Supplementary Information

Nickel-Catalyzed Stereoselective Reductive Cross-Coupling of gem-Difluoroalkenes with alkenyl-Electrophiles

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Contents

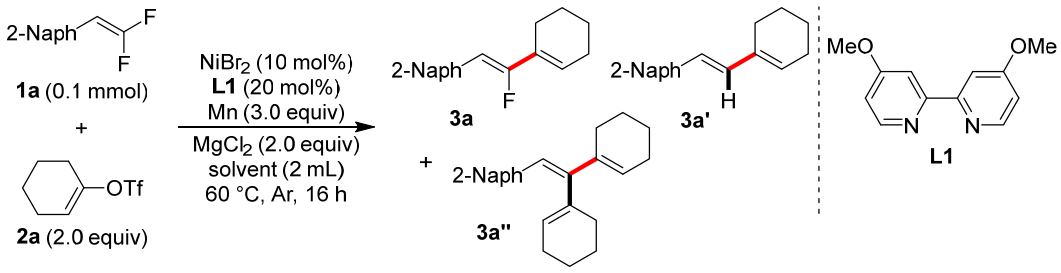
1. General information

All reactions involving air- and/or moisture-sensitive compounds were carried out in the argon-filled glove box or by standard Schlenk techniques under argon atmosphere. Unless otherwise noted, chemicals and solvents were purchased from commercial suppliers (Alfa, Adamas-beta®, Aldrich, Innochem, Stream, and so on) and used without further purification. All new compounds were fully characterized. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Column chromatography was performed on 200-300 mesh silica gel.

^{1}H, ^{13}C, and ^{19}F NMR data were recorded on Bruker AVANCE NEO (600 MHz) or AVANCE III HD (400 MHz) spectrometers. All chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Gas chromatographic (GC) analyses were acquired on a SHIMADZU GC 2030 gas chromatography instrument with a FID detector and adamantane was added as an internal standard. Melting points were determined with melting point apparatus SGW X-4A and were not corrected. High resolution mass spectra (HRMS) analysis was performed on a Thermo Fisher Q-Exactive instrument.

2. Optimization of the reaction conditions

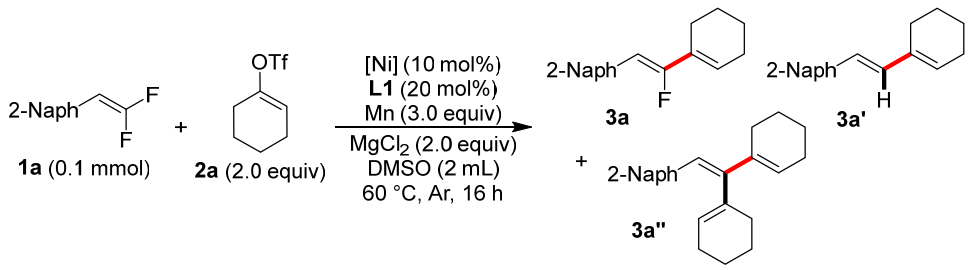
Table S1: Screening of Solvents. [a]



Entry	Solvent	Yield (%) of **3a/3a'/3a"** [b]
1	DMSO	28/2/1
2	DMF	1/1/3
3	DMA	3/1/2
4	THF	n.d.
5	MeCN	n.d.
6	1,4-dioxane	n.d.
7	EA	n.d.
8	DCE	n.d.
9	toluene	n.d.

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), $NiBr_2$ (10 mol%), **L1** (20 mol%), Mn (0.3 mmol, 3.0 equiv), and $MgCl_2$ (0.2 mmol, 2.0 equiv) in solvent (2 mL), under Ar at 60 °C for 16 h unless noted otherwise. [b] Determined by GC with adamantane as the internal standard.

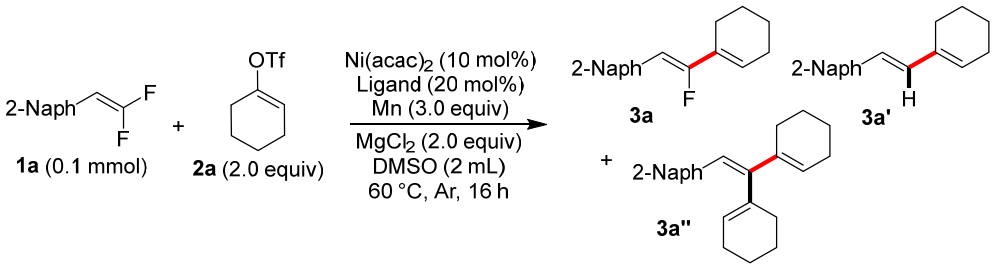
Table S2: Screening of Ni Catalysts. [a]



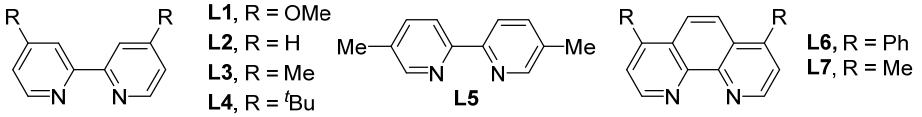
Entry	[Ni]	Yield (%) of **3a/3a'/3a''** [b]
1	$NiBr_2$	28/2/1
2	$NiCl_2$	33/3/1
3	NiI_2	39/1/1
4	NiF_2	1/1/1
5	$NiBr_2$·(diglyme)$_2$	30/3/2
6	$NiBr_2$·dme	29/4/4
7	$Ni(cod)_2$	24/1/1
8	$Ni(acac)_2$	40/3/2
9	$Ni(OTf)_2$	2/1/1
10	$Ni(OAc)_2·4H_2O$	18/8/3

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), Ni catalyst (10 mol%), **L1** (20 mol%), Mn (0.3 mmol, 3.0 equiv), and $MgCl_2$ (0.2 mmol, 2.0 equiv) in DMSO (2 mL), under Ar at 60 °C for 16 h unless noted otherwise. [b] Determined by GC with adamantane as the internal standard.

Table S3: Screening of Ligands. [a]

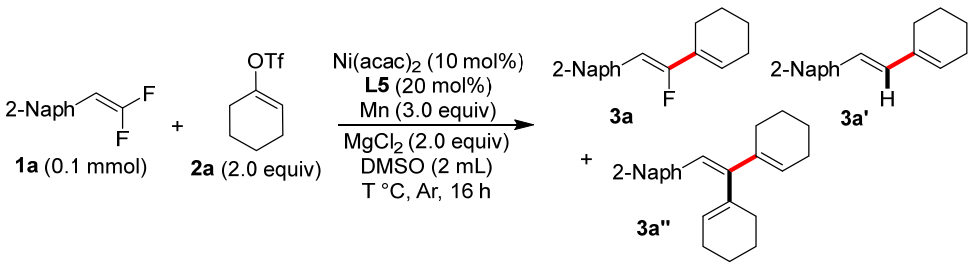


Entry	Ligand	Yield (%) of **3a/3a'/3a''** [b]
1	**L1**	40/3/2
2	**L2**	4/1/1
3	**L3**	29/3/2
4	**L4**	31/4/4
5	**L5**	43/2/5
6	**L6**	1/12/6
7	**L7**	7/1/1



[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), $Ni(acac)_2$ (10 mol%), ligand (20 mol%), Mn (0.3 mmol, 3.0 equiv), and $MgCl_2$ (0.2 mmol, 2.0 equiv) in DMSO (2 mL), under Ar at 60 °C for 16 h unless noted otherwise. [b] Determined by GC with adamantane as the internal standard.

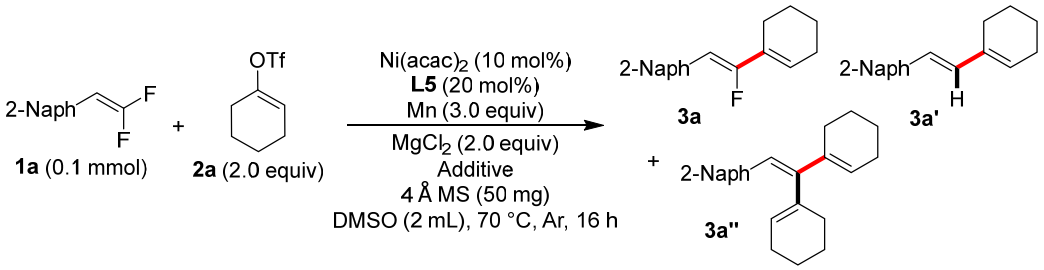
Table S4: Screening of Temperature. [a]



Entry	Temp.(ºC)	Yield (%) of **3a/3a'/3a"** [b]
1	rt	n.d.
2	50	40/1/4
3	60	43/2/3
4	70	47/1/6
5	80	20/1/4
6	90	14/1/4
7[c]	70	49/1/6

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), $Ni(acac)_2$ (10 mol%), **L5** (20 mol%), Mn (0.3 mmol, 3.0 equiv), and $MgCl_2$ (0.2 mmol, 2.0 equiv) in DMSO (2 mL), under Ar at T ℃ for 16 h unless noted otherwise. [b] Determined by GC with adamantane as the internal standard. [c] 50 mg 4 Å MS was used.

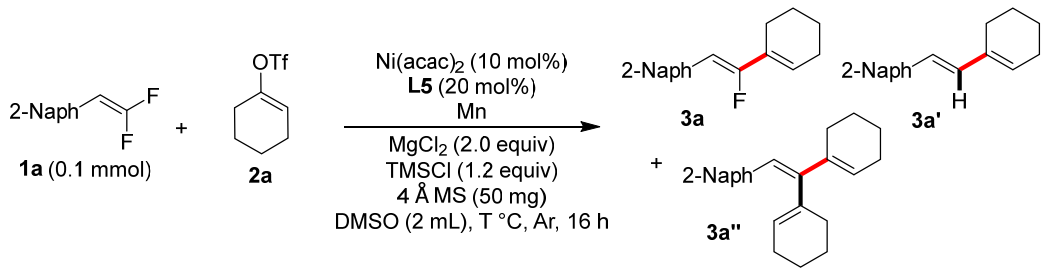
Table S5: Screening of Additives. [a]



Entry	Additive (equiv)	Yield (%) of **3a/3a'/3a"** [b]
1	TMSOTf (1.2)	51/8/2
2	TMSCl (1.2)	50/4/1
3	LiCl (2)	35/14/8
4	NaI (2)	48/2/6
5	TBAI (2)	19/1/3
6[c]	TMSOTf (1.2)	60/2/2
7 [c]	TMSCl (1.2)	72//3/3
8 [d]	TMSCl (1.2)	63/4/2

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), $Ni(acac)_2$ (10 mol%), **L5** (20 mol%), Mn (0.3 mmol, 3.0 equiv), $MgCl_2$ (0.2 mmol, 2.0 equiv), additive, and 50 mg 4 Å MS in DMSO (2 mL), under Ar at 70 ℃ for 16 h unless noted otherwise. [b] Determined by GC with adamantane as the internal standard. [c] The reaction was proceeded at 60 ℃. [d] The reaction was proceeded without 4 Å MS at 60 ℃.

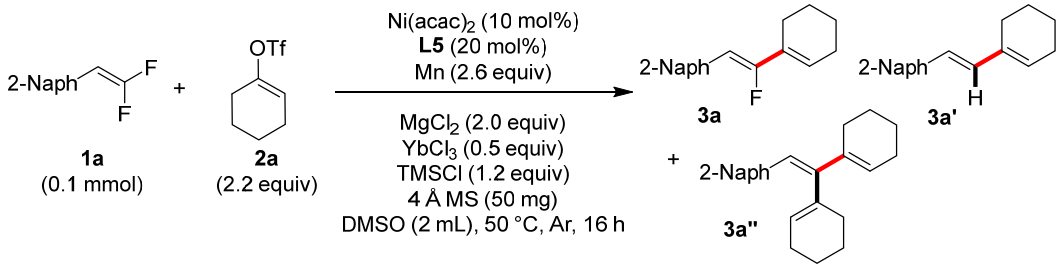
Table S6: Screening of Other Conditions. [a]



Entry	**2a** (equiv)	Mn (equiv)	Temp.(ºC)	$YbCl_3$	Yield (%) of **3a/3a'/3a''** [b]
1	2	2.5	60	-	67/3/3
2	2	3	60	-	72/3/3
3	2	3.5	60	-	62/4/2
4	2	Zn (2.5)	60	-	5/1/1
5	2.5	2.5	45	-	71/2/5
6	3	2.5	45	-	60/1/6
7	2.2	2.6	45	-	77/3/4
8	2.2	2.6	50	-	79/5/3
9	2.2	2.6	50	2	54/2/1
10	**2.2**	**2.6**	**50**	**0.5**	**88 (87)[c]/5/2**

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), $Ni(acac)_2$ (10 mol%), **L5** (20 mol%), Mn, $MgCl_2$ (0.2 mmol, 2.0 equiv), TMSCl (0.12 mmol, 1.2 equiv), and 50 mg 4 Å MS in DMSO (2 mL), under Ar at T °C for 16 h unless noted otherwise. [b] Determined by GC with adamantane as the internal standard. [c] Isolated yield.

Table S7: Control Experiments [a]

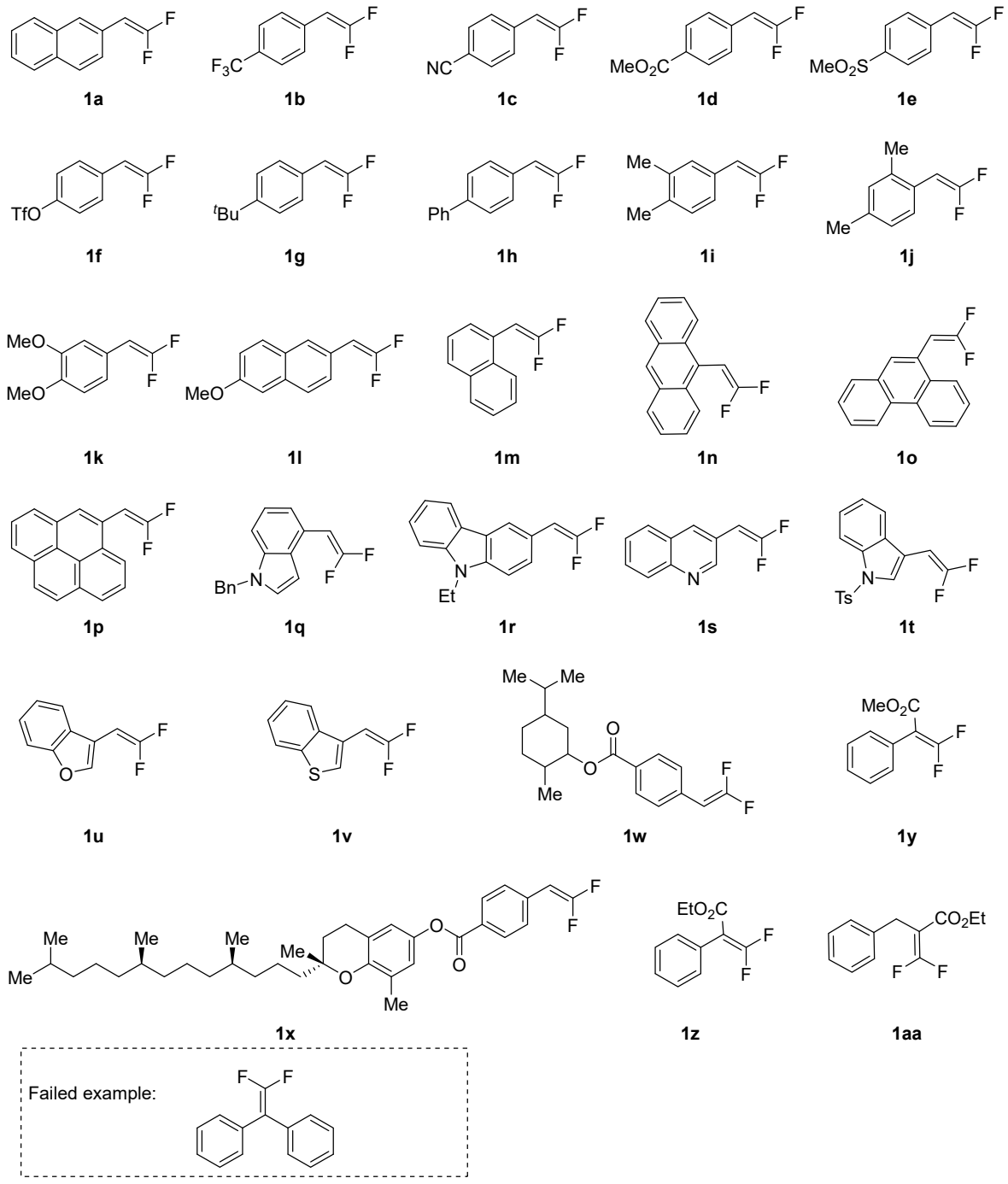


Entry	Variation of standard conditions	Yield (%) of **3a/3a'/3a''** [b]
1	no $Ni(acac)_2$/**L1**/Mn	n.d
2	no $MgCl_2$	57/2/1
3	no $YbCl_3$	79/5/3
4	no TMSCl	57/4/16
5	no 4 Å MS	84/5/7

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (2.2 equiv), $Ni(acac)_2$ (10 mol%), **L1** (20 mol%), Mn (2.6 equiv), $MgCl_2$ (2.0 equiv), $YbCl_3$ (0.5 equiv), TMSCl (1.2 equiv), and 4 Å MS (50 mg) in DMSO (2 mL), under Ar at 50 ºC for 16 h unless noted otherwise. [b] GC yield with adamantane as the internal standard.

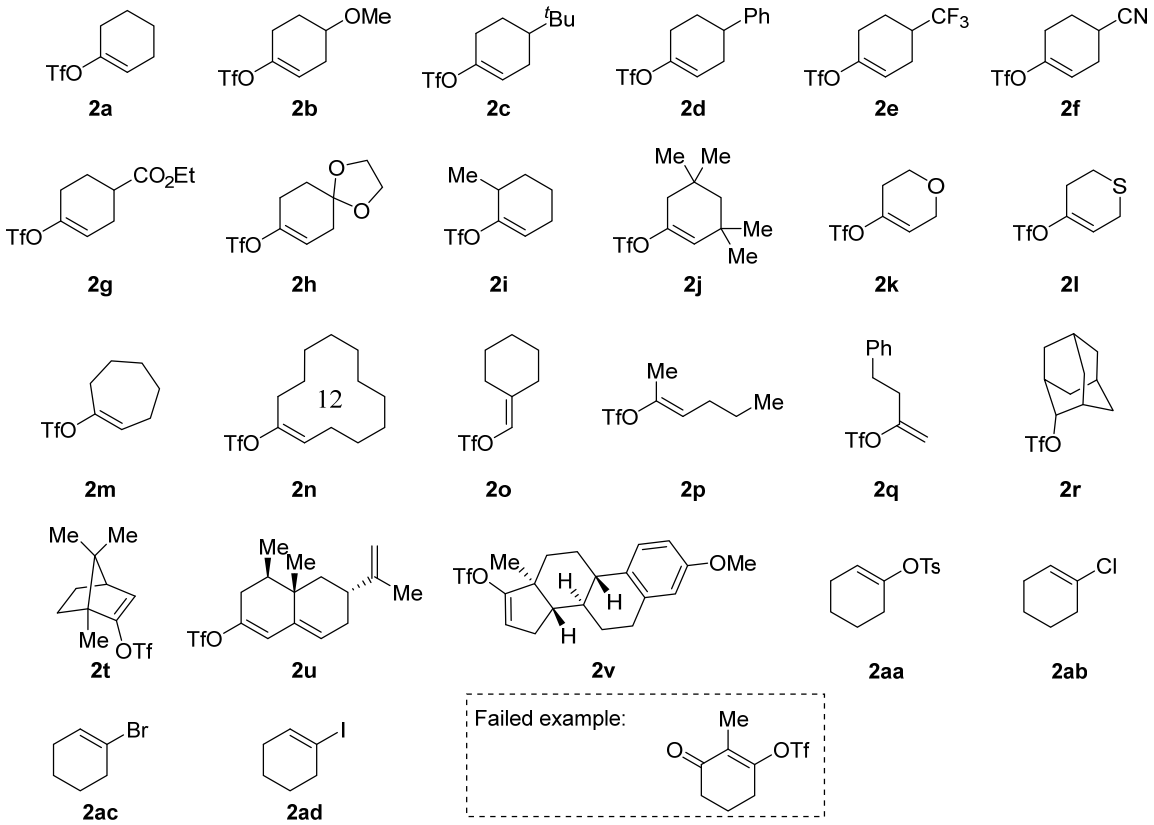
3. General procedure

3.1 Preparation of *gem*-difluoroalkene substrates



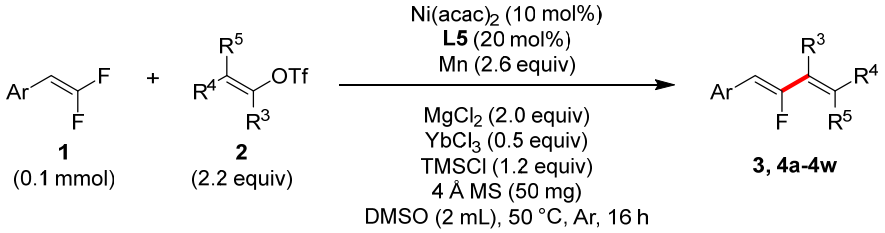
gem-Difluoroalkene substrates **1** are all known compounds and prepared according to the literature procedure.[1]

3.2 Preparation of alkenyl triflates substrates



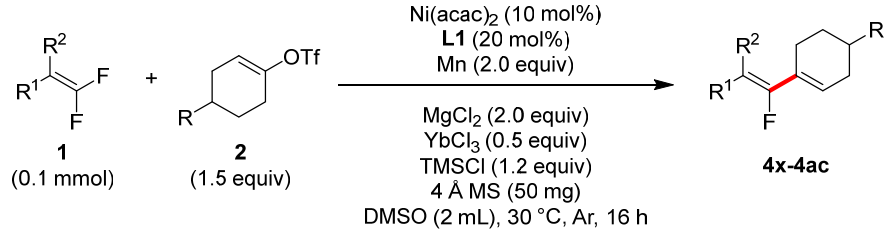
Alkenyl triflates substrates **2** are all known compounds and prepared according to the literature procedure.[2]

3.3 General procedure for Ni-catalyzed reductive cross-coupling of *gem*-difluoroalkenes with C(sp^2)-electrophiles



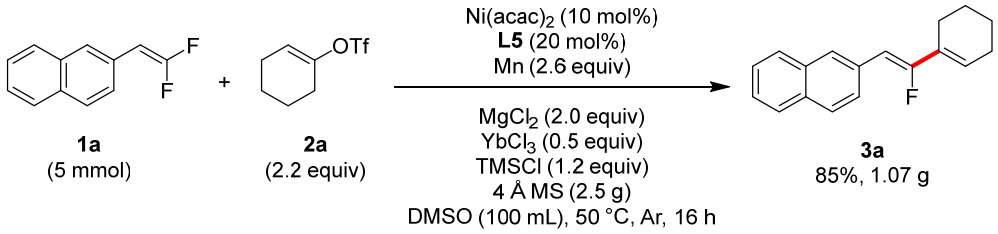
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1** (0.1 mmol) and **L5** (3.7 mg, 0.02 mmol, 20 mol%). $Ni(acac)_2$ (2.6 mg, 0.01 mmol, 10 mol%), Mn (14.0 mg, 0.26 mmol, 2.6 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), and alkenyl triflates **2** (0.22 mmol, 2.2 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 50 °C using an oil bath for 16 hours until the reaction was complete (monitored by TLC). Then 2 mL water and 1 mL 1M HCl was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic

layer was washed with brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the desired monofluoro 1,3-diene.



To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1** (0.1 mmol) and **L1** (4.3 mg, 0.02 mmol, 20 mol%). $Ni(acac)_2$ (2.6 mg, 0.01 mmol, 10 mol%), Mn (10.8 mg, 0.20 mmol, 2.0 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), and alkenyl triflates **2** (0.15 mmol, 1.5 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 30 °C using an oil bath for 16 hours until the reaction was complete (monitored by TLC). Then 2 mL water and 1 mL 1M HCl was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the desired monofluoro 1,3-diene.

3.4 Gram-scale synthesis of 3a

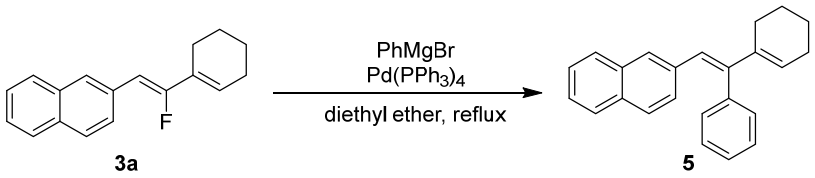


To an oven-dried 250 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1a** (950.0 mg, 5 mmol) and **L5** (184.2 mg, 1 mmol, 20 mol%). $Ni(acac)_2$ (128.5 mg, 0.5 mmol, 10 mol%), Mn (714.2 mg, 13 mmol, 2.6 equiv), $MgCl_2$ (952.1 mg, 10 mmol, 2.0 equiv), $YbCl_3$ (698.5 mg, 2.5 mmol, 0.5 equiv), and 4 Å MS (2.5 g) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (100 mL), TMSCl (760.6 μL, 0.12 mmol, 1.2 equiv), and alkenyl triflates **2a** (1.75 mL, 11 mmol, 2.2 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 50 °C using an oil bath for 16 hours until the reaction was complete (monitored by TLC). Then 100 mL water and 50 mL 1M HCl was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 200 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo.

Then the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afford monofluoro 1,3-diene **3a** as a pale yellow solid (1.07 g, 85% yield).

4. Synthetic transformations

(*Z*)-2-(2-(cyclohex-1-en-1-yl)-2-phenylvinyl)naphthalene (5)



3a **5**

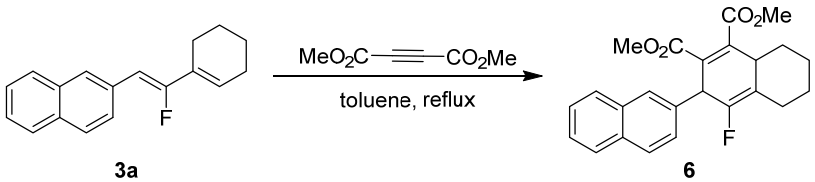
Experimental procedure:[3] To a solution of **3a** (25.2 mg, 0.1 mmol) and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 5 mol%) in diethyl ether was added dropwise a solution of PhMgBr in THF (0.24 mmol, 2.4 equiv) at room temperature under an argon atmosphere. The mixture was stirred for 2 h at reflux (monitored by TLC and GC/MS). After completion of the reaction, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with water and brine, then dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using petroleum ether as the eluent to afford target product **5** as a colorless oil (26.4 mg, 85% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 1H), 7.55 – 7.50 (m, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.36 – 7.29 (m, 6H), 7.16 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.86 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.76 (s, 1H), 5.54 (t, *J* = 4.1 Hz, 1H), 2.48 – 2.41 (m, 2H), 2.15 – 2.09 (m, 2H), 1.82 – 1.75 (m, 2H), 1.66 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.8, 140.2, 138.8, 135.4, 133.2, 131.9, 130.3, 130.2, 128.6, 128.5, 127.9, 127.4, 127.3, 126.9, 126.9, 125.7, 125.5, 123.9, 26.3, 26.3, 23.1, 22.3.

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{24}H_{23}$ 311.1794; found 311.1792.

dimethyl 1-fluoro-2,4a,5,6,7,8-hexahydro-[2,2'-binaphthalene]-3,4-dicarboxylate (6)



3a **6**

Experimental procedure:[4] To a mixture of **3a** (25.2 mg, 0.1 mmol) and dry toluene (3.0 mL) in a 10 mL oven-dried Schlenk-tube was added dimethyl but-2-ynedioate (42.6 mg, 0.3 mmol, 3.0 equiv) under an argon atmosphere. The reaction mixture was heated at 130 °C using an oil bath and stirred for 96

hours (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 - 5:1, v/v) to give the desired product **6** as a white solid (37.4 mg, 95% yield, mp. = 106-107 ºC).

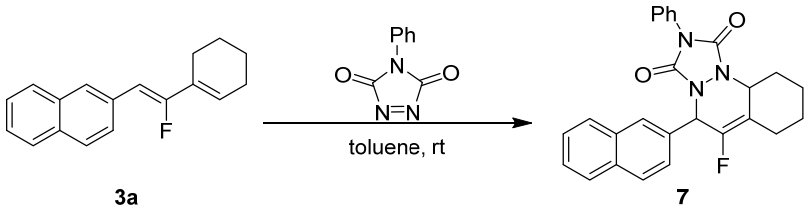
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 3H), 7.73 (s, 1H), 7.49 – 7.42 (m, 2H), 7.40 (dd, *J* = 8.5, 1.6 Hz, 1H), 4.68 – 4.62 (m, 1H), 3.83 (s, 3H), 3.52 (s, 3H), 3.19 – 3.12 (m, 1H), 2.86 (d, *J* = 13.5 Hz, 1H), 2.41 – 2.32 (m, 1H), 1.98 – 1.88 (m, 1H), 1.83 (d, *J* = 12.8 Hz, 1H), 1.64 (td, *J* = 13.3, 2.9 Hz, 1H), 1.53 – 1.44 (m, 2H), 1.33 – 1.21 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 165.8 (d, *J* = 3.6 Hz), 149.2 (d, *J* = 248.8 Hz), 140.9, 136.6, 133.4, 132.8, 130.0 (d, *J* = 9.7 Hz), 128.4, 127.9, 127.7, 127.7, 126.2, 126.1, 125.9, 113.1 (d, *J* = 13.9 Hz), 52.4, 52.2, 44.2 (d, *J* = 30.5 Hz), 41.9 (d, *J* = 4.9 Hz), 34.5, 26.6, 26.2, 24.5 (d, *J* = 4.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -121.93.

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{24}H_{24}FO_4$ 395.1653; found 395.1643.

6-fluoro-5-(naphthalen-2-yl)-2-phenyl-5,7,8,9,10,10a-hexahydro-1*H*-[1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (7)



Experimental procedure: To a mixture of **3a** (25.2 mg, 0.1 mmol) and dry toluene (3.0 mL) in a 10 mL oven-dried Schlenk-tube was added 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (52.5 mg, 0.3 mmol, 3.0 equiv) under an argon atmosphere. The reaction mixture was stirred at room temperature for 96 hours (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 - 5:1, v/v) to give the desired product **7** as a white solid (30.4 mg, 71% yield, mp. = 182-184 ºC).

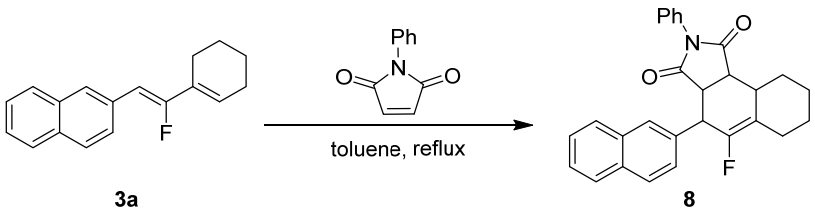
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.88 – 7.81 (m, 3H), 7.63 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.39 – 7.34 (m, 4H), 7.32 – 7.26 (m, 1H), 5.78 – 5.74 (m, 1H), 4.38 – 4.27 (m, 1H), 3.22 (d, *J* = 12.5 Hz, 1H), 3.13 – 3.07 (m, 1H), 1.99 (dd, *J* = 13.7, 1.8 Hz, 1H), 1.95 (d, *J* = 12.9 Hz, 1H), 1.82 (td, *J* = 13.9, 2.9 Hz, 1H), 1.74 (ddd, *J* = 15.8, 12.9, 3.4 Hz, 1H), 1.64 – 1.53 (m, 1H), 1.45 (qt, *J* = 13.2, 3.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.2, 149.9 (d, *J* = 2.1 Hz), 146.6 (d, *J* = 251.6 Hz), 133.7, 133.0, 131.5 (d, *J* = 2.2 Hz), 130.9, 129.0, 128.9, 128.5, 128.4, 128.1, 127.7, 126.8, 126.5, 125.4, 125.2, 114.4 (d, *J* = 13.7 Hz), 57.2 (d, *J* = 4.1 Hz), 56.7 (d, *J* = 40.7 Hz), 33.5, 25.9, 23.7 (d, *J* = 4.3 Hz), 23.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -124.04.

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{26}H_{23}FN_3O_2$ 428.1769; found 428.1760.

5-fluoro-4-(naphthalen-2-yl)-2-phenyl-3a,4,6,7,8,9,9a,9b-octahydro-1*H*-benzo[*e*]isoindole-1,3(2*H*)-dione (8)



3a **8**

Experimental procedure: To a mixture of **3a** (25.2 mg, 0.1 mmol) and dry toluene (3.0 mL) in a 10 mL oven-dried Schlenk-tube was added 1-phenyl-1*H-pyrrole*-2,5-dione (51.9 mg, 0.3 mmol, 3.0 equiv) under an argon atmosphere. The reaction mixture was heated at 130 °C using an oil bath and stirred for 96 hours (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 - 5:1, v/v) to give the desired product **8** as a white solid (39.1 mg, 92% yield, mp. = 205-207 ºC).

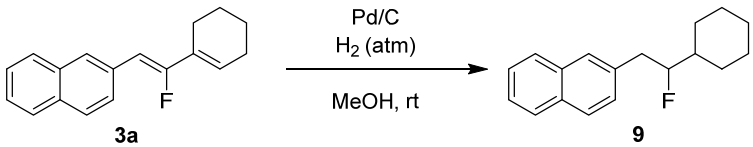
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 3H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.47 (dd, *J* = 6.0, 3.1 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.04 (t, *J* = 7.1 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 2H), 5.95 (d, *J* = 8.3 Hz, 2H), 4.26 (t, *J* = 9.0 Hz, 1H), 3.67 (t, *J* = 8.0 Hz, 1H), 3.39 – 3.33 (m, 1H), 3.10 (d, *J* = 13.9 Hz, 1H), 2.94 – 2.83 (m, 1H), 2.72 (d, *J* = 13.4 Hz, 1H), 2.14 (ddd, *J* = 25.7, 13.0, 2.9 Hz, 1H), 2.08 (d, *J* = 10.7 Hz, 1H), 1.94 (d, *J* = 10.8 Hz, 1H), 1.76 (t, *J* = 12.0 Hz, 1H), 1.53 – 1.39 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 174.8 (d, *J* = 2.7 Hz), 149.1 (d, *J* = 250.4 Hz), 133.2, 133.2, 133.1, 130.8, 128.8, 128.5, 128.4, 128.1, 128.1, 127.5, 126.7, 126.5, 126.4, 125.9, 117.7 (d, *J* = 12.1 Hz), 45.9 (d, *J* = 7.7 Hz), 41.9 (d, *J* = 29.5 Hz), 40.0, 36.4 (d, *J* = 4.1 Hz), 31.2, 26.8, 26.4, 25.1 (d, *J* = 6.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.35.

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{28}H_{25}FNO_2$ 426.1864; found 426.1859.

2-(2-cyclohexyl-2-fluoroethyl)naphthalene (9)



3a **9**

Experimental procedure:[5] To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **3a** (25.2 mg, 0.1 mmol), palladium on activated carbon (10.6 mg, 10%, 0.01 mmol, 10 mol%), and MeOH (1.0 mL). The reaction solution was purged with a hydrogen balloon for 15 minutes and then went overnight at room temperature under a hydrogen balloon. The reaction was filtered over a short

path of Celite, concentrated in vacuo, and the crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to give the desired product **9** as a white solid (15.4 mg, 60% yield, mp. = 45-46 ºC).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.67 (s, 1H), 7.48 – 7.40 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 4.52 (ddd, *J* = 48.2, 12.1, 5.6 Hz, 1H), 3.12 – 2.99 (m, 2H), 1.96 (d, *J* = 12.4 Hz, 1H), 1.85 – 1.76 (m, 2H), 1.74 (d, *J* = 10.8 Hz, 1H), 1.68 (d, *J* = 10.9 Hz, 1H), 1.61 – 1.49 (m, 1H), 1.28 – 1.13 (m, 5H).

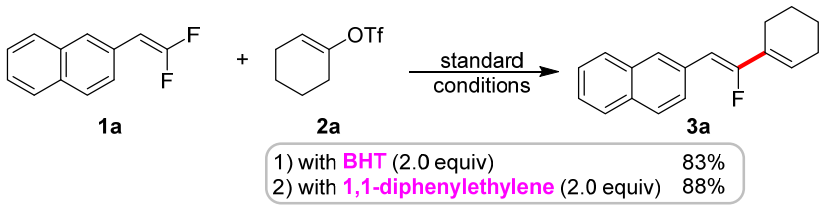
^{13}C NMR (151 MHz, $CDCl_3$) δ 135.6 (d, *J* = 2.5 Hz), 133.5, 132.2, 127.9, 127.8, 127.7, 127.6, 127.6, 125.9, 125.4, 98.3 (d, *J* = 173.3 Hz), 41.7 (d, *J* = 19.5 Hz), 38.8 (d, *J* = 22.3 Hz), 28.9 (d, *J* = 4.4 Hz), 27.4 (d, *J* = 5.5 Hz), 26.3, 26.0, 25.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -185.21 – -185.51 (m).

FTMS (ESI) m/z: $[M]^+$ calcd for $C_{18}H_{21}F$ 256.1622; found 256.1616.

5. Mechanistic studies

5.1 Radical inhibition experiments

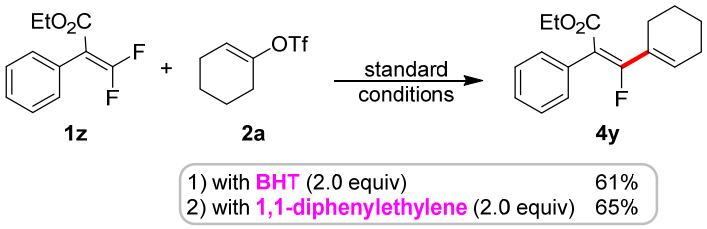


Scheme S1

1) To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1a** (19.0 mg, 0.1 mmol), **L5** (3.7 mg, 0.02 mmol, 20 mol%), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (44.1 mg, 0.2 mmol, 2.0 equiv). $Ni(acac)_2$ (2.6 mg, 0.01 mmol, 10 mol%), Mn (14.0 mg, 0.26 mmol, 2.6 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), and alkenyl triflates **2a** (35.0 μL, 0.22 mmol, 2.2 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 50 °C using an oil bath for 16 hours. Yield was determined by GC with adamantane as an internal standard.

2) To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1a** (19.0 mg, 0.1 mmol) and **L5** (3.7 mg, 0.02 mmol, 20 mol%). $Ni(acac)_2$ (2.6 mg, 0.01 mmol, 10 mol%), Mn (14.0 mg, 0.26 mmol, 2.6 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove

box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), 1,1-diphenylethylene (35.6 μL, 0.2 mmol, 2.0 equiv), and alkenyl triflates **2a** (35.0 μL, 0.22 mmol, 2.2 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 50 °C using an oil bath for 16 hours. Yield was determined by GC with adamantane as an internal standard.



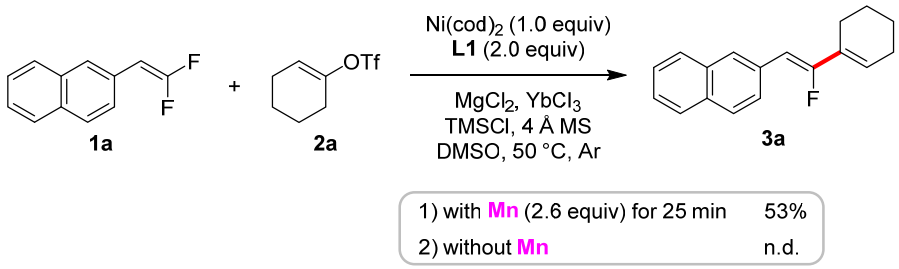
Scheme S2

1) To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1z** (21.2mg, 0.1 mmol), **L1** (4.3 mg, 0.02 mmol, 20 mol%), and BHT (44.1 mg, 0.2 mmol, 2.0 equiv). $Ni(acac)_2$ (2.6 mg, 0.01 mmol, 10 mol%), Mn (10.8 mg, 0.20 mmol, 2.0 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), and alkenyl triflates **2a** (23.9 μL, 0.15 mmol, 1.5 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 30 °C using an oil bath for 16 hours. Yield was determined by GC with adamantane as an internal standard.

2) To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1z** (21.2 mg, 0.1 mmol) and **L1** (4.3 mg, 0.02 mmol, 20 mol%). $Ni(acac)_2$ (2.6 mg, 0.01 mmol, 10 mol%), Mn (10.8 mg, 0.20 mmol, 2.0 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), 1,1-diphenylethylene (35.6 μL, 0.2 mmol, 2.0 equiv), and alkenyl triflates **2a** (23.9 μL, 0.15 mmol, 1.5 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 30 °C using an oil bath for 16 hours. Yield was determined by GC with adamantane as an internal standard.

These results showed that the radical involved process seemed to be ruled out.

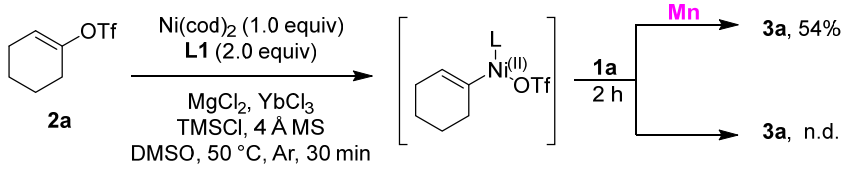
5.2 Stoichiometric experiments



Scheme S3

1) To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1a** (19.0 mg, 0.1 mmol) and **L5** (36.8 mg, 0.2 mmol, 2.0 equiv). $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 1.0 equiv), Mn (14.0 mg, 0.26 mmol, 2.6 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), and alkenyl triflates **2a** (35.0 μL, 0.22 mmol, 2.2 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 50 °C using an oil bath for 25 min. Yield was determined by GC with adamantane as an internal standard.

2) To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **1a** (19.0 mg, 0.1 mmol) and **L5** (36.8 mg, 0.2 mmol, 2.0 equiv). $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 1.0 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), and alkenyl triflates **2a** (35.0 μL, 0.22 mmol, 2.2 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 50 °C using an oil bath for 16 hours. Yield was determined by GC with adamantane as an internal standard. No desired product was found in this reaction.



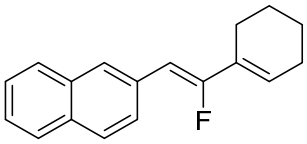
Scheme S4

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **L5** (36.8 mg, 0.2 mmol, 2.0 equiv). $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 1.0 equiv), $MgCl_2$ (19.0 mg, 0.2 mmol, 2.0 equiv), $YbCl_3$ (14.0 mg, 0.05 mmol, 0.5 equiv), and 4 Å MS (50 mg) were added to the tube in an argon-filled glove box. The tube was sealed and removed from the glove box. Then anhydrous DMSO (2 mL), TMSCl (15.2 μL, 0.12 mmol, 1.2 equiv), and alkenyl triflates **2a** (35.0 μL, 0.22 mmol, 2.2 equiv) were added in sequence under argon. The resulting mixture was allowed to heat at 50 °C using an oil bath for 30 min. Subsequently, *gem*-difluoroalkene **1a** (19.0 mg, 0.1 mmol) and Mn (14.0 mg, 0.26 mmol, 2.6 equiv) (or *gem*-difluoroalkene **1a** (19.0 mg, 0.1 mmol)) were added to the tube under

Ar, and the formed mixture was stirred at 50 °C for 2h. Yield was determined by GC with adamantane as an internal standard.

6. Characterization data of products

(*Z*)-2-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)naphthalene (3a)



According to the general procedure, the product **3a** was obtained after silica gel chromatography (petroleum ether). Pale yellow solid; 22.0 mg, 87% yield, mp. = 53-54 ºC.

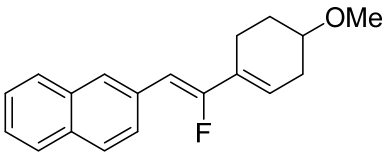
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.83 – 7.75 (m, 3H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.48 – 7.36 (m, 2H), 6.38 (s, 1H), 5.80 (d, *J* = 40.5 Hz, 1H), 2.23 (d, *J* = 5.5 Hz, 4H), 1.78 – 1.71 (m, 2H), 1.67 – 1.59 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7 (d, *J* = 260.2 Hz), 133.6, 132.3, 131.9 (d, *J* = 1.8 Hz), 129.2 (d, *J* = 19.6 Hz), 128.1, 127.9, 127.7 (d, *J* = 7.8 Hz), 127.5, 127.0 (d, *J* = 8.2 Hz), 126.8 (d, *J* = 8.4 Hz), 126.1, 125.8, 104.0 (d, *J* = 10.3 Hz), 25.5, 24.3 (d, *J* = 3.1 Hz), 22.4, 21.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.99 (d, *J* = 40.6 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}F$ 253.1387; found 253.1384.

(*Z*)-2-(2-fluoro-2-(4-methoxycyclohex-1-en-1-yl)vinyl)naphthalene (3b)



According to the general procedure, the product **3b** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). White solid; 21.1 mg, 75% yield, mp. = 49-50 ºC.

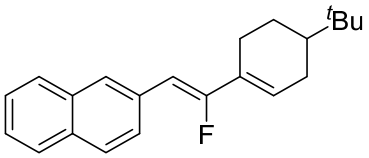
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.81 – 7.75 (m, 3H), 7.69 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.47 – 7.40 (m, 2H), 6.26 (s, 1H), 5.83 (d, *J* = 40.1 Hz, 1H), 3.59 – 3.48 (m, 1H), 3.40 (s, 3H), 2.57 (d, *J* = 17.7 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.35 – 2.18 (m, 2H), 2.07 – 1.96 (m, 1H), 1.85 – 1.72 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0 (d, *J* = 259.6 Hz), 133.5, 132.3 (d, *J* = 1.4 Hz), 131.6 (d, *J* = 2.1 Hz), 129.0 (d, *J* = 20.5 Hz), 128.0, 127.9, 127.8 (d, *J* = 7.9 Hz), 127.5, 126.9 (d, *J* = 7.8 Hz), 126.1, 125.8, 123.5 (d, *J* = 8.3 Hz), 104.7 (d, *J* = 10.6 Hz), 74.7, 55.9, 31.3, 26.8, 22.5 (d, *J* = 2.8 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.82 (d, *J* = 40.2 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}FO$ 283.1493; found 283.1487.

(*Z*)-2-(2-(4-(*tert*-butyl)cyclohex-1-en-1-yl)-2-fluorovinyl)naphthalene (3c)



According to the general procedure, the product **3c** was obtained after silica gel chromatography (petroleum ether). White solid; 24.7 mg, 80% yield, mp. = 104-105 ºC.

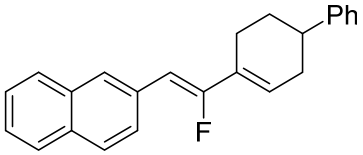
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.81 – 7.75 (m, 3H), 7.70 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.46 – 7.39 (m, 2H), 6.41 – 6.33 (m, 1H), 5.80 (d, *J* = 40.4 Hz, 1H), 2.39 (d, *J* = 15.7 Hz, 1H), 2.32 – 2.19 (m, 2H), 2.03 – 1.93 (m, 2H), 1.37 – 1.29 (m, 1H), 1.29 – 1.20 (m, 1H), 0.91 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6 (d, *J* = 259.9 Hz), 133.6, 132.3, 131.9 (d, *J* = 2.7 Hz), 129.1 (d, *J* = 19.7 Hz), 128.0, 127.9, 127.7 (d, *J* = 7.9 Hz), 127.5, 127.1 (d, *J* = 7.6 Hz), 127.0 (d, *J* = 8.2 Hz), 126.1, 125.8, 104.0 (d, *J* = 10.7 Hz), 43.7, 32.2, 27.2, 25.8 (d, *J* = 2.8 Hz), 23.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.68 (d, *J* = 40.9 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{22}H_{26}F$ 309.2013; found 309.2007.

(*Z*)-2-(2-fluoro-2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)vinyl)naphthalene (3d)



According to the general procedure, the product **3d** was obtained after silica gel chromatography (petroleum ether). White solid; 30.0 mg, 91% yield, mp. = 118-120 ºC.

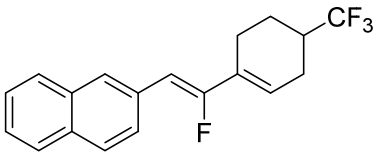
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.83 – 7.77 (m, 3H), 7.72 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 (d, *J* = 7.1 Hz, 2H), 7.24 – 7.21 (m, 1H), 6.47 (d, *J* = 2.7 Hz, 1H), 5.86 (d, *J* = 40.3 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.60 – 2.52 (m, 1H), 2.48 – 2.32 (m, 3H), 2.16 – 2.07 (m, 1H), 1.93 – 1.82 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4 (d, *J* = 259.7 Hz), 146.3, 133.6, 132.4, 131.7, 129.1 (d, *J* = 20.3 Hz), 128.5, 128.1, 127.9, 127.8 (d, *J* = 8.2 Hz), 127.5, 127.0 (d, *J* = 8.1 Hz), 126.9, 126.3, 126.2 (d, *J* = 7.8 Hz), 126.1, 125.9, 104.5 (d, *J* = 10.2 Hz), 39.6, 33.6, 29.5, 24.9 (d, *J* = 2.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.79 (d, *J* = 40.3 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}F$ 329.1700; found 329.1694.

(*Z*)-2-(2-fluoro-2-(4-(trifluoromethyl)cyclohex-1-en-1-yl)vinyl)naphthalene (3e)



According to the general procedure, the product **3e** was obtained after silica gel chromatography (petroleum ether). White solid; 26.2 mg, 82% yield, mp. = 119-120 ºC.

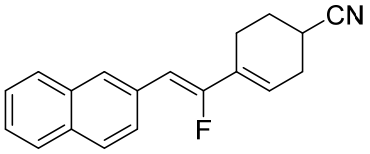
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.83 – 7.77 (m, 3H), 7.70 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.48 – 7.41 (m, 2H), 6.32 (d, *J* = 4.8 Hz, 1H), 5.83 (d, *J* = 40.1 Hz, 1H), 2.53 – 2.42 (m, 2H), 2.36 – 2.26 (m, 3H), 2.15 (dd, *J* = 11.6, 3.9 Hz, 1H), 1.69 – 1.59 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6 (d, *J* = 259.5 Hz), 133.5, 132.4, 131.3 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 20.7 Hz), 128.1, 128.0 (d, *J* = 8.5 Hz), 128.0, 127.5, 126.8 (d, *J* = 8.6 Hz), 126.2, 126.0, 123.0 (d, *J* = 8.4 Hz), 105.2 (d, *J* = 10.2 Hz), 38.1 (q, *J* = 27.7 Hz), 24.4 (d, *J* = 2.8 Hz), 23.4, 23.4, 21.2 (d, *J* = 2.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.60 (d, *J* = 8.6 Hz), -116.12 (d, *J* = 40.6 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}F_4$ 321.1261; found 321.1256.

(*Z*)-4-(1-fluoro-2-(naphthalen-2-yl)vinyl)cyclohex-3-ene-1-carbonitrile (3f)



According to the general procedure, the product **3f** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 60:1 - 10:1, v/v). White solid; 21.6 mg, 78% yield, mp. = 116-117 ºC.

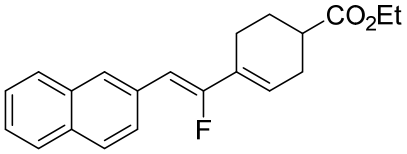
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.83 – 7.78 (m, 3H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.48 – 7.43 (m, 2H), 6.28 (s, 1H), 5.86 (d, *J* = 39.9 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.68 – 2.45 (m, 3H), 2.39 – 2.29 (m, 1H), 2.16 – 2.07 (m, 1H), 2.07 – 1.95 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2 (d, *J* = 259.6 Hz), 133.5, 132.5, 131.1, 129.2 (d, *J* = 21.5 Hz), 128.2 (d, *J* = 8.0 Hz), 128.1, 128.1, 127.6, 126.9 (d, *J* = 8.8 Hz), 126.3, 126.1, 121.9 (d, *J* = 6.4 Hz), 121.8, 105.7 (d, *J* = 10.9 Hz), 28.6, 25.3, 24.3, 22.2 (d, *J* = 3.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -116.53 (d, *J* = 39.9 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}FN$ 278.1340; found 278.1336.

ethyl (*Z*)-4-(1-fluoro-2-(naphthalen-2-yl)vinyl)cyclohex-3-ene-1-carboxylate (3g)



According to the general procedure, the product **3g** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). White solid; 24.3 mg, 75% yield, mp. = 76-77 ºC.

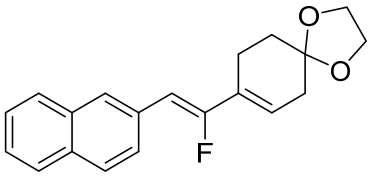
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.82 – 7.76 (m, 3H), 7.69 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.49 – 7.38 (m, 2H), 6.36 (s, 1H), 5.82 (d, *J* = 40.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.63 – 2.55 (m, 1H), 2.55 – 2.45 (m, 2H), 2.45 – 2.37 (m, 1H), 2.34 – 2.26 (m, 1H), 2.20 – 2.13 (m, 1H), 1.86 – 1.76 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 158.0 (d, *J* = 259.7 Hz), 133.5, 132.4, 131.5 (d, *J* = 2.1 Hz), 128.9 (d, *J* = 20.6 Hz), 128.0, 127.9, 127.8 (d, *J* = 7.7 Hz), 127.5, 126.9 (d, *J* = 8.2 Hz), 126.1, 125.9, 124.5 (d, *J* = 7.8 Hz), 104.7 (d, *J* = 10.6 Hz), 60.5, 38.8, 27.8, 24.9, 23.6 (d, *J* = 2.9 Hz), 14.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.99 (d, *J* = 40.2 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}FO_2$ 325.1598; found 325.1593.

(*Z*)-8-(1-fluoro-2-(naphthalen-2-yl)vinyl)-1,4-dioxaspiro[4.5]dec-7-ene (3h)



According to the general procedure, the product **3h** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v). Pale yellow solid; 21.7 mg, 70% yield, mp. = 78-79 ºC.

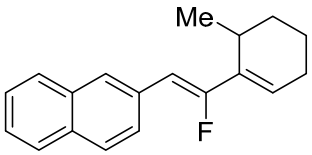
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.83 – 7.75 (m, 3H), 7.69 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.46 – 7.41 (m, 2H), 6.26 (t, *J* = 4.0 Hz, 1H), 5.87 (d, *J* = 40.0 Hz, 1H), 4.01 (s, 4H), 2.55 – 2.50 (m, 2H), 2.48 (s, 2H), 1.90 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8 (d, *J* = 259.8 Hz), 133.5, 132.4, 131.6 (d, *J* = 2.4 Hz), 128.8 (d, *J* = 20.5 Hz), 128.1, 127.9, 127.9 (d, *J* = 8.0 Hz), 127.5, 126.9 (d, *J* = 7.8 Hz), 126.1, 125.9, 123.6 (d, *J* = 7.8 Hz), 107.5, 105.1 (d, *J* = 10.7 Hz), 64.5, 35.8, 30.8, 23.8 (d, *J* = 2.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.66 (d, *J* = 40.7 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}FO_2$ 311.1442; found 311.1437.

(*Z*)-2-(2-fluoro-2-(6-methylcyclohex-1-en-1-yl)vinyl)naphthalene (3i)



According to the general procedure, the product **3i** was obtained after silica gel chromatography (petroleum ether). Colorless oil; 20.7 mg, 78% yield.

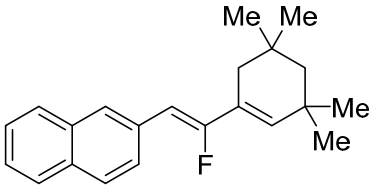
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.82 – 7.76 (m, 3H), 7.71 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 6.31 (t, *J* = 4.1 Hz, 1H), 5.88 (d, *J* = 40.7 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.30 – 2.14 (m, 2H), 1.80 – 1.69 (m, 2H), 1.68 – 1.60 (m, 2H), 1.23 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4 (d, *J* = 260.3 Hz), 134.8 (d, *J* = 19.5 Hz), 133.6, 132.3, 131.9 (d, *J* = 2.1 Hz), 128.0, 127.9, 127.6 (d, *J* = 8.1 Hz), 127.5, 127.0 (d, *J* = 7.9 Hz), 126.7 (d, *J* = 9.0 Hz), 126.1, 125.7, 104.4 (d, *J* = 11.4 Hz), 29.7, 27.5 (d, *J* = 3.0 Hz), 25.7, 20.4, 17.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.84 (d, *J* = 40.8 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}F$ 267.1544; found 267.1539.

(*Z*)-2-(2-fluoro-2-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)vinyl)naphthalene (3j)



According to the general procedure, the product **3j** was obtained after silica gel chromatography (petroleum ether). White solid; 24.5 mg, 80% yield, mp. = 106-108 ºC.

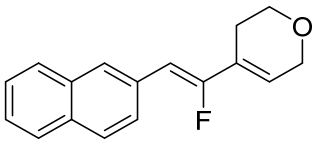
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.81 – 7.75 (m, 3H), 7.71 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.46 – 7.39 (m, 2H), 6.11 (s, 1H), 5.85 (d, *J* = 40.4 Hz, 1H), 1.99 (s, 2H), 1.40 (s, 2H), 1.10 (s, 6H), 1.04 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8 (d, *J* = 259.6 Hz), 135.2, 135.2, 133.6, 132.3 (d, *J* = 1.6 Hz), 131.9 (d, *J* = 3.2 Hz), 128.0, 127.9, 127.7 (d, *J* = 7.8 Hz), 127.5, 127.0 (d, *J* = 8.4 Hz), 126.1, 125.8, 104.7 (d, *J* = 11.2 Hz), 49.3, 37.9 (d, *J* = 2.8 Hz), 32.9, 31.4, 30.6, 30.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.45 (d, *J* = 40.5 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{22}H_{26}F$ 309.2013; found 309.2008.

(*Z*)-4-(1-fluoro-2-(naphthalen-2-yl)vinyl)-3,6-dihydro-2*H*-pyran (3k)



According to the general procedure, the product **3k** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 60:1 - 20:1, v/v). White solid; 20.2 mg, 80% yield, mp. = 112-113 ºC.

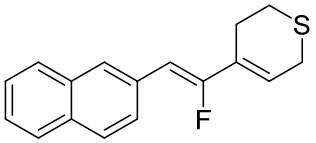
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.82 – 7.77 (m, 3H), 7.71 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48 – 7.42 (m, 2H), 6.30 (s, 1H), 5.83 (d, *J* = 39.8 Hz, 1H), 4.34 (d, *J* = 2.5 Hz, 2H), 3.89 (t, *J* = 5.5 Hz, 2H), 2.36 (d, *J* = 1.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1 (d, *J* = 259.3 Hz), 133.5, 132.5, 131.2 (d, *J* = 2.8 Hz), 128.1, 128.1, 127.6, 127.3 (d, *J* = 22.6 Hz), 126.9 (d, *J* = 8.0 Hz), 126.2, 126.1, 124.2 (d, *J* = 7.4 Hz), 105.2 (d, *J* = 9.9 Hz), 65.6, 63.8, 24.4 (d, *J* = 3.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.54 (d, *J* = 39.6 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}FO$ 255.1179; found 255.1176.

(*Z*)-4-(1-fluoro-2-(naphthalen-2-yl)vinyl)-3,6-dihydro-2*H*-thiopyran (3l)



According to the general procedure, the product **3l** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 60:1 - 20:1, v/v). Yellow solid; 14.8 mg, 55% yield, mp. = 102-103 ºC.

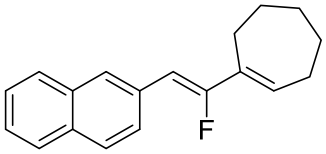
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.82 – 7.77 (m, 3H), 7.70 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.49 – 7.40 (m, 2H), 6.52 (t, *J* = 4.5 Hz, 1H), 5.89 (d, *J* = 40.2 Hz, 1H), 3.39 – 3.35 (m, 2H), 2.86 (t, *J* = 5.8 Hz, 2H), 2.60 – 2.53 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0 (d, *J* = 260.1 Hz), 133.5, 132.5, 131.2 (d, *J* = 2.7 Hz), 130.0 (d, *J* = 19.6 Hz), 128.1 (d, *J* = 6.3 Hz), 128.1, 128.0, 127.5, 126.9 (d, *J* = 7.8 Hz), 126.2, 126.0, 122.8 (d, *J* = 8.8 Hz), 105.0 (d, *J* = 10.8 Hz), 26.0, 25.1, 25.1 (d, *J* = 3.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -116.37 (d, *J* = 40.3 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}FS$ 271.0951; found 271.0947.

(*Z*)-2-(2-(cyclohept-1-en-1-yl)-2-fluorovinyl)naphthalene (3m)



According to the general procedure, the product **3m** was obtained after silica gel chromatography (petroleum ether). Pale yellow solid; 19.9 mg, 75% yield, mp. = 55-56 ºC.

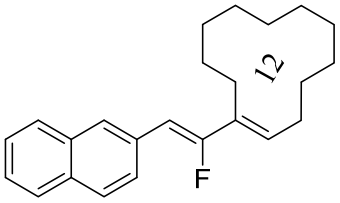
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.85 – 7.75 (m, 3H), 7.70 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48 – 7.39 (m, 2H), 6.55 (t, *J* = 7.0 Hz, 1H), 5.99 (d, *J* = 39.8 Hz, 1H), 2.49 – 2.41 (m, 2H), 2.37 – 2.30 (m, 2H), 1.87 – 1.78 (m, 2H), 1.66 – 1.59 (m, 2H), 1.59 – 1.50 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3 (d, *J* = 259.4 Hz), 136.5 (d, *J* = 18.8 Hz), 133.6, 132.3, 132.0 (d, *J* = 2.0 Hz), 131.5 (d, *J* = 9.6 Hz), 128.0, 127.9, 127.7 (d, *J* = 8.2 Hz), 127.5, 127.0 (d, *J* = 8.2 Hz), 126.1, 125.8, 104.6 (d, *J* = 12.1 Hz), 32.2, 28.4, 28.3 (d, *J* = 3.0 Hz), 26.3, 26.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.24 (d, *J* = 39.9 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}F$ 267.1544; found 267.1540.

2-((*Z*)-2-((*E*)-cyclododec-1-en-1-yl)-2-fluorovinyl)naphthalene (3n)



According to the general procedure, the product **3n** was obtained after silica gel chromatography (petroleum ether). White solid; 18.2 mg, 55% yield, mp. = 107-108 ºC.

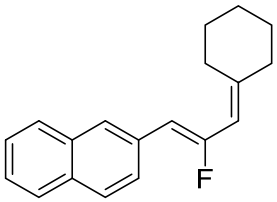
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.81 – 7.77 (m, 3H), 7.72 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.47 – 7.40 (m, 2H), 6.14 (t, *J* = 8.1 Hz, 1H), 5.91 (d, *J* = 40.6 Hz, 1H), 2.42 (t, *J* = 6.7 Hz, 2H), 2.25 (m, 2H), 1.71 – 1.65 (m, 2H), 1.60 – 1.55 (m, 2H), 1.51 – 1.42 (m, 4H), 1.42 – 1.29 (m, 8H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9 (d, *J* = 260.6 Hz), 133.6, 132.3, 132.0 (d, *J* = 2.0 Hz), 131.7 (d, *J* = 18.2 Hz), 131.1 (d, *J* = 8.8 Hz), 128.0, 127.9, 127.7 (d, *J* = 7.8 Hz), 127.5, 127.0 (d, *J* = 8.3 Hz), 126.1, 125.7, 105.6 (d, *J* = 11.7 Hz), 26.7, 26.7, 25.6, 25.3, 25.1, 25.0, 23.7, 23.5 (d, *J* = 3.0 Hz), 23.1, 22.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.59 (d, *J* = 40.5 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{24}H_{30}F$ 337.2326; found 337.2320.

(*Z*)-2-(3-cyclohexylidene-2-fluoroprop-1-en-1-yl)naphthalene (3o)



According to the general procedure, **2o** (4.0 equiv) and Mn (4.4 equiv) were used, and the product **3o** was obtained after silica gel chromatography (petroleum ether). White solid; 16.0 mg, 60% yield, mp. = 92-93 ºC.

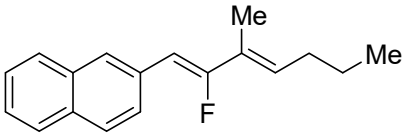
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.80 – 7.73 (m, 3H), 7.66 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.47 – 7.39 (m, 2H), 5.79 – 5.62 (m, 2H), 2.66 – 2.55 (m, 2H), 2.27 – 2.16 (m, 2H), 1.69 – 1.57 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5 (d, *J* = 263.8 Hz),148.0, 133.6, 132.3 (d, *J* = 1.5 Hz), 132.0 (d, *J* = 3.0 Hz), 128.0, 127.9, 127.5, 127.2 (d, *J* = 8.3 Hz), 126.7 (d, *J* = 7.9 Hz), 126.1, 125.7, 114.6 (d, *J* = 20.9 Hz), 109.3 (d, *J* = 10.8 Hz), 38.3, 30.6 (d, *J* = 9.4 Hz), 28.8, 28.0, 26.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -107.23 (dd, *J* = 38.5, 27.4 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}F$ 267.1544; found 267.1540.

2-((1*Z*,3*E*)-2-fluoro-3-methylhepta-1,3-dien-1-yl)naphthalene (3p)



According to the general procedure, the product **3p** was obtained after silica gel chromatography (petroleum ether). Colorless oil; 11.4 mg, 45% yield.

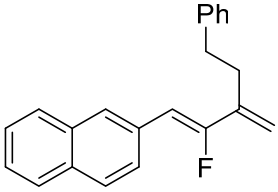
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.79 (m, 3H), 7.71 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 6.15 (t, *J* = 7.4 Hz, 1H), 5.88 (d, *J* = 40.1 Hz, 1H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.90 (s, 3H), 1.53 – 1.46 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4 (d, *J* = 259.3 Hz), 133.6, 132.3, 131.9 (d, *J* = 3.0 Hz), 129.8 (d, *J* = 8.2 Hz), 128.1, 127.9, 127.7 (d, *J* = 7.7 Hz), 127.5, 127.0 (d, *J* = 8.3 Hz), 126.9 (d, *J* = 20.0 Hz), 126.1, 125.8, 105.0 (d, *J* = 11.3 Hz), 30.4, 22.6, 13.9, 12.7 (d, *J* = 3.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.69 (d, *J* = 40.1 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}F$ 255.1544; found 255.1539.

(*Z*)-2-(2-fluoro-3-methylene-5-phenylpent-1-en-1-yl)naphthalene (3q)



According to the general procedure, the product **3q** was obtained after silica gel chromatography (petroleum ether). White solid; 17.2 mg, 57% yield, mp. = 35-36 ºC.

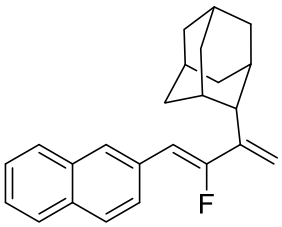
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.86 – 7.78 (m, 3H), 7.72 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.20 (m, 3H), 6.03 (d, *J* = 39.7 Hz, 1H), 5.64 (s, 1H), 5.16 (d, *J* = 3.9 Hz, 1H), 2.98 – 2.88 (m, 2H), 2.69 – 2.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.7 (d, *J* = 260.6 Hz), 141.4, 139.2 (d, *J* = 21.8 Hz), 133.5, 132.6, 131.2, 128.5, 128.4, 128.3 (d, *J* = 7.8 Hz), 128.1, 128.0, 127.5, 126.9 (d, *J* = 8.1 Hz), 126.2, 126.1, 126.1, 113.8 (d, *J* = 8.1 Hz), 106.9 (d, *J* = 10.8 Hz), 34.9, 34.1 (d, *J* = 3.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.95 (dd, *J* = 40.0, 3.2 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}F$ 303.1544; found 303.1538.

(1*R*,3*S*,5*r*,7*r*)-2-((*Z*)-3-fluoro-4-(naphthalen-2-yl)buta-1,3-dien-2-yl)adamantane (3r)



According to the general procedure, the product **3r** was obtained after silica gel chromatography (petroleum ether). White solid; 24.9 mg, 75% yield, mp. = 62-63 ºC.

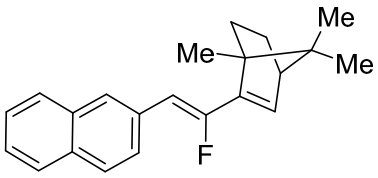
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.83 – 7.77 (m, 3H), 7.68 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48 – 7.40 (m, 2H), 5.90 (d, *J* = 37.3 Hz, 1H), 5.41 (dd, *J* = 3.1, 1.3 Hz, 1H), 5.20 – 5.13 (m, 1H), 2.04 (s, 3H), 1.86 (d, *J* = 2.4 Hz, 6H), 1.72 (q, *J* = 12.0 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9 (d, *J* = 267.0 Hz), 152.7 (d, *J* = 21.5 Hz), 133.5, 132.4, 131.6 (d, *J* = 3.8 Hz), 128.1, 127.9, 127.6 (d, *J* = 8.1 Hz), 127.6, 126.8 (d, *J* = 7.7 Hz), 126.1, 125.9, 115.7 (d, *J* = 7.5 Hz), 108.7 (d, *J* = 11.2 Hz), 41.5, 37.2 (d, *J* = 2.2 Hz), 36.8, 28.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -95.58 (d, *J* = 37.3 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{24}H_{26}F$ 333.2013; found 333.2007.

2-((*Z*)-2-fluoro-2-((4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)vinyl)naphthalene (3s)



According to the general procedure, the product **3s** was obtained after silica gel chromatography (petroleum ether). White solid; 10.7 mg, 35% yield, mp. = 39-40 ºC.

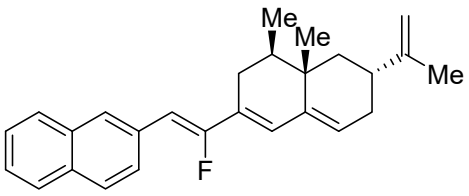
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.84 – 7.74 (m, 3H), 7.70 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48 – 7.38 (m, 2H), 6.45 (d, *J* = 3.4 Hz, 1H), 5.98 (d, *J* = 41.0 Hz, 1H), 2.43 (t, *J* = 3.6 Hz, 1H), 2.02 – 1.91 (m, 1H), 1.70 – 1.61 (m, 1H), 1.31 (s, 3H), 1.26 – 1.22 (m, 1H), 1.11 – 1.05 (m, 1H), 0.87 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0 (d, *J* = 257.1 Hz), 141.5 (d, *J* = 25.5 Hz), 135.8 (d, *J* = 6.8 Hz), 133.6, 132.3, 131.9 (d, *J* = 2.6 Hz), 128.0, 127.9, 127.7 (d, *J* = 7.9 Hz), 127.5, 127.0 (d, *J* = 7.9 Hz), 126.1, 125.7, 106.0 (d, *J* = 10.8 Hz), 57.5, 54.0 (d, *J* = 3.3 Hz), 51.5, 31.7, 25.4, 19.6, 19.5, 13.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -106.92 (d, *J* = 41.6 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}F$ 307.1857; found 307.1852.

2-((*Z*)-2-((4*R*,4a*S*,6*R*)-4,4a-dimethyl-6-(prop-1-en-2-yl)-3,4,4a,5,6,7-hexahydronaphthalen-2-yl)-2-fluorovinyl)naphthalene (3t)



According to the general procedure, the product **3t** was obtained after silica gel chromatography (petroleum ether). Yellow solid; 22.7 mg, 61% yield, mp. = 128-130 ºC.

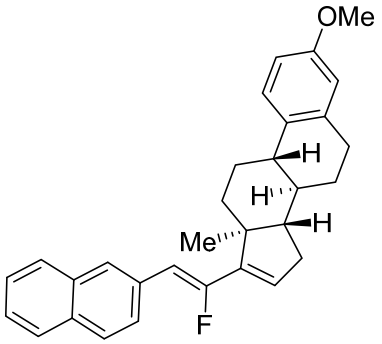
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 1H), 7.83 – 7.77 (m, 3H), 7.72 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.49 – 7.41 (m, 2H), 6.57 (s, 1H), 5.91 (d, *J* = 40.2 Hz, 1H), 5.73 (dd, *J* = 4.9, 3.0 Hz, 1H), 4.89 – 4.72 (m, 2H), 2.52 – 2.44 (m, 1H), 2.38 – 2.28 (m, 2H), 2.17 – 2.01 (m, 2H), 1.82 – 1.75 (m, 4H), 1.69 – 1.60 (m, 1H), 1.24 (t, *J* = 12.6 Hz, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3 (d, *J* = 259.2 Hz), 150.0, 141.9, 133.6, 132.3, 131.8 (d, *J* = 2.0 Hz), 128.1, 128.0, 127.8 (d, *J* = 7.8 Hz), 127.7, 127.5, 126.9 (d, *J* = 8.3 Hz), 126.6 (d, *J* = 8.2 Hz), 126.4 (d, *J* = 19.9 Hz), 126.1, 125.8, 108.9, 105.4 (d, *J* = 10.5 Hz), 39.9, 38.6, 37.2, 35.9, 31.6, 30.9 (d, *J* = 2.6 Hz), 20.7, 17.7, 14.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -116.47 (d, *J* = 40.6 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{27}H_{30}F$ 373.2326; found 373.2319.

(8*S*,9*S*,13*S*,14*S*)-17-((*Z*)-1-fluoro-2-(naphthalen-2-yl)vinyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthrene (3u)



According to the general procedure, **2u** (4.0 equiv) and Mn (4.4 equiv) were used, and the product **3u** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 200:1 - 50:1, v/v). White solid; 27.1 mg, 62% yield, mp. = 92-93 ºC.

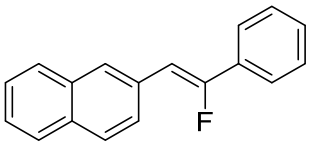
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 1H), 7.83 – 7.77 (m, 3H), 7.73 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 6.26 (s, 1H), 6.00 (d, *J* = 41.3 Hz, 1H), 3.79 (s, 3H), 3.00 – 2.85 (m, 2H), 2.44 (ddd, *J* = 11.5, 6.8, 4.2 Hz, 1H), 2.41 – 2.27 (m, 3H), 2.16 – 2.07 (m, 1H), 1.99 – 1.91 (m, 1H), 1.89 – 1.74 (m, 2H), 1.74 – 1.62 (m, 2H), 1.53 – 1.43 (m, 1H), 1.06 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 155.3 (d, *J* = 258.6 Hz), 147.2 (d, *J* = 22.3 Hz), 137.9, 133.6, 132.6, 132.4, 131.7 (d, *J* = 2.7 Hz), 130.4 (d, *J* = 4.3 Hz), 128.1, 128.0, 128.0 (d, *J* = 7.8 Hz), 127.5, 127.0 (d, *J* = 8.2 Hz), 126.1, 126.0, 125.9, 113.9, 111.5, 106.6 (d, *J* = 10.0 Hz), 56.4, 55.2, 46.7 (d, *J* = 4.1 Hz), 44.0, 37.1, 35.8, 31.1, 29.7, 27.7, 26.7, 16.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -107.82 (d, *J* = 41.1 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{31}H_{32}FO$ 439.2432; found 439.2424.

(*Z*)-2-(2-fluoro-2-phenylvinyl)naphthalene (3v)



According to the general procedure, the reaction was performed at room temperature, and the product **3v** was obtained after silica gel chromatography (petroleum ether). White solid; 16.4 mg, 66% yield, mp. = 100-101 ºC.

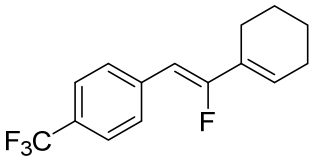
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.92 – 7.78 (m, 4H), 7.73 – 7.67 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 39.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5 (d, *J* = 259.1 Hz), 133.5, 132.9 (d, *J* = 27.9 Hz), 132.6, 131.3 (d, *J* = 2.9 Hz), 129.1, 128.6 (d, *J* = 1.8 Hz), 128.1, 128.1, 128.1 (d, *J* = 7.8 Hz), 127.6, 126.8 (d, *J* = 8.0 Hz), 126.2, 126.1, 124.3 (d, *J* = 7.6 Hz), 106.0 (d, *J* = 10.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.78 (d, *J* = 39.8 Hz).

FTMS (APCI) m/z: $[M-H]^+$ calcd for $C_{18}H_{12}F$ 247.0918; found 247.0913.

(*Z*)-1-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-4-(trifluoromethyl)benzene (4a)



According to the general procedure, **2a** (4.0 equiv) and Mn (4.4 equiv) were used, and the product **4a** was obtained after silica gel chromatography (petroleum ether). Pale yellow oil; 13.5 mg, 50% yield.

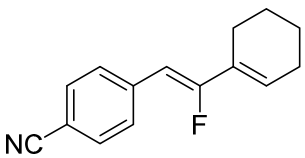
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 6.47 – 6.37 (m, 1H), 5.68 (d, *J* = 39.6 Hz, 1H), 2.27 – 2.18 (m, 4H), 1.79 – 1.71 (m, 2H), 1.69 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8 (d, *J* = 262.3 Hz), 137.8, 135.7, 135.0, 132.8, 128.9 (d, *J* = 19.6 Hz), 128.8 (d, *J* = 7.9 Hz), 128.3 (d, *J* = 8.5 Hz), 125.3 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 271.8 Hz), 102.6 (d, *J* = 10.6 Hz), 25.5, 24.2 (d, *J* = 3.1 Hz), 22.3, 21.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.51, -113.73 (d, *J* = 40.0 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}F_4$ 271.1104; found 271.1111.

(*Z*)-4-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)benzonitrile (4b)



According to the general procedure, the product **4b** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 80:1 - 20:1, v/v). White solid; 14.7 mg, 65% yield, mp. = 85-86 ºC.

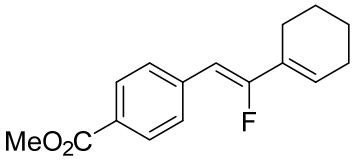
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 4H), 6.50 – 6.40 (m, 1H), 5.66 (d, *J* = 39.2 Hz, 1H), 2.27 – 2.22 (m, 2H), 2.22 – 2.17 (m, 2H), 1.77 – 1.72 (m, 2H), 1.67 – 1.61 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5 (d, *J* = 264.7 Hz), 139.0 (d, *J* = 2.0 Hz), 132.2, 129.3 (d, *J* = 8.6 Hz), 129.1 (d, *J* = 8.2 Hz), 128.8 (d, *J* = 18.8 Hz), 119.1, 109.7 (d, *J* = 2.5 Hz), 102.5 (d, *J* = 10.2 Hz), 25.6, 24.2 (d, *J* = 3.0 Hz), 22.2, 21.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.74 (d, *J* = 39.5 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}FN$ 228.1183; found 228.1181.

methyl (*Z*)-4-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)benzoate (4c)



According to the general procedure, **2a** (3.0 equiv) and Mn (3.3 equiv) were used, and the product **4c** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). Colorless oil; 16.4 mg, 63% yield.

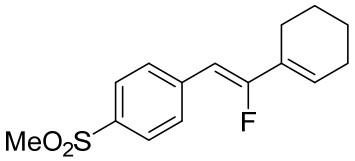
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.41 (t, *J* = 3.5 Hz, 1H), 5.69 (d, *J* = 39.9 Hz, 1H), 3.90 (s, 3H), 2.28 – 2.16 (m, 4H), 1.77 – 1.71 (m, 2H), 1.66 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 159.8 (d, *J* = 262.8 Hz), 134.0 (d, *J* = 2.0 Hz), 129.7, 129.0 (d, *J* = 19.5 Hz), 128.6 (d, *J* = 8.4 Hz), 128.3 (d, *J* = 7.9 Hz), 128.0 (d, *J* = 1.9 Hz), 103.1 (d, *J* = 10.1 Hz), 52.0, 25.6, 24.2 (d, *J* = 3.0 Hz), 22.3, 21.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.07 (d, *J* = 40.0 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{16}H_{18}FO_2$ 261.1285; found 261.1281.

(*Z*)-1-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-4-(methylsulfonyl)benzene (4d)



According to the general procedure, the product **4d** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v). White solid; 17.1 mg, 61% yield, mp. = 114-115 ºC.

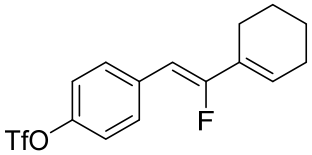
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 6.47 (s, 1H), 5.71 (d, *J* = 39.2 Hz, 1H), 3.05 (s, 3H), 2.30 – 2.18 (m, 4H), 1.79 – 1.71 (m, 2H), 1.68 – 1.62 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6 (d, *J* = 264.1 Hz), 140.0, 137.9, 129.3 (d, *J* = 9.5 Hz), 129.3 (d, *J* = 8.7 Hz), 128.8 (d, *J* = 19.2 Hz), 127.5, 102.3 (d, *J* = 10.0 Hz), 44.6, 25.6, 24.2 (d, *J* = 2.7 Hz), 22.2, 21.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.81 (d, *J* = 39.5 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}FO_2S$ 281.1006; found 281.1003.

(*Z*)-4-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)phenyl trifluoromethanesulfonate (4e)



According to the general procedure, the product **4e** was obtained after silica gel chromatography (petroleum ether). Colorless oil; 21.3 mg, 61% yield.

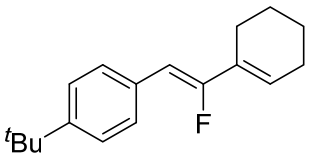
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.24 – 7.18 (m, 2H), 6.40 (s, 1H), 5.64 (d, *J* = 39.4 Hz, 1H), 2.25 – 2.17 (m, 4H), 1.77 – 1.71 (m, 2H), 1.67 – 1.62 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4 (d, *J* = 261.6 Hz), 147.8 (d, *J* = 3.4 Hz), 134.8 (d, *J* = 1.9 Hz), 130.3 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 19.0 Hz), 128.1 (d, *J* = 8.5 Hz), 121.3, 118.8 (q, *J* = 321.2 Hz), 102.0 (d, *J* = 10.7 Hz), 25.5, 24.2 (d, *J* = 3.0 Hz), 22.3, 21.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -72.82, -114.98 (d, *J* = 39.9 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}F_4O_3S$ 351.0673; found 351.0668.

(*Z*)-1-(tert-butyl)-4-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)benzene (4f)



According to the general procedure, **2a** (2.0 equiv) and Mn (2.2 equiv) were used, and the product **4f** was obtained after silica gel chromatography (petroleum ether). Colorless oil; 16.3 mg, 63% yield.

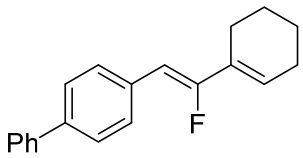
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.37 – 7.33 (m, 2H), 6.31 (s, 1H), 5.64 (d, *J* = 40.7 Hz, 1H), 2.24 – 2.17 (m, 4H), 1.76 – 1.70 (m, 2H), 1.66 – 1.60 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1 (d, *J* = 258.5 Hz), 149.8, 131.4 (d, *J* = 1.9 Hz), 129.2 (d, *J* = 19.7 Hz), 128.5 (d, *J* = 7.6 Hz), 126.1 (d, *J* = 8.1 Hz), 125.4, 103.6 (d, *J* = 11.0 Hz), 34.6, 31.3, 25.4, 24.3 (d, *J* = 3.1 Hz), 22.4, 21.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.34 (d, *J* = 40.6 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}F$ 259.1857; found 259.1852.

(*Z*)-4-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-1,1'-biphenyl (4g)



According to the general procedure, **2a** (4.0 equiv) and Mn (4.4 equiv) were used, and the product **4g** was obtained after silica gel chromatography (petroleum ether). White solid; 23.6 mg, 85% yield, mp. = 125-127 ºC.

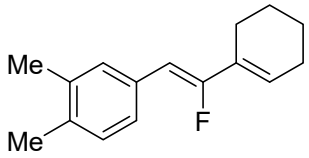
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 4H), 7.58 – 7.55 (m, 2H), 7.45 – 7.39 (m, 2H), 7.36 – 7.30 (m, 1H), 6.36 (t, *J* = 3.4 Hz, 1H), 5.70 (d, *J* = 40.5 Hz, 1H), 2.26 – 2.17 (m, 4H), 1.78 – 1.71 (m, 2H), 1.68 – 1.61 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6 (d, *J* = 259.5 Hz), 140.7, 139.3 (d, *J* = 2.6 Hz), 133.4 (d, *J* = 3.1 Hz), 129.2, 129.2, 128.8, 127.2, 127.1, 126.9, 126.7 (d, *J* = 7.9 Hz), 103.4 (d, *J* = 11.1 Hz), 25.5, 24.3 (d, *J* = 3.8 Hz), 22.4, 21.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -116.00 (d, *J* = 40.6 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}F$ 279.1544; found 279.1541.

(*Z*)-4-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-1,2-dimethylbenzene (4h)



According to the general procedure, the product **4h** was obtained after silica gel chromatography (petroleum ether). White solid; 13.3 mg, 58% yield, mp. = 47-48 ºC.

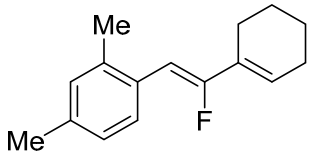
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.30 (s, 1H), 5.60 (d, *J* = 40.9 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 2.22 – 2.17 (m, 4H), 1.75 – 1.70 (m, 2H), 1.66 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (d, *J* = 258.2 Hz), 136.5, 135.3 (d, *J* = 1.6 Hz), 131.8 (d, *J* = 1.8 Hz), 130.1 (d, *J* = 7.4 Hz), 129.8, 129.3 (d, *J* = 19.7 Hz), 126.3 (d, *J* = 7.9 Hz), 125.9 (d, *J* = 8.3 Hz), 103.8 (d, *J* = 10.9 Hz), 25.4, 24.3 (d, *J* = 3.0 Hz), 22.4, 21.9, 19.8, 19.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.41 (d, *J* = 41.2 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}F$ 231.1544; found 231.1541.

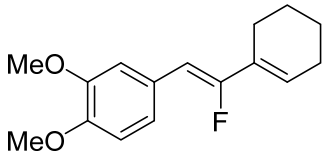
(*Z*)-1-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-2,4-dimethylbenzene (4i)



According to the general procedure, the product **4i** was obtained after silica gel chromatography (petroleum ether). Colorless oil; 12.6 mg, 55% yield.

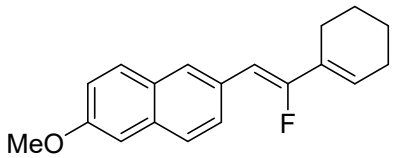
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.30 (s, 1H), 5.60 (d, *J* = 40.9 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 2.22 – 2.17 (m, 4H), 1.75 – 1.70 (m, 2H), 1.66 – 1.60 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.7 (d, *J* = 257.3 Hz), 136.6 (d, *J* = 1.5 Hz), 135.7, 130.8, 129.7, 129.2, 129.2, 126.6, 126.0 (d, *J* = 8.6 Hz), 100.9 (d, *J* = 11.9 Hz), 25.4, 24.3 (d, *J* = 3.4 Hz), 22.4, 22.0, 21.1, 20.2.
^{19}F NMR (565 MHz, $CDCl_3$) δ -119.21 (d, *J* = 40.0 Hz).
FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}F$ 231.1544; found 231.1538.

(*Z*)-4-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-1,2-dimethoxybenzene (4j)



According to the general procedure, **2a** (4.0 equiv) and Mn (4.4 equiv) were used, and the product **4j** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 60:1 - 20:1, v/v). White solid; 17.5 mg, 67% yield, mp. = 78-79 ºC.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 1.2 Hz, 1H), 7.05 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.82 (dd, *J* = 10.8, 6.6 Hz, 1H), 6.29 (s, 1H), 5.60 (d, *J* = 40.5 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.23 – 2.17 (m, 4H), 1.76 – 1.70 (m, 2H), 1.66 – 1.61 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4 (d, *J* = 257.2 Hz), 148.7, 148.0 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 19.7 Hz), 127.3 (d, *J* = 2.9 Hz), 125.7 (d, *J* = 8.0 Hz), 121.8 (d, *J* = 7.5 Hz), 111.8 (d, *J* = 9.9 Hz), 111.1, 103.6 (d, *J* = 11.0 Hz), 55.9, 55.8, 25.4, 24.3 (d, *J* = 3.6 Hz), 22.4, 21.9.
^{19}F NMR (565 MHz, $CDCl_3$) δ -118.71 (d, *J* = 41.1 Hz).
FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}FO_2$ 263.1442; found 263.1439.

(*Z*)-2-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-6-methoxynaphthalene (4k)



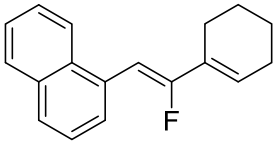
According to the general procedure, the product **4k** was obtained after silica gel chromatography (petroleum ether). White solid; 22.0 mg, 78% yield, mp. = 111-112 ºC.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.67 (s, 2H), 7.13 – 7.10 (m, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.36 (s, 1H), 5.78 (d, *J* = 40.7 Hz, 1H), 3.91 (s, 3H), 2.27 – 2.18 (m, 4H), 1.79 – 1.70 (m, 2H), 1.68 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2 (d, *J* = 258.5 Hz), 157.7, 133.4 (d, *J* = 1.2 Hz), 129.7 (d, *J* = 2.0 Hz), 129.6, 129.2 (d, *J* = 19.6 Hz), 129.0, 127.6 (d, *J* = 8.4 Hz), 127.5 (d, *J* = 8.5 Hz), 126.7, 126.2 (d, *J* = 7.8 Hz), 118.9, 105.6, 104.0 (d, *J* = 10.7 Hz), 55.3, 25.5, 24.3 (d, *J* = 3.0 Hz), 22.4, 21.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -116.96 (d, *J* = 41.2 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}FO$ 283.1493; found 283.1489.

(*Z*)-1-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)naphthalene (4l)



According to the general procedure, the product **4l** was obtained after silica gel chromatography (petroleum ether). Pale yellow solid; 16.4 mg, 65% yield, mp. = 39-40 ºC.

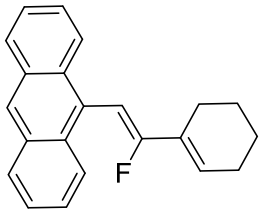
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.79 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.42 (m, 3H), 6.40 (t, *J* = 3.9 Hz, 1H), 6.32 (d, *J* = 37.9 Hz, 1H), 2.40 – 2.33 (m, 2H), 2.28 – 2.21 (m, 2H), 1.83 – 1.76 (m, 2H), 1.71 – 1.64 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8 (d, *J* = 258.4 Hz), 133.7, 131.6, 130.2, 129.2 (d, *J* = 20.2 Hz), 128.7, 127.4, 127.4 (d, *J* = 10.3 Hz), 127.0 (d, *J* = 7.8 Hz), 125.9, 125.6, 125.6, 124.1, 100.2 (d, *J* = 12.4 Hz), 25.5, 24.4 (d, *J* = 3.1 Hz), 22.4, 22.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.65 (d, *J* = 38.4 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}F$ 253.1387; found 253.1383.

(*Z*)-9-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)anthracene (4m)



According to the general procedure, **2a** (4.0 equiv) and Mn (4.4 equiv) were used, and the product **4m** was obtained after silica gel chromatography (petroleum ether). Yellow solid; 16.9 mg, 56% yield, mp. = 175-177 ºC.

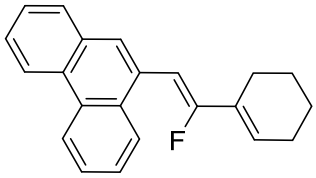
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.15 – 8.09 (m, 2H), 8.03 – 7.94 (m, 2H), 7.50 – 7.40 (m, 4H), 6.46 (d, *J* = 39.3 Hz, 1H), 6.41 (t, *J* = 4.0 Hz, 1H), 2.54 – 2.49 (m, 2H), 2.30 – 2.24 (m, 2H), 1.90 – 1.83 (m, 2H), 1.76 – 1.70 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6 (d, *J* = 255.8 Hz), 131.4, 129.9, 128.7, 128.7 (d, *J* = 20.3 Hz), 127.6, 127.2 (d, *J* = 7.4 Hz), 126.7, 126.3, 125.4, 125.1, 99.6 (d, *J* = 17.4 Hz), 25.4, 24.6 (d, *J* = 3.1 Hz), 22.4, 22.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.31 (d, *J* = 39.8 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}F$ 303.1544; found 303.1539.

(*Z*)-9-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)phenanthrene (4n)



According to the general procedure, the product **4n** was obtained after silica gel chromatography (petroleum ether). Yellow oil; 18.4 mg, 61% yield.

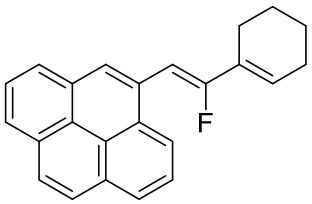
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 – 8.70 (m, 1H), 8.64 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.05 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.73 – 7.52 (m, 4H), 6.43 (s, 1H), 6.31 (d, *J* = 37.2 Hz, 1H), 2.41 – 2.35 (m, 2H), 2.29 – 2.22 (m, 2H), 1.84 – 1.77 (m, 2H), 1.72 – 1.66 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2 (d, *J* = 258.3 Hz), 131.8, 130.9, 130.5, 129.8, 129.2 (d, *J* = 19.9 Hz), 128.7, 128.4, 128.3 (d, *J* = 8.4 Hz), 127.1 (d, *J* = 7.6 Hz), 126.7, 126.5, 126.5, 126.3, 124.8, 123.1, 122.4, 100.5 (d, *J* = 12.8 Hz), 25.5, 24.4 (d, *J* = 3.1 Hz), 22.4, 21.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.26 (d, *J* = 37.9 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}F$ 303.1544; found 303.1538.

(*Z*)-4-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)pyrene (4o)



According to the general procedure, the product **4o** was obtained after silica gel chromatography (petroleum ether). Yellow solid; 18.2 mg, 56% yield, mp. = 136-138 ºC.

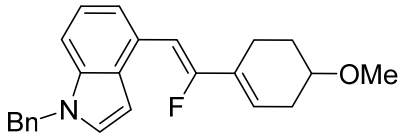
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 9.2 Hz, 1H), 8.16 – 8.12 (m, 3H), 8.07 (d, *J* = 9.2 Hz, 1H), 8.01 (s, 2H), 7.97 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 38.4 Hz, 1H), 6.50 – 6.43 (m, 1H), 2.49 – 2.39 (m, 2H), 2.32 – 2.24 (m, 2H), 1.86 – 1.80 (m, 2H), 1.73 – 1.67 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8 (d, *J* = 259.5 Hz), 131.4, 130.9, 130.3, 129.3 (d, *J* = 19.7 Hz), 128.5, 128.2, 127.5, 127.4, 127.2, 127.1 (d, *J* = 7.1 Hz), 125.9, 125.2, 124.9, 124.9, 124.9, 124.8, 123.6, 100.7 (d, *J* = 11.9 Hz), 25.5, 24.5 (d, *J* = 3.0 Hz), 22.5, 22.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.86 (d, *J* = 38.5 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}F$ 327.1544; found 327.1537.

(*Z*)-1-benzyl-4-(2-fluoro-2-(4-methoxycyclohex-1-en-1-yl)vinyl)-1H-indole (4p)



According to the general procedure, the product **4p** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 60:1 - 20:1, v/v). Yellow oil; 19.1 mg, 53% yield.

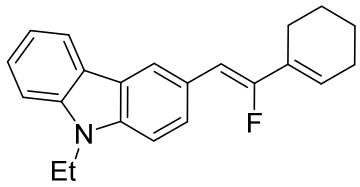
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.31 – 7.27 (m, 3H), 7.17 (d, *J* = 4.3 Hz, 2H), 7.15 (d, *J* = 3.2 Hz, 1H), 7.12 – 7.08 (m, 2H), 6.62 (d, *J* = 3.1 Hz, 1H), 6.25 (s, 1H), 6.13 (d, *J* = 40.3 Hz, 1H), 5.32 (s, 2H), 3.58 – 3.52 (m, 1H), 3.41 (s, 3H), 2.61 – 2.55 (m, 1H), 2.55 – 2.49 (m, 1H), 2.40 – 2.33 (m, 1H), 2.29 – 2.21 (m, 1H), 2.08 – 2.02 (m, 1H), 1.84 – 1.76 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (d, *J* = 259.4 Hz), 137.5, 136.3, 129.3 (d, *J* = 20.6 Hz), 128.8, 128.1, 127.9, 127.6, 126.8, 125.9 (d, *J* = 1.7 Hz), 123.0 (d, *J* = 7.9 Hz), 122.1, 120.1 (d, *J* = 12.6 Hz), 108.7, 101.8 (d, *J* = 11.4 Hz), 100.1, 74.9, 55.9, 50.2, 31.3, 27.0, 22.7 (d, *J* = 2.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.47 (d, *J* = 40.9 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}FNO$ 362.1915; found 362.1908.

(*Z*)-3-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-9-ethyl-9*H*-carbazole (4q)



According to the general procedure, **2a** (4.0 equiv) and Mn (4.4 equiv) were used, and the product **4q** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 200:1 - 50:1, v/v). Yellow oil; 19.1 mg, 60% yield.

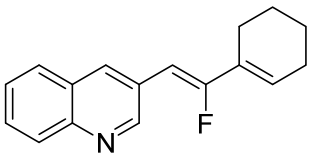
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.3 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.67 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.24 – 7.20 (m, 1H), 6.33 (t, *J* = 3.8 Hz, 1H), 5.85 (d, *J* = 41.0 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.30 – 2.25 (m, 2H), 2.25 – 2.21 (m, 2H), 1.79 – 1.73 (m, 2H), 1.68 – 1.63 (m, 2H), 1.43 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0 (d, *J* = 255.8 Hz), 140.3, 138.9, 129.4 (d, *J* = 20.2 Hz), 127.0 (d, *J* = 7.2 Hz), 125.7, 125.2 (d, *J* = 1.9 Hz), 125.0 (d, *J* = 7.7 Hz), 123.2, 123.1, 120.8 (d, *J* = 8.5 Hz), 120.5, 118.9, 108.5, 108.4, 104.6 (d, *J* = 10.9 Hz), 37.6, 25.5, 24.4 (d, *J* = 3.0 Hz), 22.5, 22.0, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -119.51 (d, *J* = 41.0 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}FN$ 320.1809; found 320.1803.

(*Z*)-3-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)quinoline (4r)



According to the general procedure, the product **4r** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 30:1 - 10:1, v/v). Pale yellow solid; 14.2 mg, 56% yield, mp. = 103-104 ºC.

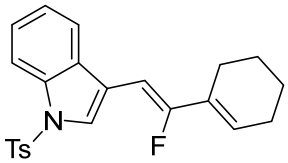
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (d, *J* = 1.5 Hz, 1H), 8.38 (d, *J* = 1.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.61 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 6.46 (s, 1H), 5.81 (d, *J* = 40.1 Hz, 1H), 2.43 – 2.06 (m, 4H), 1.82 – 1.74 (m, 2H), 1.72 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3 (d, *J* = 261.6 Hz), 151.4 (d, *J* = 5.7 Hz), 146.6, 134.3 (d, *J* = 11.2 Hz), 129.1, 129.1, 128.9 (d, *J* = 18.8 Hz), 128.2, 128.2 (d, *J* = 3.4 Hz), 128.0, 127.7 (d, *J* = 2.2 Hz), 126.8, 100.5 (d, *J* = 11.8 Hz), 25.5, 24.2 (d, *J* = 3.1 Hz), 22.3, 21.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.04 (d, *J* = 40.1 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}FN$ 254.1340; found 254.1335.

(*Z*)-3-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)-1-tosyl-1*H*-indole (4s)



According to the general procedure, the product **4s** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 60:1 - 20:1, v/v). Yellow solid; 31.2 mg, 79% yield, mp. = 139-141 ºC.

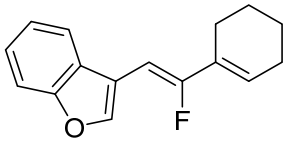
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.92 (s, 1H), 7.82 – 7.74 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.27 – 7.21 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.36 (s, 1H), 5.80 (d, *J* = 40.2 Hz, 1H), 2.31 (s, 3H), 2.26 – 2.19 (m, 4H), 1.78 – 1.70 (m, 2H), 1.68 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4 (d, *J* = 258.6 Hz), 144.9, 135.2, 134.5, 132.3 (d, *J* = 10.8 Hz), 129.9 (d, *J* = 13.6 Hz), 129.9, 128.6 (d, *J* = 16.3 Hz), 128.5 (d, *J* = 9.7 Hz), 126.8, 126.8 (d, *J* = 6.2 Hz), 124.9 (d, *J* = 15.4 Hz), 124.8, 123.2, 119.0, 115.5, 113.7, 93.1 (d, *J* = 15.3 Hz), 25.4, 24.1 (d, *J* = 3.1 Hz), 22.3, 21.9, 21.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -108.99 (d, *J* = 40.3 Hz).

FTMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}FNO_2S$ 396.1428; found 396.1421.

(*Z*)-3-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)benzofuran (4t)



According to the general procedure, the product **4t** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 400:1 - 100:1, v/v). Pale yellow solid; 18.9 mg, 78% yield, mp. = 53-55 ºC.

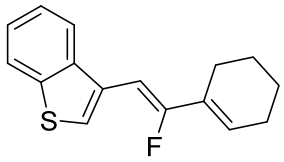
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.42 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.19 (td, *J* = 7.5, 1.1 Hz, 1H), 6.93 (s, 1H), 6.43 (t, *J* = 3.7 Hz, 1H), 5.84 (d, *J* = 38.5 Hz, 1H), 2.27 – 2.21 (m, 2H), 2.21 – 2.16 (m, 2H), 1.77 – 1.71 (m, 2H), 1.67 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6 (d, *J* = 262.7 Hz), 154.0, 151.6 (d, *J* = 1.8 Hz), 129.5, 128.5 (d, *J* = 17.8 Hz), 128.4 (d, *J* = 7.5 Hz), 124.0, 122.8, 120.7, 110.8, 105.7 (d, *J* = 12.2 Hz), 94.4 (d, *J* = 13.1 Hz), 25.6, 23.9 (d, *J* = 3.1 Hz), 22.2, 21.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -109.28 (d, *J* = 39.0 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}FO$ 243.1180; found 243.1177.

(*Z*)-3-(2-(cyclohex-1-en-1-yl)-2-fluorovinyl)benzo[b]thiophene (4u)



According to the general procedure, **2a** (2.0 equiv) and Mn (2.2 equiv) were used, and the product **4u** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 200:1 - 100:1, v/v). Yellow oil; 14.2 mg, 55% yield.

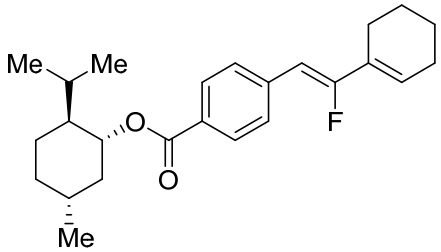
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.43 – 7.39 (m, 1H), 7.38 – 7.33 (m, 1H), 6.39 (s, 1H), 6.03 (d, *J* = 39.5 Hz, 1H), 2.33 – 2.27 (m, 2H), 2.27 – 2.21 (m, 2H), 1.80 – 1.75 (m, 2H), 1.69 – 1.64 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5 (d, *J* = 259.2 Hz), 139.3, 138.3, 128.9 (d, *J* = 19.5 Hz), 128.1, 126.8 (d, *J* = 7.6 Hz), 124.7 (d, *J* = 15.1 Hz), 124.6 124.1, 122.8, 121.2, 95.3 (d, *J* = 13.7 Hz), 25.5, 24.2 (d, *J* = 3.2 Hz), 22.3, 21.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.96 (d, *J* = 39.7 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}FS$ 259.0951; found 259.0948.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((*Z*)-2-(cyclohex-1-en-1-yl)-2-fluorovinyl)benzoate (4v)



According to the general procedure, the product **4v** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 200:1 - 100:1, v/v). White solid; 22.2 mg, 58% yield, mp. = 114-116 ºC.

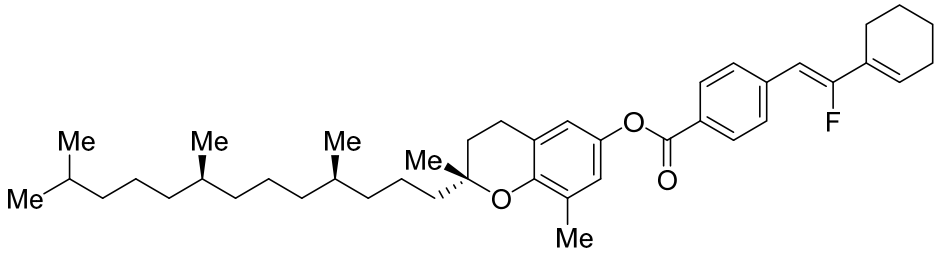
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 5.70 (d, *J* = 39.8 Hz, 1H), 4.92 (td, *J* = 10.9, 4.4 Hz, 1H), 2.27 – 2.18 (m, 4H), 2.16 – 2.10 (m, 1H), 2.02 – 1.92 (m, 1H), 1.79 – 1.70 (m, 4H), 1.67 – 1.61 (m, 2H), 1.58 – 1.50 (m, 2H), 1.18 – 1.05 (m, 2H), 0.99 – 0.89 (m, 7H), 0.79 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 159.7 (d, *J* = 262.7 Hz), 138.8 (d, *J* = 1.8 Hz), 129.7, 129.0 (d, *J* = 19.5 Hz), 128.7 (d, *J* = 1.5 Hz), 128.5 (d, *J* = 7.9 Hz), 128.2 (d, *J* = 7.9 Hz), 103.2 (d, *J* = 10.2 Hz), 74.7, 47.3, 41.0, 34.4, 31.5, 26.5, 25.5, 24.2 (d, *J* = 2.9 Hz), 23.7, 22.3, 22.1, 21.8, 20.8, 16.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.32 (d, *J* = 40.0 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{25}H_{34}FO_2$ 385.2537; found 385.2541.

(*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-((*Z*)-2-(cyclohex-1-en-1-yl)-2-fluorovinyl)benzoate (4w)



According to the general procedure, **2a** (4.0 equiv) and Mn (4.4 equiv) were used, and the product **4w** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 200:1 - 50:1, v/v). Colorless oil; 26.4 mg, 42% yield.

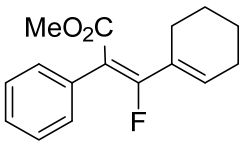
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 6.77 (dd, *J* = 30.6, 2.5 Hz, 2H), 6.44 (s, 1H), 5.73 (d, *J* = 39.8 Hz, 1H), 2.76 (dd, *J* = 12.8, 6.5 Hz, 2H), 2.27 – 2.20 (m, 4H), 2.17 (s, 3H), 1.86 – 1.79 (m, 1H), 1.78 – 1.72 (m, 3H), 1.68 – 1.62 (m, 2H), 1.61 – 1.49 (m, 3H), 1.42 – 1.35 (m, 3H), 1.33 – 1.18 (m, 12H), 1.16 – 1.10 (m, 3H), 1.10 – 1.03 (m, 3H), 0.88 – 0.86 (m, 9H), 0.85 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 160.0 (d, *J* = 263.0 Hz), 149.8, 142.7, 139.4, 130.3, 129.0 (d, *J* = 19.2 Hz), 128.7 (d, *J* = 8.1 Hz), 128.5 (d, *J* = 8.3 Hz), 127.7 (d, *J* = 1.4 Hz), 127.4, 121.3, 121.0, 119.2, 103.1 (d, *J* = 10.4 Hz), 76.2, 40.1, 39.4, 37.5, 37.4, 37.3, 32.8, 32.7, 31.0, 28.0, 25.6, 24.8, 24.5, 24.3, 24.2 (d, *J* = 2.3 Hz), 22.7, 22.6, 22.5, 22.3, 21.8, 21.0, 19.8, 19.7, 16.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.71 (d, *J* = 39.8 Hz).

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{42}H_{60}FO_3$ 631.4521; found 631.4512.

methyl (*E*)-3-(cyclohex-1-en-1-yl)-3-fluoro-2-phenylacrylate (4x)



According to the general procedure, the product **4x** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). Colorless oil; 15.1 mg, 58% yield.

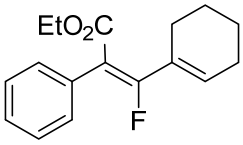
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 6.25 (dd, *J* = 3.7, 1.8 Hz, 1H), 3.73 (s, 3H), 2.22 (d, *J* = 5.9 Hz, 2H), 2.20 – 2.14 (m, 2H), 1.73 – 1.68 (m, 2H), 1.67 – 1.61 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6 (d, *J* = 15.2 Hz), 162.5 (d, *J* = 264.0 Hz), 133.2 (d, *J* = 8.6 Hz), 132.6, 130.6 (d, *J* = 24.4 Hz), 129.0 (d, *J* = 4.1 Hz), 128.3, 127.8, 114.3 (d, *J* = 22.0 Hz), 52.3, 25.6, 25.1, 22.2, 21.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -99.00.

FTMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{18}FO_2$ 261.1285; found 261.1282.

ethyl (*E*)-3-(cyclohex-1-en-1-yl)-3-fluoro-2-phenylacrylate (4y)



According to the general procedure, the product **4y** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). Colorless oil; 16.9 mg, 62% yield.

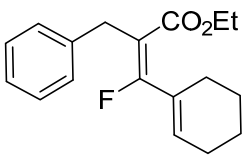
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 6.23 (dd, *J* = 3.9, 1.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.27 – 2.22 (m, 2H), 2.19 – 2.13 (m, 2H), 1.73 – 1.68 (m, 2H), 1.66 – 1.61 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2 (d, *J* = 15.2 Hz), 162.3 (d, *J* = 263.9 Hz), 133.0 (d, *J* = 8.1 Hz), 132.6, 130.8 (d, *J* = 25.0 Hz), 129.0 (d, *J* = 4.2 Hz), 128.3, 127.7, 114.7 (d, *J* = 21.6 Hz), 61.3, 25.5, 25.0, 22.1, 21.6, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -100.30.

FTMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{20}FO_2$ 275.1442; found 275.1436.

ethyl (*E*)-2-benzyl-3-(cyclohex-1-en-1-yl)-3-fluoroacrylate (4z)



According to the general procedure, the product **4z** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). Colorless oil; 21.6 mg, 75% yield.

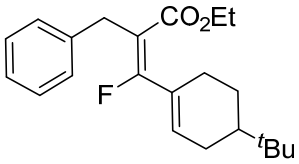
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 4H), 7.18 (t, *J* = 7.0 Hz, 1H), 6.07 – 6.02 (m, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.70 (d, *J* = 3.0 Hz, 2H), 2.22 – 2.17 (m, 2H), 2.15 – 2.08 (m, 2H), 1.71 – 1.65 (m, 2H), 1.64 – 1.59 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0 (d, *J* = 16.9 Hz), 166.1 (d, *J* = 262.8 Hz), 139.2, 132.8 (d, *J* = 8.6 Hz), 130.7 (d, *J* = 24.7 Hz), 128.5, 128.3, 126.2, 112.6 (d, *J* = 24.9 Hz), 60.6, 32.3 (d, *J* = 5.2 Hz), 25.6, 25.4, 22.1, 21.5, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -90.47.

FTMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{22}FO_2$ 289.1598; found 289.1593.

ethyl (*E*)-2-benzyl-3-(4-(*tert*-butyl)cyclohex-1-en-1-yl)-3-fluoroacrylate (4aa)



According to the general procedure, the product **4aa** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). Colorless oil; 22.0 mg, 64% yield.

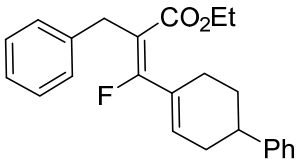
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.23 (d, *J* = 6.9 Hz, 2H), 7.19 – 7.15 (m, 1H), 6.07 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.75 – 3.64 (m, 2H), 2.31 – 2.22 (m, 2H), 2.21 – 2.12 (m, 1H), 1.93 – 1.84 (m, 2H), 1.34 – 1.28 (m, 1H), 1.25 – 1.18 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0 (d, *J* = 16.5 Hz), 165.9 (d, *J* = 262.2 Hz), 139.2, 133.3 (d, *J* = 8.4 Hz), 130.4 (d, *J* = 24.1 Hz), 128.5, 128.3, 126.2, 112.6 (d, *J* = 24.4 Hz), 60.6, 43.4, 32.4 (d, *J* = 5.0 Hz), 32.2, 27.2, 27.1, 27.1, 23.6, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -90.17.

FTMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{30}FO_2$ 345.2224; found 345.2216.

ethyl (*E*)-2-benzyl-3-fluoro-3-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)acrylate (4ab)



According to the general procedure, the product **4ab** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). Colorless oil; 22.6 mg, 62% yield.

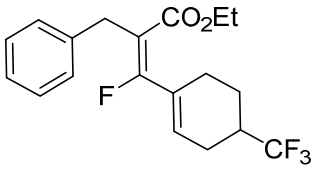
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.17 (m, 8H), 6.15 (br, 1H), 4.16 – 4.05 (m, 2H), 3.77 – 3.69 (m, 2H), 2.88 – 2.78 (m, 1H), 2.48 – 2.39 (m, 2H), 2.39 – 2.32 (m, 1H), 2.31 – 2.19 (m, 1H), 2.06 – 2.00 (m, 1H), 1.81 (ddd, *J* = 23.8, 12.2, 5.4 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.8 (d, *J* = 16.4 Hz), 165.7 (d, *J* = 262.5 Hz), 146.2, 139.1, 132.3 (d, *J* = 8.1 Hz), 130.5 (d, *J* = 24.5 Hz), 128.5, 128.5, 128.4, 126.8, 126.3, 126.2, 113.0 (d, *J* = 24.2 Hz), 60.7, 39.3, 33.6, 32.4 (d, *J* = 4.9 Hz), 29.4, 26.3, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -89.97.

FTMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{26}FO_2$ 365.1911; found 365.1904.

ethyl (*E*)-2-benzyl-3-fluoro-3-(4-(trifluoromethyl)cyclohex-1-en-1-yl)acrylate (4ac)



According to the general procedure, the product **4ac** was obtained after silica gel chromatography (petroleum ether/ethyl acetate = 100:1 - 20:1, v/v). Colorless oil; 23.1 mg, 65% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.04 (br, 1H), 4.11 – 4.05 (m, 2H), 3.75 – 3.67 (m, 2H), 2.43 – 2.28 (m, 4H), 2.26 – 2.17 (m, 1H), 2.12 – 2.05 (m, 1H), 1.65 – 1.56 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5 (d, *J* = 16.6 Hz), 164.8 (d, *J* = 262.5 Hz), 138.9, 130.6 (d, *J* = 24.9 Hz), 129.3 (d, *J* = 7.9 Hz), 128.5, 128.4, 126.3, 113.8 (d, *J* = 24.3 Hz), 60.8, 37.8 (q, *J* = 27.5 Hz), 32.3, 32.2, 24.8, 24.4 (d, *J* = 2.1 Hz), 21.1 (d, *J* = 2.2 Hz), 14.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.78 (d, *J* = 9.2 Hz), -90.43.

FTMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}F_4O_2$ 357.1472; found 357.1464.

7. References

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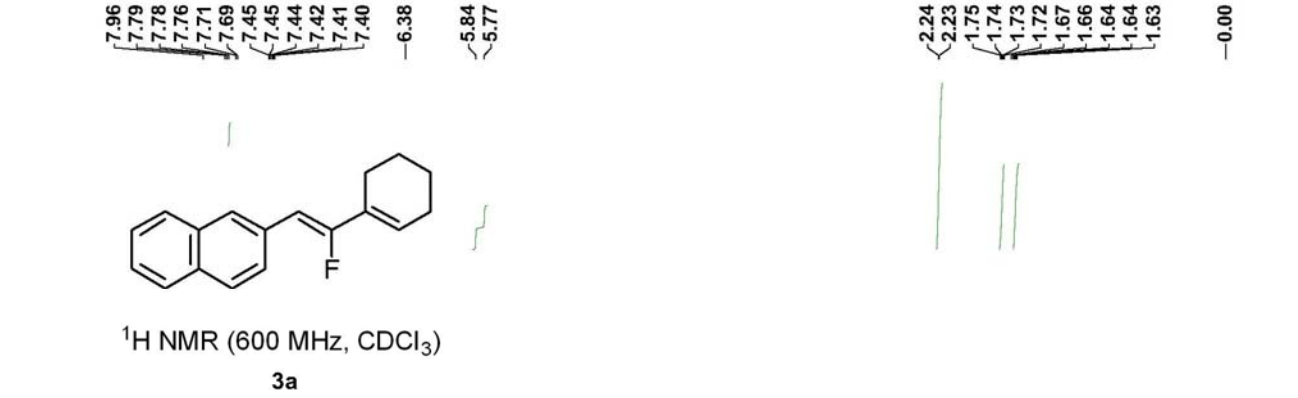
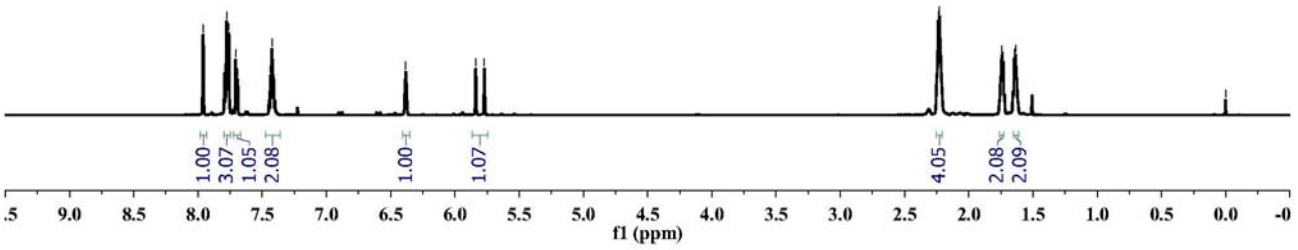
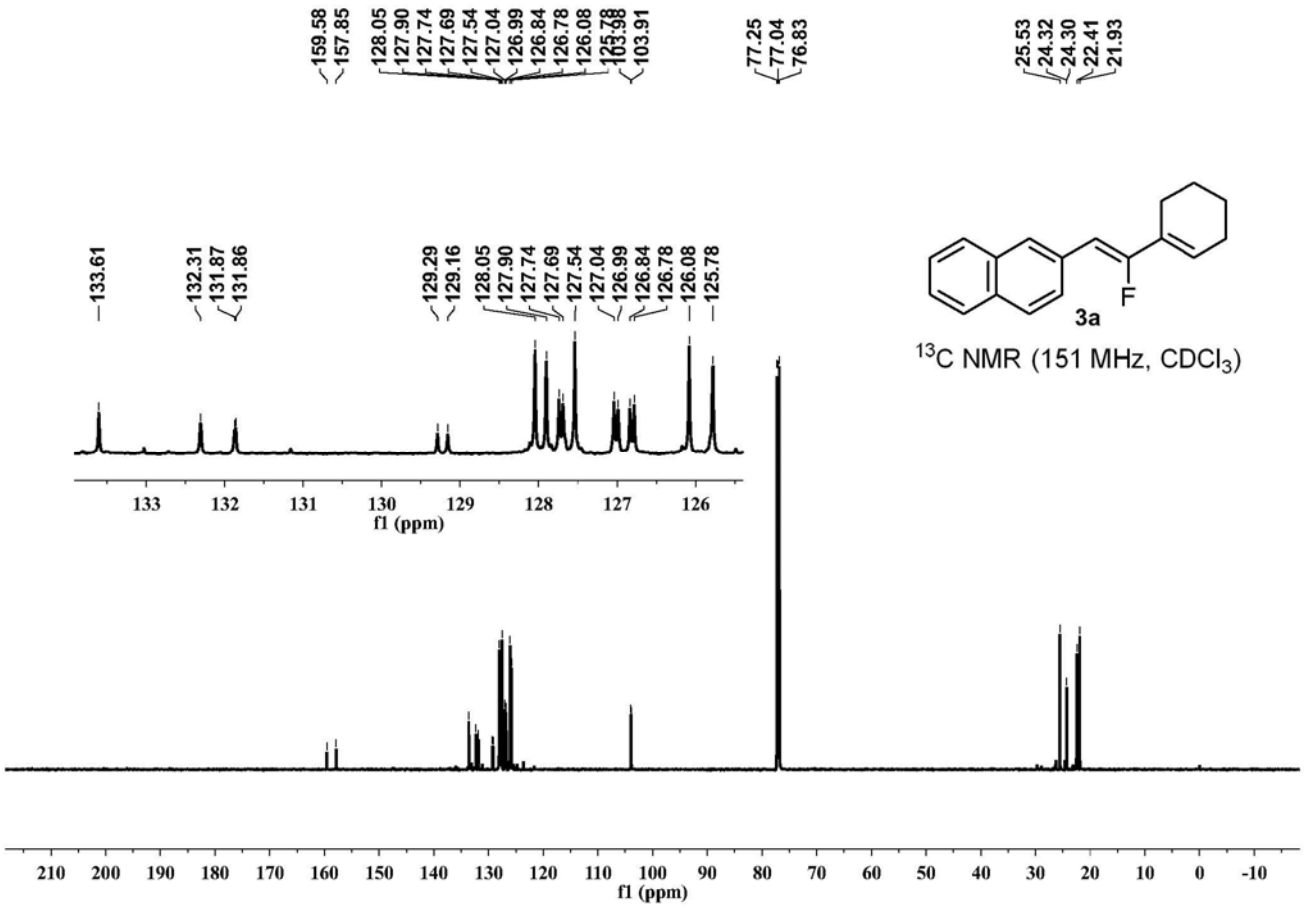
8. NMR spectra of compounds



^{1}H NMR (600 MHz, $CDCl_3$)

3a

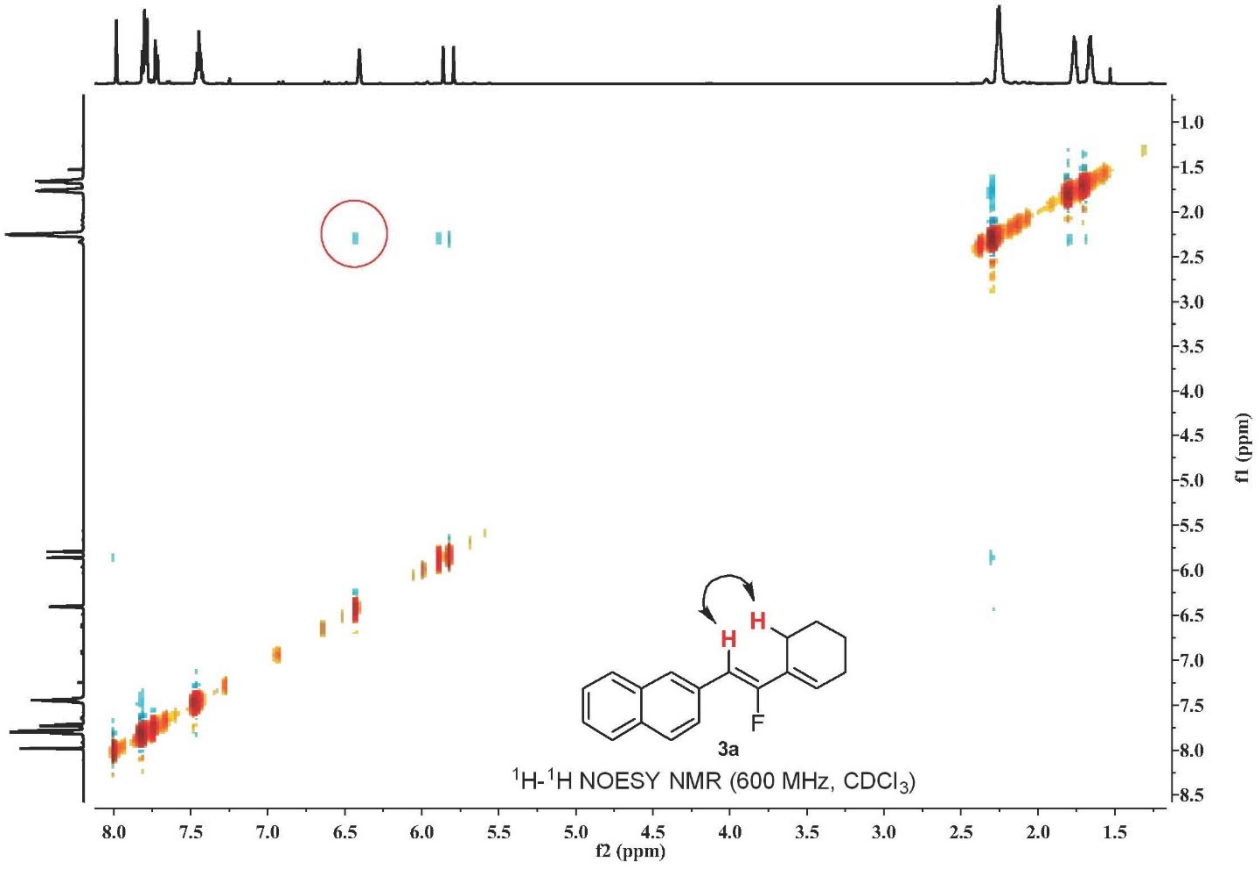


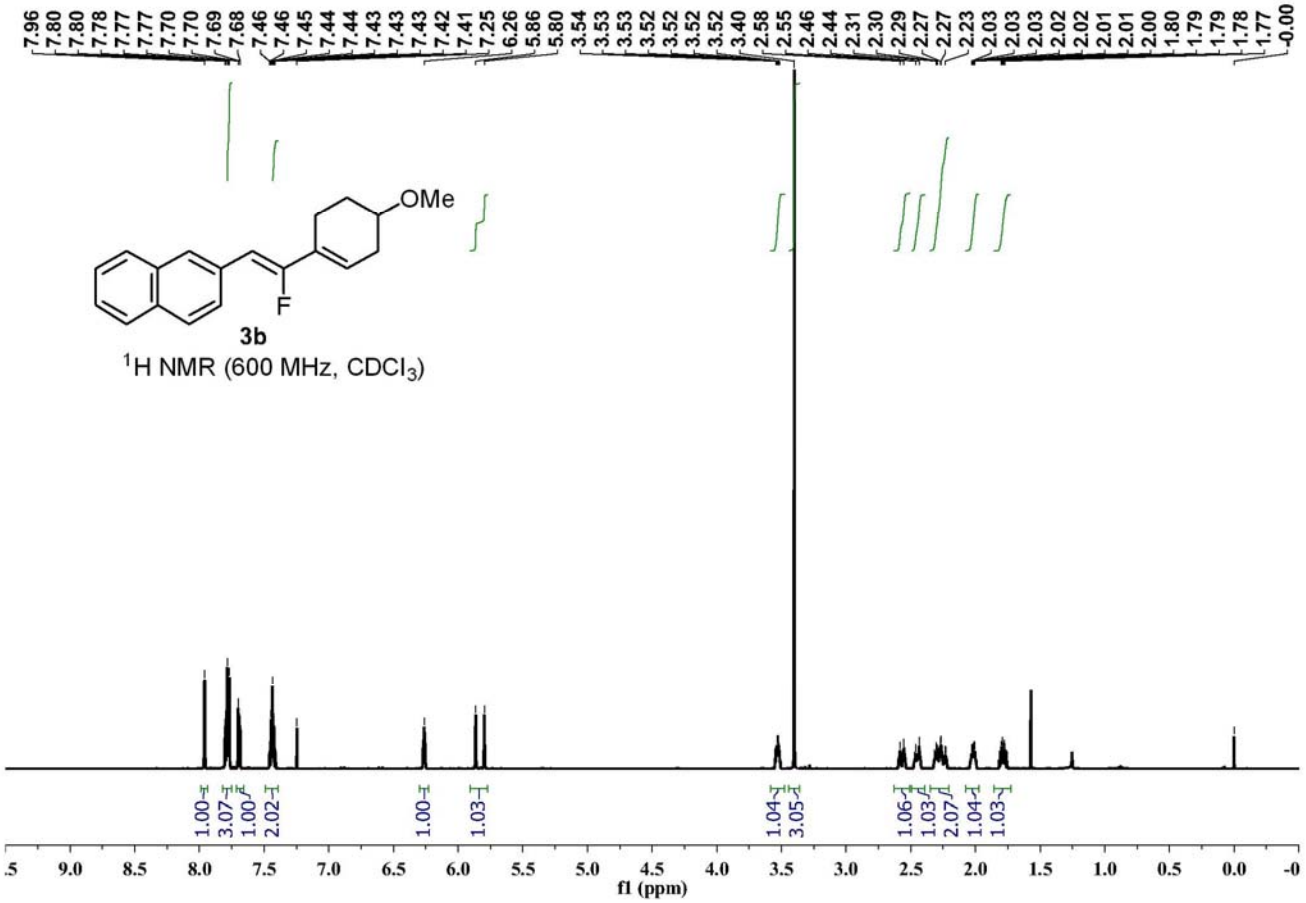


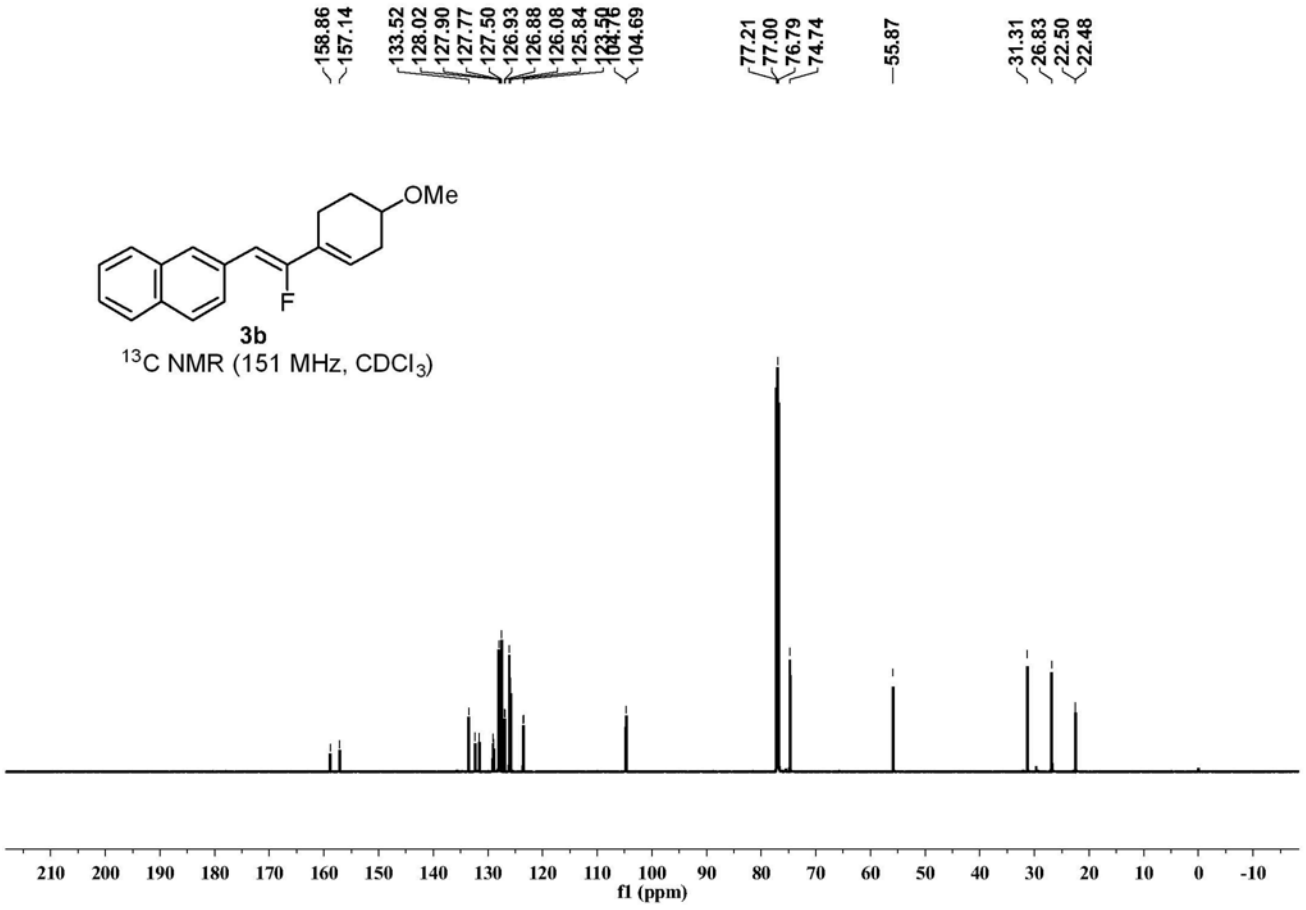
3a

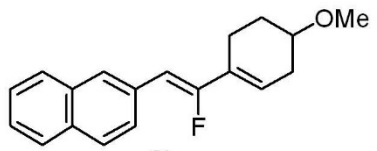
^{13}C NMR (151 MHz, $CDCl_3$)


-115.96
-116.03
F
3a
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


H
H
F
3a
1H-1H NOESY NMR (600 MHz, CDCl3)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5
f1 (ppm)

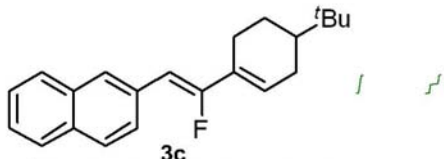

OMe
F
3b
1H NMR (600 MHz, CDCl3)
f1 (ppm)


OMe
F
3b
13C NMR (151 MHz, CDCl3)
f1 (ppm)



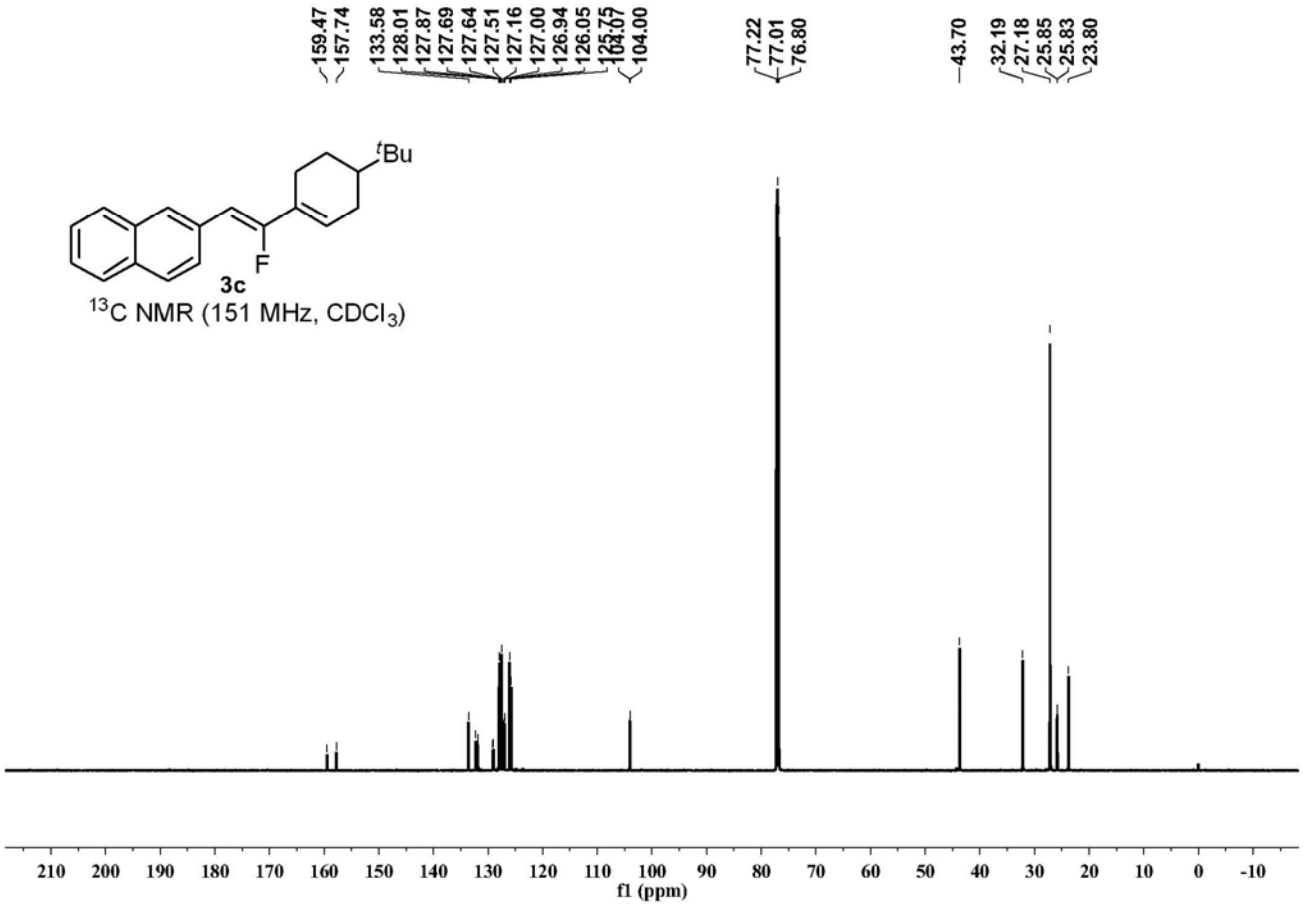
3b

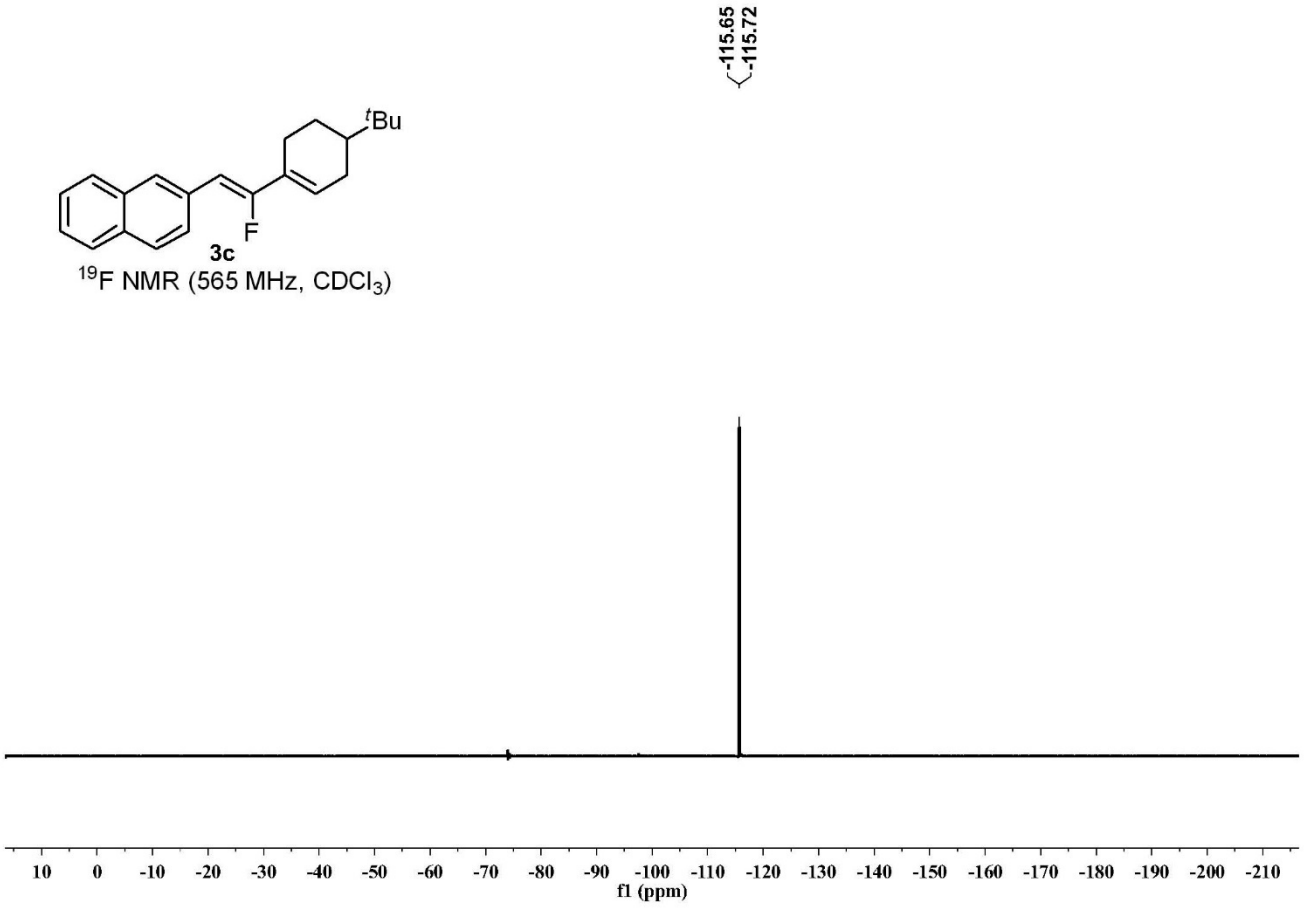
^{19}F NMR (565 MHz, $CDCl_3$)

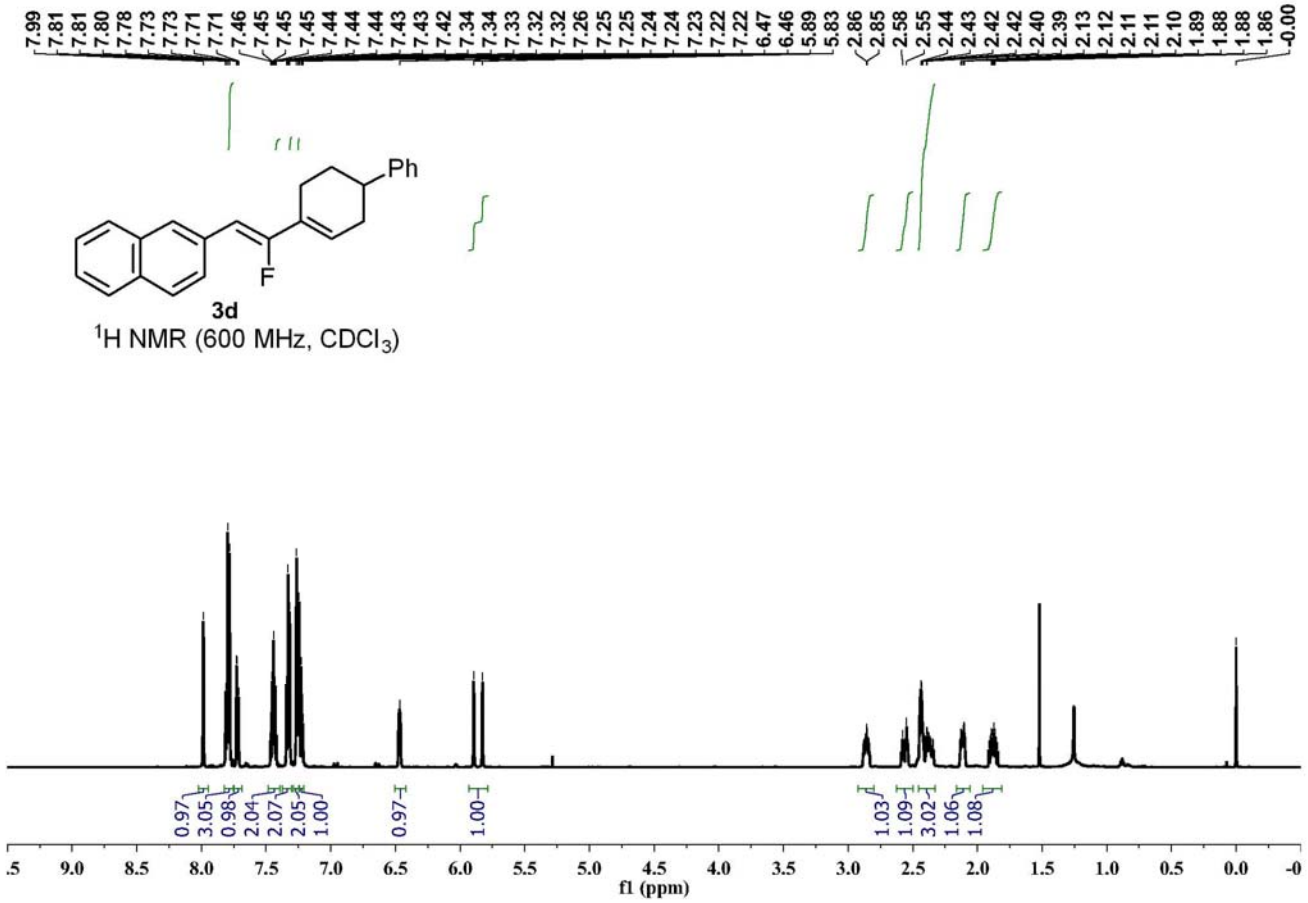


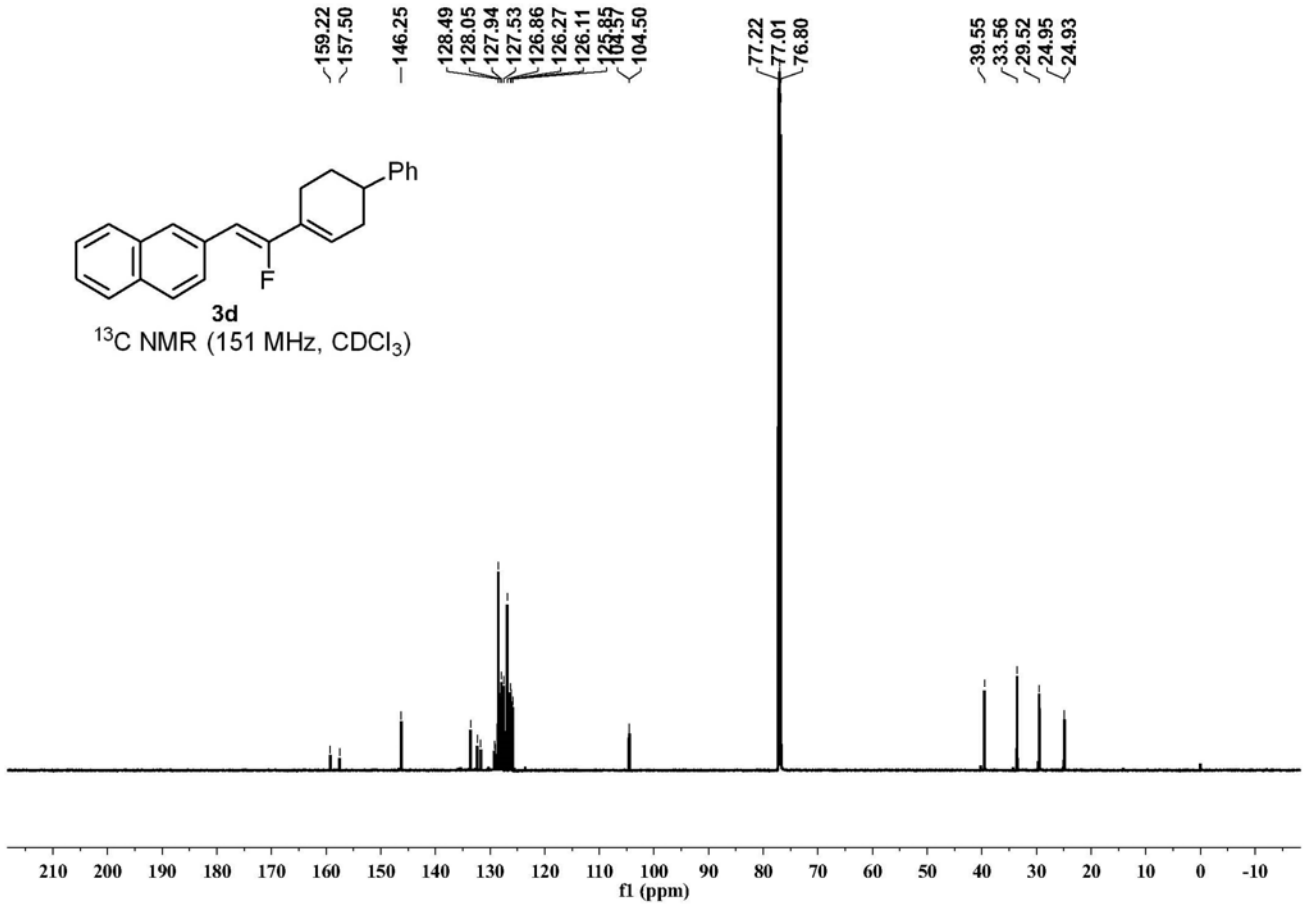
3c

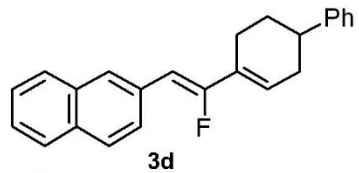
^{1}H NMR (600 MHz, $CDCl_3$)


159.47
157.74
133.58
128.01
127.87
127.69
127.64
127.51
127.16
127.00
126.94
126.05
125.75
104.07
104.00
77.22
77.01
76.80
43.70
32.19
27.18
25.85
25.83
23.80
tBu
F
3c
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-115.65
-115.72
tBu
F
3c
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

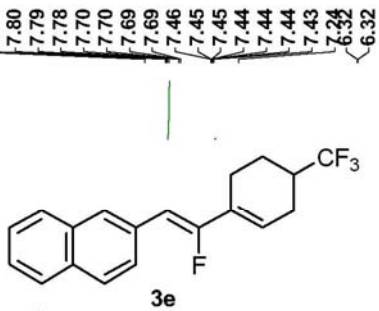

Ph
F
3d
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)


Ph
F
3d
^{13}C NMR (151 MHz, $CDCl_3$)
f1 (ppm)



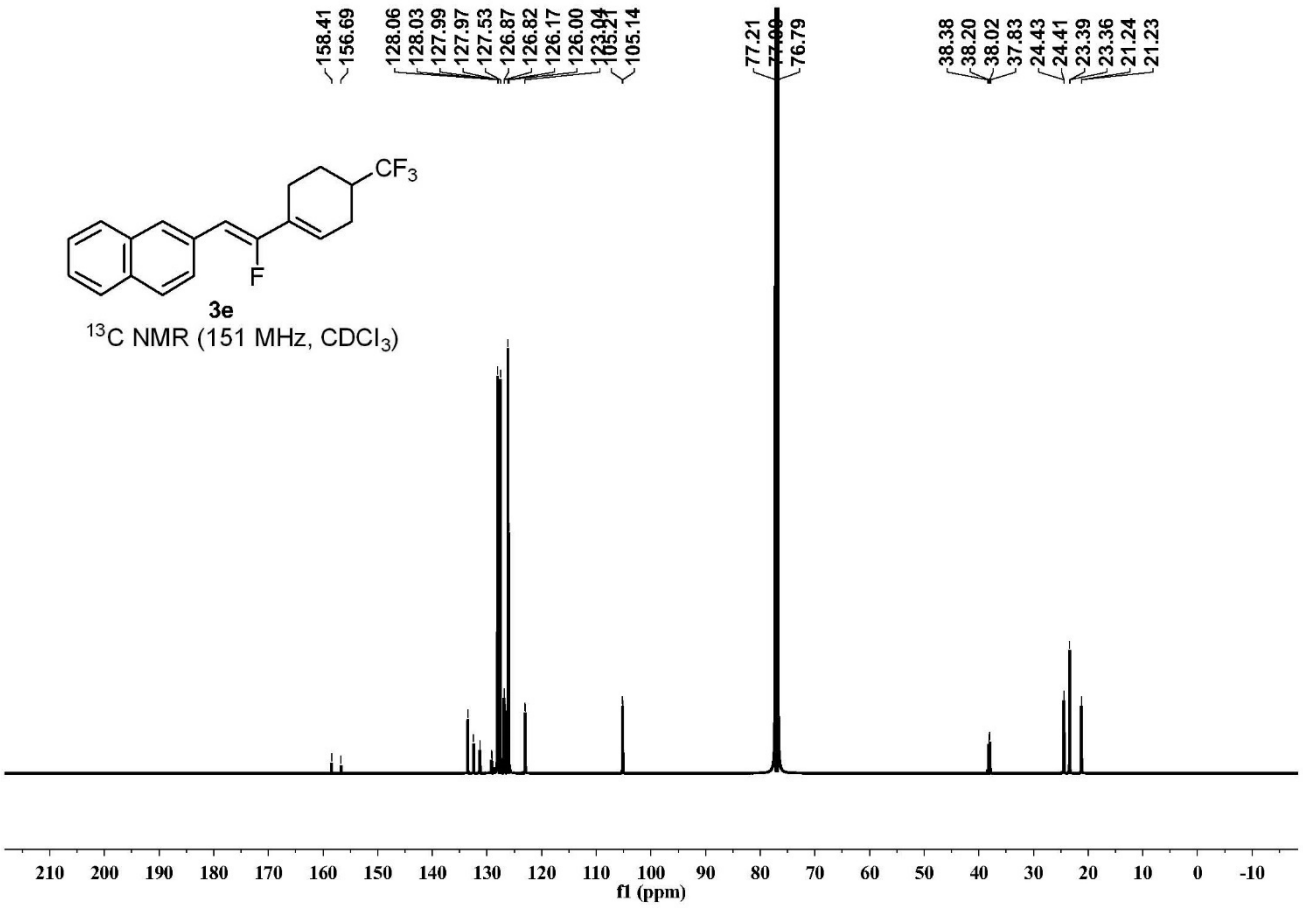
3d

^{19}F NMR (565 MHz, $CDCl_3$)



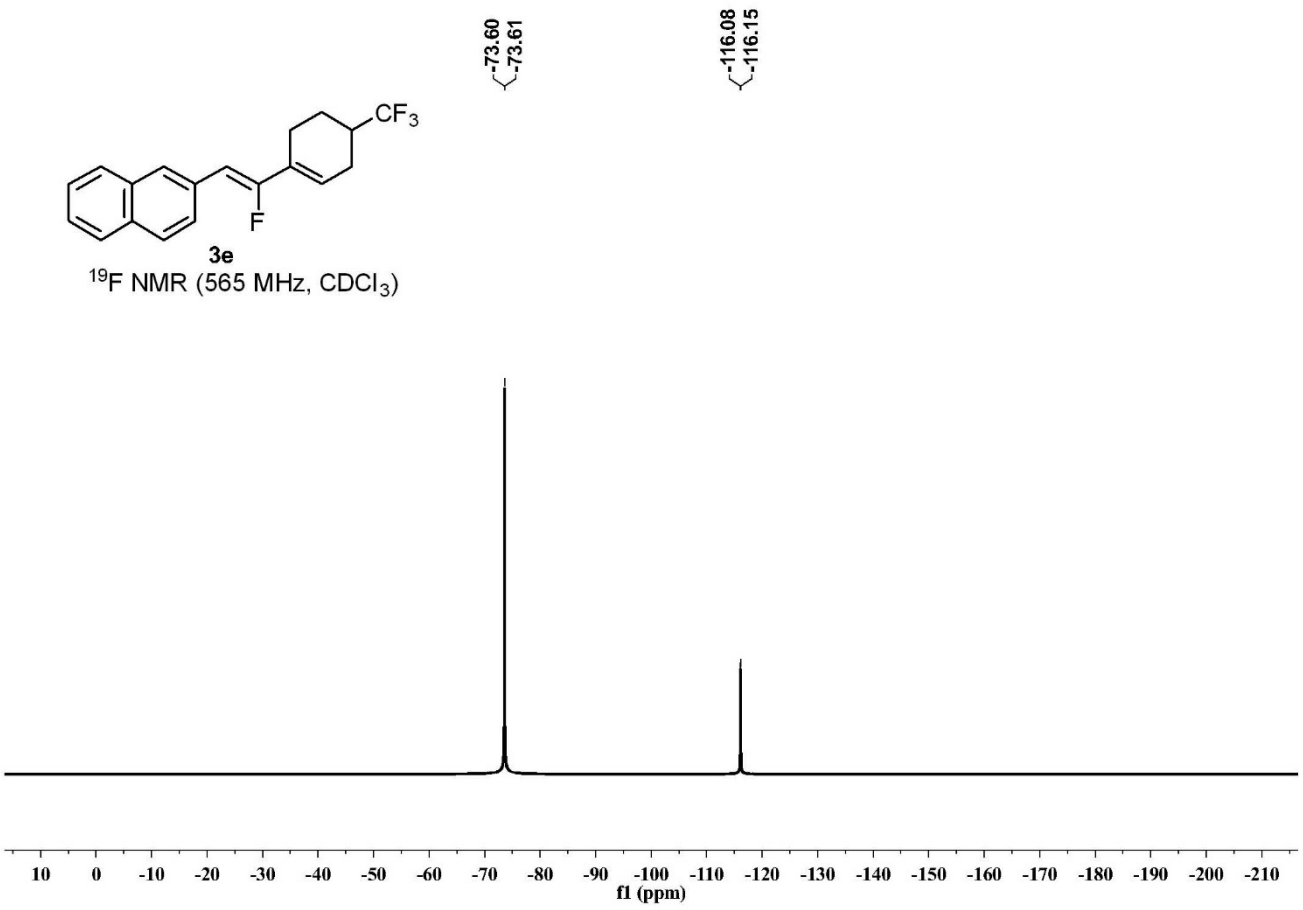
3e

^{1}H NMR (600 MHz, $CDCl_3$)



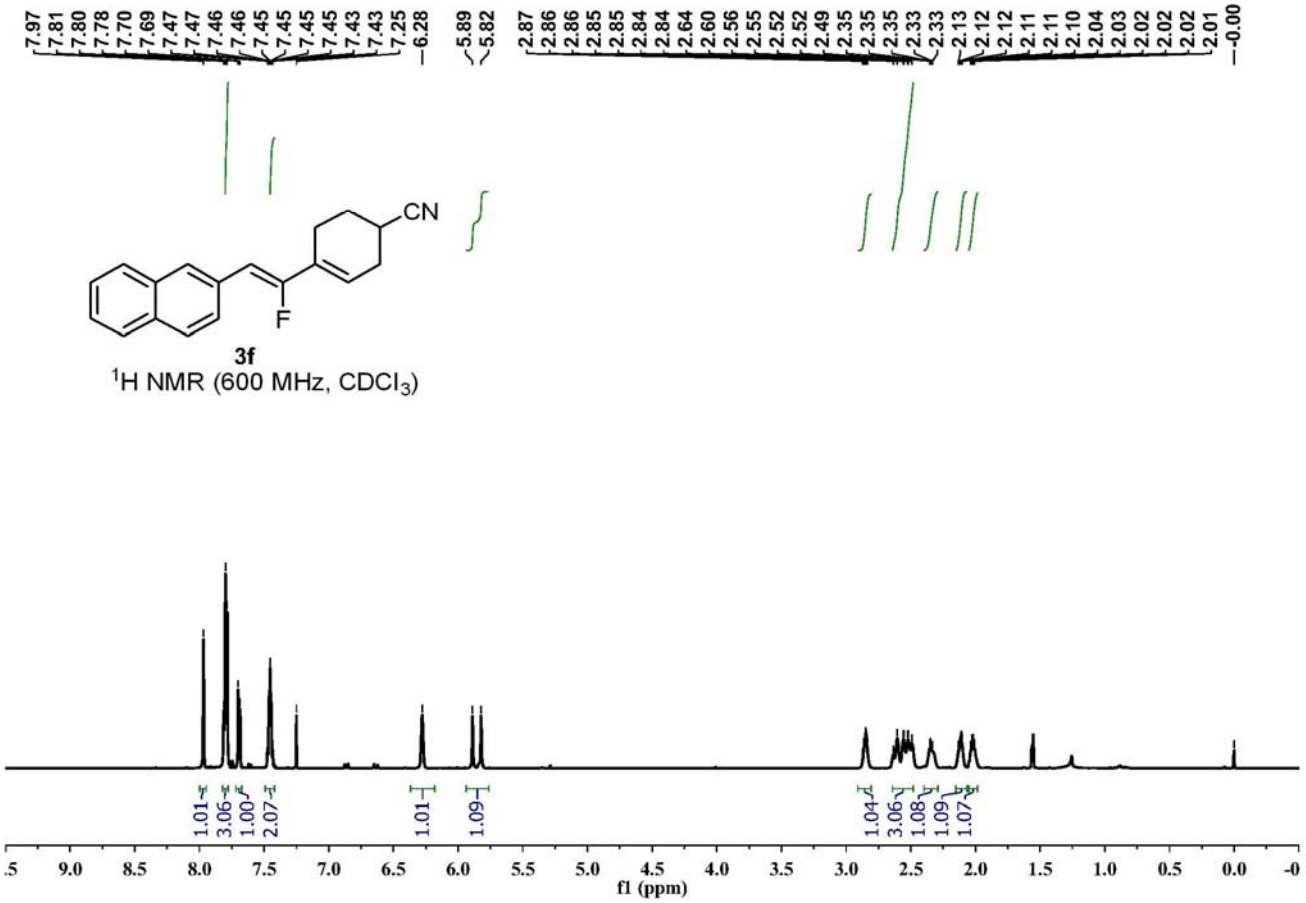
3e

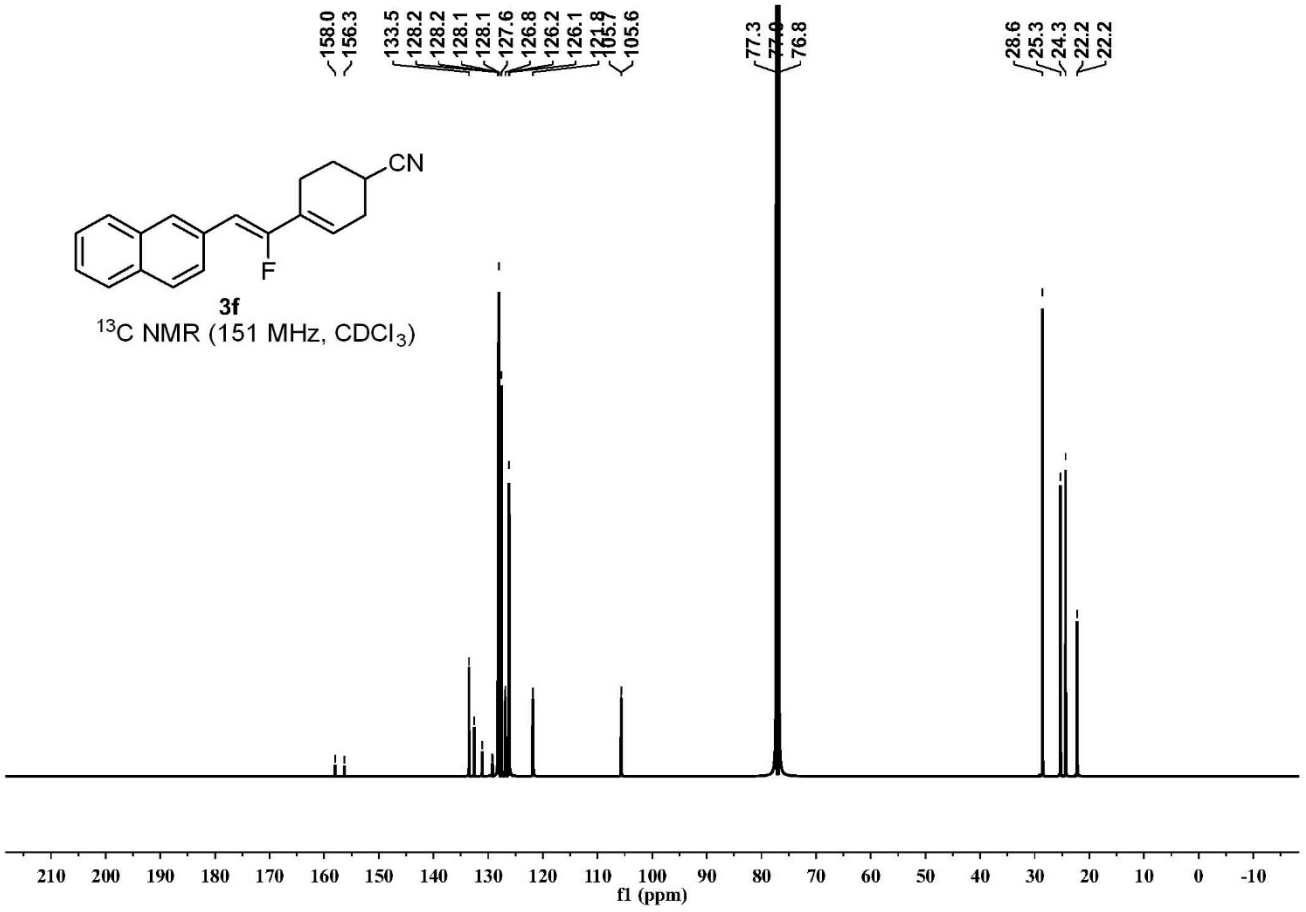
^{13}C NMR (151 MHz, $CDCl_3$)

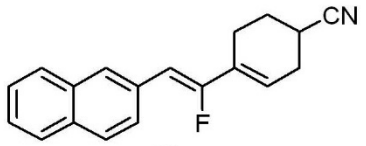


3e

^{19}F NMR (565 MHz, $CDCl_3$)

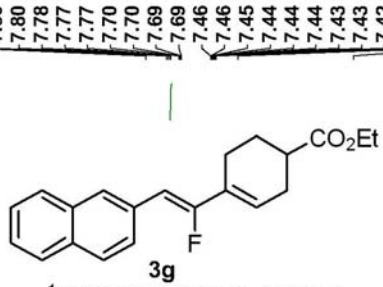

7.97
7.81
7.80
7.78
7.70
7.69
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.45
7.43
7.43
7.25
6.28
5.89
5.82
2.87
2.86
2.86
2.85
2.85
2.84
2.84
2.64
2.60
2.56
2.55
2.52
2.52
2.49
2.35
2.35
2.33
2.33
2.13
2.12
2.12
2.11
2.11
2.10
2.04
2.03
2.02
2.02
2.02
2.01
0.00
CN
F
3f
1H NMR (600 MHz, CDCl3)
1.01
3.06
1.00
2.07
1.01
1.09
1.04
3.06
1.08
1.09
1.07
f1 (ppm)


158.0
156.3
133.5
128.2
128.2
128.1
128.1
127.6
126.8
126.2
126.1
121.8
105.6
77.3
77.0
76.8
28.6
25.3
24.3
22.2
22.2
CN
F
3f
13C NMR (151 MHz, CDCl3)
f1 (ppm)



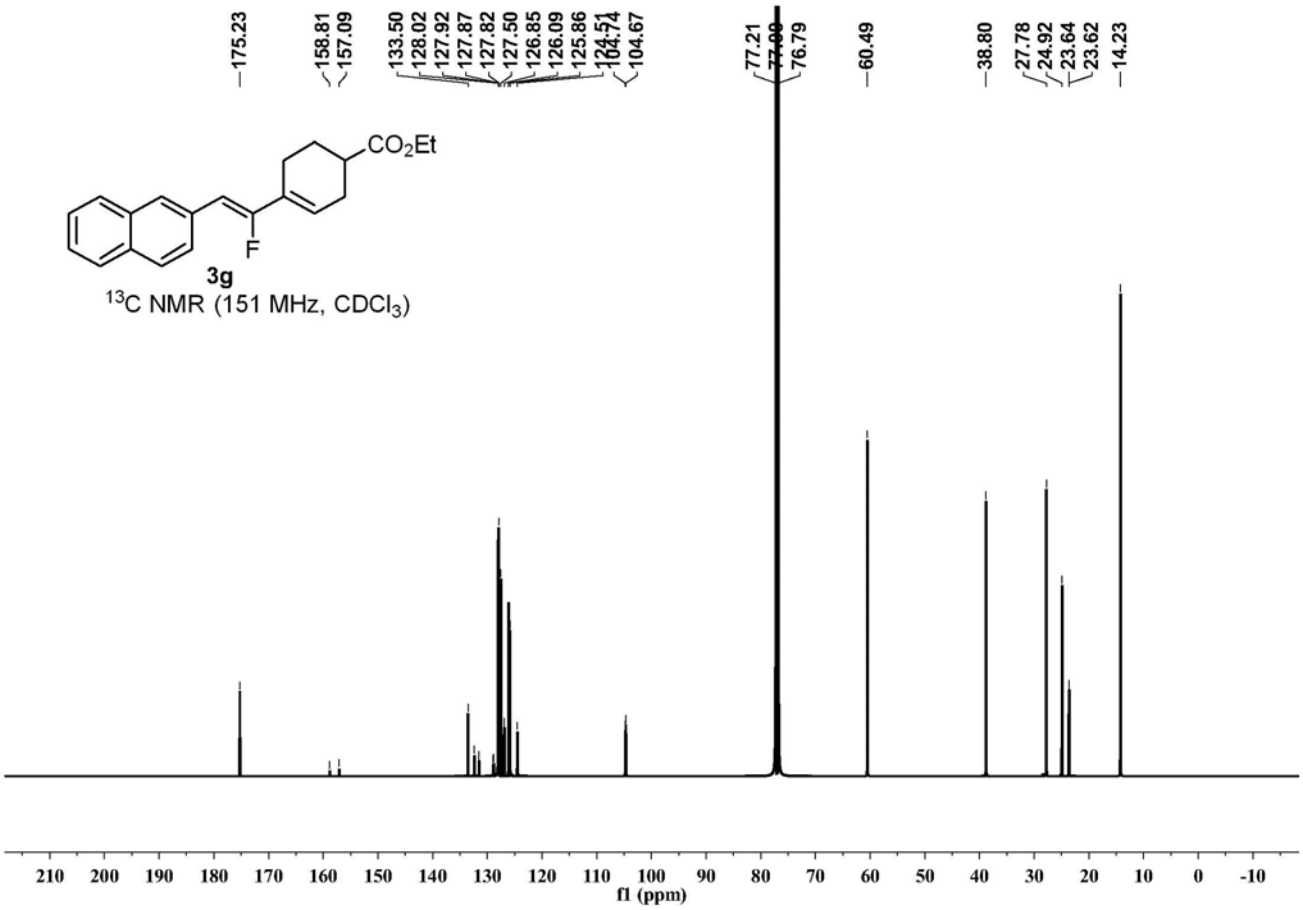
3f

^{19}F NMR (565 MHz, $CDCl_3$)



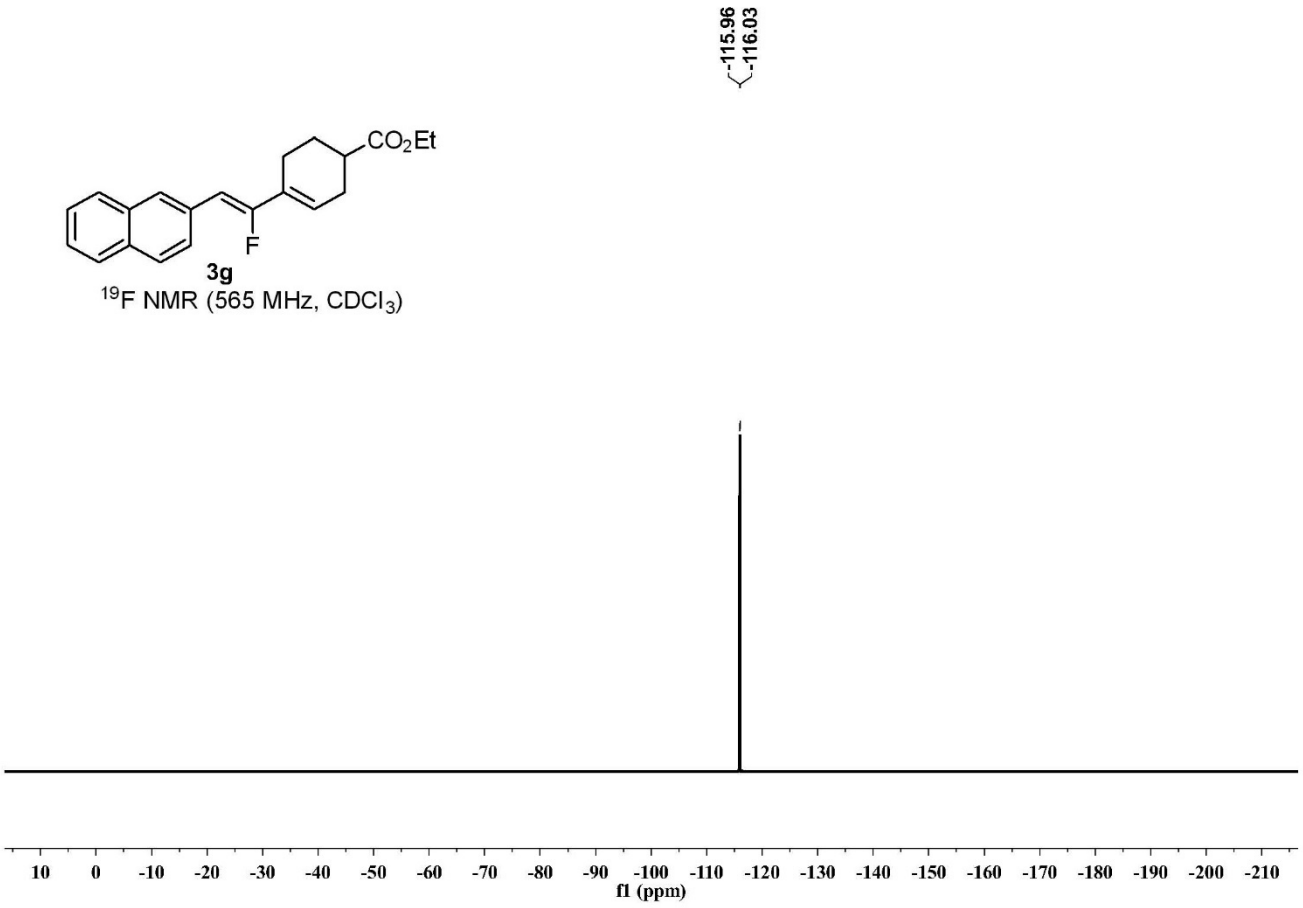
3g

^{1}H NMR (600 MHz, $CDCl_3$)



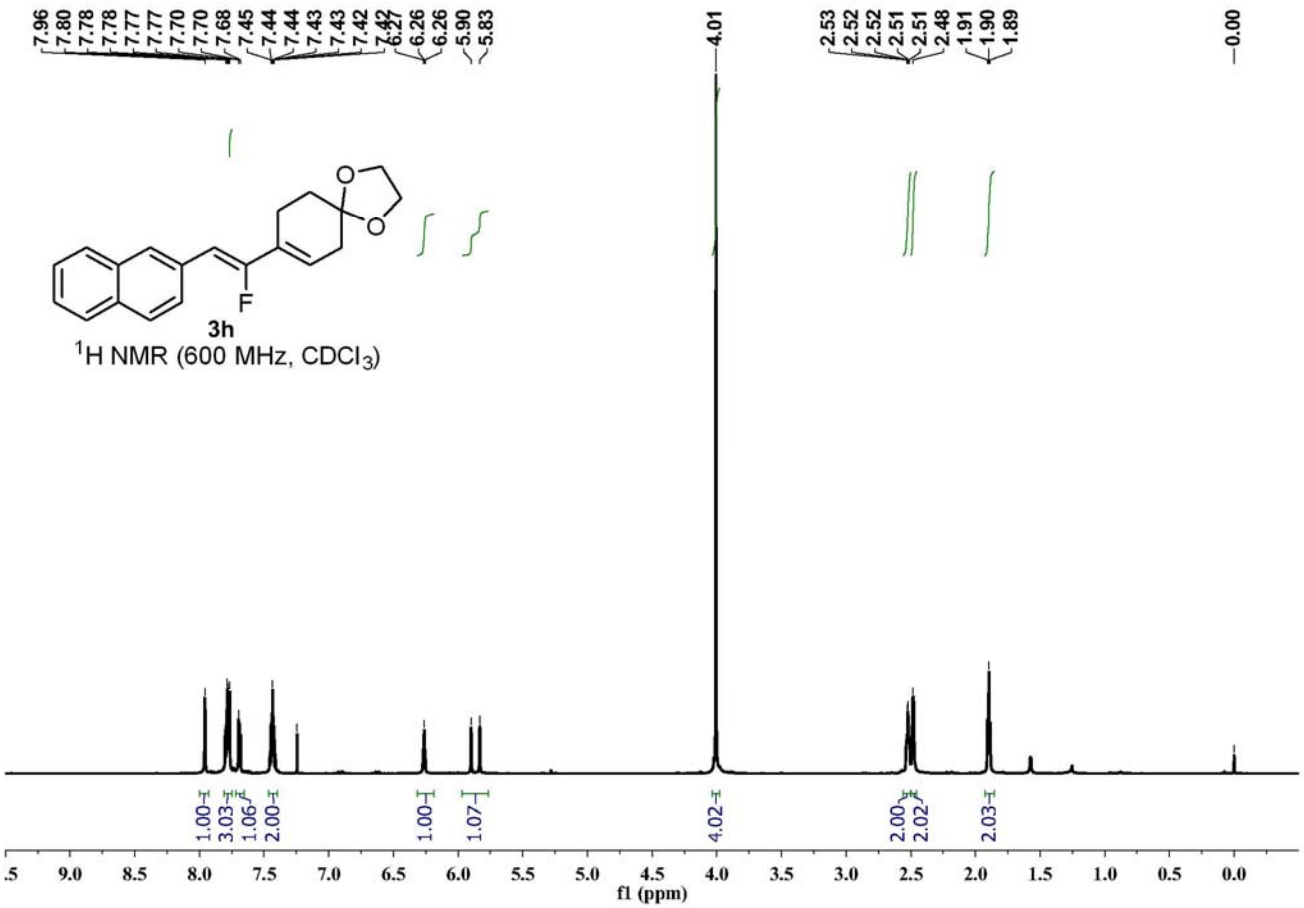
3g

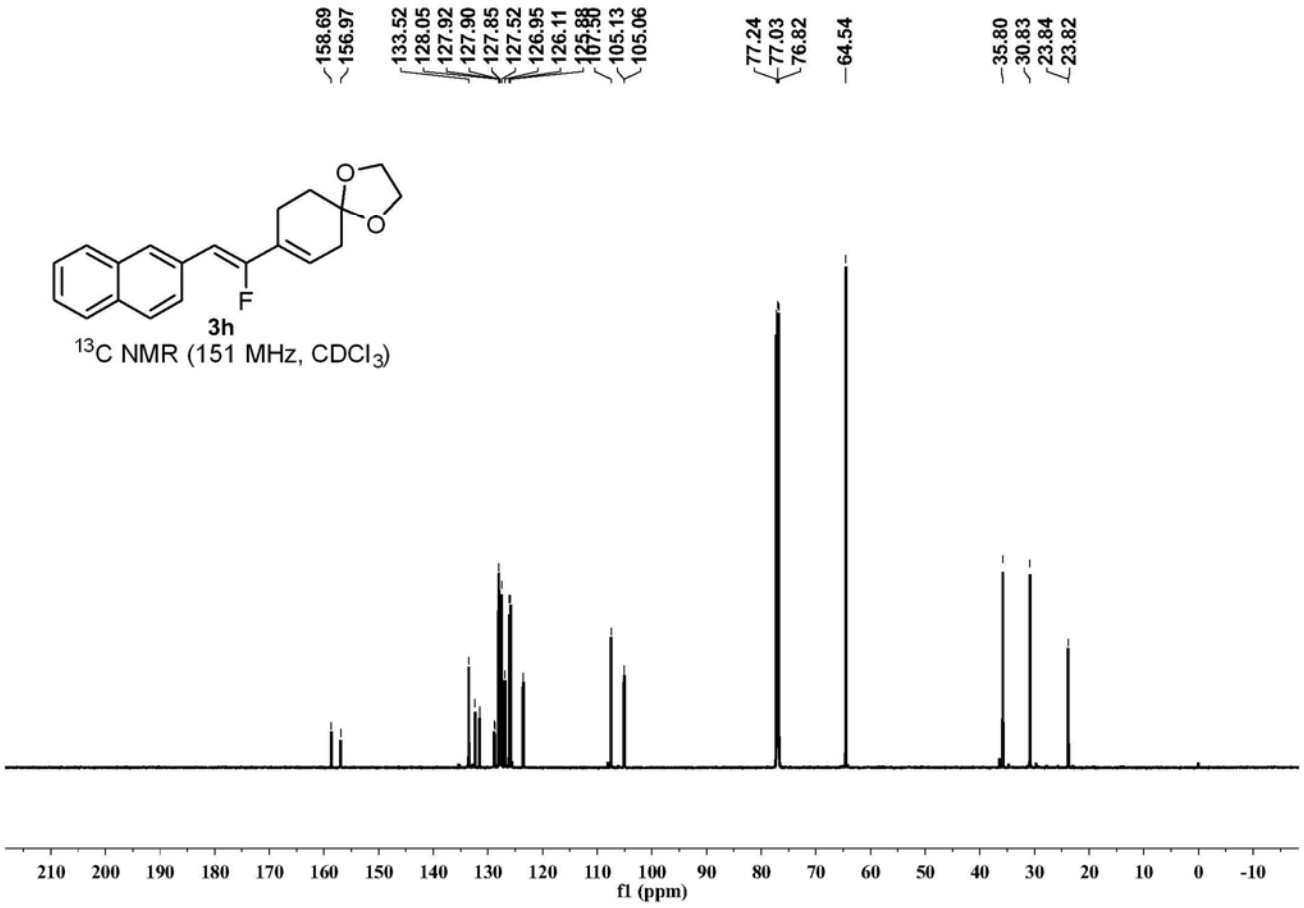
^{13}C NMR (151 MHz, $CDCl_3$)

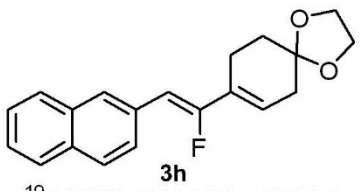


3g

^{19}F NMR (565 MHz, $CDCl_3$)

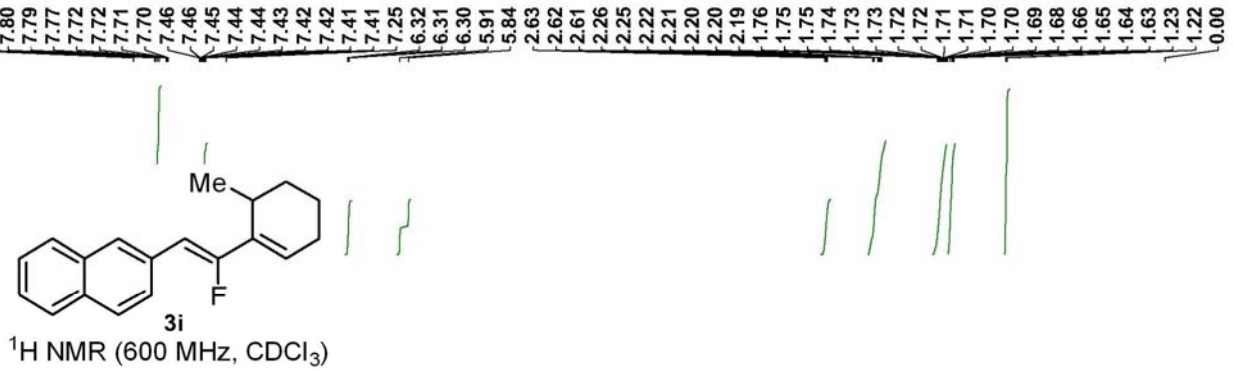

7.96
7.80
7.78
7.78
7.77
7.77
7.70
7.68
7.45
7.44
7.44
7.43
7.43
7.42
6.26
6.26
5.90
5.83
4.01
2.53
2.52
2.52
2.51
2.51
2.48
1.91
1.90
1.89
0.00
O
O
F
3h
^{1}H NMR (600 MHz, CDCl$_3$)
1.00
3.03
1.06
2.00
1.00
1.07
4.02
2.00
2.02
2.03
f1 (ppm)


158.69
156.97
133.52
128.05
127.92
127.90
127.85
127.52
126.95
126.11
105.13
105.06
77.24
77.03
76.82
64.54
35.80
30.83
23.84
23.82
O
O
F
3h
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)



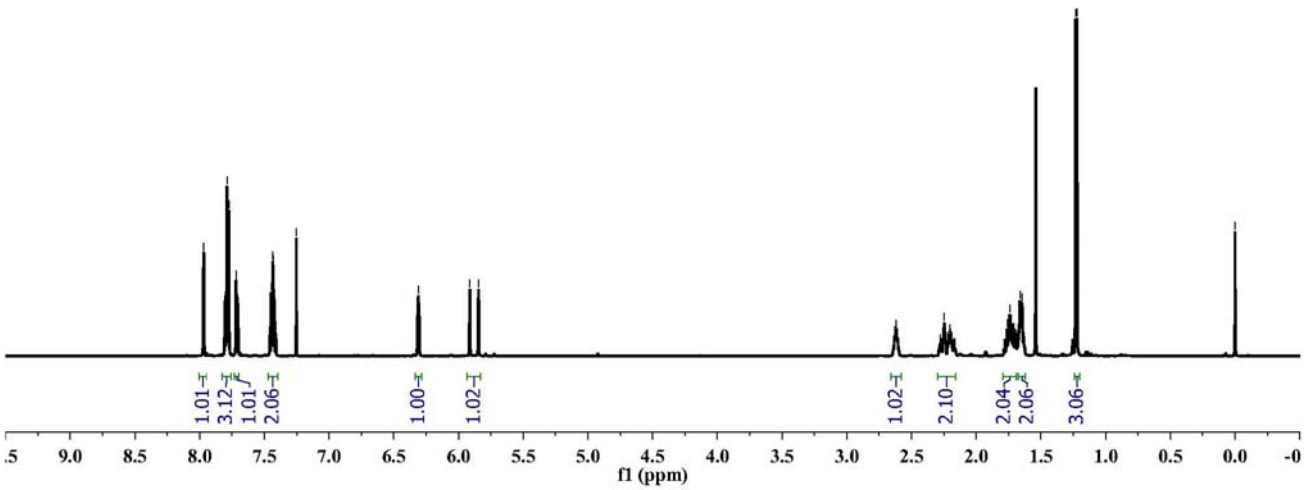
3h

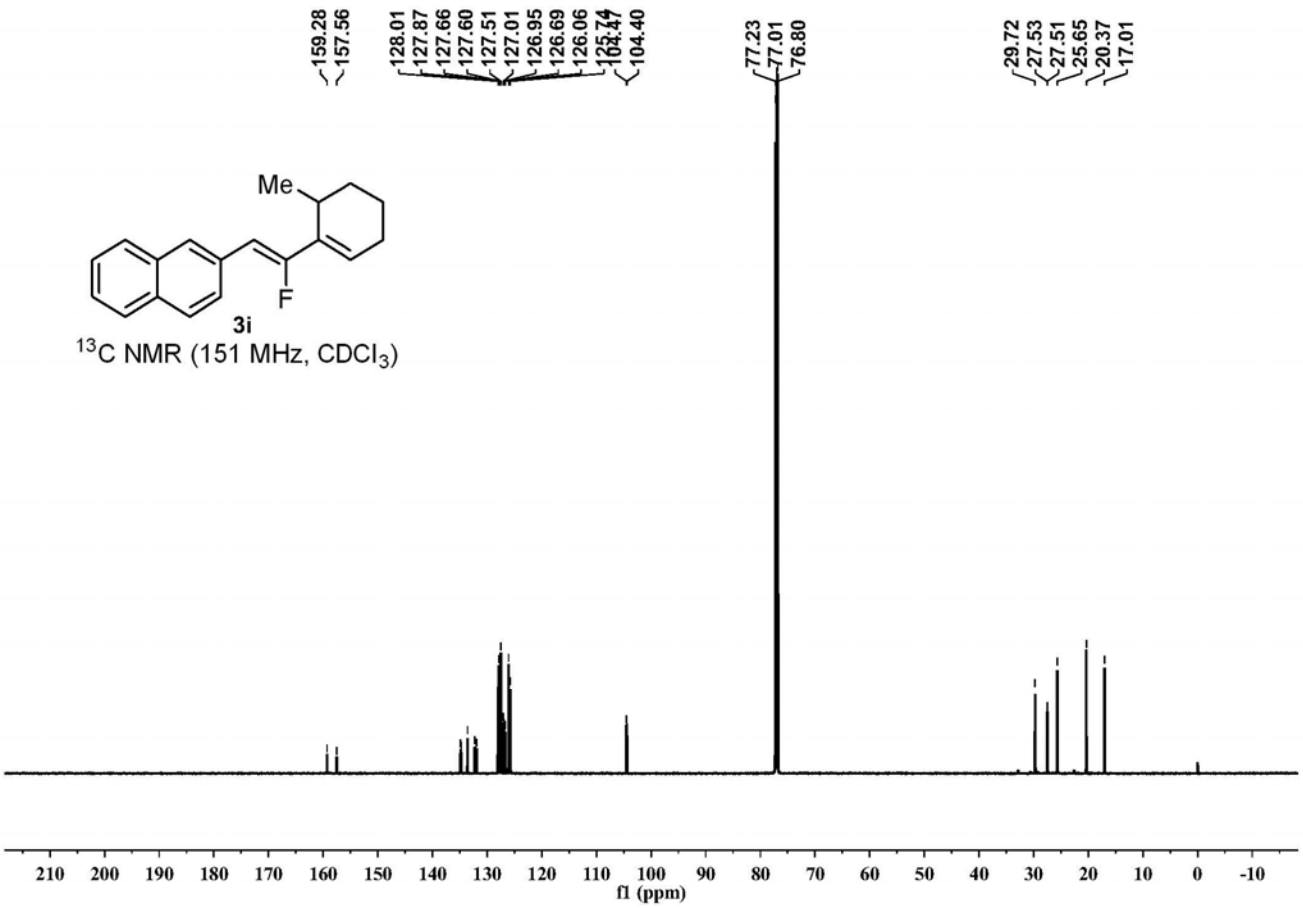
^{19}F NMR (565 MHz, $CDCl_3$)



3i

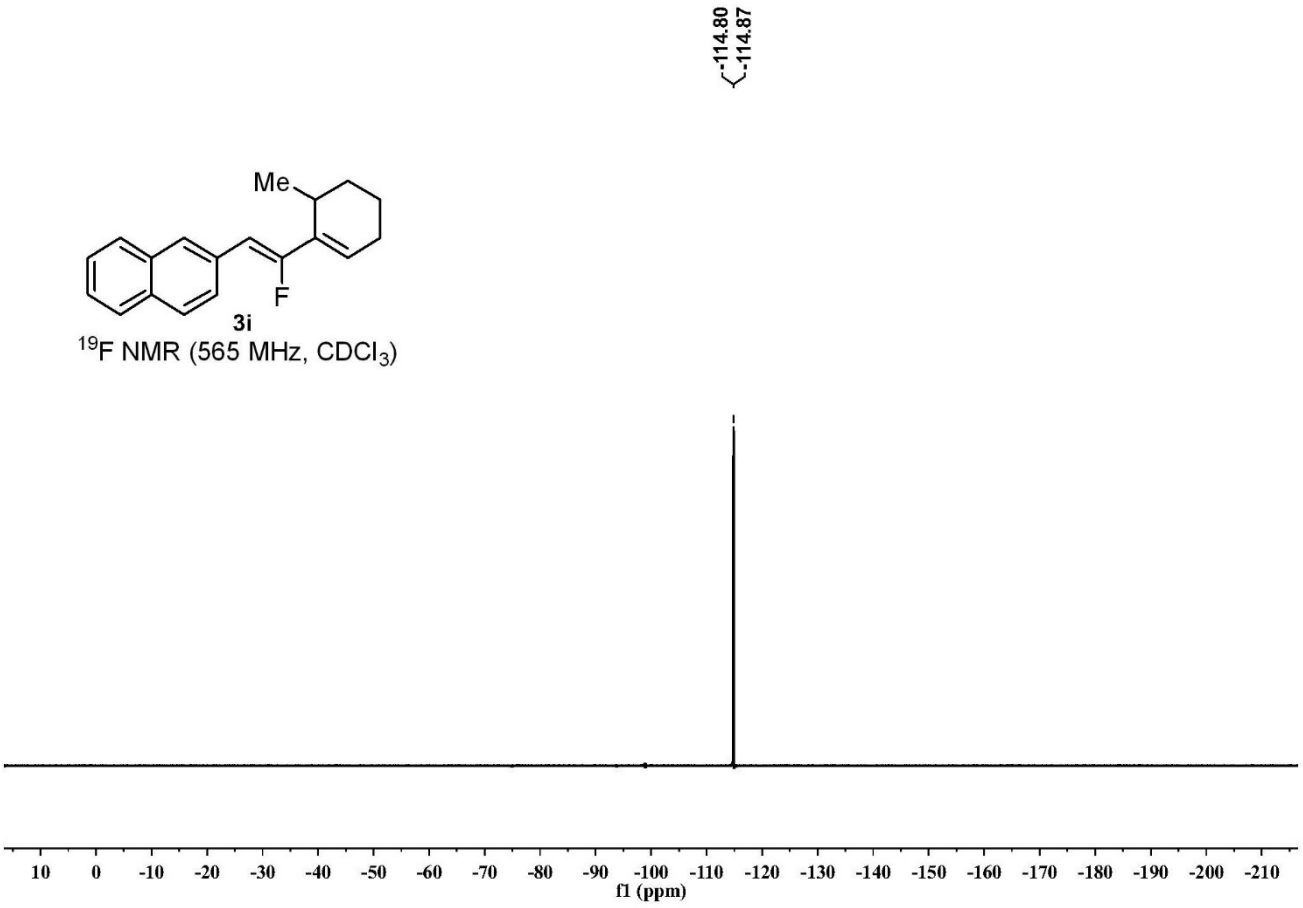
^{1}H NMR (600 MHz, $CDCl_3$)





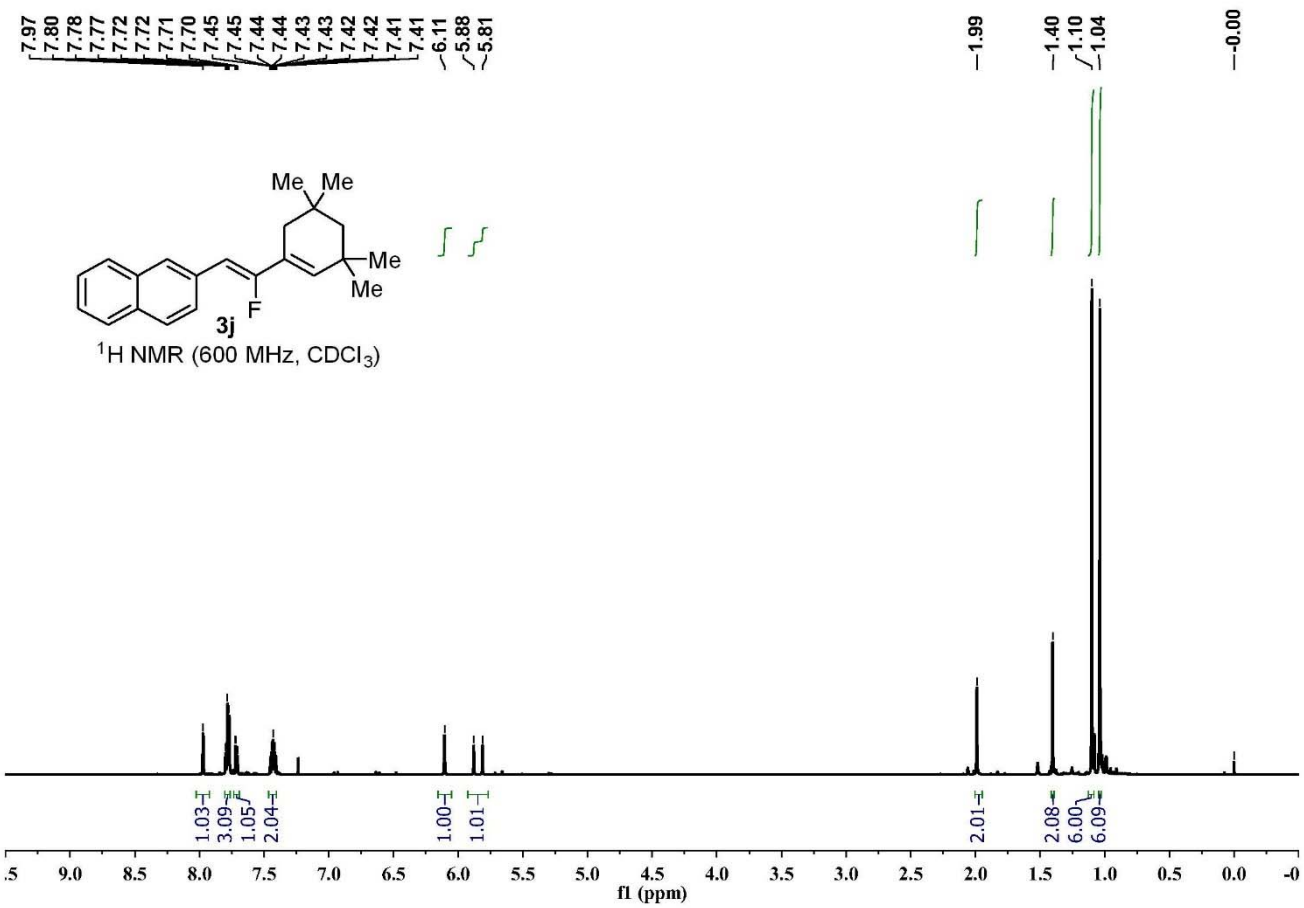
3i

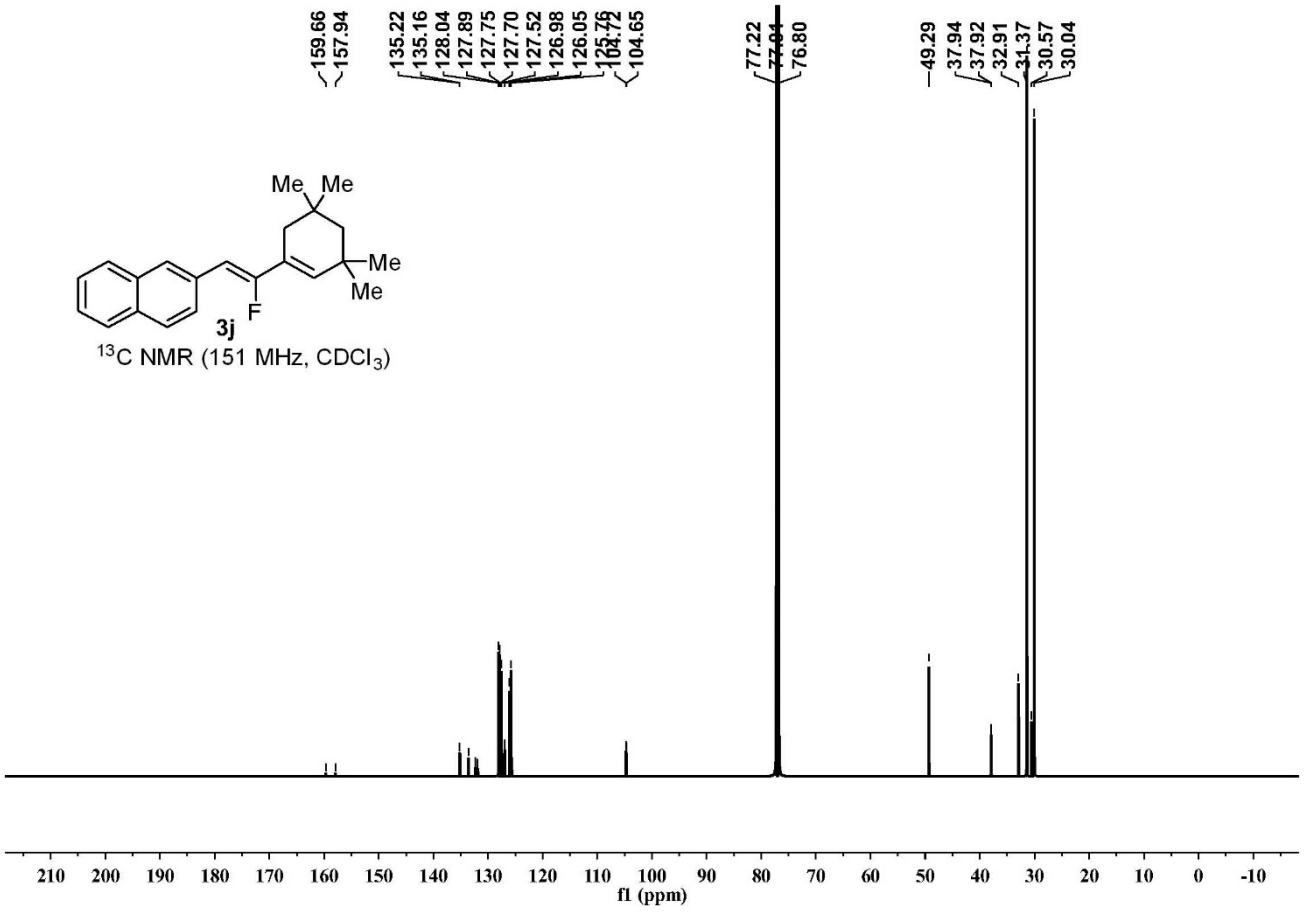
^{13}C NMR (151 MHz, $CDCl_3$)

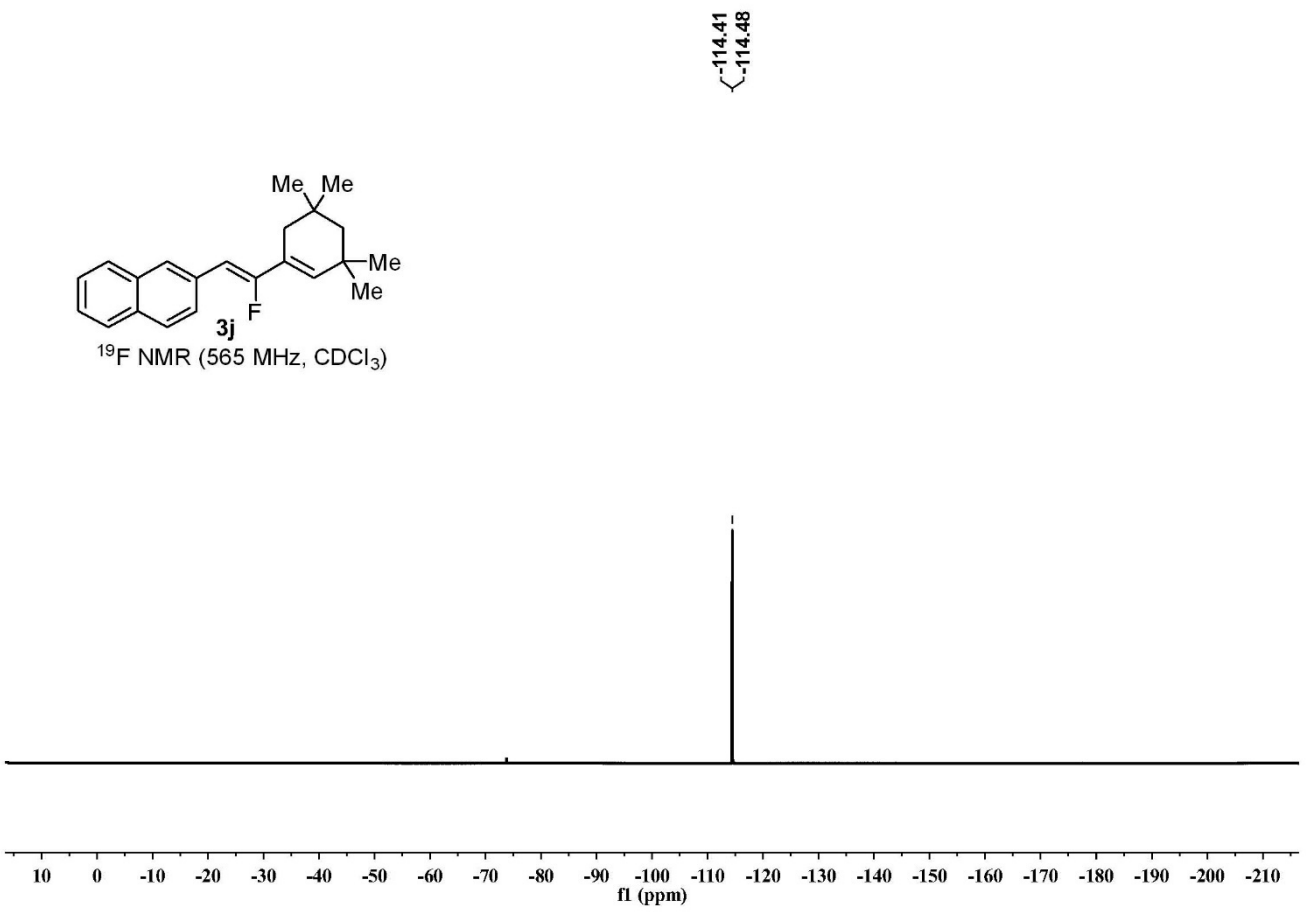


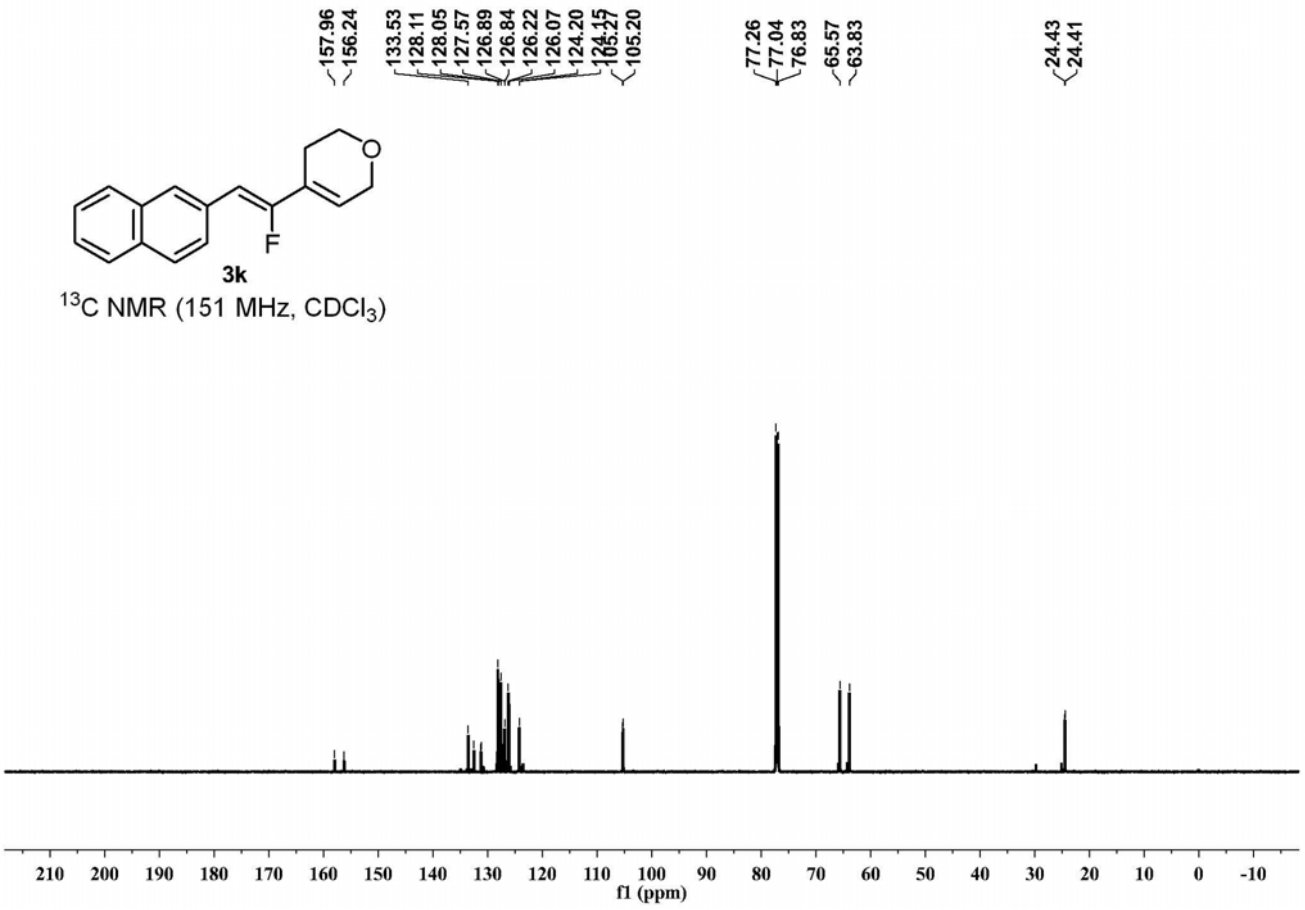
3i

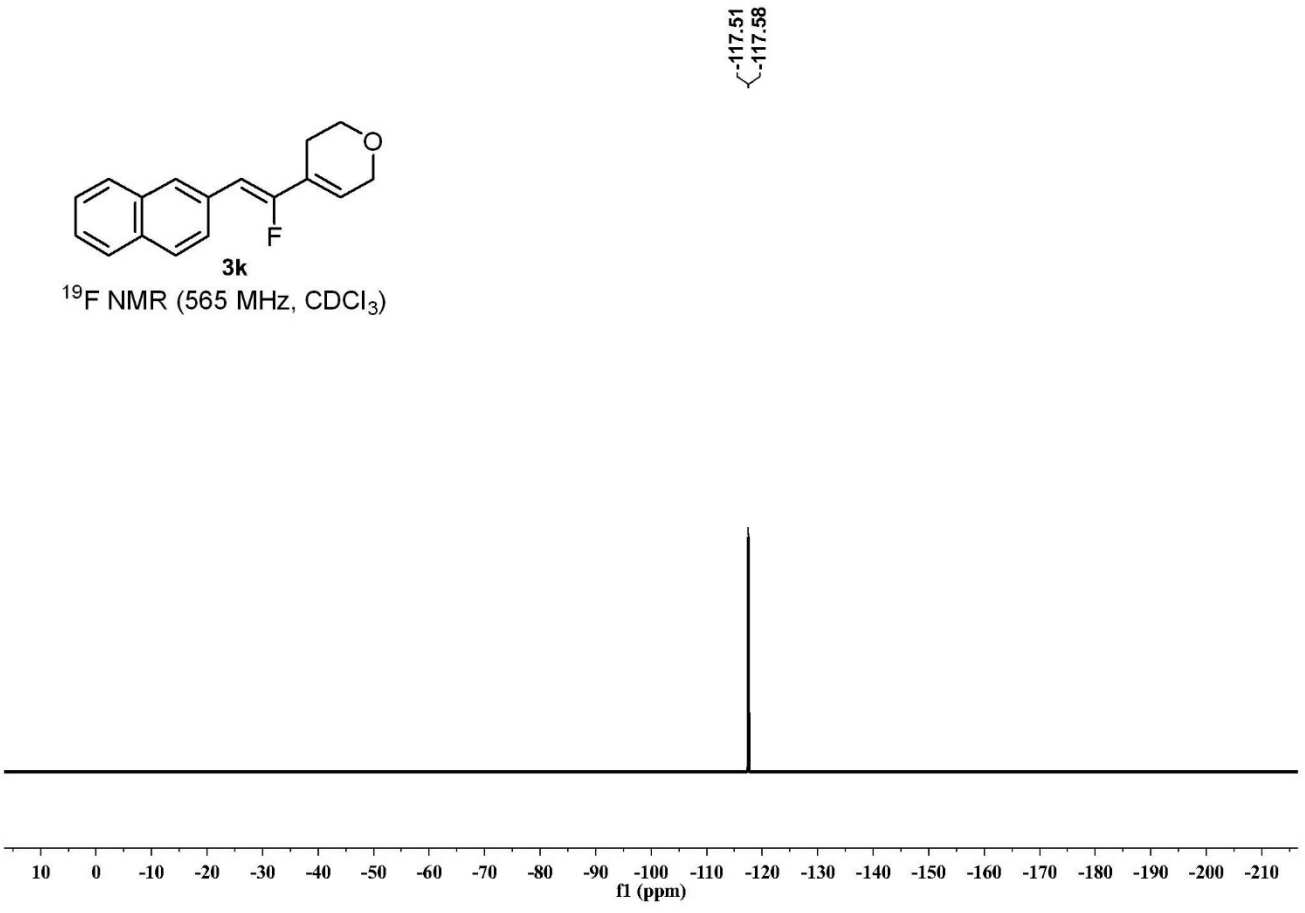
^{19}F NMR (565 MHz, $CDCl_3$)

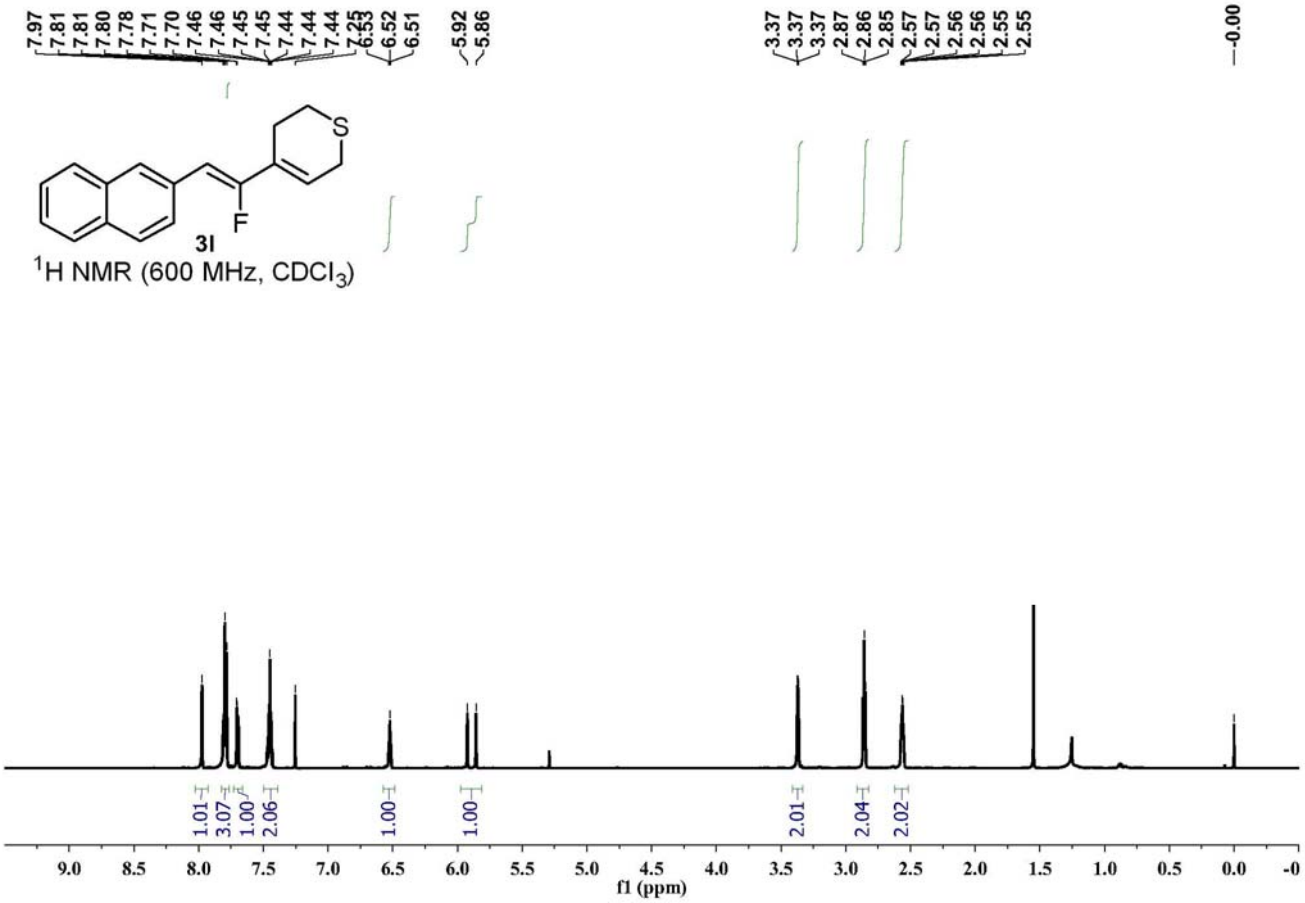

7.97
7.80
7.78
7.77
7.72
7.72
7.71
7.70
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
6.11
5.88
5.81
1.99
1.40
1.10
1.04
0.00
Me
Me
Me
Me
F
3j
1H NMR (600 MHz, CDCl3)
1.03
3.09
1.05
2.04
1.00
1.01
2.01
2.08
6.00
6.09
f1 (ppm)

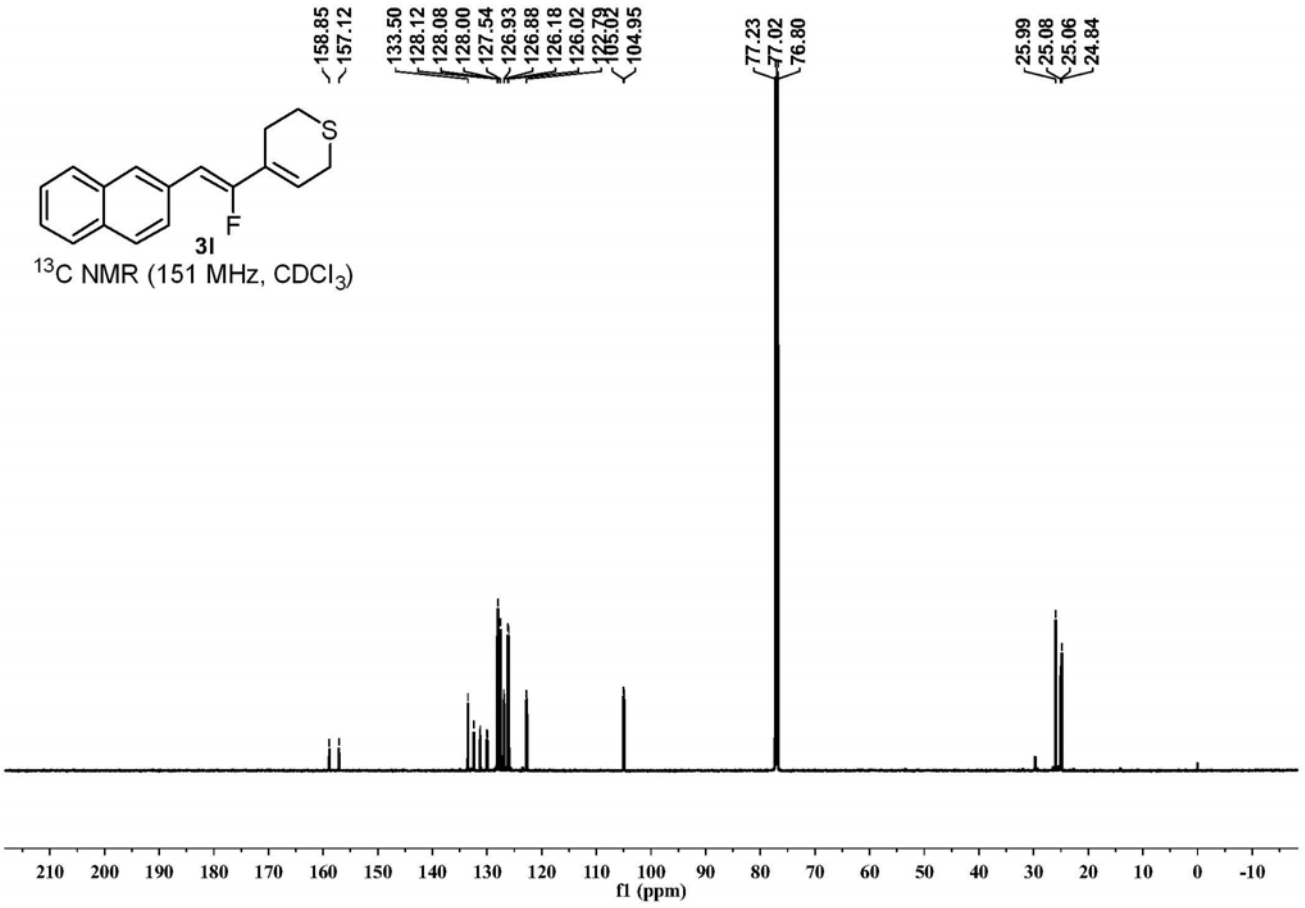

159.66
157.94
135.22
135.16
128.04
127.89
127.75
127.70
127.52
126.98
126.05
104.65
77.22
77.04
76.80
49.29
37.94
37.92
32.91
31.37
30.57
30.04
Me
Me
Me
Me
F
3j
13C NMR (151 MHz, CDCl3)
f1 (ppm)

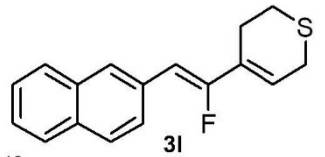

-114.41
-114.48
Me
Me
Me
Me
F
3j
^{19}F NMR (565 MHz, $CDCl_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
7.98
7.81
7.81
7.80
7.78
7.72
7.72
7.70
7.70
7.46
7.46
7.45
7.45
7.44
7.44
7.44
7.25
6.30
5.87
5.80
4.34
4.34
3.90
3.89
3.88
2.36
2.36
-0.00
O
F
3k
^{1}H NMR (600 MHz, $CDCl_3$)
1.06
3.09
1.00
2.08
1.00
1.01
2.03
2.04
2.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.96
156.24
133.53
128.11
128.05
127.57
126.89
126.84
126.22
126.07
124.20
105.20
77.26
77.04
76.83
65.57
63.83
24.43
24.41
O
F
3k
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-117.51
-117.58
O
F
3k
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

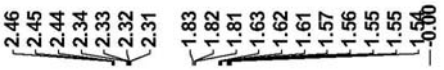

7.97
7.81
7.81
7.80
7.78
7.71
7.70
7.46
7.46
7.45
7.45
7.44
7.44
7.44
6.53
6.52
6.51
5.92
5.86
3.37
3.37
3.37
2.87
2.86
2.85
2.57
2.57
2.56
2.56
2.55
2.55
-0.00
S
F
3l
1H NMR (600 MHz, CDCl3)
1.01
3.07
1.00
2.06
1.00
1.00
2.01
2.04
2.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

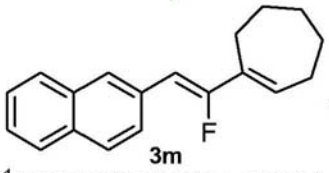

158.85
157.12
133.50
128.12
128.08
128.00
127.54
126.93
126.88
126.18
126.02
122.79
105.02
104.95
77.23
77.02
76.80
25.99
25.08
25.06
24.84
S
F
3l
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3l

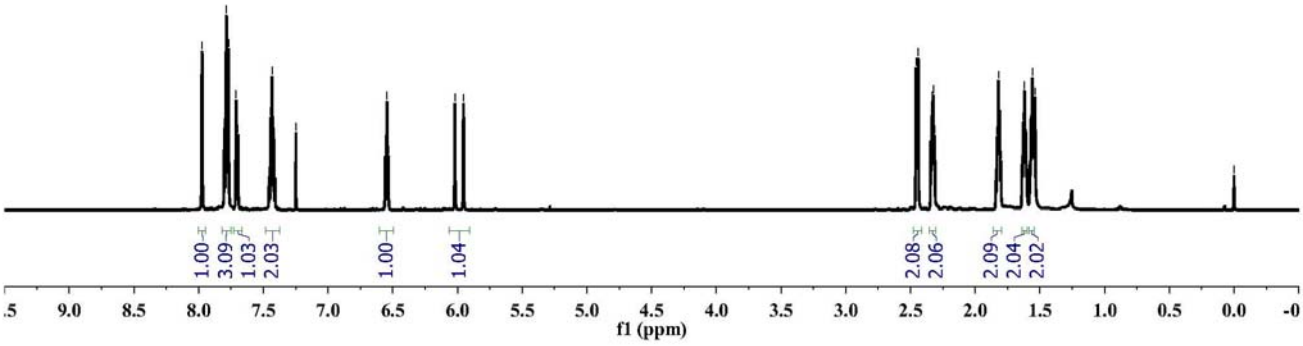
^{19}F NMR (565 MHz, $CDCl_3$)

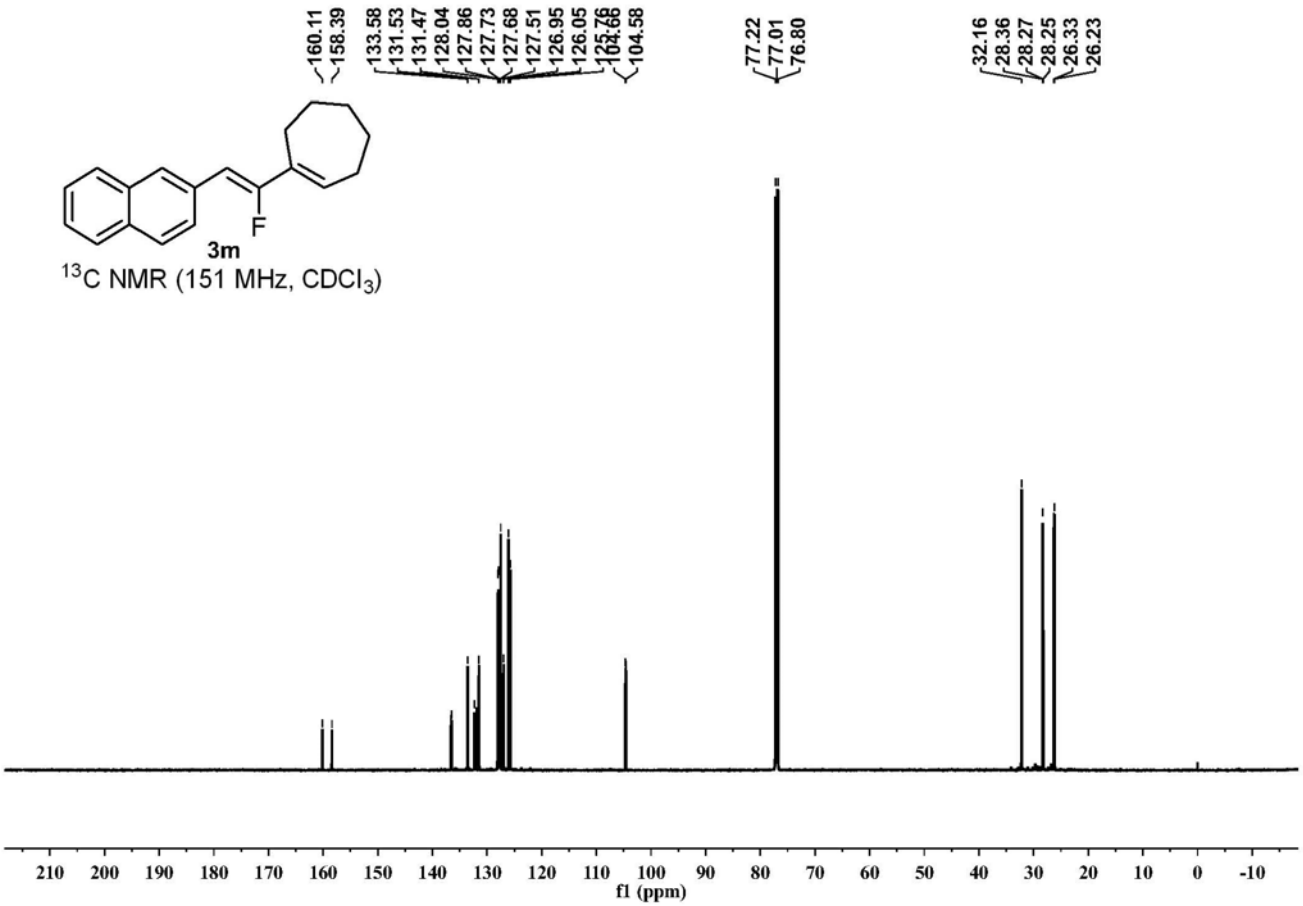


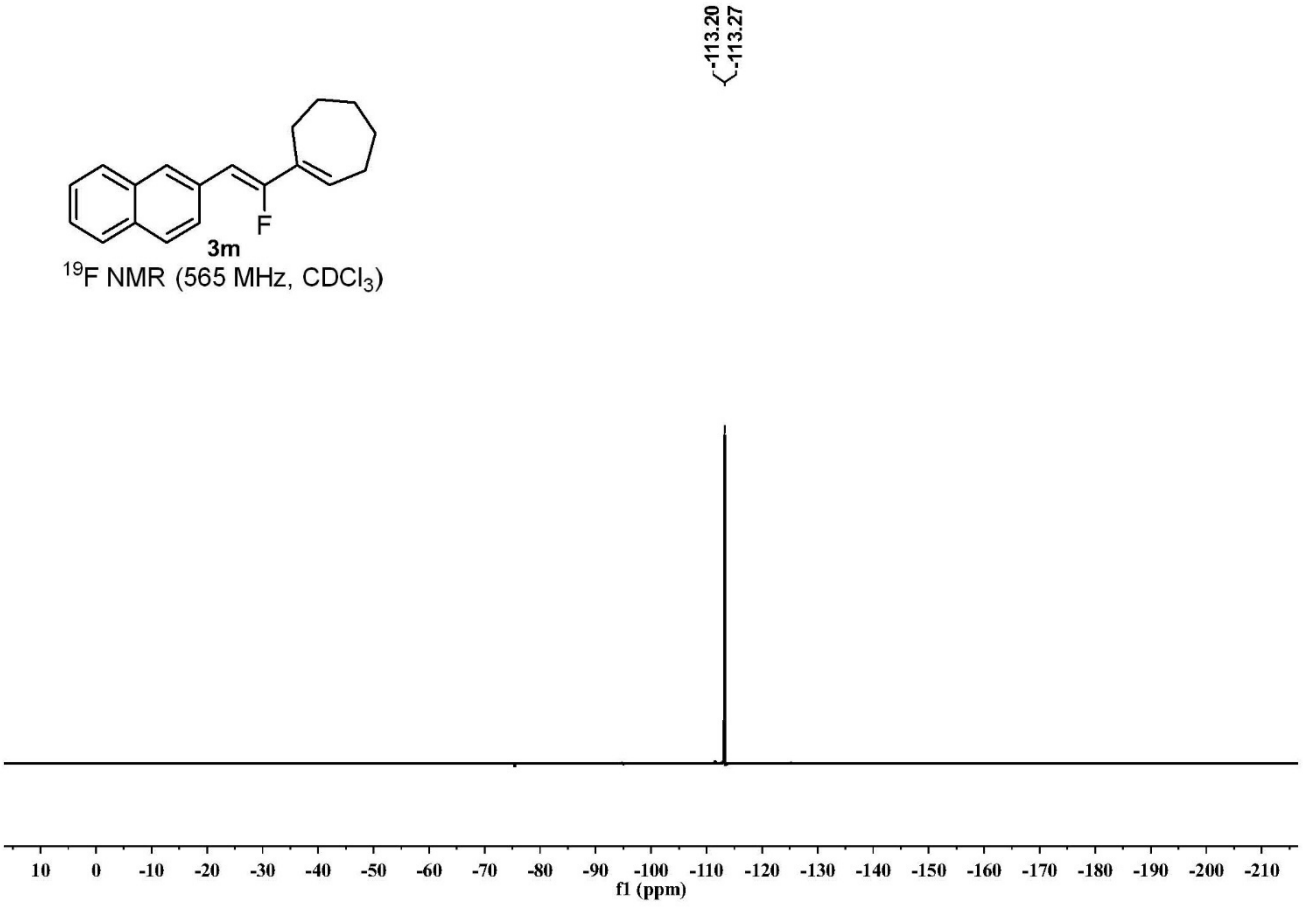


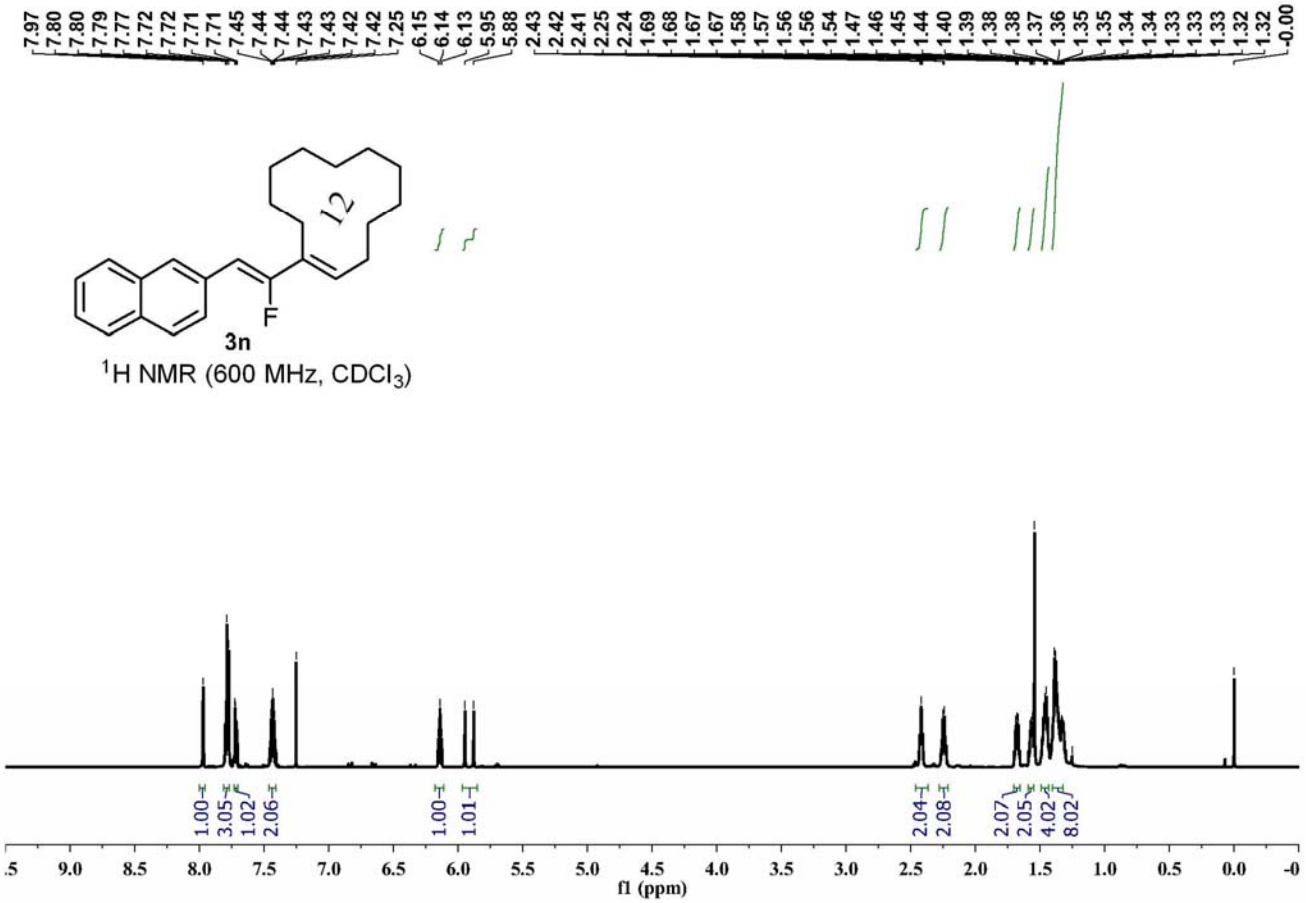
3m

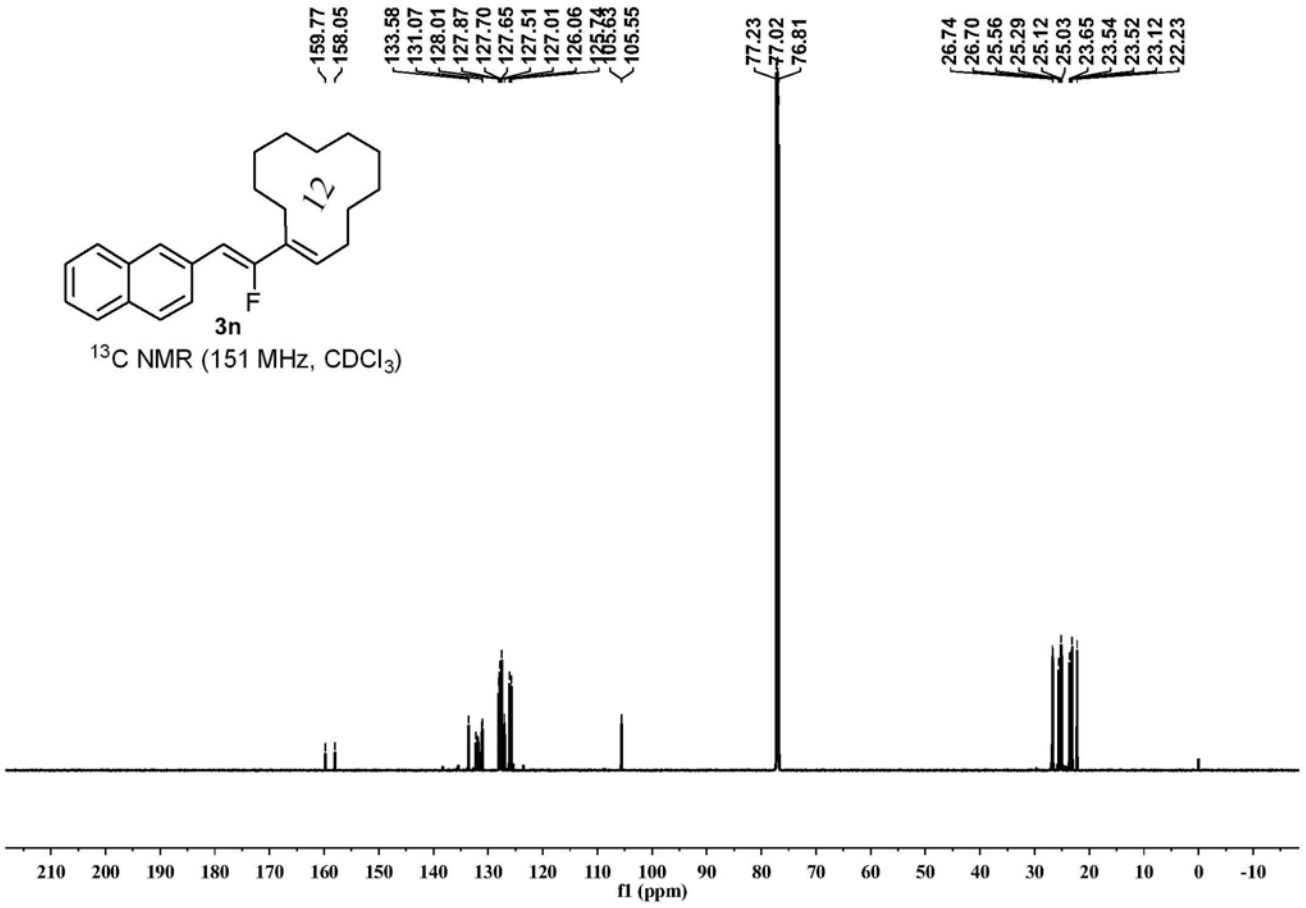
^{1}H NMR (600 MHz, $CDCl_3$)

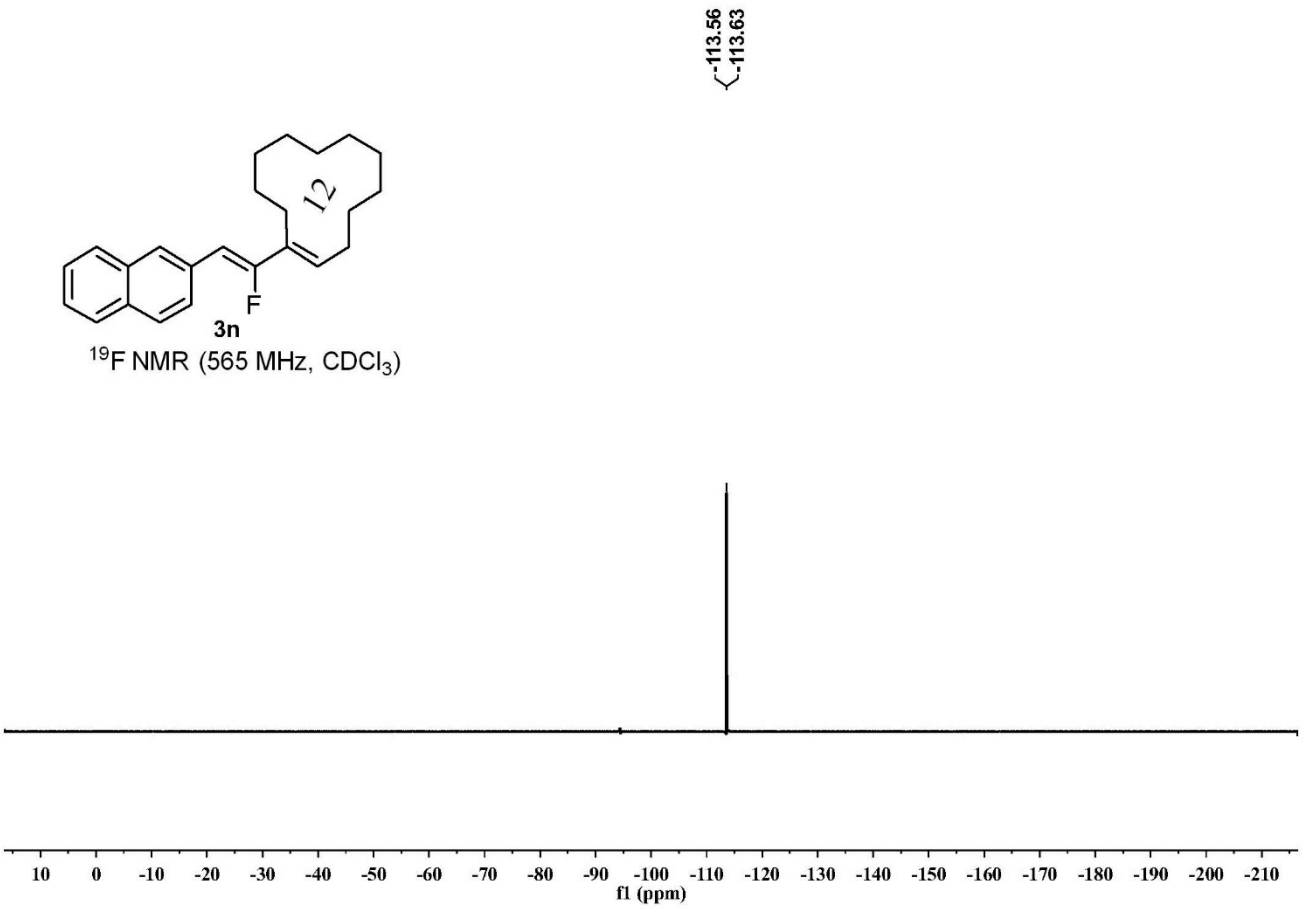


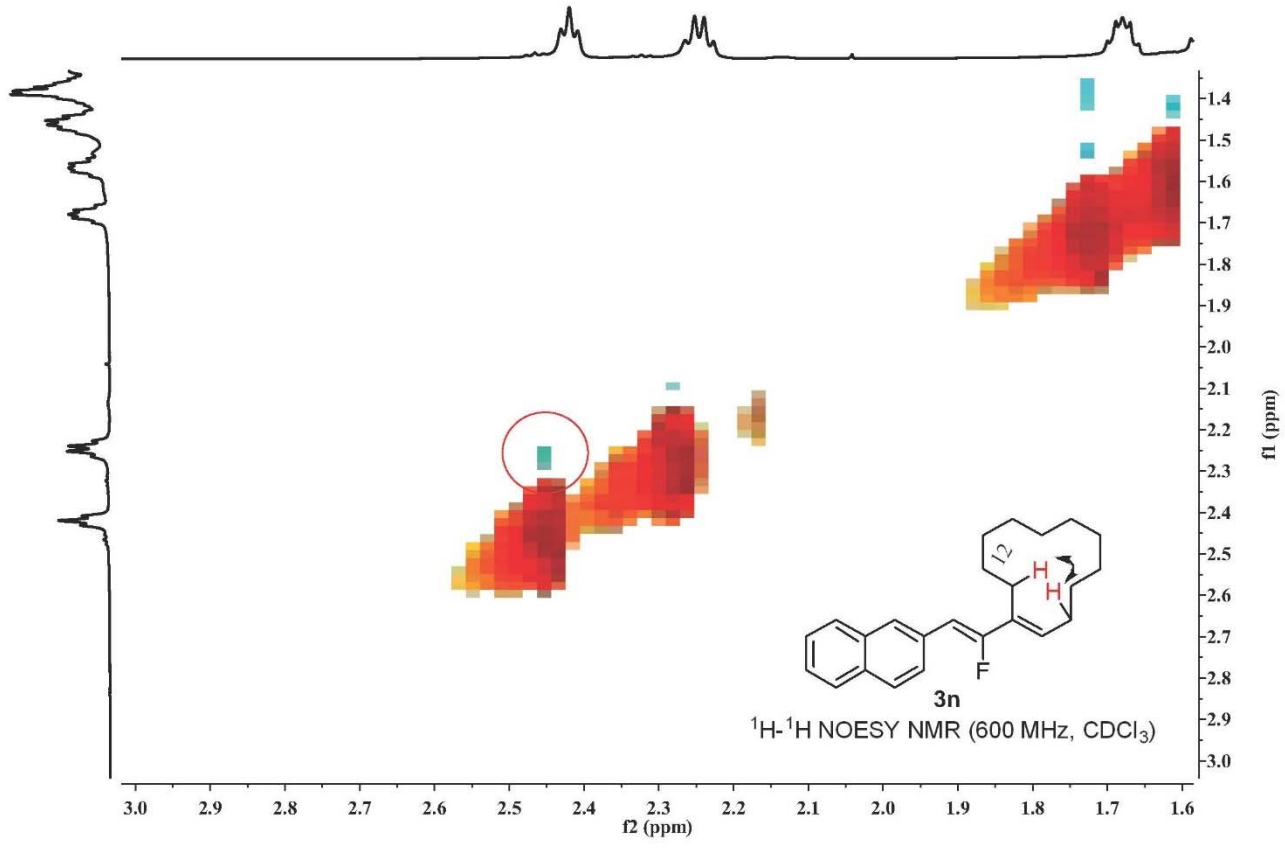

160.11
158.39
133.58
131.53
131.47
128.04
127.86
127.73
127.68
127.51
126.95
126.05
104.58
77.22
77.01
76.80
32.16
28.36
28.27
28.25
26.33
26.23
F
3m
^{13}C NMR (151 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

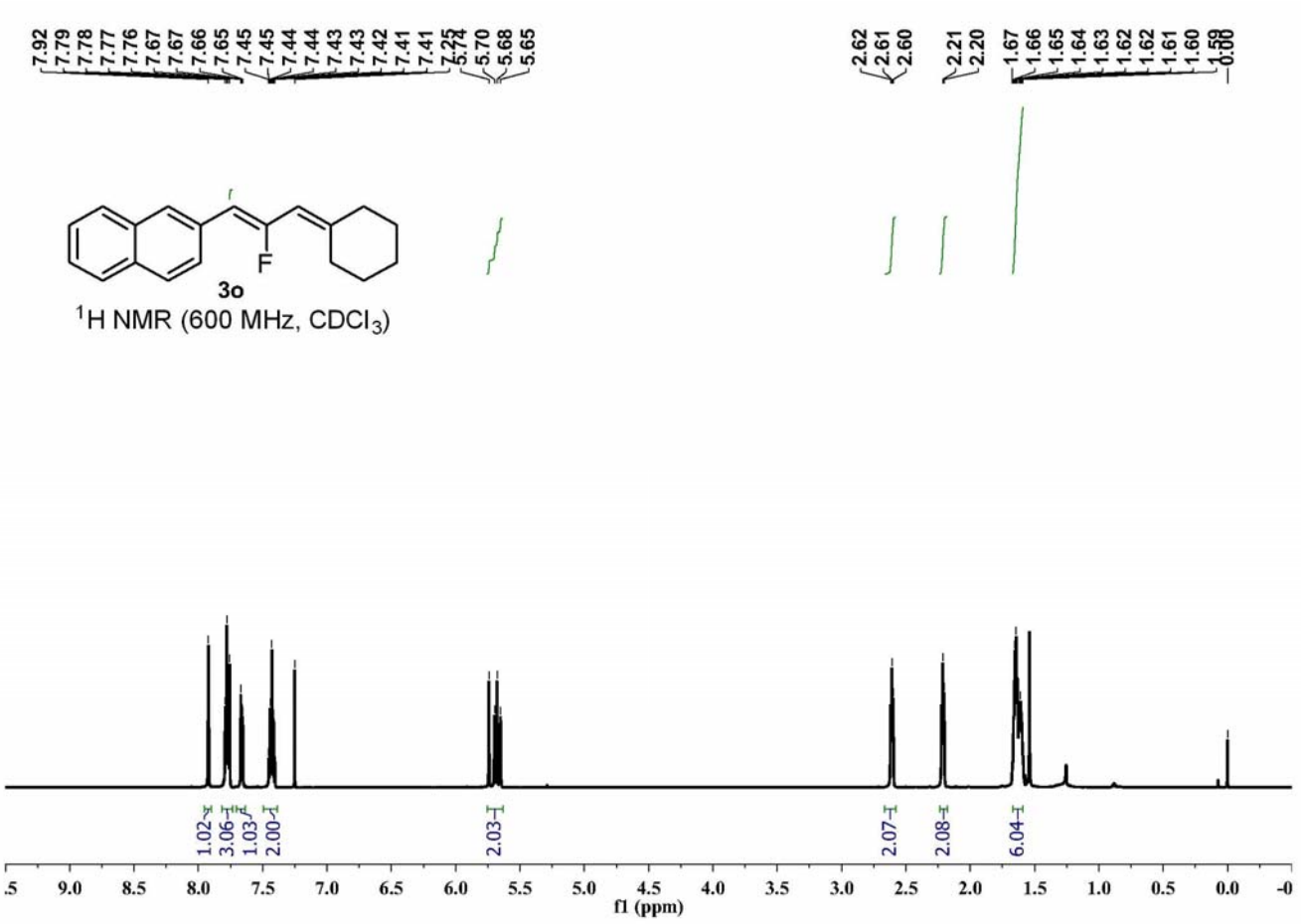

-113.20
-113.27
F
3m
^{19}F NMR (565 MHz, CDCl$_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

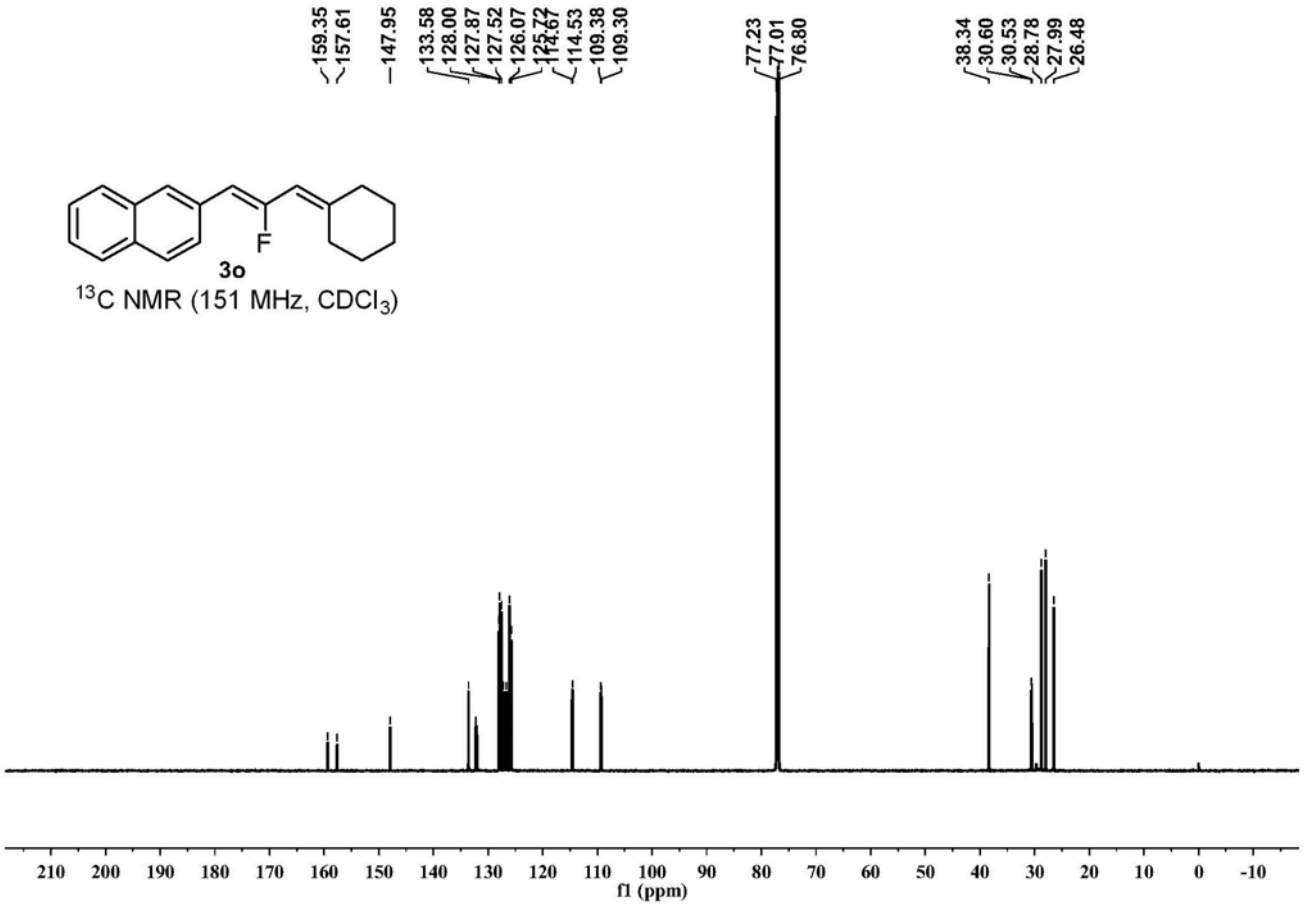

7.97 7.80 7.80 7.79 7.77 7.72 7.72 7.71 7.71 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.25 6.15 6.14 6.13 5.95 5.88 2.43 2.42 2.41 2.25 2.24 1.69 1.68 1.67 1.67 1.58 1.57 1.56 1.56 1.54 1.47 1.46 1.45 1.44 1.40 1.39 1.38 1.38 1.37 1.36 1.35 1.35 1.34 1.34 1.33 1.33 1.33 1.32 1.32 -0.00
12
F
3n
1H NMR (600 MHz, CDCl3)
1.00 3.05 1.02 2.06 1.00 1.01 2.04 2.08 2.07 2.05 4.02 8.02
f1 (ppm)


159.77 158.05 133.58 131.07 128.01 127.87 127.70 127.65 127.51 127.01 126.06 125.74 125.63 105.55 77.23 77.02 76.81 26.74 26.70 25.56 25.29 25.12 25.03 23.65 23.54 23.52 23.12 22.23
12
F
3n
13C NMR (151 MHz, CDCl3)
f1 (ppm)


-113.56
-113.63
12
F
3n
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


12
H
H
F
3n
1H-1H NOESY NMR (600 MHz, CDCl3)
3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f2 (ppm)
1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0
f1 (ppm)


7.92
7.79
7.78
7.77
7.76
7.67
7.67
7.66
7.65
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.41
5.74
5.70
5.68
5.65
2.62
2.61
2.60
2.21
2.20
1.67
1.66
1.65
1.64
1.63
1.62
1.62
1.61
1.60
0.00
F
3o
1H NMR (600 MHz, CDCl3)
1.02
3.06
1.03
2.00
2.03
2.07
2.08
6.04
f1 (ppm)


159.35
157.61
147.95
133.58
128.00
127.87
127.52
126.07
125.72
114.67
114.53
109.38
109.30
77.23
77.01
76.80
38.34
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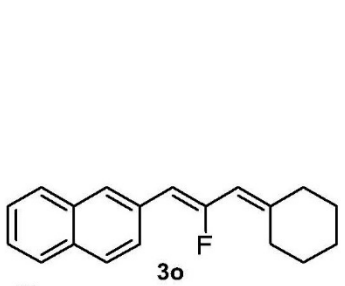
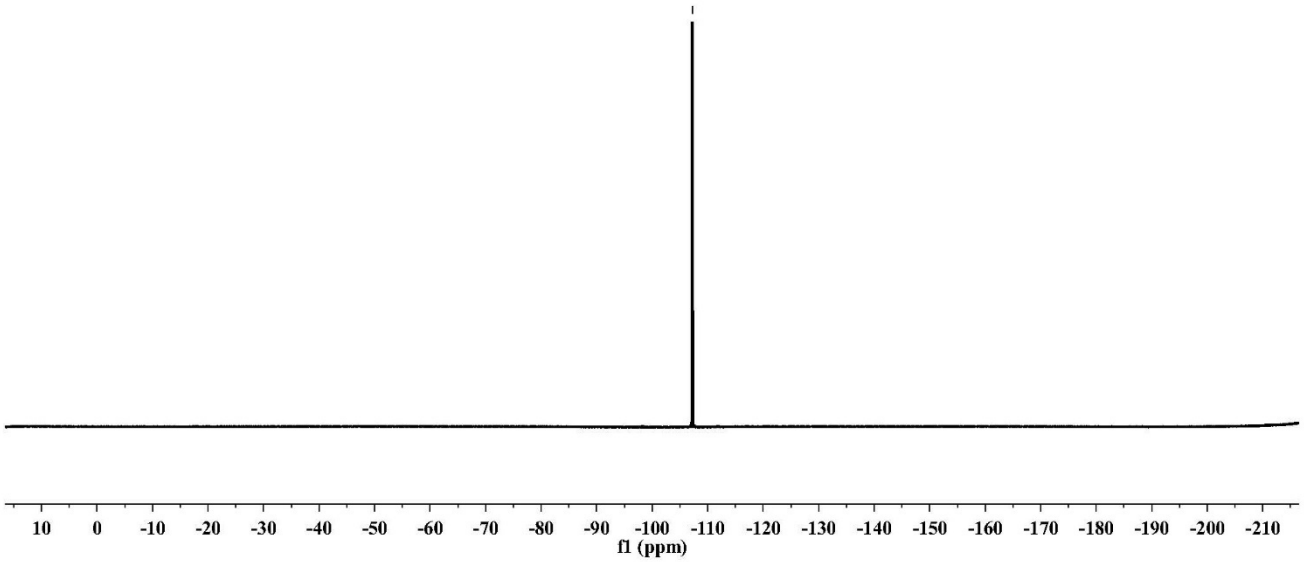
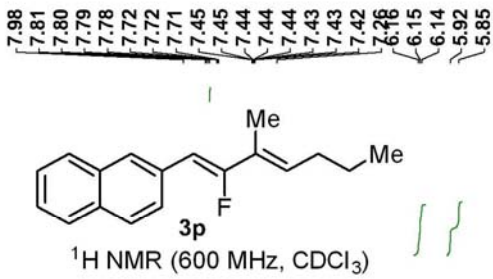
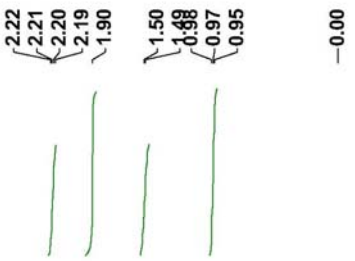
30.53
28.78
27.99
26.48
F
3o
13C NMR (151 MHz, CDCl3)
f1 (ppm)



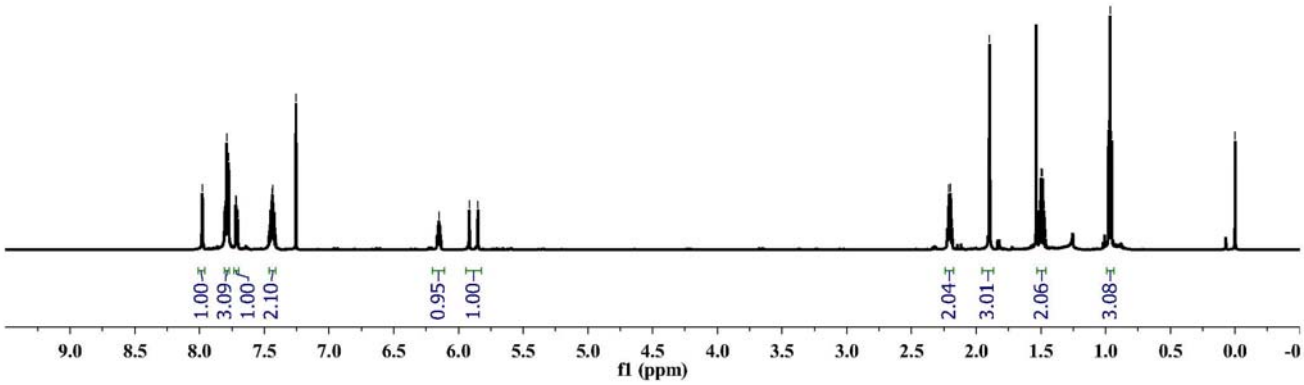
^{19}F NMR (565 MHz, $CDCl_3$)

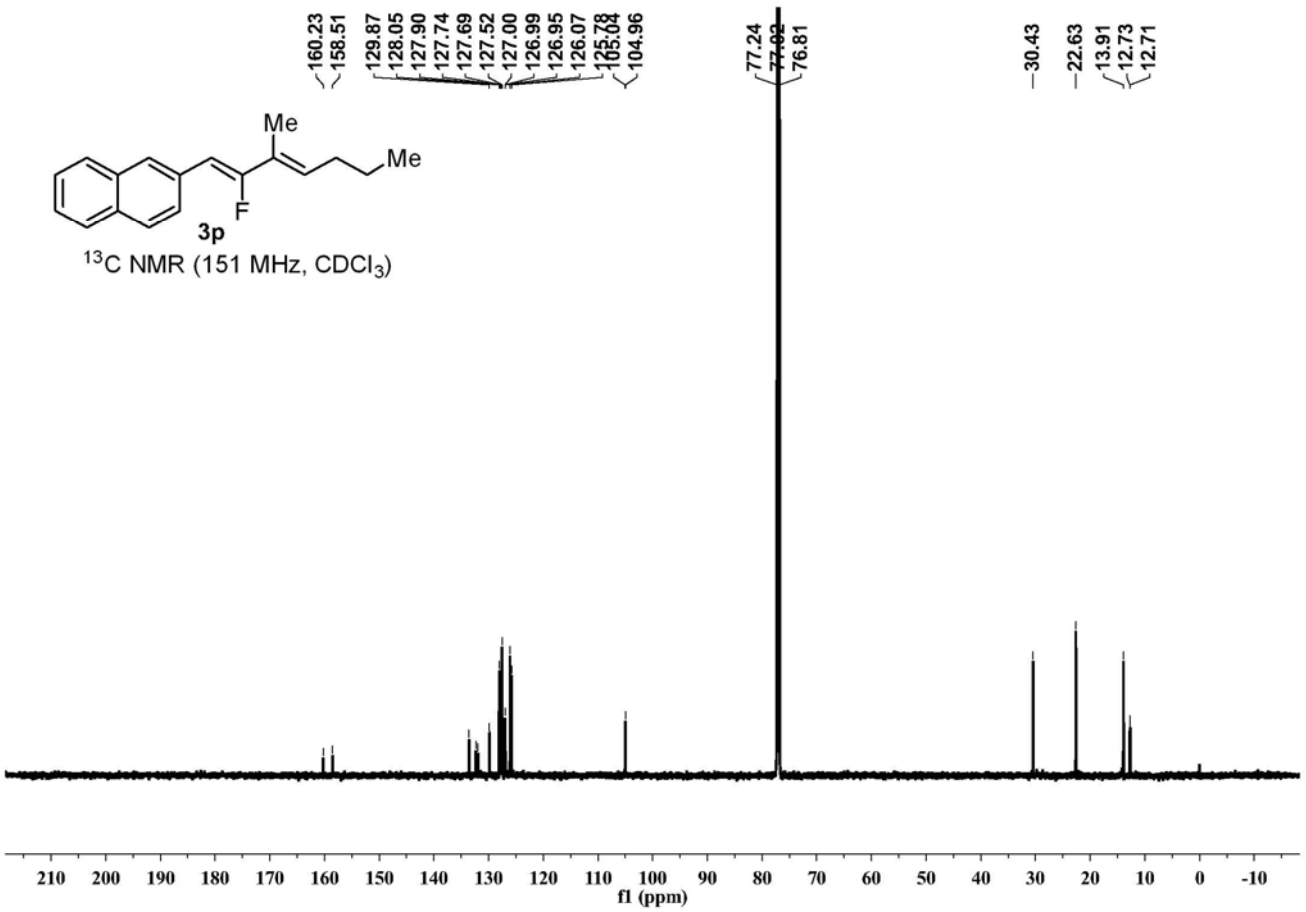




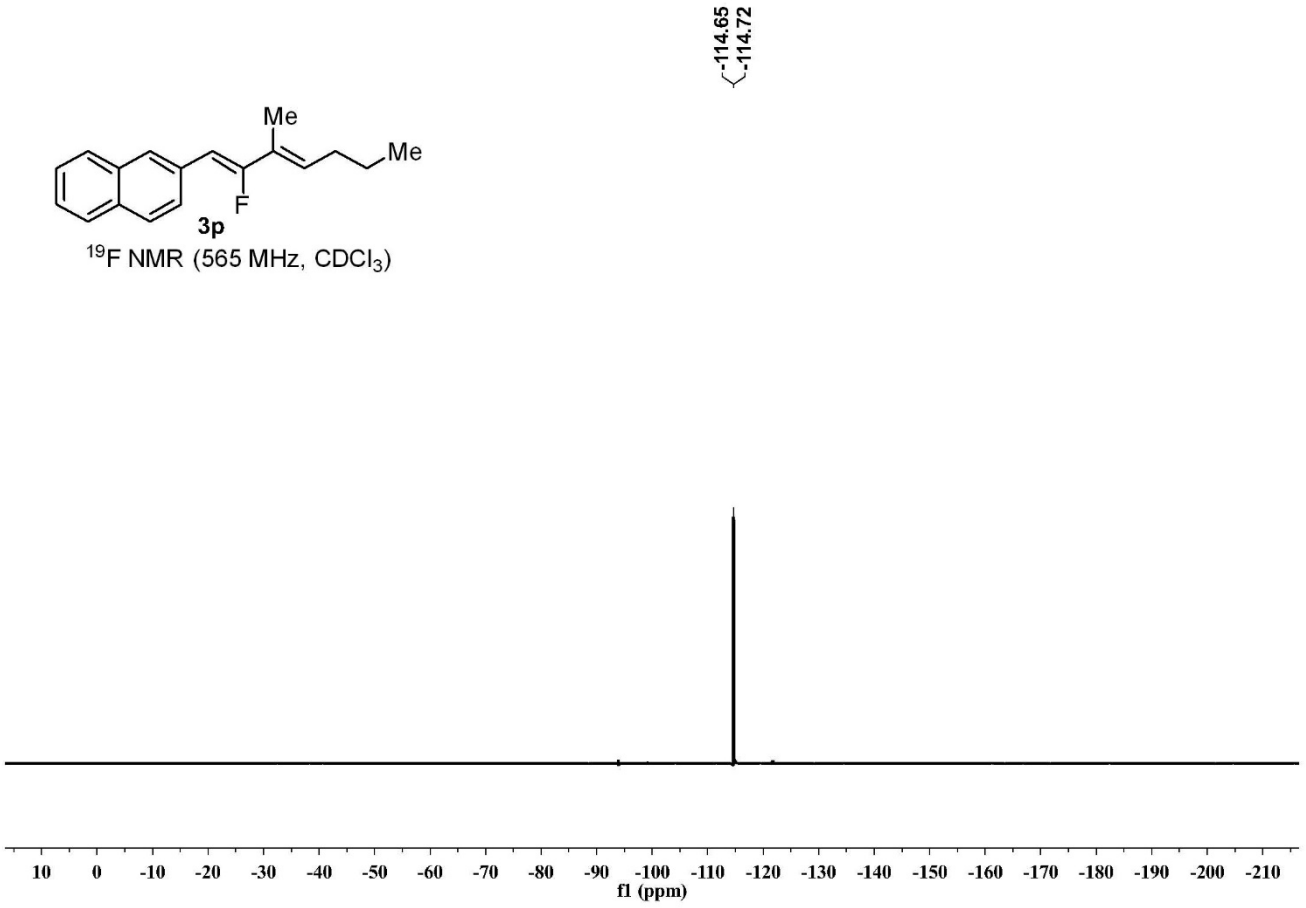


^{1}H NMR (600 MHz, $CDCl_3$)

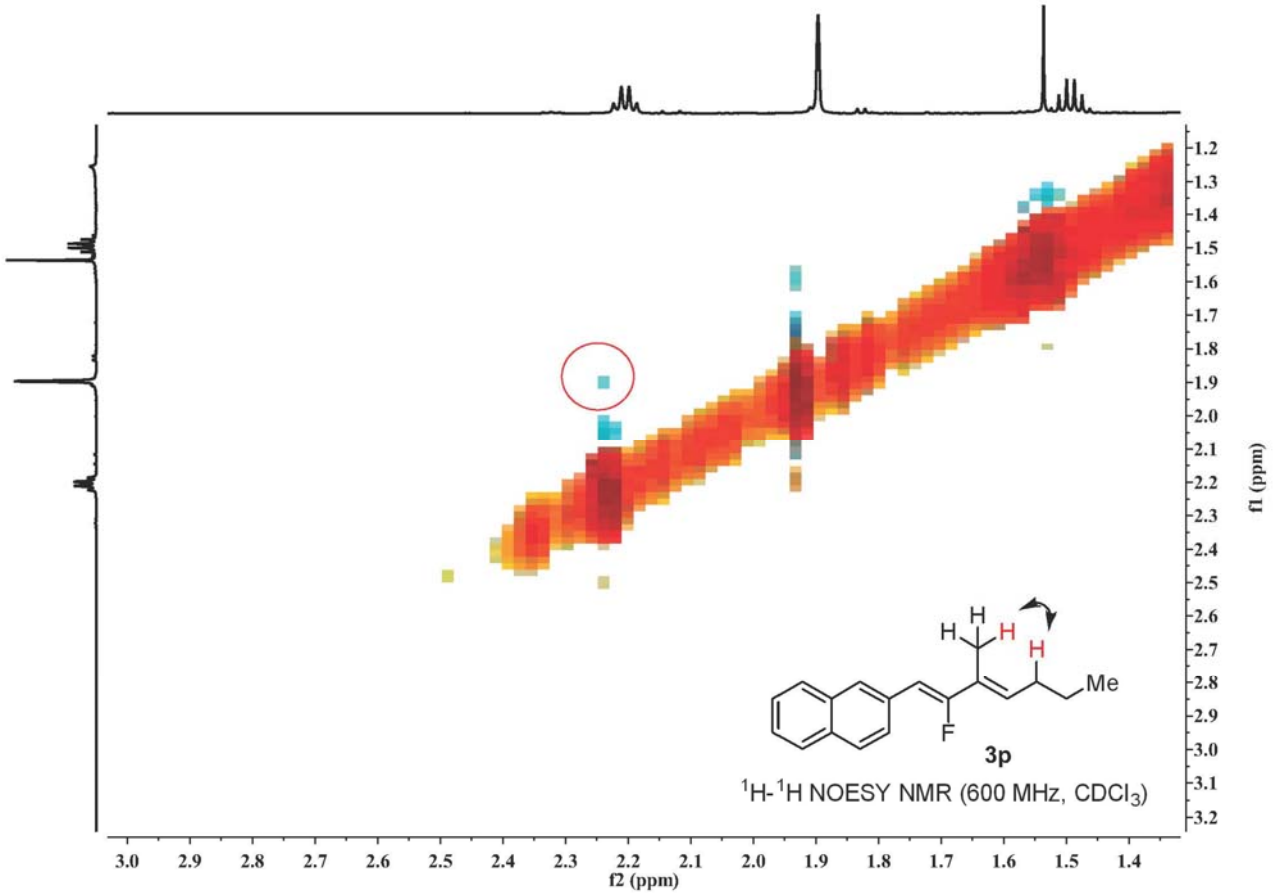




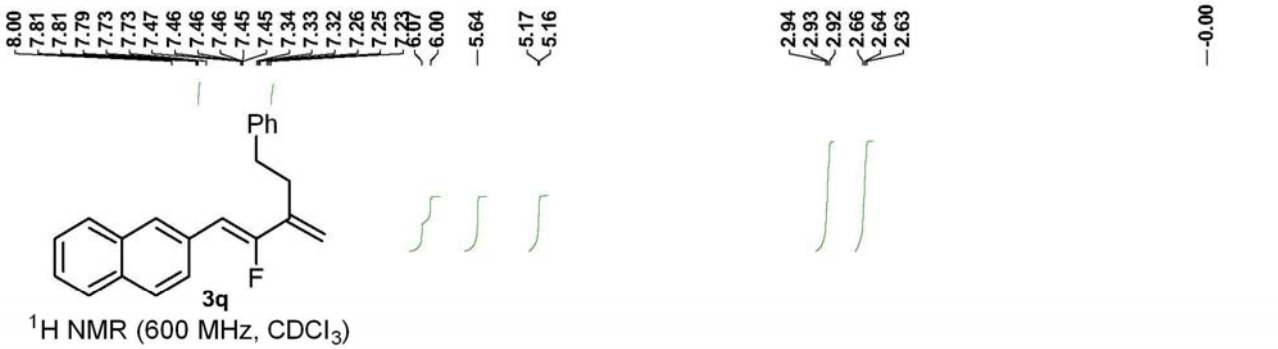
^{13}C NMR (151 MHz, $CDCl_3$)



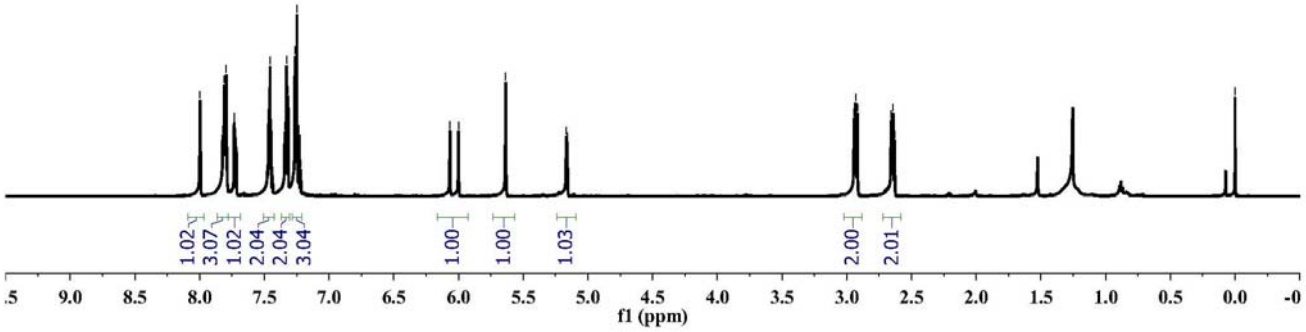
^{19}F NMR (565 MHz, $CDCl_3$)

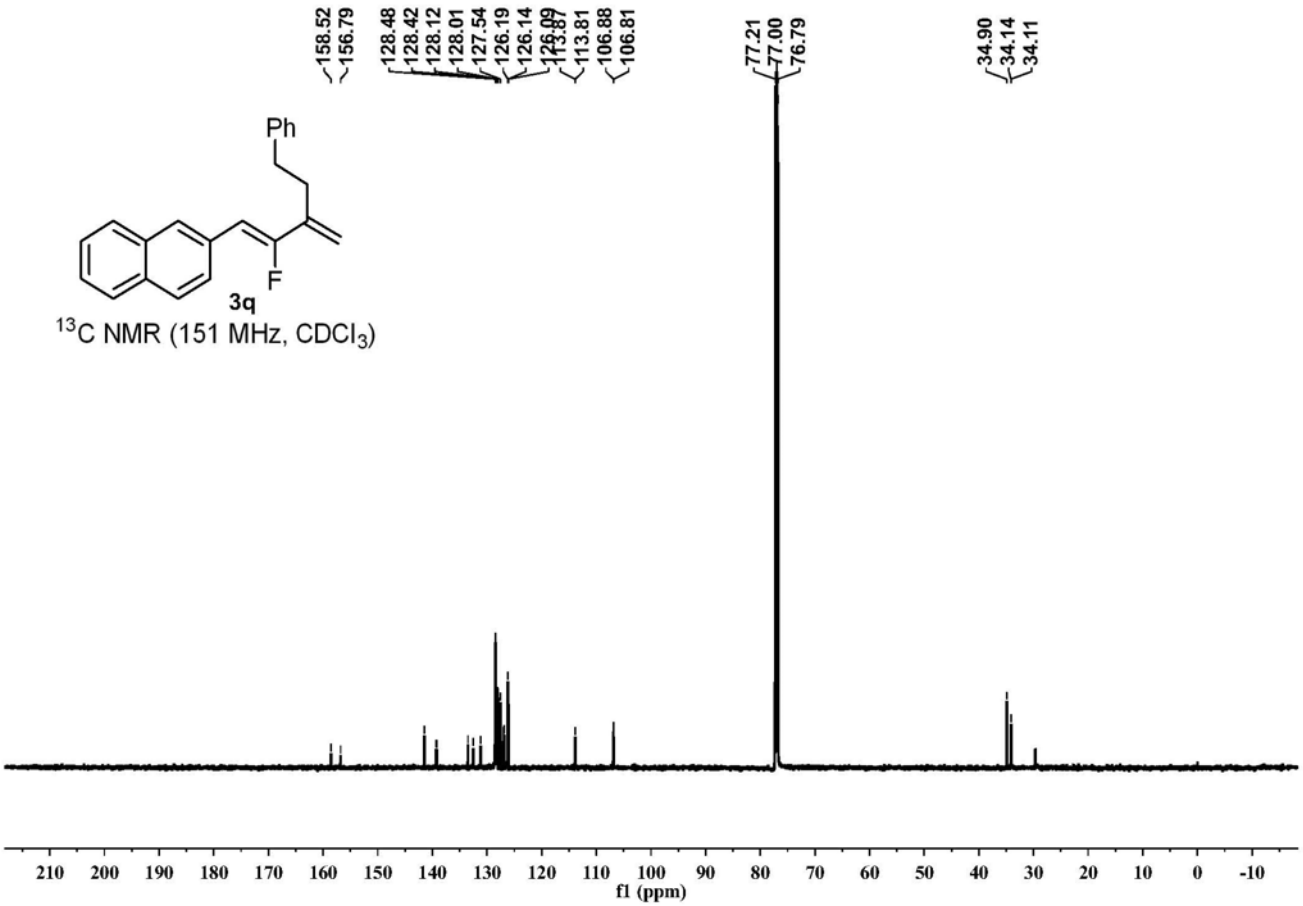


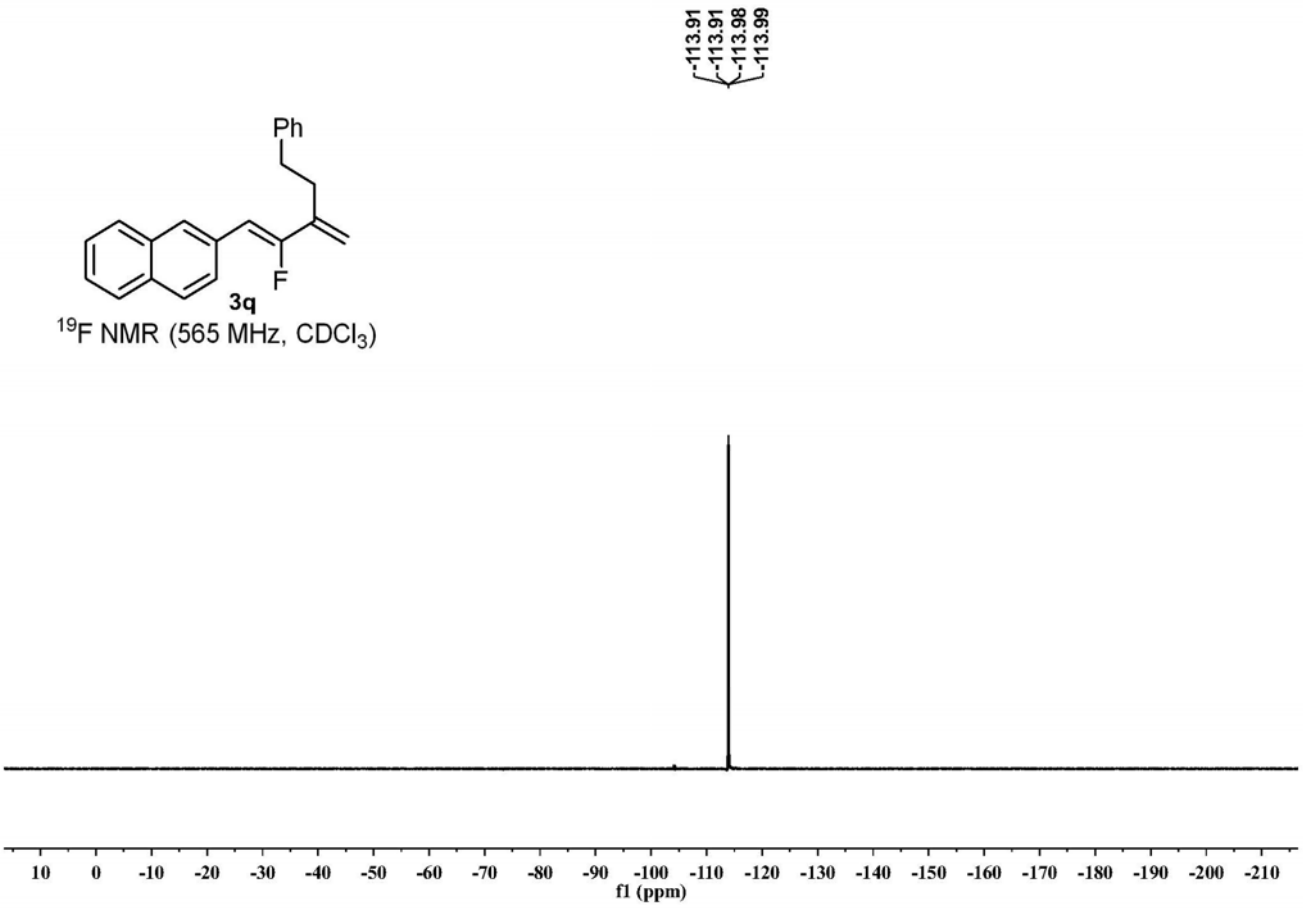
^{1}H-^{1}H NOESY NMR (600 MHz, $CDCl_3$)

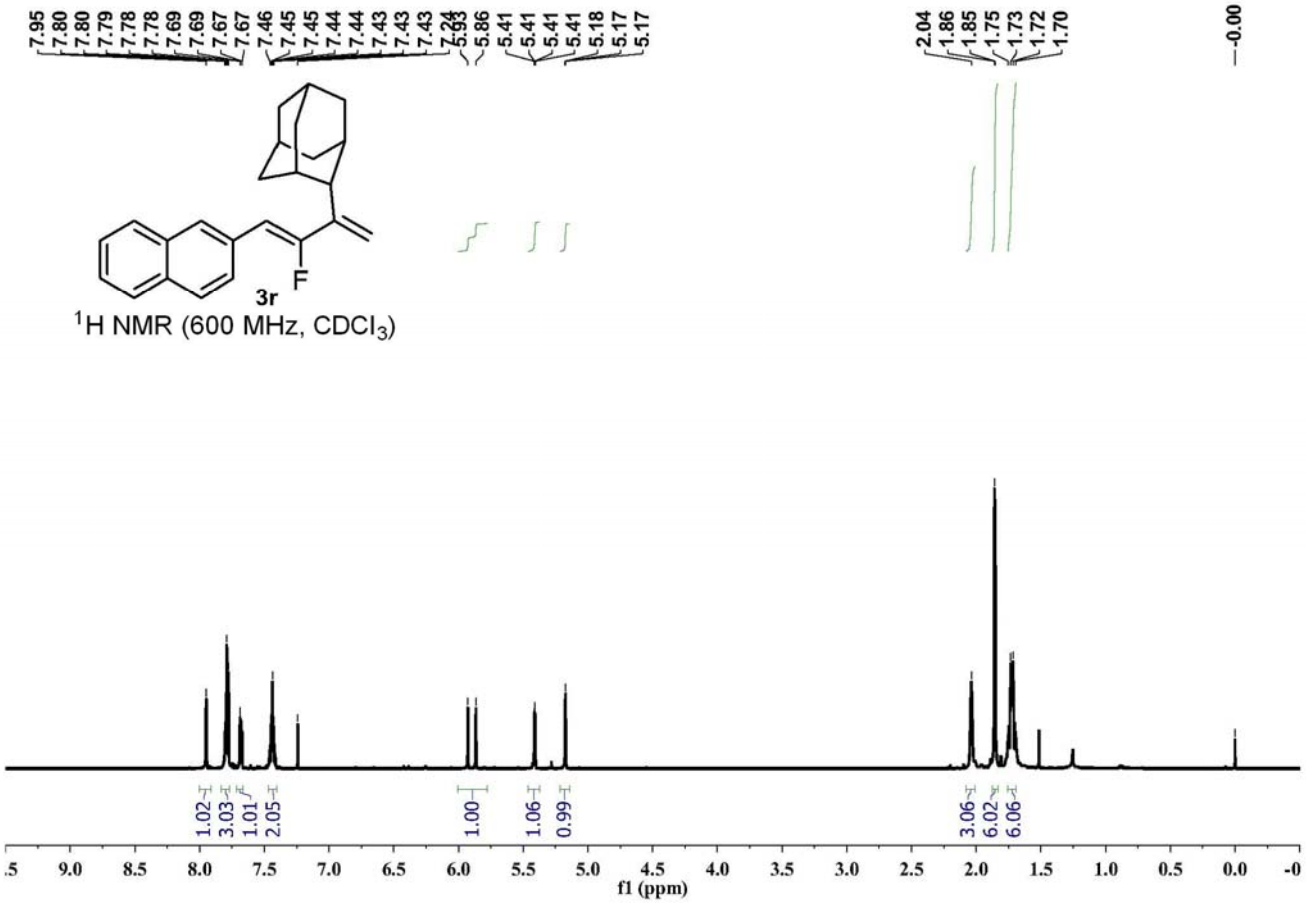


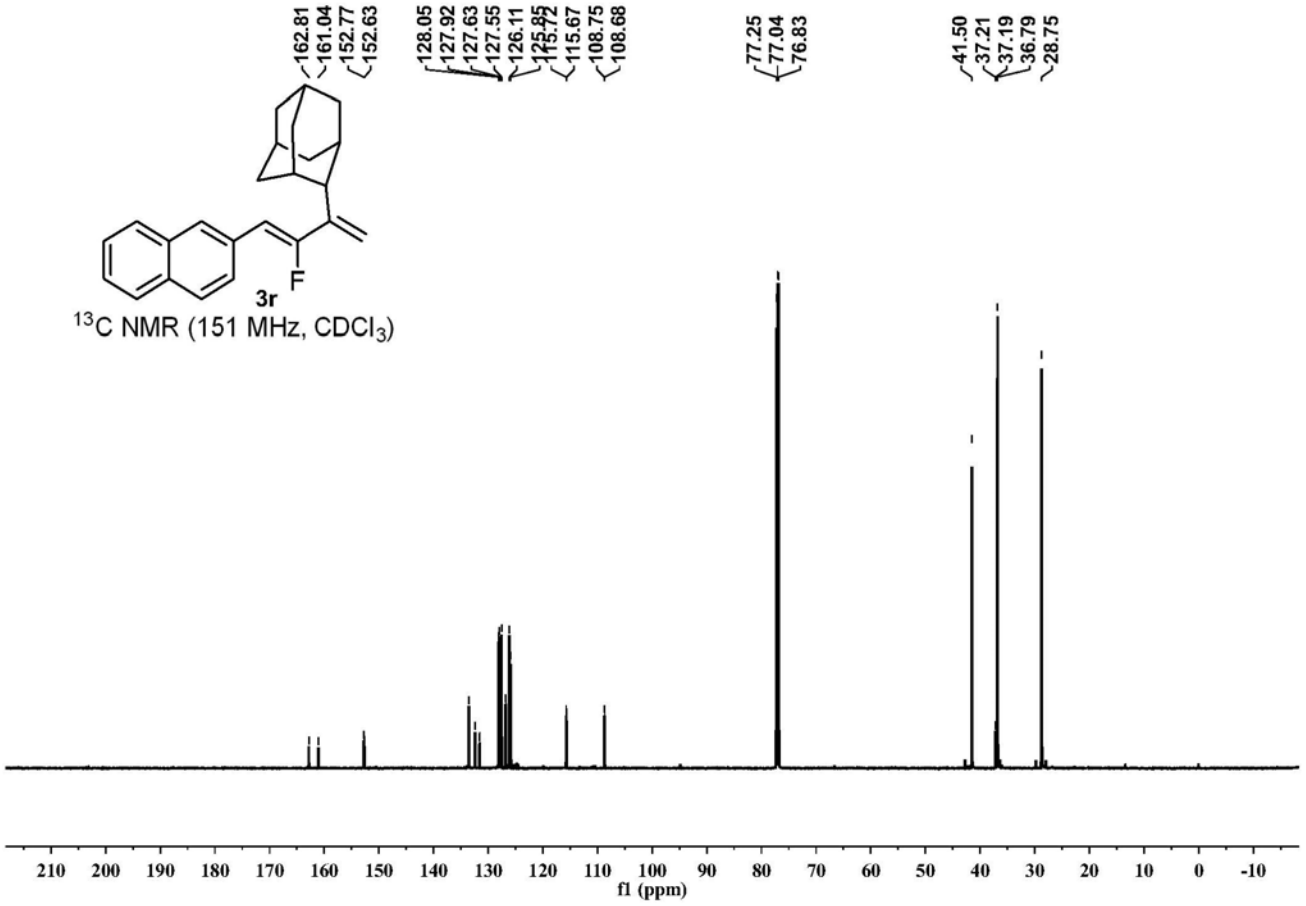
^{1}H NMR (600 MHz, $CDCl_3$)

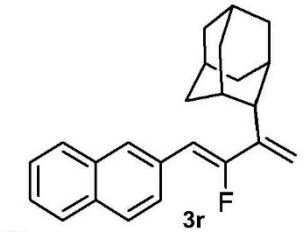



158.52
156.79
128.48
128.42
128.12
128.01
127.54
126.19
126.14
113.81
106.88
106.81
77.21
77.00
76.79
34.90
34.14
34.11
Ph
F
3q
^{13}C NMR (151 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-113.91
-113.91
-113.98
-113.99
Ph
F
3q
^{19}F NMR (565 MHz, CDCl$_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

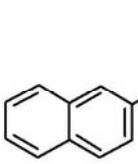

7.95
7.80
7.80
7.79
7.78
7.78
7.69
7.69
7.67
7.67
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.43
5.86
5.41
5.41
5.41
5.41
5.18
5.17
5.17
2.04
1.86
1.85
1.75
1.73
1.72
1.70
-0.00
F
3r
1H NMR (600 MHz, CDCl3)
1.02
3.03
1.01
2.05
1.00
1.06
0.99
3.06
6.02
6.06
f1 (ppm)


162.81
161.04
152.77
152.63
128.05
127.92
127.63
127.55
126.11
115.67
108.75
108.68
77.25
77.04
76.83
41.50
37.21
37.19
36.79
28.75
F
3r
13C NMR (151 MHz, CDCl3)
f1 (ppm)



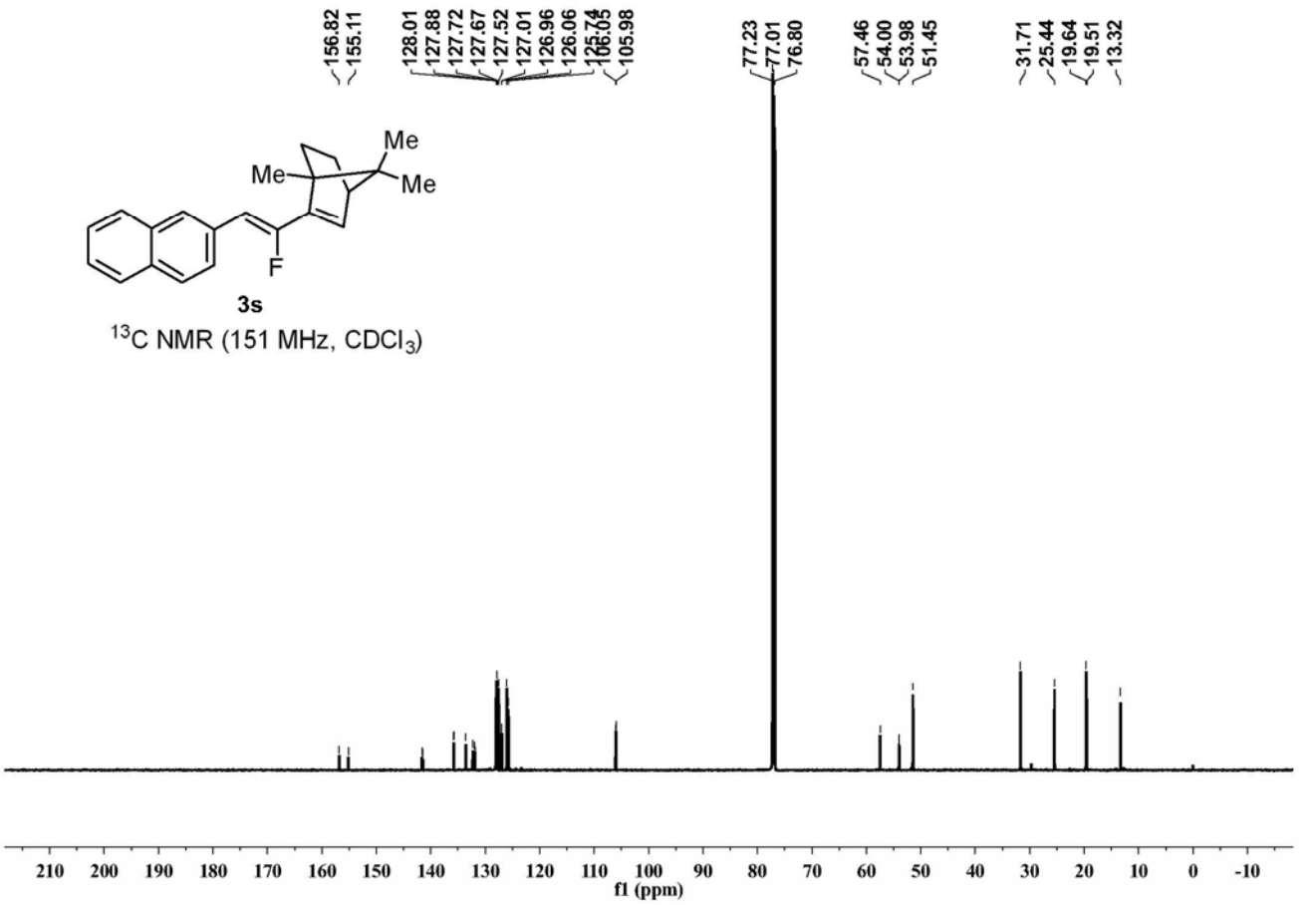
3r

^{19}F NMR (565 MHz, $CDCl_3$)



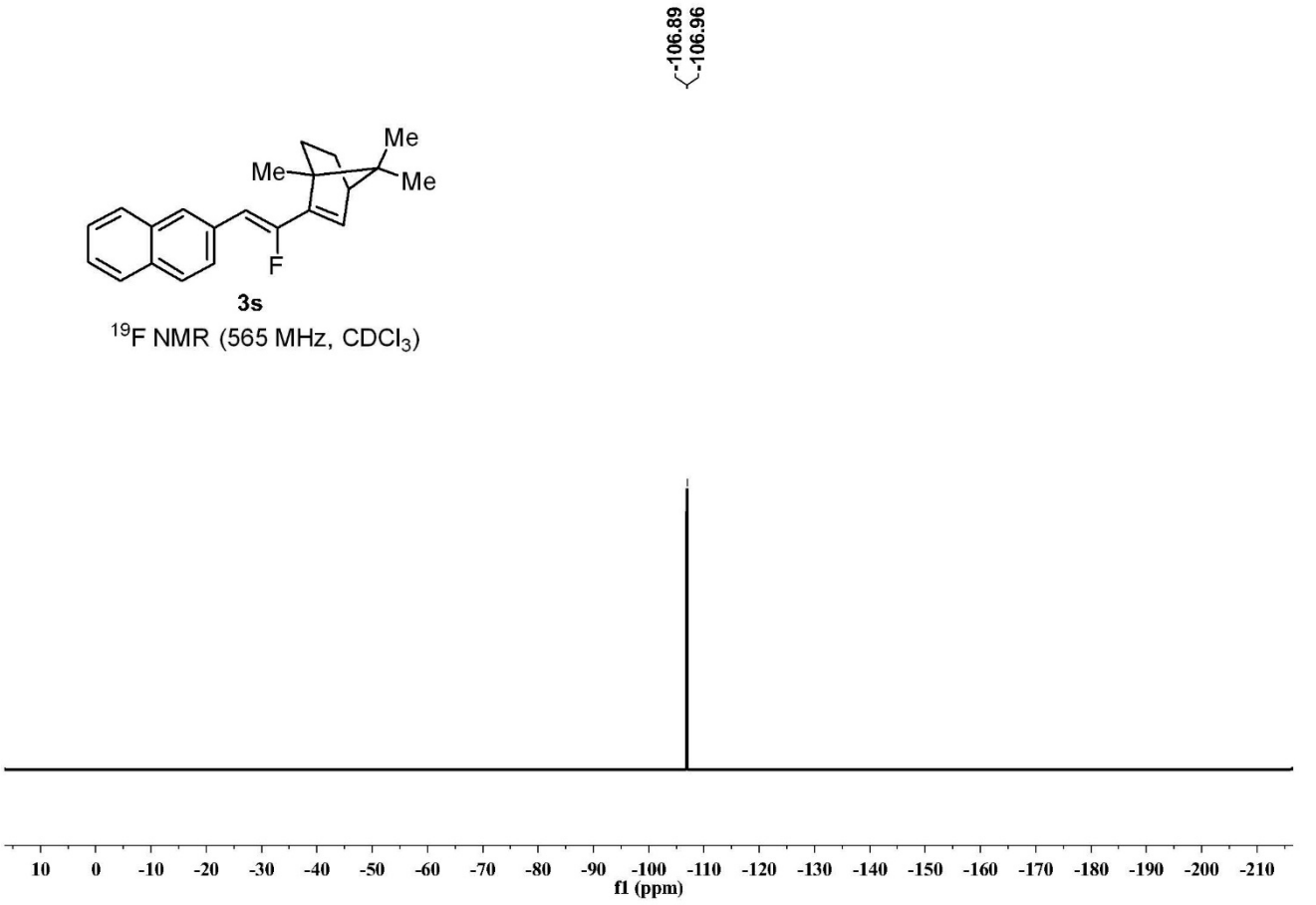
3s

^{1}H NMR (600 MHz, $CDCl_3$)



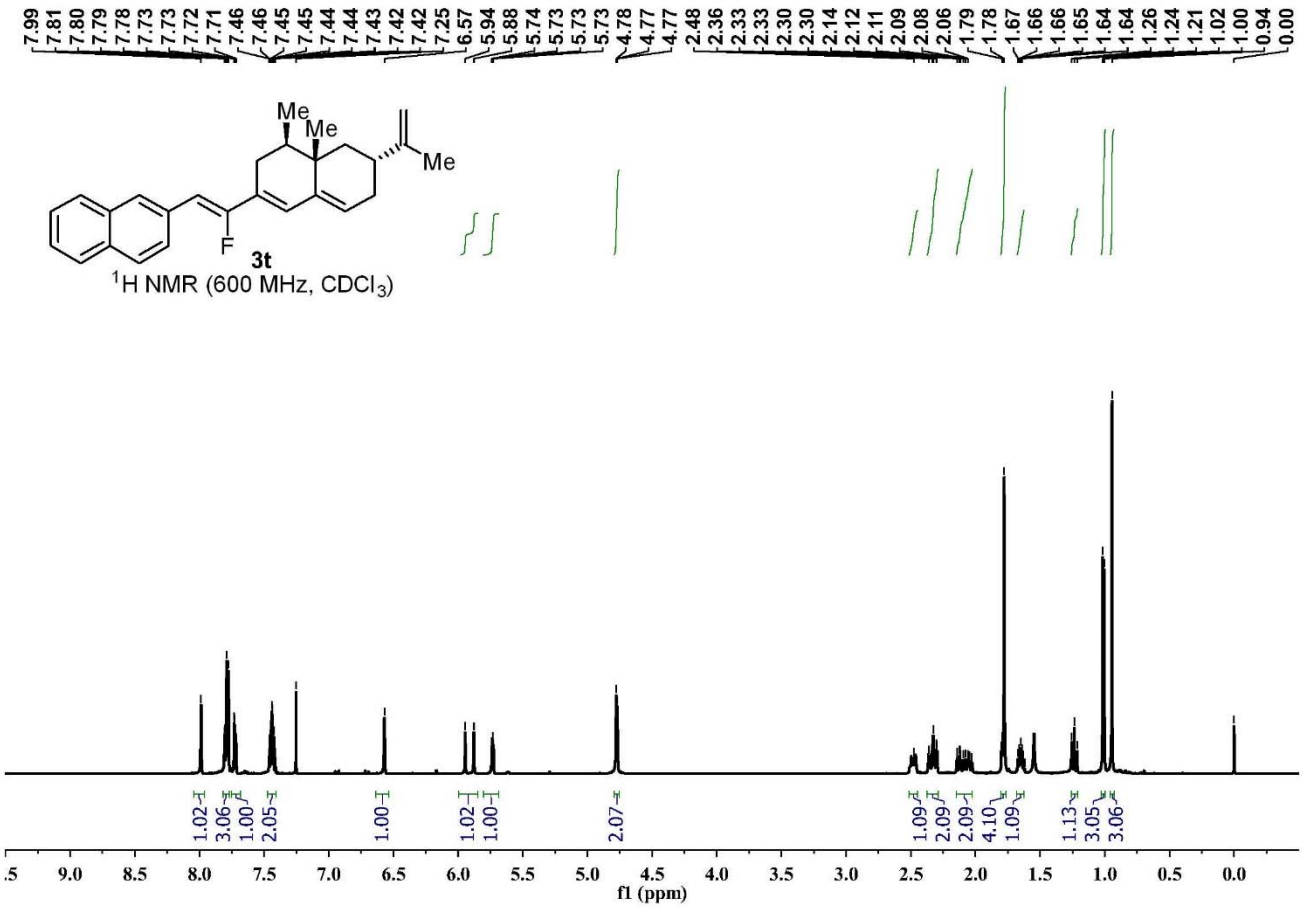
3s

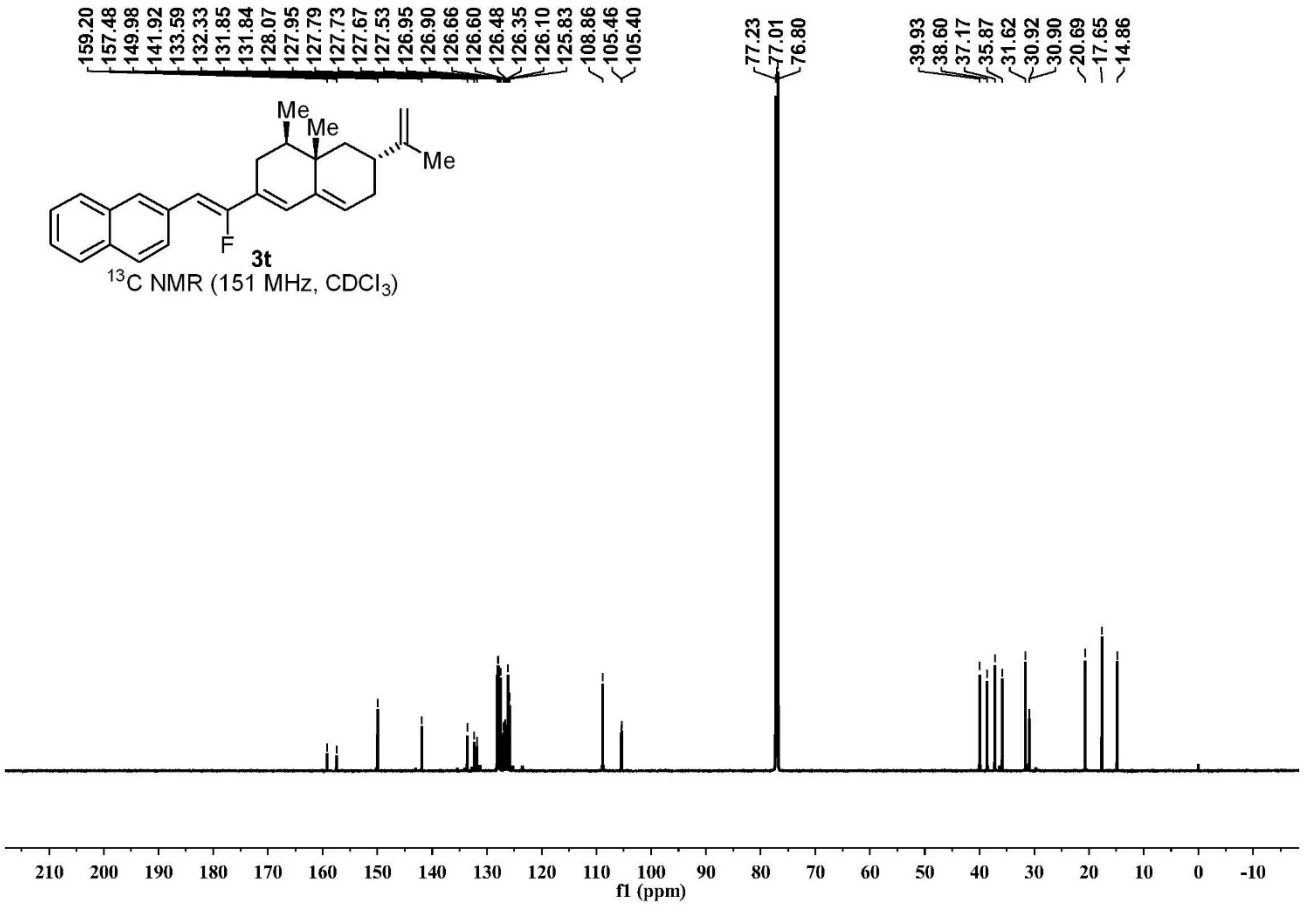
^{13}C NMR (151 MHz, $CDCl_3$)

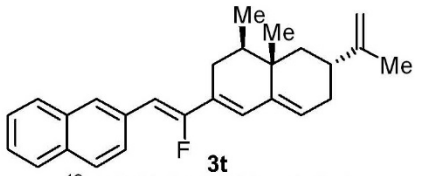


3s

^{19}F NMR (565 MHz, $CDCl_3$)

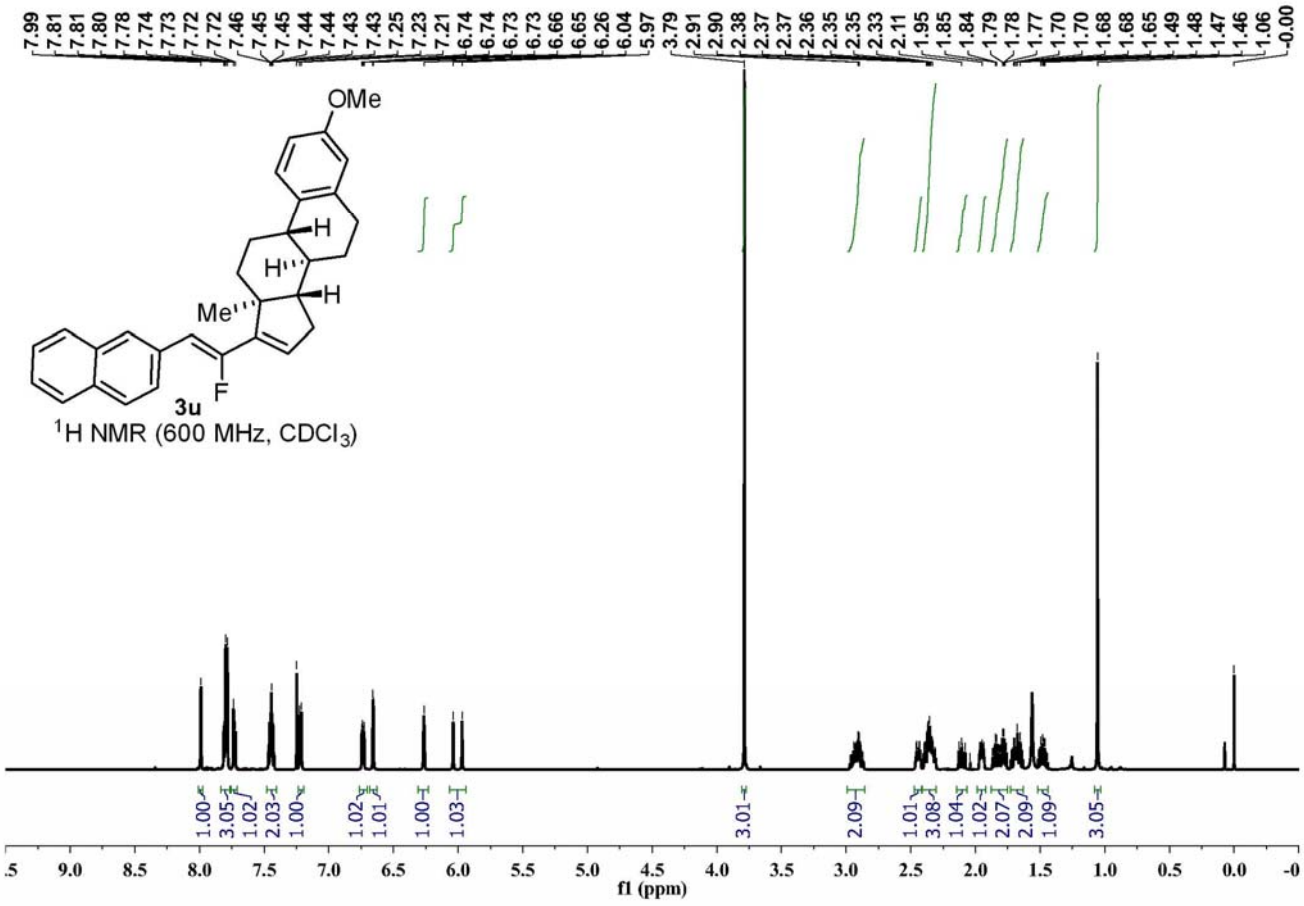

Me
Me
Me
F
3t
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


Me
Me
Me
F
3t
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)



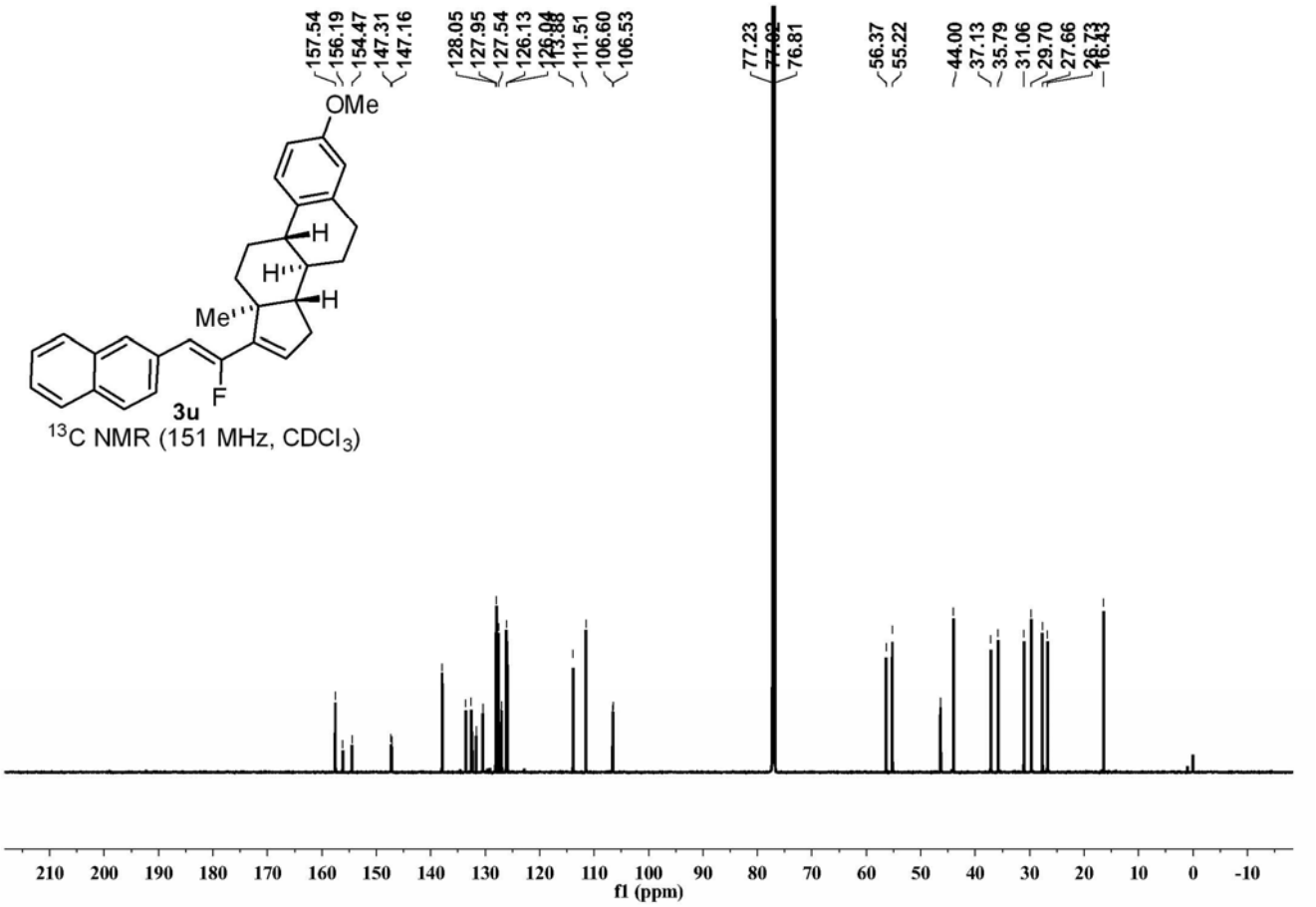
3t

^{19}F NMR (565 MHz, $CDCl_3$)

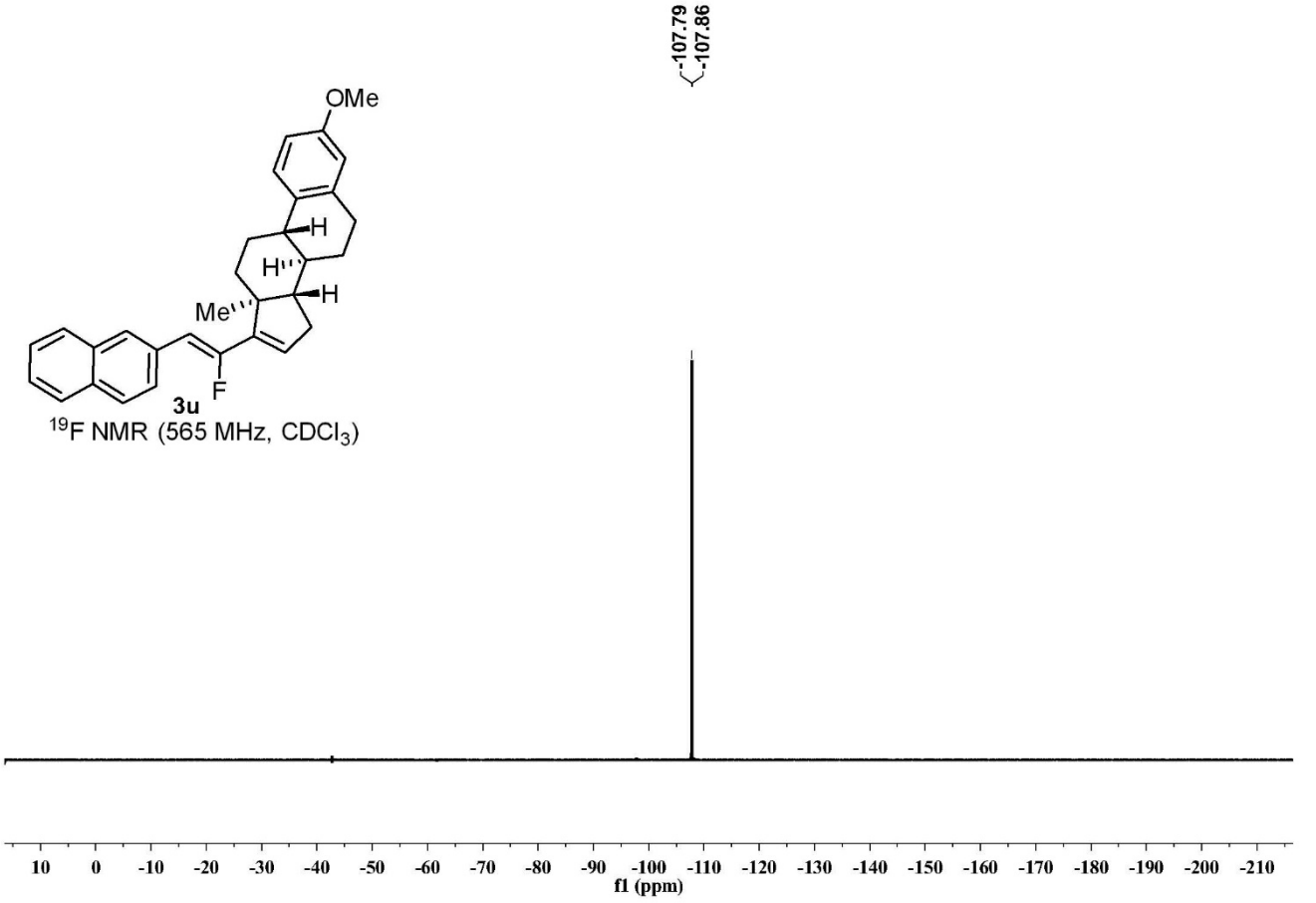


3u

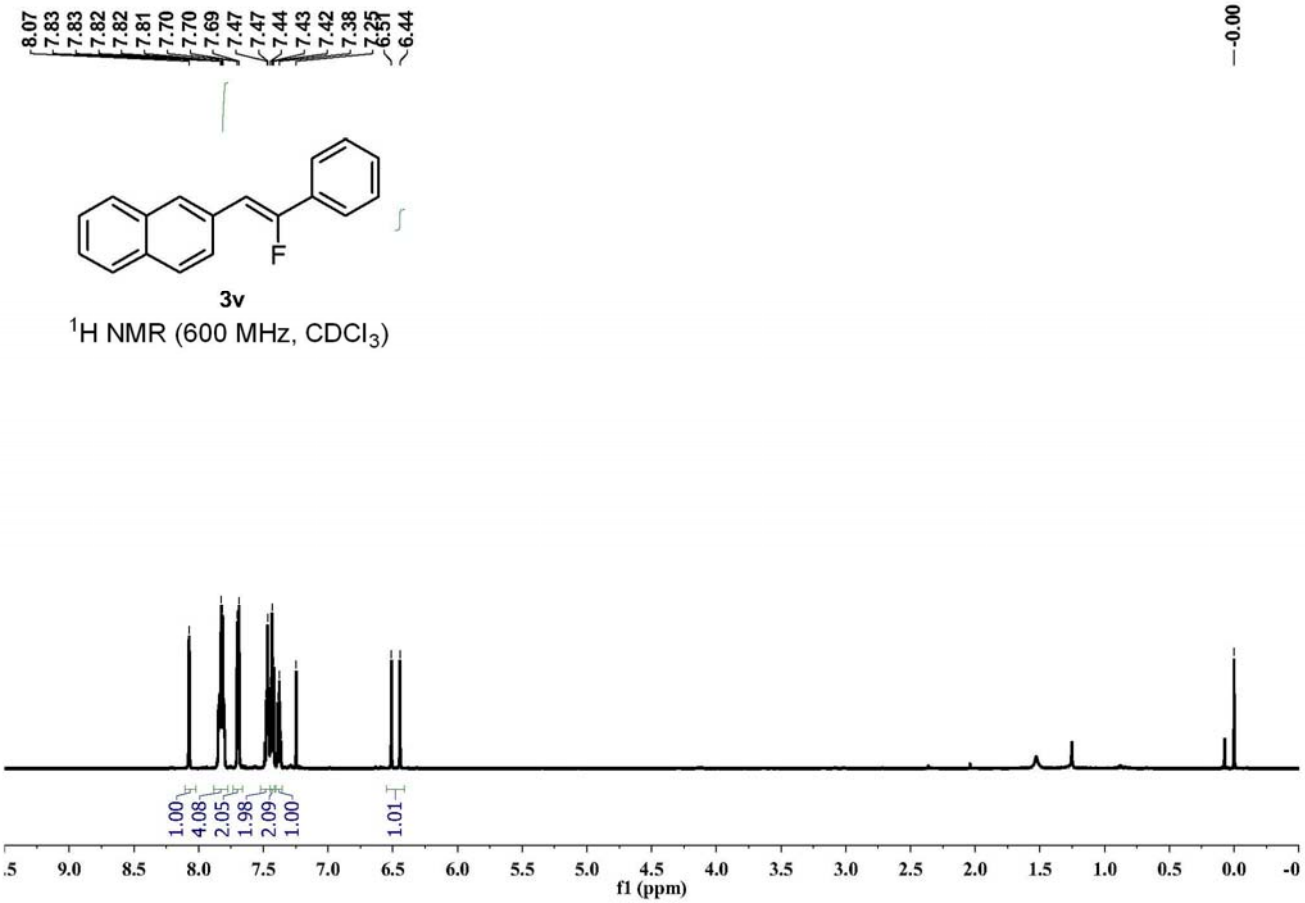
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

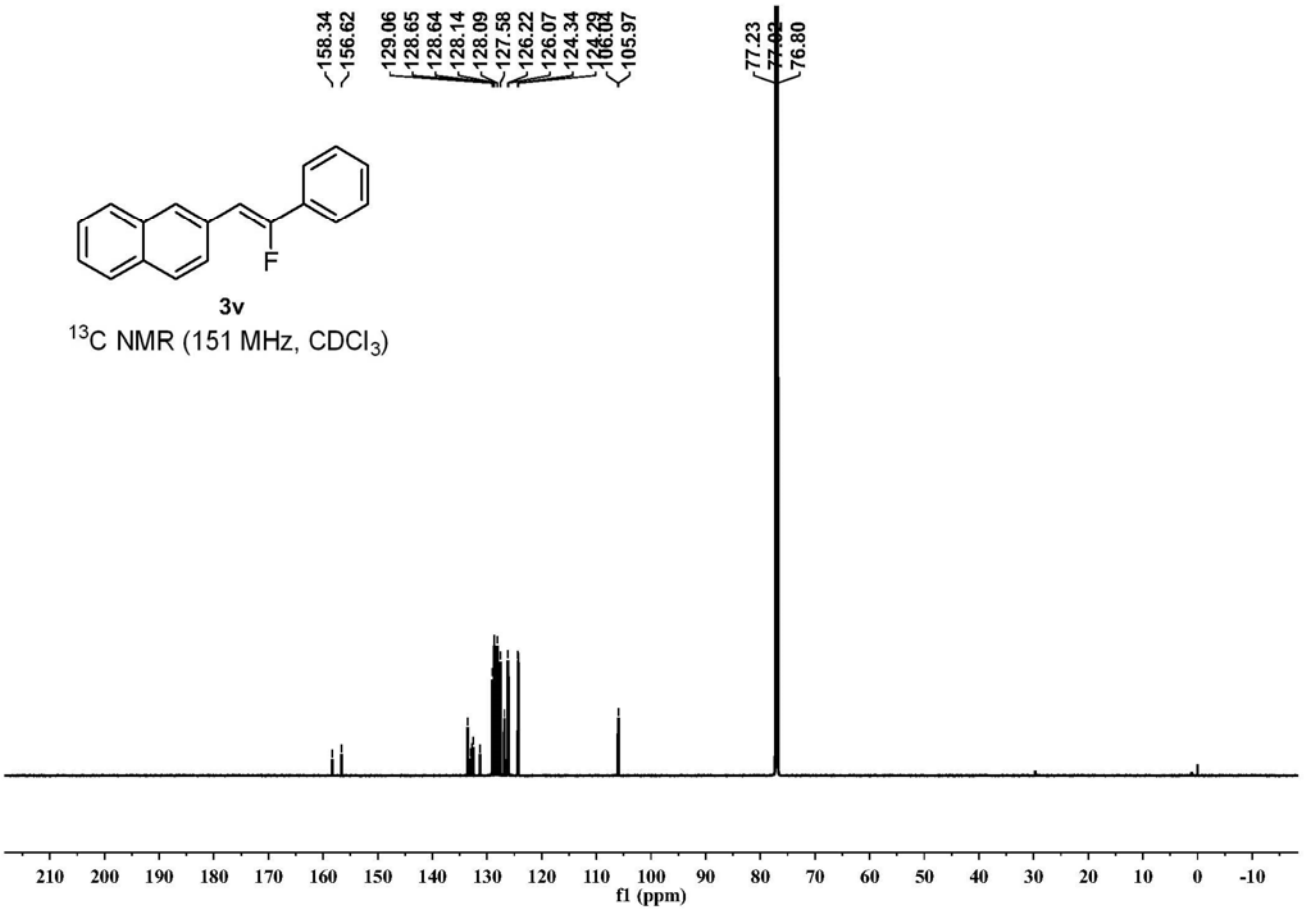


^{19}F NMR (565 MHz, $CDCl_3$)



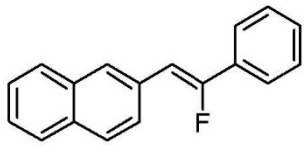
3v

^{1}H NMR (600 MHz, $CDCl_3$)



3v

^{13}C NMR (151 MHz, $CDCl_3$)

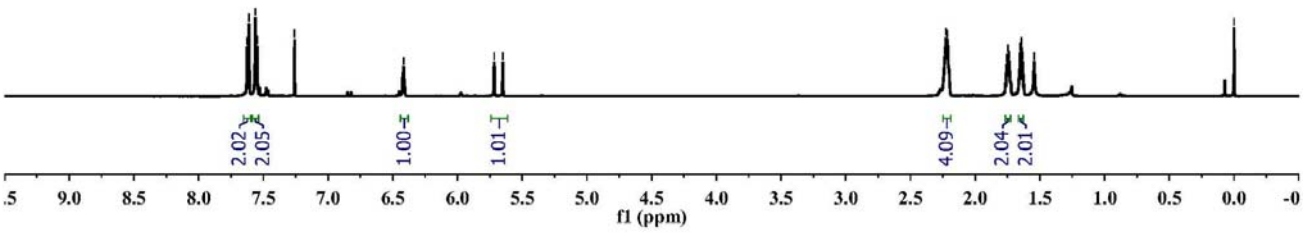


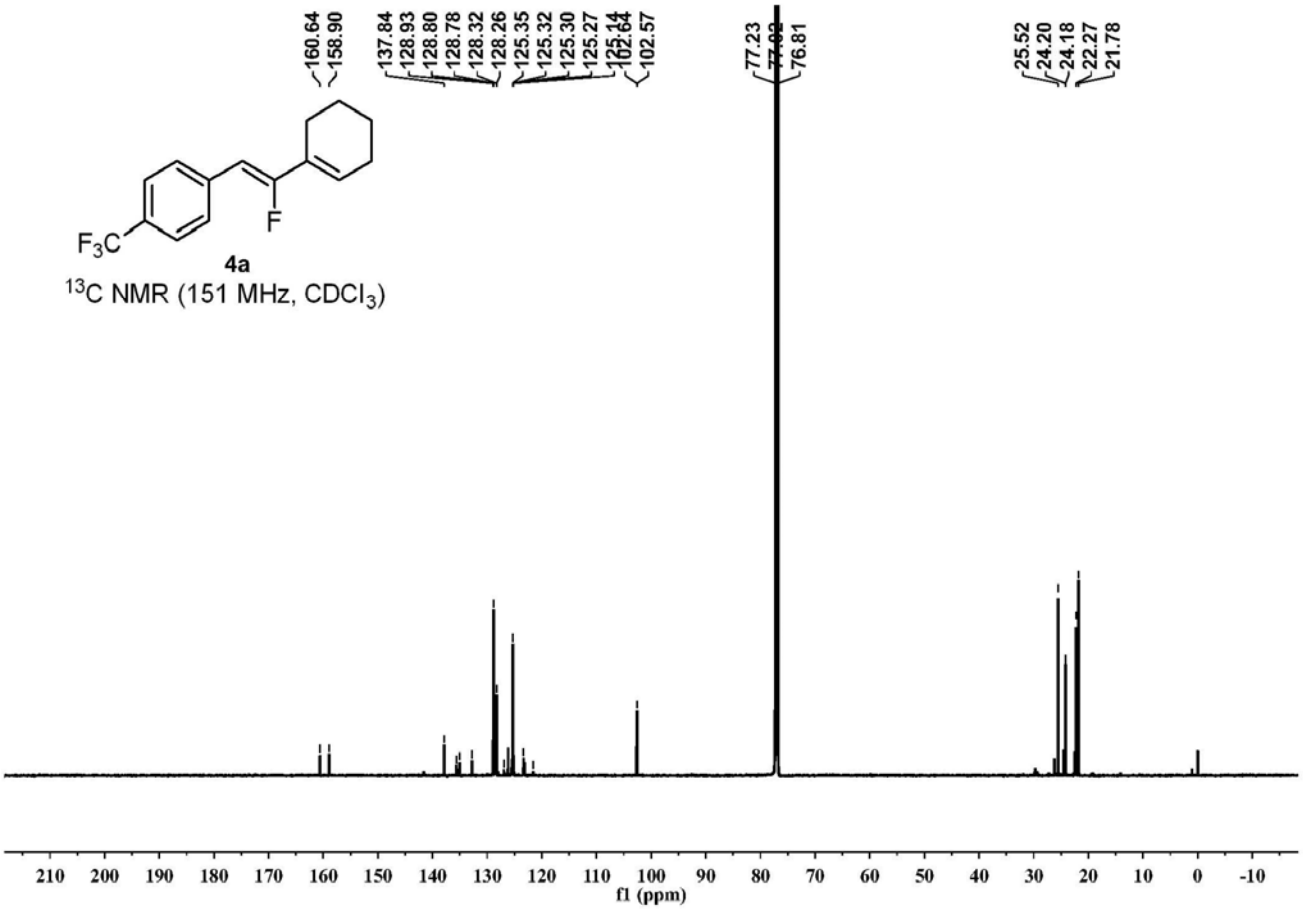
3v

^{19}F NMR (565 MHz, $CDCl_3$)

4a

^{1}H NMR (600 MHz, $CDCl_3$)

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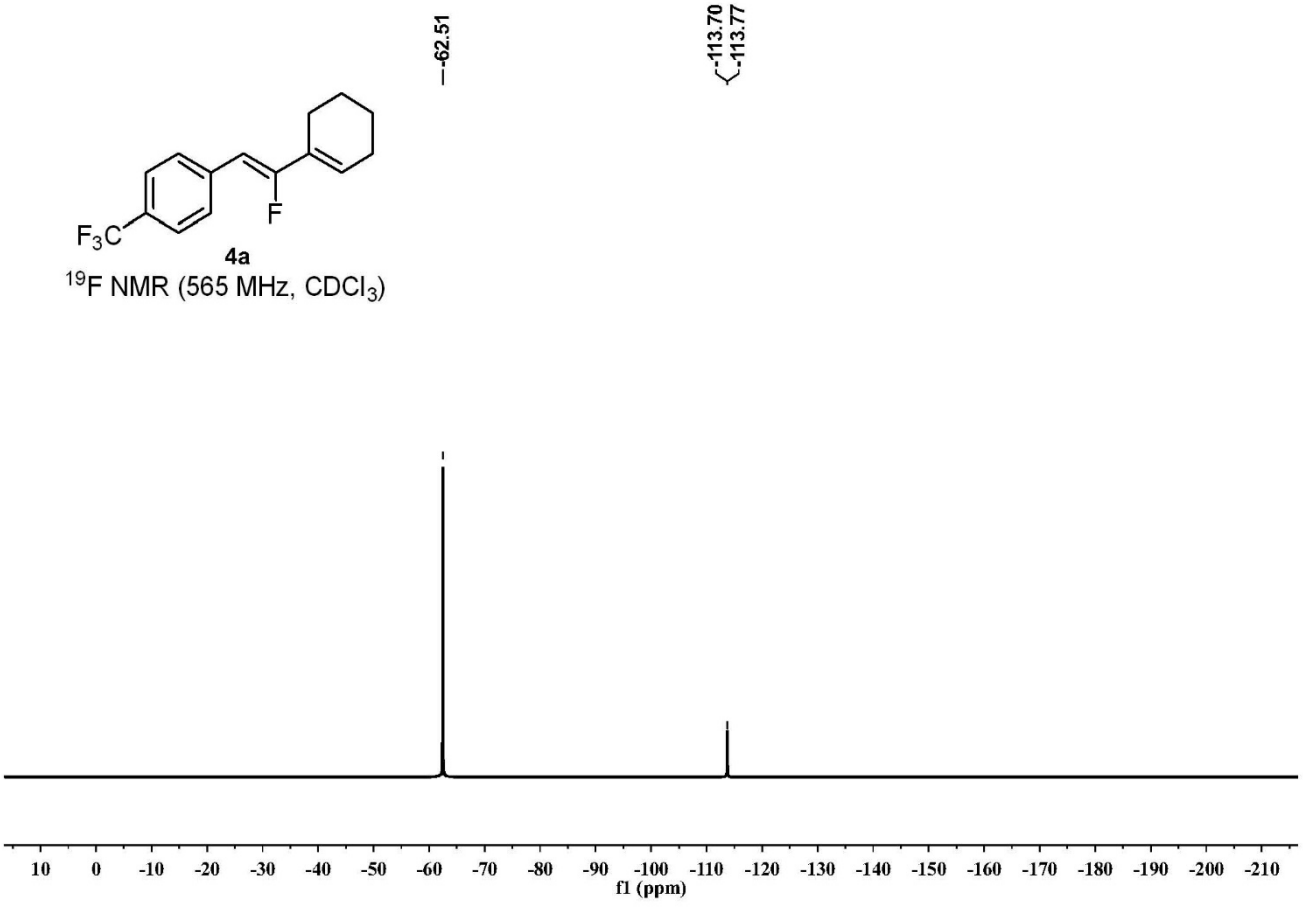
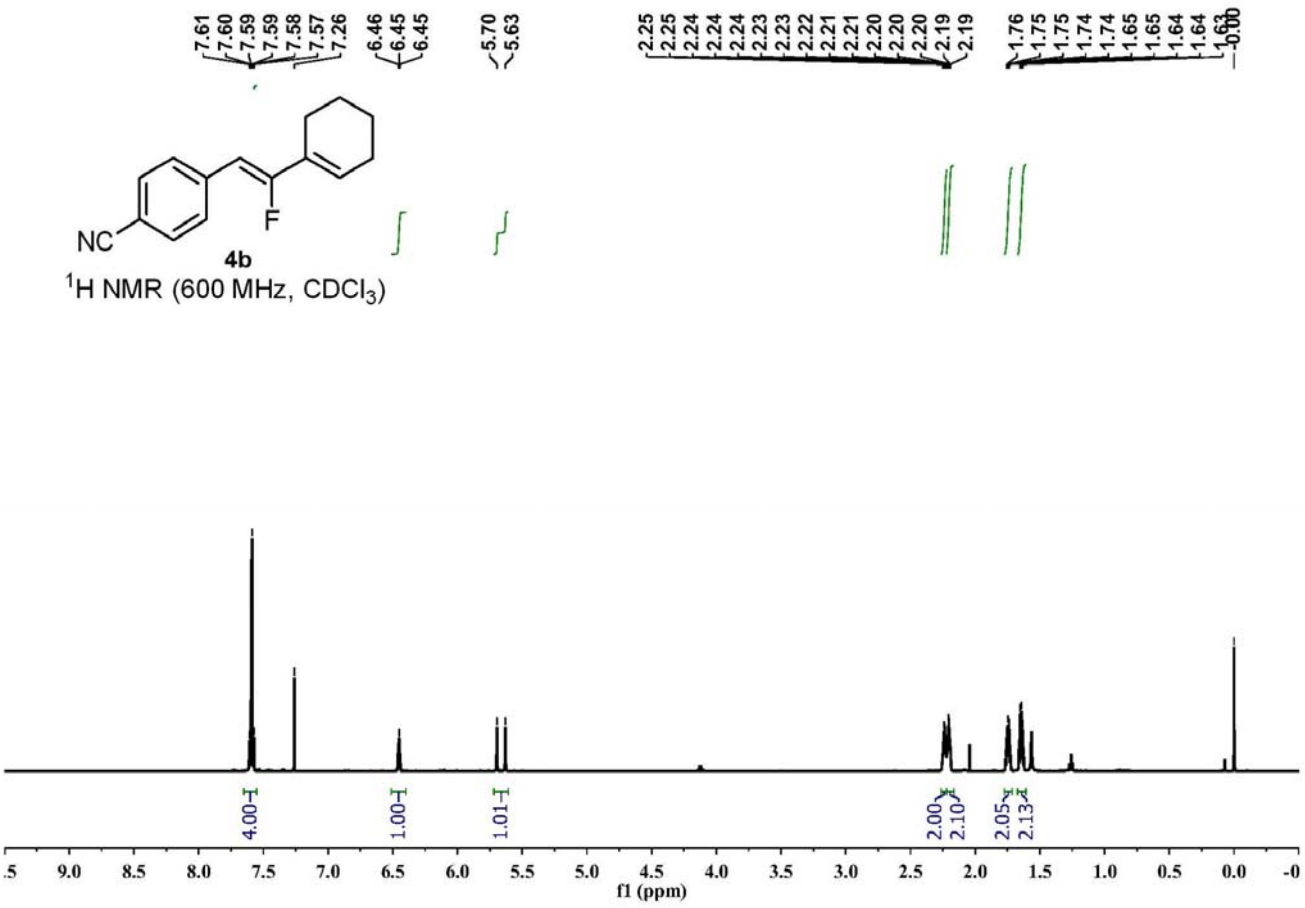
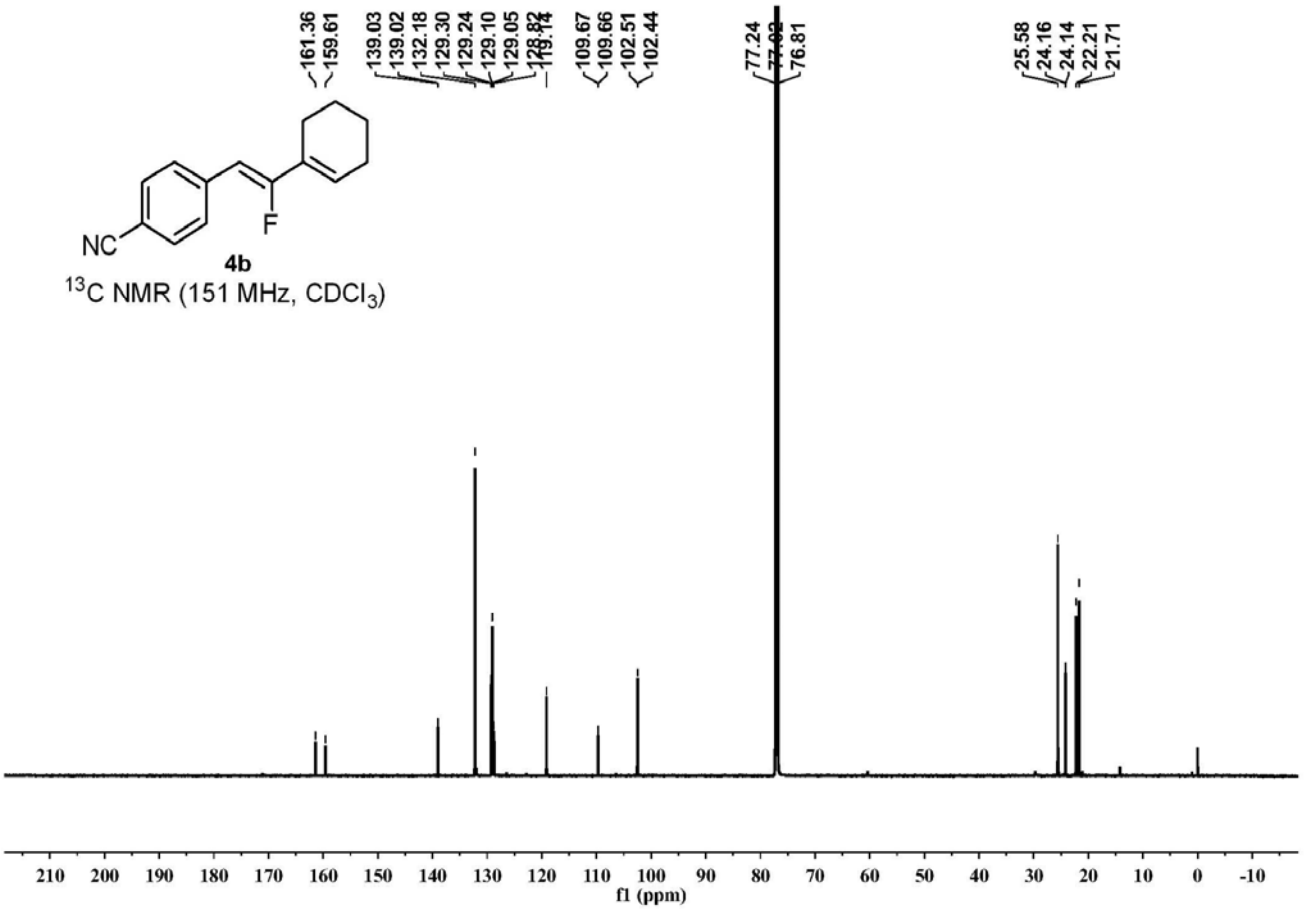
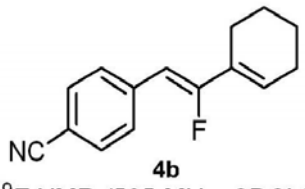
158.90
137.84
128.93
128.80
128.78
128.32
128.26
125.35
125.32
125.30
125.27
125.14
102.64
102.57
77.23
77.00
76.81
25.52
24.20
24.18
22.27
21.78
F3C
F
4a
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.51
-113.70
-113.77
F3C
F
4a
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

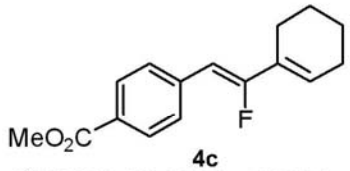

7.61
7.60
7.59
7.59
7.58
7.57
7.26
6.46
6.45
6.45
5.70
5.63
2.25
2.25
2.24
2.24
2.24
2.23
2.23
2.22
2.21
2.21
2.20
2.20
2.20
2.19
2.19
1.76
1.75
1.75
1.74
1.74
1.65
1.65
1.64
1.64
1.63
0.00
NC
F
4b
1H NMR (600 MHz, CDCl3)
4.00
1.00
1.01
2.00
2.10
2.05
2.13
f1 (ppm)


161.36
159.61
139.03
139.02
132.18
129.30
129.24
129.10
129.05
109.67
109.66
102.51
102.44
77.24
76.81
25.58
24.16
24.14
22.21
21.71
NC
F
4b
13C NMR (151 MHz, CDCl3)
f1 (ppm)



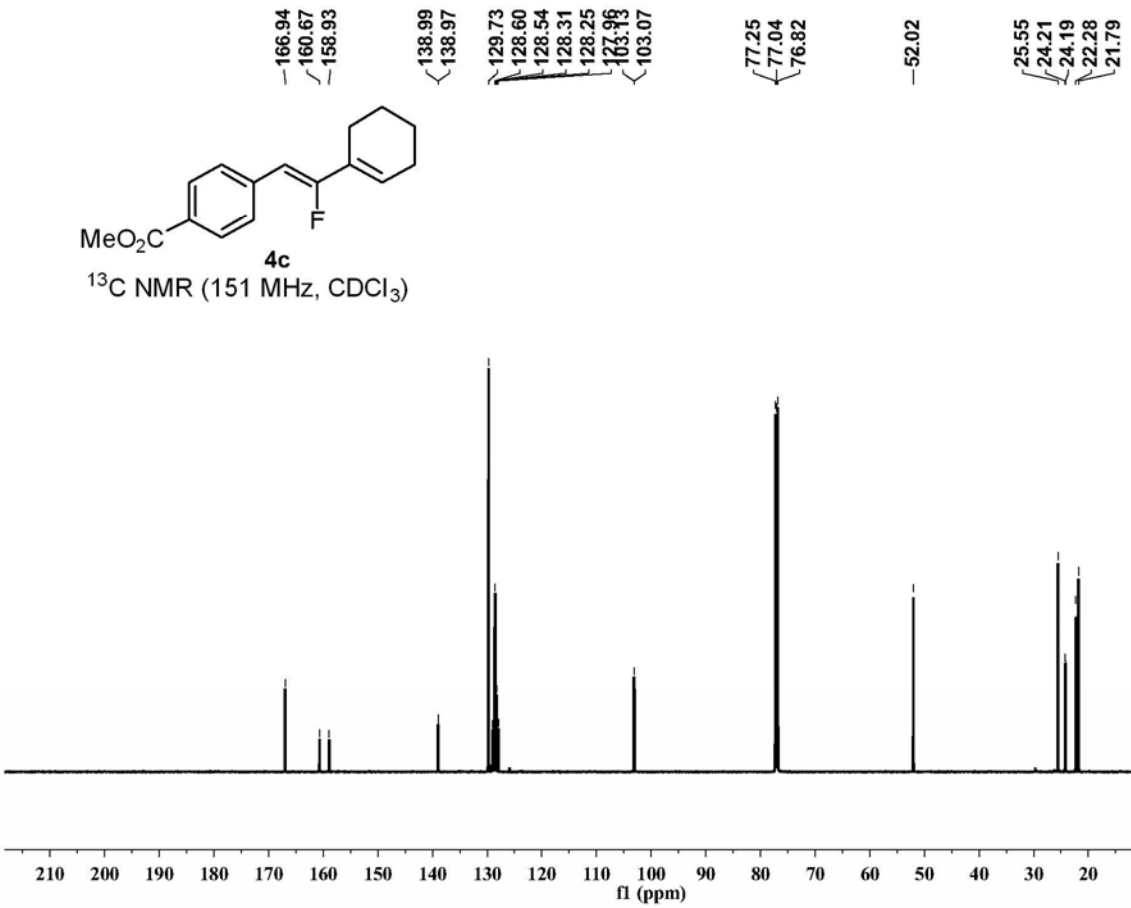
4b

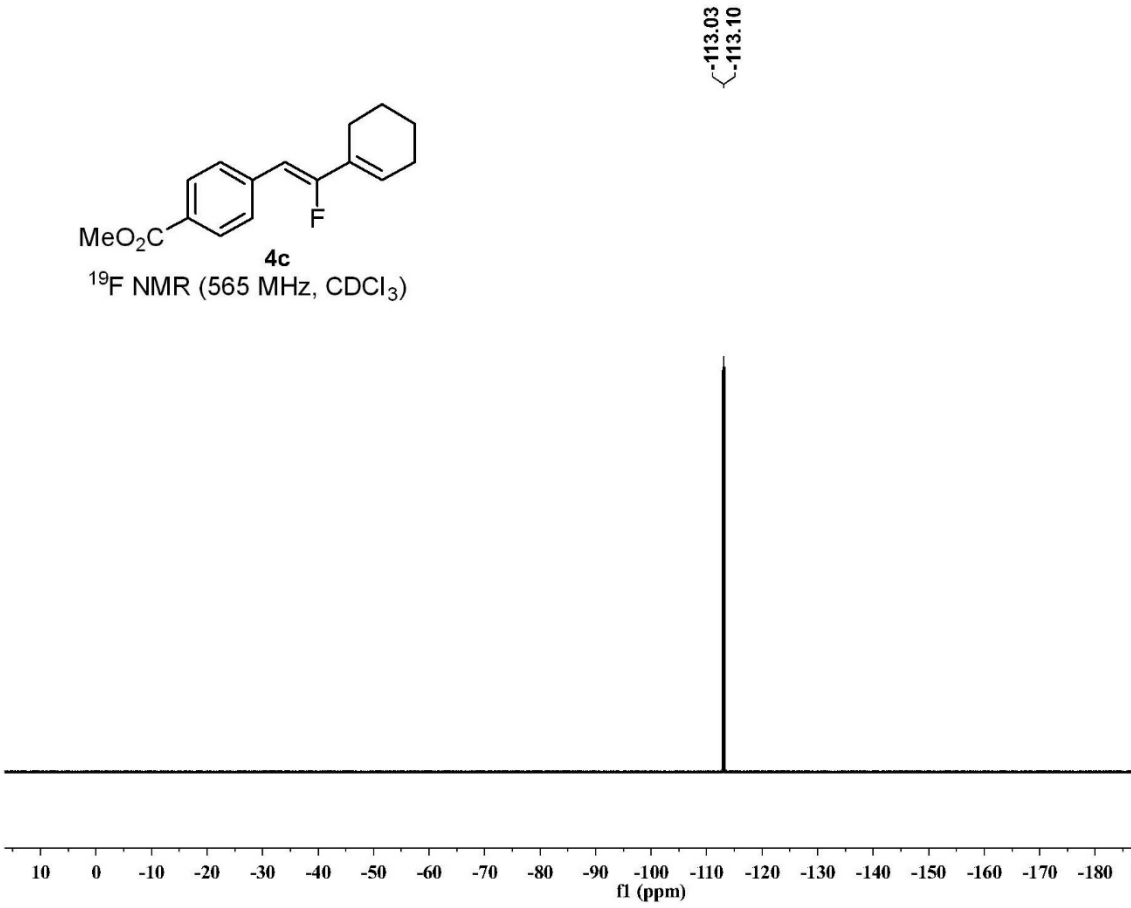
^{19}F NMR (565 MHz, $CDCl_3$)

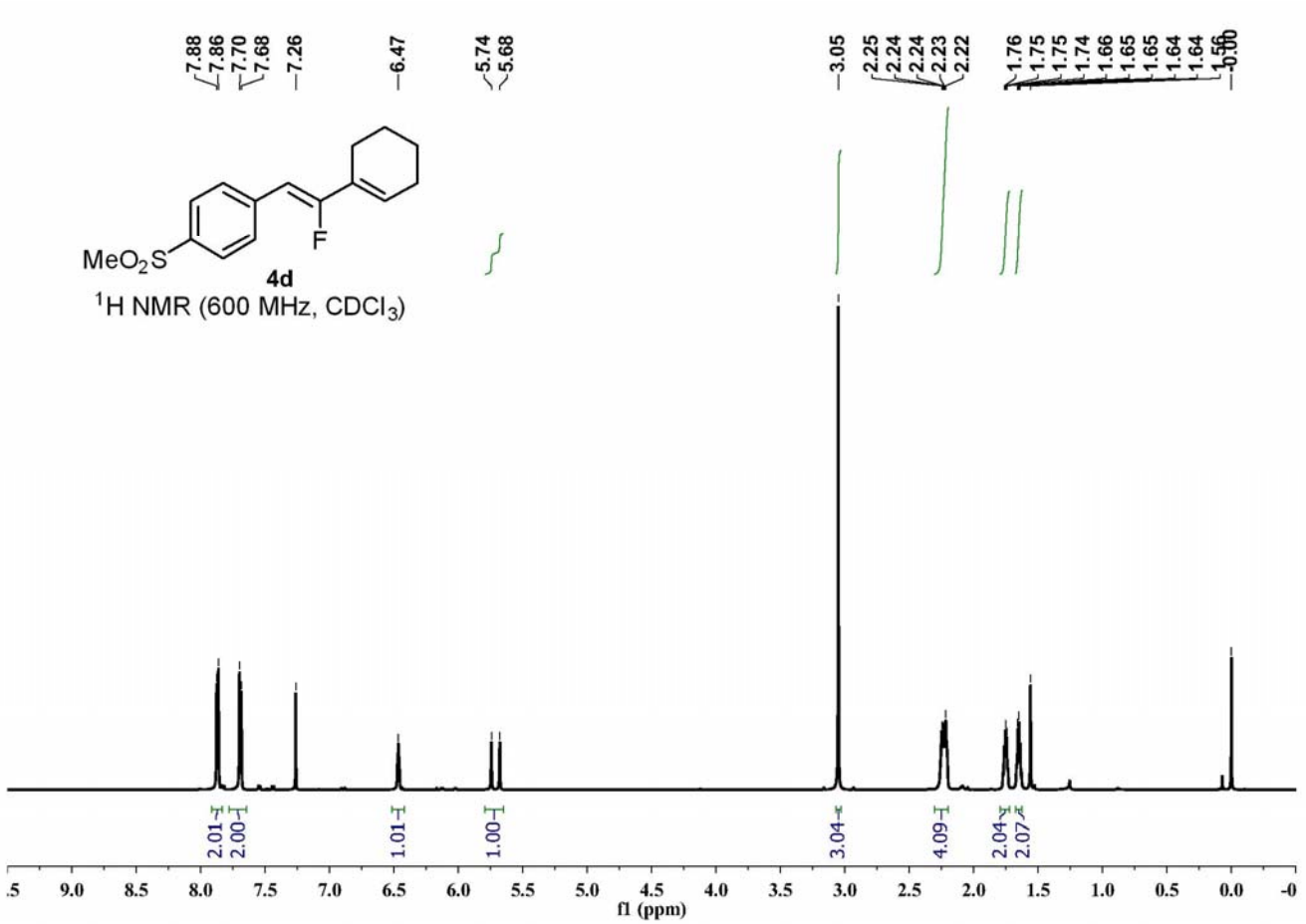


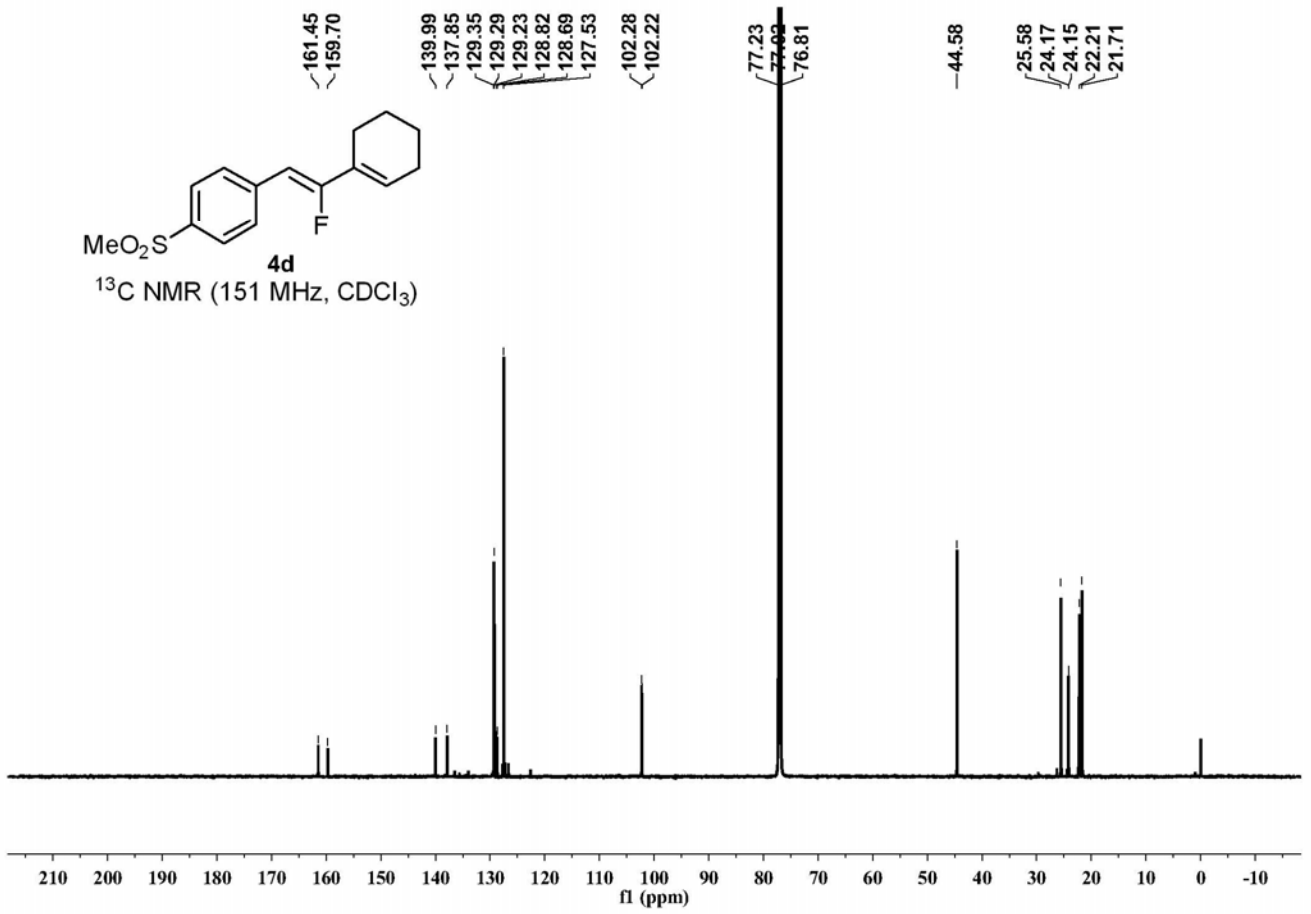
4c

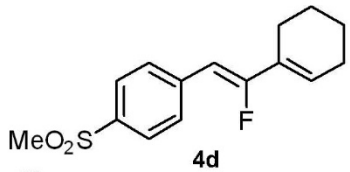
^{1}H NMR (600 MHz, $CDCl_3$)


166.94
160.67
158.93
138.99
138.97
129.73
128.60
128.54
128.31
128.25
127.96
103.13
103.07
77.25
77.04
76.82
52.02
25.55
24.21
24.19
22.28
21.79
MeO2C
F
4c
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-113.03
-113.10
MeO2C
F
4c
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

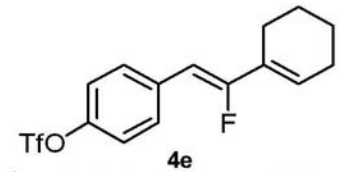

7.88
7.86
7.70
7.68
7.26
6.47
5.74
5.68
3.05
2.25
2.24
2.24
2.23
2.22
1.76
1.75
1.75
1.74
1.66
1.65
1.65
1.64
1.64
0.00
MeO2S
F
4d
1H NMR (600 MHz, CDCl3)
2.01
2.00
1.01
1.00
3.04
4.09
2.04
2.07
f1 (ppm)


161.45
159.70
139.99
137.85
129.35
129.29
129.23
128.82
128.69
127.53
102.28
102.22
77.23
77.03
76.81
44.58
25.58
24.17
24.15
22.21
21.71
MeO2S
F
4d
13C NMR (151 MHz, CDCl3)
f1 (ppm)



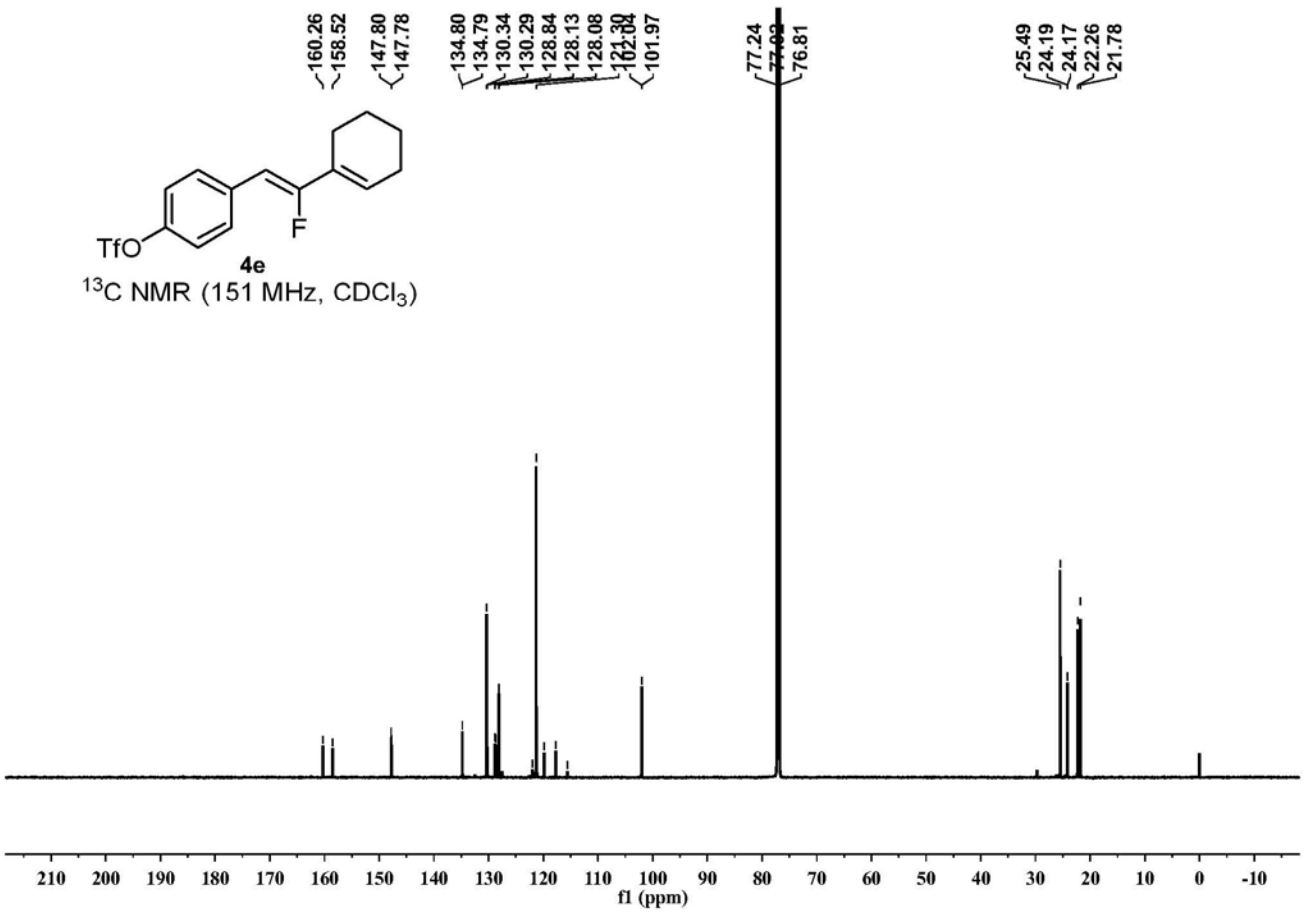
4d

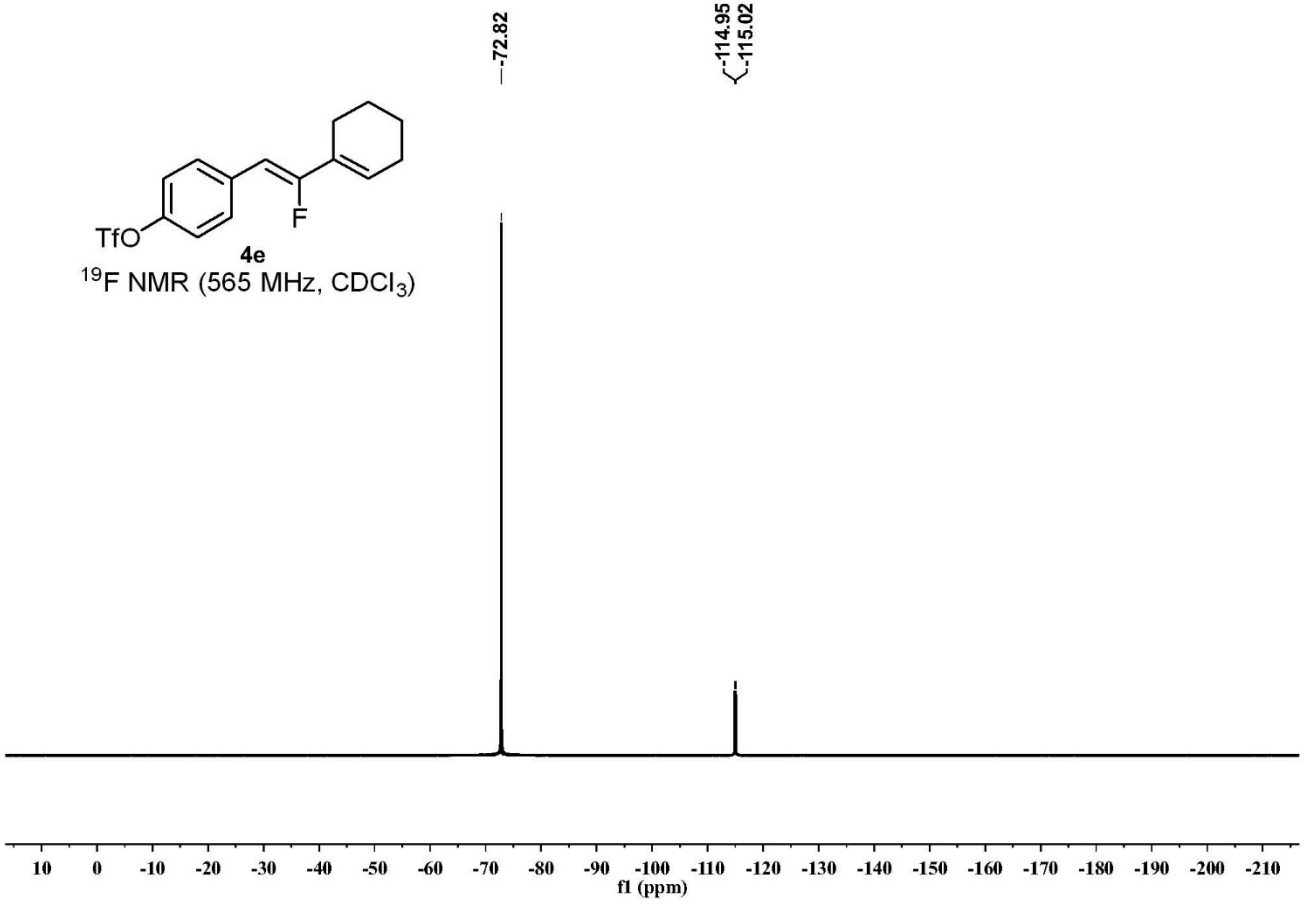
^{19}F NMR (565 MHz, $CDCl_3$)

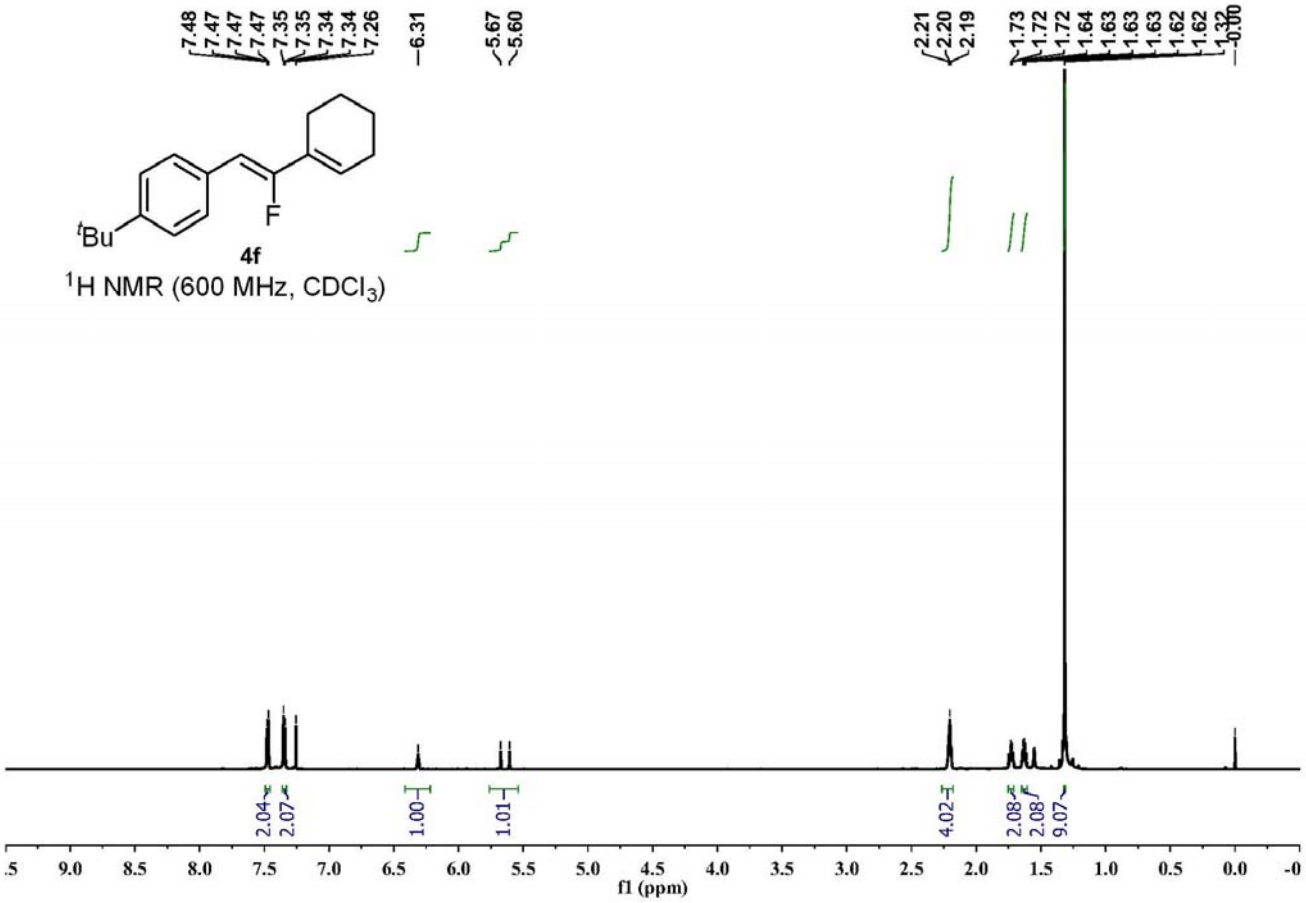


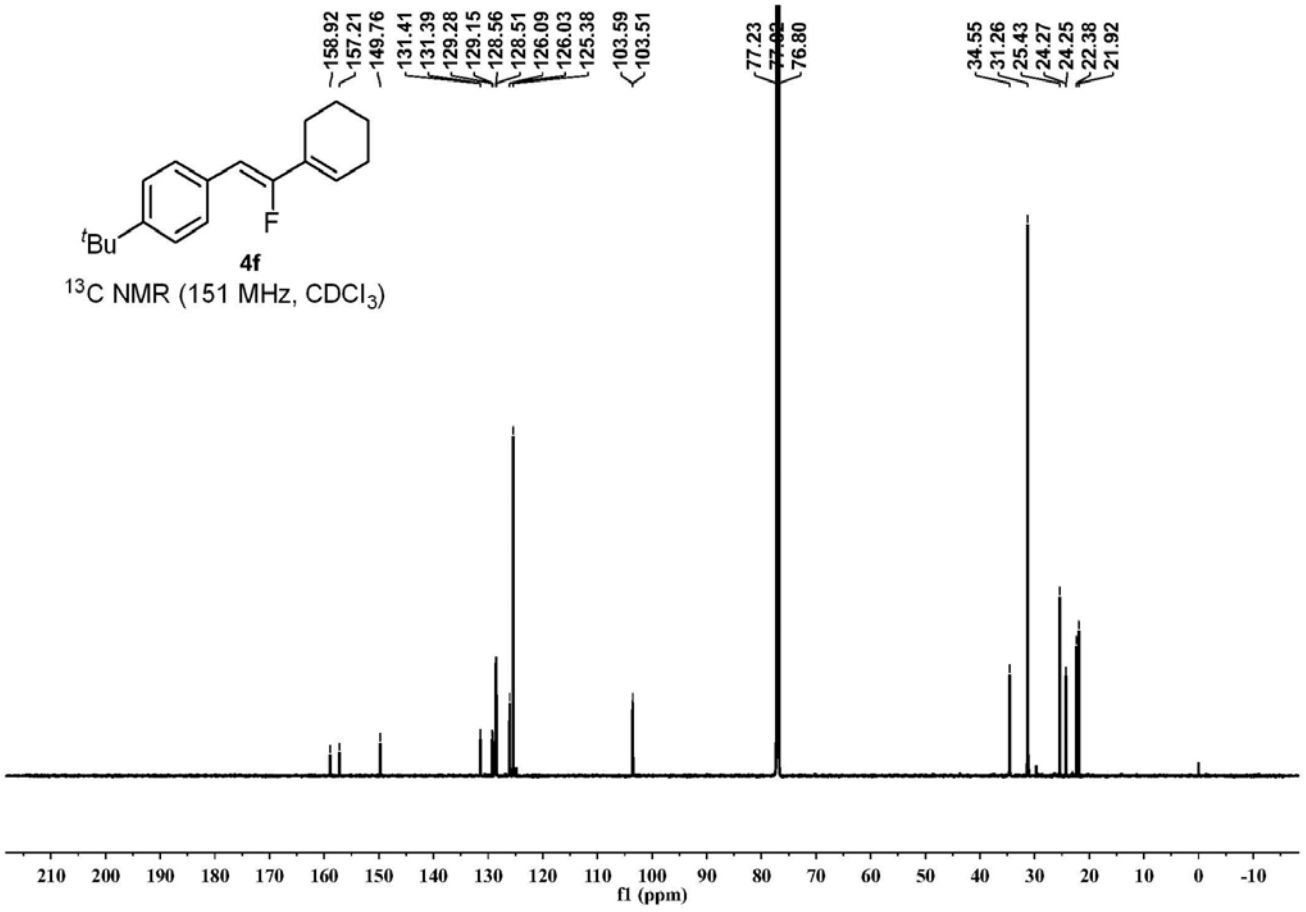
4e

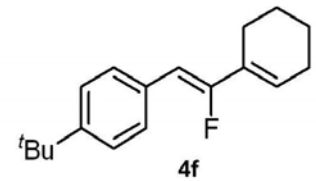
^{1}H NMR (600 MHz, $CDCl_3$)


160.26
158.52
147.80
147.78
134.80
134.79
130.34
130.29
128.84
128.13
128.08
101.97
77.24
76.81
25.49
24.19
24.17
22.26
21.78
TfO
F
4e
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-72.82
-114.95
-115.02
TfO
F
4e
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

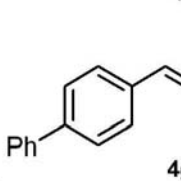

7.48
7.47
7.47
7.47
7.35
7.35
7.34
7.34
7.26
6.31
5.67
5.60
2.21
2.20
2.19
1.73
1.72
1.72
1.64
1.63
1.63
1.63
1.62
1.62
0.00
tBu
F
4f
1H NMR (600 MHz, CDCl3)
2.04
2.07
1.00
1.01
4.02
2.08
2.08
9.07
f1 (ppm)


158.92
157.21
149.76
131.41
131.39
129.28
129.15
128.56
128.51
126.09
126.03
125.38
103.59
103.51
77.23
77.03
76.80
34.55
31.26
25.43
24.27
24.25
22.38
21.92
tBu
F
4f
13C NMR (151 MHz, CDCl3)
f1 (ppm)



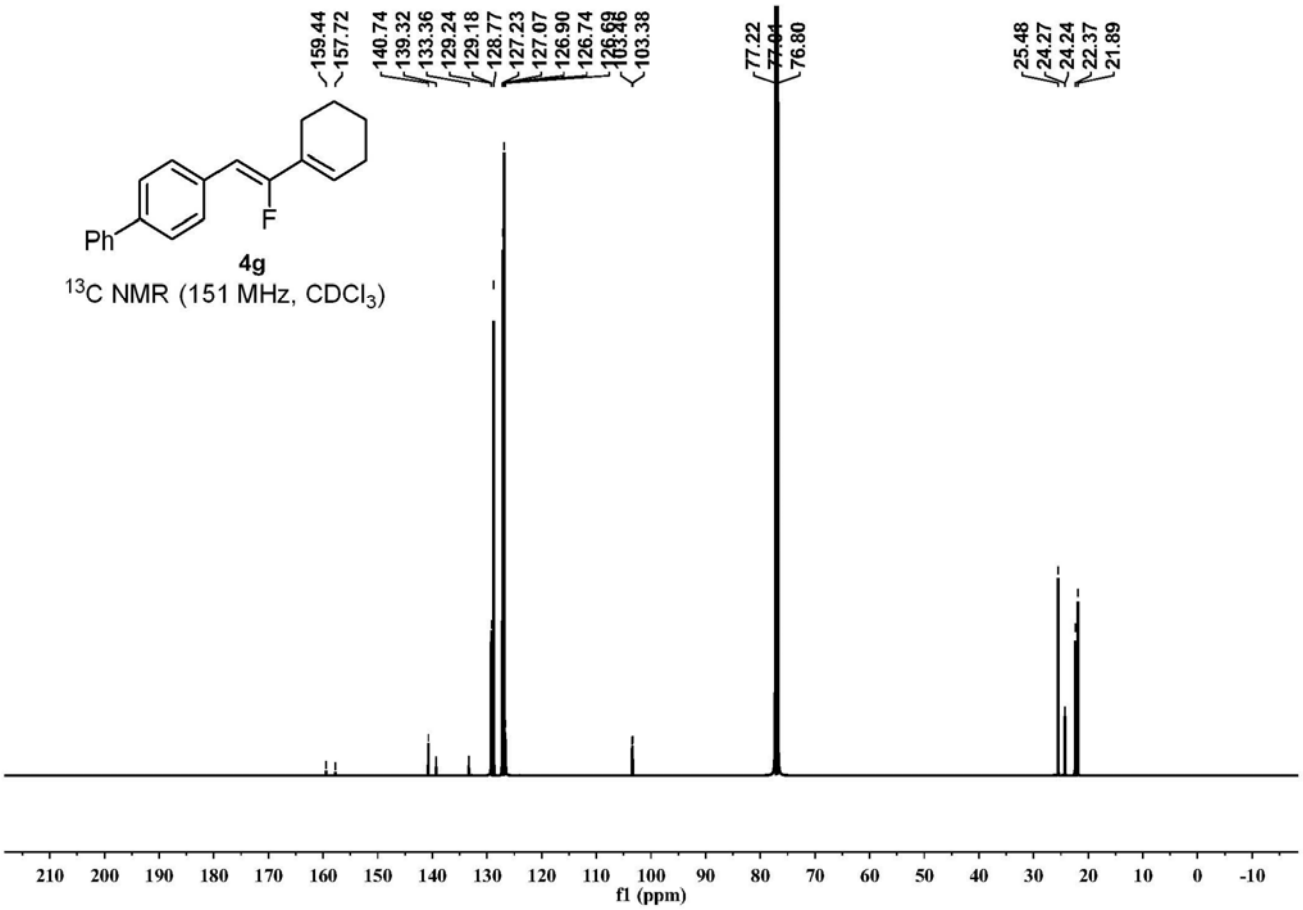
4f

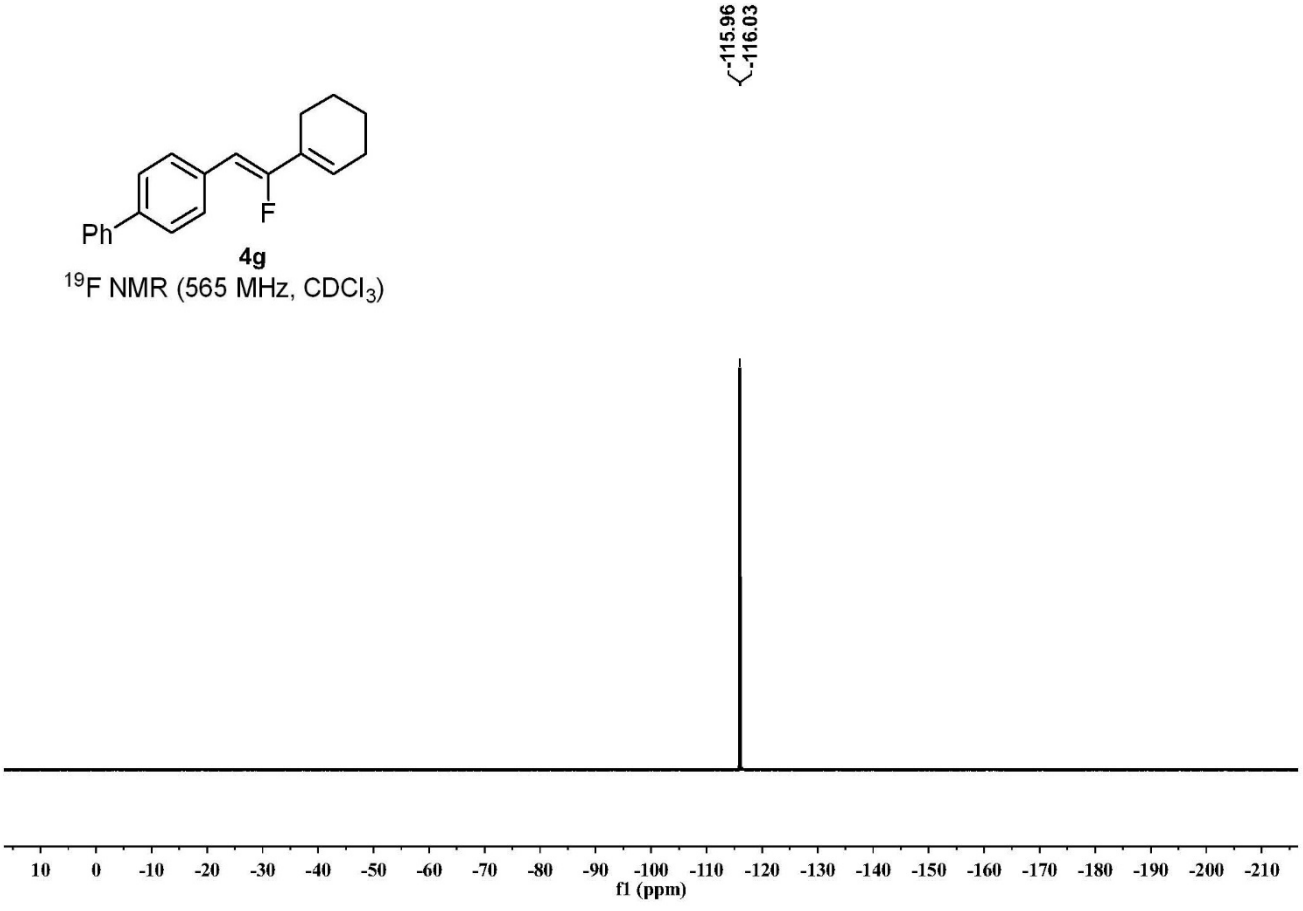
^{19}F NMR (565 MHz, $CDCl_3$)

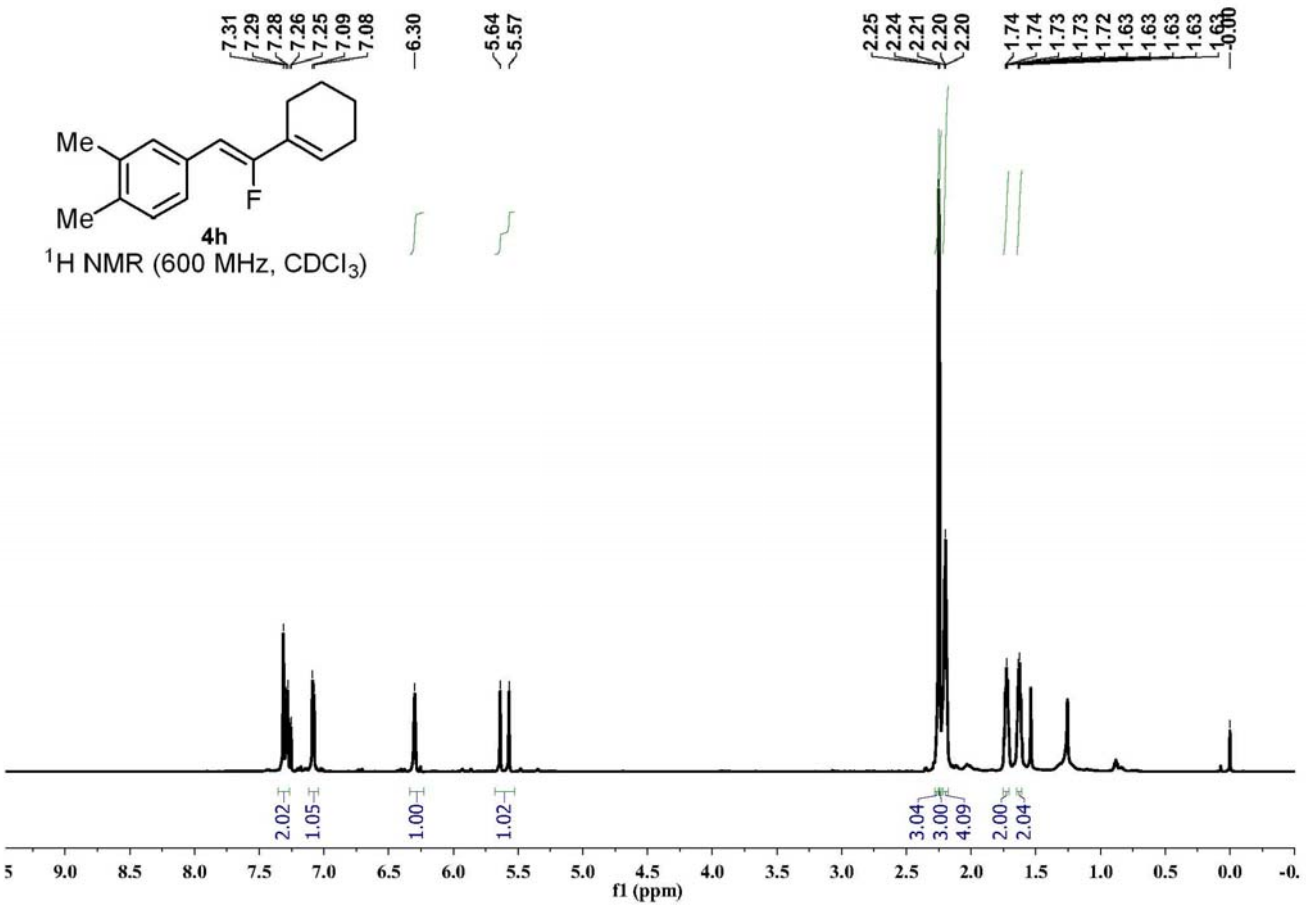


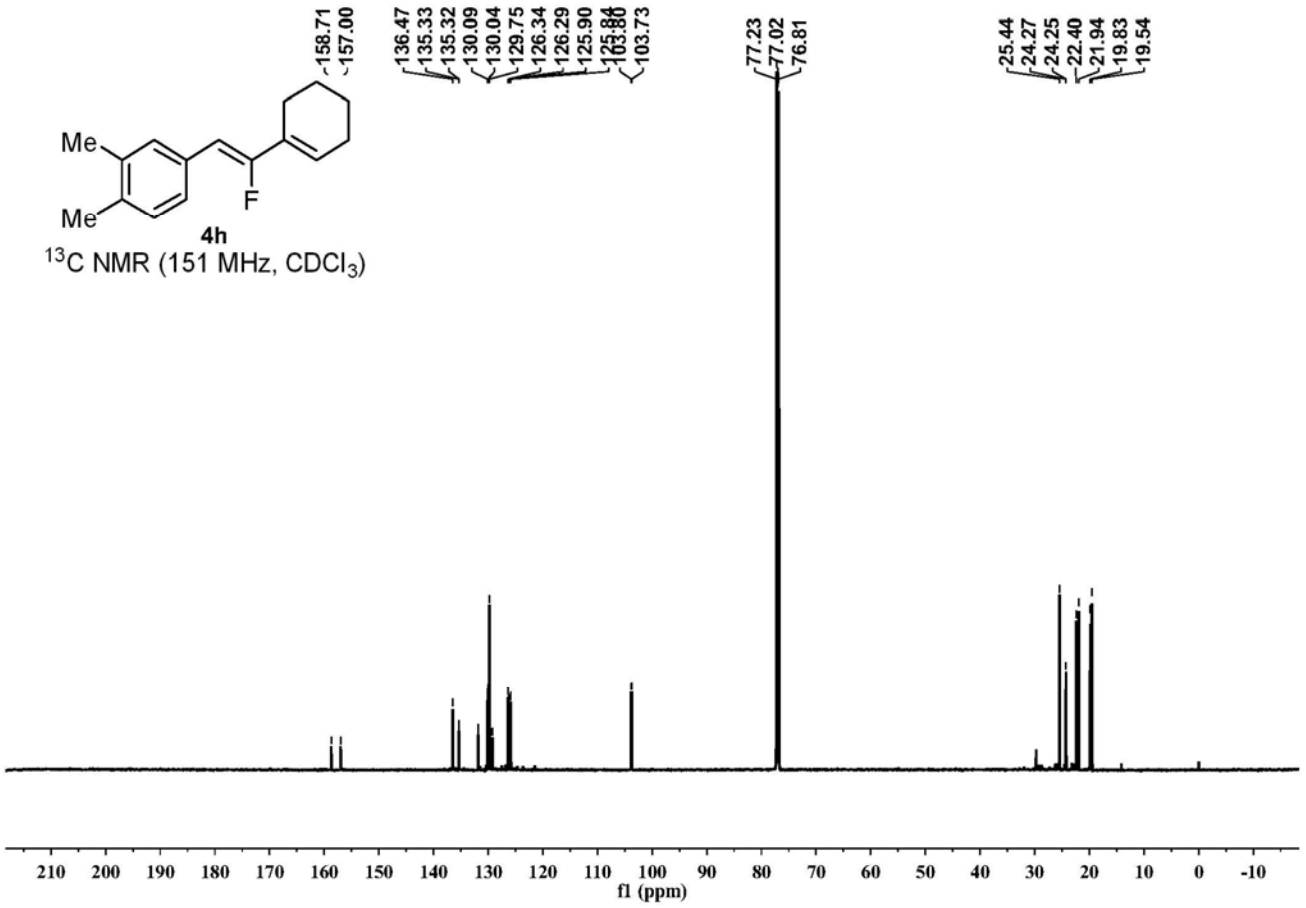
4g

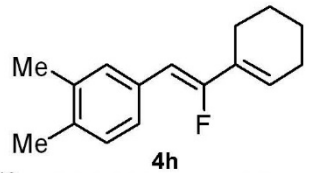
^{1}H NMR (600 MHz, $CDCl_3$)


159.44
157.72
140.74
139.32
133.36
129.24
129.18
128.77
127.23
127.07
126.90
126.74
103.38
77.22
77.04
76.80
25.48
24.27
24.24
22.37
21.89
Ph
F
4g
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-115.96
-116.03
Ph
F
4g
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

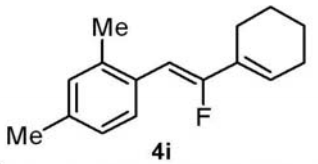

Me
Me
F
4h
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)


Me
Me
F
4h
^{13}C NMR (151 MHz, $CDCl_3$)
f1 (ppm)



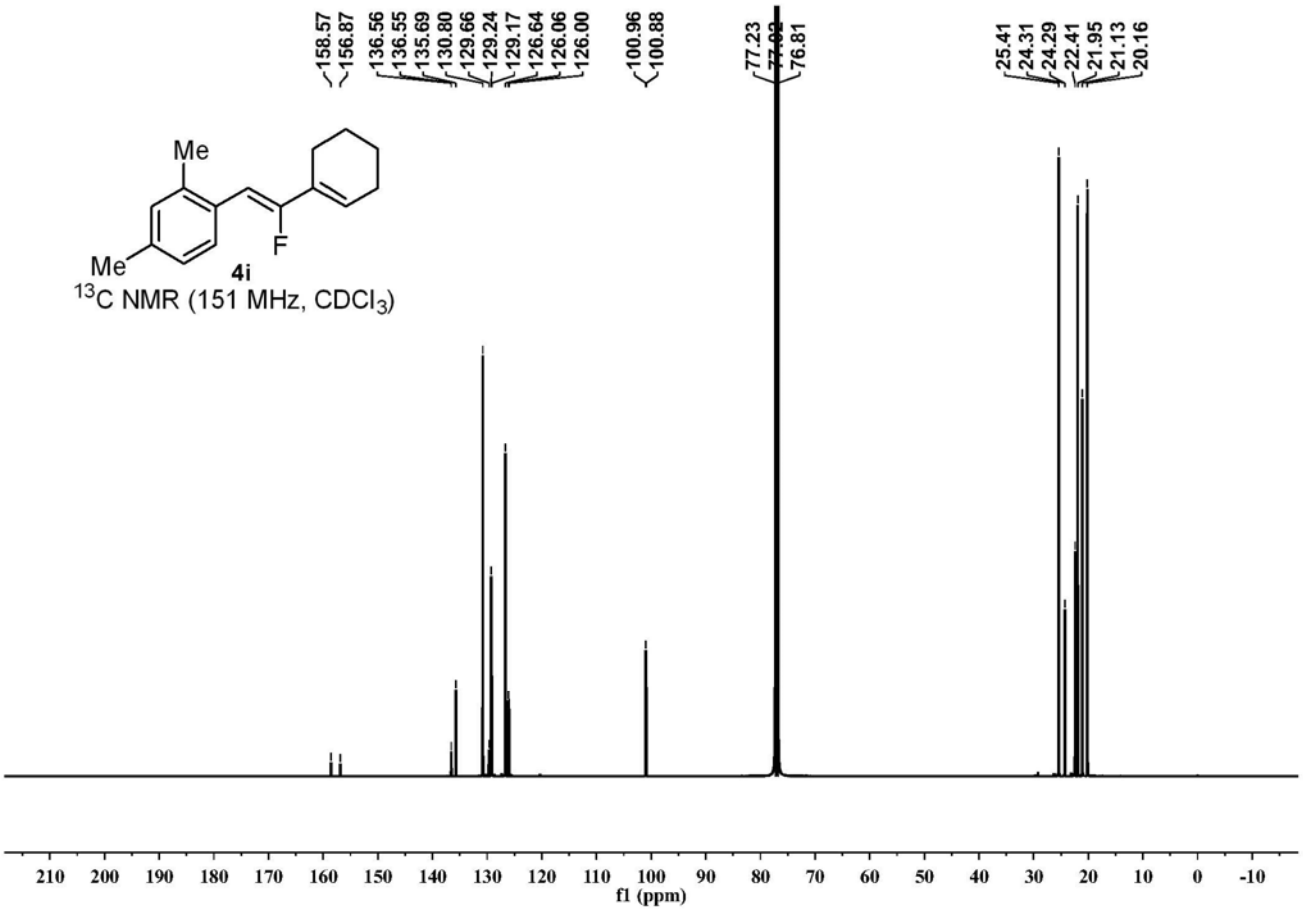
4h

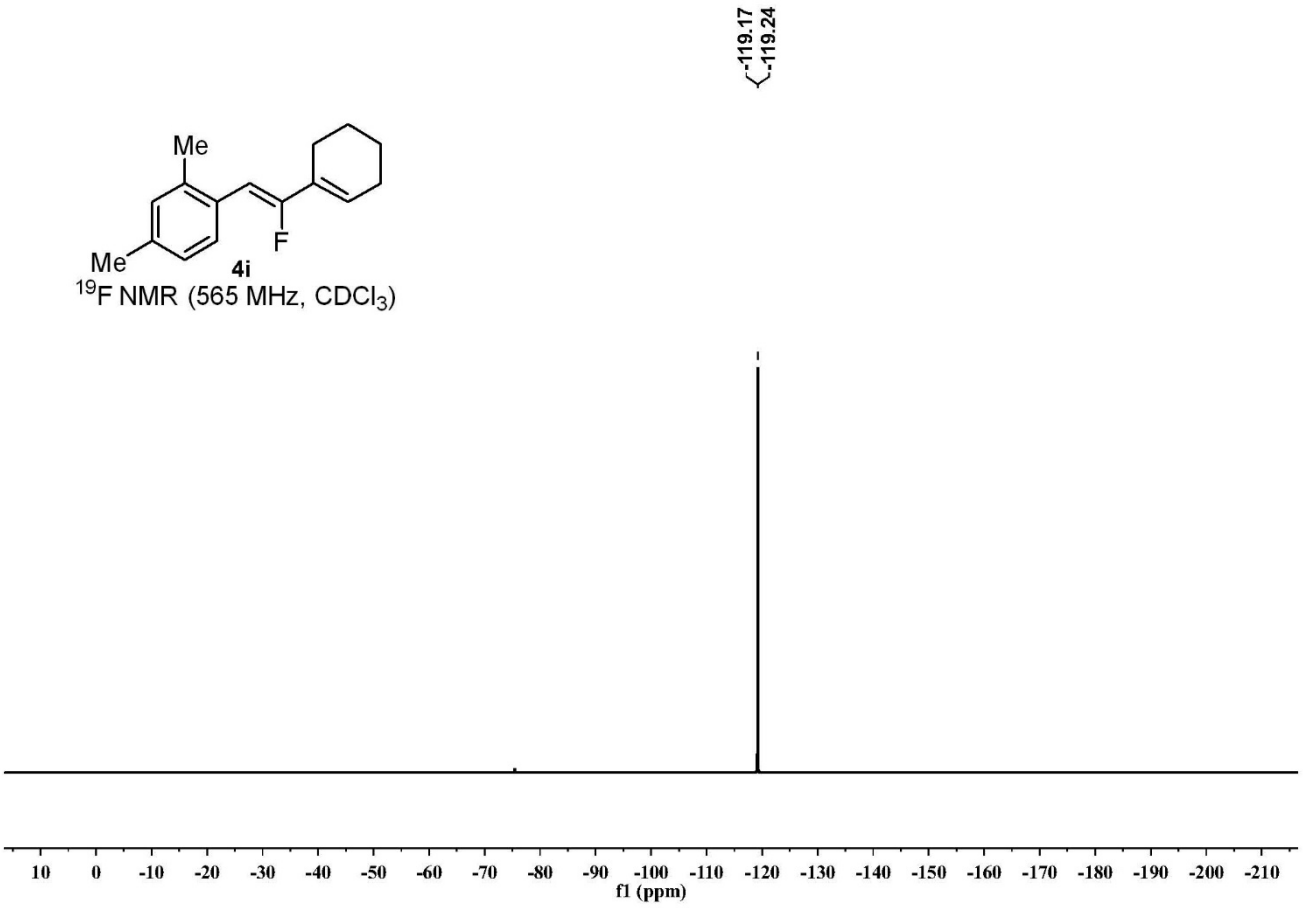
^{19}F NMR (565 MHz, $CDCl_3$)

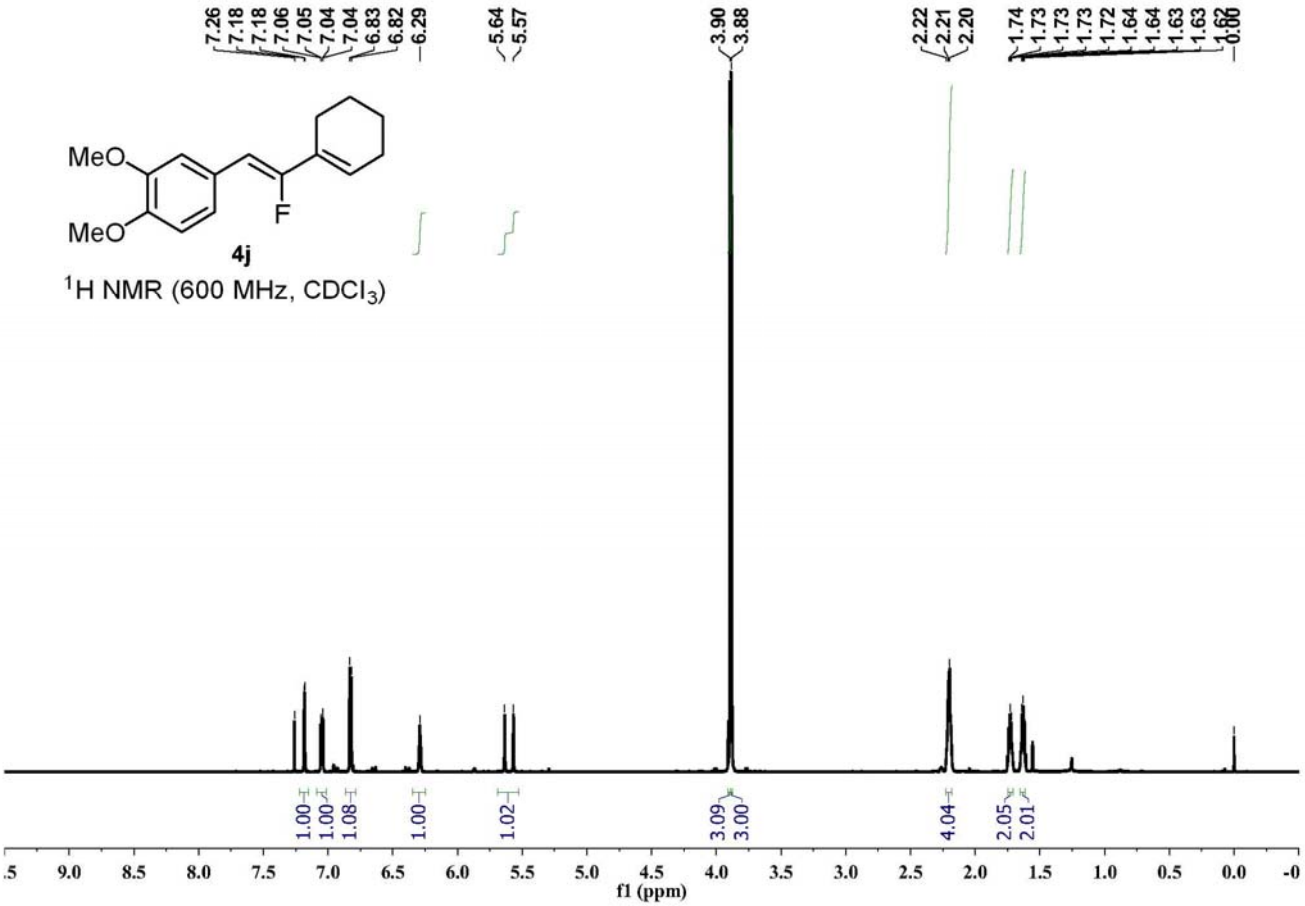


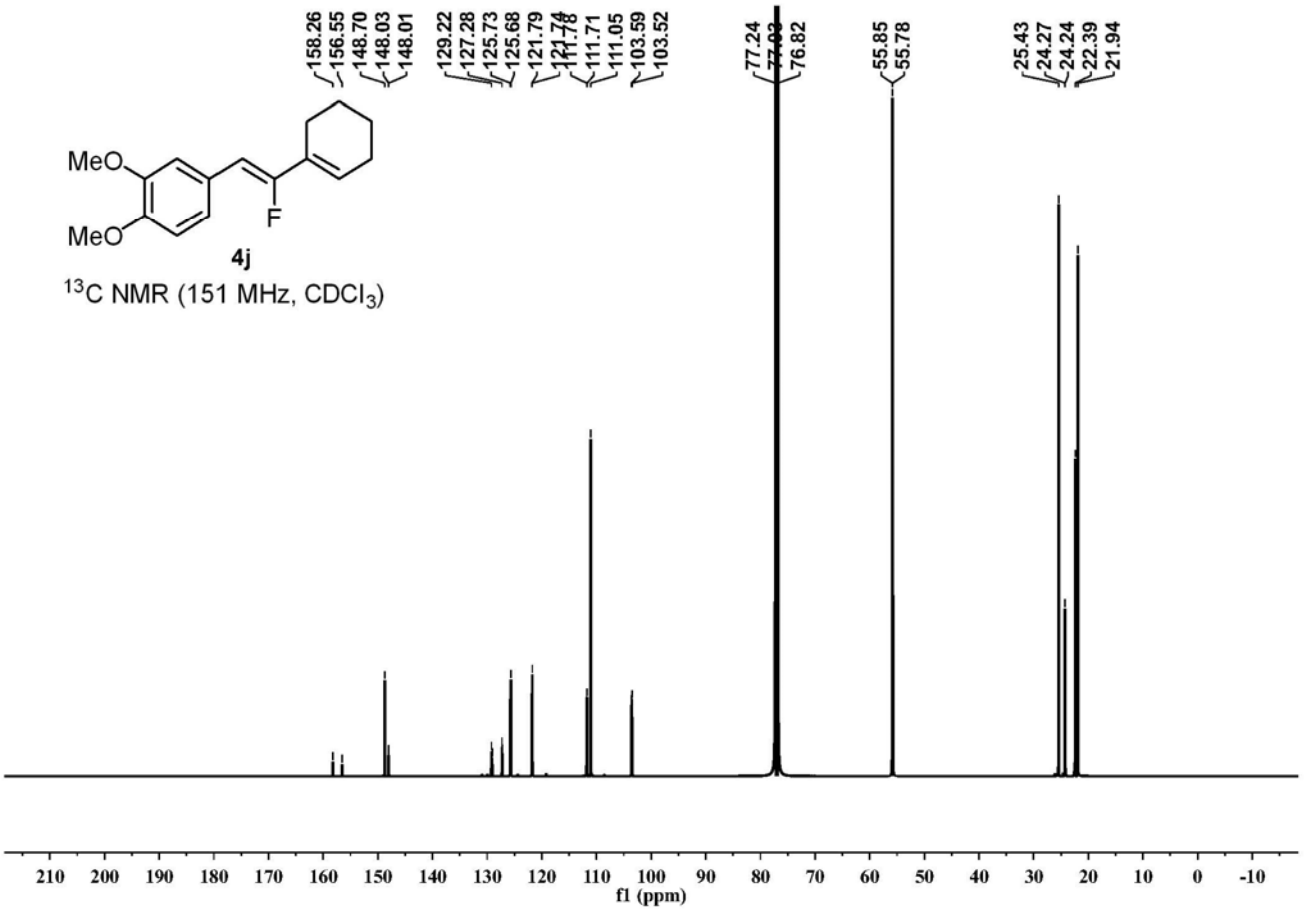
4i

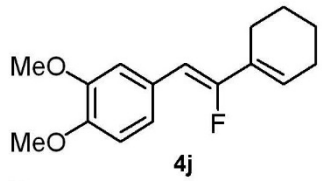
^{1}H NMR (600 MHz, $CDCl_3$)


158.57
156.87
136.56
136.55
135.69
130.80
129.66
129.24
129.17
126.64
126.06
126.00
100.96
100.88
77.23
77.02
76.81
25.41
24.31
24.29
22.41
21.95
21.13
20.16
Me
F
Me
4i
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-119.17
-119.24
Me
F
Me
4i
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

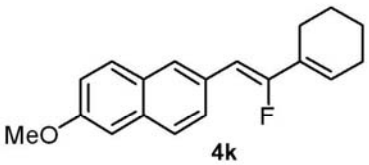

MeO
MeO
F
4j
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)


MeO
MeO
F
4j
^{13}C NMR (151 MHz, $CDCl_3$)
f1 (ppm)



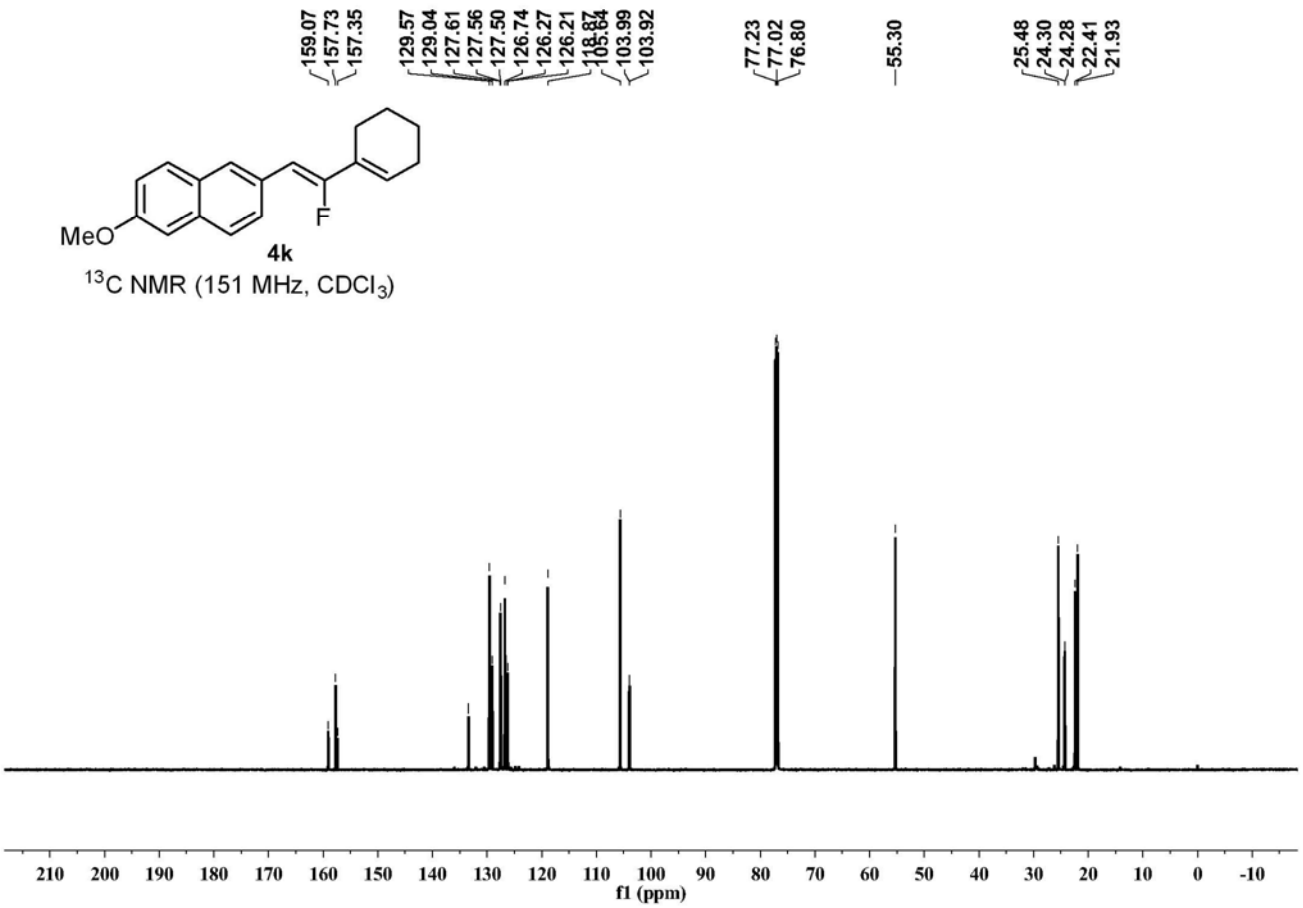
4j

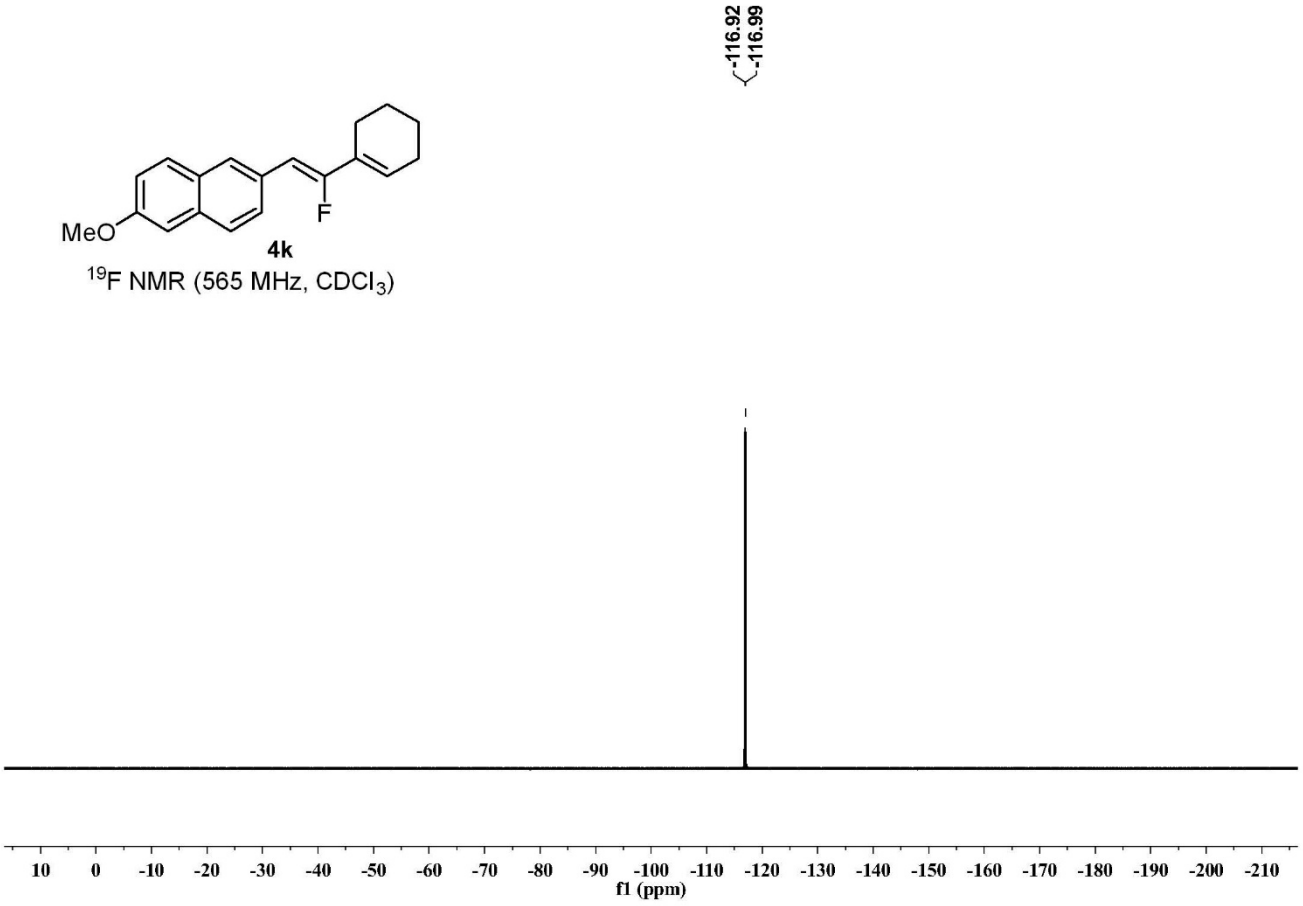
^{19}F NMR (565 MHz, $CDCl_3$)

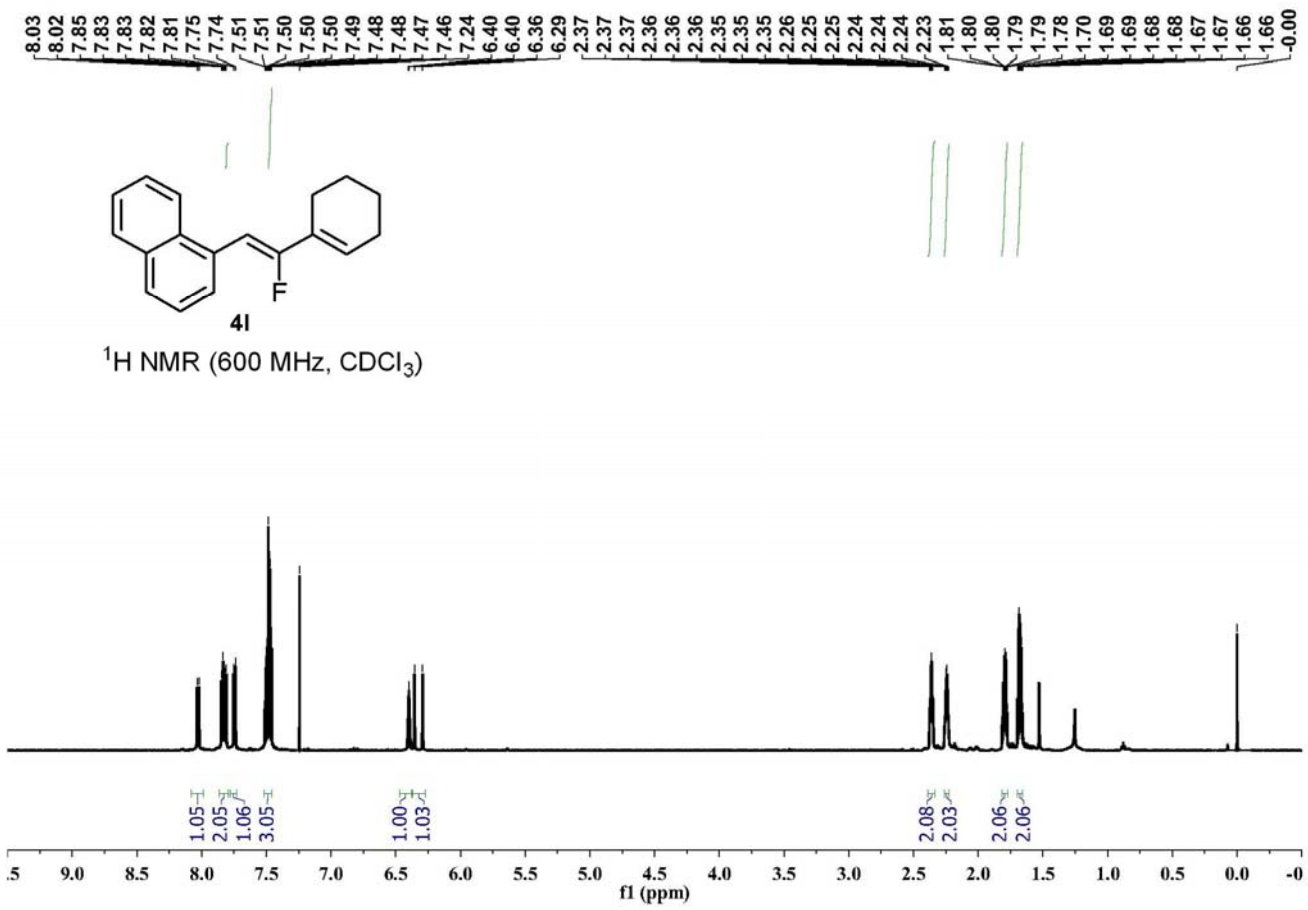


4k

^{1}H NMR (600 MHz, $CDCl_3$)

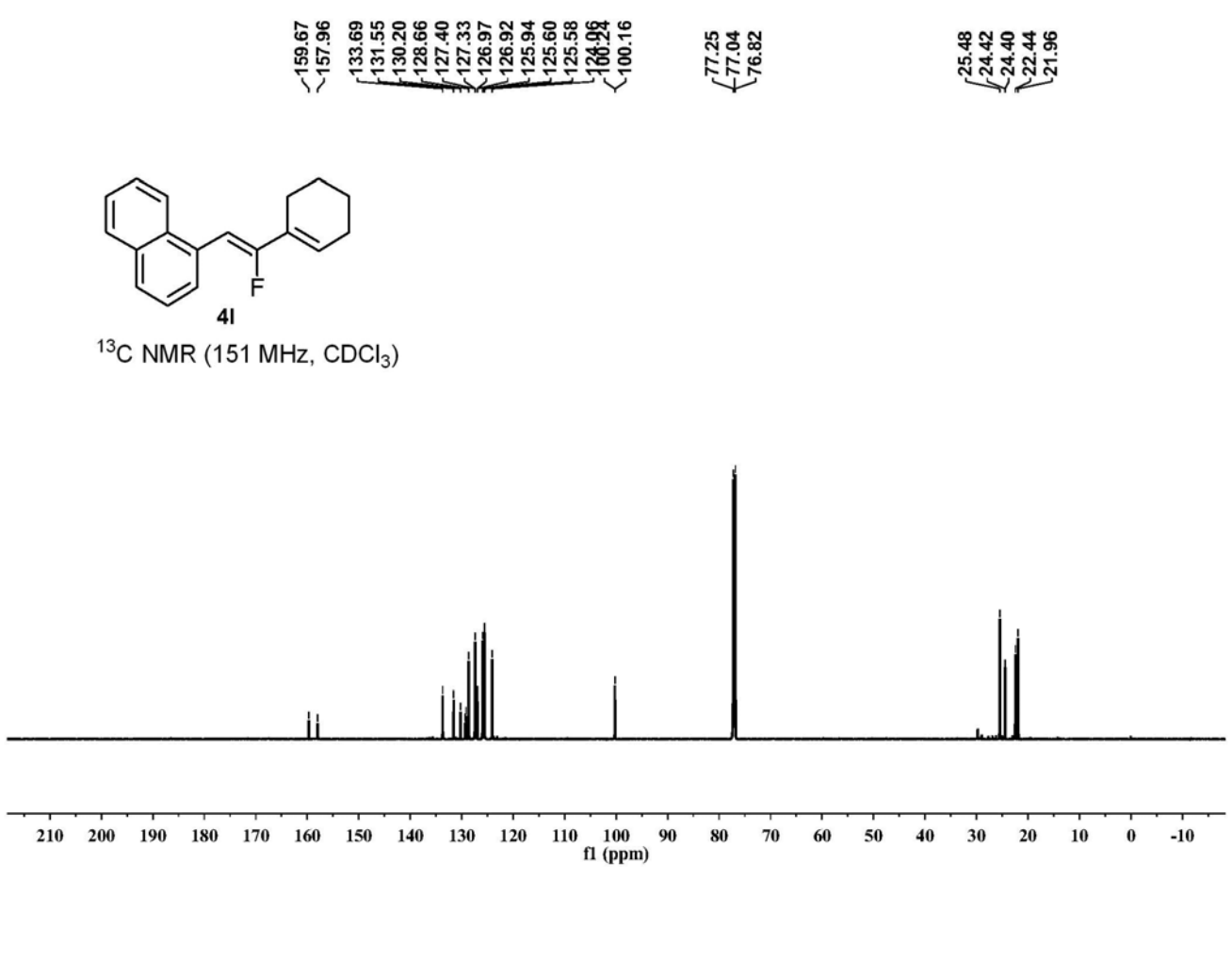

159.07
157.73
157.35
129.57
129.04
127.61
127.56
127.50
126.74
126.27
126.21
118.87
105.64
103.99
103.92
77.23
77.02
76.80
55.30
25.48
24.30
24.28
22.41
21.93
MeO
F
4k
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-116.92
-116.99
MeO
F
4k
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



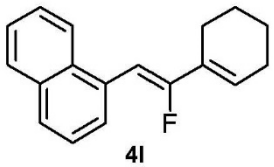
4l

^{1}H NMR (600 MHz, $CDCl_3$)



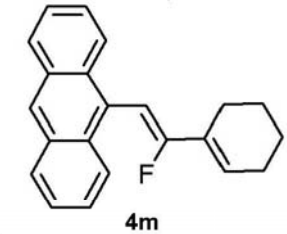
4l

^{13}C NMR (151 MHz, $CDCl_3$)



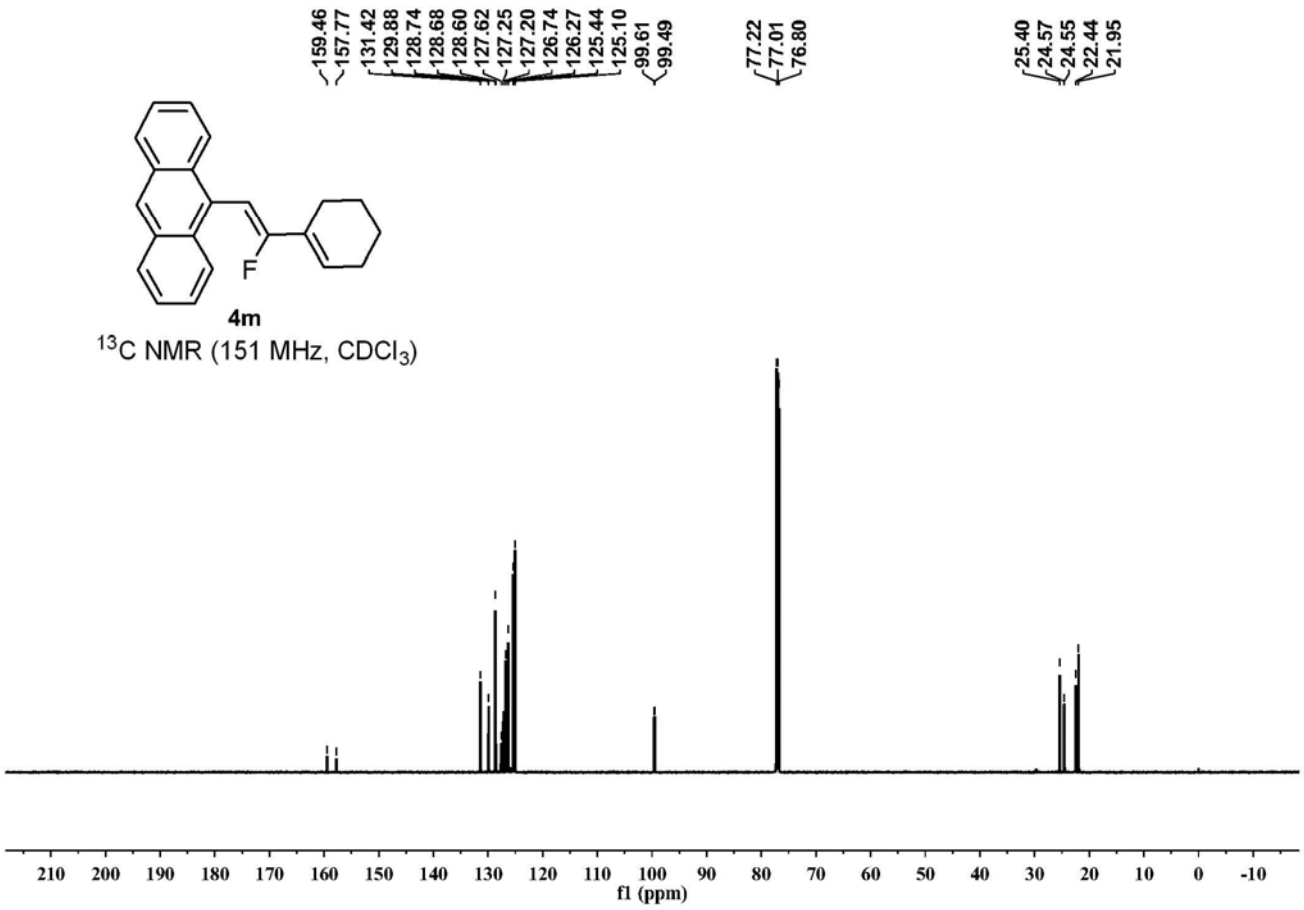
4l

^{19}F NMR (565 MHz, $CDCl_3$)



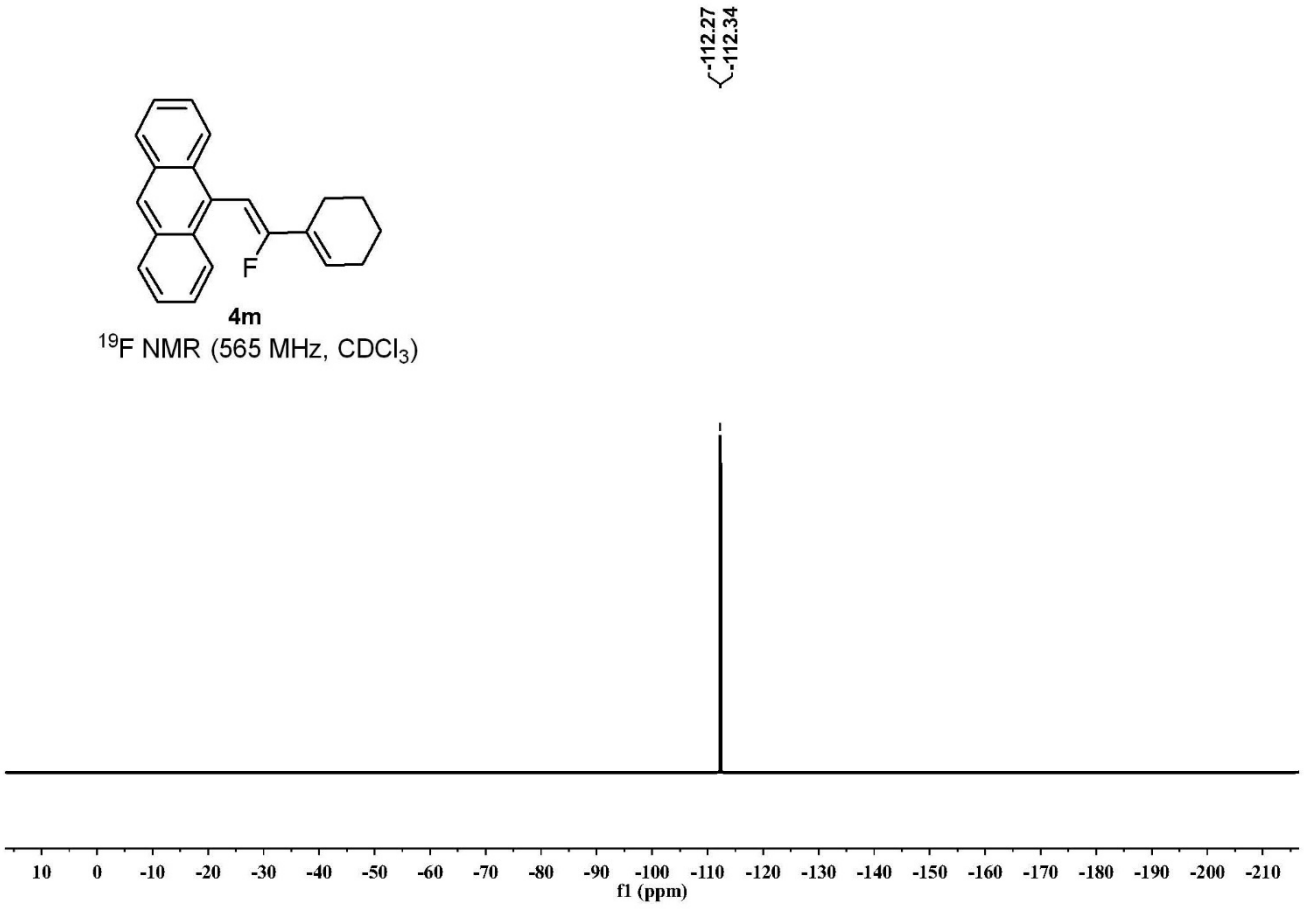
4m

^{1}H NMR (600 MHz, $CDCl_3$)



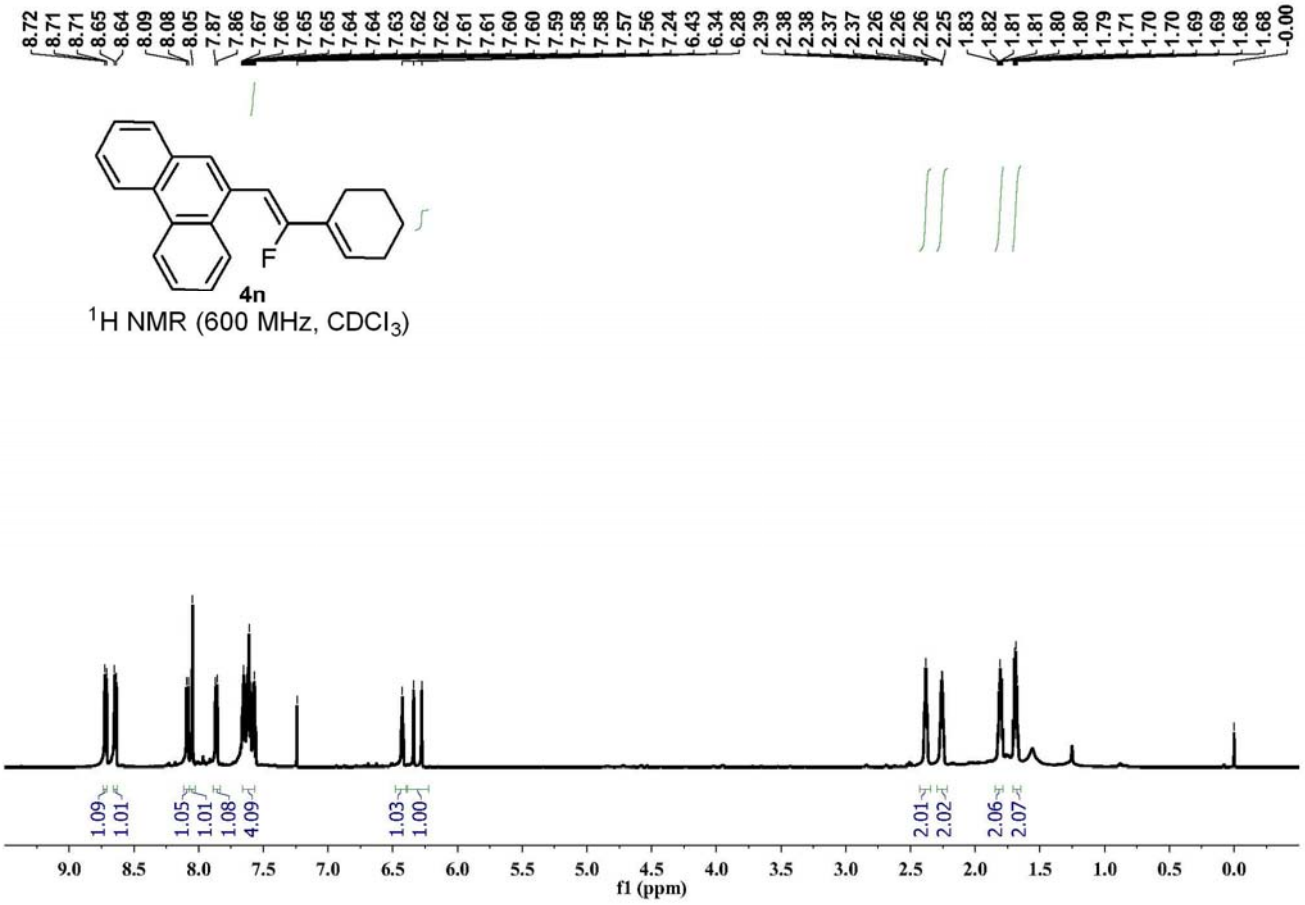
4m

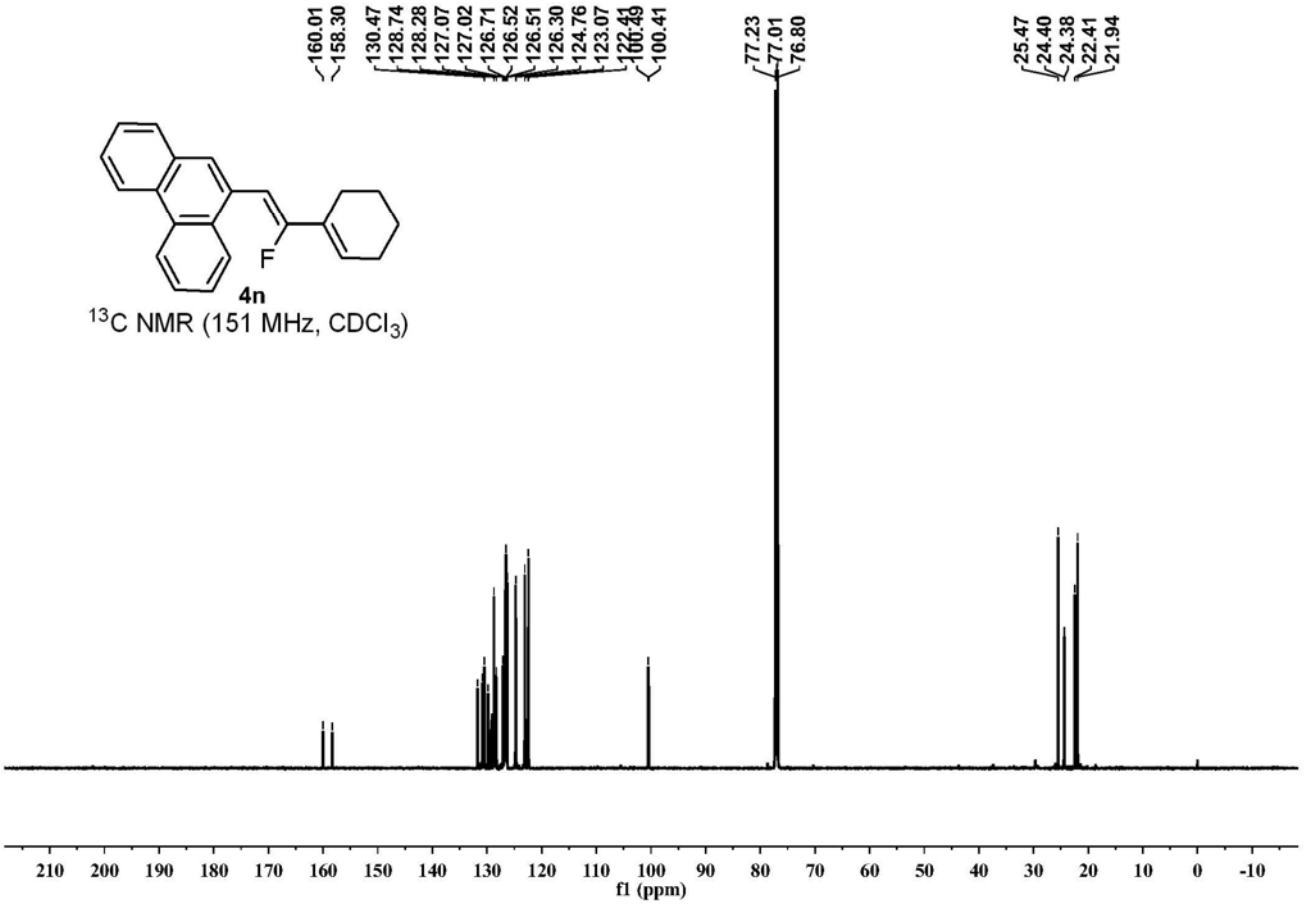
^{13}C NMR (151 MHz, $CDCl_3$)

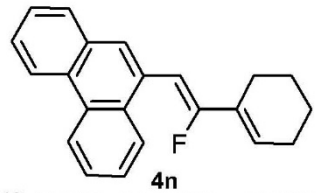


4m

^{19}F NMR (565 MHz, $CDCl_3$)

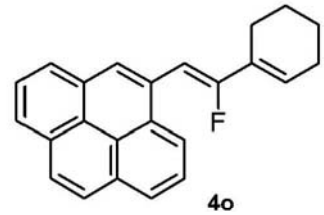

8.72 8.71 8.71 8.65 8.64 8.09 8.08 8.05 7.87 7.86 7.67 7.66 7.65 7.65 7.64 7.64 7.63 7.62 7.62 7.61 7.61 7.60 7.60 7.59 7.58 7.58 7.57 7.56 7.24 6.43 6.34 6.28 2.39 2.38 2.38 2.37 2.37 2.26 2.26 2.25 1.83 1.82 1.81 1.81 1.80 1.80 1.79 1.71 1.70 1.70 1.69 1.69 1.68 -0.00
F
4n
1H NMR (600 MHz, CDCl3)
1.09 1.01 1.05 1.01 1.08 4.09 1.03 1.00 2.01 2.02 2.06 2.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.01 158.30 130.47 128.74 128.28 127.07 127.02 126.71 126.52 126.51 126.30 124.76 123.07 100.41 77.23 77.01 76.80 25.47 24.40 24.38 22.41 21.94
F
4n
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



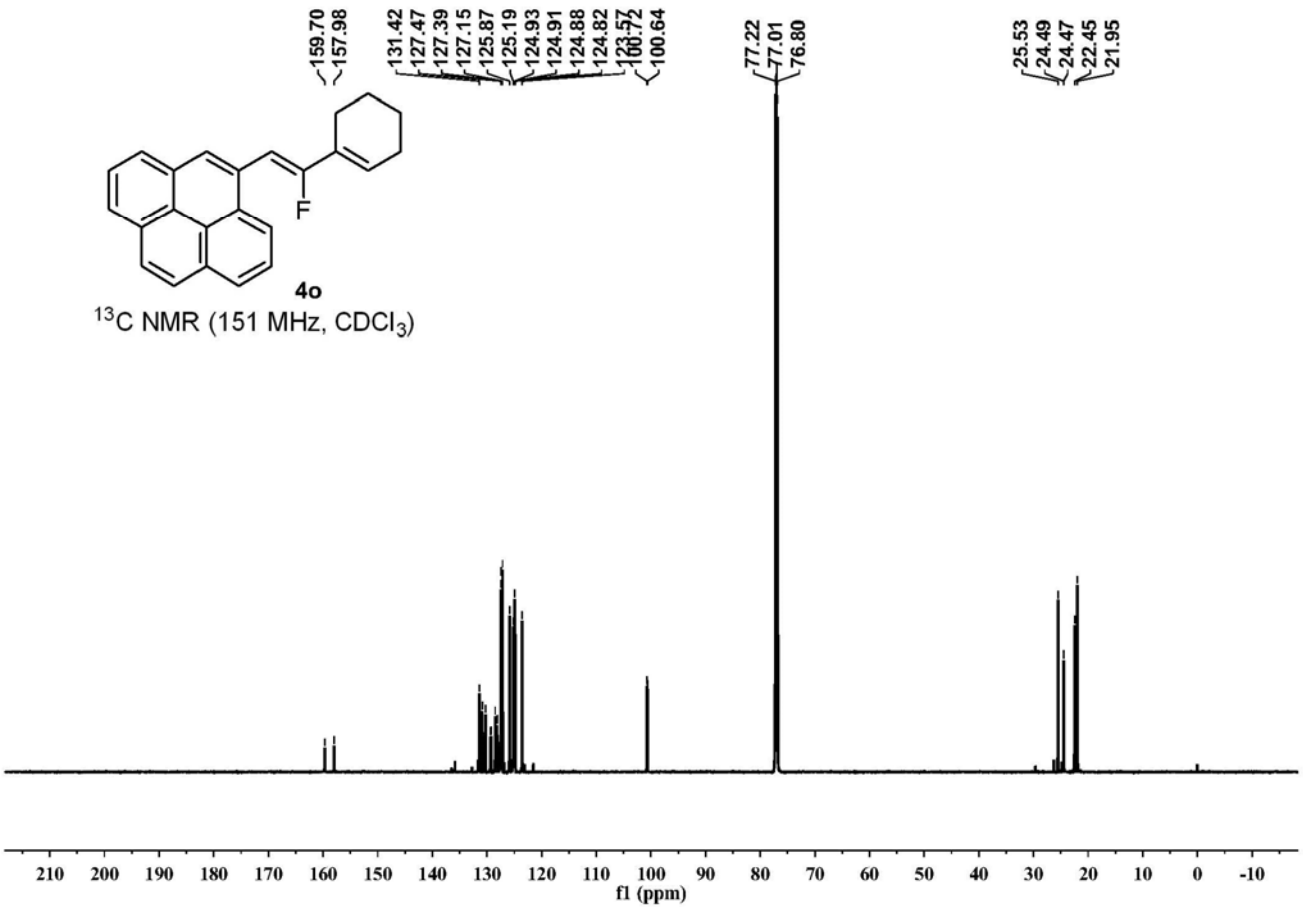
4n

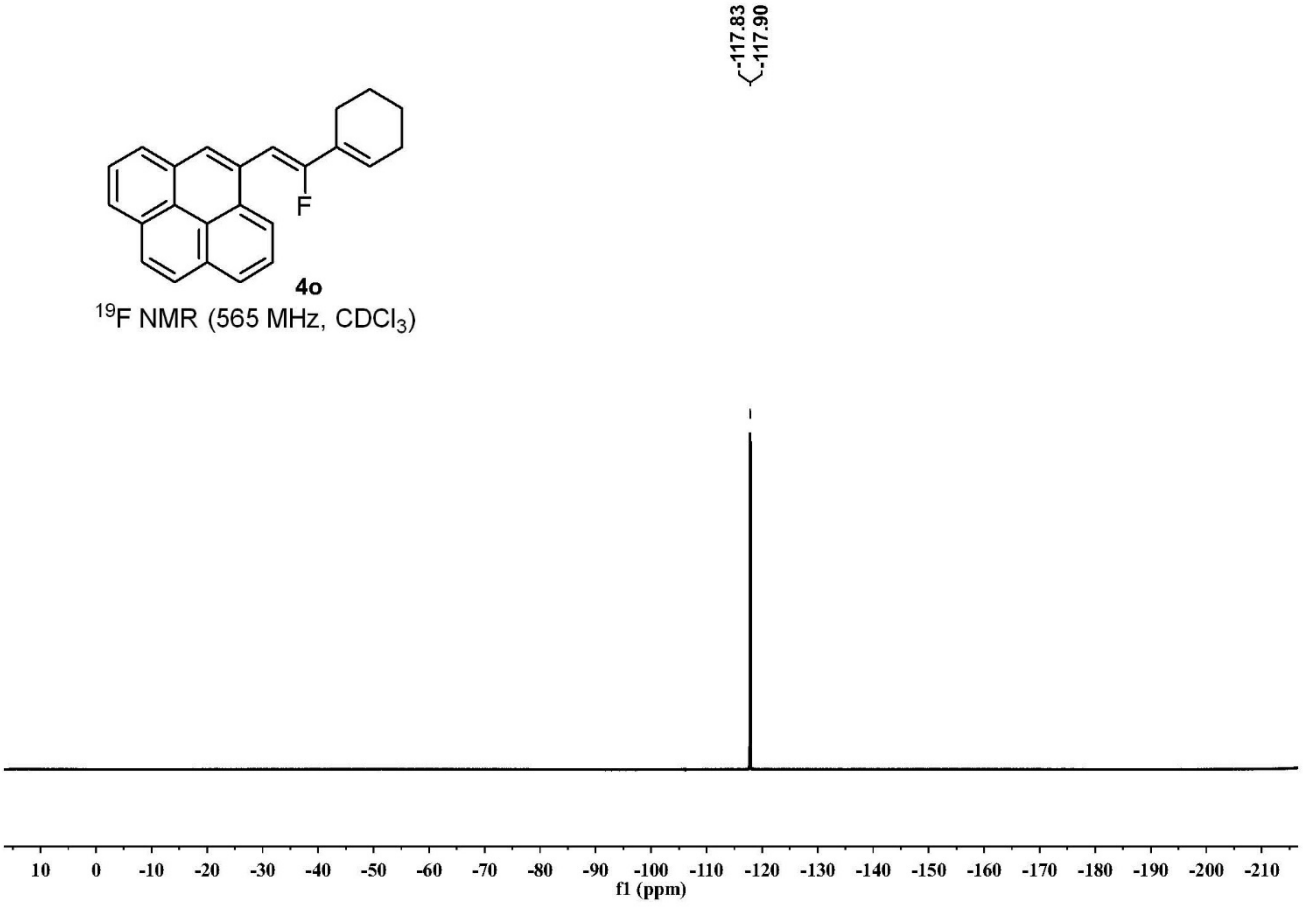
^{19}F NMR (565 MHz, $CDCl_3$)

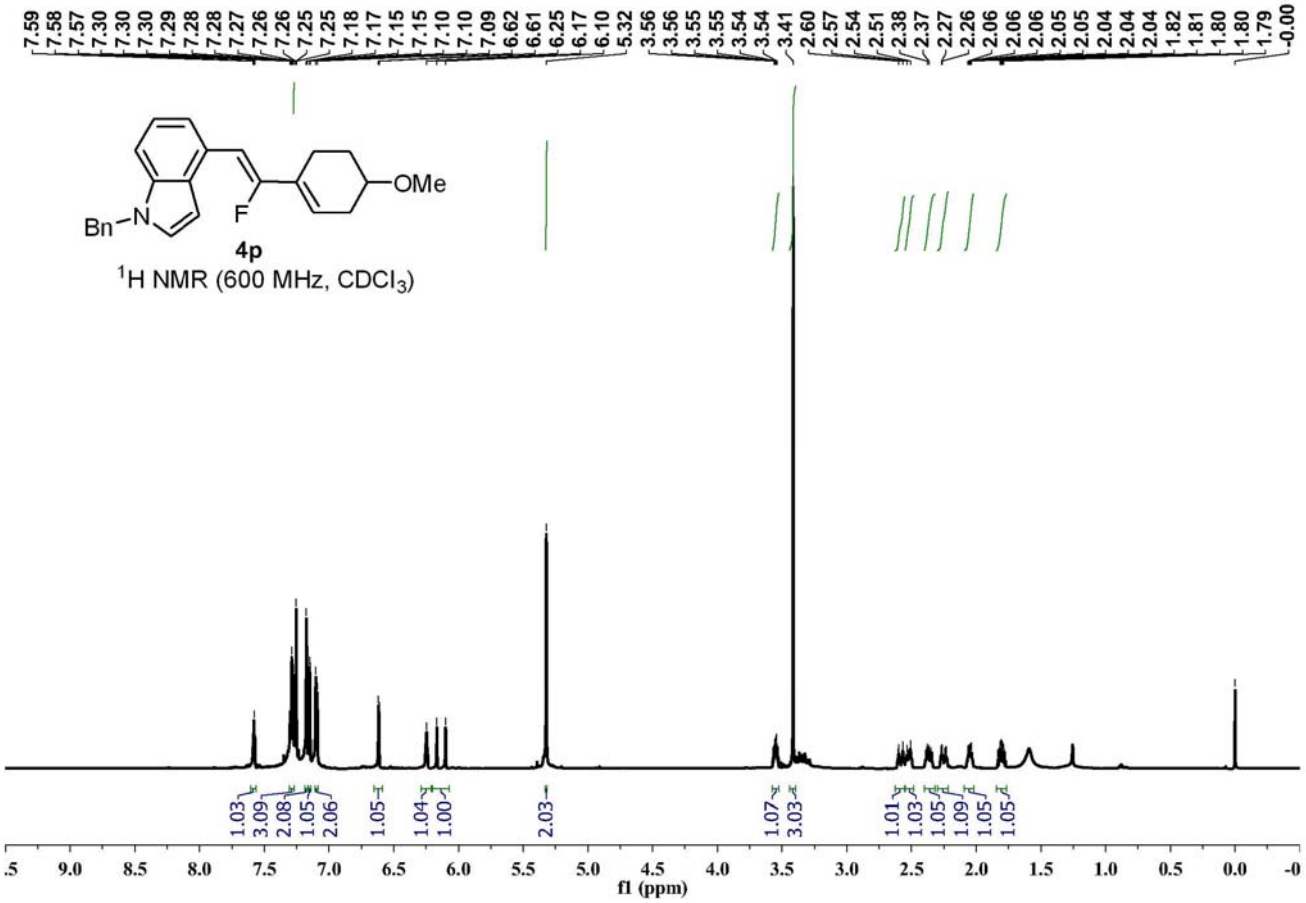


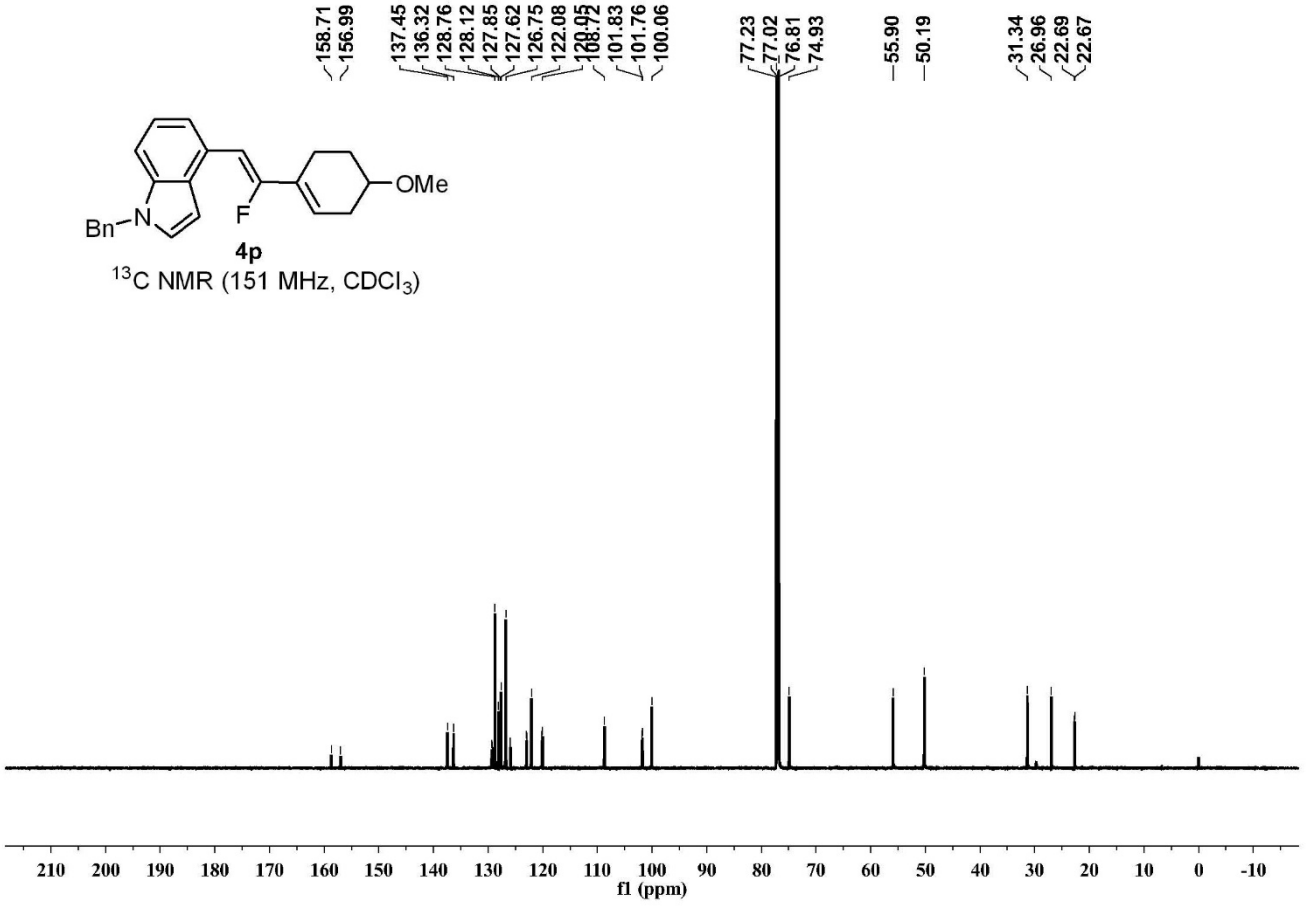
4o

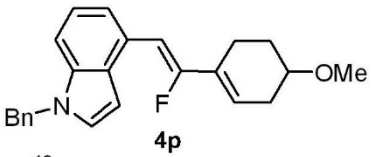
^{1}H NMR (600 MHz, $CDCl_3$)


159.70
157.98
131.42
127.47
127.39
127.15
125.87
125.19
124.93
124.91
124.88
124.82
123.57
100.72
100.64
77.22
77.01
76.80
25.53
24.49
24.47
22.45
21.95
F
4o
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-117.83
-117.90
F
4o
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

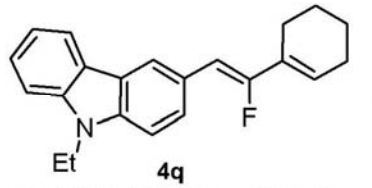

7.59 7.58 7.57 7.30 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.25 7.18 7.17 7.15 7.15 7.10 7.10 7.09 6.62 6.61 6.25 6.17 6.10 5.32 3.56 3.56 3.55 3.55 3.54 3.54 3.41 2.60 2.57 2.54 2.51 2.38 2.37 2.27 2.26 2.06 2.06 2.06 2.05 2.05 2.04 2.04 2.04 1.82 1.81 1.80 1.80 1.79 -0.00
Bn
N
F
OMe
4p
1H NMR (600 MHz, CDCl3)
1.03 3.09 2.08 1.05 2.06 1.05 1.04 1.00 2.03 1.07 3.03 1.01 1.03 1.05 1.09 1.05 1.05
f1 (ppm)


158.71 156.99 137.45 136.32 128.76 128.12 127.85 127.62 126.75 122.08 101.83 101.76 100.06 77.23 77.02 76.81 74.93 55.90 50.19 31.34 26.96 22.69 22.67
Bn
N
F
OMe
4p
13C NMR (151 MHz, CDCl3)
f1 (ppm)



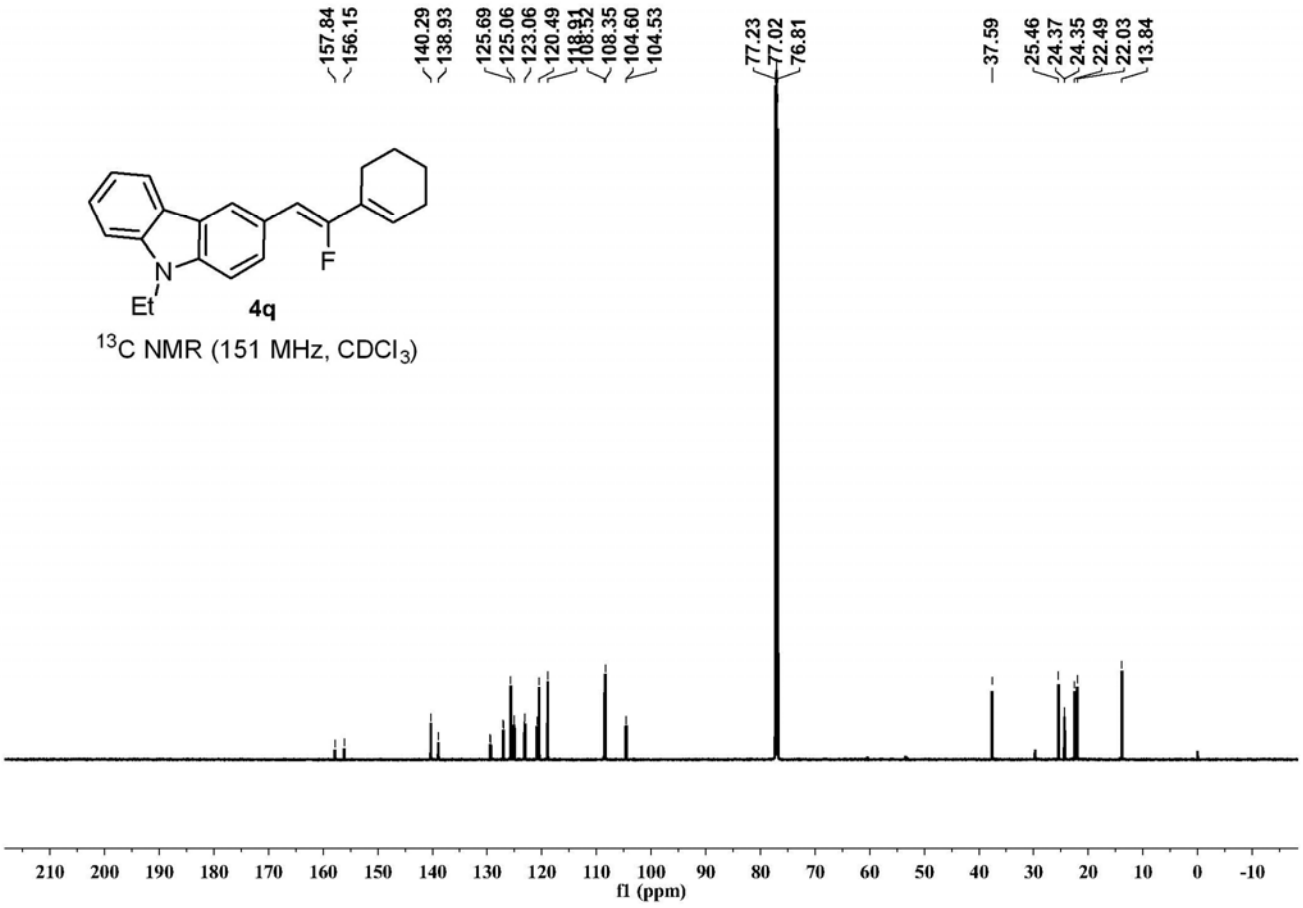
4p

^{19}F NMR (565 MHz, $CDCl_3$)

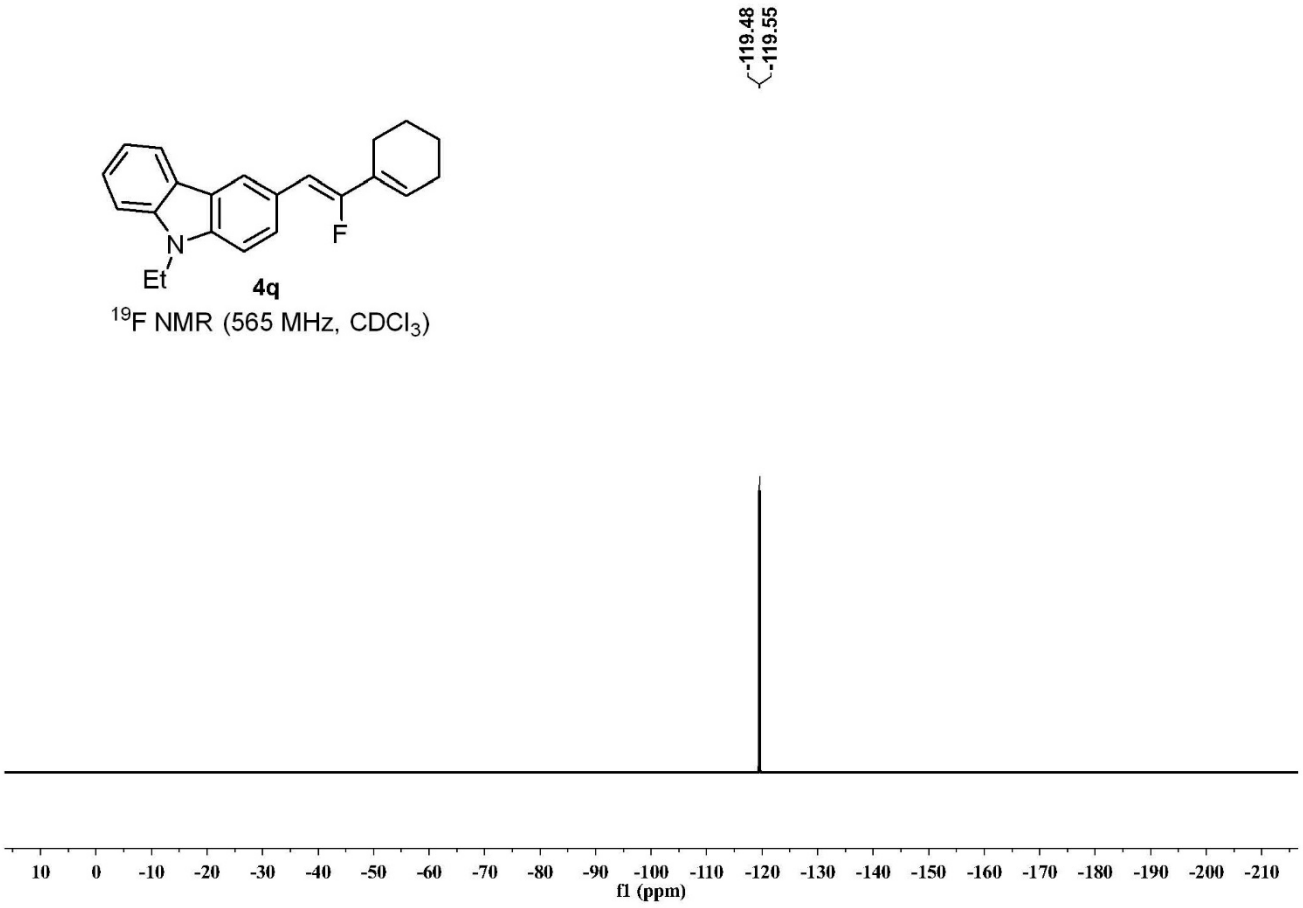


4q

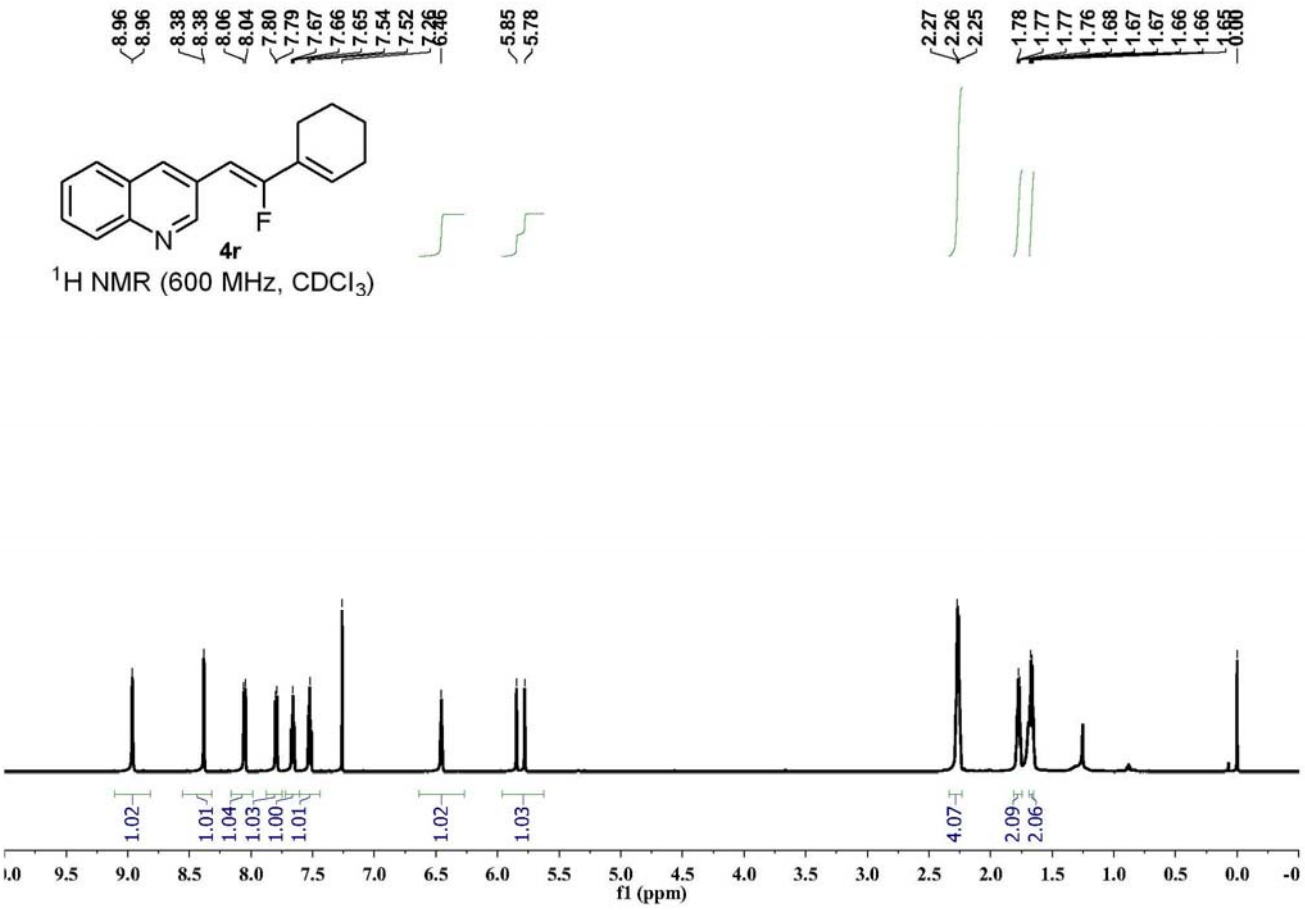
^{1}H NMR (600 MHz, $CDCl_3$)

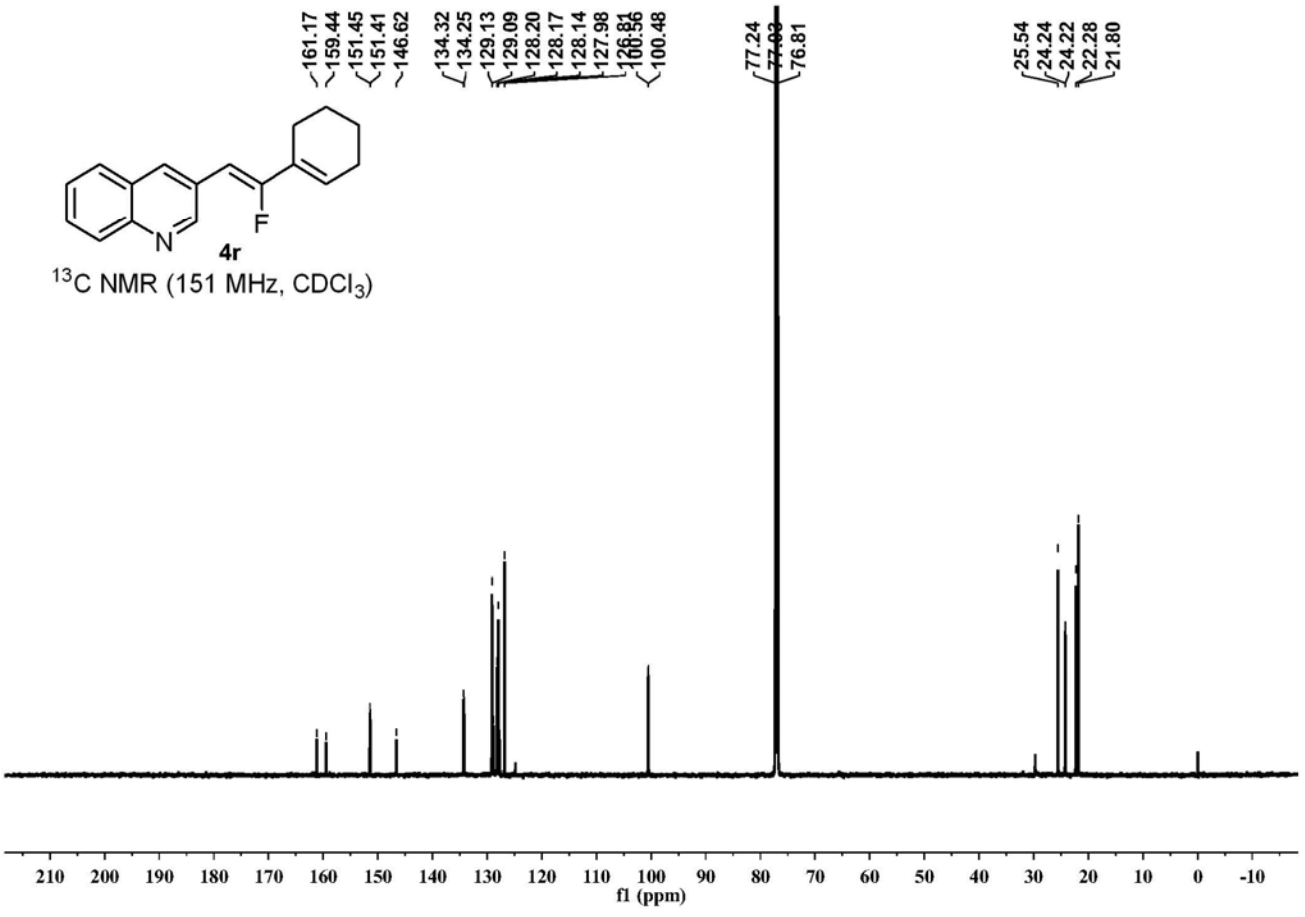


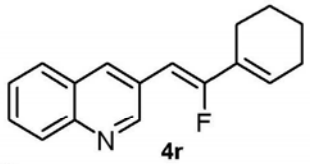
^{13}C NMR (151 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

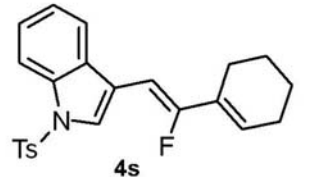

8.96
8.96
8.38
8.38
8.06
8.04
7.80
7.79
7.67
7.66
7.65
7.54
7.52
5.85
5.78
2.27
2.26
2.25
1.78
1.77
1.77
1.76
1.68
1.67
1.67
1.66
1.66
1.65
0.00
F
N
4r
1H NMR (600 MHz, CDCl3)
1.02
1.01
1.04
1.03
1.00
1.01
1.02
1.03
4.07
2.09
2.06
f1 (ppm)


161.17
159.44
151.45
151.41
146.62
134.32
134.25
129.13
129.09
128.20
128.17
128.14
127.98
126.81
100.56
100.48
77.24
77.03
76.81
25.54
24.24
24.22
22.28
21.80
F
N
4r
13C NMR (151 MHz, CDCl3)
f1 (ppm)



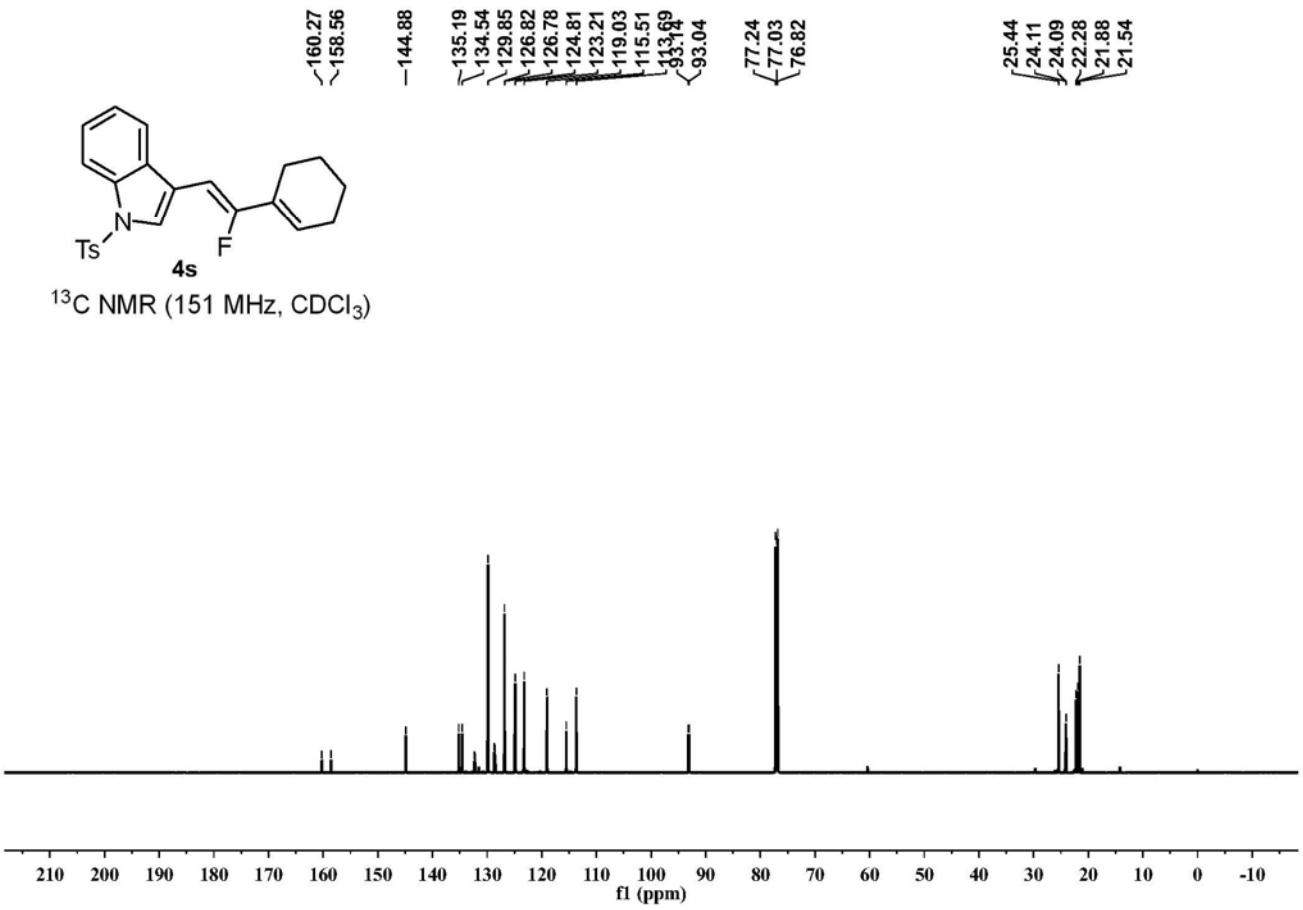
4r

^{19}F NMR (565 MHz, $CDCl_3$)

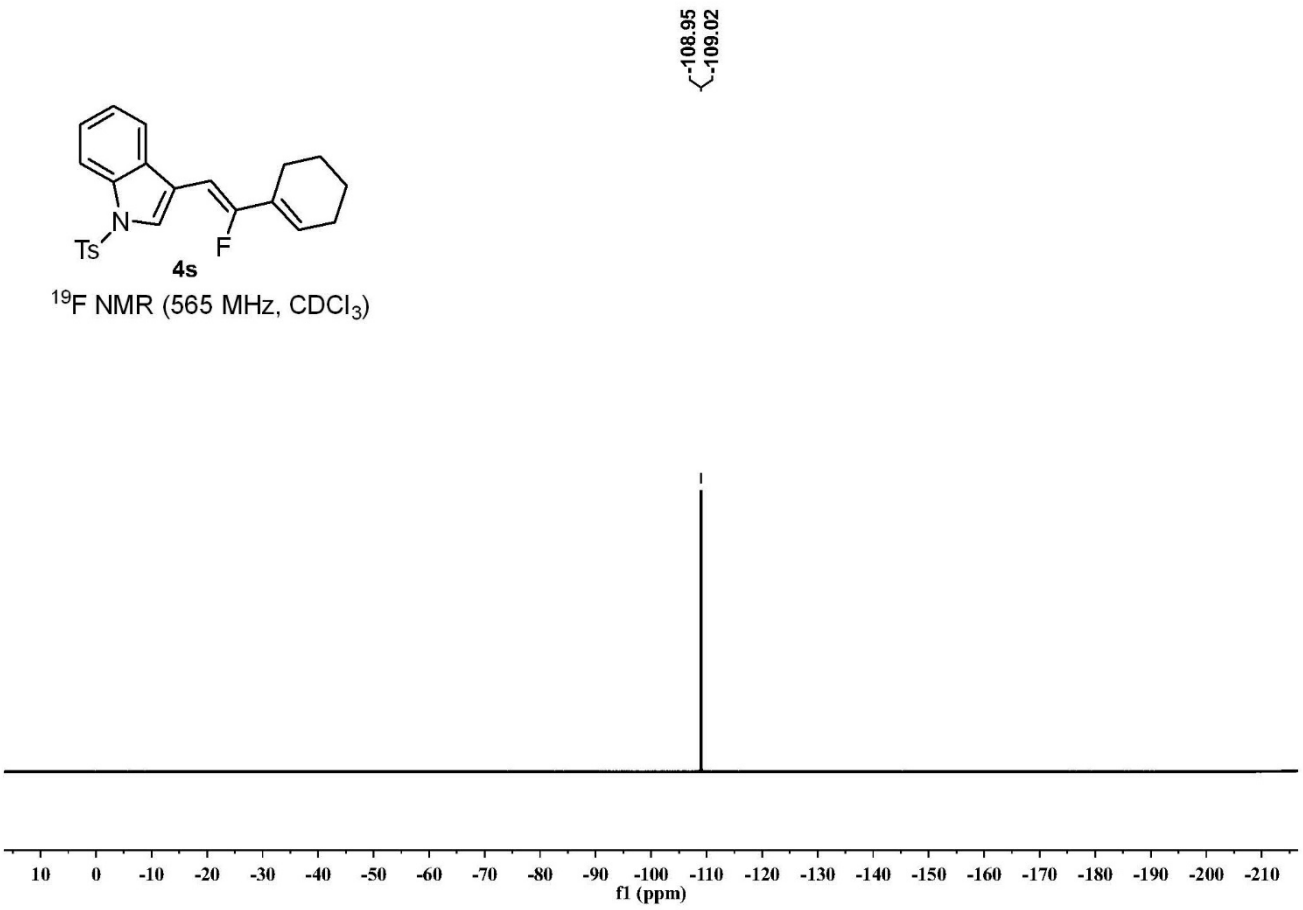


4s

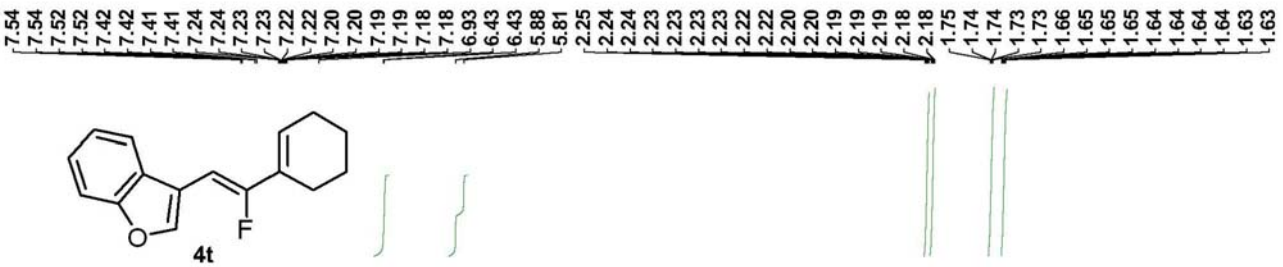
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

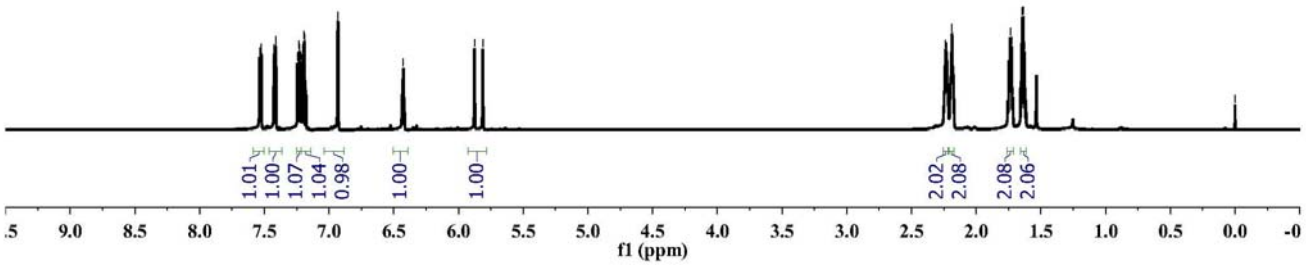


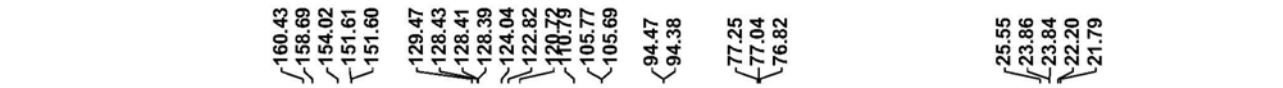
^{19}F NMR (565 MHz, $CDCl_3$)



4t

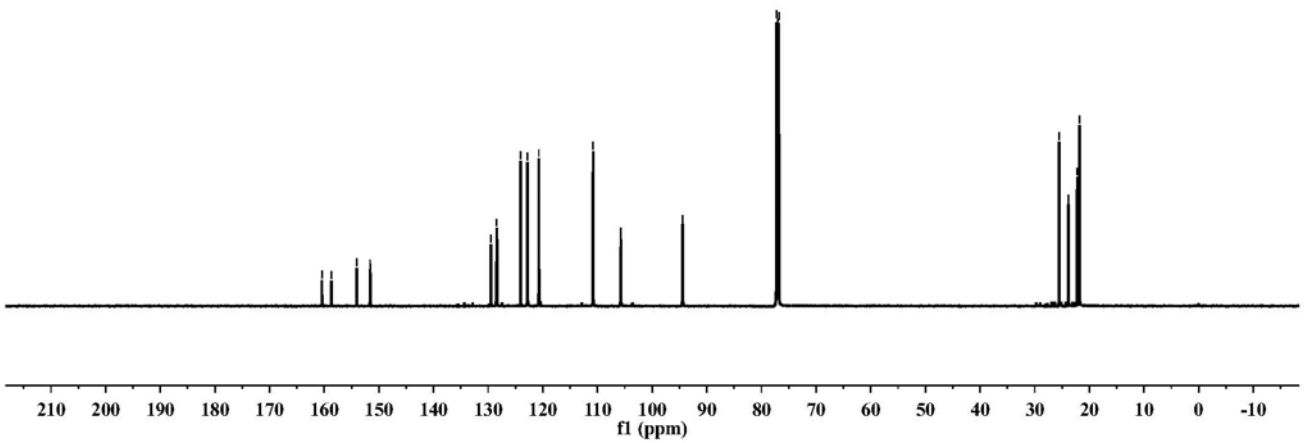
^{1}H NMR (600 MHz, $CDCl_3$)

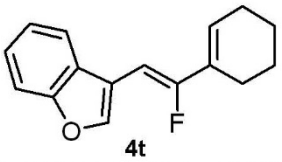




4t

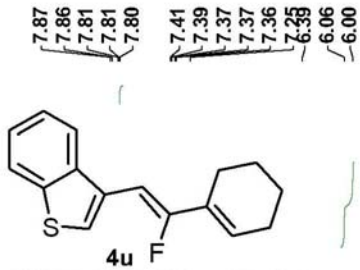
^{13}C NMR (151 MHz, $CDCl_3$)





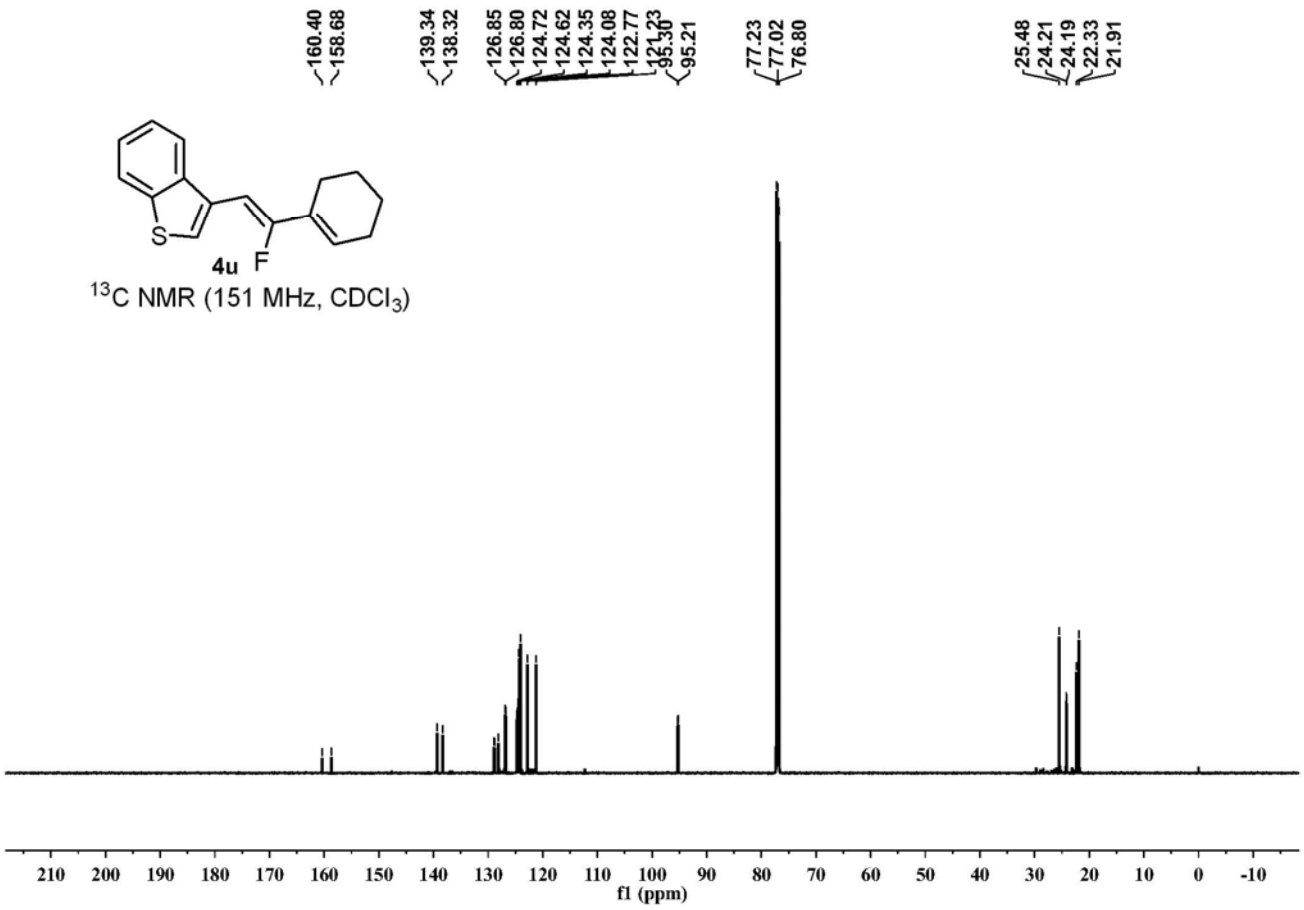
4t

^{19}F NMR (565 MHz, $CDCl_3$)

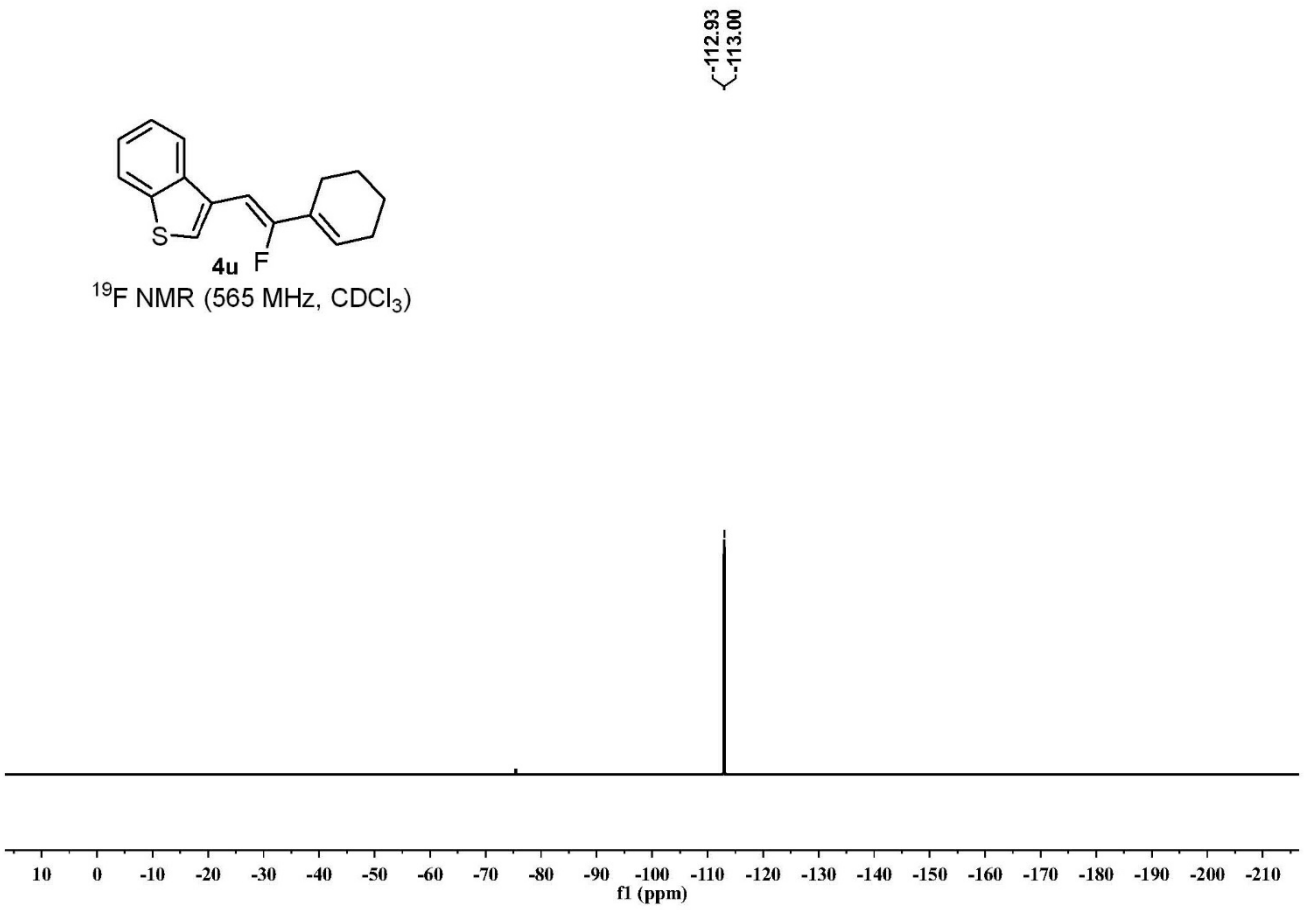


4u

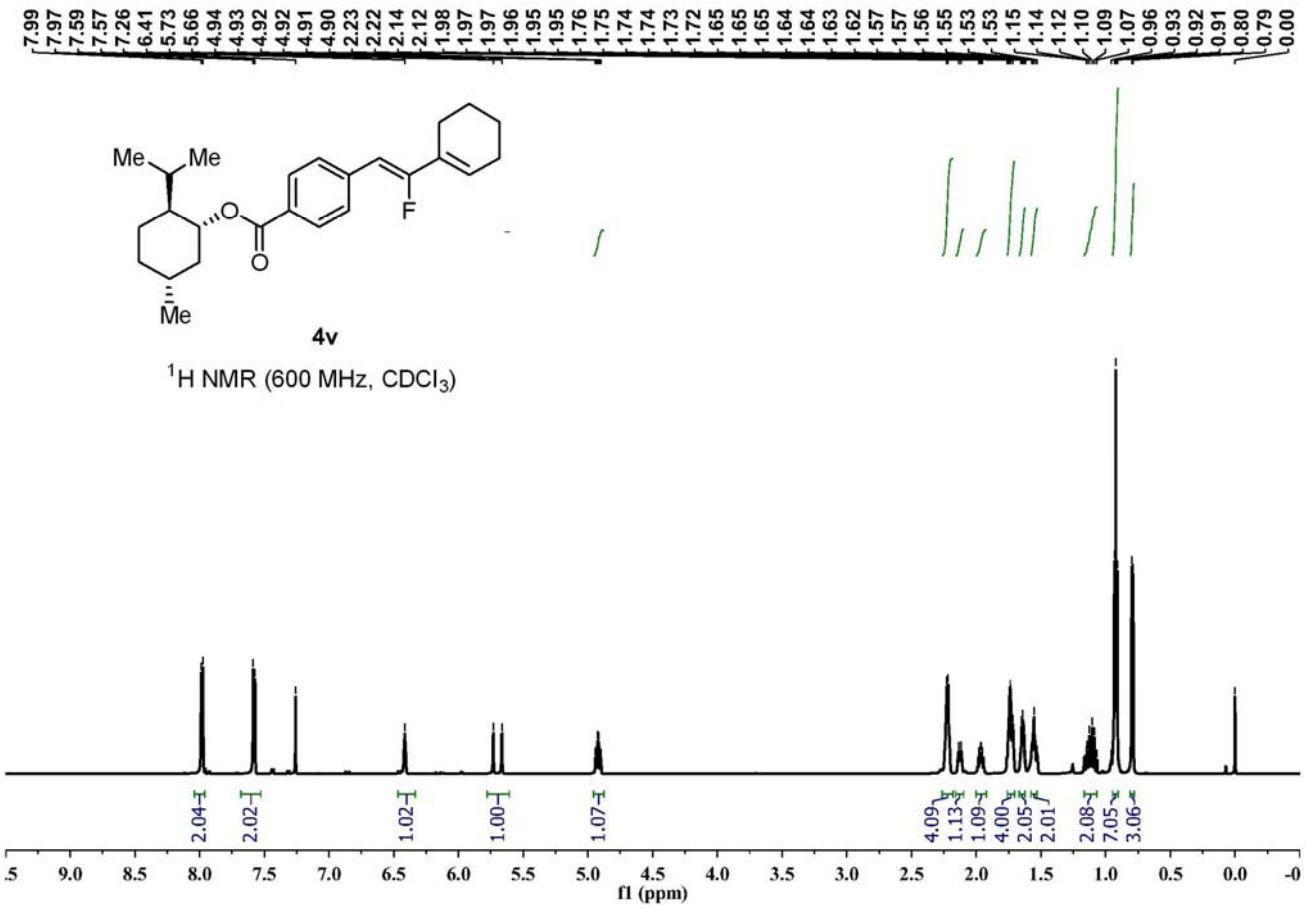
^{1}H NMR (600 MHz, $CDCl_3$)

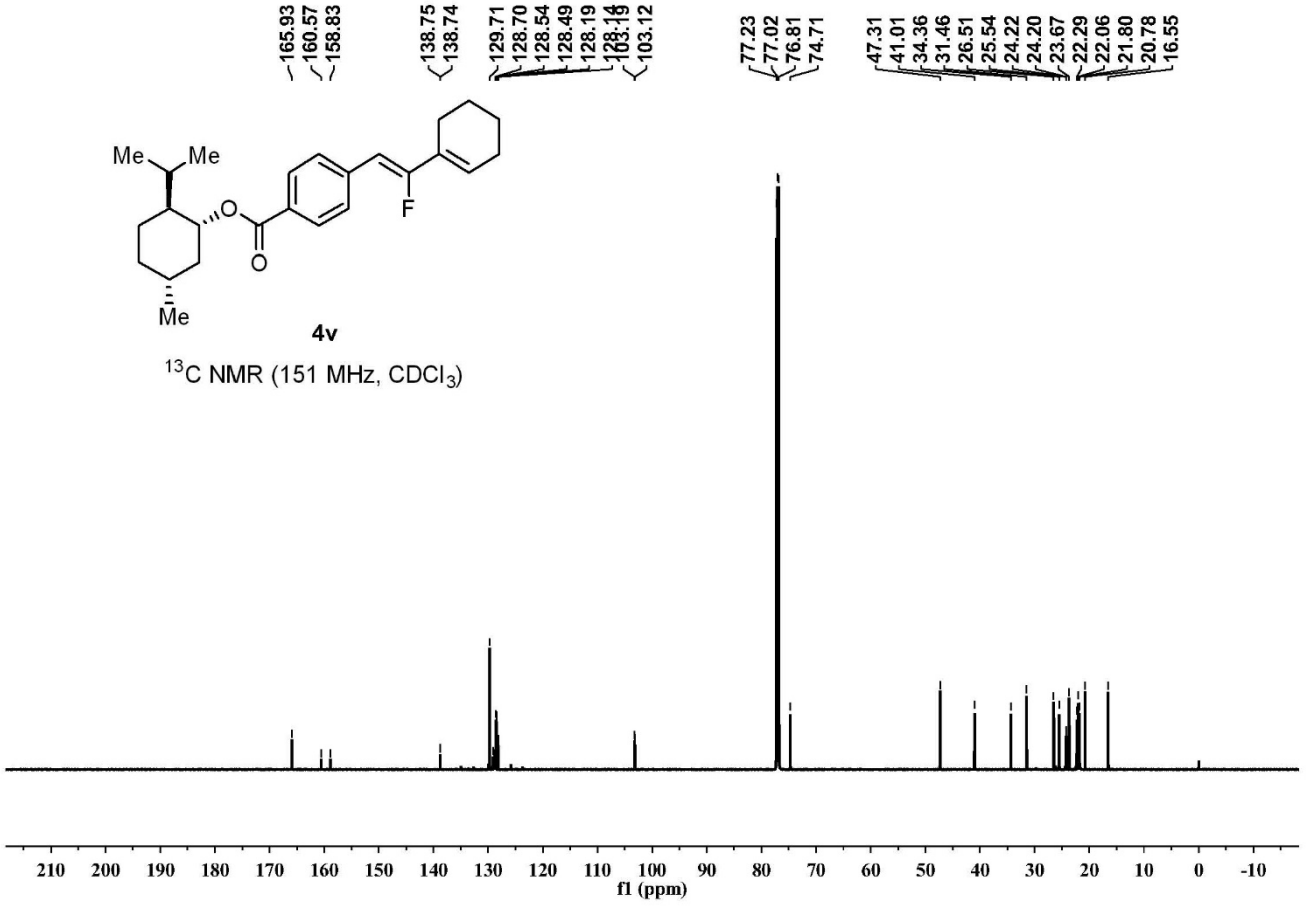


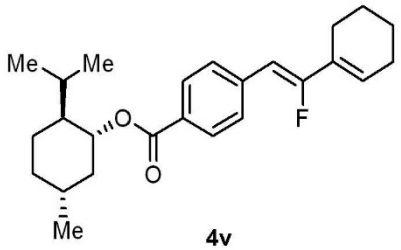
^{13}C NMR (151 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

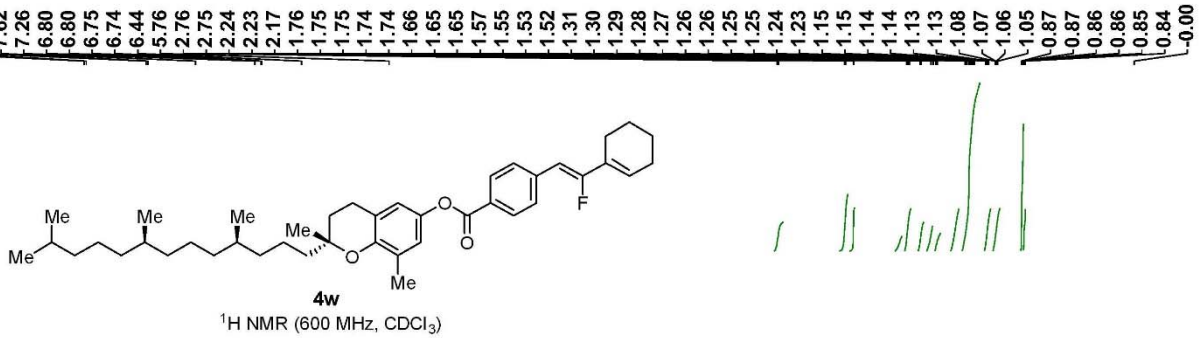

Me
Me
O
F
O
Me
4v
1H NMR (600 MHz, CDCl3)
f1 (ppm)


Me
Me
O
F
O
Me
4v
13C NMR (151 MHz, CDCl3)
f1 (ppm)



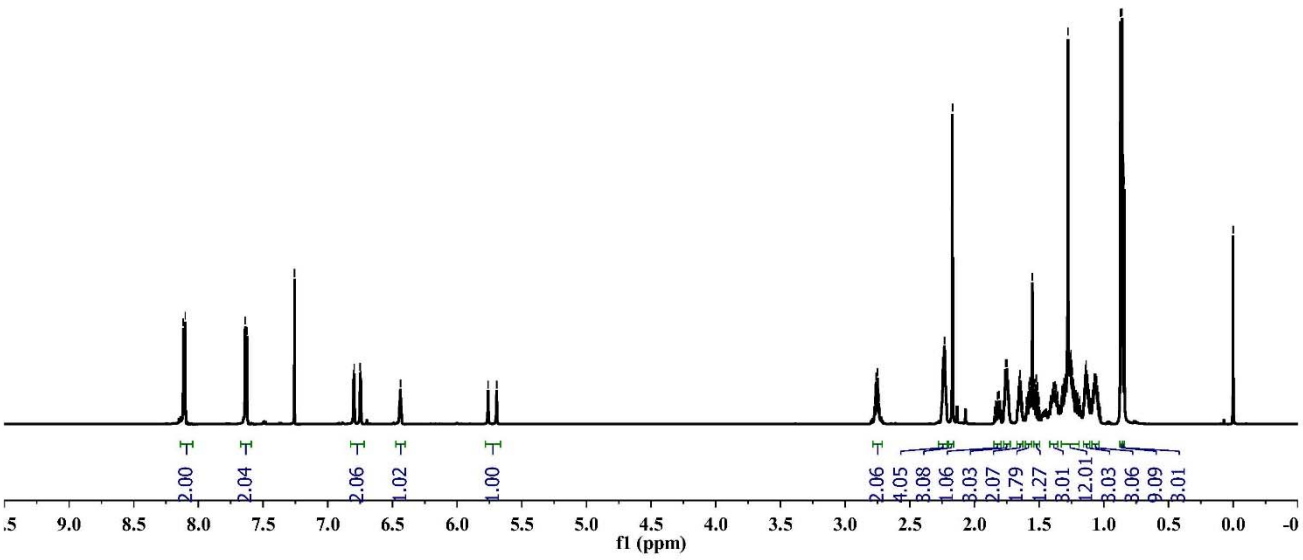
4v

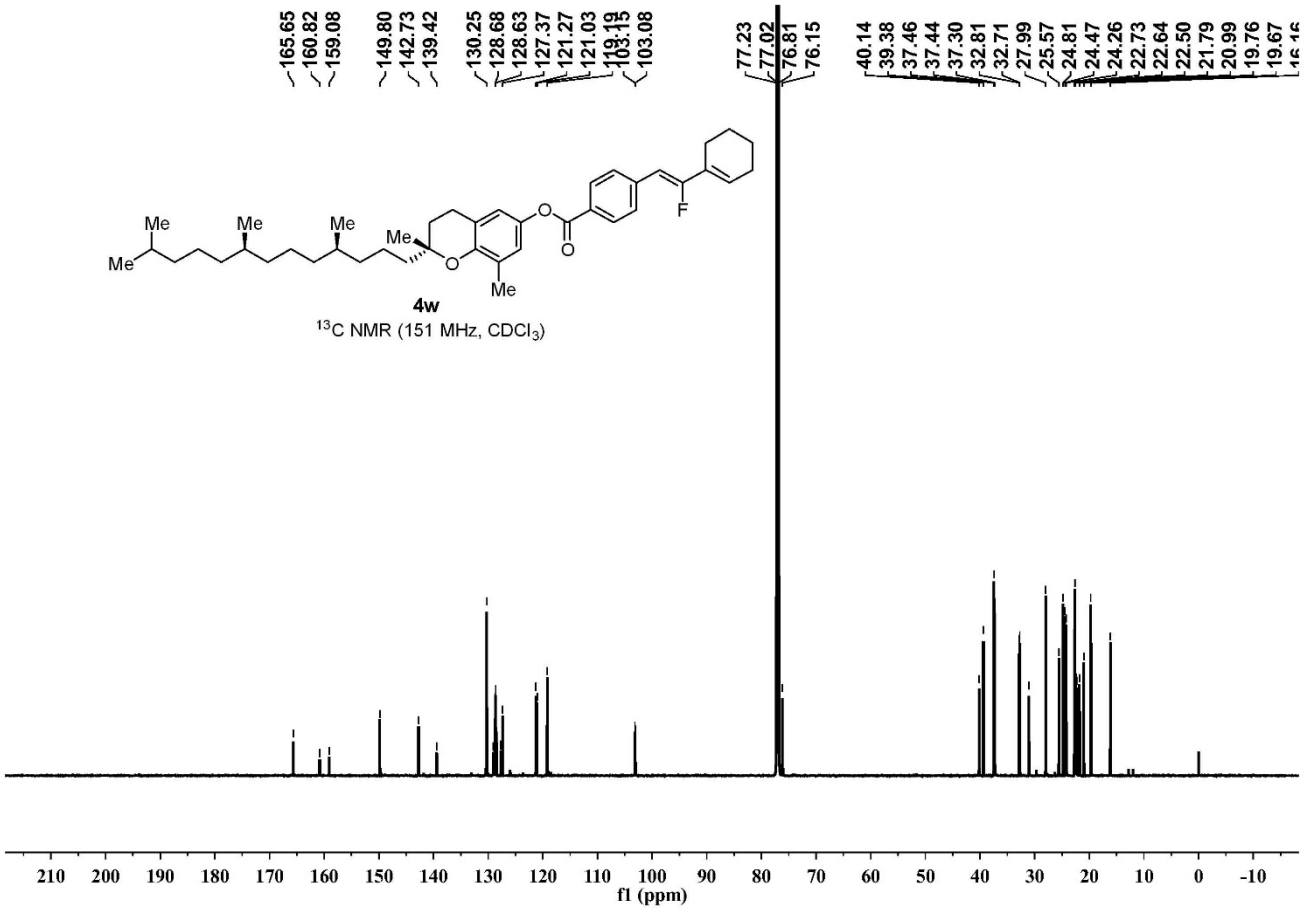
^{19}F NMR (565 MHz, $CDCl_3$)

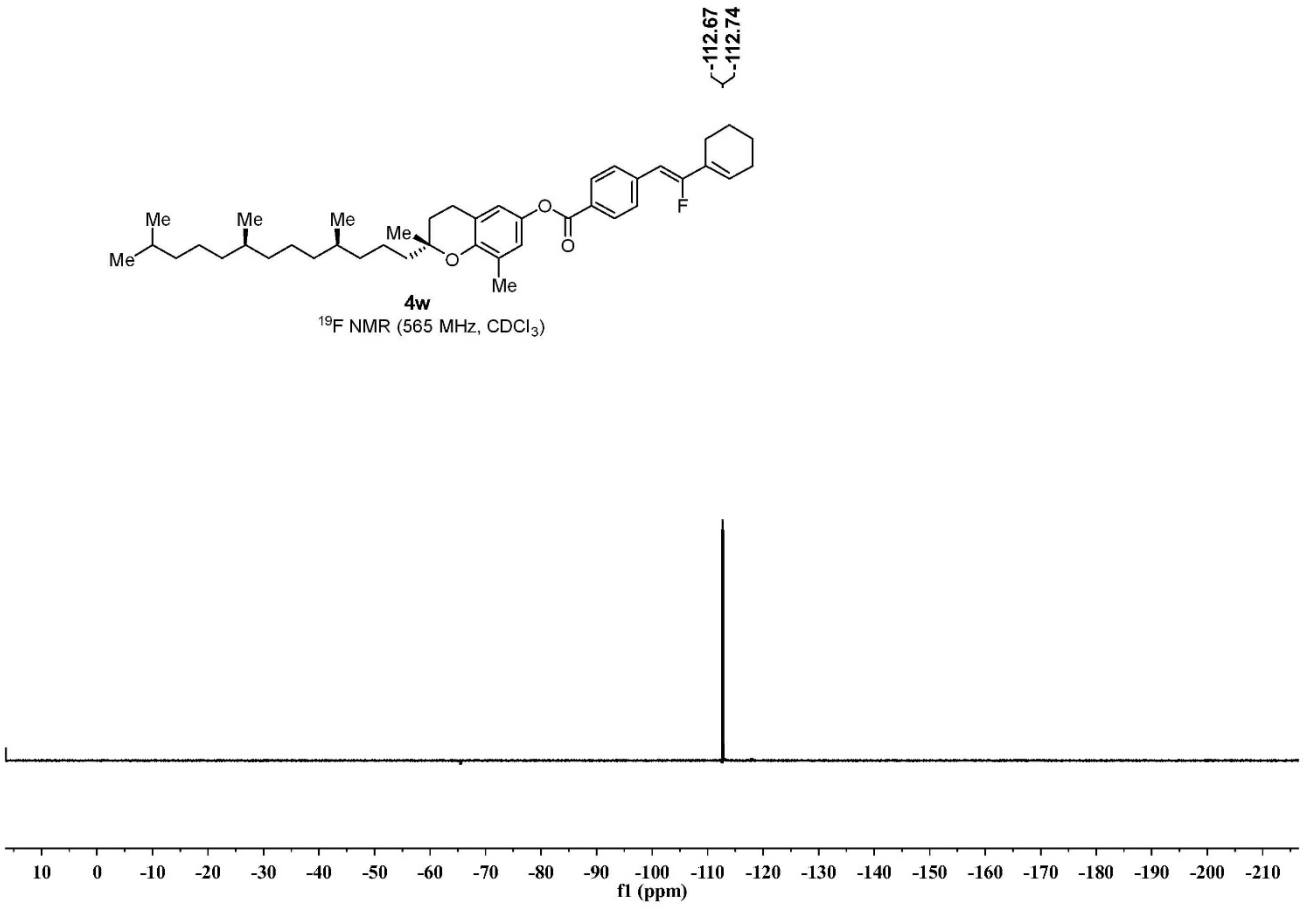


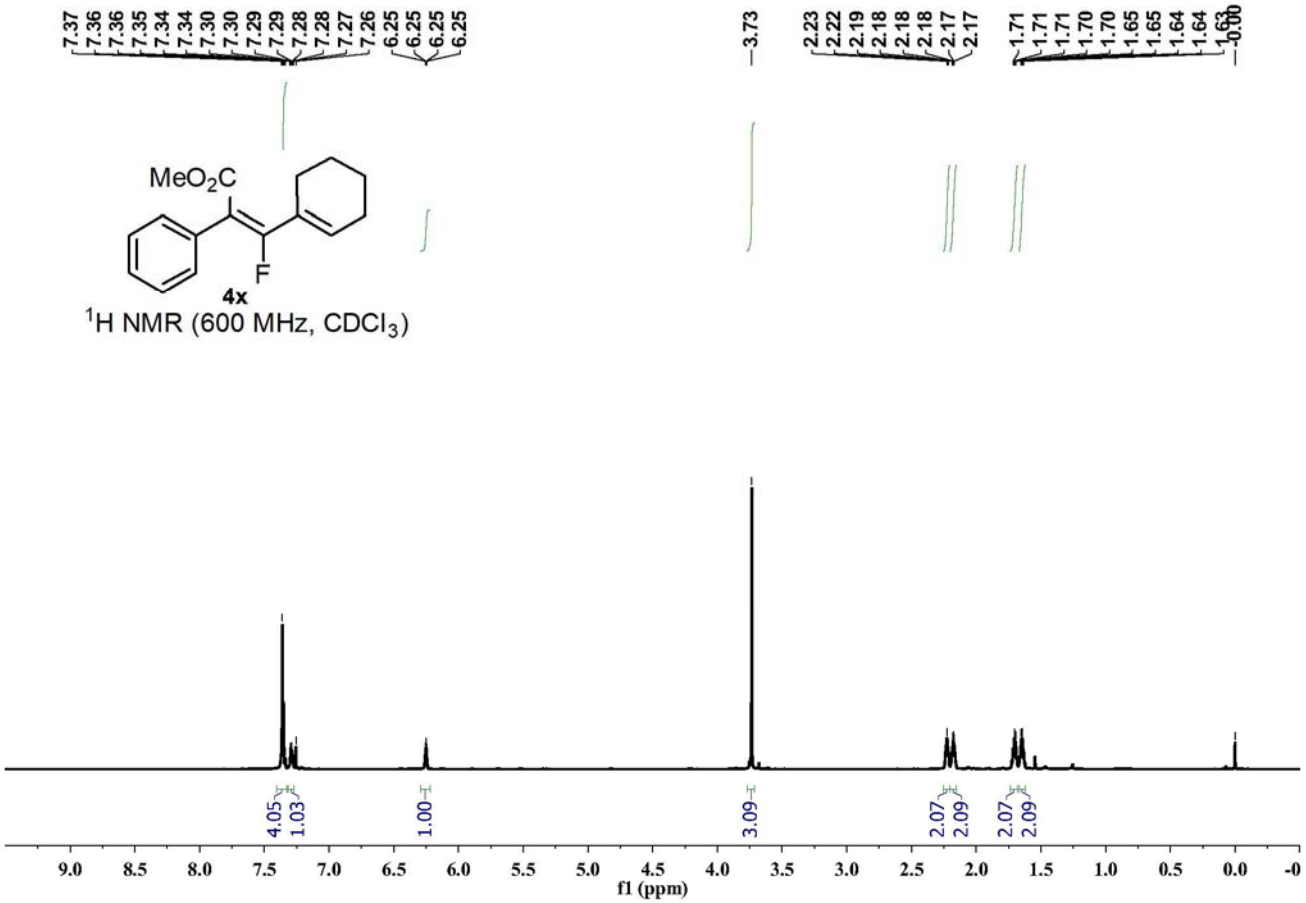
4w

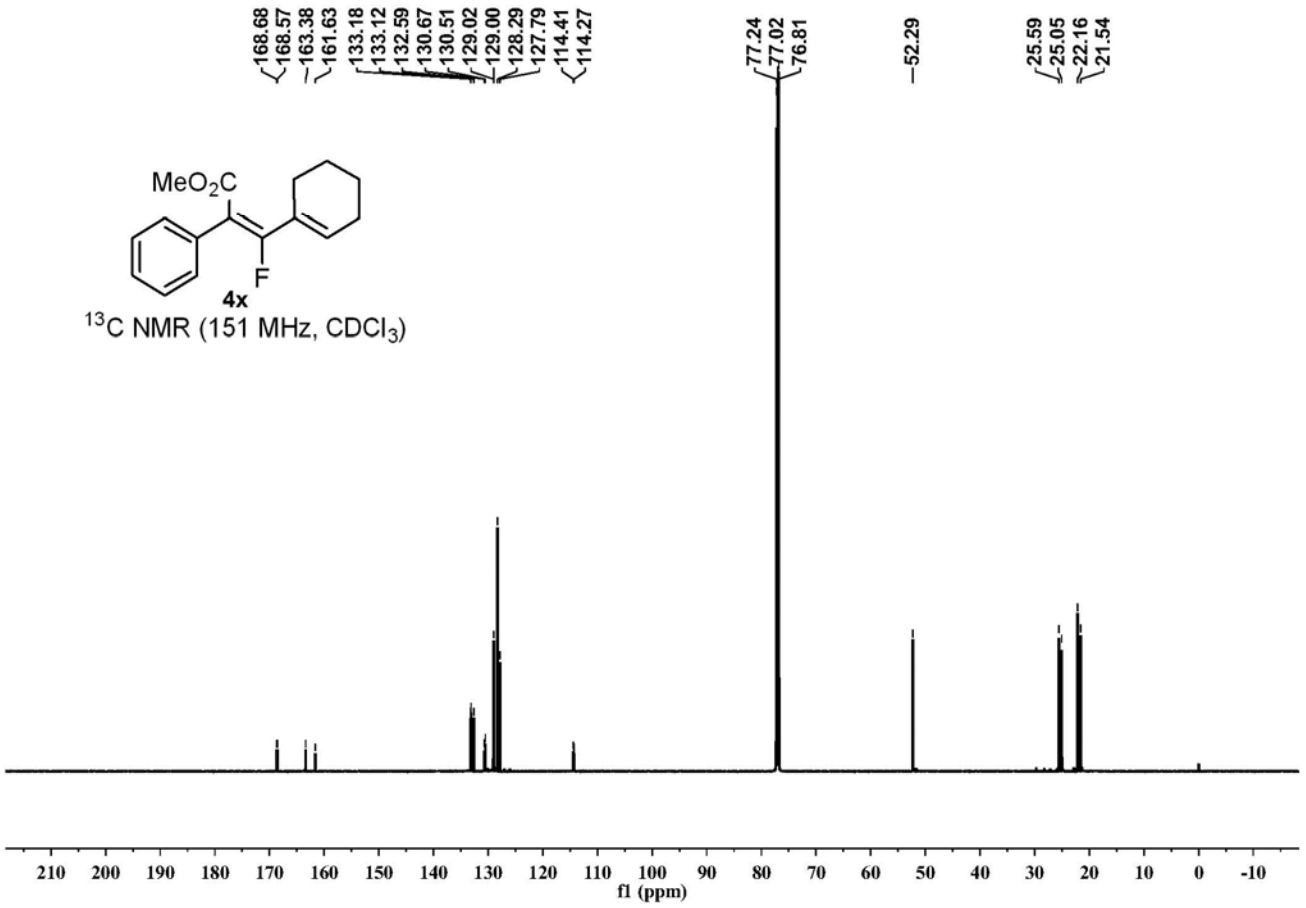
^{1}H NMR (600 MHz, $CDCl_3$)

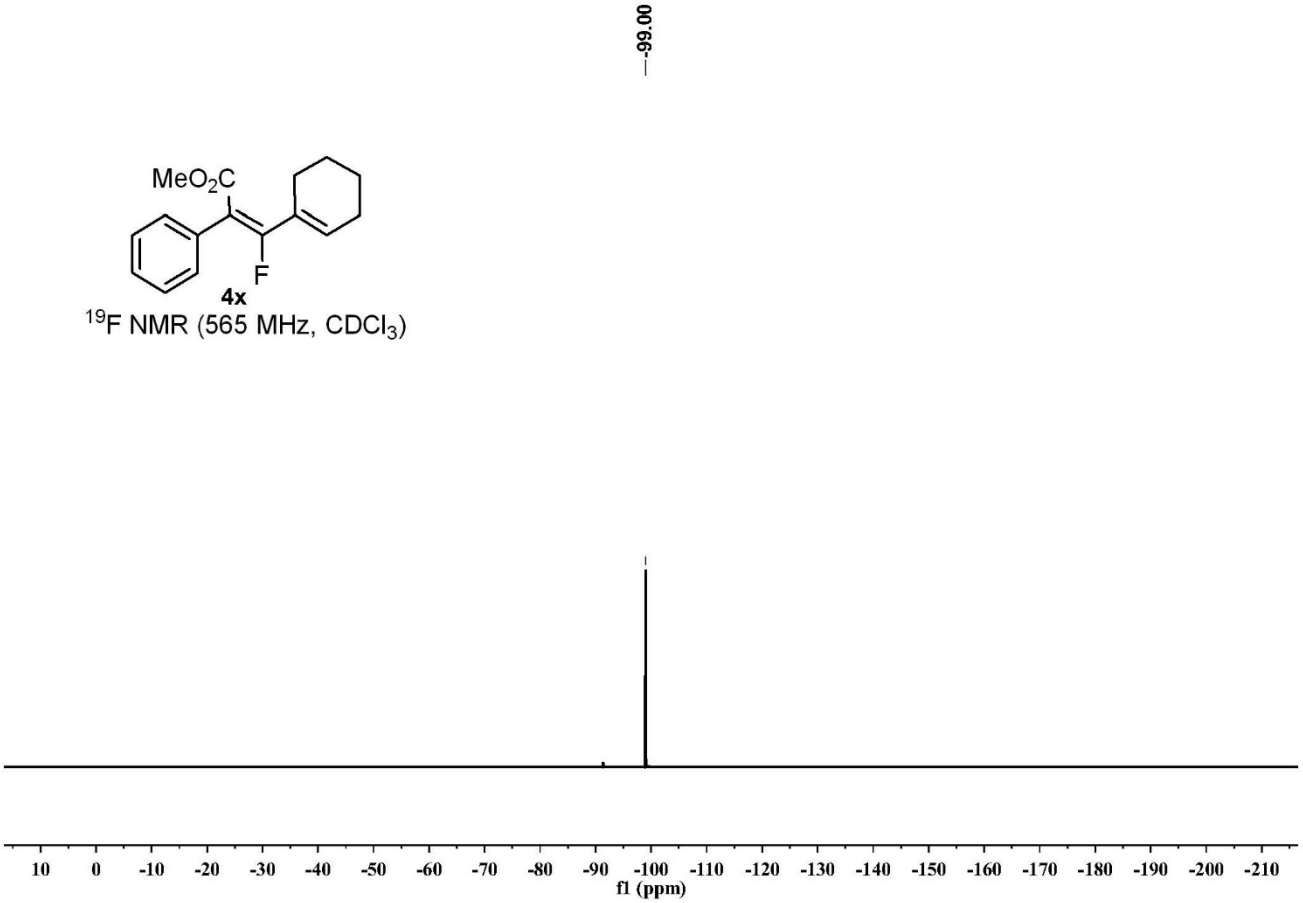


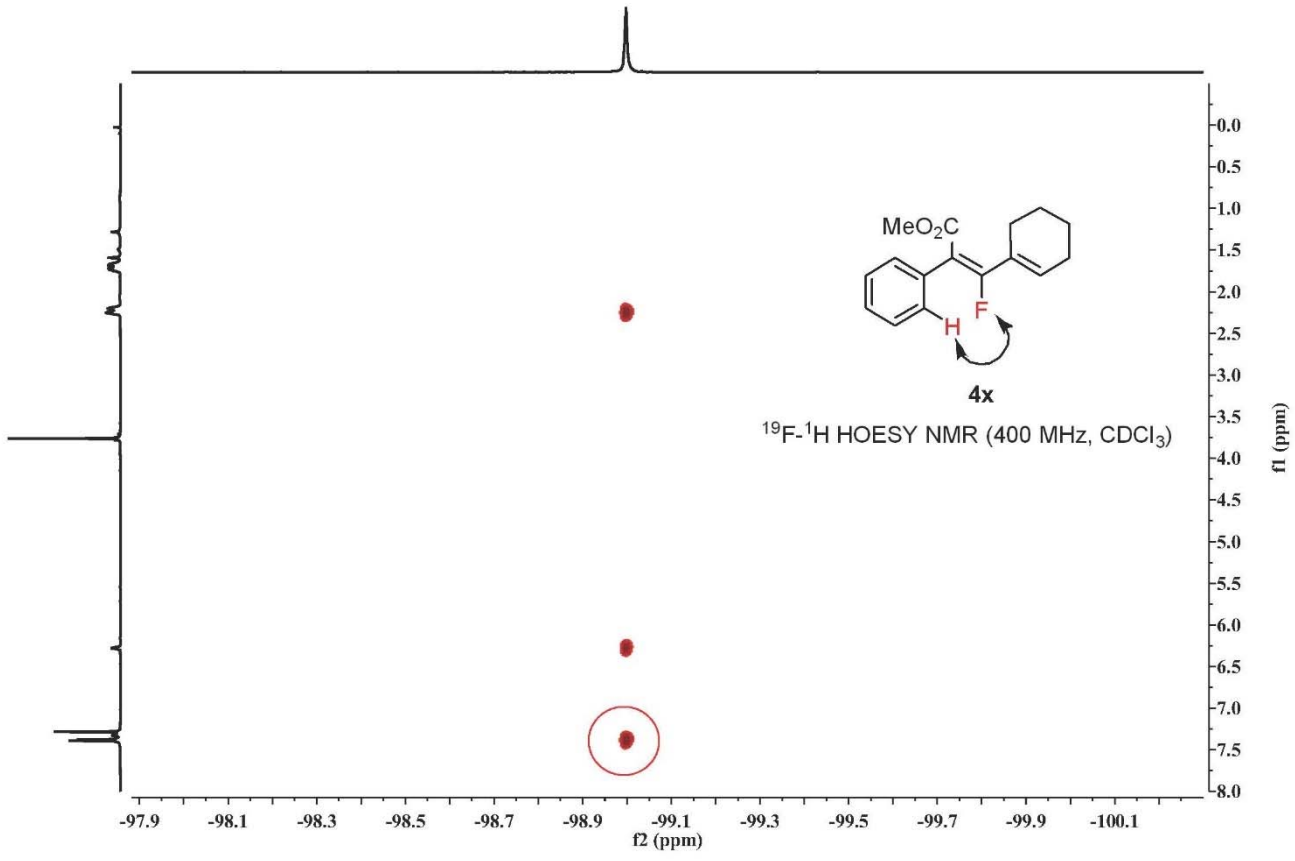

165.65
160.82
159.08
149.80
142.73
139.42
130.25
128.68
128.63
127.37
121.27
121.03
119.19
103.15
103.08
77.23
77.02
76.81
76.15
40.14
39.38
37.46
37.44
37.30
32.81
32.71
27.99
25.57
24.81
24.47
24.26
22.73
22.64
22.50
21.79
20.99
19.76
19.67
Me
Me
Me
Me
Me
O
O
O
F
Me
4w
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

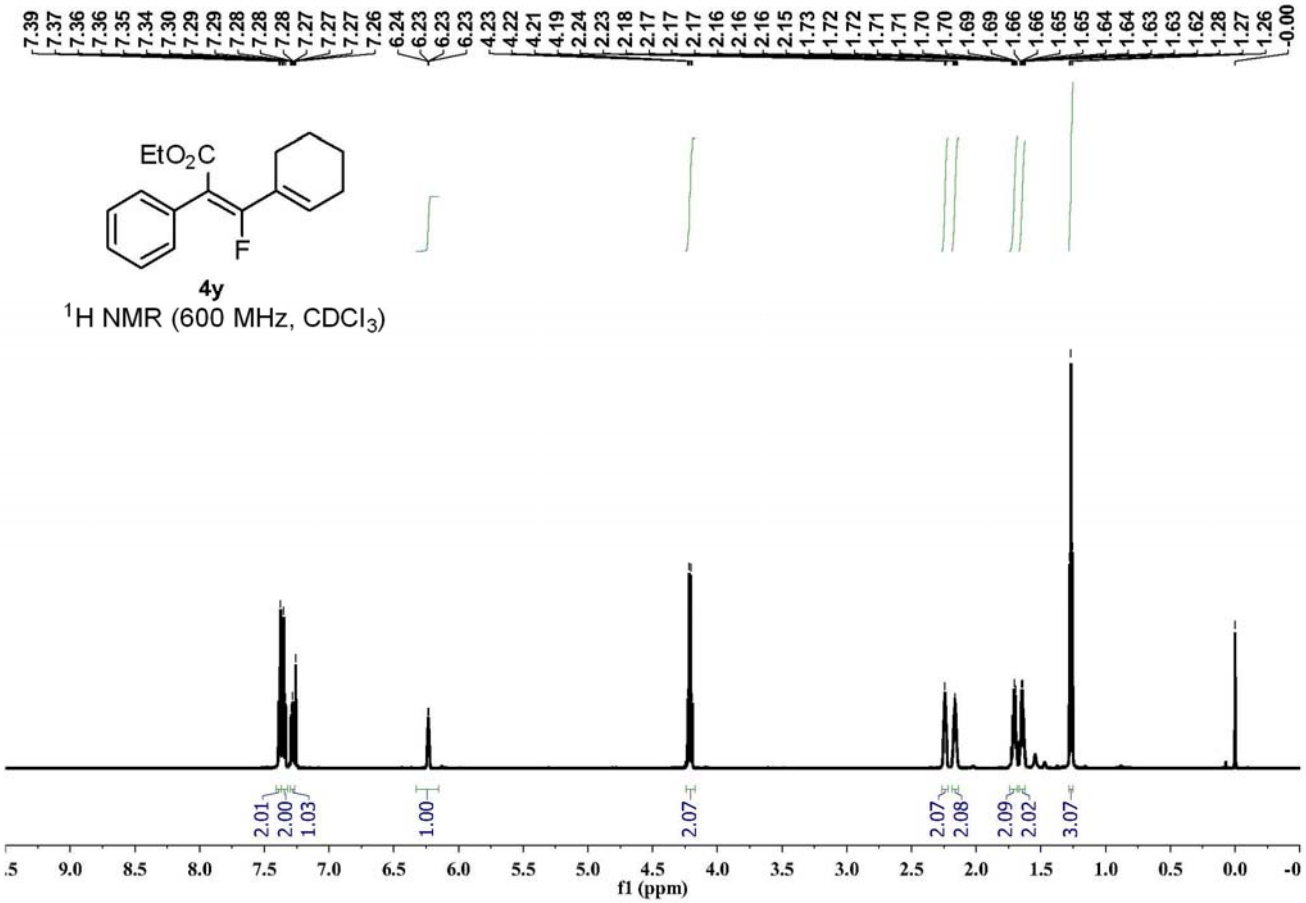

-112.67
-112.74
Me
Me
Me
Me
Me
O
O
O
F
Me
4w
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

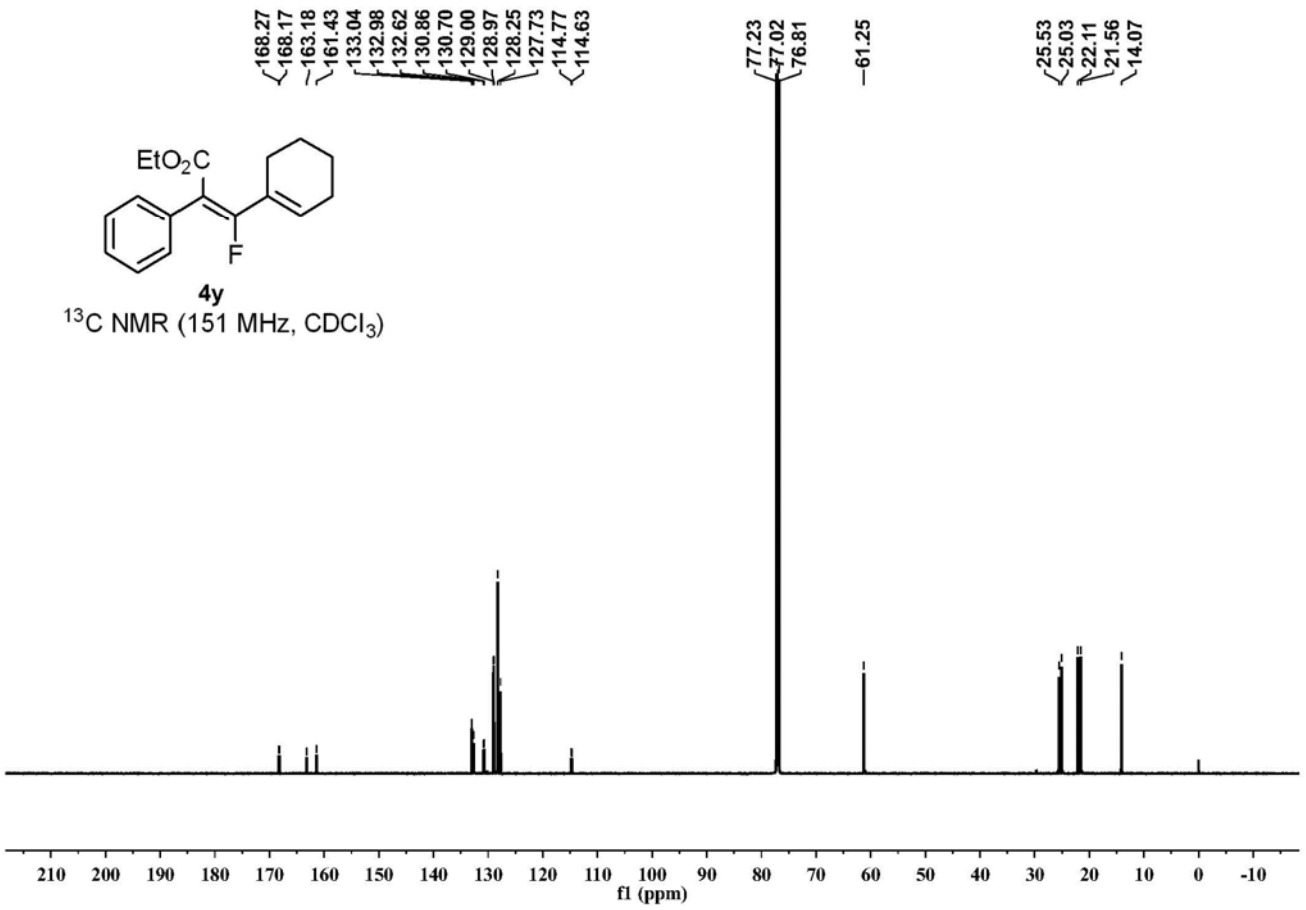

7.37
7.36
7.36
7.35
7.34
7.34
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
6.25
6.25
6.25
6.25
3.73
2.23
2.22
2.19
2.18
2.18
2.17
2.17
1.71
1.71
1.71
1.70
1.70
1.65
1.65
1.64
1.64
1.63
0.00
MeO2C
F
4x
1H NMR (600 MHz, CDCl3)
4.05
1.03
1.00
3.09
2.07
2.09
2.07
2.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

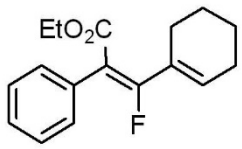

168.68
168.57
163.38
161.63
133.18
133.12
132.59
130.67
130.51
129.02
129.00
128.29
127.79
114.41
114.27
77.24
77.02
76.81
52.29
25.59
25.05
22.16
21.54
MeO2C
F
4x
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-99.00
MeO2C
F
4x
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


MeO2C
F
H
4x
19F-1H HOESY NMR (400 MHz, CDCl3)
-97.9 -98.1 -98.3 -98.5 -98.7 -98.9 -99.1 -99.3 -99.5 -99.7 -99.9 -100.1
f2 (ppm)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0
f1 (ppm)

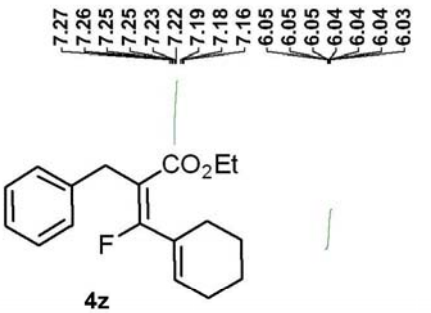

7.39 7.37 7.36 7.36 7.35 7.34 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.26 6.24 6.23 6.23 6.23 4.23 4.22 4.21 4.19 2.24 2.23 2.18 2.17 2.17 2.17 2.16 2.16 2.16 2.15 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.69 1.66 1.66 1.65 1.65 1.64 1.64 1.63 1.63 1.62 1.28 1.27 1.26 -0.00
EtO2C
F
4y
1H NMR (600 MHz, CDCl3)
2.01 2.00 1.03 1.00 2.07 2.07 2.08 2.09 2.02 3.07
f1 (ppm)


168.27 168.17 163.18 161.43 133.04 132.98 132.62 130.86 130.70 129.00 128.97 128.25 127.73 114.77 114.63
77.23 77.02 76.81 61.25
25.53 25.03 22.11 21.56 14.07
EtO2C
F
4y
13C NMR (151 MHz, CDCl3)
f1 (ppm)



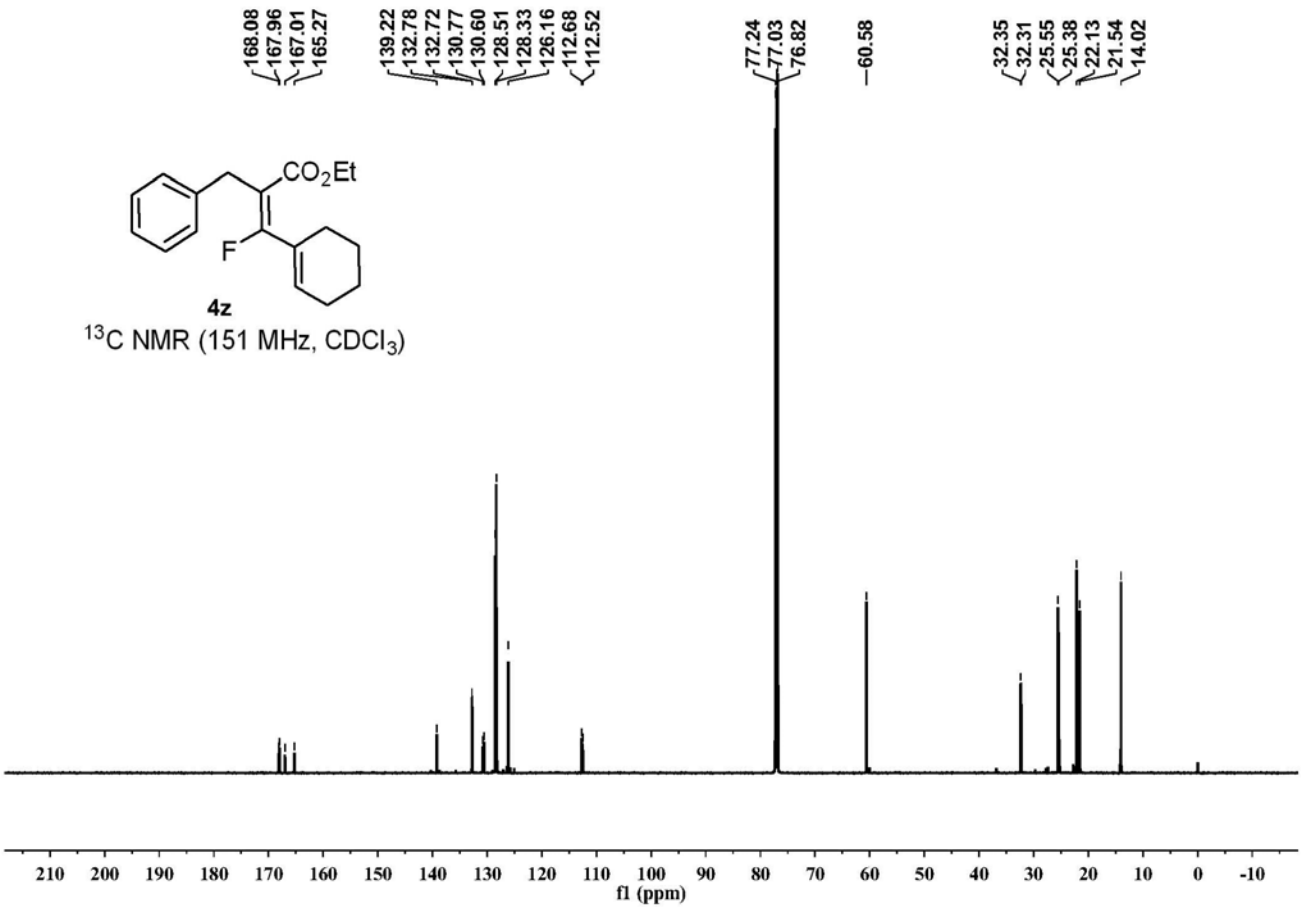
4y

^{19}F NMR (565 MHz, $CDCl_3$)



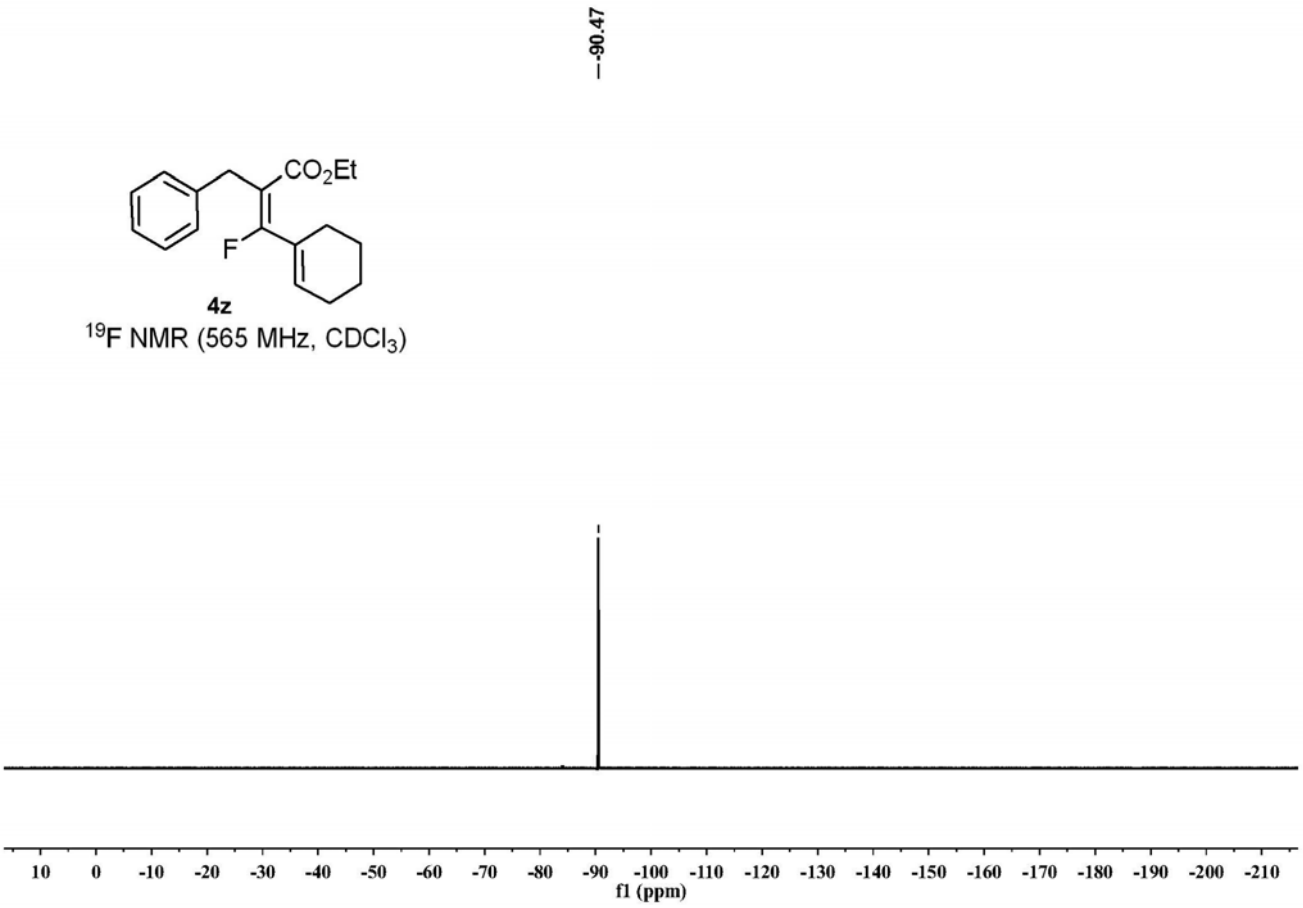
4z

^{1}H NMR (600 MHz, $CDCl_3$)



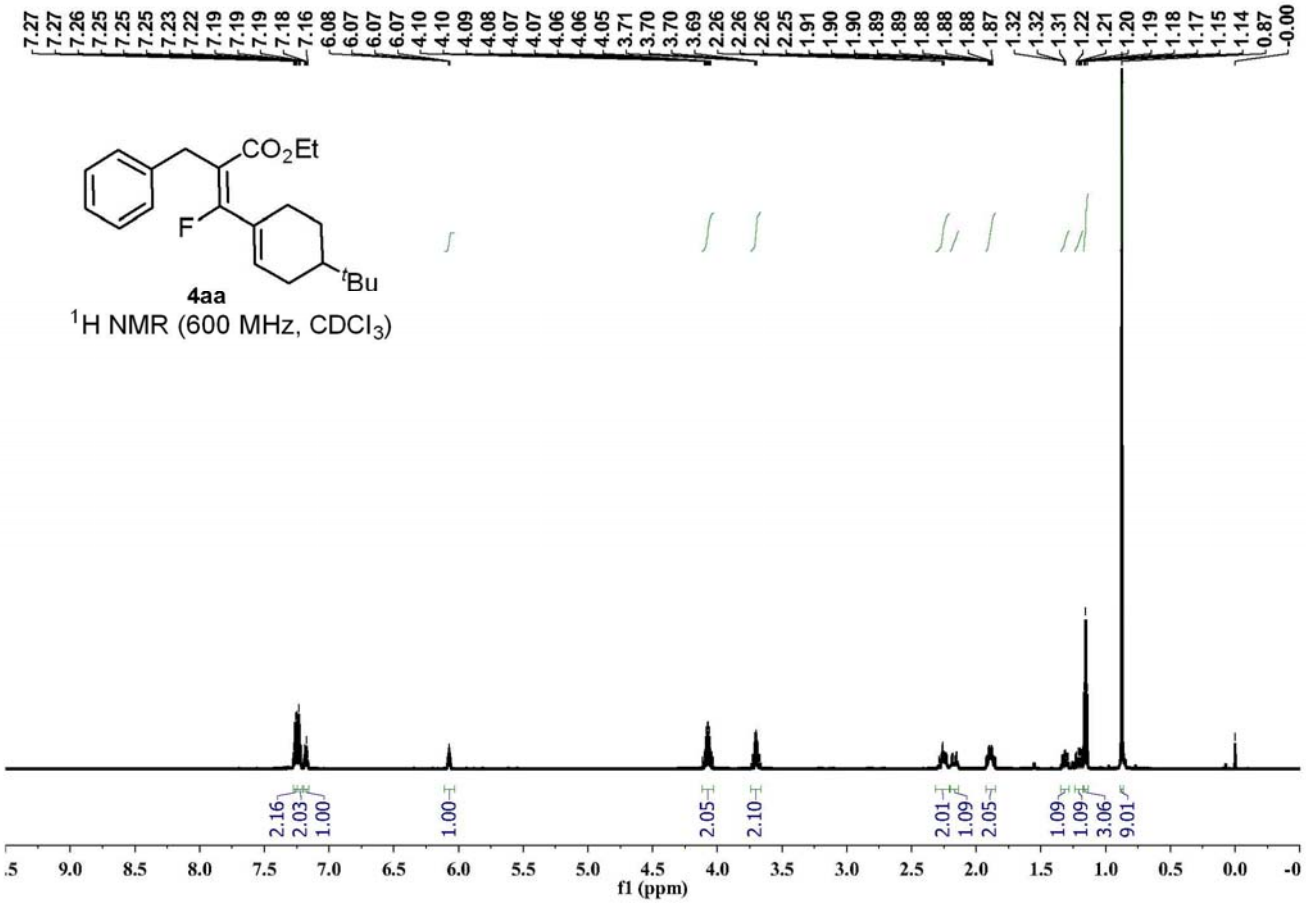
4z

^{13}C NMR (151 MHz, $CDCl_3$)



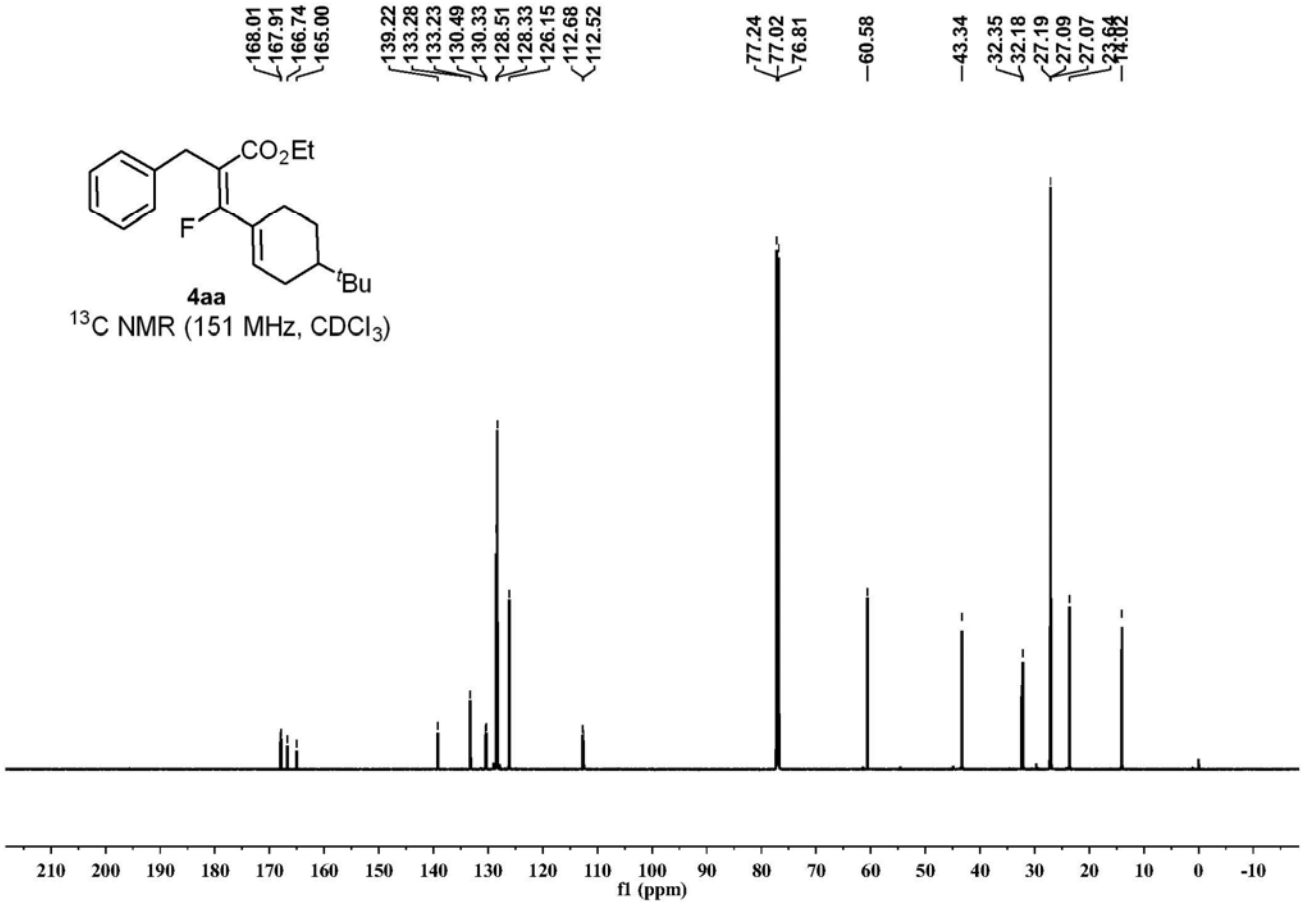
4z

^{19}F NMR (565 MHz, $CDCl_3$)



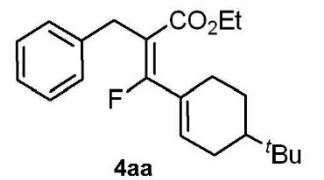
4aa

^{1}H NMR (600 MHz, $CDCl_3$)



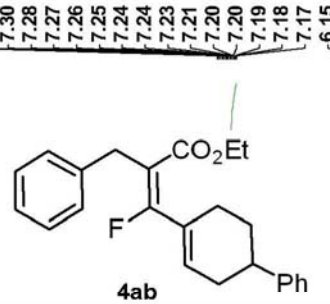
4aa

^{13}C NMR (151 MHz, $CDCl_3$)



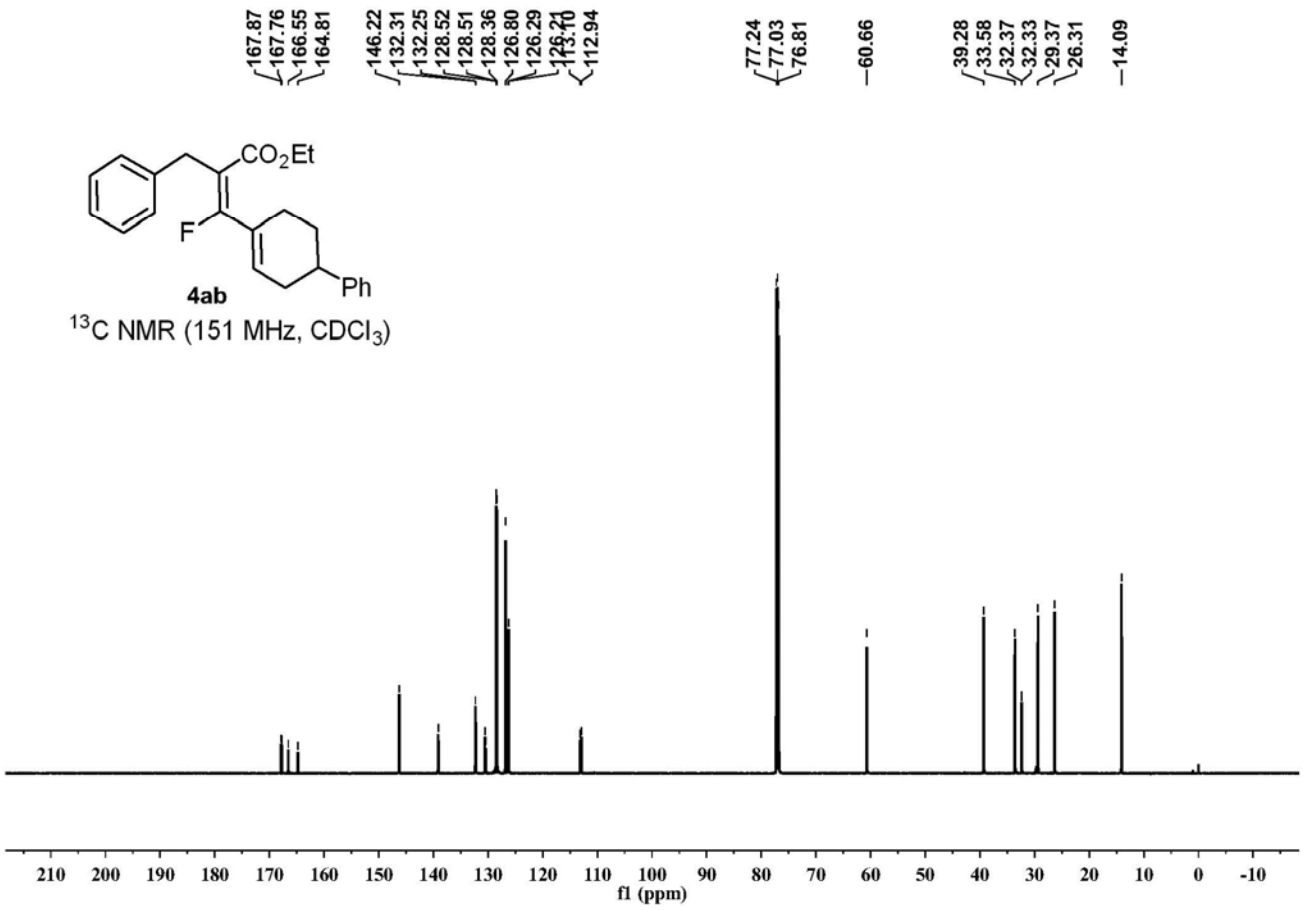
4aa

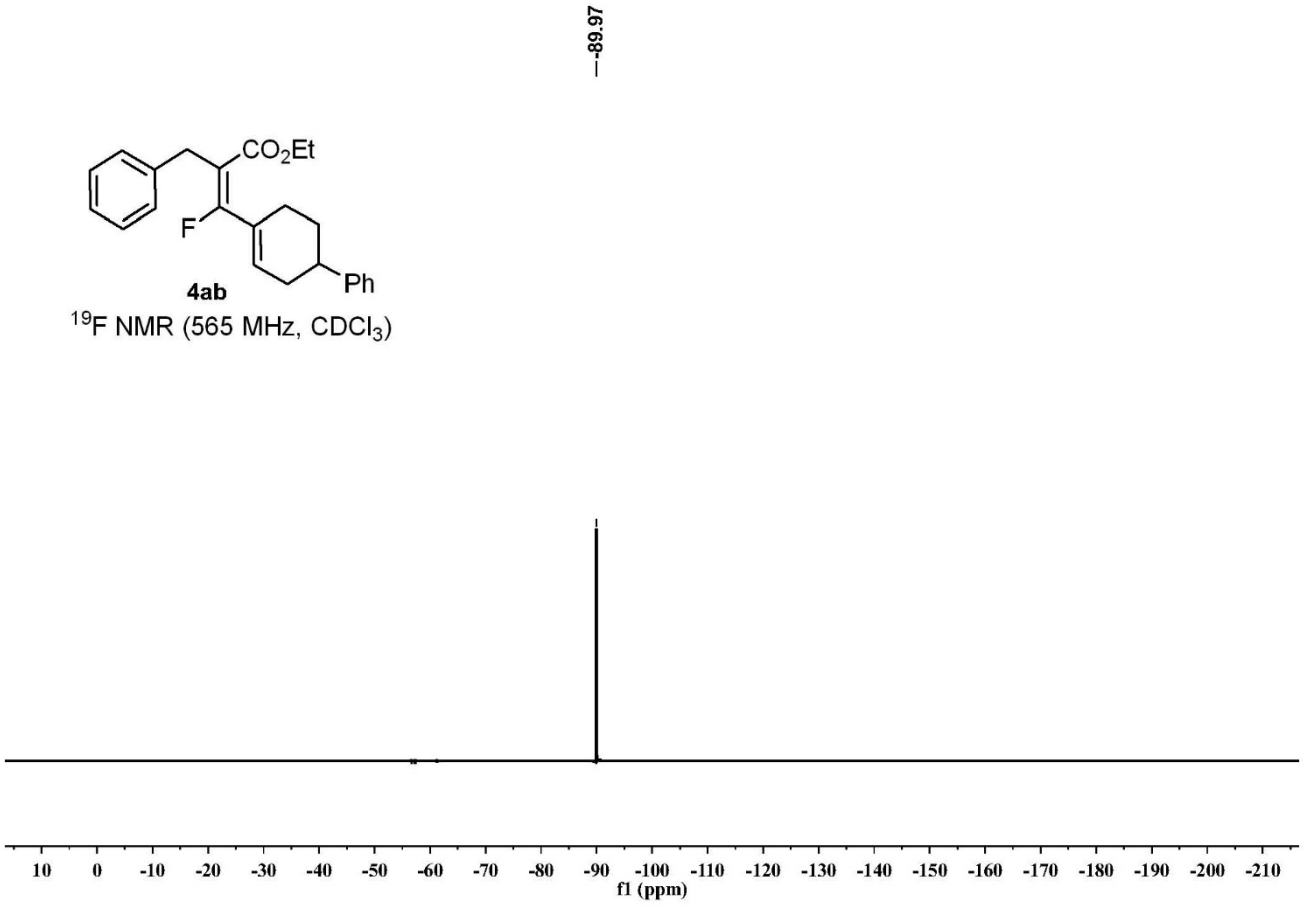
^{19}F NMR (565 MHz, $CDCl_3$)

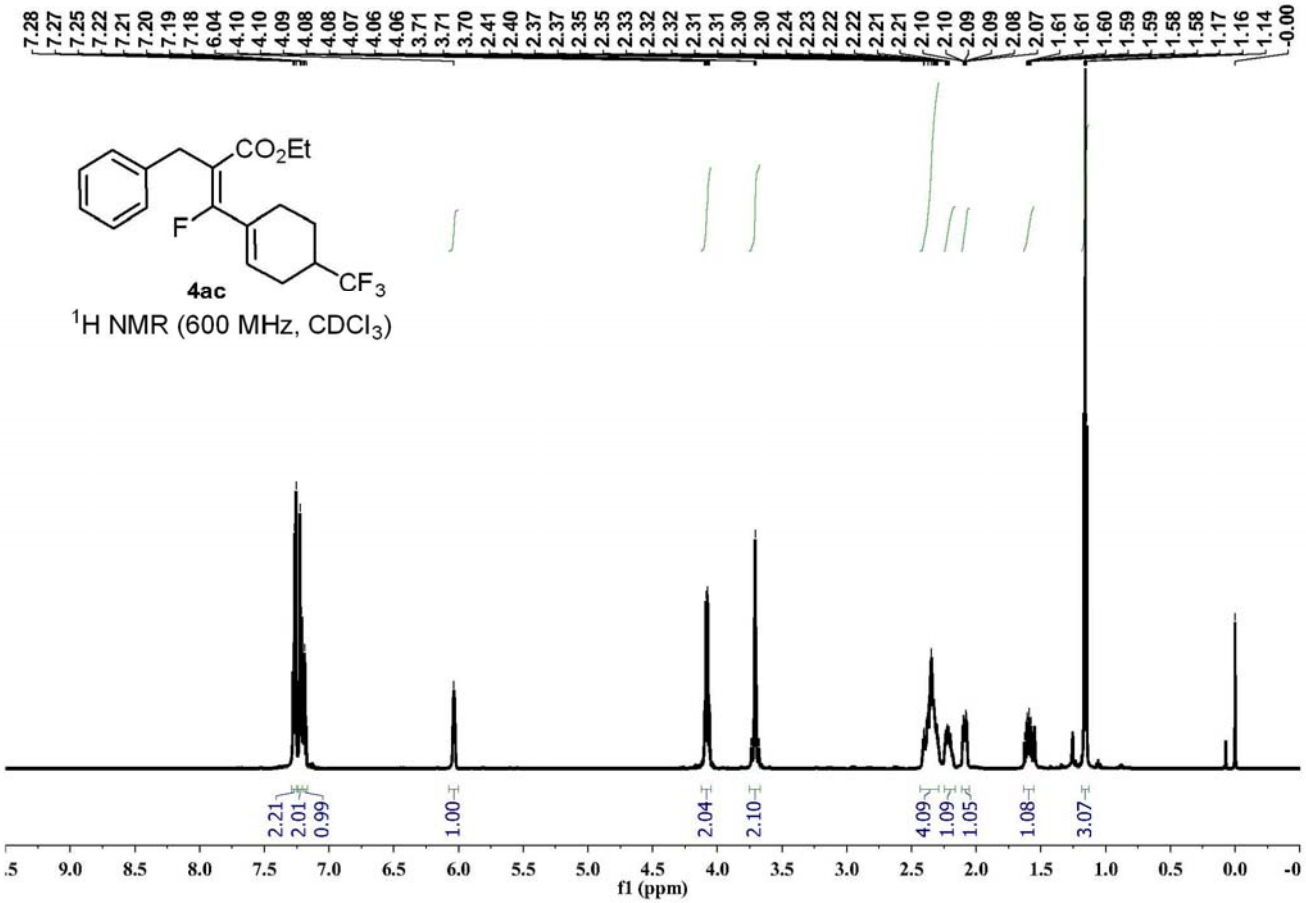


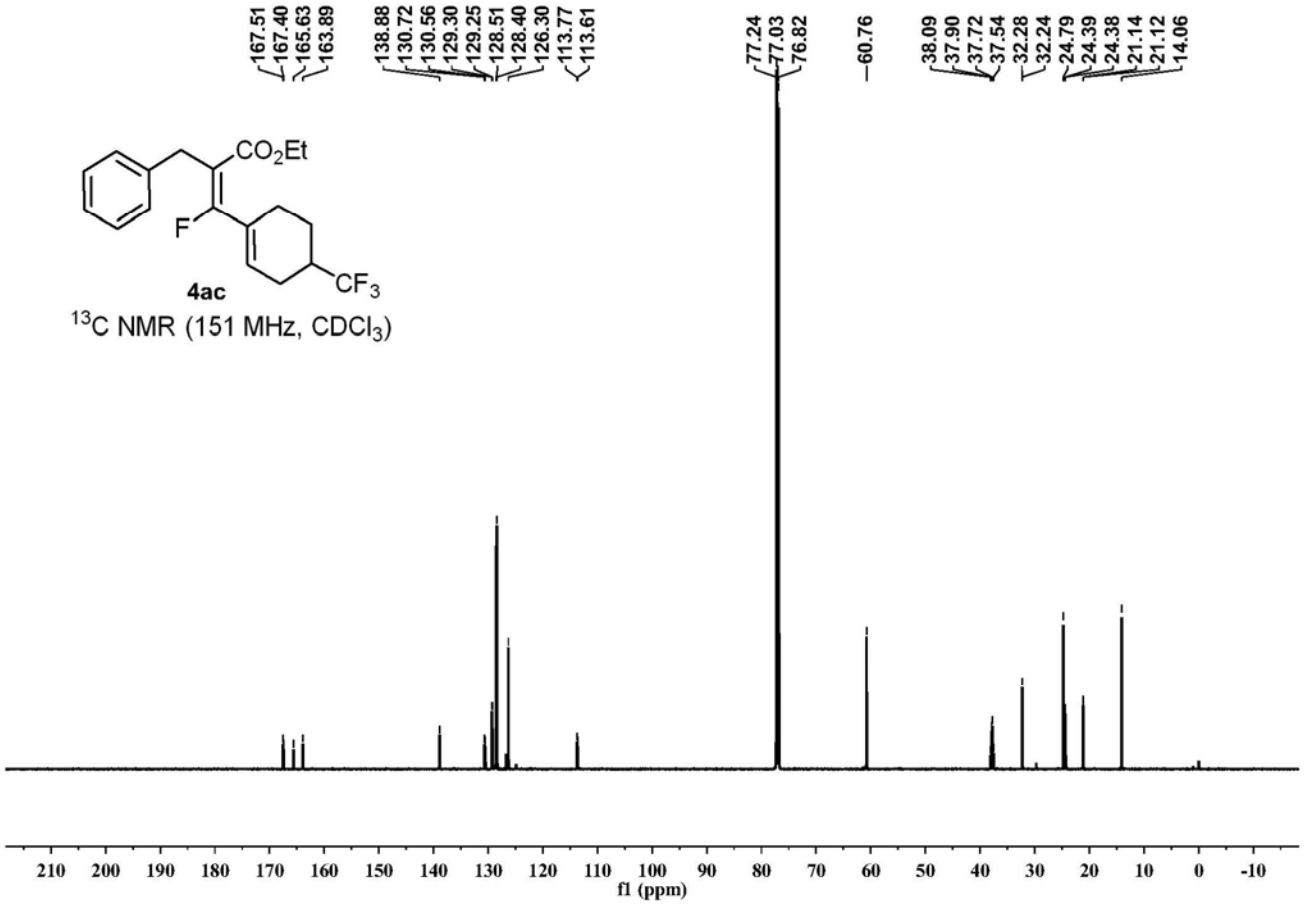
4ab

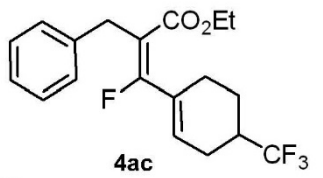
^{1}H NMR (600 MHz, $CDCl_3$)


167.87
167.76
166.55
164.81
146.22
132.31
132.25
128.52
128.51
128.36
126.80
126.29
126.21
113.10
112.94
77.24
77.03
76.81
60.66
39.28
33.58
32.37
32.33
29.37
26.31
14.09
CO2Et
F
Ph
4ab
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-89.97
CO2Et
F
Ph
4ab
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

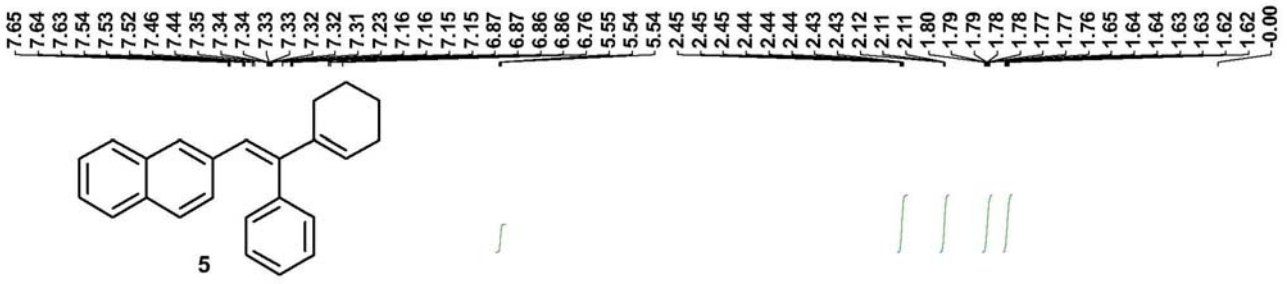

CO2Et
F
CF3
4ac
1H NMR (600 MHz, CDCl3)
f1 (ppm)


CO2Et
F
CF3
4ac
13C NMR (151 MHz, CDCl3)
f1 (ppm)



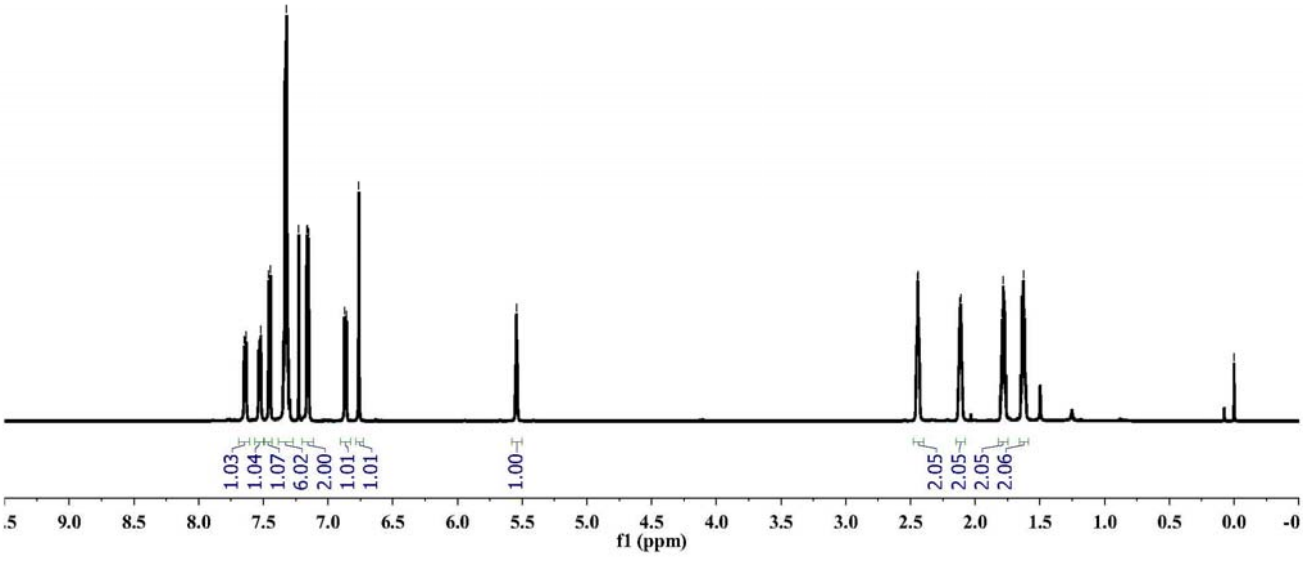
4ac

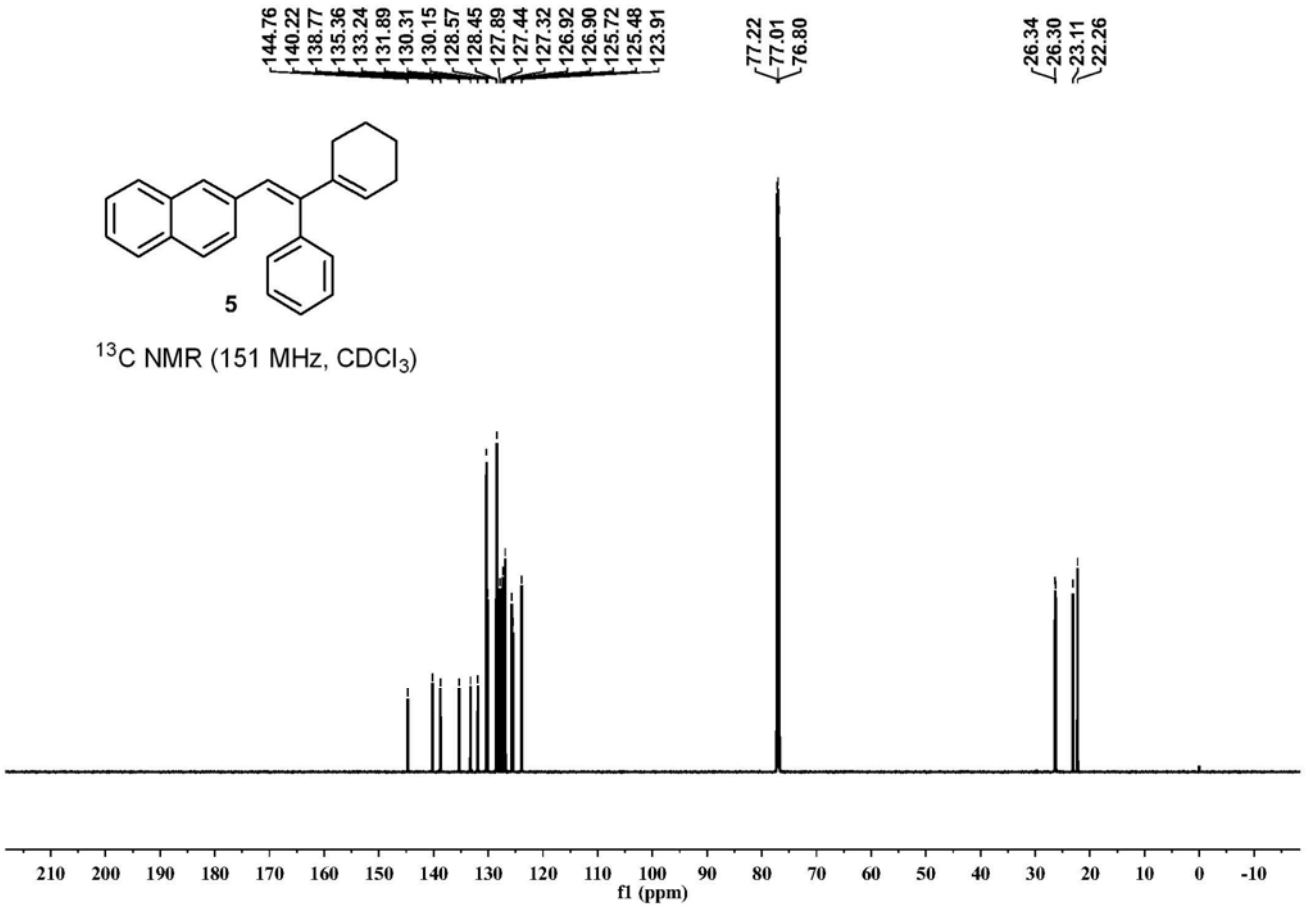
^{19}F NMR (565 MHz, $CDCl_3$)



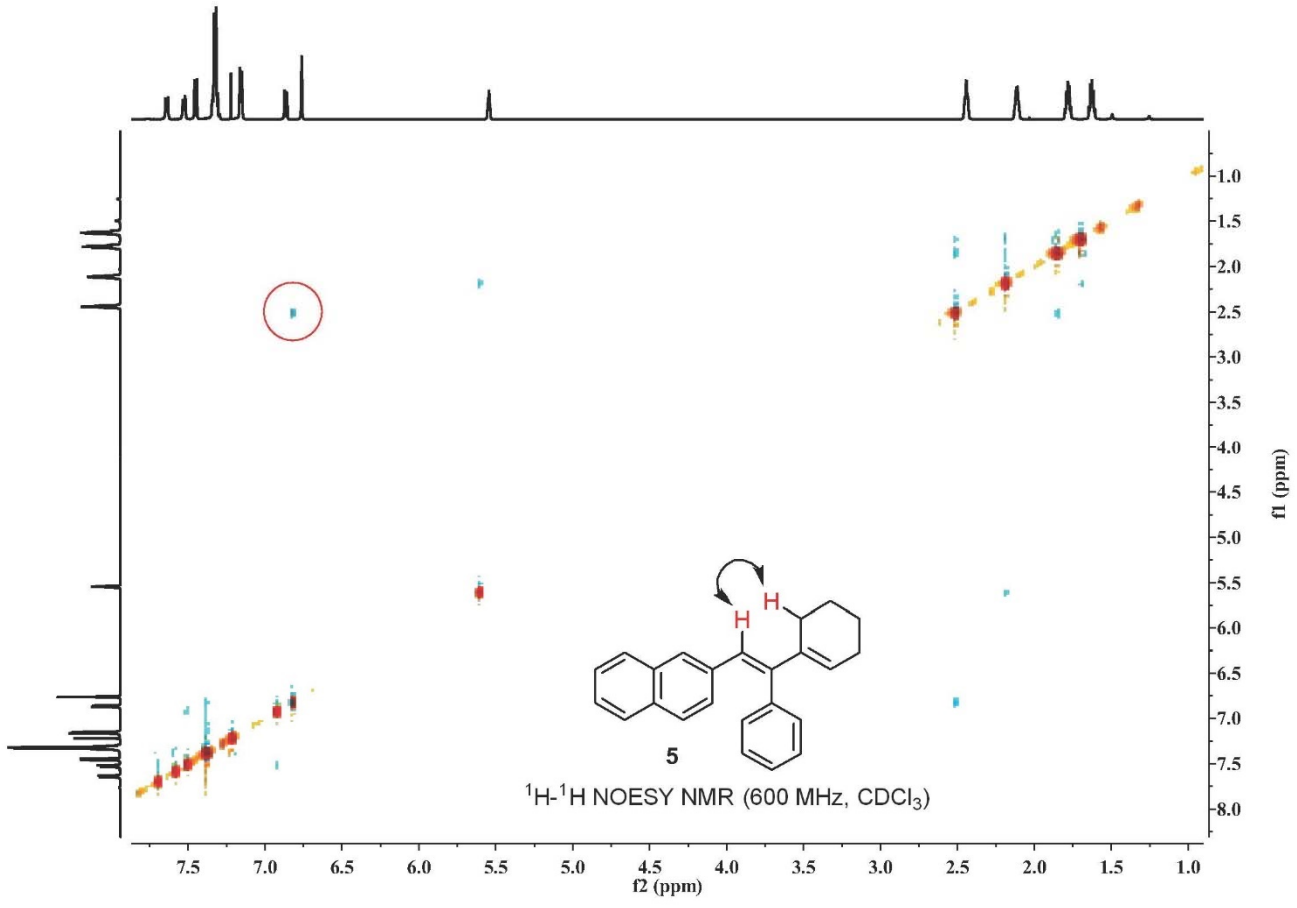
5

^{1}H NMR (600 MHz, $CDCl_3$)

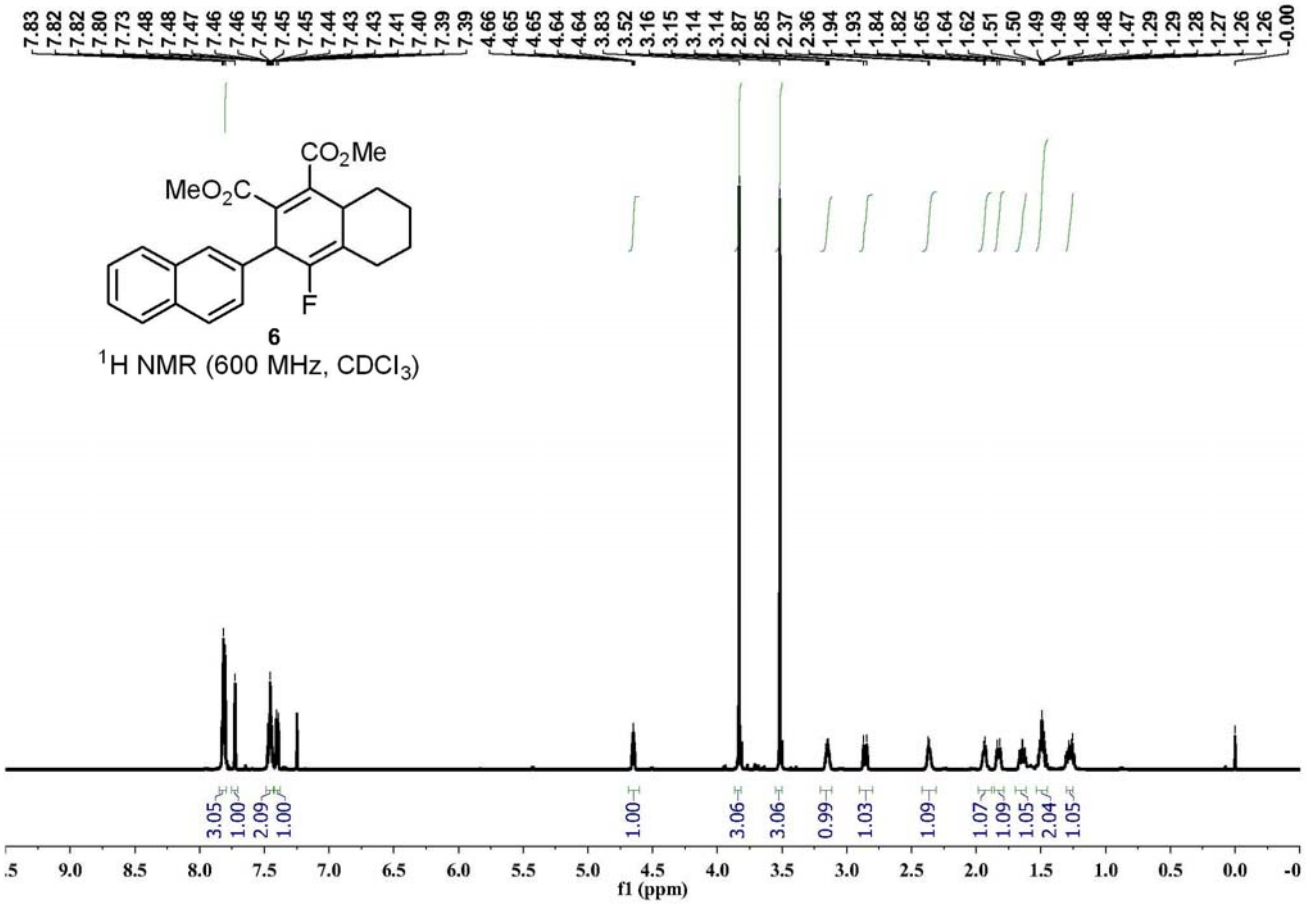


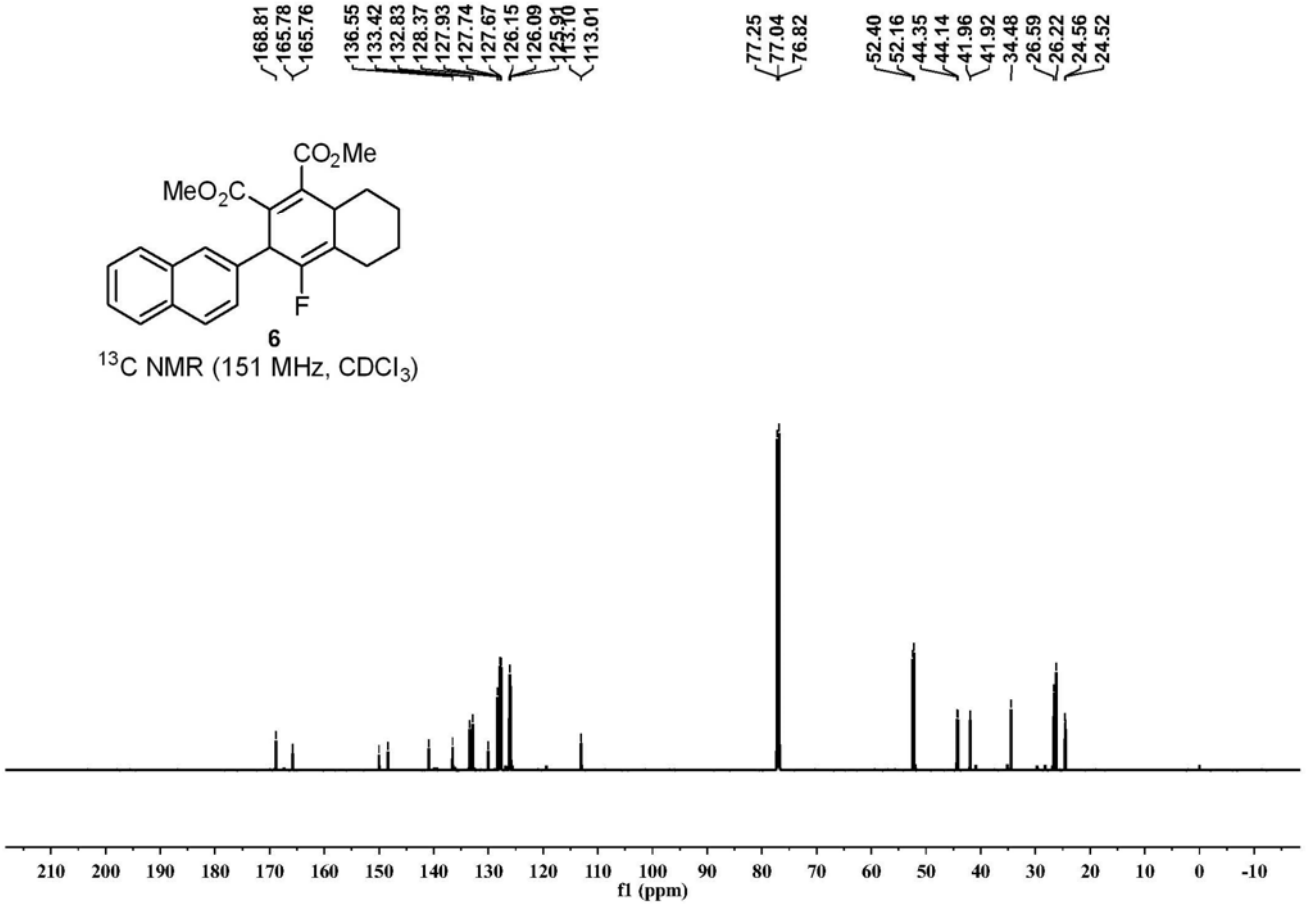


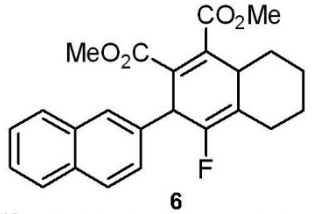
^{13}C NMR (151 MHz, $CDCl_3$)



^{1}H-^{1}H NOESY NMR (600 MHz, $CDCl_3$)

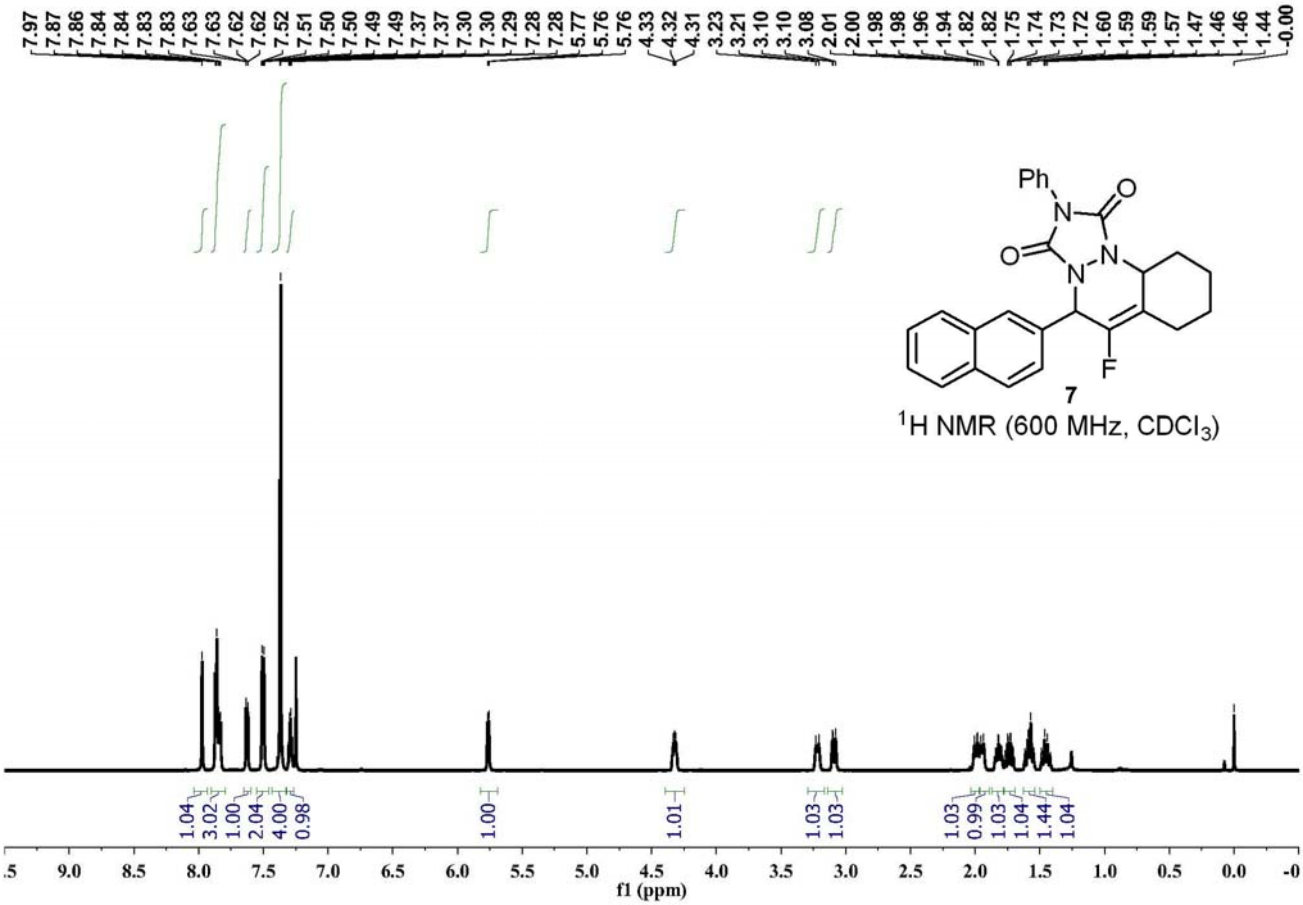

7.83 7.82 7.82 7.80 7.73 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.43 7.43 7.41 7.40 7.39 7.39
4.66 4.65 4.65 4.64 4.64 3.83 3.52 3.16 3.15 3.14 3.14 2.87 2.85 2.37 2.36 1.94 1.93 1.84 1.82 1.65 1.64 1.62 1.51 1.50 1.49 1.49 1.48 1.48 1.47 1.29 1.29 1.28 1.27 1.26 1.26 -0.00
CO2Me
MeO2C
F
6
1H NMR (600 MHz, CDCl3)
3.05 1.00 2.09 1.00 1.00 3.06 3.06 0.99 1.03 1.09 1.07 1.09 1.05 2.04 1.05
f1 (ppm)


168.81 165.78 165.76 136.55 133.42 132.83 128.37 127.93 127.74 127.67 126.15 126.09 125.91 113.10 113.01 77.25 77.04 76.82 52.40 52.16 44.35 44.14 41.96 41.92 34.48 26.59 26.22 24.56 24.52
CO2Me
MeO2C
F
6
13C NMR (151 MHz, CDCl3)
f1 (ppm)



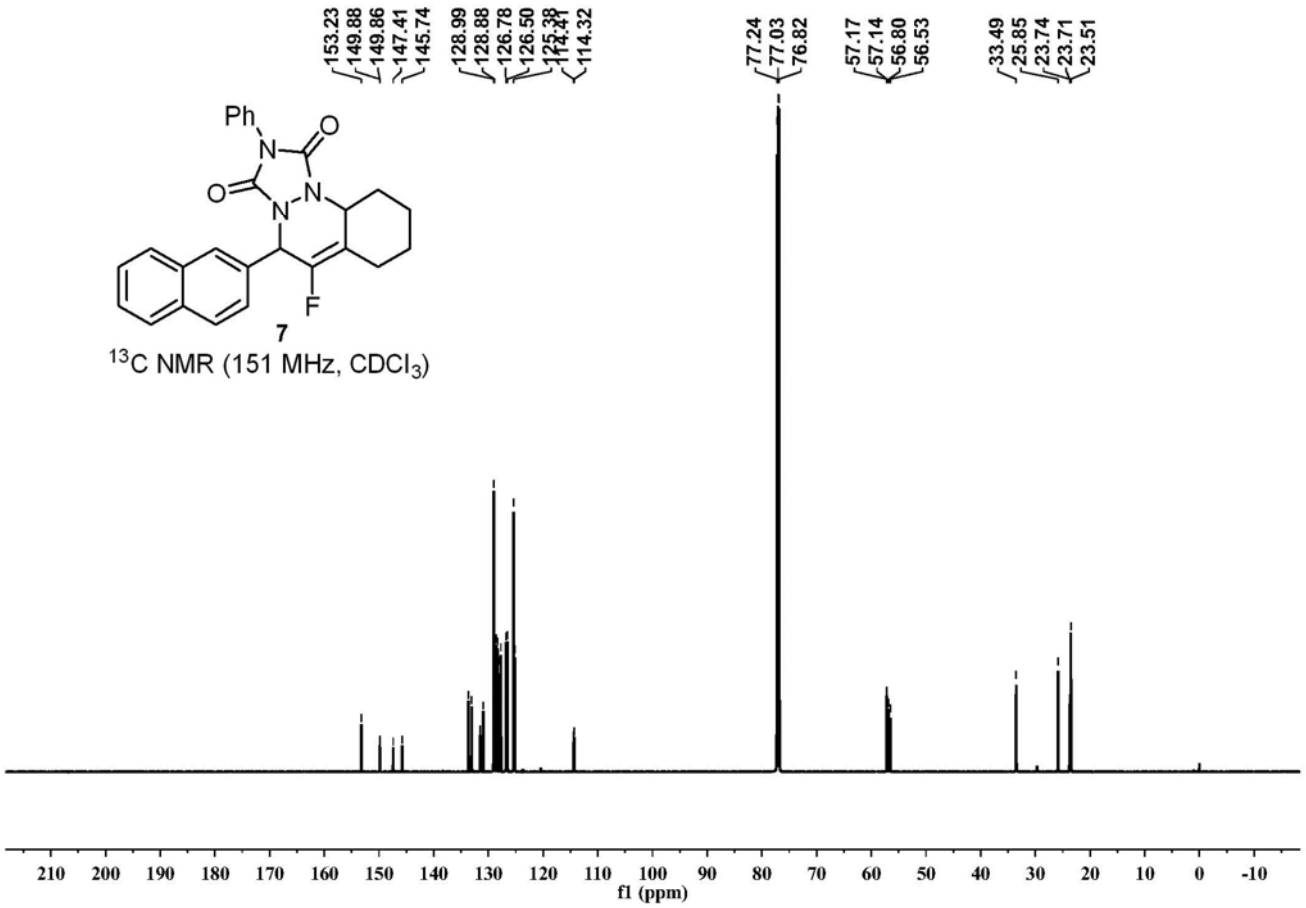
6

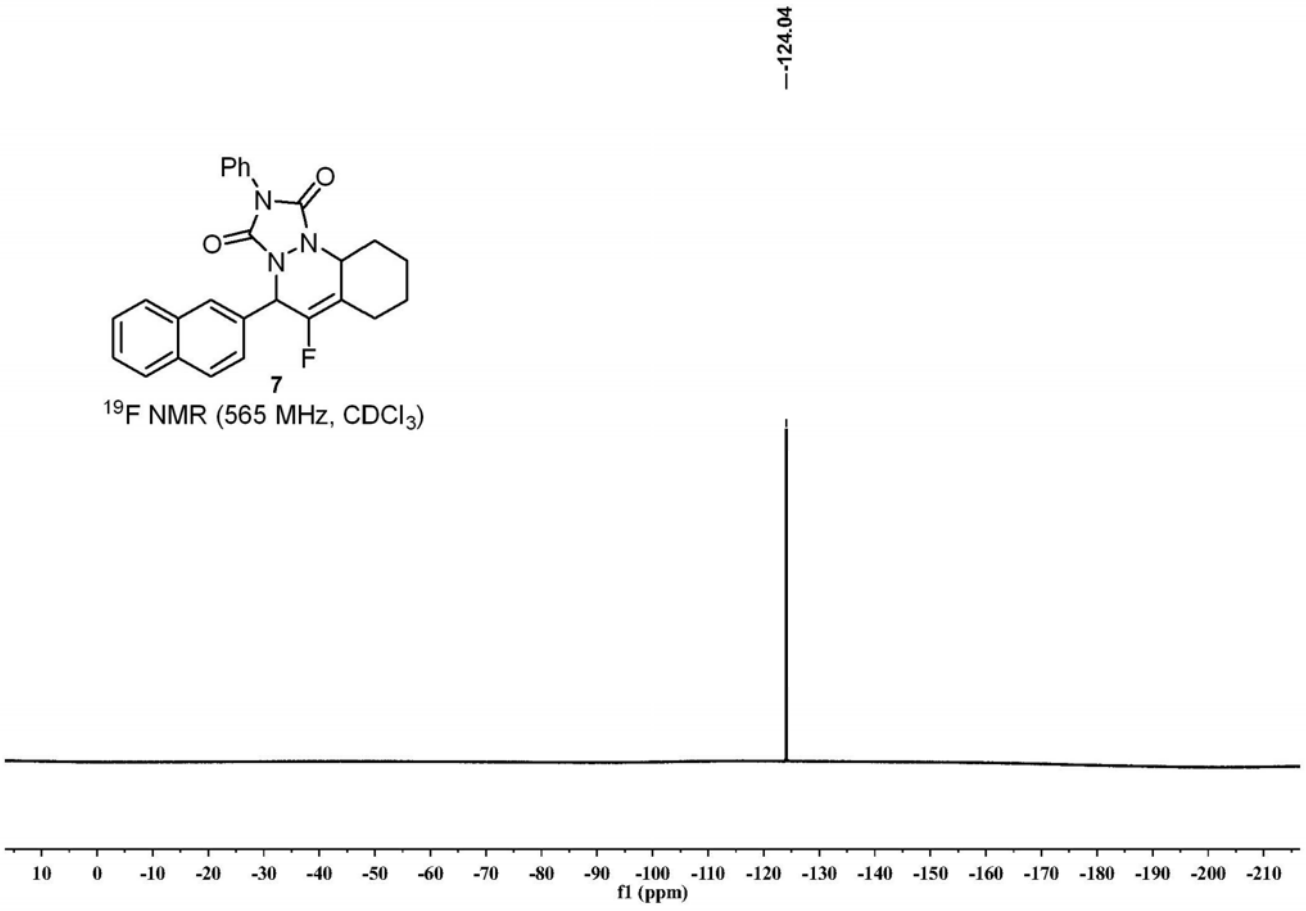
^{19}F NMR (565 MHz, $CDCl_3$)

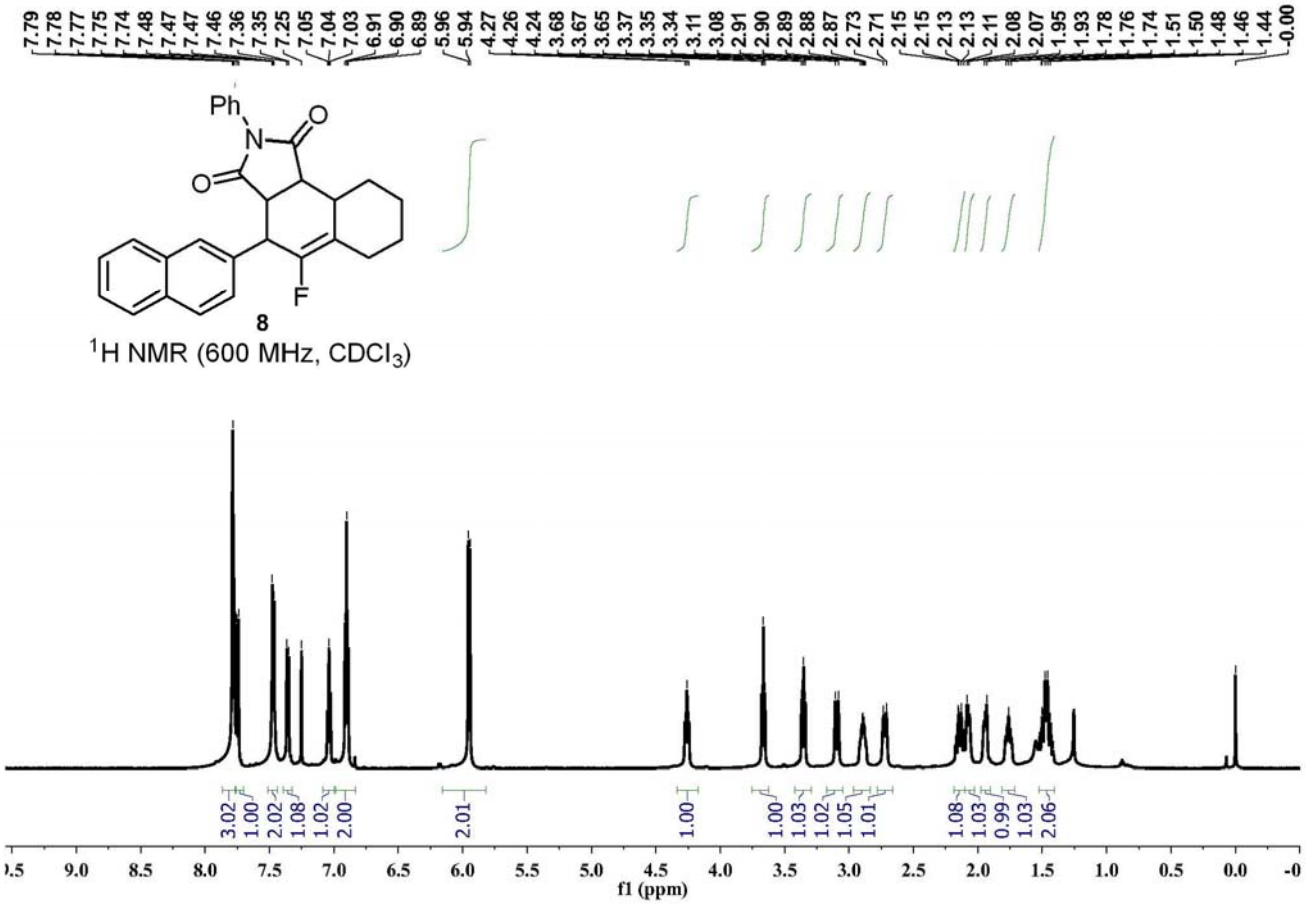


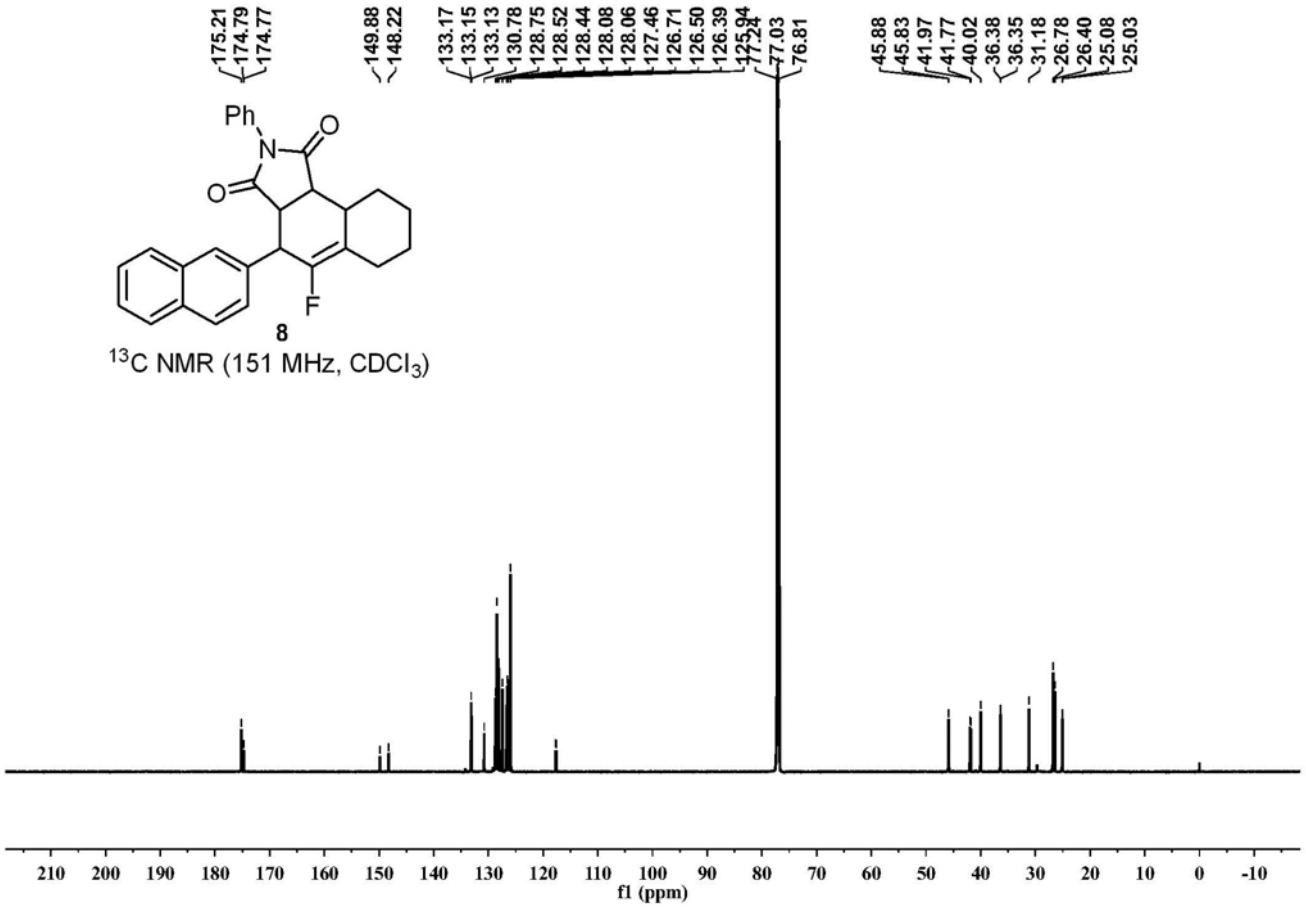
7

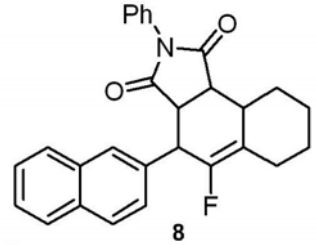
^{1}H NMR (600 MHz, $CDCl_3$)


153.23
149.88
149.86
147.41
145.74
128.99
128.88
126.78
126.50
114.32
77.24
77.03
76.82
57.17
57.14
56.80
56.53
33.49
25.85
23.74
23.71
23.51
Ph
N
O
O
N
N
F
7
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-124.04
Ph
N
O
O
N
N
F
7
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

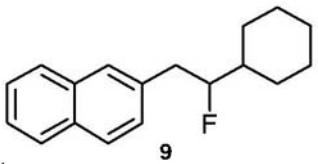

7.79 7.78 7.77 7.75 7.74 7.48 7.47 7.47 7.46 7.36 7.35 7.25 7.05 7.04 7.03 6.91 6.90 6.89 5.96 5.94 4.27 4.26 4.24 3.68 3.67 3.65 3.37 3.35 3.34 3.11 3.08 2.91 2.90 2.89 2.88 2.87 2.73 2.71 2.15 2.15 2.13 2.13 2.11 2.08 2.07 1.95 1.93 1.78 1.76 1.74 1.51 1.50 1.48 1.46 1.44 -0.00
Ph
N
O
O
F
8
^{1}H NMR (600 MHz, CDCl$_3$)
3.02 1.00 2.02 1.08 1.02 2.00 2.01 1.00 1.00 1.03 1.02 1.05 1.01 1.08 1.03 0.99 1.03 2.06
f1 (ppm)


175.21 174.79 174.77 149.88 148.22 133.17 133.15 133.13 130.78 128.75 128.52 128.44 128.08 128.06 127.46 126.71 126.50 126.39 125.94 77.24 77.03 76.81 45.88 45.83 41.97 41.77 40.02 36.38 36.35 31.18 26.78 26.40 25.08 25.03
Ph
N
O
O
F
8
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)



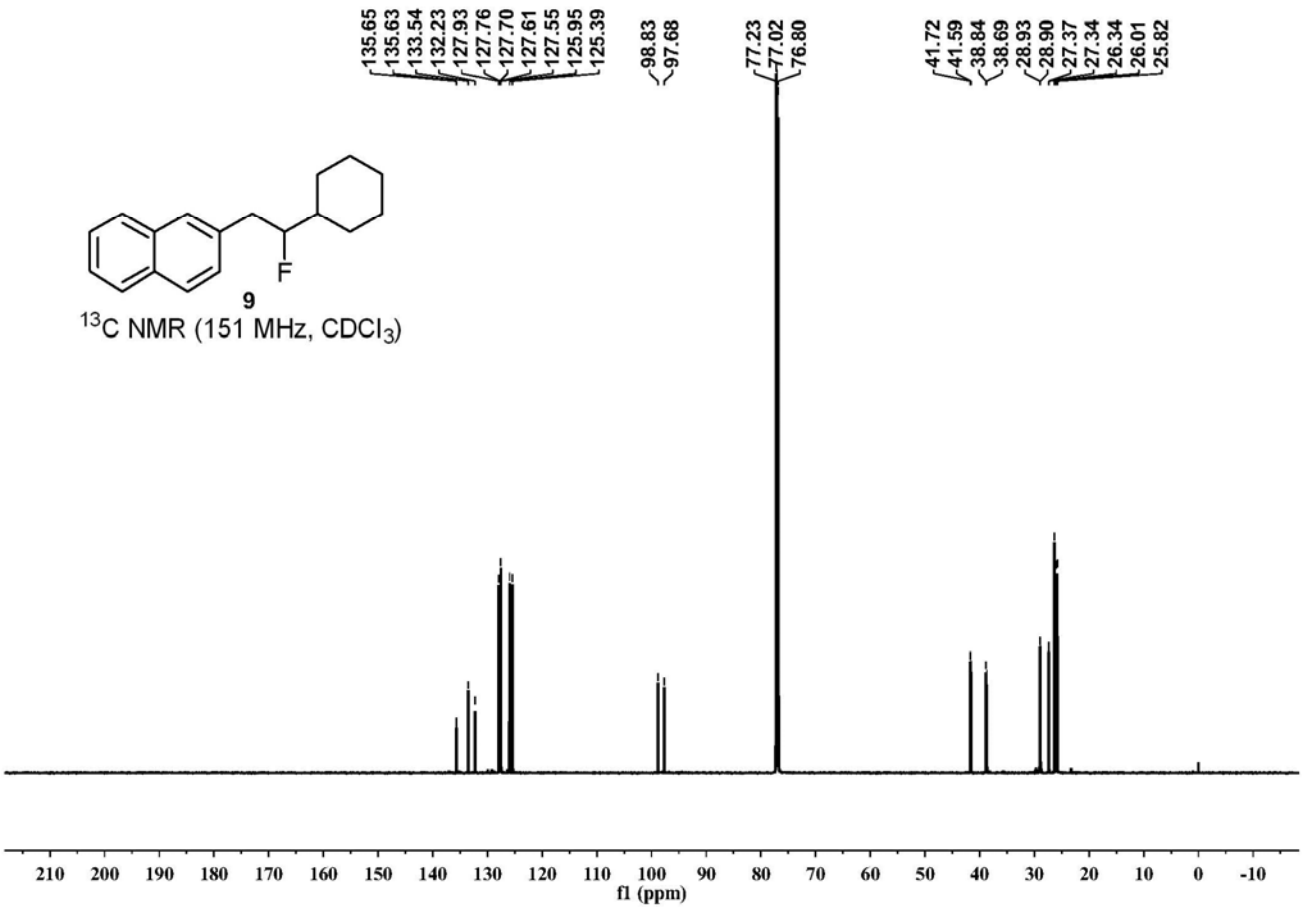
8

^{19}F NMR (565 MHz, $CDCl_3$)



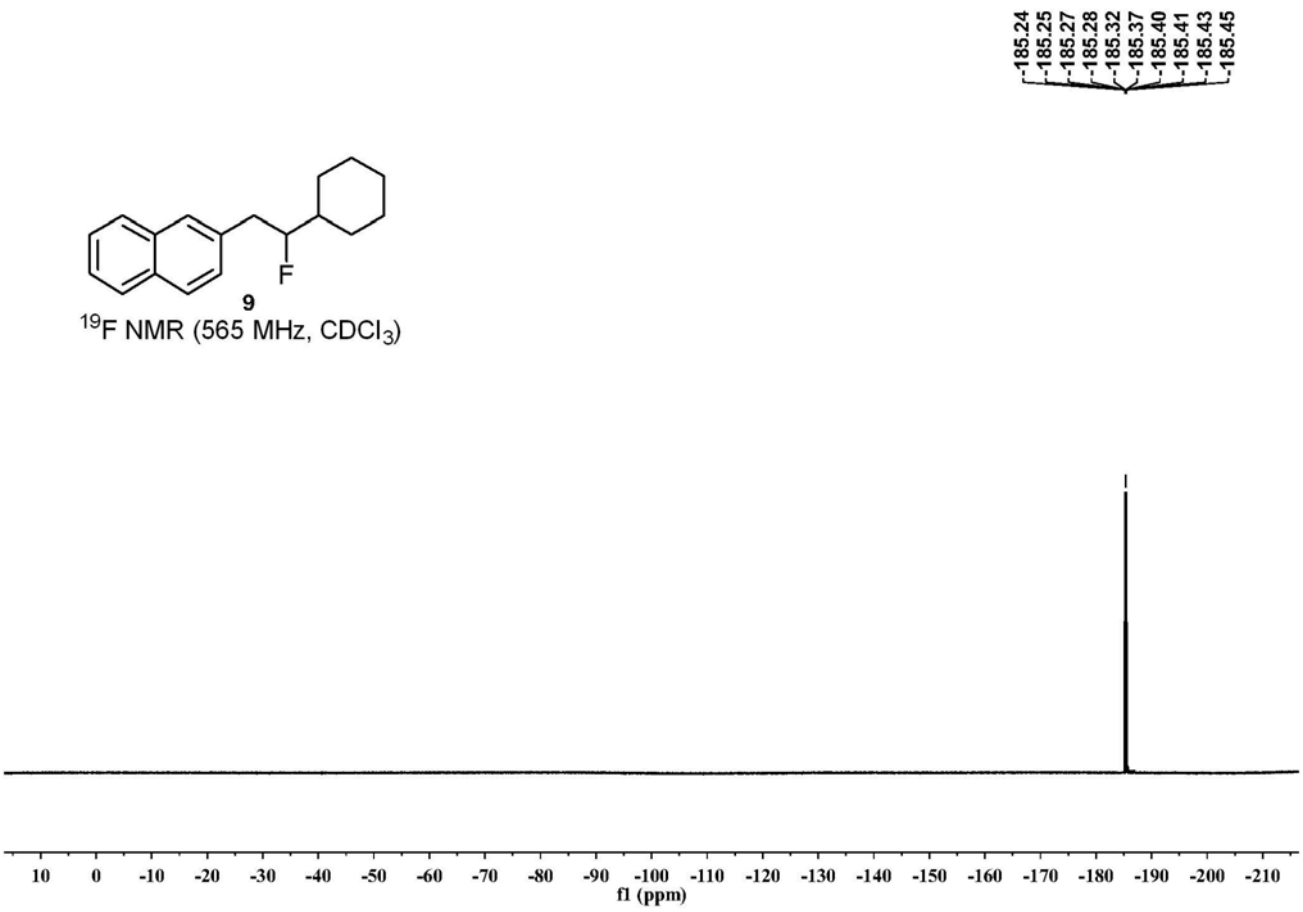
9

^{1}H NMR (600 MHz, $CDCl_3$)



9

^{13}C NMR (151 MHz, $CDCl_3$)



9

^{19}F NMR (565 MHz, $CDCl_3$)