Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Metal-Free Reductive Acyldifluoroalkylation of Alkenes through Cooperative NHC and Organophotocatalysis

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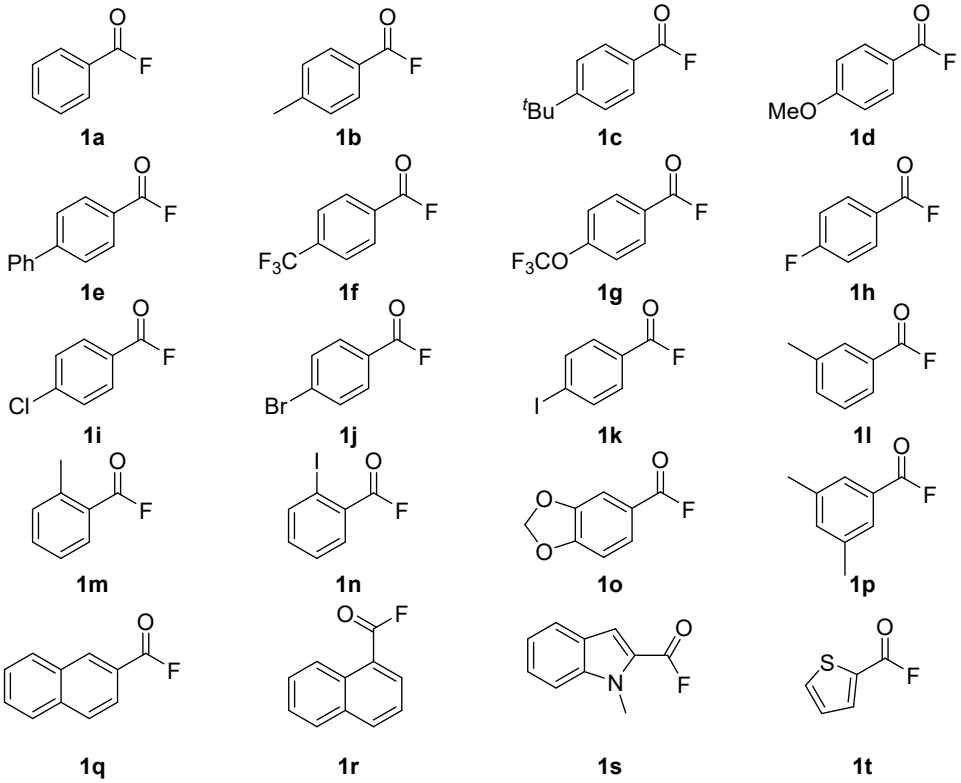
Table of Contents

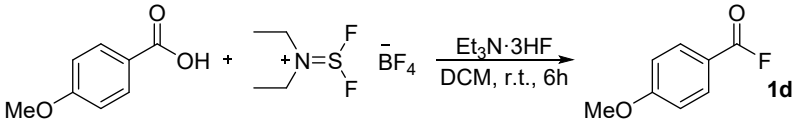
General information

All reactions at elevated temperatures were performed under heating in an oil bath. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 ^{o}C petroleum ether and analytical grade EA (without further purification). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm), and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and *J*, coupling constant in Hz. The HRMS spectrum was measured by micromass QTOF2 Quadrupole/Time of Flight Tandemmass spectrometer with electron spray ionization. The Blue LED strips were purchased from https://item.taobao.com/item.htm?spm=a1z0d.6639537/tb.1997196601.3.7d5a7484Ikjj4H&id=607819098151.

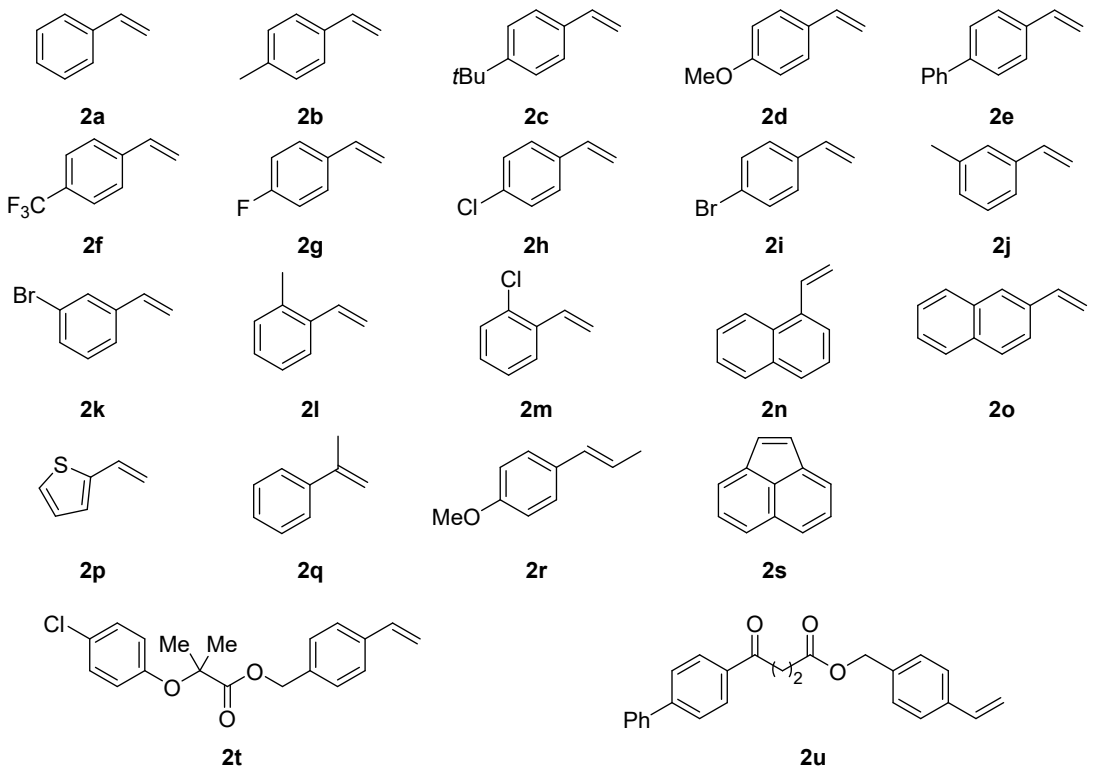
Synthesis of substrates



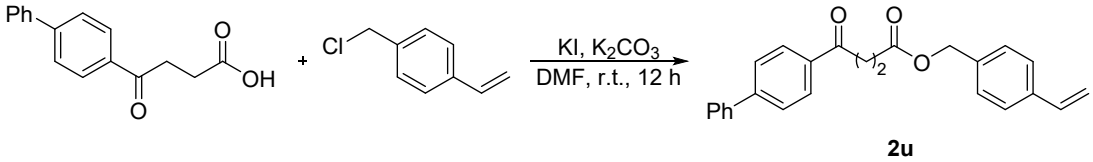
1b-**1t** were prepared according to the literature procedure[1] (Taking **1d** as an example):



A Schlenk flask filled with N_2 was added diethylaminodifluorosulfinium tetrafluoroborate (1.0 equiv) and *p*-methoxybenzoic acid in dichloromethane (5 mL/mmol substrate) at room temperature. The triethylamine trihydrofluoride (1.0 equiv) was added and the resulting mixture was stirred for 6 h at room temperature. The reaction was quenched with a 5% $NaHCO_3$ aqueous solution, stirred until the effervescence ceased. The resulting mixture was extracted three times with DCM. The organic phases were combined, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (PE:EA = 40:1), affording the product aroyl fluorides **1d** (60% yield). HRMS spectra of aroyl fluorides could not be obtained using standard ionization methods due to the lack of stability of these compounds under the experimental conditions.



2t and **2u** were prepared according to the literature procedure[2] (Taking **2u** as an example):



In a dry round-bottomed flask, the 3-(4-biphenyl carbonyl) propionic acid (1.27 g, 5.0 mmol), K_2CO_3 (1.04 g, 7.5 mmol) and KI (1.25 g, 7.5 mmol) were placed and DMF (25 mL) was added. Then, 4-chloromethyl styrene (839 mg, 5.5 mmol) was added and stirred overnight. Upon completion of the reaction, EtOAc (50 mL) and H_2O (50 mL) were added. The reaction mixture was extracted and washed three times with H_2O (50 mL). The organic layer was washed with a saturated NaCl solution (100 mL). Then, it was dried with Na_2SO_4, condensed under reduced pressure. The residue was purified by column chromatography to give the target product **2u** (82% yield).

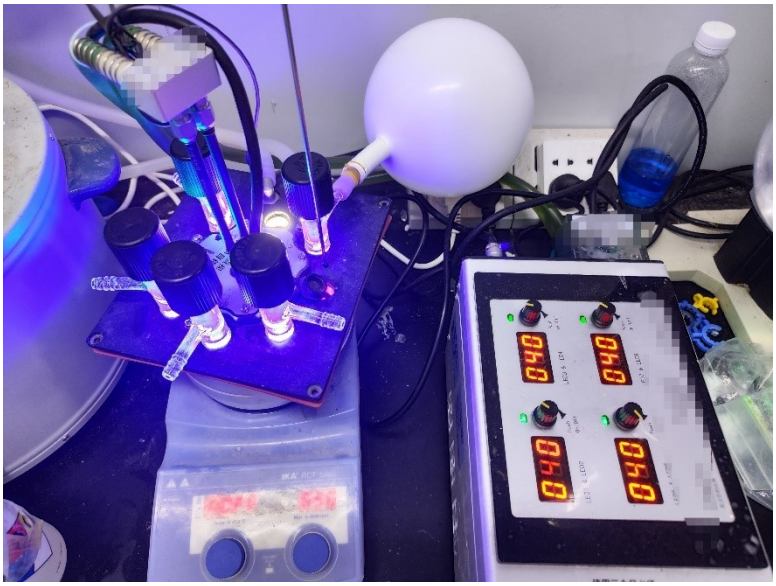
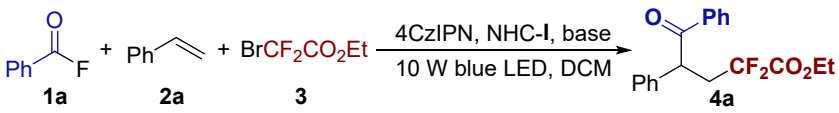


Figure S1. The set-up for the reaction (photographed by X.F. Li)

Optimization of the reaction conditions

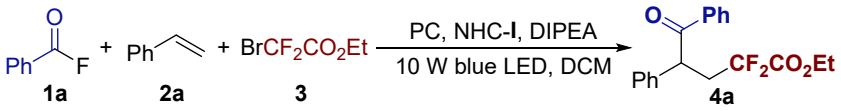
Table S1. Screening of the additive[a]



entry	base	yield [b] (%)
1	no	N.R.
2	DIPEA	27
3	DABCO	20
4	TEA	N.R.
5	DIPA	11
6	TEEDA	10
7	TMG	N.R.
8	PMDETA	8

[a]**1a** (0.40 mmol), **2a** (0.20 mmol), **3** (0.40 mmol),4CzIPN (0.005 mmol), additive (0.40 mmol), NHC-**I** (0.04 mmol) and DCM (2 mL) [b]Yields were determined by ^{19}F NMR using $PhCF_3$ as the internal standard. DIPEA = *N,N*-diisopropylethylamine, DABCO = 1,4-diazabicyclo[2.2.2]octane, TEA = triethylamine, DIPA = diisopropylamine, TEEDA = *N,N,N,N*-tetraethylethylenediamine, TMG = 1,1,3,3-Tetramethylguanidine, PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.

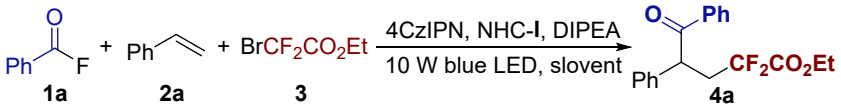
Table S2. Screening of the photocatalyst[a]



entry	PC	yield [b] (%)
1	no	N.R.
2	4CzIPN	27
3	$Ru(bpy)_3(PF_6)_2$	N.R.
4	$Ir(ppy)_3$	N.R.
5	TXO	N.R.
6	$[Ir(dtbbpy)(ppy)_2]PF_6$	Trace
7	$[Acr\text{-}Mes]^+(ClO_4)^-$	N.R.
8	EosinY	Trace

[a]**1a** (0.40 mmol), **2a** (0.20 mmol), **3** (0.40 mmol), PC (0.005 mmol), DIPEA (0.40 mmol), NHC-**I** (0.04 mmol), and DCM (2 mL) [b]Yields were determined by ^{19}F NMR using $PhCF_3$ as the internal standard.

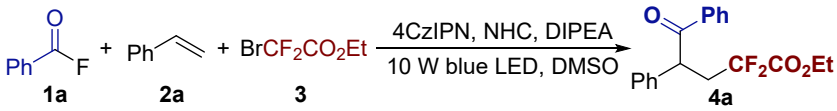
Table S3. Screening of the solvent[a]



entry	solvent	yield [b] (%)
1	DCM	27
2	DCE	25
3	THF	N.R.
4	CH_3CN	N.R.
5	toluene	N.R.
6	CH_3OH	N.R.
7	DMSO	36
8	DMF	30
9	DMAC	31
10	NMP	23
11	EA	N.R.
12	acetone	N.R.
13	^{t}BuOH	9
14	IPA	10

[a]**1a** (0.40 mmol), **2a** (0.20 mmol), **3** (0.40 mmol), 4CzIPN (0.005 mmol), DIPEA (0.40 mmol), ,NHC-**I** (0.04 mmol) and solvent (2 mL) [b]Yields were determined by ^{19}F NMR using $PhCF_3$ as the internal standard

Table S4. Screening of the NHC catalyst[a]



entry	NHC	yield [b] (%)
1	no	N.R.
2	NHC-**I**	36
3	NHC-**II**	28
4	NHC-**III**	30
5	NHC-**IV**	45
6	NHC-**V**	N.R.
7	NHC-**VI**	N.R.

[a]**1a** (0.40 mmol), **2a** (0.20 mmol), **3** (0.40 mmol), 4CzIPN (0.005 mmol), DIPEA (0.40 mmol), NHC (0.04 mmol) and DMSO (2 mL) [b]Yields were determined by ^{19}F NMR using $PhCF_3$ as the internal standard

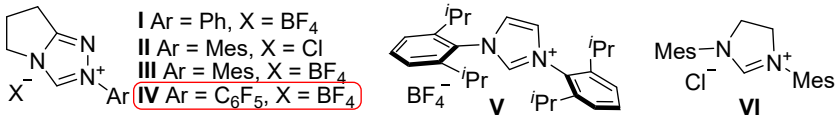
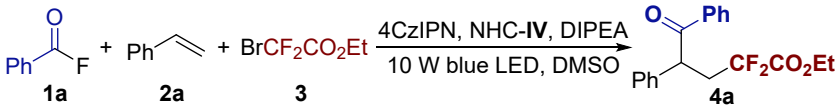


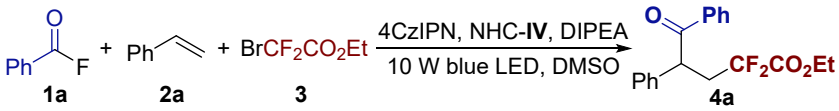
Table S5. Screening of the feed ratio



entry	1a: 2a: 3	yield [b] (%)
1	2:1:2	45
2	2:2:1	54
3	1:2:2	30
4	3:2:1	60
5	2:3:1	54
6	3:3:1	76

[a]Reaction performed on 0.2 mmol scale, 4CzIPN (0.005 mmol), DIPEA (0.40 mmol), NHC-**IV** (0.04 mmol) and DMSO (2 mL). [b]Yields were determined by ^{19}F NMR using $PhCF_3$ as the internal standard.

Table S6. Screening of the light source[a]

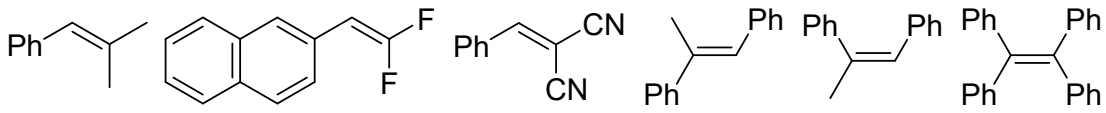


entry	LEDs	yield [b] (%)
1	no	N.R.
2	455nm,10w	76
3	white, 10w	N.R.
4	395nm, 10w	N.R.
5	520nm, 10w	N.R.
6	455nm, 30w	40
7	455nm, 8w	77
8	455nm, 6w	80
9	455nm, 4w	84 (79)
10	455nm, 2w	40
11[c]	455nm, 4w	30

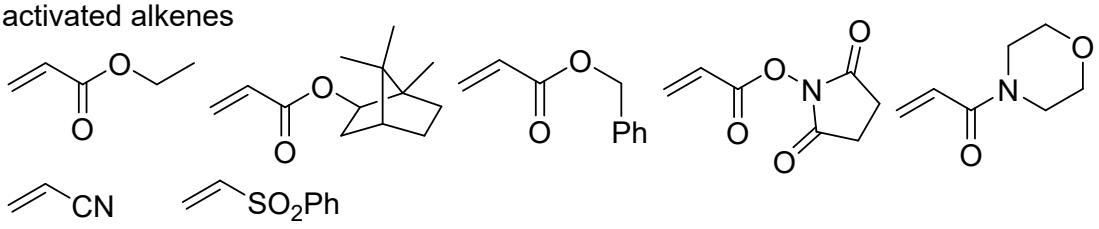
[a]**1a** (0.60 mmol), **2a** (0.60 mmol), **3** (0.20 mmol), 4CzIPN (0.005 mmol), DIPEA (0.40 mmol), NHC-**IV** (0.04 mmol) and solvent (2 mL). [b]Yields were determined by ^{19}F NMR using $PhCF_3$ as the internal standard. [c]no N_2.

Table S7. Unsuccessful substrates for the alkenes

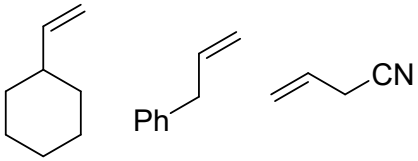
tri- and tetrasubstituted styrene derivatives



activated alkenes



alkyl alkenes



General procedures for the synthesis of products

Under an N_2 atmosphere, a 25 mL sealed tube equipped with a stir bar was charged

with **1** (0.6 mmol), **2** (0.6 mmol), **3** (0.2 mmol, 40.6 mg), NHC-**IV** (0.04 mmol, 14.5 mg), DIPEA (0.4 mmol, 51.7 mg), 4CzIPN (0.005 mmol, 4.0 mg), and DMSO (2 mL). The reaction mixture was stirred at room temperature under 4 W blue light. After 12 hours, the reaction mixture was quenched with water, extracted with ethyl acetate three times, combined with the organic layer, washed with brine three times, collected the first washed water layer, and extracted with ethyl acetate. The combined organic layer was then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Finally, the product was purified by silica gel column chromatography (PE/EA = 40:1 to 10:1).

Procedure for gram-scale reaction

Under an N_2 atmosphere, a 100 mL sealed tube equipped with a stir bar was charged with **1a** (14.4 mmol, 1.79 g), **2a** (14.4 mmol, 1.5 g), **3** (4.8 mmol, 974.4 mg), NHC-**IV** (0.96 mmol, 348 mg), DIPEA (9.6 mmol, 1.24 g), 4CzIPN (0.12 mmol, 96 mg), and DMSO (48 mL). The reaction mixture was stirred at room temperature under 4 W blue light. After 12 hours, the reaction mixture was quenched with water, extracted with ethyl acetate three times, combined with the organic layer, washed with brine three times, collected the first washed water layer, and extracted with ethyl acetate. The combined organic layer was then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Finally, the product **4a** was purified by silica gel column chromatography (PE/EA = 40:1).

Procedure for radical clock experiment

In an N_2 atmosphere, **1a** (0.60 mmol, 74.4 mg), **2a** (0.6 mmol, 62.5 mg), **3** (0.2 mmol, 40.6 mg), NHC-**IV** (0.04 mmol, 14.5 mg), DIPEA (0.4 mmol, 51.7 mg), 4CzIPN (0.005 mmol, 4.0 mg), and DMSO (2 mL) were combined with α-cyclopropyl styrene **7** (0.2 mmol, 29 mg). The reaction mixture was stirred at room temperature under 4W blue light. After 12 hours, the reaction mixture was quenched with water, extracted with ethyl acetate three times, combined with the organic layer, washed with brine three times, collected the first washed water layer, and extracted with ethyl acetate. The

combined organic layer was then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. A small number of samples were taken for HRMS analysis. Finally, the residue was purified by silica gel column chromatography to obtain **4a** (20.6 mg, 31% yield) and 8 (12.77 mg, 24% yield).

Procedure for searching possible intermediates using acylazonium ions

In the N_2 atmosphere, compound **9** (0.6 mmol, 210.0 mg), **2a** (0.6 mmol, 62.5 mg), **3** (0.2 mmol, 40.6 mg), DIPEA (0.4 mmol, 51.7 mg), 4CzIPN (0.005 mmol, 4.0 mg), and DMSO (2 mL) were combined. The reaction mixture was stirred at room temperature under 4W blue light. After 12 hours, the reaction mixture was quenched with water, extracted three times with ethyl acetate. The combined organic layers were washed three times with brine, and the first washed water layer was collected. The organic layer was further extracted with ethyl acetate and combined with the previous organic layer. Anhydrous Na_2SO_4 was added for drying, followed by filtration and concentration under reduced pressure. Finally, the product was purified by silica gel column chromatography to afford **4a** (45.8 mg, 69% yield).

Procedure for light on and off experiment

In the N_2 atmosphere, **1a** (0.60 mmol, 74.4 mg), **2a** (0.6 mmol, 62.5 mg), **3** (0.2 mmol, 40.6 mg), NHC-**IV** (0.04 mmol, 14.5 mg), DIPEA (0.4 mmol, 51.7 mg), 4CzIPN (0.005 mmol, 4.0 mg), and DMSO (2 mL) were combined. $PhCF_3$ (0.2 mmol, 29.2 mg) was added as the internal standard, and samples were taken every two hours. Simultaneously, the lamp was switched on and off, and each time 150 μL of reaction liquid was taken and dissolved in $CDCl_3$ (0.5 mL). The product was then characterized by ^{19}F NMR, and the yield of product at different times was calculated. The plotted yield transformation curve over time showed no significant change in reaction yield during the period when the light was turned off, indicating that the reaction is not a chain reaction process.

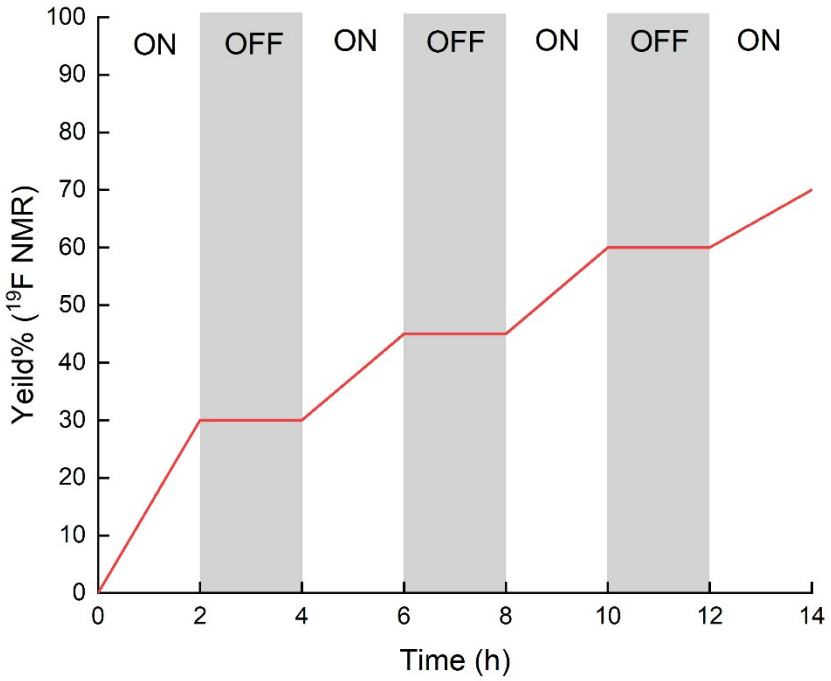
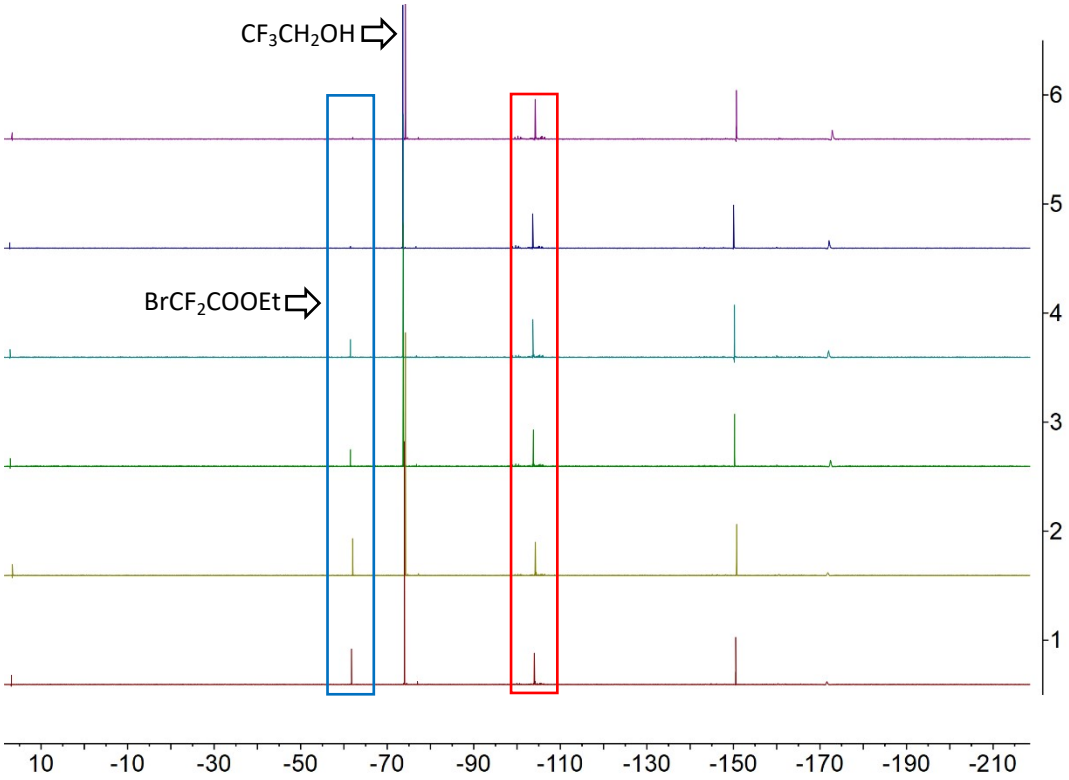


Figure S2. Time profile of the transformation with the light ON/OFF over time



Procedure for fluorescence quenching experiment

4CzIPN (0.01 mmol, 7.89 mg) was dissolved in DCE (1.0 mL), and then 100 μL of the

solution was further dissolved in DCE (900 μL). Subsequently, 250 μL of the solution was dissolved in DCE (4.750 mL), and the resulting solution was stored away from light. DIPEA (0.01 mmol, 17.28 μL) was dissolved in DCE (1.0 mL), and then 50 μL of the solution was further dissolved in DCE (950 μL) and stored away from light. $BrCF_2COOEt$ (0.01 mmol, 12.82 μL) was dissolved in DCE (1.0 mL), and then 50 μL of the solution was further dissolved in DCE (950 μL) and stored away from light.

A cuvette was filled with 4CzIPN solution (2.0 mL) to measure the fluorescence absorption and record the data. Then, DIPEA or $BrCF_2COOEt$ (20 μL) solution was added successively, and the data were recorded for each addition.

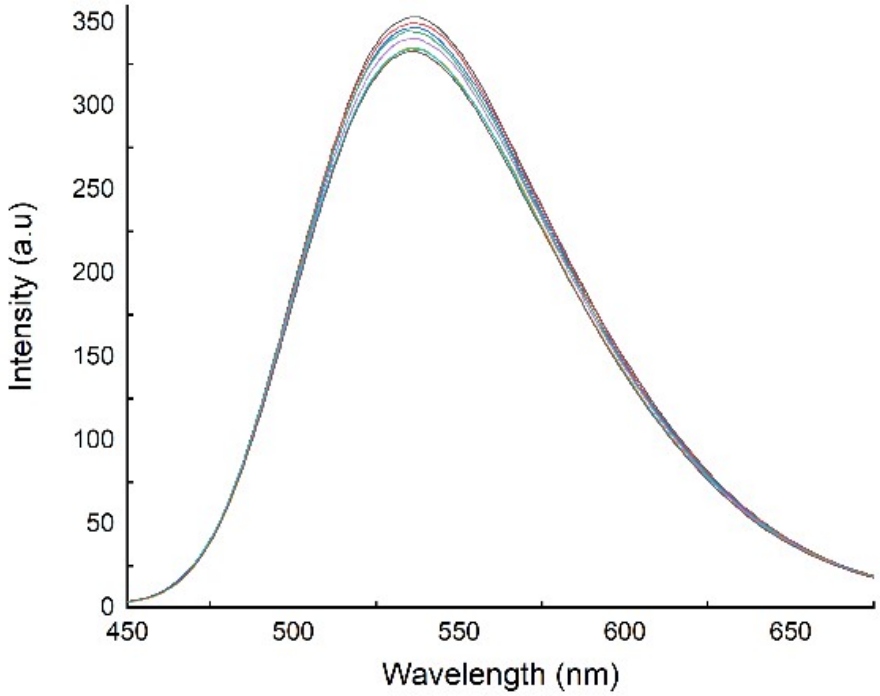


Figure S3. Fluorescence emission spectra of 4CzIPN in DCE with different concentration of 3

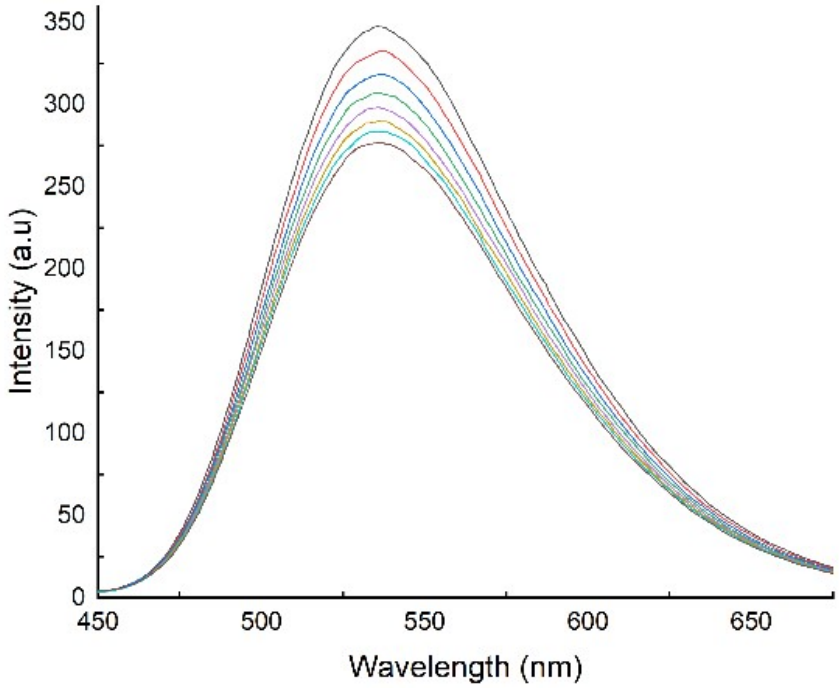


Figure S4. Fluorescence emission spectra of 4CzIPN in DCE with different concentration of DIPEA

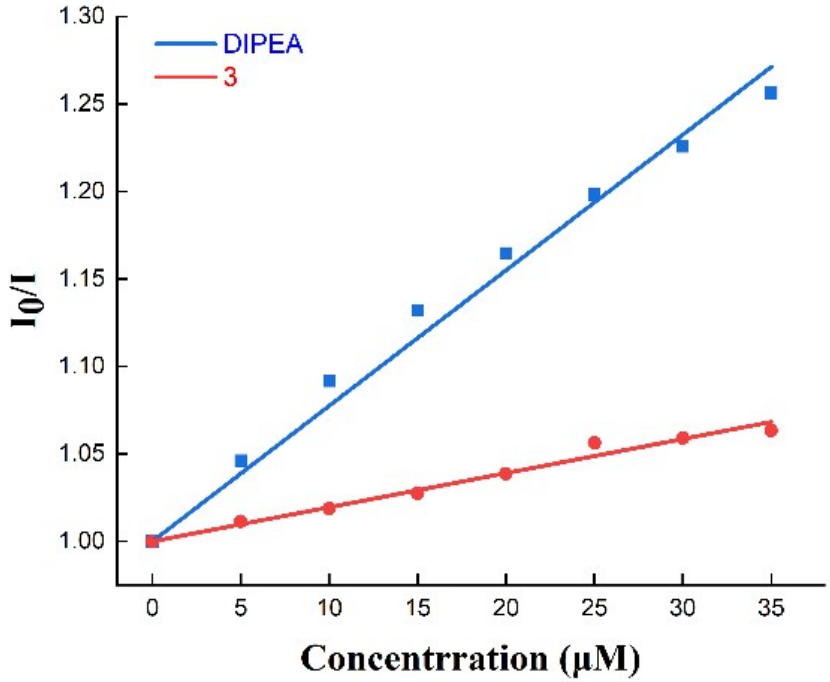
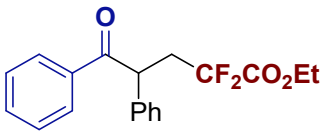
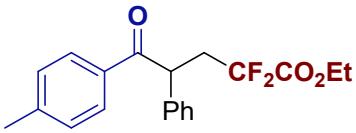


Figure S5. Stern-Volmer fluorescence quenching studies including substrate 3 and substrate DIPEA.

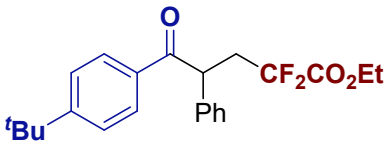
Compound characterization



ethyl 2,2-difluoro-5-oxo-4,5-diphenylpentanoate (4a). The product (52.5 mg, 79%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). This compound is known.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 - 7.86 (m, 2H), 7.41 - 7.37 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 - 7.18 (m, 4H), 7.14 - 7.09 (m, 1H), 4.88 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.07 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.95 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.19 (tdd, *J* = 16.7, 14.9, 8.1 Hz, 1H), 2.46 (tdd, *J* = 16.5, 14.9, 5.0 Hz, 1H), 1.12 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, CDCl3) δ -104.3 (d, *J* = 34.2 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.4, 163.9 (t, *J* = 32.6 Hz), 137.9, 135.9, 133.3, 129.3, 128.9, 128.7, 128.3, 127.8, 115.4 (t, *J* = 250.6 Hz), 63.0, 47.0 (t, *J* = 4.0 Hz), 38.3 (t, *J* = 23.4 Hz), 13.8.

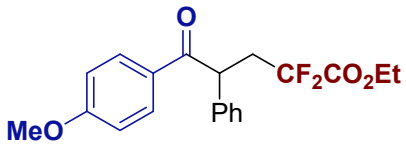


ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(p-tolyl)pentanoate (4b). The product (45 mg, 65%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). This compound is known.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.31 - 7.28 (m, 4H), 7.22 - 7.18 (m, 3H), 4.94 (dd, *J* = 7.9, 5.1 Hz, 1H), 4.16 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.04 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.26 (tdd, *J* = 16.7, 15.0, 7.9 Hz, 1H), 2.54 (tdd, *J* = 16.4, 15.0, 5.1 Hz, 1H), 2.35 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 35.9 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 163.9 (t, *J* = 32.6 Hz), 144.2, 138.1, 133.3, 129.4, 129.3, 129.1, 128.3, 127.7, 115.5 (t, *J* = 250.5 Hz), 63.0, 46.8 (t, *J* = 3.9 Hz), 38.3 (t, *J* = 23.4 Hz), 21.7, 13.8.

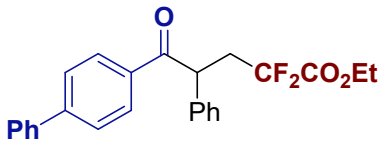


ethyl 5-(4-(tert-butyl)phenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate (4c). The product (40.4 mg, 52%) as a pale yellow oily liquid was purified with silica gel

chromatography (PE/EA = 30:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.33 - 7.28 (m, 4H), 7.23 - 7.20 (m, 1H), 4.97 (d, *J* = 5.6 Hz, 1H), 4.17 (dq, *J* = 10.5, 7.2 Hz, 1H), 4.05 (dq, *J* = 10.6, 7.2 Hz, 1H), 3.27 (qd, *J* = 16.1, 7.9 Hz, 1H), 2.54 (qd, *J* = 16.2, 5.0 Hz, 1H), 1.29 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 43.8 Hz, 2F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.9, 163.9 (t, *J* = 32.5 Hz), 157.1, 138.2, 133.2, 129.3, 128.9, 128.4, 127.7, 125.7, 115.4 (t, *J* = 250.6 Hz), 63.0, 46.8 (t, *J* = 3.9 Hz), 38.4 (t, *J* = 23.3 Hz), 35.2, 31.1, 13.8. **HRMS**: calcd for $C_{23}H_{24}F_2O_3^+$ $(M+H)^+$: 389.1923; found 389.1932.

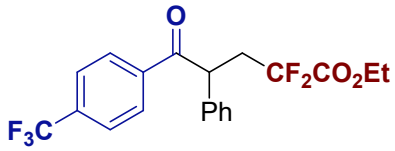


ethyl 2,2-difluoro-5-(4-methoxyphenyl)-5-oxo-4-phenylpentanoate (4d). The product (39.1 mg, 54%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 20:1). This compound is known.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.29 - 7.28 (m, 4H), 7.24 - 7.19 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.90 (dd, *J* = 7.9, 5.1 Hz, 1H), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.04 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.81 (s, 3H), 3.25 (tdd, *J* = 16.6, 14.9, 7.9 Hz, 1H), 2.53 (tdd, *J* = 16.3, 14.9, 5.1 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 24.0 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.8, 163.9 (t, *J* = 32.6 Hz), 163.7, 138.4, 131.3, 129.3, 128.8, 128.3, 127.7, 115.5 (t, *J* = 250.6 Hz), 113.9, 63.0, 55.6, 46.6 (t, *J* = 3.9 Hz), 38.3 (t, *J* = 23.3 Hz), 13.9.

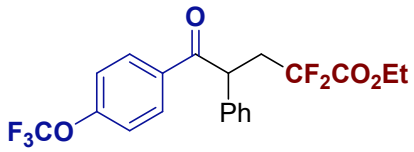


ethyl 5-([1,1'-biphenyl]-4-yl)-2,2-difluoro-5-oxo-4-phenylpentanoate (4e). The product (60.4 mg, 74%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36 - 7.28 (m, 5H), 7.21 (d, *J* = 7.5 Hz, 1H), 4.98 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.15 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.04 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.29 (qd, *J* = 16.2, 8.0 Hz, 1H), 2.55 (qd, *J* = 16.1, 5.0 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.3 (d, *J* = 36.7 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.9, 163.9 (t, *J* = 32.5 Hz),

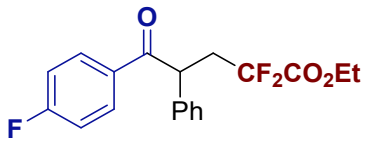
146.0, 139.8, 138.0, 134.5, 131.3, 129.5, 129.4, 129.0, 128.4, 127.8, 127.4, 127.3, 115.4 (t, J = 250.6 Hz), 63.0, 47.0 (t, J = 3.9 Hz), 38.3 (t, J = 23.4 Hz), 13.8. **HRMS**: calcd for $C_{25}H_{23}F_2O_3^+$ $(M+H)^+$: 409.1610; found 409.1618.



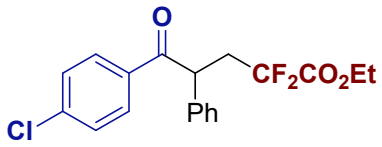
ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(4-(trifluoromethyl)phenyl)pentanoate (4f). The product (44 mg, 55%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). This compound is known.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.35 - 7.28 (m, 5H), 4.96 (dd, J = 8.2, 4.7 Hz, 1H), 4.21 (dq, J = 10.7, 7.1 Hz, 1H), 4.12 (dq, J = 10.7, 7.1 Hz, 1H), 3.32 (ddt, J = 25.1, 16.9, 8.2 Hz, 1H), 2.56 (qd, J = 15.5, 4.7 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.2 (s, 3F), -104.5 (d, J = 50.4 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 163.9 (t, J = 32.5 Hz), 138.7, 137.2, 134.5 (q, J = 32.7 Hz), 129.6, 129.2, 128.3, 128.1, 125.8 (q, J = 3.8 Hz), 123.6 (q, J = 272.7 Hz), 115.2 (t, J = 250.9 Hz), 63.2, 47.5 (t, J = 3.9 Hz), 38.2 (t, J = 23.4 Hz), 13.9.



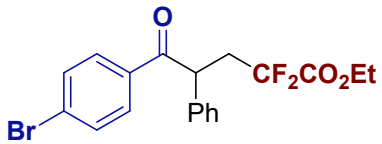
ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(4-(trifluoromethoxy)phenyl)pentanoate (4g). The product (44.9 mg, 54%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.8 Hz, 2H), 7.23 - 7.18 (m, 4H), 7.17 - 7.11 (m, 3H), 4.83 (dd, J = 8.2, 4.8 Hz, 1H), 4.09 (dq, J = 10.8, 7.1 Hz, 1H), 3.99 (dq, J = 10.8, 7.2 Hz, 1H), 3.19 (ddt, J = 24.9, 16.7, 8.1 Hz, 1H), 2.44 (ddd, J = 31.3, 16.6, 4.8 Hz, 1H), 1.15 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.6 (s, 3F), -104.5 (d, J = 38.7 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.9, 163.9 (t, J = 32.4 Hz), 152.7 (q, J = 1.8 Hz), 137.5, 134.1, 131.0, 129.5, 128.3, 128.0, 120.4, 120.3 (q, J = 259.0 Hz), 115.3 (t, J = 250.7 Hz), 63.1, 47.2 (t, J = 4.0 Hz), 38.3 (t, J = 23.4 Hz), 13.8. **HRMS**: calcd for $C_{20}H_{18}F_5O_4^+$ $(M+H)^+$: 417.1120; found 417.1126.



ethyl 2,2-difluoro-5-(4-fluorophenyl)-5-oxo-4-phenylpentanoate (4h). The product (40.6 mg, 58%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (ddd, *J* = 8.9, 5.3, 1.4 Hz, 2H), 7.36 - 7.31 (m, 4H), 7.29 - 7.26 (m, 1H), 7.10 (td, *J* = 8.6, 1.4 Hz, 2H), 4.95 (dd, *J* = 8.1, 4.9 Hz, 1H), 4.22 (dtd, *J* = 14.4, 7.8, 7.2, 4.2 Hz, 1H), 4.12 (dtd, *J* = 13.7, 7.4, 3.9 Hz, 1H), 3.32 (qd, *J* = 16.1, 8.0 Hz, 1H), 2.57 (qd, *J* = 16.0, 4.9 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (s, 1F), -104.5 (s, 1F), -104.6 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.9, 165.8 (d, *J* = 255.5 Hz), 163.9 (t, *J* = 32.5 Hz), 137.8, 132.3 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 9.4 Hz), 129.4, 128.3, 127.9, 115.9 (d, *J* = 21.9 Hz), 114.4 (d, *J* = 250.7 Hz), 63.1, 47.0 (t, *J* = 3.9 Hz), 38.3 (t, *J* = 23.4 Hz), 13.9. **HRMS**: calcd for $C_{19}H_{18}F_3O_3^+$ $(M+H)^+$: 351.1203; found 351.1200.

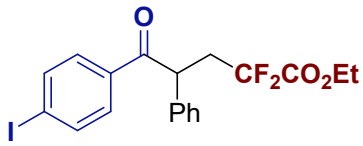


ethyl 5-(4-chlorophenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate (4i). The product (46.9 mg, 64%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). This compound is known.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.37 - 7.28 (m, 5H), 4.93 (dd, *J* = 8.1, 4.9 Hz, 1H), 4.21 (dq, *J* = 10.9, 7.2 Hz, 1H), 4.11 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.31 (tdd, *J* = 16.9, 14.9, 8.0 Hz, 1H), 2.56 (qd, *J* = 16.2, 15.8, 4.9 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 36.3 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.2, 163.8 (t, *J* = 32.5 Hz), 139.8, 137.6, 134.2, 130.3, 129.4, 129.1, 128.3, 128.0, 115.3 (t, *J* = 250.6 Hz), 63.1, 47.1 (t, *J* = 3.9 Hz), 38.2 (t, *J* = 23.4 Hz), 13.9.

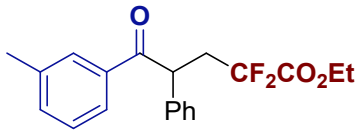


ethyl 5-(4-bromophenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate (4j). The product (56.6 mg, 69%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.56 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.36 - 7.27 (m, 5H), 4.93 (dd, *J* = 8.1, 4.9 Hz, 1H), 4.21 (dq,

J = 10.5, 7.1 Hz, 1H), 4.11 (dq, J = 10.5, 7.1 Hz, 1H), 3.31 (qd, J = 15.8, 8.0 Hz, 1H), 2.56 (qd, J = 16.0, 4.8 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, J = 39.4 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.4, 163.8 (t, J = 32.5 Hz), 137.5, 134.6, 132.1, 130.4, 129.4, 128.6, 128.3, 128.0, 115.3 (t, J = 250.7 Hz), 63.1, 47.1 (t, J = 3.9 Hz), 38.1 (t, J = 23.4 Hz), 13.9. **HRMS**: calcd for $C_{19}H_{18}BrF_2O_3^+$ $(M+H)^+$: 411.0402; found 411.0402.

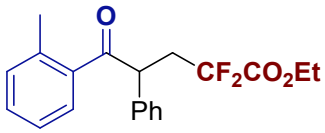


ethyl 2,2-difluoro-5-(4-iodophenyl)-5-oxo-4-phenylpentanoate (4k). The product (60.5 mg, 66%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.35 - 7.28 (m, 5H), 4.91 (dd, J = 8.1, 4.9 Hz, 1H), 4.21 (dq, J = 10.7, 7.2 Hz, 1H), 4.11 (dq, J = 10.7, 7.2 Hz, 1H), 3.30 (ddt, J = 24.9, 16.8, 8.1 Hz, 1H), 2.56 (qd, J = 16.1, 4.9 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, J = 39.4 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 163.8 (t, J = 32.5 Hz), 138.1, 137.5, 135.1, 130.3, 129.5, 128.3, 128.0, 115.3 (t, J = 250.7 Hz), 101.5, 63.1, 47.0 (t, J = 4.0 Hz), 38.1 (t, J = 23.3 Hz), 13.9. **HRMS**: calcd for $C_{19}H_{18}F_2IO_3^+$ $(M+H)^+$: 459.0264; found 459.0266.

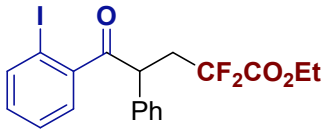


ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(m-tolyl)pentanoate (4l). The product (45.7 mg, 66%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). This compound is known.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 - 7.73 (m, 2H), 7.30 - 7.28 (m, 6H), 7.22 - 7.18 (m, 1H), 4.95 (dd, J = 8.0, 5.0 Hz, 1H), 4.16 (dq, J = 10.8, 7.2 Hz, 1H), 4.04 (dq, J = 10.8, 7.1 Hz, 1H), 3.26 (tdd, J = 16.9, 15.0, 7.9 Hz, 1H), 2.53 (tdd, J = 16.4, 14.9, 5.0 Hz, 1H), 2.34 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, J = 47.5 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 163.9 (t, J = 32.5 Hz), 138.5, 138.0, 135.9, 134.1, 129.4, 129.3, 128.6, 128.4,

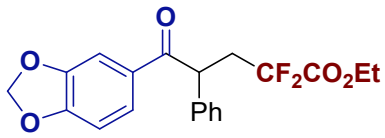
127.7, 126.2, 115.4 (t, J = 250.5 Hz), 63.0, 46.9 (t, J = 3.9 Hz), 38.3 (t, J = 23.4 Hz), 21.4, 13.8.



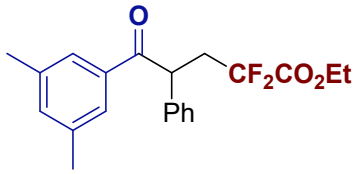
ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(o-tolyl)pentanoate (4m). The product (39.4 mg, 57%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). This compound is known.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 7.7, 1.4 Hz, 1H), 7.21 - 7.16 (m, 3H), 7.14 - 7.10 (m, 4H), 7.04 (d, J = 7.6 Hz, 1H), 4.71 (dd, J = 8.3, 4.7 Hz, 1H), 4.11 (dq, J = 10.8, 7.2 Hz, 1H), 4.03 (dq, J = 10.8, 7.1 Hz, 1H), 3.25 (dtd, J = 17.2, 15.3, 8.3 Hz, 1H), 2.44 (tdd, J = 16.7, 14.9, 4.8 Hz, 1H), 2.16 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.5 (d, J = 33.4 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.0, 164.0 (t, J = 32.4 Hz), 138.5, 137.7, 137.1, 131.7, 131.3, 129.2, 128.5, 128.1, 127.8, 125.6, 115.5 (t, J = 250.8 Hz), 63.1, 49.9 (t, J = 3.8 Hz), 37.5 (t, J = 23.3 Hz), 20.7, 13.9.



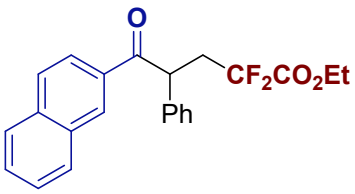
ethyl 2,2-difluoro-5-(2-iodophenyl)-5-oxo-4-phenylpentanoate (4n). The product (50.4 mg, 55%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.9, 1.1 Hz, 1H), 7.29 (tdd, J = 7.2, 5.5, 1.6 Hz, 5H), 7.22 - 7.19 (m, 2H), 7.07 (ddd, J = 7.9, 7.1, 2.0 Hz, 1H), 4.77 (t, J = 6.6 Hz, 1H), 4.16 (ddd, J = 11.9, 7.7, 4.1 Hz, 1H), 4.09 (ddd, 1H), 3.31 (dtd, J = 17.1, 15.0, 6.7 Hz, 1H), 2.69 (tdd, J = 16.8, 15.0, 6.5 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.3 (d, J = 259.0 Hz, 1F), -105.1 (d, J = 259.1 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 163.9 (t, J = 32.4 Hz), 143.2, 140.8, 135.5, 131.9, 129.2, 129.1, 128.5, 128.1, 127.8, 115.5 (t, J = 250.8 Hz), 92.5, 63.1, 50.5 (t, J = 4.0 Hz), 36.8 (t, J = 23.6 Hz), 13.9. **HRMS**: calcd for $C_{19}H_{18}F_2IO_3^+$ $(M+H)^+$: 459.0264; found 459.0261.



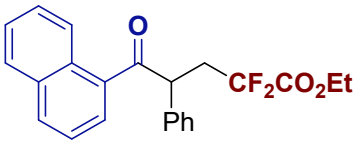
ethyl 5-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoro-5-oxo-4-phenylpentanoate (4o). The product (39.9 mg, 53%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.46 (s, 1H), 7.33 - 7.30 (m, 4H), 7.27 - 7.24 (m, 1H), 6.81 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.01 (s, 2H), 4.89 (dd, *J* = 8.1, 5.0 Hz, 1H), 4.20 (dq, *J* = 10.5, 7.2 Hz, 1H), 4.10 (dq, *J* = 10.5, 7.1 Hz, 1H), 3.28 (tdd, *J* = 16.4, 15.0, 8.0 Hz, 1H), 2.55 (qd, *J* = 16.1, 4.9 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 18.8 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.4, 163.9 (t, *J* = 32.5 Hz), 152.0, 148.3, 138.2, 130.6, 129.3, 128.2, 127.7, 125.3, 115.4 (t, *J* = 250.6 Hz), 108.7, 108.0, 102.0, 63.0, 46.7 (t, *J* = 4.0 Hz), 38.4 (t, *J* = 23.3 Hz), 13.9. **HRMS**: calcd for $C_{20}H_{19}F_2O_5^+$ $(M+H)^+$: 377.1196; found 377.1201.



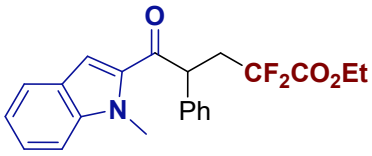
ethyl 5-(3,5-dimethylphenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate (4p). The product (45.4 mg, 63%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.7 Hz, 2H), 7.31 - 7.28 (m, 4H), 7.23 - 7.19 (m, 1H), 7.13 (s, 1H), 4.95 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.17 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.05 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.26 (ddd, *J* = 31.6, 16.6, 7.9 Hz, 1H), 2.54 (tdd, *J* = 16.4, 14.9, 5.0 Hz, 1H), 2.31 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 57.8 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.8, 163.9 (t, *J* = 32.6 Hz), 138.3, 138.1, 136.0, 135.1, 129.3, 128.4, 127.7, 126.7, 115.4 (t, *J* = 250.5 Hz), 63.0, 46.9 (t, *J* = 3.9 Hz), 38.3 (t, *J* = 23.4 Hz), 21.3, 13.8. **HRMS**: calcd for $C_{21}H_{23}F_2O_3^+$ $(M+H)^+$: 361.1610; found 361.1606.



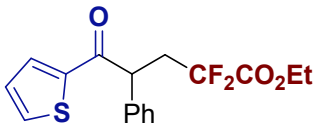
ethyl 2,2-difluoro-5-(naphthalen-2-yl)-5-oxo-4-phenylpentanoate (4q). The product (52.7 mg, 69%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). This compound is known.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.01 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.58 - 7.50 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.13 (dd, *J* = 8.0, 5.1 Hz, 1H), 4.18 (dq, *J* = 10.9, 7.2 Hz, 1H), 4.06 (dq, *J* = 10.9, 7.2 Hz, 1H), 3.35 (qd, *J* = 16.2, 7.9 Hz, 1H), 2.61 (qd, *J* = 16.2, 5.0 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.3 (d, *J* = 39.8 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.4, 163.9 (t, *J* = 32.6 Hz), 138.0, 135.7, 133.2, 132.5, 130.8, 129.8, 129.4, 128.8, 128.6, 128.4, 127.8, 127.8, 126.9, 124.5, 115.5 (t, *J* = 250.6 Hz), 63.1, 47.1 (t, *J* = 4.0 Hz), 38.3 (t, *J* = 23.4 Hz), 13.9.



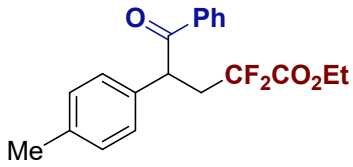
ethyl 2,2-difluoro-5-(naphthalen-1-yl)-5-oxo-4-phenylpentanoate (4r). The product (54.3 mg, 71%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.95 (dd, *J* = 7.8, 4.4 Hz, 2H), 7.84 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.56 - 7.47 (m, 3H), 7.34 - 7.28 (m, 4H), 7.23 - 7.19 (m, 1H), 5.03 (dd, *J* = 8.3, 4.7 Hz, 1H), 4.24 (dt, *J* = 10.8, 7.2 Hz, 1H), 4.14 (dt, *J* = 10.8, 7.1 Hz, 1H), 3.49 (dtd, *J* = 17.2, 15.3, 8.3 Hz, 1H), 2.65 (tdd, *J* = 16.6, 15.0, 4.7 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.3 (d, *J* = 44.0 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.7, 164.0 (t, *J* = 32.5 Hz), 137.2, 135.6, 133.9, 132.8, 130.7, 129.2, 128.4, 128.4, 128.0, 127.8, 127.5, 126.5, 125.6, 124.3, 115.5 (t, *J* = 250.7 Hz), 63.1, 50.4 (t, *J* = 3.8 Hz), 37.8 (t, *J* = 23.3 Hz), 13.9. **HRMS**: calcd for $C_{23}H_{21}F_2O_3^+$ $(M+H)^+$: 383.1454; found 383.1459.



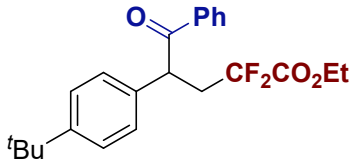
ethyl 2,2-difluoro-5-(1-methyl-1H-indol-2-yl)-5-oxo-4-phenylpentanoate (4s). The product (50.1 mg, 65%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.47 - 7.44 (m, 3H), 7.39 - 7.35 (m, 4H), 7.30 - 7.27 (m, 1H), 7.18 (ddd, *J* = 8.0, 6.2, 1.5 Hz, 1H), 5.00 (dd, *J* = 8.3, 5.0 Hz, 1H), 4.24 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.16 (dq, *J* = 10.7, 7.0 Hz, 1H), 4.07 (s, 3H), 3.36 (dtd, *J* = 18.2, 14.7, 8.2 Hz, 1H), 2.65 (dtd, *J* = 17.1, 15.6, 5.0 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.9 (d, *J* = 259.6 Hz, 1F), -105.1 (d, *J* = 259.9 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.0, 163.9 (t, *J* = 32.5 Hz), 140.5, 138.7, 133.9, 129.2, 128.1, 127.7, 126.3, 125.8, 123.2, 120.9, 115.4 (t, *J* = 250.8 Hz), 112.4, 110.4, 63.0, 48.2 (t, *J* = 3.7 Hz), 37.8 (t, *J* = 23.3 Hz), 32.3, 13.8. **HRMS**: calcd for $C_{22}H_{22}F_2NO_3^+$ $(M+H)^+$: 386.1563; found 386.1552.



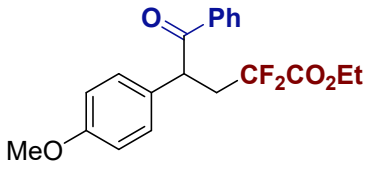
ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(thiophen-2-yl)pentanoate (4t). The product (51.4 mg, 76%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). This compound is known.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.59 (d, *J* = 4.9 Hz, 1H), 7.37 - 7.30 (m, 4H), 7.27 - 7.23 (m, 1H), 7.06 (t, *J* = 4.4 Hz, 1H), 4.77 (dd, *J* = 7.9, 5.2 Hz, 1H), 4.18 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.07 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.26 (dtd, *J* = 17.1, 15.4, 7.9 Hz, 1H), 2.56 (tdd, *J* = 16.4, 15.0, 5.2 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 86.2 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.2, 163.8 (t, *J* = 32.5 Hz), 142.9, 138.0, 134.4, 133.0, 129.3, 128.3, 128.3, 127.9, 115.3 (t, *J* = 250.7 Hz), 63.1, 48.4 (t, *J* = 3.9 Hz), 38.0 (t, *J* = 23.5 Hz), 13.8.



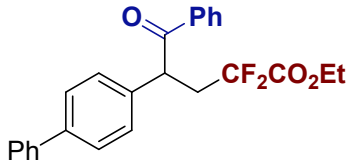
ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(p-tolyl)pentanoate (5b). The product (44.3 mg, 64%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). This compound is known.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 - 7.94 (m, 2H), 7.48 (td, *J* = 7.3, 1.5 Hz, 1H), 7.41 - 7.36 (m, 2H), 7.19 - 7.16 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 4.92 (dd, *J* = 8.0, 5.1 Hz, 1H), 4.17 (dqd, *J* = 11.8, 7.2, 1.5 Hz, 1H), 4.05 (dqd, *J* = 12.1, 7.1, 1.5 Hz, 1H), 3.25 (tddd, *J* = 16.7, 14.8, 8.0, 1.5 Hz, 1H), 2.52 (qdd, *J* = 16.4, 5.0, 1.5 Hz, 1H), 2.27 (s, 3H), 1.22 (td, *J* = 7.2, 1.5 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 15.9 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 163.9 (t, *J* = 32.5 Hz), 137.6, 136.0, 134.9, 133.3, 130.0, 128.9, 128.7, 128.2, 115.5 (t, *J* = 250.6 Hz), 63.0, 46.6 (t, *J* = 3.9 Hz), 38.3 (t, *J* = 23.4 Hz), 21.1, 13.8.



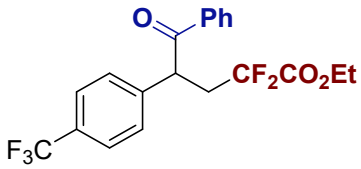
ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate (5c). The product (41.9 mg, 54%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.94 (dd, *J* = 8.1, 5.0 Hz, 1H), 4.14 (dq, *J* = 10.7, 7.2 Hz, 1H), 4.00 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.26 (qd, *J* = 16.0, 8.0 Hz, 1H), 2.55 (tdd, *J* = 16.6, 14.8, 5.0 Hz, 1H), 1.26 (s, 9H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.7 (d, *J* = 258.9 Hz, 1F), -104.9 (d, *J* = 258.9 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 163.9 (t, *J* = 32.6 Hz), 150.7, 136.0, 134.6, 133.3, 129.0, 128.7, 128.0, 126.2, 115.4 (t, *J* = 250.3 Hz), 63.0, 46.4 (t, *J* = 4.0 Hz), 38.4 (t, *J* = 23.4 Hz), 34.6, 31.3, 13.8. **HRMS**: calcd for $C_{23}H_{27}F_2O_3^+$ $(M+H)^+$: 389.1923; found 389.1934.



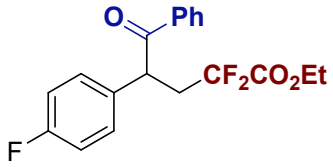
ethyl 2,2-difluoro-4-(4-methoxyphenyl)-5-oxo-5-phenylpentanoate (5d). The product (39.8 mg, 55%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 - 7.92 (m, 2H), 7.53 - 7.44 (m, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.24 - 7.17 (m, 2H), 6.85 - 6.78 (m, 2H), 4.91 (dd, *J* = 7.9, 5.2 Hz, 1H), 4.16 (dq, *J* = 11.0, 7.2 Hz, 1H), 4.05 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.72 (s, 3H), 3.23 (tdd, *J* = 16.8, 14.9, 8.0 Hz, 1H), 2.53 (tdd, *J* = 16.6, 14.9, 5.2 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.3 (d, *J* = 63.5 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 163.9 (t, *J* = 32.5 Hz), 159.1, 135.9, 133.2, 129.7, 129.5, 128.9, 128.7, 115.5 (t, *J* = 250.4 Hz), 114.7, 63.0, 55.3, 46.1 (t, *J* = 4.0 Hz), 38.3 (t, *J* = 23.3 Hz), 13.8. **HRMS**: calcd for $C_{20}H_{21}F_2O_4^+$ $(M+H)^+$: 363.1403; found 363.1415.



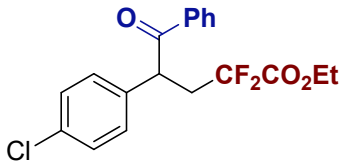
ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-5-oxo-5-phenylpentanoate (5e). The product (51.4 mg, 63%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.55 - 7.49 (m, 5H), 7.44 - 7.38 (m, 6H), 7.36 - 7.32 (m, 1H), 5.04 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.19 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.08 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.34 (tdd, *J* = 16.8, 14.9, 7.9 Hz, 1H), 2.62 (tdd, *J* = 16.4, 15.0, 5.0 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.2 (d, *J* = 48.2 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.3, 163.9 (t, *J* = 32.5 Hz), 140.7, 140.3, 136.8, 135.9, 133.4, 129.0, 128.9, 128.8, 128.8, 128.0, 127.6, 127.1, 115.4 (t, *J* = 250.7 Hz), 63.1, 46.6 (t, *J* = 3.9 Hz), 38.3 (t, *J* = 23.4 Hz), 13.8. **HRMS**: calcd for $C_{25}H_{23}F_2O_3^+$ $(M+H)^+$: 409.1610; found 409.1615.



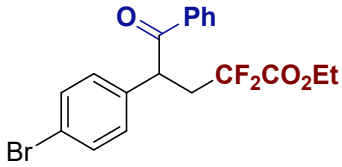
ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(4-(trifluoromethyl)phenyl)pentanoate (5f). The product (40 mg, 50%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). This compound is known.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 - 7.93 (m, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.53 - 7.51 (m, 1H), 7.45 - 7.40 (m, 4H), 5.05 (dd, *J* = 7.8, 5.2 Hz, 1H), 4.19 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.10 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.28 (tdd, *J* = 16.7, 14.9, 7.8 Hz, 1H), 2.54 (tdd, *J* = 16.6, 15.0, 5.2 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.7 (s, 2F), -104.4 (s, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 163.7 (t, *J* = 32.4 Hz), 141.9, 135.6, 133.8, 130.2 (q, *J* = 32.7 Hz), 128.9, 128.8, 126.3 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.2 Hz), 117.7, 115.2 (t, *J* = 251.0 Hz), 63.2, 46.6 (t, *J* = 3.8 Hz), 38.1 (t, *J* = 23.3 Hz), 13.9.



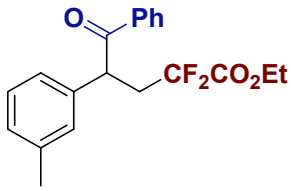
ethyl 2,2-difluoro-4-(4-fluorophenyl)-5-oxo-5-phenylpentanoate (5g). The product (39.2 mg, 56%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 - 7.85 (m, 2H), 7.44 (td, *J* = 7.2, 6.7, 1.1 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.22 - 7.18 (m, 2H), 6.93 - 6.88 (m, 2H), 4.89 (dd, *J* = 7.8, 5.2 Hz, 1H), 4.11 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.01 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.16 (tdd, *J* = 16.8, 14.9, 7.8 Hz, 1H), 2.45 (tdd, *J* = 16.3, 15.0, 5.2 Hz, 1H), 1.16 (t, *J* = 7.3 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 12.9 Hz, 2F), -114.3 (s, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.3, 164.0 (t, *J* = 32.4 Hz), 163.5, 161.1, 135.7, 133.6 (d, *J* = 3.3 Hz), 133.5, 130.0 (d, *J* = 8.1 Hz), 128.9 (d, *J* = 9.6 Hz), 116.3 (d, *J* = 21.6 Hz), 115.3 (t, *J* = 250.7 Hz), 63.1, 46.1 (t, *J* = 4.0 Hz), 38.3 (t, *J* = 23.4 Hz), 13.9. **HRMS**: calcd for $C_{19}H_{18}F_3O_3^+$ $(M+H)^+$: 351.1203; found 351.1215.



ethyl 4-(4-chlorophenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate (5h). The product (46.1 mg, 63%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 - 7.84 (m, 2H), 7.43 (td, *J* = 7.2, 1.3 Hz, 1H), 7.32 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.20 - 7.14 (m, 4H), 4.87 (dd, *J* = 7.8, 5.2 Hz, 1H), 4.11 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.01 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.16 (tdd, *J* = 16.8, 15.0, 7.8 Hz, 1H), 2.43 (tdd, *J* = 16.4, 15.0, 5.3 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (s, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.1, 163.8 (t, *J* = 32.5 Hz), 136.4, 135.6, 133.8, 133.6, 129.7, 129.5, 128.9, 128.8, 114.0 (d, *J* = 251.0 Hz), 63.2, 46.2 (t, *J* = 3.8 Hz), 38.1 (t, *J* = 23.4 Hz), 13.9. **HRMS**: calcd for $C_{19}H_{18}ClF_2O_3^+$ $(M+H)^+$: 361.1615; found 361.1608.

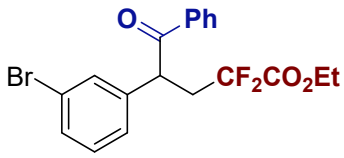


ethyl 4-(4-bromophenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate (5i). The product (46.7 mg, 57%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). This compound is known.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.42 - 7.38 (m, 4H), 7.18 (d, *J* = 8.3 Hz, 2H), 4.94 (dd, *J* = 7.8, 5.2 Hz, 1H), 4.19 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.09 (dq, *J* = 10.9, 7.2 Hz, 1H), 3.24 (qd, *J* = 16.4, 7.8 Hz, 1H), 2.51 (qd, *J* = 16.0, 5.1 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.3 (s, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 163.8 (t, *J* = 32.5 Hz), 136.9, 135.6, 133.6, 132.5, 130.1, 128.9, 128.8, 121.9, 115.3 (t, *J* = 250.9 Hz), 63.1, 46.3 (t, *J* = 3.9 Hz), 38.1 (t, *J* = 23.4 Hz), 13.8.

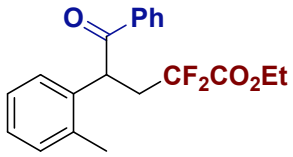


ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(m-tolyl)pentanoate (5j). The product (44.3 mg,

64%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.50 - 7.45 (m, 1H), 7.39 - 7.35 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.13 (td, *J* = 7.2, 1.8 Hz, 1H), 7.10 - 7.03 (m, 2H), 5.10 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.22 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.10 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.33 (tdd, *J* = 17.2, 15.0, 9.0 Hz, 1H), 2.56 (s, 3H), 2.32 (dtd, *J* = 18.1, 14.7, 3.5 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.7 (d, *J* = 256.9 Hz, 1F), -105.4 (d, *J* = 256.8 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.1, 164.0 (t, *J* = 32.5 Hz), 136.5, 136.3, 135.3, 133.2, 131.6, 128.7, 128.6, 127.8, 127.4, 127.0, 115.3 (t, *J* = 250.5 Hz), 63.1, 43.3 (t, *J* = 3.9 Hz), 37.7 (t, *J* = 23.6 Hz), 19.7, 13.8. **HRMS**: calcd for $C_{20}H_{21}F_2O_3^+$ $(M+H)^+$: 347.1454; found 347.1459.

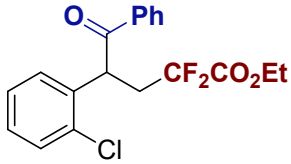


ethyl 4-(3-bromophenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate (5k). The product (49.2 mg, 60%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.38 (s, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 6.7 Hz, 1H), 7.18 - 7.15 (m, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 4.86 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.12 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.02 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.17 (qd, *J* = 16.1, 8.0 Hz, 1H), 2.44 (qd, *J* = 16.2, 15.8, 5.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, *J* = 13.8 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 163.7 (t, *J* = 32.5 Hz), 140.1, 135.6, 133.6, 131.2, 131.1, 130.9, 128.9, 128.9, 127.1, 123.3, 115.2 (t, *J* = 250.9 Hz), 63.2, 46.4 (t, *J* = 3.8 Hz), 38.2 (t, *J* = 23.4 Hz), 13.9. **HRMS**: calcd for $C_{19}H_{18}BrF_2O_3^+$ $(M+H)^+$: 361.1615; found 361.1623.

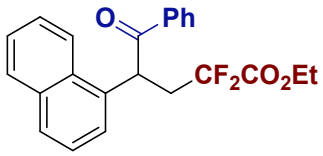


ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(o-tolyl)pentanoate (5l). The product (44.3 mg, 64%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA

= 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.50 - 7.45 (m, 1H), 7.39 - 7.35 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.13 (td, *J* = 7.2, 1.8 Hz, 1H), 7.10 - 7.03 (m, 2H), 5.10 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.22 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.10 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.33 (tdd, *J* = 17.2, 15.0, 9.0 Hz, 1H), 2.56 (s, 3H), 2.32 (dtd, *J* = 18.1, 14.7, 3.5 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.7 (d, *J* = 256.9 Hz, 1F), -105.4 (d, *J* = 256.8 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.1, 164.0 (t, *J* = 32.5 Hz), 136.5, 136.3, 135.3, 133.2, 131.6, 128.7, 128.6, 127.8, 127.4, 127.0, 115.3 (t, *J* = 250.5 Hz), 63.1, 43.3 (t, *J* = 3.9 Hz), 37.7 (t, *J* = 23.6 Hz), 19.7, 13.8. **HRMS**: calcd for $C_{20}H_{21}F_2O_3^+$ $(M+H)^+$: 347.1454; found 347.1459.

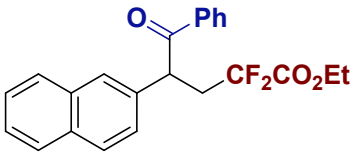


ethyl 4-(2-chlorophenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate (5m). The product (44.7 mg, 61%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). This compound is known.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 8.3, 1.1 Hz, 2H), 7.52 - 7.48 (m, 1H), 7.43 - 7.38 (m, 3H), 7.19 - 7.14 (m, 3H), 5.49 (dd, *J* = 8.8, 3.9 Hz, 1H), 4.25 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.15 (dq, *J* = 10.9, 7.2 Hz, 1H), 3.28 (tdd, *J* = 16.8, 14.8, 8.8 Hz, 1H), 2.40 (dtd, *J* = 18.0, 14.7, 4.0 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.7 (d, *J* = 258.9 Hz, 1F), -105.2 (d, *J* = 258.9 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.2, 163.9 (t, *J* = 32.4 Hz), 135.7, 135.6, 133.6, 133.4, 130.5, 129.2, 129.0, 128.8, 128.3, 127.7, 115.1 (t, *J* = 251.4 Hz), 63.1, 43.0 (t, *J* = 3.9 Hz), 37.4 (t, *J* = 23.7 Hz), 13.9.

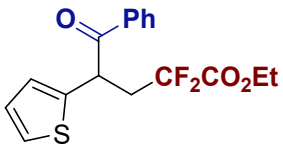


ethyl 2,2-difluoro-4-(naphthalen-1-yl)-5-oxo-5-phenylpentanoate (5n). The product (49.7 mg, 65%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.6 Hz, 1H), 7.84 - 7.78 (m, 3H), 7.69 - 7.61 (m, 2H), 7.52 - 7.48 (m, 1H), 7.34 (td, *J* = 7.4, 1.4 Hz, 1H), 7.24 - 7.13 (m, 4H), 5.65 (dd, *J* = 9.5, 2.9 Hz, 1H), 4.18 - 4.10 (m, 1H), 4.07 - 3.99 (m, 1H),

3.41 (tdd, *J* = 17.9, 15.1, 9.4 Hz, 1H), 2.39 (qd, *J* = 15.2, 2.9 Hz, 1H), 1.13 (t, *J* = 7.8 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.5 (d, *J* = 257.0 Hz, 2F), -105.7 (d, *J* = 257.1 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 164.0 (t, *J* = 32.5 Hz), 136.0, 134.7, 134.2, 133.3, 130.3, 129.5, 128.7, 128.7, 128.6, 127.4, 126.3, 125.9, 125.7, 122.4, 115.4 (t, *J* = 250.7 Hz), 63.1, 42.5 (t, *J* = 11.1 Hz), 37.7 (t, *J* = 23.5 Hz), 13.8. **HRMS**: calcd for $C_{23}H_{21}F_2O_3^+$ $(M+H)^+$: 383.1454; found 383.1443.

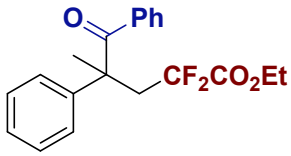


ethyl 2,2-difluoro-4-(naphthalen-2-yl)-5-oxo-5-phenylpentanoate (5o). The product (47.4 mg, 62%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). This compound is known.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.82 - 7.76 (m, 4H), 7.49 - 7.43 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 5.15 (dd, *J* = 7.9, 5.0 Hz, 1H), 4.11 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.99 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.39 (qd, *J* = 16.4, 7.9 Hz, 1H), 2.66 (qd, *J* = 16.2, 5.0 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.2 (d, *J* = 41.7 Hz, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) 197.3, 163.9 (t, *J* = 32.5 Hz), 135.9, 135.3, 133.6, 133.4, 132.7, 129.3, 129.0, 128.7, 127.9, 127.7, 127.5, 126.6, 126.4, 125.9, 115.4 (t, *J* = 250.7 Hz), 63.0, 47.1 (t, *J* = 4.0 Hz), 38.3 (t, *J* = 23.4 Hz), 13.8.

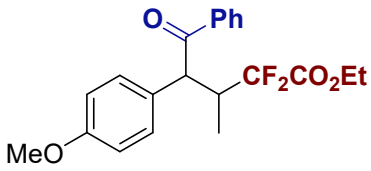


ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(thiophen-2-yl)pentanoate (5p). The product (48 mg, 71%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.56 - 7.51 (m, 1H), 7.45 - 7.41 (m, 2H), 7.18 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.92 - 6.88 (m, 2H), 5.28 (dd, *J* = 8.5, 4.6 Hz, 1H), 4.22 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.12 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.31 (tdd, *J* = 17.0, 15.1, 8.5 Hz, 1H), 2.63 (dtd, *J* = 17.3, 15.1, 4.6 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.5 (d, *J* = 22.3 Hz, 2F).

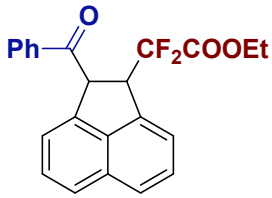
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 163.7 (t, *J* = 32.4 Hz), 139.8, 135.5, 133.6, 129.0, 128.8, 127.3, 126.6, 125.8, 115.1 (t, *J* = 251.0 Hz), 63.2, 41.4 (t, *J* = 4.2 Hz), 38.9 (t, *J* = 23.4 Hz), 13.9. **HRMS**: calcd for $C_{17}H_{17}F_2O_3S^+$ $(M+H)^+$: 361.1615; found 361.1618.



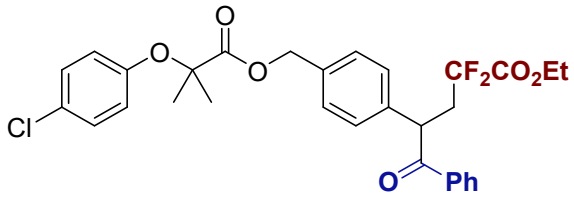
ethyl 2,2-difluoro-4-methyl-5-oxo-4,5-diphenylpentanoate (5q). The product (47.8 mg, 69%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 20:1). This compound is known.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 - 7.30 (m, 8H), 7.20 (t, *J* = 7.7 Hz, 2H), 4.08 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.95 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.00 (q, *J* = 15.7 Hz, 1H), 2.85 (dt, *J* = 21.4, 14.7 Hz, 1H), 1.85 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.7 (d, *J* = 263.6 Hz, 1F), -99.9 (d, *J* = 263.6 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.1, 164.0 (t, *J* = 32.6 Hz), 140.9, 136.3, 131.8, 129.4, 129.2, 128.1, 127.9, 126.9, 116.1 (t, *J* = 249.6 Hz), 62.8, 52.5 (d, *J* = 3.6 Hz), 44.3 (t, *J* = 22.5 Hz), 22.3 (t, *J* = 2.7 Hz), 13.9.



ethyl 2,2-difluoro-4-(4-methoxyphenyl)-3-methyl-5-oxo-5-phenylpentanoate (5r). The product (30.8 mg, 41%, dr = 5:1) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.44 - 7.40 (m, 1H), 7.33 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.21 - 7.18 (m, 2H), 6.71 - 6.69 (m, 2H), 4.63 (d, *J* = 10.5 Hz, 1H), 3.79 - 3.68 (m, 2H), 3.65 (s, 3H), 3.42 (ddt, *J* = 22.5, 10.6, 6.8 Hz, 1H), 1.13 (d, *J* = 7.1 Hz, 3H), 1.09 (d, *J* = 1.7 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.9 (d, *J* = 264.9 Hz, 1F), -115.4 (d, *J* = 264.9 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.8, 163.6 (t, *J* = 33.1 Hz), 159.4, 136.7, 133.4, 131.3, 128.8, 126.6, 117.2 (t, *J* = 248.6 Hz), 117.1, 114.1, 62.6, 55.3, 53.5 (d, *J* = 4.7 Hz), 40.8 (t, *J* = 21.5 Hz), 13.8, 12.4. **HRMS**: calcd for $C_{21}H_{23}F_2O_4^+$ $(M+H)^+$: 377.1559; found 377.1564.

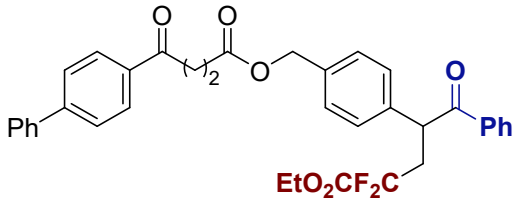


ethyl 2-(2-benzoyl-1,2-dihydroacenaphthylen-1-yl)-2,2-difluoroacetate (5s). The product (41.1 mg, 54%, dr = 9:1) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 - 8.09 (m, 2H), 7.76 - 7.66 (m, 3H), 7.63 - 7.54 (m, 4H), 7.33 and 7.23 (t, *J* = 7.6 Hz, 1H), 6.98 and 6.74 (dd, *J* = 7.0, 1.4 Hz, 1H), 5.83 (d, *J* = 3.7 Hz, 1H), 5.37 – 5.19 (m, 1H), 4.17 and 3.91 (q, *J* = 7.2 Hz, 2H), 1.06 and 0.80 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.0 and -107.1 (d, *J* = 260.4 Hz, 1F), -105.2.4 and -108.6 (d, *J* = 260.2 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$, Main product) δ 195.9, 163.7 (t, *J* = 32.9 Hz), 140.2, 138.0, 137.7 (t, *J* = 3.0 Hz), 136.5, 134.0, 131.8, 129.6, 129.2, 128.4, 127.8, 125.0, 124.6, 122.4, 120.6, 116.0 (t, *J* = 253.4 Hz), 63.2, 52.7 (t, *J* = 4.1 Hz), 50.8 (t, *J* = 23.6 Hz), 13.7. **HRMS**: calcd for $C_{23}H_{19}F_2O_3^+$ $(M+H)^+$: 381.1297; found 381.1300.

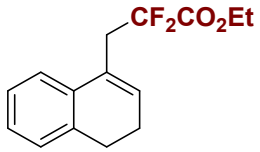


ethyl 4-(4-(((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)methyl)phenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate--ethyl 4-(4-(((4-([1,1'-biphenyl]-4-yl)-4-oxobutanoyl)oxy)methyl)phenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate (1/1) (5t). The product (59.2 mg, 53%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 10:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 5.02 (s, 2H), 4.90 (dd, *J* = 8.1, 4.9 Hz, 1H), 4.09 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.99 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.19 (qd, *J* = 16.5, 8.0 Hz, 1H), 2.43 (qd, *J* = 16.3, 4.9 Hz, 1H), 1.47 (s, 6H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.4 (d, J = 4.9 Hz, 2F). **^{13}C NMR**

(151 MHz, $CDCl_3$) δ 197.1, 173.8, 163.8 (t, *J* = 32.4 Hz), 154.0, 138.1, 135.7, 134.8, 133.5, 129.2, 129.2, 128.9, 128.8, 128.5, 127.3, 120.5, 115.3 (t, *J* = 250.7 Hz), 79.5, 66.6, 63.1, 46.5 (t, *J* = 3.7 Hz), 38.2 (t, *J* = 23.3 Hz), 25.4, 25.3, 13.8. **HRMS**: calcd for $C_{30}H_{30}ClF_2O_6^+$ $(M+H)^+$: 559.1694; found 559.1703.



ethyl 4-(4-(((4-([1,1'-biphenyl]-4-yl)-4-oxobutanoyl)oxy)methyl)phenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate (5u). The product (73.0 mg, 61%) as a pale yellow soild was purified with silica gel chromatography (PE/EA = 10:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 6.9 Hz, 2H), 7.38 - 7.33 (m, 3H), 7.29 - 7.27 (m, 3H), 7.19 (s, 4H), 4.97 (s, 2H), 4.88 (dd, *J* = 8.1, 4.9 Hz, 1H), 4.06 (dq, *J* = 10.4, 7.1 Hz, 1H), 3.95 (dq, *J* = 10.6, 7.1 Hz, 1H), 3.22 (t, *J* = 6.5 Hz, 2H), 3.19 - 3.13 (m, 1H), 2.69 (t, *J* = 6.5 Hz, 2H), 2.41 (qd, *J* = 16.2, 4.8 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.3 (s, 2F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.6, 197.2, 172.8, 163.8 (t, *J* = 32.5 Hz), 145.9, 139.8, 137.8, 135.7, 135.5, 135.2, 133.4, 129.0, 128.9, 128.7, 128.7, 128.5, 128.3, 127.3, 127.3, 115.3 (t, *J* = 250.8 Hz), 65.9, 63.0, 53.5, 46.5 (t, *J* = 3.7 Hz), 38.2 (t, *J* = 23.2 Hz), 33.4, 28.3, 13.8. **HRMS**: calcd for $C_{36}H_{33}F_2O_6^+$ $(M+H)^+$: 599.2240; found 599.2246.



ethyl 3-(3,4-dihydronaphthalen-1-yl)-2,2-difluoropropanoate (8). The product (12.77 mg, 24%) as a pale yellow oily liquid was purified with silica gel chromatography (PE/EA = 50:1). This compound is known.[7] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 - 7.12 (m, 4H), 6.08 (t, *J* = 4.7 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.25 (t, *J* = 15.8 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.31 - 2.24 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.3 (s, 2F).

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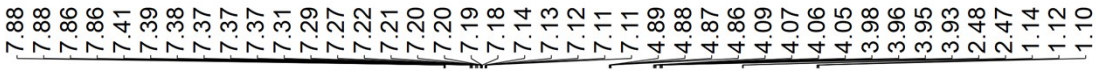
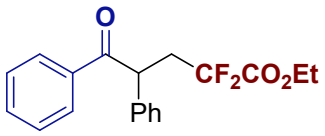
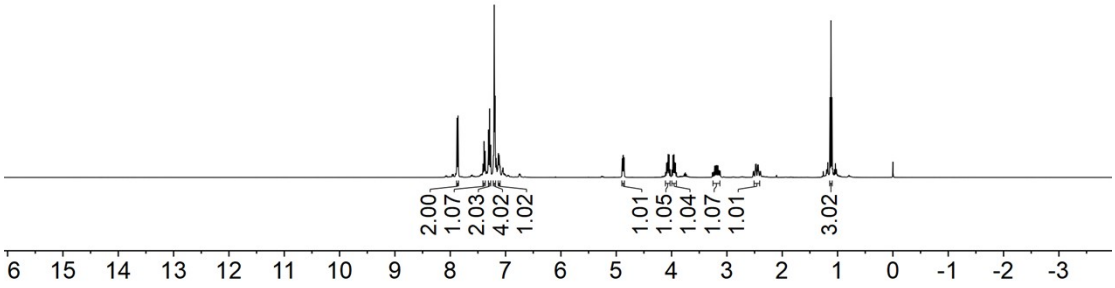
NMR spectra

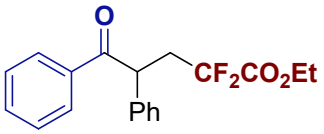




4a

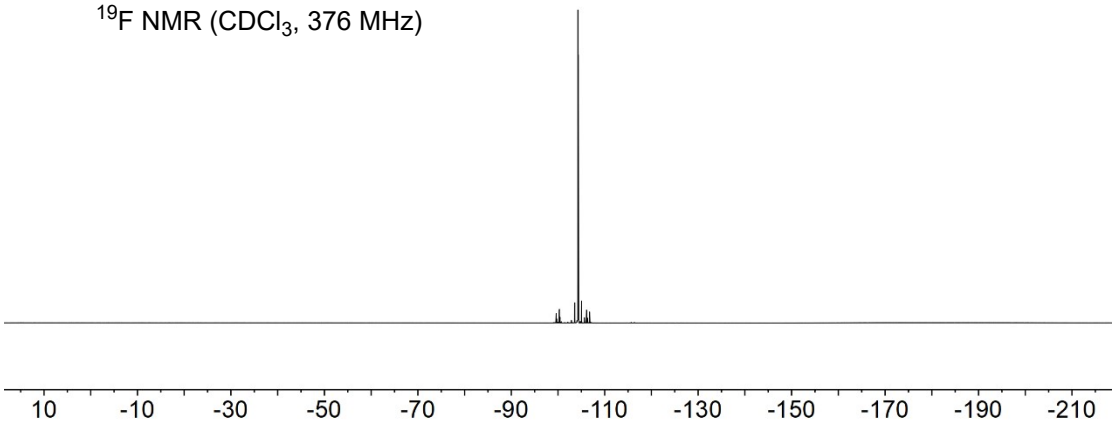
^{1}H NMR ($CDCl_3$, 400 MHz)

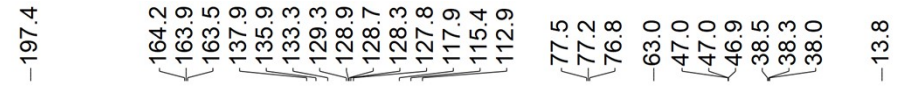


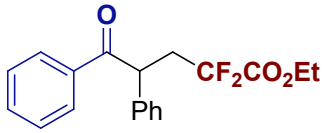


4a

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

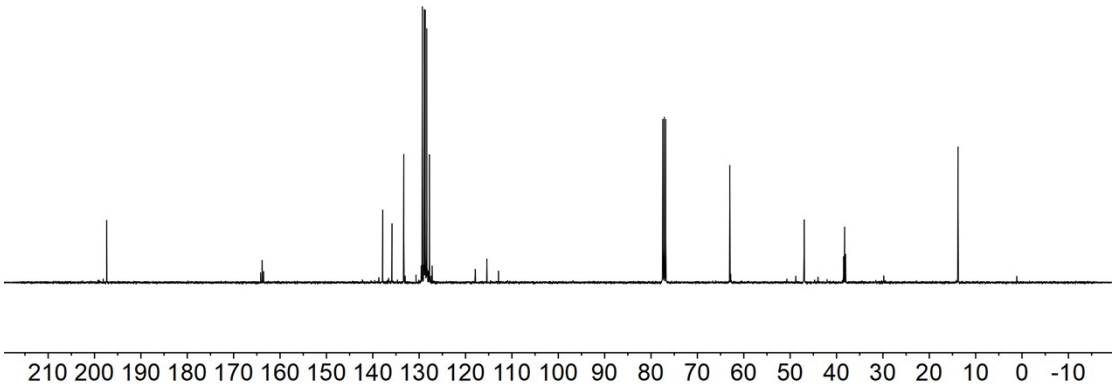


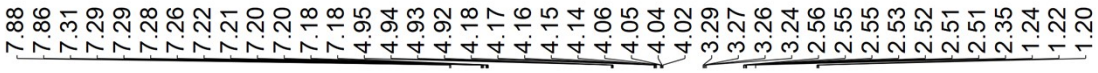


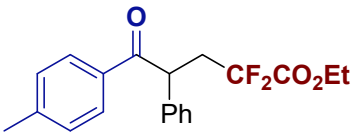


4a

^{13}C NMR ($CDCl_3$, 101 MHz)

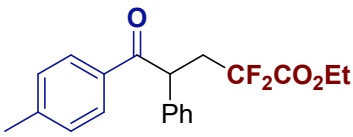






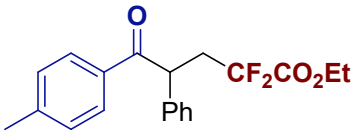
4b

^{1}H NMR ($CDCl_3$, 400 MHz)



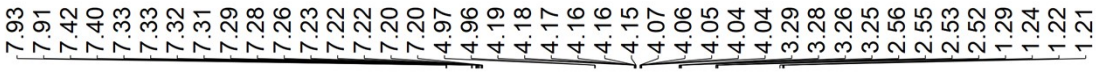
4b

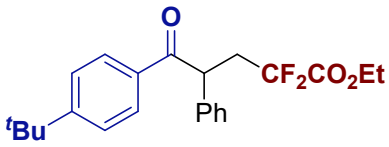
^{19}F NMR ($CDCl_3$, 376 MHz)



4b

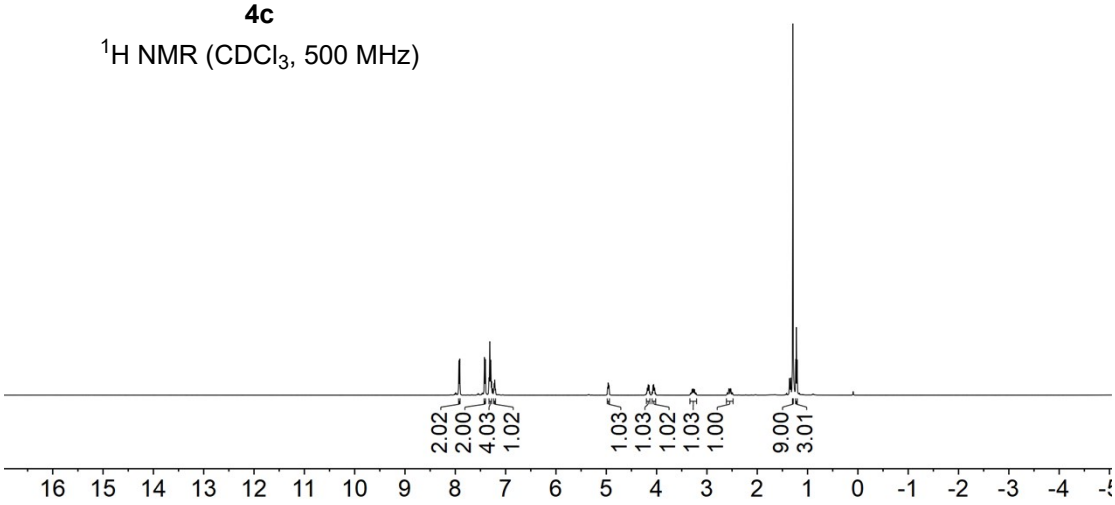
^{13}C NMR ($CDCl_3$, 101 MHz)

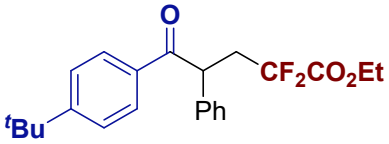




4c

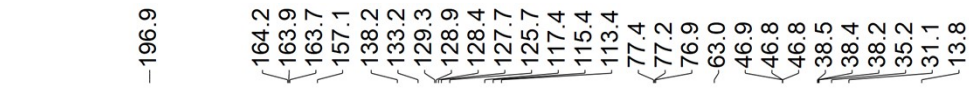
^{1}H NMR ($CDCl_3$, 500 MHz)

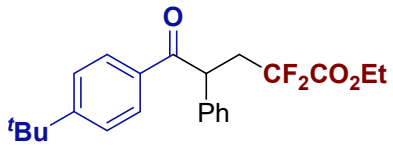




4c

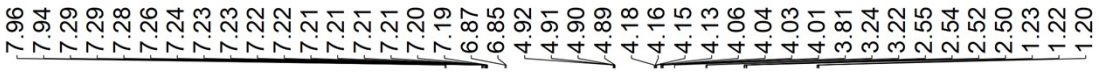
^{19}F NMR ($CDCl_3$, 376 MHz)

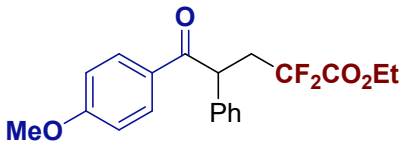




4c

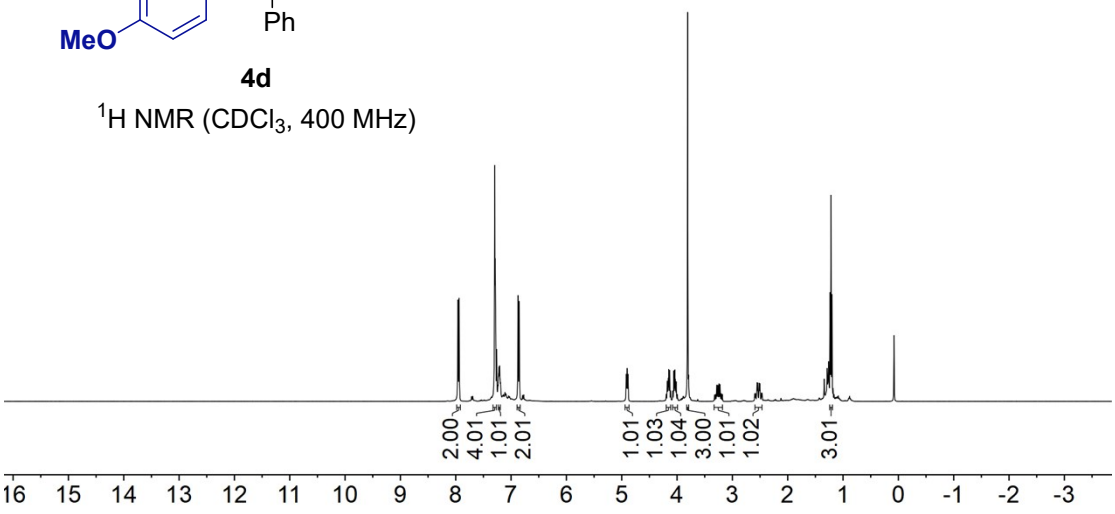
^{13}C NMR ($CDCl_3$, 126 MHz)

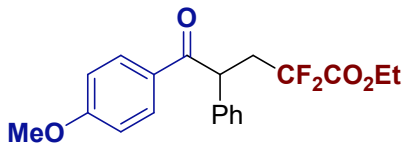




4d

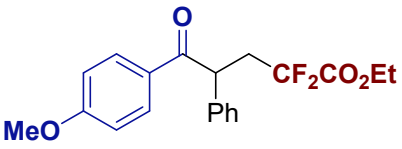
^{1}H NMR ($CDCl_3$, 400 MHz)





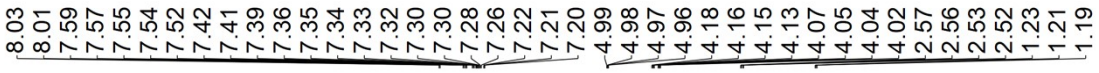
4d

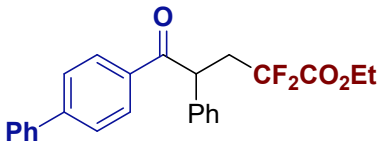
^{19}F NMR ($CDCl_3$, 376 MHz)



4d

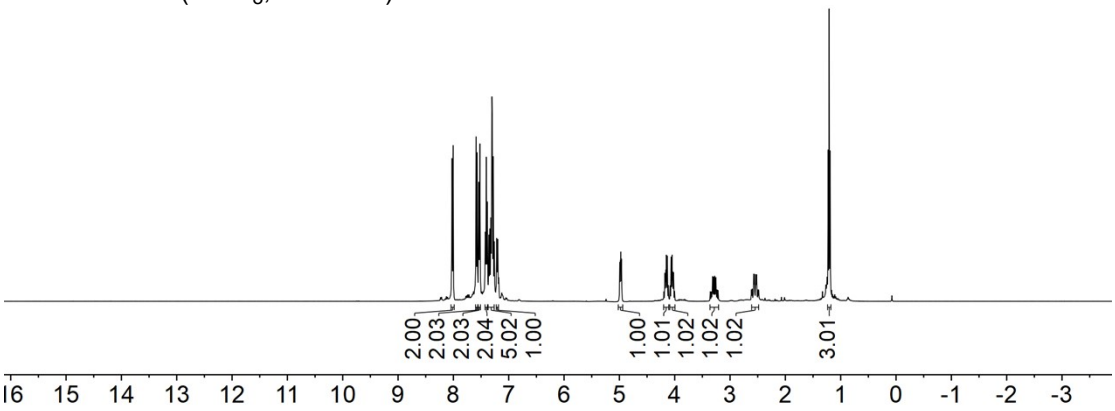
^{13}C NMR ($CDCl_3$, 101 MHz)

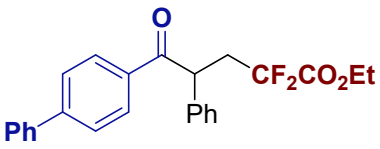




4e

^{1}H NMR ($CDCl_3$, 400 MHz)





4e

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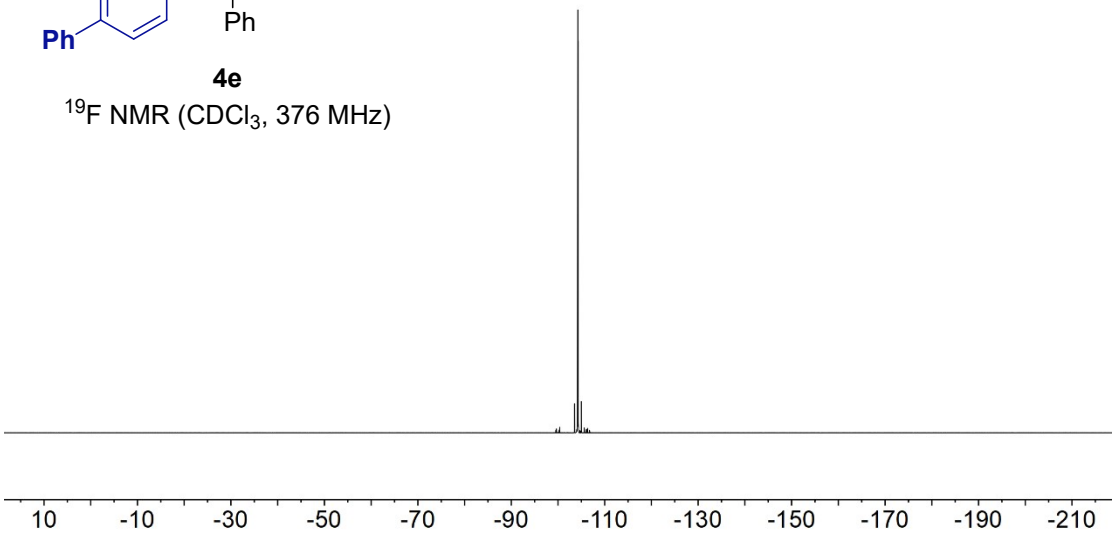
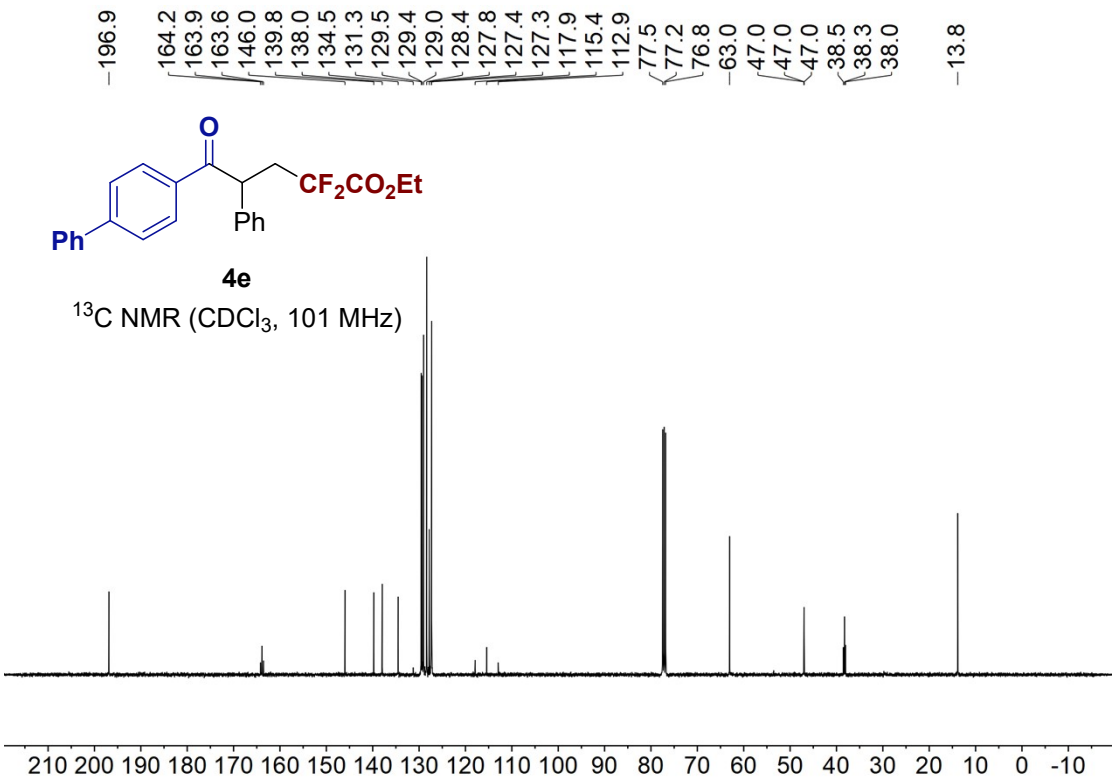
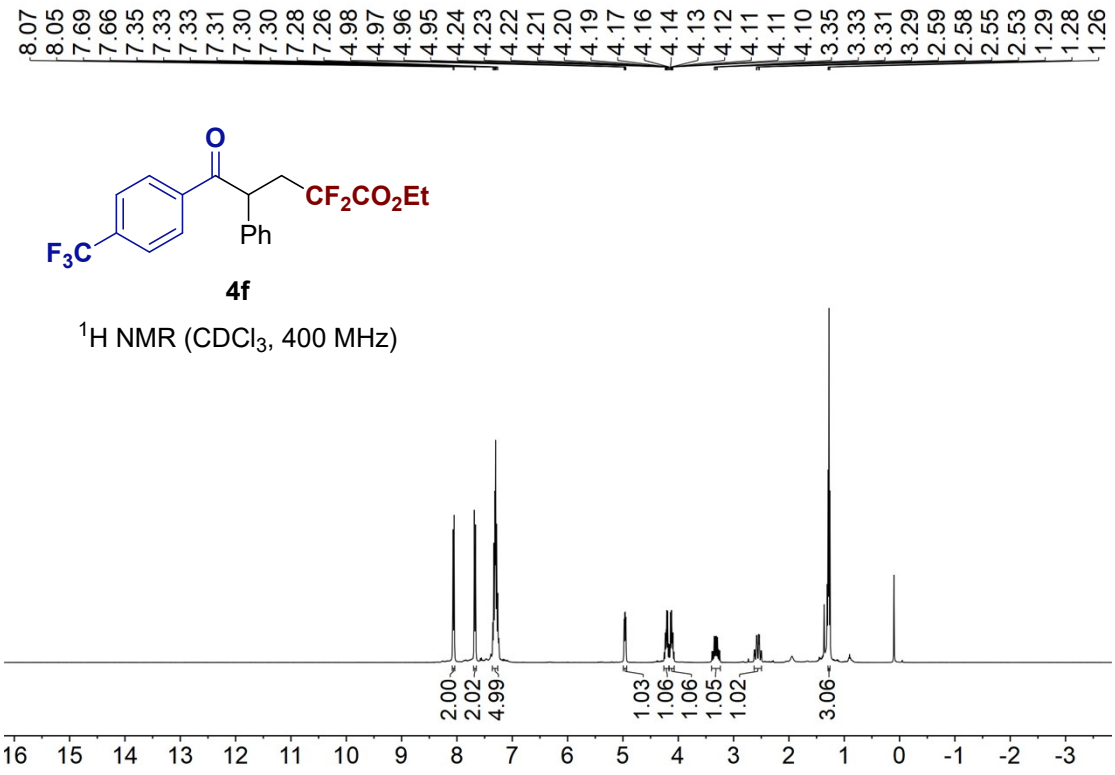




4e

^{13}C NMR ($CDCl_3$, 101 MHz)



4f

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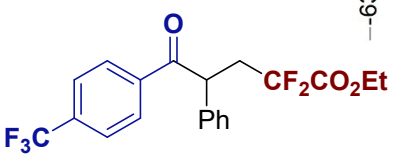

4f

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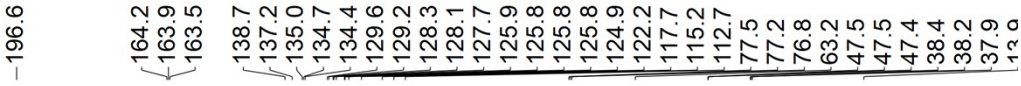

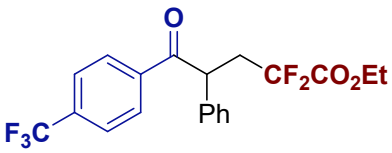

4f

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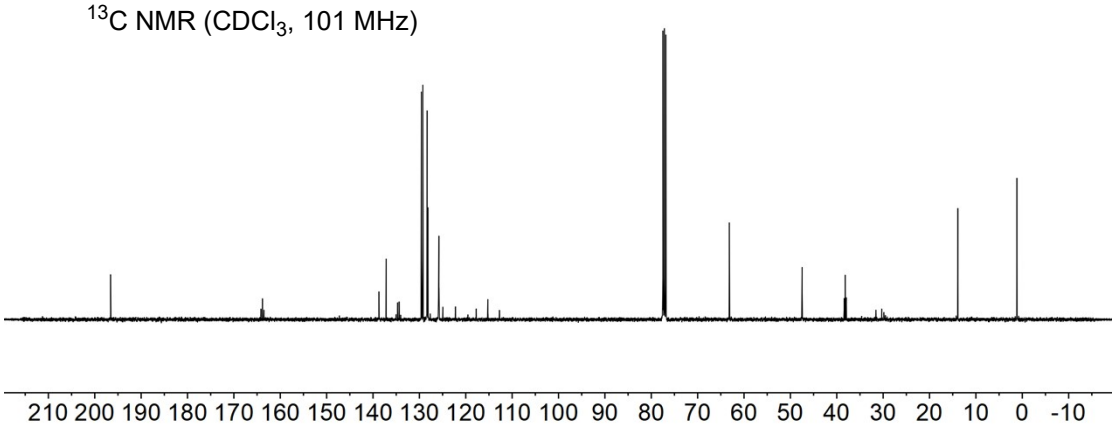
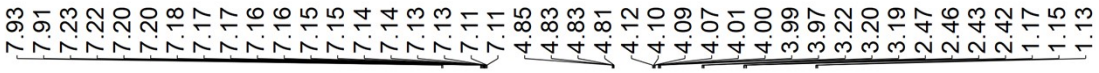
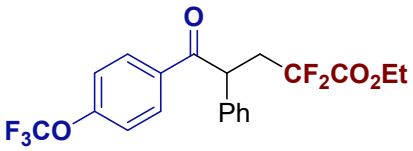
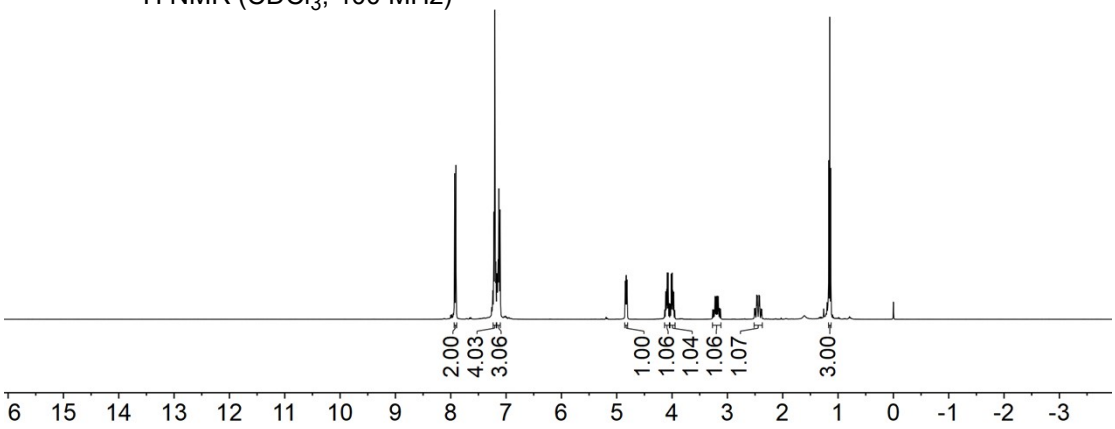


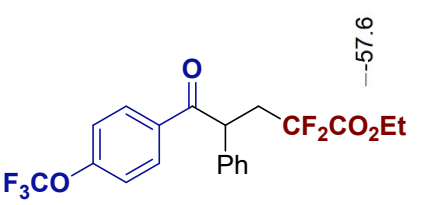




4g

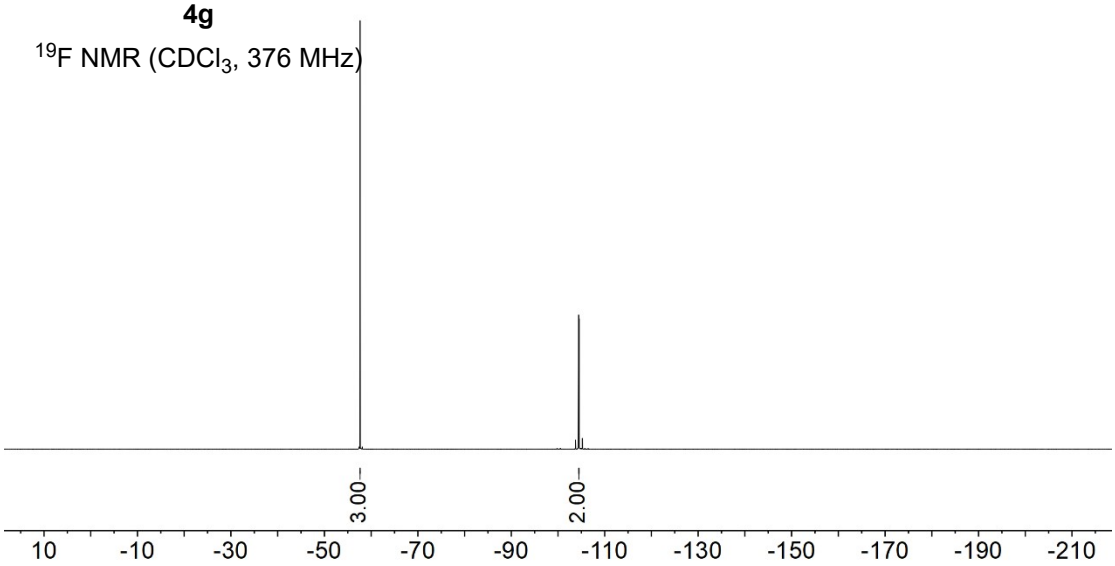
^{1}H NMR ($CDCl_3$, 400 MHz)

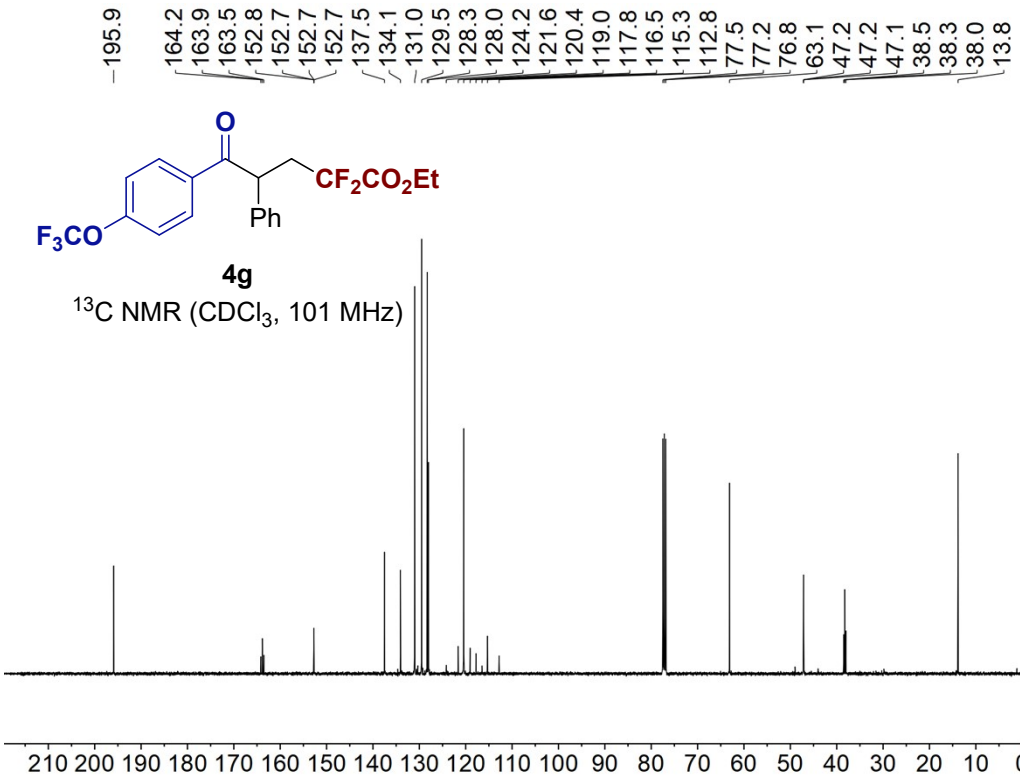




4g

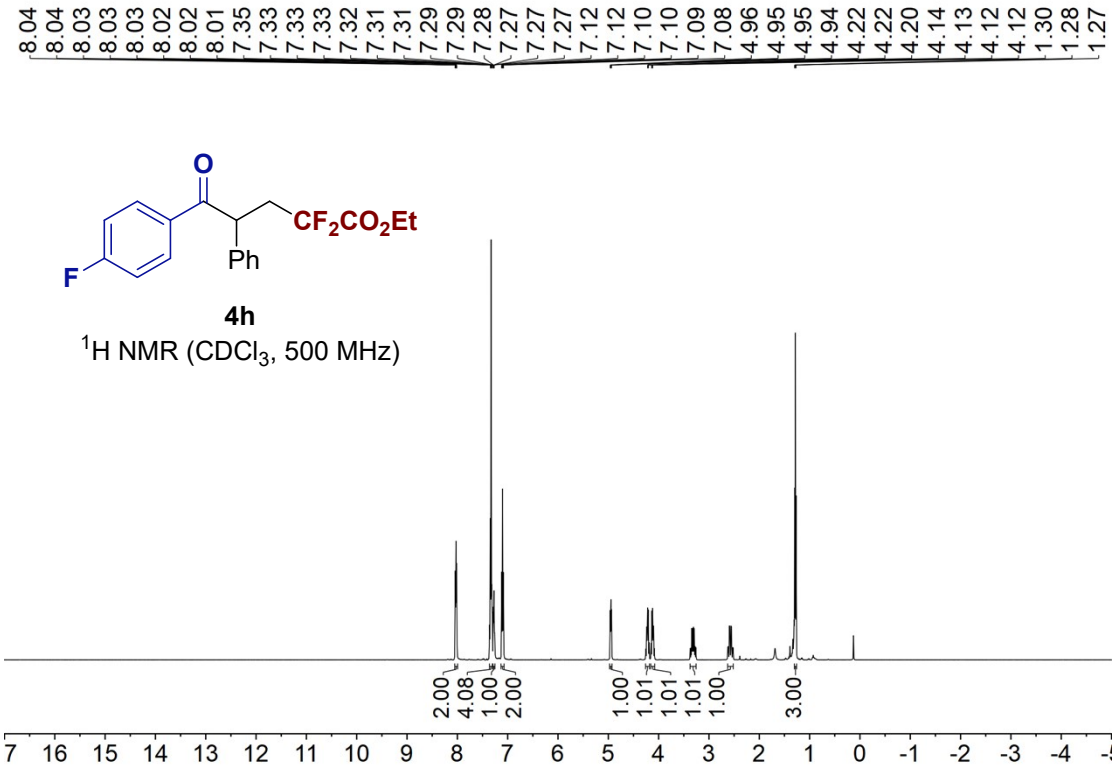
^{19}F NMR ($CDCl_3$, 376 MHz)





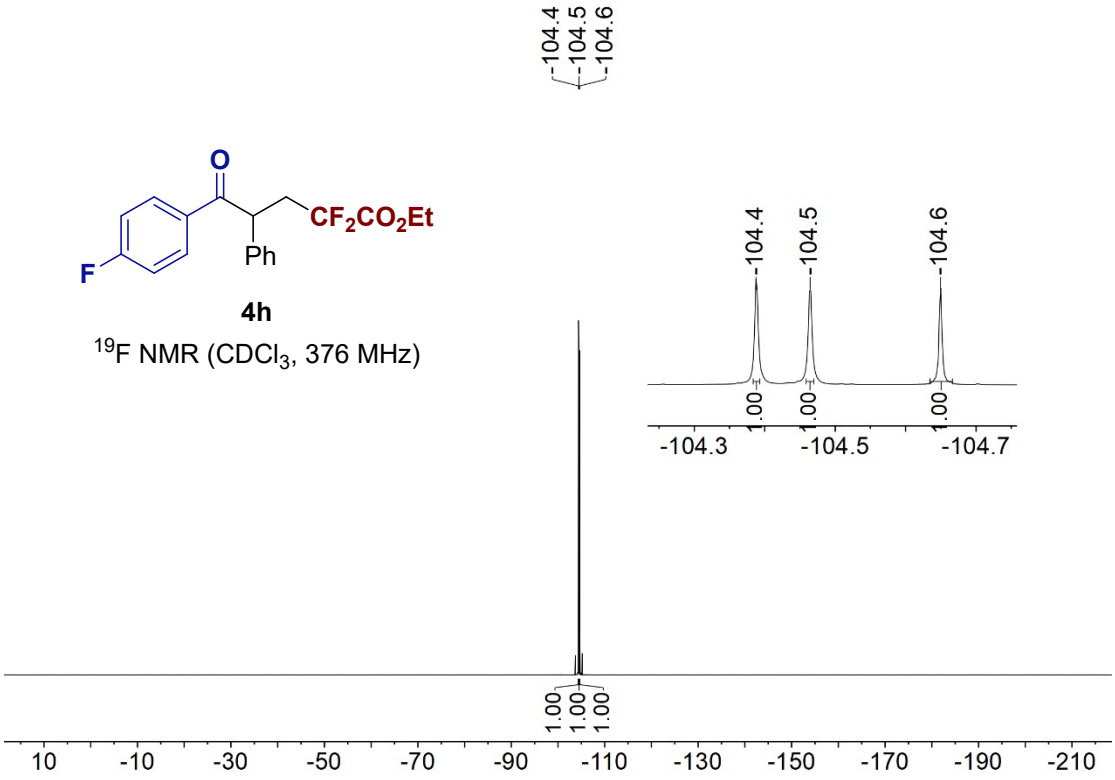
4g

^{13}C NMR ($CDCl_3$, 101 MHz)



4h

^{1}H NMR ($CDCl_3$, 500 MHz)


-104.4
-104.5
-104.6
O
CF2CO2Et
Ph
F
4h
19F NMR (CDCl3, 376 MHz)
-104.4
-104.5
-104.6
1.00
1.00
1.00
-104.3
-104.5
-104.7
1.00
1.00
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10
-10
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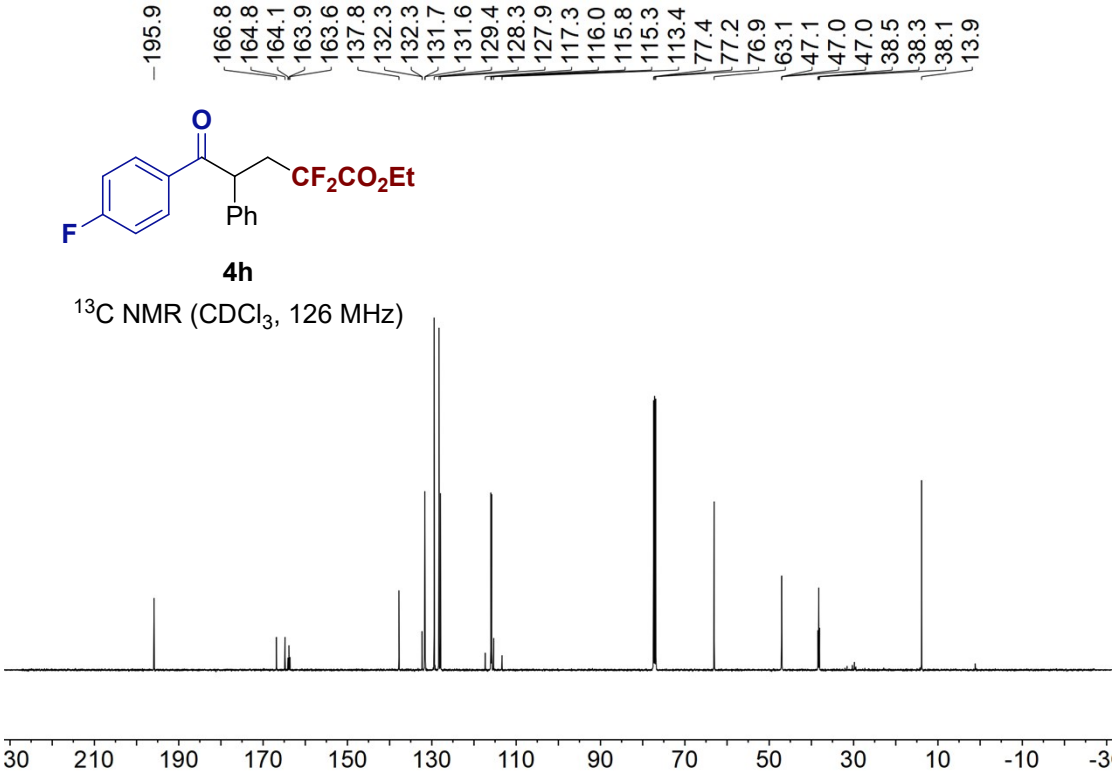
-90
-110
-130
-150
-170
-190
-210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116.0
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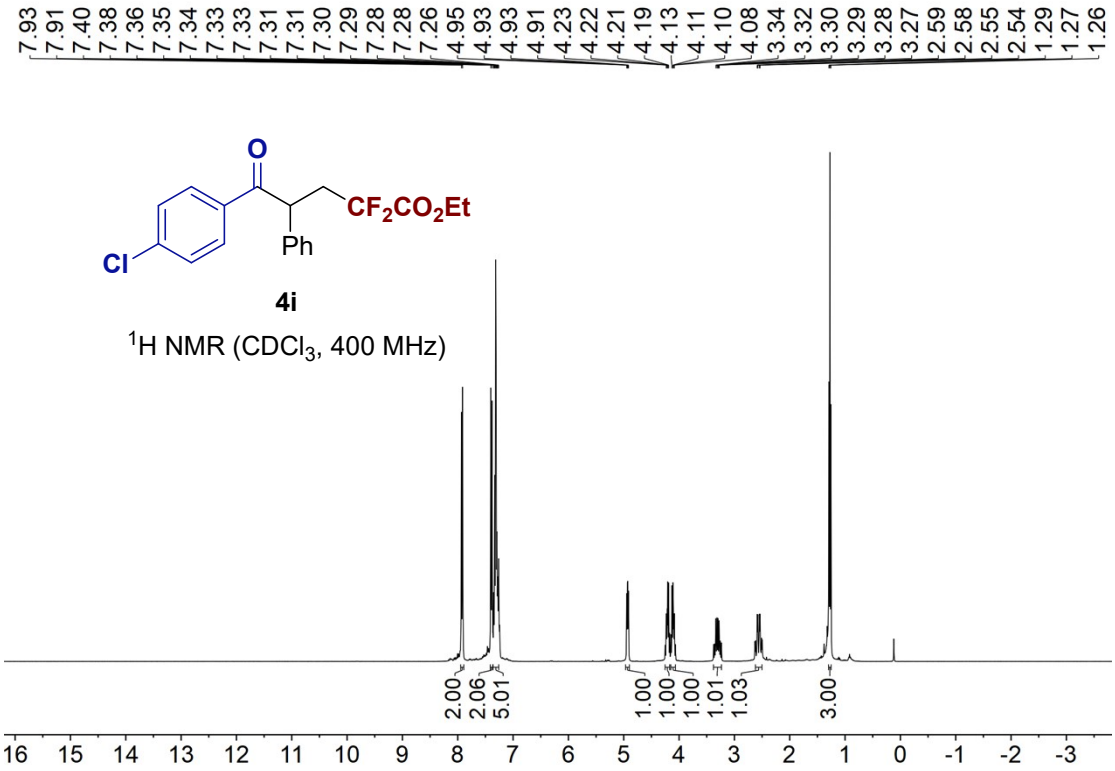
113.4
77.4
77.2
76.9
63.1
47.1
47.0
47.0
38.5
38.3
38.1
13.9
O
CF2CO2Et
Ph
F
4h
13C NMR (CDCl3, 126 MHz)
30
210
190
170
150
130
110
90
70
50
30
10
-10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7.28
7.26
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4.93
4.93
4.91
4.23
4.22
4.21
4.19
4.13
4.11
4.10
4.08
3.34
3.32
3.30
3.29
3.28
3.27
2.59
2.58
2.55
2.54
1.29
1.27
1.26
O
CF2CO2Et
Cl
Ph
4i
1H NMR (CDCl3, 400 MHz)
2.00
2.06
5.01
1.00
1.00
1.00
1.01
1.03
3.00
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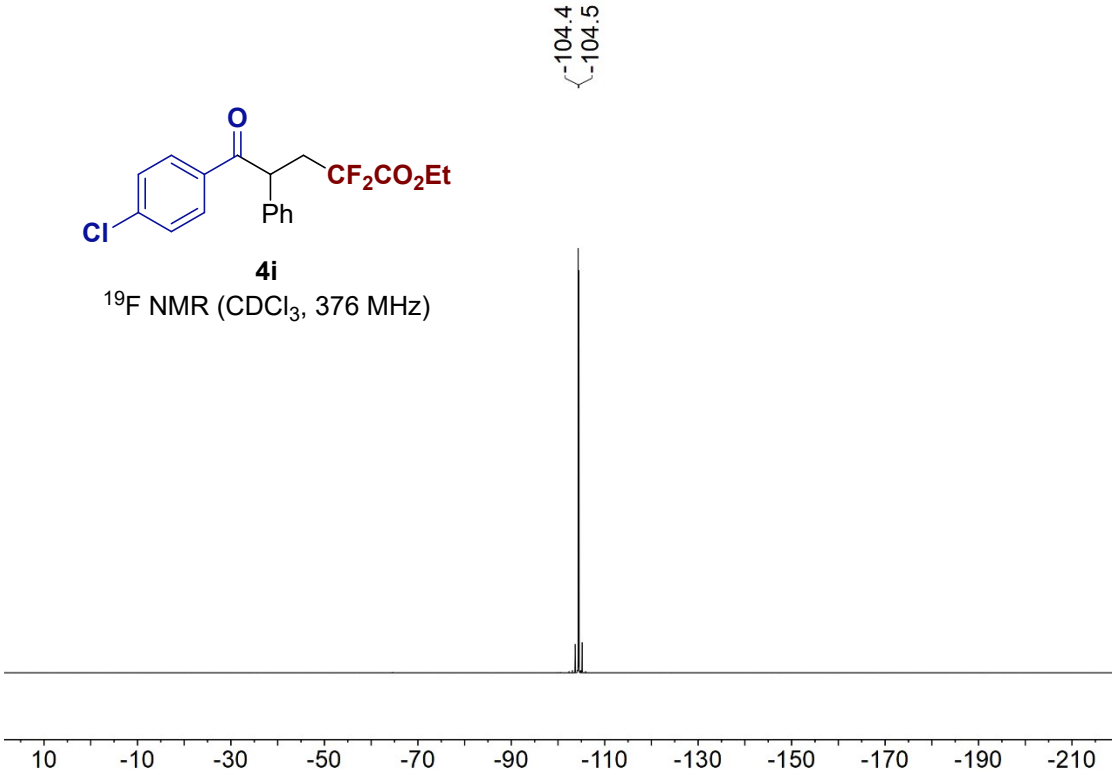
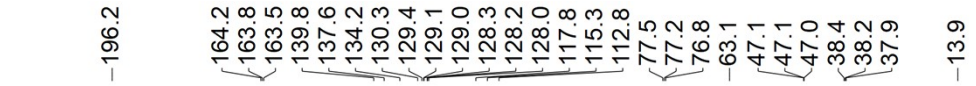
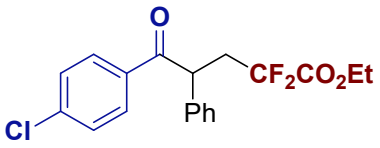
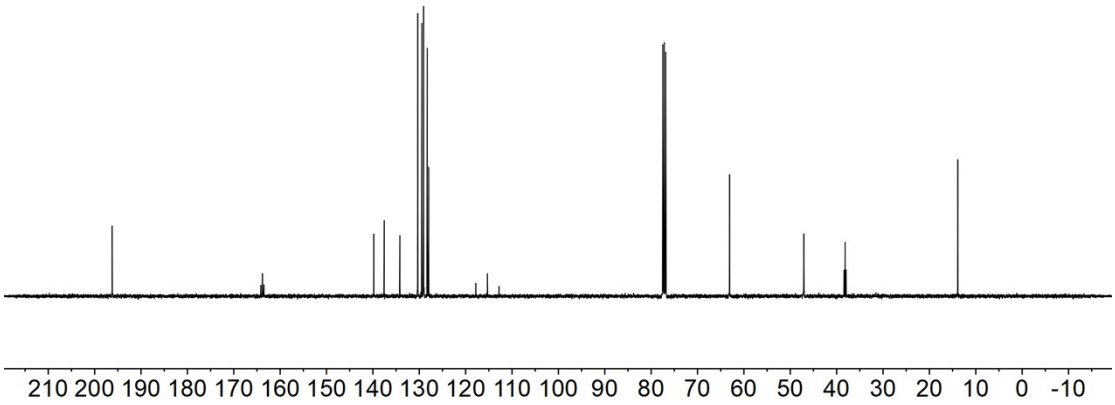

-104.4
-104.5
O
CF2CO2Et
Cl
Ph
4i
19F NMR (CDCl3, 376 MHz)
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

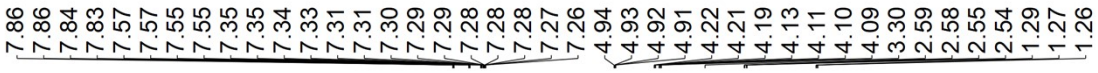


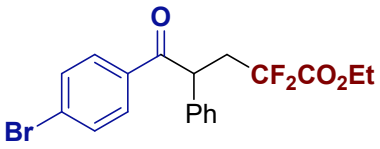


4i

^{13}C NMR ($CDCl_3$, 101 MHz)

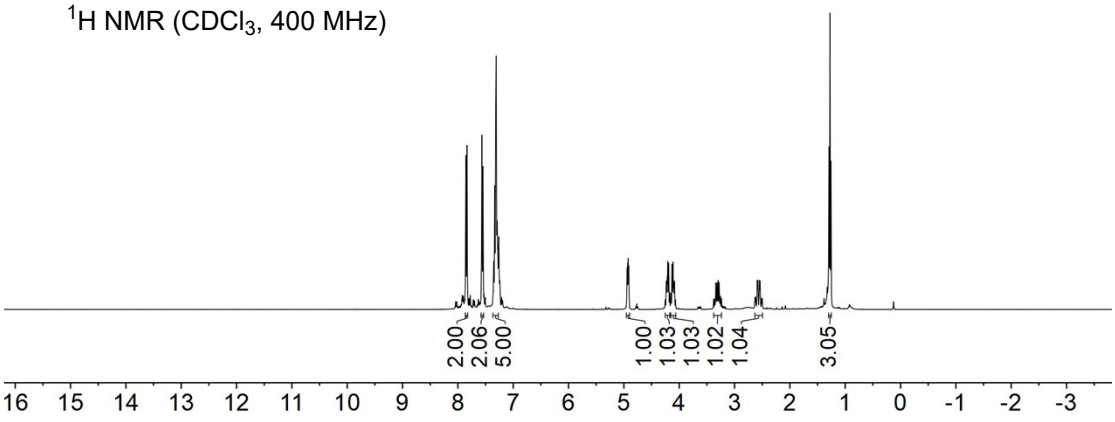


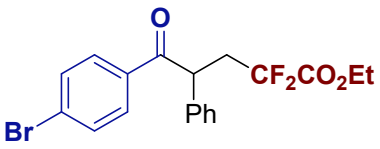




4j

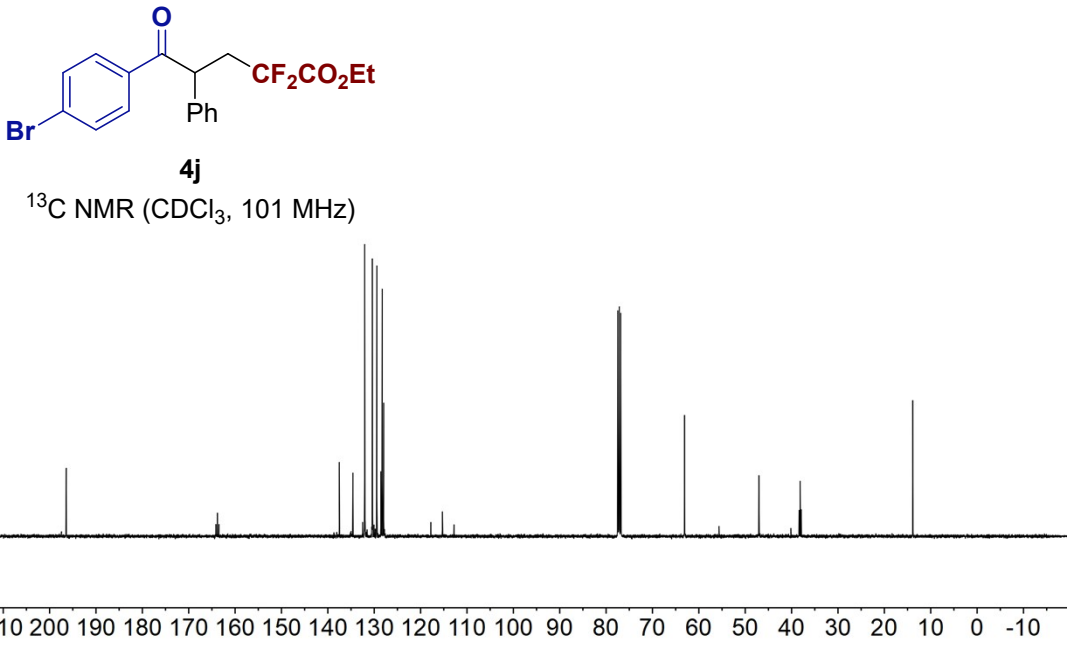
^{1}H NMR ($CDCl_3$, 400 MHz)





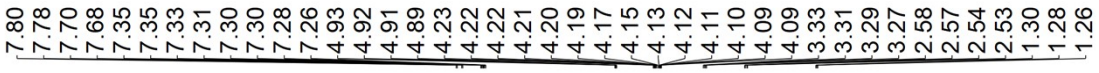
4j

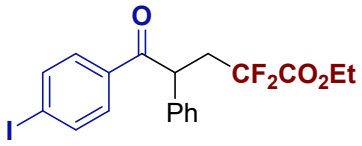
^{19}F NMR ($CDCl_3$, 376 MHz)



4j

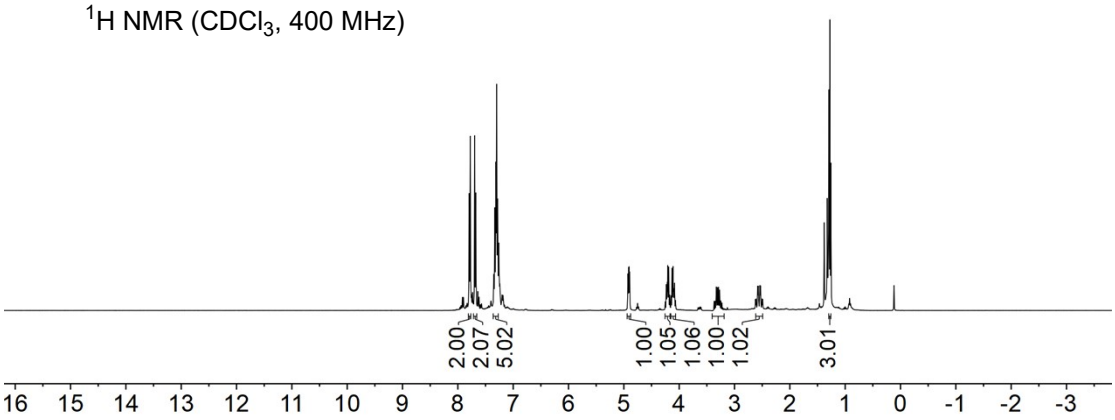
^{13}C NMR ($CDCl_3$, 101 MHz)

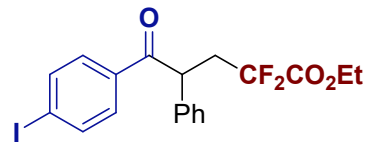




4k

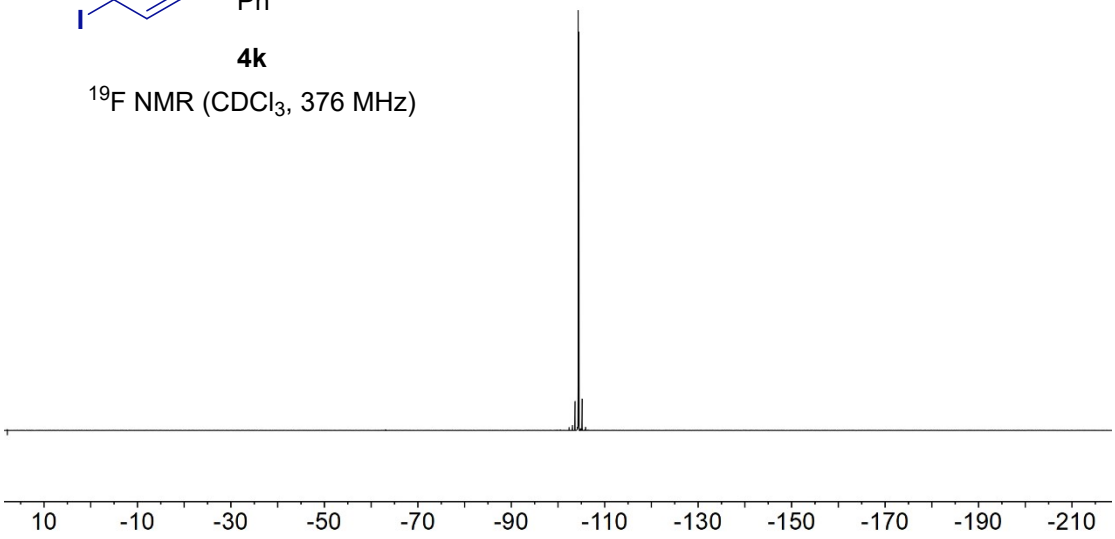
^{1}H NMR ($CDCl_3$, 400 MHz)

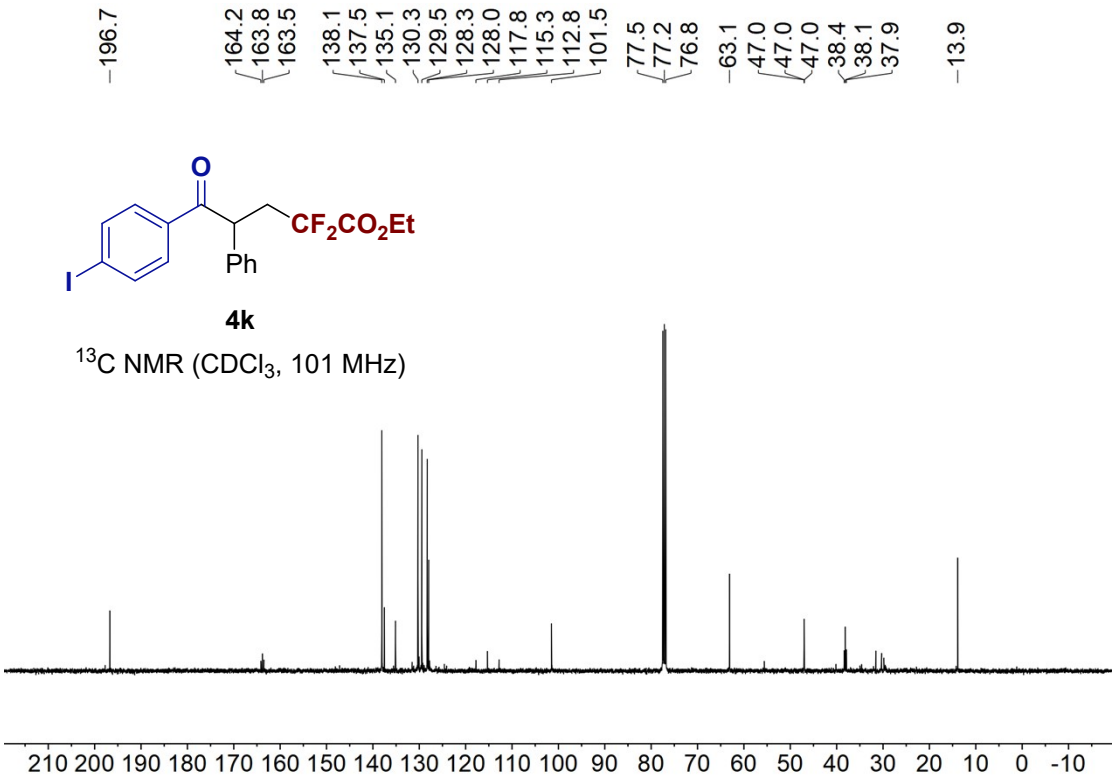




4k

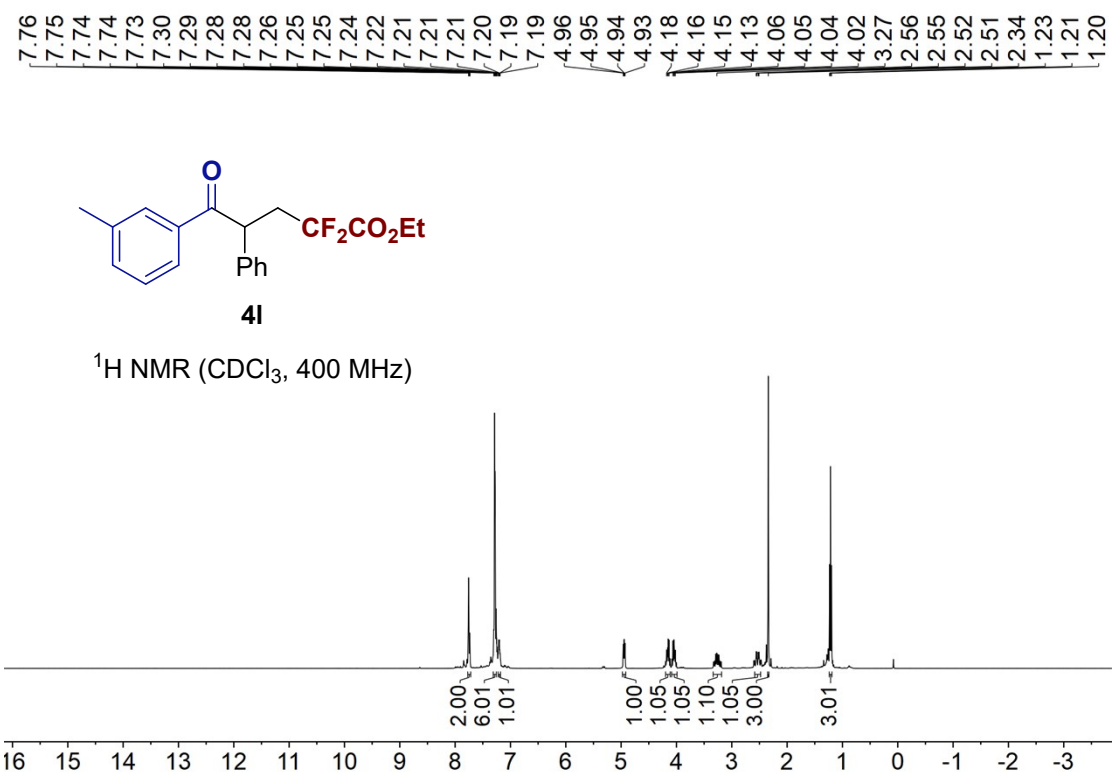
^{19}F NMR ($CDCl_3$, 376 MHz)





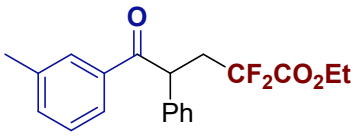
4k

^{13}C NMR ($CDCl_3$, 101 MHz)



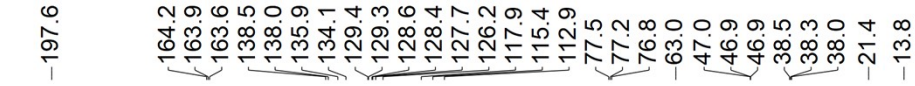
4l

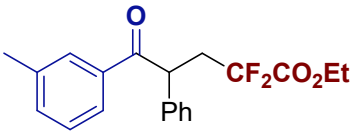
^{1}H NMR ($CDCl_3$, 400 MHz)



4l

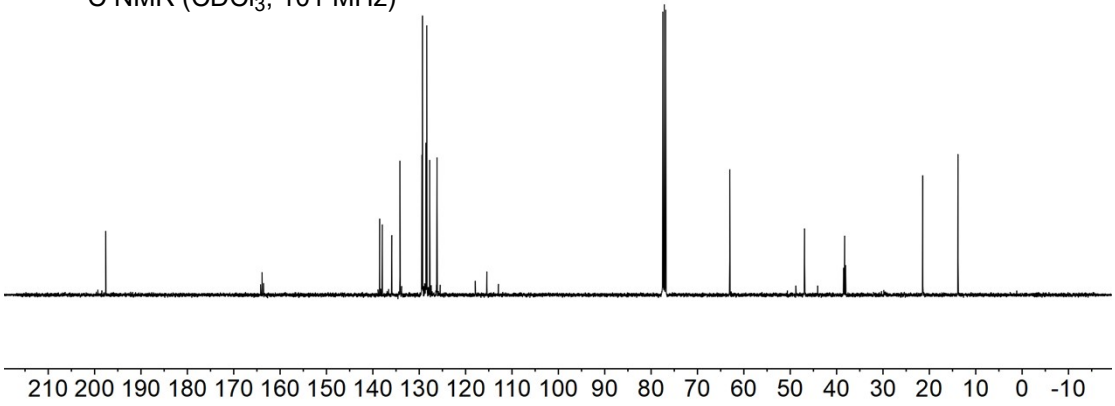
^{19}F NMR ($CDCl_3$, 376 MHz)

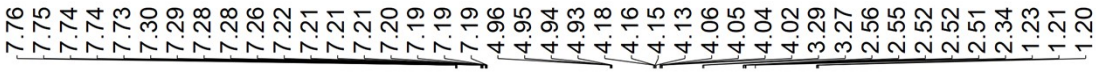


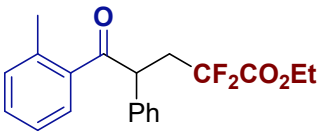


4l

^{13}C NMR ($CDCl_3$, 101 MHz)

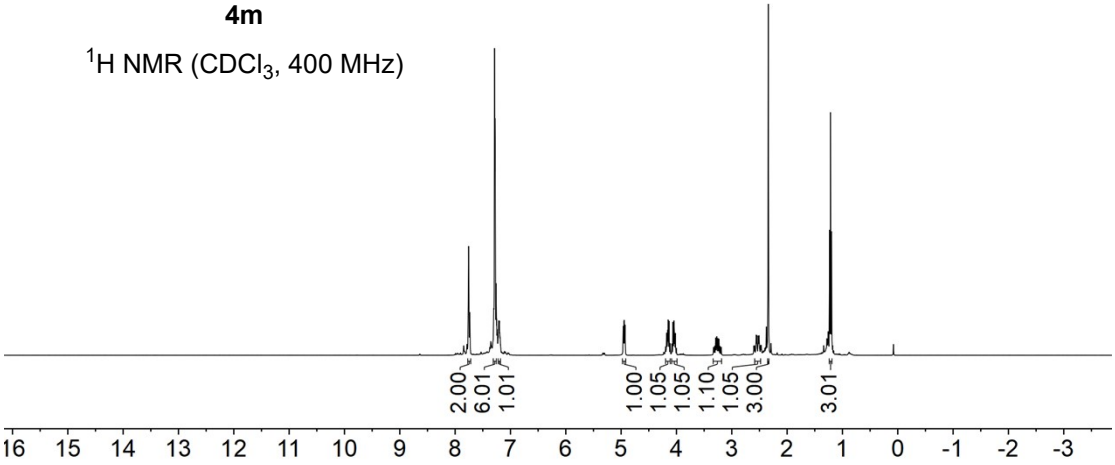


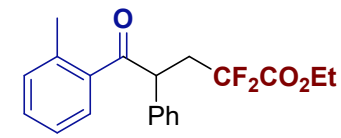




4m

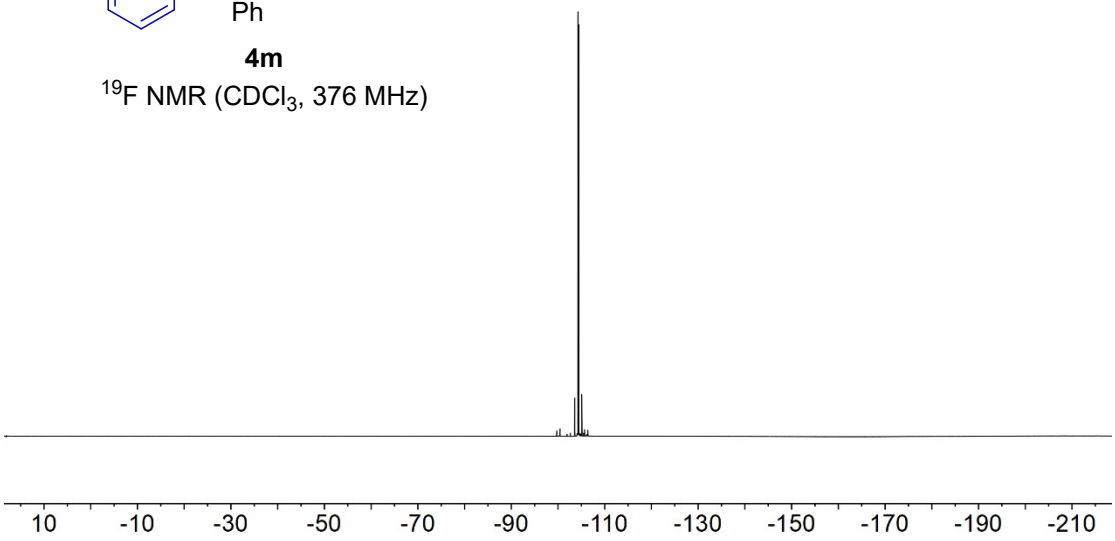
^{1}H NMR ($CDCl_3$, 400 MHz)

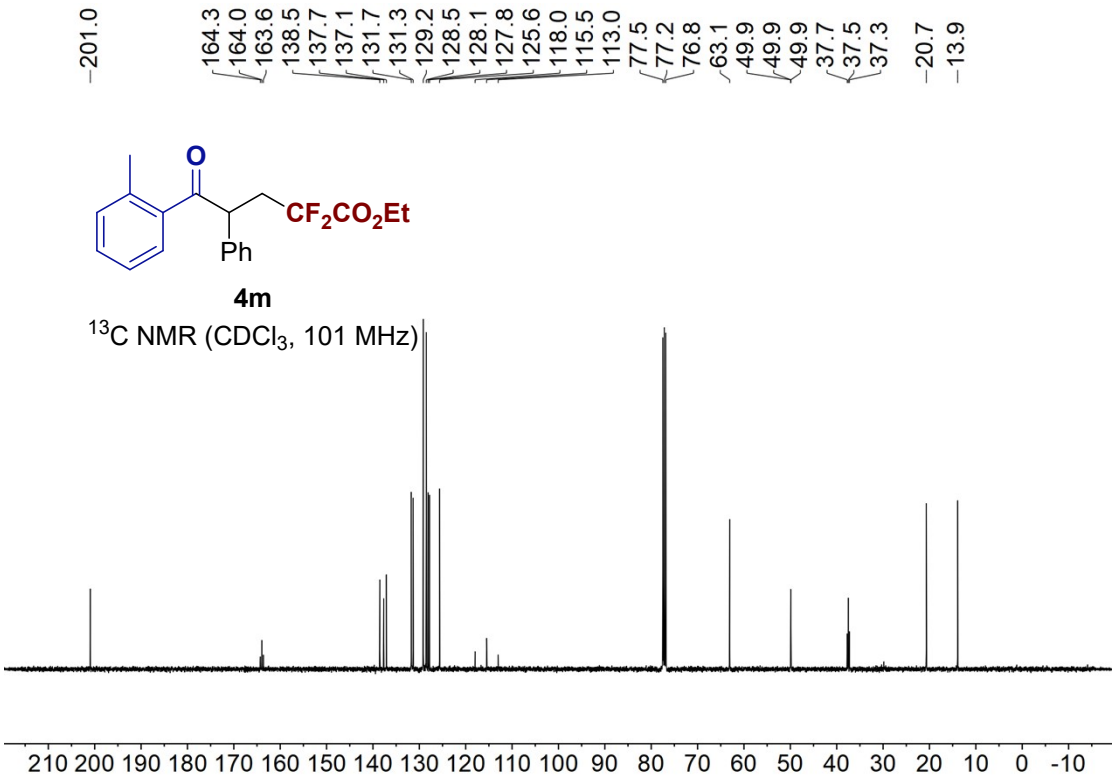




4m

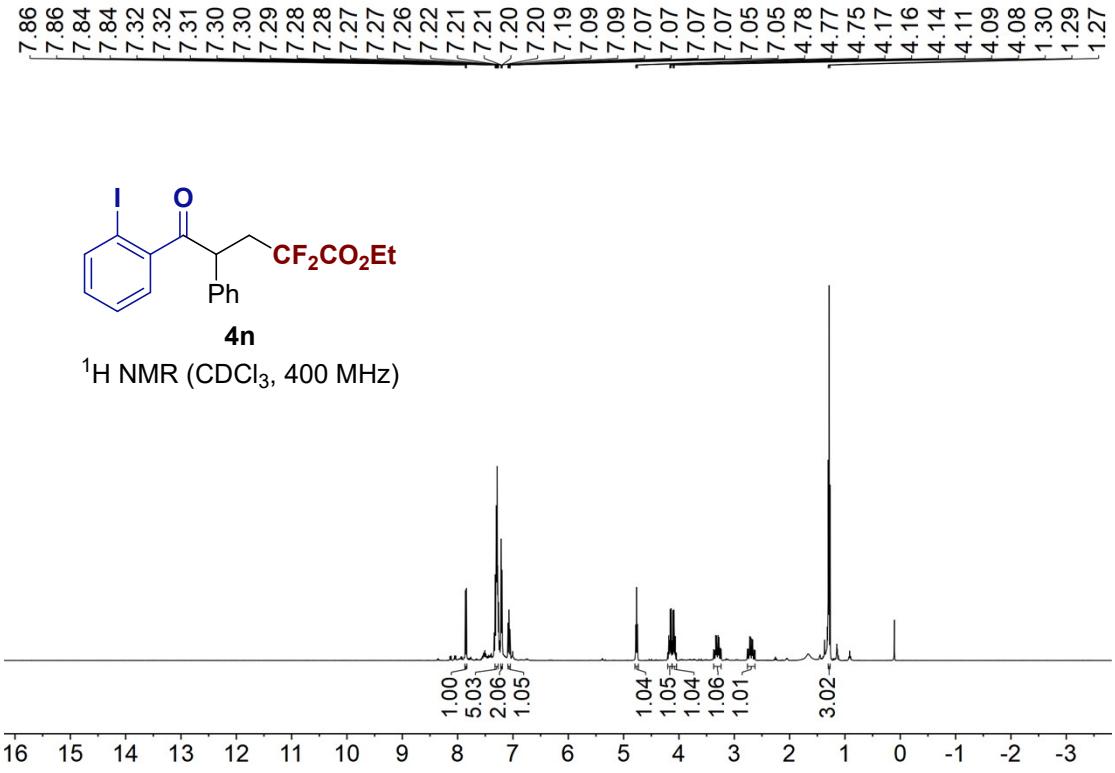
^{19}F NMR ($CDCl_3$, 376 MHz)





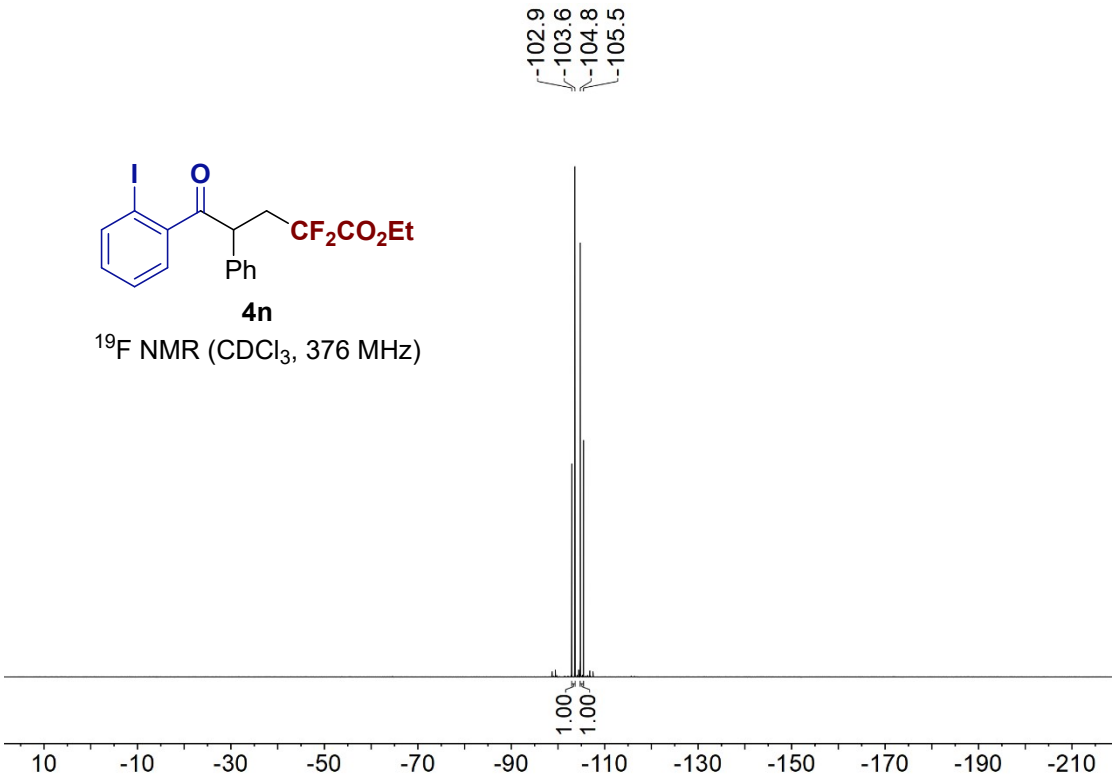
4m

^{13}C NMR ($CDCl_3$, 101 MHz)



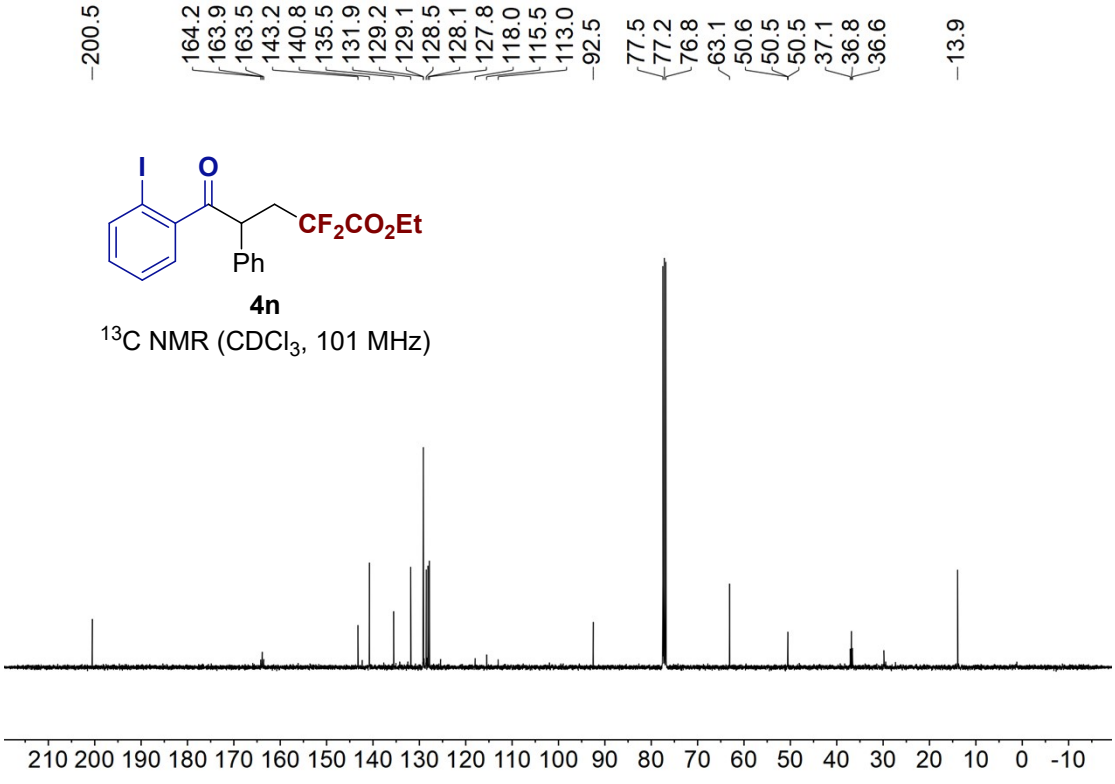
4n

^{1}H NMR ($CDCl_3$, 400 MHz)



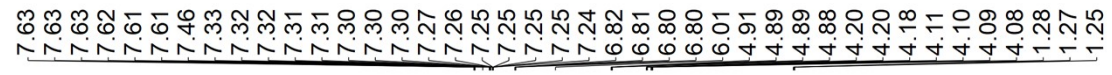
4n

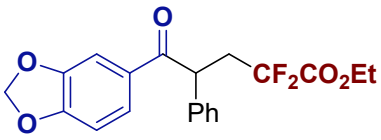
^{19}F NMR ($CDCl_3$, 376 MHz)



4n

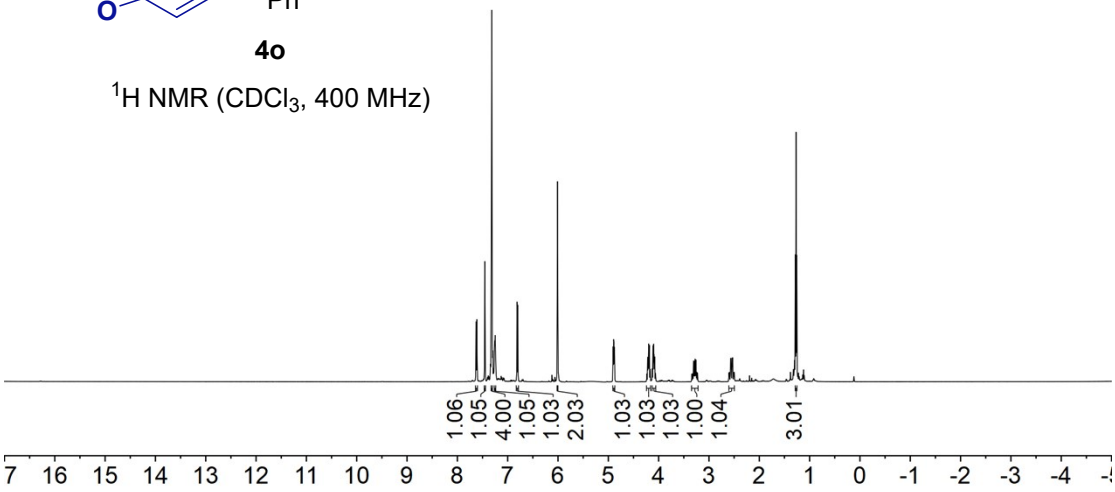
^{13}C NMR ($CDCl_3$, 101 MHz)

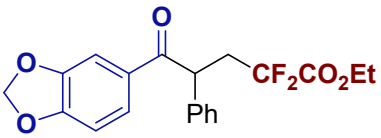




4o

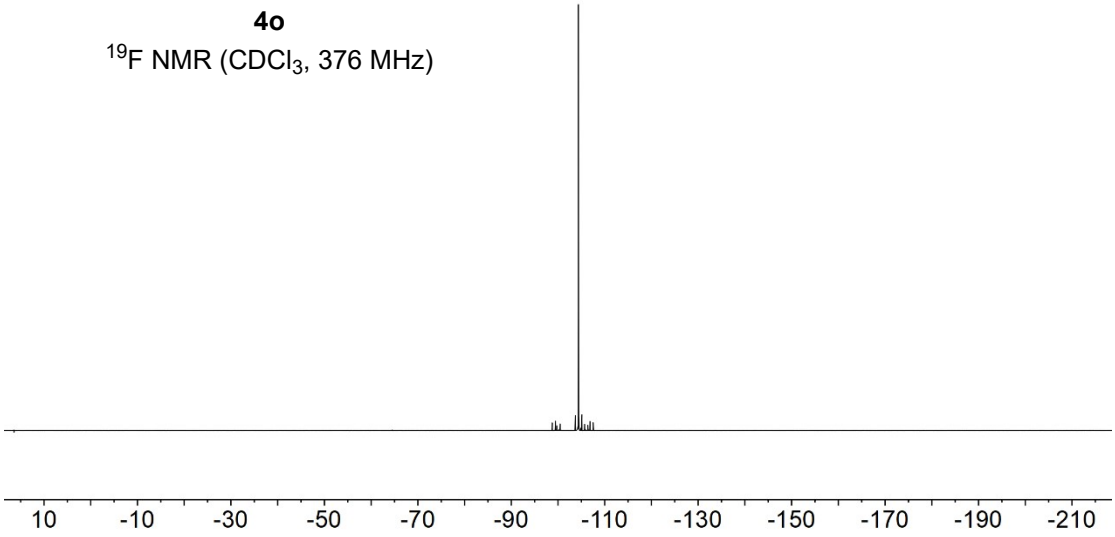
^{1}H NMR ($CDCl_3$, 400 MHz)

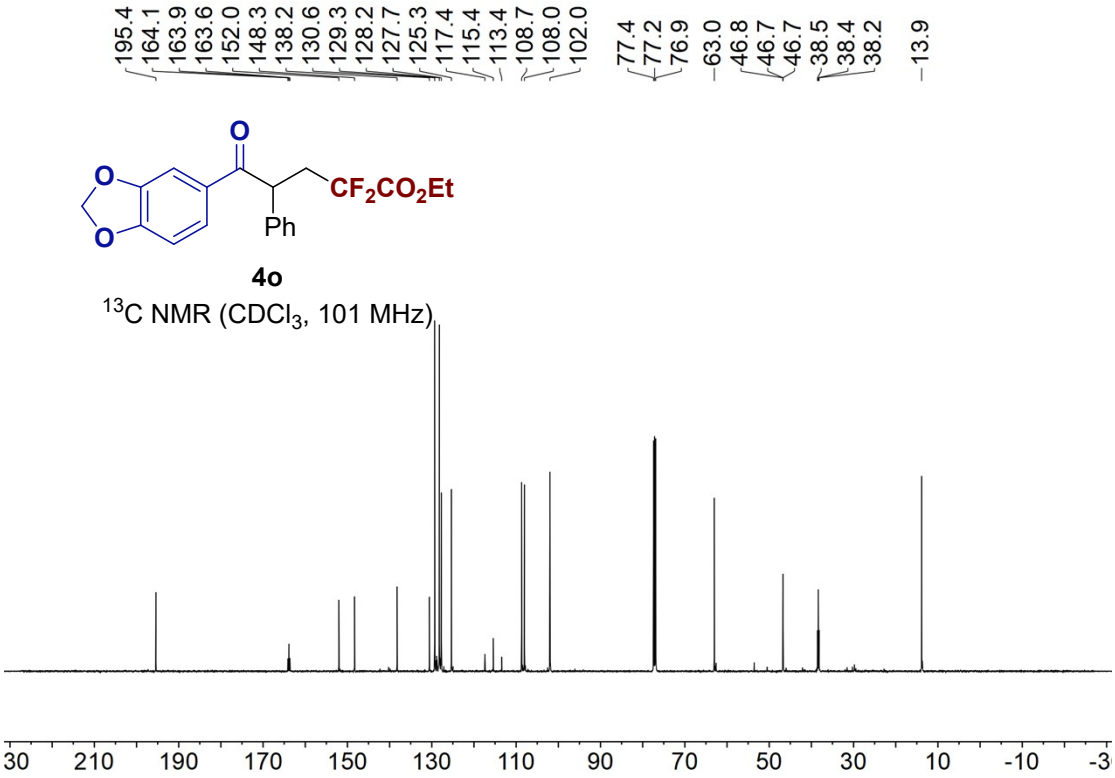




4o

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

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38.5
38.4
38.2
13.9
O
O
O
CF2CO2Et
Ph
4o
13C NMR (CDCl3, 101 MHz)
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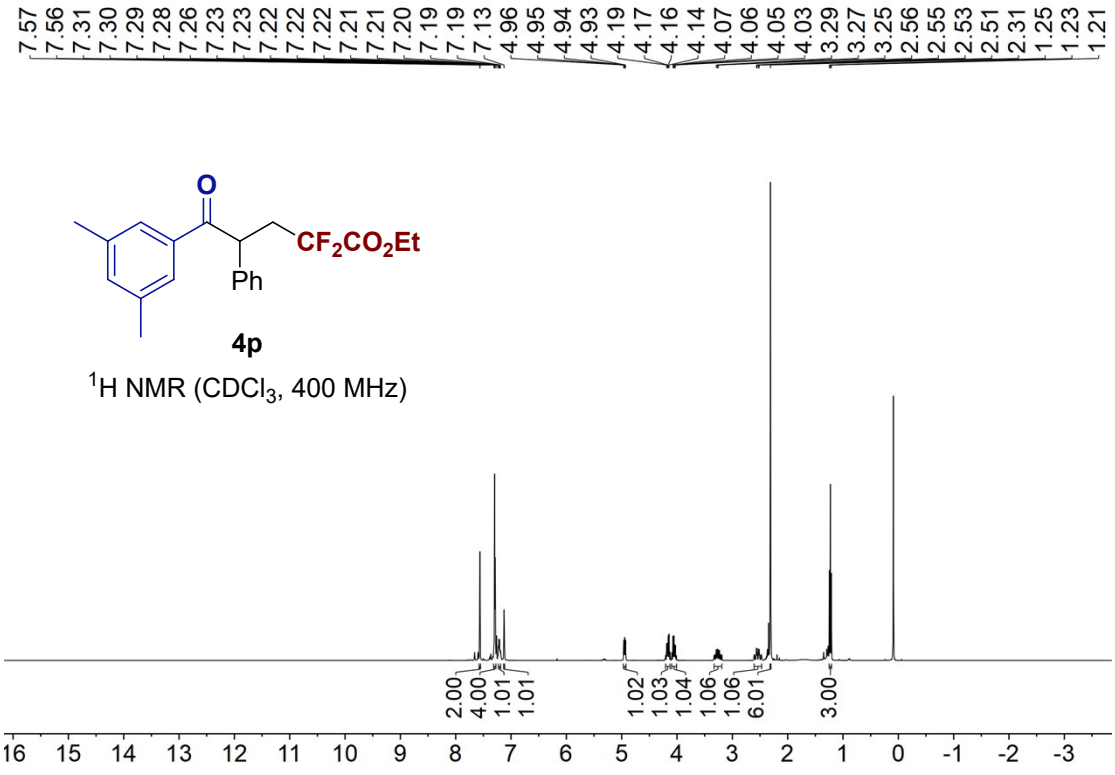
-10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2.56
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2.53
2.51
2.31
1.25
1.23
1.21
O
CF2CO2Et
Ph
4p
1H NMR (CDCl3, 400 MHz)
2.00
4.00
1.01
1.01
1.02
1.03
1.04
1.06
1.06
6.01
3.00
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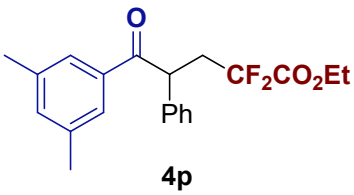
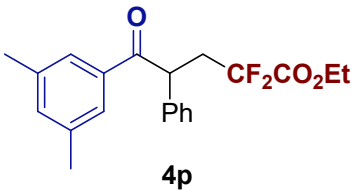


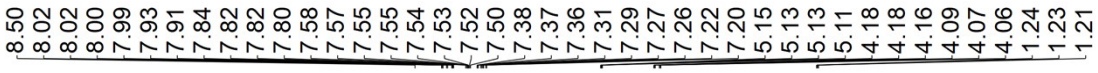
4p

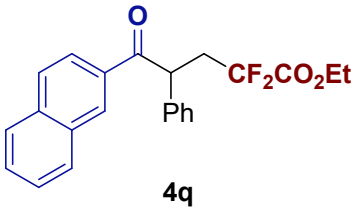
^{19}F NMR ($CDCl_3$, 376 MHz)



4p

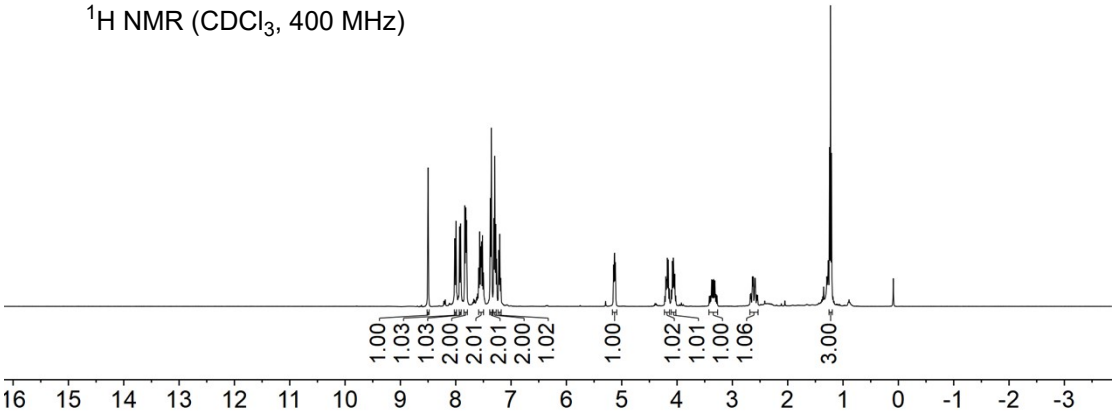
^{13}C NMR ($CDCl_3$, 101 MHz)





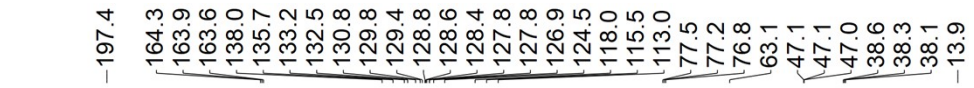
4q

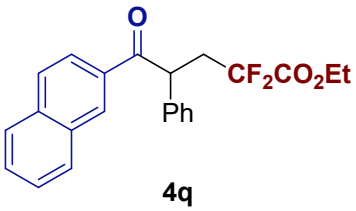
^{1}H NMR ($CDCl_3$, 400 MHz)



4q

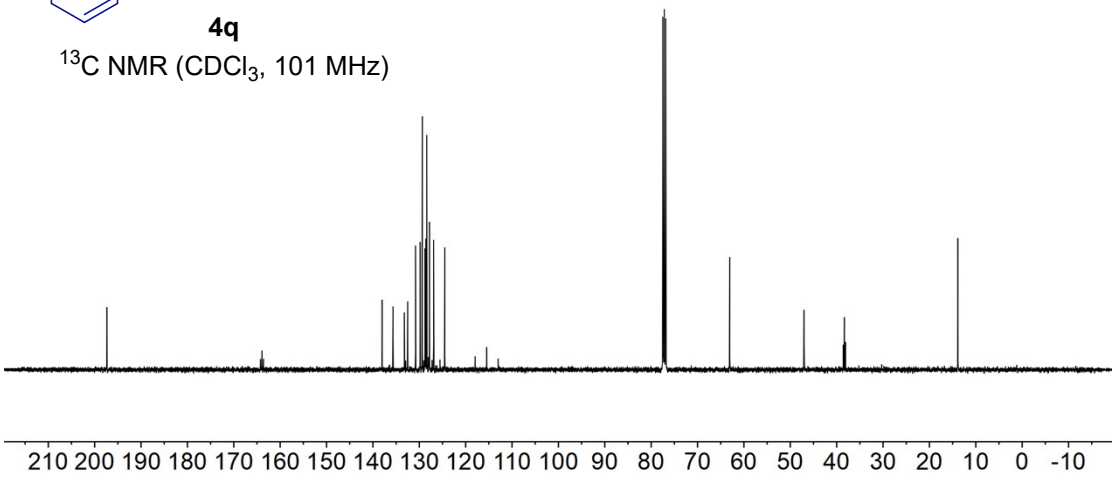
^{19}F NMR ($CDCl_3$, 376 MHz)

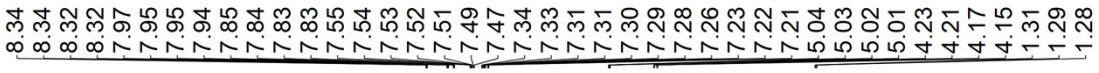


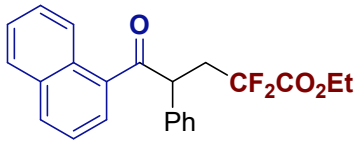


4q

^{13}C NMR ($CDCl_3$, 101 MHz)

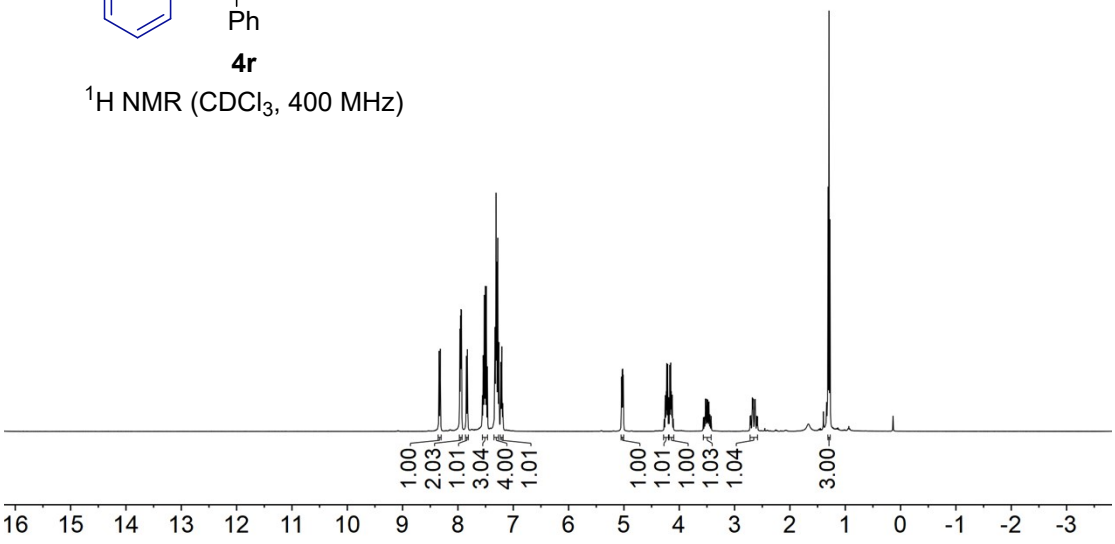


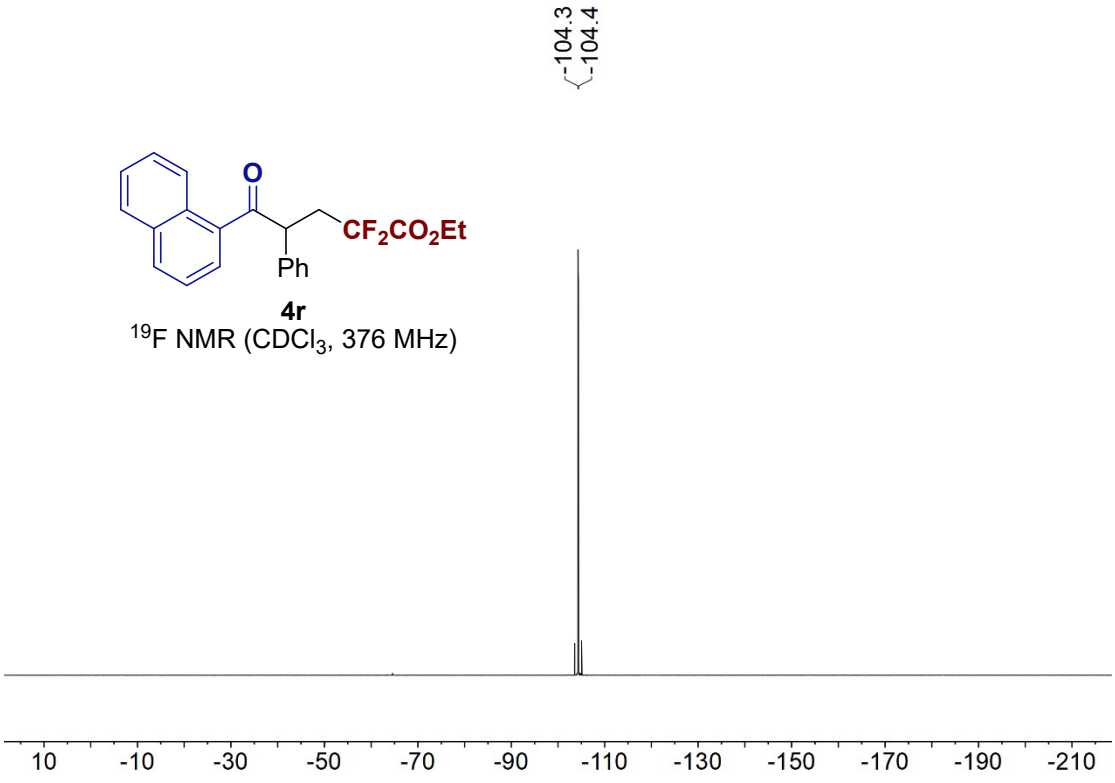




4r

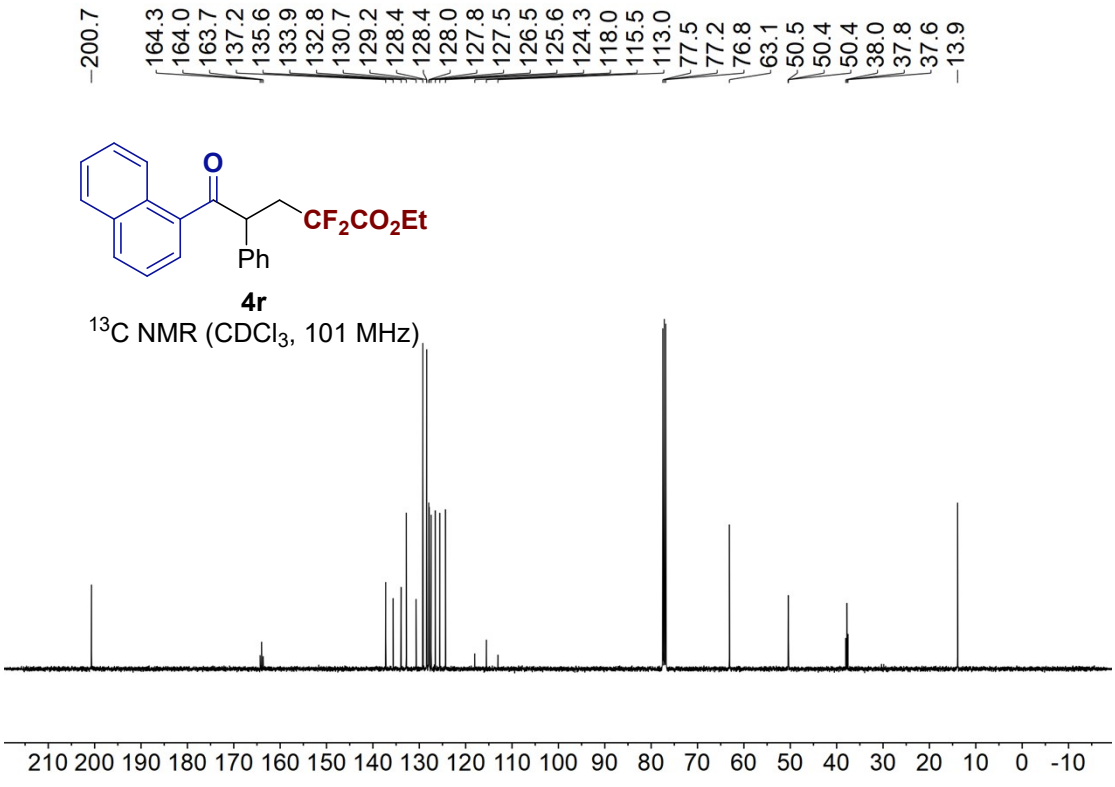
^{1}H NMR ($CDCl_3$, 400 MHz)





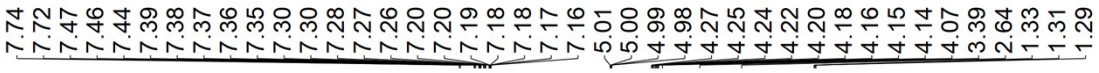
4r

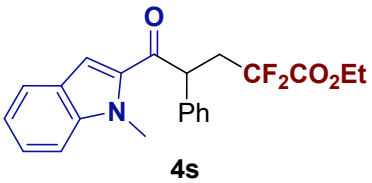
^{19}F NMR ($CDCl_3$, 376 MHz)



4r

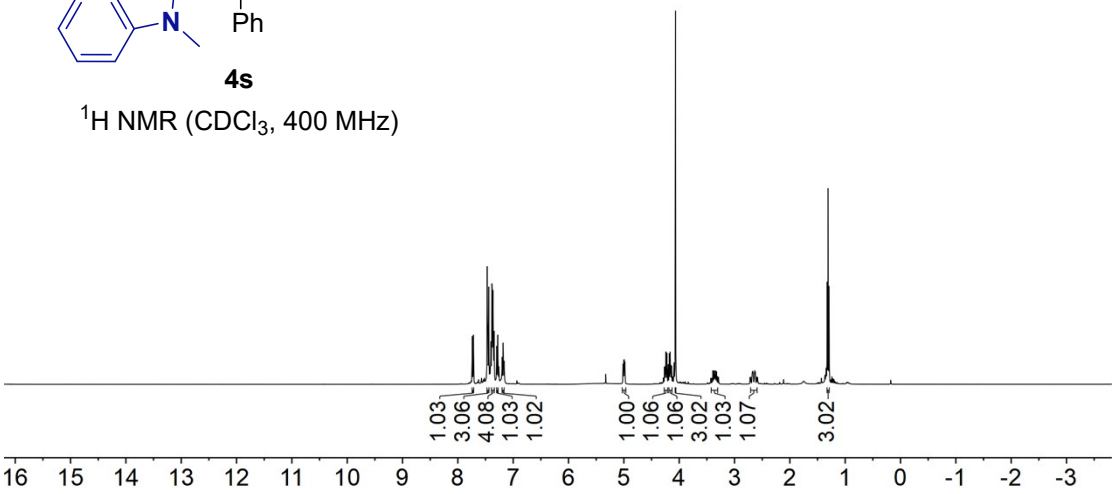
^{13}C NMR ($CDCl_3$, 101 MHz)

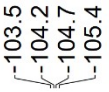


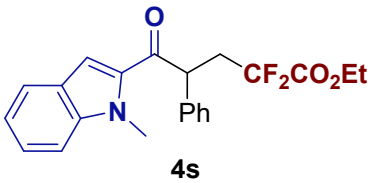


4s

^{1}H NMR ($CDCl_3$, 400 MHz)

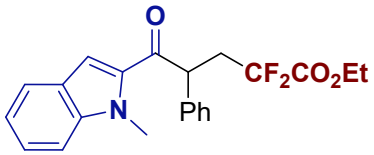






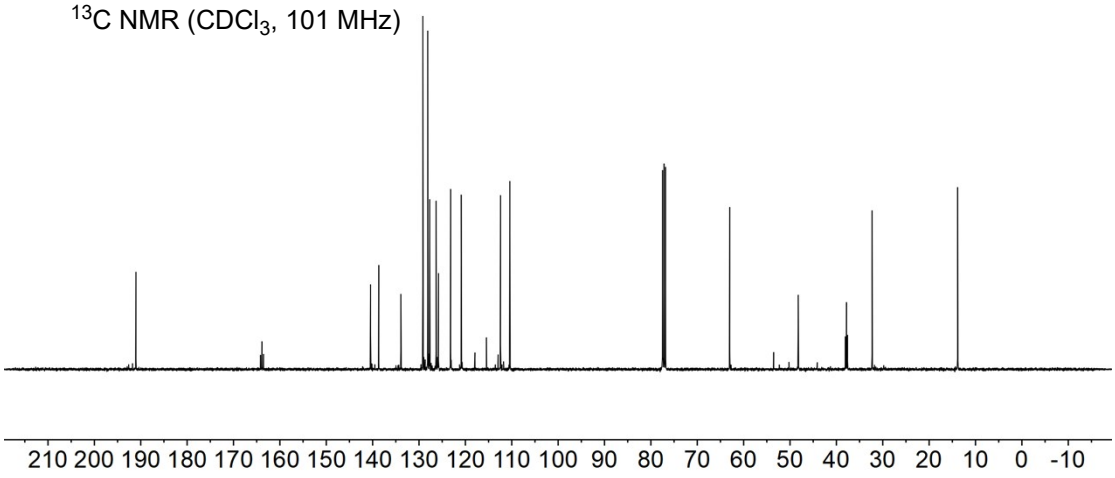
4s

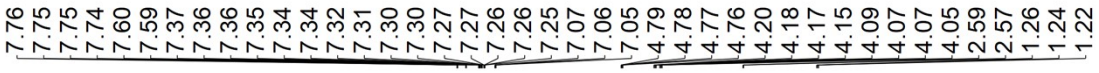
^{19}F NMR ($CDCl_3$, 376 MHz)

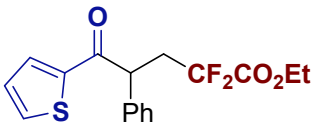


4s

^{13}C NMR ($CDCl_3$, 101 MHz)

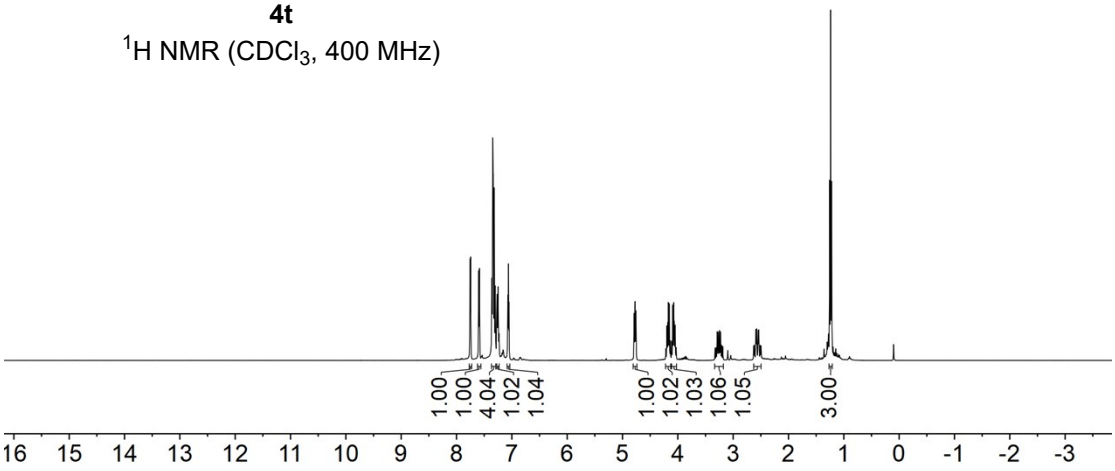


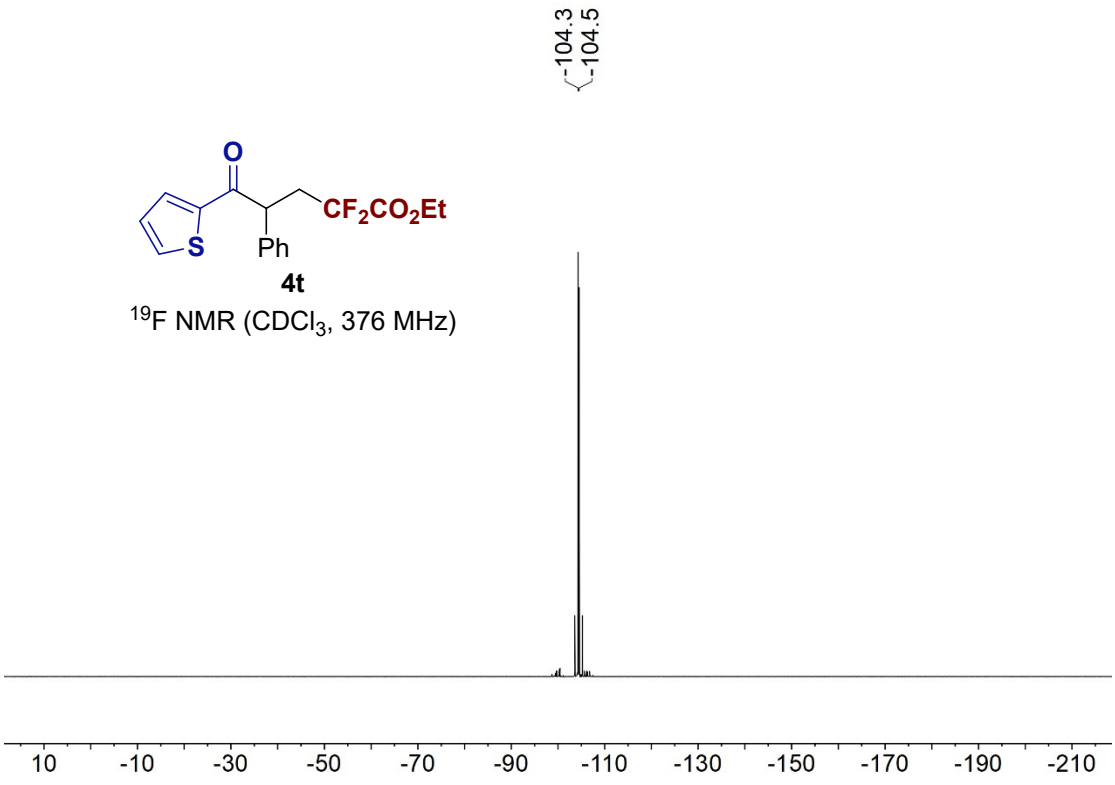




4t

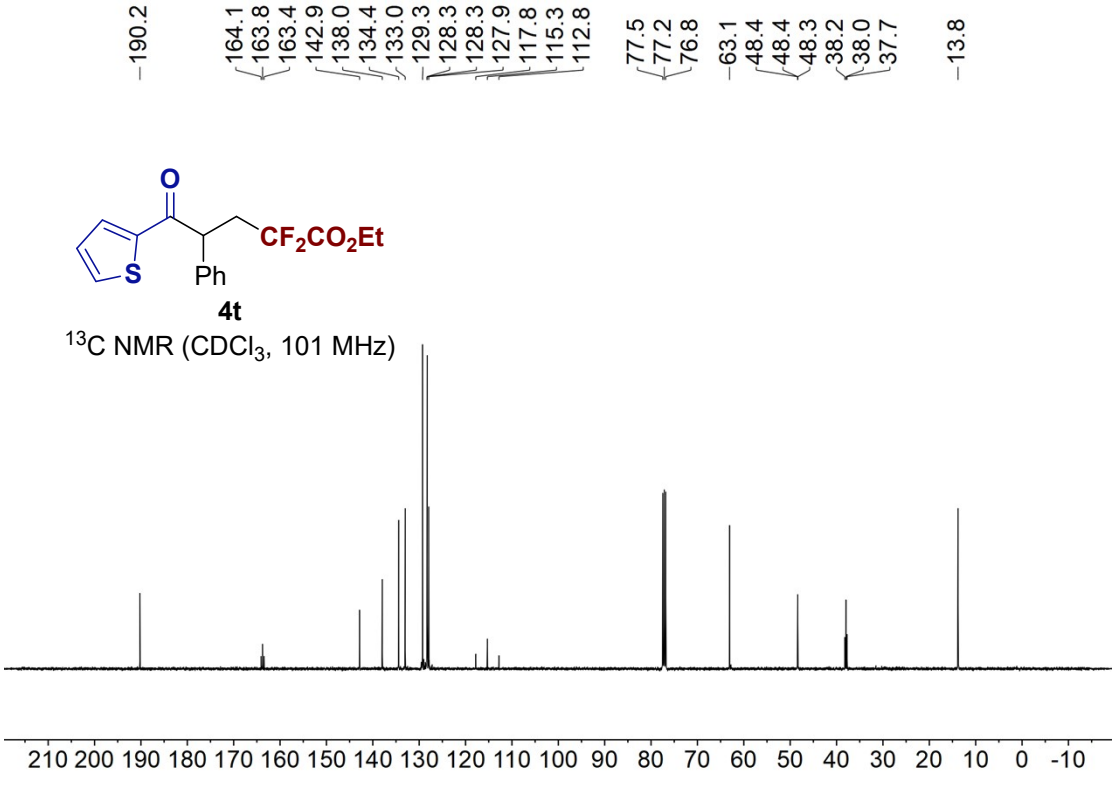
^{1}H NMR ($CDCl_3$, 400 MHz)





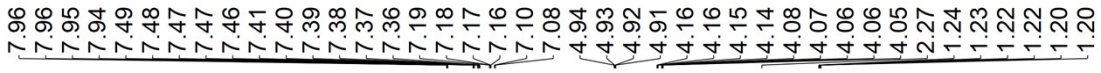
4t

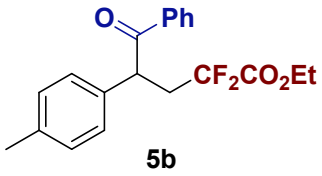
^{19}F NMR ($CDCl_3$, 376 MHz)



4t

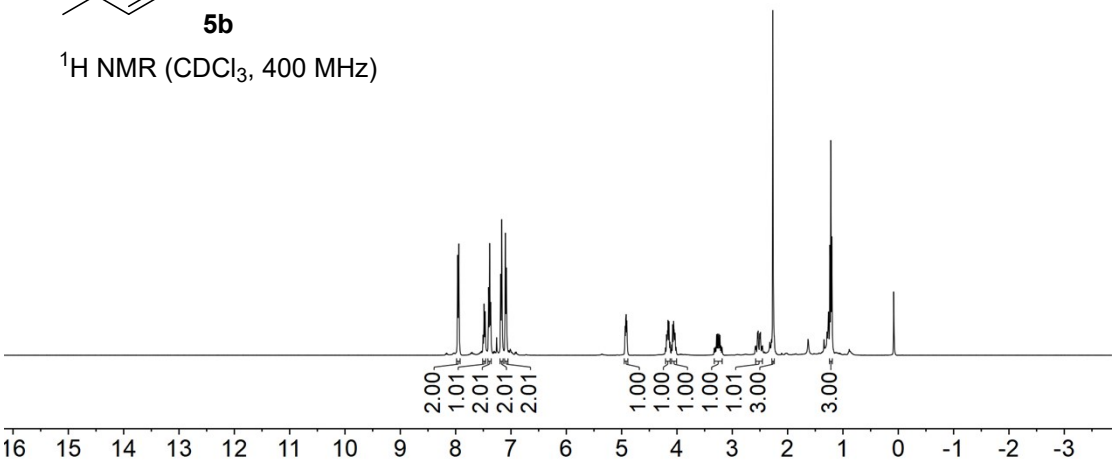
^{13}C NMR ($CDCl_3$, 101 MHz)

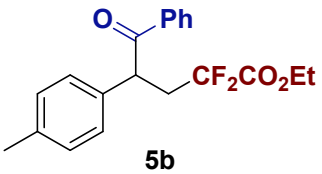




5b

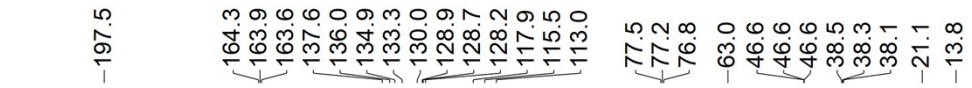
^{1}H NMR ($CDCl_3$, 400 MHz)

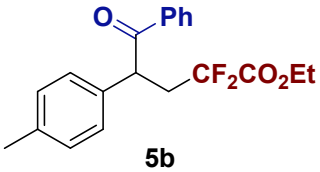




5b

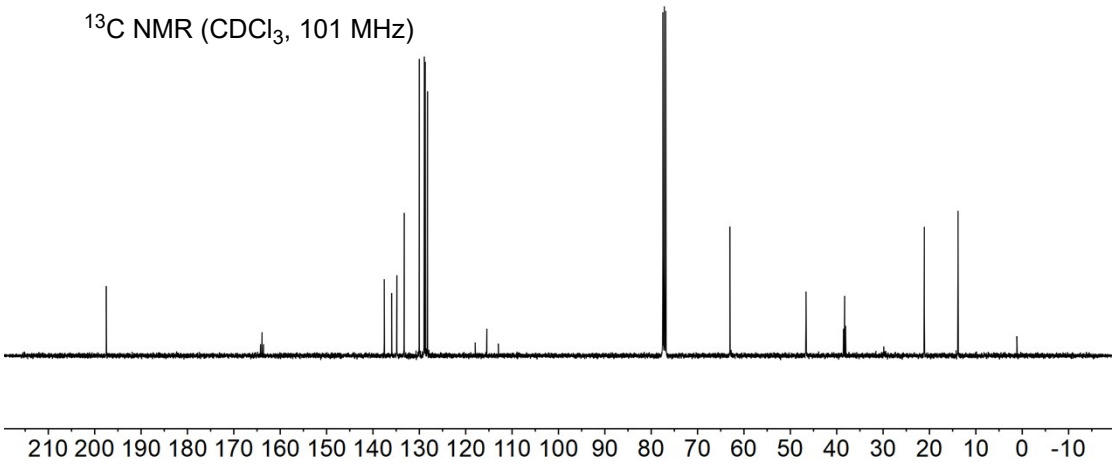
^{19}F NMR ($CDCl_3$, 376 MHz)

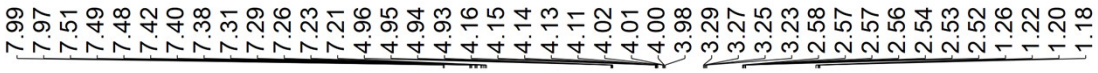


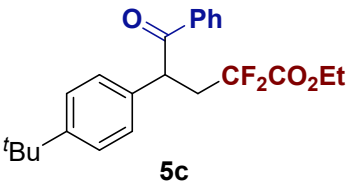


5b

^{13}C NMR ($CDCl_3$, 101 MHz)

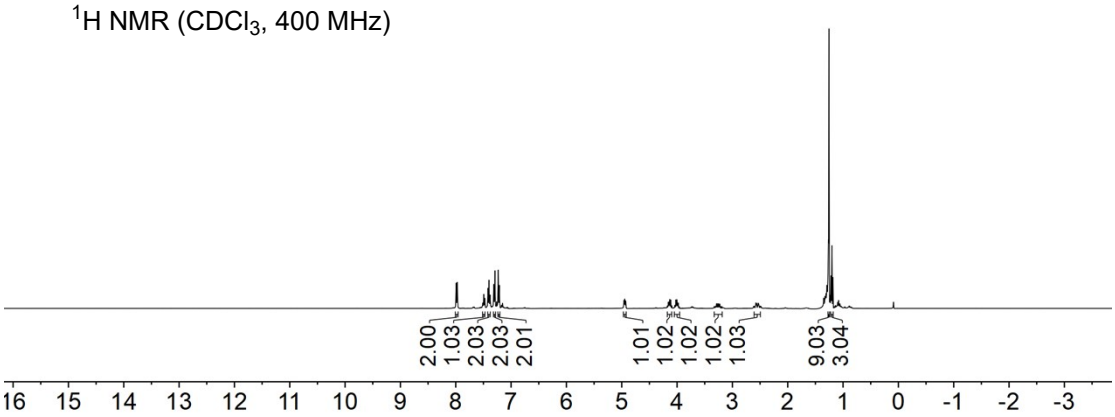


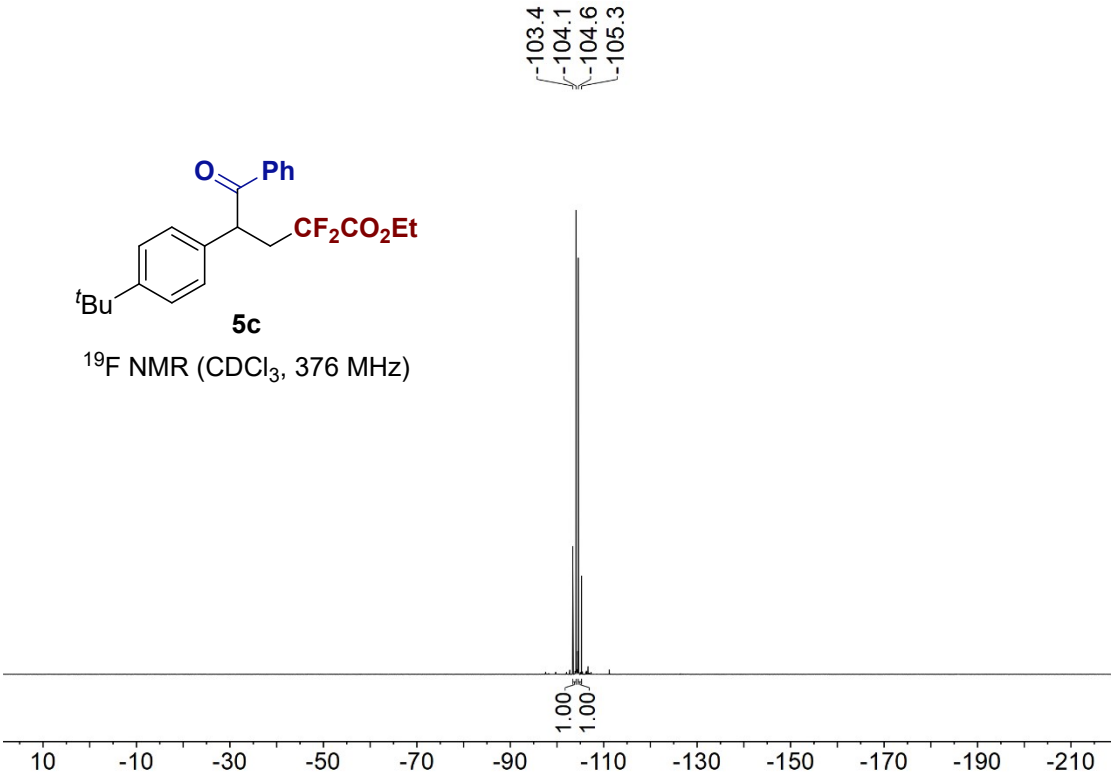




5c

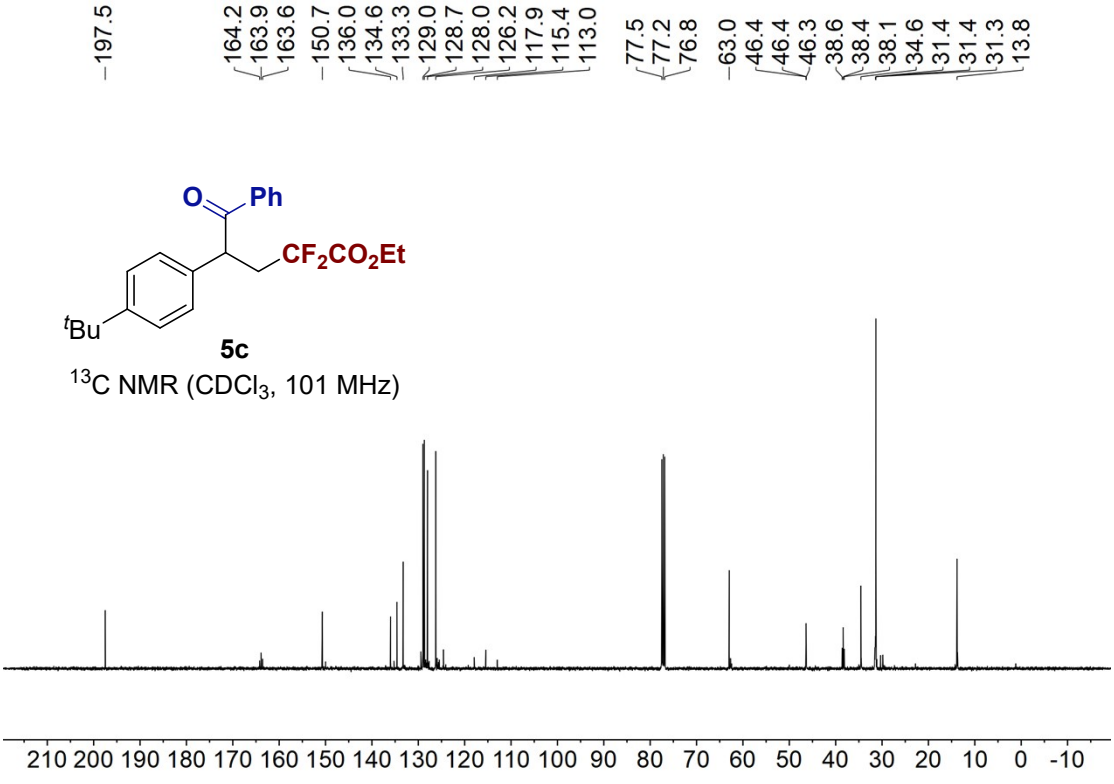
^{1}H NMR ($CDCl_3$, 400 MHz)





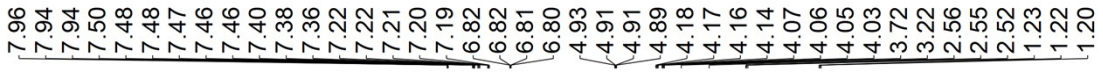
5c

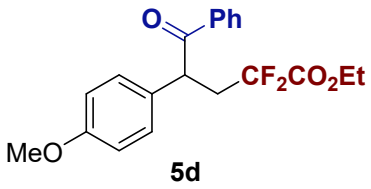
^{19}F NMR ($CDCl_3$, 376 MHz)



5c

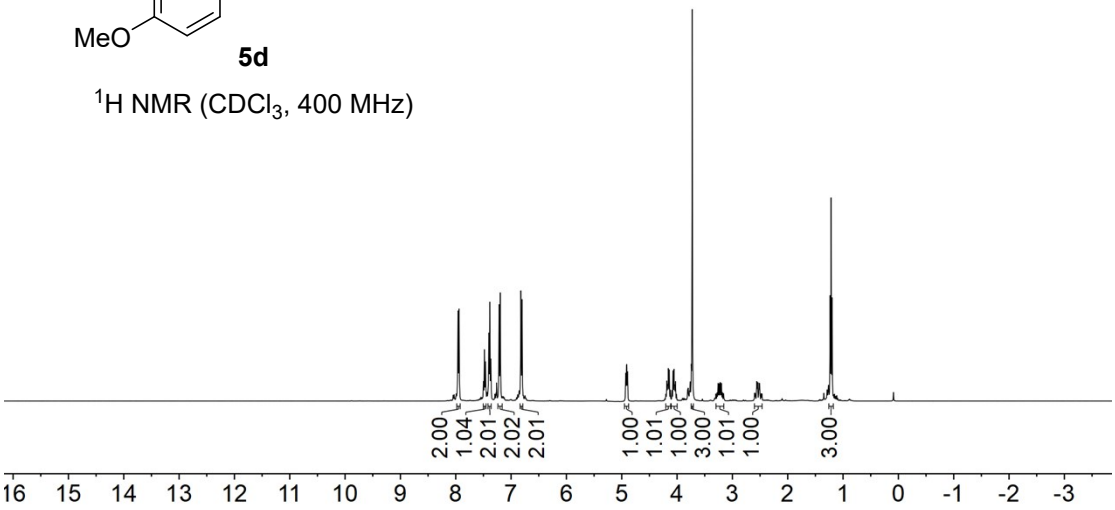
^{13}C NMR ($CDCl_3$, 101 MHz)

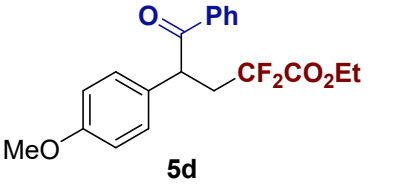




5d

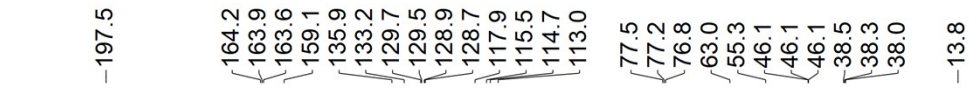
^{1}H NMR ($CDCl_3$, 400 MHz)

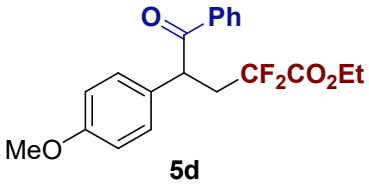




5d

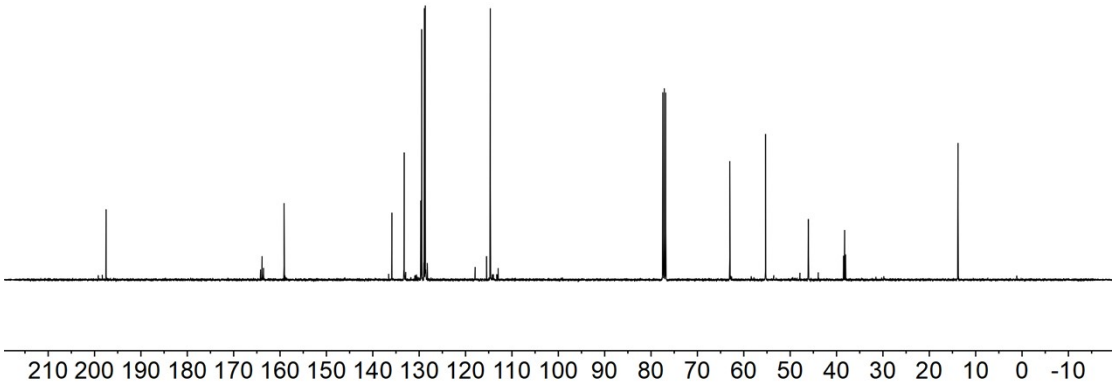
^{19}F NMR ($CDCl_3$, 376 MHz)

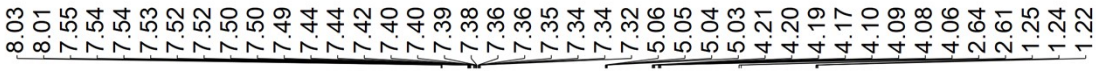


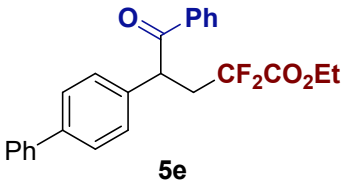


5d

^{13}C NMR ($CDCl_3$, 101 MHz)

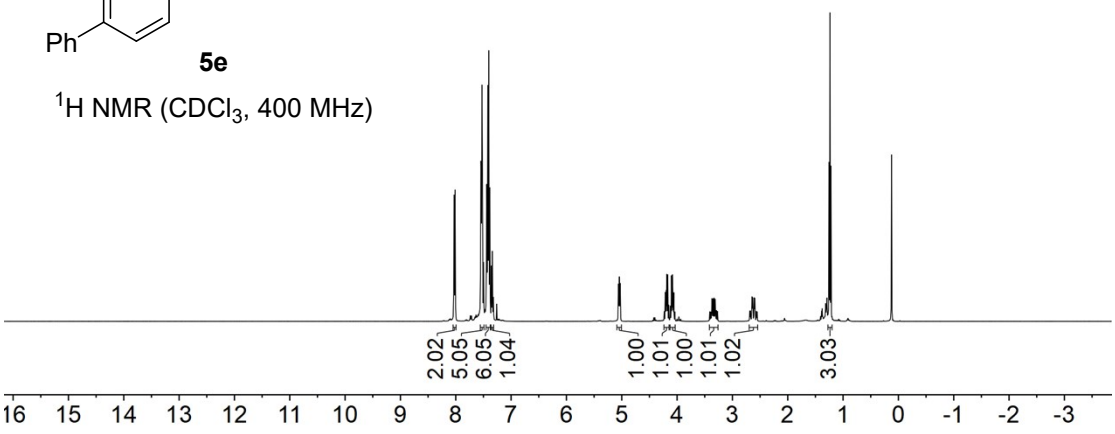


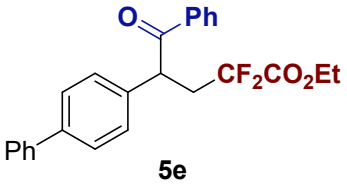




5e

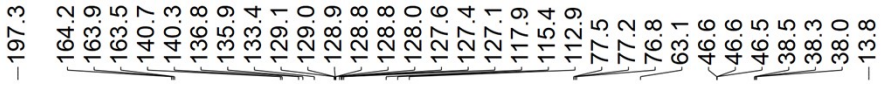
^{1}H NMR ($CDCl_3$, 400 MHz)

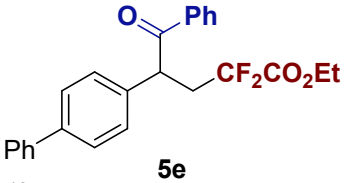




5e

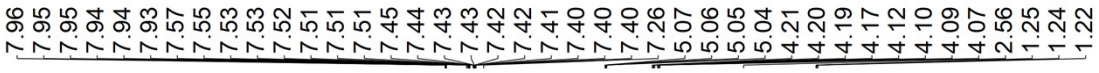
^{19}F NMR ($CDCl_3$, 376 MHz)

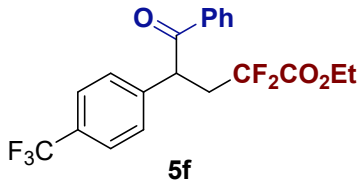




5e

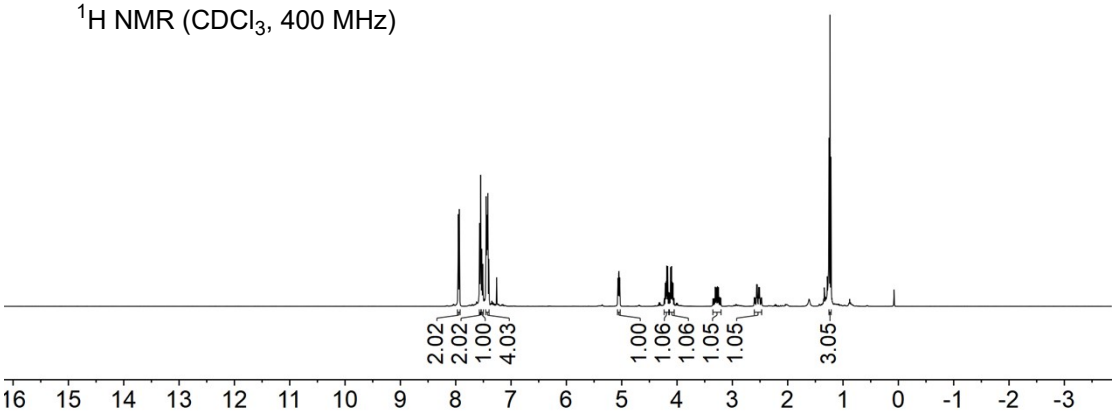
^{13}C NMR ($CDCl_3$, 101 MHz)

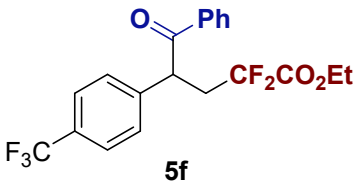




5f

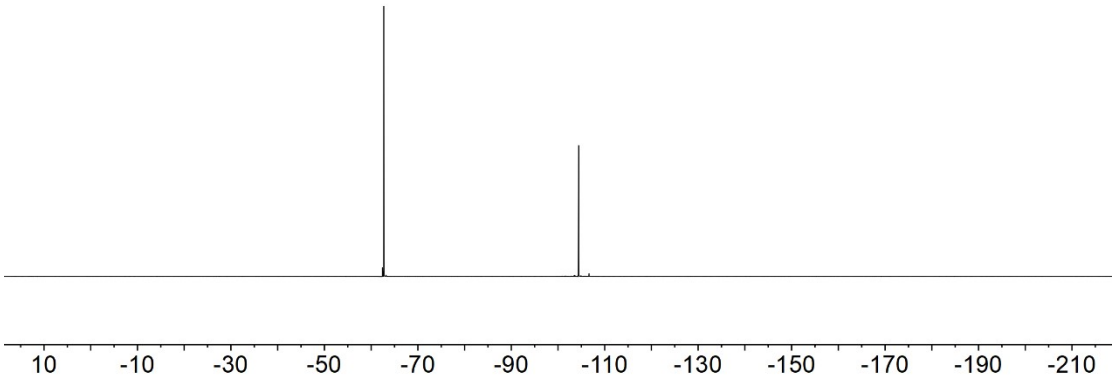
^{1}H NMR ($CDCl_3$, 400 MHz)

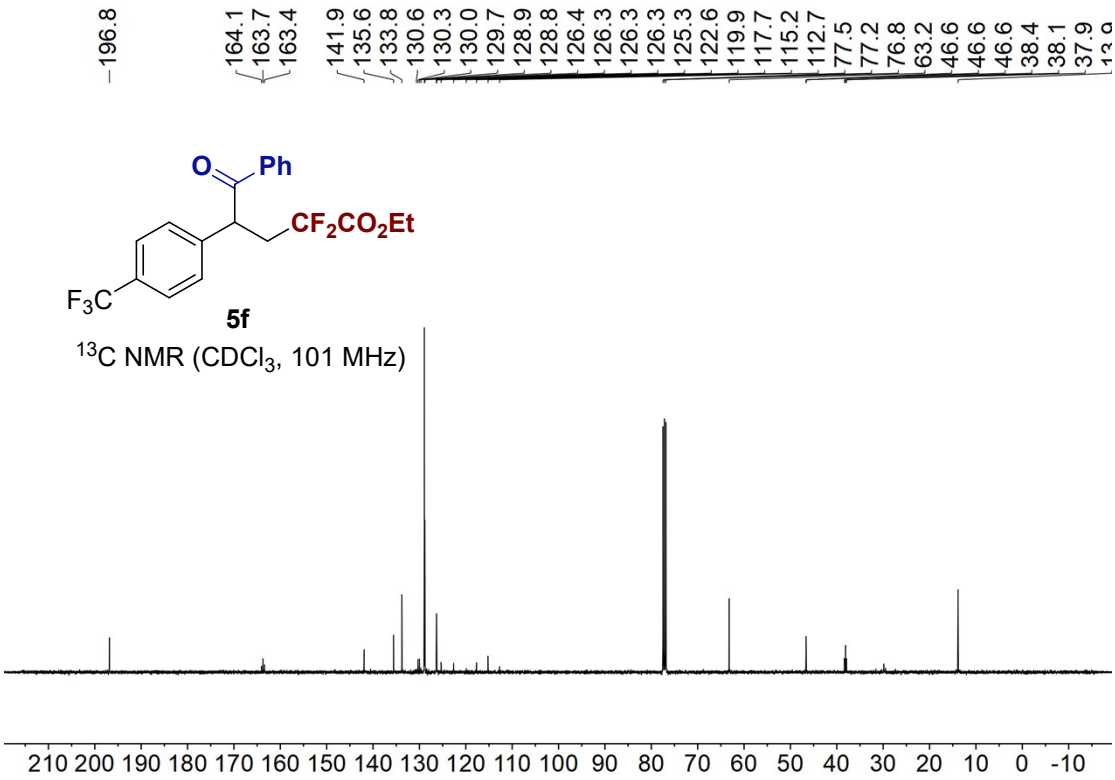




5f

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

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163.4
141.9
135.6
133.8
130.6
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130.0
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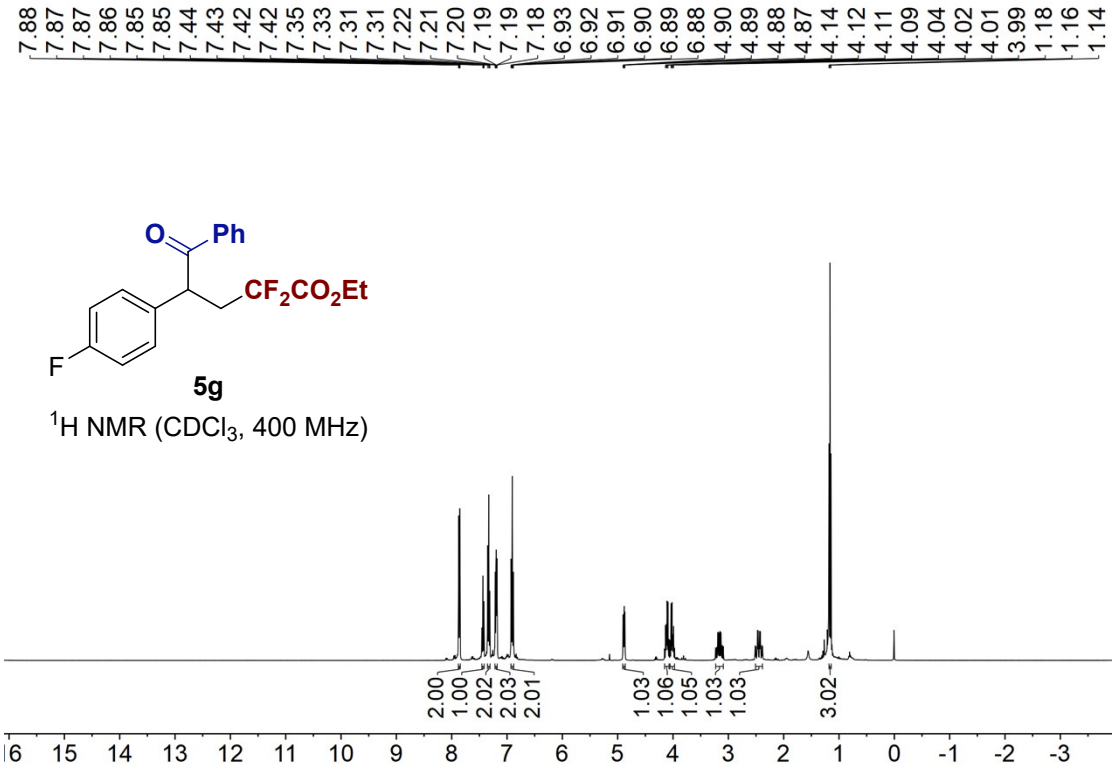
128.9
128.8
126.4
126.3
126.3
126.3
125.3
122.6
119.9
117.7
115.2
112.7
77.5
77.2
76.8
63.2
46.6
46.6
46.6
38.4
38.1
37.9
O
Ph
CF2CO2Et
F3C
5f
13C NMR (CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.88
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7.31
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7.19
7.19
7.18
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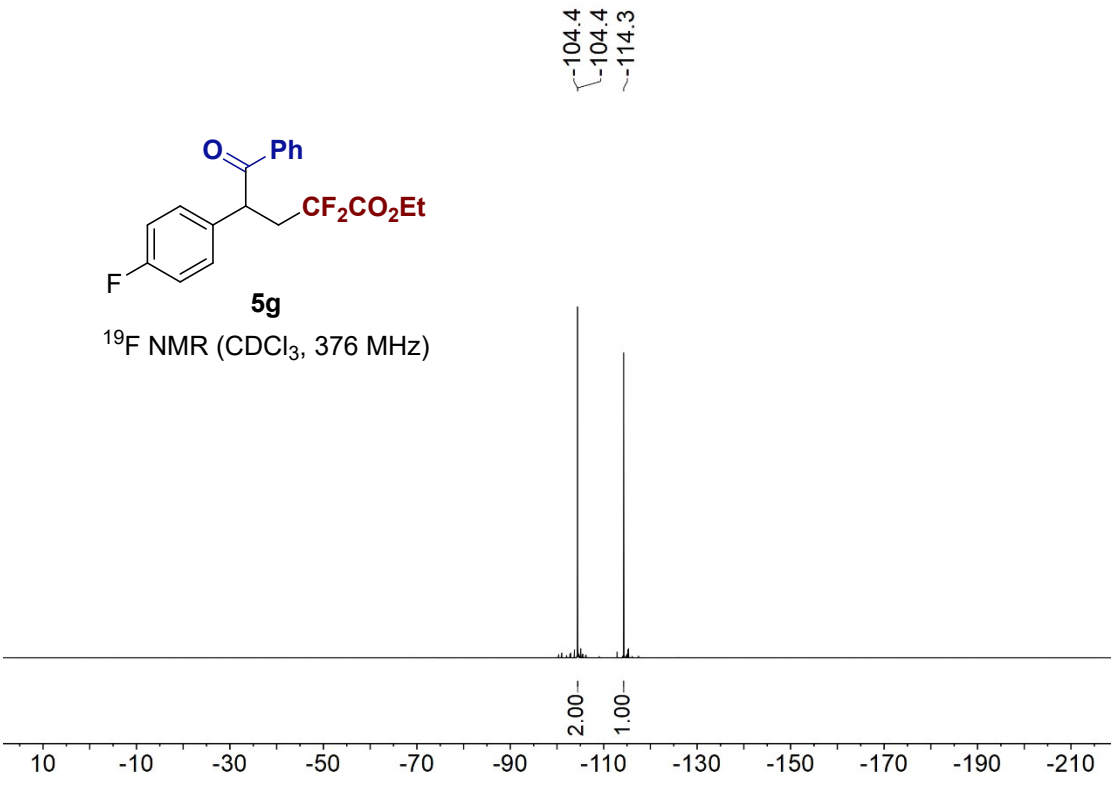
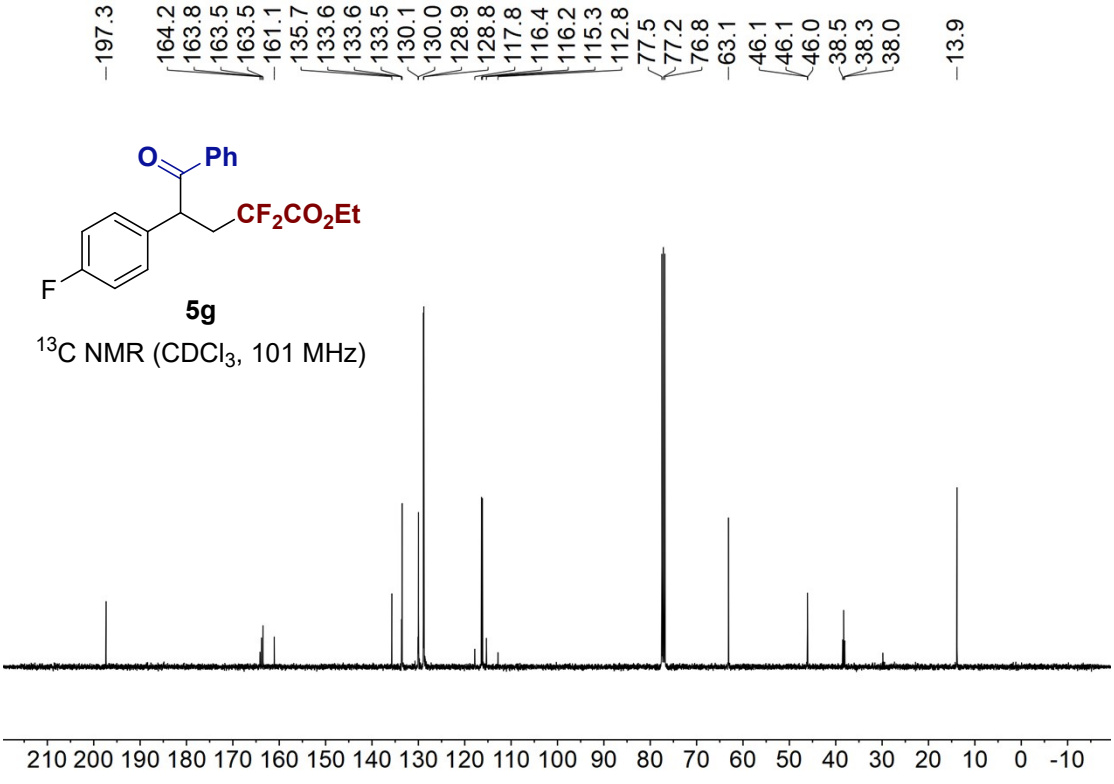
6.92
6.91
6.90
6.89
6.88
4.90
4.89
4.88
4.87
4.14
4.12
4.11
4.09
4.04
4.02
4.01
3.99
1.18
1.16
1.14
O
Ph
CF2CO2Et
F
5g
1H NMR (CDCl3, 400 MHz)
2.00
1.00
2.02
2.03
2.01
1.03
1.06
1.05
1.03
1.03
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3



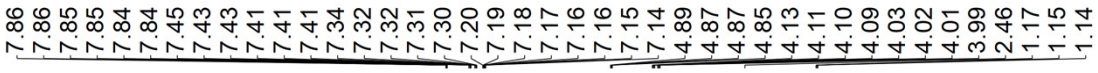
5g

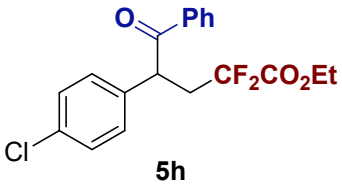
^{19}F NMR ($CDCl_3$, 376 MHz)



5g

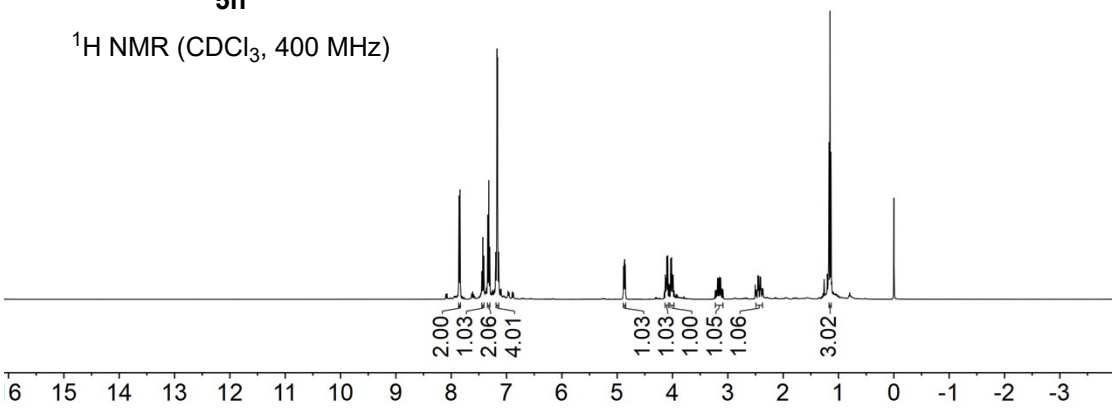
^{13}C NMR ($CDCl_3$, 101 MHz)

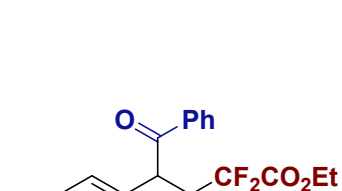




5h

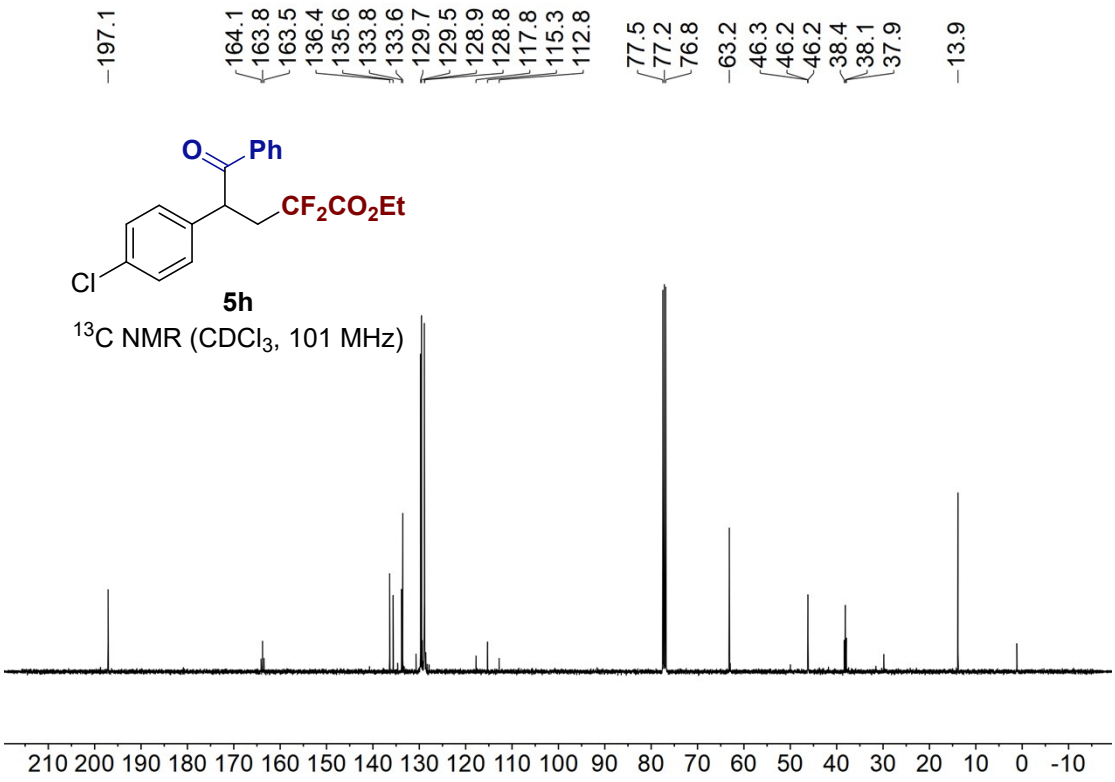
^{1}H NMR ($CDCl_3$, 400 MHz)





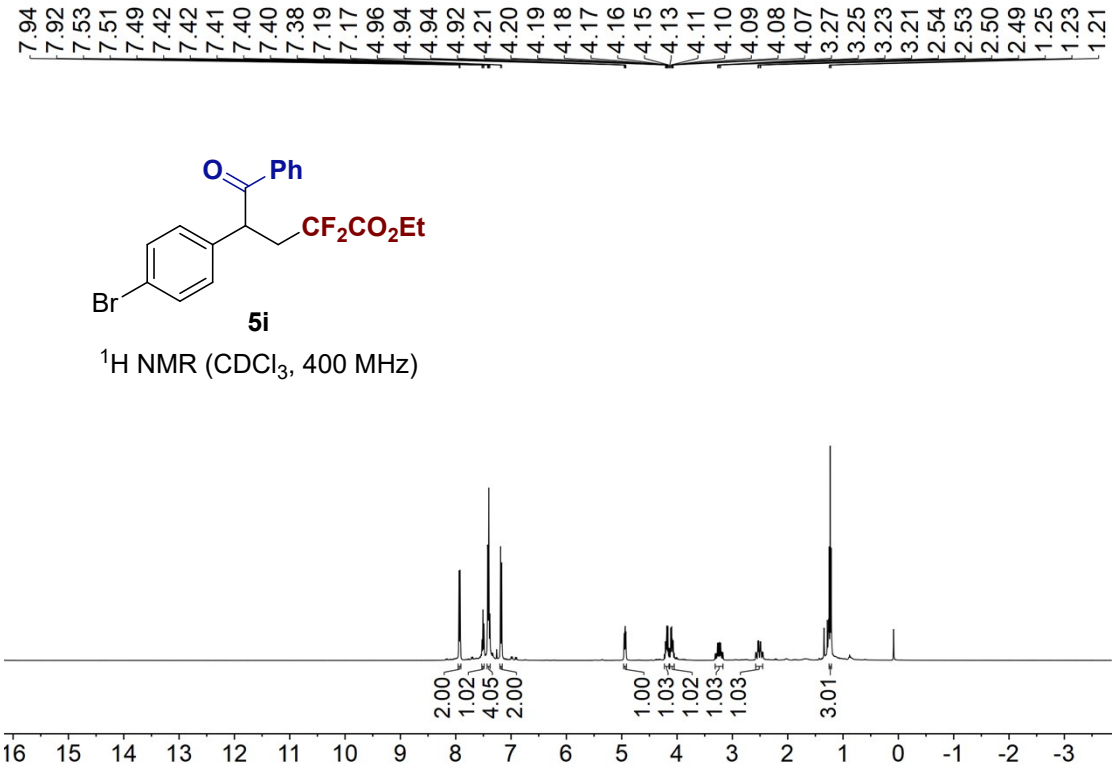
5h

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



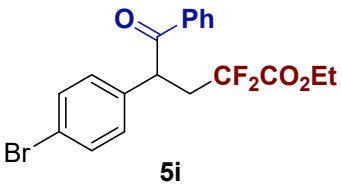
5h

^{13}C NMR ($CDCl_3$, 101 MHz)



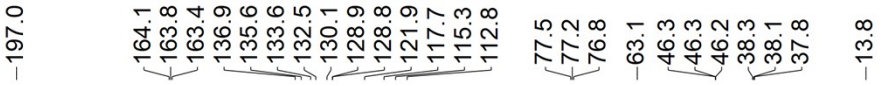
5i

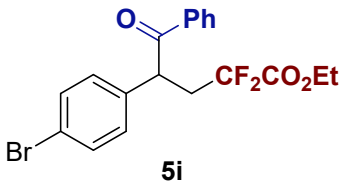
^{1}H NMR ($CDCl_3$, 400 MHz)



5i

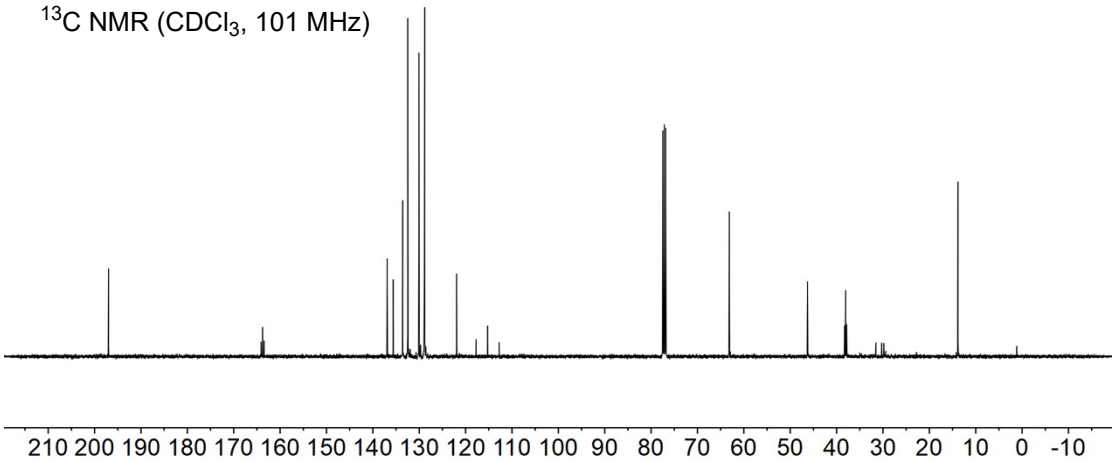
^{19}F NMR ($CDCl_3$, 376 MHz)

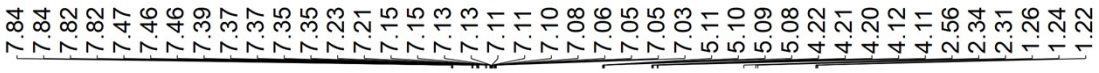


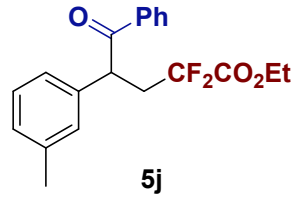


5i

^{13}C NMR ($CDCl_3$, 101 MHz)

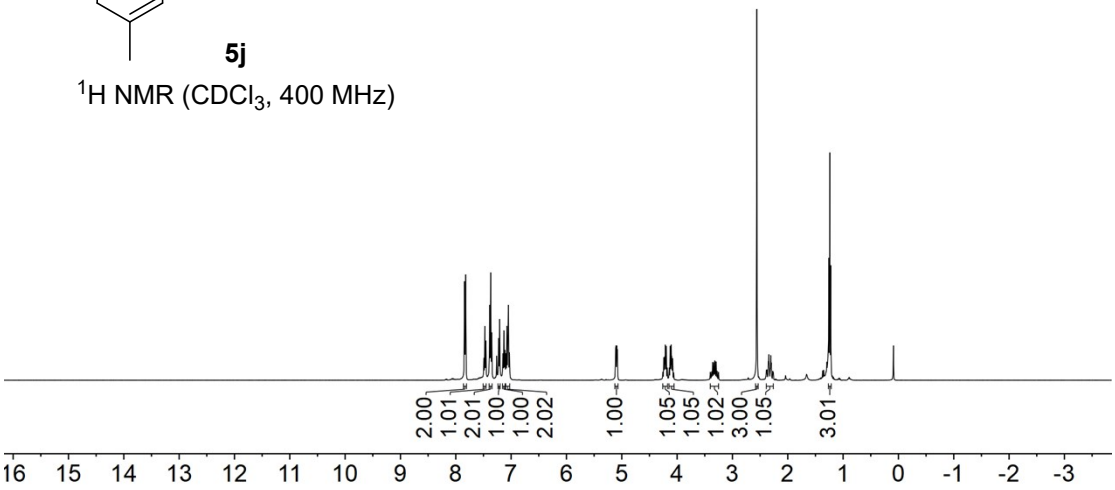


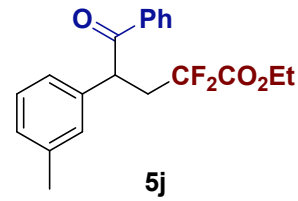




5j

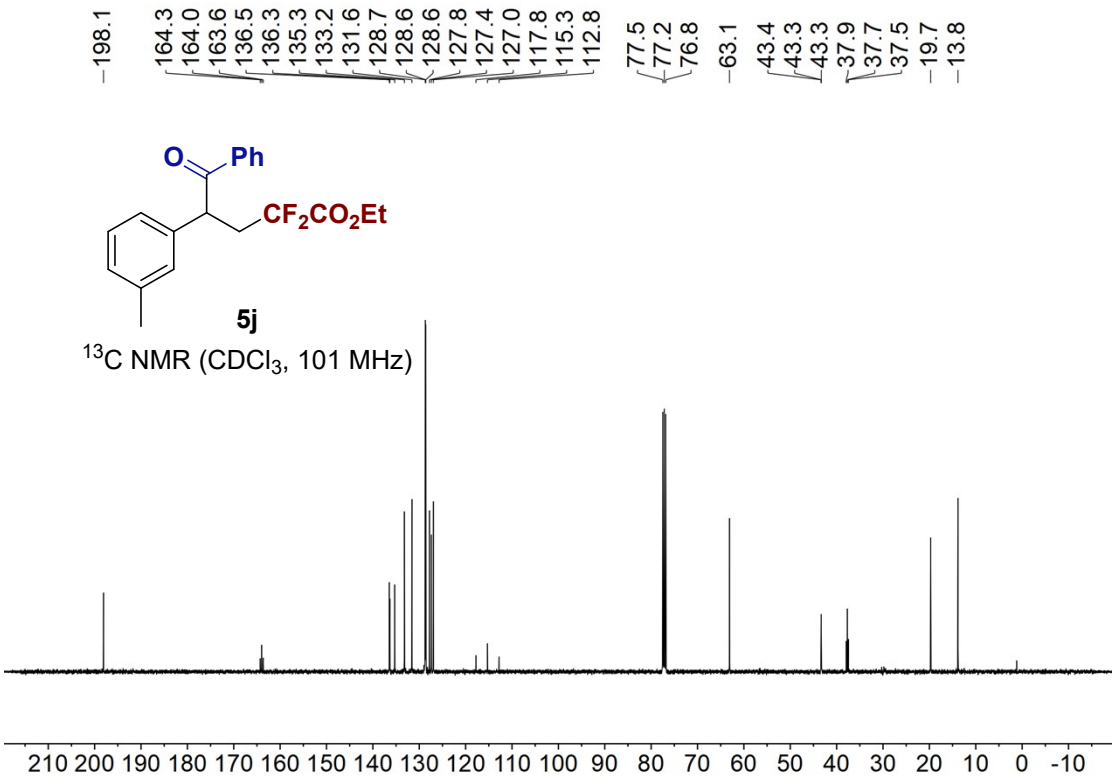
^{1}H NMR ($CDCl_3$, 400 MHz)





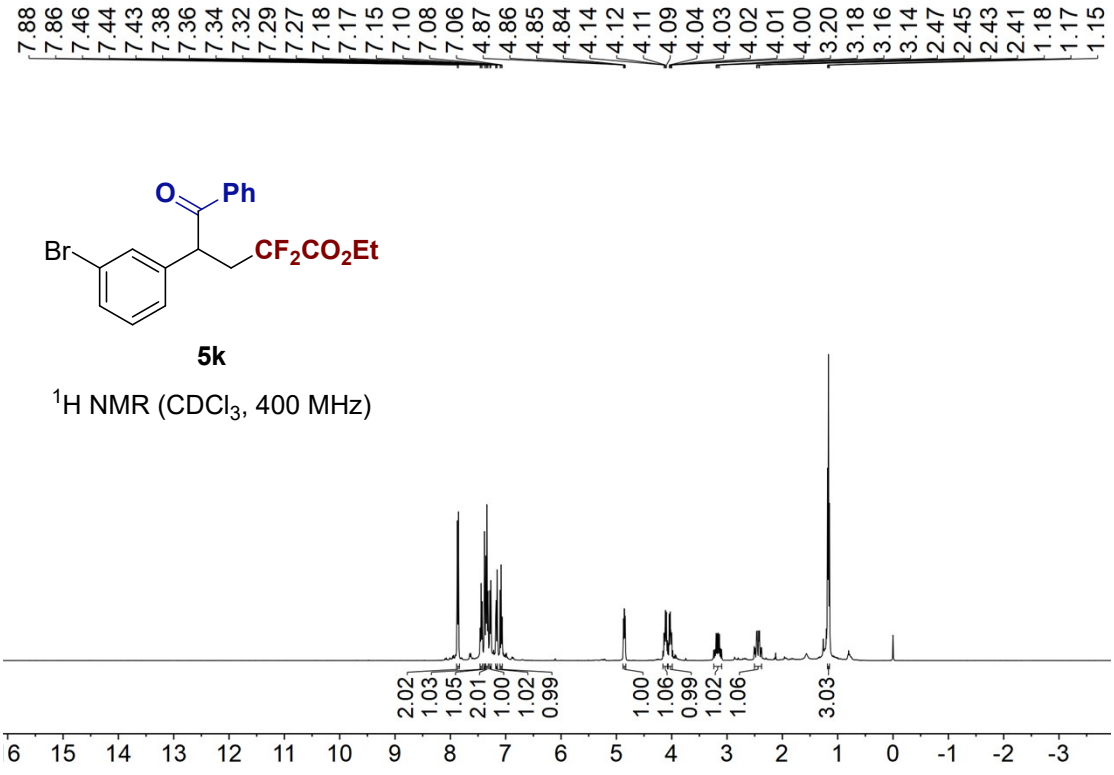
5j

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



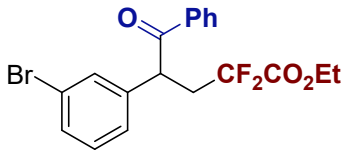
5j

^{13}C NMR ($CDCl_3$, 101 MHz)



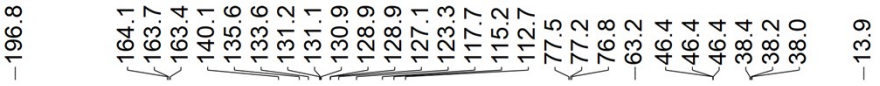
5k

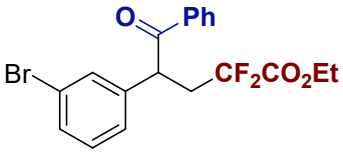
^{1}H NMR ($CDCl_3$, 400 MHz)



5k

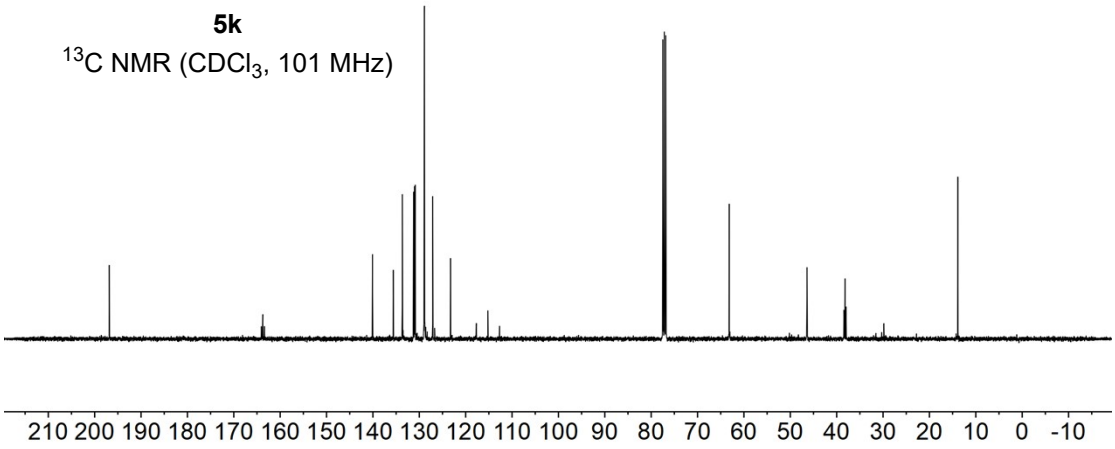
^{19}F NMR ($CDCl_3$, 376 MHz)

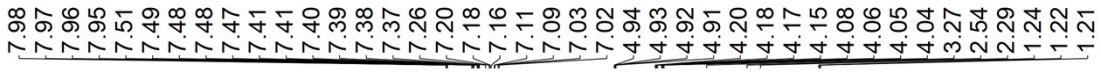


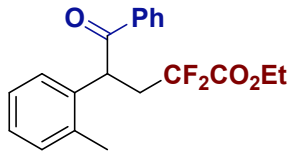


5k

^{13}C NMR ($CDCl_3$, 101 MHz)

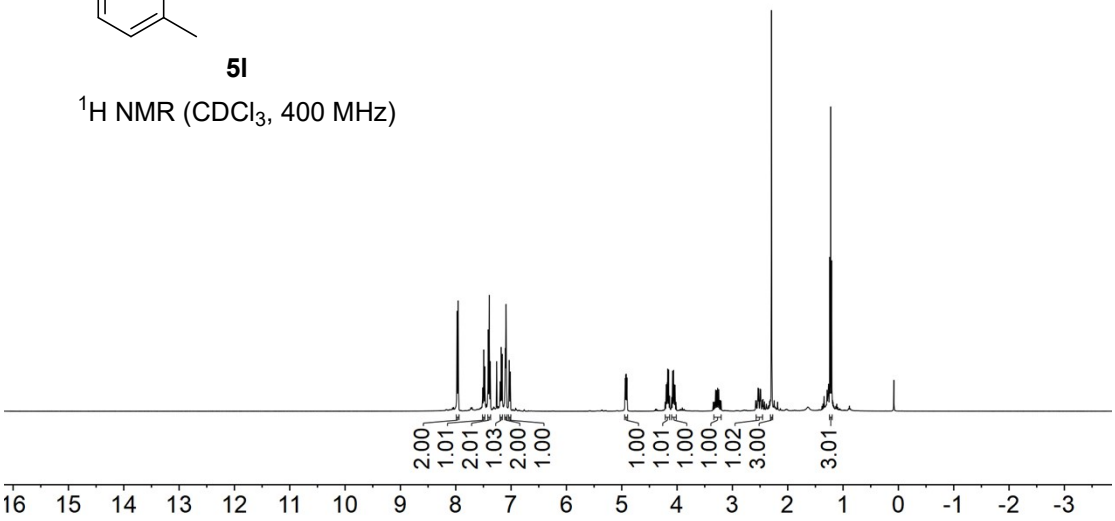


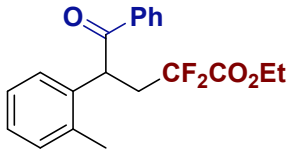




5l

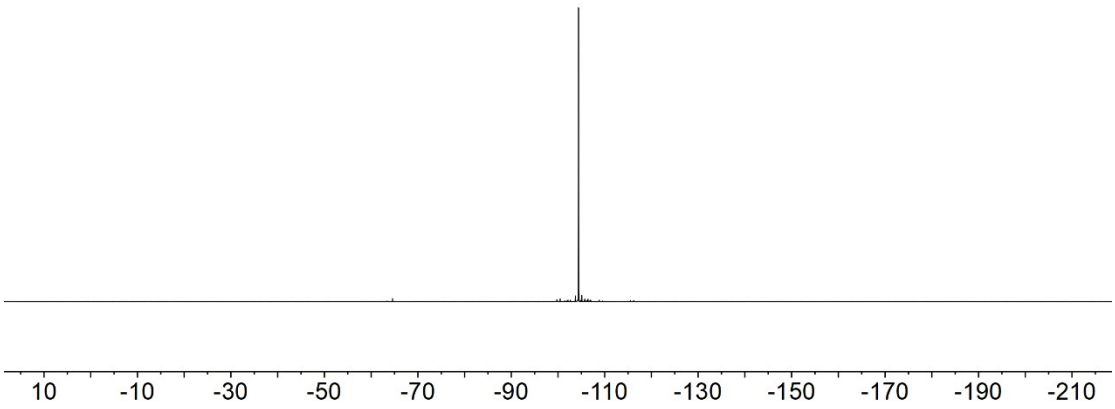
^{1}H NMR ($CDCl_3$, 400 MHz)

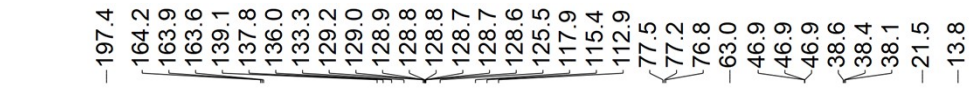


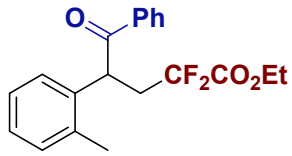


5l

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

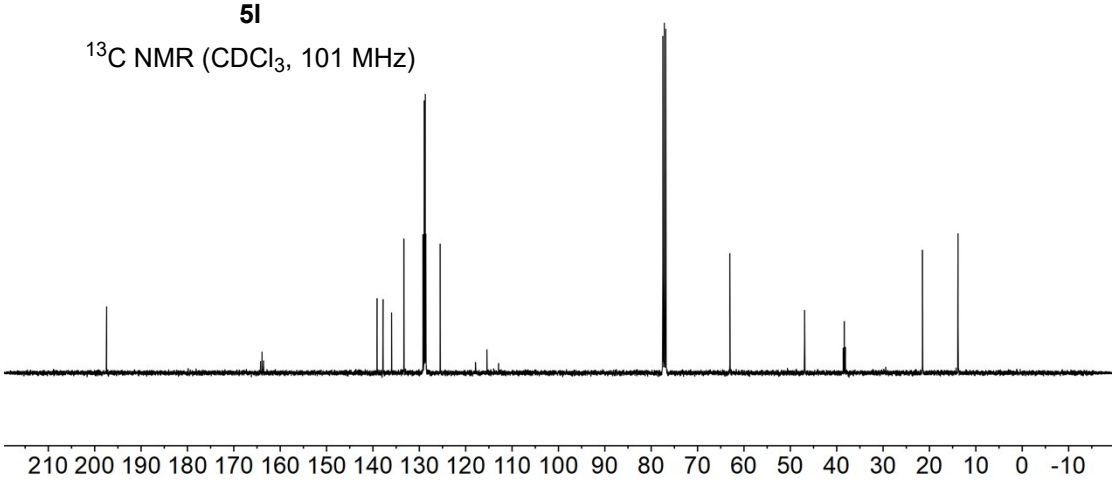


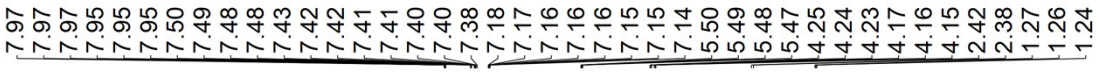


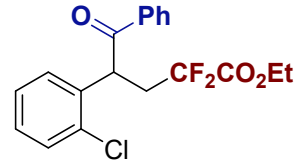


5l

^{13}C NMR ($CDCl_3$, 101 MHz)

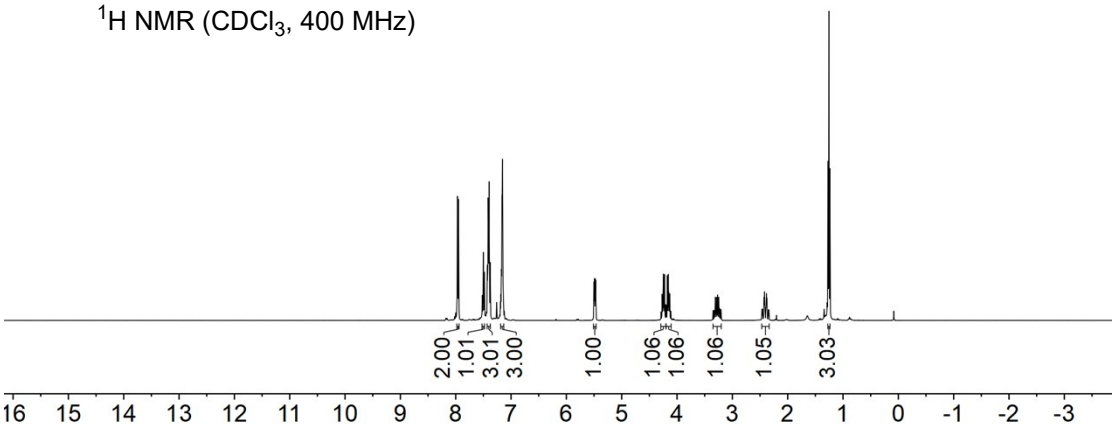


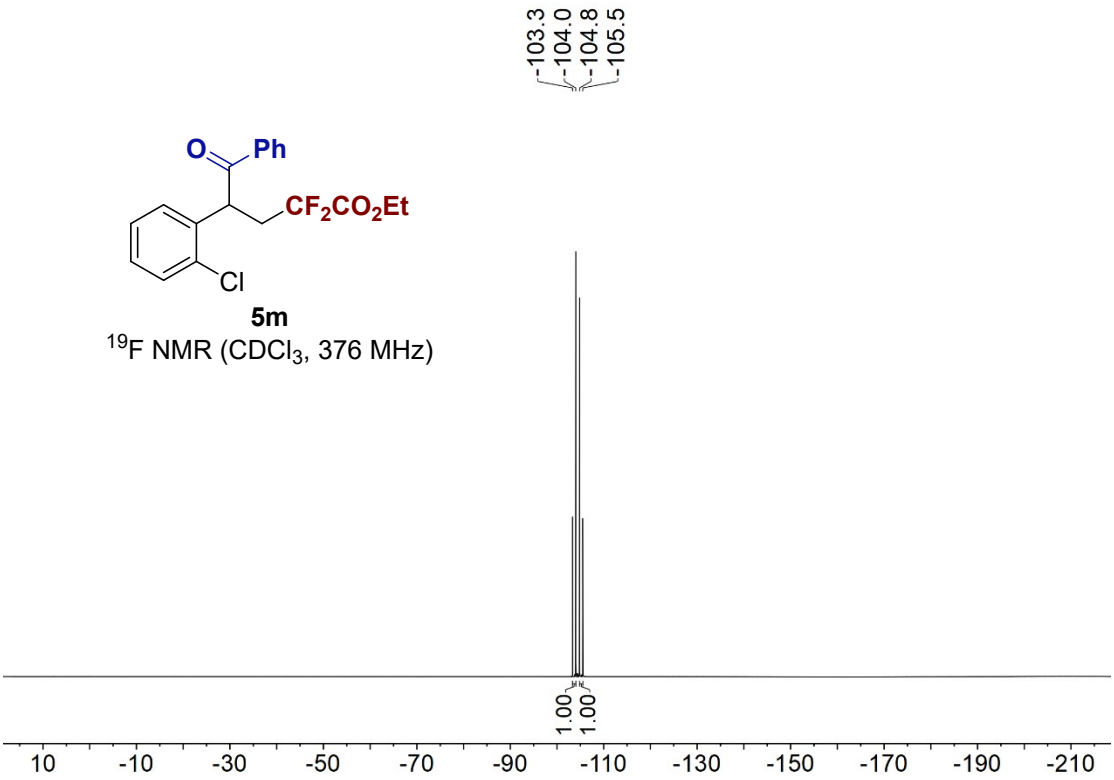




5m

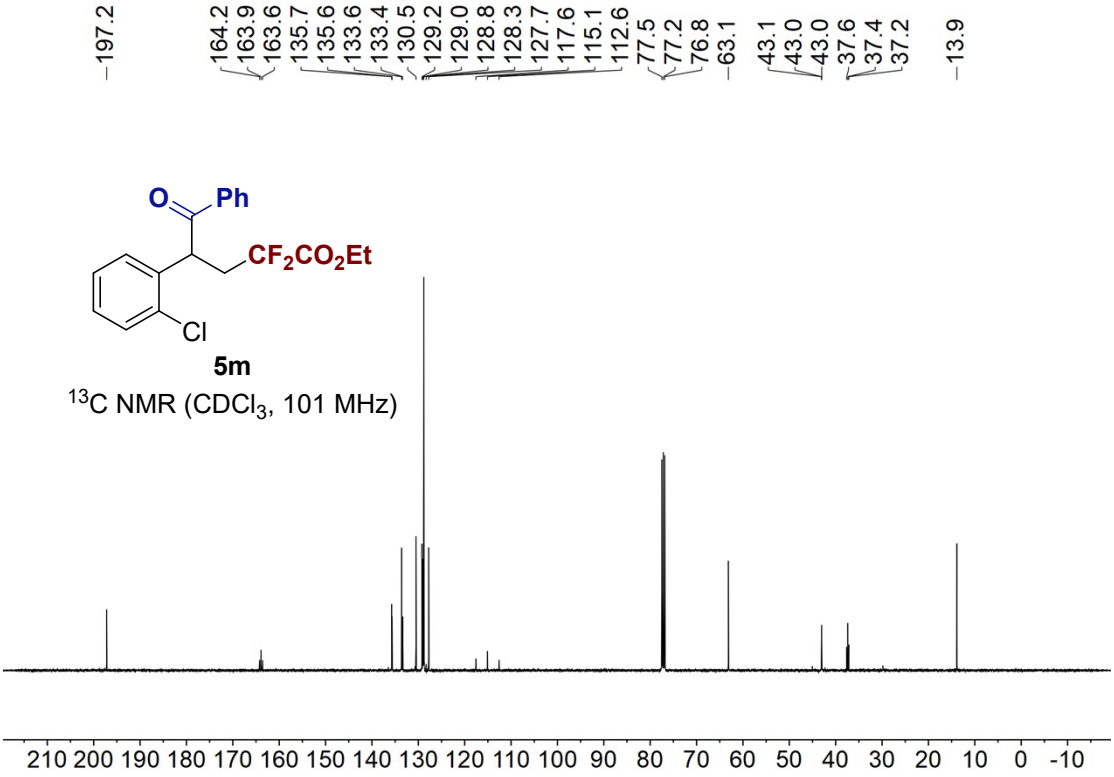
^{1}H NMR ($CDCl_3$, 400 MHz)





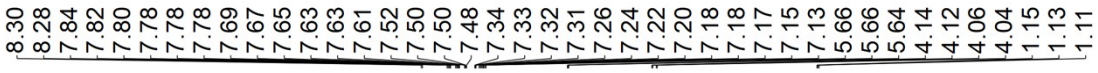
5m

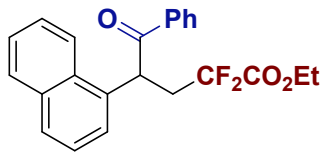
^{19}F NMR ($CDCl_3$, 376 MHz)



5m

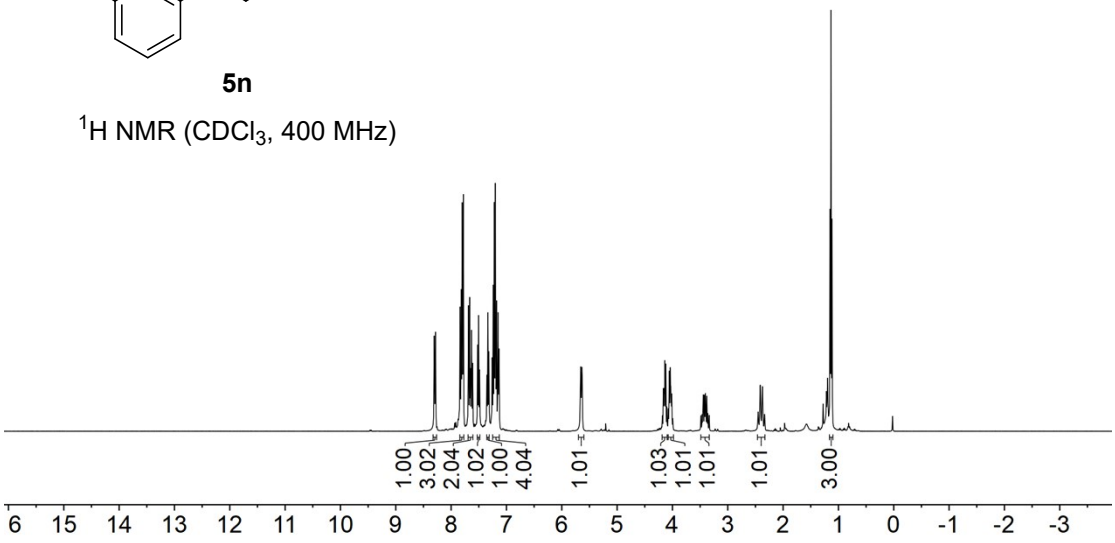
^{13}C NMR ($CDCl_3$, 101 MHz)

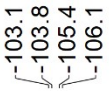


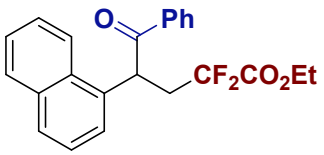


5n

^{1}H NMR ($CDCl_3$, 400 MHz)

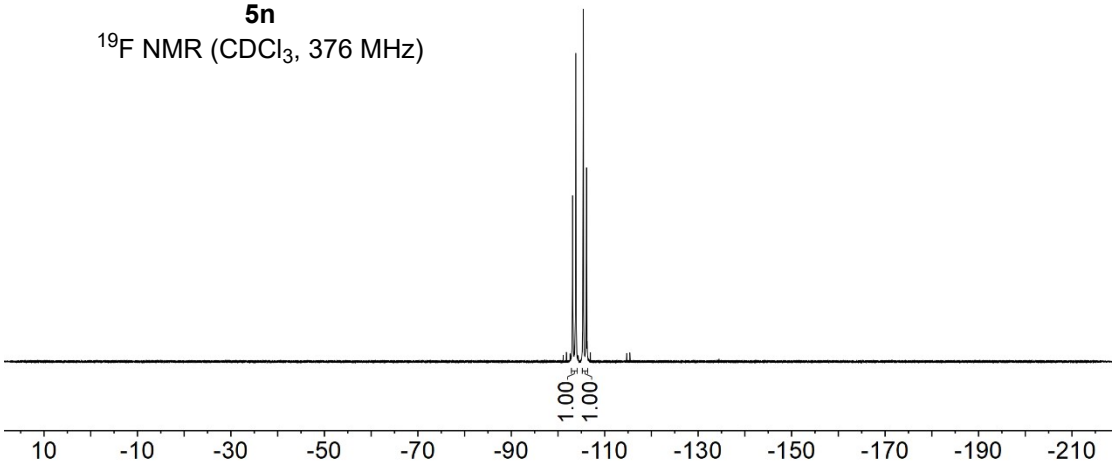


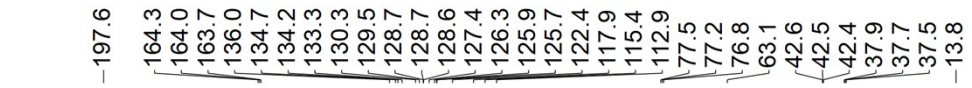


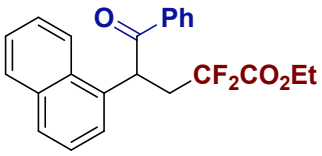


5n

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

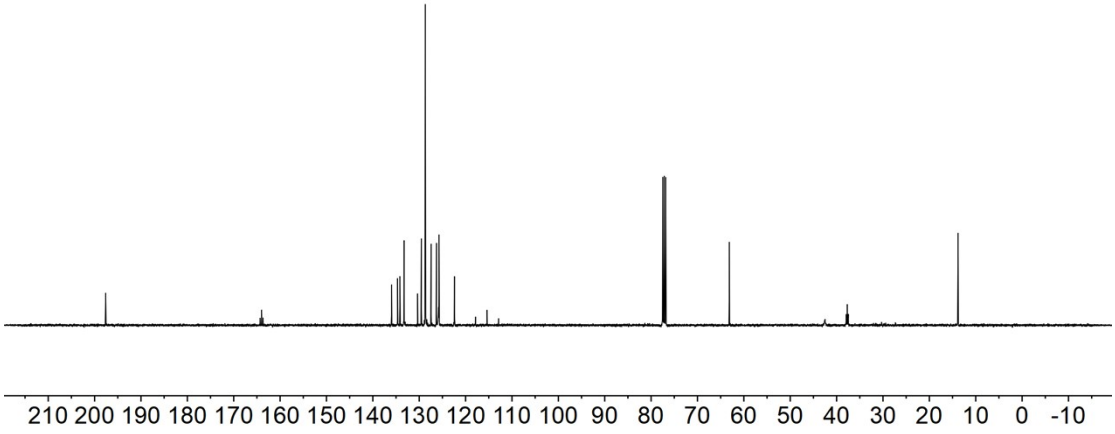


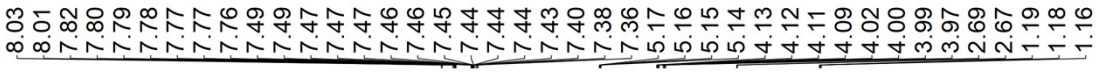


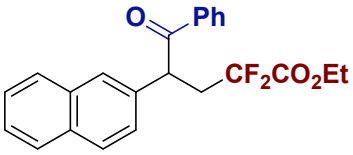


5n

^{13}C NMR ($CDCl_3$, 101 MHz)

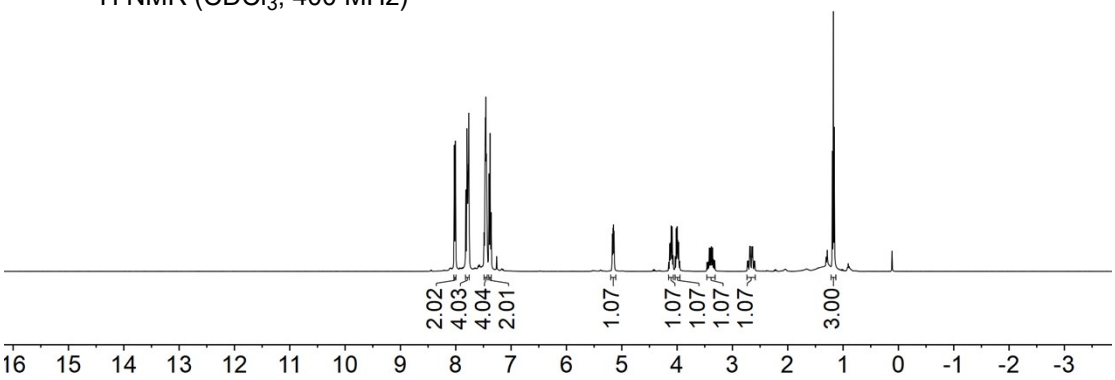


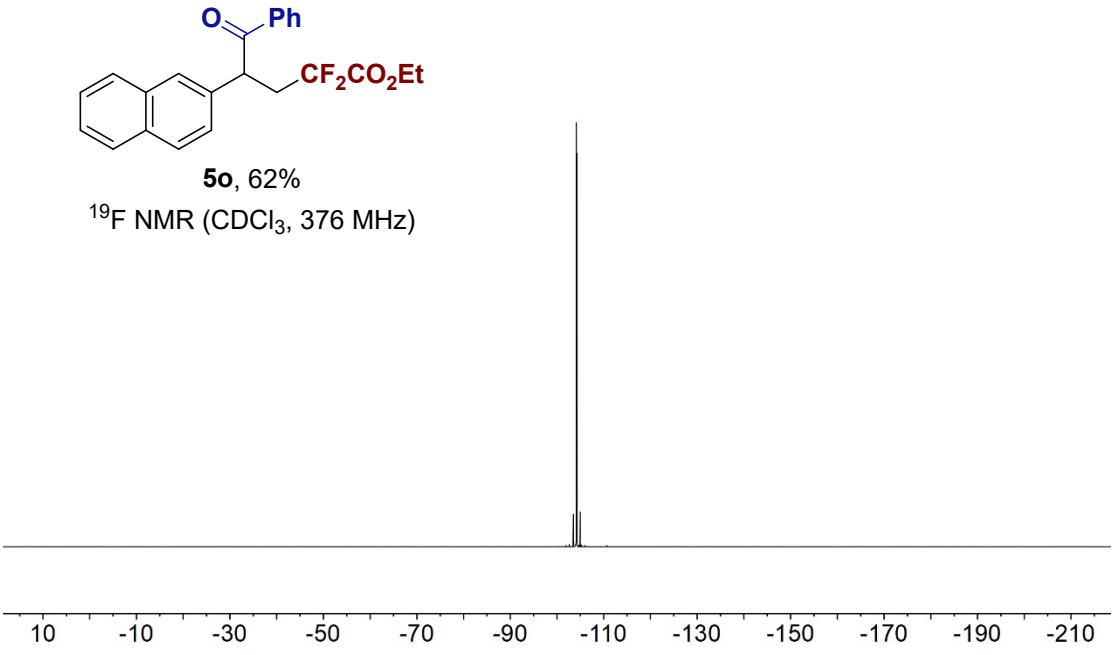




5o, 62%

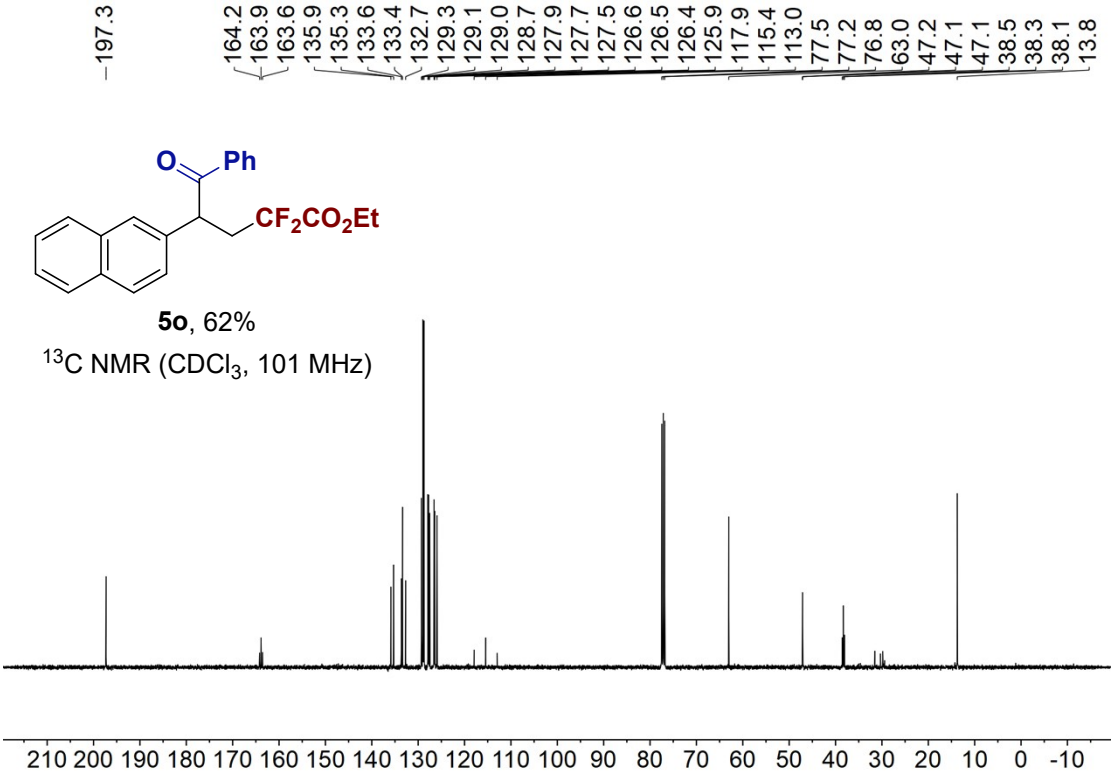
^{1}H NMR ($CDCl_3$, 400 MHz)





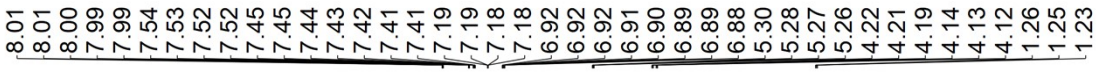
5o, 62%

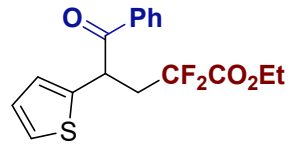
^{19}F NMR ($CDCl_3$, 376 MHz)



5o, 62%

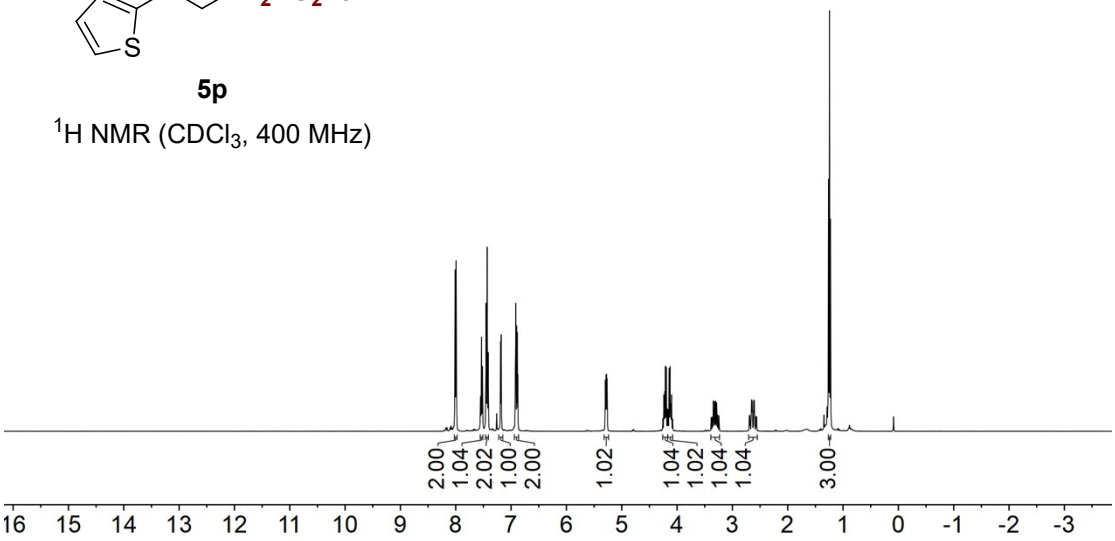
^{13}C NMR ($CDCl_3$, 101 MHz)

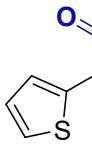




5p

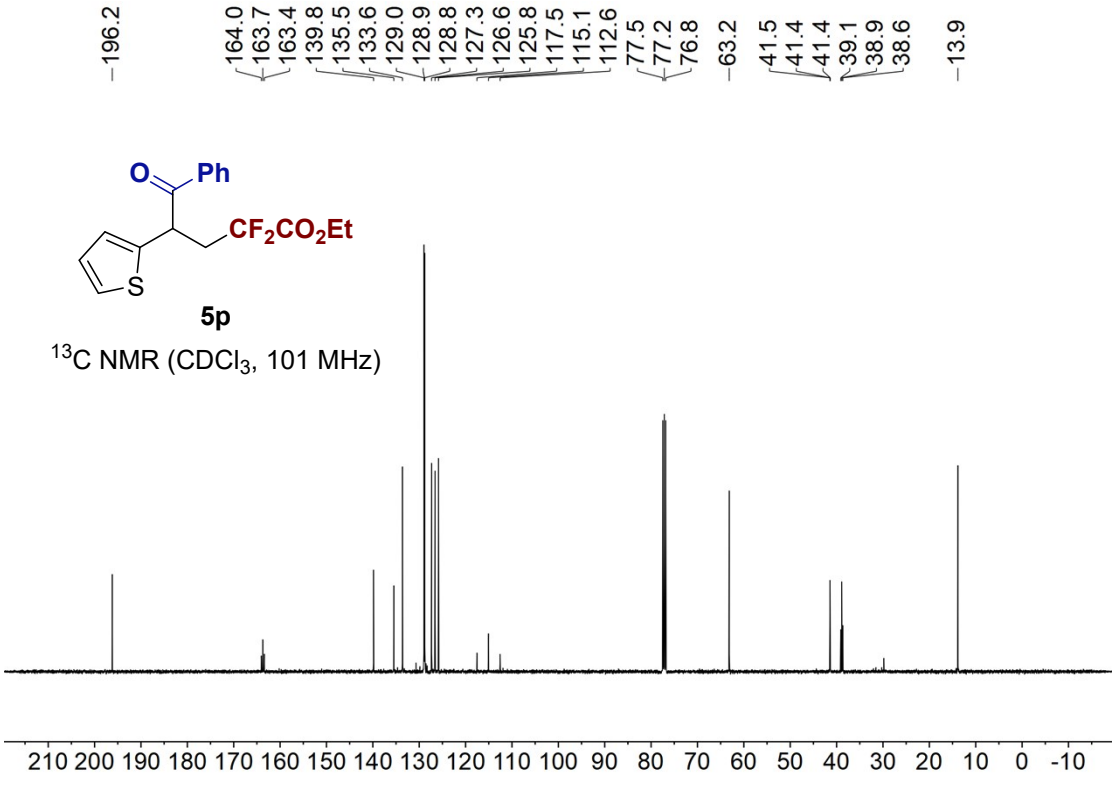
^{1}H NMR ($CDCl_3$, 400 MHz)





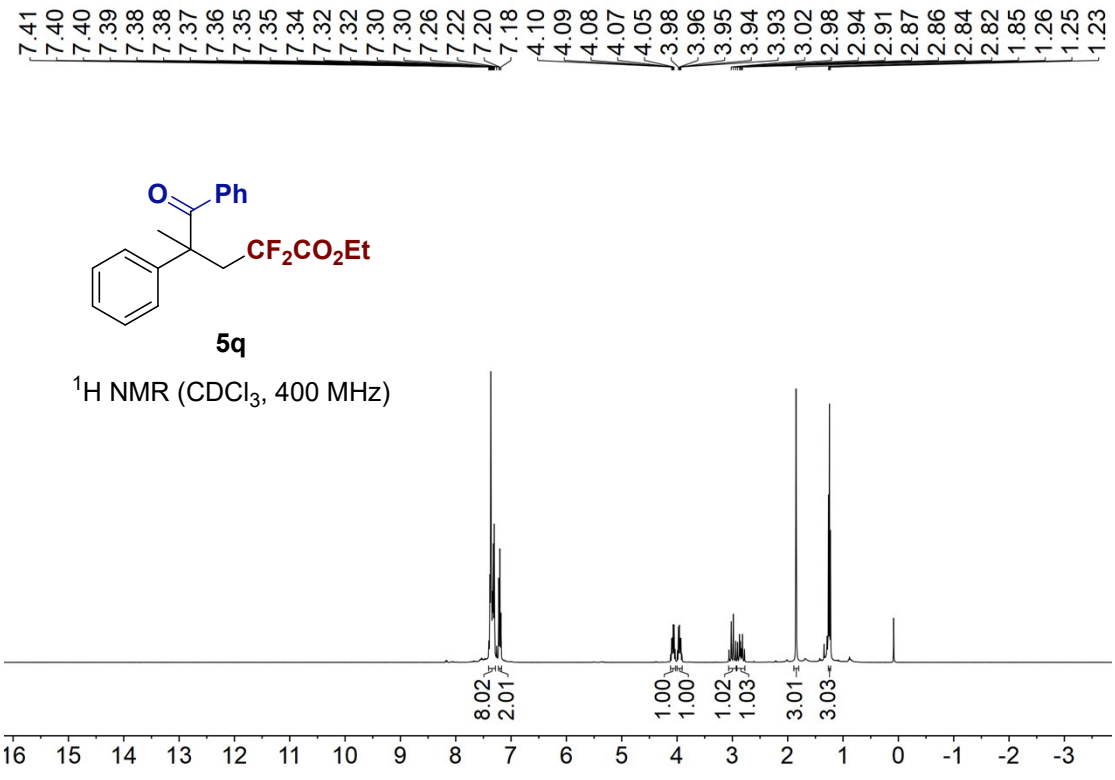
5p

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



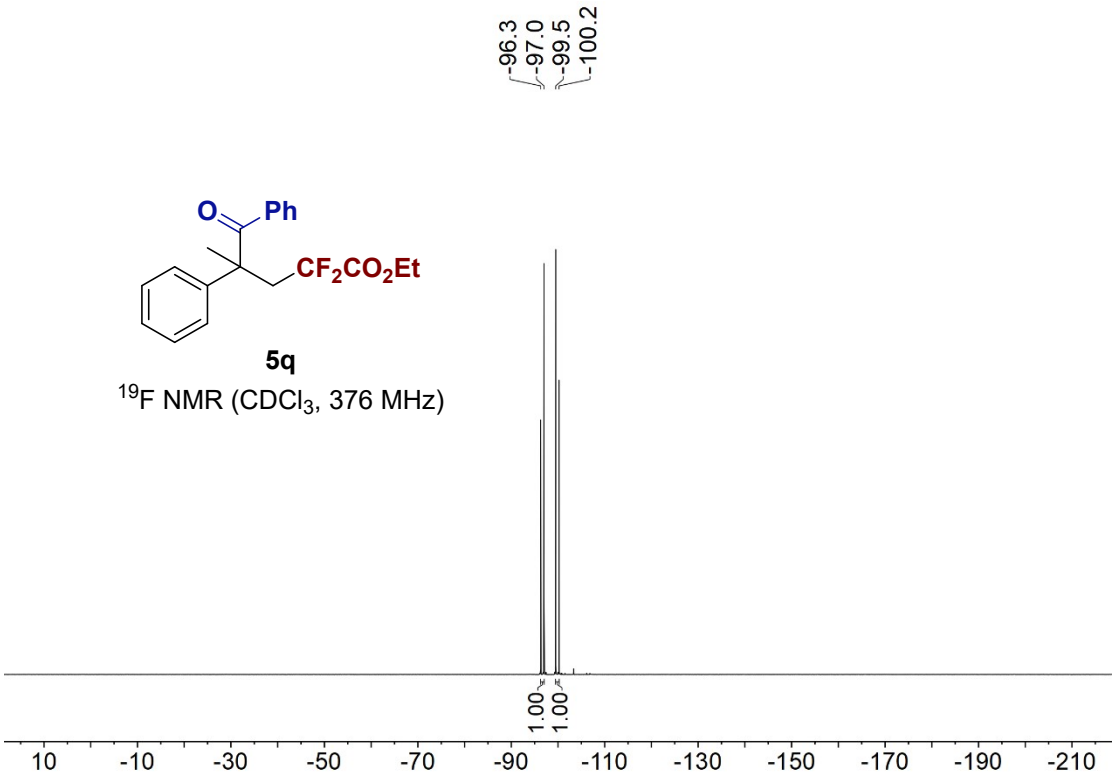
5p

^{13}C NMR ($CDCl_3$, 101 MHz)



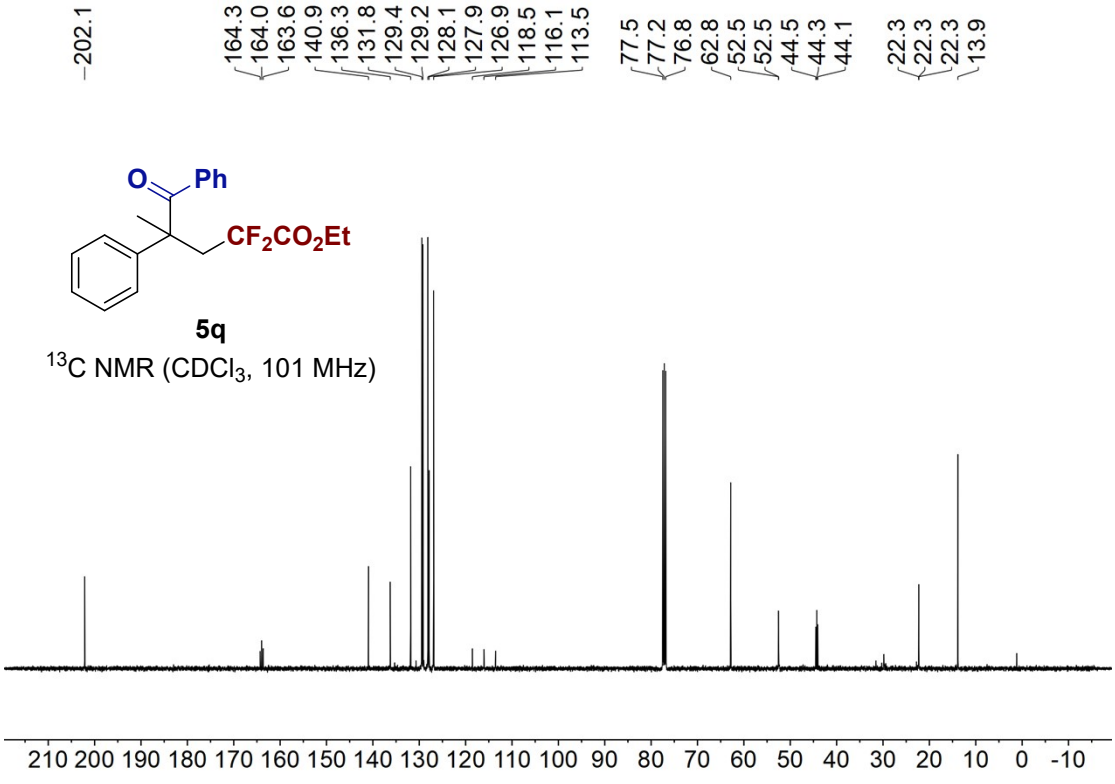
5q

^{1}H NMR ($CDCl_3$, 400 MHz)



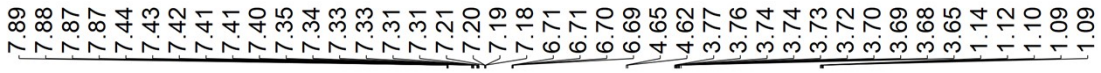
5q

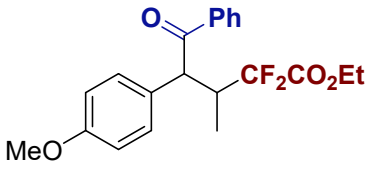
^{19}F NMR ($CDCl_3$, 376 MHz)



5q

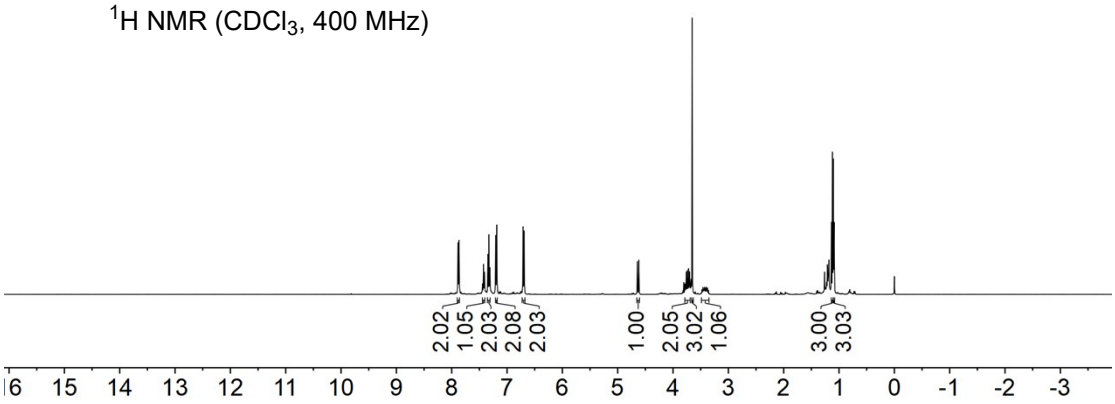
^{13}C NMR ($CDCl_3$, 101 MHz)

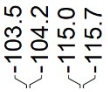


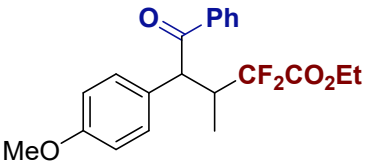


5r, dr = 5:1

^{1}H NMR ($CDCl_3$, 400 MHz)

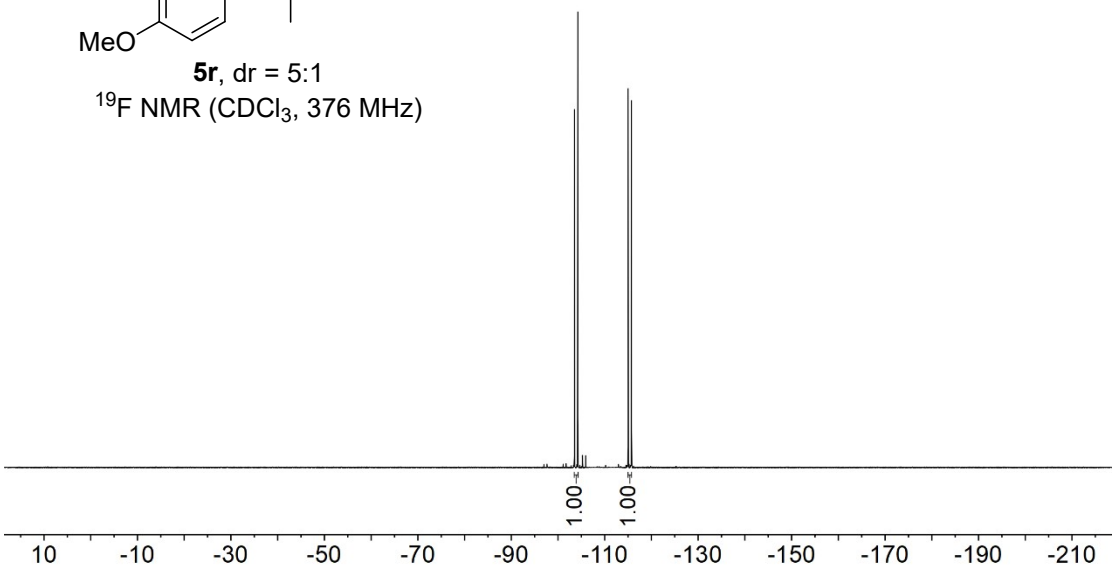


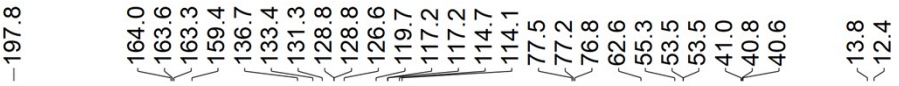


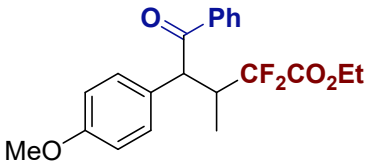


5r, dr = 5:1

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

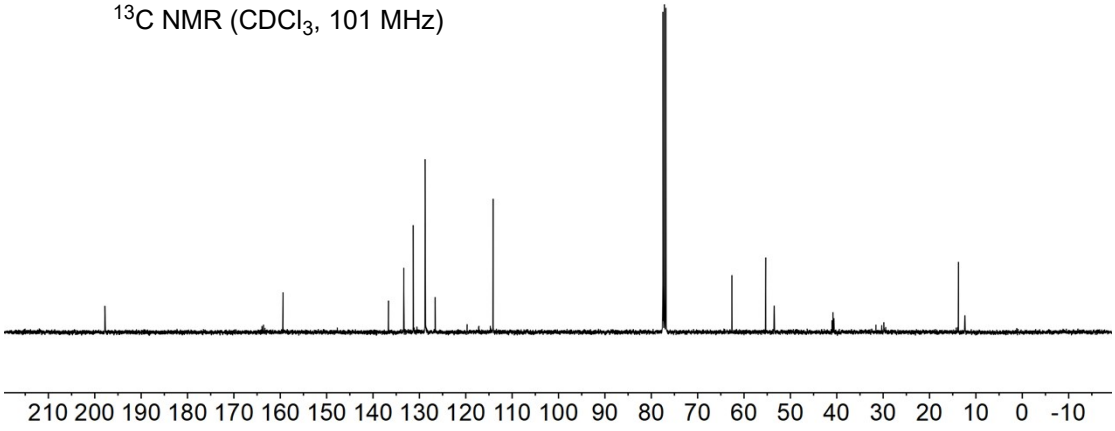


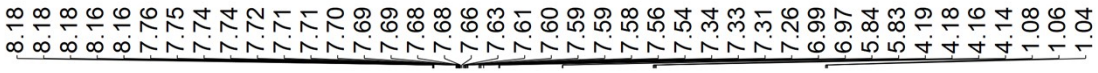


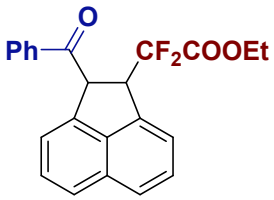


5r, dr = 5:1

^{13}C NMR ($CDCl_3$, 101 MHz)

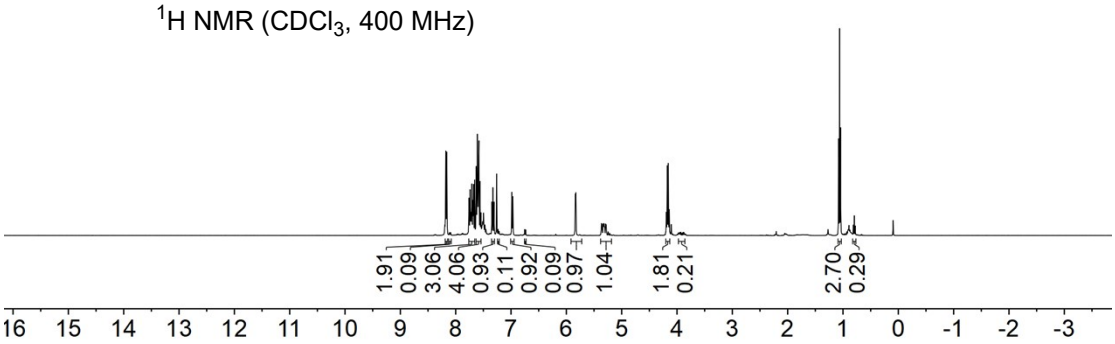


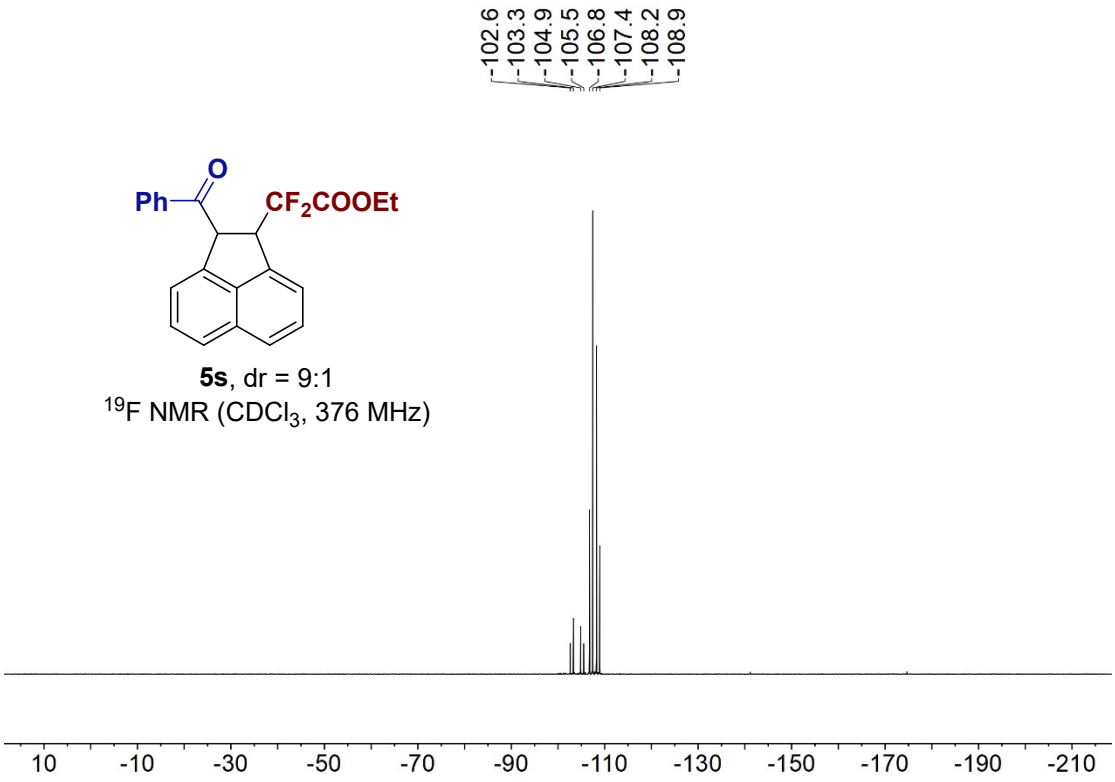




5s, dr = 9:1

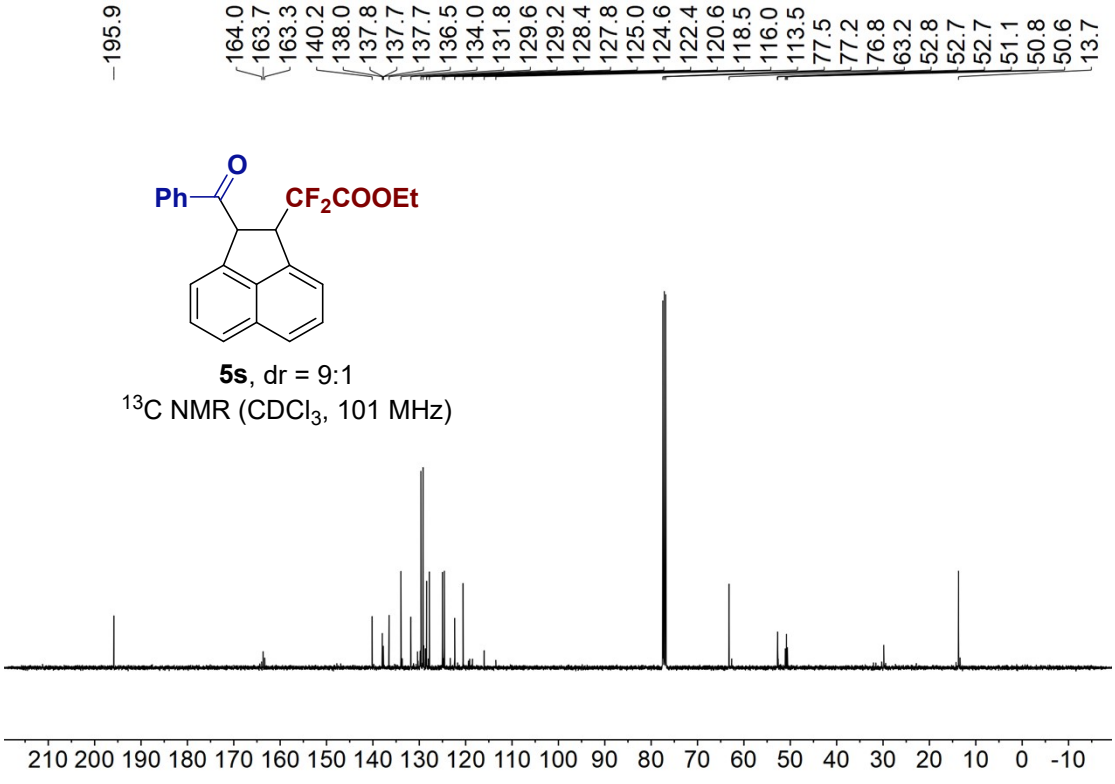
^{1}H NMR ($CDCl_3$, 400 MHz)





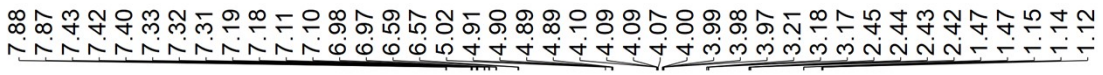
5s, dr = 9:1

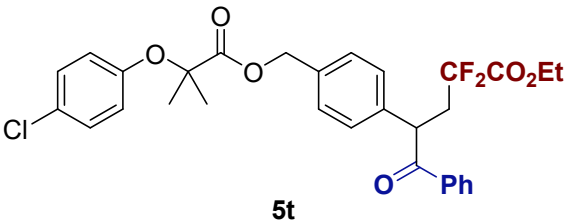
^{19}F NMR ($CDCl_3$, 376 MHz)



5s, dr = 9:1

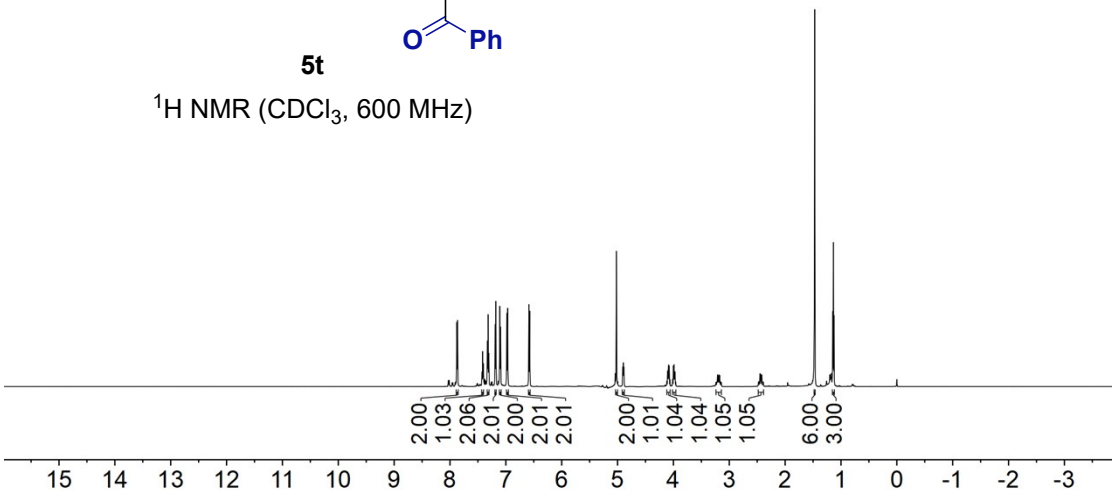
^{13}C NMR ($CDCl_3$, 101 MHz)

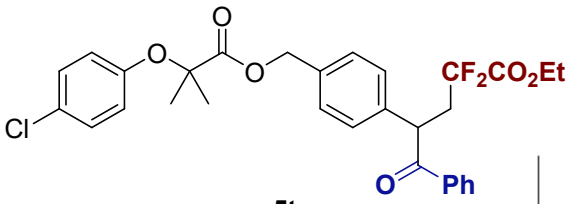




5t

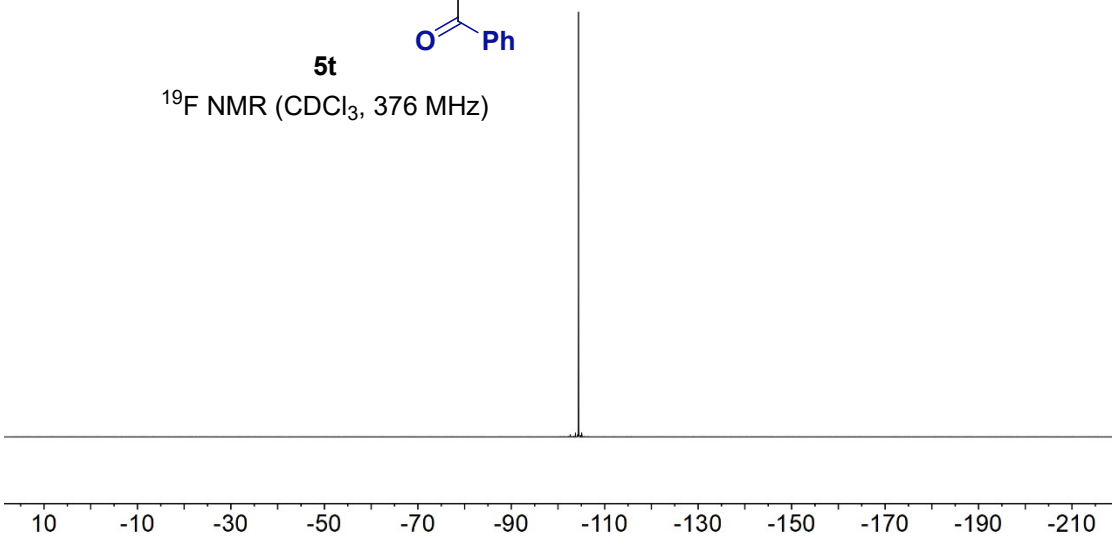
^{1}H NMR ($CDCl_3$, 600 MHz)

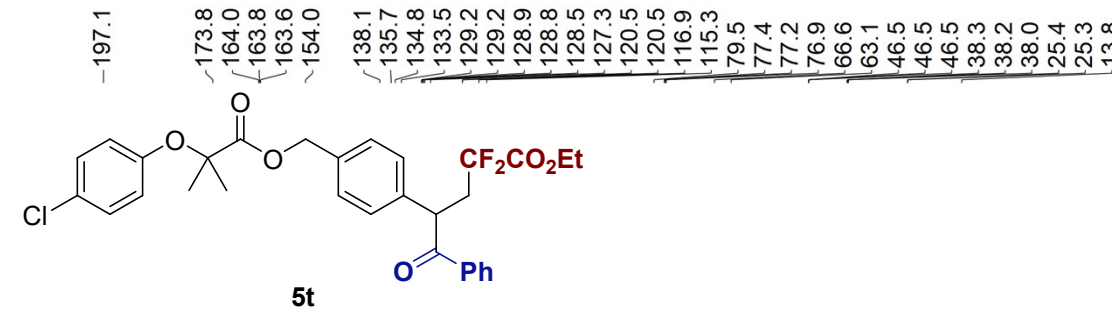




5t

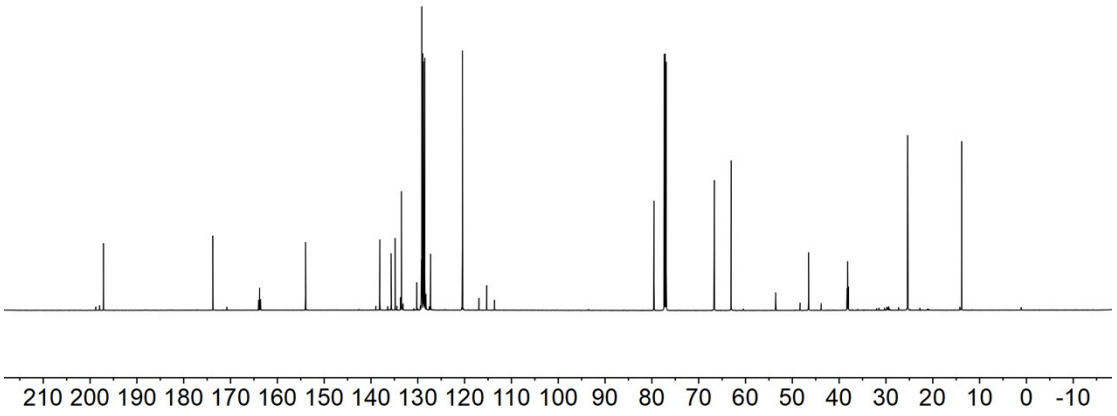
^{19}F NMR ($CDCl_3$, 376 MHz)

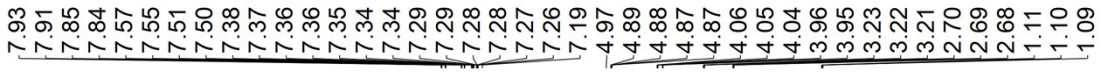


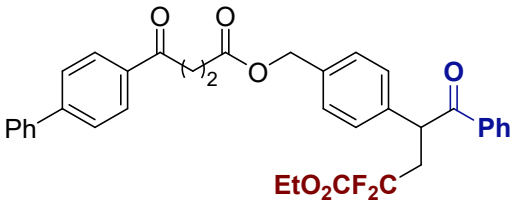


5t

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

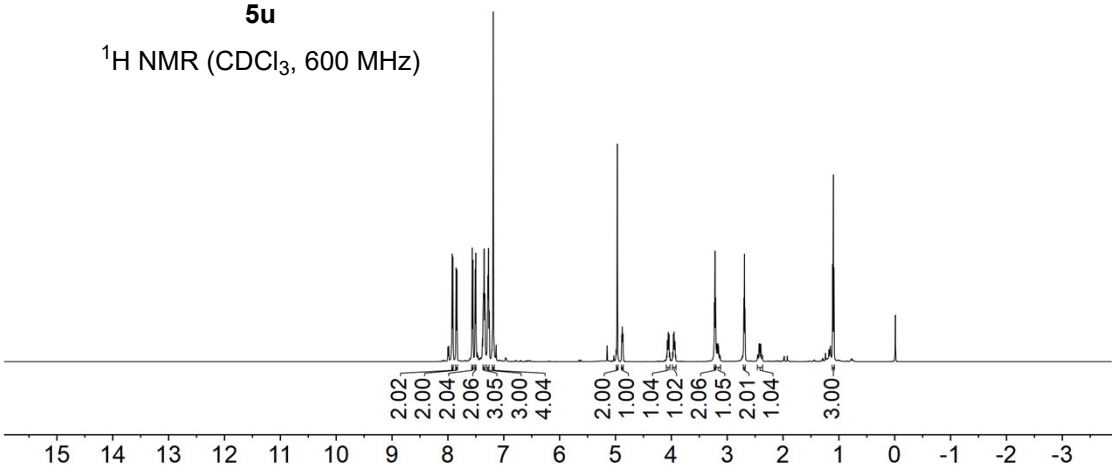


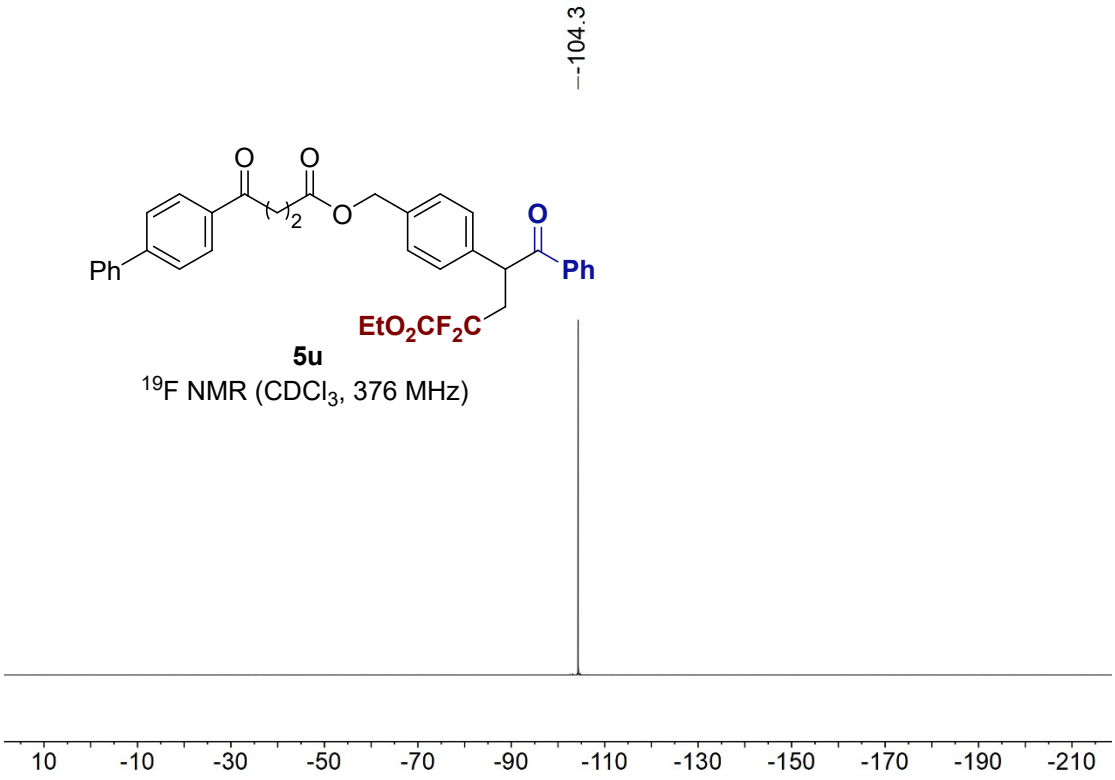




5u

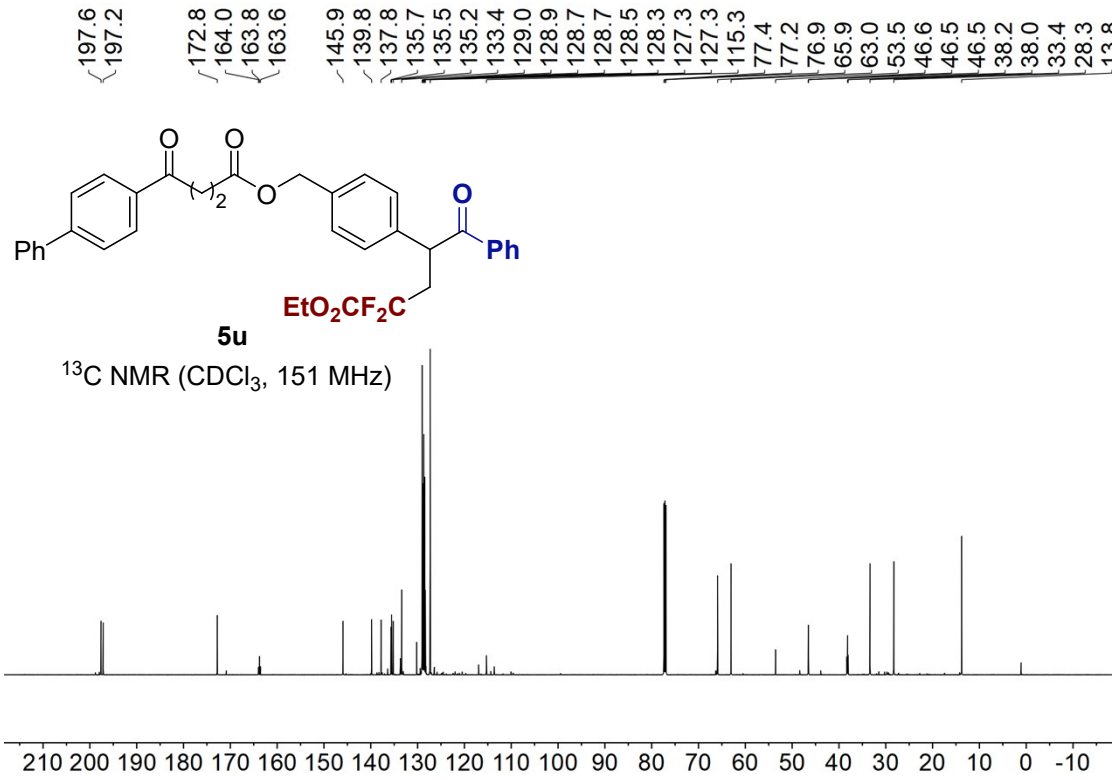
^{1}H NMR ($CDCl_3$, 600 MHz)





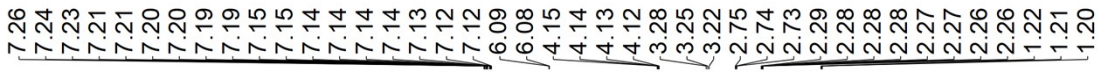
5u

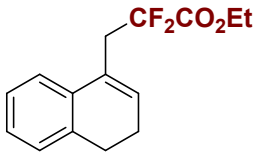
^{19}F NMR ($CDCl_3$, 376 MHz)



5u

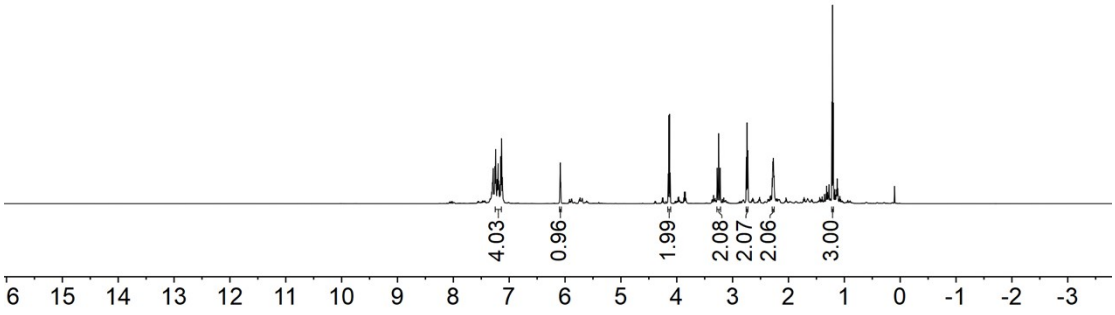
^{13}C NMR ($CDCl_3$, 151 MHz)

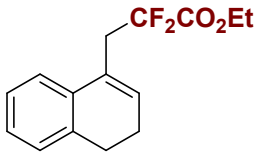




8

^{1}H NMR ($CDCl_3$, 400 MHz)





8

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

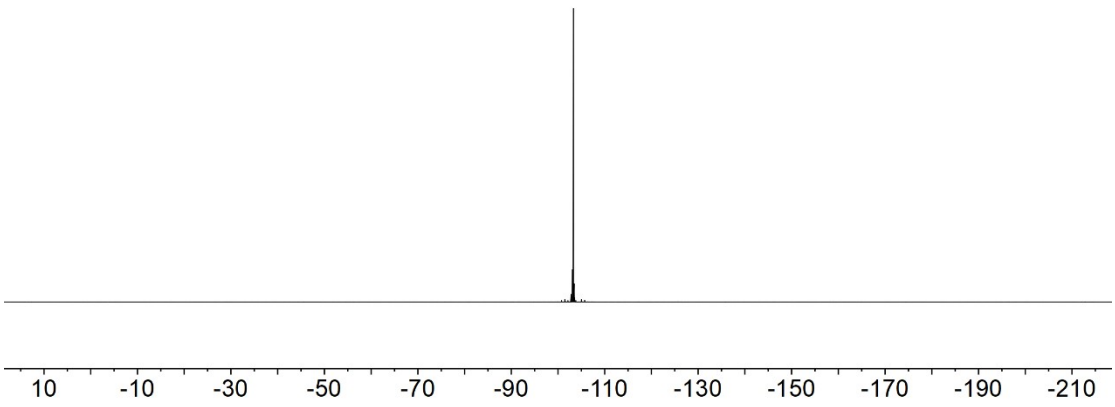
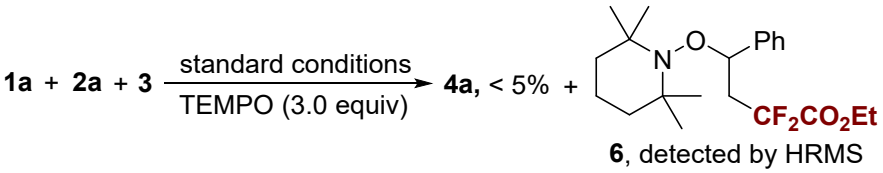
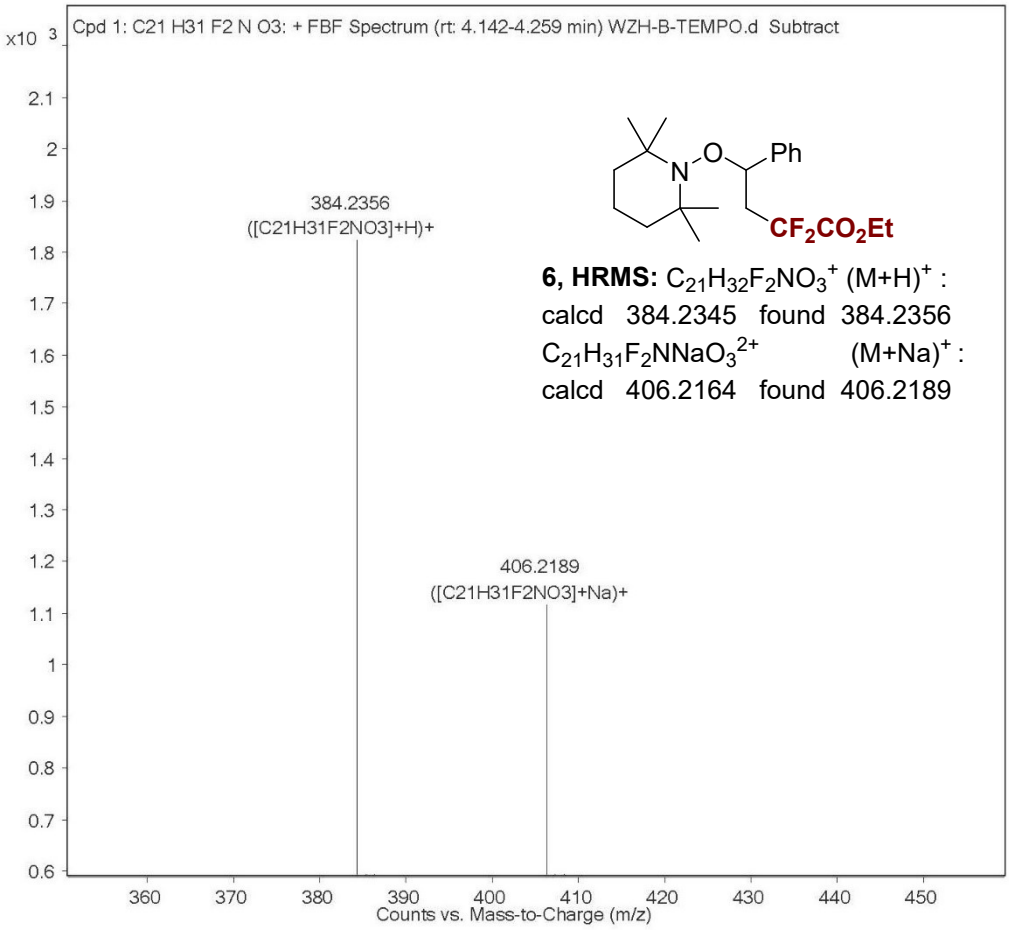


Figure S5. HRMS of TEMPO-trapped product

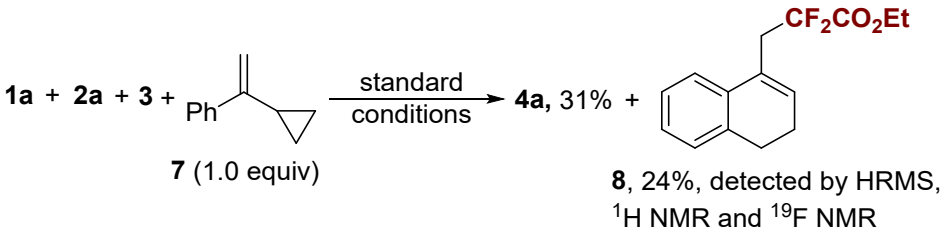


6, detected by HRMS



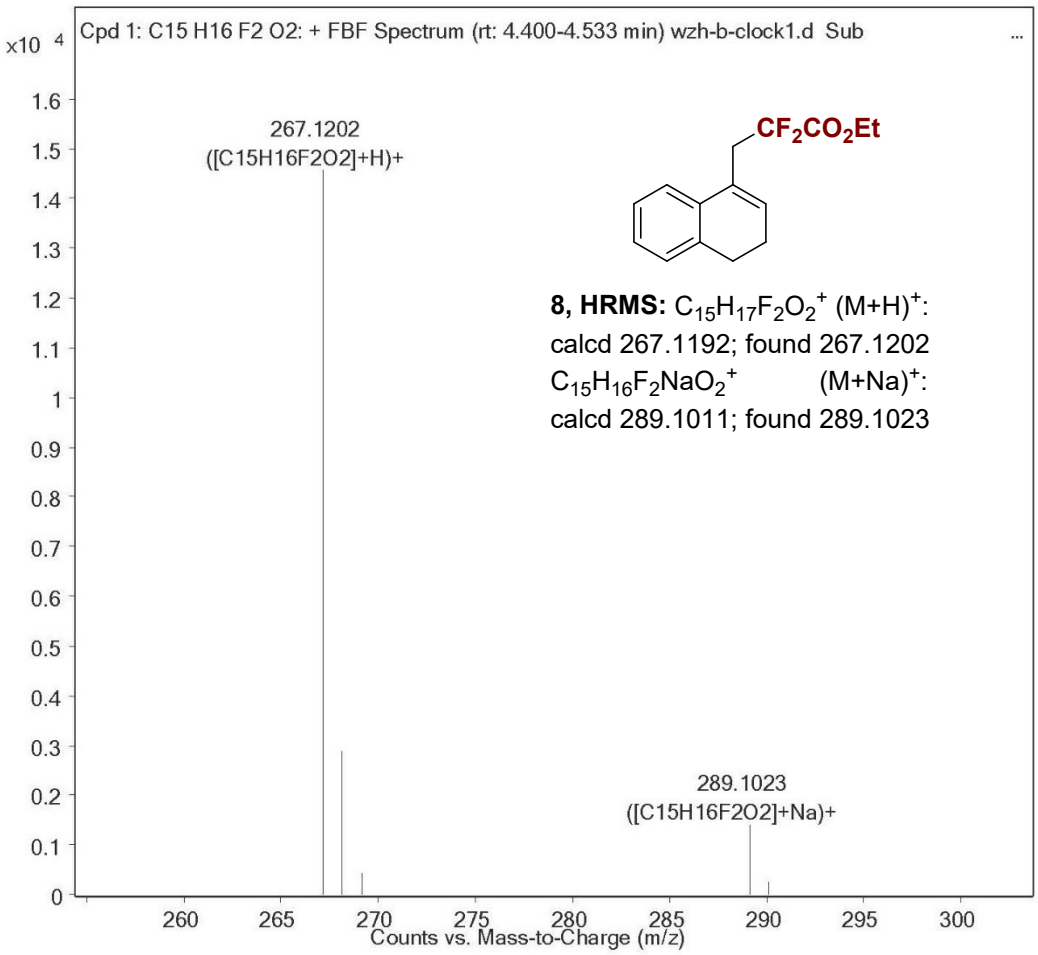
6, HRMS: $C_{21}H_{32}F_2NO_3^+$ $(M+H)^+$:
calcd 384.2345 found 384.2356
$C_{21}H_{31}F_2NNaO_3^{2+}$ $(M+Na)^+$:
calcd 406.2164 found 406.2189

Figure S6. HRMS of radical clock probe-trapped product



7 (1.0 equiv)

8, 24%, detected by HRMS, ^{1}H NMR and ^{19}F NMR



8, HRMS: $C_{15}H_{17}F_2O_2^+$ $(M+H)^+$:
calcd 267.1192; found 267.1202
$C_{15}H_{16}F_2NaO_2^+$ $(M+Na)^+$:
calcd 289.1011; found 289.1023