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Facile Access to *gem*-Difluorocyclopropanes via an *N*-Heterocyclic Carbene-Catalyzed Radical Relay/Cyclization Strategy

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Supporting Information

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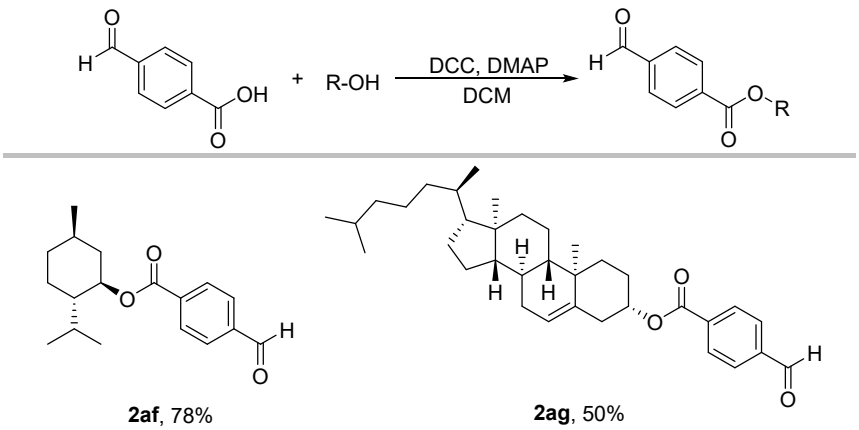
1. General information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. All the reactions were conducted using reaction tube (25 mL). The reactions were performed under nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 F25 plates. Column chromatograph was performed on silica gel 200~300 mesh. ^{1}H,^{13}C and ^{19}F NMR spectra were obtained in $CDCl_3$ using 300 MHz, 400 MHz Varian NMR spectrometer. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual $CDCl_3$ (7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant in Hertz (Hz). Chemical shifts in ^{13}C NMR spectra are reported in ppm on the δ scale from the central peak of residual $CDCl_3$ (77 ppm). Chemical shifts in ^{19}F NMR are reported in ppm on the δ scale. High-resolution mass spectra were obtained on SCIEX X500B mass spectrometer with ESI source. The redox potential was obtained on CHI660C electrochemical workstation (Shanghai ChenHua) by cyclic voltammetry.

2. Preparation of substrates

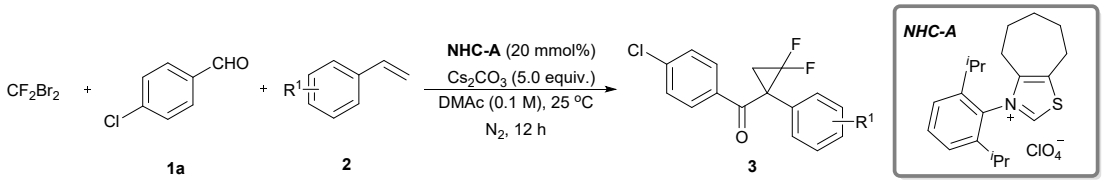
Dibromodifluoromethane, aldehydes and olefins used in this study were commercially available. Aldehydes **2af** and **2ag** were synthesized using the following methods.[1]

Preparation of aldehydes 2af and 2ag:

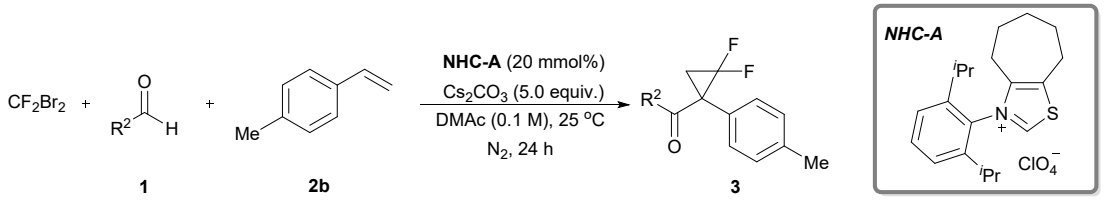


To a 100 mL round-bottom flask were added 4-formylbenzoic acid (450 mg, 3 mmol), alcohol (3 mmol), *N,N*-dicyclohexylcarbodiimide (DCC, 680.8 mg, 3.3 mmol) and DMAP (36.7 mg, 0.3 mmol). CH_2Cl_2 (15 mL) was then added at room temperature. The mixture was stirred at room temperature until the acid was consumed as monitored by TLC. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate=10:1, v/v) to yield the desired compounds **2af** and **2ag.**

3. General procedure for the synthesis of products 3

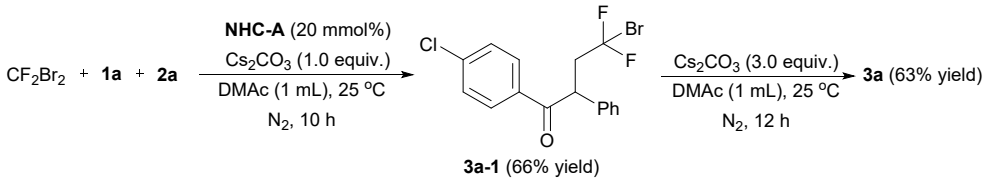


To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added aldehyde **1a** (28 mg, 0.2 mmol), NHC precatalyst **A** (16 mg, 0.04 mmol) and Cs_2CO_3 (325 mg, 1 mmol), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, dry DMAc (2 mL), olefin **2** (0.6 mmol) and dibromodifluoromethane (51 mg, 0.24 mmol) were added sequentially under the protection of nitrogen. The reaction mixture was stirred at room temperature for 12 hours. After completion of the reaction, the mixture was poured into 50 mL of water, which was extracted with EtOAc (20 mL×3). The combined organic extractions were washed by water (20 mL) and saturated brine solution (20 mL), respectively. Then, the organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 200/1) to give the products **3a-3p**.



To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added aldehyde **1** (0.15 mmol), NHC precatalyst **A** (8 mg, 0.02 mmol) and Cs_2CO_3 (325 mg, 1.0 mmol), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, dry DMAc (2 mL), olefin **2** (0.3 mmol) and dibromodifluoromethane (51 mg, 0.24 mmol) were added sequentially under the protection of nitrogen. The reaction mixture was stirred at room temperature for 12 hours, and then another portion of **A** (8 mg, 0.02 mmol) was added. The mixture was stirred under the same condition for another 12 hours. After completion of the reaction, the mixture was poured into 50 mL of water, which was extracted with EtOAc (20 mL×3). The combined organic extractions were washed by water (20 mL) and saturated brine solution (20 mL), respectively. Then, the organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 200/1) to give the products **3q-3ag**.

4. Control experiments

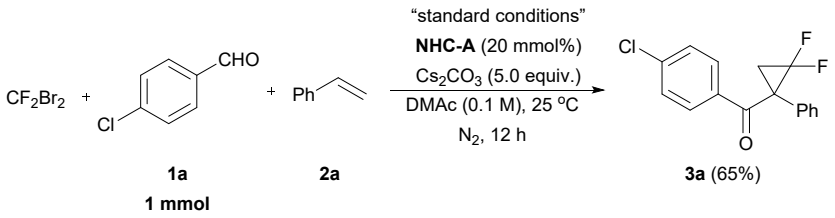


To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber

septum were added aldehyde **1a** (28mg, 0.2 mmol), NHC precatalyst **A** (16 mg, 0.04 mmol) and Cs_2CO_3 (65 mg, 0.2 mmol), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, dry DMAc (1 mL), olefin **2a** (0.6 mmol) and dibromodifluoromethane (51 mg, 0.24 mmol) were added sequentially under the protection of nitrogen. The reaction mixture was stirred at room temperature for 12 hours. After completion of the reaction, the mixture was poured into 50 mL of water, which was extracted with EtOAc (20 mL×3). The combined organic extractions were washed by water (20 mL) and saturated brine solution (20 mL), respectively. Then, the organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 200/1) to yield the products **3a-1** (50 mg, 66%).

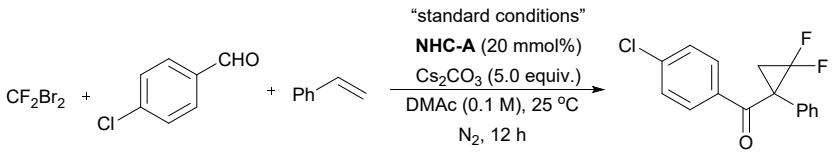
To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added Cs_2CO_3 (137 mg, 0.42 mmol), after which the tube was evacuated and back-filled with nitrogen three times. Subsequently, dry DMAc (1 mL), **3a-1** (50 mg 0.14 mmol) were added sequentially under the protection of nitrogen. After completion of the reaction, the mixture was poured into 50 mL of water, which was extracted with EtOAc (20 mL×3). The combined organic extractions were washed by water (20 mL) and saturated brine solution (20 mL), respectively. Then, the organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 200/1) to yield the products **3a** (25 mg, 63%).

5. Procedure for the scale-up synthesis of 3a



To an oven-dried reaction tube (50 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added NHC precatalyst **A** (80 mg, 0.2 mmol) and Cs_2CO_3 (1.3 g, 5 mmol), after which the tube was evacuated and back-filled with nitrogen three times. Subsequently, dry DMAc (20 mL), 4-chlorobenzaldehyde **1a** (0.141 g, 1.0 mmol), styrene **2a** (0.314 g, 3.0 mmol) and dibromodifluoromethane (1.05 g, 5.0 mmol) were added under the protection of nitrogen. The reaction mixture was stirred at room temperature for 6 hours and then NHC precatalyst **A** (80 mg, 0.2 mmol) was added. The reaction was carried out for another 6 hours at room temperature. After completion of the reaction, reaction mixture was poured into 100 mL of water, and extracted with EtOAc (50 mL×3). The combined organic extractions were washed by water (100 mL) and saturated brine solution (100 mL), respectively. Then, the organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate from 200/1) to afford **3a** (0.485 g, 65%).

6. Procedure for the synthesis of compound 4

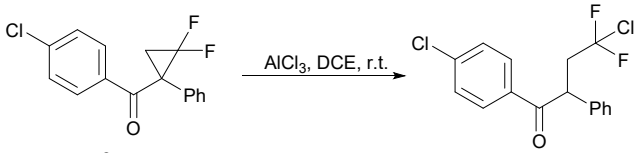


1a **2a** **3a** (65%)

1 mmol

To a 25 mL round bottom flask was charged with a solution of **3a** (59 mg, 0.2 mmol) in MeOH (5 mL). Then, $NaBH_4$ (16mg mg, 0.4 mmol) was added slowly at 0 °C. The resulting mixture was stirred at room temperature. After completion as indicated by TLC, Water (4 mL) and CH_2Cl_2 (5 mL) were added to quench the reaction. The aqueous layer was separated and extracted with CH_2Cl_2 (2×5 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by flash chromatography on silica gel with petroleum ether /ethyl acetate (50:1) to afford compound **4** (42 mg, 71 %) as a colorless oil.

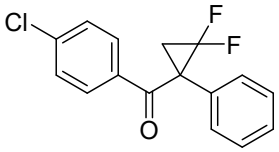
7. Procedure for the synthesis of compound 5



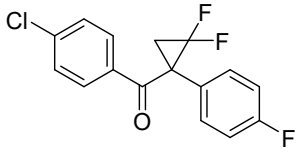
3a **5** (65%)

To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added **3a** (59 mg, 0.2 mmol) and $AlCl_3$ (67 mg, 0.5 mmol), after which the tube was evacuated and back-filled with nitrogen three times. After completion as indicated by TLC, water (2 mL) and saturated $NaHCO_3$ solution (1 mL) were added to quench the reaction. The aqueous layer was separated and extracted with CH_2Cl_2 (2×3 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by flash chromatography on silica gel with petroleum ether /ethyl acetate (1:10) to afford compound **5** (39 mg, 65%) as a colorless oil.[2]

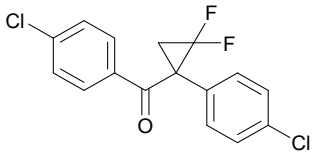
8. Characterization of products



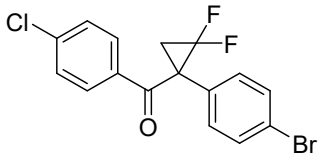
(4-chlorophenyl)(2,2-difluoro-1-phenylcyclopropyl)methanone (3a). White solid, mp: 54-55 °C, 36 mg, 62% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.35-7.27 (m, 3H), 2.62 (ddd, *J* = 13.6, 8.0, 4.6 Hz, 1H), 1.89 (ddd, *J* = 11.9, 8.0, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.94 (t, *J* = 2.5 Hz), 139.81, 133.96 (d, *J* = 2.0 Hz), 133.68, 130.81, 129.04 (t, *J* = 2.0 Hz), 129.00, 128.88, 128.19, 114.11, 111.21 (dd, *J* = 298.0, 287.9 Hz), 43.62 (dd, *J* = 13.1, 9.1 Hz), 22.53 (dd, *J* = 10.1, 9.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.5 (d, *J* = 154.0 Hz, 1F), -129.8 (d, *J* = 154.0 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{12}ClF_2O$ $[M+H]^+$: 293.0539, found 293.0536.



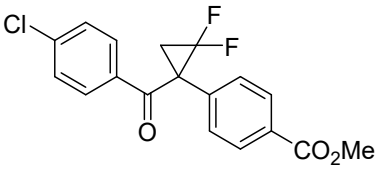
(4-chlorophenyl)(2,2-difluoro-1-(4-fluorophenyl)cyclopropyl)methanone (3b). Yellow liquid, 35 mg, 57% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dt, *J* = 8.6, 2.6 Hz 2H), 7.45-7.37 (m, 4H), 7.02-6.96 (m, 2H), 2.59 (ddd, *J* = 13.5, 8.1, 4.6 Hz, 1H), 1.82 (ddd, *J* = 11.9, 8.1, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.8 (t, *J* = 2.0 Hz), 162.3 (d, *J* = 249.5 Hz), 140.0, 133.5, 131. 0 (dt, *J* = 8.1, 2.0 Hz), 130.7, 129.7 (dd, *J* = 3.0, 2.0 Hz), 129.0, 116.1 (d, *J* = 21.2 Hz), 111.1 (dd, *J* = 296.9, 286.8 Hz), 42.9 (dd, *J* = 13.1, 9.1 Hz), 22.6 (dd, *J* = 10.1, 9.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.7, -126.6 (d, *J* = 154.3 Hz, 1F), -129.7 (d, *J* = 154.2 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{11}ClF_3O$ $[M+H]^+$: 311.0445, found: 311.0443.



(4-chlorophenyl)(1-(4-chlorophenyl)-2,2-difluorocyclopropyl)methanone (3c). Yellow liquid, 40 mg, 61% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dt, *J* = 8.6, 2.7 Hz, 2H), 7.44-7.39 (m, 4H), 7.30 (dt, *J* = 8.5, 2.7 Hz, 2H), 2.64 (ddd, *J* = 13.2, 8.1, 4.7 Hz, 1H), 1.86 (ddd, *J* = 11.9, 8.1, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 140.1, 134.4, 133.5, 132.5 (d, *J* = 2.0 Hz), 130.7, 130.4, 129.3, 129.0, 111.5 (dd, *J* =298.0, 287.6 Hz), 43.0 (dd, *J* = 13.1, 8.1 Hz), 22.6 (dd, *J* = 11.1, 9.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ (-126.3)-(-126.8) (m, 1F), (-129.5)-(-130.0) (m, 1F). HRMS (ESI) calcd for $C_{16}H_{11}Cl_2F_2O$ $[M+H]^+$: 327.0150, found 327.0146.

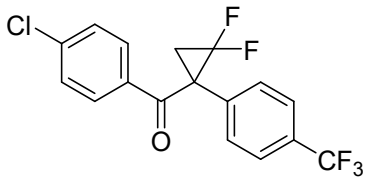


(1-(4-bromophenyl)-2,2-difluorocyclopropyl)(4-chlorophenyl)methanone (3d). Yellow liquid, 41 mg, 55% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dt, *J* = 8.2, 2.5 Hz, 2H), 7.45-7.38 (m, 4H), 7.1 (dt, *J* = 8.5, 2.4 Hz, 2H), 2.61 (ddd, *J* = 13.2, 8.1, 4.8 Hz, 1H), 1.82 (ddd, *J* = 11.9, 8.1, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5 (t, *J* = 2.0 Hz,), 140.1, 133.4, 133.0 (d, *J* = 2.0 Hz), 132.2, 130.7, 130.6 (t, *J* = 2.0 Hz), 129.0, 122.6, 110.9 (dd, *J* = 298.0, 287.9 Hz), 43.0 (dd, *J* = 13.1, 8.1 Hz), 22.6 (dd, *J* = 11.1, 9.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.5 (d, *J* = 154.6 Hz, 1F), -129.7 (d, *J* = 154.6 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{10}BrClF_2NaO$ $[M+Na]^+$: 392.9464, found 392.9470.

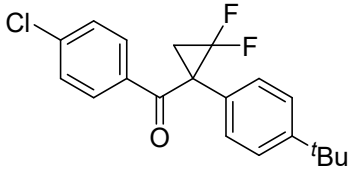


(1-(4-Methoxyformyl)-2,2-difluorocyclopropyl)(4-chlorophenyl)methanone (3e). White solid,

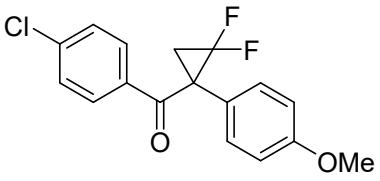
mp: 114-115 °C, 32 mg, 46% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dt, *J* = 8.4, 2.1 Hz, 2H), 7.84 (dt, *J* = 8.6, 2.6 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.37 (dt, *J* = 8.6, 2.5 Hz, 2H), 3.86 (s, 3H), 2.66 (ddd, *J* = 13.2, 8.2, 4.8 Hz 1H), 1.87 (ddd, *J* = 11.9, 8.1, 5.6 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.3, 166.2, 140.1, 138.9, 133.4, 130.7 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 2.0 Hz), 129.9 (d, *J* = 2.0 Hz), 129.0, 128.9, 111.0 (dd, *J* = 294.9, 286.8 Hz), 52.2 (d, *J* = 2.0 Hz), 43.4 (dd, *J* = 14.1, 9.1 Hz), 22.7 (dd, *J* = 11.1, 10.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.4 (dd, *J* = 154.9, 10.9 Hz), -129.6 (dd, *J* = 154.2, 11.3 Hz). HRMS (ESI) calcd for $C_{18}H_{13}ClF_2NaO_3$ $[M+Na]^+$: 373.0413, found 373.0398.



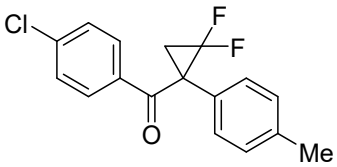
(4-chlorophenyl) (2,2-difluoro-1-(4-(trifluoromethyl)phenyl)cyclopropyl)metha none (3f). Yellow liquid, 31 mg, 43% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.57 (s, 4H), 7.40 (d, *J* = 8.5 Hz, 2H), 2.66 (dd d, *J* = 13.2, 8.2, 4.8 Hz, 1H), 1.88 (ddd, *J* = 11.9, 8.1, 5.6 Hz, 1H). ^{13}C NM R (101 MHz, Chloroform-*d*) δ 190.2 (t, *J* = 2.0 Hz), 140.3, 138.0, 133.3, 130. 8, 130.4 (q, *J* = 32.3 Hz), 129.4 (t, *J* = 2.0 Hz), 129.1, 126.0 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 273.7 Hz), 110.8 (dd, *J* = 296.9, 287.6 Hz), 43.2 (dd, *J* = 14 .1, 9.1 Hz), 22.7 (t, *J* = 10.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.9 (d, *J* = 4.6 Hz, 3F), -126.4 (d, *J* = 155.3 Hz, 1F), -129.6 (d, *J* = 155.3 Hz, 1F). HRMS (ESI) calcd for $C_{17}H_{11}ClF_5O$ $[M+H]^+$: 361.0413, found 361.0409.



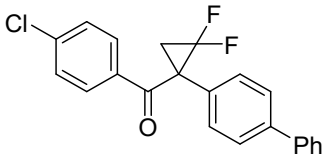
(1-(4-(*tert*-butyl)phenyl)-2,2-difluorocyclopropyl)(4-chlorophenyl)methanone (3g). Yellow solid, mp: 98-100 °C,45 mg, 65% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.38 (t, *J* = 8.6 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 2H), 2.54 (ddd, *J* = 13.8, 8.0, 4.4 Hz, 1H), 1.84 (ddd, *J* = 11.6, 8.0, 5.6 Hz, 1H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.0, 151.2, 139.8, 133.7, 130.9, 130.7 (d, *J* = 1.0 Hz), 128.9, 128.7, 125.9, 111.3 (dd, *J* = 298.0, 286.8 Hz), 43.2 (dd, *J* = 13.1, 9.1 Hz), 34.5, 31.1, 22.5 (t, *J* = 9.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.3 (d, *J* = 153.6 Hz, 1F), -130.1(d, *J* = 153.7 Hz, 1F). HRMS (ESI) calcd for $C_{20}H_{19}ClF_2NaO$ $[M+Na]^+$: 371.0985, found 371.0966.



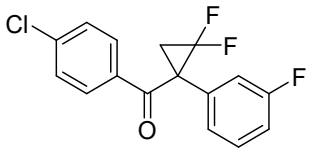
(4-chlorophenyl)(2,2-difluoro-1-(4-methoxyphenyl)cyclopropyl)methanone (3h). Yellow solid, mp: 60-61 °C, 50 mg, 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dt, *J* = 8.6, 2.5 Hz, 2H), 7.39-7.34 (m, 4H), 6.82 (dt, *J* = 8.9, 3.1 Hz, 2H), 3.74 (s, 3H), 2.56 (ddd, *J* = 13.8, 8.0, 4.5 Hz, 1H), 1.81 (ddd, *J* = 11.8, 7.9, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.2 (t, *J* = 2.0 Hz), 159.3, 139.7, 133.7, 130.8, 130.4, 128.8, 125.7 (d, *J* = 2.0 Hz), 114.4, 111.4 (dd, *J* = 298.0, 286.8 Hz), 55.2, 43.1 (dd, *J* = 13.1, 9.1 Hz), 22.4 (t, *J* = 10.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.6 (d, *J* = 153.3 Hz, 1F), -129.8 (d, *J* = 153.3 Hz, 1F). HRMS (ESI) calcd for $C_{17}H_{14}ClF_2O_2$ $[M+H]^+$: 323.0645, found 323.0646.



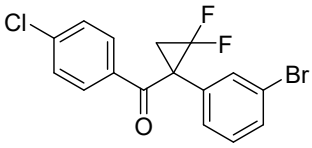
(4-chlorophenyl)(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)methanone (3i). Yellow liquid, 47 mg, 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dt, *J* = 8.6, 2.3 Hz, 2H), 7.38 (dt, *J* = 8.6, 2.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.57 (ddd, *J* = 13.7, 8.0, 4.6 Hz, 1H), 2.28 (s, 3H), 1.82 (ddd, *J* = 11.9, 8.0, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.1 (t, *J* = 3.0 Hz), 139.7, 138.1, 133.7, 130.9, 130.8, 129.7, 128.9 (t, *J* = 2.0 Hz), 128.8, 111.3 (dd, *J* = 298.0, 286.8 Hz), 43.3 (dd, *J* = 13.1, 9.1 Hz), 22.4 (dd, *J* = 10.1, 9.1 Hz), 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.6 (d, *J* = 153.4 Hz, 1F), -129.8 (d, *J* = 153.6 Hz, 1F). HRMS (ESI) calcd for $C_{17}H_{14}ClF_2O$ $[M+H]^+$: 307.0696, found 307.0682.



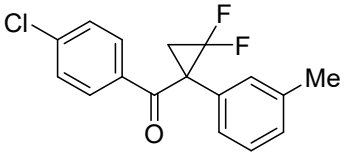
(1-([1,1'-biphenyl]-4-yl)-2,2-difluorocyclopropyl)(4-chlorophenyl)methanone (3j). Yellow liquid, 62 mg, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.56-7.52 (m, 6H), 7.44-7.40 (m, 4H), 7.35 (t, *J* = 7.2 Hz,1H), 2.64 (ddd, *J* = 13.3, 8.1, 4.6 Hz, 1H), 1.91 (ddd, *J* = 11.7, 8.1, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.9 (t, *J* = 2.0 Hz), 141.0, 140.0, 139. 9, 133.6, 132.8 (d, *J* = 2.0 Hz), 130.9, 129.4, 128.9, 128.8, 127.7, 127.6, 127.0, 111.2 (dd, *J* = 296.9, 286.8 Hz), 43.30 (dd, *J* = 13.1, 9.1 Hz), 22.6 (t, *J* = 10.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.3 (d, *J* = 154.0 Hz, 1F), -129.7 (d, *J* = 154.0 Hz, 1F). HRMS (ESI) calcd for $C_{22}H_{15}ClF_2KO$ $[M+K]^+$: 407.0411, found 407.0417.



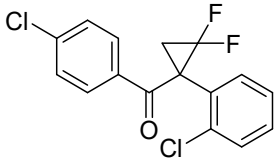
(4-chlorophenyl)(2,2-difluoro-1-(3-fluorophenyl)cyclopropyl)methanone (3k). Yellow liquid, 31 mg, 51% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (dt, *J* = 8.6, 2.5 Hz, 2H), 7.30-7.23 (dt, *J* = 8.6, 2.5 Hz, 2H), 7.27 (td, *J* = 7.6, 5.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.16 (dt, *J* = 9.7, 2.2 Hz, 2H), 6.96 (tdd, *J* = 8.3, 2.5, 1.1 Hz, 1H), 2.61 (ddd, *J* = 13.2, 8.1, 4.7 Hz, 1H), 1.85 (ddd, *J* = 11.9, 8.1, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 190.4 (t, *J* = 2.0 Hz), 162.7 (d, *J* = 248.5 Hz), 140.1, 136.2 (dd, *J* = 8.1, 2.0 Hz), 133.4, 130.8, 130.6 (d, *J* = 9.1 Hz), 129.0, 124.7 (q, *J* =2.0 Hz), 116.0 (dt, *J* = 23.2, 2.0 Hz), 115.4 (d, *J* = 21.2 Hz), 111.0 (dd, *J* = 298.0, 286.8 Hz), 43.1 (ddd, *J* = 11.1, 9.1, 2.0 Hz), 22.6 (dd, *J* = 10.1, 9.1 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -111.1 (s, 1F), -126.4 (d, *J* = 155.0 Hz, 1F), -129.9 (d, *J* = 155.1 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{11}ClF_3O$ $[M+H]^+$: 311.0445, found 311.0443.



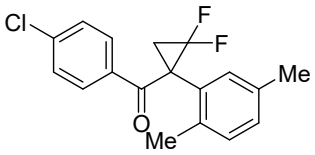
(1-(3-bromophenyl)-2,2-difluorocyclopropyl)(4-chlorophenyl)methanone (3l). White solid, mp: 79-80 °C, 41 mg, 55% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.59 (t, *J* = 1.8 Hz, 1H), 7.42-7.37 (m, 4H), 7.17 (t, *J* = 7.9 Hz, 1H), 2.60 (ddd, *J* = 13.2, 8.2, 4.8 Hz, 1H), 1.86 (ddd, *J* = 11.9, 8.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.3 (t, *J* =2.0 Hz), 140.1, 136.0 (d, *J* = 2.0 Hz), 133.3, 131.9 (t, *J* = 3.0 Hz), 131.5, 130.8, 130.5, 129.0, 127.7, 123.0, 110.8 (dd, *J* = 298.0, 287.9 Hz), 43.0 (dd, *J* = 14.1, 9.1 Hz), 22.6 (t, *J* = 11.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.4 (d, *J* = 154.8 Hz, 1F), -129.5 (d, *J* = 154.8 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{10}BrClF_2NaO$ $[M+Na]^+$: 392.9464, found 392.9470.



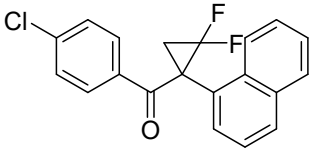
(4-chlorophenyl)(2,2-difluoro-1-(*m*-tolyl)cyclopropyl)methanone (3m). Yellow liquid, 45 mg, 74% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04-7.86 (m, 2H), 7.48-7.37 (m, 2H), 7.30 (s, 2H), 7.25-7.21 (m, 1H), 7.12 (s, 1H), 2.61 (ddt, *J* = 12.7, 8.2, 4.2 Hz, 1H), 2.35 (s, 3H), 1.90 (ddt, *J* = 12.0, 8.0, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.0, 139.8, 138.8, 133.8, 133.6, 130.9, 129.7, 129.0, 128.9, 128.8, 126.0, 111.2 (dd, *J* = 296.9, 286.8 Hz), 43.5 (dd, *J* = 12.1, 8.1 Hz), 22.4 (t, *J* = 9.1 Hz), 21.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.4 (dd, *J* = 153.9, 3.5 Hz, 1F), -129.7 (dd, *J* = 153.9, 3.7 Hz, 1F). HRMS (ESI) calcd for $C_{17}H_{14}ClF_2O$ $[M+H]^+$: 307.0696, found 307.0682.



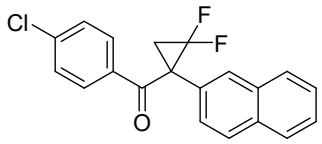
(4-chlorophenyl)(1-(2-chlorophenyl)-2,2-difluorocyclopropyl)methanone (3n). Yellow solid, mp: 73-74 °C, 31 mg, 48% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (dt, *J* = 7.1, 1.9 Hz, 1H), 7.67-7.60 (m, 2H), 7.33-7.25 (m, 4H), 7.25-7.20 (m, 1H), 3.13 (ddd, *J* = 12.8, 8.0, 6.3 Hz, 1H), 1.76 (ddd, *J* = 12.5, 8.0, 5.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.8, 138.7, 136.2 (d, *J* = 3.0 Hz), 135.3, 132.4 (d, *J* = 2.0 Hz), 132.0 (d, *J* = 4.0 Hz), 130.4, 129.90, 129.89, 128.5, 126.9, 112.7 (dd, *J* = 298.0, 289.9 Hz), 43.3 (dd, *J* = 14.1, 7.1 Hz), 23.4 (dd, *J* = 11.1, 8.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.9 (d, *J* = 148.6 Hz, 1F), -129.3 (d, *J* = 148.6 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{11}Cl_2F_2O$ $[M+H]^+$: 327.0150, found 327.0146.



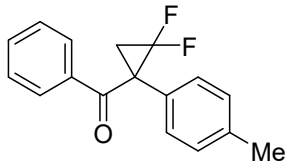
(4-chlorophenyl)(1-(2,5-dimethylphenyl)-2,2-difluorocyclopropyl)methanone (3o). Yellow liquid, 40 mg, 63% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.43 (s, 1H), 7.33 (dt, *J* = 8.6, 2.1 Hz, 2H), 6.97 (s, 2H), 2.87 (ddd, *J* = 13.1, 7.7, 5.3 Hz, 1H), 2.31 (s, 3H), 2.16 (s, 3H), 1.67 (ddd, *J* = 12.8, 7.7, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.4, 139.1, 136.3 (d, *J* = 2.0 Hz), 135.6, 134.8, 131.6 (d, *J* = 2.0 Hz), 131.2 (d, *J* = 3.0 Hz), 131.1, 130.3, 129.4, 128.6, 112.3 (dd, *J* = 295.9, 286.8 Hz), 43.6 (dd, *J* = 13.1, 8.1 Hz), 22.40 (t, *J* = 10.1 Hz), 21.06, 19.10. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.2 (d, *J* = 144.5 Hz, 1F), -128.2 (d, *J* = 149.6 Hz, 1F). HRMS (ESI) calcd for $C_{18}H_{16}ClF_2O$ $[M+H]^+$: 321.0852, found 321.0851.



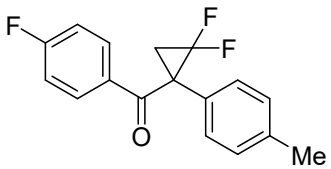
(4-chlorophenyl)(2,2-difluoro-1-(naphthalen-1-yl)cyclopropyl)methanone (3p). Yellow liquid, 32 mg, 46% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.1 Hz, 1H), 7.86-7.73 (m, 4H), 7.55 (td, *J* = 7.0, 1.0 Hz, 1H), 7.49-7.42 (m, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 3.08 (q, *J* = 8.6 Hz, 1H), 1.86 (q, *J* = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.9, 139.3, 134.3, 134.0, 132.6, 130.4, 129.4, 129.3, 129.2, 128.9, 128.6, 127.1, 126.1, 125.0, 124.3, 111.8 (t, *J* = 292.9 Hz), 43.0 (t, *J* = 11.1 Hz), 22.9 (t, *J* = 8.1 Hz).^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.7 (s, 2F). HRMS (ESI) calcd for $C_{20}H_{14}ClF_2O$ $[M+H]^+$: 343.0696, found 343.0697.



(4-chlorophenyl)(2,2-difluoro-1-(naphthalen-2-yl)cyclopropyl)methanone (3q). Yellow solid, mp: 72-73 °C, 30 mg, 44% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00-7.88 (m, 3H), 7.81-7.74 (m, 3H), 7.52-7.43 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 2H), 2.68 (ddd, *J* = 13.2, 8.0, 4.6 Hz, 1H), 1.94 (ddd, *J* = 11.9, 8.0, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.8 (*J* = 204.0 Hz), 139.8, 133.7, 133.2, 132.6, 131.32, 131.30, 130.8, 128.9, 128.5, 127.9, 127.6, 126.7, 126.6, 126.1, 111.4 (dd, *J* = 298.0, 286.8 Hz), 43.7 (dd, *J* = 13.1, 9.1 Hz), 22.7 (t, *J* = 10.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.2 (d, *J* = 154.2 Hz, 1F), -129.3 (d, *J* = 154.2 Hz, 1F). HRMS (ESI) calcd for $C_{20}H_{14}ClF_2O$ $[M+H]^+$: 343.0696, found 343.0697.

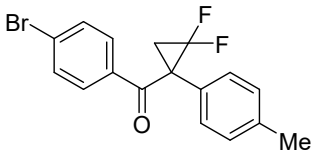


(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)(phenyl)methanone (3r). Yellow liquid, 44mg, 81% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.49 (dt, *J* = 7.3, 2.4 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.59 (ddd, *J* = 13.7, 8.0, 4.6 Hz, 1H), 2.28 (s, 3H), 1.85 (ddd, *J* = 11.8, 8.0, 5.6 Hz 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 192.1 (t, *J* = 2.3 Hz), 137.9, 135.2, 133.2, 131.0 (d, *J* = 2.2 Hz), 129.5, 129.4, 129.0 (t, *J* = 2.3 Hz), 128.4, 111.3 (dd, *J* = 294.0, 284.3 Hz), 43.4 (dd, *J* = 12.8, 9.0 Hz), 22.3 (dd, *J* = 10.5, 9.0 Hz), 20.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.4 (d, *J* = 153.3 Hz, 1F), -129.9 (d, *J* = 153.3 Hz, 1F). HRMS (ESI) calcd for $C_{17}H_{15}F_2O$ $[M+H]^+$: 273.1085, found 273.1083.

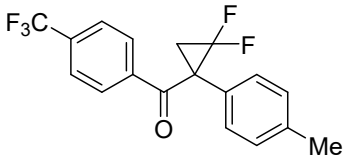


(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)(4-fluorophenyl)methanone (3s). Yellow liquid, 43 mg, 74% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.03-7.95 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.13-7.04 (m, 4H), 2.55 (ddd, *J* = 13.7, 8.0, 4.6 Hz, 1H), 2.28 (s, 3H), 1.82 (ddd, *J* = 11.8, 8.0, 5.7 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 190.7 (t, *J* = 2.3 Hz), 16 5.7 (d, *J* = 254.3 Hz), 138.1, 132.8 (d, *J* = 9.0 Hz), 132.2 (d, *J* = 9.8 Hz), 131.7 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 1.5 Hz), 129.7, 129.1, 128.9 (t, *J* = 1.5 Hz), 115.9, 115.6, (t, *J* = 21.8 Hz), 111.3 (dd, *J* = 294.8, 284.3 Hz), 43.3 (dd, *J* = 12.8, 8.3 Hz), 22.5 (dd, *J* = 10 .5, 9.0 Hz), 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -104.3 (1F), -126.5 (d, *J* = 153.8

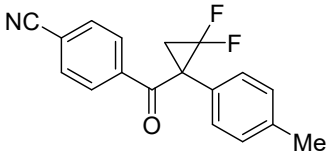
Hz, 1F), -130.0 (d, J = 153.8 Hz, 1F). HRMS (ESI) calcd for $C_{17}H_{14}F_3O$ $[M+H]^+$: 291.0991, found 291.0991.



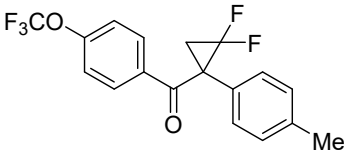
(4-bromophenyl)(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)methanone (3t). Yellow solid, mp: 72-73 °C, 34 mg, 48% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dt, J = 8.6, 2.5 Hz, 2H), 7.54 (dt, J = 8.6, 2.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.57 (ddd, J = 13.8, 8.0, 4.6 Hz, 1H), 2.28 (s, 3H), 1.82 (ddd, J = 11.8, 8.0, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.3, 138.2, 134.2, 131.8, 130.9, 129.7, 128.9, 128.5, 111.3 (dd, J = 296.9, 286.8 Hz), 43.4 (dd, J = 12.1, 7.1 Hz), 22.5 (t, J = 10.1 Hz), 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.6 (dd, J = 153.6, 5.2 Hz, 1F), -129.8 (dd, J = 153.6, 5.2 Hz, 1F). HRMS (ESI) calcd. for $C_{17}H_{14}BrF_2O$ $[M+H]^+$: 351.0191, found 351.0182.



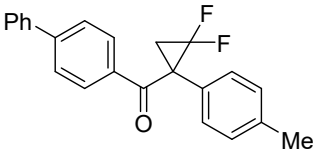
(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)(4-(trifluoromethyl)phenyl)methanone (3u). Yellow solid, mp: 60-61 °C, 40mg, 59% yield**,** ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 2.65 (ddd, J = 13.2, 8.0, 4.7 Hz, 1H), 2.28 (s, 3H), 1.86 (ddd, J = 11.8, 8.0, 5.7 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 191.5 (t, J = 2.3 Hz), 138.3, 134.3 (q, J = 32.3 Hz), 130.48, 130.46, 129.8, 129.6, 129.1 (t, J = 2.3 Hz), 125.5 (q, J = 270.8 Hz), 123.4 (q, J = 270.8 Hz), 111.3 (dd, J = 294.8, 284.3 Hz), 43.6 (dd, J = 12.8, 9.0 Hz), 22.5 (dd, J = 10.5, 9.0 Hz), 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.3 (s, 1F), -126.8(d, J = 153.6 Hz, 1F), -129.6 (d, J = 153.6 Hz, 1F). HRMS (ESI) calcd for $C_{18}H_{13}F_5NaO$ $[M+Na]^+$: 363.0779, found 363.0772.



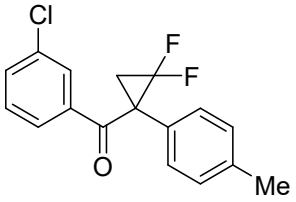
4-(2,2-difluoro-1-(*p*-tolyl)cyclopropane-1-carbonyl)benzonitrile (3v). White solid, mp: 68-69 °C, 18 mg, 30% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02-7.92 (m, 2H), 7.69 (dt, J = 8.5, 3.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.65 (ddd, J = 13.6, 8.0, 4.8 Hz, 1H), 2.27 (s, 3H), 1.85 (ddd, J = 11.9, 8.0, 5.7 Hz, H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.2 (t, J = 2.0 Hz), 138.9, 138.5, 132.3, 130.2 (d, J = 2.0 Hz), 129.8, 129.5, 129.1, 117.7, 116.3, 111.3 (dd, J = 299.0, 287.9 Hz), 43.6 (dd, J = 12.1, 9.1 Hz), 22.5 (t, J = 10.1 Hz), 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.9 (d, J = 153.24 Hz, 1F), -129.3 (d, J = 153.3 Hz, 1F). HRMS (ESI) calcd for $C_{18}H_{14}F_2NO[M+H]^+$: 298.1038, found 298.1033.



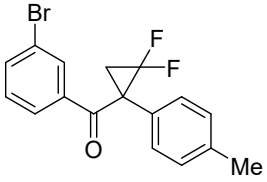
(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)(4-(trifluoromethoxy)phenyl)methanone (3w). Yellow liquid, 43 mg, 60% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.65 (ddd, *J* = 13.2, 8.0, 4.7 Hz, 1H), 2.28 (s, 3H), 1.86 (ddd, *J* = 11.8, 8.0, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.7 (t, *J* = 2.0 Hz), 152.6 (d, *J* = 2.0 Hz), 138.2, 133.5, 131.5, 130.8 (d, *J* = 1.0 Hz), 129.8, 128.9, 120.2 (q, *J* = 259.6 Hz), 120.1, 111.3 (dd, *J* = 296.9, 286.8 Hz), 43.4 (dd, *J* = 12.1, 8.1 Hz), 22.5 (t, *J* = 10.1 Hz), 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.6, -126.6 (d, *J* = 153.9 Hz, 1F), -129.9 (d, *J* = 153.9 Hz, 1F). HRMS (ESI) calcd for $C_{18}H_{14}F_5O_2$ $[M+H]^+$: 357.0908, found 357.0909.



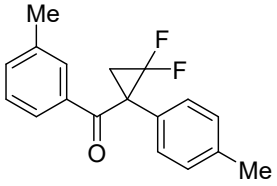
[1,1'-biphenyl]-4-yl(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)methanone (3x). White solid, mp: 67-68 °C, 32 mg, 46% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12-8.02 (m, 2H), 7. 67-7.62 (m, 2H), 7.61-7.56 (m, 2H), 7.50-7.36 (m, 5H), 7.13 (d, *J* = 7.9 Hz, 2H), 2.63-2. 56 (m, 1H), 2.29 (s, 3H), 1.920-1.80 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191. 7, 146.0, 139.7, 137.9, 134.0, 131.2, 130.1, 129.6, 129.0, 128.9, 128.3, 127.2, 127.1, 111.4 (dd, *J* = 296.9, 286.8 Hz), 43.5 (dd, *J* = 13.1, 9.1 Hz), 22.4 (t, *J* = 9.1 Hz), 21.0. ^{19}F N MR (376 MHz, Chloroform-*d*) δ -126.4 (dd, *J* = 153.5, 4.7 Hz, 1F), -130.0 (dd, *J* = 153.5, 5.1 Hz). HRMS (ESI) calcd for $C_{23}H_{19}F_2O$ $[M+H]^+$: 349.1398, found 349.1398.



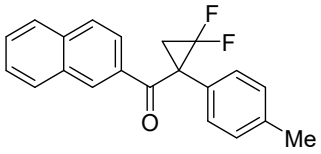
(3-chlorophenyl)(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)methanone (3y). Yellow liquid, 32 mg, 52% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.88 (t, *J* = 1.8 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.46 (ddd, *J* = 8.0, 2.2, 1.2 Hz,1H), 7.34 (t, *J* = 8.2 Hz, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.58 (ddd, *J* = 13.7, 8.0, 4.7 Hz, 1H), 2.28 (s, 3H), 1.83 (ddd, *J* = 11.8, 8.0, 5.7 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 191.1 (t, *J* = 2.3 Hz), 138.2, 137.0, 134.8, 133.1, 130.6 (d, *J* = 1.5 Hz), 129.75, 129.72, 129.3, 129.1 (t, *J* = 1.5 Hz), 127.5, 111.2 (dd, *J* = 294.8, 284.3 Hz), 43.5 (dd, *J* = 12.0, 8.3 Hz), 22.4 (dd, *J* = 9.8, 8.3 Hz), 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.7 (d, *J* = 153.42 Hz, 1F), -129.7 (d, *J* = 153.5 Hz, 1F). HRMS (ESI) calcd for $C_{17}H_{14}ClF_2O$ $[M+H]^+$: 307.0696, found 307.0682.



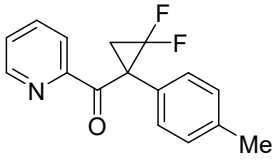
(3-bromophenyl)(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)methanone (3z). Yellow liquid, 27 mg, 39% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.06 (t, *J* = 1.7 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.61 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.36-7.27 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.60 (ddd, *J* = 13.7, 8.0, 4.7 Hz, 1H), 2.29 (s, 3H), 1.85 (ddd, *J* = 11.8, 8.0, 5.6 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 191.1 (t, *J* = 2.3 Hz), 138.2, 137.1, 136.0, 132.2, 130.6 (d, *J* = 2.3 Hz), 130.0, 129.7, 129.1 (t, *J* = 1.5 Hz), 127.9, 122.8, 111.2 (dd, *J* = 294.0, 284.3 Hz), 43.5 (dd, *J* = 13.5, 9.0 Hz), 22.4 (dd, *J* = 10.5, 9.0 Hz), 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.7 (d, *J* = 153.31 Hz, 1F), -129.6 (d, *J* = 153.3 Hz, 1F). HRMS (ESI) calcd. for $C_{17}H_{14}BrF_2O$ $[M+H]^+$: 351.0191, found 351.0182.



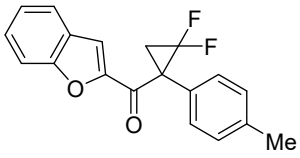
(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)(*m*-tolyl)methanone (3aa). Yellow liquid, 40 mg, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.37-7.27 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.55 (ddd, *J* = 13.7, 7.9, 4.5 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.82 (ddd, *J* = 11.8, 8.0, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.4, 138.3, 137.8, 135.4, 134.0, 131.3, 129.9, 129.5, 129.0, 128.3, 126.8, 111.3 (dd, *J* = 296.9, 286.8 Hz), 43.6 (dd, *J* = 13.1, 9.1 Hz), 22.4 (t, *J* = 10.1 Hz), 21.3, 21.0.^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.5 (d, *J* = 153.2 Hz, 1F), -130.0 (d, *J* = 153.2 Hz, 1F). HRMS (ESI) calcd for $C_{18}H_{17}F_2O$ $[M+H]^+$: 287.1242, found 287.1241.



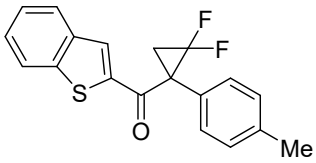
(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)(naphthalen-2-yl)methanone (3ab). Yellow liquid, 26 mg, 41% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 8.00-7.94 (m, 2H), 7.85-7.81 (m, 2H), 7.61-7.50 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.63 (ddd, *J* = 13.7, 8.0, 4.6 Hz, 1H), 2.25 (s, 3H), 1.89 (ddd, 11.9, 7.9, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.2 (t, *J* = 2.0 Hz), 137.9, 135.6, 132.7, 132.3, 131.6, 131.3, 129.7, 129.6, 129.0, 128.7, 128.3, 127.7, 126.8, 124.8, 111.5 (dd, *J* = 296.9, 286.8 Hz), 43.6 (dd, *J* = 13.1, 9.1 Hz), 22.5 (t, *J* = 10.1 Hz), 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.2 (d, *J* = 153.3 Hz, 1F), -129.8 (d, *J* = 153.3 Hz, 1F). HRMS (ESI) calcd for $C_{21}H_{17}F_2O$ $[M+H]^+$: 323.1242, found 323.1237.



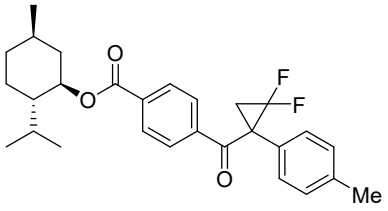
(2,2-difluoro-1-(*p* -tolyl)cyclopropyl)(pyridin-2-yl)methanone (3ac). Black solid, mp: 58-60 °C, 24 mg, 44% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 4.7 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.40-7.37 (m, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 2.48 (ddd, *J* = 12.8, 8.0, 4.4 Hz, 1H), 2.27 (s, 3H), 1.81 (ddd, *J* = 11.4, 7.9, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.7 (t, *J* = 2.0 Hz), 152.1, 149.0, 137.8, 136.6, 130.8 (d, *J* = 2.0 Hz), 130.7, 129.0, 127.0, 123.5, 110.8 (dd, *J* = 295.9, 285.8 Hz), 43.6 (dd, *J* = 12.1, 9.1 Hz), 21.7 (dd, *J* = 11.1, 10.1 Hz), 21.1.^{19}F NMR (376 MHz, Chloroform-*d*) δ -128.3(d, *J* = 153.2 Hz, 1F), -130.6 (d, *J* = 153.3 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{14}F_2NO$ $[M+H]^+$: 274.1038, found 274.1037.



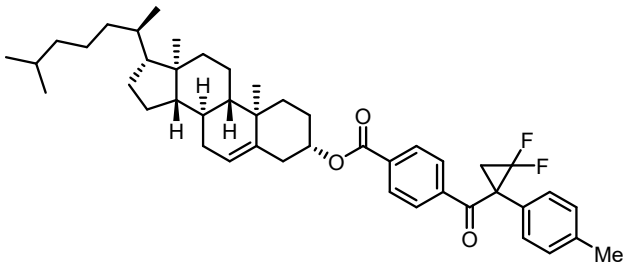
Benzofuran-2-yl(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)methanone (3ad). Yellow solid, mp: 75-76 °C,21 mg, 33% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 16.2, 8.2 Hz, 3H), 7.46 (td, *J* = 7.4, 1.2 Hz, 1H), 7.41 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.67 (q, *J* = 9.0 Hz, 1H), 2.32 (s, 3H), 1.88 (q, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.9, 155.6, 151.1, 138.5, 130.3, 129.7, 129.6, 128.6, 126.7, 123.9, 123.4, 115.8, 112.4, 111.1 (t, *J* = 291.9 Hz), 43.4 (t, *J* = 11.1 Hz), 22.4 (t, *J* = 10.1 Hz), 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -128.8 (s, 2F). HRMS (ESI) calcd for $C_{19}H_{15}F_2O_2$ $[M+H]^+$: 313.1035, found 313.1020.



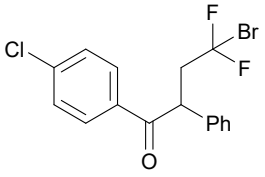
Benzo[b]thiophen-2-yl(2,2-difluoro-1-(*p*-tolyl)cyclopropyl)methanone (3ae). Yellow liquid, 24 mg, 36% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.83 (dd, *J* = 13.4, 7.9 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.44-7.34 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.63 (ddd, *J* = 13.2, 8.0, 4.9 Hz, 1H), 2.32 (s, 3H), 1.90 (ddd, *J* = 11.8, 7.9, 5.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.0 (t, *J* = 3.0 Hz), 142.6, 141.6, 138.8, 138.4, 131.8, 130.9, 129.7, 129.2, 127.7, 126.3, 125.0, 122.7, 111.2 (dd, *J* = 295.9, 287.9 Hz), 43.7 (dd, *J* = 12.1, 9.1 Hz), 23.1 (t, *J* = 10.1 Hz), 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -127.3 (d, *J* = 152.5 Hz, 1F), -129.1 (d, *J* = 152.5 Hz, 1F). HRMS (ESI) calcd for $C_{19}H_{15}F_2OS$ $[M+H]^+$: 329.0806, found 329.0805.



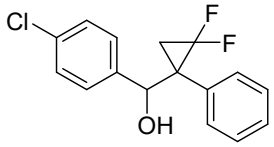
(*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-(2,2-difluoro-1-(*p*-tolyl)cyclopropane-1-carbonyl)benzoate (3af). Yellow liquid, 27 mg, 30% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.98 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.34 (d, *J* = 6.4 Hz, 2H), 7.09 (dd, *J* = 8.3, 2.3 Hz, 2H), 4.94 (tdd, *J* = 10.8, 4.1, 1.4 Hz, 1H), 2.62 (ddt, *J* = 13.0, 7.9, 4.8 Hz, 1H), 2.26 (s, 3H), 2.12-2.07 (m, 1H), 1.96-1.88 (m, 1H), 1.87-1.80 (m, 1H), 1.73 (d, *J* = 11.8 Hz, 2H), 1.58-1.51 (m, 2H), 1.15-1.07 (m, 2H), 0.93-0.90 (m, 7H), 0.91-0.88 (m, 1H), 0.78 (dd, *J* = 6.9, 2.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.8 (t, *J* = 2.0 Hz), 165.0 (t, *J* = 2.1 Hz), 138.7 (d, *J* = 4.0 Hz), 138.1, 134.6 (d, *J* = 3.0 Hz), 130.7 (dd, *J* = 5.1, 1.0 Hz), 129.7, 129.6, 129.2 (d, *J* = 2.0 Hz), 114.2 (d, *J* = 4.0 Hz), 111.3 (ddd, *J* = 290.9, 286.8, 4.0 Hz), 75.4, 47.2 (d, *J* = 1.0 Hz), 43.7 (ddd, *J* = 13.1, 9.1, 3.0 Hz), 40.8, 34.2, 31.4, 26.4 (d, *J* = 3.0 Hz), 23.5 (d, *J* = 2.0 Hz), 22.4 (t, *J* = 8.1 Hz), 22.0, 21.0, 20.7 (d, *J* = 1.0 Hz), 16.4 (d, *J* = 2.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.7 (dd, *J* = 153.5, 11.9 Hz, 1F), -129.6 (dd, *J* = 153.5, 40.6 Hz, 1F). HRMS (ESI) calcd for $C_{28}H_{33}F_2O_3$ $[M+H]^+$ 455.2392, found 455.2398.



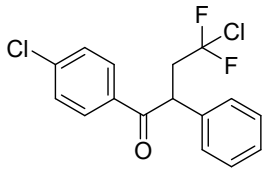
(*3S,8S,9S,10R,13R,14S,17R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*α*]phenanthren-3-yl 4-(2,2-difluoro-1-(*p*-tolyl)cyclopropane-1-carbonyl)benzoate (3ag). White solid, mp: 135-136 °C, 67 mg, 49% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 5.41 (d, *J* = 4.9 Hz, 1H), 4.90 -4.79 (m, 1H), 2.62 (ddd, *J* = 13.1, 8.0, 4.6 Hz, 1H), 2.44 (d, *J* = 8.2 Hz, 2H), 2.26 (s, 3H), 2.05-1.69 (m, 8H), 1.61-1.44 (m, 6H), 1.40-1.19 (m, 8H), 1.09-0.978 (m, 8H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.9, 164.9, 139.4, 138.8, 138.1, 134.5, 130.7, 129.7, 129.6, 129.1, 122.9, 111.3 (dd, *J* = 296.9, 286.8 Hz), 75.1, 56.7, 56.1, 50.0, 43.7 (dd, *J* = 13.1, 9.1 Hz), 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 22.4 (t, *J* = 9.1 Hz), 21.0, 19.3, 18.7, 11.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.7 (d, *J* = 153.5 Hz, 1F), -129.5 (d, *J* = 153.4 Hz, 1F). HRMS (ESI) calcd for $C_{45}H_{58}F_2NaO_3$ $[M+Na]^+$: 707.4246, found 707.4270.



4-bromo-1-(4-chlorophenyl)-4,4-difluoro-2-phenylbutan-1-one (3a-1). White solid, mp: 64-65 ^{o}C,, 50 mg, 66% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dt, *J* = 8.6, 2.6 Hz, 2H), 7.38 (dt, *J* = 8.6, 2.5 Hz, 2H), 7.34-7.22 (m, 5H), 4.92 (dd, *J* = 7.7, 4.5 Hz, 1H), 3.68 (tdd, *J* = 15.1, 12.9, 7.7 Hz, 1H), 2.80 (tdd, *J* = 15.1, 13.1, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.5, 139.9, 137.1, 134.0, 130.2, 129.4, 129.0, 128.0, 127.98, 121.5 (t, *J* = 307.0 Hz), 48.8 (t, *J* = 2.0 Hz), 47.4 (t, *J* = 21.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.8 (d, *J* = 156.7 Hz, 1F), -43.6 (d, *J* = 156.7 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{13}BrClF_2O[M+H]^+$: 372.9801, found 372.9802.



(4-chlorophenyl)(2,2-difluoro-1-phenylcyclopropyl)methanol (4). White solid, mp: 86-87 ^{o}C, 42 mg, 71% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.30-7.17 (m, 3H), 7.15 (t, *J* = 2.6 Hz, 1H), 7.02-6.98 (m, 1H), 6.88-6.84 (m, 2H), 4.77 (s, 1H), 2.34 (s, 1H), 1.84 (ddd, *J* = 13.0, 7.9, 3.9 Hz, 1H), 1.65 (ddd, *J* = 12.1, 8.0, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.5 (d, *J* = 1.0 Hz), 133.6, 132.1 (t, *J* = 2.0 Hz), 131.3 (d, *J* = 2.0 Hz), 128.1, 128.0, 127.8, 127.7, 114.0 (dd, *J* = 289.9, 287.9 Hz), 75.1 (dd, *J* = 8.1, 2.0 Hz), 41.2 (dd, *J* = 10.1, 9.1 Hz), 21.8 (t, *J* = 10.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -128.8 (d, *J* = 154.8 Hz, 1F), -137.8 (d, *J* = 154.8 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{13}ClF_2NaO$ $[M+Na]^+$: 317.0515, found 317.0515.



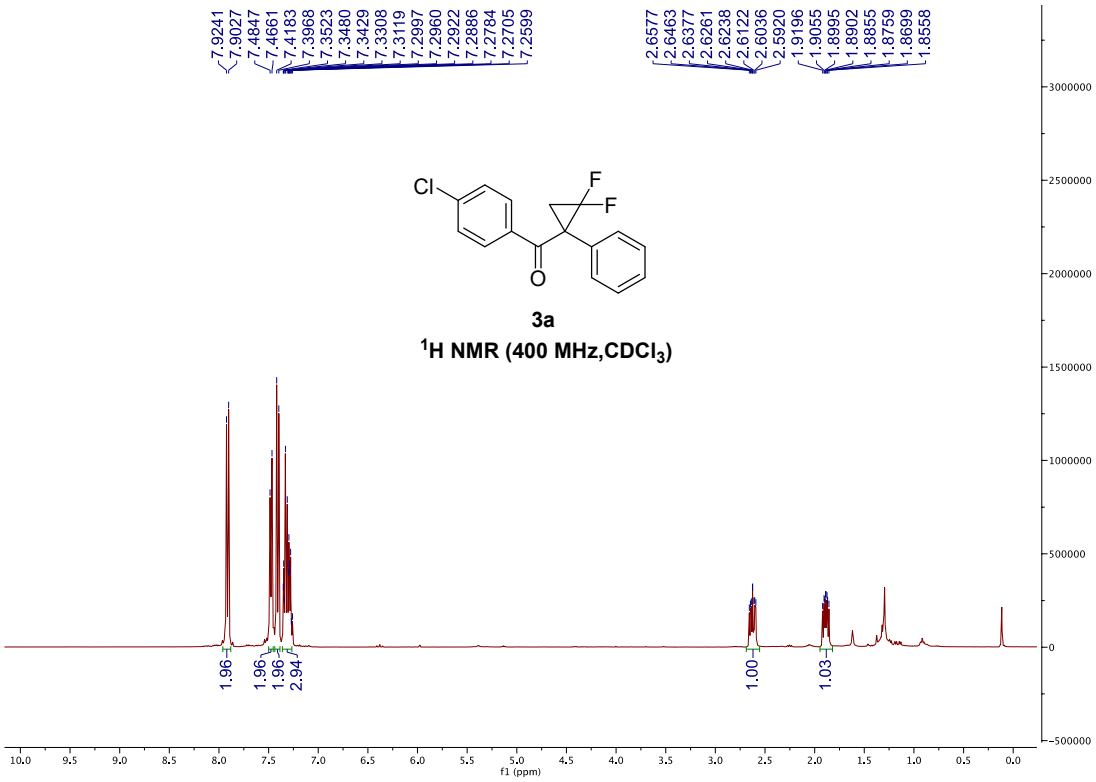
4-chloro-1-(4-chlorophenyl)-4,4-difluoro-2-phenylbutan-1-one (5). White solid, mp: 81-82 ^{o}C, 39 mg, 65% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (dt, *J* = 8.6, 1.9 Hz, 1H), 7.40 (dt, *J* = 8.6, 2.3 Hz, 2H), 7.36-7.25 (m, 5H), 4.95 (dd, *J* = 7.7, 4.6 Hz, 1H), 3.63 (ddd, *J* = 27.2, 14.6, 7.8 Hz, 1H), 2.75 (tdd, *J* = 14.7, 12.4, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.6, 139.8, 137.1, 134.0, 130.2, 129.4, 129.0, 128.8 (t, *J* = 293.9 Hz), 127.99, 127.95, 48.3 (t, *J* = 2.0 Hz), 45.0 (t, *J* = 24.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -49.5 (d, *J* = 161.3 Hz, 1F), -50.2 (d, *J* = 161.2 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{13}Cl_2F_2O$ $[M+H]^+$: 329.0306, found 329.0314.

9. References

1. Chen, L.; Jin, S. Y.; Gao, J.; Liu, T. T.; Shao, Y. B.; Feng, J.; Wang, K.; Lu, T.; Du, D., *N*-Heterocyclic Carbene/Magnesium Cocatalyzed Radical Relay Assembly of Aliphatic Keto Nitriles. *Org Lett* **2021**, *23*, 394-399.

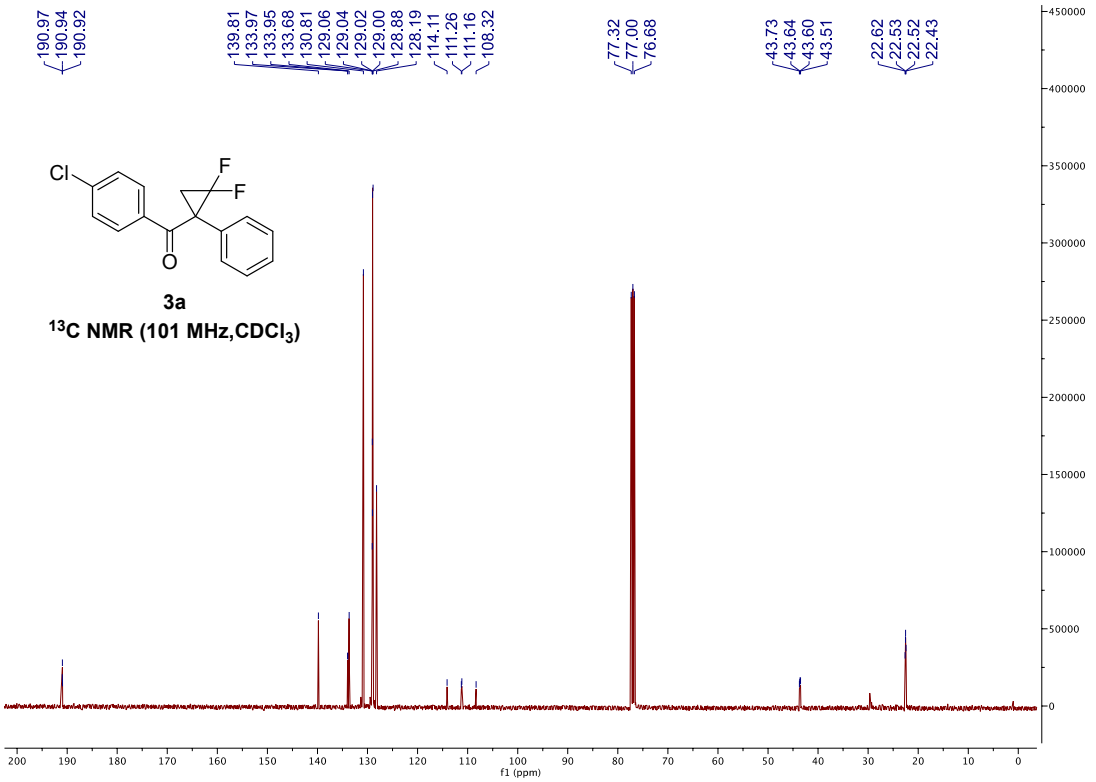
2. Xiao, J.C.; Lin, J.H.;Li, Q.; Yang, T.P.; Boron-trihalide-promoted regioselective ring-opening reactions of *gem*-difluorocyclopropyl ketones. *Chem. Commun.* **2014**, *50*, 1077-1079.

10. Copies of the NMR spectra



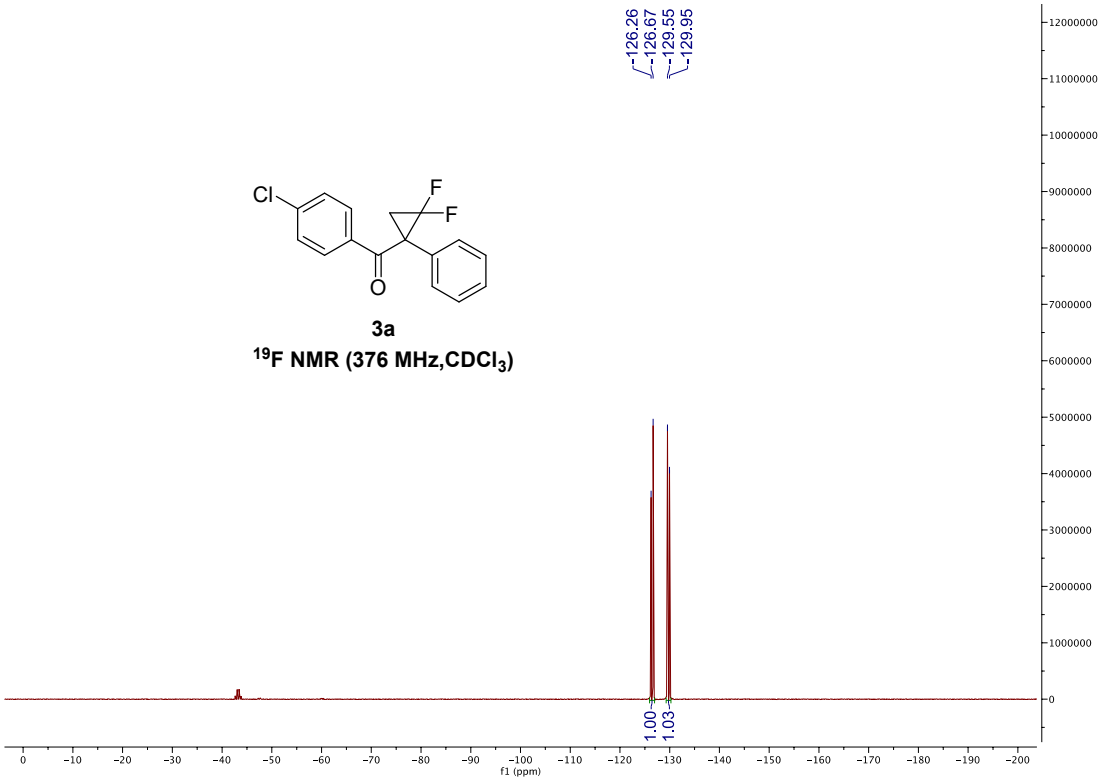
3a

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



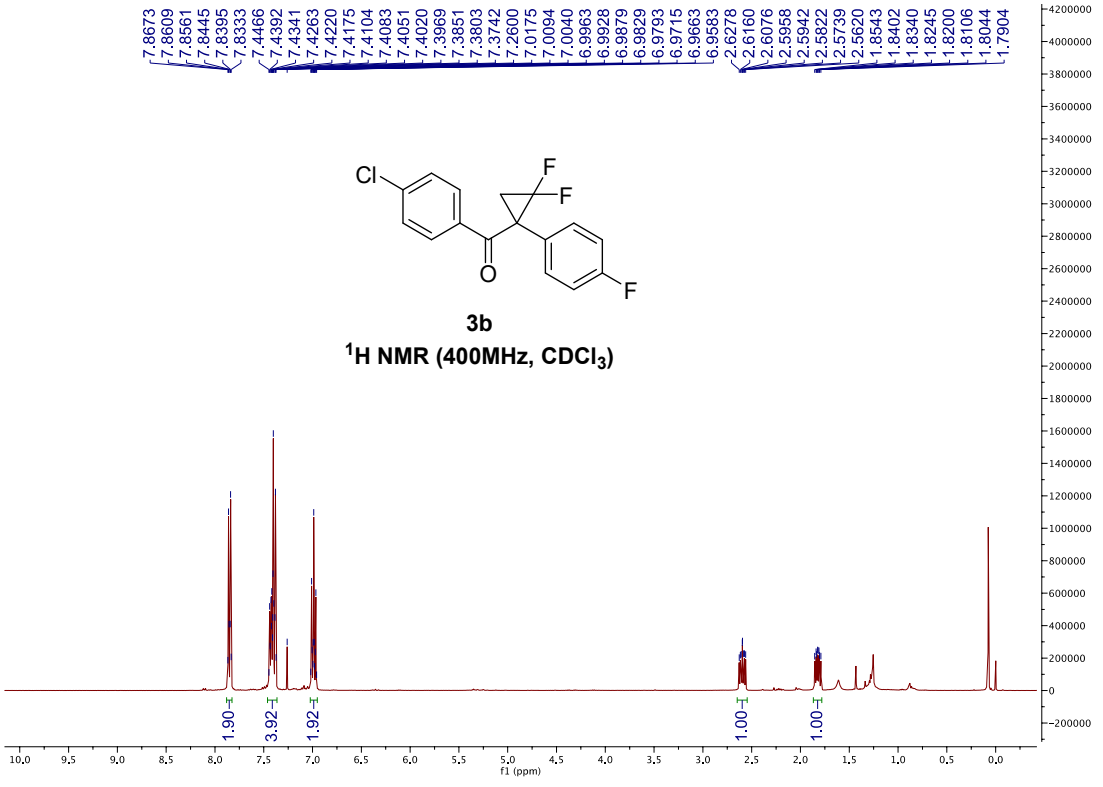
3a

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



3a

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



3b

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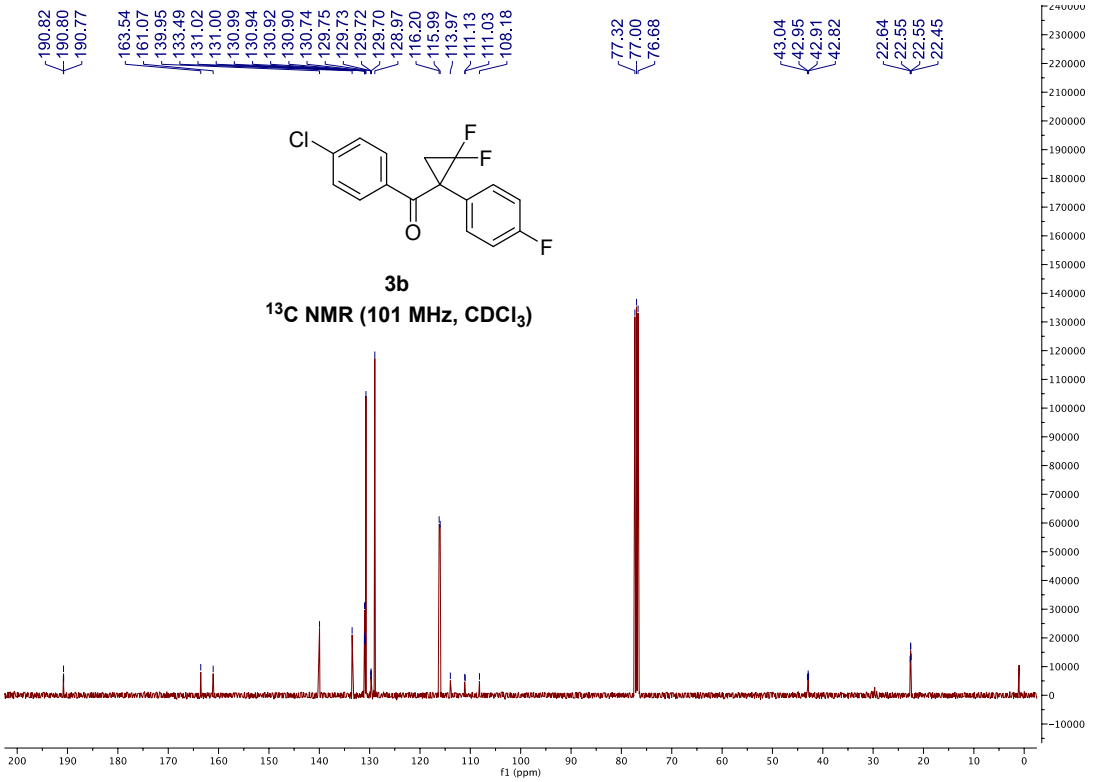

3b

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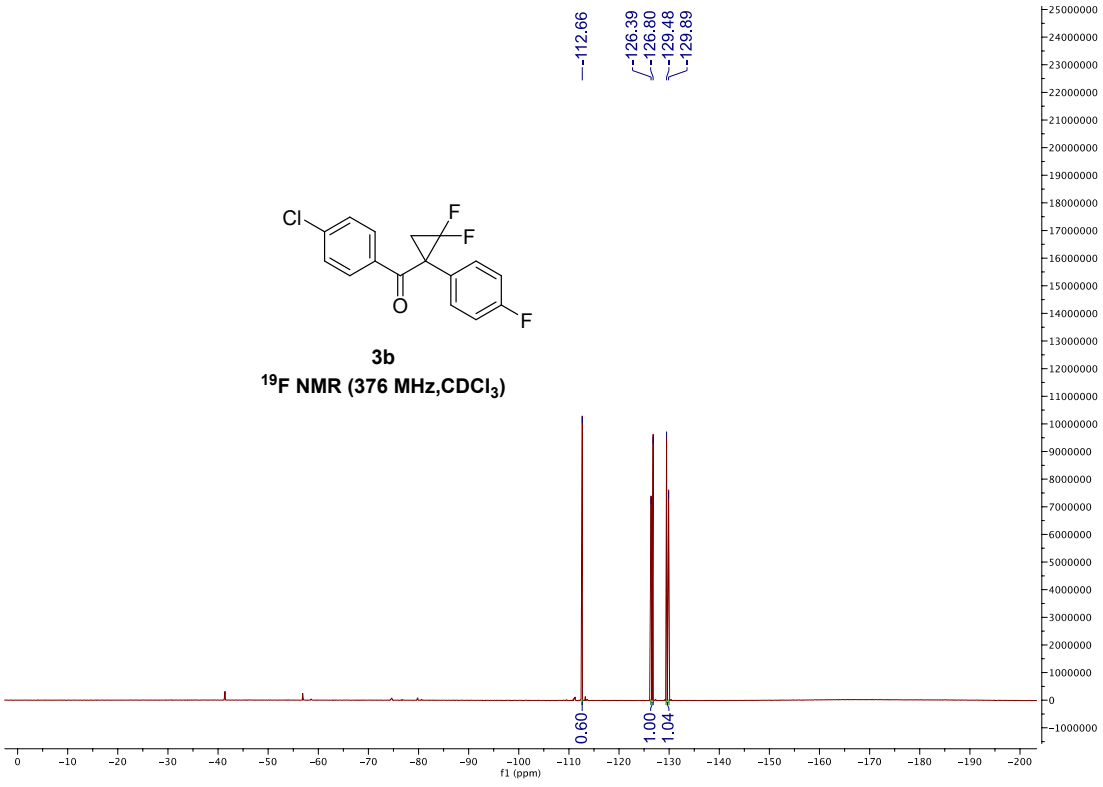

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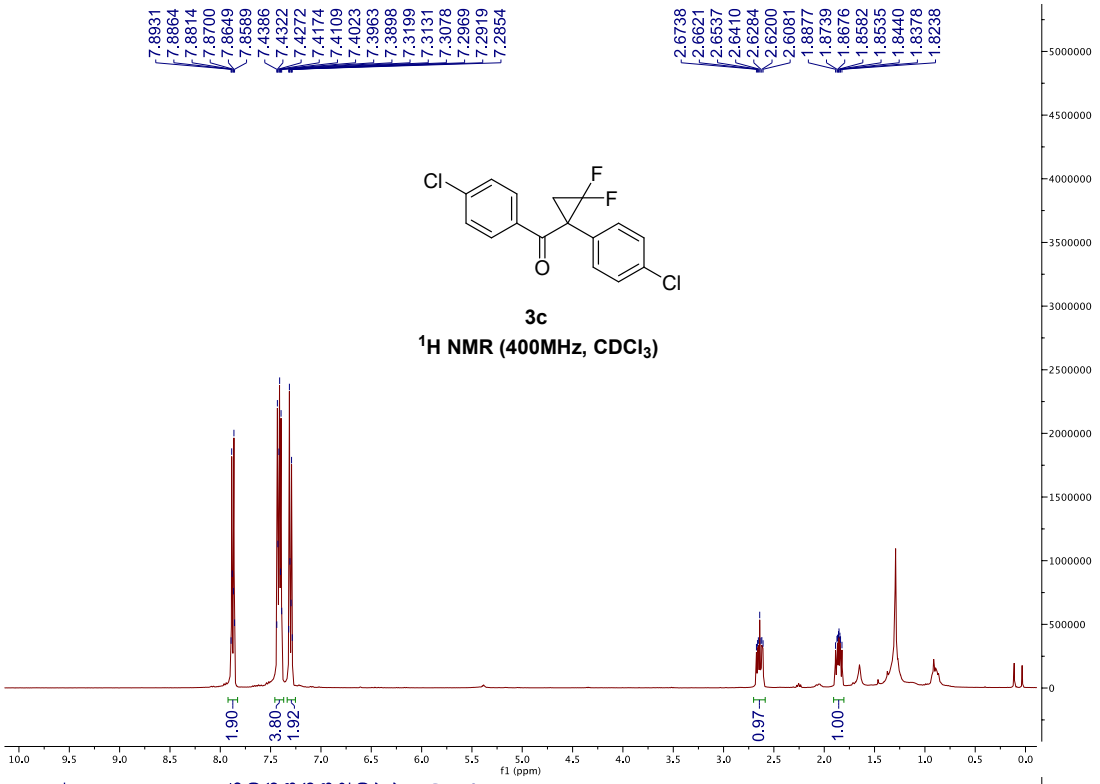
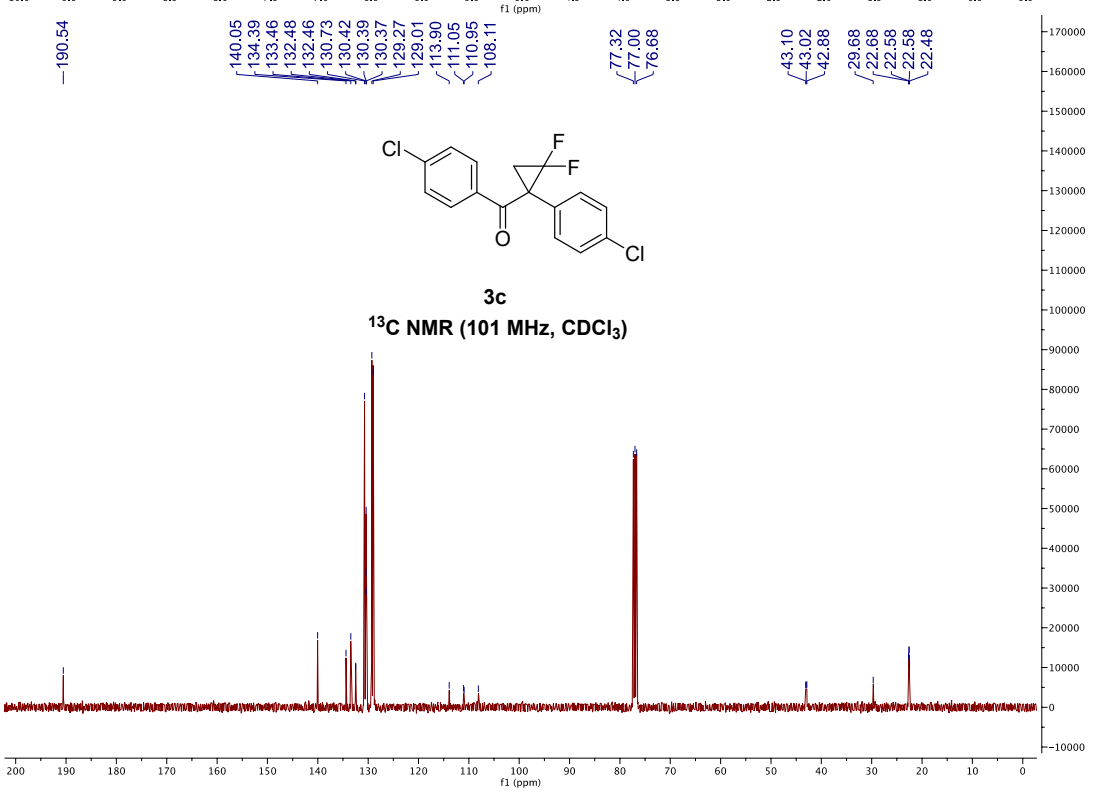


3c

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



3c

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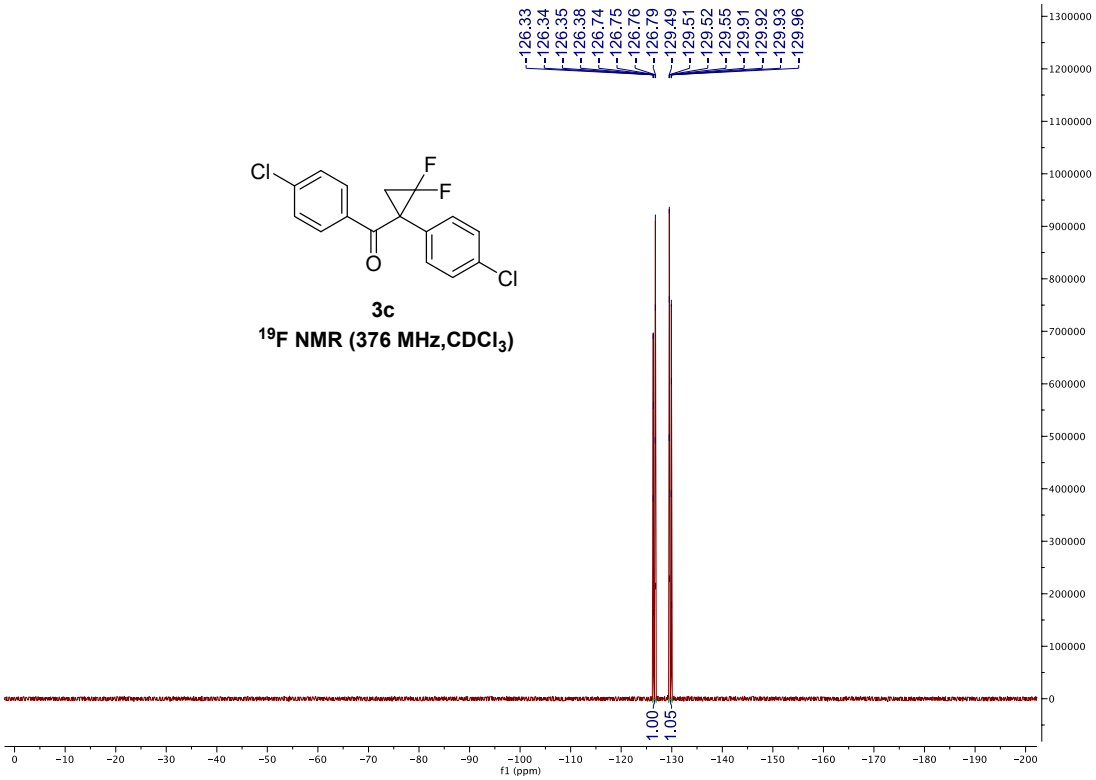

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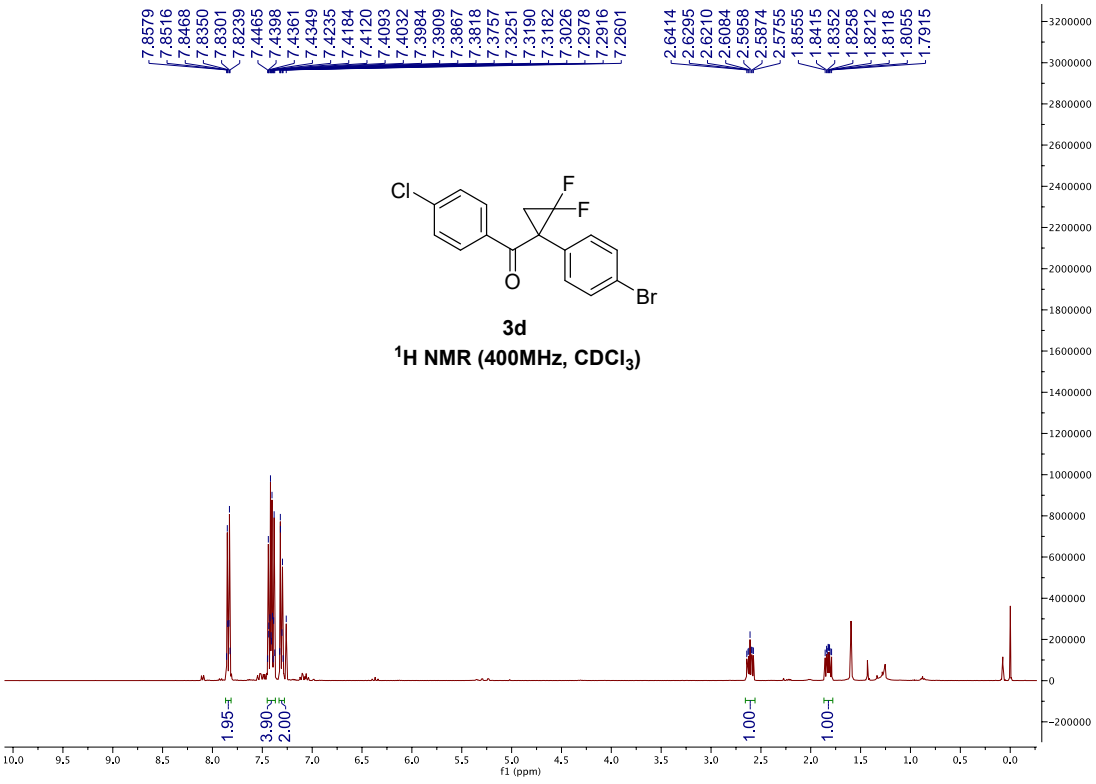

3d

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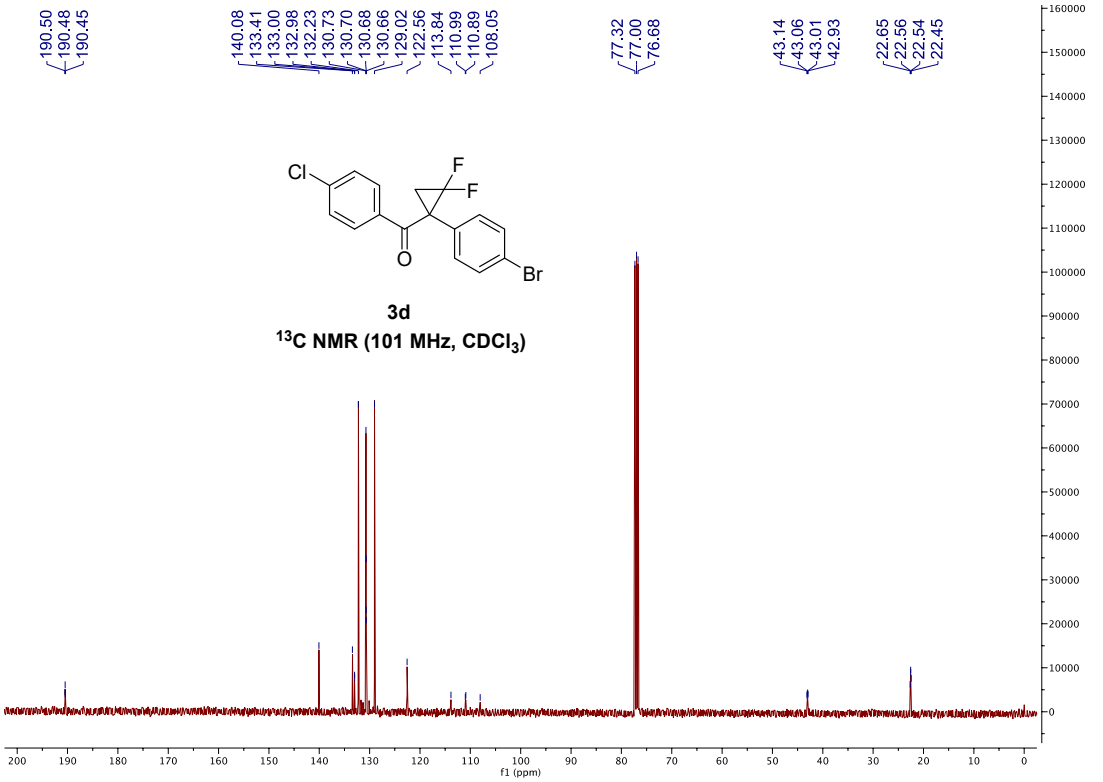

3d

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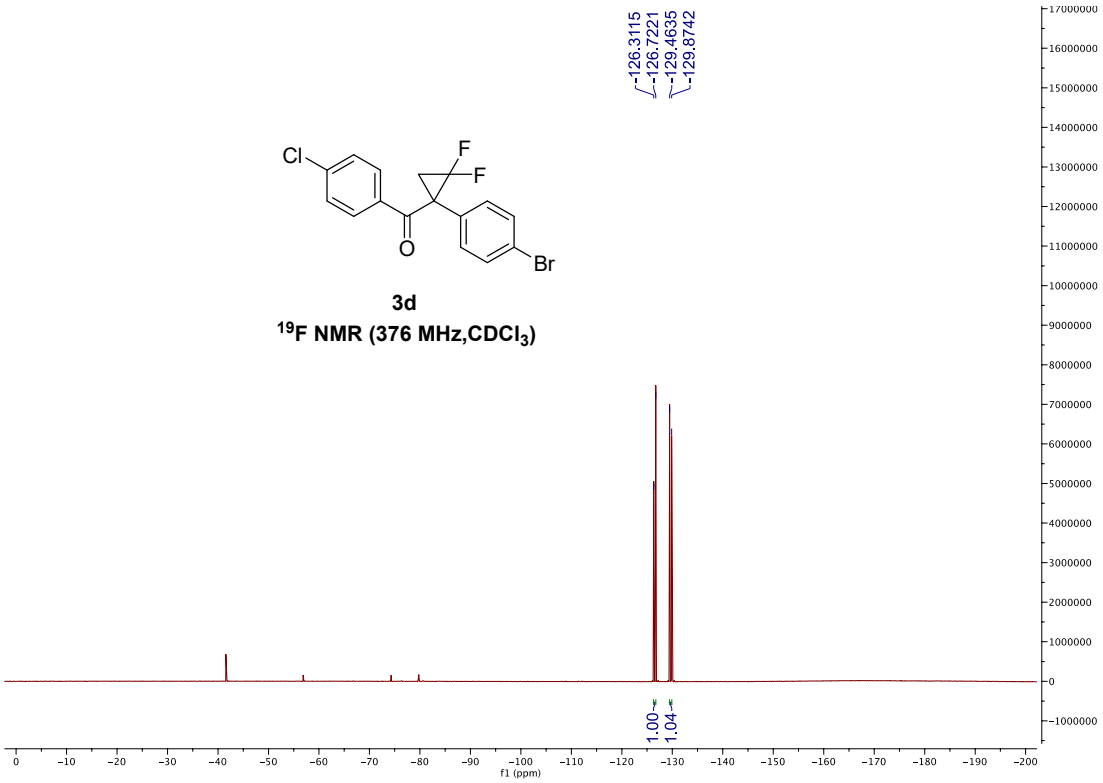

3d

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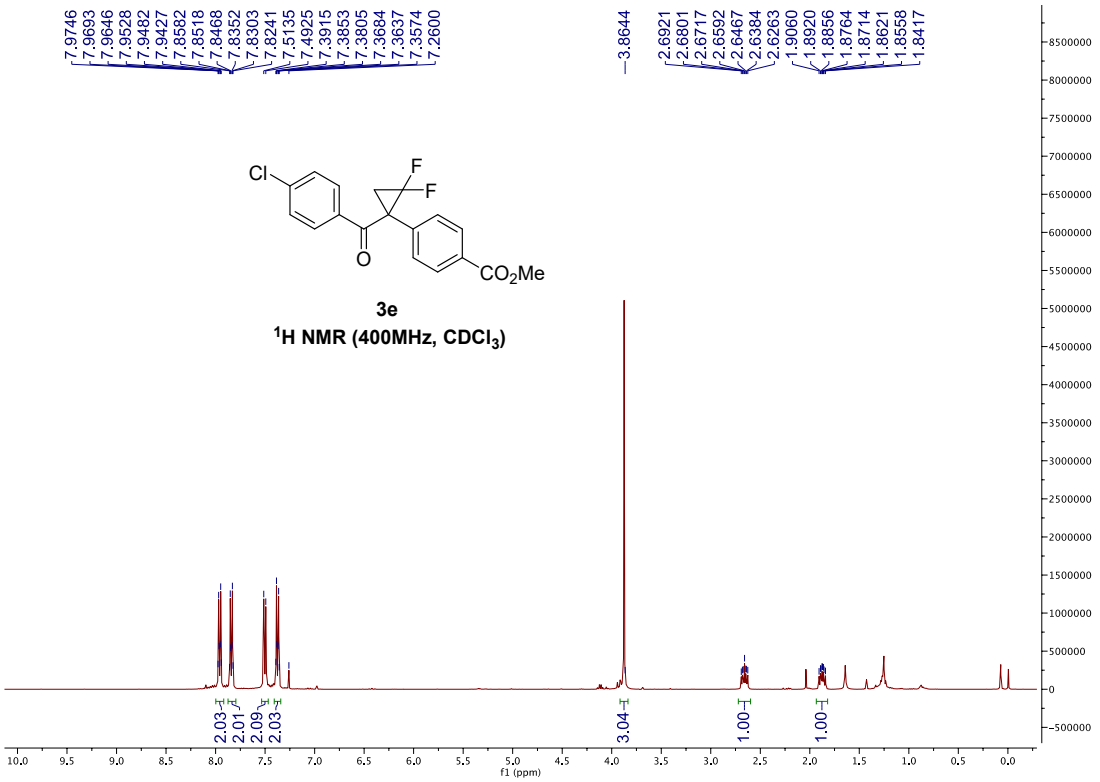

3e

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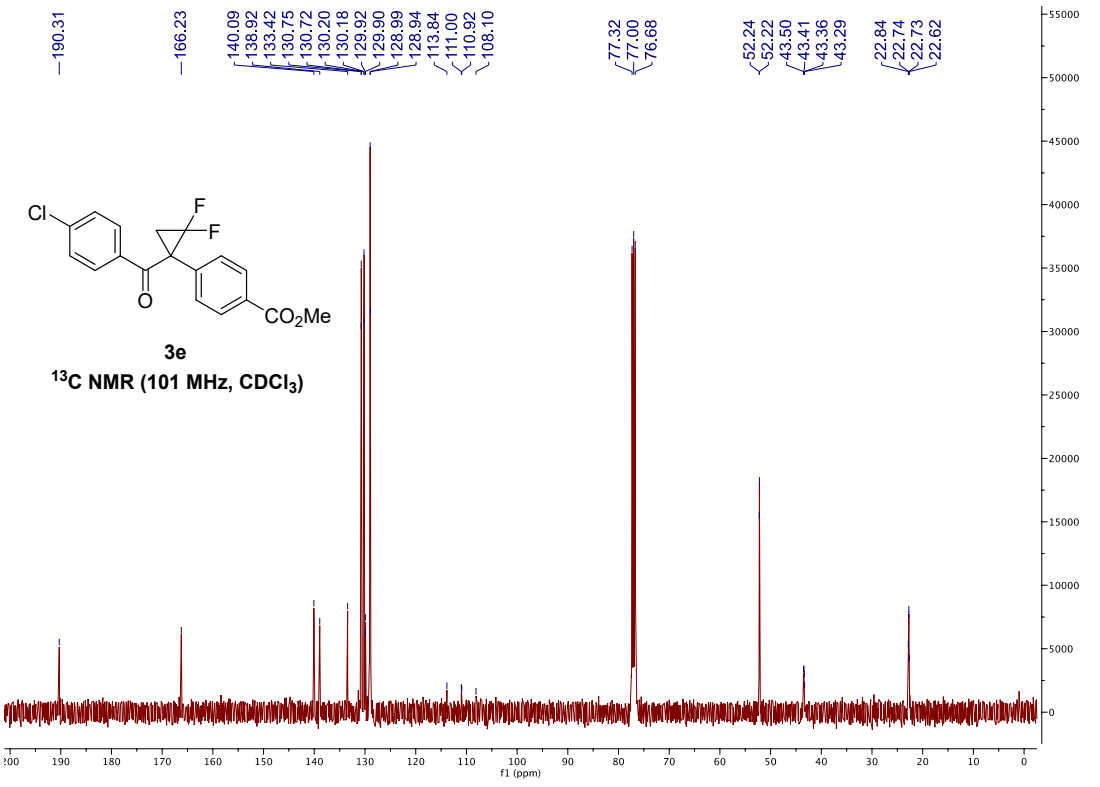

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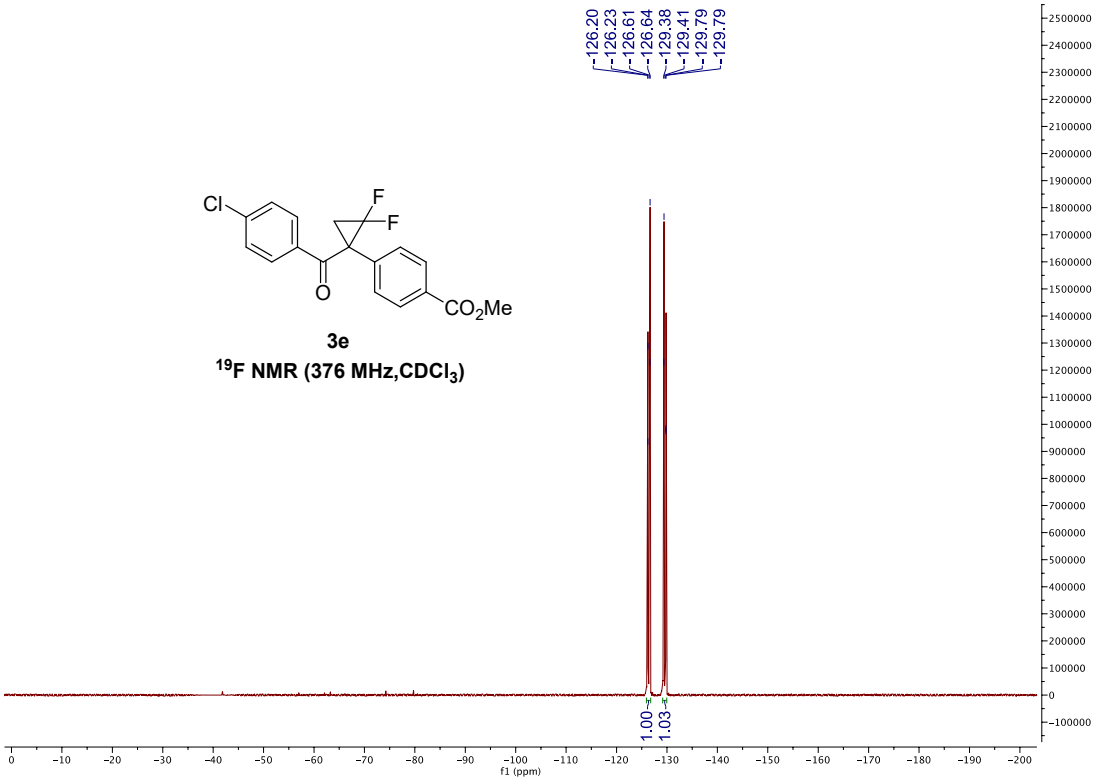

3e

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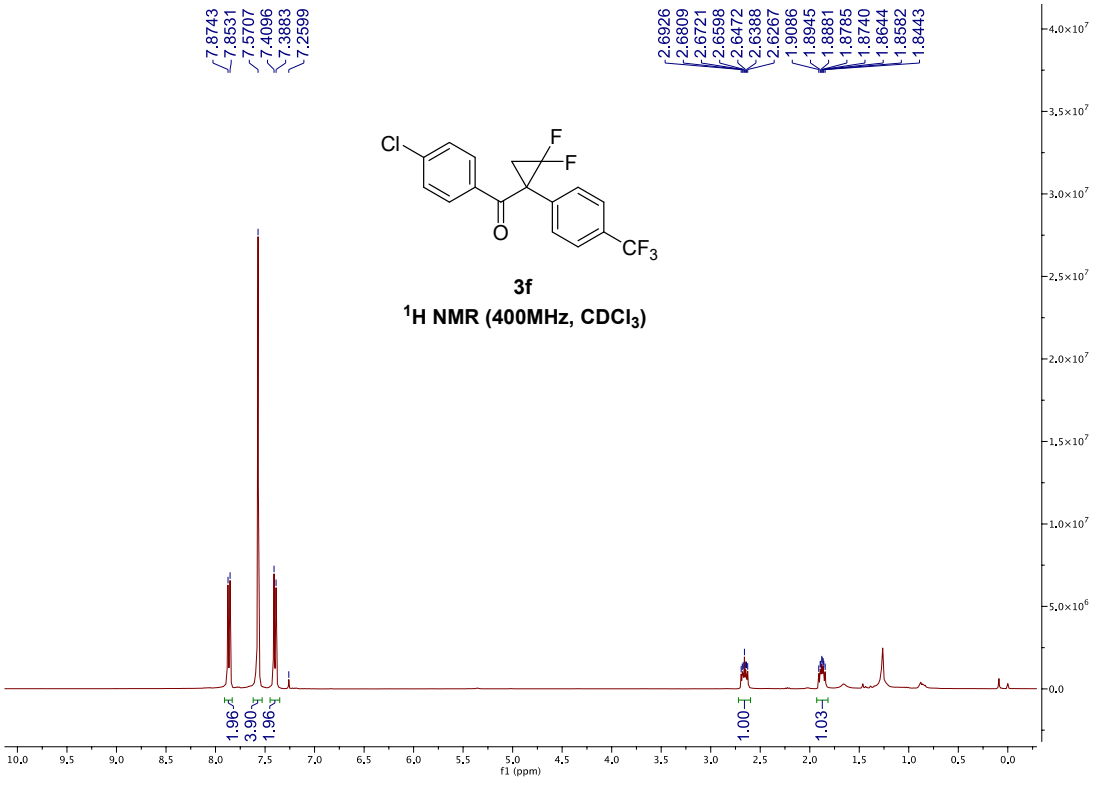

3f

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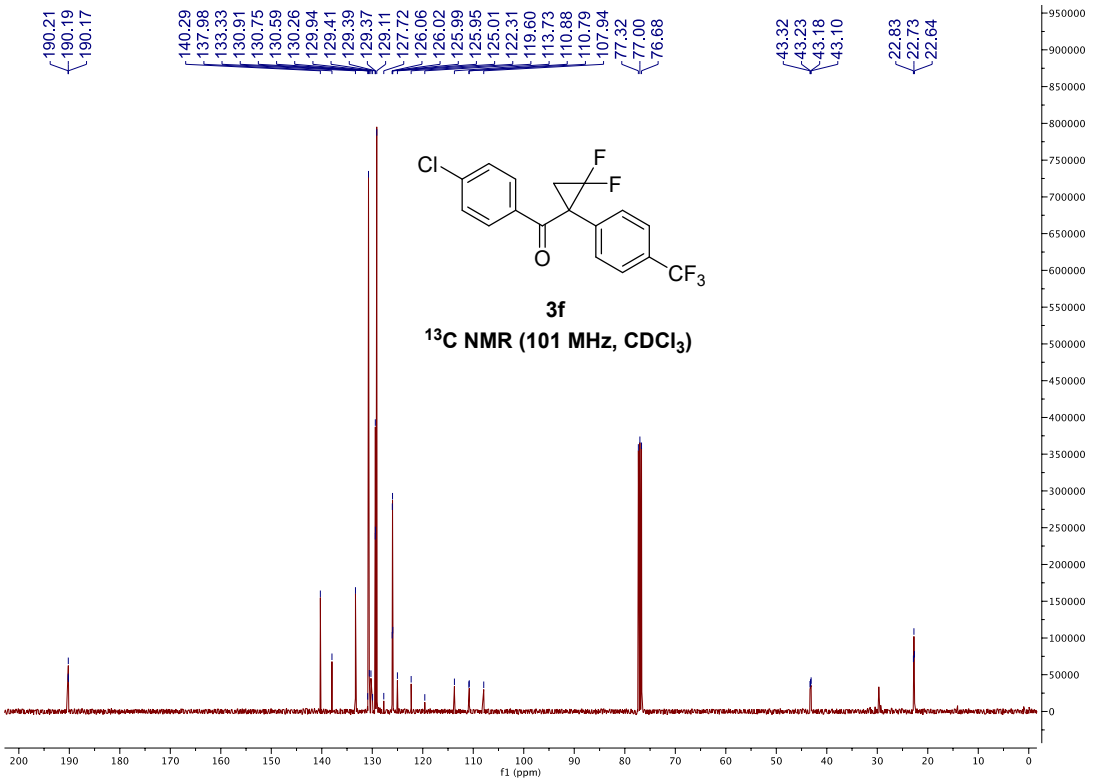

3f

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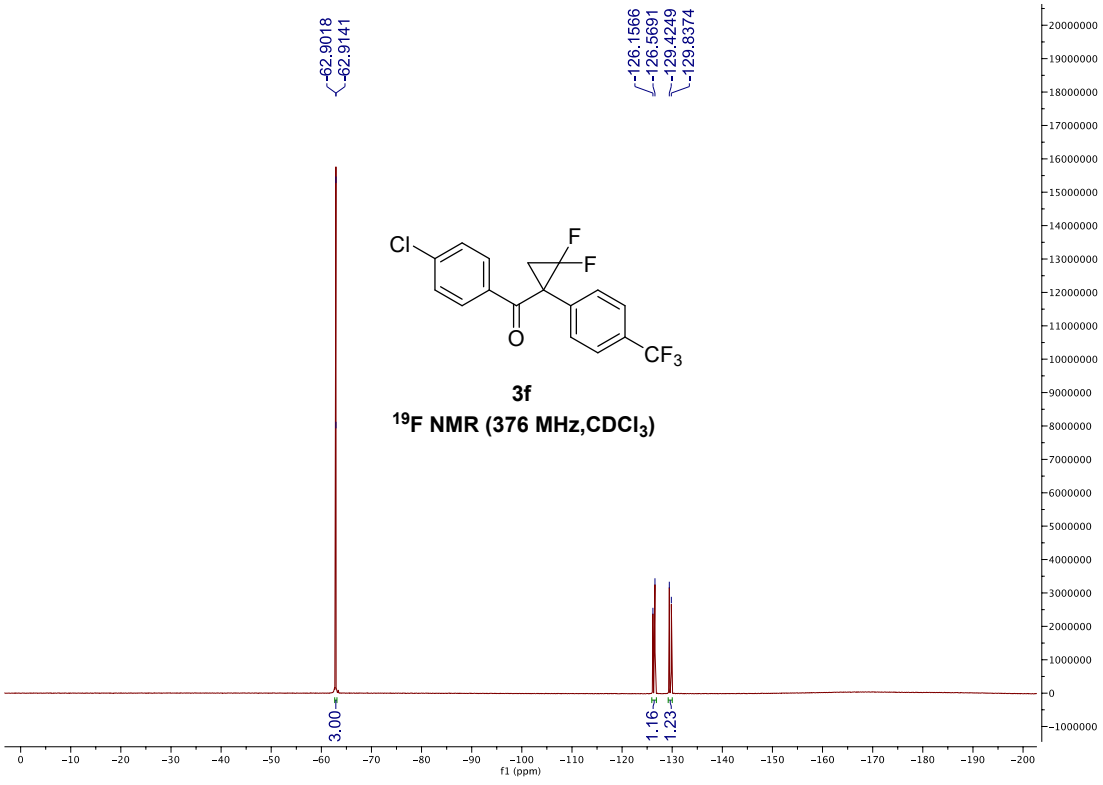

3f

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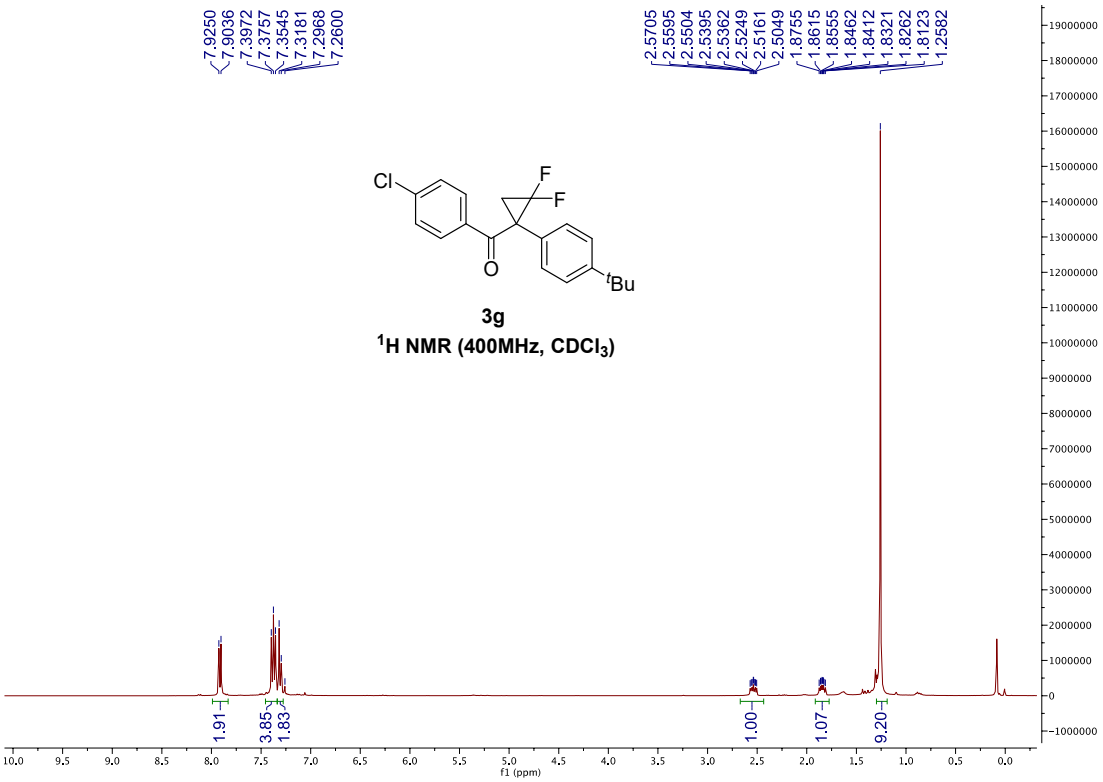

3g

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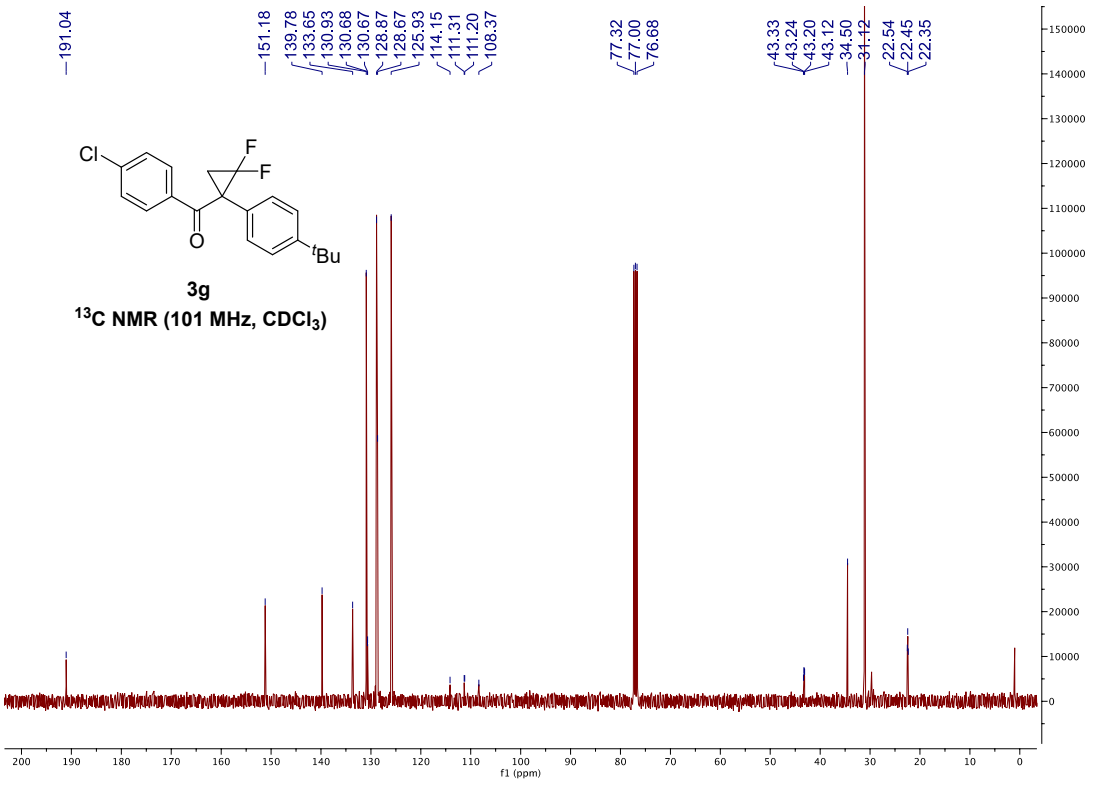

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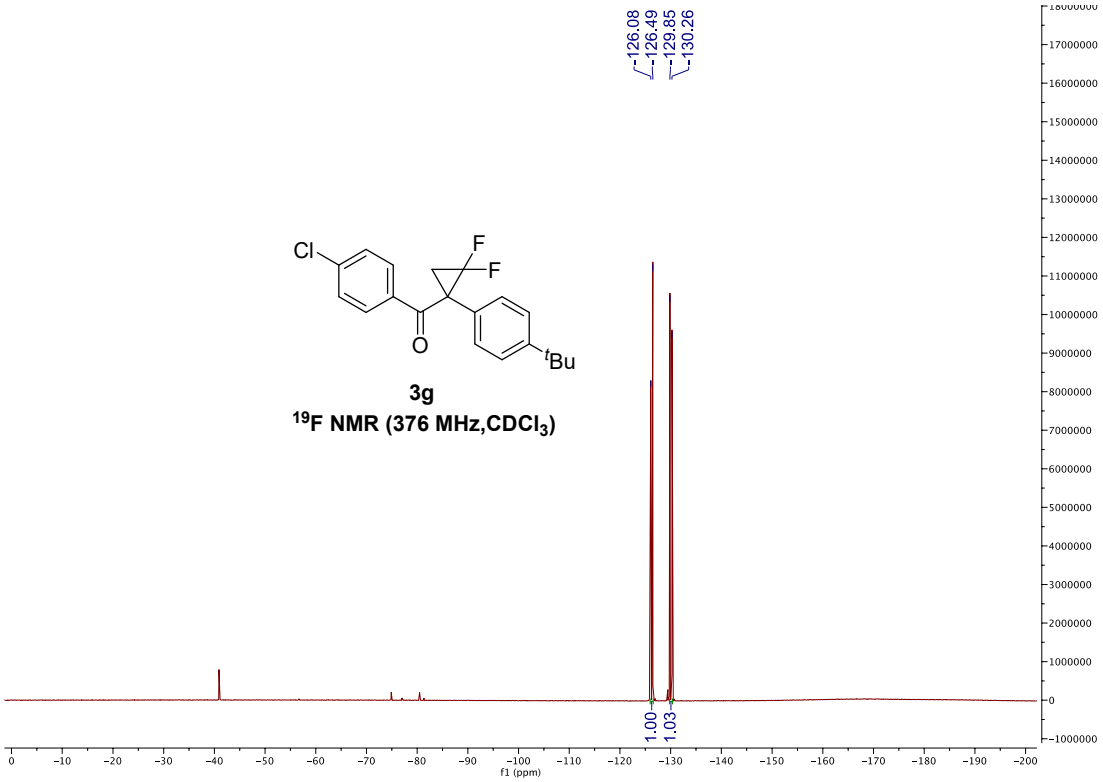

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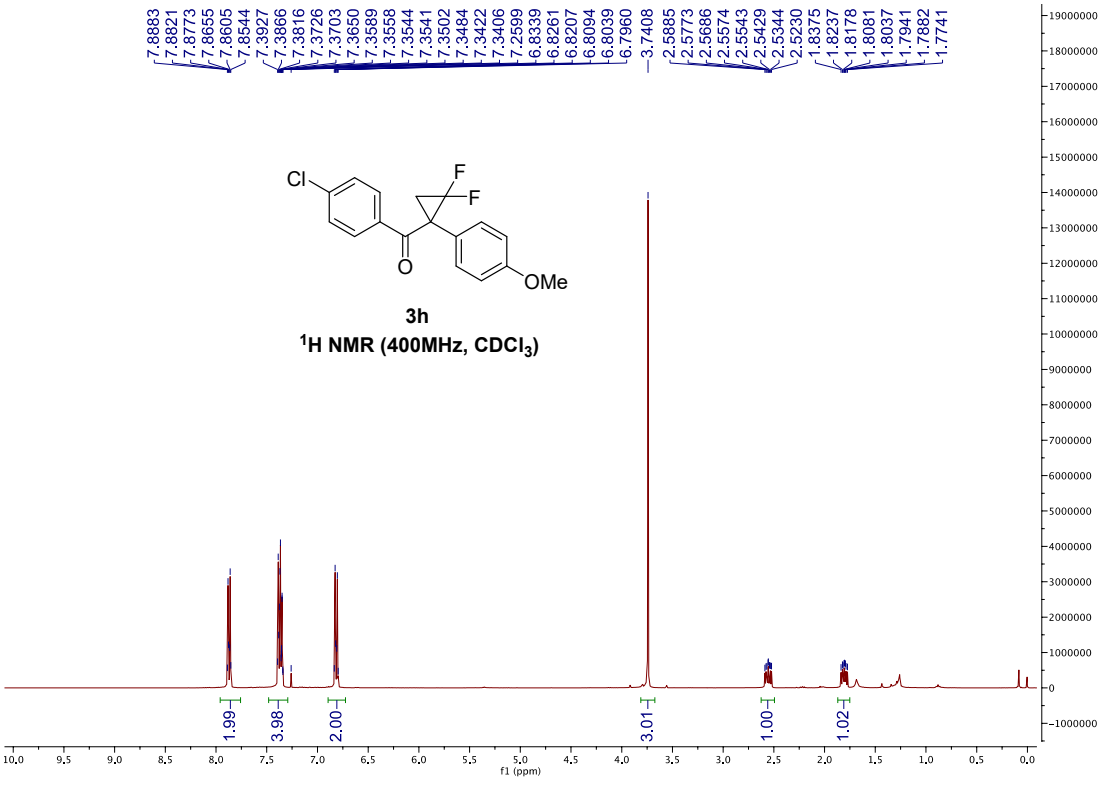

3h

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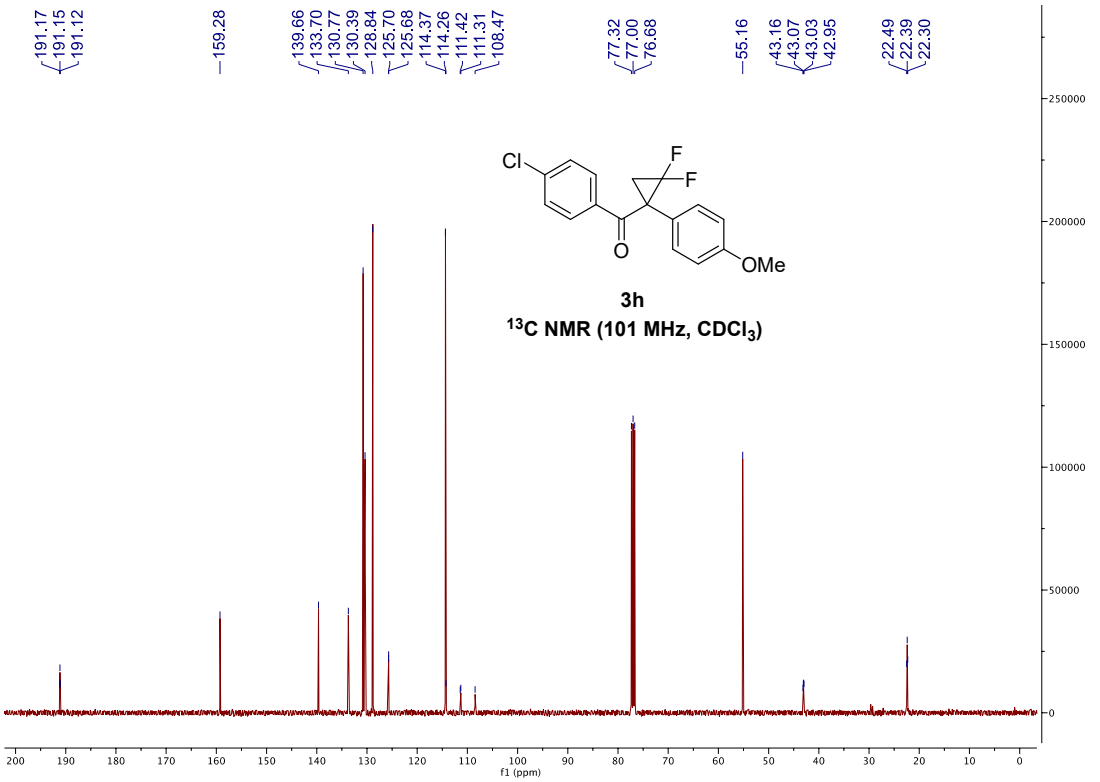

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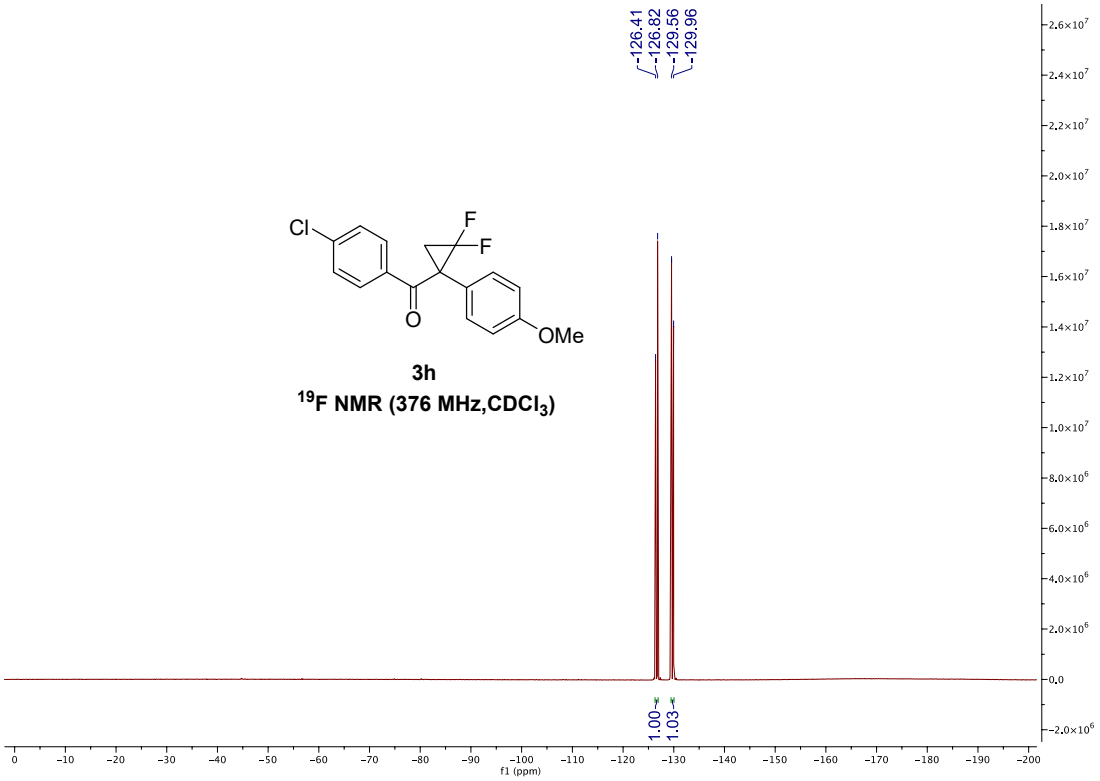

3h

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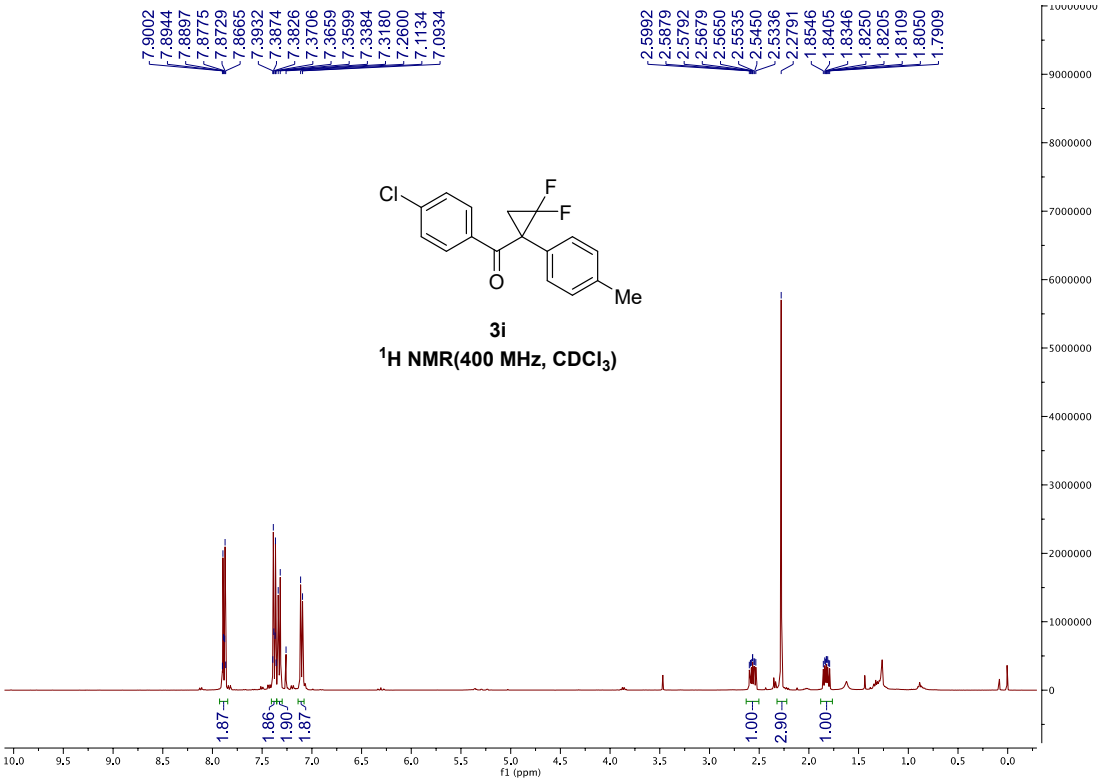

3i

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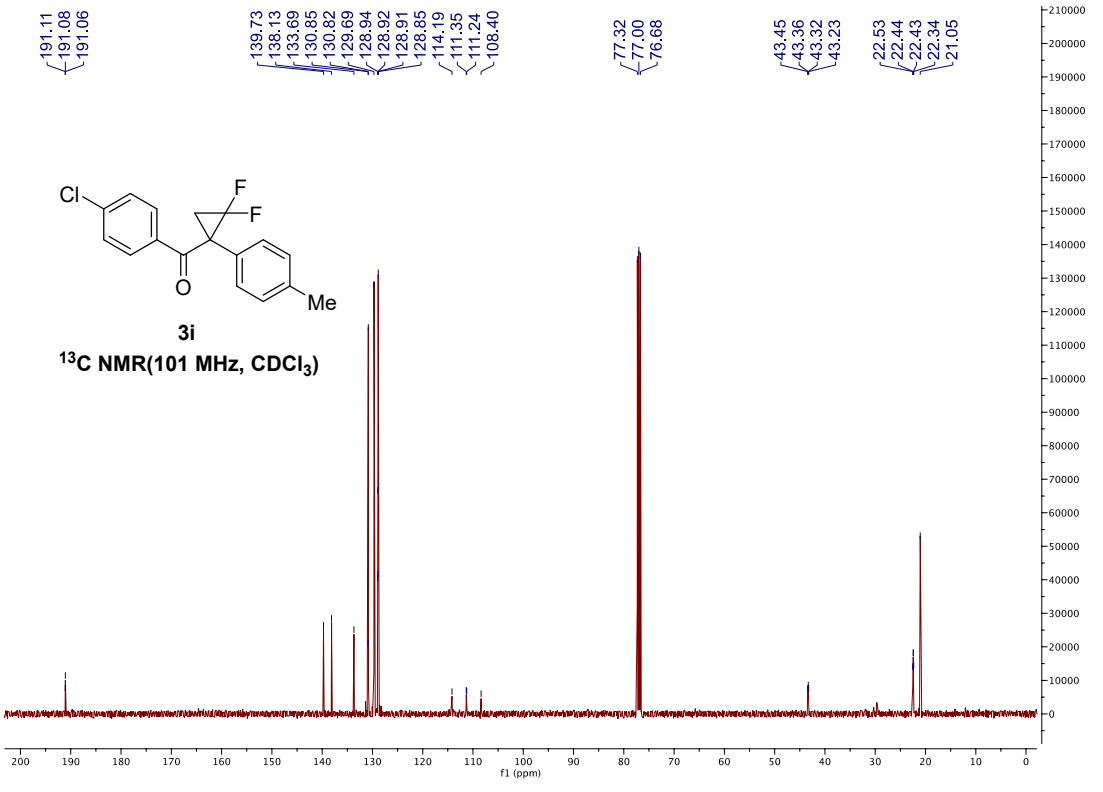

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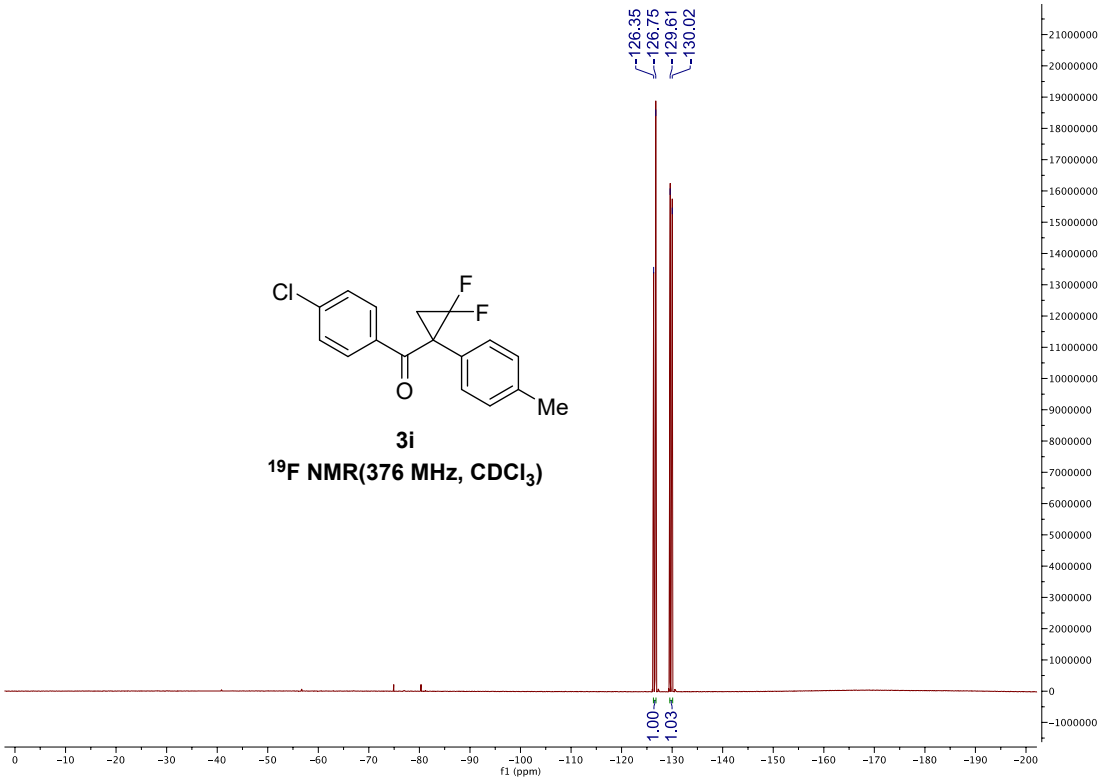

3i

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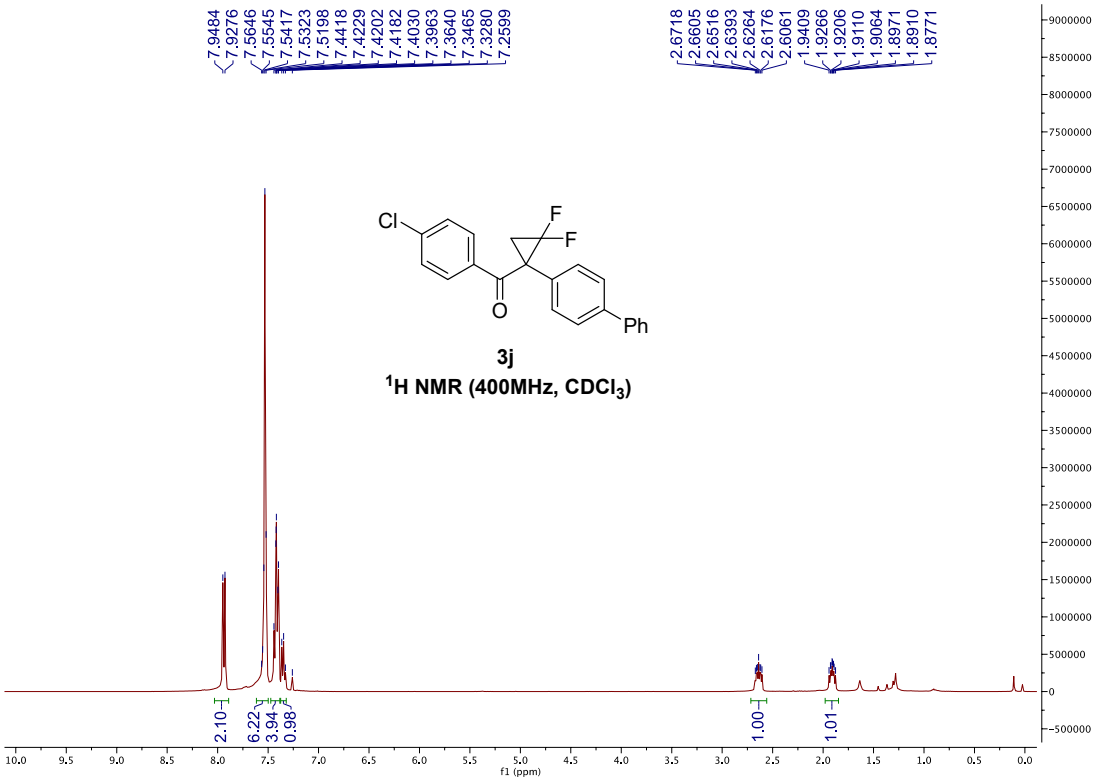

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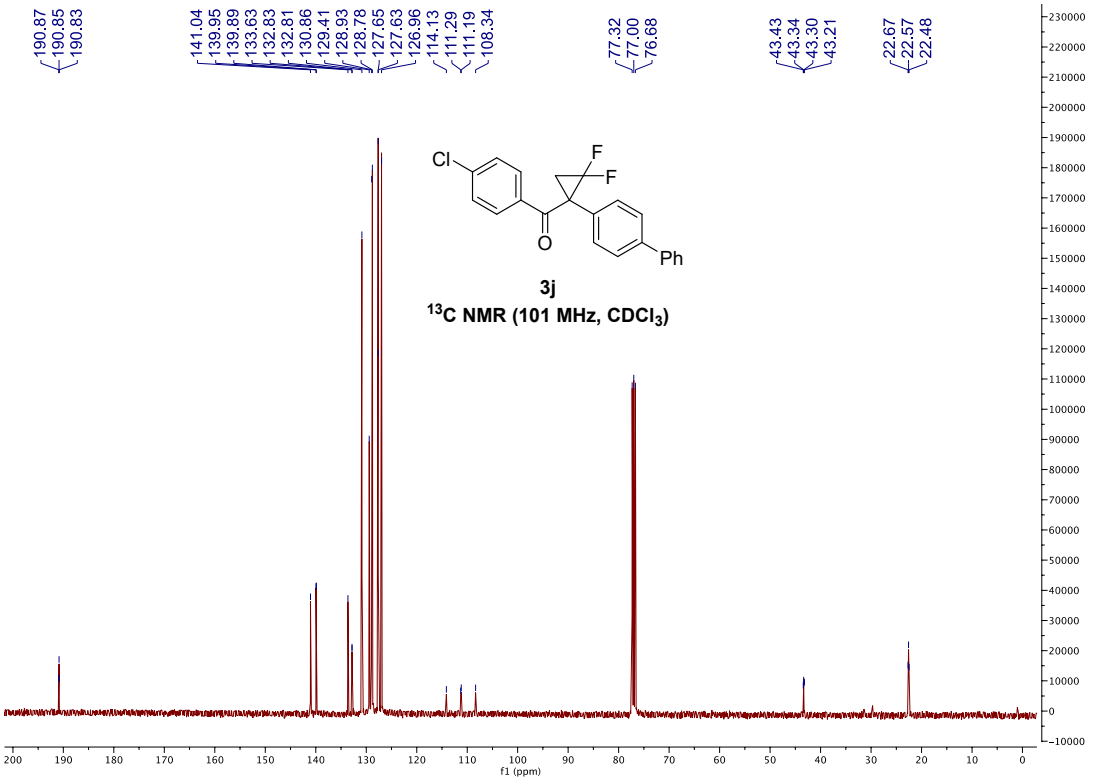

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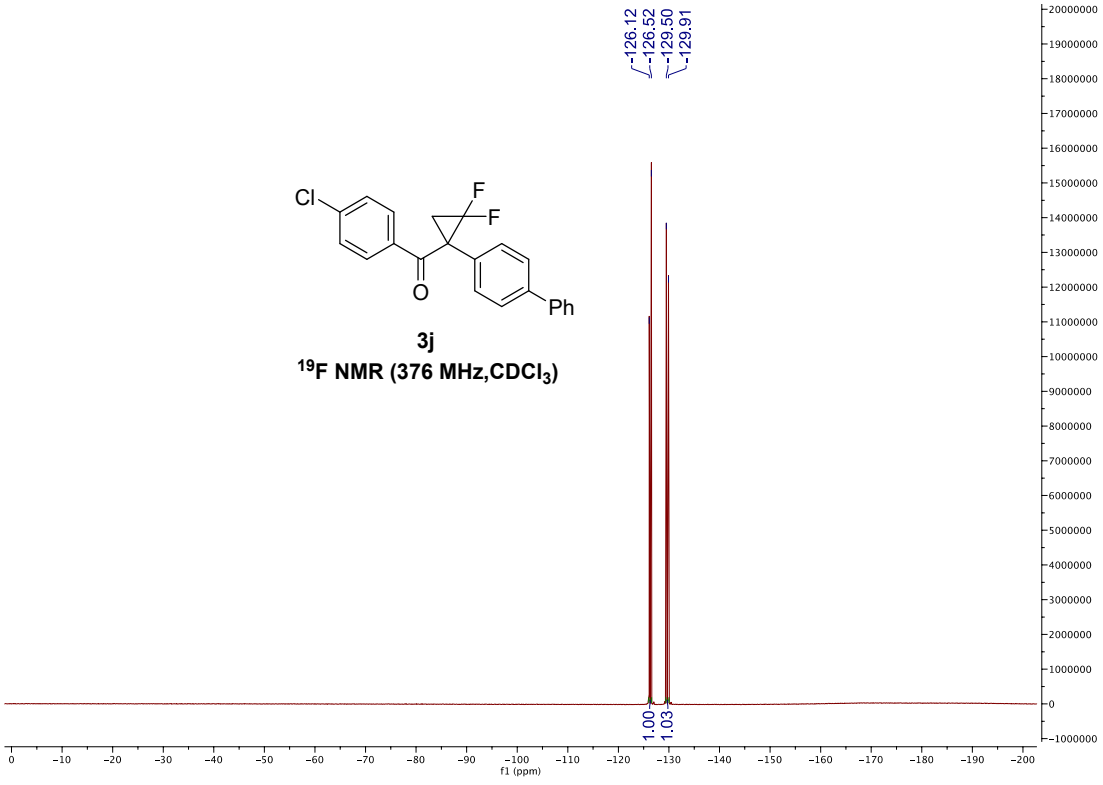

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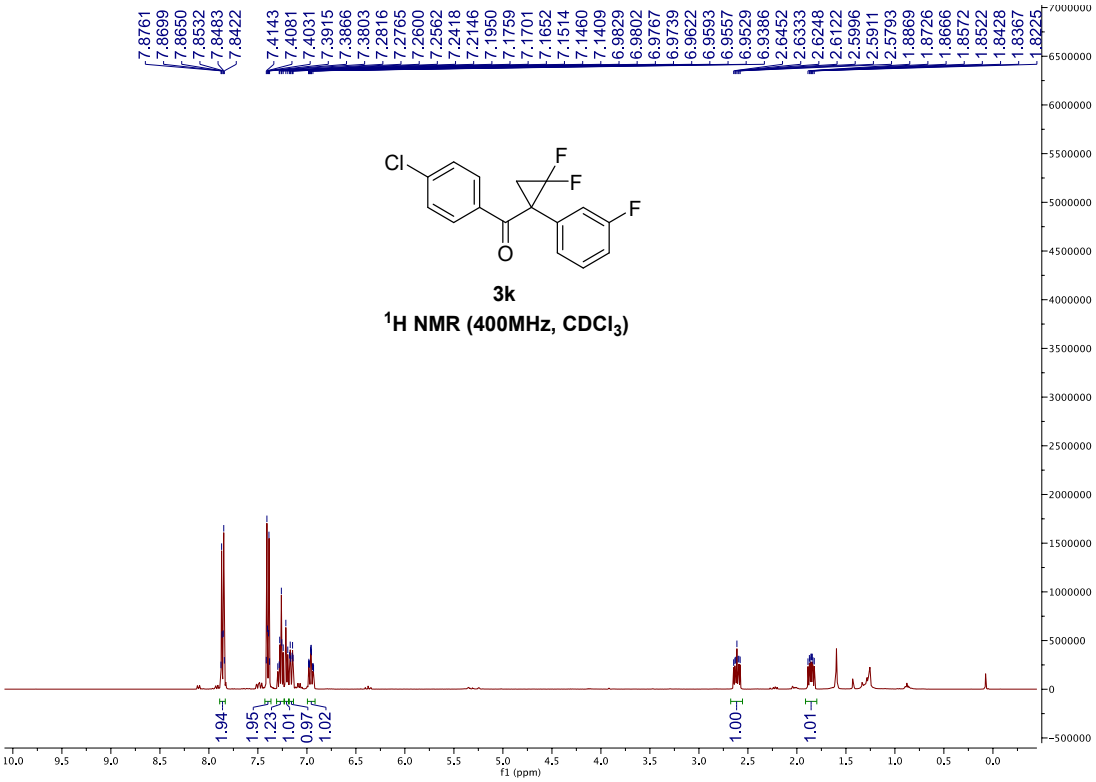

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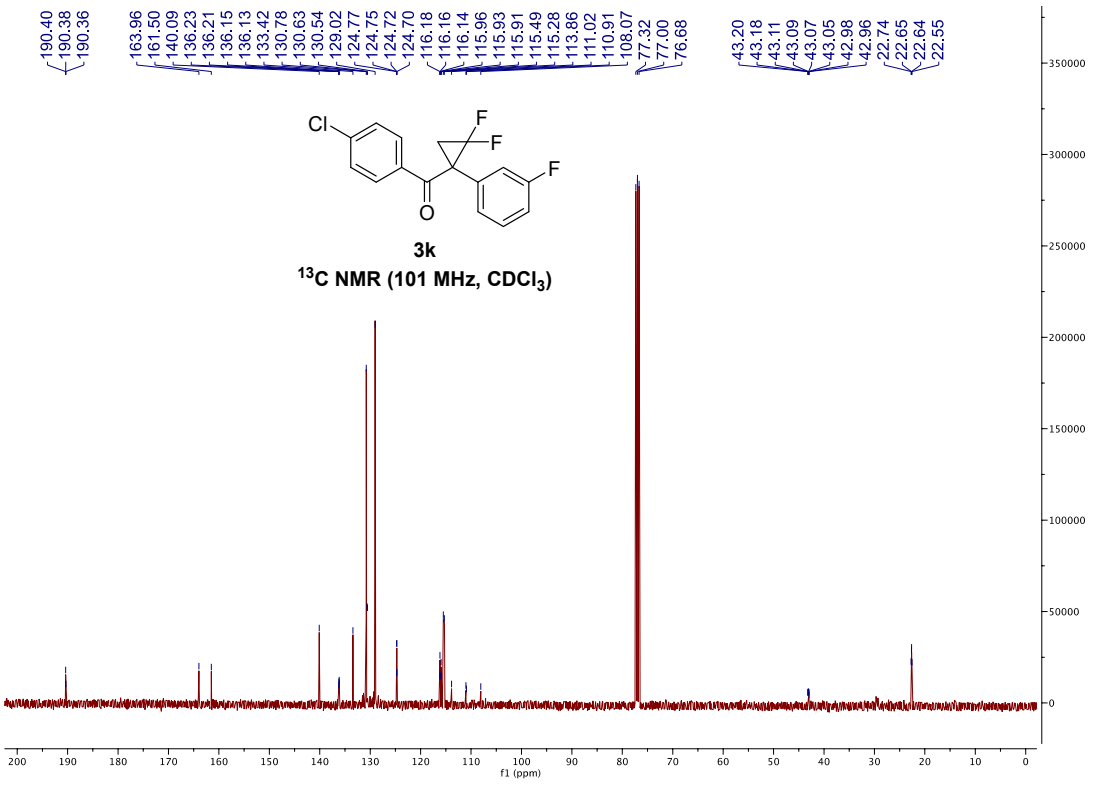

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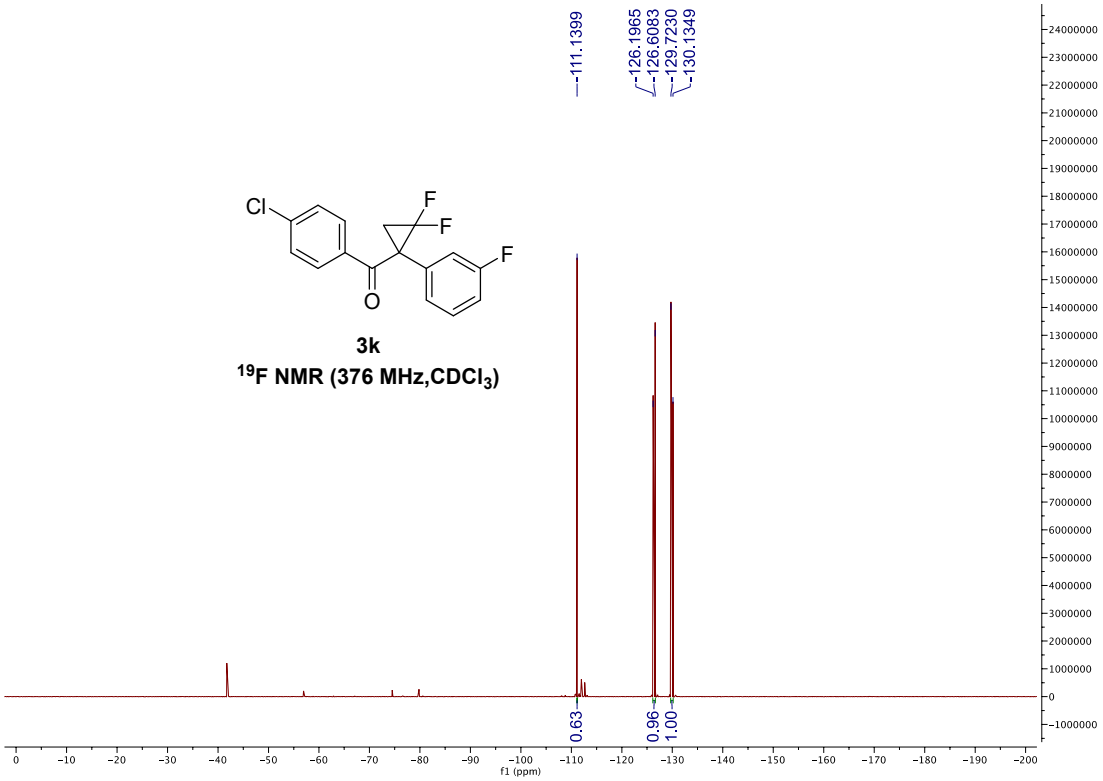

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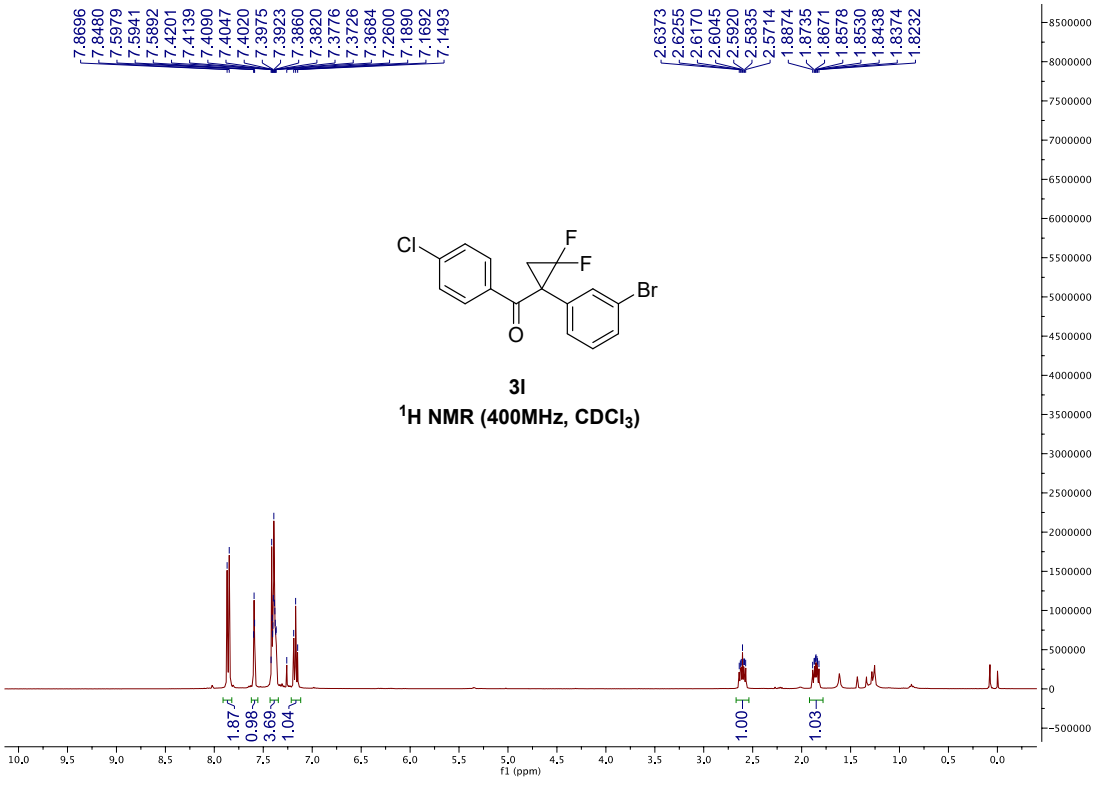

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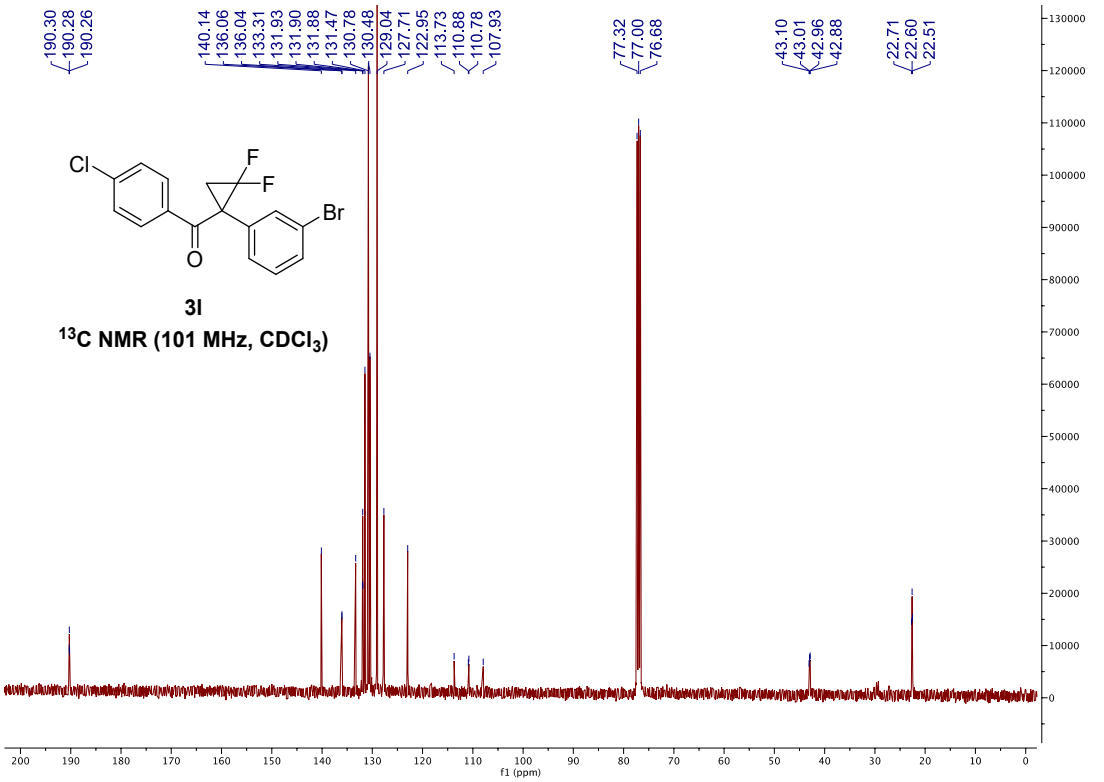

3l

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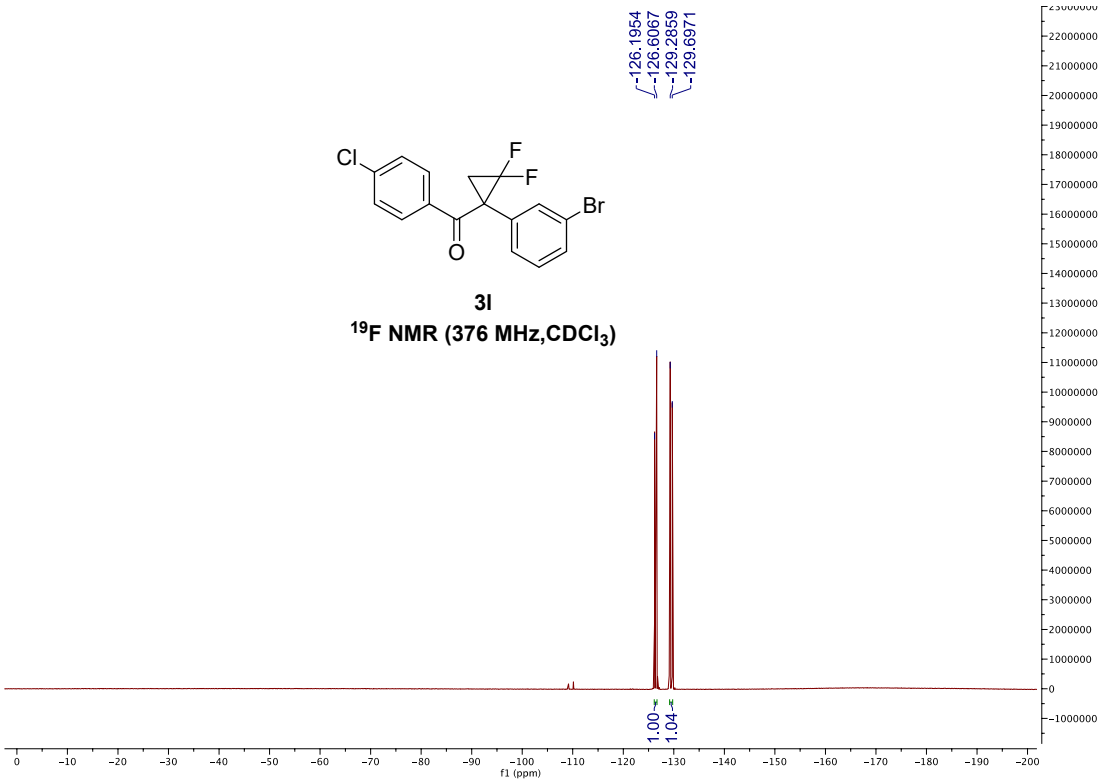

3l

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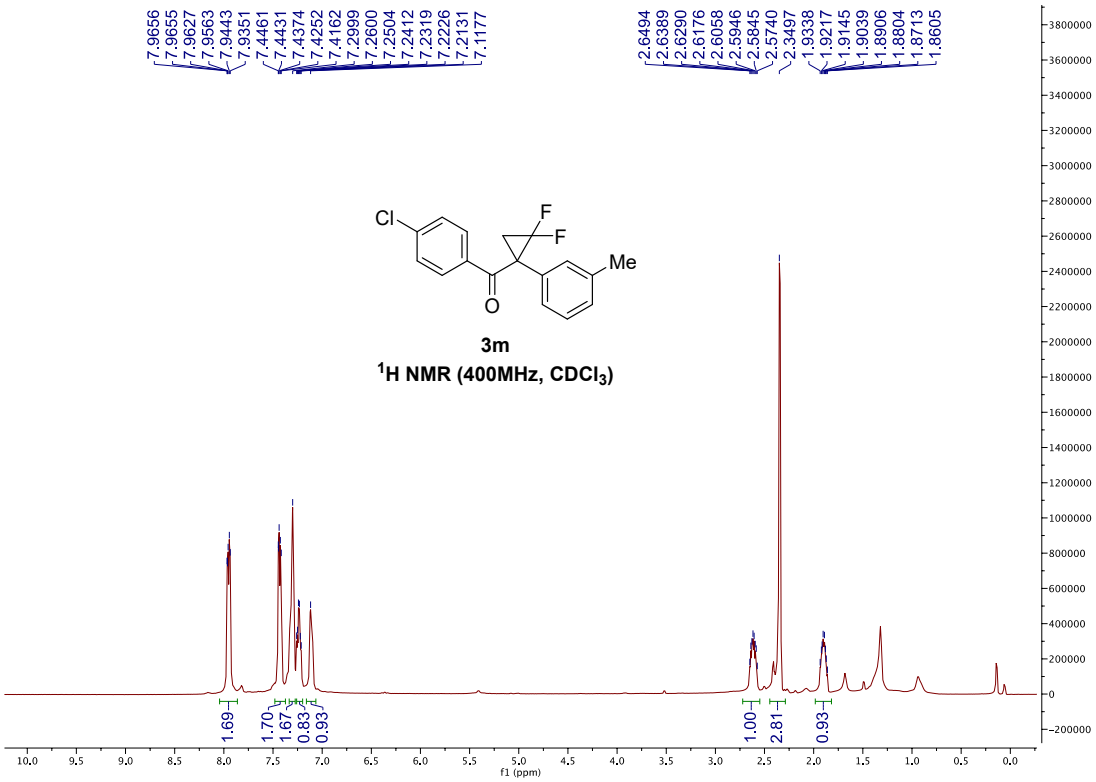
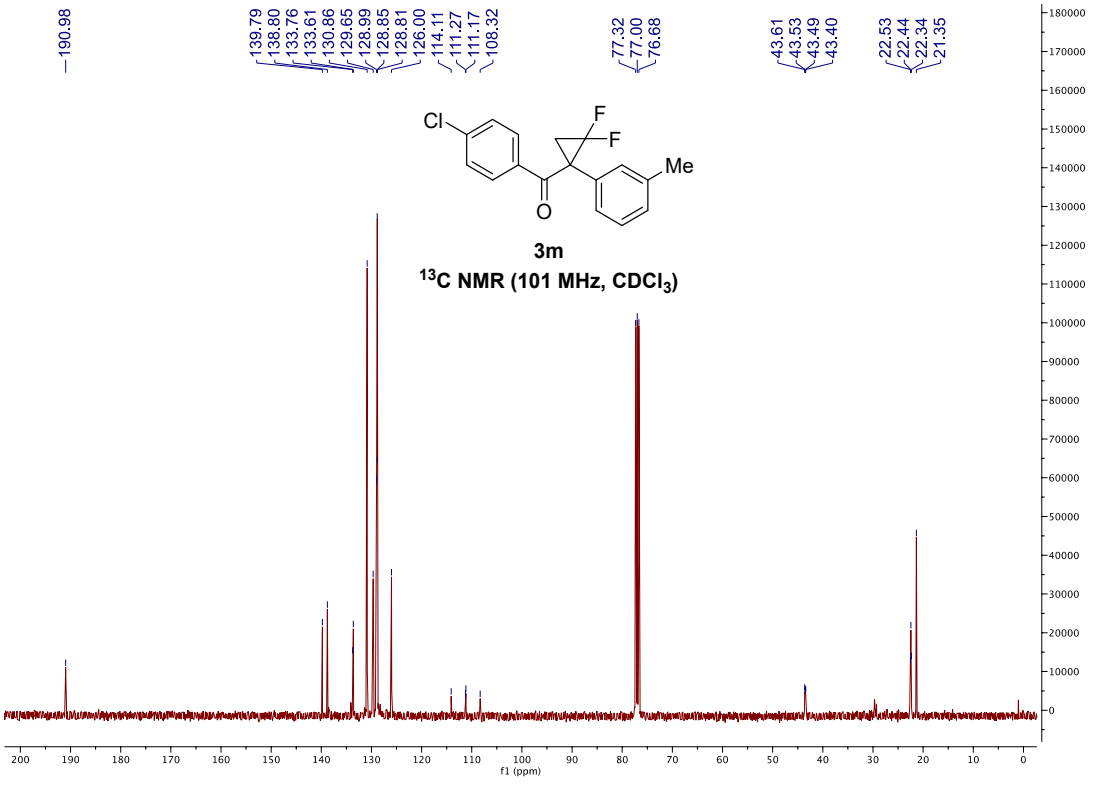


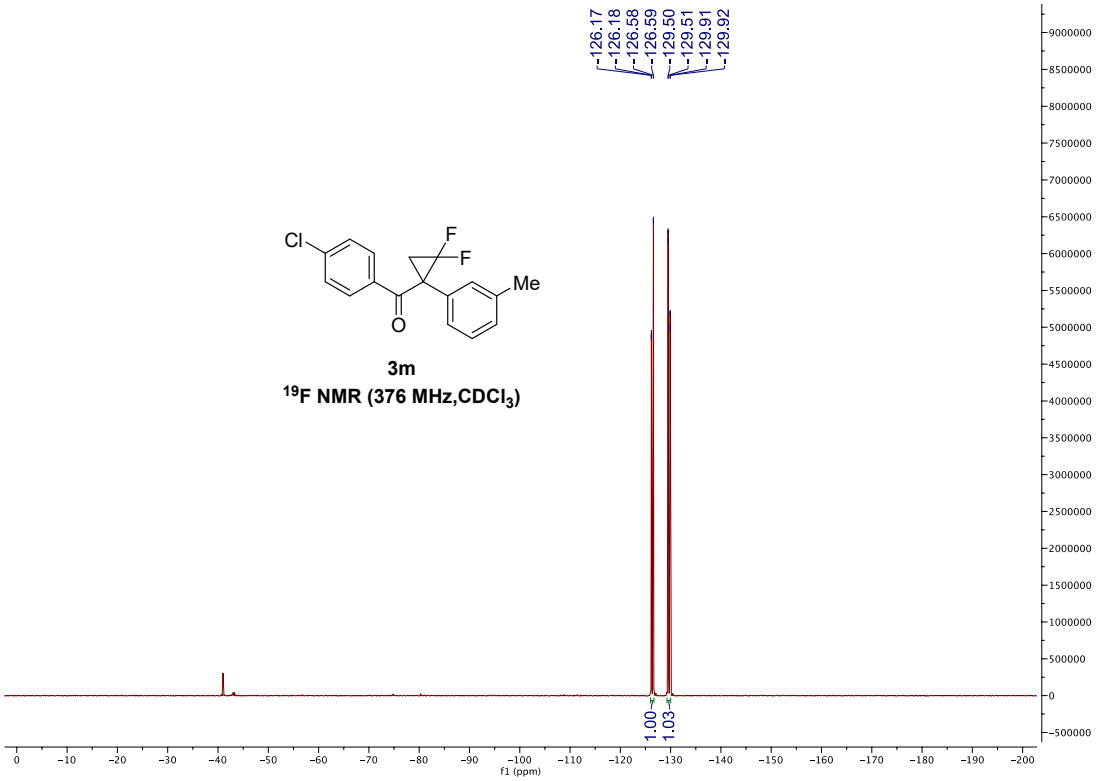
3m

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



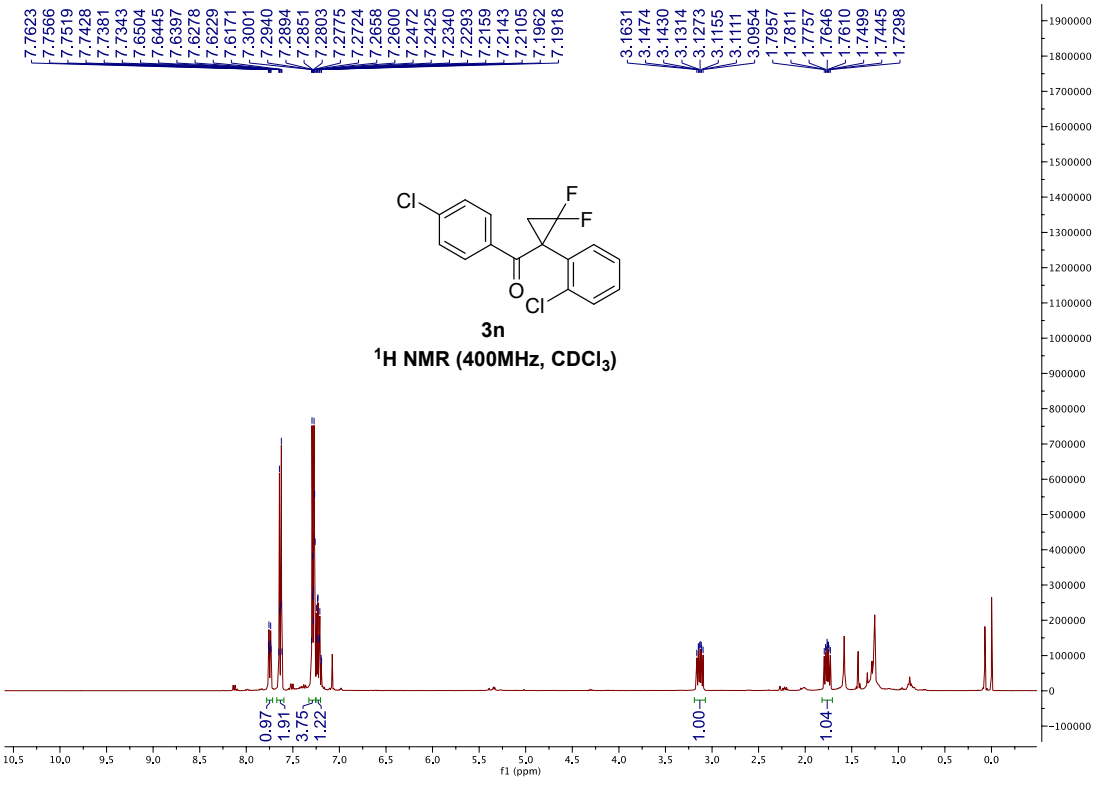
3m

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



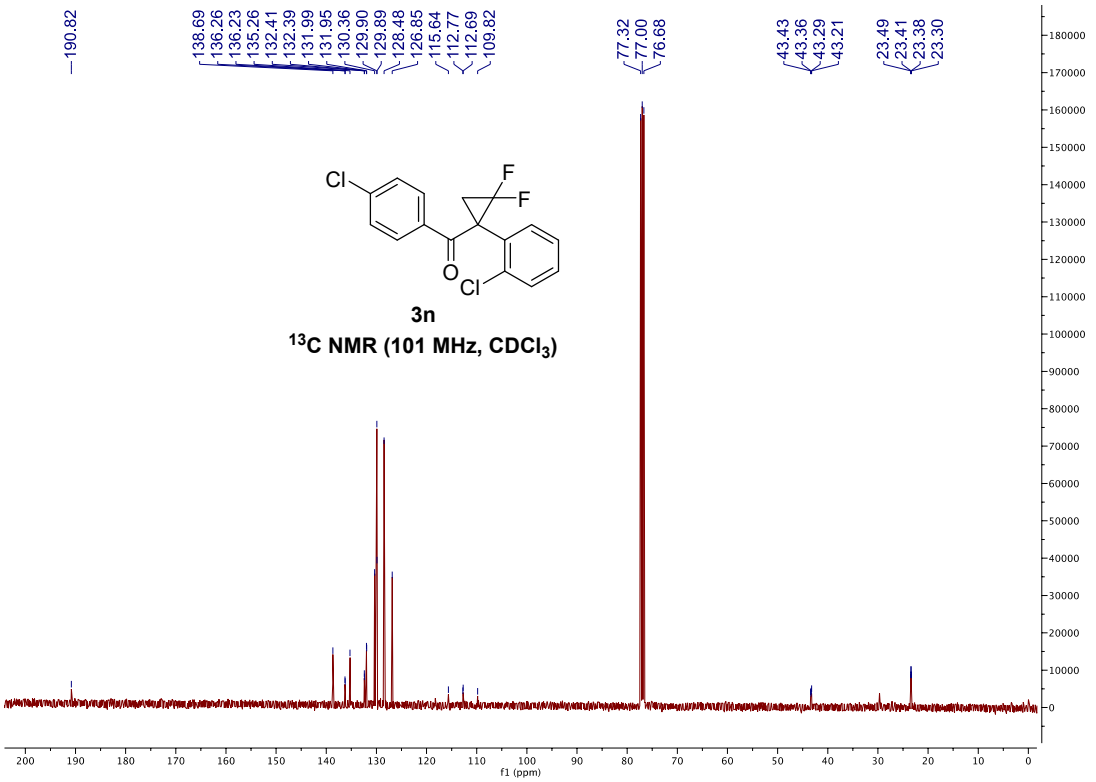
3m

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



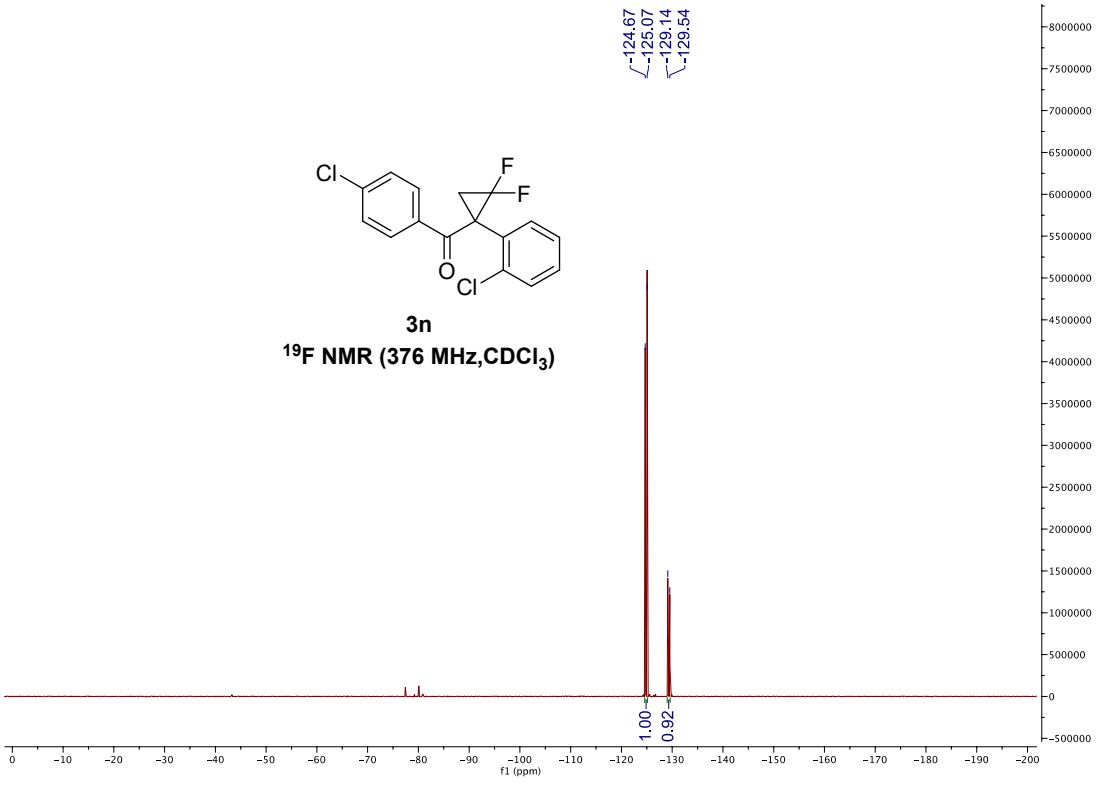
3n

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



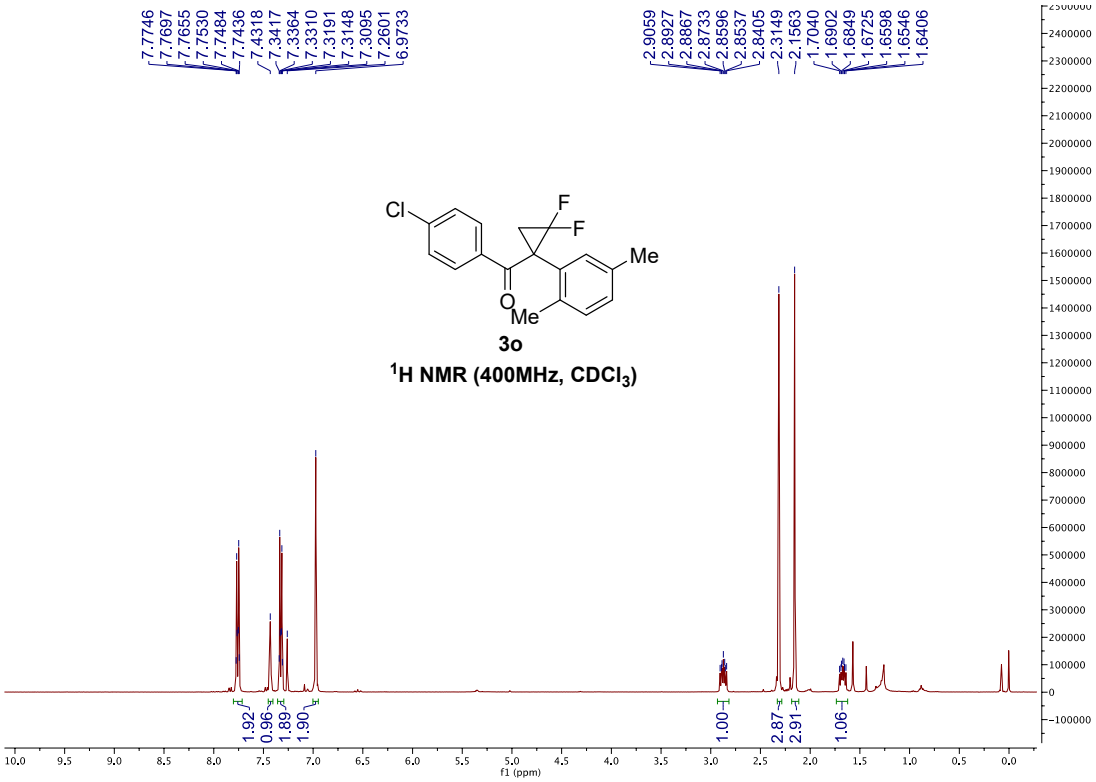
3n

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



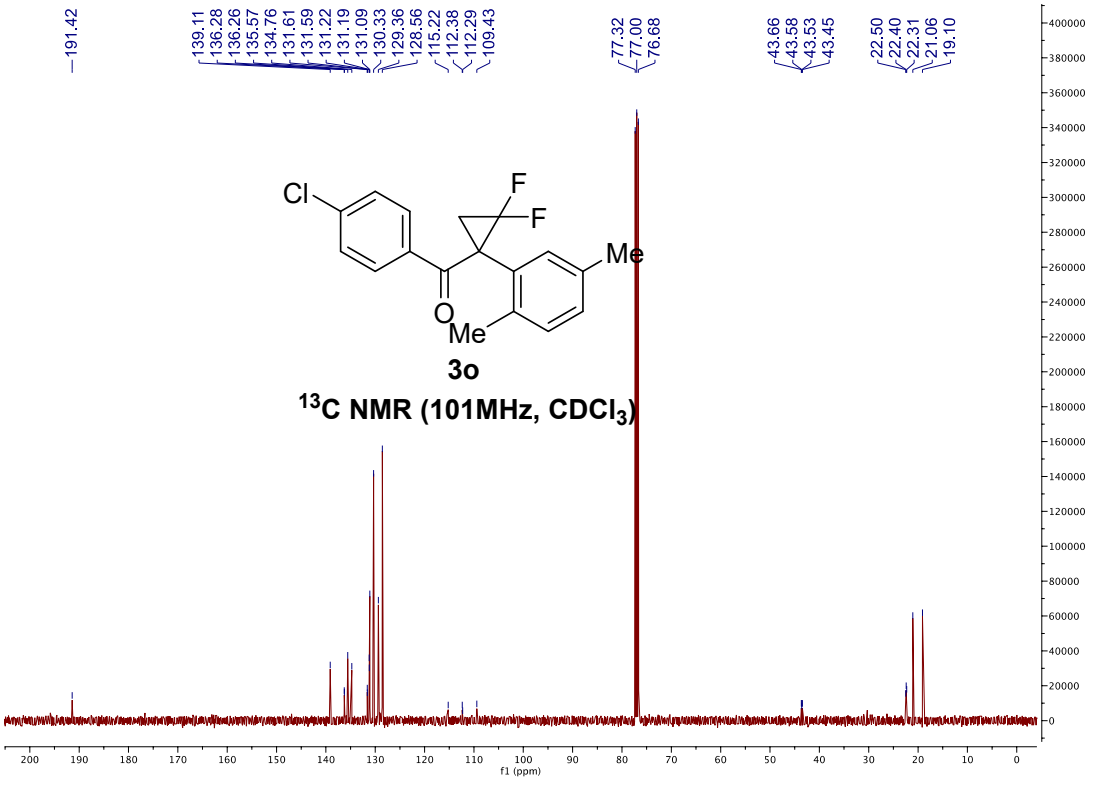
3n

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



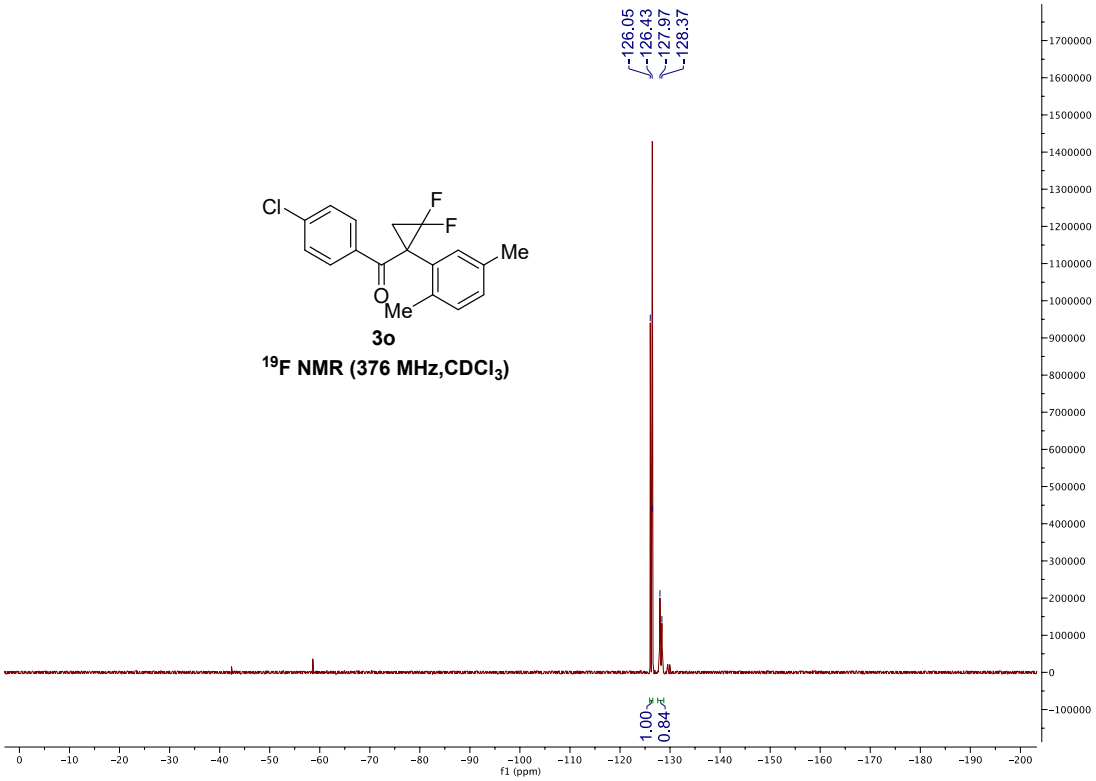
3o

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



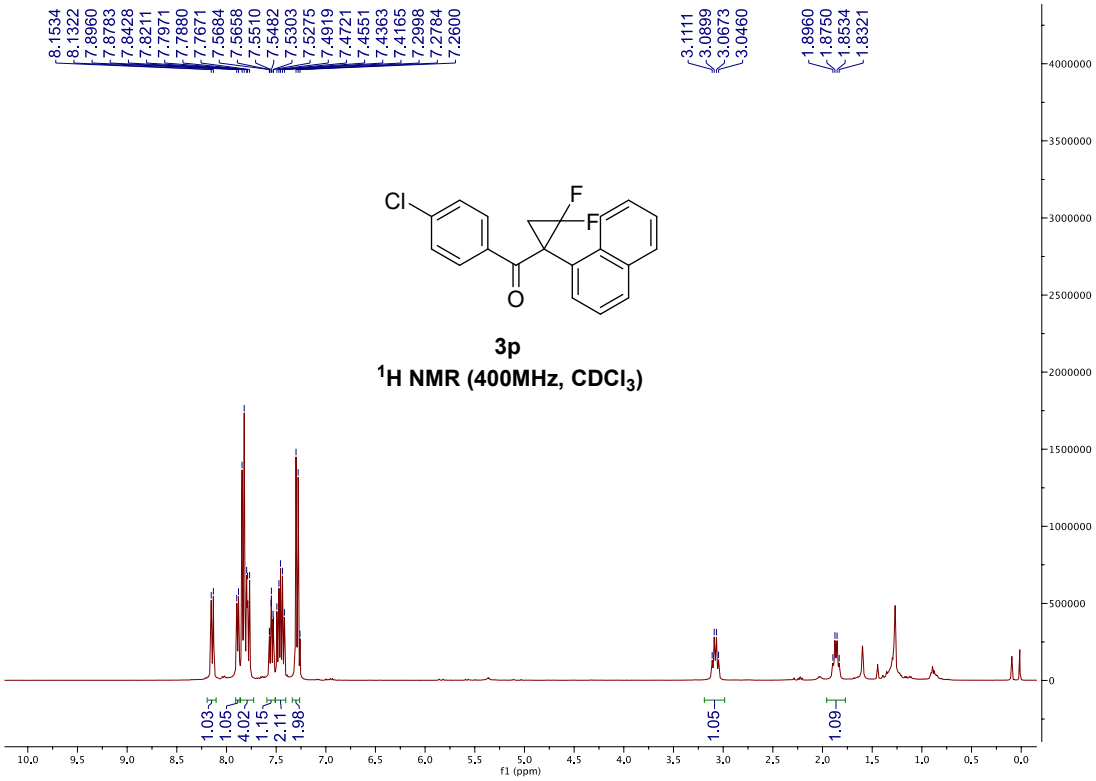
3o

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



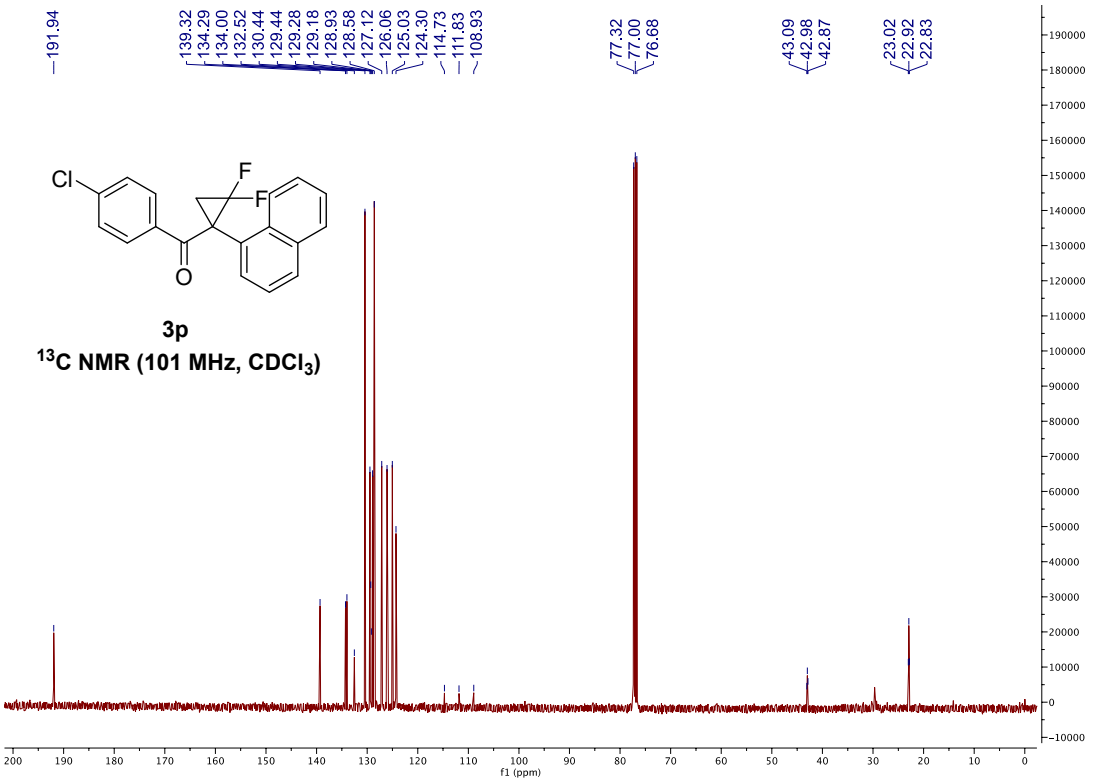
3o

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



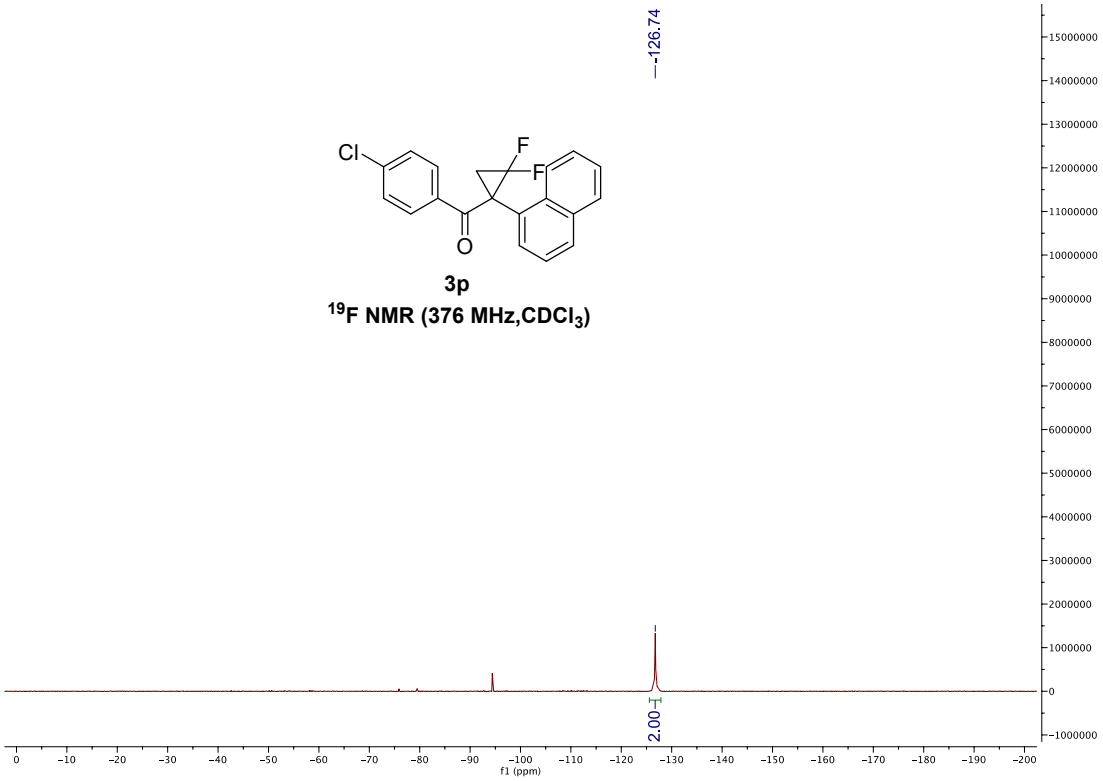
3p

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



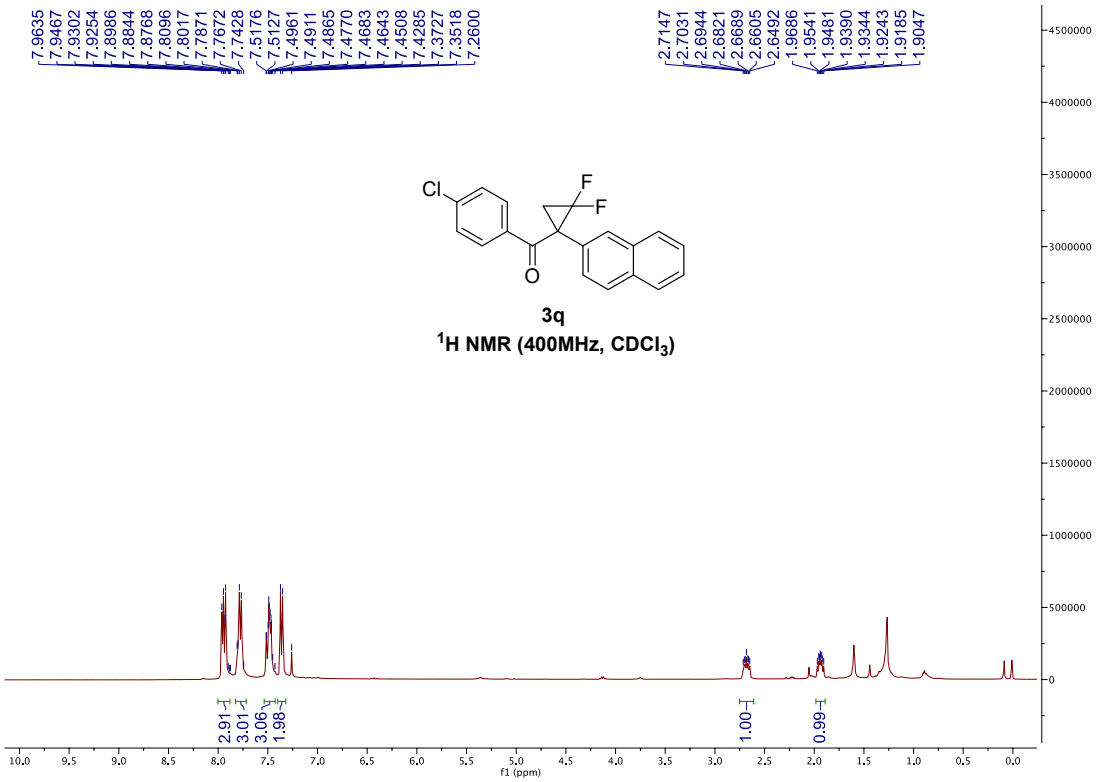
3p

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



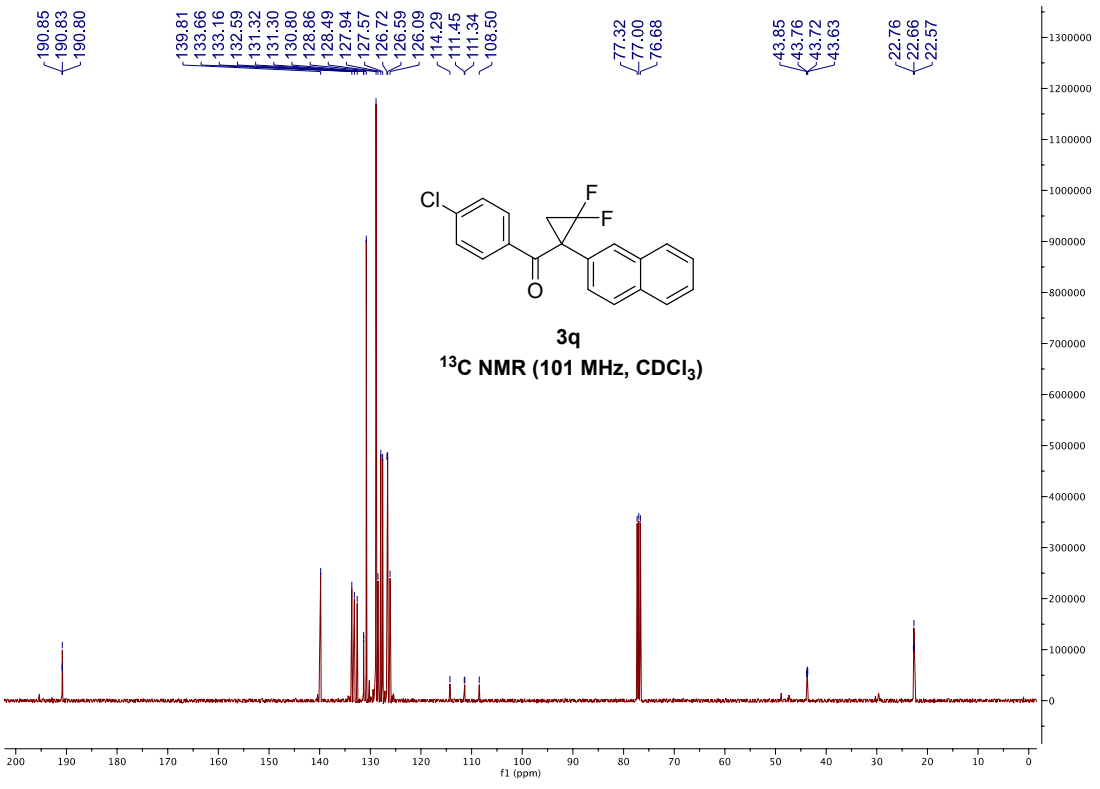
3p

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



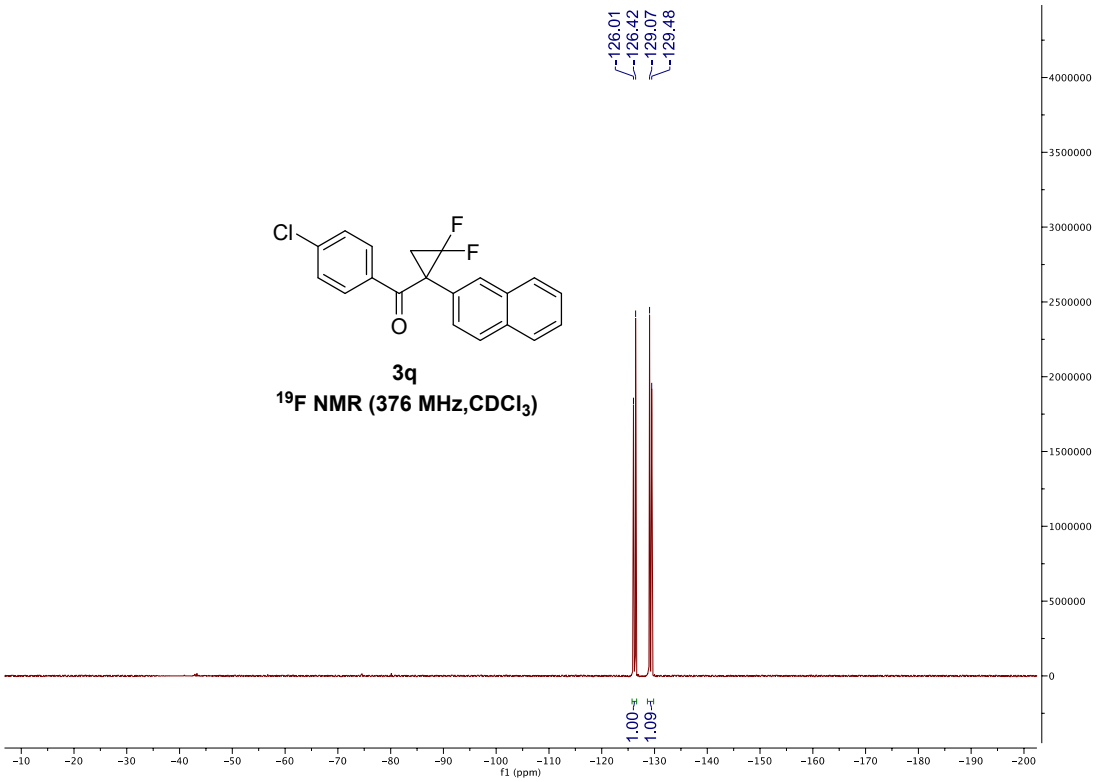
3q

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



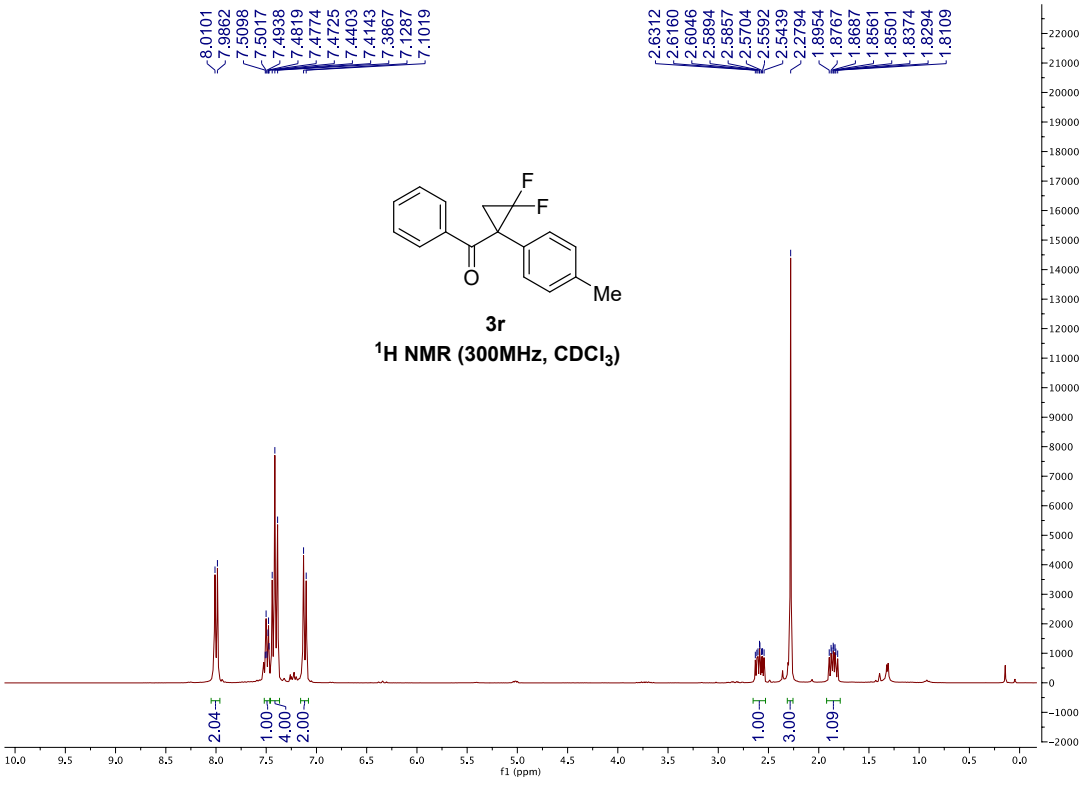
3q

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



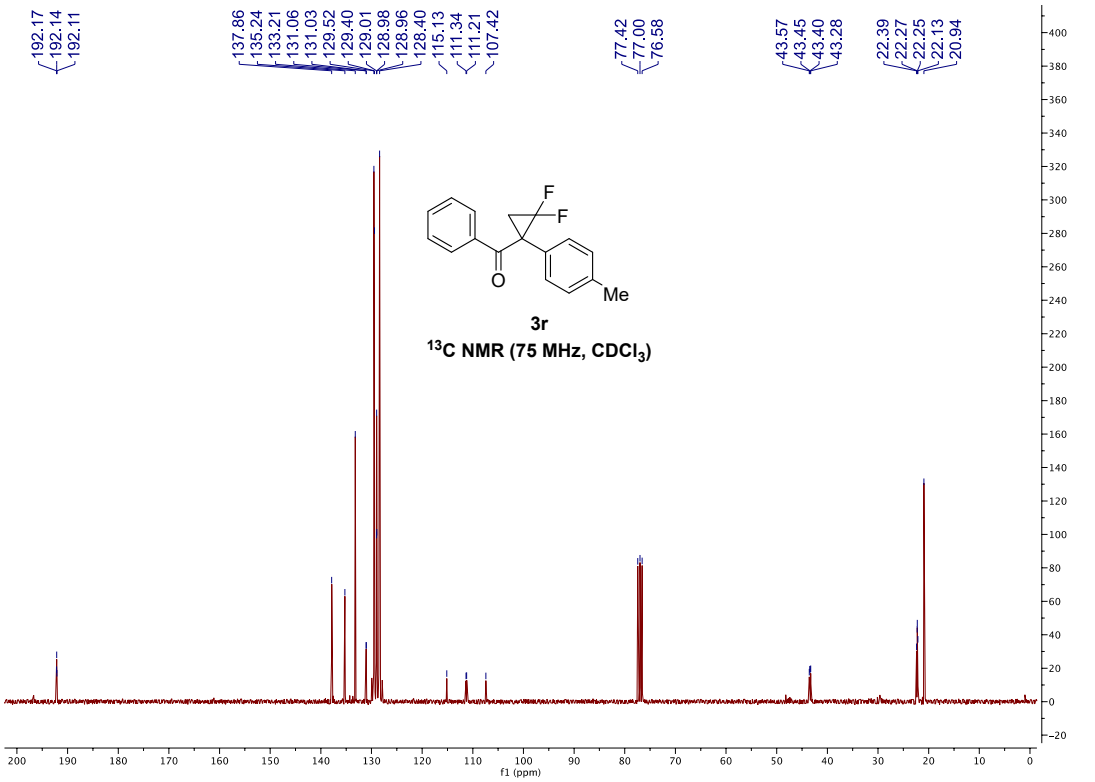
3q

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



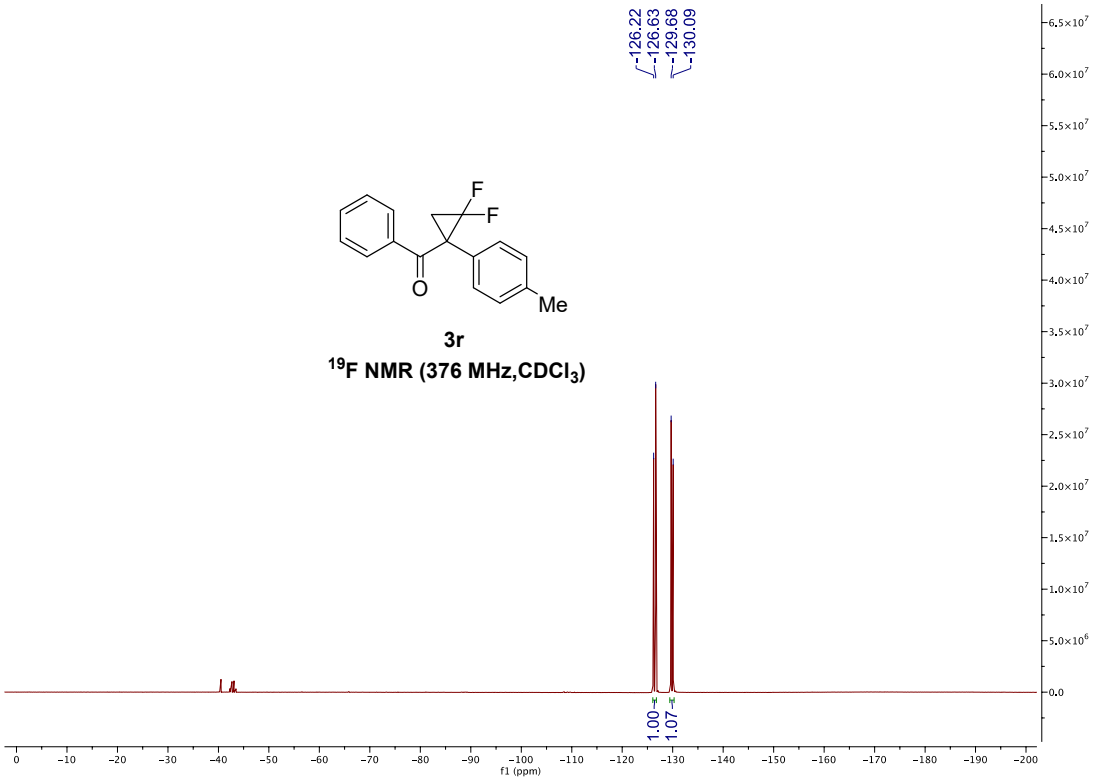
3r

^{1}H NMR (300MHz, $CDCl_3$)



3r

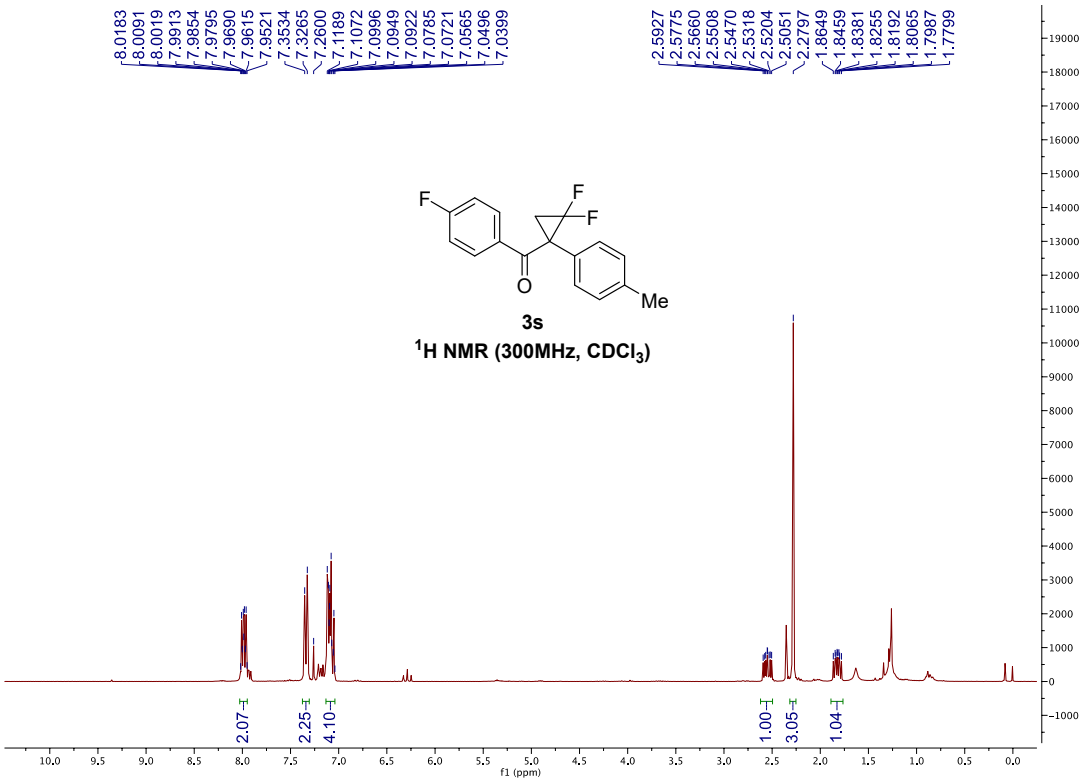
^{13}C NMR (75 MHz, $CDCl_3$)



3r

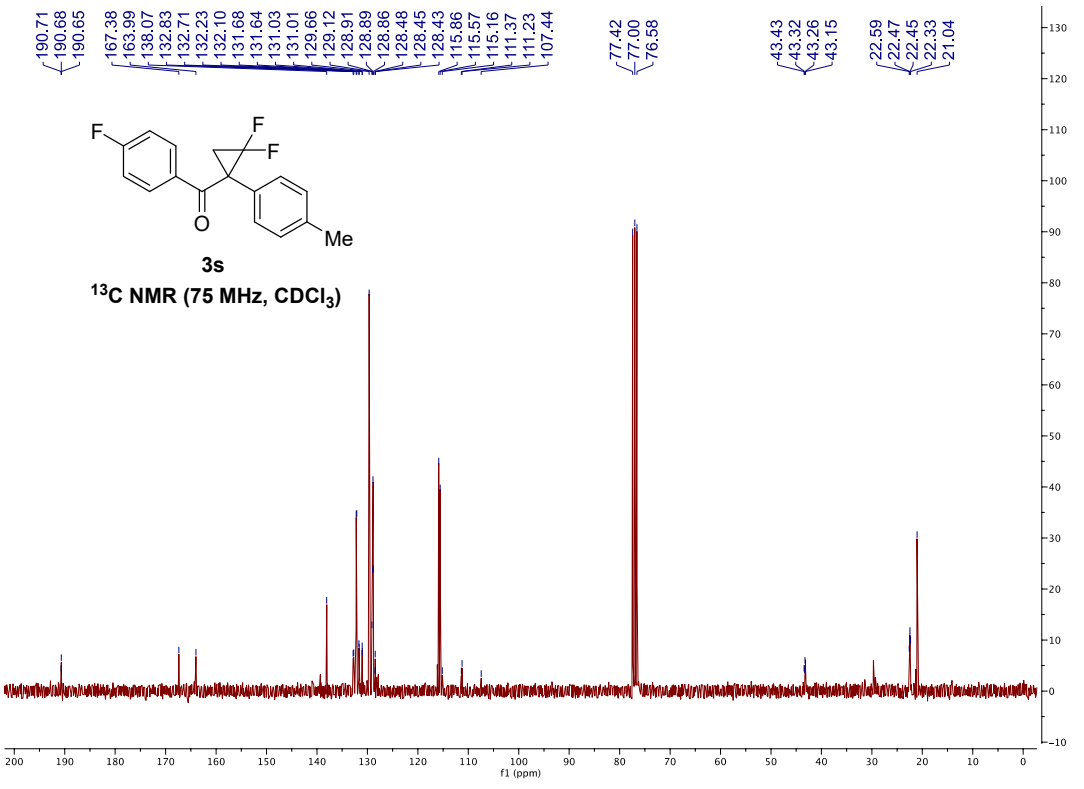
^{19}F NMR (376 MHz,$CDCl_3$)

3r



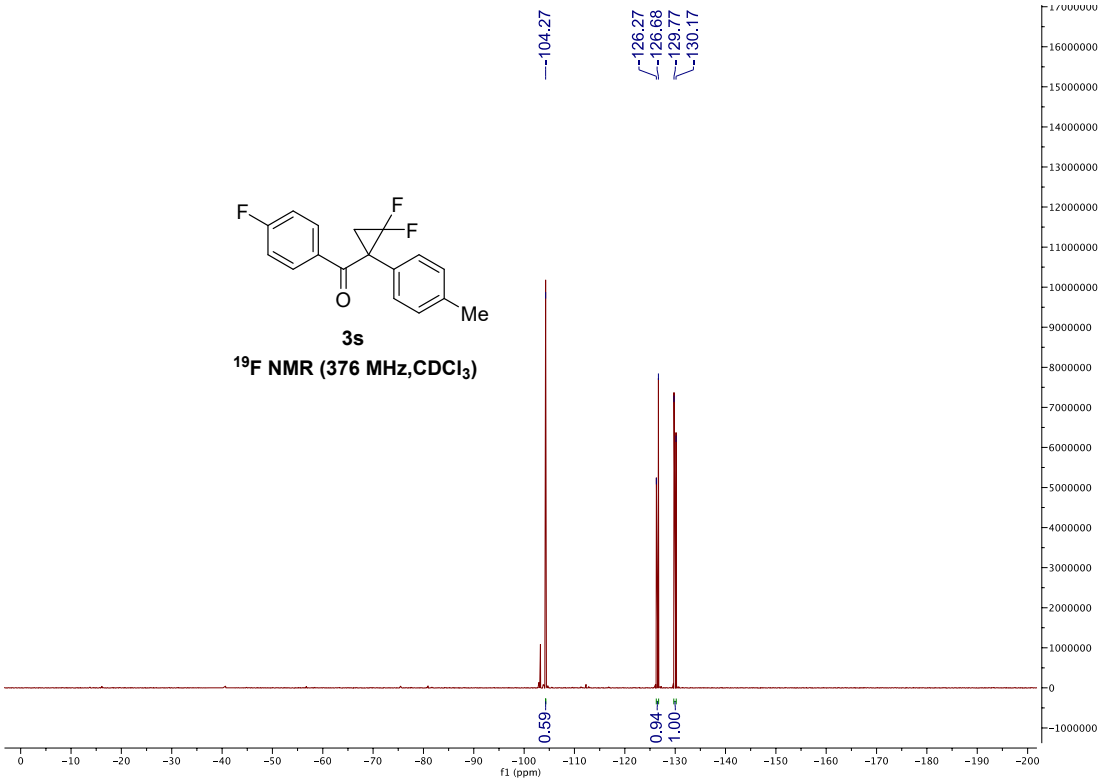
3s

^{1}H NMR (300MHz, CDCl$_3$)



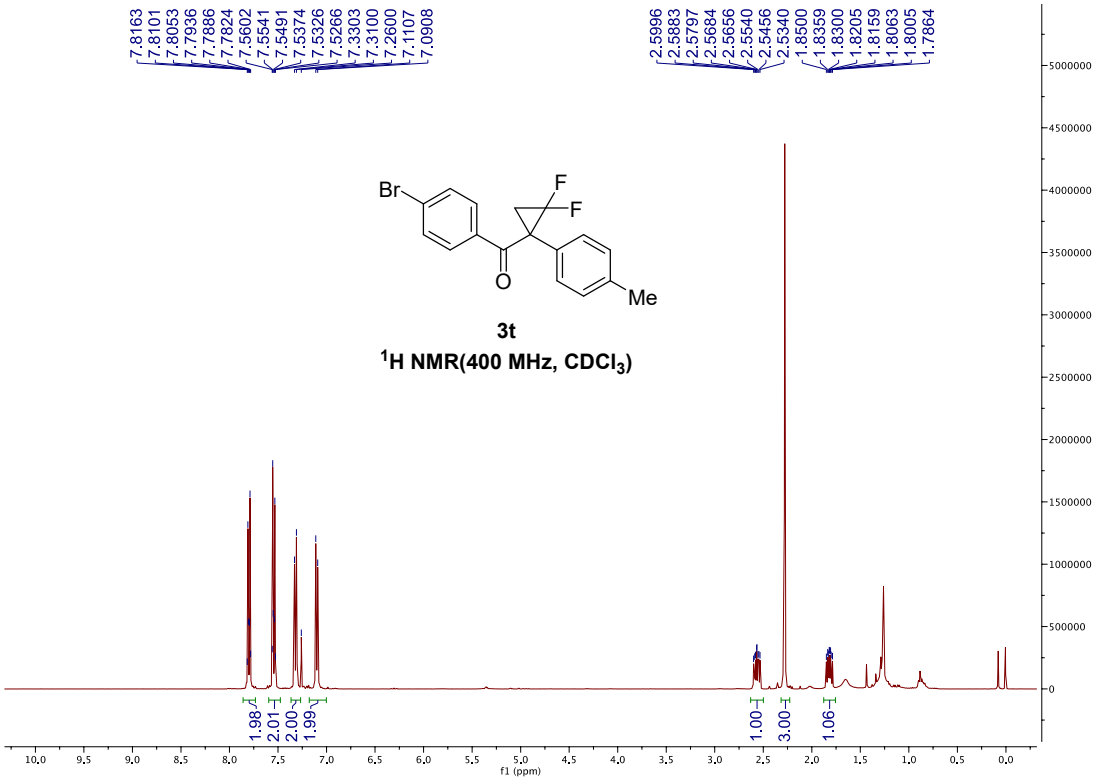
3s

^{13}C NMR (75 MHz, CDCl$_3$)



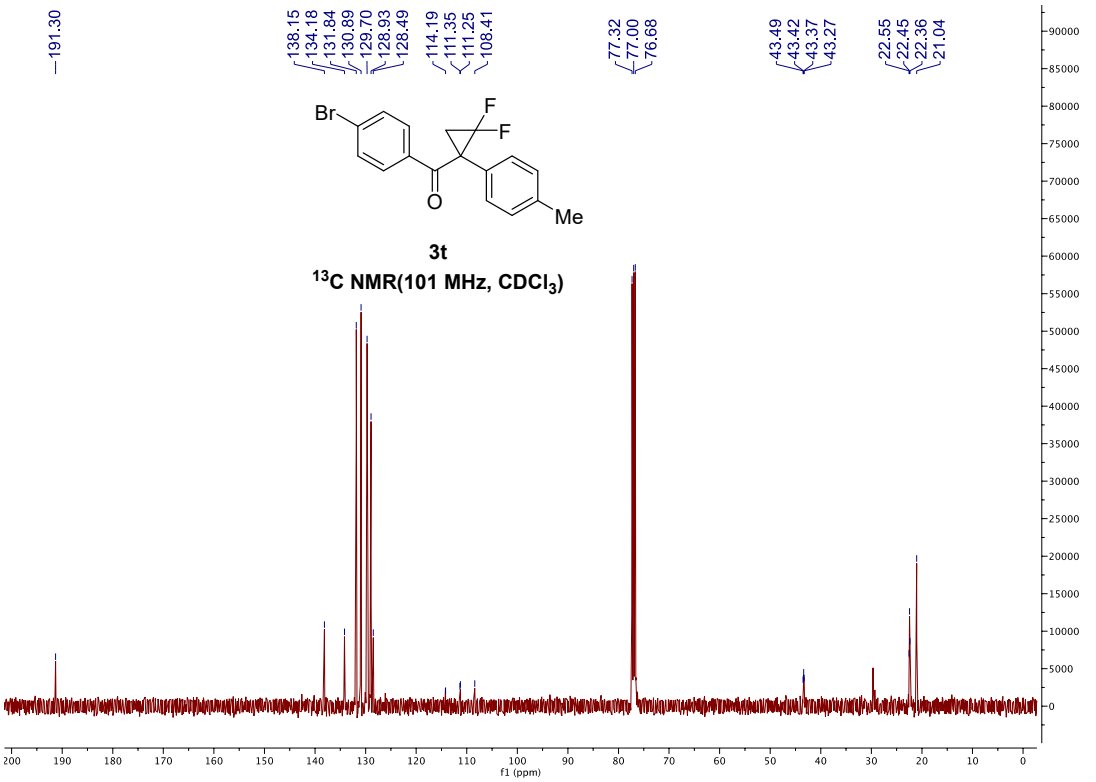
3s

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



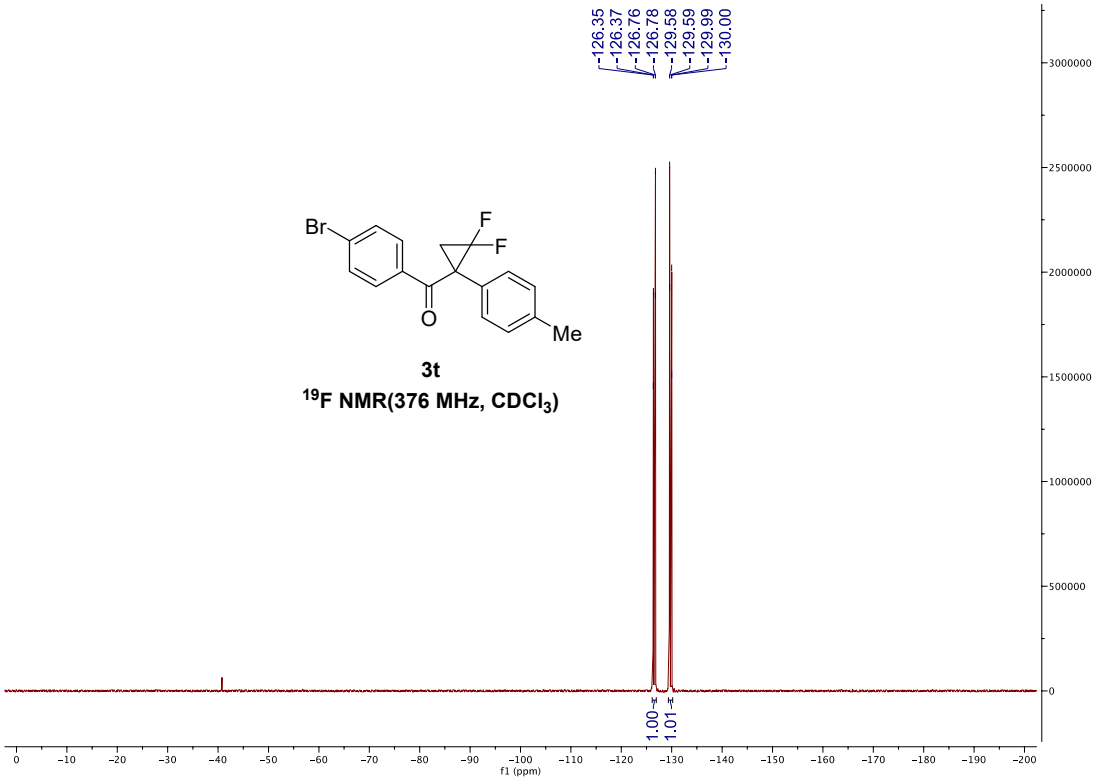
3t

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



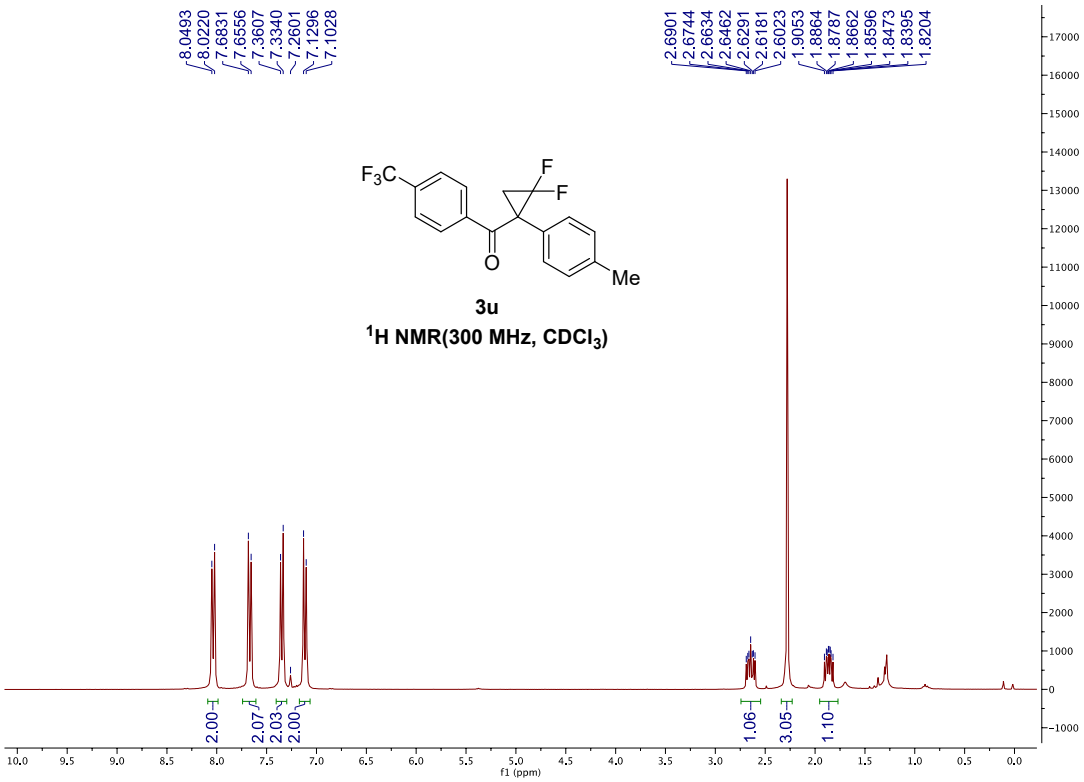
3t

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



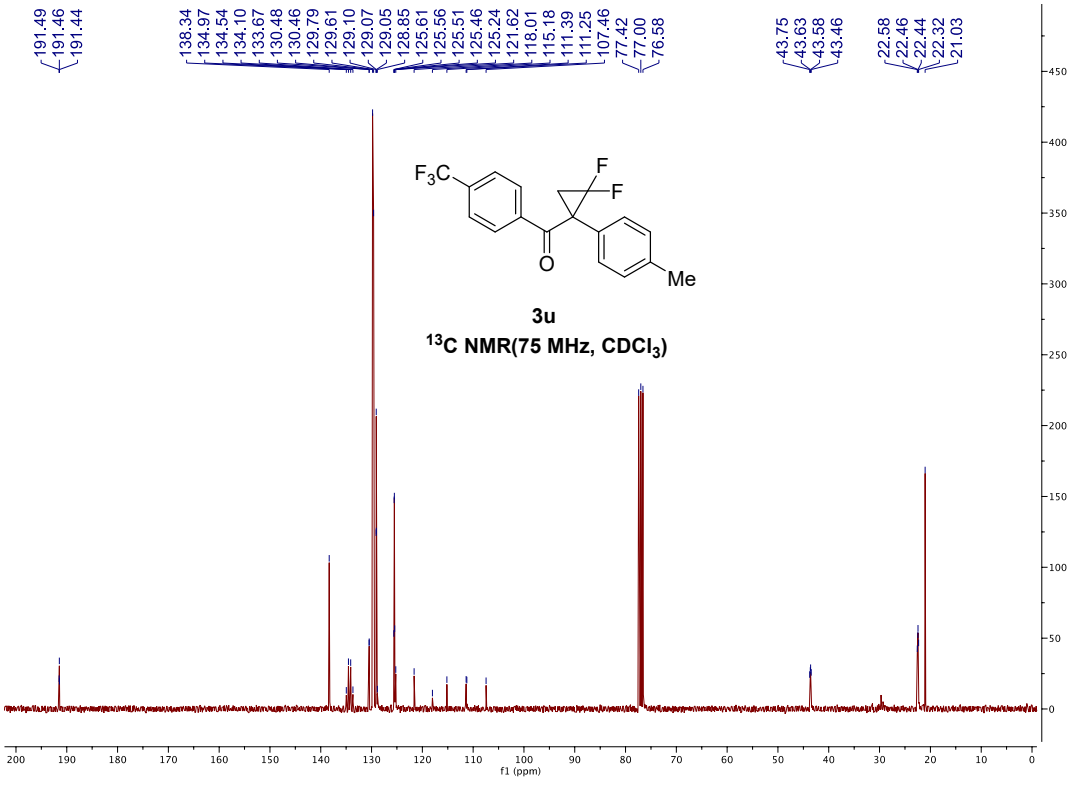
3t

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



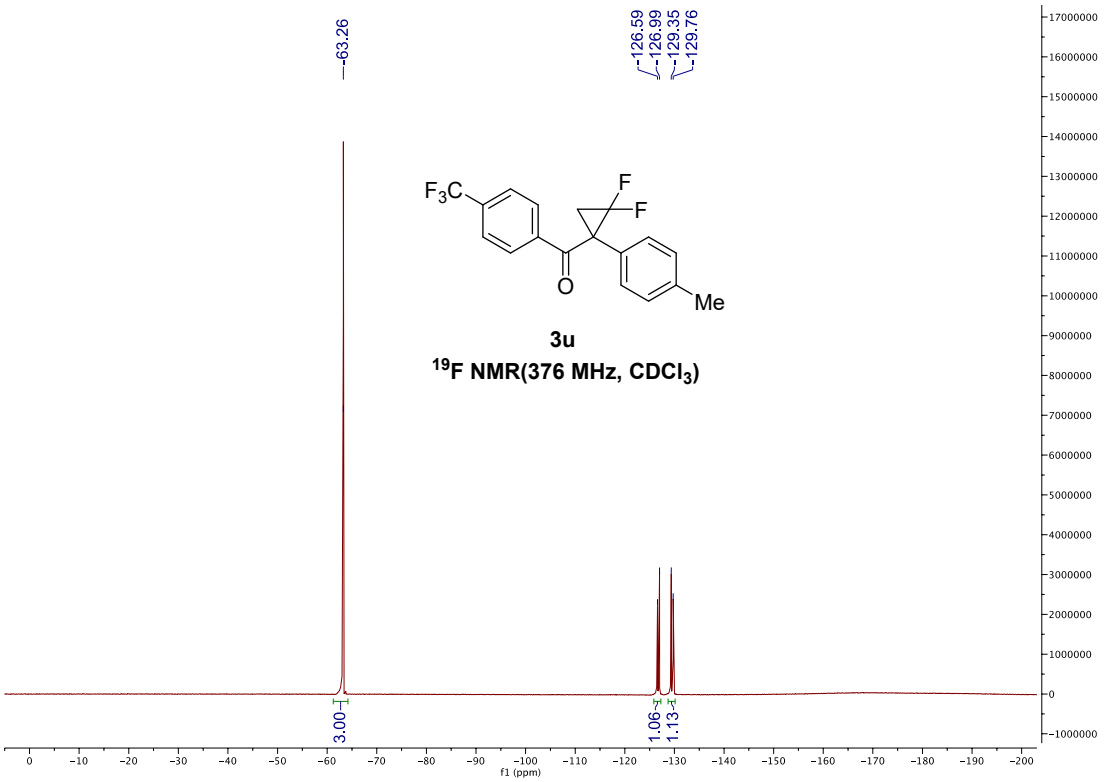
3u

^{1}H NMR(300 MHz, $CDCl_3$)



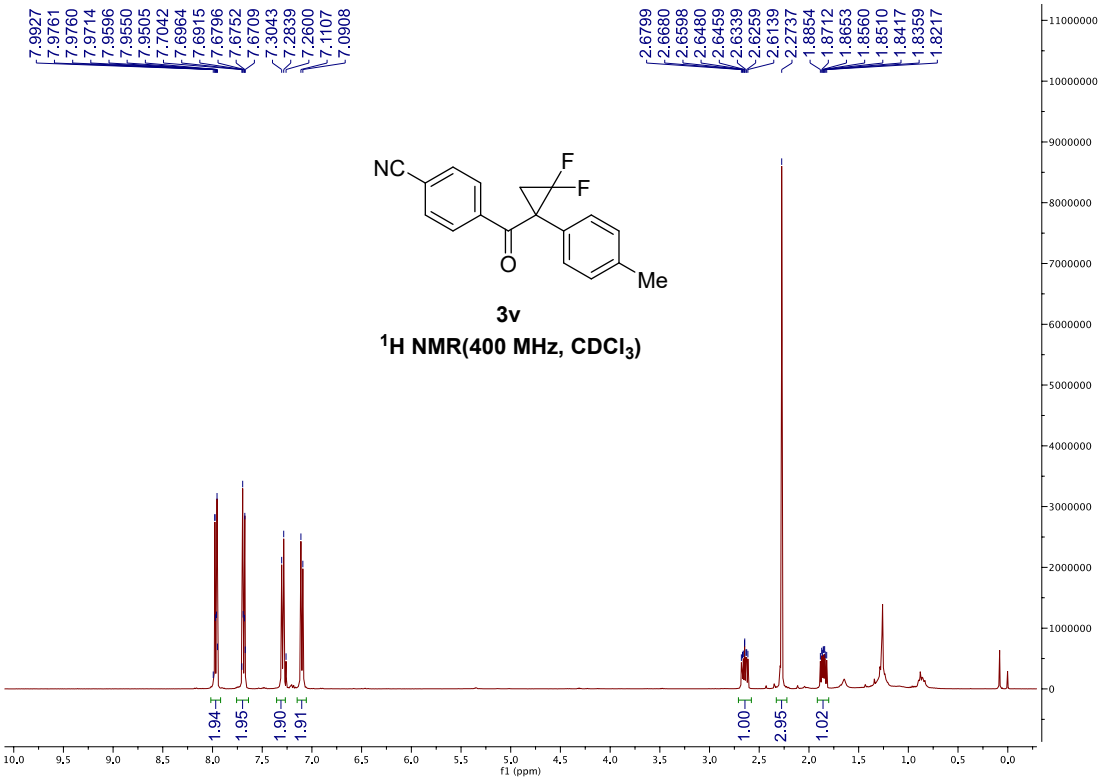
3u

^{13}C NMR(75 MHz, $CDCl_3$)



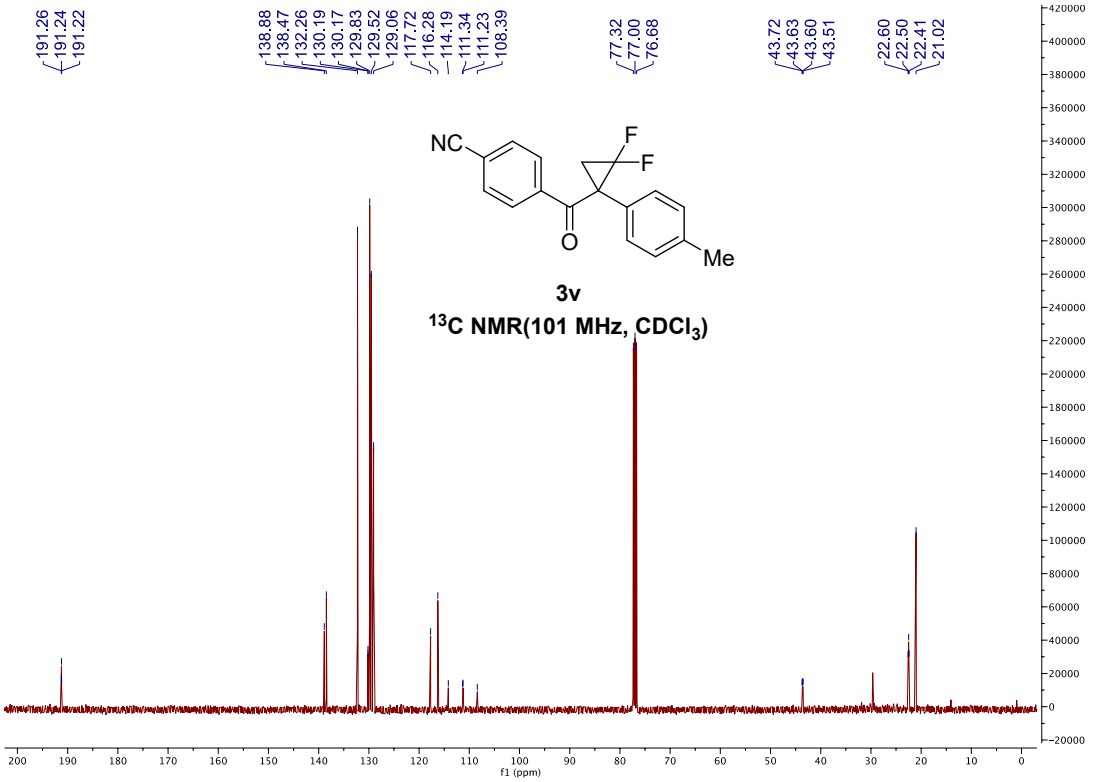
3u

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



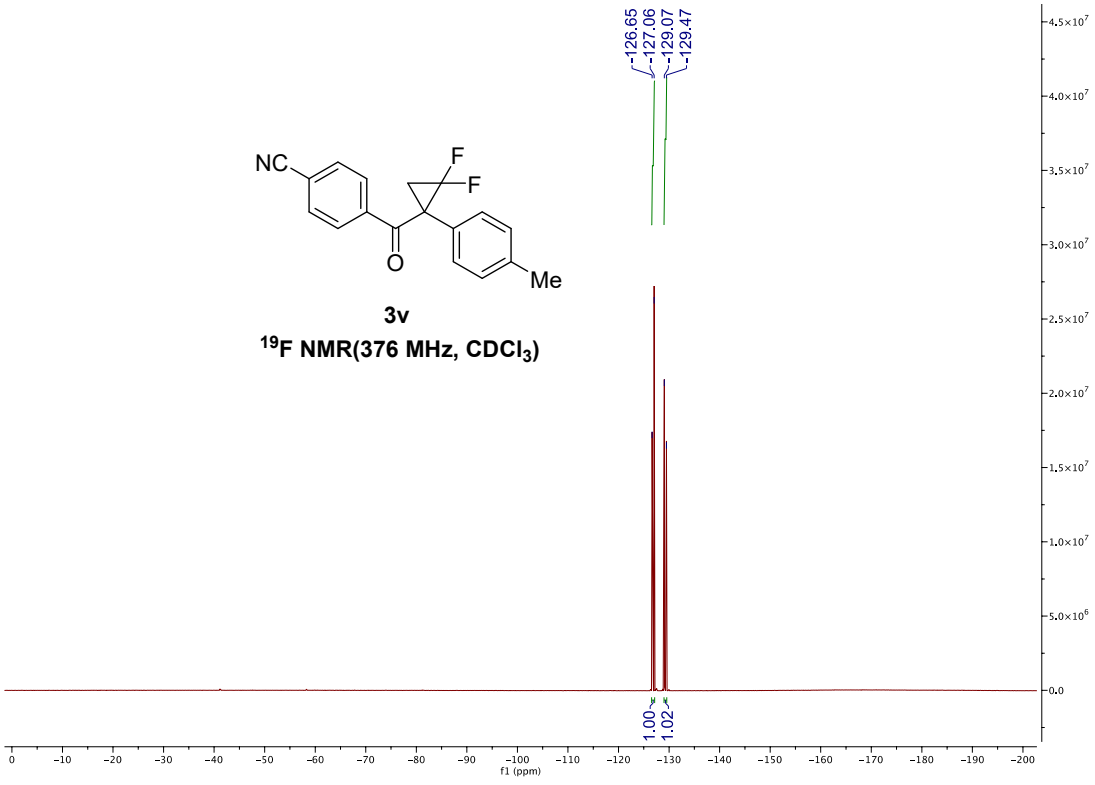
3v

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



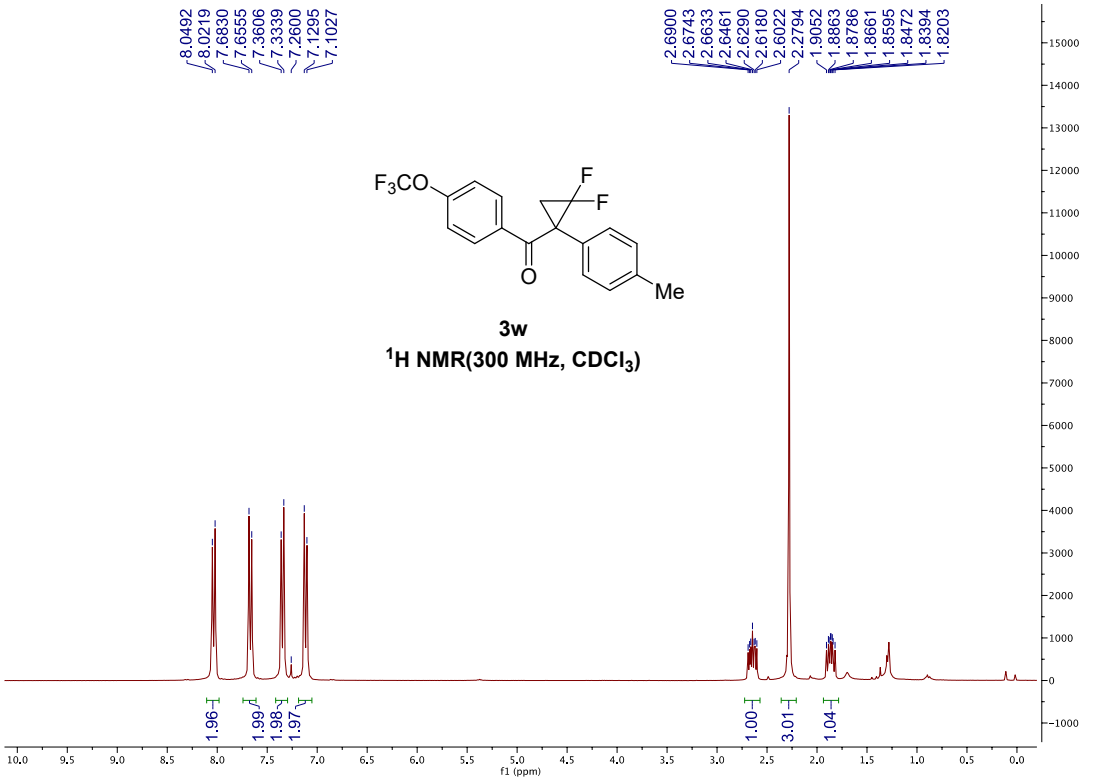
3v

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



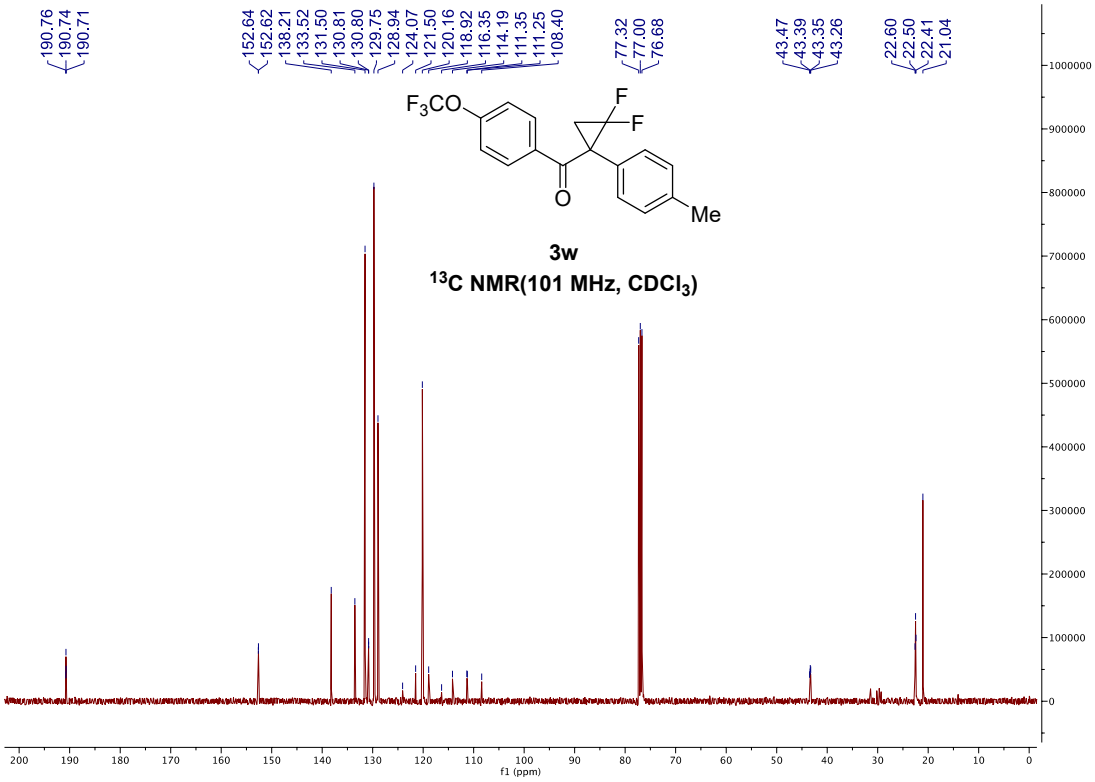
3v

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



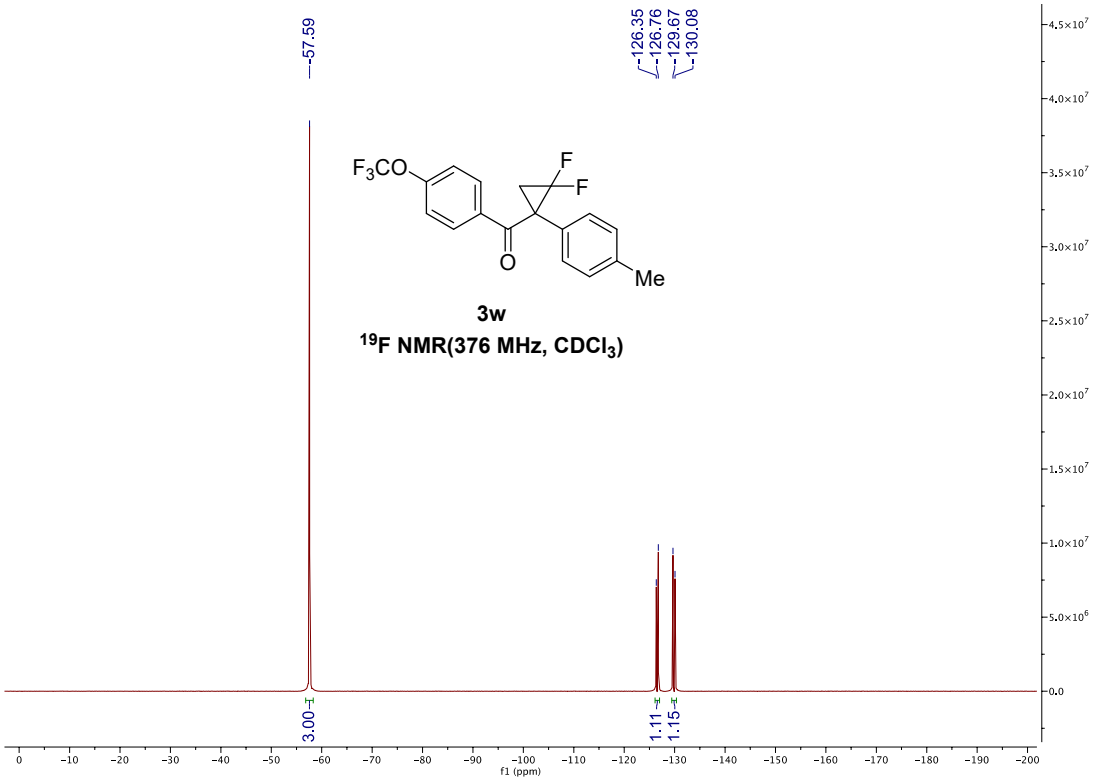
3w

^{1}H NMR(300 MHz, $CDCl_3$)



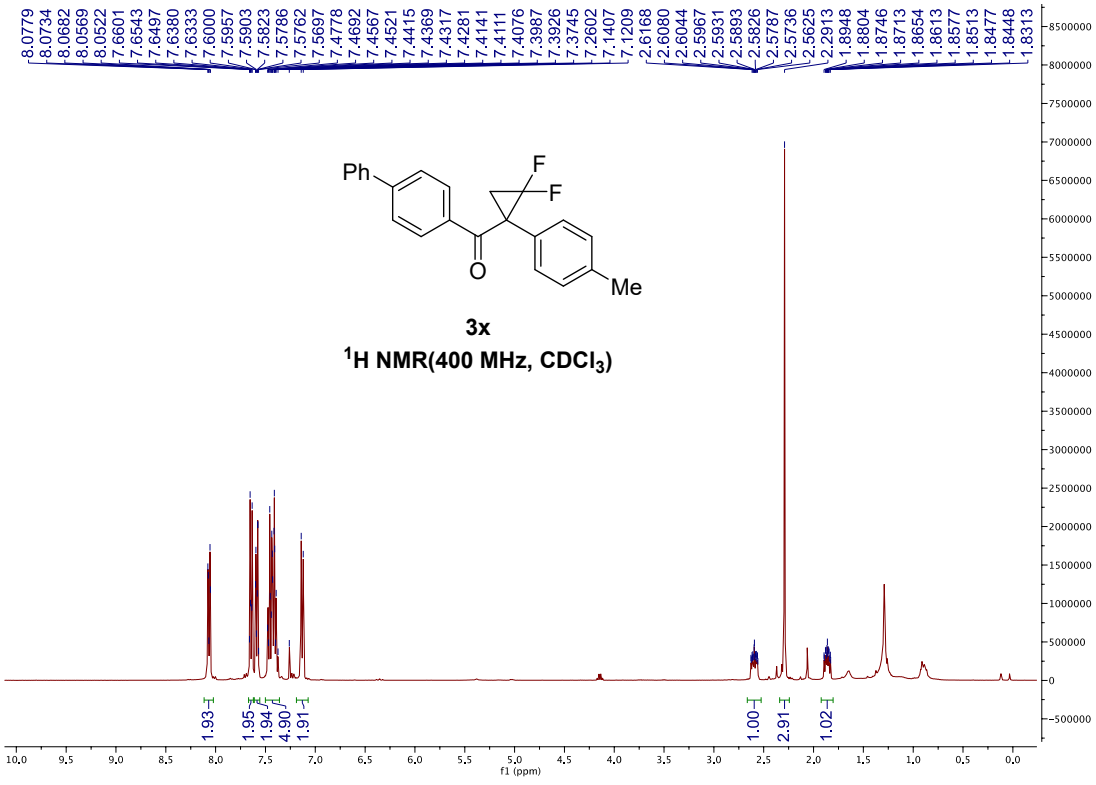
3w

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



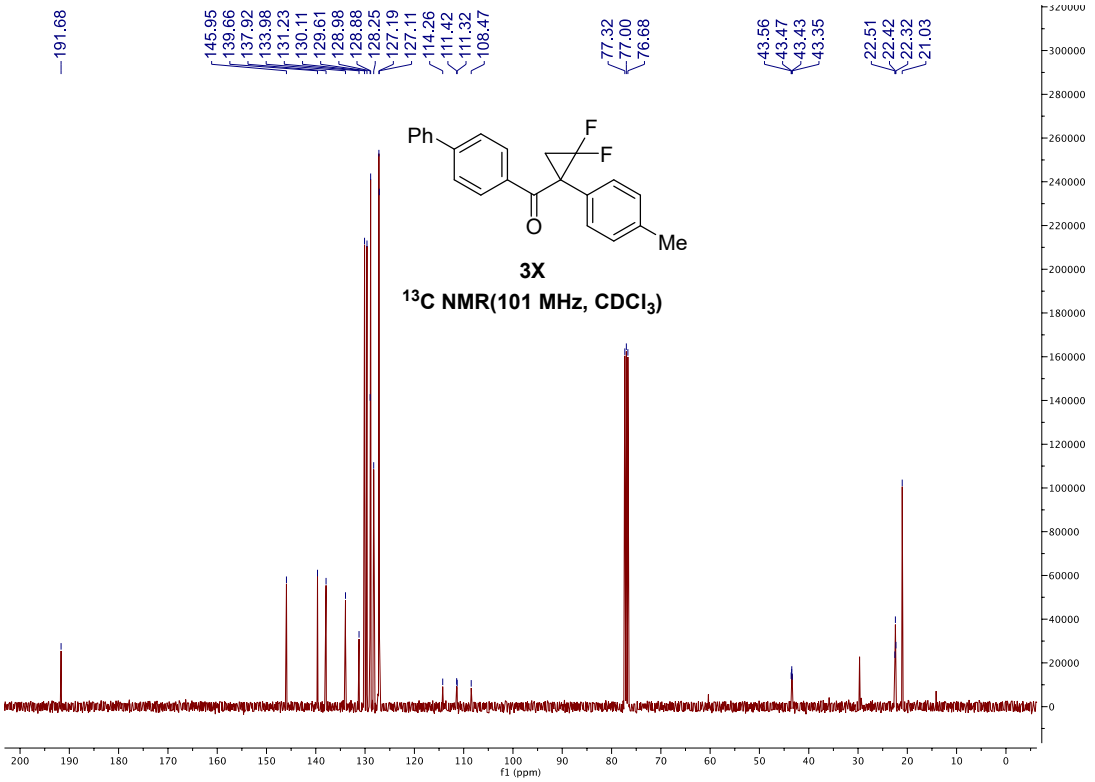
3w

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



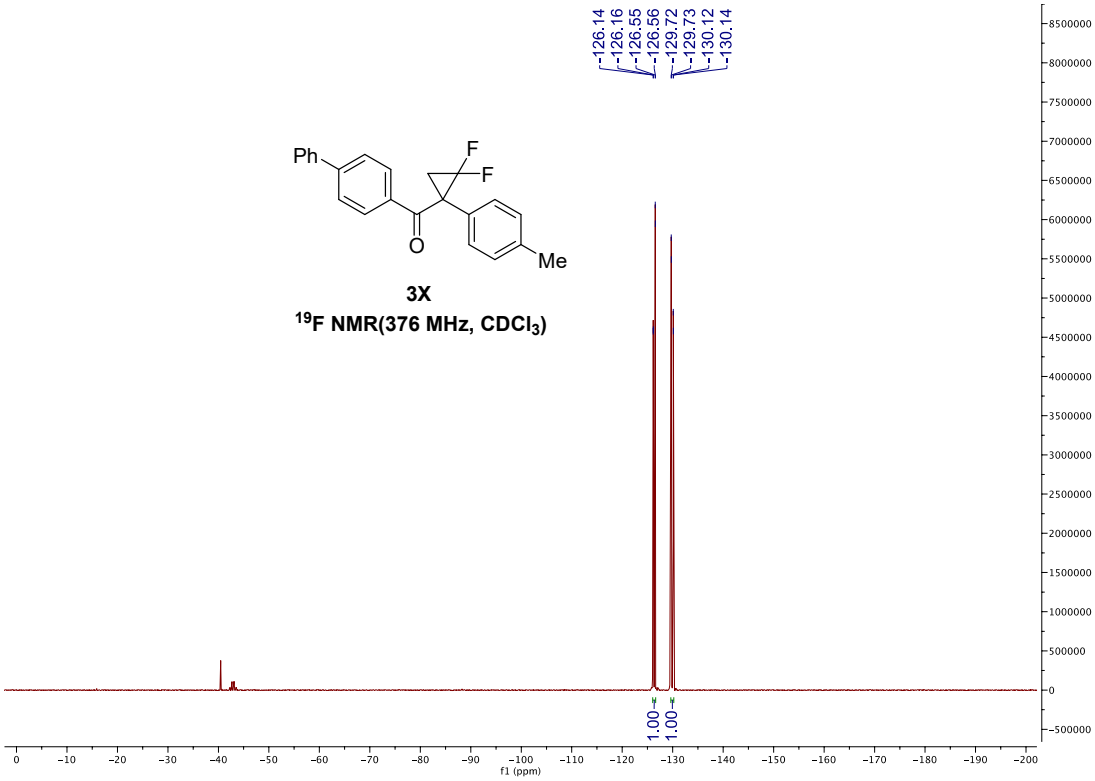
3x

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



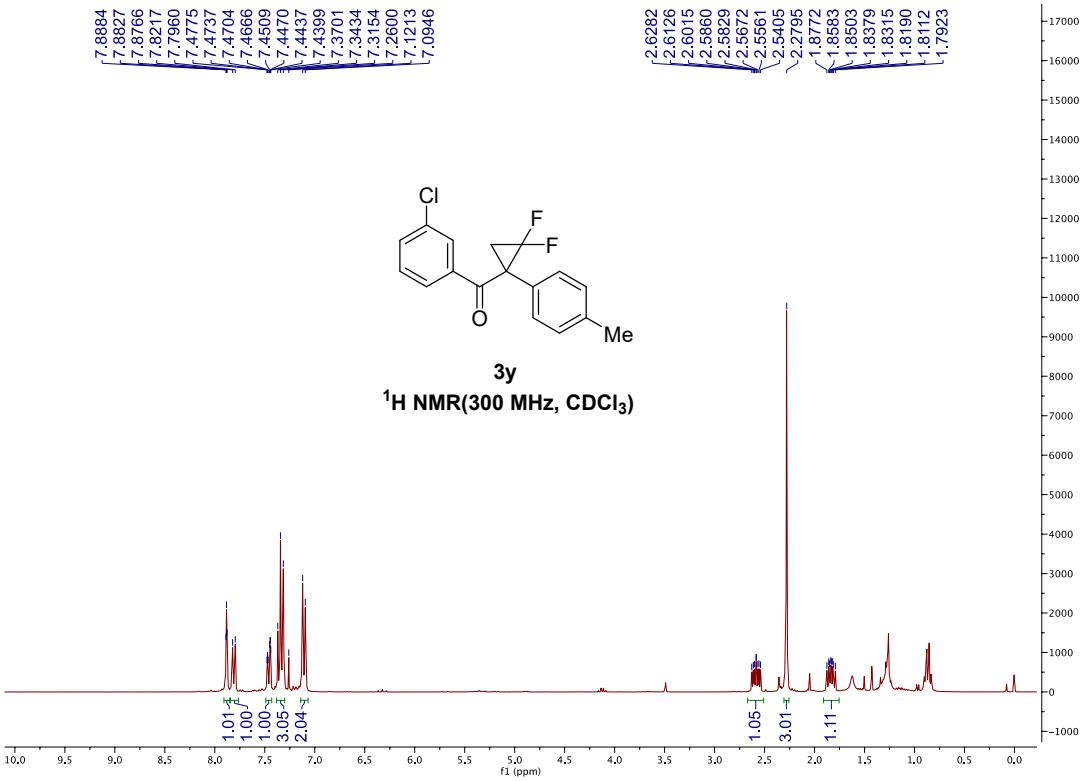
3X

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



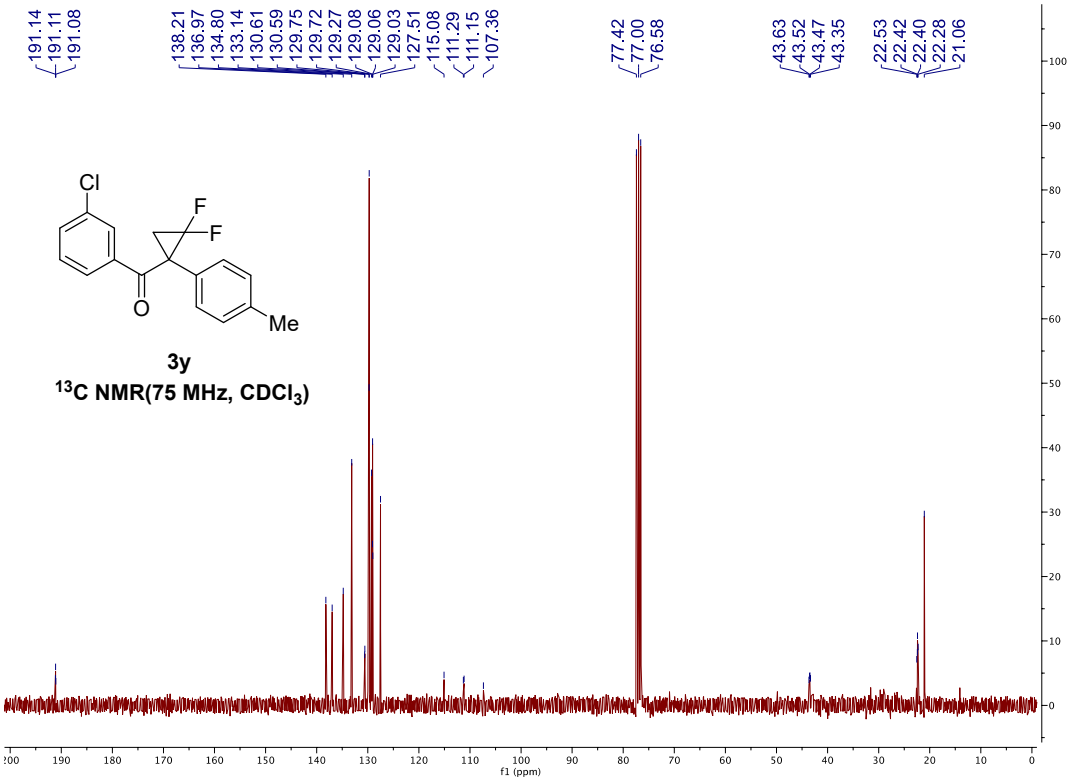
3X

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



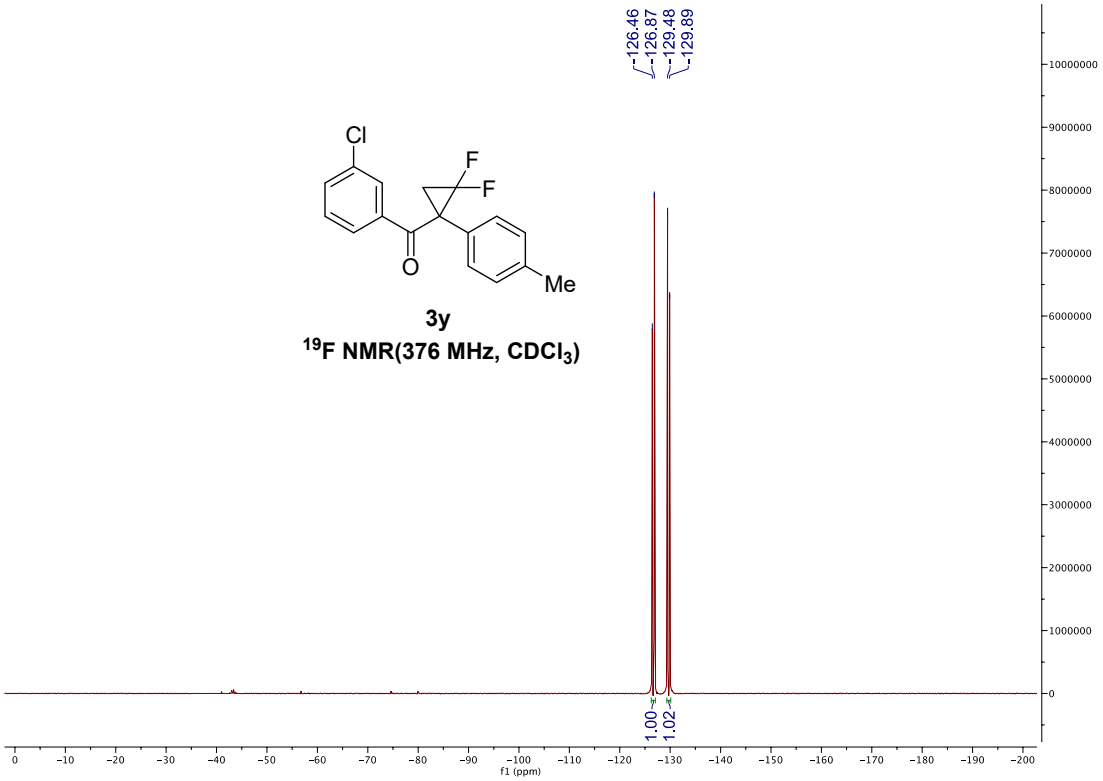
3y

^{1}H NMR(300 MHz, $CDCl_3$)



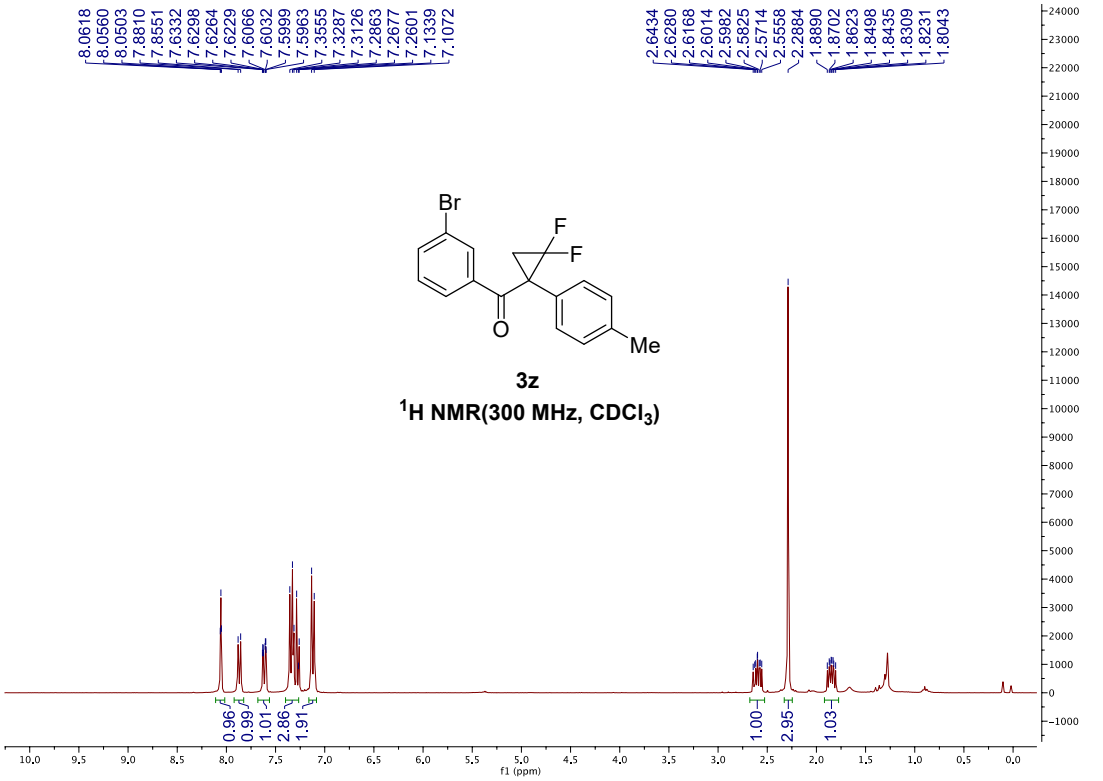
3y

^{13}C NMR(75 MHz, $CDCl_3$)



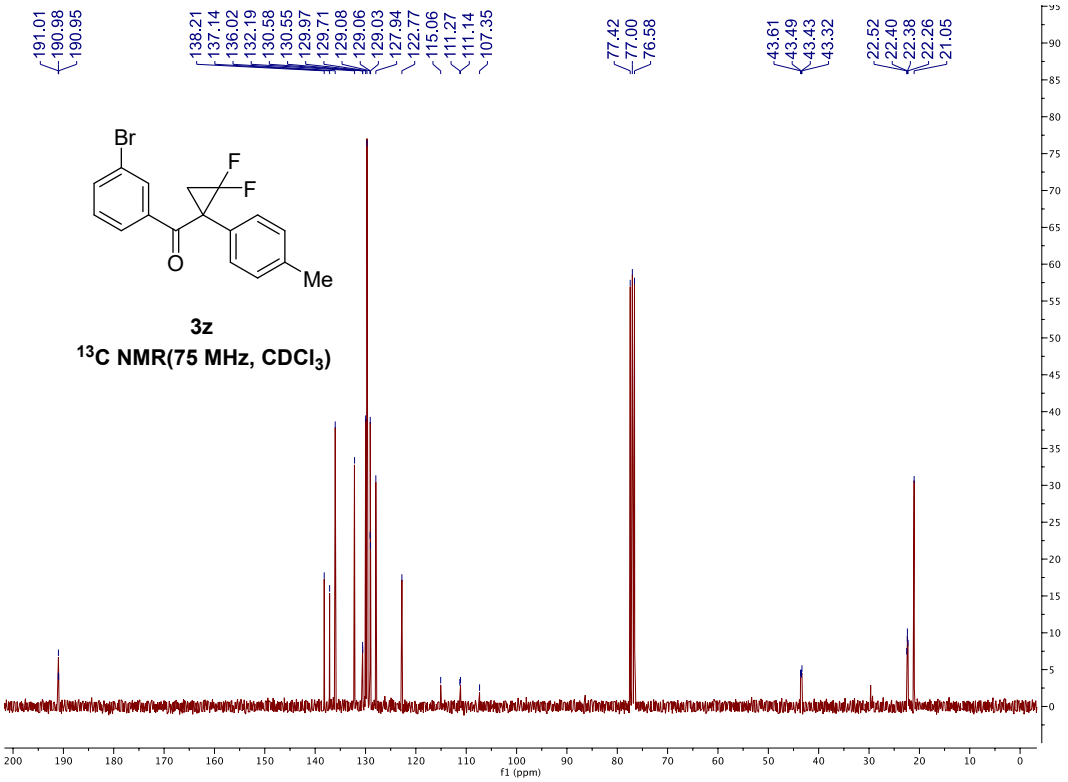
3y

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



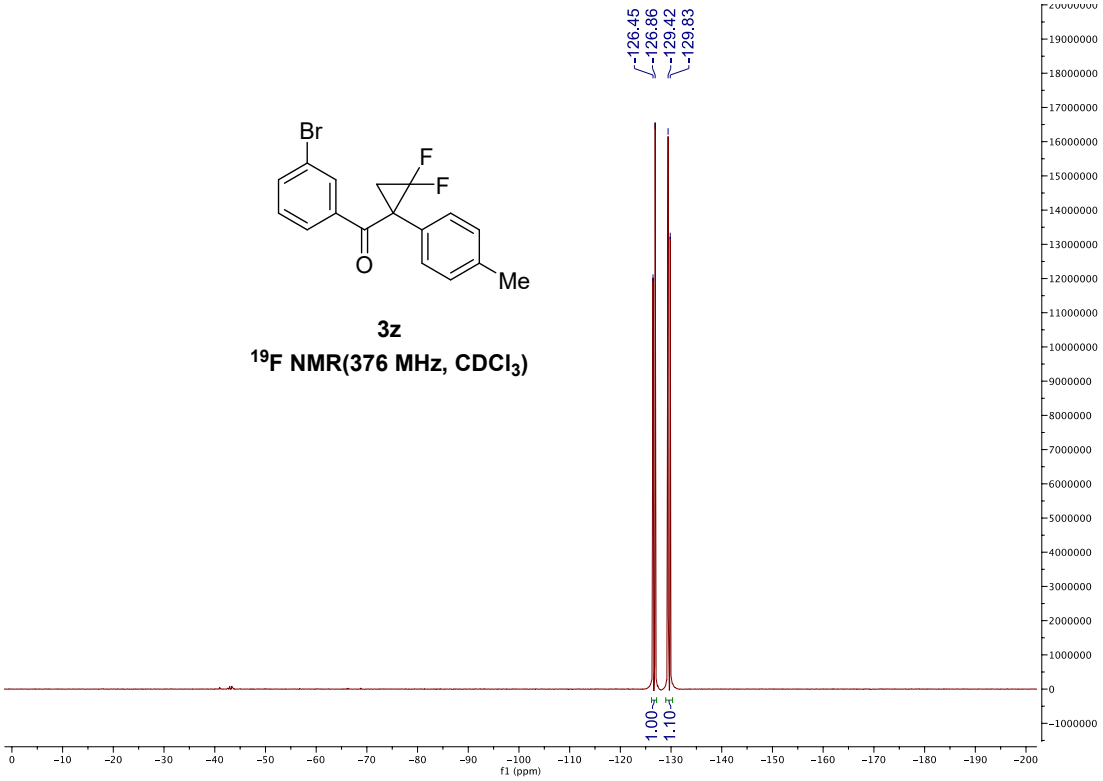
3z

^{1}H NMR(300 MHz, $CDCl_3$)



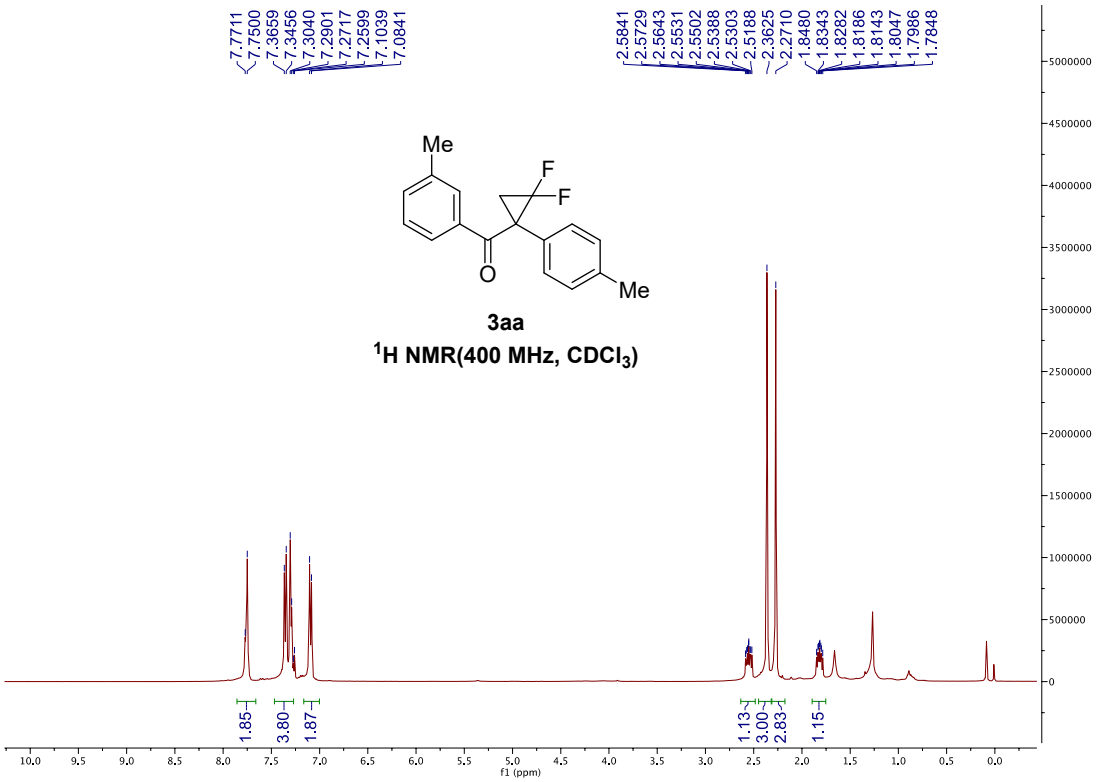
3z

^{13}C NMR(75 MHz, $CDCl_3$)



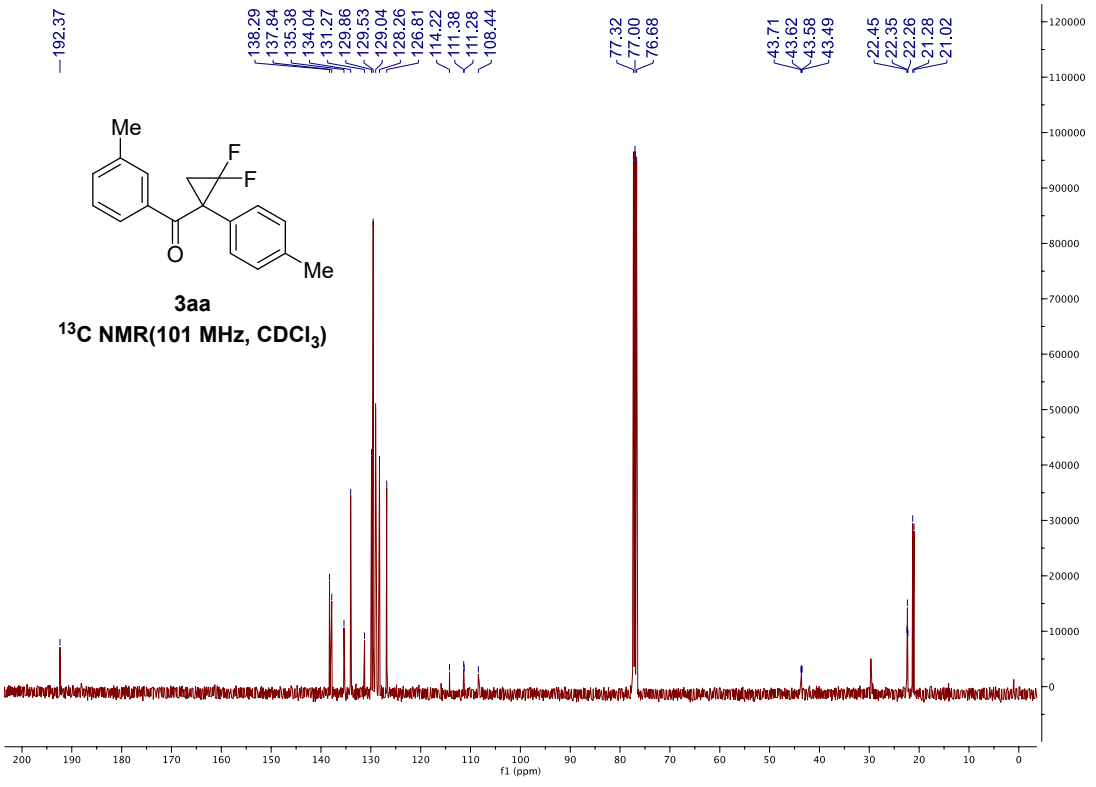
3z

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



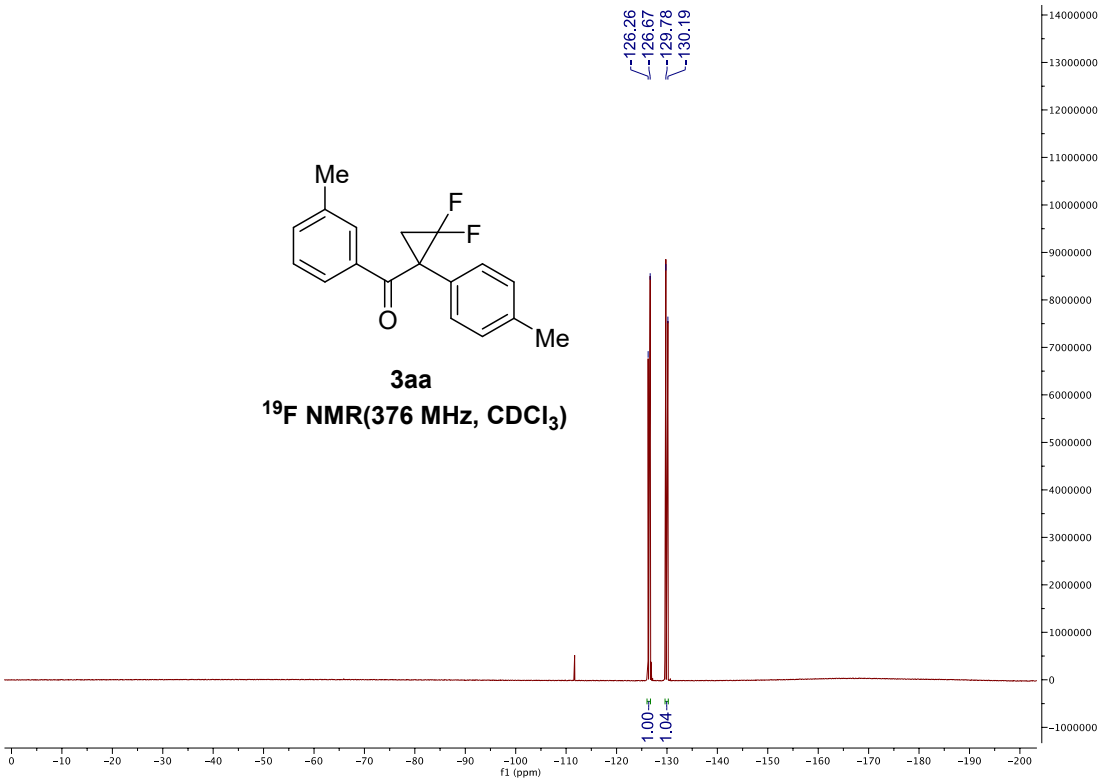
3aa

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



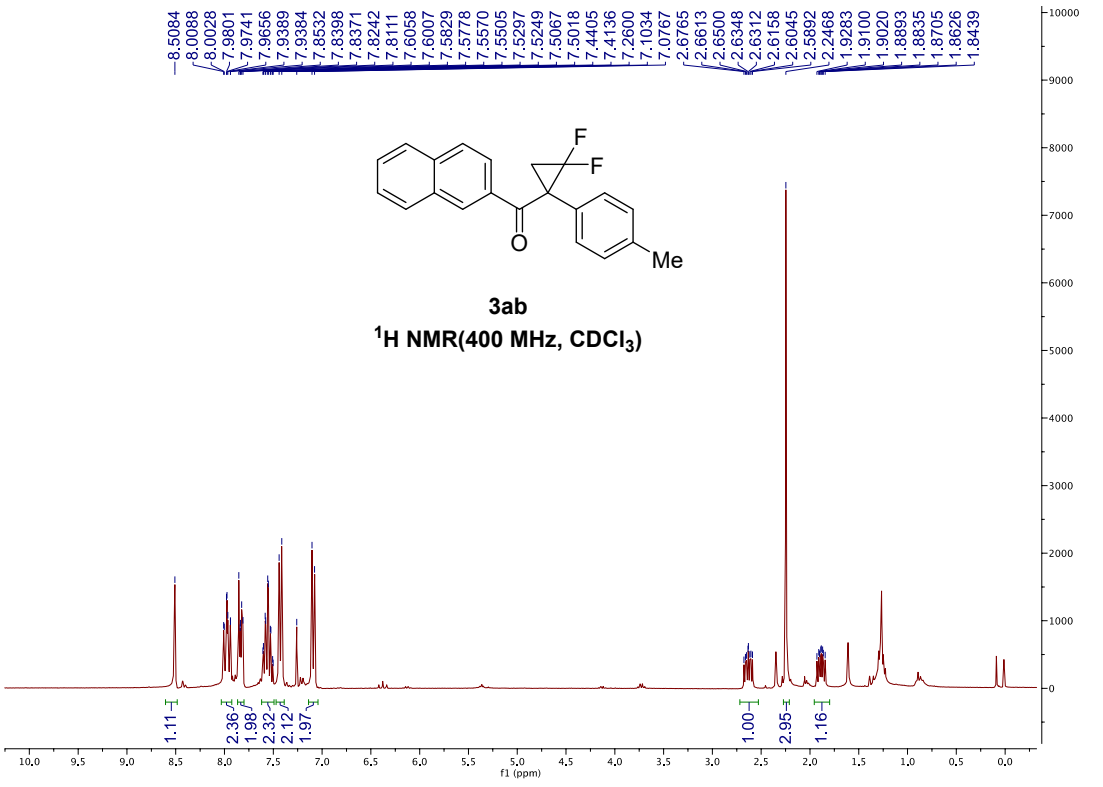
3aa

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



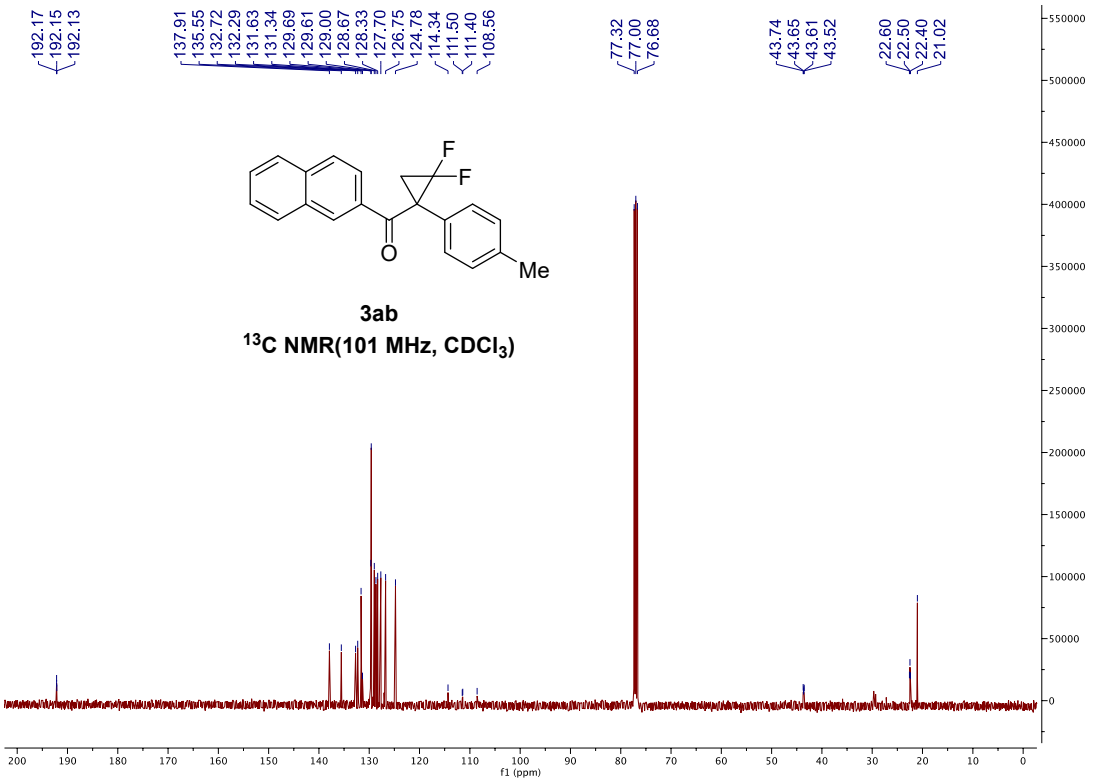
3aa

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



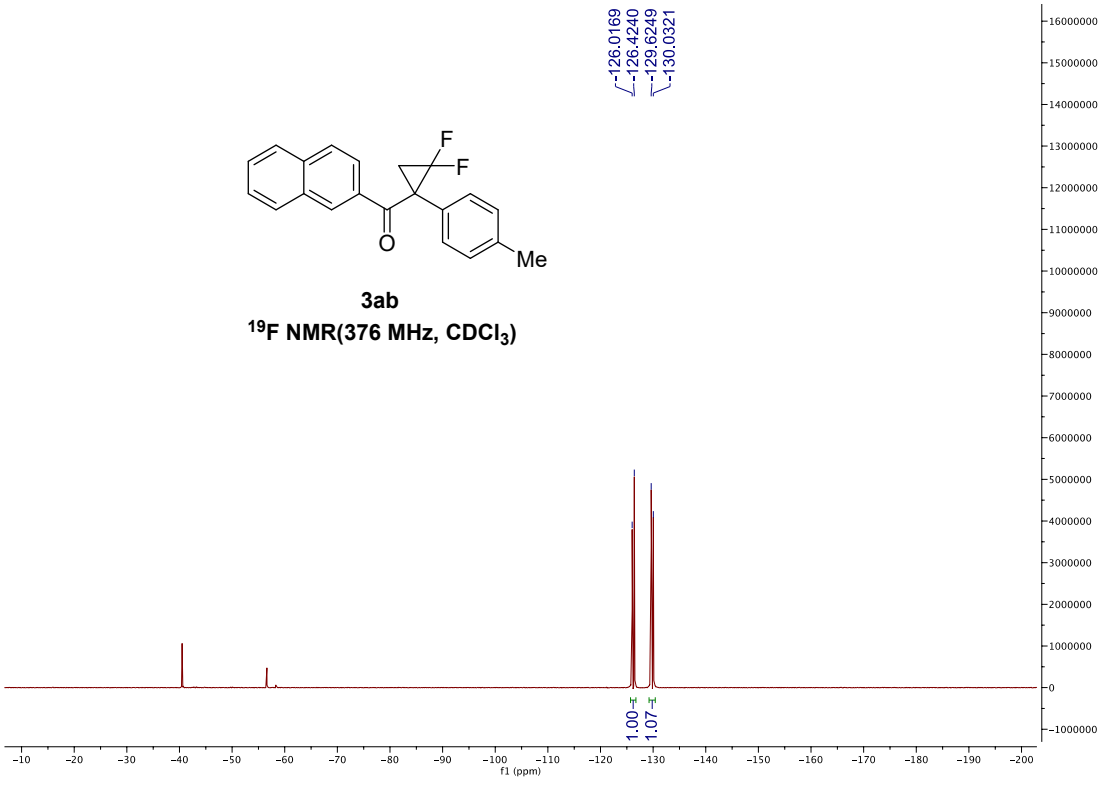
3ab

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



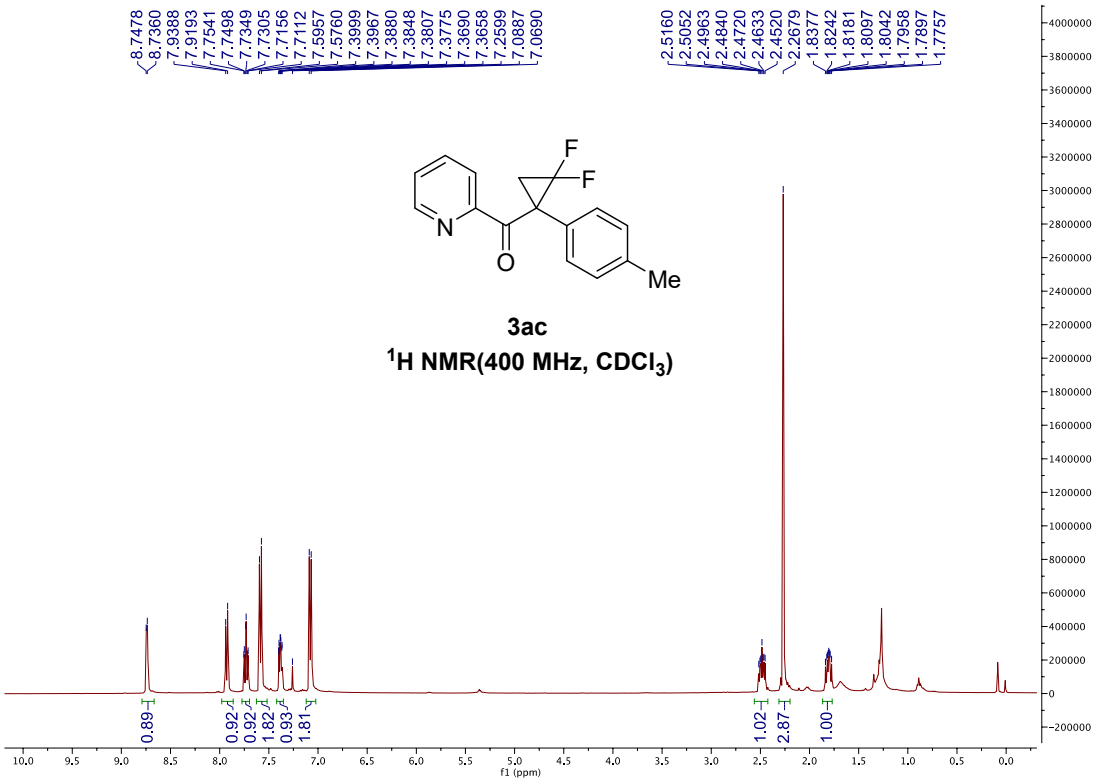
3ab

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



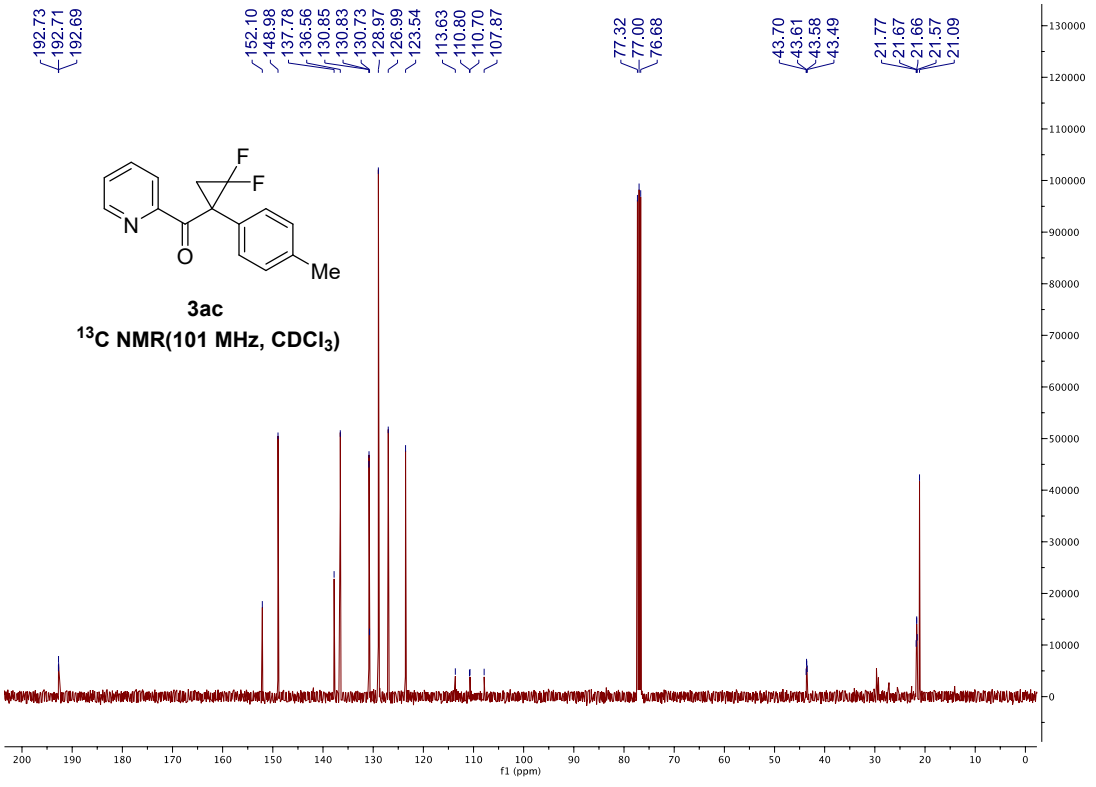
3ab

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



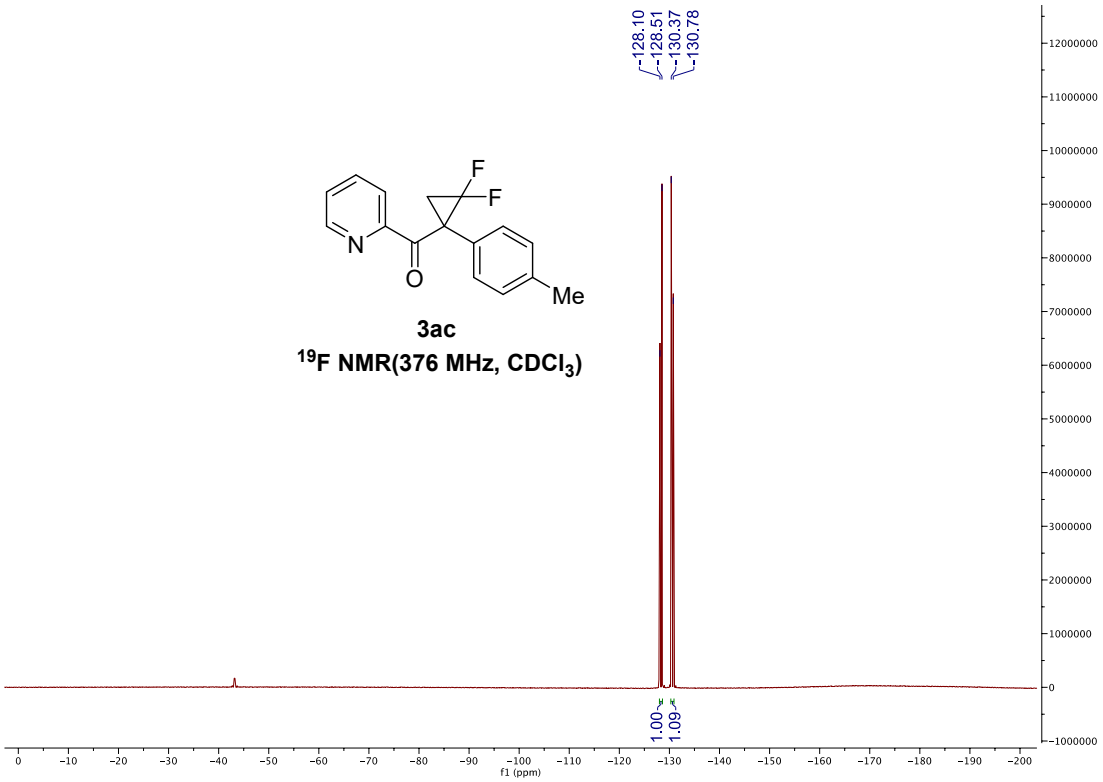
3ac

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



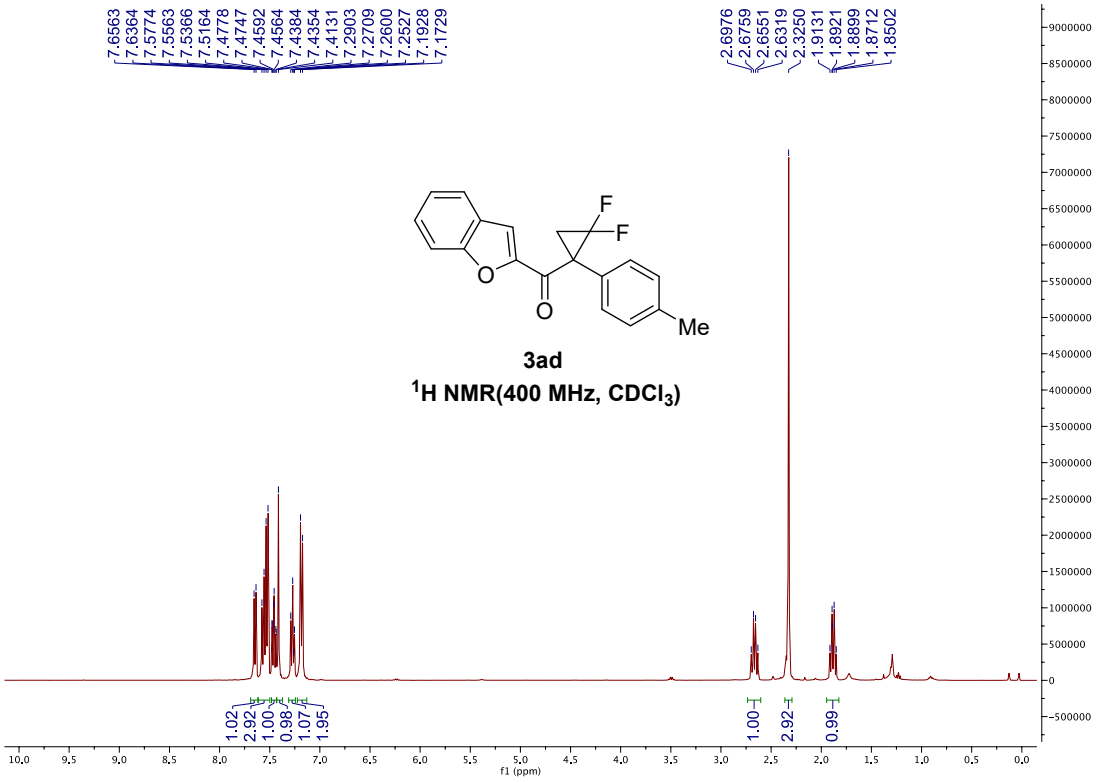
3ac

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



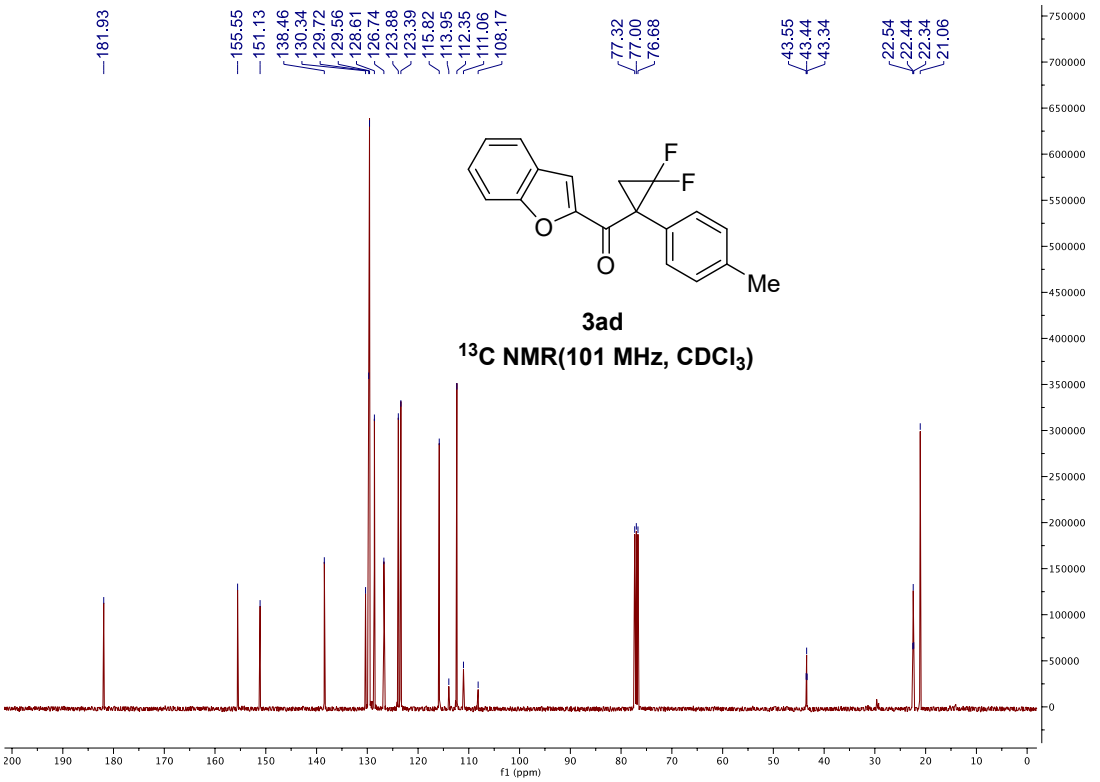
3ac

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



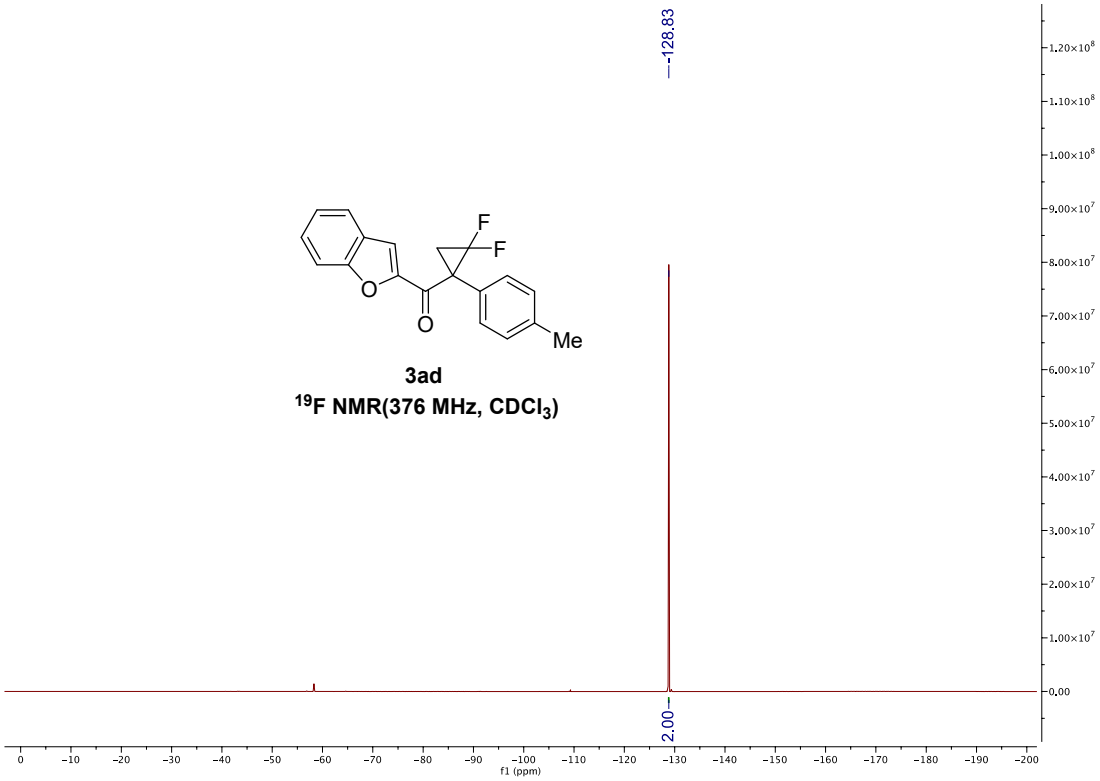
3ad

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



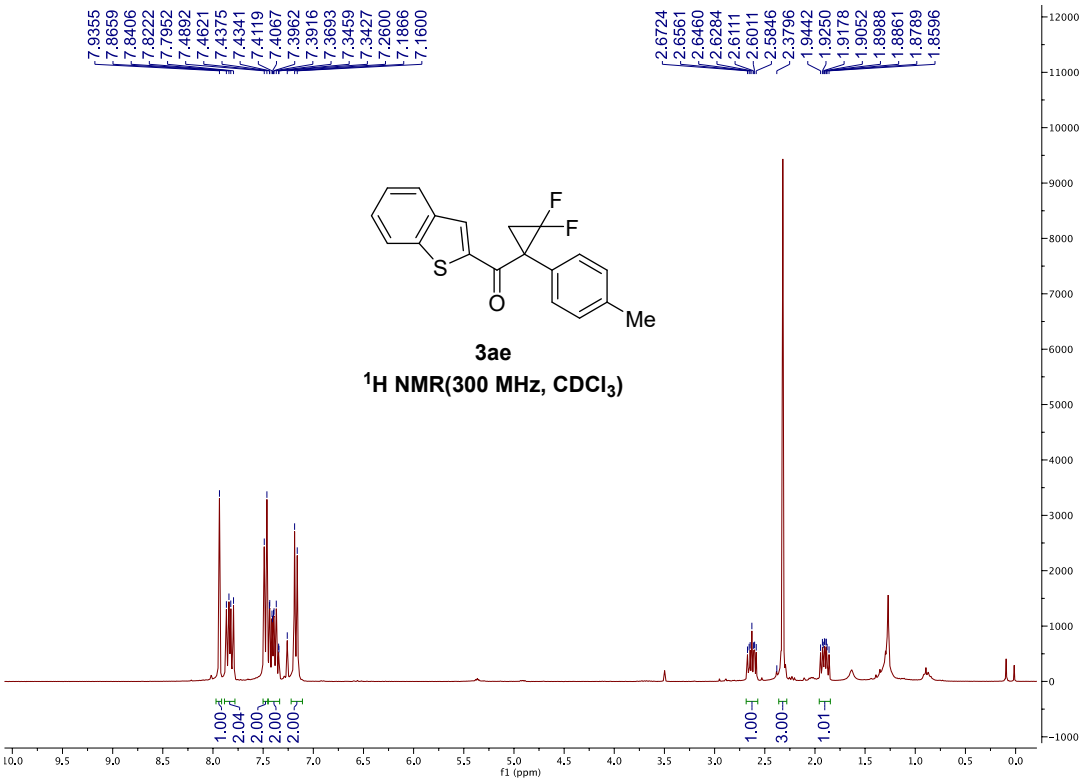
3ad

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



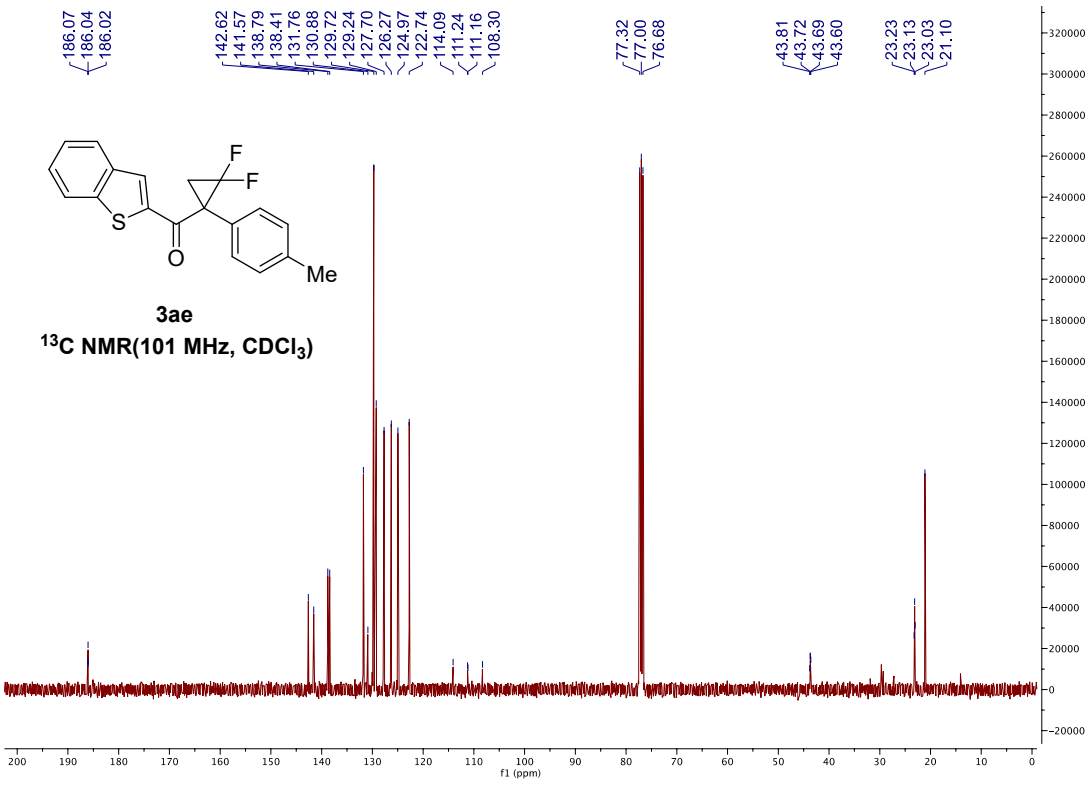
3ad

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



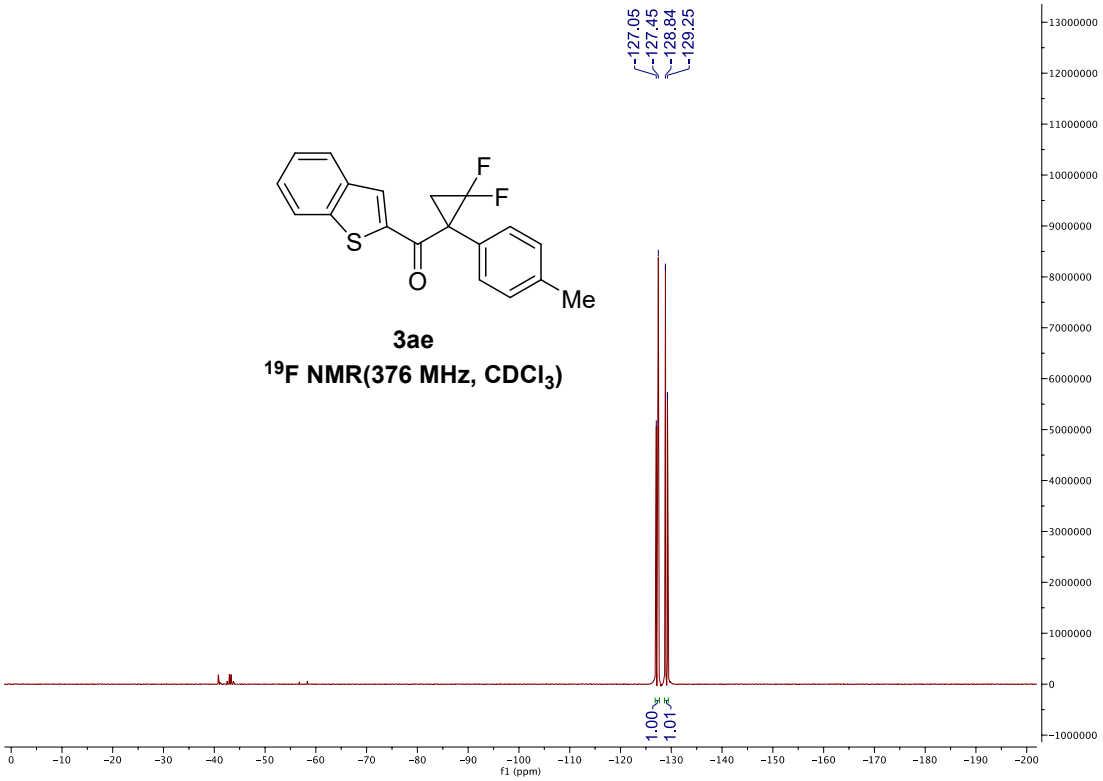
3ae

^{1}H NMR(300 MHz, $CDCl_3$)



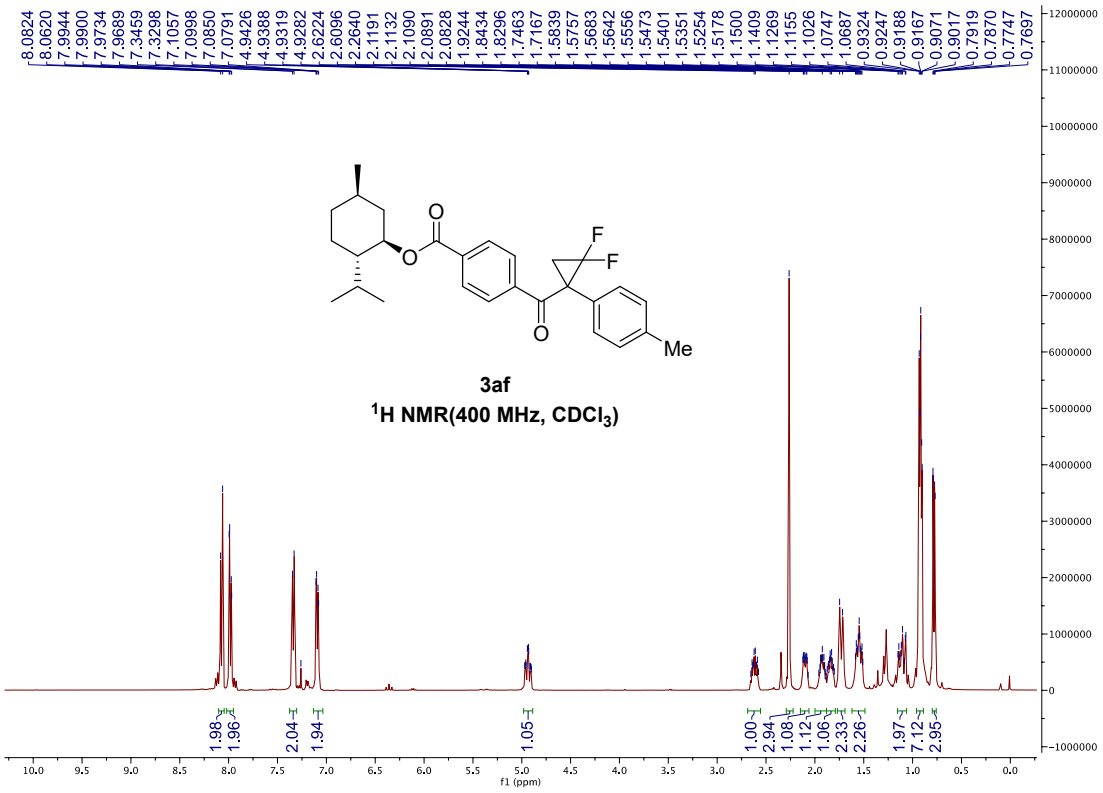
3ae

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



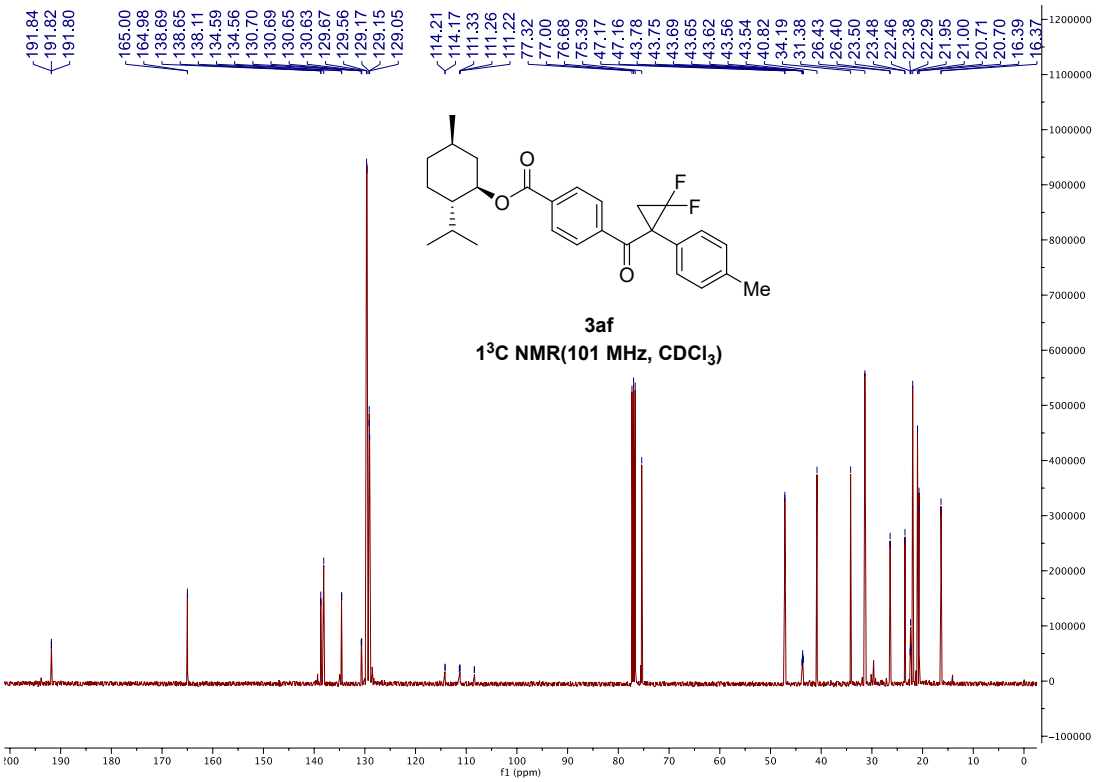
3ae

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



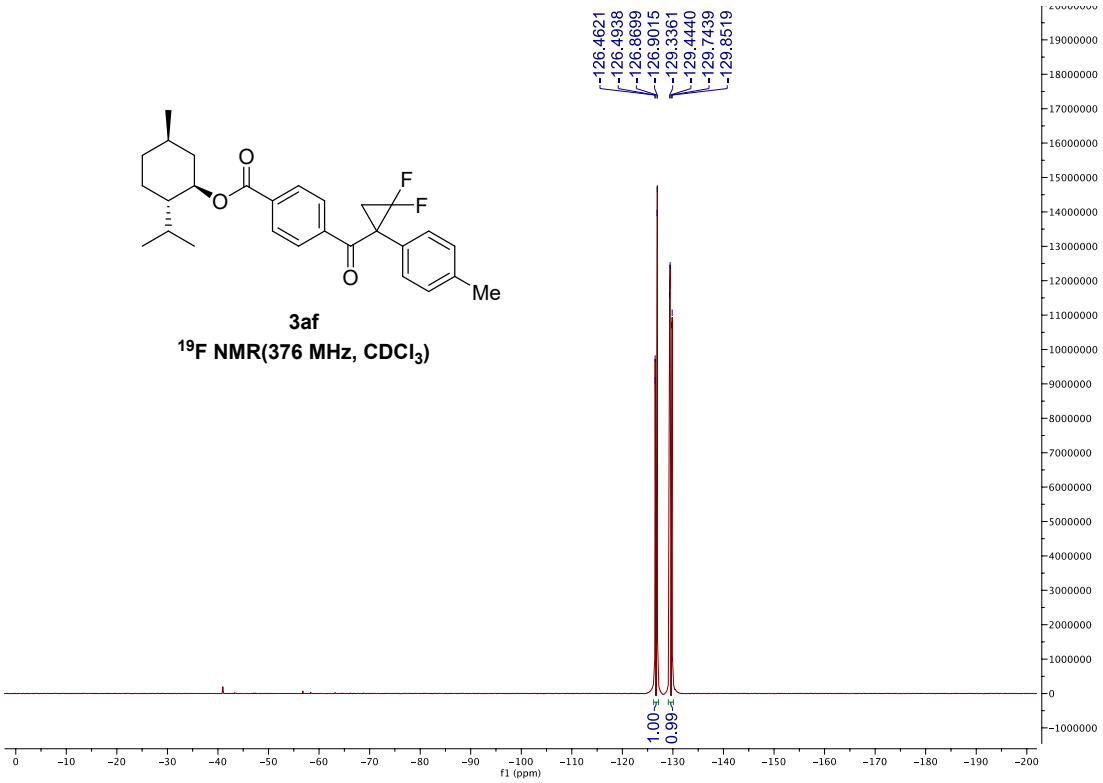
3af

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



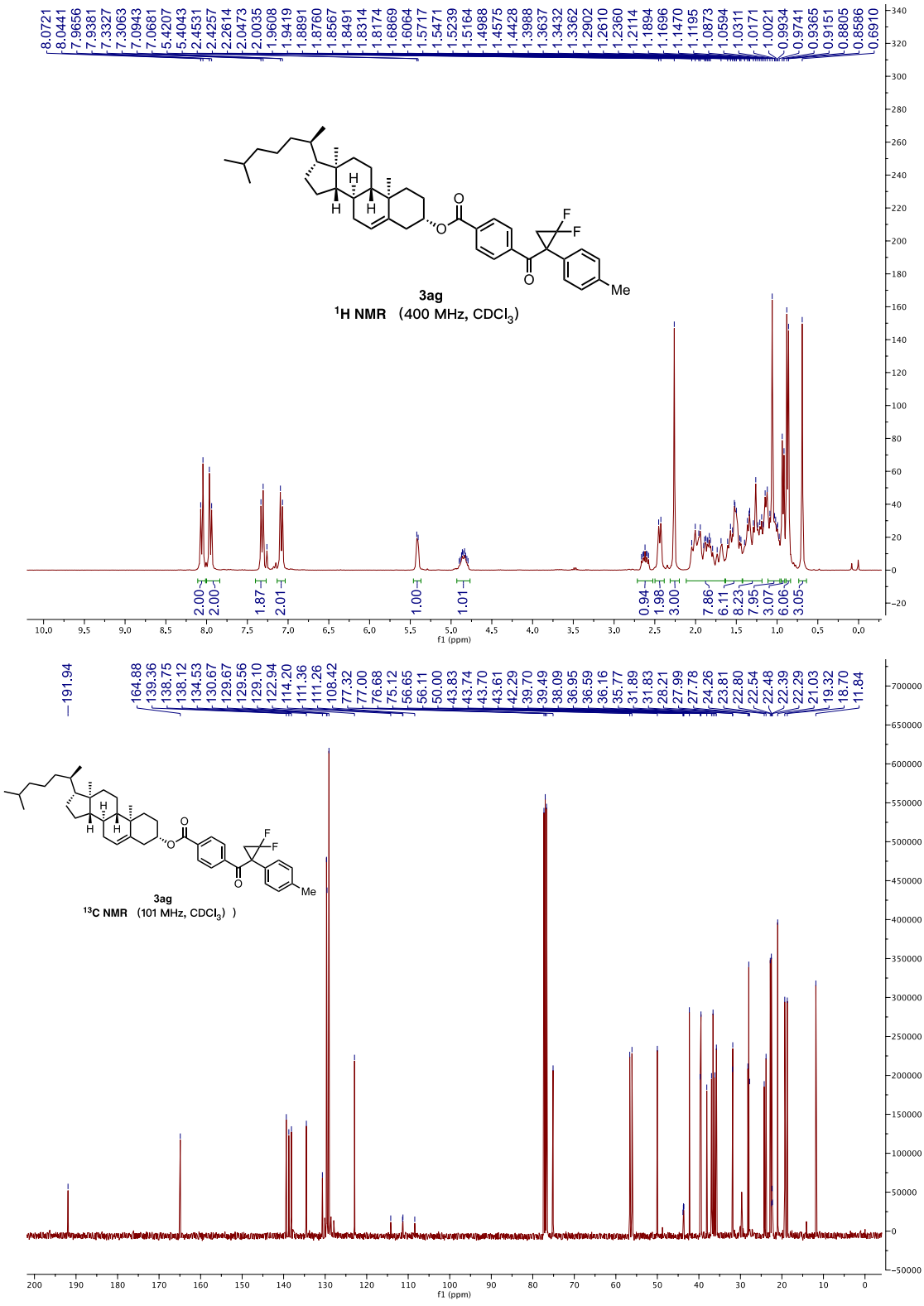
3af

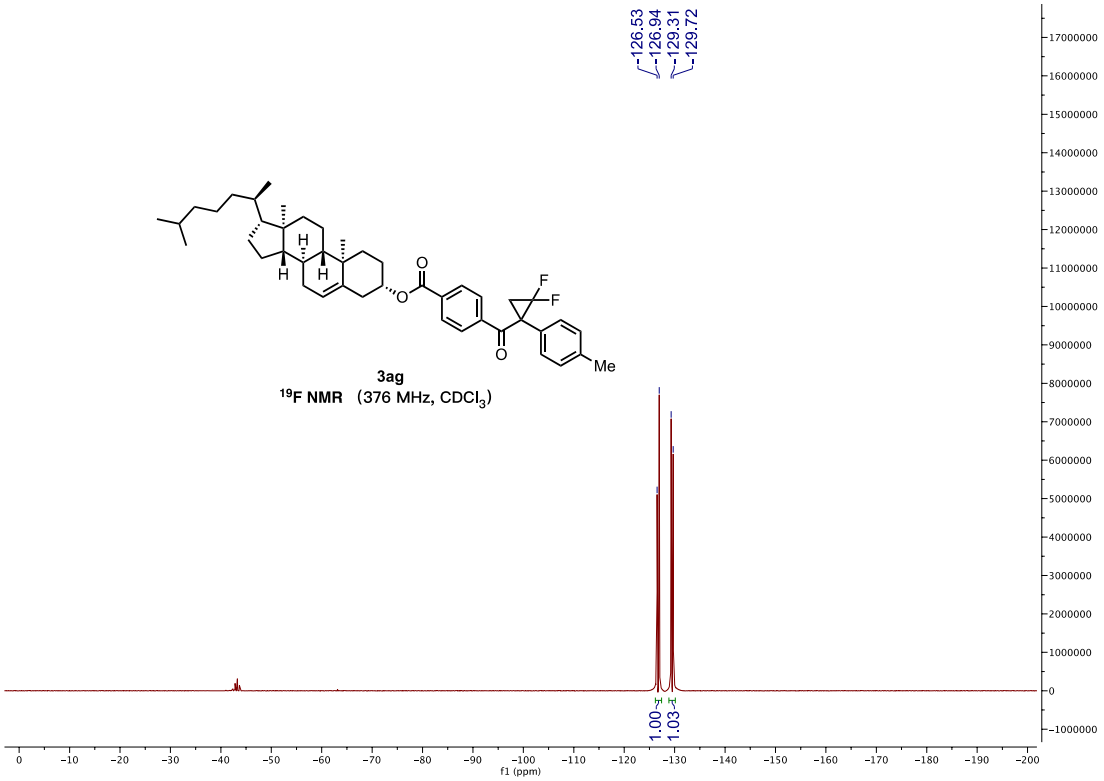
^{13}C NMR(101 MHz, $CDCl_3$)



3af

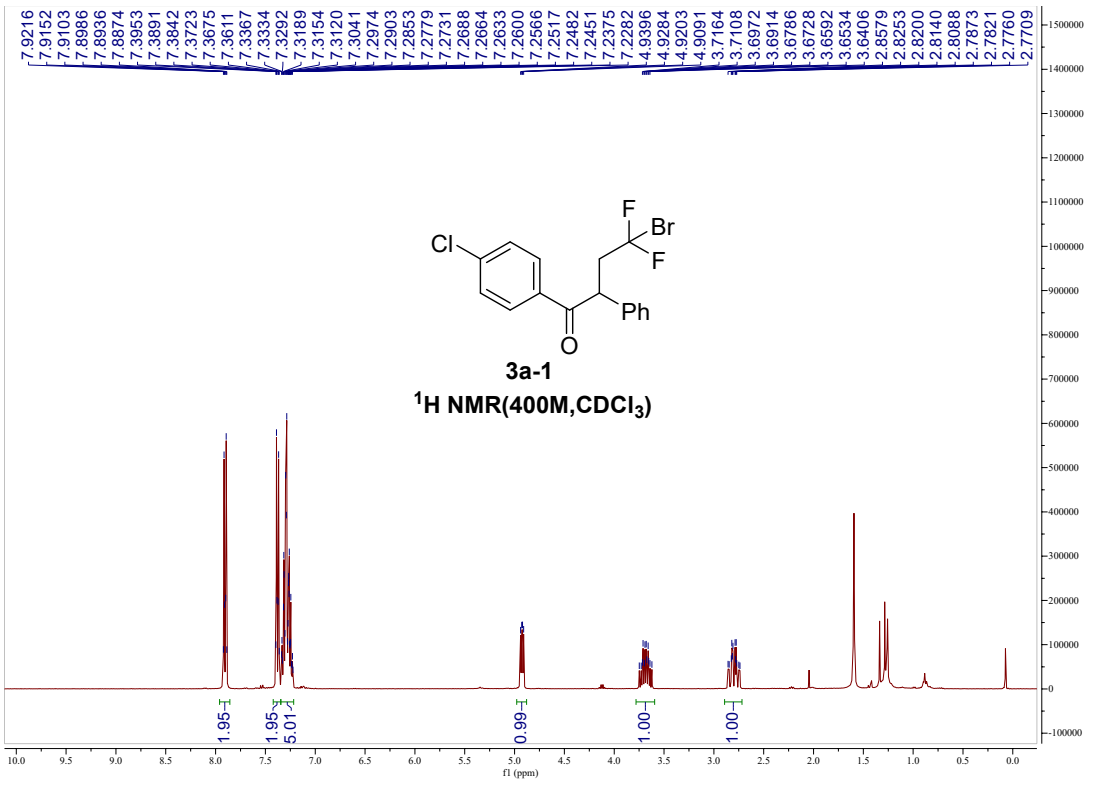
^{19}F NMR(376 MHz, $CDCl_3$)


3ag
1H NMR (400 MHz, CDCl3)
3ag
13C NMR (101 MHz, CDCl3))



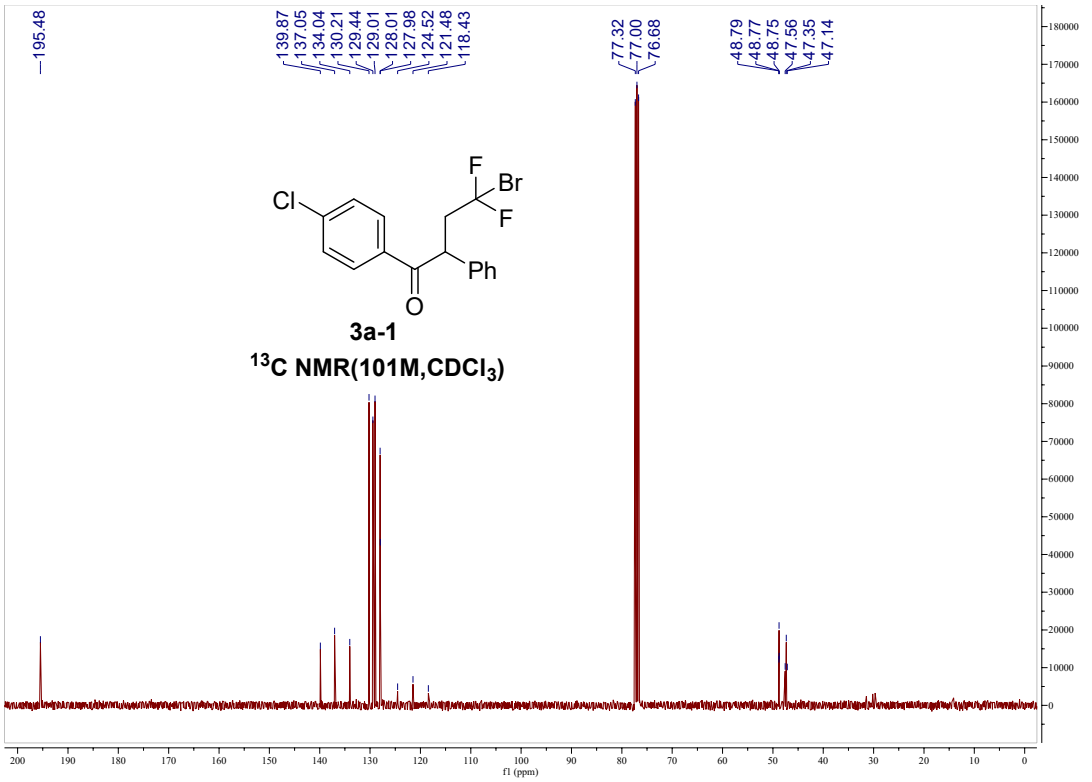
3ag

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



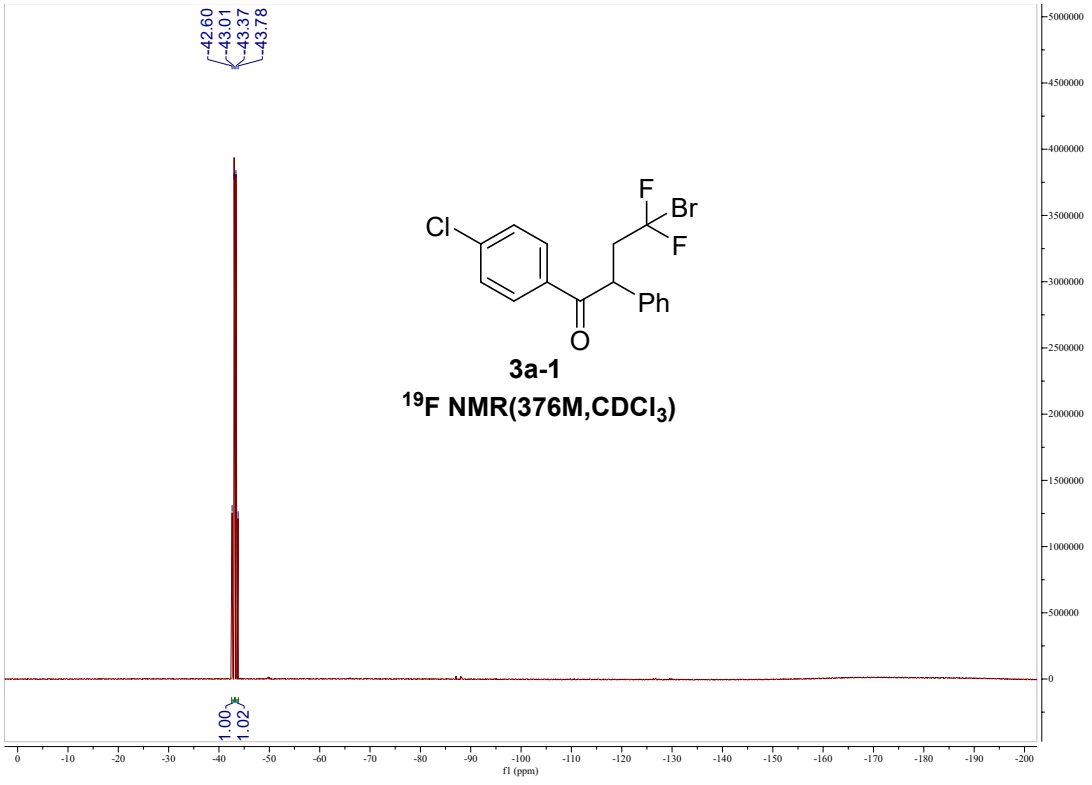
3a-1

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



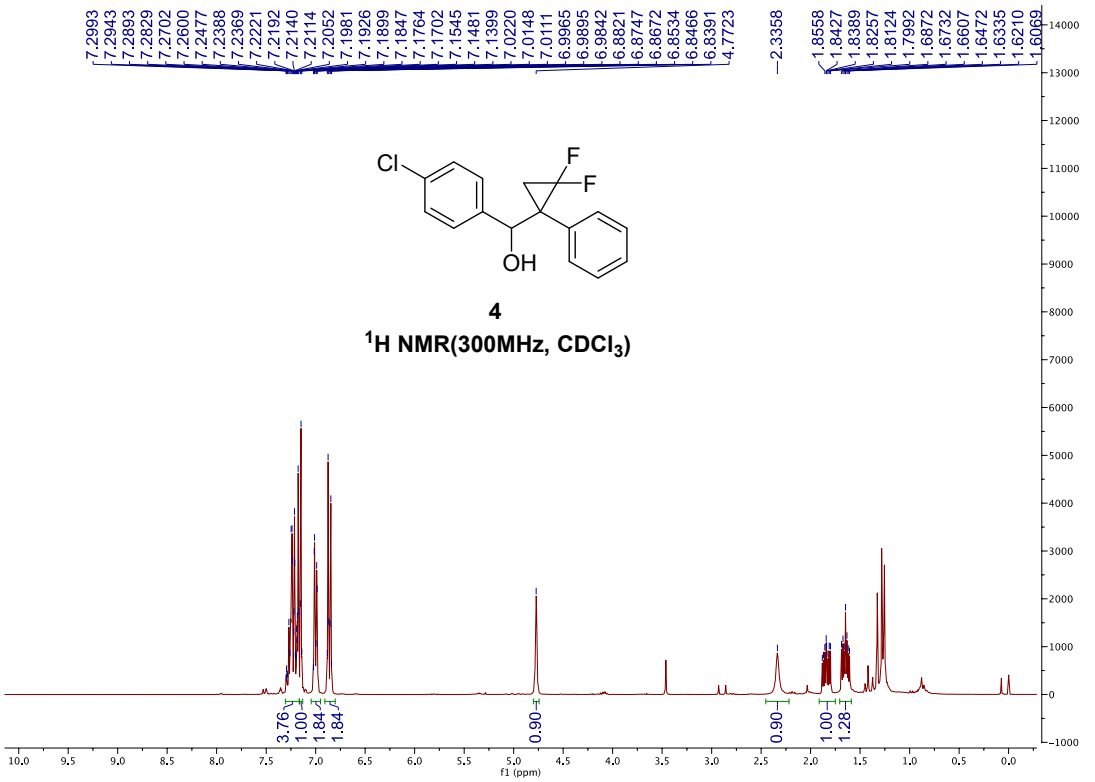
3a-1

^{13}C NMR(101M,CDCl$_3$)



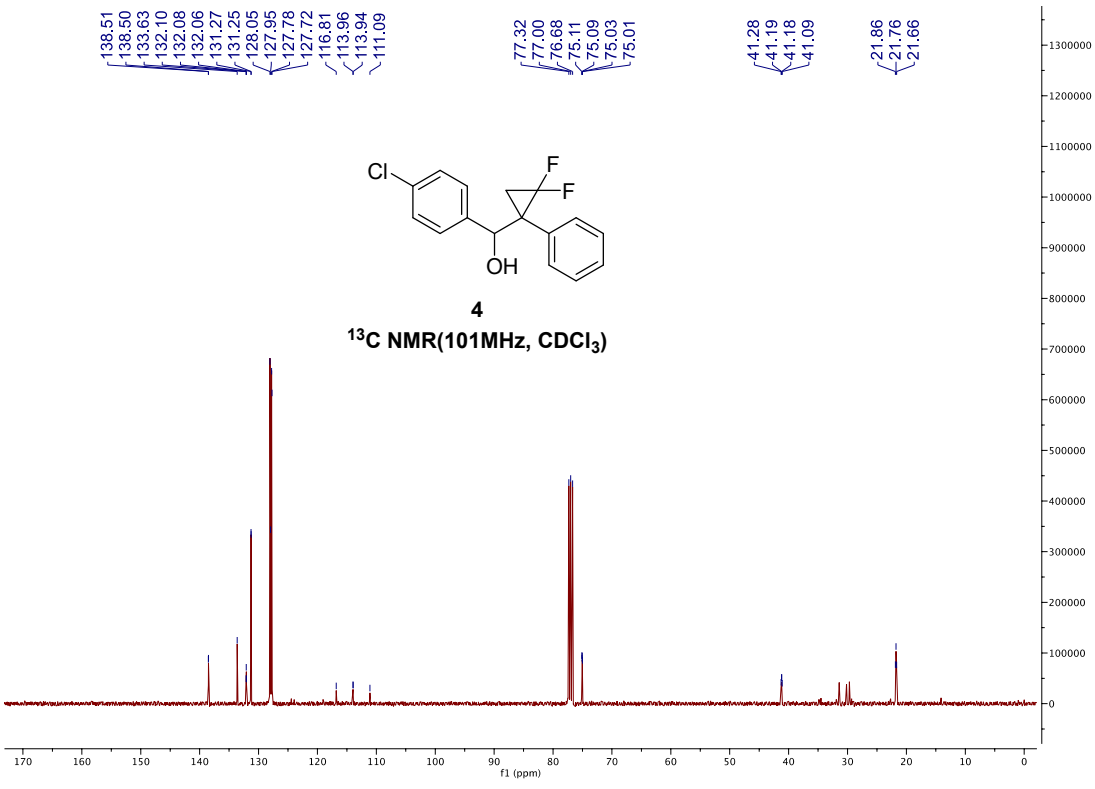
3a-1

^{19}F NMR(376M,CDCl$_3$)



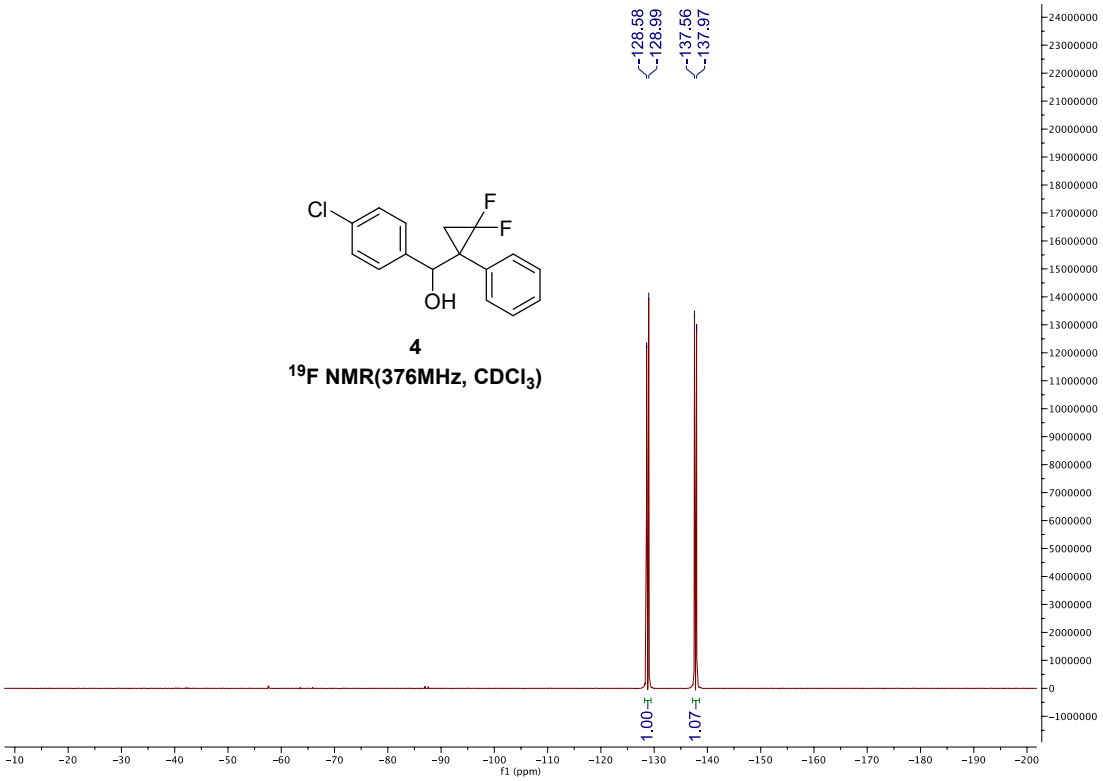
4

^{1}H NMR(300MHz, $CDCl_3$)



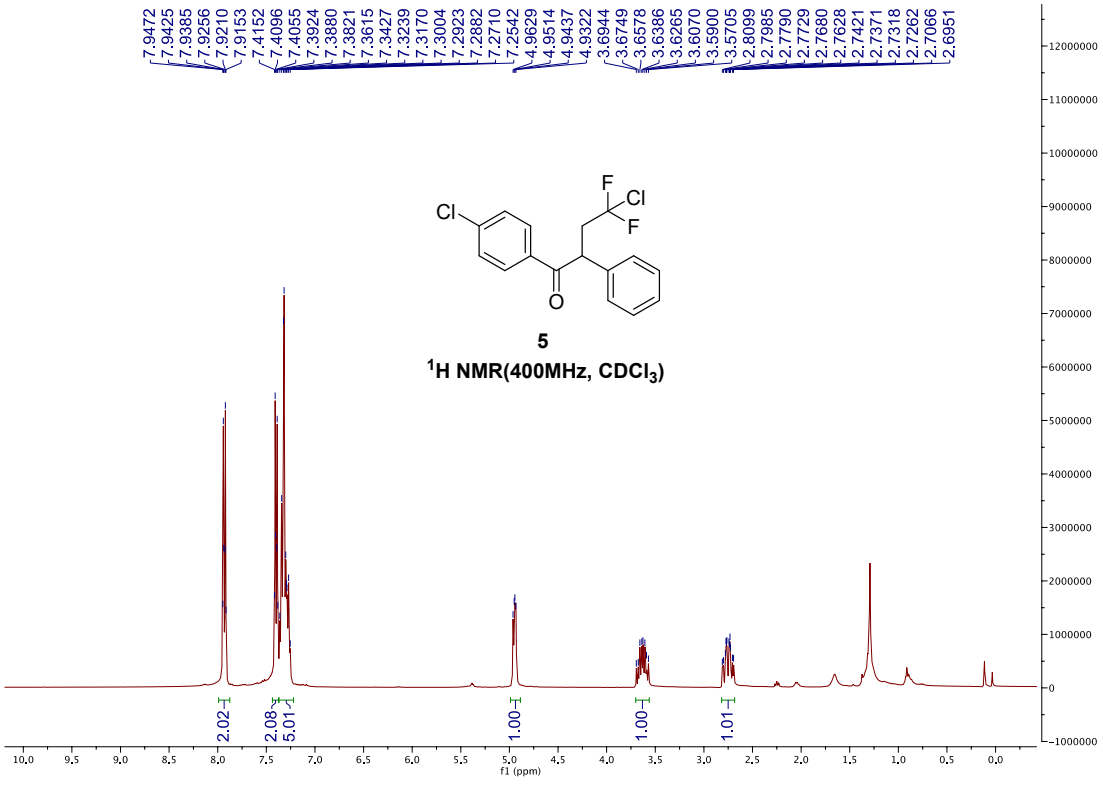
4

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



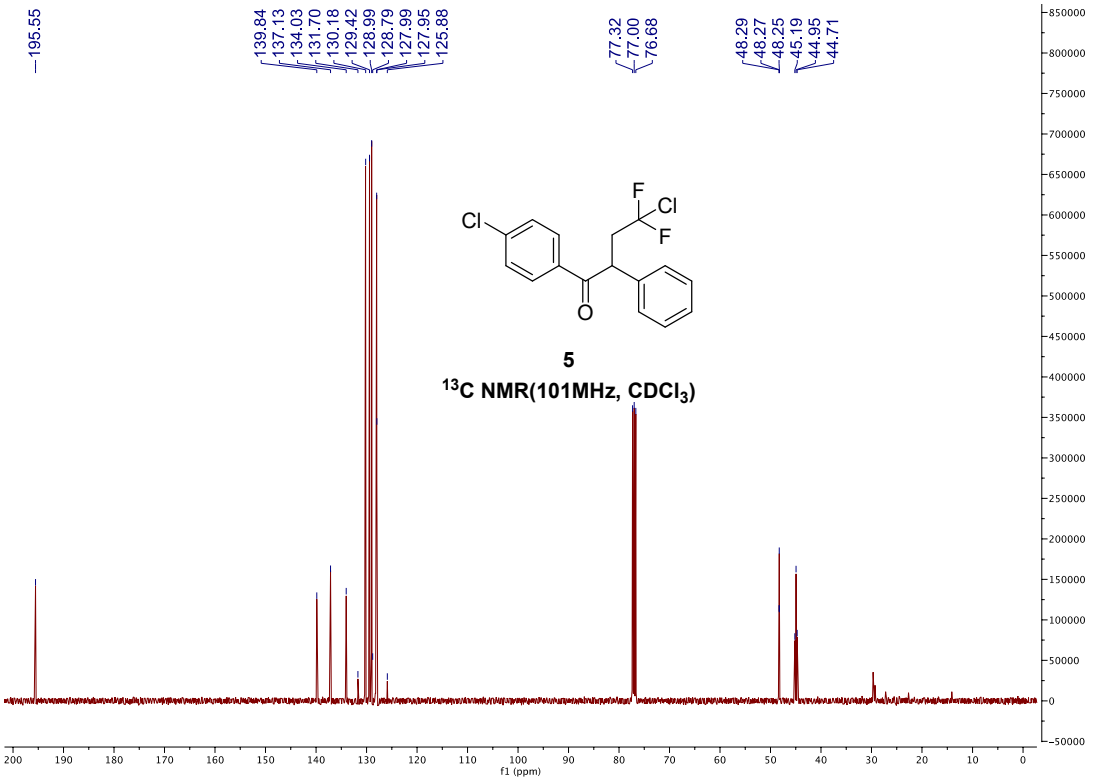
4

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



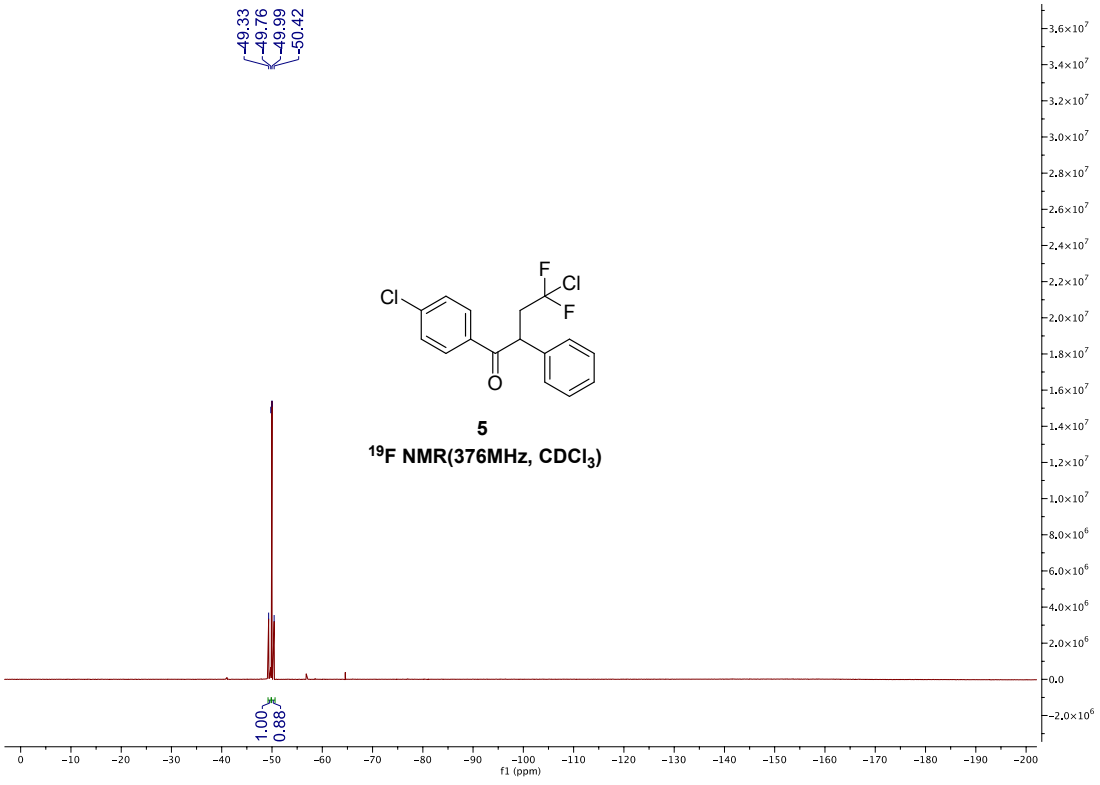
5

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



5

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



5

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

11. Cyclic voltammogram of CF_2Br_2

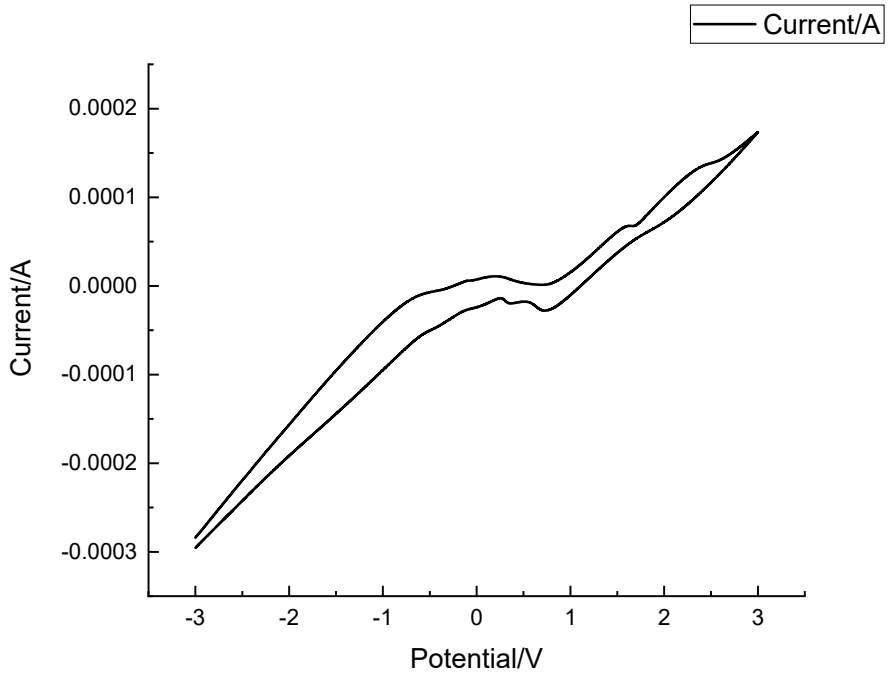


Figure S1. Cyclic voltammograms of CF_2Br_2 (1.82 M solution in DMAc employing saturated KCl solution in Ag/AgCl electrolyte; 50 mV/s rate).