Supporting Information

$HP(O)Ph_2/H_2O$-Promoted Hydrodefluorination of Trifluoromethyl Alkenes

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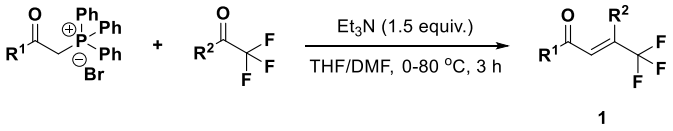
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N_2 atmosphere using undistilled solvent. Melting points were recorded on an electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI source). Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

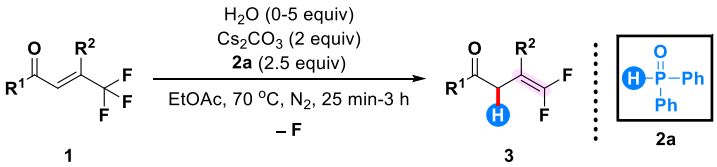
General procedure for the synthesis of trifluoromethyl alkenes 1[1]



1

According to Zhang's reported method, a solution of triphenylphosphonium salt (7.5 mmol) and triethylamine (759 mg, 7.5 mmol) in THF (20 mL) was added a solution of a trifluoromethyl ketone (5.0 mmol) in DMF (1.6 mL) at 0 ℃ (ice bath). The mixture was stirred for 15 min at this temperature. After warming to room temperature, the solution was heated at 80 °C for 3 h. The solution was quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate: 100/1) to give the pure trifluoromethyl alkenes **1**.

General procedure for the hydrodefluorination of trifluoromethyl alkenes 1



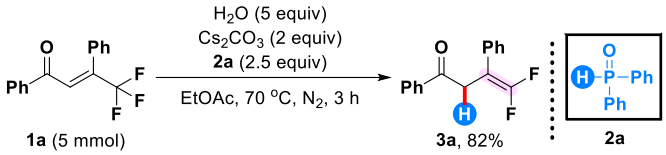
1 3 2a

Reaction conditions A: A solution of trifluoromethyl alkene **1** (0.3 mmol),[1] diphenylphosphine oxide **2a** (151.6 mg, 0.75 mmol), Cs_2CO_3 (195.6 mg, 0.6 mmol), and H_2O (27.0 mg, 1.5 mmol) in EtOAc (3.5 mL) was stirred at 70 °C under N_2 for 3 h.

Reaction conditions B: A solution of trifluoromethyl alkene **1** (0.3 mmol), diphenylphosphine oxide **2a** (151.6 mg, 0.75 mmol), and Cs_2CO_3 (195.5 mg, 0.6 mmol) in EtOAc (3.5 mL) was stirred at 70 °C under N_2 for 25 min.

The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate as eluent to afford the pure products **3**.

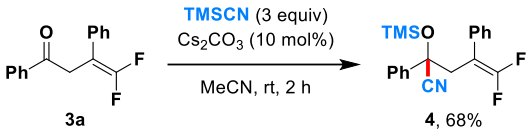
General procedure for the scale-up synthesis of product 3a



A solution of (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one **1a** (1.38 g, 5 mmol), diphenylphosphine oxide **2a** (2.53 g, 12.5 mmol), Cs_2CO_3 (3.26 g, 10 mmol), and H_2O (0.45 g, 25 mmol) in EtOAc (50 mL) was stirred at 70 °C under N_2 for 3 h. The reaction was then quenched by saturated NH_4Cl solution (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **3a** (1.06 g, 82% yield).

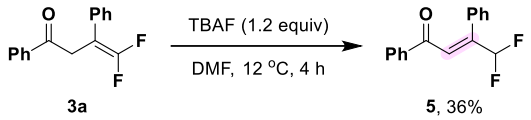
Further transformation of products

a) The reaction of product 3a with TMSCN



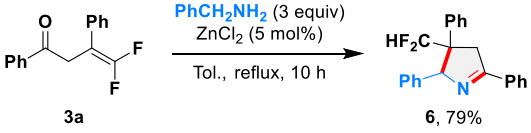
A solution of 4,4-difluoro-1,3-diphenylbut-3-en-1-one **3a** (77.5 mg, 0.3 mmol), TMSCN (89.3 mg, 0.9 mmol), and Cs_2CO_3 (9.8 mg, 0.03 mmol) in MeCN (1 mL) was stirred at room temperature under N_2 for 2 h. The reaction solvent was concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **4** (73.2 mg, 68% yield).

b) The isomerization of product 3a



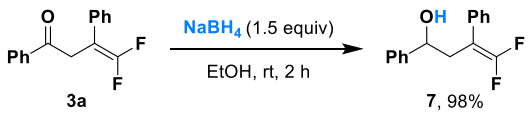
A solution of 4,4-difluoro-1,3-diphenylbut-3-en-1-one **3a** (77.5 mg, 0.3 mmol) and TBAF (1 M in THF, 0.36 mL, 0.36 mmol) in DMF (2 mL) was stirred at 12 °C under N_2 for 4 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **5** (27.8 mg, 36% yield).

c) The reaction of product 3a with $PhCH_2NH_2$



A solution of 4,4-difluoro-1,3-diphenylbut-3-en-1-one **3a** (77.5 mg, 0.3 mmol), $PhCH_2NH_2$ (96.4 mg, 0.9 mmol), and $ZnCl_2$ (2.0 mg, 0.015 mmol) in toluene (2 mL) was stirred at 110 °C under N_2 for 10 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (50/1) as eluent to afford the pure product **6** (81.9 mg, 79% yield).

d) The reduction reaction of product 3a

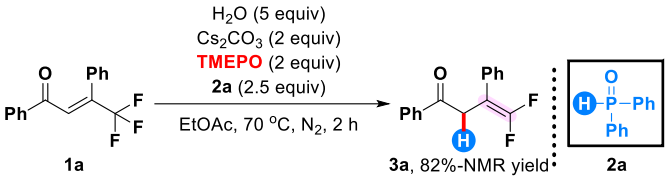


A solution of 4,4-difluoro-1,3-diphenylbut-3-en-1-one **3a** (77.5 mg, 0.3 mmol), and $NaBH_4$ (17.0 mg, 0.45 mmol) in EtOH (2 mL) was stirred at room temperature under N_2 for 2 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3).

The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1) as eluent to afford the pure product **7** (76.4 mg, 98% yield).

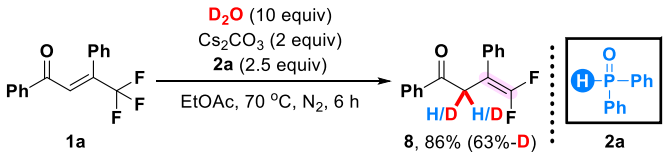
Mechanistic studies

1) Radical trapping experiment

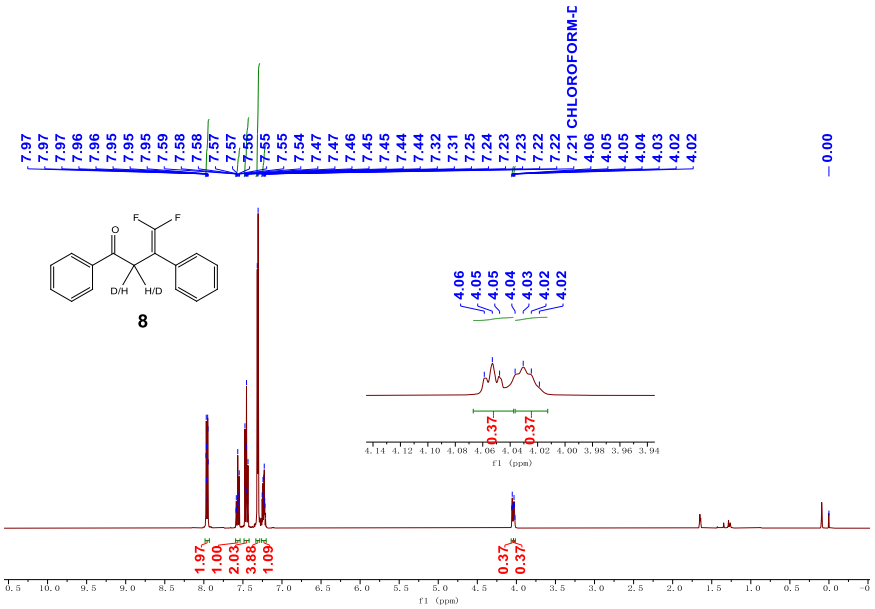


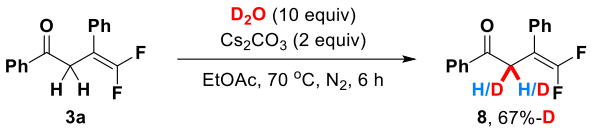
A solution of (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one **1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide **2a** (151.6 mg, 0.75 mmol), Cs_2CO_3 (195.6 mg, 0.6 mmol), H_2O (27.0 mg, 1.5 mmol), and 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 93.7 mg, 0.6 mmol) in EtOAc (3.5 mL) was stirred at 70 °C under N_2 for 2 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). 82%-NMR yield of product **3a** was obtained as determined by ^{19}F NMR analysis of the reaction mixture with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard. **This result suggested that hydrodefluorination of trifluoromethyl alkenes might not proceed through a radical pathway.**

2) D-labeling experiments

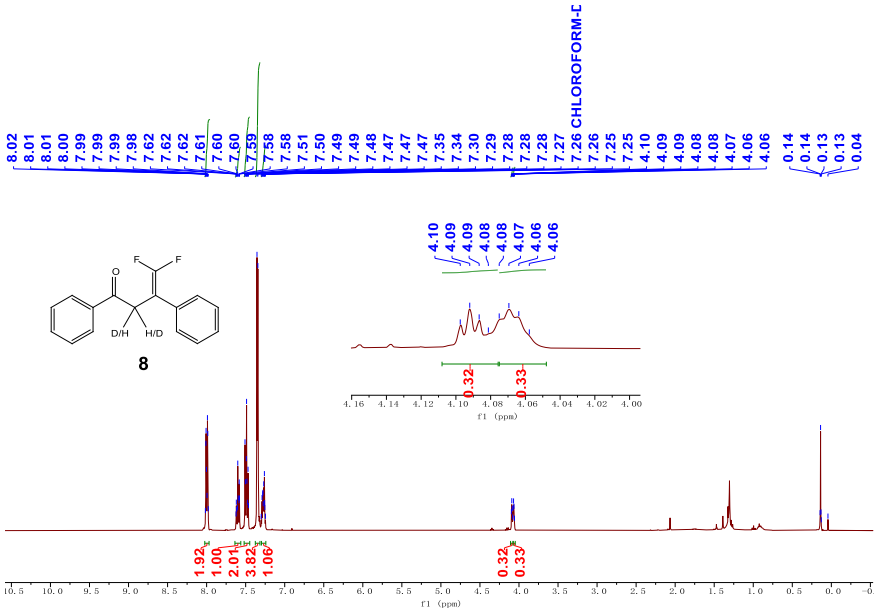


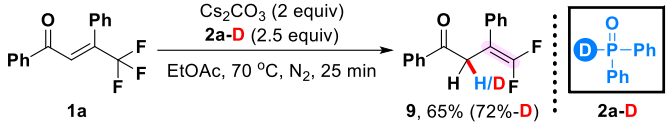
A solution of (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one **1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide **2a** (151.6 mg, 0.75 mmol), Cs_2CO_3 (195.6 mg, 0.6 mmol), and D_2O (54.0 mg, 3.0 mmol) in EtOAc (3.5 mL) was stirred at 70 °C under N_2 for 6 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **8** (86% yield, 63%-D incorporation). The ^1H NMR analysis of product **8** showed that two deuterium atoms were incorporated into the α-position of carbonyl group with a ratio of 1:1.



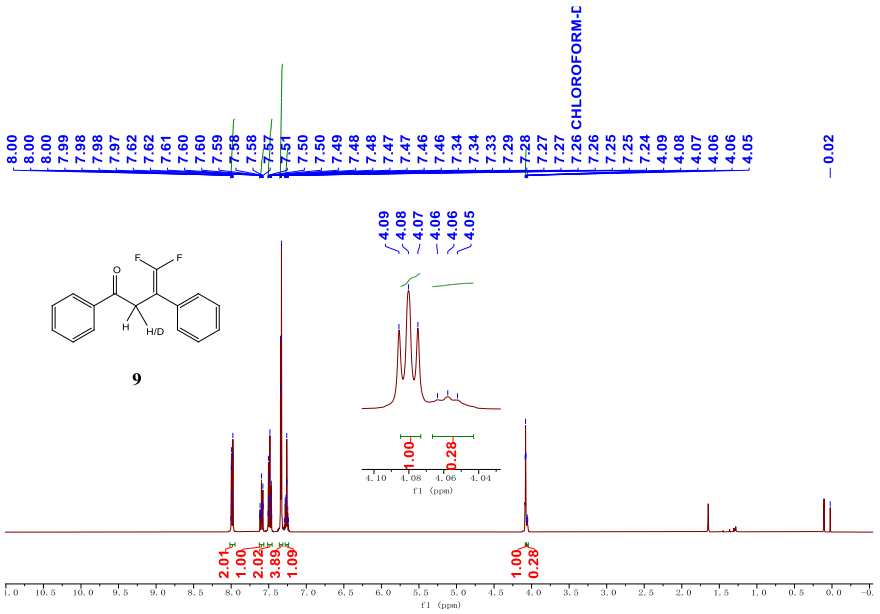


A solution of 4,4-difluoro-1,3-diphenylbut-3-en-1-one **3a** (77.5 mg, 0.3 mmol), Cs_2CO_3 (195.6 mg, 0.6 mmol), and D_2O (54.0 mg, 3.0 mmol) in EtOAc (3.5 mL) was stirred at 70 °C under N_2 for 6 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product **8** was directly analyzed by ^1H NMR, which showed that two deuterium atoms were incorporated into the α-position of carbonyl group with a ratio of 1:1 (67%-D incorporation). **These results suggested that the deuterium atoms might be incorporated by keto-enol tautomerism of product 3a under basic conditions rather than direct hydrodefluorination by using water as a hydrogen source.**

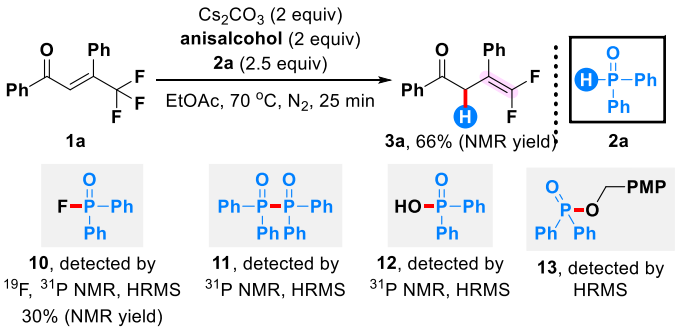




A solution of (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one **1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide-*d* **2a-D** (151.6 mg, 0.75 mmol),[2] and Cs_2CO_3 (195.6 mg, 0.6 mmol) in EtOAc (3.5 mL) was stirred at 70 °C under N_2 for 25 min. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **9** (65% yield, 72%-D incorporation). The ^1H NMR analysis of product **9** showed that only one deuterium atom was incorporated into the α-position of carbonyl group. **This result suggested that the hydrogen atom in the product might come from the $HP(O)Ph_2$ component.**



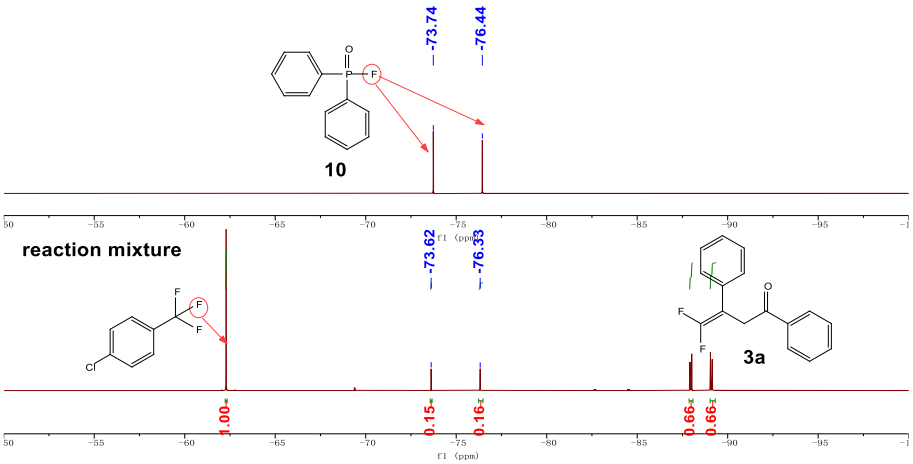
3) Analysis of possible reaction intermediates



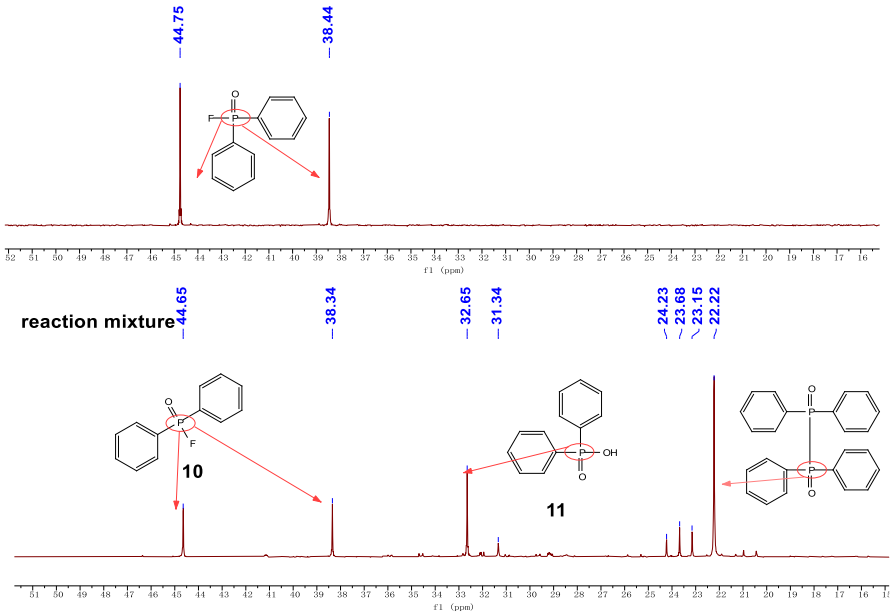
A solution of (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one **1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide **2a** (151.6 mg, 0.75 mmol), Cs_2CO_3 (195.6 mg, 0.6 mmol), and (4-methoxyphenyl)methanol (41.4 mg, 0.3 mmol) in EtOAc (3.5 mL) was stirred at 70 °C under N_2 for 25 min. 66%-NMR yield of product **3a** and 30%-NMR yield of diphenylphosphinic

fluoride (**10**)[2] were formed as determined by ^{19}F NMR analysis of the reaction mixture with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard. The existence of diphenylphosphinic fluoride (**10**) was also determined by ^{31}P analysis of the reaction mixture.

^{19}F NMR[1-3] analysis of the reaction mixture:



^{31}P NMR analysis of the reaction mixture:



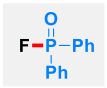
In addition, HRMS analysis of the reaction mixture suggested the involvement of intermediates **10**-**13**.

Elemental Composition Report

Single Mass Analysis

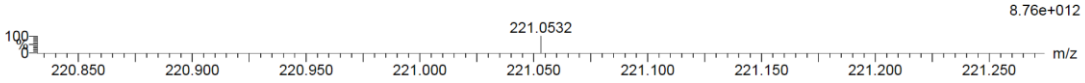
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
46 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 12-13 H: 10-11 N: 0-2 O: 1-2 F: 1-4 P: 1-2



10
$C_{12}H_{11}FOP^+$
$[M+H]^+$: 221.0526
found: 221.0532

slw-1112-1 (1.900) Is (1.00,1.00) C12H10FOP
2: TOF MS ES+



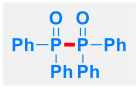
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
221.0532	221.0532	0.0	0.0	7.5	75.6	n/a	n/a	C12 H11 O F P

Elemental Composition Report

Single Mass Analysis

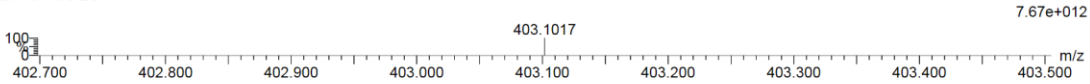
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 24-25 H: 20-22 O: 1-2 P: 1-2



11
$C_{24}H_{21}O_2P_2^+$
$[M+H]^+$: 403.1011
found: 403.1017

slw-1112-1 (2.071) Is (1.00,1.00) C24H20O2P2
2: TOF MS ES+



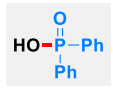
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
403.1017	403.1017	0.0	0.0	15.5	75.7	n/a	n/a	C24 H21 O2 P2

Elemental Composition Report

Single Mass Analysis

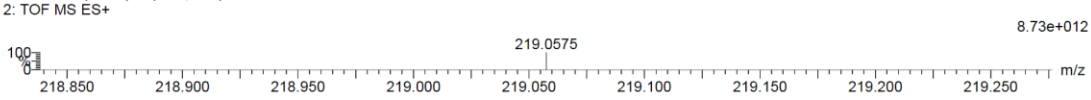
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 10-25 H: 10-22 O: 1-2 P: 1-2



12
$C_{12}H_{12}O_2P^+$
$[M+H]^+$: 219.0569
found: 219.0575

slw-1112-1 (1.388) Is (1.00,1.00) C12H11O2P
2: TOF MS ES+

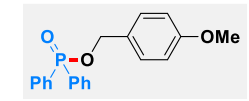


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
219.0575	219.0575	0.0	0.0	7.5	75.5	n/a	n/a	C12 H12 O2 P

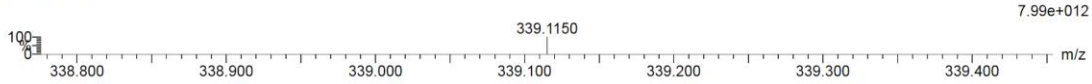
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 10-25 H: 10-22 O: 1-3 P: 1-2
slw-1112-1 (1.217) Is (1.00,1.00) C20H19O3P
2: TOF MS ES+



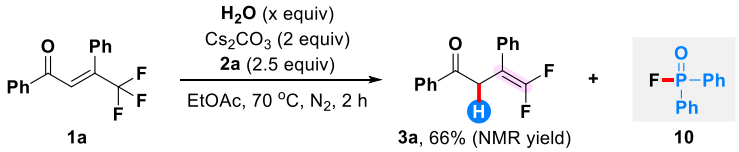
13
$C_{20}H_{20}O_3P^+$
$[M+H]^+$: 339.1145
found: 339.1150



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
339.1150	339.1150	0.0	0.0	11.5	75.7	n/a	n/a	C20 H20 O3 P

These results suggested that intermediates 10-13 might involve in the reaction mixture.

4) Investigation on the effect of the H_2O

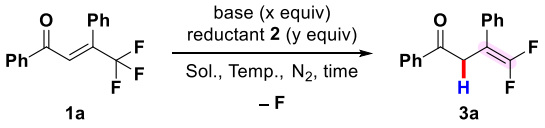


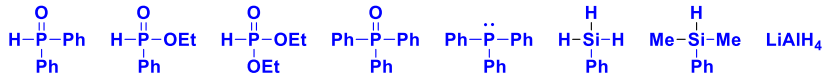
H_2O (x)	**3a**	**10** (NMR yield)
0	67%	52%
5	87%	24%

A solution of (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one **1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide **2a** (151.6 mg, 0.75 mmol), Cs_2CO_3 (195.6 mg, 0.6 mmol), and H_2O (0-1.5 mmol) in EtOAc (3.5 mL) was stirred at 70 °C under N_2 for 2 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). NMR yield of product **3a** and diphenylphosphinic fluoride (**10**) were determined by ^{19}F NMR analysis of the reaction mixture with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard. **These results suggested that the addition of water might promote the transformation of *in situ* formed diphenylphosphinic fluoride (10) to increase the yield of desired product 3a.**

Optimization of reaction conditions

Table S1. Optimization of reaction conditions[a]





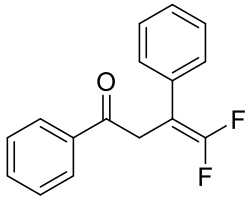
Entry	**2** (y equiv)	Base (x equiv)	Solvent	Temp. (°C)	Time	Yield (%)[b]
1	**2a** (2)	Cs_2CO_3 (3)	DCE	70	12 h	56
2	**2a** (2)	Cs_2CO_3 (3)	MeCN	70	12 h	4
3	**2a** (2)	Cs_2CO_3 (3)	DMSO	70	12 h	0
4	**2a** (2)	Cs_2CO_3 (3)	DMF	70	12 h	0
5	**2a** (2)	Cs_2CO_3 (3)	EtOH	70	12 h	0
6	**2a** (2)	Cs_2CO_3 (3)	EtOAc	70	12 h	58
7	**2a** (2)	Cs_2CO_3 (3)	$MeNO_2$	70	12 h	25
8	**2a** (2)	Cs_2CO_3 (3)	NMP	70	12 h	10
9	**2a** (2)	Cs_2CO_3 (3)	DMA	70	12 h	10
10	**2a** (2)	Cs_2CO_3 (3)	NMP	r.t.	24 h	18
11	**2a** (2)	Cs_2CO_3 (3)	NMP	50	24 h	18
12	**2a** (2)	Cs_2CO_3 (3)	NMP	100	24 h	trace
13	**2a** (2)	Cs_2CO_3 (3)	NMP	120	24 h	trace
14	**2a** (2)	Cs_2CO_3 (3)	EtOAc	70	25 min	57 (53)[c]
15	--	Cs_2CO_3 (3)	EtOAc	70	12 h	trace
16	**2a** (0.1)	Cs_2CO_3 (3)	EtOAc	70	25 min	0
17	**2a** (1)	Cs_2CO_3 (3)	EtOAc	70	25 min	32
18	**2a** (1.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	43
19	**2a** (2.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	62 (60)[c]
20	**2a** (2.5)	Cs_2CO_3 (3)	EtOAc	rt	25 min	57
21	**2a** (2.5)	Cs_2CO_3 (3)	EtOAc	70	3.5 h	58 (55)[c]
22	**2a** (2.5)	$NaHCO_3$ (3)	EtOAc	70	25 min	0
23	**2a** (2.5)	K_3PO_4 (3)	EtOAc	70	25 min	0
24	**2a** (2.5)	K_3PO_4 (3)	EtOAc	70	24 h	trace
25	**2a** (2.5)	NaOAc (3)	EtOAc	70	25 min	0
26	**2a** (2.5)	Et_3N (3)	EtOAc	70	25 min	0
27	**2a** (2.5)	DABCO (3)	EtOAc	70	25 min	0
28	**2a** (2.5)	LiOH (3)	EtOAc	70	25 min	0
29	**2b** (2.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	0
30	**2c** (2.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	0
31	**2d** (2.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	<5 (>90)[d]
32	**2e** (2.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	<5 (>90)[d]

Table S1. *Continued.*

Entry	**2** (y equiv)	Base (x equiv)	Solvent	Temp. (°C)	Time	Yield (%)[b]
33	**2f** (2.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	trace
34	**2g** (2.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	trace
35	**2h** (2.5)	Cs_2CO_3 (3)	EtOAc	70	25 min	trace
36	**2a** (2.5)	Cs_2CO_3 (0.5)	EtOAc	70	25 min	49
37	**2a** (2.5)	Cs_2CO_3 (1.2)	EtOAc	70	25 min	62
38	**2a** (2.5)	Cs_2CO_3 (1.5)	EtOAc	70	25 min	65
39	**2a** (2.5)	Cs_2CO_3 (2.0)	EtOAc	70	25 min	70 (67)[c]
40	**2a** (2.5)	Cs_2CO_3 (2.0)	EtOAc	70	3 h	84 (81)[c,e]
41	**2a** (2.5)	Cs_2CO_3 (2.0)	EtOAc	70	3 h	90 (87)[c,f]
42	**2a** (1.0)	Cs_2CO_3 (1.0)	EtOAc	70	3 h	65[f]
43	**2a** (2.5)	Cs_2CO_3 (2.0)	EtOAc	70	3 h	trace[c,g]
44	**2a** (2.5)	K_2CO_3 (2.0)	EtOAc	70	3 h	48[f]
45	PhCHO (2.5)	Cs_2CO_3 (2.0)	EtOAc	70	3 h	0[f]

[a] Reaction conditions: **1a** (0.3 mmol), **2** (0-0.75 mmol), and base (0-0.9 mmol) in solvent (3.5 mL) at r.t.-120 °C under N_2. [b] Yields were determined by ^{19}F NMR analysis with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard. [c] Isolated yield. [d] Recovery yield of **1a**. [e] H_2O (10 equiv.) was added. [f] H_2O (5 equiv.) was added. [g] H_2O (20 equiv.) was added.

Characterization data for products[1,3]



4,4-Difluoro-1,3-diphenylbut-3-en-1-one (3a):

Yield = 87% (67.5 mg). White solid. M.p. 66.7–68.4 °C.

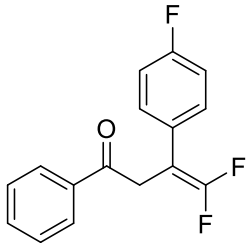
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02-7.96 (m, 2H), 7.63-7.56 (m, 1H), 7.52-7.45 (m, 2H), 7.37-7.31 (m, 4H), 7.30-7.22 (m, 1H), 4.08 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.93 (d, J = 37.2 Hz, 1F), -89.08 (d, J = 37.3 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.3 (t, $J_{C\text{-}F}$ = 2.7 Hz), 154.7 (dd, $J_{C\text{-}F}$ = 292.4, 288.0 Hz), 136.2, 133.4, 128.7, 128.5, 128.1, 128.0 (t, $J_{C\text{-}F}$ = 3.6 Hz), 127.4, 87.1 (dd, $J_{C\text{-}F}$ = 21.7, 17.3 Hz), 38.3 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{13}F_2O$ $[M+H]^+$ 259.0929, found: 259.0934.



4,4-Difluoro-3-(4-fluorophenyl)-1-phenylbut-3-en-1-one (3b):

Yield = 82% (67.8 mg). Yellow oil.

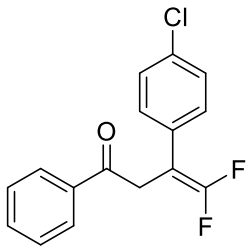
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01-7.94 (m, 2H), 7.64-7.55 (m, 1H), 7.53-7.44 (m, 2H), 7.33-7.27 (m, 2H), 7.08-6.96 (m, 2H), 4.05 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -88.25 (d, J = 37.2 Hz, 1F), -89.16 (d, J = 37.2 Hz, 1F), -114.15 (td, J = 8.9, 4.0 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.3, 161.9 (d, $J_{C\text{-}F}$ = 247.1 Hz), 154.6 (dd, $J_{C\text{-}F}$ = 290.7, 289.0 Hz), 136.1, 133.5, 129.8 (dt, $J_{C\text{-}F}$ = 7.3, 3.4 Hz), 129.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 128.7, 128.1, 115.4 (d, $J_{C\text{-}F}$ = 21.7 Hz), 86.4 (dd, $J_{C\text{-}F}$ = 22.3, 17.7 Hz), 38.4 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{12}F_3O$ $[M+H]^+$ 277.0835, found: 277.0836.



3-(4-Chlorophenyl)-4,4-difluoro-1-phenylbut-3-en-1-one (3c):

Yield = 69% (60.7 mg). Yellow oil.

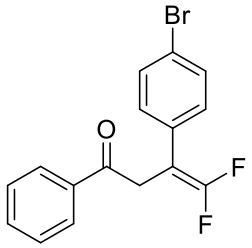
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00-7.92 (m, 2H), 7.63-7.54 (m, 1H), 7.52-7.43 (m, 2H), 7.33-7.21 (m, 4H), 4.04 (t, J = 2.1 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.27 (d, J = 35.6 Hz, 1F), -88.17 (d, J = 35.4 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.1 (t, $J_{C\text{-}F}$ = 2.8 Hz), 154.6 (dd, $J_{C\text{-}F}$ = 292.8, 289.0 Hz), 136.0, 133.6, 133.3, 131.9 (t, $J_{C\text{-}F}$ = 4.2 Hz), 129.3 (t, $J_{C\text{-}F}$ = 3.4 Hz), 128.7, 128.7, 128.1, 86.5 (dd, $J_{C\text{-}F}$ = 22.6, 16.9 Hz), 38.1 (d, $J_{C\text{-}F}$ = 1.9 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{12}ClF_2O$ $[M+H]^+$ 293.0539, found: 293.0545.



3-(4-Bromophenyl)-4,4-difluoro-1-phenylbut-3-en-1-one (3d):

Yield = 68% (68.7 mg). Yellow oil.

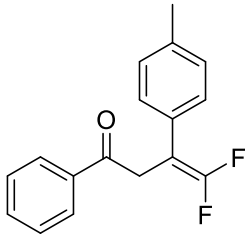
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01-7.94 (m, 2H), 7.65-7.56 (m, 1H), 7.53-7.41 (m, 4H), 7.24-7.16 (m, 2H), 4.06 (t, J = 2.1 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.09 (d, J = 34.5 Hz, 1F), -88.01 (d, J = 34.7 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.1 (t, $J_{C\text{-}F}$ = 2.5 Hz), 154.6 (dd, $J_{C\text{-}F}$ = 292.8, 289.1 Hz), 136.0, 133.6, 132.3 (t, $J_{C\text{-}F}$ = 4.0 Hz), 131.6, 129.6 (t, $J_{C\text{-}F}$ = 3.6 Hz), 128.7, 128.1, 121.4, 86.5 (dd, $J_{C\text{-}F}$ = 22.6, 17.4 Hz), 38.0 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{12}BrF_2O$ $[M+H]^+$ 337.0034, found: 337.0040.



4,4-Difluoro-1-phenyl-3-(p-tolyl)but-3-en-1-one (3e):

Yield = 80% (65.0 mg). Yellow oil.

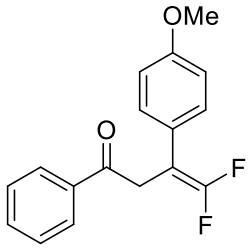
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-7.96 (m, 2H), 7.64-7.56 (m, 1H), 7.53-7.45 (m, 2H), 7.26-7.21 (m, 2H), 7.19-7.12 (m, 2H), 4.07 (t, J = 2.2 Hz, 2H), 2.34 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -88.08 (d, J = 40.1 Hz, 1F), -89.10 (d, J = 41.0 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4 (t, $J_{C\text{-}F}$ = 2.5 Hz), 154.6 (dd, $J_{C\text{-}F}$ = 291.8, 287.5 Hz), 137.2, 136.2, 133.4, 130.3 (t, $J_{C\text{-}F}$ = 4.5 Hz), 129.2, 128.7, 128.1, 127.8 (t, $J_{C\text{-}F}$ = 3.4 Hz), 87.0 (dd, $J_{C\text{-}F}$ = 21.4, 17.6 Hz), 38.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 21.0 ppm.

HRMS (m/z): calcd for $C_{17}H_{15}F_2O$ $[M+H]^+$ 273.1085, found: 273.1085.



4,4-Difluoro-3-(4-methoxyphenyl)-1-phenylbut-3-en-1-one (3f):

Yield = 75% (65.2 mg). Yellow oil.

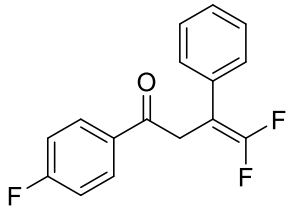
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99-7.92 (m, 2H), 7.61-7.53 (m, 1H), 7.49-7.42 (m, 2H), 7.27-7.20 (m, 2H), 6.89-6.81 (m, 2H), 4.02 (t, J = 2.2 Hz, 2H), 3.76 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.16 (d, J = 39.9 Hz, 1F), -90.00 (d, J = 39.5 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5 (t, $J_{C\text{-}F}$ = 2.2 Hz), 158.7, 154.5 (dd, $J_{C\text{-}F}$ = 291.2, 287.4 Hz), 136.3, 133.4, 129.1 (t, $J_{C\text{-}F}$ = 3.5 Hz), 128.7, 128.1, 125.5 (t, $J_{C\text{-}F}$ = 3.9 Hz), 113.9, 86.7 (dd, $J_{C\text{-}F}$ = 21.9, 17.6 Hz), 55.1, 38.4 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{17}H_{15}F_2O_2$ $[M+H]^+$ 289.1035, found: 289.1040.



4,4-Difluoro-1-(4-fluorophenyl)-3-phenylbut-3-en-1-one (3g):

Yield = 78% (64.9 mg). Colorless oil.

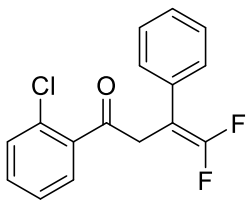
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05-7.96 (m, 2H), 7.38-7.30 (m, 4H), 7.30-7.23 (m, 1H), 7.20-7.08 (m, 2H), 4.05 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.89 (d, J = 36.9 Hz, 1F), -88.92 (d, J = 36.2 Hz, 1F), -104.28 (ddd, J = 13.4, 9.0, 4.6 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.8 (t, $J_{C\text{-}F}$ = 2.7 Hz), 165.9 (d, $J_{C\text{-}F}$ = 255.3 Hz), 154.7 (dd, $J_{C\text{-}F}$ = 292.3, 288.1 Hz), 133.3 (t, $J_{C\text{-}F}$ = 3.3 Hz), 132.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.8 (d, $J_{C\text{-}F}$ = 9.6 Hz), 128.5, 127.9 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.5, 115.8 (d, $J_{C\text{-}F}$ = 22.2 Hz), 87.1 (dd, $J_{C\text{-}F}$ = 21.7, 17.8 Hz), 38.2 (d, $J_{C\text{-}F}$ = 2.9 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{12}F_3O$ $[M+H]^+$ 277.0835, found: 277.0833.



1-(2-Chlorophenyl)-4,4-difluoro-3-phenylbut-3-en-1-one (3h):

Yield = 91% (80.3 mg). Colorless oil.

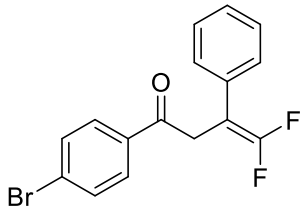
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.33 (m, 4H), 7.33-7.23 (m, 5H), 4.06 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.21 (d, J = 34.5 Hz, 1F), -88.81 (d, J = 34.4 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8 (t, $J_{C\text{-}F}$ = 2.6 Hz), 154.8 (dd, $J_{C\text{-}F}$ = 293.1, 288.8 Hz), 138.6, 133.0 (t, $J_{C\text{-}F}$ = 3.9 Hz), 131.9, 130.8, 130.4, 128.9, 128.5, 127.9 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.5, 126.9, 86.9 (dd, $J_{C\text{-}F}$ = 21.9, 17.6 Hz), 42.3 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{12}ClF_2O$ $[M+H]^+$ 293.0539, found: 293.0534.



1-(4-Bromophenyl)-4,4-difluoro-3-phenylbut-3-en-1-one (3i):

Yield = 84% (85.2 mg). White solid. M.p. 39.7–40.5 °C.

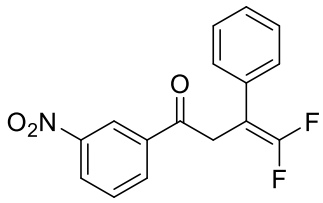
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.78 (m, 2H), 7.63-7.56 (m, 2H), 7.36-7.27 (m, 4H), 7.26-7.21 (m, 1H), 4.01 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.71 (d, J = 35.9 Hz, 1F), -88.74 (d, J = 36.0 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.4 (t, $J_{C\text{-}F}$ = 2.7 Hz), 154.7 (dd, $J_{C\text{-}F}$ = 292.6, 288.3 Hz), 134.9, 133.2 (t, $J_{C\text{-}F}$ = 4.1 Hz), 132.0, 129.6, 128.6, 128.5, 127.9 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.5, 87.0 (dd, $J_{C\text{-}F}$ = 21.7, 17.8 Hz), 38.3 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{12}BrF_2O$ $[M+H]^+$ 337.0034, found: 337.0036.



4,4-Difluoro-1-(3-nitrophenyl)-3-phenylbut-3-en-1-one (3j):

Yield = 51% (46.3 mg). Yellow solid. M.p. 40.8–41.3 °C.

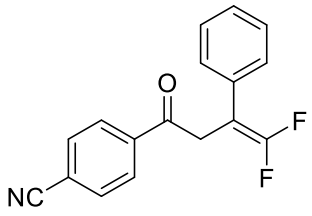
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 30/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (t, J = 2.0 Hz, 1H), 8.47-8.41 (m, 1H), 8.31-8.26 (m, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.39-7.24 (m, 5H), 4.13 (t, J = 2.1 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.38 (d, J = 36.1 Hz, 1F), -88.35 (d, J = 36.0 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3 (t, $J_{C\text{-}F}$ = 2.9 Hz), 154.7 (dd, J = 293.1, 288.8 Hz), 148.4, 137.3, 133.6, 132.9 (t, $J_{C\text{-}F}$ = 3.7 Hz), 130.0, 128.6, 127.9 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.7, 127.7, 123.0, 86.6 (dd, $J_{C\text{-}F}$ = 21.5, 18.1 Hz), 38.7 (d, $J_{C\text{-}F}$ = 2.9 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{12}F_2NO_3$ $[M+H]^+$ 304.0780, found: 304.0785.



4-(4,4-Difluoro-3-phenylbut-3-enoyl)benzonitrile (3k):

Yield = 51% (43.2 mg). Yellow solid. M.p. 79.4–80.9 °C.

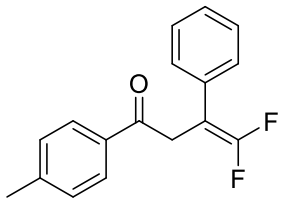
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 30/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.01 (m, 2H), 7.81-7.72 (m, 2H), 7.38-7.24 (m, 5H), 4.07 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.39 (d, J = 35.5 Hz, 1F), -88.41 (d, J = 35.4 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.2 (t, $J_{C\text{-}F}$ = 2.6 Hz), 154.7 (dd, J = 292.8, 288.5 Hz), 139.1, 132.8 (t, $J_{C\text{-}F}$ = 3.9 Hz), 132.6, 128.6, 128.5, 127.9 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.7, 117.8, 116.7, 86.7 (dd, $J_{C\text{-}F}$ = 21.5, 18.0 Hz), 38.7 (d, $J_{C\text{-}F}$ = 2.9 Hz) ppm.

HRMS (m/z): calcd for $C_{17}H_{12}F_2NO$ $[M+H]^+$ 284.0881, found: 284.0887.



4,4-Difluoro-3-phenyl-1-(p-tolyl)but-3-en-1-one (3l):

Yield = 81% (66.1 mg). Yellow solid. M.p. 31.5–33.0 °C.

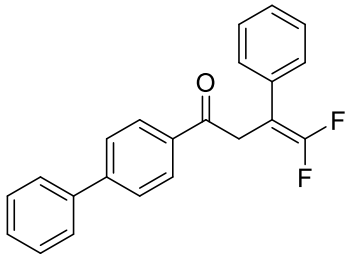
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = δ = 7.93-7.87 (m, 2H), 7.36-7.32 (m, 4H), 7.31-7.24 (m, 3H), 4.06 (t, J = 2.2 Hz, 2H), 2.43 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -88.06 (d, J = 37.1 Hz, 1F), -89.10 (d, J = 37.0 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.0 (t, $J_{C\text{-}F}$ = 2.6 Hz), 154.7 (dd, $J_{C\text{-}F}$ = 292.1, 287.8 Hz), 144.3, 133.8, 133.5 (t, $J_{C\text{-}F}$ = 3.8 Hz), 129.3, 128.4, 128.2, 127.9 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.4, 87.2 (dd, $J_{C\text{-}F}$ = 21.9, 17.1 Hz), 38.1 (d, $J_{C\text{-}F}$ = 2.4 Hz), 21.6 ppm.

HRMS (m/z): calcd for $C_{17}H_{15}F_2O$ $[M+H]^+$ 273.1085, found: 273.1090.



1-([1,1'-Biphenyl]-4-yl)-4,4-difluoro-3-phenylbut-3-en-1-one (3m):

Yield = 84% (84.5 mg). White solid. M.p. 115.3–116.2 °C.

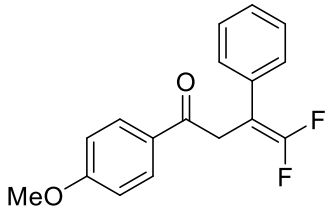
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-8.04 (m, 2H), 7.75-7.69 (m, 2H), 7.68-7.63 (m, 2H), 7.54-7.47 (m, 2H), 7.46-7.41 (m, 1H), 7.40-7.32 (m, 4H), 7.31-7.26 (m, 1H), 4.12 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.85 (d, J = 36.4 Hz, 1F), -88.89 (d, J = 36.7 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9 (t, $J_{C\text{-}F}$ = 2.6 Hz), 154.7 (dd, $J_{C\text{-}F}$ = 292.4, 288.0 Hz), 146.1, 139.7, 134.9, 133.4, 129.0, 128.7, 128.5, 128.3, 128.0 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.4, 127.3, 127.2, 87.2 (dd, $J_{C\text{-}F}$ = 21.9, 17.6 Hz), 38.3 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{22}H_{17}F_2O$ $[M+H]^+$ 335.1242, found: 335.1248.



4,4-Difluoro-1-(4-methoxyphenyl)-3-phenylbut-3-en-1-one (3n):

Yield = 85% (73.1 mg). White solid. M.p. 56.6–57.4 °C.

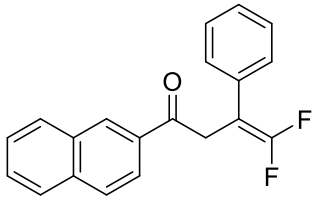
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97-7.91 (m, 2H), 7.34-7.27 (m, 4H), 7.26-7.20 (m, 1H), 6.96-6.89 (m, 2H), 4.00 (t, J = 2.2 Hz, 2H), 3.84 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -88.14 (d, J = 37.1 Hz, 1F), -89.15 (d, J = 37.1 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.8 (t, $J_{C\text{-}F}$ = 2.8 Hz), 163.7, 154.7 (dd, $J_{C\text{-}F}$ = 292.2, 287.8 Hz), 133.5 (t, $J_{C\text{-}F}$ = 4.1 Hz), 130.4, 129.3, 128.4, 127.9 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.3, 113.8, 89.4 (dd, $J_{C\text{-}F}$ = 21.9, 17.1 Hz), 55.4, 37.9 (d, $J_{C\text{-}F}$ = 2.5 Hz) ppm.

HRMS (m/z): calcd for $C_{17}H_{15}F_2O_2$ $[M+H]^+$ 289.1035, found: 289.1032.



4,4-Difluoro-1-(naphthalen-2-yl)-3-phenylbut-3-en-1-one (3o):

Yield = 86% (79.7 mg). White solid. M.p. 87.4–89.0 °C.

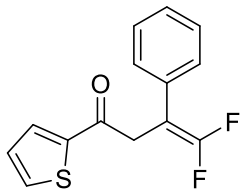
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 1H), 8.05 (dd, J = 8.6, 1.8 Hz, 1H), 7.96 (d, J = 6.8 Hz, 1H), 7.93-7.86 (m, 2H), 7.67-7.54 (m, 2H), 7.45-7.33 (m, 4H), 7.32-7.24 (m, 1H), 4.22 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.80 (d, J = 36.7 Hz, 1F), -88.85 (d, J = 36.2 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.2 (t, $J_{C\text{-}F}$ = 2.2 Hz), 154.7 (dd, $J_{C\text{-}F}$ = 292.4, 288.0 Hz), 135.6, 133.5, 133.4 (d, $J_{C\text{-}F}$ = 3.8 Hz), 132.4, 129.9, 129.5, 128.6, 128.5, 128.5, 127.9 (t, $J_{C\text{-}F}$ = 3.6 Hz), 127.7, 127.4, 126.9, 123.7, 87.3 (dd, $J_{C\text{-}F}$ = 21.7, 17.3 Hz), 38.3 (d, $J_{C\text{-}F}$ = 2.9 Hz) ppm.

HRMS (m/z): calcd for $C_{20}H_{15}F_2O$ $[M+H]^+$ 309.1085, found: 309.1091.



4,4-Difluoro-3-phenyl-1-(thiophen-2-yl)but-3-en-1-one (3p):

Yield = 88% (69.8 mg). Yellow oil.

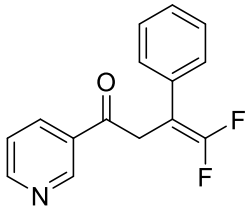
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (dd, J = 3.8, 1.1 Hz, 1H), 7.66 (dd, J = 4.9, 1.1 Hz, 1H), 7.39-7.31 (m, 4H), 7.30-7.24 (m, 1H), 7.14 (dd, J = 5.0, 3.8 Hz, 1H), 4.01 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.63 (d, J = 35.7 Hz, 1F), -88.71 (d, J = 35.7 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.2 (t, $J_{C\text{-}F}$ = 3.1 Hz), 154.8 (dd, $J_{C\text{-}F}$ = 292.5, 288.8 Hz), 143.1, 134.1, 133.2 (t, $J_{C\text{-}F}$ = 4.1 Hz), 132.1, 128.5, 128.2, 128.0 (t, $J_{C\text{-}F}$ = 3.6 Hz), 127.5, 87.1 (dd, $J_{C\text{-}F}$ = 21.7, 17.8 Hz), 38.8 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{14}H_{11}F_2OS$ $[M+H]^+$ 265.0493, found: 265.0499.



4,4-Difluoro-3-phenyl-1-(pyridin-3-yl)but-3-en-1-one (3q):

Yield = 68% (52.8 mg). White solid. M.p. 57.7–58.6 °C.

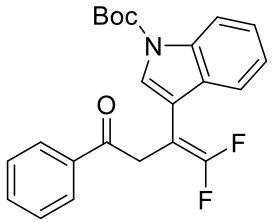
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.18 (s, 1H), 8.79 (d, J = 3.6 Hz, 1H), 8.21 (dt, J = 8.0, 2.1 Hz, 1H), 7.42 (dd, J = 8.0, 4.8 Hz, 1H), 7.36-7.28 (m, 4H), 7.28-7.22 (m, 1H), 4.07 (t, J = 2.1 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.50 (d, J = 35.8 Hz, 1F), -88.55 (d, J = 35.8 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.3 (t, $J_{C\text{-}F}$ = 2.5 Hz), 154.6 (dd, $J_{C\text{-}F}$ = 292.7, 286.7 Hz), 153.8, 149.5, 135.4, 132.9 (t, $J_{C\text{-}F}$ = 3.9 Hz), 131.4, 128.5, 127.9 (t, $J_{C\text{-}F}$ = 3.4 Hz), 127.6, 123.7, 86.6 (dd, $J_{C\text{-}F}$ = 21.7, 18.3 Hz), 38.6 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{15}H_{12}F_2NO$ $[M+H]^+$ 260.0881, found: 260.0882.

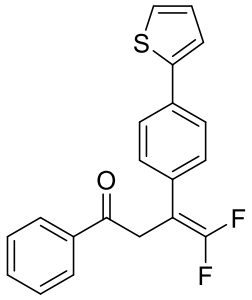


***tert*-Butyl 3-(1,1-difluoro-4-oxo-4-phenylbut-1-en-2-yl)-1*H*-indole-1-carboxylate (3r):**

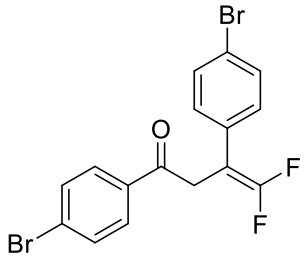
Yield = 62% (73.6 mg). Pink oil.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 7.1 Hz, 1H), 8.00-7.93 (m, 2H), 7.63-7.52 (m, 3H), 7.50-7.42 (m, 2H), 7.37-7.30 (m, 1H), 7.29-7.24 (m, 1H), 4.09 (t, J = 2.1 Hz, 2H), 1.66 (s, 9H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -85.15 (d, J = 35.8 Hz, 1F), -88.24 (d, J = 35.8 Hz, 1F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.3 (t, $J_{C\text{-}F}$ = 2.9 Hz), 154.6 (dd, $J_{C\text{-}F}$ = 289.3, 287.6 Hz), 149.4, 136.2, 135.1, 133.4, 128.8, 128.7, 128.1, 124.9 (d, $J_{C\text{-}F}$ = 2.9 Hz), 124.6, 122.8, 119.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 115.3, 113.5 (d, $J_{C\text{-}F}$ = 5.2 Hz), 84.0, 79.6 (dd, $J_{C\text{-}F}$ = 25.5, 20.7 Hz), 38.7 (d, $J_{C\text{-}F}$ = 2.4 Hz), 28.1 ppm.
HRMS (m/z): calcd for $C_{23}H_{22}F_2NO_3$ $[M+H]^+$ 398.1562, found: 398.1560.

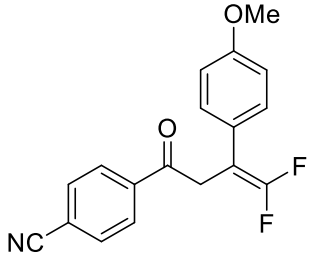


4,4-Difluoro-1-phenyl-3-(4-(thiophen-2-yl)phenyl)but-3-en-1-one (3s):
Yield = 70% (71.2 mg). White solid. M.p. 94.9–96.1 °C.
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-7.98 (m, 2H), 7.64-7.55 (m, 3H), 7.53-7.46 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.29 (m, 1H), 7.29-7.26 (m, 1H), 7.08 (dd, J = 5.2, 3.6 Hz, 1H), 4.10 (t, J = 2.2 Hz, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.12 (d, J = 35.8 Hz, 1F), -88.01 (d, J = 35.8 Hz, 1F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5 (t, $J_{C\text{-}F}$ = 2.5 Hz), 154.7 (dd, $J_{C\text{-}F}$ = 292.9, 288.4 Hz), 143.6, 136.1, 133.5, 133.4, 132.4 (t, $J_{C\text{-}F}$ = 4.2 Hz), 128.7, 128.3 (t, $J_{C\text{-}F}$ = 3.9 Hz), 128.1, 128.0, 125.9, 124.9, 123.2, 86.9 (dd, $J_{C\text{-}F}$ = 22.2, 16.9 Hz), 38.0 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.
HRMS (m/z): calcd for $C_{20}H_{15}F_2OS$ $[M+H]^+$ 341.0806, found: 341.0803.



1,3-Bis(4-bromophenyl)-4,4-difluorobut-3-en-1-one (3t):
Yield = 67% (83.1 mg). Yellow solid. M.p. 53.8–54.8 °C.
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.76 (m, 2H), 7.66-7.57 (m, 2H), 7.48-7.41 (m, 2H), 7.21-7.13 (m, 2H), 4.00 (t, J = 2.2 Hz, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -86.88 (d, J = 34.2 Hz, 1F), -87.78 (d, J = 34.3 Hz, 1F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1 (t, $J_{C\text{-}F}$ = 2.6 Hz), 154.6 (dd, $J_{C\text{-}F}$ = 293.1, 289.2 Hz), 134.7, 132.1 (t, $J_{C\text{-}F}$ = 3.8 Hz), 132.1, 131.7, 129.6, 129.5, 128.8, 121.5, 86.3 (dd, $J_{C\text{-}F}$ = 22.4, 17.1 Hz), 38.0 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{11}Br_2F_2O$ $[M+H]^+$ 414.9139, found: 414.9145.



4-(4,4-Difluoro-3-(4-methoxyphenyl)but-3-enoyl)benzonitrile (3u):

Yield = 56% (52.6 mg). Yellow oil.

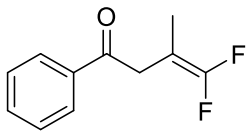
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 30/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05-7.99 (m, 2H), 7.80-7.74 (m, 2H), 7.24-7.17 (m, 2H), 6.89-6.82 (m, 2H), 4.03 (t, J = 2.2 Hz, 2H), 3.78 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -88.58 (d, J = 38.3 Hz, 1F), -89.40 (d, J = 38.2 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.4 (t, $J_{C\text{-}F}$ = 2.7 Hz), 158.9, 154.5 (dd, $J_{C\text{-}F}$ = 291.5, 287.9 Hz), 139.1, 132.6, 129.1 (t, $J_{C\text{-}F}$ = 3.4 Hz), 128.5, 124.9 (t, $J_{C\text{-}F}$ = 3.7 Hz), 117.8, 116.6, 114.0, 86.2 (dd, $J_{C\text{-}F}$ = 21.6, 18.4 Hz), 55.2, 38.8 (d, $J_{C\text{-}F}$ = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{18}H_{14}F_2NO_2$ $[M+H]^+$ 314.0987, found: 314.0981.



4,4-Difluoro-3-methyl-1-phenylbut-3-en-1-one (3y):

Yield = 25% (14.7 mg). Colorless oil.

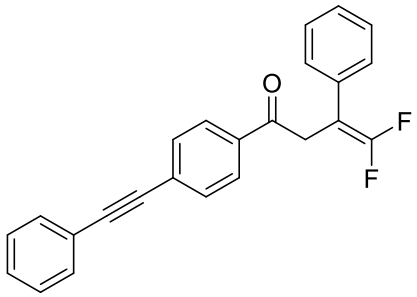
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99-7.94 (m, 2H), 7.62-7.56 (m, 1H), 7.52-7.45 (m, 2H), 3.64 (t, J = 1.9 Hz, 2H), 1.65 (t, J = 3.2 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -94.06 (d, J = 55.2 Hz, 1F), -94.41 (d, J = 53.7 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.3 (t, $J_{C\text{-}F}$ = 2.7 Hz), 153.7 (dd, $J_{C\text{-}F}$ = 281.6, 280.2 Hz), 136.3, 133.4, 128.1, 128.1, 80.5 (dd, $J_{C\text{-}F}$ = 22.9, 19.0 Hz), 38.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 12.6 ppm.

HRMS (m/z): calcd for $C_{11}H_{11}F_2O$ $[M+H]^+$ 197.0772, found: 197.0778.



4,4-Difluoro-3-phenyl-1-(4-(phenylethynyl)phenyl)but-3-en-1-one (3z):

Yield = 67% (72.3 mg). White solid. M.p. 140.8–141.4 °C.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl

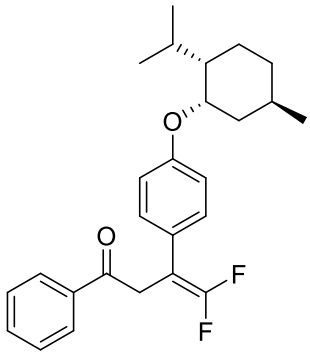
acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00-7.93 (m, 2H), 7.67-7.61 (m, 2H), 7.60-7.55 (m, 2H), 7.42-7.37 (m, 3H), 7.36-7.32 (m, 4H), 7.31-7.25 (m, 1H), 4.07 (t, J = 2.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.77 (d, J = 37.3 Hz, 1F), -88.81 (d, J = 35.8 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6 (t, $J_{C\text{-}F}$ = 2.6 Hz), 154.7 (dd, J = 292.4, 288.0 Hz), 135.2, 133.3 (t, $J_{C\text{-}F}$ = 3.8 Hz), 131.8, 131.7, 128.9, 128.5, 128.5, 128.4, 128.1, 127.9 (t, J = 3.6 Hz), 127.5, 122.5, 93.0, 88.5, 87.0 (dd, J = 21.9, 17.6 Hz), 38.3 (d, J = 2.4 Hz) ppm.

HRMS (m/z): calcd for $C_{24}H_{17}F_2O$ $[M+H]^+$ 359.1242, found: 359.1245.



4,4-Difluoro-3-(4-(((1S,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)-1-phenylbut-3-en-1-one (3a'):

Yield = 61% (75.9 mg). Colorless oil.

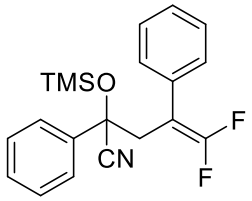
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01-7.94 (m, 2H), 7.63-7.54 (m, 1H), 7.52-7.44 (m, 2H), 7.24-7.17 (m, 2H), 6.88-6.80 (m, 2H), 4.60 (d, J = 2.9 Hz, 1H), 4.03 (t, J = 2.2 Hz, 2H), 2.12-2.01 (m, 1H), 1.81-1.69 (m, 2H), 1.69-1.59 (m, 2H), 1.57-1.48 (m, 1H), 1.09-0.92 (m, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H), 0.80 (d, J = 6.6 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.23 (d, J = 41.9 Hz, 1F), -90.05 (d, J = 42.3 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6 (t, $J_{C\text{-}F}$ = 2.5 Hz), 157.5, 154.5 (dd, $J_{C\text{-}F}$ = 288.9, 285.1 Hz), 136.3, 133.4, 129.1 (t, $J_{C\text{-}F}$ = 3.4 Hz), 128.7, 128.1, 124.8 (t, $J_{C\text{-}F}$ = 3.9 Hz), 115.5, 86.7 (dd, $J_{C\text{-}F}$ = 21.6, 17.5 Hz), 73.1, 47.7, 38.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 37.5, 34.9, 29.2, 26.1, 24.8, 22.2, 21.0, 20.8 ppm.

HRMS (m/z): calcd for $C_{26}H_{31}F_2O_2$ $[M+H]^+$ 413.2287, found: 413.2289.



(S)-5,5-Difluoro-2,4-diphenyl-2-((trimethylsilyl)oxy)pent-4-enenitrile (4):

Yield = 68% (73.2 mg). Colorless oil.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

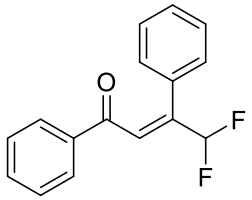
^{1}H NMR (400 MHz, DMSO): δ = 7.49-7.36 (m, 5H), 7.35-7.30 (m, 4H), 7.29-7.24 (m, 1H), 3.22 (dt, J = 14.6, 2.3 Hz, 1H), 3.10 (dt, J = 14.7, 1.9 Hz, 1H), -0.11 (s, 9H) ppm.

^{19}F NMR (376 MHz, DMSO): δ = -87.94 (d, J = 34.2 Hz, 1F), -90.01 (d, J = 34.5 Hz, 1F) ppm.

^{13}C NMR (100 MHz, DMSO): δ = 154.6 (t, $J_{C\text{-}F}$ = 287.9 Hz), 139.6, 132.8 (t, $J_{C\text{-}F}$ = 3.5 Hz), 129.1,

128.7, 128.5 (t, J_{C-F} = 2.9 Hz), 128.1, 127.4, 124.9, 119.9, 88.7 (dd, J_{C-F} = 19.1, 17.7 Hz), 74.6 (t, J_{C-F} = 3.0 Hz) , 43.0, 0.4 ppm.

HRMS (m/z): calcd for $C_{20}H_{22}F_2NOSi$ $[M+H]^+$ 358.1433, found: 358.1430.



(E)-4,4-difluoro-1,3-diphenylbut-2-en-1-one (5):

Yield = 36% (27.8 mg). Colorless oil.

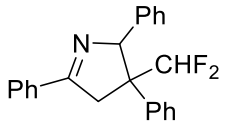
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.81 (m, 2H), 7.55-7.48 (m, 1H), 7.42-7.35 (m, 2H), 7.28-7.26 (m, 5H), 7.05 (t, J = 2.1 Hz, 1H), 6.42 (t, J = 13.8 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -114.62 (s, 1F), -114.76 (s, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 143.2 (t, J_{C-F} = 19.9 Hz), 136.4, 133.6, 132.5, 129.1 (t, J_{C-F} = 8.6 Hz), 129.1, 128.9, 128.7, 128.6, 128.4, 114.5 (t, J_{C-F} = 242.5 Hz) ppm.

HRMS (m/z): calcd for $C_{16}H_{13}F_2O$ $[M+H]^+$ 259.0929, found: 259.0934.



3-(Difluoromethyl)-2,3,5-triphenyl-3,4-dihydro-2H-pyrrole (6):

Yield = 79% (81.9 mg). White solid. M.p. 123.2–124.7 ºC.

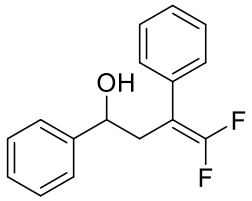
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 50/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.02 (m, 2H), 7.58-7.48 (m, 3H), 7.14-7.05 (m, 6H), 7.02-6.91 (m, 4H), 6.26 (t, J = 56.2 Hz, 1H), 5.83 (s, 1H), 3.79 (s, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -122.91 (d, J = 273.1 Hz, 1F), -125.28 (d, J = 272.8 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 138.3, 136.6, 133.5, 131.2, 128.7, 128.4, 128.2, 127.9, 127.9, 127.7, 127.2, 126.8, 117.9 (t, J_{C-F} = 247.6 Hz), 80.4 (t, J_{C-F} = 2.9 Hz), 59.3 (t, J_{C-F} = 17.6 Hz), 41.5 (t, J_{C-F} = 3.7 Hz) ppm.

HRMS (m/z): calcd for $C_{23}H_{20}F_2N$ $[M+H]^+$ 348.1558, found: 348.1564.



4,4-Difluoro-1,3-diphenylbut-3-en-1-ol (7):

Yield = 98% (76.4 mg). Colorless oil.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.38 (m, 2H), 7.38-7.27 (m, 8H), 4.62 (dd, J = 8.2, 5.7 Hz, 1H), 2.96-2.87 (m, 1H), 2.82-2.73 (m, 1H), 2.13 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.89 (s, 1F), -88.90 (s, 1F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (t, $J_{C\text{-}F}$ = 287.5 Hz), 143.4, 133.2, 128.5, 128.4, 128.3 (t, $J_{C\text{-}F}$ = 3.1 Hz), 127.8, 127.4, 125.8, 89.5 (dd, $J_{C\text{-}F}$ = 19.0, 17.0 Hz), 72.2 (t, $J_{C\text{-}F}$ = 2.9 Hz), 37.5 ppm.
HRMS (m/z): calcd for $C_{16}H_{15}F_2O$ $[M+H]^+$ 261.1085, found: 261.1091.

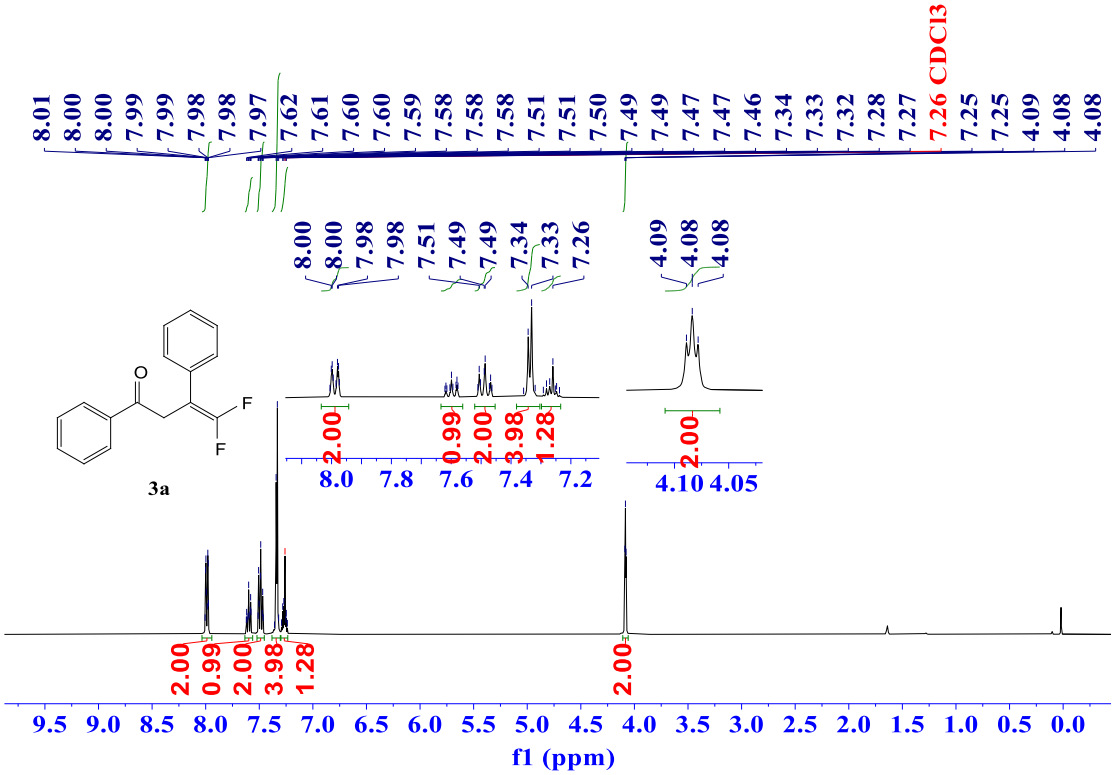
Reference

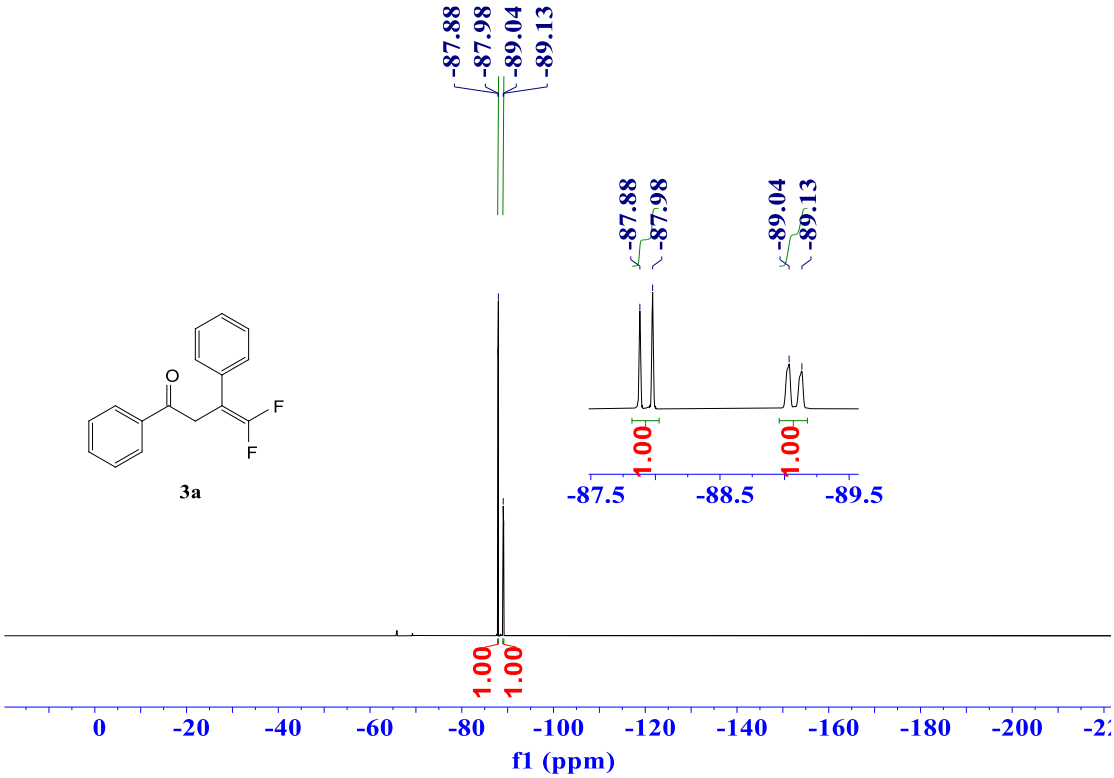
[1] Wu, X.; Xie, F.; Gridnev, I. D.; Zhang, W. A copper-catalyzed reductive defluorination of β-trifluoromethylated enones *via* oxidative homocoupling of Grignard reagents, *Org. Lett.* **2018**, *20*, 1638−1642.

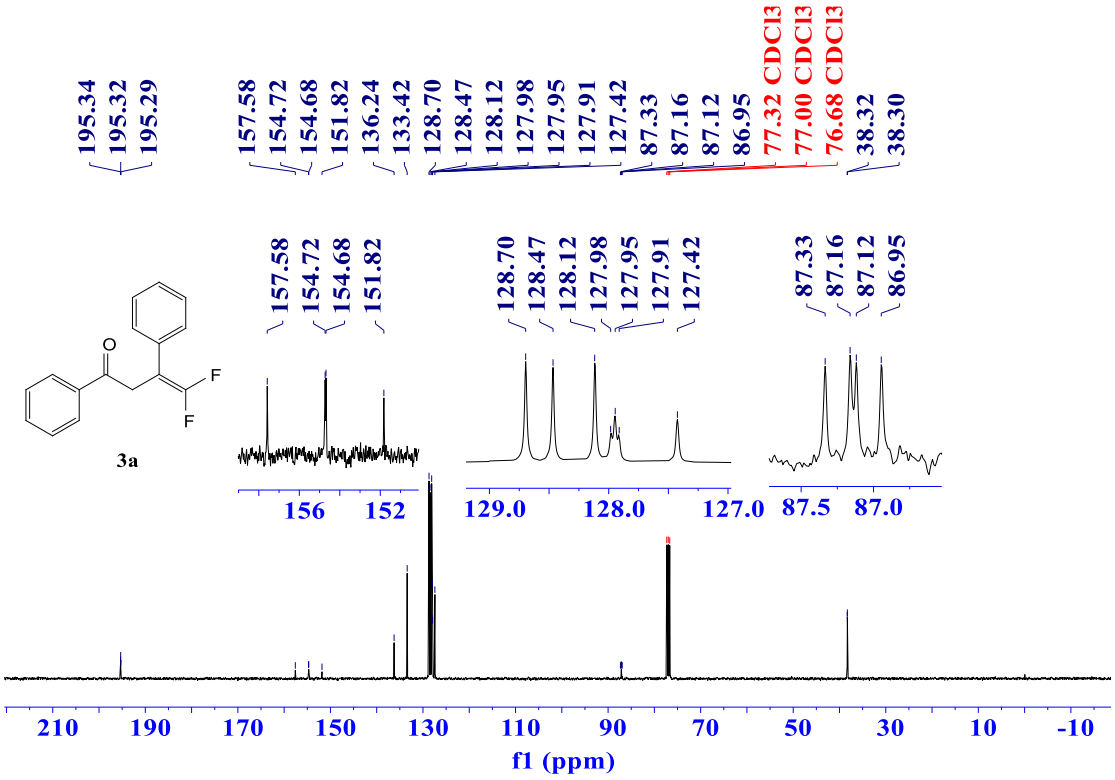
[2] Liu, N.; Mao, L.-L.; Yang, B.; Yang, S.-D. Copper-promoted oxidative-fluorination of arylphosphine under mild conditions, *Chem. Commun*. **2014**, *50*, 10879−10882.

[3] Yao, C.; Wang, S.; Norton, J.; Hammond, M. Catalyzing the hydrodefluorination of CF_3-substituted alkenes by $PhSiH_3$. H• transfer from a nickel hydride. *J. Am. Chem. Soc.* **2020**, *142*, 4793−4799.

^{1}H, ^{19}F, and ^{13}C NMR spectra of products



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127.98
127.95
127.91
127.42
87.33
87.16
87.12
86.95
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.32
38.30
O
F
F
3a
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70
50
30
10
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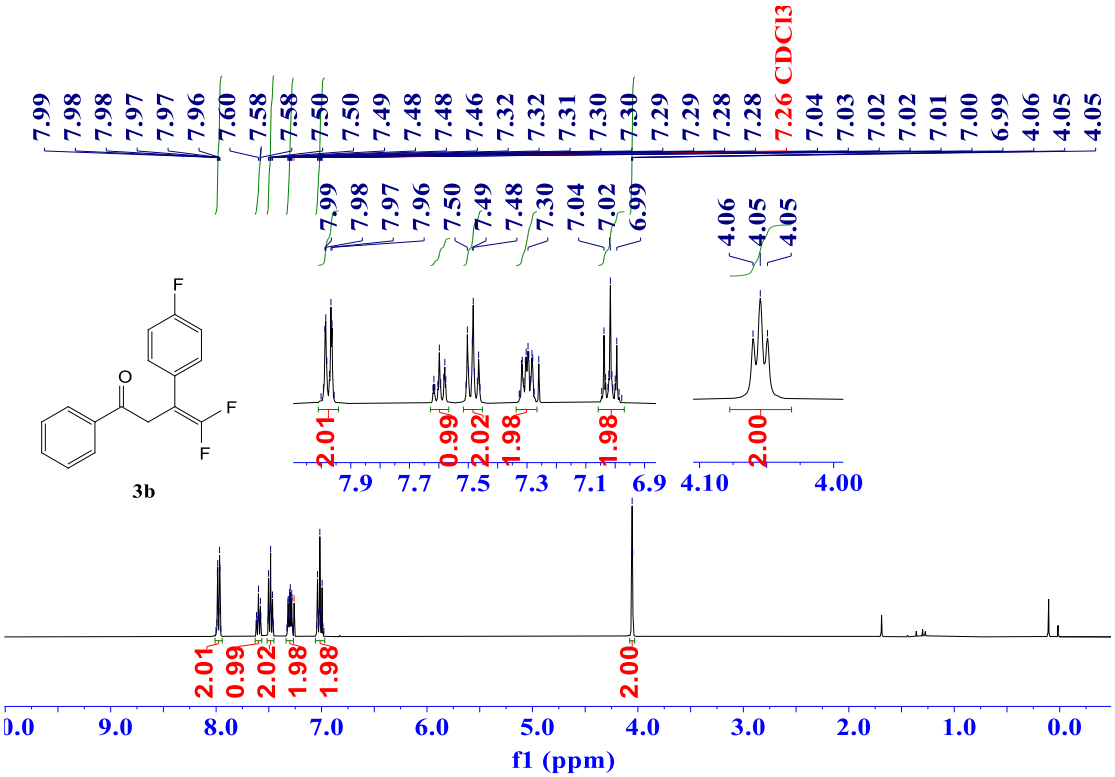
f1 (ppm)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7.29
7.28
7.28
7.26 CDCl3
7.04
7.03
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7.01
7.00
6.99
4.06
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F
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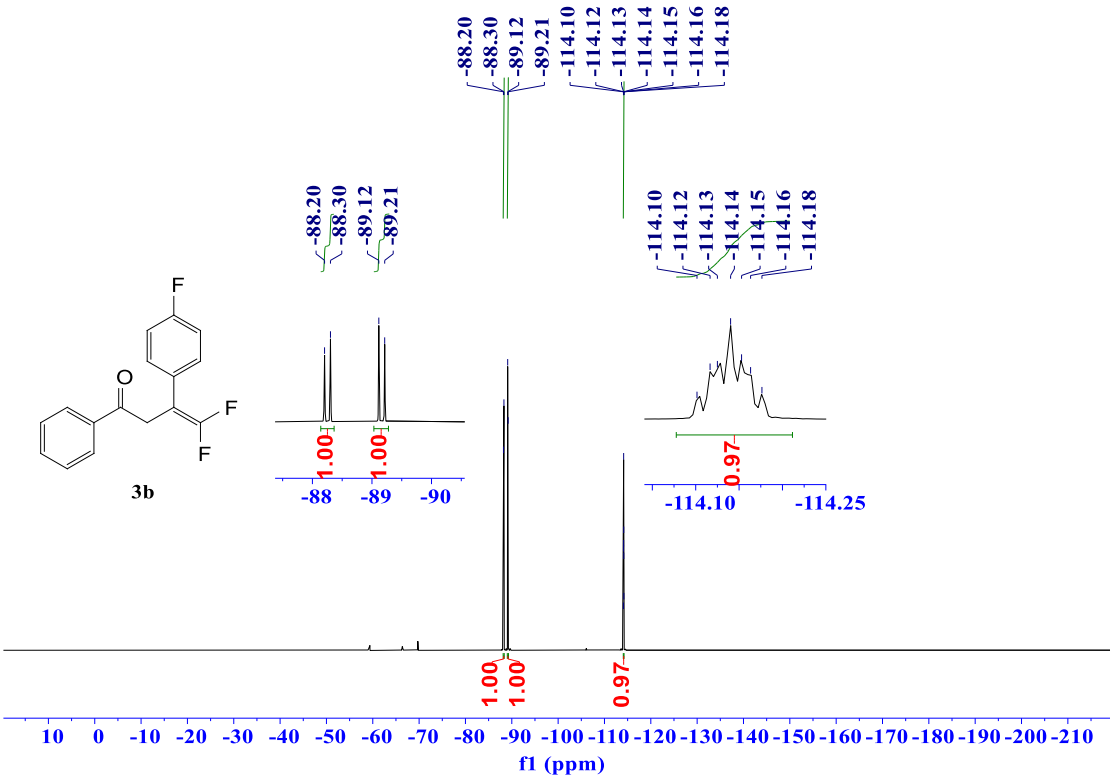
2.00
f1 (ppm)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O
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3b
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1.00
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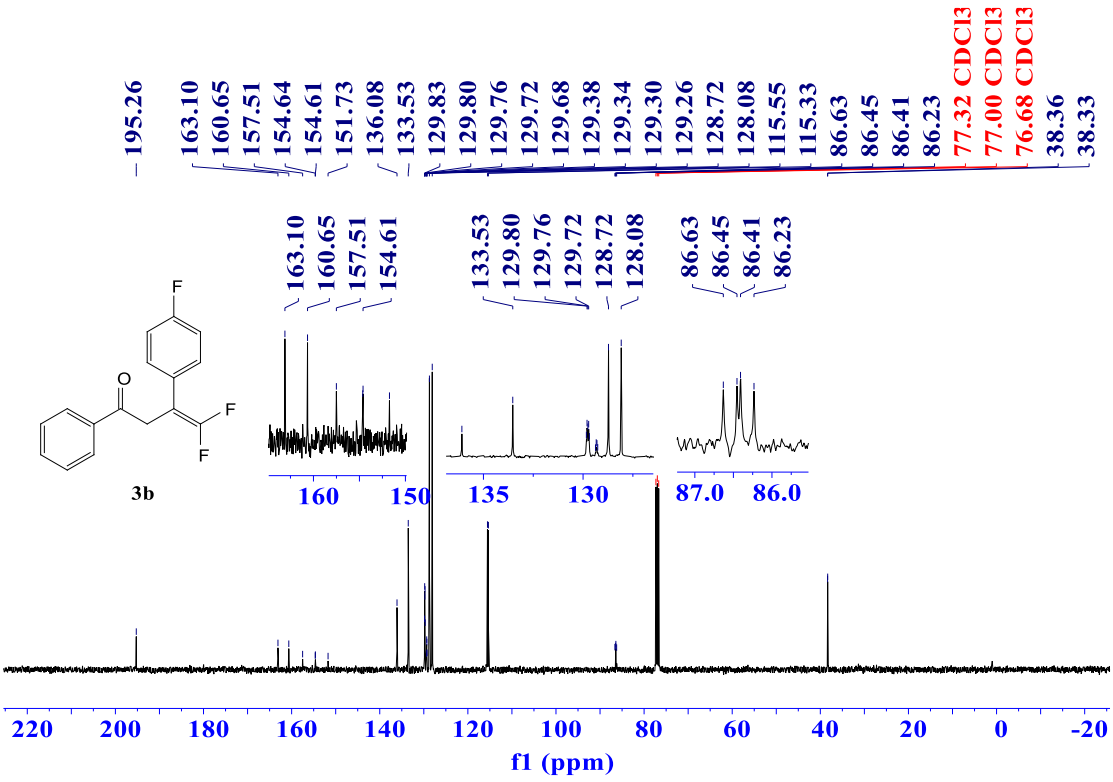
f1 (ppm)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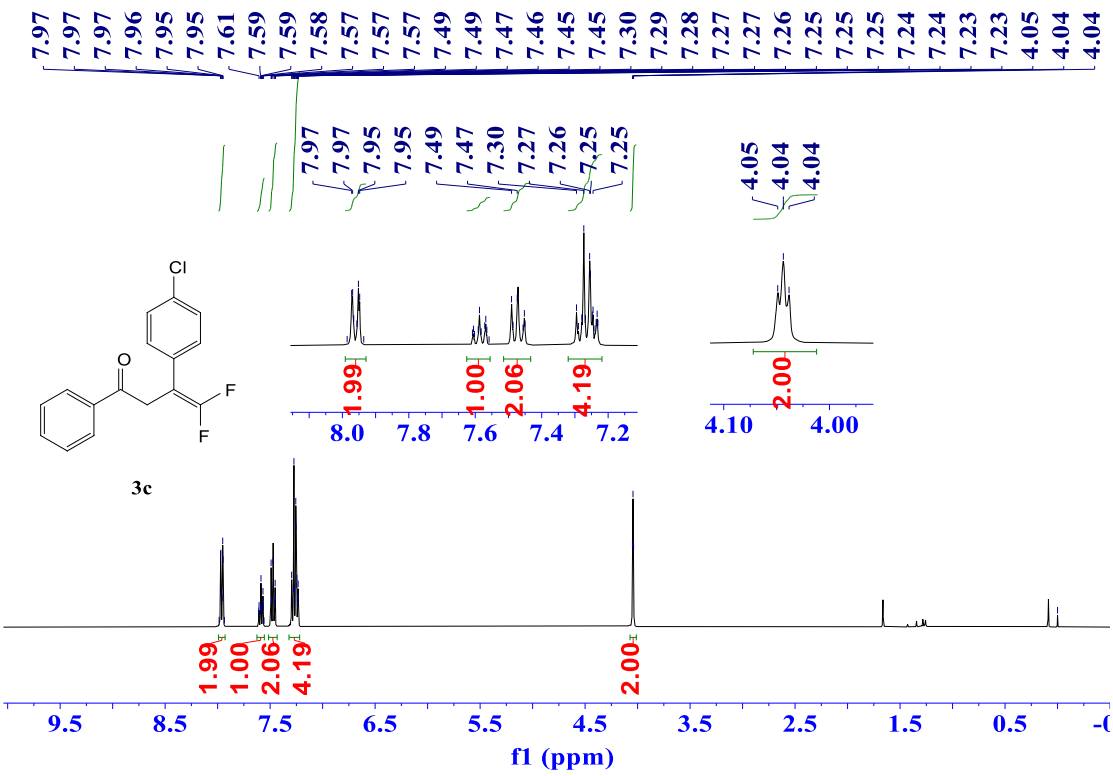
f1 (ppm)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Cl
O
F
F
3c
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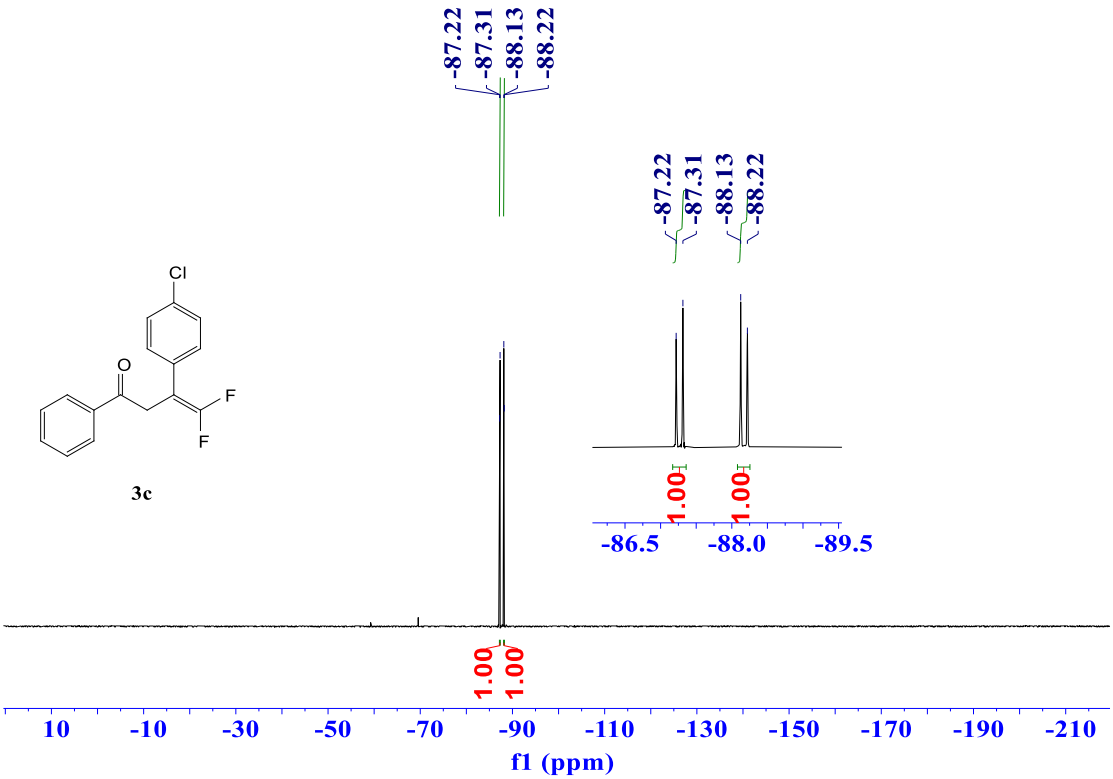
f1 (ppm)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F
F
3c
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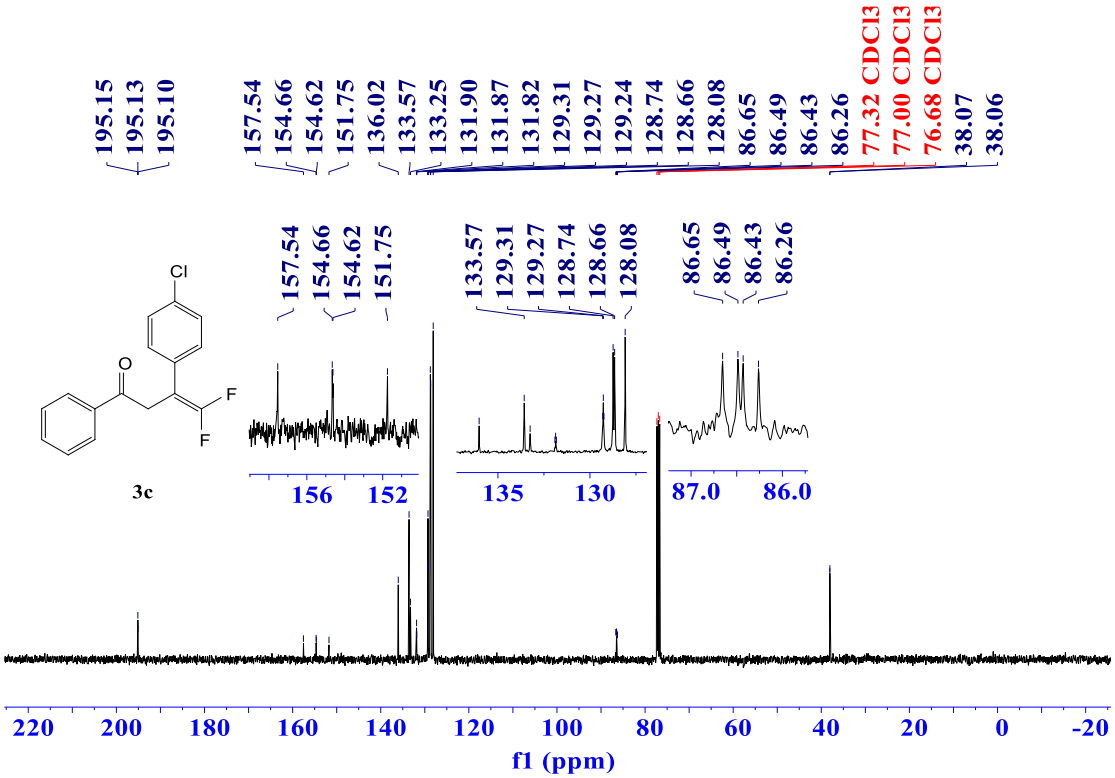
f1 (ppm)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86.26
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77.00 CDCl3
76.68 CDCl3
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F
3c
156
152
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200
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160
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120
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80
60
40
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0
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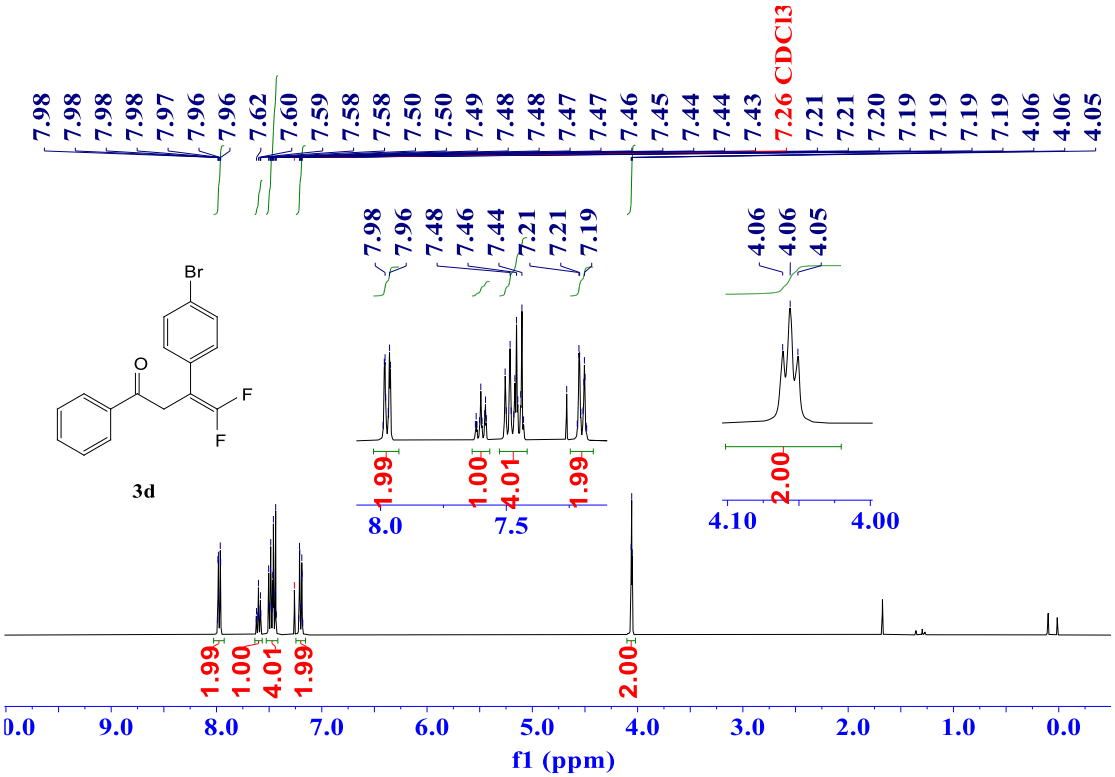
f1 (ppm)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4.06
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O
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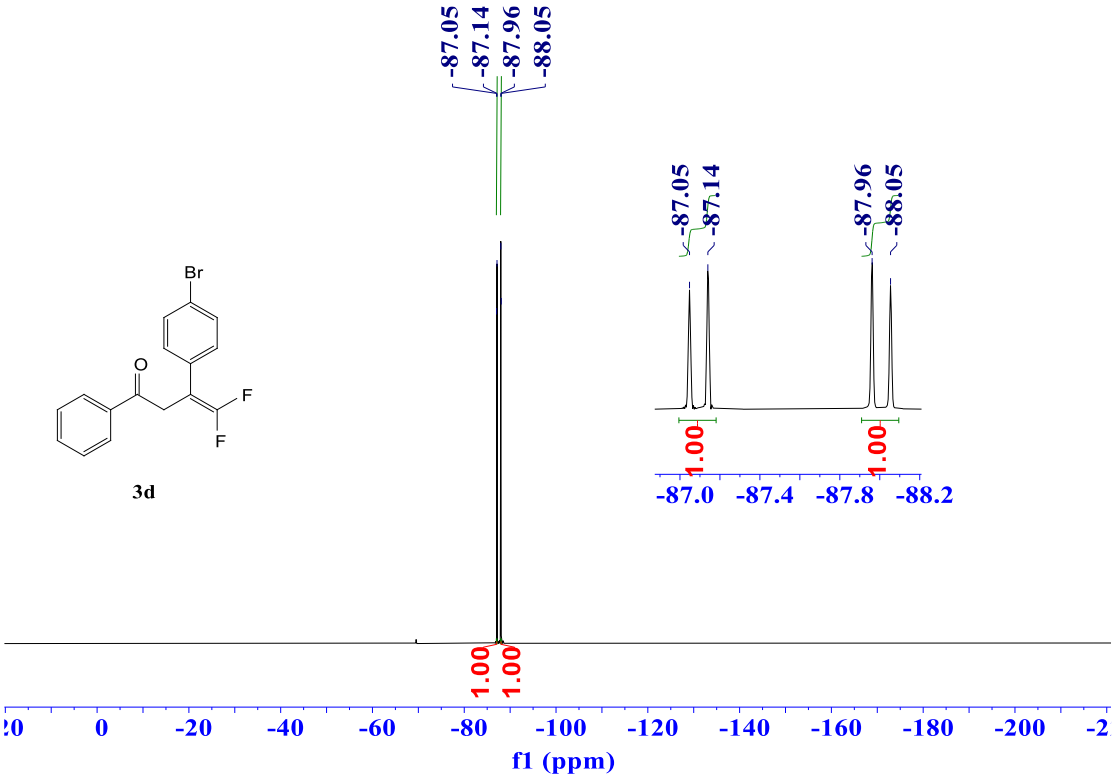
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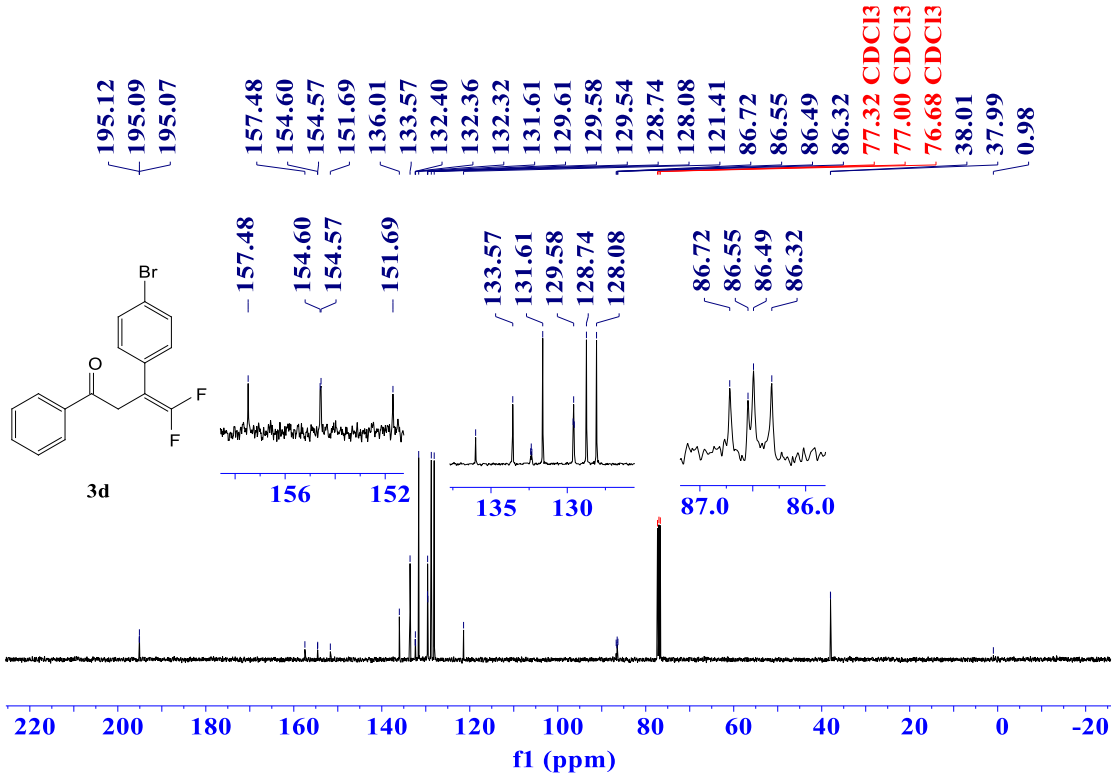
f1 (ppm)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86.32
77.32 CDCl3
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37.99
0.98
Br
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F
3d
156
152
135
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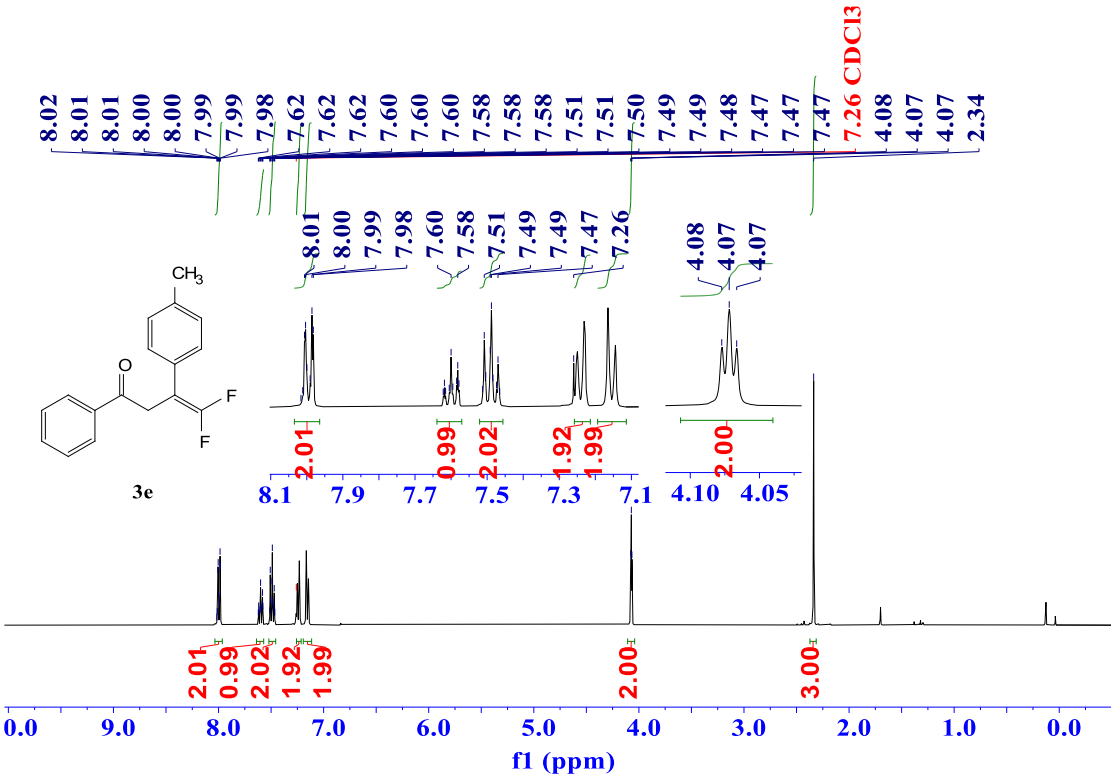
f1 (ppm)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3e
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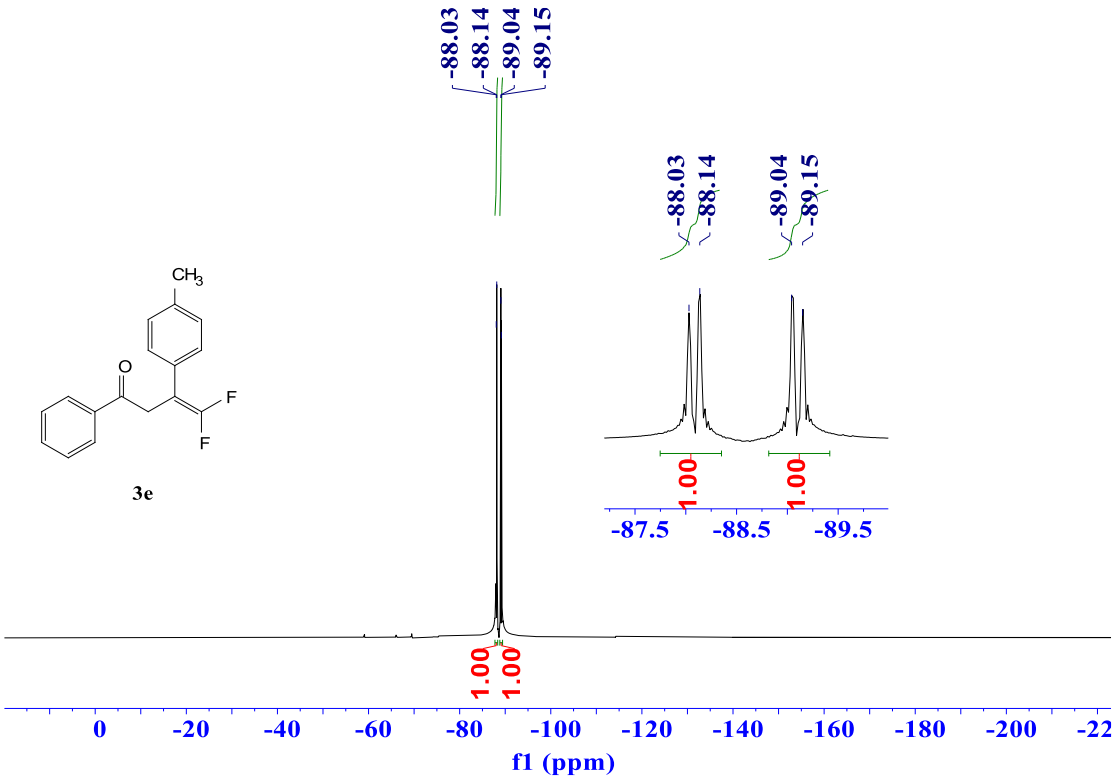
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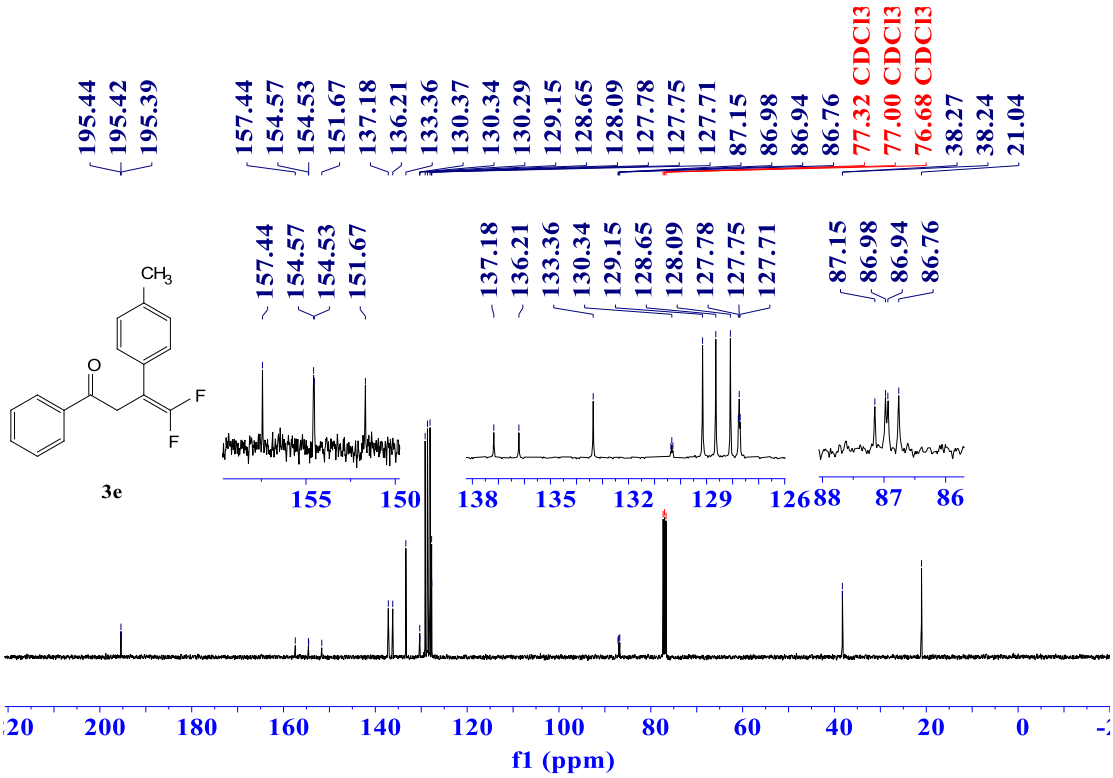
1.00 1.00
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -22
f1 (ppm)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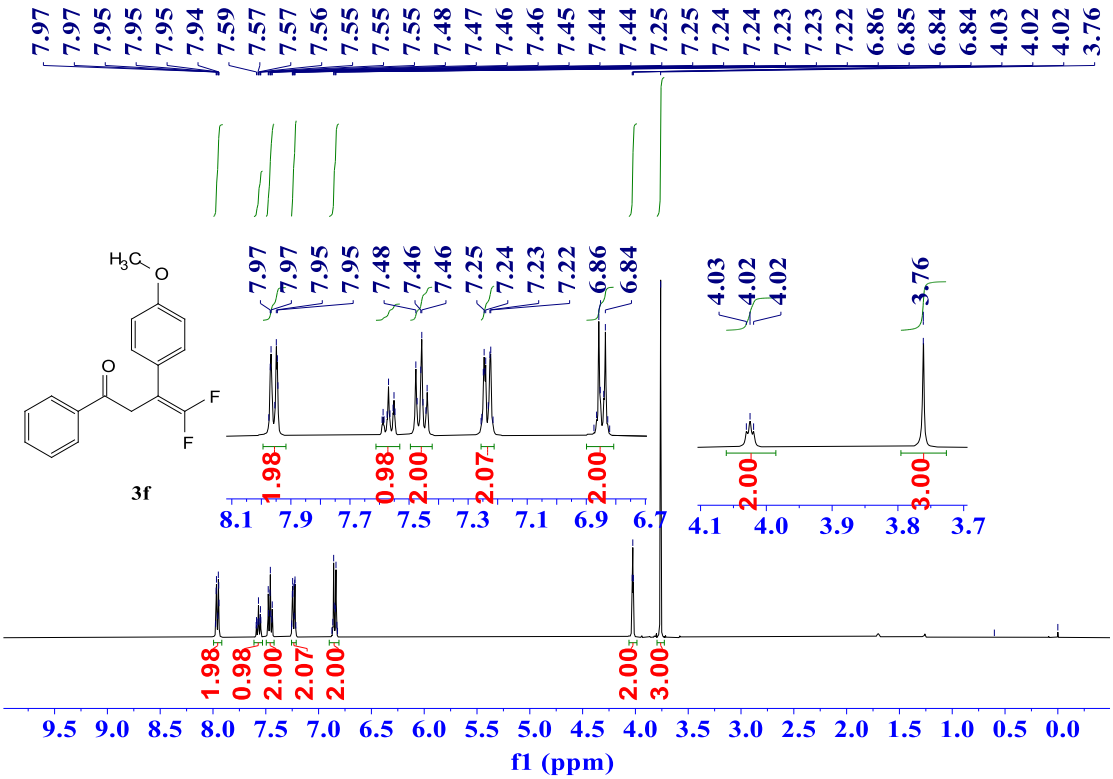
f1 (ppm)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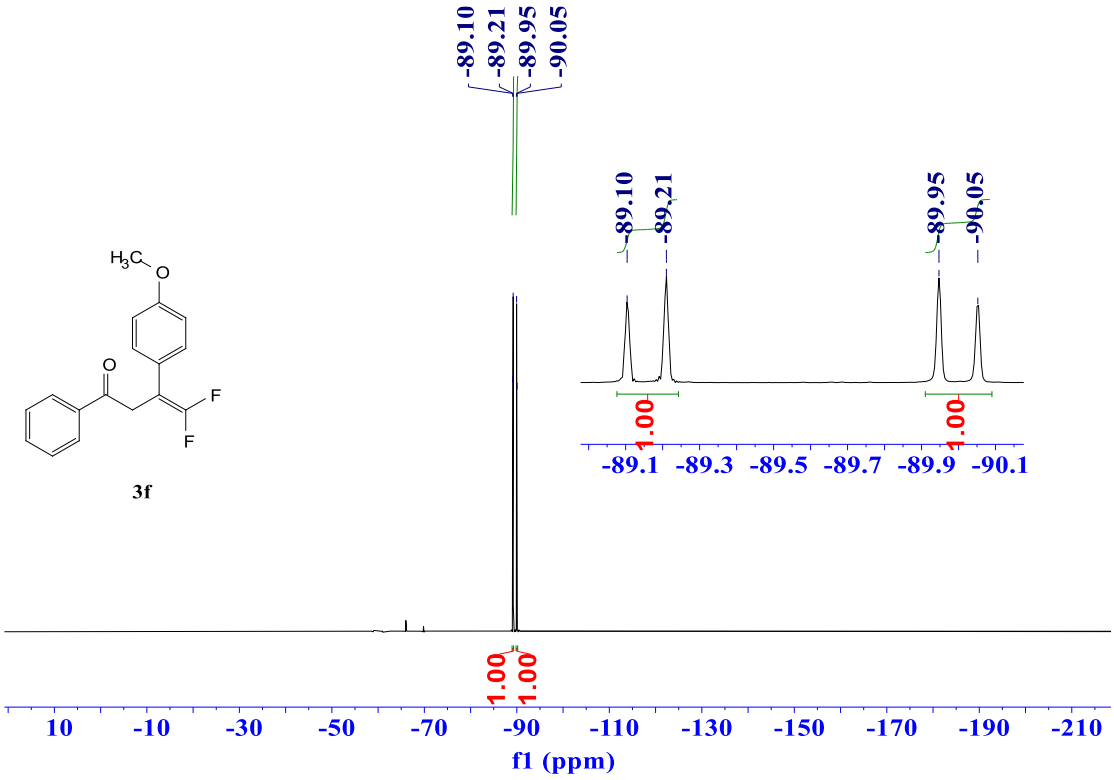
7.94
7.59
7.57
7.56
7.55
7.48
7.47
7.46
7.45
7.44
7.25
7.24
7.23
7.22
6.86
6.85
6.84
4.03
4.02
3.76
H3C
O
O
F
F
3f
1.98
0.98
2.00
2.07
2.00
3.00
f1 (ppm)


-89.10
-89.21
-89.95
-90.05
H3C
O
O
F
F
3f
1.00
1.00
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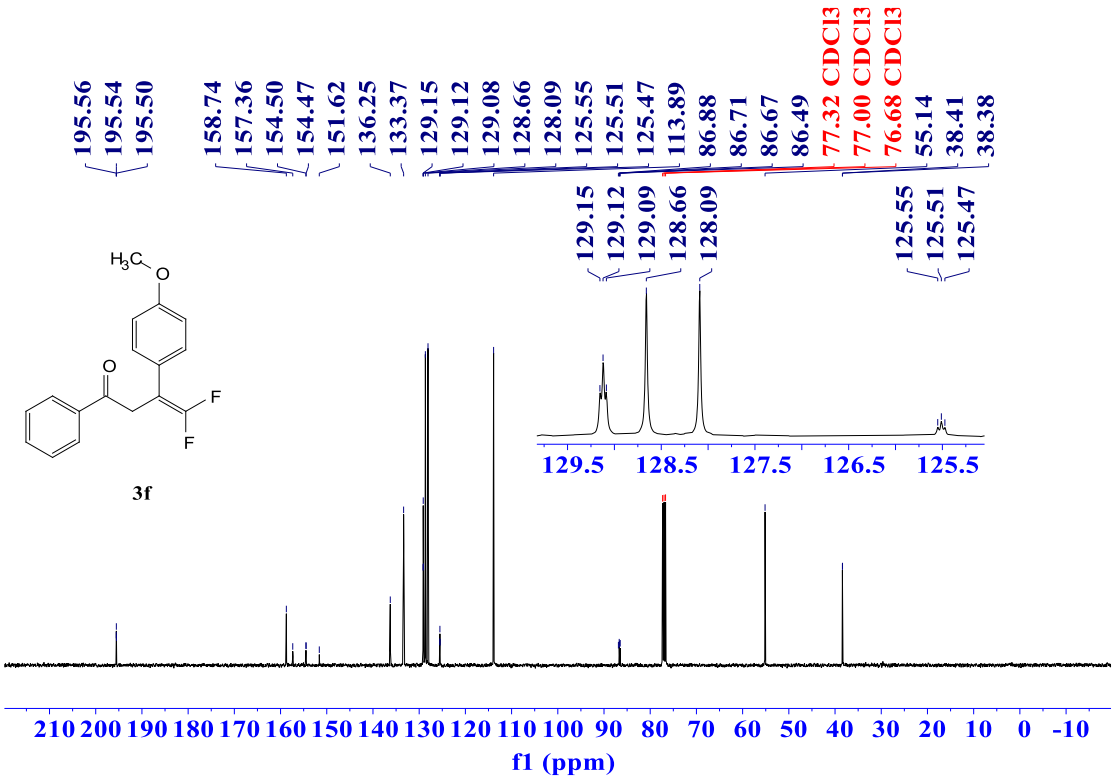
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)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133.37
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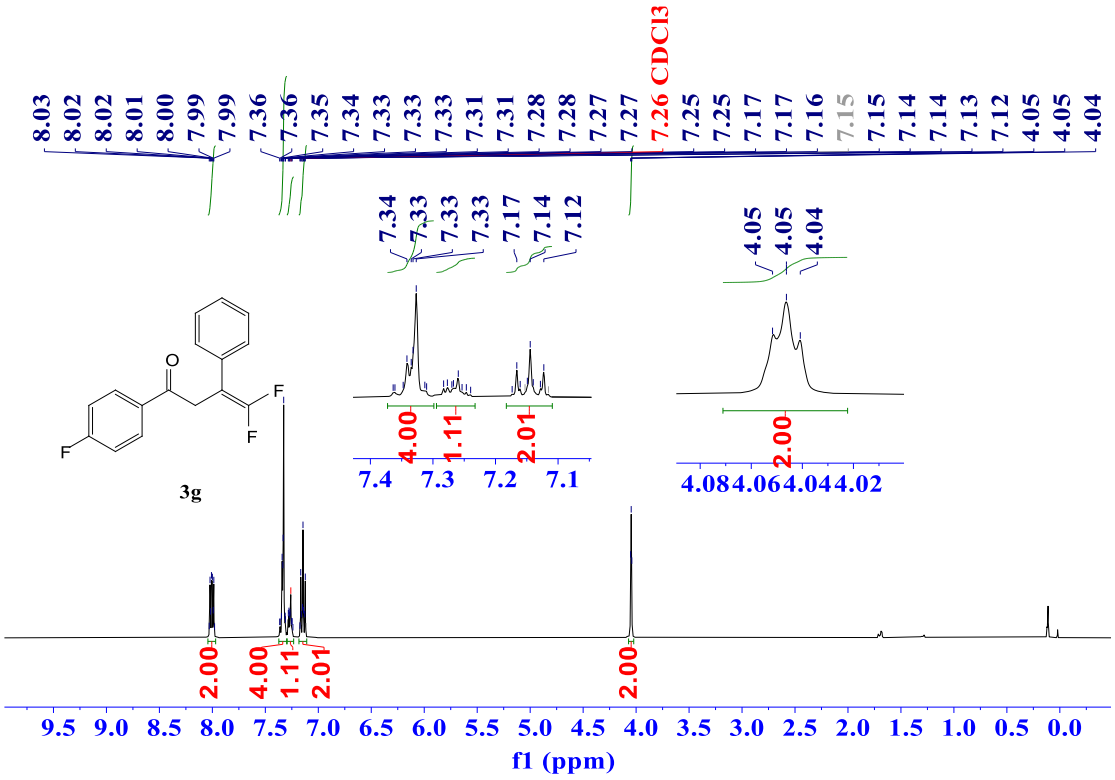
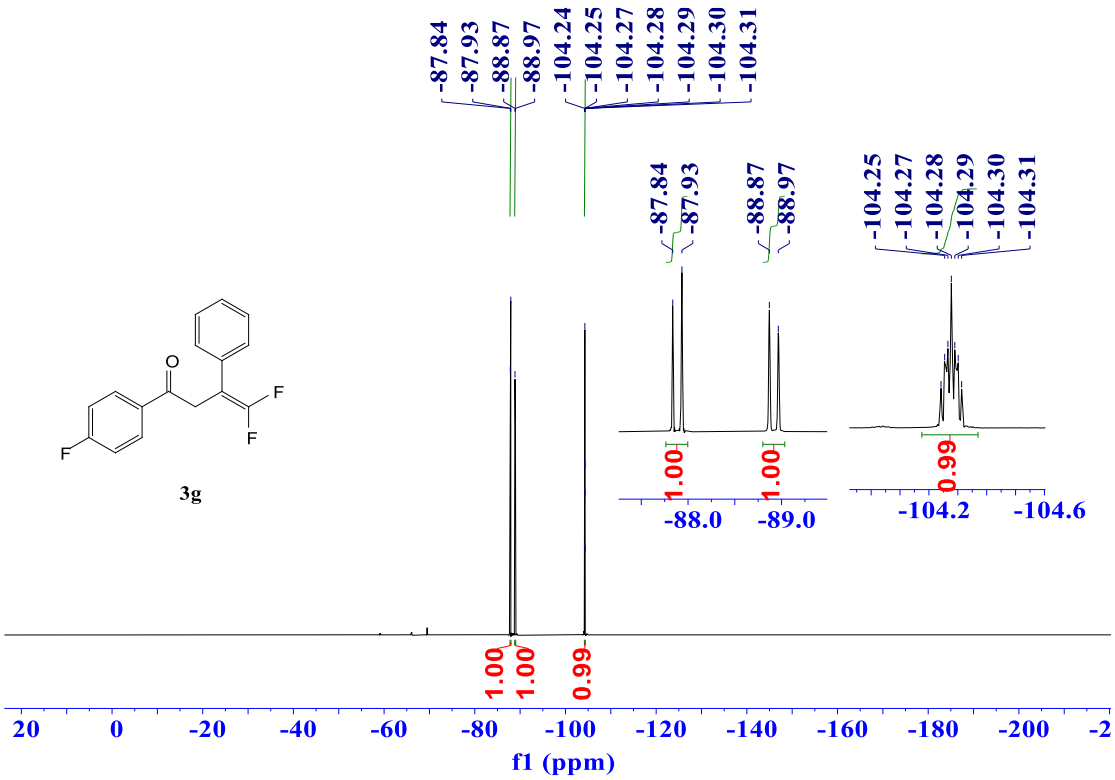
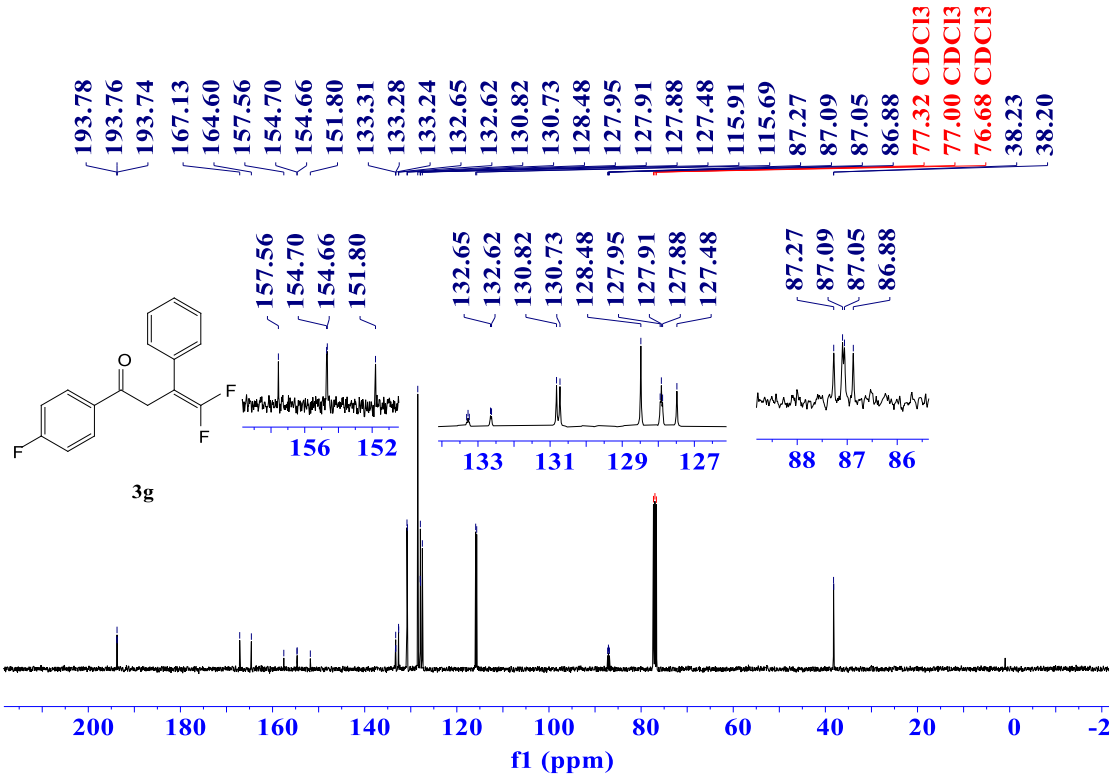
129.12
129.08
128.66
128.09
125.55
125.51
125.47
113.89
86.88
86.71
86.67
86.49
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.14
38.41
38.38
H3C
O
O
F
F
3f
129.5 128.5 127.5 126.5 125.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.03 8.02 8.02 8.01 8.00 7.99 7.99 7.36 7.36 7.35 7.34 7.33 7.33 7.33 7.31 7.31 7.28 7.28 7.27 7.27 7.26 CDCl3 7.25 7.25 7.17 7.17 7.16 7.15 7.15 7.14 7.14 7.13 7.12 4.05 4.05 4.04
7.34 7.33 7.33 7.33 7.17 7.14 7.12
4.05 4.05 4.04
O
F
F
F
3g
4.00 1.11 2.01
7.4 7.3 7.2 7.1
2.00
4.08 4.06 4.04 4.02
2.00 4.00 1.11 2.01 2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-87.84 -87.93 -88.87 -88.97 -104.24 -104.25 -104.27 -104.28 -104.29 -104.30 -104.31
-87.84 -87.93
-88.87 -88.97
-104.25 -104.27 -104.28 -104.29 -104.30 -104.31
O
F
F
F
3g
1.00 1.00
-88.0 -89.0
0.99
-104.2 -104.6
1.00 1.00 0.99
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)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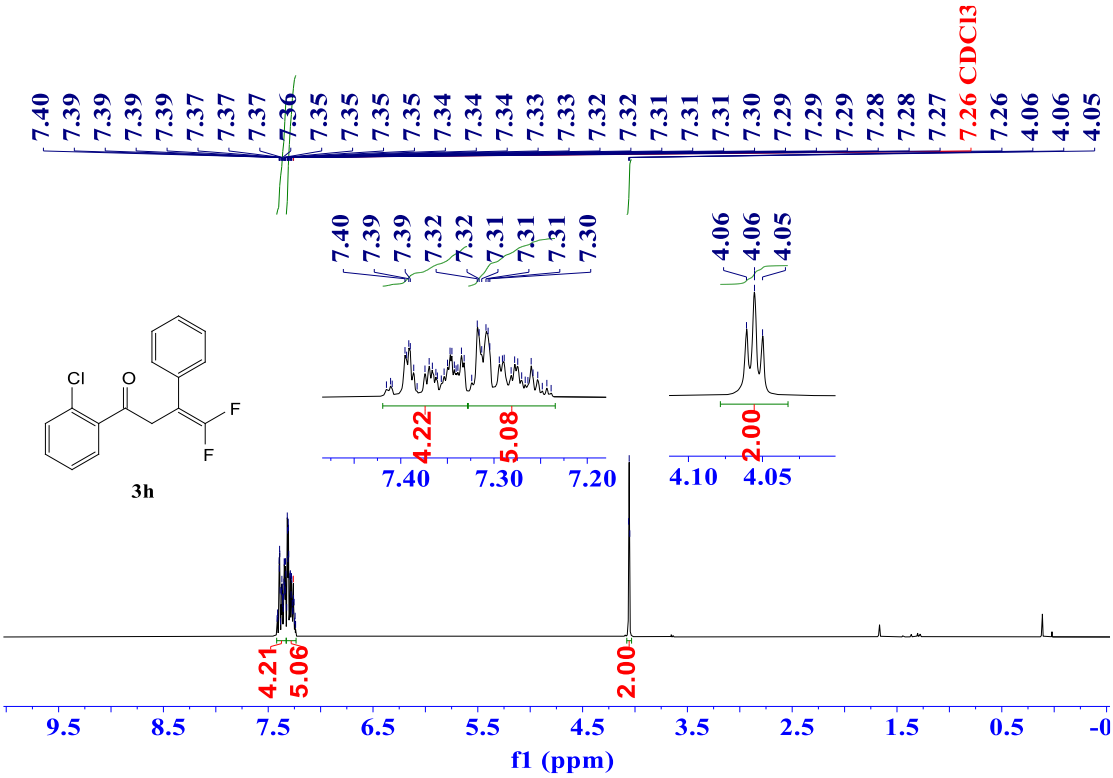
193.76
193.74
167.13
164.60
157.56
154.70
154.66
151.80
133.31
133.28
133.24
132.65
132.62
130.82
130.73
128.48
127.95
127.91
127.88
127.48
115.91
115.69
87.27
87.09
87.05
86.88
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.23
38.20
O
F
F
F
3g
156 152
133 131 129 127
88 87 86
200 180 160 140 120 100 80 60 40 20 0 -2
f1 (ppm)


7.40
7.39
7.39
7.39
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7.37
7.37
7.37
7.36
7.35
7.35
7.35
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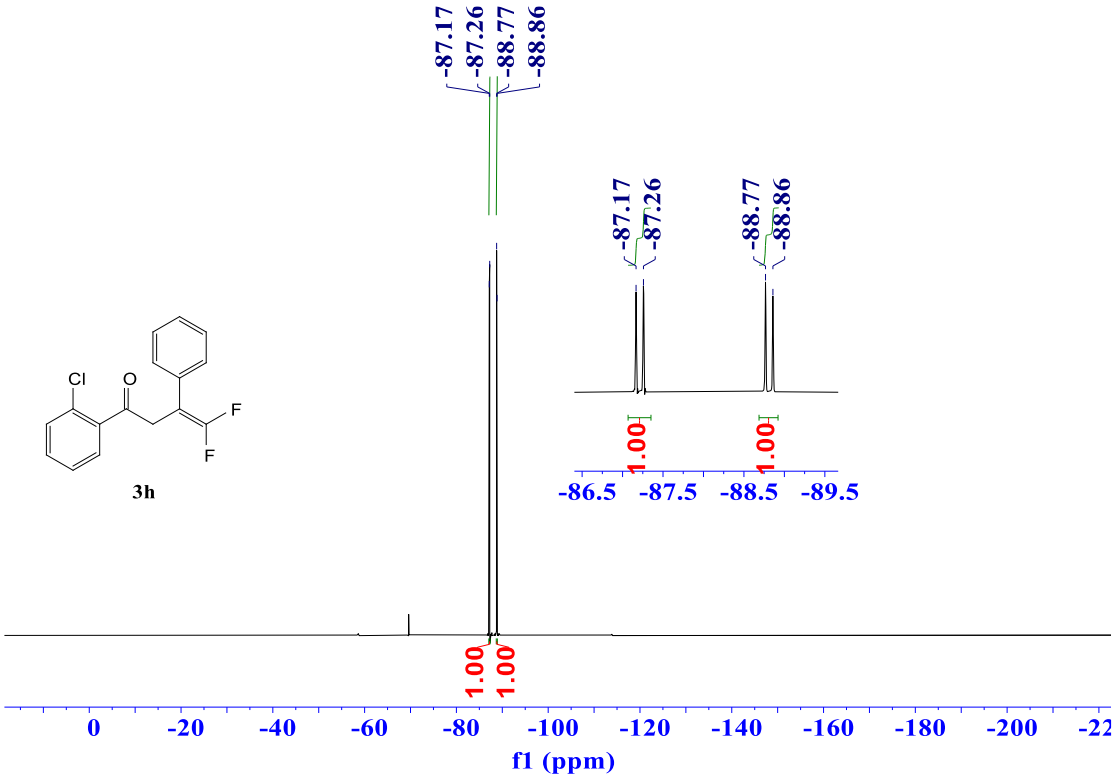
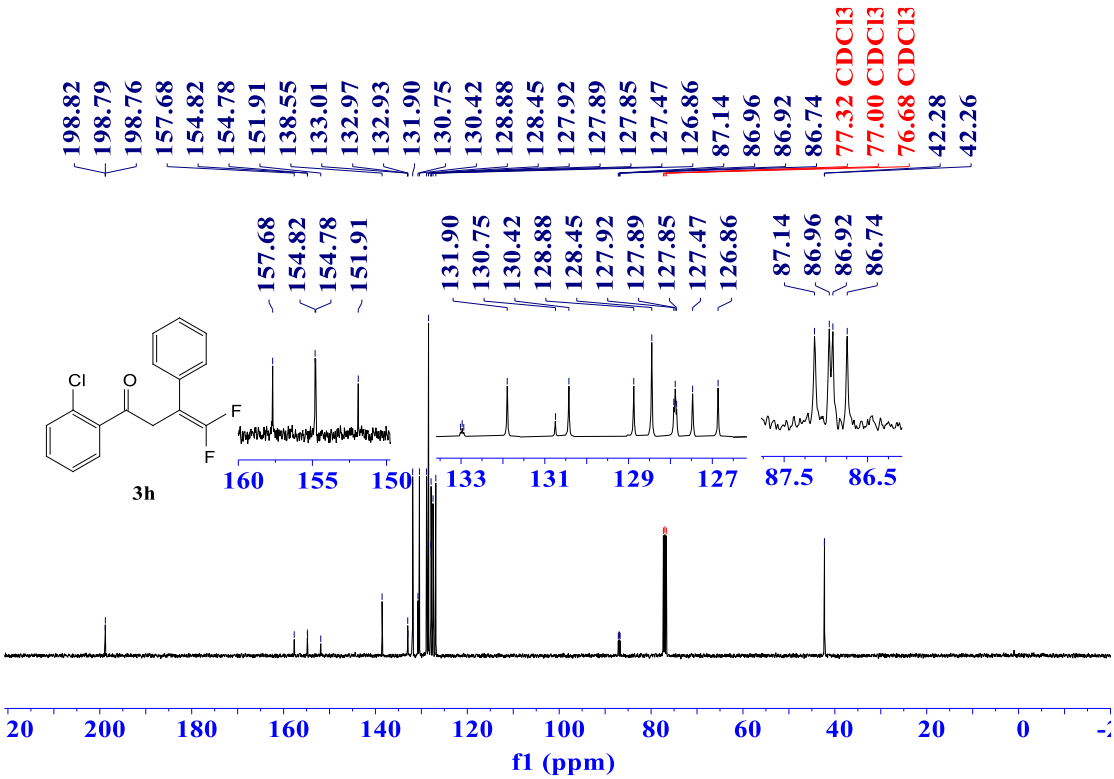
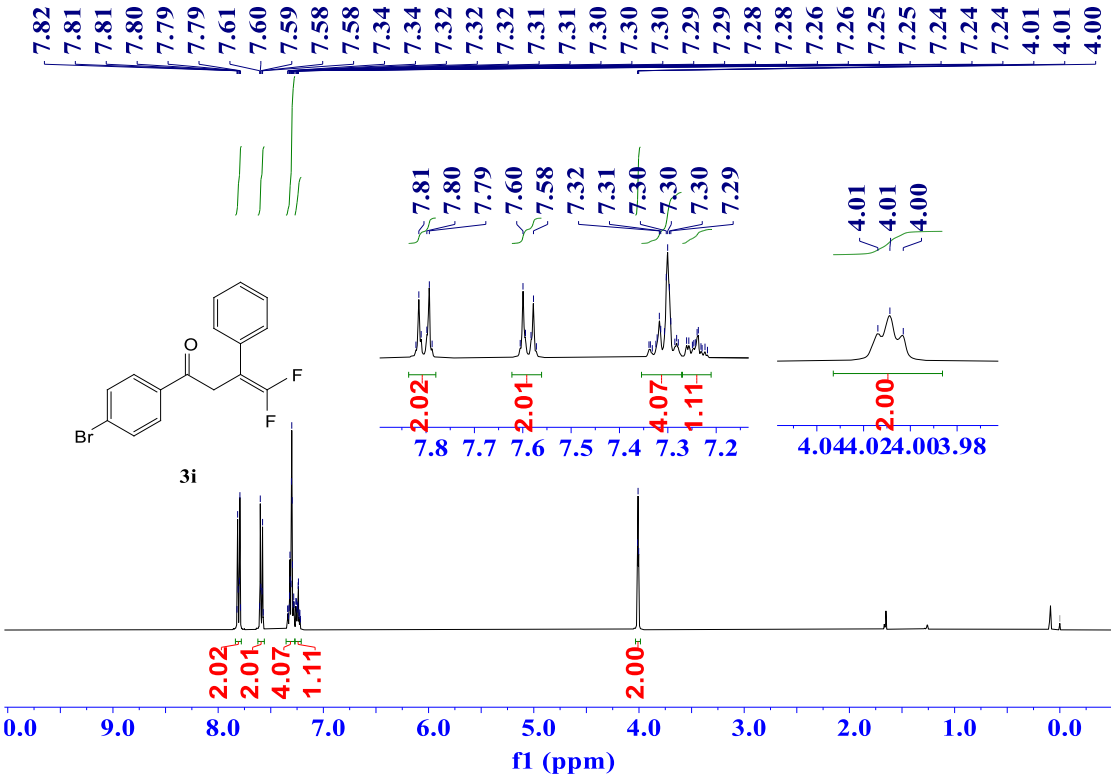
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26 CDCl3
7.26
4.06
4.06
4.05
Cl
O
F
F
3h
4.22
5.08
2.00
7.40 7.30 7.20
4.10 4.05
4.21
5.06
2.00
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0
f1 (ppm)


-87.17
-87.26
-88.77
-88.86
Cl
O
F
F
3h
1.00
1.00
-86.5
-87.5
-88.5
-89.5
f1 (ppm)


198.82
198.79
198.76
157.68
154.82
154.78
151.91
138.55
133.01
132.97
132.93
131.90
130.75
130.42
128.88
128.45
127.92
127.89
127.85
127.47
126.86
87.14
86.96
86.92
86.74
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
42.28
42.26
Cl
O
F
F
3h
f1 (ppm)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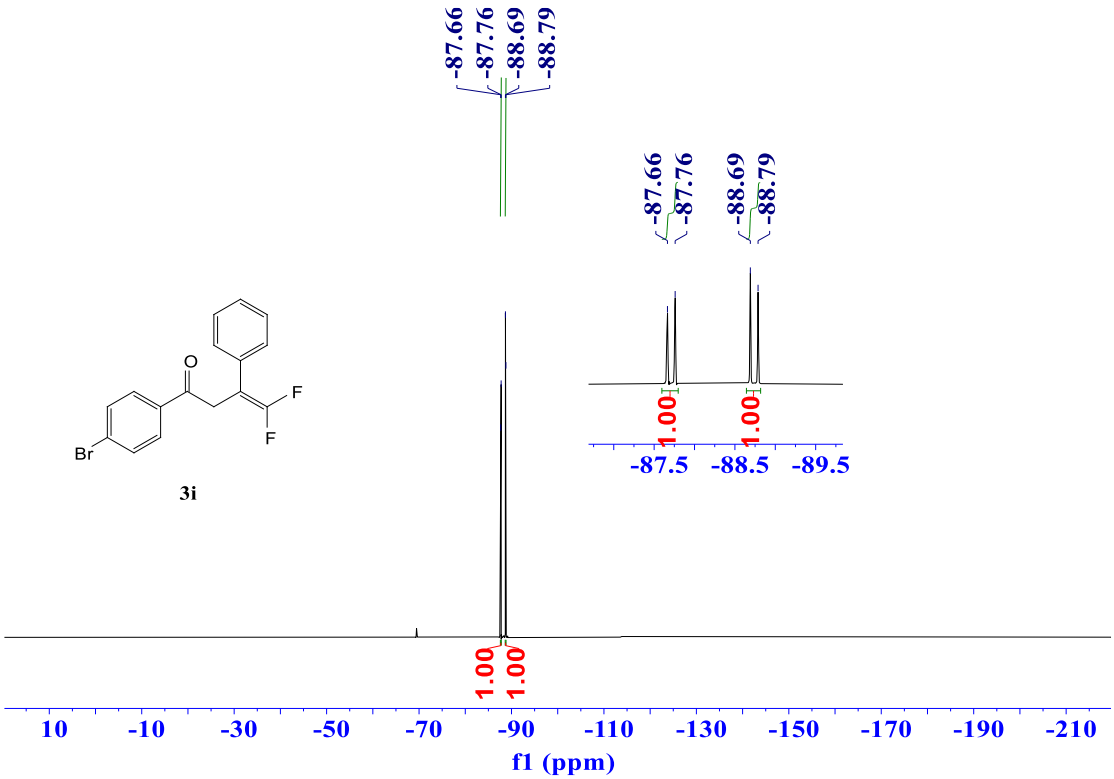
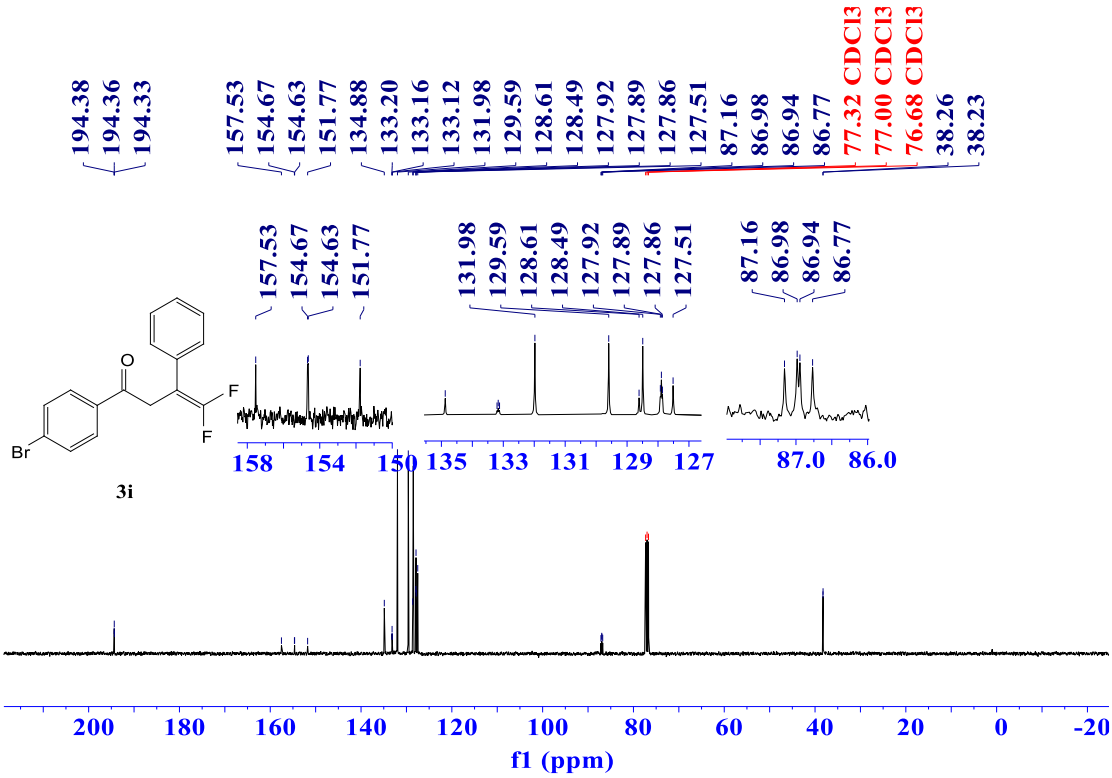
7.81 7.80 7.79 7.60 7.58 7.32 7.31 7.30 7.30 7.30 7.29
4.01 4.01 4.00
O
F
F
Br
3i
2.02 2.01 4.07 1.11
2.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2
4.04 4.02 4.00 3.98
0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


-87.66 -87.76 -88.69 -88.79
-87.66 -87.76 -88.69 -88.79
O
F
F
Br
3i
1.00 1.00
-87.5 -88.5 -89.5
1.00 1.00
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)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134.88
133.20
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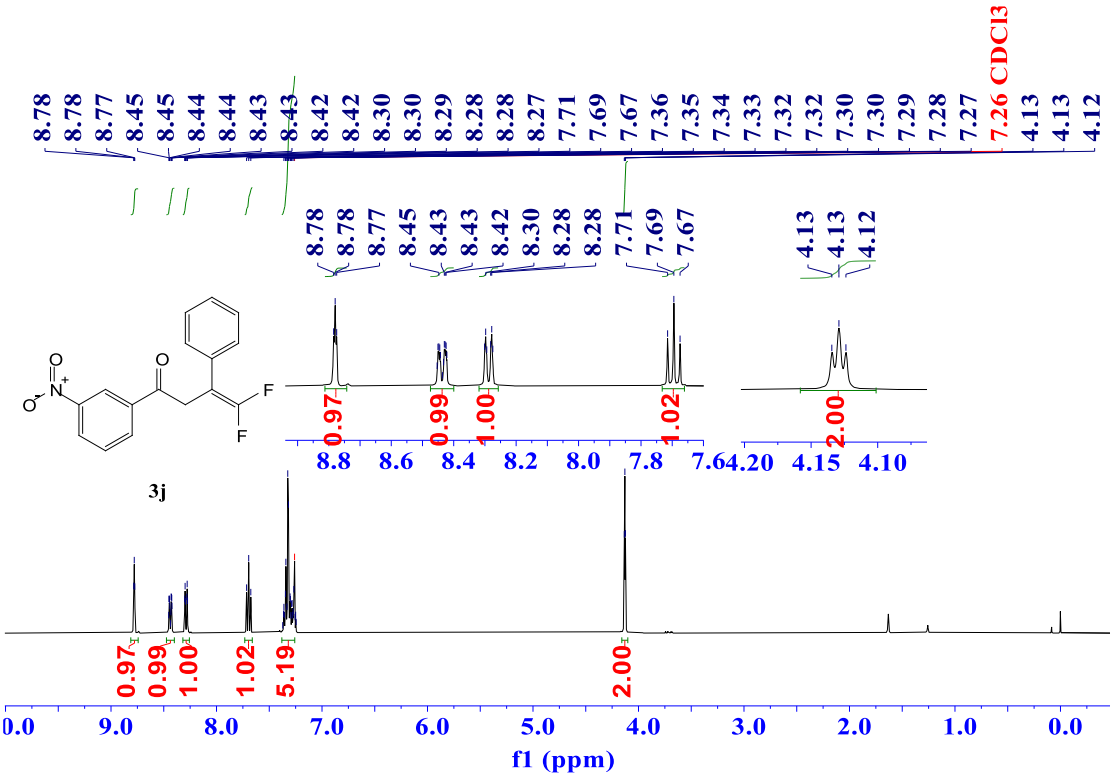
133.12
131.98
129.59
128.61
128.49
127.92
127.89
127.86
127.51
87.16
86.98
86.94
86.77
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.26
38.23
O
F
F
Br
3i
158
154
150
135
133
131
129
127
87.0
86.0
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)


8.78
8.78
8.77
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8.44
8.44
8.43
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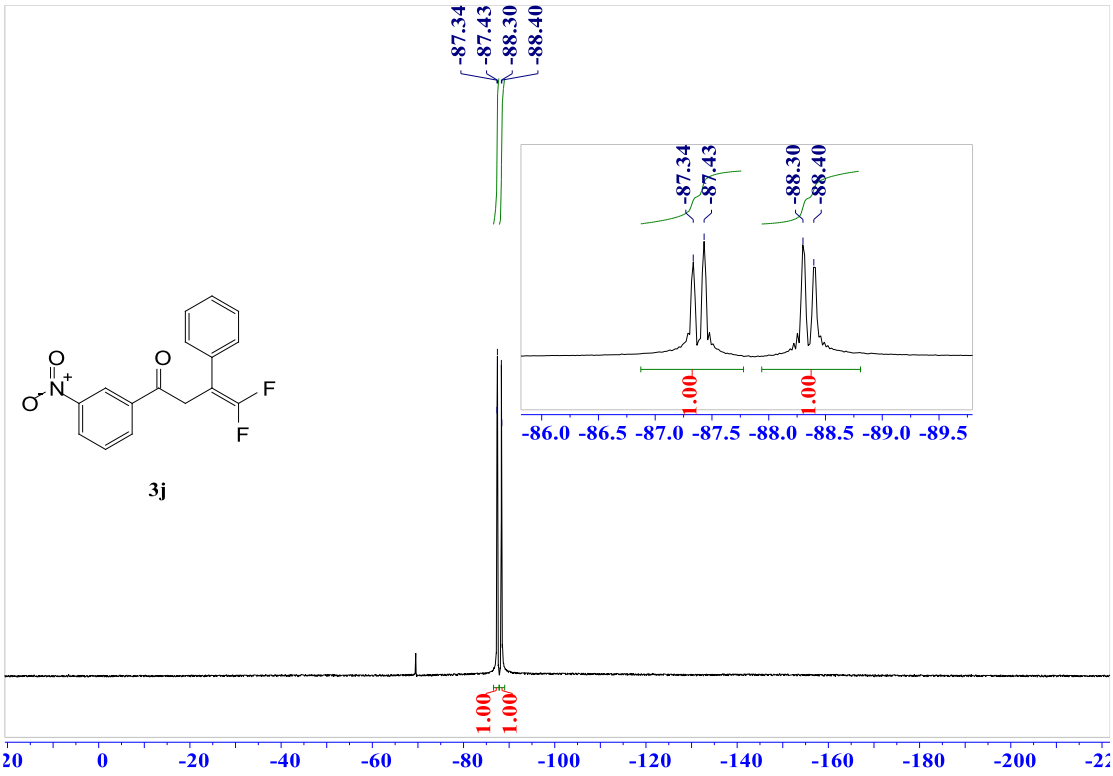
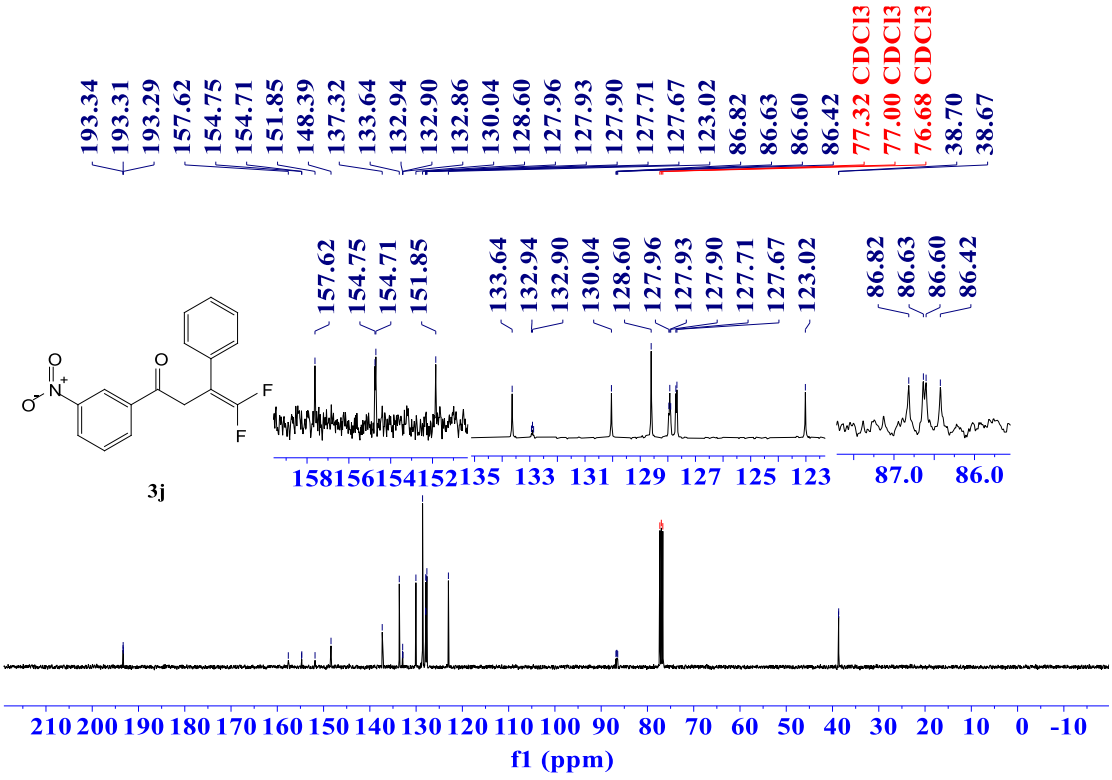
8.42
8.42
8.30
8.30
8.29
8.28
8.28
8.27
7.71
7.69
7.67
7.36
7.35
7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.28
7.27
7.26 CDCl3
4.13
4.13
4.12
O
O
N
O
F
F
0.97
0.99
1.00
1.02
2.00
8.8
8.6
8.4
8.2
8.0
7.8
7.6
4.20
4.15
4.10
3j
0.97
0.99
1.00
1.02
5.19
2.00
0.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


-87.34
-87.43
-88.30
-88.40
1.00
1.00
-86.0 -86.5 -87.0 -87.5 -88.0 -88.5 -89.0 -89.5
3j
1.00
1.00
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200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154.71
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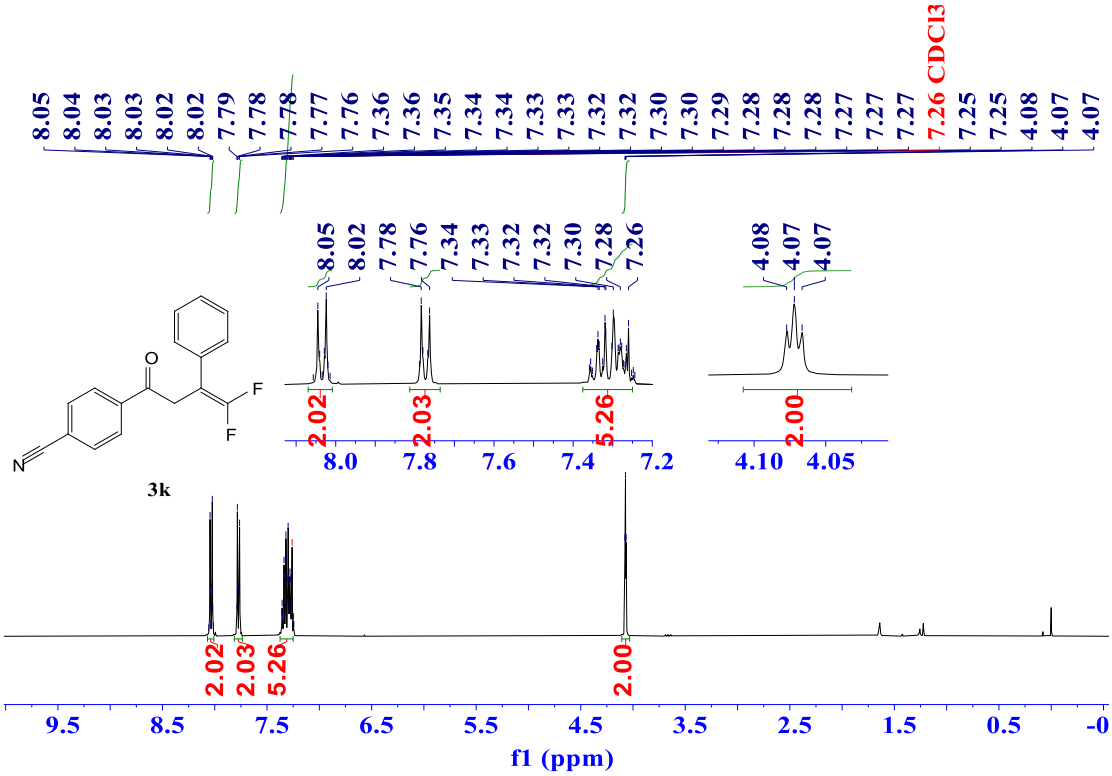
148.39
137.32
133.64
132.94
132.90
132.86
130.04
128.60
127.96
127.93
127.90
127.71
127.67
123.02
86.82
86.63
86.60
86.42
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.70
38.67
3j
158 156 154 152
135 133 131 129 127 125 123
87.0 86.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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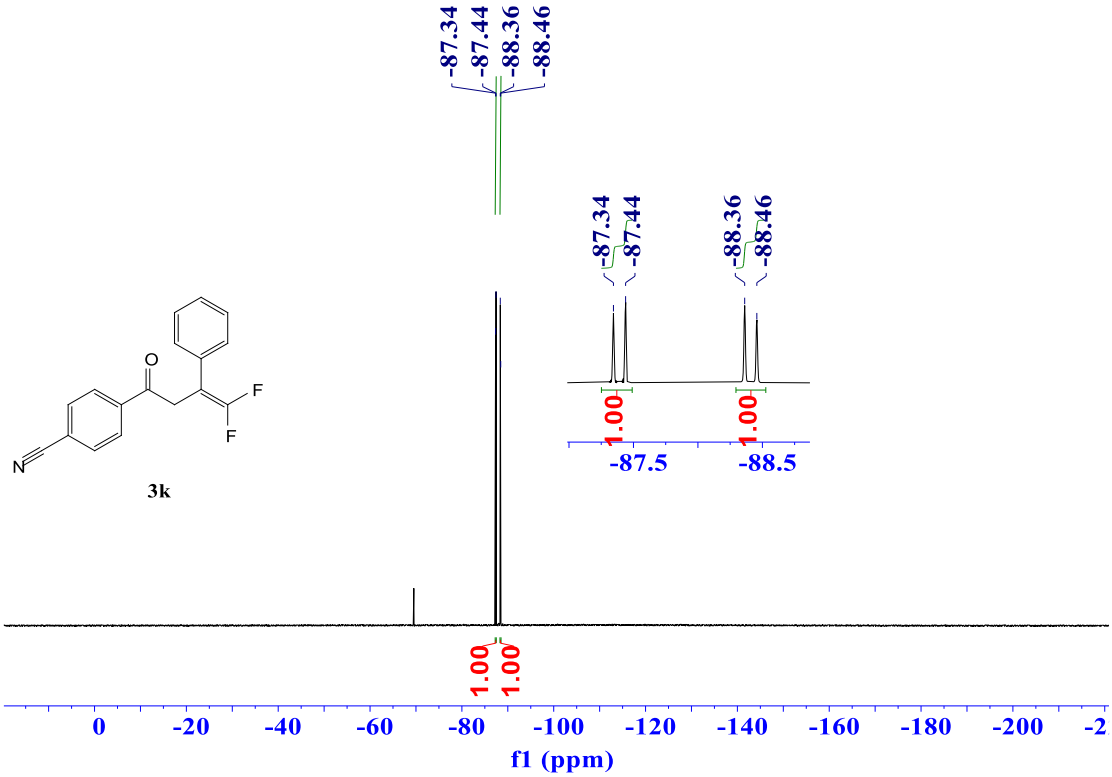
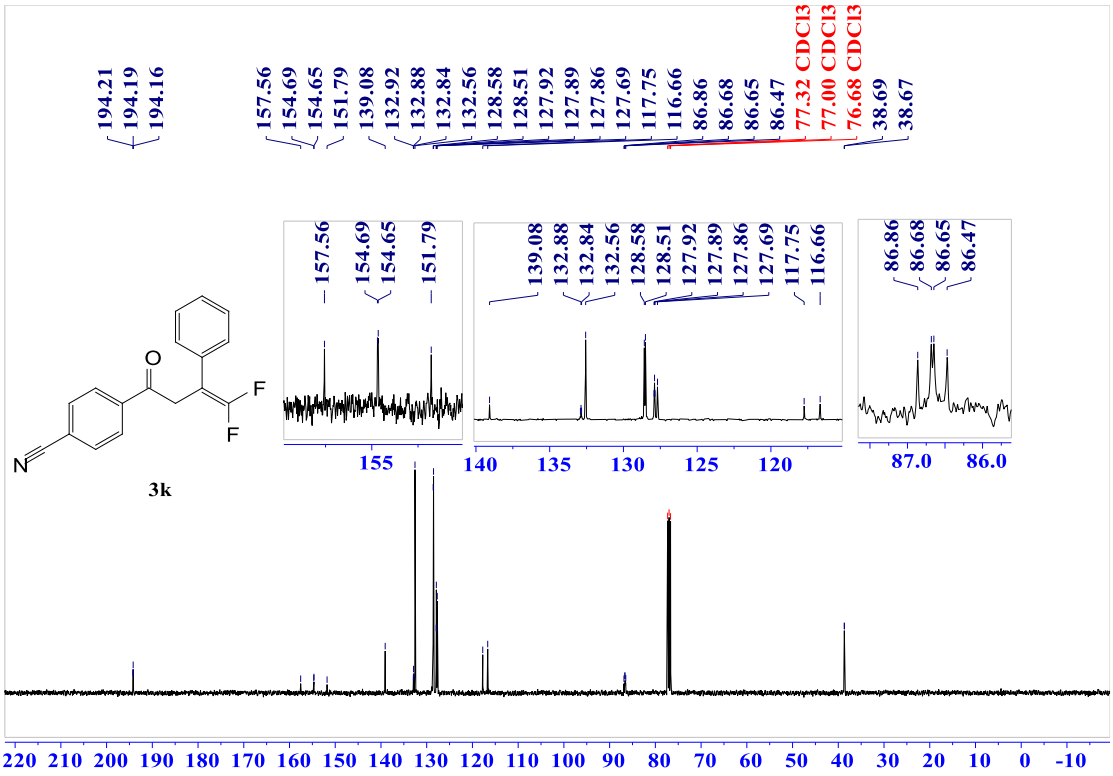
8.05 8.02 7.78 7.76 7.34 7.33 7.32 7.32 7.30 7.28 7.26
4.08 4.07 4.07
2.02 2.03 5.26 2.00
8.0 7.8 7.6 7.4 7.2 4.10 4.05
O F F N
3k
2.02 2.03 5.26 2.00
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0
f1 (ppm)


-87.34 -87.44 -88.36 -88.46
-87.34 -87.44 -88.36 -88.46
1.00 1.00
-87.5 -88.5
O F F N
3k
1.00 1.00
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)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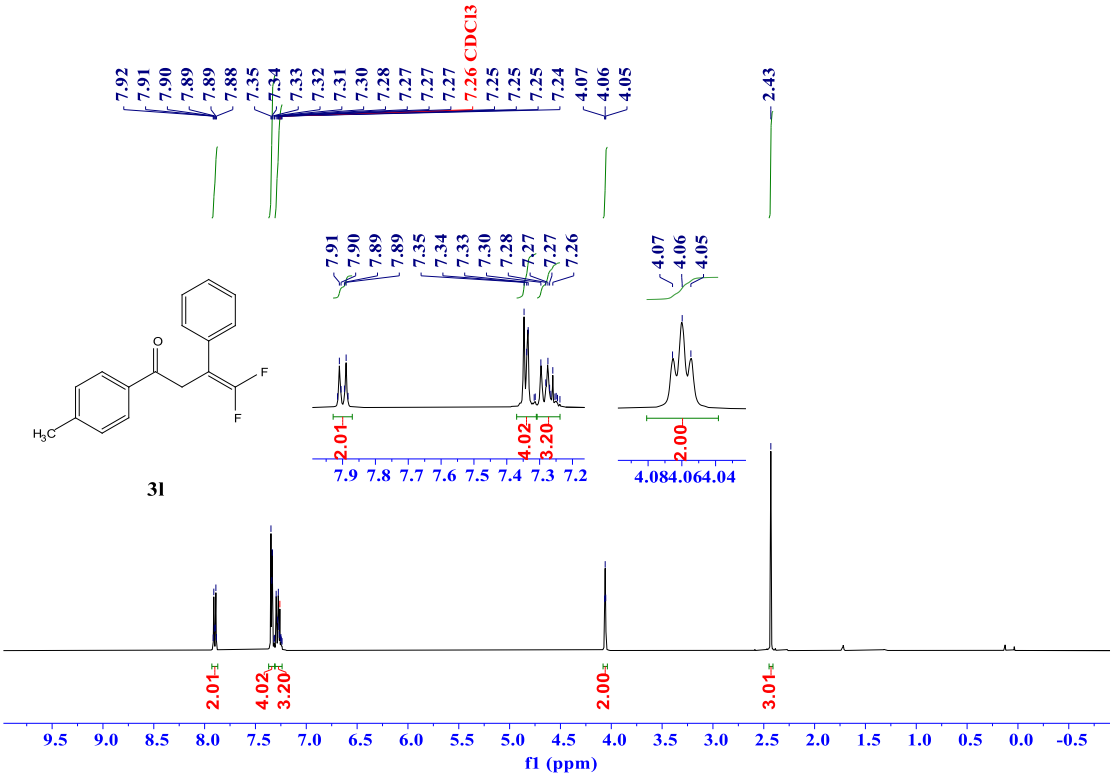
139.08
132.92
132.88
132.84
132.56
128.58
128.51
127.92
127.89
127.86
127.69
117.75
116.66
86.86
86.68
86.65
86.47
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.69
38.67
O
F
F
N
3k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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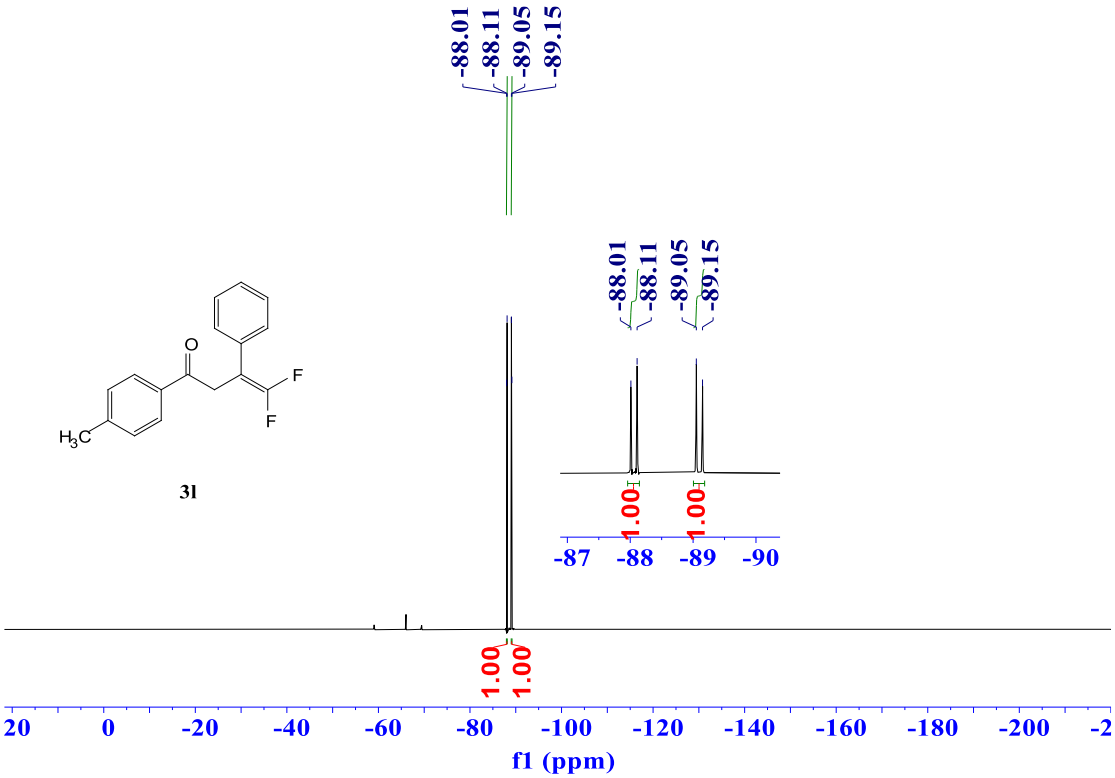
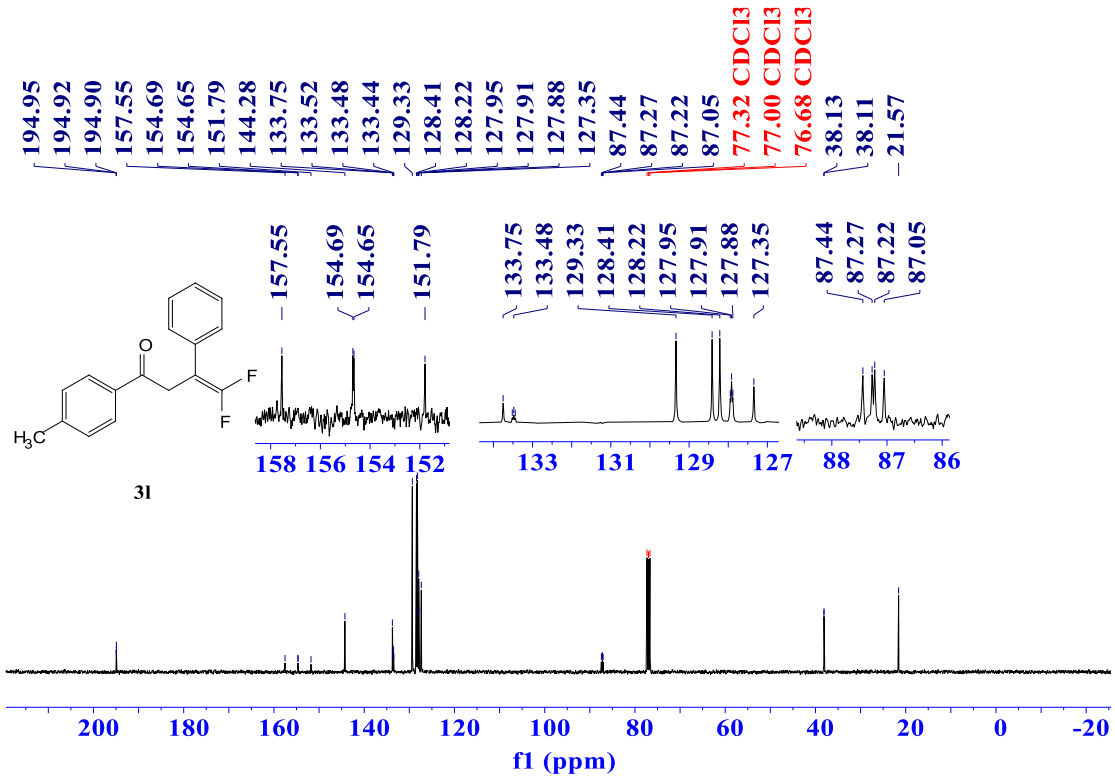
7.90
7.89
7.89
7.88
7.35
7.34
7.33
7.32
7.31
7.30
7.28
7.27
7.27
7.27
7.26 CDCl3
7.25
7.25
7.25
7.24
4.07
4.06
4.05
2.43
O
F
F
H3C
3l
2.01
4.02
3.20
2.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-88.01
-88.11
-89.05
-89.15
O
F
F
H3C
3l
1.00
1.00
-87
-88
-89
-90
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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194.90
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154.65
151.79
144.28
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133.52
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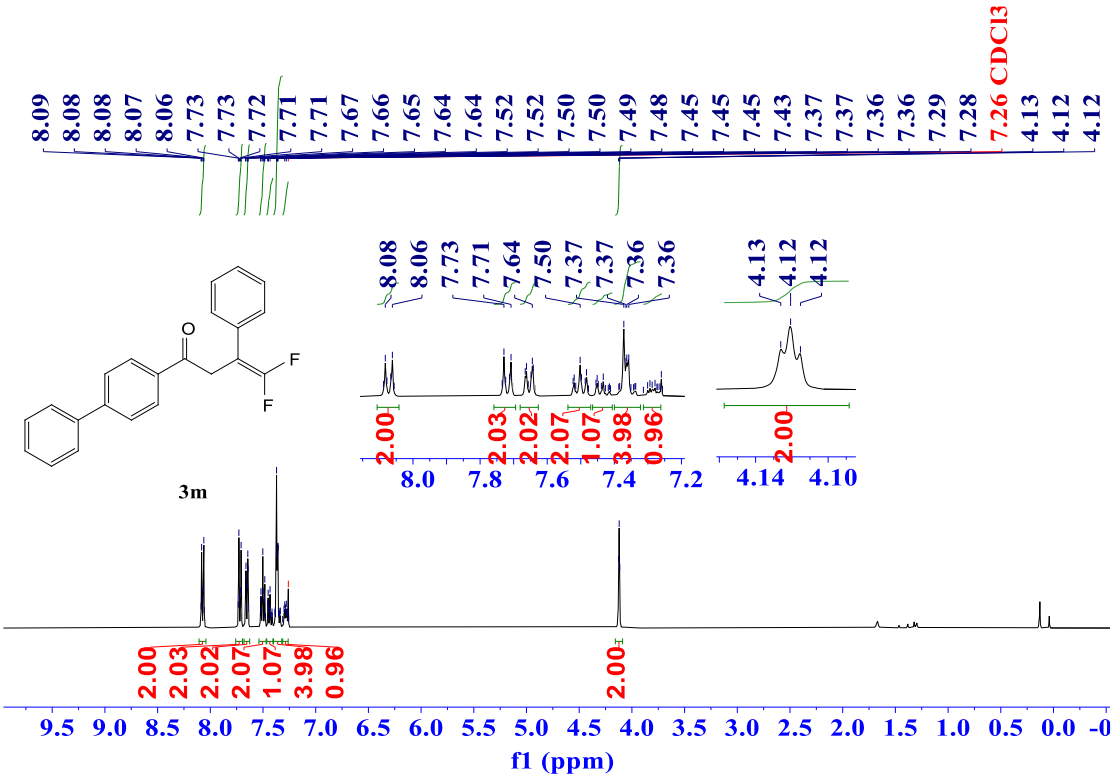
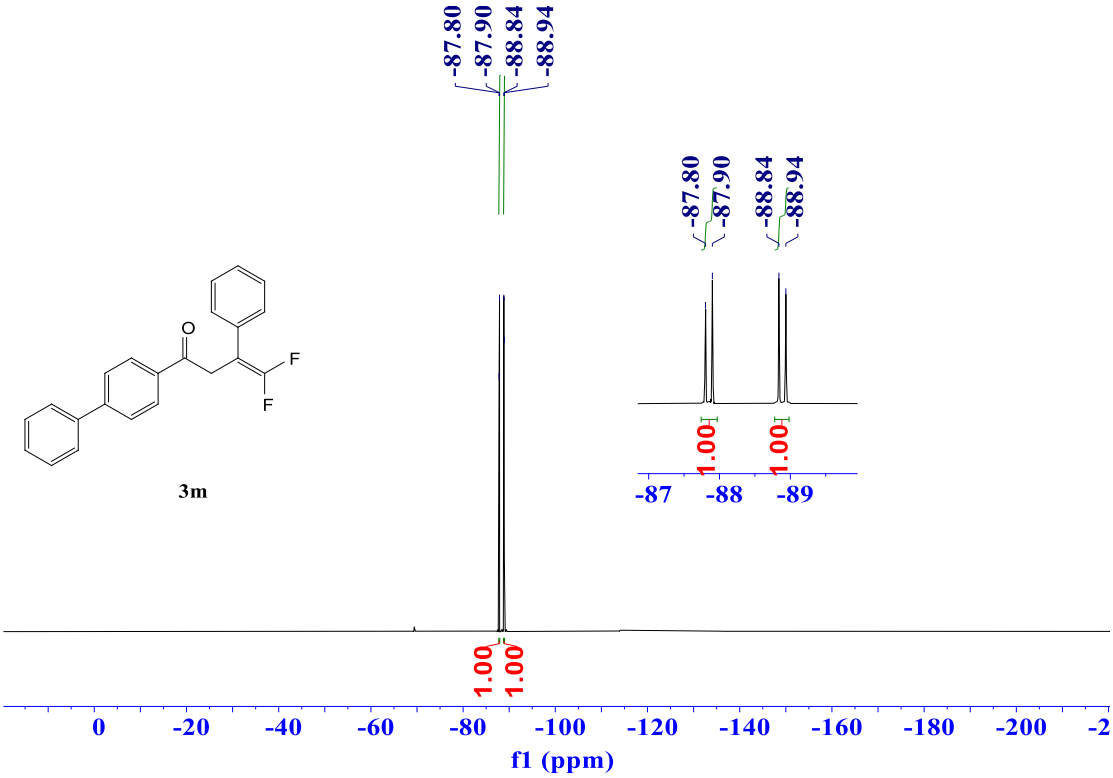
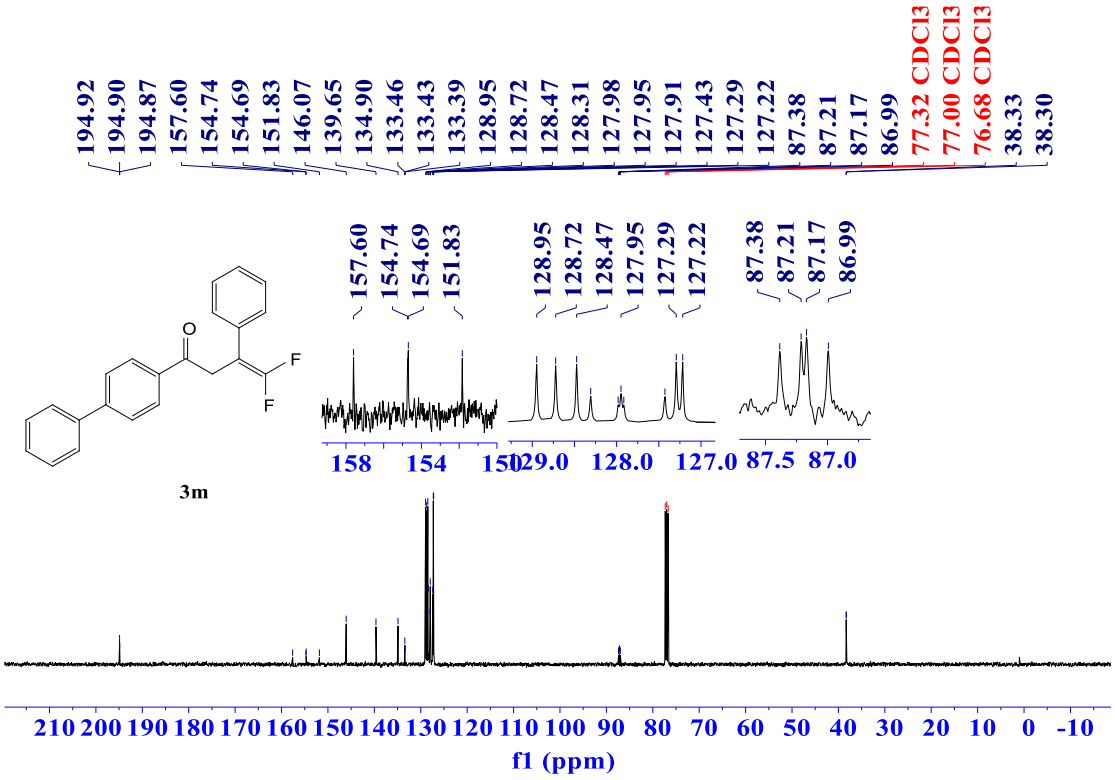
133.44
129.33
128.41
128.22
127.95
127.91
127.88
127.35
87.44
87.27
87.22
87.05
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.13
38.11
21.57
O
F
F
H3C
3l
158 156 154 152
133
131
129
127
88
87
86
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)


8.09 8.08 8.08 8.07 8.06 7.73 7.73 7.72 7.71 7.71 7.67 7.66 7.65 7.64 7.64 7.52 7.52 7.50 7.50 7.49 7.48 7.45 7.45 7.45 7.43 7.37 7.37 7.36 7.36 7.29 7.28 7.26 CDCl3 4.13 4.12 4.12
O
F
F
3m
2.00 2.03 2.02 2.07 1.07 3.98 0.96
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


-87.80 -87.90 -88.84 -88.94
O
F
F
3m
1.00 1.00
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)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134.90
133.46
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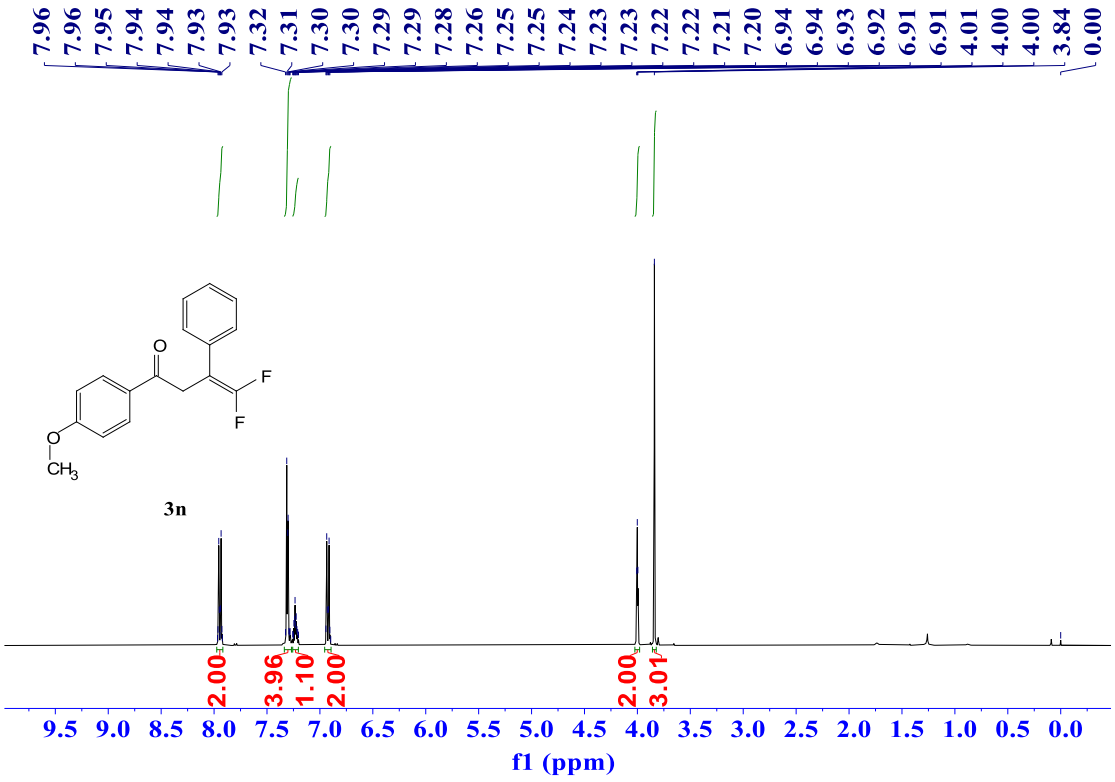
128.95
128.72
128.47
128.31
127.98
127.95
127.91
127.43
127.29
127.22
87.38
87.21
87.17
86.99
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.33
38.30
O
F
F
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.96
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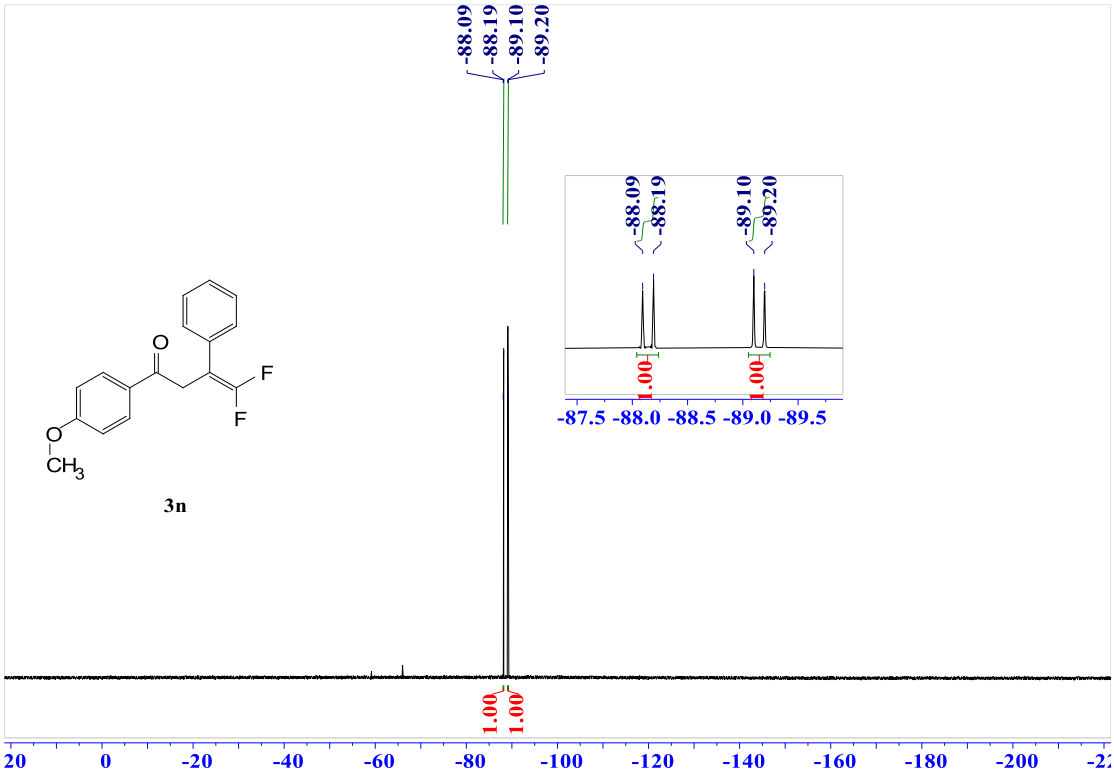
7.21
7.20
6.94
6.94
6.93
6.92
6.91
6.91
4.01
4.00
4.00
3.84
0.00
O
F
F
O
CH3
3n
2.00
3.96
1.10
2.00
2.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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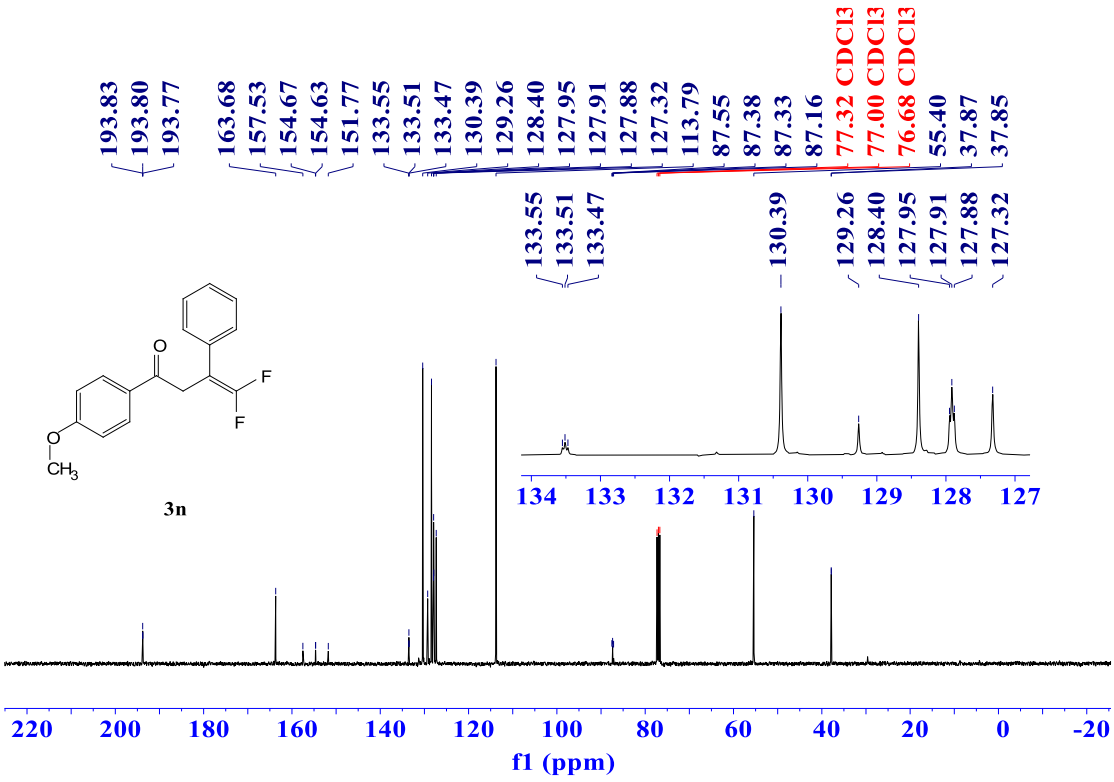
-88.19
-89.10
-89.20
O
F
F
O
CH3
3n
1.00
1.00
-87.5 -88.0 -88.5 -89.0 -89.5
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200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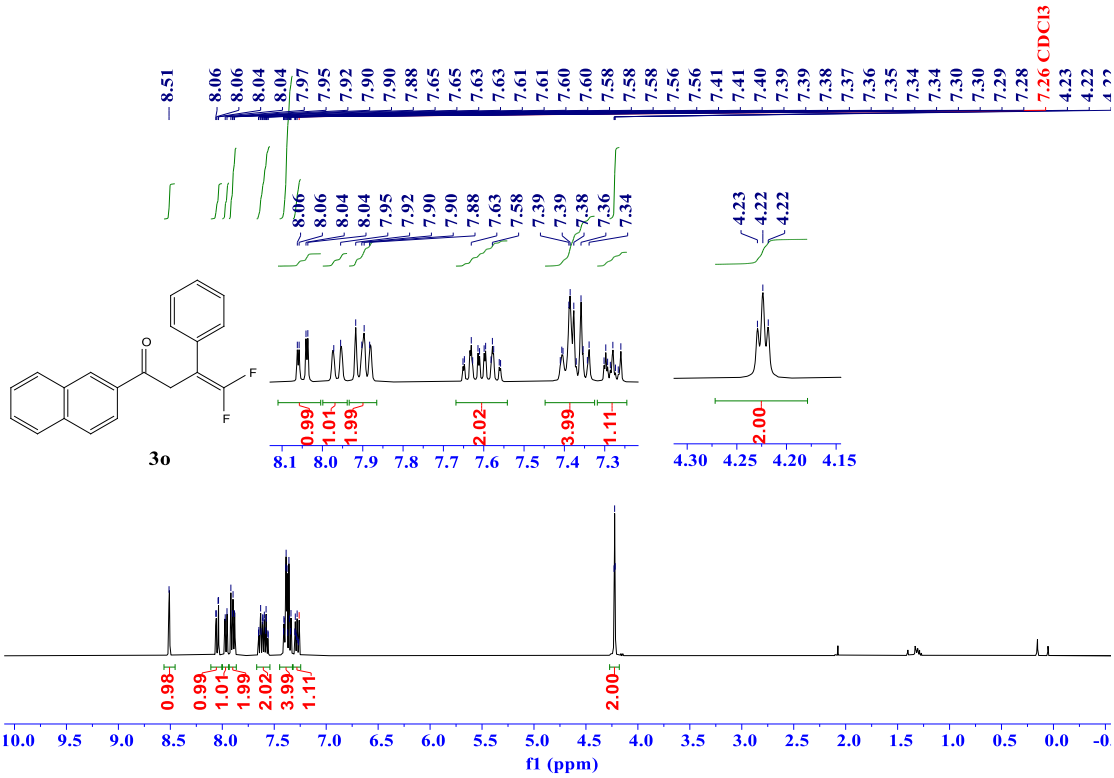
130.39
129.26
128.40
127.95
127.91
127.88
127.32
113.79
87.55
87.38
87.33
87.16
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.40
37.87
37.85
O
F
F
O
CH3
3n
134 133 132 131 130 129 128 127
220 200 180 160 140 120 100 80 60 40 20 0 -20
f1 (ppm)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7.97
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7.88
7.65
7.65
7.63
7.63
7.61
7.61
7.60
7.60
7.58
7.58
7.58
7.56
7.56
7.41
7.41
7.40
7.39
7.39
7.38
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7.36
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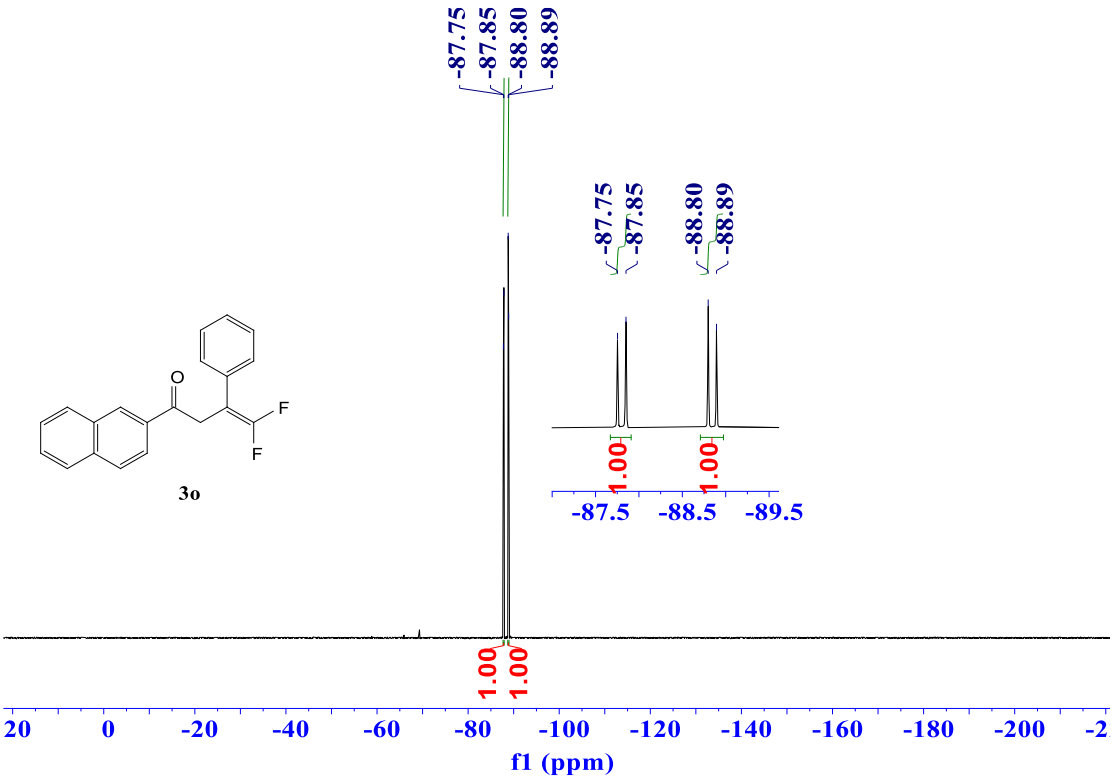
7.34
7.34
7.30
7.30
7.29
7.28
7.26 CDCl3
4.23
4.22
4.22
O
F
F
3o
0.99
1.01
1.99
2.02
3.99
1.11
2.00
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
4.30 4.25 4.20 4.15
0.98
0.99
1.01
1.99
2.02
3.99
1.11
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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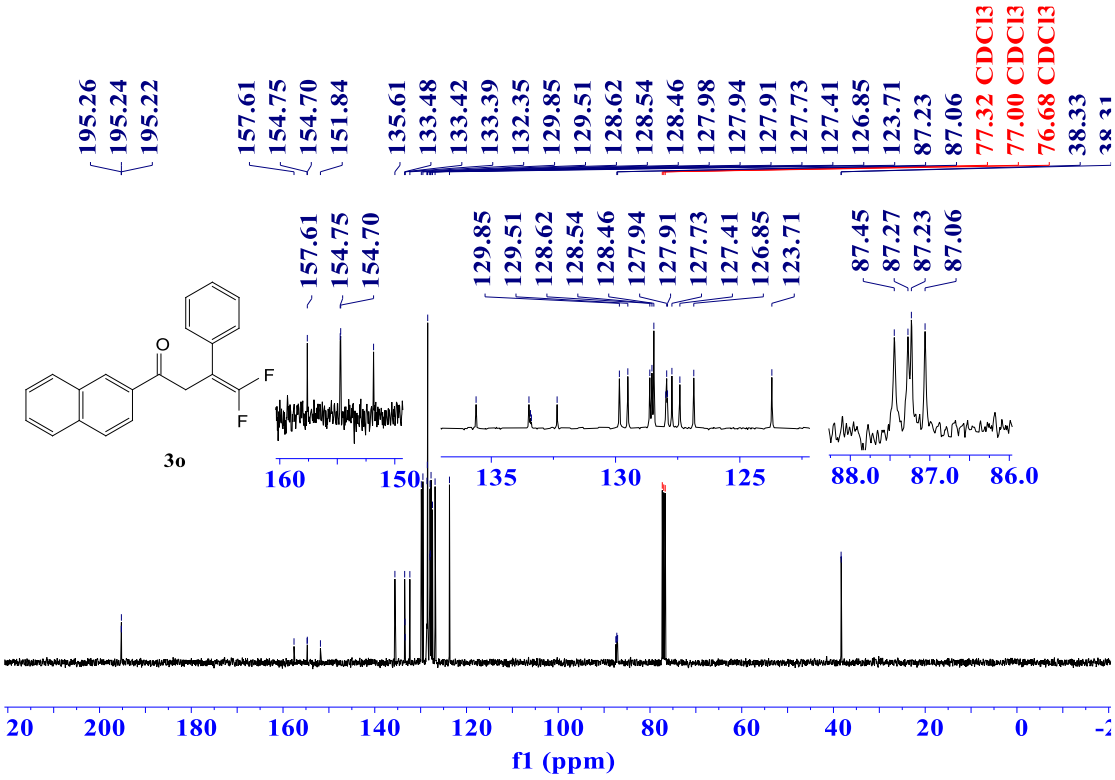
-88.80
-88.89
O
F
F
3o
1.00
1.00
-87.5 -88.5 -89.5
1.00
1.00
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)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154.70
151.84
135.61
133.48
133.42
133.39
132.35
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129.51
128.62
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128.46
127.98
127.94
127.91
127.73
127.41
126.85
123.71
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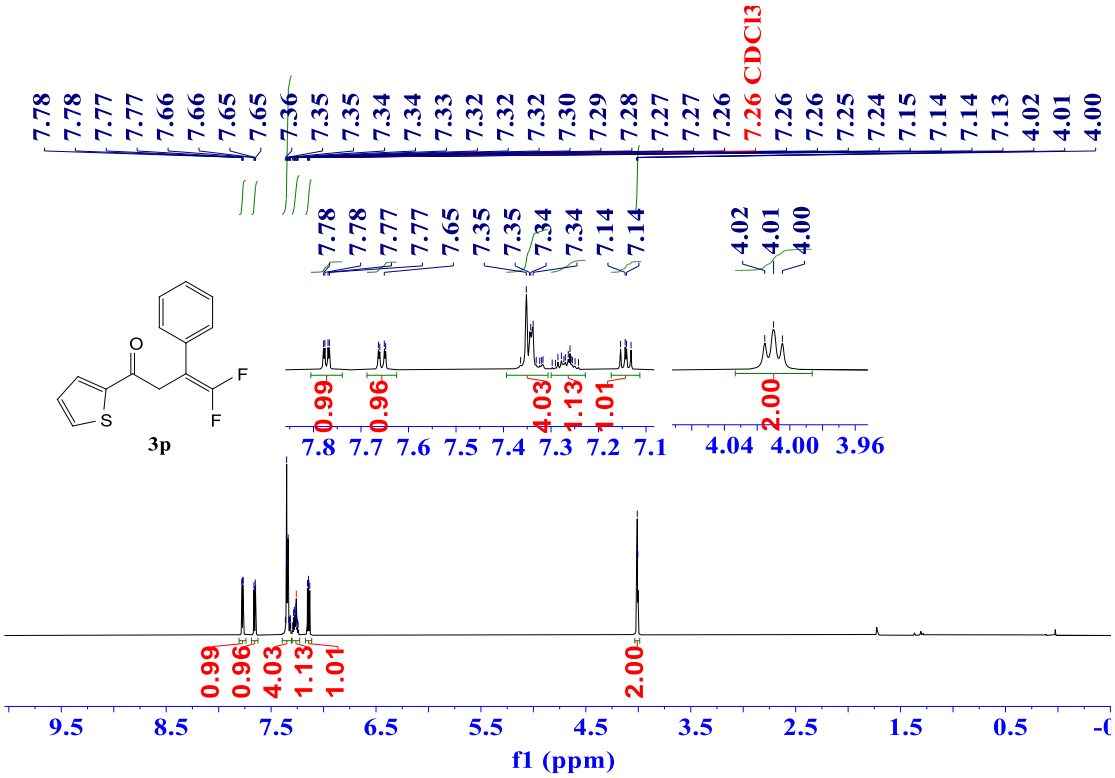
87.06
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.33
O
F
F
3o
f1 (ppm)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7.65
7.65
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7.33
7.32
7.32
7.32
7.30
7.29
7.28
7.27
7.27
7.26
7.26 CDCl3
7.26
7.25
7.24
7.15
7.14
7.14
7.13
4.02
4.01
4.00
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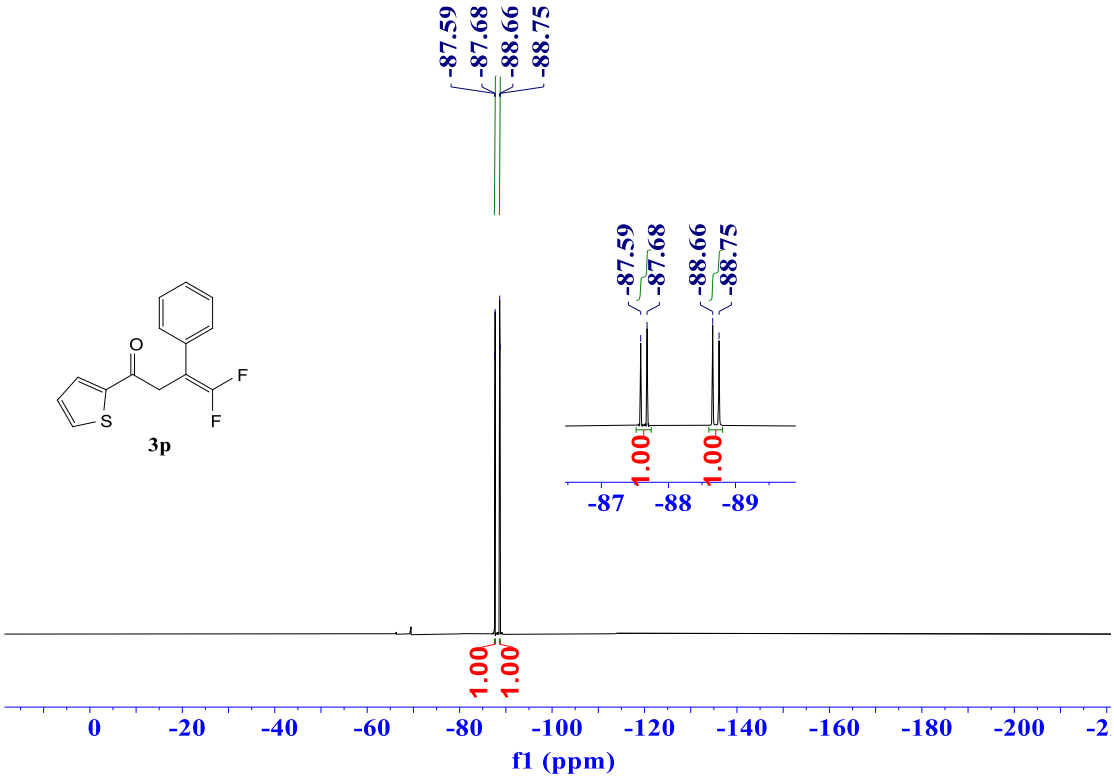
0.96
4.03
1.13
1.01
2.00
O
F
S
F
3p
f1 (ppm)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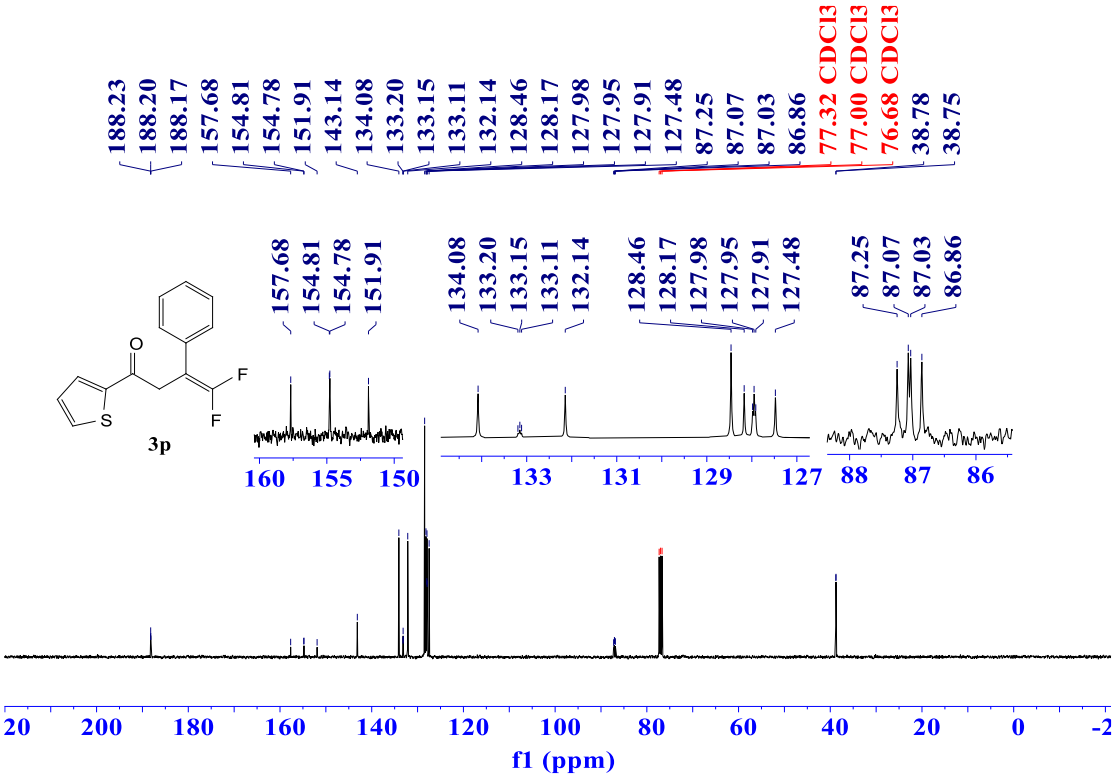
-87.68
-88.66
-88.75
O
S
F
F
3p
1.00
1.00
-87
-88
-89
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


188.23
188.20
188.17
157.68
154.81
154.78
151.91
143.14
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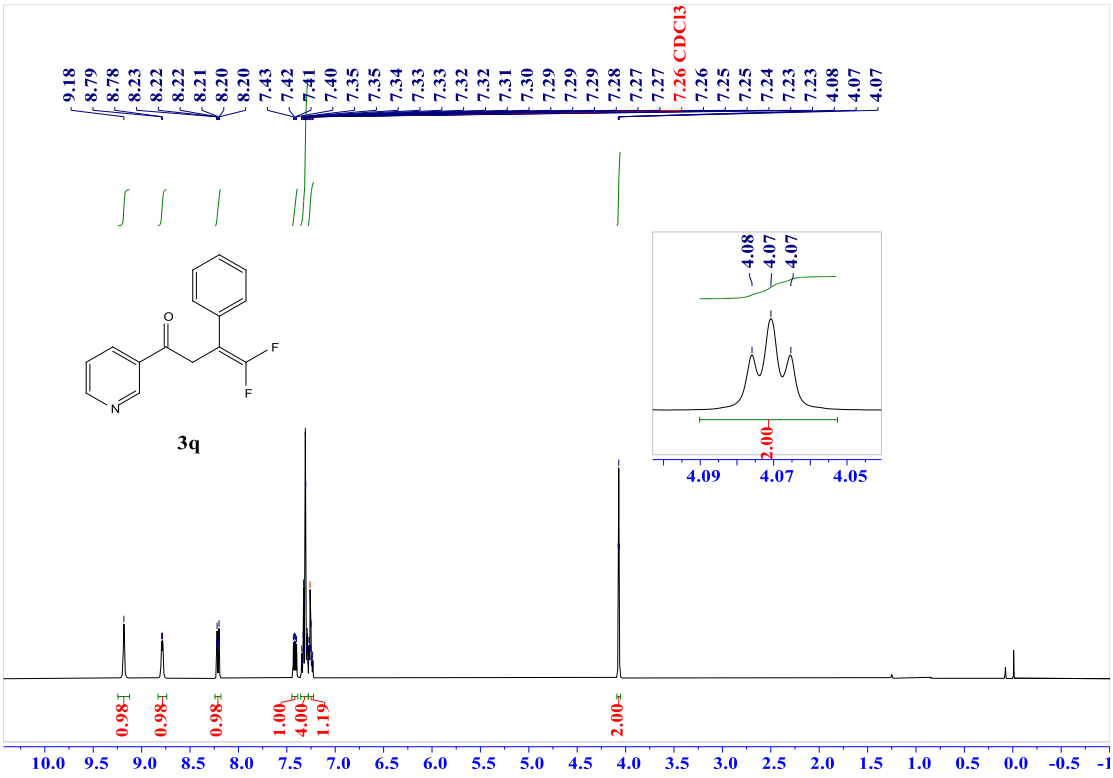
133.15
133.11
132.14
128.46
128.17
127.98
127.95
127.91
127.48
87.25
87.07
87.03
86.86
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.78
38.75
O
S
F
F
3p
160
155
150
133
131
129
127
88
87
86
20
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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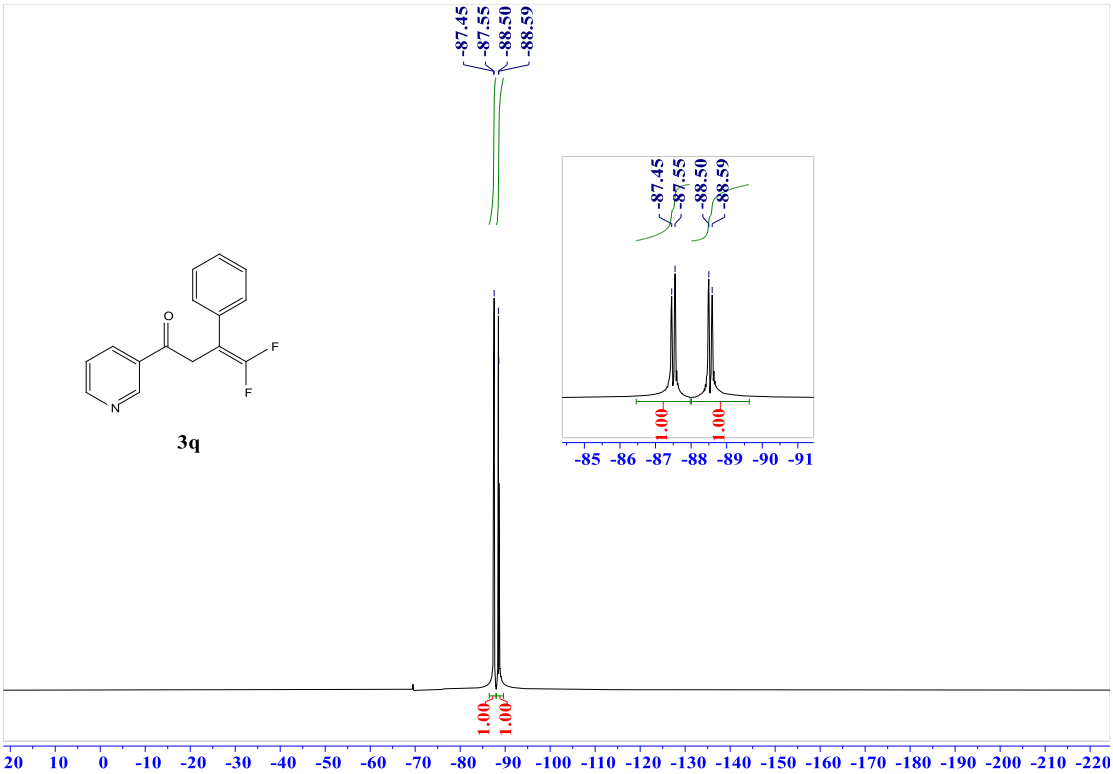
7.40
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.26 CDCl3
7.26
7.25
7.25
7.24
7.23
7.23
4.08
4.07
4.07
O
F
F
N
3q
4.08
4.07
4.07
2.00
4.09
4.07
4.05
0.98
0.98
0.98
1.00
4.00
1.19
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1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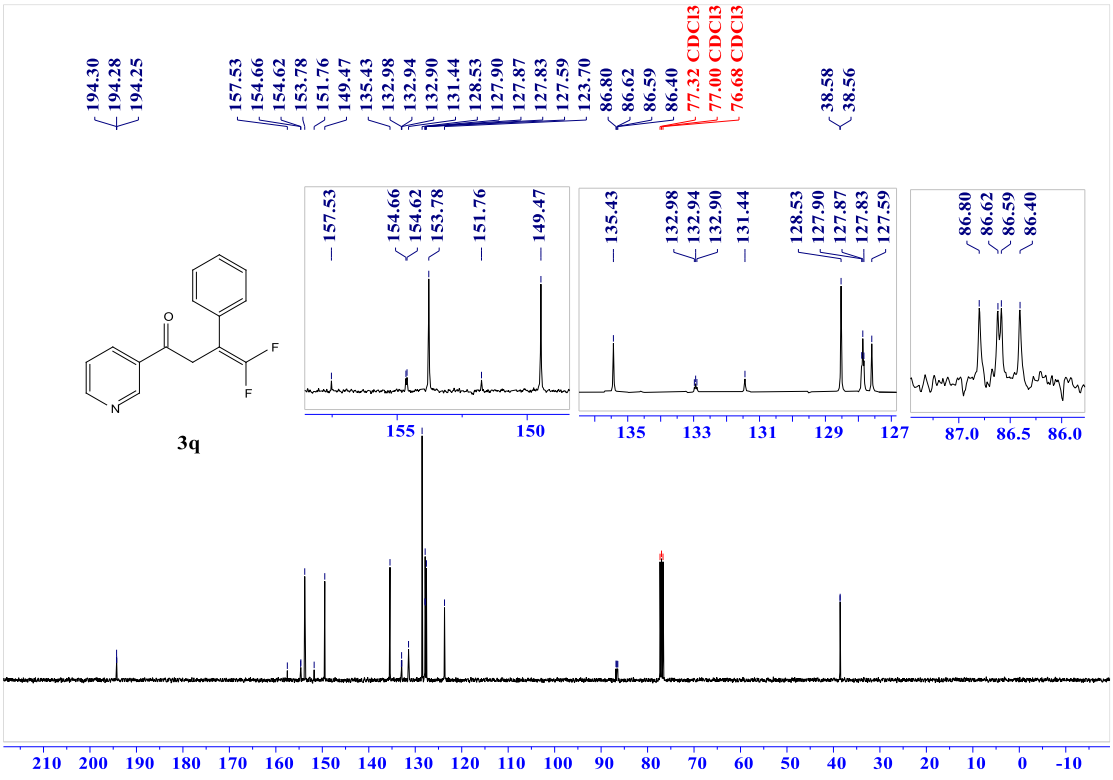
-87.55
-88.50
-88.59
O
F
F
N
3q
-87.45
-87.55
-88.50
-88.59
1.00
1.00
-85 -86 -87 -88 -89 -90 -91
1.00
1.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220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132.90
131.44
128.53
127.90
127.87
127.83
127.59
123.70
86.80
86.62
86.59
86.40
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
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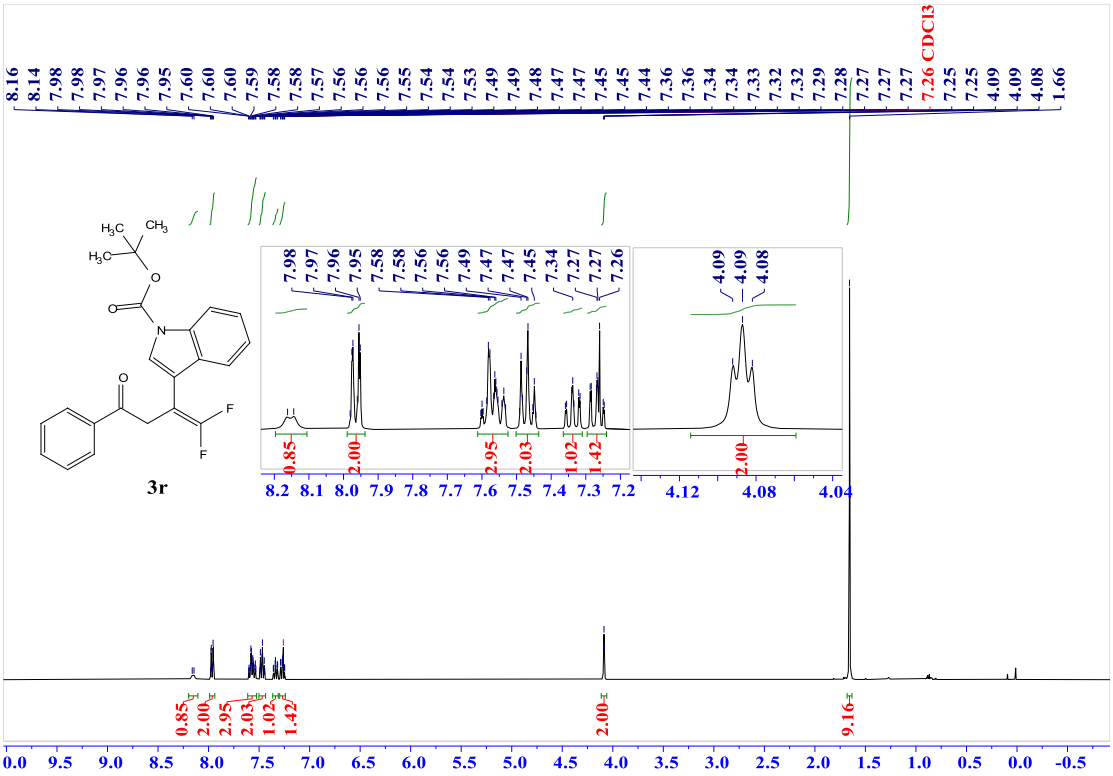
38.56
O
F
F
N
3q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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7.60
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7.58
7.58
7.57
7.56
7.56
7.56
7.55
7.54
7.54
7.53
7.49
7.49
7.48
7.47
7.47
7.45
7.45
7.44
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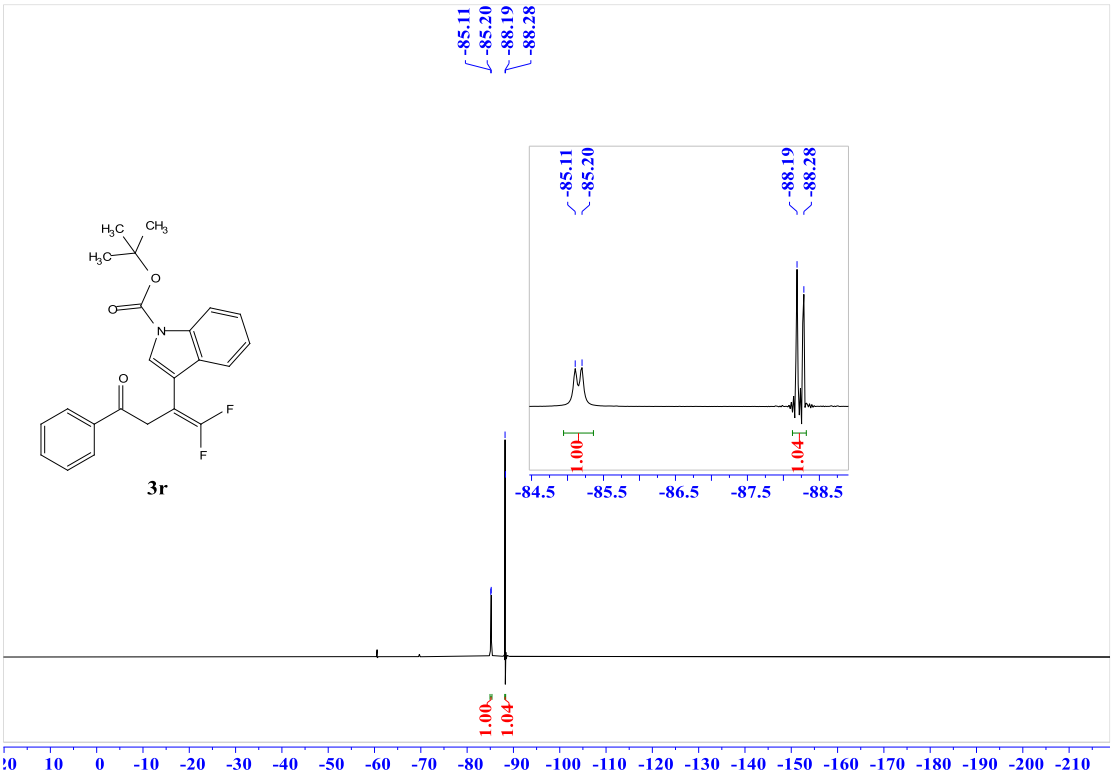
7.36
7.34
7.34
7.33
7.32
7.29
7.28
7.27
7.27
7.27
7.26 CDCl3
7.25
4.09
4.09
4.08
1.66
H3C
CH3
H3C
O
O
N
O
F
F
3r
0.85
2.00
2.95
2.03
1.02
1.42
2.00
9.16
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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-88.19
-88.28
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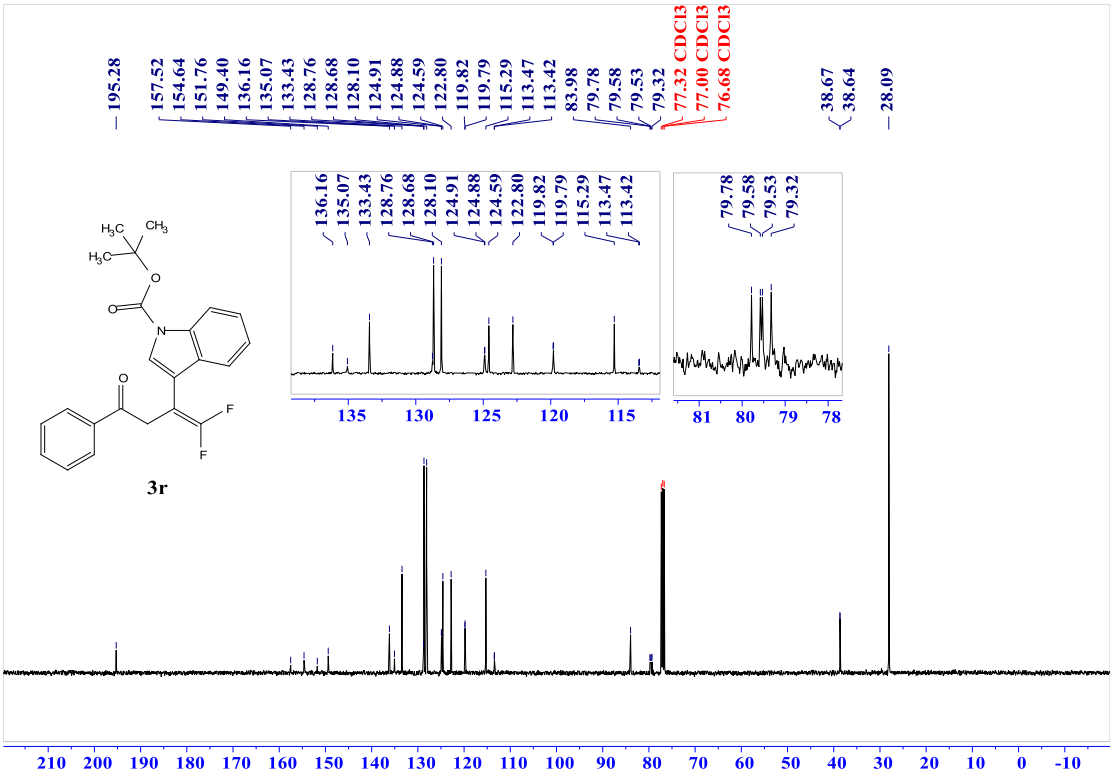
1.04
-84.5
-85.5
-86.5
-87.5
-88.5
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210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128.10
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124.88
124.59
122.80
119.82
119.79
115.29
113.47
113.42
83.98
79.78
79.58
79.53
79.32
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.67
38.64
28.09
3r
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130
125
120
115
81
80
79
78
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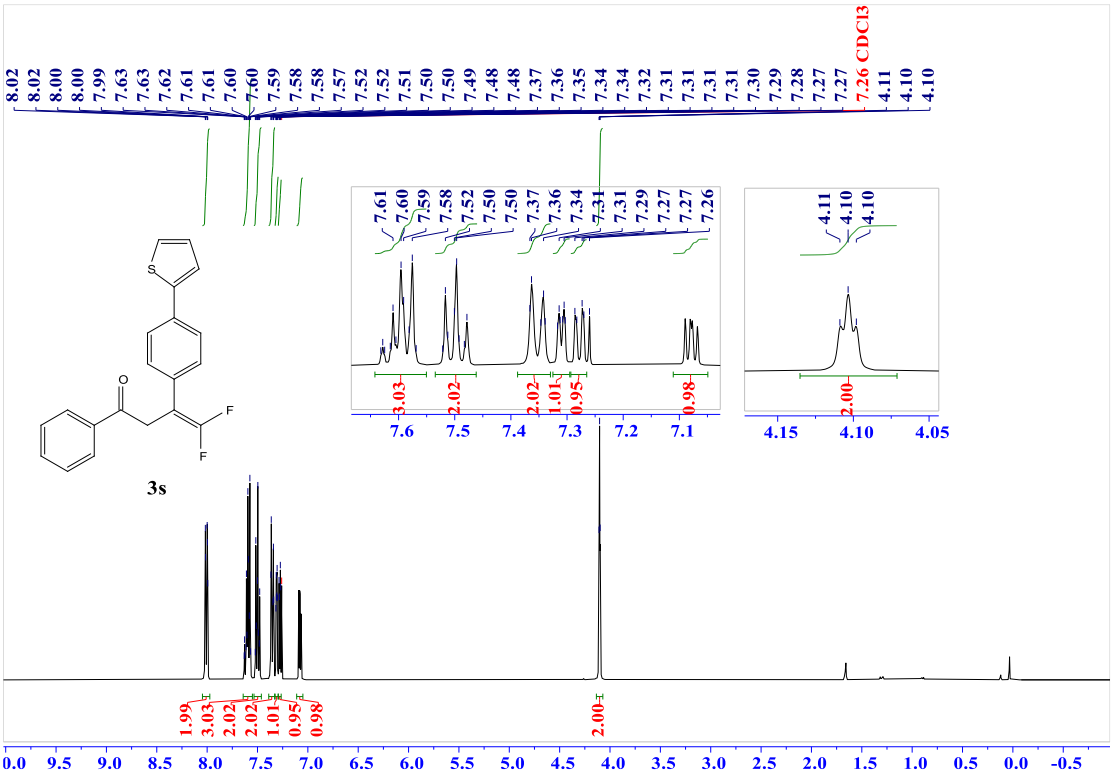
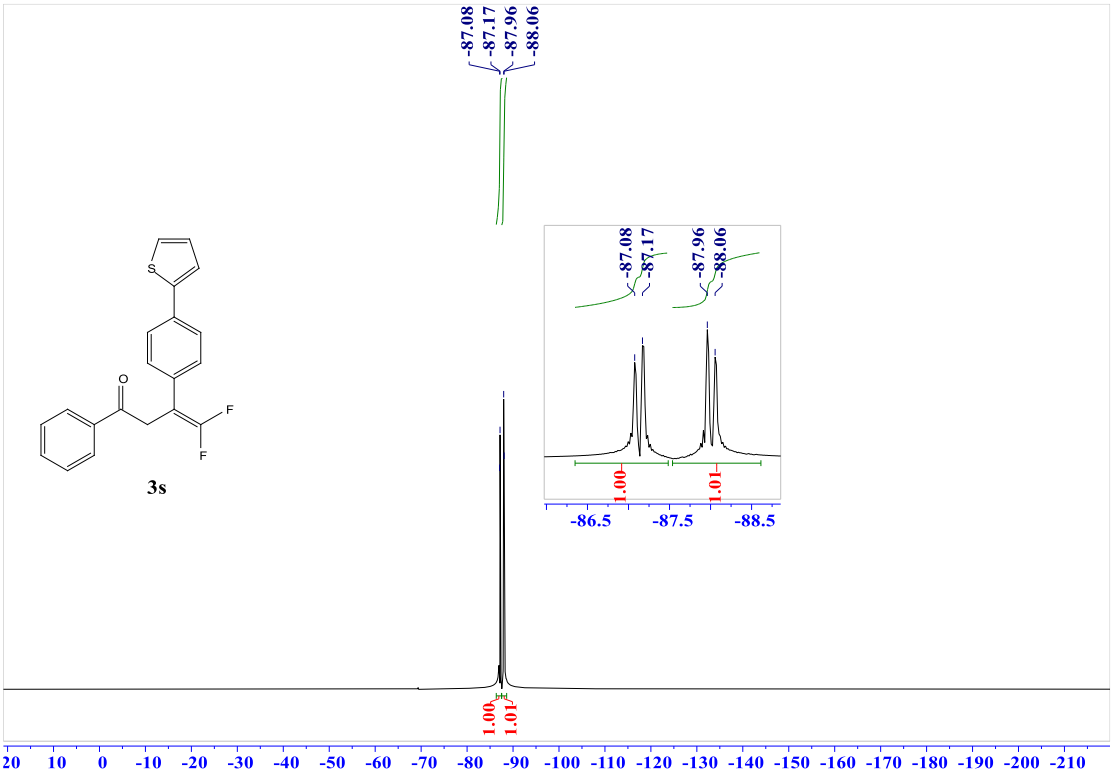
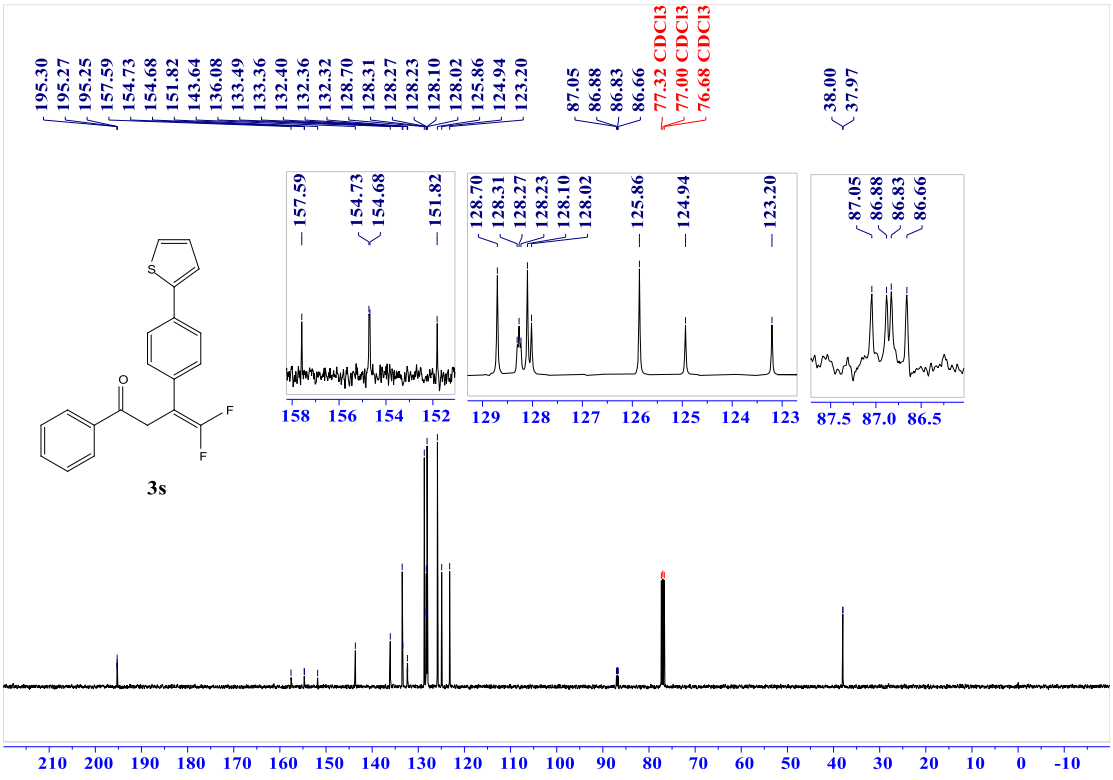

3s


3s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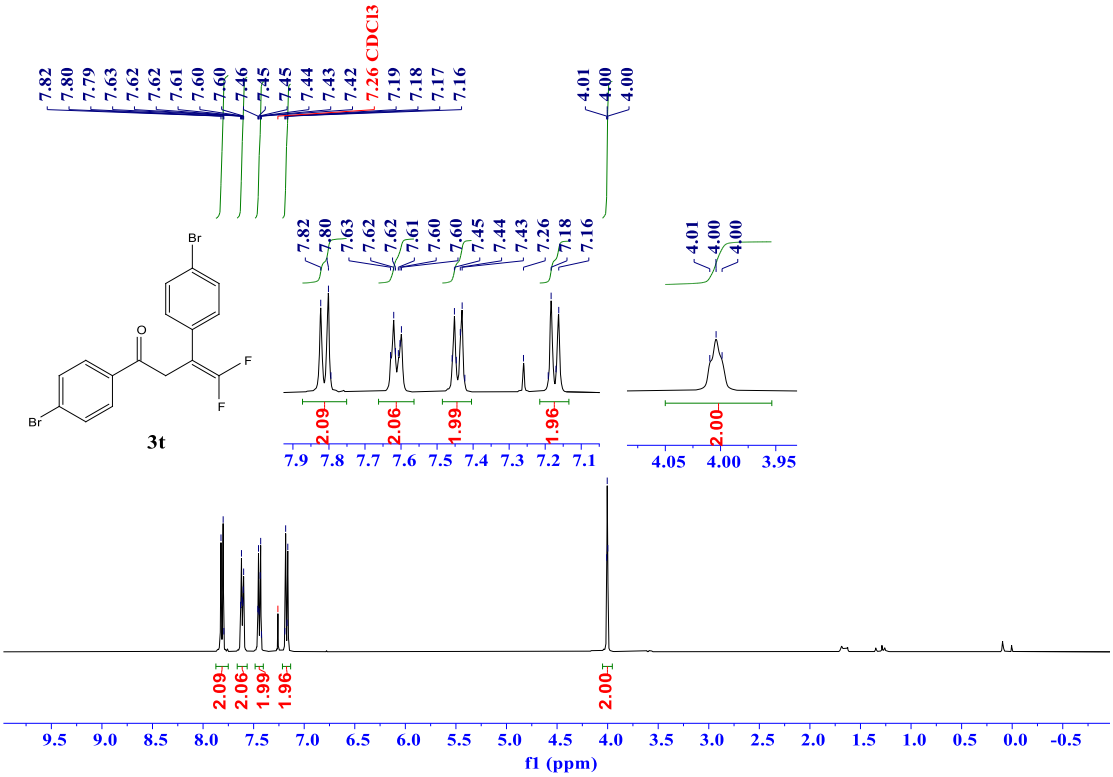
132.36
132.32
128.70
128.31
128.27
128.23
128.10
128.02
125.86
124.94
123.20
87.05
86.88
86.83
86.66
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.00
37.97
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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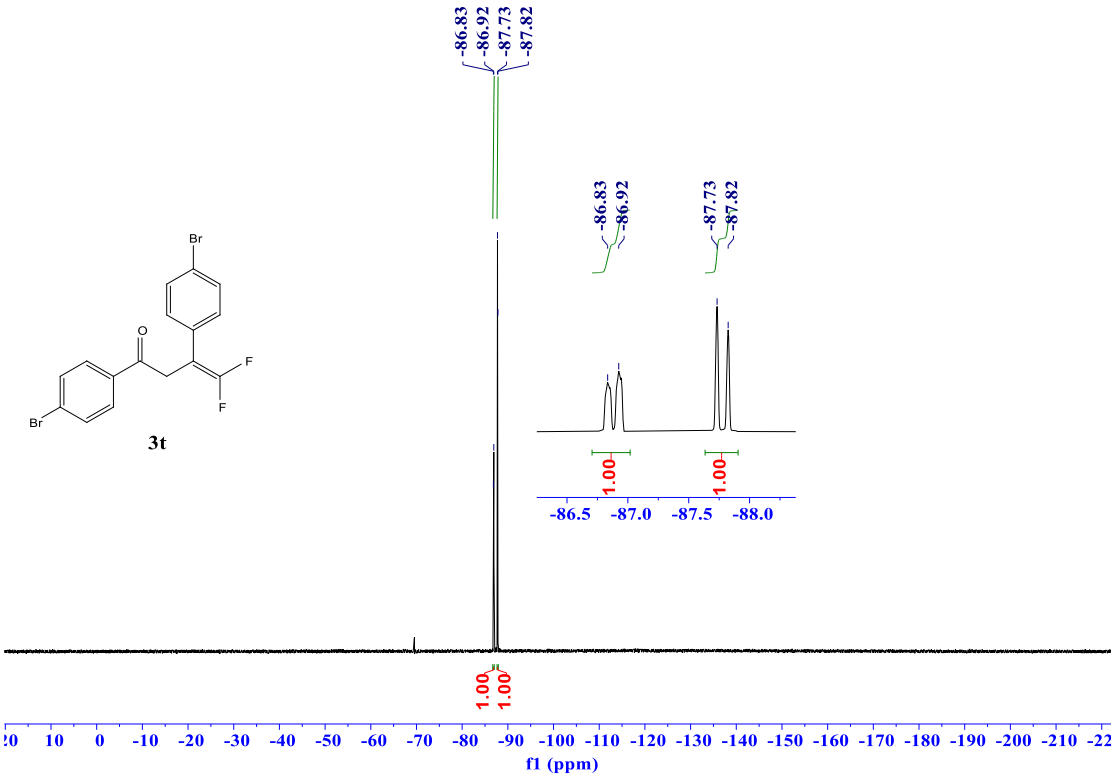
7.45
7.44
7.43
7.42
7.26 CDCl3
7.19
7.18
7.17
7.16
4.01
4.00
4.00
2.09
2.06
1.99
1.96
2.00
3t
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
4.05 4.00 3.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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-86.92
-87.73
-87.82
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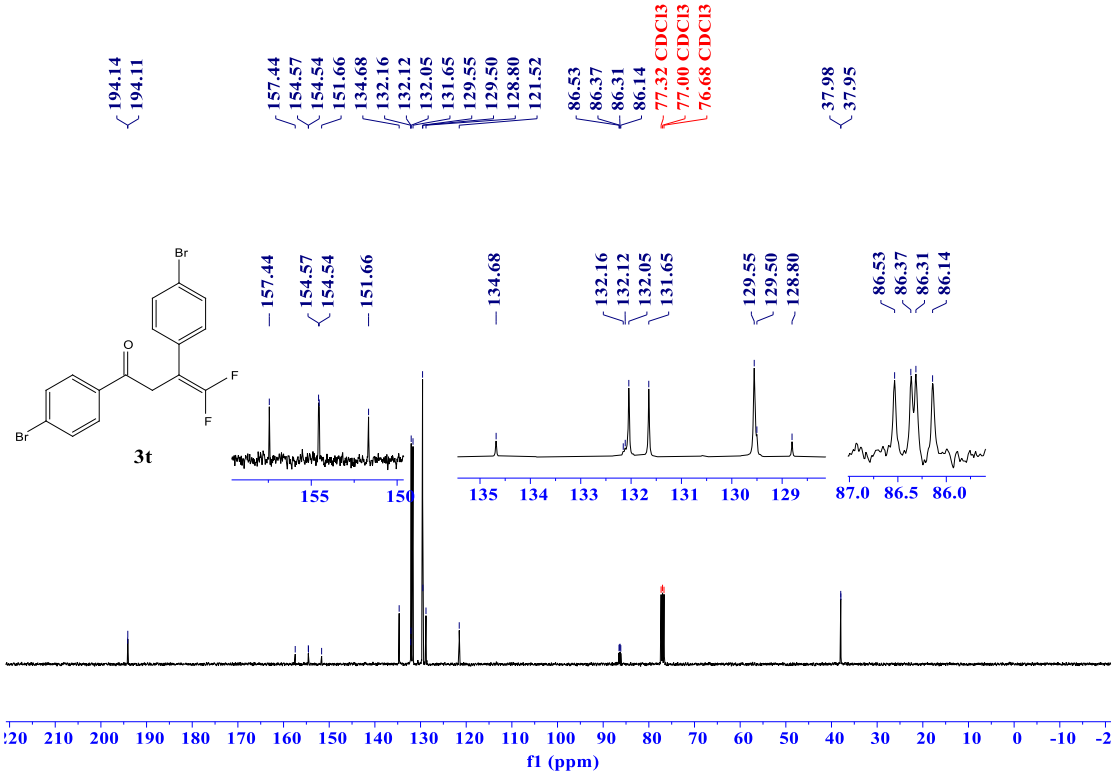
F
F
Br
3t
1.00
1.00
-86.5
-87.0
-87.5
-88.0
f1 (ppm)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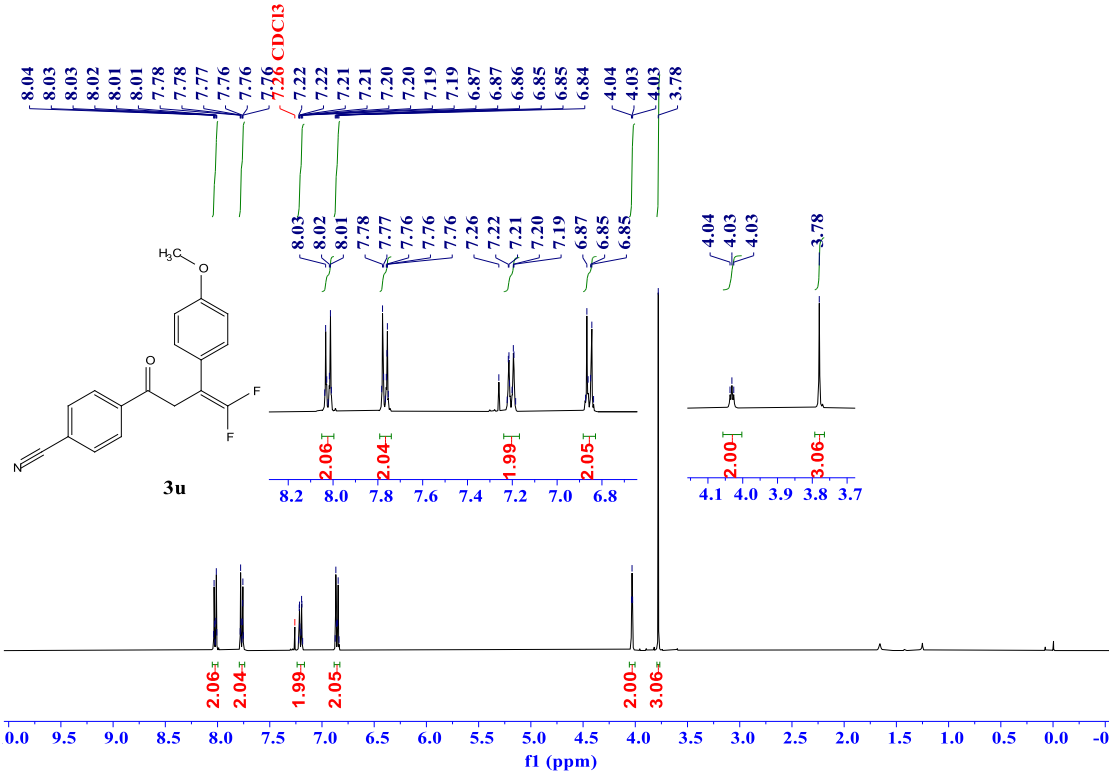
128.80
121.52
86.53
86.37
86.31
86.14
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
37.98
37.95
Br
O
F
F
Br
3t
f1 (ppm)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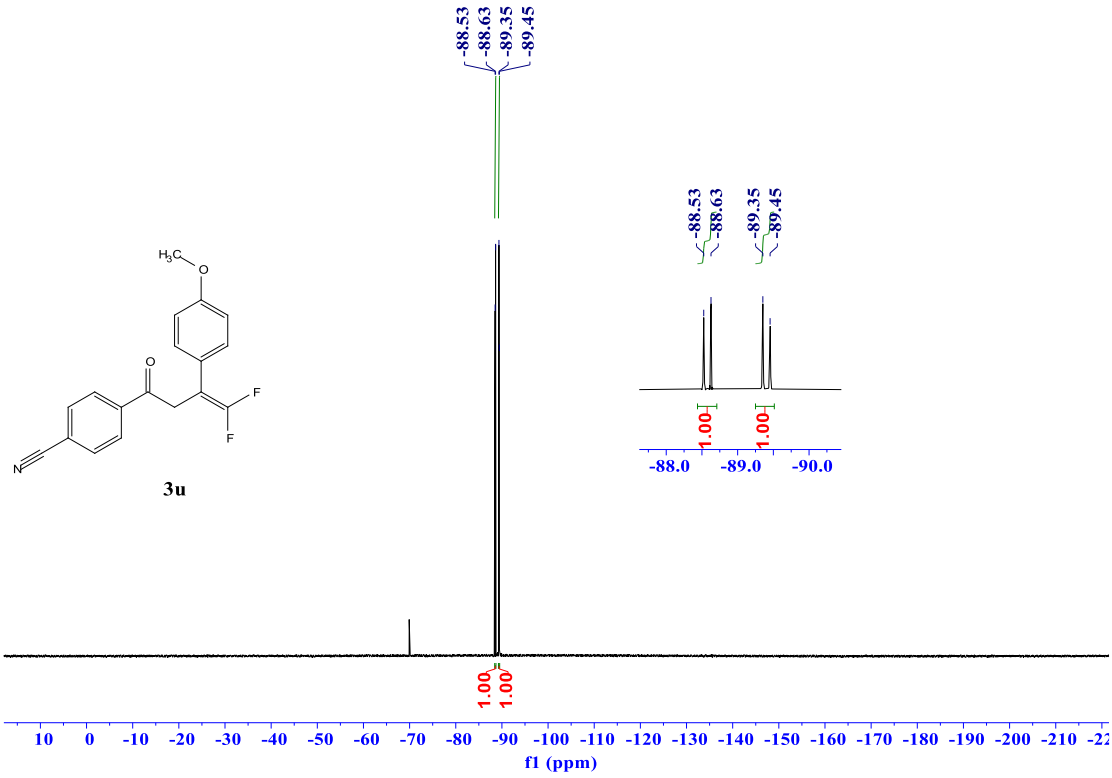
3u
2.06 2.04 1.99 2.05 2.00 3.06
f1 (ppm)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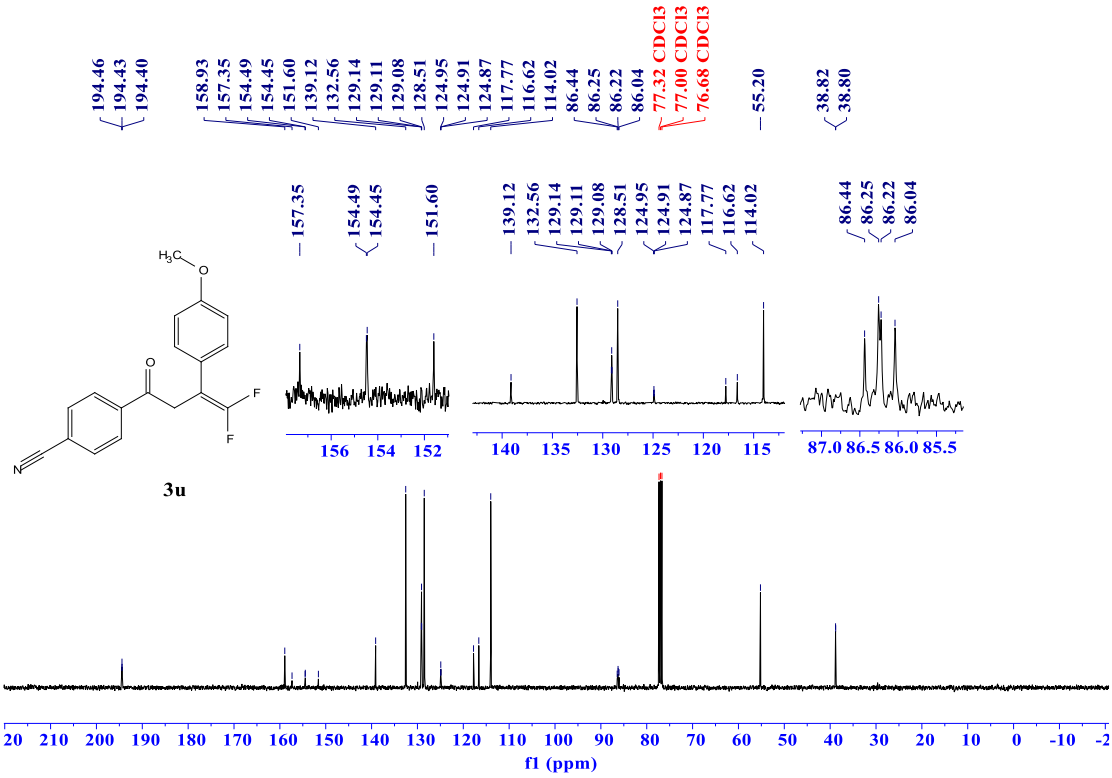
1.00 1.00
f1 (ppm)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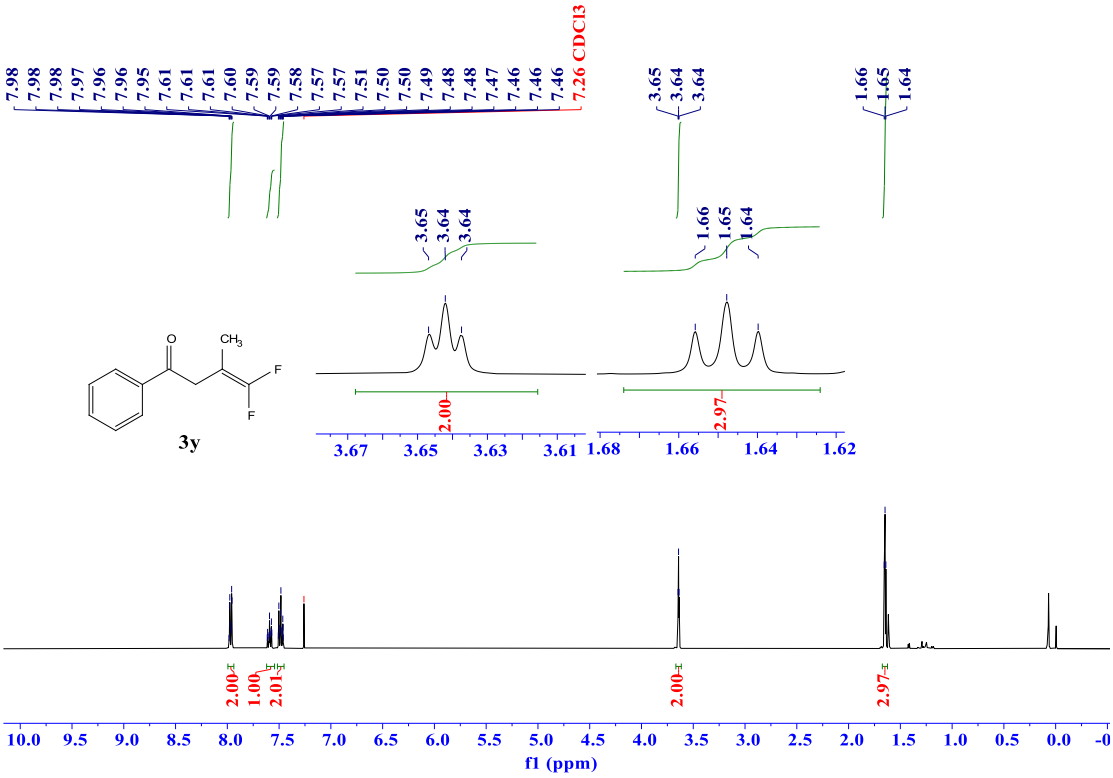
129.11
129.08
128.51
124.95
124.91
124.87
117.77
116.62
114.02
86.44
86.25
86.22
86.04
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.20
38.82
38.80
3u
f1 (ppm)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7.48
7.47
7.46
7.46
7.46
7.26 CDCl3
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3.64
3.64
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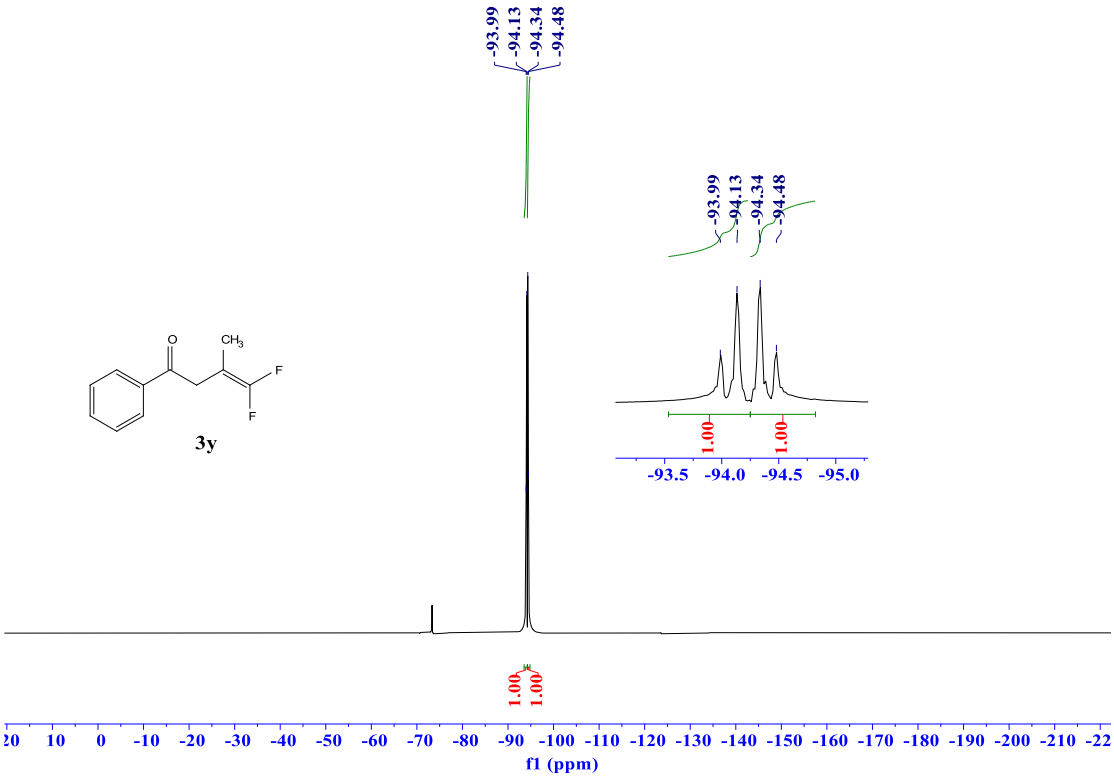
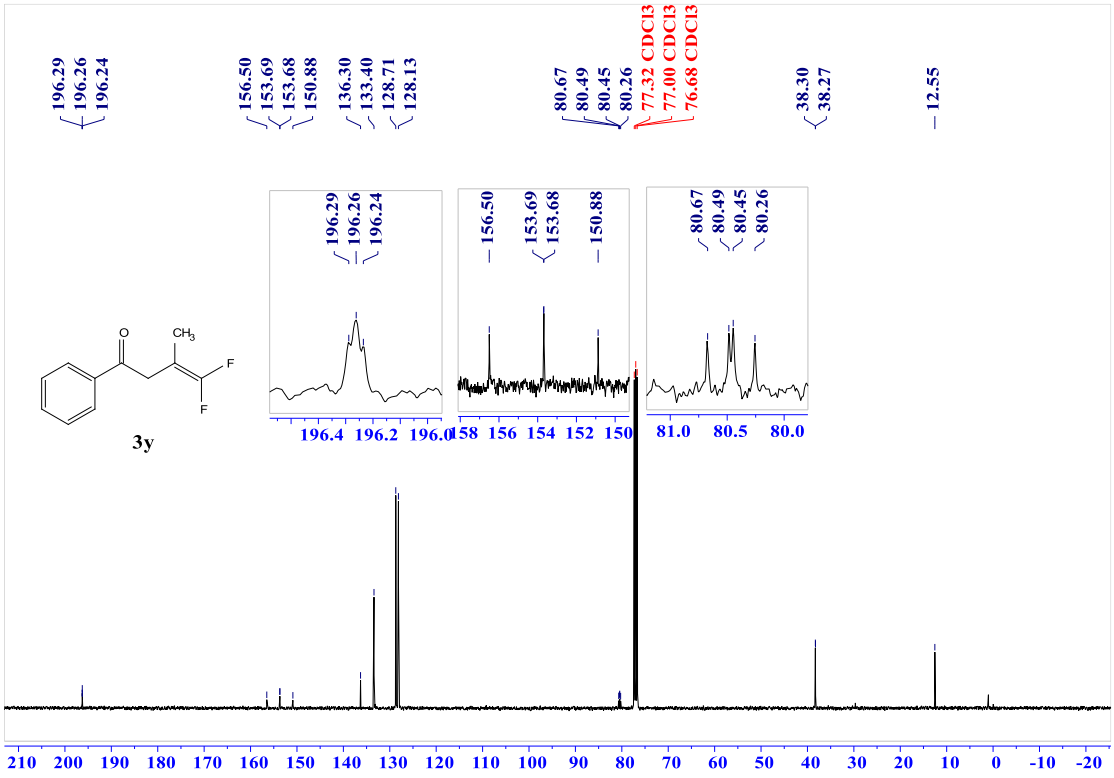
1.64
2.00
2.97
3y
2.00
1.00
2.01
2.00
2.97
f1 (ppm)


-93.99
-94.13
-94.34
-94.48
O
CH3
F
F
3y
1.00
1.00
-93.5 -94.0 -94.5 -95.0
f1 (ppm)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133.40
128.71
128.13
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80.26
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
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38.27
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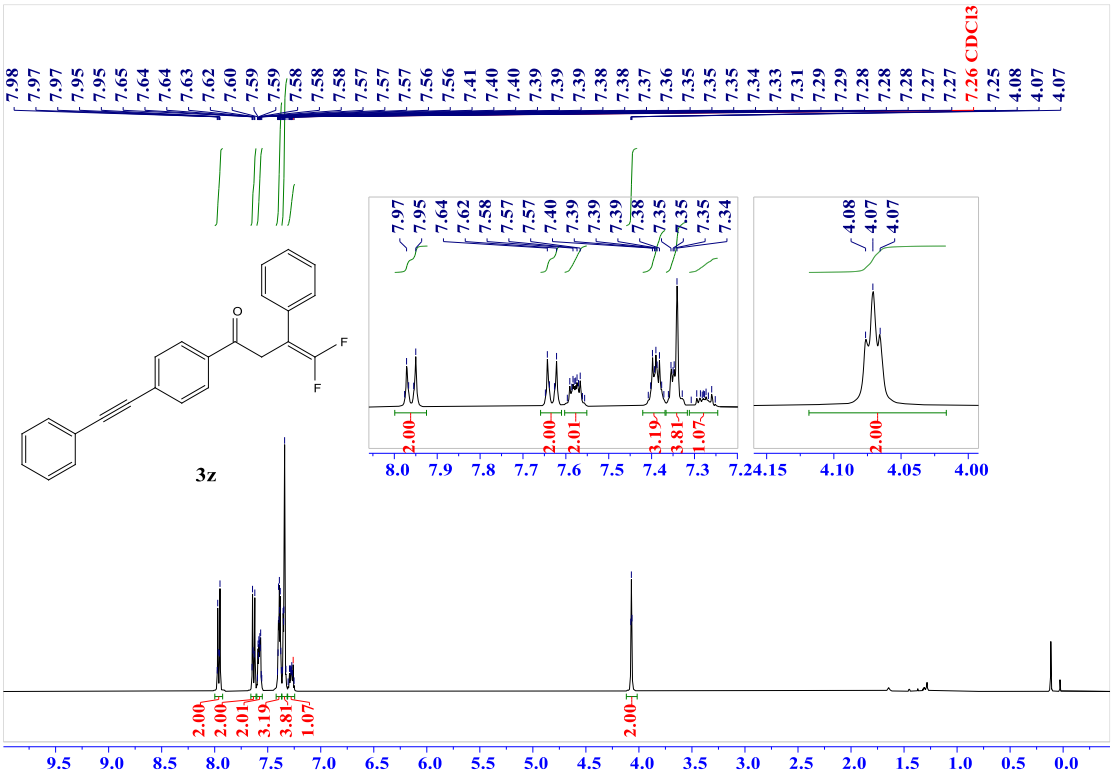
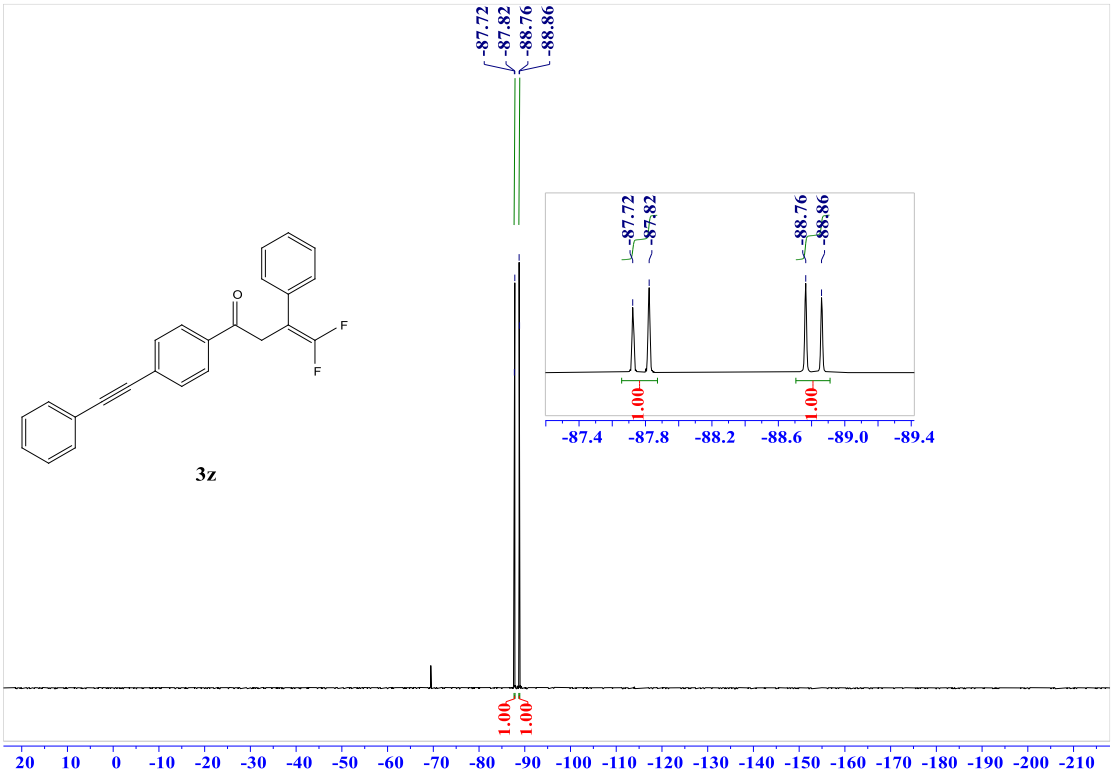
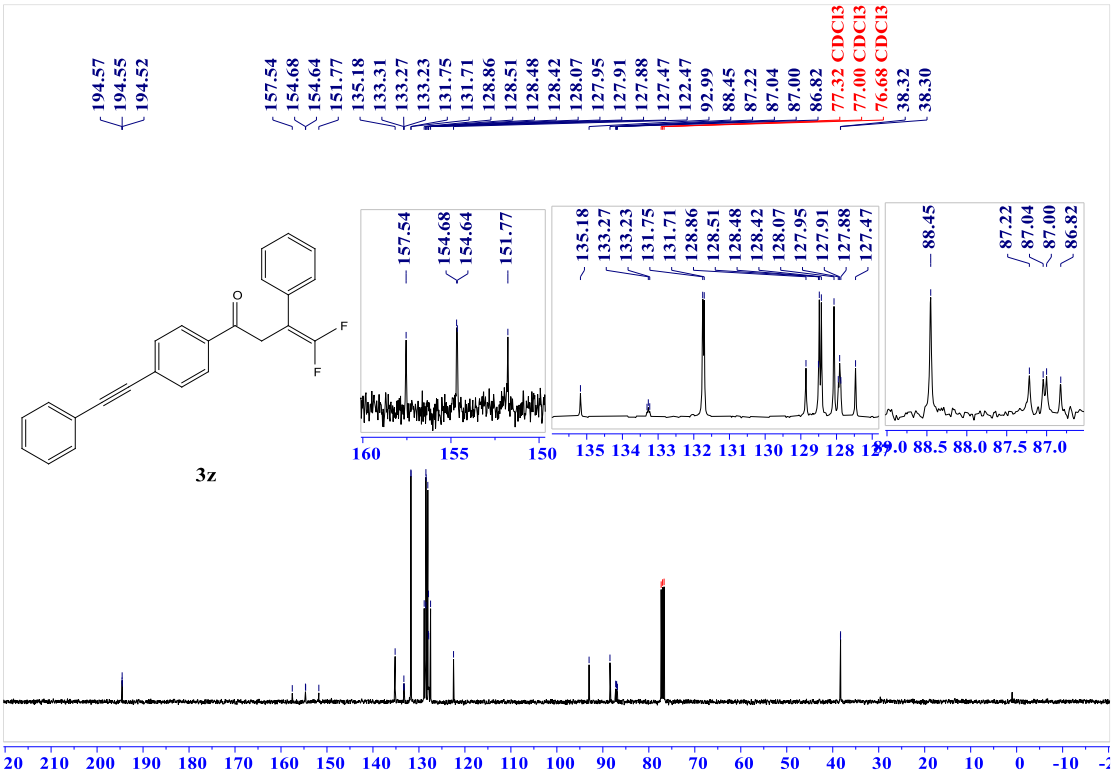
3y


3z


3z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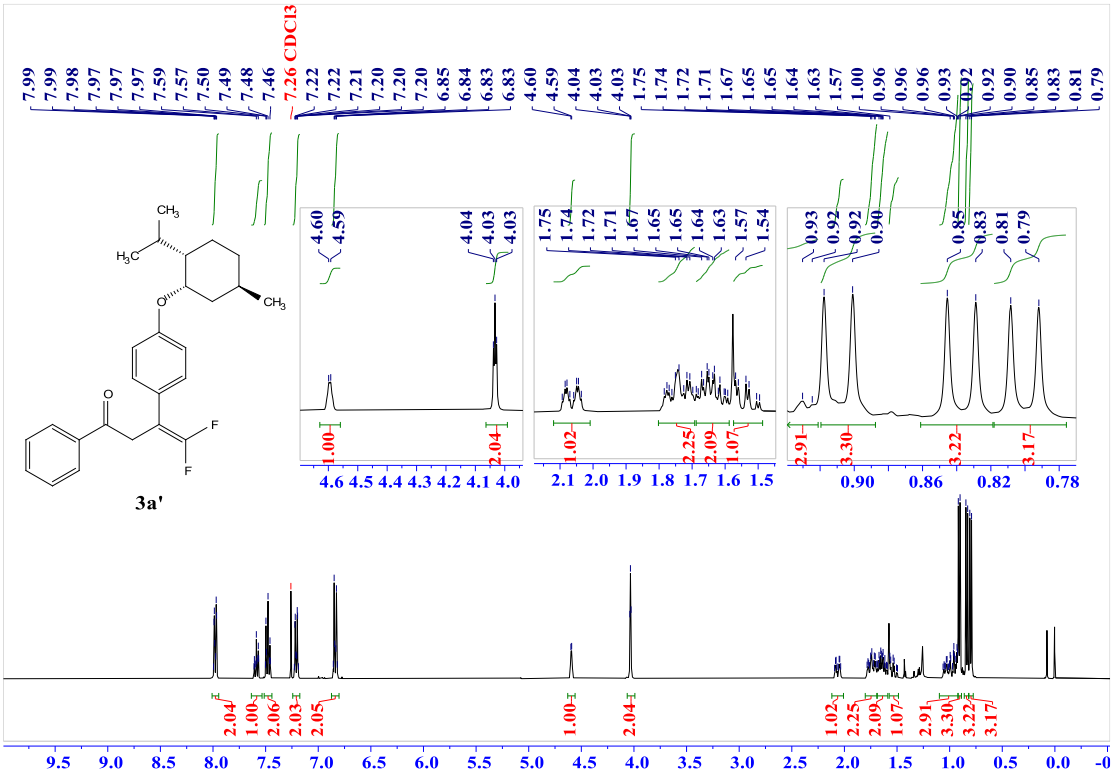
133.27
133.23
131.75
131.71
128.86
128.51
128.48
128.42
128.07
127.95
127.91
127.88
127.47
122.47
92.99
88.45
87.22
87.04
87.00
86.82
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.32
38.30
O
F
F
3z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7.98
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7.97
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7.57
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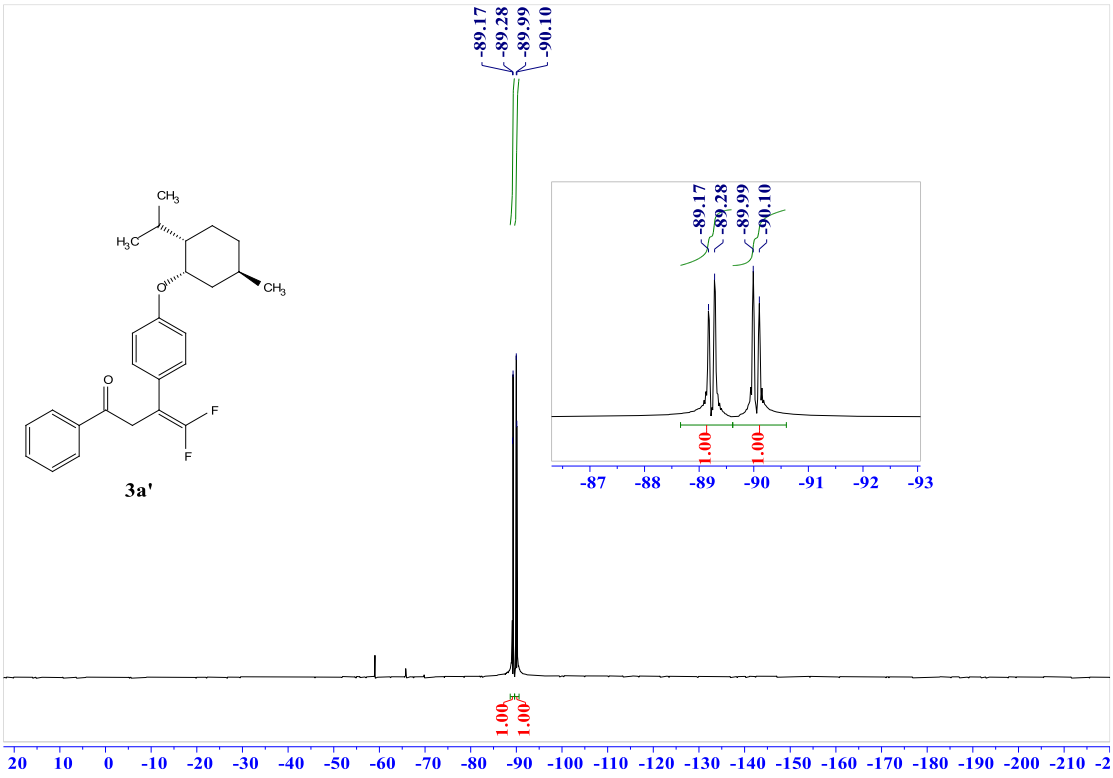
7.49
7.48
7.46
7.26 CDCl3
7.22
7.22
7.21
7.20
7.20
7.20
6.85
6.84
6.83
6.83
4.60
4.59
4.04
4.03
4.03
1.75
1.74
1.72
1.71
1.67
1.65
1.65
1.64
1.63
1.57
1.54
1.00
0.96
0.96
0.96
0.93
0.92
0.92
0.90
0.85
0.83
0.81
0.79
CH3
H3C
CH3
O
O
F
F
3a'
2.04
1.00
2.06
2.03
2.05
1.00
2.04
1.02
2.25
2.09
1.07
2.91
3.30
3.22
3.17


-89.17
-89.28
-89.99
-90.10
3a'
1.00
1.00
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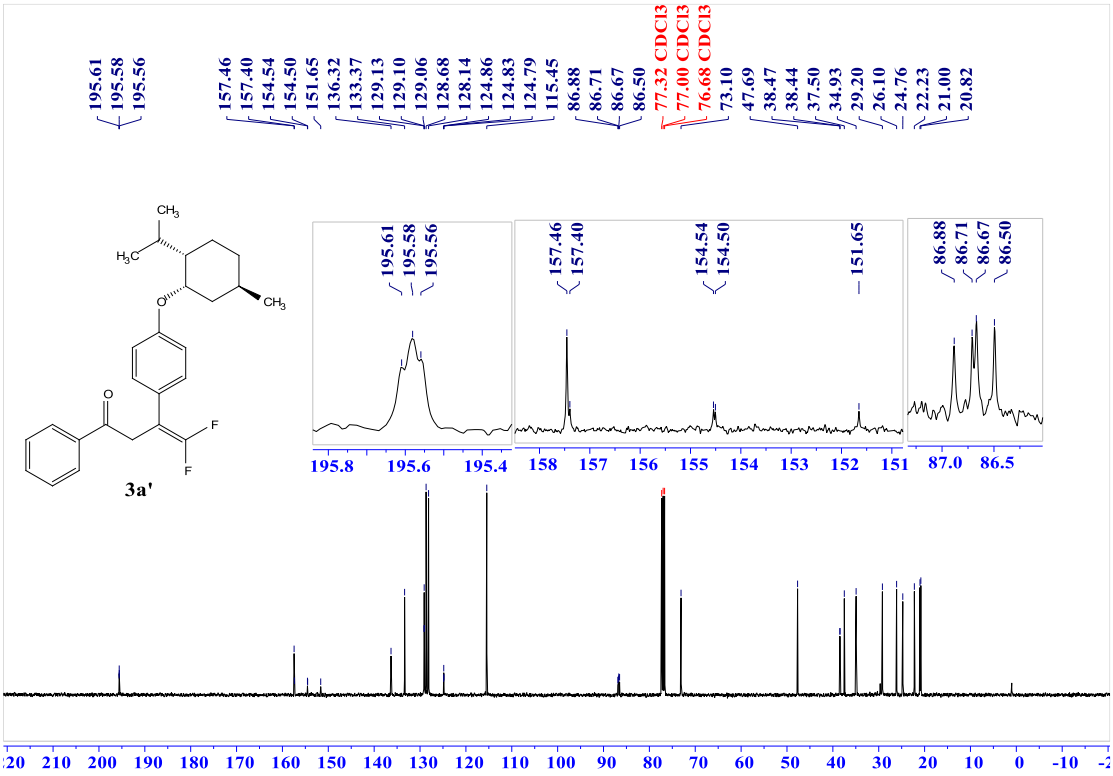
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195.56
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154.50
151.65
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133.37
129.13
129.10
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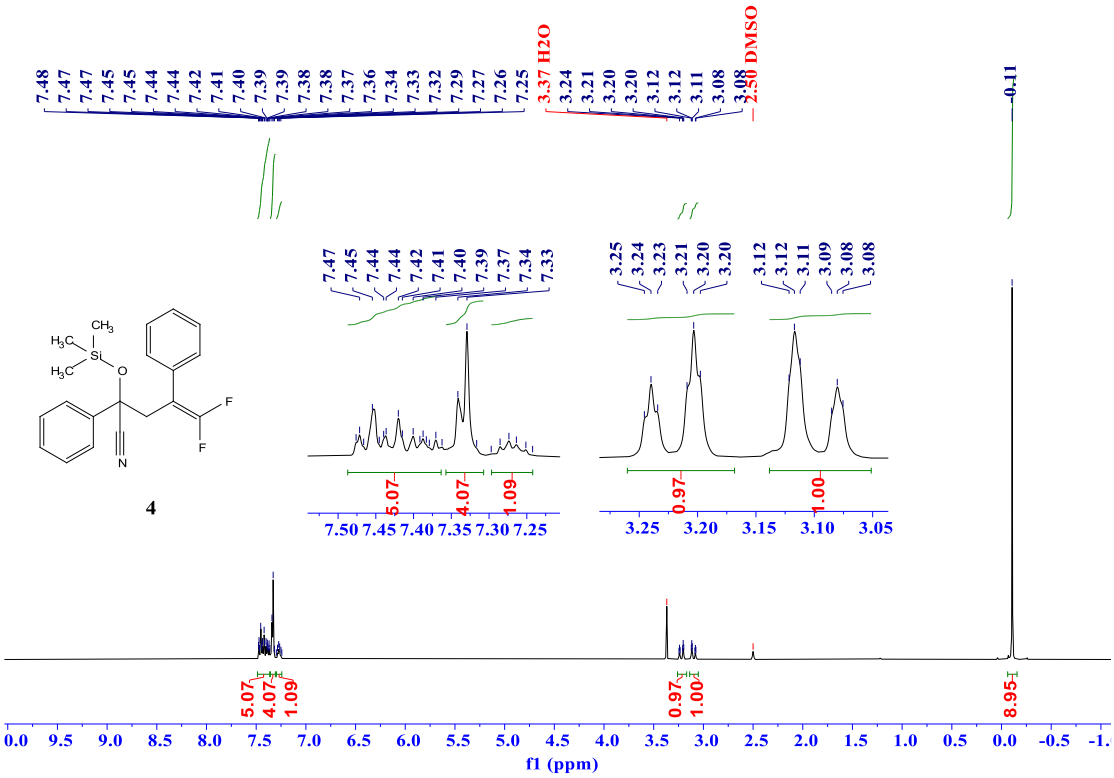
128.68
128.14
124.86
124.83
124.79
115.45
86.88
86.71
86.67
86.50
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.10
47.69
38.47
38.44
37.50
34.93
29.20
26.10
24.76
22.23
21.00
20.82
3a'
195.8 195.6 195.4
158 157 156 155 154 153 152 151
87.0 86.5
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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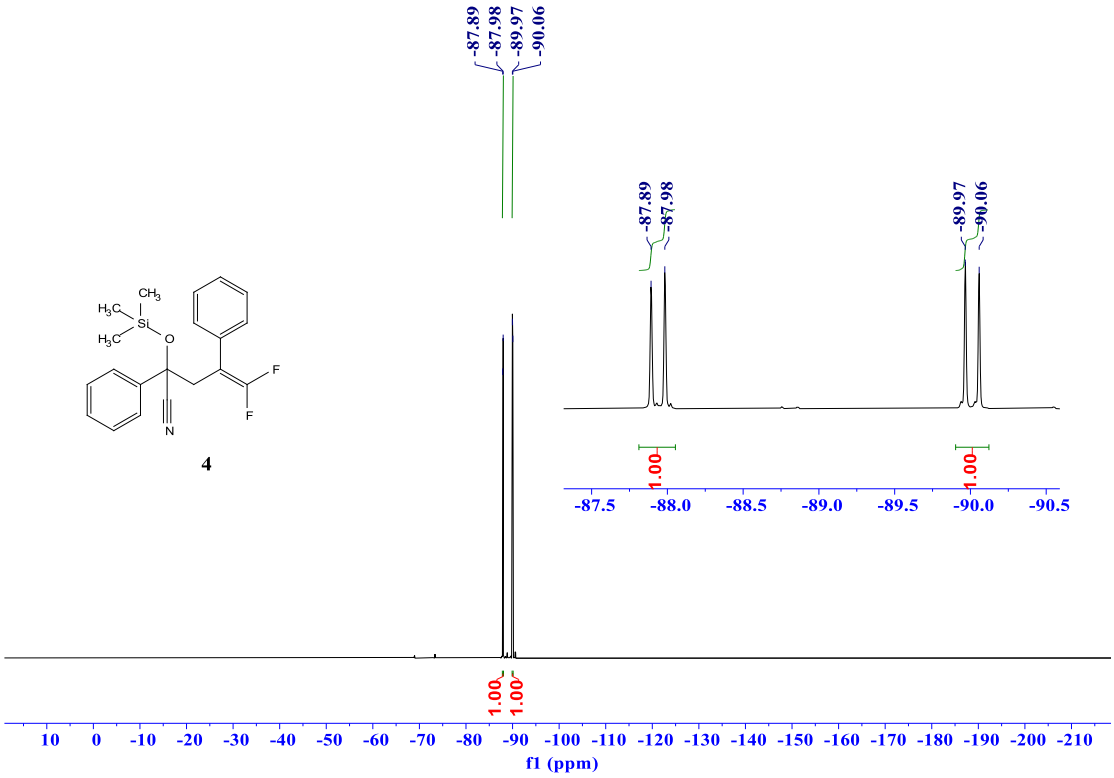
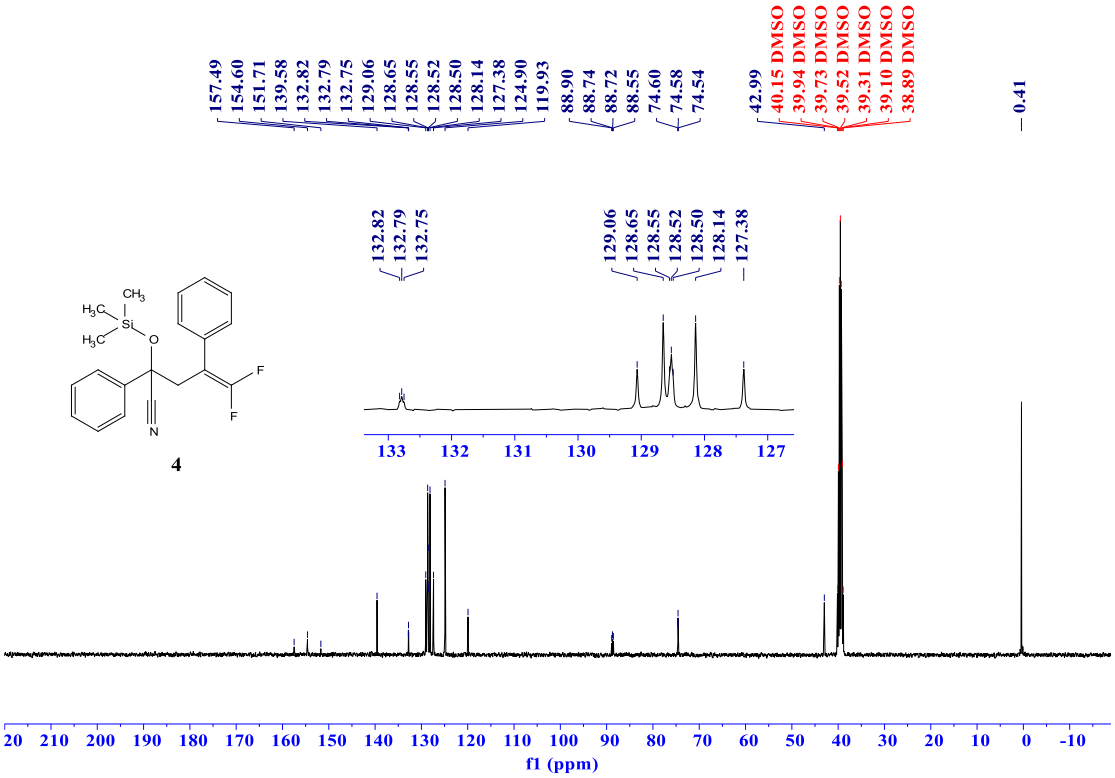
3.37 H2O
3.24 3.21 3.20 3.20 3.12 3.12 3.11 3.08 3.08
2.50 DMSO
-0.11
7.47 7.45 7.44 7.44 7.42 7.41 7.40 7.39 7.37 7.34 7.33
3.25 3.24 3.23 3.21 3.20 3.20 3.12 3.12 3.11 3.09 3.08 3.08
4
5.07 4.07 1.09
0.97 1.00
8.95
f1 (ppm)


-87.89 -87.98 -89.97 -90.06
4
1.00 1.00
f1 (ppm)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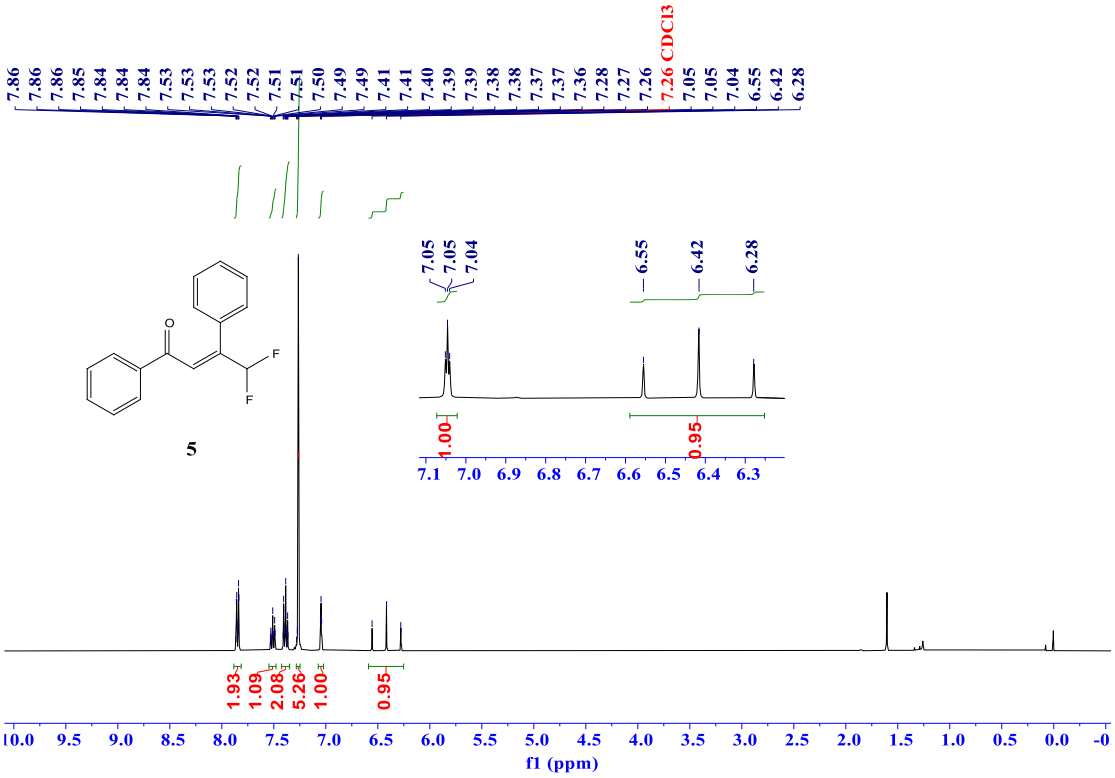
154.60
151.71
139.58
132.82
132.79
132.75
129.06
128.65
128.55
128.52
128.50
128.14
127.38
124.90
119.93
88.90
88.74
88.72
88.55
74.60
74.58
74.54
42.99
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
0.41
4
f1 (ppm)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7.86
7.86
7.85
7.84
7.84
7.84
7.53
7.53
7.53
7.52
7.52
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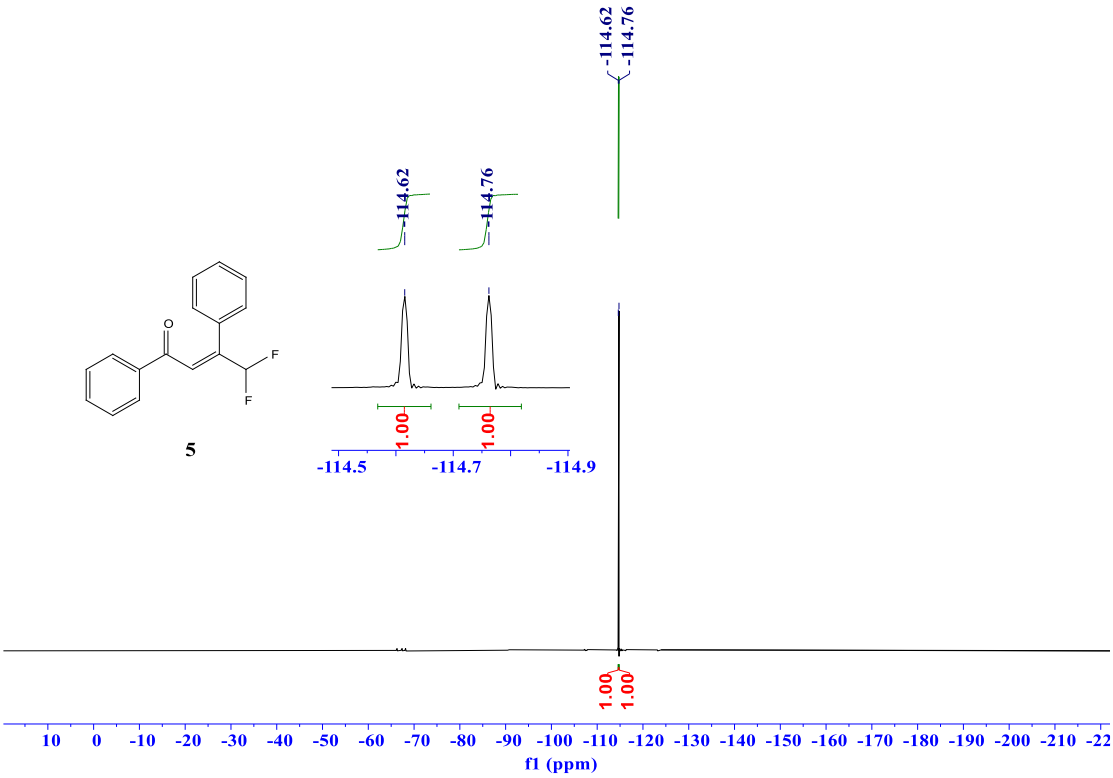
7.51
7.50
7.49
7.49
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.28
7.27
7.26 CDCl3
7.05
7.05
7.04
6.55
6.42
6.28
1.93
1.09
2.08
5.26
1.00
0.95
5
f1 (ppm)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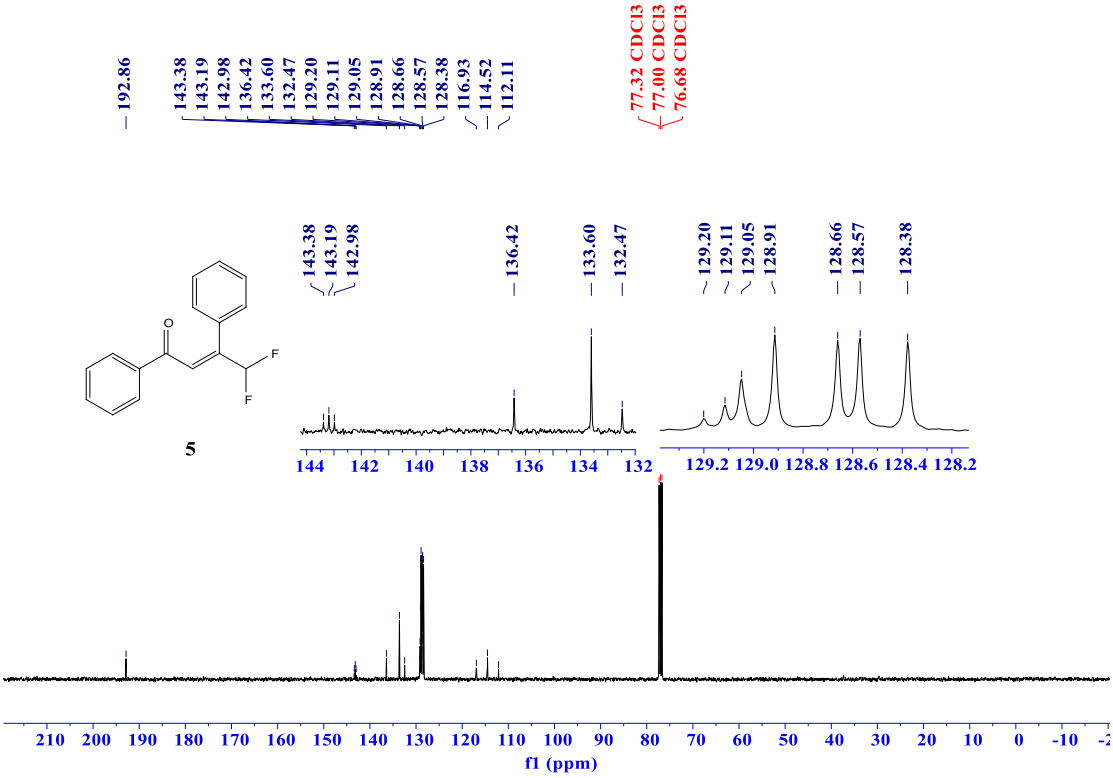
-114.76
-114.62
-114.76
1.00
1.00
-114.5
-114.7
-114.9
O
F
F
5
1.00
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)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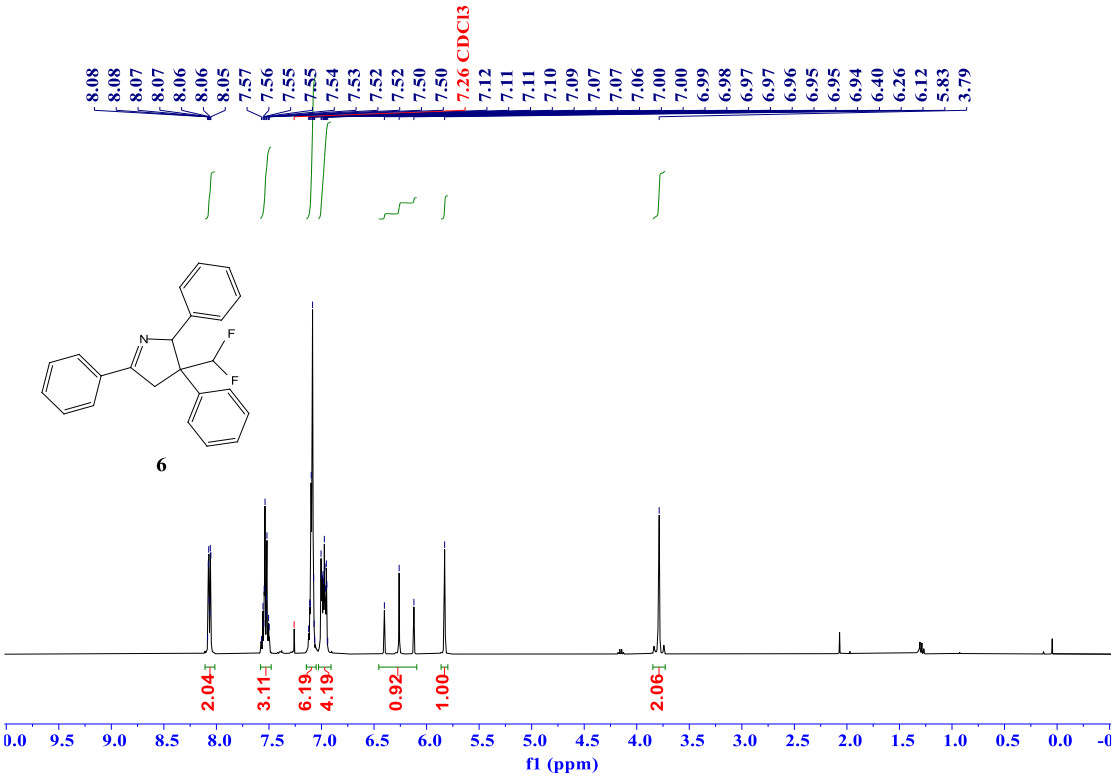
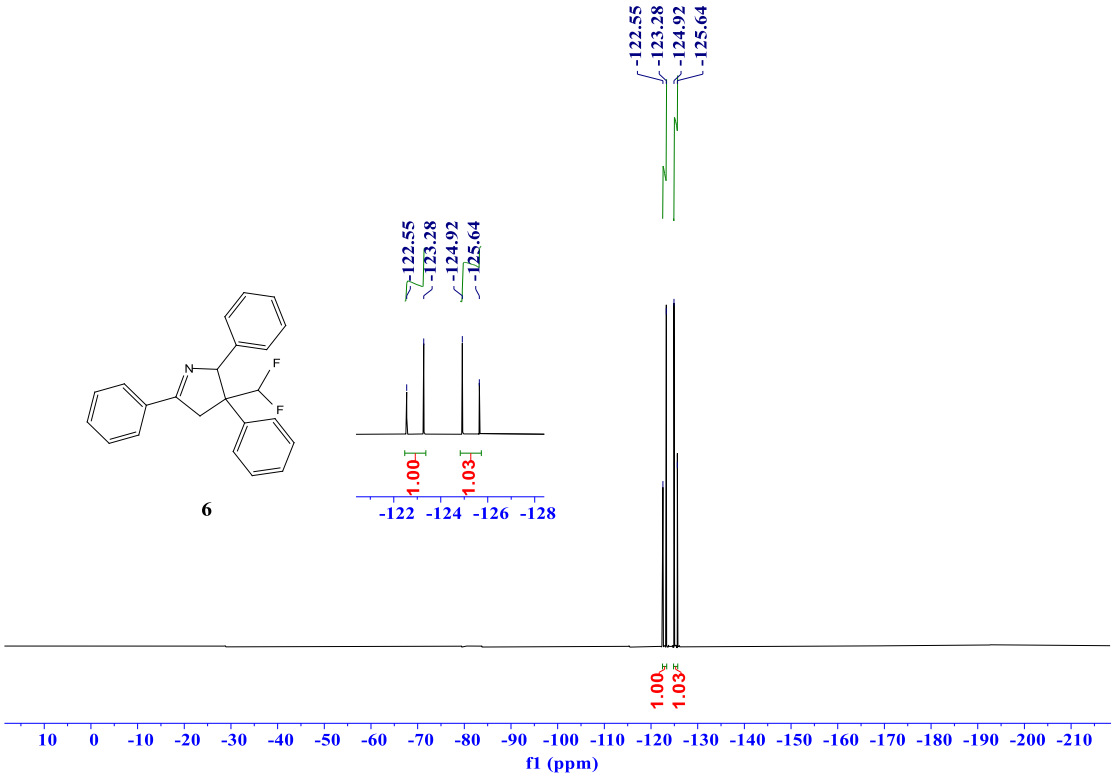
143.19
142.98
136.42
133.60
132.47
129.20
129.11
129.05
128.91
128.66
128.57
128.38
116.93
114.52
112.11
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
143.38
143.19
142.98
136.42
133.60
132.47
129.20
129.11
129.05
128.91
128.66
128.57
128.38
O
F
F
5
144 142 140 138 136 134 132
129.2 129.0 128.8 128.6 128.4 128.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.08 8.08 8.07 8.07 8.06 8.06 8.05 7.57 7.56 7.55 7.55 7.54 7.53 7.52 7.52 7.50 7.50 7.26 CDCl3 7.12 7.11 7.11 7.10 7.09 7.07 7.07 7.06 7.00 7.00 6.99 6.98 6.97 6.97 6.96 6.95 6.95 6.94 6.40 6.26 6.12 5.83 3.79
N
F
F
6
2.04 3.11 6.19 4.19 0.92 1.00 2.06
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-122.55 -123.28 -124.92 -125.64
N
F
F
6
1.00 1.03
-122 -124 -126 -128
1.00 1.03
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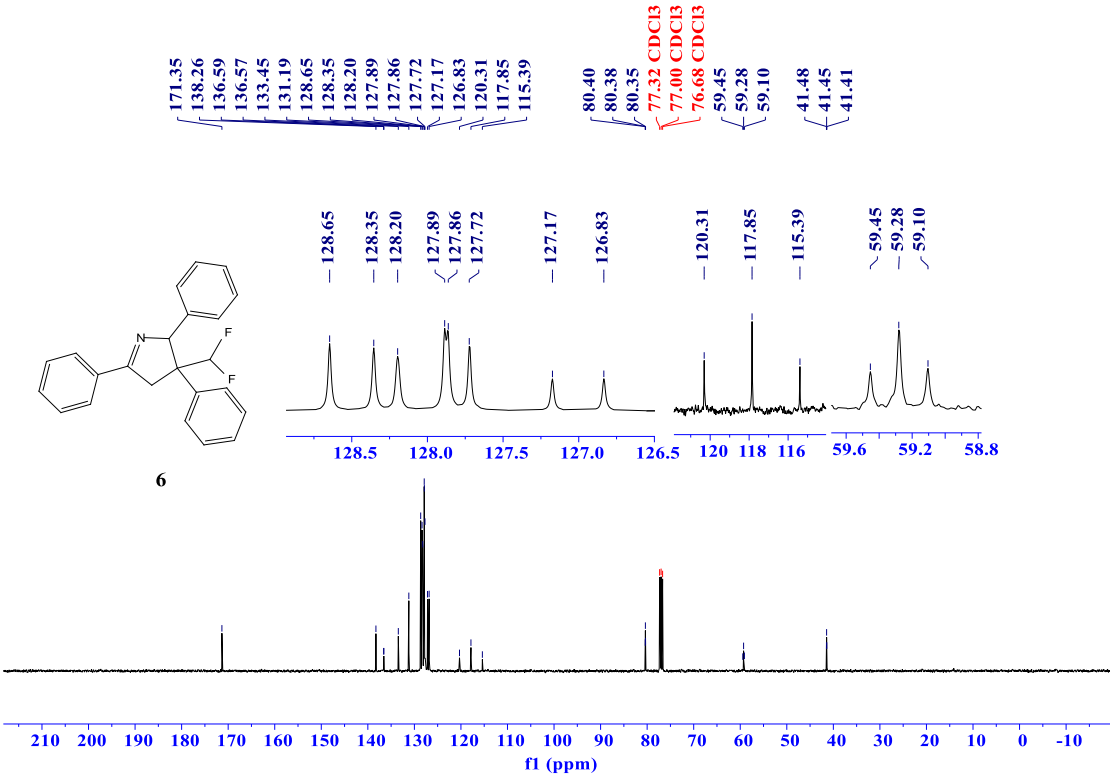
f1 (ppm)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128.35
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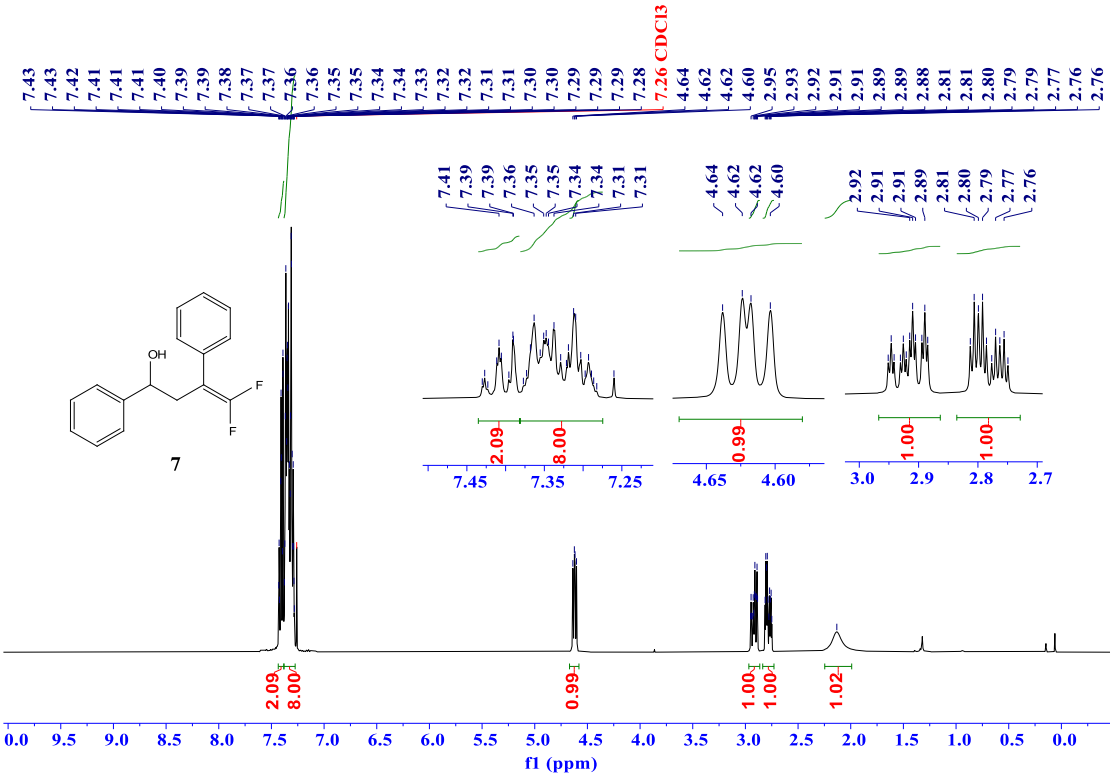
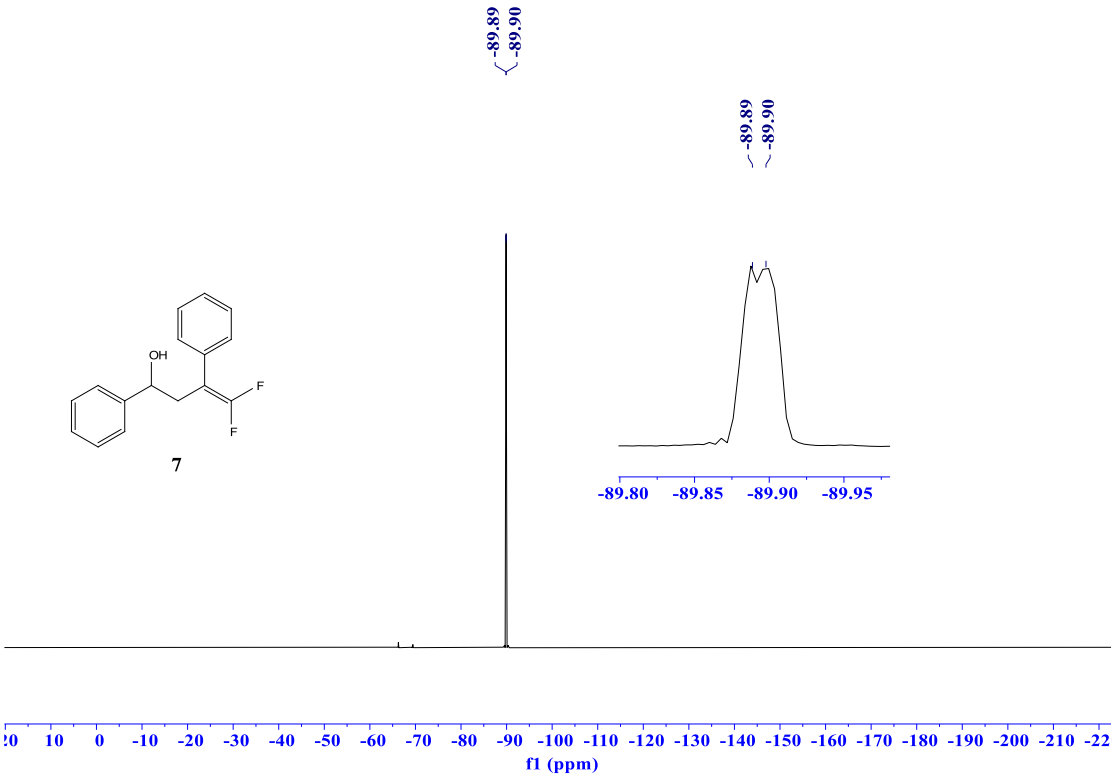
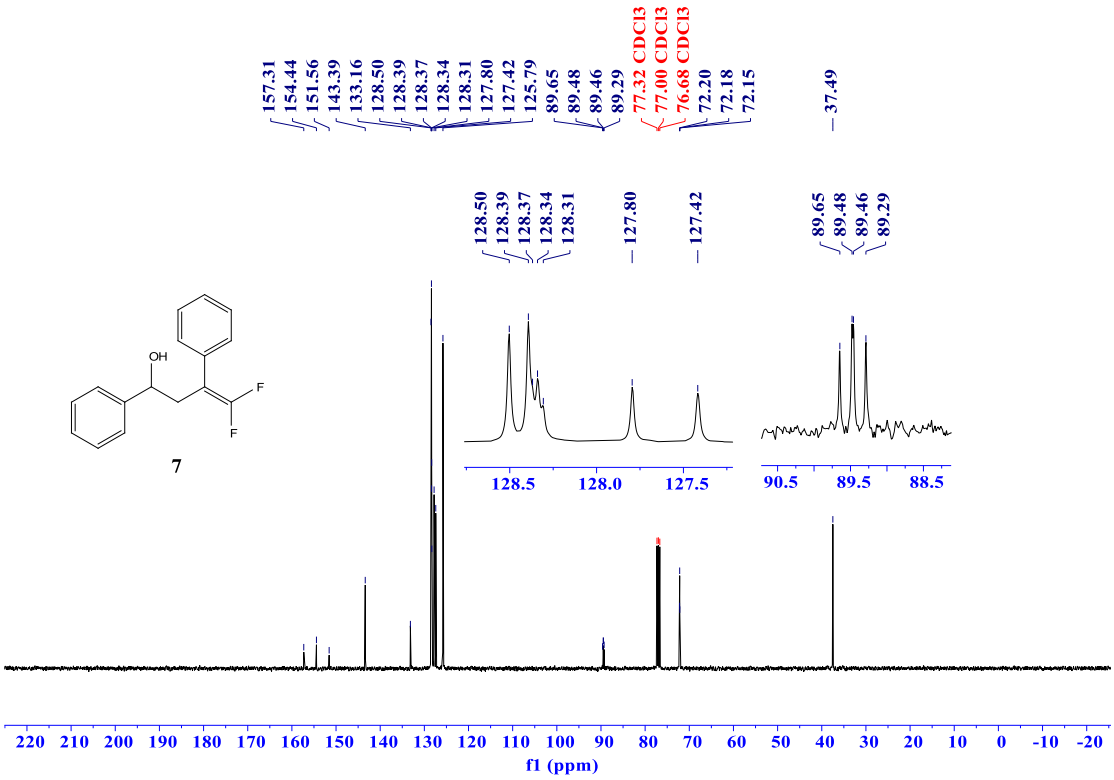
127.89
127.86
127.72
127.17
126.83
120.31
117.85
115.39
80.40
80.38
80.35
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
59.45
59.28
59.10
41.48
41.45
41.41
N
F
F
6
f1 (ppm)


7.26 CDCl3
OH
F
F
7
2.09
8.00
0.99
1.00
1.00
1.02
f1 (ppm)


-89.89
-89.90
-89.89
-89.90
OH
F
F
7
-89.80
-89.85
-89.90
-89.95
f1 (ppm)


157.31
154.44
151.56
143.39
133.16
128.50
128.39
128.37
128.34
128.31
127.80
127.42
125.79
89.65
89.48
89.46
89.29
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
72.20
72.18
72.15
37.49
128.50
128.39
128.37
128.34
128.31
127.80
127.42
89.65
89.48
89.46
89.29
OH
F
F
7
128.5
128.0
127.5
90.5
89.5
88.5
f1 (ppm)