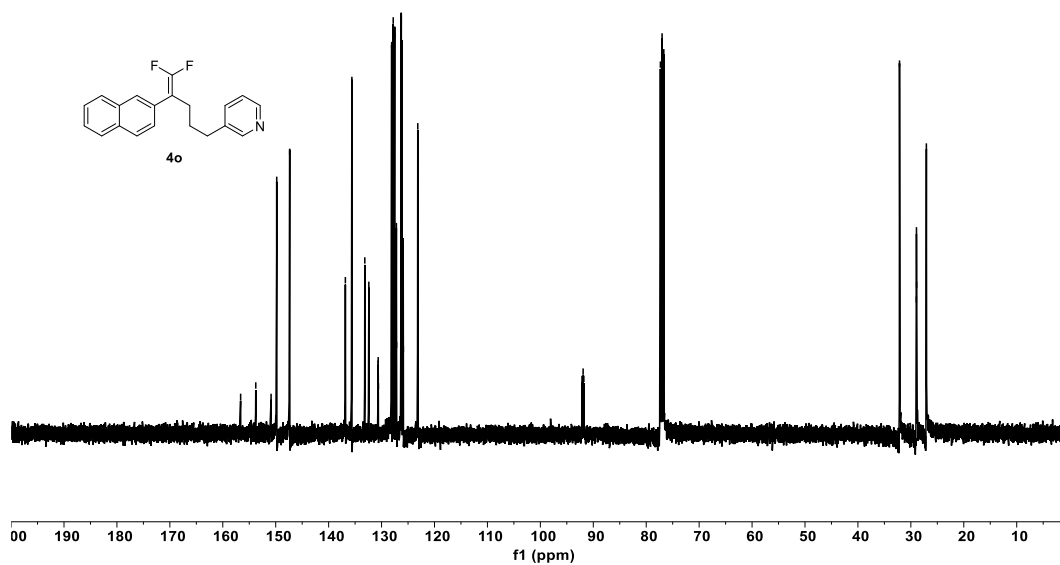
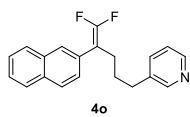
2.65
2.63
2.61
2.58
2.57
1.77
1.76
1.74
1.72
1.70



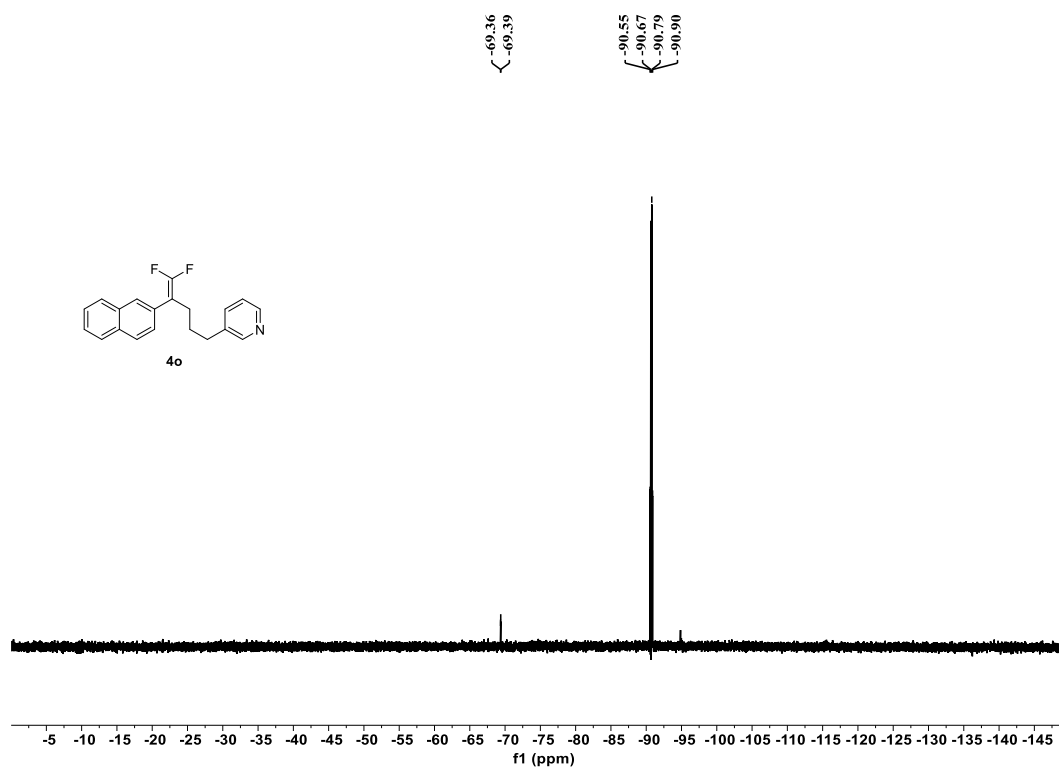
^{13}C NMR (100 MHz, CDCl_3)

156.63
153.77
153.74
150.88
149.81
147.36
136.84
135.61
133.17
132.41
130.66
130.64
130.62
130.60
128.09
127.80
127.52
127.23
127.20
127.17
126.28
126.13
125.94
125.91
125.88
123.16
92.13
92.00
91.92
91.78
77.32
77.00
76.68

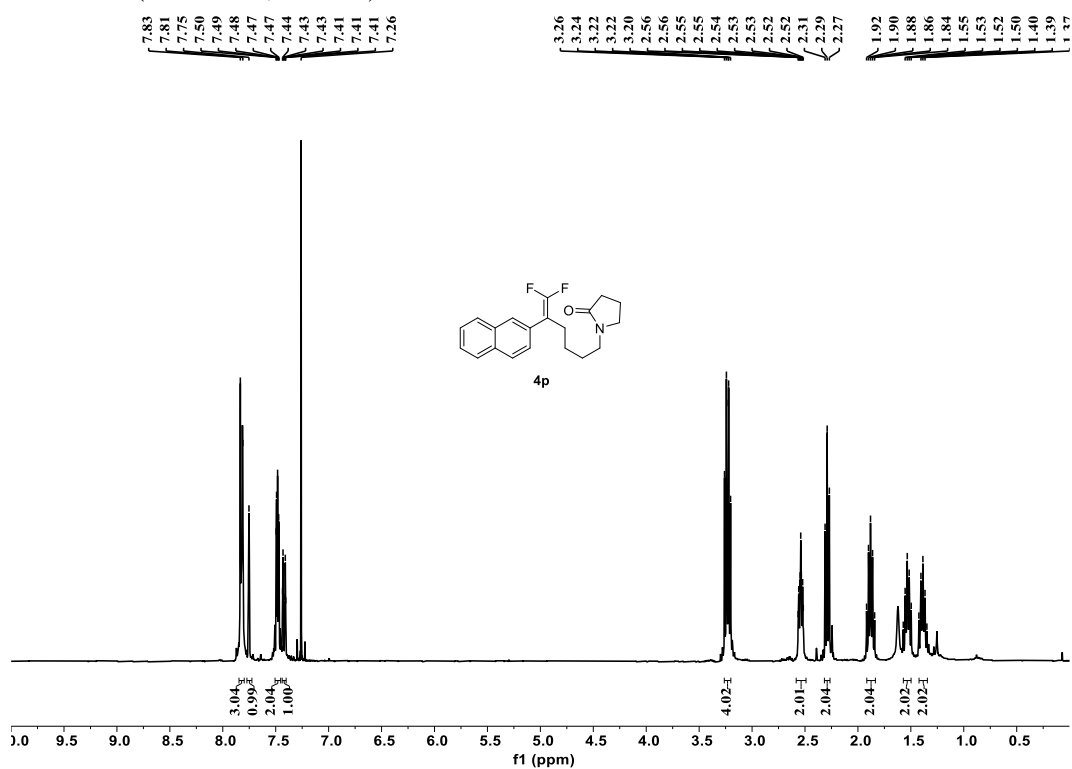
32.14
28.96
28.94
28.91
27.07



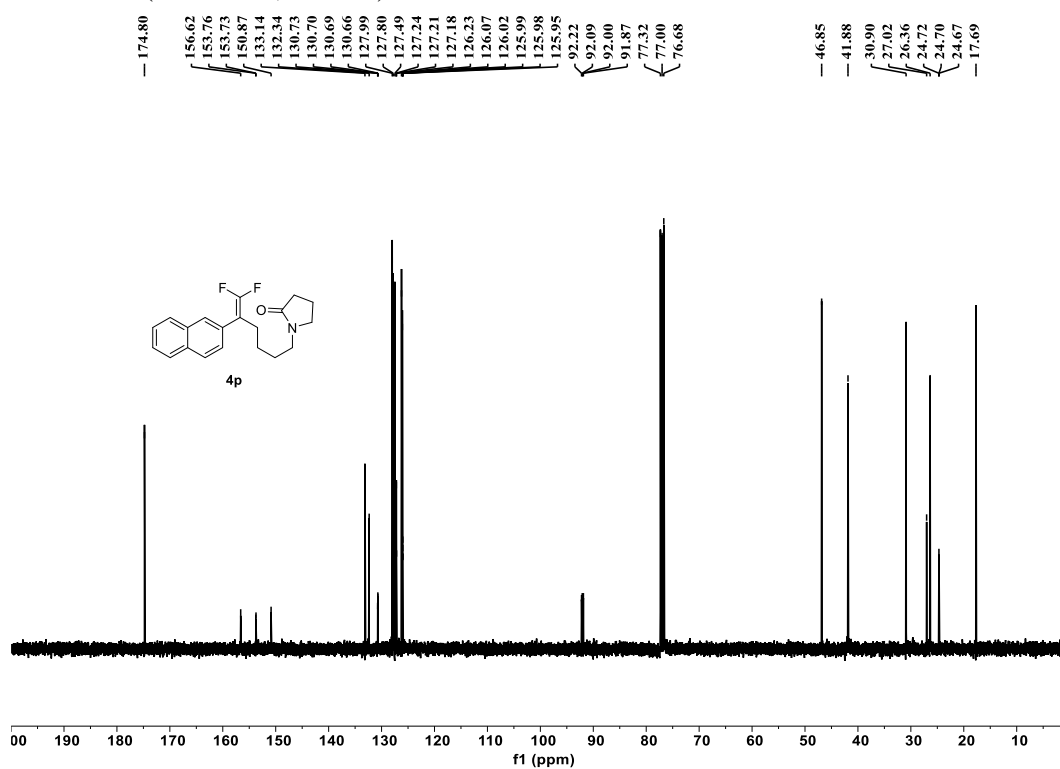
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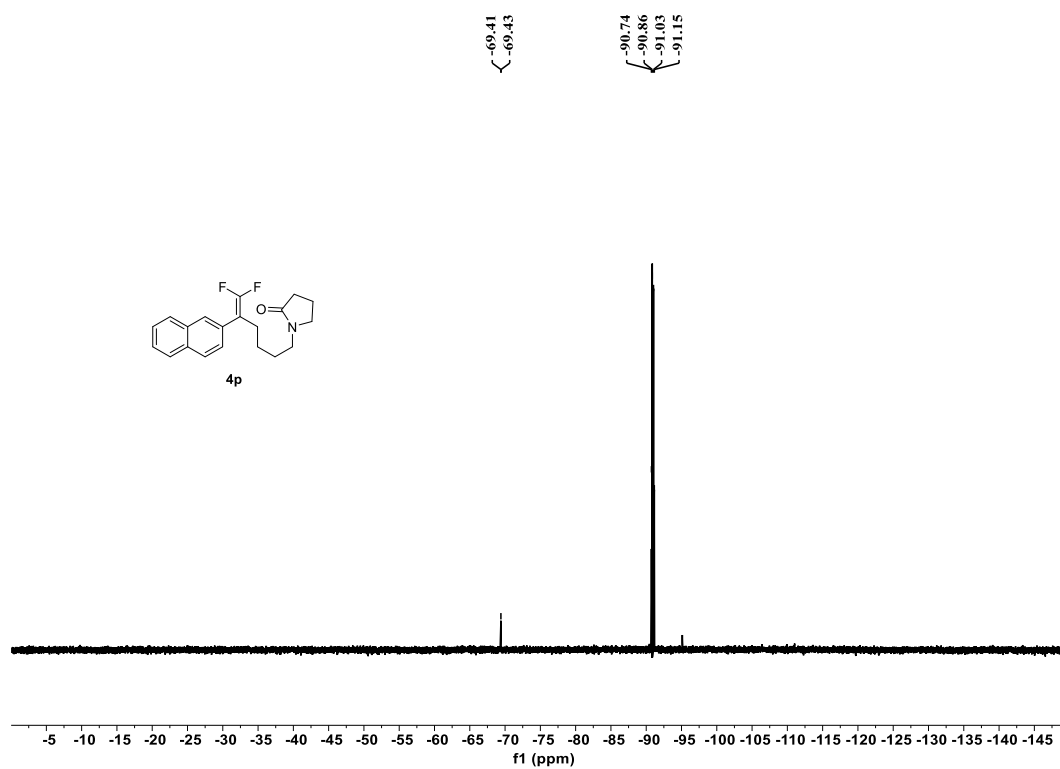
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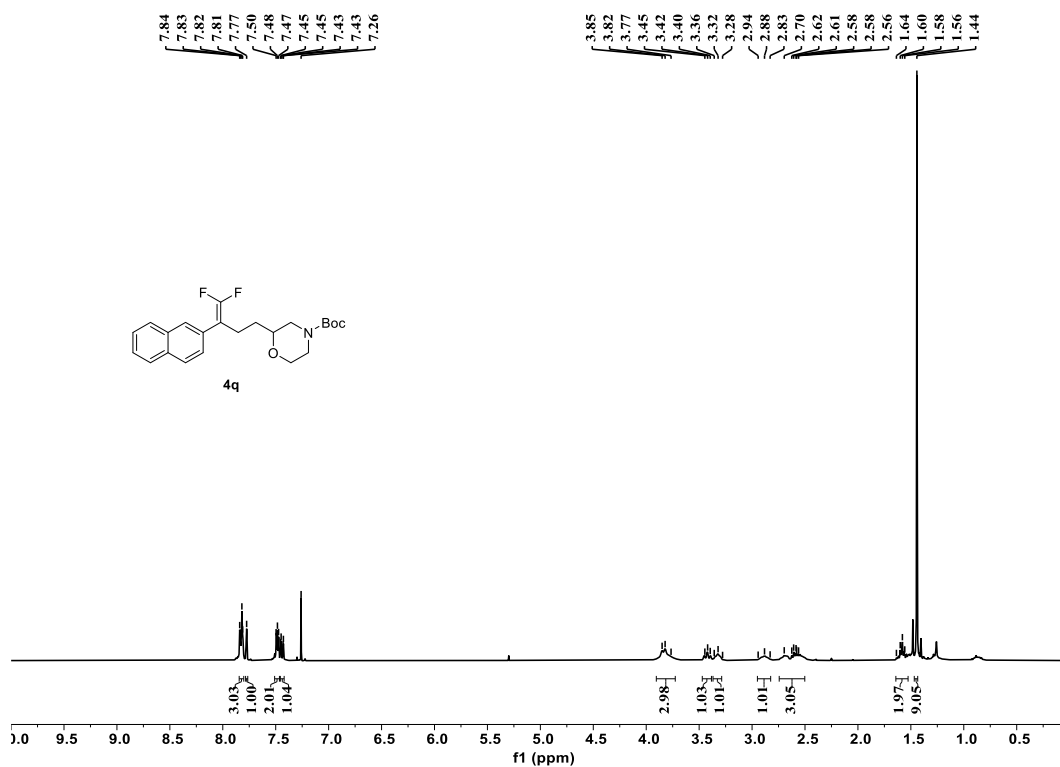
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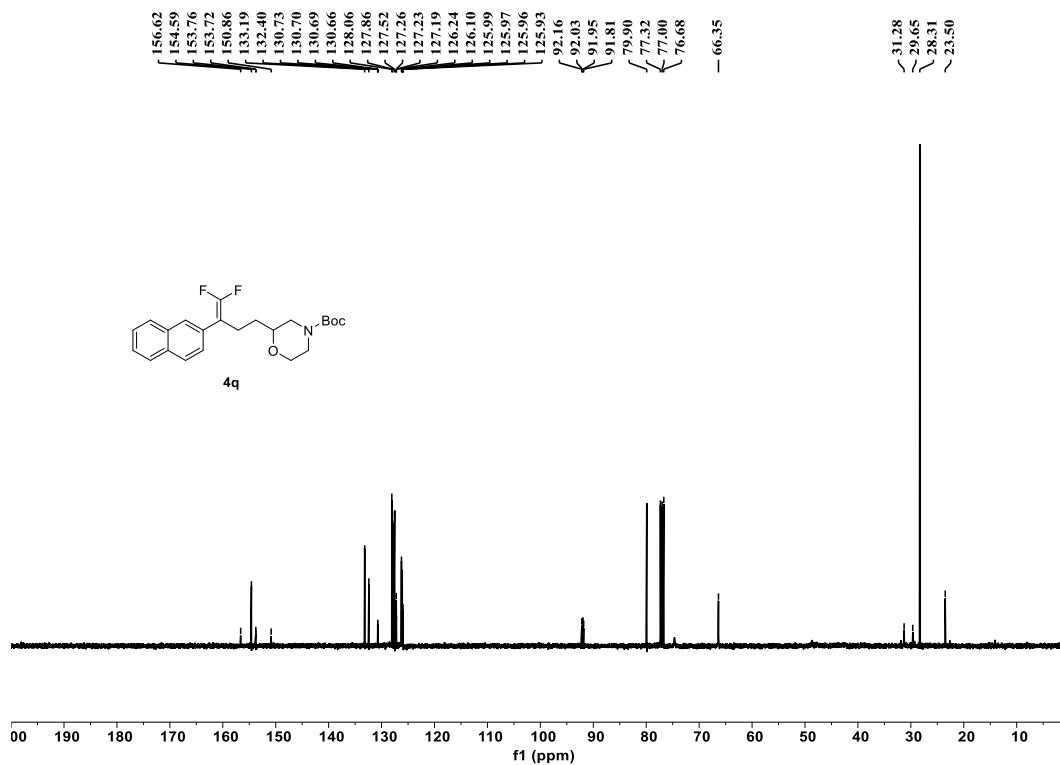
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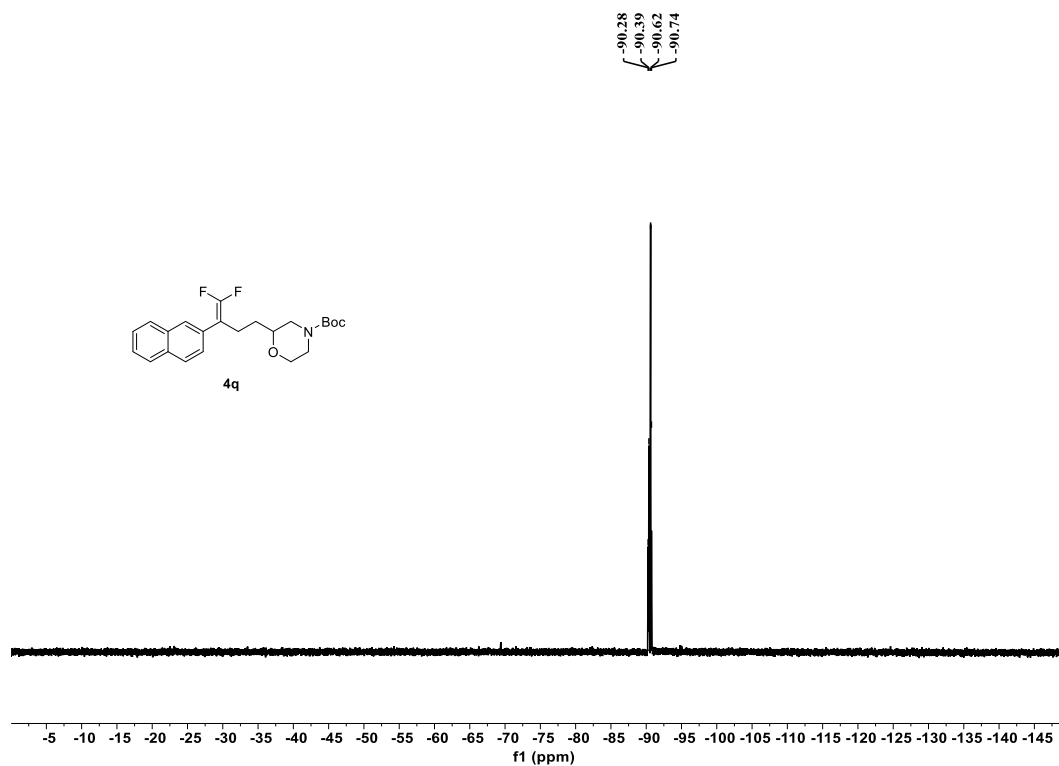
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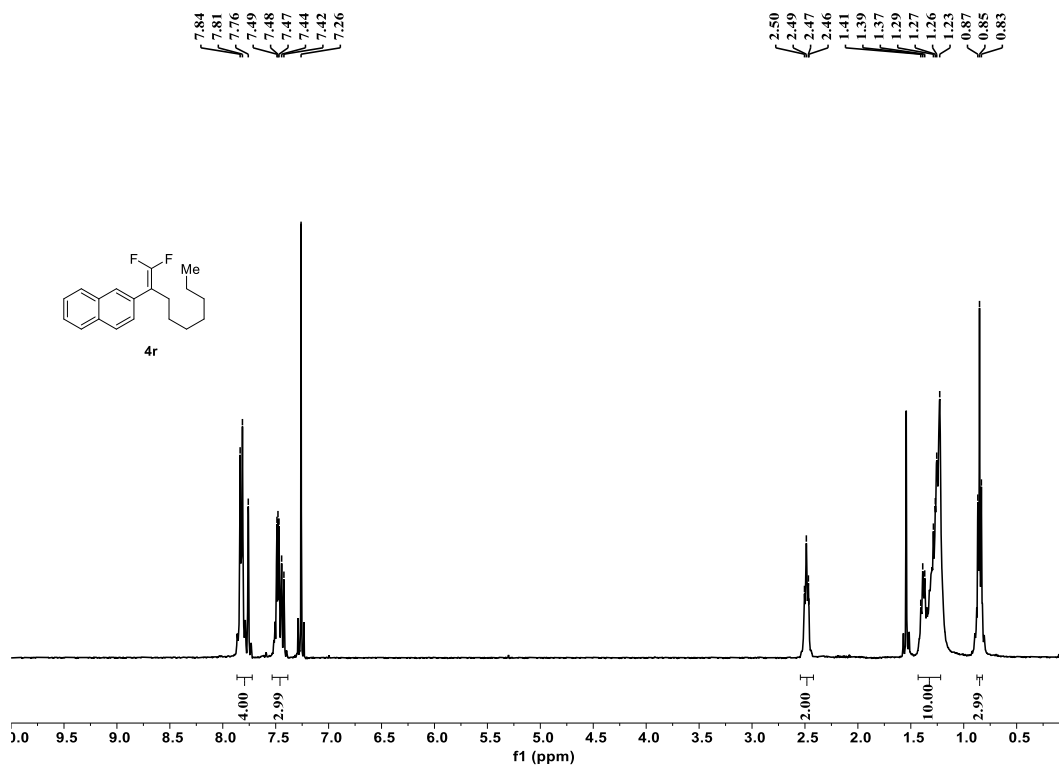
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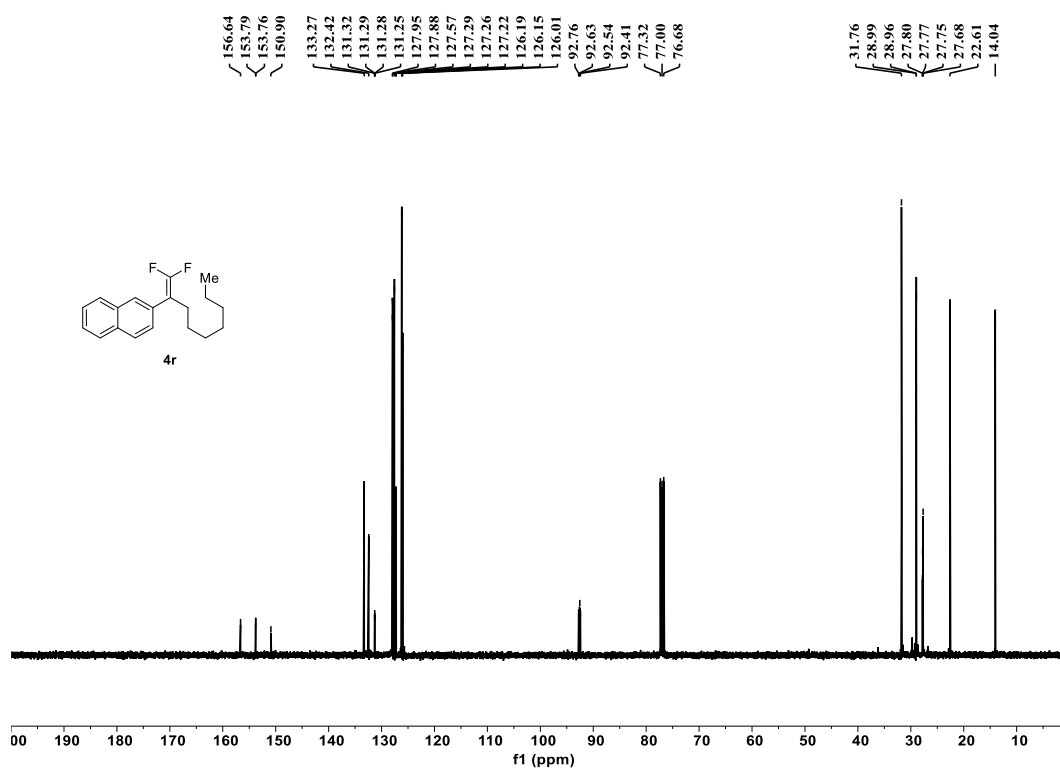
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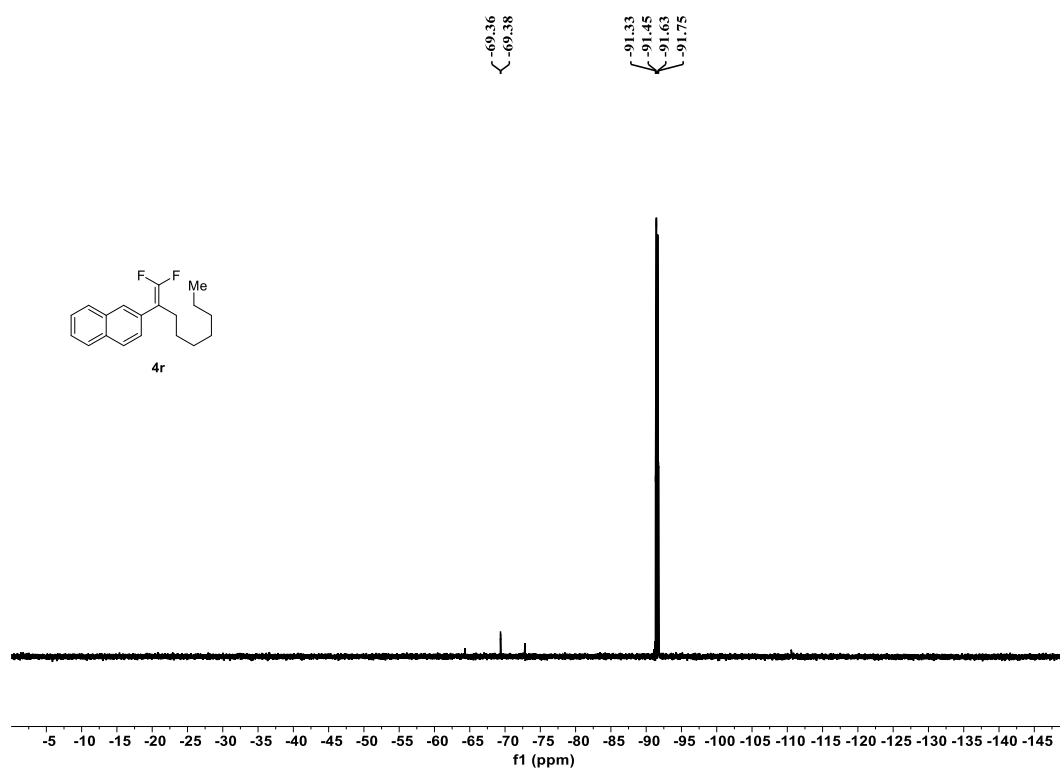
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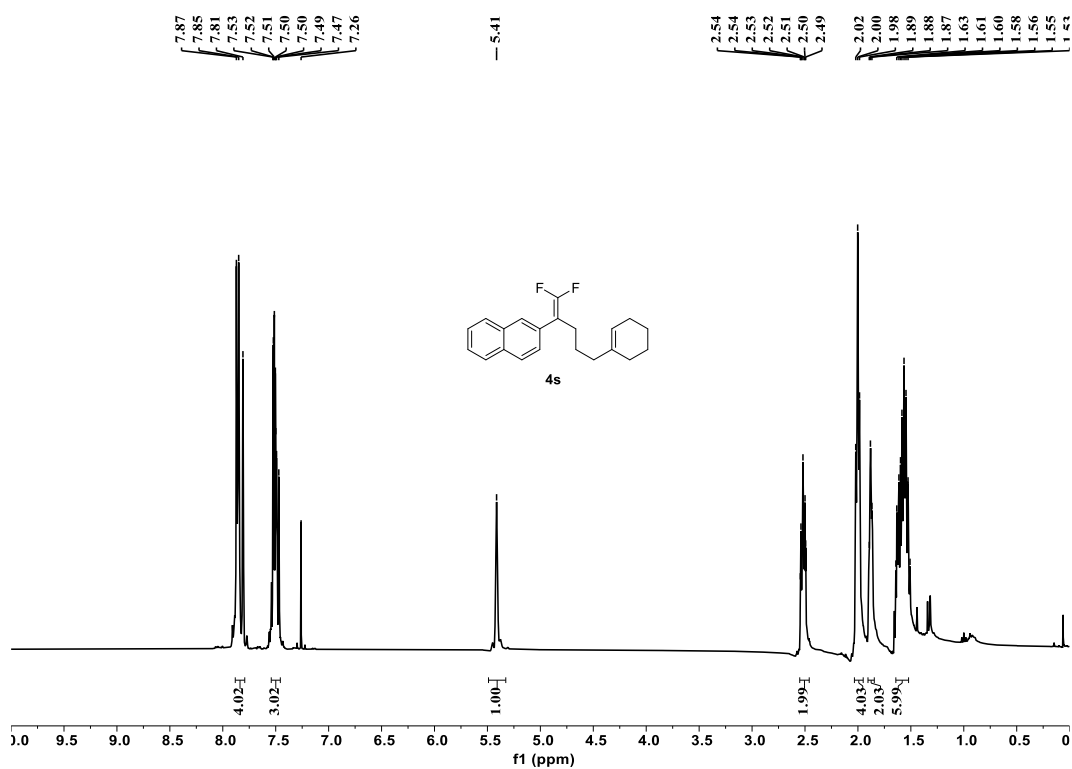
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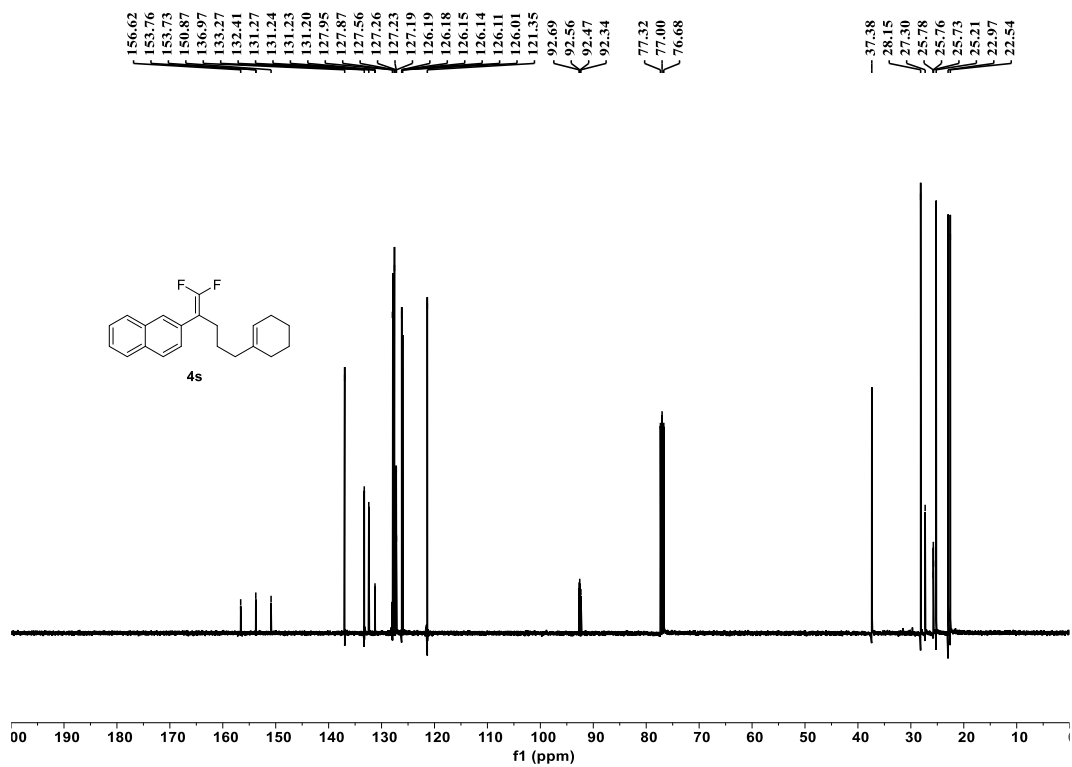
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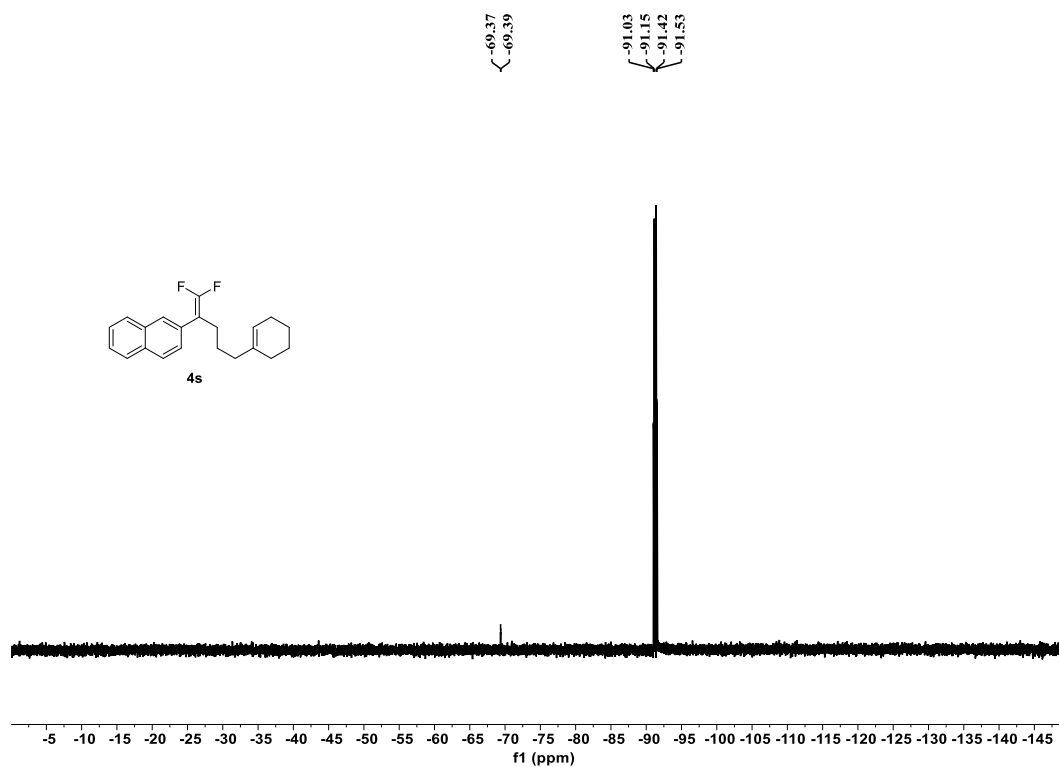
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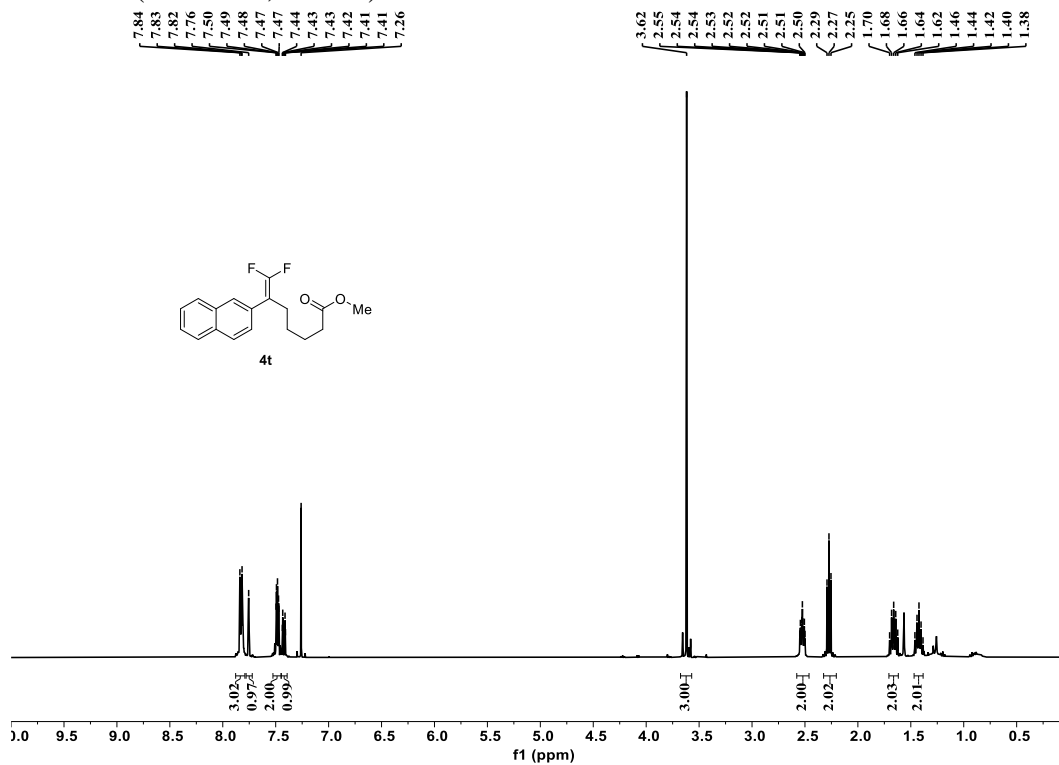
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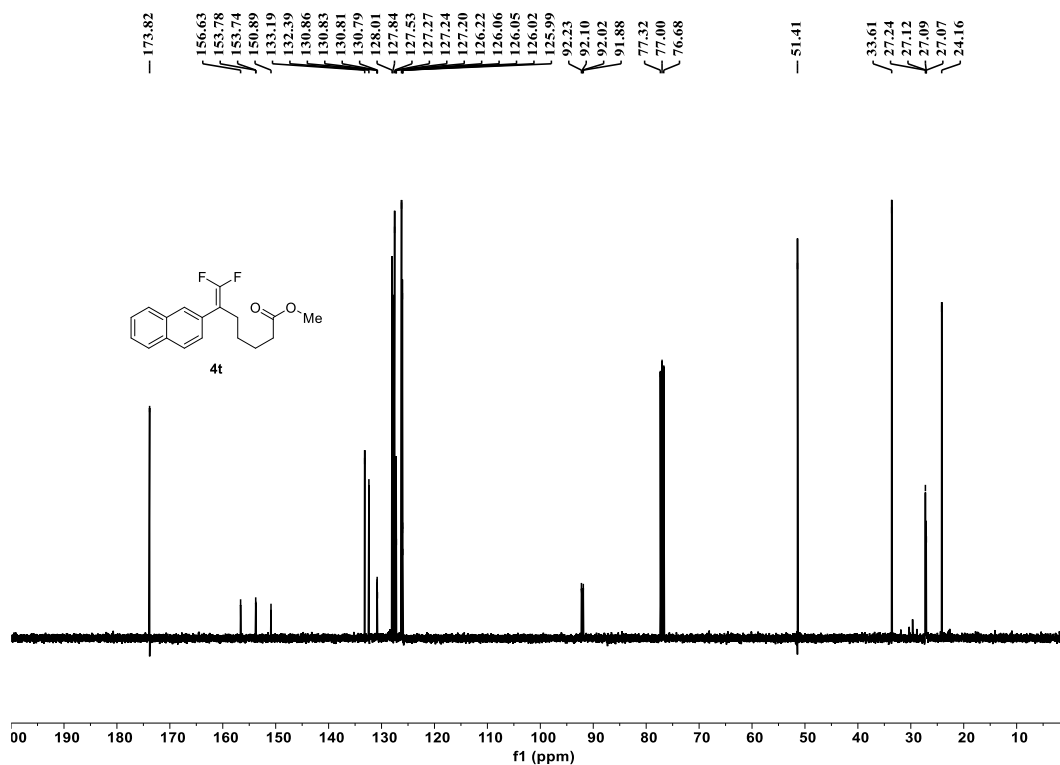
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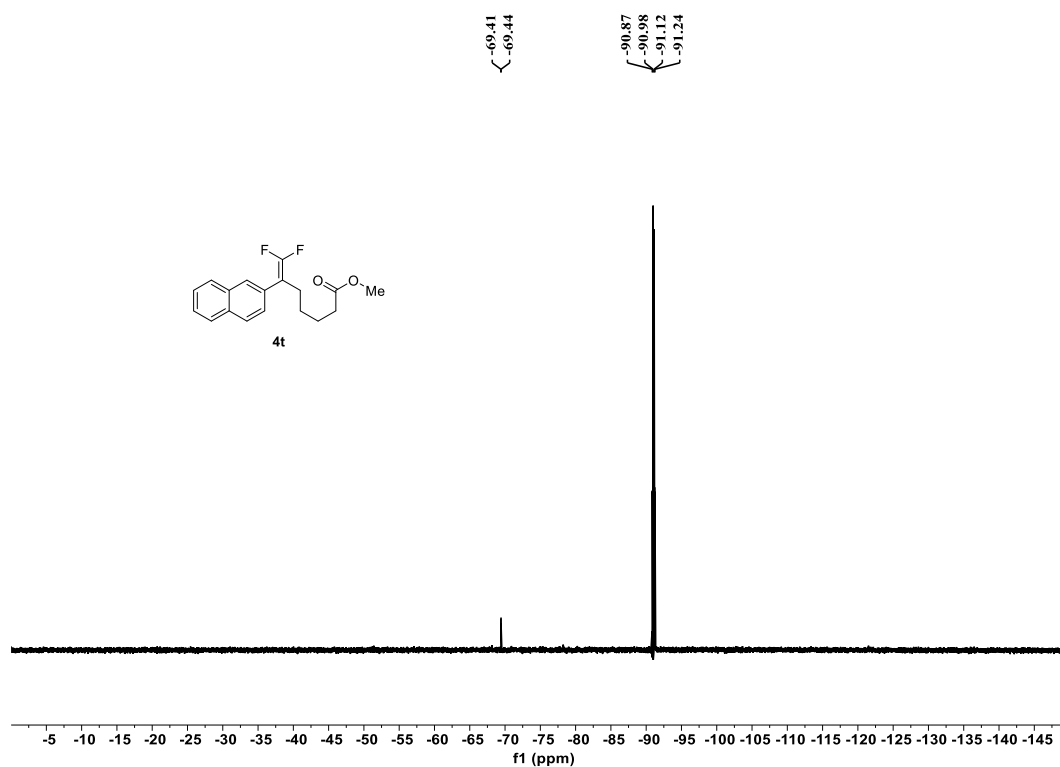
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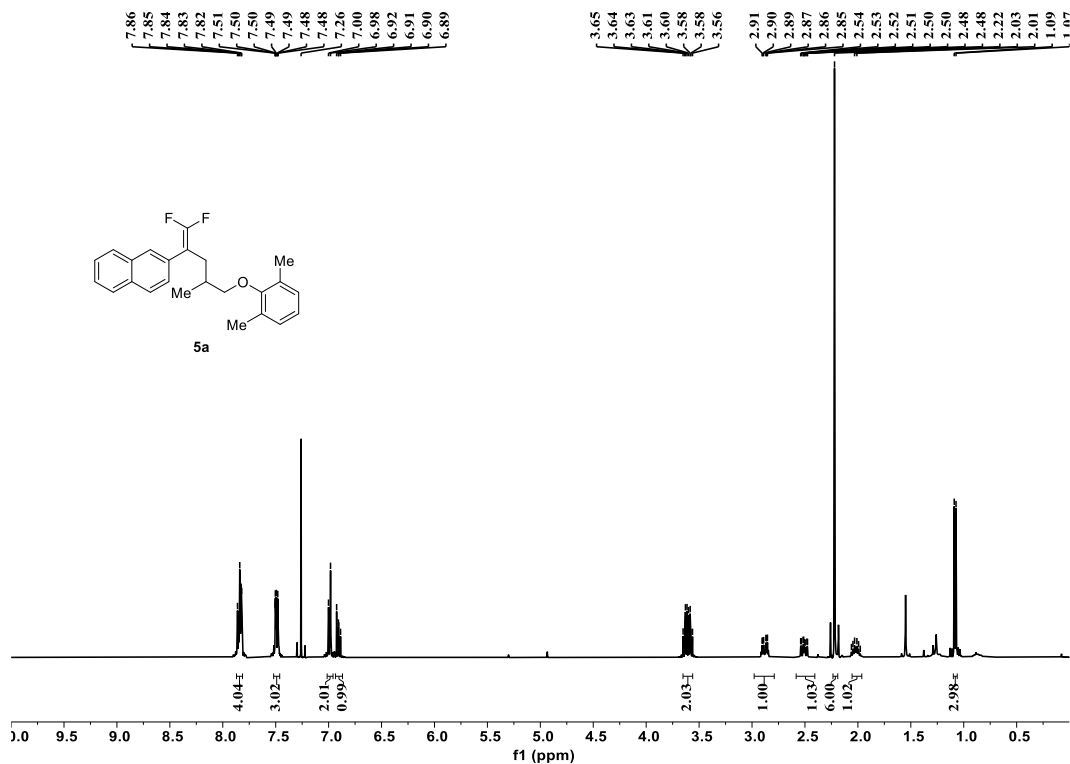
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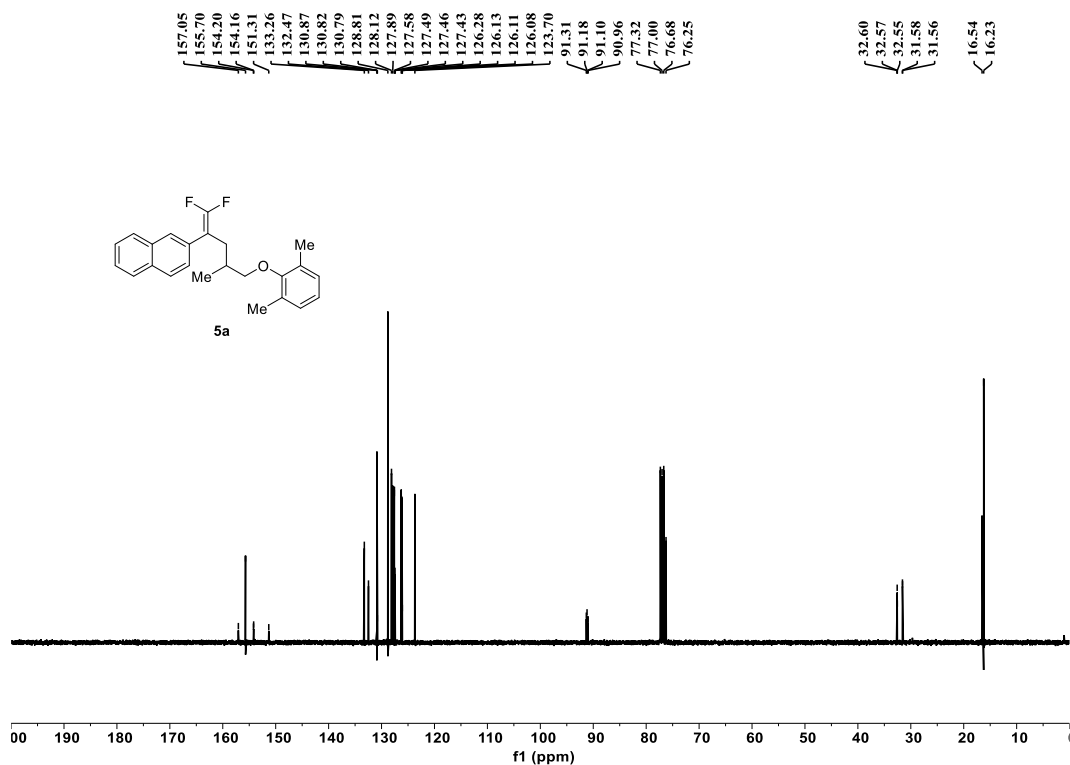
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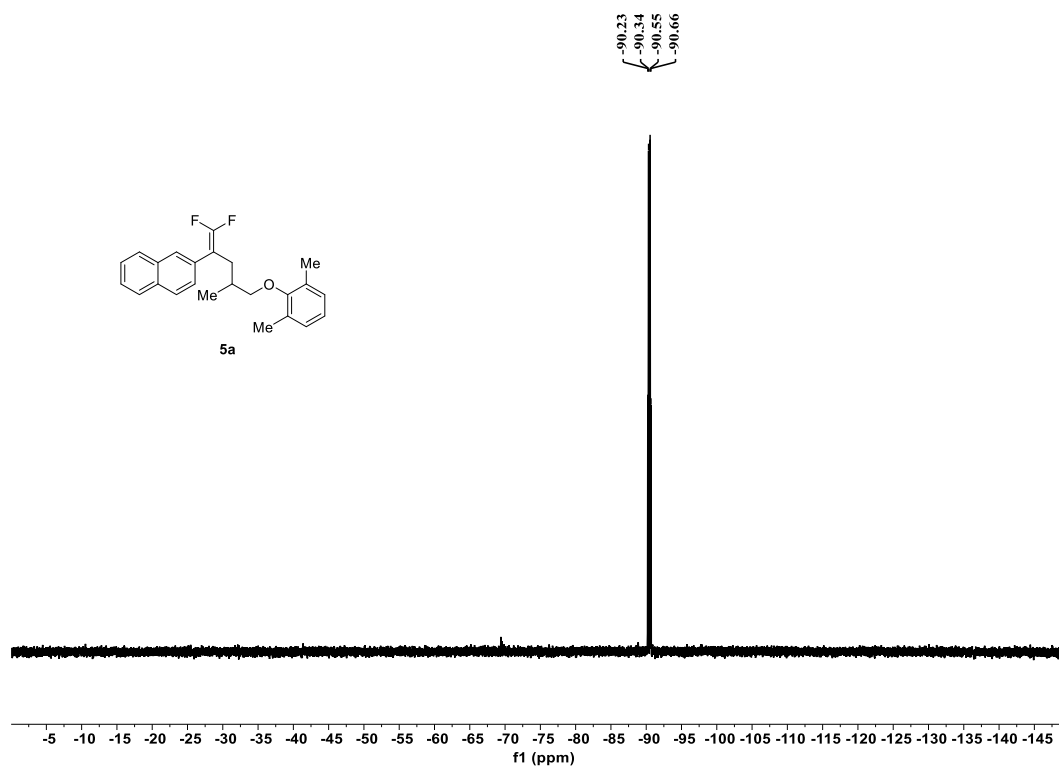
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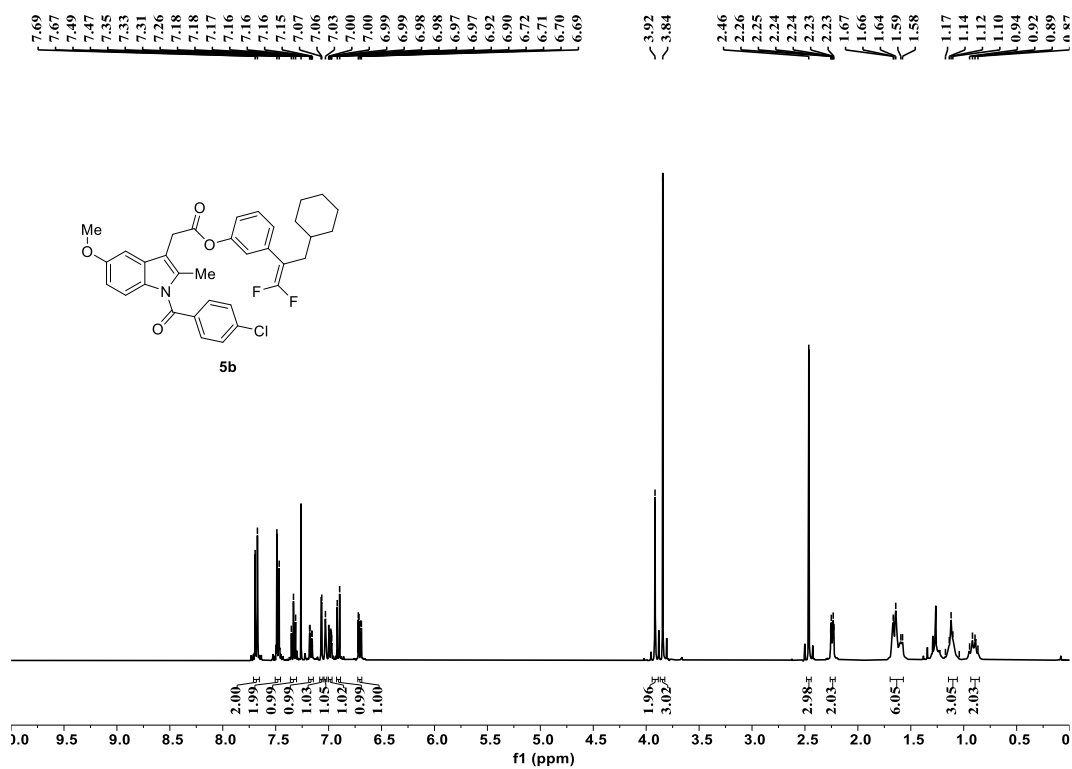
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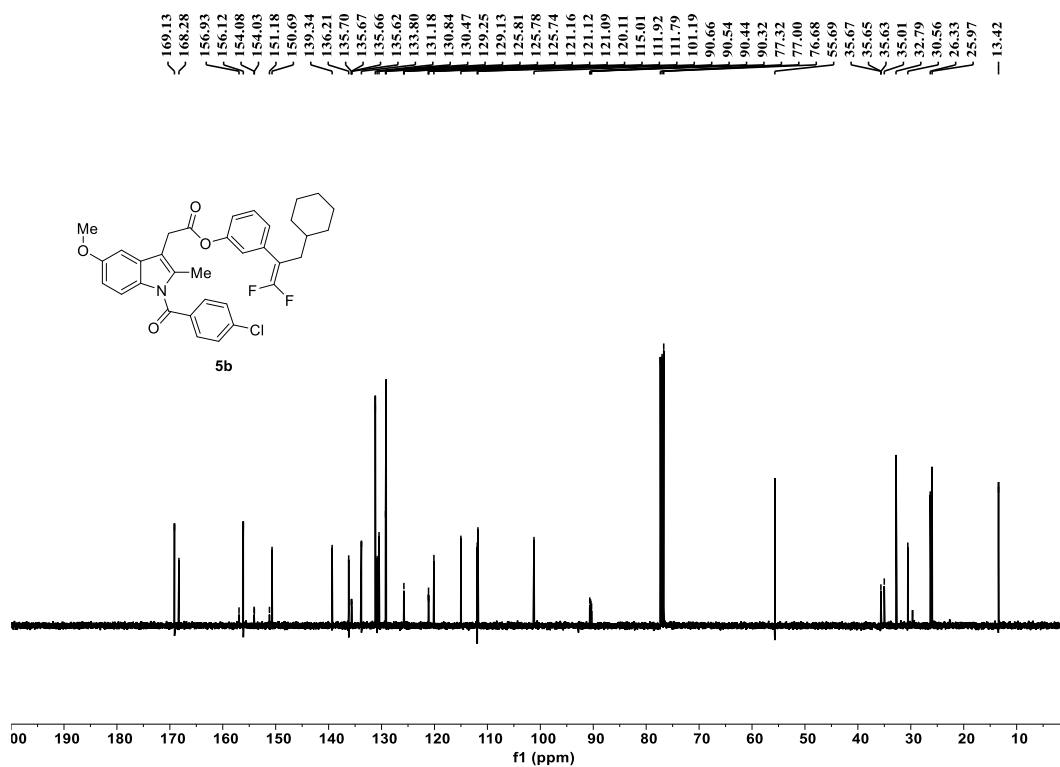
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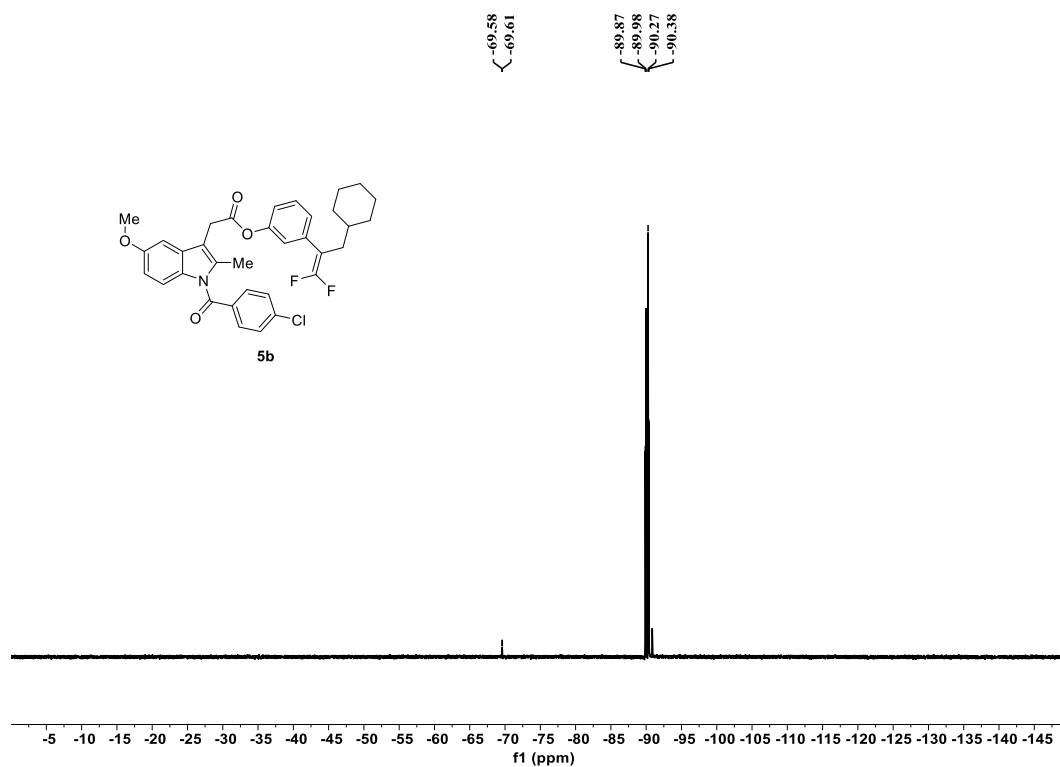
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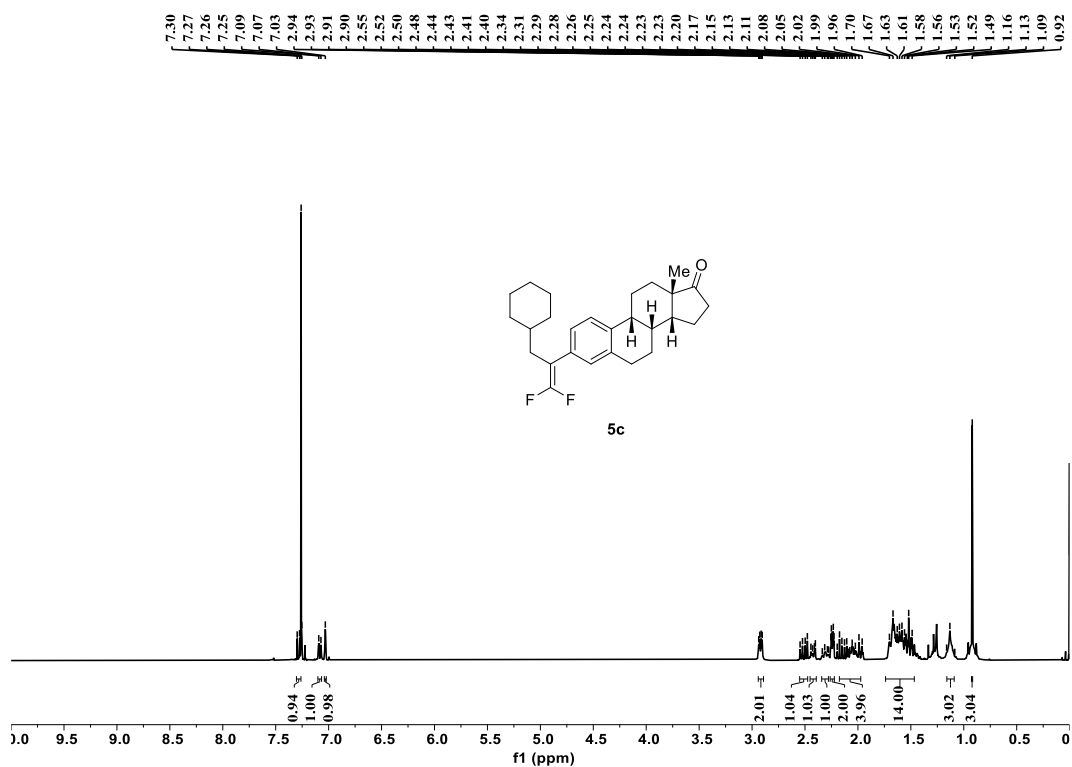
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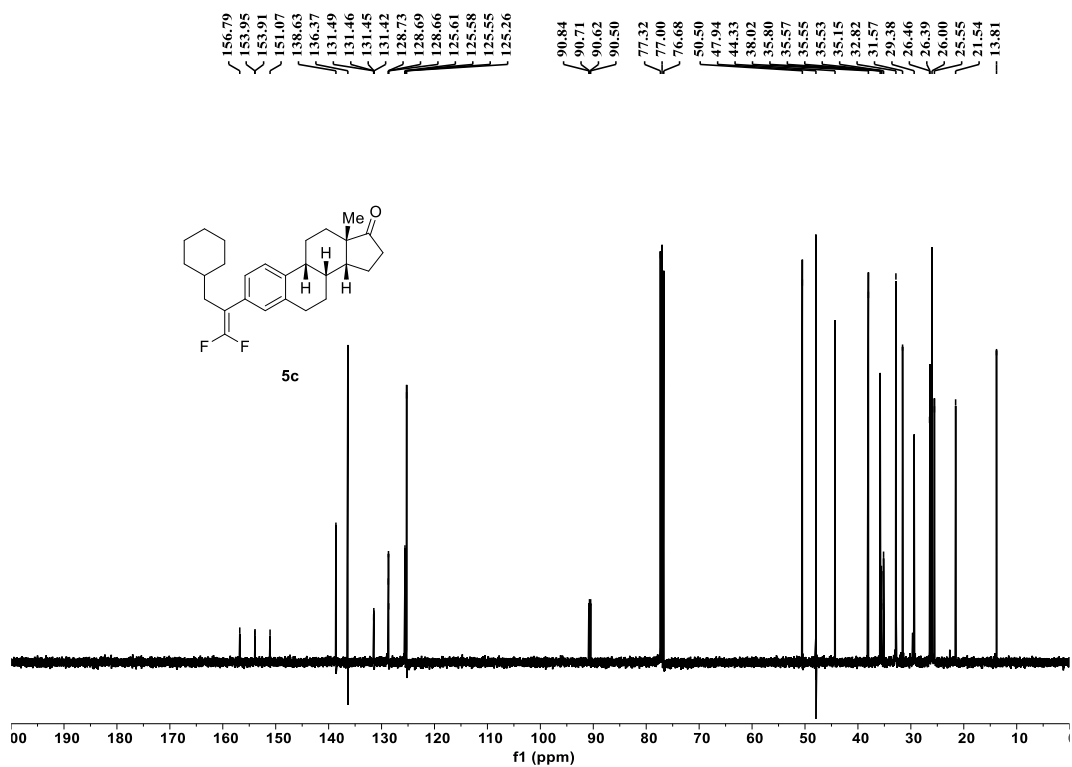
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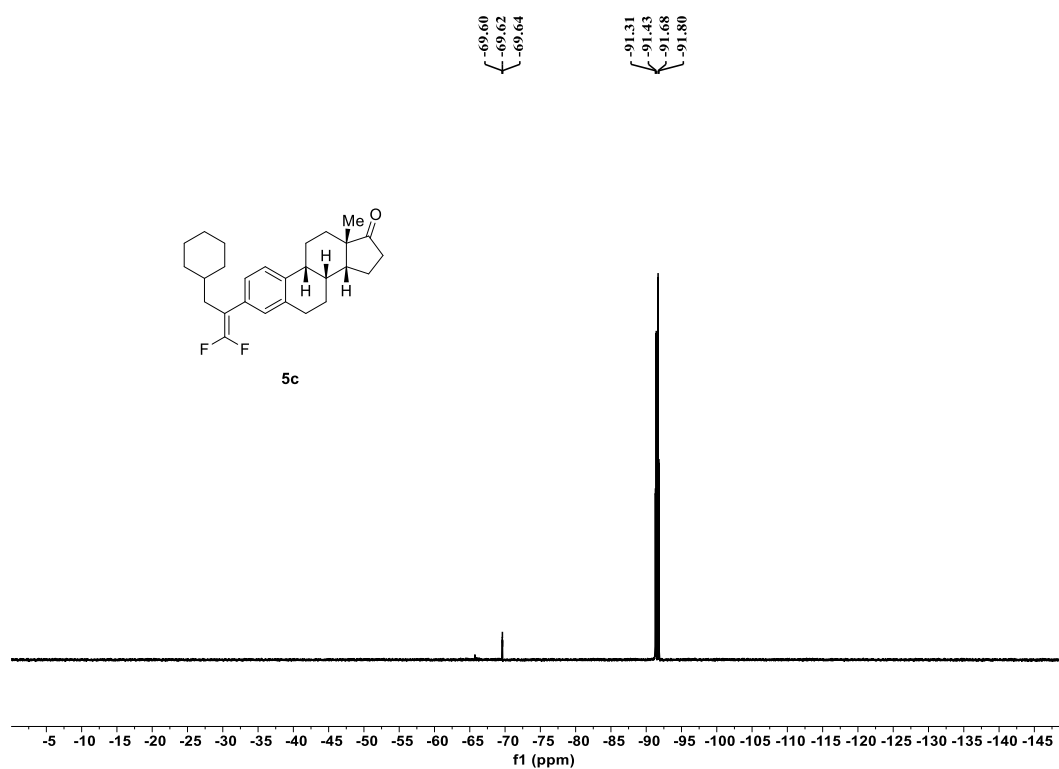
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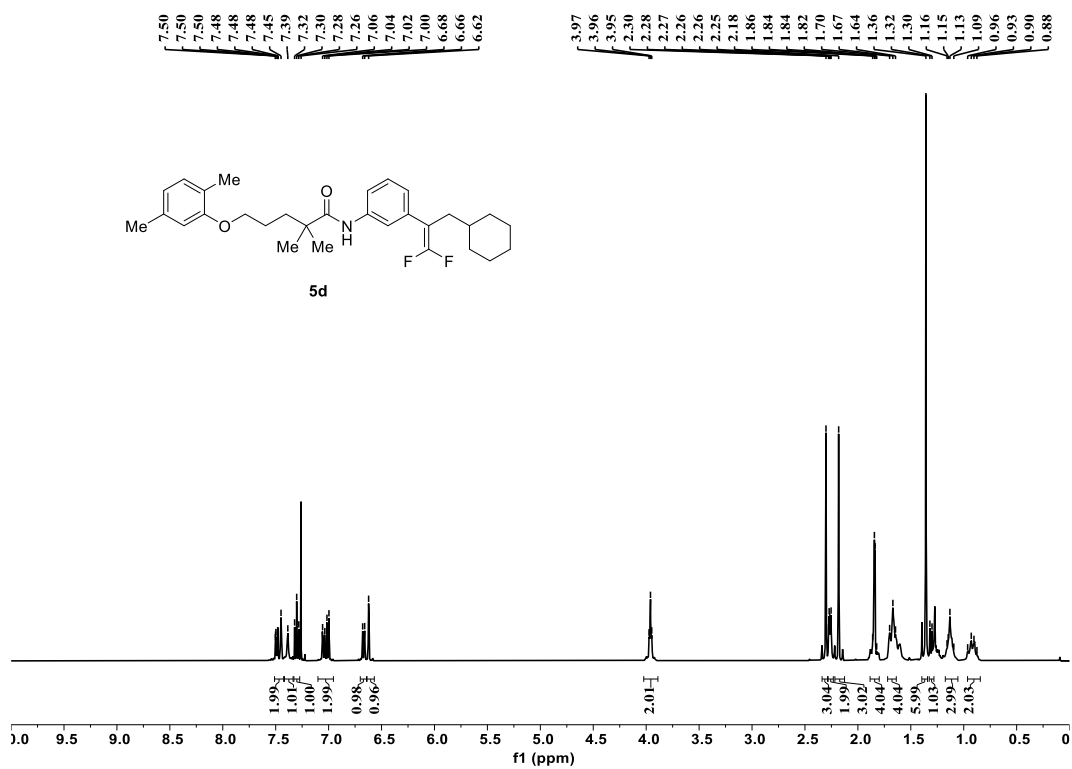
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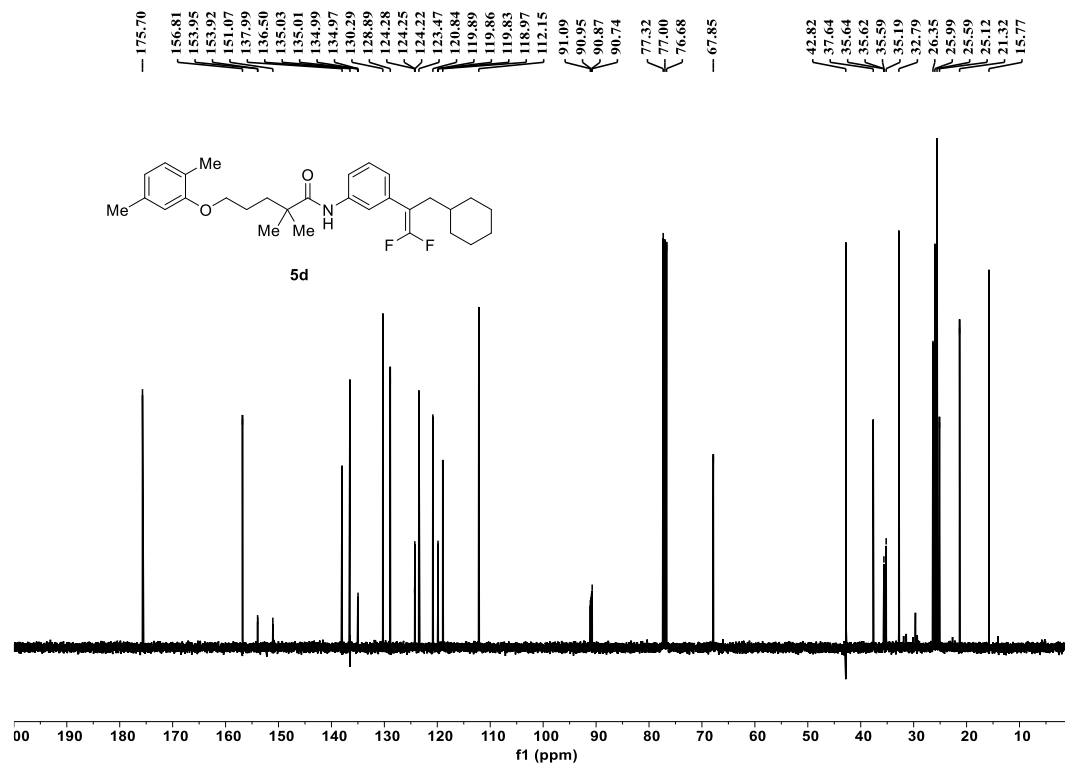
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^1H NMR (400 MHz, CDCl_3)



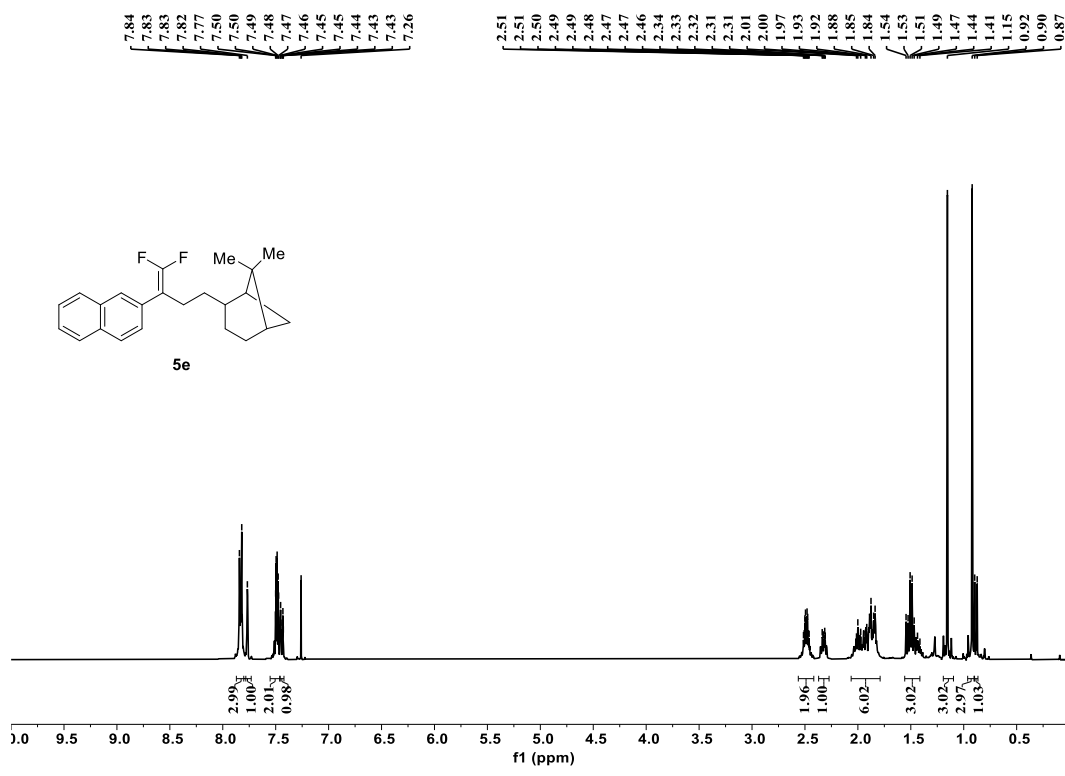
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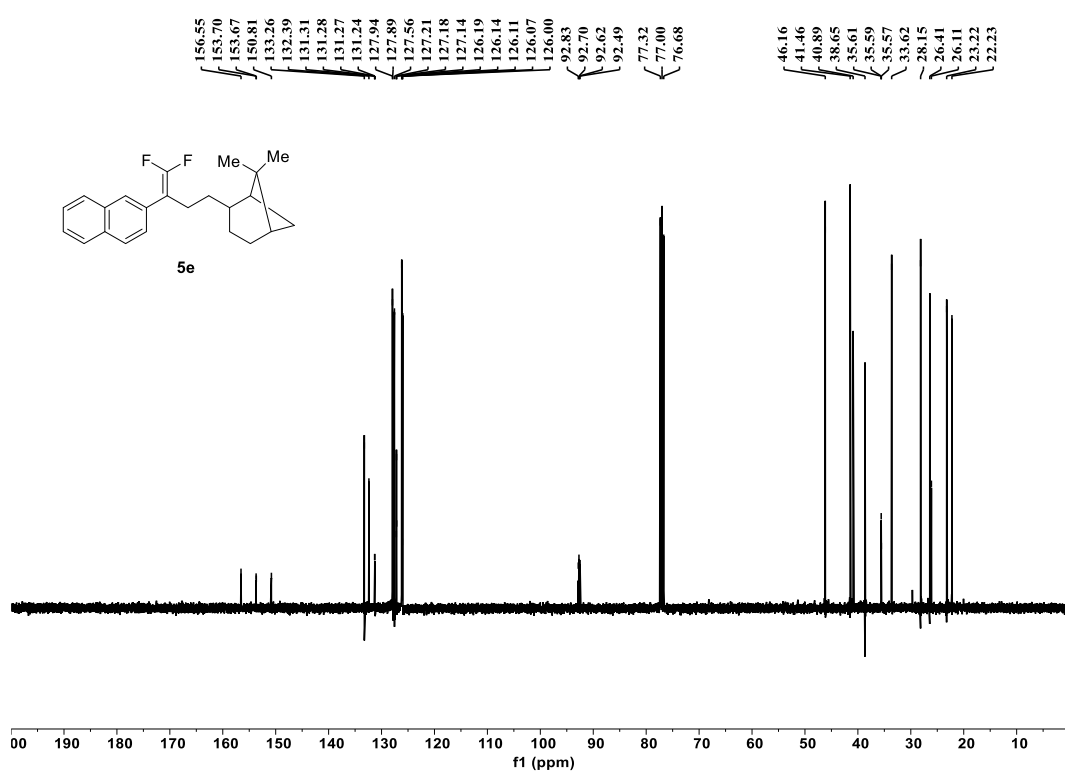
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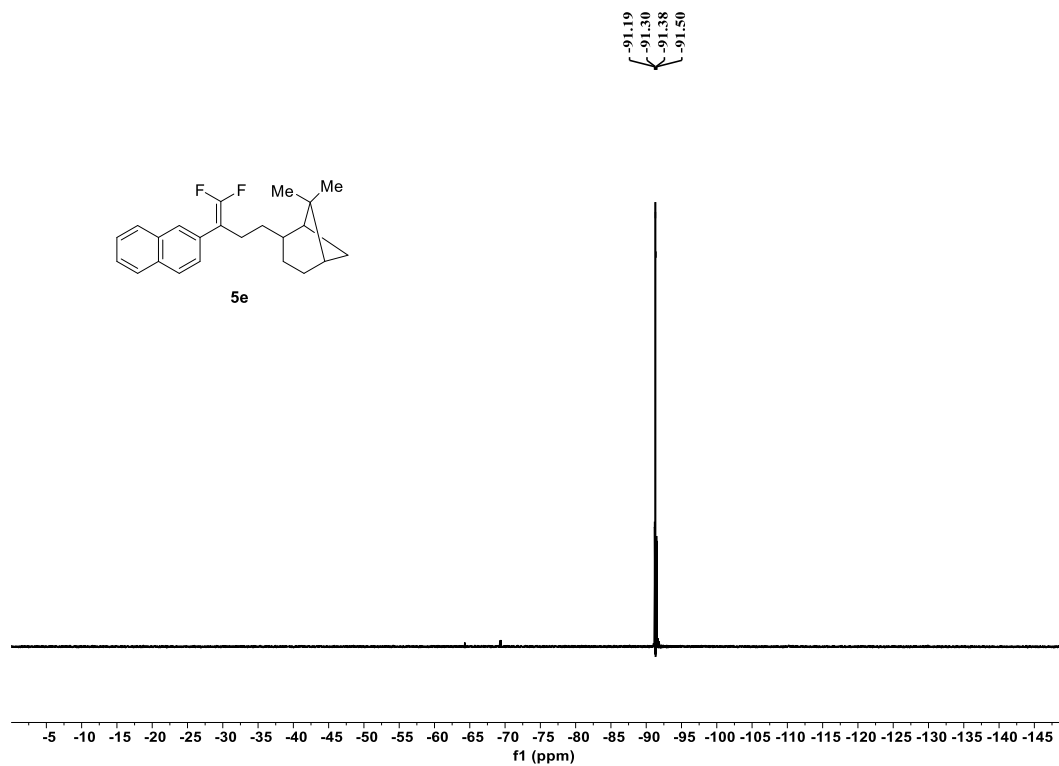
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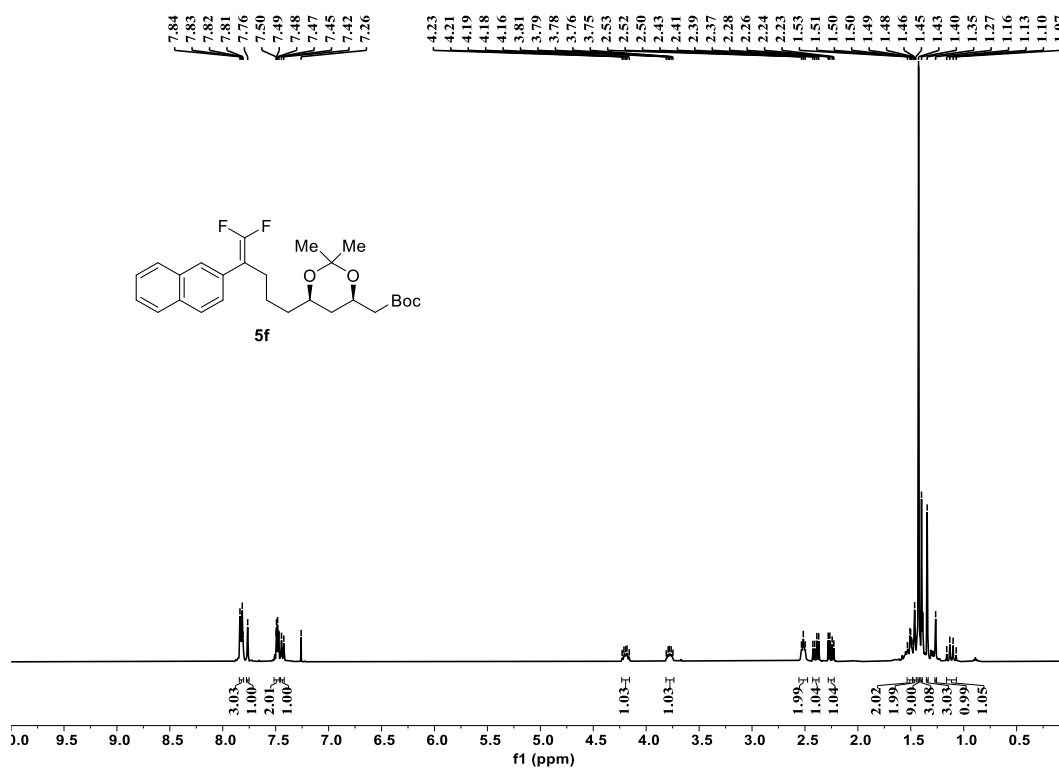
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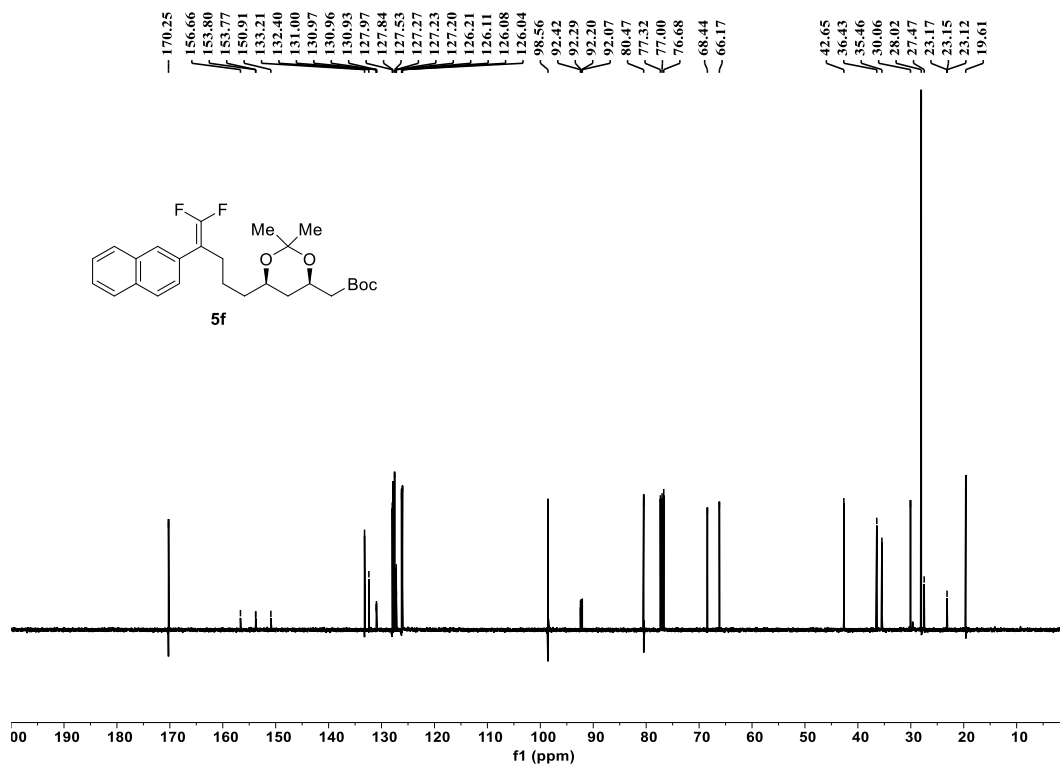
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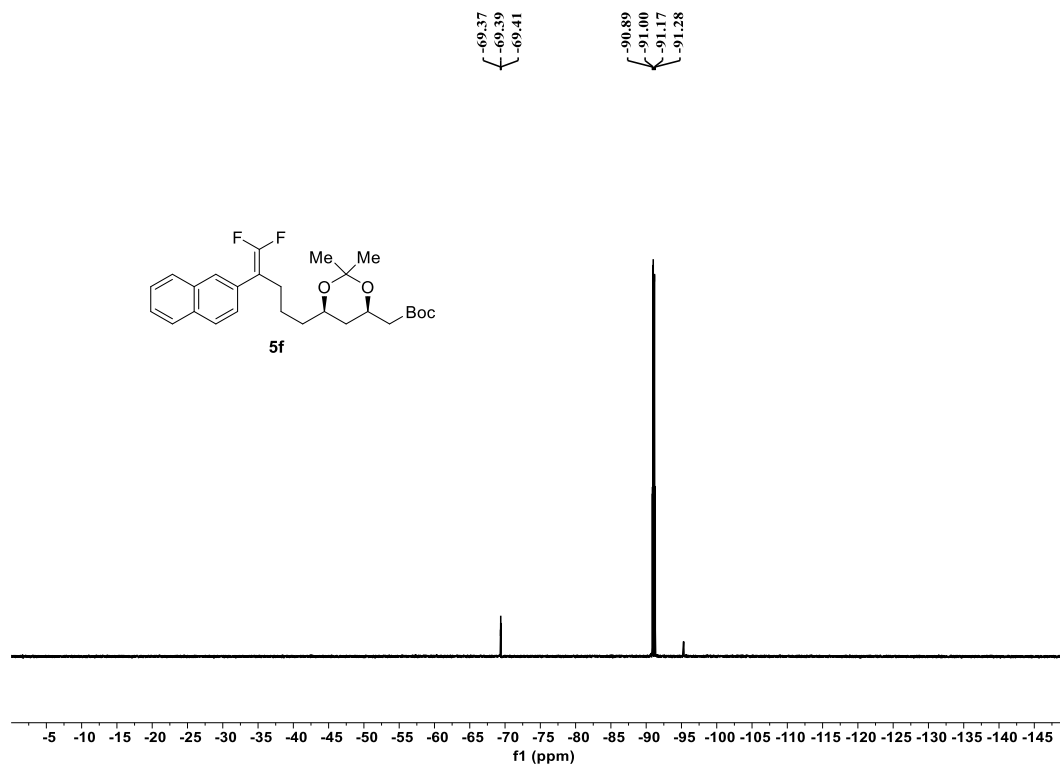
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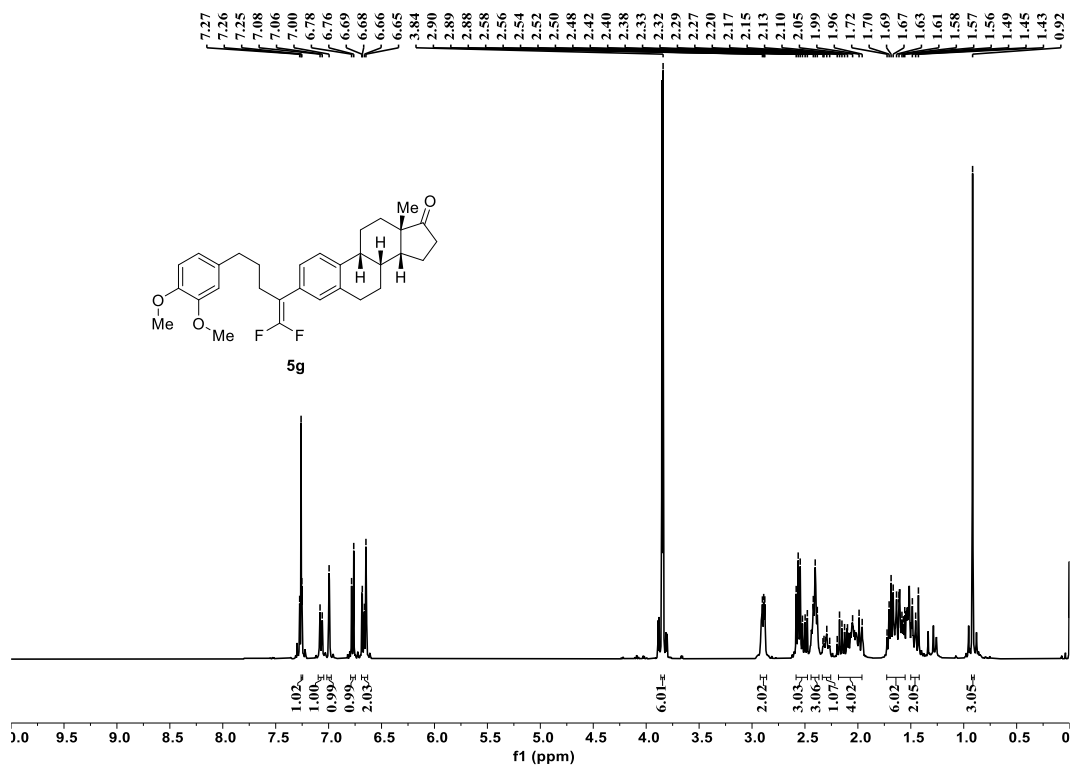
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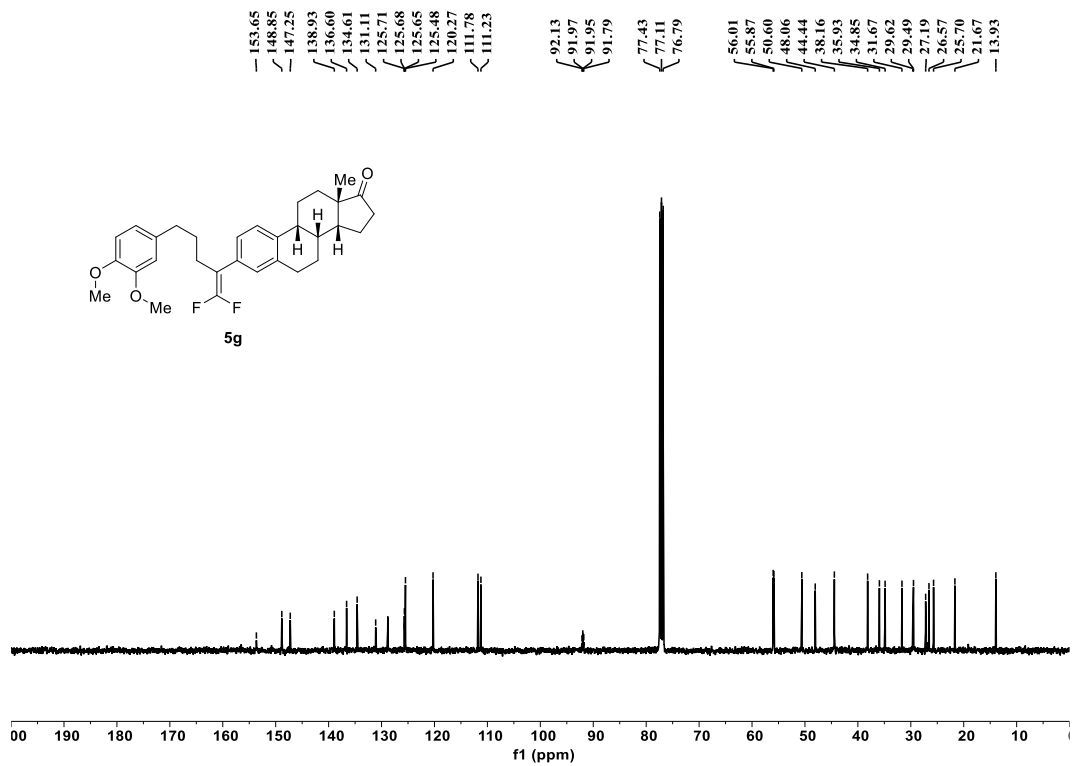
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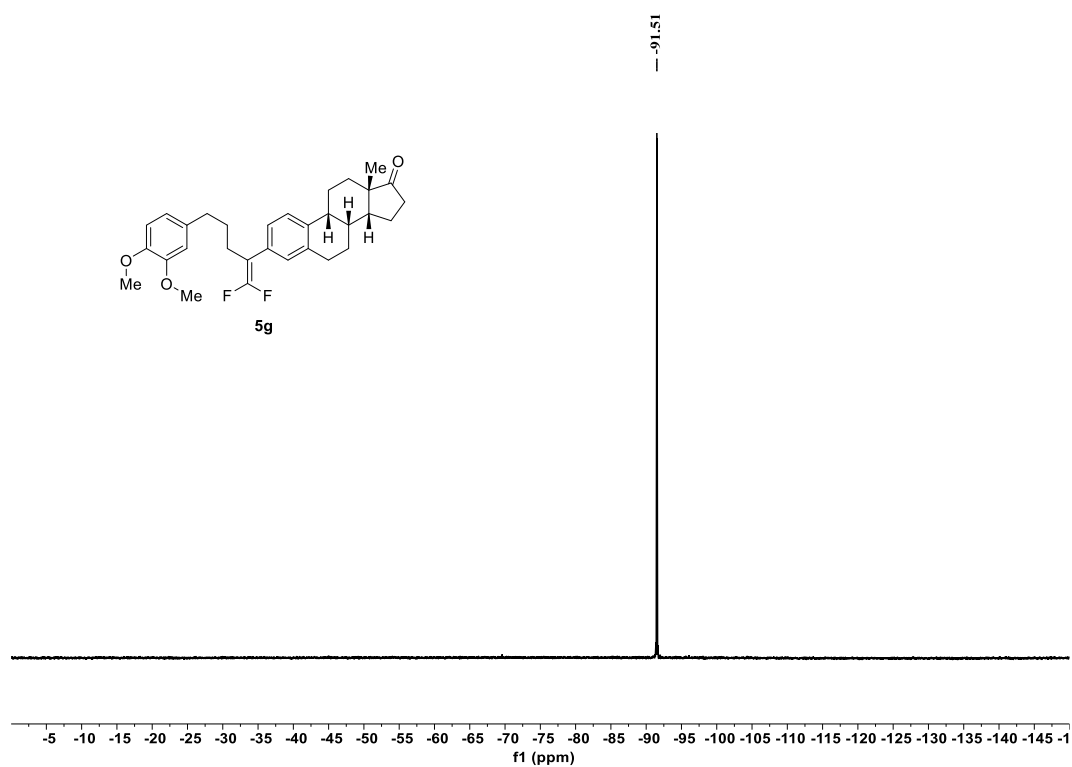
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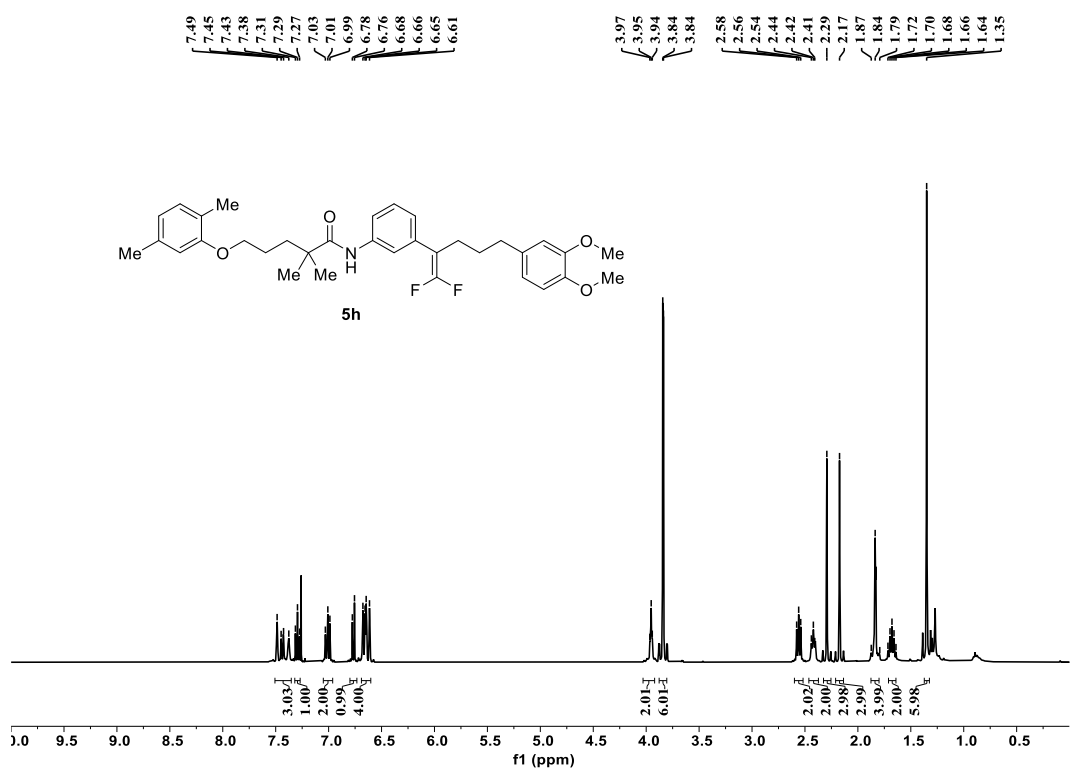
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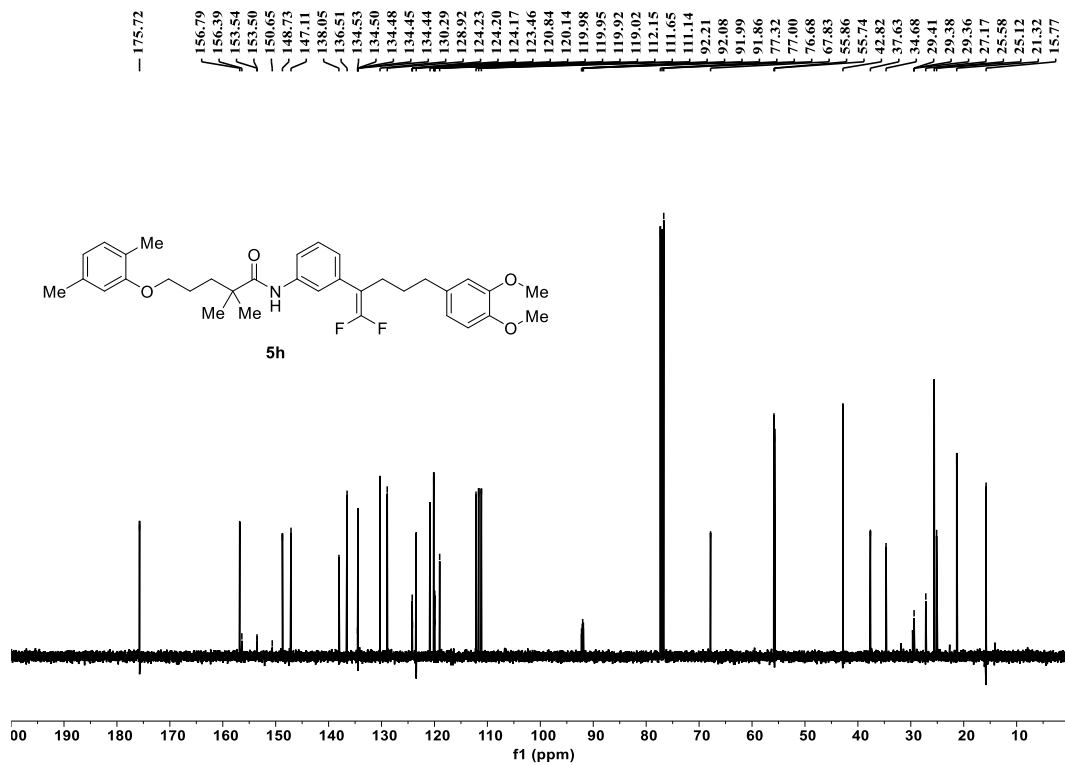
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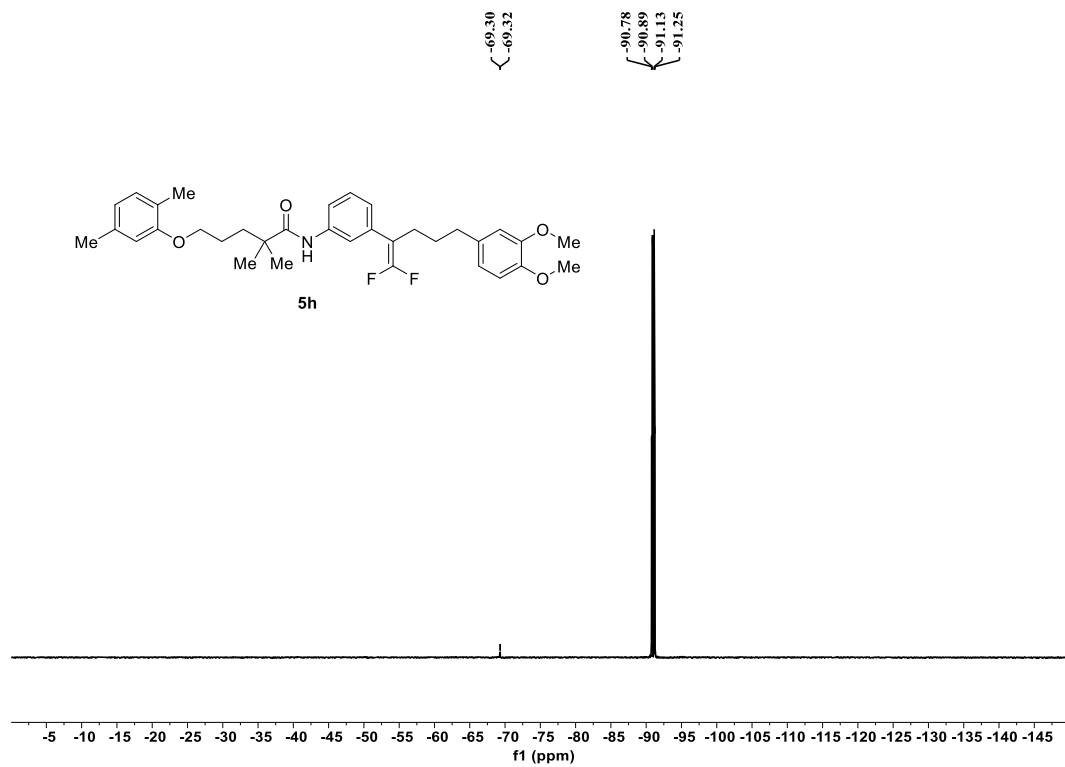
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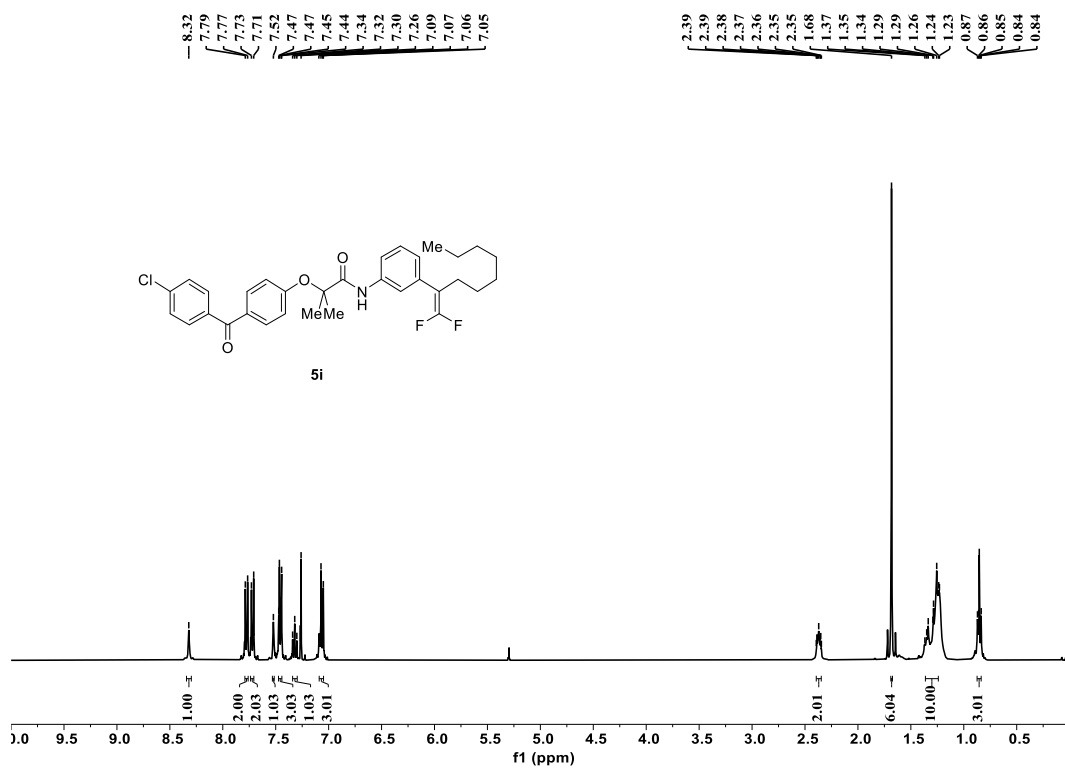
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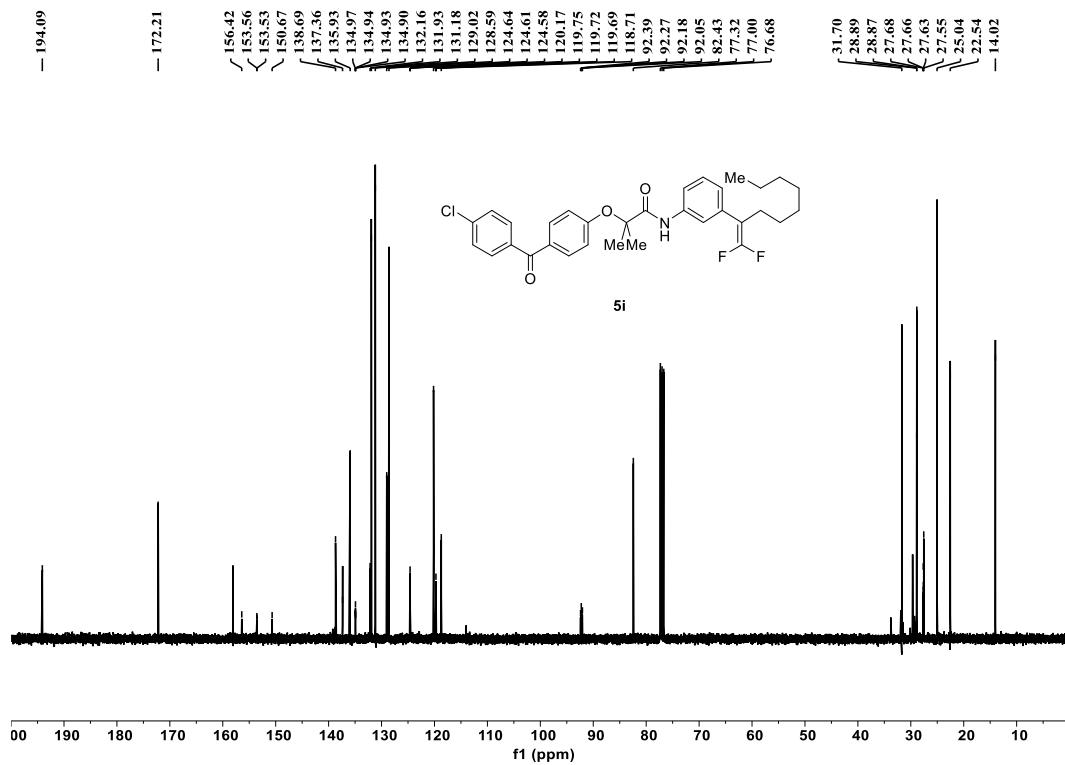
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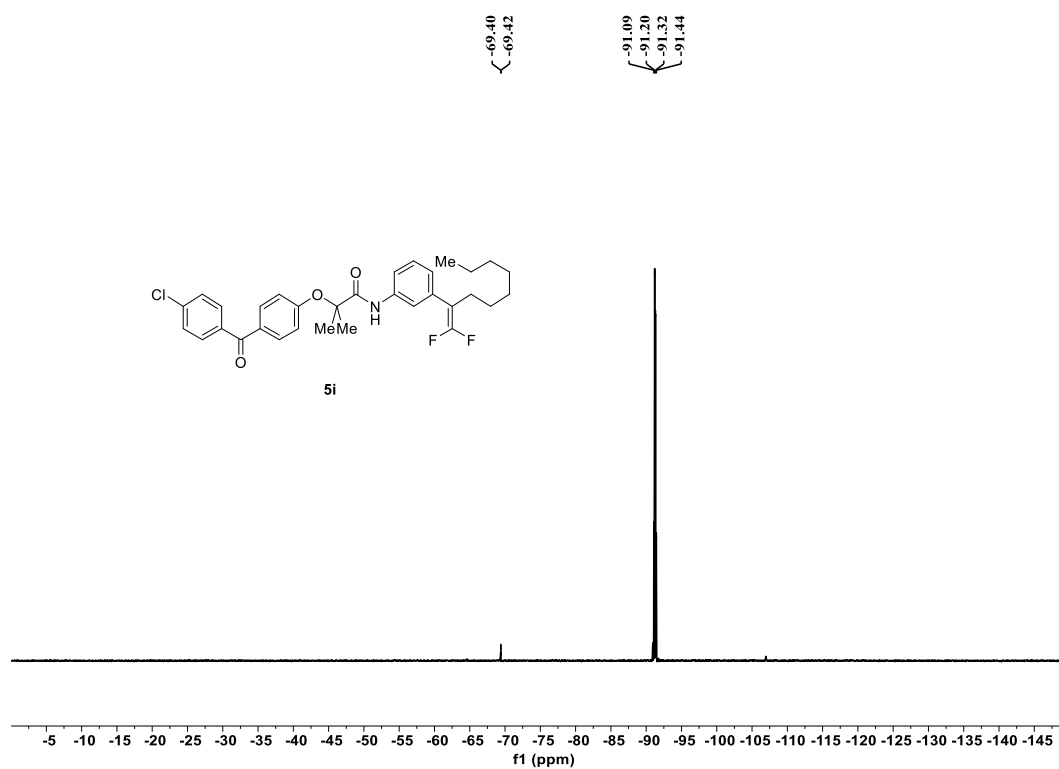
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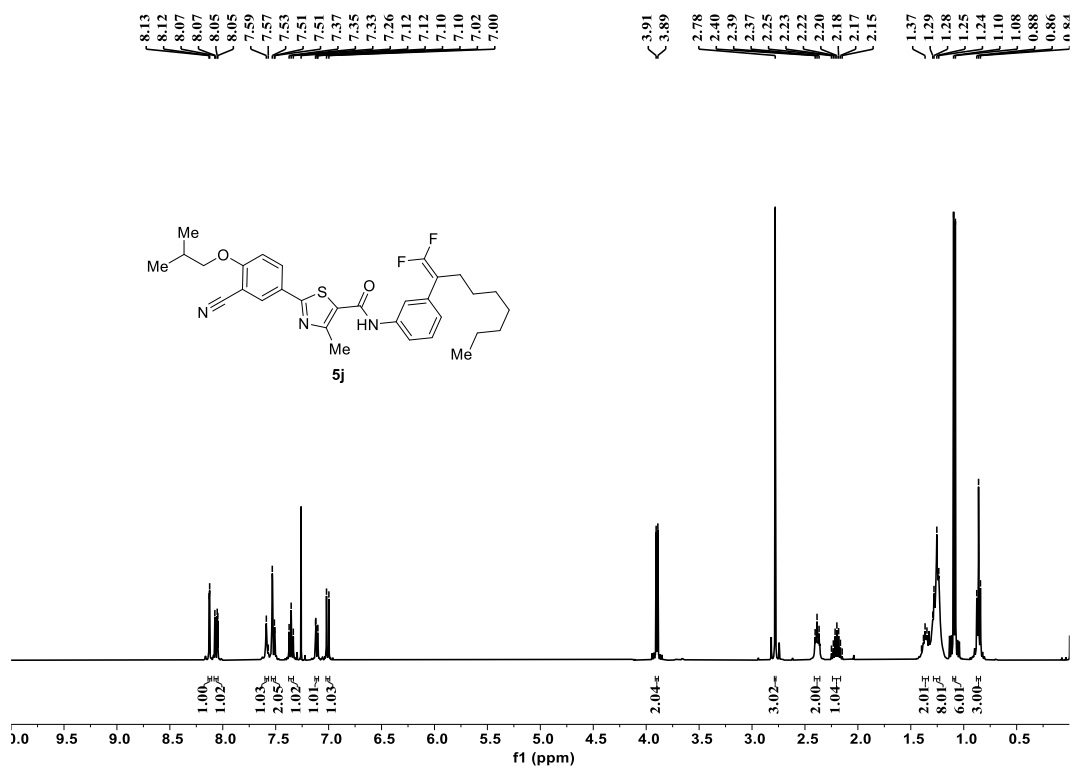
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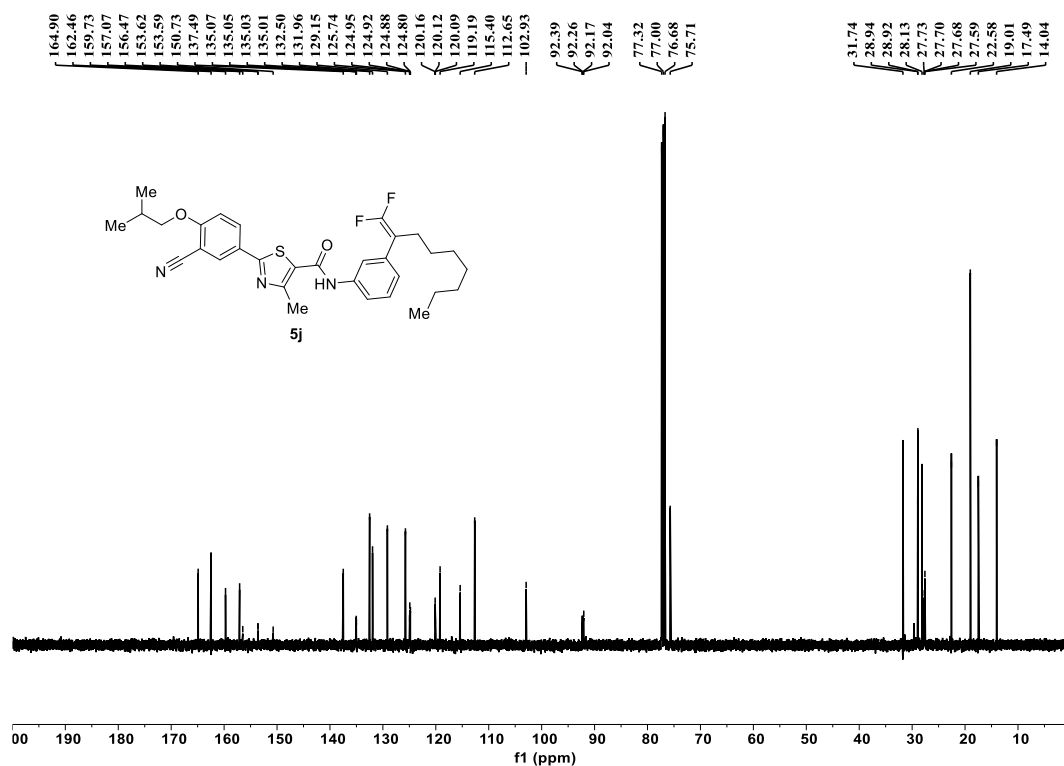
^{19}F NMR (376 MHz, CDCl_3)



^1H NMR (400 MHz, CDCl_3)



¹³C NMR (100 MHz, CDCl₃)



¹⁹F NMR (376 MHz, CDCl₃)

