Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Visible-Light promoted desulfonylative radical difluoroalkylation between difluoroenol silyl ethers and difluoroalkyl sulfones to construct functionalized aryltetrafluoroethane derivatives

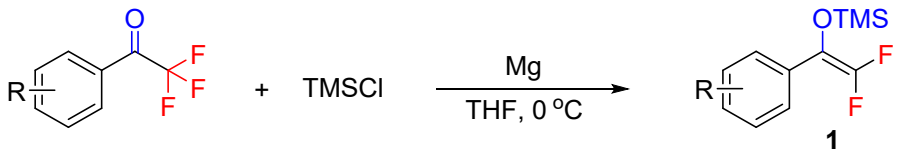
Contents

1. General Information

^{1}H NMR (TMS as the internal standard), ^{13}C NMR and ^{19}F NMR ($CFCl_3$ as outside standard and low field is positive) spectra were recorded on a Bruker AM 400 MHz spectrometer. For the determination of ^{19}F NMR yield, $PhCF_3$ was used as an internal standard and the relaxation delay (d1) was set to 5 s. Chemical shifts (δ) were reported in per million (ppm), and coupling constants (*J*) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (HRMS) were obtained on a GC-TOF mass spectrometer.

Materials: Unless otherwise noted, all reagents were obtained commercially and used without further purification. Substrates were prepared according to literature procedures. Reactions were performed using glassware that was flame-dried under vacuum.

2. Preparation of Difluoroenol Silyl Ethers



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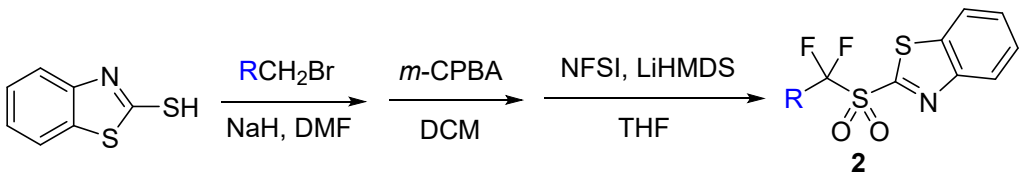
The difluoroenol silyl ethers **1** were freshly prepared from the corresponding trifluoroketones according to the literature procedures.[1] To a mixture of TMSCl (4.0 equiv) and Mg (4.0 equiv) in dry THF (0.25 M) was cooled down to 0 °C under N_2 atmosphere, then trifluoroacetophenone (1.0 equiv) was added dropwise. The reaction mixture was stirred for additional 30 min. After evaporation of solvent, hexane was added to the residue, and the resulting salt was filtered. The filtrate was concentrated to give crude difluoroenol silyl ethers, which could be used directly without further purification.

3. Preparation of α, α-difluorobenzyl/alkyl sulfones 2 (2b[2], 2c[3], 2k[4], 2l[4])

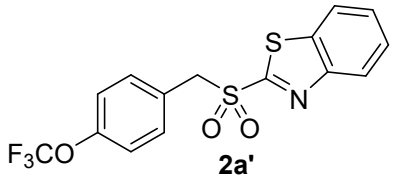


A 50-mL flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added benzo[*d*]thiazole-2-thiol (1.67 g, 10 mmol, 1.0 equiv) and dry DMF (20 mL) under a stream of argon. NaH (60% dispersion in mineral oil, 440 mg, 11 mmol, 1.1 equiv) was added to this mixture at 0 ºC. After stirring at 0 ºC for 10 min, corresponding benzyl or alkyl bromide (11 mmol, 1.1 equiv) was added at this temperature and the mixture was stirred at room temperature for 12 h. The mixture was quenched with cold water and extracted with ether (3 times). The combined extracts were dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was dissolved in DCM (50 mL). *m*-CPBA (85%, 5.08 g, 25 mmol, 2.5 equiv) was slowly added to this solution at 0 ºC and the mixture was stirred at room temperature for 12 h. The mixture was quenched with sat. Na_2SO_3 solution (~6 mL) and was washed with 1N NaOHaq (3 times). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography or recrystallization to afford the corresponding sulfones **2'**.

A 50-mL Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added sulfones **2'** (3 mmol, 1.0 equiv) and dry THF (20 mL). LiHMDS (1.0 M in THF solution, 8 mL, 8 mmol, 2.67 equiv) was added dropwise to the reaction mixture at -78 °C under argon. After stirring at -78 ºC for 30 min, a solution of NFSI (2.84 g, 9 mmol) in dry THF (10 mL) was added, the mixture was stirred at -78 °C for 30 min and then warmed to r.t. and stirring was continued for an additional 30 min. Sat. NH_4Claq (~20 mL) was added and the solvent was evaporated under reduced pressure. The mixture was extracted with EtOAc (3 times), and the combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was

purified by column chromatography to afford the corresponding α, α-difluorobenzyl/alkyl sulfones **2**.

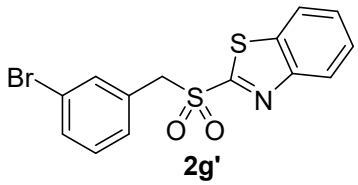
2-((4-(trifluoromethoxy)benzyl)sulfonyl)benzo[*d*]thiazole (2a')



2a'

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 8:1) to afford **2a'** as a white solid. m.p. 134-136 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.24 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.52 (m, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.77 (s, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.81 (s, 3F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 164.9, 152.5, 149.9, 137.0, 132.7, 128.2, 127.8, 125.5, 125.1, 122.4, 121.2, 120.3 (q, *J* = 257.9 Hz), 60.1; **IR** (thin film) *v* 1746, 1677, 1531, 1473, 1338, 1211, 1129, 948, 850, 666 cm^{-1}; **MS** (ESI): *m/z* 374.0 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{15}H_{11}F_3NO_3S_2$ $[M+H]^+$: 374.0127; Found: 374.0129.

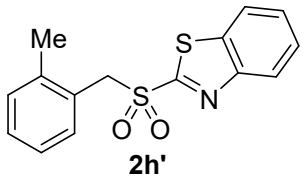
2-((3-bromobenzyl)sulfonyl)benzo[*d*]thiazole (2g')



2g'

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 8:1) to afford **2g'** as a white solid. m.p. 149-151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.25 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J*= 8.0 Hz, 1H), 7.62 (dt, *J* = 26.2, 7.4 Hz, 2H), 7.45 – 7.43 (m, 2H), 7.25 – 7.11 (m, 2H), 4.71 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 164.8, 152.5, 137.0, 134.1, 132.4, 130.4, 129.8, 128.5, 128.2, 127.8, 125.5, 122.8, 122.4, 60.3; **IR** (thin film) *v* 1568, 1470, 1317, 1144, 850, 793, 760, 728, 690, 638 cm^{-1}; **MS** (ESI): *m/z* 367.9 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{14}H_{11}F_3BrNO_2S_2$ $[M+H]^+$: 367.9409; Found: 367.9411.

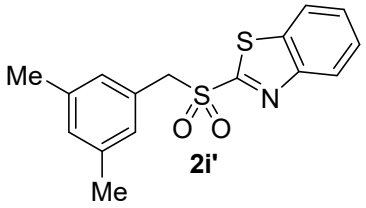
2-((2-methylbenzyl)sulfonyl)benzo[*d*]thiazole (2h')



2h'

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 8:1) to afford **2g'** as a white solid. m.p. 124-126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.29 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.64 (dt, *J* = 27.2, 7.4 Hz, 2H), 7.29 – 7.16 (m, 3H), 7.10 (t, *J* = 7.2 Hz, 1H), 4.85 (s, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 165.7, 152.6, 138.9, 137.1, 132.1, 131.1, 129.5, 128.1, 127.7, 126.3, 125.5, 124.8, 122.4, 58.4, 19.8; **IR** (thin film) *v* 1468，1326，1137，1023，854，766，728，692，641 cm^{-1}; **MS** (ESI): *m*/*z* 304.0 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{15}H_{14}NO_2S_2$ $[M+H]^+$: 304.0460; Found: 304.0461.

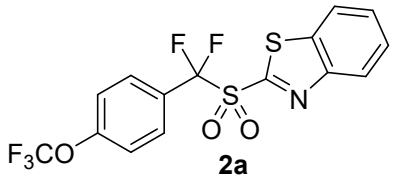
2-((3,5-dimethylbenzyl)sulfonyl)benzo[*d*]thiazole (2i')



2i'

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 8:1) to afford **2i'** as a white solid. m.p. 158-160 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.29 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.63 (dt, *J* = 27.8, 7.5 Hz, 2H), 6.95 (s, 1H), 6.89 (s, 2H), 4.69 (s, 2H), 2.20 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 165.5, 152.6, 138.5, 137.1, 130.9, 128.9, 128.0, 127.7, 125.9, 125.4, 122.3, 61.2, 21.1; **IR** (thin film) *v* 1470，1316，1153，1127，873，858，764，729，703，602 cm^{-1}; **MS** (ESI): *m*/*z* 318.1 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{16}H_{16}NO_2S_2$ $[M+H]^+$: 318.0617; Found: 318.0619.

2-((difluoro(4-(trifluoromethoxy)phenyl)methyl)sulfonyl)benzo[*d*]thiazole (2a)

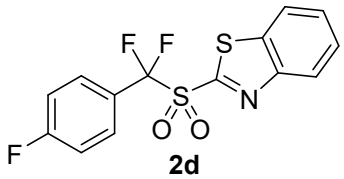


2a

The product mixture was purified by silica gel column chromatography (hexane/DCM = 1:1) to afford **2a** as a white solid. m.p. 159-161 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.36 (dd, *J* = 7.3, 1.7 Hz, 1H), 8.07 (dd, *J* = 7.2, 1.7 Hz, 1H),

7.83 (d, *J* = 8.8 Hz, 2H), 7.72 – 7.65 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.67 (s, 3F), -99.69 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 158.7, 153.0, 152.8, 138.3, 130.2 (t, *J* = 5.9 Hz), 129.0, 128.1, 126.3, 123.9 (t, *J* = 22.5 Hz), 122. 3, 122.0 (t, *J* = 290.5 Hz), 120.9, 120.3 (q, *J* = 260.3 Hz) ; **IR** (thin film) *v* 1463，1357，1221，1162，1100，1067，922，842，761，728，618 cm^{-1}; **MS** (ESI): *m/z* 410.0 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{15}H_9F_5NO_3S_2$ $[M+H]^+$: 409.9939; Found: 409.9941.

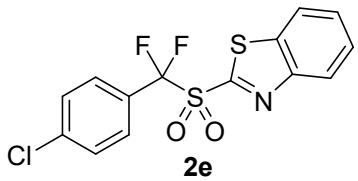
2-((difluoro(4-fluorophenyl)methyl)sulfonyl)benzo[*d*]thiazole (2d)



2d

The product mixture was purified by silica gel column chromatography (hexane/DCM = 1:1) to afford **2d** as a white solid. m.p. 171-173 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.44 – 8.32 (m, 1H), 8.19 – 8.03 (m, 1H), 7.77 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.24 (t, *J* = 9.2 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -99.24 (s, 2F), -104.87 – -104.91 (m, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 165.7 (d, *J*= 255.8), 159.0, 153.0, 138.3, 130.6 (dt, *J* = 9.5, 6.0 Hz), 128.9, 128.1, 126.3, 122.3, 122.2 (t, *J* = 290.3 Hz), 121.5 (td, *J* = 22.4, 3.3 Hz), 116.4 (d, *J*= 22.5 Hz); **IR** (thin film) *v* 1604，1462，1353，1278，1168，1060，839，758，720，620 cm^{-1}; **MS** (ESI): *m/z* 366.0 $[M+Na]^+$. **HRMS** (ESI): m/z Calculated for $C_{14}H_8F_3NNaO_2S_2$ $[M+Na]^+$: 365.9841; Found: 365.9841.

2-(((4-chlorophenyl)difluoromethyl)sulfonyl)benzo[*d*]thiazole (2e)

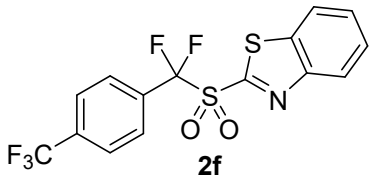


2e

The product mixture was purified by silica gel column chromatography (hexane/DCM = 1:1) to afford **2e** as a white solid. m.p. 227-229 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.30 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 7.4 Hz, 1H), 7.74 – 7.56 (m, 4H), 7.47 (d, *J* = 8.4 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -99.91 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 158.1, 152.0, 138.9, 137.3, 128.4 (t, *J* = 5.9 Hz), 128.3, 127.9, 127.1, 125.3, 122.9 (t, *J* = 22.5 Hz), 121.4 (t, *J* = 308.1 Hz), 121.3; **IR** (thin film) *v*

1597，1462，1356，1280，1169，1068，1011，819，764，616 cm^{-1}; **MS** (ESI): *m/z* 360.0 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{14}H_9ClF_2NO_2S_2$ $[M+H]^+$: 359.9726; Found: 359.9729.

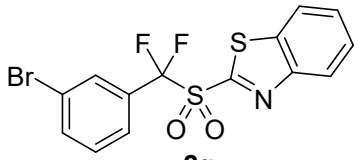
2-((difluoro(4-(trifluoromethyl)phenyl)methyl)sulfonyl)benzo[*d*]thiazole (2f)



2f

The product mixture was purified by silica gel column chromatography (hexane/DCM = 1:1) to afford **2f** as a white solid. m.p. 186-188 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.28 (dd, *J* = 7.3, 1.6 Hz, 1H), 8.00 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.84 – 7.73 (m, 4H), 7.65 – 7.58 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -63.27 (s, 3F), -100.35 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 158.5, 153.0, 138.4, 134.9 (q, *J* = 33.3 Hz), 129.3 (t, *J* = 21.4 Hz), 129.0, 128.7 (t, *J* = 5.9 Hz), 128.2, 126.4, 126.0 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 274.0 Hz), 122.3, 122.0 (q, *J* = 291.6 Hz); **IR** (thin film) *v* 1457，1367，1321，1276，1172，1102，1063，823，764，622 cm^{-1}; **MS** (ESI): *m/z* 394.0 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{15}H_9F_5NO_2S_2$ $[M+H]^+$: 393.9989; Found: 393.9995.

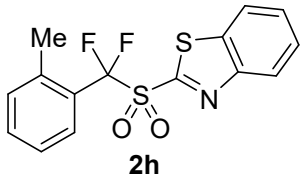
2-(((3-bromophenyl)difluoromethyl)sulfonyl)benzo[*d*]thiazole (2g)



2g

The product mixture was purified by silica gel column chromatography (hexane/DCM = 1:1) to afford **2g** as a white solid. m.p. 149-151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.37 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.07 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.88 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.67 (m, 3H), 7.43 (t, *J* = 7.9 Hz, 1H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -99.89 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 158.7, 153.0, 138.3, 136.2, 131.0 (t, *J* = 6.2 Hz), 130.4, 129.0, 128.2, 127.6 (t, *J* = 22.0 Hz), 126.7 (t, *J* = 5.9 Hz), 126.3, 123.0, 122.3, 121.6 (t, *J* = 290.0 Hz); **IR** (thin film) *v* 1459，1359，1260，1169，1078，951，795，764，748，612 cm^{-1}; **MS** (ESI): *m/z* 403.9 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{14}H_9F_2BrNO_2S_2$ $[M+H]^+$: 403.9221; Found: 403.9224.

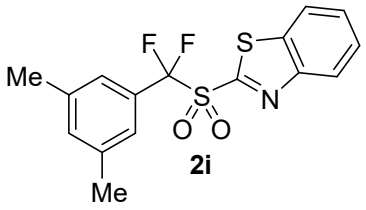
2-((difluoro(*o*-tolyl)methyl)sulfonyl)benzo[*d*]thiazole (2h)



2h

The product mixture was purified by silica gel column chromatography (hexane/DCM = 2:1) to afford **2h** as a white solid. m.p. 170-172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.97 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.64 – 7.54 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 6.6 Hz, 2H), 2.59 (t, *J* = 3.3 Hz, 1H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -93.82 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 158.6, 152.0, 138.6, 137.3, 131.9, 131.7, 128.8 (t, *J* = 8.3 Hz), 127.7, 126.9, 125.2, 125.1, 123.1 (t, *J* = 291.8 Hz), 122.7 (t, *J* = 19.7 Hz), 121.2, 19.8; **IR** (thin film) *v* 1461, 1351，1255，1166，1045，920，753，723，694，609 cm^{-1}; **MS** (ESI): *m/z* 362.0 $[M+Na]^+$. **HRMS** (ESI): m/z Calculated for $C_{15}H_{11}F_2NNaO_2S_2$ $[M+Na]^+$: 362.0091; Found: 362.0093.

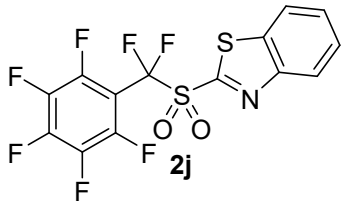
2-(((3,5-dimethylphenyl)difluoromethyl)sulfonyl)benzo[*d*]thiazole (2i)



2i

The product mixture was purified by silica gel column chromatography (hexane/DCM = 2:1) to afford **2i** as a white solid. m.p. 174-176 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.35 (d, *J* = 7.7 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.73 – 7.54 (m, 2H), 7.35 (s, 2H), 7.24 (s, 1H), 2.36 (s, 6H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -99.13 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 159.5, 153.0, 138.8, 138.3, 134.8, 128.7, 128.0, 126.2, 125.6 (t, *J* = 5.9 Hz), 125.2 (t, *J* = 21.3 Hz), 122.8 (t, *J* = 289.9 Hz), 122.2, 21.2; **IR** (thin film) *v* 1460，1354，1166，1097，962，858，758，726，696，618 cm^{-1}; **MS** (ESI): *m/z* 376.0 $[M+Na]^+$. **HRMS** (ESI): m/z Calculated for $C_{16}H_{13}F_2NNaO_2S_2$ $[M+Na]^+$: 376.0248; Found: 376.0250.

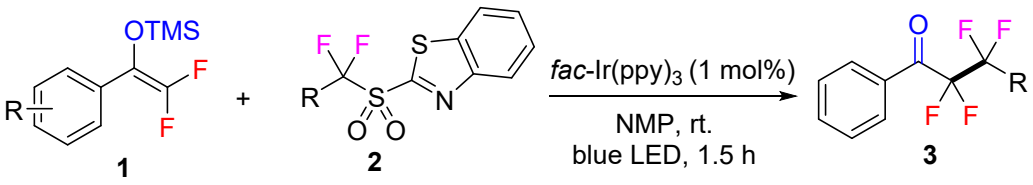
2-((difluoro(perfluorophenyl)methyl)sulfonyl)benzo[*d*]thiazole (2j)



2j

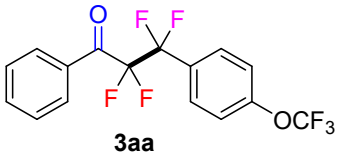
The product mixture was purified by silica gel column chromatography (hexane/DCM = 2:1) to afford **2j** as a white solid. m.p. 155-157 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.27 – 8.07 (m, 1H), 8.06 – 7.80 (m, 1H), 7.72 – 7.35 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -95.15 (t, *J* = 31.5 Hz, 2F), -131.83 – -137.83 (m, 2F), -143.51 (tt, *J* = 21.4, 6.7 Hz, 1F), -155.38 – -162.79 (m, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 157.5, 153.1, 147.5 – 144.5 (m), 146.0 – 143.2 (m), 139.6 – 136.7 (m), 138.5, 129.3, 128.4, 126.3, 122.4, 120.1 (t, *J* = 295.6 Hz), 103.10 – 101.13 (m); **IR** (thin film) *v* 1654，1505，1463，1361，1168，1095，977，817，771，630 cm^{-1}; **MS** (ESI): *m*/*z* 416.0 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{14}H_5F_7NO_2S_2$ $[M+H]^+$: 415.9644; Found: 415.9649.

4. General procedure for reactions of sulfones 2 with difluoroenol silyl ethers



A 25 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, *fac*-Ir(ppy)$_3$ (2.6 mg, 0.004 mmol, 1 mol %) and difluoroalkyl sulfone **2** (0.4 mmol, 1.0 equiv) were dissolved in dry NMP (2.0 mL), then difluoroenol silyl ethers **1** (0.8 mmol, 2.0 equiv) was added. The mixture was degassed three times by the freeze-pump-thaw procedure. The flask was placed at a distance of 2 cm from the blue LEDs. After 1.5 hours, the reaction was quenched by water, extracted by Et_2O. The organic phase was dried by anhydrous sodium sulfate, then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired products **3**.

2,2,3,3-tetrafluoro-1-phenyl-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3aa)

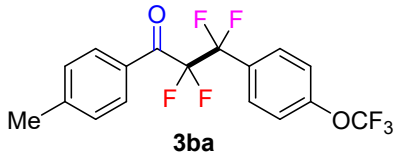


3aa

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3aa** (87.9 mg, 60%) as a yellowlish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.99 (d, *J* = 7.9 Hz, 2H), 7.60 – 7.56 (m, 3H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.78 (s, 3F), -109.56 (s, 2F), -112.86 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.6 (t, *J* = 26.7 Hz), 150.5, 133.9, 131.4, 129.3 (t, *J* = 3.4 Hz), 128.0 (t, *J* = 6.4 Hz), 127.8, 127.5 (t, *J* = 25.0 Hz), 119.6, 119.3 (q, *J* = 258.5 Hz), 114.5 (tt, *J* = 255.3, 31.7 Hz), 110.8 (tt, *J* = 266.6, 38.2 Hz); **IR** (thin film) *v* 1704, 1598, 1513, 1255, 1211, 1149, 1079, 975, 838, 713, 660 cm^{-1}; **MS** (EI): *m*/*z*

366.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{16}H_9F_7O_2$ $[M]^+$: 366.0491; Found: 366.0480.

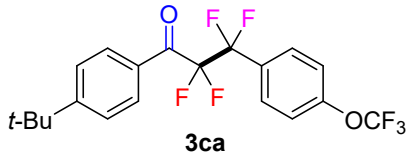
2,2,3,3-tetrafluoro-1-(p-tolyl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ba)



3ba

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ba** (85.1 mg, 56%) as a yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.88 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.18 (m, 4H), 2.34 (s, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.80 (s, 3F), -109.63 (s, 2F), -112.86 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.1 (t, *J* = 26.5 Hz), 150.5, 145.3, 129.4 (t, *J* = 3.2 Hz), 128.9, 128.5, 128.0 (t, *J* = 6.3 Hz), 127.6 (t, *J* = 25.1 Hz), 119.5, 119.3 (q, *J* = 258.7 Hz), 114.7 (tt, *J* = 255.3, 31.8 Hz), 110.9 (tt, *J* = 266.4, 38.2 Hz); **IR** (thin film) *v* 1698, 1607, 1513, 1255, 1211, 1146, 1079, 974, 845, 751, 609 cm^{-1}; **MS** (EI): *m/z* 380.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{17}H_{11}F_7O_2$ $[M]^+$: 380.0647; Found: 380.0648.

1-(4-(tert-butyl)phenyl)-2,2,3,3-tetrafluoro-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ca)

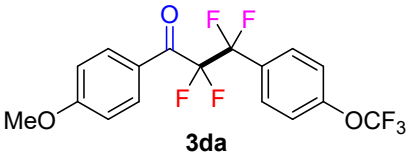


3ca

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ca** (99.6 mg, 59%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.93 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 1.25 (s, 9H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.78 (s, 3F), -109.59 (s, 2F), -112.85 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.1 (t, *J* = 26.5 Hz), 158.1, 150.4, 129.3 (t, *J* = 3.1 Hz), 128.8, 128.0 (t, *J* = 6.4 Hz), 127.6 (t, *J* = 25.1 Hz), 124.8, 119.5, 119.3 (q, *J* = 258.5 Hz), 115.0 (tt, *J* = 255.3, 31.7 Hz), 110.9 (tt, *J* = 266.4, 38.0 Hz), 34.3, 29.8; **IR** (thin film) *v* 1679, 1604, 1514, 1257, 1213, 1153, 1027, 976, 877, 692 cm^{-1}; **MS** (ESI): *m/z* 423.1

[M+H]$^+$. **HRMS** (ESI): m/z Calculated for $C_{20}H_{18}F_7O_2$ [M+H]$^+$: 423.1190; Found: 423.1189.

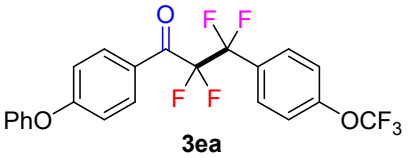
2,2,3,3-tetrafluoro-1-(4-methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3da)



3da

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **3da** (104.6 mg, 66%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.97 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.81 (s, 3F), -109.67 (s, 2F), -112.65 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 182.7 (t, *J* = 26.2 Hz), 164.0, 150.4, 132.0 (t, *J* = 3.4 Hz), 127.9 (t, *J* = 6.3 Hz), 127.6 (t, *J* = 25.1 Hz), 124.3, 119.5, 119.3 (q, *J* = 258.7 Hz), 114.8 (tt, *J* = 255.3, 31.7 Hz), 113.1, 111.5 (tt, *J* = 266.3, 37.8 Hz), 54.6; **IR** (thin film) *v* 1690, 1599, 1512, 1254, 1211, 1142, 1028, 974, 842, 701 cm^{-1}; **MS** (ESI): *m/z* 397.1 [M+H]$^+$. **HRMS** (ESI): m/z Calculated for $C_{17}H_{12}F_7O_3$ [M+H]$^+$: 397.0669; Found: 397.0670.

2,2,3,3-tetrafluoro-1-(4-phenoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ea)

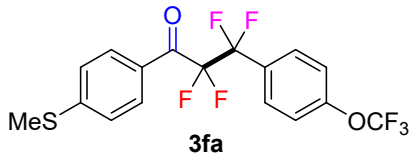


3ea

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **3ea** (119.1 mg, 65%) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.97 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.75 (s, 3F), -109.56 (s, 2F), -112.65 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 182.8 (t, *J* = 26.4 Hz), 162.8, 153.6, 150.4, 131.9 (t, *J* = 3.4 Hz), 129.2, 127.9 (t, *J* = 6.4 Hz), 127.5 (t, *J* = 25.1 Hz), 125.6, 124.2, 119.6, 119.5, 119.3 (q, *J* = 258.6 Hz), 116.0, 114.7 (tt, *J* =

255.3, 31.9 Hz), 111.0 (tt, J = 266.2, 38.3 Hz); **IR** (thin film) v 1694, 1585, 1489, 1248, 1145, 1079, 975, 876, 750, 692 cm^{-1}; **MS** (ESI): m/z 459.1 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{12}H_{14}F_7O_3$ $[M+H]^+$: 459.0826; Found: 459.0826.

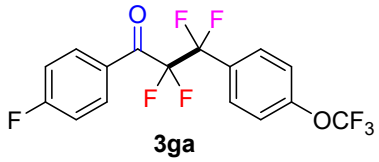
2,2,3,3-tetrafluoro-1-(4-(methylthio)phenyl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3fa)



3fa

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 80:1) to afford **3fa** (100.5 mg, 61%) as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.88 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.19 – 7.16 (m, 2H), 2.42 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.79 (s, 3F), -109.58 (s, 2F), -112.79 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 183.3 (t, J = 26.4 Hz), 150.5, 148.3, 129.6 (t, J = 3.4 Hz), 127.9 (t, J = 6.3 Hz), 127.5 (t, J = 25.0 Hz), 127.4, 123.7, 119.5, 119.3 (q, J = 258.6 Hz), 114.7 (tt, J = 255.2, 31.7 Hz), 111.0 (tt, J = 266.2, 38.2 Hz); **IR** (thin film) v 1691, 1587, 1255, 1211, 1149, 1092, 974, 840, 753, 674 cm^{-1}; **MS** (ESI): m/z 413.0 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{17}H_{12}F_7O_2S$ $[M+H]^+$: 413.0441; Found: 413.0443.

2,2,3,3-tetrafluoro-1-(4-fluorophenyl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ga)

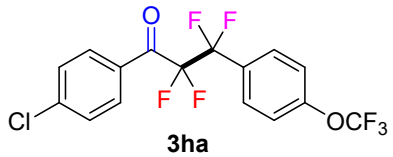


3ga

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ga** (90.6 mg, 59%) as a yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.03 (dd, J = 8.8, 5.4 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 7.13 – 7.04 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.86 (s, 3F), -100.88 – -100.94 (m, 1F), -109.56 (s, 2F), -112.84 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 183.0 (t, J = 26.9 Hz), 165.8 (d, J = 260.0 Hz), 150.6, 132.3 (dt, J = 9.9, 5.2 Hz), 128.0 (t, J = 6.4 Hz), 127.3 (t, J = 25.0 Hz), 119.6, 119.3 (q, J = 258.7 Hz), 115.3, 115.1, 114.7 (tt, J = 255.2, 31.9 Hz), 110.9 (tt, J = 266.1,

38.5 Hz); **IR** (thin film) *v* 1705, 1561, 1508, 1257, 1211, 1151, 1078, 975, 848, 608 cm^{-1}; **MS** (EI): *m/z* 384.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{16}H_8F_8O_2$ $[M]^+$: 384.0397; Found: 384.0387.

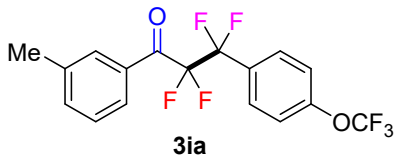
1-(4-chlorophenyl)-2,2,3,3-tetrafluoro-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ha)



3ha

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ha** (88.0 mg, 55%) as a yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.93 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.81 (s, 3F), -109.49 (s, 2F), -112.95 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 183.5 (t, *J* = 27.1 Hz), 150.6, 140.9, 130.7 (t, *J* = 3.3 Hz), 129.7, 128.2, 127.9 (t, *J* = 6.4 Hz), 127.2 (t, *J* = 24.9 Hz), 119.6, 119.3 (q, *J* = 258.7 Hz), 114.7 (tt, *J* = 255.4, 31.9 Hz), 110.8 (tt, *J* = 266.4, 38.8 Hz); **IR** (thin film) *v* 1706, 1589, 1255, 1211, 1154, 1095, 975, 839, 753 cm^{-1}; **MS** (EI): *m/z* 400.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{16}H_8ClF_7O_2$ $[M]^+$: 400.0101; Found: 400.0095.

2,2,3,3-tetrafluoro-1-(*m*-tolyl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ia)

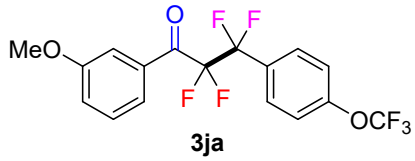


3ia

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ia** (95.8 mg, 63%) as a yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.77 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 2.31 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) -57.82 (s, 3F), -109.62 (s, 2F), -112.79 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.7 (t, *J* = 26.7 Hz), 150.5, 137.7, 134.7 , 131.4, 129.6 (t, *J* = 2.8 Hz), 128.0 (t, *J* = 6.4 Hz), 127.6, 127.5 (t, *J* = 25.1 Hz), 126.5 (t, *J* = 3.7 Hz), 119.5, 119.3 (q, *J* = 258.6 Hz), 114.7 (tt, *J* = 255.5, 31.6 Hz), 110.9 (tt, *J* = 266.7, 38.0 Hz), 20.2; **IR** (thin film) *v* 1702, 1513, 1255, 1212, 1136, 1079, 978, 742, 661

cm^{-1}; **MS** (EI): *m/z* 380.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{17}H_{11}F_7O_2$ $[M]^+$: 380.0647; Found: 380.0641.

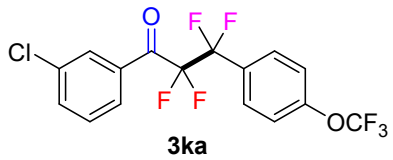
2,2,3,3-tetrafluoro-1-(3-methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ja)



3ja

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **3ja** (93.5 mg, 59%) as a yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.59 – 7.57 (m, 2H), 7.47 (s, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.11 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 3.75 (s, 1H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.82 (s, 3F), -109.54 (s, 2F), -112.66 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.4 (t, *J* = 26.9 Hz), 158.8, 150.5, 132.5, 128.8, 128.0 (t, *J* = 6.4 Hz), 127.5 (t, *J* = 25.0 Hz), 121.9 (t, *J* = 4.3 Hz), 120.5, 119.5, 119.3 (q, *J* = 258.6 Hz), 114.7 (tt, *J* = 255.4, 31.8 Hz), 113.3, 110.8 (tt, *J* = 266.8, 38.2 Hz); **IR** (thin film) *v* 1702, 1598, 1253, 1211, 1153, 1079, 981, 850, 753, 662 cm^{-1}; **MS** (EI): *m/z* 396.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{17}H_{11}F_7O_3$ $[M]^+$: 396.0596; Found: 396.0593.

1-(3-chlorophenyl)-2,2,3,3-tetrafluoro-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ka)

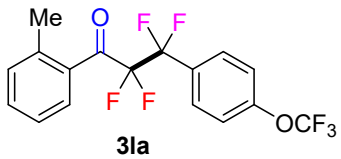


3ka

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ka** (92.8 mg, 58%) as a colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.93 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.54 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.82 (s, 3F), -109.50 (s, 2F), -113.02 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 183.6 (t, *J* = 27.3 Hz), 150.6, 134.2, 133.8, 132.8, 129.1, 128.0 (t, *J* = 6.3 Hz), 127.3 (t, *J* = 3.5 Hz), 127.2 (t, *J* = 24.9 Hz), 119.6, 119.3 (q, *J* = 258.8 Hz), 114.7 (tt, *J* = 255.3, 31.7 Hz), 110.7 (tt, *J* = 266.7, 38.6 Hz);

IR (thin film) *v* 1709, 1513, 1255, 1211, 1154, 1079, 980, 879, 748, 672 cm^{-1}; **MS** (EI): *m/z* 400.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{16}H_8ClF_7O_2$ $[M]^+$: 400.0101; Found: 400.0099.

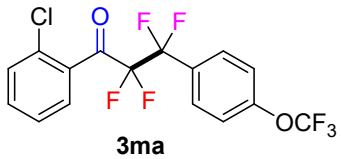
2,2,3,3-tetrafluoro-1-(o-tolyl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3la)



3la

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3la** (82.1 mg, 54%) as a yellowish liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ ppm 7.65 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.22 –7.17(m, 4H), 2.31 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.82 (s, 3F), -109.46 (s, 2F), -113.28 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 188.1 (t, *J* = 26.7 Hz), 150.5, 138.9, 131.9, 131.7, 131.0, 128.1 (t, *J* = 5.6 Hz), 127.9 (t, *J* = 6.3 Hz), 119.3 (t, *J* = 25.1 Hz), 124.5, 119.5, 119.3 (q, *J* = 258.6 Hz), 114.9 (tt, *J* = 255.3, 32.0 Hz), 109.9 (tt, *J* = 266.7, 38.0 Hz), 19.7; **IR** (thin film) *v* 1708, 1513, 1255, 1211, 1154, 1078, 972, 849, 737, 656 cm^{-1};**MS** (EI): *m/z* 380.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{17}H_{11}F_7O_2$ $[M]^+$: 380.0647; Found: 380.0643.

1-(2-chlorophenyl)-2,2,3,3-tetrafluoro-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3ma)

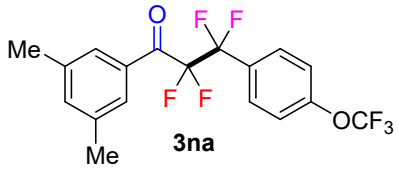


3ma

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ma** (88.0 mg, 55%) as a colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.54 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.28 – 7.19 (m, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.84 (s, 3F), -109.68 (s, 2F), -115.31 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 187.5 (t, *J* = 28.9 Hz), 150.6, 132.9, 131.9, 131.4, 129.8, 128.0 (t, *J* = 6.4 Hz), 127.7 (t, *J* = 3.1 Hz), 127.1 (t, *J* = 24.9 Hz), 125.5, 119.6, 119.3 (q, *J* = 258.6 Hz), 114.9 (tt, *J* = 255.4, 32.2 Hz), 109.3 (tt, *J* = 267.1, 38.5 Hz); **IR** (thin film) *v* 1734, 1513, 1255, 1211,

1156, 1080, 974, 844, 737, 656 cm^{-1}; **MS** (EI): *m/z* 400.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{16}H_8ClF_7O_2$ $[M]^+$: 400.0101; Found: 400.0102.

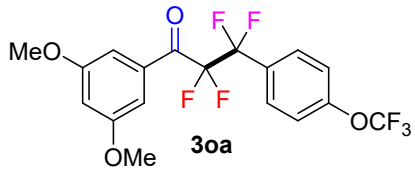
1-(3,5-dimethylphenyl)-2,2,3,3-tetrafluoro-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3na)



3na

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3na** (107.2 mg, 68%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.58 – 7.56 (m, 4H), 7.21 (s, 1H), 7.19 (s, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.83 (s, 3F), -109.68 (s, 2F), -112.70 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.9 (t, *J* = 26.7 Hz), 150.5, 137.5, 135.7, 131.5, 128.0 (t, *J* = 6.1 Hz), 127.7 (t, *J* = 25.1 Hz), 126.9 (t, *J* = 3.3 Hz), 119.5, 119.3 (q, *J* = 258.5 Hz), 114.7 (tt, *J* = 255.4, 31.7 Hz), 110.9 (tt, *J* = 267.7, 37.8 Hz), 20.12; **IR** (thin film) *v* 1701, 1599, 1513, 1255, 1211, 1176, 1082, 909, 786, 674 cm^{-1}; **MS** (EI): *m/z* 394.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{18}H_{13}F_7O_2$ $[M]^+$: 394.0804; Found: 394.0801.

1-(3,5-dimethoxyphenyl)-2,2,3,3-tetrafluoro-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3oa)

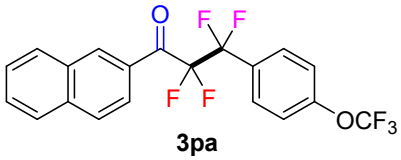


3oa

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 40:1) to afford **3oa** (100.6 mg, 59%) as a colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.58 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.13 – 7.06 (m, 2H), 6.65 (t, *J* = 2.3 Hz, 1H), 3.74 (s, 6H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.83 (s, 3F), -109.52 (s, 2F), -112.49 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.2 (t, *J* = 26.8 Hz), 159.8, 150.5, 132.9, 128.0 (t, *J* = 6.4 Hz), 127.5 (t, *J* = 25.0 Hz), 119.5, 119.3 (q, *J* = 258.6 Hz), 114.7 (tt, *J* = 255.6, 31.7 Hz), 110.8 (tt, *J* = 266.9, 38.0 Hz), 107.0 (t, *J* = 3.5 Hz), 106.4, 54.6; **IR** (thin film) *v* 1704, 1593, 1458,

1254, 1206, 1157, 993, 849, 786, 673 cm^{-1}; **MS** (ESI): *m/z* 427.1 $[M+H]^+$. **HRMS** (ESI): m/z Calculated for $C_{18}H_{14}F_7O_4$ $[M+H]^+$: 427.0775; Found: 427.0776.

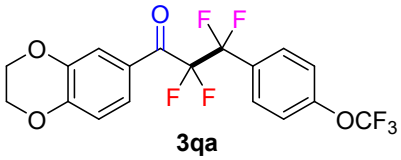
2,2,3,3-tetrafluoro-1-(naphthalen-2-yl)-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3pa)



3pa

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 80:1) to afford **3pa** (104.8 mg, 63%) as a yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.53 (s, 1H), 7.93 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.53 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.20 (d, *J* = 8.3 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.76 (s, 3F), -109.43 (s, 2F), -112.25 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) 184.4 (t, *J* = 26.7 Hz), 150.5, 135.2, 132.3 (t, *J* = 4.6 Hz), 131.2, 129.2, 128.8, 128.6, 128.0 (t, *J* = 6.4 Hz), 127.7, 127.5 (t, *J* = 24.9 Hz), 126.7, 126.2, 123.6, 119.5, 119.3 (q, *J* = 258.6 Hz), 114.8 (tt, *J* = 255.5, 31.6 Hz), 111.1 (tt, *J* = 266.8, 38.0 Hz); **IR** (thin film) *v* 1697, 1627, 1513, 1255, 1211, 1149, 979, 799, 776, 699 cm^{-1}; **MS** (EI): *m/z* 416.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{20}H_{11}F_7O_2$ $[M]^+$: 416.0647; Found: 416.0648.

1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2,2,3,3-tetrafluoro-3-(4-(trifluoromethoxy)phenyl)propan-1-one (3qa)

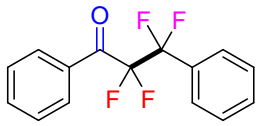


3qa

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **3qa** (88.2 mg, 52%) as a light yellow solid, m.p. 60-62 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.61 – 7.50 (m, 4H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 1H), 4.27 – 4.23 (m, 2H), 4.21 – 4.17 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.79 (s, 3F), -109.60 (s, 2F), -112.52 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 182.6 (t, *J* = 26.3 Hz), 150.4, 148.9, 142.4, 127.9 (t, *J* = 6.5

Hz), 127.6 (t, J = 25.0 Hz), 124.9, 123.9 (t, J = 3.7 Hz), 119.5, 119.3 (q, J = 258.6 Hz), 118.9 (t, J = 3.4 Hz), 116.5, 114.7 (tt, J = 255.2, 32.0 Hz), 111.0 (tt, J = 266.2, 38.0 Hz), 63.9, 63.0; **IR** (thin film) ν 1698, 1605, 1508, 1305, 1252, 1122, 887, 732, 663, 620 cm^{-1}; **MS** (ESI): m/z 447.0 $[M+Na]^+$. **HRMS** (ESI): m/z Calculated for $C_{18}H_{11}F_7NaO_4$ $[M+Na]^+$: 447.0438; Found: 447.0440.

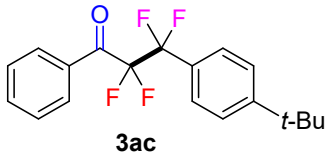
2,2,3,3-tetrafluoro-1,3-diphenylpropan-1-one (3ab)



3ab

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ab** (67.7 mg, 60%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.98 (d, J = 7.6 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.43 – 7.35 (m, 5H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -109.74 (s, 2F), -112.98 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 185.0 (t, J = 26.5 Hz), 133.7, 131.6, 130.4, 129.3 (t, J = 3.2 Hz), 128.9 (t, J = 24.4 Hz), 127.7, 127.4, 125.8 (t, J = 6.5 Hz), 115.1 (tt, J = 254.7, 31.7 Hz), 111.1 (tt, J = 265.8, 38.9 Hz); **IR** (thin film) ν 1700, 1598, 1451, 1297, 1143, 1071, 967, 859, 713, 660 cm^{-1}; **MS** (EI): m/z 282.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{15}H_{10}F_4O$ $[M]^+$: 282.0668; Found: 282.0665.

3-(4-(tert-butyl)phenyl)-2,2,3,3-tetrafluoro-1-phenylpropan-1-one (3ac)

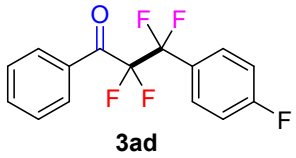


3ac

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ac** (83.9 mg, 62%) as a white solid, m.p. 59-61 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ ppm 7.98 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.42 – 7.35 (m, 4H), 1.24 (s, 9H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -109.30 (s, 2F), -113.04 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 186.2 (t, J = 26.6 Hz), 154.8, 134.7, 132.8, 130.4 (t, J = 3.4 Hz), 128.7, 127.0 (t, J = 24.5 Hz), 126.7 (t, J = 6.2 Hz), 125.5, 116.3 (tt, J = 254.5, 31.9 Hz), 112.3 (tt, J = 265.6, 39.6 Hz), 34.9, 31.2; **IR** (thin film) ν 1705, 1598, 1451, 1312, 1272, 1145,

1081, 846, 791, 661 cm^{-1}; **MS** (EI): *m/z* 338.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{19}H_{18}F_4O$ $[M]^+$: 338.1294; Found: 338.1292.

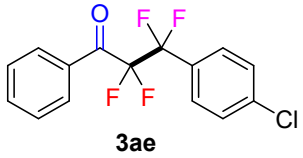
2,2,3,3-tetrafluoro-3-(4-fluorophenyl)-1-phenylpropan-1-one (3ad)



3ad

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ad** (79.2 mg, 66%) as a yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.98 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.51 (m, 3H), 7.44 – 7.35 (m, 2H), 7.06 (t, *J* = 8.6 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -108.23 – -108.30 (m, 1F), -109.03 (s, 2F), -112.92 (s, 2F); **^{13}C NMR** (151 MHz, $CDCl_3$) δ ppm 184.8 (t, *J* = 26.8 Hz), 163.6 (d, *J* = 251.8 Hz), 133.8, 131.5, 129.3 (t, *J* = 3.4 Hz), 128.3 (dt, *J* = 8.5, 6.7 Hz), 127.7, 124.9 (td, *J* = 25.1, 3.4 Hz), 114.9 (tt, *J* = 254.9, 31.9 Hz), 114.7 (d, *J* = 22.1 Hz), 110.9 (tt, *J* = 266.2, 38.8 Hz); **IR** (thin film) *v* 1701, 1598, 1515, 1299, 1236, 1145, 1077, 970, 838, 685 cm^{-1}; **MS** (EI): *m/z* 300.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{15}H_9F_5O$ $[M]^+$: 300.0574; Found: 300.0573.

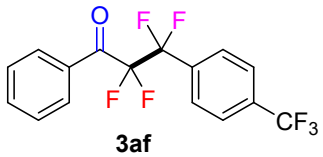
3-(4-chlorophenyl)-2,2,3,3-tetrafluoro-1-phenylpropan-1-one (3ae)



3ae

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ae** (56.9 mg, 45%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.99 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.37 (d, *J* = 8.7 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -109.73 (s, 2F), -112.88 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.7 (t, *J* = 26.9 Hz), 136.9 (t, *J* = 1.9 Hz), 133.9, 131.4, 129.3 (t, *J* = 3.4 Hz), 127.8 , 127.5, 127.4, 127.3 (t, *J* = 6.6 Hz), 114.8 (tt, *J* = 255.2, 31.6 Hz), 110.9 (tt, *J* = 266.7, 38.5 Hz); **IR** (thin film) *v* 1702, 1598, 1495, 1298, 1146, 1093, 973, 824, 721, 658 cm^{-1}; **MS** (EI): *m/z* 316.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{15}H_9ClF_4O$ $[M]^+$: 316.0278; Found: 316.0276.

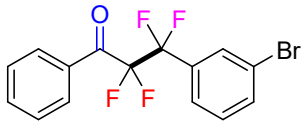
2,2,3,3-tetrafluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (3af)



3af

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3af** (98.0 mg, 70%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.99 (d, *J* = 7.6 Hz, 2H), 7.69 – 7.63 (m, 4H), 7.59 – 7.53 (m, 1H), 7.43 – 7.39 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -63.16 (s, 2F), -110.32 (s, 2F), -112.75 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.4 (t, *J* = 26.8 Hz), 134.0, 133.7 (t, *J* = 24.2 Hz) , 132.5 (q, *J* = 32.9 Hz), 131.3, 129.3 (t, *J* = 3.4 Hz), 127.8, 126.6 (t, *J* = 6.5 Hz), 124.5 (q, *J* = 3.7 Hz), 122.5 (q, *J* = 272.6 Hz), 114.6 (tt, *J* = 255.7, 31.8 Hz), 110.8 (tt, *J* = 266.9, 37.8 Hz); **IR** (thin film) *v* 1702, 1598, 1415, 1324, 1297, 1131, 1066, 976, 834, 662 cm^{-1}; **MS** (EI): *m/z* 350.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{16}H_9F_7O$ $[M]^+$: 350.0542; Found: 350.0541.

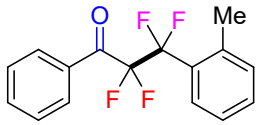
3-(3-bromophenyl)-2,2,3,3-tetrafluoro-1-phenylpropan-1-one (3ag)



3ag

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ag** (95.0 mg, 66%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.99 (d, *J* = 7.9 Hz, 2H), 7.69 (s, 1H), 7.58 – 7.55 (t, *J* = 6.8 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.26 (t, *J* = 7.9 Hz, 1H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -109.78 (s, 2F), -112.69 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.5 (t, *J* = 26.7 Hz), 133.9, 133.6, 131.4, 130.9 (t, *J* = 24.7 Hz), 129.3 (t, *J* = 3.2 Hz), 129.1 (t, *J* = 6.7 Hz), 129.0, 127.8, 124.6 (t, *J* = 6.3 Hz), 121.5, 114.3 (tt, *J* = 255.6, 31.8 Hz), 110.8 (tt, *J* = 266.6, 38.4 Hz); **IR** (thin film) *v* 1701, 1597, 1293, 1142, 1069, 974, 841, 790, 716, 658 cm^{-1}; **MS** (EI): *m/z* 360.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{15}H_9BrF_4O$ $[M]^+$: 359.9773; Found: 359.7770.

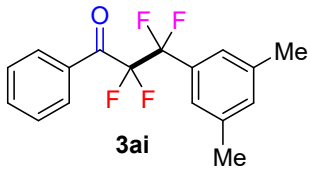
2,2,3,3-tetrafluoro-1-phenyl-3-(o-tolyl)propan-1-one (3ah)



3ah

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ah** (53.3 mg, 45%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.00 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.21 – 7.12 (m, 2H), 2.45 (t, *J* = 2.9 Hz, 1H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -104.70 (s, 2F), -112.23 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 185.2 (t, *J* = 26.4 Hz), 136.9, 133.6, 131.8, 131.4, 130.3, 129.3 (t, *J* = 3.3 Hz), 127.7, 127.4 (t, *J* = 8.8 Hz), 126.8 (t, *J* = 22.4 Hz), 124.7, 116.7 (tt, *J* = 255.5, 33.6 Hz), 111.9 (tt, *J* = 265.5, 40.4 Hz), 19.76 – 19.62 (m); **IR** (thin film) *v* 1699, 1597, 1449, 1298, 1140, 1107, 966, 858, 753, 660 cm^{-1}; **MS** (EI): *m/z* 296.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{16}H_{12}F_4O$ $[M]^+$: 296.0824; Found: 296.0823.

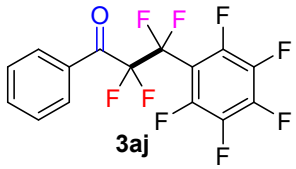
3-(3,5-dimethylphenyl)-2,2,3,3-tetrafluoro-1-phenylpropan-1-one (3ai)



3ai

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ai** (76.9 mg, 62%) as a white solid, m.p. 61-63 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm ; **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -109.28 (s, 2F), -112.95 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 185.1 (t, *J* = 26.5 Hz), 137.2, 133.6, 132.1, 131.8, 129.3, 129.2 (t, *J* = 3.0 Hz), 128.7 (t, *J* = 23.9 Hz), 127.6, 123.5 (t, *J* = 6.3 Hz), 115.2 (tt, *J* = 254.5, 31.9 Hz), 111.2 (tt, *J* = 265.4, 39.5 Hz), 20.2; **IR** (thin film) *v* 1689, 1597, 1449, 1327, 1297, 1131, 1066, 976, 834, 662 cm^{-1}; **MS** (EI): *m/z* 310.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{17}H_{14}F_4O$ $[M]^+$: 310.0981; Found: 310.0980.

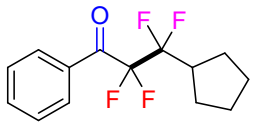
2,2,3,3-tetrafluoro-3-(perfluorophenyl)-1-phenylpropan-1-one (3aj)



3aj

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3aj** (99.7 mg, 67%) as a white solid, m.p. 61-63 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.01 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -106.01 (t, *J* = 30.6 Hz, 2F), -113.90 (t, *J* = 7.8 Hz, 2F), -136.95 – -137.38 (m, 2F), -146.85 (tt, *J* = 21.1, 5.5 Hz, 1F), -159.68 – -159.88 (m, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 184.0 (t, *J* = 26.0 Hz), 146.1 – 143.2 (m), 144.0 – 143.2 (m), 138.4 – 135.6 (m), 134.2, 131.1, 129.3 (t, *J* = 3.4 Hz), 127.9, 113.5 (tt, *J* = 260.8, 35.4 Hz), 110.6 (tt, *J* = 267.8, 36.7 Hz), 104.3 – 103.6 (m); **IR** (thin film) *v* 1698, 1505, 1332, 1282, 1138, 1092, 985, 894, 732, 623 cm^{-1}; **MS** (EI): *m/z* 372.0 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{15}H_5F_9O$ $[M]^+$: 372.0197; Found: 372.0185.

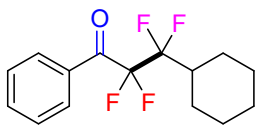
3-cyclopentyl-2,2,3,3-tetrafluoro-1-phenylpropan-1-one (3ak)



3ak

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3ak** (61.4 mg, 56%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.00 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 2.71 – 2.39 (m, 1H), 1.85 – 1.77 (m, 2H), 1.69 – 1.48 (m, 6H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -112.83 (s, 2F), -115.63 (d, *J* = 16.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 185.8 (t, *J* = 26.3 Hz), 133.6, 131.7, 129.4 (t, *J* = 3.1 Hz), 127.6, 118.4 (tt, *J* = 253.3, 31.6 Hz), 112.0 (tt, *J* = 264.7, 38.0 Hz), 40.2 (t, *J* = 21.8 Hz), 24.9 (t, *J* = 3.8 Hz), 24.5; **IR** (thin film) *v* 1703, 1598, 1449, 1286, 1133, 1067, 912, 845, 713, 662 cm^{-1}; **MS** (EI): *m/z* 274.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{14}H_{14}F_4O$ $[M]^+$: 274.0981; Found: 274.0980.

3-cyclohexyl-2,2,3,3-tetrafluoro-1-phenylpropan-1-one (3al)



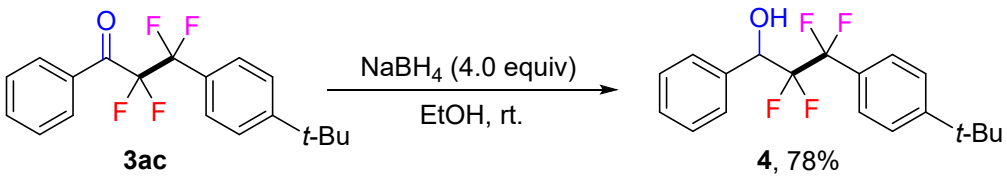
3al

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **3al** (72.6 mg, 63%) as a yellowish liquid; **^{1}H NMR**

(400 MHz, $CDCl_3$) δ ppm 8.00 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 2.20 – 2.06 (m, 1H), 1.93 – 1.90 (m, 2H), 1.76 – 1.74 (m, 2H), 1.33 – 1.07 (m, 6H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -111.75 (s, 2F), -116.22 (d, *J* = 15.2 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 185.6 (t, *J* = 26.6 Hz), 133.6, 131.6, 129.4 (t, *J* = 3.0 Hz), 127.6, 117.8 (tt, *J* = 254.6, 31.1 Hz), 112.4 (tt, *J* = 265.7, 38.6 Hz), 39.6 (t, *J* = 21.2 Hz), 24.7, 24.4, 23.9 – 23.3 (m); **IR** (thin film) *v* 1704, 1598, 1449, 1284, 1143, 1072, 898, 812, 713, 660 cm^{-1}; **MS** (EI): *m*/*z* 288.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{15}H_{16}F_4O$ $[M]^+$: 288.1137; Found: 288.1134.

5. Transformation of compound 3ac.

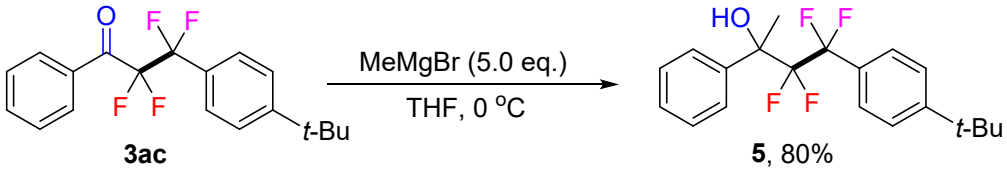
5.1 Reduction of compound 3ac



3ac **4**, 78%

To a solution of compound **3ac** (67.6 mg, 0.20 mmol, 1.0 equiv) in EtOH (2 mL) was added $NaBH_4$ (30.4 mg, 0.8 mmol, 4.0 equiv) at room temperature. After the reaction was stirred for 2 h, aqueous solution HCl (1 M) was added. The resulting mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 8: 1) to give product **4** (53.1 mg, 78%) a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.42 – 7.29 (m, 6H), 7.26 – 7.20 (m, 3H), 5.02 (dd, J = 17.0, 7.3 Hz, 1H), 2.75 (brs, 1H), 1.22 (s, 9H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -108.95 (d, J = 4.2 Hz, 2F), -117.73 (dd, J = 275.1, 7.3 Hz, 1F), -126.51 (dd, J = 275.1, 16.9 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 153.3, 134.3, 128.0, 127.2, 127.1, 126.9 (t, J = 24.8 Hz), 125.4 (t, J = 6.4 Hz), 124.2, 116.4 (tt, J = 253.4, 34.2 Hz), 114.4 (ddt, J = 260.9, 35.8, 6.0 Hz), 71.1 (dd, J = 28.6, 22.8 Hz), 33.8, 30.1; **IR** (thin film) v 2966, 1615, 1457, 1290, 1100, 943, 834, 711, 613 cm^{-1}; **MS** (ESI): m/z 363.1 $[M+Na]^+$; **HRMS** (ESI-TOF): m/z Calculated for $C_{19}H_{20}F_4NaO$ $[M+Na]^+$: 363.1342; Found: 363.1340.

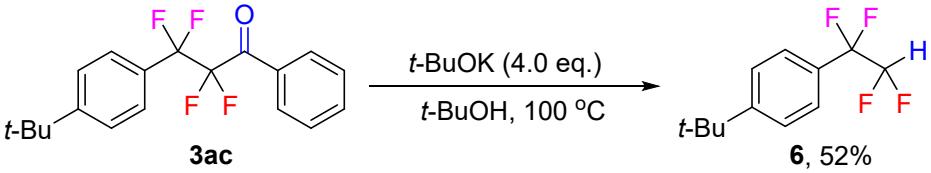
5.2 Grignard reaction of compound 3ac



3ac **5**, 80%

To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was added compound **3ac** (67.6 mg, 0.2 mmol, 1.0 equiv.), the tube was evacuated and backfilled with argon three times, followed by anhydrous THF (2.0 mL) were added. The solution was cooled to 0 °C and methylmagnesium bromide (1.0 mL, 1.0 mol/L in THF) was added dropwise. The reaction was allowed to stir at 0 °C for 10 hours. The reaction was then quenched with saturated NH_4Cl (aq.), and extracted with dichloromethane three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10: 1) to provide **5** (56.7 mg, 80%) as a colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.43 (d, *J* = 7.5 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.24 – 7.13 (m, 3H), 2.48 (brs, 1H), 1.69 (s, 3H), 1.20 (s, 9H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -105.6 (AB, *J* = 265.2 Hz, 2F), -117.1 (AB, *J* = 279.0 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 152.9, 139.2, 127.8 (t, *J* = 24.9 Hz), 126.8, 126.8, 125.4 (t, *J* = 6.5 Hz), 125.2, 124.0, 117.1 (tt, *J* = 255.3, 34.8 Hz), 115.5 (tt, *J* = 261.4, 35.0 Hz), 75.2 (t, *J* = 24.8 Hz), 33.7, 30.1, 24.3; **IR** (thin film) *v* 2965, 1615, 1449, 1286, 1100, 911, 833, 762, 699 cm^{-1}; **MS** (ESI): *m/z* 377.1 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{12}H_{13}F_2NNaO_2$ $[M+Na]^+$: 377.1499; Found: 377.1498.

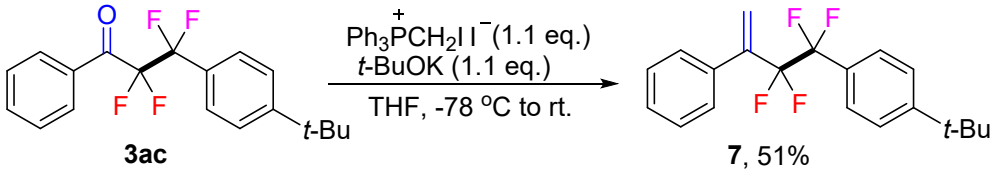
5.3 Haller-Bauer reaction of compound 3ac



To a 25 mL sealed tube equipped with a magnetic stirrer bar was added compound **3ac** (135.2 mg, 0.4 mmol, 1.0 equiv.), *t*-BuOK (179.4 mg, 1.6 mmol, 4.0 eq.)，the tube was evacuated and backfilled with argon three times, followed by *t*-BuOH (4.0 mL) were added. The reaction was allowed to stir at 100 °C in an oil bath for 6 hours. After that, the reaction mixture was cooled to room temperature, then quenched with saturated NH_4Cl (aq.), and extracted with dichloromethane three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 100: 1) to provide **6** (48.7 mg, 52%) as a yellowish liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.44 – 7.38 (m, 4H), 5.82 (tt, *J* = 54.2, 2.6 Hz, 1H), 1.26 (s, 9H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -

113.40 – -113.50 (m, 2F), -134.24 (dt, J = 54.1, 4.1 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 153.6, 125.9 (t, J = 24.5 Hz), 125.1 (t, J = 6.3 Hz), 124.5, 114.6 (tt, J = 248.8, 28.7 Hz), 109.3 (tt, J = 251.4, 43.7 Hz), 33.8, 30.1 ; **IR** (thin film) v 2960, 1601, 1384, 1283, 1217, 1101, 991, 815, 676 cm^{-1}. Known compound[5].

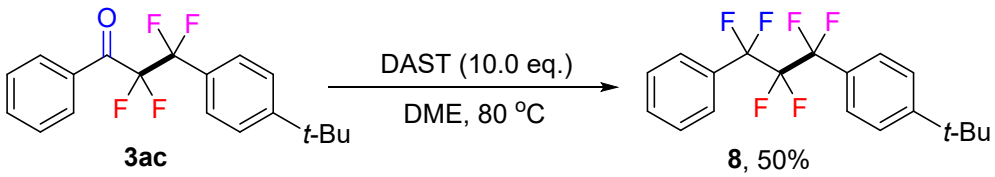
5.4 Wittig reaction of compound 3ac



3ac **7**, 51%

To a 25 mL flask equipped with a magnetic stirrer bar was charged with $Ph_3P^+CH_2II^-$ (233.3 mg, 0.44 mmol, 1.1 eq.), anhydrous THF (2.0 mL). *t*-BuOK (233.3 mg, 0.44 mmol, 1.1 eq.) was added portionwise and the resulting yellow solution was stirred for 1 h before cooling to -78 ° C. compound **3ac** (135.2 mg, 0.4 mmol, 1.0 equiv.) in anhydrous THF was added dropwise and the reaction mixture was allowed to warm to ambient temperature and was stirred overnight. water was added and extracted with EtOAc three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 100: 1) to provide **7** (68.6 mg, 51%) as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.36 – 7.30 (m, 4H), 7.24 – 7.22 (m, 5H), 5.74 (s, 1H), 5.58 (s, 1H), 1.24 (s, 9H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -109.23 (s, 2F), -109.52 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 153.1, 139.5 (t, J = 22.8 Hz), 139.2, 135.5, 127.6, 127.1, 127.0, 125.6 (t, J = 6.1 Hz), 124.0, 122.9 (t, J = 8.6 Hz), 115.9 (tt, J = 253.0, 33.9 Hz), 115.1 (tt, J = 255.2, 37.0 Hz), 33.7, 30.1; **IR** (thin film) v 2965, 1285, 1223, 1101, 1074, 1017, 939, 833, 774, 697 cm^{-1}; **MS** (EI): m/z 336.1 $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{20}H_{20}F_4$ $[M]^+$: 336.1501; Found: 336.1500.

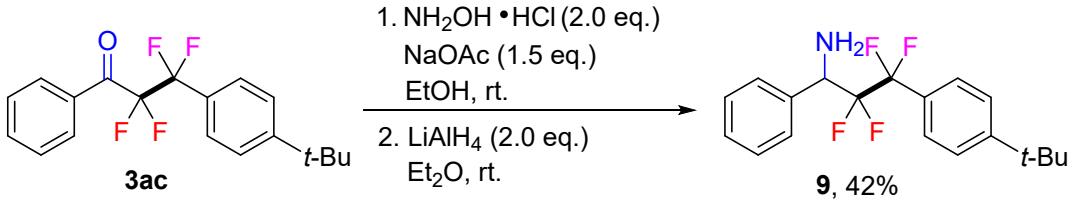
5.5 Deoxofluorination of compound 3ac



3ac **8**, 50%

To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was added compound **3ac** (135.2 mg, 0.4 mmol, 1.0 equiv.), the tube was evacuated and backfilled with argon three times, followed by anhydrous DME (2.0 mL) were added. The solution was cooled to -78 °C and DAST (645 mg, 4 mmol) was added dropwise with stirring. The reaction was stirred at room temperature for 10 min, then slowly heated to 80 °C and stirred for 12 hours. After cooling to room temperature, the reaction was quenched with saturated $NaHCO_3$ (aq.), and extracted with dichloromethane three times. The combined organic phase were washed with aqueous HCl (2 M), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc = 100: 1) to afford product **8** (72.0 mg, 50%) as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.91 – 7.87 (m, 1H), 7.77 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.43 – 7.36 (m, 1H), 7.34 – 7.27 (m, 2H), 7.12 (dd, *J* = 4.9, 4.1 Hz, 1H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -86.48 (t, *J* = 6.4 Hz, 2F), -112.37 (s, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 176.8 (t, *J* = 27.8 Hz), 137.6, 136.7, 136.2, 135.8 (t, *J* = 5.5 Hz), 129.7, 128.3, 128.0, 122.3 (t, *J* = 2.3 Hz), 121.9 (tt, *J* = 290.9, 34.3 Hz), 111.6 (tt, *J* = 267.1, 34.7 Hz); **IR** (thin film) *v* 3106, 2248, 1672, 1410, 1356, 1183, 1061, 837, 730, 700 cm^{-1}; **MS** (EI): *m/z* 360.1 $[M]^+$. $[M]^+$. **HRMS** (EI): m/z Calculated for $C_{19}H_{18}F_6$ $[M]^+$: 360.1313; Found: 360.1310.

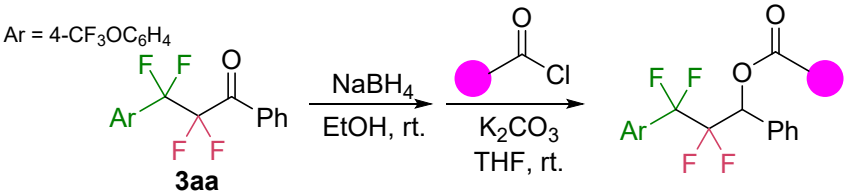
5.6 Amination of compound 3ac



To a 25 mL flask equipped with a magnetic stirrer bar was added compound **3ac** (135.2 mg, 0.4 mmol, 1.0 equiv.), hydroxylamine hydrochloride (55.6 mg, 0.8 mmol, 2.0 equiv), NaOAc (49.2 mg, 0.6 mmol, 1.5 eq.), followed by EtOH (4.0 mL) were added. After stirring for 2 h, the solvent was evaporated under reduced pressure. Anhydrous Et_2O (4.0 mL) was added, then $LiAlH_4$ (30.4 mg, 0.8 mmol, 2.0 eq.) was added in one portion. After stirring for 2 h, the reaction was quenched with saturated NH_4Cl (aq.), and extracted with Et_2O three times. The combined organic phase were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc = 10: 1) to afford product **9** (57.0 mg, 42%) as a yellowish liquid; **^{1}H**

NMR (400 MHz, $CDCl_3$) δ ppm 7.37 – 7.32 (m, 6H), 7.30 – 7.25 (m, 3H), 5.06 (brs, 2H), 4.58 (t, *J* = 13.4 Hz, 1H), 1.25 (s, 9H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -108.5 (dt, *J* = 265.7, 5.1 Hz, 1F), -109.4 (dt, *J* = 265.7, 3.9 Hz, 1F), -115.6 (dd, *J* = 276.6, 13.9 Hz, 1F), -118.6 (dd, *J* = 276.7, 12.5 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 153.3, 132.6 (d, *J* = 2.9 Hz), 128.3, 127.9, 127.4, 126.6 (t, *J* = 24.8 Hz), 125.5 (t, *J* = 6.3 Hz), 124.2, 116.2 (tt, *J* = 269.5, 34.7 Hz), 114.6 (tt, *J* = 259.3, 17.3 Hz), 65.9 (dd, *J* = 22.7, 20.0 Hz), 33.8, 30.1; **IR** (thin film) *v* 3284, 1290, 1186, 1141, 1101, 1015, 894, 830, 749, 665 cm^{-1}; **MS** (ESI): *m/z* 362.1 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{19}H_{21}F_4NNa$ $[M+Na]^+$: 362.1502; Found: 362.1501.

5.7 late-stage functionalization

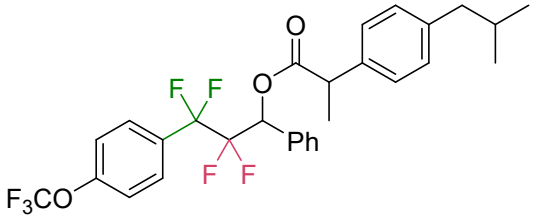


To a solution of compound **3aa** (146.4 mg, 0.4 mmol, 1.0 equiv) in EtOH (2 mL) was added $NaBH_4$ (60.8 mg, 1.6 mmol, 4.0 equiv) at room temperature. After the reaction was stirred for 2 h, aqueous solution HCl (1 M) was added. The resulting mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The obtained mixture was used in the next step without further purification.

To a solution of carboxylic acid (0.4 mmol, 1.0 equiv) in DCM (2 mL) was added oxalyl chloride (152.3 mg, 1.2 mmol, 3.0 equiv) at room temperature. Then 1 drop of DMF was added and the reaction mixture was stirred for 2 h. The solvent was removed under reduced pressure. The obtained mixture was used in the next step without further purification.

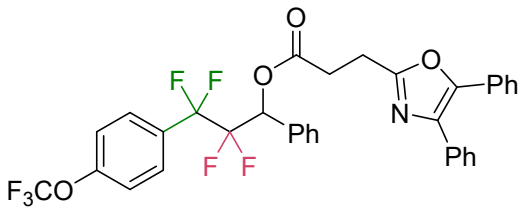
To a 25 mL flask equipped with a magnetic stirrer bar was added the fluorinated alcohol, K_2CO_3 (55.2 mg, 0.4 mmol, 1.0 equiv), followed by THF (4.0 mL) were added. The mixture was cooled to 0°C for 10 min, then the freshly prepared acyl chloride in 2 mL THF was added dropwise. After stirring for 2 h at room temperature, the solvent was evaporated under reduced pressure. The obtained reside was added 10 mL H_2O, and extracted with EA three times. The combined organic phase were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography to afford the product.

2,2,3,3-tetrafluoro-1-phenyl-3-(4-(trifluoromethoxy)phenyl)propyl 2-(4-isobutylphenyl)propanoate (10)



The product mixture was purified by silica gel column chromatography (hexane/EA = 30:1) to afford **10** (186.9 mg, 84%) as a colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 1.38H), 7.30–7.24 (m, 1.31H), 7.23–7.19 (m, 0.93H), 7.16–7.12 (m, 2.73H), 7.08–7.05 (m, 2.04H), 7.02–7.00 (m, 1.98H), 6.96–6.92 (m, 2.73H), 6.16 (dd, *J* = 18.2, 6.6 Hz, 0.69H), 6.09 (dd, *J* = 18.0, 6.5 Hz, 0.34H), 3.68 (q, *J* = 7.1 Hz, 0.33H), 3.48 (q, *J* = 7.1 Hz, 0.68H), 2.35 (d, *J* = 7.1 Hz, 0.67H), 2.33 (d, *J* = 7.1 Hz, 1.34H), 1.78–1.68 (m, 1.06H), 1.39 (d, *J* = 7.2 Hz, 1.1H), 1.36 (d, *J* = 7.2 Hz, 1.97H), 0.78 (d, *J* = 6.8 Hz, 4.13H). 0.76 (d, *J* = 6.8 Hz, 2.06H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.8 (s, 3F), -109.7 (ddt, *J* = 312.9, 269.1, 3.8 Hz, 0.67F), -109.9 (qt, *J* = 268.4, 5.9 Hz, 1.34F), -115.8 (dt, *J* = 279.9, 5.6 Hz, 0.33F), -115.9 (dq, *J* = 275.2, 5.7 Hz, 0.67F), -123.1 (ddt, *J* = 280.0, 17.4, 3.8 Hz, 0.33F), -123.5 (ddt, *J* = 279.2, 18.0, 4.4 Hz, 0.67F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 172.5, 172.2, 151.3, 141.0, 140.9, 136.7, 136.6, 132.2, 131.8, 129.5, 129.4, 129.3, 128.7 (t, *J* = 5.0 Hz), 128.5, 128.4, 128.3, 128.2, 127.5, 127.4, 120.6, 120.5, 120.4 (q, *J* = 259.4 Hz), 120.3 (q, *J* = 259.4 Hz), 117.5 (tt, *J* = 255.1, 33.4 Hz), 116.0 (dt, *J* = 259.3, 36.0 Hz), 113.4 (dt, *J* = 253.3, 35.4 Hz), 71.6 (dd, *J* = 31.6, 22.2 Hz), 71.3 (dd, *J* = 32.0, 22.0 Hz), 45.2, 45.1, 45.0, 44.9, 30.3, 22.4, 22.3, 17.9, 17.8; **MS** (ESI): *m/z* 579.2 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{29}H_{27}F_7NaO_3$ $[M+Na]^+$: 579.1741; Found: 579.1735.

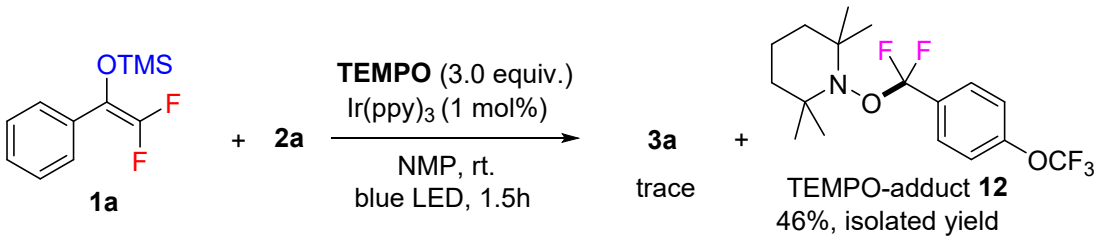
2,2,3,3-tetrafluoro-1-phenyl-3-(4-(trifluoromethoxy)phenyl)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate (11)



The product mixture was purified by silica gel column chromatography (hexane/EA = 8:1) to afford **11** (185.2 mg, 72%) as a colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 6.8 Hz, 2H), 7.41–7.39 (m, 4H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.23–7.12 (m, 4H), 7.07 (d, J = 8.3 Hz, 2H), 6.28 (dd, *J* = 17.5, 7.0 Hz, 1H), 3.07 – 2.93 (m, 2H),

2.83 (t, J = 7.2 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -57.7 (s, 3F), -109.7 (ddt, J = 394.0, 268.5, 5.1 Hz, 2F), -115.8 (dq, J = 280.3, 5.7 Hz, 1F), -122.8 (ddt, J = 280.3, 17.1, 5.3 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 169.9, 161.3, 151.3, 145.6, 135.2, 132.5, 132.0, 129.6, 129.2 (t, J = 25.3 Hz), 129.0, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.1, 128.0, 126.6, 120.6, 120.4 (q, J = 258.6 Hz), 117.7 (tt, J = 254.5, 34.3 Hz), 113.4 (tt, J = 253.5, 36.4 Hz), 71.4 (dd, J = 31.5, 21.7 Hz), 30.8, 23.2; **MS** (ESI): m/z 666.1 $[M+Na]^+$; **HRMS** (ESI-TOF): m/z Calculated for $C_{34}H_{24}F_7NNaO_4$ $[M+Na]^+$: 666.1486; Found: 666.1480.

6. Mechanistic experiments.



A 25 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, *fac*-Ir(ppy)$_3$ (2.6 mg, 0.004 mmol, 1 mol %) and difluoroalkyl sulfone **2a** (0.4 mmol, 1.0 equiv), and TEMPO (187.2 mg, 1.2 mmol, 3.0 equiv) were dissolved in dry NMP (2.0 mL), then difluoroenol silyl ethers **1a** (0.8 mmol, 2.0 equiv) was added. The mixture was degassed three times by the freeze-pump-thaw procedure. The flask was placed at a distance of 2 cm from the blue LEDs. After 1.5 hours, the reaction was quenched by water, extracted by Et_2O. The organic phase was dried by anhydrous sodium sulfate, then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the TEMPO-adduct **12** in 46% yield.

7. References

1. Prakash, S. G. K.; Hu, J.; Olah, G. A. Facile Preparation of Di- and Monofluoromethyl Ketones from Trifluoromethyl Ketones via Fluorinated Enol Silyl Ethers. *J. Fluorine Chem*. **2001**, *112*, 355 – 360.

1. He, Z.; Tan, P.; Ni, C.; Hu, J. Fluoroalkylative Aryl Migration of Conjugated *N*-Arylsulfonylated Amides Using Easily Accessible Sodium Di- and Monofluoroalkanesulfinate. *Org. Lett*. **2015**, *17*, 1838 − 1841.

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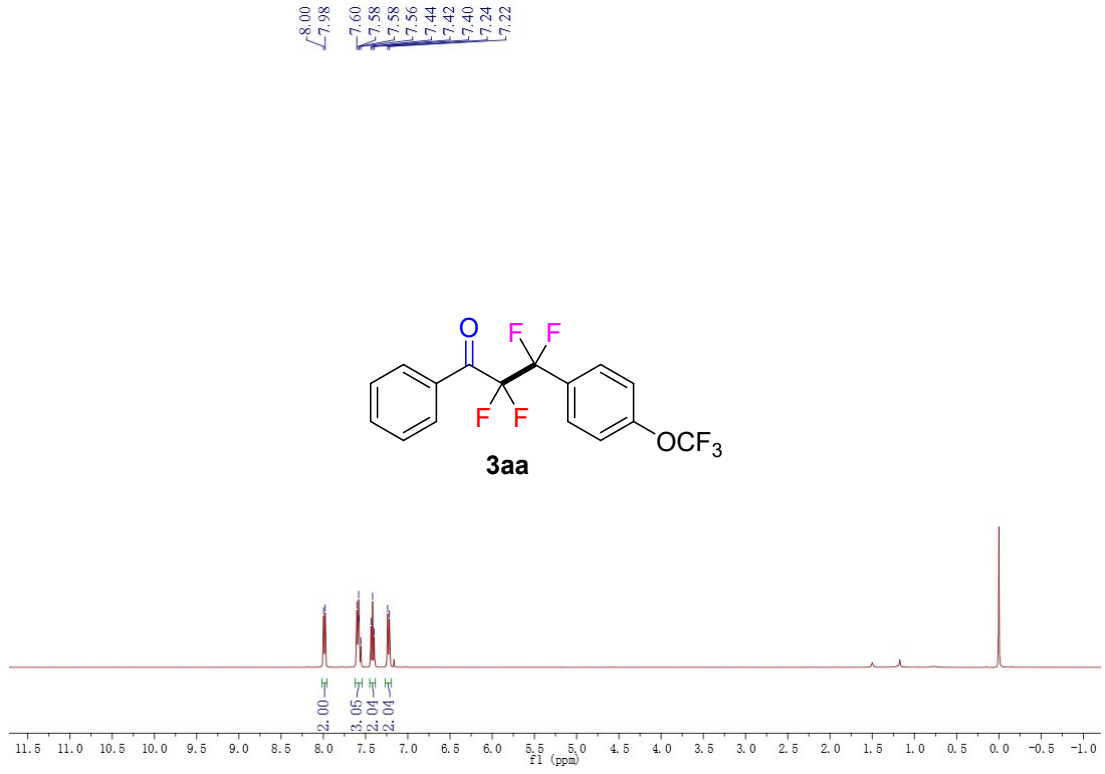
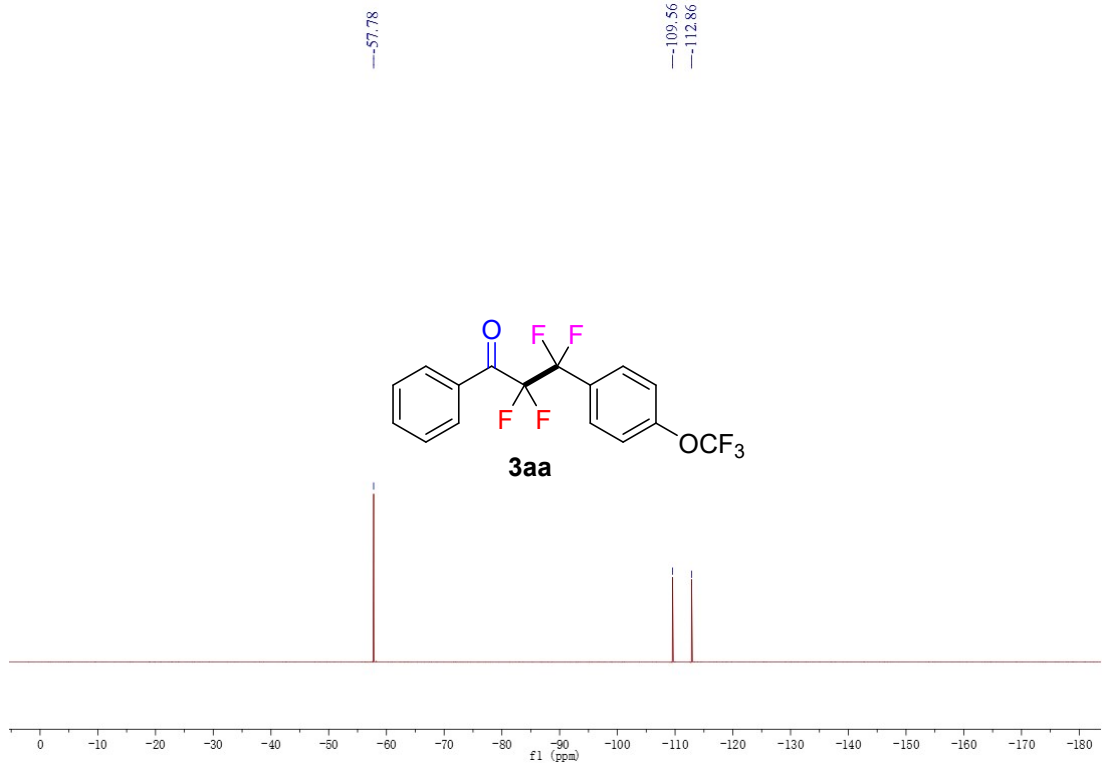
5. Fu, X.-P.; Xue, X.-S.; Zhang, X.-Y.; Xiao, Y.-L.; Zhang, S.; Guo, Y.-L.; Leng, X.; Houk, K. N.; Zhang, X. Controllable Catalytic Difluorocarbene Transfer Enables Access to Diversified fluoroalkylated arenes. *Nat. Chem.* **2019**, *11*, 948 – 956.

8. Copies of ^{1}H, ^{19}F, and ^{13}C NMR spectra for the products

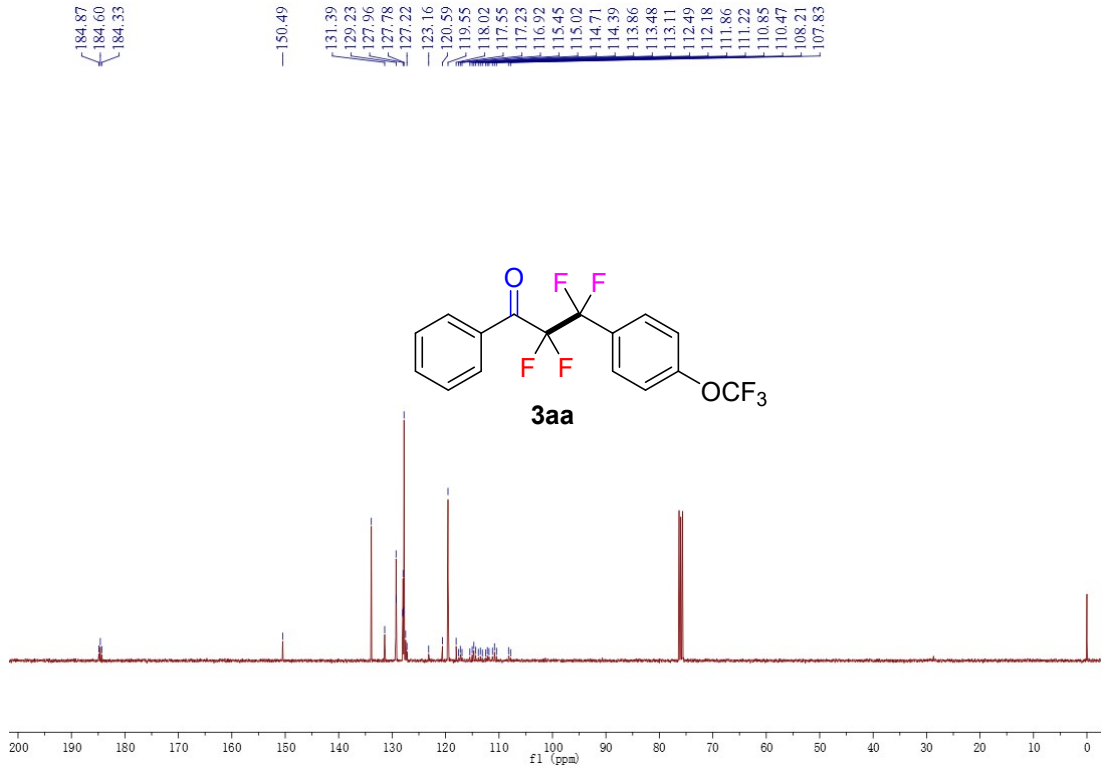
^{1}H NMR (400 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$)



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



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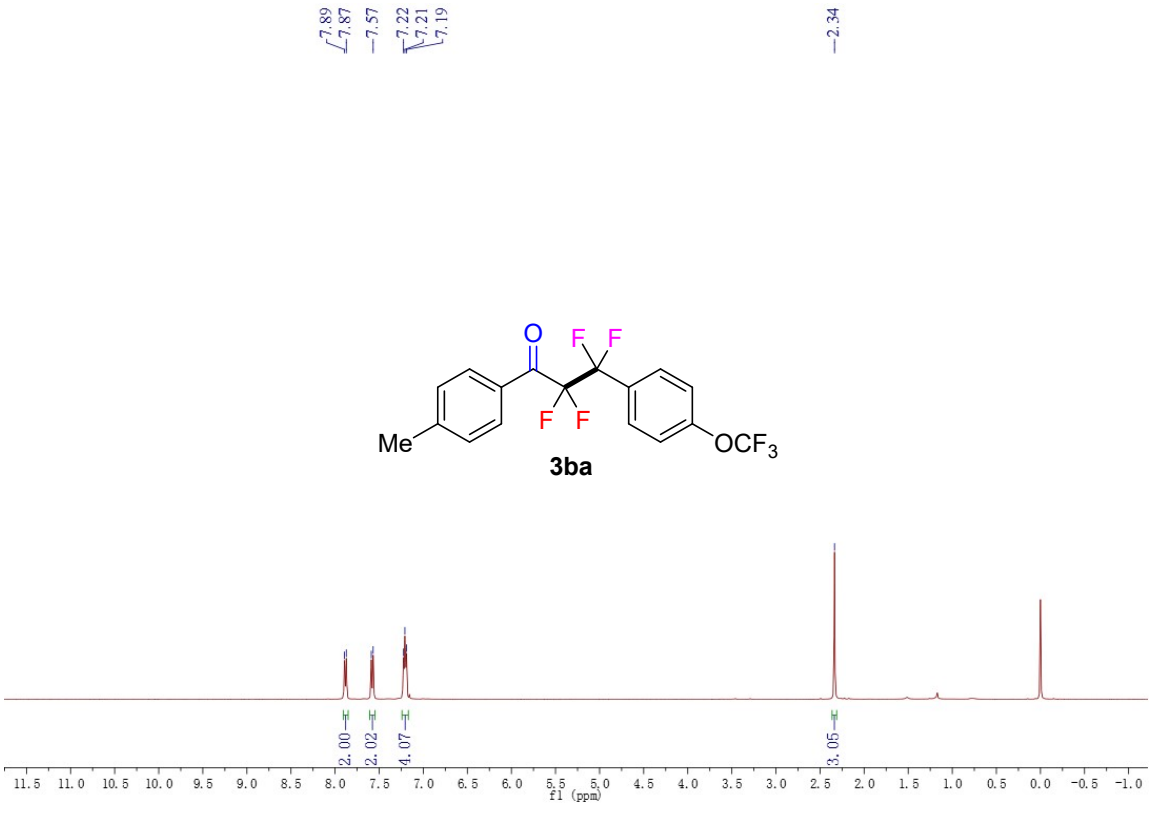

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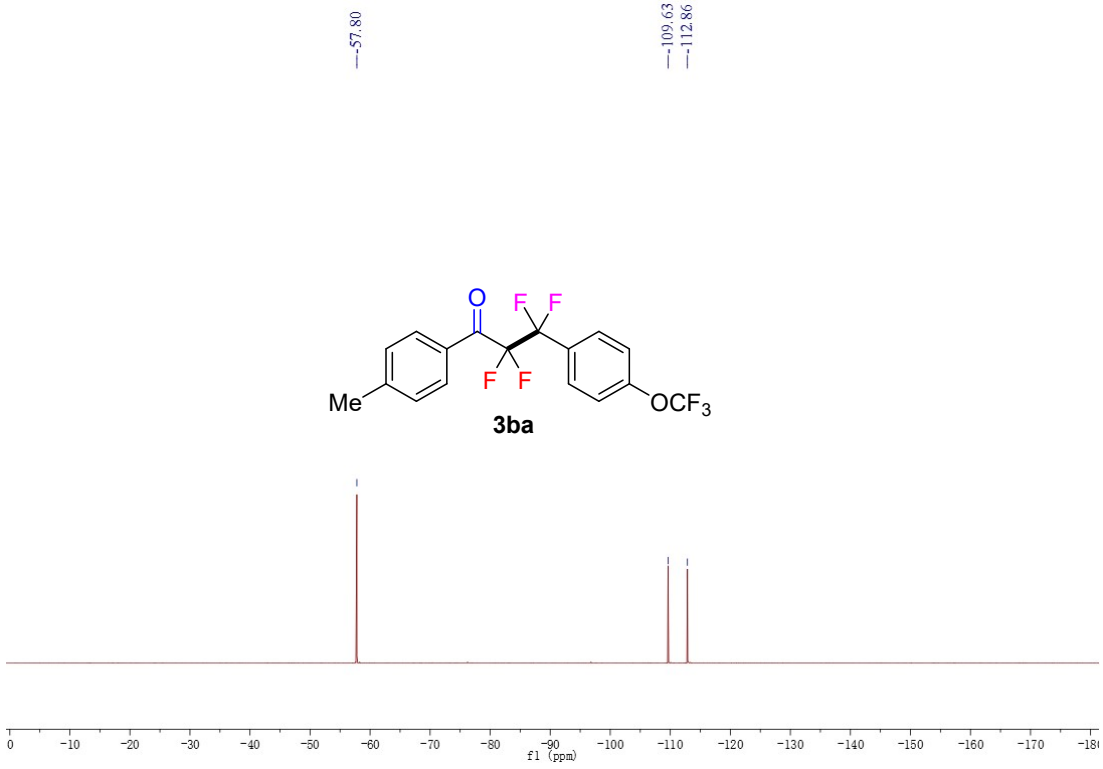

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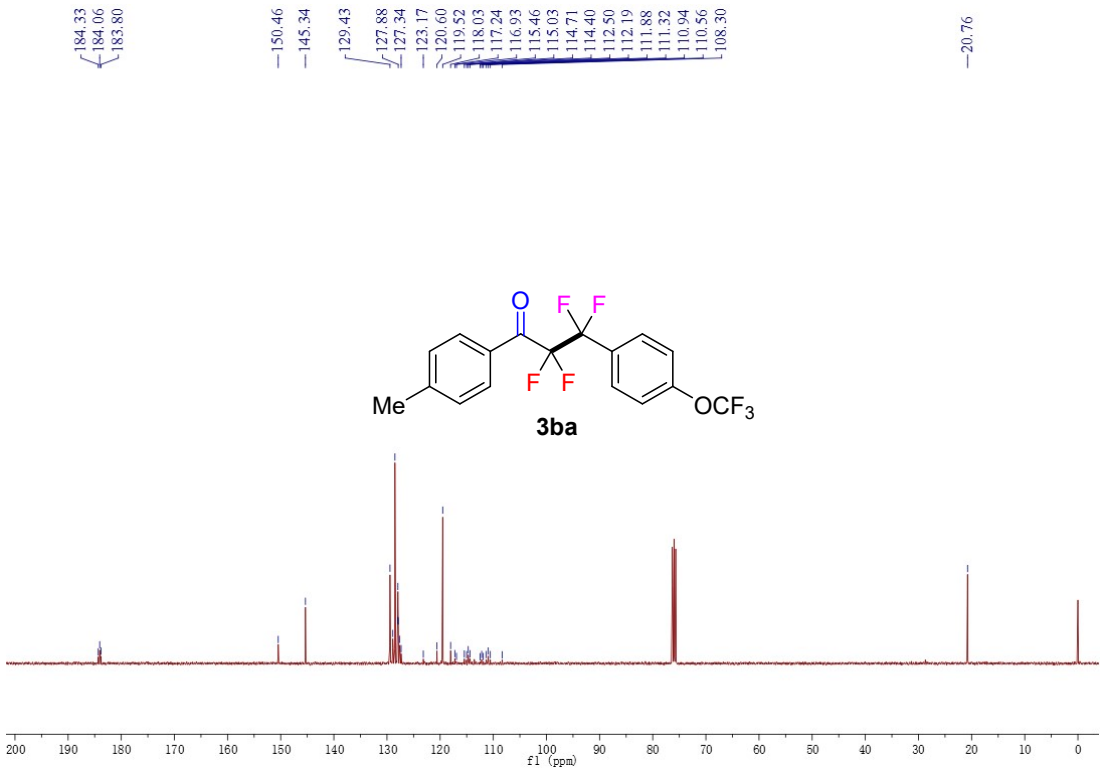

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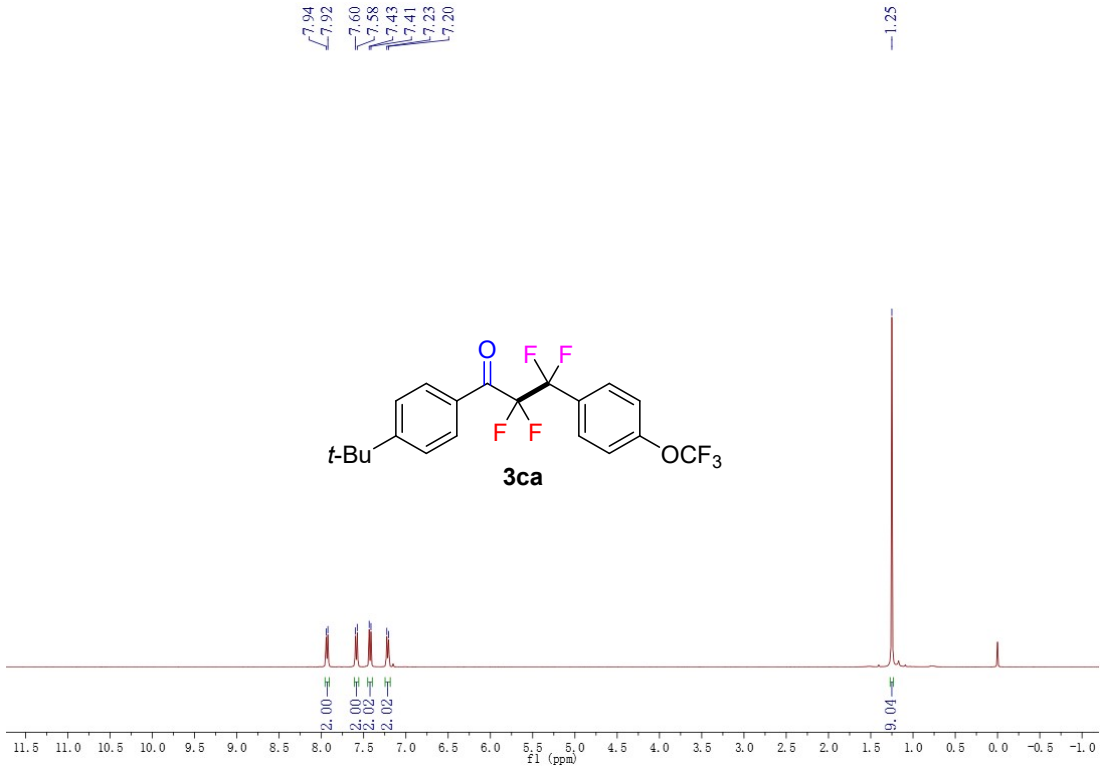

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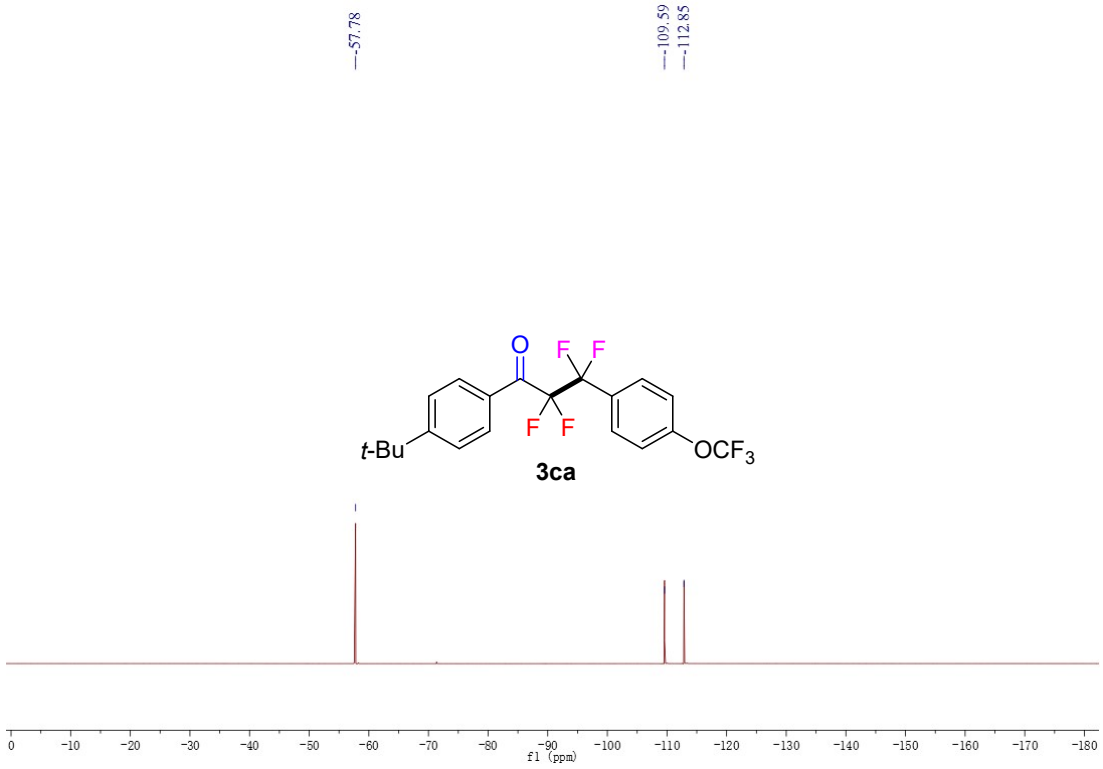

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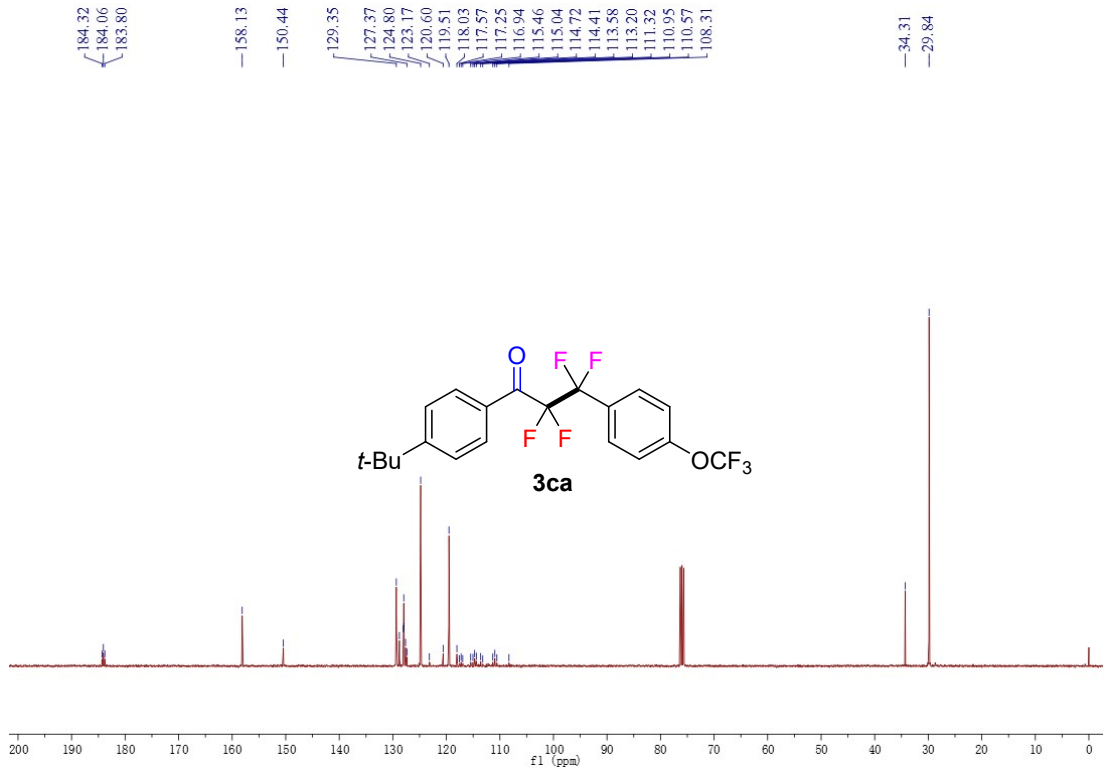

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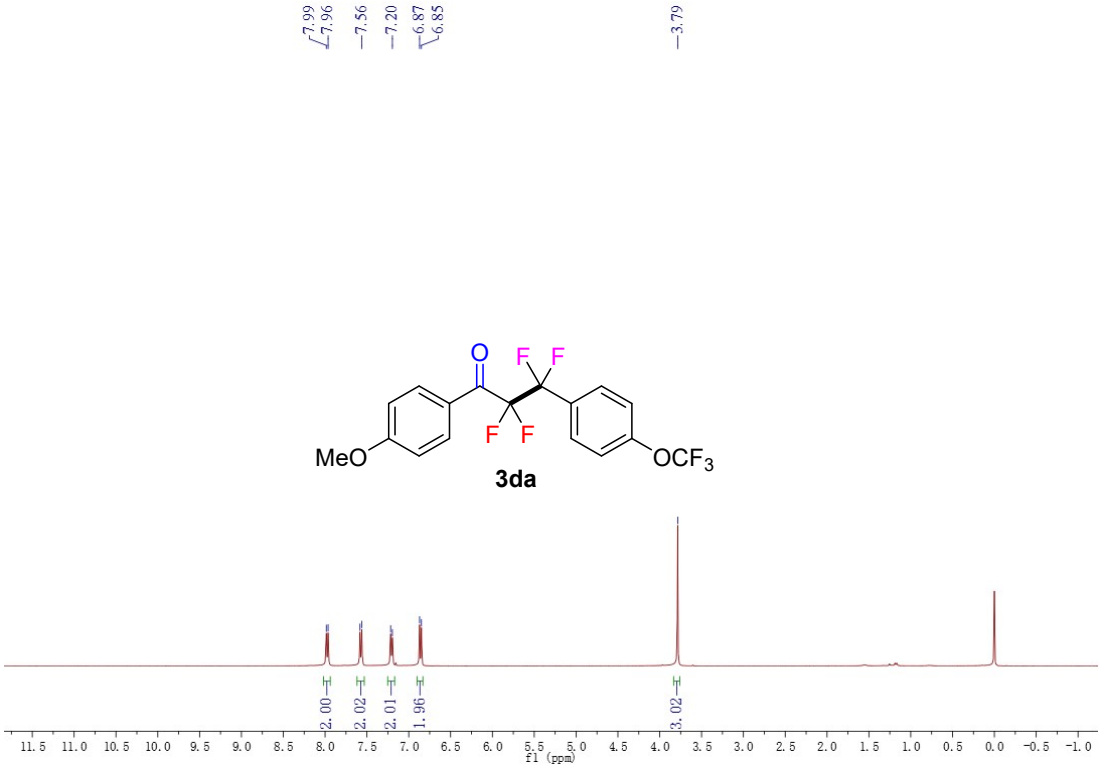

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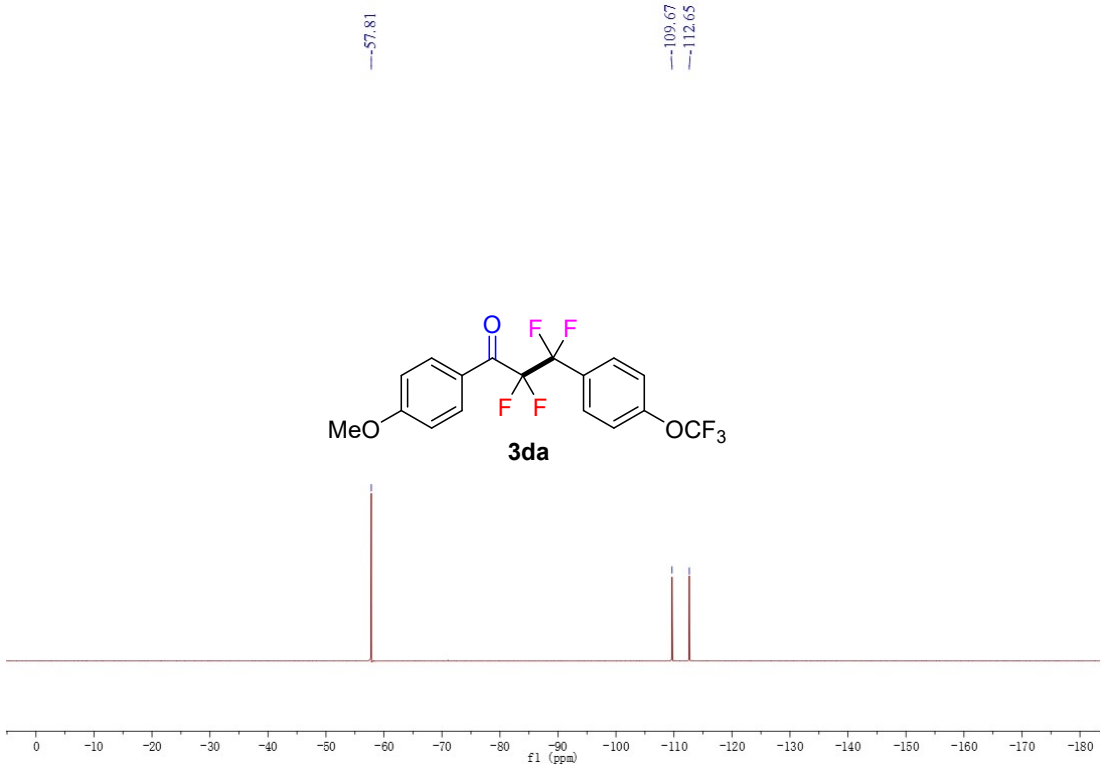

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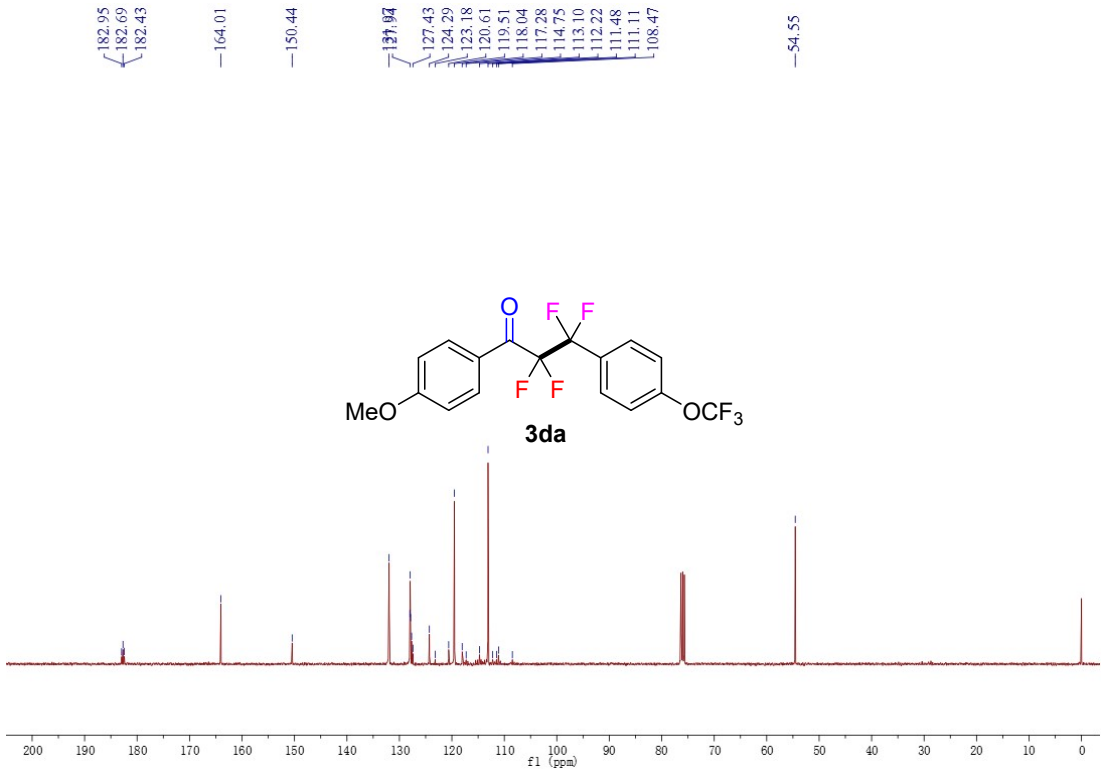

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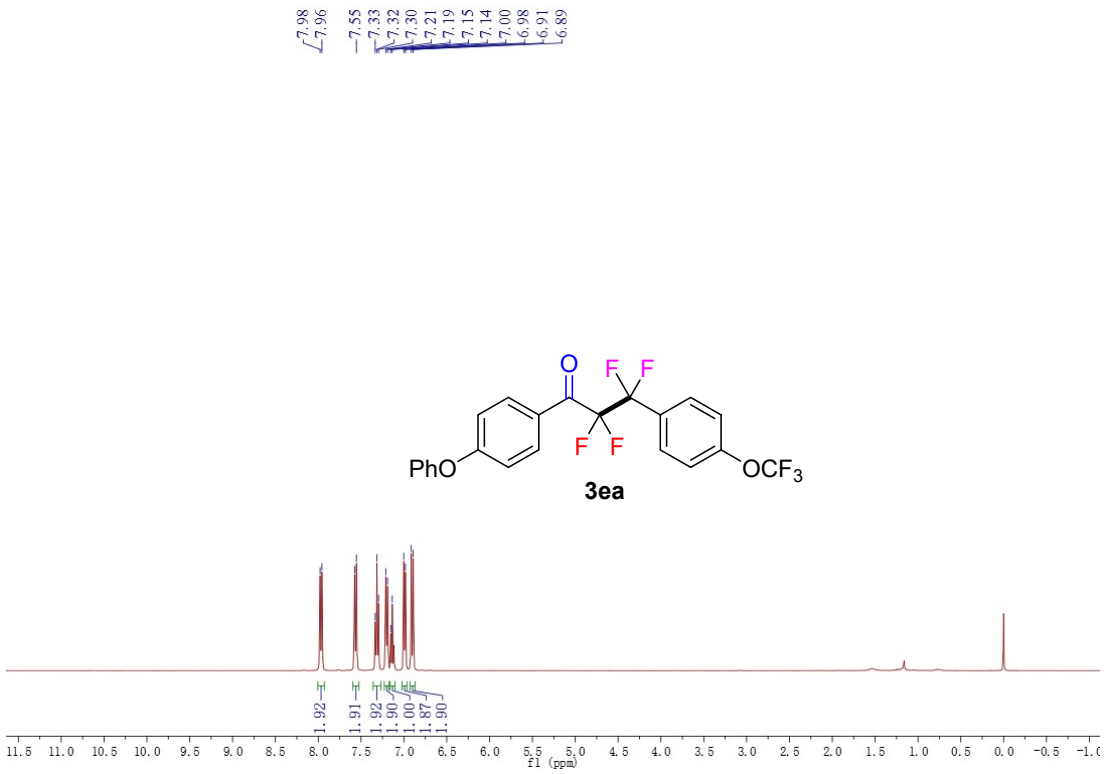

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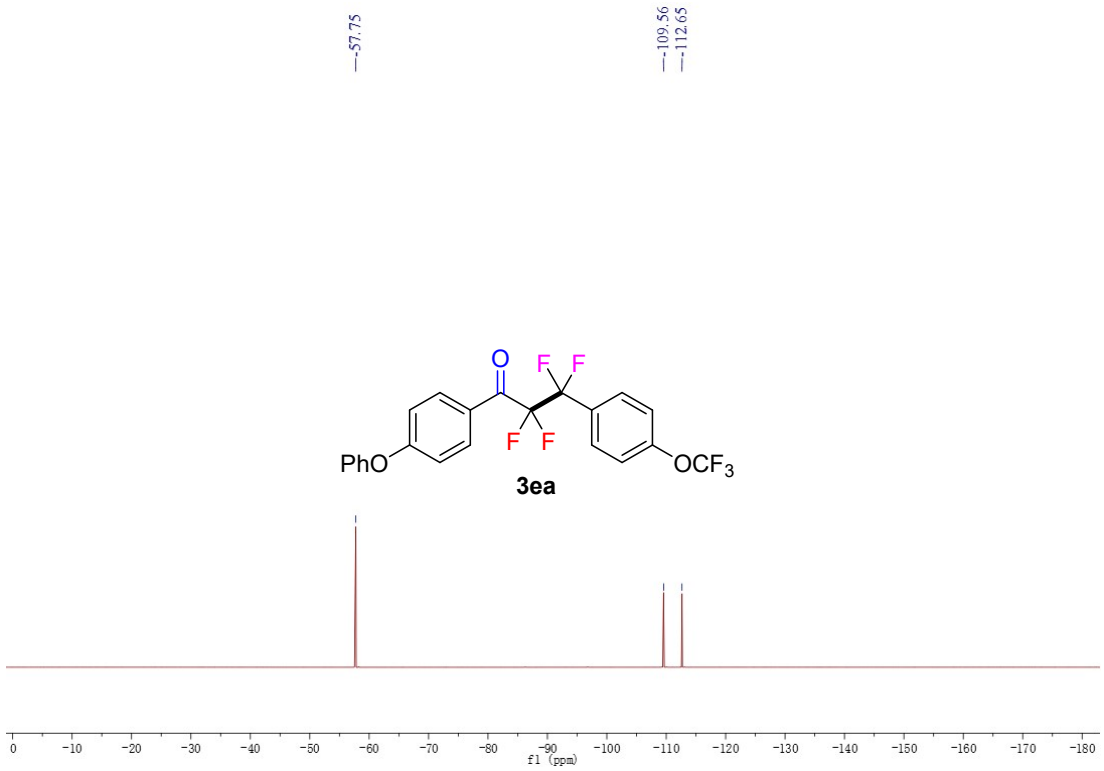

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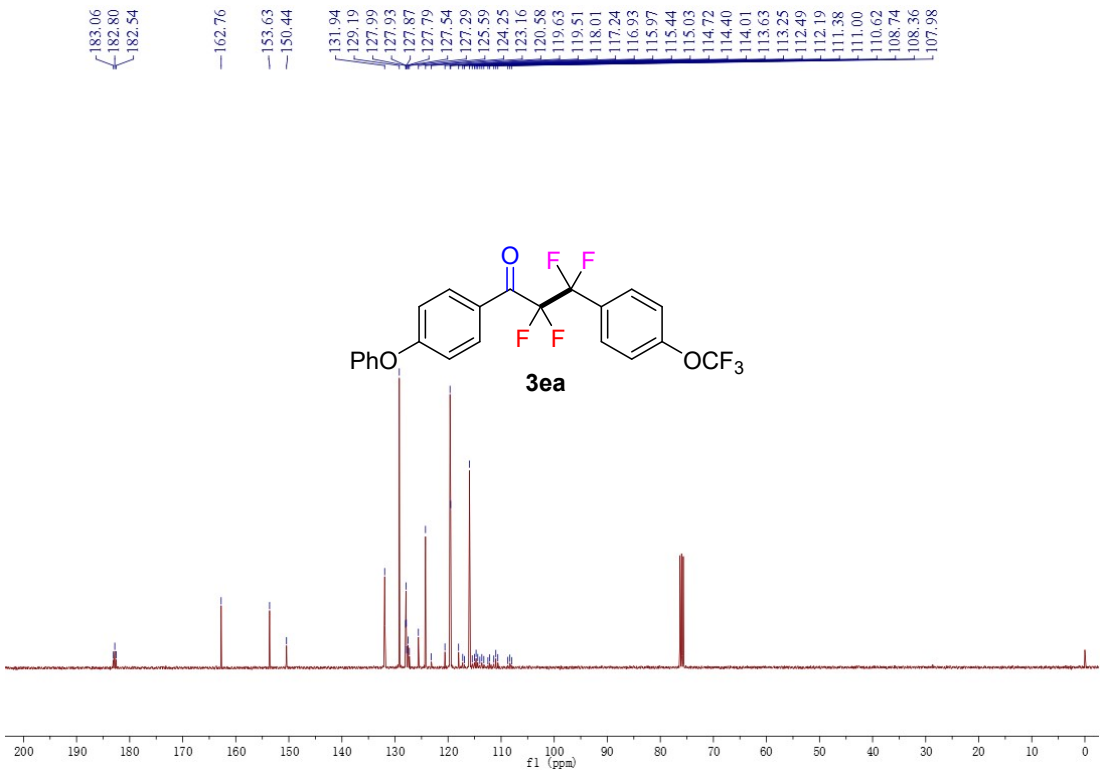

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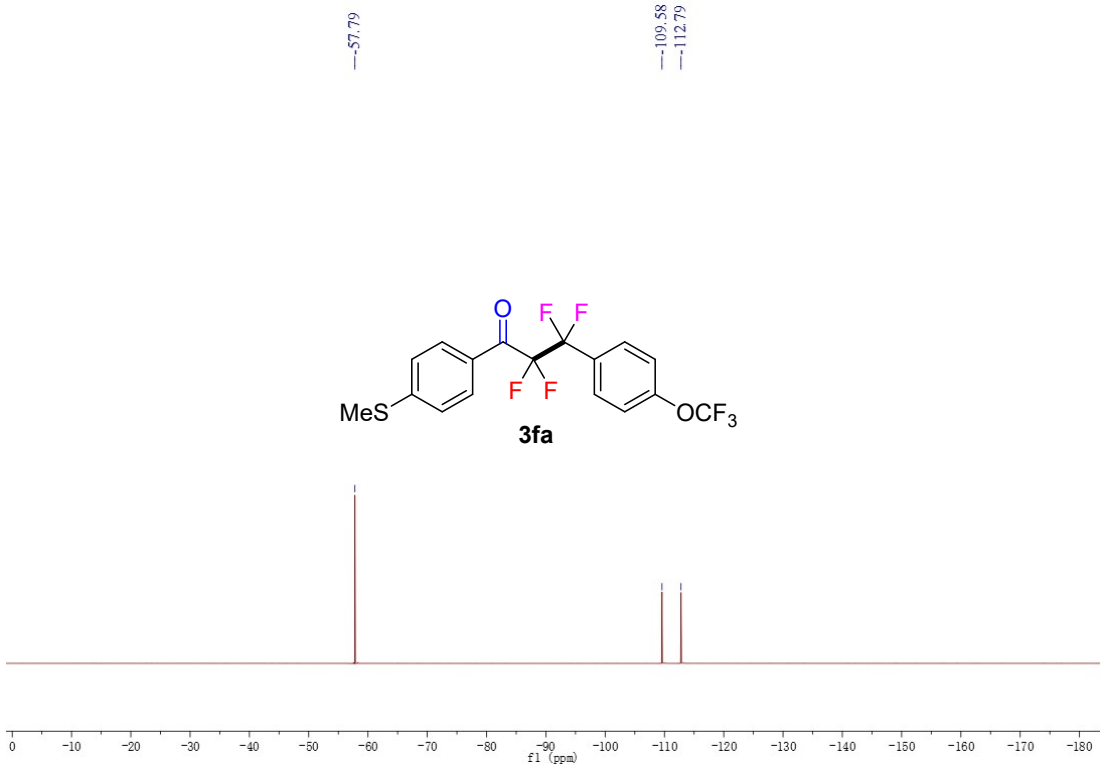

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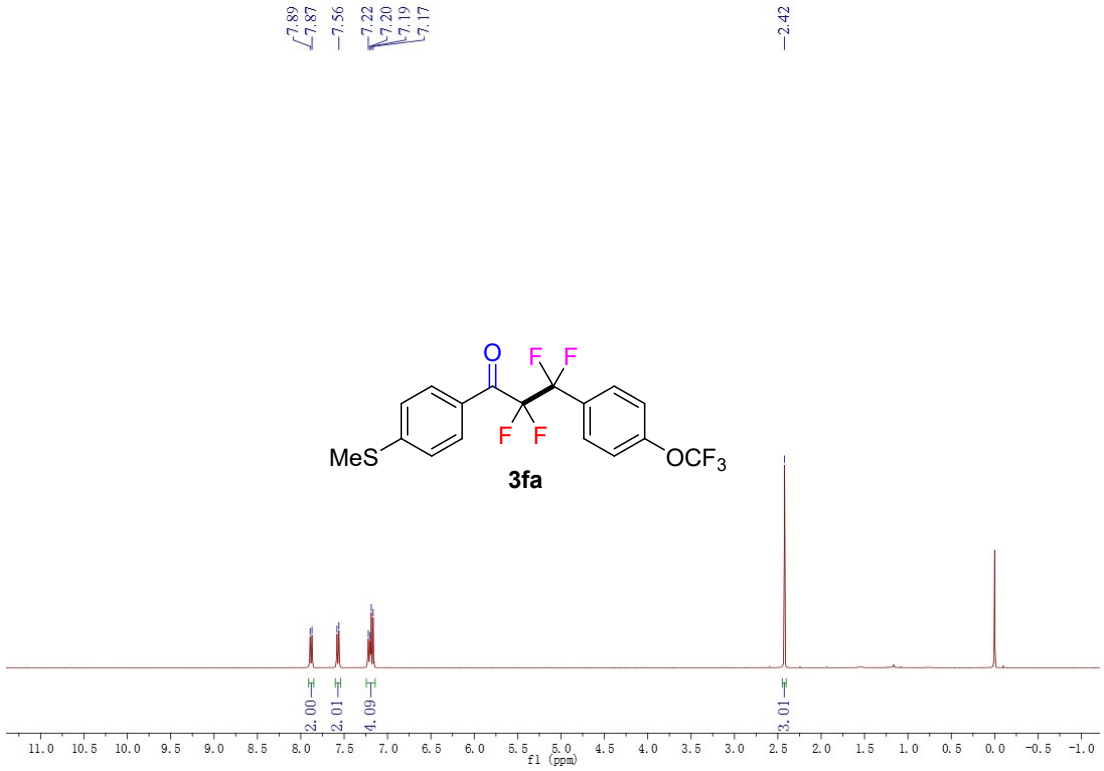

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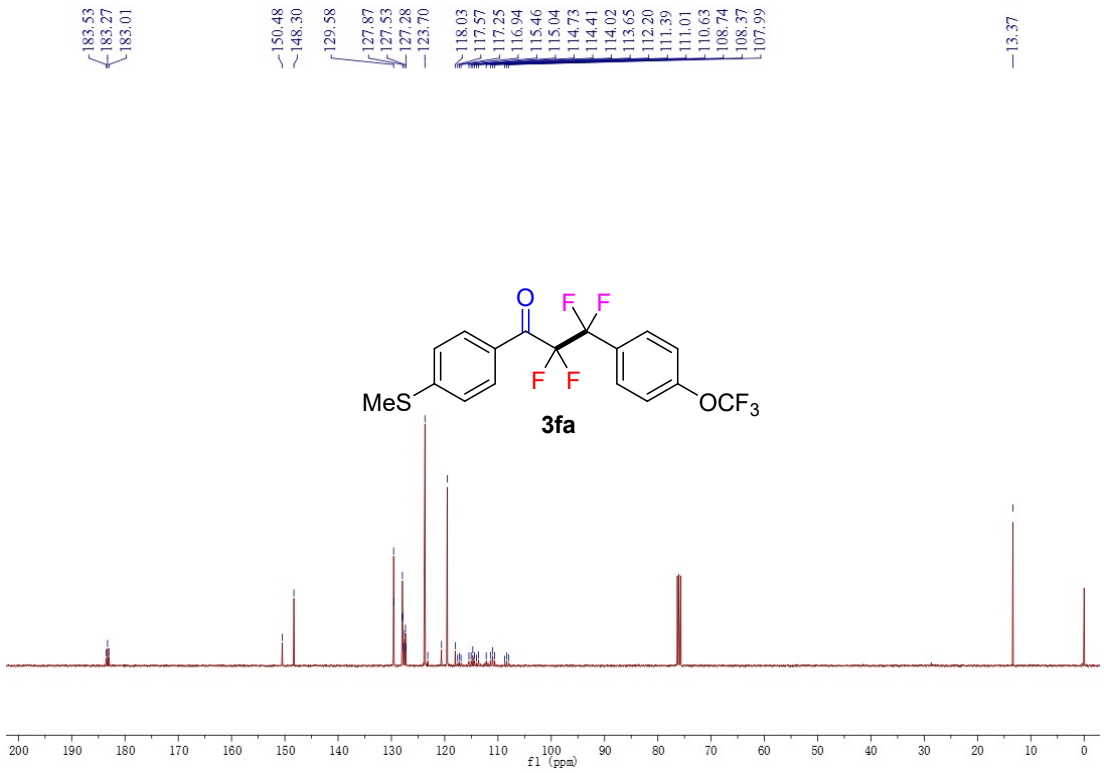

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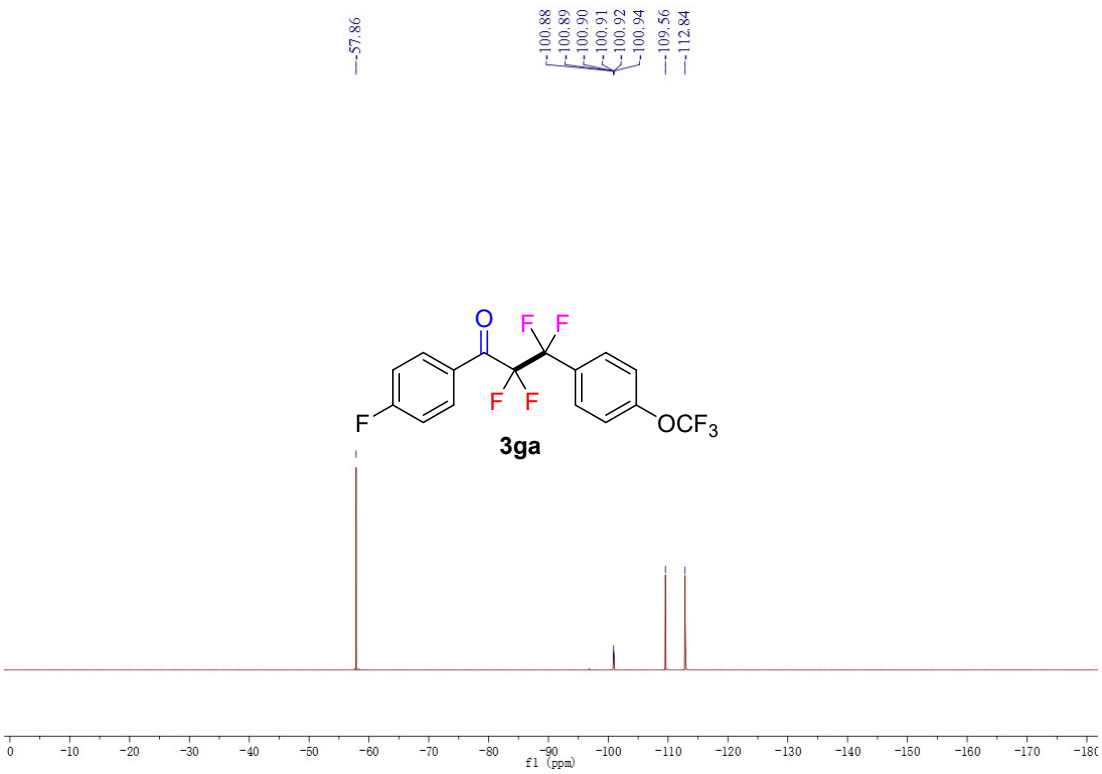

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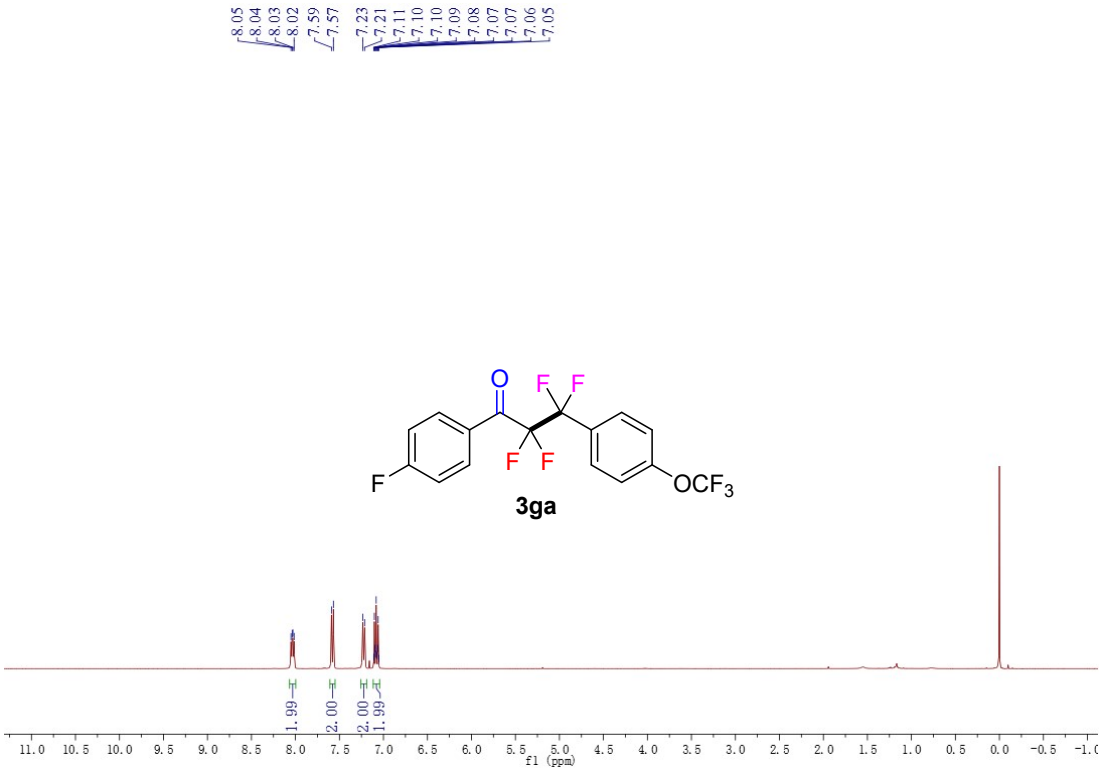

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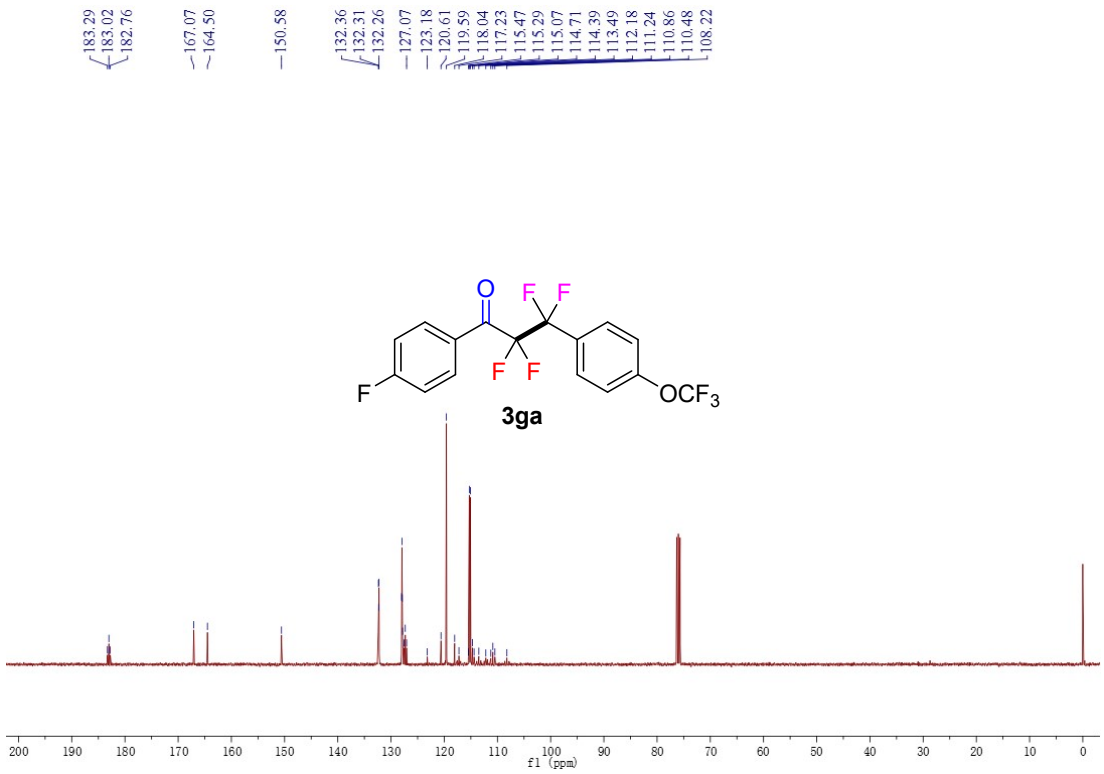

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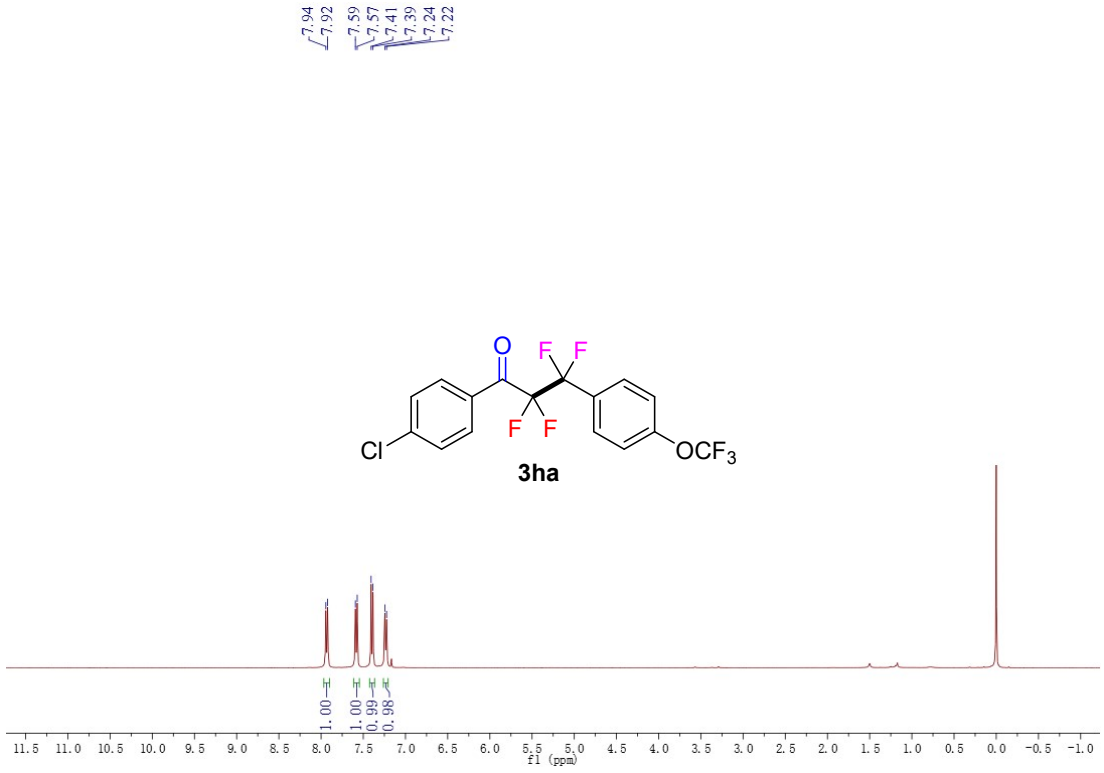

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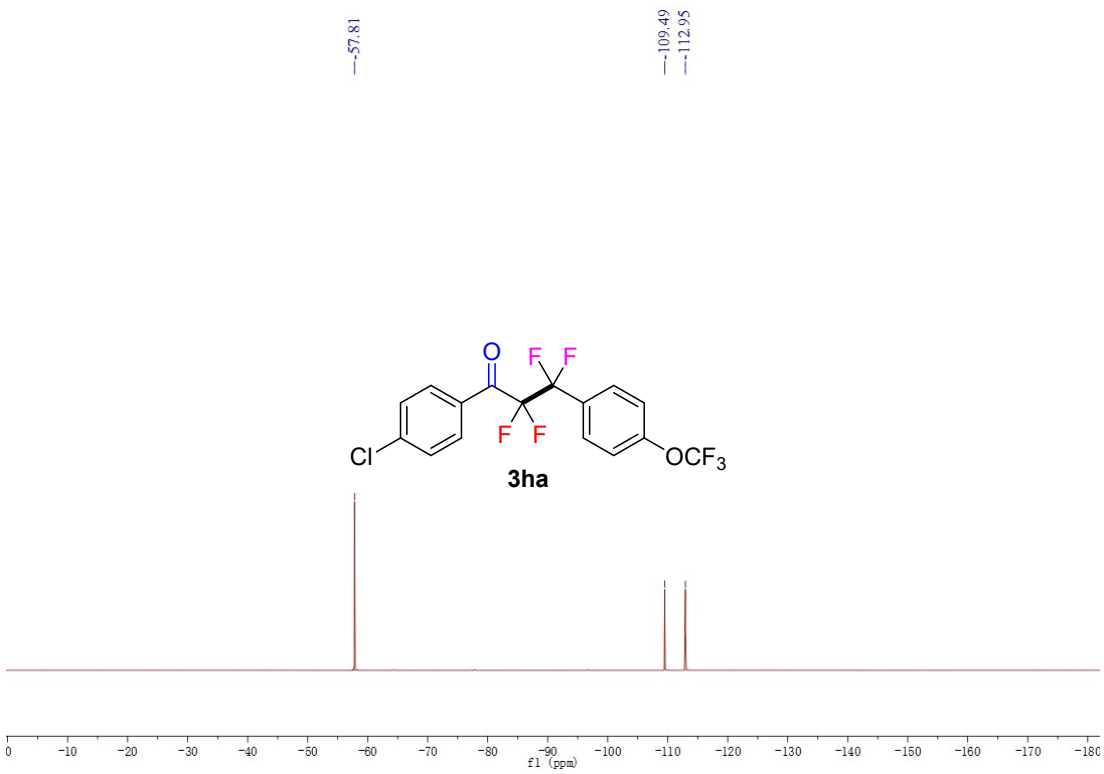

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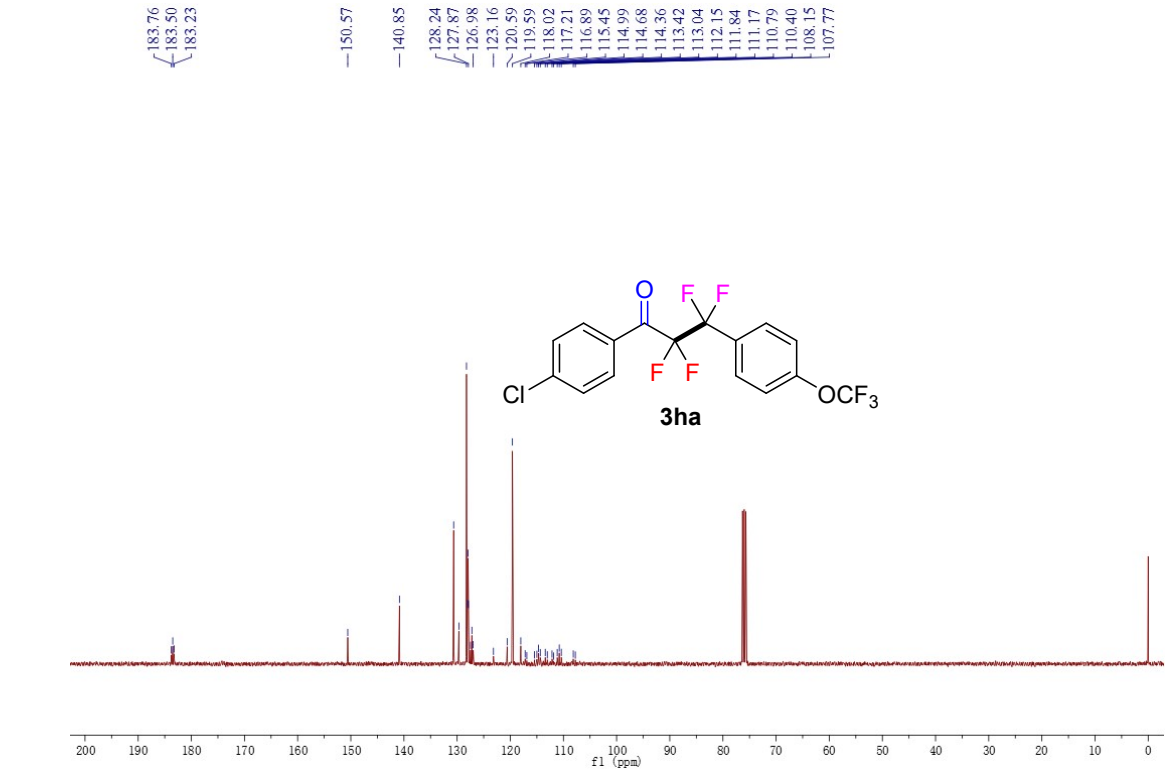

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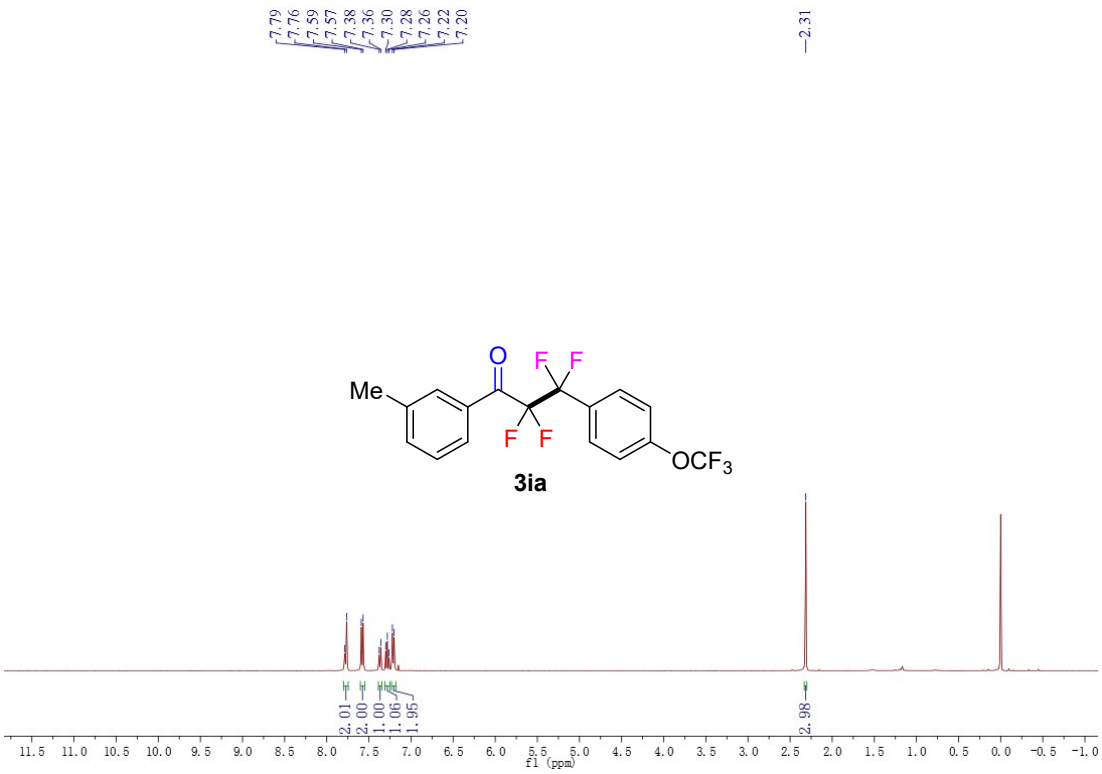

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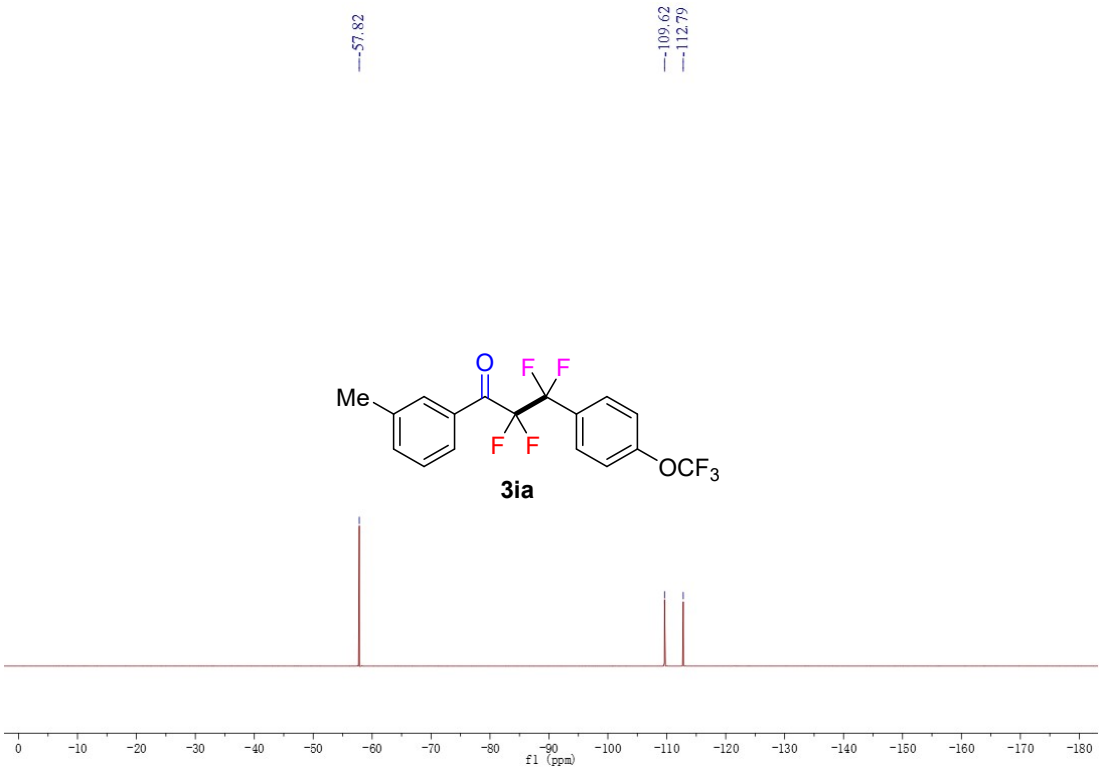

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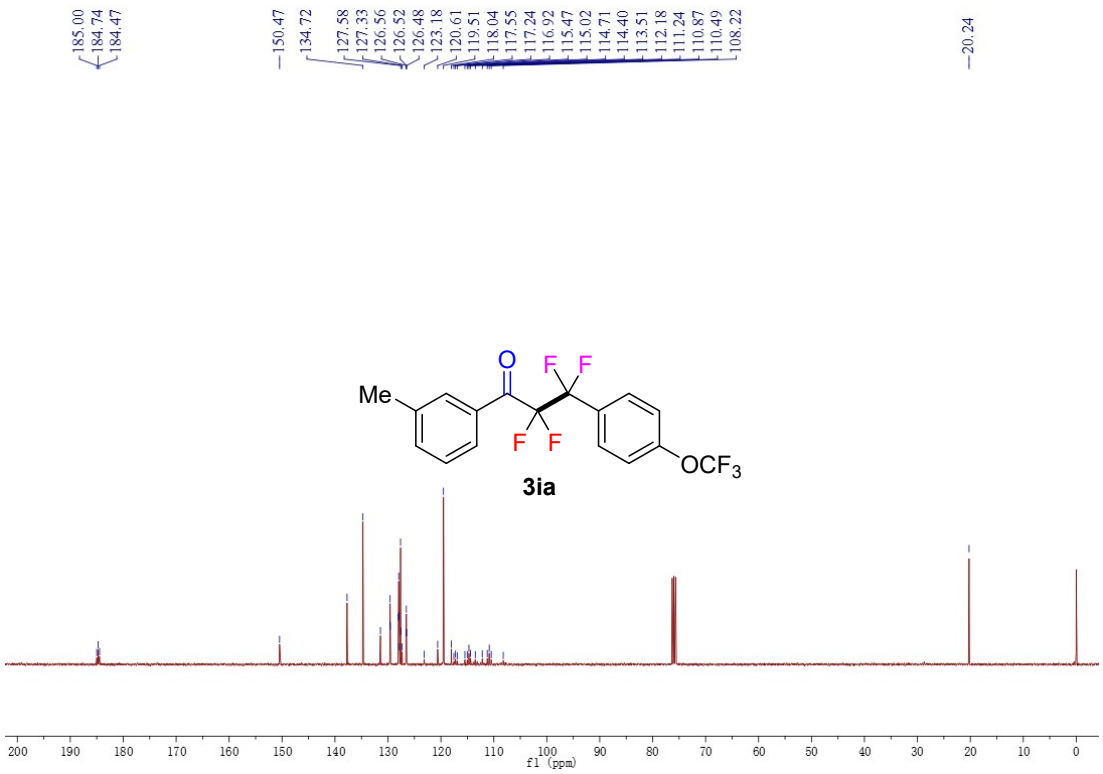

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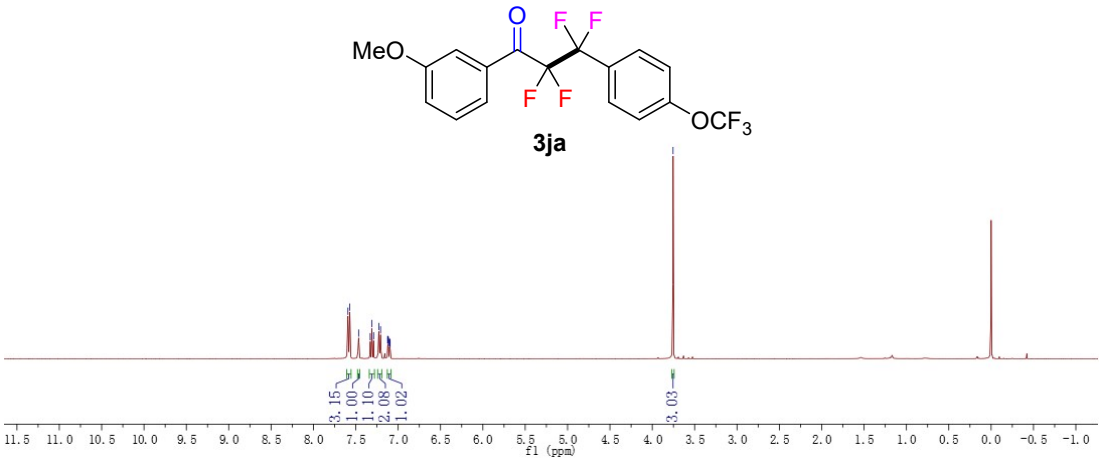

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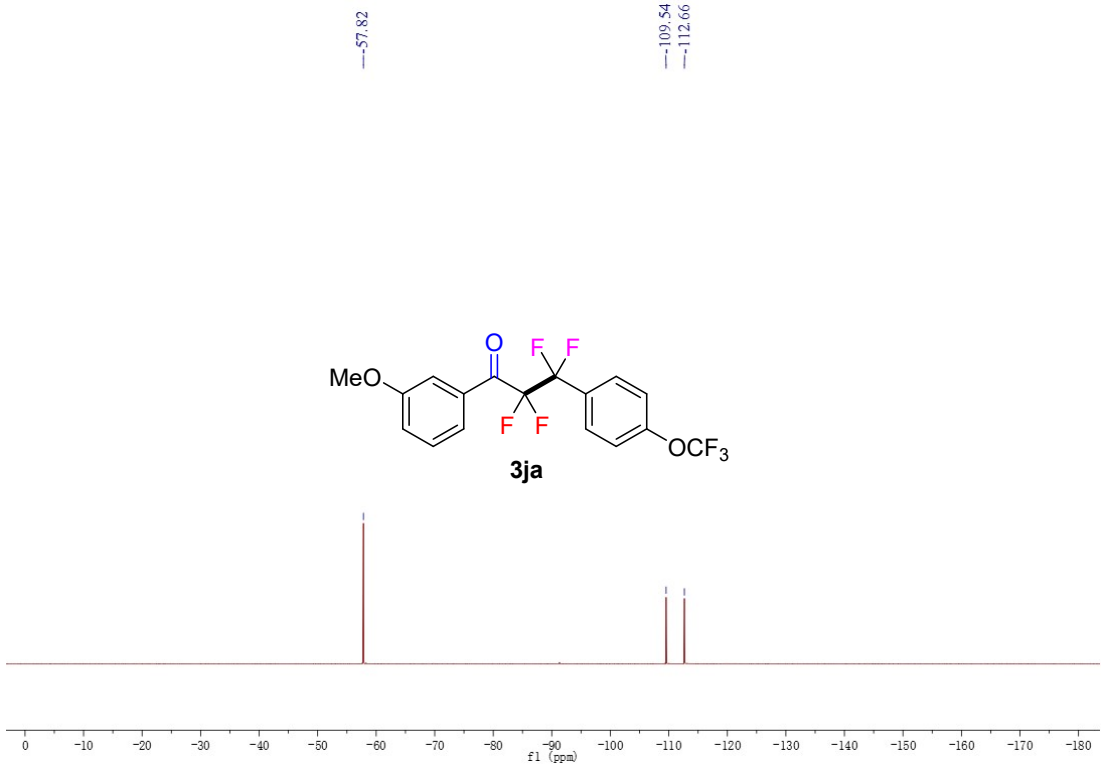

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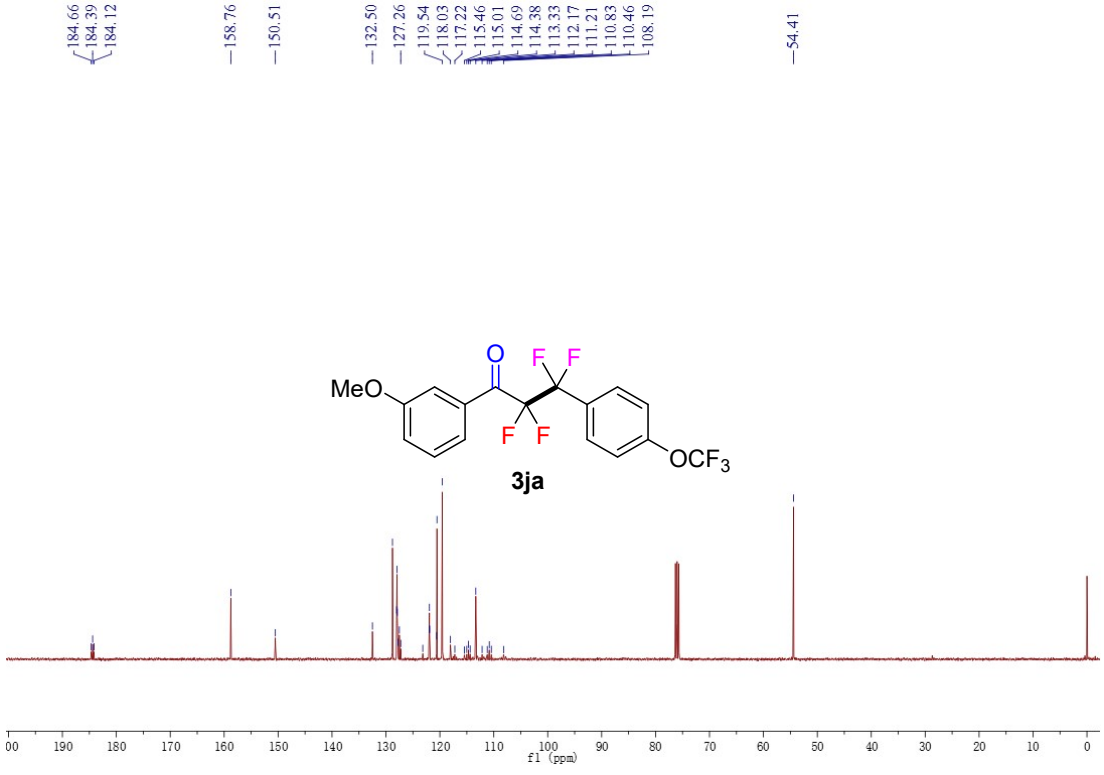

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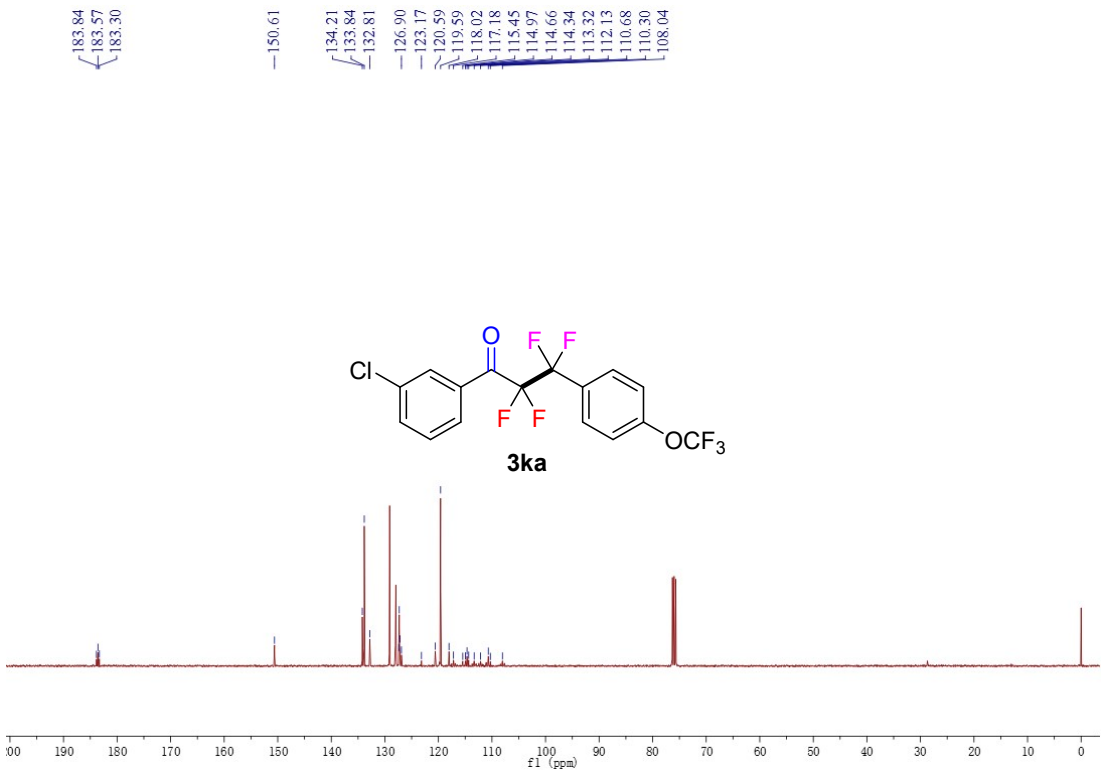

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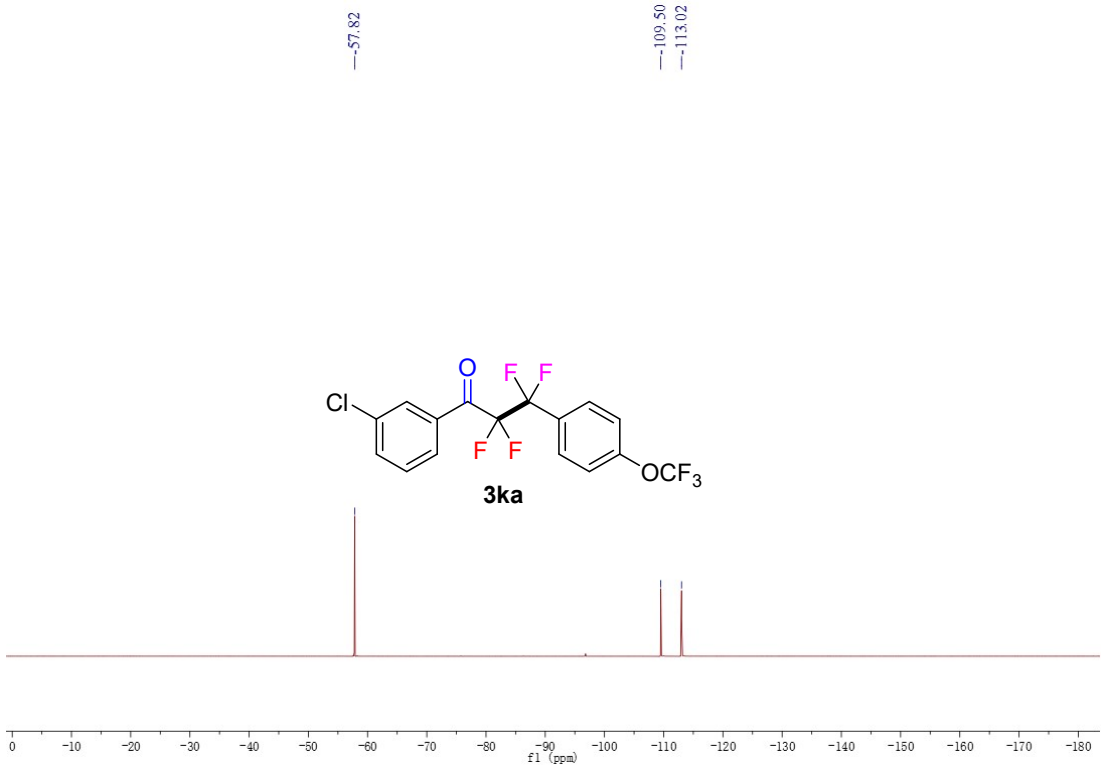

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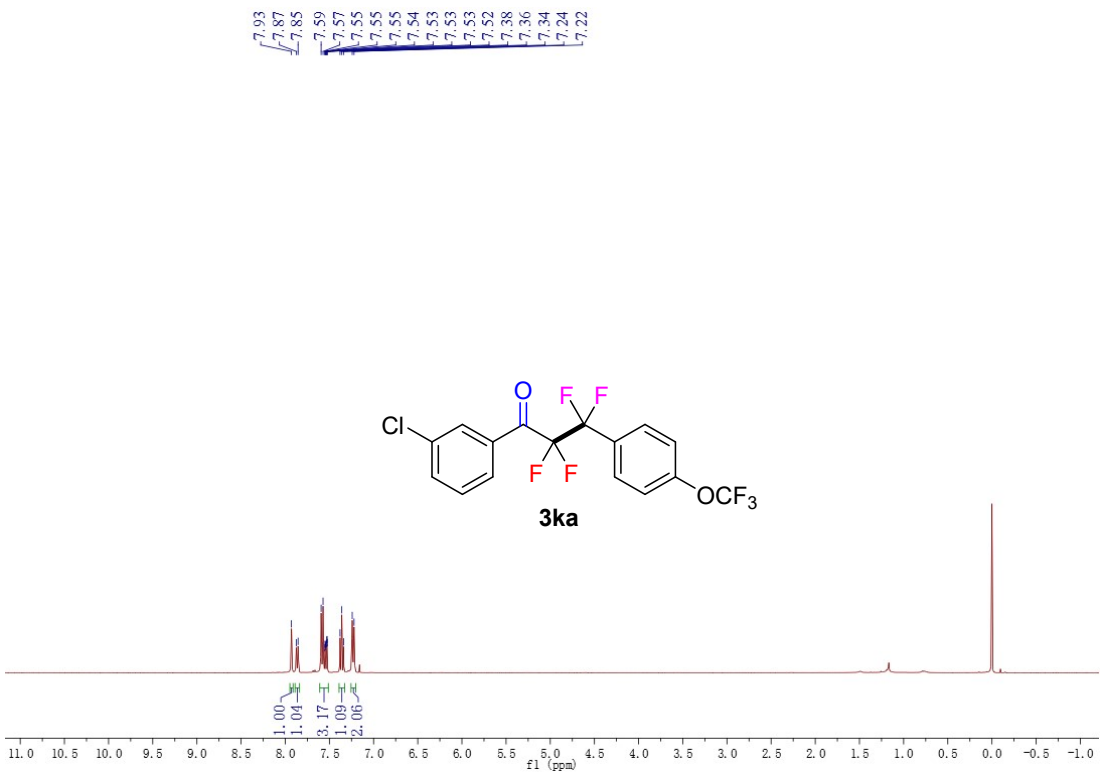

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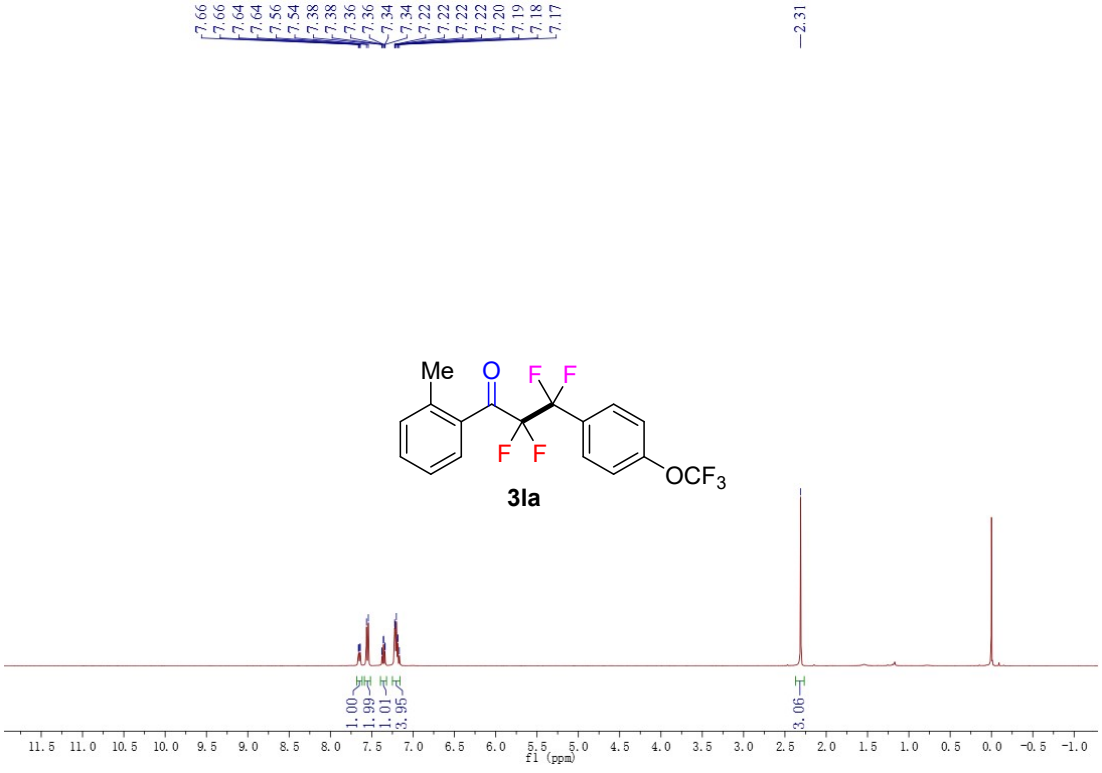
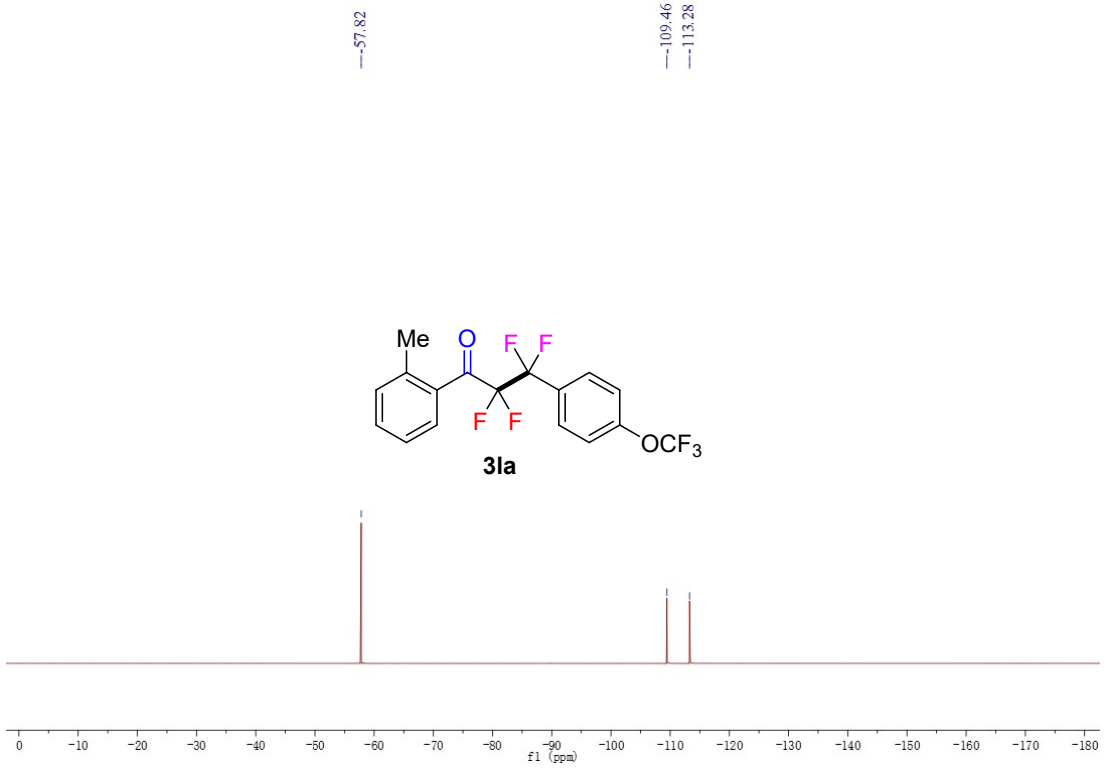


[19]F NMR (377 MHz, CDCl3)



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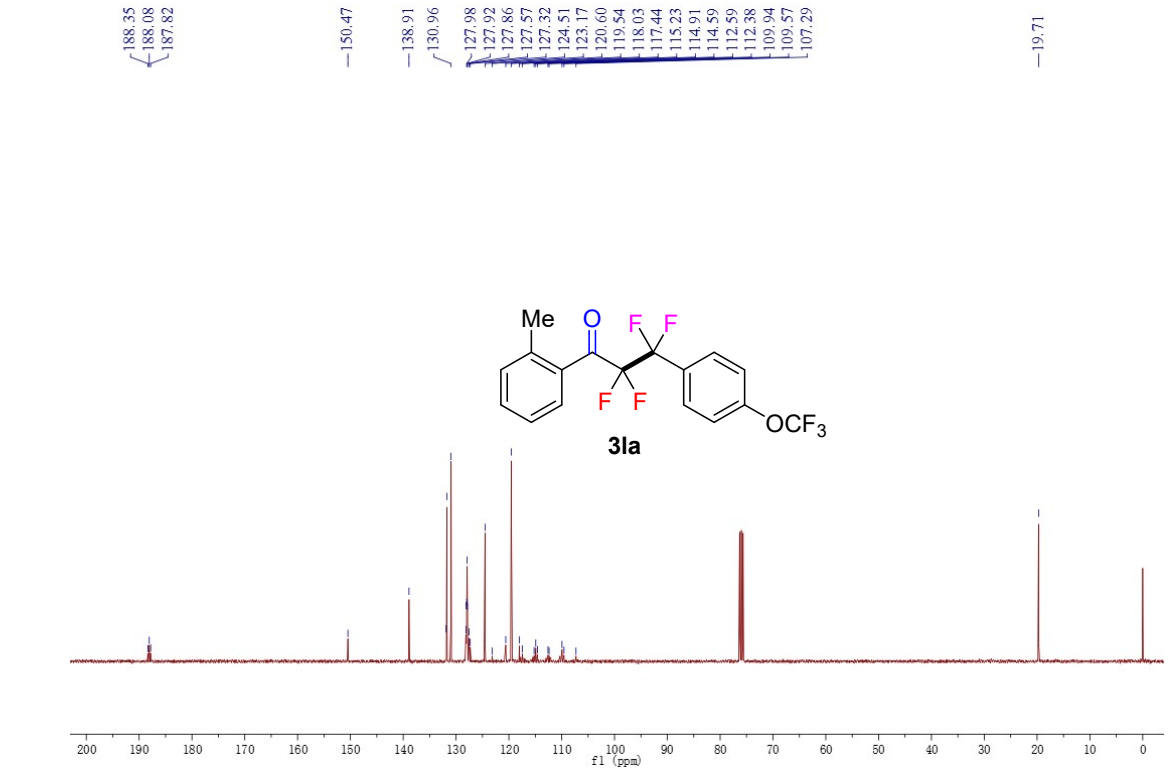

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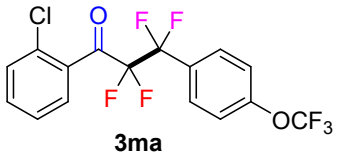

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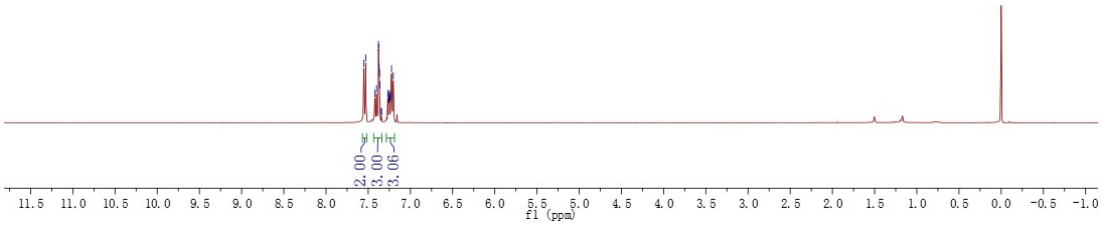
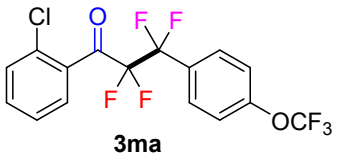


^{19}F NMR (377 MHz, $CDCl_3$)



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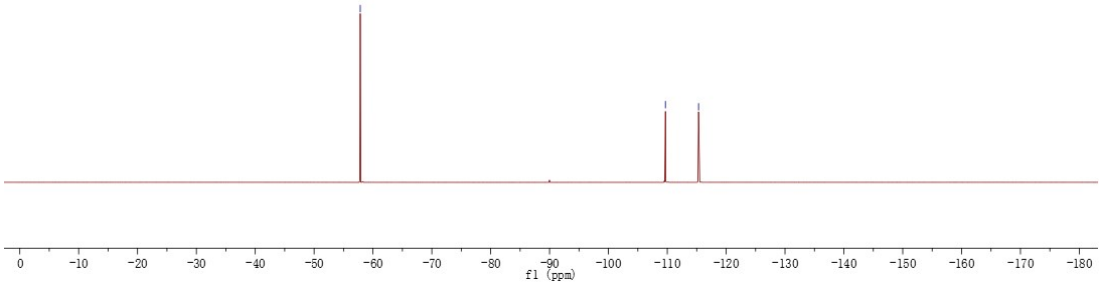
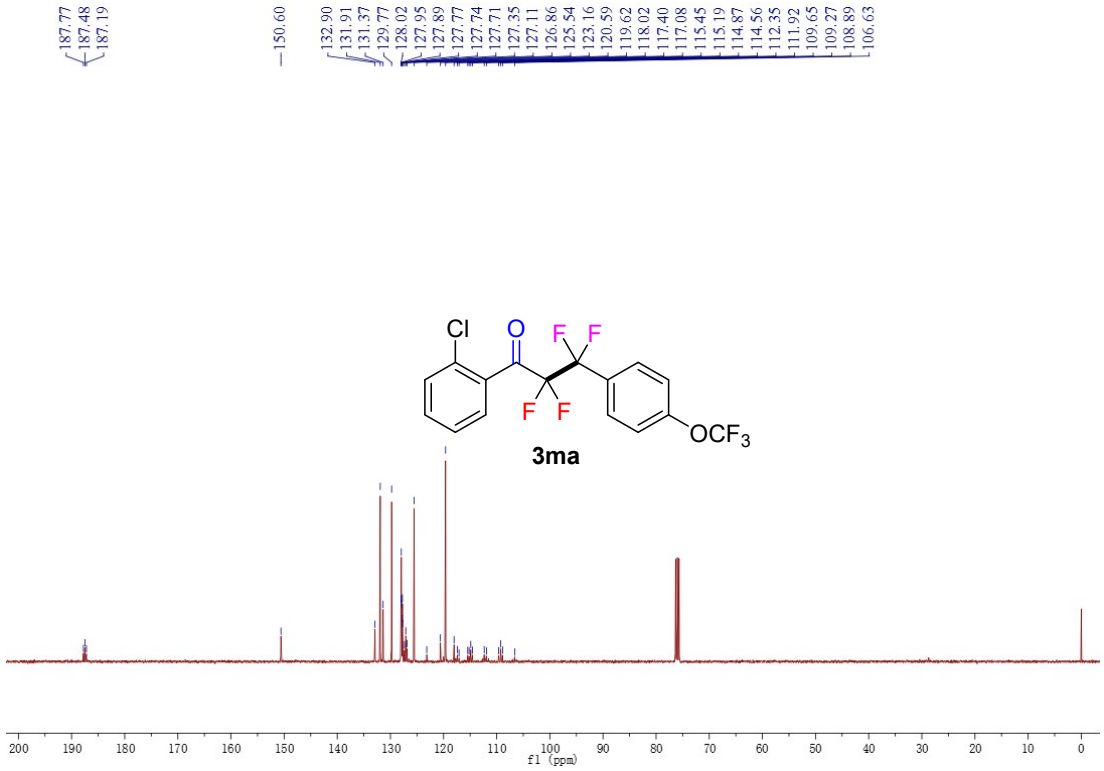


^{13}C NMR (101 MHz, $CDCl_3$)



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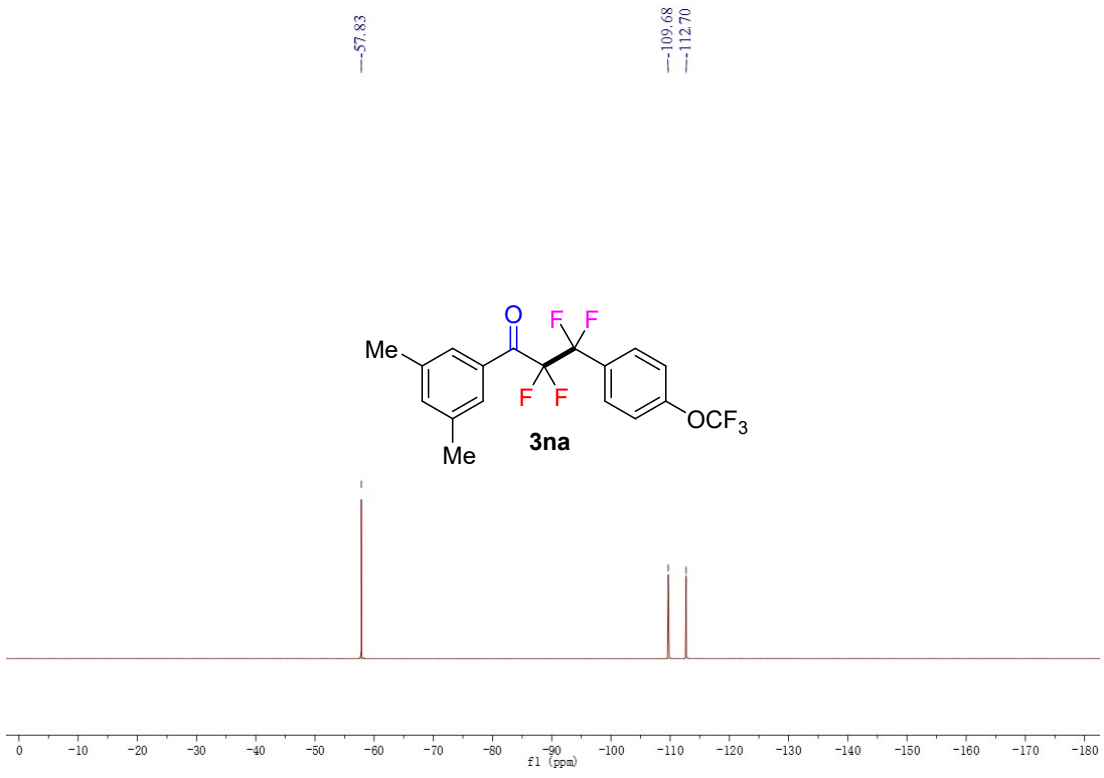

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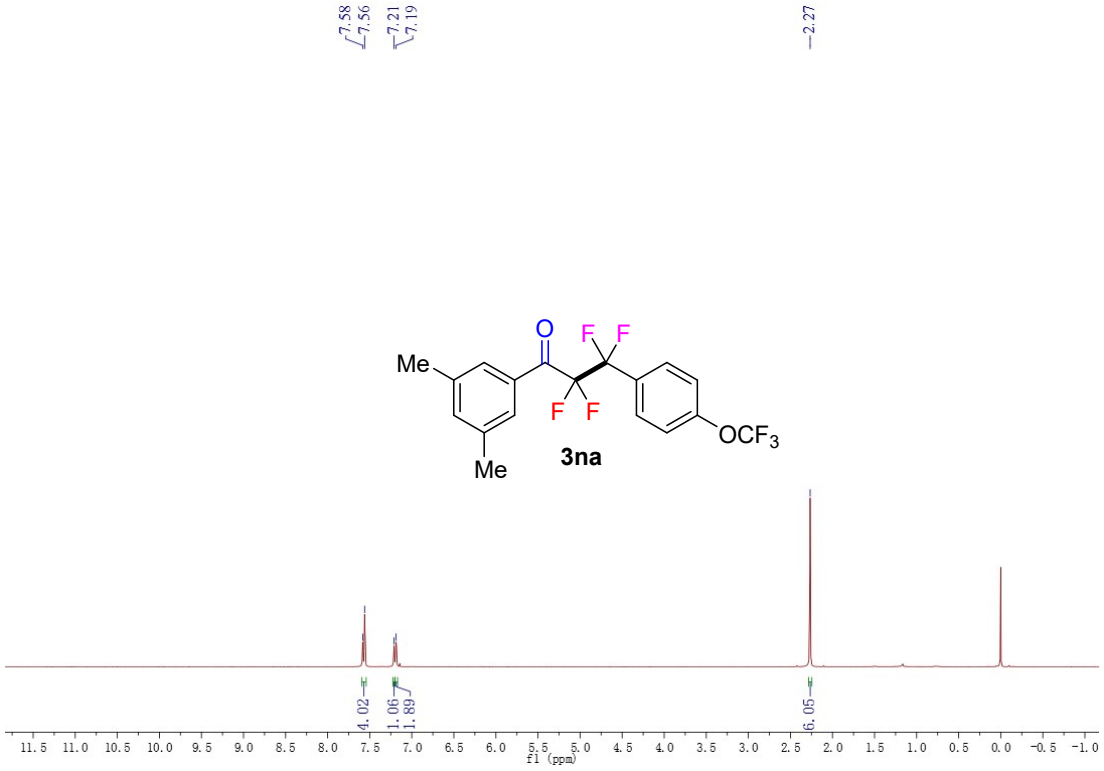

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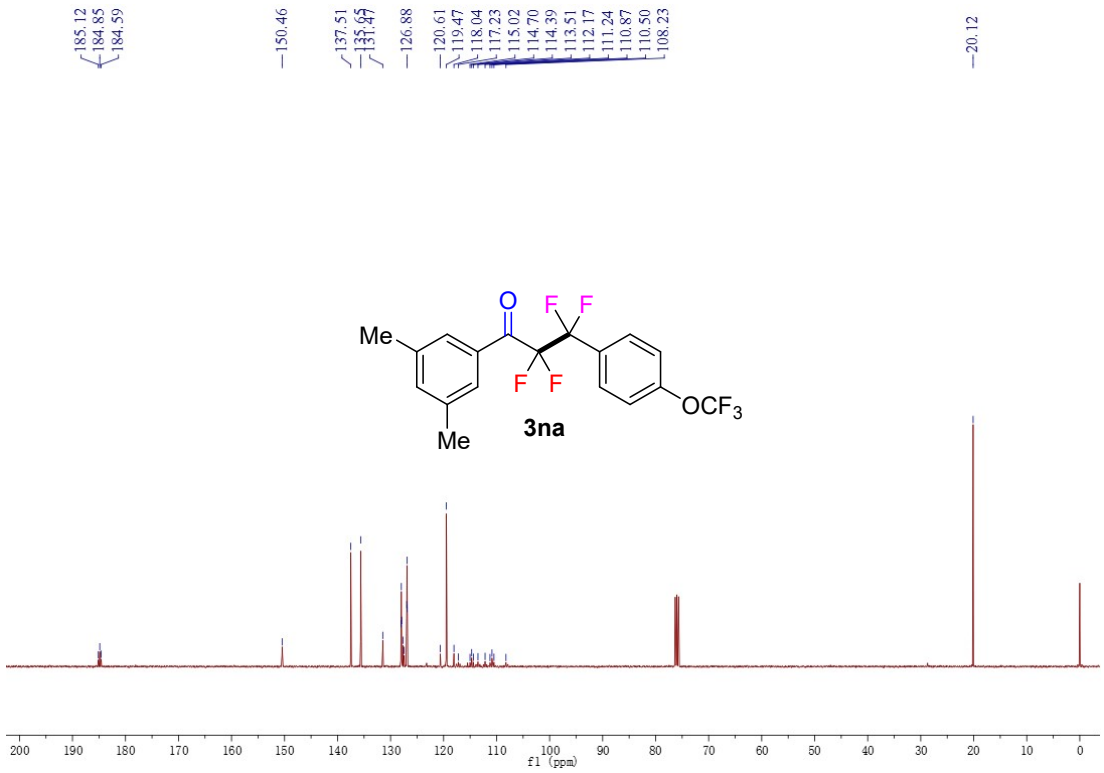

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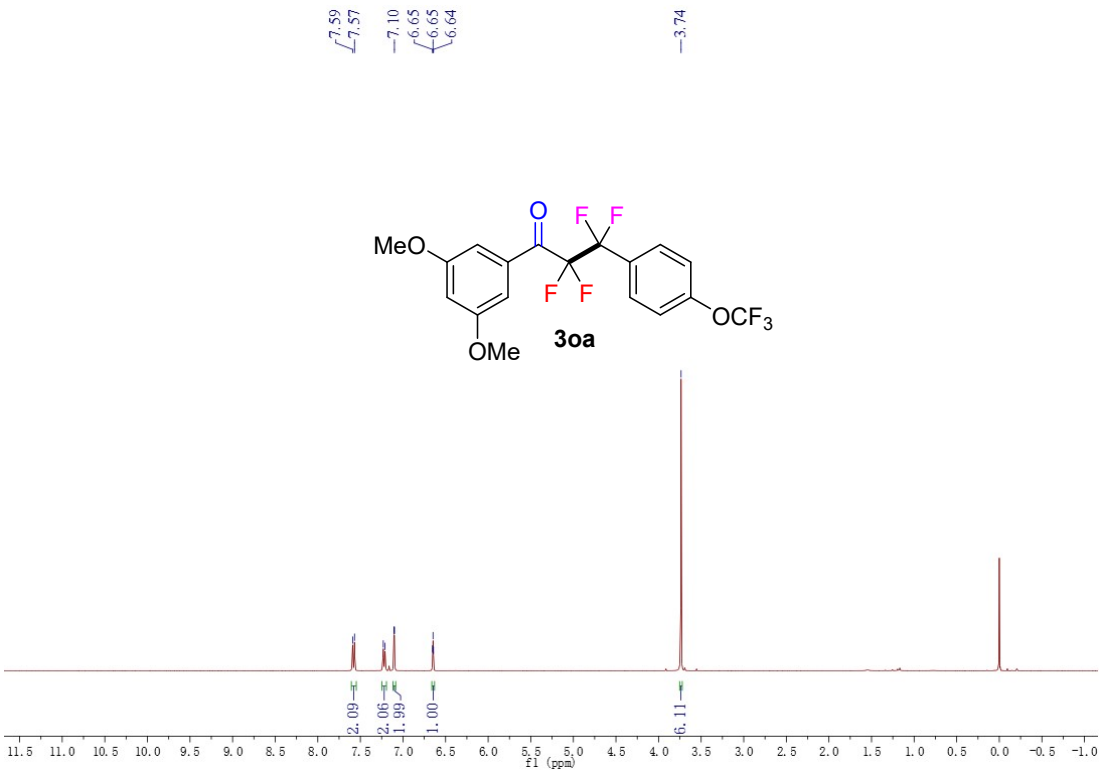
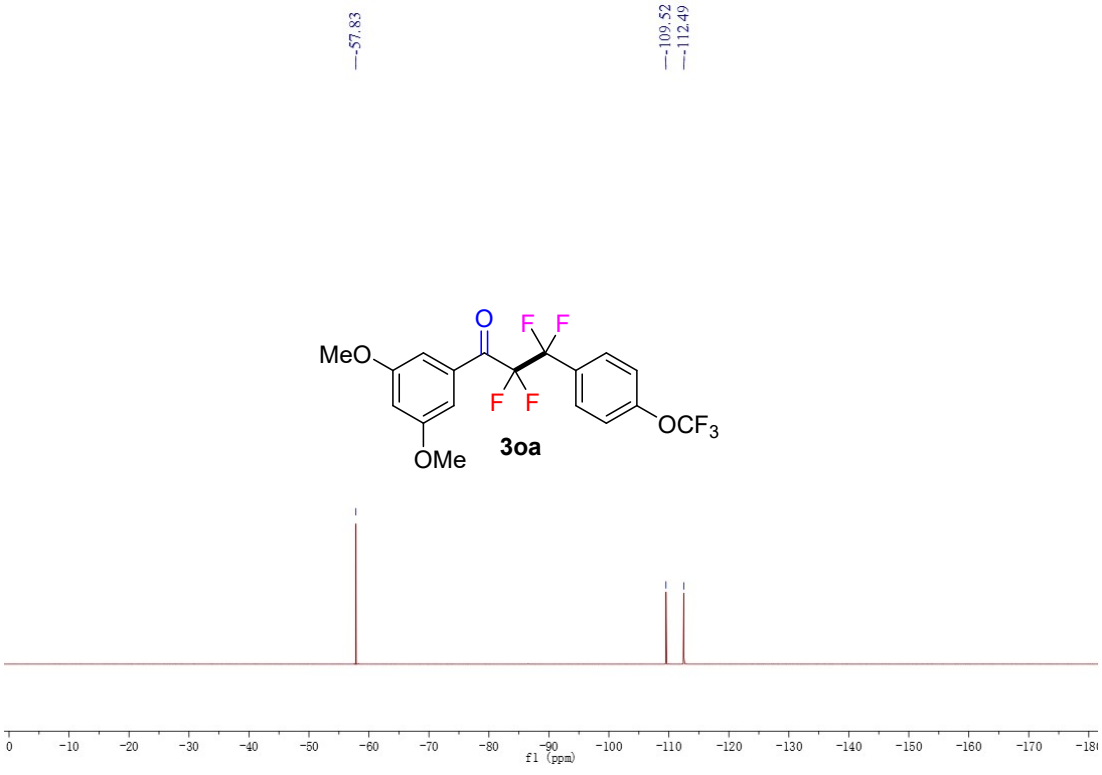


^{19}F NMR (377 MHz, $CDCl_3$)



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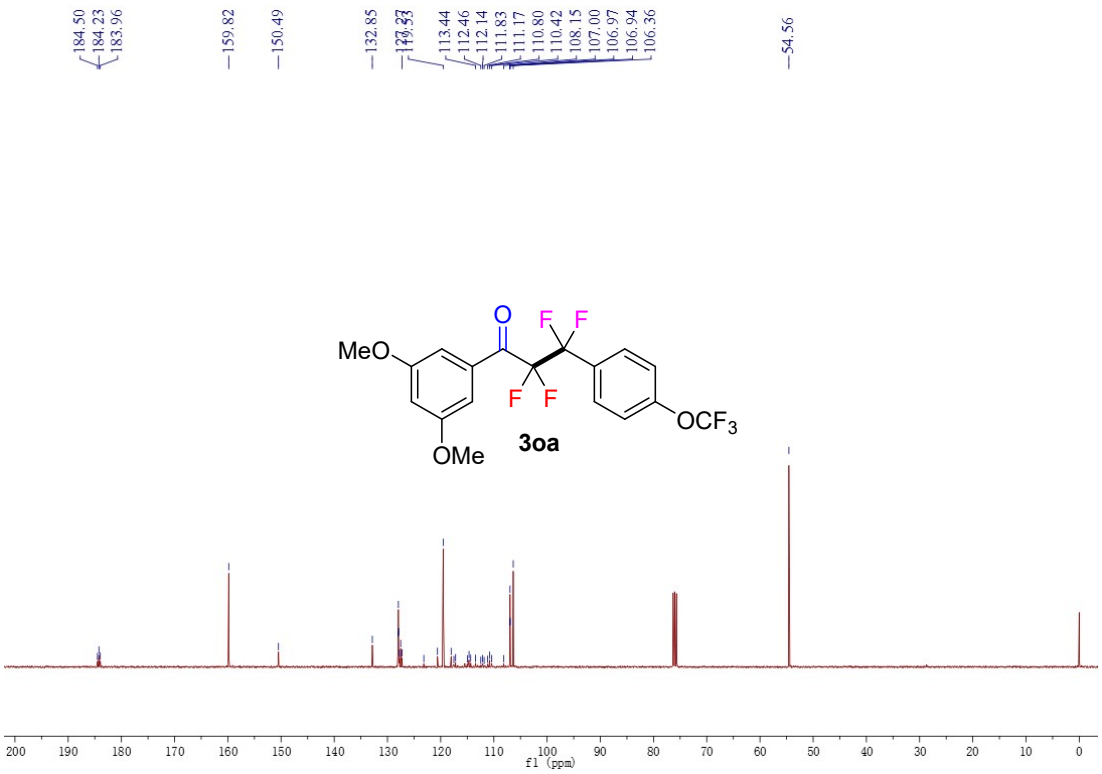

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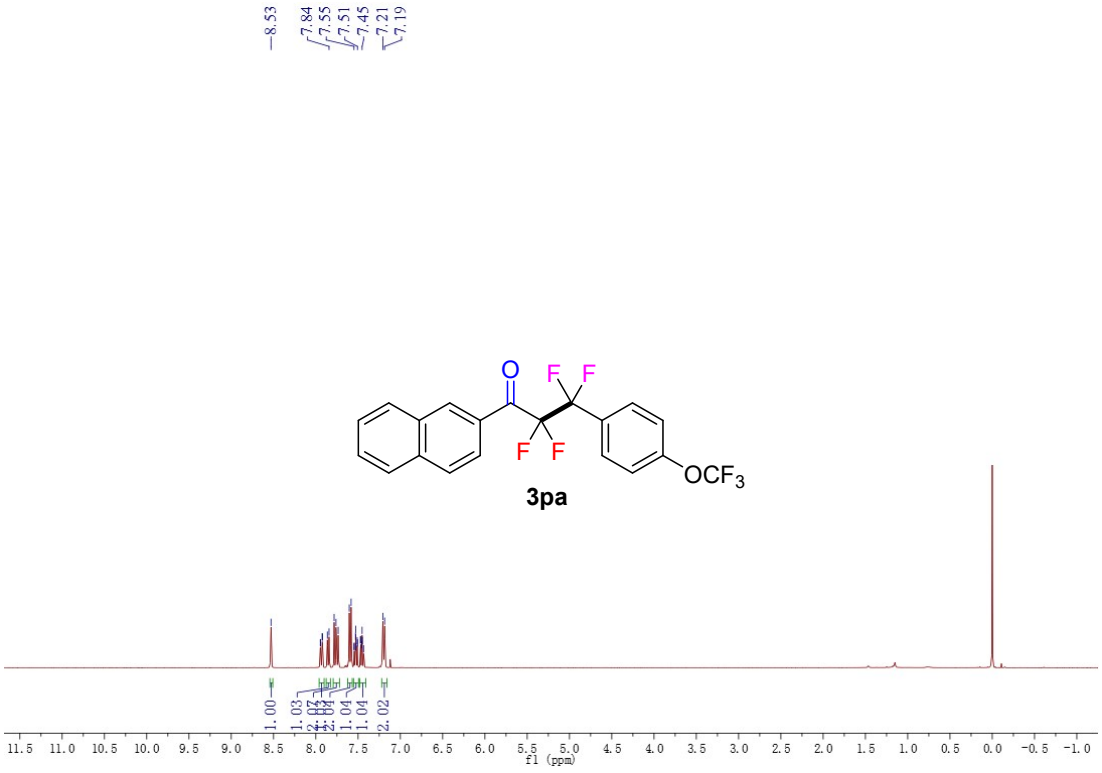

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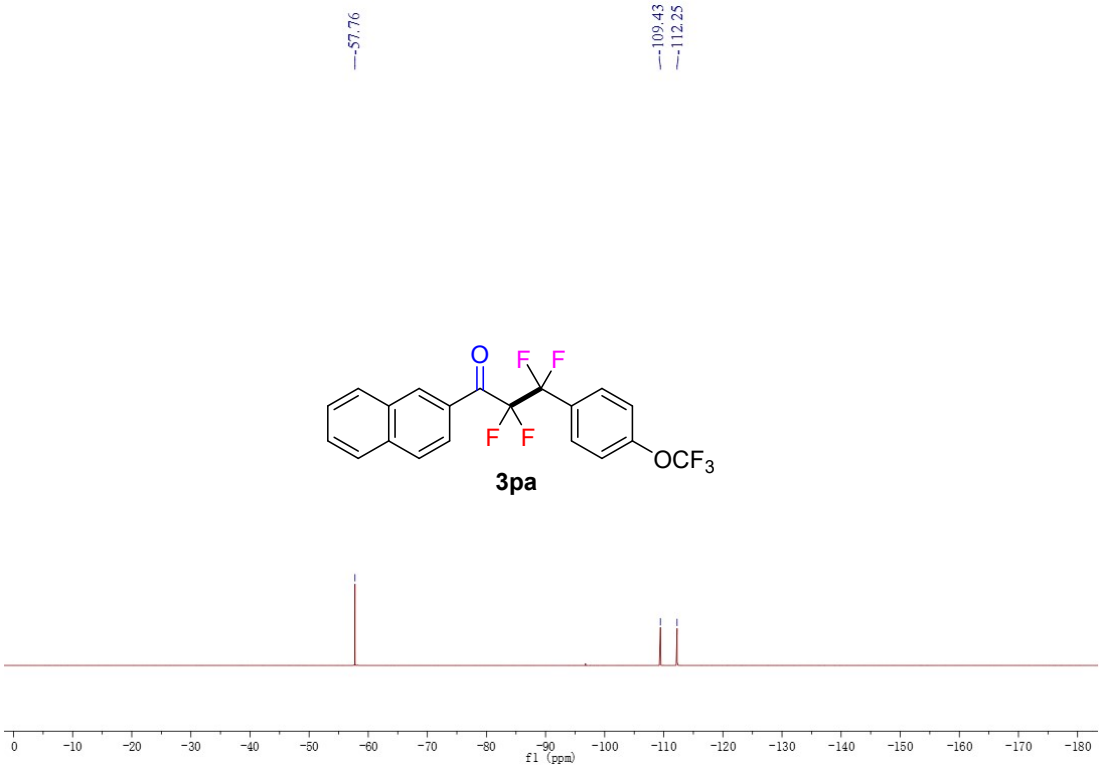

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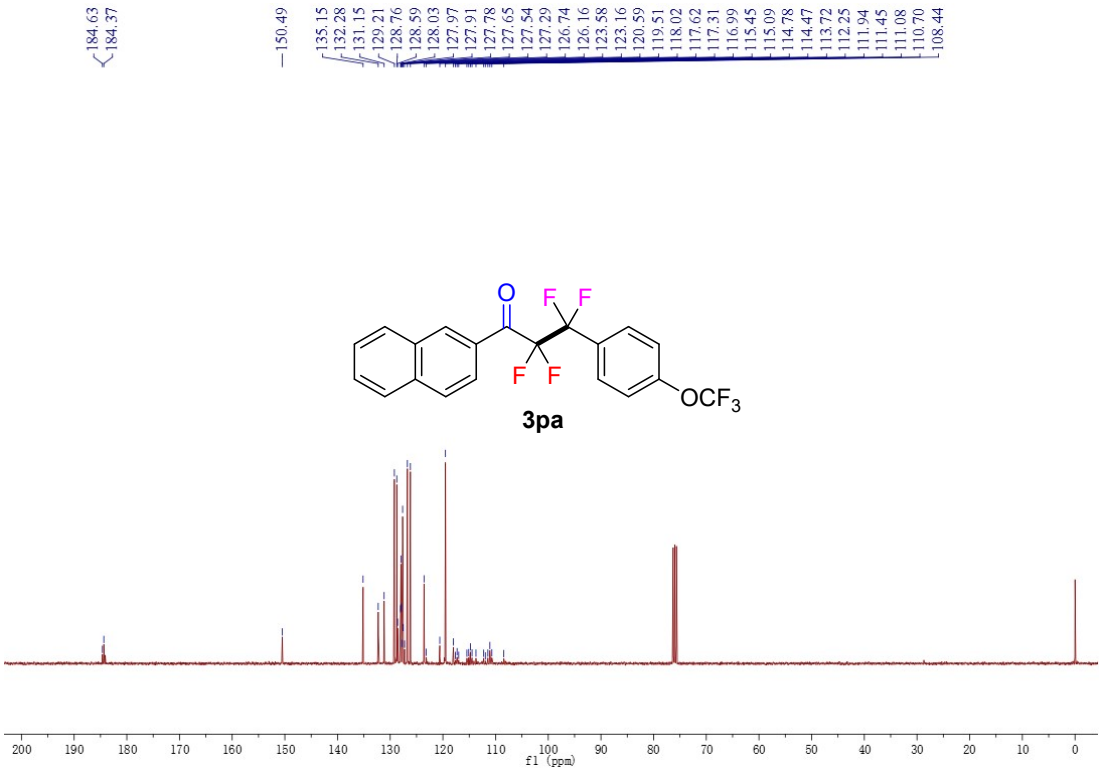

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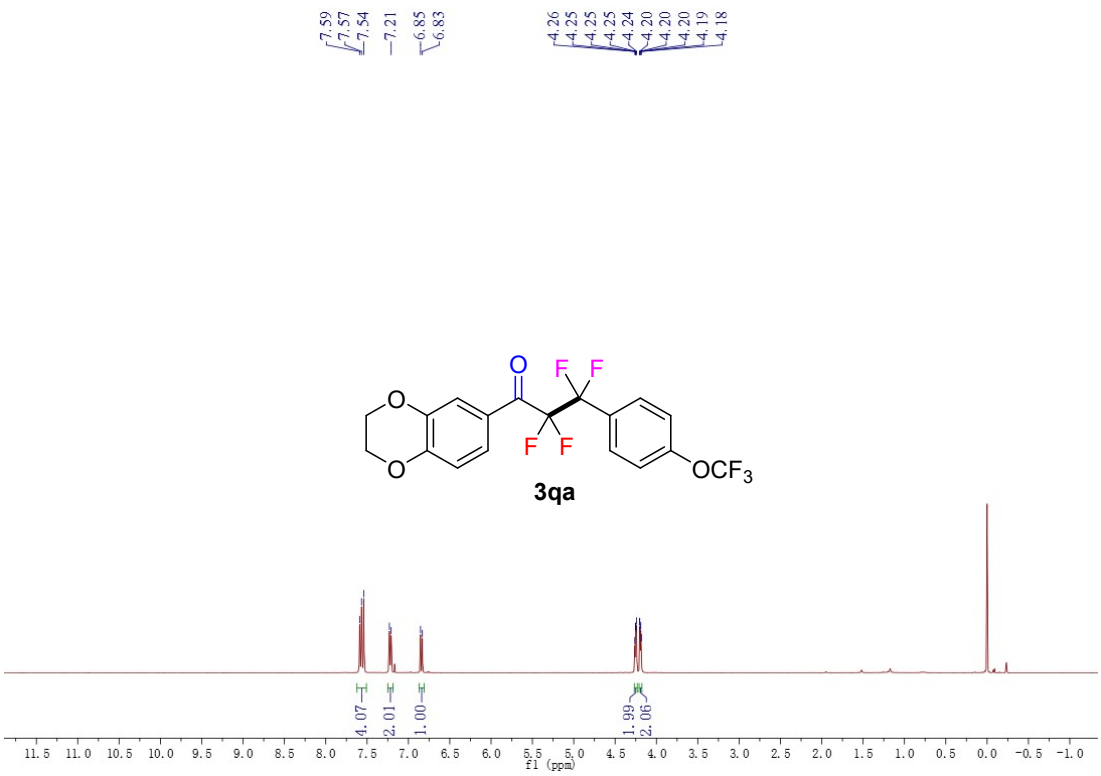

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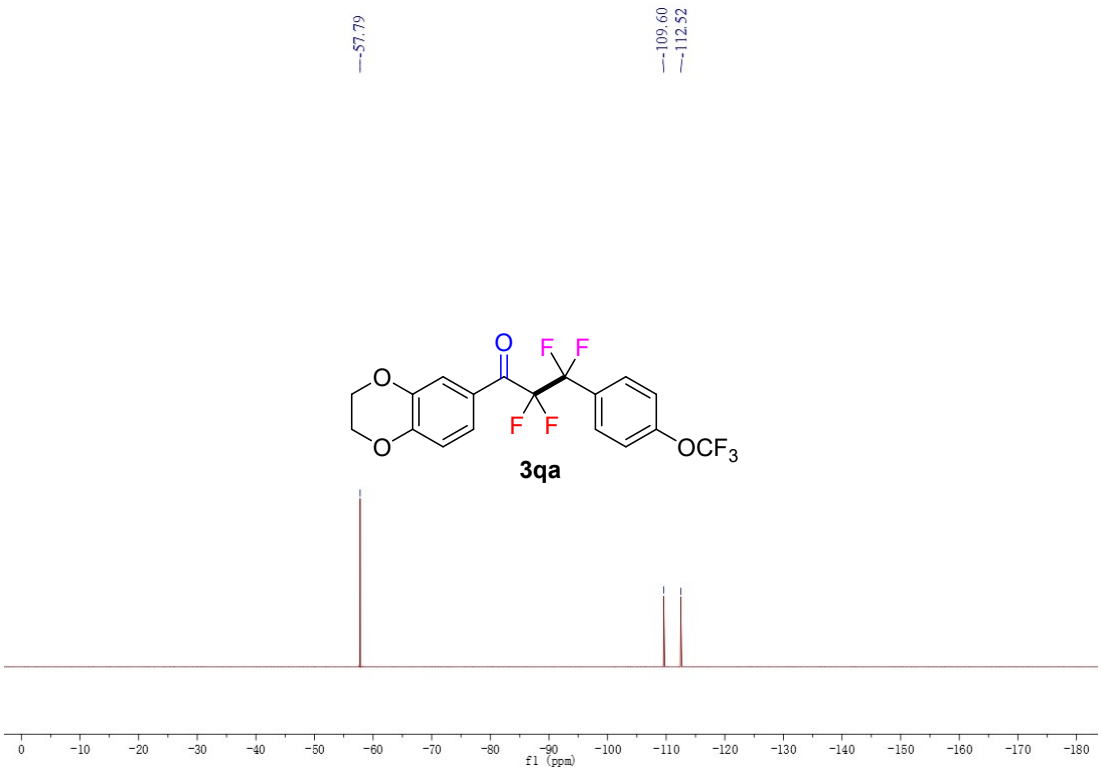

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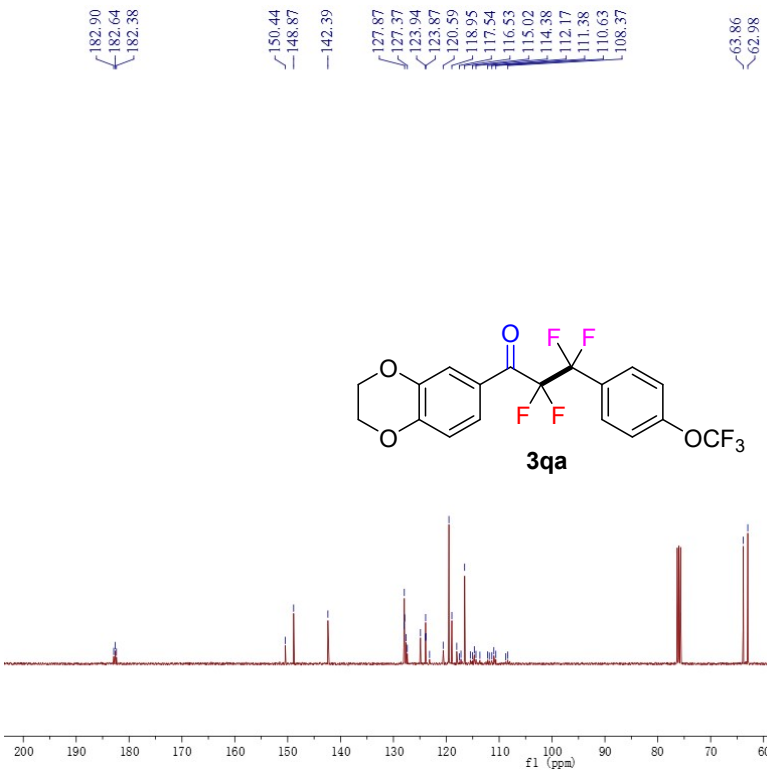

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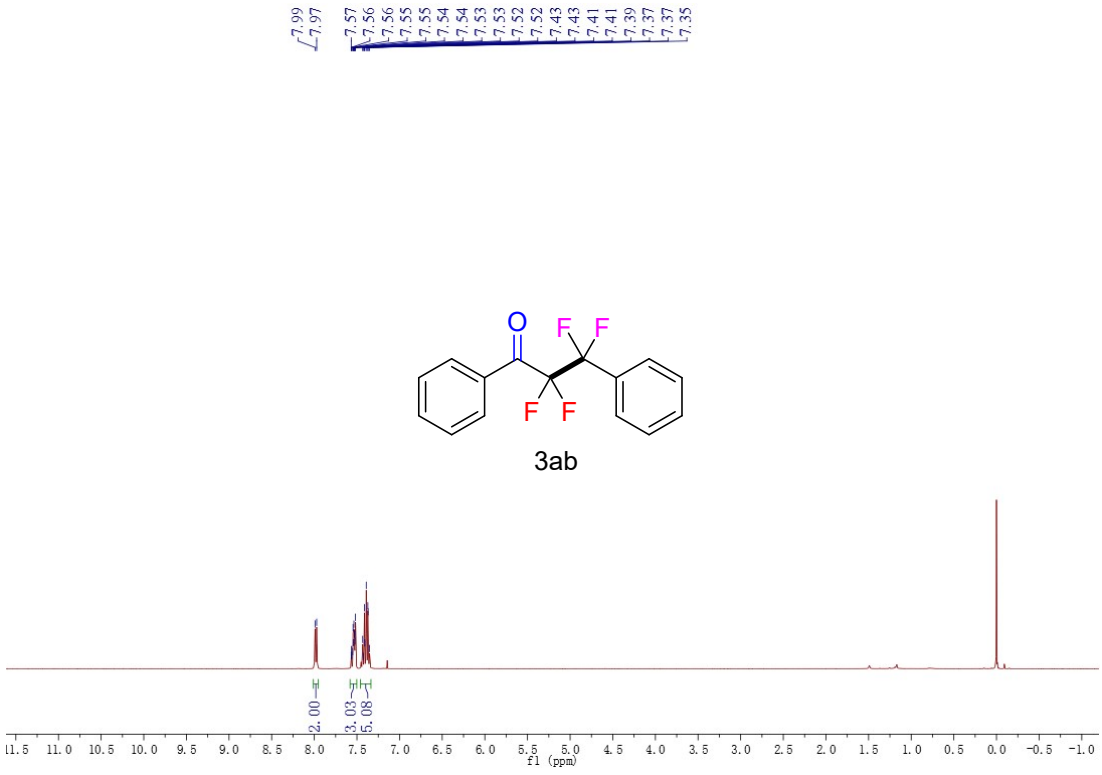

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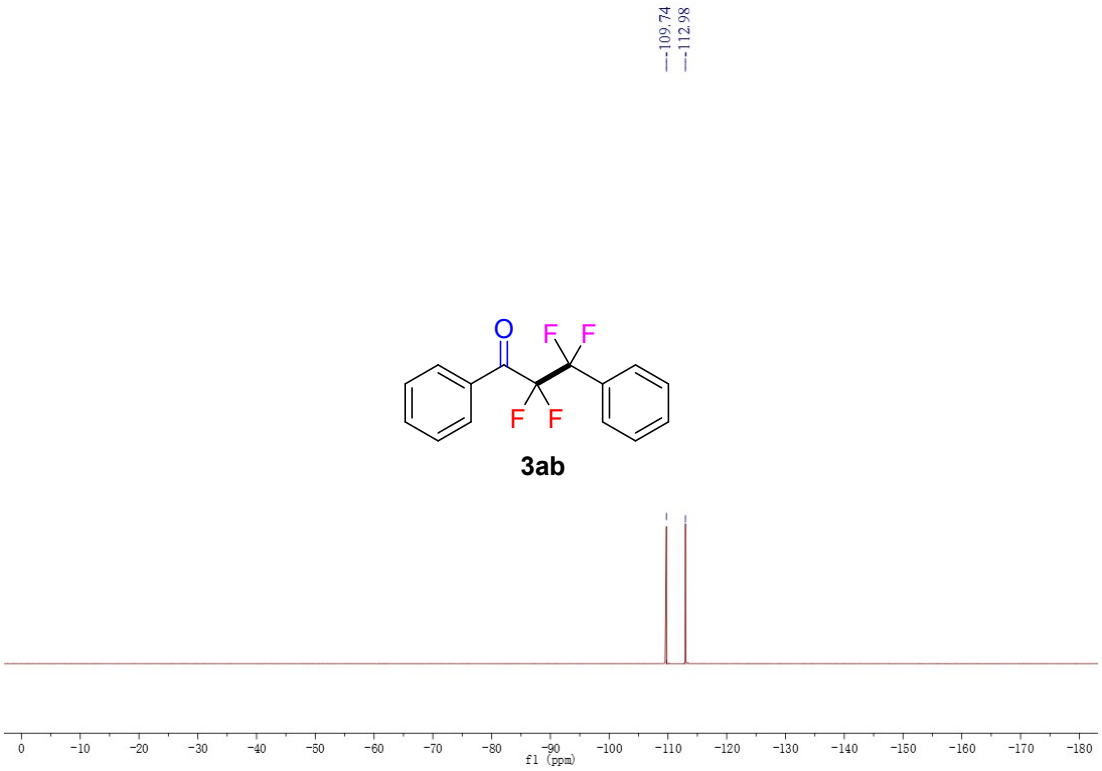

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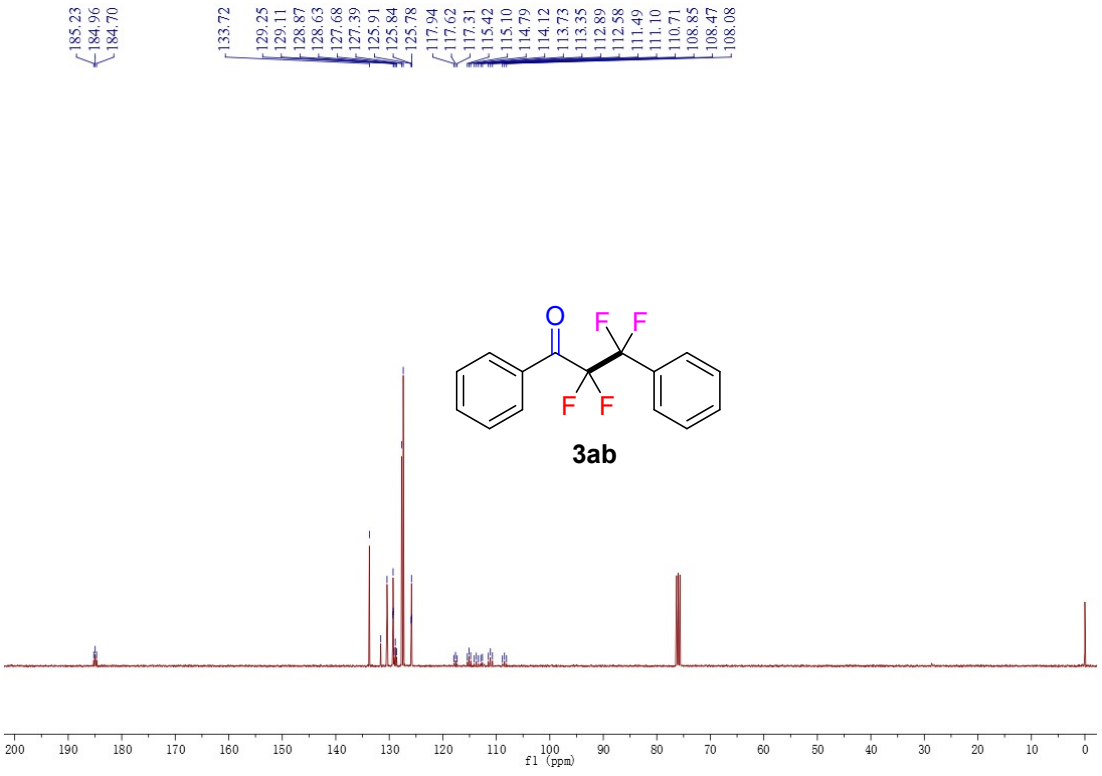

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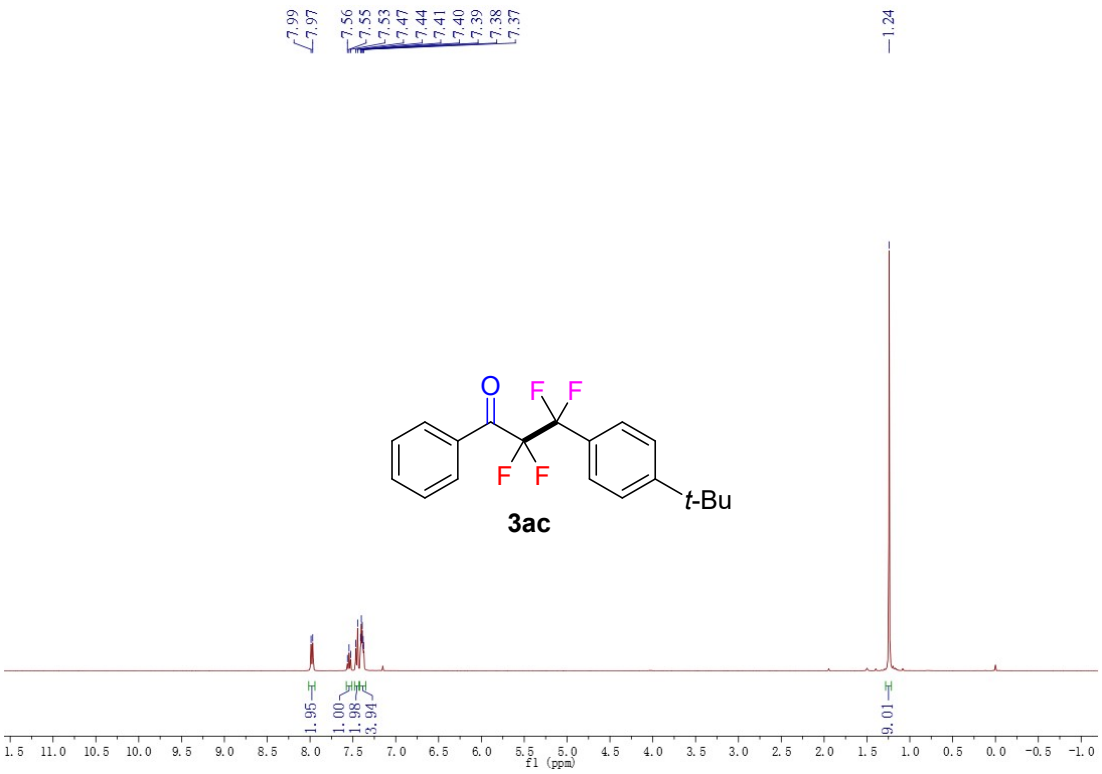

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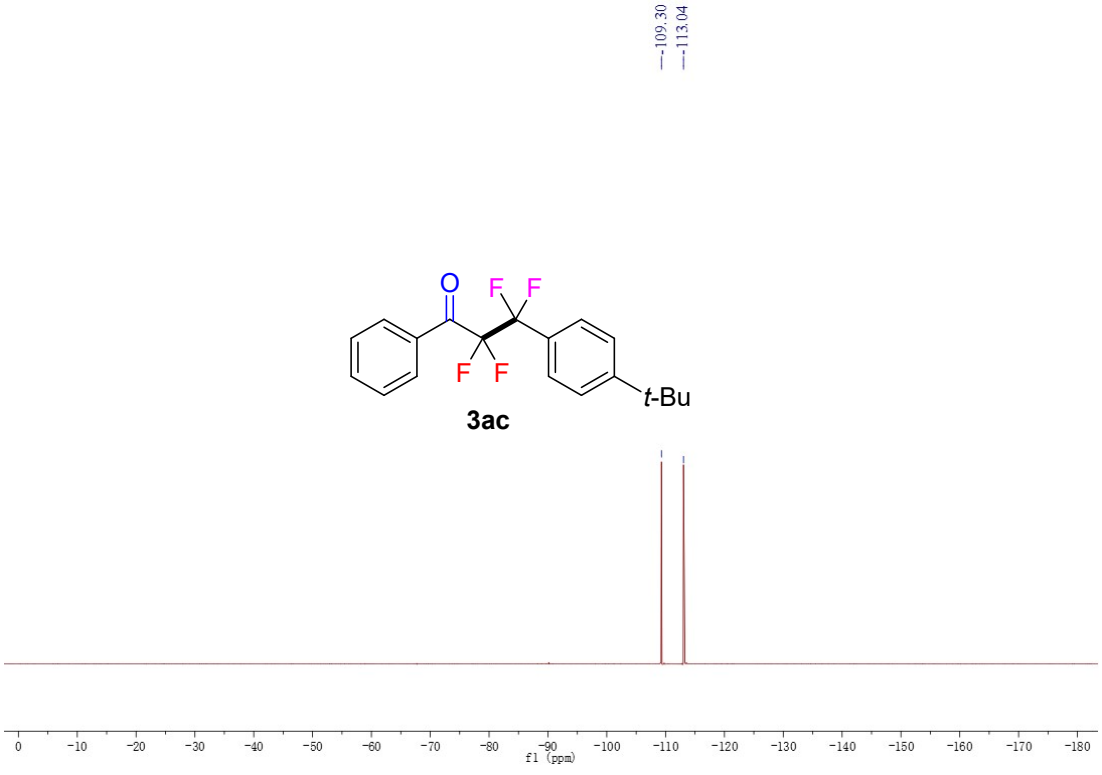

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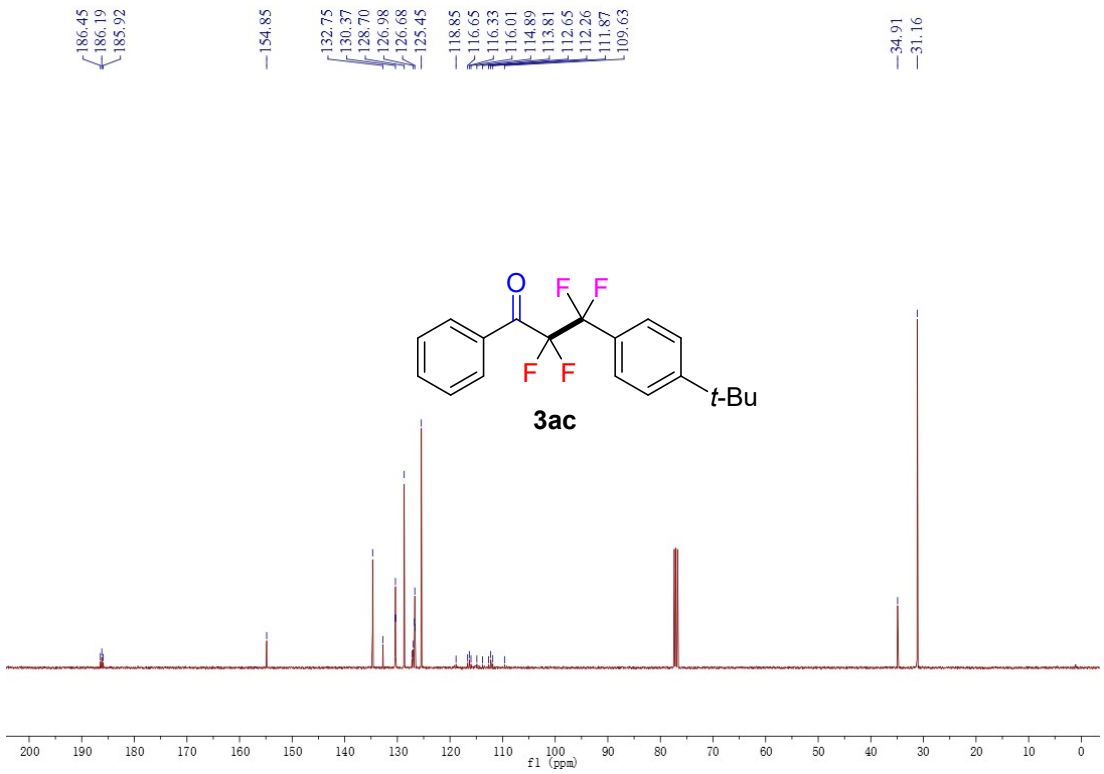

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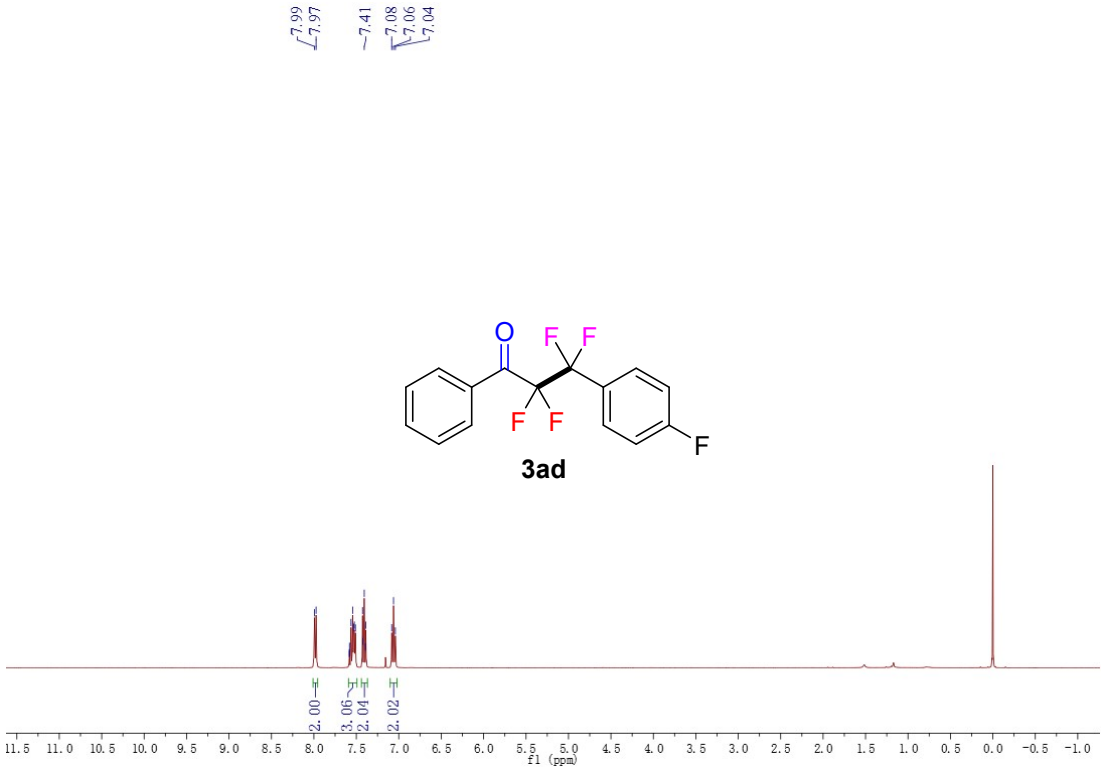

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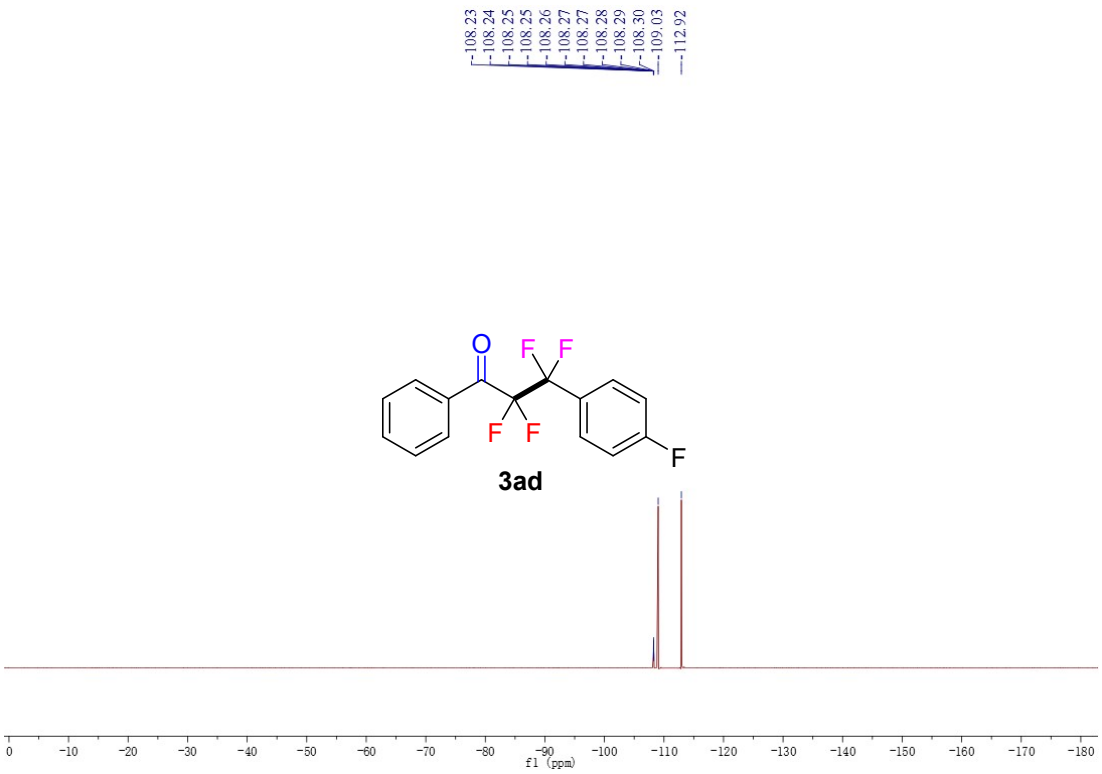

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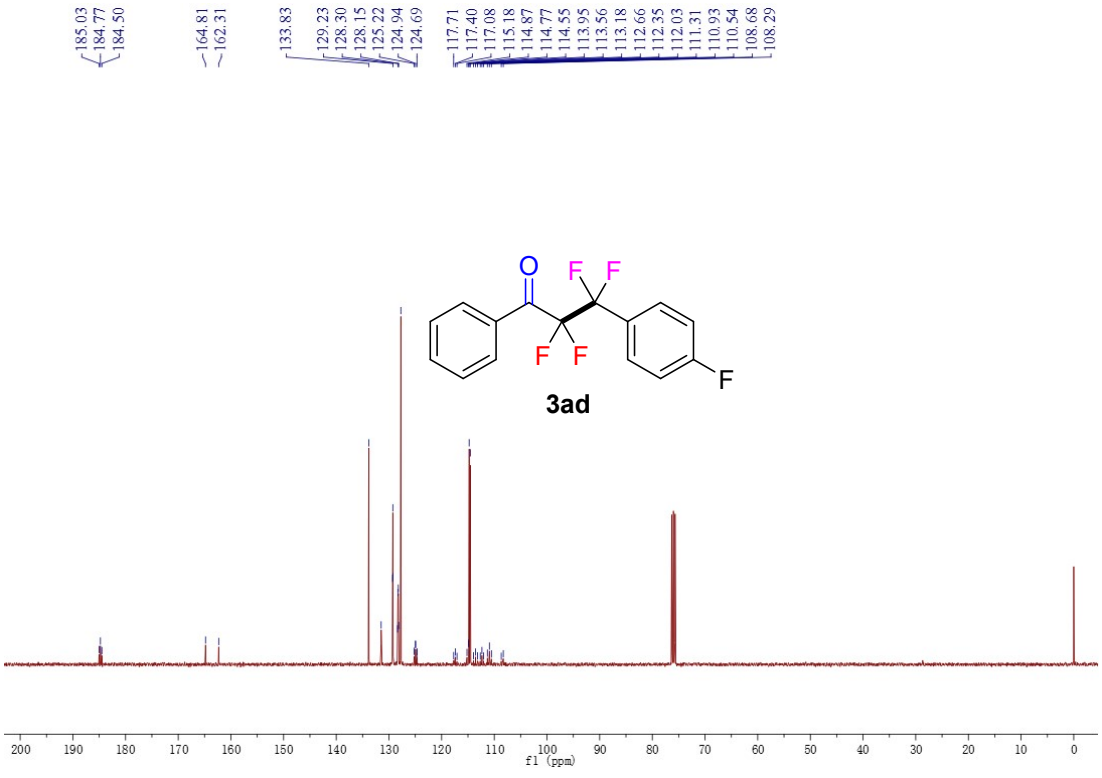

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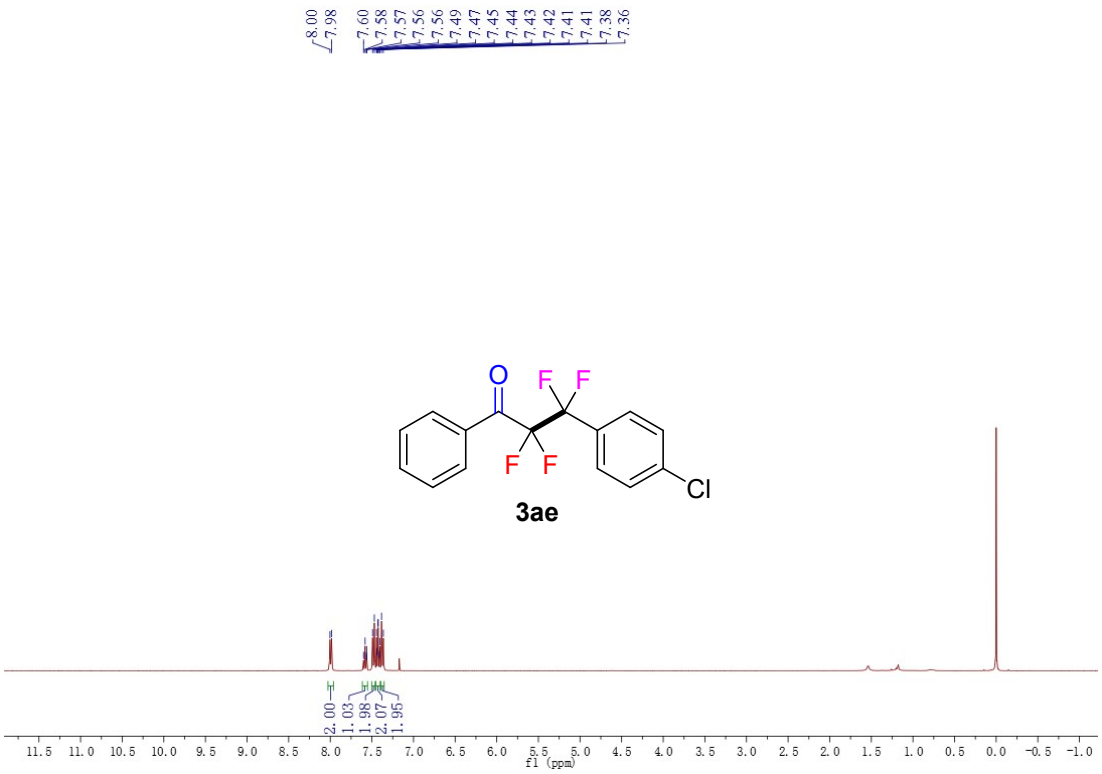

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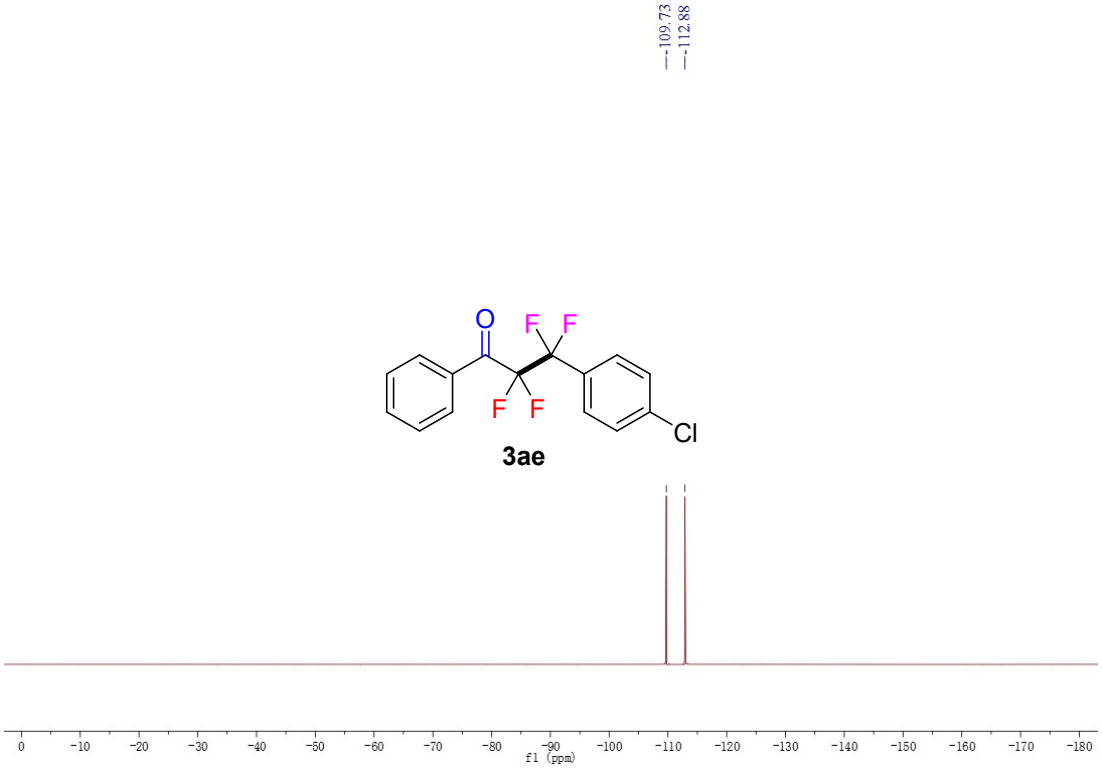

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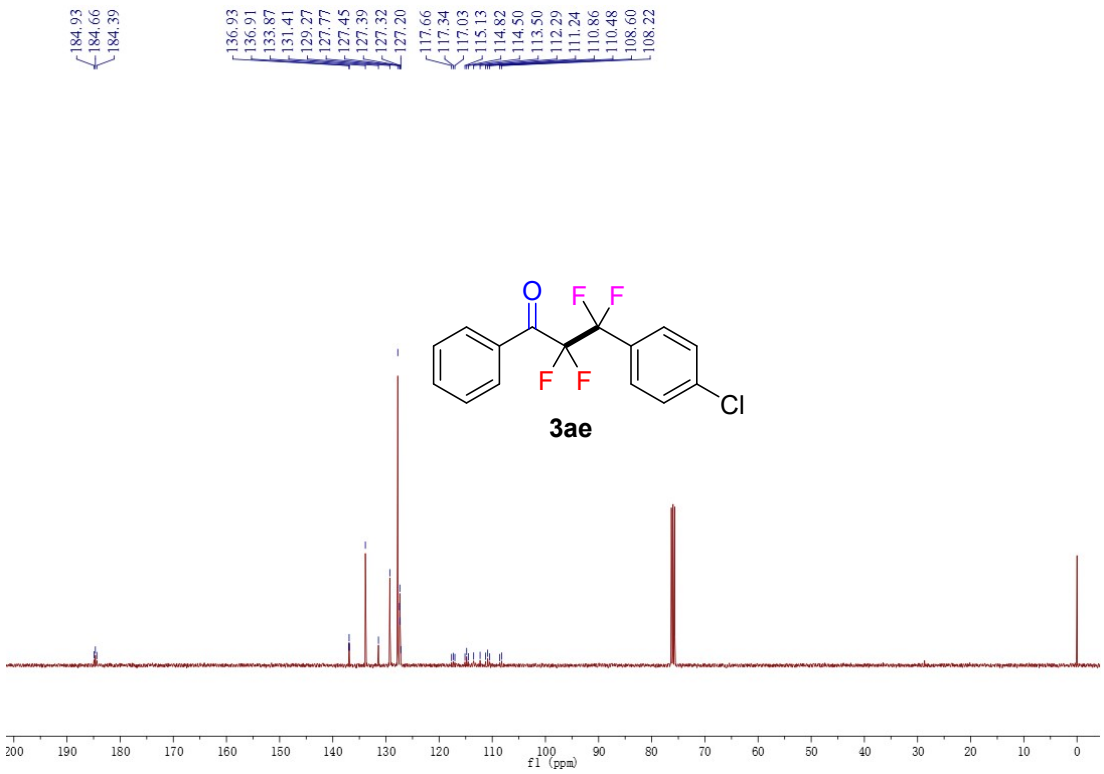

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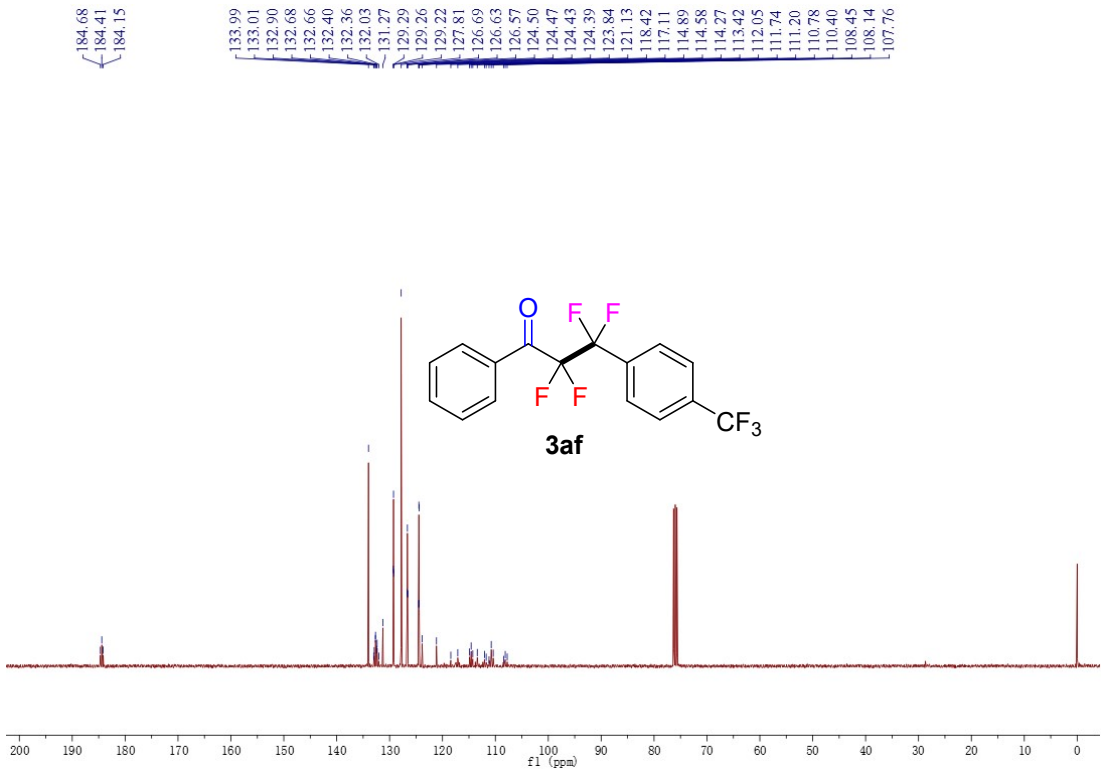

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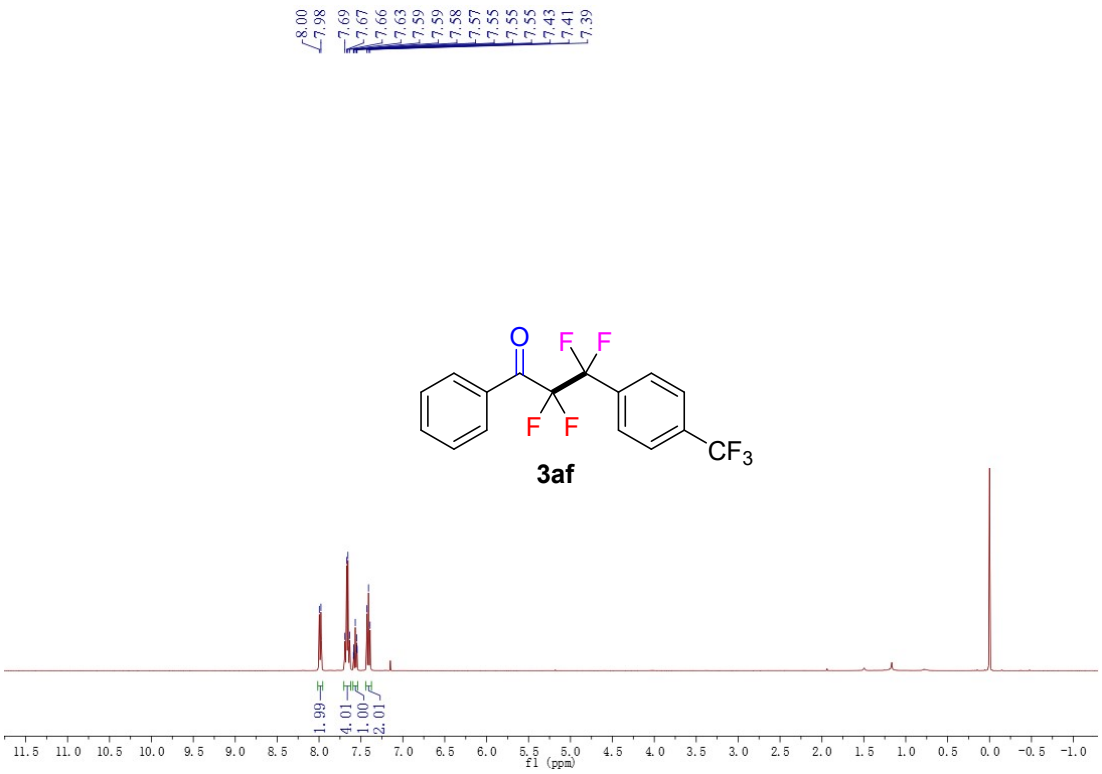

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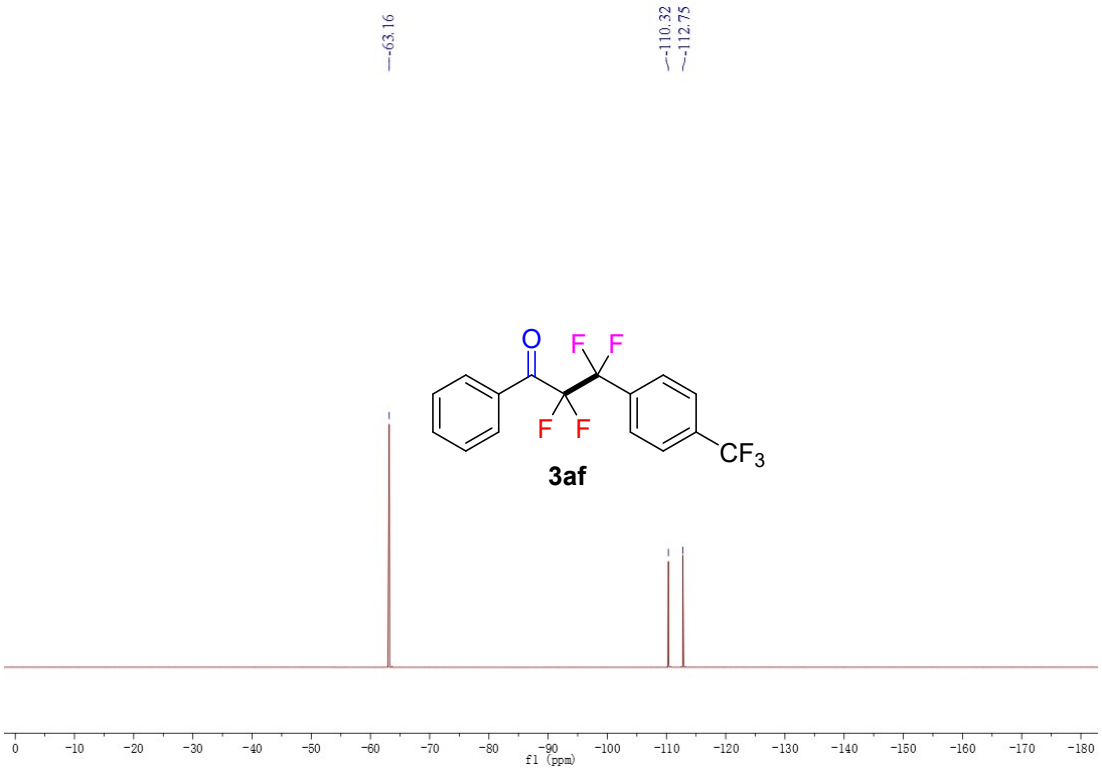

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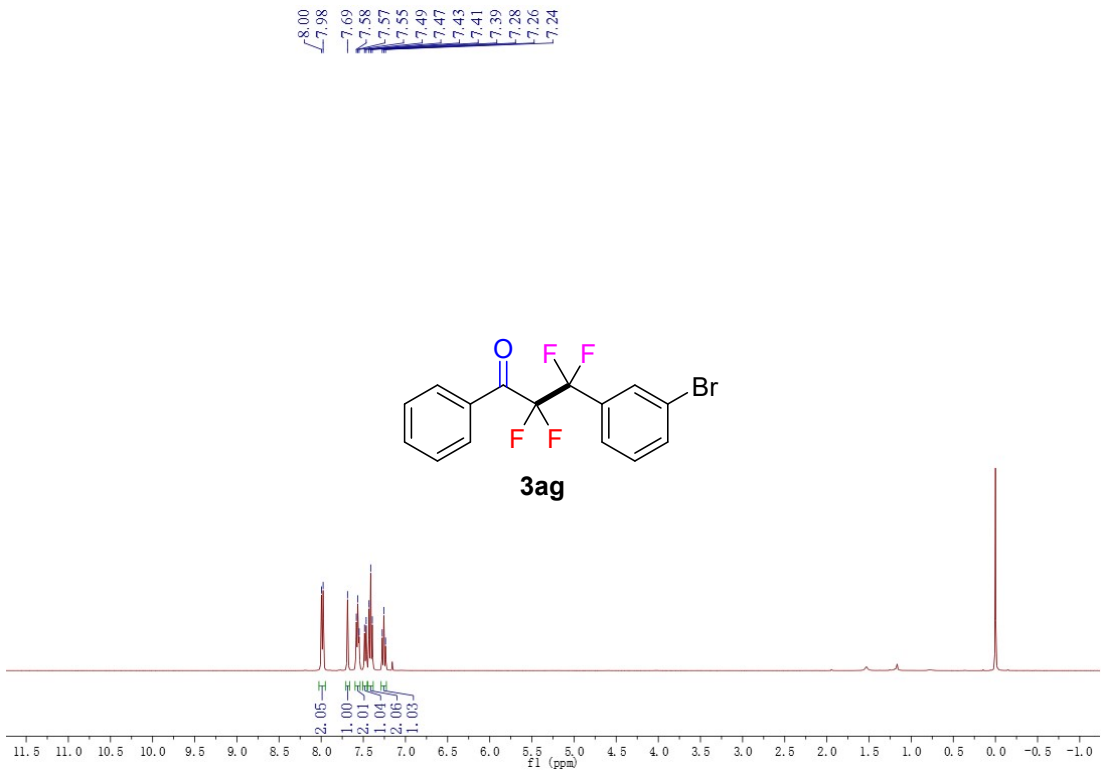

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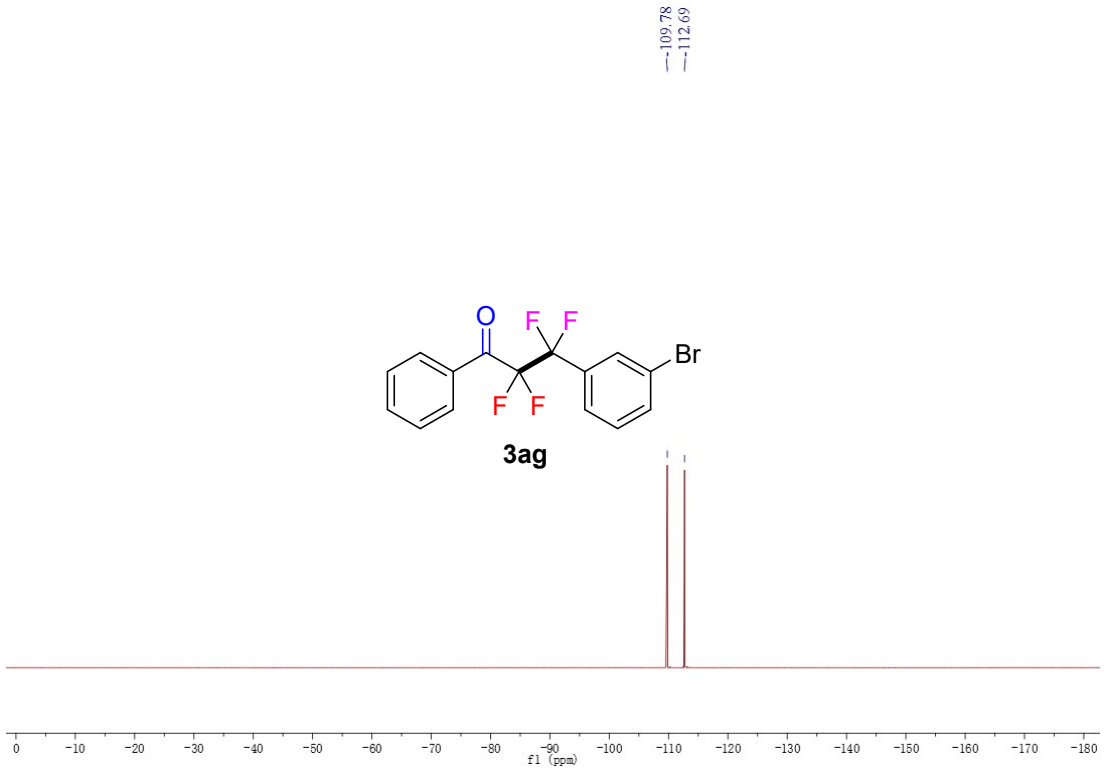

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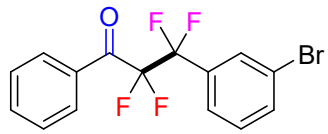

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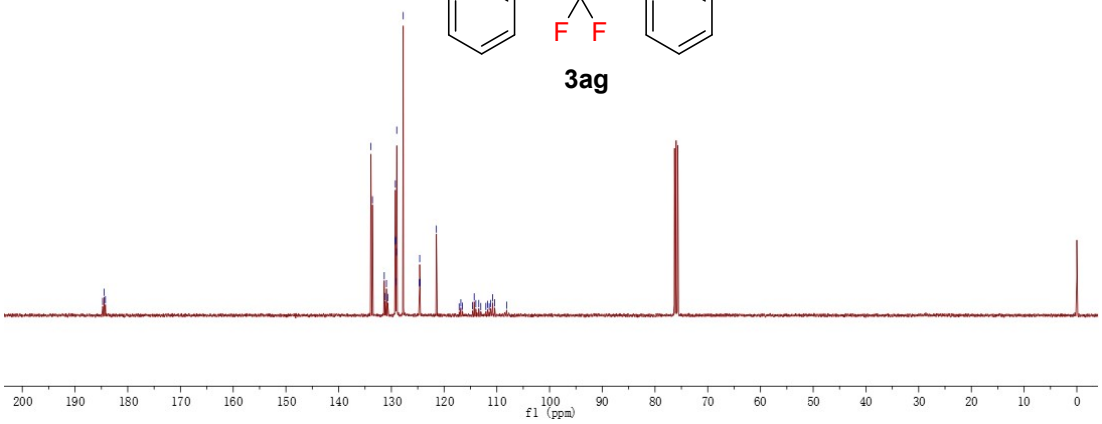

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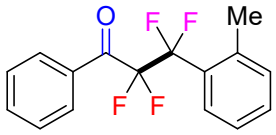

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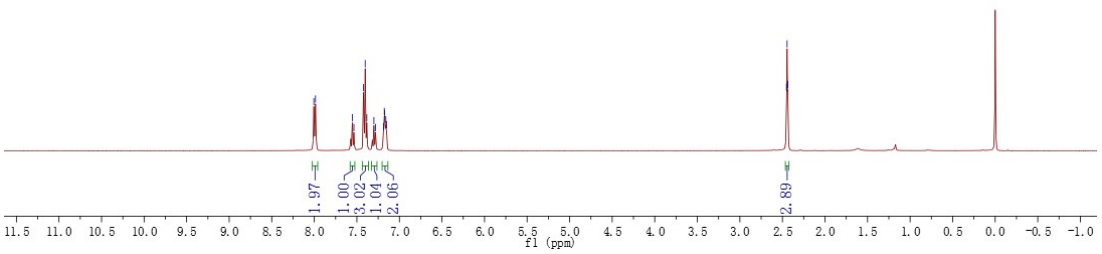

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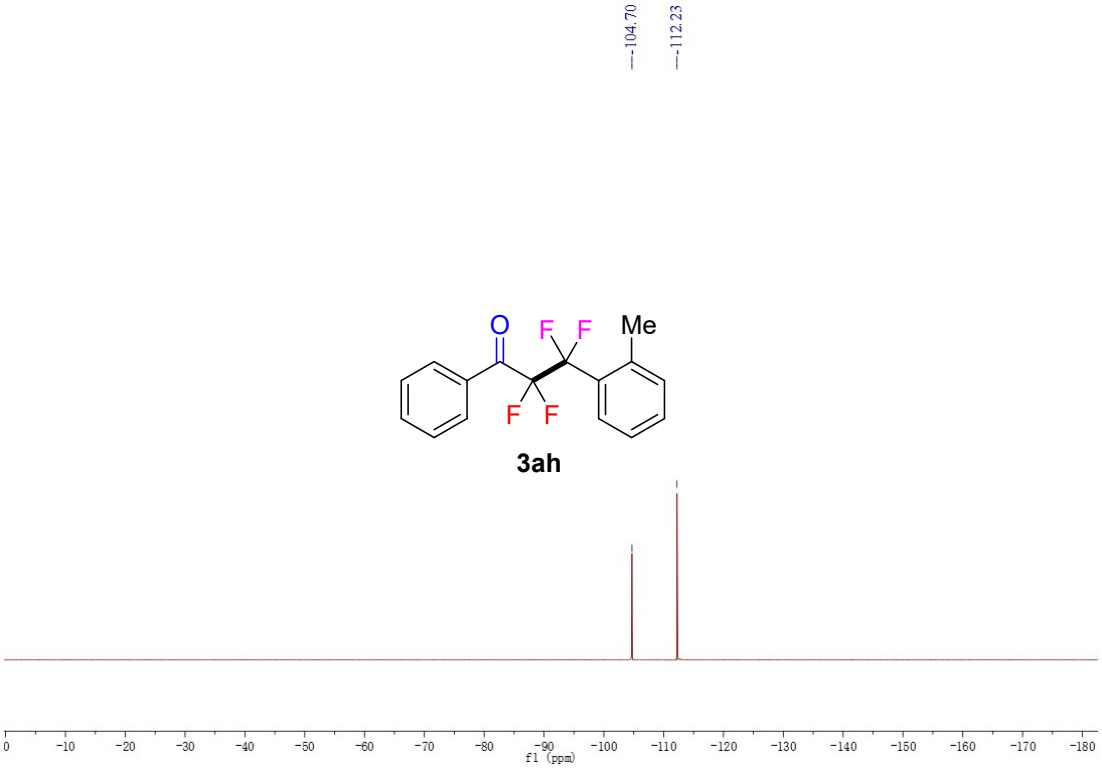

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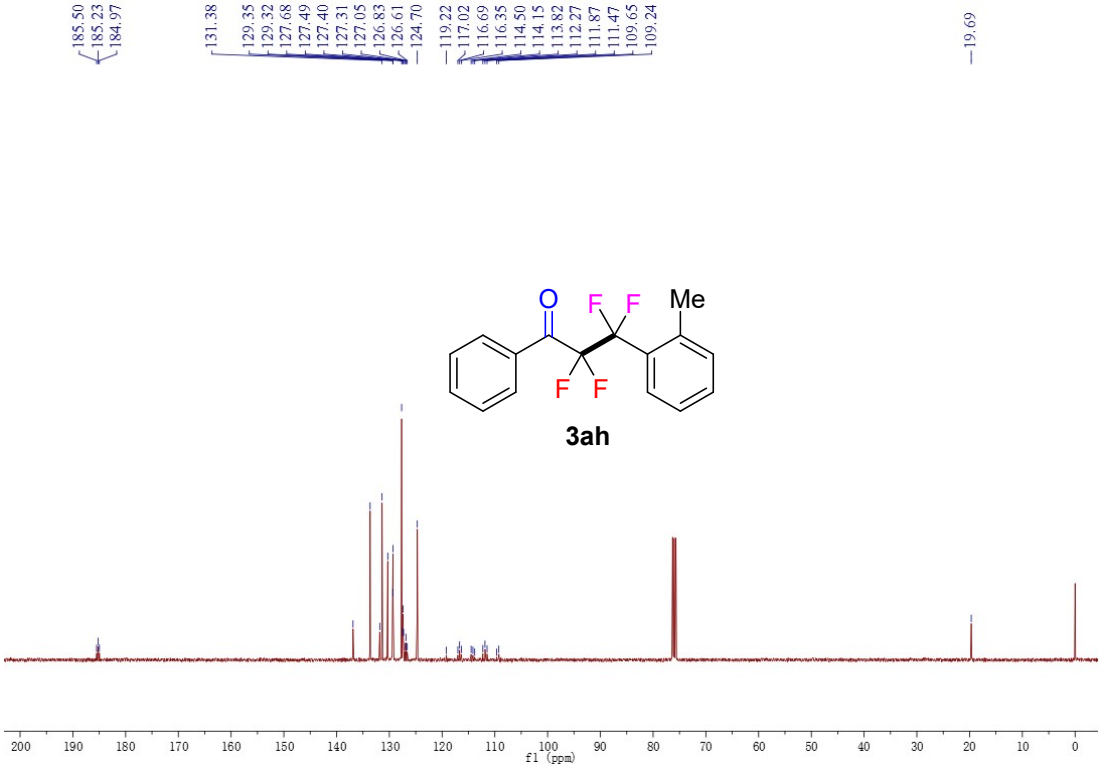

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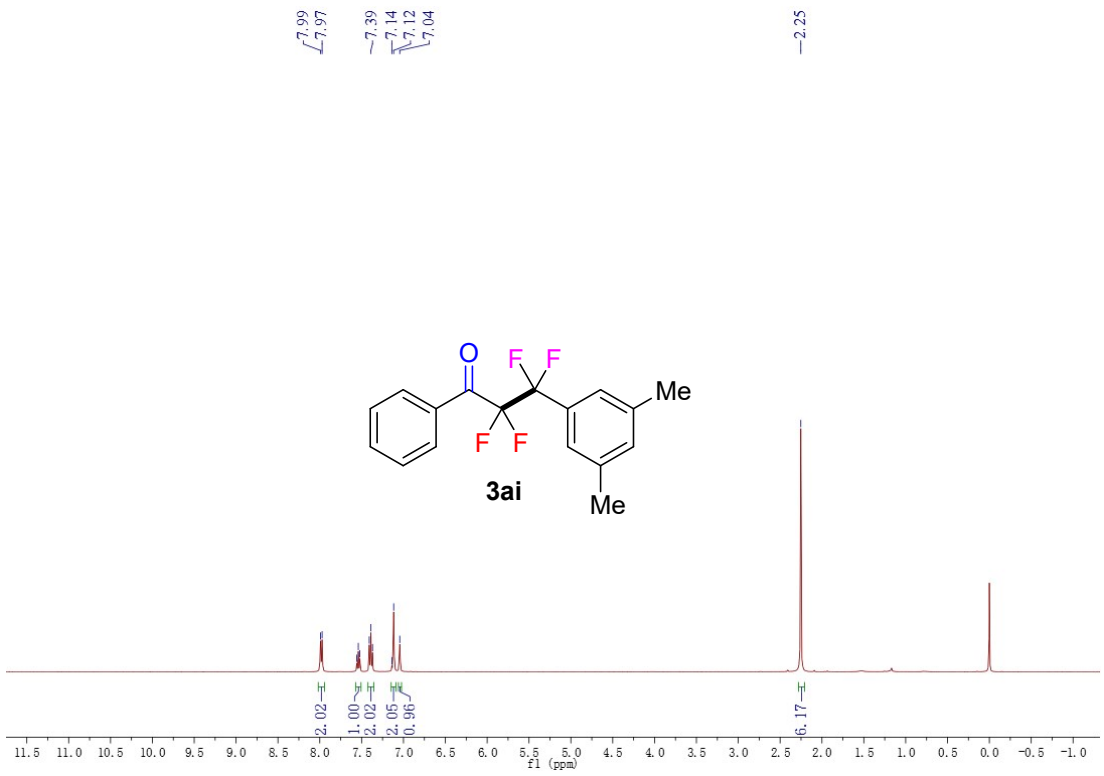

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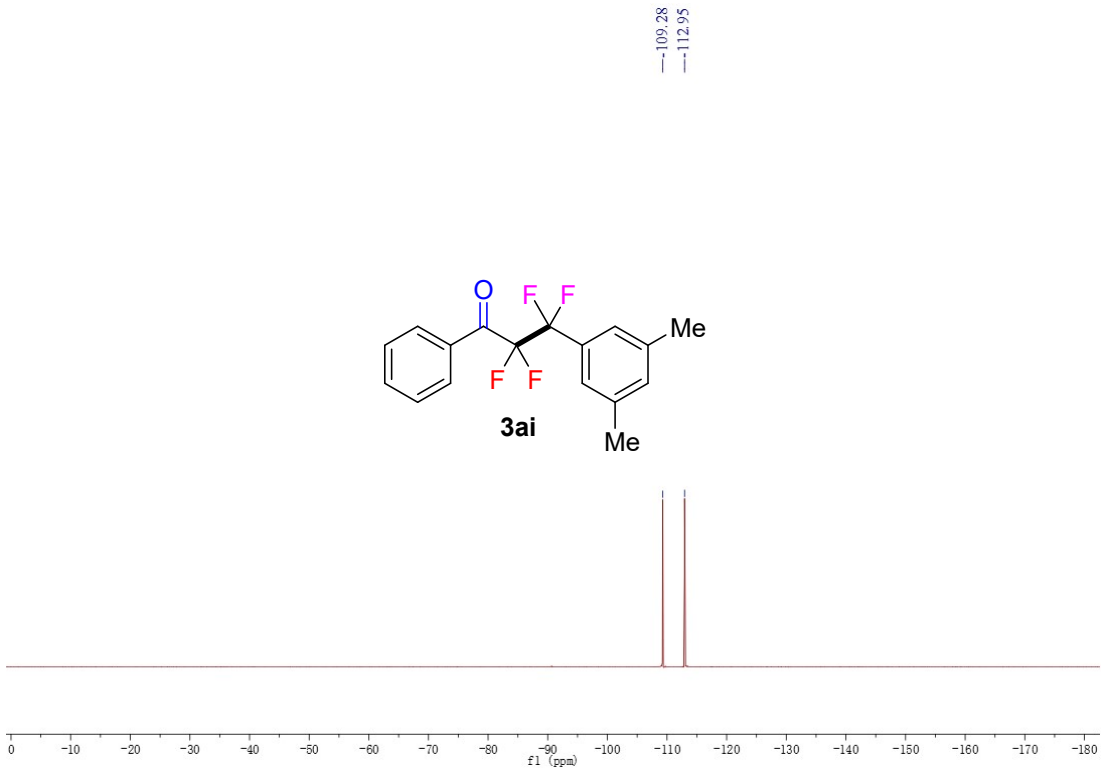

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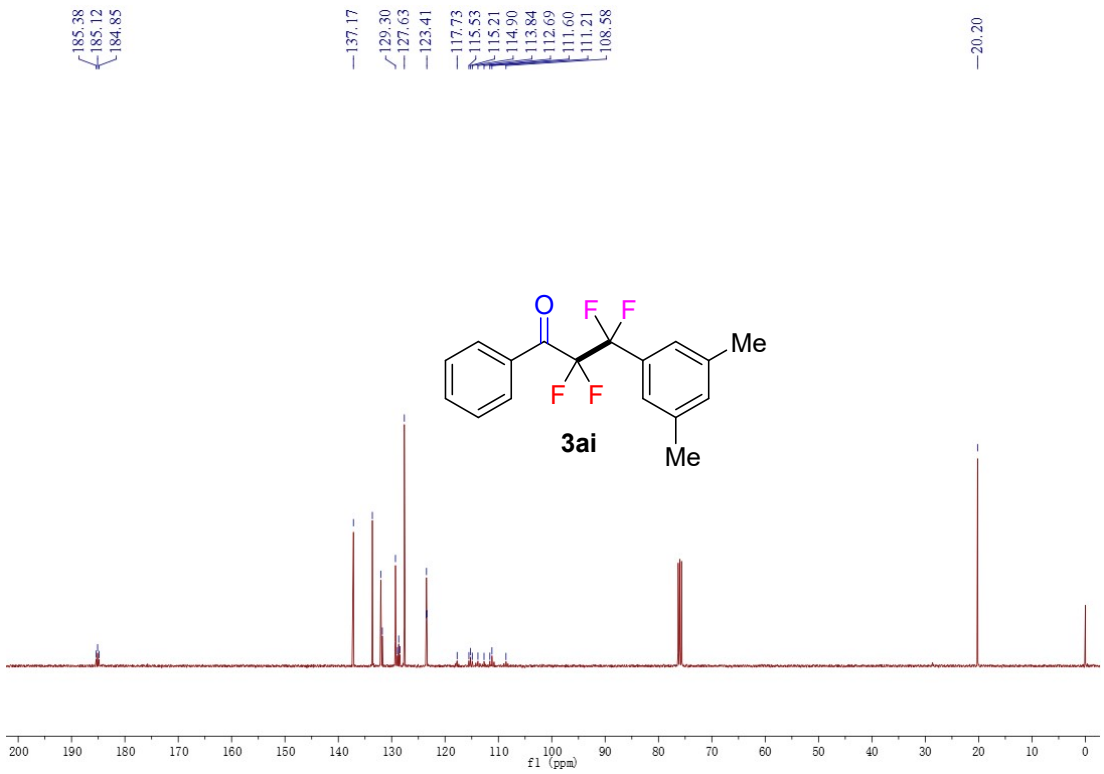

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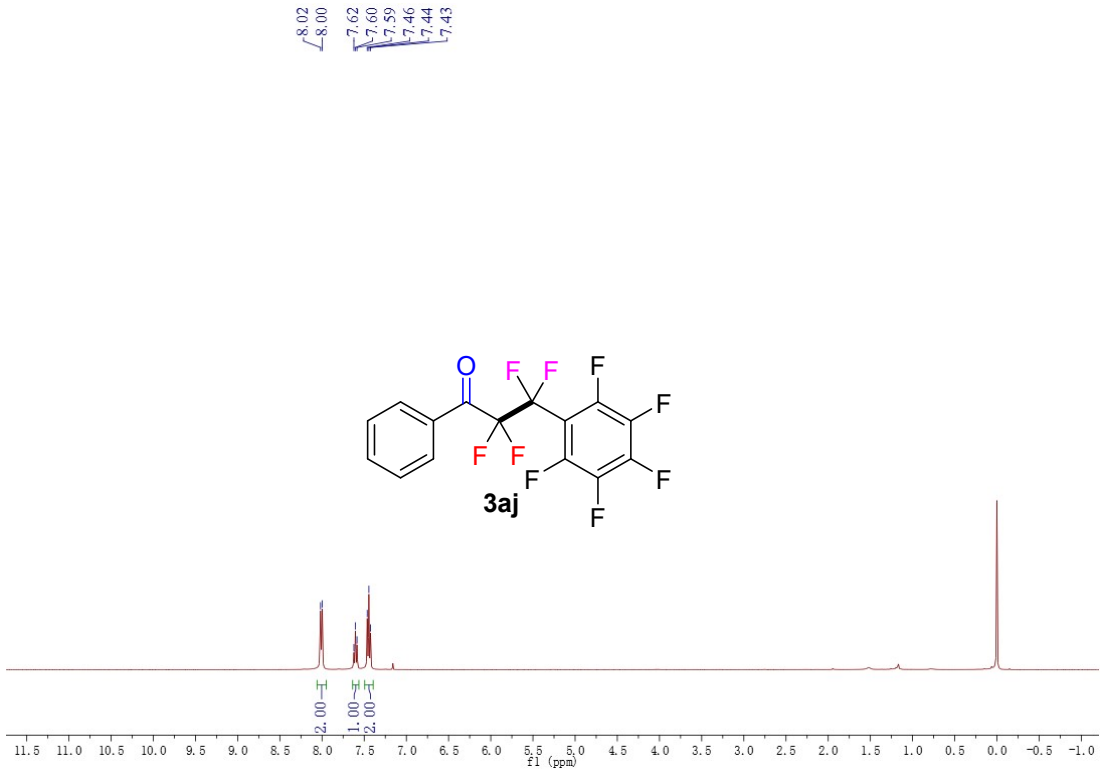
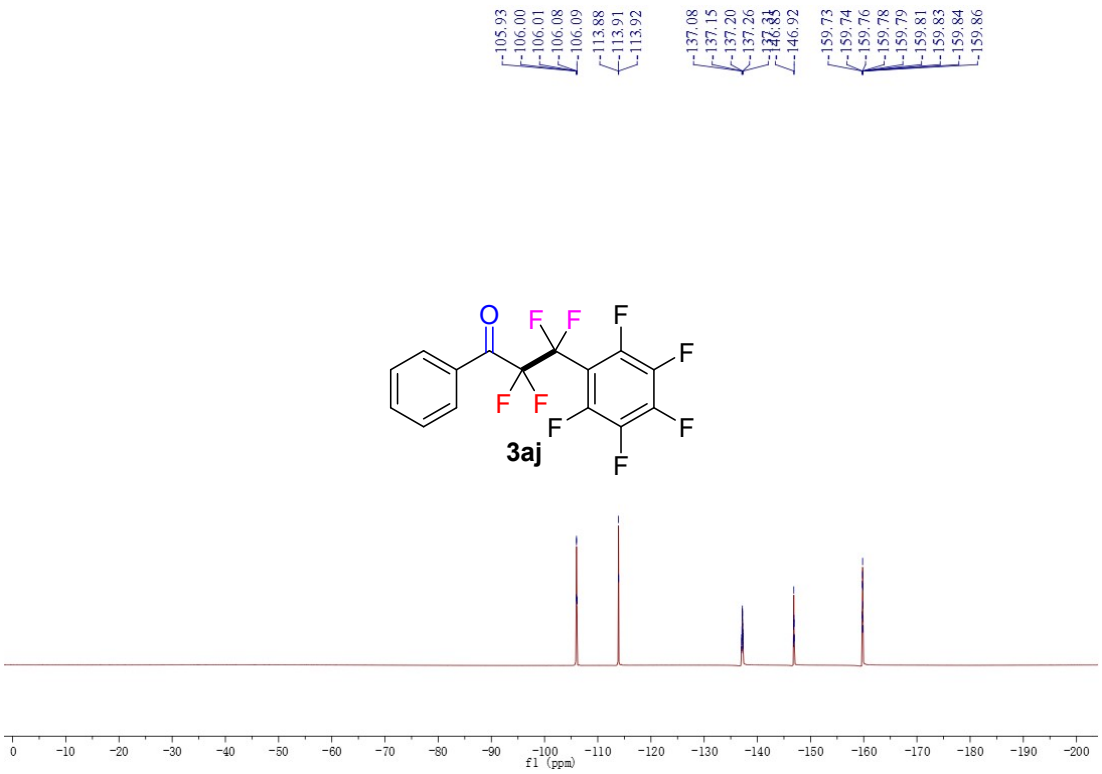


[19]F NMR (377 MHz, CDCl3)



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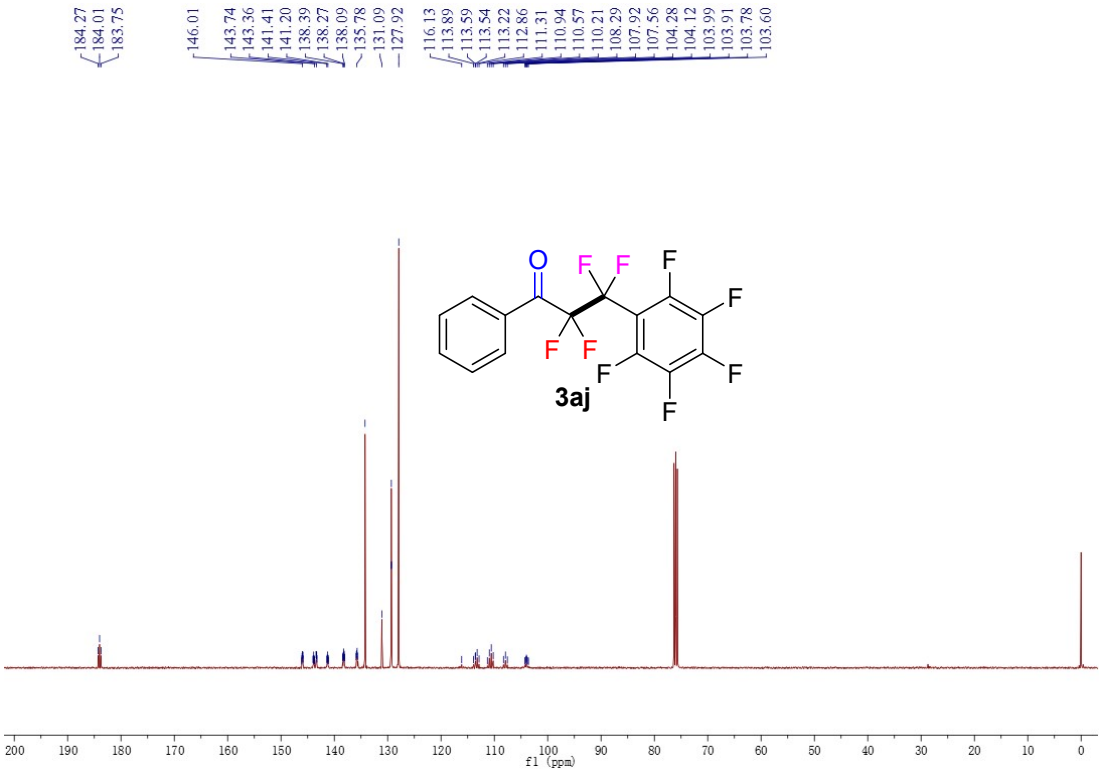

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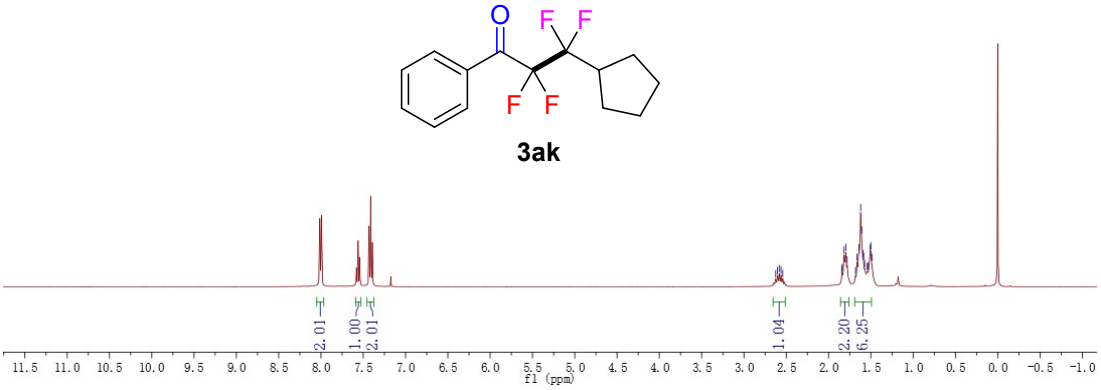

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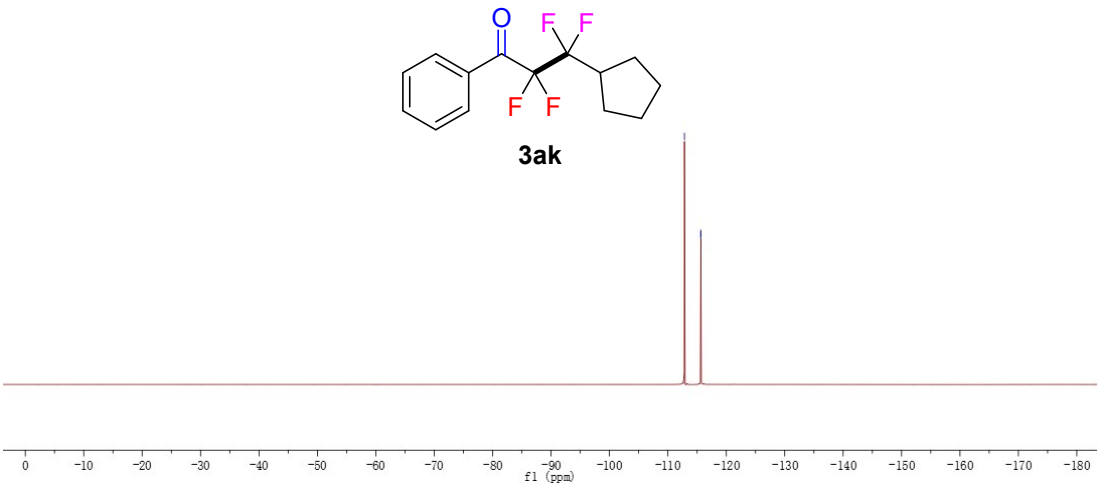

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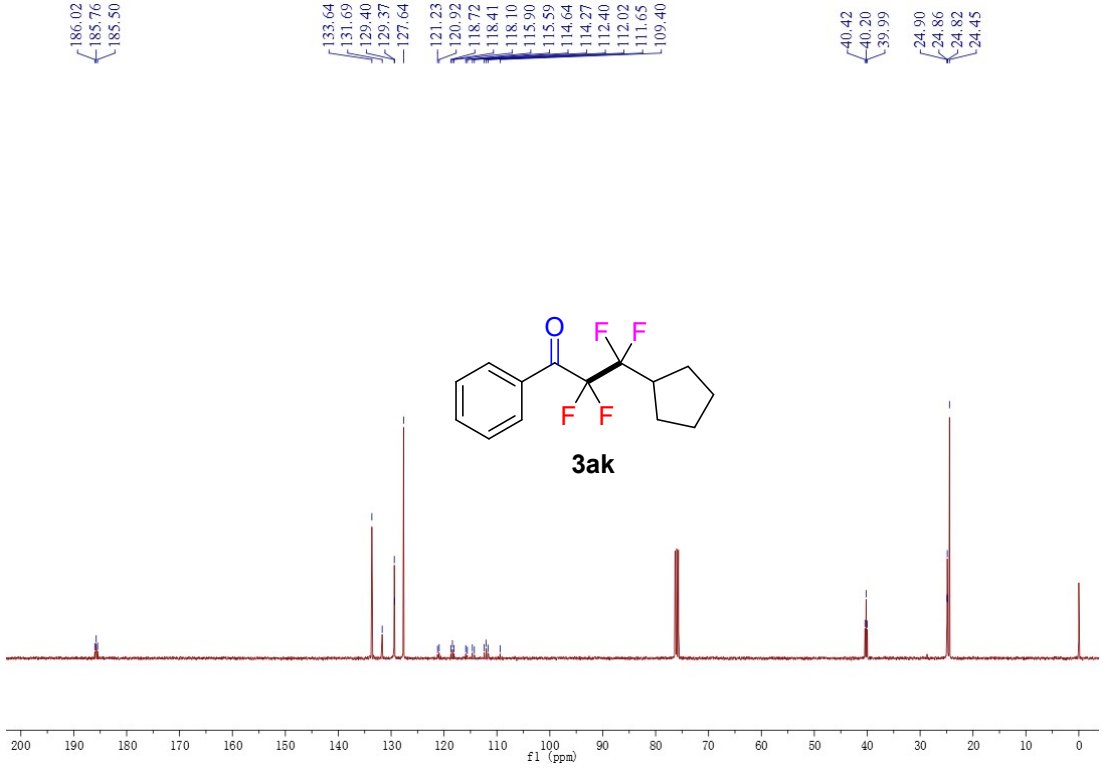

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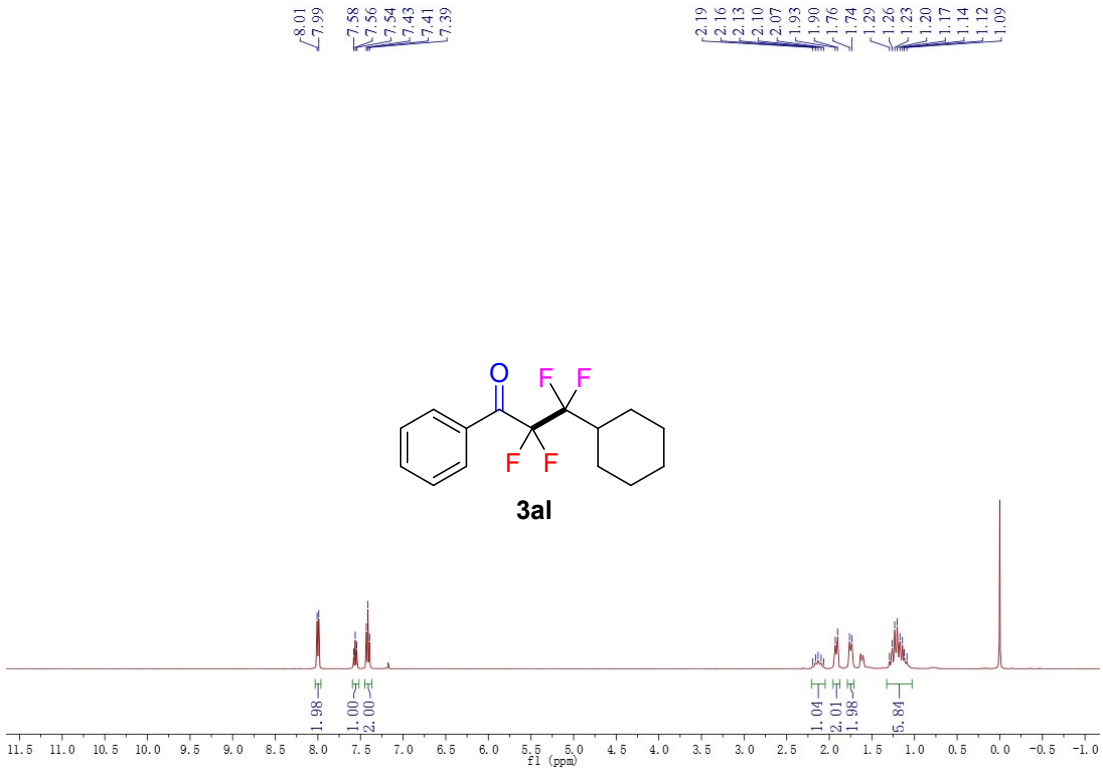

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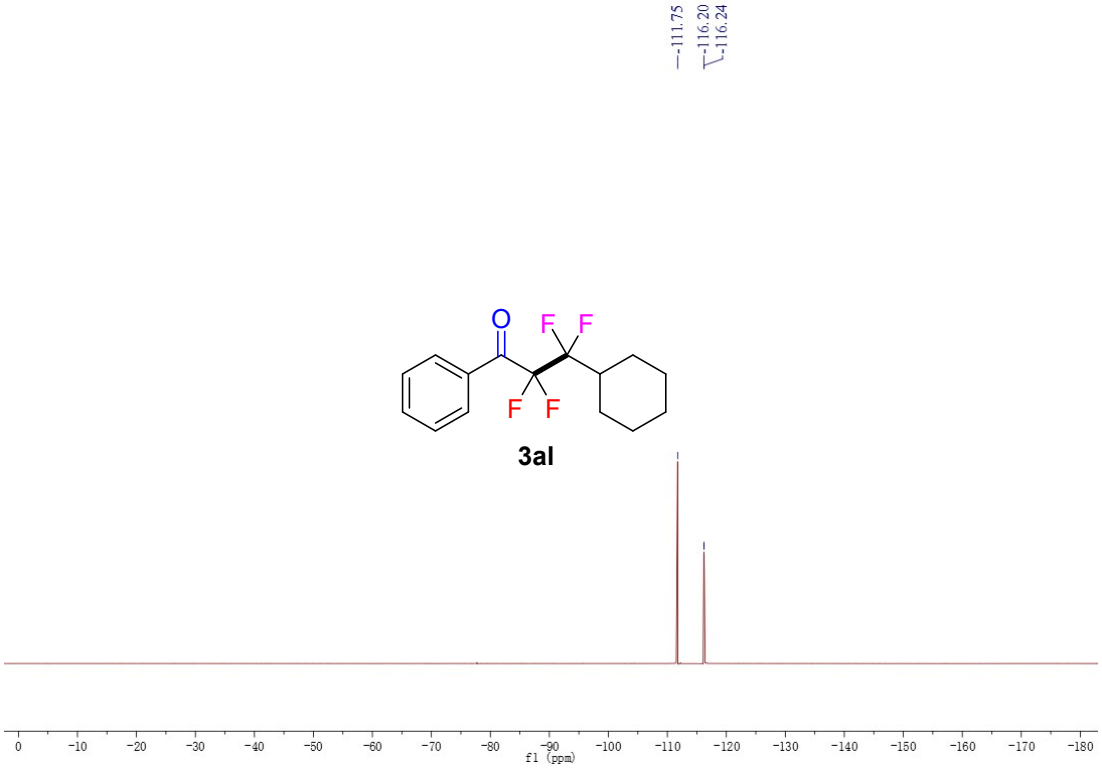

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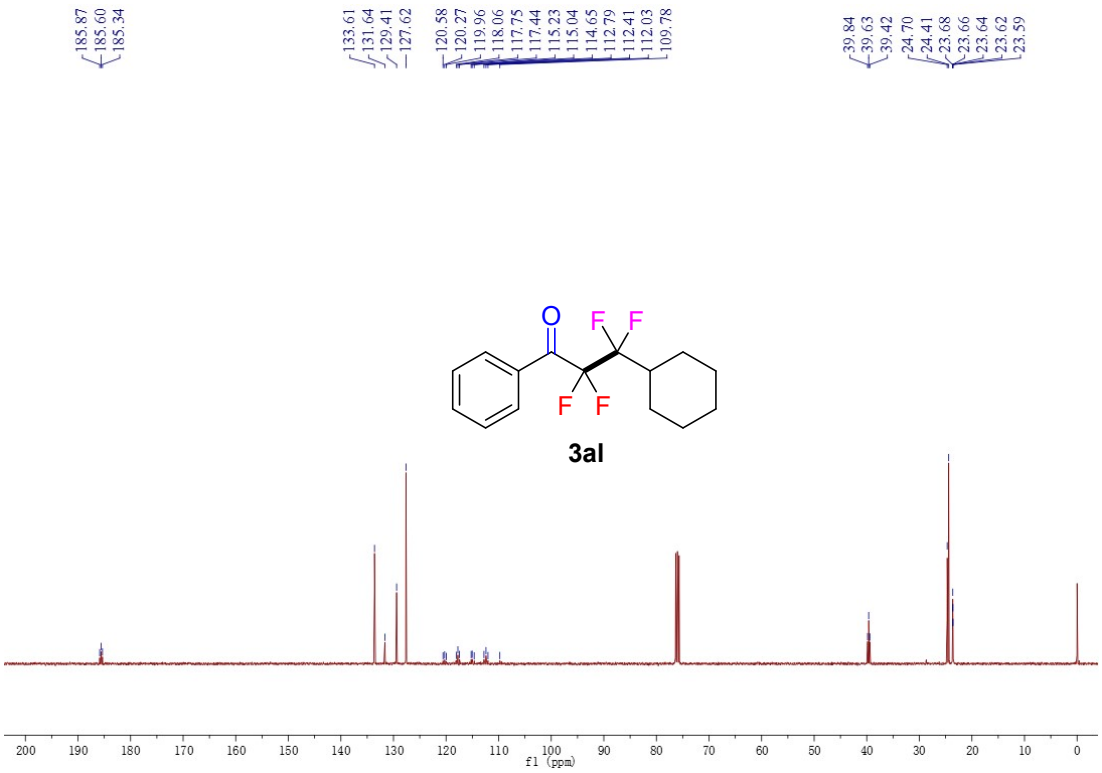

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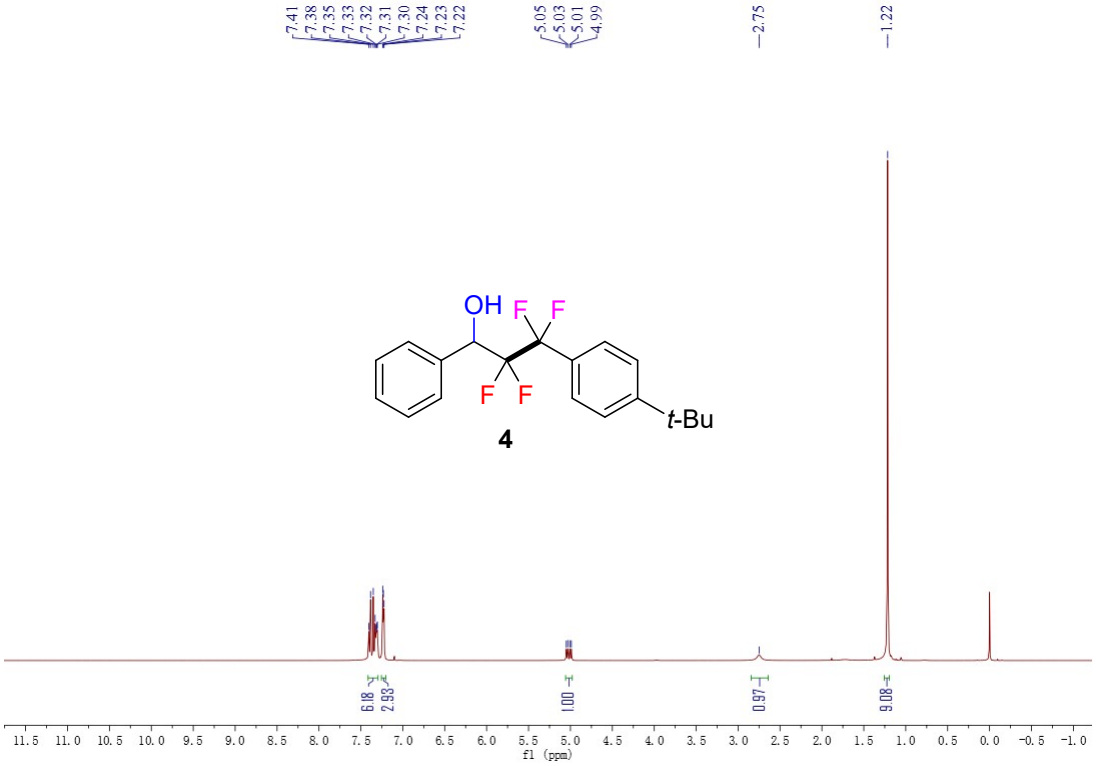

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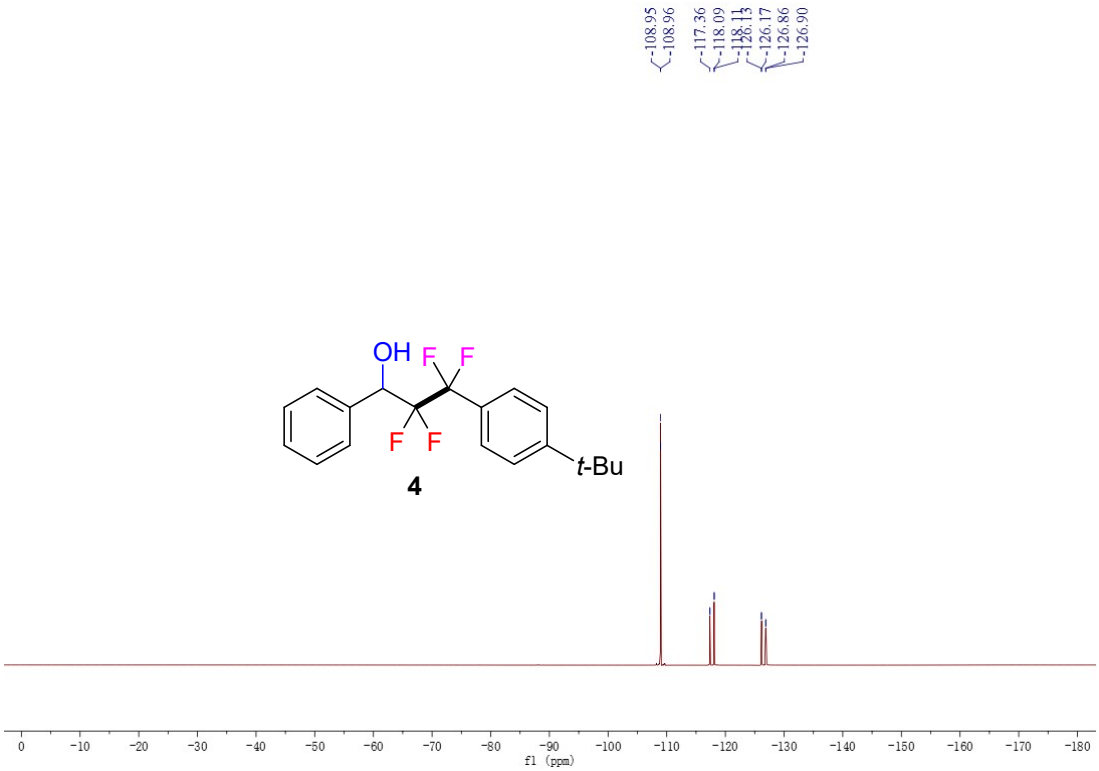

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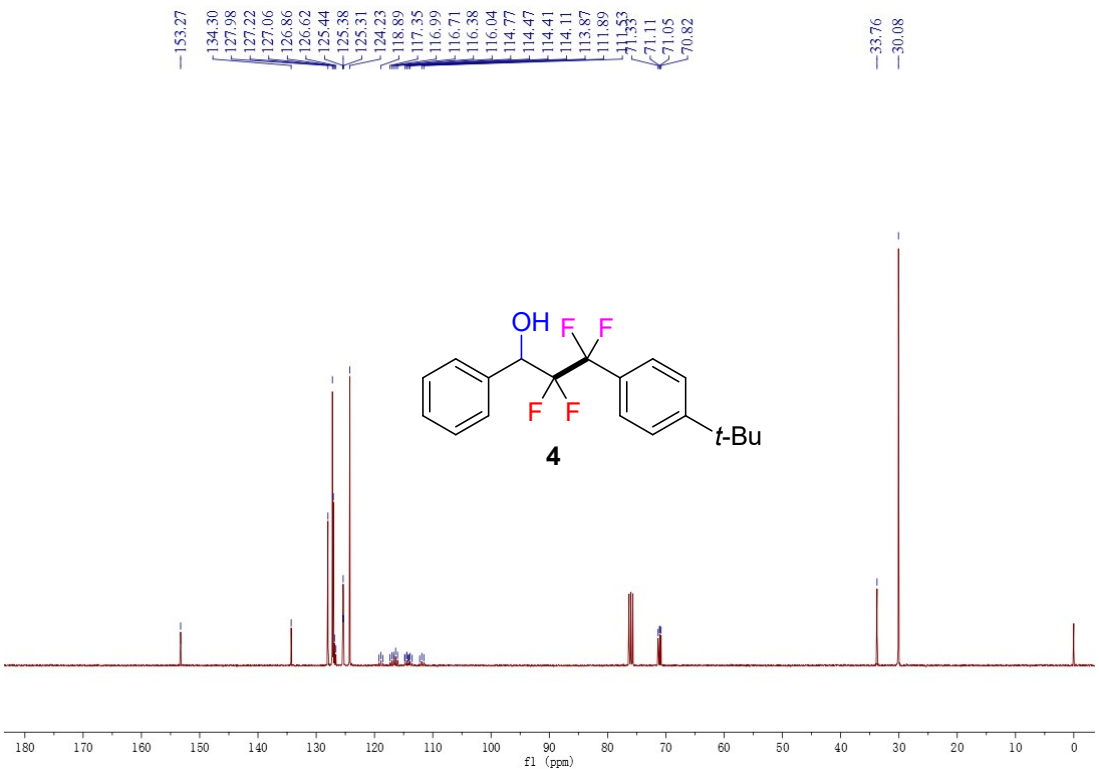

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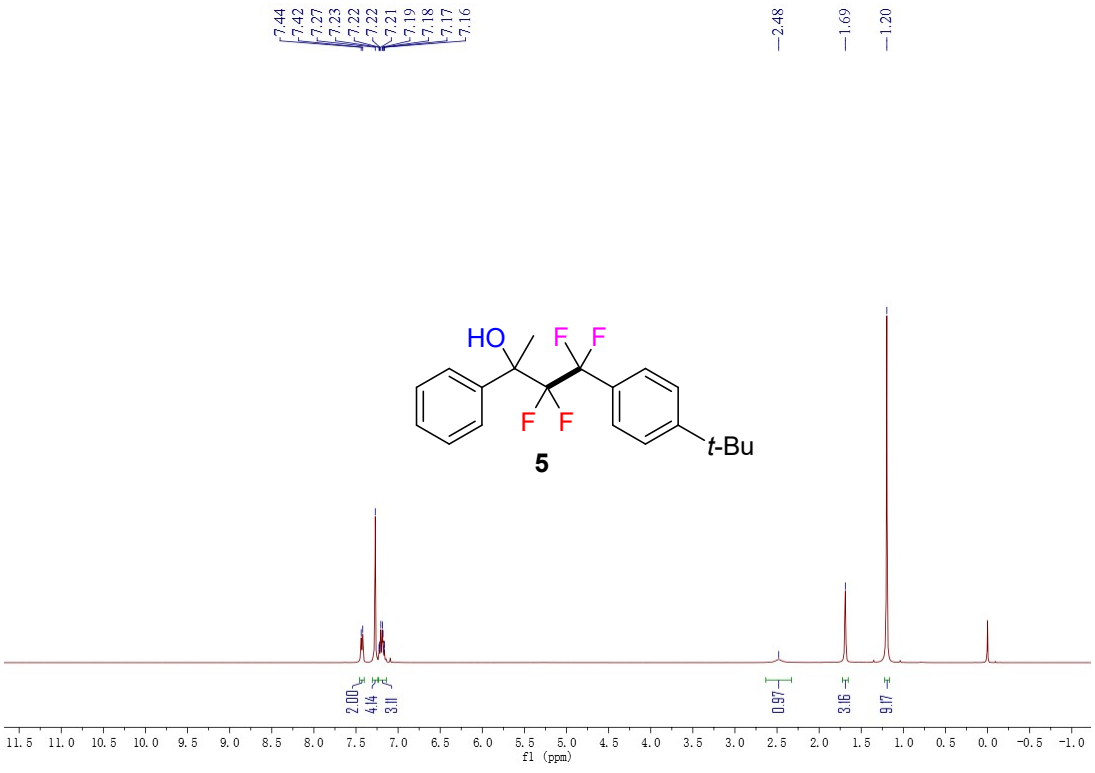

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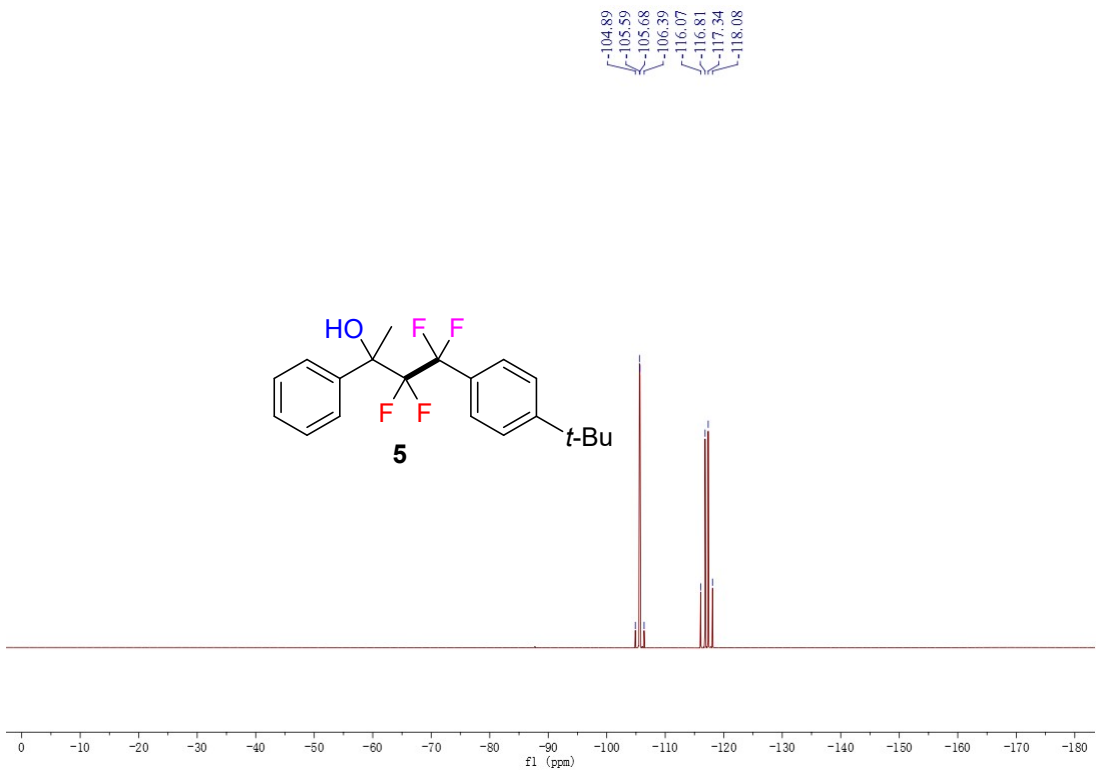
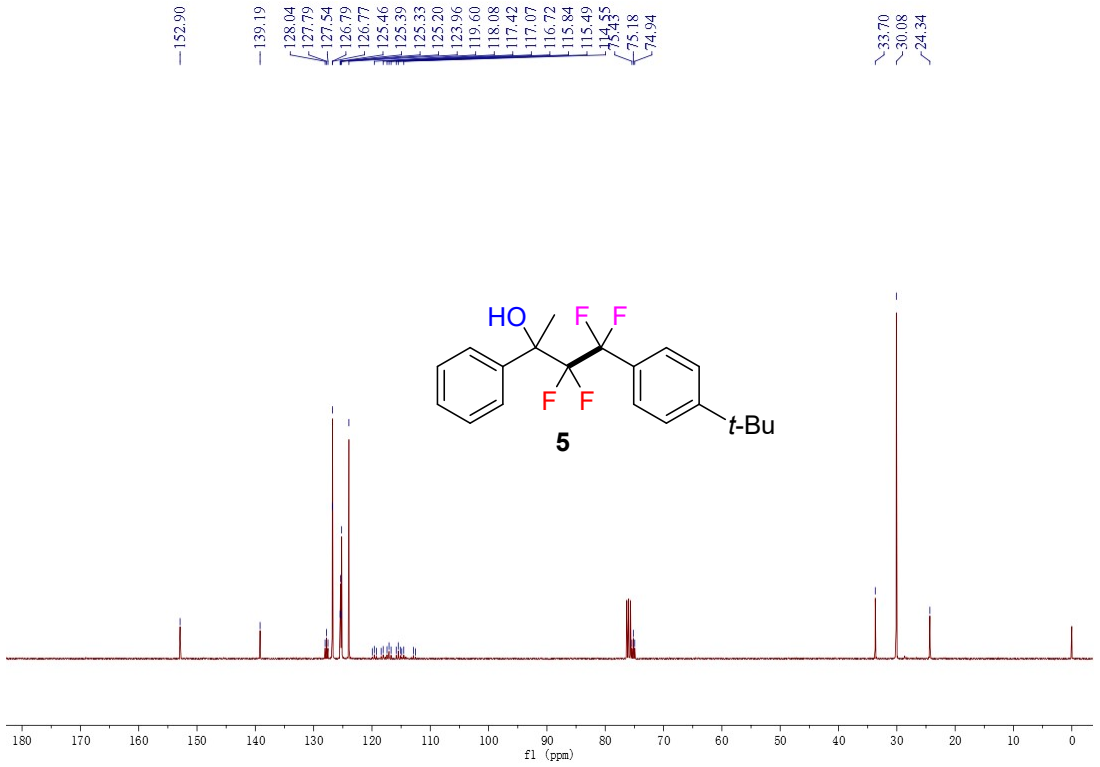
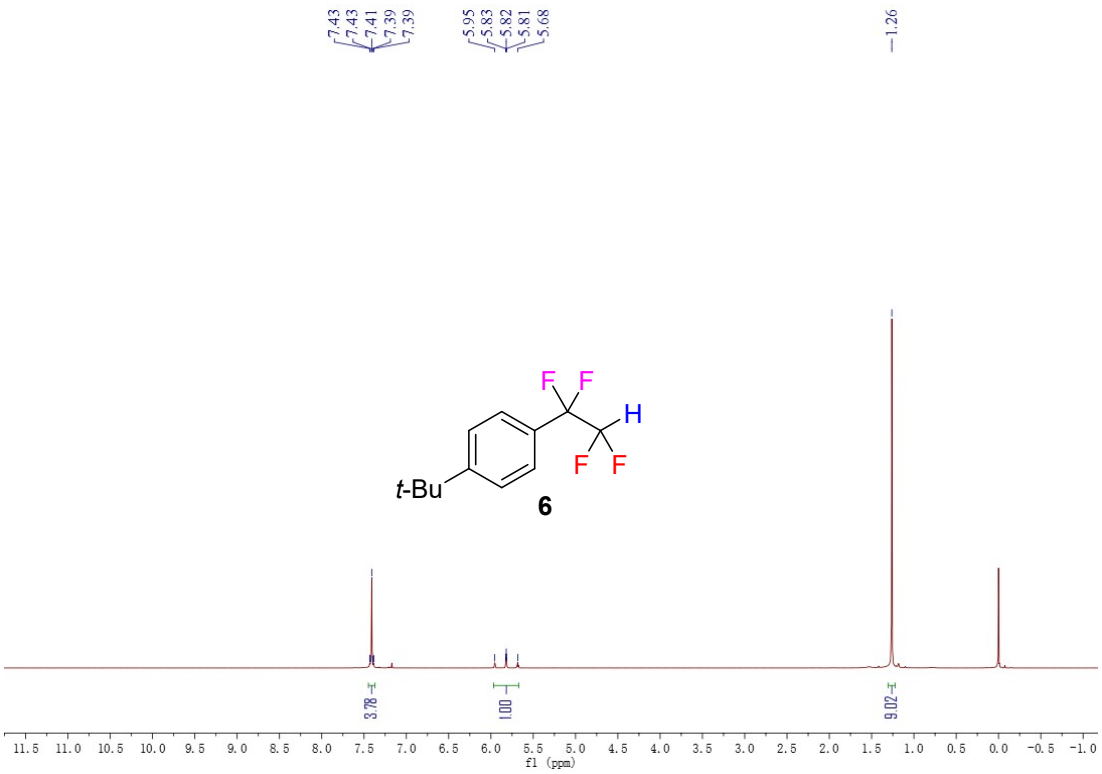


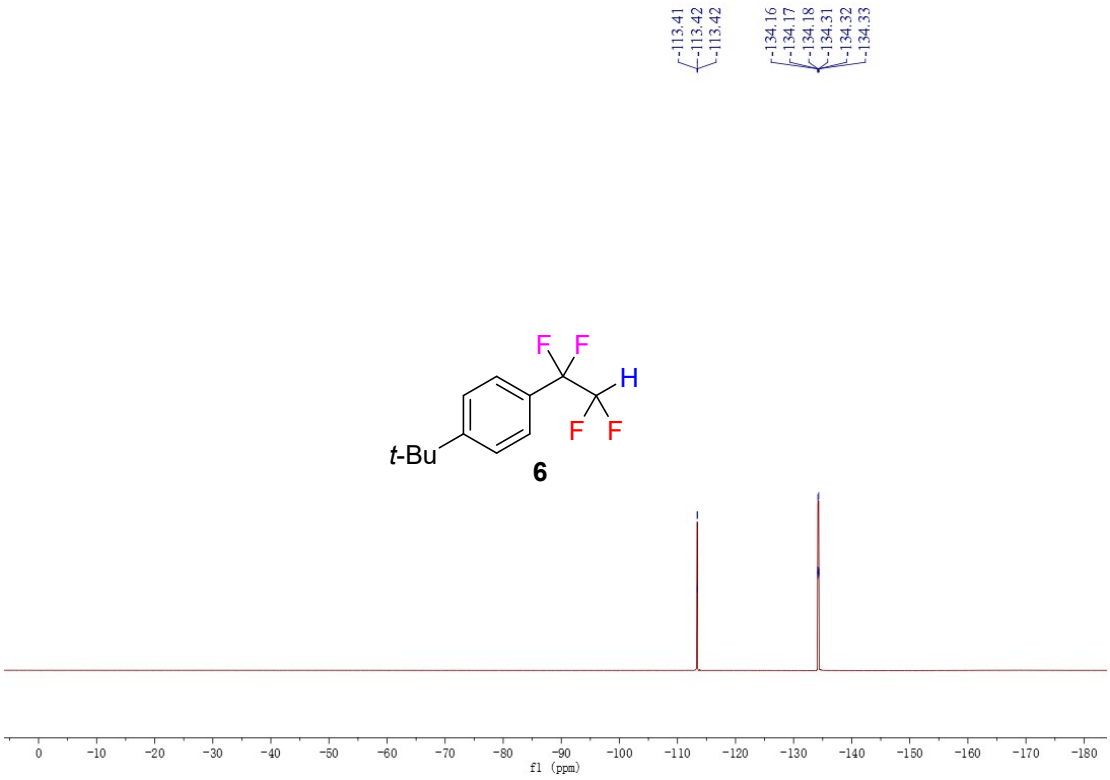
^{13}C NMR (101 MHz, $CDCl_3$)



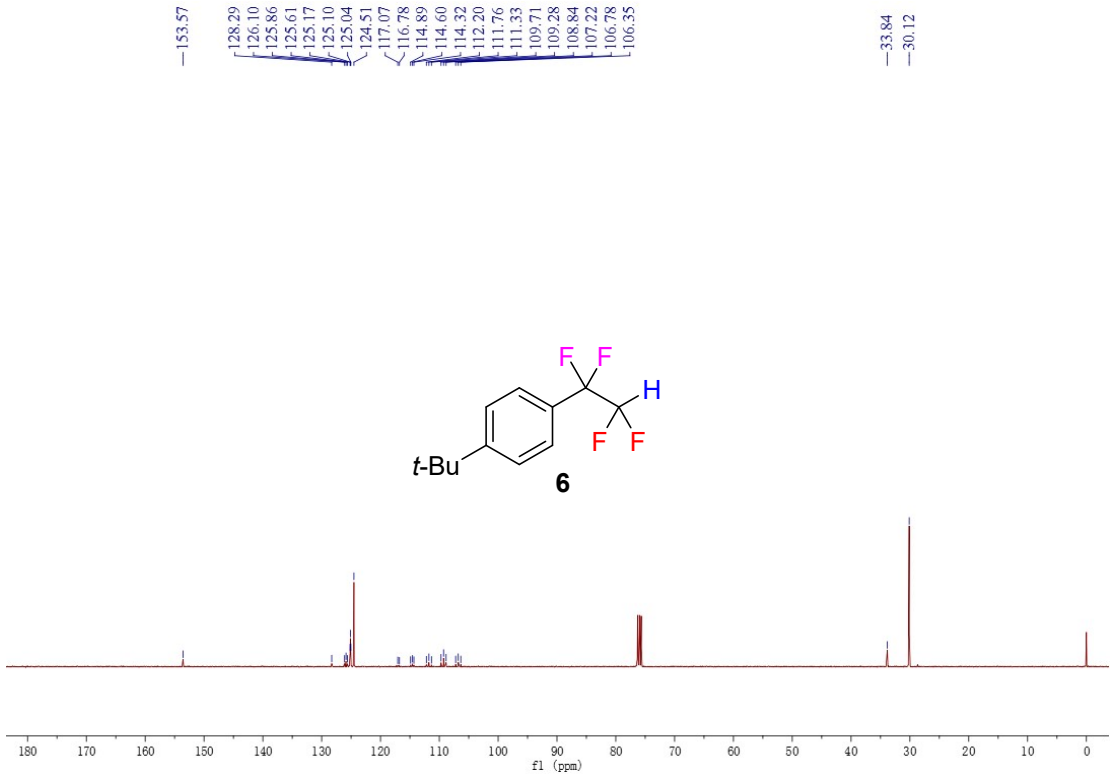
^{1}H NMR (400 MHz, $CDCl_3$)



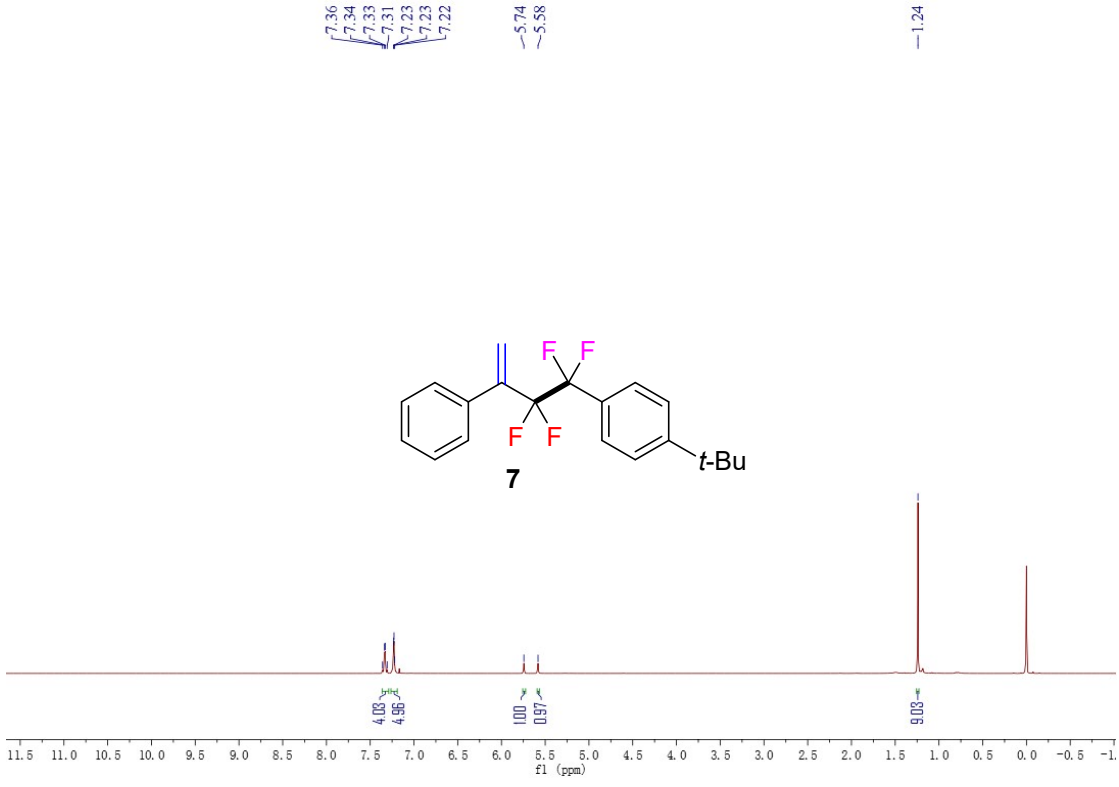
^{19}F NMR (377 MHz, $CDCl_3$)



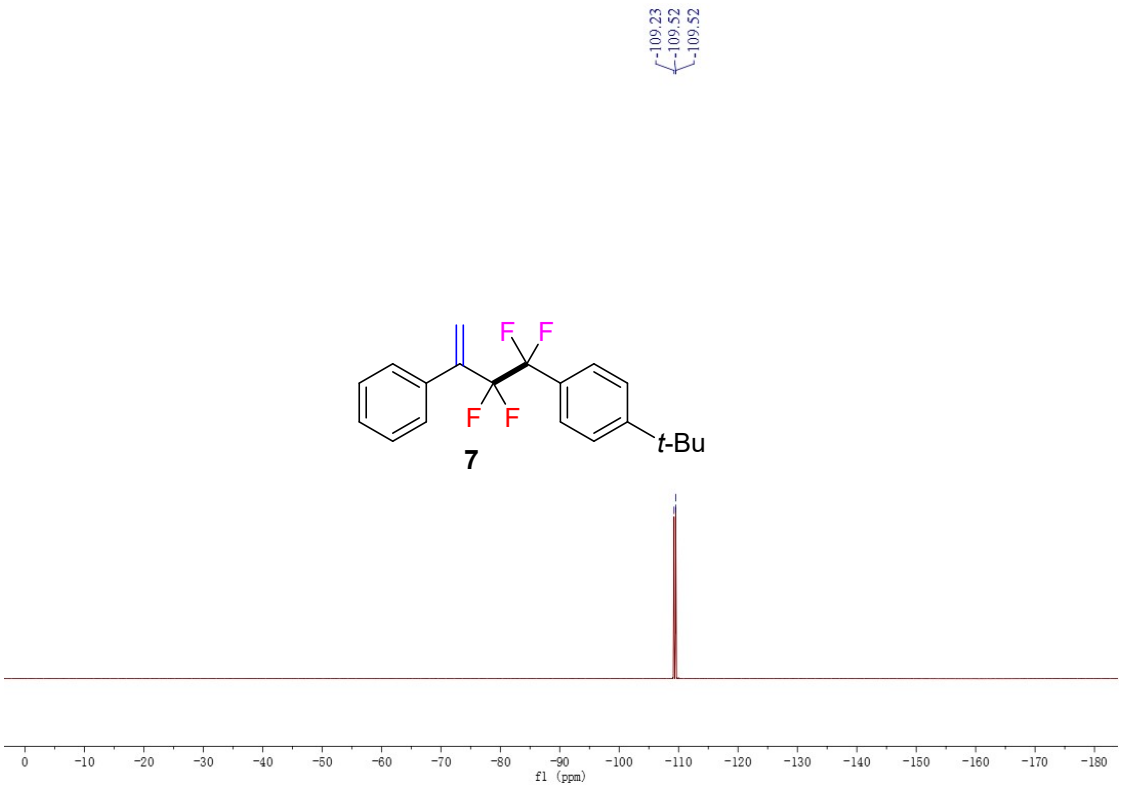
^{13}C NMR (101 MHz, $CDCl_3$)



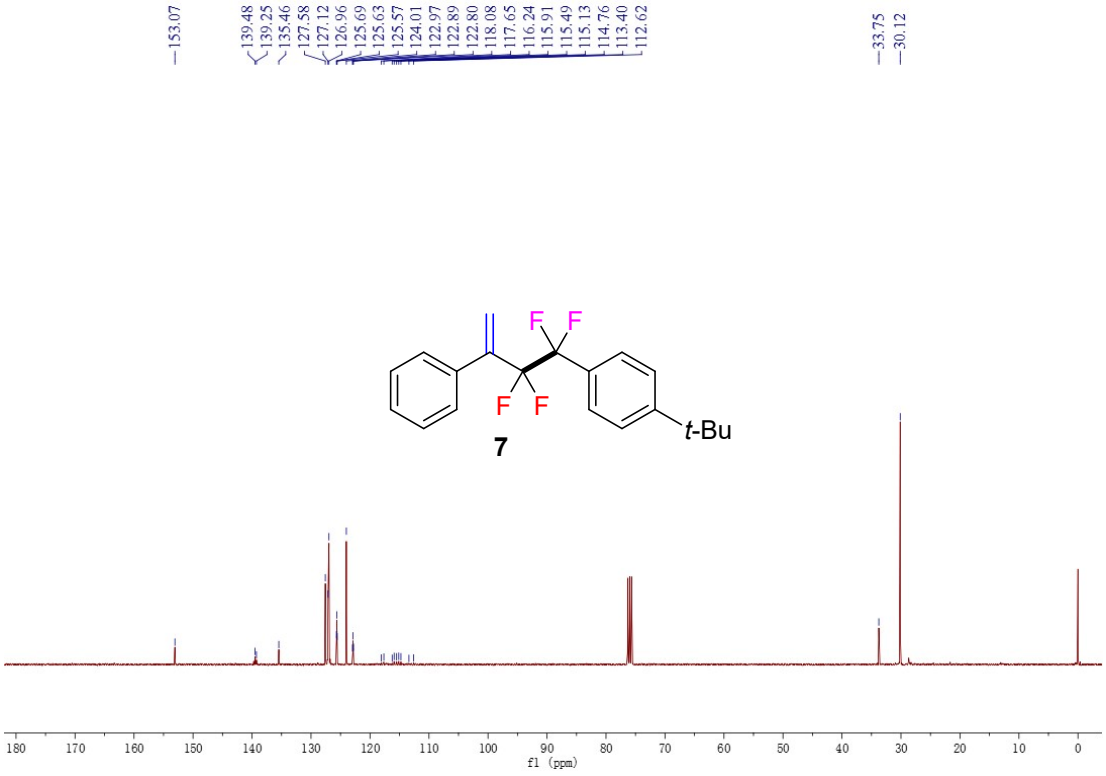
^{1}H NMR (400 MHz, $CDCl_3$)



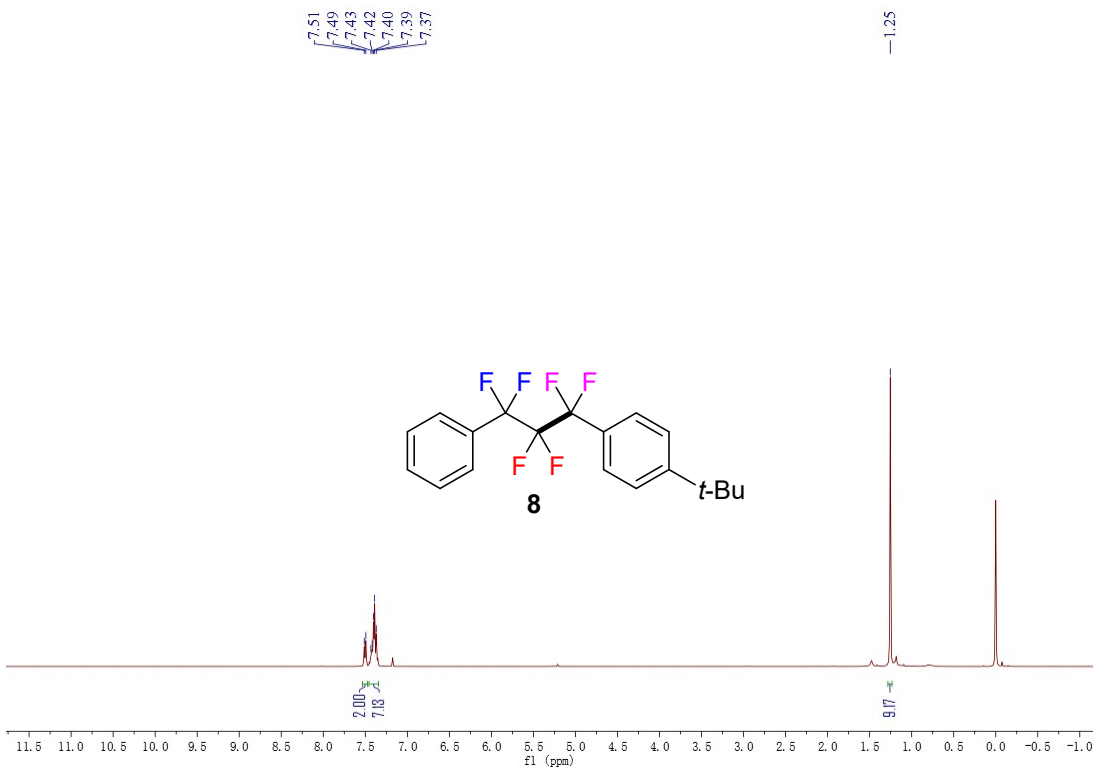
^{19}F NMR (377 MHz, $CDCl_3$)



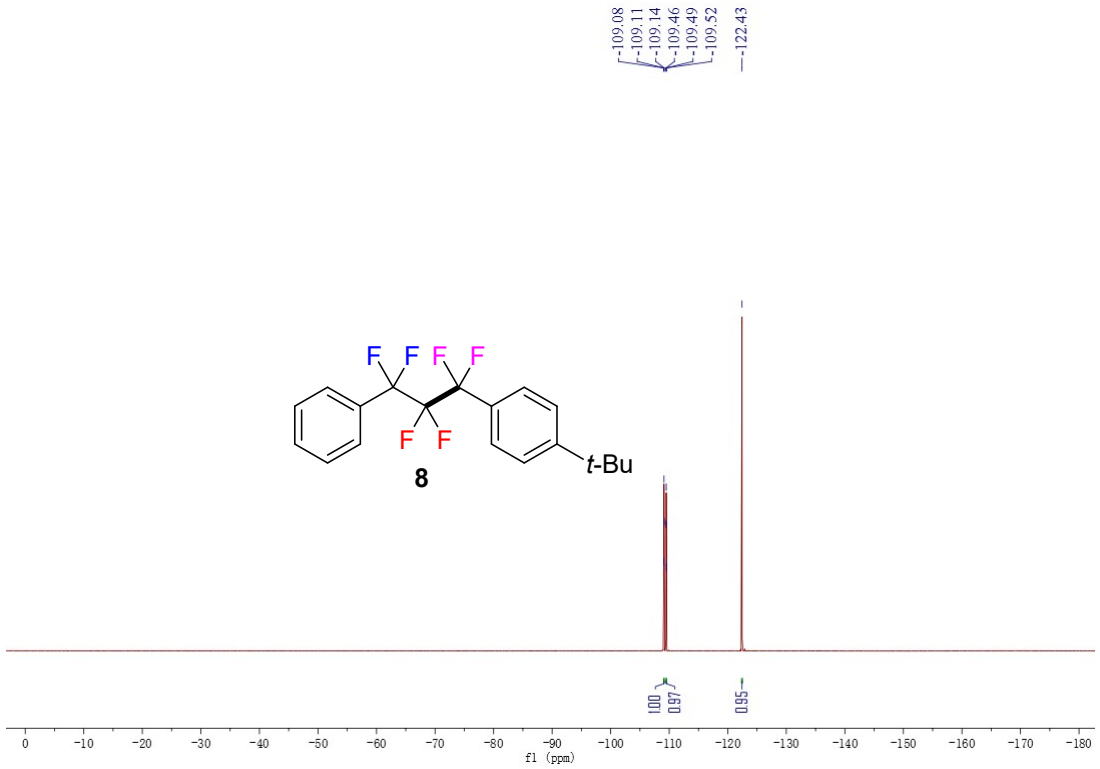
^{13}C NMR (101 MHz, $CDCl_3$)



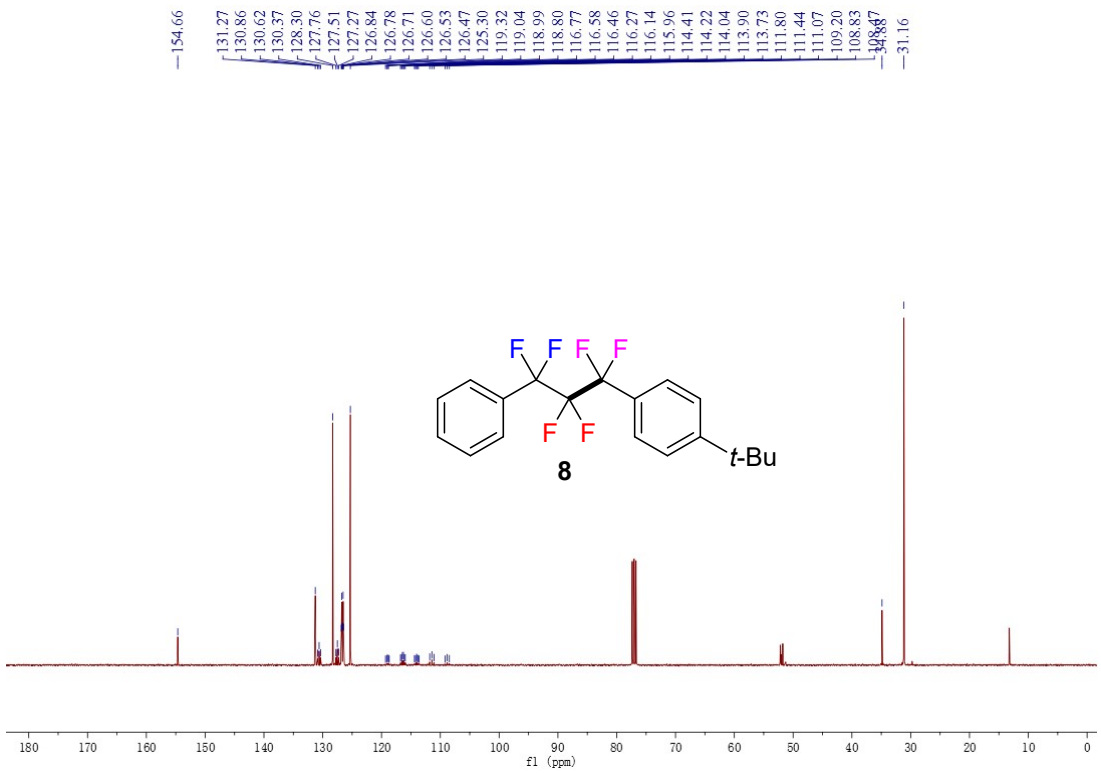
^{1}H NMR (400 MHz, $CDCl_3$)



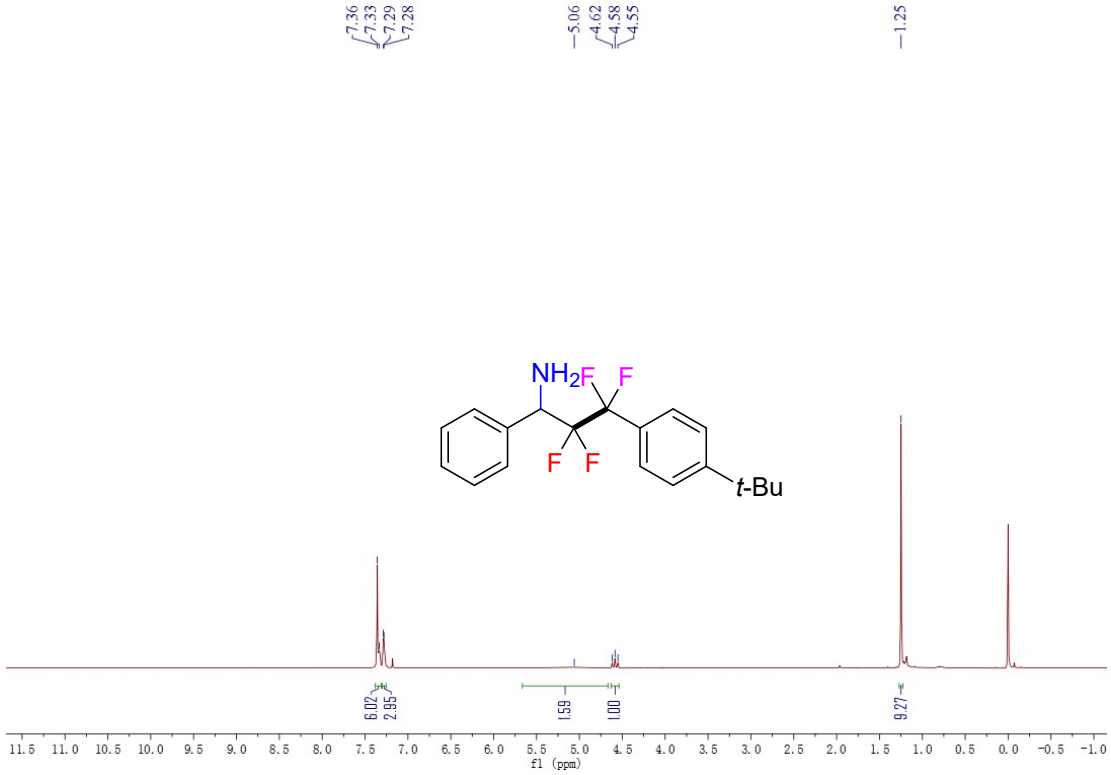
^{19}F NMR (377 MHz, $CDCl_3$)



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



[1]H NMR (400 MHz, CDCl3)



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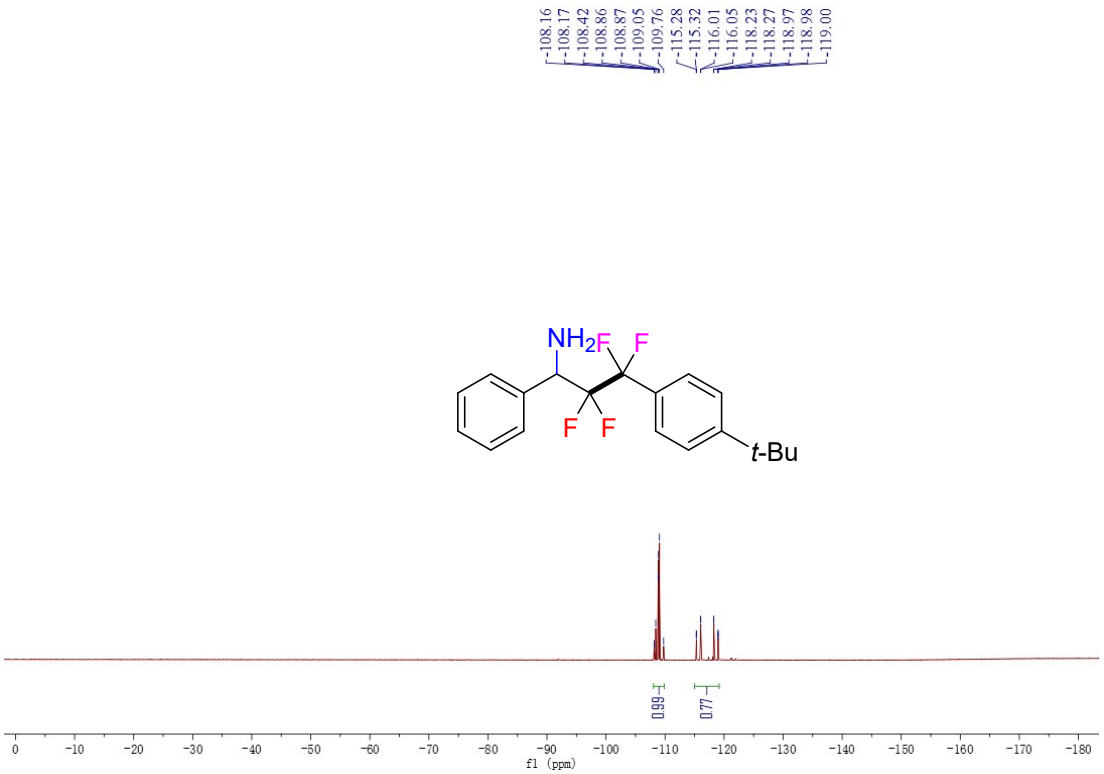
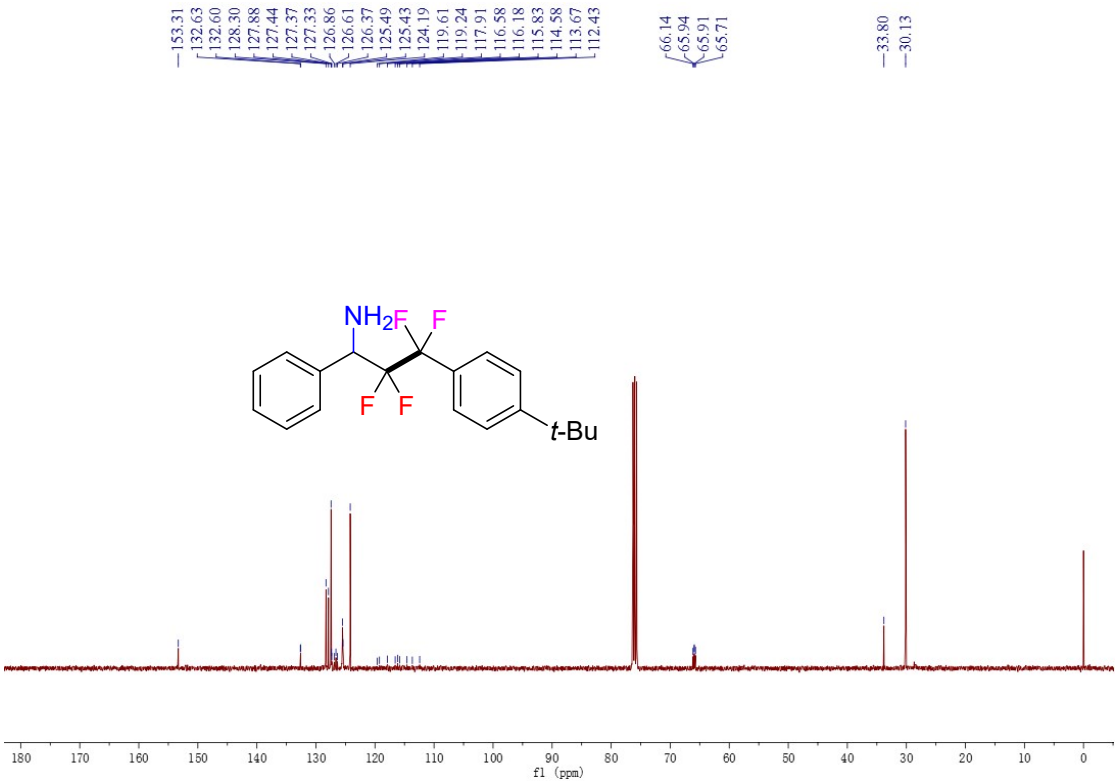
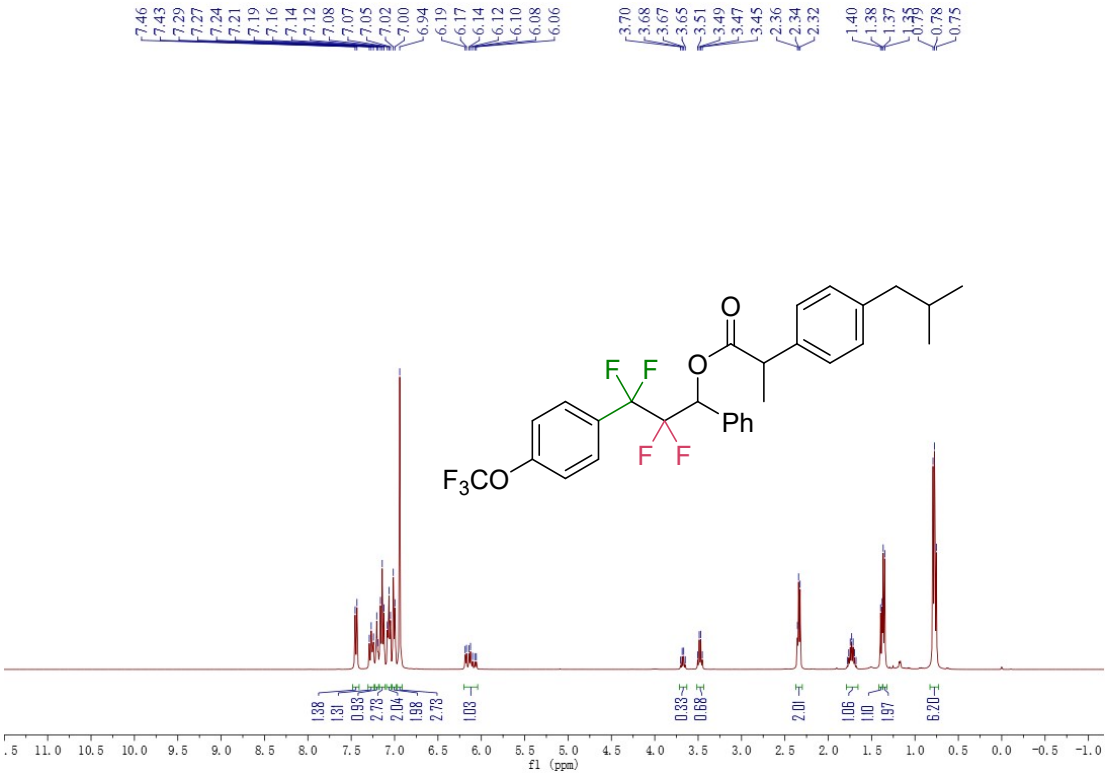


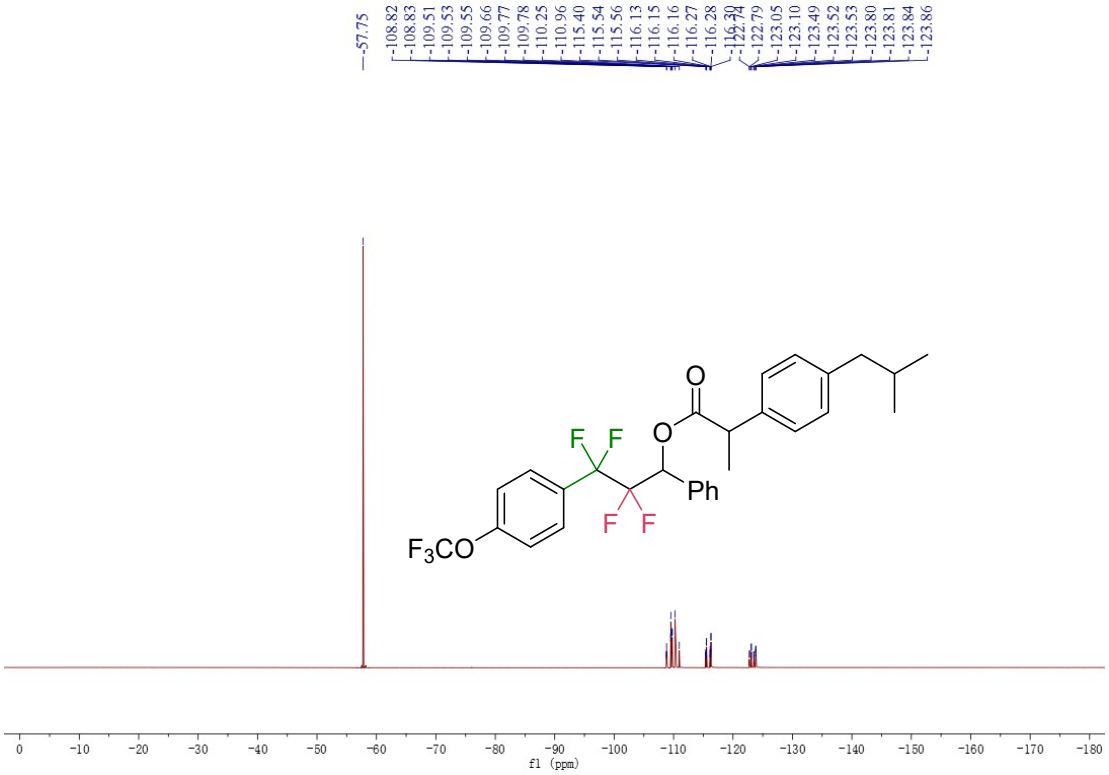
^{13}C NMR (101 MHz, $CDCl_3$)



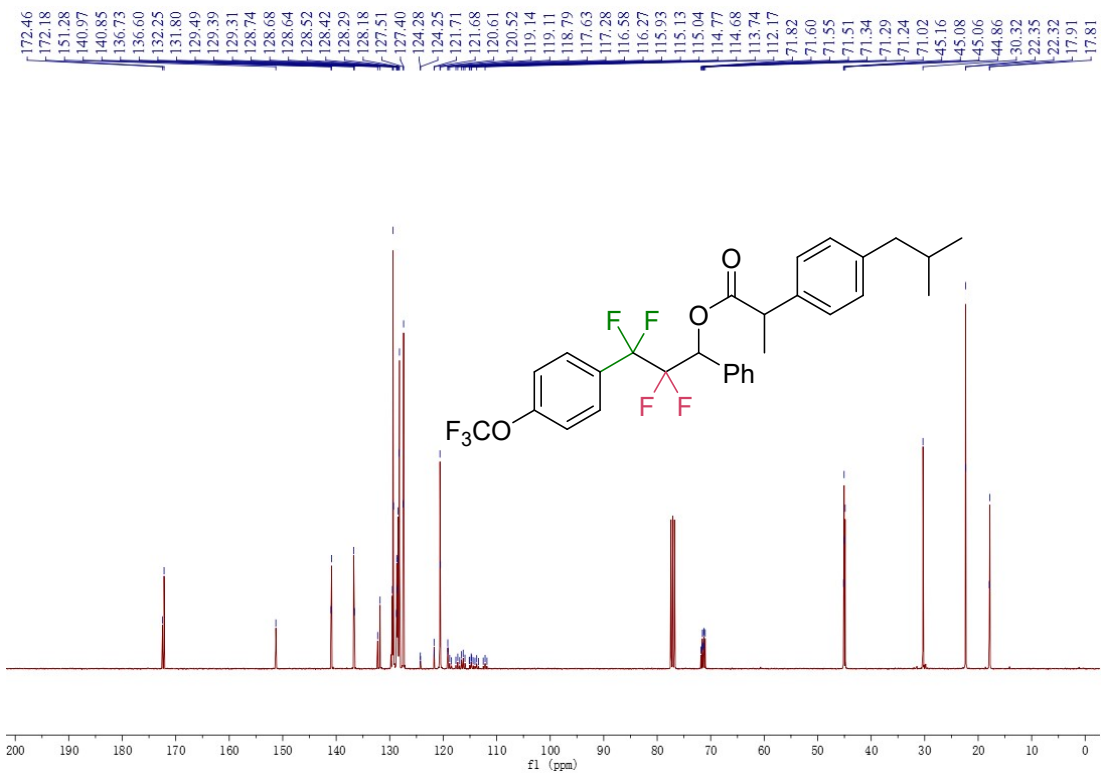
^{1}H NMR (400 MHz, $CDCl_3$)



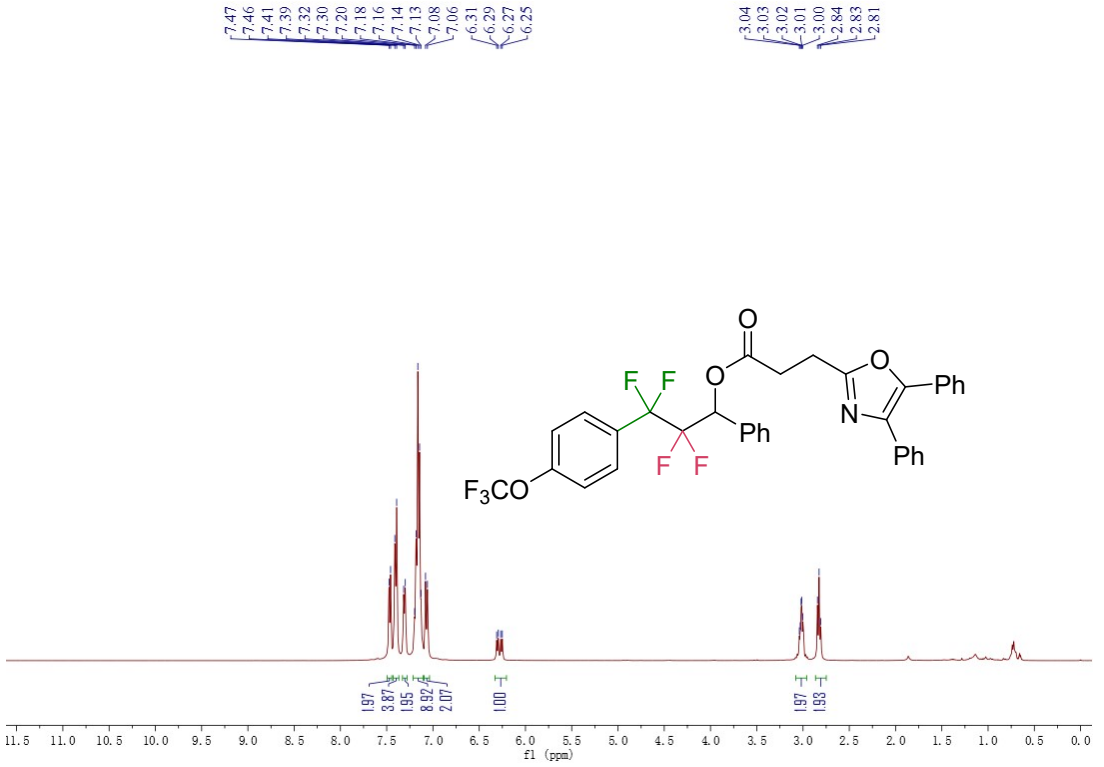
^{19}F NMR (377 MHz, $CDCl_3$)



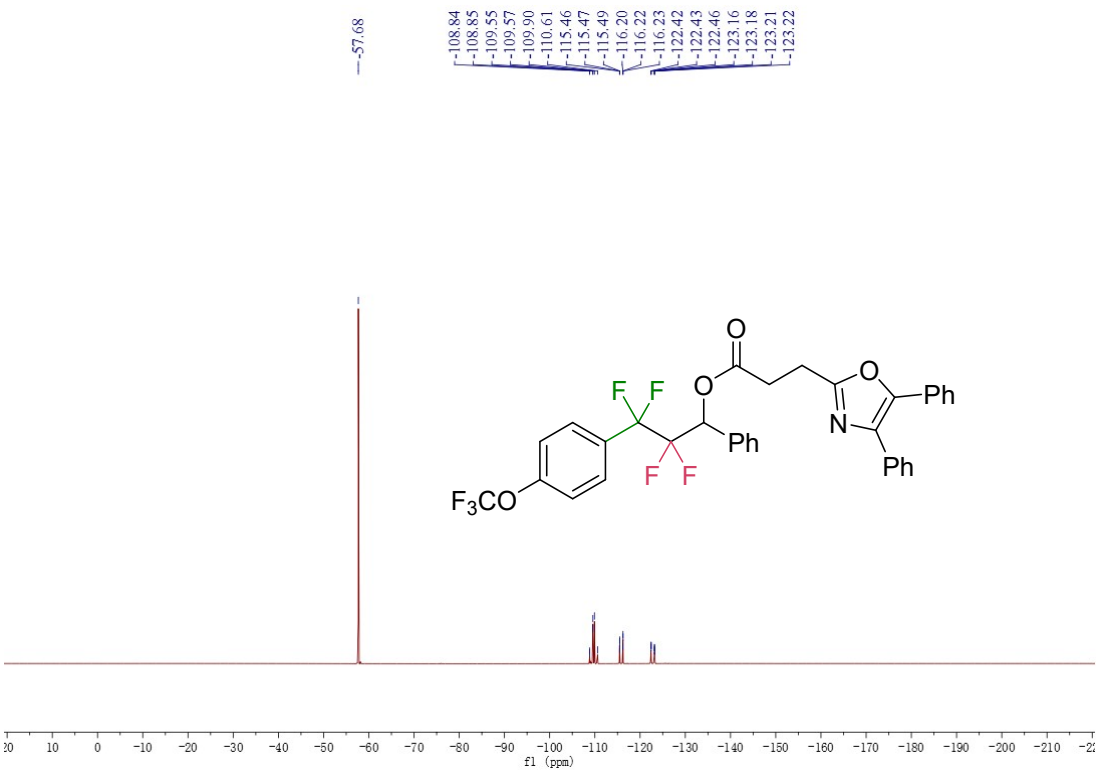
^{13}C NMR (101 MHz, $CDCl_3$)



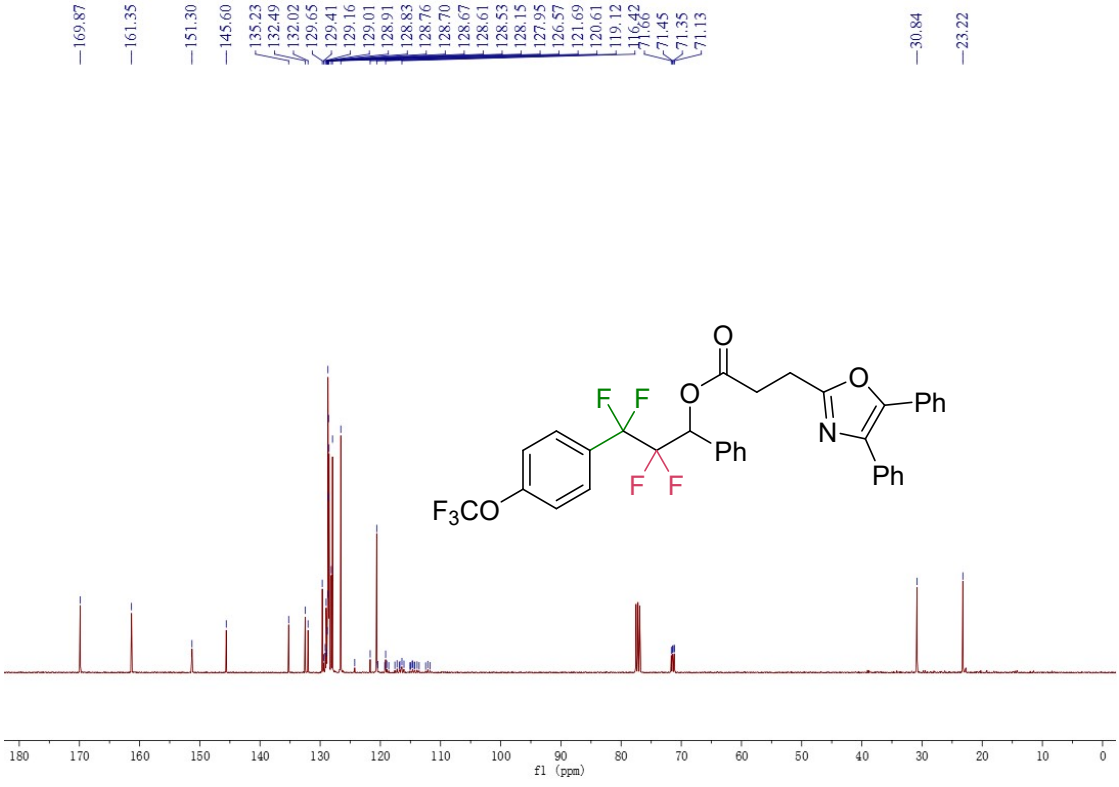
[1]H NMR (400 MHz, CDCl3)



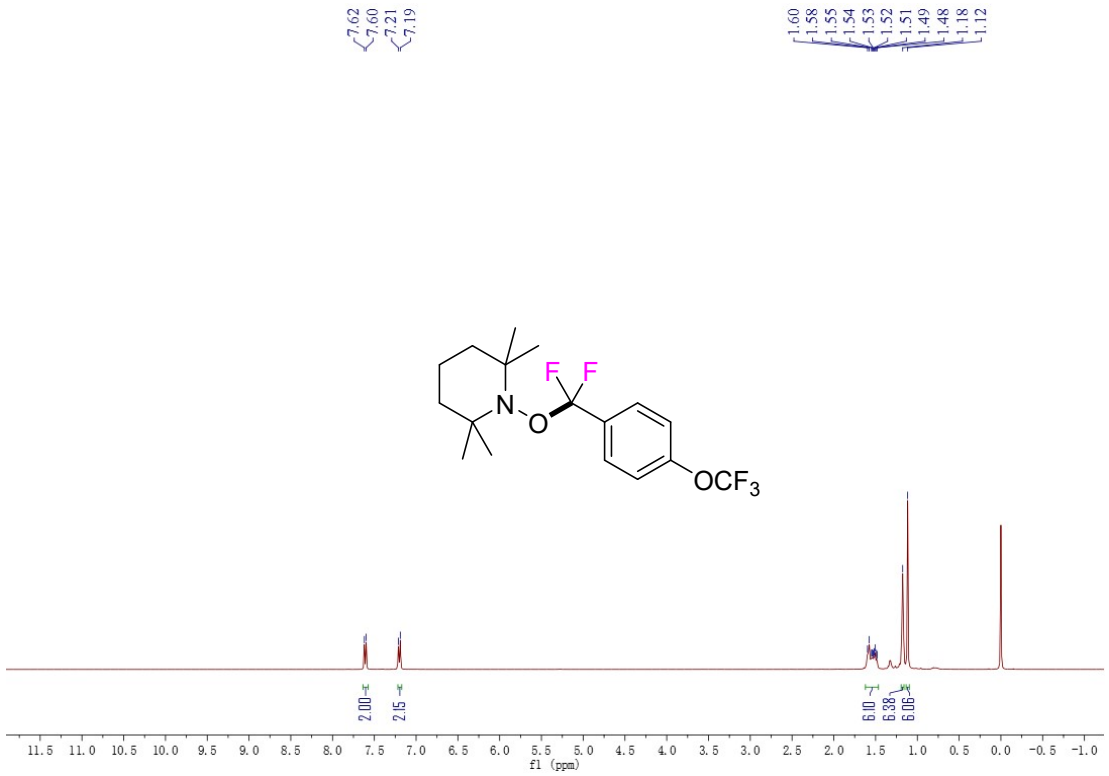
[19]F NMR (377 MHz, CDCl3)



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



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



^{19}F NMR (377 MHz, $CDCl_3$)