Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Halogen bond promoted aryl migration of allyl alcohols under visible light irradiation

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1. General information

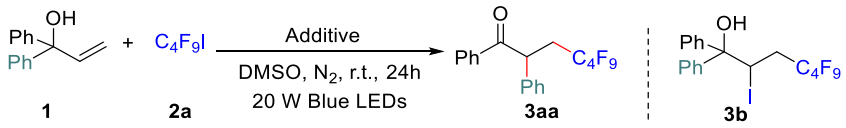
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance and JEOL III–400 spectrometer at 25 ^{o}C in solvents as indicated. Chemical shift values are reported in ppm with the solvent resonance refereed to the standard position ($CDCl_3$: ^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.16$). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and dd, doublet of doublets. The coupling constants *J* are reported in Hertz (Hz). HRMS were obtained on a QTOF micro spectrometer. Melting points were measured using open glass capillaries in SGW® X–4A apparatus.

All reactions were conducted in oven–dried Round bottom flask under an atmosphere of nitrogen. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Conversion of the reactions was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (230-400 mesh). All the allylic alcohols were prepared according to reported method.[1]

2. Optimization of the reaction conditions

2.1 Optimization of reaction conditions for perfluorobutyl iodide 2a

Table S1: Screening of the additives

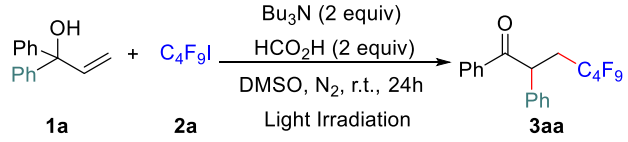


Entry [a]	Additive	Yield of **3aa** [b] (%)
1	Et_3N (2.0 equiv)	30
2	DIPEA (2.0 equiv)	35
3	Bu_3N (2.0 equiv)	73
4	Bu_3N (2.0 equiv) + HCOOH (2.0 equiv.)	82
5	HCOOH (2.0 equiv.)	26
6	_	NR

[a] All reactions were carried out with 1,1–diphenylprop–2–en–1–ol **1a** (0.1 mmol), perfluorobutyl iodide **2a** (0.2 mmol), and the additive as indicated in DMSO (2.0 mL) under N_2 at rt for 24 h. [b] Isolated yield. NR means no reaction occurred.

Note: For the reactions running under conditions indicated in entries 1-3, the atom transfer radical addition (ATRA) product **3b** was also formed as the main side-product. While only trace amount of **3b** was observed when the combination of Bu_3N and HCOOH were employed as the additive, and the yield was further improved to 82%. Control experiment revealed that additive was crucial to the transformation, since no reaction occurred when the reaction mixture was irradiated with blue LEDs without additives.

Table S2: Screening of light source

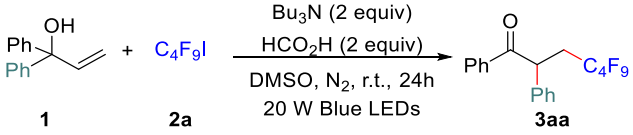


1a 2a 3aa

Entry [a]	Light source	Yield of **3aa** [b] (%)
1	10 W blue LEDs (465nm)	67
2	20 W blue LEDs (465 nm)	82
3	30 W blue LEDs (465nm)	58
4	30 W purple LEDs (390 nm)	58

[a] All reactions were carried out with 1,1–diphenylprop–2–en–1–ol **1a** (0.1 mmol), perfluorobutyl iodide **2a** (0.2 mmol), Bu_3N (0.2 mmol), HCOOH (0.2mmol) in DMSO (2.0 mL) under N_2 at rt for 24 h. [b] Isolated yield.

Table S3: Control experiments



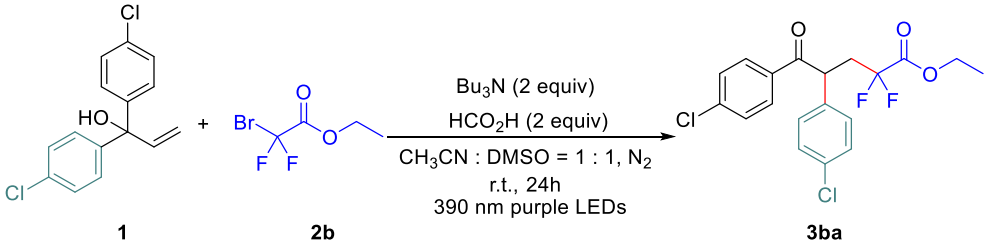
1 2a 3aa

Entry [a]	Variations of the reaction conditions	Yield of **3aa** [b] (%)
1	_	82
2	Without HCOOH	73
3	Without Bu_3N	26
4	HCOONa instead of Bu_3N/HCOOH	trace
5	No light	trace
6	With 20% Bu_3N/HCOOH	20

[a] All reactions were carried out with 1,1–diphenylprop–2–en–1–ol **1a** (0.1 mmol), perfluorobutyl iodide **2a** (0.2 mmol the additive as indicated in DMSO (2.0 mL) under N_2 at rt for 24 h. [b] Isolated yield.

2.2 Optimization of reaction conditions for ethyl 2–bromo–2,2–difluoroacetate 2b

Table S4: Screening of concentration

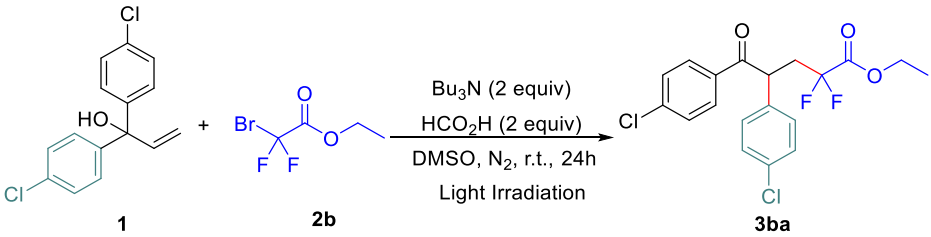


1 **2b** **3ba**

Entry [a]	Concentration (M)	Yield of **3ba** [b] (%)
1	0.1	51
2	0.2	54
3	0.05	75

[a] All reactions were carried out with 1,1–bis(4–chlorophenyl)prop–2–en–1–ol **1c** (0.1 mmol), ethyl 2–bromo–2,2–difluoroacetate **2b** (0.2 mmol), Bu_3N (0.2 mmol), HCOOH (0.2mmol) in MeCN/DMSO (1:1, v/v) (2.0 mL) under N_2 at rt for 24 h. [b] Isolated yield.

Table S5: Screening of light source

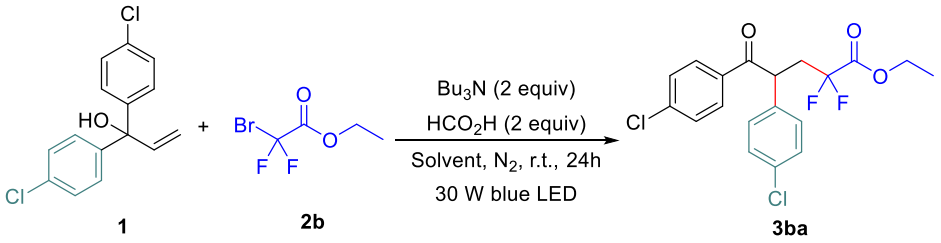


1 **2b** **3ba**

Entry [a]	Light source	Yield of **3ba** [b] (%)
1	30 W blue LEDs	88
2	10 W blue LEDs	76
3	20 W blue LEDs	88

[a] All reactions were carried out with 1,1–bis(4–chlorophenyl)prop–2–en–1–ol **1c** (0.1 mmol), ethyl 2–bromo–2,2–difluoroacetate **2b** (0.2 mmol), Bu_3N (0.2 mmol), HCOOH (0.2mmol) in DMSO (2.0 mL) under N_2 at rt for 24 h. [b] Isolated yield.

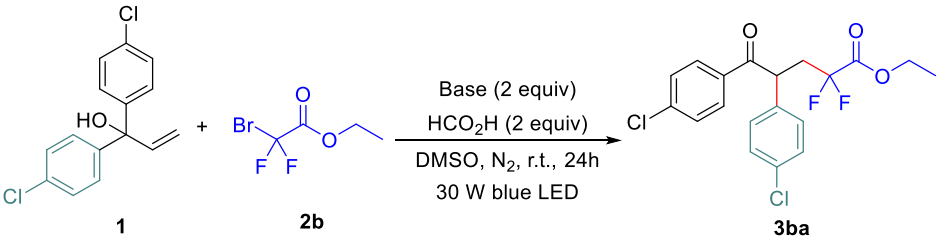
Table S6: Screening of the solvents



Entry [a]	Solvent	Yield of **3ba** [b] (%)
1	DMSO	88
2	CH_3CN	55

[a] All reactions were carried out with 1,1–bis(4–chlorophenyl)prop–2–en–1–ol **1c** (0.1 mmol), ethyl 2–bromo–2,2–difluoroacetate **2b** (0.2 mmol), Bu_3N (0.2 mmol), HCOOH (0.2mmol) in Solvent (2.0 mL) under N_2 at rt for 24 h. [b] Isolated yield.

Table S7: Screening of the base



Entry [a]	Base (2.0 equiv)	Yield of **3ba** [b] (%)
1	Et_3N	67
2	DIPEA	57
3	Bu_3N	88

[a] All reactions were carried out with 1,1–bis(4–chlorophenyl)prop–2–en–1–ol **1c** (0.1 mmol), ethyl 2–bromo–2,2–difluoroacetate **2b** (0.2 mmol), base (0.2 mmol), HCOOH (0.2mmol) in DMSO (2.0 mL) under N_2 at rt for 24 h. [b] Isolated yield.

3. General procedure

General procedure for the preparation of allyl alcohols

Following the reported procedure,[1] to a solution of aldehyde/ketone (5 mmol) in dry THF was added vinylmagnesium bromide (1 M in THF, 1.2 equiv.) under nitrogen atmosphere by a syringe over 5 min at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for additional 3 hours. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with a saturated NH_4Cl aqueous solution (20 mL) and extracted with ethyl acetate (3×70 mL). The combined organic layer was washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduce pressure

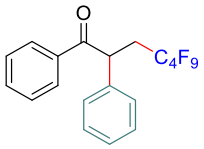
to give the crude allylic alcohols which was purified by a flash chromatograph (PE/EA) on silica gel with petroleum ether/ethyl acetate mixture as eluent to afford the corresponding pure products. The NMR data were consistent with the reported reference.

General procedure for the synthesis of aryl migration products

A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with α,α–diaryl allylic alcohols (1, 0.1 mol). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of perfluorobutyl iodide **2a** (0.2 mmol, 34.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 20 W blue LEDs light irradiation with a water chiller to maintain the temperature at 25 °C. After 24 hours, the reaction was then quenched with satd. NH_4Cl solution (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was concentrated, the crude residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate mixture as eluent to give the corresponding products.

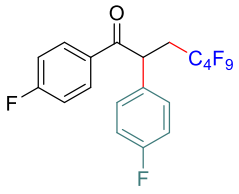
4. Characterization of products

4,4,5,5,6,6,7,7,7–Nonafluoro–1,2–diphenylheptan–1–one (3aa)



82% yield, 35.1 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.55 – 7.51 (m, 1H), 7.43 (t, J_1 = 7.5 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.29 – 7.25 (m, 1H), 5.05 (dd, J_1 = 8.4 Hz, J_2 = 4.2 Hz, 1H), 3.54 – 3.39 (m, 1H), 2.53 – 2.38 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 81.0 to − 81.1 (m, 3F), − 111.8 to − 113.9 (m, 2F), − 124.3 to − 124.4 (m, 2F), − 125.9 to − 126.1 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 137.8, 135.7, 133.5, 129.6, 129.0, 128.8, 128.2, 128.0, 45.7, 34.4 (t, J_{C-F} = 26.0 Hz); The spectra data are consistent with the reported reference.[2]

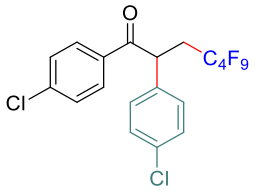
4,4,5,5,6,6,7,7,7–Nonafluoro–1,2–bis(4–fluorophenyl)heptan–1–one (3ab)



35% yield, 16.3 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.30 – 7.26 (m, 2H), 7.12 – 7.07 (m, 2H), 7.04 – 7.00 (m, 2H), 4.97 (dd, J_1 = 8.2 Hz, J_2 = 4.6 Hz, 1H), 3.46 – 3.31 (m, 1H), 2.50 – 2.35 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 81.0 to − 81.1 (m, 3F), − 103.9 to − 104.0 (m, 2F), − 113.6 to − 113.7 (m, 2F), − 124.4 to − 124.5 (m, 2F), − 125.9 to − 126.0 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 166.0 (d, J_{C-F} = 254.7 Hz), 162.5 (d, J_{C-F} = 246.5 Hz), 133.3 (d, J_{C-F} = 3.6 Hz), 131.9 (d, J_{C-F} = 3.5 Hz), 131.6 (d, J_{C-F} = 9.6 Hz), 129.8 (d, J_{C-F} = 8.4 Hz), 116.7 (d, J_{C-F} = 21.6 Hz),

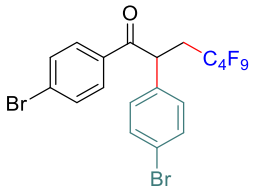
116.1 (d, J_{C-F} = 21.9 Hz), 44.9, 34.5 (t, J_{C-F} = 22.1 Hz); The spectra data are consistent with the reported reference.[2]

1,2–Bis(4–chlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluoroheptan–1–one (3ac)



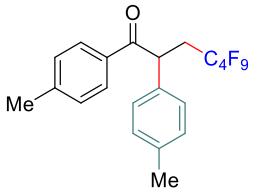
83% yield, 41.3 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.41 – 7.38 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 2H), 4.95 (dd, J_1 = 8.4 Hz, J_2 = 4.6 Hz, 1H), 3.46 – 3.31 (m, 1H), 2.50 – 2.36 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 81.0 (t, J = 9.5, 3F), − 111.6 to − 114.0 (m, 2F), − 124.3(9) to − 124.4(3) (m, 2F), − 125.9 to − 126.0 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 140.4, 135.8, 134.3, 133.7, 130.3, 129.9, 129.5, 129.3, 45.1, 34.3 (t, J_{C-F} = 20.8 Hz); The spectra data are consistent with the reported reference.[2]

1,2–Bis(4–bromophenyl)–4,4,5,5,6,6,7,7,7–nonafluoroheptan–1–one (3ad)



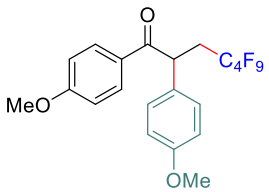
58% yield, 34.0 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.58 – 7.55 (m, 2H), 7.47 – 7.44 (m, 2H), 7.19 – 7.15 (m, 2H), 4.92 (dd, J_1 = 8.0 Hz, J_2 = 4.6 Hz, 1H), 3.45 – 3.30 (m, 1H), 2.50 – 2.35 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 80.9(7) to − 81.0(2) (m, 3F), − 111.5 to − 113.9 (m, 2F), − 124.3 to − 124.4 (m, 2F), − 125.9 to − 126.0 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 136.3, 134.1, 132.9, 132.3, 130.4, 129.8, 129.2, 122.4, 45.2, 34.2 (t, J_{C-F} = 20.6 Hz); The spectra data are consistent with the reported reference.[2]

4,4,5,5,6,6,7,7,7–Nonafluoro–1,2–di–p–tolylheptan–1–one (3ae)



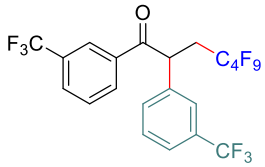
69% yield, 31.7 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.22 – 7.19 (m, 4H), 7.13 – 7.10 (m, 2H), 4.99 (dd, J_1 = 8.3 Hz, J_2 = 4.2 Hz, 1H), 3.51 – 3.35 (m, 1H), 2.44 – 2.36 (m, 4H), 2.28 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 81.0 (t, J = 10.0, 3F), − 111.8 to − 114.1 (m, 2F), − 124.3 to − 124.5 (m, 2F), − 125.9 to − 126.0 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 144.4, 137.7, 135.0, 133.2, 130.2, 129.5, 129.1, 128.0, 45.1, 34.4 (t, J_{C-F} = 20.2 Hz), 21.8, 21.1; The spectra data are consistent with the reported reference.[2]

4,4,5,5,6,6,7,7,7–Nonafluoro–1,2–bis(4–methoxyphenyl)heptan–1–one (3af)



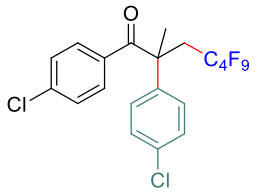
31% yield, 15.1 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.25 – 7.21 (m, 2H), 6.90 – 6.80 (m, 4H), 4.94 (dd, J_1 = 8.2 Hz, J_2 = 4.4 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.47 – 3.31 (m, 1H), 2.47 – 2.33 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 81.0 to − 81.1 (m, 3F), − 111.8 to − 114.1 (m, 2F), − 124.4 to − 124.5 (m, 2F), − 125.9 to − 126.0 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 163.8, 159.2, 131.3, 130.2, 129.2, 128.6, 114.9, 114.0, 55.6, 55.4, 44.5, 34.4 (t, J_{C-F} = 20.6 Hz); The spectra data are consistent with the reported reference.[2]

4,4,5,5,6,6,7,7,7–Nonafluoro–1,2–bis(4–(trifluoromethyl)phenyl)heptan–1–one (3ag)



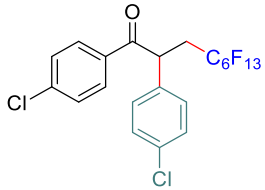
80% yield, 45.0 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.62 – 7.47 (m, 5H), 5.09 (dd, J_1 = 8.4 Hz, J_2 = 4.4 Hz, 1H), 3.54 – 3.38 (m, 1H), 2.56 – 2.42 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 62.8 (s, 3F), − 63.1 (s, 3F), − 81.1 (t, J_1 = 9.6 Hz, 3F), − 111.5 to − 113.7 (m, 2F), − 124.3 to − 124.4 (m, 2F), − 125.9 to − 126.0 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 138.0. 135.8, 132.3 (q, J_{C-F} =32.5), 131.9, 131.8 (q, J_{C-F} = 32.9), 131.5, 130.4 (q, J_{C-F} = 3.9), 130.3, 129.8, 126.5 (q, J_{C-F} = 245.2 Hz), 125.8 (q, J_{C-F} = 3.9 Hz), 125.4 (q, J_{C-F} = 3.7 Hz), 125.0 (q, J_{C-F} = 3.8 Hz), 123.8 (q, J_{C-F} = 270.8 Hz), 123.6 (d, J_{C-F} = 278.9 Hz), 45.7, 34.5 (t, J_{C-F} = 20.7 Hz); HRMS (ESI) m/z calcd for $C_{21}H_{12}F_{15}O^+$ $[M + H]^+$ m/z 565.0643, found m/z 565.0607.

1,2–Bis(4–chlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluoro–2–methylheptan–1–one (3ah)



41% yield, 21.2 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.30 – 7.27 (m, 4H), 7.25 – 7.20 (m, 2H), 3.10 – 2.97 (m, 1H), 2.73 – 2.59 (m, 1H), 1.86 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 81.1 (t, J = 9.8 Hz, 3F), − 107.4 to − 111.3 (m, 2F), − 124.6 (s, 2F), − 125.7 to − 125.8 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 139.5 138.7, 134.3, 134.0, 130.9, 129.8, 128.7, 127.8, 52.1, 39.7 (t, J_{C-F} = 18.3 Hz), 22.5; The spectra data are consistent with the reported reference.[2]

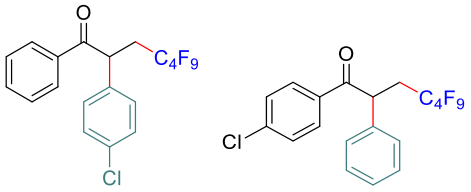
1,2–Bis(4–chlorophenyl)–4,4,5,5,6,6,7,7,8,8,9,9,9–tridecafluorononan–1–one (3ai)



53% yield, 31.1 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.41 – 7.39 (m, 2H), 7.33 – 7.22 (m, 4H), 4.94 (dd, J_1 = 8.1 Hz, J_2 = 4.6 Hz, 1H), 3.46 – 3.31 (m, 1H), 2.50 – 2.36 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 80.6 to − 80.7 (m, 3F), − 111.2 to − 113.6 (m, 2F), − 121.6(6) to − 121.7(5) (m, 2F), − 121.8 (s, 2F), − 123.3 to − 123.4 (m, 2F), − 126.0 to − 126.1 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 140.4, 135.9, 134.3, 133.7, 130.3, 129.9, 129.5, 129.3, 45.1, 34.4 (t, J_{C-F} = 19.3 Hz); HRMS (ESI) m/z calcd for $C_{21}H_{12}{}^{35}Cl_2F_{13}O^+$ $[M + H]^+$ m/z 597.0052, found m/z 597.0066.

2–(4–Chlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluoro–1–phenylheptan–1–one (3aj)

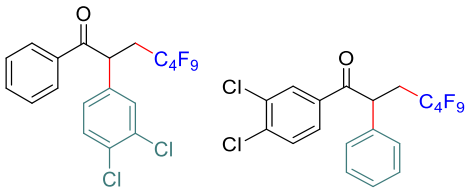
1–(4–Chlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluoro–2–phenylheptan–1–one (3aj')



69% yield, 30.5 mg; **3i/3i'** = 3 : 1; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer 7.96 – 7.94 (m, 2H), 7.56 – 7.52 (m, 1H), 7.45 – 7.43 (overlapped, 1H), 7.41 – 7.37 (overlapped, 1H), 7.31 – 7.25 (overlapped, 4H), 5.02 (dd, J_1 = 8.0 Hz, J_2 = 4.7 Hz, 1H), 3.50 – 3.32 (overlapped, 1H), 2.51 – 2.37 (overlapped, 1H); minor isomer 7.92 – 7.89 (m, 2H), 7.45 – 7.43 (overlapped, 2H), 7.41 – 7.37 (overlapped, 1H), 7.31 – 7.25 (overlapped, 4H), 4.96 (dd, J_1 = 8.3 Hz, J_2 = 4.1 Hz, 1H), 3.50 – 3.32 (overlapped, 1H), 2.51 – 2.37 (overlapped, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ major isomer − 80.9 to − 81.0 (overlapped, 3F), − 111.5 to − 113.8 (overlapped, 2F), − 124.2 to − 124.3 (overlapped, 2F), − 125.8 to − 125.9 (overlapped, 2F); minor isomer − 80.9 to − 81.0 (overlapped, 3F), − 111.5 to − 113.8 (overlapped, 2F), − 124.2 to − 124.3 (overlapped, 2F), − 125.8 to − 125.9 (overlapped, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer 196.5, 136.2, 135.5, 134.1, 133.8, 129.8, 129.6, 129.0, 128.1, 45.0, 34.4 (overlapped, $J_{C–F}$ = 20.9 Hz); minor isomer 195.6, 140.1, 137.5, 134.0, 130.4, 129.7, 129.2, 128.8, 128.2, 45.8, 34.4 (overlapped, $J_{C–F}$ = 20.9 Hz); The spectra data are consistent with the reported reference.[2]

2–(3,4–Dichlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluoro–1–phenylheptan–1–one (3ak)

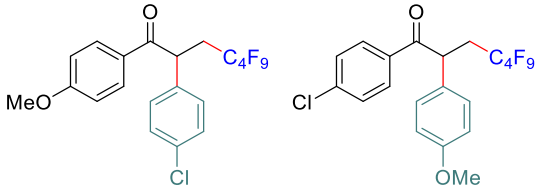
1–(3,4–Dichlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluoro–2–phenylheptan–1–one (3ak')



77% yield, 38.1 mg; **3j/3j'** = 6 : 1; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer 7.97 – 7.90 (m, 2H), 7.59 – 7.50 (m, 1H), 7.47 – 7.39 (overlapped, 4H), 7.20 – 7.17 (m, 1H), 5.00 (dd, J_1 = 8.0 Hz, J_2 = 4.7 Hz, 1H), 3.45 – 3.30 (overlapped, 1H), 2.52 – 2.38 (overlapped, 1H); minor isomer 8.04 (d, J_1 = 2.0 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.52 – 7.50 (m, 1H), 7.47 – 7.39 (overlapped, 4H), 7.30 – 7.29 (m, 1H), 4.91 (dd, J_1 = 8.5 Hz, J_2 = 4.1 Hz, 1H), 3.45 – 3.30 (overlapped, 1H), 2.52 – 2.38 (overlapped, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ major isomer − 80.9 to − 81.0 (overlapped, 3F), − 111.5 to − 113.8 (overlapped, 2F), − 124.2 to − 124.3 (overlapped, 2F), − 125.8 to − 126.0 (overlapped, 2F); minor isomer − 80.9 to − 81.0 (overlapped, 3F), − 111.5 to − 113.8 (overlapped, 2F), − 124.2 to − 124.3 (overlapped, 2F), − 125.8 to − 126.0 (overlapped, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer 196.1, 137.7, 135.2, 134.0, 133.7, 132.6, 131.5, 130.1, 129.1, 128.9, 127.5, 44.6, 34.4 (t, $J_{C–F}$ = 20.6 Hz); HRMS (ESI) m/z calcd for $C_{19}H_{12}{}^{35}Cl_2F_9O^+$ $[M + H]^+$ m/z 497.0116, found m/z 497.0123.

2–(4–Chlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluoro–1–(4–methoxyphenyl)heptan–1–one (3al)

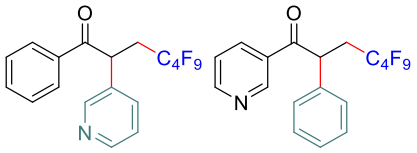
1–(4–Chlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluoro–2–(4–methoxyphenyl)heptan–1–one (3al')



43% yield, 21.4 mg, **3j**/**3j'** = 14 : 1; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer 7.96 – 7.91 (m, 2H), 7.30 – 7.25 (m, 4H), 6.91 – 6.88 (overlapped, 2H), 4.96 (dd, J_1 = 7.9 Hz, J_2 = 4.7 Hz, 1H), 3.84 (s, 1H), 3.45 – 3.30 (overlapped, 1H), 2.50 – 2.35 (overlapped, 1H); minor isomer 7.91 – 7.89 (m, 2H), 7.39 – 7.37 (m, 2H), 7.21 – 7.18 (m, 2H), 6.85 – 6.83 (m, 2H), 7.30 – 7.29 (m, 1H), 4.91 (dd, J_1 = 8.2 Hz, J_2 = 4.7 Hz, 1H), 3.76 (s, 1H), 3.45 – 3.30 (overlapped, 1H), 2.50 – 2.35 (overlapped, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ major isomer − 80.9(9) to − 81.0(4) (overlapped, 3F), − 111.6 to − 114.1 (overlapped, 2F), − 124.3(5) to − 124.4(3) (overlapped, 2F), − 125.9 to − 126.0 (overlapped, 2F); minor isomer − 80.9(9) to − 81.0(4) (overlapped, 3F), − 111.6 to − 114.1 (overlapped, 2F), − 124.3(5) to − 124.4(3) (overlapped, 2F), − 125.9 to − 126.0 (overlapped, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 164.0, 136.7, 133.9, 131.3, 129.7, 129.5, 128.3, 114.1, 55.6, 44.6, 34.3 (t, J_{C-F} = 20.5 Hz); HRMS (ESI) m/z calcd for $C_{20}H_{15}{}^{35}ClF_9O_2^+$ [M + H] $^+$ m/z 493.0611, found m/z 493.0610.

4,4,5,5,6,6,7,7,7–Nonafluoro–1–phenyl–2–(pyridin–2–yl)heptan–1–one (3am)

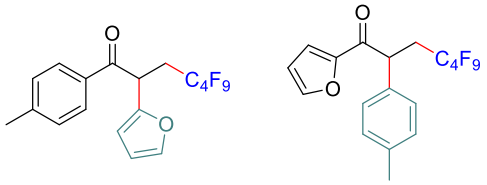
4,4,5,5,6,6,7,7,7–Nonafluoro–2–phenyl–1–(pyridin–3–yl)heptan–1–one (3am')



71% yield, 30.5 mg; **3i**/**3i'** = 3 : 1; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer 8.66 (d, J = 2.4 Hz, 1H), 8.52 – 8.50 (m, 1H), 7.78 – 7.75 (overlapped, 1H), 7.65 – 7.62 (m, 1H), 7.58 – 7.53 (m, 1H), 7.46 – 7.42 (m, 2H), 7.38 – 7.25 (overlapped, 2H), 5.09 (dd, J_1 = 8.2 Hz, J_2 = 5.0 Hz, 1H), 3.54 – 3.33 (overlapped, 1H), 2.56 – 2.39 (overlapped, 1H); minor isomer 9.18 (d, J = 1.7 Hz, 1H), 8.72 – 8.70 (m, 1H), 8.24 – 8.21 (overlapped, 1H), 7.98 – 7.95 (overlapped, 2H), 7.38 – 7.25 (overlapped, 4H), 4.97 (dd, J_1 = 8.4 Hz, J_2 = 4.0 Hz, 1H), 3.54 – 3.33 (overlapped, 1H), 2.56 – 2.39 (overlapped, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ major isomer − 81.0 (overlapped, J = 10.5 Hz, 3F), − 111.5 to − 113.8 (overlapped, 2F), − 124.3 to − 124.4 (overlapped, 2F), − 125.9 to − 126.0 (overlapped, 2F); minor isomer − 81.0 (overlapped, J = 10.5 Hz, 3F), − 111.5 to − 113.8 (overlapped, 2F), − 124.3 to − 124.4 (overlapped, 2F), − 125.9 to − 126.0 (overlapped, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer 196.2, 149.8, 149.4, 136.3, 135.3, 134.0, 129.8, 129.1 128.2, 124.3, 42.9, 34.3 (t, J_{C-F} = 20.4 Hz); minor isomer 195.7, 153.8, 150.2, 136.8, 135.1, 133.6, 131.1, 128.9, 128.4, 123.8, 46.3, 34.2 (t, J_{C-F} = 21.1 Hz); The spectra data are consistent with the reported reference.[2]

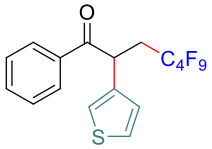
4,4,5,5,6,6,7,7,7-nonafluoro-2-(furan-2-yl)-1-(p-tolyl)heptan-1-one (3an)

4,4,5,5,6,6,7,7,7-nonafluoro-1-(furan-2-yl)-2-(p-tolyl)heptan-1-one (3an')



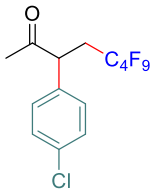
40% yield, 17.3 mg; **3an**/**3an'** = 10 : 1; yellow oil; specture date of the major one; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 2H), 7.33 – 7.32 (m, 1H), 7.26 – 7.23 (m, 2H), 6.27 – 6.26 (m, 1H), 6.15 – 6.14 (m, 1H), 5.14 (dd, J_1 = 7.8 Hz, J_2 = 5.0 Hz, 1H), 3.36 – 3.21 (m, 1H), 2.69 – 2.54 (m, 1H), 2.39 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 80.9 to − 81.0 (m, 3F), − 113.1 to − 113.4 (m, 2F), − 124.2(5) to − 124.3(3) (m, 2F), − 125.8 to − 125.9 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 150.3, 144.9, 142.8, 132.8, 129.6, 129.1, 111.1, 108.2, 39.2, 31.9 (t, J_{C-F} = 20.4 Hz), 21.8; HRMS (ESI) m/z calcd for $C_{18}H_{14}F_9O_2^+$ [M + H] $^+$ m/z 433.0839, found m/z 433.0835.

4,4,5,5,6,6,7,7,7–Nonafluoro–1–phenyl–2–(thiophen–3–yl)heptan–1–one (3ao)



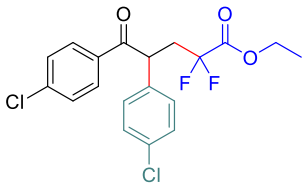
40% yield, 17.3 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 7.23 – 7.21 (m, 1H), 6.96 – 6.91 (m, 2H), 5.34 (dd, J_1 = 8.9 Hz, J_2 = 3.8 Hz, 1H), 3.55 – 3.40 (m, 1H), 2.62 – 2.48 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 80.9 to − 81.0 (m, 3F), − 112.7 to − 113.1 (m, 2F), − 124.3 to − 124.4 (m, 2F), − 125.9 to − 126.0 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 139.5, 135.3, 133.8, 129.2, 129.0, 127.6, 126.6, 126.1, 40.2, 35.1 (t, $J_{C–F}$ = 21.4 Hz); HRMS (ESI) m/z calcd for $C_{17}H_{12}F_9OS^+$ $[M + H]^+$ m/z 435.0460, found m/z 435.0431.

3–(4–Chlorophenyl)–5,5,6,6,7,7,8,8,8–nonafluorooctan–2–one (3ap)



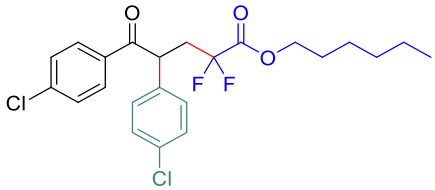
31% yield, 12.4 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.19 – 7.15 (m, 2H), 4.06 (dd, J_1 = 7.0 Hz, J_2 = 5.5 Hz, 1H), 3.27 – 3.11 (m, 1H), 2.35 – 2.12 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 80.9 (t, J = 10.2 Hz, 3F), − 111.5 to − 114.3 (m, 2F), − 124.3 to − 124.4 (m, 2F), 125.8 to − 125.9 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 135.7, 134.4, 129.8, 129.5, 50.7, 32.9 (t, $J_{C–F}$ = 20.4 Hz), 28.9; HRMS (ESI) m/z calcd for $C_{14}H_{10}{}^{35}ClF_9ONa^+$ $[M + Na]^+$ m/z 423.0169, found m/z 423.0109.

Ethyl 4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoate (3ba)



88% yield, 35.2 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87– 7.85 (m, 2H), 7.40 – 7.37 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.19 (m, 2H), 4.88 (dd, J_1 = 7.8 Hz, J_2 = 5.1 Hz, 1H), 4.24 – 4.07 (m, 2H), 3.30 – 3.15 (m, 1H), 2.55 – 2.42 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 104.9 to − 105.0 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 163.8 (t, $J_{C–F}$ = 32.0 Hz), 140.1, 136.1, 134.1 134.0, 130.3, 129.7 (two peaks overlapped), 129.2, 115.2 (t, $J_{C–F}$ = 249.5 Hz), 63.2, 46.3 (t, $J_{C–F}$ = 3.3 Hz), 38.1 (t, $J_{C–F}$ = 23.0 Hz), 13.9; The spectra data are consistent with the reported reference.[3]

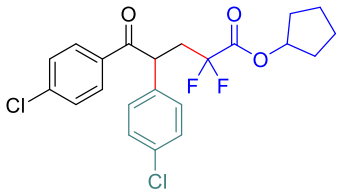
Hexyl 4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoate (3bb)



77% yield, 35.1 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.39 – 7.36 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 – 7.19 (m, 2H), 4.87 (dd, J_1 = 7.8 Hz, J_2 = 5.2 Hz, 1H), 4.16 − 3.99 (m, 2H), 3.29 – 3.15 (m, 1H), 2.55 – 2.42 (m, 1H), 1.65 – 1.54 (m, 2H), 1.34 – 1.22 (m, 7H), 0.90 – 0.86 (m, 2H);

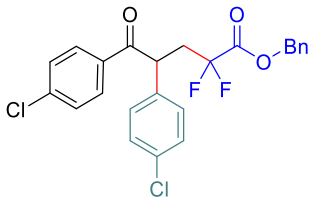
^{19}F NMR (376 MHz, $CDCl_3$) δ − 104.3 to − 104.4 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 163.8 (t, J_{C-F} = 31.8 Hz), 140.1, 136.1, 134.0, 133.9, 130.3, 129.7 (two peaks overlapped), 129.2, 115.2 (t, J_{C-F} = 249.6 Hz), 67.3, 46.3 (t, J_{C-F} = 3.6 Hz), 38.1 (t, J_{C-F} = 23.1 Hz), 31.4, 28.2, 25.4, 22.6, 14.1; HRMS (ESI) m/z calcd for $C_{23}H_{25}{}^{35}Cl_2F_2O_3^+$ $[M + H]^+$ m/z 457.1143, found m/z 457.1161.

Cyclopentyl 4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoate (3bc)



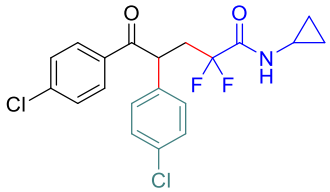
75% yield, 33.0 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.38 – 7.36 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 – 7.19 (m, 2H), 5.14 – 5.10 (m, 1H), 4.87 (dd, J_1 = 7.8 Hz, J_2 = 5.2 Hz, 1H), 3.27 – 3.13 (m, 1H), 2.53 – 2.40 (m, 1H), 1.88 – 1.54 (m, 8H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 104.3 to − 104.5 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 163.6 (t, J_{C-F} = 32.1 Hz), 140.1, 136.2, 134.0(1), 133.9(7), 130.3, 129.6 (two peaks overlapped), 129.2, 115.2 (t, J_{C-F} = 249.7 Hz), 80.7, 46.3 (t, J_{C-F} = 3.7 Hz), 38.0 (t, J_{C-F} = 23.1 Hz), 32.6, 32.5, 23.8, 23.7; HRMS (ESI) m/z calcd for $C_{22}H_{20}{}^{35}Cl_2F_2O_3Na^+$ $[M + Na]^+$ m/z 463.0650, found m/z 463.0655.

Benzyl 4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoate (3bd)



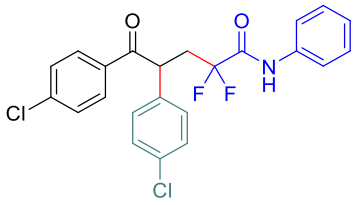
56% yield, 26.0 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.38 – 7.30 (m, 7H), 7.24 – 7.22 (m, 2H), 7.16 – 7.12 (m, 2H), 5.19 – 5.04 (m, 2H), 4.81 (dd, J_1 = 7.9 Hz, J_2 = 5.1 Hz, 1H), 3.30 – 3.16 (m, 1H), 2.55 – 2.42 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 104.1 (t, J = 16.3 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 163.6 (t, J_{C-F} = 32.9 Hz), 140.1, 136.0, 134.1, 134.0, 133.9, 130.3, 129.6(4), 129.6(0), 129.2, 129.0, 128.9, 128.7, 115.2 (t, J_{C-F} = 249.8 Hz), 68.6, 46.3 (t, J_{C-F} = 3.8 Hz), 38.1 (t, J_{C-F} = 23.1 Hz); HRMS (ESI) m/z calcd for $C_{24}H_{19}{}^{35}Cl_2F_2O_3^+$ $[M + H]^+$ m/z 463.0674, found m/z 463.0690.

4,5–Bis(4–chlorophenyl)–N–cyclopropyl–2,2–difluoro–5–oxopentanamide (3be)



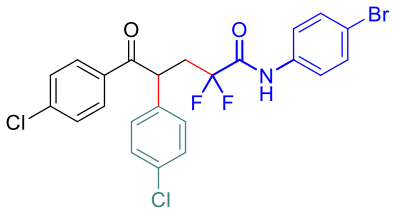
66% yield, 27.1 mg; white solid; mp. 133–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.24 (m, 2H), 7.22 – 7.18 (m, 2H), 6.34 (s, 1H), 4.99 (dd, J_1 = 8.4 Hz, J_2 = 4.4 Hz, 1H), 3.24 – 3.18 (m, 1H), 2.70 – 2.66 (m, 1H), 2.53 – 2.47 (m, 1H), 0.83 – 0.80 (m, 2H), 0.55 – 0.54 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 104.2 to − 104.3 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 165.1 (t, J_{C-F} = 28.1 Hz), 139.9, 136.4, 134.1, 133.8, 130.3, 129.6, 129.5, 129.1, 116.8 (t, J_{C-F} = 252.0 Hz), 46.2 (t, J_{C-F} = 3.6 Hz), 37.6 (t, J_{C-F} = 23.0 Hz), 22.6, 6.5(3), 6.5(1); HRMS (ESI) m/z calcd for $C_{20}H_{18}{}^{35}Cl_2F_2NO_2^+$ $[M + H]^+$ m/z 412.0677, found m/z 412.0671.

4,5–Bis(4–chlorophenyl)–2,2–difluoro–5–oxo–N–phenylpentanamide (3bf)



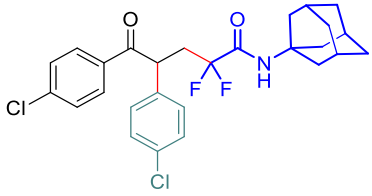
88% yield, 39.6 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 3H), 7.59 – 7.47 (m, 3H), 7.38 – 7.33 (m, 4H), 7.27 – 7.17 (m, 4H), 5.02 (dd, J_1 = 8.3 Hz, J_2 = 4.8 Hz, 1H), 3.39 – 3.24 (m, 1H), 2.71 – 2.58 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 103.5 (t, J = 16.8 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 161.6 (t, J = 28.0 Hz), 140.1, 136.2, 135.8, 134.1, 134.0, 130.3, 129.6(2), 129.6(0), 129.4, 129.2, 125.9, 120.4, 117.0 (t, J_{C-F} = 253.3 Hz), 46.3 (t, J_{C-F} = 3.7 Hz), 37.6 (t, J_{C-F} = 22.7 Hz); HRMS (ESI) m/z calcd for $C_{23}H_{18}{}^{35}Cl_2F_2NO_2^+$ [M + H]$^+$ m/z 448.0677, found m/z 448.0673.

***N*–(4–Bromophenyl)–4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanamide (3bg)**



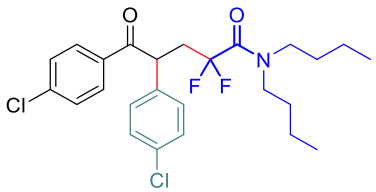
99% yield, 52.0 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.88 – 7.85 (m, 2H), 7.48 – 7.44 (m, 2H), 7.39 – 7.35 (m, 4H), 7.26 – 7.20 (m, 4H), 4.99 (dd, J_1 = 8.3 Hz, J_2 = 4.9 Hz, 1H), 3.37 – 3.23 (m, 5H), 2.70 – 2.56 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 104.9 to − 105.0 (m, 1F), − 105.2 – − 105.3 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 161.7 (t, J_{C-F} = 28.8 Hz), 140.1, 136.1, 134.9, 134.1, 134.0, 132.4, 130.3, 129.7, 129.6, 129.2, 121.9, 118.7, 116.9 (t, J_{C-F} = 253.7 Hz), 46.3, 37.6 (t, J_{C-F} = 23.3 Hz); HRMS (ESI) m/z calcd for $C_{23}H_{17}{}^{79}Br^{35}Cl_2F_2NO_2^+$ [M + H]$^+$ m/z 525.9782, found m/z 525.9785.

***N*–((3s,5s,7s)–Adamantan–1–yl)–4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanamide (3bh)**



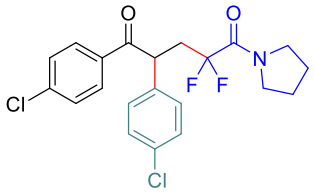
83% yield,42.0 mg; white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.24 (m, 2H), 7.22 – 7.20 (m, 2H), 5.90 (s, 1H), 4.97 (dd, J_1 = 8.3 Hz, J_2 = 4.4 Hz, 1H), 3.23 – 3.13 (m, 1H), 2.55 – 2.42 (m, 1H), 2.08 (s, 3H), 1.95 (d, J = 3.0, 6H), 1.67 (t, J = 3.1, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 103.6 to − 103.8 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 162.6 (t, J_{C-F} = 27.7 Hz), 139.9, 136.5, 134.3, 133.8, 130.3, 129.6, 129.5, 129.1, 116.7 (t, J_{C-F} = 253.3 Hz), 52.7, 46.3 (t, J_{C-F} = 3.8 Hz), 41.2, 37.6 (t, J_{C-F} = 23.9 Hz), 36.2, 29.4; HRMS (ESI) m/z calcd for $C_{27}H_{28}{}^{35}Cl_2F_2NO_2^+$ [M + H]$^+$ m/z 506.1460, found m/z 506.1456.

***N,N*–Dibutyl–4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanamide (3bi)**



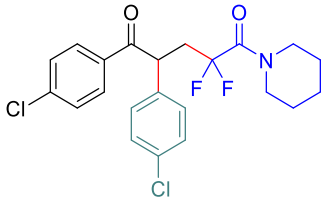
78% yield, 37.6 mg; white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.22 (m, 4H), 4.98 (dd, J_1 = 8.6 Hz, J_2 = 3.8 Hz, 1H), 3.44 – 3.26 (m, 5H), 2.58 – 2.45 (m, 1H), 1.55 – 1.46 (m, 4H), 1.32 – 1.24 (m, 4H), 0.91 (q, J = 7.3 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 97.6 to − 97.7 (m, 1F), − 97.9 to − 98.0 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 162.6 (t, J_{C-F} = 41.6 Hz), 139.8, 137.0, 134.4, 133.6, 130.3, 129.6, 129.5, 129.1, 118.7 (t, J_{C-F} = 239.0 Hz), 47.5 (t, J_{C-F} = 6.5 Hz), 47.0, 46.4 (t, J_{C-F} = 4.2 Hz), 38.7 (t, J_{C-F} = 22.7 Hz), 31.1, 29.2, 20.3, 20.0, 13.9, 13.8; HRMS (ESI) m/z calcd for $C_{25}H_{30}{}^{35}Cl_2F_2NO_2^+$ [M + H]$^+$ m/z 484.1616, found m/z 484.1615.

4,5–Bis(4–chlorophenyl)–2,2–difluoro–1–(pyrrolidin–1–yl)pentane–1,5–dione (3bj)



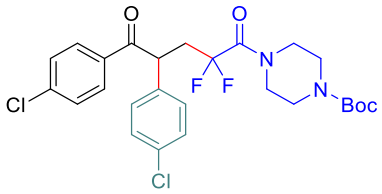
55% yield, 23.4 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.39 – 7.35 (m, 2H), 7.27 – 7.21 (m, 4H), 4.99 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H), 3.64 – 3.60 (m, 2H), 3.48 – 3.42 (m, 2H), 3.39 – 3.27 (m, 1H), 2.57 – 2.43 (m, 1H), 1.96 – 1.91 (m, 2H), 1.85 – 1.81 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 101.1 (t, J = 18.2 Hz, 1F), –101.5 (t, J = 18.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 161.8 (t, J_{C-F} = 29.4 Hz), 139.9, 136.8, 134.4, 133.7, 130.3, 129.6, 129.5, 129.1, 118.0 (t, J_{C-F} = 251.8 Hz), 47.5, 46.7 (t, J_{C-F} = 5.8 Hz), 46.4 (t, J_{C-F} = 3.3 Hz), 38.0 (t, J_{C-F} = 22.9 Hz), 26.6, 23.4; HRMS (ESI) m/z calcd for $C_{21}H_{20}{}^{35}Cl_2F_2NO_2^+$ [M + H]$^+$ m/z 426.0834, found m/z 426.0832.

4,5–Bis(4–chlorophenyl)–2,2–difluoro–1–(piperidin–1–yl)pentane–1,5–dione (3bk)



65% yield, 28.8 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 7.28 – 7.22 (m, 4H), 4.97 (dd, J_1 = 8.6 Hz, J_2 = 3.8 Hz, 1H), 3.59 – 3.46 (m, 4H), 3.44 – 3.35 (m, 1H), 2.57 – 2.43 (m, 1H), 1.68 – 1.54 (m, 7H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 98.1 (t, J = 17.7, 1F), − 98.2 (t, J = 17.7, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 161.4 (t, J_{C-F} = 28.3 Hz), 139.9, 137.0, 134.4, 133.7, 130.3, 129.6, 129.5, 129.1, 118.8 (t, J_{C-F} = 253.5 Hz), 47.0 (t, J_{C-F} = 6.5 Hz), 46.4 (t, J_{C-F} = 3.3 Hz), 44.6, 38.6 (t, J_{C-F} = 22.7 Hz), 26.5 25.7, 24.5; HRMS (ESI) m/z calcd for $C_{22}H_{22}{}^{35}Cl_2F_2NO_2^+$ [M + H]$^+$ m/z 440.0990, found m/z 440.0982.

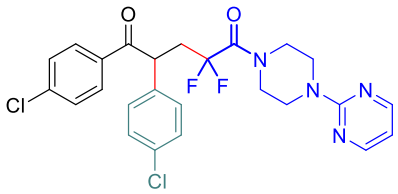
***tert*–Butyl 4–(4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoyl)piperazine–1–carboxylate (3bl)**



65% yield, 35.2 mg; white solid; mp. 124–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.39 – 7.35 (m, 2H), 7.27 – 7.21 (m, 4H), 4.94 (dd, J_1 = 8.7 Hz, J_2 = 3.7 Hz, 1H), 3.75 – 3.72 (m, 2H), 3.63 (t, J = 5.3 Hz, 2H), 3.55 (t, J = 5.5 Hz, 2H), 3.50 – 3.38 (m, 3H), 2.56 – 2.43 (m, 1H), 1.46 (s. 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 97.5 to − 97.8 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 161.8 (t,

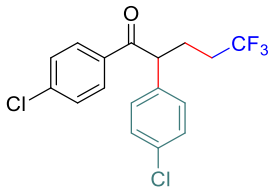
J_{C-F} = 28.8 Hz), 154.5, 140.0, 136.8, 134.2, 133.8, 130.3, 129.6, 129.5, 129.1, 118.5 (t, J_{C-F} = 253.4 Hz), 80.6, 46.3 (t, J_{C-F} = 3.4 Hz), 45.8 (t, J_{C-F} = 4.9 Hz), 43.1, 38.4 (t, J_{C-F} = 22.6 Hz), 28.5; HRMS (ESI) m/z calcd for $C_{26}H_{28}{}^{35}Cl_2F_2N_2O_4Na^+$ $[M + Na]^+$ m/z 563.1286, found m/z 563.1296.

4,5–Bis(4–chlorophenyl)–2,2–difluoro–1–(4–(pyrimidin–2–yl)piperazin–1–yl)pentane–1,5–dione (3bm)



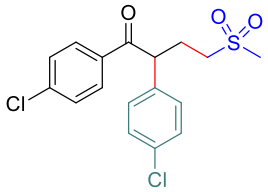
78% yield, 40.0 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 4.7 Hz, 2H), 7.89 – 7.86 (m, 2H), 7.39 – 7.35 (m, 2H), 7.28 – 7.22 (m, 4H), 6.55 (t, J = 4.7 Hz, 1H), 4.97 (dd, J_1 = 8.6 Hz, J_2 = 3.7 Hz, 1H), 3.93 – 3.81 (m, 4H), 3.74 (t, J = 5.1 Hz, 2H), 3.67 (t, J = 5.2 Hz, 2H), 3.50 – 3.35 (m, 1H), 2.56 – 2.50 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 98.0 to − 98.3 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 161.8 (t, J_{C-F} = 28.6 Hz), 161.3, 157.9, 139.9, 136.8, 134.2, 133.8, 130.3, 129.6, 129.5, 129.1, 118.6 (t, J_{C-F} = 253.4 Hz), 110.8, 46.3 (t, J_{C-F} = 3.5 Hz), 45.7 (t, J_{C-F} =6.0 Hz), 44.0, 43.4, 43.1, 38.4 (t, J_{C-F} = 22.3 Hz); HRMS (ESI) m/z calcd for $C_{25}H_{23}{}^{35}Cl_2F_2N_4O_2^+$ $[M + H]^+$ m/z 519.1161, found m/z 519.1160.

5,5,5–Trifluoro–1,2–diphenylpentan–1–one (3bn)



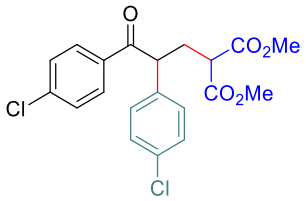
37% yield, 13.4 mg; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.39 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.21 – 7.17 (m, 2H), 4.52 (t, J = 7.0 Hz, 1H), 2.40 – 2.34 (m, 1H), 2.14 – 2.00 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 66.7 (m, J = 7.9, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 140.0, 136.6, 134.4, 133.9, 130.2, 129.8, 129.5, 129.2, 51.6, 31.5 (d, J_{C-F} = 28.9 Hz), 26.1 (q, J_{C-F} = 3.4 Hz); HRMS (ESI) m/z calcd for $C_{17}H_{14}{}^{35}Cl_2F_3O_2^+$ $[M + H]^+$ m/z 361.0368, found m/z 361.0376.

1,2–Bis(4–chlorophenyl)–4–(methylsulfonyl)butan–1–one (3bo)



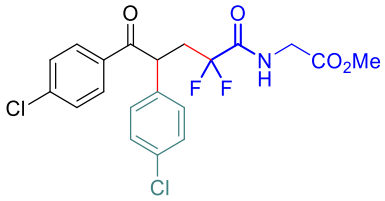
66% yield, 24.5 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.37 – 7.34 (m, 2H), 7.30 – 7.27 (m, 2H), 7.22 – 7.19 (m, 2H), 4.84 (t, J = 7.4 Hz, 1H), 3.06 – 2.94 (m, 2H), 2.91 (s, 3H), 2.66 – 2.57 (m, 1H), 2.39 – 2.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 140.1, 136.2, 134.2, 134.1, 130.3, 129.8, 129.6, 129.2, 52.1, 50.9, 41.0, 26.6; HRMS (ESI) m/z calcd for $C_{17}H_{17}{}^{35}Cl_2O_3S^+$ $[M + H]^+$ m/z 371.0270, found m/z 371.0260.

Dimethyl 2–(2,3–bis(4–chlorophenyl)–3–oxopropyl)malonate (3bp)



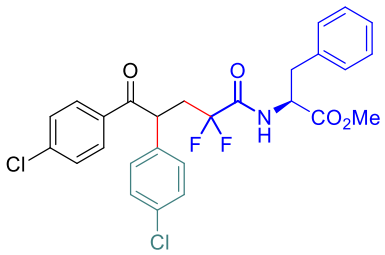
20% yield, 8.0 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.38 – 7.34 (m, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.17 (m, 2H), 4.65 (t, J = 7.4 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.30 (dd, J_1 = 8.1 Hz, J = 6.7 Hz, 1H), 2.73 – 2.66 (m, 1H), 2.42 – 2.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 169.6(2) 169.5(5), 139.9, 136.4, 134.4, 133.9, 130.3, 129.8, 129.6, 129.1, 52.9, 52.8, 50.2, 49.2, 32.3; HRMS (ESI) m/z calcd for $C_{20}H_{18}{}^{35}Cl_2O_5Na^+$ $[M + Na]^+$ m/z 431.0424, found m/z 431.0409.

Methyl (4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoyl)glycinate (3bq)



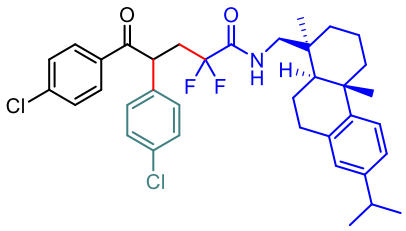
90% yield, 40.0 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.21 (m, 4H), 6.79 (s, 1H), 4.98 (dd, J_1 = 8.0 Hz, J_2 = 5.2 Hz, 1H), 4.08 – 3.97 (m, 2H), 3.80 (s, 3H), 3.31 – 3.17 (m, 1H), 2.63 – 2.50 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ − 104.5 to − 104.7 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 169.3, 164.1 (t, J_{C-F} = 28.9 Hz), 140.0, 136.3, 134.1, 133.9, 130.4, 129.7, 129.6, 129.2, 117.0 (t, J_{C-F} = 250.2 Hz), 52.9, 46.1 (t, J_{C-F} = 3.9 Hz), 41.1, 37.5 (t, J_{C-F} = 23.2 Hz); HRMS (ESI) m/z calcd for $C_{20}H_{18}{}^{35}Cl_2F_2NO_4^+$ $[M + H]^+$ m/z 444.0575, found m/z 444.0566.

Methyl (4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoyl)–L–phenylalaninate (3br)



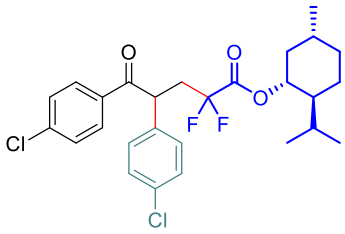
82% yield, 43.8 mg; yellow oil; dr = 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.16 (m, 7H), 7.12 – 7.05 (m, 2H), 6.72 (d, J = 7.8 Hz, 1H), 4.95 – 4.90 (m, 1H), 4.84 – 4.74 (m, 1H), 3.77 (d, J = 6.5 Hz, 3H), 3.21 – 3.07 (m, 3H), 2.56 – 2.42 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, two diastereoisomers) δ one isomer –102.9 to–103.5 (m, 1F), –105.5 to –106.1 (m, 1F); another isomer –102.2 to –102.8 (m, 1F), –106.2 to –106.8 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$, two diastereoisomers) δ one isomer 196.1, 170.9(overlapped), 163.5 (t, J_{C-F} = 29.3 Hz), 140.0(overlapped), 136.4, 135.1,134.1, 133.8, 130.3, 129.6, 129.5, 129.3,129.1, 128.9, 127.6, 116.9 (t, J_{C-F} = 252.0 Hz), 53.2, 52.8, 46.1, 37.9, 37.6, 37.4 (t, J_{C-F} =23.4 Hz); another isomer 196.1, 170.9(overlapped), 163.4 (t, J_{C-F} = 28.5 Hz), 140.0(overlapped), 136.2, 135.0, 134.1, 133.8, 130.3, 129.6, 129.5, 129.3, 129.1, 128.9, 127.6, 116.8 (t, J_{C-F} = 252.6 Hz), 53.1, 52.8, 46.0, 37.9, 37.6, 37.4 (t, J_{C-F} =23.4 Hz); HRMS (ESI) m/z calcd for $C_{27}H_{24}{}^{35}Cl_2F_2NO_4^+$ $[M + H]^+$ m/z 534.1045, found m/z 534.1045.

4,5–Bis(4–chlorophenyl)–2,2–difluoro–N–(((*1S,4aS,10aS*)–7–isopropyl–1,4a,10a–trimethyl–1,2,3,4,4a,9, 10,10a–octahydrophenanthren–1–yl)methyl)–5–oxopentanamide (3bs)



56% yield, 35.8 mg; yellow oil, dr = 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.39 – 7.34 (m, 2H), 7.26 – 7.22 (m, 2H), 7.20 – 7.16 (m, 3H), 7.03 – 6.99 (m, 1H), 6.89 – 6.87 (m, 1H), 6.25 (s, 1H), 5.00 – 4.93 (m, 1H), 3.31 – 3.13 (m, 3H), 2.95 – 2.75 (m, 3H), 2.56 – 2.43 (m, 1H), 2.32 – 2.28 (m, 1H), 1.87 – 1.63 (m, 5H), 1.46 – 1.32 (m, 3H), 1.23 – 1.20 (m, 9H), 0.95 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$, two diastereoisomers) δ one isomer –103.5 to –103.6 (m, 2F); another isomer –103.6(5) to –103.7(4) (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ one isomer 196.3, 164.1 (overlapped, t, J_{C-F} =28.23 Hz), 146.9(overlapped), 145.9(overlapped), 140.0(overlapped), 136.4(overlapped), 134.6(overlapped), 134.2(overlapped), 133.9(overlapped), 130.3, 129.6, 129.2(overlapped), 127.1, 124.4(overlapped), 124.1(overlapped), 117.2 (t, J_{C-F} =251.8 Hz), 50.1, 46.3, 46.1, 38.3(overlapped), 37.7, 37.5, 36.3, 33.6(overlapped), 30.4, 25.5, 24.1(overlapped), 19.2(overlapped), 18.6; another isomer 196.3, 164.1 (overlapped, t, J_{C-F} =28.23 Hz), 146.9(overlapped), 145.9(overlapped), 140.0(overlapped), 136.4(overlapped), 134.6(overlapped), 134.2(overlapped), 133.9(overlapped), 130.3, 129.6, 129.2(overlapped), 127.0, 124.4(overlapped), 124.1(overlapped), 117.1 (t, J_{C-F} =251.8 Hz), 50.1, 46.2, 46.0, 38.3(overlapped), 37.6, 37.5, 36.2, 33.6(overlapped), 30.3, 25.5, 24.1(overlapped), 19.2(overlapped), 18.6; HRMS (ESI) m/z calcd for $C_{37}H_{42}{}^{35}Cl_2F_2NO_2^+$ $[M + H]^+$ m/z 640.2555, found m/z 640.2556.

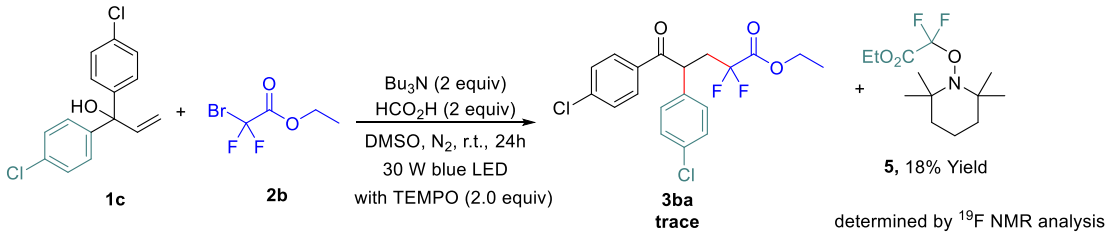
(*1R,2S,5R*)–2–Isopropyl–5–methylcyclohexyl 4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoate (3bt)



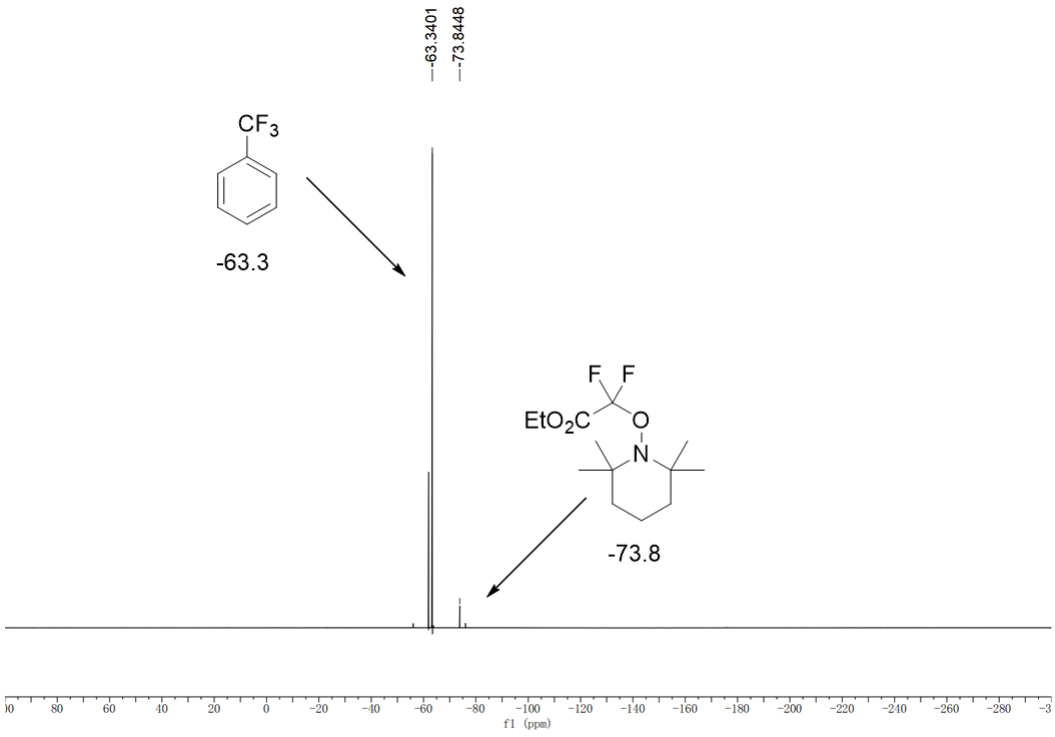
95% yield, 48.5 mg; yellow oil, dr = 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, two diastereoisomers) δ one isomer 7.88 – 7.84 (overlapped, 2H), 7.40 – 7.36 (overlapped, 2H), 7.28 – 7.25 (overlapped, 2H), 7.23 – 7.19 (overlapped, 2H), 4,92 – 4.87 (overlapped, 1H), 4.80 – 4.70 (overlapped, 1H), 3.34 – 3.17 (overlapped, 1H), 2.53 – 2.38 (overlapped, 1H), 1.98 – 1.79 (overlapped, 2H), 1.72 – 1.65 (overlapped, 2H), 1.51 – 1.39 (overlapped, 2H), 0.93 – 0.86 (overlapped, 9H), 0.75 – 0.73 (overlapped, 3H); ^{19}F NMR (376 MHz, $CDCl_3$, two diastereoisomers) δ one isomer –104.0 (overlapped, J = 16.8 Hz, 1F), –104.1 to –104.2 (m, 1F); another isomer –104.0 (overlapped, J = 16.8 Hz, 1F), –104.3 to –104.4 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$, two diastereoisomers) δ one isomer 195.9, 163.3 (t, J_{C-F} = 32.2 Hz), 139.9(overlapped), 136.2, 133.9(2), 133.8(5)(overlapped), 130.2, 129.5(2), 129.4(8), 129.0(overlapped), 115.2 (t, J_{C-F} = 250.3 Hz), 46.7(overlapped), 46.0 (t, J_{C-F} =7.5 Hz), 40.1, 37.8 (t, J_{C-F} =23.3 Hz), 33.9, 31.4, 26.1, 23.3, 21.9, 20.6 (overlapped), 16.1 (overlapped); another isomer 195.8, 163.3 (t, J_{C-F} = 31.3 Hz), 139.9(overlapped), 136.1, 133.8(5)(overlapped), 133.8(2), 130.1, 129.51, 129.41, 129.0(overlapped), 115.2 (t, J_{C-F} = 249.9 Hz), 46.7(overlapped), 46.0 (t, J_{C-F} =7.5 Hz), 40.2, 37.8 (t, J_{C-F} =22.9 Hz), 33.9, 31.3, 26.1, 23.2, 21.9, 20.6 (overlapped), 16.1 (overlapped); HRMS (ESI) m/z calcd

for $C_{27}H_{31}{}^{35}Cl_2F_2O_3^+$ $[M + H]^+$ m/z 511.1613, found m/z 511.1659.

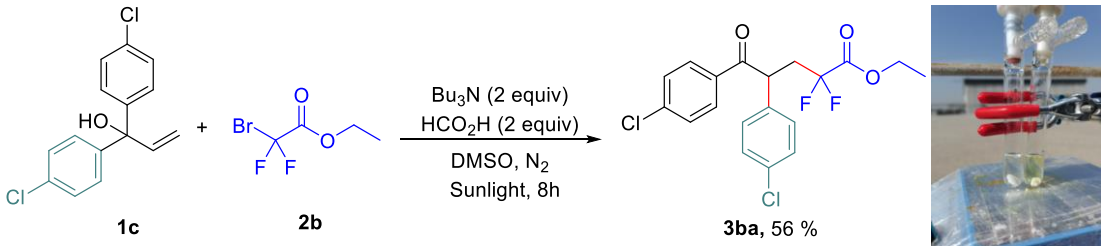
5. TEMPO inhibition experiment



A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with TEMPO (0.2 mmol, 31.2 mg) and 1,1–bis(4–chlorophenyl) prop–2–en–1–ol **1c** (0.1 mmol, 27.9 mg,). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate **2a** (0.2 mmol, 25.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 30 W blue LEDs light irradiation with a water chiller to maintain the temperature at 25 ºC. After 24 hours, the reaction was then quenched satd. NH_4Cl solution (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was concentrated. The yield of product formed was determined by ^{19}F NMR with trifluorotoluene as internal standard**.** The ^{19}F NMR signal of compound **5** was consistent with the reported data.[4]

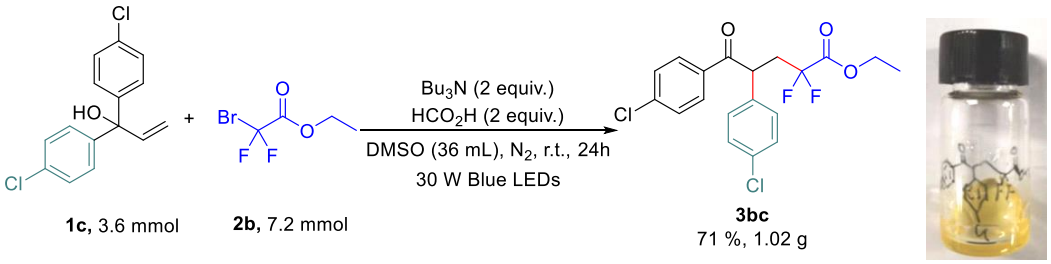


6. Sunlight irradiation experiment



A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with 1,1–bis(4–chlorophenyl) prop–2–en–1–ol **1c** (0.1 mol, 27.9mg). The vessel was then evacuated and filled with nitrogen three times. Next, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate **2a** (0.2 mmol, 25.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. The tube was then sealed and irradiated with sunlight for 8 hours. The reaction was quenched with satd. NH_4Cl solution (15 mL) and extracted with ethyl acetate (3 x 10 mL). The organic layer was concentrated to give the crude product, which was purified by column chromatography on silica gel with petroleum ether/ethyl acetate mixtures to give the product in 54% yield.

7. Scaleup experiment



A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with 1,1–bis(4–chlorophenyl) prop–2–en–1–ol **1c** (3.6 mol, 1.04g, 1 equiv.). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate **2a** (7.2 mmol, 0.92 mL, 2 equiv.), tributylamine (7.2 mmol, 1.7mL, 2 equiv.) and formic acid (7.2 mmol, 0.24mL, 2 equiv.) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 30 W blue LEDs light irradiation with a water chiller to maintain the temperature at 25 °C. After 24 hours, the reaction was then quenched with satd. NH_4Cl solution (100 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was concentrated, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to give compound **3ba** (1.02 g, 71% yield).

8. Quantum yield measurement

Quantum yield experiments were performed according to the procedure of Yoon.[5, 6]

8.1 Determination of the photo flux of the light source:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were covered in foil and stored in dark. To determine the photon flux of our lamp source, 2.0 mL of the ferrioxalate solution was placed in a 5 mL screw–top test tube and irradiated for 10.0s with the photoreactor 2 cm away from a 30 W blue LEDs light irradiation. After irradiation, 0.35 mL of the phenanthroline solution was added to the test tube. The solution was then allowed to rest for 1 h in dark to make sure the ferrous ions completely coordinating to phenanthroline. The absorbance of the solution was then measured at 510 nm. Conversion was calculated using eq. 1

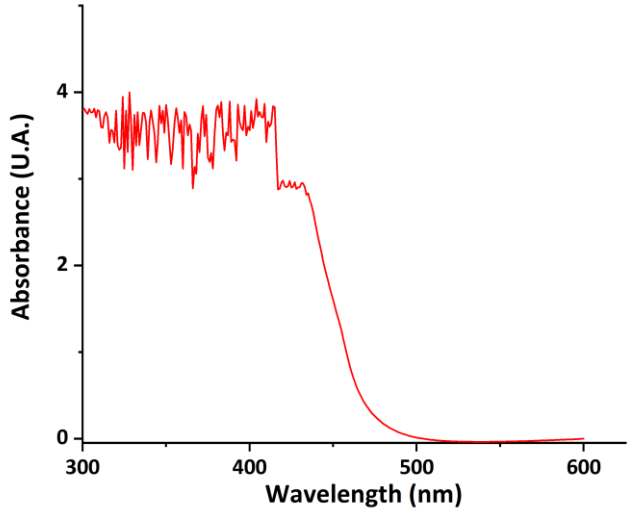
$$\text{mol } Fe^{2+} = \frac{V \bullet \Delta A}{l \bullet \varepsilon} \qquad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in the absorbance at 510 nm between the irradiated and non–irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq. 2

$$\text{Photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \bullet t \bullet f} \qquad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 460 nm),[6] t is the irradiation time (10.0 s), and f is the fraction of light absorbed at λ = 460 nm. The fraction of light absorbed (f) by this solution was calculated using eq. 3, where A is the measured absorbance at 460 nm.

$$f = 1 - 10^{-A} \qquad (3)$$



The absorbance of the above ferrioxalate solution at 460 nm was measured to be 0.840, which means $f = 0.840$, *vide infra*. Then, the photo flux of the light source could be calculated:

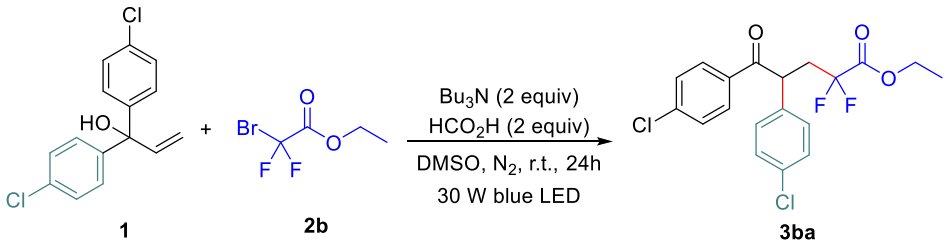
Sample calculation:

$$\text{Mol } Fe^{2+} = \frac{0.00235\ L \cdot 1.233}{1\ cm \cdot 11100\ L\ mol^{-1}\ cm^{-1}} = 2.61 \times 10^{-7}\ \text{mol}$$

$$\text{Photon flux} = \frac{2.61 \times 10^{-7}\ \text{mol}}{0.845 \cdot 10\ \text{s} \cdot 0.85546} = 3.61 \times 10^{-8}\ \text{einsteins s}^{-1}$$

The photon flux was calculated (average of three experiments) to be 3.61 x 10^{-8} einsteins s^{-1}.

8.2 Determination of quantum yield



A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with 1,1–bis(4–chlorophenyl) prop–2–en–1–ol **1c** (0.1 mol, 27.9mg). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate **2a** (0.2 mmol, 25.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 30 W blue LEDs light irradiation with a water chiller to maintain the temperature at 25

°C. After 20 min, the reaction was then quenched with satd. NH_4Cl solution (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was concentrated. The yield of product formed was determined by ^1H NMR with a 1,3,5–Trimethoxybenzene as internal standard. Average yield of three experiments was 24% yield. The fraction of light absorbed (*f*) by this solution was calculated to be 0.89 using eq. 3. The quantum yield was calculated using eq. 4 the average yield of three experiments to be 0.62.

$$\Phi = \frac{\text{moles of product formed}}{\text{einsteins of light absorbed}} \qquad (4)$$

Sample quantum yield calculation:

$$\Phi = \frac{2.4 \times 10^{-5} \text{ mol}}{3.61 \times 10^{-8} \text{ einsteins s}^{-1} \cdot 1200 \text{ s} \cdot 1.00 \cdot 0.89183} = 0.62$$

9. Light on/off Experiment

A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with 1,1–bis(4–chlorophenyl) prop–2–en–1–ol **1c** (0.1 mol, 27.9 mg). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate **2a** (0.2 mmol, 25.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 30 W blue LEDs light irradiation and kept in the dark in 1 hour intervals with a water chiller to maintain the temperature at 25 °C. The reaction was then quenched satd. NH_4Cl solution (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was concentrated. The yield of **3ba** was determined by ^1H NMR with 1,3,5–trimethoxybenzene as internal standard**.**

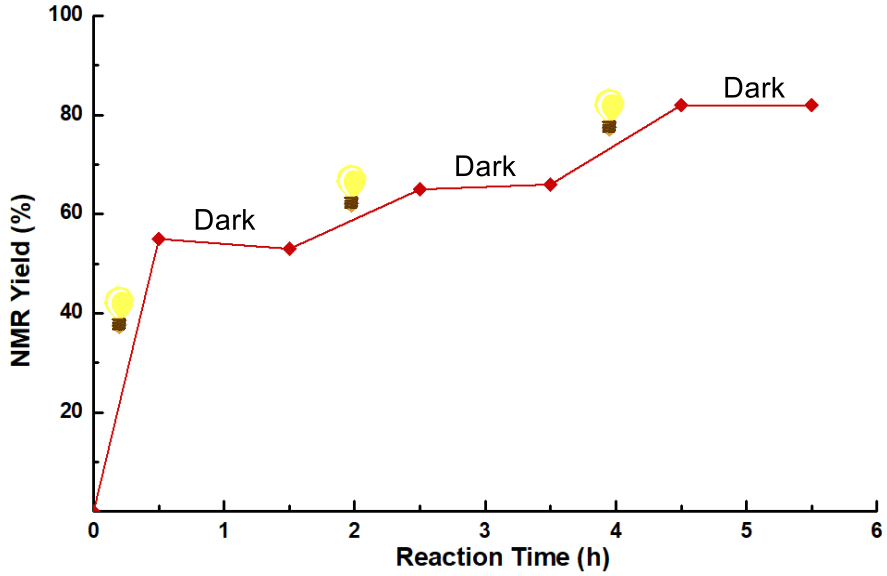


Figure S1. Reaction profile of light on/off experiment

10. UV–vis absorption spectra

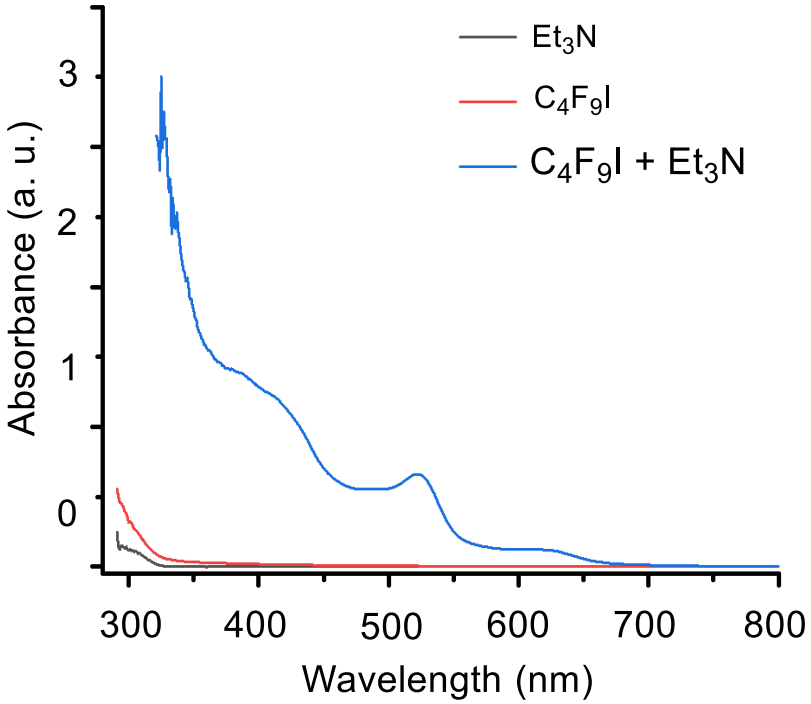


Figure S2. UV–visible absorption spectra of Et_3N, C_4F_9I and mixture solution of Et_3N/C_4F_9I in DMSO / CH_3OH (99:1, v/v) (c = 0.01 M).

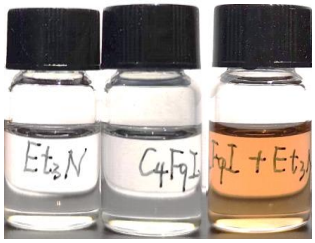


Figure S3. Photograph of solution of Et_3N, C_4F_9I and mixture solution of Et_3N/C_4F_9I in DMSO / CH_3OH (99:1, v/v) (c = 0.01 M).

Conclusion: *UV-Vis spectrum of the mixture of Et_3N/C_4F_9I shows a strong bathochromic shift and a charge transfer band, which support the formation of halogen bonded complex in the reaction mixture between Et_3N and C_4F_9I.*

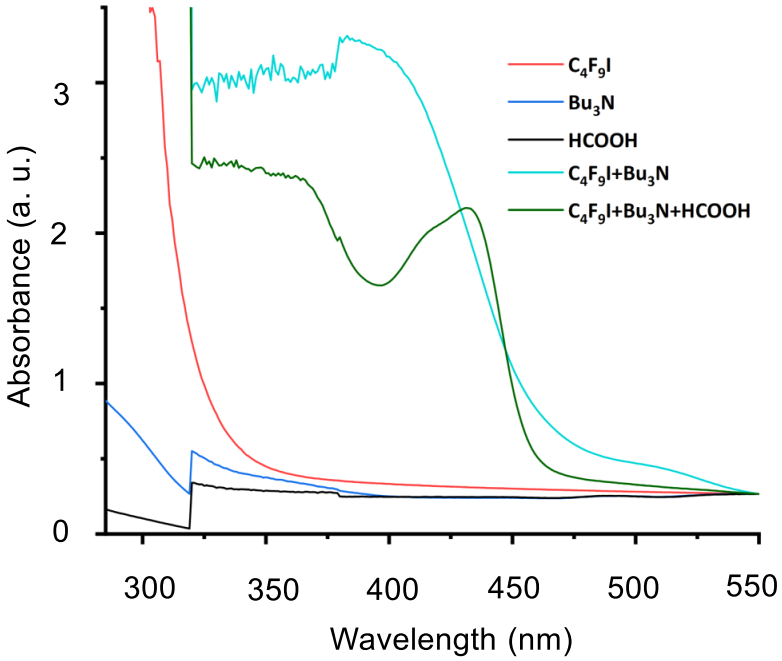


Figure S4. UV–visible absorption spectra of Bu_3N, C_4F_9I, HCOOH, mixture solution of Bu_3N/C_4F_9I and mixture solution of Bu_3N/C_4F_9I/HCOOH in DMSO (c = 0.01 M)

Figure S5. Photograph of solution of Bu_3N, C_4F_9I and mixture solution of Bu_3N/C_4F_9I in DMSO (c = 0.01 M).

Conclusion: *UV-Vis spectrum of the mixture of Bu_3N/C_4F_9I/HCOOH shows a strong bathochromic shift and a charge transfer band, which support the formation of halogen bonded complex in the reaction mixture.*

11. ^{19}FNMR Titration of C_4F_9I (2a) with Et_3N.

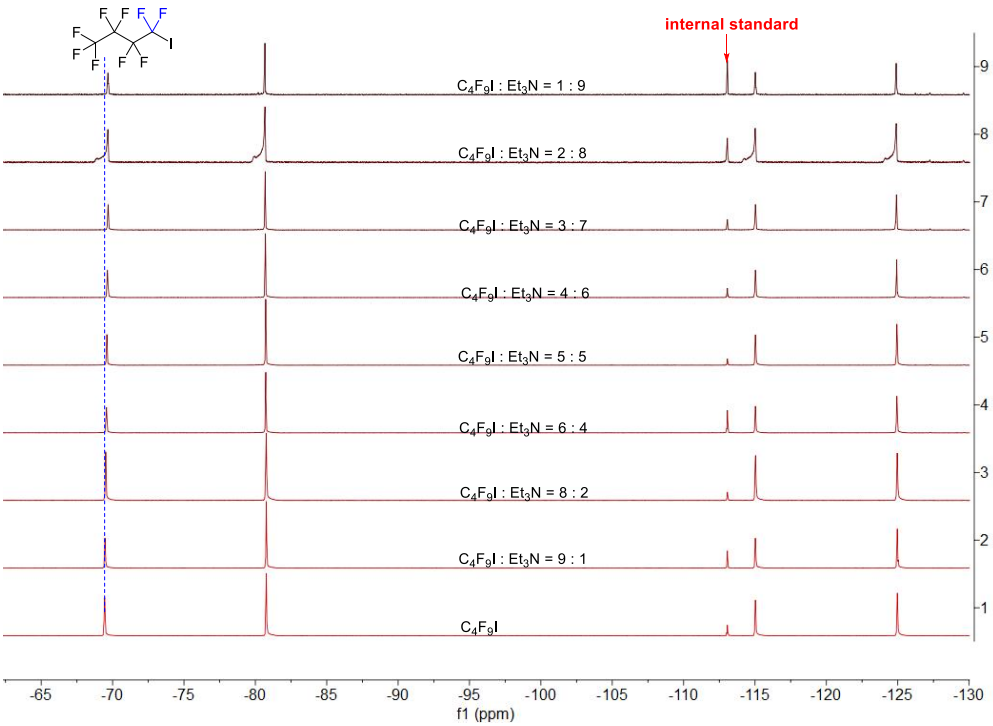


Figure S6. ^{19} F NMR shift of C_4F_9I with the addition of Et_3N in DMSO/CH_3OH (90:10, v/v)

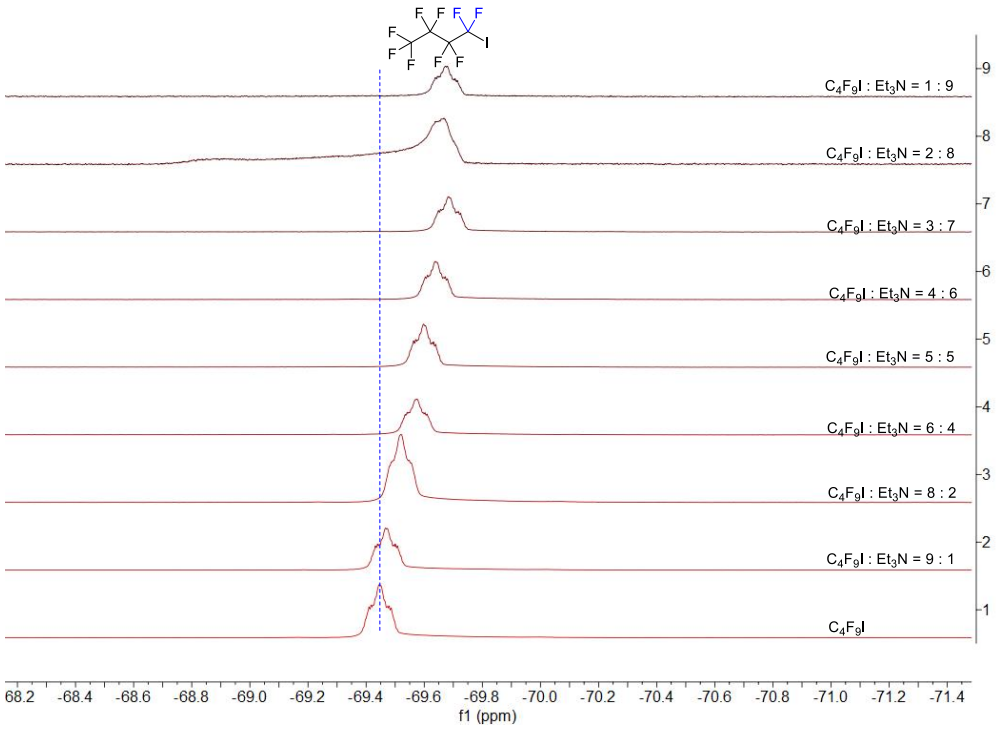


Figure S7. ^{19} F NMR shift of C_4F_9I with the addition of Et_3N in DMSO/CH_3OH (90:10, v/v)

Conclusion: *A clear upfiled-shift of the ^{19} F NMR signal was observed with the addition of Et_3N into C_4F_9I. which indicated the interaction, namely, halogen bond between Et_3N and C_4F_9I.*

12. Determination of binding stoichiometry of halogen bond between C_4F_9I (2a) and Et_3N.

Determination of binding stoichiometry experiments were performed by Job's method according to the reported procedure.[7,8] The binding stoichiometry between C_4F_9I (**2a**) and Et_3N was evaluated using a Job's plot in 1.0 mL of DMSO/CH_3OH (90:10, v/v) solution. In an NMR tube, total constant concentration [**2a** + Et_3N] = 0.1 M. Samples were prepared for molar fractions χ (**2a**) = 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.80, 0.90, 1.00. ^{19}F NMR for each sample was recorded to measure the change in chemical shift for the F of C_4F_9I. Fluorobenzene was used as internal standard and $\delta_{F\text{-}Ph}$ = -113.066 ppm. The data show formation of a 1:1 adduct (maximum in the plot at χ (2a) = 0.5).

x (**2a**)	0	0.10	0.20	0.30	0.40
△δ	0	0.2325	0.2308	0.2344	0.1891
[2a]*△δ	0	0.02325	0.04616	0.07032	0.07564
x (**2a**)	0.50	0.60	0.80	0.90	1.00
△δ	0.1536	0.1258	0.0723	0.0231	0
[2a]*△δ	0.0768	0.07548	0.05784	0.02079	0

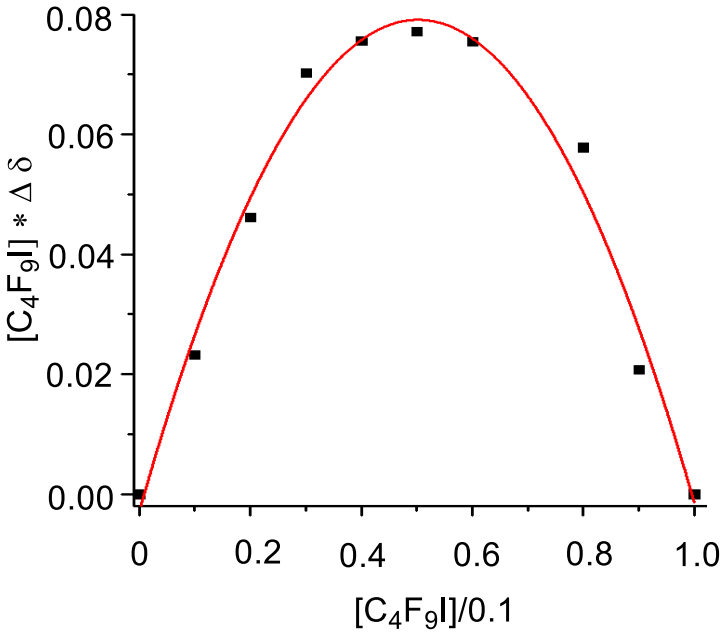


Figure S8. Job's plot

Conclusion: *A clear upfiled-shift of the ^{19}F NMR signal of C_4F_9I was observed with the addition of Et_3N, which indicated the formation of halogen bonded complex between C_4F_9I and Et_3N. This is in consistent with the redshift of the UV-Vis spectrum. And the halogen bond donor:acceptor ratio in the solution was calculated to be 1:1 via Job's method.*

13. Reference

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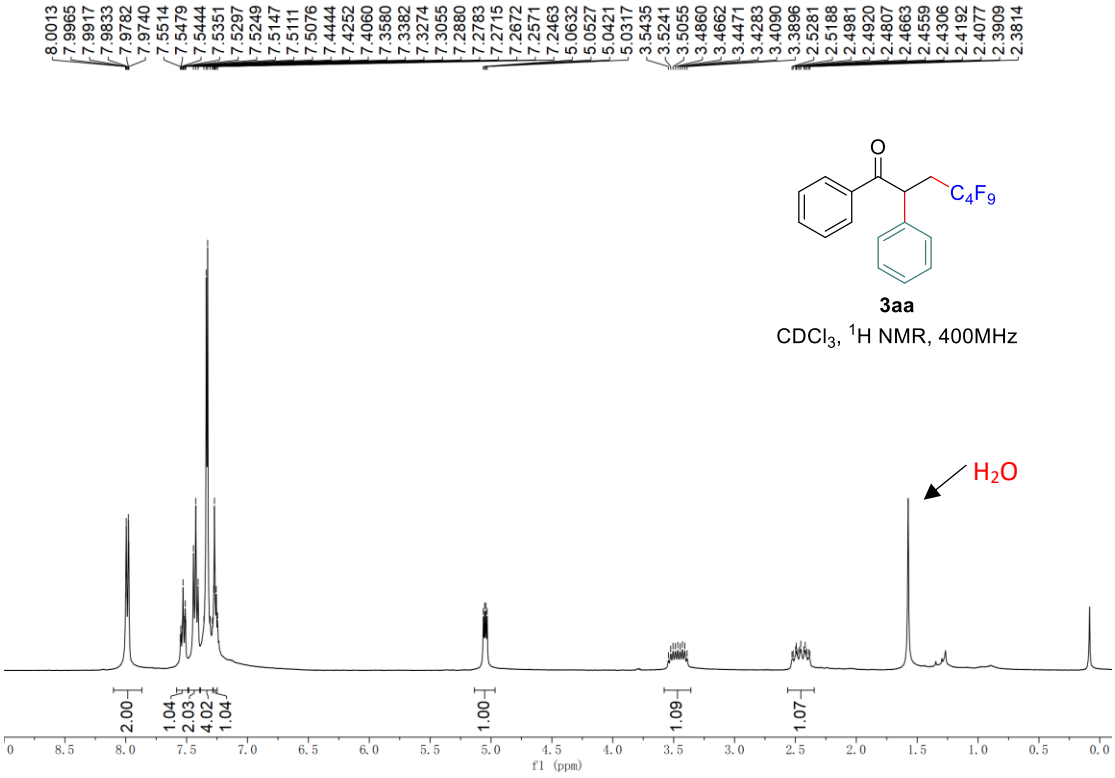
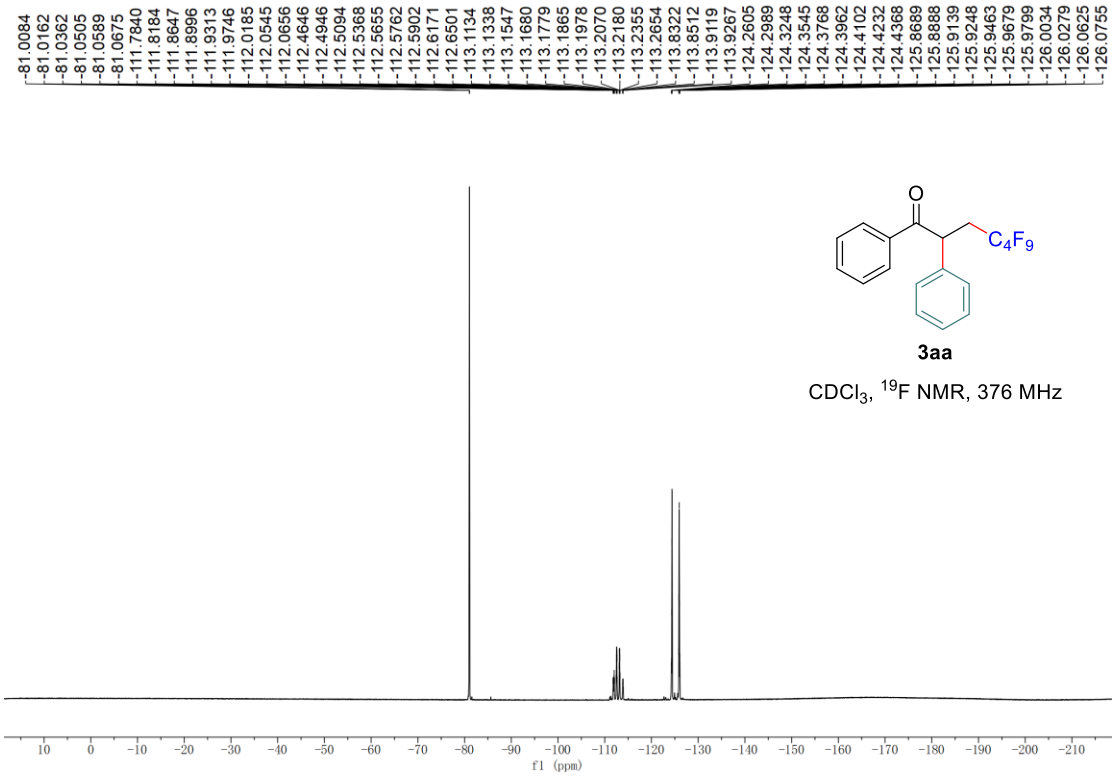
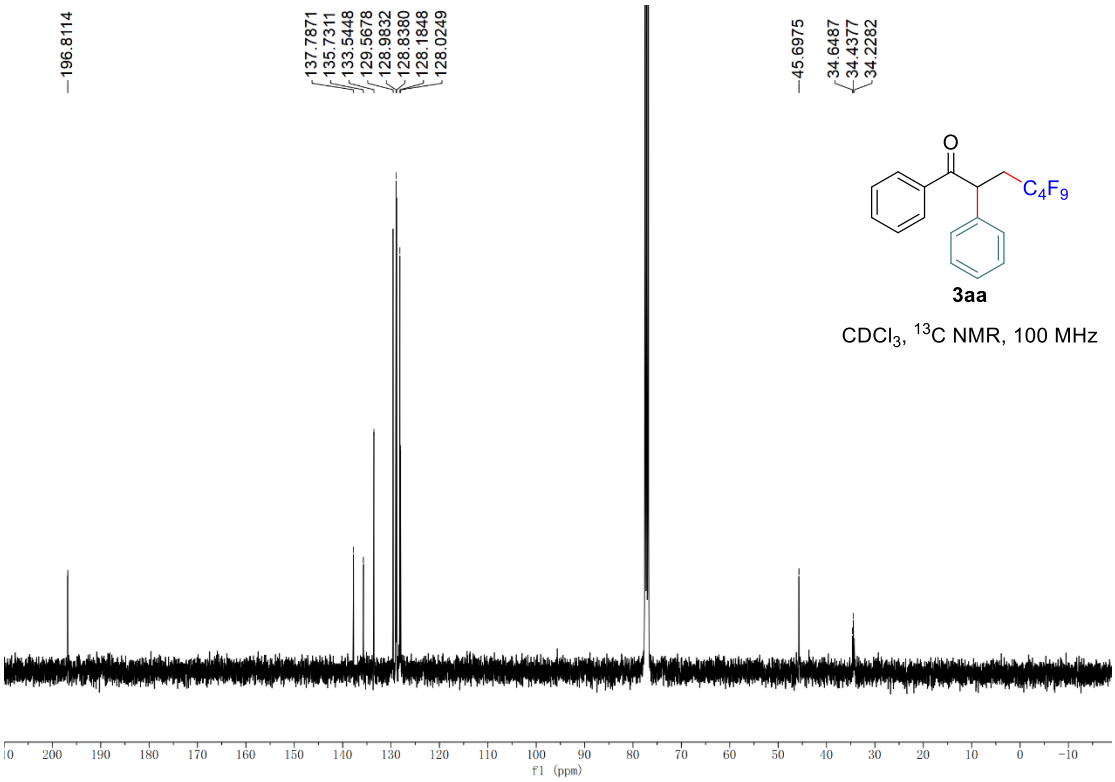
14. NMR Spectra

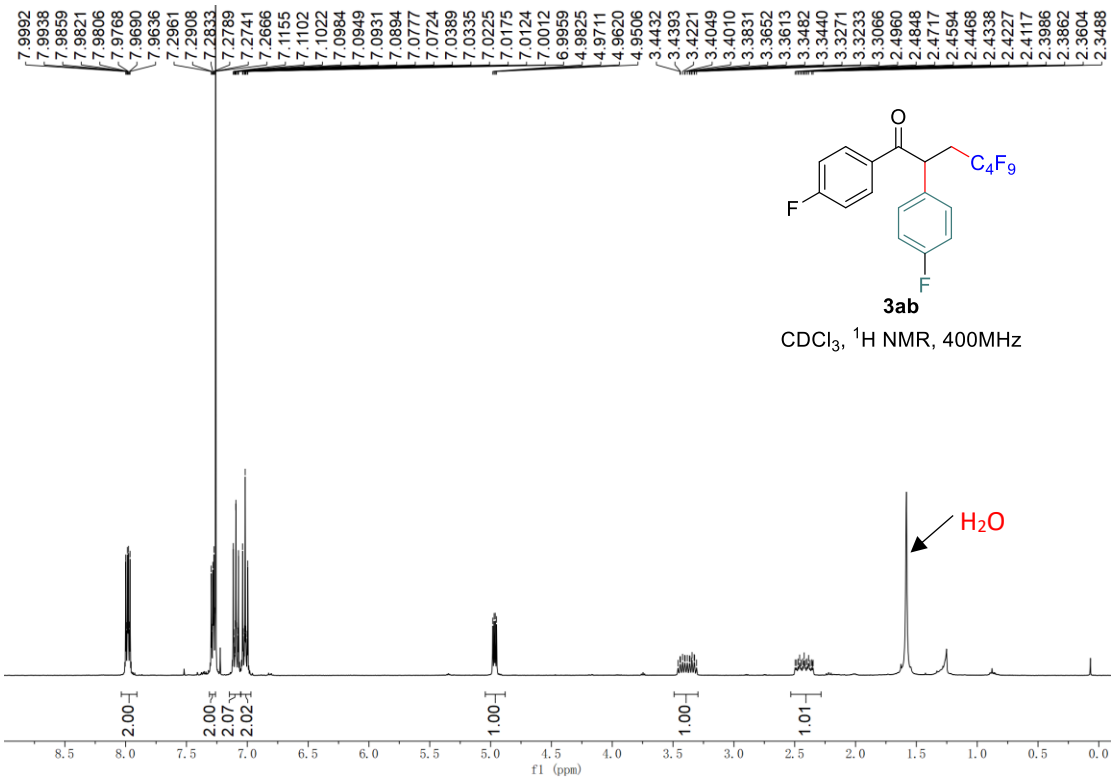






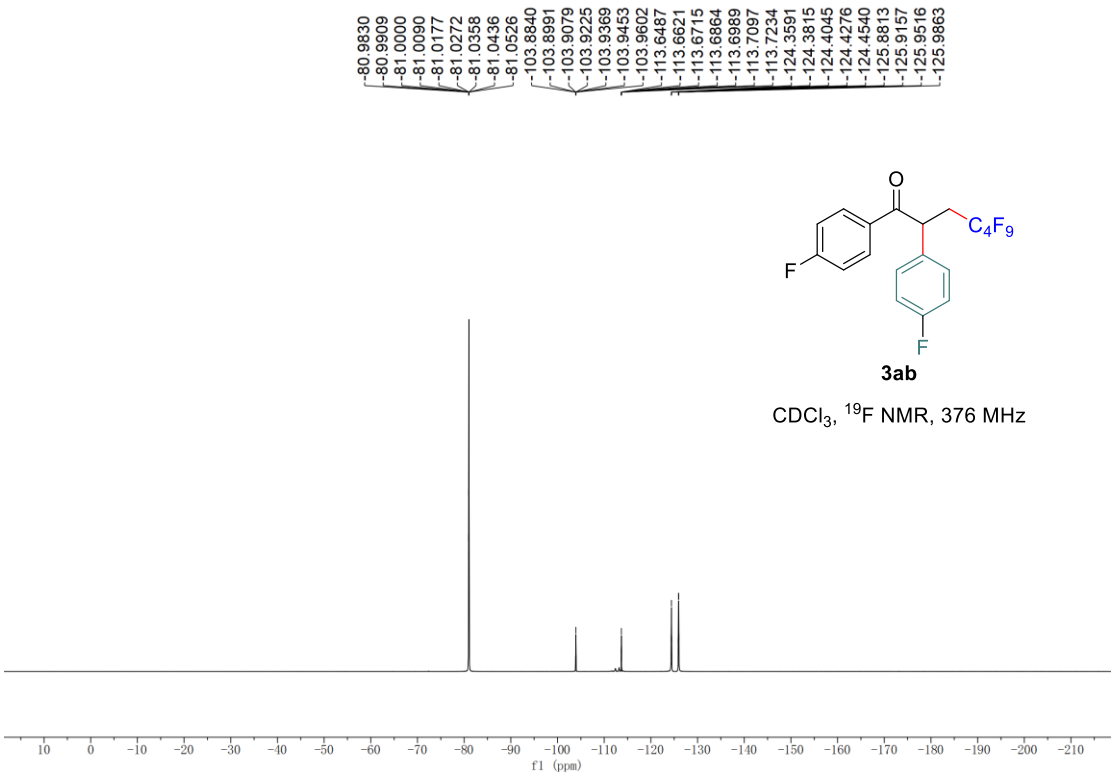
3aa

$CDCl_3$, ^{13}C NMR, 100 MHz



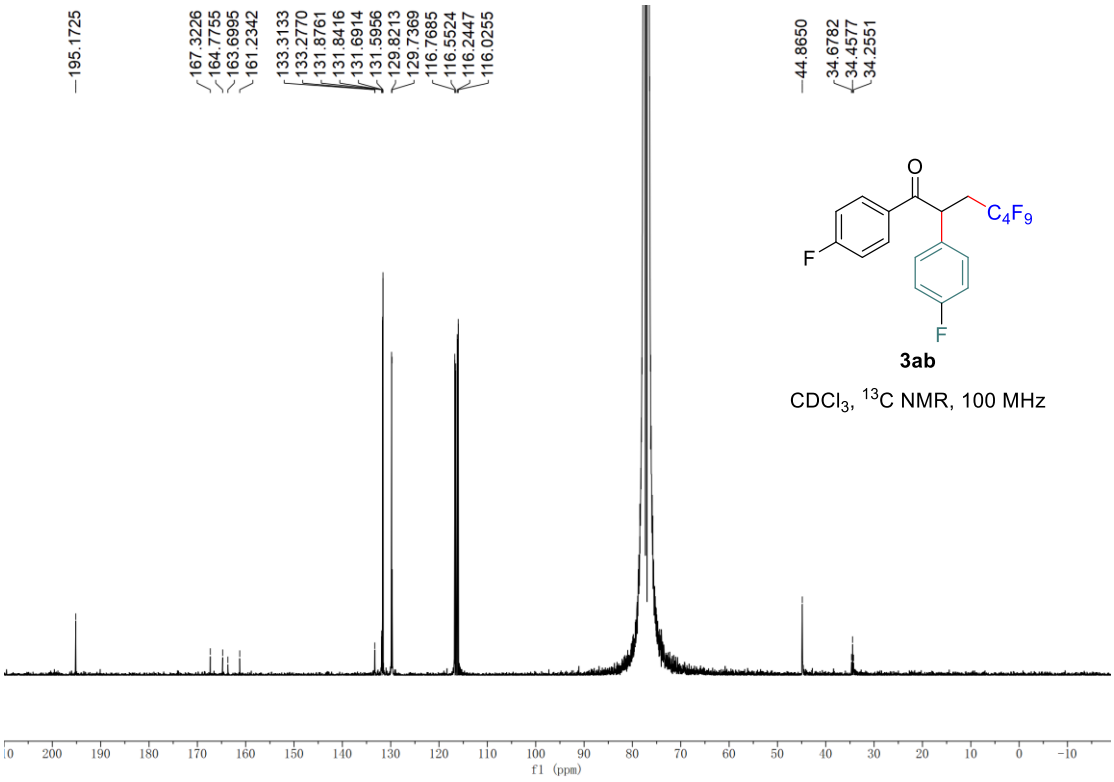
3ab

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



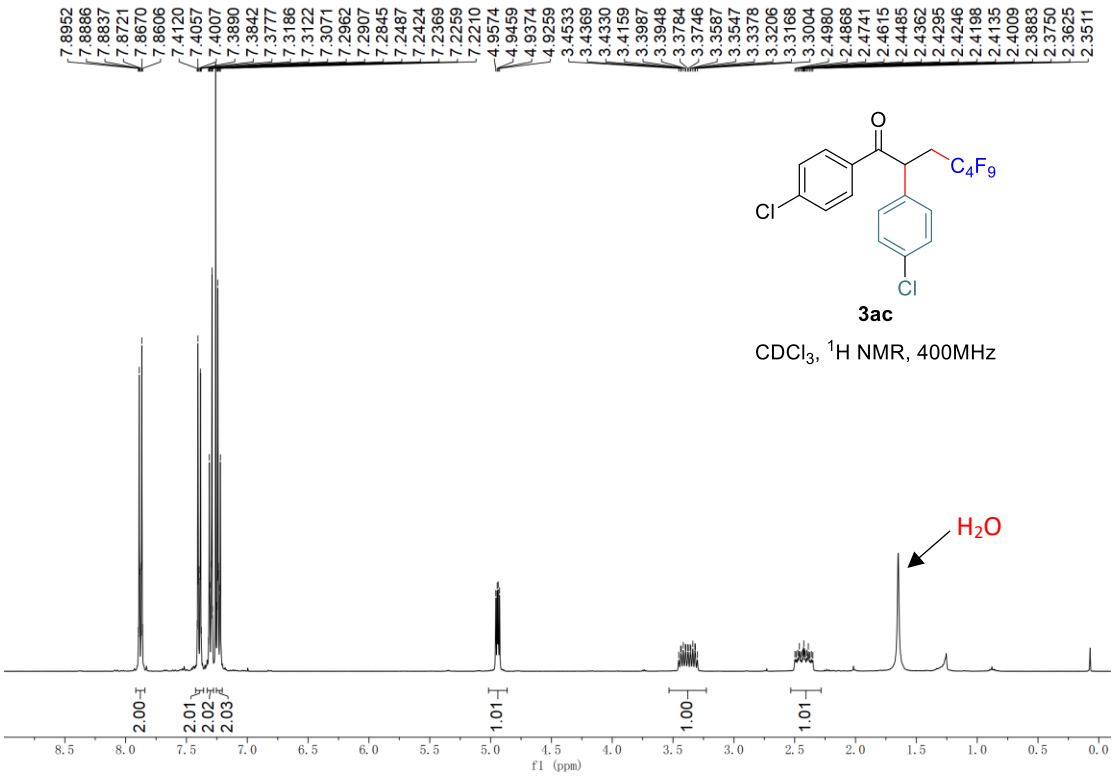
3ab

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



3ab

$CDCl_3$, ^{13}C NMR, 100 MHz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7.8837
7.8721
7.8670
7.8606
7.4120
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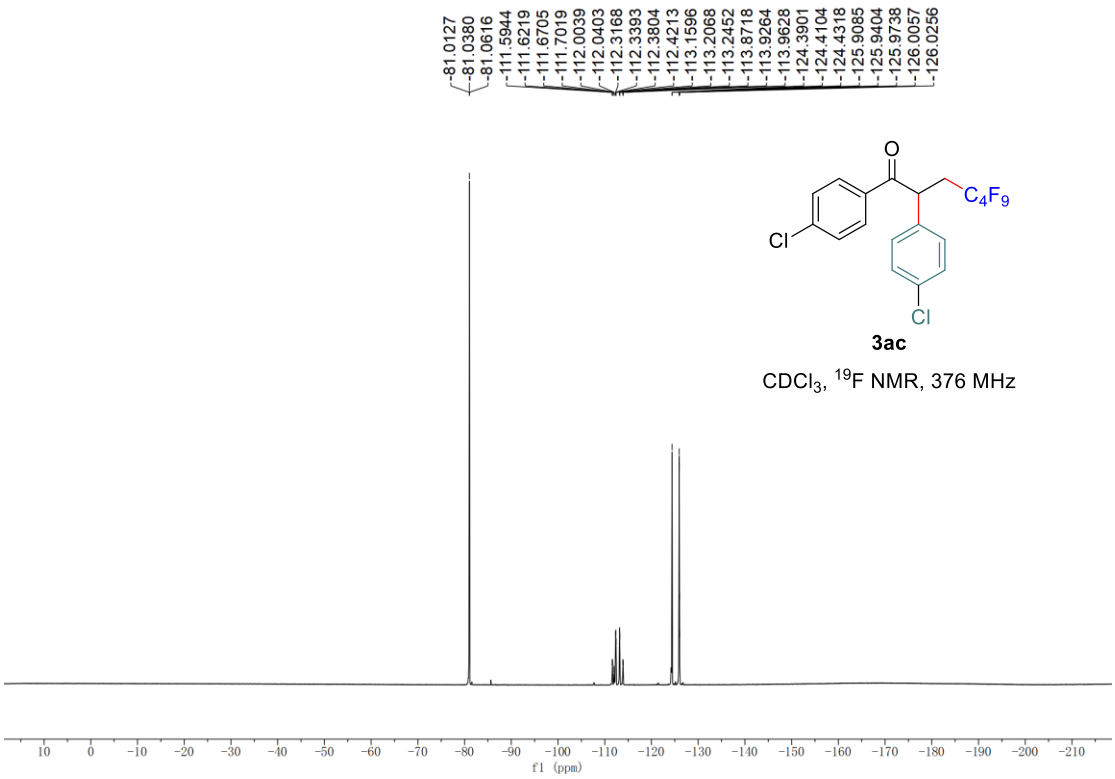
7.4007
7.3890
7.3842
7.3777
7.3186
7.3122
7.3071
7.2962
7.2907
7.2845
7.2487
7.2424
7.2369
7.2259
7.2210
4.9574
4.9459
4.9374
4.9259
3.4533
3.4369
3.4330
3.4159
3.3987
3.3948
3.3784
3.3746
3.3587
3.3547
3.3378
3.3206
3.3168
3.3004
2.4980
2.4868
2.4741
2.4615
2.4485
2.4362
2.4295
2.4246
2.4198
2.4135
2.4009
2.3883
2.3750
2.3625
2.3511
O
C4F9
Cl
Cl
3ac
CDCl3, 1H NMR, 400MHz
H2O
2.00
2.01
2.02
2.03
1.01
1.00
1.01
f1 (ppm)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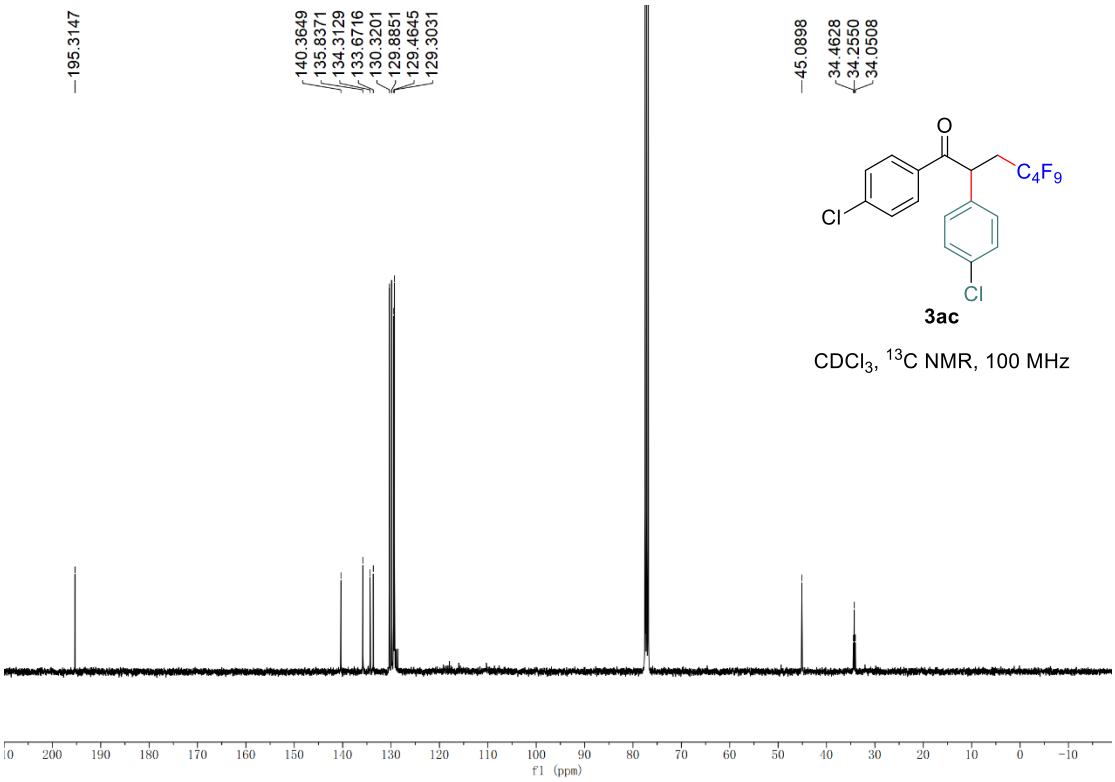
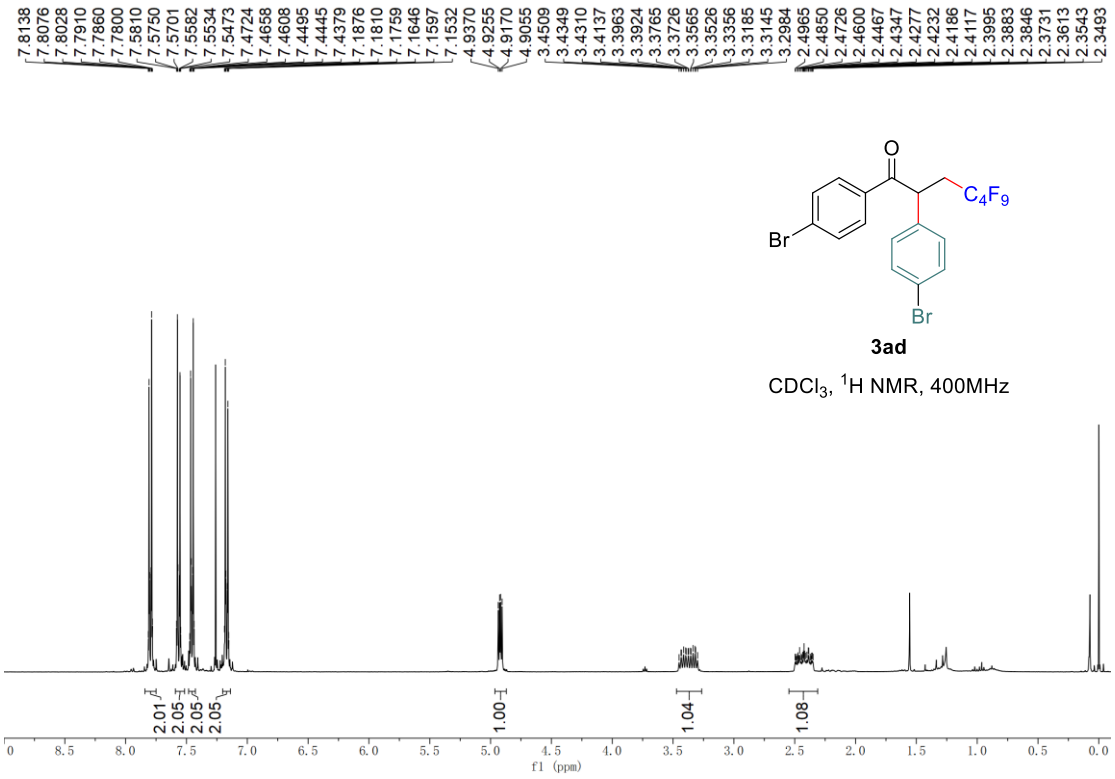
-111.6219
-111.6705
-111.7019
-112.0039
-112.0403
-112.3168
-112.3393
-112.3804
-112.4213
-113.1596
-113.2068
-113.2452
-113.8718
-113.9264
-113.9628
-124.3901
-124.4104
-124.4318
-125.9085
-125.9404
-125.9738
-126.0057
-126.0256
O
C4F9
Cl
Cl
3ac
CDCl3, 19F NMR, 376 MHz
f1 (ppm)



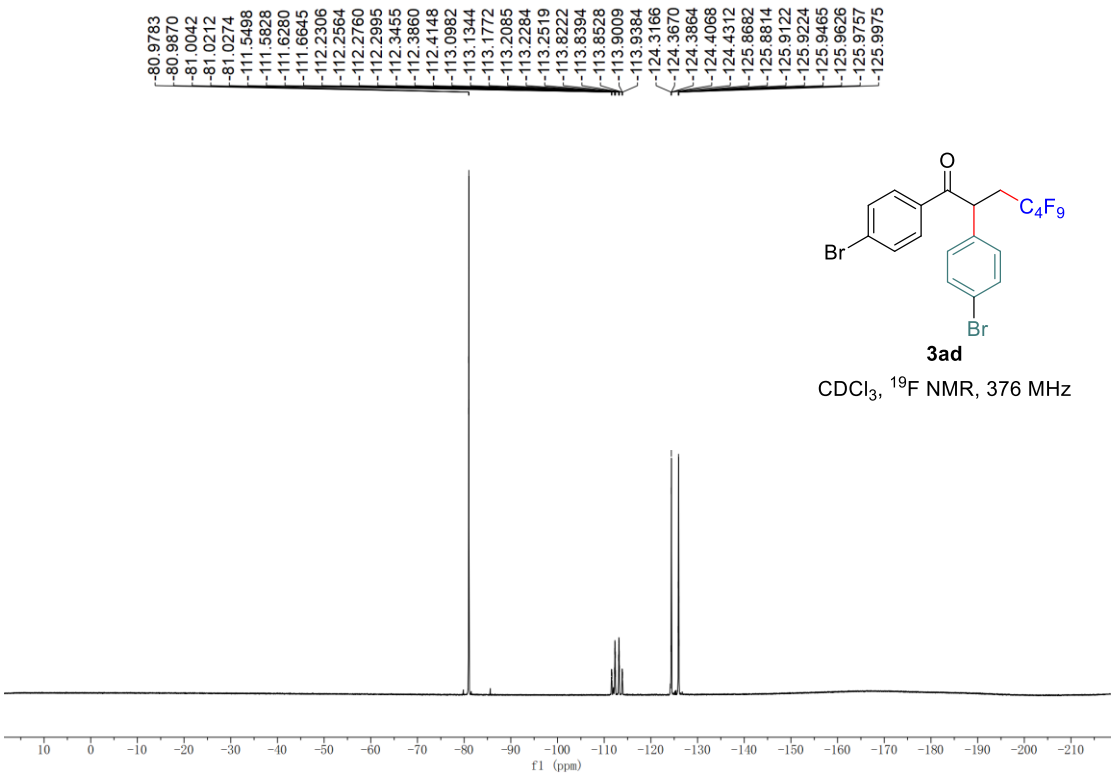
3ac

$CDCl_3$, ^{13}C NMR, 100 MHz



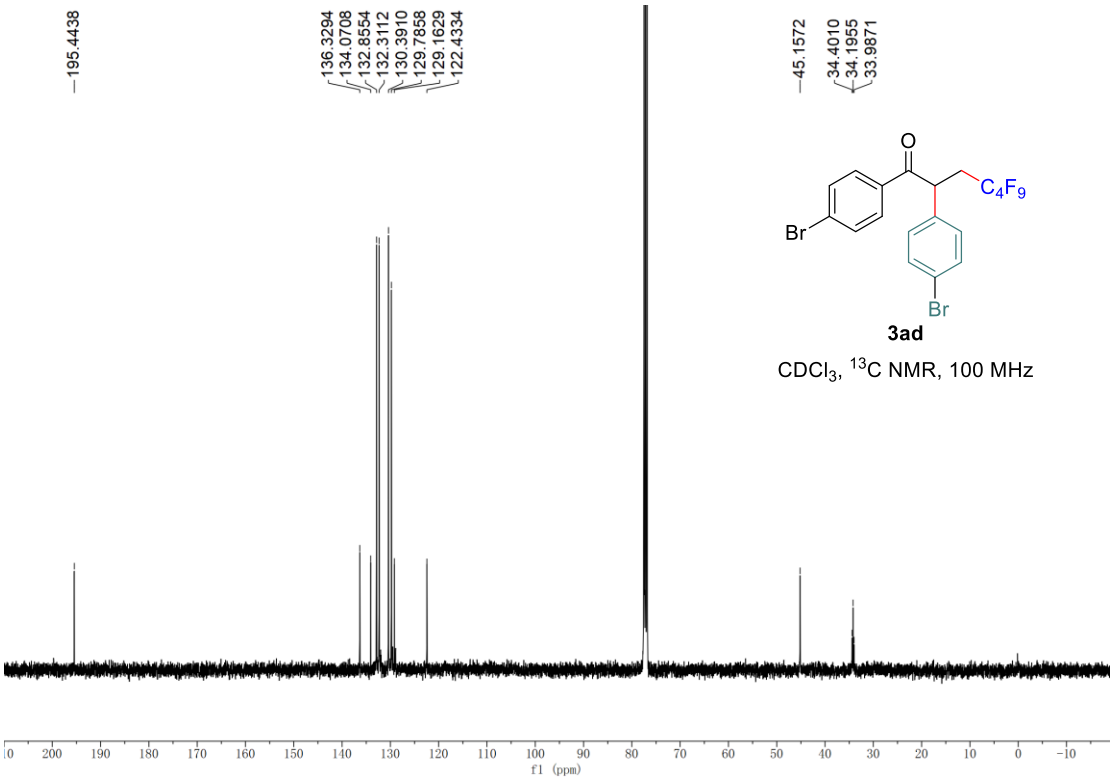
3ad

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



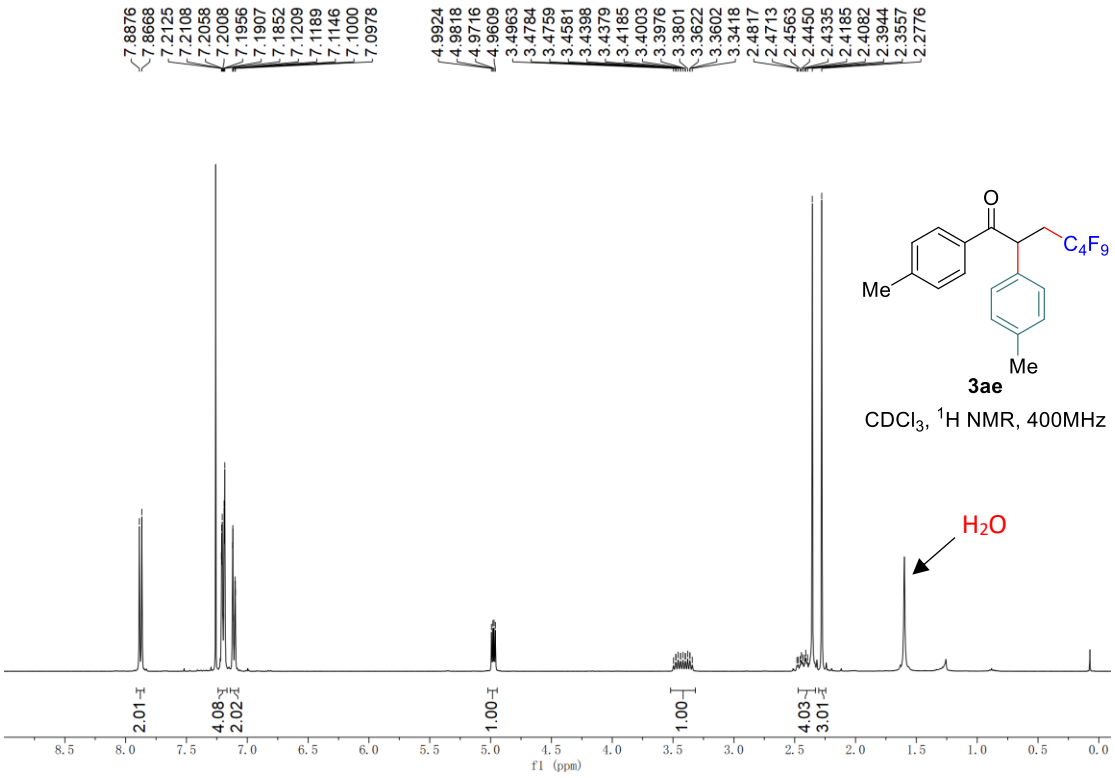
3ad

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



3ad

$CDCl_3$, ^{13}C NMR, 100 MHz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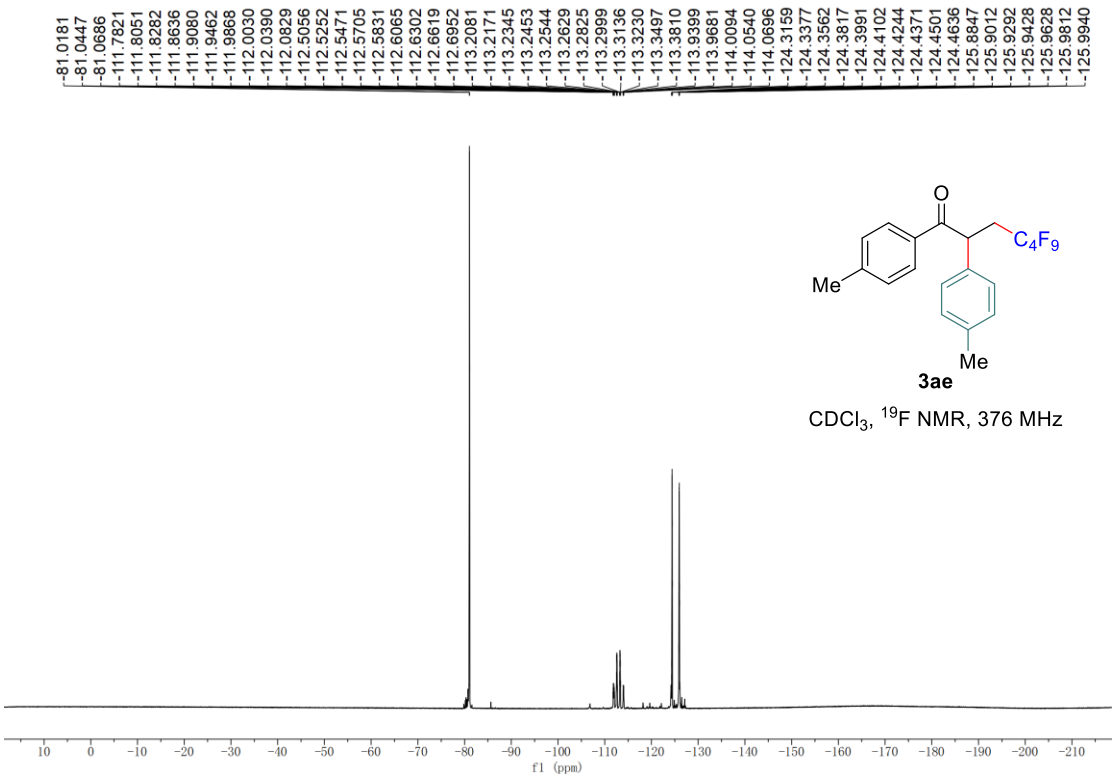
7.8668
7.2125
7.2108
7.2058
7.2008
7.1956
7.1907
7.1852
7.1209
7.1189
7.1146
7.1000
7.0978
4.9924
4.9818
4.9716
4.9609
3.4963
3.4784
3.4759
3.4581
3.4398
3.4379
3.4185
3.4003
3.3976
3.3801
3.3622
3.3602
3.3418
2.4817
2.4713
2.4563
2.4450
2.4335
2.4185
2.4082
2.3944
2.3557
2.2776
O
C4F9
Me
Me
3ae
CDCl3, 1H NMR, 400MHz
H2O
2.01
4.08
2.02
1.00
1.00
4.03
3.01
f1 (ppm)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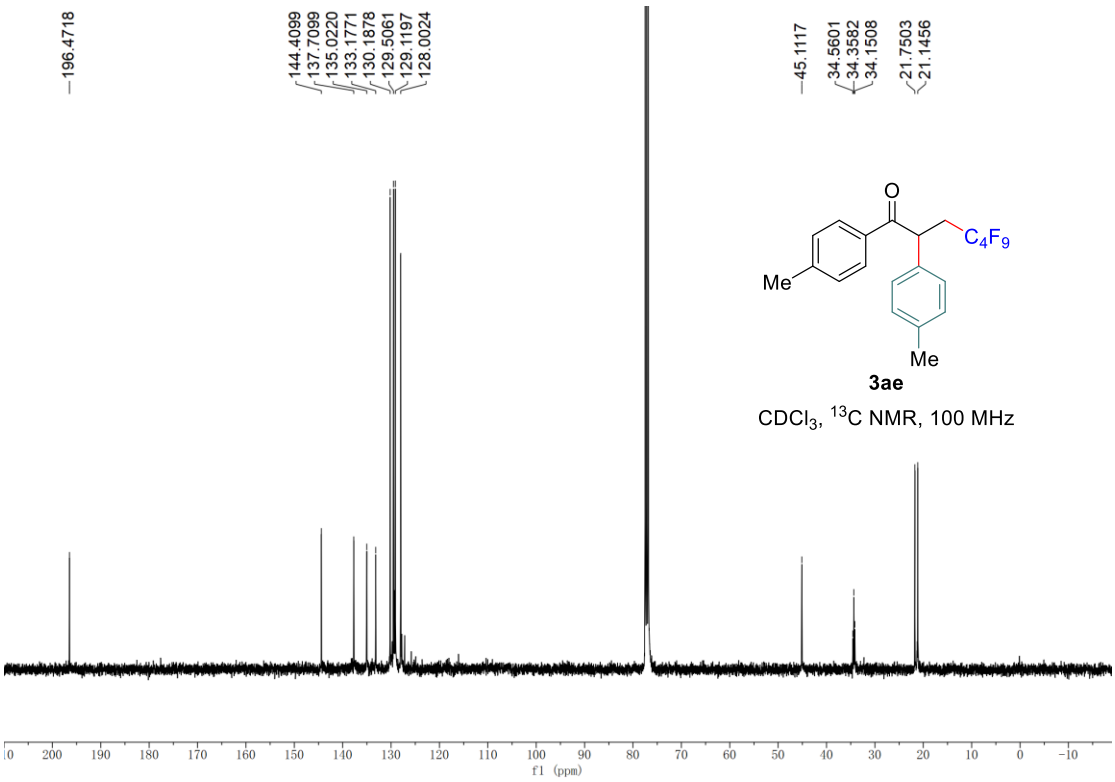
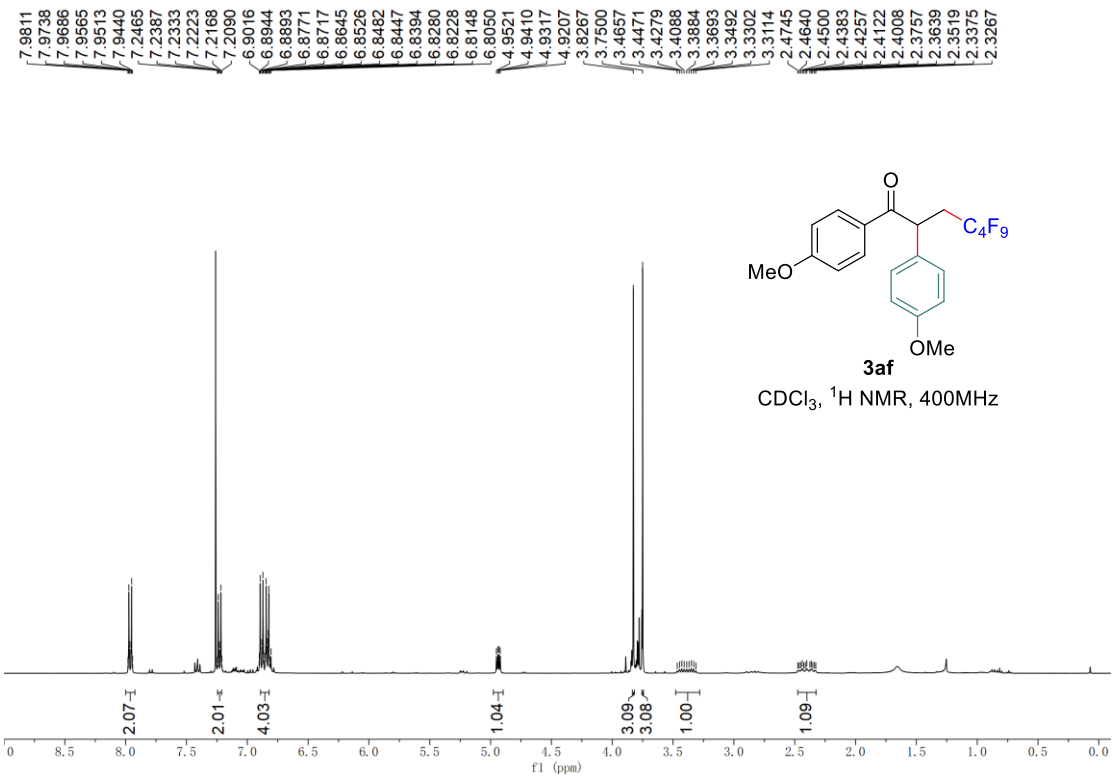
-81.0447
-81.0686
-111.7821
-111.8051
-111.8282
-111.8636
-111.9080
-111.9462
-111.9868
-112.0030
-112.0390
-112.0829
-112.5056
-112.5252
-112.5471
-112.5705
-112.5831
-112.6065
-112.6302
-112.6619
-112.6952
-113.2081
-113.2171
-113.2345
-113.2453
-113.2544
-113.2629
-113.2825
-113.2999
-113.3136
-113.3230
-113.3497
-113.3810
-113.9399
-113.9681
-114.0094
-114.0540
-114.0696
-124.3159
-124.3377
-124.3562
-124.3817
-124.3991
-124.4102
-124.4244
-124.4371
-124.4501
-124.4636
-125.8847
-125.9012
-125.9292
-125.9428
-125.9628
-125.9812
-125.9940
O
C4F9
Me
Me
3ae
CDCl3, 19F NMR, 376 MHz
f1 (ppm)



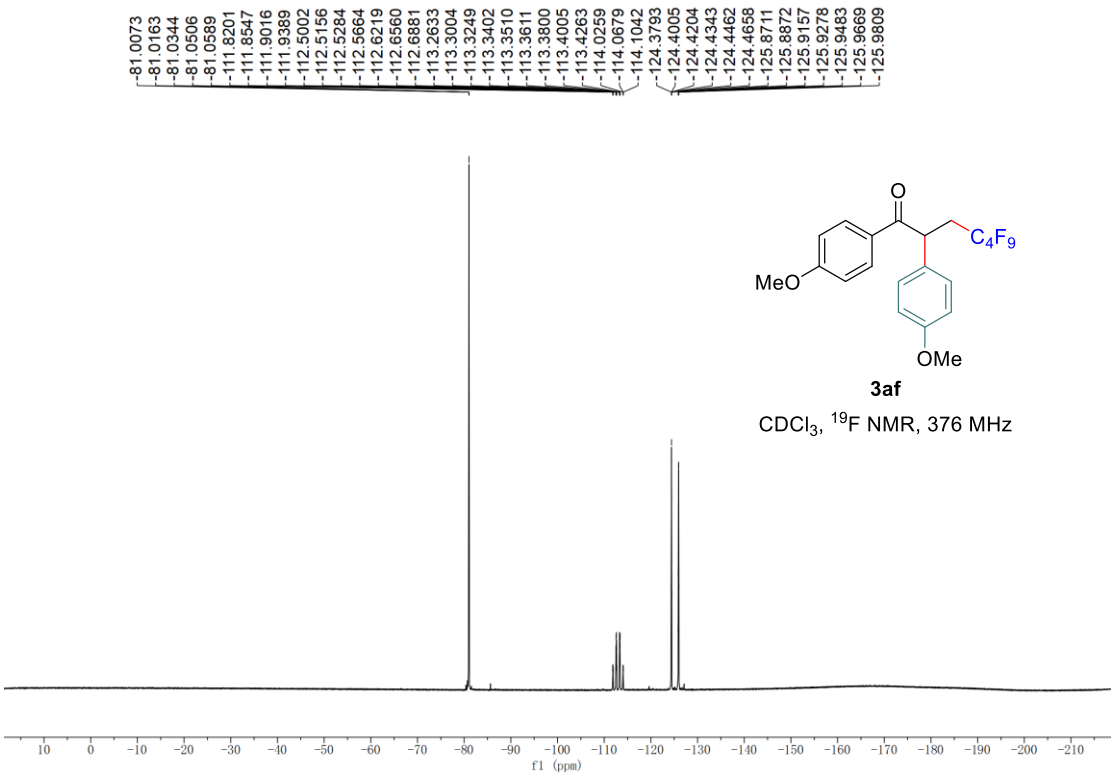
3ae

$CDCl_3$, ^{13}C NMR, 100 MHz



3af

$CDCl_3$, ^{1}H NMR, 400MHz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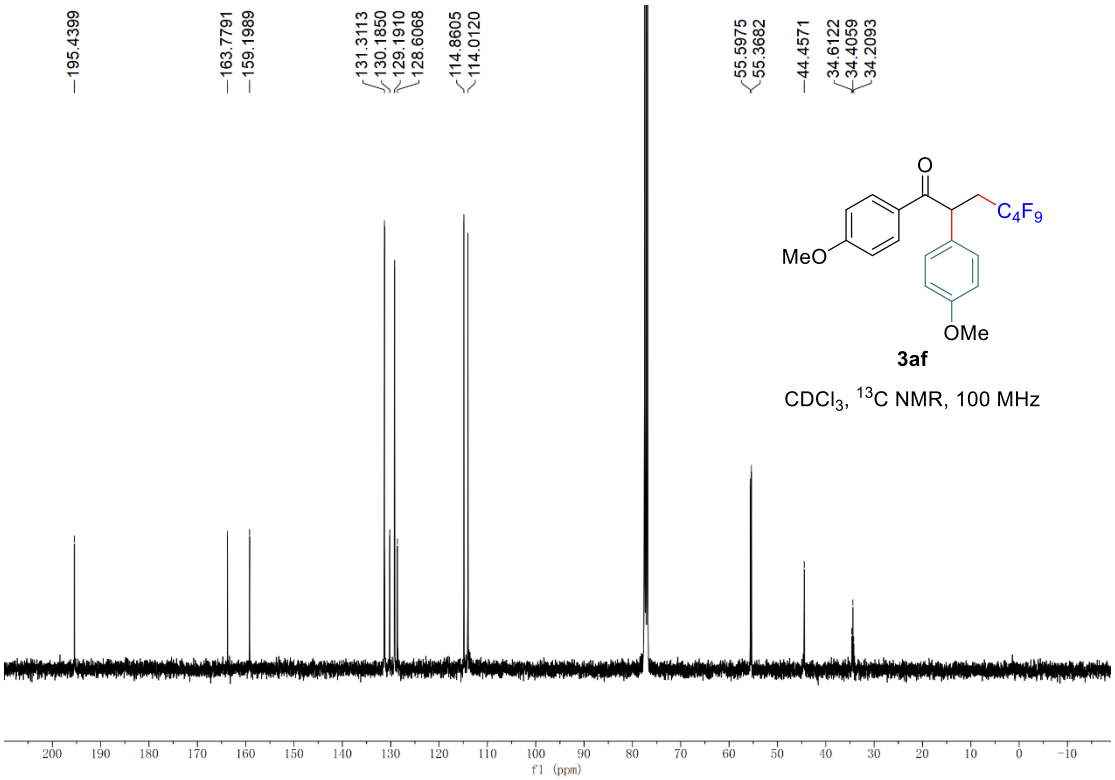
-81.0163
-81.0344
-81.0506
-81.0589
-111.8201
-111.8547
-111.9016
-111.9389
-112.5002
-112.5156
-112.5284
-112.5664
-112.6219
-112.6560
-112.6881
-113.2633
-113.3004
-113.3249
-113.3402
-113.3510
-113.3611
-113.3800
-113.4005
-113.4263
-114.0259
-114.0679
-114.1042
-124.3793
-124.4005
-124.4204
-124.4343
-124.4462
-124.4658
-125.8711
-125.8872
-125.9157
-125.9278
-125.9483
-125.9669
-125.9809
O
C4F9
MeO
OMe
3af
CDCl3, 19F NMR, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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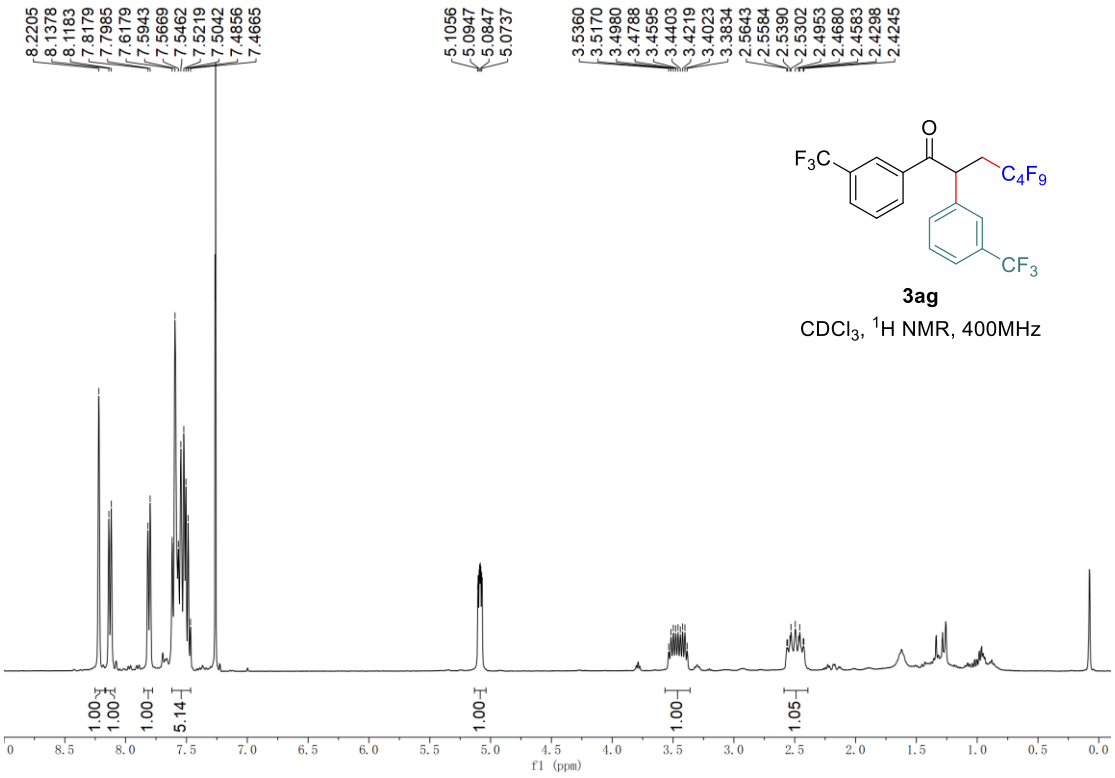
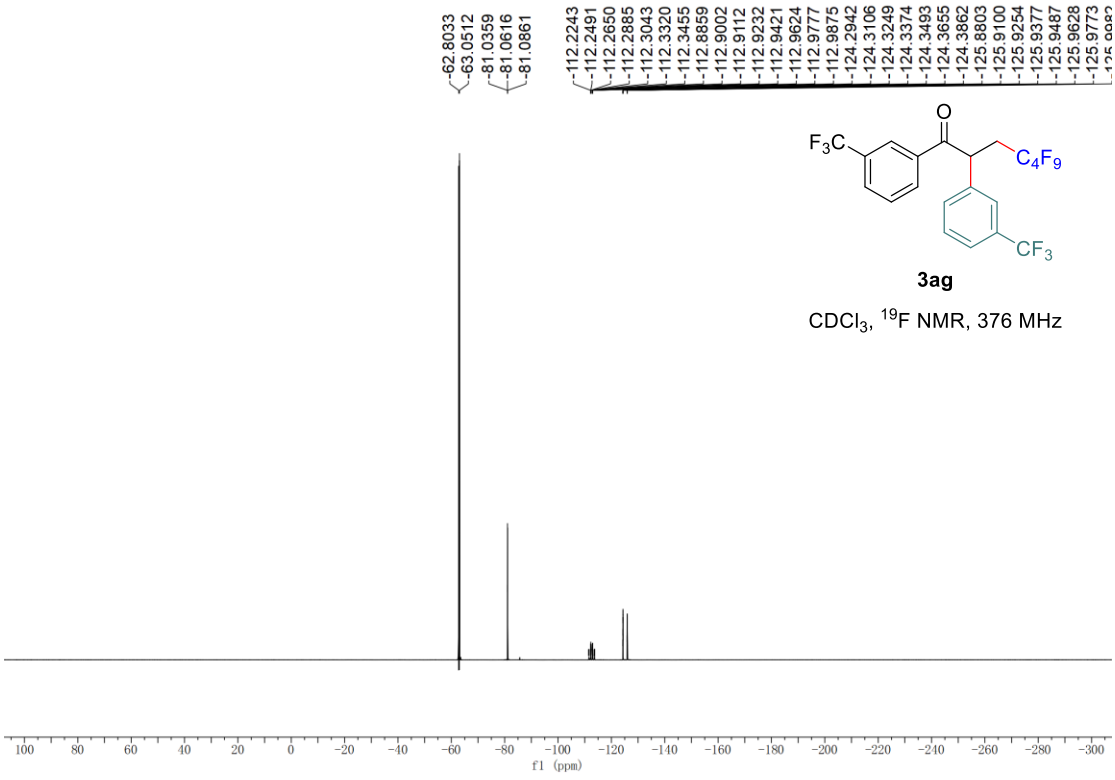
163.7791
159.1989
131.3113
130.1850
129.1910
128.6068
114.8605
114.0120
55.5975
55.3682
44.4571
34.6122
34.4059
34.2093
O
C4F9
MeO
OMe
3af
CDCl3, 13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



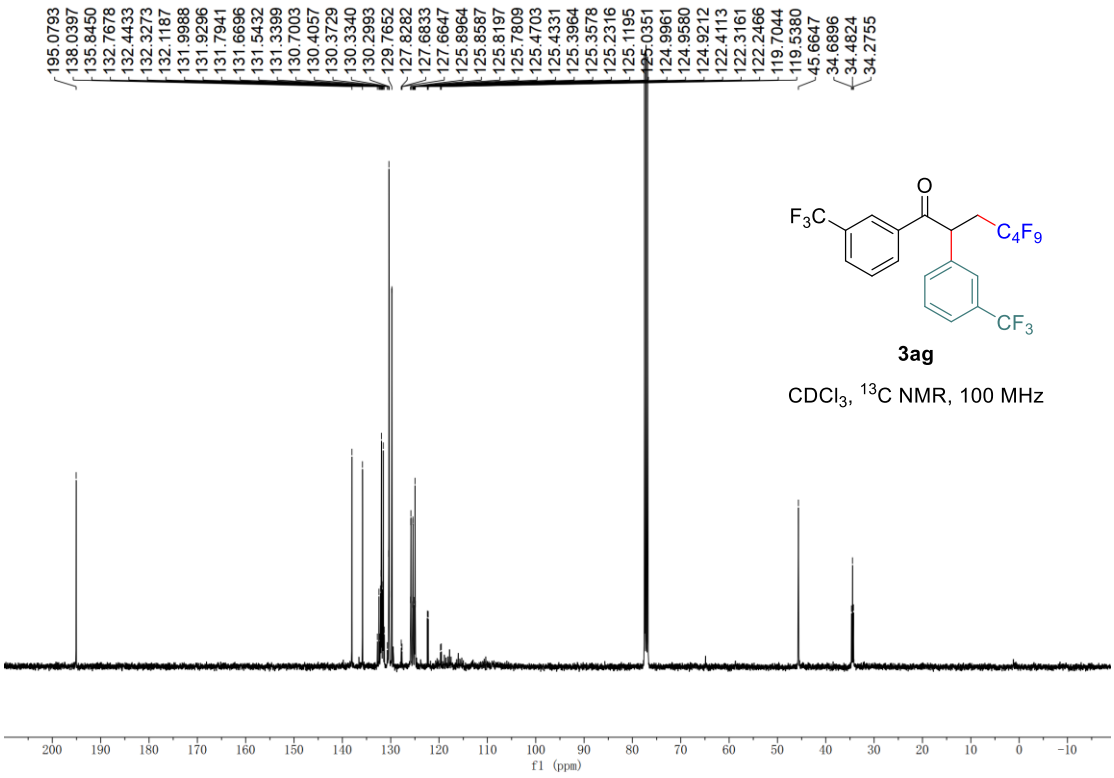
3ag

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



3ag

$CDCl_3$, ^{19}F NMR, 376 MHz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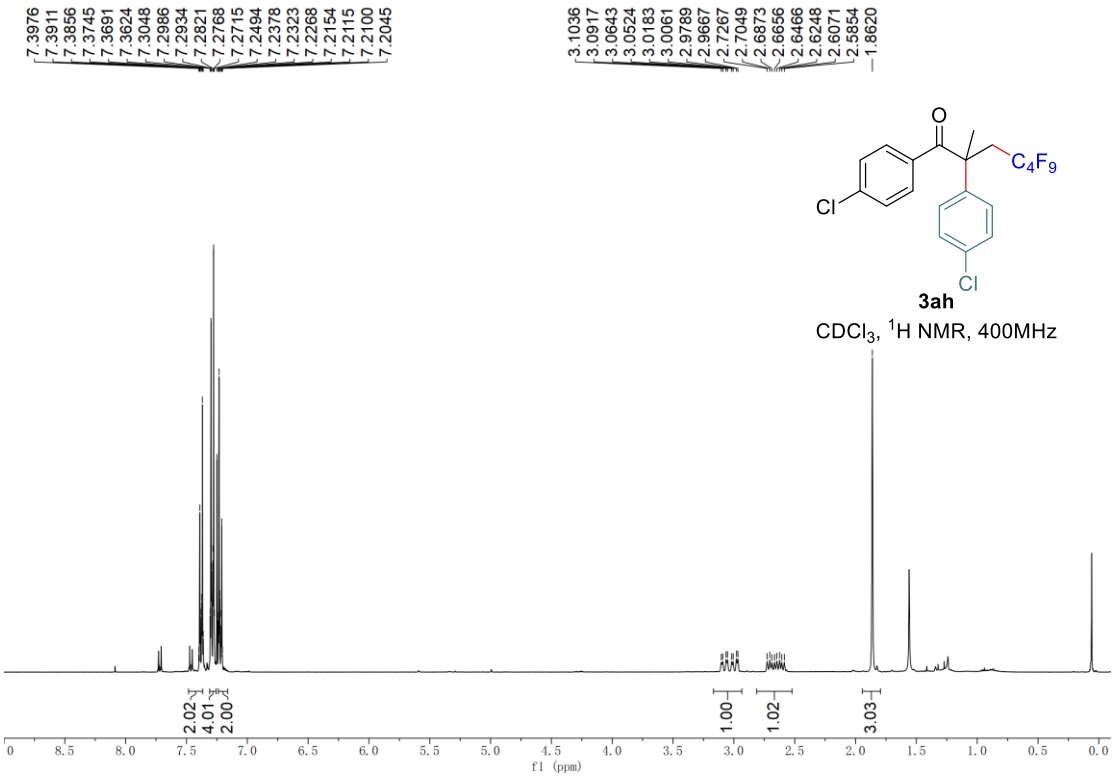
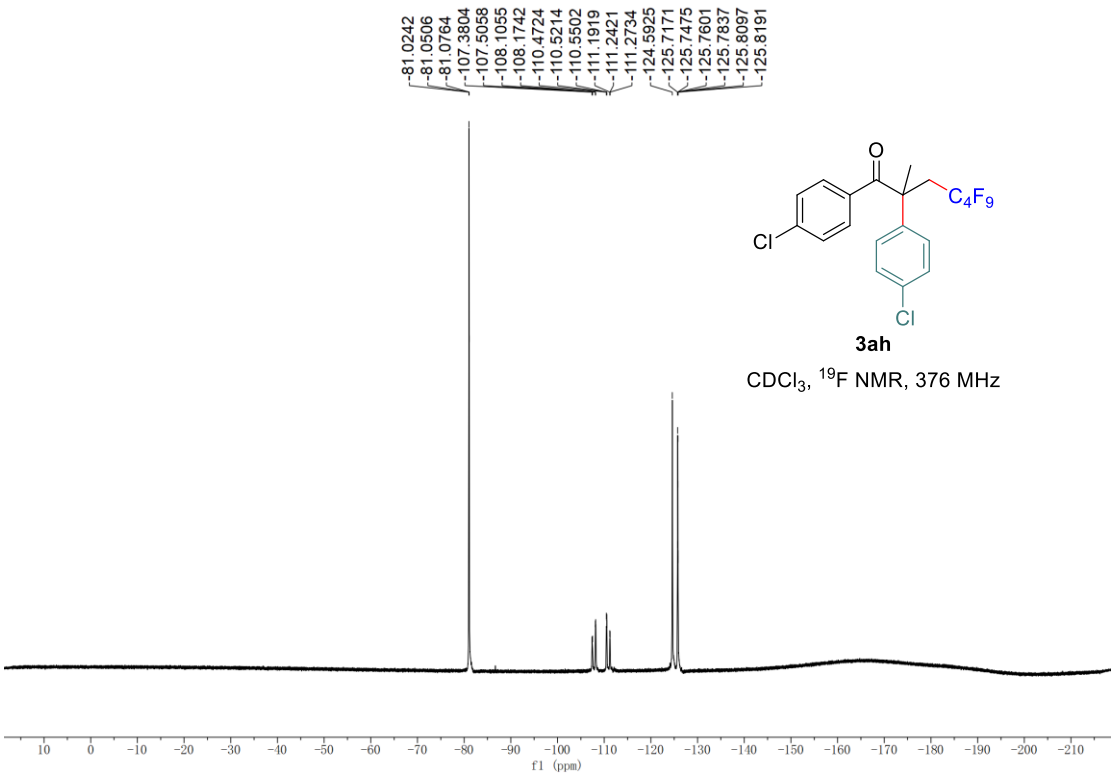
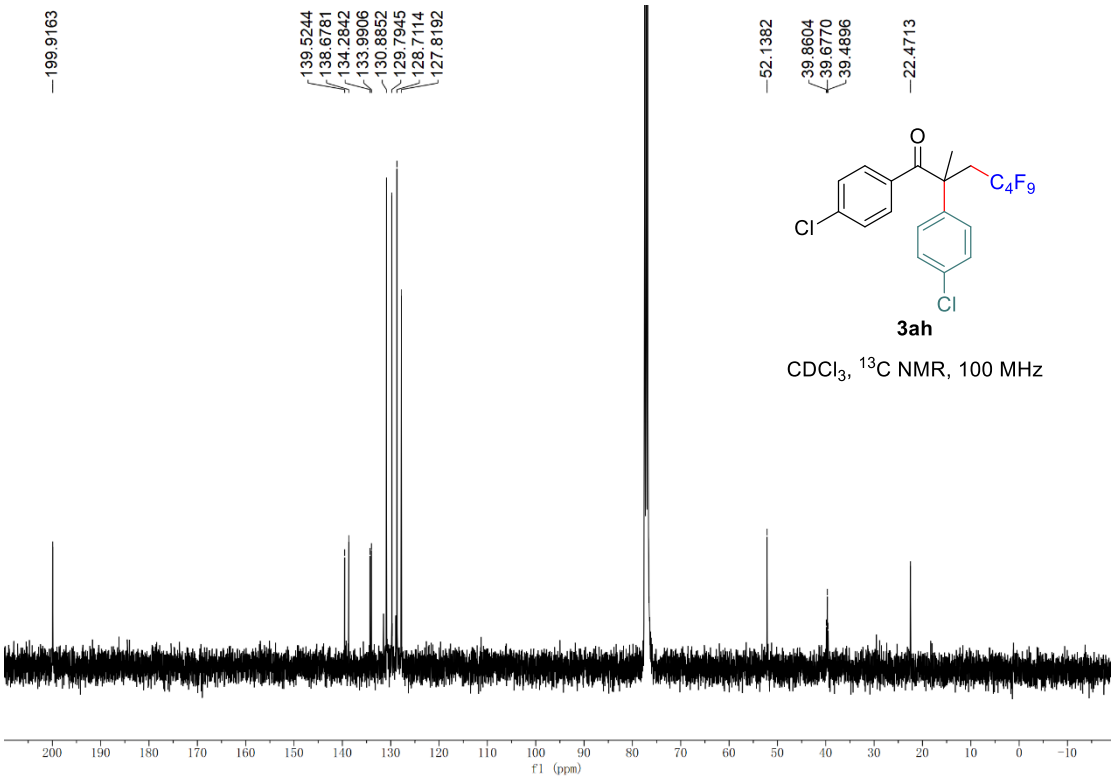
132.7678
132.4433
132.3273
132.1187
131.9988
131.9296
131.7941
131.6696
131.5432
131.3399
130.7003
130.4057
130.3729
130.3340
130.2993
129.7652
127.8282
127.6833
127.6647
125.8964
125.8587
125.8197
125.7809
125.4703
125.4331
125.3964
125.3578
125.2316
125.1195
125.0351
124.9961
124.9580
124.9212
122.4113
122.3161
122.2466
119.7044
119.5380
45.6647
34.6896
34.4824
34.2755
O
F3C
C4F9
CF3
3ag
CDCl3, 13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.3976
7.3911
7.3856
7.3745
7.3691
7.3624
7.3048
7.2986
7.2934
7.2821
7.2768
7.2715
7.2494
7.2378
7.2323
7.2268
7.2154
7.2115
7.2100
7.2045
3.1036
3.0917
3.0643
3.0524
3.0183
3.0061
2.9789
2.9667
2.7267
2.7049
2.6873
2.6656
2.6466
2.6248
2.6071
2.5854
1.8620
O
C4F9
Cl
Cl
3ah
CDCl3, 1H NMR, 400MHz
2.02
4.01
2.00
1.00
1.02
3.03
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)



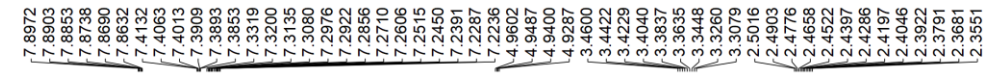
3ah

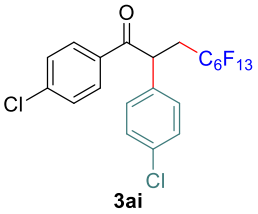
$CDCl_3$, ^{19}F NMR, 376 MHz



3ah

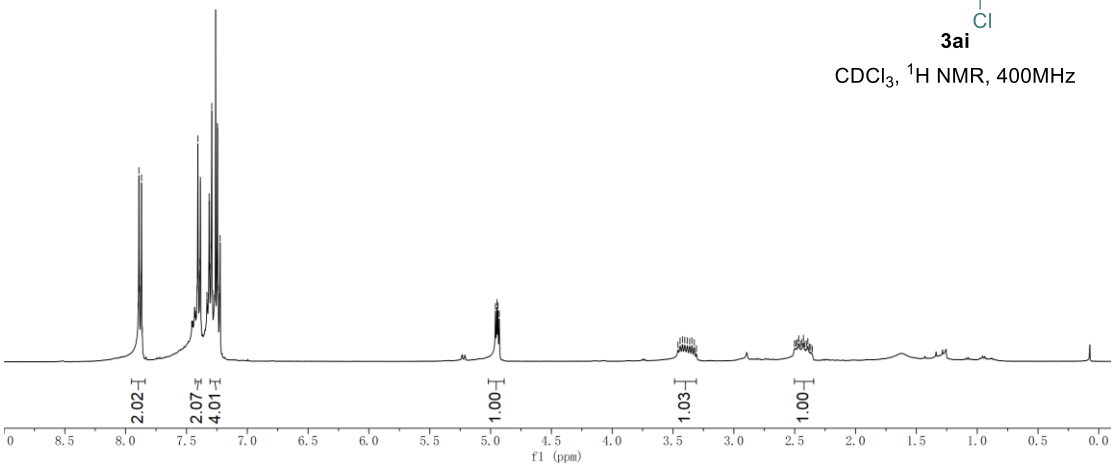
$CDCl_3$, ^{13}C NMR, 100 MHz

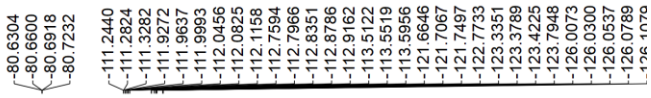


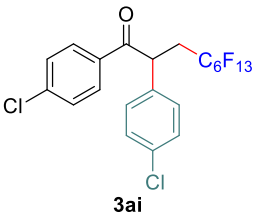


3ai

$CDCl_3$, ^1H NMR, 400MHz

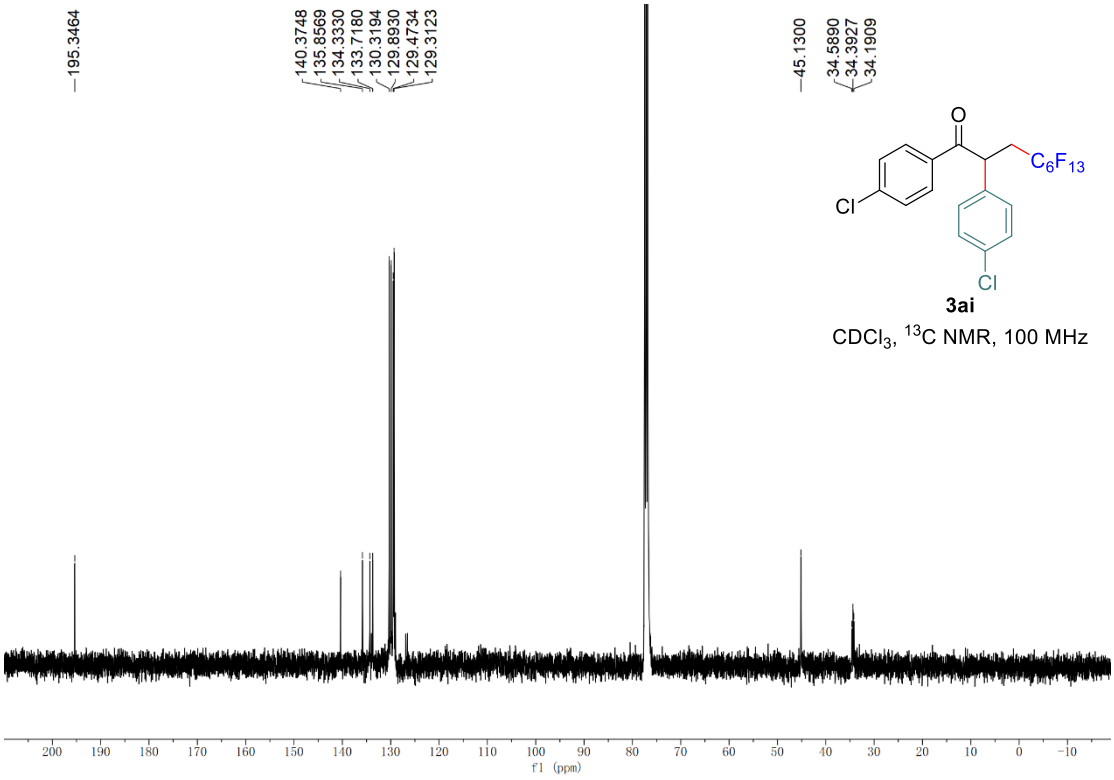






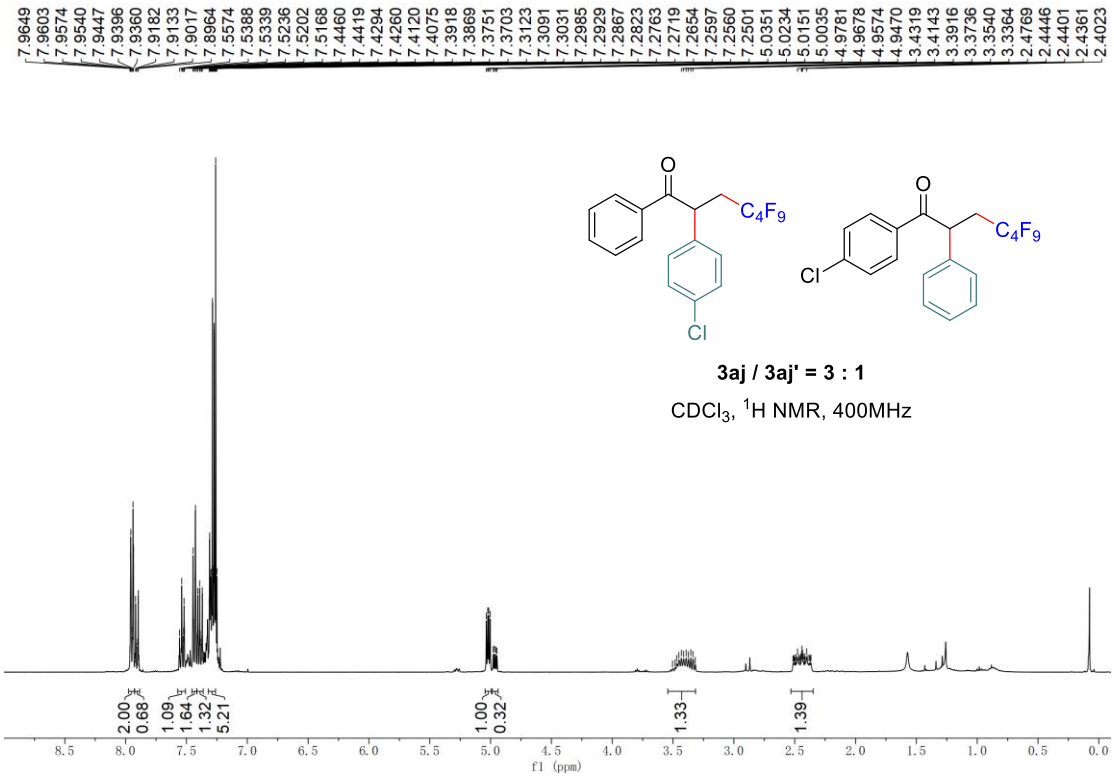
3ai

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



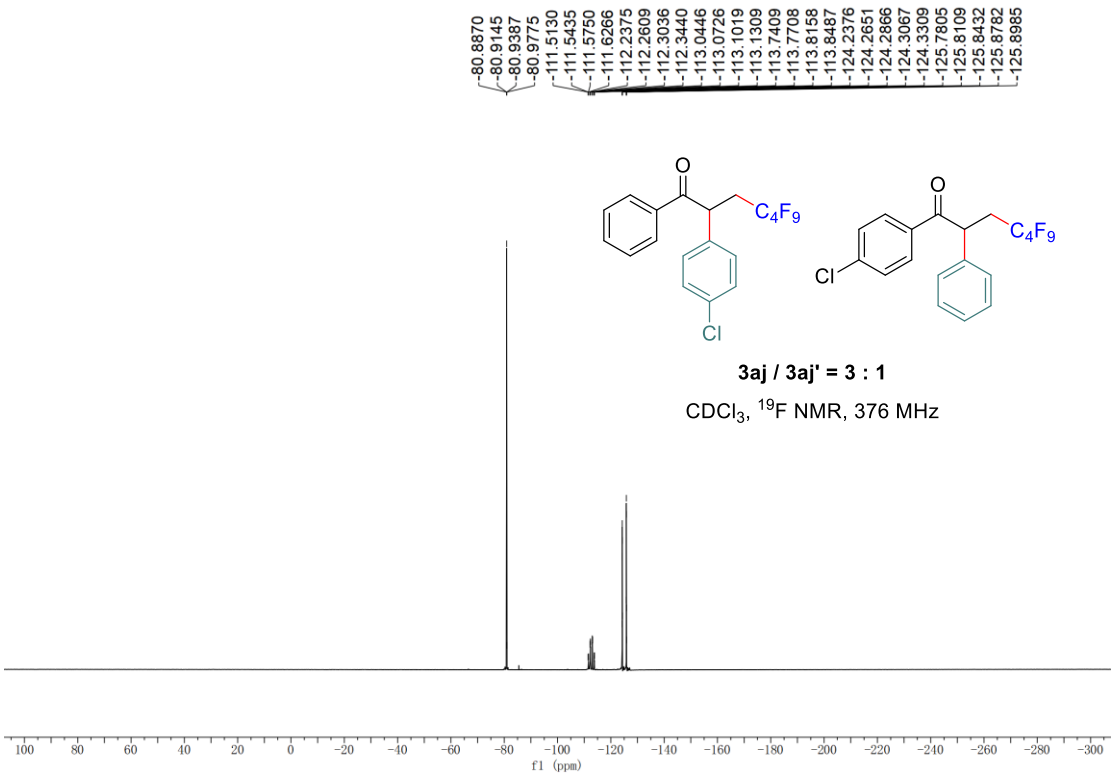
3ai

$CDCl_3$, ^{13}C NMR, 100 MHz



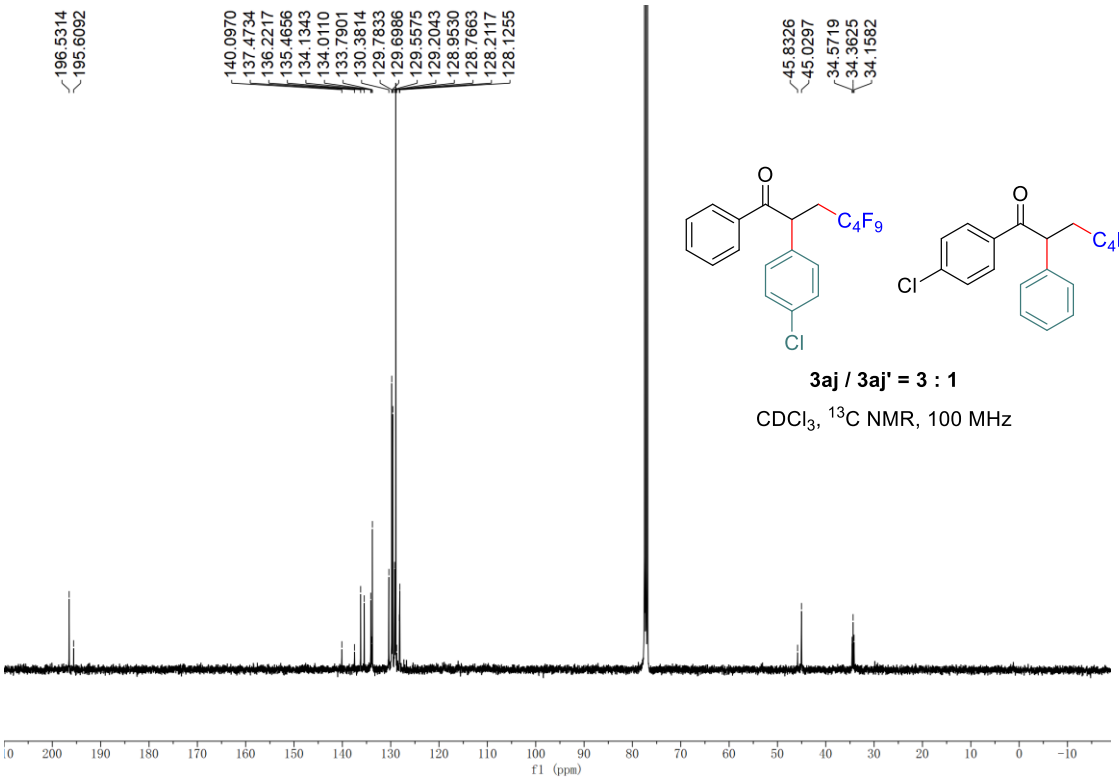
3aj / 3aj' = 3 : 1

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



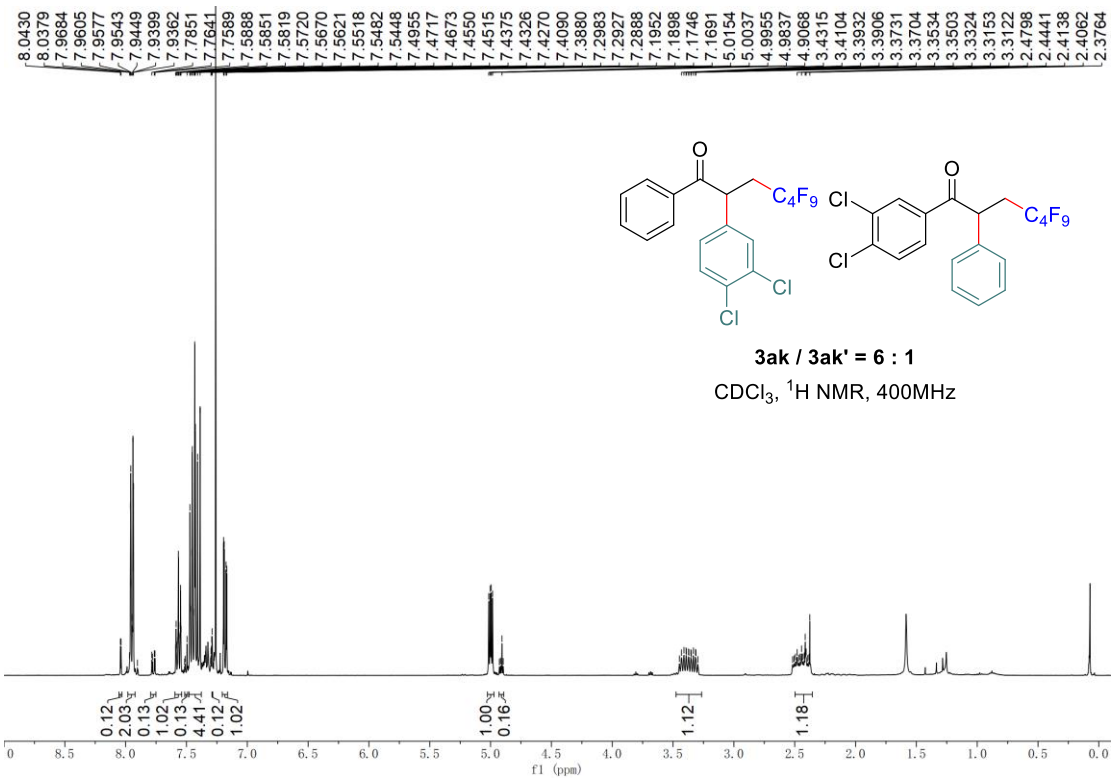
3aj / 3aj' = 3 : 1

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



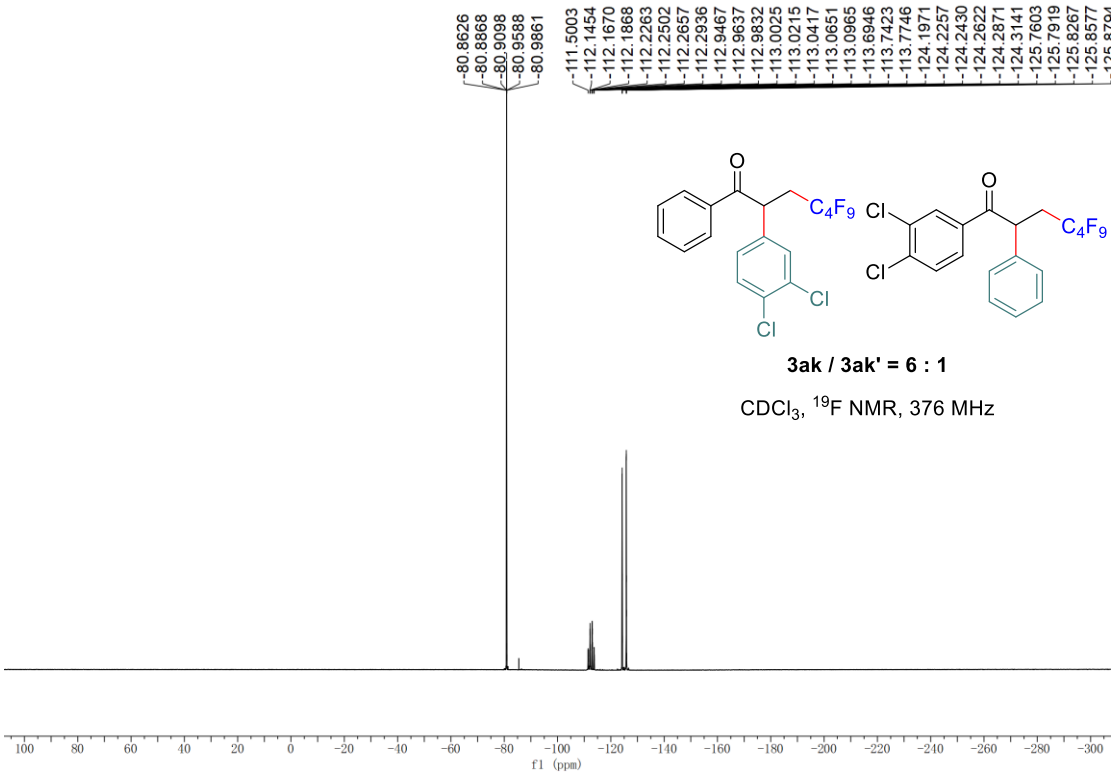
3aj / 3aj' = 3 : 1

$CDCl_3$, ^{13}C NMR, 100 MHz



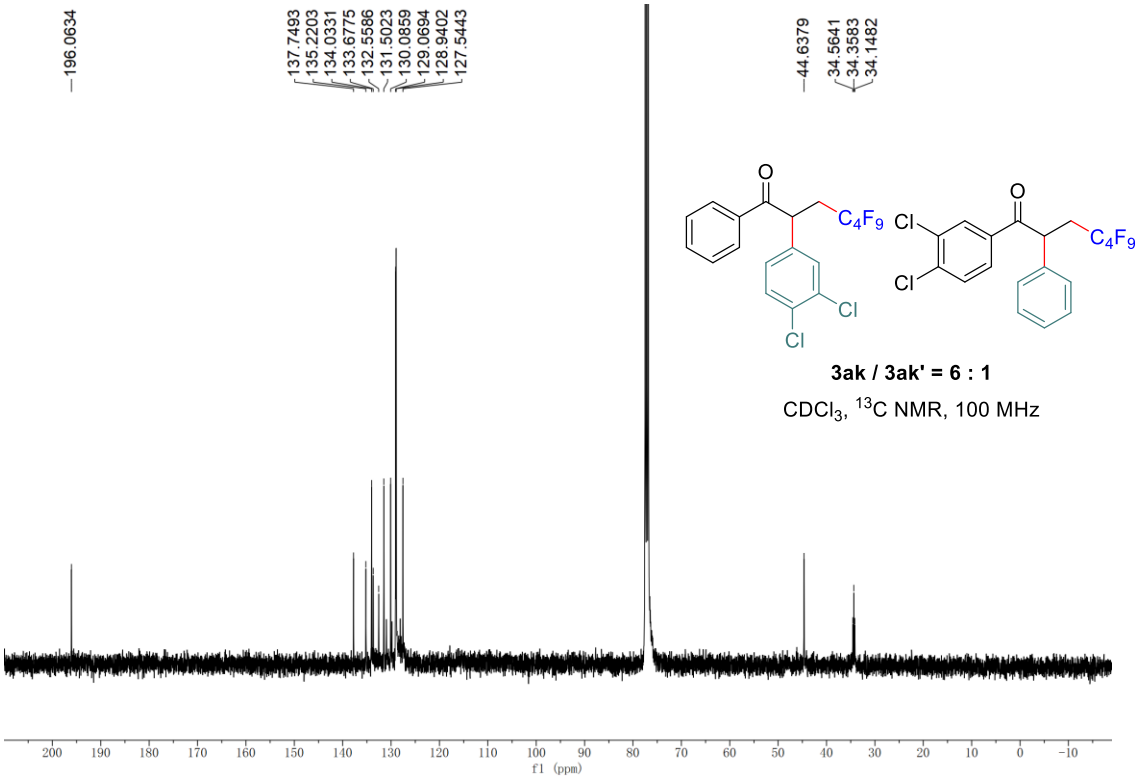
3ak / 3ak' = 6 : 1

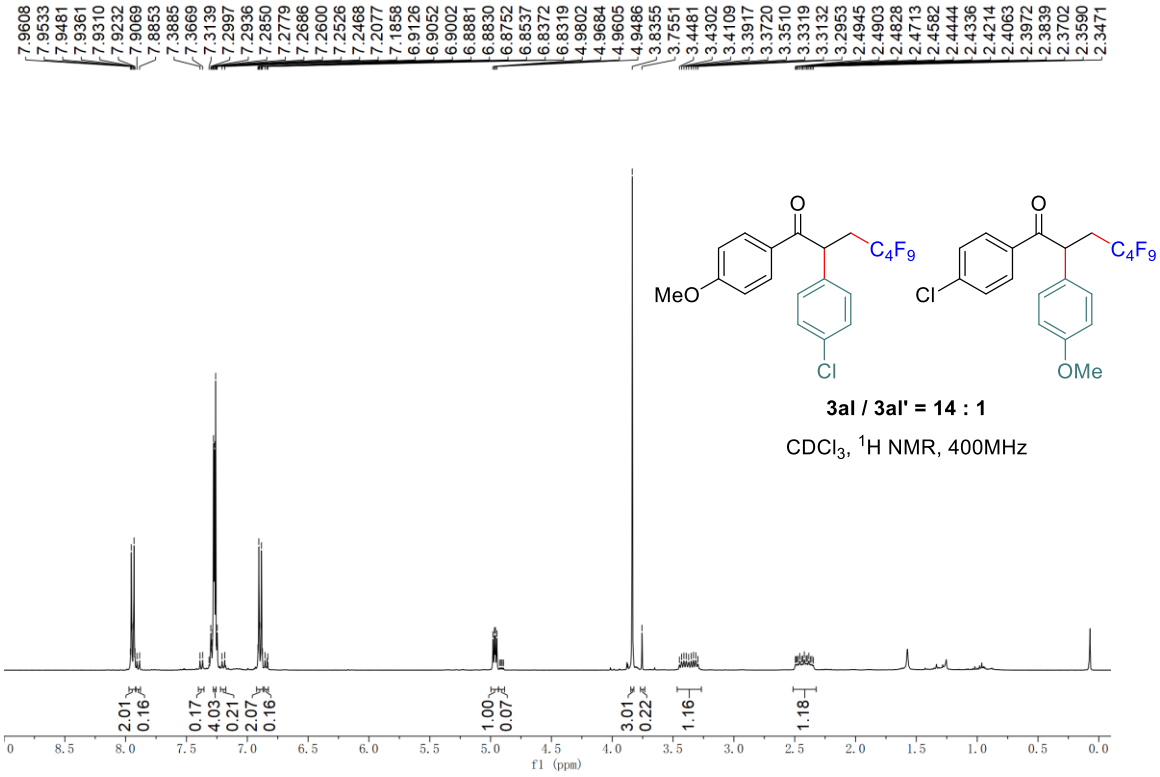
$CDCl_3$, ^{1}H NMR, 400MHz

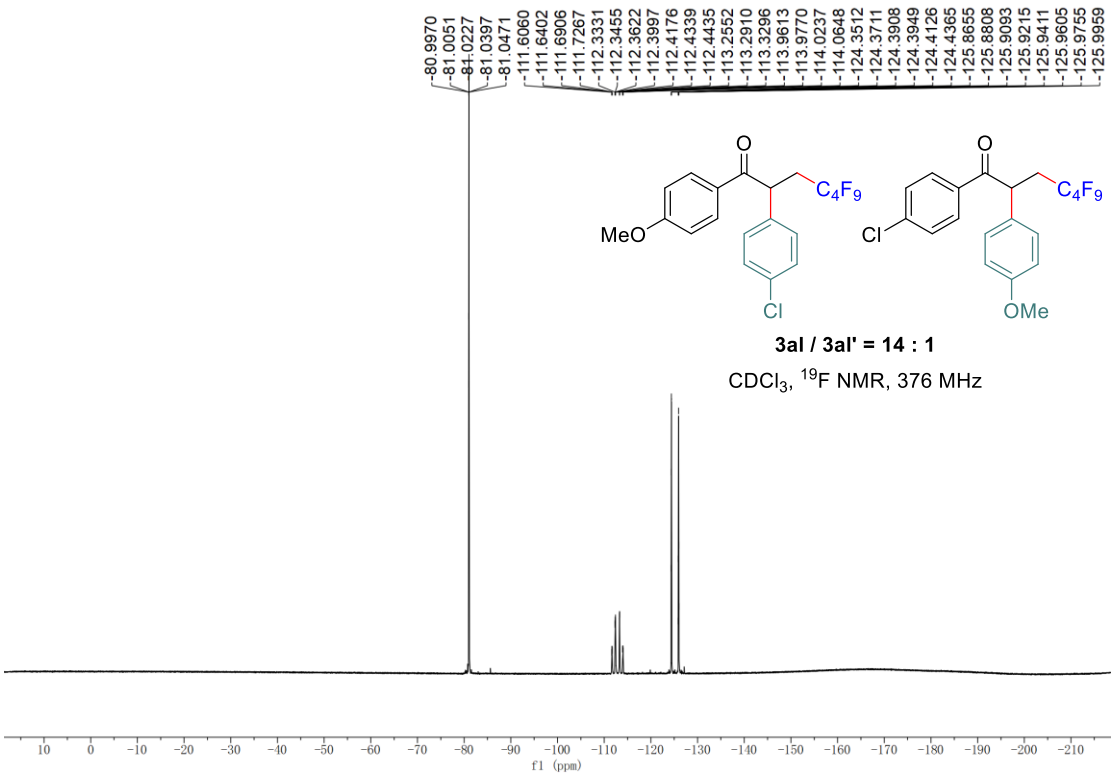


3ak / 3ak' = 6 : 1

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


196.0634
137.7493
135.2203
134.0331
133.6775
132.5586
131.5023
130.0859
129.0694
128.9402
127.5443
44.6379
34.5641
34.3583
34.1482
O
C4F9
Cl
Cl
O
Cl
Cl
C4F9
3ak / 3ak' = 6 : 1
CDCl3, 13C NMR, 100 MHz
f1 (ppm)


7.9608
7.9533
7.9481
7.9361
7.9310
7.9232
7.9069
7.8853
7.3885
7.3669
7.3139
7.2997
7.2936
7.2850
7.2779
7.2686
7.2600
7.2526
7.2468
7.2077
7.1858
6.9126
6.9052
6.9002
6.8881
6.8830
6.8752
6.8537
6.8372
6.8319
4.9802
4.9684
4.9605
4.9486
3.8355
3.7551
3.4481
3.4302
3.4109
3.3917
3.3720
3.3510
3.3319
3.3132
3.2953
2.4945
2.4903
2.4828
2.4713
2.4582
2.4444
2.4336
2.4214
2.4063
2.3972
2.3839
2.3702
2.3590
2.3471
O
C4F9
MeO
Cl
O
C4F9
Cl
OMe
3al / 3al' = 14 : 1
CDCl3, 1H NMR, 400MHz
2.01
0.16
0.17
4.03
0.21
2.07
0.16
1.00
0.07
3.01
0.22
1.16
1.18
f1 (ppm)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-111.6060
-111.6402
-111.6906
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-112.3331
-112.3455
-112.3622
-112.3997
-112.4176
-112.4339
-112.4435
-113.2552
-113.2910
-113.3296
-113.9613
-113.9770
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-114.0648
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-124.3711
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-124.4126
-124.4365
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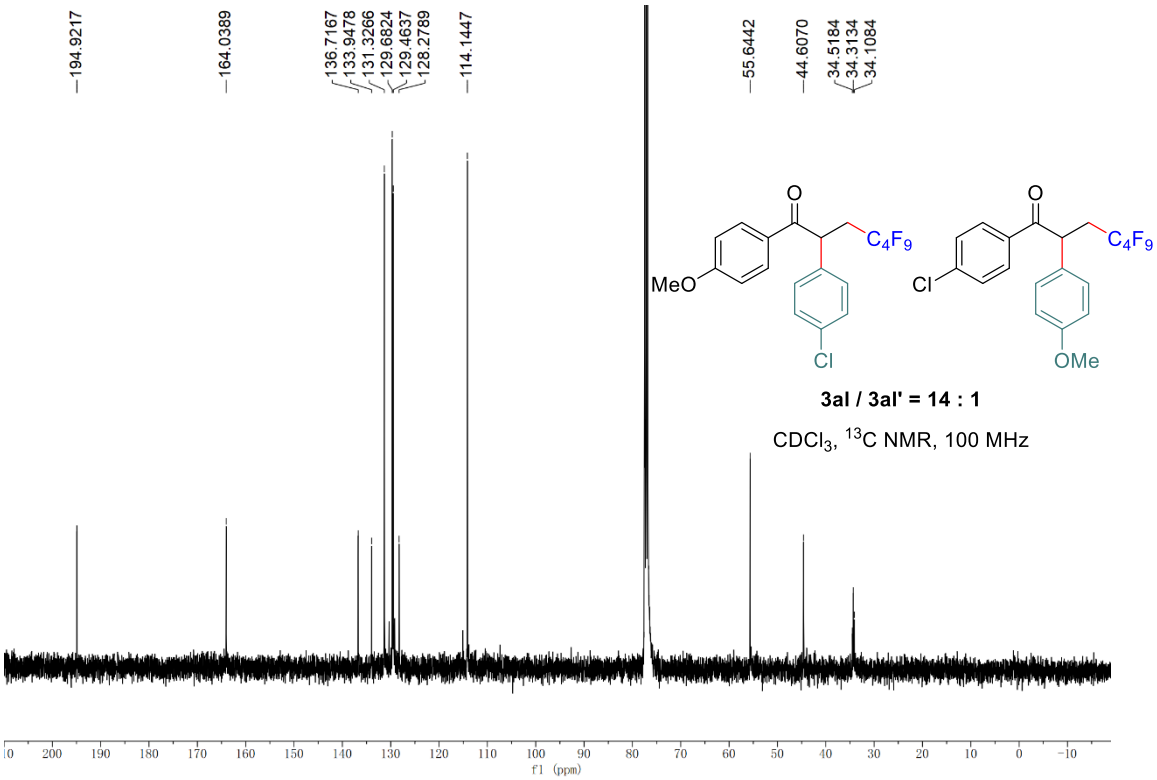
-125.8808
-125.9093
-125.9215
-125.9411
-125.9605
-125.9755
-125.9959
O
C4F9
MeO
Cl
O
C4F9
Cl
OMe
3al / 3al' = 14 : 1
CDCl3, 19F NMR, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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131.3266
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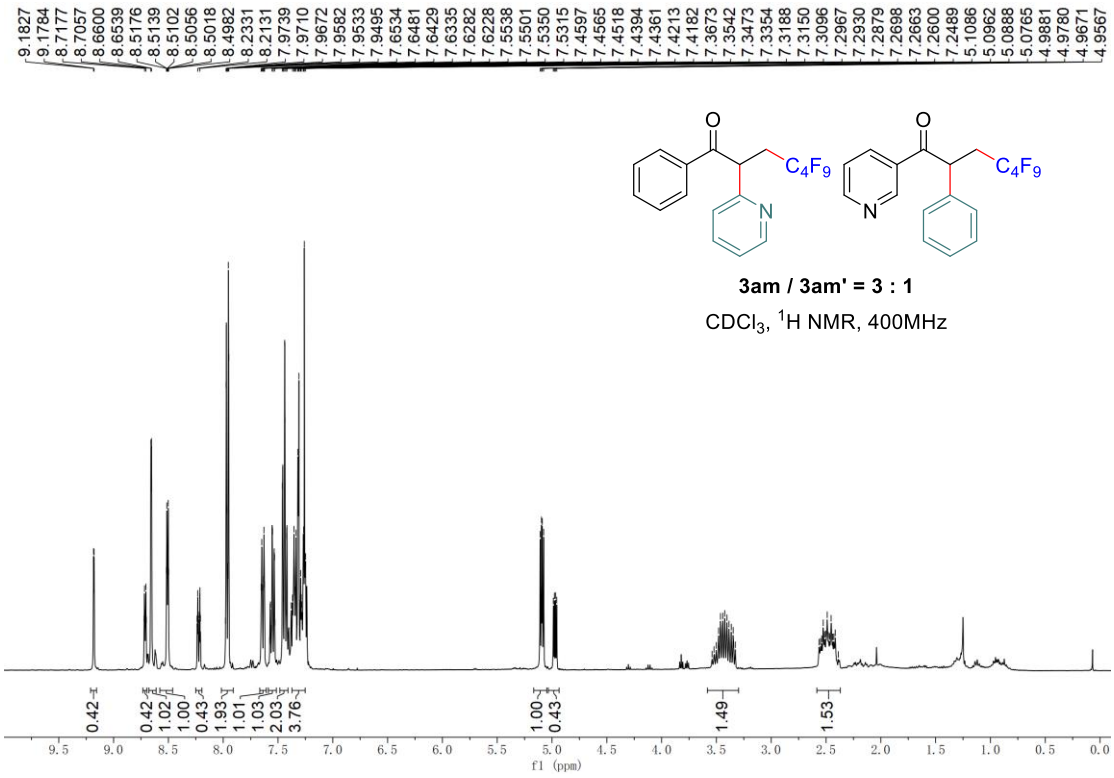
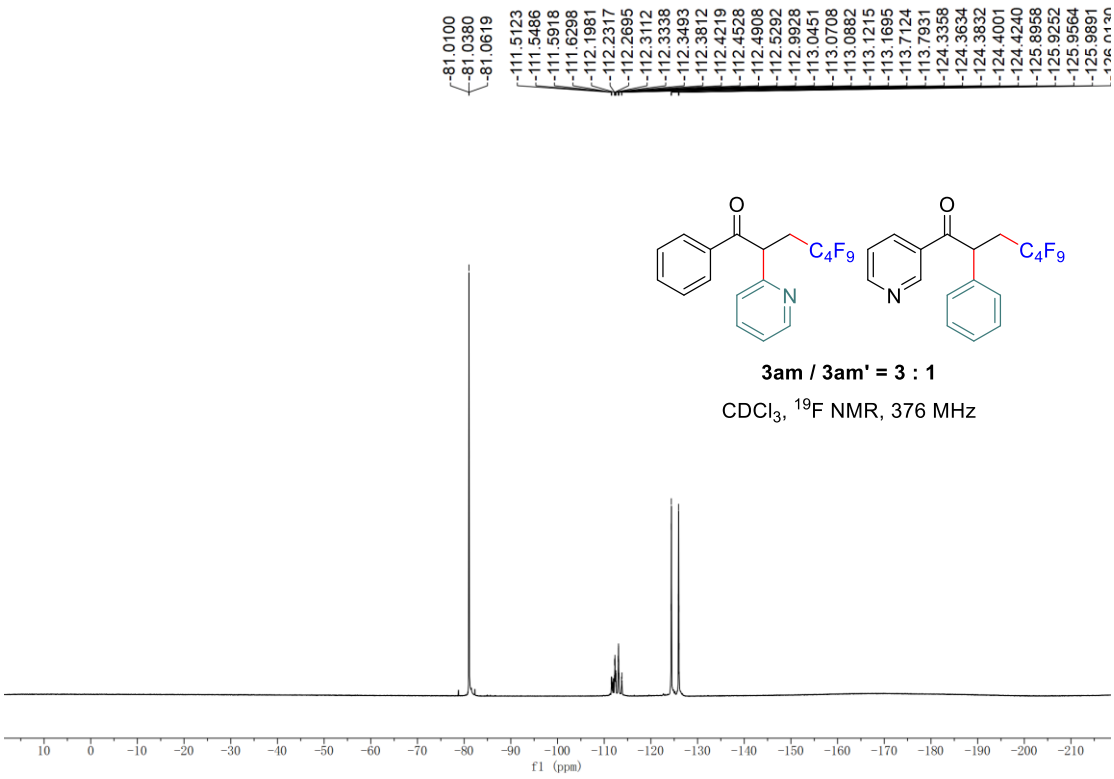
114.1447
55.6442
44.6070
34.5184
34.3134
34.1084
O
C4F9
MeO
Cl
O
C4F9
Cl
OMe
3al / 3al' = 14 : 1
CDCl3, 13C NMR, 100 MHz
0 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



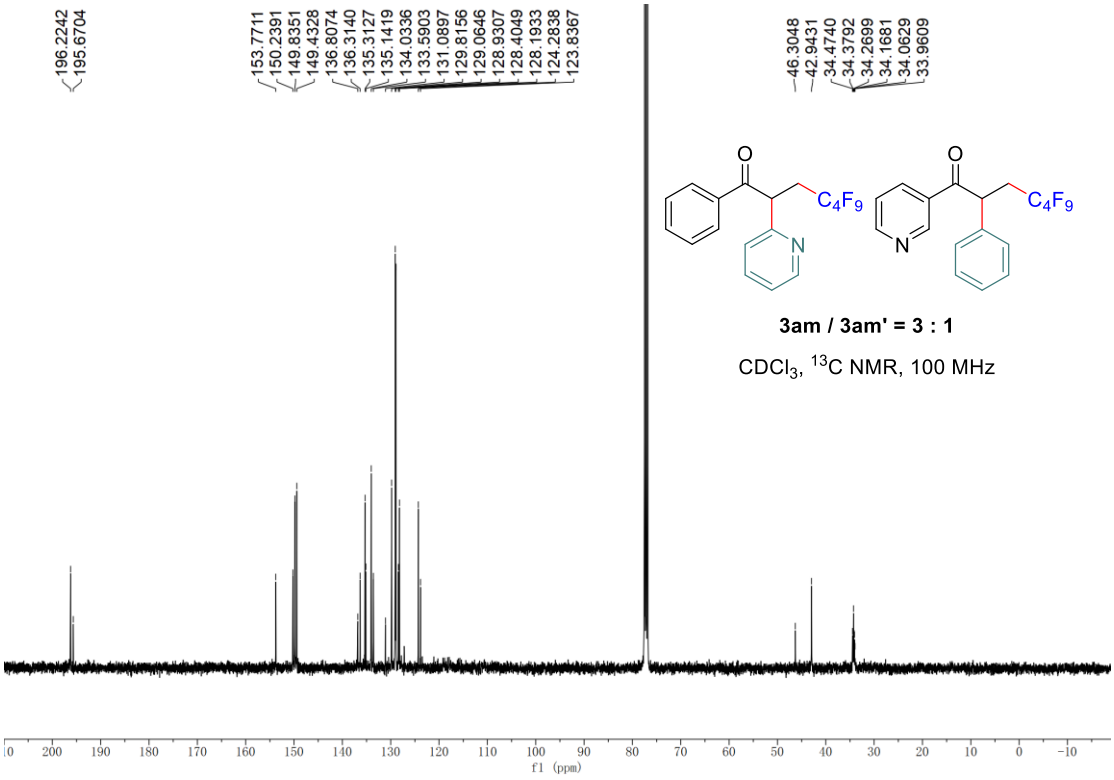
3am / 3am' = 3 : 1

$CDCl_3$, ^1H NMR, 400MHz



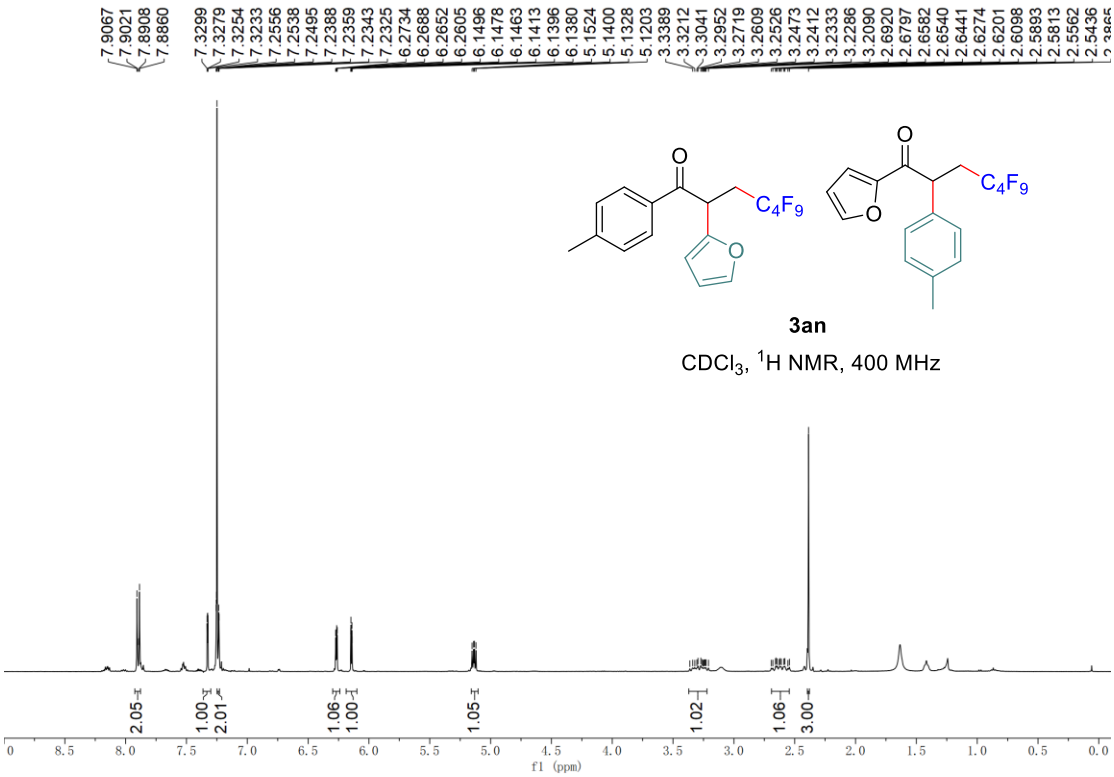
3am / 3am' = 3 : 1

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



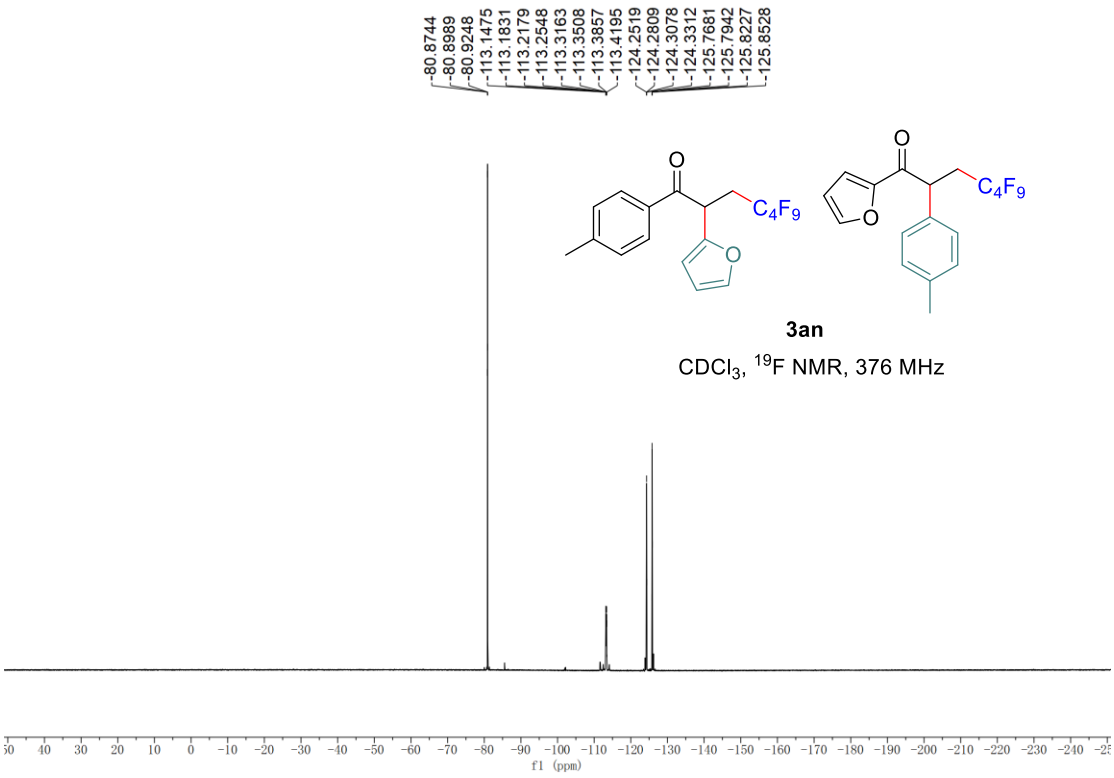
3am / 3am' = 3 : 1

$CDCl_3$, ^{13}C NMR, 100 MHz



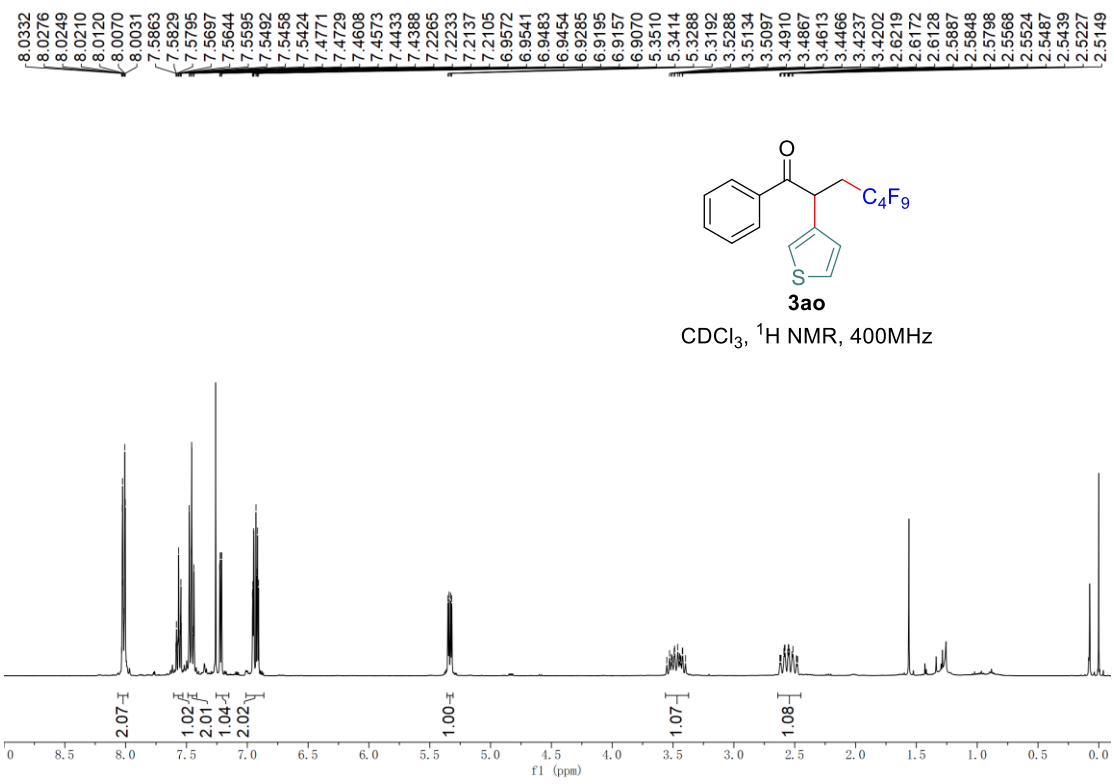
3an

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



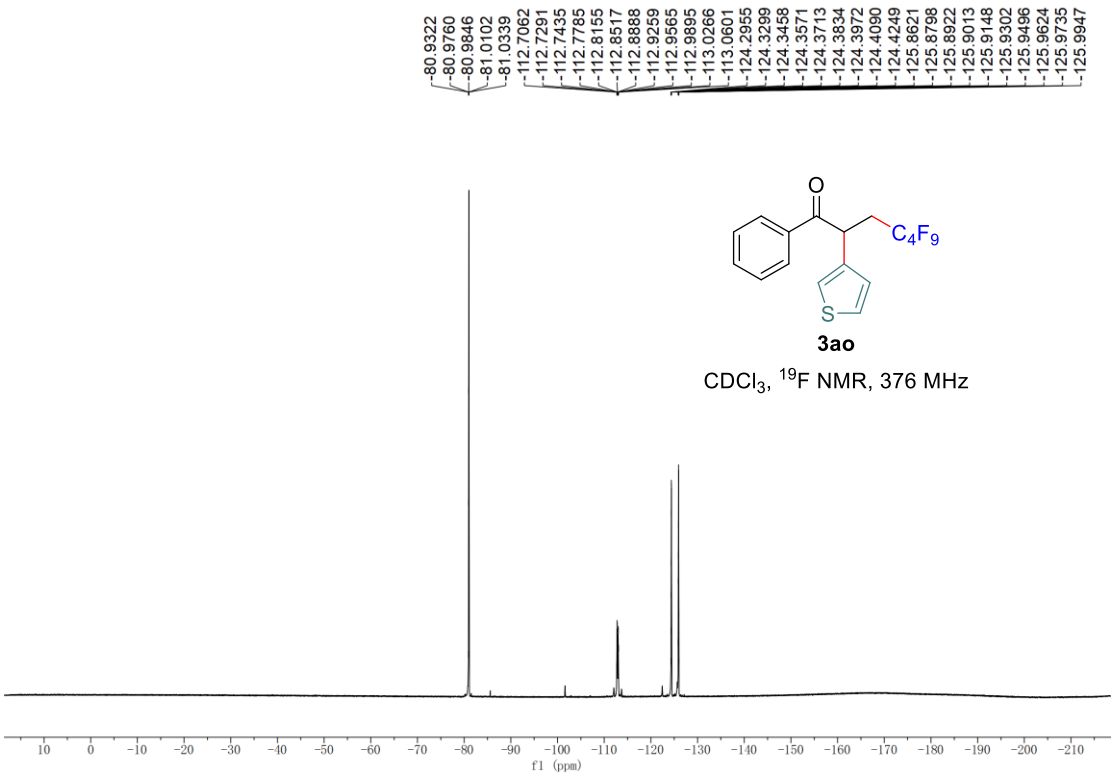
3an

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



3ao

$CDCl_3$, ^{1}H NMR, 400MHz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-112.8517
-112.8888
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-112.9565
-112.9895
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-124.3458
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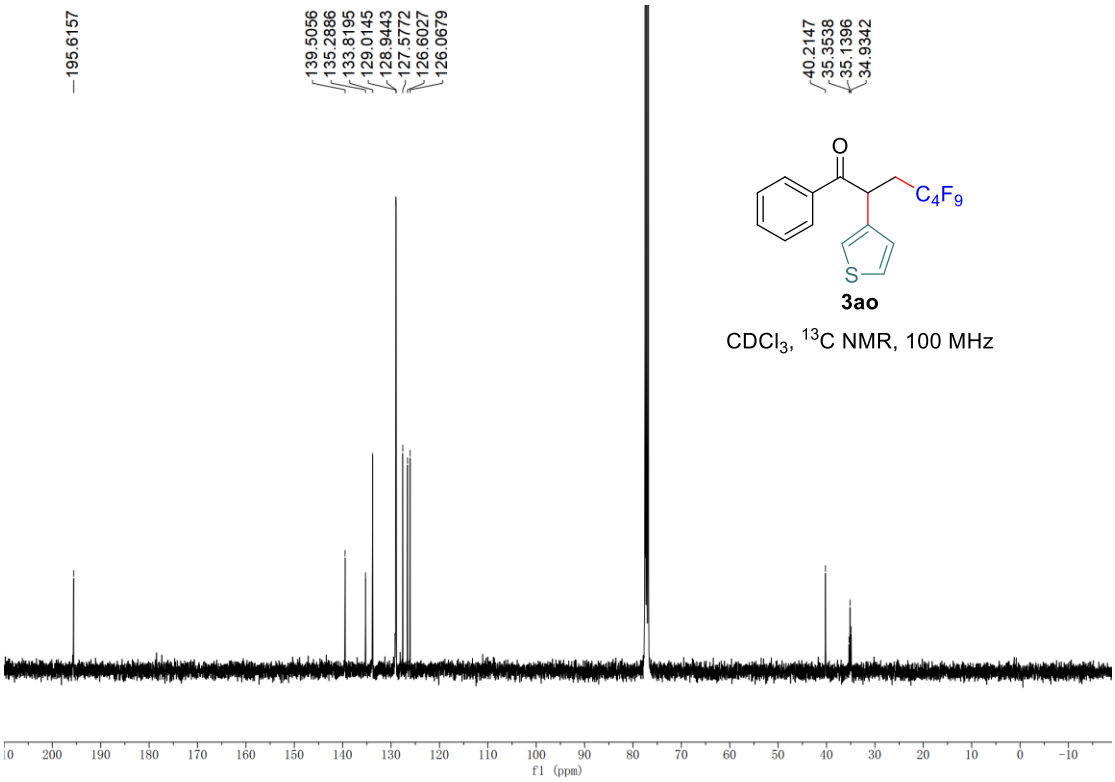
-124.4090
-124.4249
-125.8621
-125.8798
-125.8922
-125.9013
-125.9148
-125.9302
-125.9496
-125.9624
-125.9735
-125.9947
O
C4F9
S
3ao
CDCl3, 19F NMR, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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129.0145
128.9443
127.5772
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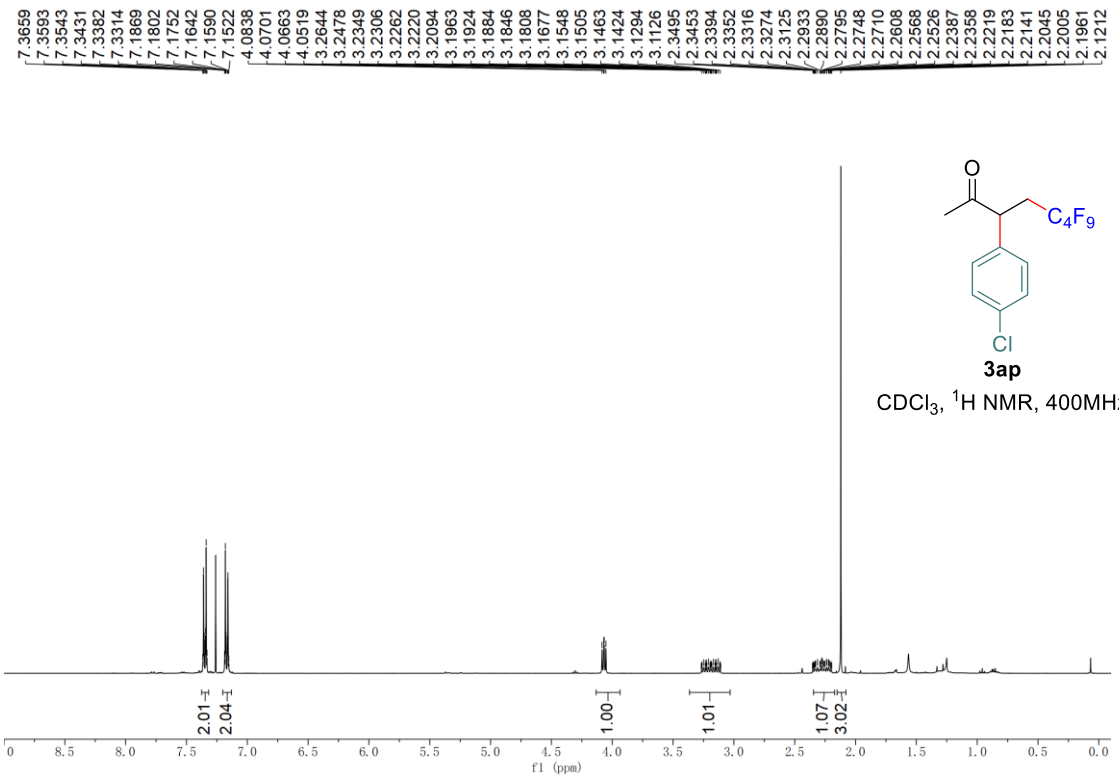
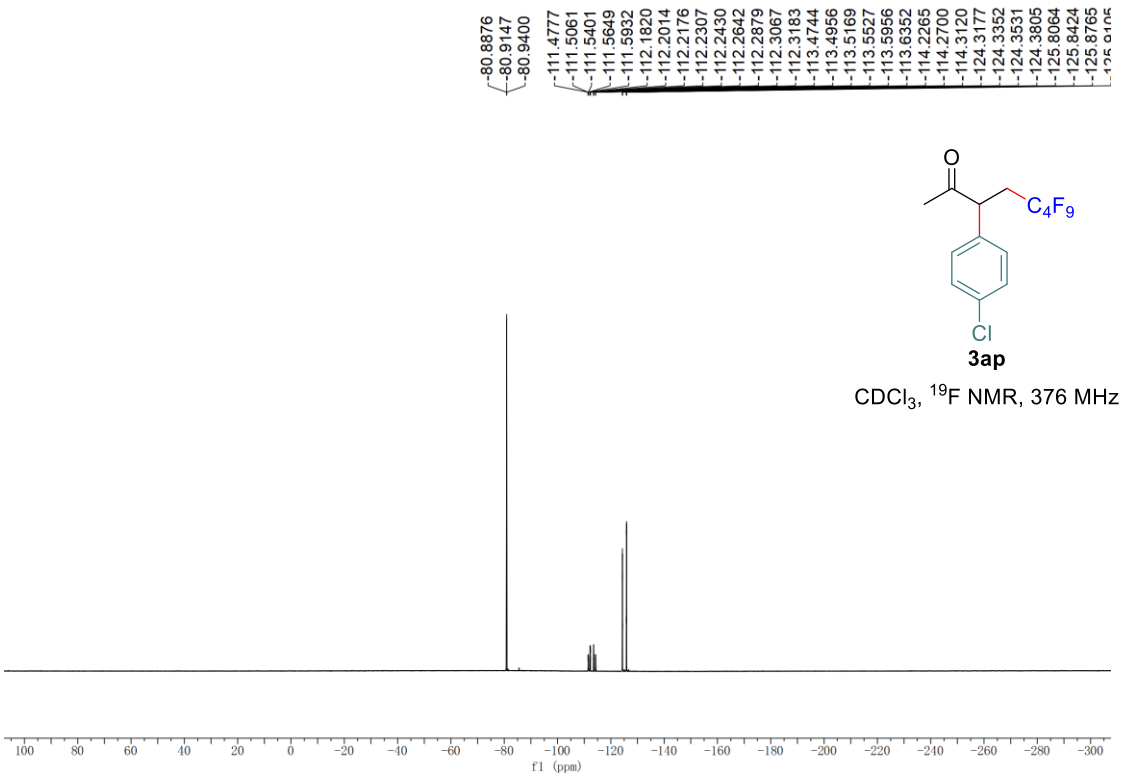
35.3538
35.1396
34.9342
O
C4F9
S
3ao
CDCl3, 13C NMR, 100 MHz
0 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



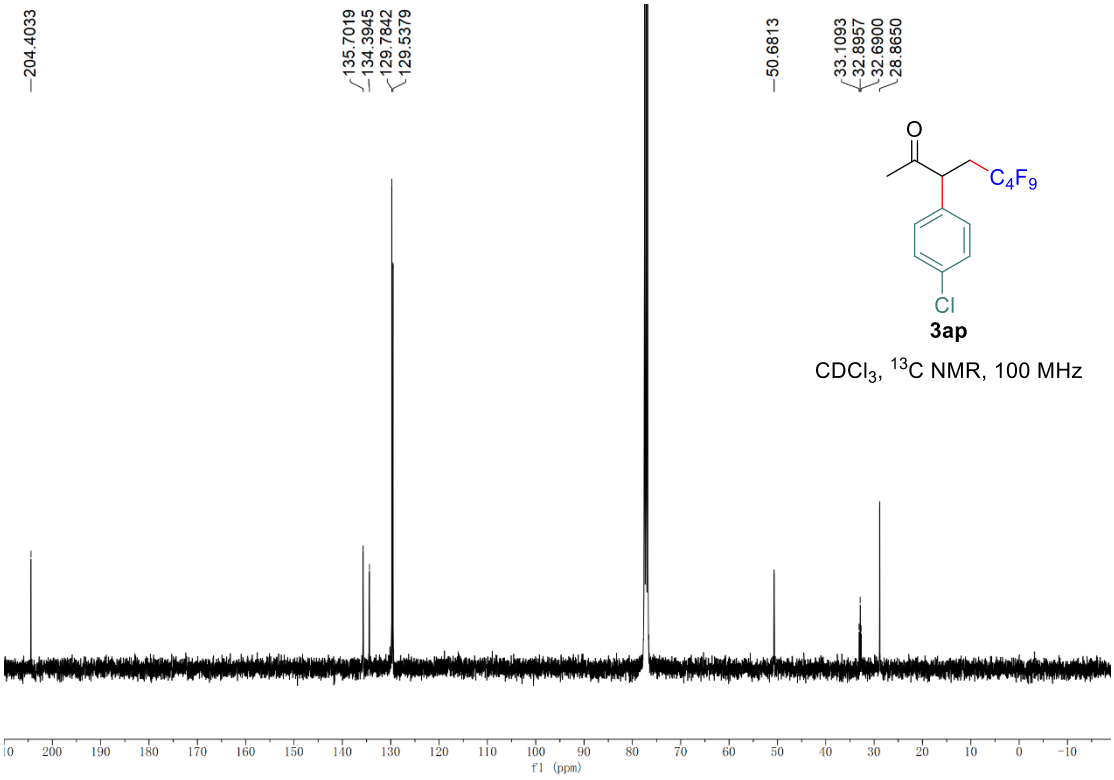
3ap

$CDCl_3$, ^1H NMR, 400MHz



3ap

$CDCl_3$, ^{19}F NMR, 376 MHz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134.3945
129.7842
129.5379
50.6813
33.1093
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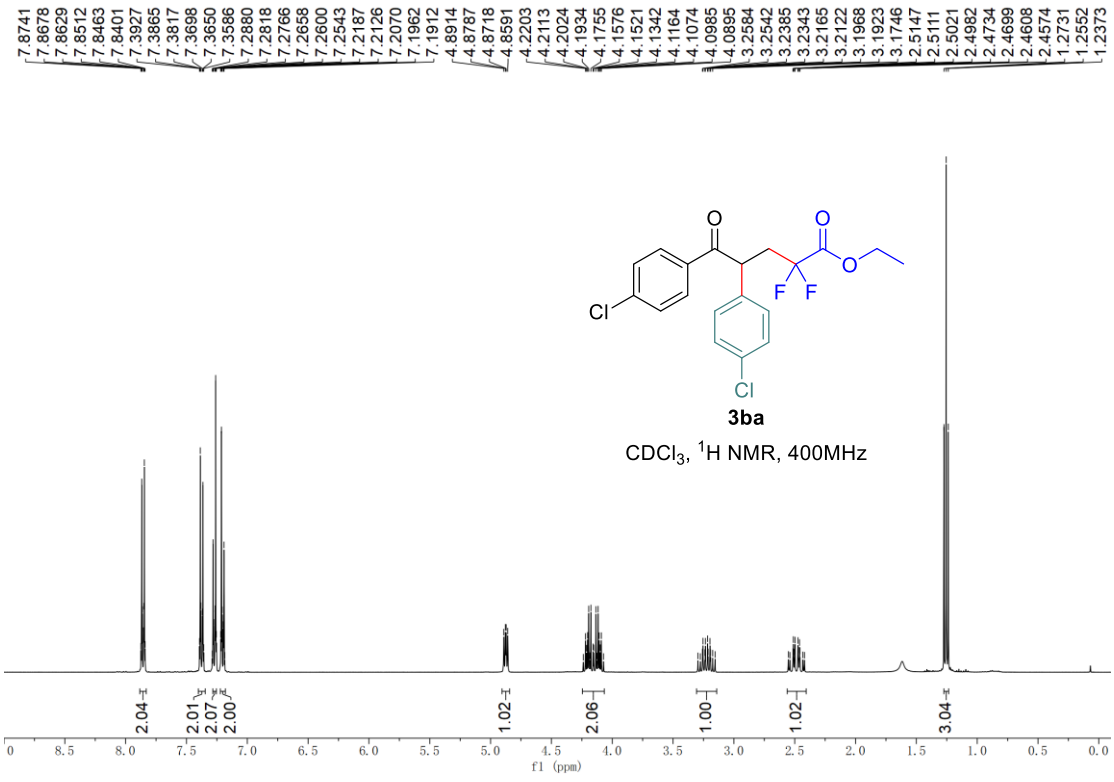
32.6900
28.8650
O
C4F9
Cl
3ap
CDCl3, 13C NMR, 100 MHz
f1 (ppm)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7.8629
7.8512
7.8463
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7.3927
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7.3817
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7.3586
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7.2818
7.2766
7.2658
7.2600
7.2543
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7.2126
7.2070
7.1962
7.1912
4.8914
4.8787
4.8718
4.8591
4.2203
4.2113
4.2024
4.1934
4.1755
4.1576
4.1521
4.1342
4.1164
4.1074
4.0985
4.0895
3.2584
3.2542
3.2385
3.2343
3.2165
3.2122
3.1968
3.1923
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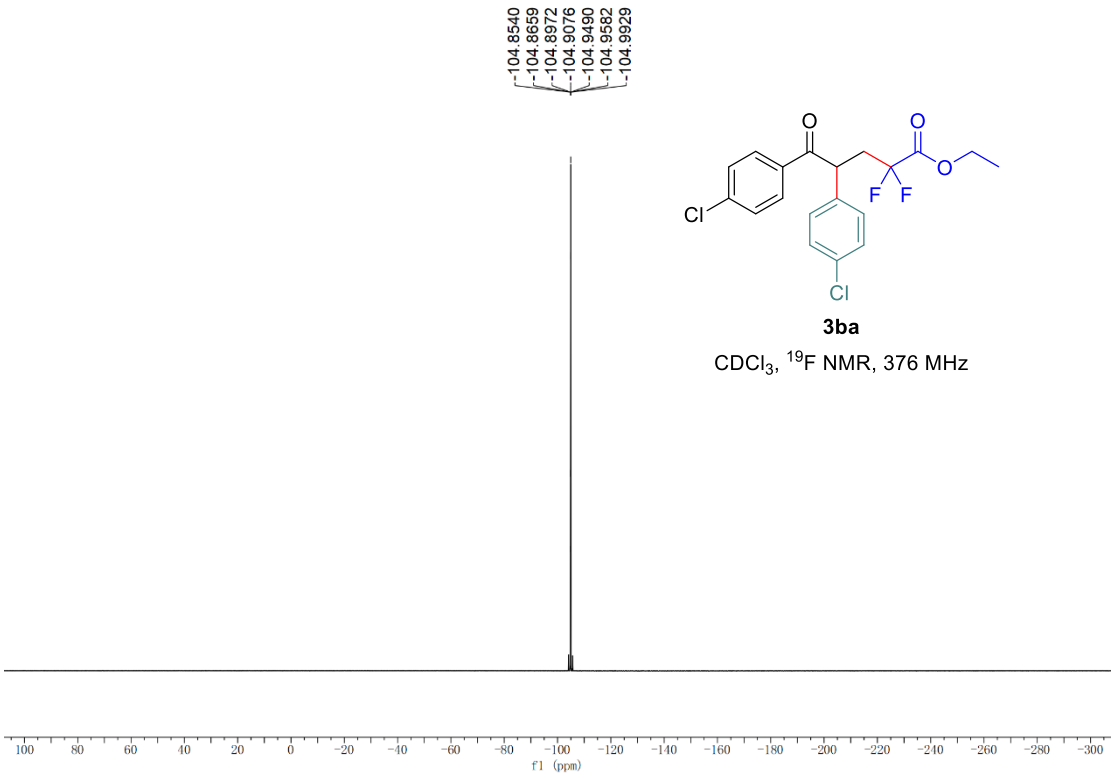
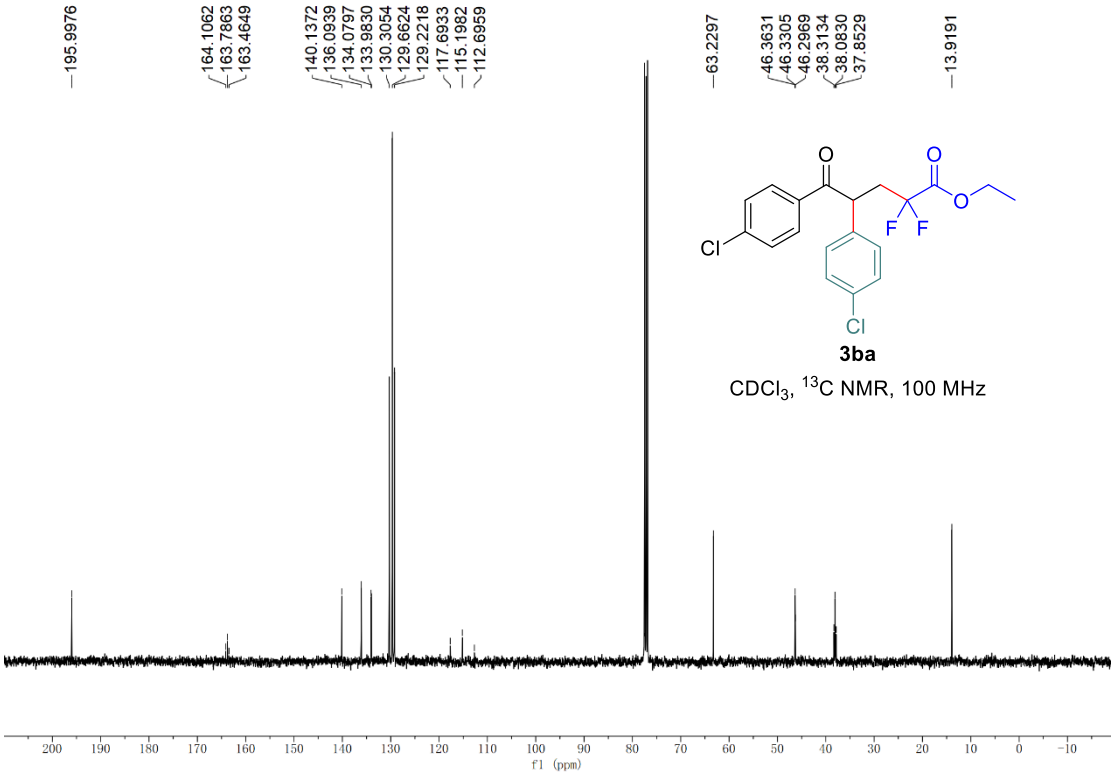
2.5147
2.5111
2.5021
2.4982
2.4734
2.4699
2.4608
2.4574
1.2731
1.2552
1.2373
O
O
O
F
F
Cl
Cl
3ba
CDCl3, 1H NMR, 400MHz
2.04
2.01
2.07
2.00
1.02
2.06
1.00
1.02
3.04
f1 (ppm)



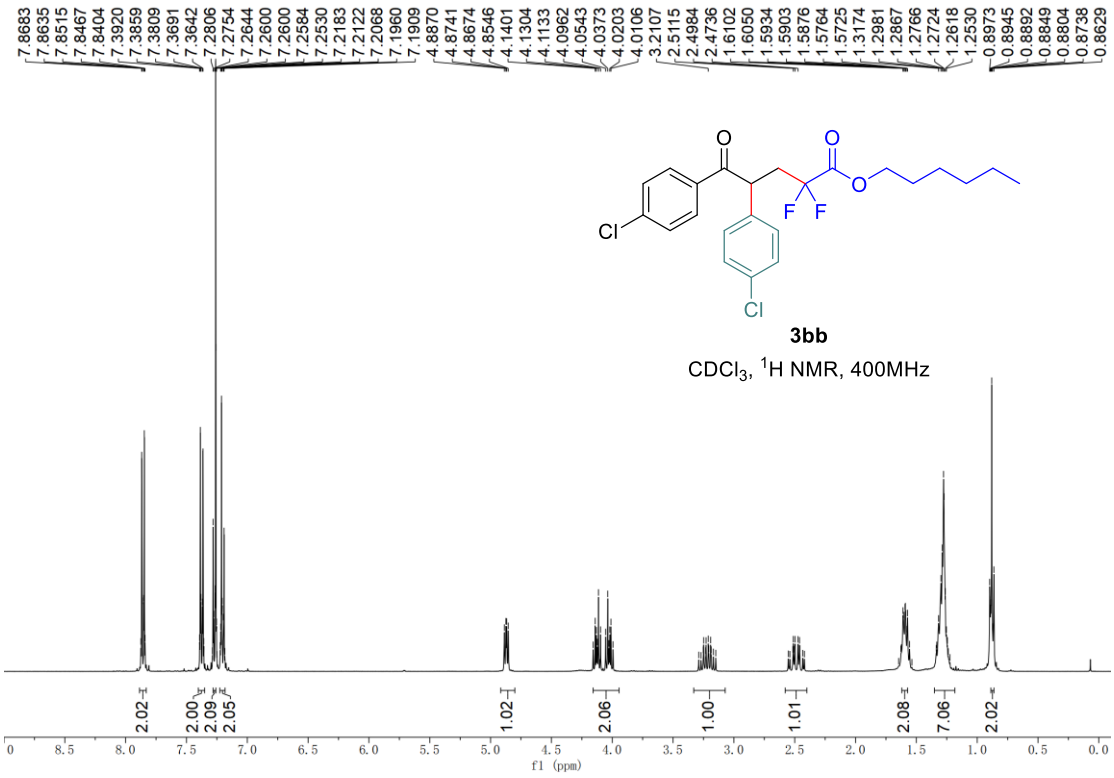
3ba

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



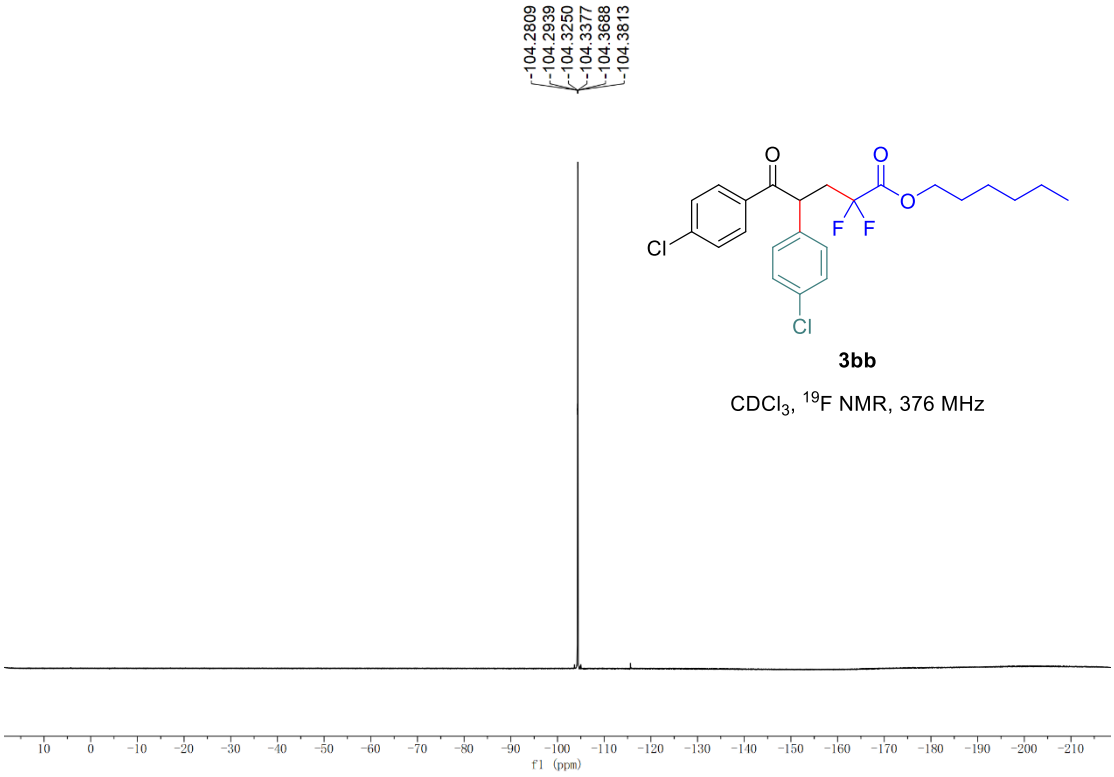
3ba

$CDCl_3$, ^{13}C NMR, 100 MHz



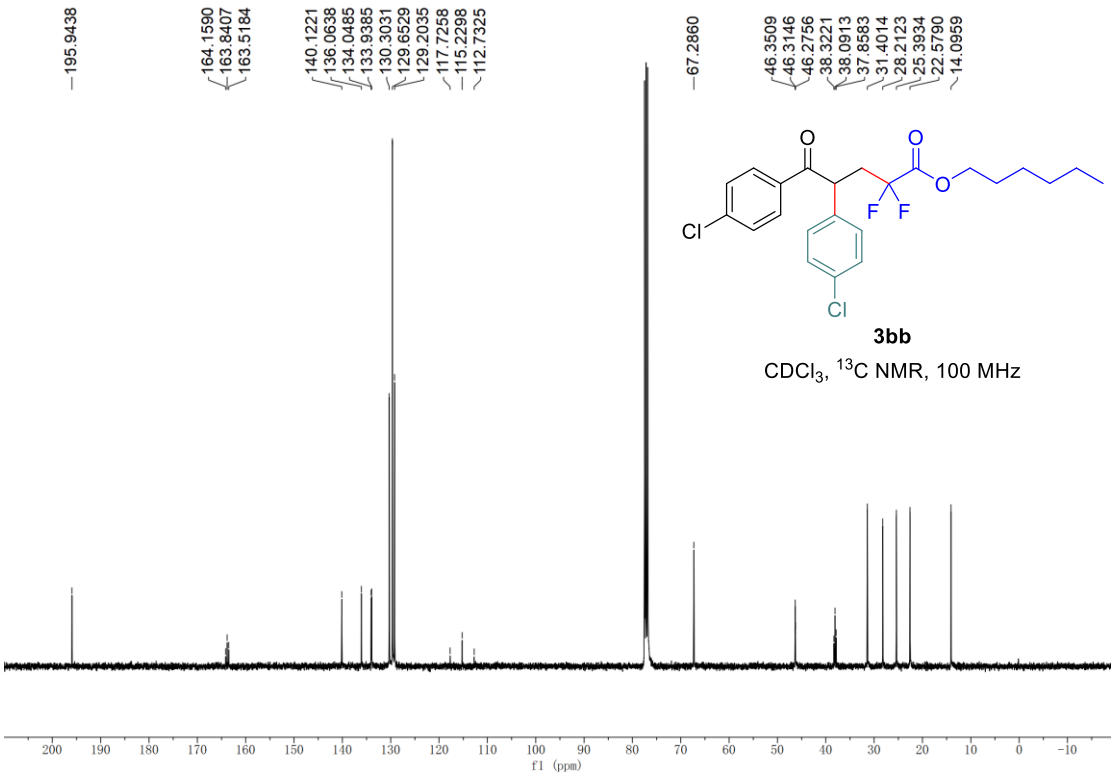
3bb

$CDCl_3$, ^1H NMR, 400MHz



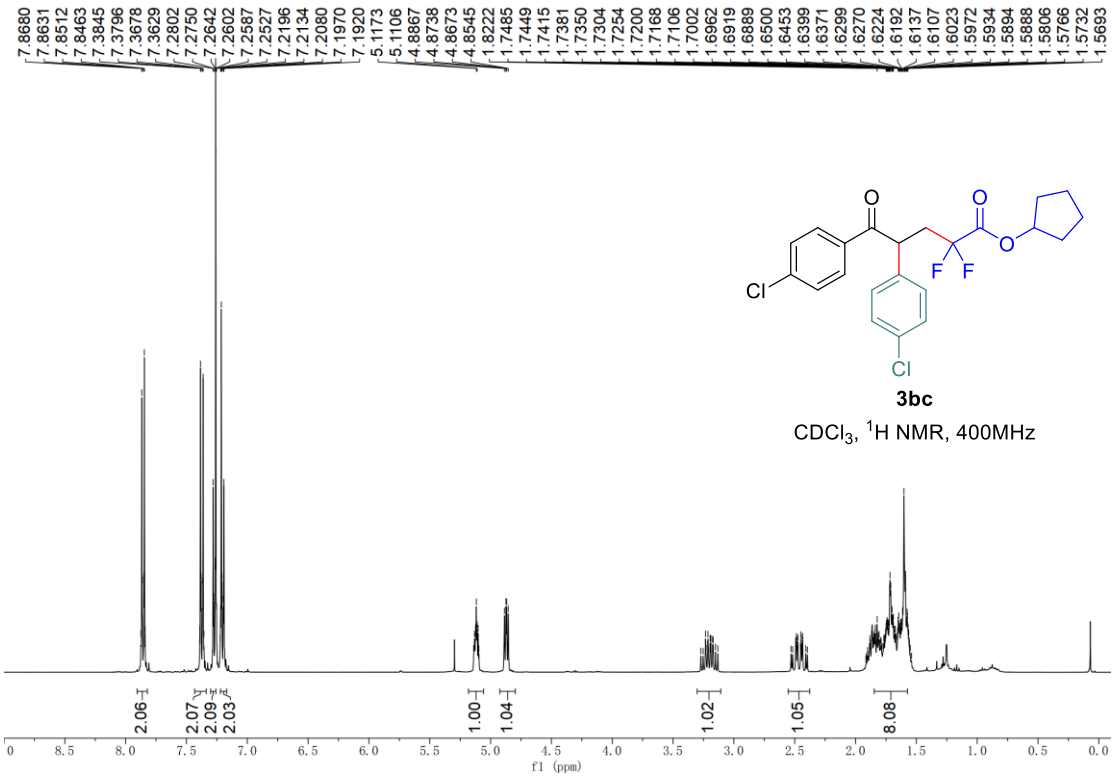
3bb

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



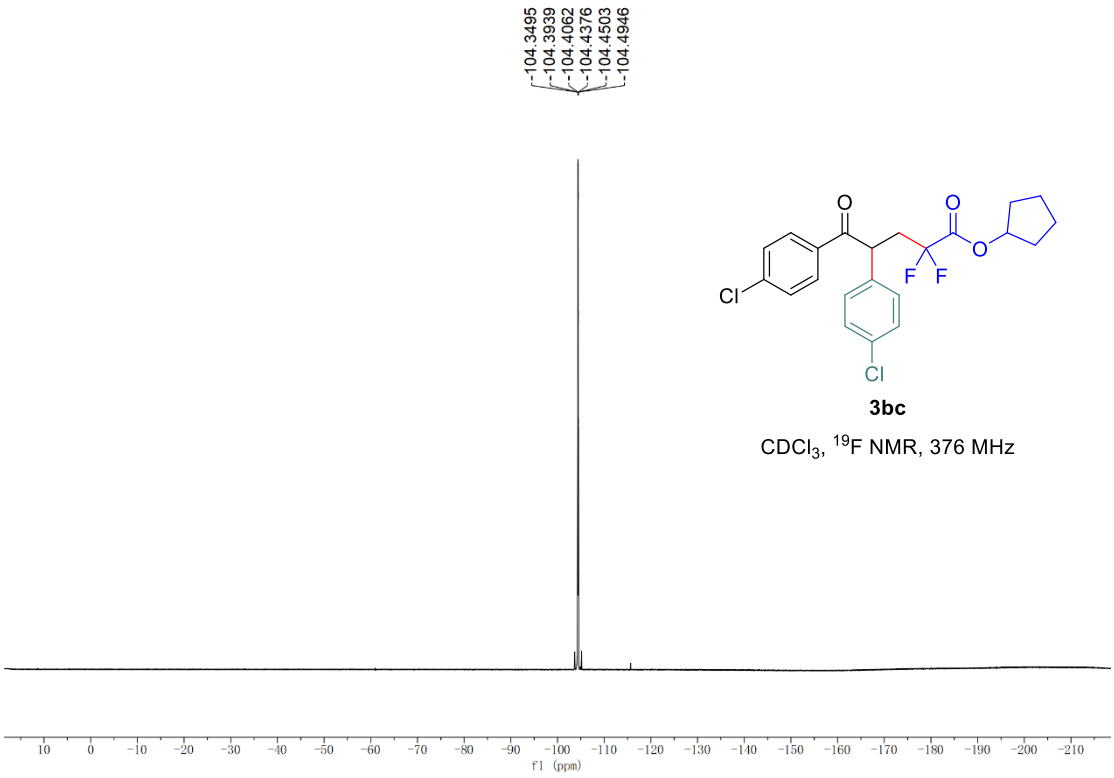
3bb

$CDCl_3$, ^{13}C NMR, 100 MHz



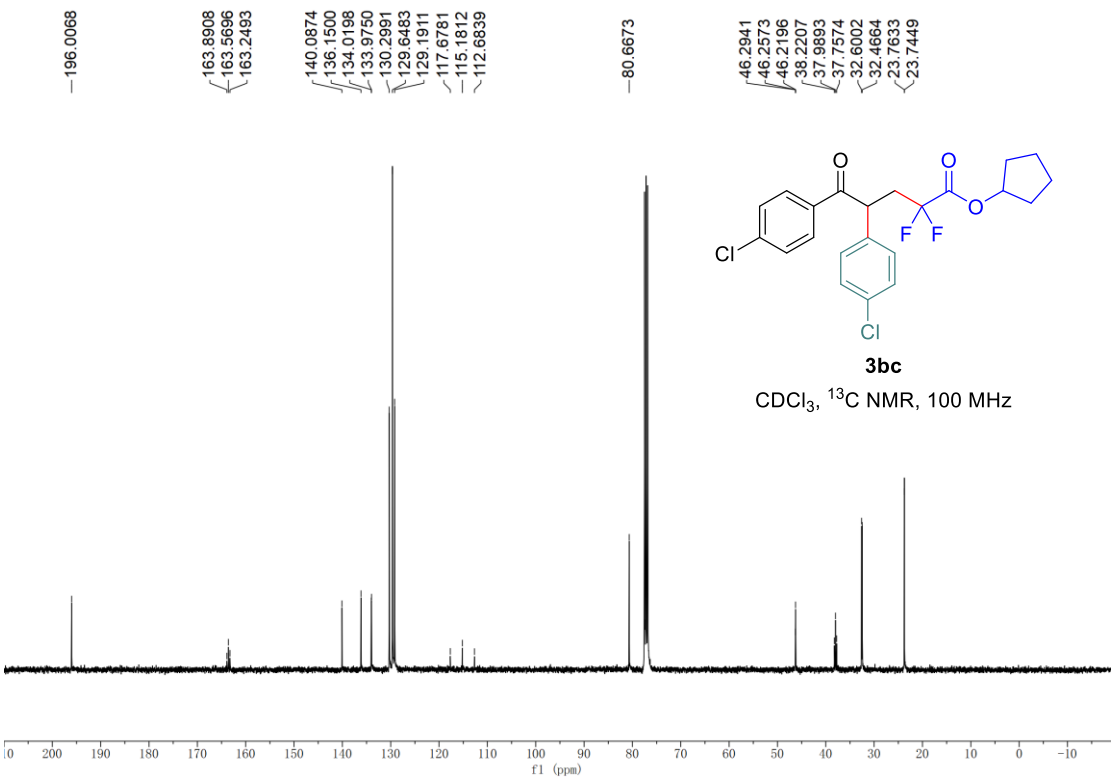
3bc

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



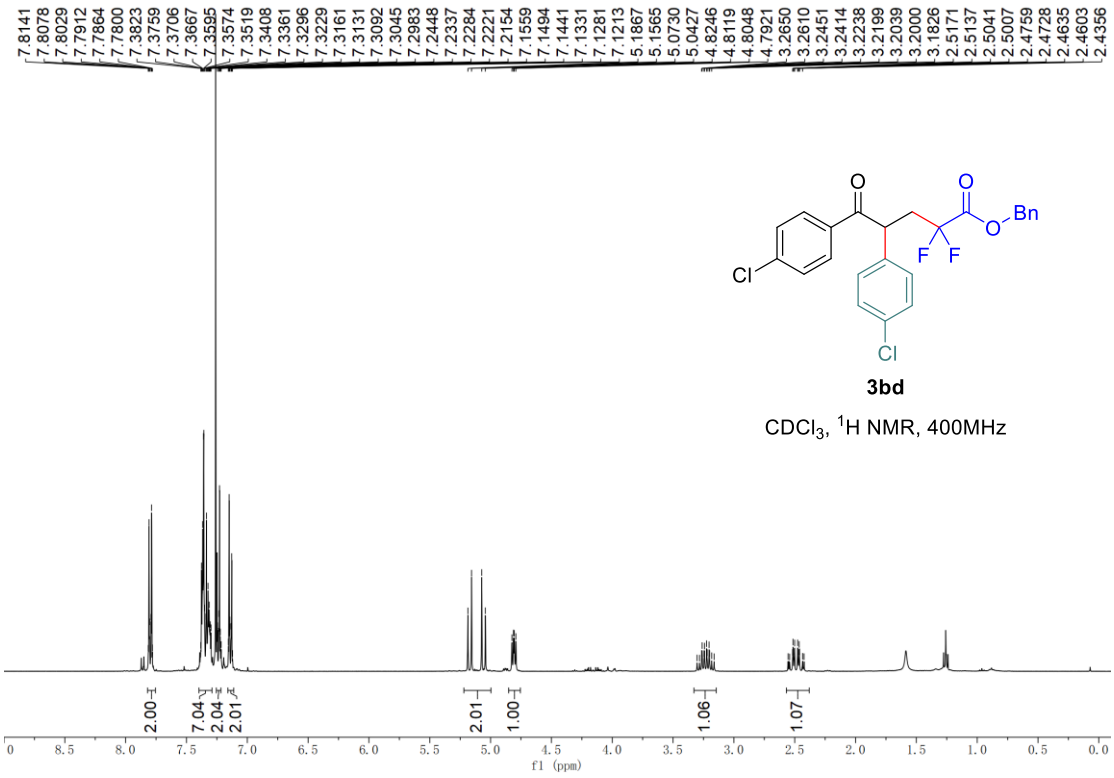
3bc

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



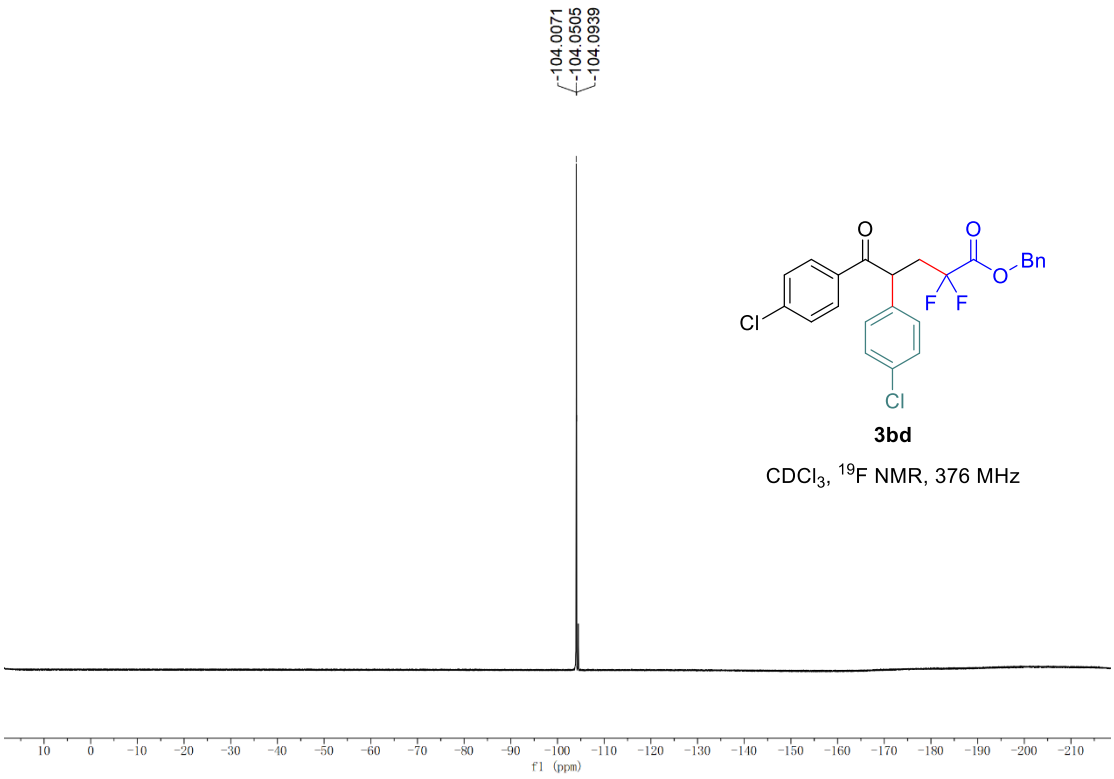
3bc

$CDCl_3$, ^{13}C NMR, 100 MHz



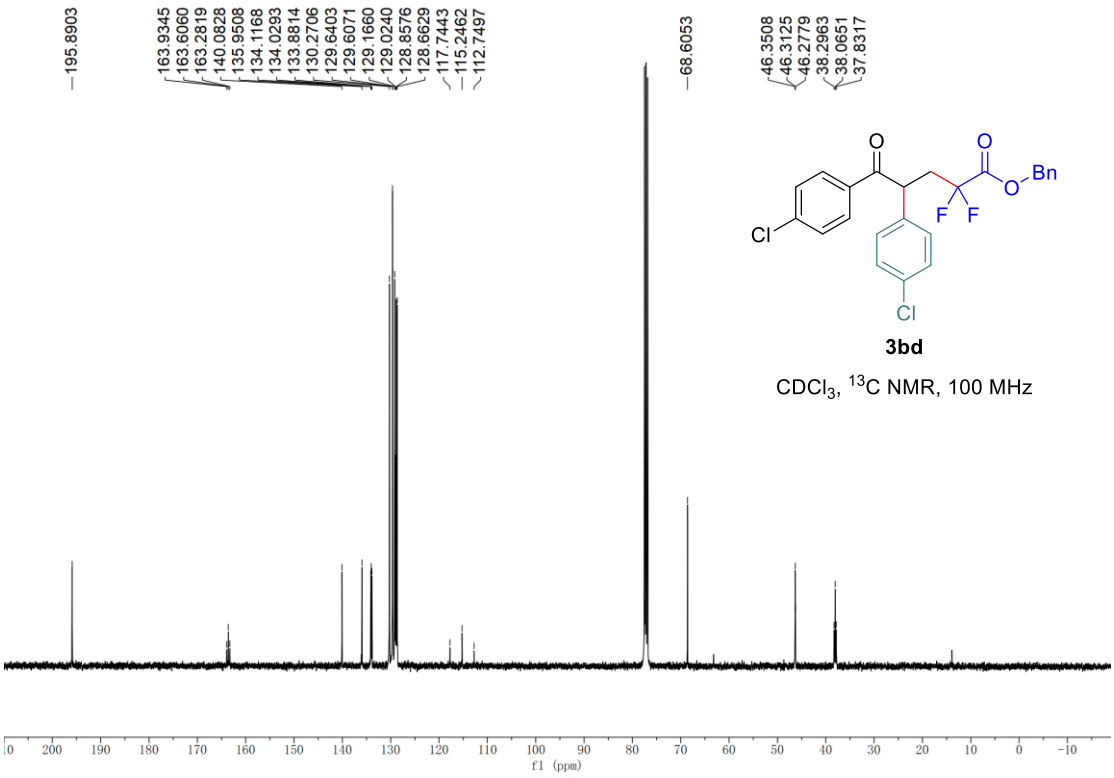
3bd

$CDCl_3$, ^1H NMR, 400MHz



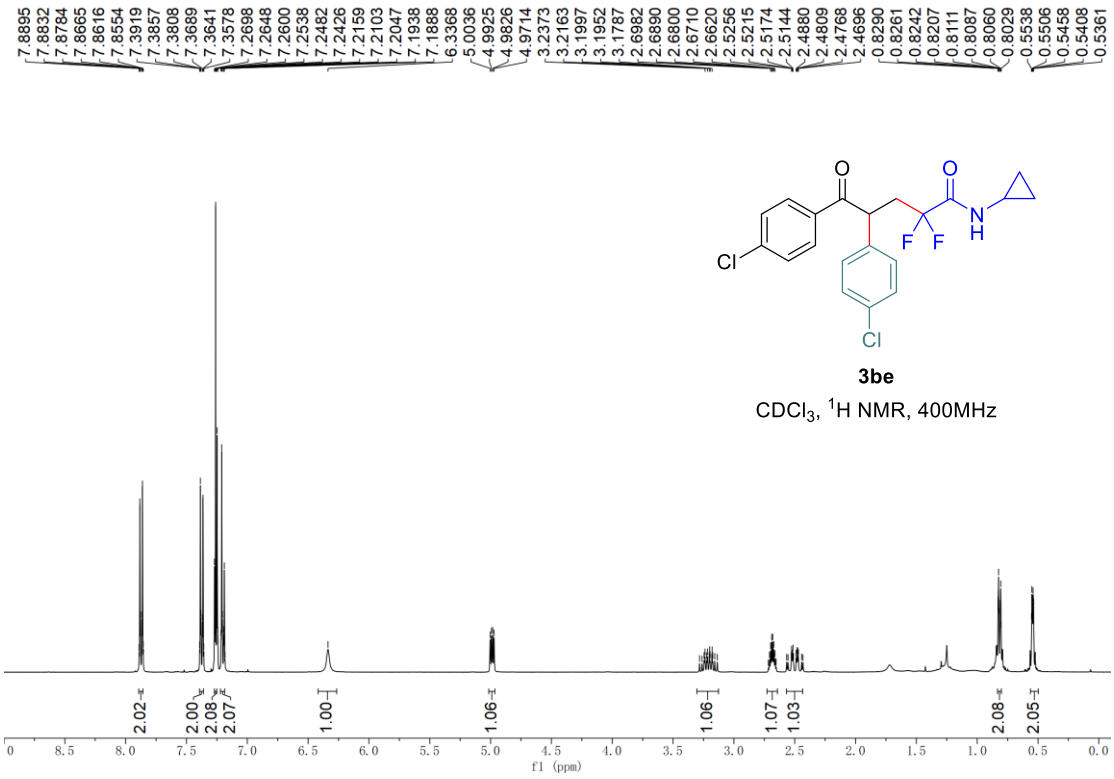
3bd

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



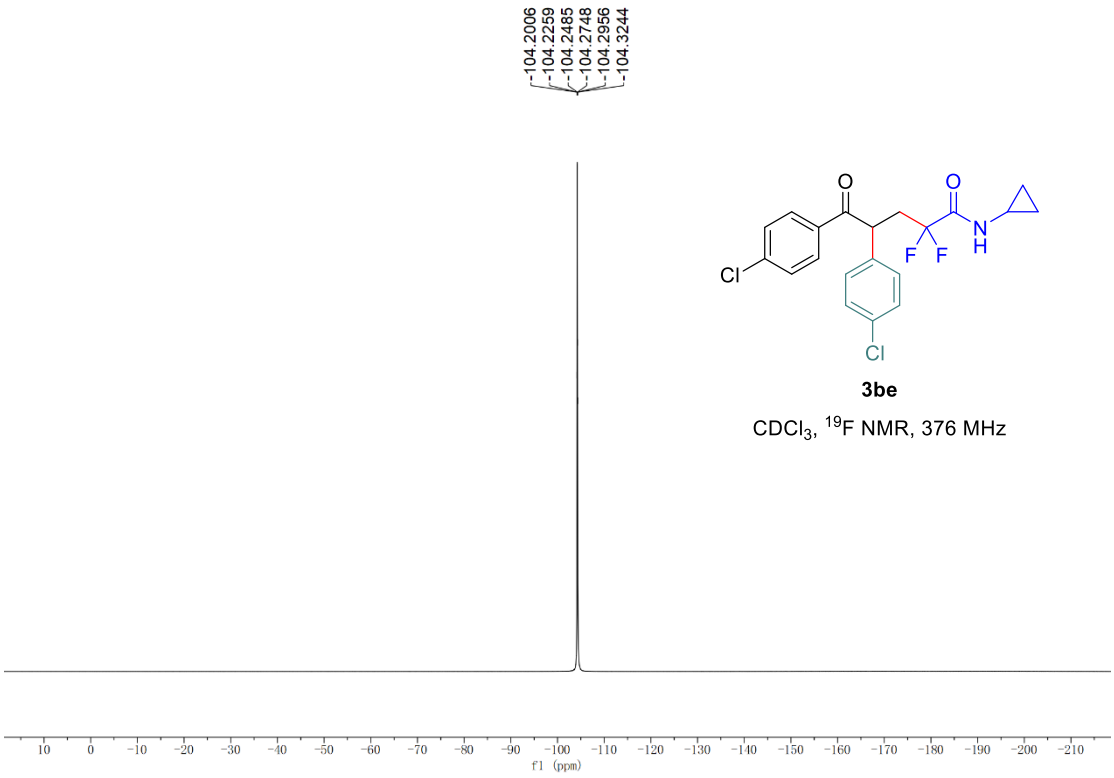
3bd

$CDCl_3$, ^{13}C NMR, 100 MHz



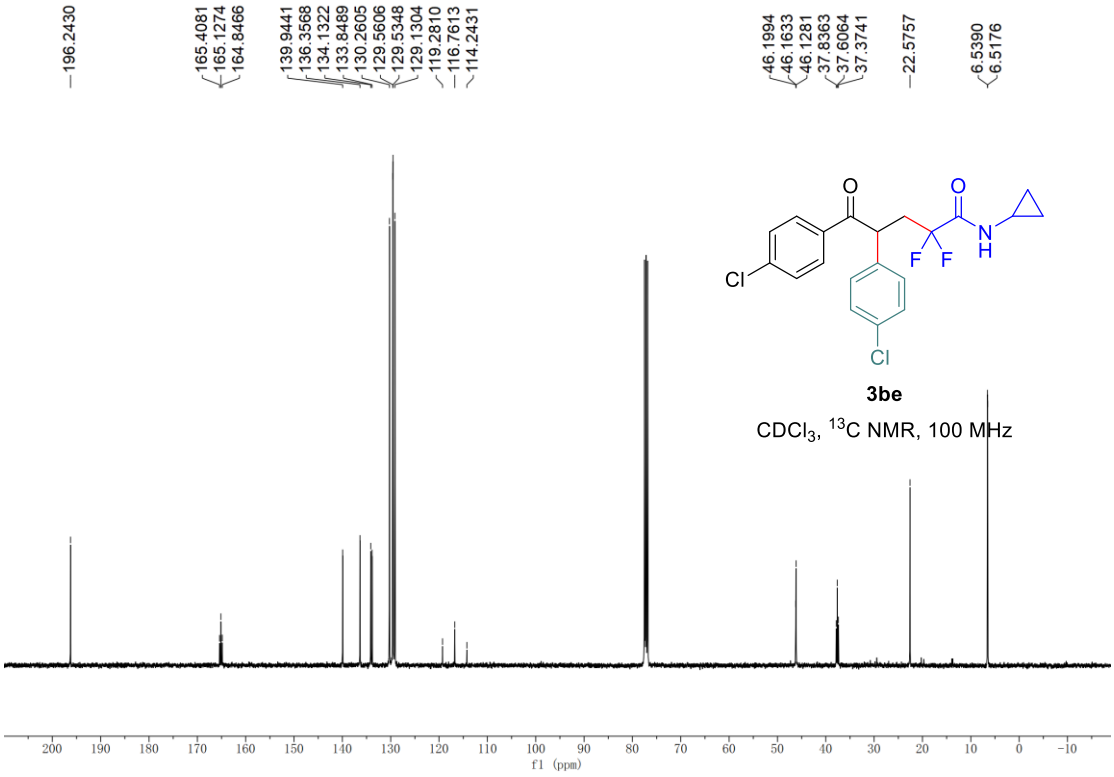
3be

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



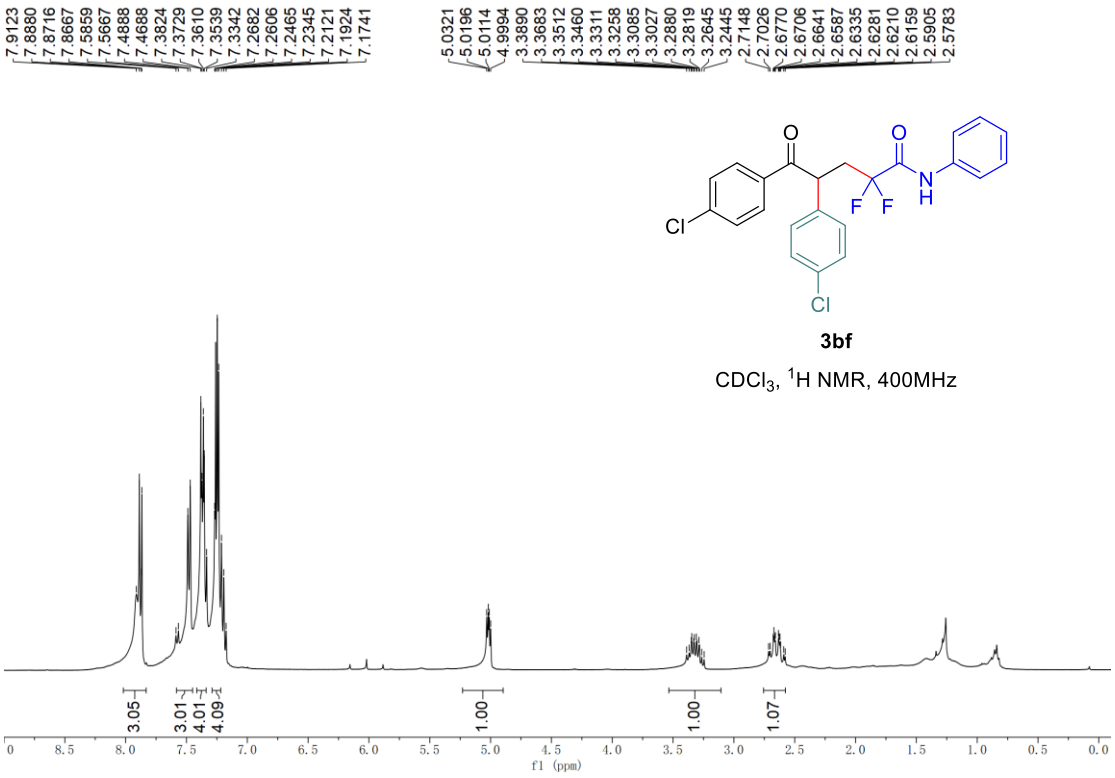
3be

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



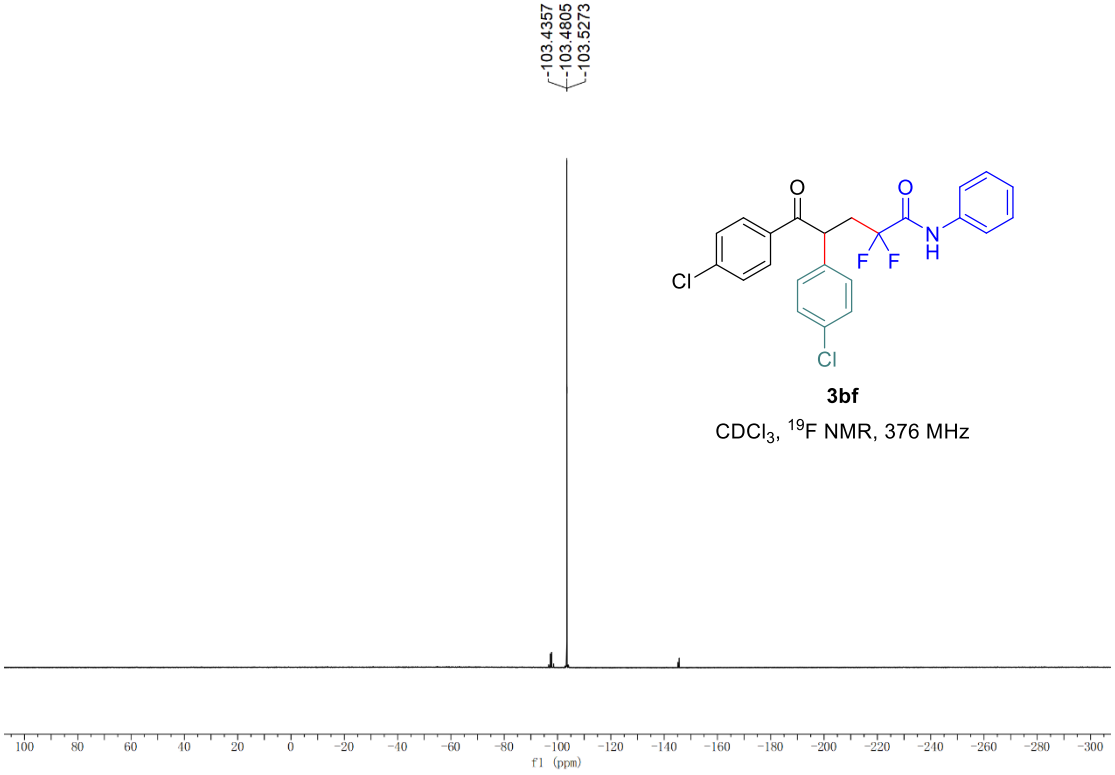
3be

$CDCl_3$, ^{13}C NMR, 100 MHz



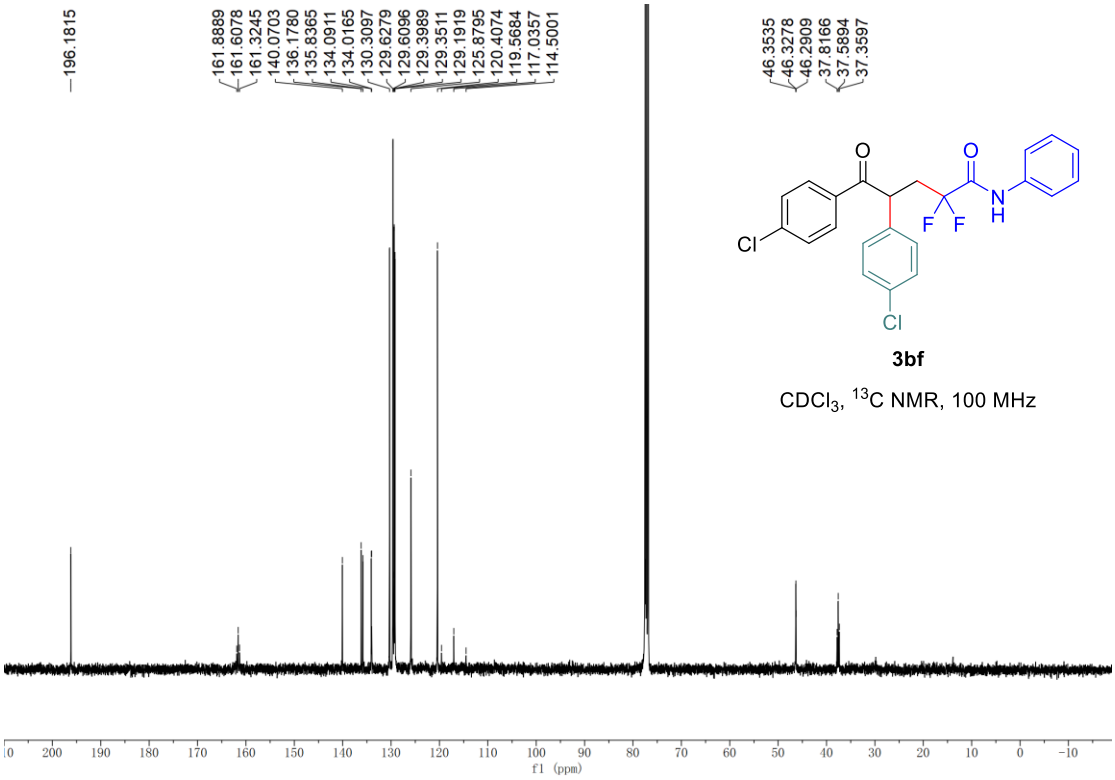
3bf

$CDCl_3$, ^1H NMR, 400MHz



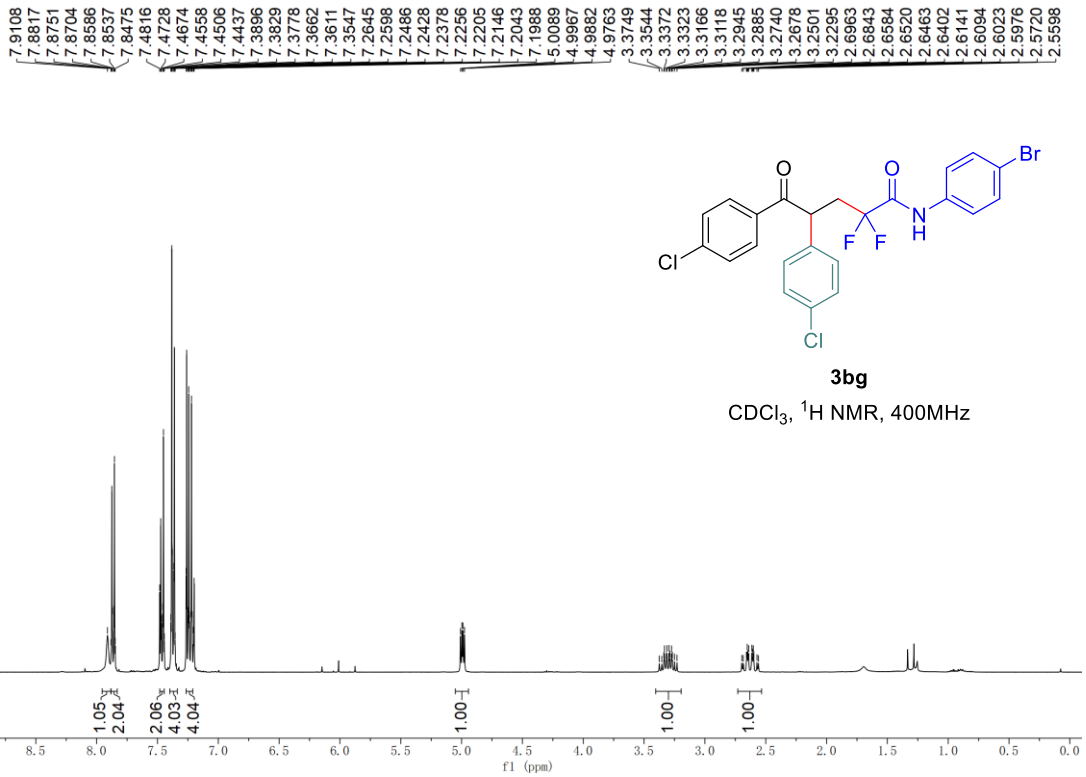
3bf

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



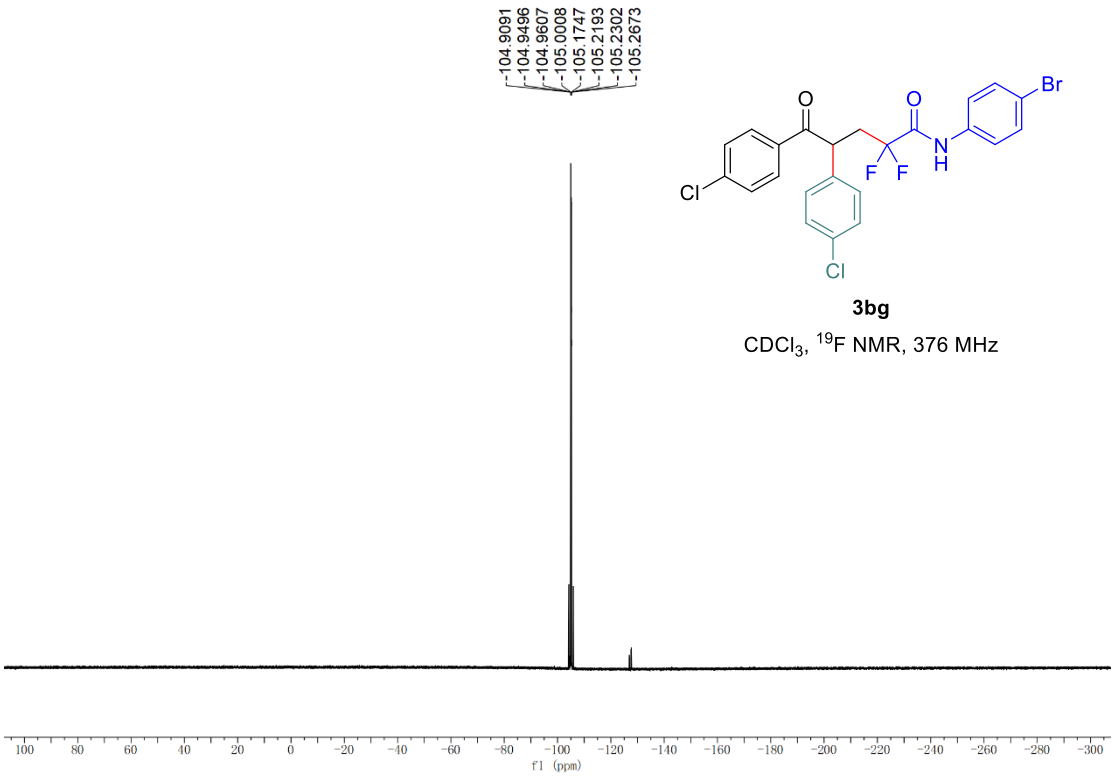
3bf

$CDCl_3$, ^{13}C NMR, 100 MHz



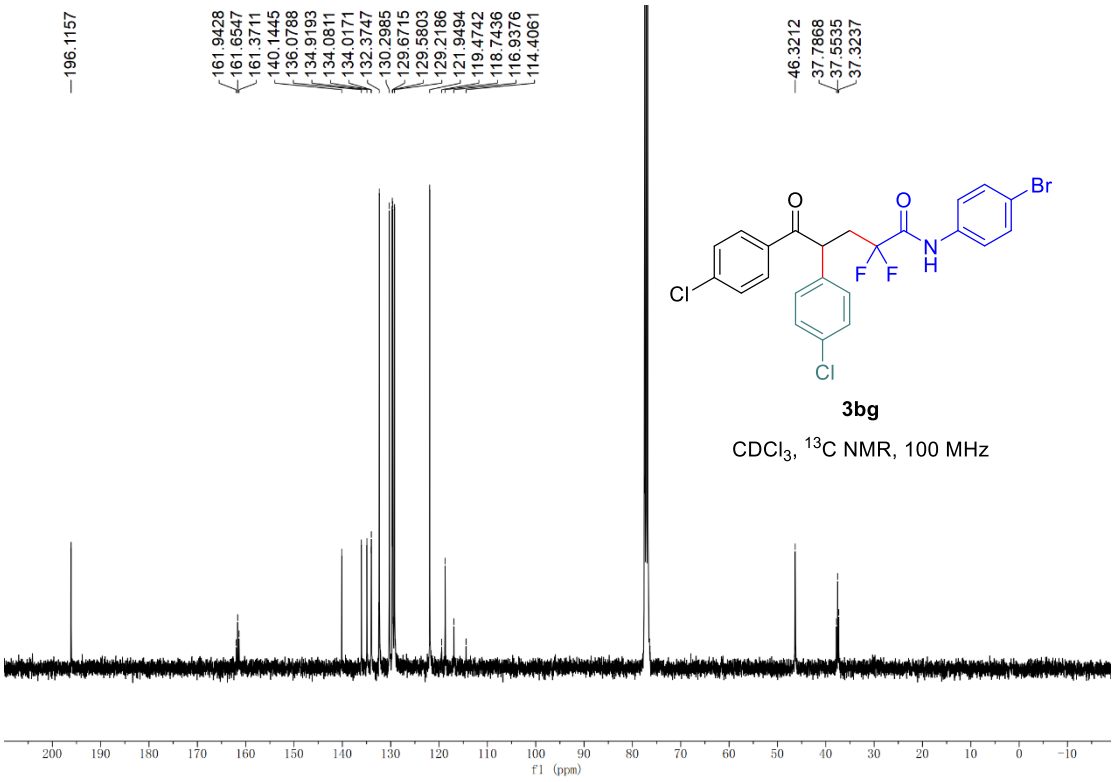
3bg

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



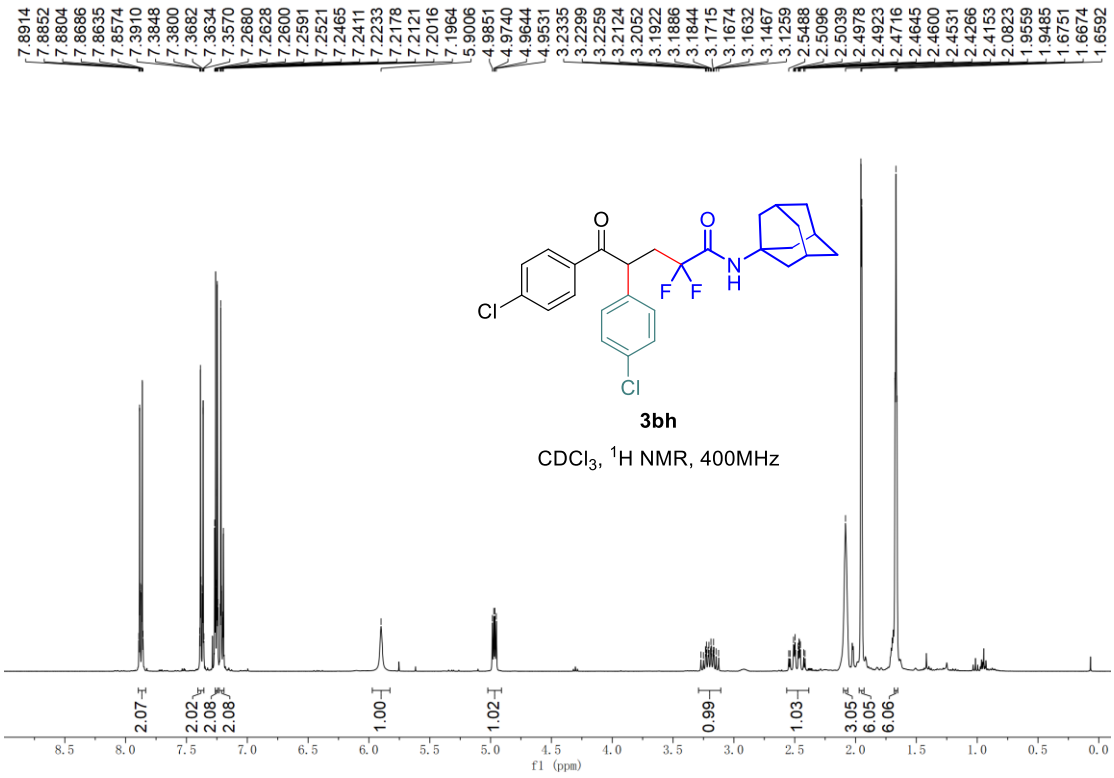
3bg

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



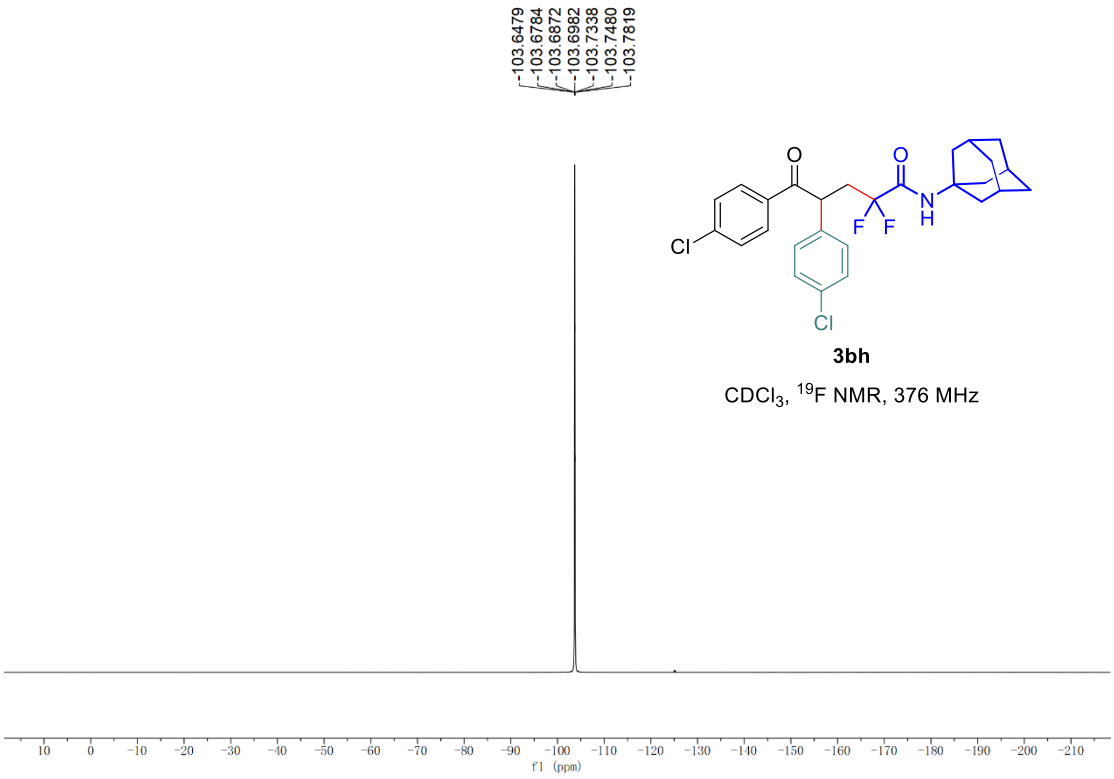
3bg

$CDCl_3$, ^{13}C NMR, 100 MHz



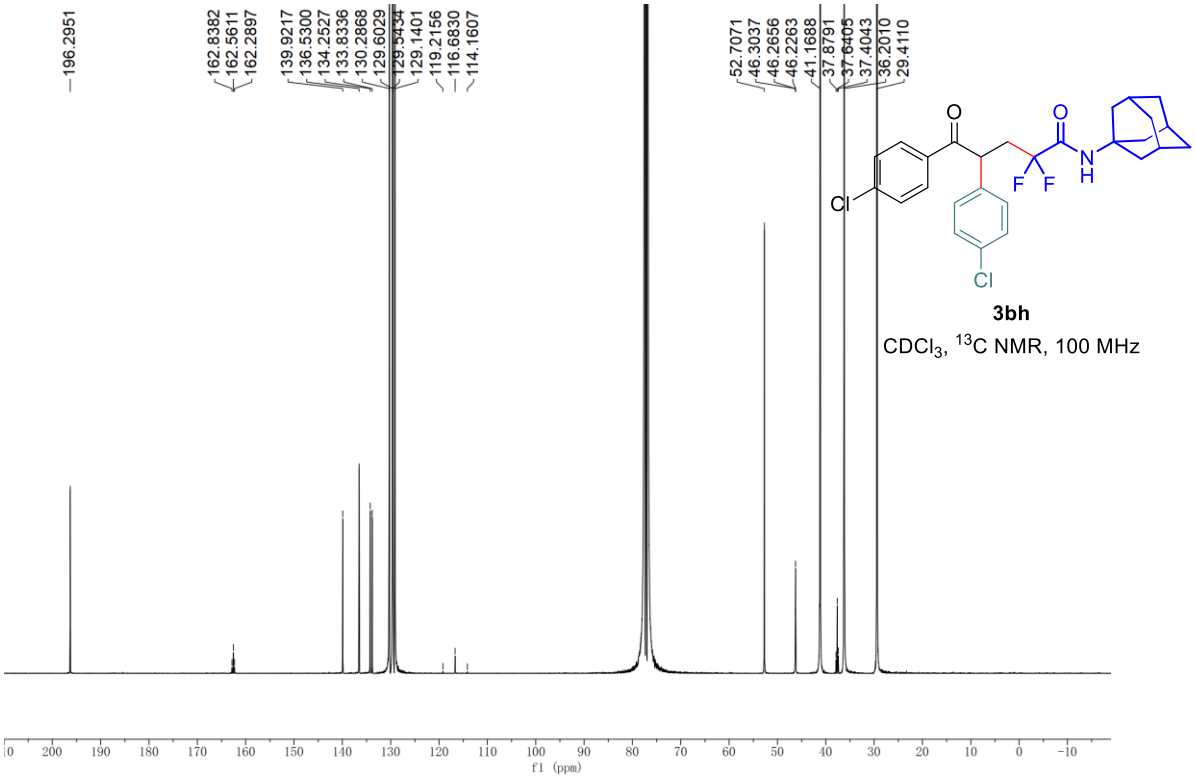
3bh

$CDCl_3$, ^1H NMR, 400MHz



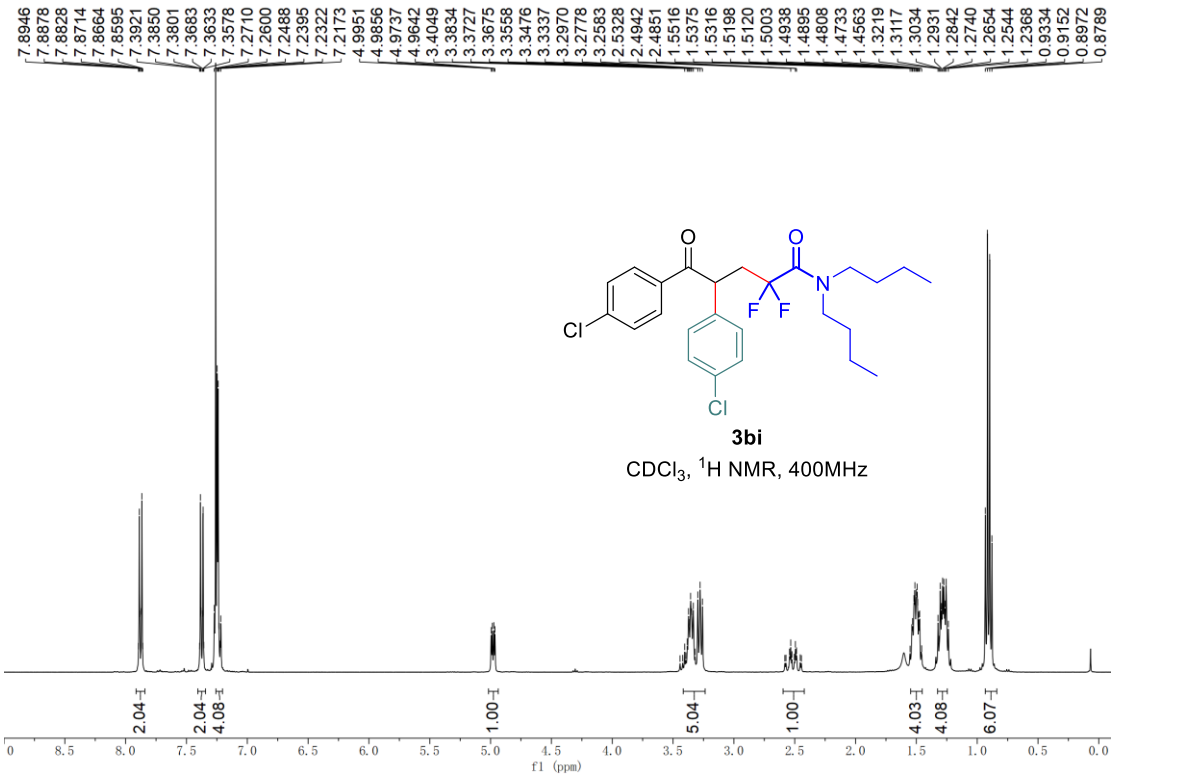
3bh

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



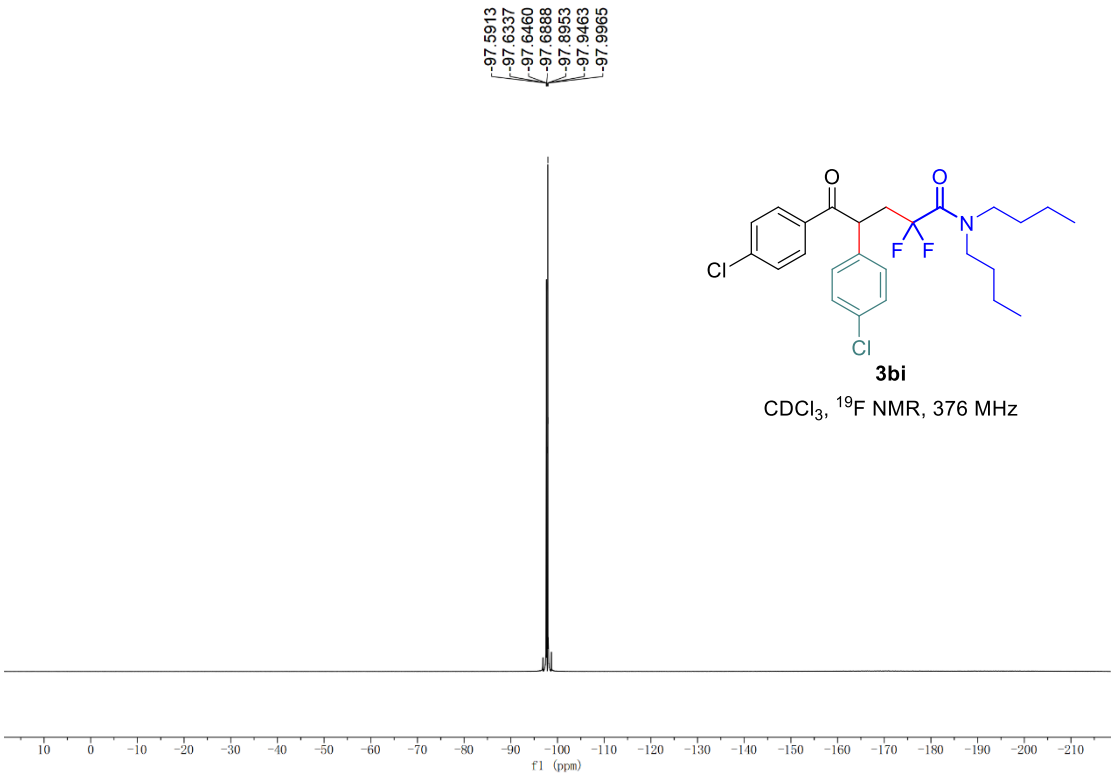
3bh

$CDCl_3$, ^{13}C NMR, 100 MHz



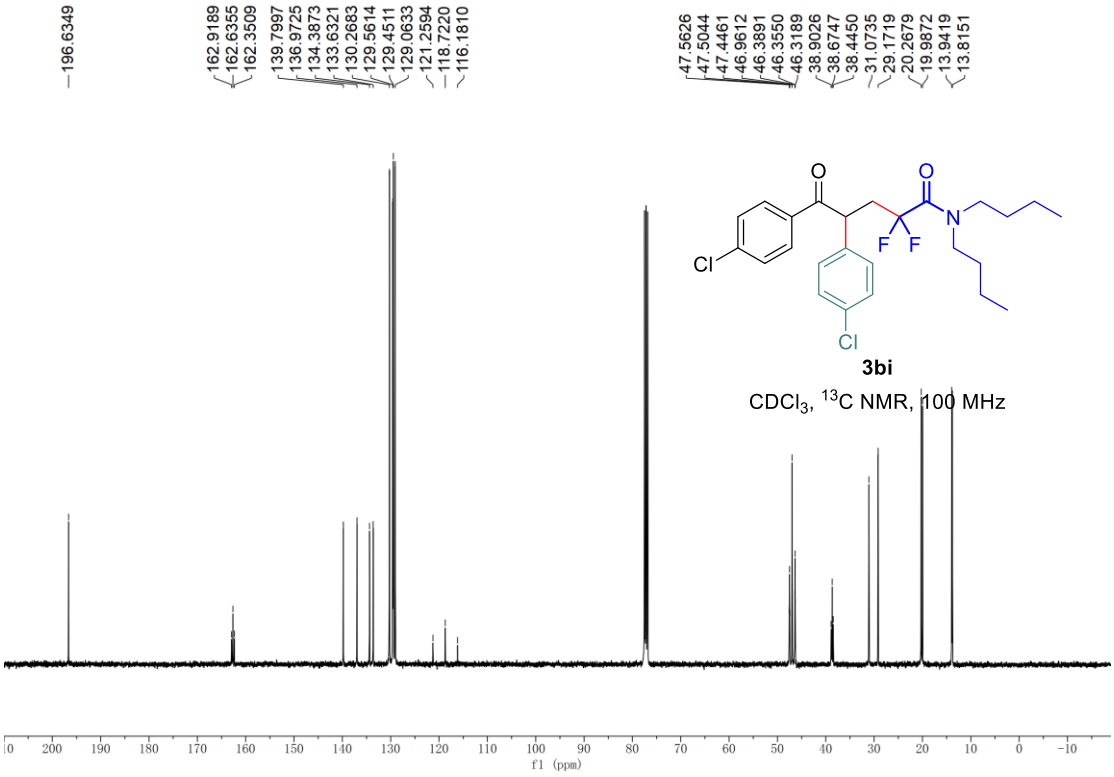
3bi

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



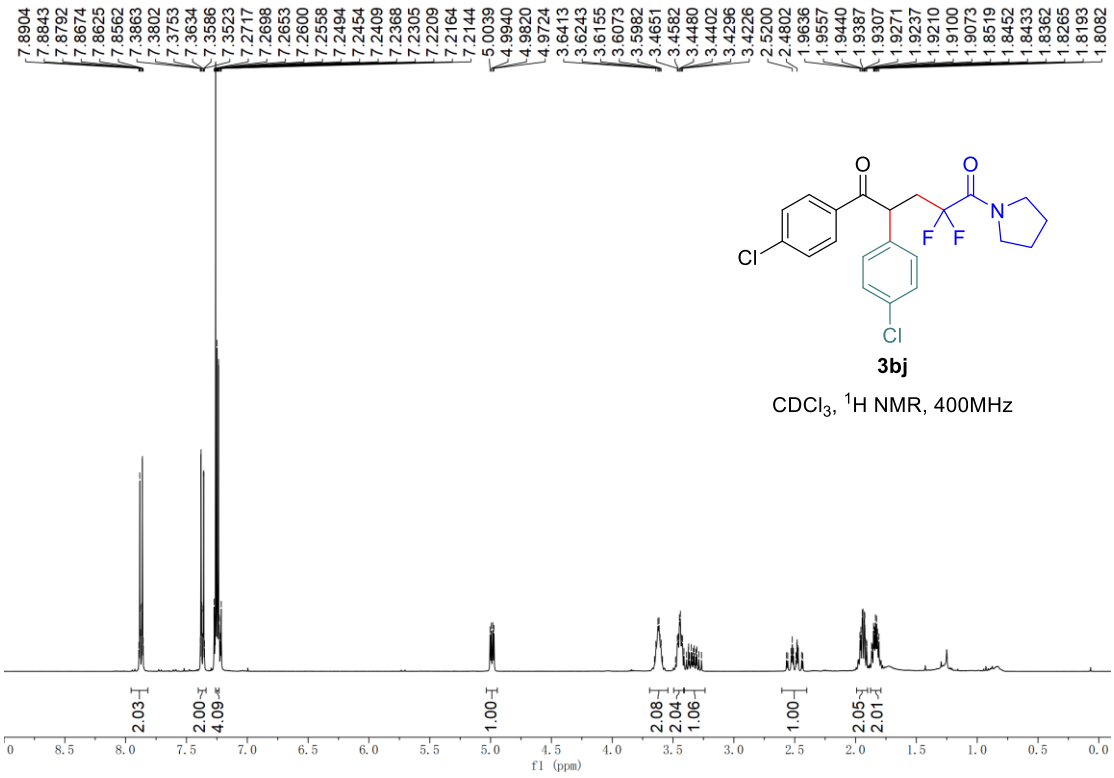
3bi

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



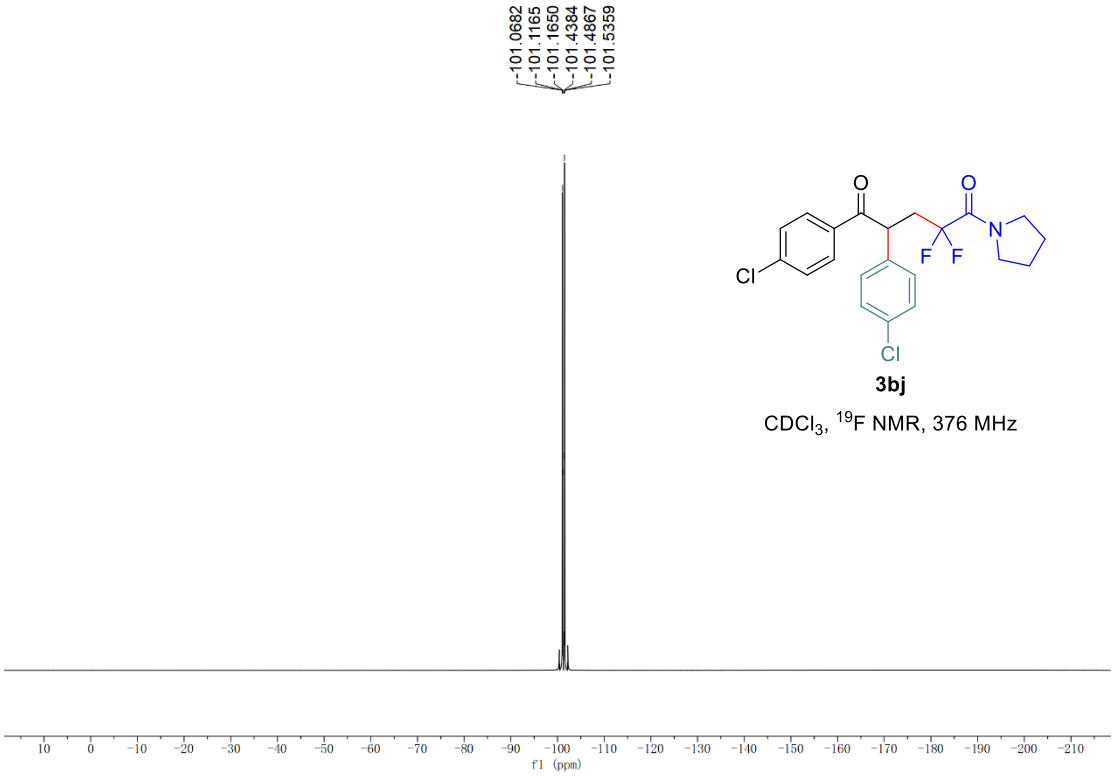
3bi

$CDCl_3$, ^{13}C NMR, 100 MHz



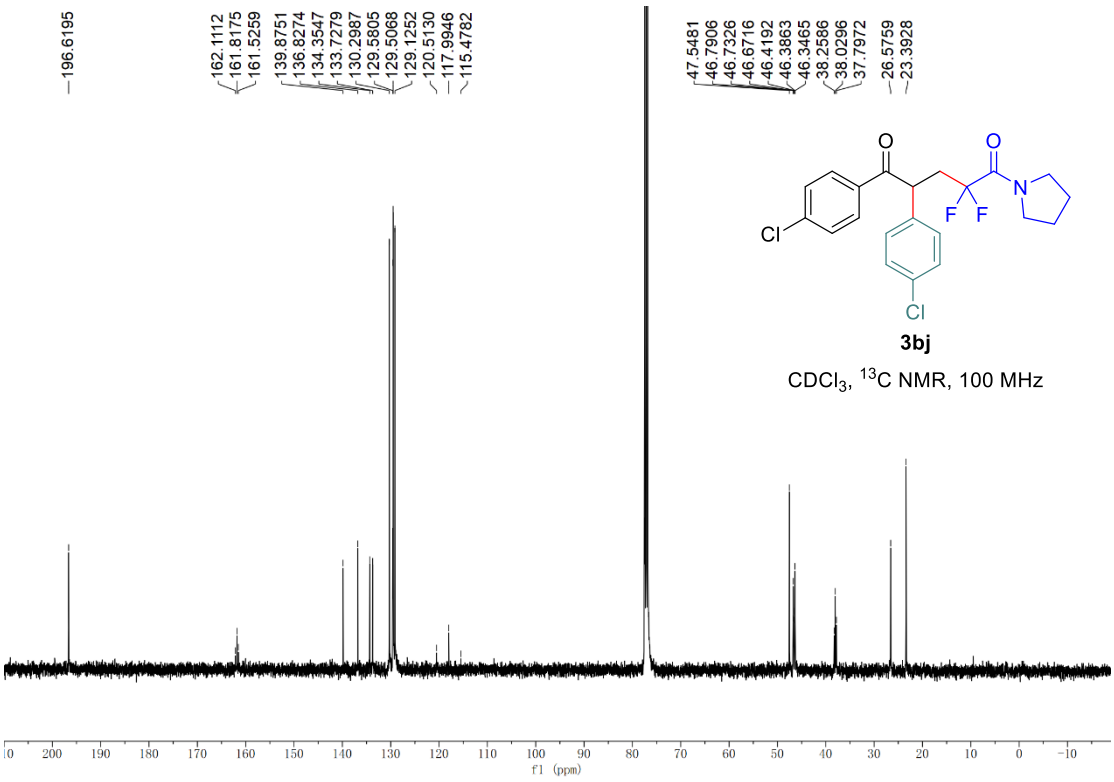
3bj

$CDCl_3$, ^1H NMR, 400MHz



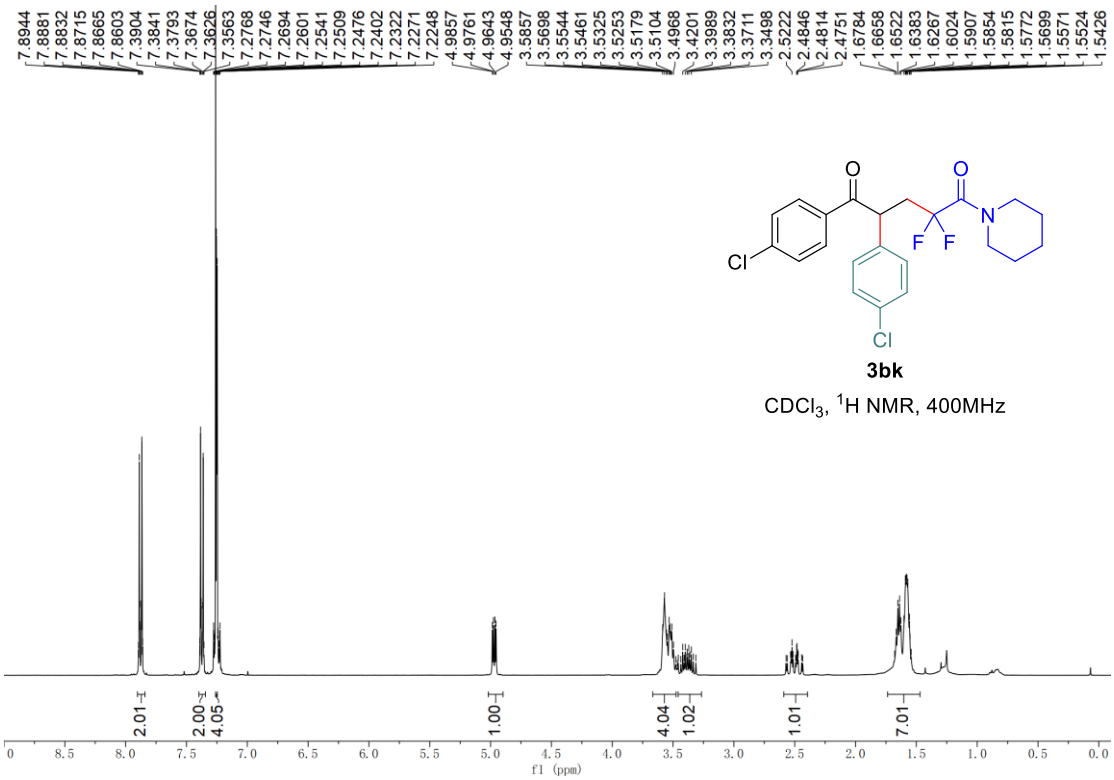
3bj

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



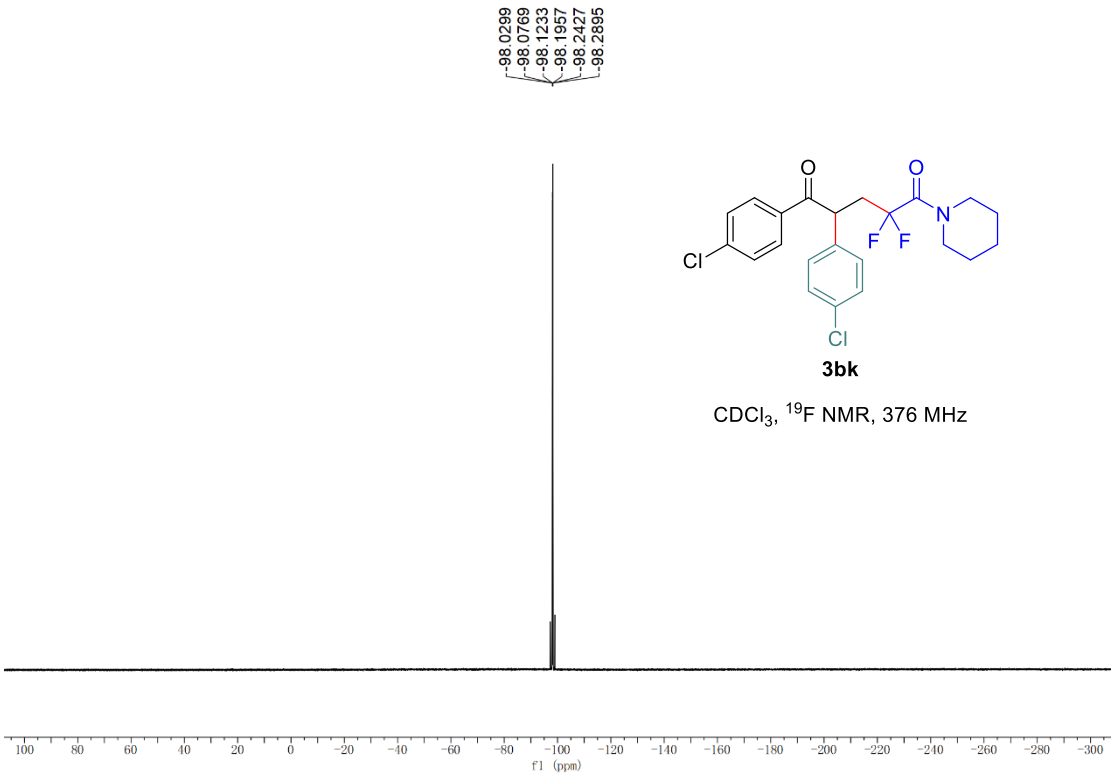
3bj

$CDCl_3$, ^{13}C NMR, 100 MHz



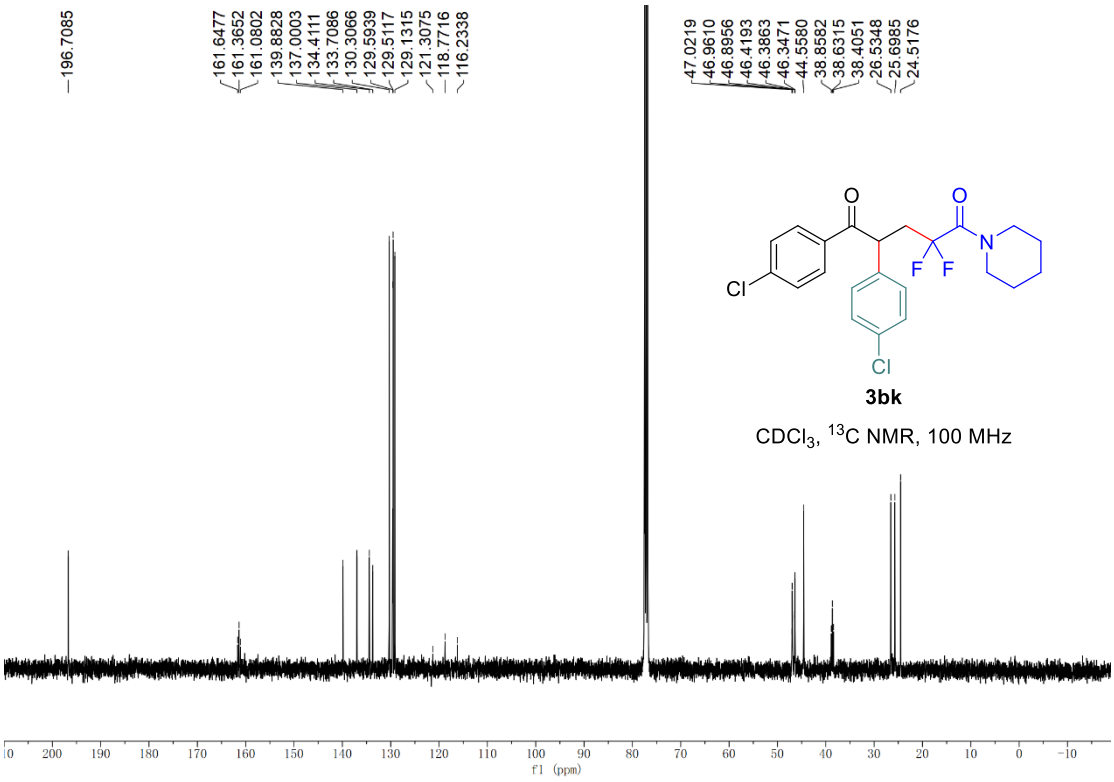
3bk

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



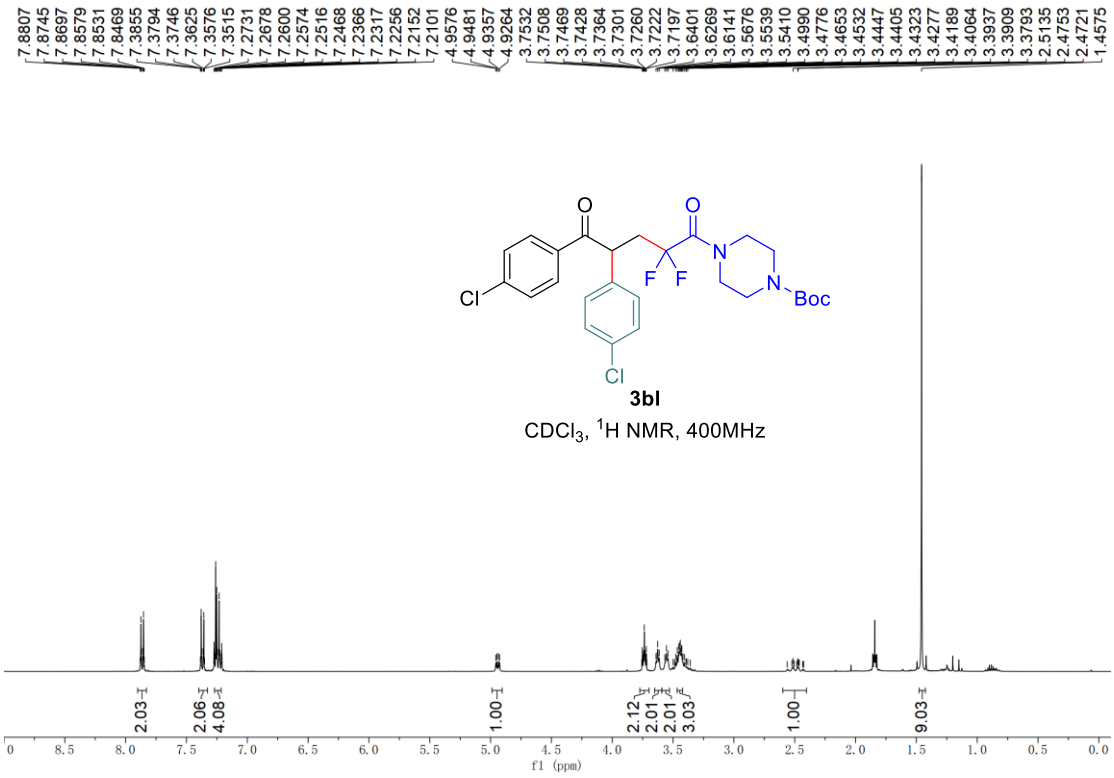
3bk

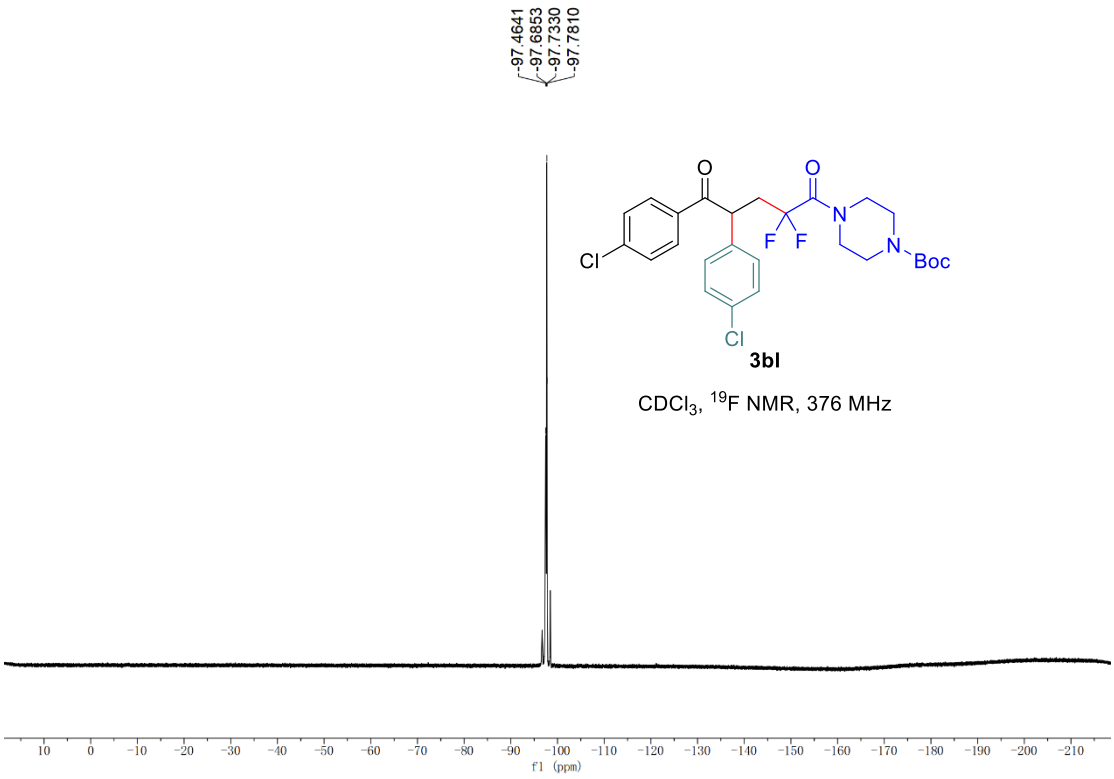
$CDCl_3$, ^{19}F NMR, 376 MHz

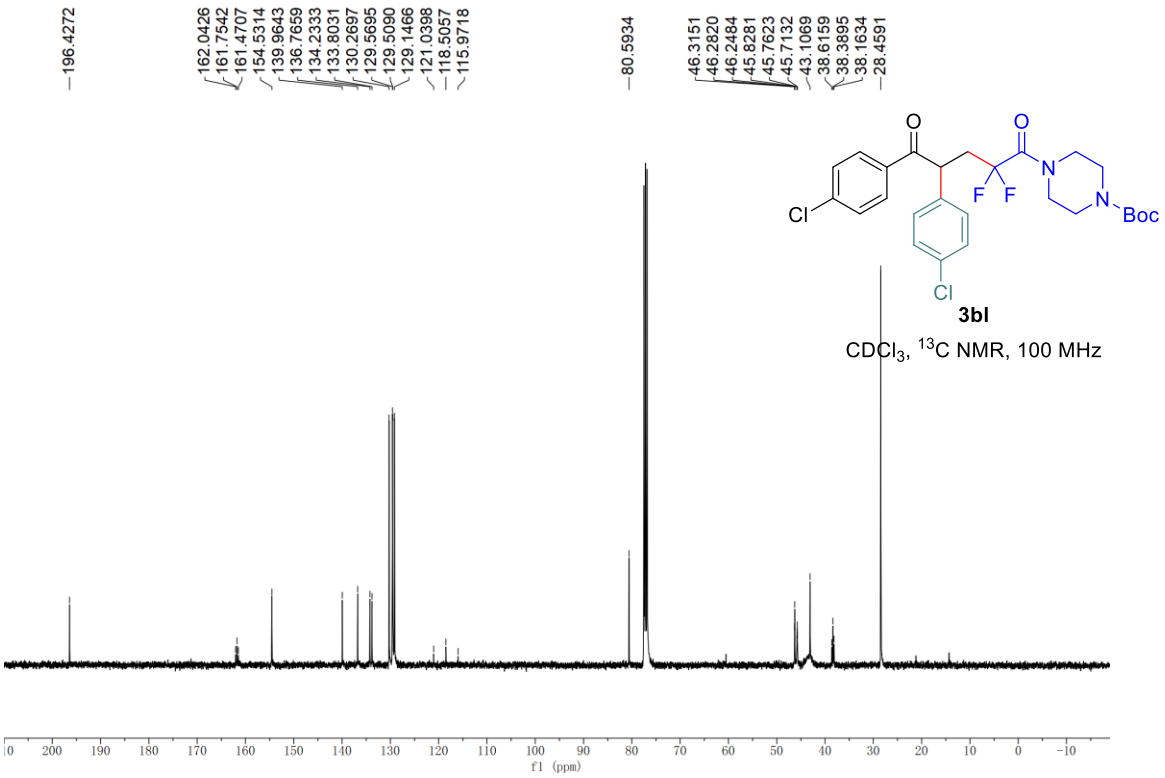


3bk

$CDCl_3$, ^{13}C NMR, 100 MHz

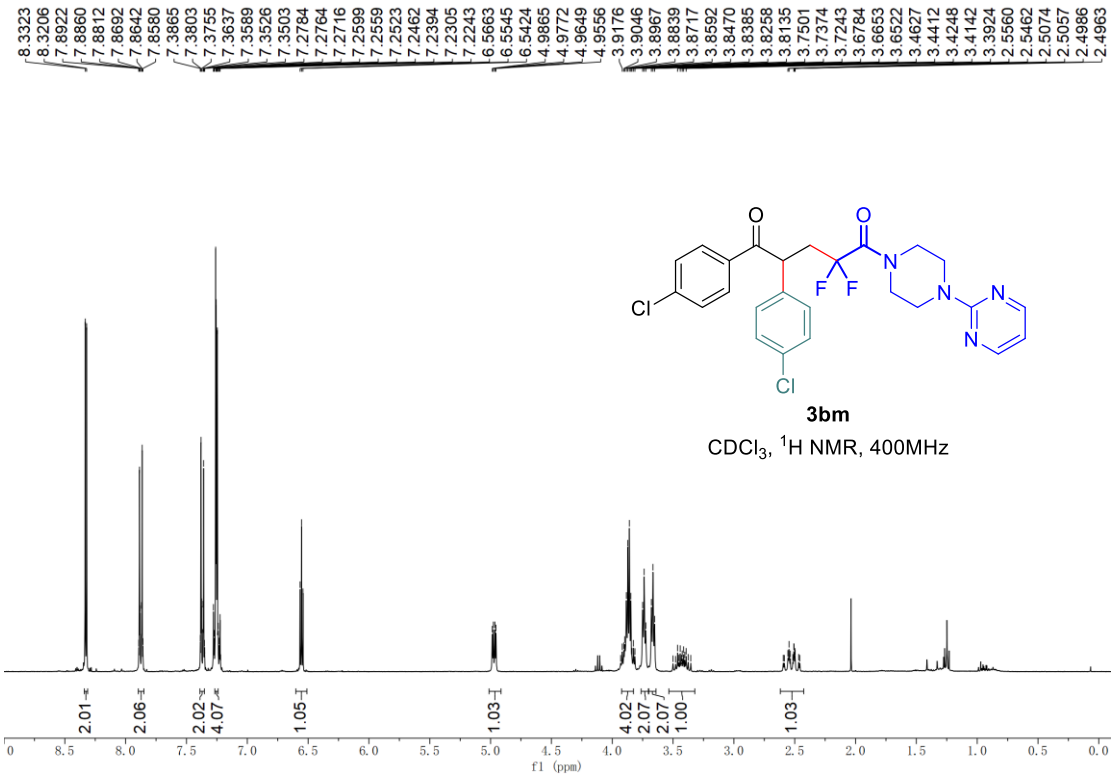

7.8807
7.8745
7.8697
7.8579
7.8531
7.8469
7.3855
7.3794
7.3746
7.3625
7.3576
7.3515
7.2731
7.2678
7.2600
7.2574
7.2516
7.2468
7.2366
7.2317
7.2256
7.2152
7.2101
4.9576
4.9481
4.9357
4.9264
3.7532
3.7508
3.7469
3.7428
3.7364
3.7301
3.7260
3.7222
3.7197
3.6401
3.6269
3.6141
3.5676
3.5539
3.5410
3.4990
3.4776
3.4653
3.4532
3.4447
3.4405
3.4323
3.4277
3.4189
3.4064
3.3937
3.3909
3.3793
2.5135
2.4753
2.4721
1.4575
O
O
N
F
F
N
Boc
Cl
Cl
3bl
CDCl3, 1H NMR, 400MHz
2.03
2.06
4.08
1.00
2.12
2.01
2.01
3.03
1.00
9.03
f1 (ppm)


-97.4641
-97.6853
-97.7330
-97.7810
O
O
N
F
F
N
Boc
Cl
Cl
3bl
CDCl3, 19F NMR, 376 MHz
f1 (ppm)



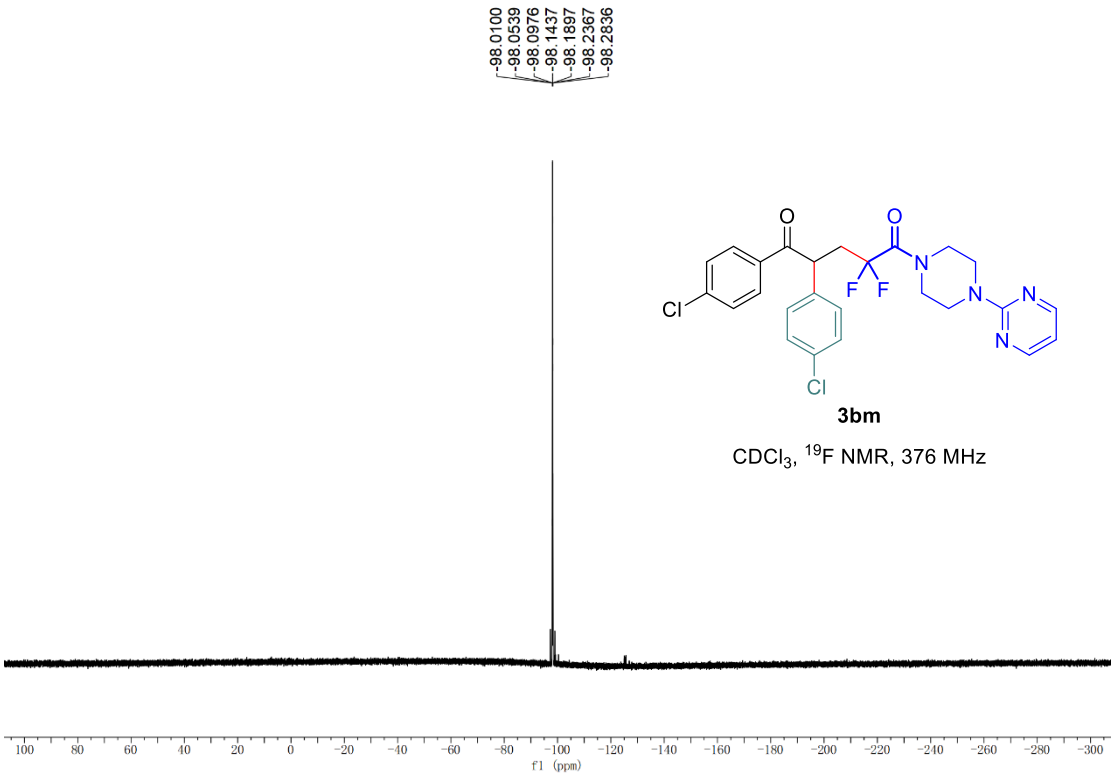
3bl

$CDCl_3$, ^{13}C NMR, 100 MHz



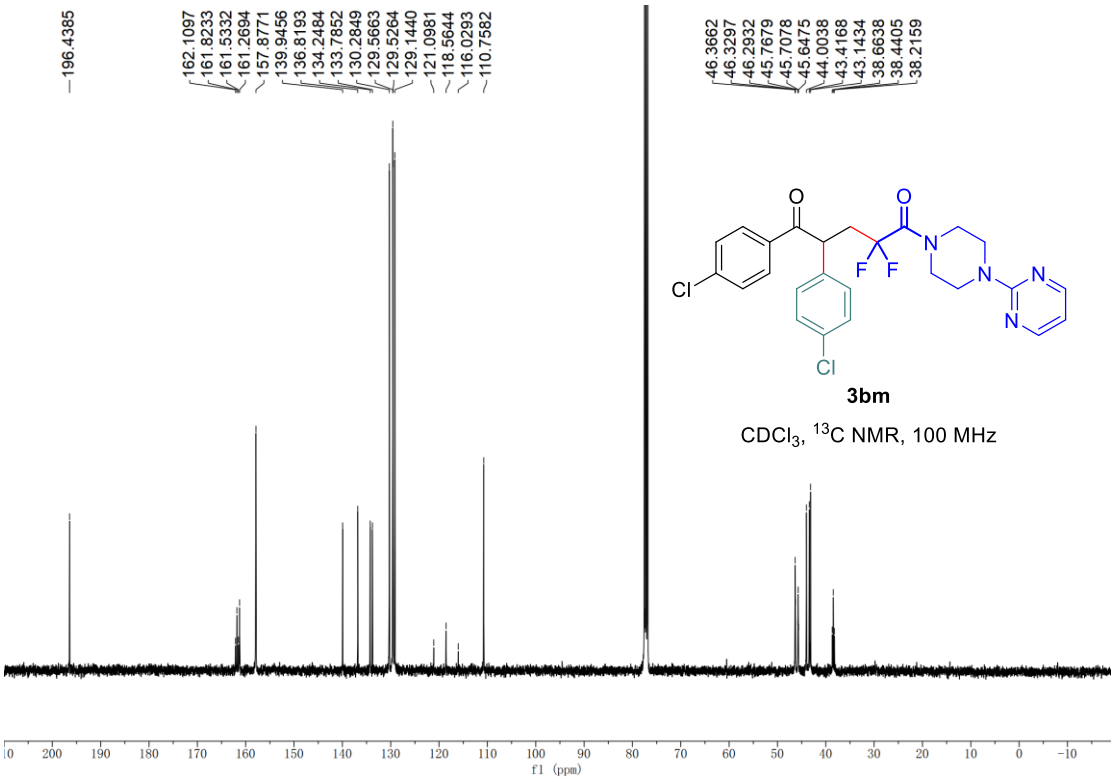
3bm

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



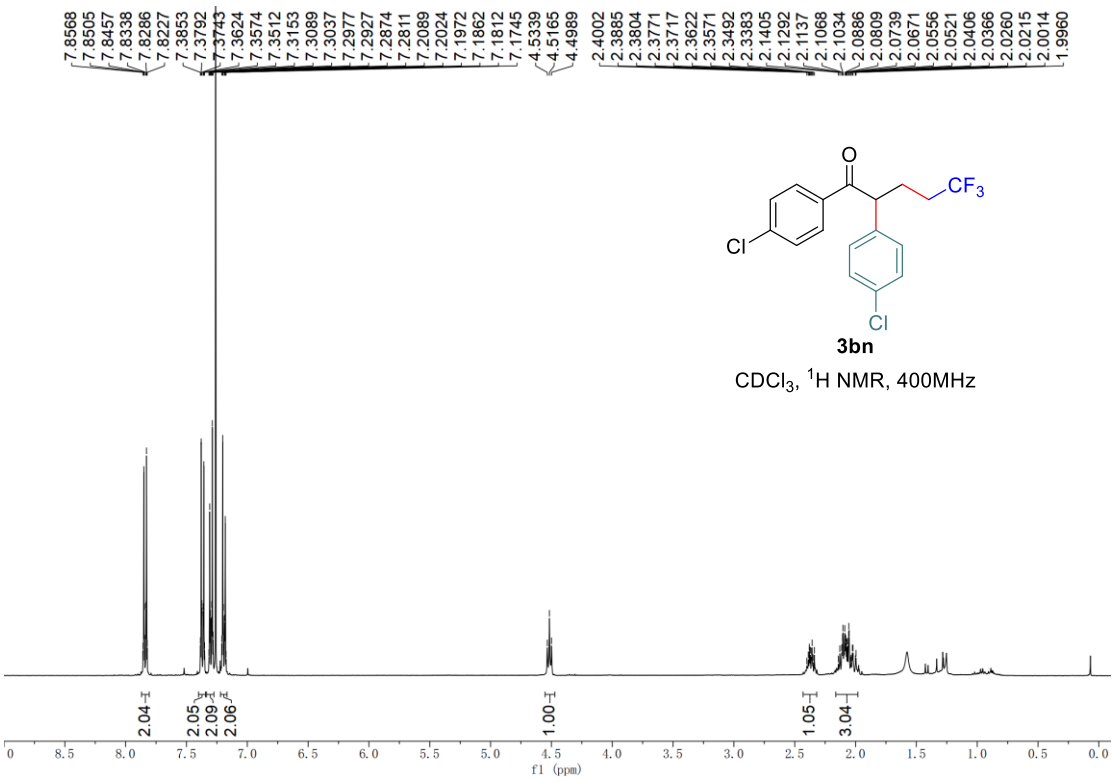
3bm

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



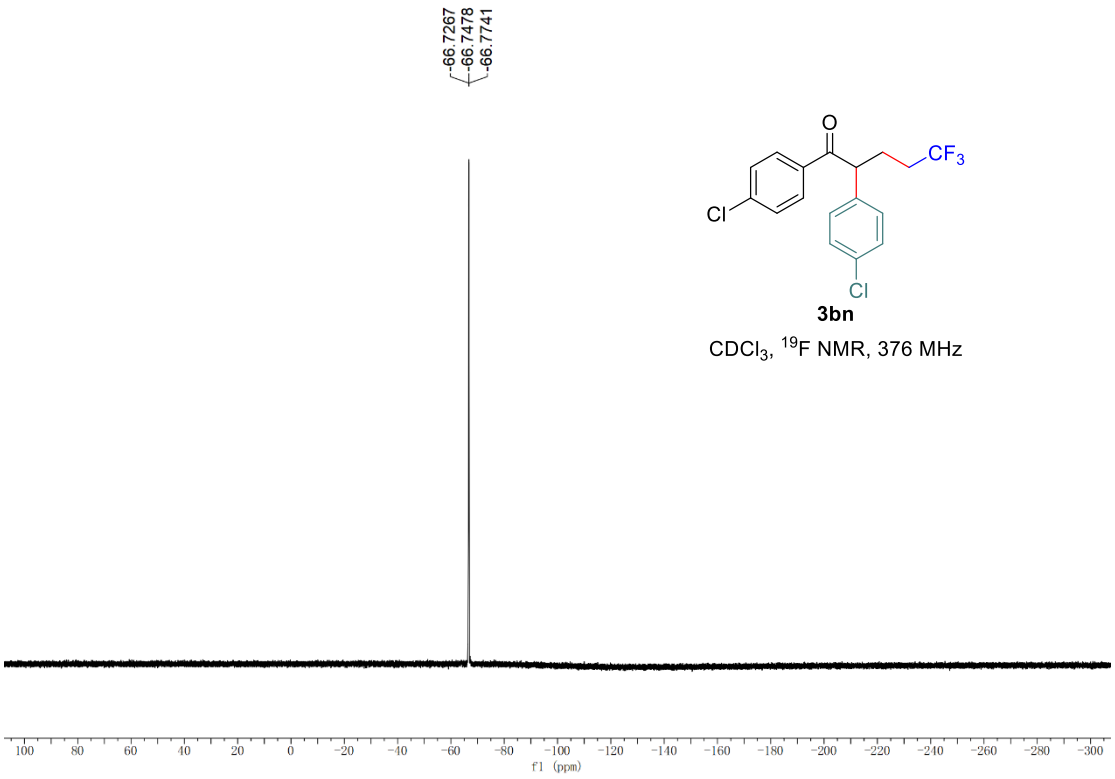
3bm

$CDCl_3$, ^{13}C NMR, 100 MHz



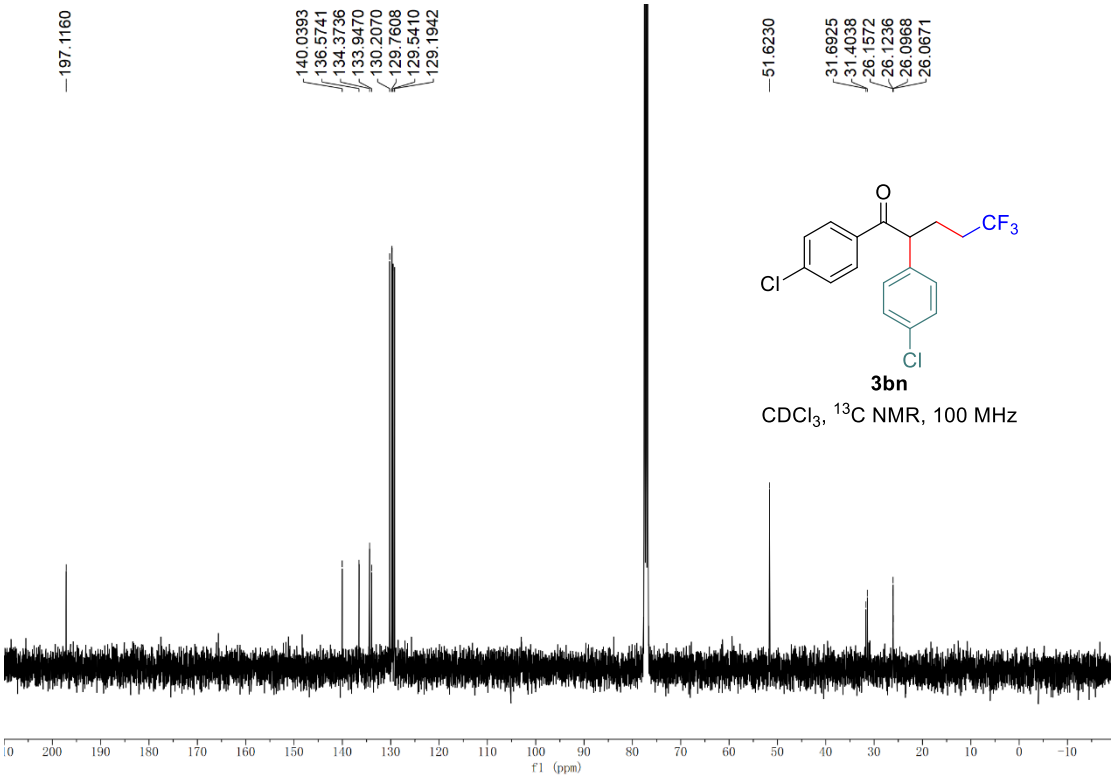
3bn

$CDCl_3$, ^1H NMR, 400MHz



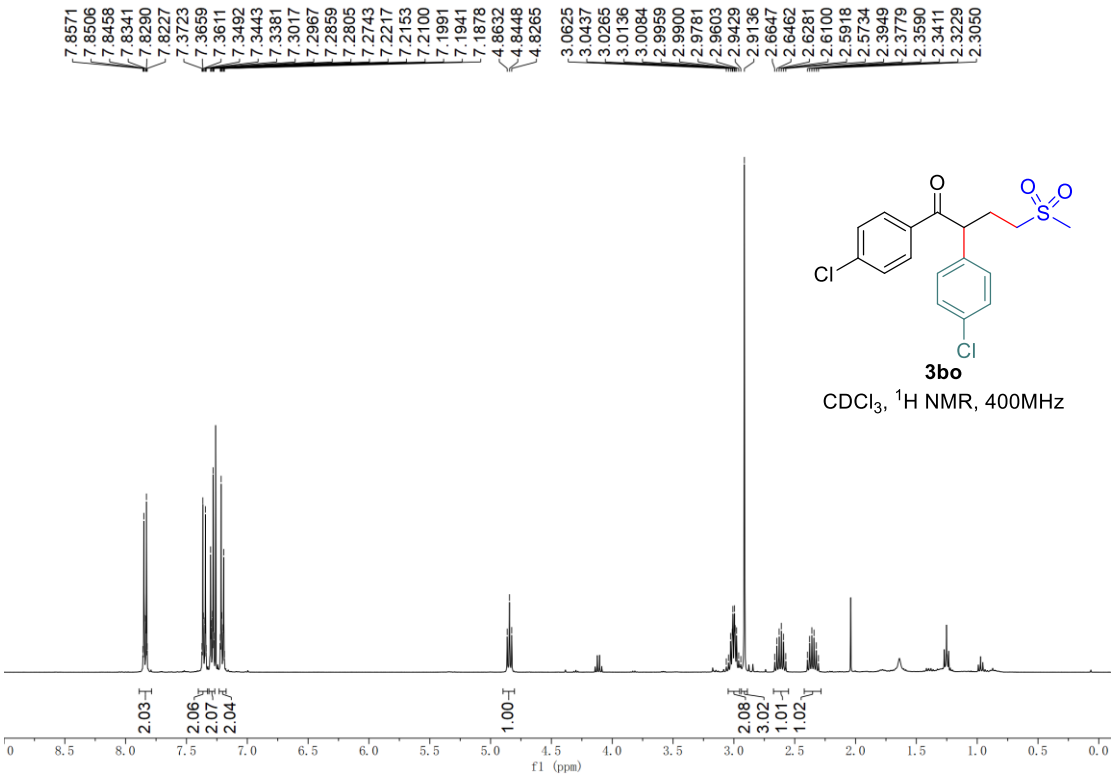
3bn

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



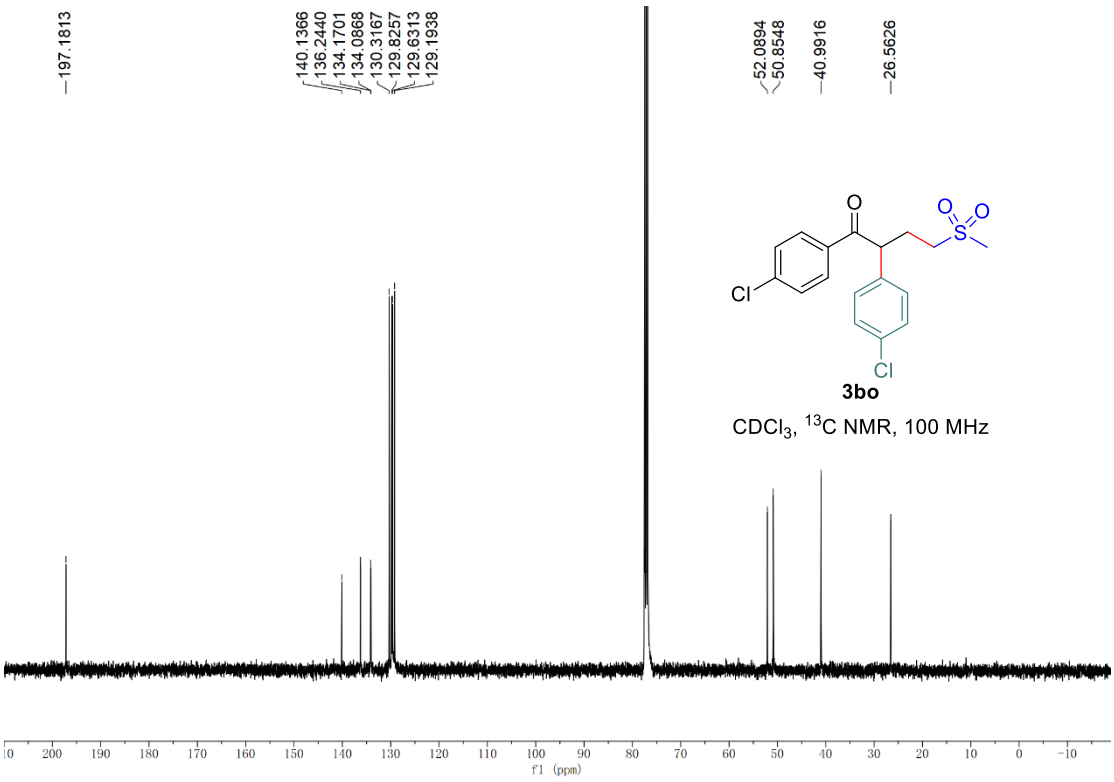
3bn

$CDCl_3$, ^{13}C NMR, 100 MHz



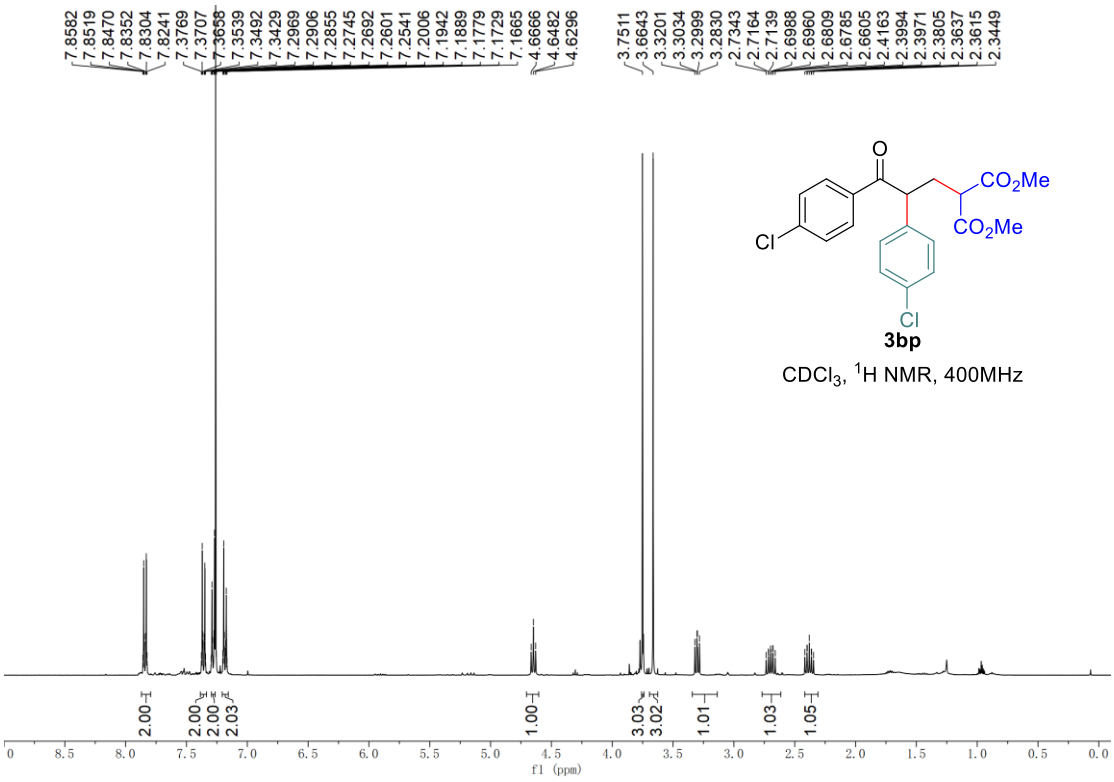
3bo

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



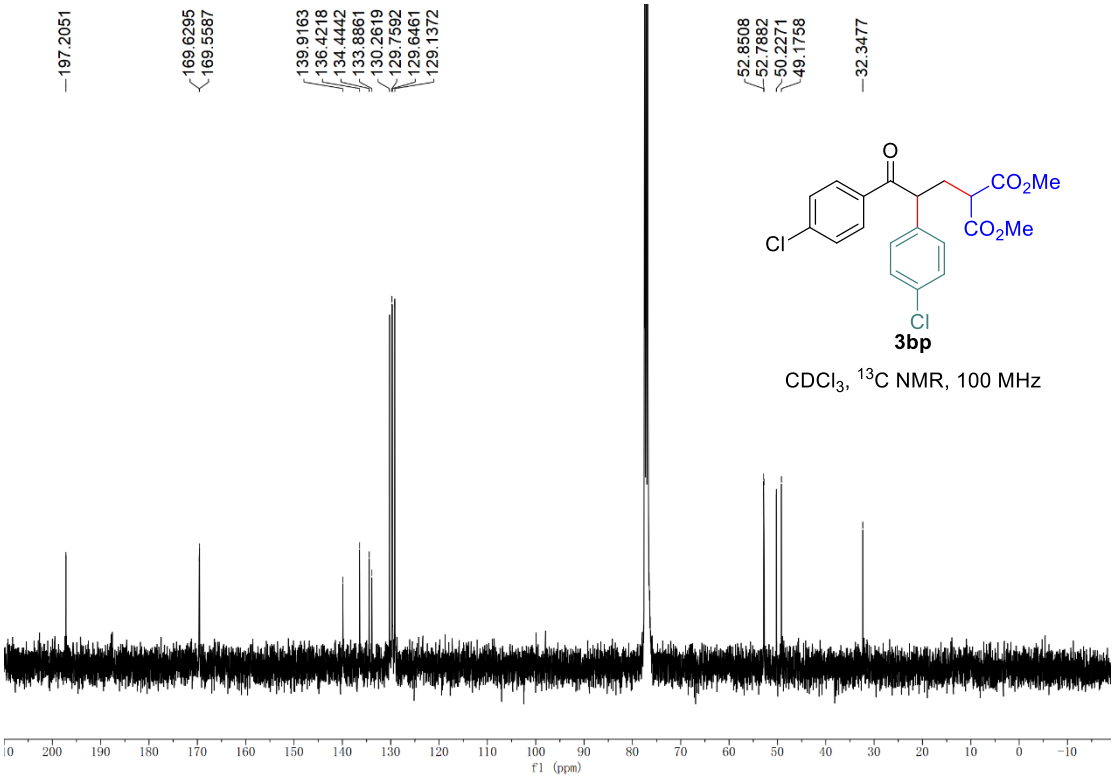
3bo

$CDCl_3$, ^{13}C NMR, 100 MHz



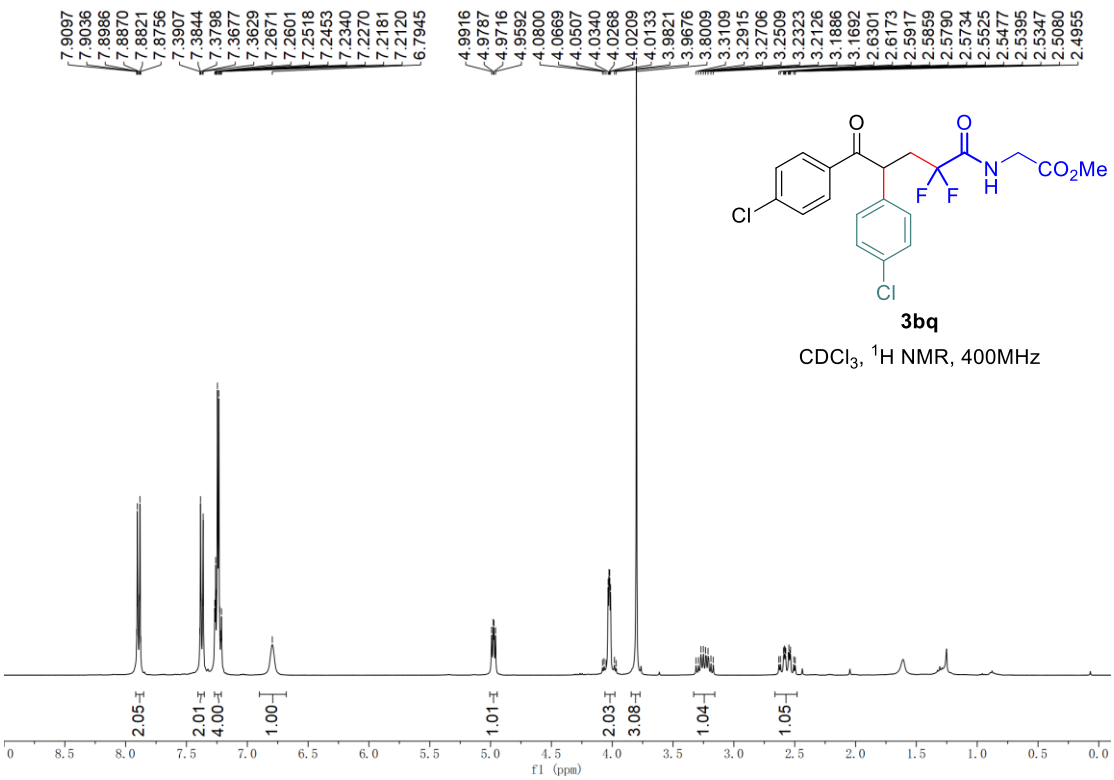
3bp

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



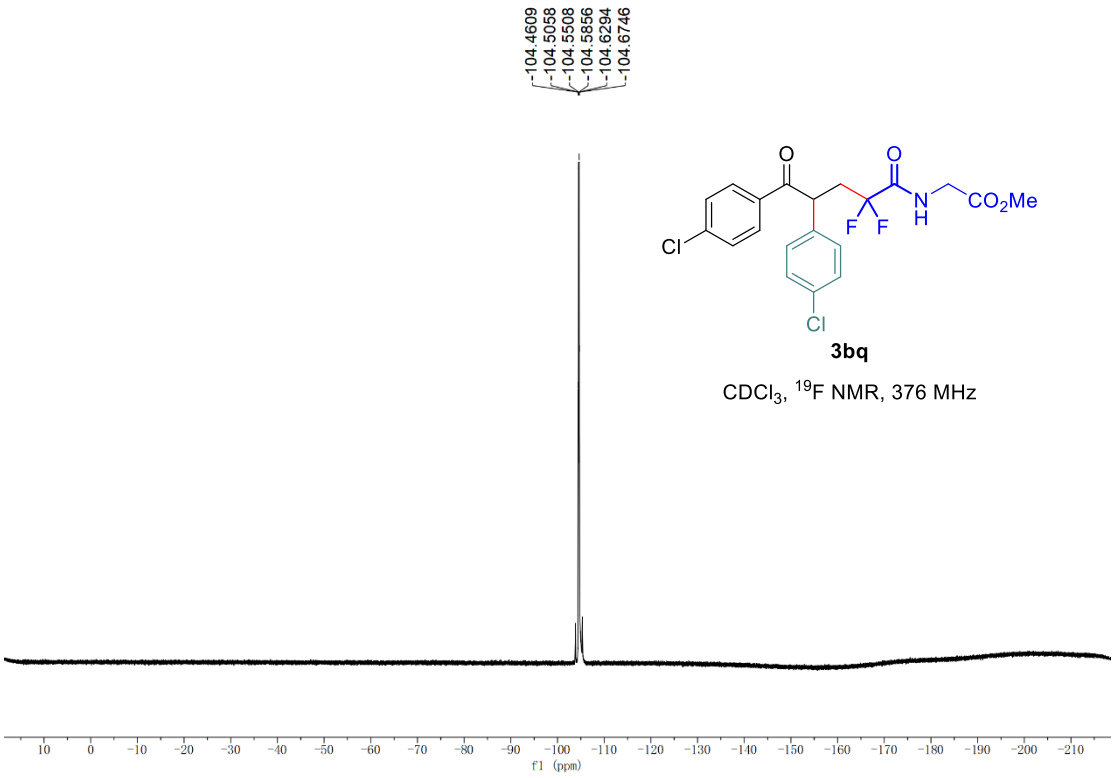
3bp

$CDCl_3$, ^{13}C NMR, 100 MHz



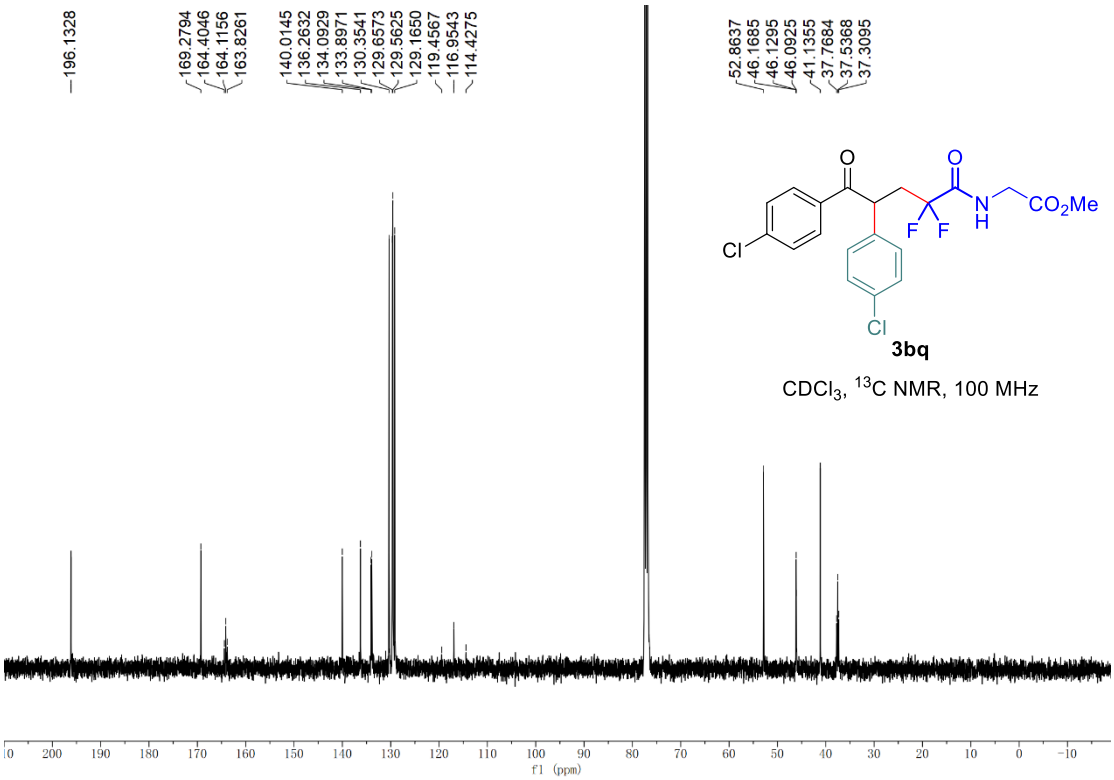
3bq

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



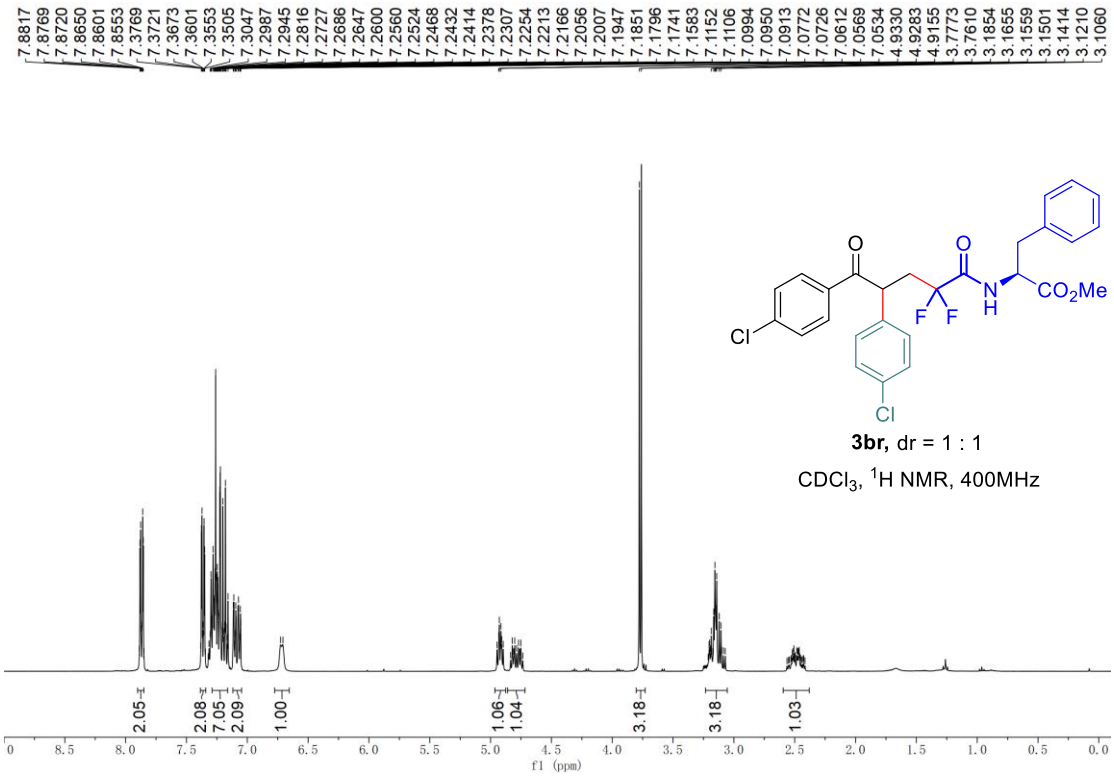
3bq

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



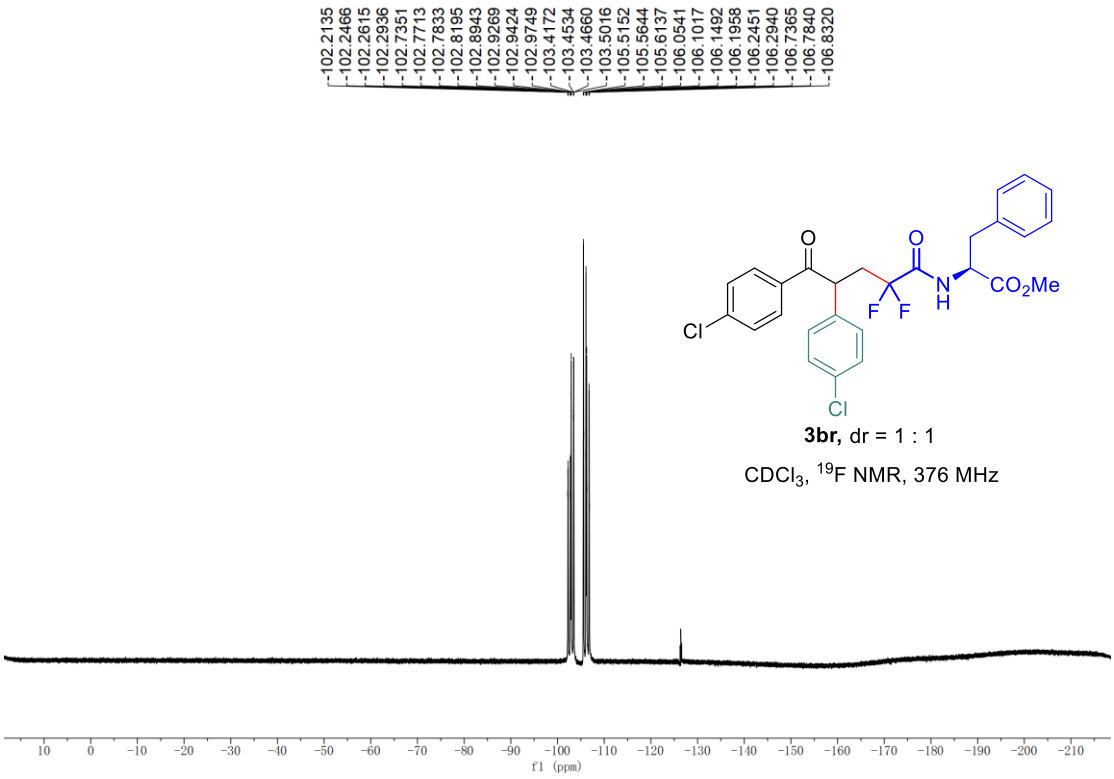
3bq

$CDCl_3$, ^{13}C NMR, 100 MHz



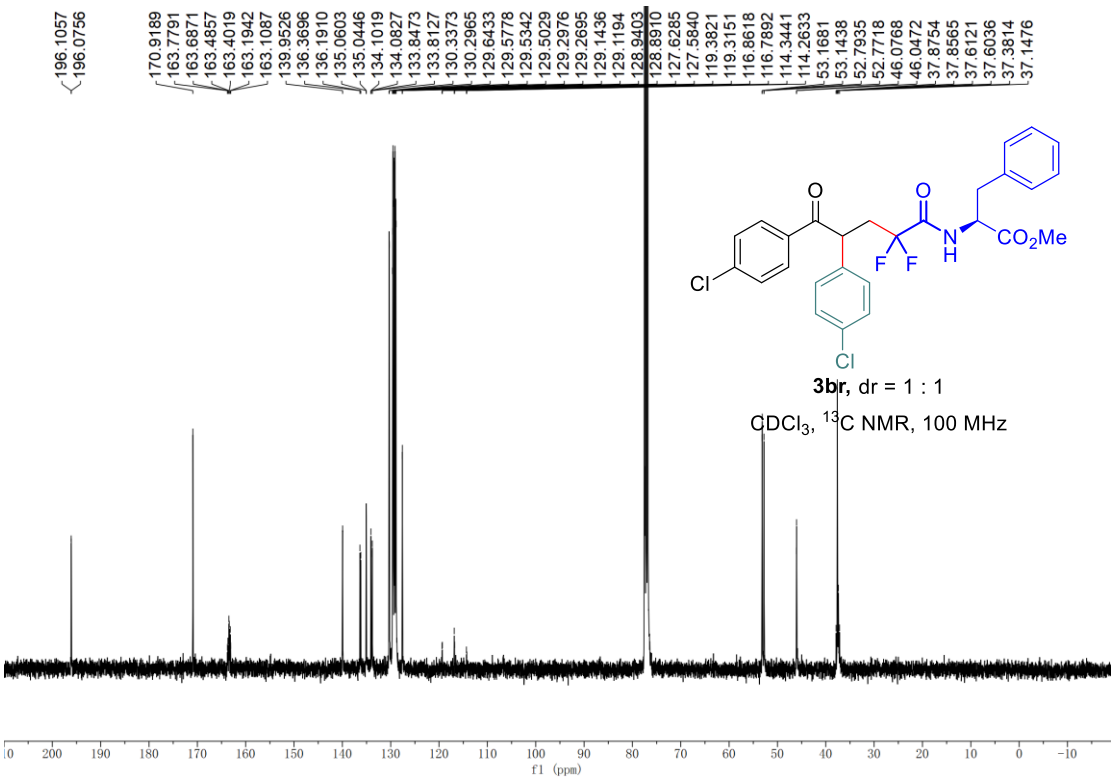
3br, dr = 1 : 1

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



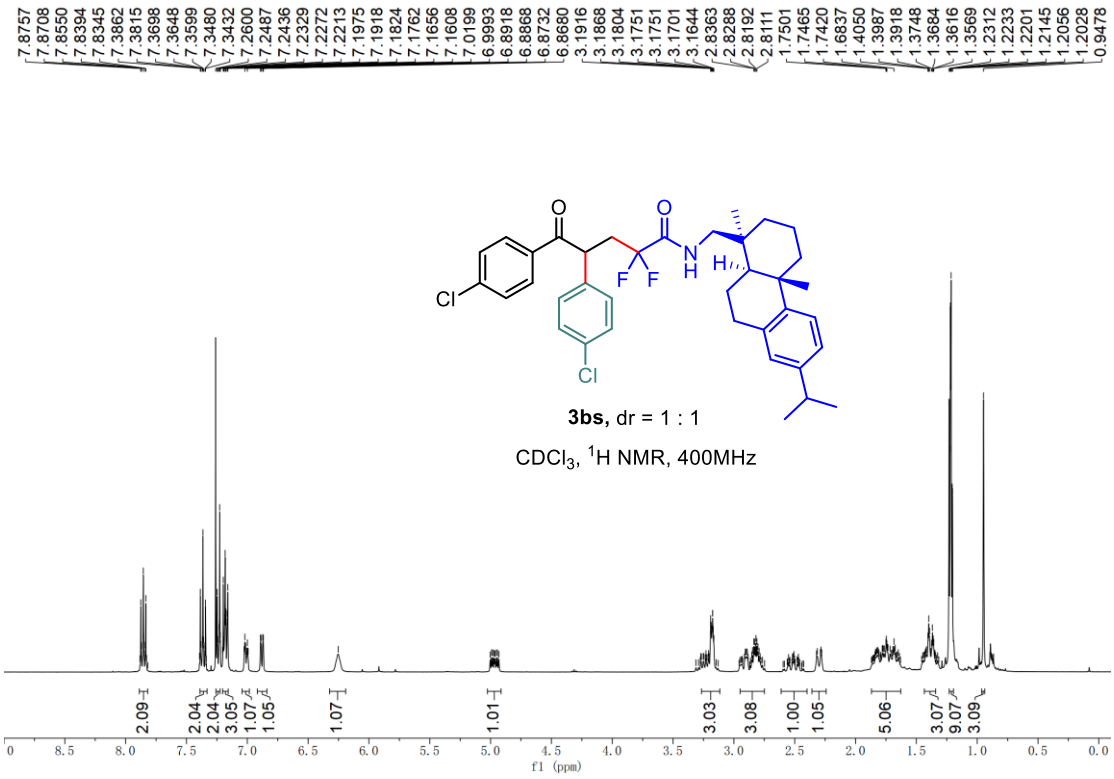
3br, dr = 1 : 1

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



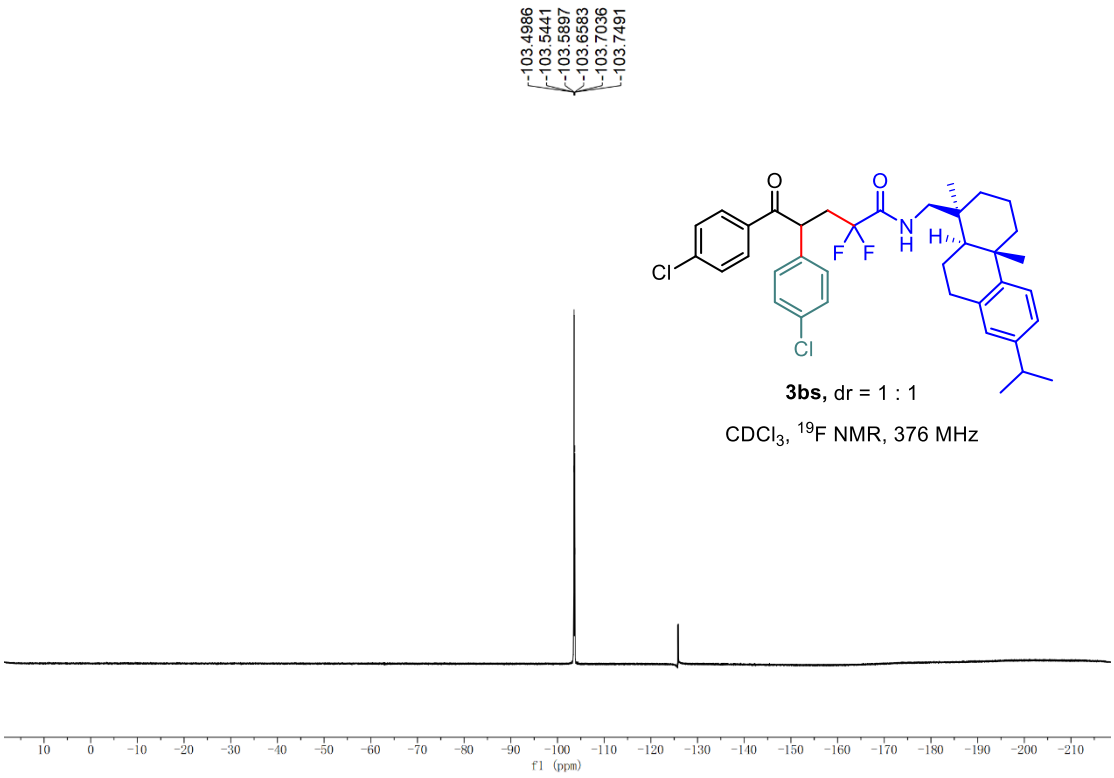
3br, dr = 1 : 1

$CDCl_3$, ^{13}C NMR, 100 MHz



3bs, dr = 1 : 1

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



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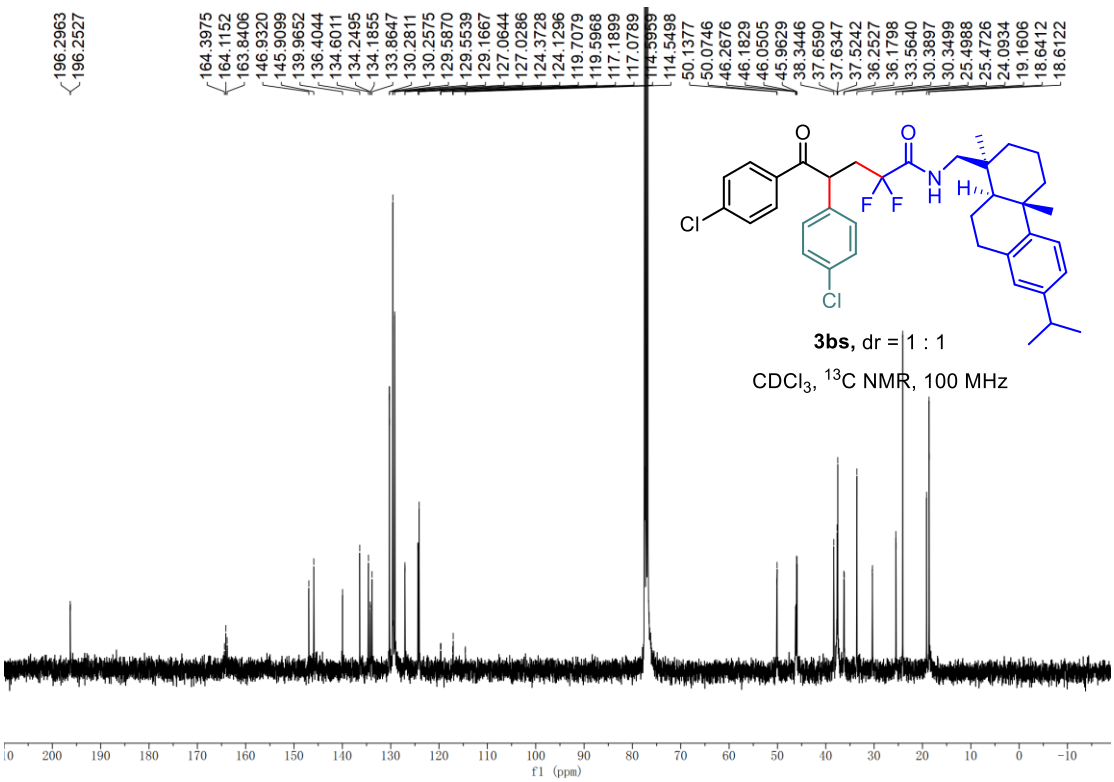
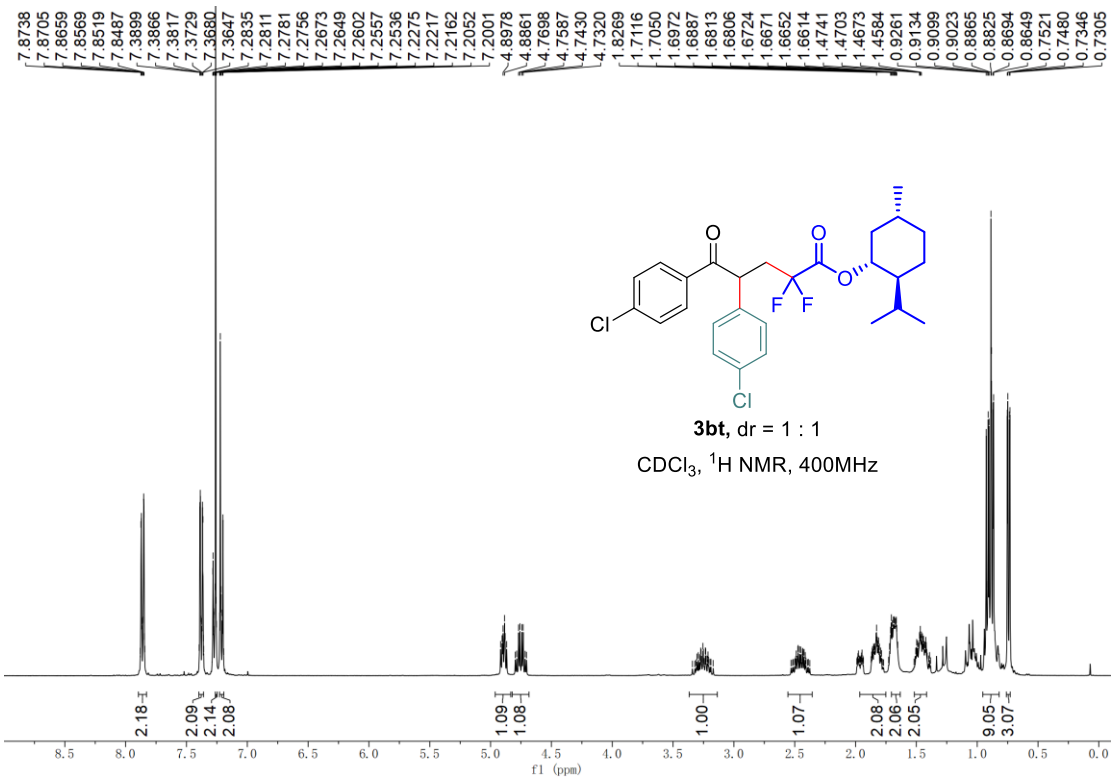
$CDCl_3$, ^{19}F NMR, 376 MHz



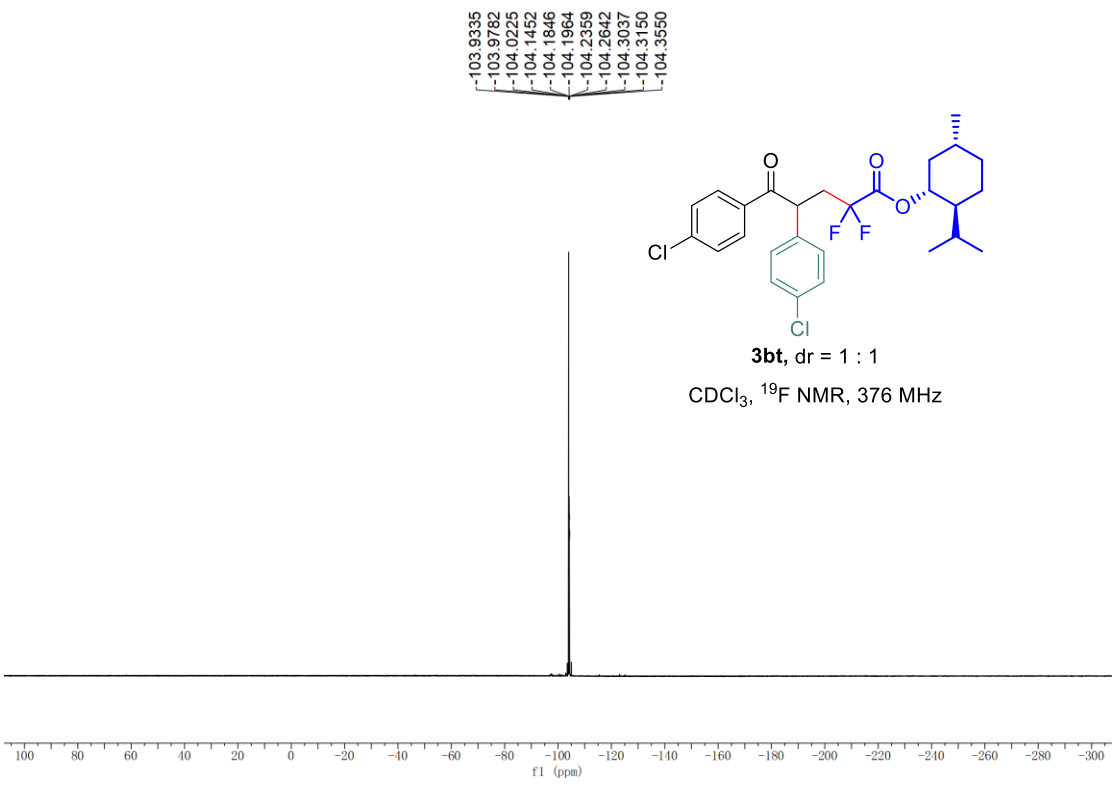
3bs, dr = 1 : 1

$CDCl_3$, ^{13}C NMR, 100 MHz



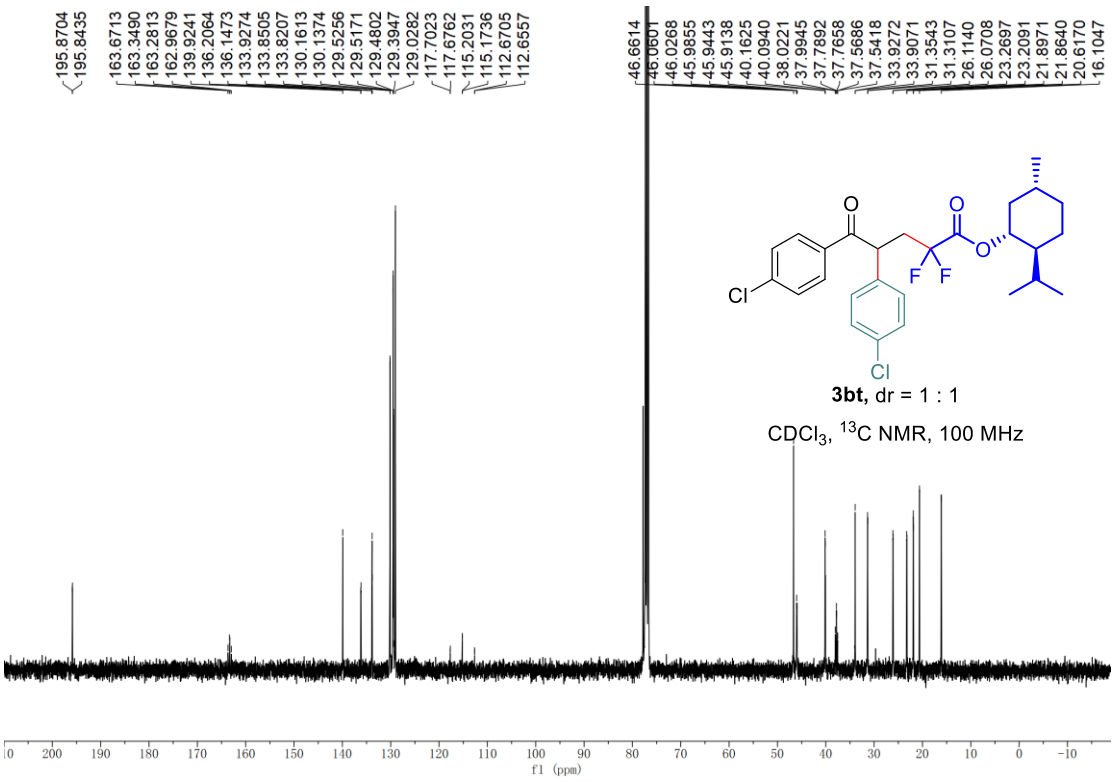
3bt, dr = 1 : 1

$CDCl_3$, ^1H NMR, 400MHz



3bt, dr = 1 : 1

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



3bt, dr = 1 : 1

$CDCl_3$, ^{13}C NMR, 100 MHz