Supporting Information

Iron-catalysed reductive coupling for the synthesis of polyfluorinated compounds

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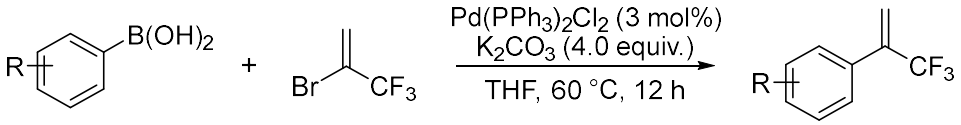
1. General remarks

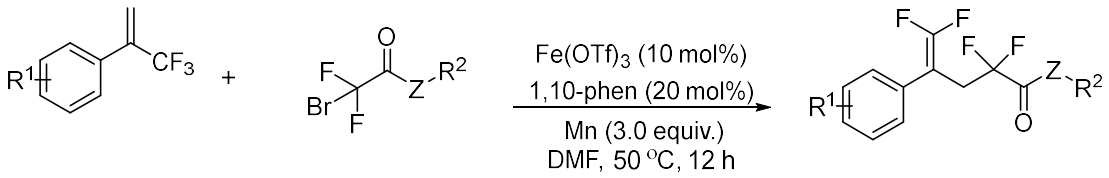
^{1}H NMR, ^{13}C NMR data were obtained on AVANCE III Bruker 500 MHz nuclear resonance spectrometers unless otherwise noted. Chemical shifts (in ppm) were referenced to tetramethylsilane (TMS) (δ = 0.00 ppm) in $CDCl_3$ or dimethyl sulfoxide (δ = 2.50 ppm) in DMSO-d_6 as an internal standard. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (J values) in Hz and integration. ^{13}C NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.16 ppm) or DMSO-d_6 (δ = 39.50 ppm). Flash chromatography was performed using 300-400 mesh silica gel with the indicated eluent according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) unless otherwise noted. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI) mode.

2. General procedure

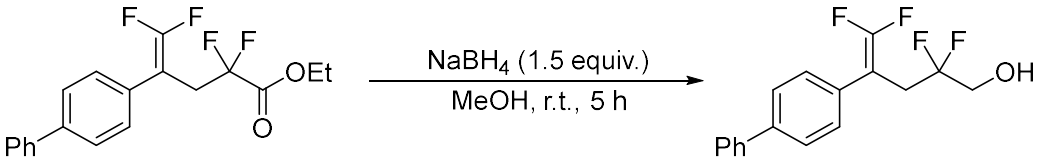


General procedure for the synthesis of trifluoromethyl-substituted alkene 1: [1, 2] To a Schlenk tube equipped with stir bar, arylboronic acid (1.0 equiv., 3 mmol) and $Pd(PPh_3)_2Cl_2$ (3 mol%, 0.09 mmol, 63.2 mg) were added. The vessel was evacuated and filled with argon (three times), and then aqueous K_2CO_3 (2.0 M, 6 mL) and THF (9 mL) were added. After addition of 2-bromo-3,3,3-trifluoro-1-propene (1.5 equiv., 4.5mmol, 0.47 mL), the solution was stirred at 60 ℃ with heating mantle for 12 hours

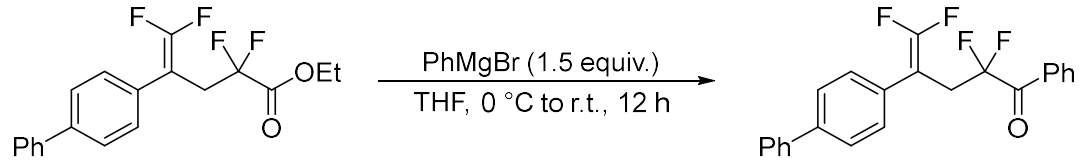
(TLC tracking detection). The solvent was quenched with water, diluted with EtOAc (10 mL) and washed with brine (15 mL) The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkene.



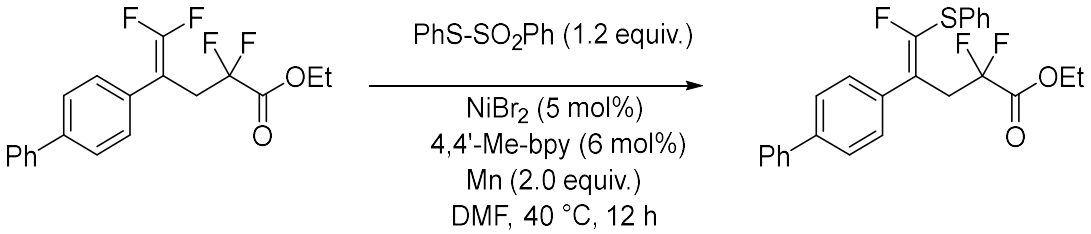
General procedure for the Fe-catalysed reductive cross-coupling of Product 3: To a 10 mL Schlenk tube was added sequentially $Fe(OTf)_3$ (10.07 mg, 0.02 mmol), 1,10-phenanthroline (6.80 mg, 0.04 mmol), Mn power (32.90 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMF (0.20 mL) was added via syringe and the mixture was stirred at room temperature for 10 min. The trifluoromethyl-substituted alkene **1** (0.20 mmol) was added, followed by the bromodifluoroacetate **2** (0.40 mmol) in one portion. DMF (0.30 mL) was subsequently added via syringe. The resulting solution was stirred for 12 h at 50 ˚C. After this time, the crude reaction mixture was diluted with ethyl acetate (5 mL) and washed with water (2.0 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.



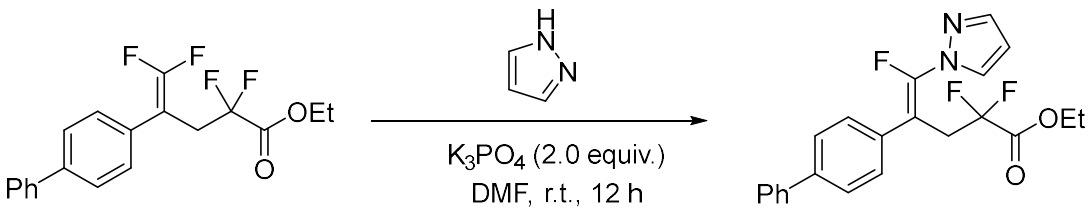
General procedure for the Product 5: To a 25mL round-bottomed flask ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate **3aa** (1.0 mmol) was added, followed by methanol 10 mL in one portion. $NaBH_4$ (1.5 mmol) was subsequently added. The resulting solution was stirred for 5 h at room temperature. After this time, the crude reaction mixture was concentrated in vacuum and the residue was purified by column chromatography to afford the corresponding product.



General procedure for the Product 6: To a 10 mL Schlenk tube was added ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate **3aa** (0.2 mmol). The vessel was evacuated and filled with argon (three times), THF (0.50 mL) was added via syringe and the mixture was stirred at room temperature for 10 min. The phenylmagnesium bromide (0.3 mmol) was added under 0 ˚C. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (5 mL) and washed with water (2.0 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.



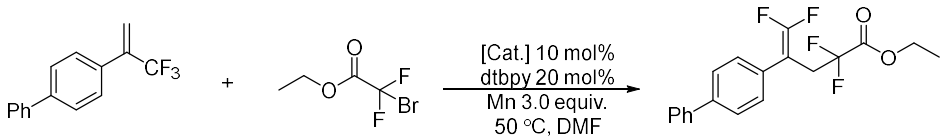
General procedure for the Product 7:[3] To a 10 mL Schlenk tube was added ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate **3aa** (0.2 mmol), S-phenyl 4-methylbenzenesulfonothioate (0.24 mmol), $NiBr_2$ (2.2 mg, 0.01 mmol), 4,4'-dimethyl-2,2'-bipyridine (2.2 mg, 0.012 mmol) and Mn powder (22.0 mg, 0.4 mmol). DMF (0.5 mL) was added via syringe. The resulting solution was stirred for 12 h at 40 °C. After this time, the crude reaction mixture was diluted with ethyl acetate (100 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.



General procedure for the Product 8:[4] A solution of 1*H*-imidazole (1.0 mmol) in DMF (1 mL) was added dropwise to a mixture of ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate **3aa** (1.2 mmol) and K_3PO_4 (424.0 mg, 2.0 mmol) in DMF (1 mL) via syring and then stirred at room temperature for 12 h (monitored by TLC). After completion of the reaction, the mixture was quenched with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel using a hexane/dichloromethane (10:1) mixture as eluent to afford the pure target compound.

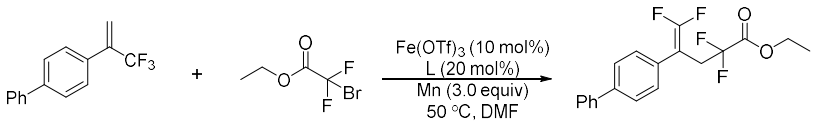
3. Optimization of the reaction conditions

Table S1. Optimization of the catalysts



entry	[Cat.]	yield
1	$NiCl_2$	16 %
2	$NiBr_2$	12 %
3	NiI_2	3 %
4	$NiBr_2$-DME	31 %
5	$NiBr_2$-bpy	6 %
6	$Ni(acac)_2$	3 %
7	$CoCl_2$	20 %
8	$CrCl_3$	13 %
9	$Fe(OTf)_3$	45 %
10	$FeCl_3$	41 %
11	$FeCl_2$	45 %
12	$Fe(acac)_3$	37 %
13	dppf	20 %
14	$Fe(OTf)_3$	49 %
15	none	n.d.

Table S2. Optimization of the ligands



entry	L	yield
1	L1	91 %
2	L2	51 %
3	L3	92 %
4	L4	53 %
5	L5	88 %
6	L6	74 %
7	L7	92 %
8	L8	65 %
9	L9	93 %
10	L10	92 %
11	L11	36 %
12	L12	42 %
13	L13	35%
14	L14	31%
15	L15	trace

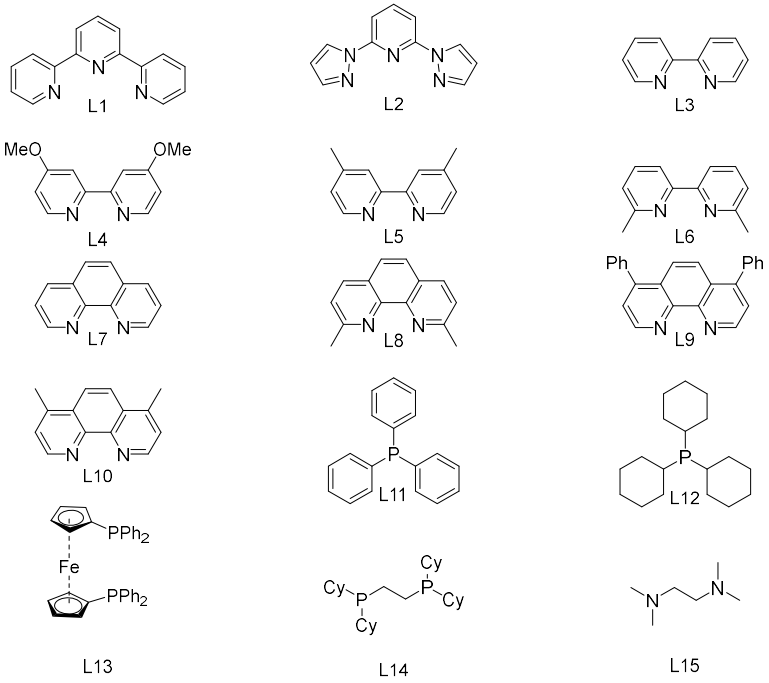
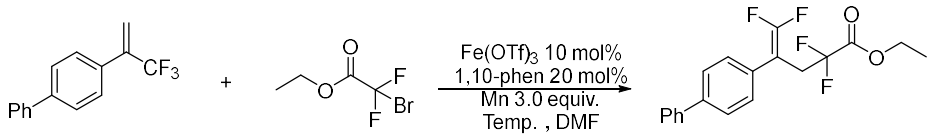
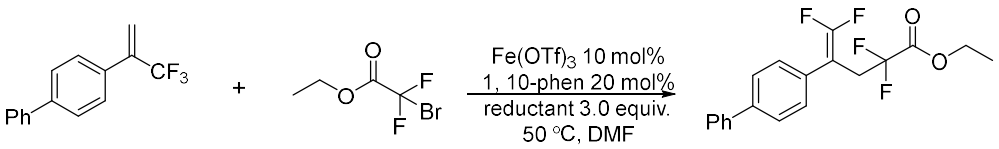


Table S3. Optimization of reaction temperature



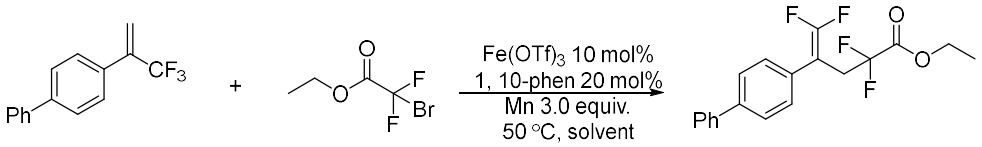
entry	Temp.	yield
1	r.t.	57 %
2	35 °C	60 %
3	50 °C	92 %

Table S4. Optimization of the reducing agents



entry	reductant	yield
1	Mn	92 %
2	Zn	56 %
3	B_2pin_2	trace

Table S5. Optimization of the solvents

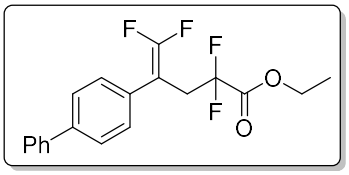


1a **2a** **3aa**

entry	solvent	yield
1	DMF	92 %
2	DMA	87 %
3	DMSO	88 %
4	dioxane	25 %
5	toluene	n.d.
6	MeCN	33 %
7	THF	35 %
8	DCE	7 %
9[a]	DMF	65 %

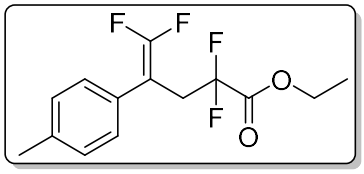
Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), catalyst (10 mol%), ligand (20 mol%), reducing agent (0.60 mmol), solvent (0.5 mL) for 12 h. Isolated yields. [a]chlorodifluoroacetic ester was used instead of **2a**.

4. Characterization data for all products

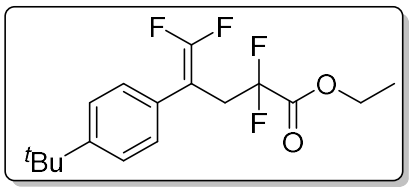


Ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (3aa). The

representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 50 : 1) yielded **3aa** (64.8 mg, 92 %) as a white solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 – 7.50 (m, 2H), 7.50 – 7.48 (m, 2H), 7.36 – 7.33 (m, 2H), 7.29 – 7.26 (m, 3H), 3.94 (q, *J* = 7.0 Hz, 2H), 3.18 – 3.12 (m, 2H), 1.10 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.39 (t, *J* = 26.2 Hz), 155.37 (t, *J* = 232.0 Hz), 140.71, 140.28, 131.00, 128.87, 128.82, 127.55, 127.10, 126.97, 114.49 (t, *J* = 198.0 Hz), 84.60 (t, *J* = 16.3 Hz), 62.95, 33.92 (t, *J* = 20.5 Hz), 13.62; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.19, -104.17; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{19}H_{17}F_4O_2$ 353.1159, found: 353.1156.

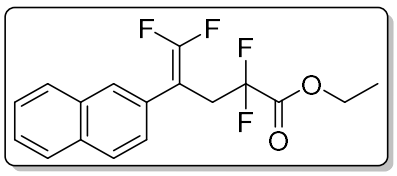


Ethyl 2,2,5,5-tetrafluoro-4-(*p*-tolyl)pent-4-enoate (3ba). The representative procedure was followed using 1-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1b**) (37.24 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 100 : 1) yielded **3ba** (53.9 mg, 90 %) as a colorless oil; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.12 – 7.07 (m, 4H), 3.94 (q, *J* = 7.2 Hz, 2H), 3.14 – 3.07 (m, 2H), 2.26 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.41 (t, *J* = 40.1 Hz), 155.21 (t, *J* = 362.5 Hz), 137.73, 129.14, 129.04, 128.32, 114.52 (t, *J* = 313.8 Hz), 84.63 (t, *J* = 24.5 Hz), 62.88, 34.02 (t, *J* = 31.8 Hz), 21.08, 13.60; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -87.16, -104.25; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{14}H_{15}F_4O_2$ 291.1003, found: 291.1001.

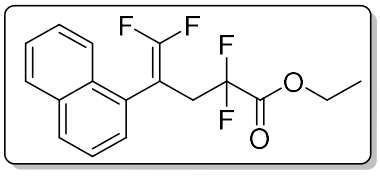


Ethyl 4-(4-[*tert*-butyl]phenyl)-2,2,5,5-tetrafluoropent-4-enoate (3ca). The

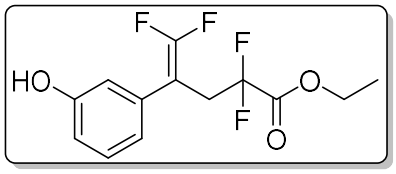
representative procedure was followed using 1-(*tert*-butyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1c**) (45.65 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 100 : 1) yielded **3ca** (67.7 mg, 87 %) as a colorless oil; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31 – 7.28 (m, 2H), 7.16 – 7.14 (m, 2H), 3.84 (q, J = 9.0 Hz, 2H), 3.15 – 3.08 (m, 2H), 1.23 (s, 9H), 1.08 – 1.04 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.39 (t, J = 40.0 Hz), 155.30 (t, J = 362.8 Hz), 150.88, 128.93, 128.14, 125.37, 114.49 (t, J = 313.2 Hz), 84.53 (t, J = 24.8 Hz), 62.82, 34.54, 34.00 (t, J = 33.0 Hz), 37.18, 13.58; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.96 , -104.35; **HRMS** (ESI) m/z ([M+ Na]$^+$) Calcd. for $C_{17}H_{20}F_4O_2Na$ 355.1292, found: 355.1293.



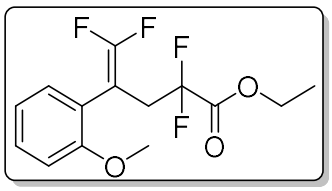
Ethyl 2,2,5,5-tetrafluoro-4-(naphthalen-2-yl)pent-4-enoate (3da). The representative procedure was followed using 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (**1d**) (44.44 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 50 : 1) yielded **3da** (47.0 mg, 72%) as a white solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 – 7.65 (m, 4H), 7.37 – 7.28 (m, 3H), 3.78 (q, J = 7.0 Hz, 2H), 3.23 – 3.20 (m, 2H), 0.96 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.36 (t, J = 25.6 Hz), 155.52 (t, J = 232.6 Hz), 133.05, 132.62, 129.43, 128.13, 127.89, 127.82, 127.55, 126.47, 126.44, 125.94, 114.52 (t, J = 201.1 Hz), 84.99 (t, J = 16.0 Hz), 62.85, 34.06 (t, J = 20.0 Hz), 13.42; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.39, -104.10; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{17}H_{15}F_4O_2$ 327.1003, found: 327.1002.



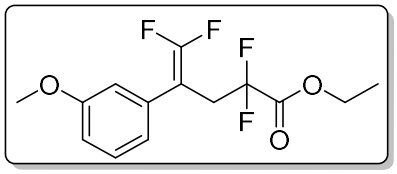
Ethyl 2,2,5,5-tetrafluoro-4-(naphthalen-1-yl)pent-4-enoate (3ea). The representative procedure was followed using 1-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (**1e**) (44.44 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 50 : 1) yielded **3ea** (45.7 mg, 70%) as a white solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 – 7.71 (m, 3H), 7.46 –7.30 (m, 4H), 3.83 – 3.71 (m, 2H), 3.29 – 3.16 (m, 2H), 0.91 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.21 (t, J = 32.3 Hz), 155.34 (t, J = 287.6 Hz), 133.76, 131.18, 129.42, 128.96, 128.66, 128.09, 126.62, 126.06, 125.22, 124.44, 114.52 (t, J = 250.8 Hz), 82.73 (t, J = 23.8 Hz), 62.80, 35.00 (t, J = 27.9 Hz), 13.37; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.58, -104.24, -113.55; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{17}H_{15}F_4O_2$ 327.1003, found: 327.1001.



Ethyl 2,2,5,5-tetrafluoro-4-(3-hydroxyphenyl)pent-4-enoate (3fa). The representative procedure was followed using 3-(3,3,3-trifluoroprop-1-en-2-yl)phenol (**1f**) (37.63 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 10 : 1) yielded **3fa** (43.8 mg, 75%) as a yellow oil; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.21 (m, 1H), 6.86 – 6.84 (m, 1H), 6.78 – 6.77 (m, 2H), 5.79 (s, 1H), 4.04 (q, J = 7.0 Hz, 2H), 3.20 – 3.14 (m, 2H), 1.20 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.74 (t, J = 25.7 Hz), 155.66, 155.32 (t, J = 232.6 Hz), 133.54, 129.71, 120.81, 115.69, 115.05,114.43 (t, J = 201.1 Hz), 84.56 (t, J = 16.2 Hz), 63.19, 33.93 (t, J = 20.6 Hz), 13.54; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.89, -104.23; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{13}H_{13}F_4O_3$ 293.0795, found: 293.0794.

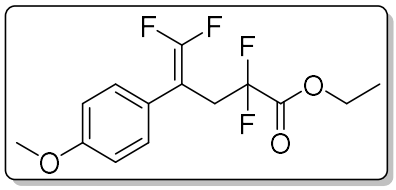


Ethyl 2,2,5,5-tetrafluoro-4-(2-methoxyphenyl)pent-4-enoate (3ga). The representative procedure was followed using 1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1g**) (40.44 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 10 : 1) yielded **3ga** (47.8 mg, 78%) as a colorless oil; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.25 – 7.20 (m, 1H), 7.09 – 7.06 (m, 1H), 6.88 – 6.86 (m, 1H), 6.84 – 6.80 (m, 1H), 3.93 (q, J = 9.0 Hz, 2H), 3.75 (s, 3H), 3.18 – 3.09 (m, 2H), 1.10 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.46 (t, J = 40.0 Hz), 157.18, 155.06 (t, J = 359.4 Hz), 131.55, 129.79, 120.44, 117.31, 114.81(t, J = 179.0 Hz), 110.73, 82.34 (t, J = 34.1 Hz), 62.72, 55.36, 33.11 (t, J = 31.5 Hz), 13.63; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.09, -89.20, -103.97.; **HRMS** (ESI) m/z ($[M+ H]^+$) Calcd. for $C_{14}H_{15}F_4O_3$ 307.0952, found: 307.0954.

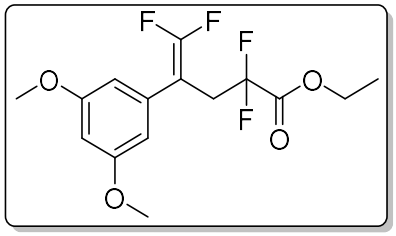


Ethyl 2,2,5,5-tetrafluoro-4-(3-methoxyphenyl)pent-4-enoate (3ha). The representative procedure was followed using 1-methoxy-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1h**) (40.44 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 10 : 1) yielded **3ha** (49.0 mg, 80%) as a colorless oil; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29 – 7.25 (m, 1H), 6.89 – 6.83 (m, 3H), 4.03 (q, J = 7.0 Hz, 2H), 3.80 (s, 3H), 3.22 – 3.15 (m, 2H), 1.20 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.37 (t, J = 32.0 Hz), 159.51, 155.30 (t, J = 290.5 Hz), 133.41, 129.44, 120.83, 114.54 (t, J = 248.1 Hz), 114.40, 113.29, 84.76 (t, J = 19.9 Hz), 62.93, 55.23, 34.02 (t, J = 26.5 Hz), 13.62; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.93, -86.41, -104.30; **HRMS** (ESI) m/z ($[M+ H]^+$)

Calcd. for $C_{14}H_{15}F_4O_3$ 307.0952, found: 307.0947.

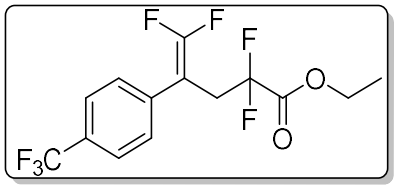


Ethyl 2,2,5,5-tetrafluoro-4-(4-methoxyphenyl)pent-4-enoate (3ia). The representative procedure was followed using 1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1i**) (40.44 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 10 : 1) yielded **3ia** (51.2 mg, 80%) as a colorless oil; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.22 – 7.20 (m, 2H), 6.89 – 6.88 (m, 2H), 4.04 (q, J = 7.0 Hz, 2H), 3.80 (s, 3H), 3.19 – 3.13 (m, 2H), 1.20 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.42 (t, J = 31.9 Hz), 159.16, 155.19 (t, J = 289.6 Hz), 129.69, 124.14, 114.54 (t, J = 251.6 Hz), 113.90, 84.33 (t, J = 20.4 Hz), 62.89, 55.22, 34.11 (t, J = 24.8 Hz), 13.64; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.59, -106.17; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{14}H_{15}F_4O_3$ 307.0952, found: 307.0950.

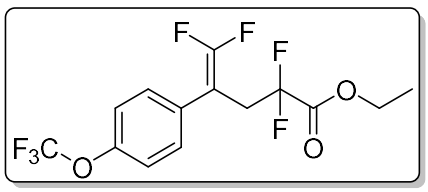


Ethyl 4-(3,5-dimethoxyphenyl)-2,2,5,5-tetrafluoropent-4-enoate (3ja). The representative procedure was followed using 1,3-dimethoxy-5-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1j**) (46.44 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 5 : 1) yielded **3ja** (57.2 mg, 85 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.36 – 6.35 (m, 2H), 6.33 – 6.31 (m, 1H), 4.00 (q, J = 9.0 Hz, 2H), 3.71 (s, 6H), 3.13 – 3.06 (m, 2H), 1.14 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.40 (t, J = 40.5 Hz), 160.68, 155.31 (t, J = 362.9 Hz), 134.01, 114.41 (t, J = 315.1 Hz), 106.81, 99.86,

84.85 (t, J = 19.8 Hz), 62.96, 55.34, 34.06 (t, J = 32.8 Hz), 13.62; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.34, -86.27, -104.29; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{15}H_{17}F_4O_4$ 337.1057, found: 337.1056.

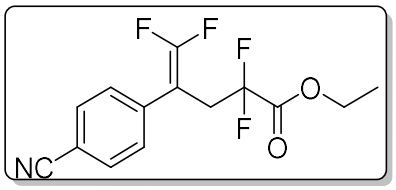


Ethyl 2,2,5,5-tetrafluoro-4-(4-[trifluoromethyl]phenyl)pent-4-enoate (3ka). The representative procedure was followed using 1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1k**) (48.03 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 20 : 1) yielded **3ka** (44.7 mg, 65 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 – 7.55 (m, 2H), 7.37 – 7.35 (m, 2H), 4.03 (q, J = 7.0 Hz, 2H), 3.18 – 3.12 (m, 2H), 1.15 (t, J = 7.0 Hz, 3H).; **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.30 (t, J = 32.0 Hz), 155.55 (t, J = 292.0 Hz), 136.06, 129.91 (t, J = 33.8 Hz), 128.88, 125.46, 124.93 (t, J = 270.4 Hz), 114.28 (t, J = 251.4 Hz), 84.31 (t, J = 23.1 Hz), 63.12, 33.73 (t, J = 24.3 Hz), 13.67; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.80, -84.77, -104.30; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{14}H_{12}F_7O_2$ 345.0720, found: 345.0721.

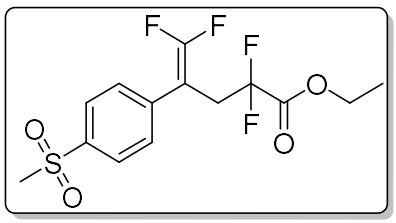


Ethyl 2,2,5,5-tetrafluoro-4-(4-[trifluoromethoxy]phenyl)pent-4-enoate (3la). The representative procedure was followed using 1-(trifluoromethoxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1l**) (51.23 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 20 : 1) yielded **3la** (45.4 mg, 63 %) as a yellow solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 – 7.25 (m, 2H), 7.15 – 7.13 (m, 2H), 3.99 (q, J = 9.0 Hz, 2H), 3.15 – 3.08 (m, 2H), 1.13 (t, J = 9.0 Hz, 3H).; **^{13}C NMR (125 MHz, $CDCl_3$)** δ

163.29 (t, J = 40.1 Hz), 155.43 (t, J = 363.8 Hz), 148.66, 130.87, 130.08, 121.68, 119.12 (t, J = 280.9 Hz), 114.33 (t, J = 313.8 Hz), 84.15 (t, J = 25.3 Hz), 63.05, 33.96 (t, J = 32.0 Hz), 13.63; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -57.92, -85.76, -104.33; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{14}H_{12}F_7O_3$ 361.0669, found: 361.0671.

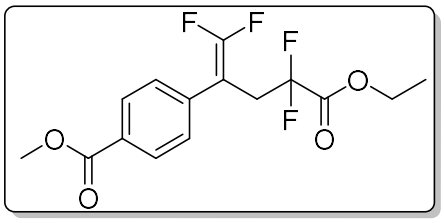


Ethyl 4-(4-cyanophenyl)-2,2,5,5-tetrafluoropent-4-enoate (3ma). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)benzonitrile (**1m**) (39.43 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 10 : 1) yielded **3ma** (45.2 mg, 75 %) as a yellow solid.; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.68 – 7.66 (m, 2H), 7.45 – 7.43 (m, 2H), 4.15 (q, J = 9.0 Hz, 2H), 3.25 – 3.18 (m, 2H), 1.27 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 163.17 (t, J = 39.4 Hz), 155.60 (t, J = 367.8 Hz), 132.26, 131.77, 129.13, 118.31, 114.20 (t, J = 311.9 Hz), 111.71, 84.34 (t, J = 41.3 Hz), 63.21, 33.42 (t, J = 28.8 Hz), 13.75; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -83.23, -83.60, -104.31; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{14}H_{12}F_4NO_2$ 302.0799, found: 302.0796.

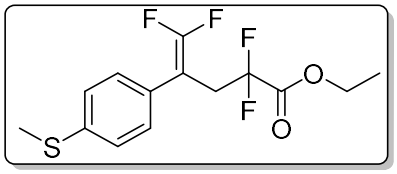


Ethyl 2,2,5,5-tetrafluoro-4-(4-[methylsulfonyl]phenyl)pent-4-enoate (3na). The representative procedure was followed using 1-(methylsulfonyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1n**) (50.05 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 5 : 1) yielded **3na** (48.2 mg, 68 %) as a yellow solid.; **^{1}H NMR (500**

MHz, $CDCl_3$) δ 7.95 – 7.94 (m, 2H), 7.53 – 7.52 (m, 2H), 4.18 (q, J = 9.0 Hz, 2H), 3.27 – 3.20 (m, 2H), 3.07 (s, 3H), 1.27 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.13 (t, J = 31.8 Hz), 155.60 (t, J = 293.0 Hz), 139.80, 129.35, 127.57, 127.05, 114.17 (t, J = 251.0 Hz), 84.20 (t, J = 21.8 Hz), 63.20, 44.43, 33.72 (t, J = 25.3 Hz), 13.71; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -83.25, -83.70, -104.17; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{14}H_{15}F_4O_4S$ 355.0622, found: 355.0624.

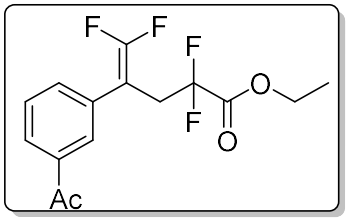


Methyl 4-(5-ethoxy-1,1,4,4-tetrafluoro-5-oxopent-1-en-2-yl)benzoate (3oa). The representative procedure was followed using methyl 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (**1o**) (46.04 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 10 : 1) yielded **3oa** (46.8 mg, 70 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.98 – 7.95 (m, 2H), 7.33 – 7.30 (m, 2H), 4.00 (q, J = 9.0 Hz, 2H), 3.85 (s, 3H), 3.19 – 3.12 (m, 2H), 1.15 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 166.50, 163.25 (t, J = 32.0 Hz), 155.47 (t, J = 292.4 Hz), 136.93, 129.91, 129.68, 128.40, 114.29 (t, J = 251.9 Hz), 84.56 (t, J = 21.1 Hz), 63.18, 52.24, 33.63 (t, J = 25.4 Hz), 13.67; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -84.55, -104.30; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{15}H_{15}F_4O_4$ 355.0901, found: 335.0899.

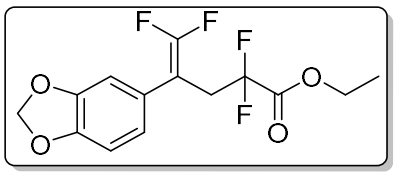


Ethyl 2,2,5,5-tetrafluoro-4-(4-[methylthio]phenyl)pent-4-enoate (3pa). The representative procedure was followed using methyl(4-[3,3,3-trifluoroprop-1-en-2-yl]phenyl)sulfane (**1p**) (43.65 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate

(**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 30 : 1) yielded **3pa** (60.6 mg, 94 %) as a yellow solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.23 – 7.21 (m, 4H), 4.04 (q, J = 9.0 Hz, 2H), 3.22 – 3.14 (m, 2H), 2.48 (s, 3H), 1.21 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.36 (t, J = 40.5 Hz), 155.25 (t, J = 363.0 Hz), 138.57, 128.82, 128.79, 126.19, 114.44 (t, J = 314.1 Hz), 84.37 (t, J = 25.0 Hz), 62.96, 33.85 (t, J = 32.0 Hz), 15.47, 13.65; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.47, -104.28; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{14}H_{15}F_4O_2S$ 323.0722, found: 323.0715.

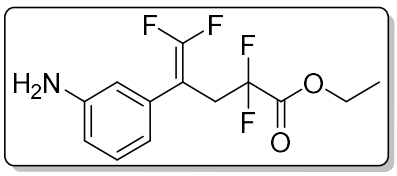


Ethyl 4-(3-acetylphenyl)-2,2,5,5-tetrafluoropent-4-enoate (3qa). The representative procedure was followed using 1-(3-[3,3,3-trifluoroprop-1-en-2-yl]phenyl)ethan-1-one (**1q**) (42.84 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 30 : 1) yielded **3qa** (51.9 mg, 79 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 – 7.88 (m, 2H), 7.53 – 7.45 (m, 2H), 4.08 (q, J = 9.0 Hz, 2H), 3.29 – 3.20 (m, 2H), 2.61 (s, 3H), 1.21 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 197.38, 163.17 (t, J = 39.9 Hz), 155.40 (t, J = 363.8 Hz), 137.27, 133.05, 132.80, 128.76, 128.10, 127.78, 114.32 (t, J = 318.9 Hz), 84.35 (t, J = 25.3 Hz), 62.95, 33.76 (t, J = 31.6 Hz), 26.45, 13.53; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.89, -104.26; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{15}H_{15}F_4O_3$ 319.0952, found: 319.0949.

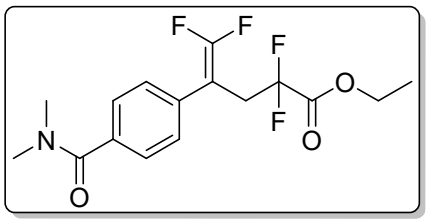


Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-2,2,5,5-tetrafluoropent-4-enoate (3ra). The

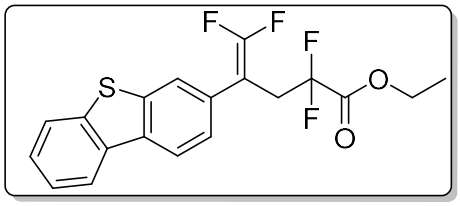
representative procedure was followed using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole (**1r**) (43.23 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 50 : 1) yielded **3ra** (53.2 mg, 83 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.73 – 6.66 (m, 3H), 5.89 (s, 2H), 4.04 (q, J = 9.0 Hz, 2H), 3.10 – 3.02 (m, 2H), 1.17 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.38 (t, J = 32.0 Hz), 155.24 (t, J = 289.9 Hz), 147.70, 147.21, 125.64, 122.22, 114.46 (t, J = 251.1 Hz), 109.02, 108.26, 101.25, 84.58 (t, J = 20.8 Hz), 62.97, 34.24 (t, J = 25.5 Hz), 13.68; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.80, -87.25, -104.22; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{14}H_{13}F_4O_4$ 321.0744, found: 321.0746.



Ethyl 4-(3-aminophenyl)-2,2,5,5-tetrafluoropent-4-enoate (3sa). The representative procedure was followed using 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (**1s**) (37.43 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 5 : 1) yielded **3sa** (51.3 mg, 88 %) as a yellow oil.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.07 – 7.03 (m, 1H), 6.60 – 6.58 (m, 1H), 6.54 – 6.52 (m, 2H), 3.97 (q, J = 9.0 Hz, 2H), 3.81 – 3.16 (m, 2H), 3.13 – 3.04 (m, 2H), 1.13 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.43 (t, J = 32.0 Hz), 155.21 (t, J = 290.1 Hz), 146.45 133.05, 129.32, 118.60, 115.14, 114.60, 114.43 (t, J = 251.3 Hz), 84.83 (t, J = 19.9 Hz), 62.93, 34.02 (t, J = 25.5 Hz), 13.64; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.21, -86.91, -104.35; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{13}H_{14}F_4NO_2$ 292.0955, found: 292.0951.

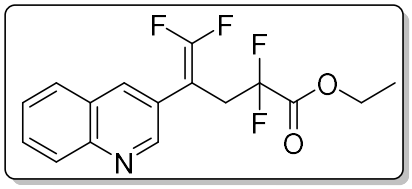


Ethyl 4-(4-[dimethylcarbamoyl]phenyl)-2,2,5,5-tetrafluoropent-4-enoate (3ta). The representative procedure was followed using *N*,*N*-dimethyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzamide (**1t**) (48.65 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (DCM : MeOH = 50 : 1) yielded **3ta** (59.7 mg, 86 %) as a yellow oil.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 – 7.34 (m, 2H), 7.30 – 7.26 (m, 2H), 4.04 (q, J = 9.0 Hz, 2H), 3.17 – 3.09 (m, 2H), 3.03 (s, 3H), 2.91 (s, 3H), 1.17 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.83, 163.27 (t, J = 39.9 Hz), 155.38(t, J = 364.3 Hz), 135.75, 133.51, 128.37, 127.25, 114.33 (t, J = 314.3 Hz), 84.46 (t, J = 25.3 Hz), 63.01, 39.44, 35.27, 33.71 (t, J = 29.0 Hz), 13.66; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.45, -104.28; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{16}H_{18}F_4NO_3$ 348.1217, found: 348.1216.

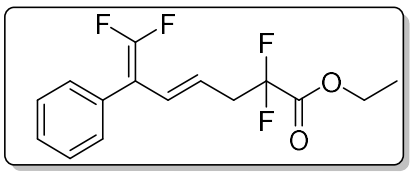


Ethyl 4-(dibenzo[*b*,*d*]thiophen-3-yl)-2,2,5,5-tetrafluoropent-4-enoate (3ua). The representative procedure was followed using 3-(3,3,3-trifluoroprop-1-en-2-yl)dibenzo[b,d]thiophene (**1u**) (55.66 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 30 : 1) yielded **3ua** (61.2 mg, 80 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09 – 8.04 (m, 2H), 7.79 – 7.77 (m, 1H), 7.42 – 7.40 (m, 3H), 7.29 – 7.27 (m, 1H), 3.92 (q, J = 9.0 Hz, 2H), 3.32 – 3.25 (m, 2H), 1.00 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.20 (t, J = 39.9 Hz), 155.41 (t, J = 362.8 Hz), 139.47, 138.92, 136.12, 135.53, 128.14, 127.09, 126.84, 124.73, 124.60, 122.75, 121.78, 121.54, 114.45 (t, J = 308.6 Hz), 83.69 (t, J = 27.8 Hz), 62.95, 33.01 (t, J = 31.9 Hz),

13.52; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -81.56, -86.31, -104.15; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{19}H_{15}F_4O_2S$ 383.0723, found: 383.0726.

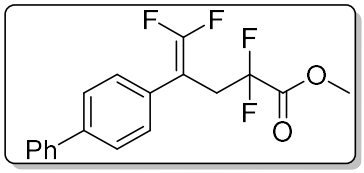


Ethyl 2,2,5,5-tetrafluoro-4-(quinolin-3-yl)pent-4-enoate (3va). The representative procedure was followed using 3-(3,3,3-trifluoroprop-1-en-2-yl)quinoline (**1v**) (44.64 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 20 : 1) yielded **3va** (50.4 mg, 77 %) as a yellow oil.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.87 – 8.86 (m, 1H), 8.12 – 8.09 (m, 2H), 7.84 – 7.82 (m, 1H), 7.76 – 7.73 (m, 1H), 7.60 – 7.57 (m, 1H), 4.07 (q, J = 7.5 Hz, 2H), 3.36 – 3.29 (m, 2H), 1.19 (t, J = 7.5 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.25 (t, J = 32.1 Hz), 155.88 (t, J = 292.1 Hz), 149.86, 147.12, 135.55, 130.10, 129.14, 127.82, 127.38, 127.28, 125.53, 114.33 (t, J = 252.2 Hz), 82.70 (t, J = 33.4 Hz), 63.18, 33.75 (t, J = 23.4 Hz), 13.65; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -84.71, -84.78, -104.11; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{16}H_{14}F_4NO_2$ 328.0955, found: 328.0958.

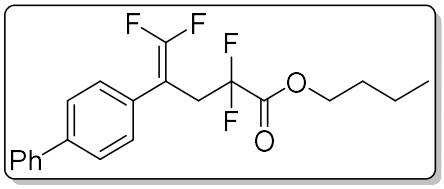


Ethyl (*E*)-2,2,7,7-tetrafluoro-6-phenylhepta-4,6-dienoate (3wa). The representative procedure was followed using (*Z*)-(1,1,1-trifluoropenta-2,4-dien-2-yl)benzene (**1w**) (39.64 mg, 0.20 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 50 : 1) yielded **3wa** (39.3 mg, 65 %) as a colorless oil.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 – 7.30 (m, 2H), 7.29 – 7.27 (m, 1H), 7.16 – 7.15 (m, 2H), 6.40 – 6.36 (m, 1H), 5.23 – 5.17 (m, 1H), 4.22 (q, J = 9.0 Hz, 2H), 2.83 – 2.76 (m, 2H), 1.22 (t, J = 9.0 Hz, 3H); **^{13}C NMR (125**

MHz, $CDCl_3$) δ 163.71 (t, J = 32.3 Hz), 153.85 (t, J = 291.3 Hz), 130.60, 129.98, 128.81, 128.63, 128.54, 128.13, 115.03 (t, J = 250.0 Hz), 95.34 (t, J = 16.1 Hz), 62.83, 38.40 (t, J = 24.3 Hz), 13.85; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.65, -89.05, -105.37; **HRMS** (ESI) m/z ([M+ Na]$^+$) Calcd. for $C_{15}H_{14}F_4O_2Na$ 325.0822, found: 325.0829.

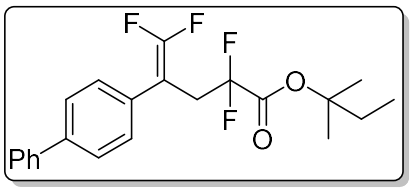


Methyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (3ab). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and methyl 2-bromo-2,2-difluoroacetate (**2b**) (75.58 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 50 : 1) yielded **3ab** (49.4 mg, 73 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.61 – 7.58 (m, 4H), 7.47 – 7.43 (m, 2H), 7.38 – 7.36 (m, 3H), 3.58 (s, 3H), 3.29 – 3.20 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.83 (t, J = 32.4 Hz), 155.39 (t, J = 291.0 Hz), 140.69, 140.23, 135.35, 132.05, 130.87, 128.84, 127.59, 127.11, 126.98, 114.44 (t, J = 254.3 Hz), 84.47 (t, J = 19.4 Hz), 53.18; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.15, -104.41; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{18}H_{15}F_4O_2$ 339.1003, found: 339.1002.

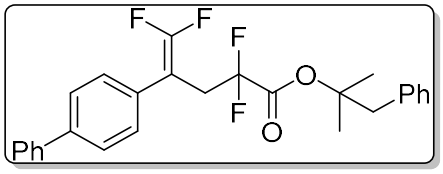


Butyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (3ac). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and butyl 2-bromo-2,2-difluoroacetate (**2c**) (92.42 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 50 : 1) yielded **3ac** (67.7 mg, 89 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.60 – 7.57 (m, 4H), 7.45 – 7.42 (m, 2H), 7.38 – 7.35 (m, 3H), 3.97 (t, J = 7.0 Hz, 2H), 3.26 – 3.20 (m, 2H), 1.57 – 1.52 (m, 2H), 1.35 – 1.27 (m, 2H), 0.88 (t, J = 7.0 Hz, 3H); **^{13}C**

NMR (125 MHz, $CDCl_3$) δ 163.50 (t, J = 32.1 Hz), 155.37 (t, J = 290.8 Hz), 140.67, 140.26, 131.03, 128.85, 128.82, 127.55, 127.11, 126.97, 114.52 (t, J = 241.3 Hz), 84.56 (t, J = 19.8 Hz), 66.77, 33.94 (t, J = 24.1 Hz), 30.07, 18.84, 13.54; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.12, -104.15; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{21}H_{21}F_4O_2$ 381.1472, found: 381.1475.

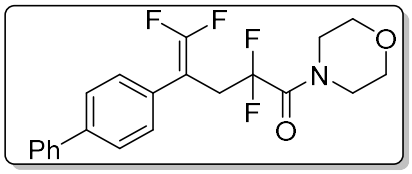


***tert*-pentyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (3ad).** The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and *tert*-pentyl 2-bromo-2,2-difluoroacetate (**2d**) (98.02 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 30 : 1) yielded **3ad** (48.1 mg, 61 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 – 7.49 (m, 4H), 7.38 – 7.35 (m, 2H), 7.32 – 7.28 (m, 3H), 3.15 – 3.09 (m, 2H), 1.65 (q, J = 7.5 Hz, 2H), 1.27 (s, 6H), 0.78 (t, J = 7.5 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.25 (t, J = 31.4 Hz), 155.30 (t, J = 290.6 Hz), 140.70, 140.42, 131.28, 128.86, 128.80, 127.48, 127.19, 127.02, 114.47 (t, J = 242.3 Hz), 87.38, 84.80 (t, J = 19.8 Hz), 33.68 (t, J = 26.1 Hz), 33.28, 24.77, 8.04; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.86, -86.50, -103.38; **HRMS** (ESI) m/z ([M+ Na]$^+$) Calcd. for $C_{22}H_{22}F_4O_2Na$ 417.1488, found: 417.1489.

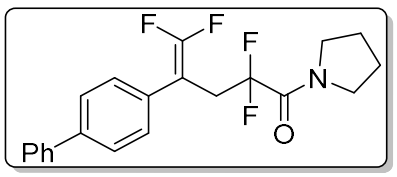


2-methyl-1-phenylpropan-2-yl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (3ae). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and 2-methyl-1-phenylpropan-2-yl 2-bromo-2,2-difluoroacetate (**2e**) (122.85 mg, 0.4 mmol). Isolation by column

chromatography (hexane : EtOAc = 20 : 1) yielded **3ae** (48.4 mg, 58 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47 – 7.41 (m, 4H), 7.36 – 7.33 (m, 2H), 7.27 – 7.25 (m, 1H), 7.24 – 7.16 (m, 5H), 7.08 – 7.06 (m, 2H), 3.09 – 3.03 (m, 2H), 2.84 (s, 2H), 1.24 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.26 (t, J = 31.6 Hz), 155.33 (t, J = 290.8 Hz), 140.62, 140.36, 136.15, 130.65, 128.84, 128.81, 128.78, 128.04, 127.47, 127.15, 126.98, 126.79, 114.35 (t, J = 250.8 Hz), 86.34, 84.66 (t, J = 19.5 Hz), 46.97, 36.63 (t, J = 25.4 Hz), 24.86; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.85, -86.41, -103.73; **HRMS** (ESI) m/z ([M+ Na]$^+$) Calcd. for $C_{27}H_{24}F_4O_2Na$ 479.1605, found: 479.1604.

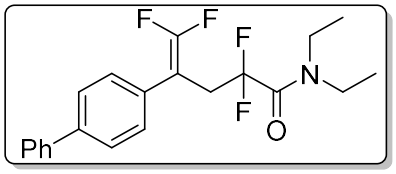


4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoro-1-morpholinopent-4-en-1-one (3af). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and 2-bromo-2,2-difluoro-1-morpholinoethan-1-one (**2f**) (97.62 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 10 : 1) yielded **3af** (63.7 mg, 81 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.60 – 7.58 (m, 4H), 7.45 – 7.40 (m, 4H), 7.36 – 7.33 (m, 1H), 3.69 – 3.58 (m, 8H), 3.41 – 3.33 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 161.47 (t, J = 28.6 Hz), 155.29 (t, J = 290.4 Hz), 140.32, 140.31, 132.17, 128.76, 128.57, 127.43, 127.05, 126.96, 117.89 (t, J = 255.1 Hz), 84.83 (t, J = 19.8 Hz), 66.62, 66.57, 46.34, 43.29, 33.43 (t, J = 22.8 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.36, -98.73; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{21}H_{20}F_4NO_2$ 394.1425, found: 394.1429.

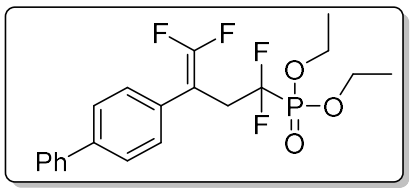


4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoro-1-(pyrrolidin-1-yl)pent-4-en-1-one

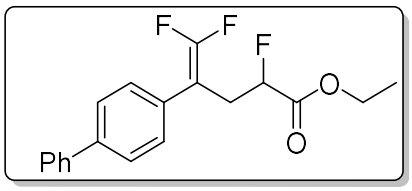
(3ag). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and 2-bromo-2,2-difluoro-1-(pyrrolidin-1-yl)ethan-1-one (**2g**) (91.22 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 30 : 1) yielded **3ag** (57.4 mg, 76 %) as a white solid.; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.60 – 7.57 (m, 4H), 7.45 – 7.41 (m, 4H), 7.36 – 7.33 (m, 1H), 3.60 – 3.56 (m, 2H), 3.41 – 3.31 (m, 4H), 1.86 (q, J = 7.0 Hz, 2H), 1.76 (q, J = 7.0 Hz, 2H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 161.60 (t, J = 29.0 Hz), 155.26 (t, J = 290.4 Hz), 140.30, 140.26, 131.86, 128.76, 128.58, 127.42, 126.98, 126.94, 117.30 (t, J = 254.0 Hz), 84.98 (t, J = 20.9 Hz), 47.37, 46.45, 33.15 (t, J = 24.3 Hz), 26.36, 23.12; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -86.50, -102.03; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{21}H_{20}F_4NO$ 378.1476, found: 378.1472.



4-([1,1'-biphenyl]-4-yl)-*N*,*N*-diethyl-2,2,5,5-tetrafluoropent-4-enamide (3ah). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and 2-bromo-*N*,*N*-diethyl-2,2-difluoroacetamide (**2h**) (92.02 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 20 : 1) yielded **3ah** (54.6 mg, 76 %) as a white solid.; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.52 – 7.50 (m, 4H), 7.37 – 7.33 (m, 4H), 7.28 – 7.25 (m, 1H), 3.37 (q, J = 7.0 Hz, 2H), 3.33 – 3.28 (m, 2H), 3.26 (q, J = 7.0 Hz, 2H), 1.08 (t, J = 7.0 Hz, 3H), 1.03 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.28 (t, J = 28.4 Hz), 155.27 (t, J = 289.9 Hz), 140.41, 140.20, 132.27, 128.75, 128.60, 127.38, 127.02, 126.97, 118.04 (t, J = 252.6 Hz), 85.13 (t, J = 18.6 Hz), 41.71, 41.47, 33.58 (t, J = 23.5 Hz), 14.17, 12.16; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -86.55, -99.39; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{21}H_{22}F_4NO$ 380.1632, found: 380.1637.

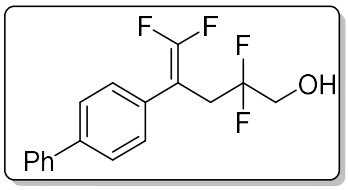


Diethyl (3-([1,1'-biphenyl]-4-yl)-1,1,4,4-tetrafluorobut-3-en-1-yl)phosphonate (3ai). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and diethyl (bromodifluoromethyl)phosphonate (**2i**) (106.80 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 20 : 1) yielded **3ai** (66.6 mg, 80 %) as a yellow solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.60 – 7.58 (m, 4H), 7.44 – 7.41 (m, 4H), 7.36 – 7.33 (m, 1H), 4.27 – 4.23 (m, 4H), 3.26 – 3.19 (m, 2H), 1.38 – 1.35 (m, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.32 (t, J = 290.4 Hz), 140.40, 140.33, 131.98, 128.76, 128.59, 127.42, 127.06, 126.99, 84.31 (t, J = 21.1 Hz), 64.67, 64.62, 32.80 (q, J = 21.0 Hz), 16.34; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.64, -86.01, -110.61; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 6.45 (t, J = 84.4 Hz); **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{20}H_{22}F_4O_3P$ 417.1237, found: 417.1239.

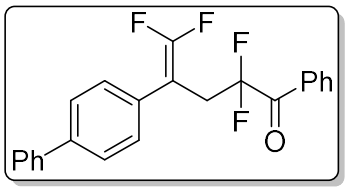


Ethyl 4-([1,1'-biphenyl]-4-yl)-2,5,5-trifluoropent-4-enoate (3aj). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol) and ethyl 2-bromo-2-fluoroacetate (**2j**) (74.00 mg, 0.4 mmol). Isolation by column chromatography (hexane : EtOAc = 50 : 1) yielded **3aj** (38.8 mg, 58 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54 – 7.50 (m, 4H), 7.39 – 7.33 (m, 4H), 7.28 (m, 1H), 4.86 – 4.74 (m, 1H), 4.08 – 4.00 (m, 2H), 3.00 – 2.93 (m, 2H), 1.16 (m, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 167.92 (d, J = 23.25 Hz), 153.74 (t, J = 289.0 Hz), 139.65, 139.32, 129.99, 127.85, 127.82, 126.52, 126.27, 125.99, 86.13 (t, J = 19.06 Hz), 84.68, 60.72, 30.35 (d, J = 22.63 Hz), 12.97; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -87.76, -191.04; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{19}H_{18}F_3O_2$

335.1253, found: 335.1258.

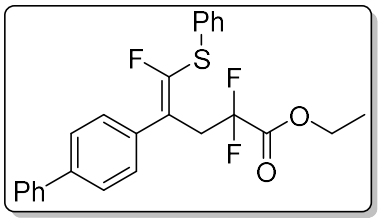


4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-en-1-ol (5). The representative procedure was followed using ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (**3aa**) (352.33 mg, 1.0 mmol) and $NaBH_4$ (56.75 mg, 1.5 mmol). Isolation by column chromatography (hexane : EtOAc = 5 : 1) yielded **5** (285.29 mg, 92 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 – 7.49 (m, 4H), 7.36 – 7.32 (m, 4H), 7.27 – 7.24 (m, 1H), 3.58 – 3.53(m, 2H), 3.04 – 2.97 (m, 2H), 1.91 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.21 (t, J = 290.2 Hz), 140.46, 140.25, 131.86, 128.79, 128.56, 127.50, 127.18, 126.97, 121.92 (t, J = 242.9 Hz), 85.50 (t, J = 20.9 Hz), 63.63 (t, J = 31.1 Hz), 32.19 (t, J = 25.6 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.48, -87.03, -106.07; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{17}H_{15}F_4O$ 311.1054, found: 311.1056.

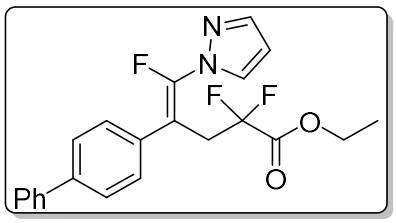


4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoro-1-phenylpent-4-en-1-one (6). The representative procedure was followed using ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (**3aa**) (49.65 mg, 0.20 mmol) and phenylmagnesium bromide (0.30 mmol). Isolation by column chromatography (hexane : EtOAc = 10 : 1) yielded **7** (54.6 mg, 71 %) as a white solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58 – 7.53 (m, 6H), 7.44 – 7.41 (m, 2H), 7.35 – 7.28 (m, 6H), 3.41 – 3.35 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.14 (t, J = 289.9 Hz), 141.18, 140.48, 140.00, 132.70, 128.74, 128.43, 128.14, 128.10, 127.92, 127.38, 127.35, 126.98, 126.97, 124.56 (t, J = 253.9 Hz) 79.91 (t, J = 25.1 Hz), 31.72 (t, J = 23.1 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -86.91, -87.03, -104.97; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{23}H_{17}F_4O$ 385.1210,

found: 385.1212.



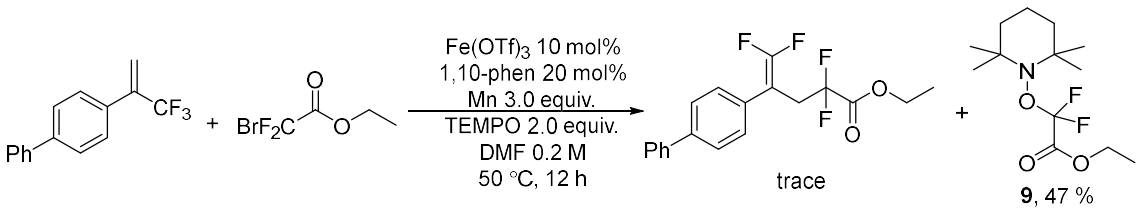
Ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)-2,2,5-trifluoro-5-(phenylthio)pent-4-enoate (7). The representative procedure was followed using ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (**3aa**) (49.65 mg, 0.20 mmol) and S-phenyl 4-methylbenzenesulfonothioate (63.44 mg, 0.24 mmol). Isolation by column chromatography (hexane : EtOAc = 20 : 1) yielded **6** (50.4 mg, 57 %) as a yellow solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 – 7.50 (m, 4H), 7.39 – 7.34 (m, 2H), 7.32 – 7.25 (m, 6H), 7.22 – 7.15 (m, 2H), 3.98 (q, J = 7.0 Hz, 2H), 3.41 – 3.35 (m, 2H), 1.12 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.45 (t, J = 31.9 Hz), 154.73 (t, J = 96.8 Hz), 152.31, 140.96, 140.35, 135.36, 134.17, 131.41, 129.87, 129.45, 129.02, 128.80 (t, J = 28.0 Hz), 127.56, 127.02, 126.88, 114.27 (t, J = 248.5 Hz), 62.95, 29.69, 13.69; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -84.10, -103.00; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{25}H_{22}F_3O_2S$ 443.1287, found: 443.1289.



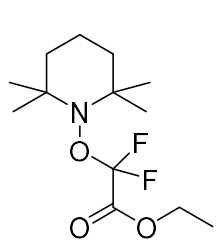
Ethyl (*Z*)-4-([1,1'-biphenyl]-4-yl)-2,2,5-trifluoro-5-(1*H*-pyrazol-1-yl)pent-4-enoate (8). The representative procedure was followed using ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-enoate (**3aa**) (297.9 mg, 1.20 mmol) and 1*H*-imidazole (68.1 mg, 1.0 mmol). Isolation by column chromatography (hexane : DCM = 3 : 1) yielded **8** (201.6 mg, 42 %) as a yellow solid.; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.64 (s, 1H), 7.55 – 7.53 (m, 2H), 7.47 – 7.46 (m, 2H), 7.43 – 7.40 (m, 2H), 7.35 – 7.34 (m, 1H), 7.24 – 7.23 (m, 1H), 7.11 – 7.09 (m, 2H), 6.20 (s, 1H), 4.10 (q, J = 7.0 Hz, 2H), 3.53 – 3.47

(m, 2H), 1.27 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 163.38 (t, J = 32.1 Hz), 148.71, 146.59, 142.28, 140.65 (t, J = 47.6 Hz), 139.97, 131.85, 131.20, 128.77, 128.64, 127.56, 127.04, 126.84, 114.43 (t, J = 251.8 Hz), 107.43, 63.07, 35.82 (t, J = 25.9 Hz), 13.69; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -88.00, -103.07; **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_{22}H_{20}F_3N_2O_2$ 401.1471, found: 401.1473.

5. Mechanistic studies



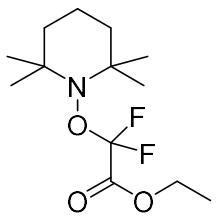
Ethyl 2,2-difluoro-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate (9). The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) (49.65 mg, 0.20 mmol), ethyl 2-bromo-2,2-difluoroacetate (**2a**) (81.19 mg, 0.4 mmol) and TEMPO (62.5 mg, 0.4 mmol). Then we found that TEMPO can capture ester radical in 47% isolated yield. Isolation by column chromatography (hexane : DCM = 3 : 1) yielded **9** as a colorless liquid.; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 4.31 – 4.26 (q, J = 7.0 Hz, 2H), 1.52 – 1.47 (m, 6H), 1.32 – 1.28 (t, J = 7.0 Hz, 3H), 1.12 (s, 6H), 1.10 (s, 6H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 160.73 (t, J = 42.1 Hz), 115.48 (t, J = 269.8 Hz), 63.00, 61.38, 40.19, 33.41, 20.75, 16.90, 13.92; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.46.



9

^{1}H NMR, 500 MHz

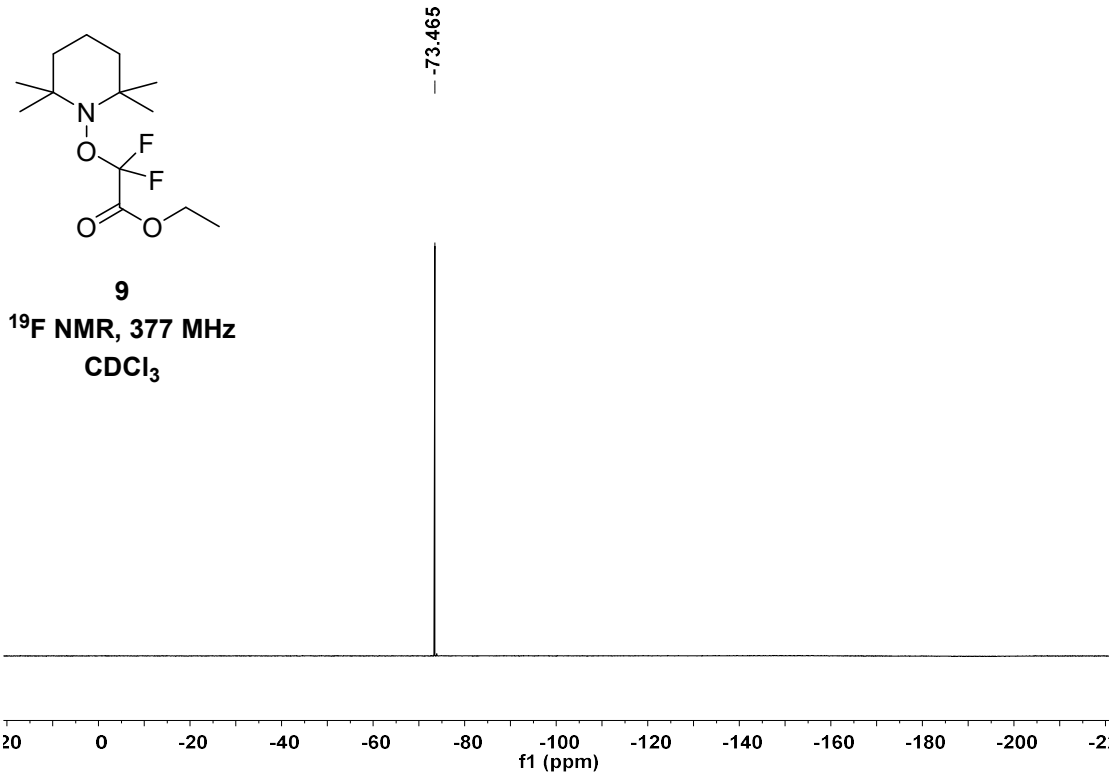
$CDCl_3$



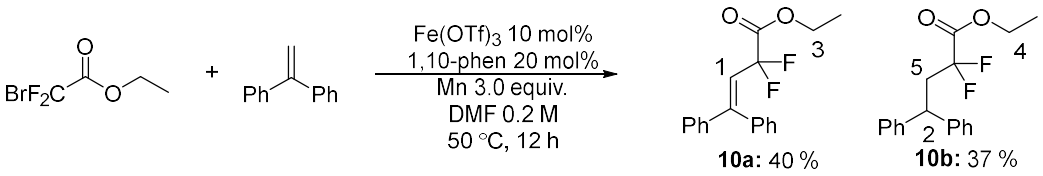
9

^{13}C NMR, 125 MHz

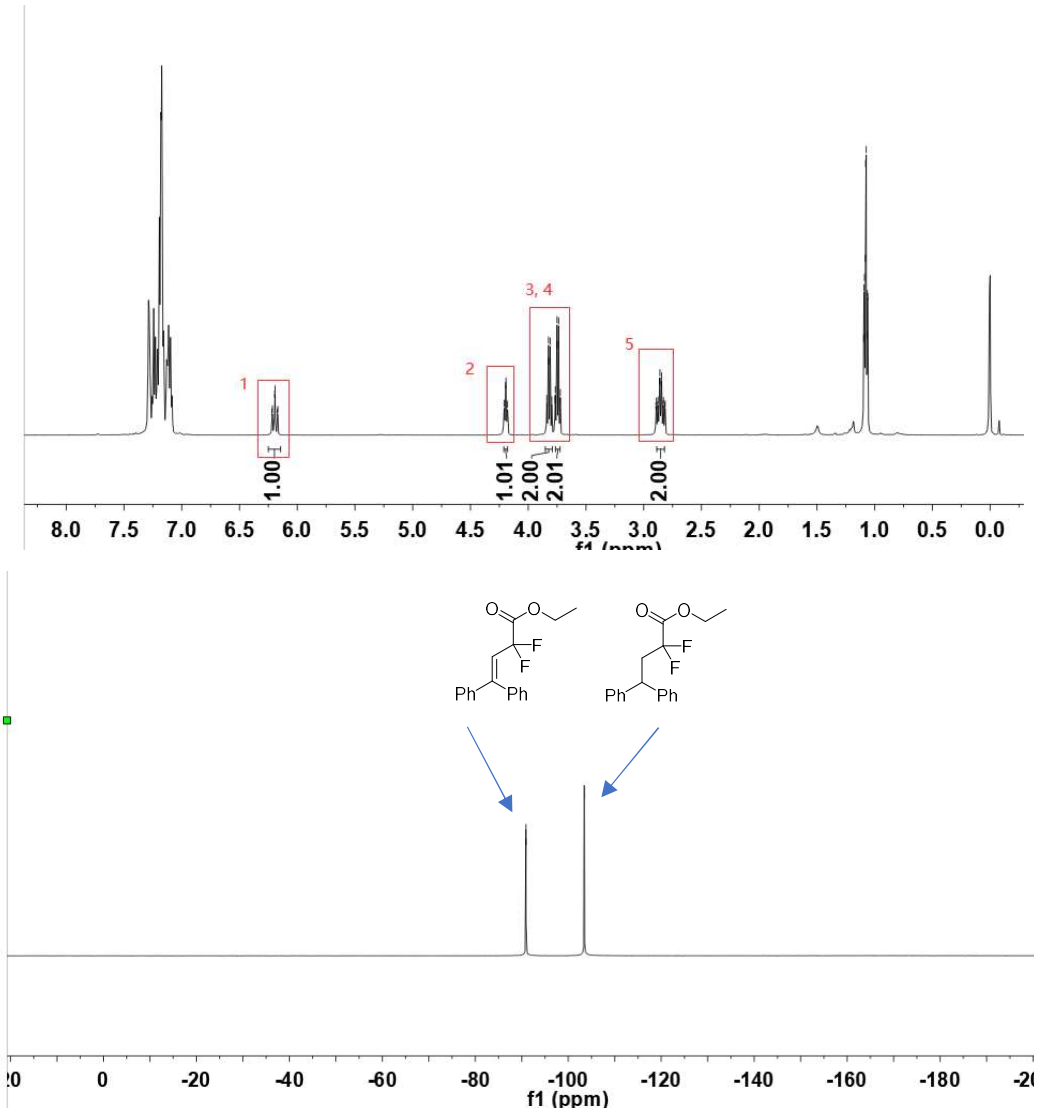
$CDCl_3$



9
^{19}F NMR, 377 MHz
$CDCl_3$



To a 10 mL Schlenk tube was added sequentially $Fe(OTf)_3$ (10.07 mg, 0.02 mmol), 1,10-Phenanthroline (6.80 mg, 0.04 mmol), Mn power (32.90 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMF (0.20 mL) was added via syringe and the mixture was stirred at room temperature for 10 min, ethyl 2-bromo-2,2-difluoroacetate (0.4 mmol, 81.2 mg) and 1,1-diphenylethylene (0.4 mmol, 72.0 mg) was added. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (5 mL) and washed with water (2.0 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.



References:

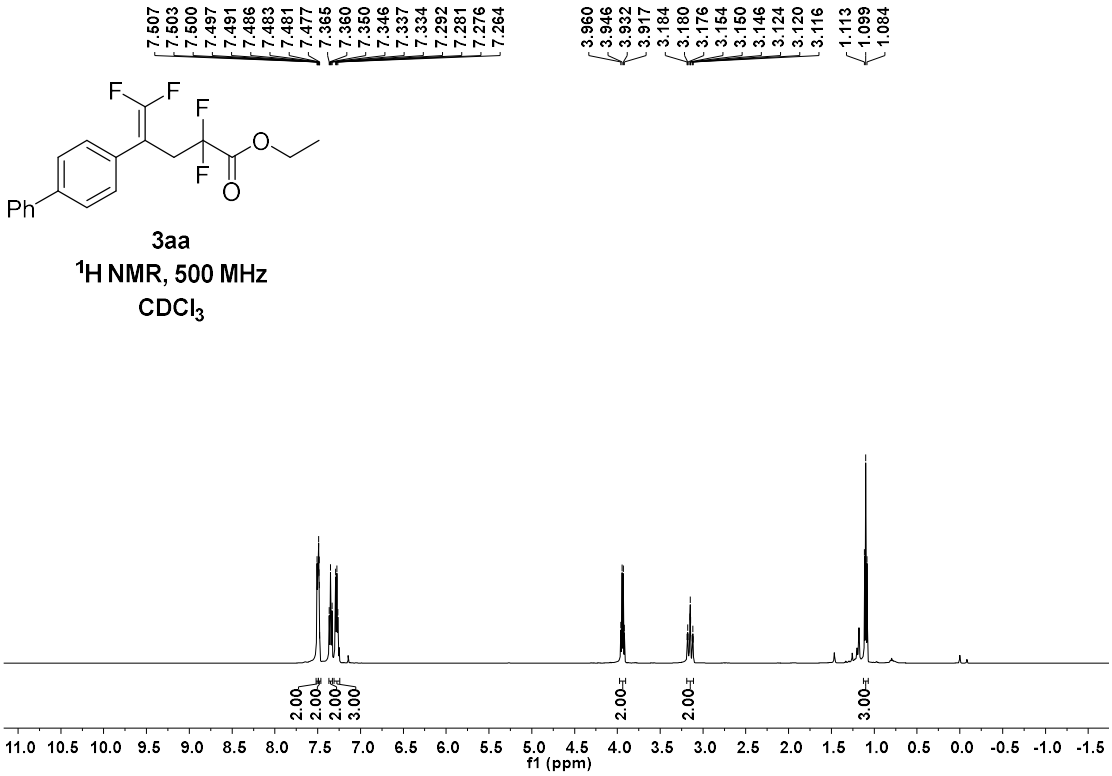
[1] B. M. Trost and L. Debien, *J. Am. Chem. Soc*., 2015, **137**, 11606.

[2] S. B. Lang, R. J. Wiles, C. B. Kelly and G. A. Molander, *Angew. Chem. Int. Ed*., 2017, **56**, 15073.

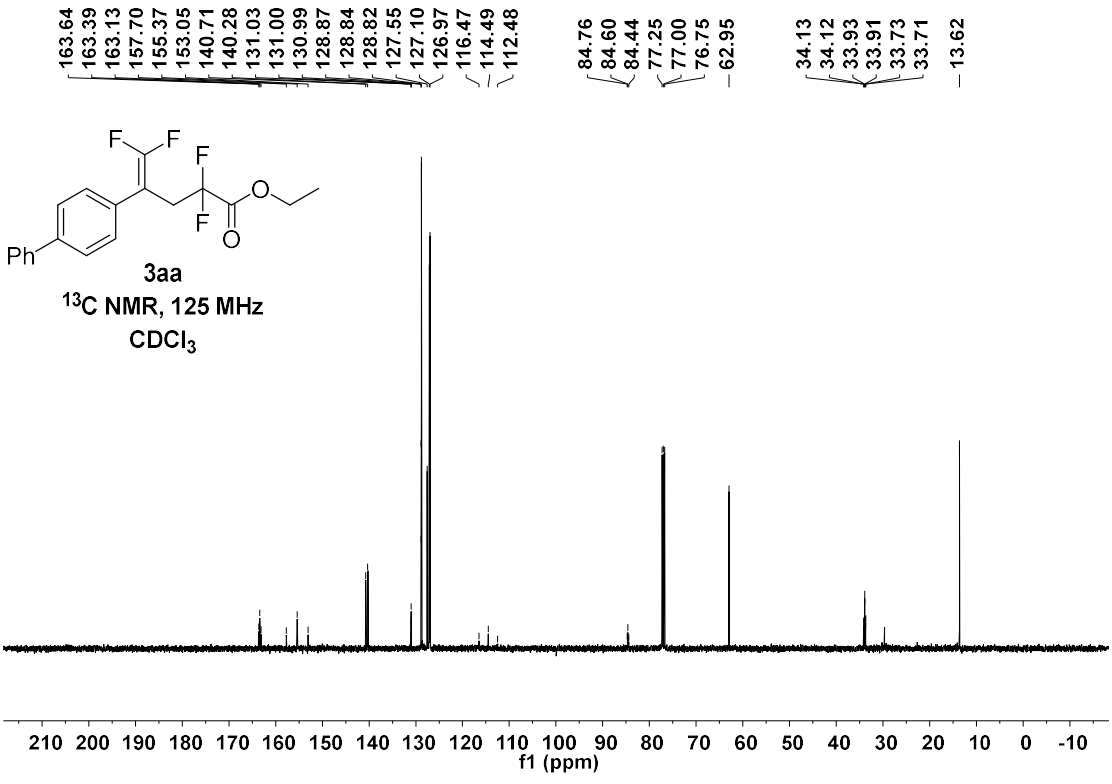
[3] J. Li, W. Rao, S.-Y. Wang and S.-J. Ji, *J. Org. Chem*., 2019, **84**, 11542.

[4] Y. Xiong, X. Zhang, T. Huang and S. Cao, *J. Org. Chem*., 2014, **79**, 6395.

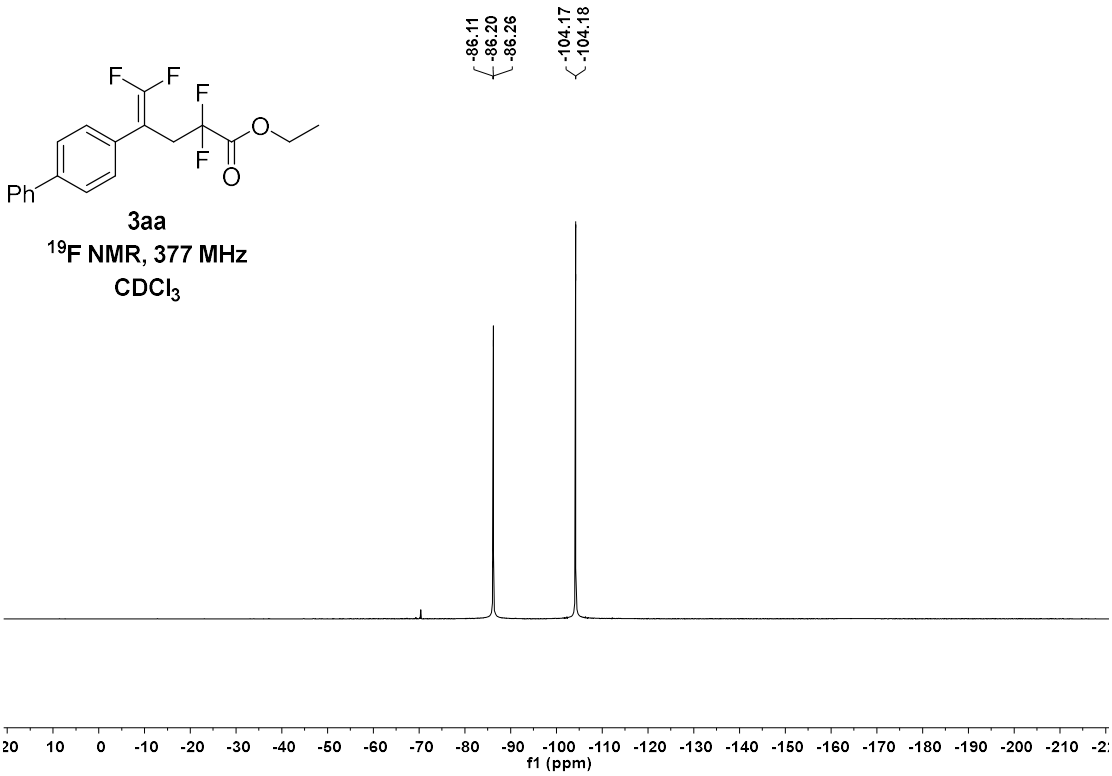
6. NMR Spectra for all the products

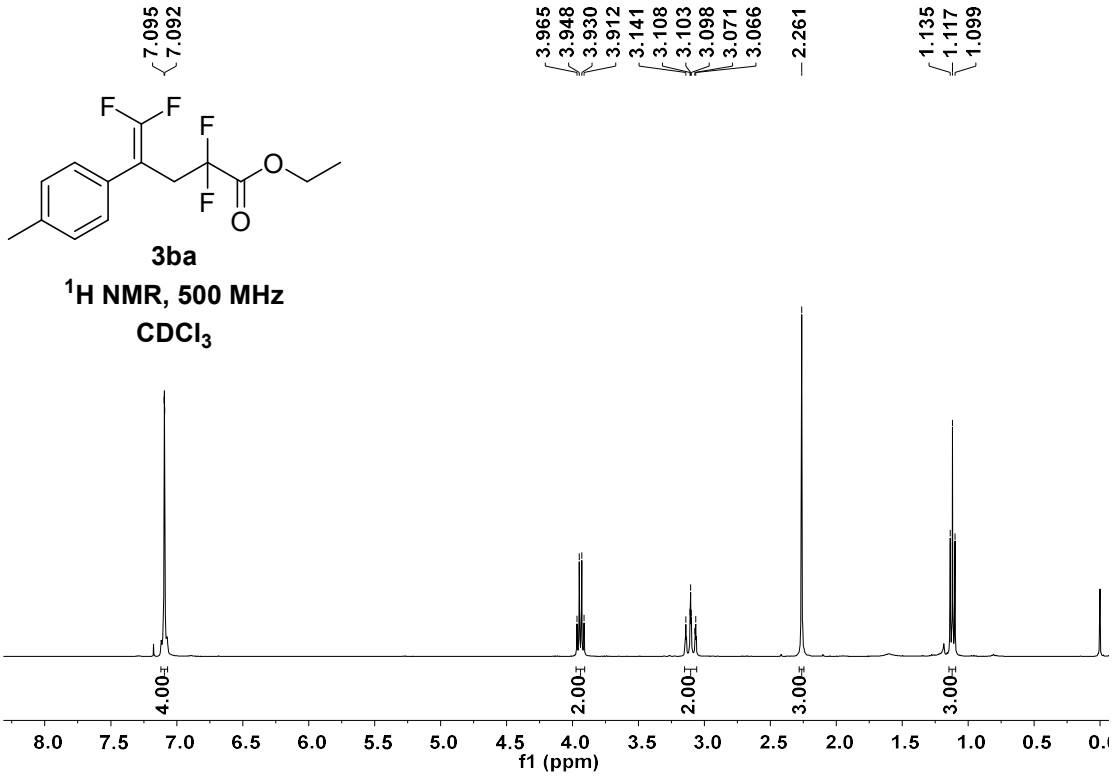


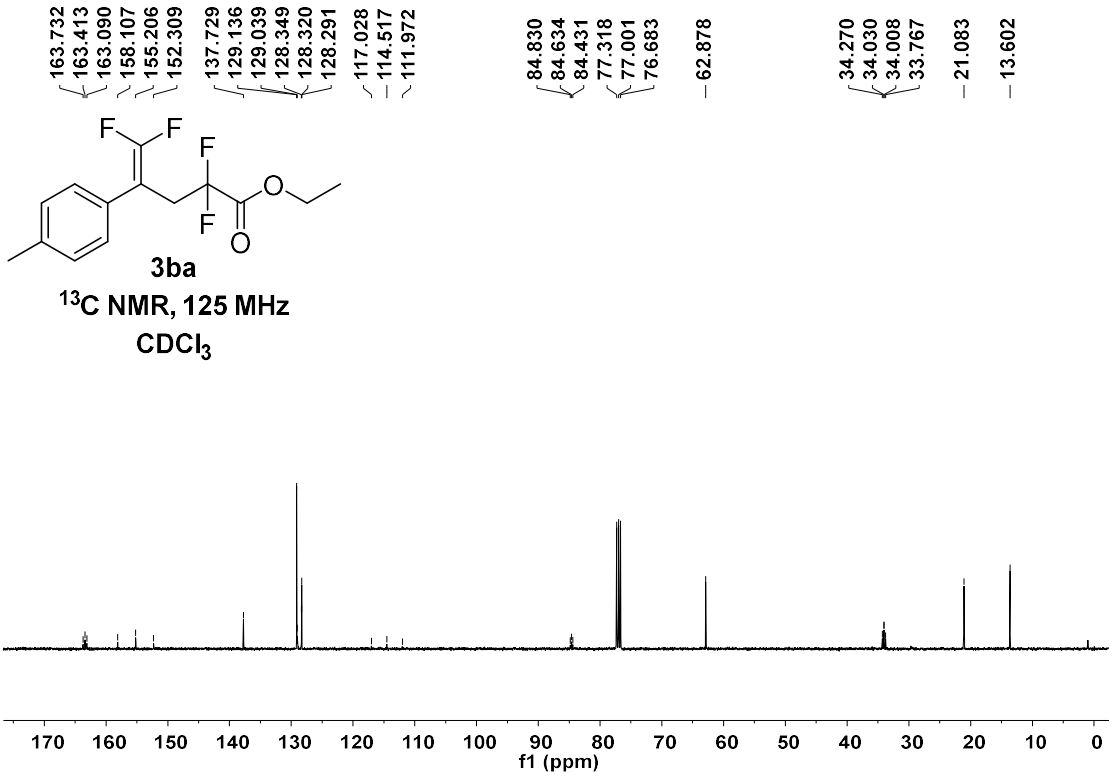
3aa
^{1}H NMR, 500 MHz
$CDCl_3$

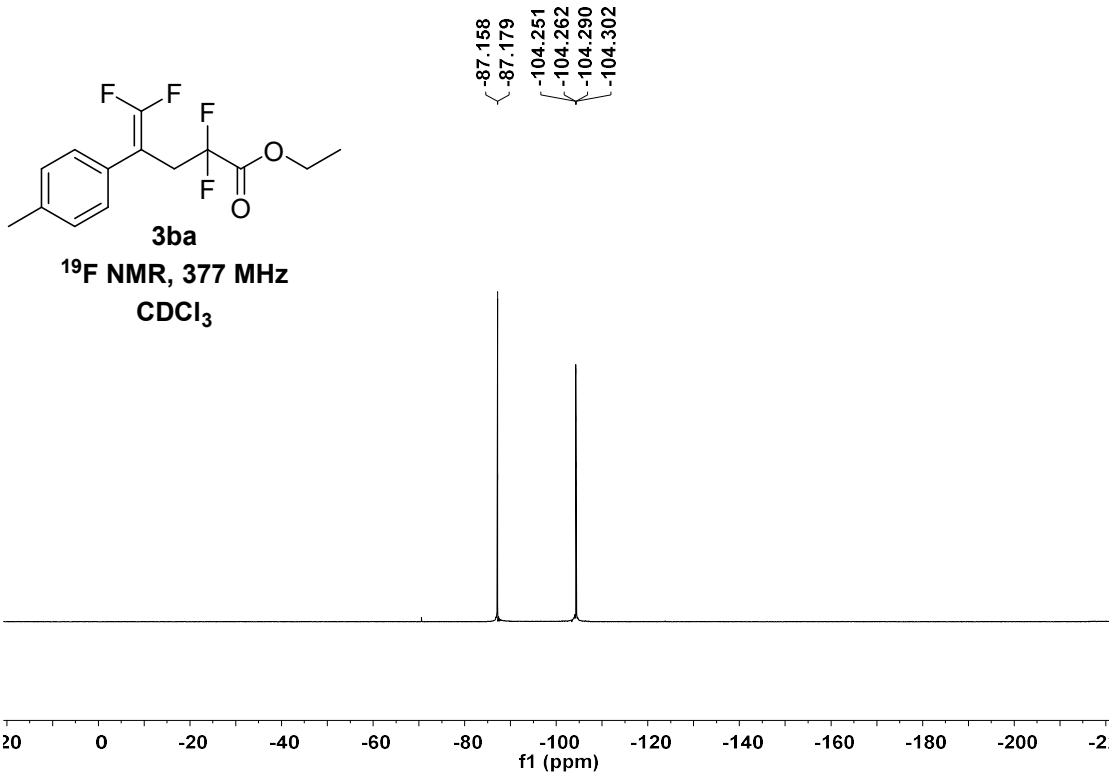


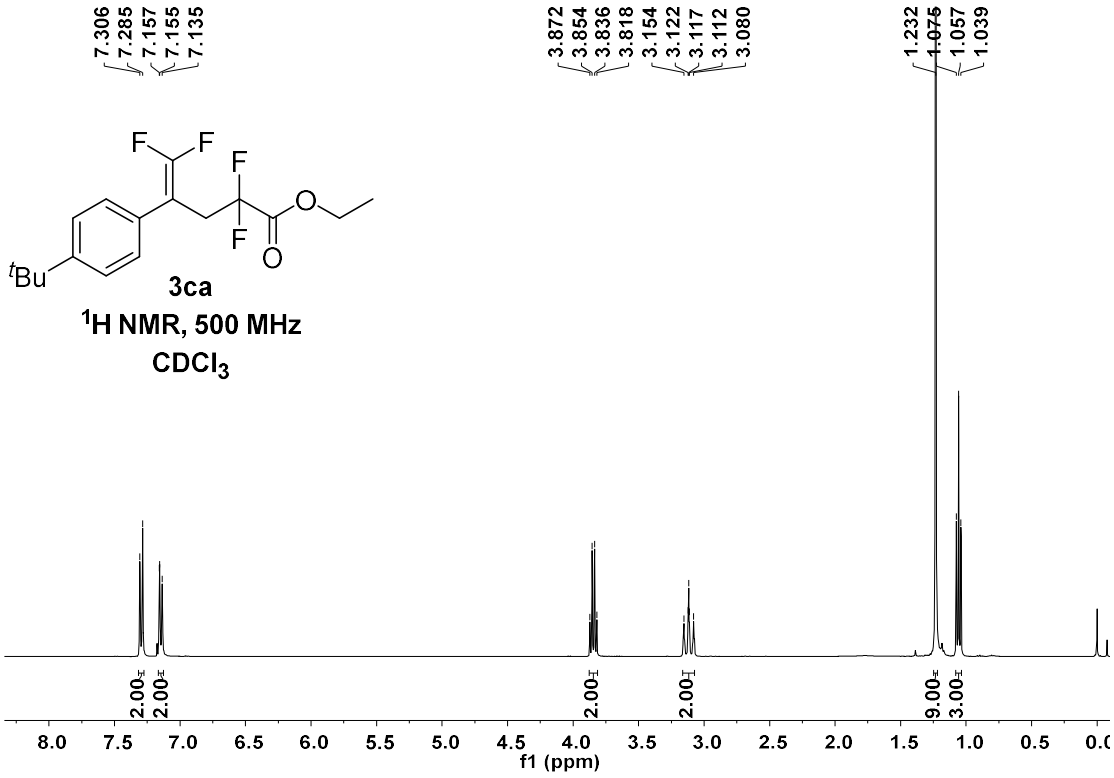
3aa
^{13}C NMR, 125 MHz
$CDCl_3$

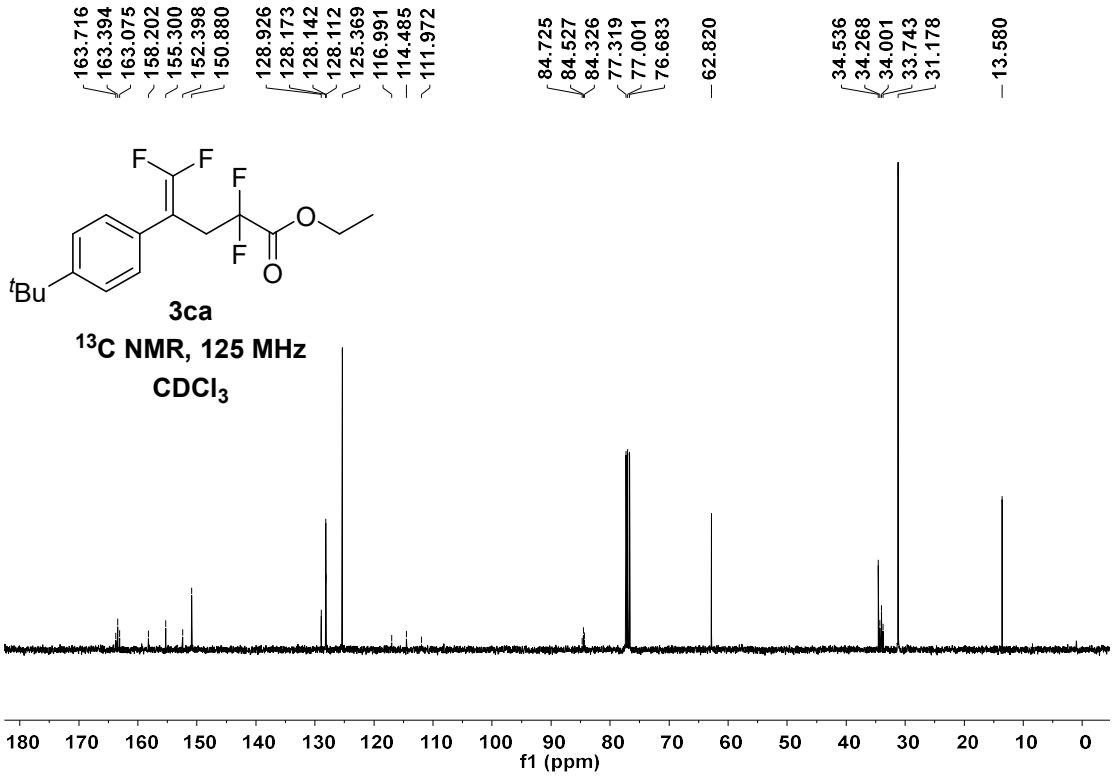

-86.11
-86.20
-86.26
-104.17
-104.18
F
F
F
F
O
O
Ph
3aa
19F NMR, 377 MHz
CDCl3
f1 (ppm)

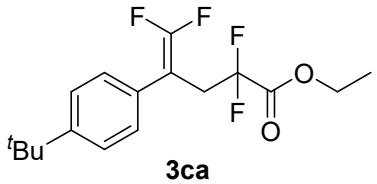

7.095
7.092
3.965
3.948
3.930
3.912
3.141
3.108
3.103
3.098
3.071
3.066
2.261
1.135
1.117
1.099
F
F
F
F
O
O
3ba
1H NMR, 500 MHz
CDCl3
4.00
2.00
2.00
3.00
3.00
f1 (ppm)


163.732
163.413
163.090
158.107
155.206
152.309
137.729
129.136
129.039
128.349
128.320
128.291
117.028
114.517
111.972
84.830
84.634
84.431
77.318
77.001
76.683
62.878
34.270
34.030
34.008
33.767
21.083
13.602
F
F
F
F
O
O
3ba
13C NMR, 125 MHz
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-87.158
-87.179
-104.251
-104.262
-104.290
-104.302
F
F
F
F
O
O
3ba
19F NMR, 377 MHz
CDCl3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.306
7.285
7.157
7.155
7.135
3.872
3.854
3.836
3.818
3.154
3.122
3.117
3.112
3.080
1.232
1.076
1.057
1.039
F
F
F
F
O
O
tBu
3ca
1H NMR, 500 MHz
CDCl3
2.00
2.00
2.00
2.00
9.00
3.00
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)

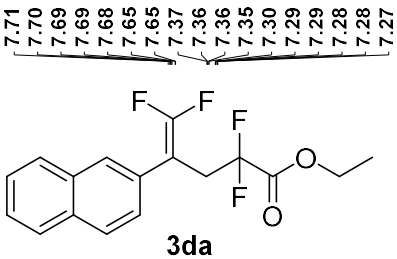

163.716
163.394
163.075
158.202
155.300
152.398
150.880
128.926
128.173
128.142
128.112
125.369
116.991
114.485
111.972
84.725
84.527
84.326
77.319
77.001
76.683
62.820
34.536
34.268
34.001
33.743
31.178
13.580
F
F
F
F
O
O
tBu
3ca
13C NMR, 125 MHz
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3ca

^{19}F NMR, 377 MHz

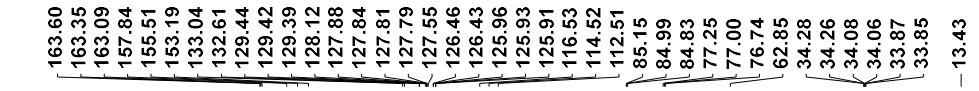
$CDCl_3$

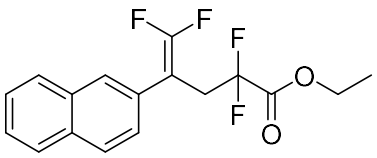


3da

^{1}H NMR, 500 MHz

$CDCl_3$

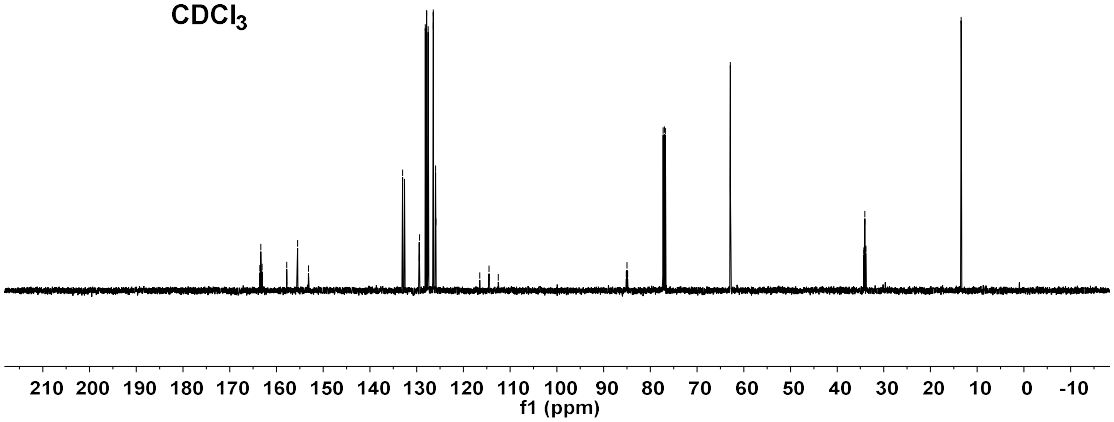


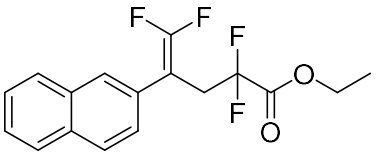


3da

^{13}C NMR, 125 MHz

$CDCl_3$

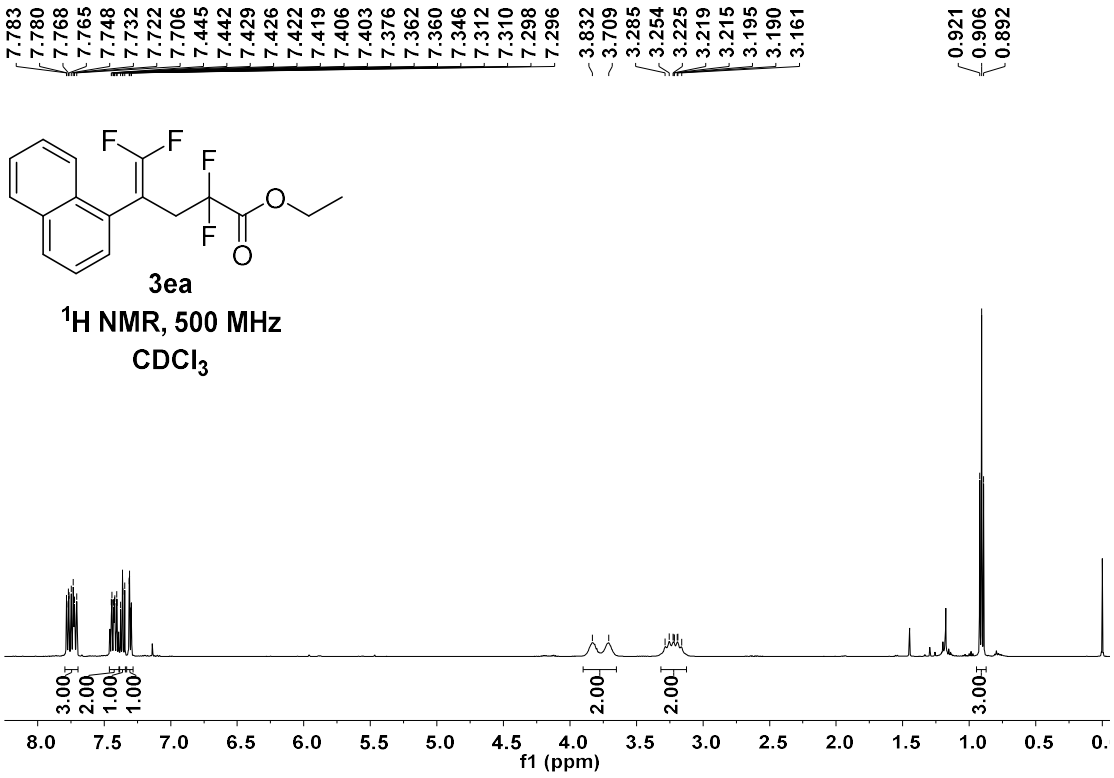




3da

^{19}F NMR, 377 MHz

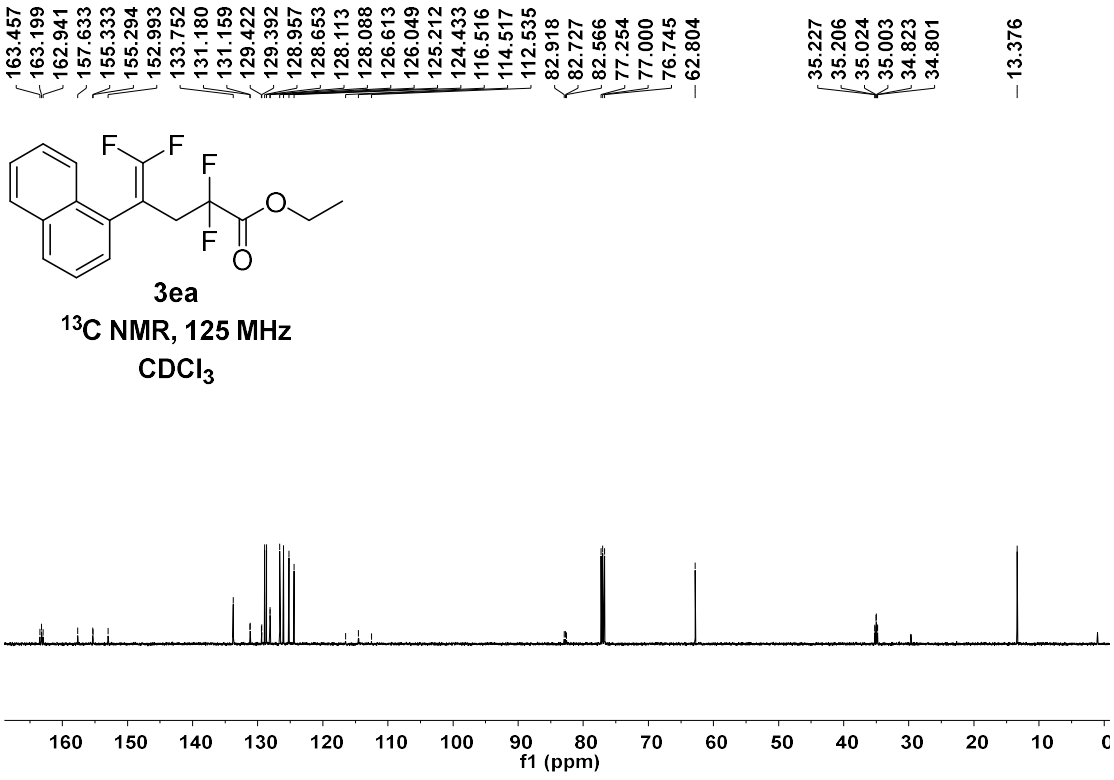
$CDCl_3$



3ea

^{1}H NMR, 500 MHz

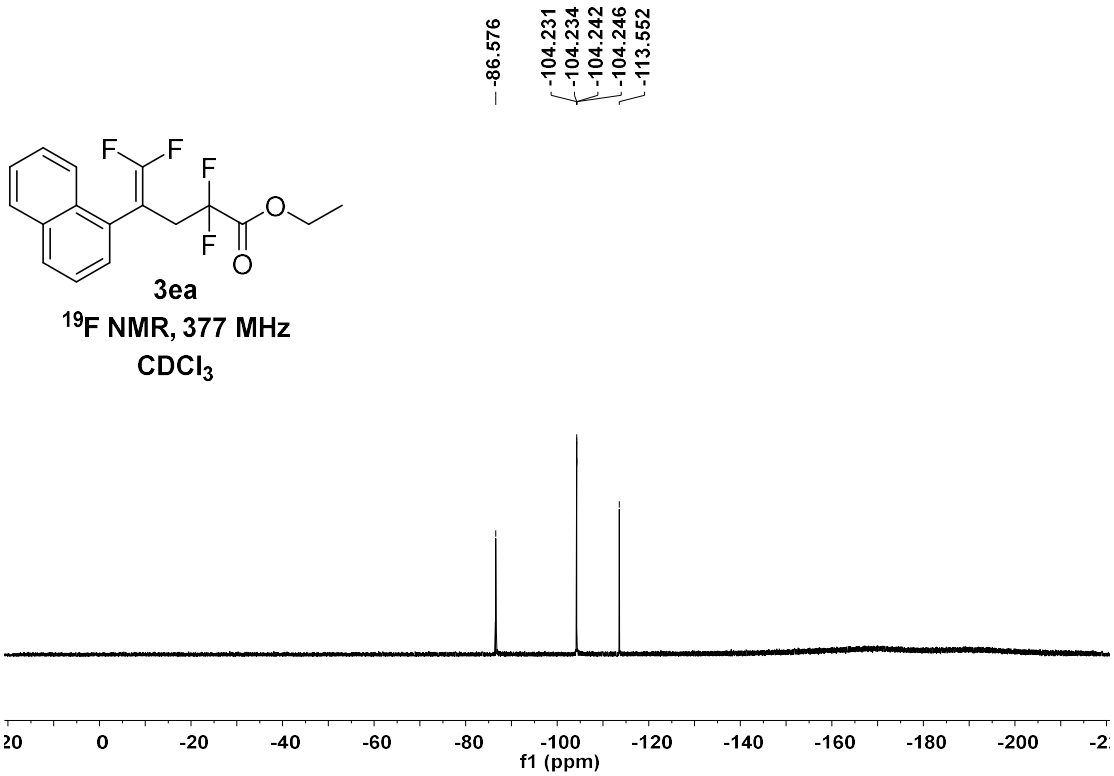
$CDCl_3$

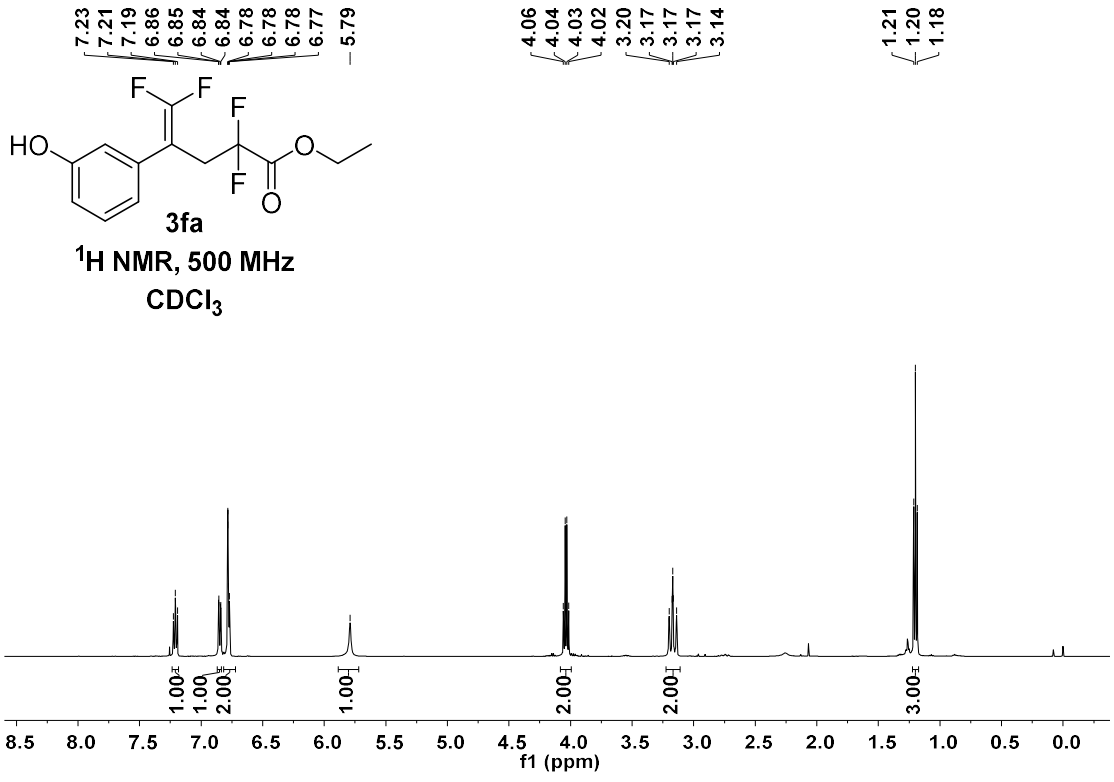


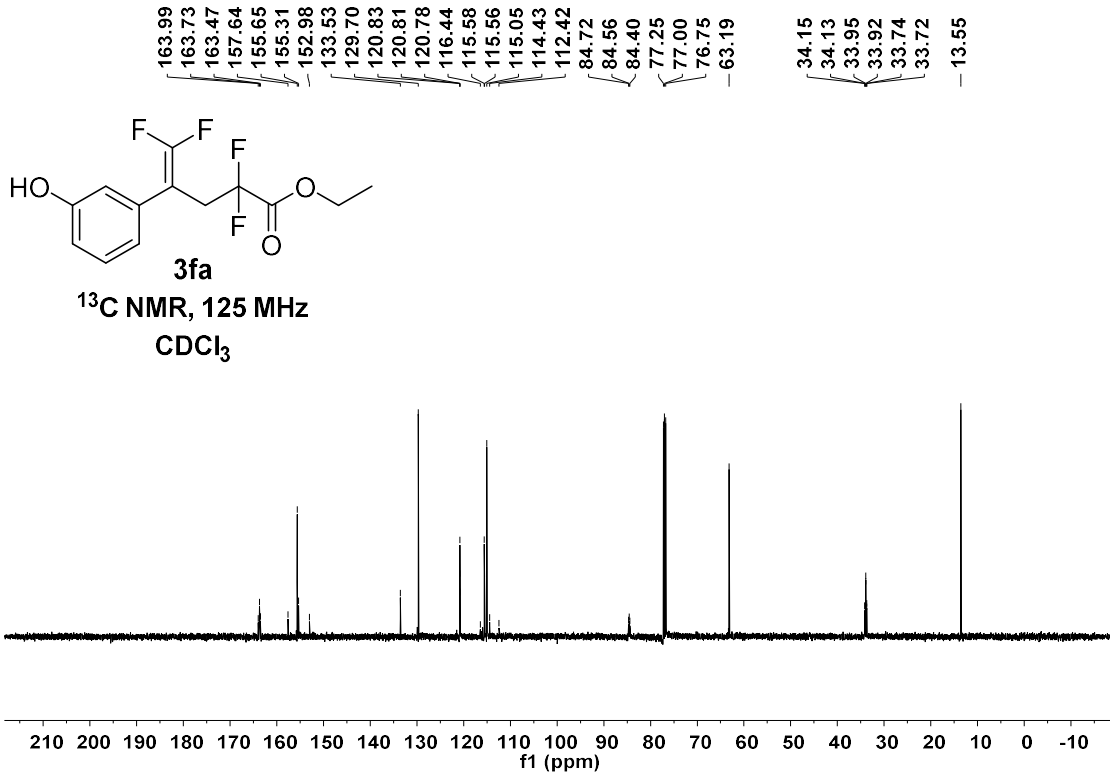
3ea

^{13}C NMR, 125 MHz

$CDCl_3$


-86.576
-104.231
-104.234
-104.242
-104.246
-113.552
F
F
F
F
O
O
3ea
19F NMR, 377 MHz
CDCl3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.23
7.21
7.19
6.86
6.85
6.84
6.84
6.78
6.78
6.77
5.79
4.06
4.04
4.03
4.02
3.20
3.17
3.17
3.17
3.14
1.21
1.20
1.18
F
F
F
F
HO
O
O
3fa
1H NMR, 500 MHz
CDCl3
1.00
1.00
2.00
1.00
2.00
2.00
3.00
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)


163.99
163.73
163.47
157.64
155.65
155.31
152.98
133.53
129.70
120.83
120.81
120.78
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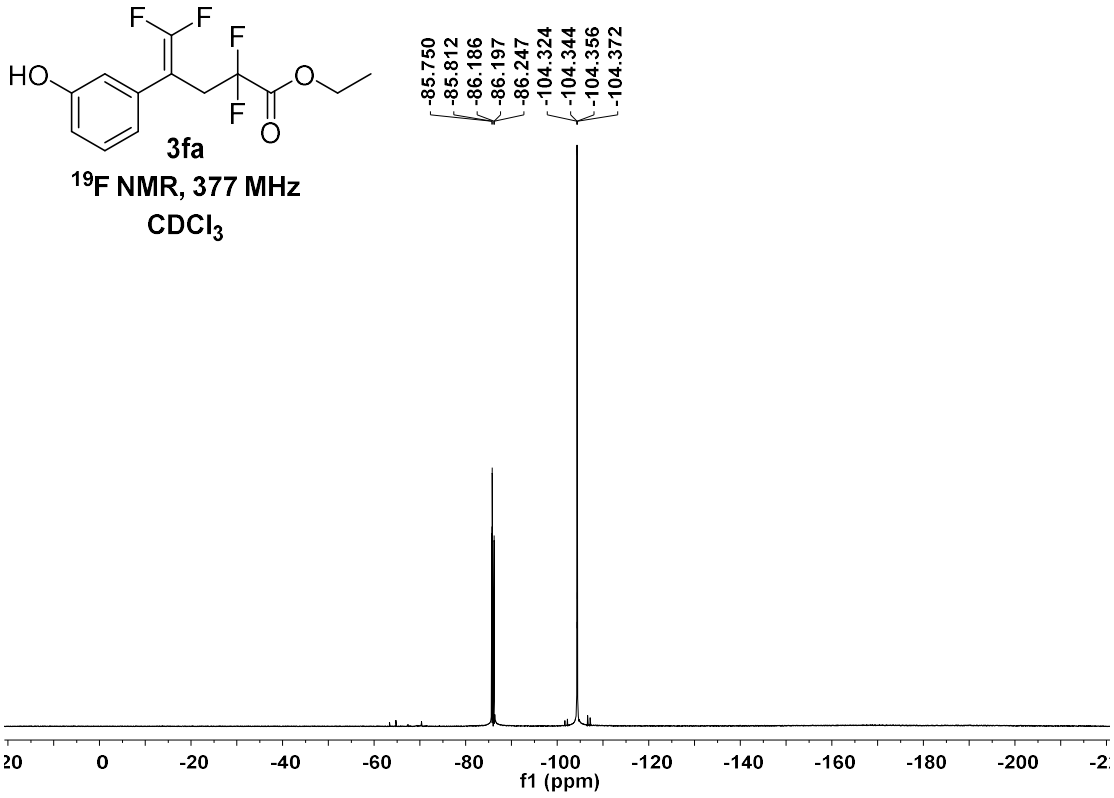
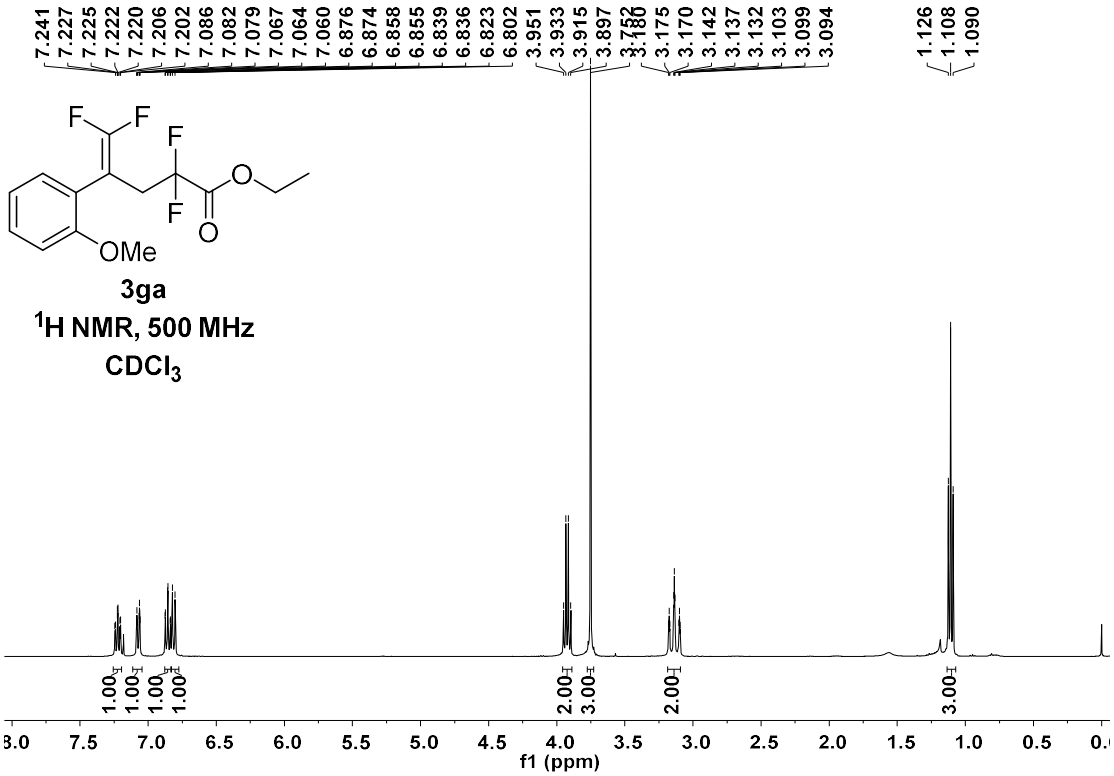
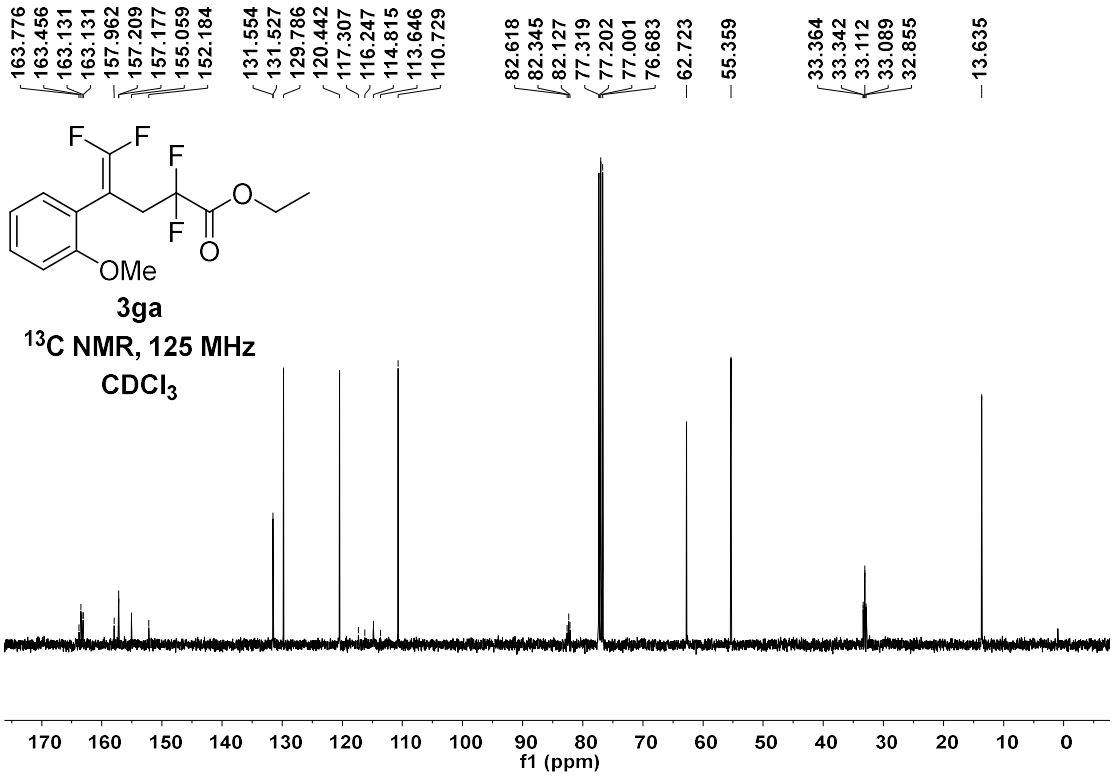
115.58
115.56
115.05
114.43
112.42
84.72
84.56
84.40
77.25
77.00
76.75
63.19
34.15
34.13
33.95
33.92
33.74
33.72
13.55
F
F
F
HO
O
F
O
3fa
13C NMR, 125 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
F
F
HO
O
F
O
3fa
19F NMR, 377 MHz
CDCl3
-85.750
-85.812
-86.186
-86.197
-86.247
-104.324
-104.344
-104.356
-104.372
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.241
7.227
7.225
7.222
7.220
7.206
7.202
7.086
7.082
7.079
7.067
7.064
7.060
6.876
6.874
6.858
6.855
6.839
6.836
6.823
6.802
3.951
3.933
3.915
3.897
3.175
3.170
3.142
3.137
3.132
3.103
3.099
3.094
1.126
1.108
1.090
F
F
F
F
O
O
OMe
3ga
1H NMR, 500 MHz
CDCl3
1.00
1.00
1.00
1.00
2.00
3.00
2.00
3.00
f1 (ppm)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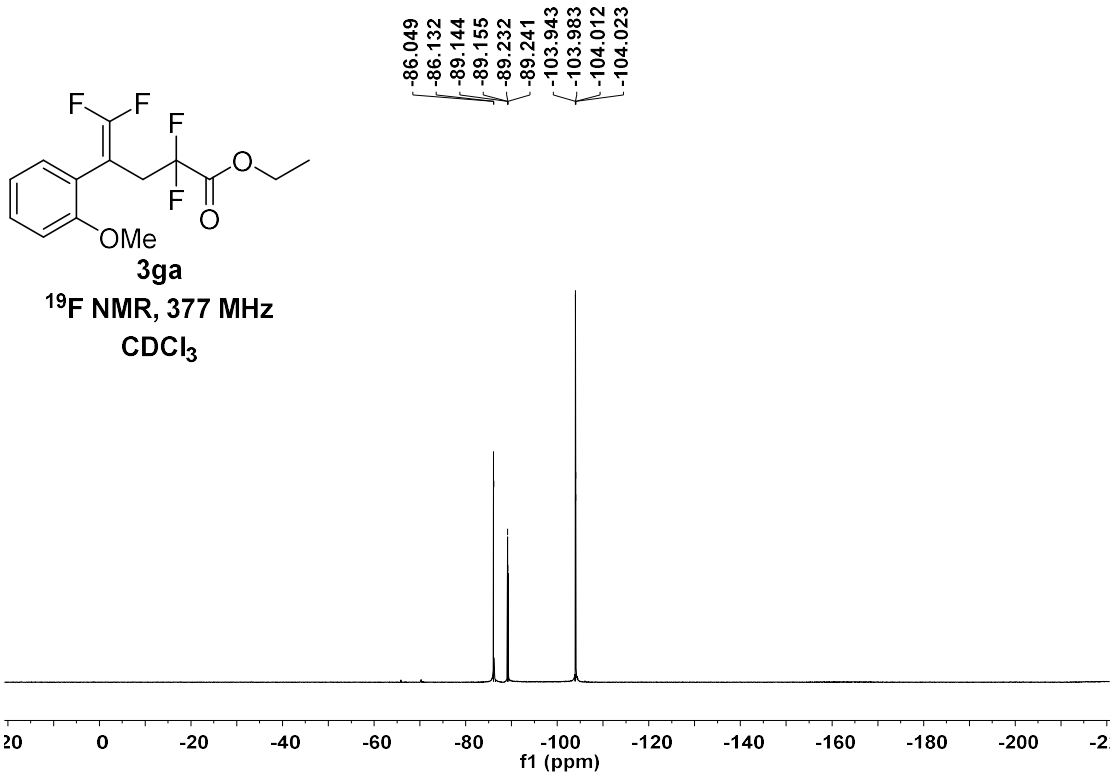
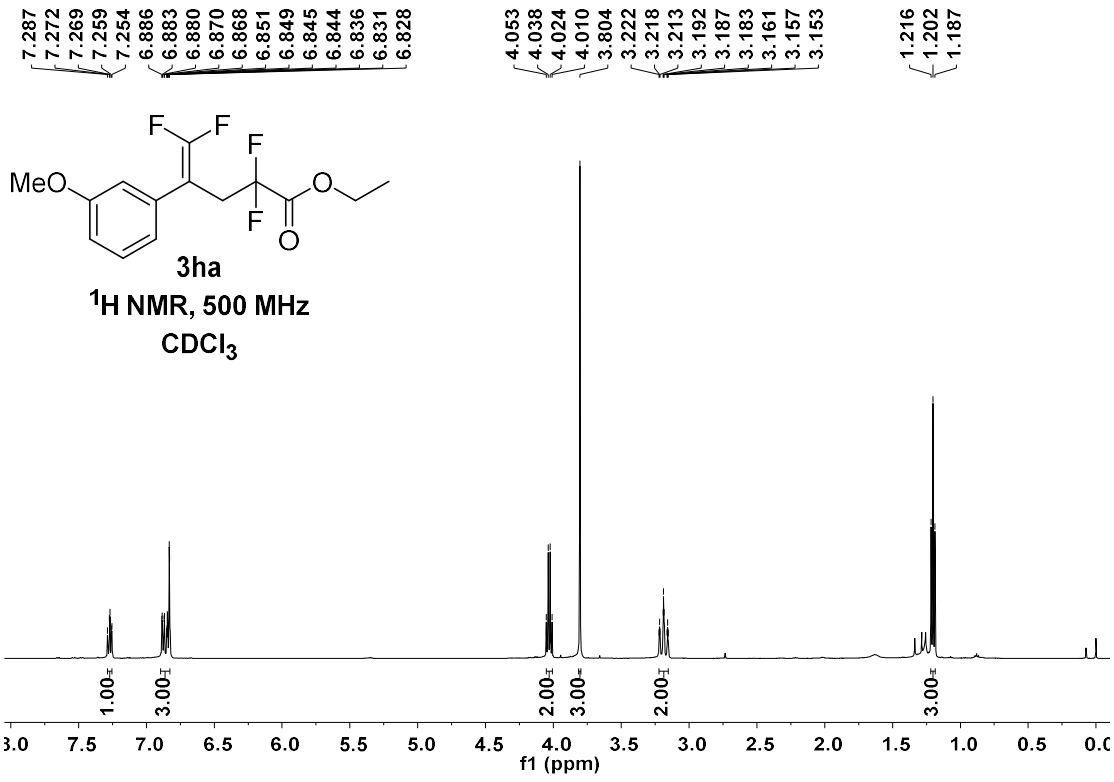
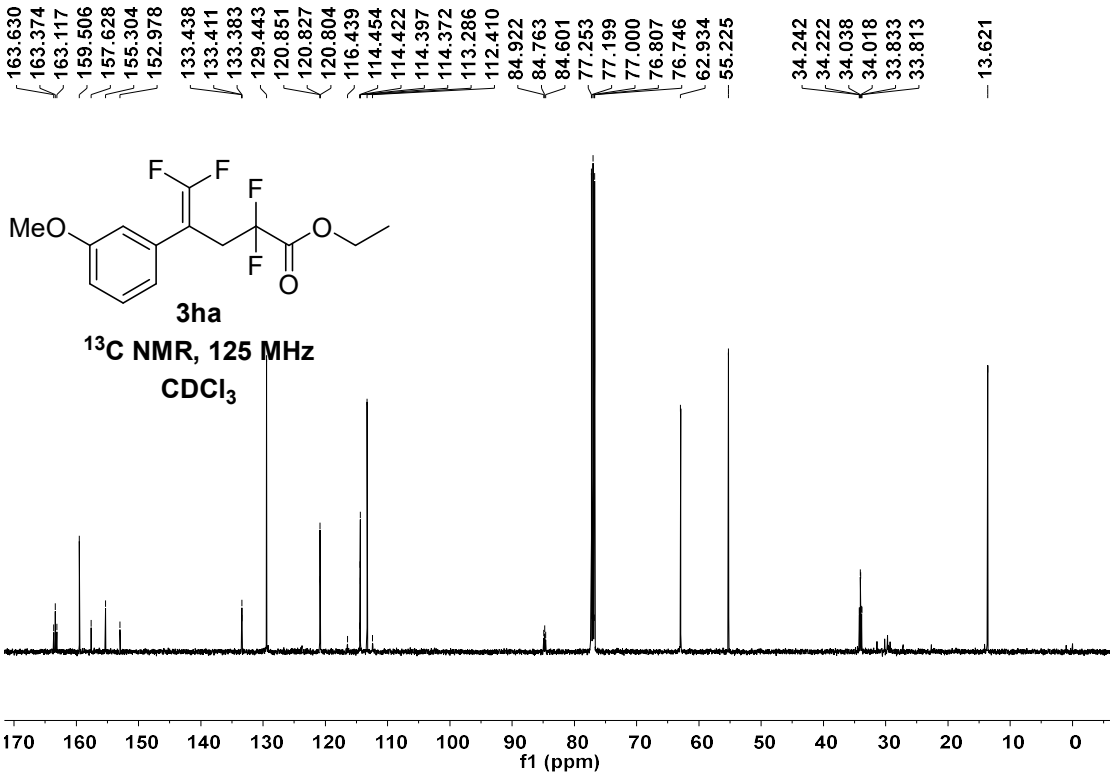
163.456
163.131
163.131
157.962
157.209
157.177
155.059
152.184
131.554
131.527
129.786
120.442
117.307
116.247
114.815
113.646
110.729
82.618
82.345
82.127
77.319
77.202
77.001
76.683
62.723
55.359
33.364
33.342
33.112
33.089
32.855
13.635
F
F
F
F
O
O
OMe
3ga
13C NMR, 125 MHz
CDCl3
f1 (ppm)


-86.049
-86.132
-89.144
-89.155
-89.232
-89.241
-103.943
-103.983
-104.012
-104.023
F
F
F
F
O
O
OMe
3ga
19F NMR, 377 MHz
CDCl3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.287
7.272
7.269
7.259
7.254
6.886
6.883
6.880
6.870
6.868
6.851
6.849
6.845
6.844
6.836
6.831
6.828
4.053
4.038
4.024
4.010
3.804
3.222
3.218
3.213
3.192
3.187
3.183
3.161
3.157
3.153
1.216
1.202
1.187
F
F
F
F
O
O
MeO
3ha
1H NMR, 500 MHz
CDCl3
1.00
3.00
2.00
3.00
2.00
3.00
3.0
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
f1 (ppm)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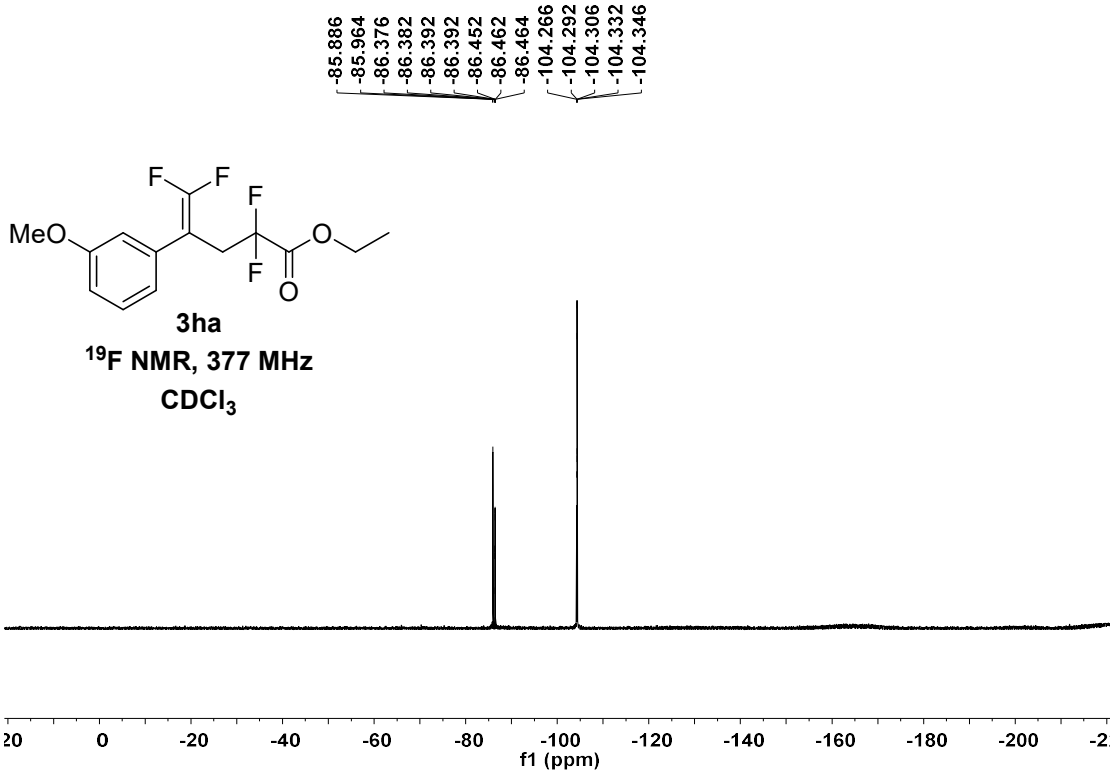
163.374
163.117
159.506
157.628
155.304
152.978
133.438
133.411
133.383
129.443
120.851
120.827
120.804
116.439
114.454
114.422
114.397
114.372
113.286
112.410
84.922
84.763
84.601
77.253
77.199
77.000
76.807
76.746
62.934
55.225
34.242
34.222
34.038
34.018
33.833
33.813
13.621
F
F
F
MeO
O
F
O
3ha
13C NMR, 125 MHz
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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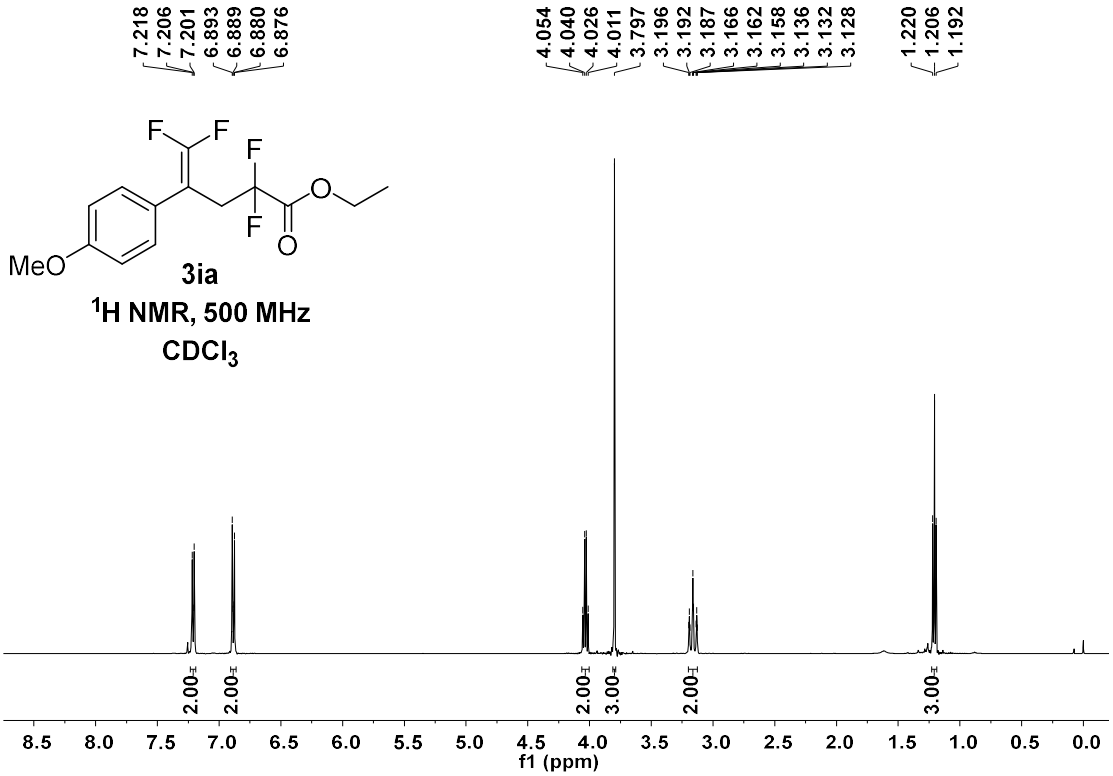
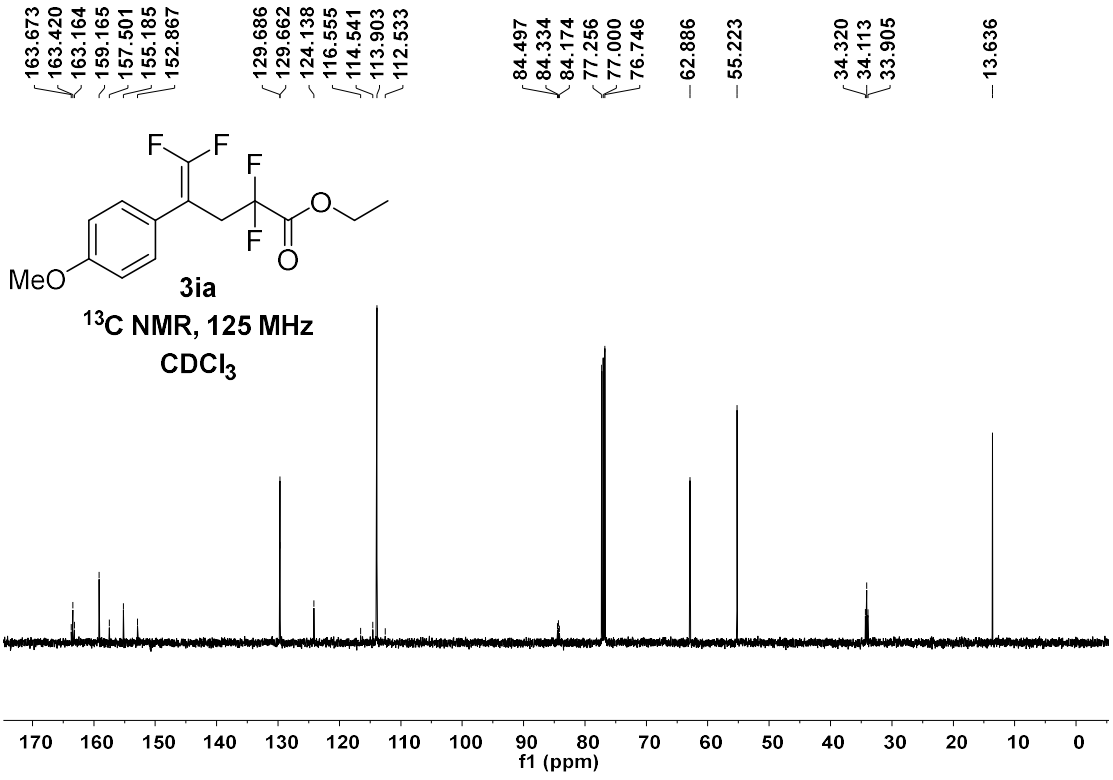
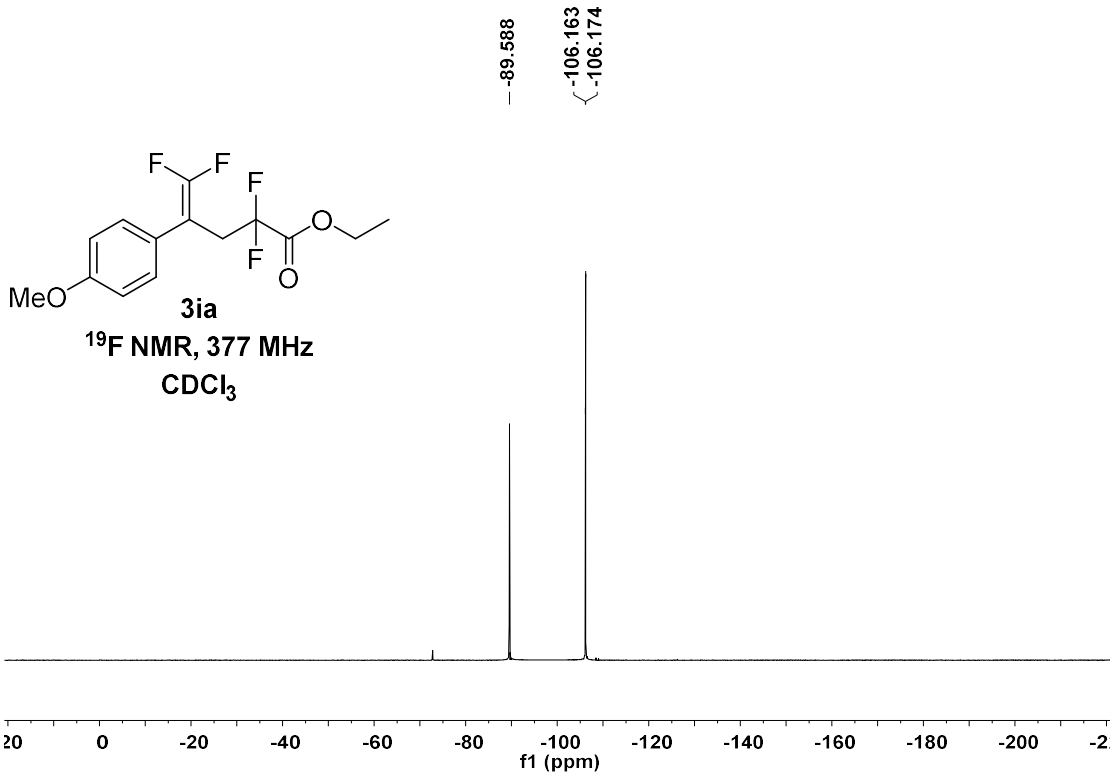
-85.964
-86.376
-86.382
-86.392
-86.392
-86.452
-86.462
-86.464
-104.266
-104.292
-104.306
-104.332
-104.346
F
F
F
MeO
O
F
O
3ha
19F NMR, 377 MHz
CDCl3
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.218
7.206
7.201
6.893
6.889
6.880
6.876
4.054
4.040
4.026
4.011
3.797
3.196
3.192
3.187
3.166
3.162
3.158
3.136
3.132
3.128
1.220
1.206
1.192
F
F
F
F
O
O
MeO
3ia
1H NMR, 500 MHz
CDCl3
2.00
2.00
2.00
3.00
2.00
3.00
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)

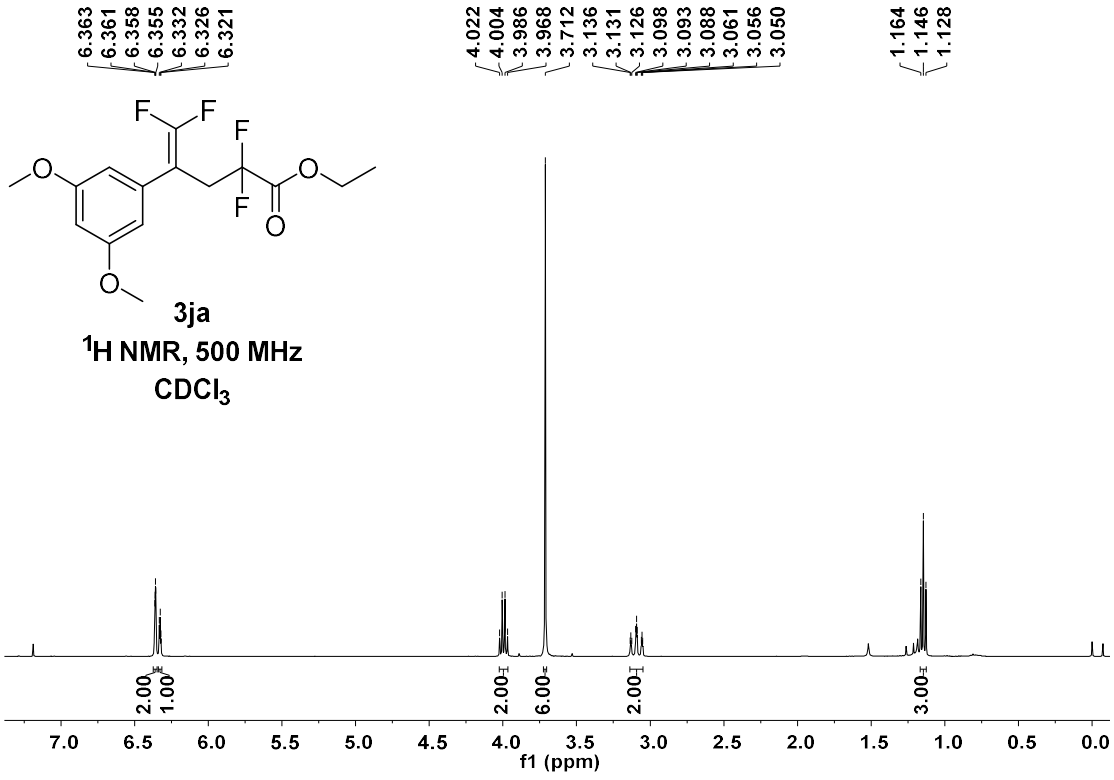

163.673
163.420
163.164
159.165
157.501
155.185
152.867
129.686
129.662
124.138
116.555
114.541
113.903
112.533
84.497
84.334
84.174
77.256
77.000
76.746
62.886
55.223
34.320
34.113
33.905
13.636
F
F
F
F
O
O
MeO
3ia
13C NMR, 125 MHz
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3ia

^{19}F NMR, 377 MHz

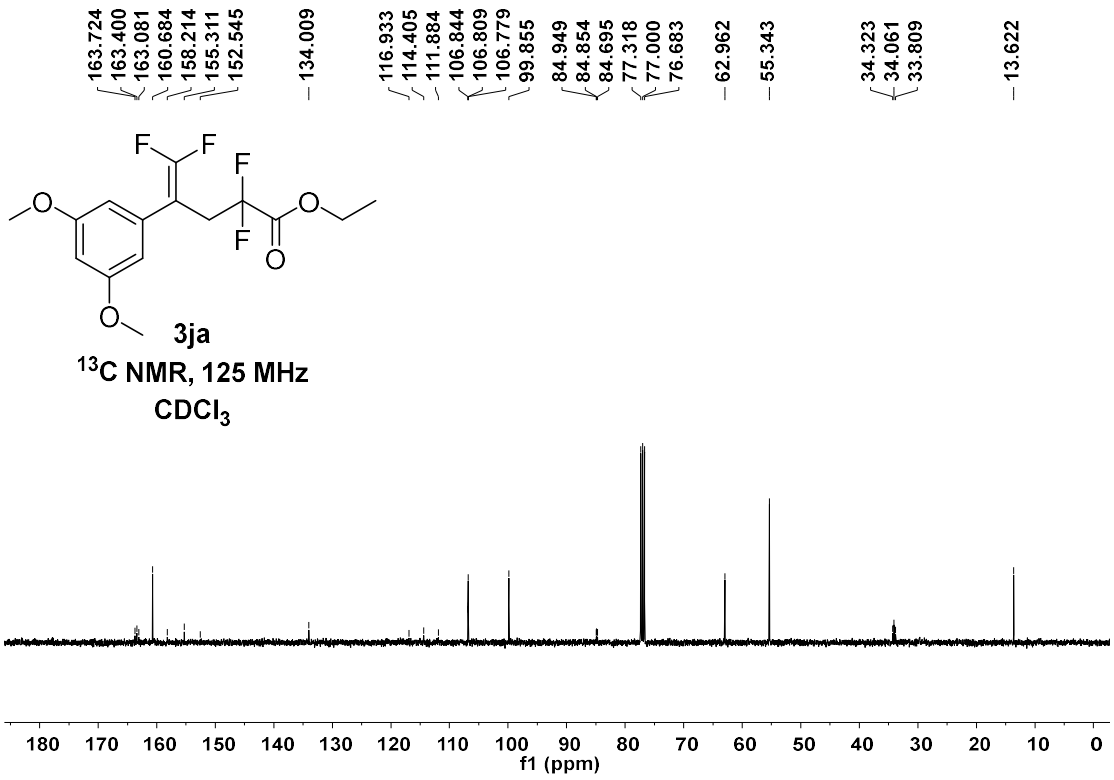
$CDCl_3$



3ja

^{1}H NMR, 500 MHz

$CDCl_3$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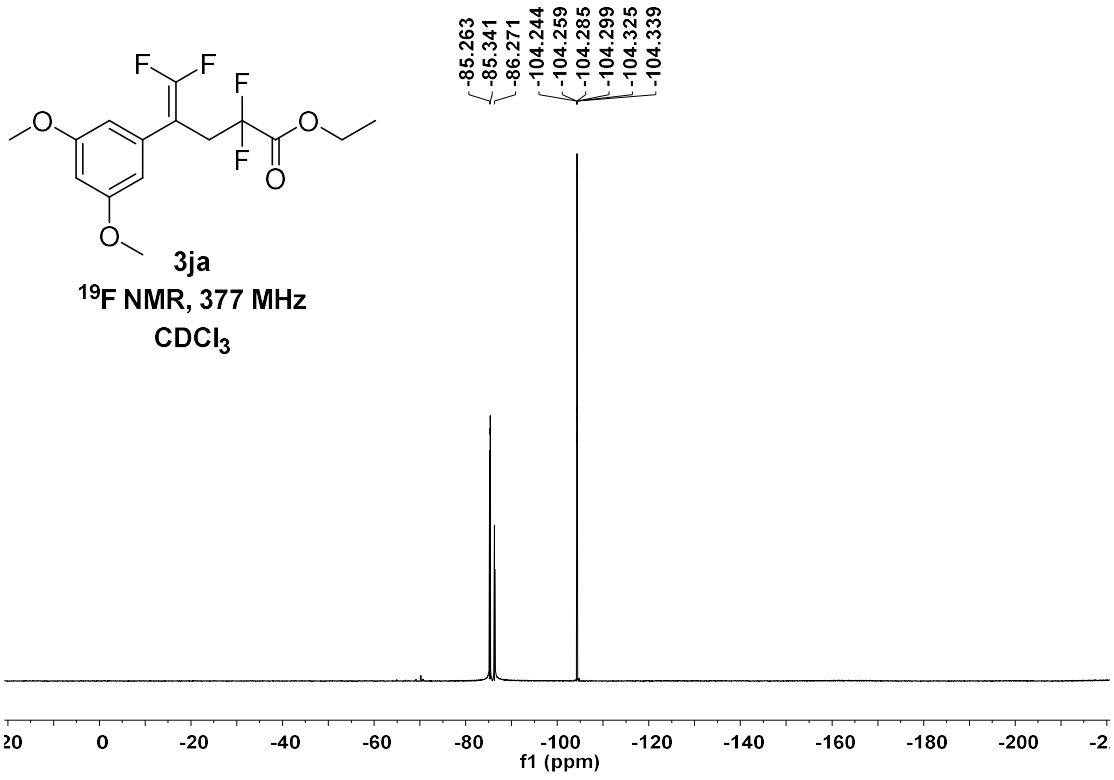
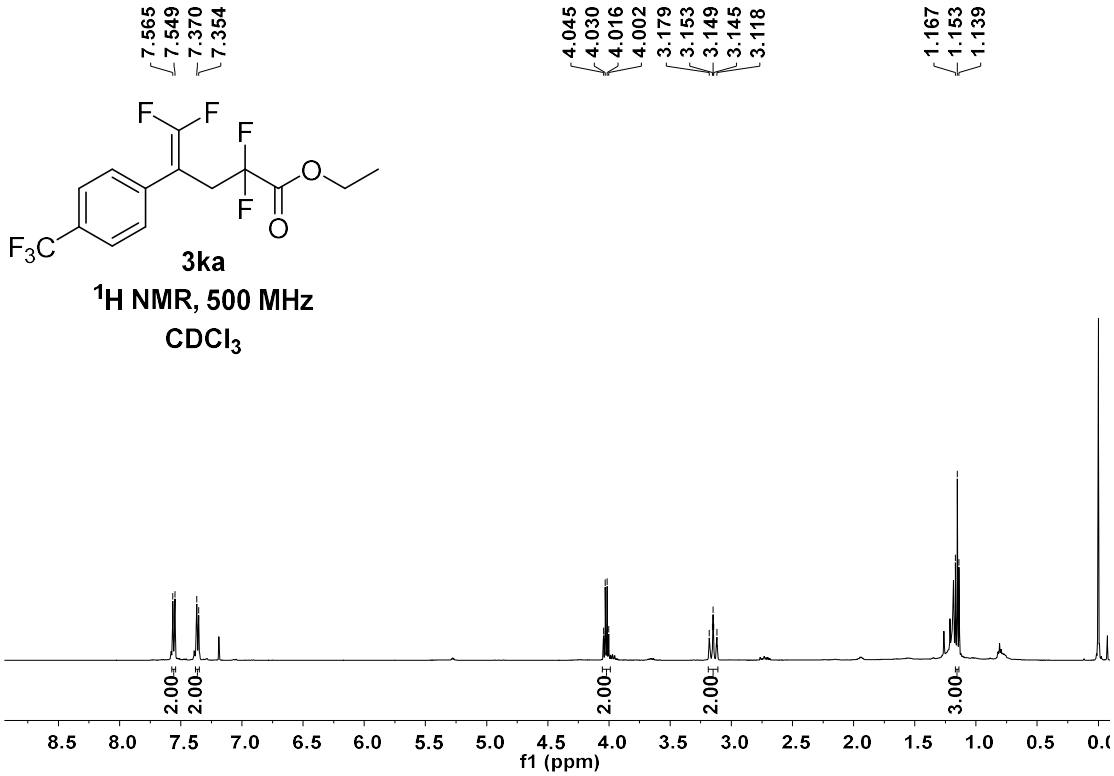
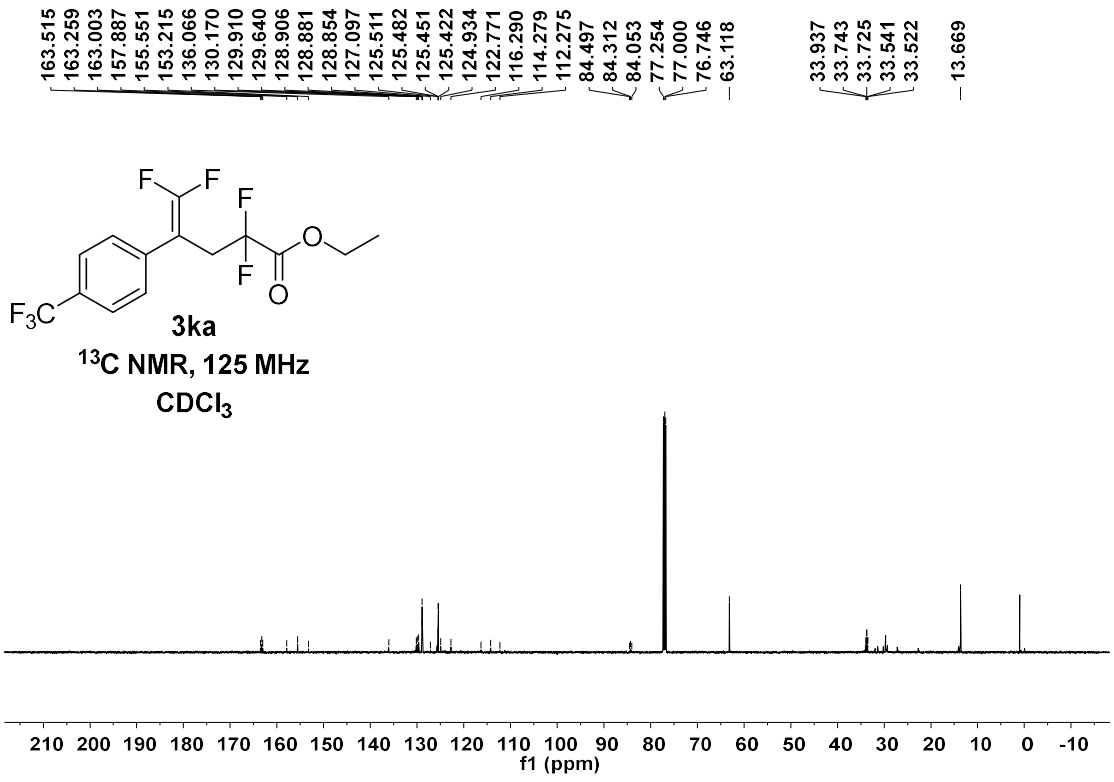
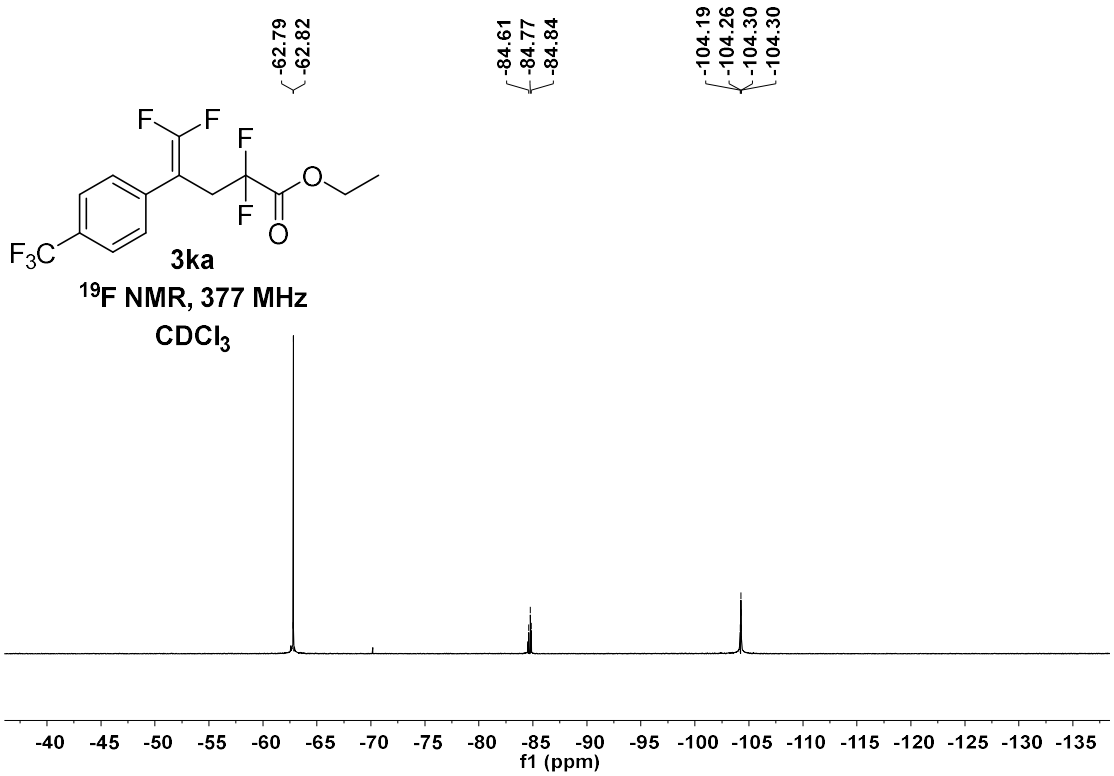
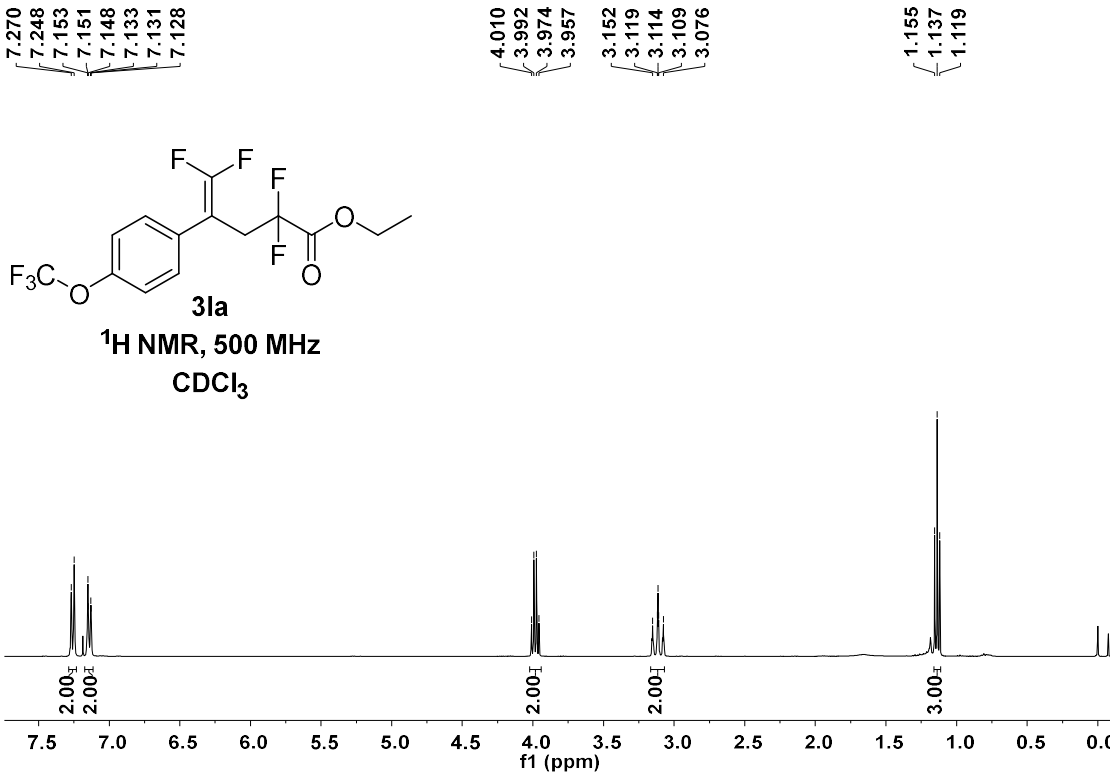
163.400
163.081
160.684
158.214
155.311
152.545
134.009
116.933
114.405
111.884
106.844
106.809
106.779
99.855
84.949
84.854
84.695
77.318
77.000
76.683
62.962
55.343
34.323
34.061
33.809
13.622
3ja
13C NMR, 125 MHz
CDCl3
f1 (ppm)

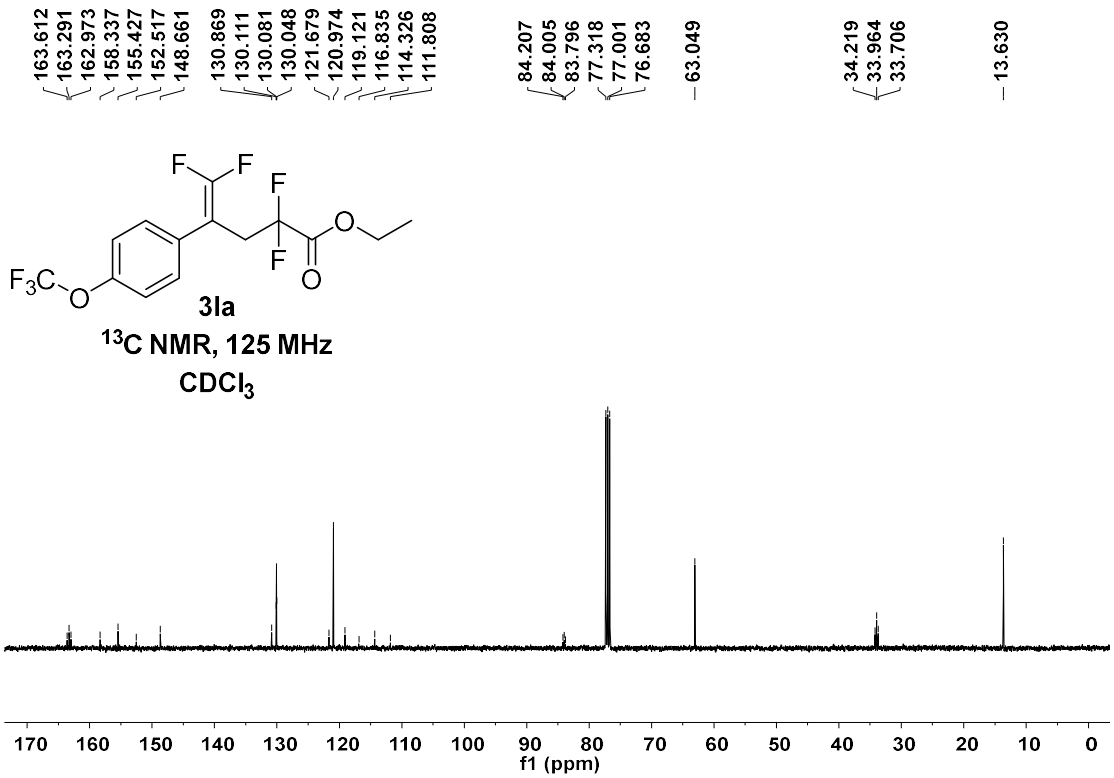

-85.263
-85.341
-86.271
-104.244
-104.259
-104.285
-104.299
-104.325
-104.339
3ja
19F NMR, 377 MHz
CDCl3
f1 (ppm)


7.565
7.549
7.370
7.354
4.045
4.030
4.016
4.002
3.179
3.153
3.149
3.145
3.118
1.167
1.153
1.139
F
F
F
F
O
O
F3C
3ka
1H NMR, 500 MHz
CDCl3
2.00
2.00
2.00
2.00
3.00
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
f1 (ppm)


163.515
163.259
163.003
157.887
155.551
153.215
136.066
130.170
129.910
129.640
128.906
128.881
128.854
127.097
125.511
125.482
125.451
125.422
124.934
122.771
116.290
114.279
112.275
84.497
84.312
84.053
77.254
77.000
76.746
63.118
33.937
33.743
33.725
33.541
33.522
13.669
F
F
F
F
O
O
F3C
3ka
13C NMR, 125 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)


-62.79
-62.82
-84.61
-84.77
-84.84
-104.19
-104.26
-104.30
-104.30
F
F
F
F
O
O
F3C
3ka
19F NMR, 377 MHz
CDCl3
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)


7.270
7.248
7.153
7.151
7.148
7.133
7.131
7.128
4.010
3.992
3.974
3.957
3.152
3.119
3.114
3.109
3.076
1.155
1.137
1.119
F
F
F
F
O
O
F3C
O
3la
1H NMR, 500 MHz
CDCl3
2.00
2.00
2.00
2.00
3.00
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
f1 (ppm)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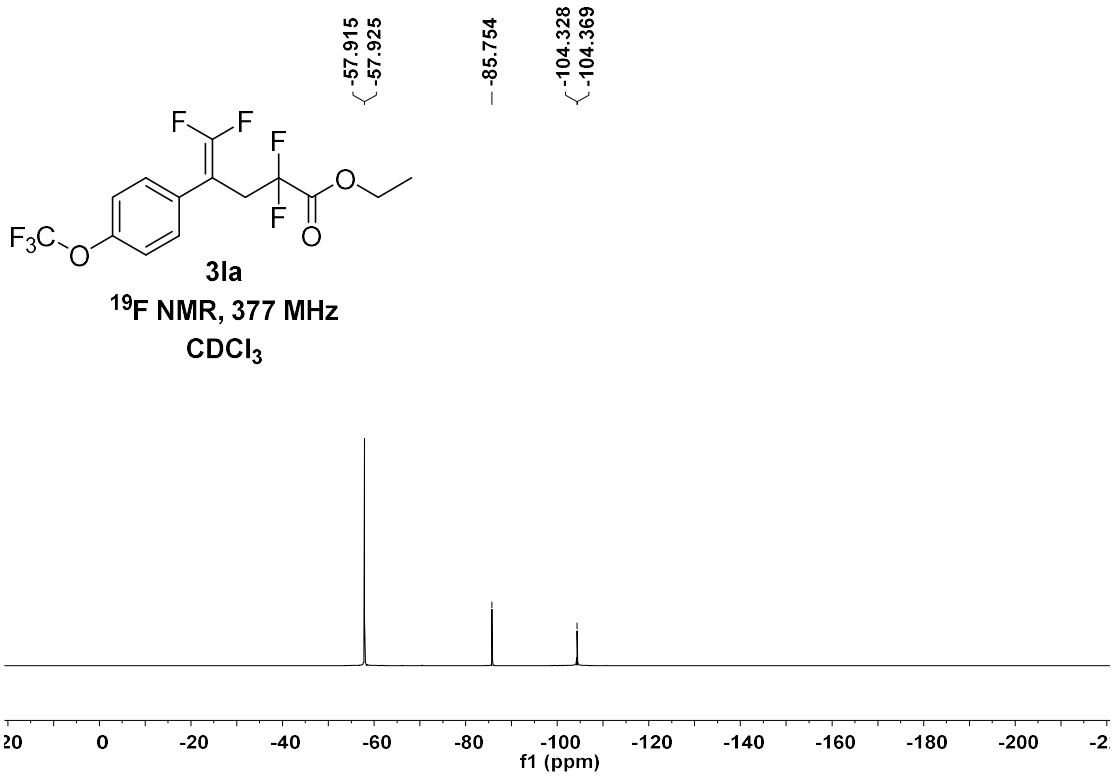
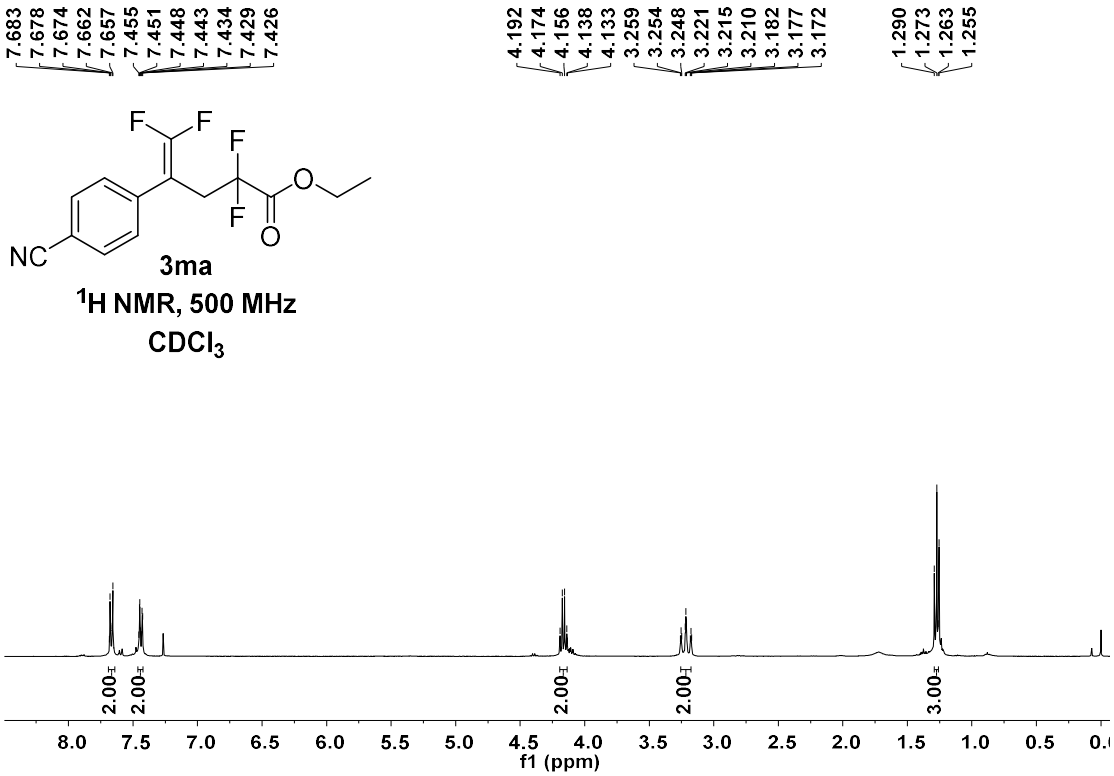
162.973
158.337
155.427
152.517
148.661
130.869
130.111
130.081
130.048
121.679
120.974
119.121
116.835
114.326
111.808
84.207
84.005
83.796
77.318
77.001
76.683
63.049
34.219
33.964
33.706
13.630
F
F
F
F
O
O
F3C
O
3la
13C NMR, 125 MHz
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

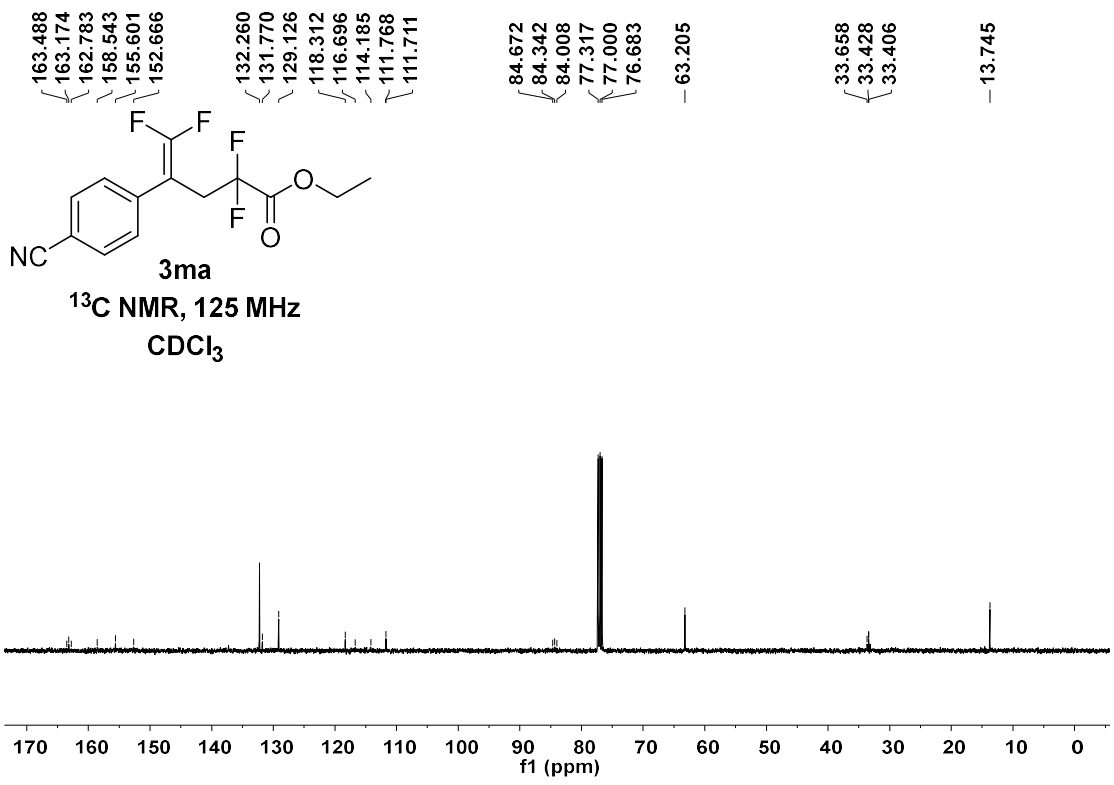

-57.915
-57.925
-85.754
-104.328
-104.369
F
F
F
F
O
O
F3C
O
3la
19F NMR, 377 MHz
CDCl3
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)



3ma

^{1}H NMR, 500 MHz

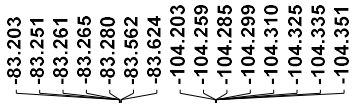
$CDCl_3$

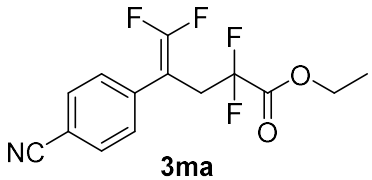


3ma

^{13}C NMR, 125 MHz

$CDCl_3$

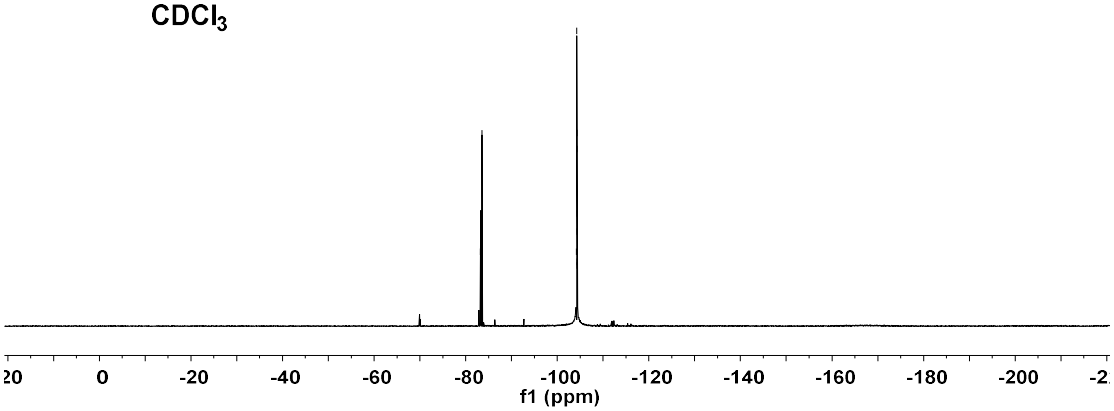


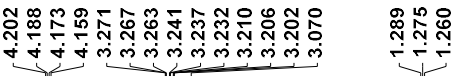


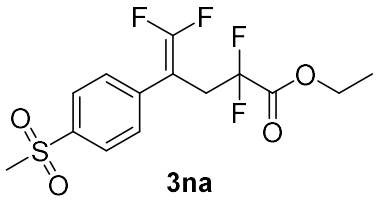
3ma

^{19}F NMR, 377 MHz

$CDCl_3$



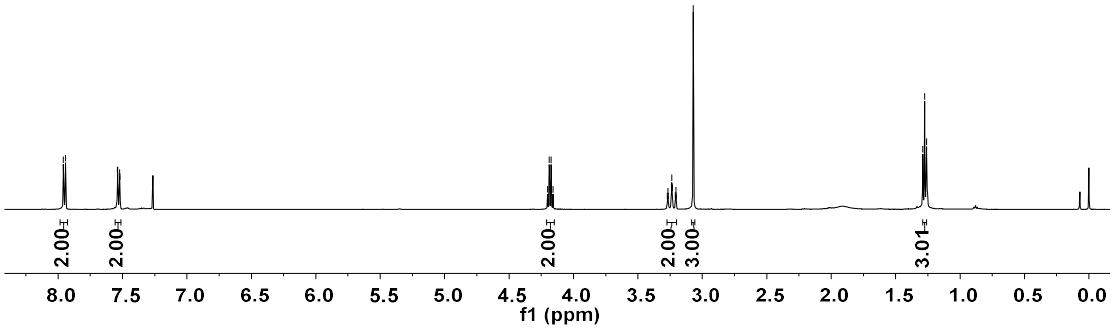


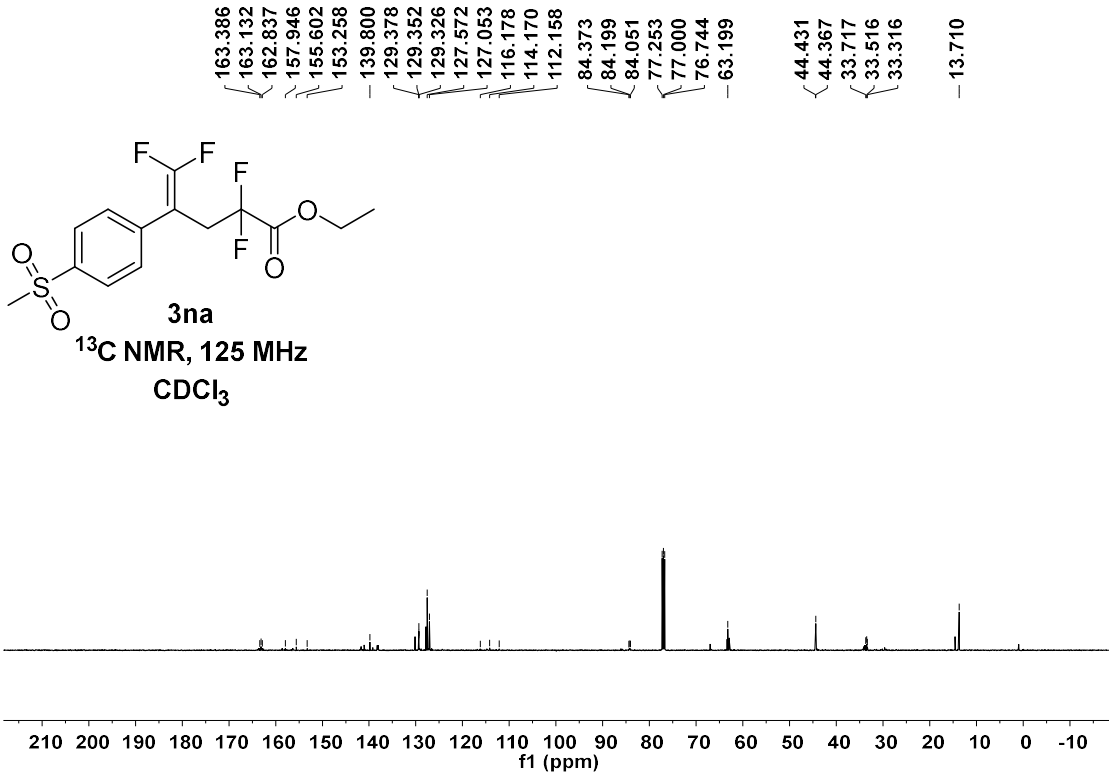


3na

^{1}H NMR, 500 MHz

$CDCl_3$

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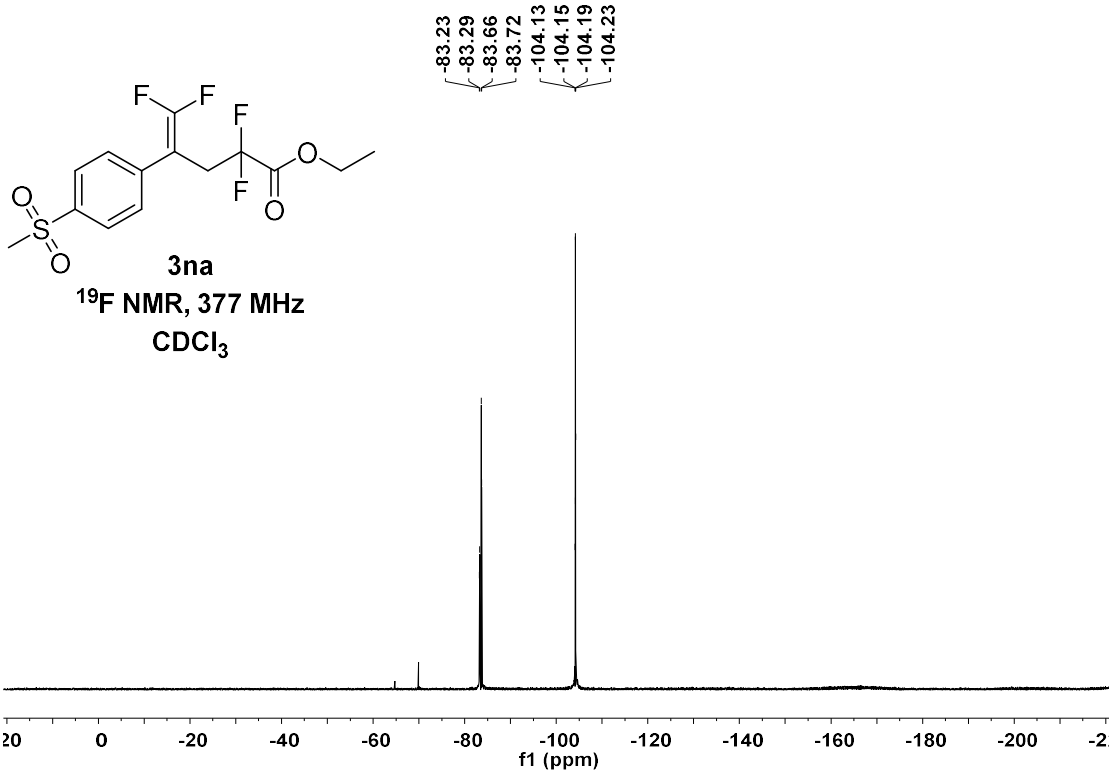
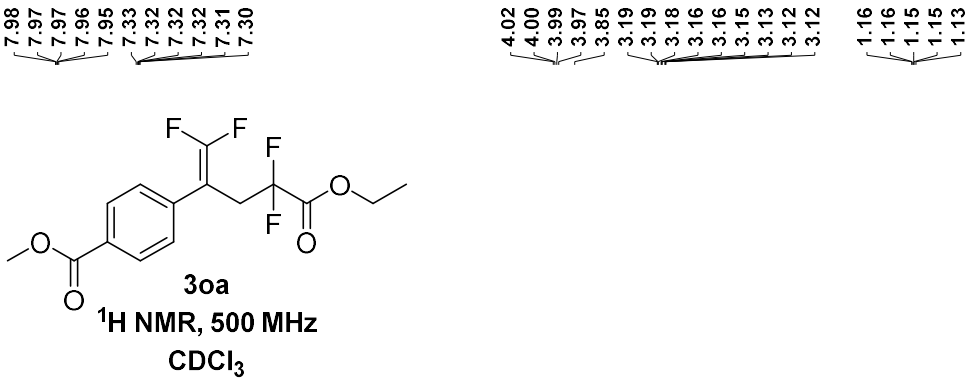
157.946
155.602
153.258
139.800
129.378
129.352
129.326
127.572
127.053
116.178
114.170
112.158
84.373
84.199
84.051
77.253
77.000
76.744
63.199
44.431
44.367
33.717
33.516
33.316
13.710
F
F
F
F
O
O
O
O
S
O
3na
13C NMR, 125 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-83.23
-83.29
-83.66
-83.72
-104.13
-104.15
-104.19
-104.23
F
F
F
F
O
O
O
O
S
O
3na
19F NMR, 377 MHz
CDCl3
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)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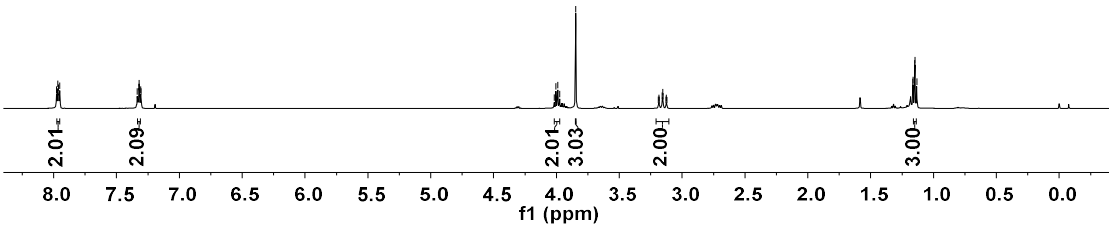
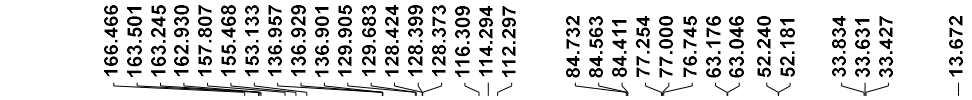
7.97
7.96
7.95
7.33
7.32
7.32
7.32
7.31
7.30
4.02
4.00
3.99
3.97
3.85
3.19
3.19
3.18
3.16
3.16
3.15
3.13
3.12
3.12
1.16
1.16
1.15
1.15
1.13
F
F
F
F
O
O
O
O
3oa
^{1}H NMR, 500 MHz
$CDCl_3$


2.01
2.09
2.01
3.03
2.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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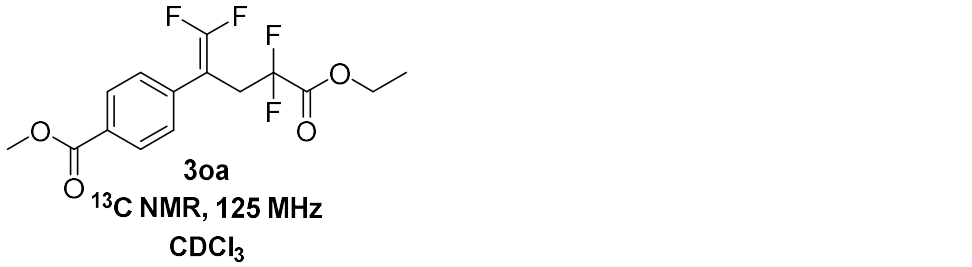
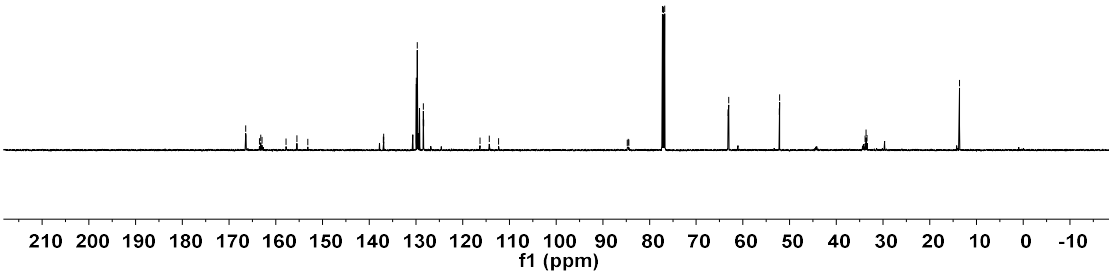
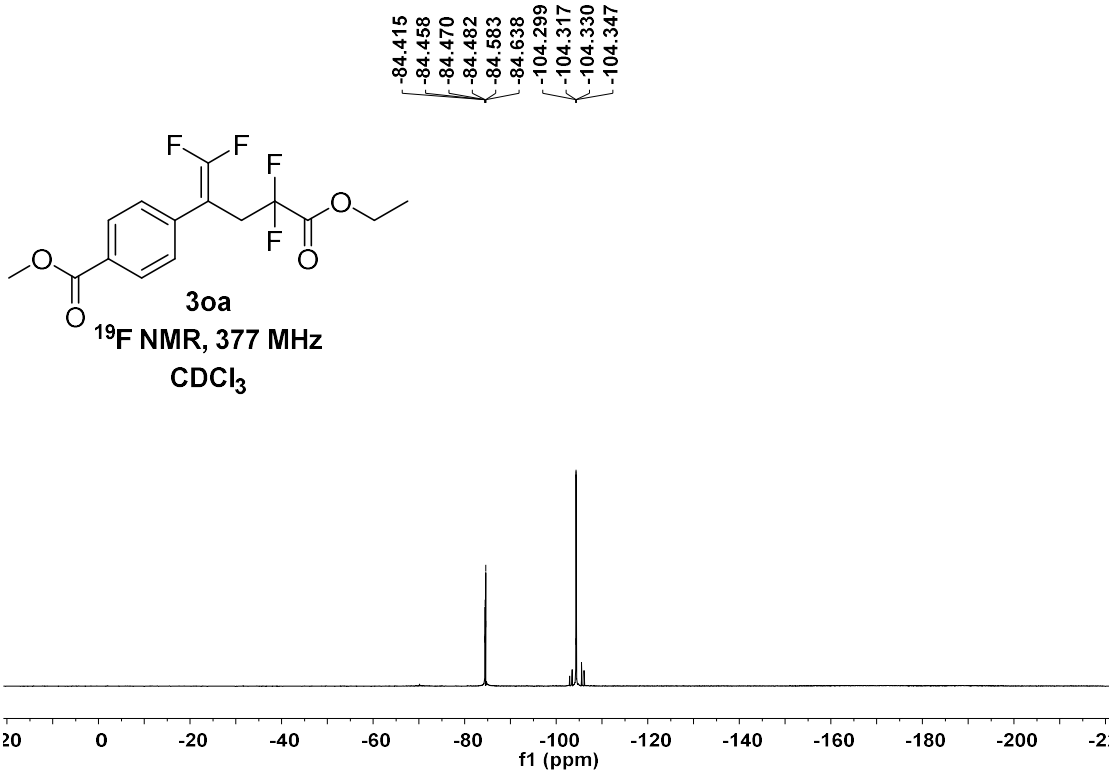
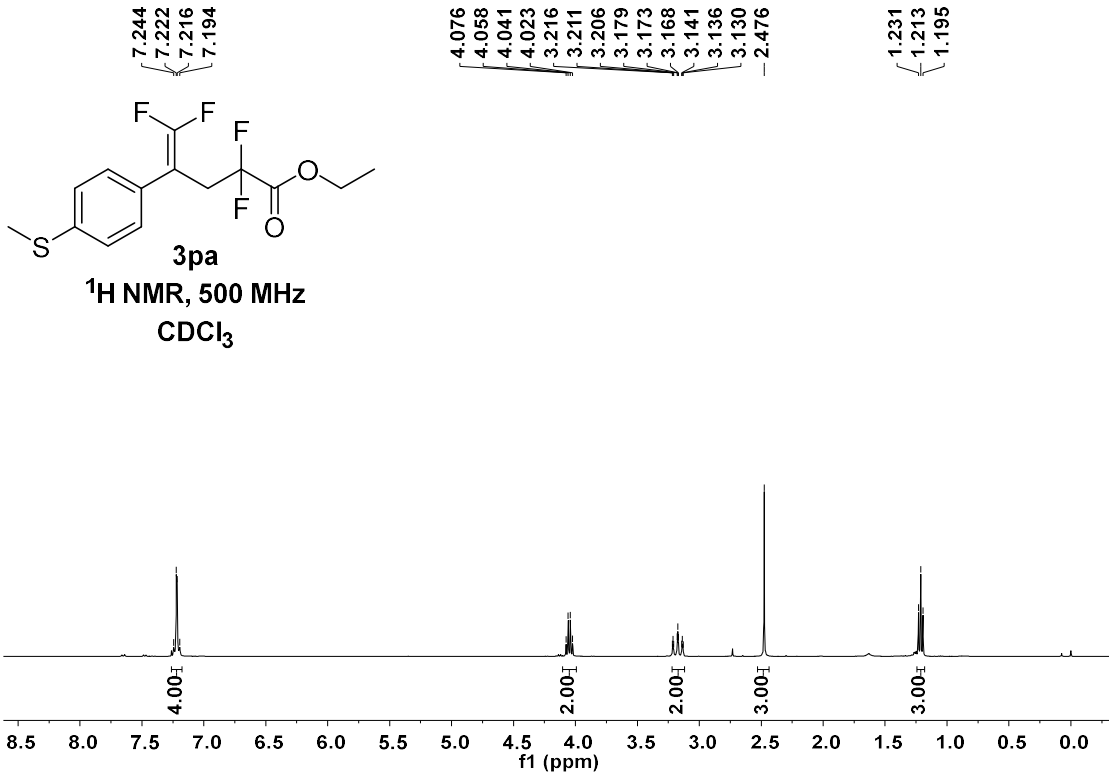
163.501
163.245
162.930
157.807
155.468
153.133
136.957
136.929
136.901
129.905
129.683
128.424
128.399
128.373
116.309
114.294
112.297
84.732
84.563
84.411
77.254
77.000
76.745
63.176
63.046
52.240
52.181
33.834
33.631
33.427
13.672


F
F
F
F
O
O
O
O
3oa
^{13}C NMR, 125 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)


-84.415
-84.458
-84.470
-84.482
-84.583
-84.638
-104.299
-104.317
-104.330
-104.347
F
F
F
F
O
O
O
O
3oa
19F NMR, 377 MHz
CDCl3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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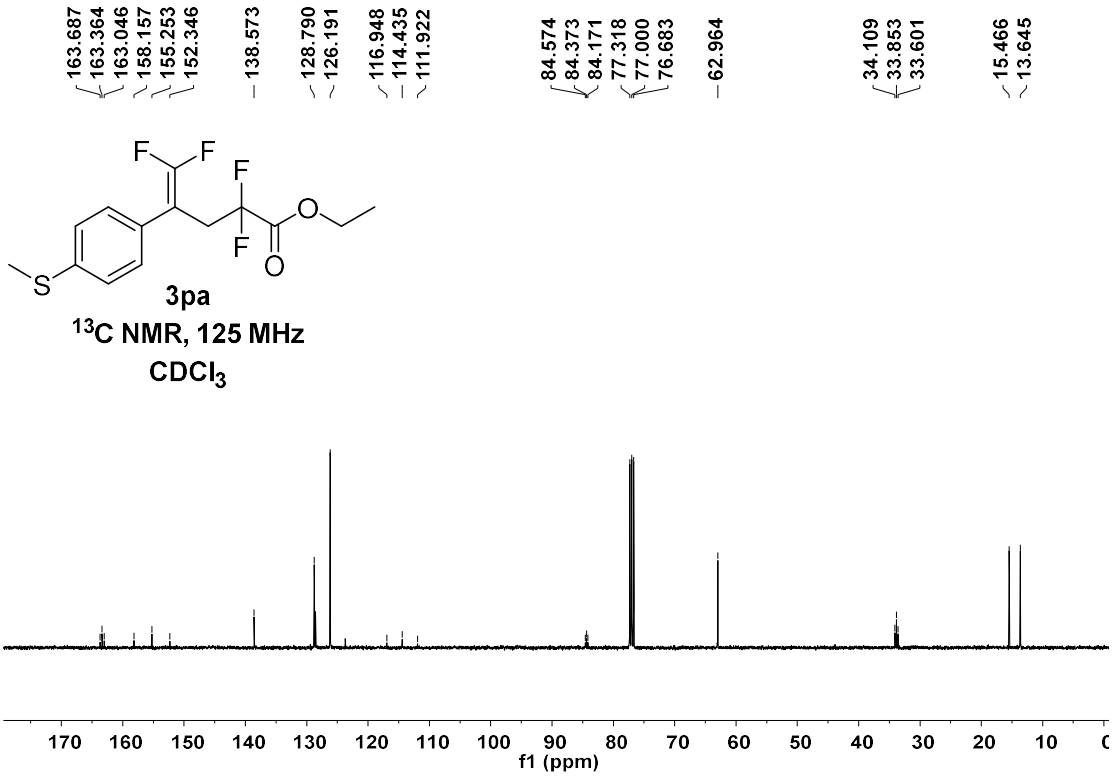
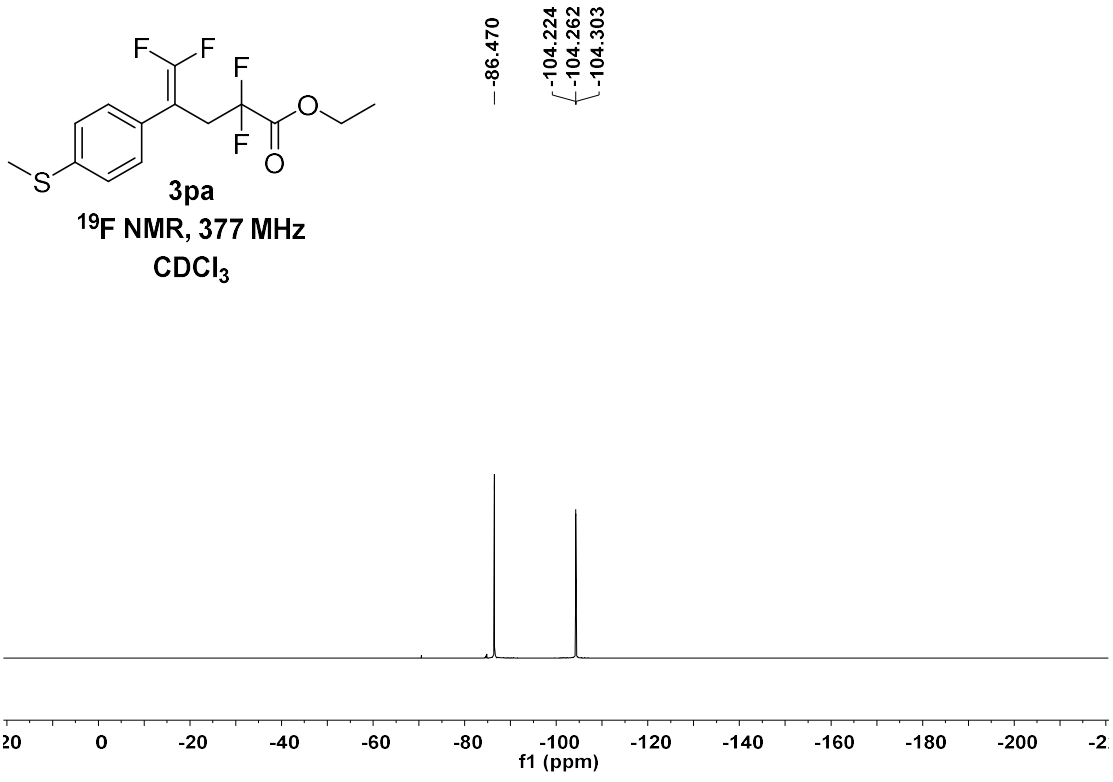
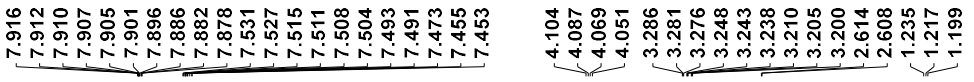
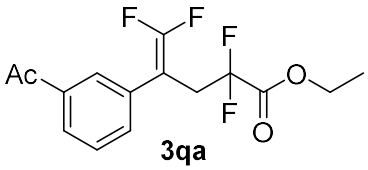
7.222
7.216
7.194
4.076
4.058
4.041
4.023
3.216
3.211
3.206
3.179
3.173
3.168
3.141
3.136
3.130
2.476
1.231
1.213
1.195
F
F
F
F
O
O
S
3pa
1H NMR, 500 MHz
CDCl3
4.00
2.00
2.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.687
163.364
163.046
158.157
155.253
152.346
138.573
128.790
126.191
116.948
114.435
111.922
84.574
84.373
84.171
77.318
77.000
76.683
62.964
34.109
33.853
33.601
15.466
13.645
F
F
F
F
O
O
S
3pa
13C NMR, 125 MHz
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-86.470
-104.224
-104.262
-104.303
F
F
F
F
O
O
S
3pa
19F NMR, 377 MHz
CDCl3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

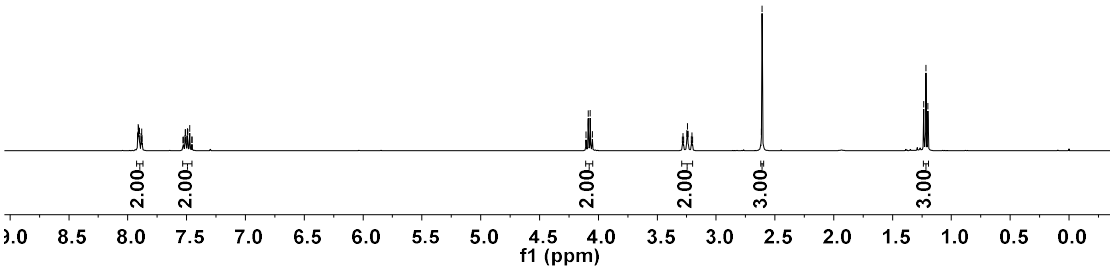


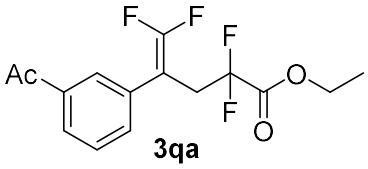


3qa

^{1}H NMR, 500 MHz

$CDCl_3$

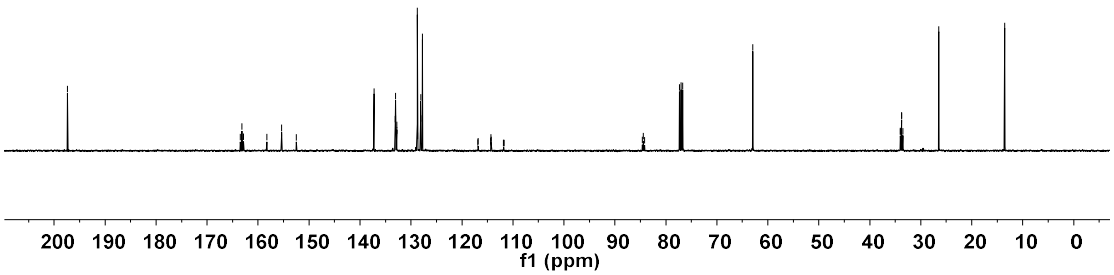


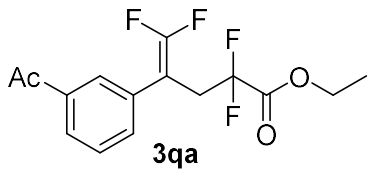


3qa

^{13}C NMR, 125 MHz

$CDCl_3$

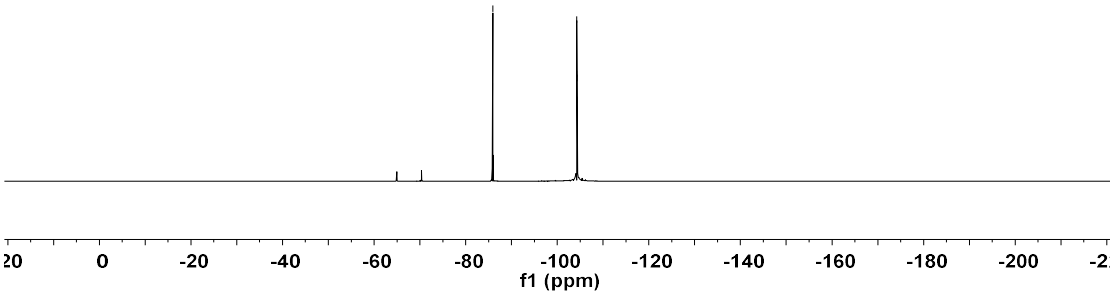


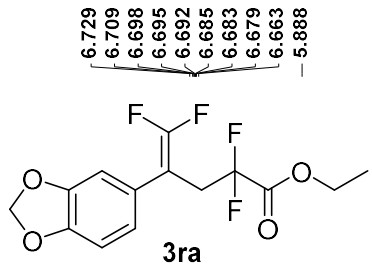


3qa

^{19}F NMR, 377 MHz

$CDCl_3$

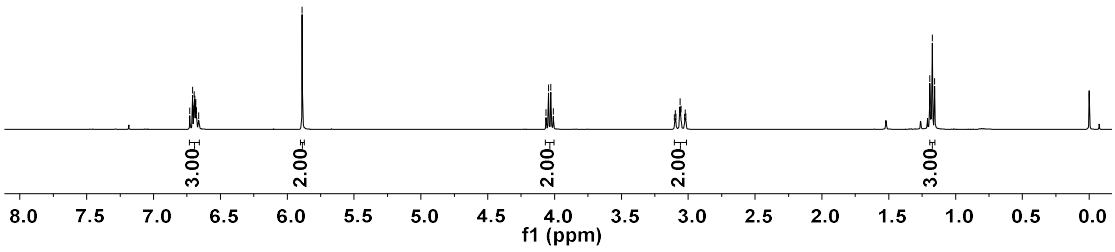


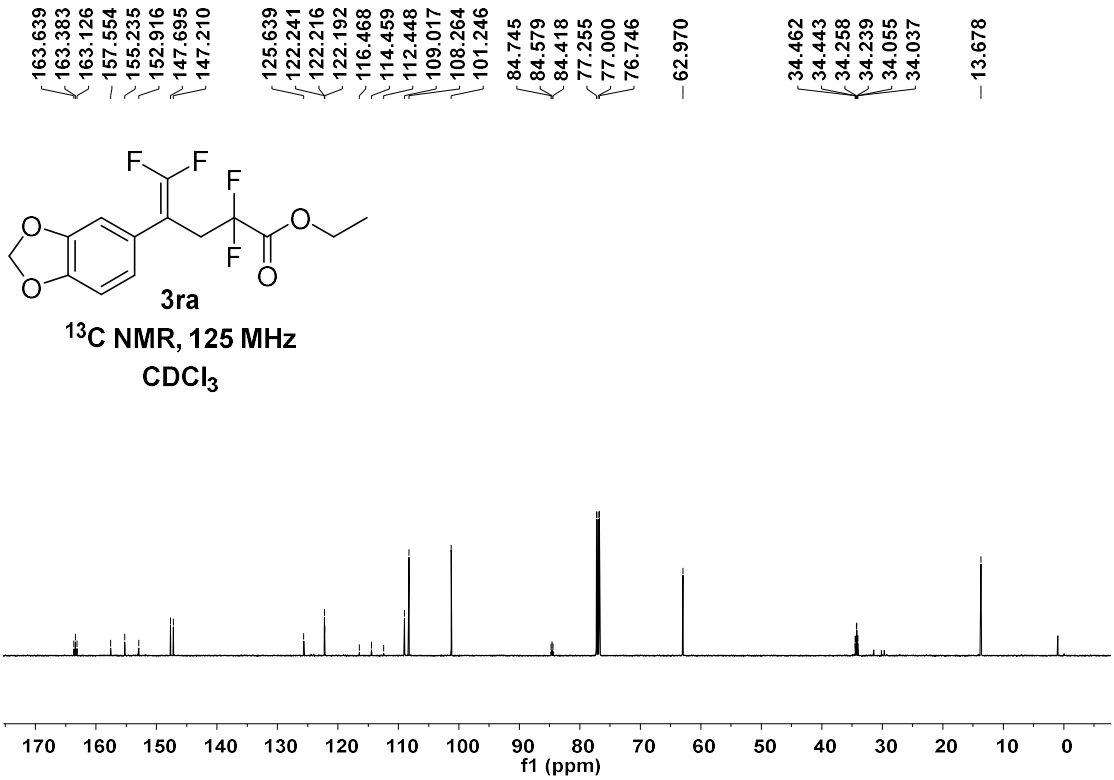


3ra

^{1}H NMR, 500 MHz

$CDCl_3$

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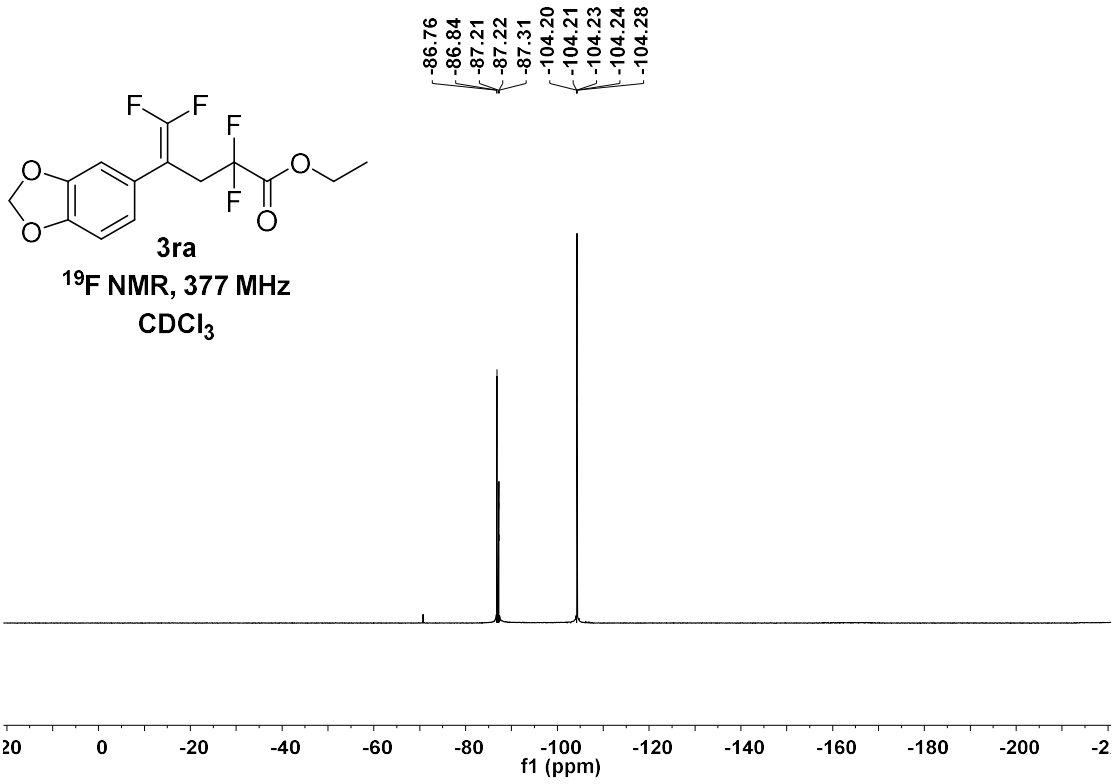
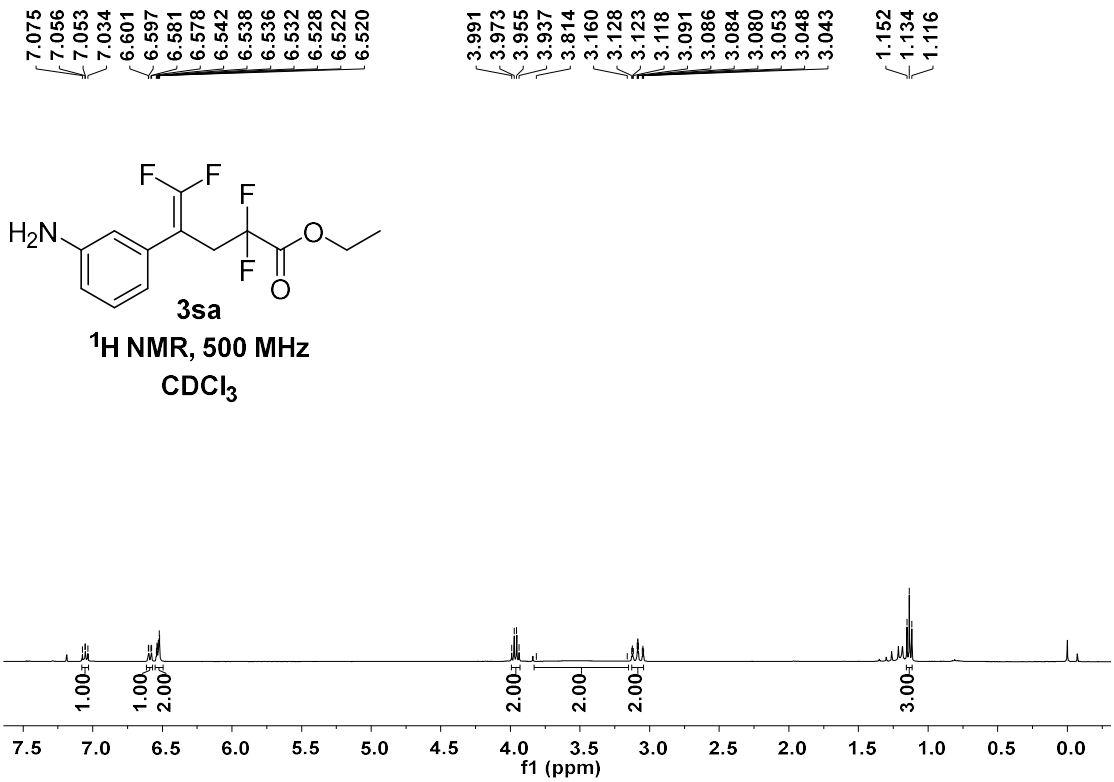
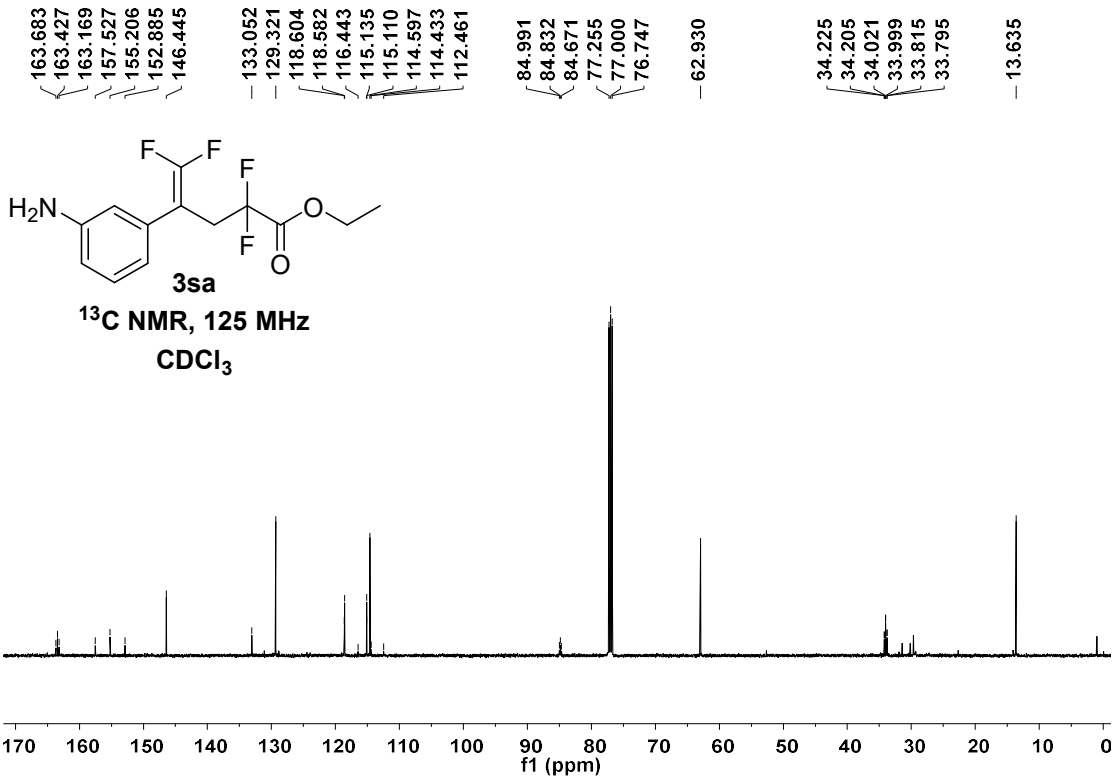
163.126
157.554
155.235
152.916
147.695
147.210
125.639
122.241
122.216
122.192
116.468
114.459
112.448
109.017
108.264
101.246
84.745
84.579
84.418
77.255
77.000
76.746
62.970
34.462
34.443
34.258
34.239
34.055
34.037
13.678
F
F
F
O
O
F
O
O
3ra
13C NMR, 125 MHz
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-86.76
-86.84
-87.21
-87.22
-87.31
-104.20
-104.21
-104.23
-104.24
-104.28
F
F
F
O
O
F
O
O
3ra
19F NMR, 377 MHz
CDCl3
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)


7.075
7.056
7.053
7.034
6.601
6.597
6.581
6.578
6.542
6.538
6.536
6.532
6.528
6.522
6.520
3.991
3.973
3.955
3.937
3.814
3.160
3.128
3.123
3.118
3.091
3.086
3.084
3.080
3.053
3.048
3.043
1.152
1.134
1.116
F
F
F
H2N
O
F
O
3sa
1H NMR, 500 MHz
CDCl3
1.00
1.00
2.00
2.00
2.00
2.00
2.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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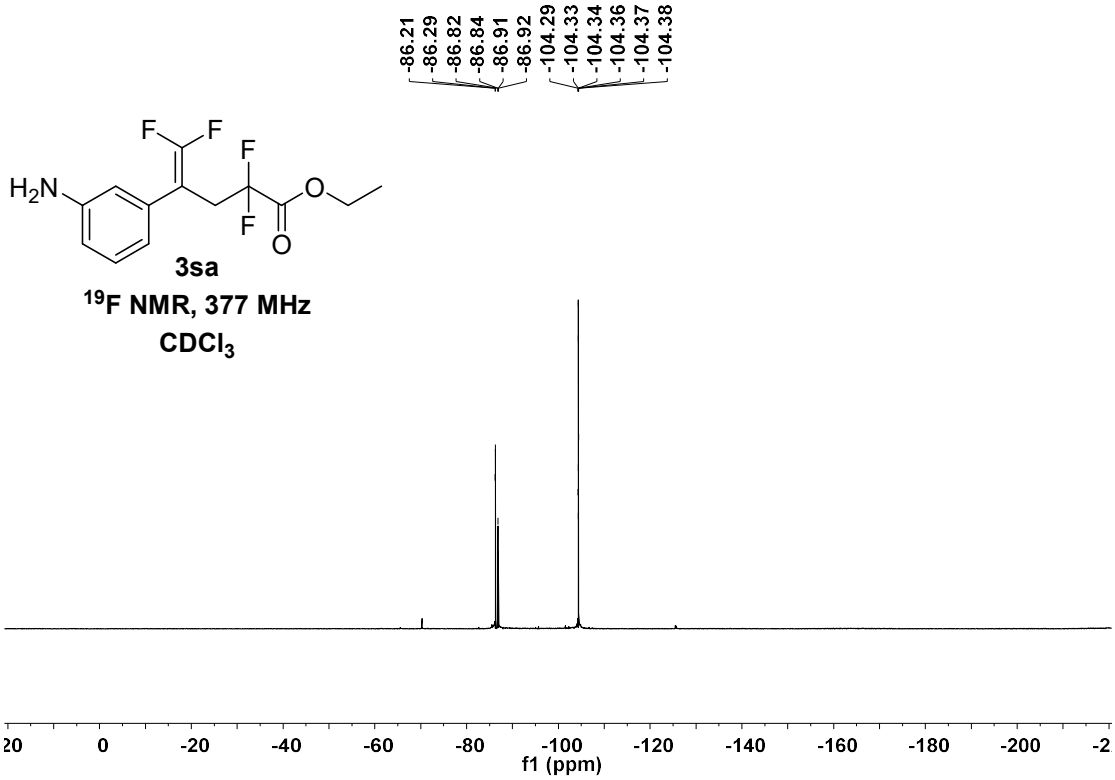
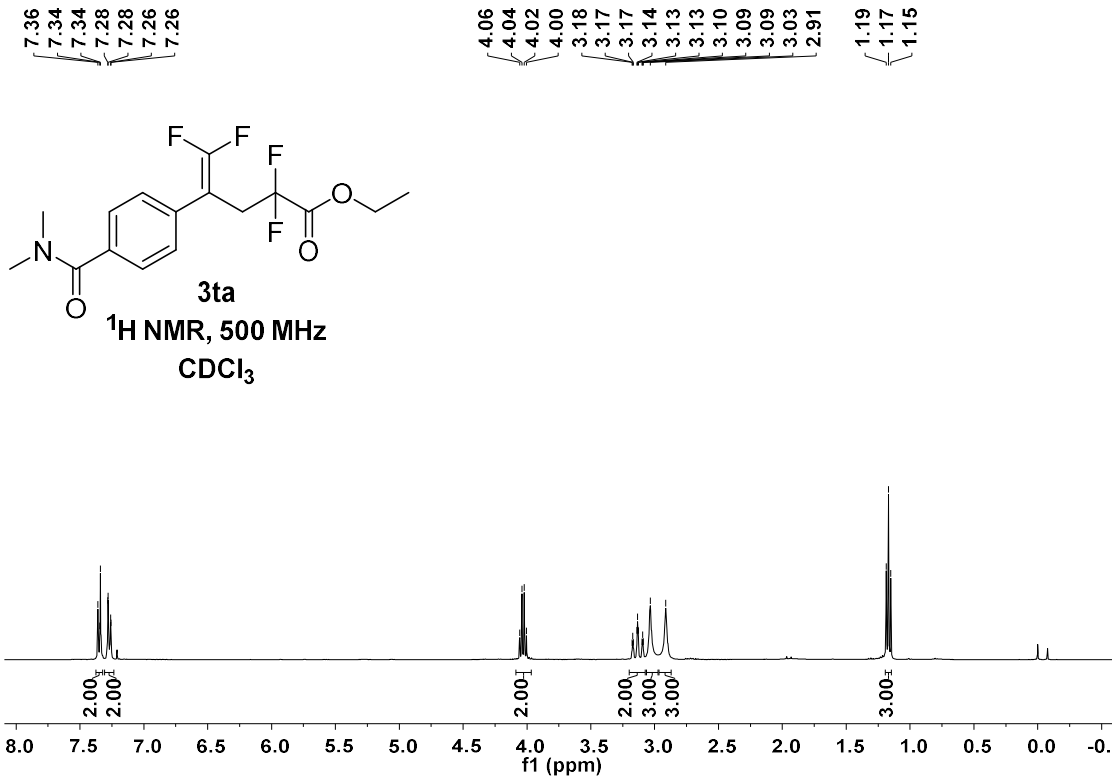
163.427
163.169
157.527
155.206
152.885
146.445
133.052
129.321
118.604
118.582
116.443
115.135
115.110
114.597
114.433
112.461
84.991
84.832
84.671
77.255
77.000
76.747
62.930
34.225
34.205
34.021
33.999
33.815
33.795
13.635
F
F
F
H2N
O
F
O
3sa
13C NMR, 125 MHz
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-86.21
-86.29
-86.82
-86.84
-86.91
-86.92
-104.29
-104.33
-104.34
-104.36
-104.37
-104.38
F
F
F
H2N
O
F
O
3sa
19F NMR, 377 MHz
CDCl3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)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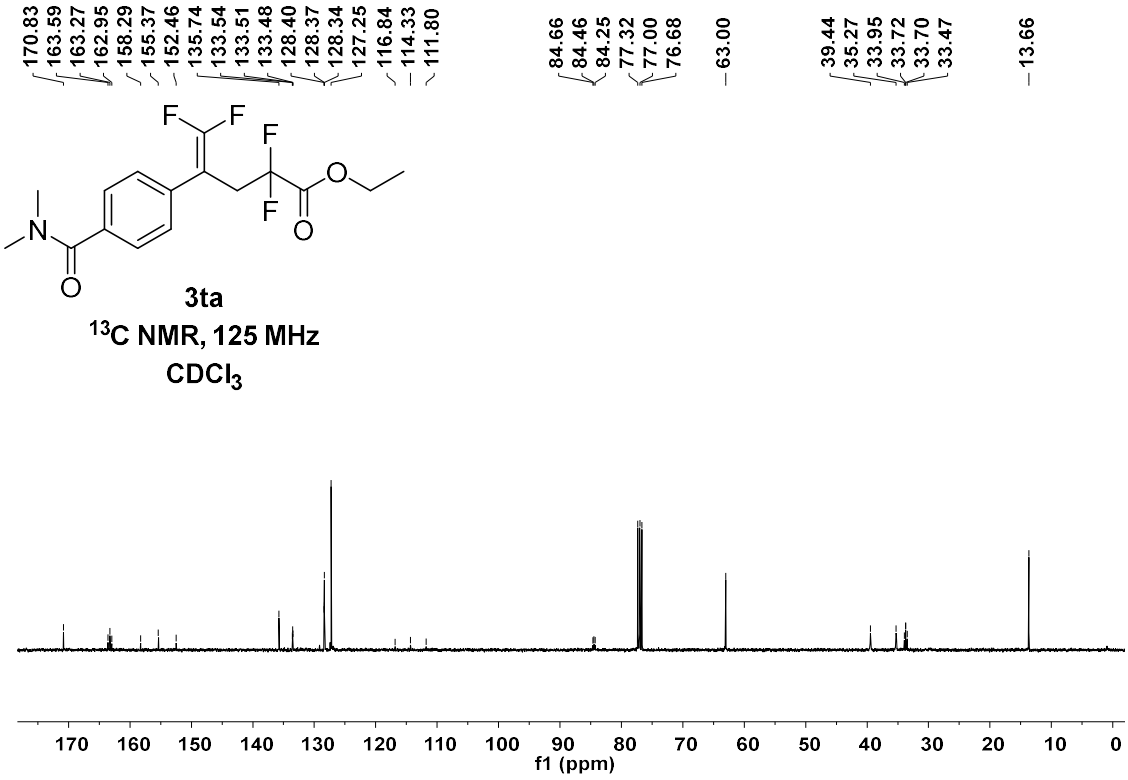
7.34
7.34
7.28
7.28
7.26
7.26
4.06
4.04
4.02
4.00
3.18
3.17
3.17
3.14
3.13
3.13
3.10
3.09
3.09
3.03
2.91
1.19
1.17
1.15
F
F
F
F
O
N
O
O
3ta
1H NMR, 500 MHz
CDCl3
2.00
2.00
2.00
2.00
3.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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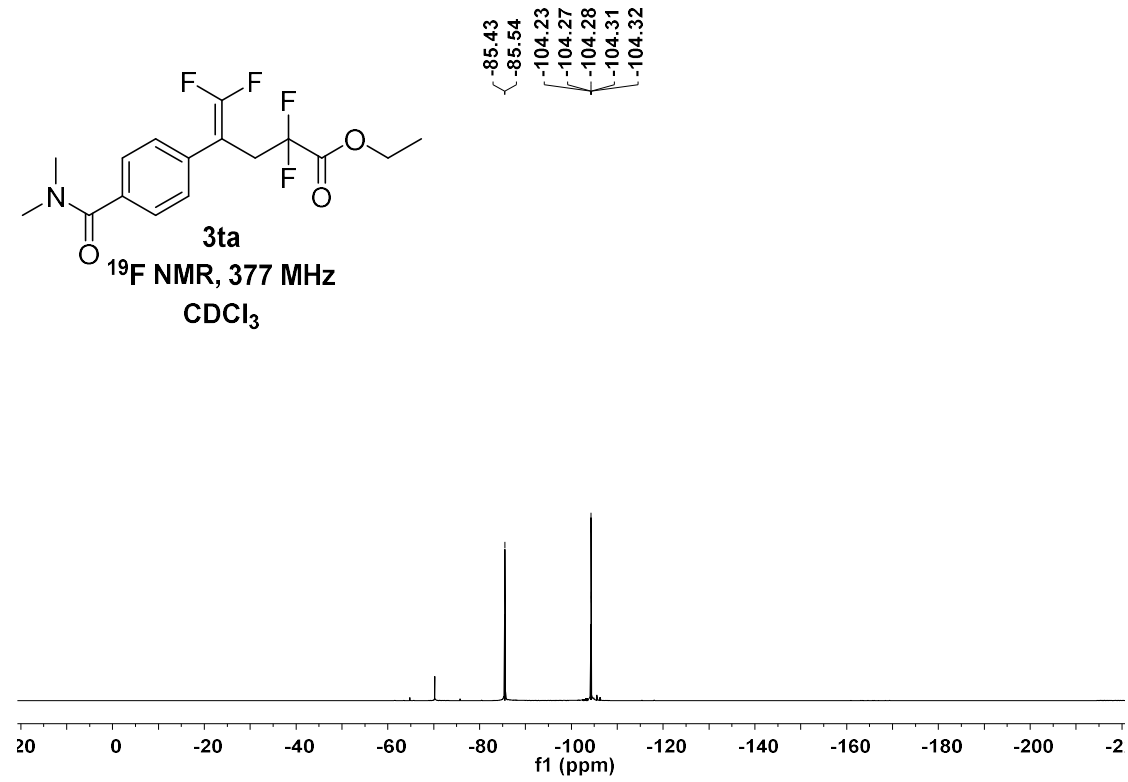
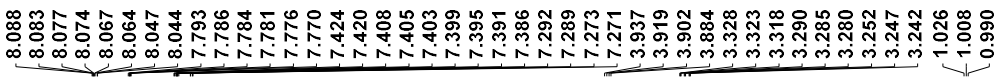
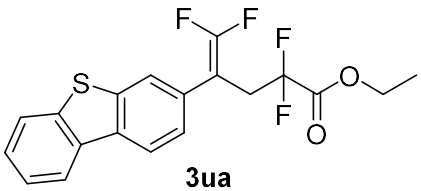
152.46
135.74
133.54
133.51
133.48
128.40
128.37
128.34
127.25
116.84
114.33
111.80
84.66
84.46
84.25
77.32
77.00
76.68
63.00
39.44
35.27
33.95
33.72
33.70
33.47
13.66
F
F
F
F
O
O
N
O
3ta
13C NMR, 125 MHz
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-85.43
-85.54
-104.23
-104.27
-104.28
-104.31
-104.32
F
F
F
F
O
O
N
O
3ta
19F NMR, 377 MHz
CDCl3
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

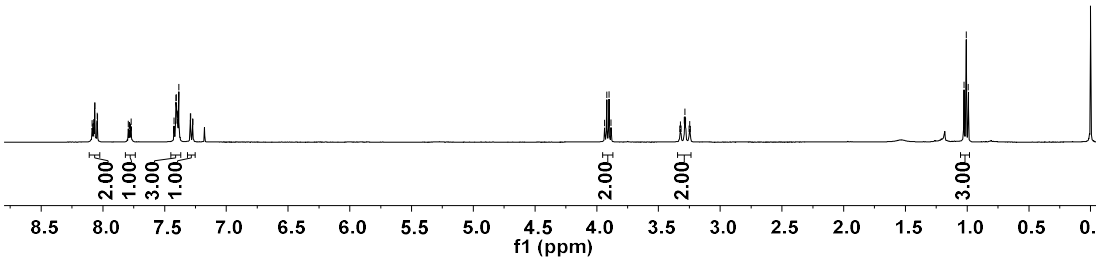


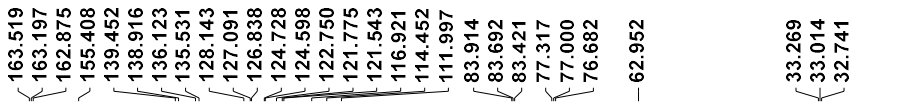


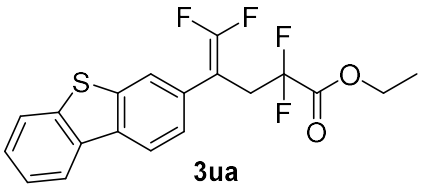
3ua

^{1}H NMR, 500 MHz

$CDCl_3$



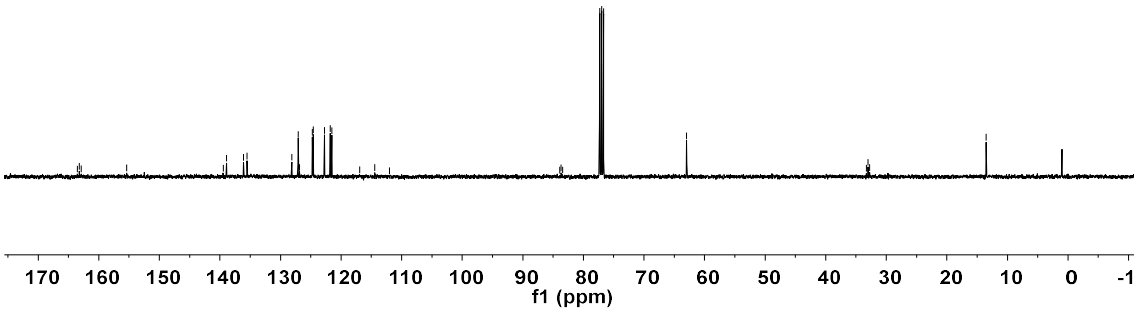


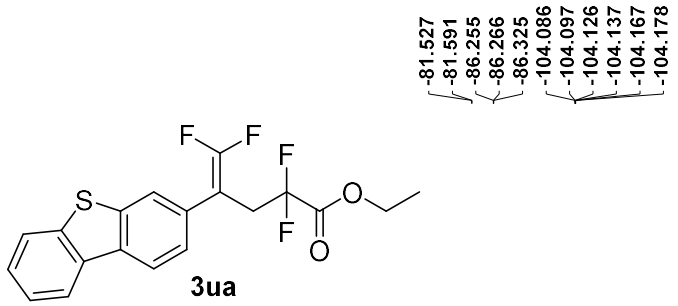


3ua

^{13}C NMR, 125 MHz

$CDCl_3$

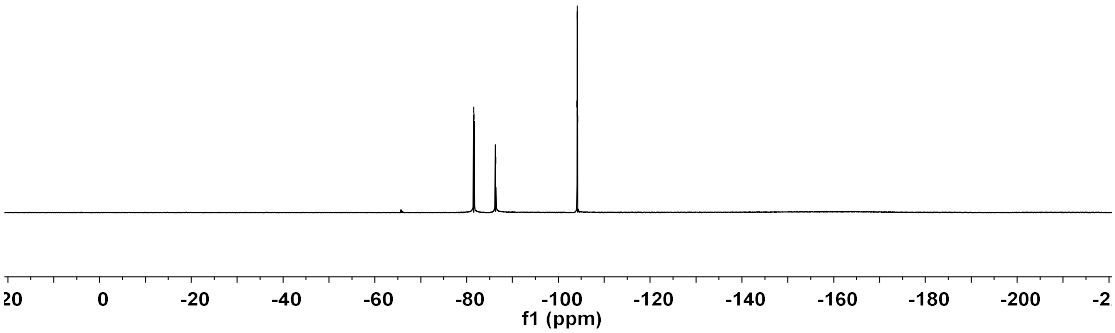


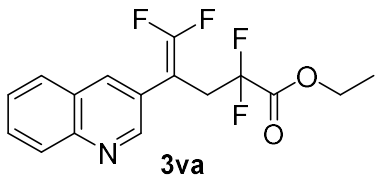


3ua

^{19}F NMR, 377 MHz

$CDCl_3$

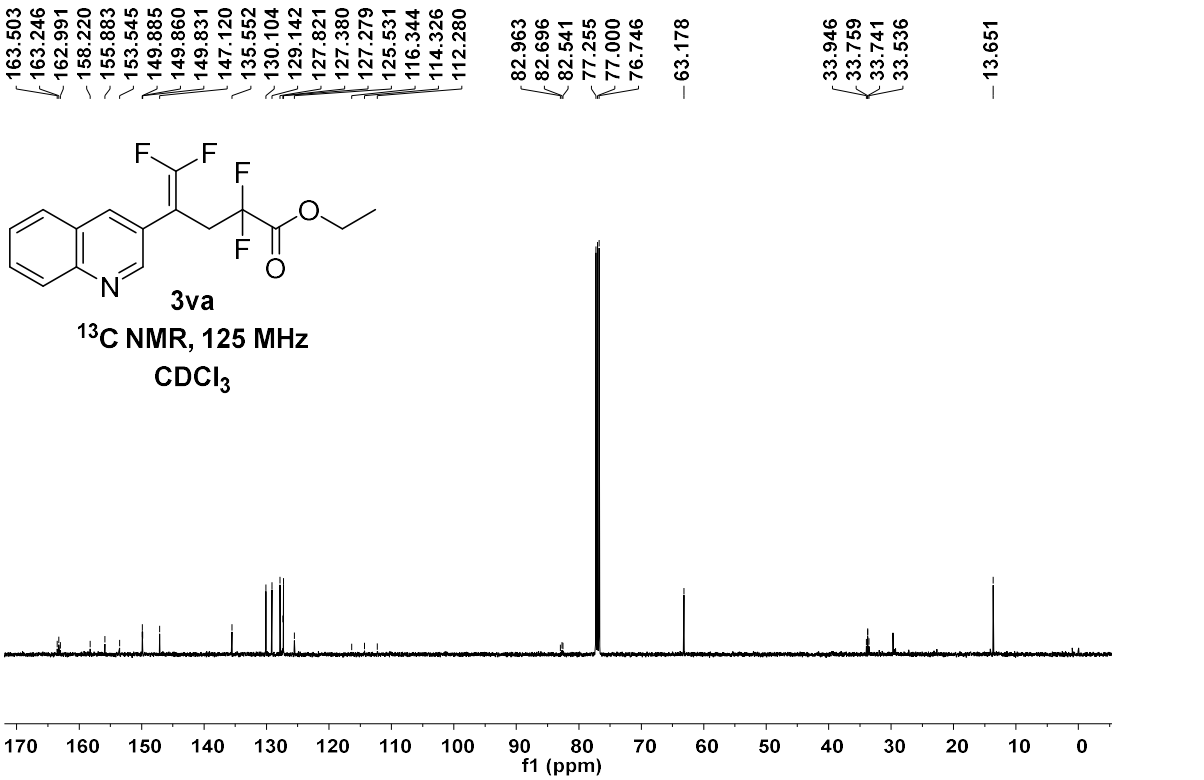




3va

^{1}H NMR, 500 MHz

$CDCl_3$


163.503
163.246
162.991
158.220
155.883
153.545
149.885
149.860
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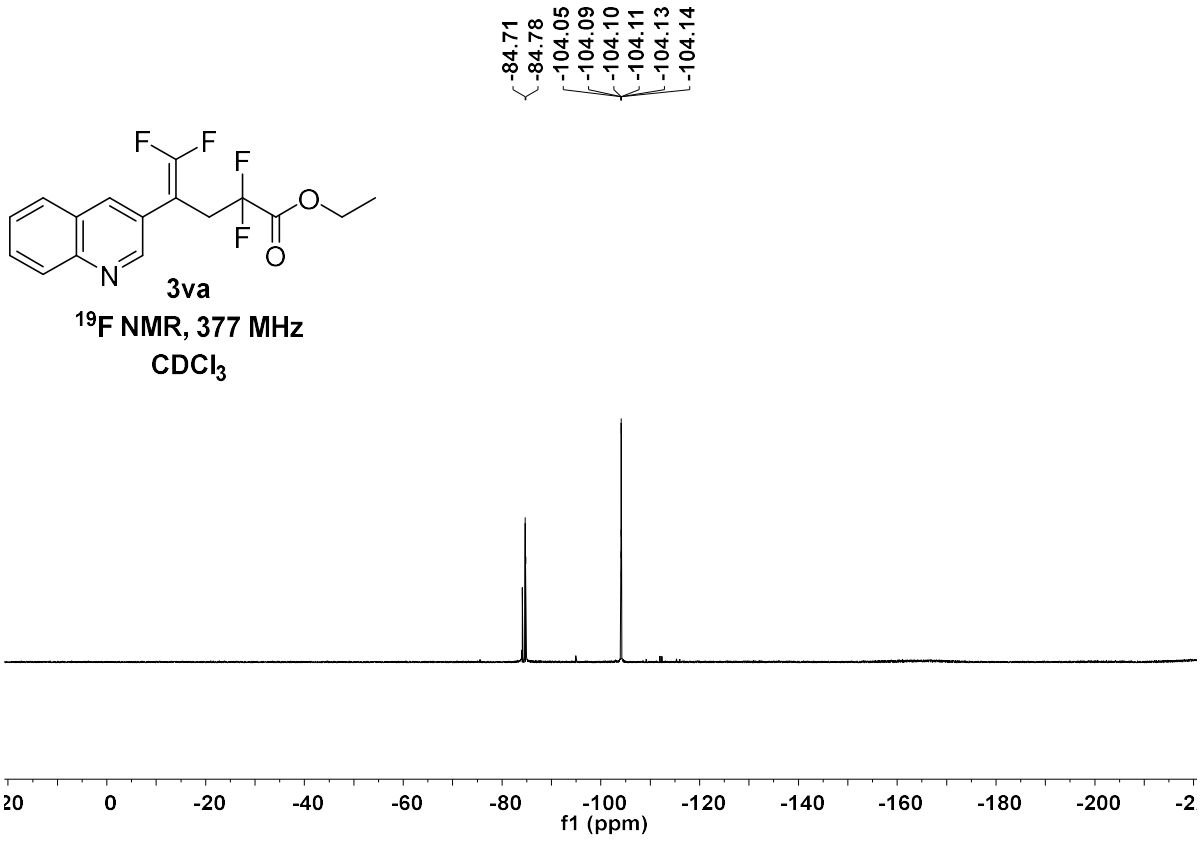
147.120
135.552
130.104
129.142
127.821
127.380
127.279
125.531
116.344
114.326
112.280
82.963
82.696
82.541
77.255
77.000
76.746
63.178
33.946
33.759
33.741
33.536
13.651
F
F
F
F
O
O
N
3va
^{13}C NMR, 125 MHz
$CDCl_3$
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-84.71
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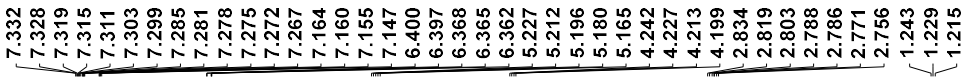
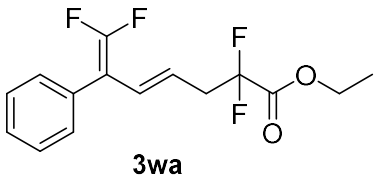
-104.05
-104.09
-104.10
-104.11
-104.13
-104.14
F
F
F
F
O
O
N
3va
^{19}F NMR, 377 MHz
$CDCl_3$
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

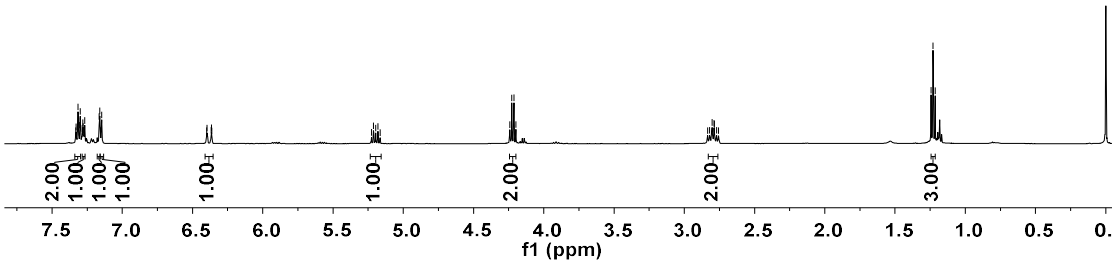


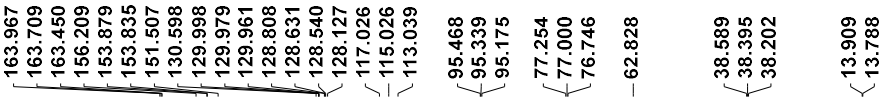


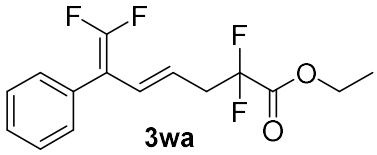
3wa

^{1}H NMR, 500 MHz

$CDCl_3$



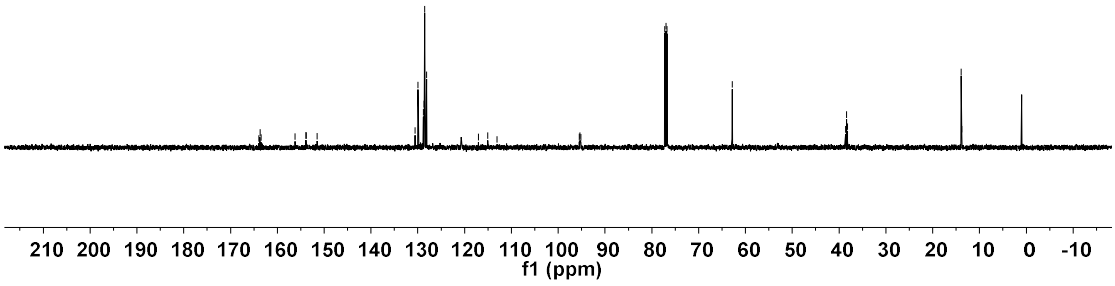


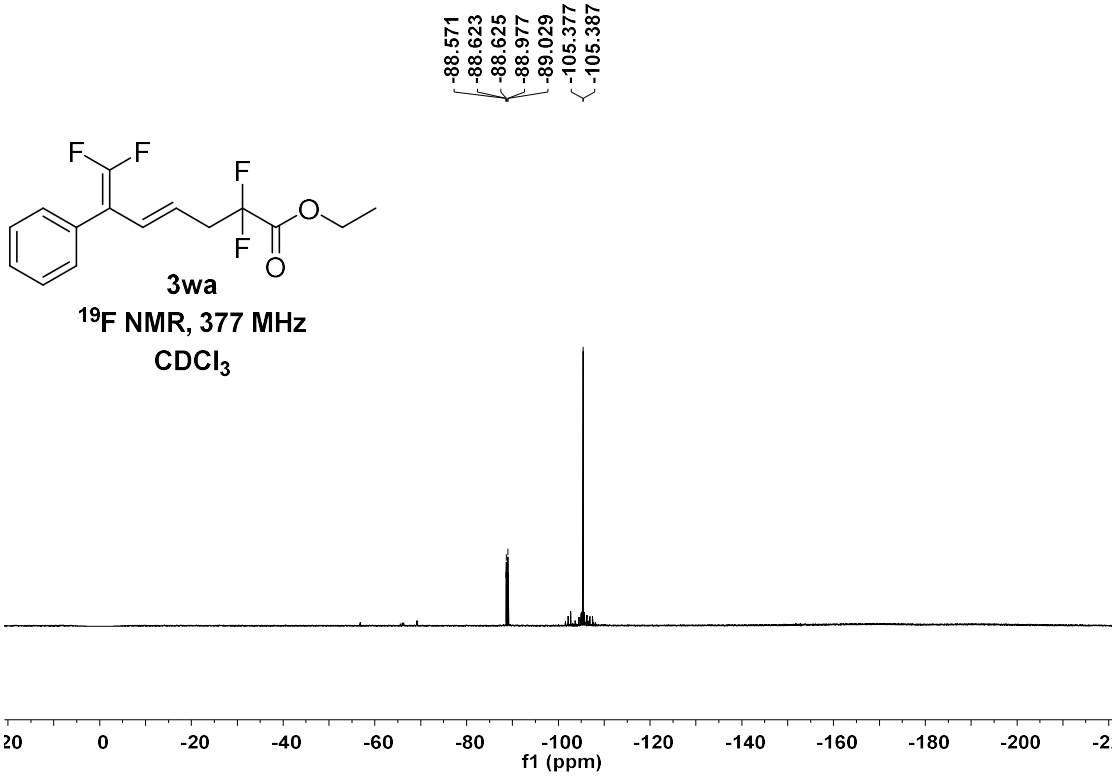


3wa

^{13}C NMR, 125 MHz

$CDCl_3$

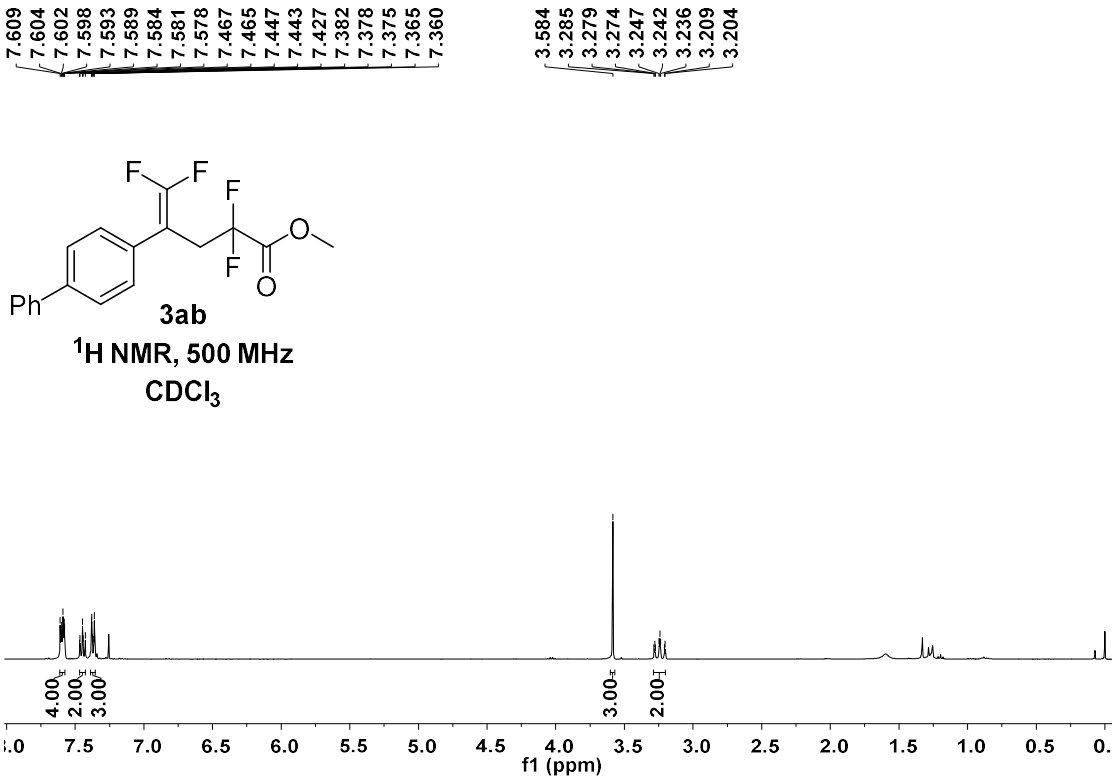




3wa

^{19}F NMR, 377 MHz

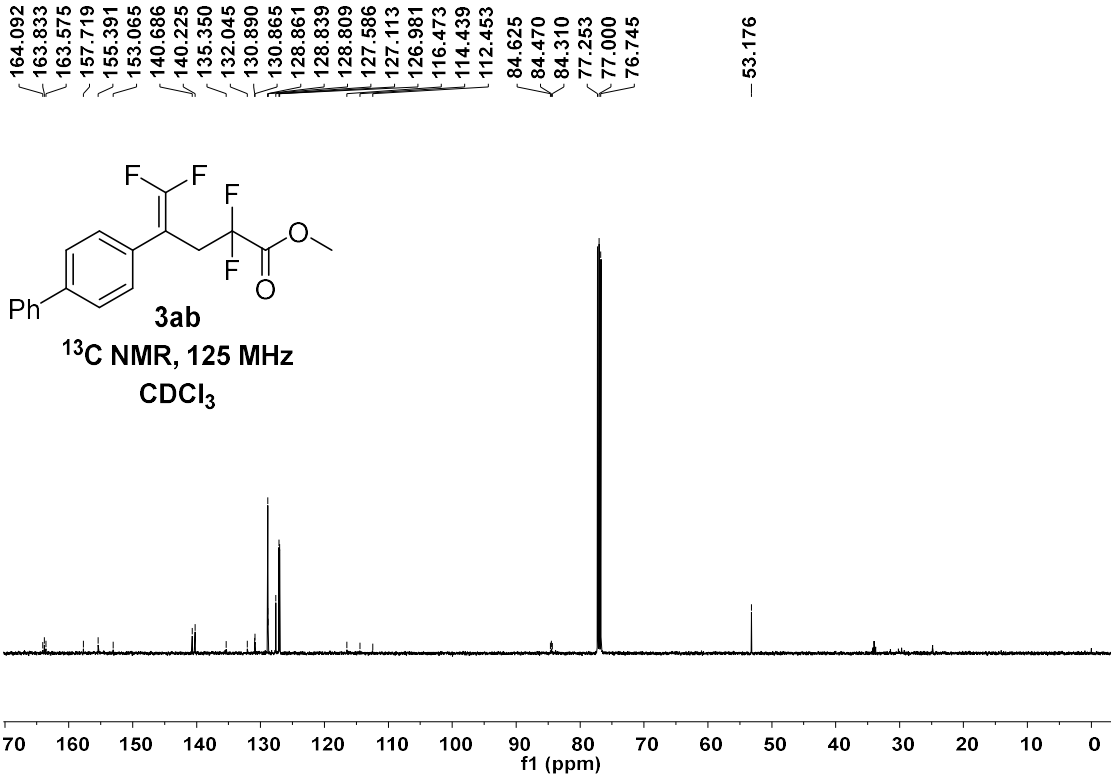
$CDCl_3$

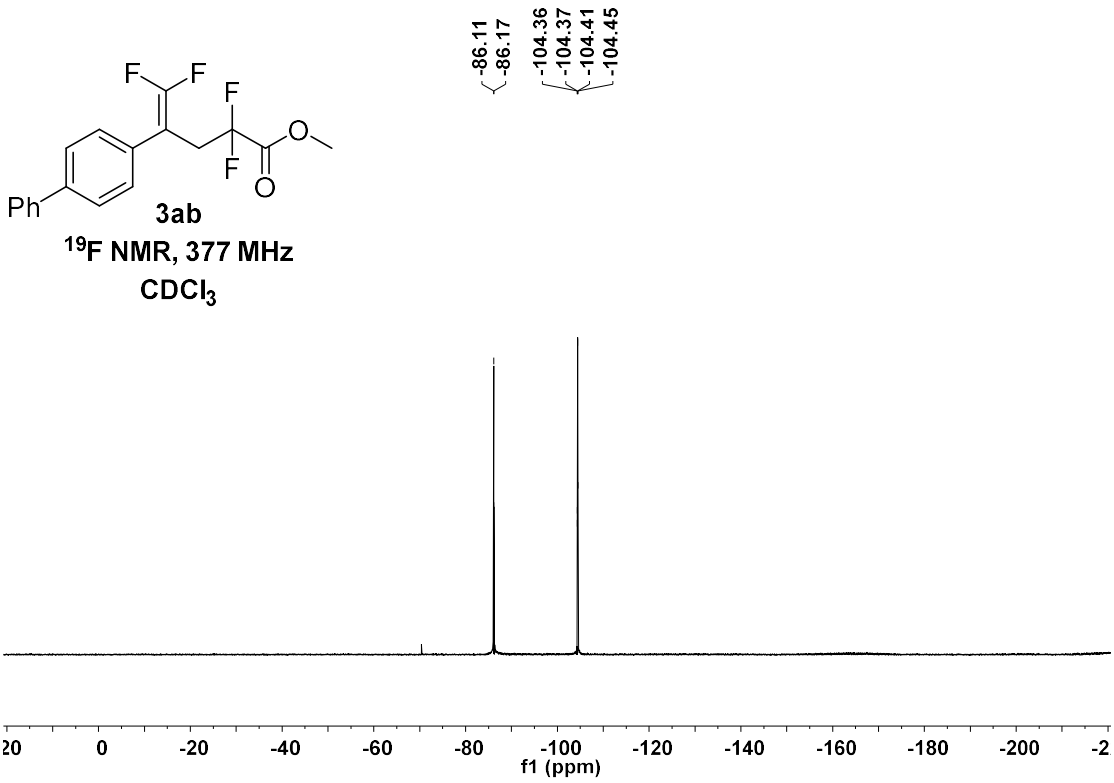


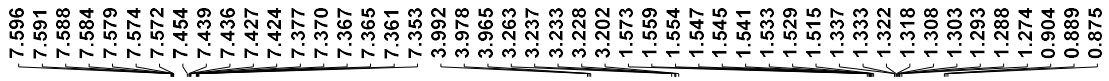
3ab

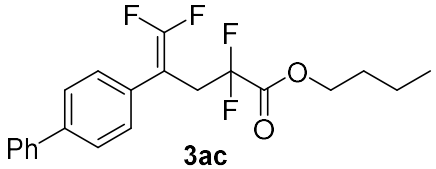
^{1}H NMR, 500 MHz

$CDCl_3$


164.092
163.833
163.575
157.719
155.391
153.065
140.686
140.225
135.350
132.045
130.890
130.865
128.861
128.839
128.809
127.586
127.113
126.981
116.473
114.439
112.453
84.625
84.470
84.310
77.253
77.000
76.745
53.176
F
F
F
F
O
O
Ph
3ab
13C NMR, 125 MHz
CDCl3
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-86.11
-86.17
-104.36
-104.37
-104.41
-104.45
F
F
F
F
O
O
Ph
3ab
19F NMR, 377 MHz
CDCl3
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

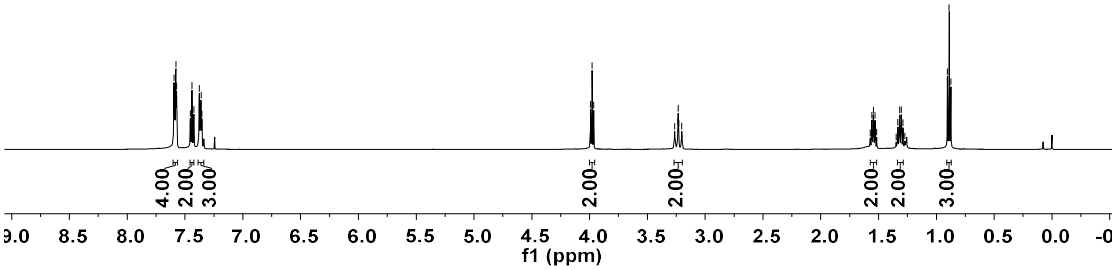


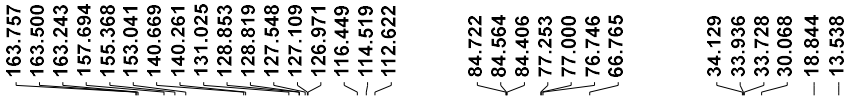


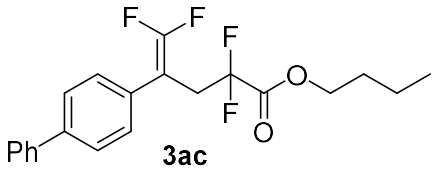
3ac

^{1}H NMR, 500 MHz

$CDCl_3$



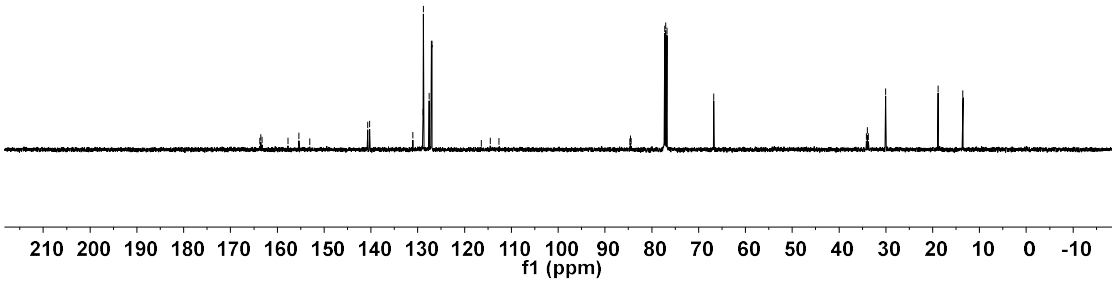


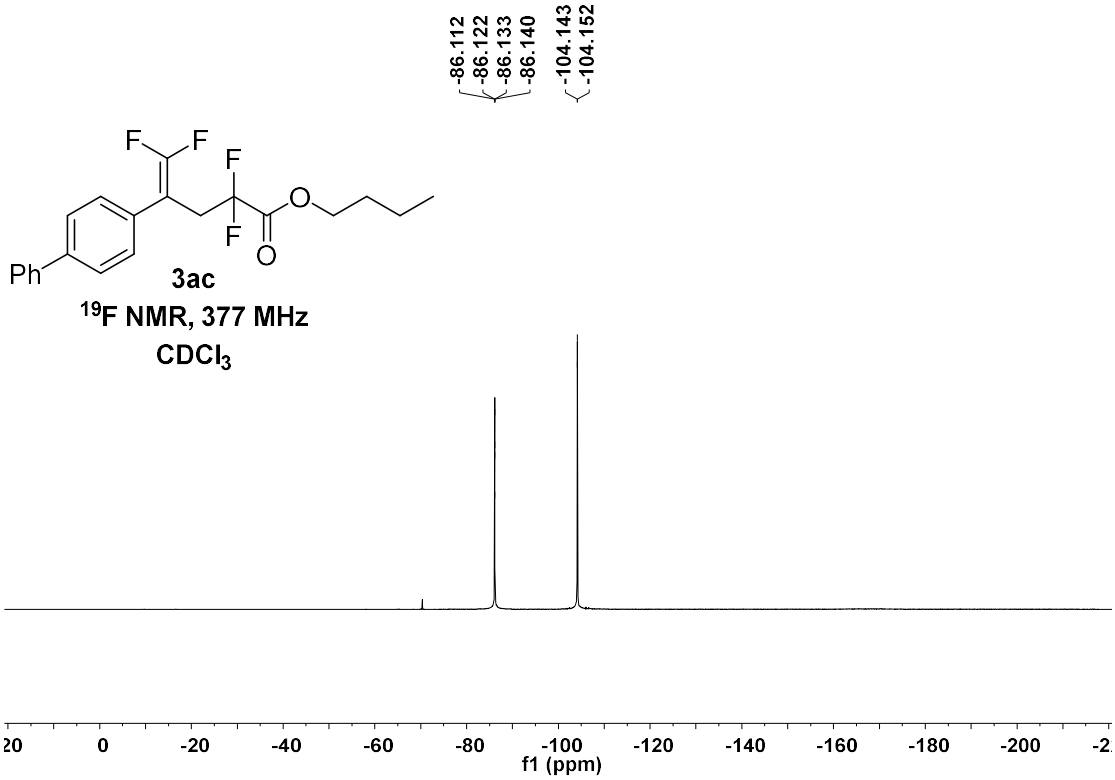


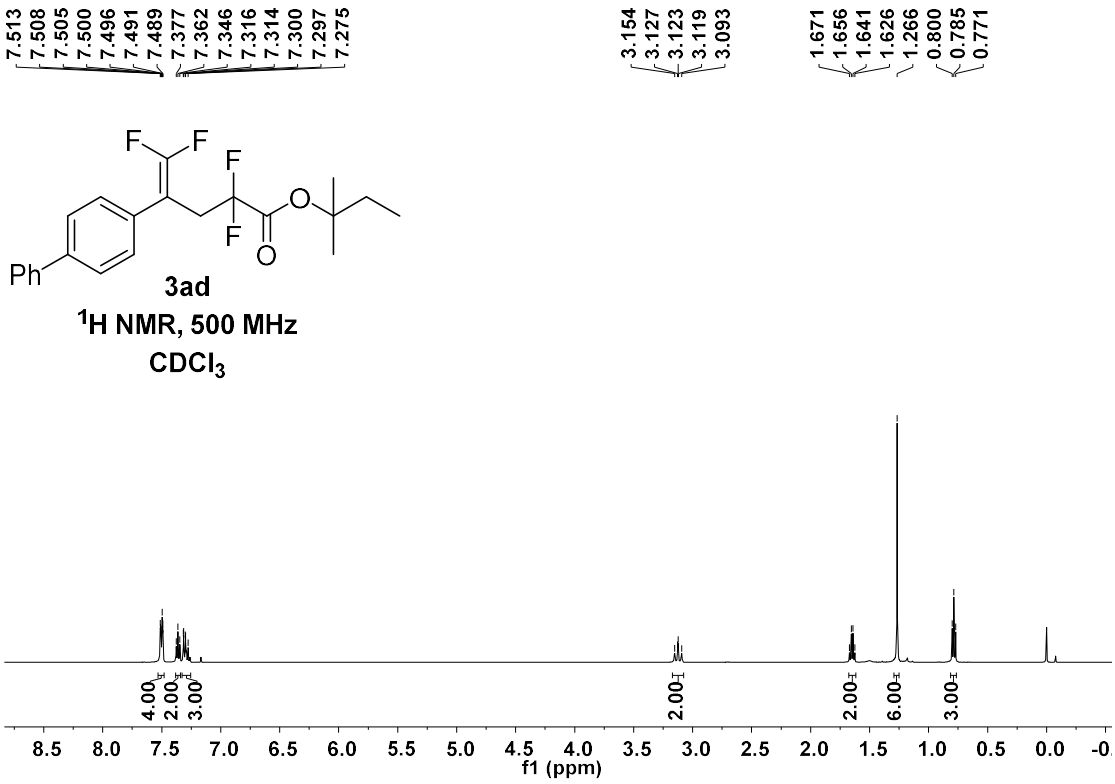
3ac

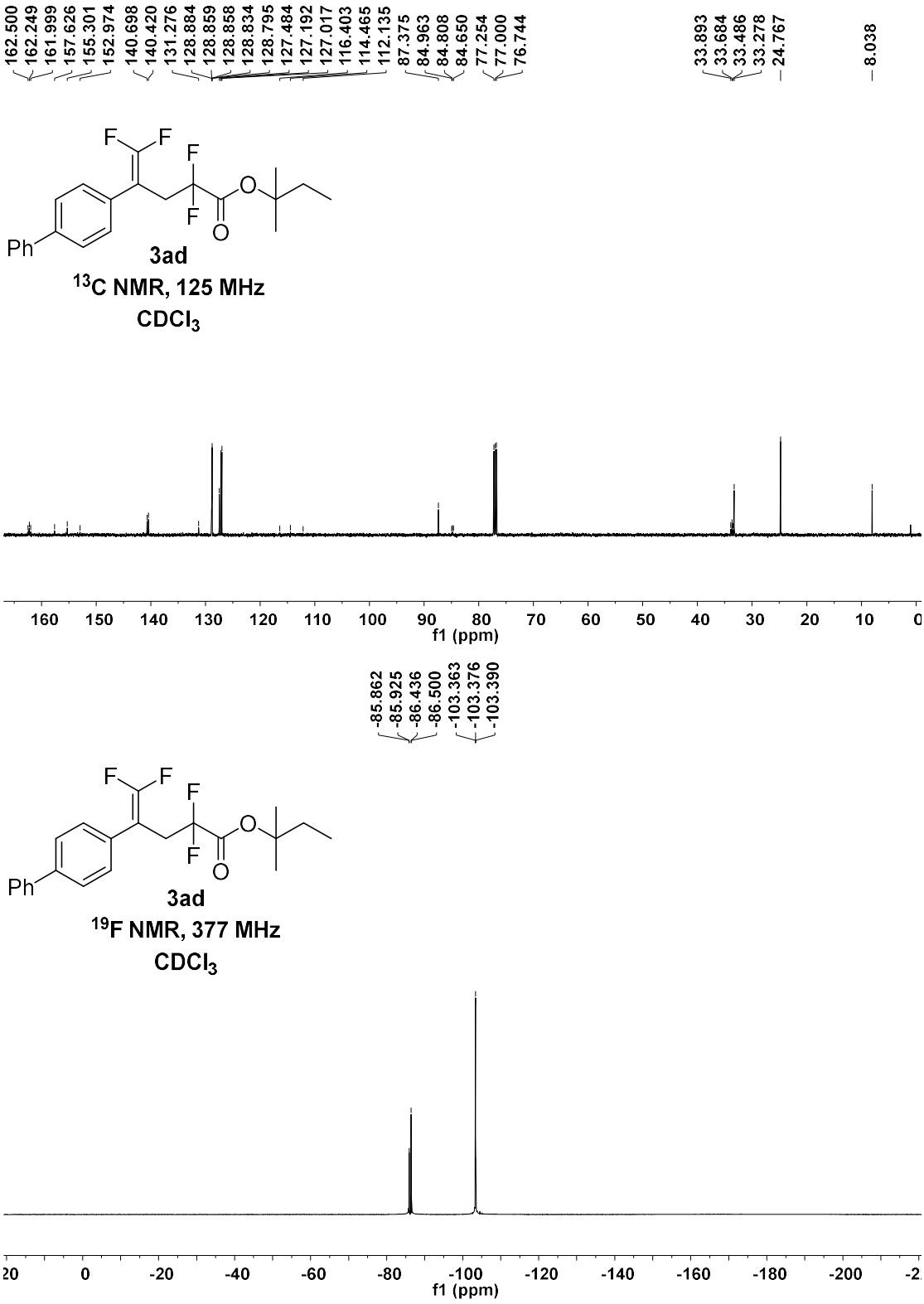
^{13}C NMR, 125 MHz

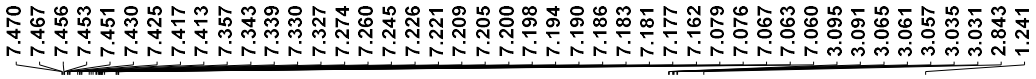
$CDCl_3$

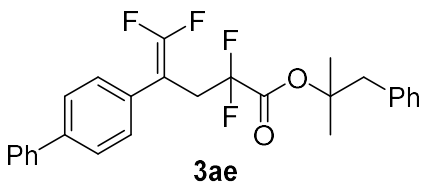



-86.112
-86.122
-86.133
-86.140
-104.143
-104.152
F
F
F
F
O
O
Ph
3ac
19F NMR, 377 MHz
CDCl3
f1 (ppm)


7.513
7.508
7.505
7.500
7.496
7.491
7.489
7.377
7.362
7.346
7.316
7.314
7.300
7.297
7.275
3.154
3.127
3.123
3.119
3.093
1.671
1.656
1.641
1.626
1.266
0.800
0.785
0.771
F
F
F
F
O
O
Ph
3ad
1H NMR, 500 MHz
CDCl3
4.00
2.00
3.00
2.00
2.00
6.00
3.00
f1 (ppm)


162.500
162.249
161.999
157.626
155.301
152.974
140.698
140.420
131.276
128.884
128.859
128.858
128.834
128.795
127.484
127.192
127.017
116.403
114.465
112.135
87.375
84.963
84.808
84.650
77.254
77.000
76.744
33.893
33.684
33.486
33.278
24.767
8.038
F
F
F
F
O
O
Ph
3ad
13C NMR, 125 MHz
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
-85.862
-85.925
-86.436
-86.500
-103.363
-103.376
-103.390
F
F
F
F
O
O
Ph
3ad
19F NMR, 377 MHz
CDCl3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

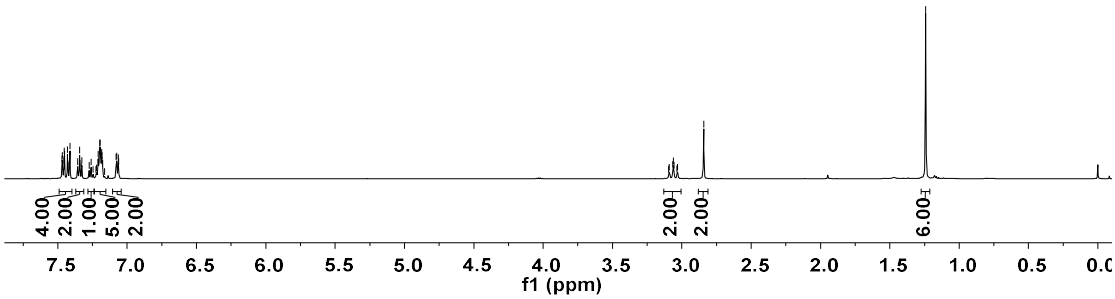


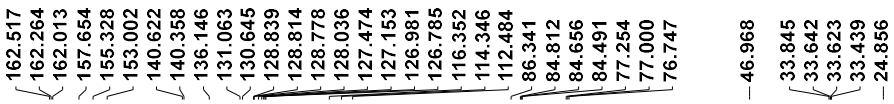


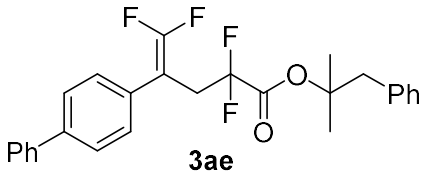
3ae

^{1}H NMR, 500 MHz

$CDCl_3$



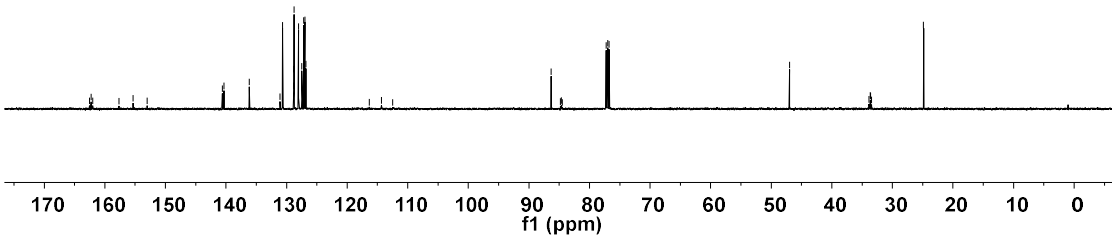


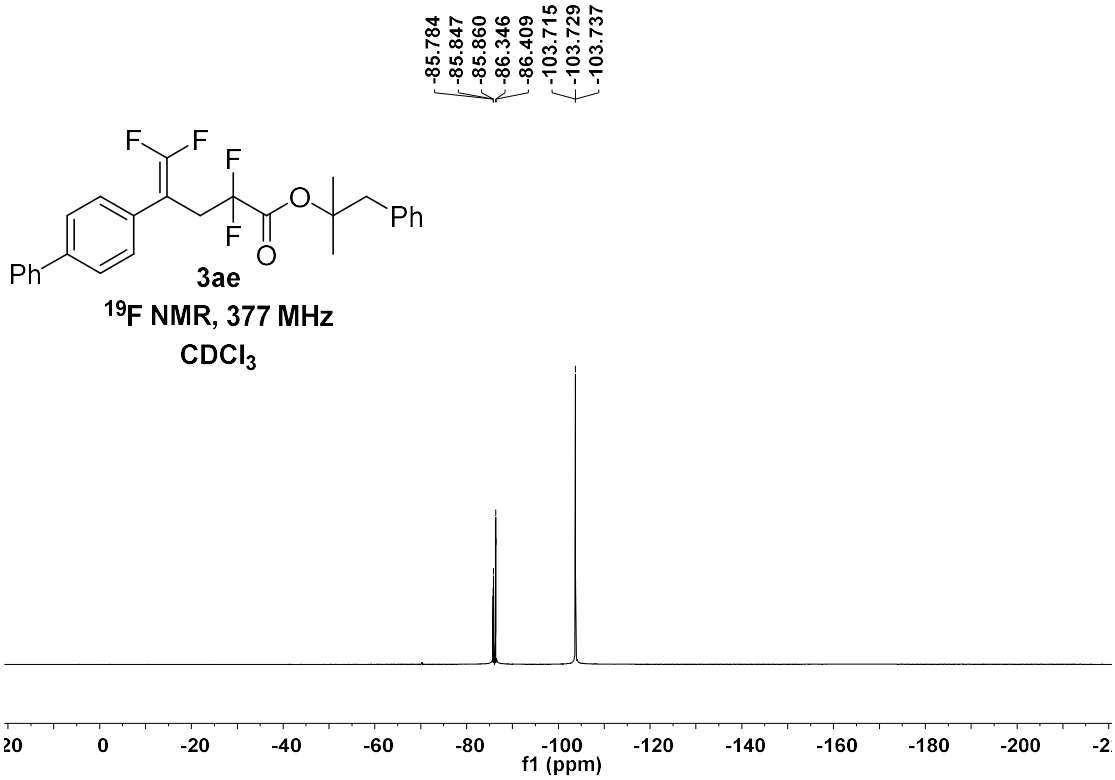


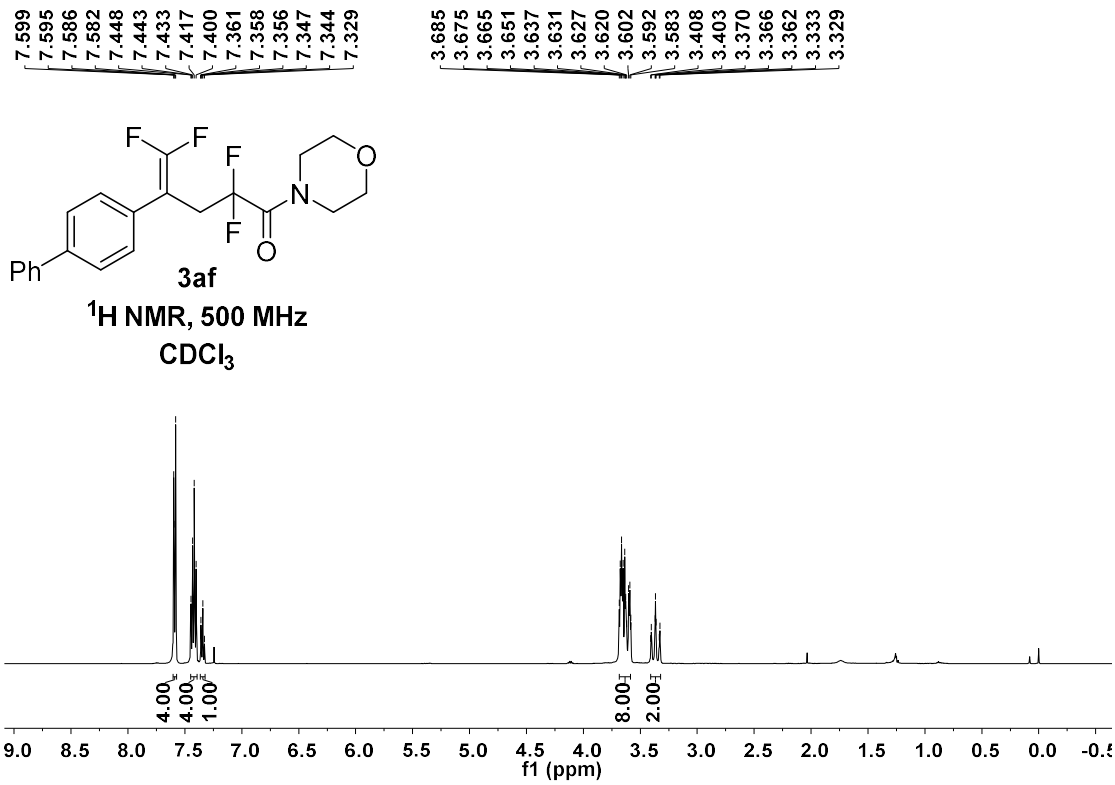
3ae

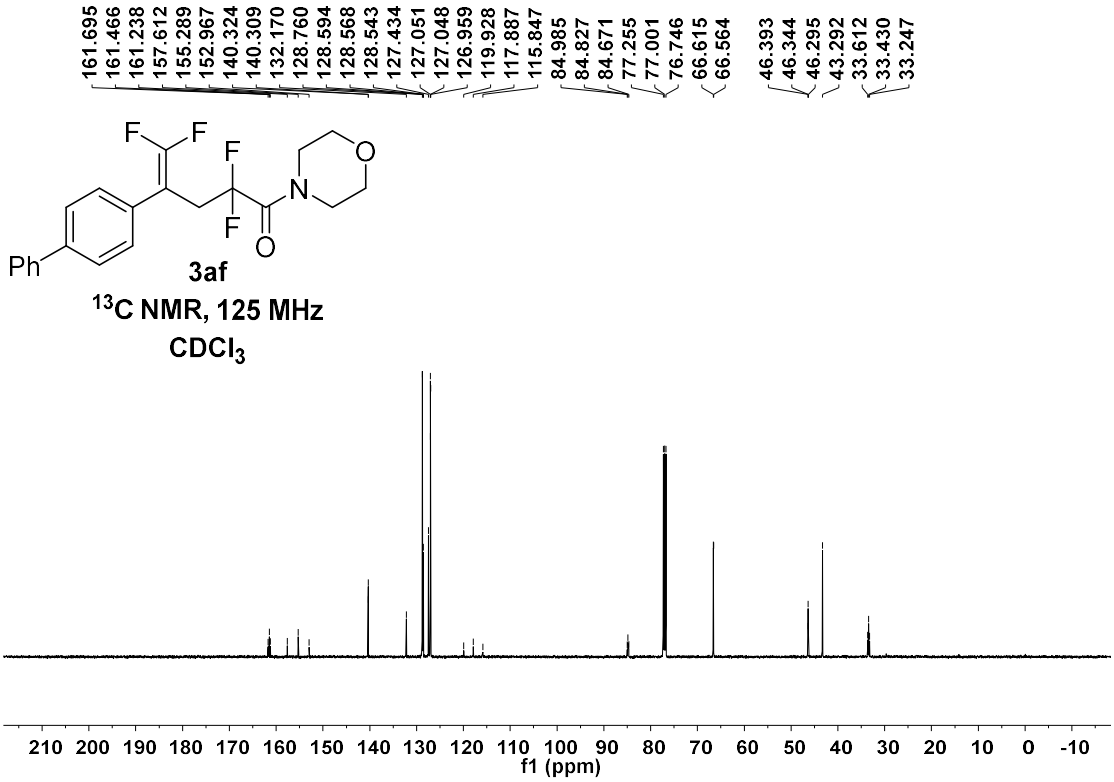
^{13}C NMR, 125 MHz

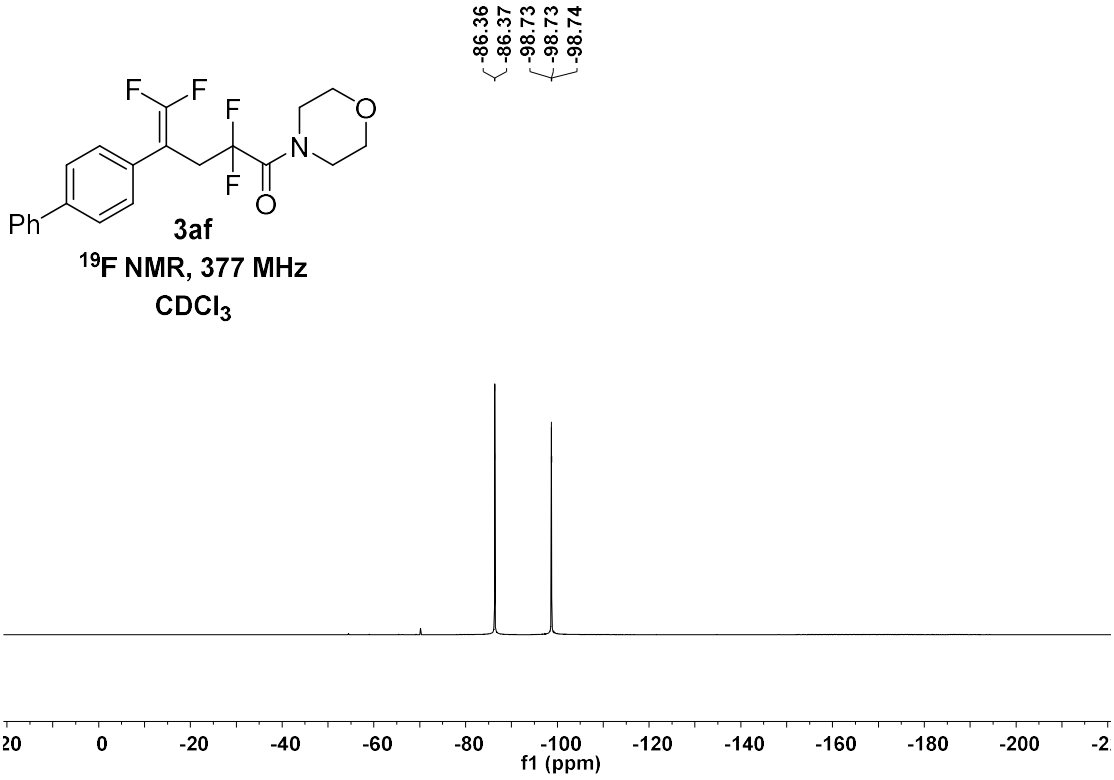
$CDCl_3$

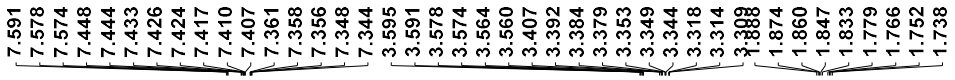


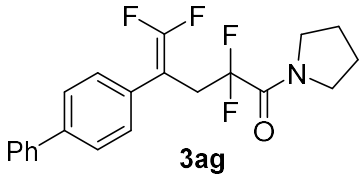

-85.784
-85.847
-85.860
-86.346
-86.409
-103.715
-103.729
-103.737
F
F
F
F
O
O
Ph
Ph
3ae
19F NMR, 377 MHz
CDCl3
f1 (ppm)


7.599
7.595
7.586
7.582
7.448
7.443
7.433
7.417
7.400
7.361
7.358
7.356
7.347
7.344
7.329
3.685
3.675
3.665
3.651
3.637
3.631
3.627
3.620
3.602
3.592
3.583
3.408
3.403
3.370
3.366
3.362
3.333
3.329
F
F
F
F
O
N
O
Ph
3af
1H NMR, 500 MHz
CDCl3
4.00
4.00
1.00
8.00
2.00
f1 (ppm)


161.695
161.466
161.238
157.612
155.289
152.967
140.324
140.309
132.170
128.760
128.594
128.568
128.543
127.434
127.051
127.048
126.959
119.928
117.887
115.847
84.985
84.827
84.671
77.255
77.001
76.746
66.615
66.564
46.393
46.344
46.295
43.292
33.612
33.430
33.247
F
F
F
F
O
N
O
Ph
3af
13C NMR, 125 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)


-86.36
-86.37
-98.73
-98.73
-98.74
F
F
F
F
O
N
O
Ph
3af
19F NMR, 377 MHz
CDCl3
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

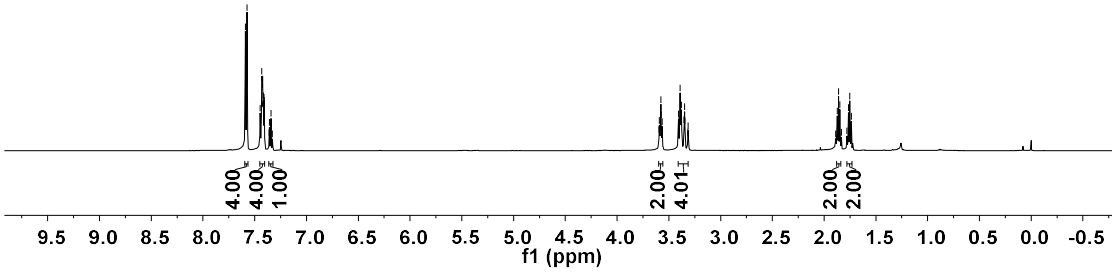


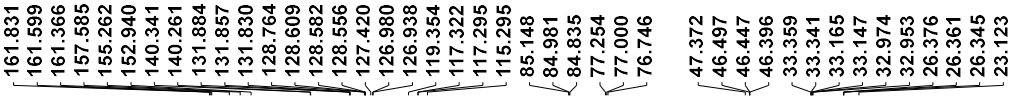


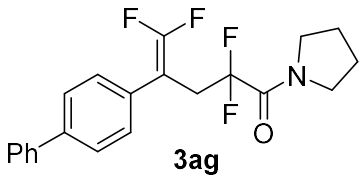
3ag

^{1}H NMR, 500 MHz

$CDCl_3$



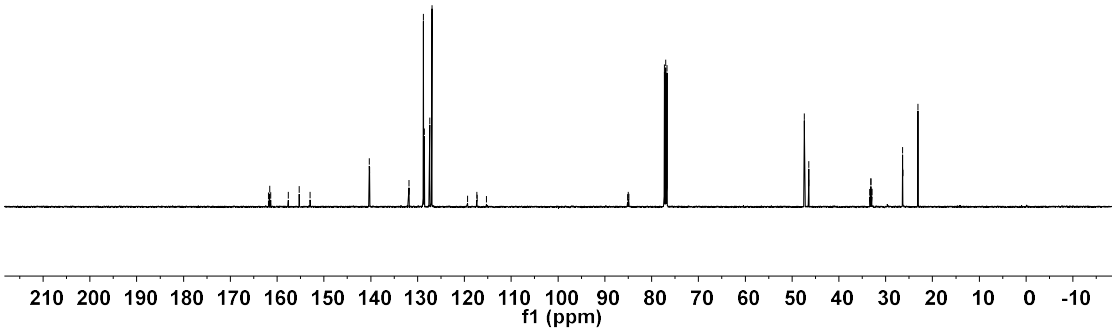


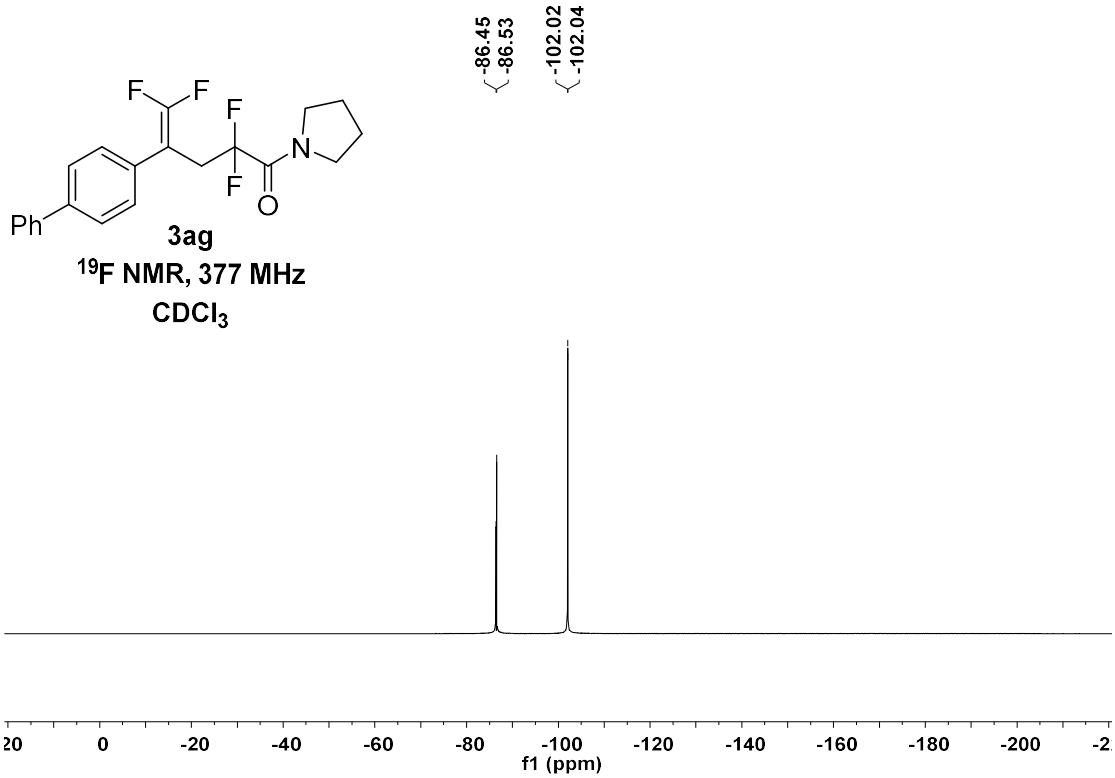


3ag

^{13}C NMR, 125 MHz

$CDCl_3$

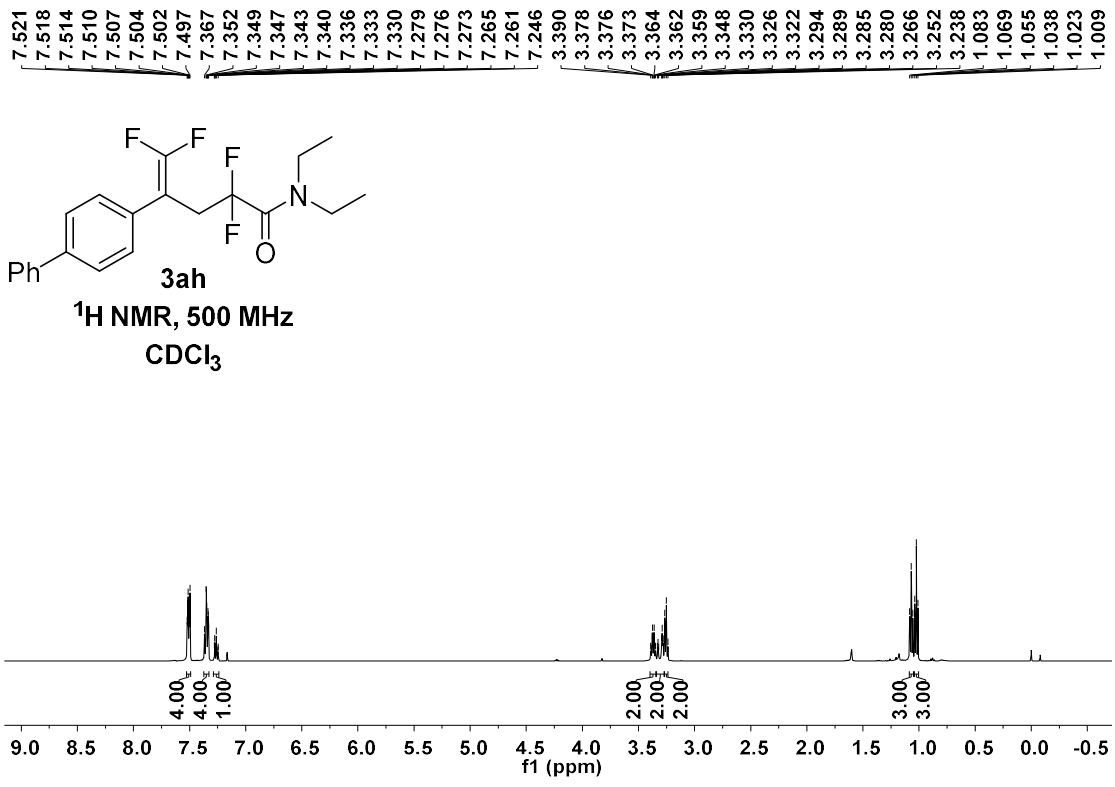




3ag

^{19}F NMR, 377 MHz

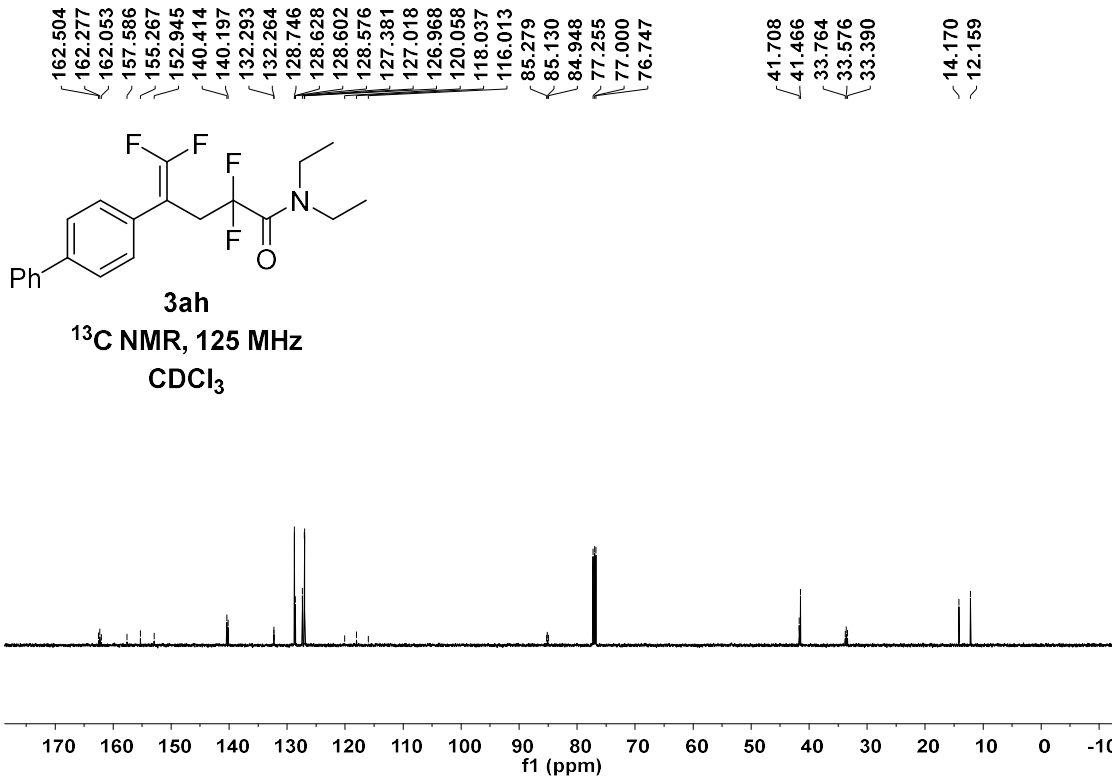
$CDCl_3$



3ah

^{1}H NMR, 500 MHz

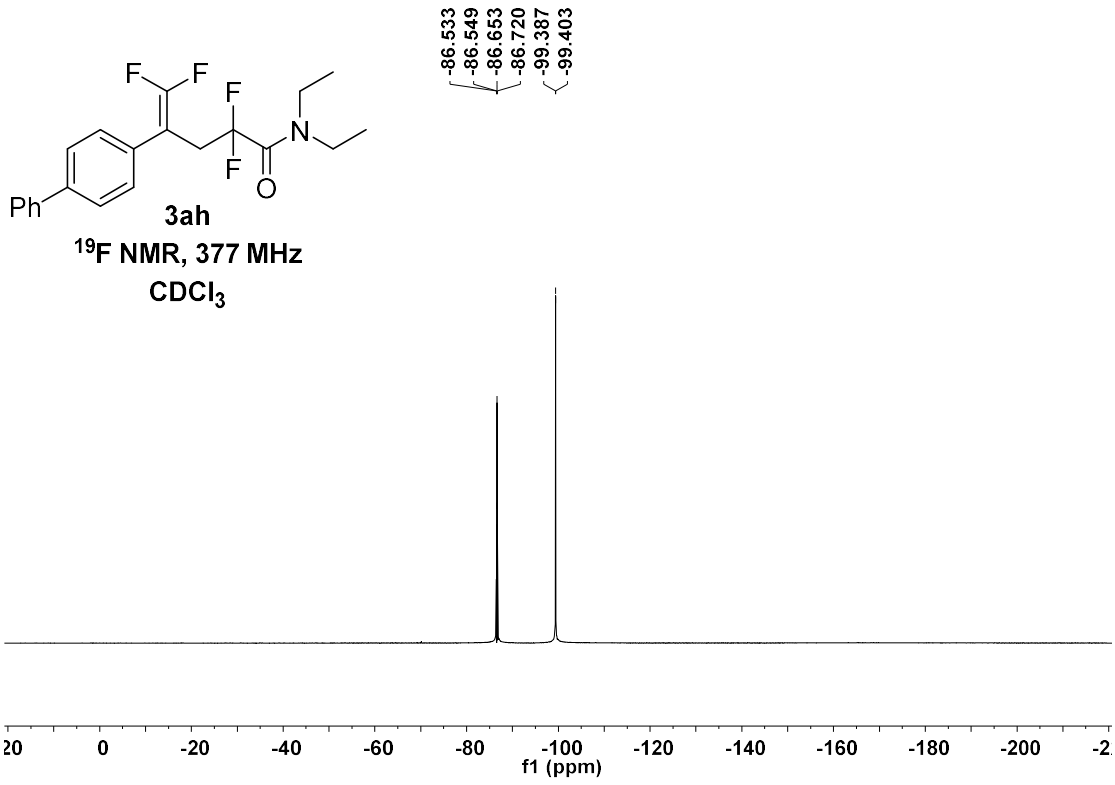
$CDCl_3$



3ah

^{13}C NMR, 125 MHz

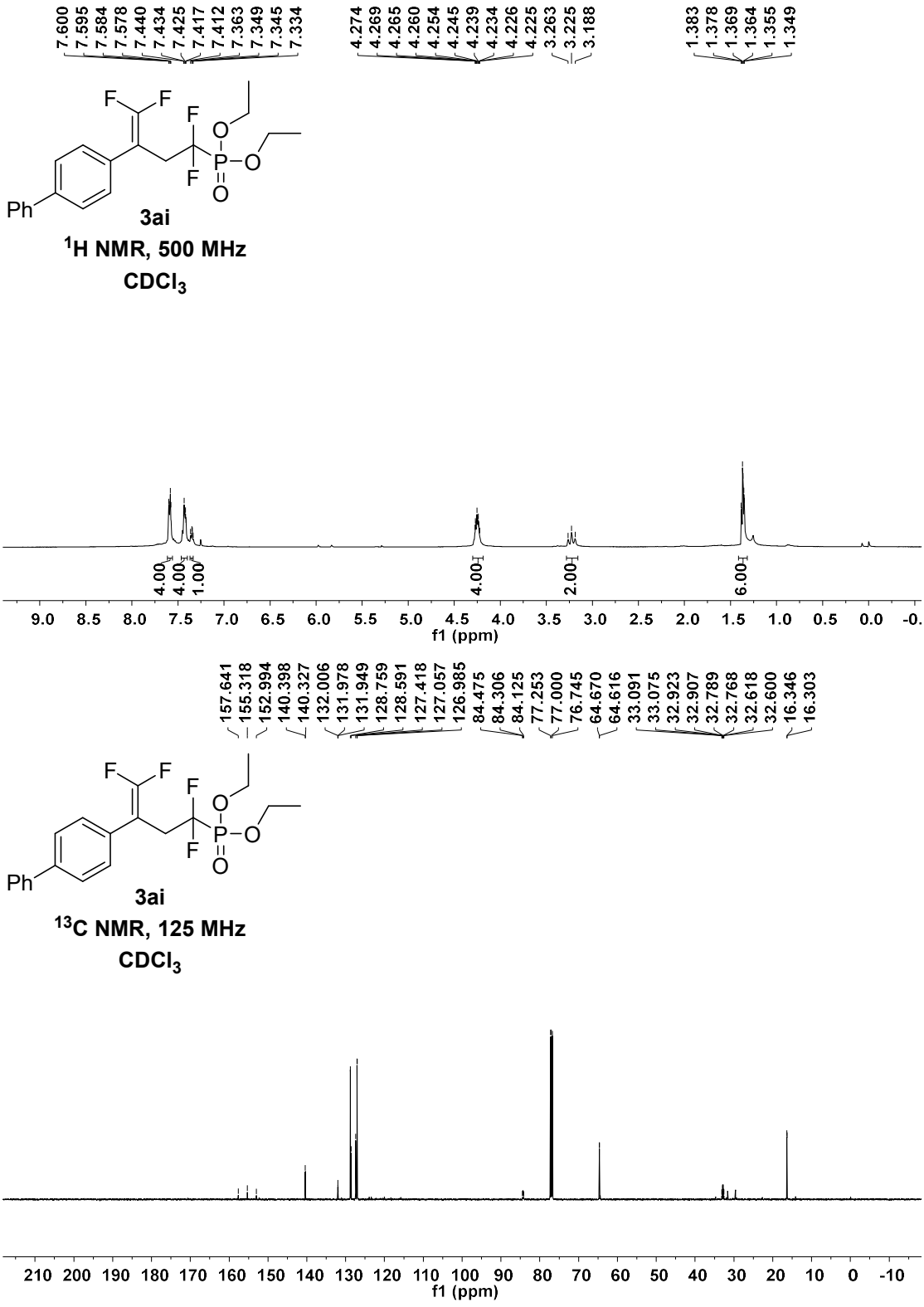
$CDCl_3$



3ah

^{19}F NMR, 377 MHz

$CDCl_3$



3ai

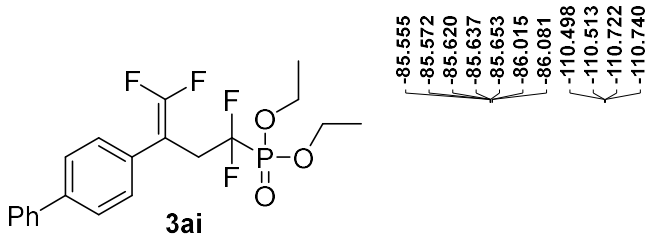
^{1}H NMR, 500 MHz

$CDCl_3$

3ai

^{13}C NMR, 125 MHz

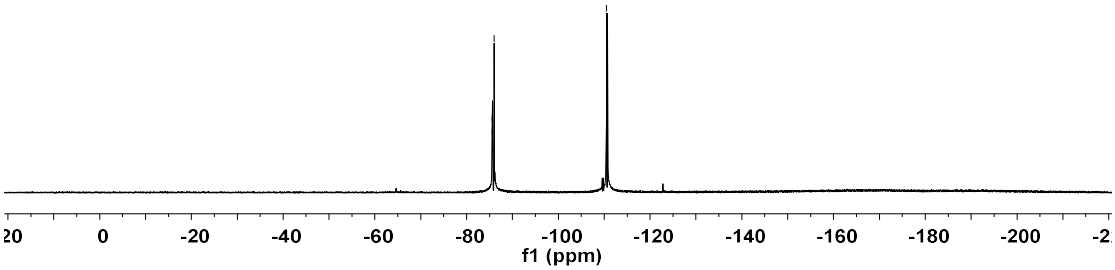
$CDCl_3$

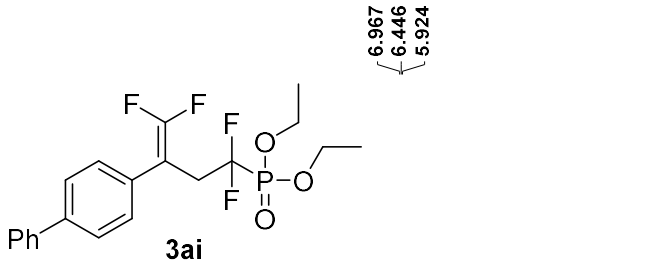


3ai

^{19}F NMR, 377 MHz

$CDCl_3$

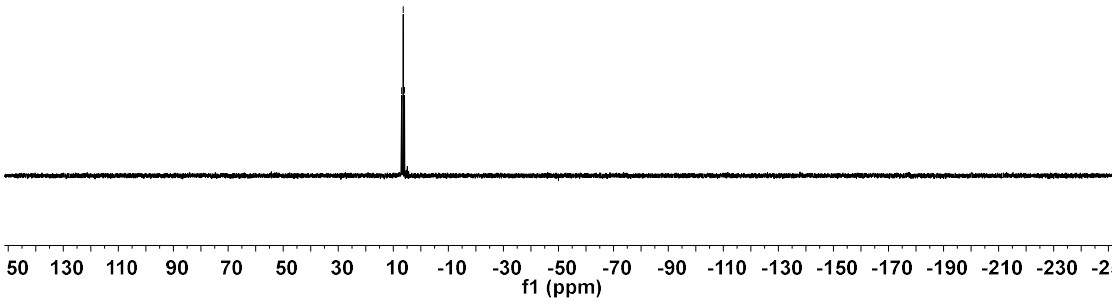


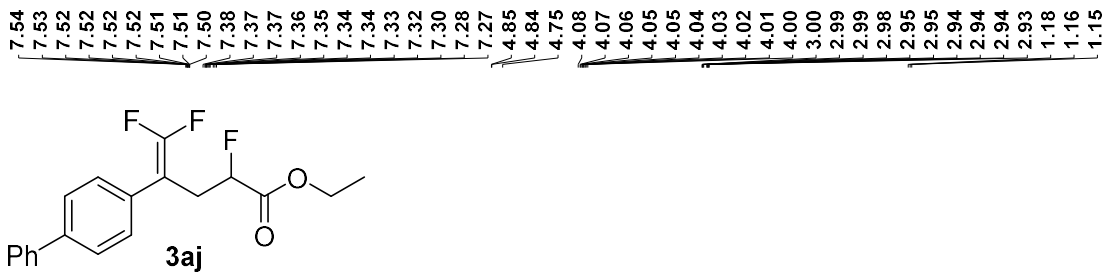


3ai

^{31}P NMR, 162 MHz

$CDCl_3$

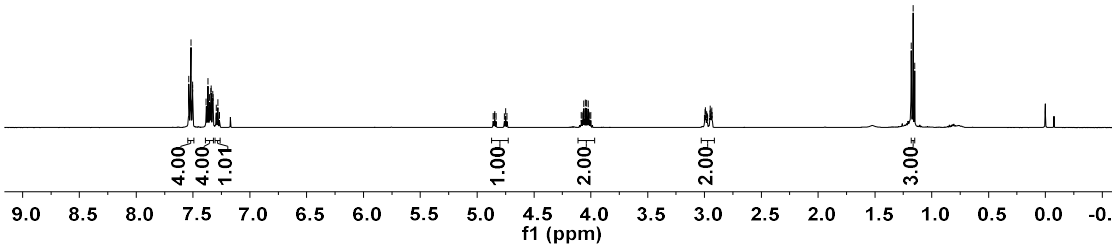


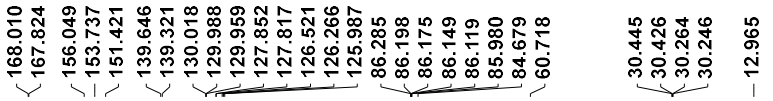


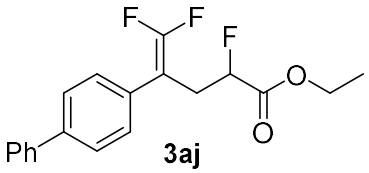
3aj

^{1}H NMR, 500 MHz

$CDCl_3$



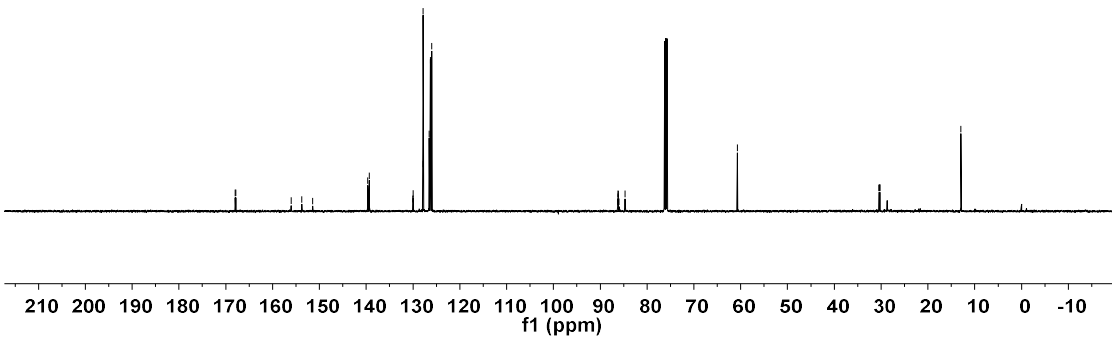


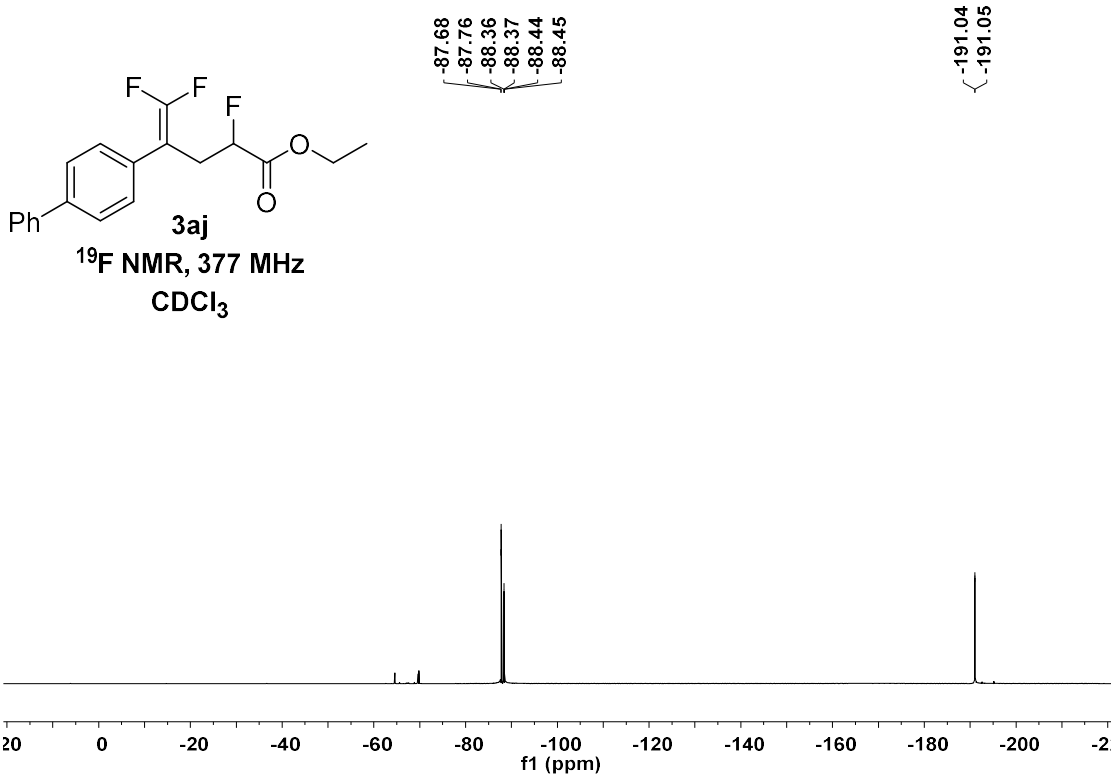


3aj

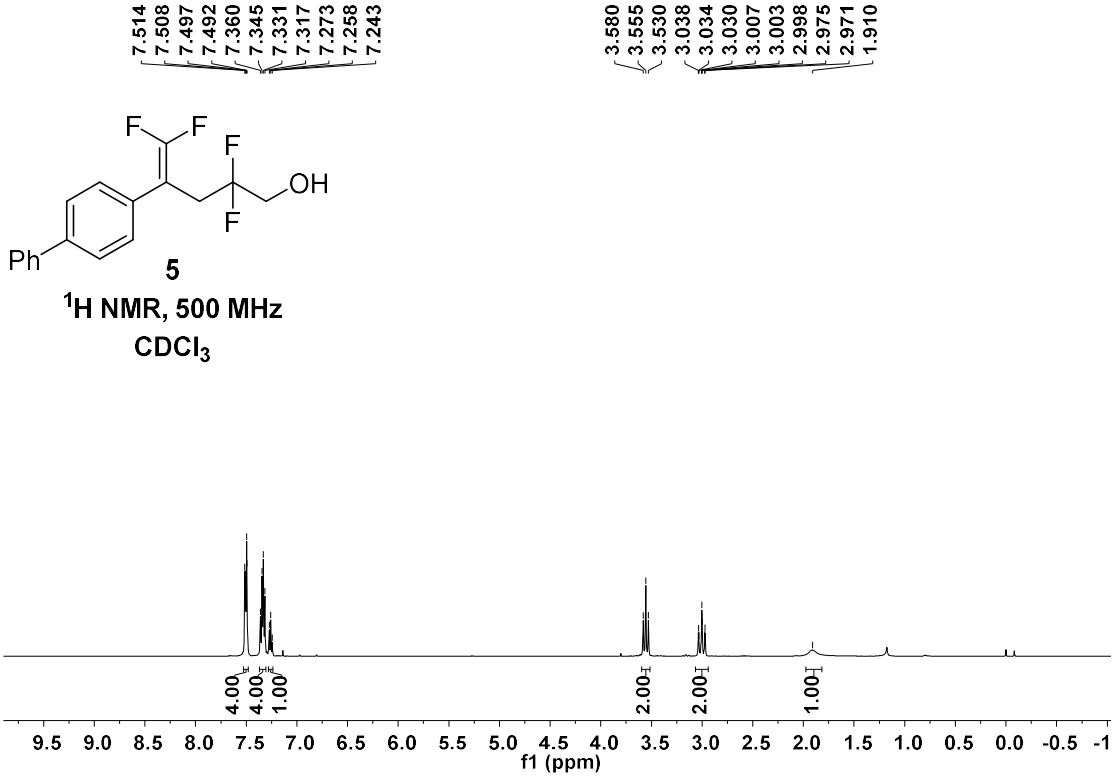
^{13}C NMR, 125 MHz

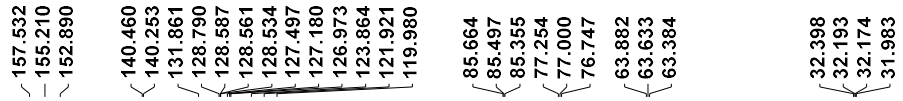
$CDCl_3$

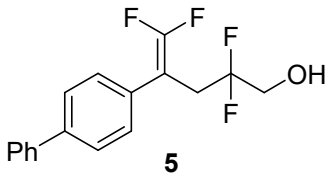




4-([1,1'-biphenyl]-4-yl)-2,2,5,5-tetrafluoropent-4-en-1-ol (5)



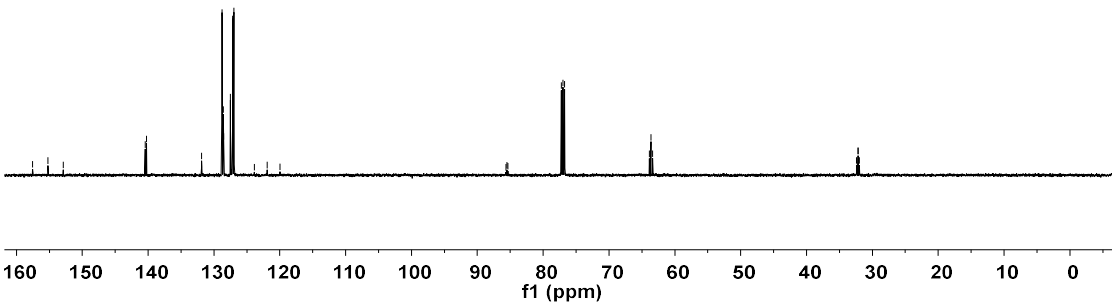


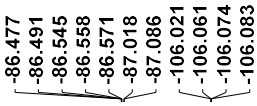


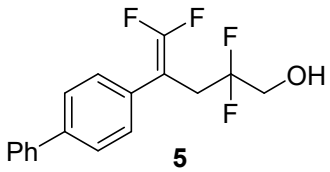
5

^{13}C NMR, 125 MHz

$CDCl_3$



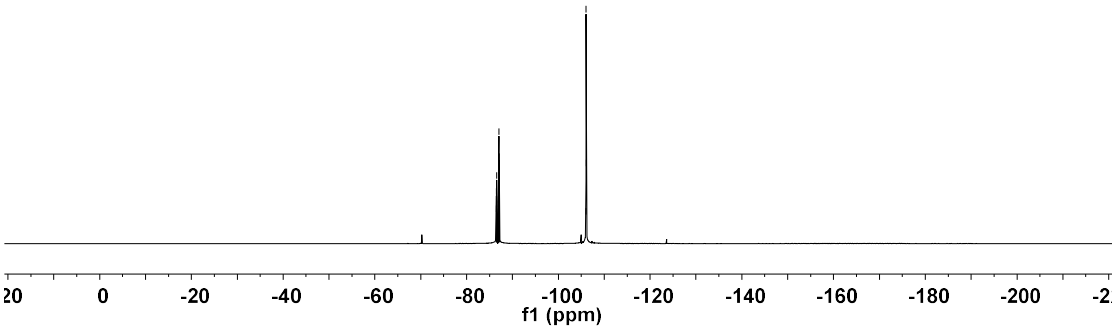




5

^{19}F NMR, 377 MHz

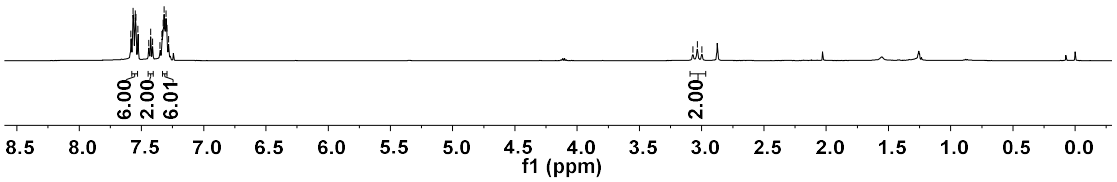
$CDCl_3$

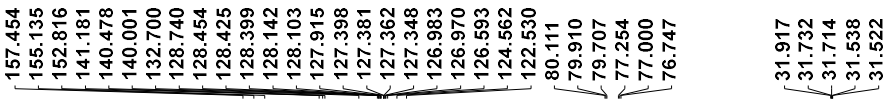


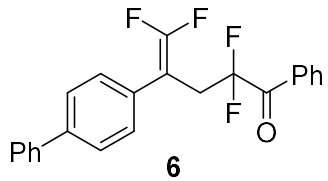
6

^{1}H NMR, 500 MHz

$CDCl_3$



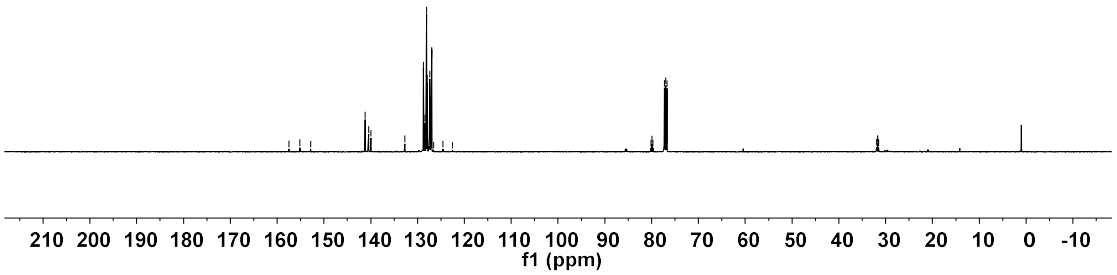


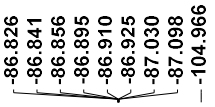


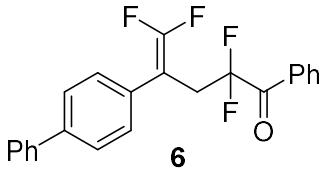
6

^{13}C NMR, 125 MHz

$CDCl_3$



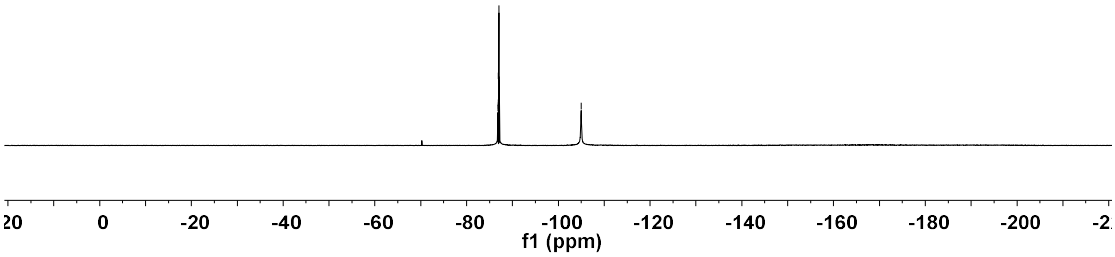


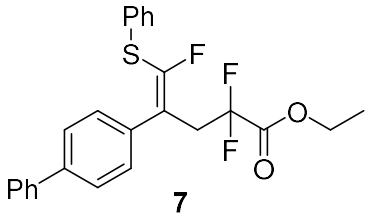


6

^{19}F NMR, 377 MHz

$CDCl_3$

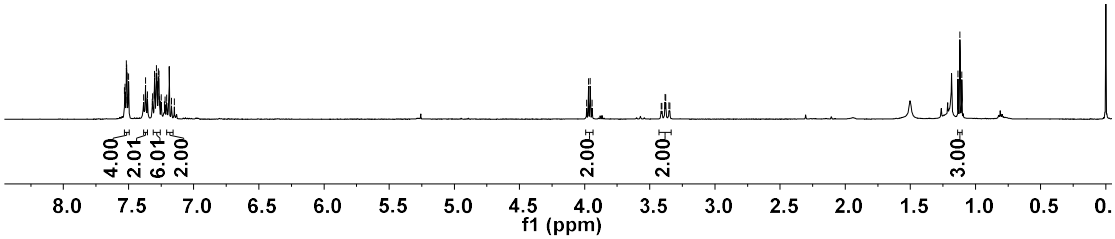


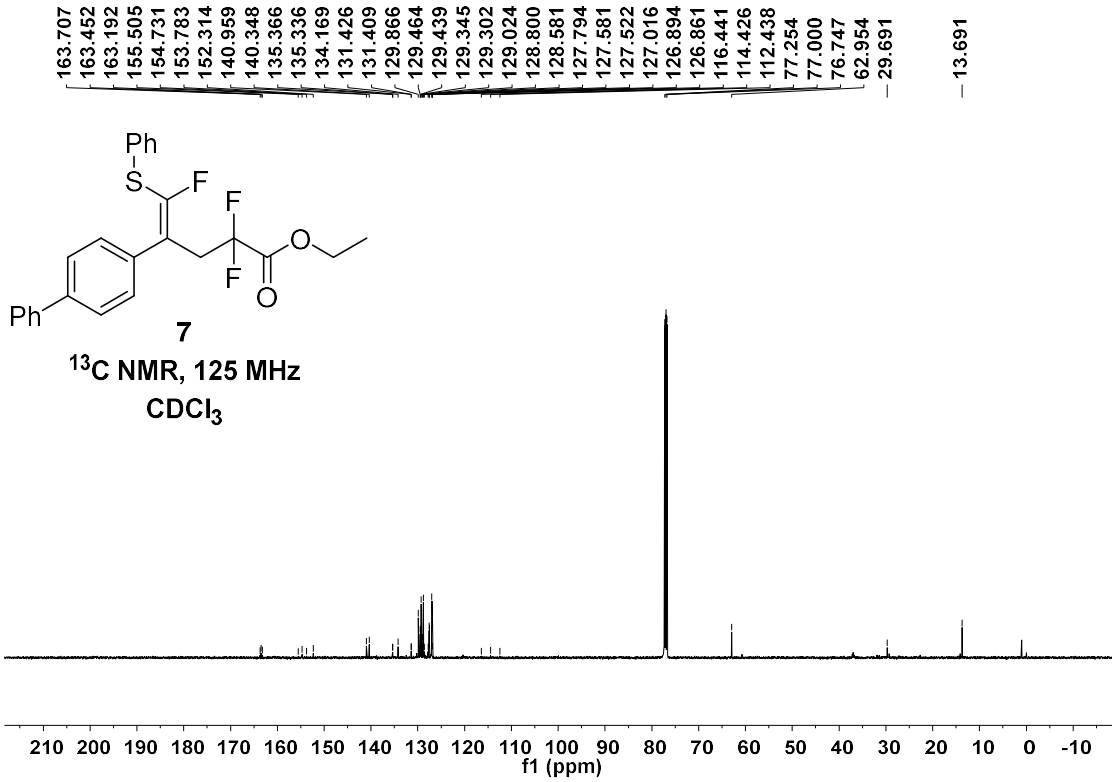


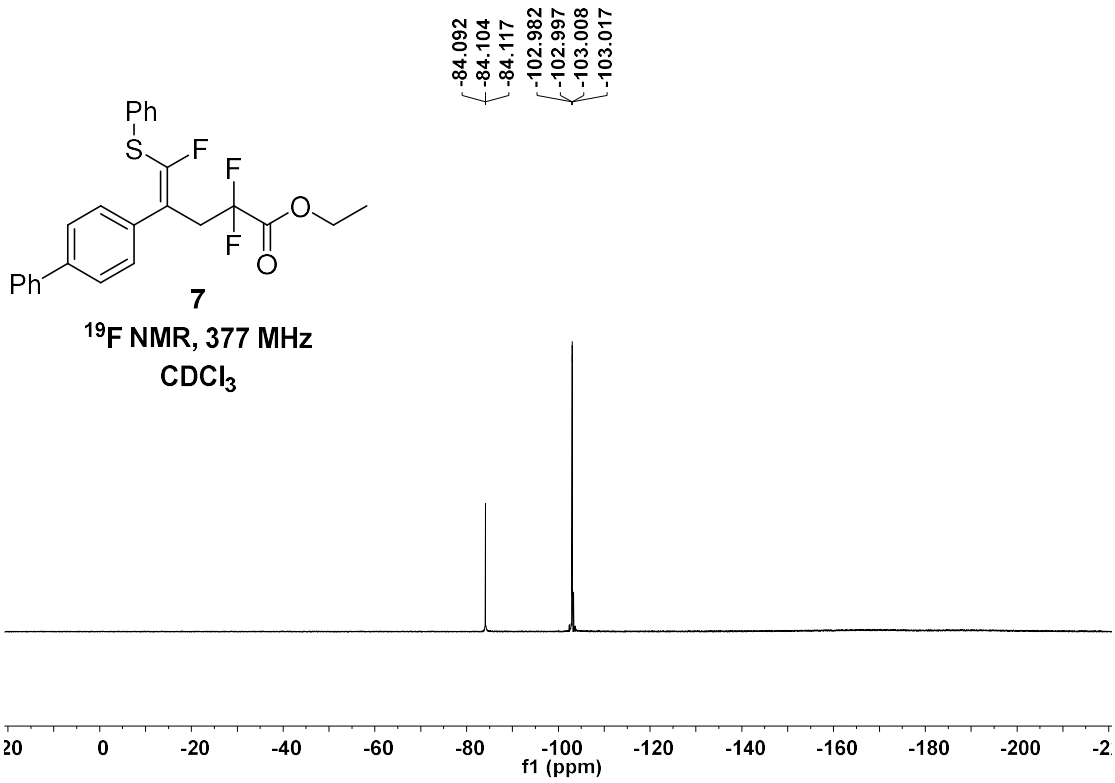
7

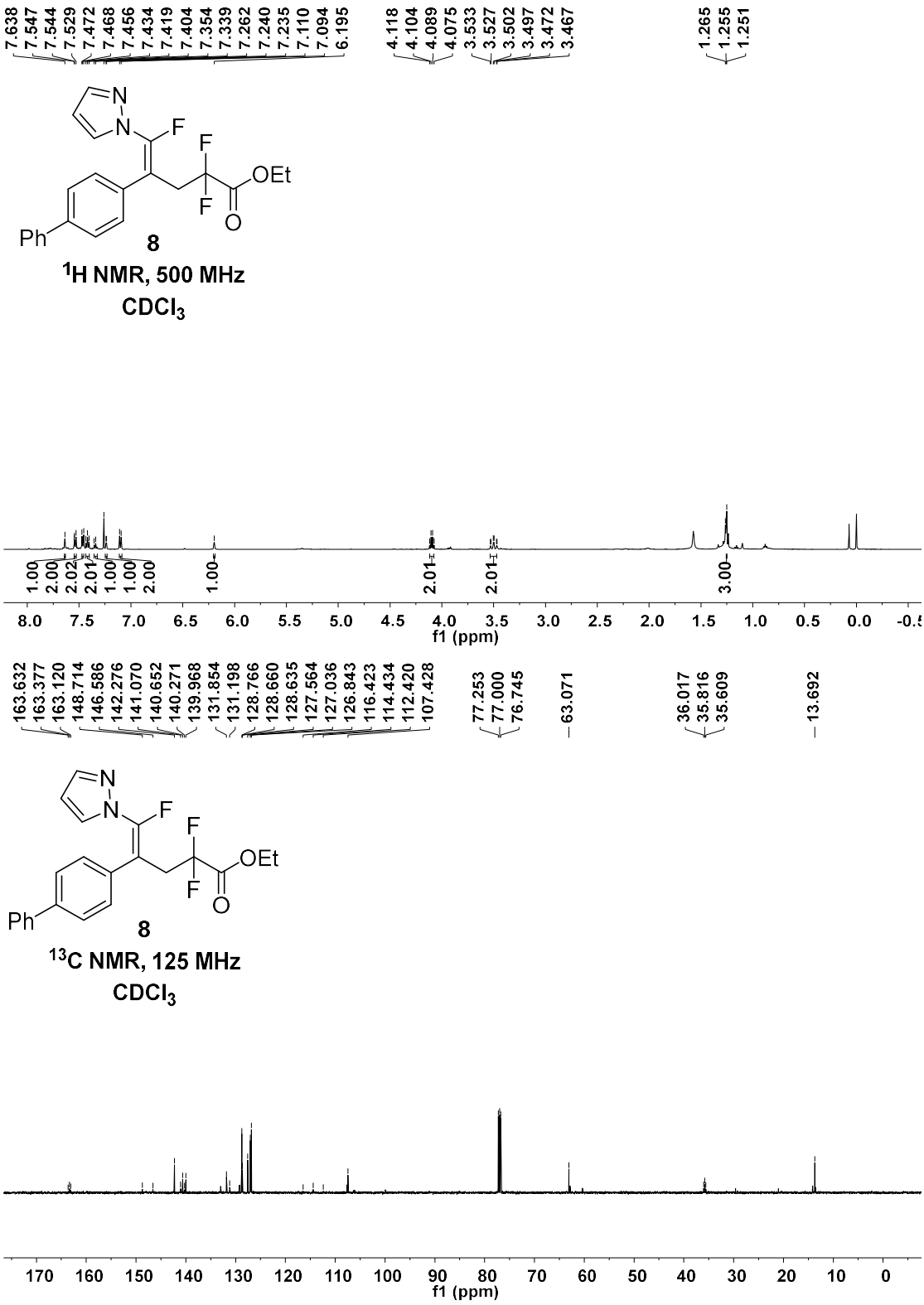
^{1}H NMR, 500 MHz

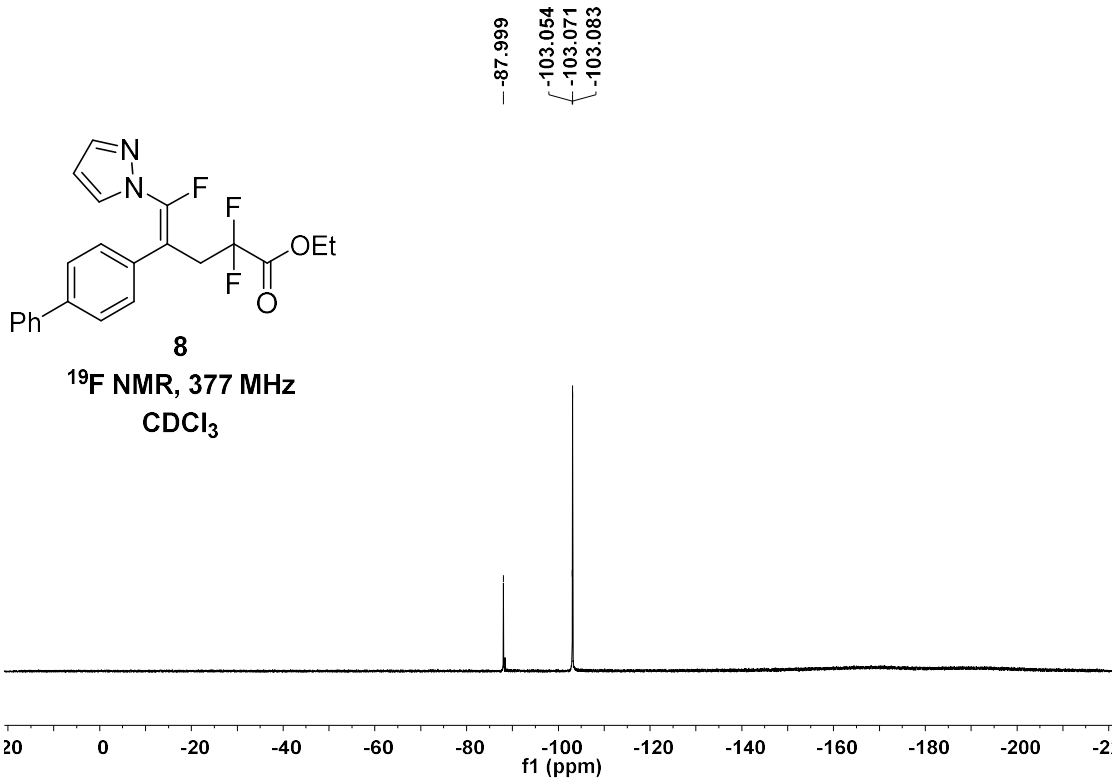
$CDCl_3$




163.707
163.452
163.192
155.505
154.731
153.783
152.314
140.959
140.348
135.366
135.336
134.169
131.426
131.409
129.866
129.464
129.439
129.345
129.302
129.024
128.800
128.581
127.794
127.581
127.522
127.016
126.894
126.861
116.441
114.426
112.438
77.254
77.000
76.747
62.954
29.691
13.691
Ph
S
F
F
O
F
O
Ph
7
13C NMR, 125 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)


-84.092
-84.104
-84.117
-102.982
-102.997
-103.008
-103.017
Ph
S
F
F
O
F
O
Ph
7
19F NMR, 377 MHz
CDCl3
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)


7.638
7.547
7.544
7.529
7.472
7.468
7.456
7.434
7.419
7.404
7.354
7.339
7.262
7.240
7.235
7.110
7.094
6.195
4.118
4.104
4.089
4.075
3.533
3.527
3.502
3.497
3.472
3.467
1.265
1.255
1.251
N
N
F
F
F
OEt
O
Ph
8
1H NMR, 500 MHz
CDCl3
1.00
2.00
2.02
2.01
1.00
1.00
2.00
1.00
2.01
2.01
3.00
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)
163.632
163.377
163.120
148.714
146.586
142.276
141.070
140.652
140.271
139.968
131.854
131.198
128.766
128.660
128.635
127.564
127.036
126.843
116.423
114.434
112.420
107.428
77.253
77.000
76.745
63.071
36.017
35.816
35.609
13.692
N
N
F
F
F
OEt
O
Ph
8
13C NMR, 125 MHz
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



8

^{19}F NMR, 377 MHz

$CDCl_3$