Visible Light Promoted Deaminative Difluoroalkylation of Aliphatic Amines with Difluoroenoxysilanes

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Supporting Information

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List of Contents

1. General information.

^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent MR400 spectrometer. ^{19}F NMR was recorded on an Agilent MR400 spectrometer ($CFCl_3$ as outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using *p*-fluorotoluene as an internal standard before working up the reaction.

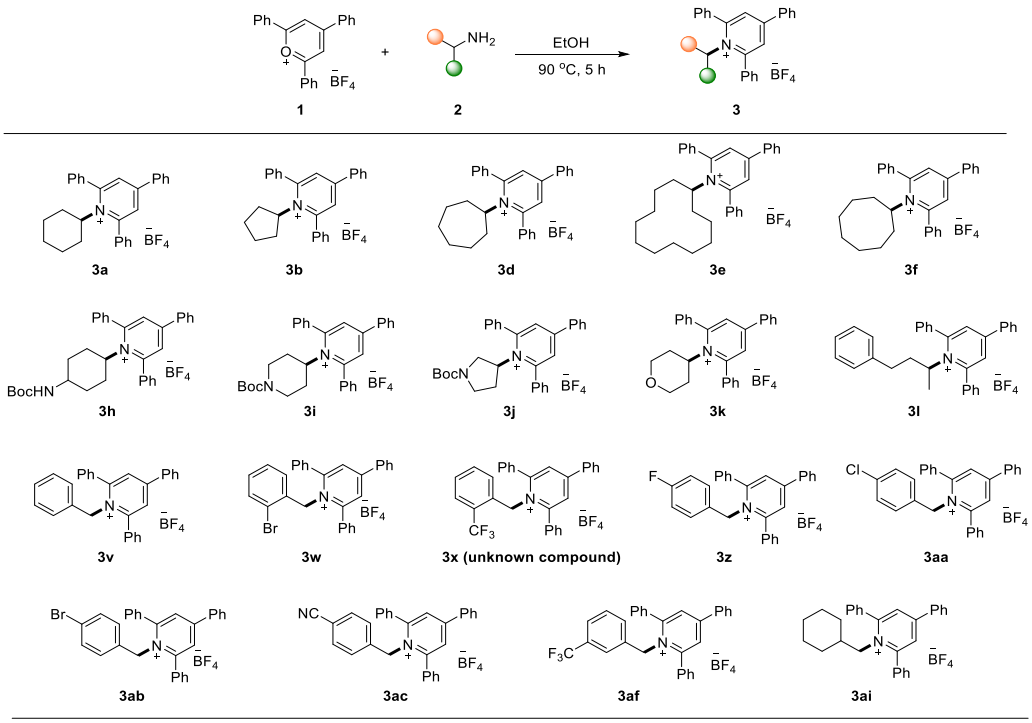
Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air at room temperature.

2. General procedure for the synthesis of Katritzky salts 3.

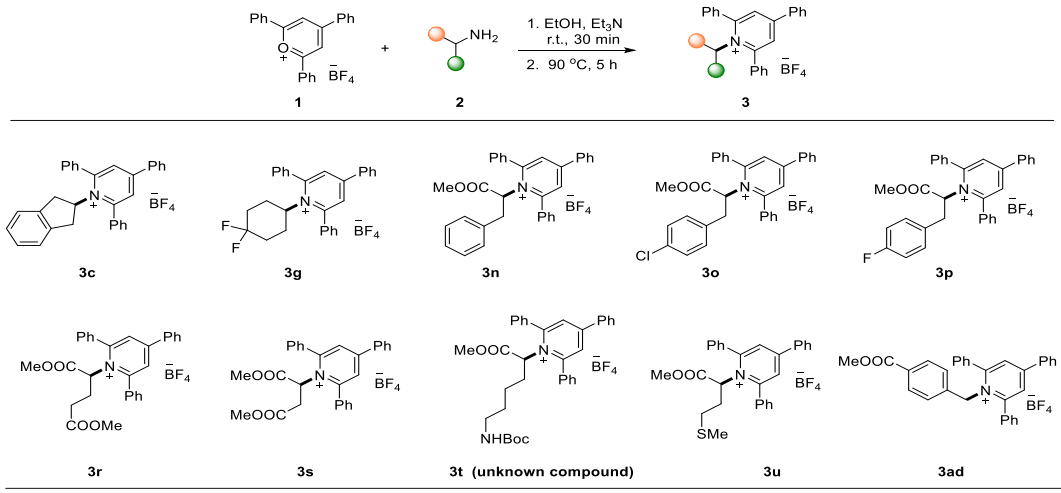
3a, [1] **3b**, [1] **3c**, [2] **3d**, [1] **3e**, [1] **3f**, [3] **3g**, [1] **3h** , [4] **3i**, [1] **3j**, [5] **3k**, [1] **3l**, [2] **3m**, [1] **3n**, [1] **3o**, [1] **3p**, [6] **3r**, [7] **3s**, [7] **3u**, [1] **3v**, [2] **3w**, [8] **3z**, [8] **3aa**, [8] **3ab**, [9] **3ac**, [8] **3ad**, [8] **3ae**, [8] **3af**, [8] **3ag**, [10] **3ai** [11] were prepared according to previous reported procedures. [1], [5] **3q**, **3t**, **3x**, **3y**, **3ah** (unkown Katritzky salts) were prepared according to literature procedures [1], [5] as described as follows:

Procedure 2a [1]**.** A 25 mL Schlenk tube equipped with a magnetic stirrer bar was charged with triphenylpyrylium tetrafluoroborate (**1**) (2.5 mmol, 1.0 equiv.) and the corresponding primary amine (**2**) (3.0 mmol, 1.2 equiv., if solid,). Ethanol (2.5 mL, 1.0 M) was added followed by the corresponding primary amine (**2**) (3.0 mmol, 1.2 equiv., if liquid). No precautions were taken to exclude oxygen or water. The reaction mixture was stirred and heated at reflux in an oil bath at 90 ºC for 5 h. If precipitation occurred during the reaction, the solid was collected by filtration and washed with Et_2O (3×25 mL). If no precipitation occurred, Et_2O (7.5 mL) was added and the crude mixture was stirred for 1 h. The resulting solid was collected by filtration and washed with Et_2O (3×25 mL). If precipitation did still not take place, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography,

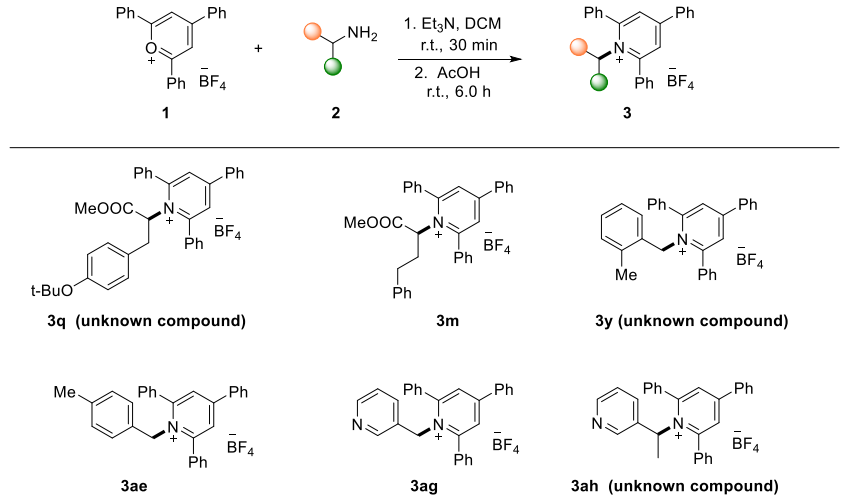
eluting with CH_2Cl_2/MeOH.



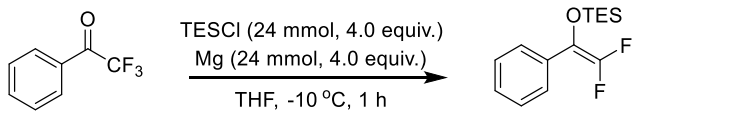
Amine hydrochlorides as starting materials: The corresponding amine hydrochloride (**2**) (3.0 mmol, 1.2 equiv.) was weighed into a 25 mL Schlenk tube containing a magnetic stirring bar. EtOH (2.5 mL, 1.0 M) and Et_3N (3.0 mmol, 1.2 equiv.) were added successively. The resulting suspension was stirred at room temperature for 30 min. 2,4,6-Triphenylpyrylium tetrafluoroborate (**1**) (2.5 mmol, 1.0 equiv.) was added in one portion and the reaction mixture was stirred and heated at reflux in an oil bath at 90 ºC for 5 h. If precipitation occurred during the reaction, the solid was collected by filtration and washed with H_2O (3×25 mL, to remove Et_3N·HCl salts) and Et_2O (3×25 mL). If no precipitation occurred, Et_2O (7.5 mL) was added and the crude mixture was stirred for 1 h. The resulting solid was collected by filtration and washed with H_2O (3×25 mL, to remove Et_3N·HCl salts) and Et_2O (3×25 mL). If precipitation did still not take place, the solvent was removed under reduced pressure. The crude product was then dissolved in CH_2Cl_2, washed with H_2O and concentrated under reduced pressure. The crude product was purified by flash column chromatography, eluting with CH_2Cl_2/MeOH.



Procedure 2b [5]**.** The triphenylpyrylium tetrafluoroborate (**1**) (2.5 mmol, 1.0 equiv.) and the corresponding primary amine (**2**) (2.5 mmol, 1.0 equiv.) was weighed into a 25 ml Schlenk tube containing a magnetic stirring bar. CH_2Cl_2 (5.0 mL, 0.5 M) and then Et_3N (1.0 equiv. for free base amines; 2.0 equiv. for amine hydrochloride salts) were added successively. The mixture was stirred at room temperature for 30 min. Acetic acid (2.0 equiv.) was added and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with CH_2Cl_2, washed successively with aq. HCl (1.0 M, 2×25 mL), aq. $NaHCO_3$ (sat., 2×25 mL) and brine (3×25 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography, eluting with CH_2Cl_2/MeOH.



3. Detail procedure for the synthesis of Difluoroenoxytriethylsilane (4) [12].

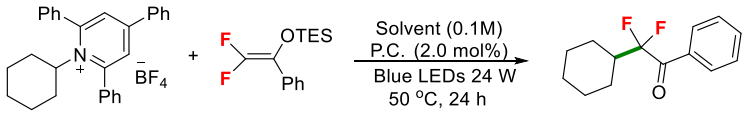


1.0 equiv

Difluoroenoxytriethylsilane (**4**)

A 100 mL oven-dried reaction bottle equipped with a magnetic stirrer bar was charged with the Mg (0.58 g, 24 mmol). The bottle was evacuated and backfilled with argon three times, followed by THF (24 mL) were added with stirring, Chlorotriethylsilane (4.0 mL, 24 mmol) was added subsequently. The bottle was capped and cooled down to -10 °C under an argon atmosphere, trifluoroacetophenone (843 μL, 6.0 mmol) was added dropwise and then the reaction mixture was stirred for additional 1 h. After evaporation of solvent, Et_3N (3.3 mL, 24 mmol) was added and the mixture was stirred for 10 min. The mixture was filtered by petroleum ether, concentrated in vacuo, and purified by flash column chromatography on silica gel (pretreated with 3% Et_3N/Petroleum ether), eluting with petroleum ether, afforded to pure product difluoroenoxytriethylsilane **(4)** (1.3 g, 80% yield). The reagent should be used as soon as possible after preparation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.65 (d, *J* = 68.8 Hz, 1F), -112.49 (d, *J* = 68.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (t, *J* = 287.6 Hz), 132.87 (dd, *J* = 6.9, 1.8 Hz), 128.2, 127.8 (t, *J* = 1.4 Hz), 126.1 (dd, *J* = 6.6, 3.5 Hz), 114.22 (dd, *J* = 35.1, 19.0 Hz), 6.5, 4.9.

4. Detail Results for the Condition Optimization [a,b]

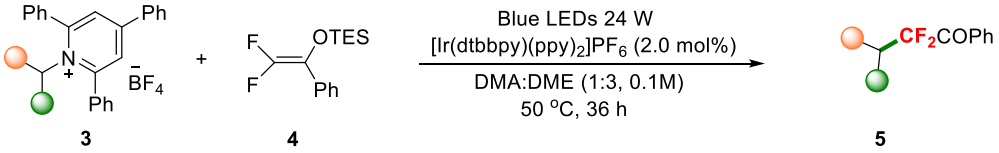


3a **4** **5a**

Entry	Catalyst	Solvent	Yield (5a %)[b]
1	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA	68
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	NMP	64
3	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMF	36
4	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMSO	----
5	$[Ir(dtbbpy)(ppy)_2]PF_6$	MeCN	9
6	$[Ir(dtbbpy)(ppy)_2]PF_6$	THF	43
7	$[Ir(dtbbpy)(ppy)_2]PF_6$	DME	11
8	$[Ir(dtbbpy)(ppy)_2]PF_6$	1,4-Dioxane	10
9	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : MeCN (1:1)	59
10	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : DCE (1:1)	50
11	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : PhCl (1:1)	70
12	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : 1,4-Dioxane (1:1)	73
13	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : DME (1:1)	85
14	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : THF (1:1)	85
15	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : DME (1:3)	97
16	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : DME (3:1)	75
17	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : THF (1:3)	84
18	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : THF (3:1)	72
19	$Ru(bpy)_3Cl_2$	DMA : DME (1:3)	9
20	$Ir(ppy)_3$	DMA : DME (1:3)	19
21	$[Ir(ppy)_2(bpy)]PF_6$	DMA : DME (1:3)	36
22[c]	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : DME (1:3)	75
23[d]	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : DME (1:3)	----
24	----	DMA : DME (1:3)	----
25[e]	$[Ir(dtbbpy)(ppy)_2]PF_6$	DMA : DME (1:3)	97 (92)

[a] Reaction conditions (unless otherwise specified): 3a (0.1 mmol, 1.0 equiv.), 4 (0.2 mmol, 2.0 equiv.), P.C. (2.0 mol%), Solvent (1.0 mL), blue LEDs 24 W, 50 °C, 24 h, under argon atmosphere. [b] NMR yield determined by ^{19}F NMR using *p*-fluorotoluene as internal standard. [c] The reaction was performed at 35 °C. [d] The reaction was performed in the dark. [e] Reaction performed on a 0.2 mmol scale, 36 h, yield of isolated product given in parentheses.

5. General procedure for visible light promoted deaminative difluoroalkylation of aliphatic amines.



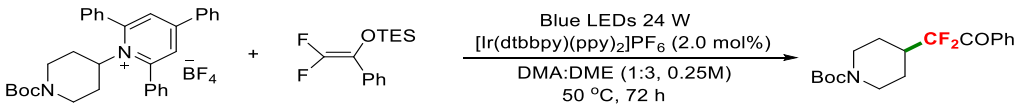
3 **4** **5**

A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with the Katritzky salt (**3**) (0.2 mmol, 1.0 equiv.), $[Ir(dtbbpy)(ppy)_2]PF_6$ (0.004 mmol, 2.0 mol%). The tube was evacuated and backfilled with argon three times, followed by DMA and DME (1:3, 2.0 mL) with stirring. Difluoroenoxytriethylsilane (**4**) (0.4 mmol, 2.0 equiv.) was added subsequently. The tube was screw capped and heated to 50 °C under irradiation of blue LEDs. After stirring for 36 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

6. Detailed procedure for the gram scale synthesis of compound 5a, 5i.

3a **4** **5a**

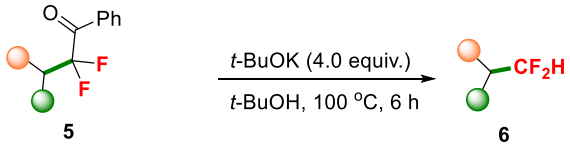
A 50 mL oven-dried Schlenk bottle equipped with a magnetic stirrer bar was charged with the **3a** (4.0 mmol, 1.0 equiv.), $[Ir(dtbbpy)(ppy)_2]PF_6$ (0.08 mmol, 2.0 mol%). The bottle was evacuated and backfilled with argon three times, followed by DMA and DME (1:3, 16.0 mL) with stirring. Difluoroenoxytriethylsilane **(4)** (8.0 mmol, 2.0 equiv.) was added subsequently. The bottle was capped and heated to 50 °C under irradiation of blue LEDs. After stirring for 72 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The product **5a** (707 mg, 74% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as colorless oil.



3i **4** **5i**

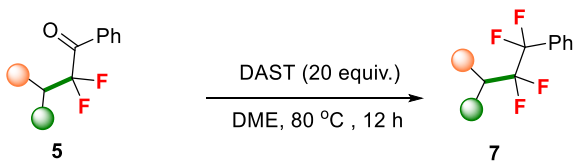
A 50 mL oven-dried Schlenk bottle equipped with a magnetic stirrer bar was charged with the **3i** (4.0 mmol, 1.0 equiv.), $[Ir(dtbbpy)(ppy)_2]PF_6$ (0.08 mmol, 2.0 mol%). The bottle was evacuated and backfilled with argon three times, followed by DMA and DME (1:3, 16.0 mL) with stirring. Difluoroenoxytriethylsilane **(4)** (8.0 mmol, 2.0 equiv.) was added subsequently. The bottle was capped and heated to 50 °C under irradiation of blue LEDs. After stirring for 72 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The product **5i** (828 mg, 61% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as pale yellow oil.

7. General procedure for the transformation of Compounds 5.



5 **6**

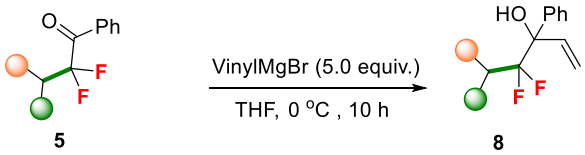
General procedure 7a: A mixture of **5** (0.2 mmol, 1.0 equiv.), *t*-BuOK (89.8 mg, 0.4 mmol) in *t*-BuOH (2.0 mL) was stirred at 100 °C for 6 h in a 25 ml sealed Schlenk tube. After that, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography to afford product **6.**



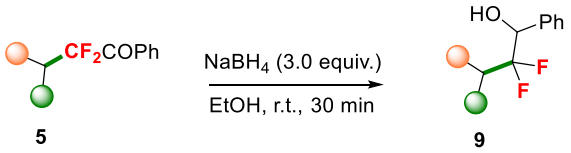
5 **7**

General procedure 7b: To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was added compound **5** (0.2 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 to afford product **7**.



General procedure 7c: To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was added compound **5** (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 vinylmagnesium bromide (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 organics were washed with brine, dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. The unpurified reaction mixture was purified on silica gel to afford product **8.**

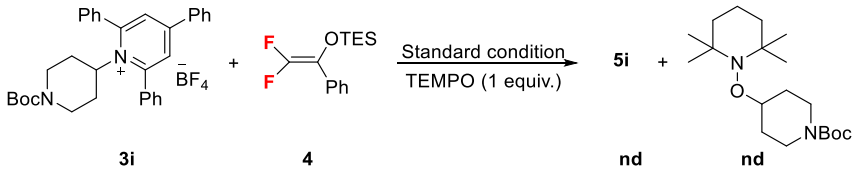


General procedure 7d: Compound **5** (0.2 mmol, 1.0 equiv.) was dissolved in 2.0 mL anhydrous EtOH, followed by the addition of $NaBH_4$ (22.7 mg, 0.6 mmol) in one portion at room temperature. The resulting mixture was stirred until the complete consumption of **5** as indicated by TLC analysis. Then the reaction was quenched by saturated NH_4Cl (aq.), and extracted with CH_2Cl_2 three times. The combined organic layer was washed with saturated brine, respectively. The solution was dried over

anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography to afford product **9**.

8. Mechanism studies

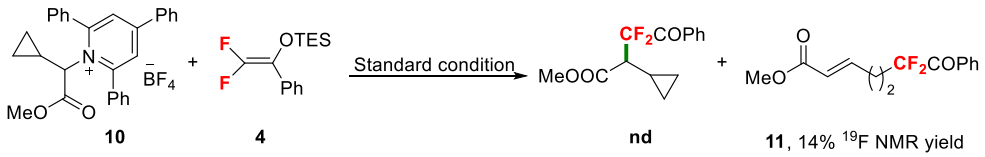
8.1 Addition of radical and SET inhibitors



3i **4** **nd** **nd**

Typical procedure: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with the Katritzky salt (**3i**) (0.2 mmol, 1.0 equiv.), $[Ir(dtbbpy)(ppy)_2]PF_6$ (0.004 mmol, 2.0 mol%). The tube was evacuated and backfilled with argon three times, followed by DMA and DME (1:3, 2.0 mL) were added with stirring. Difluoroenoxytriethylsilane (**4**) (0.4 mmol, 2.0 equiv.) was added subsequently. The tube was screw capped and heated to 50 °C under irradiation of blue LEDs. After stirring for 36 h, the reaction mixture was cooled to room temperature, monitored by TLC. The reaction was totally suppressed by the addition of a radical scavenger TEMPO (100 mol%), which suggests that the involvement of radical intermediates is likely during the reaction.

8.2 Trapping of intermediates:

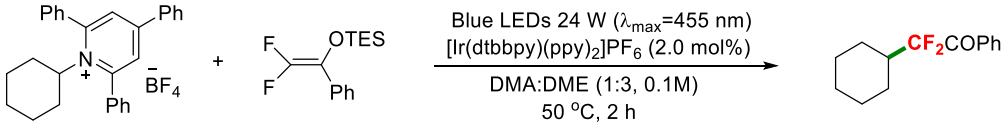


10 **4** **nd** **11**, 14% ^{19}F NMR yield

Typical procedure: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with the Katritzky salt (**10**) [13] (0.2 mmol, 1.0 equiv.), $[Ir(dtbbpy)(ppy)_2]PF_6$ (0.004 mmol, 2.0 mol%). The tube was evacuated and backfilled with argon three times, followed by DMA and DME (1:3, 2.0 mL) were added with stirring. Difluoroenoxytriethylsilane (**4**) (0.4 mmol, 2.0 equiv.) was added subsequently. The tube was screw capped and heated to 50 °C under irradiation of blue LEDs. After

stirring for 36 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide product **11**. (The yield of the crude ring-opened product **11** was determined to be 14% by ^{19}F-NMR analysis with p-fluorotoluene as an internal standard). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.02 – 6.95 (m, 1H), 5.90 (dt, *J* = 15.6, 1.5 Hz, 1H), 3.73 (s, 3H), 2.53 – 2.48 (m, 2H), 2.42 – 2.30 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.16 (t, *J* = 17.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9 (t, *J* = 31.6 Hz), 166.7, 146.5, 134.4, 131.7, 130.3 (t, *J* = 3.2 Hz), 128.7, 122.0, 119.1 (t, *J* = 255.1 Hz), 51.5, 32.2 (t, *J* = 23.1 Hz), 24.3 (t, *J* = 5.1 Hz). MS (ESI): m/z (%) 269 ($[M+H]^+$, 100). HRMS (ESI): calculated for $C_{14}H_{15}O_3F_2$ ($[M+H]^+$): 269.0984; Found: 269.0981.

8.3 **Determination of the quantum yield** [1]



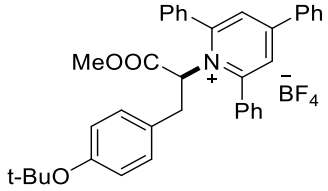
3a **4** **5a**
1.4% yield

A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with the **3a** (1.0 mmol, 1.0 equiv.), $[Ir(dtbbpy)(ppy)_2]PF_6$ (0.02 mmol, 2.0 mol%). The tube was evacuated and backfilled with argon three times, followed by DMA and DME (1:3, 10.0 mL) with stirring. Difluoroenoxytriethylsilane **(4)** (2.0 mmol, 2.0 equiv.) was added subsequently. The tube was stored protected from light. 2.0 mL of this stock solution was transferred to a quartz cuvette under an argon atmosphere. The cuvette was capped with a stopper and sealed with parafilm. The reaction mixture was heated to 50 °C under irradiation of blue LEDs (λ_{max} = 455 nm). After stirring for 2 h, the yield determined by HPLC analysis with styrene as an internal standard. The yield of the desired product **5a** was determined to be 1.4 % ($2.4 * 10^{-6}$ mol). The reaction quantum yield (Φ) was determined using eq 1.

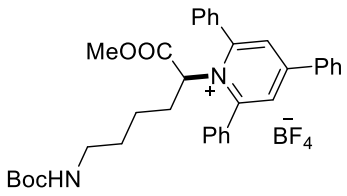
$$\Phi = \frac{\text{mol of product}}{\text{Photon flux} \bullet t \bullet f} \qquad (1)$$

$$\Phi = \frac{2.4 \bullet 10^{-6}\,\text{mol}}{2.25 * 10^{-9}\,\text{E s}^{-1} * 7200\,\text{s} * 0.981} = 0.15$$

9. Data for compounds 3, 5, 6, 7, 8, 9

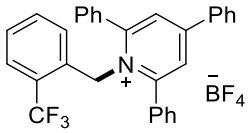


1-(3-(4-(Tert-butoxy)phenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (3q). The product (677 mg, 43% yield) was purified with silica gel chromatography (DCM/MeOH = 100:1) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.77 (br, 2H), 7.59 – 7.46 (m, 11H), 6.69 (s, 4H), 5.57 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.69 (s, 3H), 3.38 (dd, *J* = 14.6, 4.2 Hz, 1H), 2.94 (dd, *J* = 14.4, 7.6 Hz, 1H), 1.25 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -152.80 (minor, $^{11}BF_4$), -152.85 (major, $^{10}BF_4$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 156.9, 156.8, 154.4, 133.7, 132.4, 132.2, 131.5, 131.1, 129.7, 129.4, 129.0, 128.5, 127.8, 124.1, 78.5, 70.2, 53.7, 37.0, 28.7 (one carbon signal missing due to signal broadening). MS (ESI): m/z (%) 542 ($[M\text{-}BF_4]^+$, 100). HRMS (ESI): calculated for $C_{37}H_{36}O_3N$ ($[M\text{-}BF_4]^+$): 542.2690; Found: 542.2692.

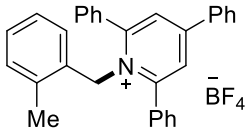


1-(6-((Tert-butoxycarbonyl)amino)-1-methoxy-1-oxohexan-2-yl)-2,4,6-triphenyl pyridin-1-ium tetrafluoroborate (3t). The product (1.1 g, 70% yield) was purified with silica gel chromatography (DCM/MeOH = 100:1) as off-white solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.84 – 7.82 (m, 2H), 7.72 (br, 2H), 7.63 – 7.51 (m,

11H), 5.31 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.91 – 4.89 (m, 1H), 3.69 (s, 3H), 2.97 – 2.92 (m, 2H), 1.95 – 1.89 (m, 2H), 1.69 – 1.61 (m, 2H), 1.40 (s, 9H), 1.27 – 1.16 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -152.68 (minor, $^{11}BF_4$), -152.73 (major, $^{10}BF_4$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 157.0, 156.2, 133.8, 132.5, 132.3, 131.5, 129.7, 129.2, 128.5, 127.9, 78.7, 69.0, 53.7, 39.6, 31.2, 28.8, 28.4, 24.5. (two carbon signal missing due to signal broadening). MS (ESI): m/z (%) 551 ($[M-BF_4]^+$, 100). HRMS (ESI): calculated for $C_{35}H_{39}O_4N_2$ ($[M-BF_4]^+$): 551.2904; Found: 551.2900.



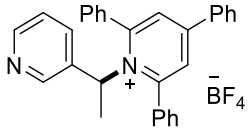
2,4,6-Triphenyl-1-(2-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate (3x). The product (941 mg, 68% yield) was purified with silica gel chromatography (DCM/MeOH = 100:1) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.49 (m, 6H), 7.45 – 7.41 (m, 4H), 7.38 – 7.29 (m, 6H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.81 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.70 (s, 3F), -152.61 (minor, $^{11}BF_4$), -152.67 (major, $^{10}BF_4$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 157.1, 133.9, 132.9, 132.2, 132.0, 131.86 – 131.83 (m), 130.9, 129.6, 128.9, 128.7, 128.4, 128.3, 127.4, 127.1, 126.3 – 126.1 (m), 125.6, 123.1 (q, *J* = 275.2 Hz), 55.0 – 54.9 (m). MS (ESI): m/z (%) 466 ($[M-BF_4]^+$, 100). HRMS (ESI): calculated for $C_{31}H_{23}NF_3$ ($[M-BF_4]^+$): 466.1777; Found: 466.1779.



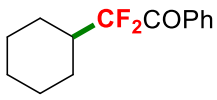
1-(2-Methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate （3y）.

The product (974 mg, 78% yield) was purified with silica gel chromatography (DCM/MeOH = 100:1) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.79 – 7.76 (m, 2H), 7.60 – 7.58 (m, 4H), 7.55 – 7.44 (m, 5H), 7.41 – 7.37 (m, 4H), 7.13 – 7.05 (m, 2H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 1H), 5.65 (s, 2H),

1.59 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -152.88 (minor, $^{11}BF_4$), -152.93 (major, $^{10}BF_4$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 156.2, 134.9, 133.6, 132.7, 132.4, 132.3, 130.8, 130.3, 129.7, 128.9, 128.8, 128.1, 126.5, 126.4, 124.9, 55.8, 18.4. MS (ESI): m/z (%) 412 ([M-BF_4]$^+$, 100). HRMS (ESI): calculated for $C_{31}H_{26}N$ ([M-BF_4]$^+$): 412.2060; Found: 412.2061.

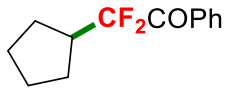


2,4,6-Triphenyl-1-(1-(pyridin-3-yl)ethyl)pyridin-1-ium tetrafluoroborate (3ah). The product (500 mg, 40% yield) was purified with silica gel chromatography (DCM/MeOH = 100:1) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.88 – 7.80 (m, 3H), 7.75 (s, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.45 (m, 5H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 4H), 7.07 (br, 2H), 6.16 (q, *J* = 7.1 Hz, 1H), 1.95 (d, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -152.36 (minor, $^{11}BF_4$), -152.42 (major, $^{10}BF_4$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 156.1, 149.2, 146.9, 134.8, 133.7, 133.2, 132.9, 132.0, 130.7, 129.4, 129.1, 128.9, 128.7, 128.3, 124.0, 63.9, 19.0. MS (ESI): m/z (%) 413 ([M-BF_4]$^+$, 100). HRMS (ESI): calculated for $C_{30}H_{25}N_2$ ([M-BF_4]$^+$): 413.2012; Found: 413.2014.

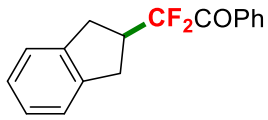


2-Cyclohexyl-2,2-difluoro-1-phenylethan-1-one (5a). The product (43.8 mg, 92% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 2.30 – 2.18 (m, 1H), 1.84 – 1.80 (m, 4H), 1.70 – 1.66 (m, 1H), 1.34 – 1.16 (m, 5H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.56 (d, *J* = 14.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3 (t, *J* = 30.3 Hz), 134.1, 132.8, 130.0 (t, *J* = 3.6 Hz), 128.6, 120.3 (t, *J* = 255.5 Hz), 42.1 (t, *J* = 21.8 Hz), 25.8, 25.4, 24.8 (t, *J* = 4.2 Hz). MS (EI): m/z (%) 238 (M$^+$), 105 (100). HRMS (EI): calculated for

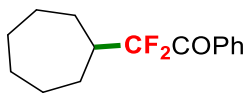
$C_{14}H_{16}OF_2$: 238.1169; Found: 238.1160.



2-Cyclopentyl-2,2-difluoro-1-phenylethan-1-one (5b). The product (24.7 mg, 55% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 2.88 – 2.71 (m, 1H), 1.86 – 1.79 (m, 2H), 1.73 – 1.64 (m, 4H), 1.61 – 1.58 (m. 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.17 (d, *J* = 16.9 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9 (t, *J* = 31.7 Hz), 134.1, 132.5, 130.1 (t, *J* = 3.6 Hz), 128.6, 120.8 (t, *J* = 254.8 Hz), 42.7 (t, *J* = 22.1 Hz), 26.02, 25.97, 25.9. MS (EI): m/z (%) 224 (M^+), 105 (100). HRMS (EI): calculated for $C_{13}H_{14}OF_2$: 224.1013; Found: 224.1012.

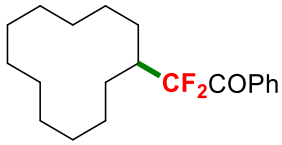


2-(2,3-Dihydro-1H-inden-2-yl)-2,2-difluoro-1-phenylethan-1-one (5c). The product (34.3 mg, 63% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.17 (m, 4H), 3.54 – 3.37 (m, 1H), 3.20 – 3.18 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.5 (d, *J* = 16.2 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3 (t, *J* = 31.9 Hz), 141.3, 134.3, 132.2 (t, *J* = 2.7 Hz), 130.1 (t, *J* = 3.4 Hz), 128.7, 126.6, 124.4, 120.2 (t, *J* = 255.9 Hz), 42.4 (t, *J* = 22.4 Hz), 32.8 (t, *J* = 4.6 Hz). MS (EI): m/z (%) 272 (M^+), 116 (100). HRMS (EI): calculated for $C_{17}H_{14}OF_2$: 272.1013; Found: 272.1008.

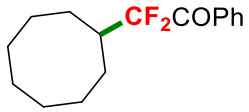


2-Cycloheptyl-2,2-difluoro-1-phenylethan-1-one (5d). The product (43.4 mg, 86% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane

= 200:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 2.49 – 2.35 (m, 1H), 1.88 – 1.82 (m, 2H), 1.77 – 1.74 (m, 2H), 1.59 – 1.41 (m, 8H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.18 (d, *J* = 16.5 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5 (t, *J* = 30.9 Hz), 134.0, 132.9, 129.9 (t, *J* = 3.6 Hz), 128.6, 121.1 (t, *J* = 256.6 Hz), 43.3 (t, *J* = 20.6 Hz), 28.2, 26.5, 26.45, 26.41. MS (EI): m/z (%) 252 (M^+), 105 (100). HRMS (EI): calculated for $C_{15}H_{18}OF_2$: 252.1326; Found: 252.1317.

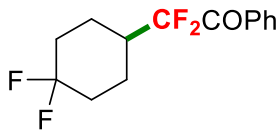


2-Cyclododecyl-2,2-difluoro-1-phenylethan-1-one (5e). The product (50.3 mg, 78% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 2.54 – 2.40 (m, 1H), 1.59 – 1.43 (m, 9H), 1.38 – 1.29 (s, 13H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.37 (d, *J* = 16.5 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4 (t, *J* = 30.5 Hz), 134.0, 132.8 (t, *J* = 1.9 Hz), 129.9 (t, *J* = 3.5 Hz), 128.6, 121.6 (t, *J* = 256.5 Hz), 38.4 (t, *J* = 20.6 Hz), 24.3, 23.6, 23.53, 23.5, 23.4, 22.5. MS (EI): m/z (%) 322 (M^+), 105 (100). HRMS (EI): calculated for $C_{20}H_{28}OF_2$: 322.2108; Found: 322.2115.

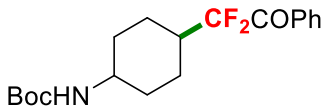


2-Cyclooctyl-2,2-difluoro-1-phenylethan-1-one (5f). The product (42.6 mg, 80% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 2.59 – 2.45 (m, 1H), 1.80 – 1.71 (m, 4H), 1.61 – 1.45 (m, 10H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.3 (d, *J* = 16.5 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5 (t, *J* = 31.2 Hz), 134.0, 132.9 (t, *J* = 2.0 Hz), 129.9 (t, *J* = 3.5 Hz), 128.6, 121.4 (t, *J* = 256.8 Hz), 41.2 (t, *J* = 20.4 Hz), 26.6, 26.2, 25.6 (t, *J* =

4.0 Hz), 25.4. MS (EI): m/z (%) 266 (M^+), 105 (100). HRMS (EI): calculated for $C_{16}H_{20}OF_2$: 266.1482; Found: 266.1479.

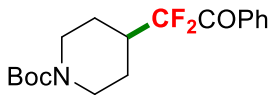


2-(4,4-Difluorocyclohexyl)-2,2-difluoro-1-phenylethan-1-one (5g). The product (37.8 mg, 69% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 2.45 – 2.33 (m, 1H), 2.21 –2.18 (m, 2H), 1.97 – 1.95 (m, 2H), 1.83 – 1.63 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.24 (d, *J* = 236.9 Hz, 1F), -102.44 – -103.24 (m, 1F), -107.04 (d, *J* = 14.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3 (t, *J* = 31.1 Hz), 134.4, 132.3 (t, *J* = 2.1 Hz), 130.1 (t, *J* = 3.6 Hz), 128.7, 122.5 (dd, *J* = 243.5, 240.9 Hz), 120.3 (td, *J* = 257.0, 2.2 Hz), 39.6 (td, *J* = 22.0, 1.1 Hz), 32.7 (dd, *J* = 25.8, 23.8 Hz), 21.5 – 21.3 (m). MS (EI): m/z (%) 274 (M^+), 105 (100). HRMS (EI): calculated for $C_{14}H_{14}OF_4$: 274.0981; Found: 274.0990.

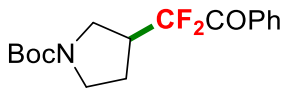


Tert-butyl (4-(1,1-difluoro-2-oxo-2-phenylethyl)cyclohexyl)carbamate (5h). The product (35.3 mg, 50% yield, as a 1.5:1 ratio of cis-trans isomers) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow oil. For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.8 Hz, 4H), 7.64 – 7.61 (m, 2H), 7.51 – 7.47 (m, 4H), 4.73 – 4.40 (m, 2H), 3.85 – 3.40 (m, 2H), 2.33 – 2.19 (m, 2H), 2.10 – 2.07 (m, 2H), 1.91 – 1.85 (m, 4H), 1.72 – 1.70 (m, 2H), 1.58 – 1.38 (m, 6H), 1.44 (s, 9H), 1.43 (s, 9H), 1.15 – 1.06 (m, 2H). For the mixture: ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.76 (d, *J* = 15.8 Hz, 2F), -107.52 (d, *J* = 15.0 Hz, 2F). For the mixture: ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9 (t, *J* = 30.8 Hz), 189.8 (t, *J* = 30.2 Hz), 155.15, 155.09, 134.24, 134.2, 132.6, 130.0, 128.69, 128.66, 120.0 (t, *J* = 256.1 Hz),

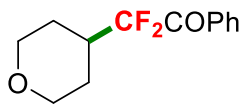
119.9 (t, J = 256.3 Hz), 79.2, 49.1, 44.9, 40.9 (t, J = 21.8 Hz), 40.8 (t, J = 21.8 Hz), 32.3, 29.2, 28.4, 23.7 (t, J = 3.9 Hz), 19.5. MS (ESI): m/z (%) 376 ([M+Na]$^+$, 100). HRMS (ESI): calculated for $C_{19}H_{25}O_3NF_2Na$ ([M+Na]$^+$): 376.1695; Found: 376.1692.



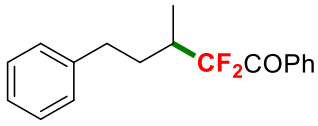
Tert-butyl 4-(1,1-difluoro-2-oxo-2-phenylethyl)piperidine-1-carboxylate (5i). The product (55 mg, 81% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 4.22 – 4.19 (m, 2H), 2.69 (t, J = 12.8 Hz, 2H), 2.51 – 2.38 (m, 1H), 1.80 – 1.77 (m, 2H), 1.56 – 1.48 (m, 2H), 1.45 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.86 (t, J = 12.6 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5 (t, J = 31.0 Hz), 154.6, 134.3, 132.4 (t, J = 2.1 Hz), 130.0 (t, J = 3.5 Hz), 128.7, 119.4 (t, J = 256.5 Hz), 79.7, 43.1 (br), 40.2 (t, J = 22.2 Hz), 28.4, 24.2. MS (ESI): m/z (%) 362 ([M+Na]$^+$, 100). HRMS (ESI): calculated for $C_{18}H_{23}O_3NF_2Na$ ([M+Na]$^+$): 362.1538; Found: 362.1540.



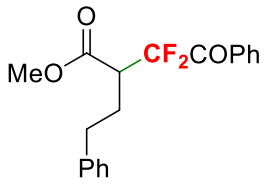
Tert-butyl 3-(1,1-difluoro-2-oxo-2-phenylethyl)pyrrolidine-1-carboxylate (5j). The product (29.3 mg, 45% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 3.71 – 3.66 (m, 2H), 3.56 (br, 1H), 3.42 – 3.32 (m, 2H), 3.21 – 3.09 (m, 1H), 2.17 – 2.00 (m, 1H), 1.46 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.61 – -105.86 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7 (t, J = 31.9 Hz), 154.3, 134.5, 131.7, 130.2 (t, J = 3.3 Hz), 128.7, 119.1 (t, J = 257.3 Hz), 79.5, 45.2, 45.1, 41.6 (br), 28.4, 24.7. MS (ESI): m/z (%) 348 ([M+Na]$^+$,100). HRMS (ESI): calculated for $C_{17}H_{21}O_3NF_2Na$ ([M+Na]$^+$): 348.1382; Found: 348.1381.



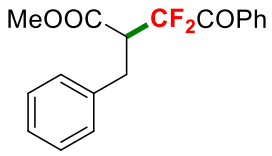
2,2-Difluoro-1-phenyl-2-(tetrahydro-2H-pyran-4-yl)ethan-1-one (5k). The product (28.8 mg, 60% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 4.04 – 4.03 (m, 2H), 3.44 – 3.38 (m, 2H), 2.62 – 2.51 (m, 1H), 1.74 – 1.69 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.68 (d, *J* = 14.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4 (t, *J* = 31.0 Hz), 134.3, 132.4 (t, *J* = 2.2 Hz), 130.0 (t, *J* = 3.6 Hz), 128.7, 119.2 (t, *J* = 256.2 Hz), 67.0, 39.2 (t, *J* = 22.5 Hz), 24.8 (t, *J* = 4.4 Hz). MS (EI): m/z (%) 240 (M^+), 105 (100). HRMS (EI): calculated for $C_{13}H_{14}O_2F_2$: 240.0962; Found: 240.0954.



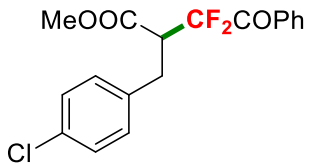
2,2-Difluoro-3-methyl-1,5-diphenylpentan-1-one (5l). The product (38.1 mg, 66% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 150:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 6.8 Hz, 2H), 7.18 – 7.12 (m, 3H), 2.82 – 2.75 (m, 1H), 2.60 – 2.53 (m, 1H), 2.50 – 2.34 (m, 1H), 2.04 – 1.95 (m, 1H), 1.66 – 1.56 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.7 – -107.8 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0 (t, *J* = 30.6 Hz), 141.3, 134.1, 132.6, 129.9 (t, *J* = 3.5 Hz), 128.6, 128.4, 128.3, 126.0, 120.7 (t, *J* = 256.4 Hz), 37.0 (t, *J* = 21.8 Hz), 32.9, 30.5 (t, *J* = 3.7 Hz), 12.1 (t, *J* = 5.0 Hz). MS (EI): m/z (%) 288 (M^+), 105 (100). HRMS (EI): calculated for $C_{18}H_{18}OF_2$: 288.1326; Found: 288.1321.



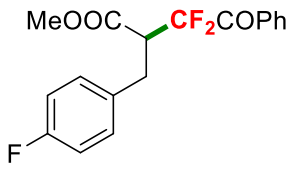
Methyl 3,3-difluoro-4-oxo-2-phenethyl-4-phenylbutanoate (5m). The product (62.5 mg, 94% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 140:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.23 – 7.21 (m, 3H), 3.72 (s, 3H), 3.51 – 3.40 (m, 1H), 2.88– 2.80 (m, 1H), 2.75 – 2.67 (m, 1H), 2.33 – 2.15 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.09 (dd, *J* = 293.8, 11.8 Hz, 1F), -105.00 (dd, *J* = 294.0, 17.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7 (t, *J* = 30.9 Hz), 170.0 – 169.9 (m), 140.5, 134.3, 131.8, 130.1 (t, *J* = 3.0 Hz), 128.6, 128.5, 128.4, 126.2, 117.8 (dd, *J* = 263.7, 257.3 Hz), 52.2, 48.6 (dd, *J* = 23.6, 21.5 Hz), 33.3, 27.1 (t, *J* = 3.3 Hz). MS (ESI): m/z (%) 333 ([M+H]$^+$, 100). HRMS (ESI): calculated for $C_{19}H_{19}O_3F_2$ ([M+H]$^+$): 333.1297; Found: 333.1298.



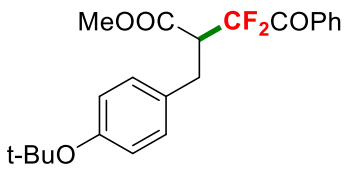
Methyl 2-benzyl-3,3-difluoro-4-oxo-4-phenylbutanoate (5n). The product (51.6 mg, 81% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 120:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.23 (m, 3H), 3.77 – 3.66 (m, 1H), 3.57 (s, 3H), 3.19 (d, *J* = 7.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.94 (dd, *J* = 295.5, 13.2 Hz, 1F), -103.74 (dd, *J* = 295.5, 15.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3 (t, *J* = 30.9 Hz), 169.4 (dd, *J* = 7.9, 1.5 Hz), 137.4, 134.5, 131.7 (t, *J* = 2.9 Hz), 130.1 (t, *J* = 3.4 Hz), 128.9, 128.7, 128.5, 126.8, 117.5 (dd, *J* = 263.2, 259.6 Hz), 52.1, 51.4 (dd, *J* = 23.0, 21.0 Hz), 31.7 (t, *J* = 4.4 Hz). MS (ESI): m/z (%) 341 ([M+Na]$^+$, 100). HRMS (ESI): calculated for $C_{18}H_{16}O_3F_2Na$ ([M+Na]$^+$): 341.0960; Found: 341.0960.



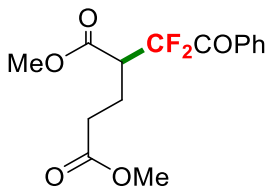
Methyl 2-(4-chlorobenzyl)-3,3-difluoro-4-oxo-4-phenylbutanoate (5o). The product (56.4 mg, 80% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 120:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.70 – 3.61 (m, 1H), 3.54 (s, 3H), 3.11 (d, *J* = 7.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.80 (dd, *J* = 296.1, 13.7 Hz, 1F), -103.59 (dd, *J* = 296.3, 15.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3 (t, *J* = 30.9 Hz), 169.2 (dd, *J* = 7.7, 1.5 Hz), 135.9, 134.6, 132.7, 131.6 (t, *J* = 2.8 Hz), 130.3, 130.1 (t, *J* = 3.3 Hz), 128.73, 128.69, 117.5 (dd, *J* = 263.5, 259.8 Hz), 52.2, 51.2 (dd, *J* = 22.8, 21.1 Hz), 31.1 (t, *J* = 4.4 Hz). MS (ESI): m/z (%) 375 ([M+Na]$^+$, 100). HRMS (ESI): calculated for $C_{18}H_{15}O_3ClF_2Na$ ([M+Na]$^+$): 375.0570; Found: 375.0570.



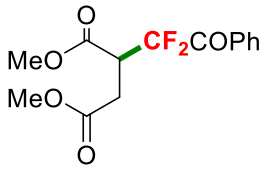
Methyl 3,3-difluoro-2-(4-fluorobenzyl)-4-oxo-4-phenylbutanoate (5p). The product (57.2 mg, 85% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 120:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.18 (m, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.74 – 3.63 (m, 1H), 3.58 (s, 3H), 3.16 (d, *J* = 7.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.91 (dd, *J* = 296.1, 13.7 Hz, 1F), -103.57 (dd, *J* = 296.1, 15.2 Hz, 1F), -115.97 – -116.05 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3 (t, *J* = 30.9 Hz), 169.3 (dd, *J* = 7.7, 1.5 Hz), 161.8 (d, *J* = 246.1 Hz), 134.6, 133.1 (d, *J* = 3.3 Hz), 131.6 (t, *J* = 2.8 Hz), 130.4 (d, *J* = 8.0 Hz), 130.2 (t, *J* = 3.3 Hz), 128.7, 117.5 (dd, *J* = 263.4, 259.7 Hz), 115.4 (d, *J* = 21.4 Hz), 52.2, 51.5 (t, *J* = 22.0 Hz), 30.9 (t, *J* = 4.4 Hz). MS (EI): m/z (%) 336 (M$^+$, 100). HRMS (EI): calculated for $C_{18}H_{15}O_3F_3$: 336.0973; Found: 336.0980.



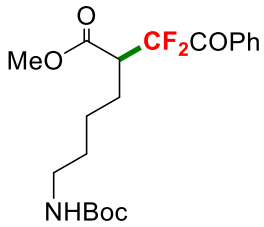
Methyl-2-(4-(tert-butoxy)benzyl)-3,3-difluoro-4-oxo-4-phenylbutanoate (5q). The product (50 mg, 64% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 120:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 3.73 – 3.62 (m, 1H), 3.54 (s, 3H), 3.15 – 3.13 (m, 2H), 1.32 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.00 (dd, *J* = 295.5, 13.5 Hz, 1F), -103.73 (dd, *J* = 295.5, 15.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4 (t, *J* = 31.1 Hz), 169.6 – 169.5 (m,), 154.1, 134.5, 132.2, 131.7 (t, *J* = 2.8 Hz), 130.2 (t, *J* = 3.3 Hz), 129.3, 128.7, 124.3, 117.5 (dd, *J* = 263.1, 259.6 Hz), 78.4, 52.0, 51.5 (dd, *J* = 23.0, 20.6 Hz), 31.1 (t, *J* = 4.3 Hz), 28.8. MS (ESI): m/z (%) 413 ($[M+Na]^+$, 100). HRMS (ESI): calculated for $C_{22}H_{24}O_4F_2Na$ ($[M+Na]^+$): 413.1535; Found: 413.1536.



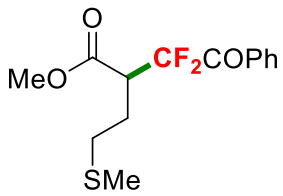
Dimethyl 2-(1,1-difluoro-2-oxo-2-phenylethyl)pentanedioate (5r). The product (54.7 mg, 87% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 3.70 (s, 3H), 3.69 (s, 3H), 3.56 – 3.46 (m, 1H), 2.60 – 2.43 (m, 2H), 2.27 – 2.17 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.75 (dd, *J* = 295.5, 10.5 Hz, 1F), -106.28 (dd, *J* = 295.3, 19.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6 (dd, *J* = 31.3, 29.9 Hz), 172.7, 169.6 (d, *J* = 10.2 Hz), 134.5, 131.7 (t, *J* = 2.8 Hz), 130.1 (dd, *J* = 3.6, 2.8 Hz), 128.7, 117.7 (dd, *J* = 264.8, 256.9 Hz), 52.3, 51.8, 48.1 (t, *J* = 22.7 Hz), 31.3, 20.5 (t, *J* = 4.2 Hz). MS (EI): m/z (%) 314 (M^+, 100). HRMS (EI): calculated for $C_{15}H_{16}O_5F_2$: 314.0966; Found: 314.0968.



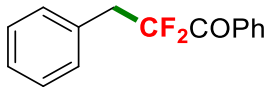
Dimethyl 2-(1,1-difluoro-2-oxo-2-phenylethyl)succinate (5s). The product (42.6 mg, 71% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 4.12 – 4.01 (m, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 3.07 – 3.01 (m, 1H), 2.86 – 2.81 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.76 (dd, J = 288.4, 10.5 Hz, 1F), -105.59 (dd, J = 288.0, 18.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1 (dd, J = 30.4, 29.2 Hz), 171.2, 168.5 – 168.4 (m), 134.4, 131.9, 130.0 (t, J = 3.2 Hz), 128.7, 117.3 (dd, J = 262.6, 259.1 Hz), 52.7, 52.2, 46.0 (t, J = 23.0 Hz), 30.0 (t, J = 4.1 Hz). MS (ESI): m/z (%) 301 ([M+H]$^+$, 100). HRMS (ESI): calculated for $C_{14}H_{15}O_5F_2$ ([M+H]$^+$): 301.0882; Found: 301.0882.



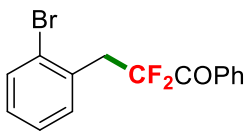
Methyl 6-((tert-butoxycarbonyl)amino)-2-(1,1-difluoro-2-oxo-2-phenylethyl)hexanoate (5t). The product (55.1 mg, 69% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 4.57 (br, 1H), 3.69 (s, 3H), 3.43 – 3.32 (m, 1H), 3.11 (m, 2H), 1.96 – 1.79 (m, 2H), 1.53 – 1.45 (m, 4H), 1.42(s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.46 (dd, J = 295.2, 12.4 Hz, 1F), -104.97 (dd, J = 295.2, 17.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7 (dd, J = 31.7, 30.6 Hz), 170.2, 155.9, 134.4, 131.7 (t, J = 2.8 Hz), 130.1 (t, J = 3.3 Hz), 128.6, 117.7 (dd, J = 263.7, 257.3 Hz), 79.1, 52.2, 49.0 (dd, J = 23.8, 21.1 Hz), 40.1, 29.8, 28.3, 25.1 (t, J = 3.6 Hz), 24.5. MS (ESI): m/z (%) 422 ([M+Na]$^+$, 100). HRMS (ESI): calculated for $C_{20}H_{27}O_5NF_2Na$ ([M+Na]$^+$): 422.1750; Found: 422.1746.



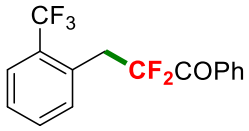
Methyl 3,3-difluoro-2-(2-(methylthio)ethyl)-4-oxo-4-phenylbutanoate (5u). The product (40.5 mg, 67% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 3.70 (s, 3H), 3.69 – 3.64 (m, 1H), 2.72 – 2.66 (m, 1H), 2.61 – 2.54 (m, 1H), 2.28 – 2.13 (m, 2H), 2.10 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.57 (dd, *J* = 293.3, 11.7 Hz, 1F), -105.04 (dd, *J* = 293.3, 18.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6 (dd, *J* = 31.6, 29.7 Hz), 169.7 – 169.6 (m), 134.4, 131.8 (t, *J* = 2.9 Hz), 130.0 (dd, *J* = 3.8, 2.8 Hz), 128.7, 117.8 (dd, *J* = 263.9, 257.2 Hz), 52.4, 47.8 (dd, *J* = 23.7, 21.6 Hz), 31.6, 24.7 (t, *J* = 3.5), 15.0. MS (ESI): m/z (%) 303 ([M+H]$^+$, 100). HRMS (ESI): calculated for $C_{14}H_{17}O_3F_2S$ ([M+H]$^+$): 303.0861; Found: 303.0856.



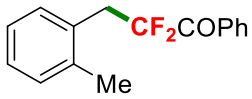
2,2-Difluoro-1,3-diphenylpropan-1-one (5v). This compound is known [14]. The product (37.9 mg, 77% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.33 (s, 5H), 3.54 (t, *J* = 17.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.75 (t, *J* = 17.9 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5 (t, *J* = 31.3 Hz), 134.2, 132.1 (t, *J* = 2.5 Hz), 131.2 (t, *J* = 3.7 Hz), 130.8, 130.1 (t, *J* = 3.3 Hz), 128.6, 128.4, 127.6, 118.3 (t, *J* = 255.7 Hz), 40.1 (t, *J* = 23.3 Hz).



3-(2-Bromophenyl)-2,2-difluoro-1-phenylpropan-1-one (5w). The product (46 mg, 71% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.3 (t, *J* = 7.4 Hz, 1H), 7.19 – 7.15 (m, 1H), 3.77 (t, *J* = 18.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.87 (t, *J* = 18.0 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1 (t, *J* = 32.9 Hz), 134.4, 133.1, 132.6, 131.8 (t, *J* = 2.5 Hz), 131.5 (t, *J* = 2.4 Hz), 130.2 (t, *J* = 3.3 Hz), 129.3, 128.6, 127.3, 126.1, 118.2 (t, *J* = 256.6 Hz), 39.3 (t, *J* = 23.1 Hz). MS (ESI): m/z (%) 325 ($[M+H]^+$, 100). HRMS (ESI): calculated for $C_{15}H_{12}OBrF_2$ ($[M+H]^+$): 325.0034; Found: 325.0034.

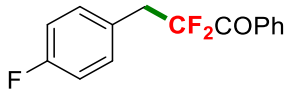


2,2-Difluoro-1-phenyl-3-(2-(trifluoromethyl)phenyl)propan-1-one (5x). The product (38.3 mg, 61% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.51 – 7.48 (m, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 3.77 (t, *J* = 18.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.66 (t, *J* = 6.2 Hz, 3F), -98.34 – -98.49 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9 (t, *J* = 31.3 Hz), 134.4, 133.1, 131.6, 130.3 (q, *J* = 30.0 Hz), 130.2 (t, *J* = 2.8 Hz), 130.0, 128.7, 127.7, 126.4 (q, *J* = 5.5 Hz), 124.1 (q, *J* = 275.1 Hz), 117.7 (t, *J* = 256.9 Hz), 35.7 (t, *J* = 22.9 Hz). MS (ESI): m/z (%) 337 ($[M+Na]^+$, 100). HRMS (ESI): calculated for $C_{16}H_{11}OF_5Na$ ($[M+Na]^+$): 337.0622; Found: 337.0624.

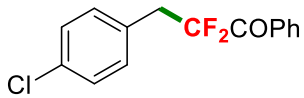


2,2-Difluoro-1-phenyl-3-(o-tolyl)propan-1-one (5y). This compound is known. [14] The product (29.2 mg, 56% yield) was purified with silica gel chromatography Petroleum ether/Dichloromethane = 200:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.06 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.15 (m, 3H), 3.57 (t, *J* = 18.4 Hz, 2H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.67 (t, *J* = 18.0 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8 (t, *J* = 31.4 Hz), 138.0, 134.2, 132.0 (t, *J* = 2.3 Hz), 131.7, 130.5, 130.1 (t, *J* = 3.2 Hz), 129.8 (t, *J* = 2.5 Hz), 128.6, 127.7, 125.8, 118.8 (t, *J* = 255.8 Hz), 36.7 (t, *J* = 23.3 Hz), 20.0.

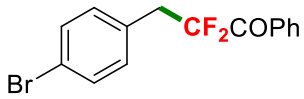


2,2-Difluoro-3-(4-fluorophenyl)-1-phenylpropan-1-one (5z). The product (29.1 mg, 55% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 3.49 (t, *J* = 17.6 Hz, 2H). ^{19}F NMR (367 MHz, $CDCl_3$) δ -98.86 (t, *J* = 17.5 Hz, 2F), -114.98 – -115.08 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2 (t, *J* = 31.3 Hz), 162.3 (d, *J* = 247.3 Hz), 134.3, 132.4 (d, *J* = 8.2 Hz), 131.9 (t, *J* = 2.7 Hz), 130.1 (t, *J* = 3.3 Hz), 128.6, 127.0 – 126.9 (m), 118.1 (t, *J* = 256.0 Hz), 115.3 (d, *J* = 21.5 Hz), 39.2 (t, *J* = 23.4 Hz). MS (EI): m/z (%) 264 (M^+), 105 (100). HRMS (EI): calculated for $C_{15}H_{11}OF_3$: 264.0762; Found: 264.0752.

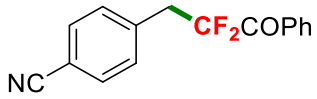


3-(4-Chlorophenyl)-2,2-difluoro-1-phenylpropan-1-one (5aa). The product (30.3 mg, 54% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.21 (m, 4H), 3.46 (t, *J* = 17.6 Hz, 2H). ^{19}F NMR (367 MHz, $CDCl_3$) δ -98.61 (t, *J* = 17.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1 (t, *J* = 31.4 Hz), 134.4, 133.6, 132.2, 131.8 (t, *J* = 2.7 Hz), 130.1 (t, *J* = 3.3 Hz), 129.7 (t, *J* = 3.7 Hz), 128.7, 128.6, 118.1 (t, *J* = 256.1 Hz), 39.3 (t, *J* = 23.4 Hz). MS (EI): m/z (%) 280 (M^+), 105 (100). HRMS (EI):

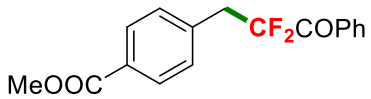
calculated for $C_{15}H_{11}OF_2Cl$: 280.0466; Found: 280.0470.



3-(4-Bromophenyl)-2,2-difluoro-1-phenylpropan-1-one (5ab). The product (39 mg, 60% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.0 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.19 (d, *J* = 7.6 Hz, 2H), 3.47 (t, *J* = 17.6 Hz, 2H). ^{19}F NMR (367 MHz, $CDCl_3$) δ -98.56 (t, *J* = 17.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0 (t, *J* = 31.5 Hz), 134.4, 132.5, 131.8 (t, *J* = 2.9 Hz), 131.5, 130.3 (t, *J* = 3.7 Hz), 130.1 (t, *J* = 3.3 Hz), 128.7, 121.8, 118.0 (t, *J* = 256.2 Hz), 39.4 (t, *J* = 23.4 Hz). MS (EI): m/z (%) 105 (100), 304. HRMS (EI): calculated for $C_{15}H_{11}OF_2Br$: 323.9961; Found: 323.9968.

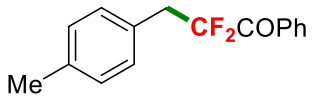


4-(2,2-Difluoro-3-oxo-3-phenylpropyl)benzonitrile (5ac). This compound is known [14]. The product (33.1 mg, 61% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 30:1) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.62 (m, 3H), 7.51 – 7.45 (m, 4H), 3.58 (t, *J* = 17.4 Hz, 2H). ^{19}F NMR (367 MHz, $CDCl_3$) δ -98.01 (t, *J* = 17.5 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5 (t, *J* = 33.5 Hz), 136.9 (t, *J* = 3.5 Hz), 134.6, 132.0, 131.6, 131.5 (t, *J* = 2.9 Hz), 130.1 (t, *J* = 3.3 Hz), 128.7, 118.6, 117.9 (t, *J* = 257.1 Hz), 111.6, 39.8 (t, *J* = 23.4 Hz).

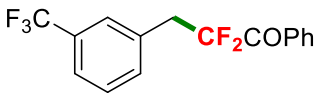


Methyl 4-(2,2-difluoro-3-oxo-3-phenylpropyl)benzoate (5ad). This compound is known**.** [15] The product (46.3 mg, 76% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as white solid. ^{1}H NMR (400

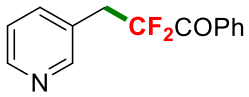
MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.57 (t, *J* = 17.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.2 (t, *J* = 17.5 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9 (t, *J* = 31.3 Hz), 166.8, 136.6 (t, *J* = 3.5 Hz), 134.4, 131.8 (t, *J* = 2.8 Hz), 130.9, 130.1 (t, *J* = 3.3 Hz), 129.6, 129.4, 128.6, 118.1 (t, *J* = 256.6 Hz), 52.1, 39.9 (t, *J* = 23.4 Hz).



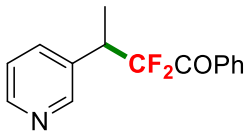
2,2-Difluoro-1-phenyl-3-(p-tolyl)propan-1-one (5ae). This compound is known. [14] The product (21.3 mg, 41% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.12 (m, 4H), 3.48 (t, *J* = 18.0 Hz, 2H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.85 (t, *J* = 17.9 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5 (t, *J* = 31.3 Hz), 137.3, 134.2, 132.1 (t, *J* = 2.4 Hz), 130.7, 130.1 (t, *J* = 3.3 Hz), 129.1, 128.6, 128.0 (t, *J* = 3.6 Hz), 118.3 (t, *J* = 255.5 Hz), 39.7 (t, *J* = 23.3 Hz), 21.1.



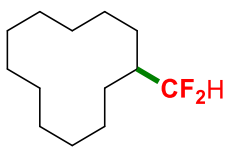
2,2-Difluoro-1-phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one (5af). This compound is known. [14] The product (47 mg, 75% yield) was purified with silica gel chromatography (Petroleum ether/Dichloromethane = 200:1) as pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.60 – 7.44 (m, 6H), 3.58 (t, *J* = 17.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.95 (s, 3F), -105.78 (t, *J* = 17.5 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8 (t, *J* = 31.5 Hz), 134.5, 134.3, 132.3 (t, *J* = 3.6 Hz), 131.7 (t, *J* = 2.8 Hz), 130.8 (q, *J* = 32.5 Hz), 130.1 (t, *J* = 3.2 Hz), 128.8, 128.7, 127.6 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 273.6 Hz), 118.0 (t, *J* = 256.5 Hz), 39.6 (t, *J* = 23.4 Hz).



2,2-Difluoro-1-phenyl-3-(pyridin-3-yl)propan-1-one (5ag). The product (32 mg, 65% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.54 (m, 2H), 8.07 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.26 (m, 1H), 3.53 (t, *J* = 17.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.34 (t, *J* = 16.9 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6 (t, *J* = 31.4 Hz), 151.5, 148.7, 138.4, 134.5, 131.6 (t, *J* = 3.0 Hz), 130.1 (t, *J* = 3.3 Hz), 128.7, 127.5, 123.3, 117.9 (t, *J* = 256.6 Hz), 37.2 (t, *J* = 23.7 Hz). MS (ESI): m/z (%) 248 ([M+H]$^+$, 100). HRMS (ESI): calculated for $C_{14}H_{12}ONF_2$ ([M+H]$^+$): 248.0881; Found: 248.0879.

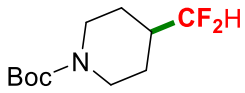


2,2-Difluoro-1-phenyl-3-(pyridin-3-yl)butan-1-one (5ah). The product (23 mg, 44% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.51 (m, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.26 (m, 1H), 3.87 – 3.74 (m, 1H), 1.51 (d, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.06 (dd, *J* = 282.9, 15.6 Hz, 1F), -105.64 (dd, *J* = 282.8, 15.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2 (t, *J* = 30.7 Hz), 150.3, 148.7, 136.7, 134.3, 133.4, 132.3 129.9 (t, *J* = 3.2 Hz), 128.7, 123.4, 119.0 (t, *J* = 259.3 Hz), 41.3 (t, *J* = 22.6 Hz), 14.3. MS (ESI): m/z (%) 262 ([M+H]$^+$, 100). HRMS (ESI): calculated for $C_{15}H_{14}ONF_2$ ([M+H]$^+$): 262.1038; Found: 262.1039.

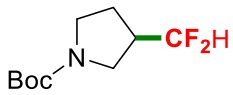


(Difluoromethyl)cyclododecane (6e). The product (28.4 mg, 65% yield) was purified

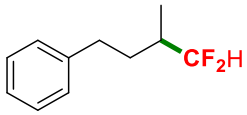
with silica gel chromatography (Petroleum ether) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (td, *J* = 57.0, 4.4 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.43 – 1.31 (m, 22H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.83 (dd, *J* = 57.0, 15.2 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.7 (t, *J* = 243.3 Hz), 38.1 (t, *J* = 18.1 Hz), 24.1, 23.58, 23.56, 23.41, 23.40, 23.3, 22.2. MS (EI): m/z (%) 218 (M^+), 97 (100). HRMS (EI): calculated for $C_{13}H_{24}F_2$: 218.1841; Found: 218.1844.



Tert-butyl 4-(difluoromethyl)piperidine-1-carboxylate (6i). This compound is known. [16] The product (38.1 mg, 81% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (td, *J* = 56.7, 4.5 Hz, 1H), 4.17 (br, 2H), 2.68 (t, *J* = 11.8 Hz, 2H), 1.97 – 1.84 (m, 1H), 1.74 – 1.70 (m, 2H), 1.45 (s, 9H), 1.38 – 1.29 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.13 – -119.39 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 118.2 (t, *J* = 242.9 Hz), 79.6, 42.8 (br), 40.1 (t, *J* = 20.3 Hz), 28.3, 24.6 (t, *J* = 4.7 Hz).

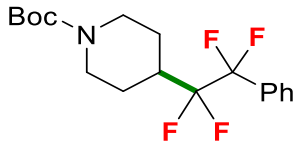


Tert-butyl-3-(difluoromethyl)pyrrolidine-1-carboxylate (6j). This compound is known. [16] The product (31.4 mg, 71% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 15:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (td, *J* = 56.4, 5.2 Hz, 1H), 3.53 – 3.44 (m, 2H), 3.37 – 3.29 (m, 2H), 2.68 – 2.56 (m, 1H), 2.06 – 1.98 (m, 1H), 1.93 – 1.84 (m, 1H), 1.44 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.24 – -121.30 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 117.0 (t, *J* = 242.3 Hz), 79.5, 45.1 (t, *J* = 5.5 Hz), 45.0, 42.2 (br), 28.4, 25.0.

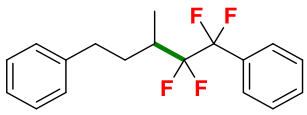


(4,4-difluoro-3-methylbutyl)benzene (6l). The product (23 mg, 63% yield) was

purified with silica gel chromatography (Petroleum ether) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 7.4 Hz, 2H), 7.21 (t, J = 7.8 Hz, 3H), 5.65 (td, J = 56.9, 3.5 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.67 – 2.59 (m, 1H), 1.96 – 1.86 (m, 2H), 1.61 – 1.52 (m, 1H), 1.07 (d, J = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.6 (ddd, J = 276.7, 56.8, 13.5 Hz, 1F), -124.17 (ddd, J = 276.7, 57.0, 16.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 128.4, 128.3, 126.0, 119.2 (t, J = 243.4 Hz), 36.7 (t, J = 19.5 Hz), 32.8, 31.4 (t, J = 4.3 Hz), 12.3 (t, J = 5.4 Hz). MS (EI): m/z (%) 184 (M^+), 91 (100). HRMS (EI): calculated for $C_{11}H_{14}F_2$: 184.1058; Found: 184.1055.

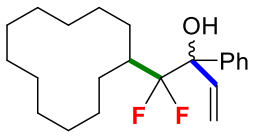


Tert-butyl 4-(1,1,2,2-tetrafluoro-2-phenylethyl)piperidine-1-carboxylate (7i). The product (40 mg, 55% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 25:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.44 (m, 5H), 4.20 (br, 2H), 2.70 – 2.65 (m, 2H), 2.34 – 2.21 (m, 1H), 1.94 – 1.91 (m, 2H), 1.57 – 1.52 (m, 2H), 1.46 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.41 – -109.42 (m, 2F), -117.74 – -117.77 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 130.94 – 130.86 (m), 129.83 – 129.8 (m), 128.2, 126.7 – 126.5 (m), 122.0 – 116.9 (m), 79.7, 43.1 (br), 38.8 (t, J = 22.8 Hz), 28.4, 24.5. MS (ESI): m/z (%) 384 ($[M+Na]^+$, 100). HRMS (ESI): calculated for $C_{18}H_{23}O_2NF_4Na$ ($[M+Na]^+$): 384.1557; Found: 384.1556.

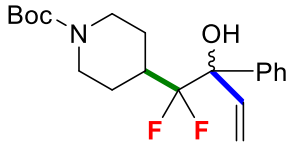


(1,1,2,2-Tetrafluoro-3-methylpentane-1,5-diyl)dibenzene (7l). The product (34.8 mg, 56% yield) was purified with silica gel chromatography (Petroleum ether) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.43 (m, 5H), 7.31 (t, J = 7.4 Hz, 2H), 7.24 – 7.19 (m, 3H), 2.85 – 2.77 (m, 1H), 2.63 – 2.55 (m, 1H), 2.33 – 2.21 (m, 1H), 2.19 – 2.11 (m, 1H), 1.73 – 1.63 (m, 1H), 1.23 (d, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$)

δ -108.05 – -109.99 (m, 2F), -114.93 – -117.57 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 131.7 (t, *J* = 25.2 Hz), 130.7 (t, *J* = 1.4 Hz), 128.4, 128.35, 128.2, 126.6 – 126.5 (m), 126.0, 122.0 – 117.0 (m), 35.5 (t, *J* = 22.1 Hz), 33.0, 31.0, 12.7 – 12.5 (m). MS (EI): m/z (%) 310 (M^+, 100). HRMS (EI): calculated for $C_{18}H_{18}F_4$: 310.1339; Found: 310.1343.

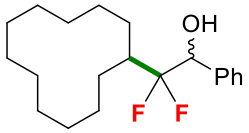


1-Cyclododecyl-1,1-difluoro-2-phenylbut-3-en-2-ol (8e). The product (57.5 mg, 82% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 80:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* =7.6 Hz, 2H), 7.38 – 7.29 (m, 3H), 6.70 – 6.62 (m, 1H), 5.45 – 5.33 (m, 2H), 2.43 (br, 1H), 2.09 – 1.97 (m, 1H), 1.72 – 1.65 (m, 1H), 1.43 – 1.19 (m, 19H), 1.13 – 0.99 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.91 – -106.63 (m 1F), -112.28 – -113.02 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7 (d, *J* = 3.4 Hz), 139.1 (d, *J* = 5.3 Hz), 128.0, 127.7, 126.33 – 126.3 (m), 125.5 (t, *J* = 257.8 Hz), 115.5, 79.4 (t, *J* = 27.8 Hz), 37.4 (t, *J* = 21.8 Hz), 24.5, 24.4, 23.9, 23.6, 23.07, 23.06, 22.8, 22.2. MS (EI): m/z (%) 350 (M^+), 134 (100). HRMS (EI): calculated for $C_{22}H_{32}OF_2$: 350.2416; Found: 350.2420.

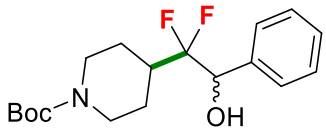


Tert-butyl 4-(1,1-difluoro-2-hydroxy-2-phenylbut-3-en-1-yl)piperidine-1-carboxylate (8i). The product (44 mg, 60% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.39 – 7.31 (m, 3H), 6.64 – 6.57 (m, 1H), 5.44 – 5.33 (m, 2H), 4.06 – 3.98 (m, 2H), 2.56 (br, 1H), 2.44 (t, *J* = 12.8, 2H), 2.00 – 1.85 (m, 2H), 1.45 – 1.32 (m, 3H), 1.42 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.01 – -110.72 (m, 1F), -116.26 – -116.97 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6,

139.44 – 139.4 (m), 138.7 – 138.67 (m), 128.2, 127.9, 126.1 – 126.0 (m), 123.3 (t, J = 255.7 Hz), 115.8, 79.4, 79.1 (t, J = 27.2 Hz), 43.3 (br), 39.8 (t, J = 23.6 Hz), 28.4, 25.6, 24.9. MS (ESI): m/z (%) 390 ([M+Na]$^+$, 100). HRMS (ESI): calculated for $C_{20}H_{27}O_3NF_2Na$ ([M+Na]$^+$): 390.1851; Found: 390.1854.

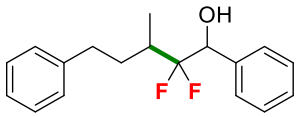


2-Cyclododecyl-2,2-difluoro-1-phenylethan-1-ol (9e). The product (57 mg, 88% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.40 – 7.37 (m, 3H), 4.96 – 4.90 (m, 1H), 2.34 (br, 1H), 2.08 – 1.99 (m, 1H), 1.65 – 1.58 (m, 1H), 1.54 – 1.31 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.00 – -113.75 (m 1F), -114.04 – -114.77 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0 (d, J = 2.6 Hz), 128.6, 128.2, 127.8, 125.0 (t, J = 251.1 Hz), 74.1 (dd, J = 29.5, 27.3 Hz), 37.6 (t, J = 21.5 Hz), 24.7 (d, J = 1.9 Hz), 24.0, 23.5 (t, J = 4.1 Hz), 23.4, 23.3, 23.2, 23.1, 22.3. MS (EI): m/z (%) 324 (M$^+$), 107 (100). HRMS (EI): calculated for $C_{20}H_{30}OF_2$: 324.2259; Found: 324.2258.



Tert-butyl 4-(1,1-difluoro-2-hydroxy-2-phenylethyl)piperidine-1-carboxylate (9i). The product (64.2 mg, 94% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.36 – 7.34 (m, 3H), 4.85 (t, J = 12.2, 1H), 4.11 – 4.09 (m, 2H), 3.07 (br, 1H), 2.61 – 2.55 (m, 2H), 2.09 – 2.00 (m, 1H), 1.84 (d, J = 13.2, 1H), 1.70 (d, J = 13.2, 1H), 1.51 – 1.43 (m, 2H), 1.41 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.13 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 136.8, 128.6, 128.3, 127.7, 122.8 (t, J = 249.7 Hz), 79.7, 73.5 (t, J = 28.3 Hz), 43.1 (br), 39.3 (t, J = 23.5 Hz), 28.4, 25.0 (t, J =

4.6 Hz), 24.2 (t, J = 4.4 Hz). MS (ESI): m/z (%) 364 ([M+Na]$^+$, 100). HRMS (ESI): calculated for $C_{18}H_{25}O_3NF_2Na$ ([M+Na]$^+$): 364.1695; Found: 364.1691.



2,2-Difluoro-3-methyl-1,5-diphenylpentan-1-ol (9l). The product (56.3 mg, 97% yield, as a 1.1:1 ratio of diastereoisomers) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow oil. For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 10H), 7.31 – 7.26 (m, 4H), 7.22 – 7.14 (m, 6H), 4.97 – 4.91 (m, 2H), 2.80 – 2.73 (m, 2H), 2.56 – 2.49 (m, 2H), 2.33 (br, 2H), 2.11 – 1.96 (m, 4H), 1.67 – 1.54 (m, 2H), 1.17 (d, J = 7.2 Hz, 3H), 1.10 (d, J = 6.8 Hz, 3H). For the mixture: ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.64 (dt, J = 250.4, 14.1 Hz, 1F), -117.57 (dt, J = 250.0, 13.7 Hz, 1F), -116.49 (dt, J = 250.4, 14.1 Hz, 1F), -117.08 – -117.82 (m, 1F). For the mixture: ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 141.7, 136.8, 136.7, 128.7, 128.6, 128.36, 128.35, 128.32, 128.30, 128.28, 127.73 – 127.68 (m), 125.9, 125.86, 124.1 (dd, J = 251.0, 249.9 Hz), 73.8 (dd, J = 29.3, 27.1 Hz), 73.7 (dd, J = 30.0, 27.2 Hz), 36.1 (t, J = 22.8 Hz), 36.0 (t, J = 22.9 Hz), 33.2, 33.1, 31.4 (t, J = 4.2 Hz), 31.1 (t, J = 4.0 Hz), 12.7 (t, J = 5.3 Hz), 12.3 (t, J = 5.2 Hz). MS (EI): m/z (%) 290.2 (M$^+$), 107.7 (100). HRMS (EI): calculated for $C_{18}H_{20}OF_2$: 290.1477; Found: 290.1484.

10. References

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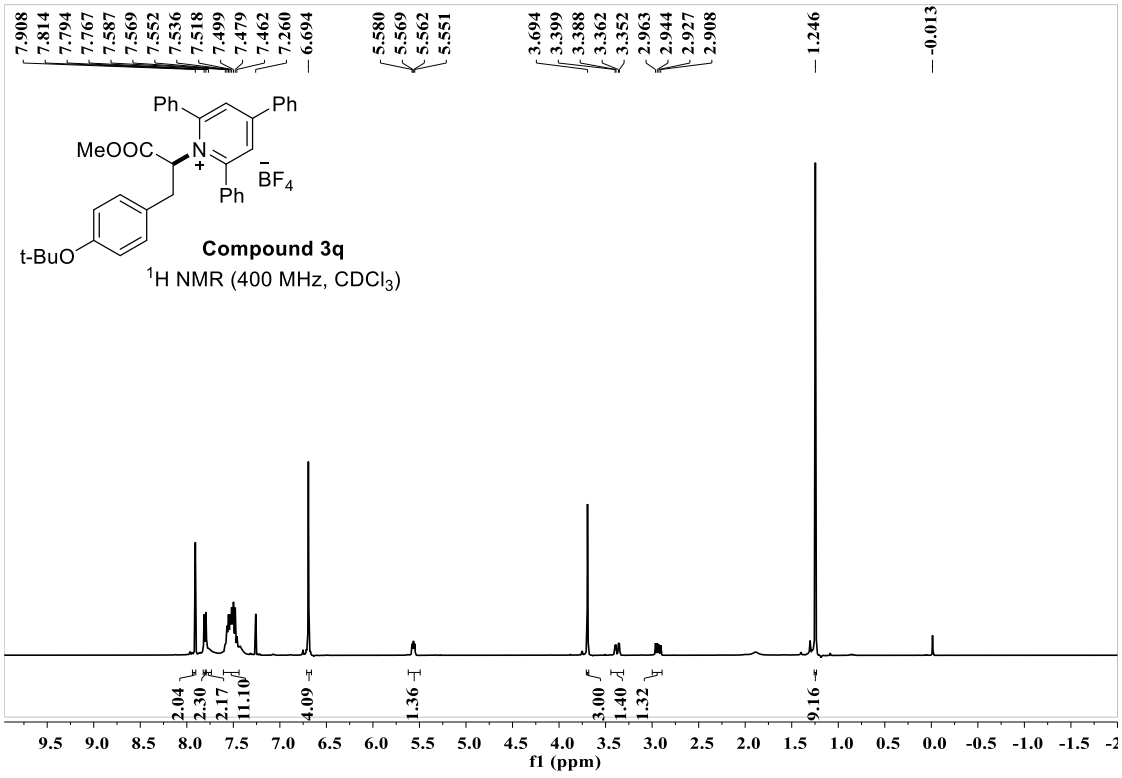
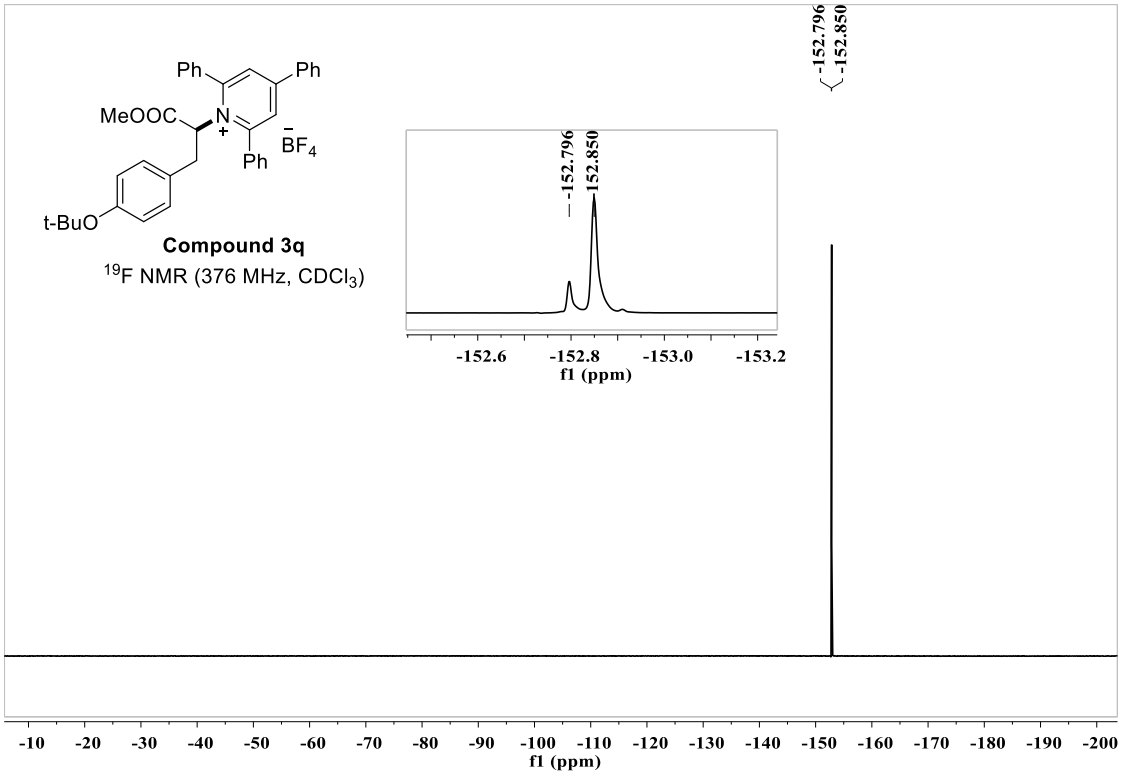
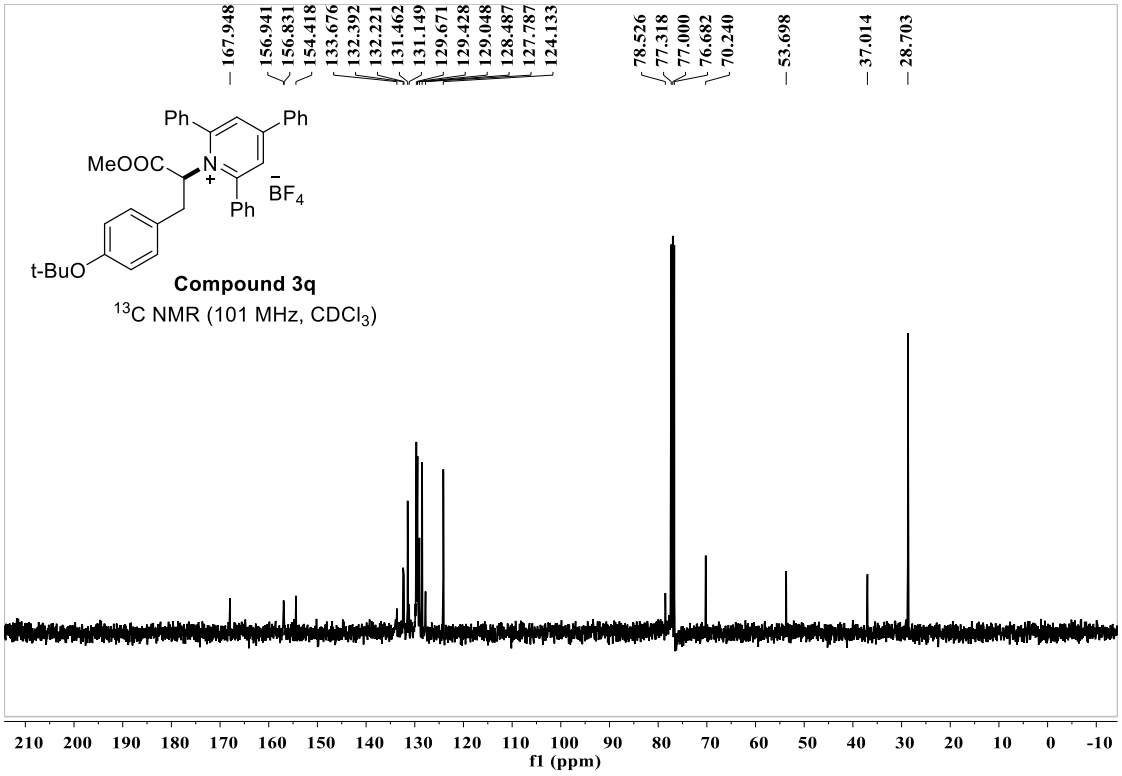
11. Copies of NMR spectra of 3, 4, 5, 6, 7, 8, 9, 11

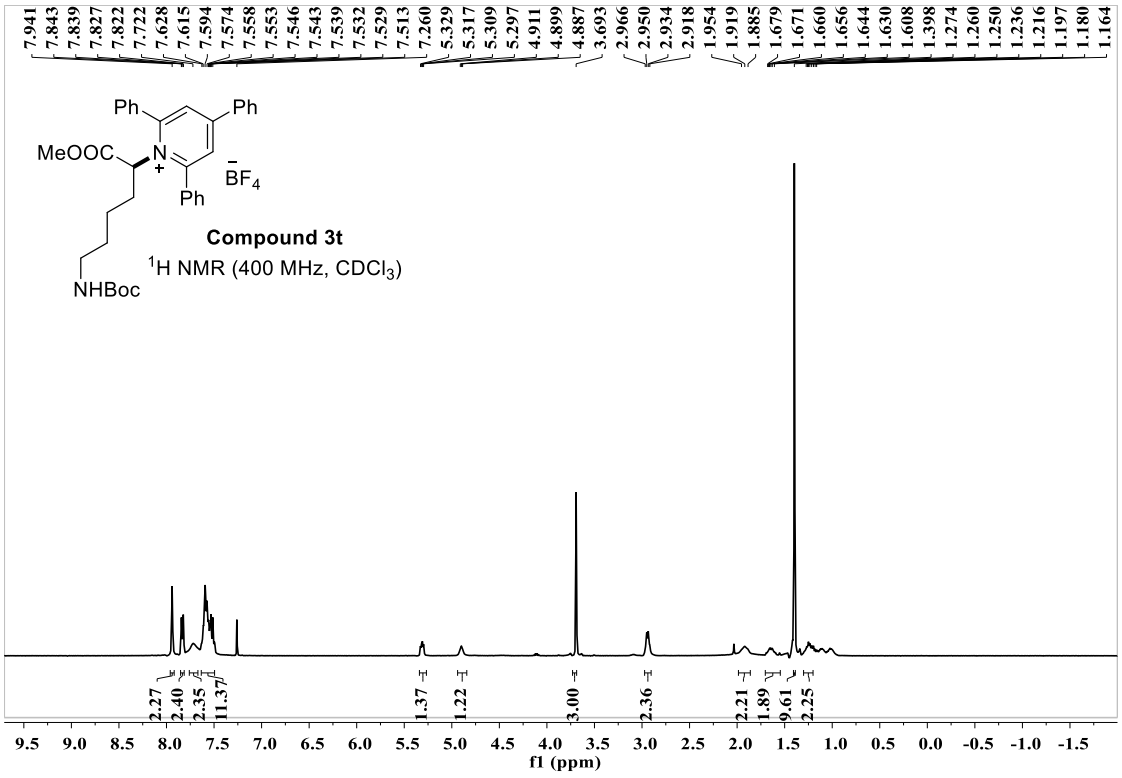
1-(3-(4-(Tert-butoxy)phenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (3q).

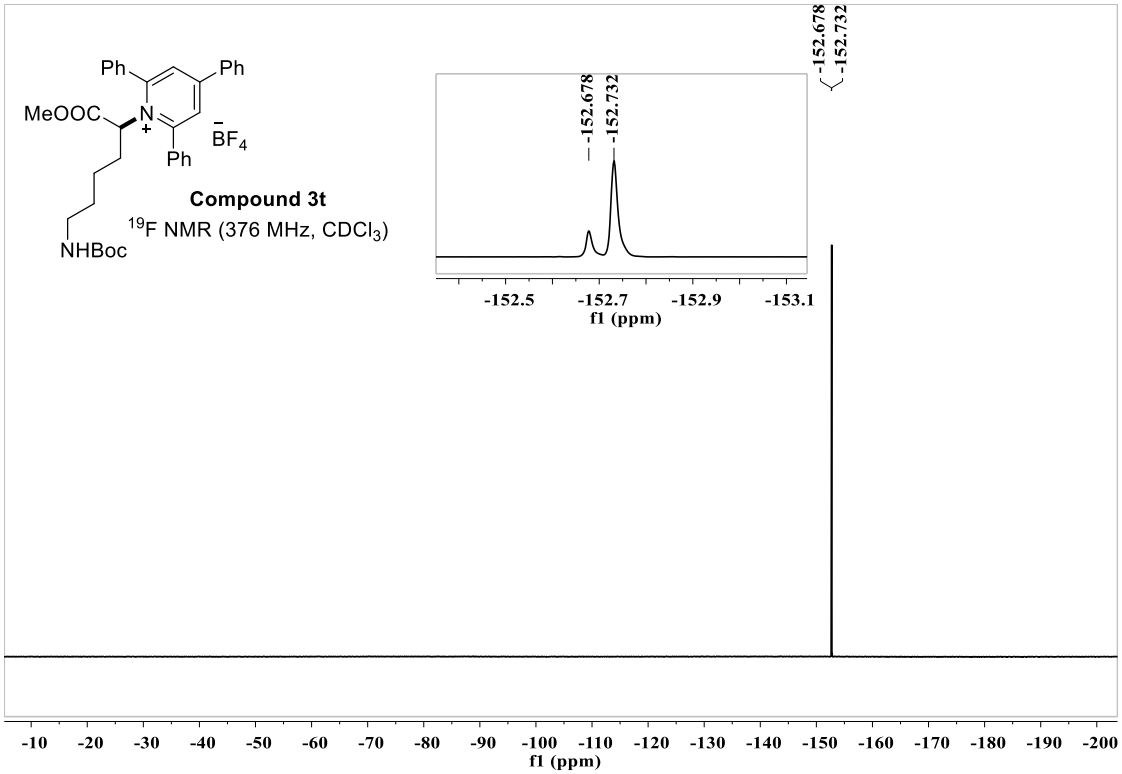


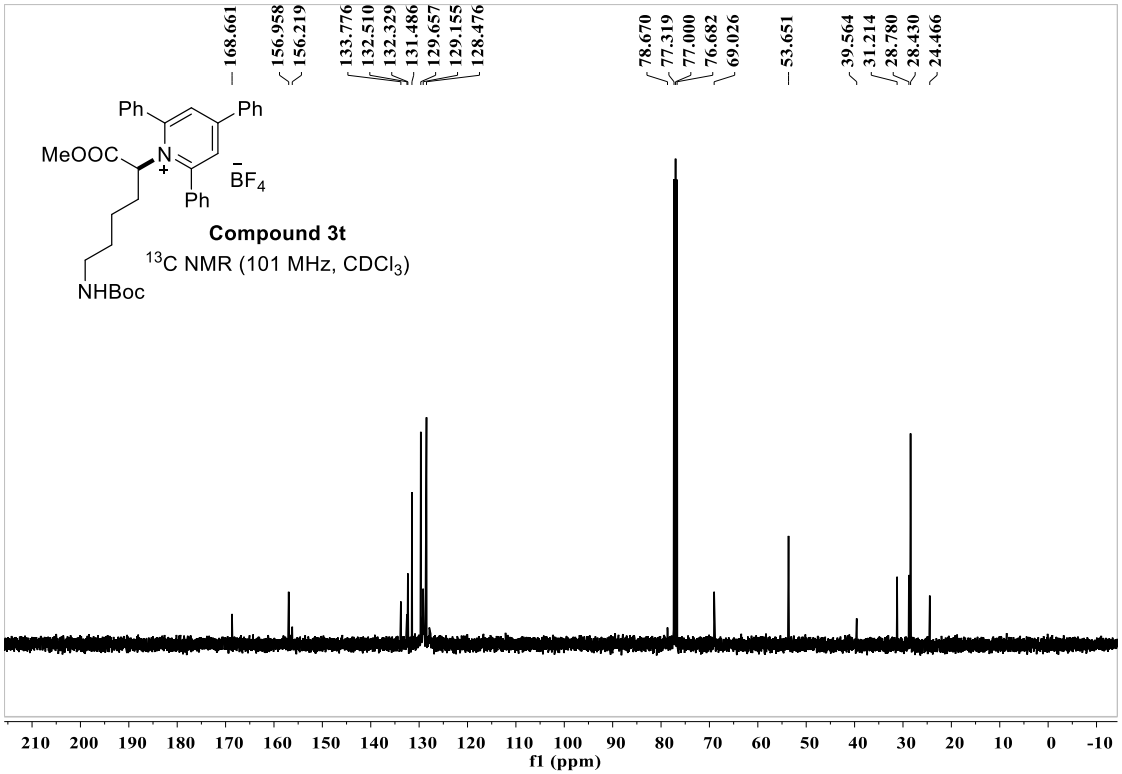




1-(6-((Tert-butoxycarbonyl)amino)-1-methoxy-1-oxohexan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (3t).




Ph
Ph
MeOOC
N
+
BF4
Ph
NHBoc
Compound 3t
19F NMR (376 MHz, CDCl3)
-152.678
-152.732
-152.5
-152.7
-152.9
-153.1
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


168.661
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156.219
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132.510
132.329
131.486
129.657
129.155
128.476
78.670
77.319
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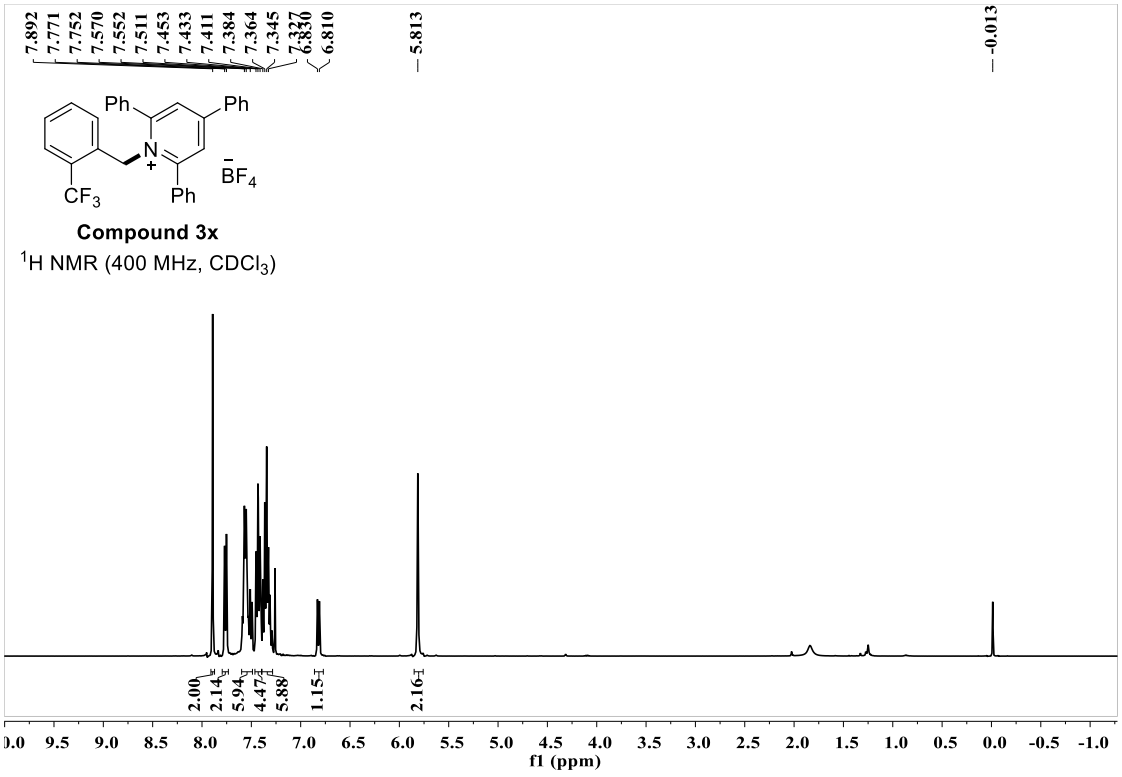
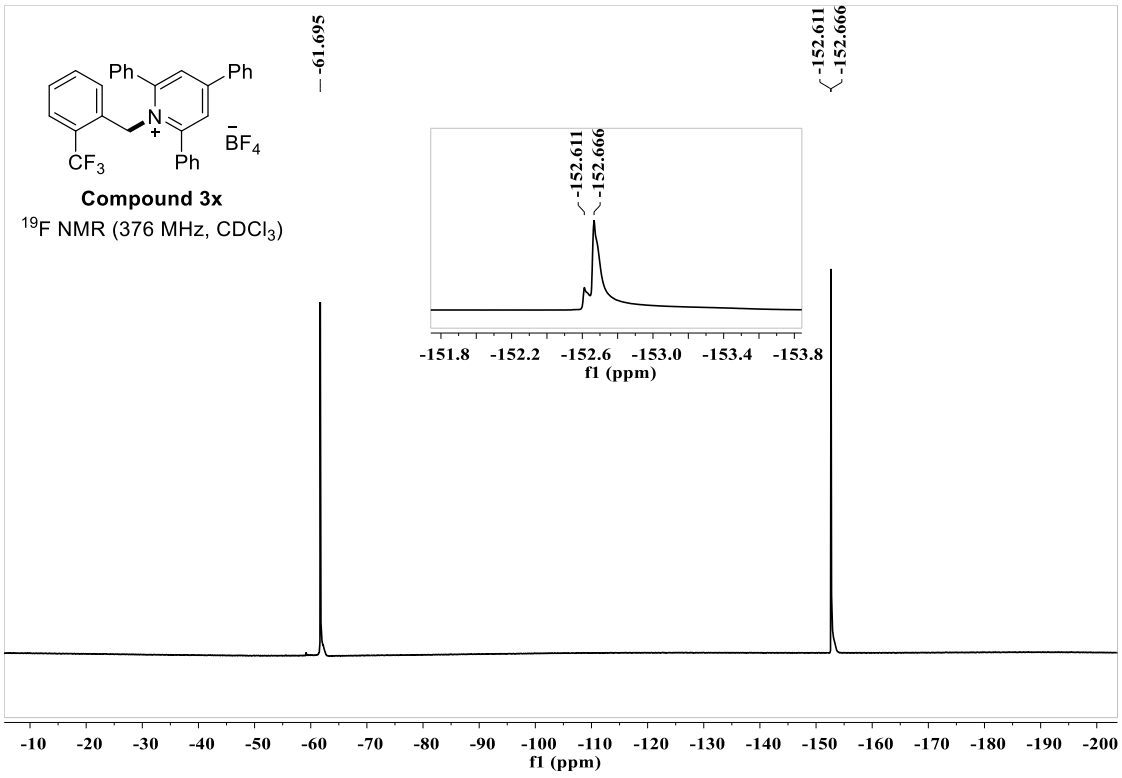
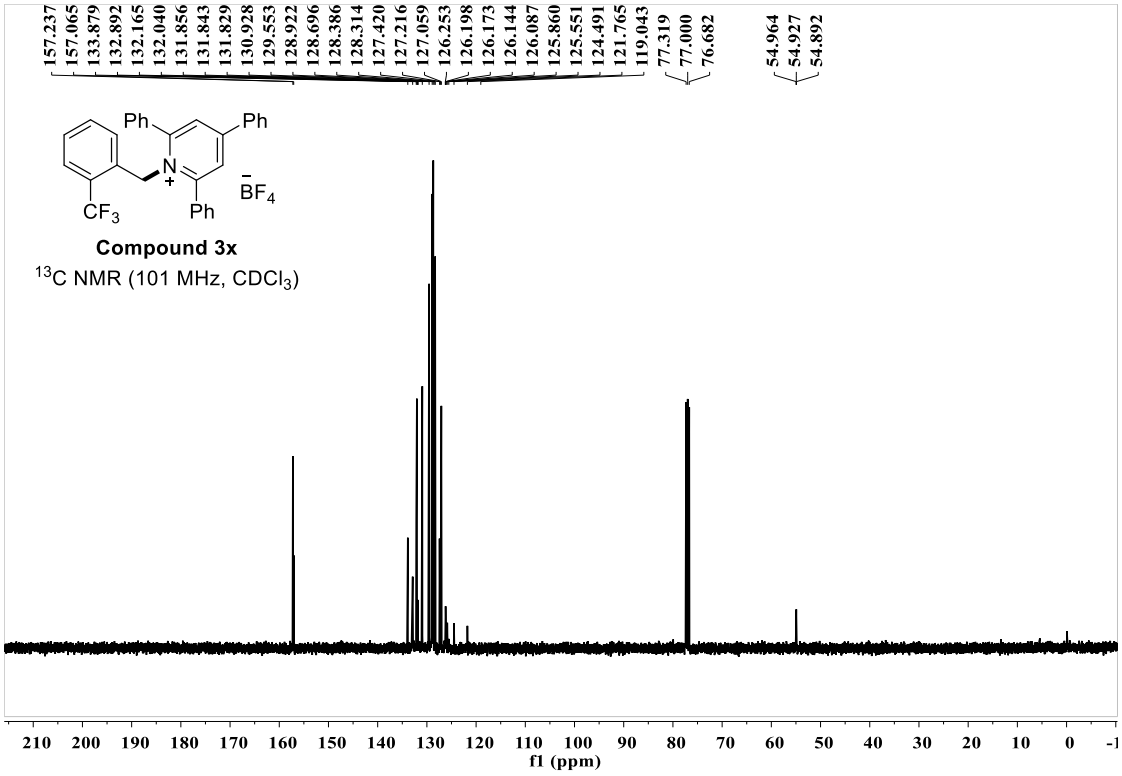
76.682
69.026
53.651
39.564
31.214
28.780
28.430
24.466
Ph
Ph
MeOOC
N
+
BF4
Ph
NHBoc
Compound 3t
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

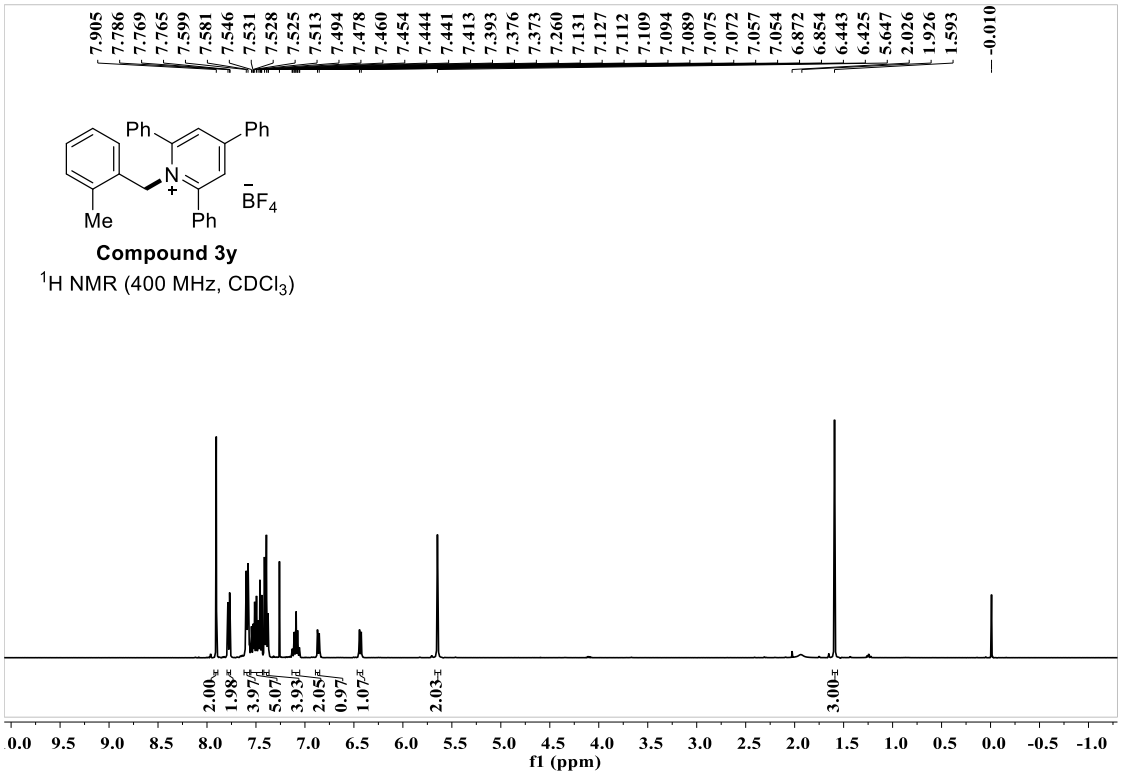
2,4,6-Triphenyl-1-(2-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate (3x).

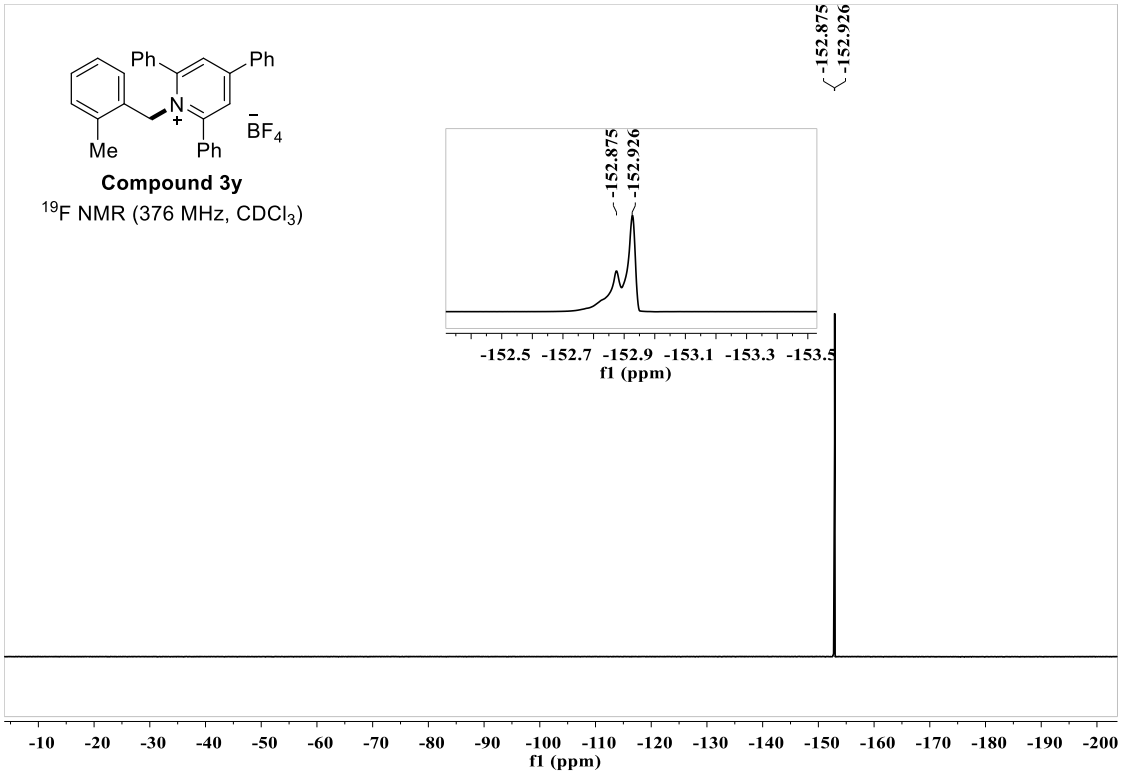






1-(2-Methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate （3y）.

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Ph
N
+
Me
Ph
BF4
Compound 3y
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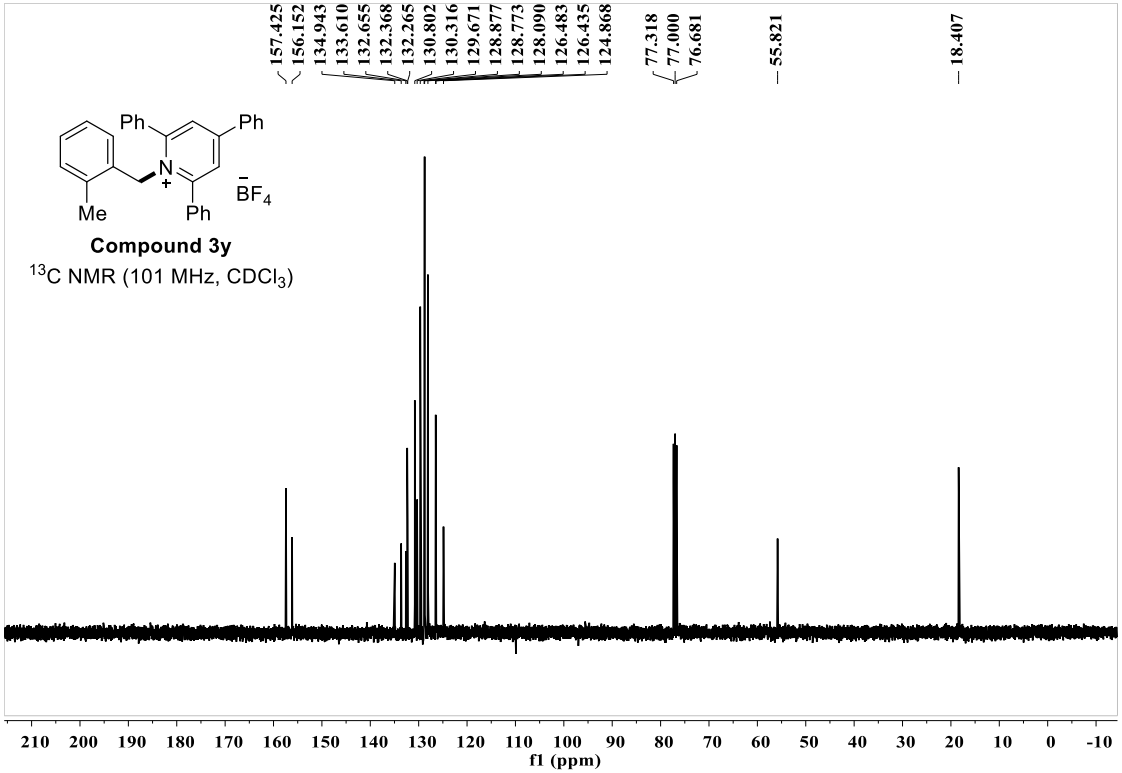
-152.875
-152.926
-152.5 -152.7 -152.9 -153.1 -153.3 -153.5
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)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132.655
132.368
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129.671
128.877
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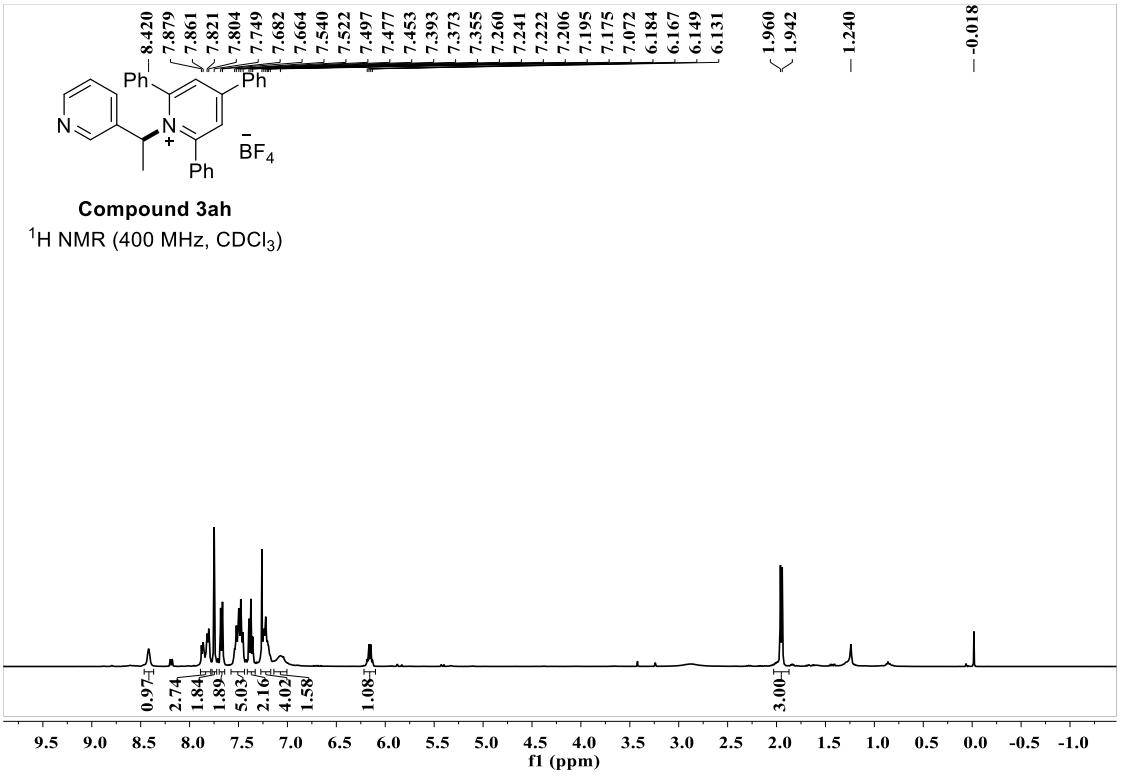
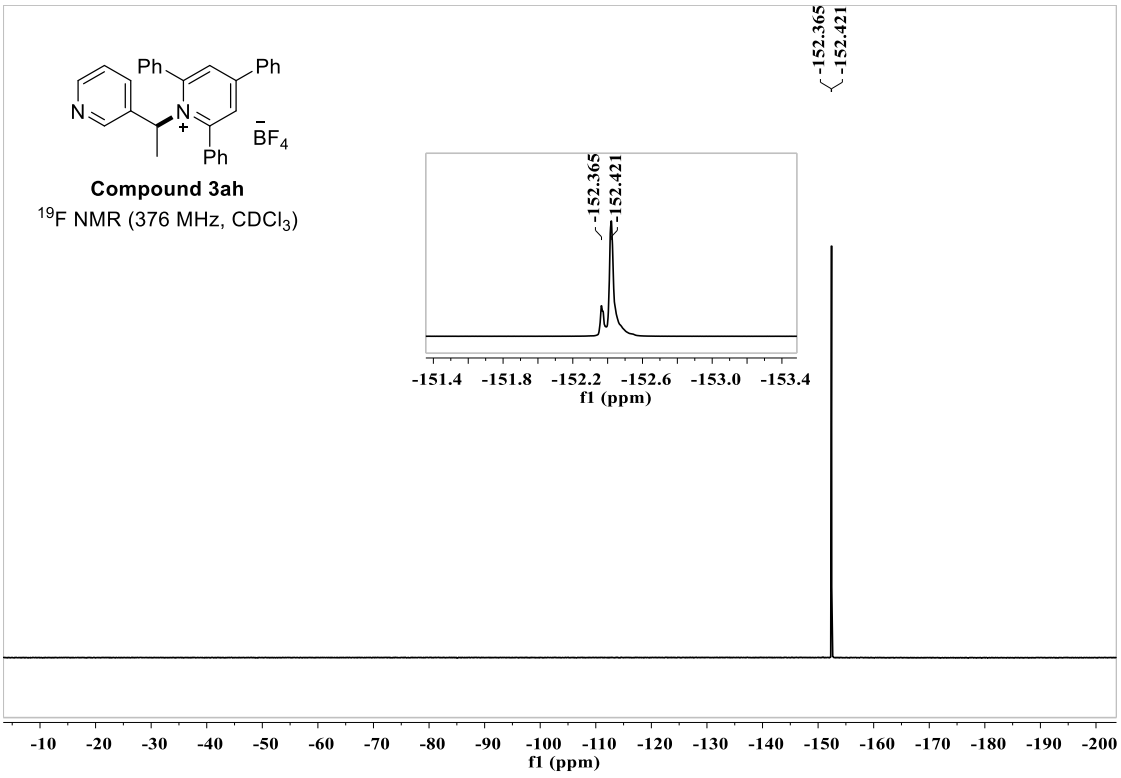
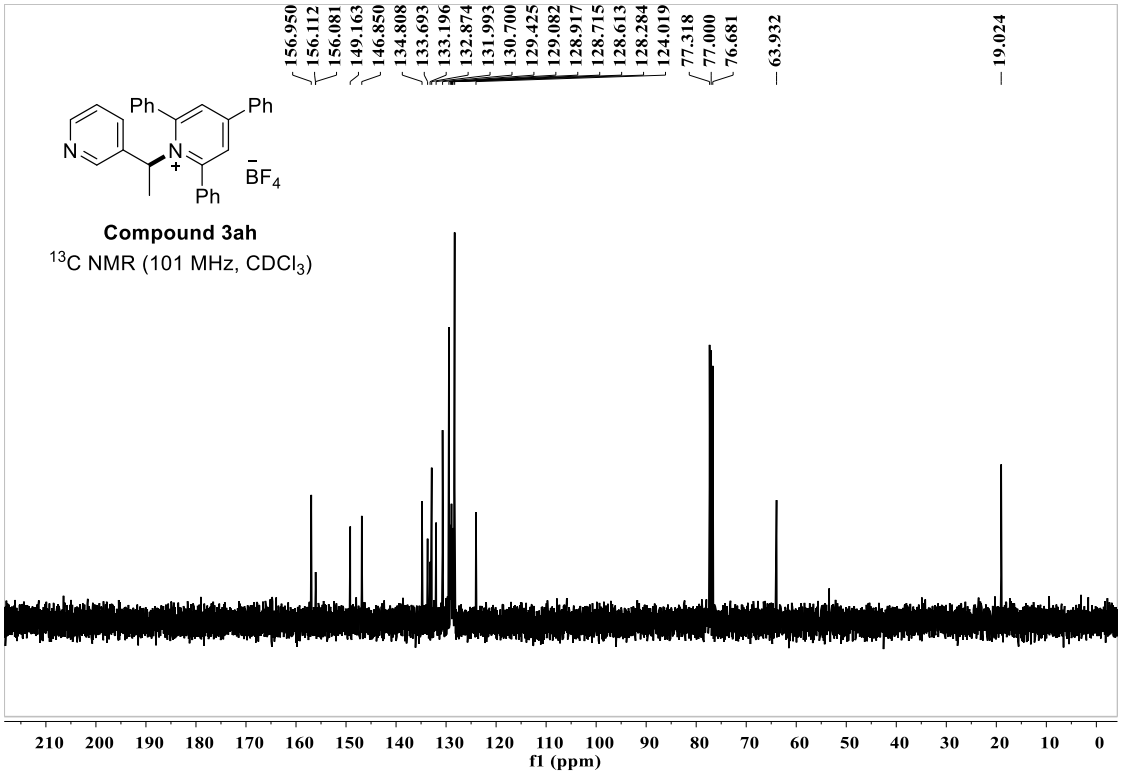
126.483
126.435
124.868
77.318
77.000
76.681
55.821
18.407
Ph
Ph
N
+
Me
Ph
BF4
Compound 3y
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

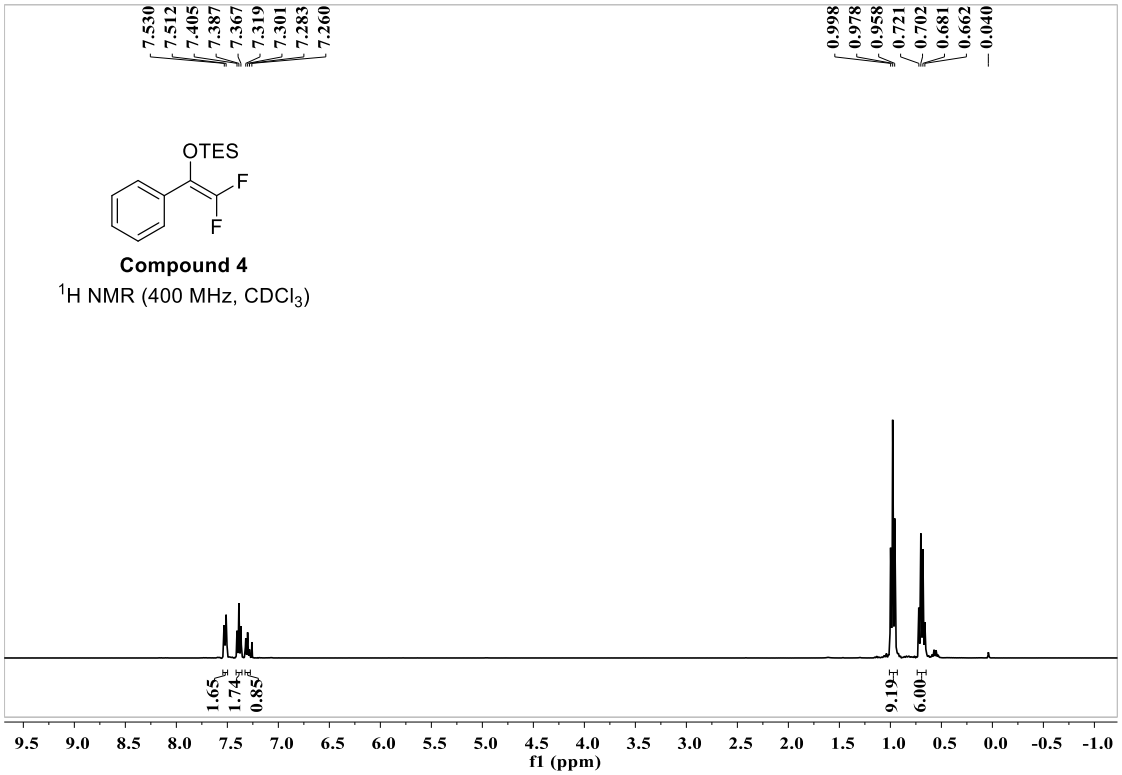
2,4,6-Triphenyl-1-(1-(pyridin-3-yl)ethyl)pyridin-1-ium tetrafluoroborate (3ah).

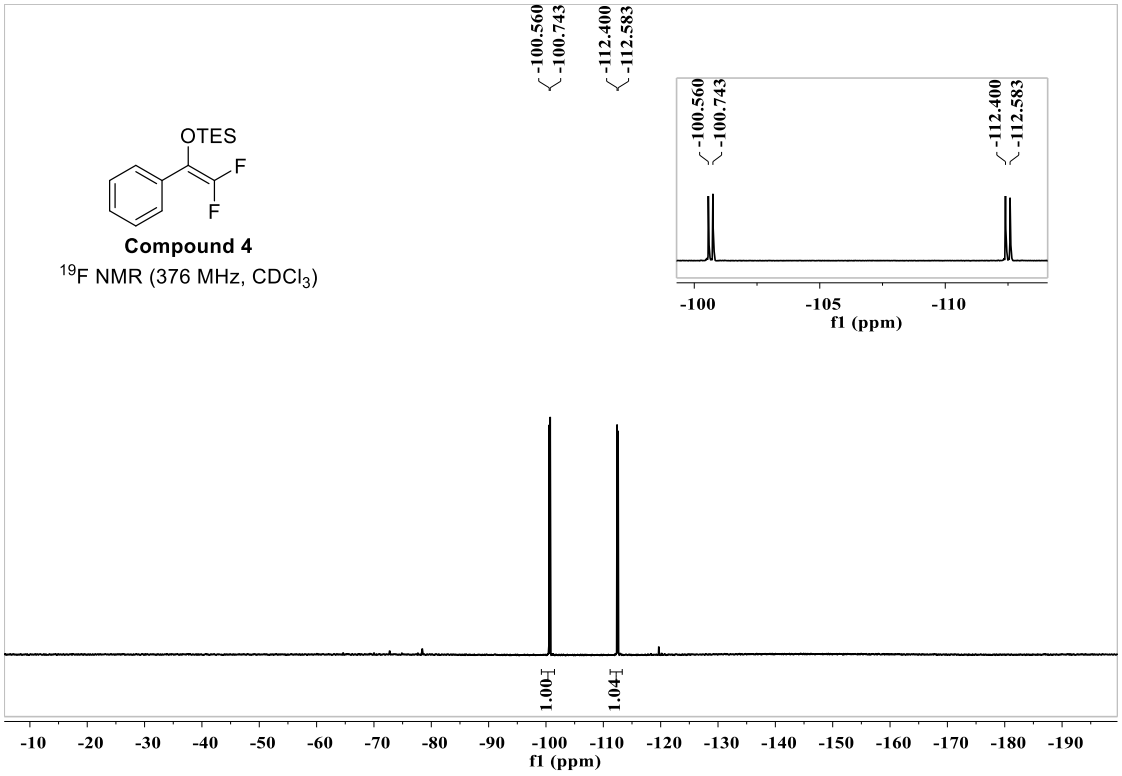


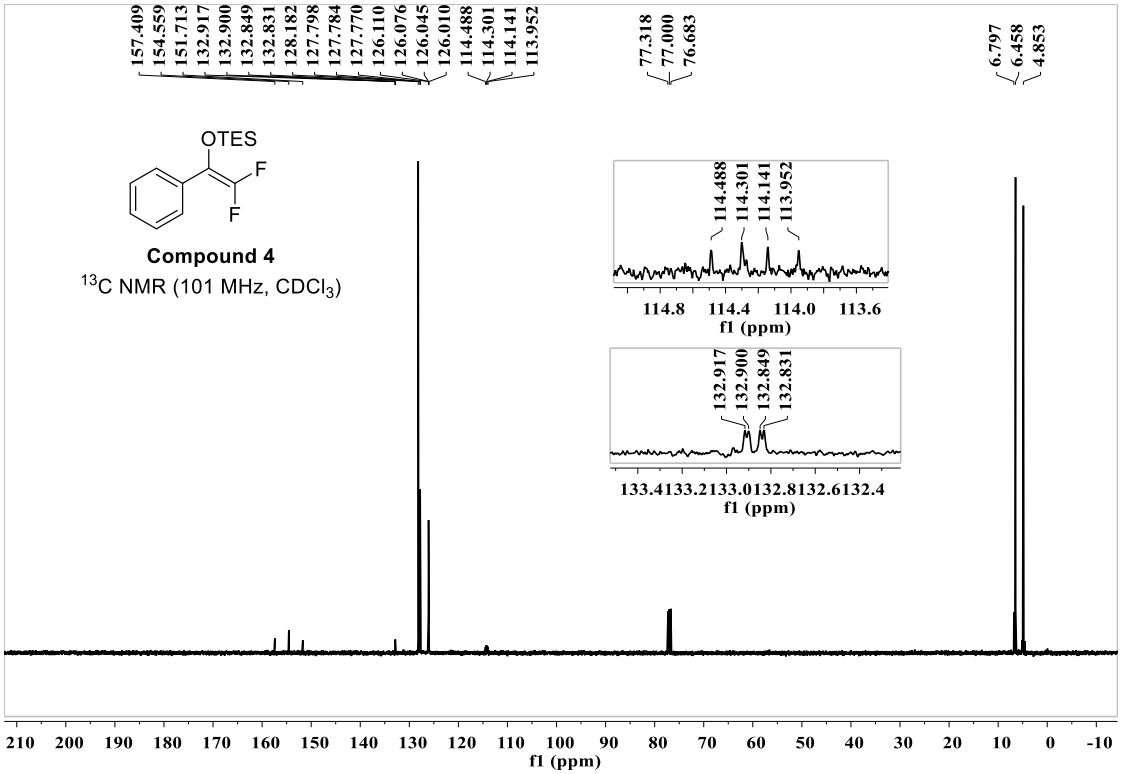




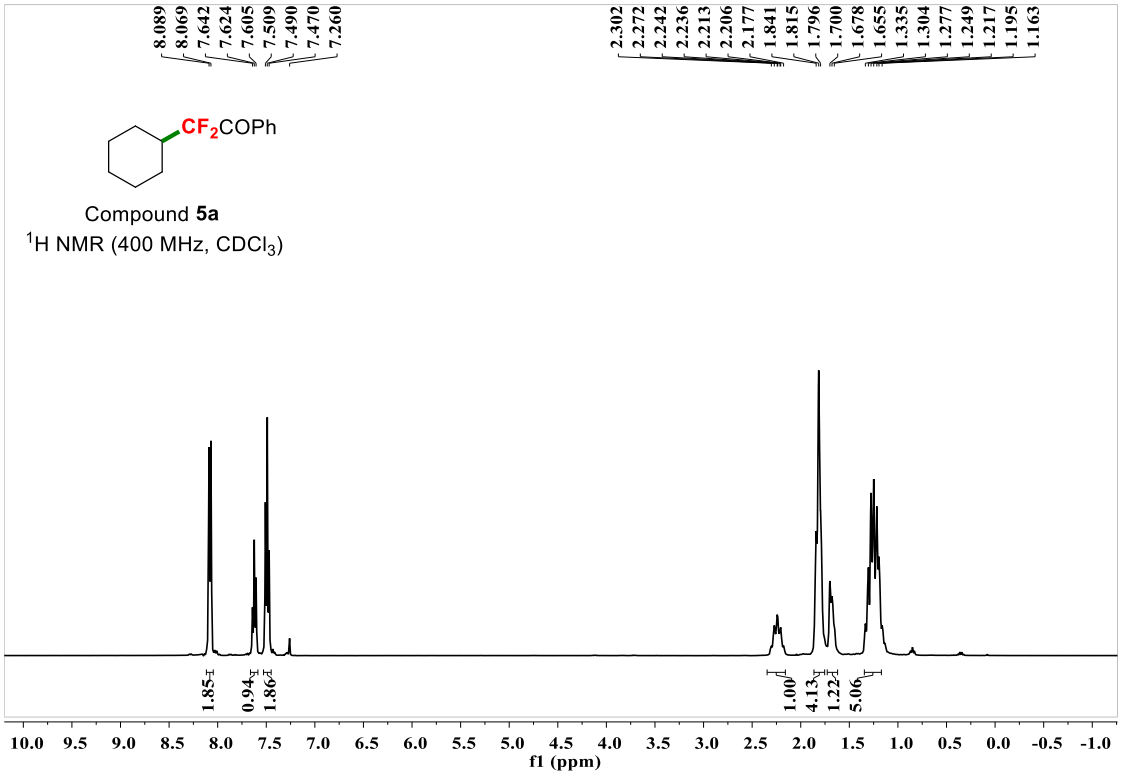
Difluoroenoxytriethylsilane (4).

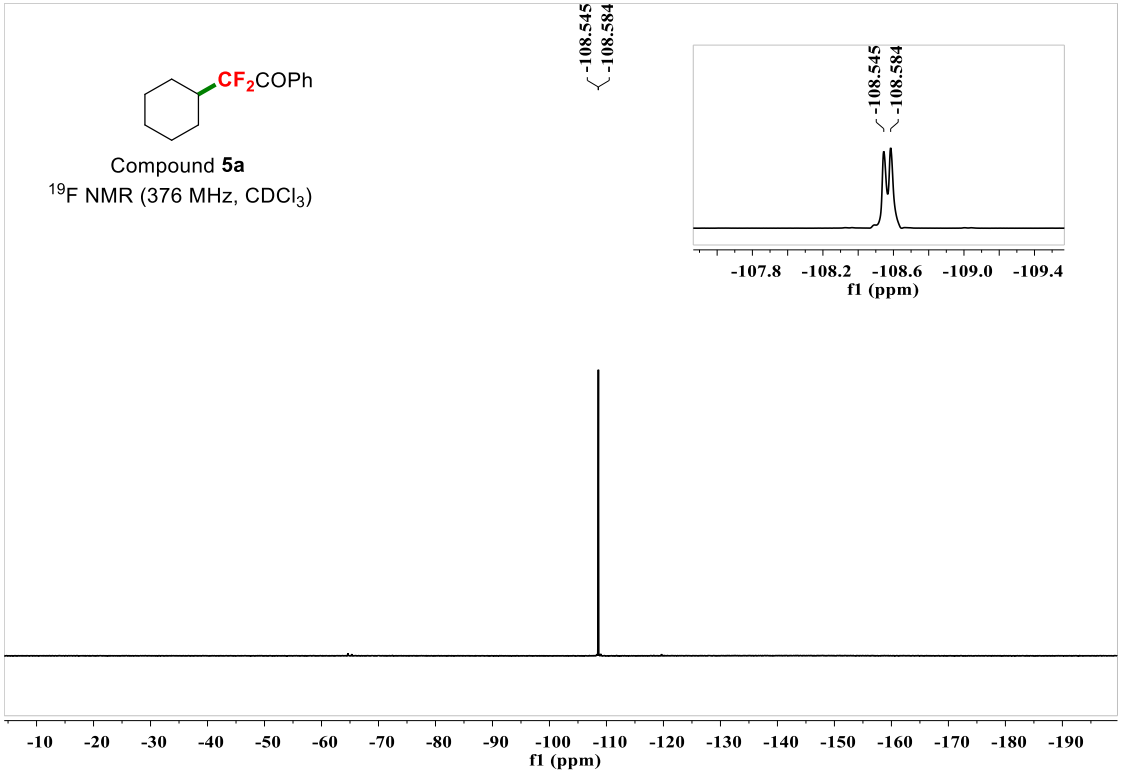


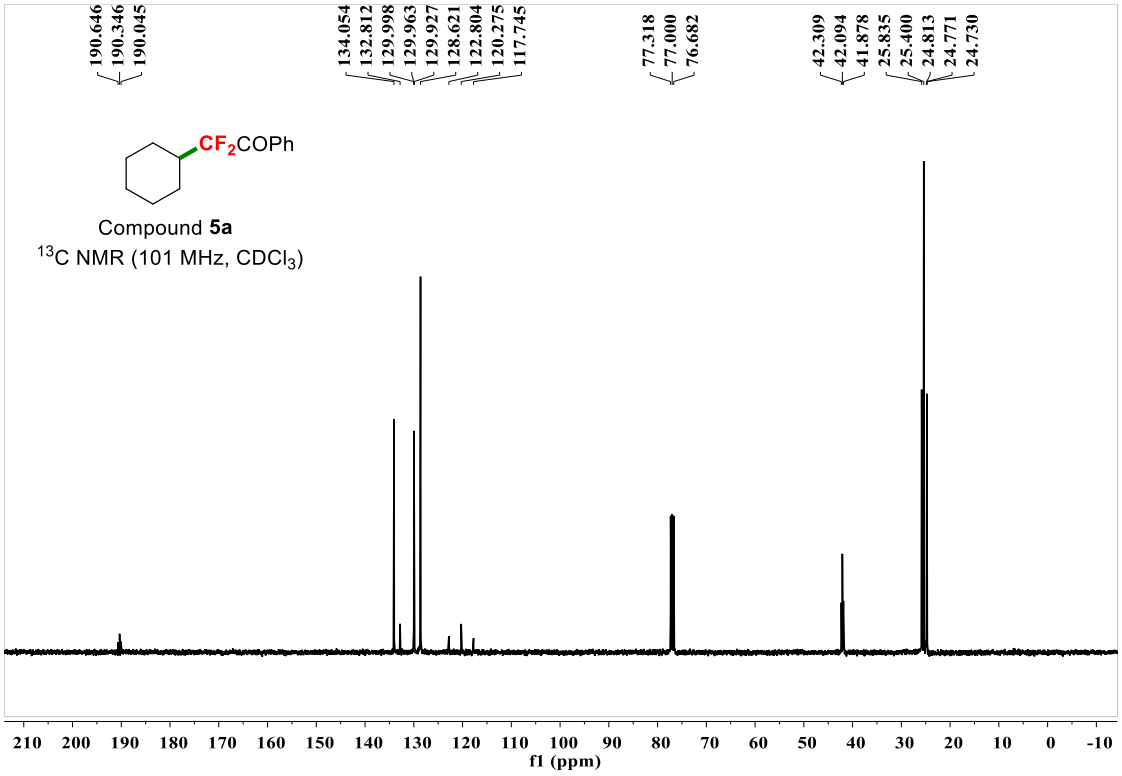

-100.560
-100.743
-112.400
-112.583
OTES
F
F
Compound 4
19F NMR (376 MHz, CDCl3)
1.00
1.04
f1 (ppm)


157.409
154.559
151.713
132.917
132.900
132.849
132.831
128.182
127.798
127.784
127.770
126.110
126.076
126.045
126.010
114.488
114.301
114.141
113.952
77.318
77.000
76.683
6.797
6.458
4.853
OTES
F
F
Compound 4
13C NMR (101 MHz, CDCl3)
f1 (ppm)

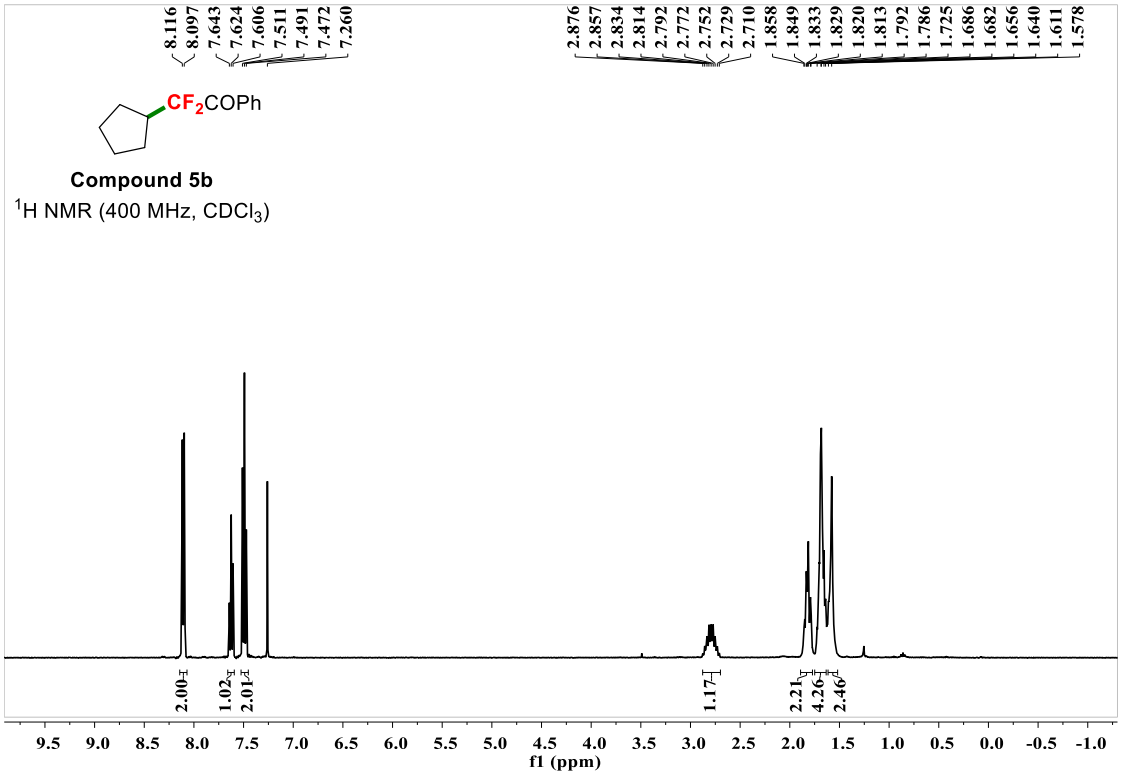
2-Cyclohexyl-2,2-difluoro-1-phenylethan-1-one (5a)

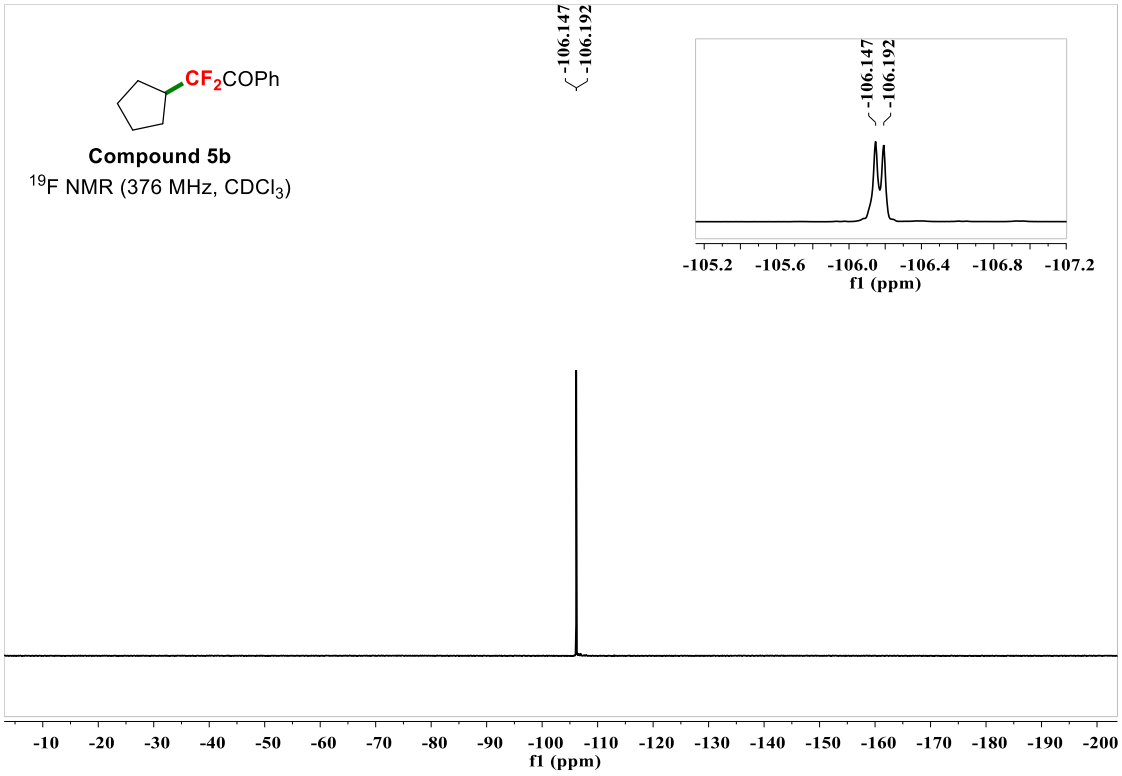


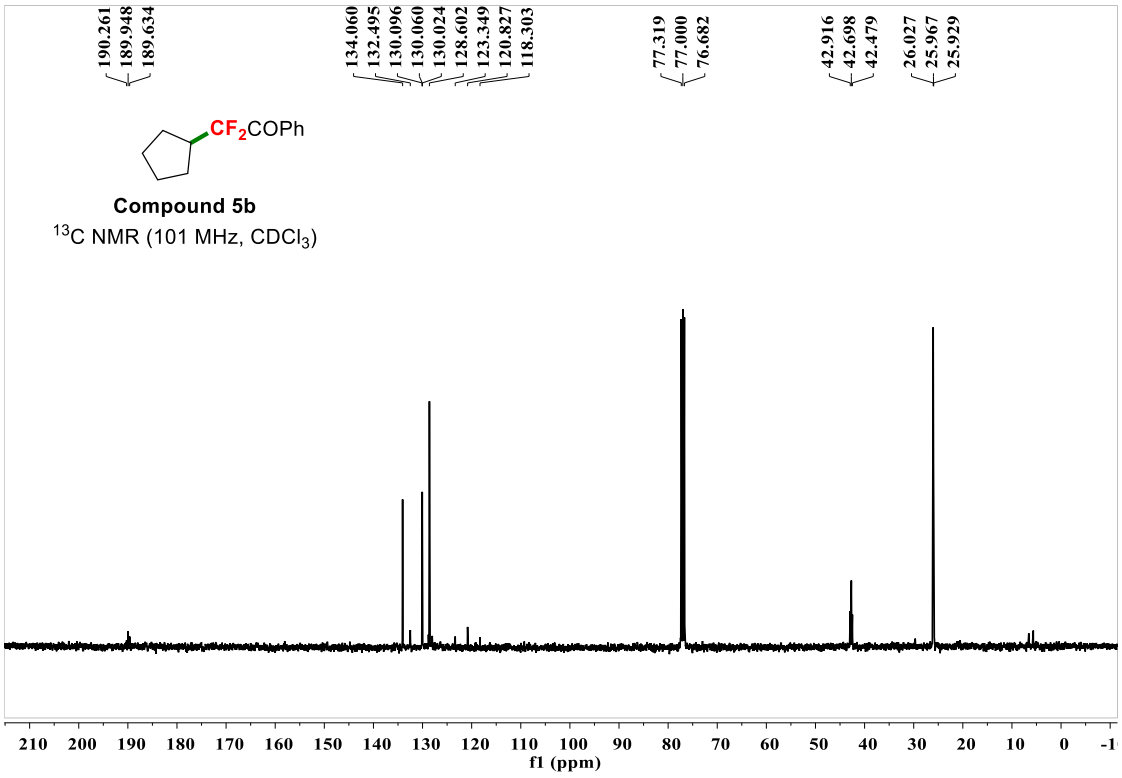




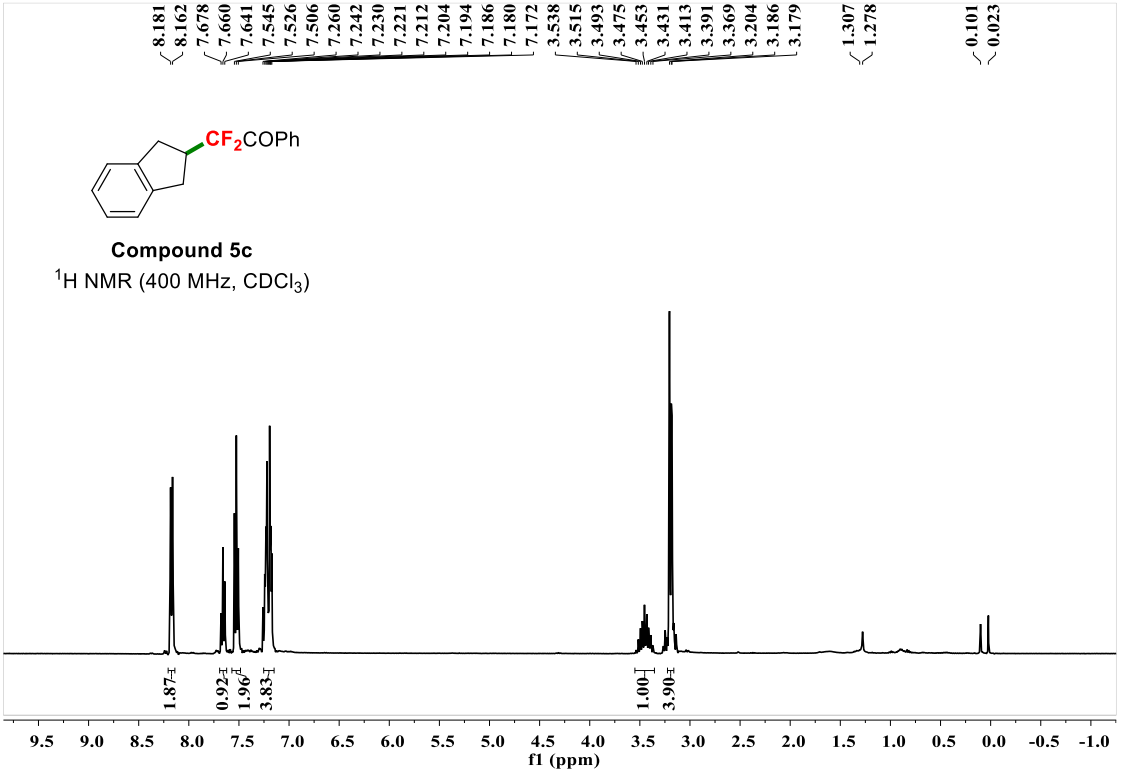
2-Cyclopentyl-2,2-difluoro-1-phenylethan-1-one (5b)

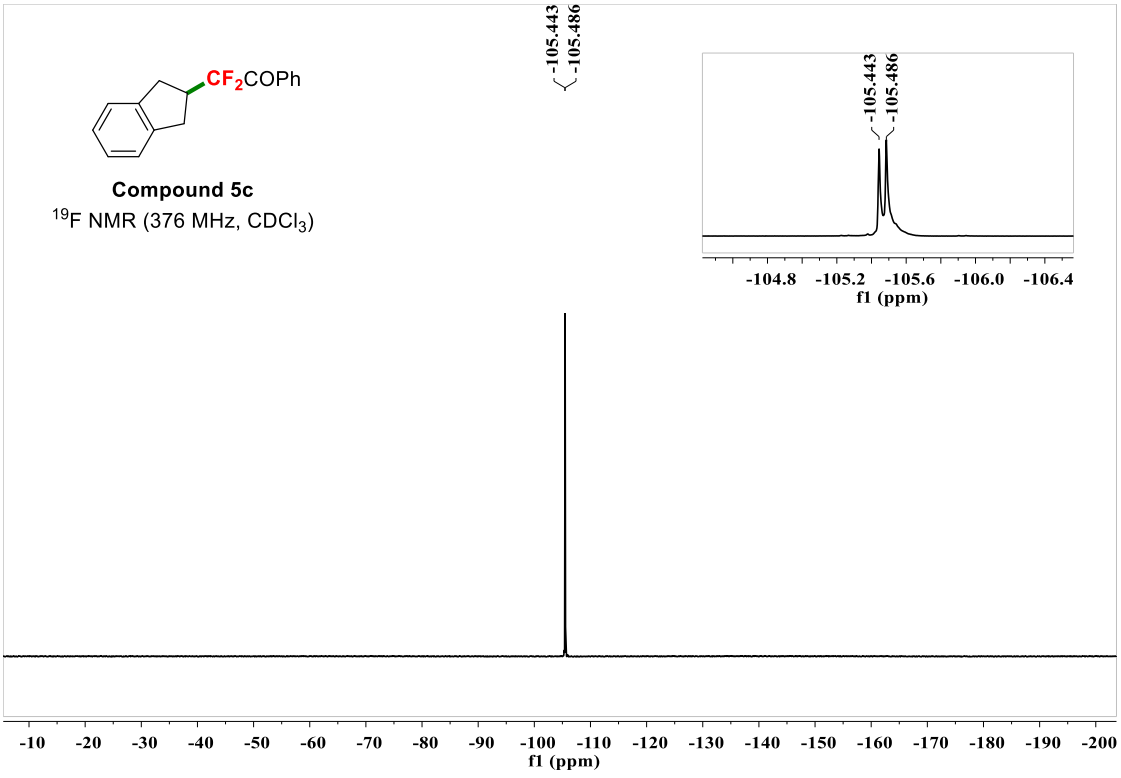


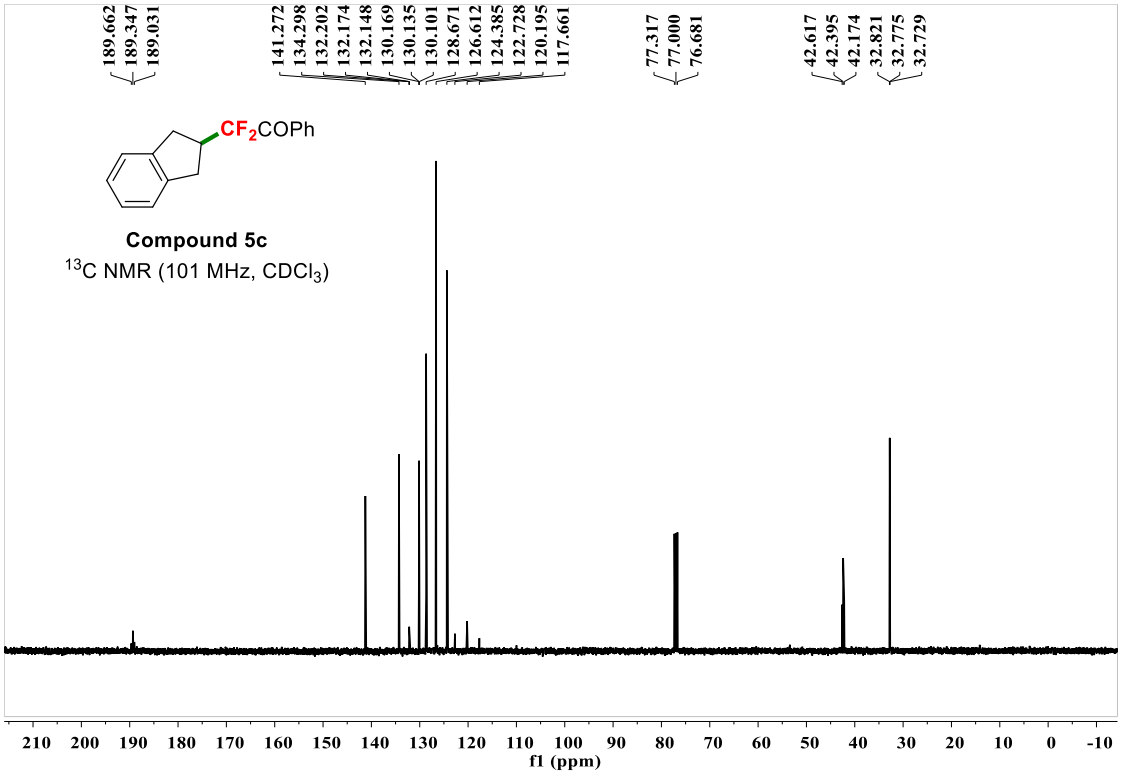

CF2COPh
Compound 5b
19F NMR (376 MHz, CDCl3)
-106.147
-106.192
-105.2 -105.6 -106.0 -106.4 -106.8 -107.2
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


190.261
189.948
189.634
134.060
132.495
130.096
130.060
130.024
128.602
123.349
120.827
118.303
77.319
77.000
76.682
42.916
42.698
42.479
26.027
25.967
25.929
CF2COPh
Compound 5b
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

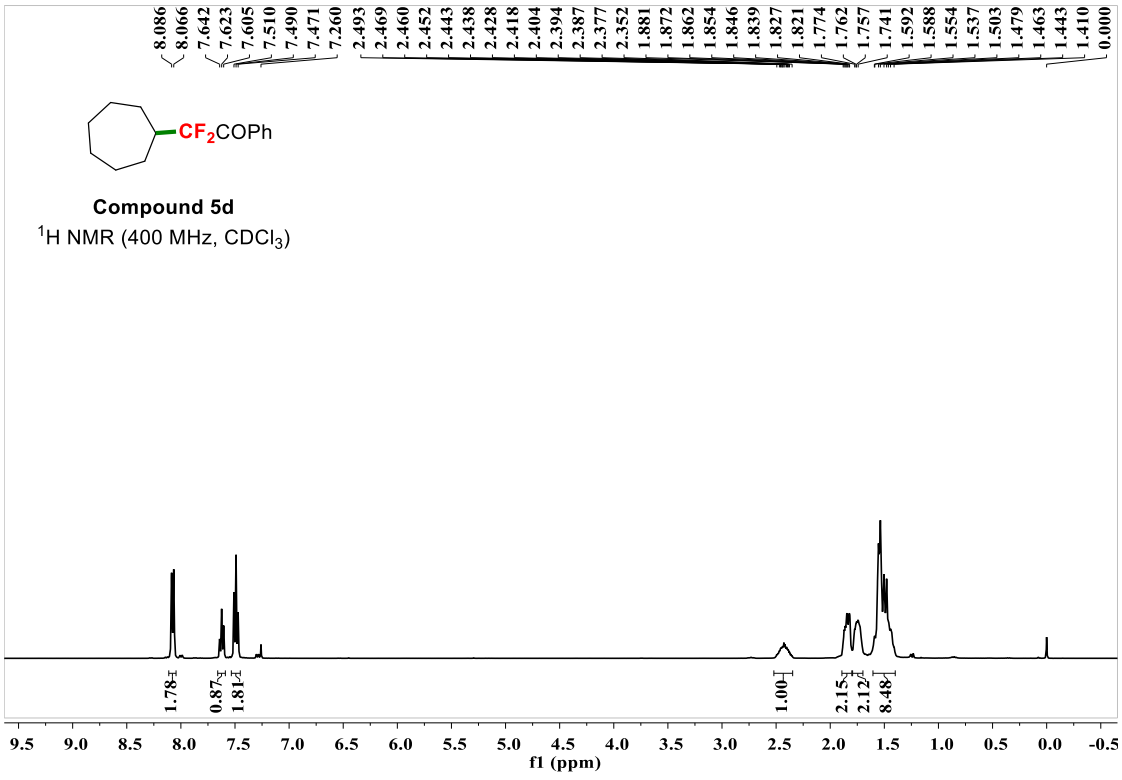
2-(2,3-Dihydro-1H-inden-2-yl)-2,2-difluoro-1-phenylethan-1-one (5c).

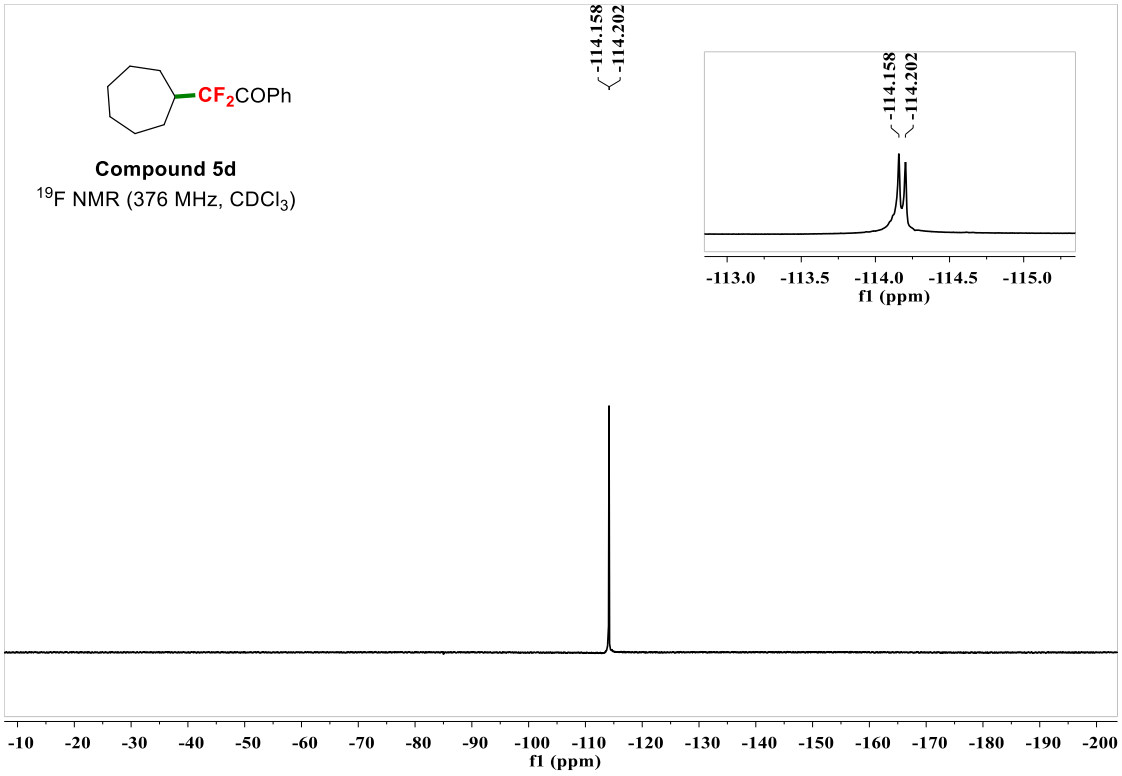


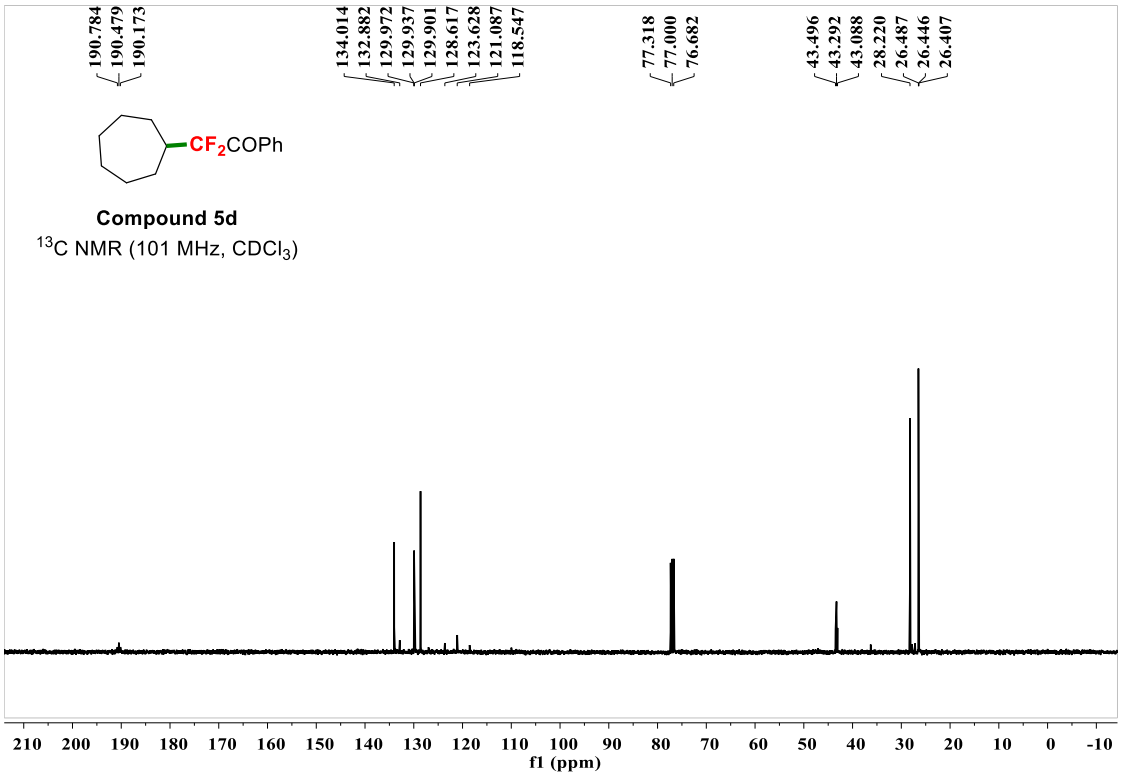




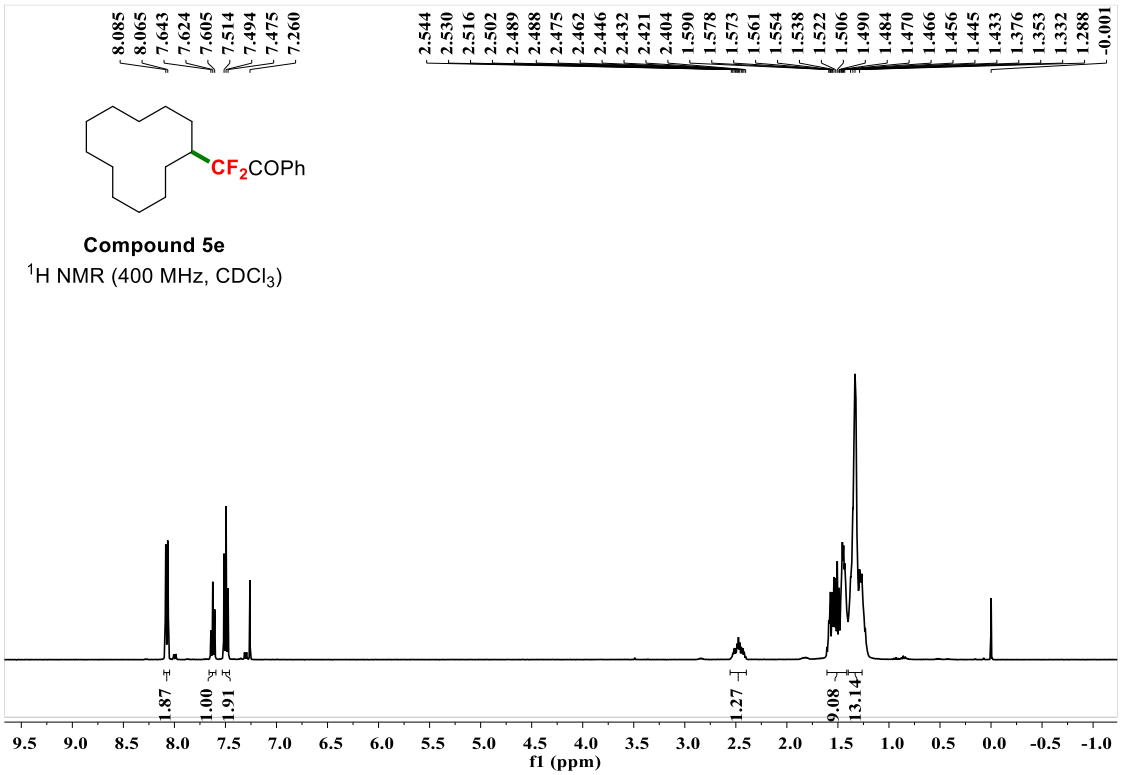
2-Cycloheptyl-2,2-difluoro-1-phenylethan-1-one (5d).

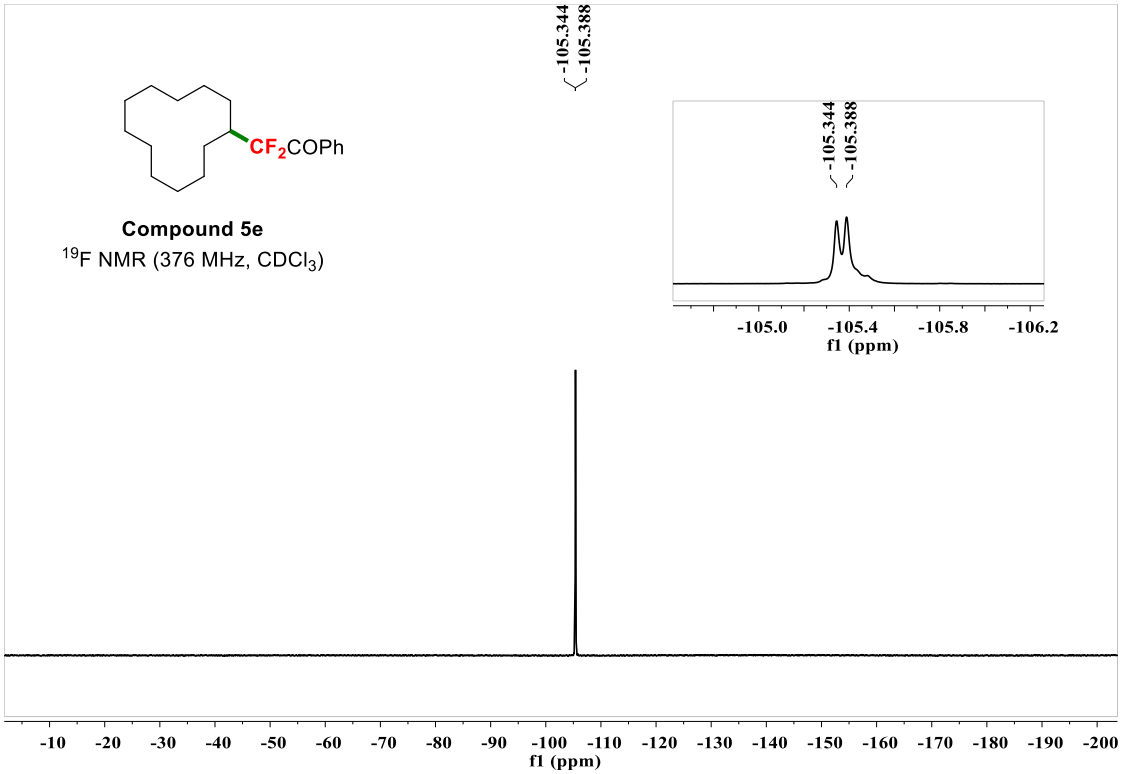


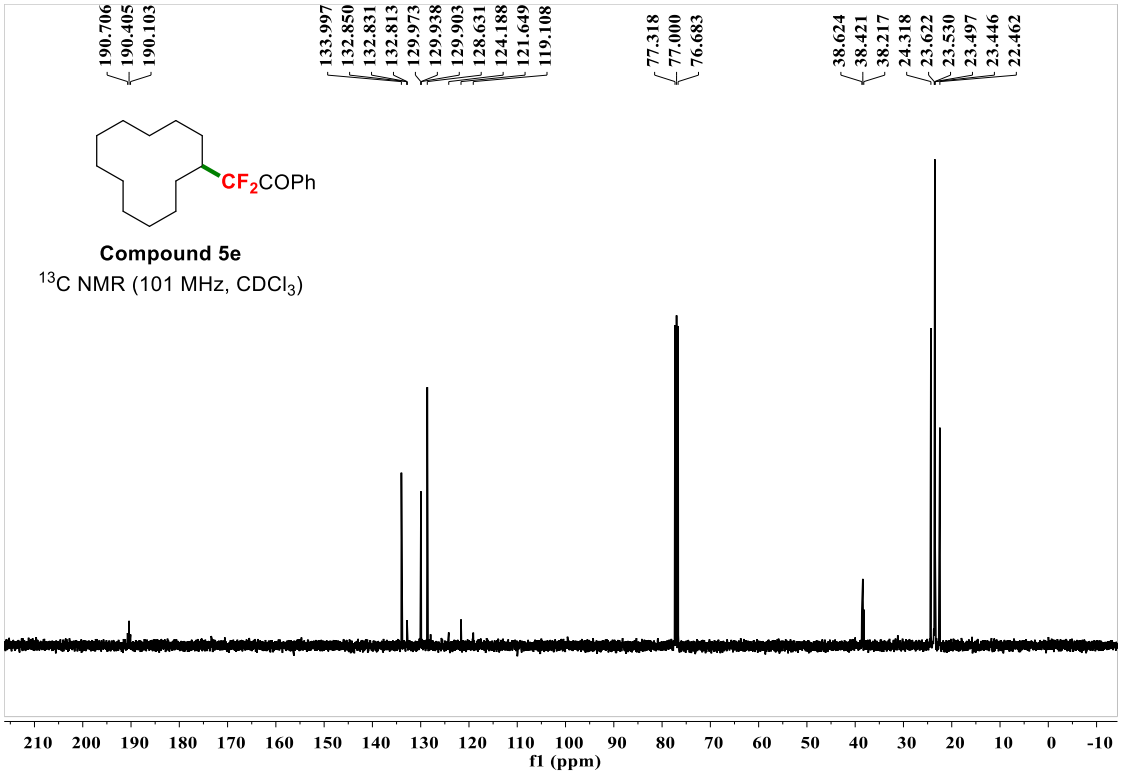

-114.158
-114.202
CF2COPh
Compound 5d
19F NMR (376 MHz, CDCl3)
-114.158
-114.202
-113.0 -113.5 -114.0 -114.5 -115.0
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


190.784
190.479
190.173
134.014
132.882
129.972
129.937
129.901
128.617
123.628
121.087
118.547
77.318
77.000
76.682
43.496
43.292
43.088
28.220
26.487
26.446
26.407
CF2COPh
Compound 5d
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

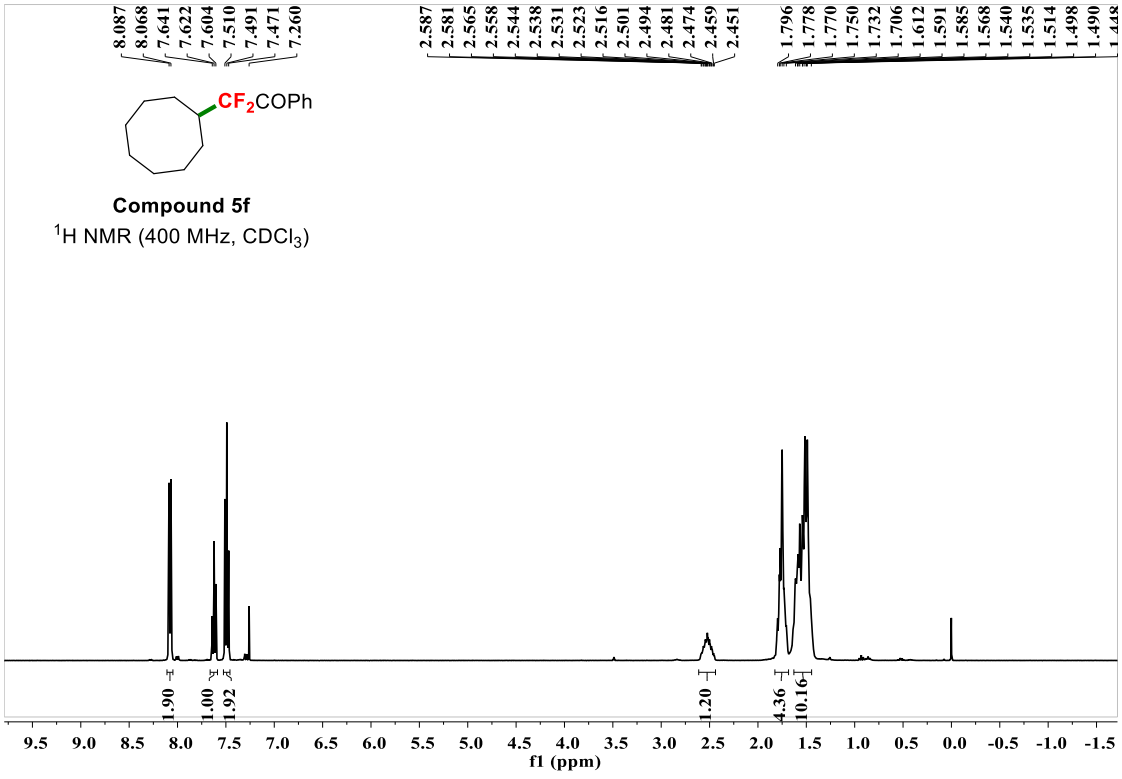
2-Cyclododecyl-2,2-difluoro-1-phenylethan-1-one (5e).

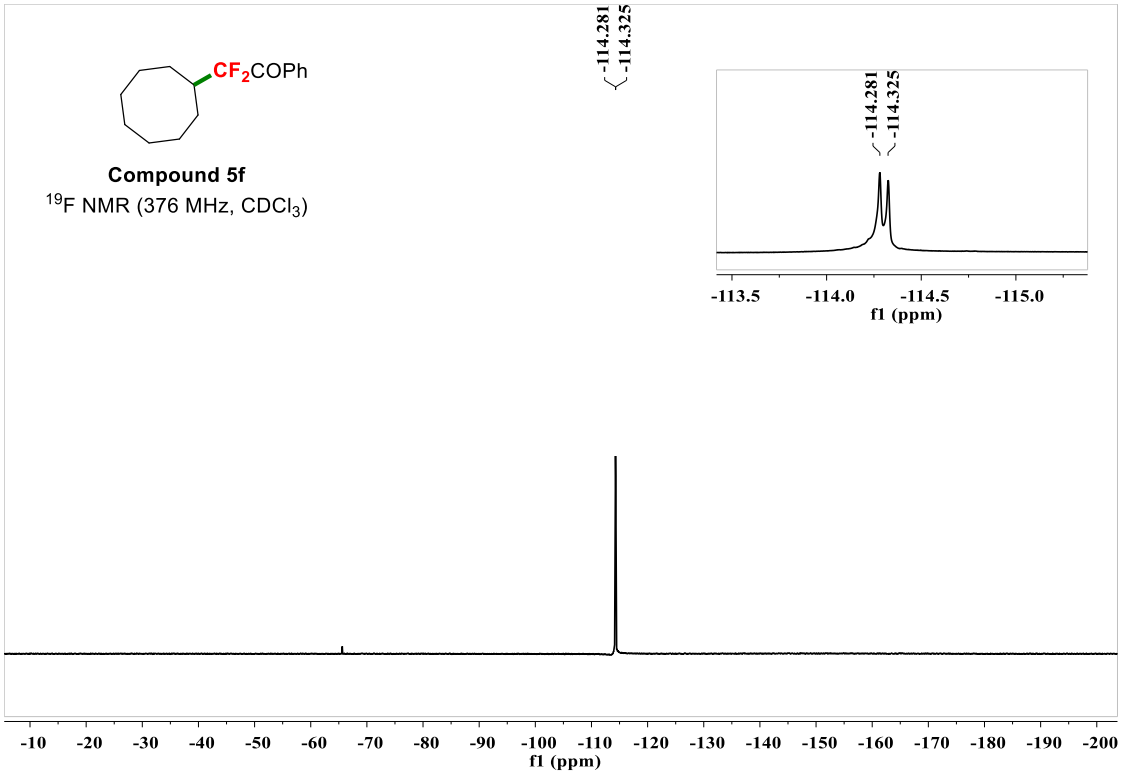


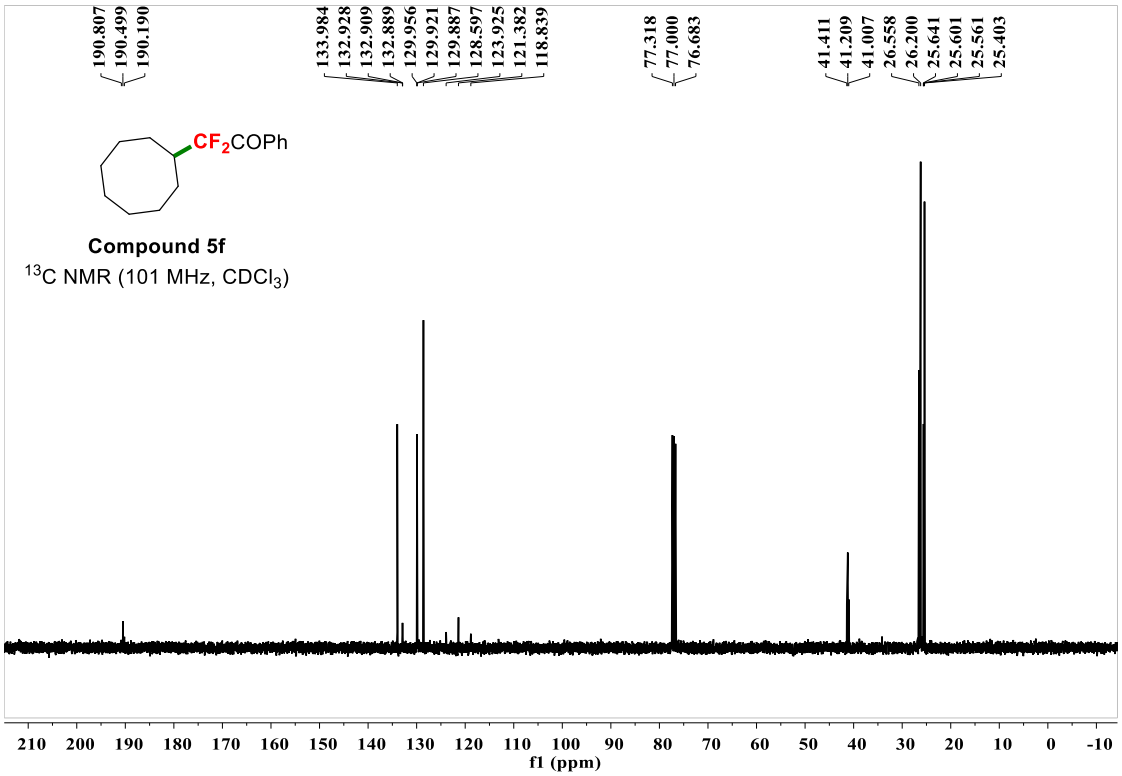




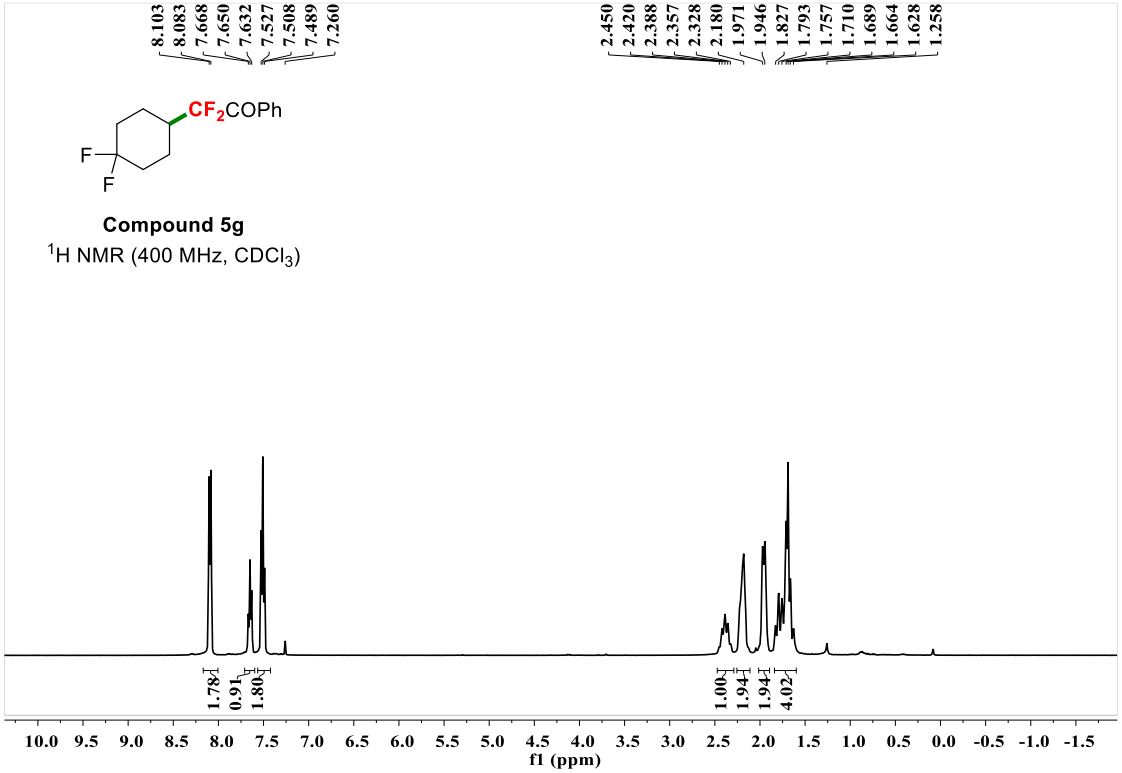
2-Cyclooctyl-2,2-difluoro-1-phenylethan-1-one (5f)

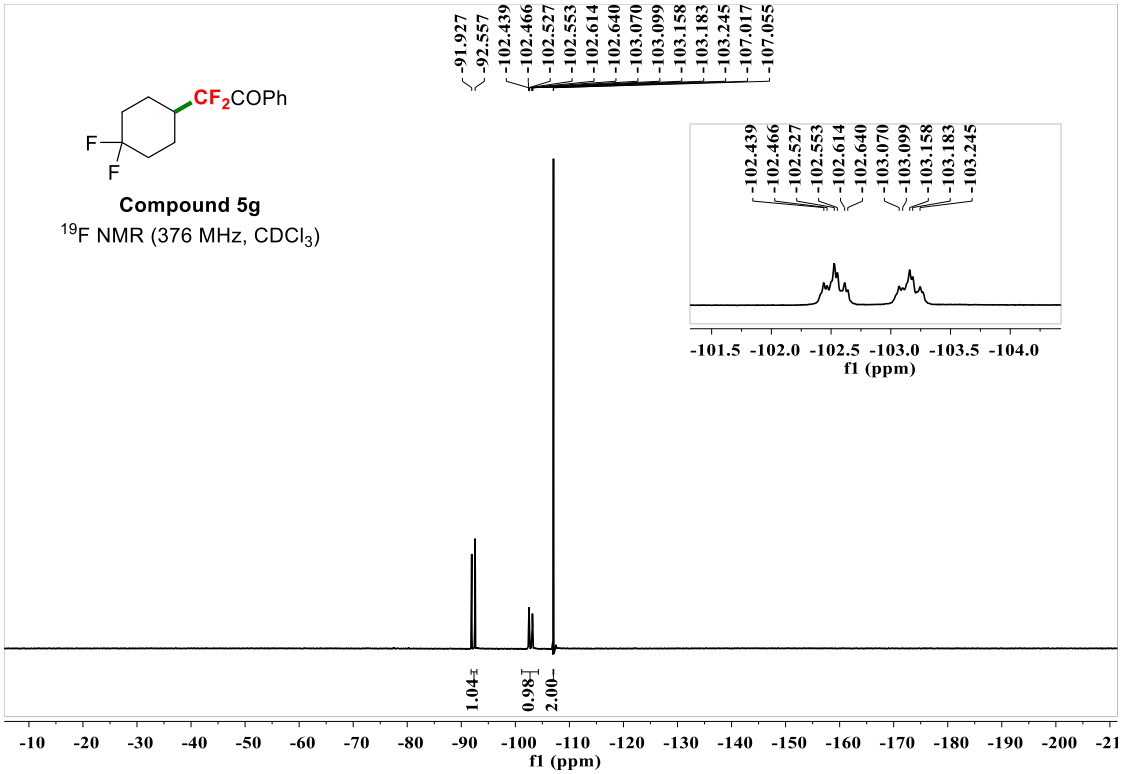


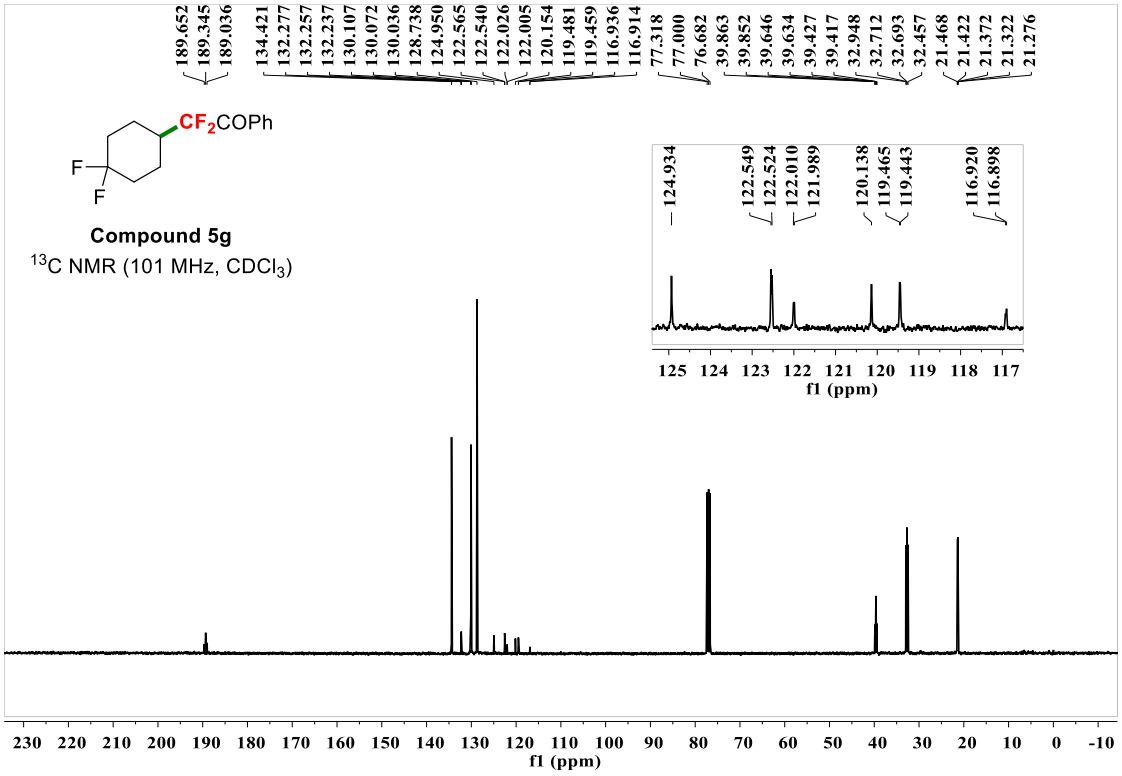

CF2COPh
Compound 5f
19F NMR (376 MHz, CDCl3)
-114.281
-114.325
-113.5
-114.0
-114.5
-115.0
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


190.807
190.499
190.190
133.984
132.928
132.909
132.889
129.956
129.921
129.887
128.597
123.925
121.382
118.839
77.318
77.000
76.683
41.411
41.209
41.007
26.558
26.200
25.641
25.601
25.561
25.403
CF2COPh
Compound 5f
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

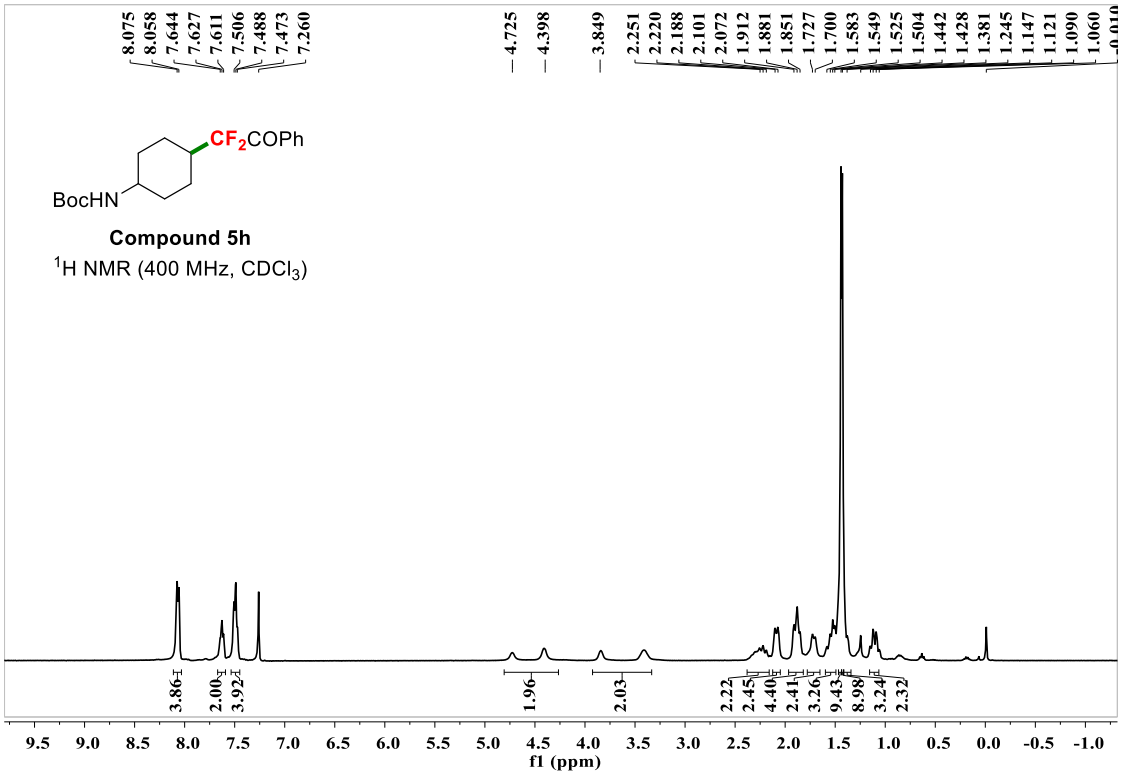
2-(4,4-Difluorocyclohexyl)-2,2-difluoro-1-phenylethan-1-one (5g).

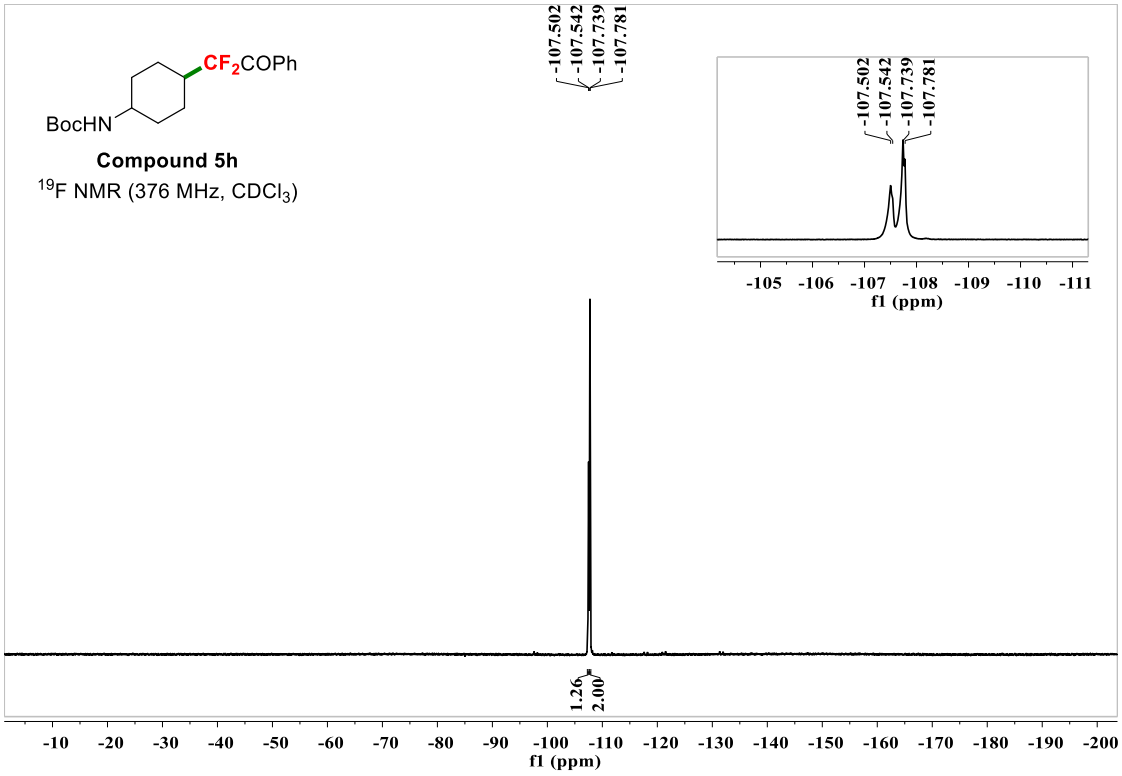


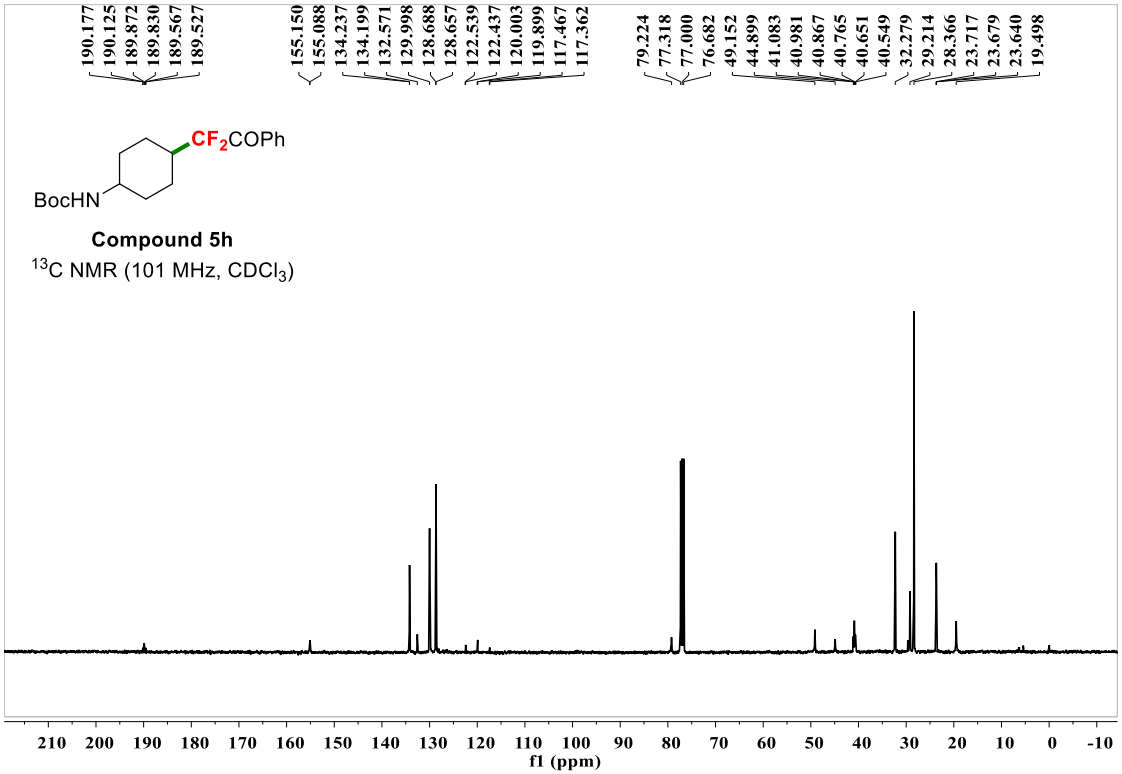




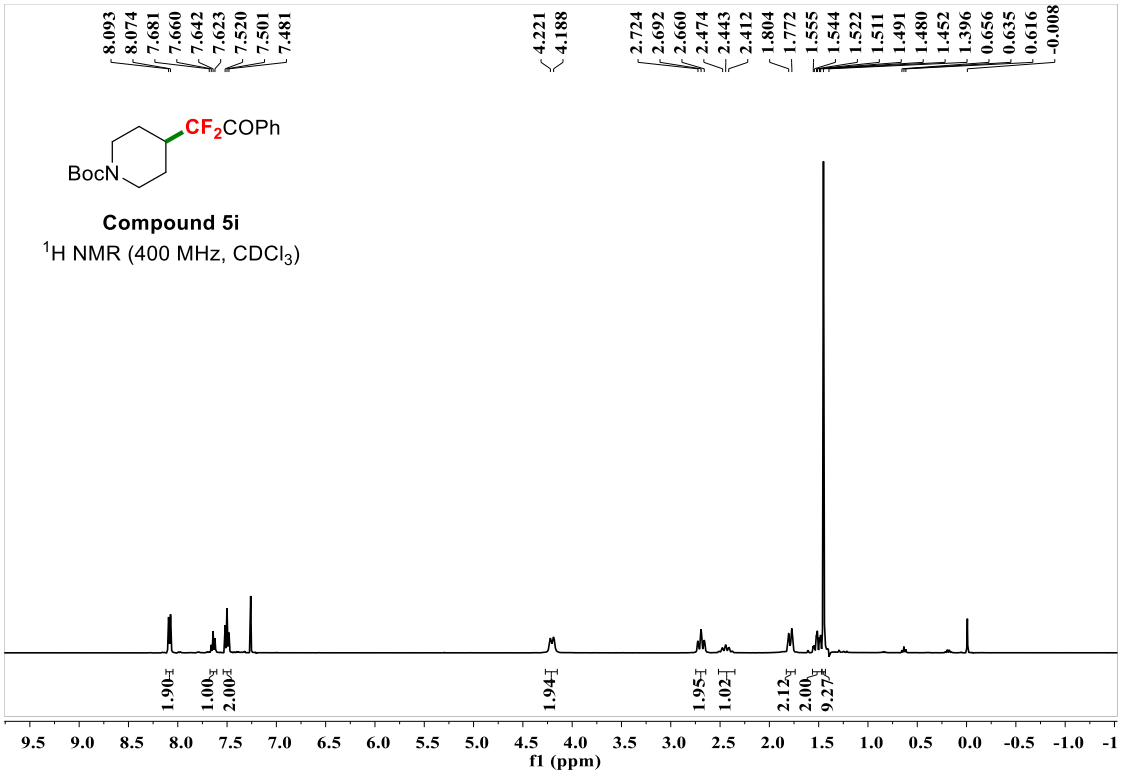
Tert-butyl (4-(1,1-difluoro-2-oxo-2-phenylethyl)cyclohexyl)carbamate (5h).

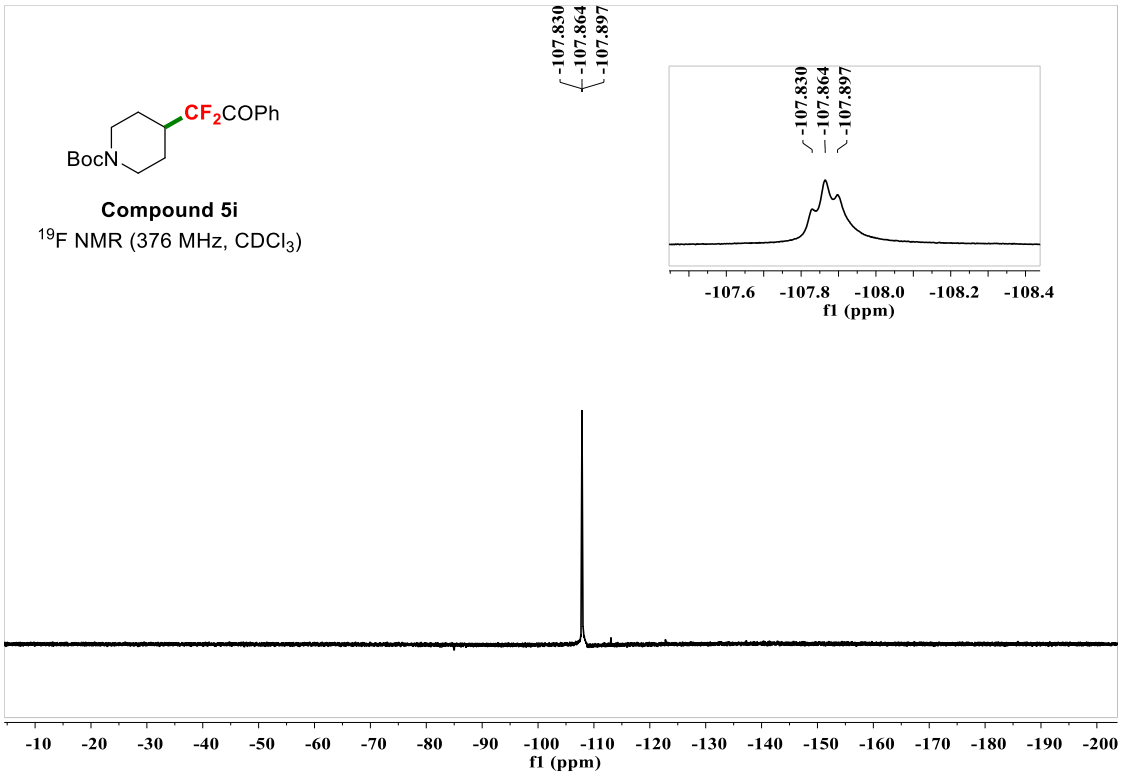


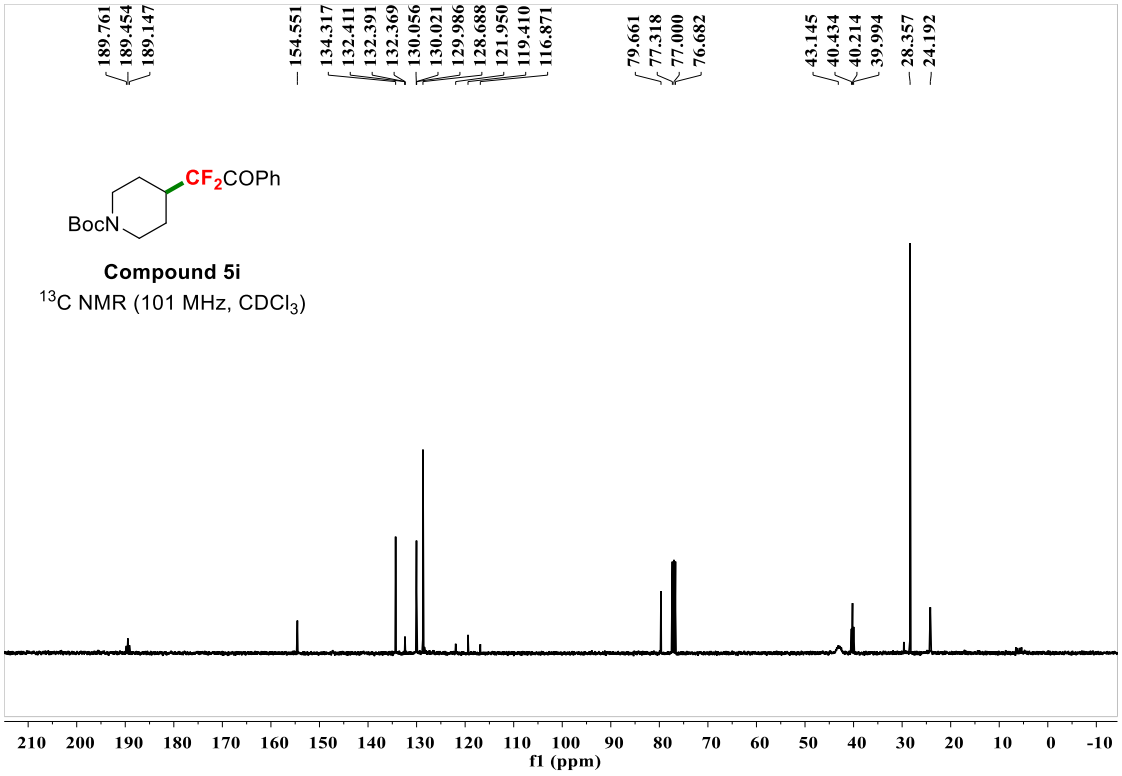

CF2COPh
BocHN
Compound 5h
19F NMR (376 MHz, CDCl3)
-107.502
-107.542
-107.739
-107.781
1.26
2.00
f1 (ppm)


CF2COPh
BocHN
Compound 5h
13C NMR (101 MHz, CDCl3)
f1 (ppm)

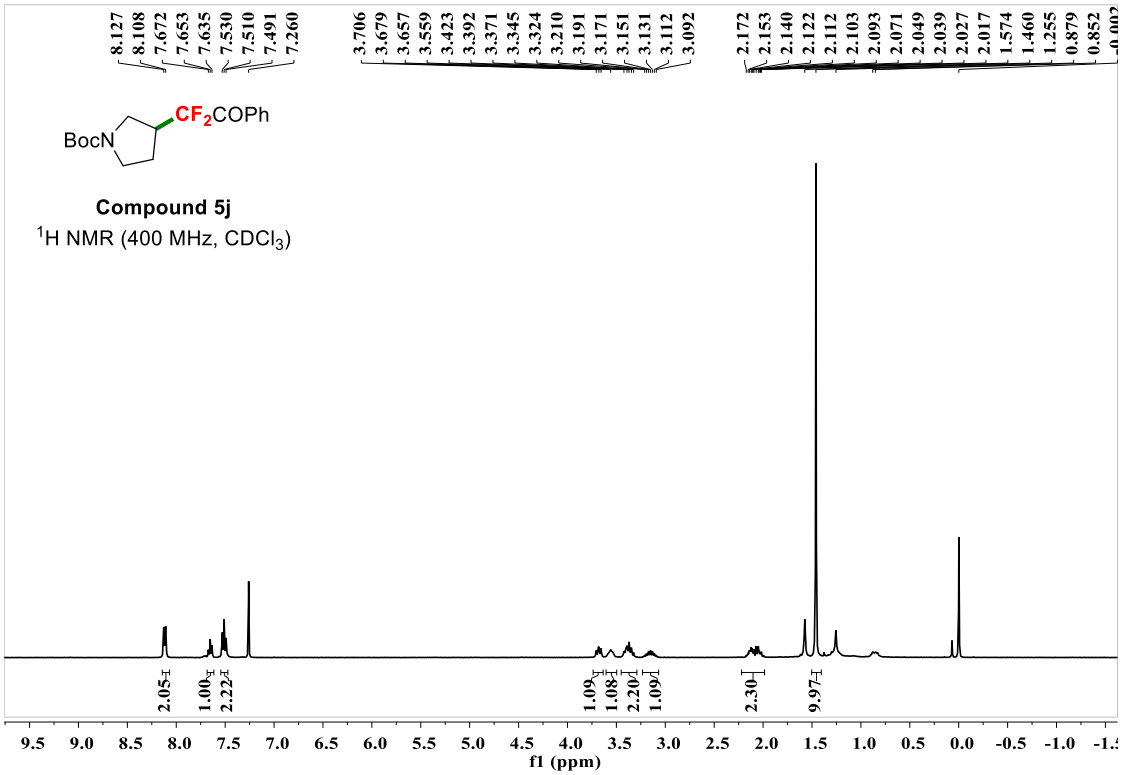
Tert-butyl 4-(1,1-difluoro-2-oxo-2-phenylethyl)piperidine-1-carboxylate (5i).

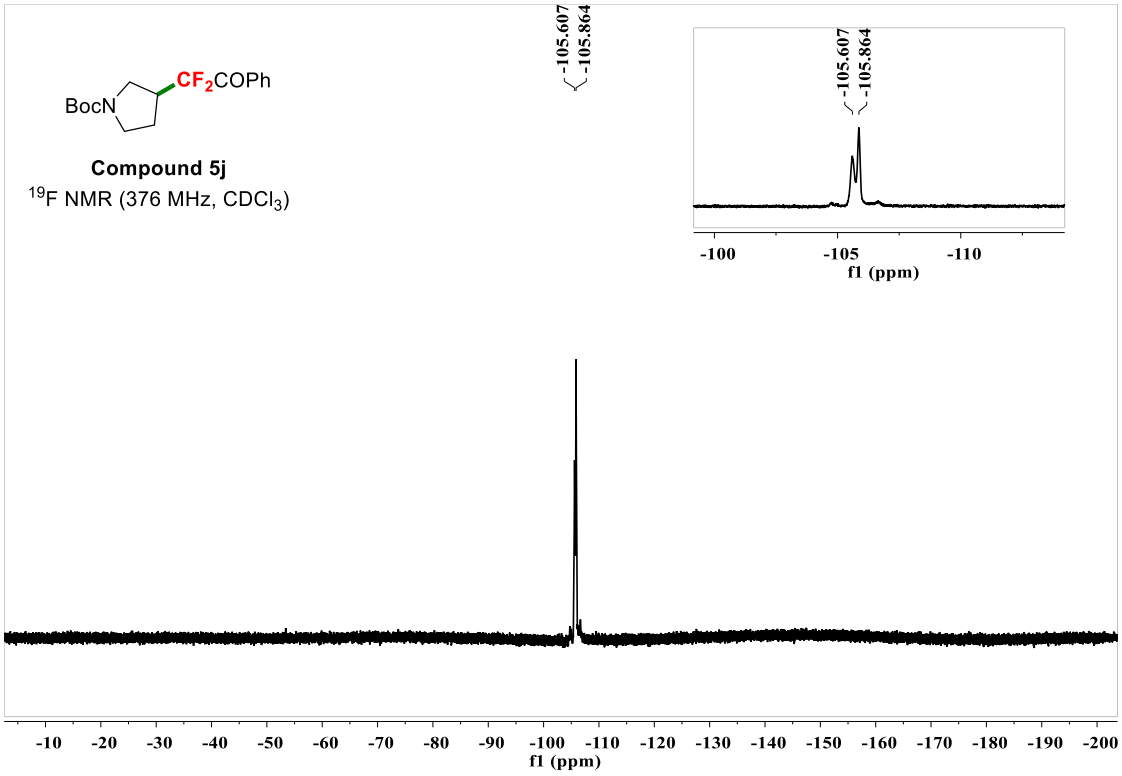


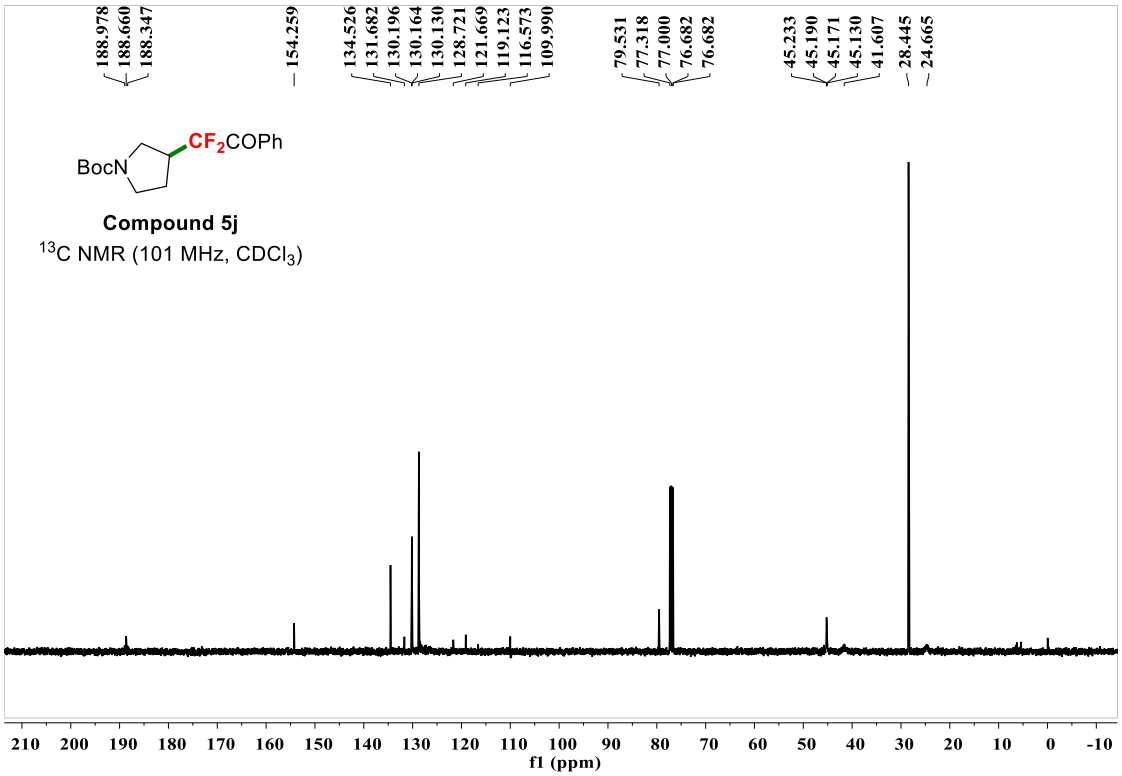




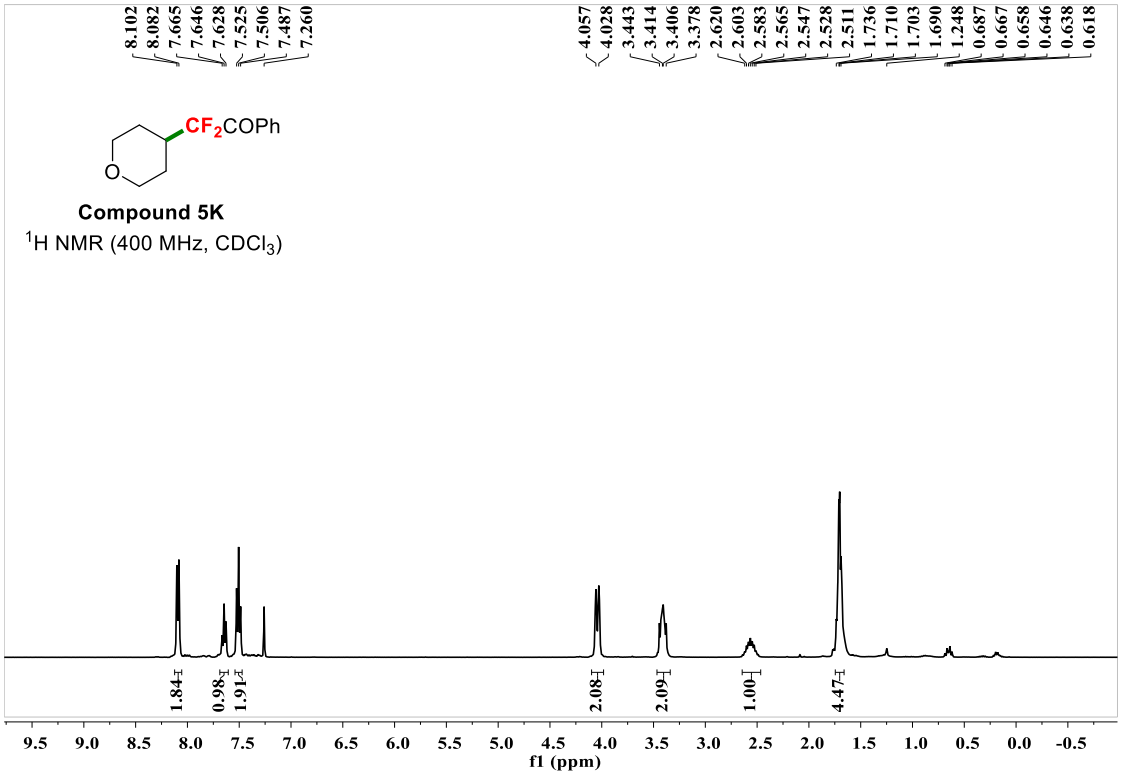
Tert-butyl 3-(1,1-difluoro-2-oxo-2-phenylethyl)pyrrolidine-1-carboxylate (5j).

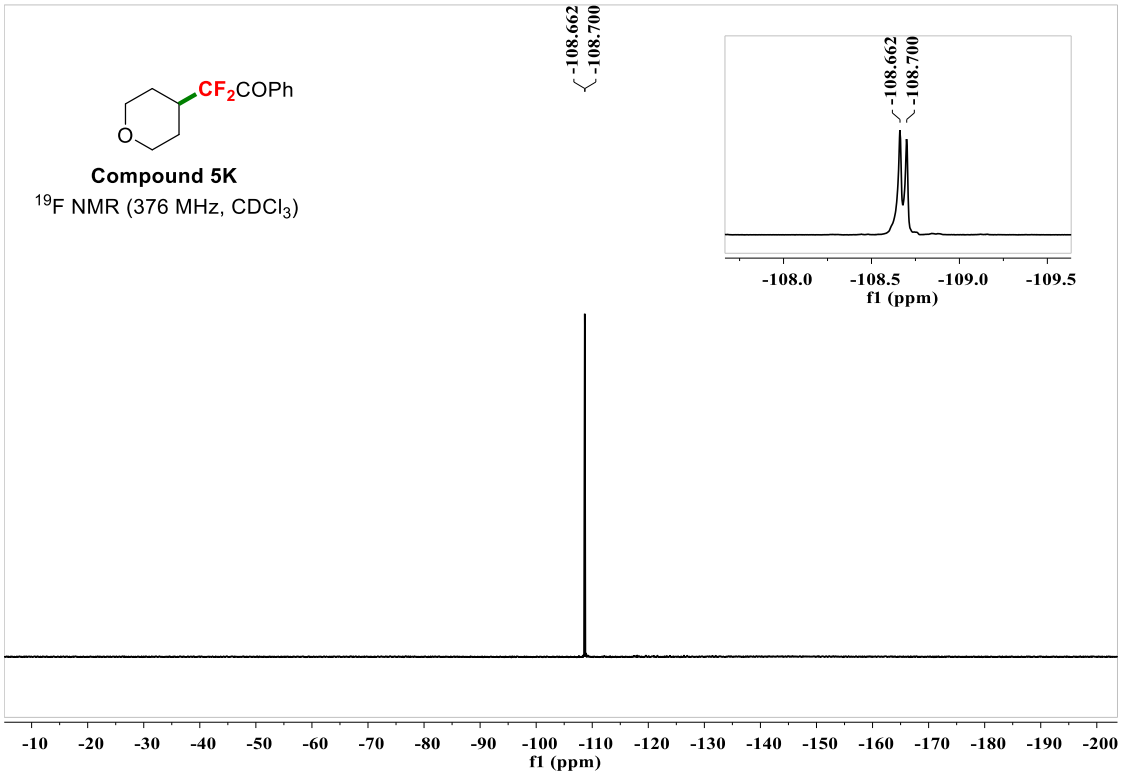


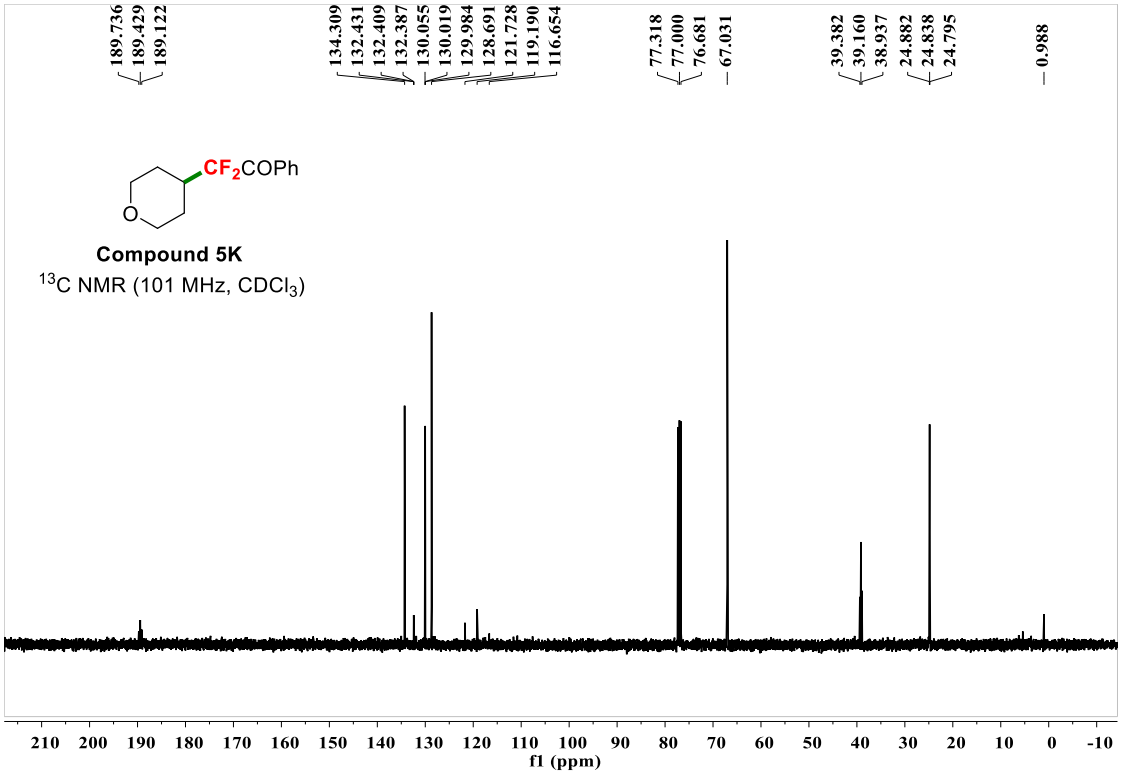

BocN
CF2COPh
Compound 5j
19F NMR (376 MHz, CDCl3)
-105.607
-105.864
-100
-105
-110
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


188.978
188.660
188.347
154.259
134.526
131.682
130.196
130.164
130.130
128.721
121.669
119.123
116.573
109.990
79.531
77.318
77.000
76.682
76.682
45.233
45.190
45.171
45.130
41.607
28.445
24.665
BocN
CF2COPh
Compound 5j
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

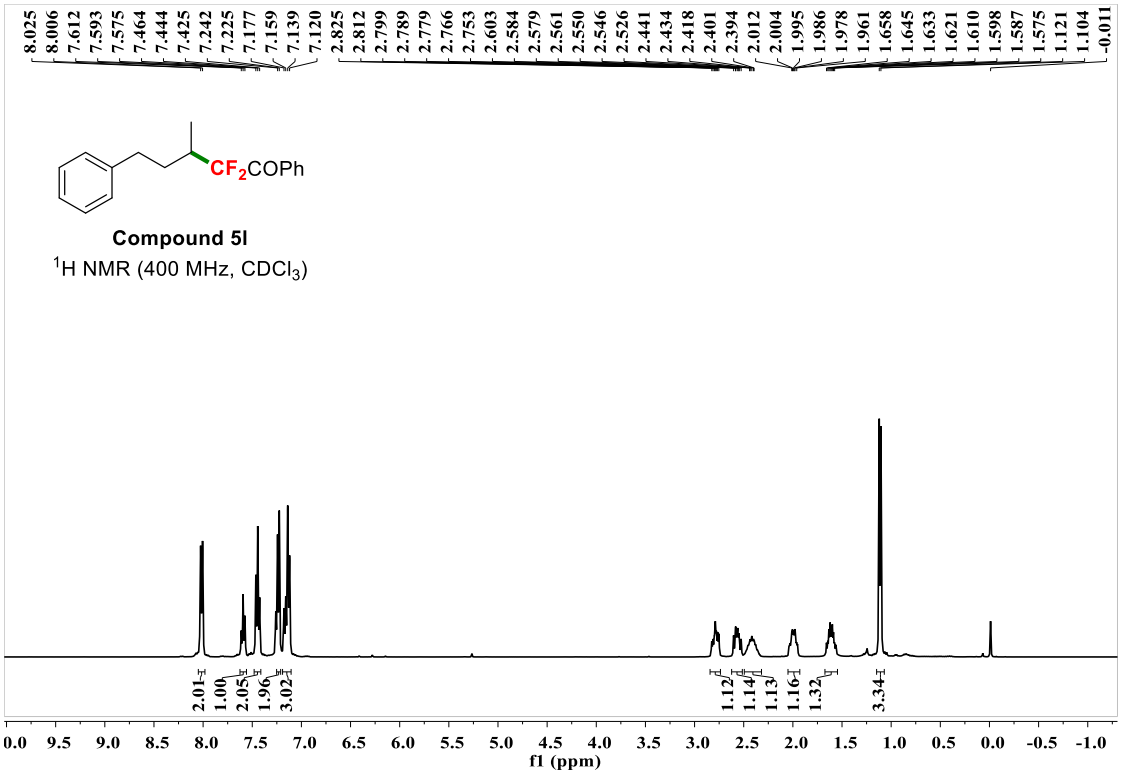
2,2-Difluoro-1-phenyl-2-(tetrahydro-2H-pyran-4-yl)ethan-1-one (5k).

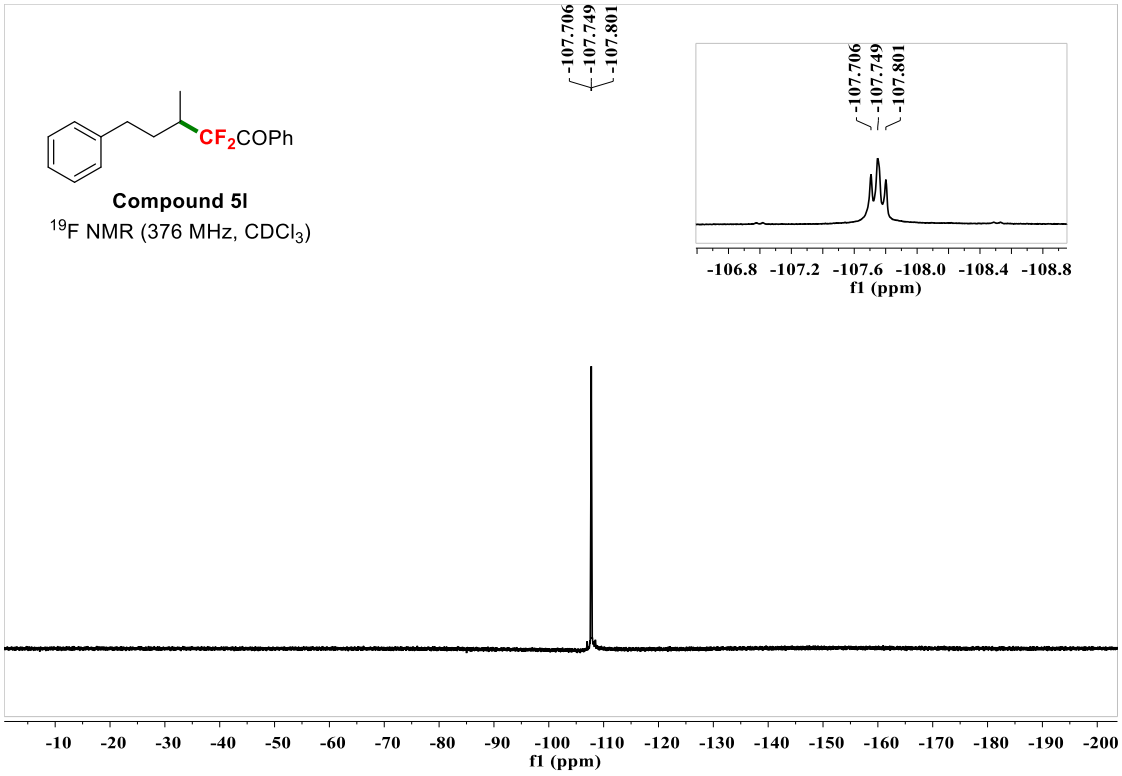


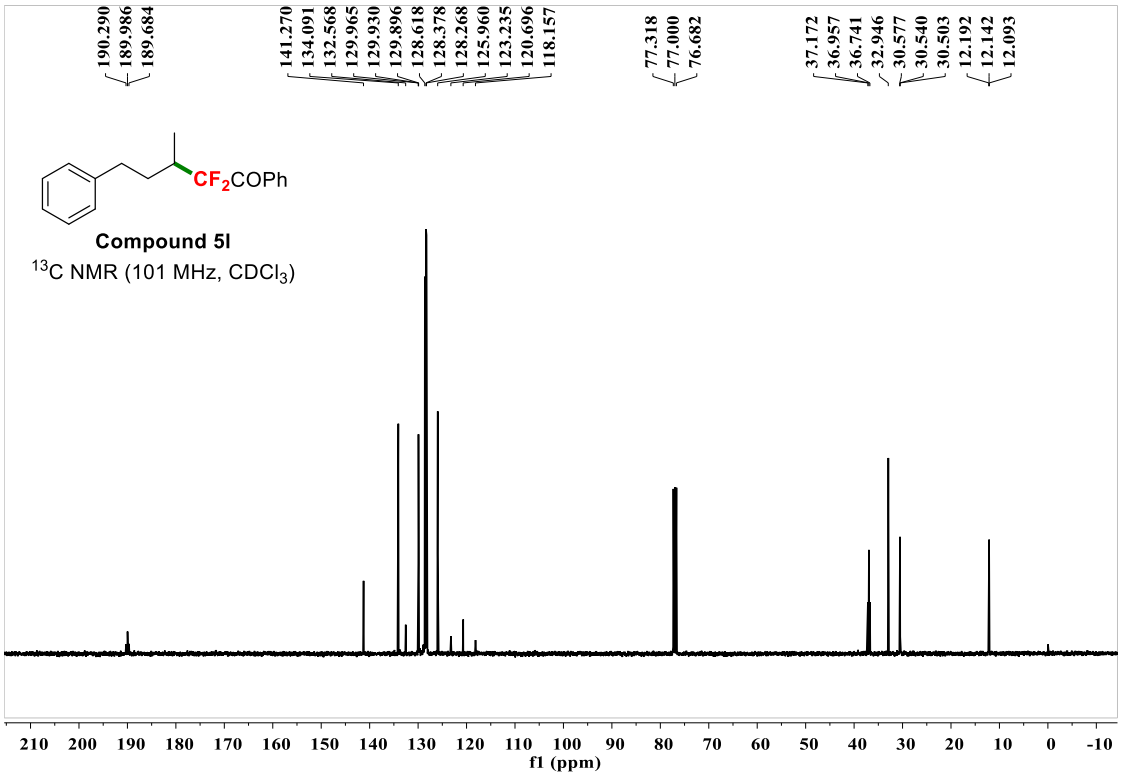




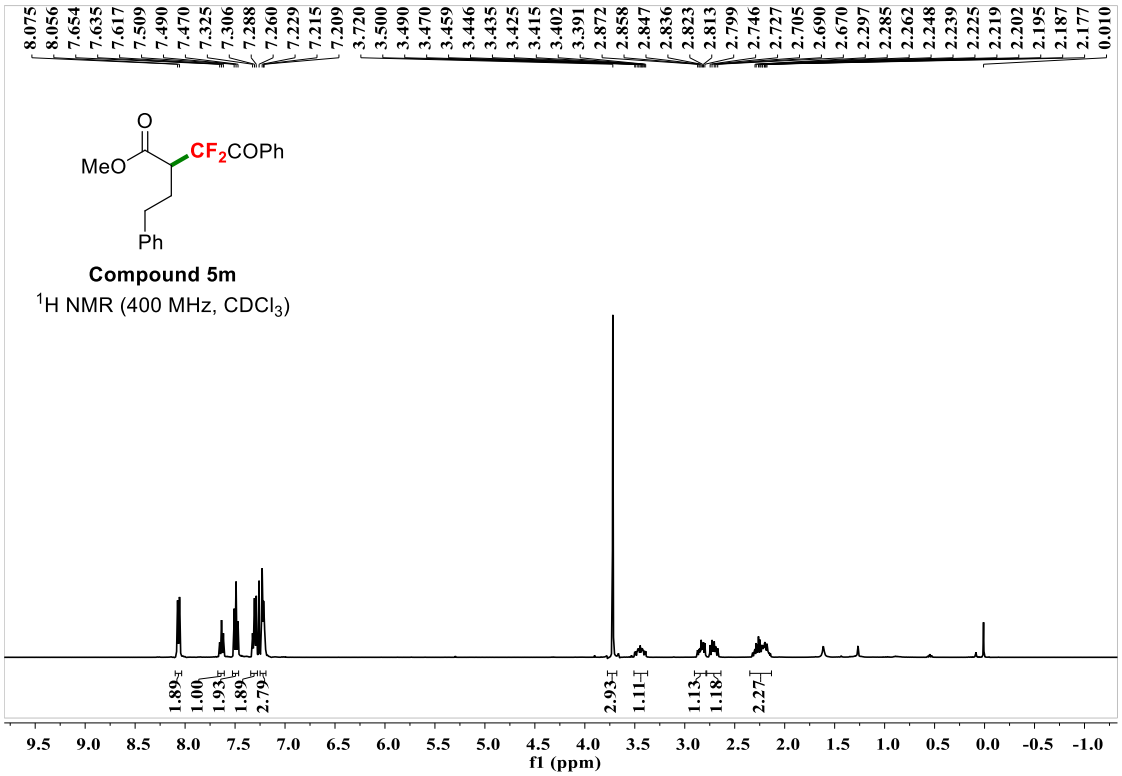
2,2-Difluoro-3-methyl-1,5-diphenylpentan-1-one (5l).

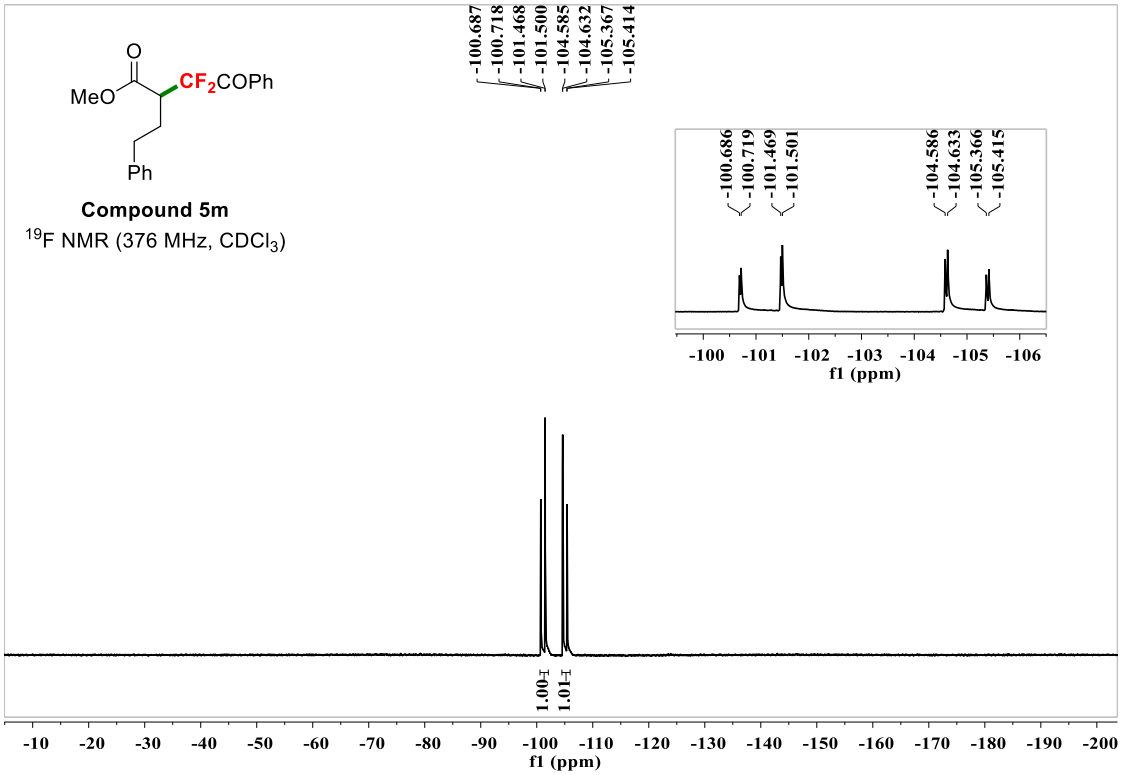


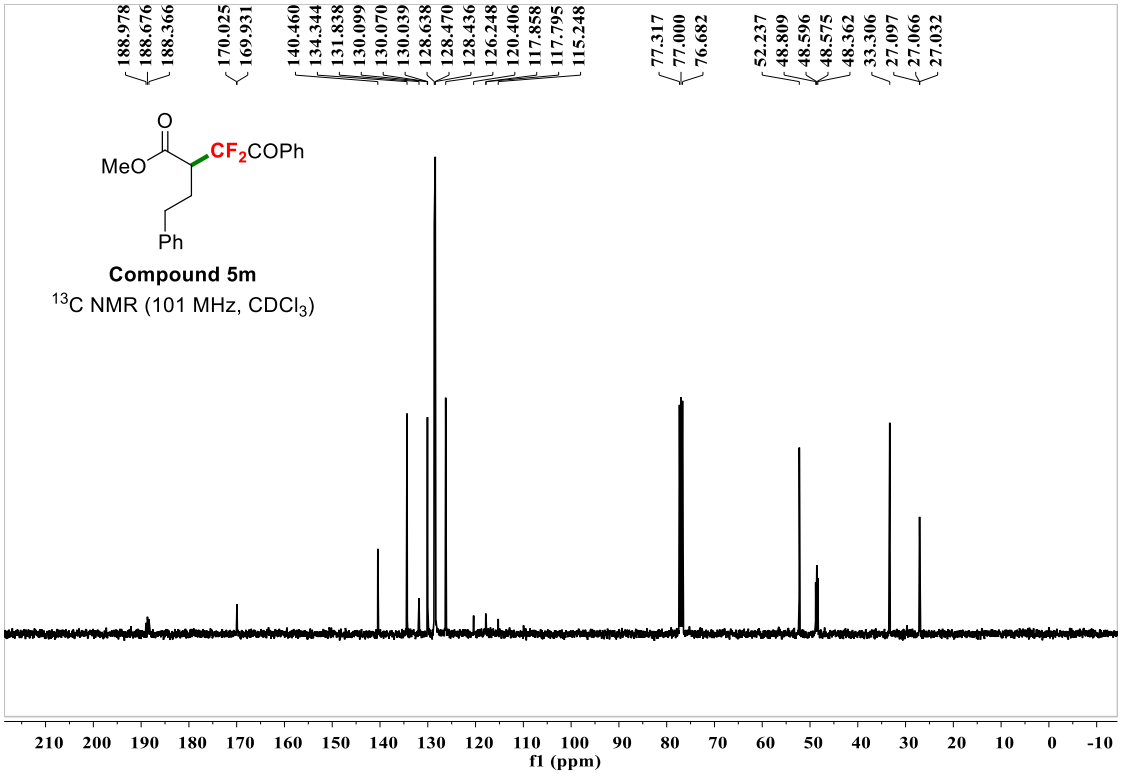

-107.706
-107.749
-107.801
CF2COPh
Compound 5l
19F NMR (376 MHz, CDCl3)
-106.8 -107.2 -107.6 -108.0 -108.4 -108.8
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


190.290
189.986
189.684
141.270
134.091
132.568
129.965
129.930
129.896
128.618
128.378
128.268
125.960
123.235
120.696
118.157
77.318
77.000
76.682
37.172
36.957
36.741
32.946
30.577
30.540
30.503
12.192
12.142
12.093
CF2COPh
Compound 5l
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

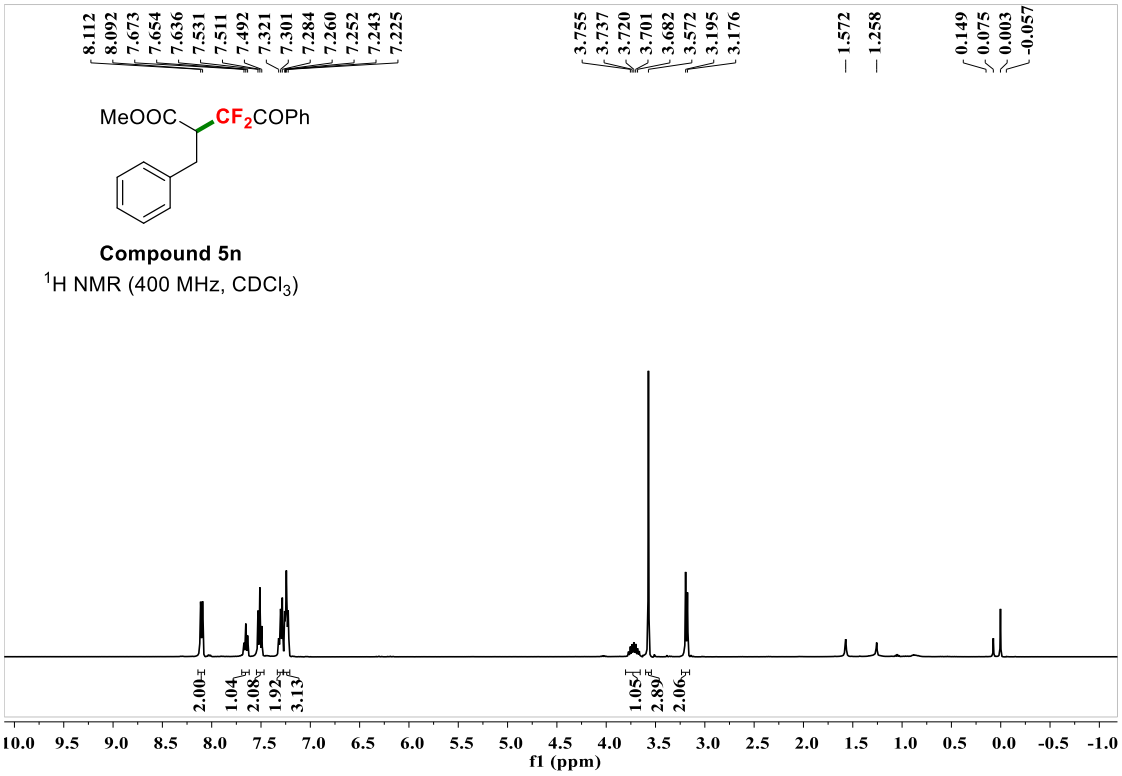
Methyl 3,3-difluoro-4-oxo-2-phenethyl-4-phenylbutanoate (5m).

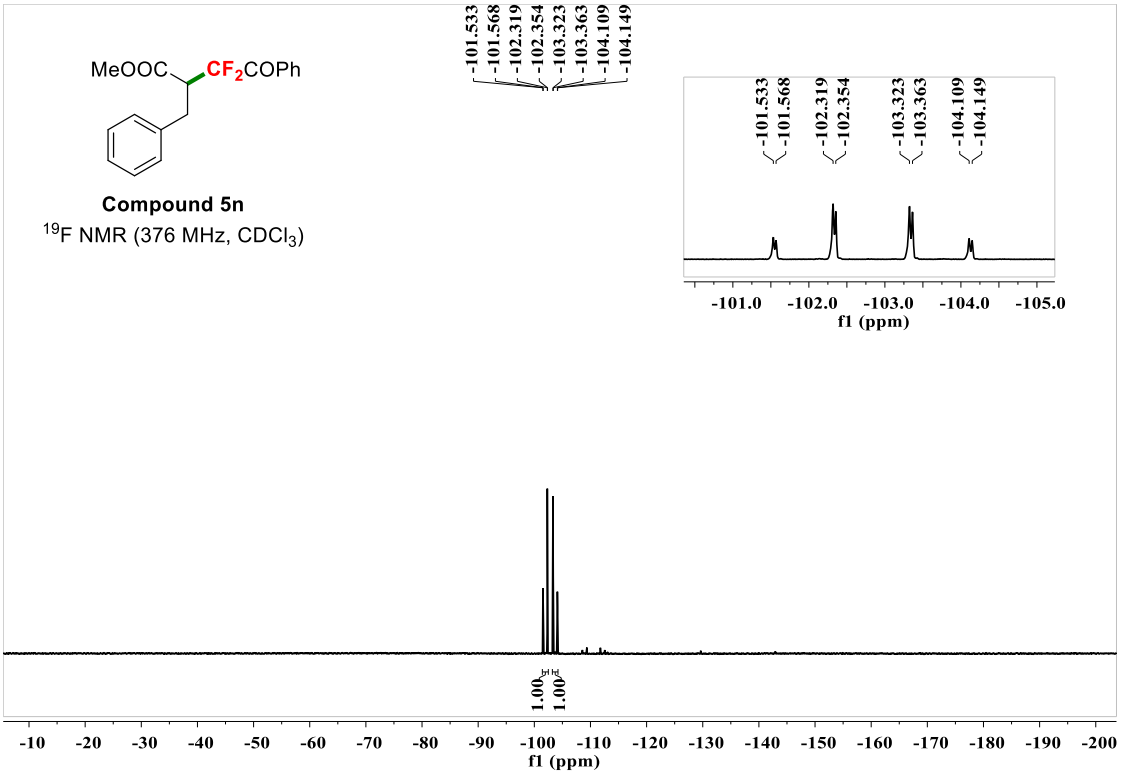


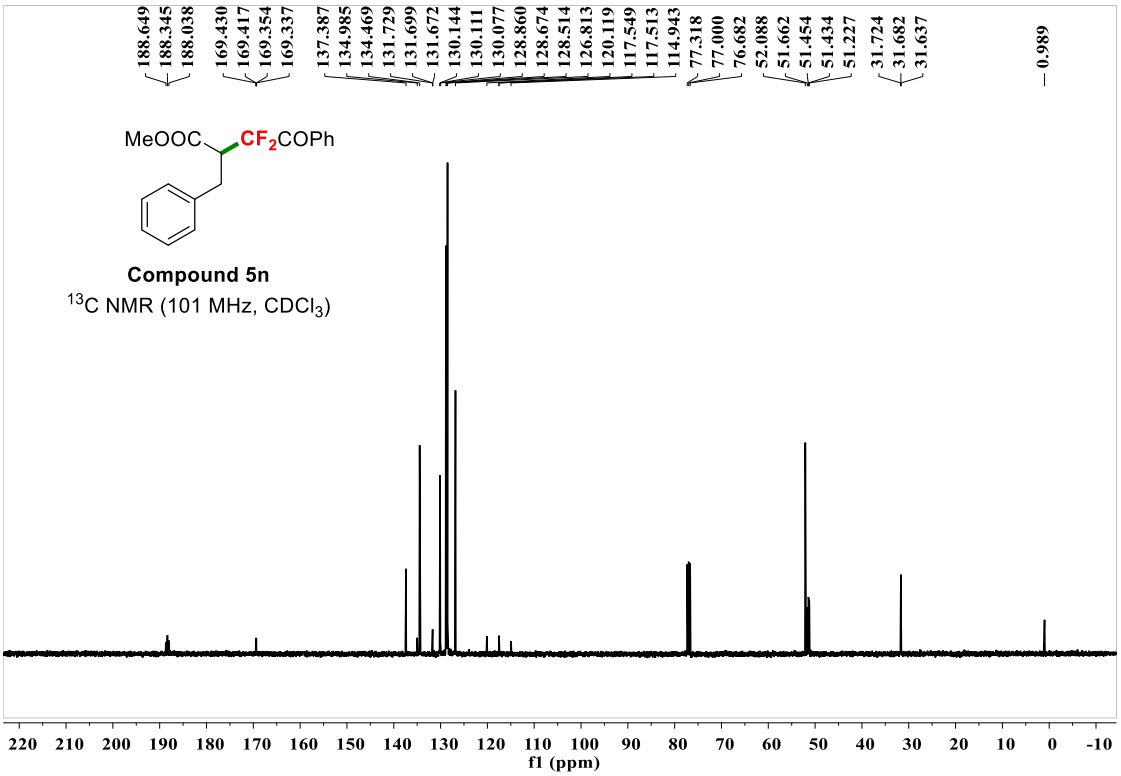




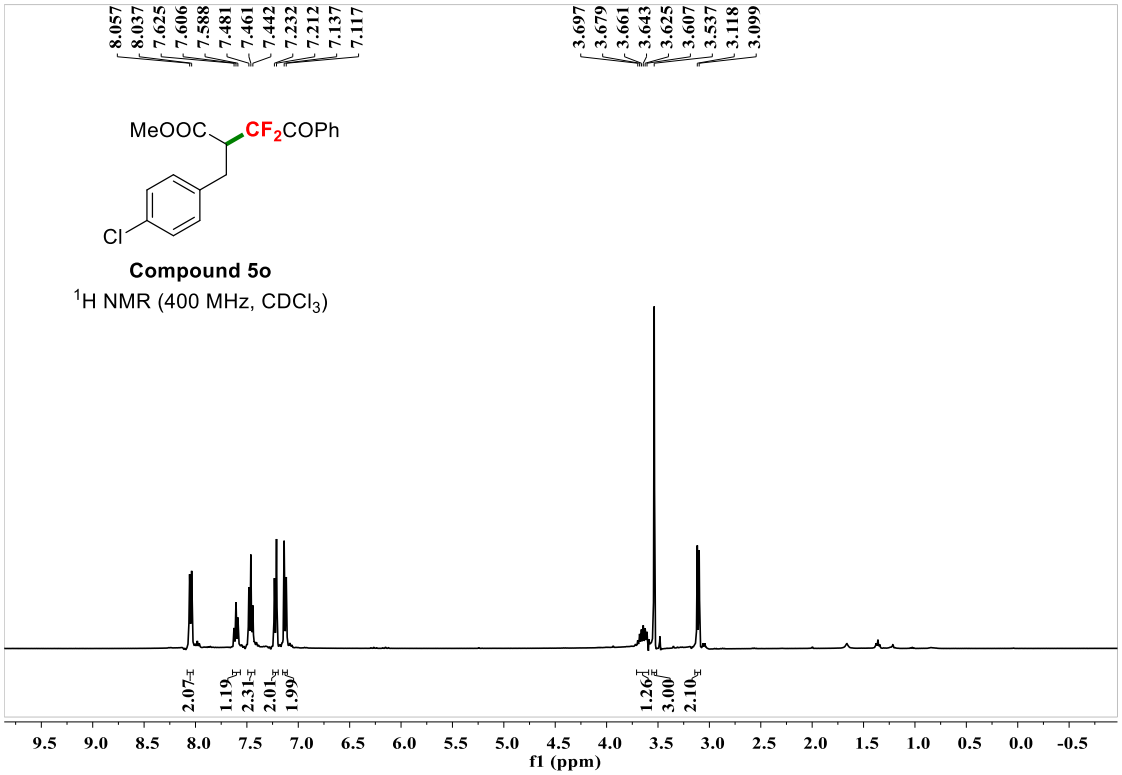
Methyl 2-benzyl-3,3-difluoro-4-oxo-4-phenylbutanoate (5n).

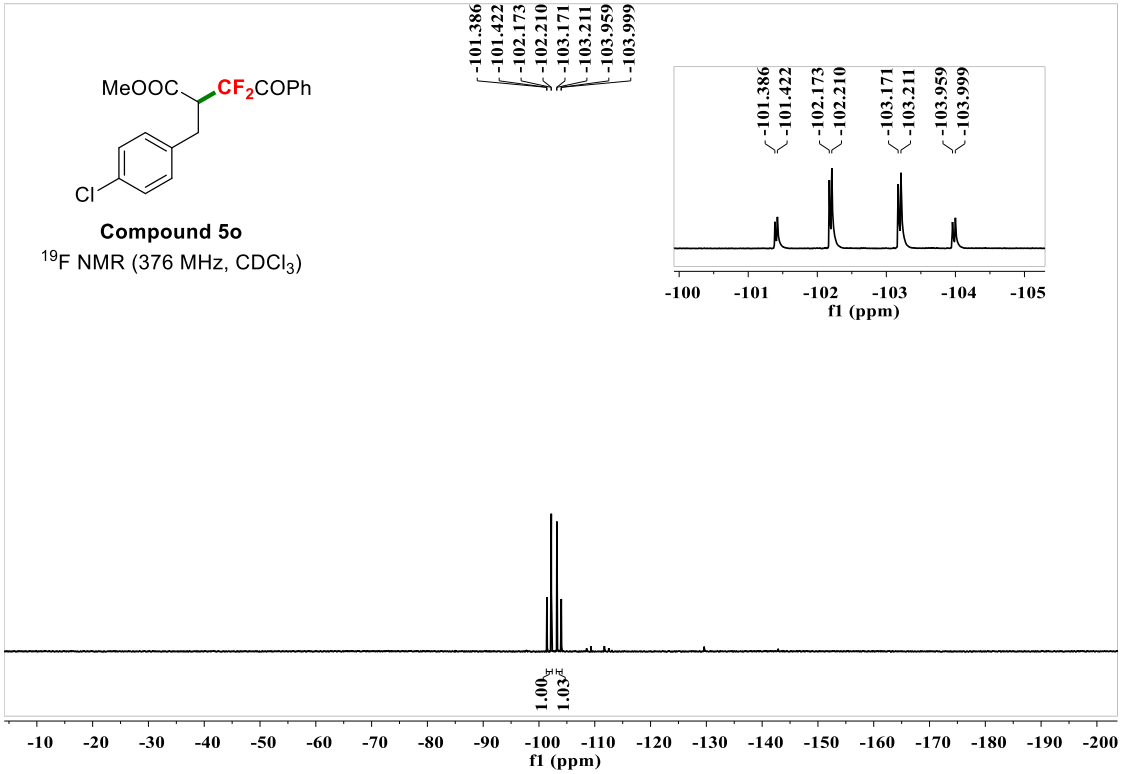


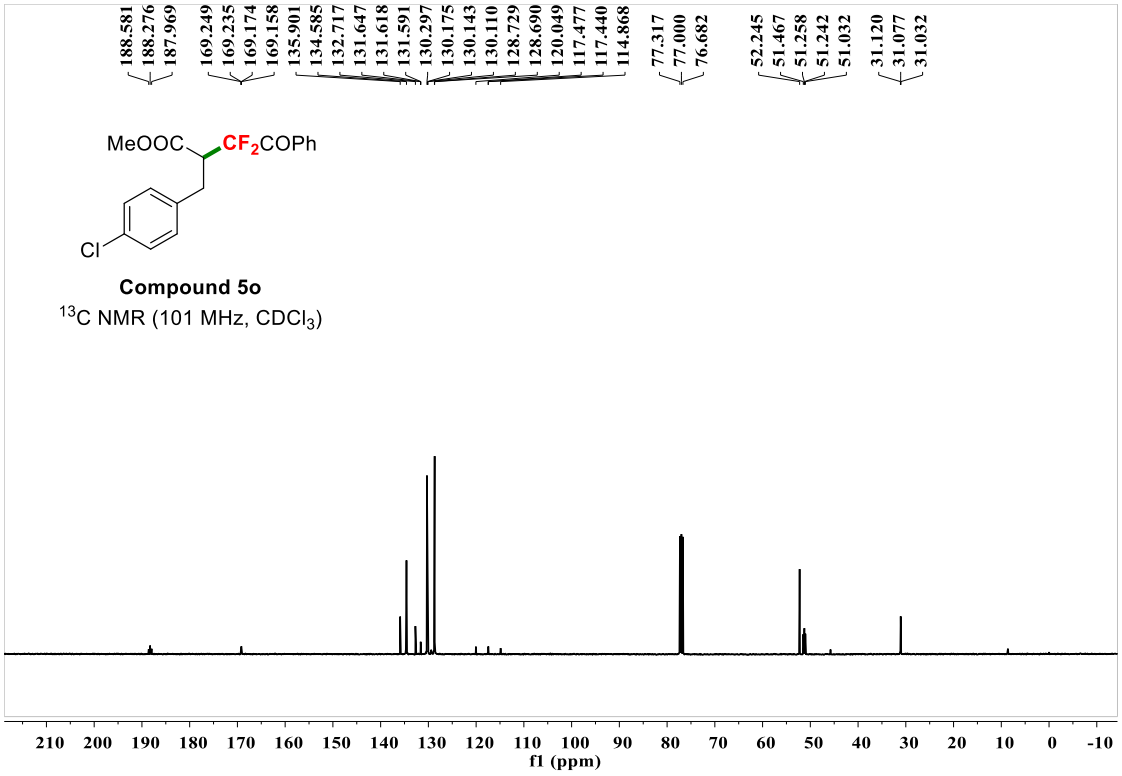

MeOOC
CF2COPh
Compound 5n
19F NMR (376 MHz, CDCl3)
-101.533
-101.568
-102.319
-102.354
-103.323
-103.363
-104.109
-104.149
1.00
1.00
f1 (ppm)


MeOOC
CF2COPh
Compound 5n
13C NMR (101 MHz, CDCl3)
f1 (ppm)

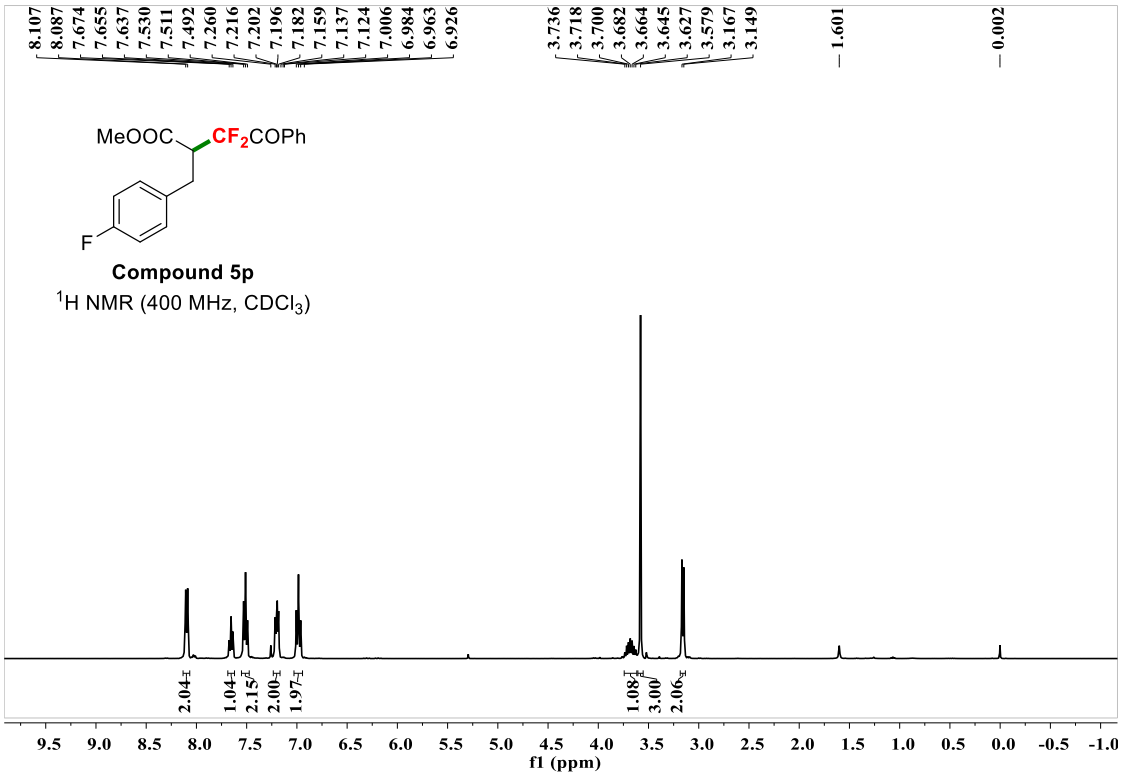
Methyl 2-(4-chlorobenzyl)-3,3-difluoro-4-oxo-4-phenylbutanoate (5o).

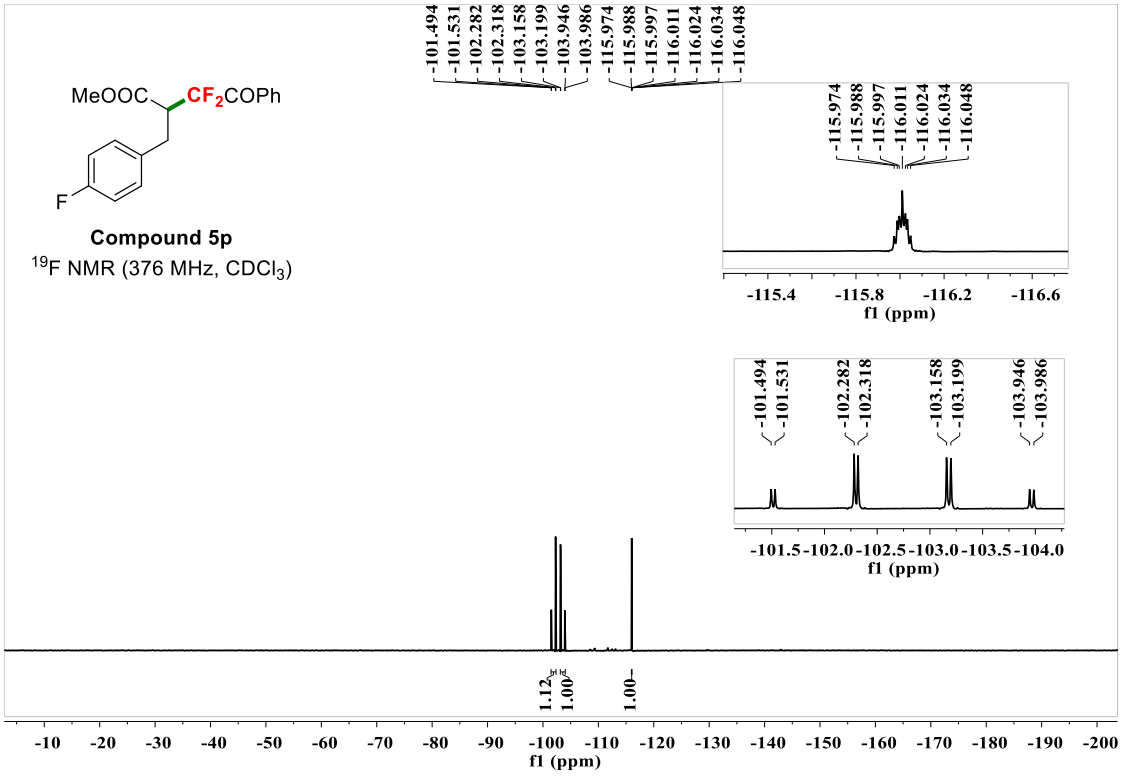


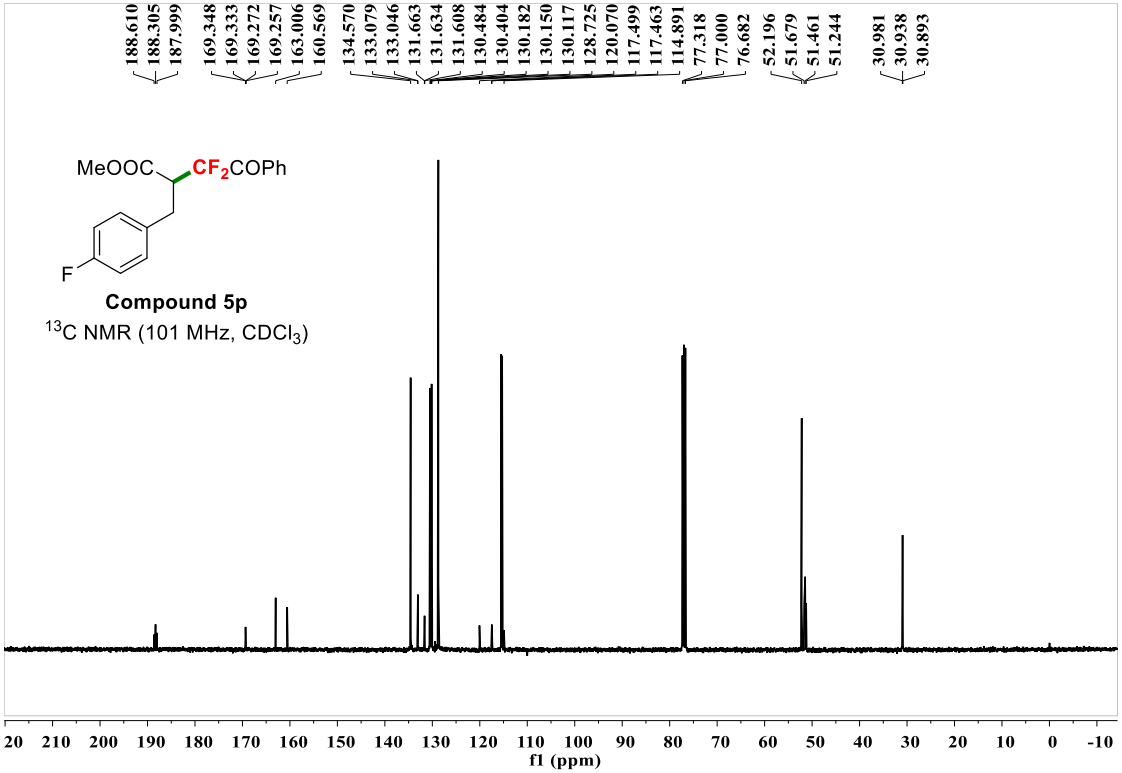




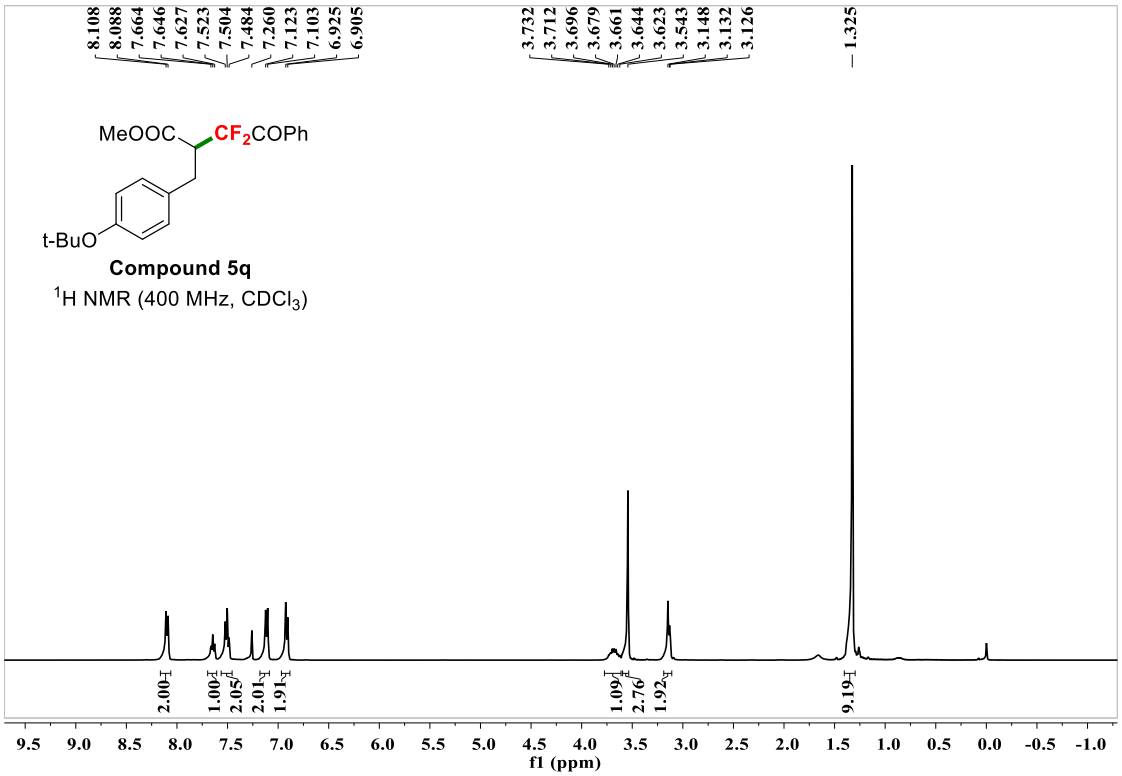
Methyl 3,3-difluoro-2-(4-fluorobenzyl)-4-oxo-4-phenylbutanoate (5p).

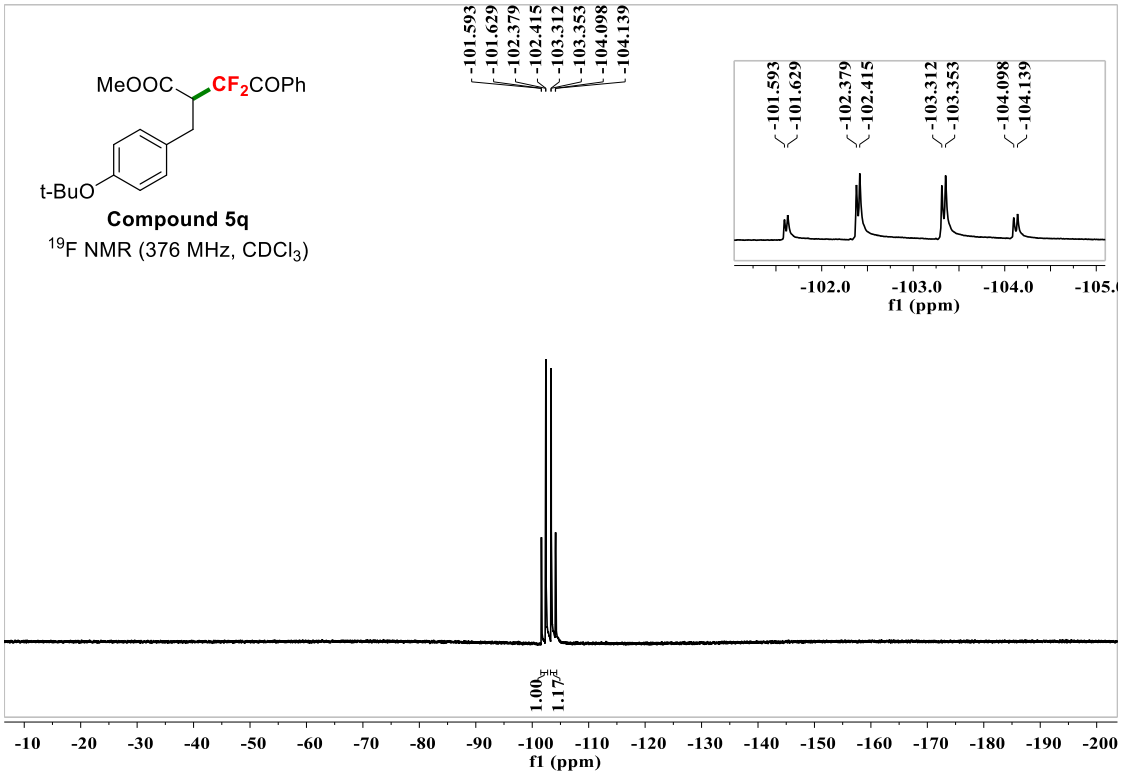


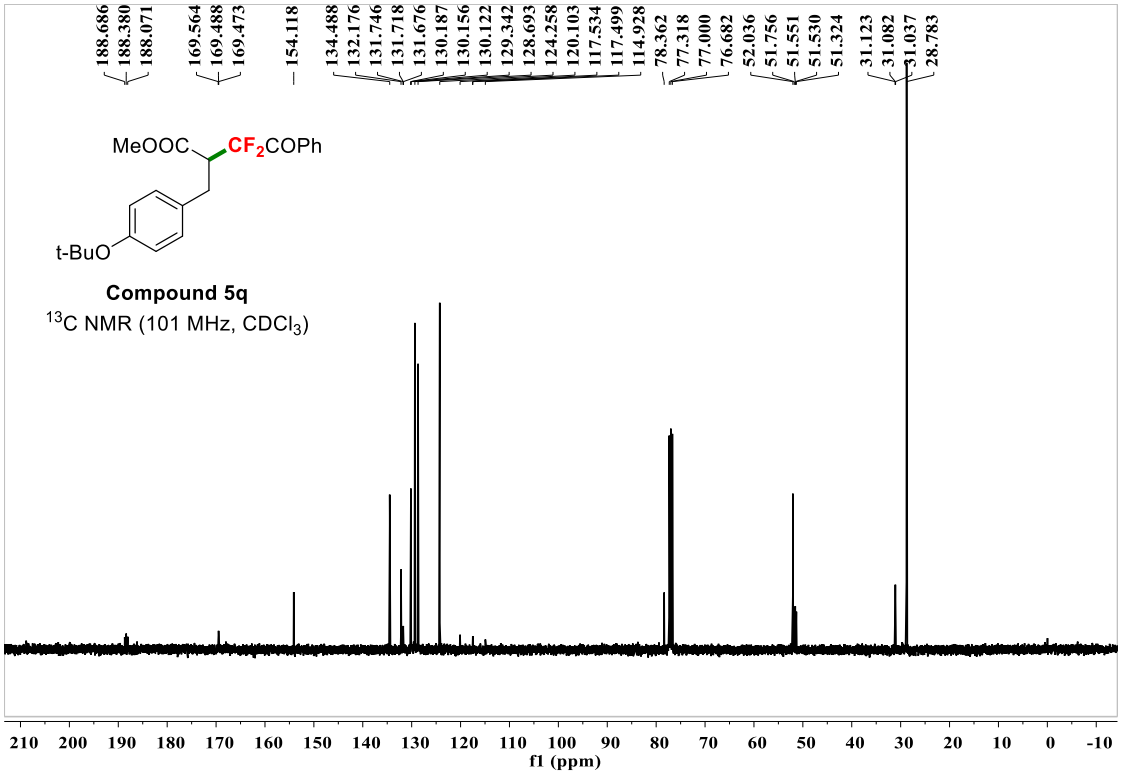

MeOOC
CF2COPh
F
Compound 5p
19F NMR (376 MHz, CDCl3)
-101.494
-101.531
-102.282
-102.318
-103.158
-103.199
-103.946
-103.986
-115.974
-115.988
-115.997
-116.011
-116.024
-116.034
-116.048
-115.4
-115.8
-116.2
-116.6
f1 (ppm)
-101.5
-102.0
-102.5
-103.0
-103.5
-104.0
1.12
1.00
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200


188.610
188.305
187.999
169.348
169.333
169.272
169.257
163.006
160.569
134.570
133.079
133.046
131.663
131.634
131.608
130.484
130.404
130.182
130.150
130.117
128.725
120.070
117.499
117.463
114.891
77.318
77.000
76.682
52.196
51.679
51.461
51.244
30.981
30.938
30.893
MeOOC
CF2COPh
F
Compound 5p
13C NMR (101 MHz, CDCl3)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

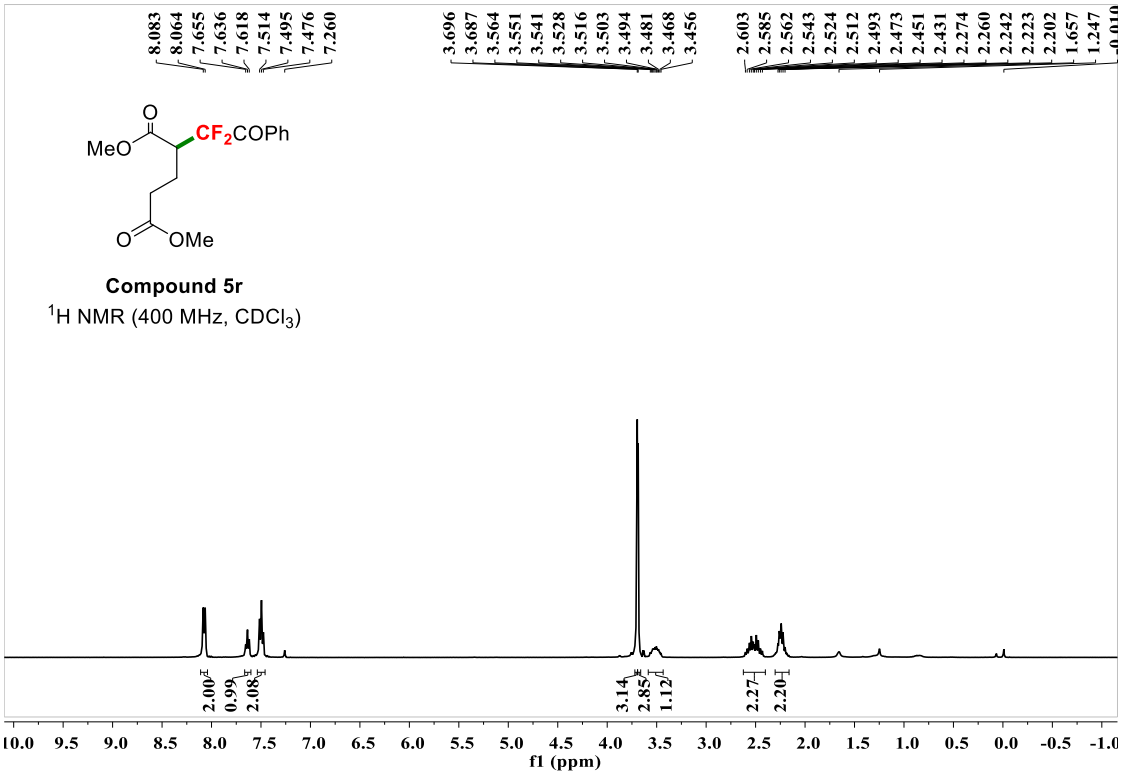
Methyl-2-(4-(tert-butoxy)benzyl)-3,3-difluoro-4-oxo-4-phenylbutanoate (5q).

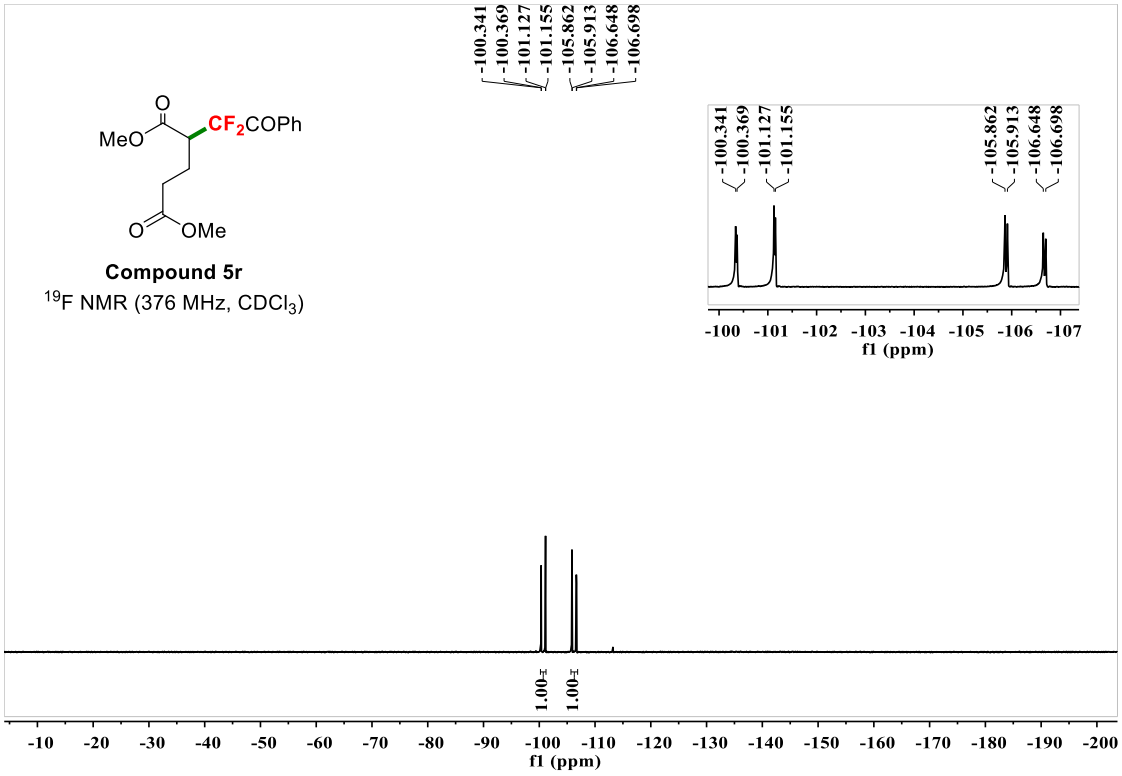


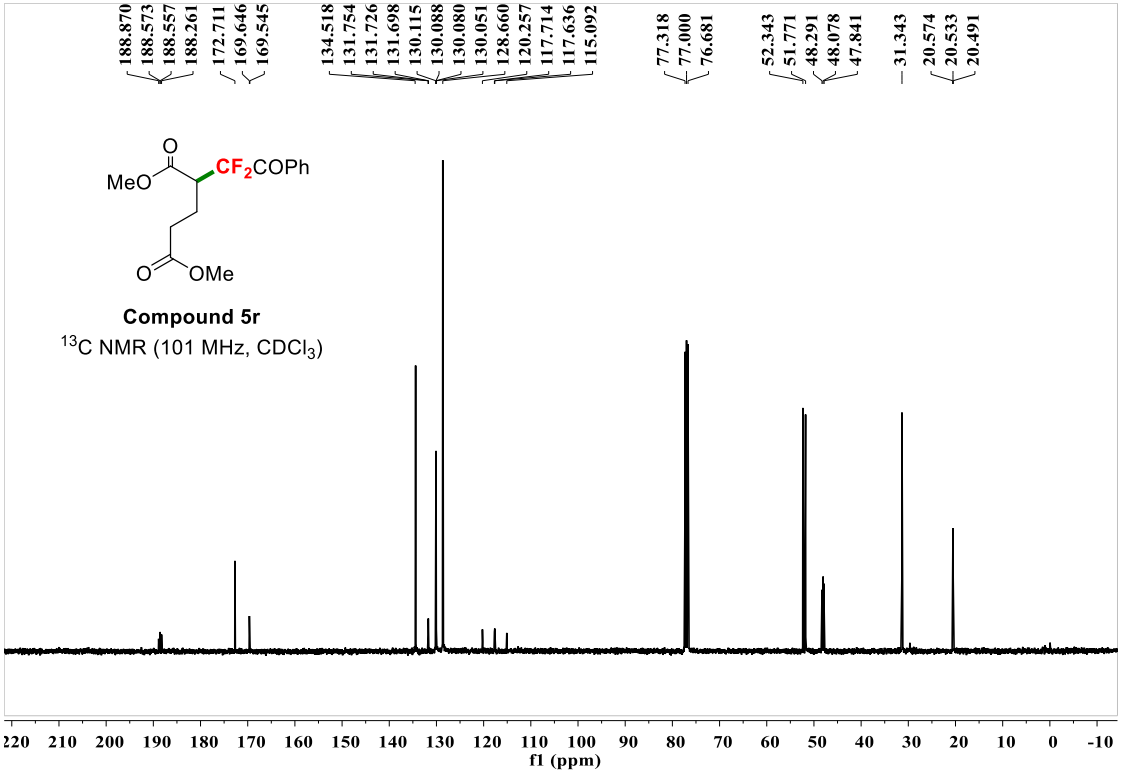




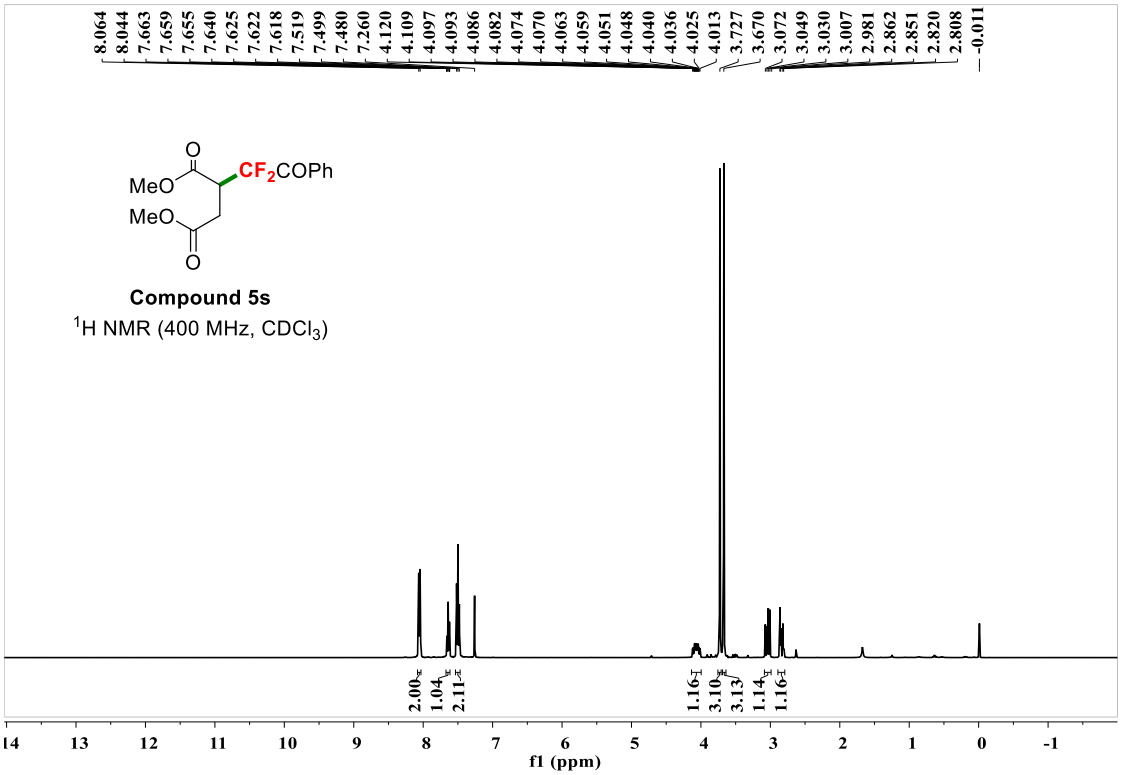
Dimethyl 2-(1,1-difluoro-2-oxo-2-phenylethyl)pentanedioate (5r).

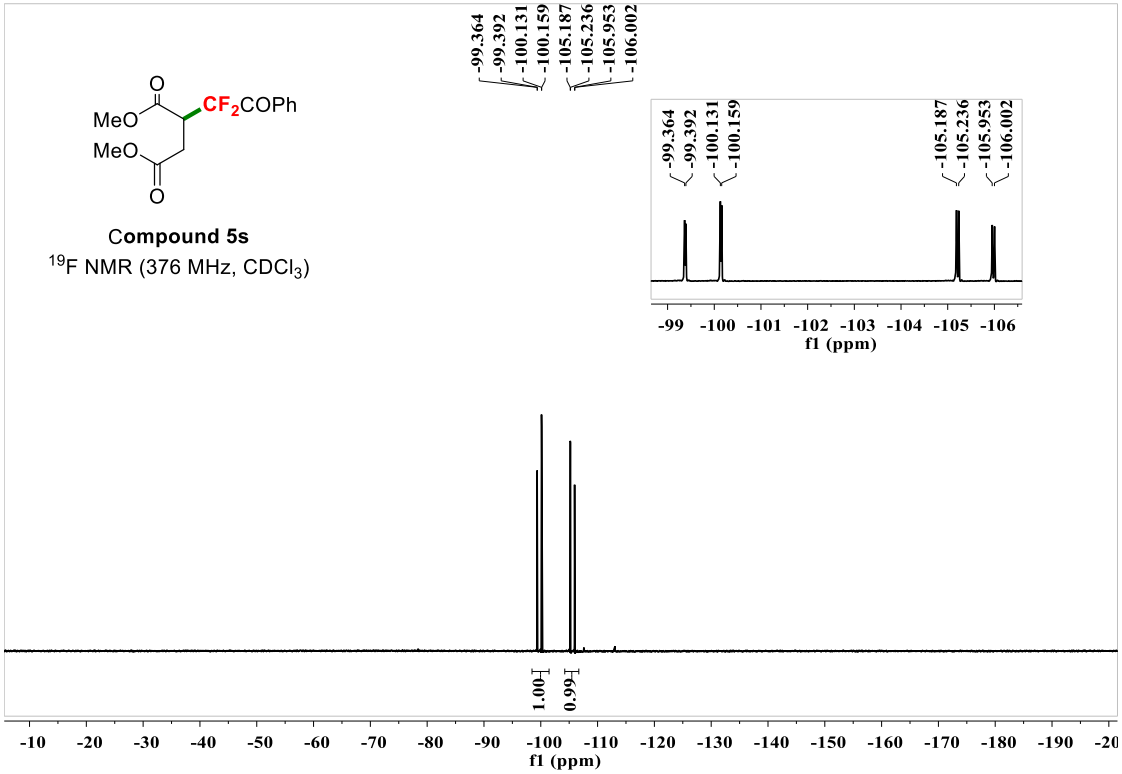


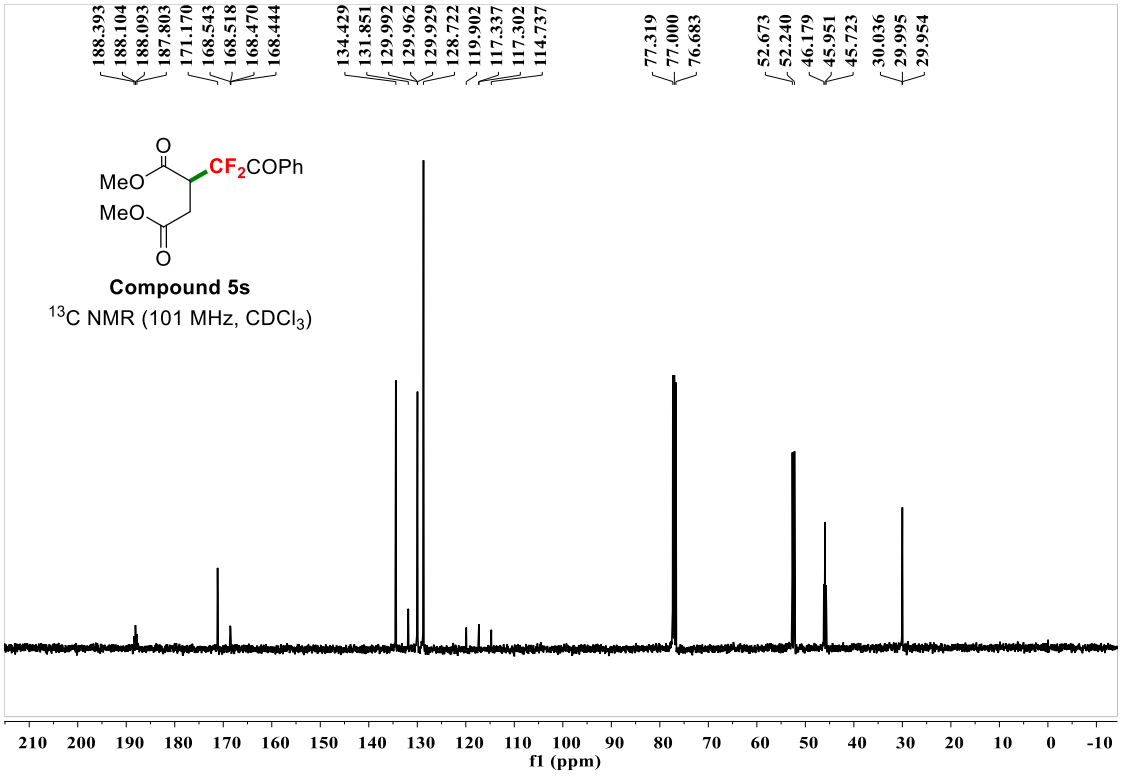

-100.341
-100.369
-101.127
-101.155
-105.862
-105.913
-106.648
-106.698
MeO
CF2COPh
O
OMe
Compound 5r
19F NMR (376 MHz, CDCl3)
1.00
1.00
f1 (ppm)


188.870
188.573
188.557
188.261
172.711
169.646
169.545
134.518
131.754
131.726
131.698
130.115
130.088
130.080
130.051
128.660
120.257
117.714
117.636
115.092
77.318
77.000
76.681
52.343
51.771
48.291
48.078
47.841
31.343
20.574
20.533
20.491
MeO
CF2COPh
O
OMe
Compound 5r
13C NMR (101 MHz, CDCl3)
f1 (ppm)

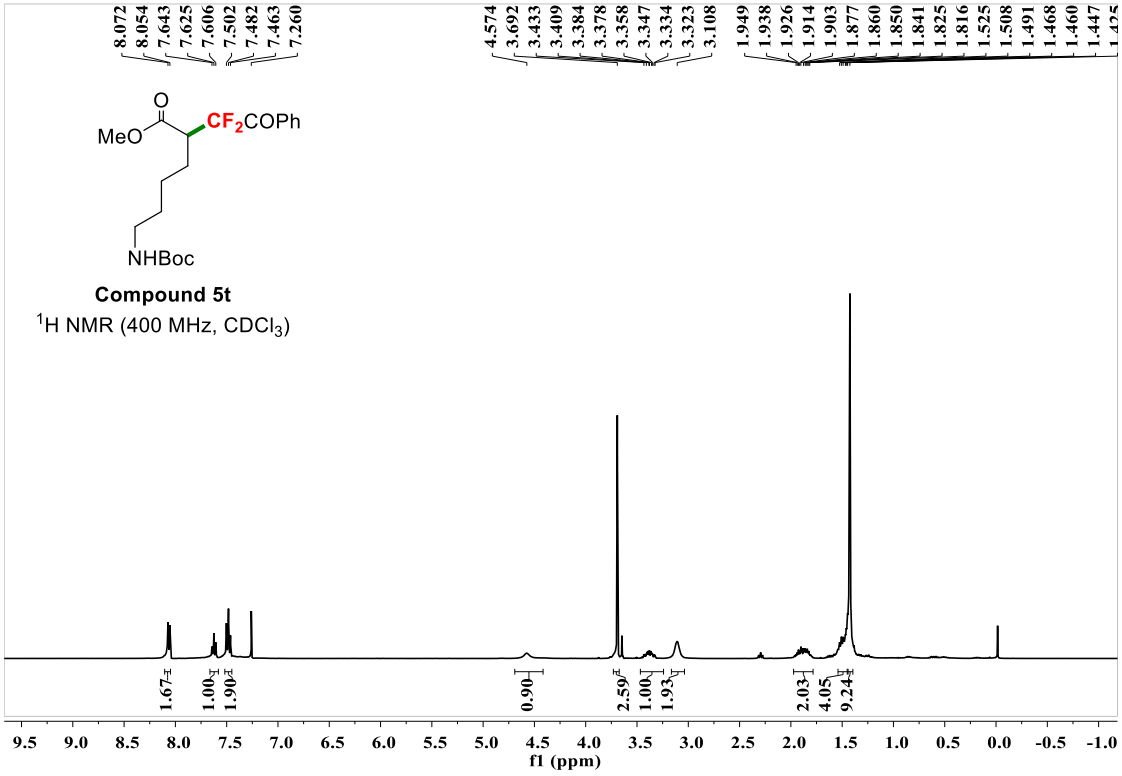
Dimethyl 2-(1,1-difluoro-2-oxo-2-phenylethyl)succinate (5s).

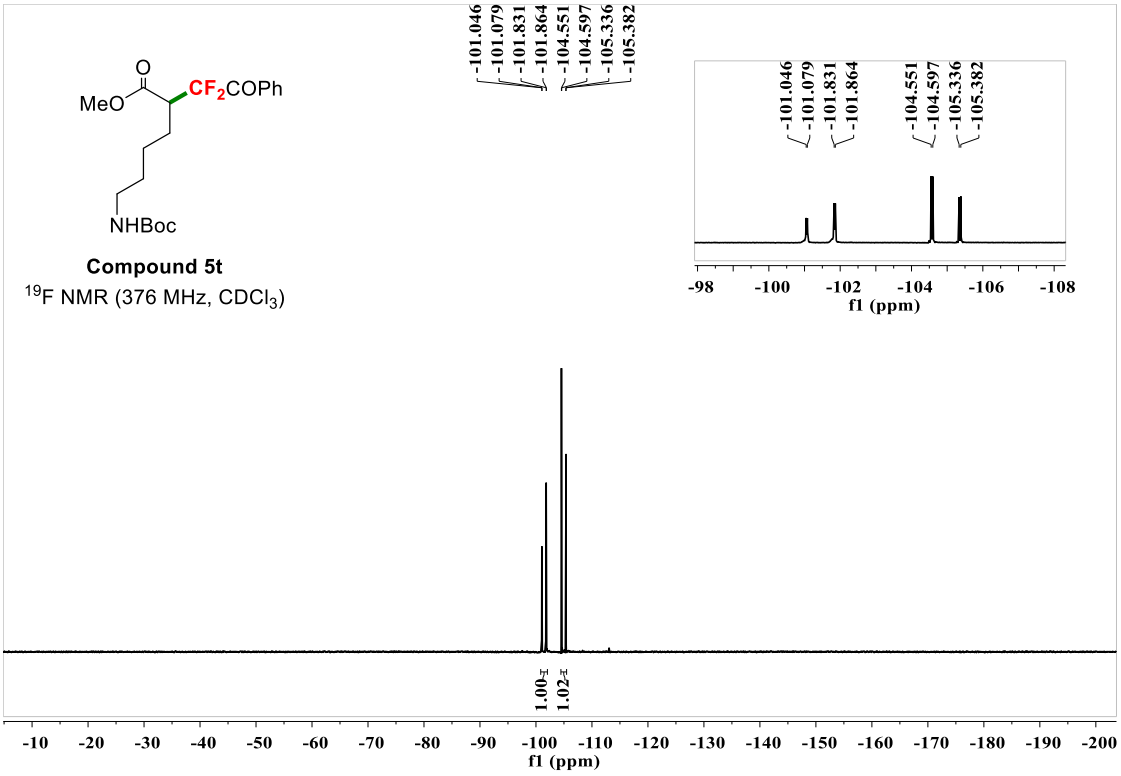






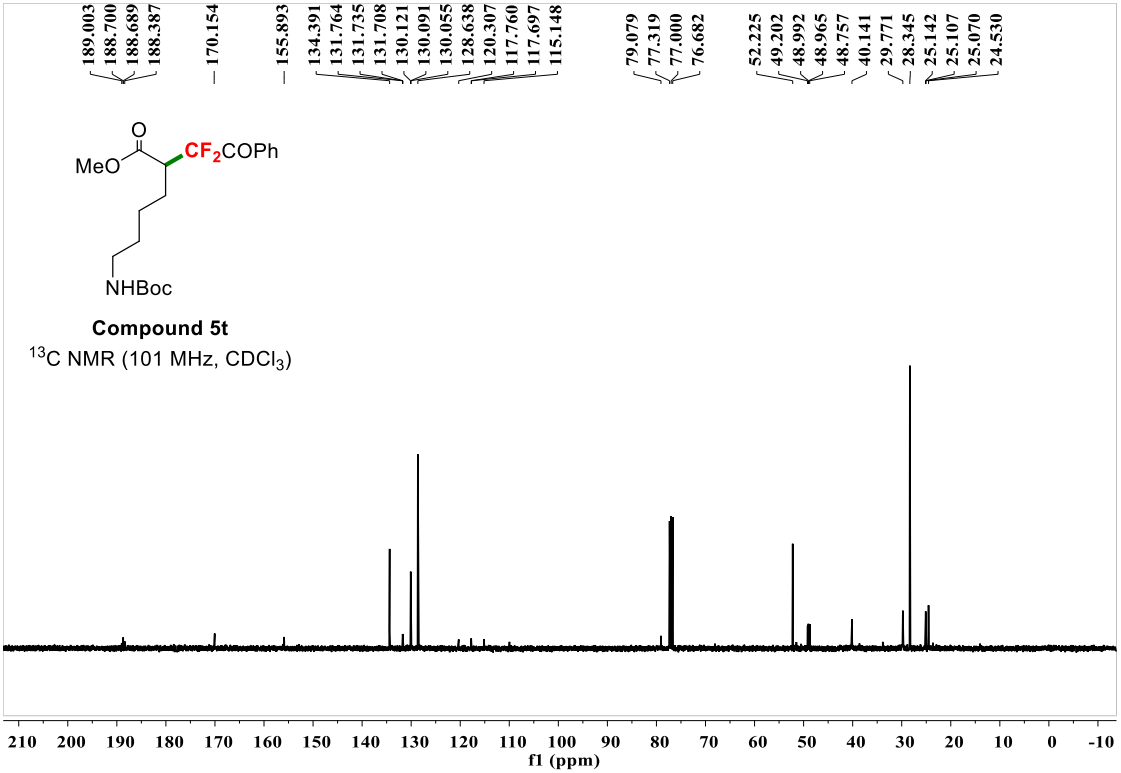
Methyl 6-((tert-butoxycarbonyl)amino)-2-(1,1-difluoro-2-oxo-2-phenylethyl)hexanoate (5t).





Compound 5t

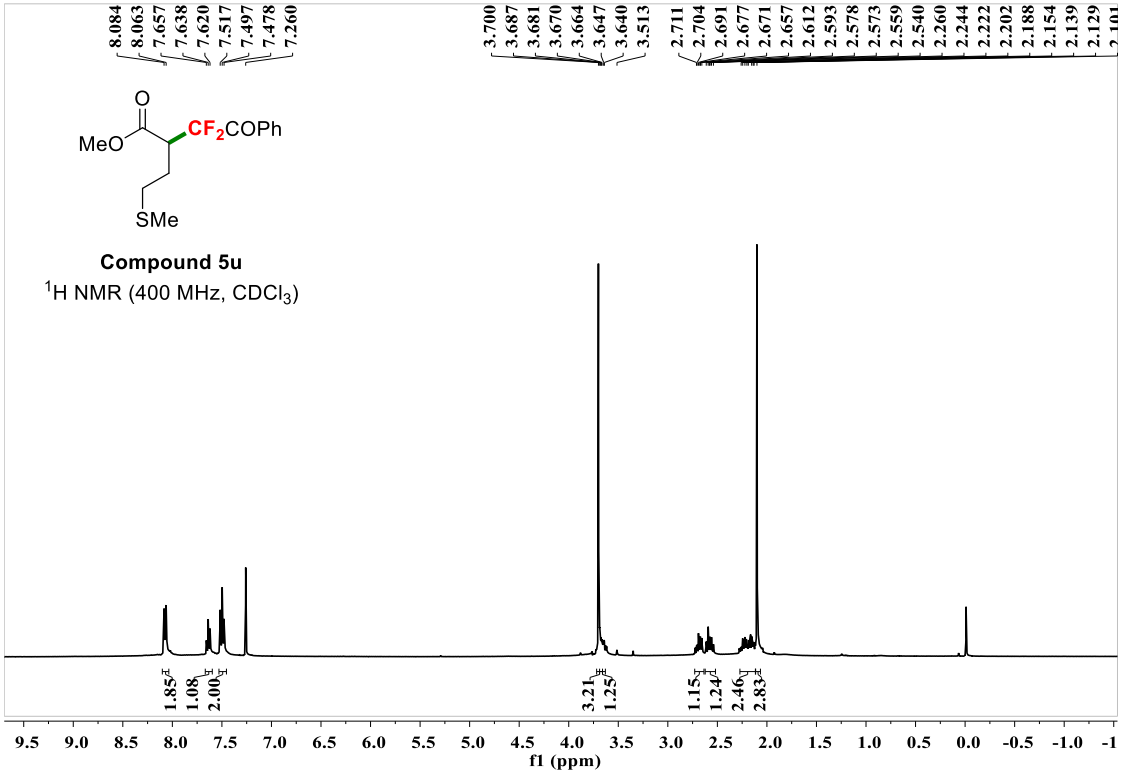
^{19}F NMR (376 MHz, $CDCl_3$)

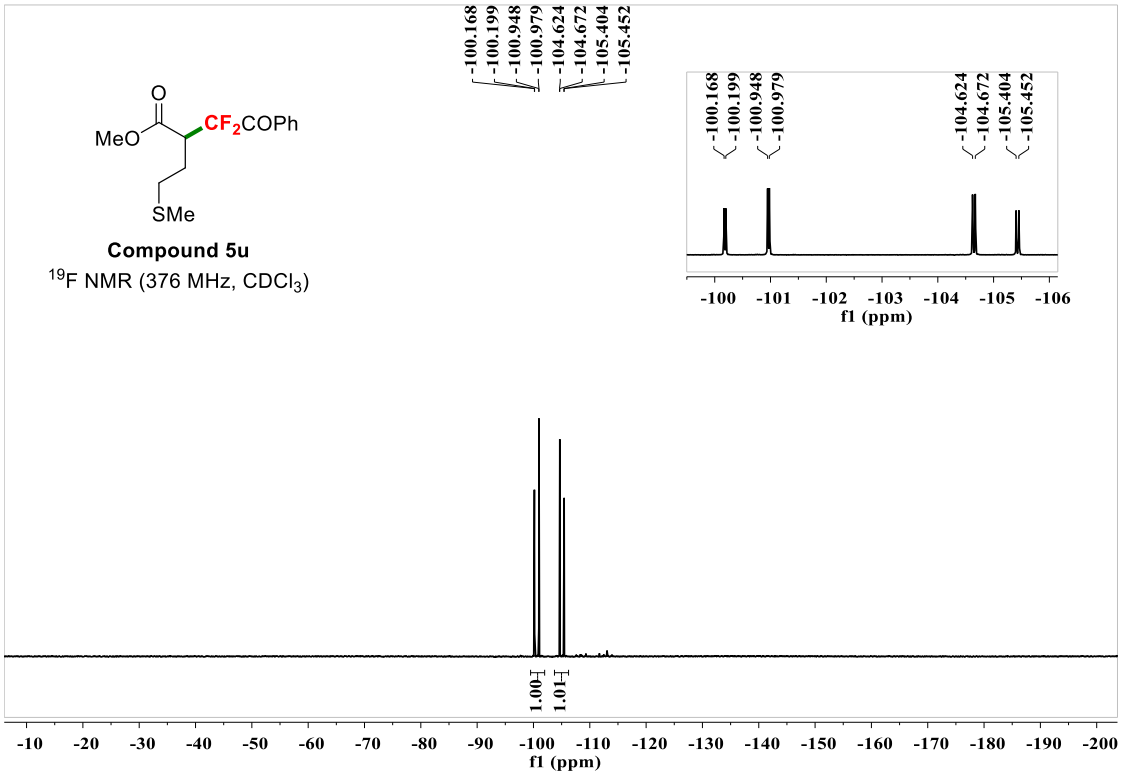


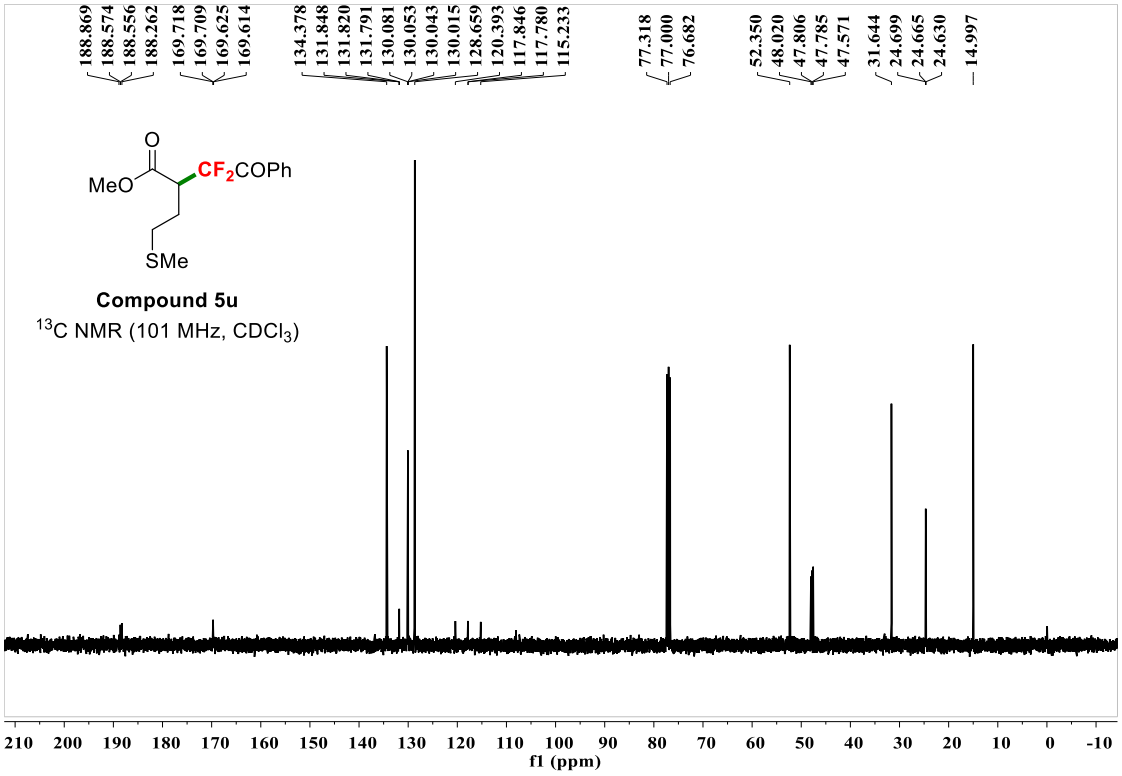
Compound 5t

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

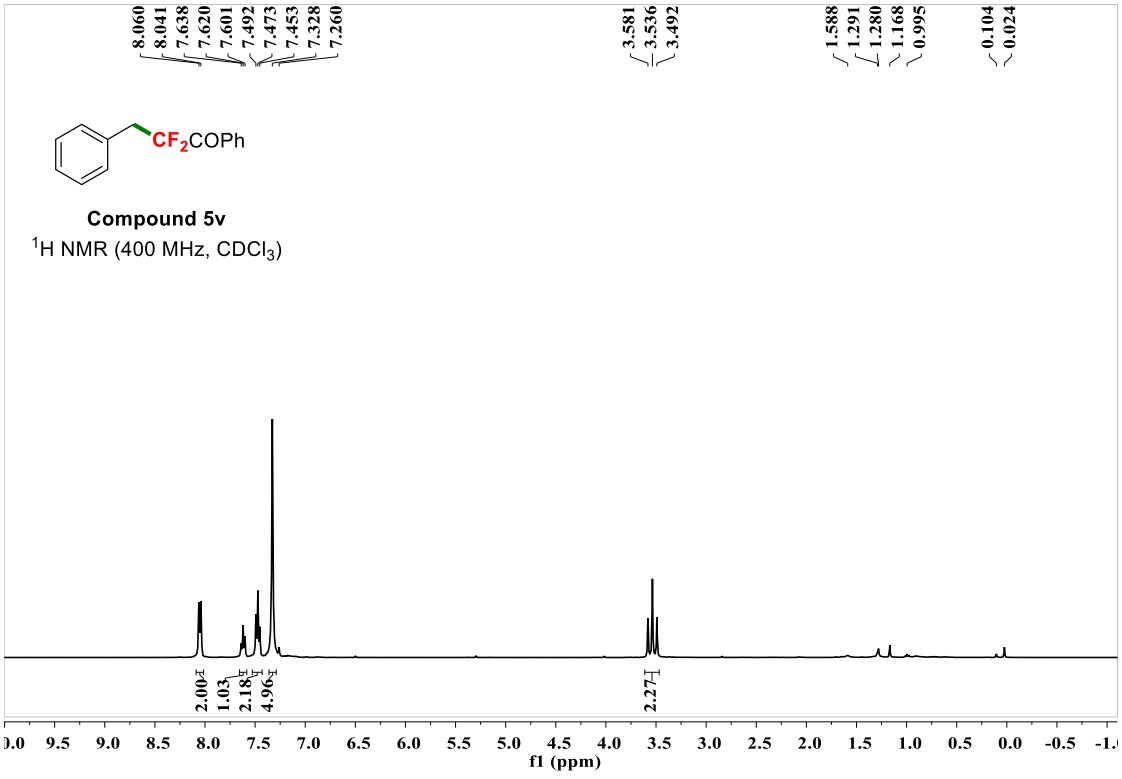
Methyl 3,3-difluoro-2-(2-(methylthio)ethyl)-4-oxo-4-phenylbutanoate (5u).

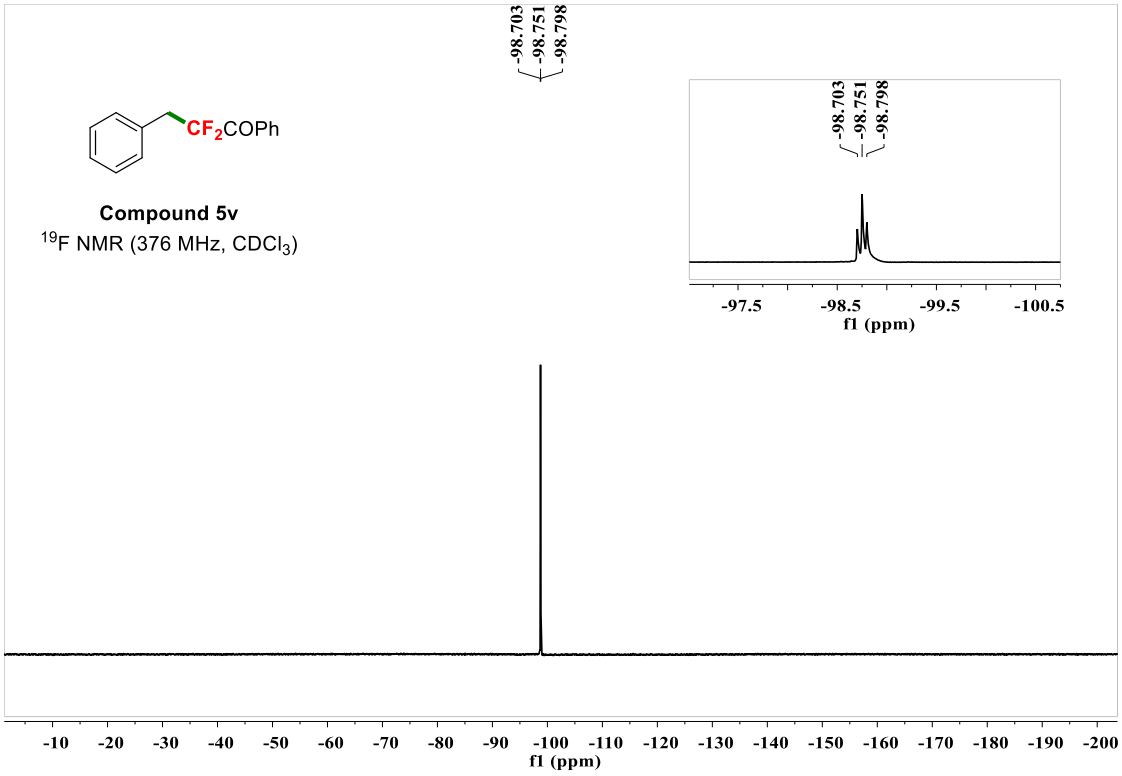


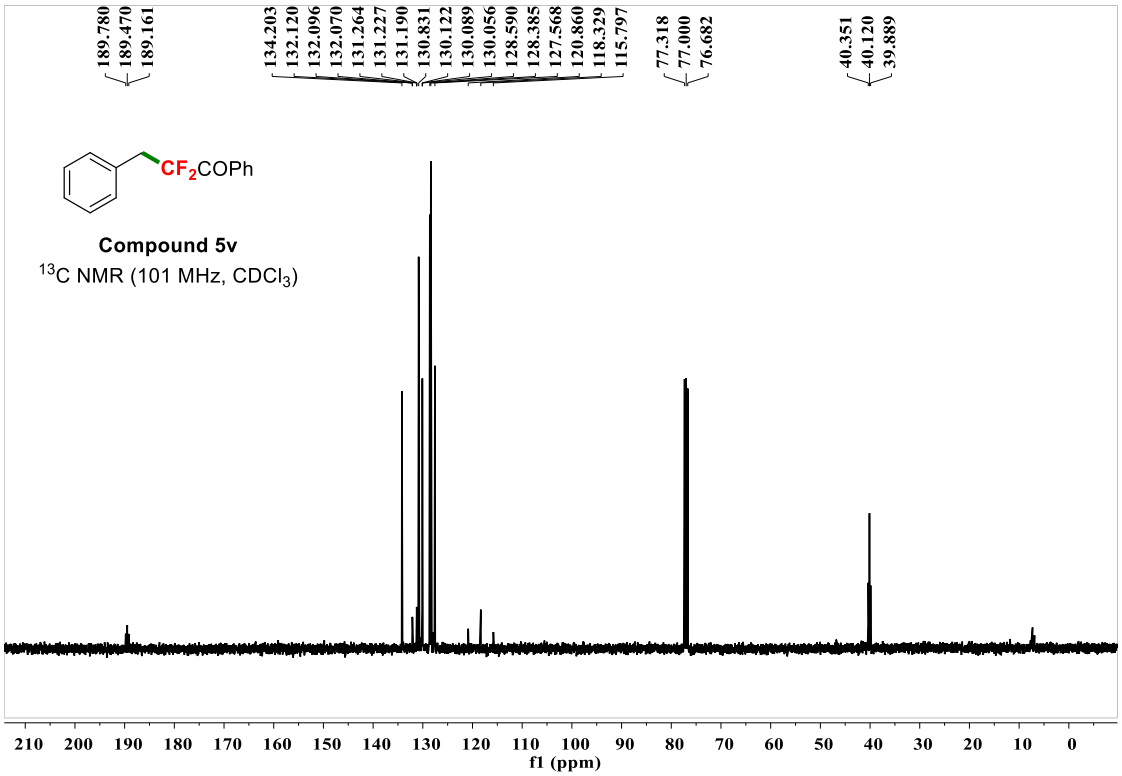




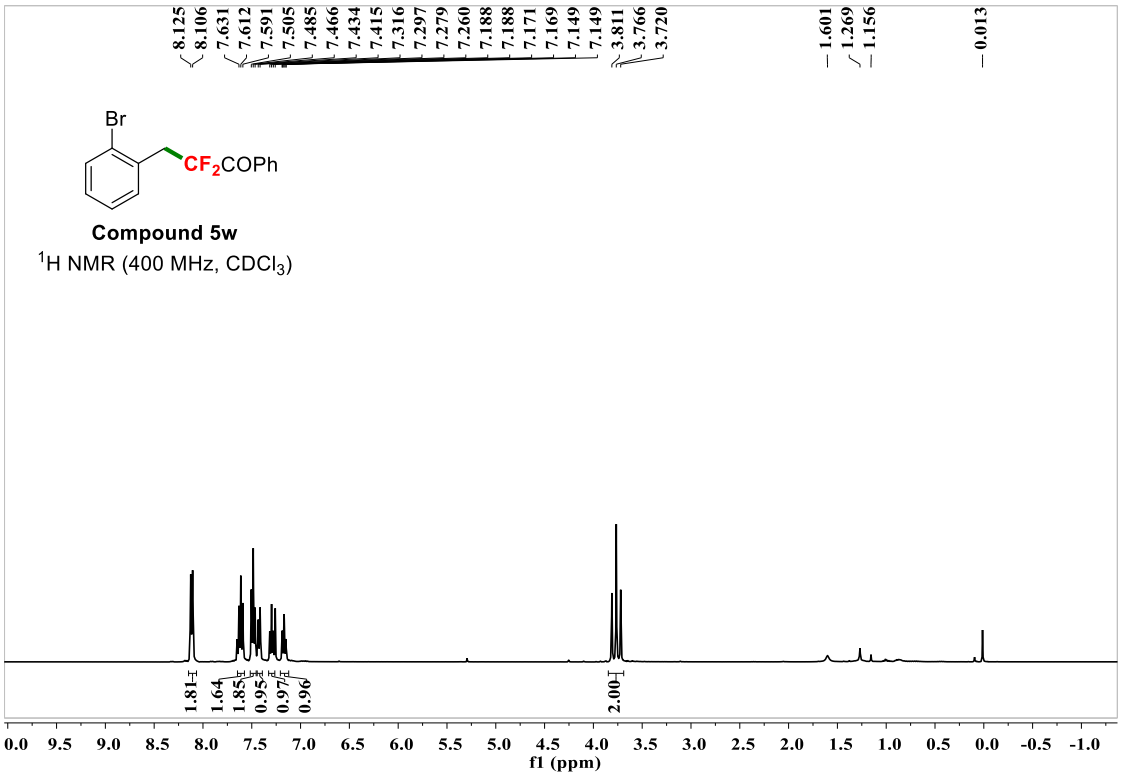
2,2-Difluoro-1,3-diphenylpropan-1-one (5v).

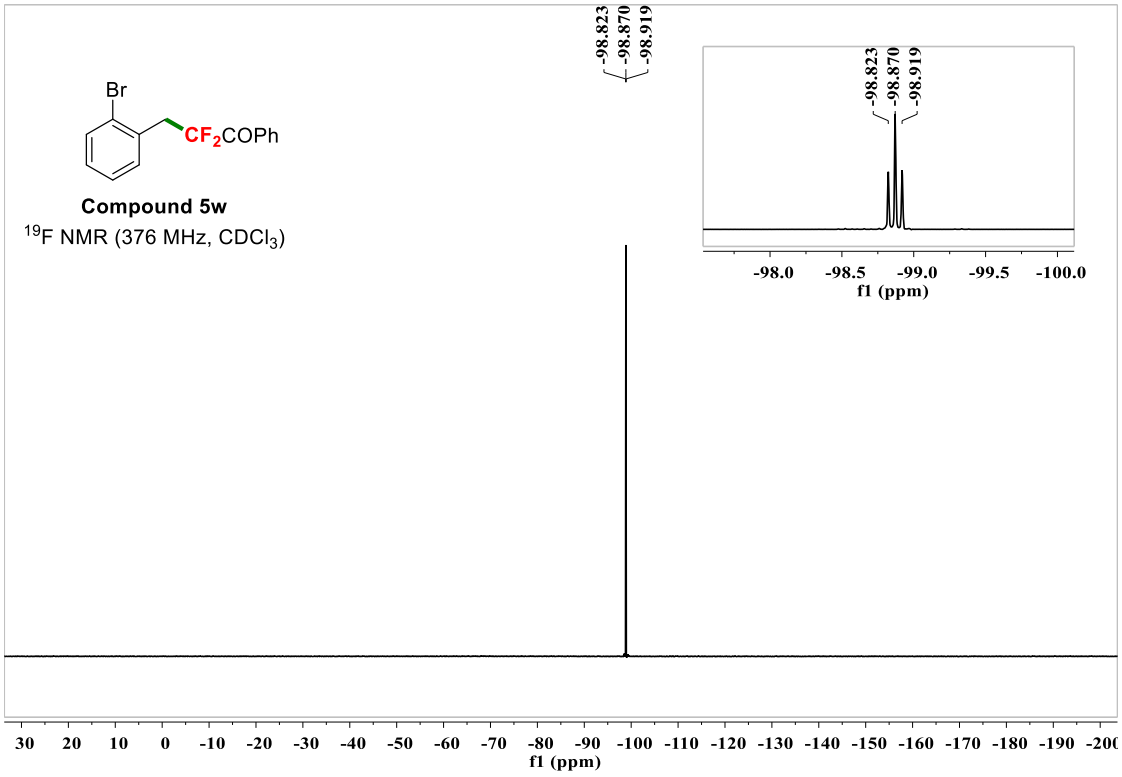


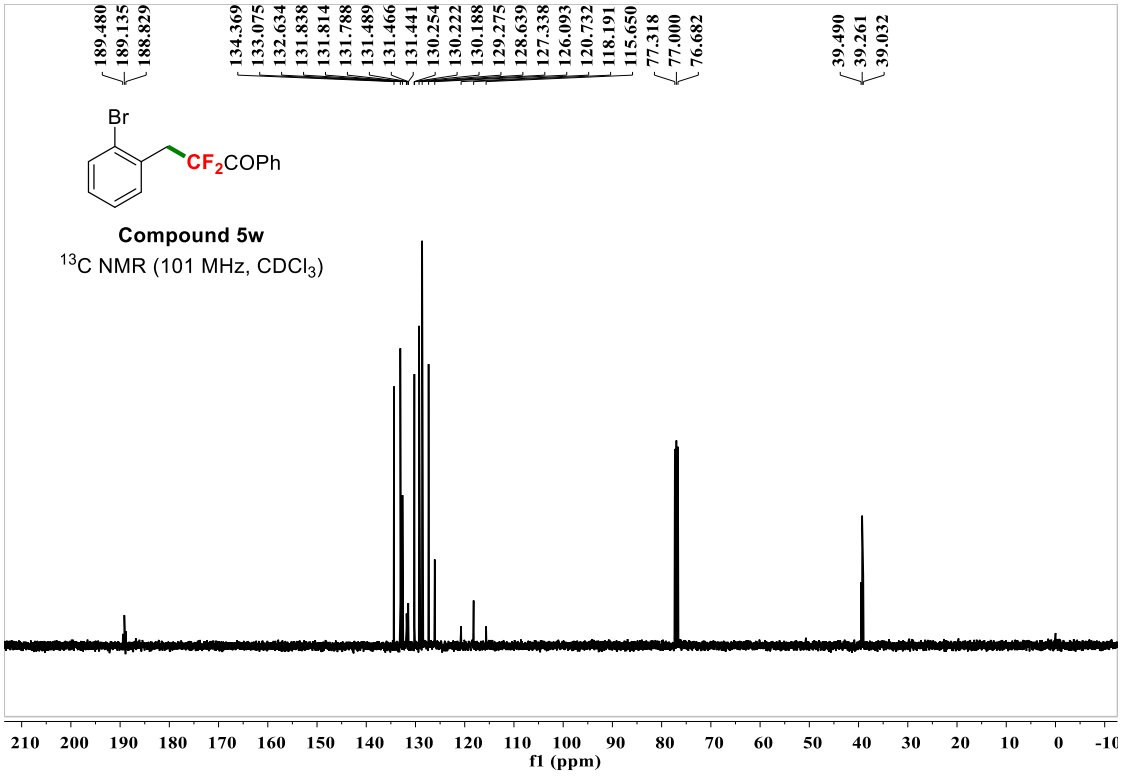

-98.703
-98.751
-98.798
CF2COPh
Compound 5v
19F NMR (376 MHz, CDCl3)
-98.703
-98.751
-98.798
-97.5
-98.5
-99.5
-100.5
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


189.780
189.470
189.161
134.203
132.120
132.096
132.070
131.264
131.227
131.190
130.831
130.122
130.089
130.056
128.590
128.385
127.568
120.860
118.329
115.797
77.318
77.000
76.682
40.351
40.120
39.889
CF2COPh
Compound 5v
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

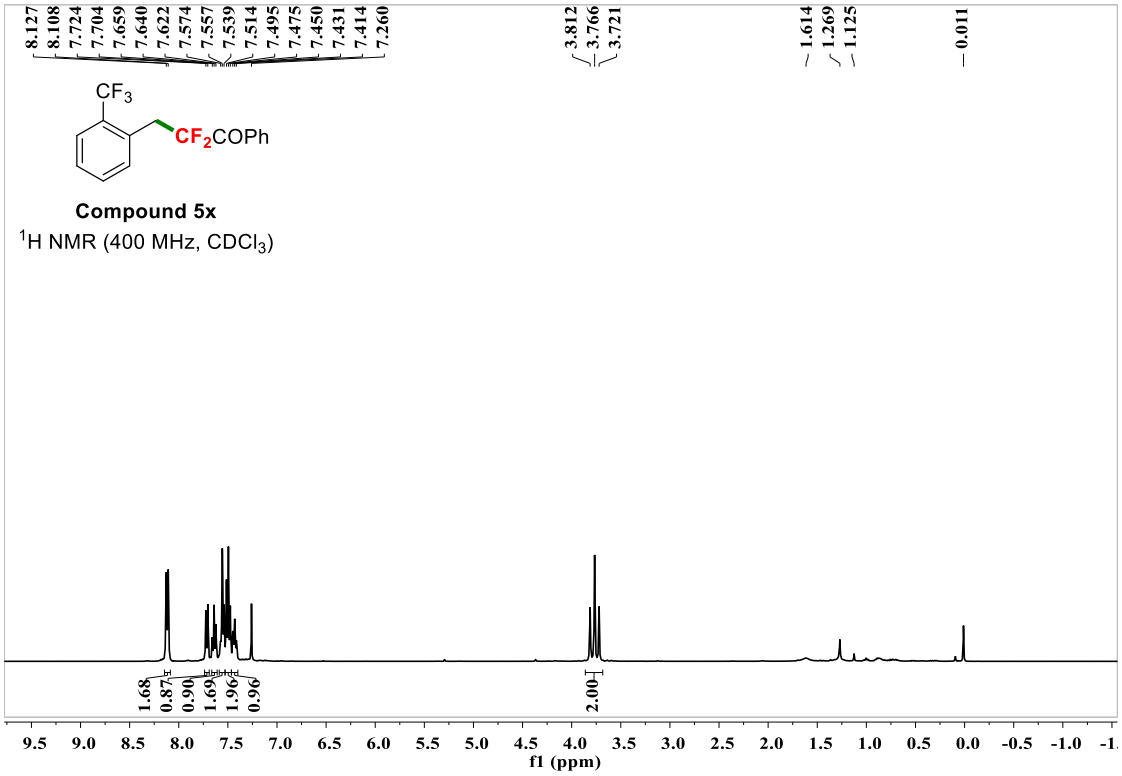
3-(2-Bromophenyl)-2,2-difluoro-1-phenylpropan-1-one (5w).

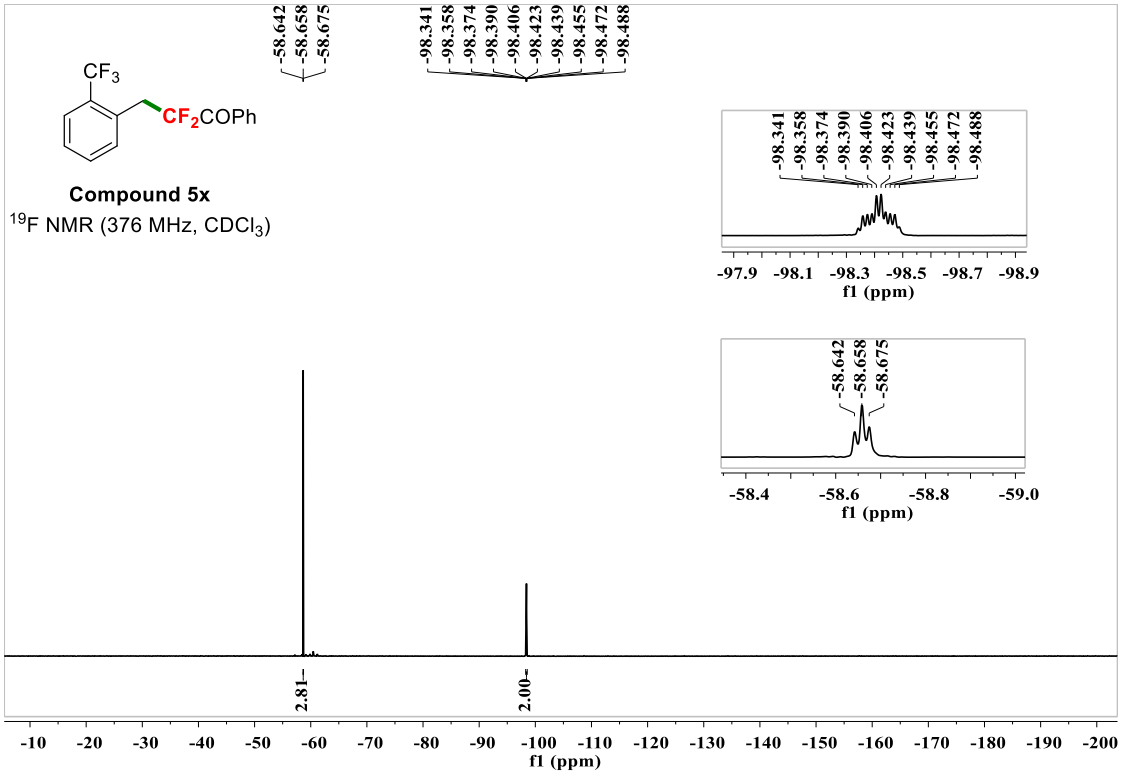


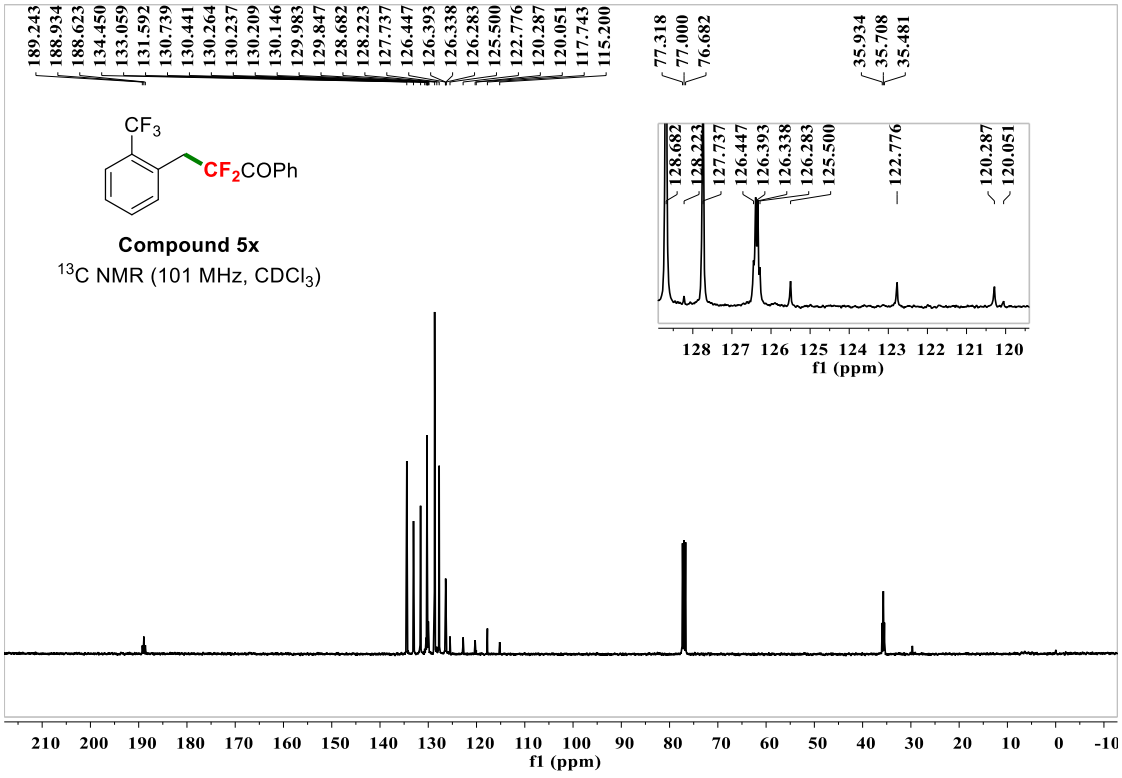




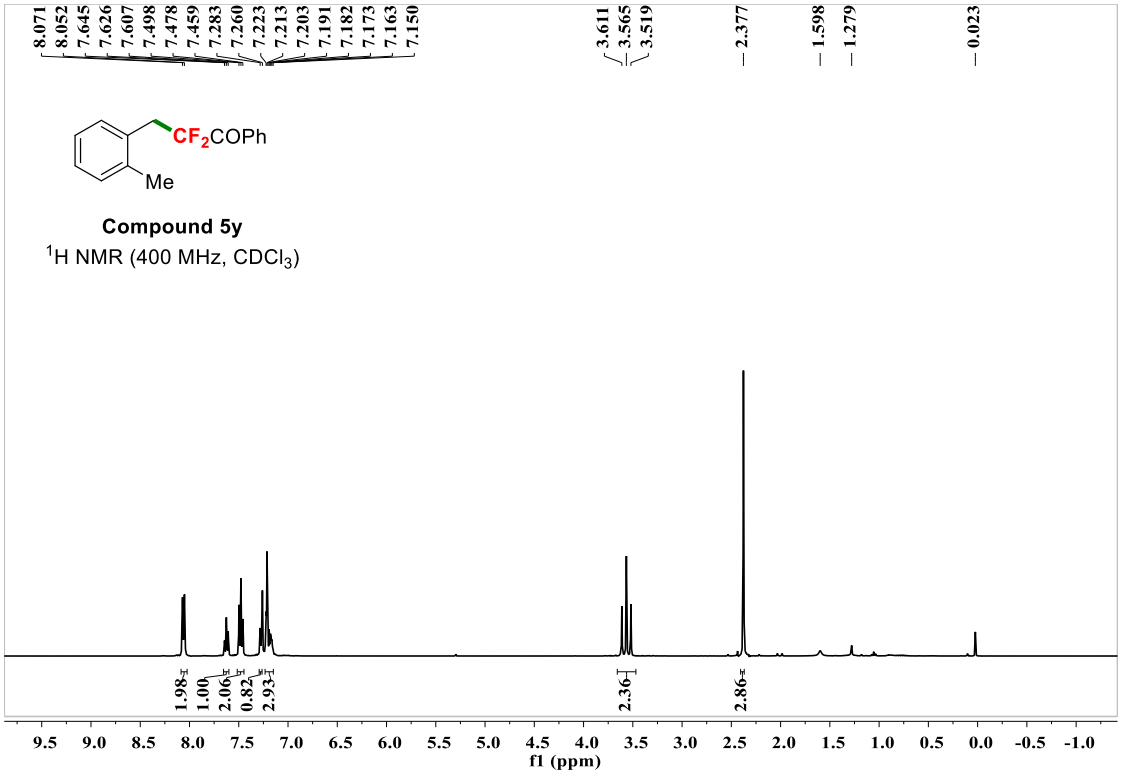
2,2-Difluoro-1-phenyl-3-(2-(trifluoromethyl)phenyl)propan-1-one (5x).

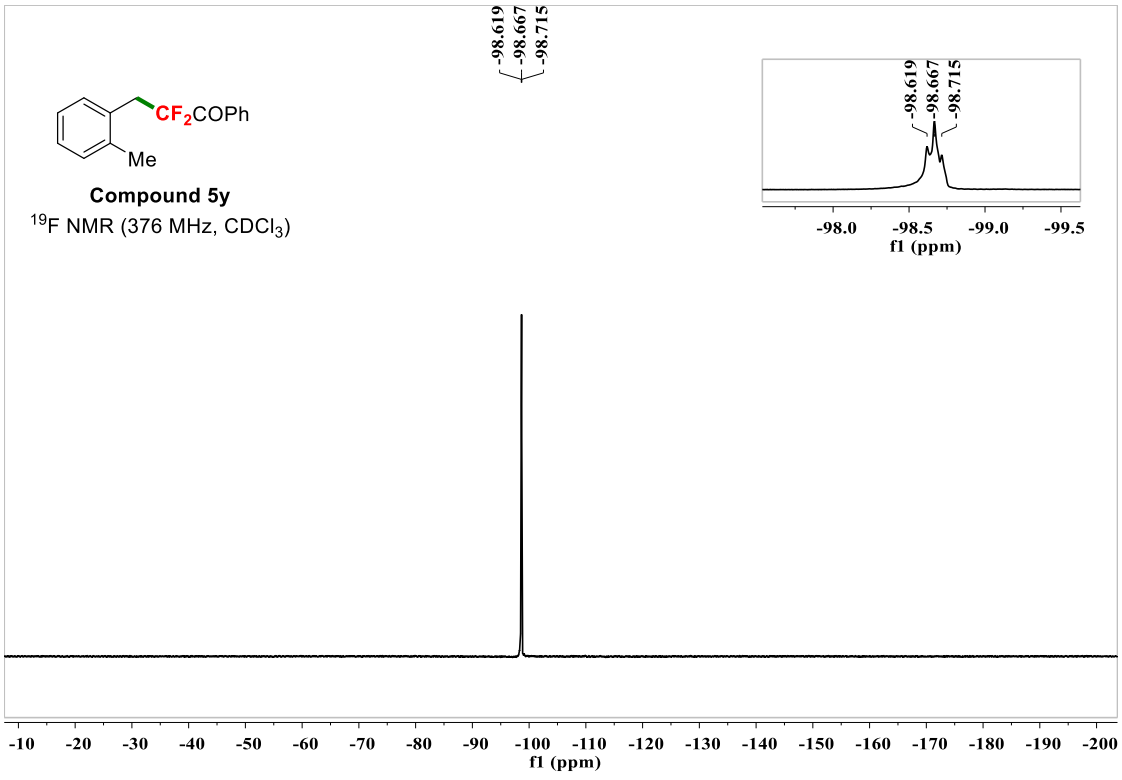


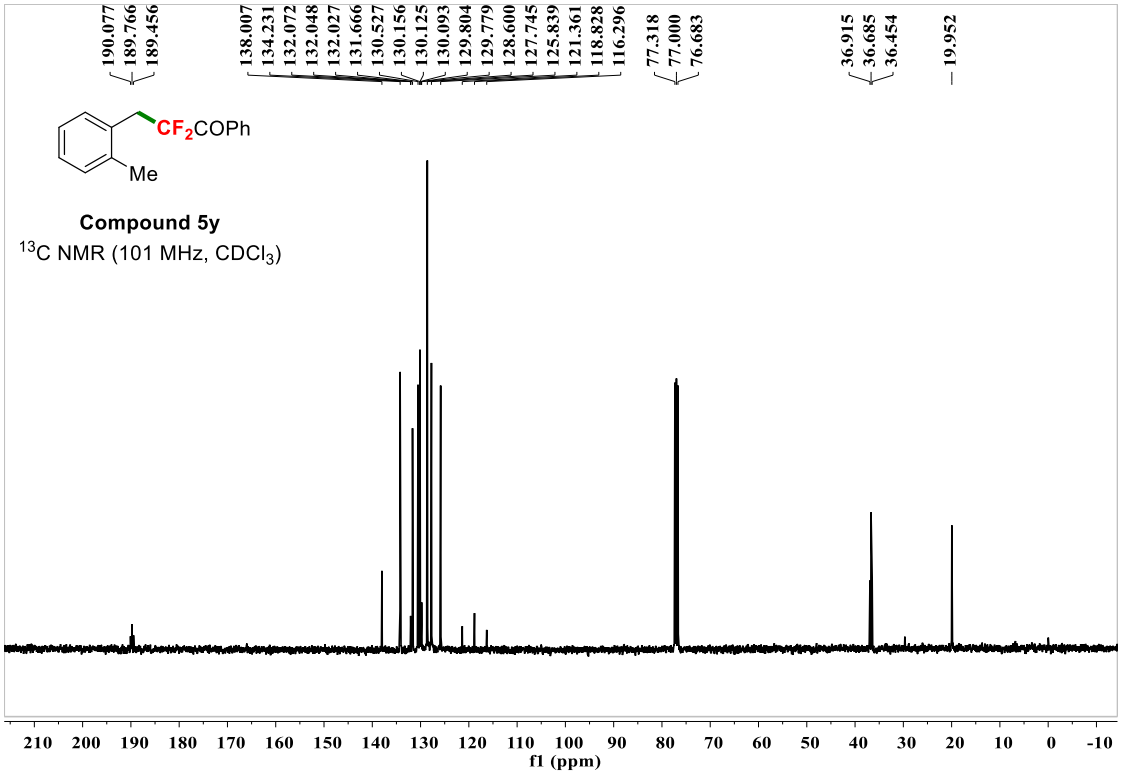

-58.642
-58.658
-58.675
-98.341
-98.358
-98.374
-98.390
-98.406
-98.423
-98.439
-98.455
-98.472
-98.488
CF3
CF2COPh
Compound 5x
19F NMR (376 MHz, CDCl3)
-97.9 -98.1 -98.3 -98.5 -98.7 -98.9
f1 (ppm)
-58.4 -58.6 -58.8 -59.0
f1 (ppm)
2.81
2.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


189.243
188.934
188.623
134.450
133.059
131.592
130.739
130.441
130.264
130.237
130.209
130.146
129.983
129.847
128.682
128.223
127.737
126.447
126.393
126.338
126.283
125.500
122.776
120.287
120.051
117.743
115.200
77.318
77.000
76.682
35.934
35.708
35.481
CF3
CF2COPh
Compound 5x
13C NMR (101 MHz, CDCl3)
128 127 126 125 124 123 122 121 120
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

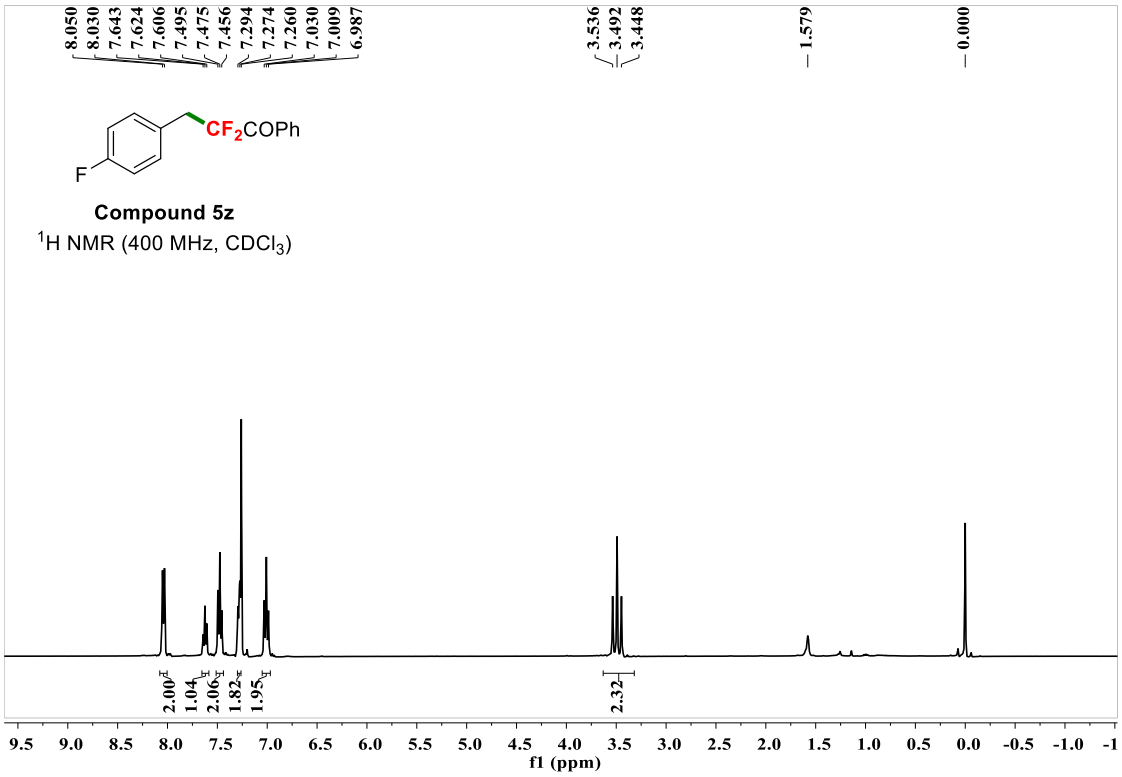
2,2-Difluoro-1-phenyl-3-(o-tolyl)propan-1-one (5y).

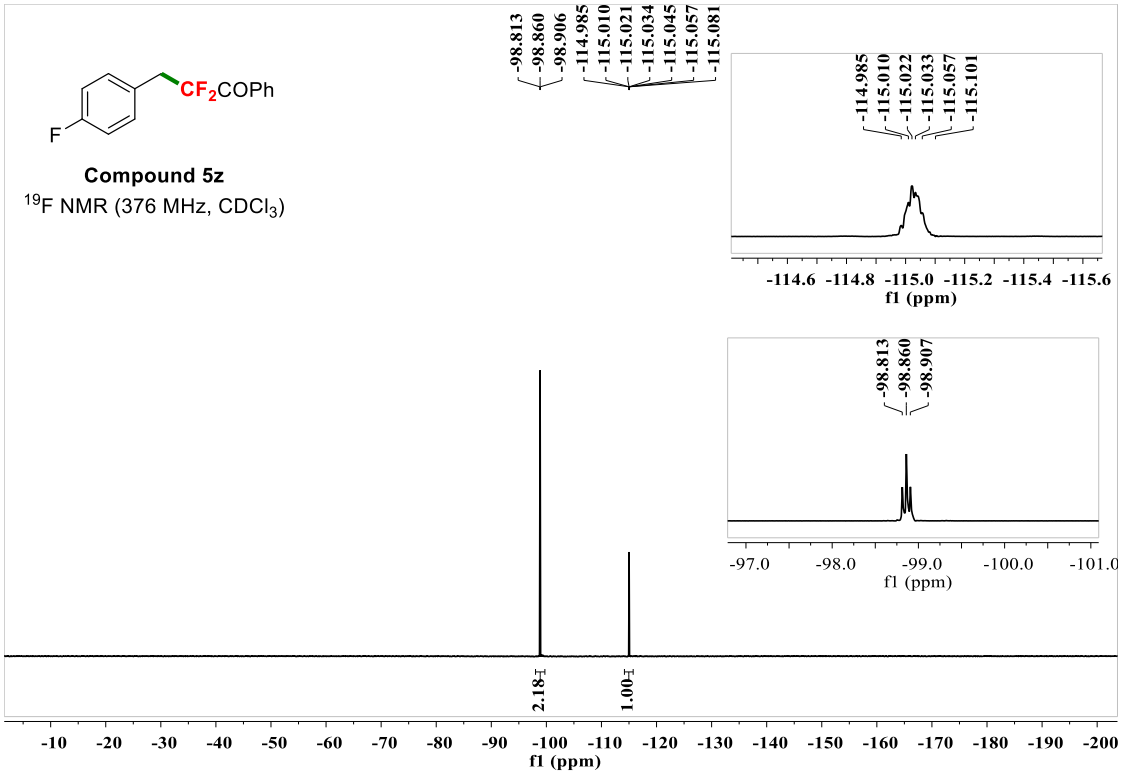


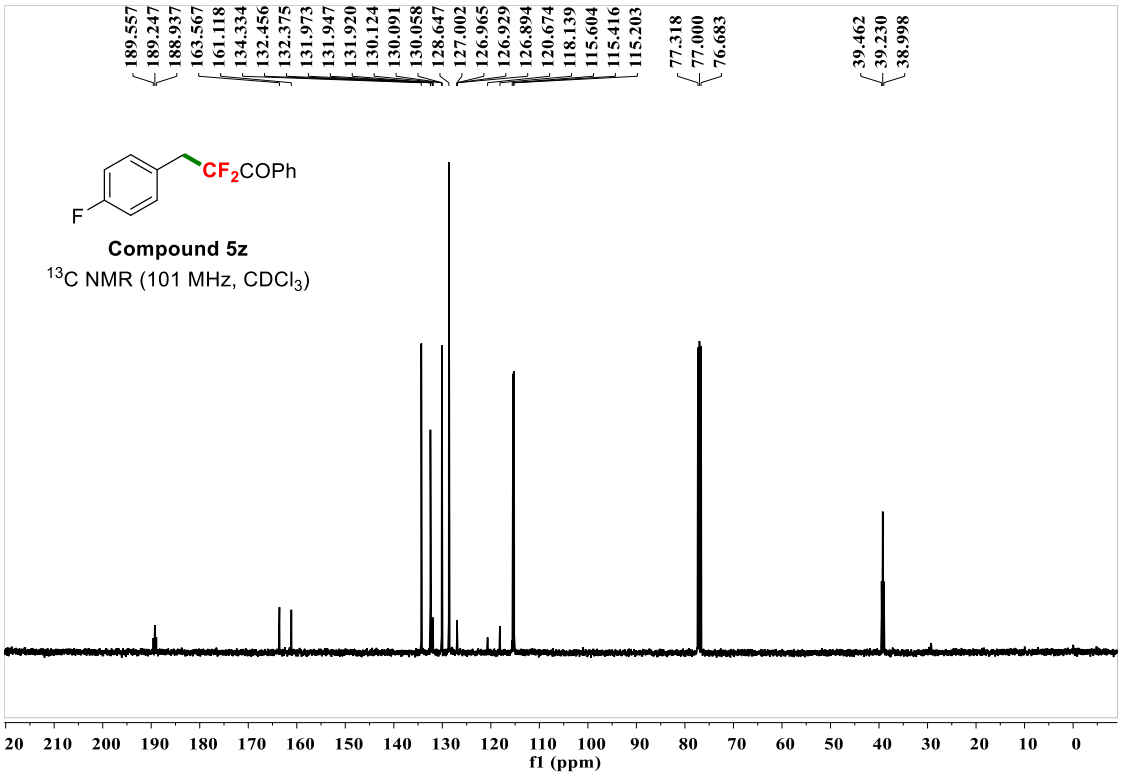




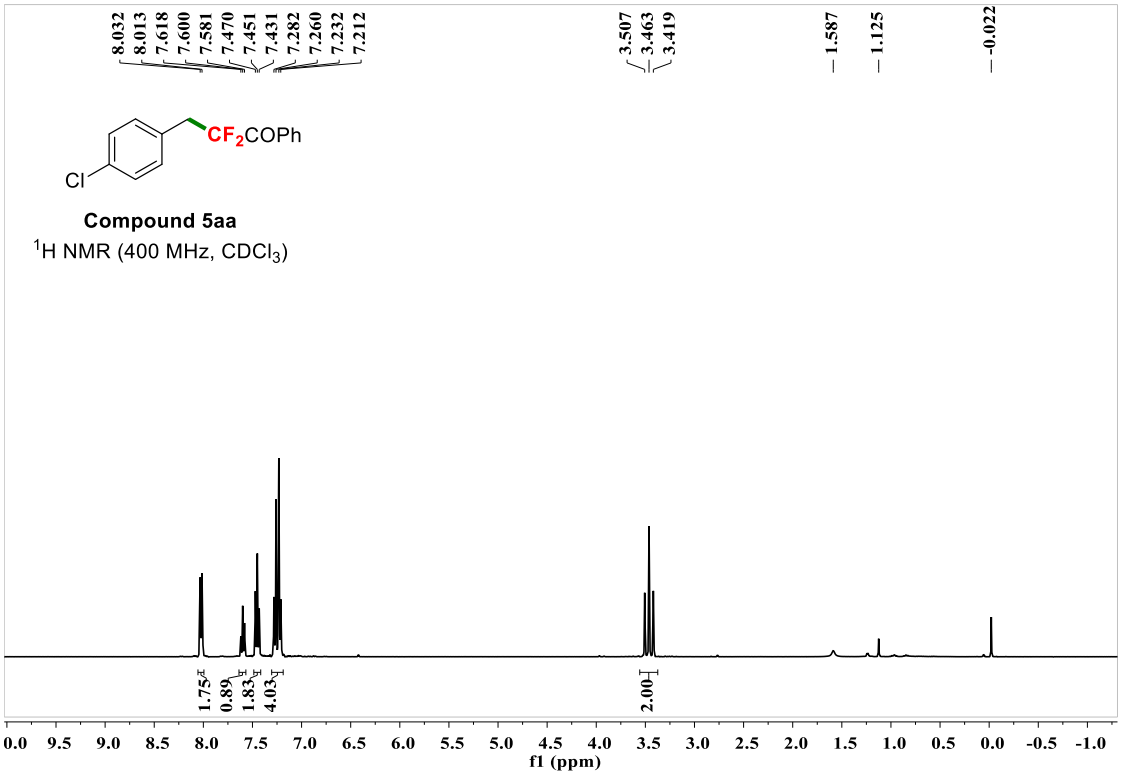
2,2-Difluoro-3-(4-fluorophenyl)-1-phenylpropan-1-one (5z).

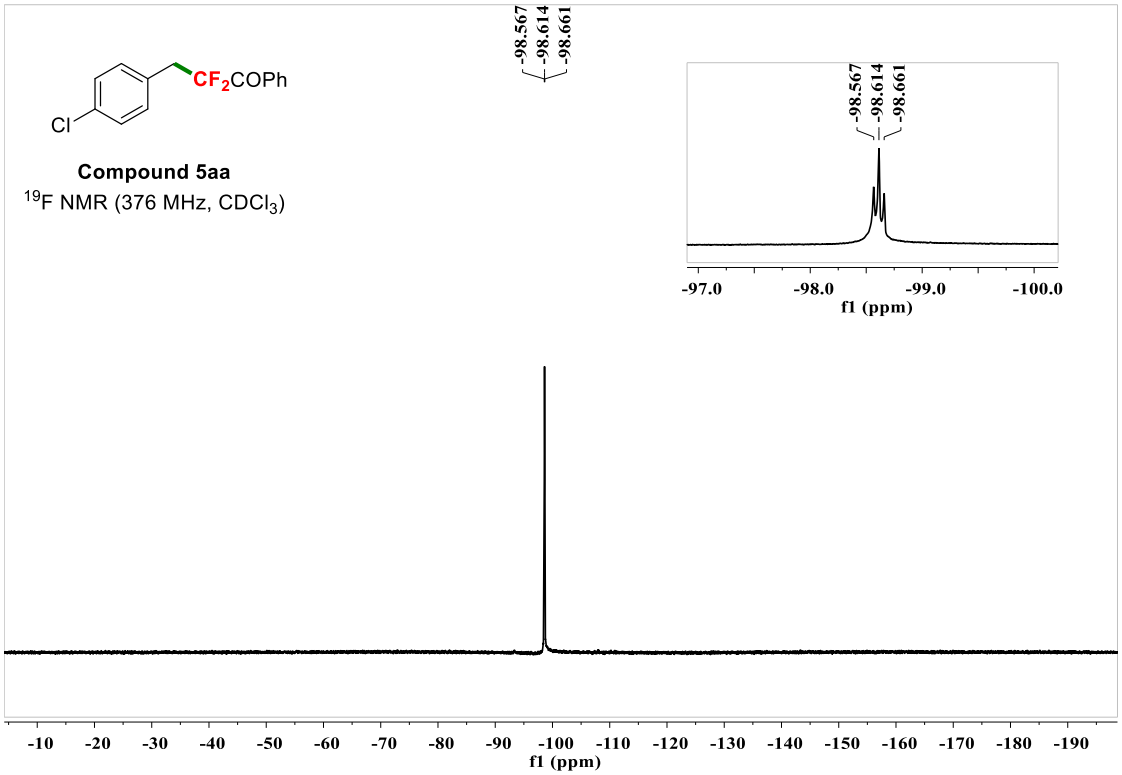


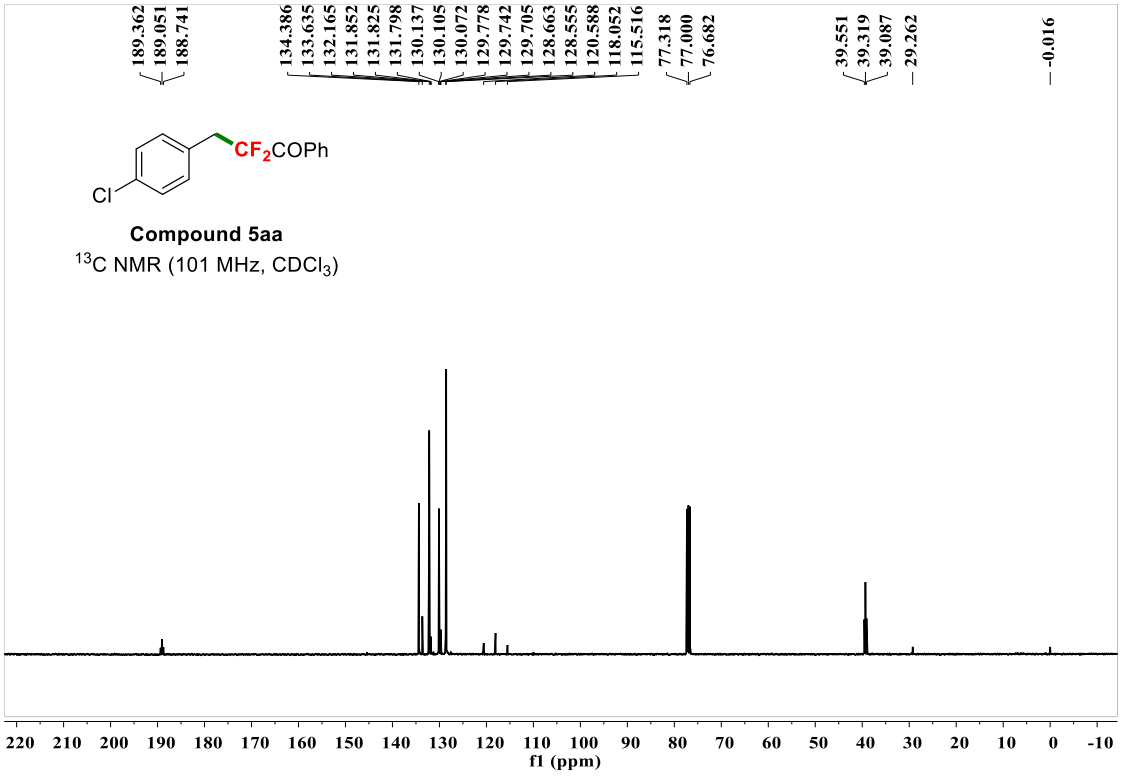

CF2COPh
F
Compound 5z
19F NMR (376 MHz, CDCl3)
-98.813
-98.860
-98.906
-114.985
-115.010
-115.021
-115.034
-115.045
-115.057
-115.081
-114.985
-115.010
-115.022
-115.033
-115.057
-115.101
-114.6 -114.8 -115.0 -115.2 -115.4 -115.6
f1 (ppm)
-98.813
-98.860
-98.907
-97.0 -98.0 -99.0 -100.0 -101.0
f1 (ppm)
2.18
1.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


189.557
189.247
188.937
163.567
161.118
134.334
132.456
132.375
131.973
131.947
131.920
130.124
130.091
130.058
128.647
127.002
126.965
126.929
126.894
120.674
118.139
115.604
115.416
115.203
77.318
77.000
76.683
39.462
39.230
38.998
CF2COPh
F
Compound 5z
13C NMR (101 MHz, CDCl3)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

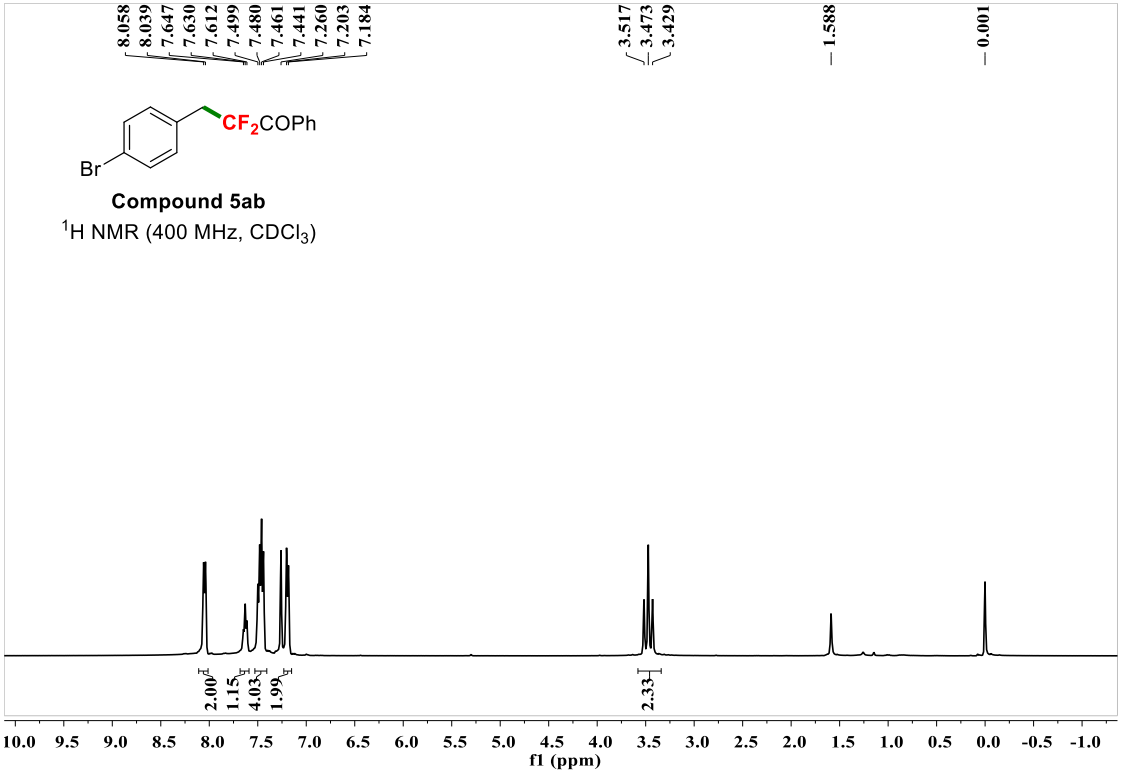
3-(4-Chlorophenyl)-2,2-difluoro-1-phenylpropan-1-one (5aa).

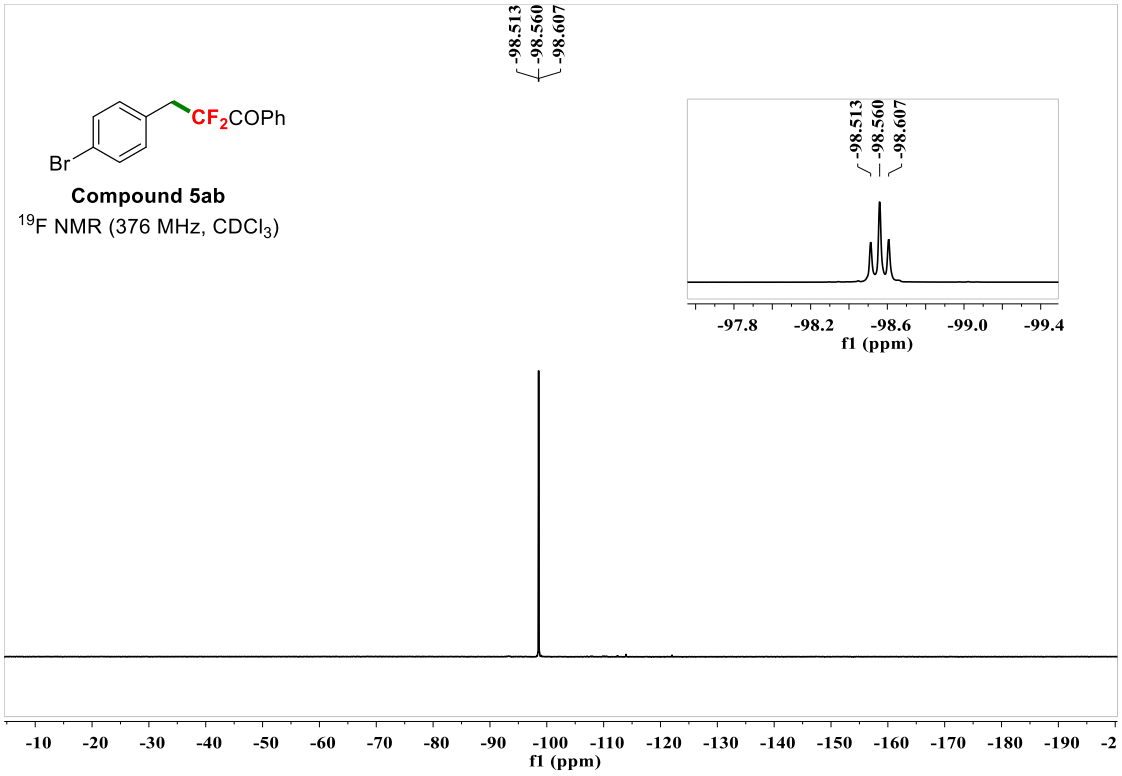


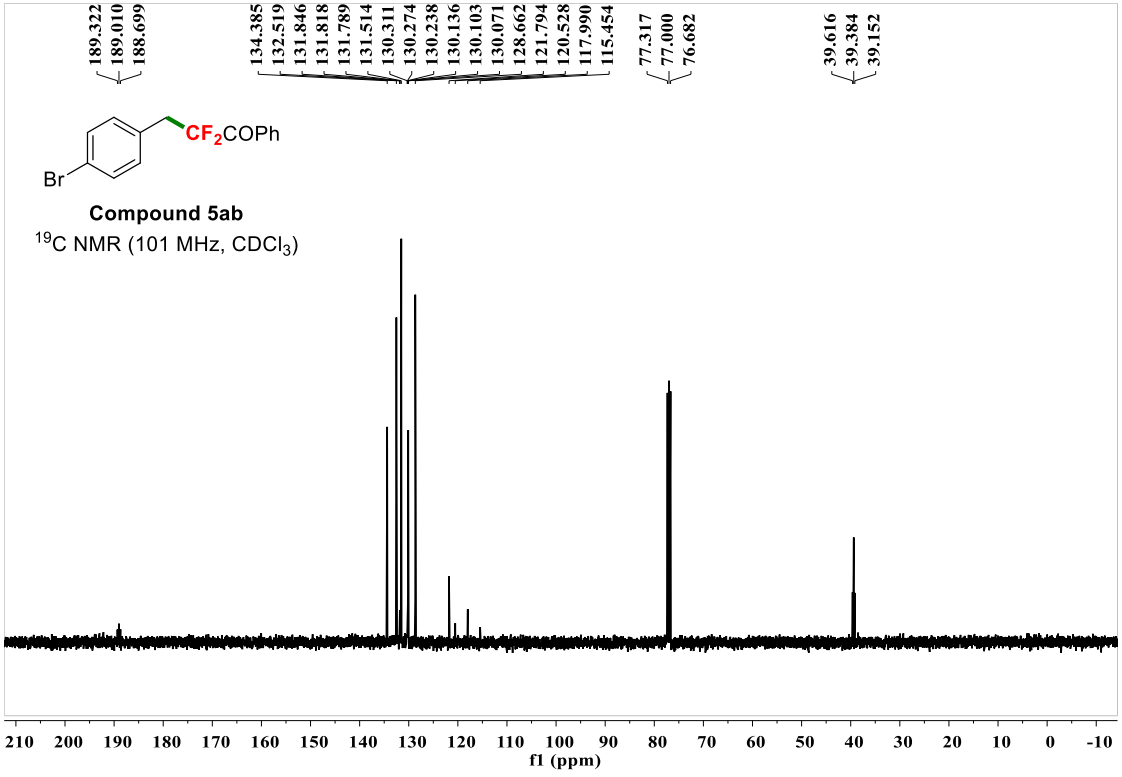




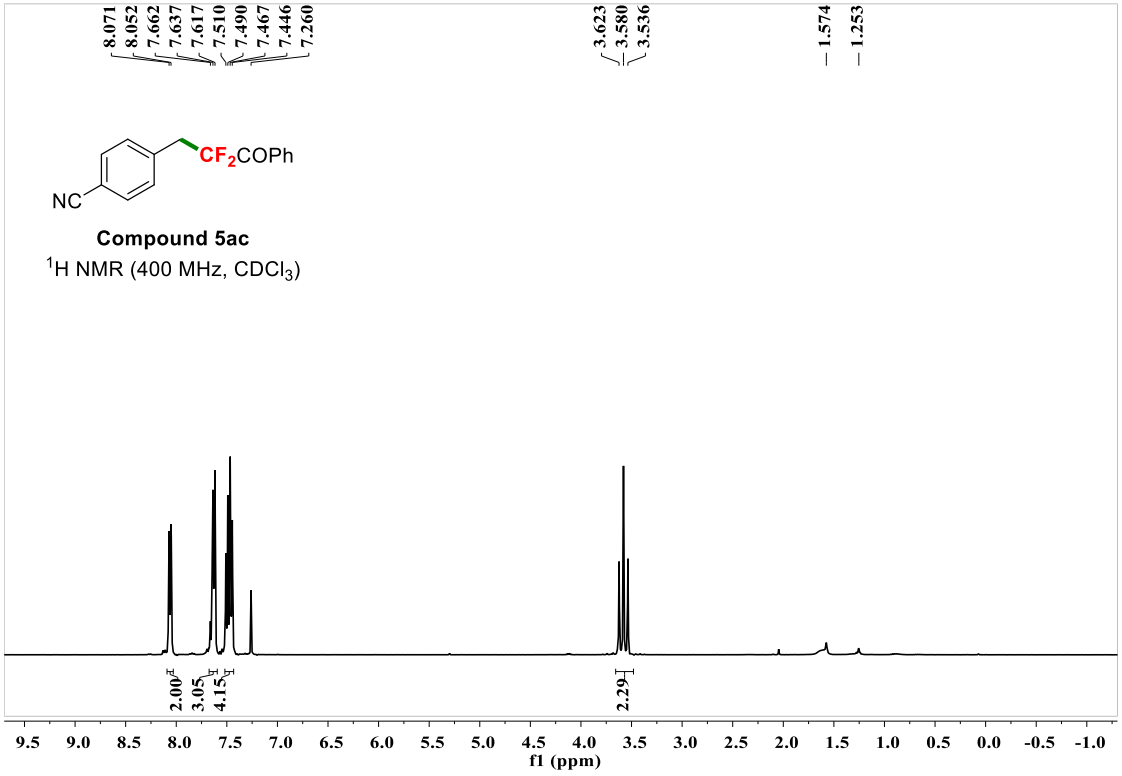
3-(4-Bromophenyl)-2,2-difluoro-1-phenylpropan-1-one (5ab).

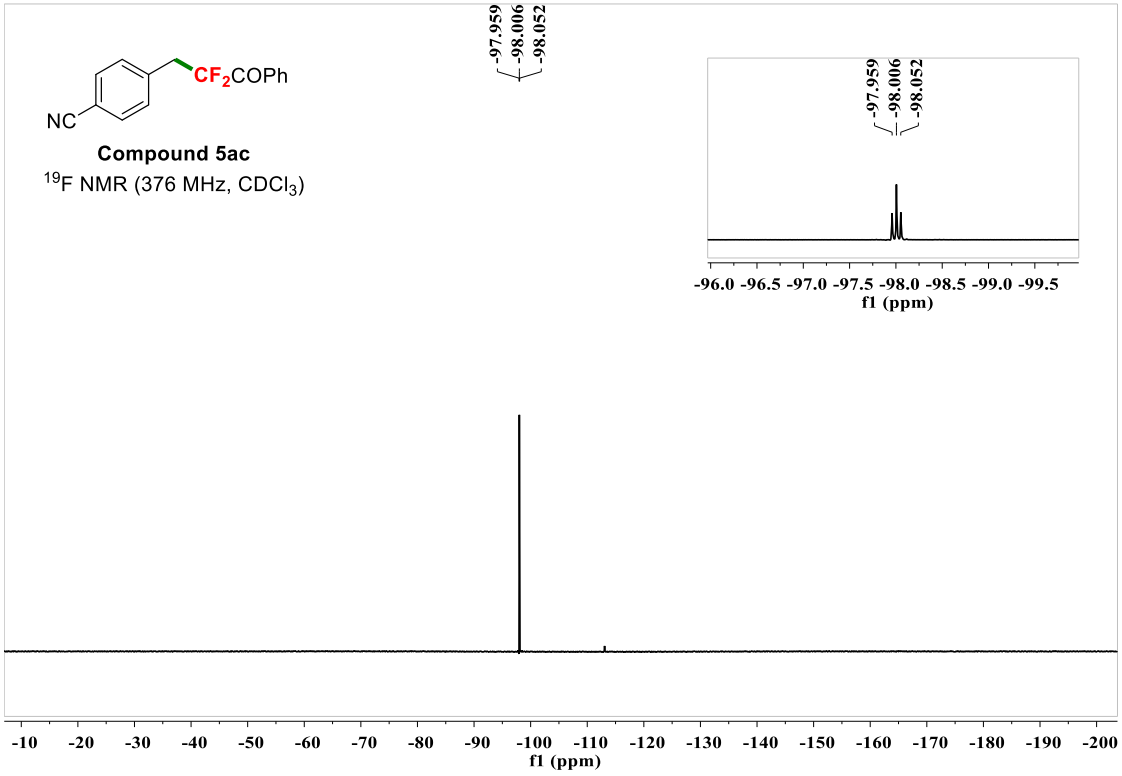


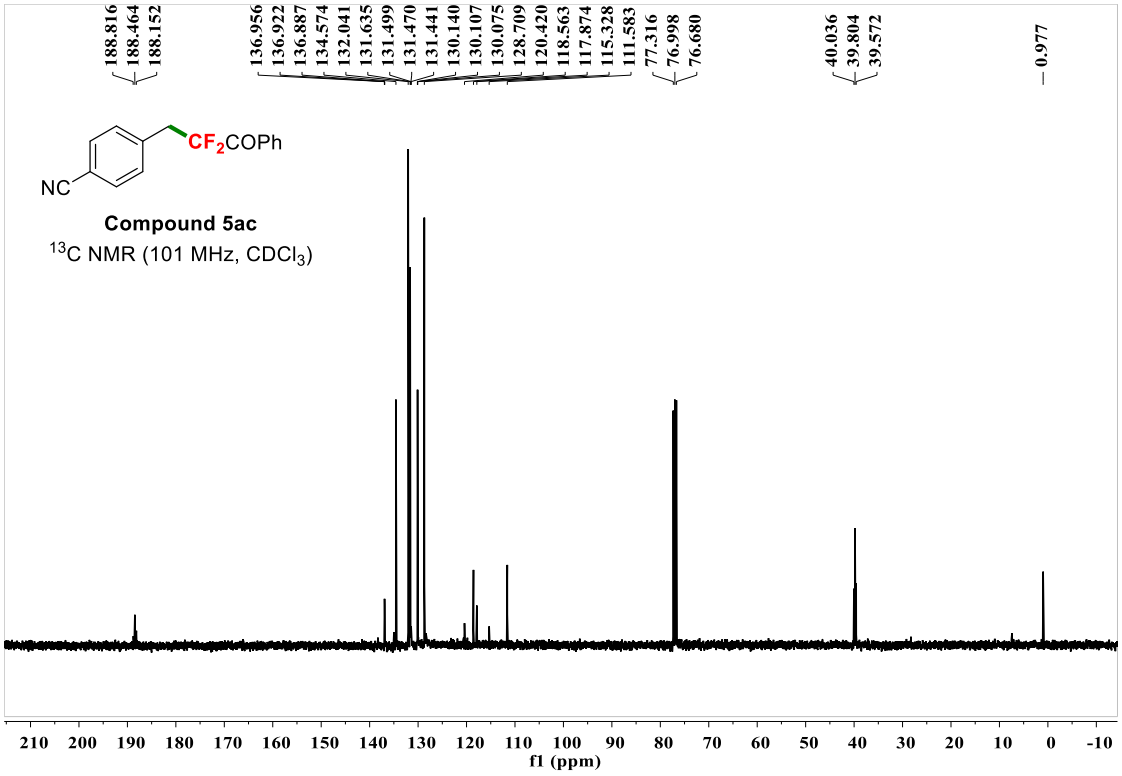

-98.513
-98.560
-98.607
CF2COPh
Br
Compound 5ab
19F NMR (376 MHz, CDCl3)
-98.513
-98.560
-98.607
-97.8
-98.2
-98.6
-99.0
-99.4
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)


189.322
189.010
188.699
134.385
132.519
131.846
131.818
131.789
131.514
130.311
130.274
130.238
130.136
130.103
130.071
128.662
121.794
120.528
117.990
115.454
77.317
77.000
76.682
39.616
39.384
39.152
CF2COPh
Br
Compound 5ab
19C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

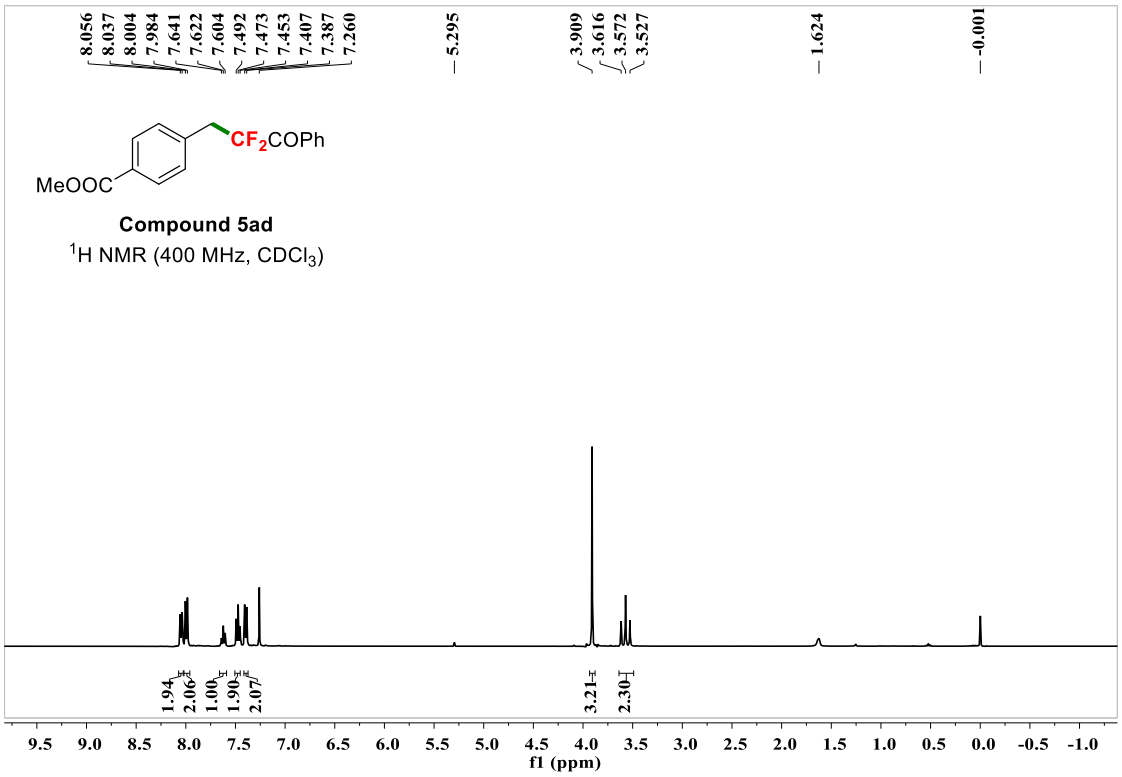
4-(2,2-Difluoro-3-oxo-3-phenylpropyl)benzonitrile (5ac).

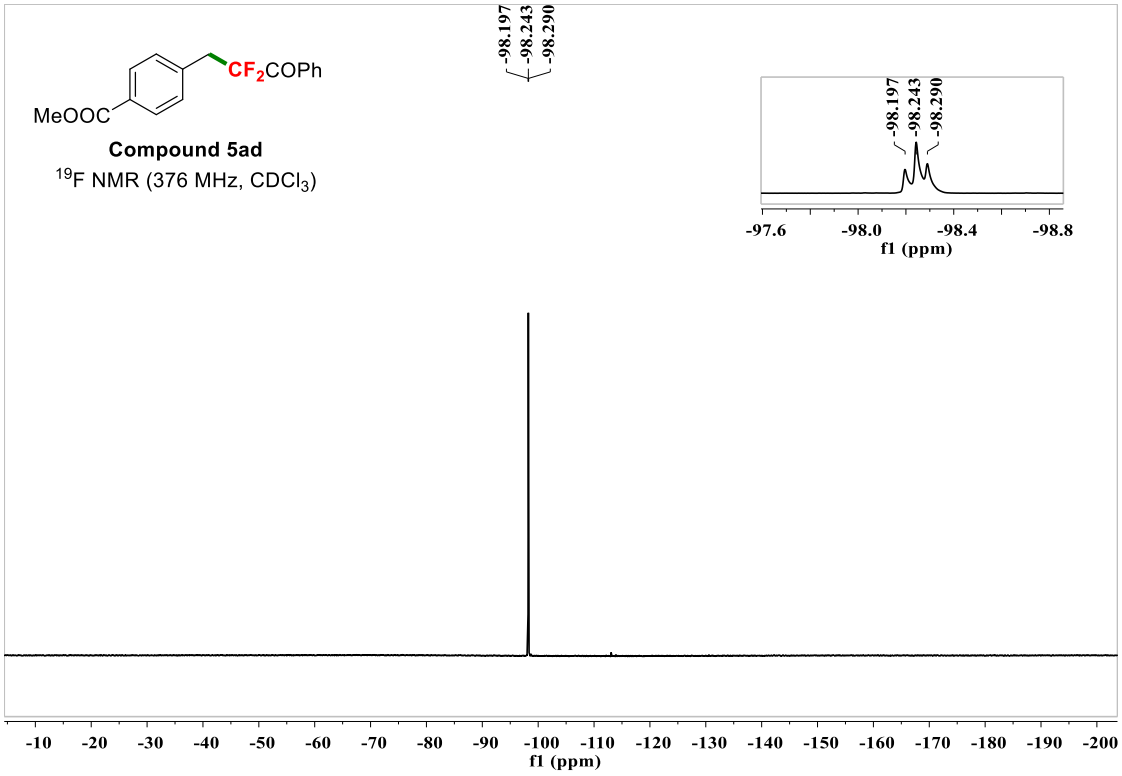


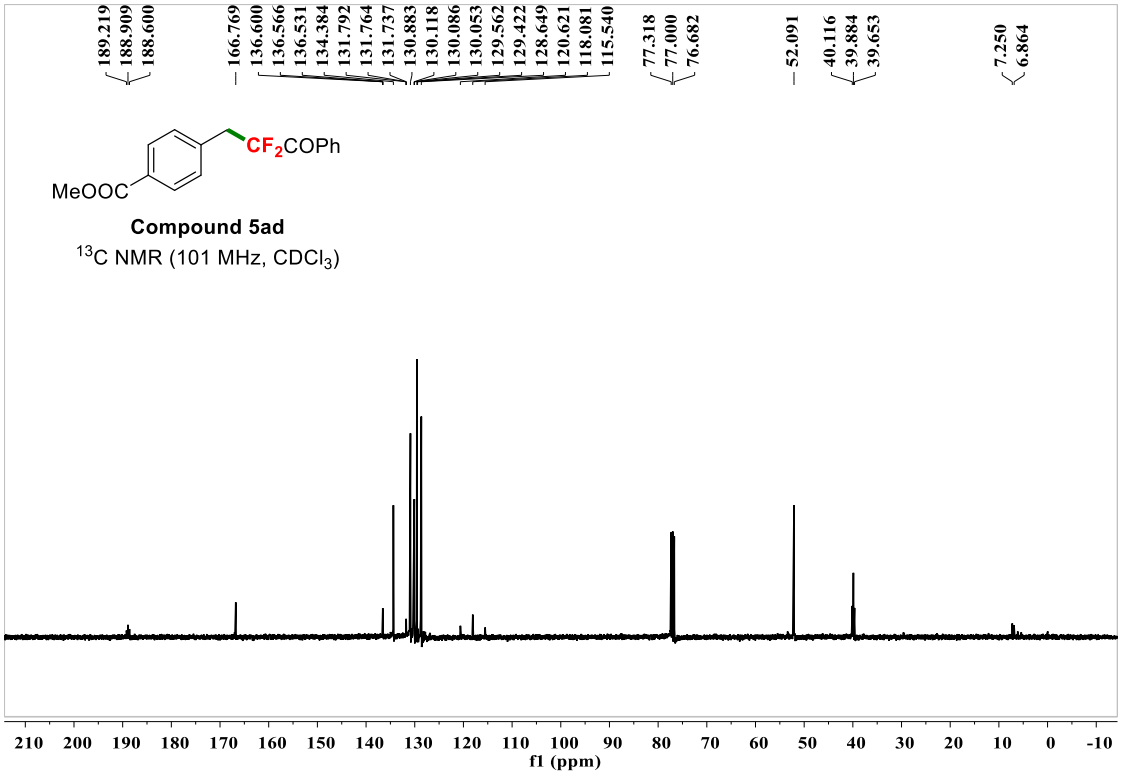




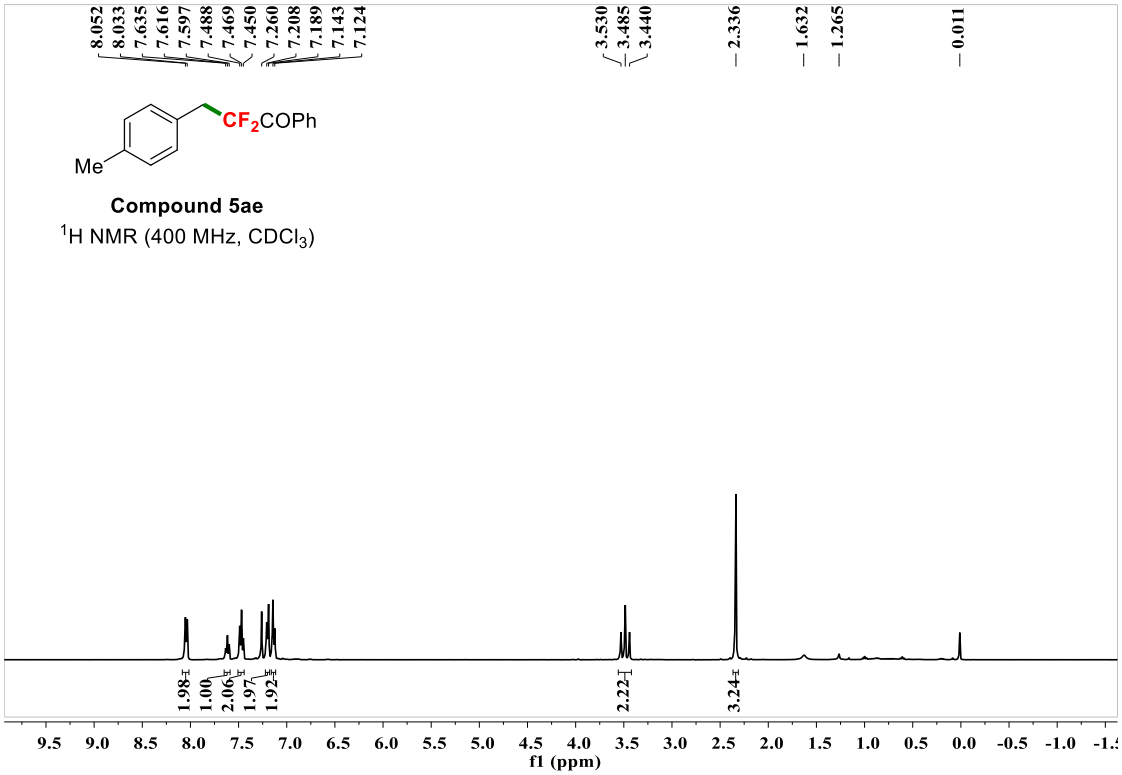
Methyl 4-(2,2-difluoro-3-oxo-3-phenylpropyl)benzoate (5ad).

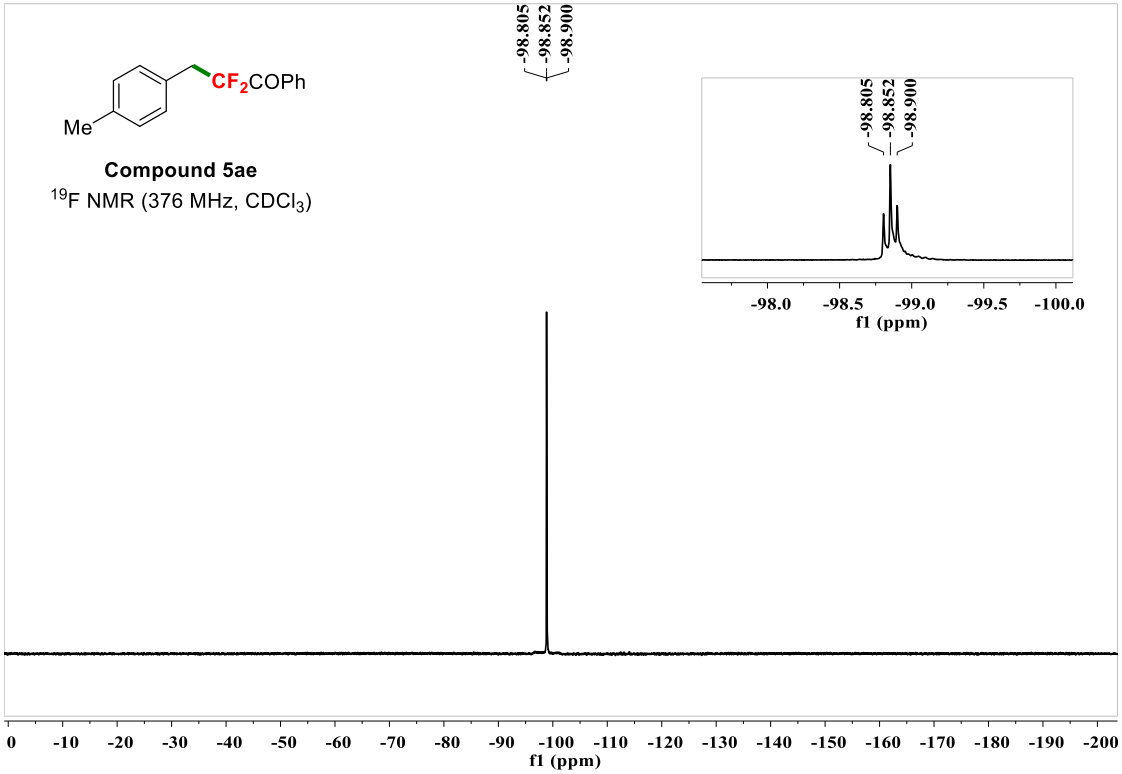


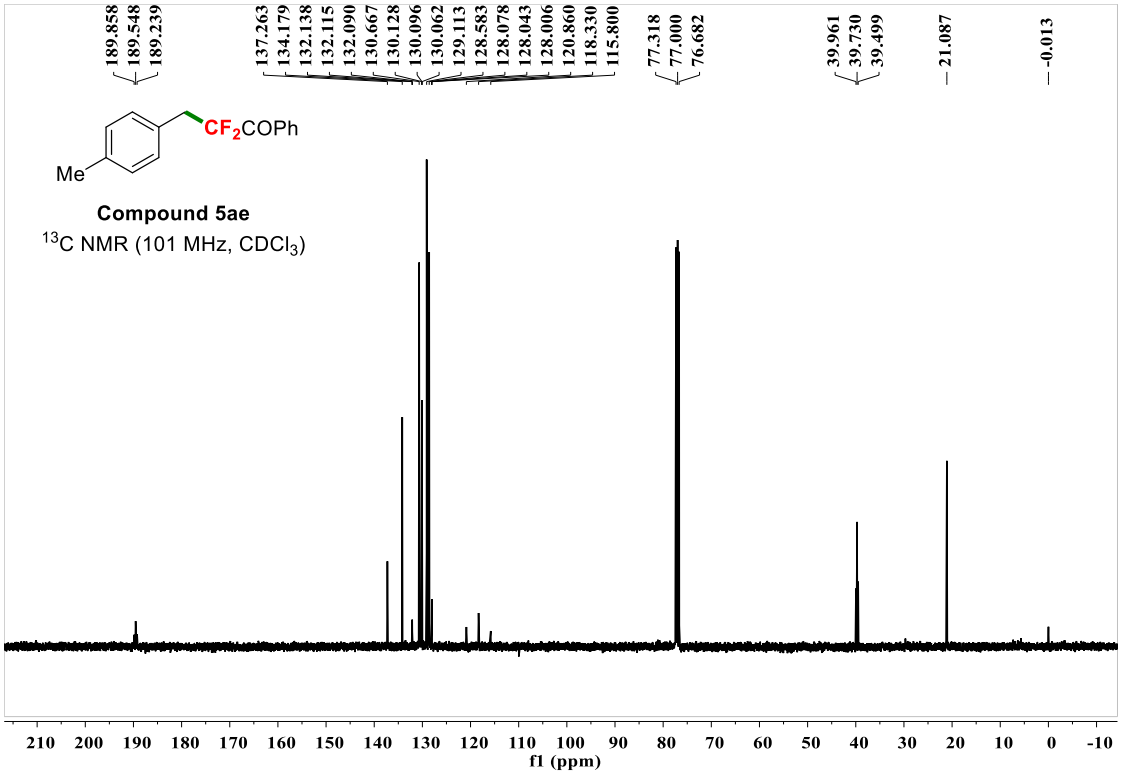

-98.197
-98.243
-98.290
CF2COPh
MeOOC
Compound 5ad
19F NMR (376 MHz, CDCl3)
-98.197
-98.243
-98.290
-97.6
-98.0
-98.4
-98.8
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


189.219
188.909
188.600
166.769
136.600
136.566
136.531
134.384
131.792
131.764
131.737
130.883
130.118
130.086
130.053
129.562
129.422
128.649
120.621
118.081
115.540
77.318
77.000
76.682
52.091
40.116
39.884
39.653
7.250
6.864
CF2COPh
MeOOC
Compound 5ad
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

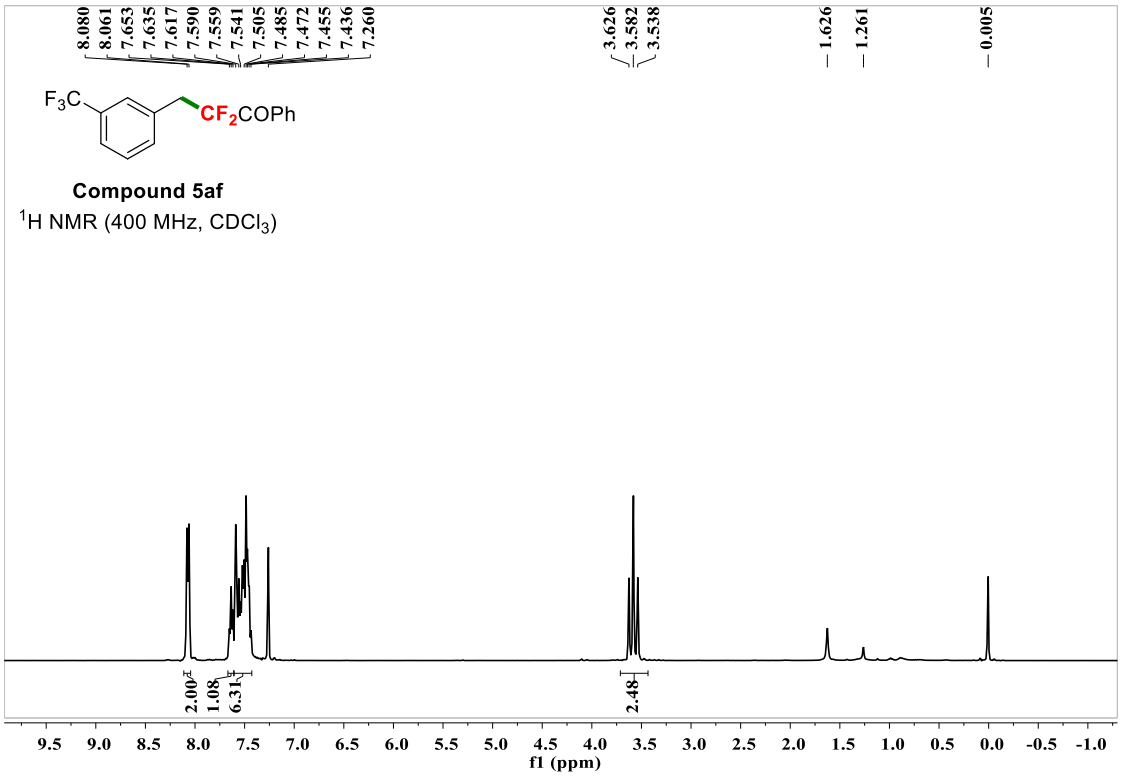
2,2-Difluoro-1-phenyl-3-(p-tolyl)propan-1-one (5ae).

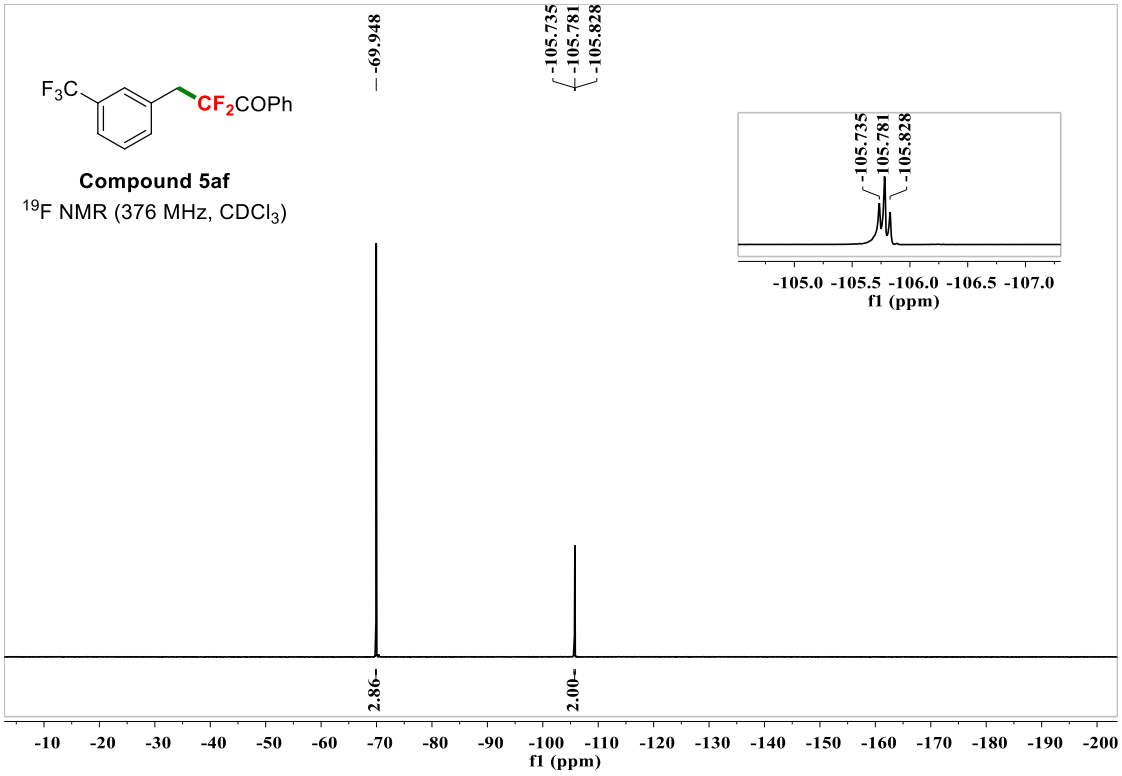


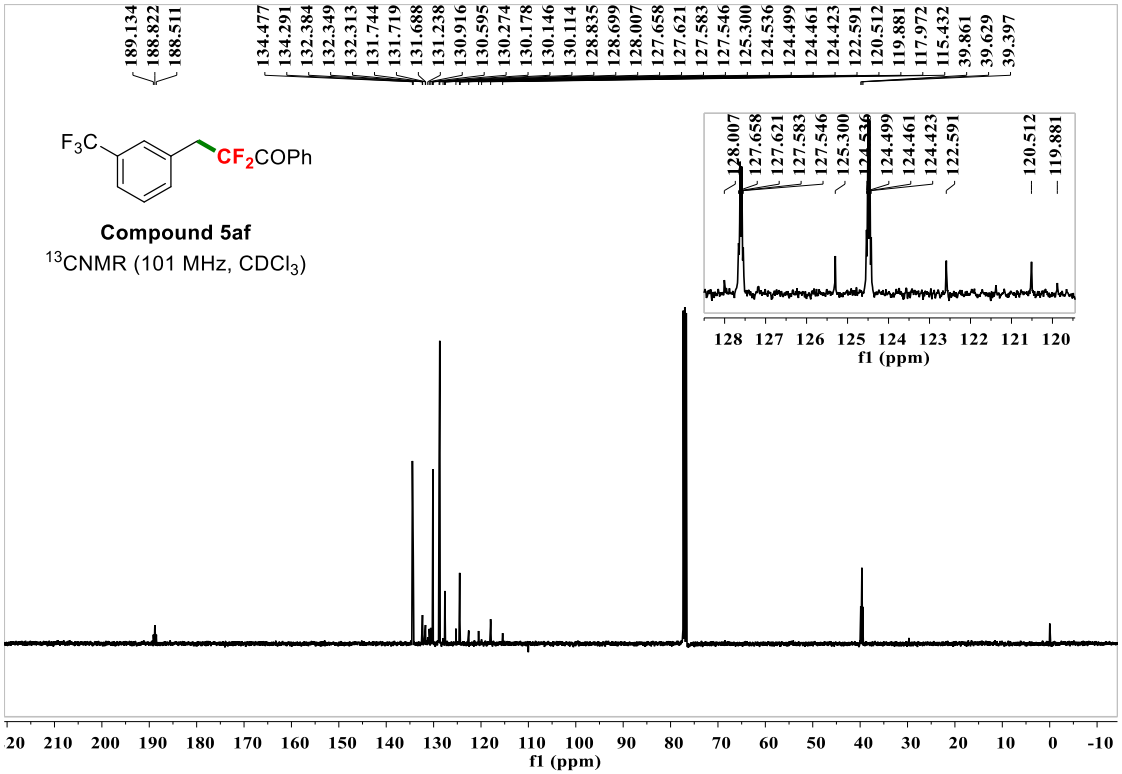




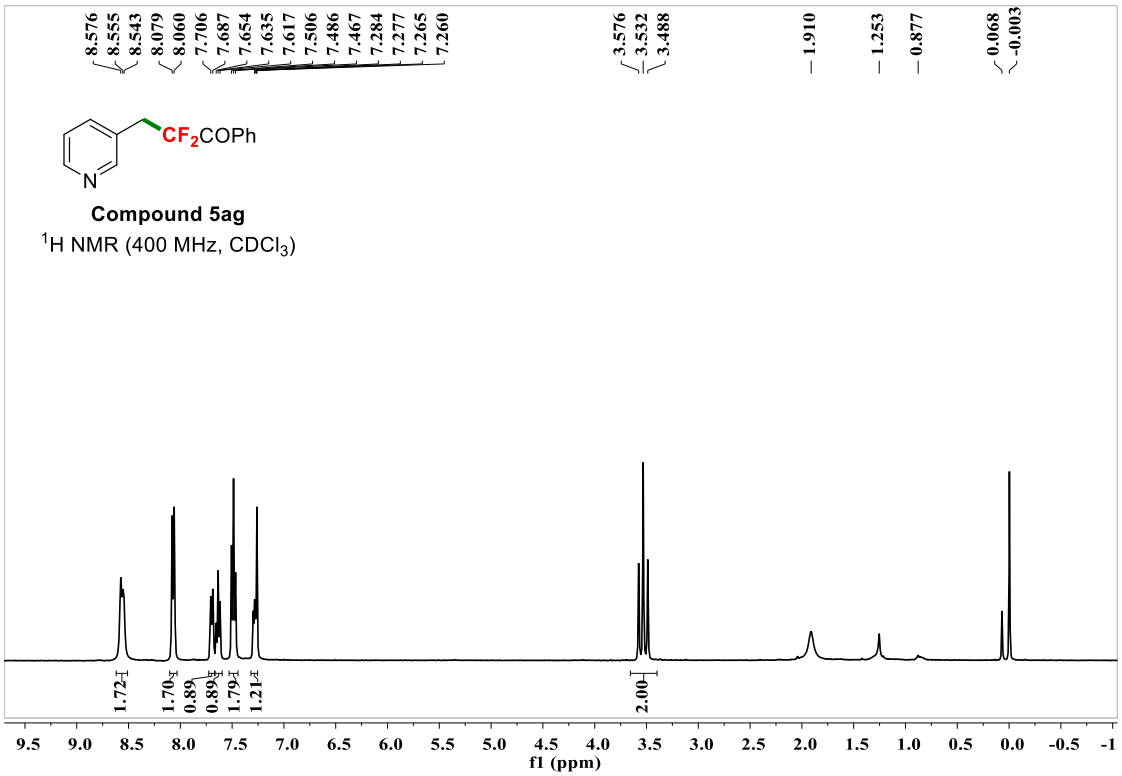
2,2-Difluoro-1-phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one (5af).

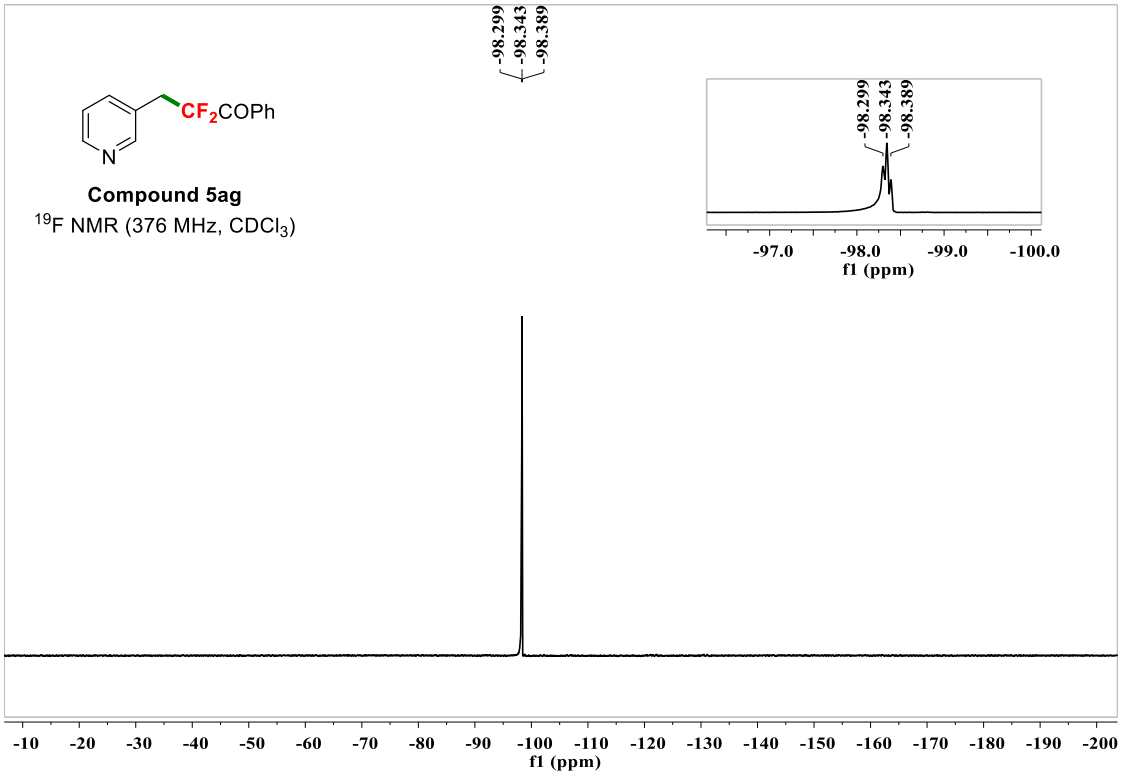


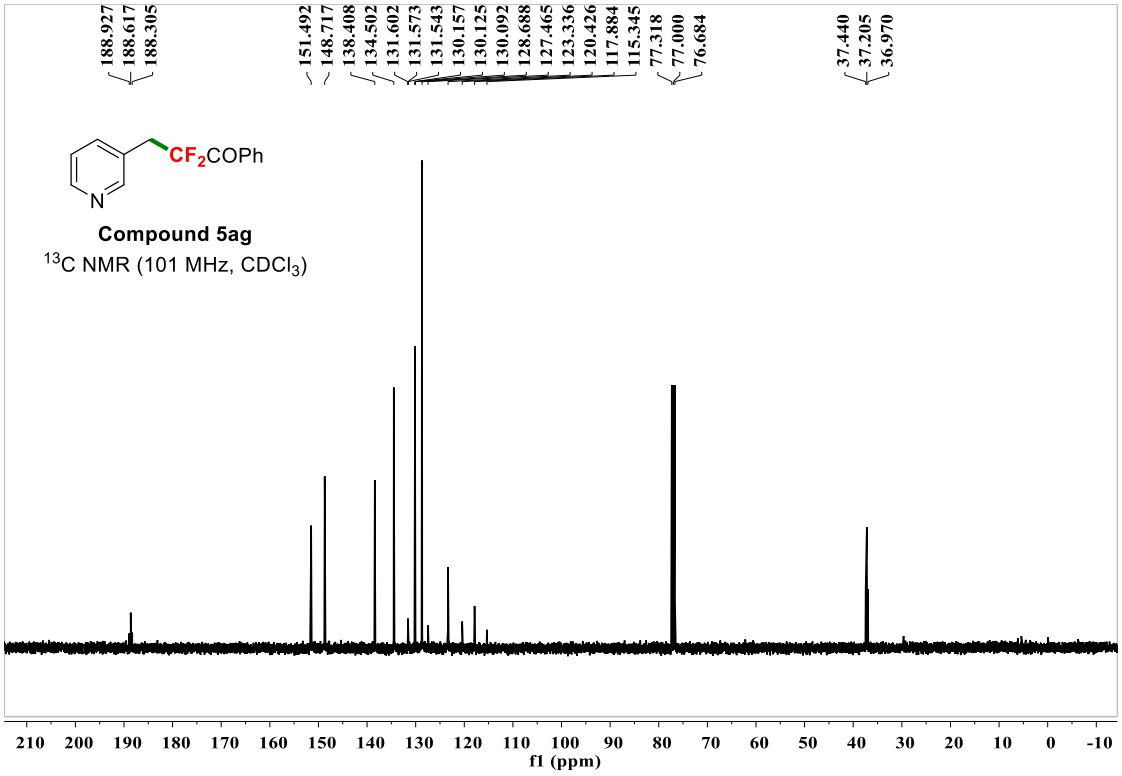

-69.948
-105.735
-105.781
-105.828
F3C
CF2COPh
Compound 5af
19F NMR (376 MHz, CDCl3)
-105.735
-105.781
-105.828
-105.0 -105.5 -106.0 -106.5 -107.0
f1 (ppm)
2.86
2.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


189.134
188.822
188.511
134.477
134.291
132.384
132.349
132.313
131.744
131.719
131.688
131.238
130.916
130.595
130.274
130.178
130.146
130.114
128.835
128.699
128.007
127.658
127.621
127.583
127.546
125.300
124.536
124.499
124.461
124.423
122.591
120.512
119.881
117.972
115.432
39.861
39.629
39.397
F3C
CF2COPh
Compound 5af
13CNMR (101 MHz, CDCl3)
128.007
127.658
127.621
127.583
127.546
125.300
124.536
124.499
124.461
124.423
122.591
120.512
119.881
128 127 126 125 124 123 122 121 120
f1 (ppm)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

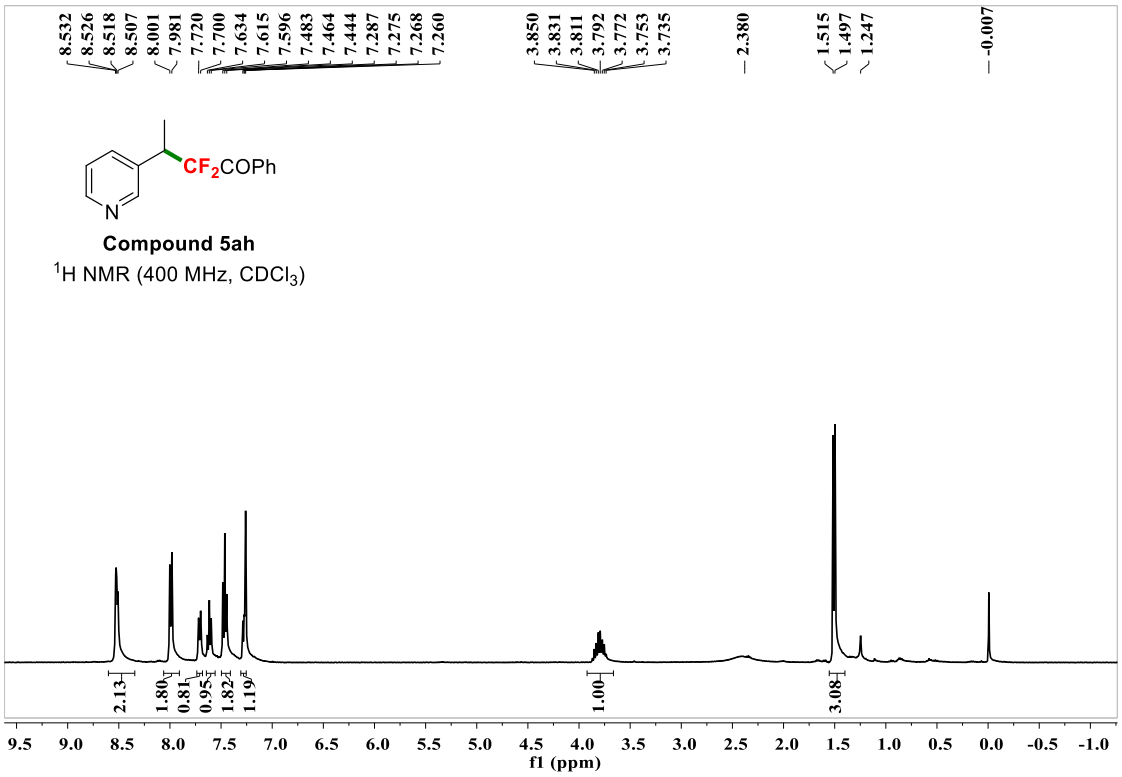
2,2-Difluoro-1-phenyl-3-(pyridin-3-yl)propan-1-one (5ag).

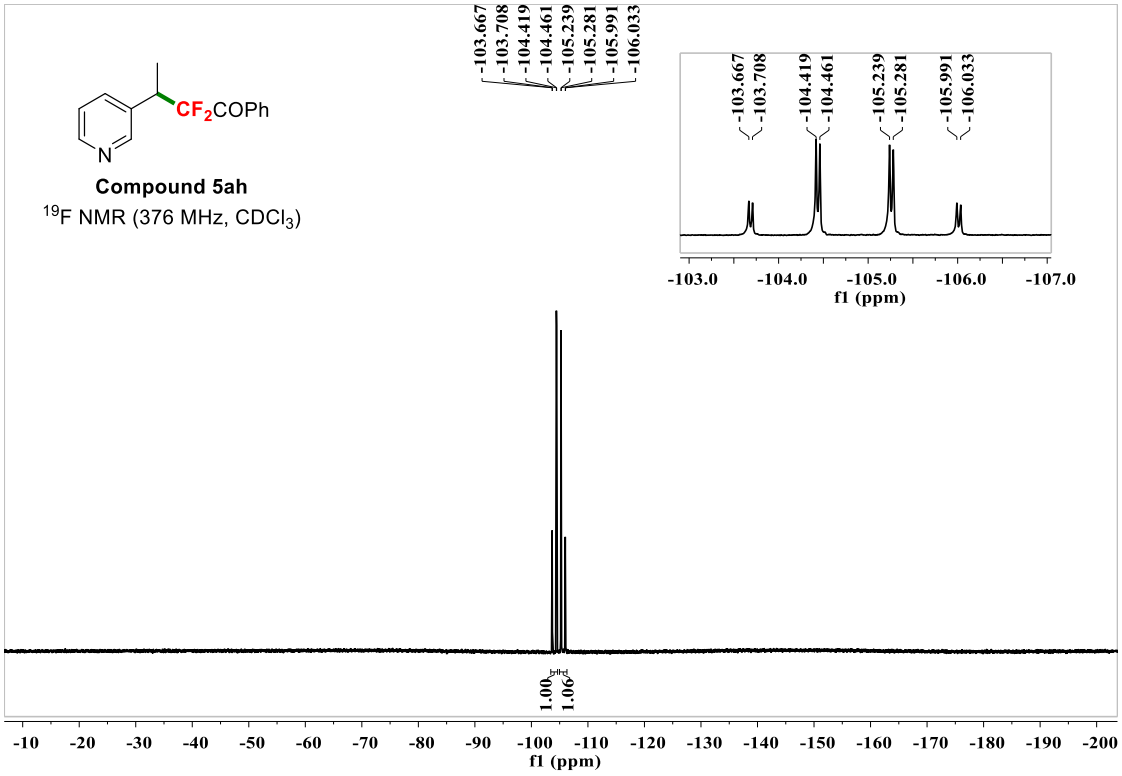


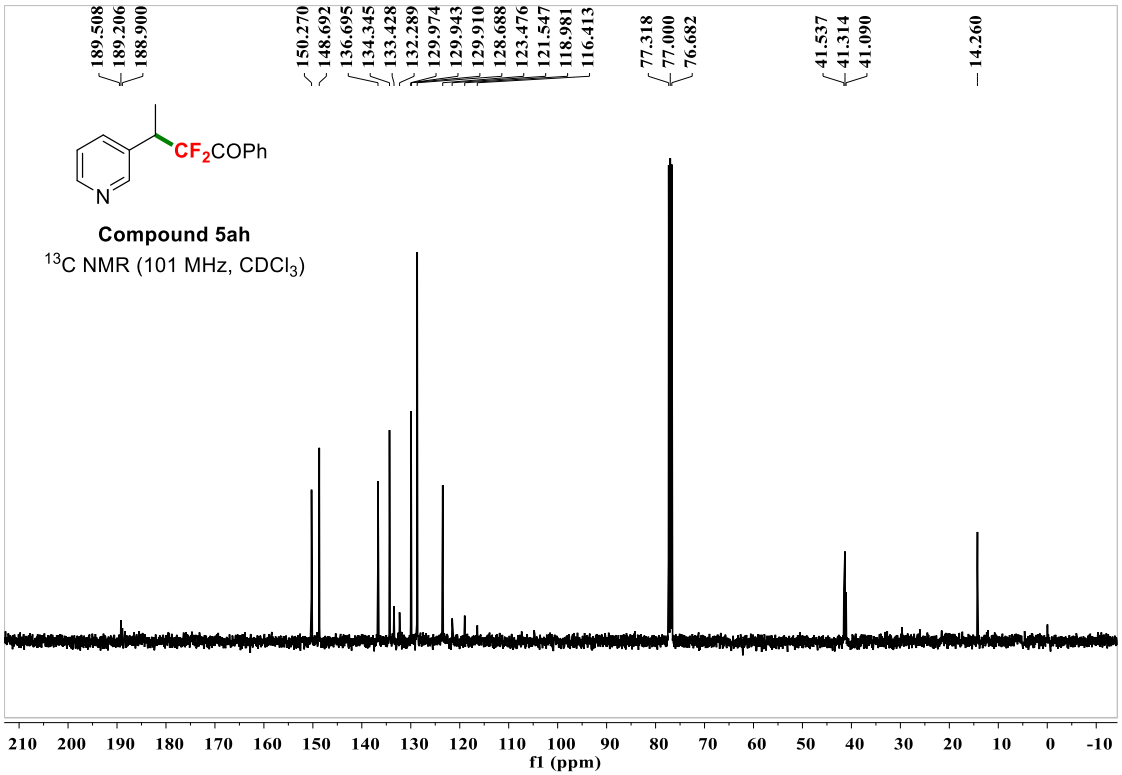




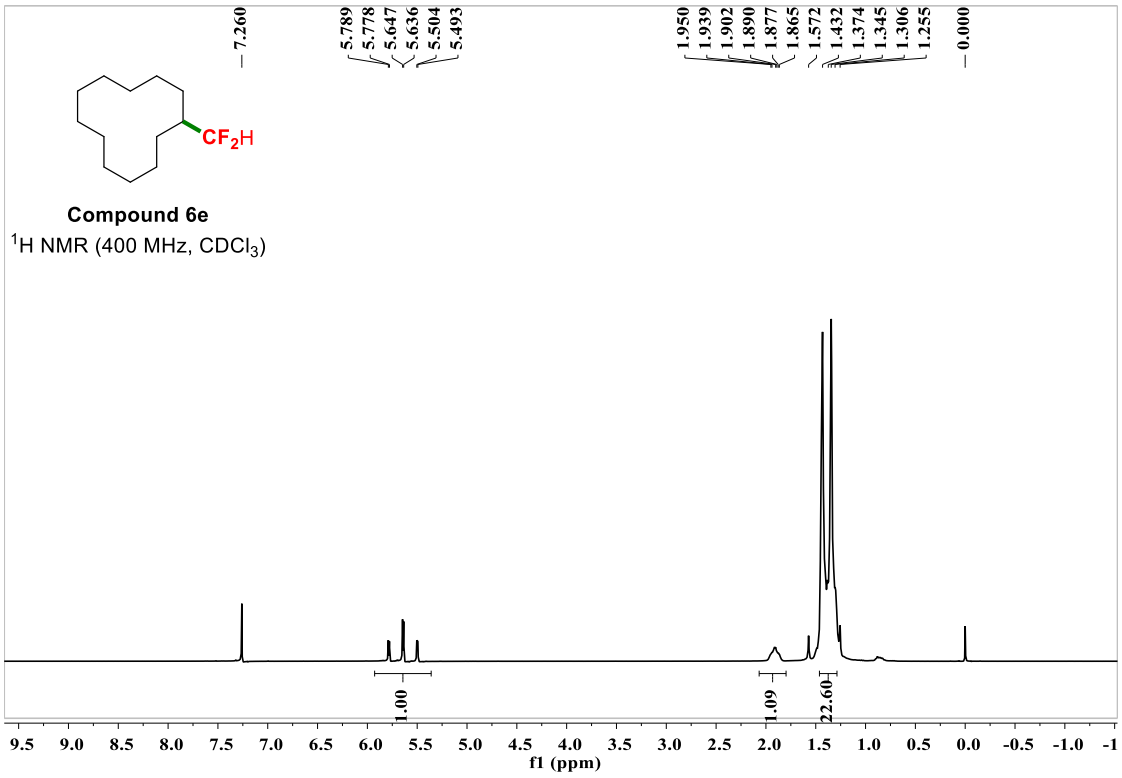
2,2-Difluoro-1-phenyl-3-(pyridin-3-yl)butan-1-one (5ah).

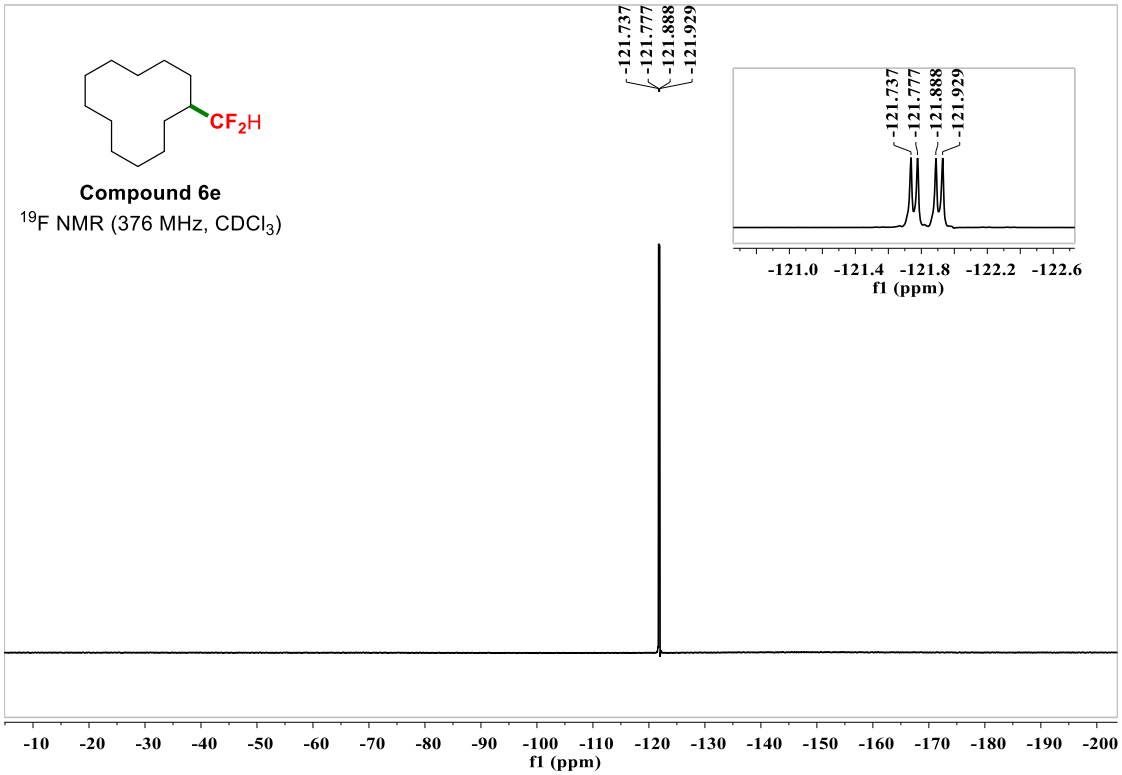


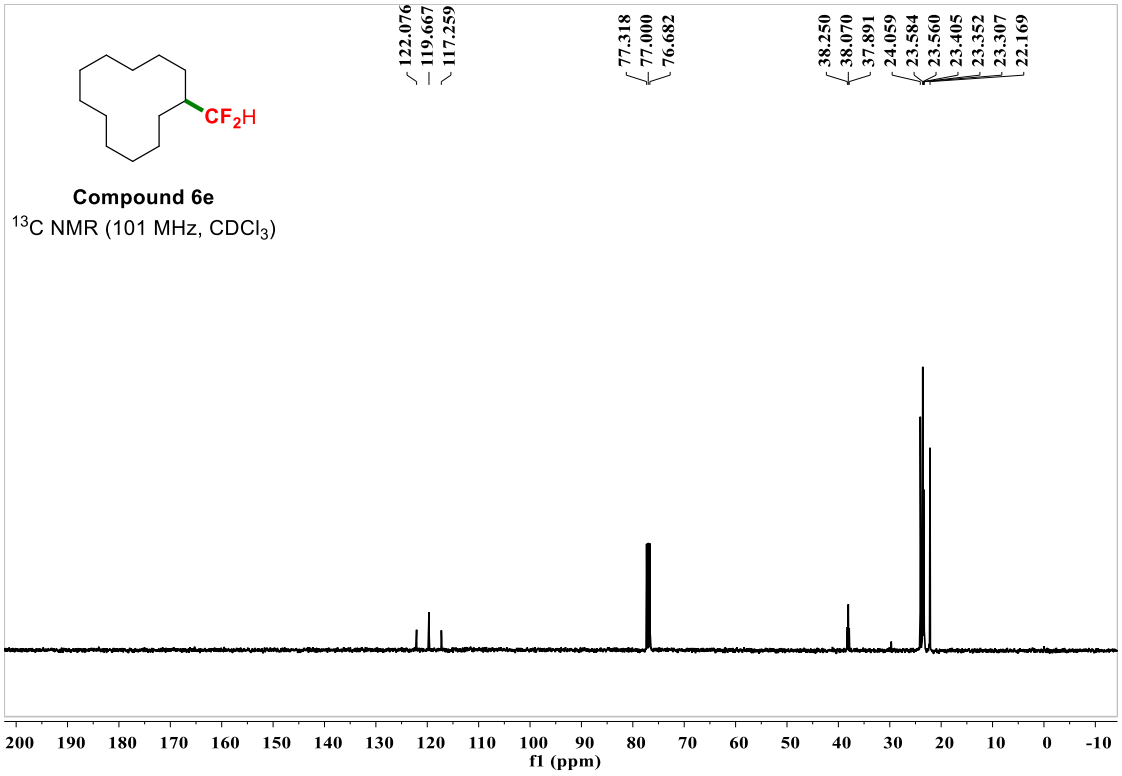

-103.667
-103.708
-104.419
-104.461
-105.239
-105.281
-105.991
-106.033
CF2COPh
N
Compound 5ah
19F NMR (376 MHz, CDCl3)
-103.0
-104.0
-105.0
-106.0
-107.0
f1 (ppm)
1.00
1.06
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


189.508
189.206
188.900
150.270
148.692
136.695
134.345
133.428
132.289
129.974
129.943
129.910
128.688
123.476
121.547
118.981
116.413
77.318
77.000
76.682
41.537
41.314
41.090
14.260
CF2COPh
N
Compound 5ah
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

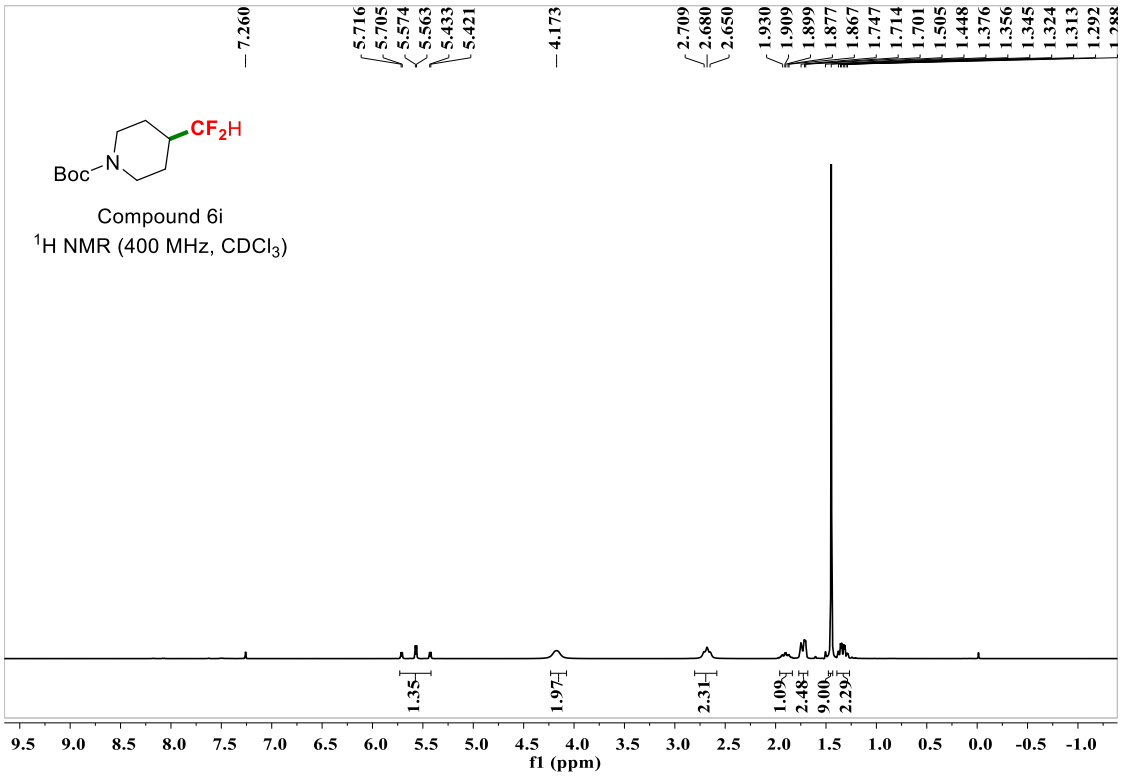
(Difluoromethyl)cyclododecane (6e).

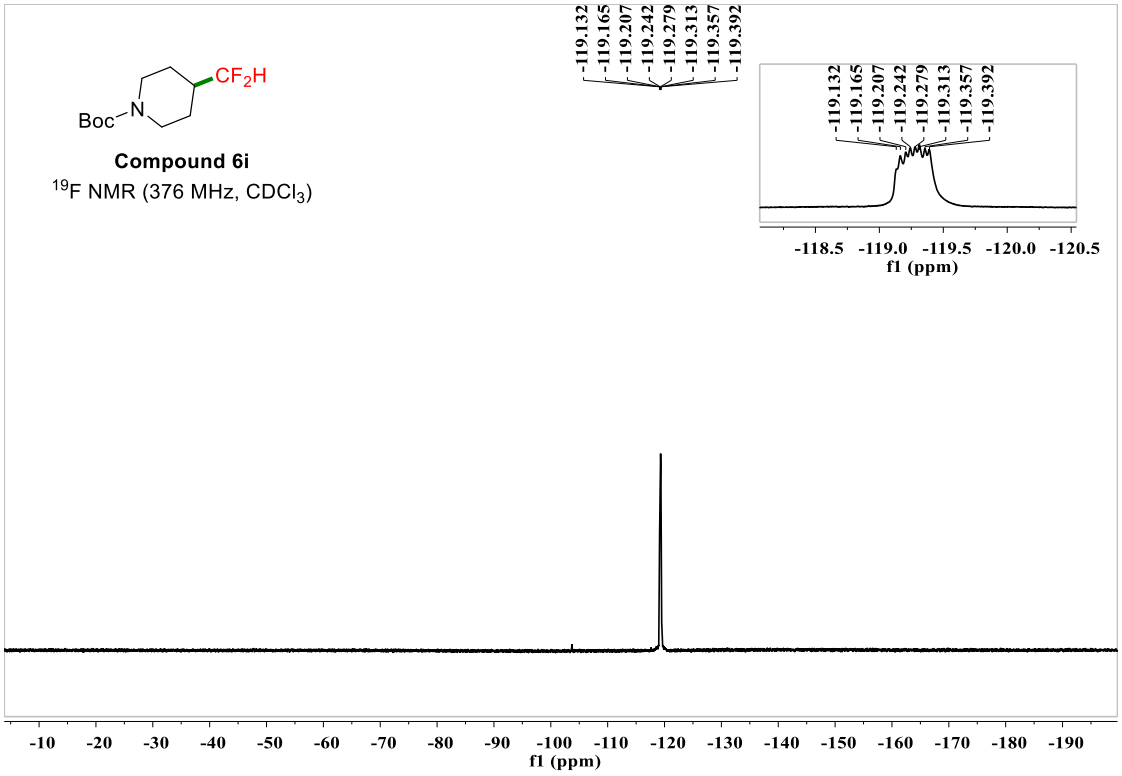






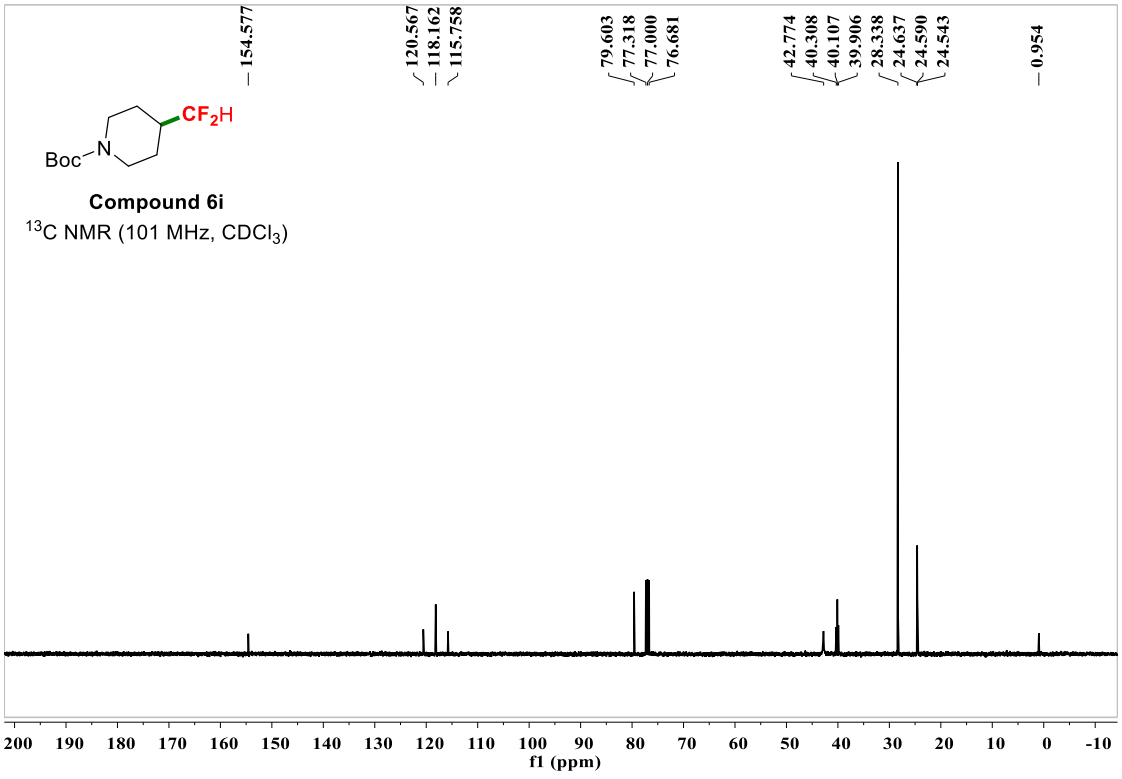
Tert-butyl 4-(difluoromethyl)piperidine-1-carboxylate (6i).





Compound 6i

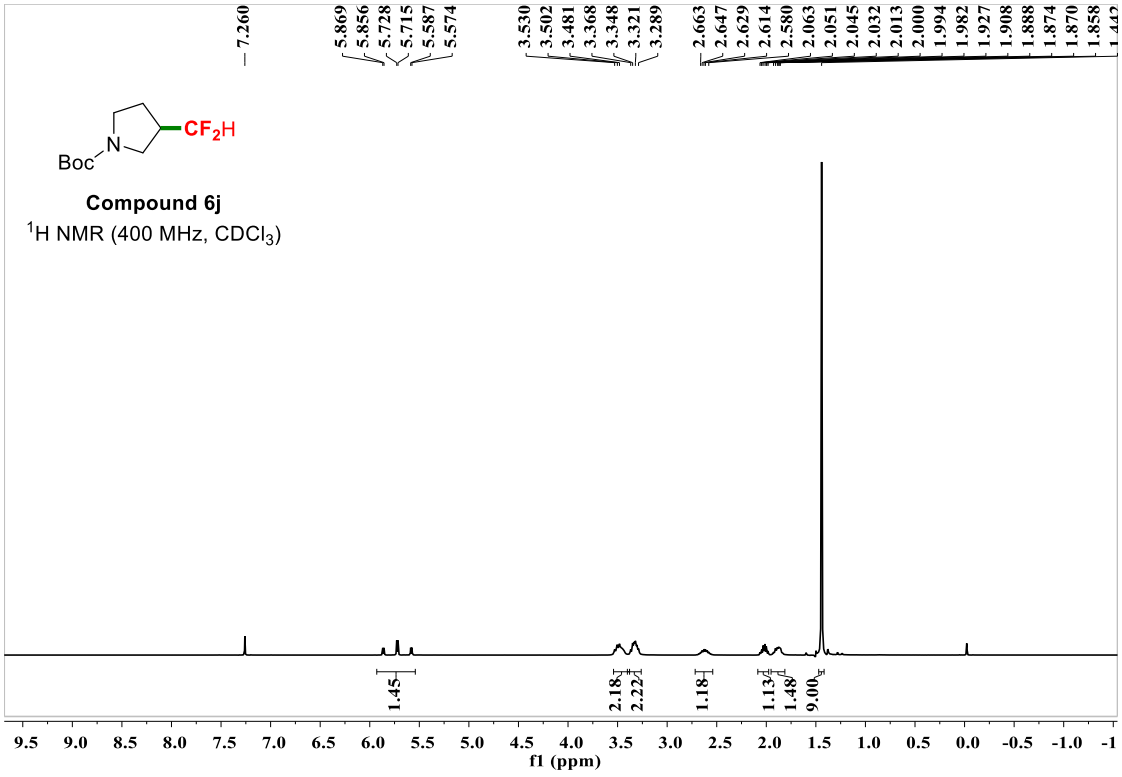
^{19}F NMR (376 MHz, $CDCl_3$)

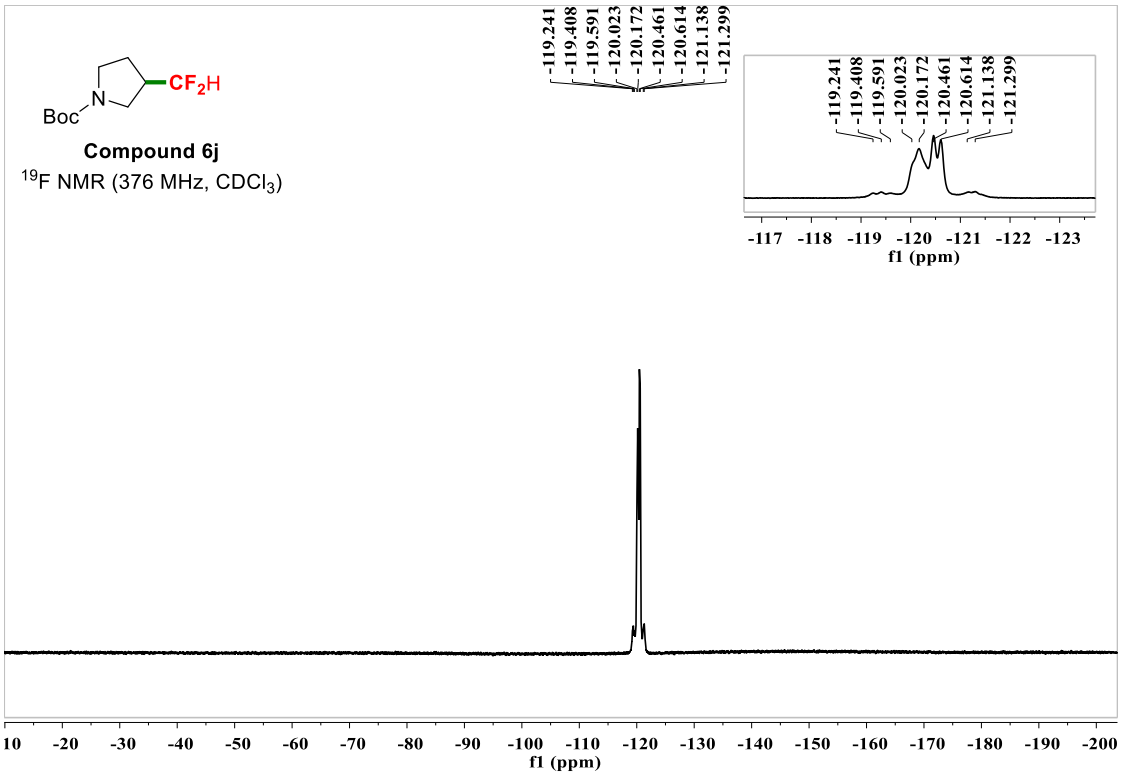


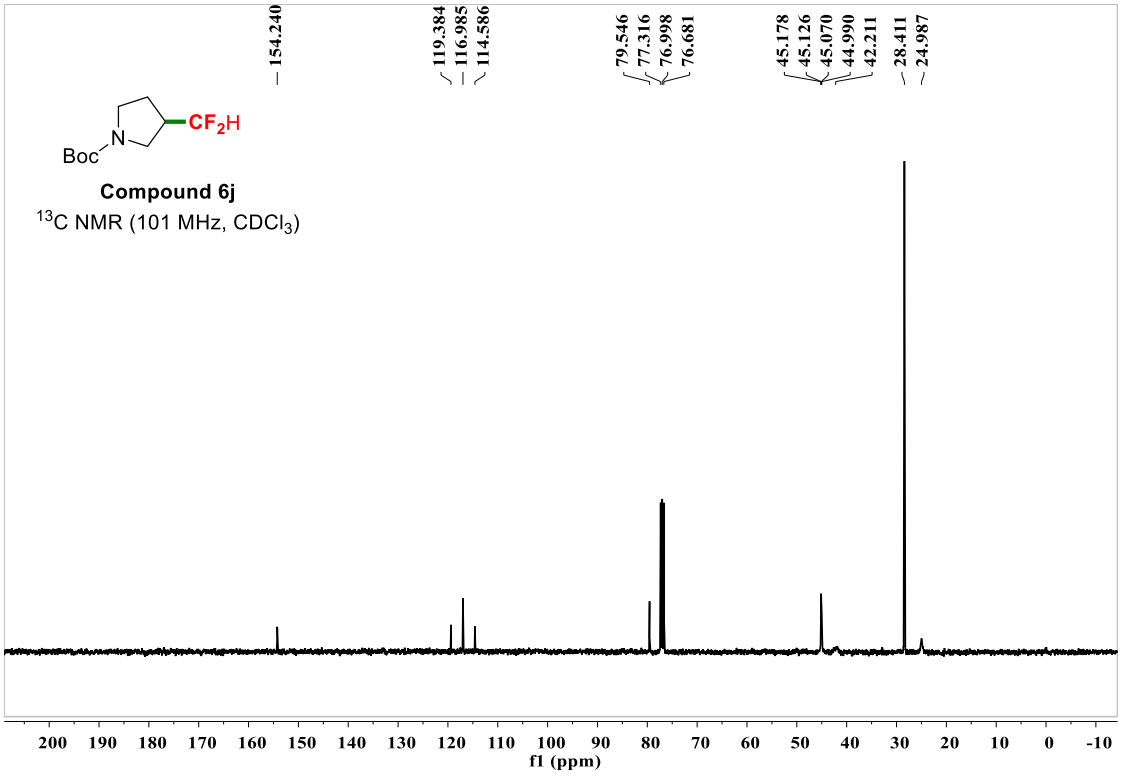
Compound 6i

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

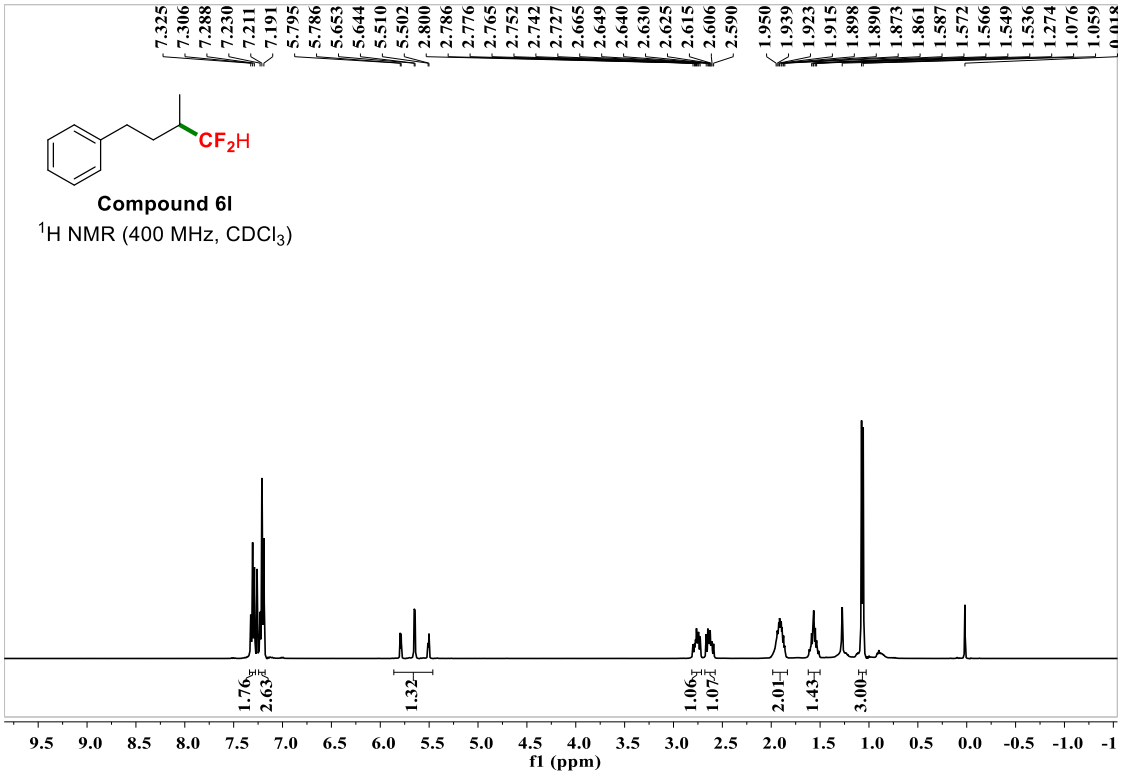
Tert-butyl-3-(difluoromethyl)pyrrolidine-1-carboxylate (6j).

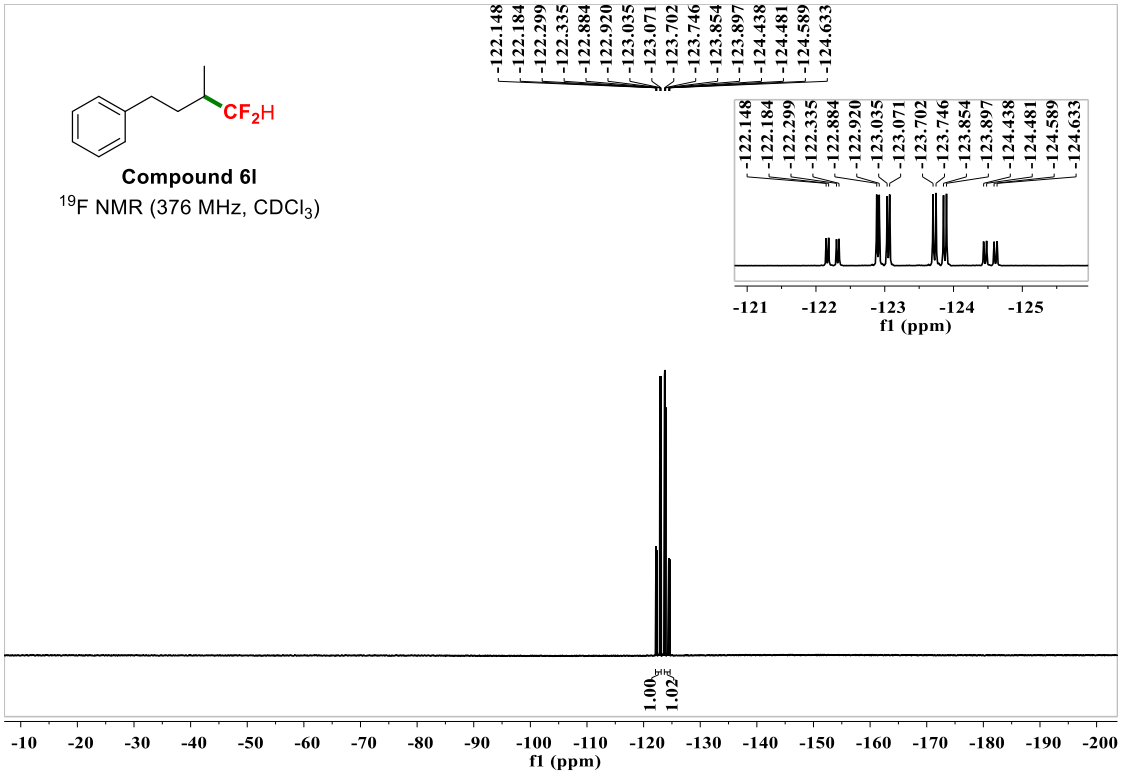


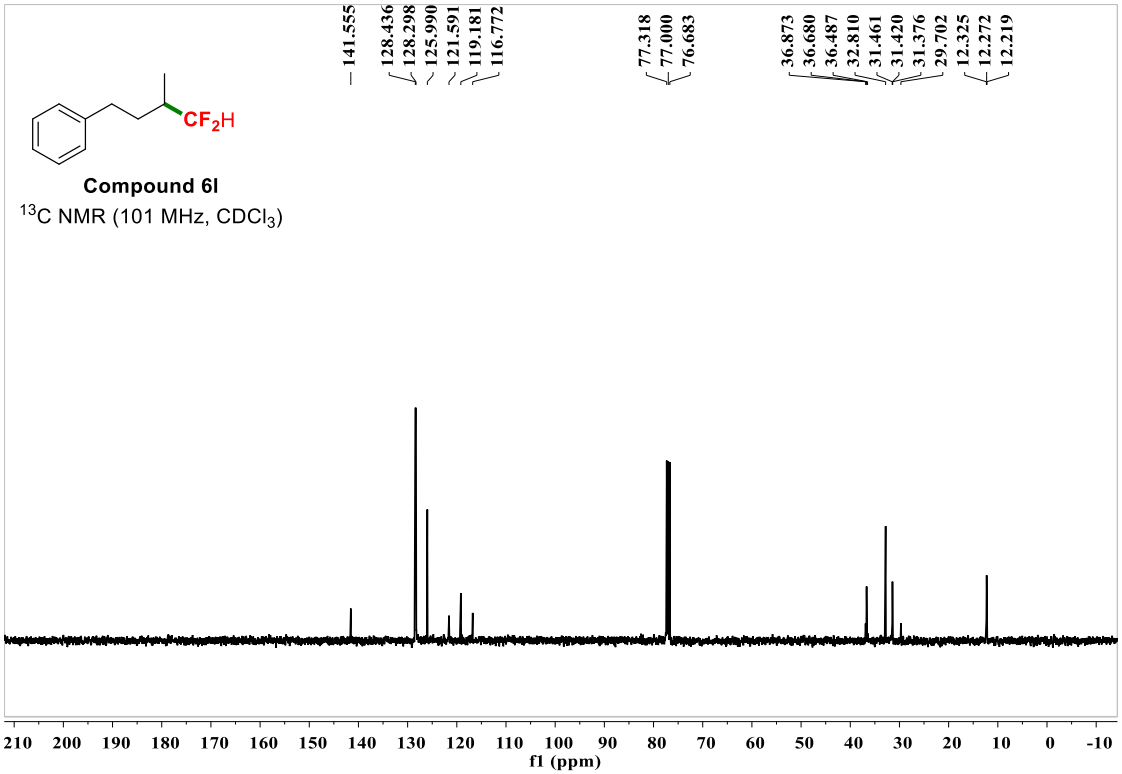




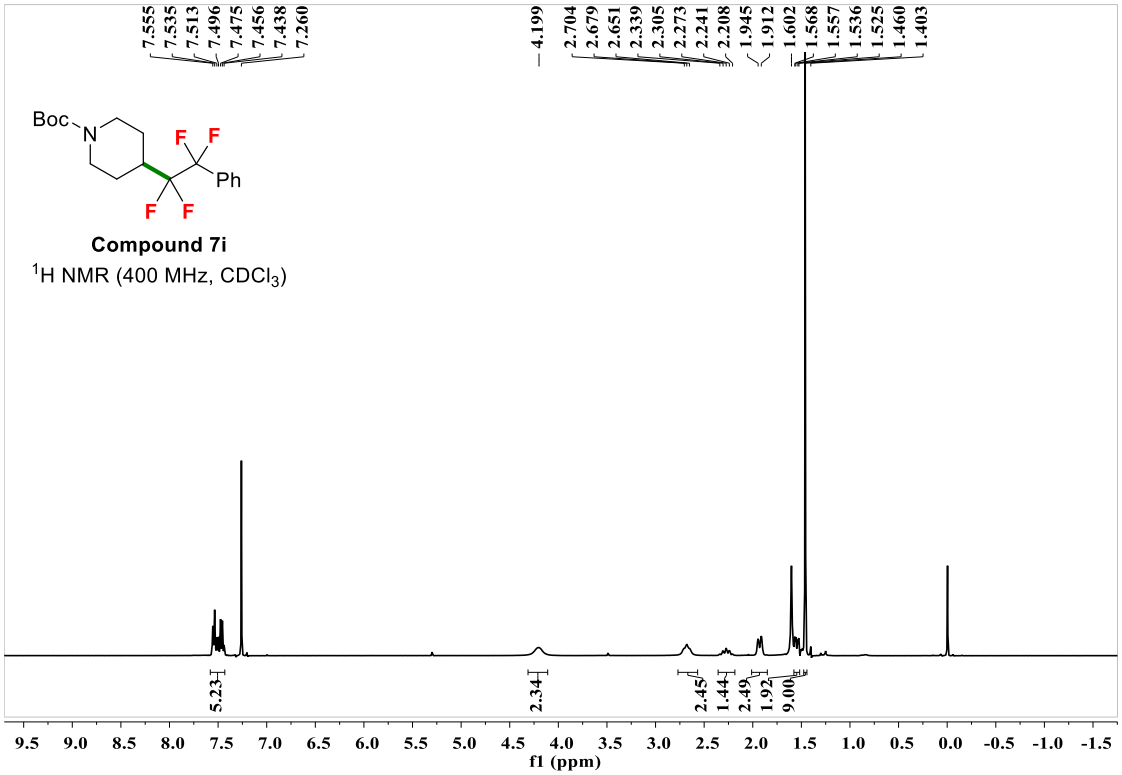
(4,4-Difluoro-3-methylbutyl)benzene (6l).

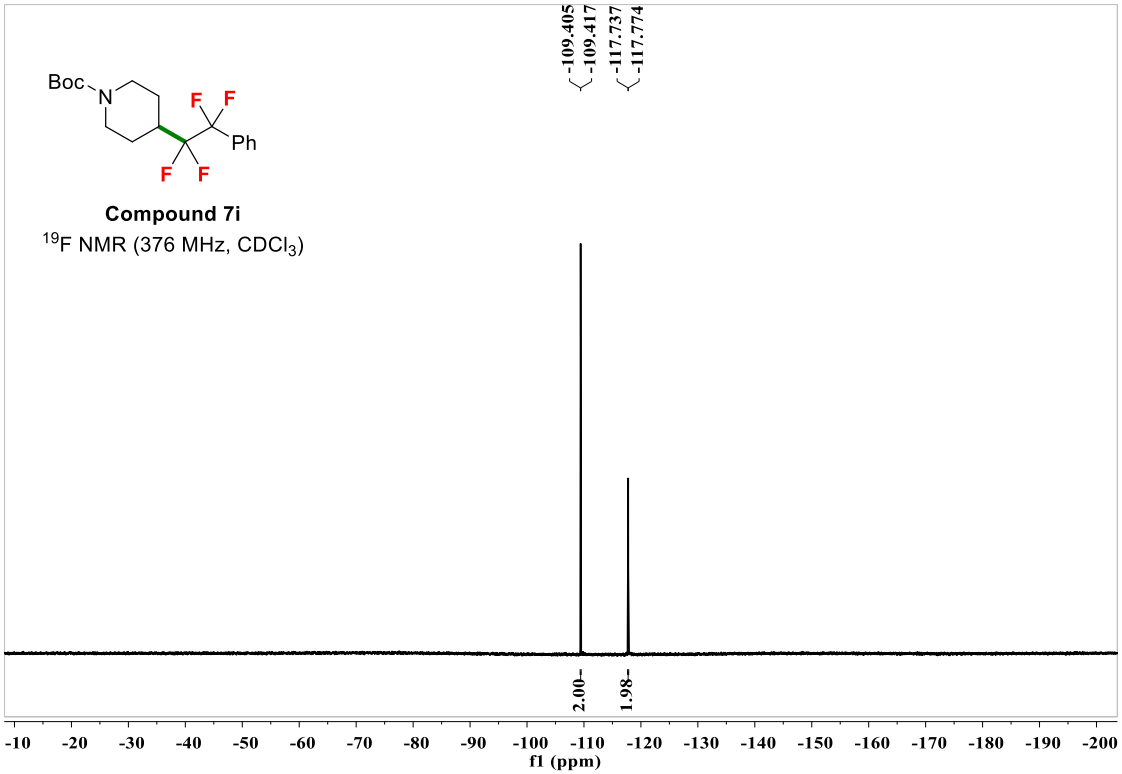


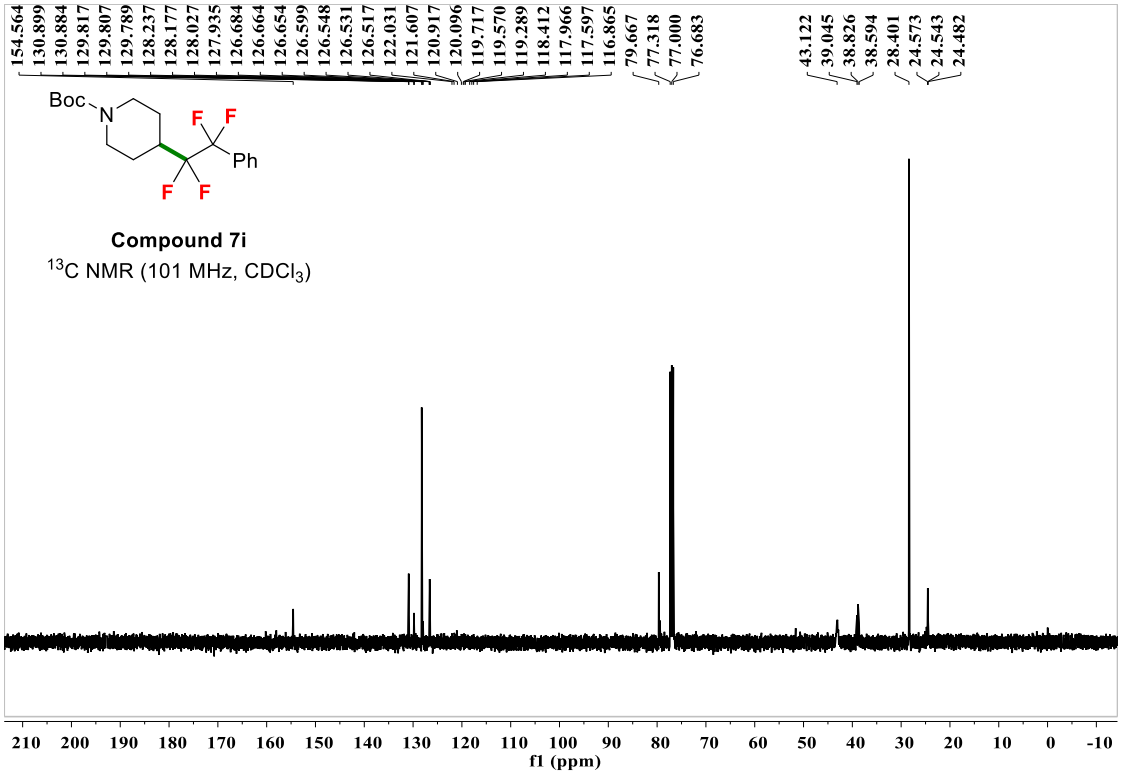

-122.148
-122.184
-122.299
-122.335
-122.884
-122.920
-123.035
-123.071
-123.702
-123.746
-123.854
-123.897
-124.438
-124.481
-124.589
-124.633
CF2H
Compound 6l
19F NMR (376 MHz, CDCl3)
1.00
1.02
-121
-122
-123
-124
-125
f1 (ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


141.555
128.436
128.298
125.990
121.591
119.181
116.772
77.318
77.000
76.683
36.873
36.680
36.487
32.810
31.461
31.420
31.376
29.702
12.325
12.272
12.219
CF2H
Compound 6l
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

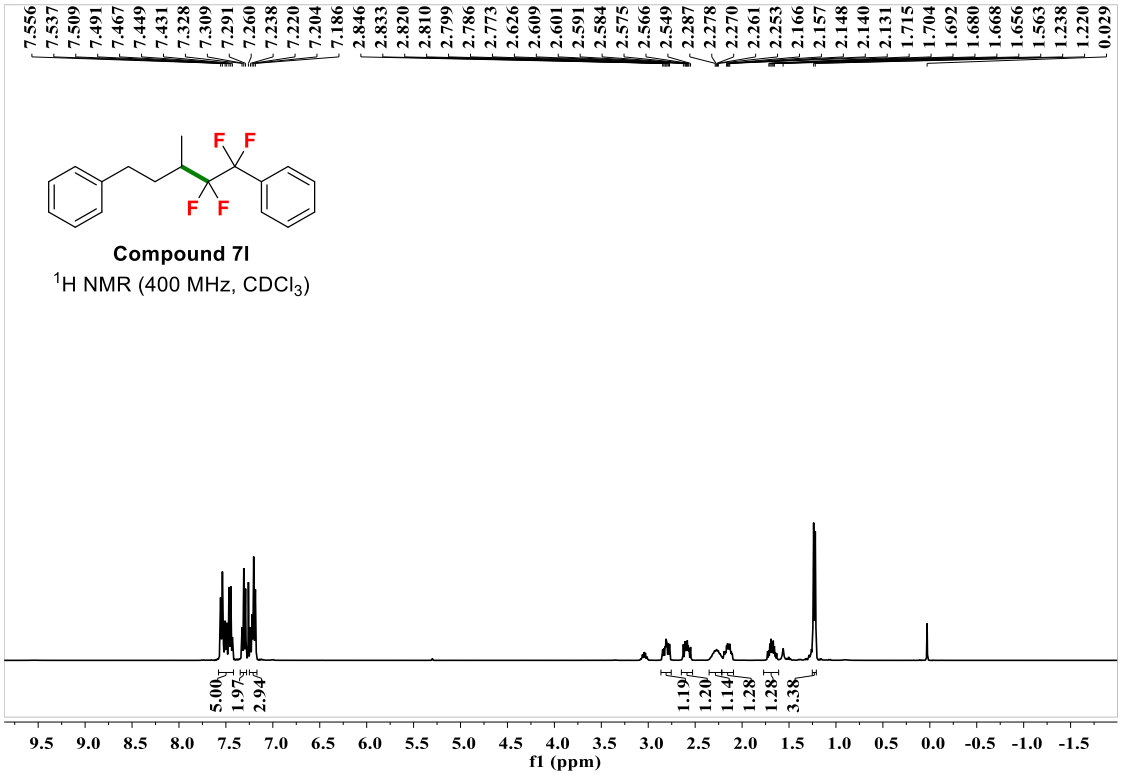
Tert-butyl 4-(1,1,2,2-tetrafluoro-2-phenylethyl)piperidine-1-carboxylate (7i).

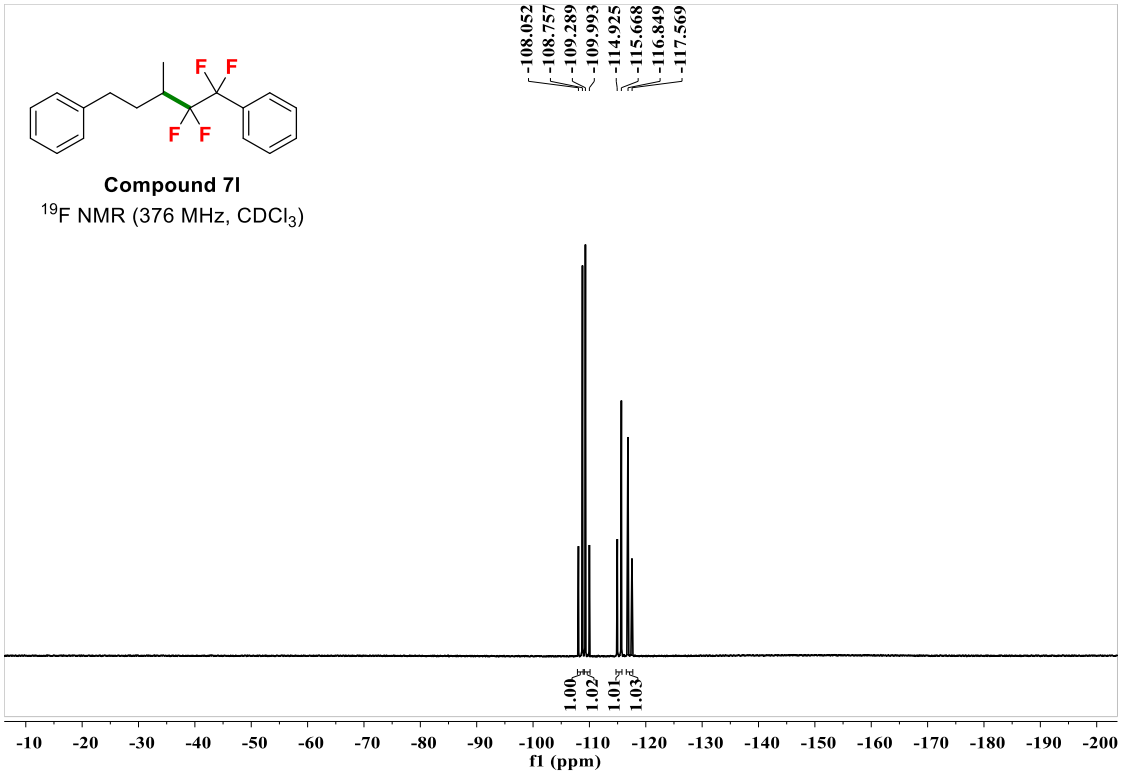


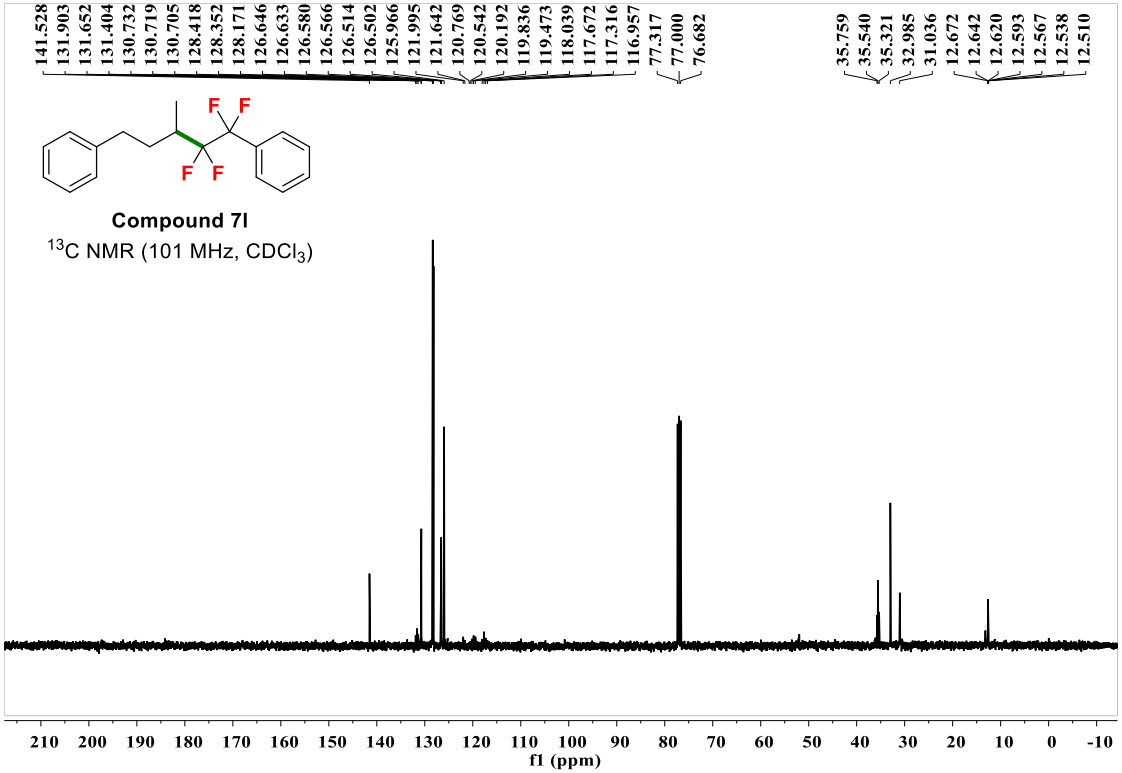




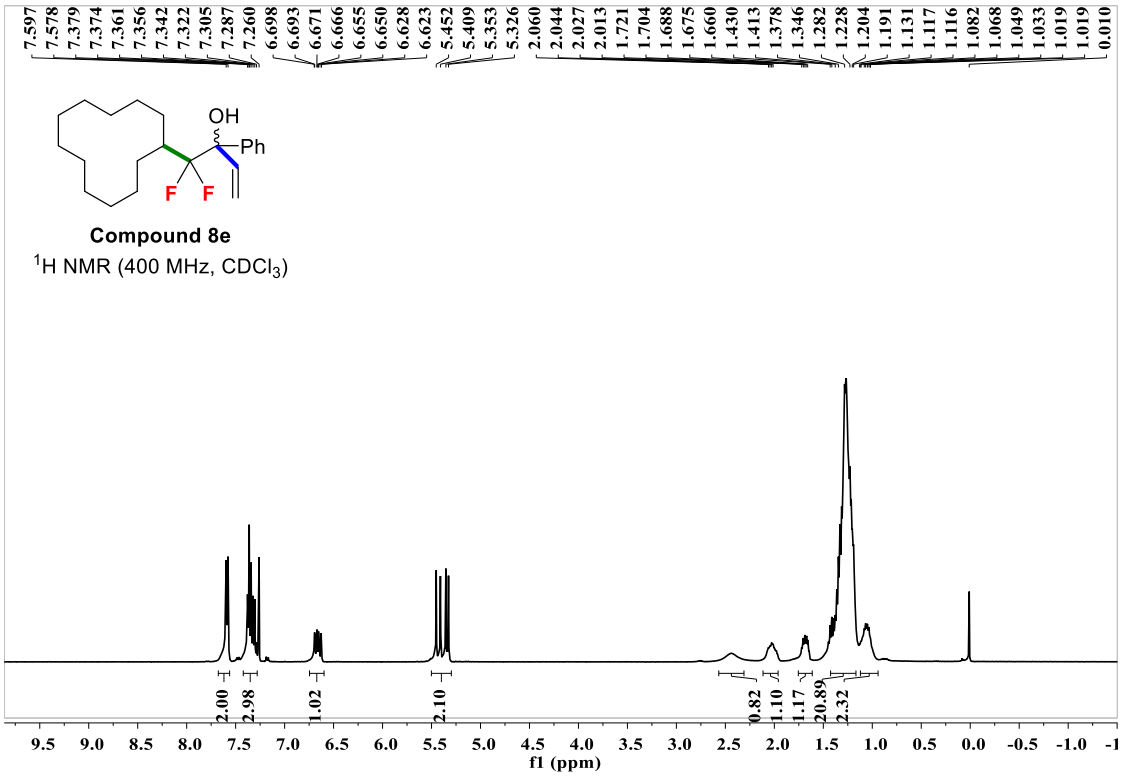
(1,1,2,2-tetrafluoro-3-methylpentane-1,5-diyl)dibenzene (7l).

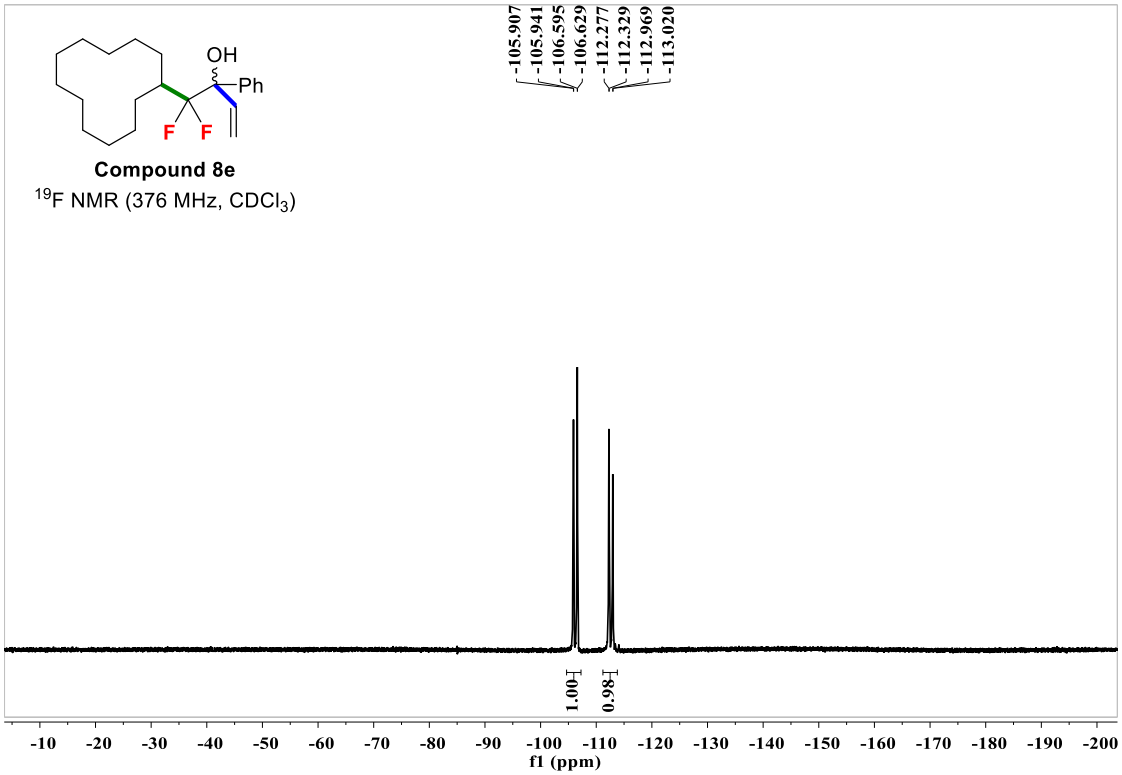


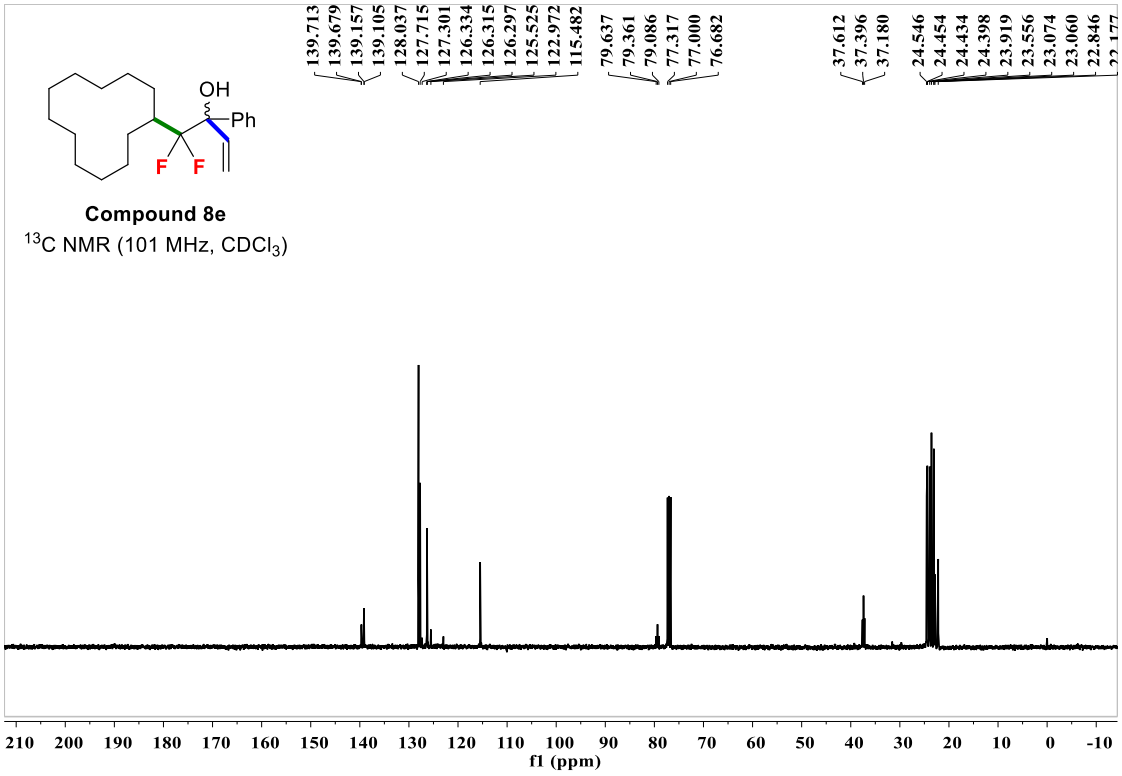

-108.052
-108.757
-109.289
-109.993
-114.925
-115.668
-116.849
-117.569
F F
F F
Compound 7l
19F NMR (376 MHz, CDCl3)
1.00
1.02
1.01
1.03
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


141.528
131.903
131.652
131.404
130.732
130.719
130.705
128.418
128.352
128.171
126.646
126.633
126.580
126.566
126.514
126.502
125.966
121.995
121.642
120.769
120.542
120.192
119.836
119.473
118.039
117.672
117.316
116.957
77.317
77.000
76.682
35.759
35.540
35.321
32.985
31.036
12.672
12.642
12.620
12.593
12.567
12.538
12.510
F F
F F
Compound 7l
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

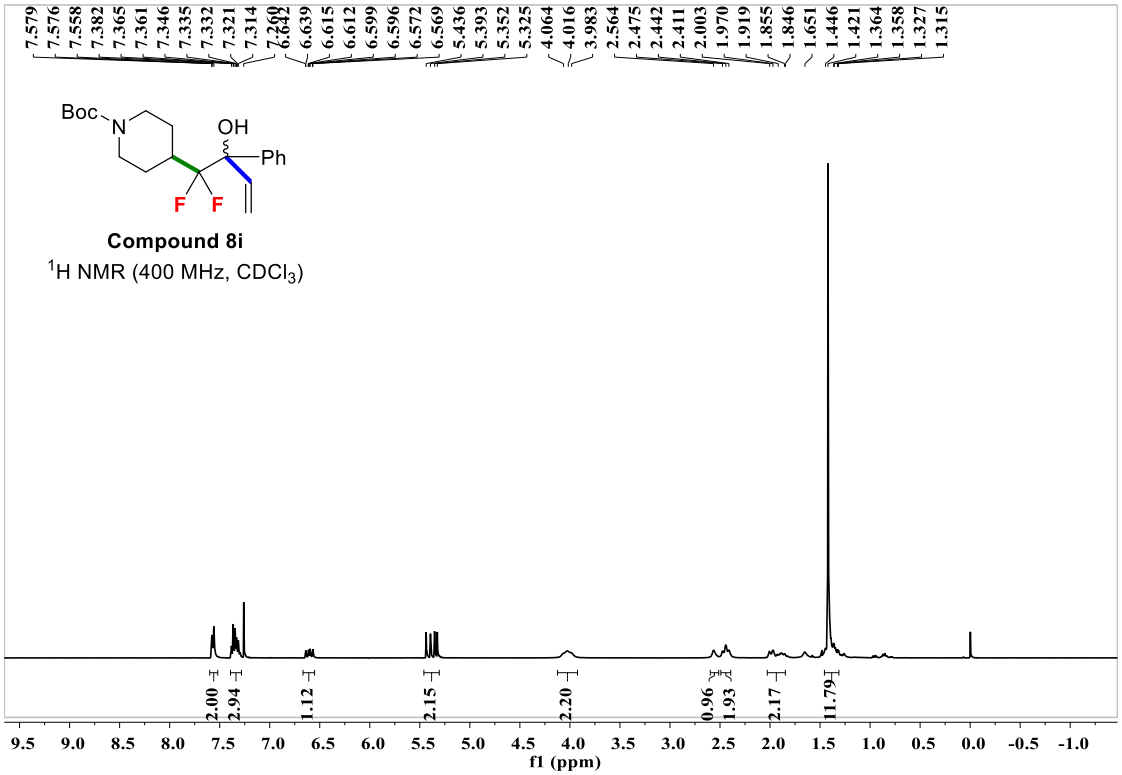
1-Cyclododecyl-1,1-difluoro-2-phenylbut-3-en-2-ol (8e).

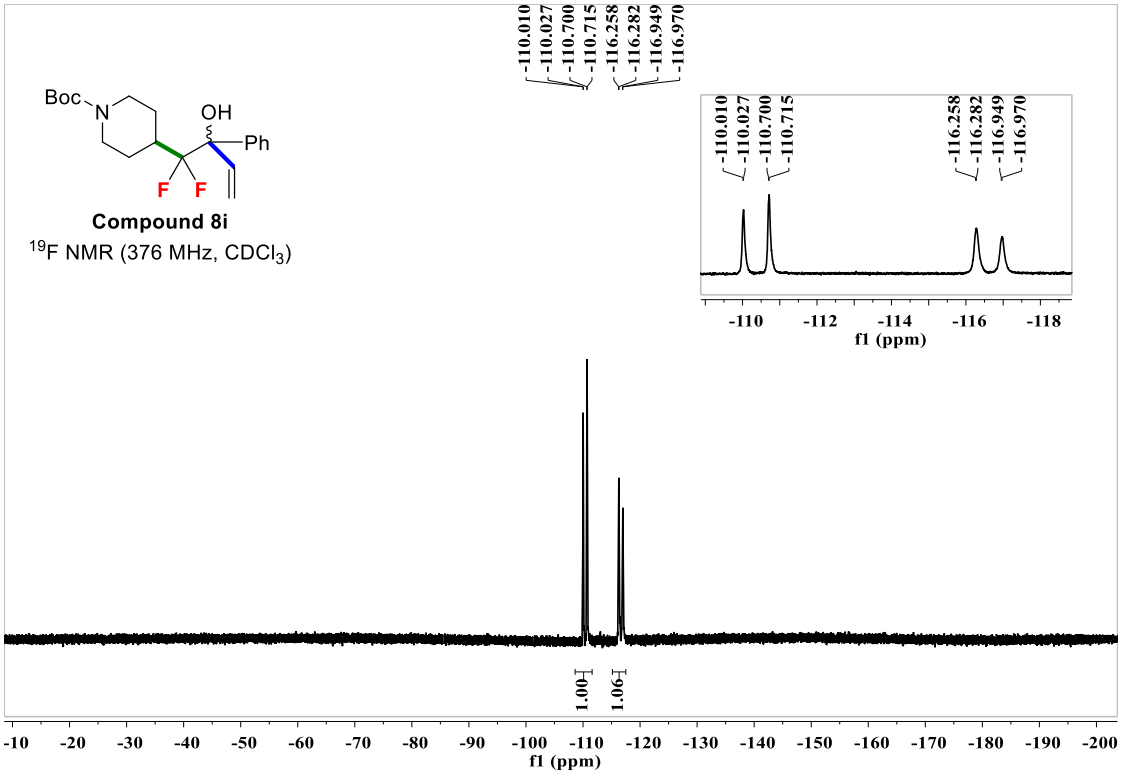


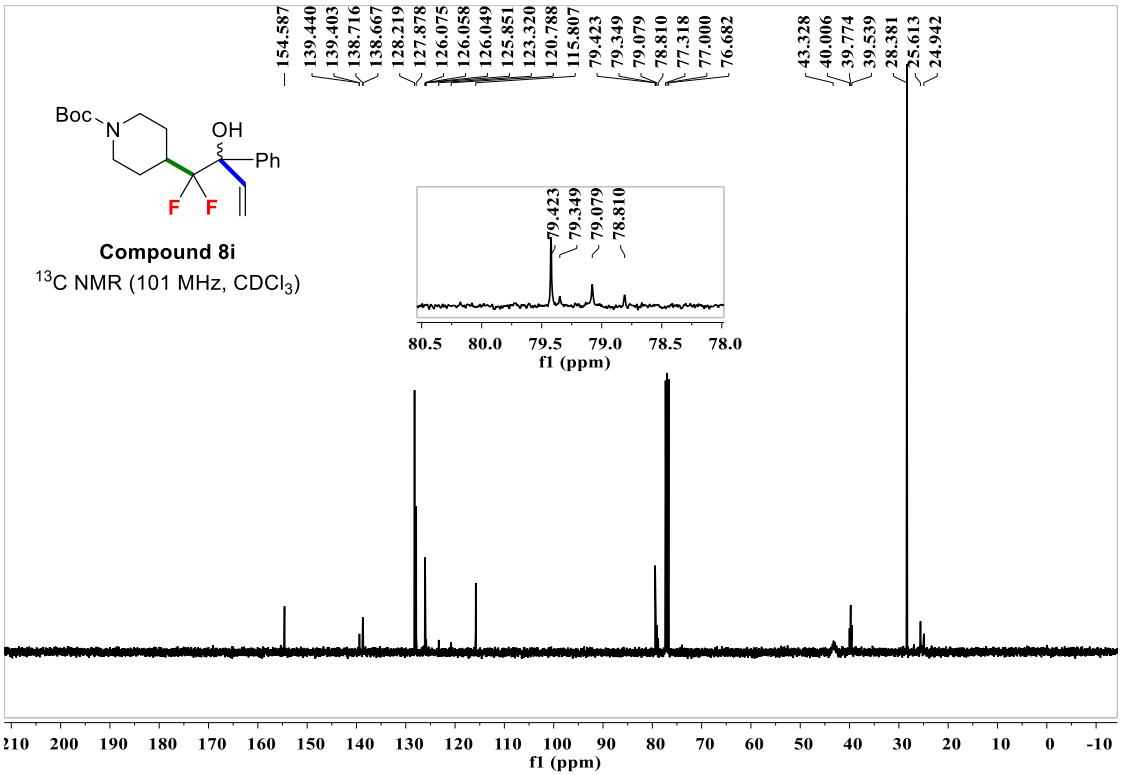




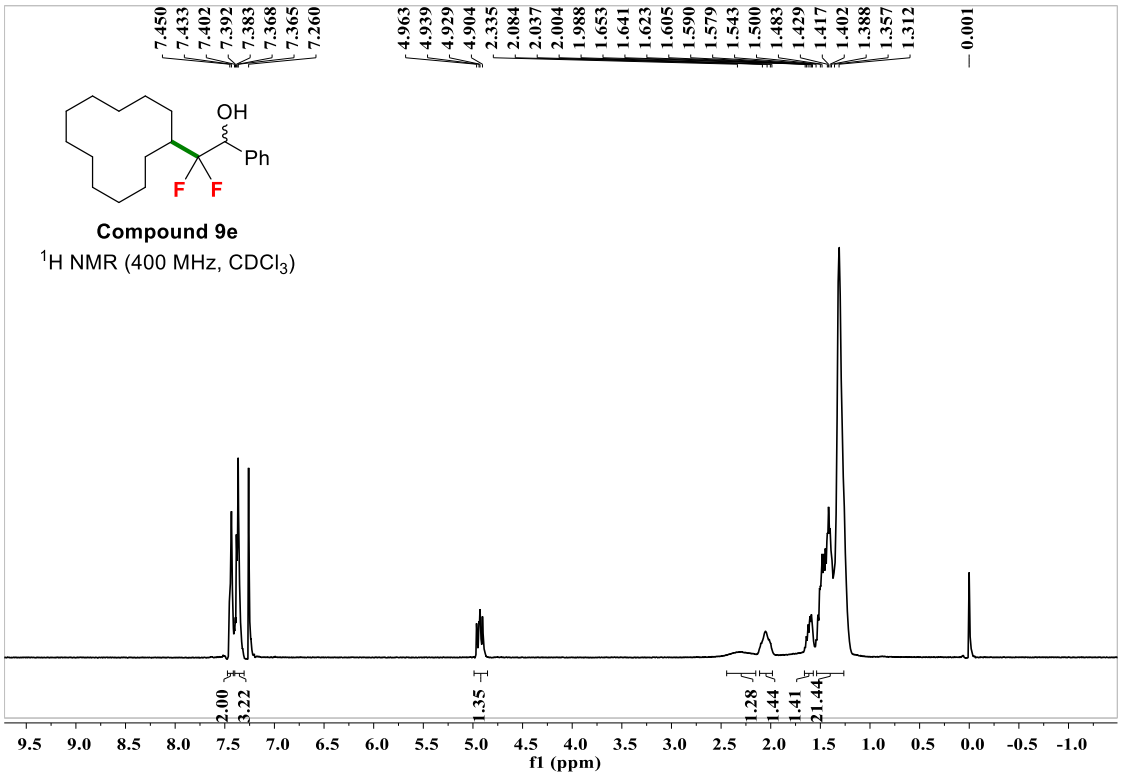
Tert-butyl 4-(1,1-difluoro-2-hydroxy-2-phenylbut-3-en-1-yl)piperidine-1-carboxylate (8i).

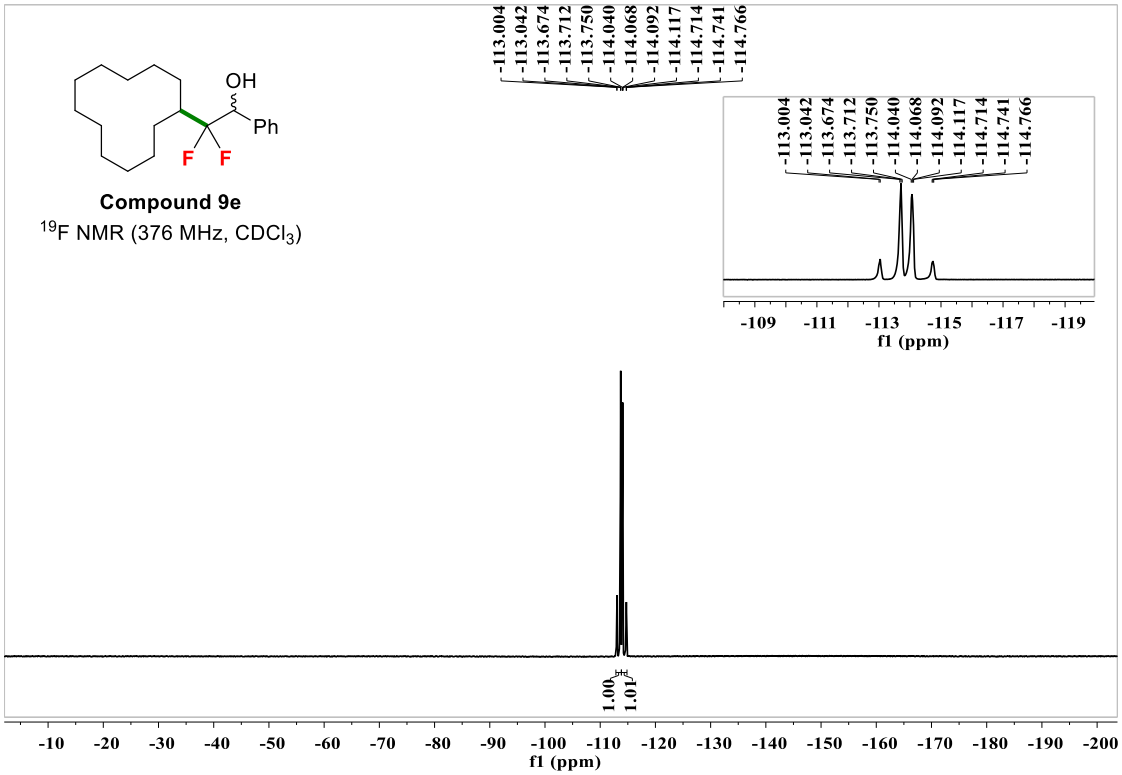


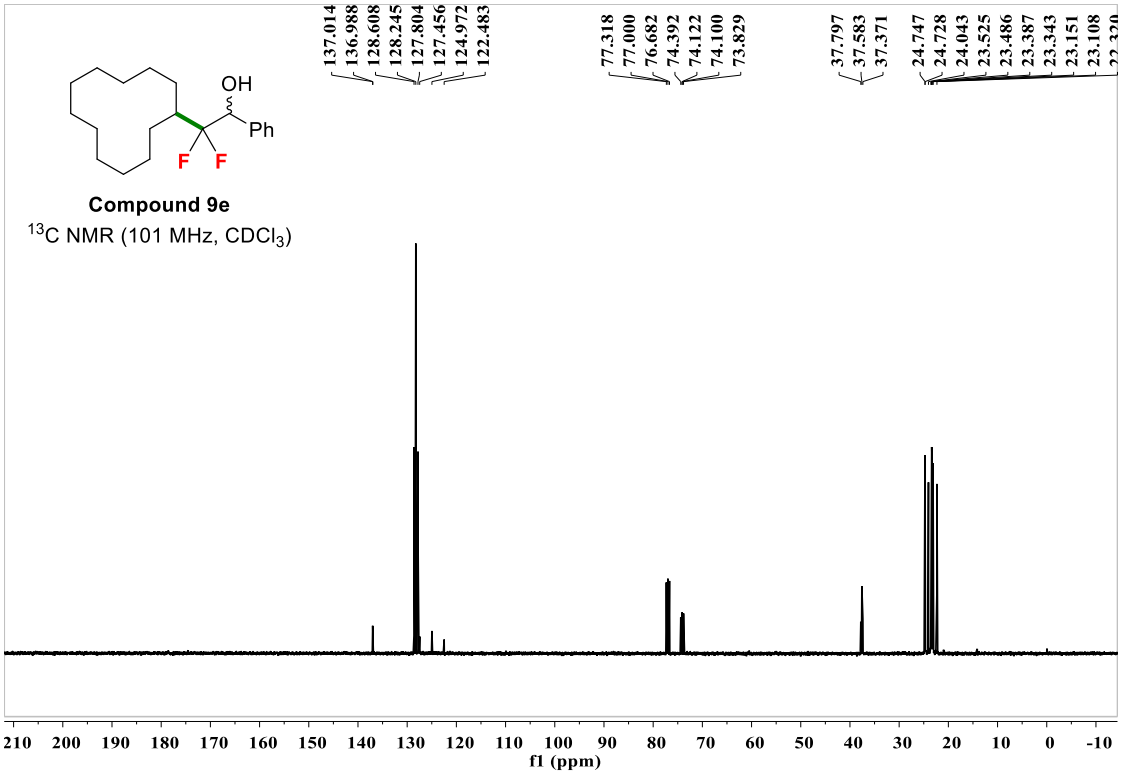

-110.010
-110.027
-110.700
-110.715
-116.258
-116.282
-116.949
-116.970
Boc
N
OH
Ph
F F
Compound 8i
19F NMR (376 MHz, CDCl3)
-110.010
-110.027
-110.700
-110.715
-116.258
-116.282
-116.949
-116.970
-110 -112 -114 -116 -118
f1 (ppm)
1.00
1.06
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


154.587
139.440
139.403
138.716
138.667
128.219
127.878
126.075
126.058
126.049
125.851
123.320
120.788
115.807
79.423
79.349
79.079
78.810
77.318
77.000
76.682
43.328
40.006
39.774
39.539
28.381
25.613
24.942
Boc
N
OH
Ph
F F
Compound 8i
13C NMR (101 MHz, CDCl3)
79.423
79.349
79.079
78.810
80.5 80.0 79.5 79.0 78.5 78.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

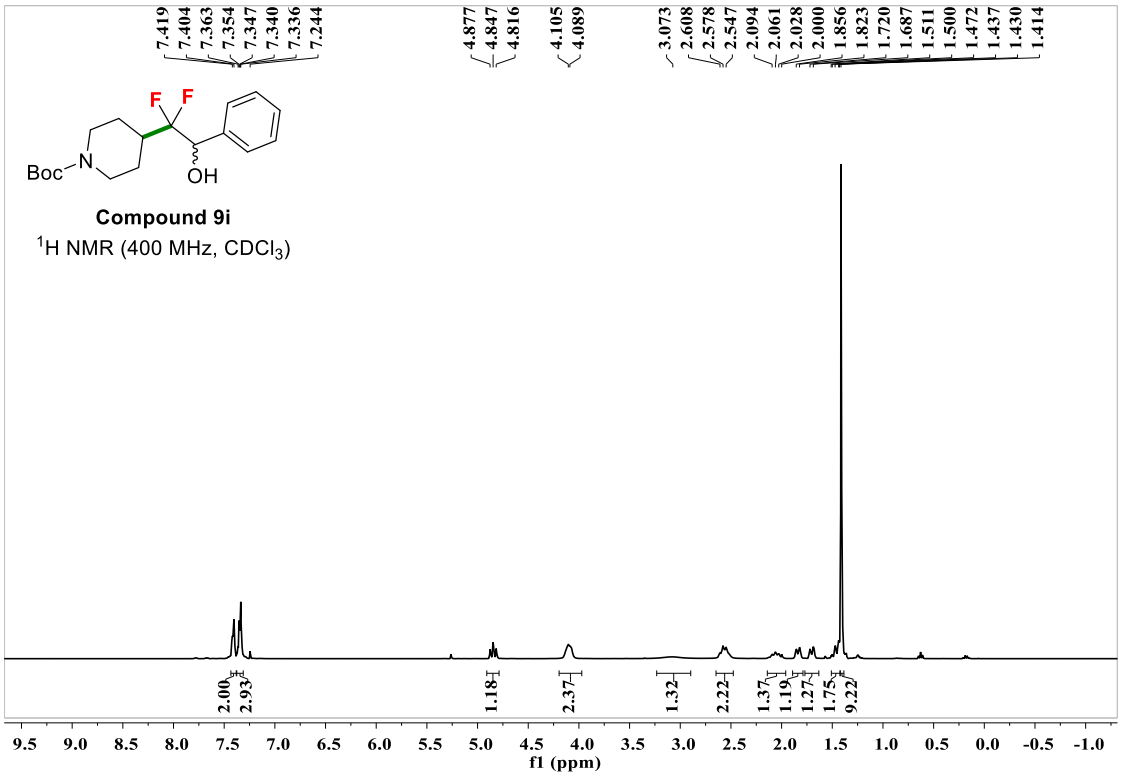
2-Cyclododecyl-2,2-difluoro-1-phenylethan-1-ol (9e).

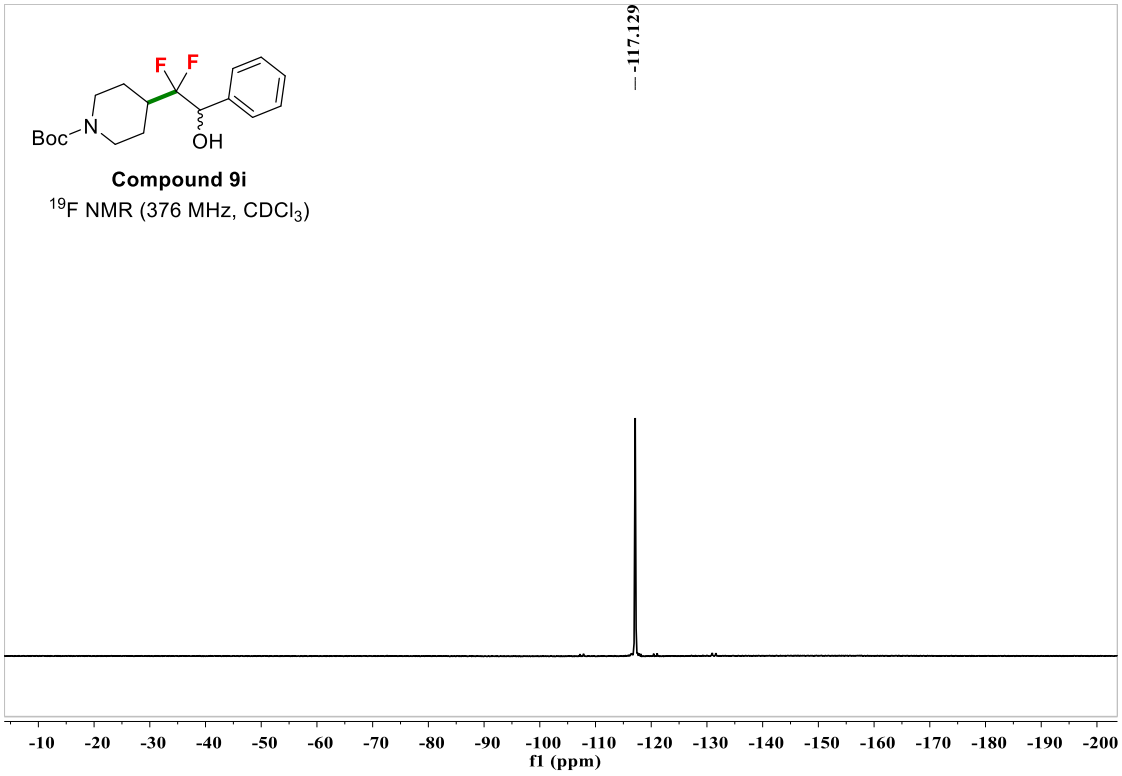






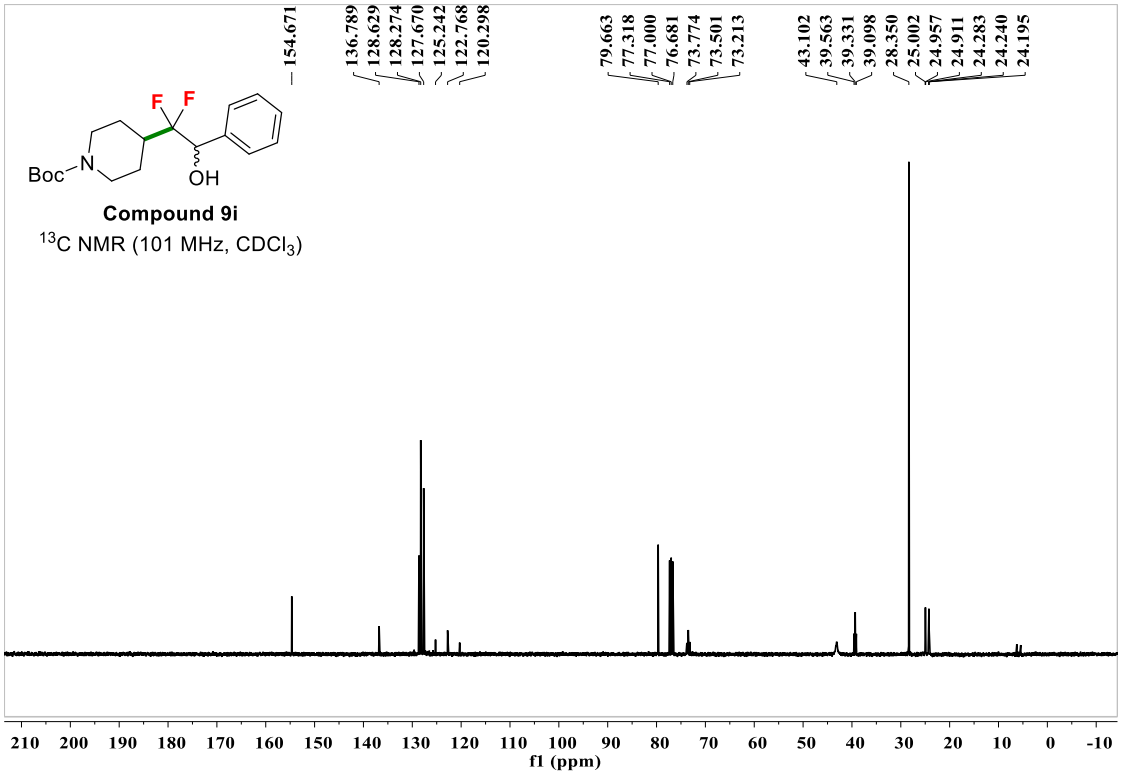
Tert-butyl 4-(1,1-difluoro-2-hydroxy-2-phenylethyl)piperidine-1-carboxylate (9i).





Compound 9i

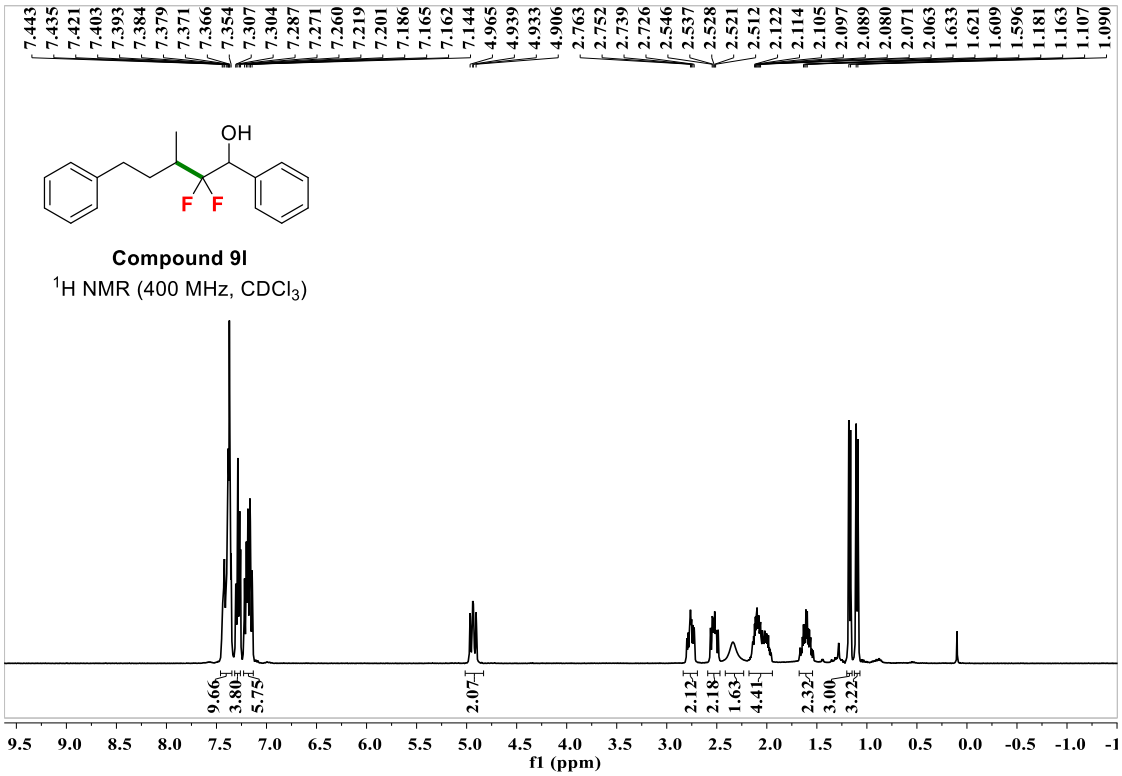
^{19}F NMR (376 MHz, $CDCl_3$)

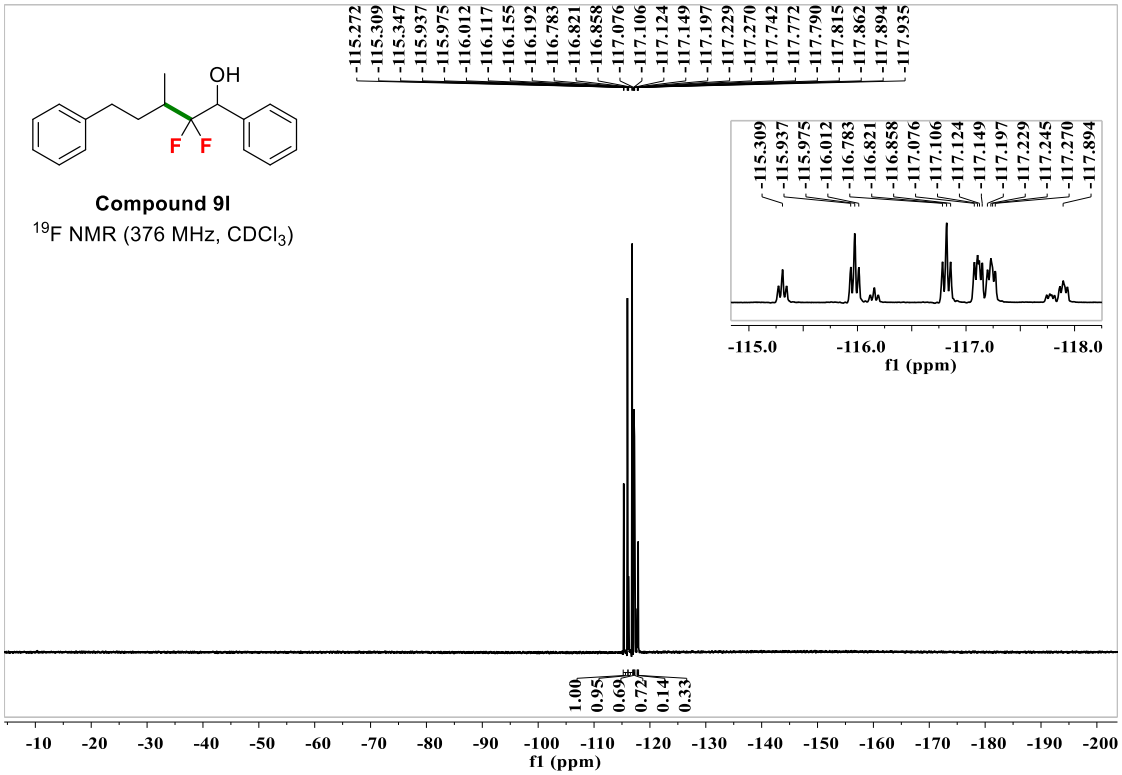


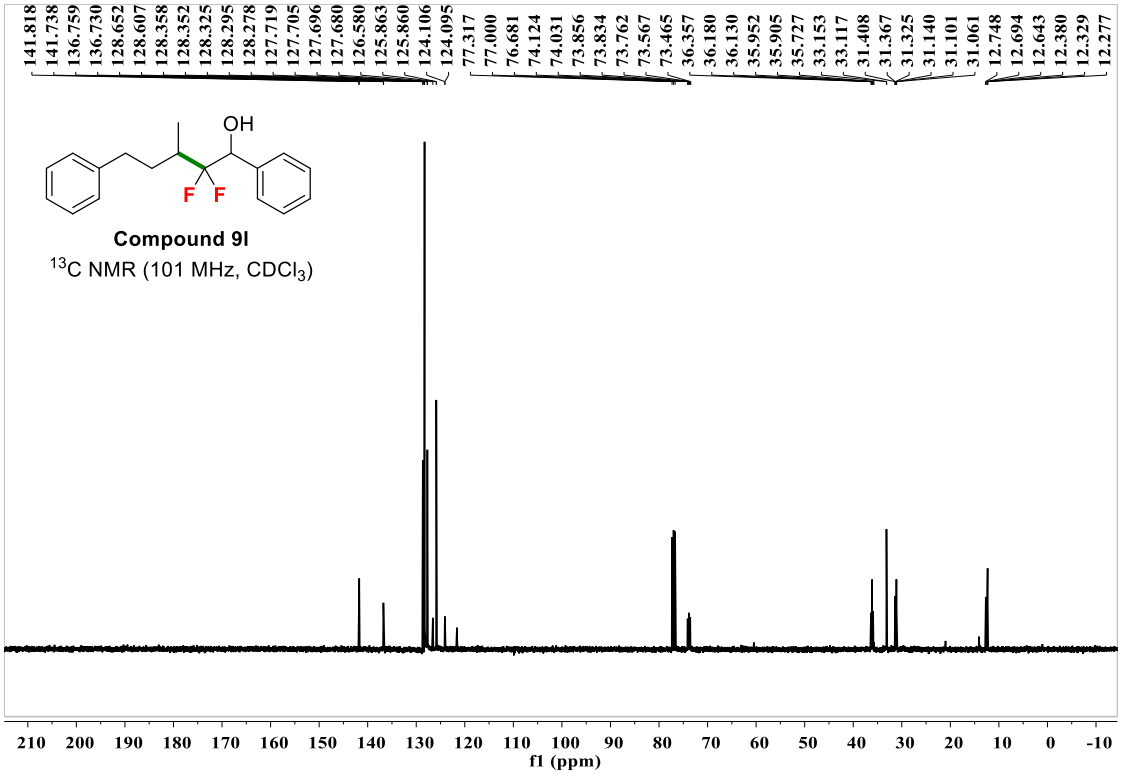
Compound 9i

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

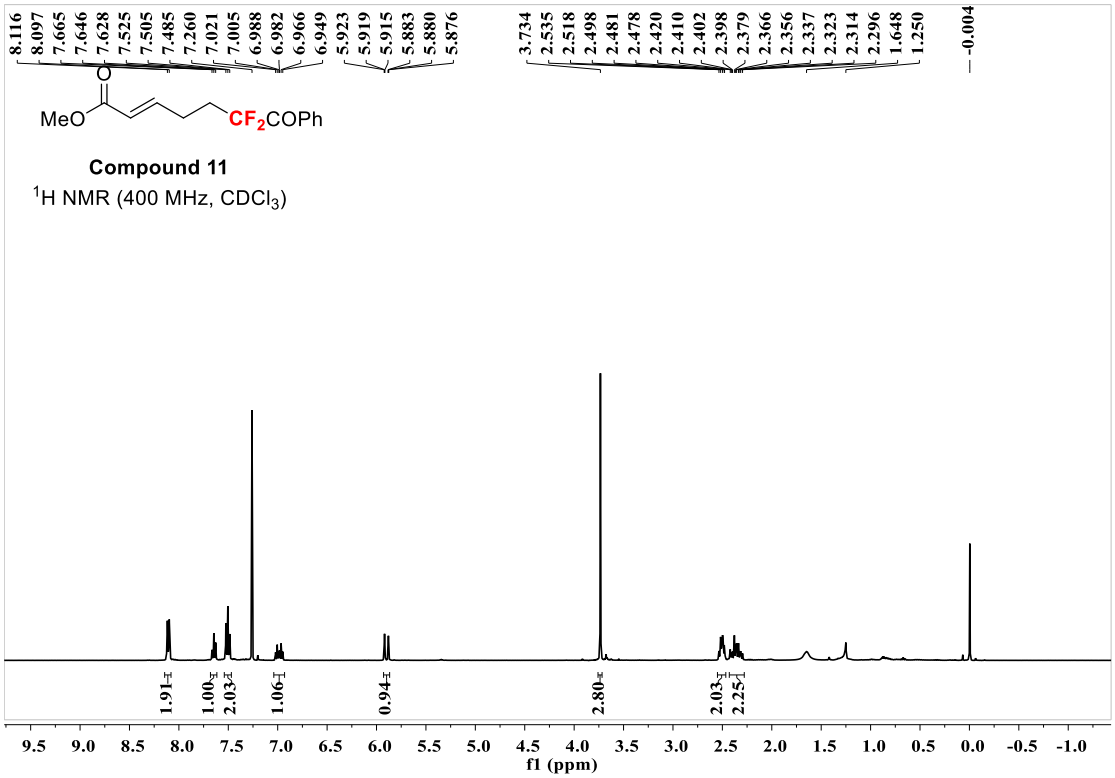
2,2-Difluoro-3-methyl-1,5-diphenylpentan-1-ol (9l).

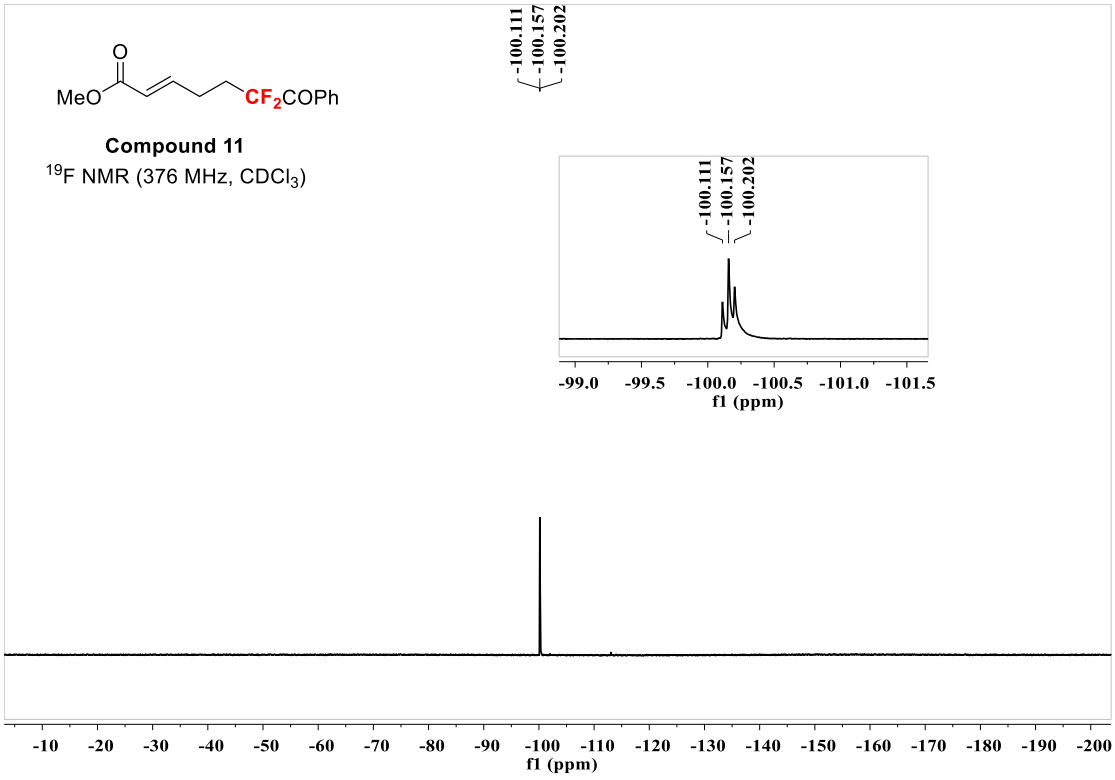


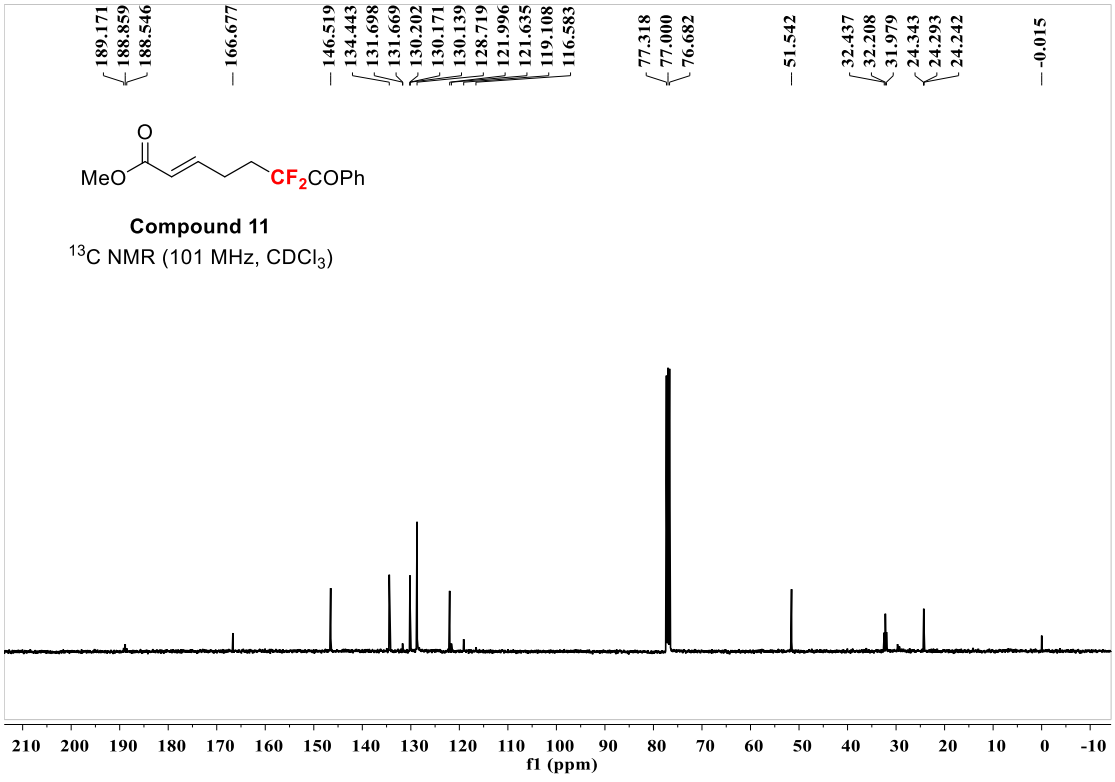




Methyl (E)-6,6-difluoro-7-oxo-7-phenylhept-2-enoate (11).




-100.111
-100.157
-100.202
MeO
CF2COPh
Compound 11
19F NMR (376 MHz, CDCl3)
-99.0 -99.5 -100.0 -100.5 -101.0 -101.5
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


189.171
188.859
188.546
166.677
146.519
134.443
131.698
131.669
130.202
130.171
130.139
128.719
121.996
121.635
119.108
116.583
77.318
77.000
76.682
51.542
32.437
32.208
31.979
24.343
24.293
24.242
-0.015
MeO
CF2COPh
Compound 11
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)