

Supporting Information

Visible-light-promoted defluorinated alkylation of trifluoromethyl alkenes initiated by radical [1,2]-Brook rearrangement: facile synthesis of gem-difluoro homoallylic alcohol derivatives

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1. General Information

All reactions were performed under nitrogen atmosphere in flame dried flasks. All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^1H , ^{13}C , ^{19}F spectra were recorded with, Varian 500 MHz (Inova-500), or Bruker 600 MHz (Avance-600) instrument. All ^1H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm (CDCl_3). All ^{13}C NMR spectra are decoupled and reported in ppm relative to the solvent signal at 77.16 ppm (CDCl_3). High-resolution mass spectra HRMS (ESI-TOF) were recorded on Bruker microtof. Compounds were visualized by irradiation with UV light, or stained with iodine/silica gel, or potassium permanganate. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 \times 20 cm, 1000 microns, from Yantai Jiang you Silica Gel Development Co., Ltd.) and visualized with UV light.

Materials. Reaction solvents THF and toluene were distilled over sodium and stored under nitrogen atmosphere. While DCM, DCE and CH_3CN was distilled over CaH_2 and stored under nitrogen atmosphere. Compounds **1a-1m** and **2a-2u** were known and prepared according to the previously reported procedures.^{S1-S3} All other commercial reagents and solvents were purchased from Energy-Chemical Ltd, and used as received unless otherwise noted.

2. Detailed Optimization Studies

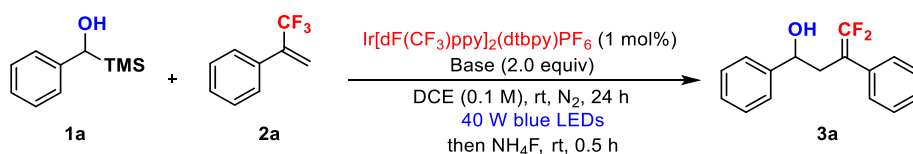
Table S1. Screening of photocatalysts^a



Entry	Photocatalyst (%)	Yield (%) ^b
1	Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆ (1)	81
2	[Ir(ppy) ₂ (dtbbpy)]PF ₆ (1)	49
3	[Ir(ppy) ₃]PF ₆ (1) (1)	trace
4	Ru(bpy) ₃ (PF ₆) ₂ (1)	7
5	9-Fluorenone (5)	NR
6	Mes-Acr ⁺ ClO ₄ ⁻ (5)	NR
7	EosinY (5)	NR

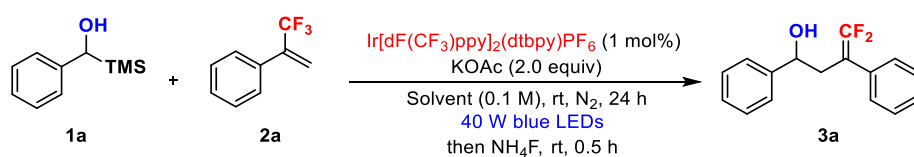
^aReactions were run with **1a** (0.1 mmol, 1 equiv), **2a** (0.2 mmol, 2 equiv), photocatalyst (1 mol%), KOAc (0.2 mmol, 2 equiv) in 1 mL of DCE was irradiated with 40 W blue LEDs at room temperature under N₂ for 24 h. The reaction mixture was quenched with saturated NH₄F/MeOH solution and stirred for 30 min. ^bIsolated yields are provided.

Table S2. Screening of base^a



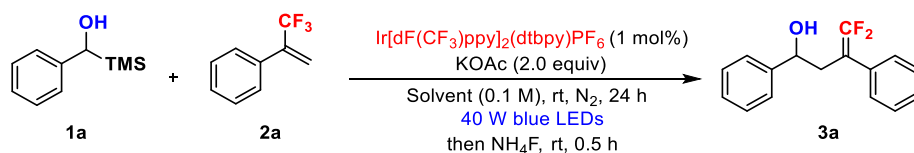
Entry	Base (x equiv)	Yield (%) ^b
1	CsOAc (2)	23
2	NaOAc (2)	10
3	NH ₄ OAc (2)	25
5	Na ₂ CO ₃ (2)	12
6	K ₂ CO ₃ (2)	32
7	Li ₂ CO ₃ (2)	32
8	KOPiv (2)	13
9	Et ₃ N (2)	trace
10	KOAc (1)	41
11	KOAc (1.5)	54
12	KOAc (2.5)	70

^aReactions were run with **1a** (0.1 mmol, 1 equiv), **2a** (0.2 mmol, 2 equiv), photocatalyst (1 mol%), Base (x equiv) in 1 mL of DCE was irradiated with 40 W blue LEDs at room temperature under N₂ for 24 h. The reaction mixture was quenched with saturated NH₄F/MeOH solution and stirred for 30 min. ^bIsolated yields are provided.

Table S3. Screening of solvent and 2a^a

Entry	2a (x equiv)	Solvent	Yield (%) ^b
1	2	DCM	41
2	2	CH ₃ CN	10
3	2	DMSO	29
5	2	DMA	10
6	2	Acetone	24
7	2	Tol	14
8	3	DCE	83
9	2.5	DCE	79
10	1.5	DCE	59
11	1.3	DCE	54
12	1.0	DCE	38

^aReactions were run with **1a** (0.1 mmol, 1 equiv), **2a** (0.2 mmol, 2 equiv), photocatalyst (1 mol%), Base (x equiv) in 1 mL of DCE was irradiated with 40 W blue LEDs at room temperature under N₂ for 48 h. The reaction mixture was quenched with saturated NH₄F/MeOH solution and stirred for 30 min. ^bIsolated yields are provided.

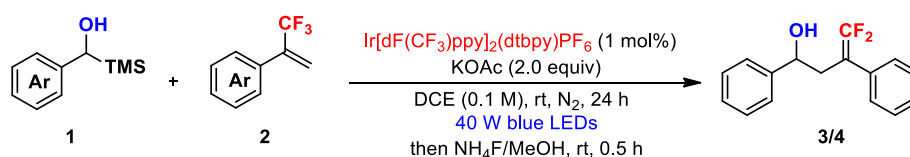
Table S4. Control experiments^a

Entry	<i>hν</i>	Photocatalyst	KOAc	Yield (%) ^b
1 ^c	-	+	+	NR
2 ^d	+	-	+	NR
3 ^e	+	+	-	5%

^aReactions were run with **1a** (0.1 mmol, 1 equiv), **2a** (0.2 mmol, 2 equiv), photocatalyst (1 mol%), Base (x equiv) in 1 mL of DCE was irradiated with 40 W blue LEDs at room temperature under N₂ for 24 h. The reaction mixture was quenched with saturated NH₄F/MeOH solution and stirred for 30 min. ^bIsolated yields are provided. ^cWithout visible light irradiation. ^dWithout photocatalyst. ^eWithout KOAc.

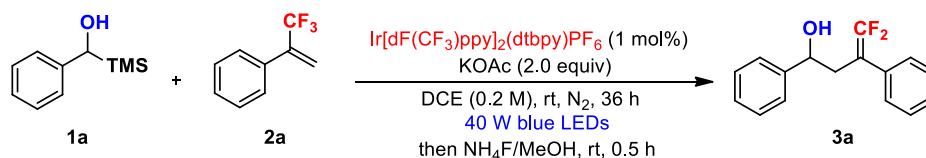
3. Experimental Procedures

a) General Procedure for 3/4



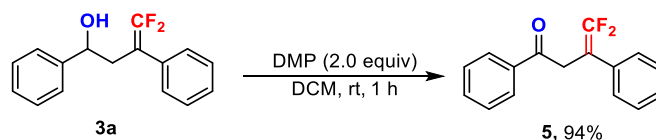
In a nitrogen-filled glovebox, a flame-dried seal reaction tube equipped with a teflon-coated magnetic stir bar was charged with phenyl(trimethylsilyl)methanol **1a** (18 mg 0.1 mmol, 1.0 equiv), KOAc (19.6 mg, 2.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.1 mg, 0.01 equiv.) and 1.0 mL 1,2-dichloroethane were added to the tube in sequence, followed by (3,3,3-trifluoroprop-1-en-2-yl)benzene (34.4 mg, 2.0 equiv.). Then the vial was sealed and exposed to blue LEDs at room temperature with stirring for 24 hours. The reaction mixture was quenched with saturated NH₄F/MeOH solution and stirred for another 30 min, after extracted with CH₂Cl₂ (3×10 mL) and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

b) Gram-scale experiment.



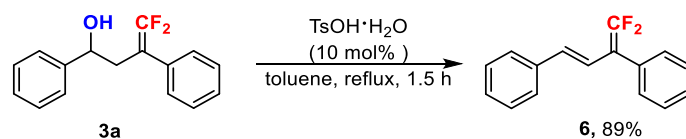
In a nitrogen-filled glovebox, a flame-dried seal reaction tube equipped with a teflon-coated magnetic stir bar was charged with phenyl(trimethylsilyl)methanol **1a** (900 mg 5 mmol, 1.0 equiv), KOAc (980 mg, 2.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (55 mg, 0.01 equiv.) and 25 mL 1,2-dichloroethane were added to the tube in sequence, followed by (3,3,3-trifluoroprop-1-en-2-yl)benzene **2a** (1.5 g, 1.8 equiv). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 36 hours. The reaction mixture was quenched with saturated NH₄F/MeOH solution and stirred for 30 min, after extracted with CH₂Cl₂ (3×50 mL) and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

c) General Procedure for 5



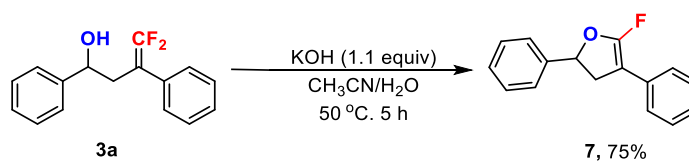
In a separated flask charged with the **3a** (52 mg, 0.2 mmol) and DCM (1.0 mL), DMP (170 mg 0.4 mmol, 2.0 equiv) was added dropwise and stirred at room temperature. Monitored by TLC until full conversion to the product was observed, the saturated sodium thiosulfate was added to the mixture. The mixture was filtrated through celite. Then the filtrate was extracted with CH₂Cl₂, and concentrated under reduced pressure. The residue was chromatographed on silica gel to afford the product **5**.

d) General Procedure for 6



A separate flask was charged with the requisite **3a** (52 mg, 0.2 mmol), toluene (5.0 mL) and *p*-toluenesulfonic acid monohydrate (10 mol%) were added sequentially. Then the reaction mixture was stirred at room temperature for 2 min. Subsequently, the resultant mixture was heated and refluxed for 1.5 h. The mixture was then cooled to room temperature, diluted with CH_2Cl_2 , washed with brine, dried over NaSO_4 , filtrated and concentrated *in vacuo*. The residue was chromatographed on silica gel to afford the product **6**.

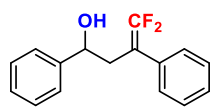
e) General Procedure for 7



A separate flask was charged with the requisite **3a** (52 mg, 0.2 mmol), acetonitrile (2.0 mL), water (50 μL) and KOH (12.3 mg, 0.22 mmol). After the reaction mixture was stirred at room temperature for 2 min, the resultant mixture was then heated to 50 °C with stirring, and monitored by TLC until full conversion to the product was observed. The mixture was then cooled to room temperature, filtrated through celite, and concentrated. The residue was chromatographed on silica gel to afford the product **7**.

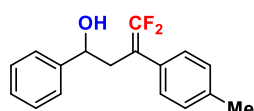
4. Analytical data of New Compounds

4,4-Difluoro-1,3-diphenylbut-3-en-1-ol (**3a**)



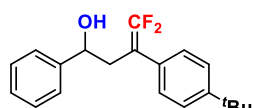
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3a** as colorless oil (21.1 mg, 81% yield), TLC: R_f = 0.16 (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.37 (t, J = 7.8 Hz, 2H), 7.35 – 7.24 (m, 8H), 4.63 (t, J = 7.2 Hz, 1H), 2.92 – 2.87 (m, 1H), 2.79 – 2.75 (m, 1H), 1.87 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.7 (dd, J = 287.7, 285.5 Hz), 143.6, 133.4, 128.7, 128.6, 128.5 (t, J = 3.0 Hz), 128.0, 127.6, 126.0, 89.7 (dd, J = 18.8, 17.4 Hz), 72.5 (t, J = 2.7 Hz), 37.8. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -90.02 (s, 2F) ppm. **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 283.0905, found, 283.0900. **IR**: 3152.54, 2851.42, 1771.12, 1601.98, 1479.92, 1401.47, 1317.87, 1214.12, 1034.65, 871.65, 771.48, 611.41.

4,4-Difluoro-1-phenyl-3-(*p*-tolyl)but-3-en-1-ol (**3b**)



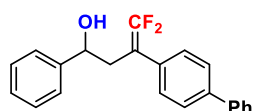
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3b** as colorless oil (17.0 mg, 62% yield), TLC: R_f = 0.17 (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 5H), 7.22 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 4.63 (dd, J = 8.4, 5.4 Hz, 1H), 2.93 – 2.83 (m, 1H), 2.76 – 2.73 (m, 1H), 2.36 (s, 3H), 1.87 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.6 (dd, J = 288.3, 286.2 Hz), 143.7, 137.5, 130.3 (t, J = 3.3 Hz), 129.5, 128.6, 128.4 (t, J = 3.0 Hz), 128.0, 126.0, 89.5 (dd, J = 20.7, 15.3 Hz), 72.5 (t, J = 2.7 Hz), 37.8, 21.3. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -90.32 (d, J = 41.2 Hz), -90.49 (d, J = 40.1 Hz) ppm. **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 297.1061, found, 297.1066. **IR**: 3211.31, 2895.64, 2877.12, 2460.64, 1688.24, 1677.03, 1554.69, 1377.08, 1165.70, 1008.06, 679.01, 612.83, 563.51.

3-(4-(*tert*-Butyl)phenyl)-4,4-difluoro-1-phenylbut-3-en-1-ol (**3c**)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3c** as colorless oil (19.3 mg, 61% yield), TLC: R_f = 0.17 (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 2H), 7.35 – 7.32 (m, 4H), 7.31 – 7.26 (m, 3H), 4.67 (dd, J = 8.0, 5.0 Hz, 1H), 2.92 – 2.86 (m, 1H), 2.80 – 2.75 (m, 1H), 1.89 (s, 1H), 1.35 (s, 9H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.7 (dd, J = 289.2, 286.8 Hz), 150.6, 143.7, 130.2 (t, J = 2.7 Hz), 128.6, 128.1 (t, J = 3.2 Hz), 128.0, 126.0, 125.7, 89.4 (dd, J = 19.8, 15.2 Hz), 72.5 (t, J = 2.9 Hz), 37.8, 34.7, 31.4. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -90.04 (d, J = 40.0 Hz, 1F), -90.15 (d, J = 40.4 Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{20}\text{H}_{22}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 339.1531, found, 339.1533. **IR**: 3405.11, 3031.67, 2923.61, 1732.49, 1605.61, 1490.02, 1454.45, 1265.34, 1120.48, 1046.98, 787.98, 699.23.

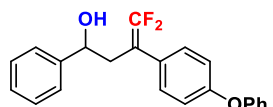
3-([1,1'-Biphenyl]-4-yl)-4,4-difluoro-1-phenylbut-3-en-1-ol (**3d**)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3d** as colorless oil (24.5 mg, 73% yield), TLC: R_f = 0.16 (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.65 – 7.56 (m, 4H), 7.45 (t, J = 7.2 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.39 – 7.25 (m,

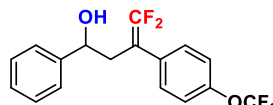
6H), 4.69 (t, $J = 7.2$ Hz, 1H), 2.95 – 2.91 (m, 1H), 2.82 – 2.78 (m, 1H), 1.91 (s, 1H). ^{13}C NMR (150 MHz, Chloroform- d) δ 154.8 (dd, $J = 289.4, 287.3$ Hz), 143.6, 140.6, 140.4, 132.3 (t, $J = 2.9$ Hz), 129.0, 128.9 (t, $J = 3.2$ Hz), 128.7, 128.1, 127.6, 127.4, 127.2, 126.0, 89.4 (dd, $J = 20.6, 15.6$ Hz), 72.5 (t, $J = 2.9$ Hz), 37.7. ^{19}F NMR (565 MHz, Chloroform- d) δ -89.35 (d, $J = 38.7$ Hz, 1F), -89.46 (d, $J = 38.2$ Hz, 1F). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 359.1218, found, 359.1210. IR: 3312.76, 2841.55, 1431.97, 1681.22, 1677.12, 1501.42, 1317.87, 1224.12, 1134.26, 1094.23, 1076.21, 898.03, 762.65, 785.43, 671.43, 661.54.

4,4-Difluoro-3-(4-phenoxyphenyl)-1-phenylbut-3-en-1-ol (**3e**)



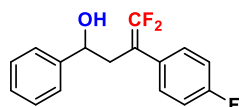
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **3e** as colorless oil (29.6 mg, 84% yield), TLC: $R_f = 0.15$ (Petroleum ether : Ethyl acetate = 40:1) [UV]. ^1H NMR (500 MHz, Chloroform- d) δ 7.40 – 7.26 (m, 9H), 7.15 (t, $J = 7.5$ Hz, 1H), 7.06 (d, $J = 7.5$ Hz, 2H), 7.00 (d, $J = 8.5$ Hz, 2H), 4.68 (t, $J = 6.8$ Hz, 1H), 2.92 – 2.87 (m, 1H), 2.79 – 2.74 (m, 1H), 1.92 (s, 1H). ^{13}C NMR (150 MHz, Chloroform- d) δ 156.9 (d, $J = 9.9$ Hz), 154.6 (t, $J = 287.3$ Hz), 143.6, 130.0, 129.9 (t, $J = 3.2$ Hz), 128.6, 128.0 (d, $J = 5.1$ Hz), 126.0, 123.8, 119.4, 118.7, 89.1 (t, $J = 18.0$ Hz), 72.5 (t, $J = 2.9$ Hz), 37.8. ^{19}F NMR (565 MHz, Chloroform- d) δ -90.20 (s, 2F). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{22}\text{H}_{19}\text{F}_2\text{O}_2$ ($[\text{M} + \text{H}]^+$), 353.1348, found, 353.1355. IR: 3420.85, 3036.01, 2925.09, 1731.25, 1589.27, 1508.57, 1498.42, 1239.42, 1024.26, 842.53, 796.91, 697.83.

4,4-Difluoro-1-phenyl-3-(4-(trifluoromethoxy)phenyl)but-3-en-1-ol (**3f**)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **3f** as colorless oil (31.6 mg, 92% yield), TLC: $R_f = 0.17$ (Petroleum ether : Ethyl acetate = 30:1) [UV]. ^1H NMR (600 MHz, Chloroform- d) δ 7.33 – 7.31 (m, 4H), 7.29 – 7.24 (m, 3H), 7.23 – 7.15 (m, 2H), 4.63 (dd, $J = 7.8, 5.4$ Hz, 1H), 2.91 – 2.86 (m, 1H), 2.77 – 2.72 (m, 1H), 1.91 (s, 1H). ^{13}C NMR (150 MHz, Chloroform- d) δ 154.8 (dd, $J = 289.5, 286.5$ Hz), 148.4, 143.4, 132.2 (t, $J = 4.1$ Hz), 130.0 (t, $J = 3.3$ Hz), 128.7, 128.2, 126.0, 121.1, 120.6 (d, $J = 255.9$ Hz), 88.9 (dd, $J = 21.9, 14.7$ Hz), 72.6 (t, $J = 2.7$ Hz), 37.7. ^{19}F NMR (565 MHz, Chloroform- d) δ -57.83 (s, OCF_3), -89.03 (d, $J = 37.7$ Hz, 1F), -89.36 (d, $J = 37.7$ Hz, 1F). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{13}\text{F}_5\text{NaO}_2$ ($[\text{M} + \text{Na}]^+$), 367.0728, found, 367.0720. IR: 3393.85, 3033.70, 1732.91, 1511.18, 1454.85, 1220.35, 853.32, 700.17, 580.51.

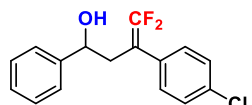
4,4-Difluoro-3-(4-fluorophenyl)-1-phenylbut-3-en-1-ol (**3g**)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3g** as colorless oil (23.6 mg, 83% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. ^1H NMR (600 MHz, Chloroform- d) δ 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 5H), 7.08 – 7.02 (m, 2H), 4.64 – 4.61 (m, 1H), 2.92 – 2.83 (m, 1H), 2.78 – 2.69 (m, 1H), 1.87 (d, $J = 3.0$ Hz, 1H). ^{13}C NMR (150 MHz, Chloroform- d) δ 162.1 (d, $J = 245.4$ Hz), 162.1 (t, $J = 287.3$ Hz), 143.5, 130.2 (ddd, $J = 8.0$ Hz, $J = 6.3$ Hz, $J = 3.0$ Hz), 129.4 (q, $J = 4.0$ Hz), 128.7, 128.1, 126.0, 115.7 (d, $J = 21.3$ Hz), 130.2 (dd, $J = 21.5$ Hz, $J = 15.8$ Hz), 72.5 (t, $J = 2.9$ Hz), 37.9. ^{19}F NMR (565 MHz, Chloroform- d) δ -90.03 (d, $J = 39.8$ Hz, 1F), -90.16 (d, $J = 39.7$ Hz, 1F), -114.33 – -114.38 (m, 1F). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 301.0811, found, 301.0801. IR: 3391.71, 3032.42, 2925.97, 1732.82, 1604.92, 1511.80,

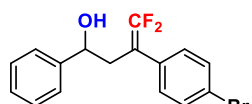
1454.37, 1240.50, 1044.04, 837.97, 701.26, 580.88, 519.28.

3-(4-Chlorophenyl)-4,4-difluoro-1-phenylbut-3-en-1-ol (3h)



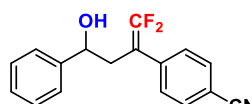
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3h** as colorless oil (25.9 mg, 88% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.32 (dd, $J = 8.4, 6.6$ Hz, 4H), 7.30 – 7.26 (m, 3H), 7.24 (d, $J = 7.8$ Hz, 2H), 4.61 (dd, $J = 8.4, 6.0$ Hz, 1H), 2.89 – 2.84 (m, 1H), 2.75 – 2.70 (m, 1H), 1.90 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.6 (dd, $J = 289.5, 287.3$ Hz), 143.4, 133.4, 132.0 (t, $J = 3.5$ Hz), 129.9 (t, $J = 3.0$ Hz), 128.9, 128.7, 128.2, 125.9, 89.0 (dd, $J = 21.5, 14.6$ Hz), 72.5 (t, $J = 2.9$ Hz), 37.6. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -89.12 (d, $J = 38.4$ Hz, 1F), -89.32 (d, $J = 37.7$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{13}\text{ClF}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 317.0515, found, 317.0510. **IR**: 3385.69, 3031.87, 1730.91, 1493.61, 1454.11, 1315.08, 1242.67, 1092.62, 1014.24, 831.40, 758.10, 701.00, 487.42.

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



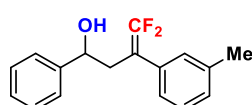
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3i** as colorless oil (31.4 mg, 93% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.34 – 7.32 (m, 4H), 7.29 – 7.27 (m, 3H), 7.24 (d, $J = 8.4$ Hz, 2H), 4.61 (dd, $J = 9.6, 6.0$ Hz, 1H), 2.89 – 2.85 (m, 1H), 2.75 – 2.71 (m, 1H), 1.89 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.6 (dd, $J = 289.7, 287.0$ Hz), 143.4, 133.4, 132.0 (t, $J = 3.5$ Hz), 130.0 (t, $J = 3.3$ Hz), 128.9, 128.7, 128.2, 126.0, 89.0 (dd, $J = 21.7, 14.9$ Hz), 72.5 (t, $J = 3.2$ Hz), 37.6. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -89.12 (d, $J = 36.7$ Hz, 1F), -89.32 (d, $J = 38.4$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{13}\text{BrF}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 361.0010, found, 361.0018. **IR**: 3121.34, 2981.12, 2910.22, 1632.42, 1531.96, 1465.23, 1307.29, 1247.63, 947.51, 865.22, 739.21, 408.32, 554.38.

4-(1,1-Difluoro-4-hydroxy-4-phenylbut-1-en-2-yl)benzonitrile (3j)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 25:1 to afford **3j** as colorless oil (12.8 mg, 45% yield), TLC: $R_f = 0.15$ (Petroleum ether : Ethyl acetate = 25:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.84 – 7.78 (m, 2H), 7.51 – 7.44 (m, 2H), 7.37 – 7.26 (m, 5H), 4.68 – 4.65 (m, 1H), 3.03 – 2.98 (m, 1H), 2.89 – 2.84 (m, 1H), 1.88 (d, $J = 3.0$ Hz, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.8 (dd, $J = 292.5, 289.5$ Hz), 143.1, 133.4, 132.0 (t, $J = 3.5$ Hz), 129.9 (t, $J = 3.0$ Hz), 128.9, 128.7, 128.2, 125.5, 118.6, 89.2 (dd, $J = 24.0, 13.5$ Hz), 72.6 (t, $J = 3.0$ Hz), 37.0. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -89.12 (d, $J = 38.4$ Hz, 1F), -89.32 (d, $J = 37.7$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{13}\text{F}_2\text{NNaO}$ ($[\text{M} + \text{Na}]^+$), 308.0857, found, 308.0850. **IR**: 3243.75, 2933.66, 2360.42, 2341.12, 1735.68, 1603.90, 1532.55, 1508.38, 1434.71, 1284.89, 1226.36, 1048.01, 820.20, 701.65, 475.55.

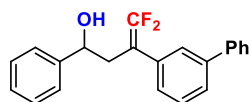
4,4-Difluoro-1-phenyl-3-(*m*-tolyl)but-3-en-1-ol (3k)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3k** as colorless oil (21.1 mg, 77% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.35 – 7.24 (m, 6H), 7.13 – 7.10 (m, 3H), 4.63 (dd, $J = 8.5, 7.5$ Hz, 1H), 2.91 – 2.86

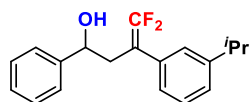
(m, 1H), 2.77 – 2.72 (m, 1H), 2.36 (s, 3H), 1.87 (s, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 154.6 (dd, $J = 288.9, 286.4$ Hz), 143.6, 138.4, 133.3 (t, $J = 3.9$ Hz), 129.3 (t, $J = 3.0$ Hz), 128.6, 128.5, 128.0, 126.0, 125.6 (t, $J = 3.3$ Hz), 89.7 (dd, $J = 21.0, 15.0$ Hz), 72.4 (t, $J = 2.6$ Hz), 37.9, 21.6. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.00 (d, $J = 39.8$ Hz, 1F), -90.29 (d, $J = 39.8$ Hz, 1F). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 297.1061, found, 297.1060. IR: 3422.32, 2932.44, 2826.13, 2462.54, 1732.65, 1619.01, 1478.65, 1322.19, 1254.78, 1088.17, 710.34, 617.42, 513.47.

3-([1,1'-Biphenyl]-3-yl)-4,4-difluoro-1-phenylbut-3-en-1-ol (**3l**)



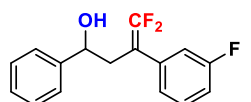
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3l** as colorless oil (29.6 mg, 88% yield), TLC: $R_f = 0.15$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 2H), 7.52 – 7.50 (m, 2H), 7.46 – 7.42 (m, 3H), 7.40 – 7.34 (m, 1H), 7.34 – 7.23 (m, 6H), 4.68 (dd, $J = 8.4, 5.4$ Hz, 1H), 2.96 – 2.92 (m, 1H), 2.82 – 2.78 (m, 1H), 1.89 (s, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 154.8 (dd, $J = 288.0, 286.5$ Hz), 143.6, 141.7, 140.9, 133.93 (t, $J = 4.5$ Hz), 129.1, 129.0, 128.6, 128.1, 127.7, 127.4 (dd, $J = 7.5, 4.5$ Hz), 127.3, 126.5, 126.0, 89.7 (dd, $J = 19.5, 15.0$ Hz), 72.5 (t, $J = 2.9$ Hz), 37.9. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -89.57 (d, $J = 33.9$ Hz, 1F), -89.32 (d, $J = 39.6$ Hz, 1F). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 359.1218, found, 359.1210. IR: 3232.25, 2875.86, 1736.38, 1600.16, 1481.77, 1453.47, 1321.71, 1274.32, 1122.57, 1044.24, 898.00, 791.79, 758.37, 699.40, 607.09.

4,4-Difluoro-3-(3-isopropylphenyl)-1-phenylbut-3-en-1-ol (**3m**)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3m** as colorless oil (18.7 mg, 62% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 6H), 7.17 – 7.13 (m, 3H), 4.64 (dd, $J = 8.5, 5.5$ Hz, 1H), 2.99 – 2.84 (m, 2H), 2.78 – 2.74 (m, 1H), 1.86 (s, 1H), 1.26 (dd, $J = 7.0, 2.0$ Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 154.7 (dd, $J = 289.4, 286.2$ Hz), 149.3, 143.6, 133.2 (t, $J = 3.5$ Hz), 128.7, 128.6, 128.0, 126.7 (t, $J = 3.0$ Hz), 125.9, 126.0, 125.7, 89.8 (dd, $J = 20.7, 15.2$ Hz), 72.5 (t, $J = 2.9$ Hz), 37.9, 34.3, 24.2, 24.1. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -89.99 (d, $J = 39.7$ Hz, 1F), -90.25 (d, $J = 40.0$ Hz, 1F). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{19}\text{H}_{20}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 325.1374, found, 325.1377. IR: 3392.66, 2961.65, 2870.85, 1731.41, 1603.59, 1488.79, 1241.26, 1122.44, 1048.50, 793.18, 700.27.

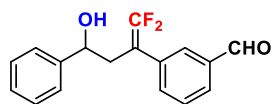
4,4-Difluoro-3-(3-fluorophenyl)-1-phenylbut-3-en-1-ol (**3n**)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3n** as colorless oil (24.2 mg, 87% yield), TLC: $R_f = 0.15$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.26 (m, 6H), 7.11 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.03 (dt, $J = 12.0, 1.8$ Hz, 1H), 7.00 – 6.97 (m, 1H), 4.66 – 4.63 (m, 1H), 2.90 – 2.85 (m, 1H), 2.76 – 2.72 (m, 1H), 1.89 (d, $J = 3.0$ Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 162.9 (d, $J = 244.2$ Hz), 154.8 (dd, $J = 289.5, 288.0$ Hz), 143.5, 135.7 (d, $J = 6.6$ Hz), 130.1 (d, $J = 8.3$ Hz), 128.7, 128.2, 125.9, 124.2 (d, $J = 3.0$ Hz), 115.7 (t, $J = 3.3$ Hz), 115.5 (t, $J = 3.2$ Hz), 114.5 (d, $J = 21.0$ Hz), 89.1 (dd, $J = 17.1, 3.3$ Hz), 72.5 (t, $J = 2.9$ Hz), 37.6. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -88.63 (d, $J = 6.7$ Hz, 2F), -112.75 – 112.80 (m,

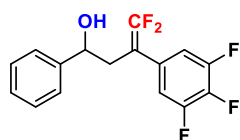
1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}F_3NaO$ ($[M + Na]^+$), 301.0811, found, 301.0810. **IR**: 3337.11, 3063.19, 3027.57, 2897.53, 2359.71, 1732.75, 1613.49, 1584.68, 1491.33, 1437.26, 1250.71, 1118.89, 1035.17, 851.22, 722.86, 546.20.

3-(1,1-Difluoro-4-hydroxy-4-phenylbut-1-en-2-yl)benzaldehyde (3o)



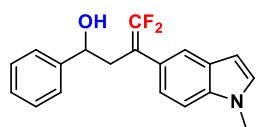
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **3o** as colorless oil (23.9 mg, 83% yield), TLC: R_f = 0.13 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **1H NMR** (500 MHz, Chloroform- d) δ 9.99 (s, 1H), 7.83 – 7.76 (m, 2H), 7.63 – 7.50 (m, 2H), 7.36 – 7.23 (m, 5H), 4.67 – 4.64 (m, 1H), 2.97 – 2.92 (m, 1H), 2.83 – 2.78 (m, 1H), 1.99 (d, J = 3.5 Hz, 1H). **^{13}C NMR** (150 MHz, Chloroform- d) δ 192.1, 154.9 (dd, J = 290.3, 287.7 Hz), 143.4, 136.8, 134.8 (t, J = 4.1 Hz, 1H), 134.5 (t, J = 3.3 Hz, 1H), 129.7 (t, J = 3.0 Hz, 1H), 129.4, 128.8, 128.7, 128.2, 125.9, 89.1 (dd, J = 22.2, 14.3 Hz), 72.6 (t, J = 2.9 Hz, 1H), 37.5. **^{19}F NMR** (565 MHz, Chloroform- d) δ -88.32 (d, J = 36.2 Hz, 1F), -88.84 (d, J = 36.7 Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}F_3NaO_2$ ($[M + Na]^+$), 311.0854, found, 311.0850. **IR**: 3440.28, 3031.13, 2838.79, 1698.26, 1601.17, 1580.45, 1453.74, 1316.07, 1277.18, 1176.76, 1051.79, 716.33.

4,4-Difluoro-1-phenyl-3-(3,4,5-trifluorophenyl)but-3-en-1-ol (3p)



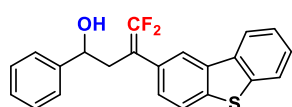
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **3p** as colorless oil (30.8 mg, 98% yield), TLC: R_f = 0.16 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **1H NMR** (600 MHz, Chloroform- d) δ 7.35 – 7.33 (m, 2H), 7.31 – 7.26 (m, 3H), 6.94 (dd, J = 8.4, 6.6 Hz, 2H), 4.66 (dd, J = 7.8, 5.4 Hz, 1H), 2.84 – 2.79 (m, 1H), 2.70 – 2.66 (m, 1H), 1.92 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform- d) δ 154.9 (dd, J = 290.7, 288.8 Hz), 152.1 (dd, J = 9.6, 4.1 Hz), 152.0 (dd, J = 9.9, 4.2 Hz), 143.2, 139.8 (t, J = 15.0 Hz), 138.2 (t, J = 14.9 Hz), 129.8 (t, J = 3.9 Hz), 128.8, 128.4, 125.9, 112.9 (t, J = 3.8 Hz), 112.8 (t, J = 4.1 Hz), 88.5 (dd, J = 23.4, 13.1 Hz), 72.7 (t, J = 2.7 Hz), 37.4. **^{19}F NMR** (565 MHz, Chloroform- d) δ -87.25 (d, J = 34.1 Hz, 1F), -87.67 (d, J = 34.4 Hz, 1F), -134.15 – -134.23 (m, 2F), -161.27 – -161.36 (m, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{11}F_5NaO$ ($[M + Na]^+$), 337.0622, found, 337.0612. **IR**: 3303.62, 2959.35, 1735.84, 1618.50, 1531.83, 1496.23, 1110.77, 863.71, 751.67, 703.14, 587.23.

4,4-Difluoro-3-(1-methyl-1H-indol-5-yl)-1-phenylbut-3-en-1-ol (3q)



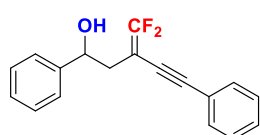
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 10:1 to afford **3q** as colorless oil (11.9 mg, 38% yield), TLC: R_f = 0.16 (Petroleum ether : Ethyl acetate = 10:1) [UV]. **1H NMR** (600 MHz, Chloroform- d) δ 7.59 (s, 1H), 7.35 – 7.30 (m, 5H), 7.29 – 7.26 (m, 1H), 7.19 (dt, J = 8.4, 1.8 Hz, 1H), 7.08 (d, J = 3.0 Hz, 1H), 6.49 (d, J = 3.0 Hz, 1H), 4.65 (dd, J = 8.4, 5.4 Hz, 1H), 3.81 (s, 3H), 2.96 – 2.92 (m, 1H), 2.83 – 2.79 (m, 1H), 1.74 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform- d) δ 154.6 (dd, J = 286.5, 285.0 Hz), 143.8, 136.2, 129.7, 128.7, 127.9, 126.0, 122.3 (t, J = 3.0 Hz), 121.1 (t, J = 3.0 Hz), 109.5, 101.3, 90.2 (dd, J = 19.5, 15.0 Hz), 72.4 (t, J = 3.0 Hz), 38.7, 33.1. **^{19}F NMR** (565 MHz, Chloroform- d) δ -91.12 (d, J = 39.6 Hz, 1F), -89.32 (d, J = 39.6 Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{19}H_{17}F_2NNaO$ ($[M + Na]^+$), 336.1170, found, 336.1177. **IR**: 3232.25, 2875.86, 736.38, 1600.16, 1481.77, 1453.47, 1321.71, 1274.32, 1122.57, 1042.42, 889.98, 791.79, 774.54, 699.41.

3-(Dibenzo[*b,d*]thiophen-2-yl)-4,4-difluoro-1-phenylbut-3-en-1-ol (**3r**)



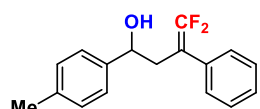
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **3r** as colorless oil (35.7 mg, 98% yield), TLC: $R_f = 0.14$ (Petroleum ether : Ethyl acetate = 40:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.17 – 8.10 (m, 1H), 8.08 – 8.02 (m, 1H), 7.89 – 7.80 (m, 2H), 7.46 (dt, $J = 7.2, 3.6$ Hz, 2H), 7.39 (dt, $J = 8.4, 1.2$ Hz, 1H), 7.35 – 7.25 (m, 5H), 4.69 – 4.66 (m, 1H), 3.03 – 2.98 (m, 1H), 2.87 – 2.83 (m, 1H), 1.93 (d, $J = 3.6$ Hz, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.8 (t, $J = 287.6$ Hz), 143.6, 140.0, 138.8, 136.0, 135.3, 129.8 (t, $J = 2.6$ Hz), 128.7, 128.1, 127.13, 127.1, 127.08, 126.0, 124.6, 123.0, 121.8, 121.7 (t, $J = 3.3$ Hz), 89.8 (dd, $J = 20.7, 15.9$ Hz), 72.5 (t, $J = 2.9$ Hz), 38.2. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -88.58 (d, $J = 39.5$ Hz, 1F), -88.84 (d, $J = 39.5$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{22}\text{H}_{16}\text{F}_2\text{NaOS}$ ($[\text{M} + \text{Na}]^+$), 389.0782, found, 389.0780. **IR**: 3214.63, 2958.91, 2887.45, 2360.54, 1736.66, 1492.37, 1068.09, 995.52, 988.64, 826.44, 764.31, 699.43, 439.89.

3-(Difluoromethylene)-1,5-diphenylpent-4-yn-1-ol (**3s**)



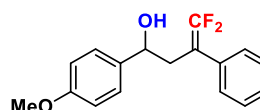
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3s** as colorless oil (12.2 mg, 43% yield), TLC: $R_f = 0.12$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 4H), 7.40 – 7.35 (m, 2H), 7.35 – 7.28 (m, 4H), 5.03 – 4.98 (m, 1H), 2.69 – 2.63 (m, 1H), 2.54 – 2.49 (m, 1H), 2.05 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 159.8 (dd, $J = 295.1, 292.8$ Hz), 143.2, 131.6, 128.7, 128.5, 128.1, 126.0, 122.8, 94.3 (t, $J = 5.6$ Hz), 80.7 (dd, $J = 7.8, 4.2$ Hz), 75.8 (dd, $J = 4.1, 1.7$ Hz), 72.7 (t, $J = 2.7$ Hz), 37.8 (d, $J = 2.1$ Hz). $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -77.95 (d, $J = 13.0$ Hz, 1F), -83.48 (d, $J = 12.4$ Hz, 1F) ppm. **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{18}\text{H}_{14}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 307.0905, found, 307.0911. **IR**: 3062.02, 2956.75, 2925.20, 2360.72, 1718.72, 1491.35, 1450.62, 1208.10, 1177.66, 721.53, 691.99.

4,4-Difluoro-3-phenyl-1-(*p*-tolyl)but-3-en-1-ol (**4a**)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4a** as colorless oil (19.7 mg, 72% yield), TLC: $R_f = 0.15$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.43 – 7.28 (m, 5H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 4.61 (dd, $J = 8.5, 5.5$ Hz, 1H), 2.92 – 2.87 (m, 1H), 2.79 – 2.74 (m, 1H), 2.35 (s, 3H), 1.83 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.6 (t, $J = 287.6$ Hz), 140.7, 137.7, 133.4, 129.3, 128.7, 128.6 (t, $J = 3.0$ Hz), 127.6, 125.9, 89.8 (t, $J = 18.2$ Hz), 72.3 (t, $J = 2.9$ Hz), 37.7, 21.3. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -90.14 (s, 2F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 297.1061, found, 297.1051. **IR**: 3394.89, 2923.75, 1731.69, 1498.72, 1446.51, 1305.34, 1201.57, 1044.48, 818.57, 727.56, 697.48.

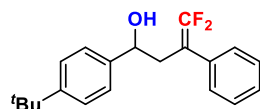
4,4-Difluoro-1-(4-methoxyphenyl)-3-phenylbut-3-en-1-ol (**4b**)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **4b** as colorless oil (25.2 mg, 87% yield), TLC: $R_f = 0.14$ (Petroleum ether : Ethyl acetate = 40:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 7.21 (d, $J = 8.4$ Hz, 2H),

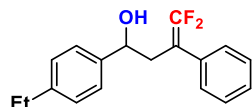
6.86 (d, $J = 8.4$ Hz, 2H), 4.58 (dd, $J = 7.8, 5.4$ Hz, 1H), 3.80 (s, 3H), 2.91 – 2.87 (m, 1H), 2.76 – 2.72 (m, 1H), 1.81 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 159.4, 154.7 (t, $J = 286.5$ Hz), 135.7, 133.4 (d, $J = 3.0$ Hz), 128.7, 128.6 (d, $J = 3.0$ Hz), 127.6, 127.3, 89.7 (dd, $J = 19.5, 16.5$ Hz), 72.3 (t, $J = 1.5$ Hz), 55.4, 37.7. $^{19}\text{F NMR}$ (565 MHz, Chloroform- d) δ -90.04 (d, $J = 50.9$ Hz, 1F), -90.17 (d, $J = 45.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{NaO}_2$ ($[\text{M} + \text{Na}]^+$), 313.1011, found, 313.1010. **IR**: 3215.76, 2891.69, 2933.43, 2277.16, 1713.65, 1423.69, 1306.31, 1209.11, 1199.31, 1183.28, 787.98, 631.86.

1-(4-(*tert*-Butyl)phenyl)-4,4-difluoro-3-phenylbut-3-en-1-ol (**4c**)



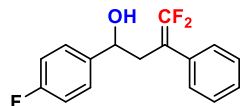
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4c** as colorless oil (23.1 mg, 73% yield), TLC: $R_f = 0.15$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (500 MHz, Chloroform- d) δ 7.39 – 7.27 (m, 7H), 7.25 – 7.20 (m, 2H), 4.61 (dd, $J = 8.5, 5.5$ Hz, 1H), 2.93 – 2.87 (m, 1H), 2.77 – 2.72 (m, 1H), 1.84 (s, 1H), 1.31 (s, 9H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 154.6 (dd, $J = 288.0, 286.5$ Hz), 151.0, 140.6, 133.5, 128.7, 128.6 (t, $J = 3.0$ Hz), 127.6, 125.7, 125.5, 89.8 (dd, $J = 19.5, 15.0$ Hz), 72.2 (t, $J = 3.0$ Hz), 37.7, 34.7, 31.5. $^{19}\text{F NMR}$ (565 MHz, Chloroform- d) δ -90.06 (d, $J = 39.6$ Hz, 1F), -90.17 (d, $J = 39.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{20}\text{H}_{22}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 339.1531, found, 339.1525. **IR**: 2963.32, 2869.15, 1732.21, 1446.41, 1292.17, 1047.26, 835.12, 731.85, 697.34, 577.81.

1-(4-Ethylphenyl)-4,4-difluoro-3-phenylbut-3-en-1-ol (**4d**)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4d** as colorless oil (24.2 mg, 84% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 7.21 (d, $J = 7.8$ Hz, 2H), 7.16 (d, $J = 8.4$ Hz, 2H), 4.61 (ddd, $J = 7.8, 5.4, 3.0$ Hz, 1H), 2.91 – 2.86 (m, 1H), 2.77 – 2.72 (m, 1H), 2.64 (q, $J = 7.8$ Hz, 2H), 1.82 (d, $J = 3.0$ Hz, 1H), 1.23 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 154.7 (t, $J = 288.0$ Hz), 144.1, 140.9, 133.5 (d, $J = 1.5$ Hz), 128.7, 128.6 (d, $J = 3.0$ Hz), 128.1, 127.6, 126.0, 89.8 (dd, $J = 18.0, 16.5$ Hz), 72.3 (t, $J = 3.0$ Hz), 37.7, 28.7, 15.7. $^{19}\text{F NMR}$ (565 MHz, Chloroform- d) δ -90.13 (t, $J = 50.9$ Hz, 2F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{18}\text{H}_{18}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 311.1218, found, 311.1210. **IR**: 3385.16, 2995.61, 2931.27, 2360.36, 1731.13, 1512.64, 1446.37, 1305.39, 1237.88, 1123.88, 833.10, 697.32.

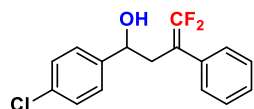
4,4-Difluoro-1-(4-fluorophenyl)-3-phenylbut-3-en-1-ol (**4e**)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4e** as colorless oil (25.0 mg, 90% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.37 (t, $J = 7.8$ Hz, 2H), 7.30 (d, $J = 7.2$ Hz, 3H), 7.27 – 7.23 (m, 2H), 7.07 – 6.96 (m, 2H), 4.62 (dd, $J = 8.4, 6.0$ Hz, 1H), 2.90 – 2.86 (m, 1H), 2.76 – 2.72 (m, 1H), 1.84 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 162.5 (d, $J = 244.5$ Hz), 154.7 (t, $J = 288.0$ Hz), 139.3 (d, $J = 3.0$ Hz), 133.2, 128.8, 128.5 (t, $J = 3.0$ Hz), 127.7, 127.6, 115.4 (d, $J = 21.0$ Hz), 89.5 (dd, $J = 19.5, 18.0$ Hz), 71.9 (t, $J = 3.0$ Hz), 37.8. $^{19}\text{F NMR}$ (565 MHz, Chloroform- d) δ -88.63 (s, 2F), -114.53 – 114.57 (m, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 301.0811, found, 301.0810. **IR**: 3387.94, 2919.86, 2360.54, 1723.19, 1607.73, 1446.56, 1278.89, 1122.83, 850.96,

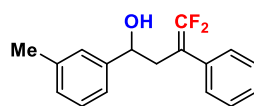
697.58,

1-(4-Chlorophenyl)-4,4-difluoro-3-phenylbut-3-en-1-ol (4f)



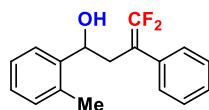
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4f** as colorless oil (20.0 mg, 68% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.30 (t, $J = 7.0$ Hz, 5H), 7.25 – 7.20 (m, 2H), 4.62 (dd, $J = 8.5, 6.0$ Hz, 1H), 2.90 – 2.84 (m, 1H), 2.77 – 2.70 (m, 1H), 1.88 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 156.6 (dd, $J = 289.5, 288.0$ Hz), 142.0, 133.7, 133.2, 128.8, 128.7, 128.5 (t, $J = 3.0$ Hz), 127.8, 127.4, 89.4 (dd, $J = 19.5, 16.5$ Hz), 71.8 (t, $J = 3.0$ Hz), 37.8. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -89.57 (d, $J = 39.6$ Hz, 1F), -89.32 (d, $J = 39.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{13}\text{ClF}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 317.0515, found, 317.0520. **IR**: 3370.59, 3060.42, 2925.99, 2359.79, 1732.76, 1599.49, 1493.50, 1446.19, 1293.71, 1122.98, 1013.92, 830.38, 768.35, 697.86, 544.51.

4,4-Difluoro-3-phenyl-1-(*m*-tolyl)but-3-en-1-ol (4g)



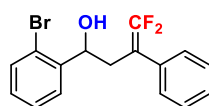
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4g** as colorless oil 17.8 mg, 65% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 5H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.13 – 7.06 (m, 3H), 4.60 (dd, $J = 8.5, 5.0$ Hz, 1H), 2.91 – 2.86 (m, 1H), 2.80 – 2.70 (m, 1H), 2.34 (s, 3H), 1.84 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 156.6 (dd, $J = 289.5, 288.0$ Hz), 143.6, 138.3, 133.4 (t, $J = 3.0$ Hz), 128.8, 128.7, 128.6 (t, $J = 3.0$ Hz), 127.6, 126.6, 123.0, 89.8 (dd, $J = 21.0, 16.5$ Hz), 72.4 (t, $J = 3.0$ Hz), 37.8, 21.6. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -89.57 (d, $J = 39.6$ Hz, 1F), -89.32 (d, $J = 39.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 297.1061, found, 297.1060. **IR**: 3394.97, 3027.51, 2922.85, 1731.40, 1606.89, 1446.33, 1305.61, 1236.98, 1123.04, 1044.55, 721.21, 697.76, 609.30.

4,4-Difluoro-3-phenyl-1-(*o*-tolyl)but-3-en-1-ol (4h)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4h** as colorless oil (17.3 mg, 63% yield), TLC: $R_f = 0.15$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.50 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.42 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 7.23 (ddd, $J = 9.0, 7.2, 1.8$ Hz, 1H), 7.17 (ddd, $J = 9.0, 7.2, 1.2$ Hz, 1H), 7.12 – 7.08 (m, 1H), 4.93 – 4.87 (m, 1H), 2.84 – 2.79 (m, 1H), 2.76 – 2.72 (m, 1H), 2.17 (s, 3H), 1.75 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.7 (dd, $J = 289.5, 286.5$ Hz), 141.8, 134.6, 133.4 (dd, $J = 4.5, 3.0$ Hz), 130.6, 128.7, 128.5 (t, $J = 3.0$ Hz), 127.8, 127.6, 126.5, 125.4, 90.0 (dd, $J = 21.0, 13.5$ Hz), 71.8 (t, $J = 3.0$ Hz), 36.8, 19.0. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -89.93 (d, $J = 39.6$ Hz, 1F), -90.14 (d, $J = 39.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 297.1061, found, 297.1062. **IR**: 3026.81, 2927.76, 2361.19, 1732.10, 1469.01, 1446.60, 1237.74, 1124.89, 1045.78, 798.26, 713.20, 697.99, 457.51.

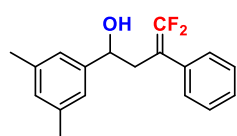
1-(2-Bromophenyl)-4,4-difluoro-3-phenylbut-3-en-1-ol (4i)



The crude was purified by flash chromatography using Petroleum ether/

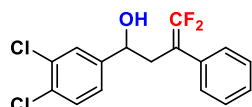
Ethyl acetate 50:1 to afford **4i** as colorless oil (17.2 mg, 51% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.59 (dd, $J = 9.0, 1.2$ Hz, 1H), 7.48 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.42 – 7.35 (m, 4H), 7.34 – 7.28 (m, 2H), 7.12 (td, $J = 7.8, 1.8$ Hz, 1H), 5.03 – 5.00 (m, 1H), 2.91 – 2.87 (m, 1H), 2.74 – 2.70 (m, 1H), 1.96 (d, $J = 3.6$ Hz, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.8 (dd, $J = 289.5, 286.5$ Hz), 142.7, 132.8, 129.2, 128.7 (t, $J = 3.0$ Hz), 128.6, 127.9, 127.7, 127.6, 121.7, 89.6 (dd, $J = 21.0, 15.0$ Hz), 71.0 (t, $J = 1.5$ Hz), 36.1. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -90.06 (d, $J = 39.6$ Hz, 1F), -90.17 (d, $J = 39.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{13}\text{BrF}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 361.0010, found, 361.0015. **IR**: 3060.74, 2927.03, 2360.31, 1731.06, 1568.39, 1442.18, 1239.46, 1125.31, 1020.59, 756.50, 734.59, 697.50, 450.98.

1-(3,5-Dimethylphenyl)-4,4-difluoro-3-phenylbut-3-en-1-ol (**4j**)



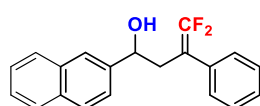
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4j** as colorless oil (20.5 mg, 71% yield), TLC: $R_f = 0.14$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 (ddd, $J = 9.0, 7.2, 1.8$ Hz, 1H), 6.90 (s, 3H), 4.56 (dd, $J = 9.0, 5.4$ Hz, 1H), 2.93 – 2.83 (m, 1H), 2.79 – 2.72 (m, 1H), 2.29 (s, 6H), 1.82 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.7 (dd, $J = 288.9, 286.4$ Hz), 143.6, 138.2, 133.5 (t, $J = 3.0$ Hz), 129.6, 128.5, 128.4 (d, $J = 6.2$ Hz), 127.6, 123.7, 89.9 (dd, $J = 20.6, 15.01$ Hz), 72.4 (t, $J = 2.9$ Hz), 37.8, 21.4. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -90.19 (s, 2F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{18}\text{H}_{18}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 311.1218, found, 311.1220. **IR**: 3318.67, 2955.94, 2835.63, 2360.51, 1734.97, 1611.02, 1510.02, 1305.77, 1244.70, 1038.09, 729.03, 697.82, 553.53.

1-(3,4-Dichlorophenyl)-4,4-difluoro-3-phenylbut-3-en-1-ol (**4k**)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4k** as colorless oil (15.1 mg, 46% yield), TLC: $R_f = 0.15$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.40 – 7.37 (m, 4H), 7.32 – 7.29 (m, 3H), 7.12 (dd, $J = 8.4, 1.8$ Hz, 1H), 4.60 (dd, $J = 8.4, 5.4$ Hz, 1H), 2.87 – 2.83 (m, 1H), 2.75 – 2.71 (m, 1H), 1.92 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.7 (dd, $J = 289.5, 286.5$ Hz), 143.8, 132.7, 131.8, 130.6, 128.9, 128.5 (dd, $J = 3.0$ Hz), 128.4, 128.1, 127.9, 125.3, 89.2 (dd, $J = 19.5, 5.0$ Hz), 71.3 (t, $J = 3.0$ Hz), 37.8. $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -89.36 (d, $J = 39.6$ Hz, 1F), -89.53 (d, $J = 39.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 351.0125, found, 351.0120. **IR**: 2928.75, 2360.55, 2341.35, 1708.29, 1470.93, 1298.47, 1030.17, 823.57, 734.22, 698.31.

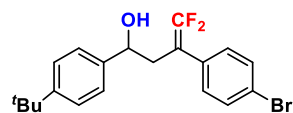
4,4-Difluoro-1-(naphthalen-2-yl)-3-phenylbut-3-en-1-ol (**4l**)



The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **4l** as colorless oil (16.7 mg, 54% yield), TLC: $R_f = 0.16$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.85 – 7.70 (m, 3H), 7.71 (s, 1H), 7.50 – 7.44 (m, 3H), 7.41 – 7.34 (m, 4H), 7.30 (t, $J = 7.2$ Hz, 1H), 4.82 – 4.79 (m, 1H), 3.00 – 2.94 (m, 1H), 2.89 – 2.84 (m, 1H), 1.96 (d, $J = 3.0$ Hz, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.5 (dd, $J = 288.9, 287.3$ Hz), 140.8, 133.2, 133.1, 128.6, 128.5, 128.4 (d, $J = 6.0$ Hz), 128.4, 127.9, 127.7, 127.5, 126.2, 126.0, 124.7, 123.8,

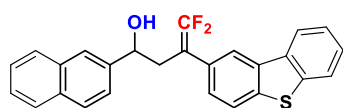
89.6 (dd, $J = 20.0, 16.1$ Hz), 71.5 (t, $J = 2.9$ Hz), 37.6. **^{19}F NMR** (565 MHz, Chloroform- d) δ -89.87.06 (d, $J = 39.6$ Hz, 1F), -89.96 (d, $J = 39.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{20}\text{H}_{16}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 333.1061, found, 333.1060. **IR**: 3485.55, 3063.88, 2964.98, 2360.74, 2230.39, 1762.28, 1607.51, 1454.28, 1247.78, 1113.41, 844.26, 758.92, 701.76, 551.47.

3-(4-Bromophenyl)-1-(4-(*tert*-butyl)phenyl)-4,4-difluorobut-3-en-1-ol (**4m**)



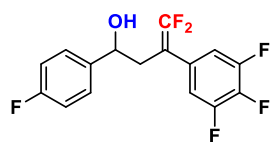
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4m** as colorless oil (38.2 mg, 97% yield), TLC: $R_f = 0.14$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^1H NMR** (500 MHz, Chloroform- d) δ 7.36 – 7.27 (m, 4H), 7.24 – 7.17 (m, 4H), 4.60 (dd, $J = 8.5, 6.0$ Hz, 1H), 2.90 – 2.85 (m, 1H), 2.76 – 2.66 (m, 1H), 1.84 (s, 1H), 1.30 (s, 9H). **^{13}C NMR** (125 MHz, Chloroform- d) δ 154.6 (dd, $J = 290.0, 287.5$ Hz), 151.2, 140.4, 133.3, 132.1 (t, $J = 3.0$ Hz), 129.9 (t, $J = 3.75$ Hz), 128.8, 125.7 (d, $J = 18.85$ Hz), 89.1 (dd, $J = 21.0, 15.0$ Hz), 72.3 (t, $J = 2.8$ Hz), 37.5, 34.7, 31.5. **^{19}F NMR** (565 MHz, Chloroform- d) δ -89.25 (d, $J = 45.2$ Hz, 1F), -89.42 (d, $J = 45.2$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{20}\text{H}_{21}\text{BrF}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 417.0636, found, 417.0630. **IR**: 3374.37, 2964.23, 2905.13, 2361.11, 1731.77, 1493.84, 1400.52, 1241.31, 1092.67, 829.11, 579.01.

3-(Dibenzo[*b,d*]thiophen-2-yl)-4,4-difluoro-1-(naphthalen-2-yl)but-3-en-1-ol (**4n**)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4n** as colorless oil (29.5 mg, 71% yield), TLC: $R_f = 0.12$ (Petroleum ether : Ethyl acetate = 20:1) [UV]. **^1H NMR** (600 MHz, Chloroform- d) δ 8.09 – 8.04 (m, 1H), 8.03 – 7.98 (m, 1H), 7.90 – 7.75 (m, 5H), 7.71 (s, 1H), 7.49 – 7.40 (m, 5H), 7.41 (dt, $J = 7.8, 1.2$ Hz, 1H), 4.86 (dd, $J = 8.4, 6.0$ Hz, 1H), 3.12-3.08 (m, 1H), 2.98-2.93 (m, 1H), 2.02 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform- d) δ 154.8 (t, $J = 288.0$ Hz), 140.9, 140.0, 138.8, 136.0, 135.3, 133.3 (d, $J = 4.5$ Hz), 129.8, 128.6, 128.1, 127.8, 127.1 (t, $J = 3.0$ Hz), 126.4, 126.2, 125.0, 124.6, 123.9, 123.0 (d, $J = 3.0$ Hz), 121.9, 121.8, 121.7, 89.8 (dd, $J = 21.0, 16.5$ Hz), 72.7 (t, $J = 30$ Hz), 38.1. **^{19}F NMR** (565 MHz, Chloroform- d) δ -89.79 (d, $J = 39.6$ Hz, 1F), -89.90 (d, $J = 39.6$ Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{26}\text{H}_{18}\text{F}_2\text{NaOS}$ ($[\text{M} + \text{Na}]^+$), 439.0939, found, 439.0940. **IR**: 3227.58, 2959.27, 2926.76, 1737.45, 1617.38, 1531.56, 1374.52, 1268.85, 1047.82, 844.43, 731.52, 477.55.

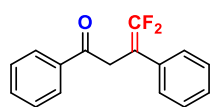
4,4-Difluoro-1-(4-fluorophenyl)-3-(3,4,5-trifluorophenyl)but-3-en-1-ol (**4o**)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4o** as colorless oil (31.2 mg, 94% yield), TLC: $R_f = 0.14$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^1H NMR** (500 MHz, Chloroform- d) δ 7.29 – 7.24 (m, 2H), 7.03 (t, $J = 8.5$ Hz, 2H), 6.96 (dd, $J = 8.5, 6.5$ Hz, 2H), 4.66 (dd, $J = 8.0, 5.5$ Hz, 1H), 2.79 (ddt, $J = 14.5, 8.0, 2.0$ Hz, 1H), 2.73 – 2.62 (m, 1H), 1.92 (s, 1H). **^{13}C NMR** (125 MHz, Chloroform- d) δ 154.6 (dd, $J = 290.0, 287.5$ Hz), 151.2, 140.4, 133.3, 132.1 (t, $J = 3.0$ Hz), 129.9 (t, $J = 3.75$ Hz), 128.8, 125.7 (d, $J = 18.85$ Hz), 89.1 (dd, $J = 21.0, 15.0$ Hz), 72.3 (t, $J = 2.8$ Hz), 37.5, 34.7, 31.5. **^{19}F NMR** (471 MHz, Chloroform- d) δ -87.08 (d, $J = 34.4$ Hz, 1F), -87.47 (d, $J = 34.2$ Hz, 1F), -113.84 – -113.90 (m, 1F), -133.93 (d, $J = 9.4$ Hz, 1F), -133.97 (d, $J = 9.4$ Hz, 1F), -161.00 – -161.09 (m, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{10}\text{F}_6\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 355.0528, found, 355.0530. **IR**: 3393.78, 2928.90, 2359.67, 1729.61,

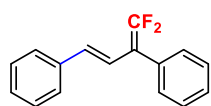
1616.19, 1501.72, 1433.14, 1374.08, 1279.07, 1222.93, 1114.11, 1042.30, 706.78, 688.18, 594.54, 553.74.

4,4-Difluoro-1,3-diphenylbut-3-en-1-one (5)



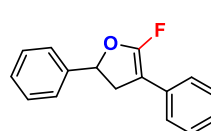
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 100:1 to afford **5** as colorless oil (49.0 mg, 94% yield), TLC: R_f = 0.21 (Petroleum ether : Ethyl acetate = 100:1) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 2H), 7.61 – 7.56 (m, 1H), 7.50 – 7.45 (m, 2H), 7.36 – 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 4.06 (t, J = 2.4 Hz, 2H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 195.5, 154.9 (dd, J = 289.5, 285.0 Hz), 136.4, 133.6, 128.9, 128.6, 128.3, 128.1 (t, J = 3.0 Hz), 127.6, 87.3 (dd, J = 21.0, 16.5 Hz), 38.5 (d, J = 1.5 Hz). $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -88.13 (d, J = 37.3 Hz, 1F), -89.14 (d, J = 36.7 Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{12}\text{F}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$), 281.0748, found, 281.0750. **IR**: 3215.76, 2891.69, 2933.43, 2277.16, 1752.67, 1703.69, 1444.60, 1356.87, 1279.19, 1198.21, 1173.21, 765.45, 619.43.

(*E*)-(4,4-Difluorobuta-1,3-diene-1,3-diyl)dibenzene (6)



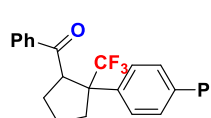
The crude was purified by flash chromatography using Petroleum ether to afford **6** as colorless oil (43.1 mg, 89% yield), TLC: R_f = 0.33 (Petroleum ether) [UV]. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.41 – 7.37 (m, 1H), 7.35 – 7.31 (m, 4H), 7.28 (t, J = 7.8 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.01 (d, J = 16.2 Hz, 1H), 6.21 (d, J = 15.6 Hz, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.2 (dd, J = 297.0, 291.0 Hz), 137.1, 131.3 (d, J = 3.0 Hz), 131.2 (d, J = 4.5 Hz), 130.4 (t, J = 3.0 Hz), 128.8, 128.7, 128.3, 127.8, 126.4, 121.3, 96.6 (dd, J = 21.0, 16.5 Hz). $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -86.98 (d, J = 39.6 Hz, 1F), -87.25 (d, J = 39.6 Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{12}\text{F}_2\text{Na}$ ($[\text{M} + \text{Na}]^+$), 265.0799, found, 265.0780. **IR**: 3086.69, 2914.66, 1746.51, 1688.14, 1448.61, 1237.97, 1000.67, 754.50, 729.01, 685.40.

5-Fluoro-2,4-diphenyl-2,3-dihydrofuran (7)



The crude was purified by flash chromatography using Petroleum ether to afford **7** as colorless oil (36.2 mg, 75% yield), TLC: R_f = 0.35 (Petroleum ether) [UV]. $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.46 – 7.39 (m, 4H), 7.38 – 7.28 (m, 5H), 7.14 (tt, J = 7.0, 1.5 Hz, 1H), 5.72 (dd, J = 10.5, 8.0 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.15 – 3.08 (m, 1H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 157.1, 155.3, 140.9, 132.5 (d, J = 6.0 Hz), 129.0, 128.6 (d, J = 1.5 Hz), 125.8, 125.3 (d, J = 1.5 Hz), 124.9 (d, J = 4.5 Hz), 80.3 (d, J = 3.0 Hz), 38.0 (d, J = 3.0 Hz). $^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -106.63 (t, J = 39.6 Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{11}\text{FONa}$ ($[\text{M} + \text{Na}]^+$), 261.0686, found, 261.0688. **IR**: 3011.72, 2894.42, 1796.59, 1514.54, 1448.61, 1237.97, 1109.43, 980.43, 712.76, 677.541, 591.42.

(2-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)cyclopentyl)(phenyl)methanone (9)

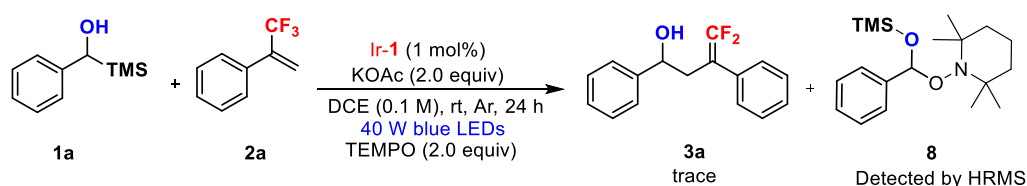


The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 200:1 to afford **9** as colorless oil (12.2 mg, 31% yield), TLC: R_f = 0.21 (Petroleum ether: Ethyl acetate = 200:1) [UV]. $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.44 – 7.36 (m, 4H), 7.30 (t, J = 7.3 Hz, 1H), 7.28 – 7.24 (m, 2H), 4.84 (d, J = 10.0 Hz, 1H), 2.99

- 2.88 (m, 1H), 2.72 - 2.63 (m, 1H), 2.47 (dt, $J = 18.0, 9.0$ Hz, 1H), 2.20 - 2.05 (m, 1H), 2.00 - 1.91 (m, 1H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 200.3, 140.6, 140.2, 137.6, 137.2, 133.3, 129.4, 128.9, 128.8, 128.4, 127.4, 127.2, 126.7, 60.7 (q, $J = 23.3$ Hz), 50.1, 32.7, 30.7, 23.3. **¹⁹F NMR** (565 MHz, Chloroform-*d*) δ -72.48 (s, CF₃). **HRMS** (ESI-TOF) (m/z): Calcd for C₂₅H₂₁F₃ONa ([M-H]⁻), 393.14717, found, 393.14267. **IR**: 2958.62, 1685.21, 1595.79, 1487.84, 1447.85, 1302.46, 1263.43, 1146.38, 1002.75, 766.53, 697.97, 608.51.

5. Mechanistic Experiments

a) Radical inhibition experiment



In a nitrogen-filled glovebox, a flame-dried seal reaction tube equipped with a teflon-coated magnetic stir bar was charged with phenyl(trimethylsilyl)methanol **1a** (18 mg 0.1mmol, 1.0 equiv), KOAc (19.6 mg, 2.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.1 mg, 0.01 equiv.) and 1.0 mL 1,2-dichloroethane were added to the tube in sequence, followed by (3,3,3-trifluoroprop-1-en-2-yl)benzene (34.4 mg, 2.0 equiv.). TEMPO (2.0 equiv) was added. Then the vial was sealed and exposed to blue LEDs at room temperature with stirring for 24 hours. The reaction mixture was quenched with NH₄F and stirred for 30 min, after extracted with CH₂Cl₂ (3×10 mL) and the combined organic layers were concentrated in vacuo.

In the system of TEMPO, the formation of **3a** was almost completely suppressed. The TEMPO-trapped product **8** was detected by high-resolution mass. This result suggested that an alkyl radical intermediate is probably involved in this transformation. The corresponding high-resolution mass spectrometry (HRMS) analysis and spectroscopic analysis were offered as follows.

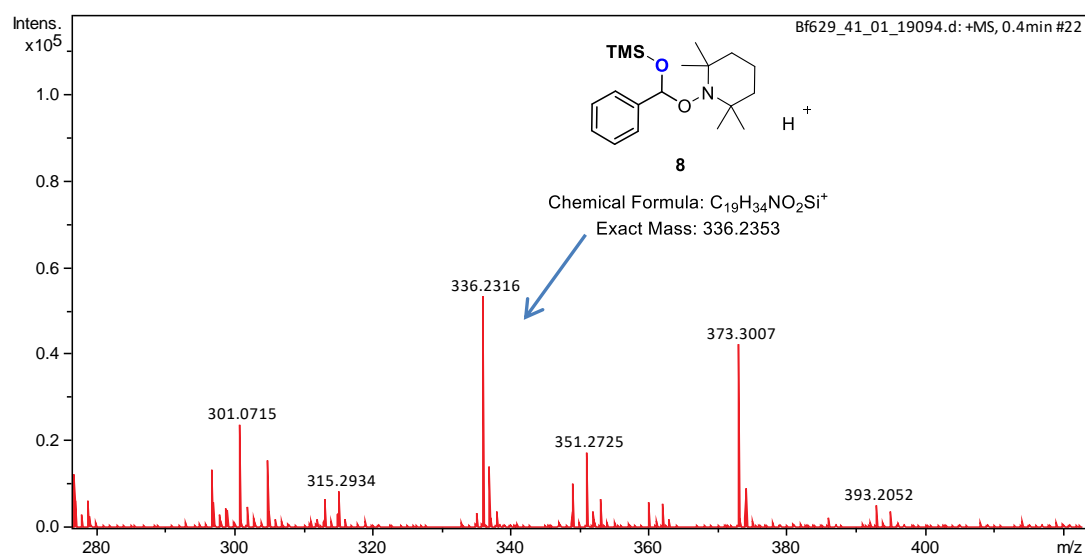
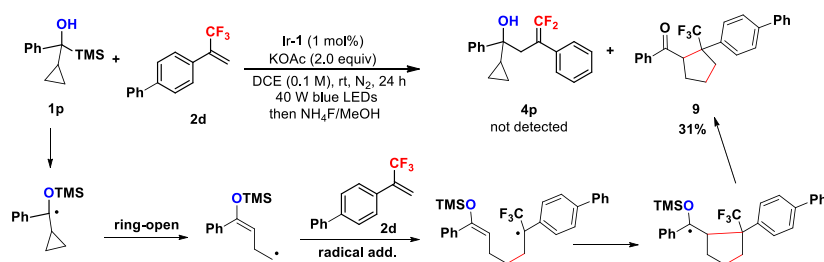


Fig. S1 TEMPO trapped alkyl radical intermediate

b) Radical clock experiment



c) Light ON/OFF experiment

Standard reactions were set up parallel on a 0.10 mmol scale according to the general procedure and extra 1 equiv. of benzotrifluoride was added as the internal standard. After being irradiated for 2 h, an aliquot (150 μ L) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.5 mL of CDCl₃. The yield of product was determined by ¹⁹F NMR. Then the reaction mixture was stirred for 2 h with light-off. All of the following yields were analyzed in the identical way after a 2 hour light on or off.

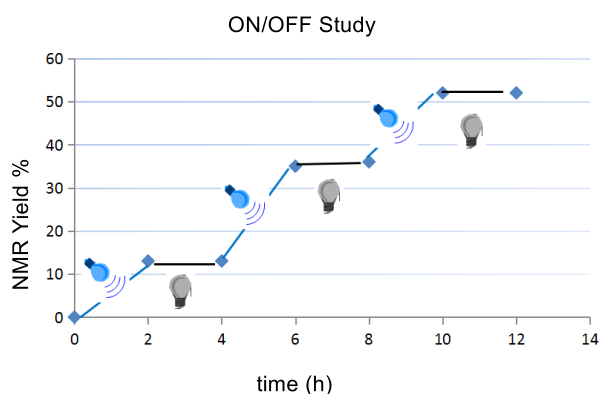
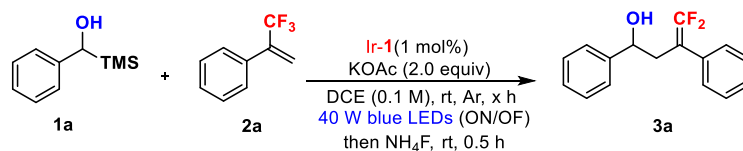
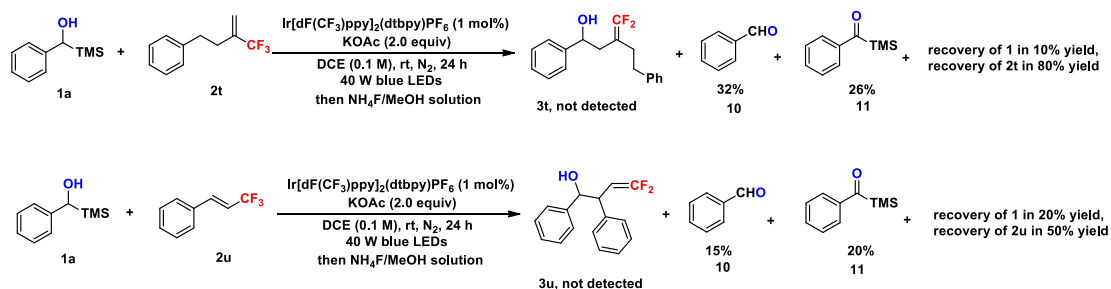


Fig. S2 Light on-off Experiment

d) The reaction of other trifluoromethyl alkenes



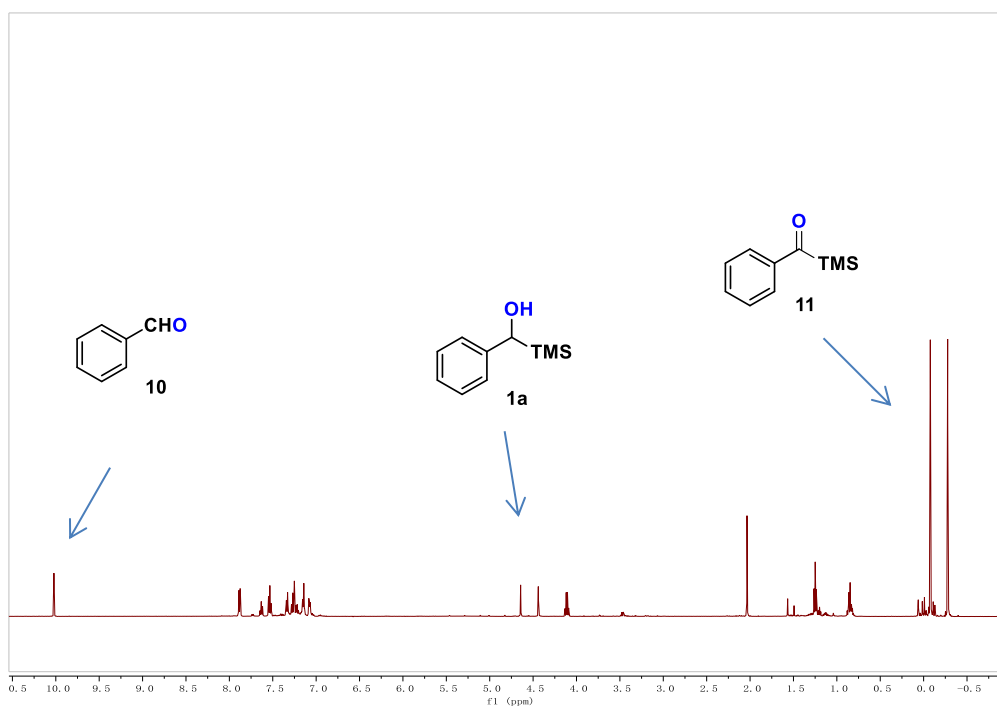
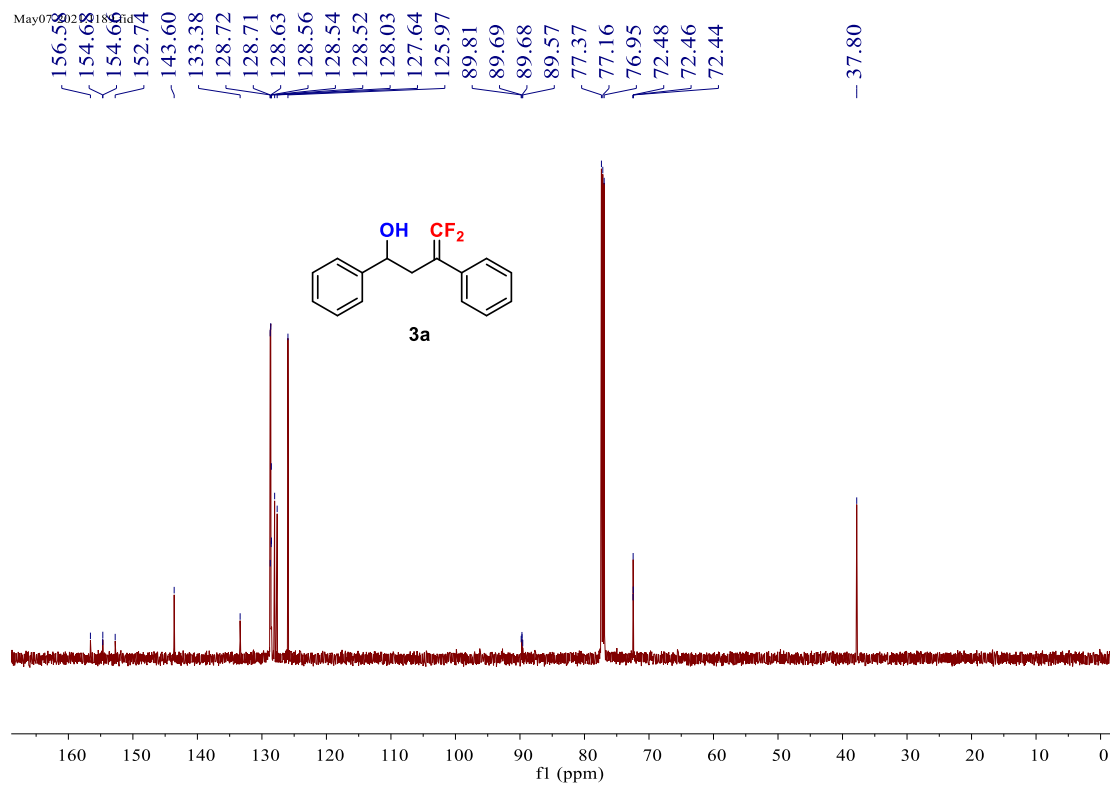
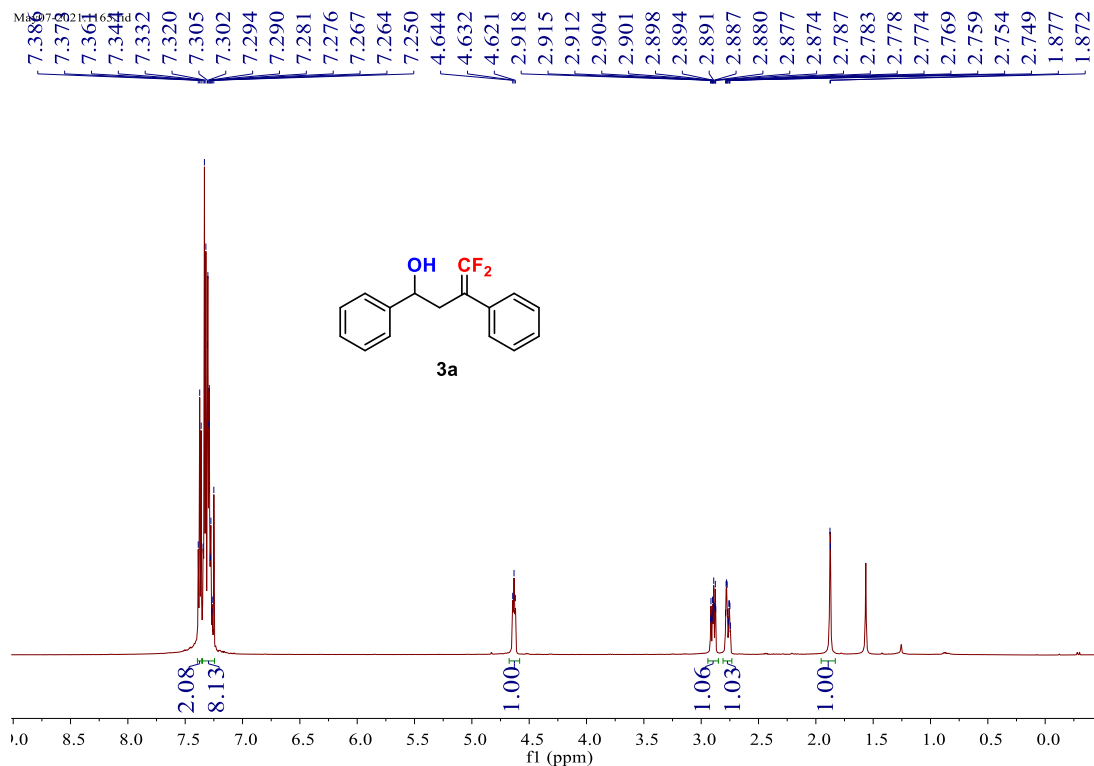


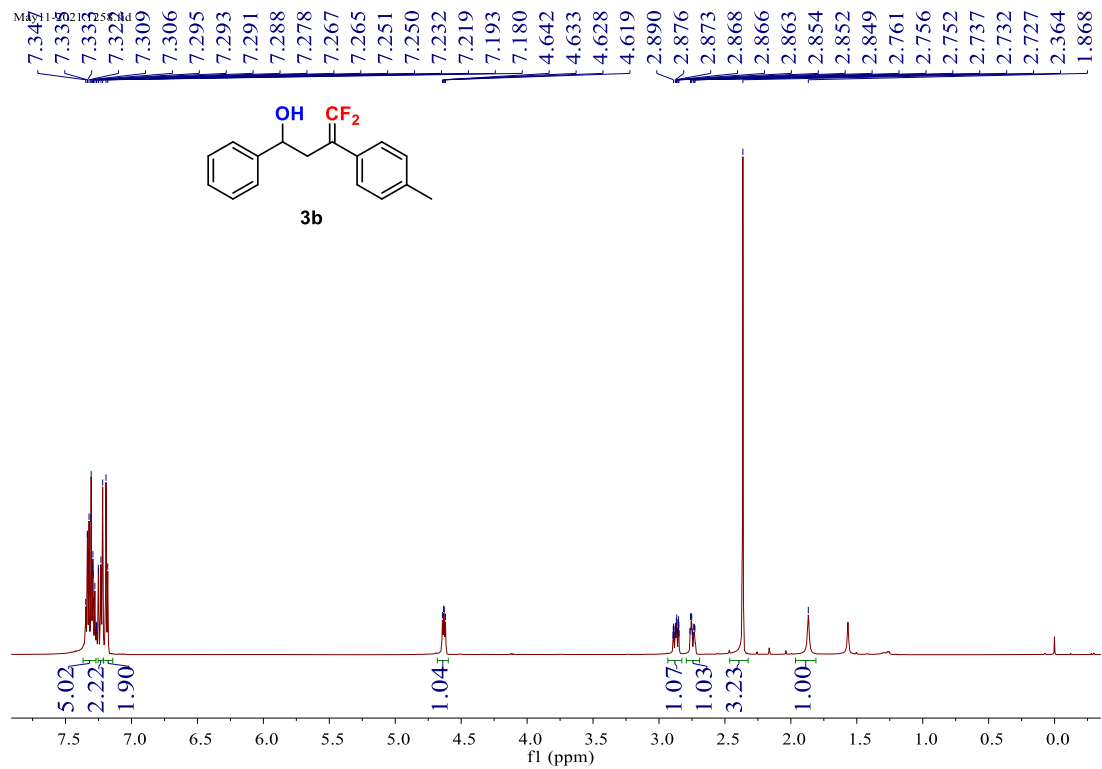
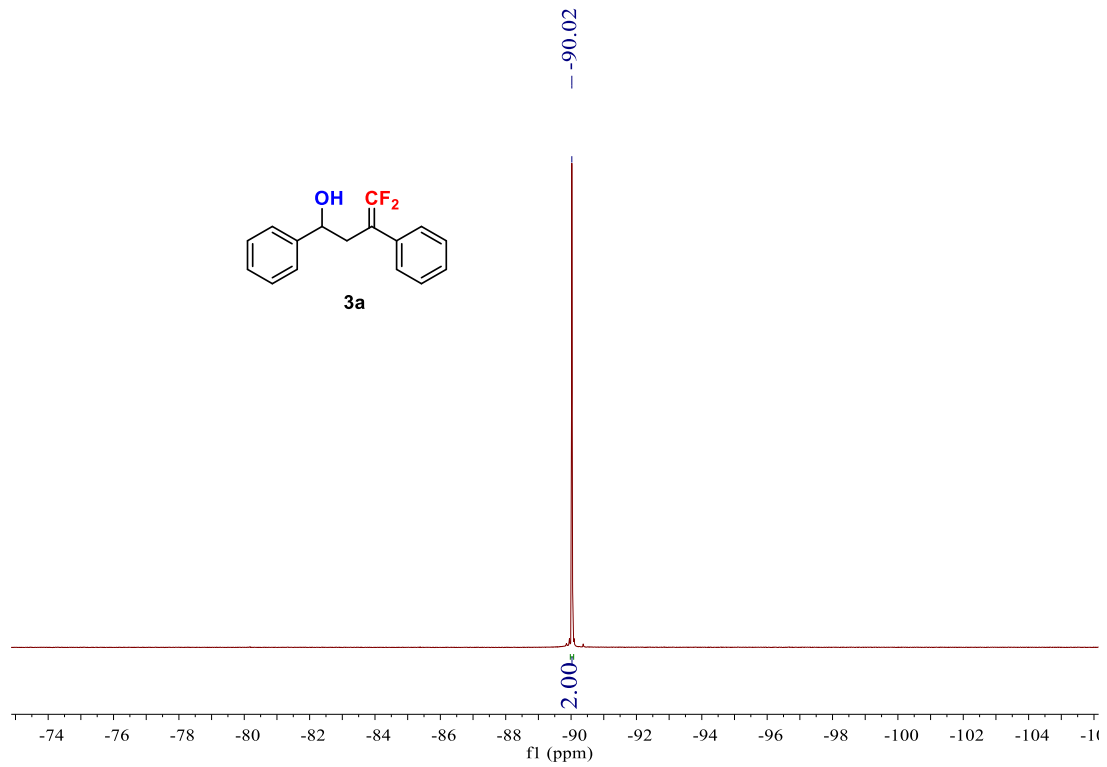
Fig. S3 ^1H NMR of **1a**, **10**, **11**

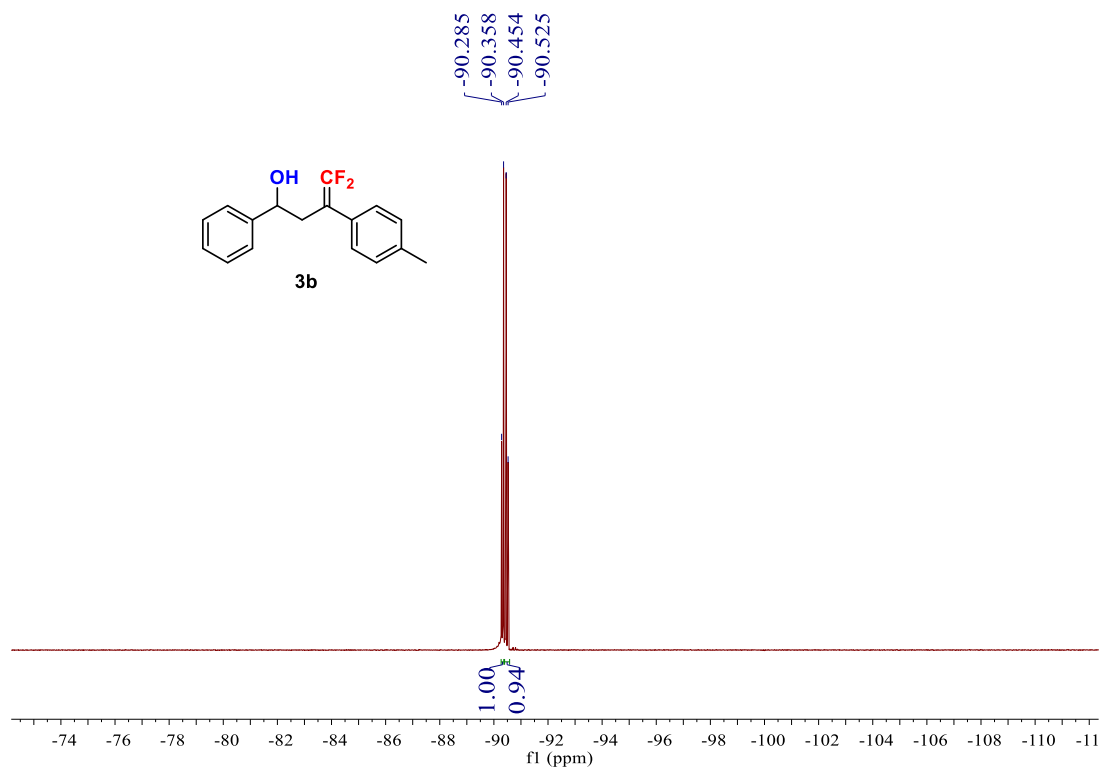
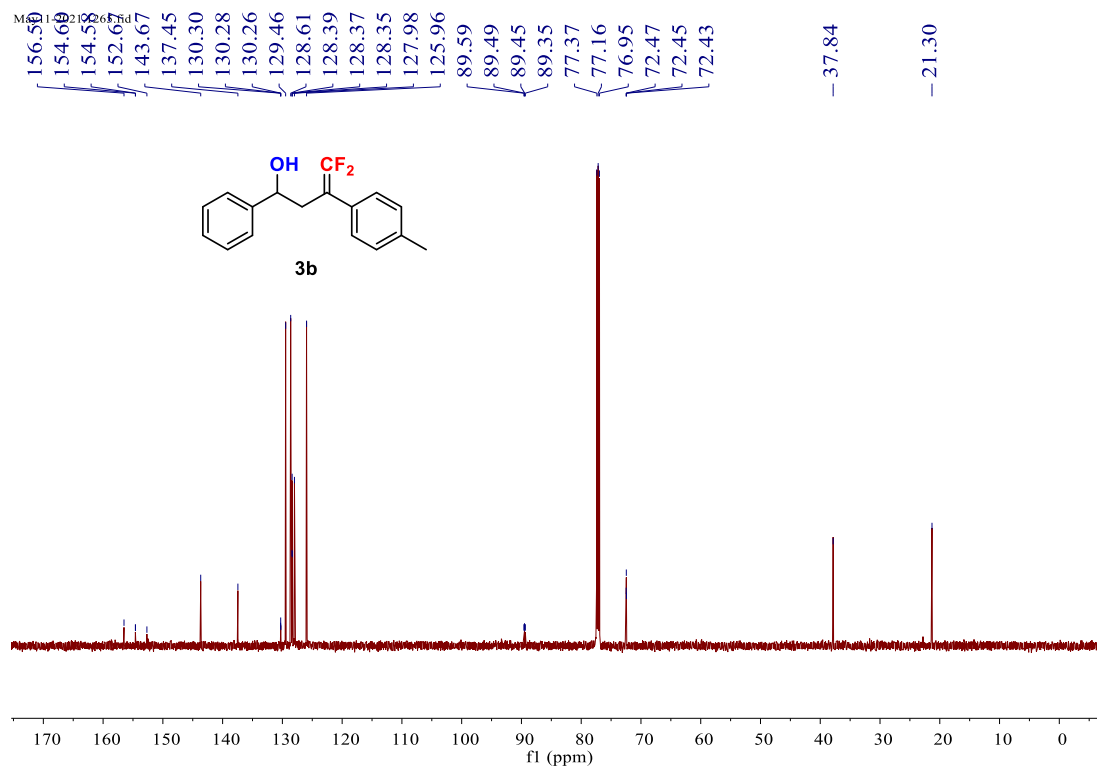
6. References

- [S1] Guo, Y.; Wang, R.; Song, H.; Liu, Y.; Wang, Q. *Org. Lett.* 2020, **22**, 709–713.
[S2] Deng, Y., Liu, Q., and Smith, A.B. *J. Am. Chem. Soc.* 2017, **139**, 9487–9490.
[S3] Lu, X.; Zhang, J.; Xu, L.; Shen, W.; Yu, F.; Ding, L.; Zhong, G. *Org. Lett.* 2020, **22**, 5610–5616.

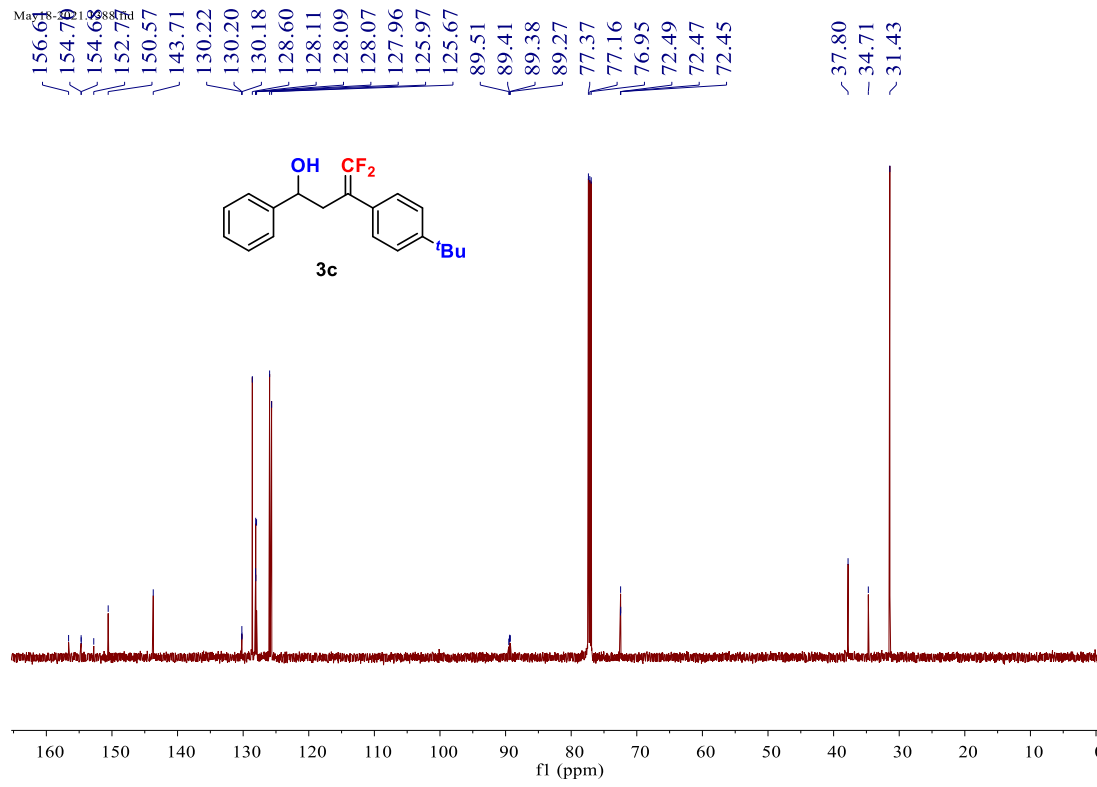
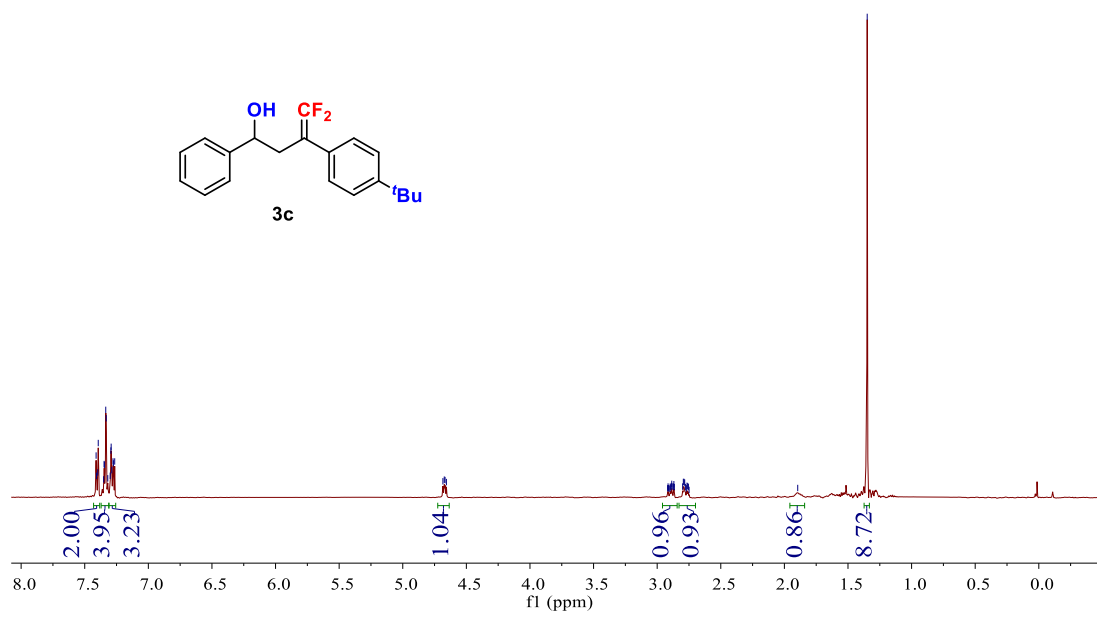
7. ¹H, ¹³C, ¹⁹F Spectra of New Compounds

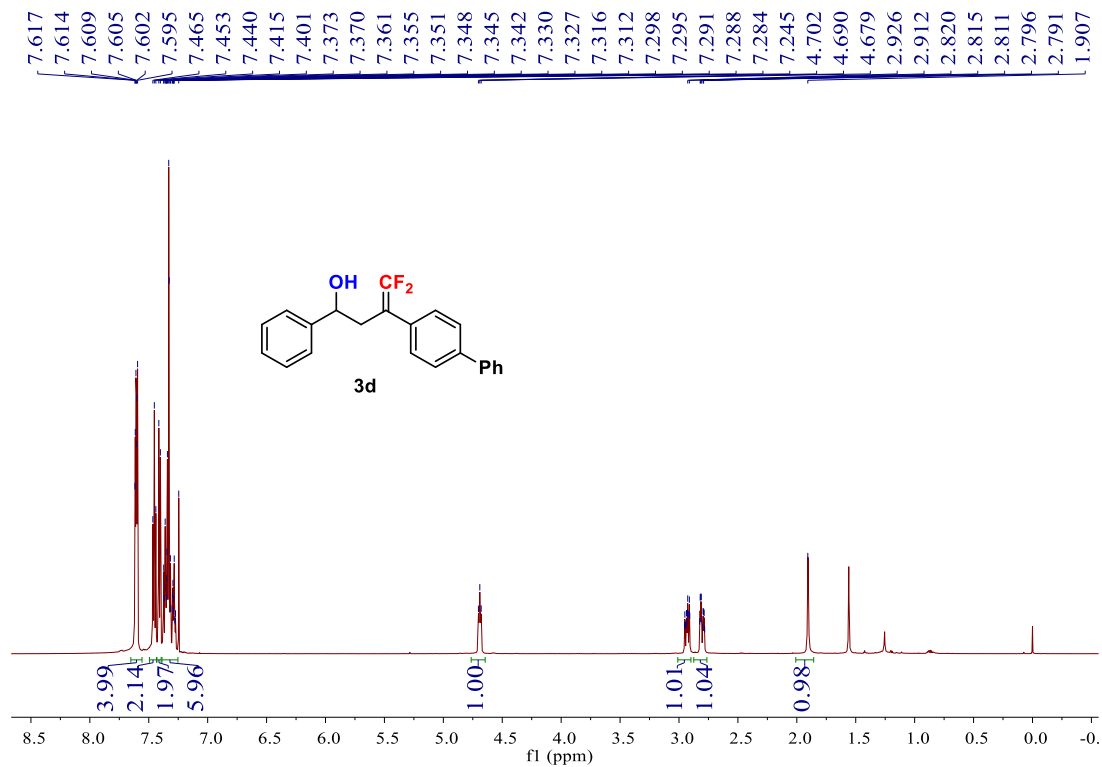
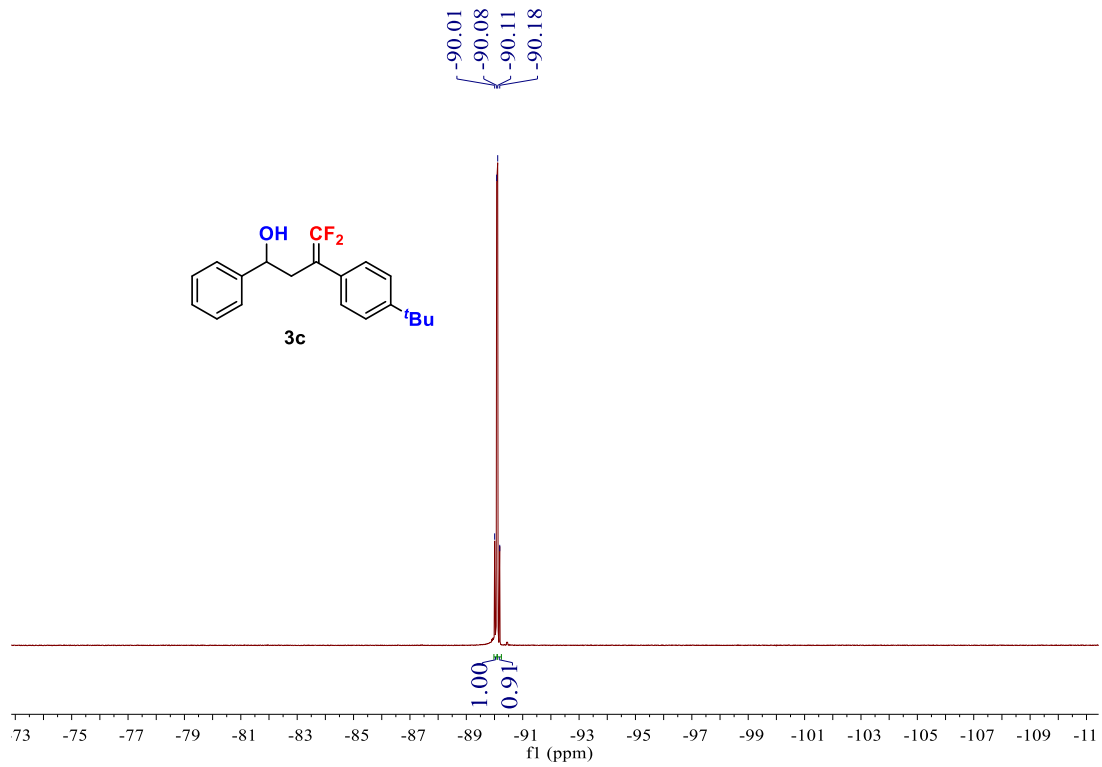


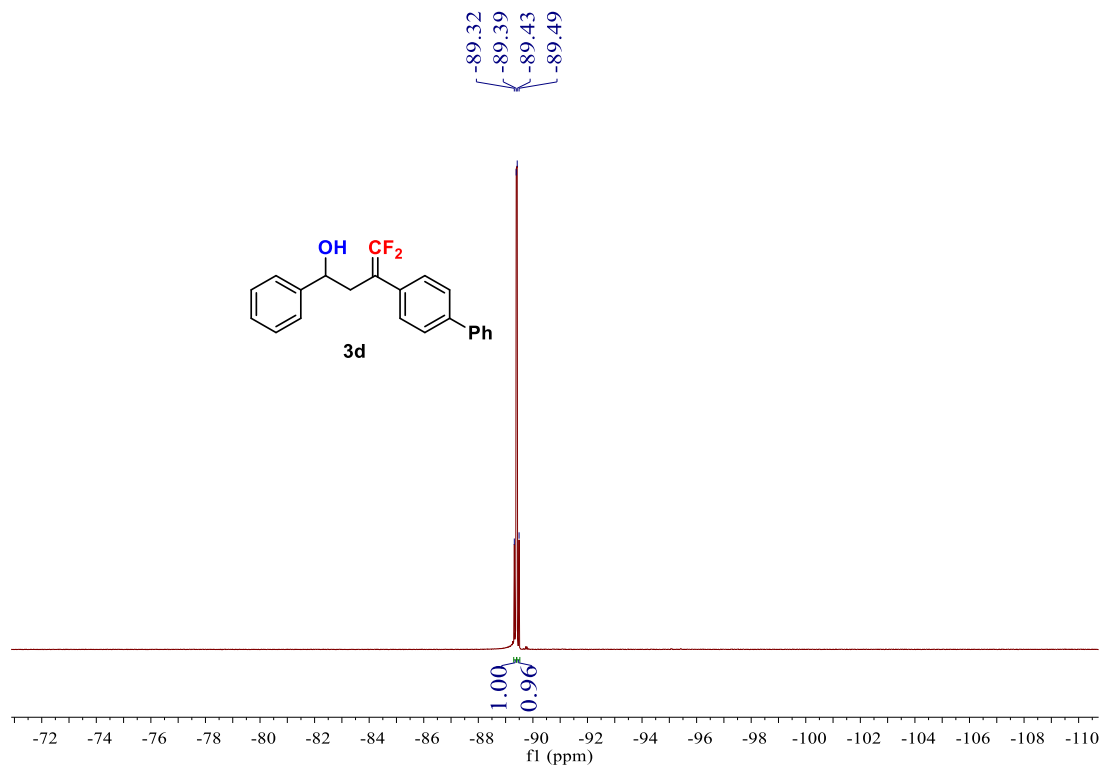
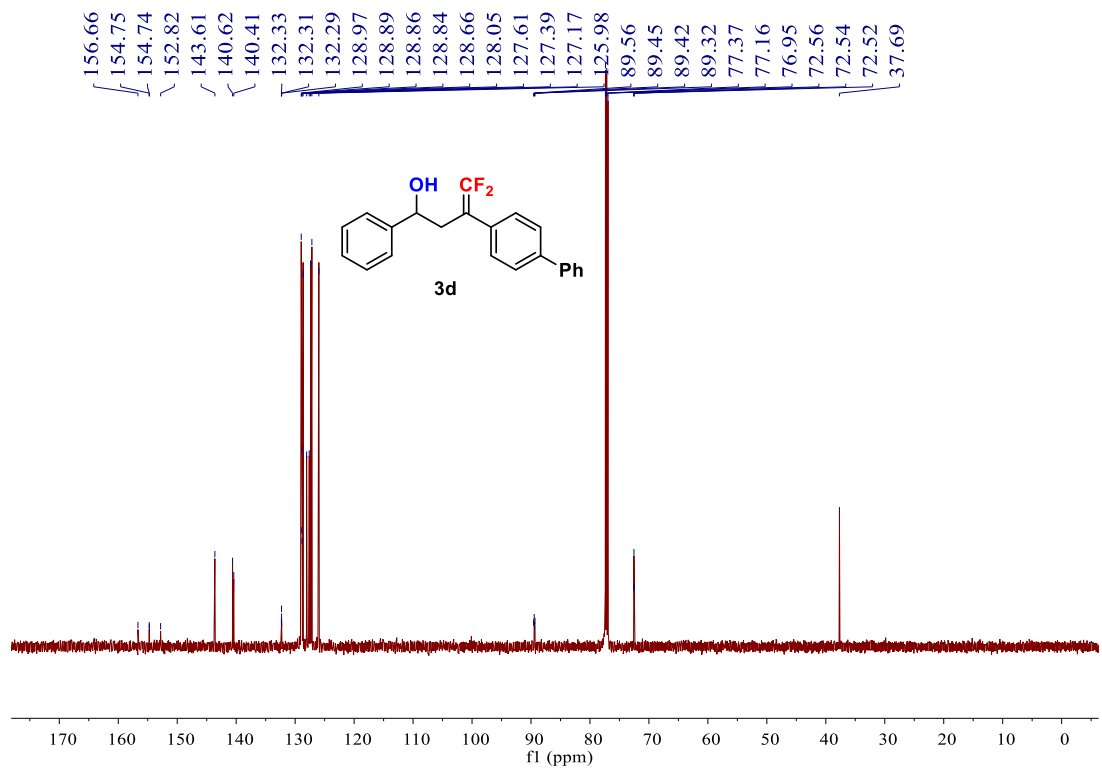


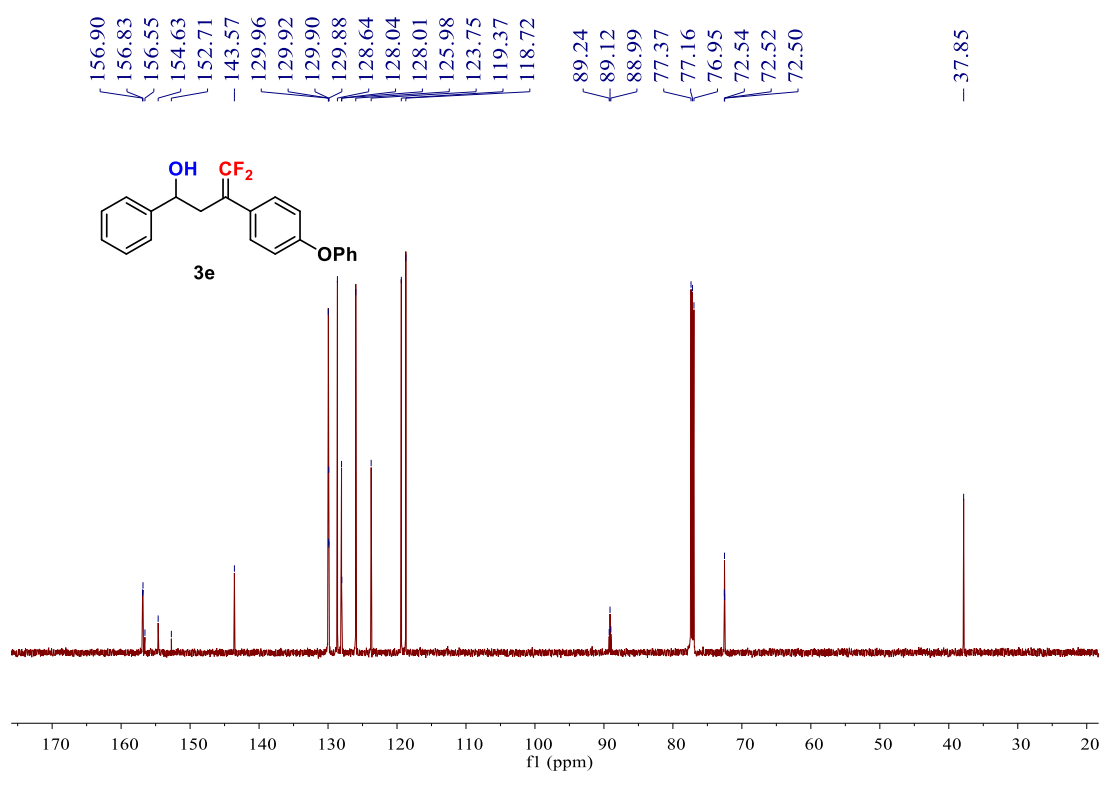
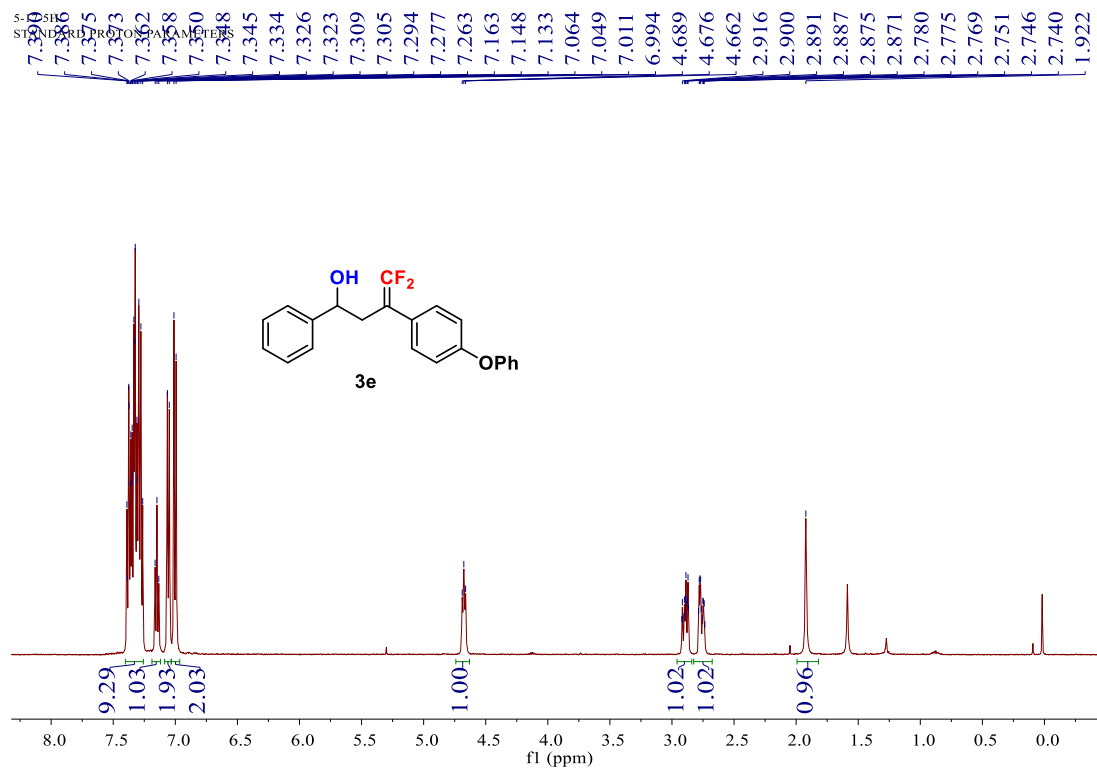


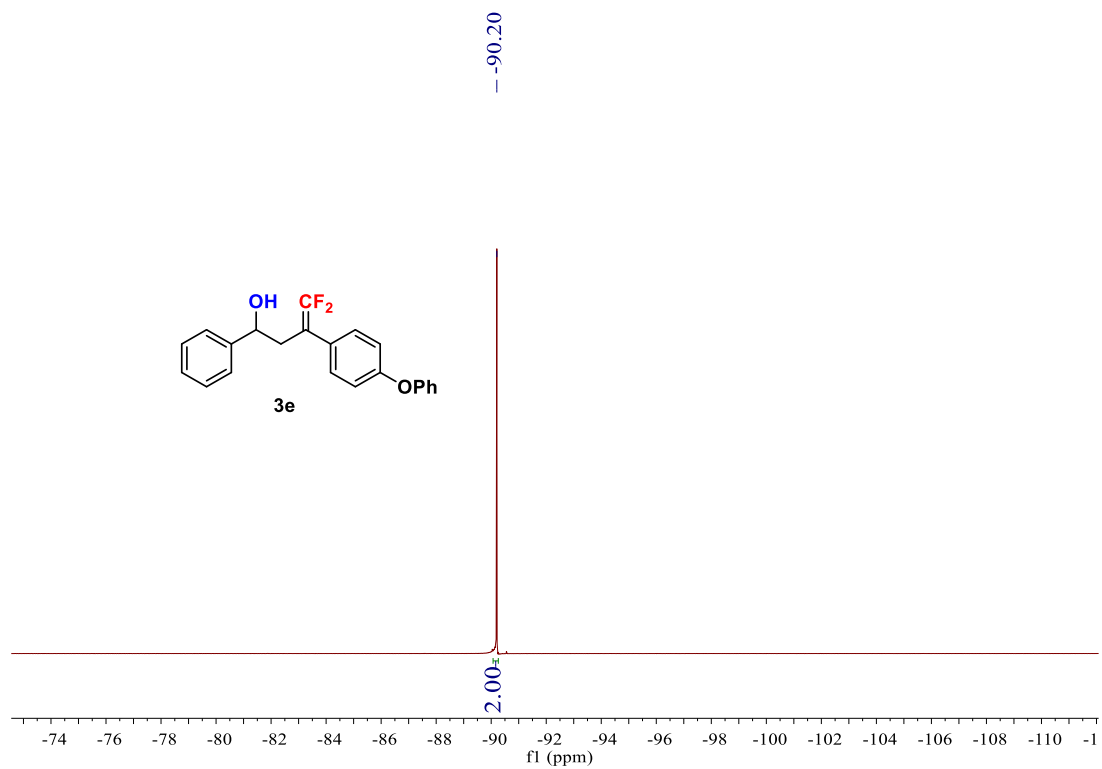
5-13
STANDARD PROTON PARAMETERS



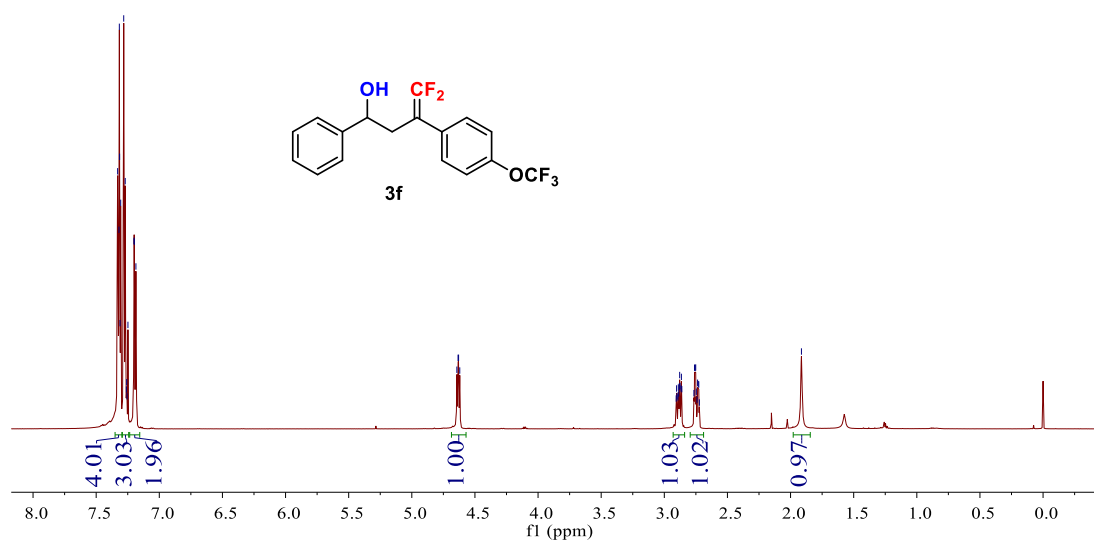


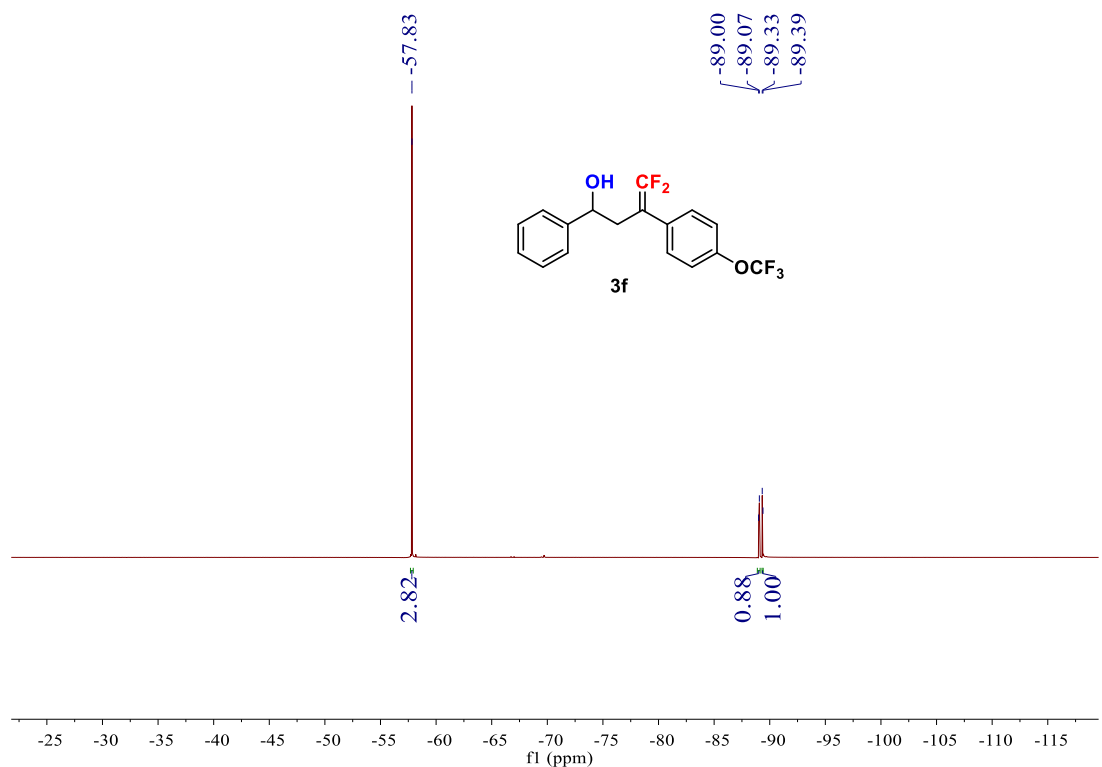
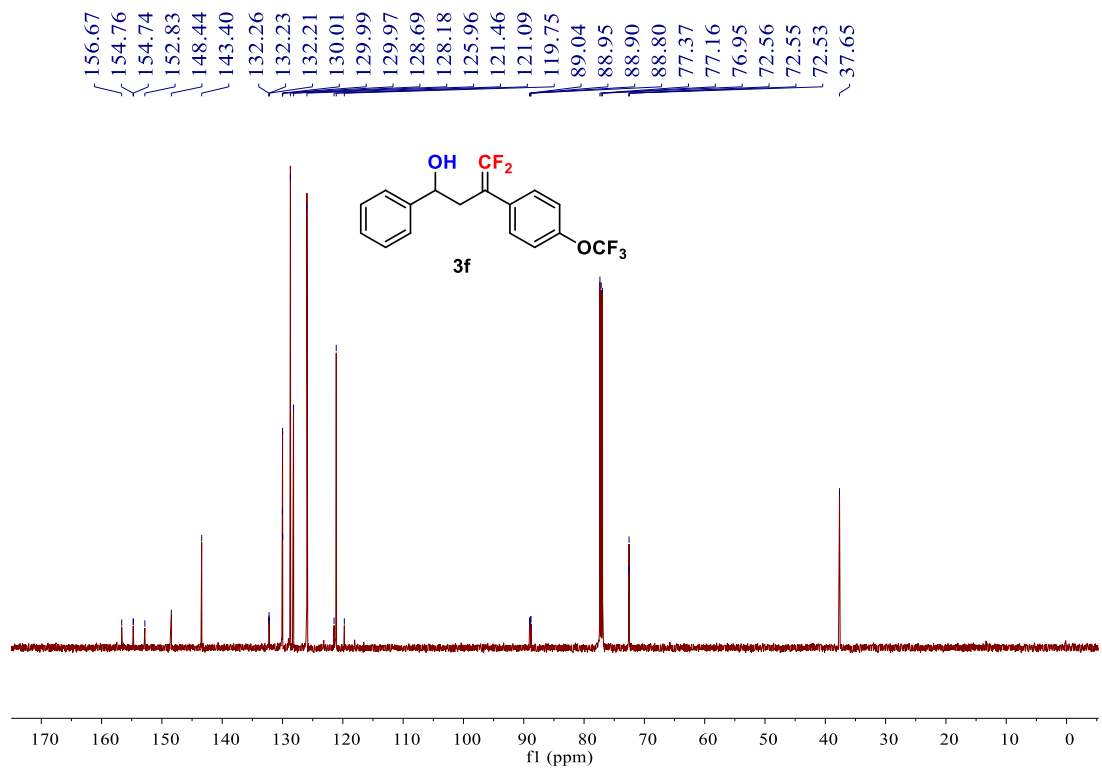


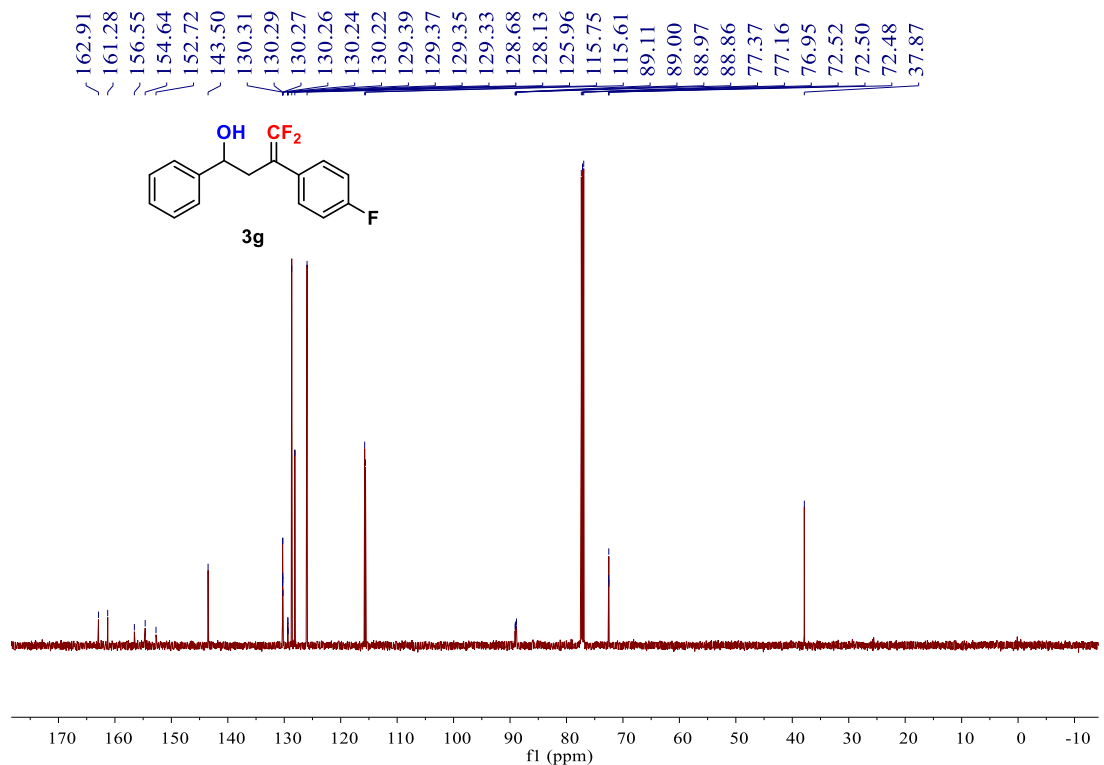
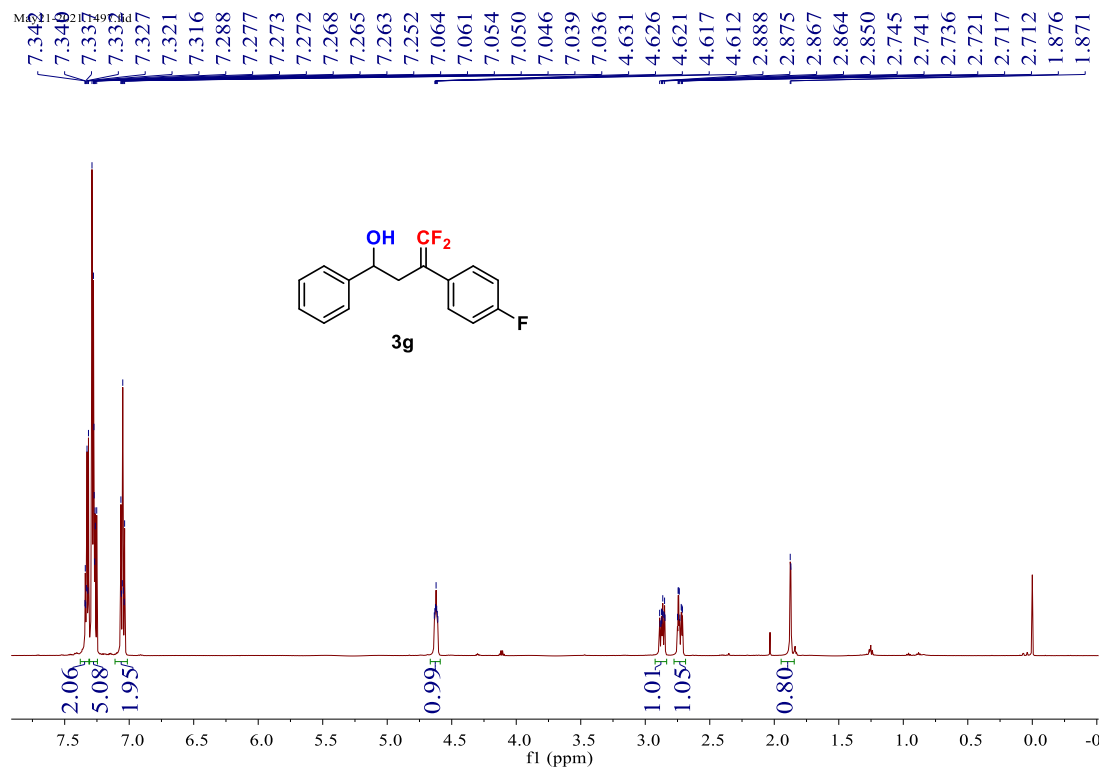


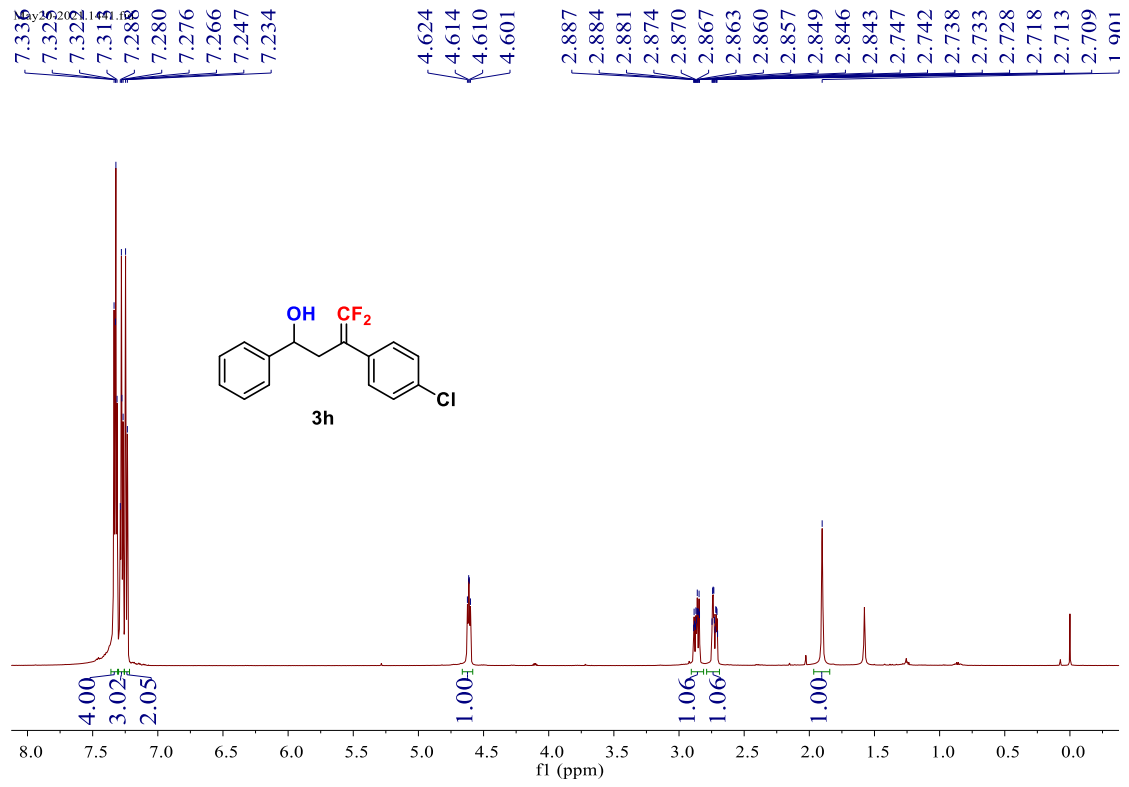
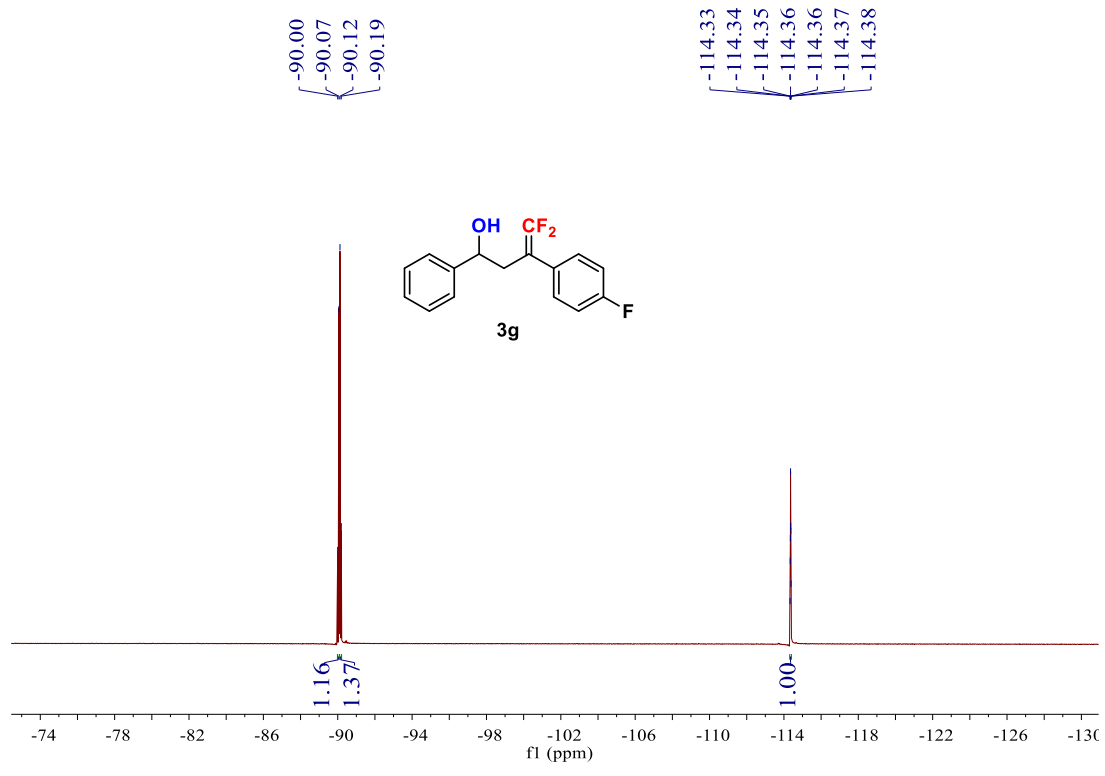


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4.620
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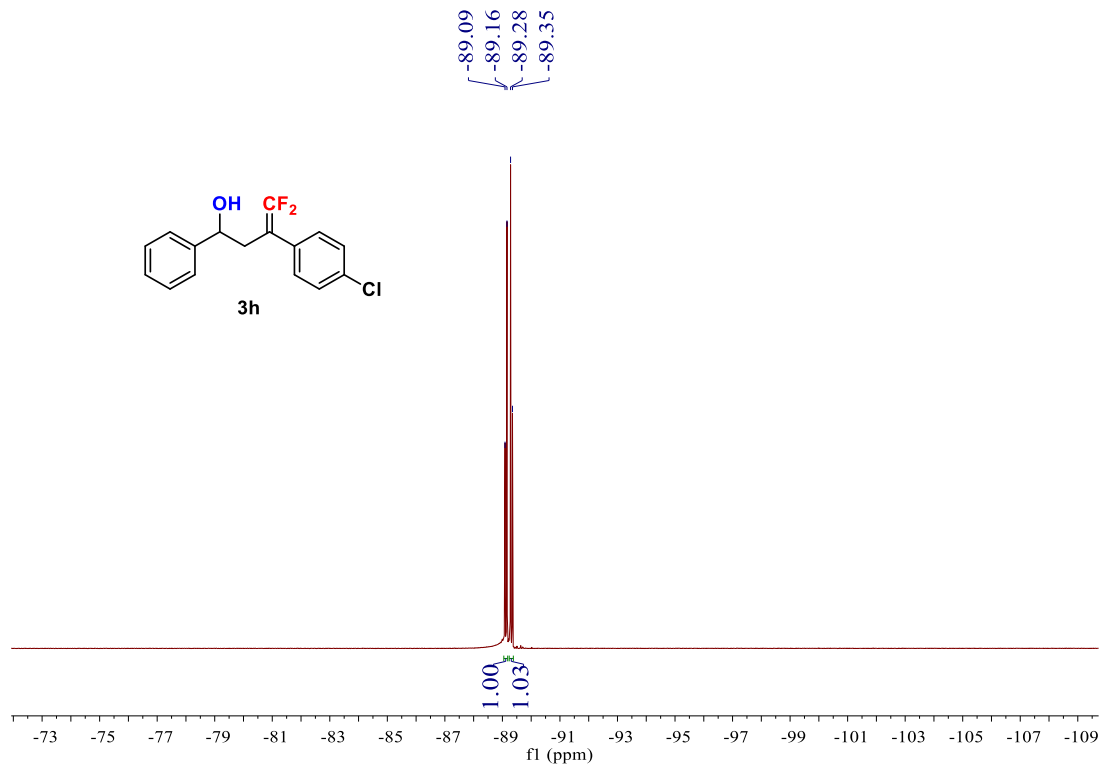
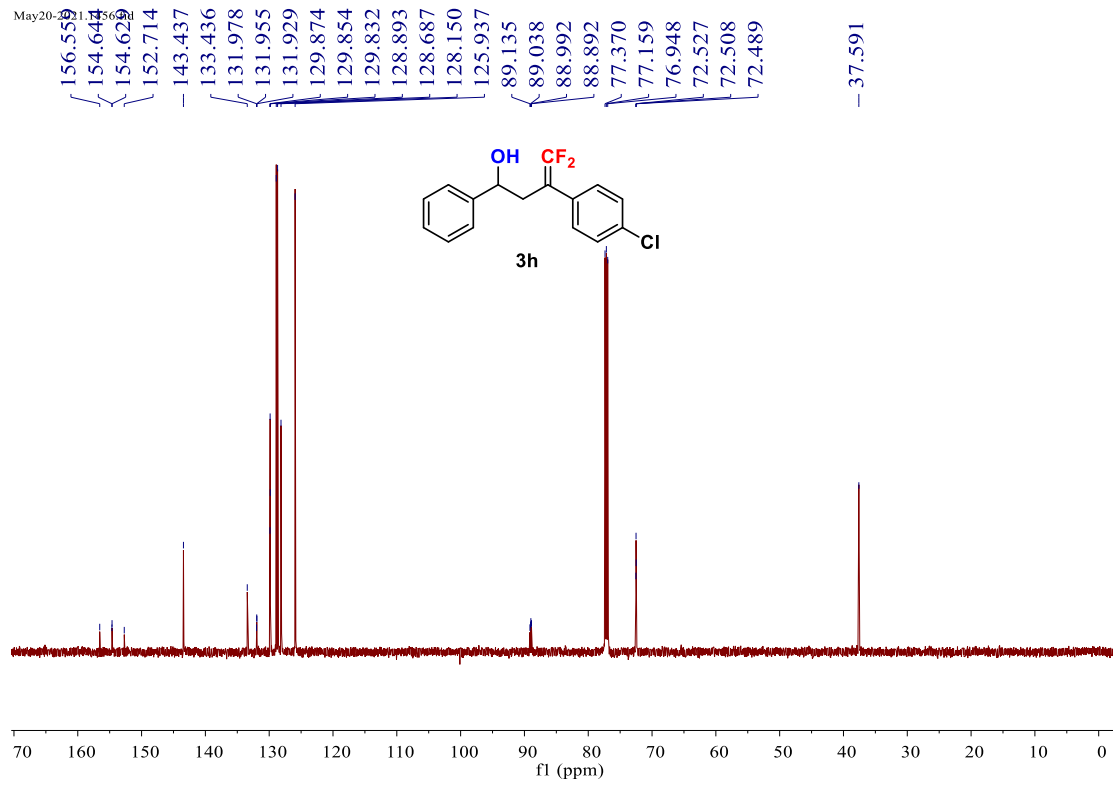


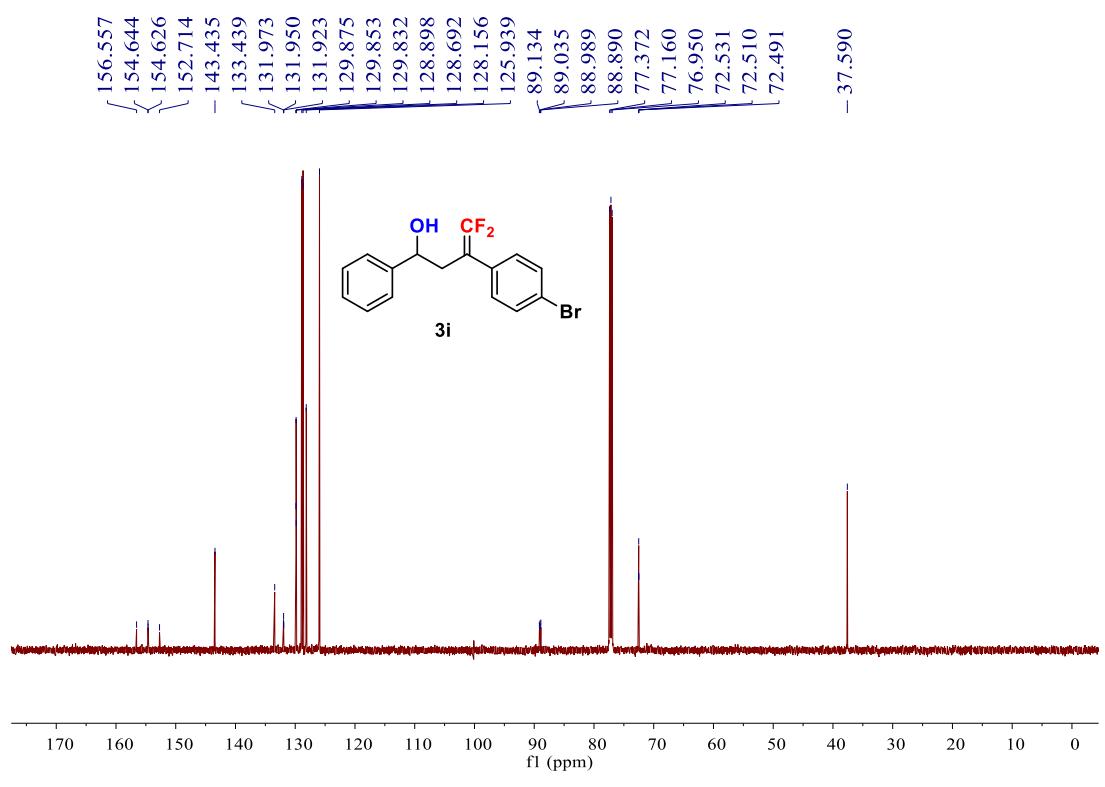
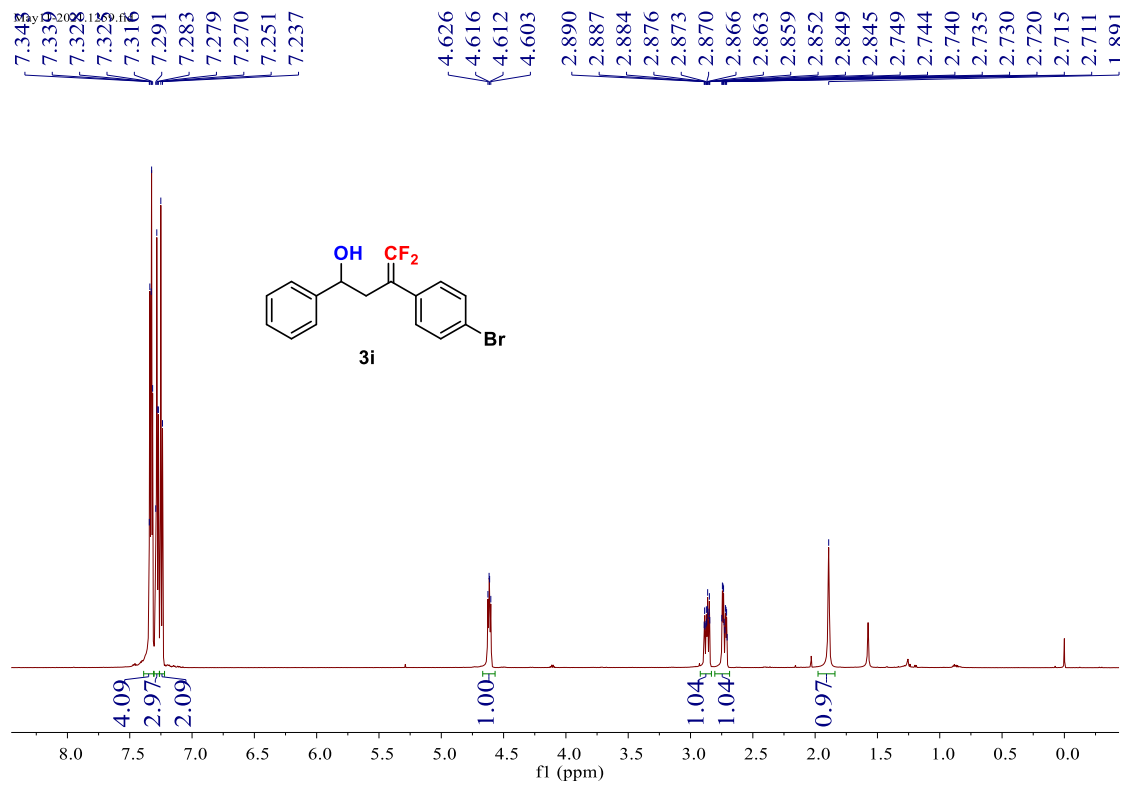


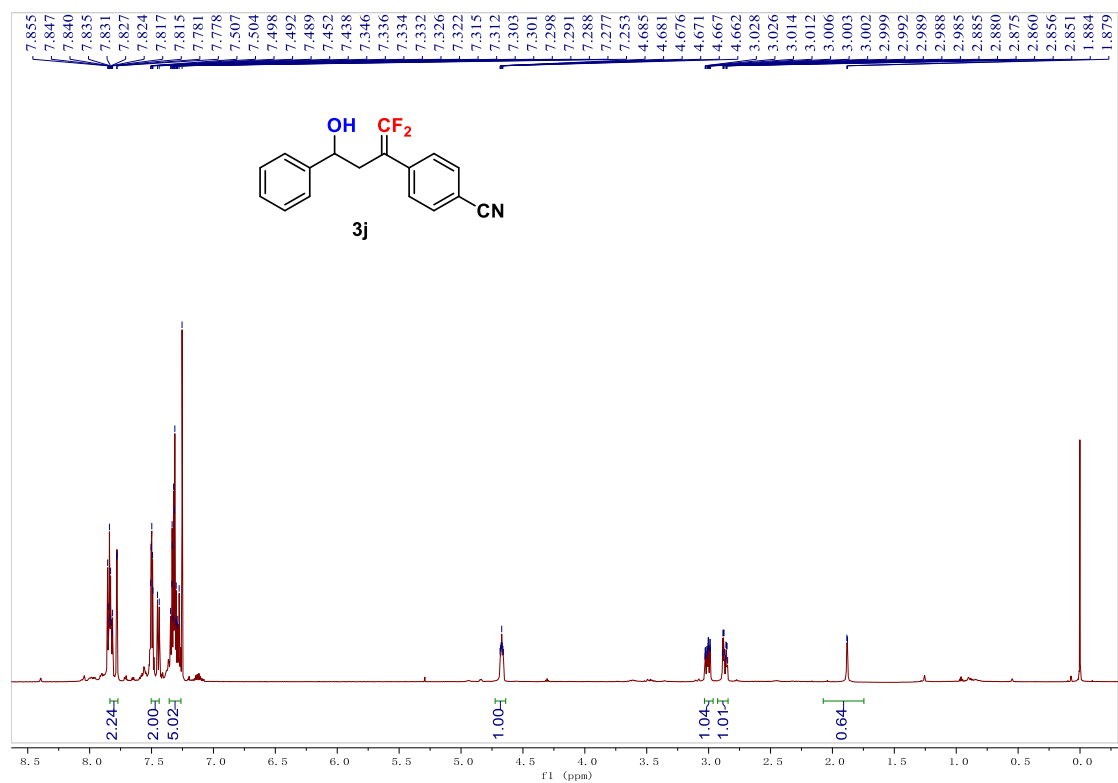
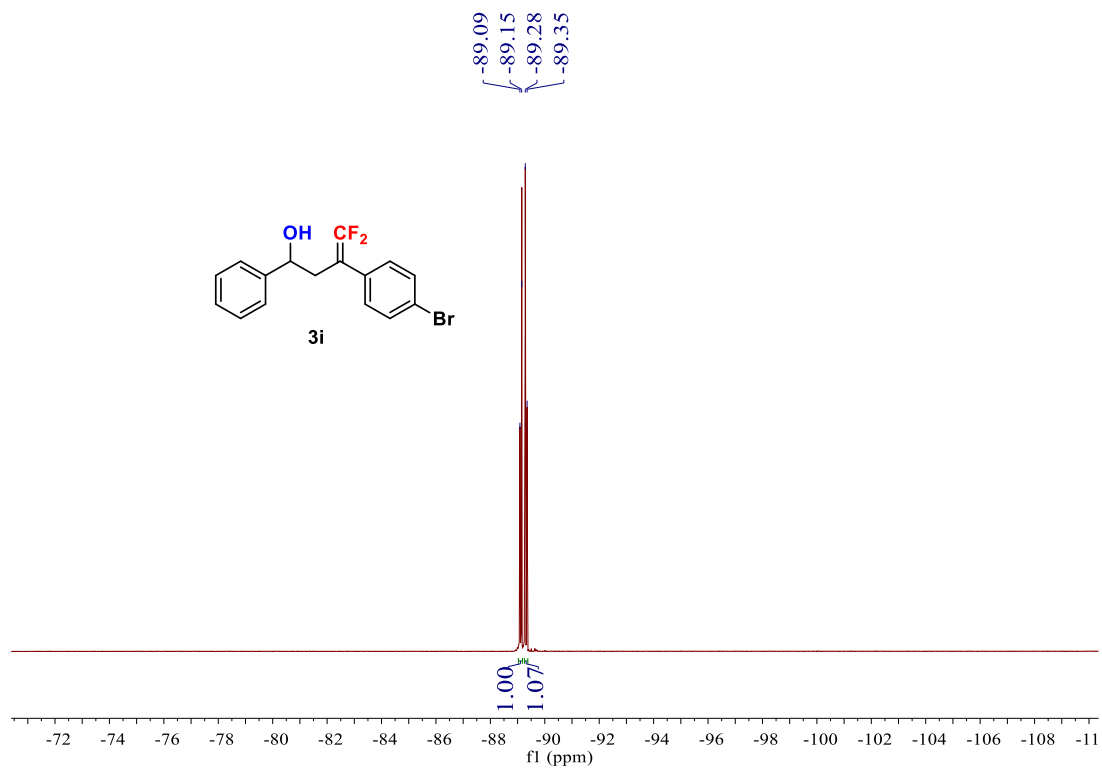


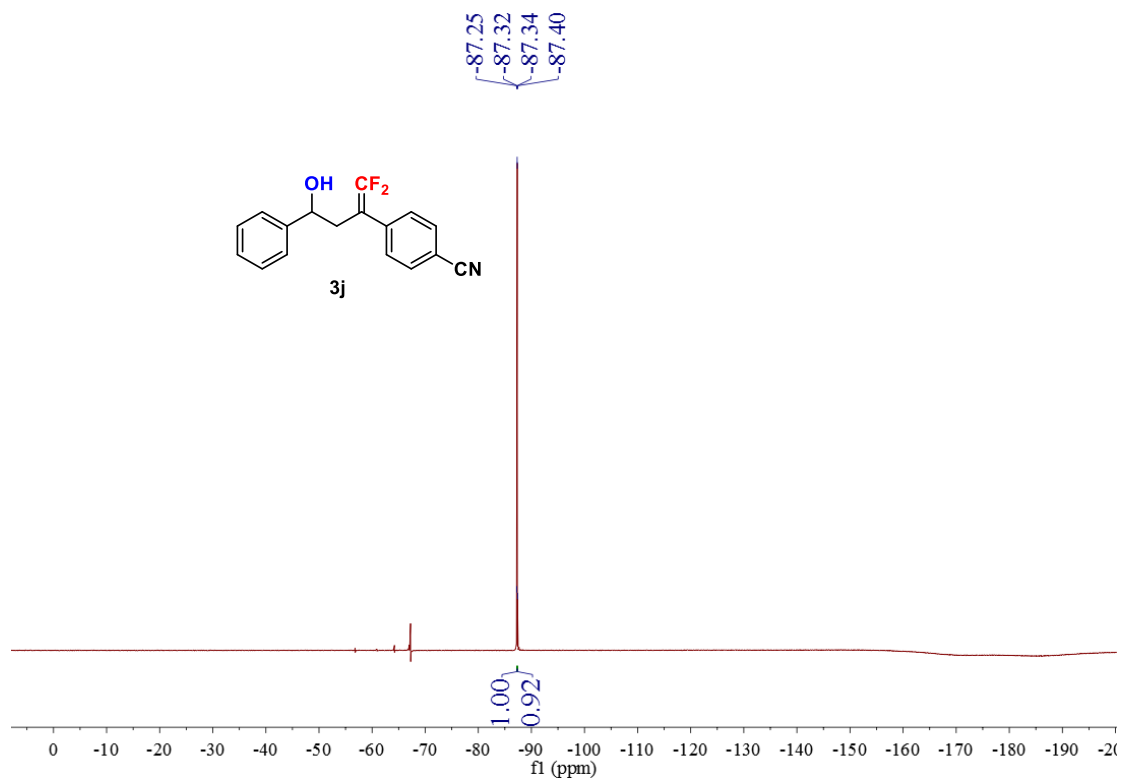
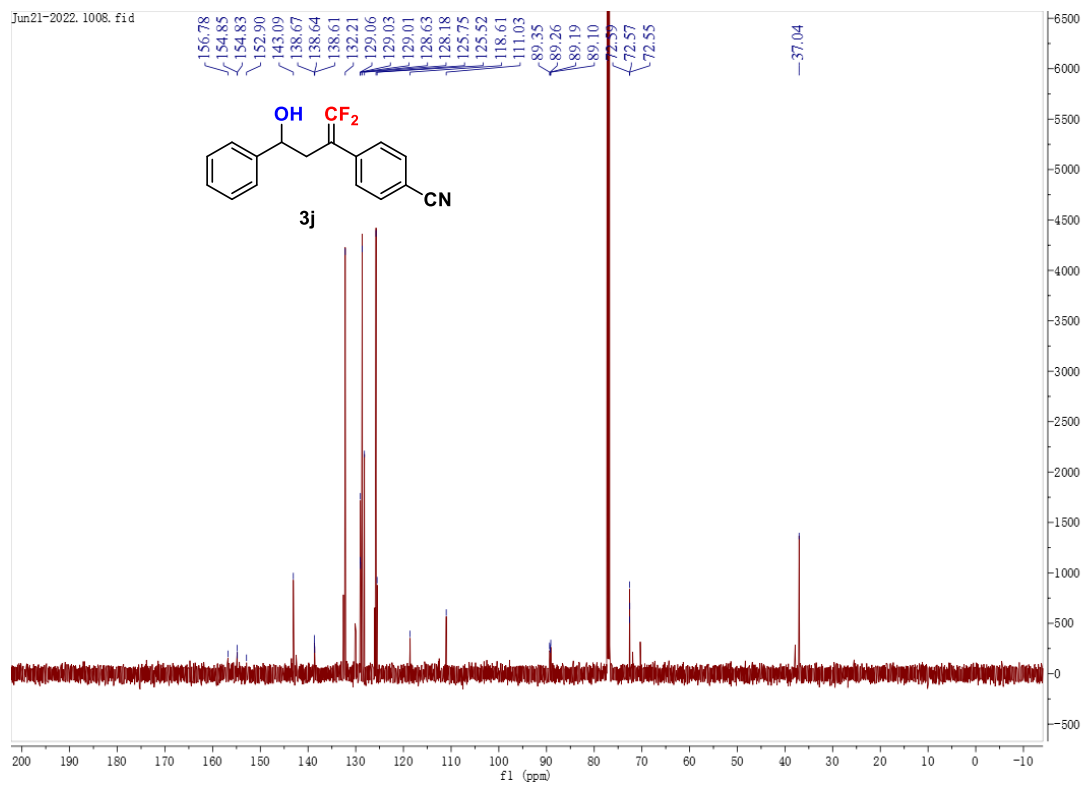


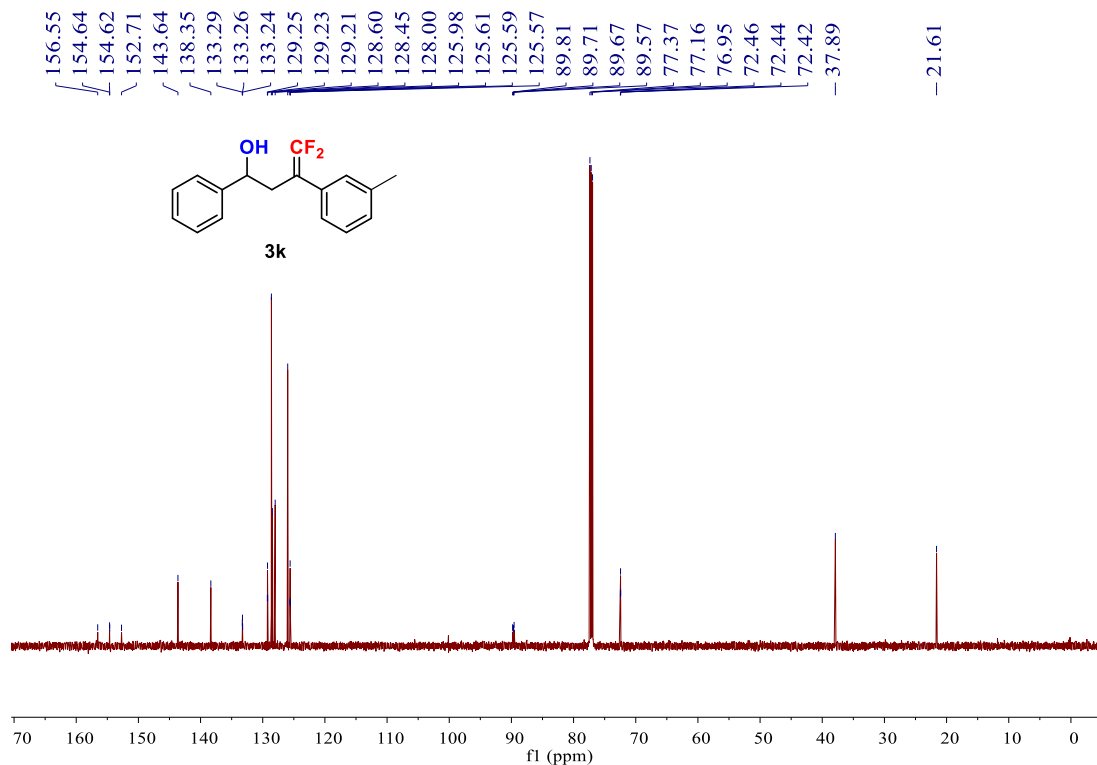
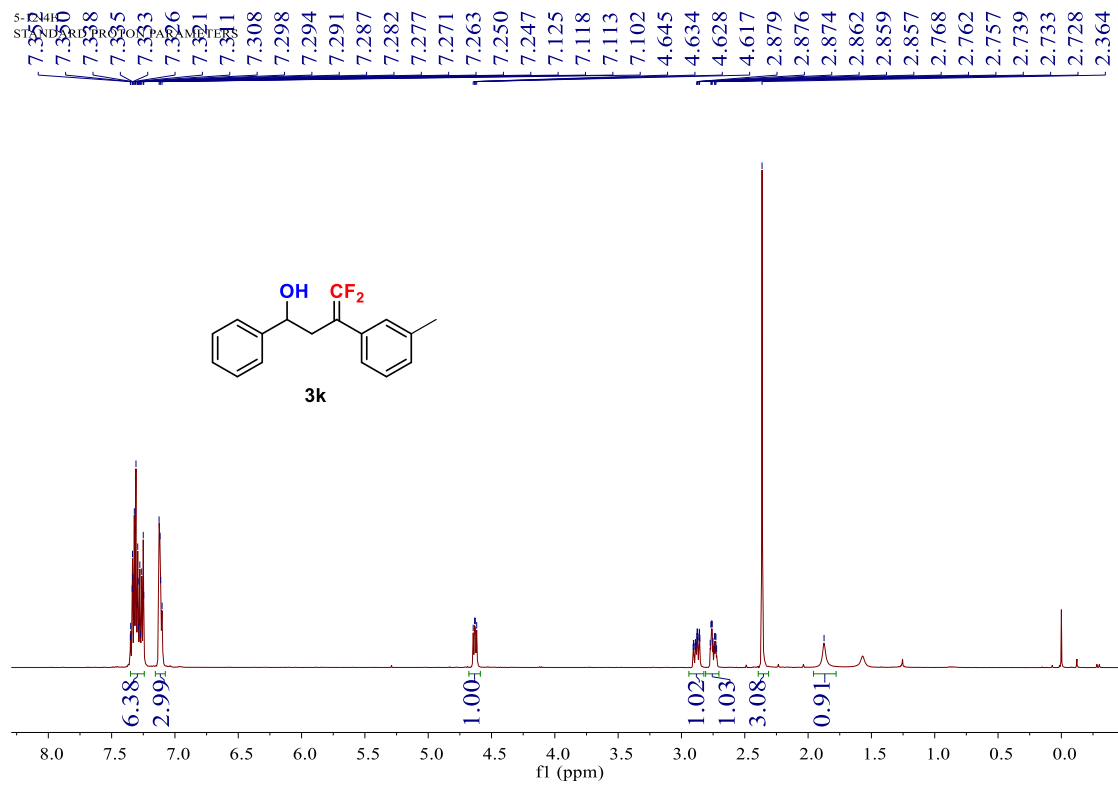
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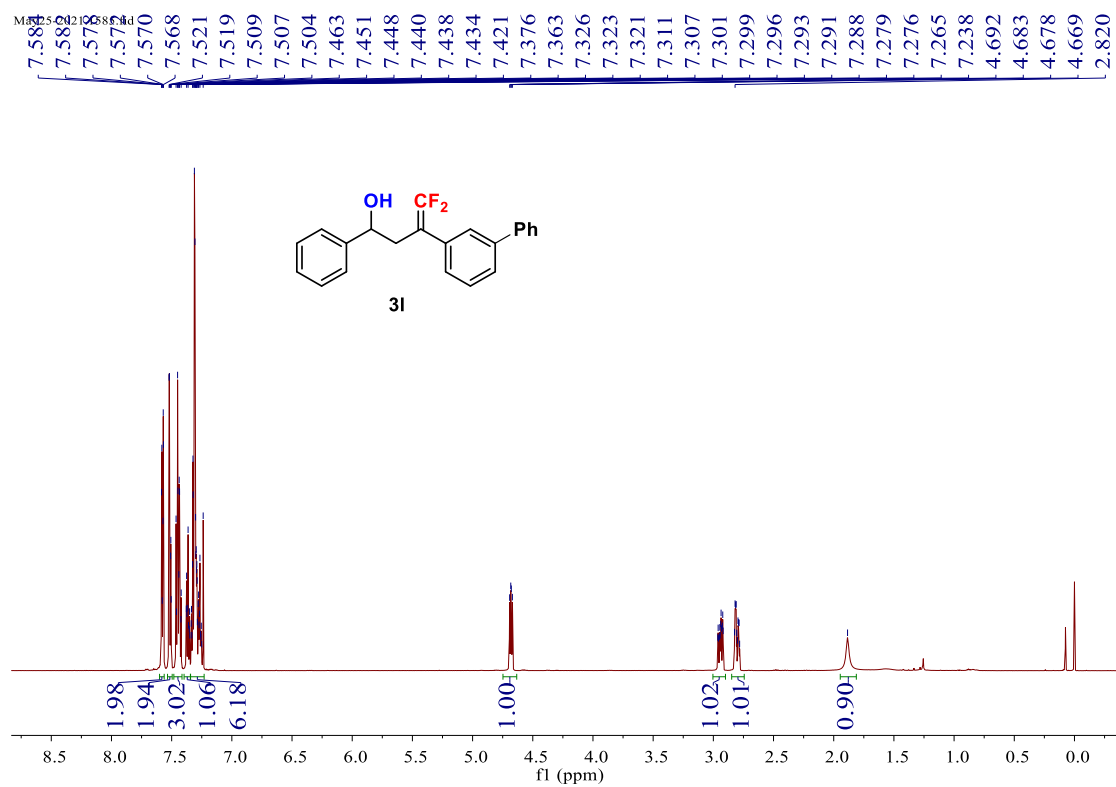
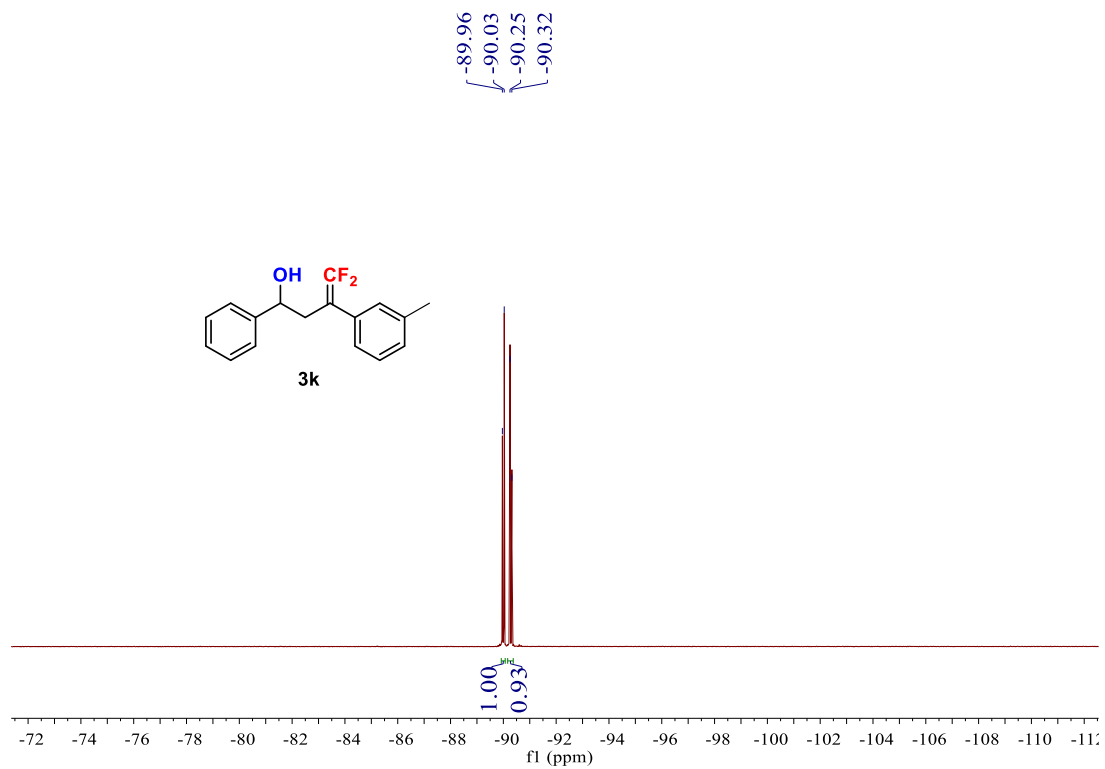


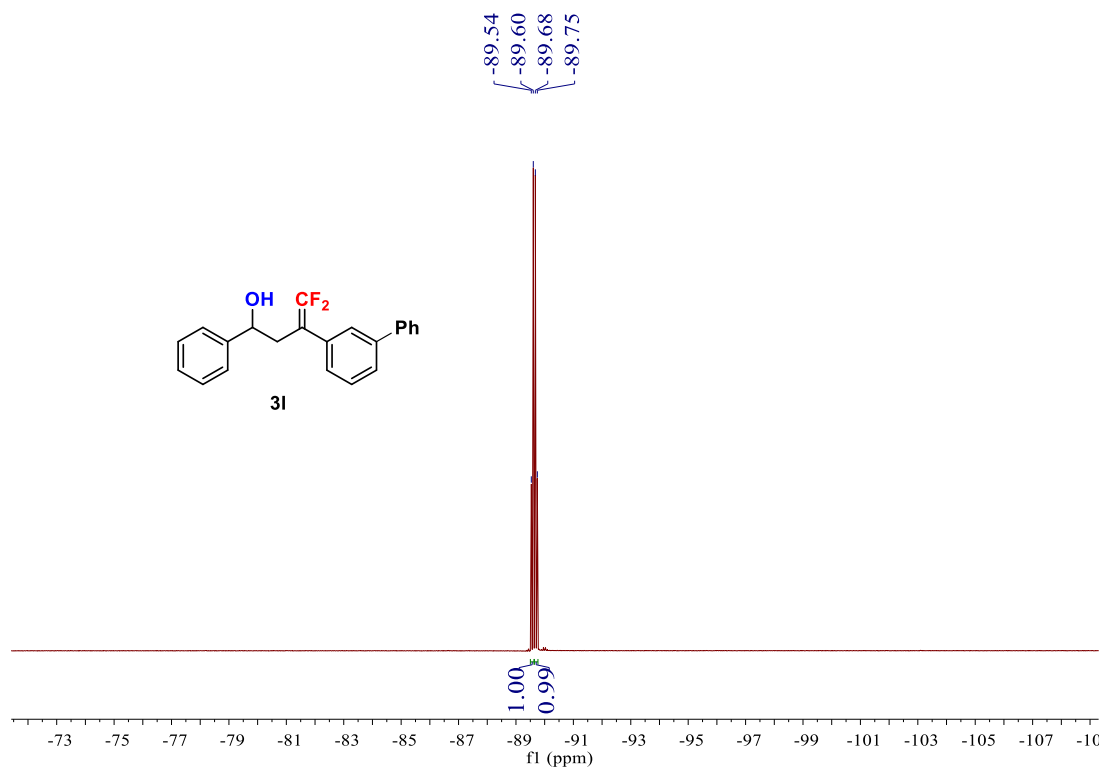
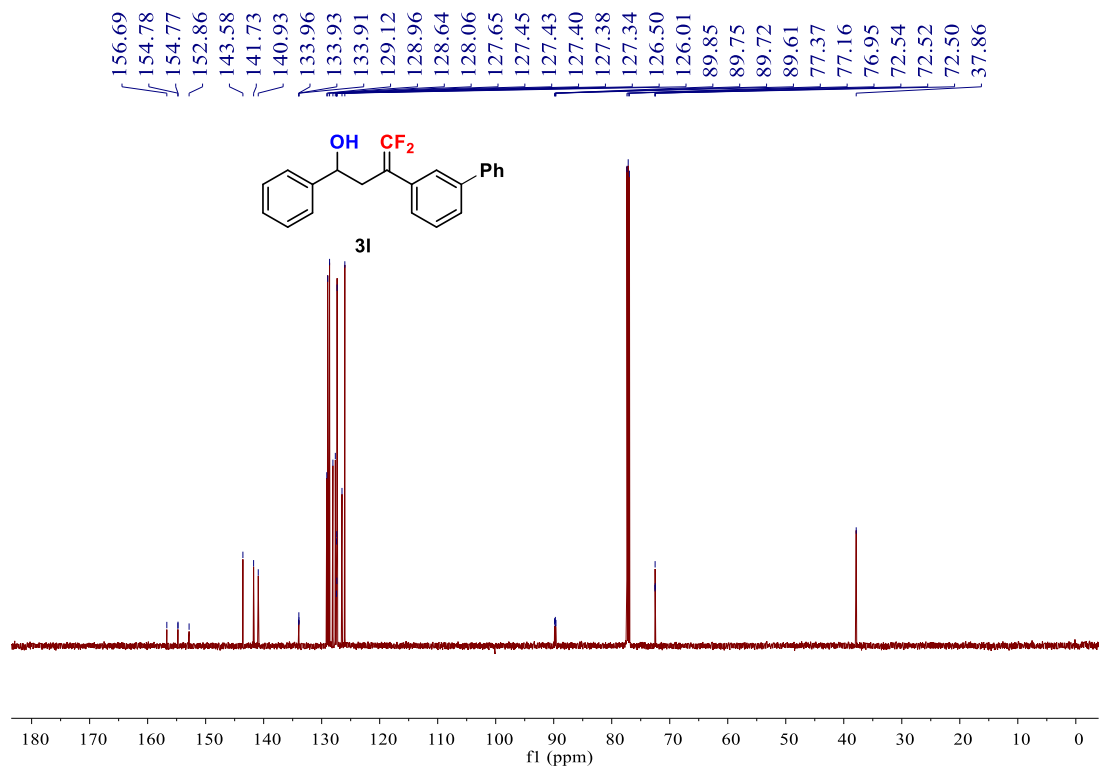


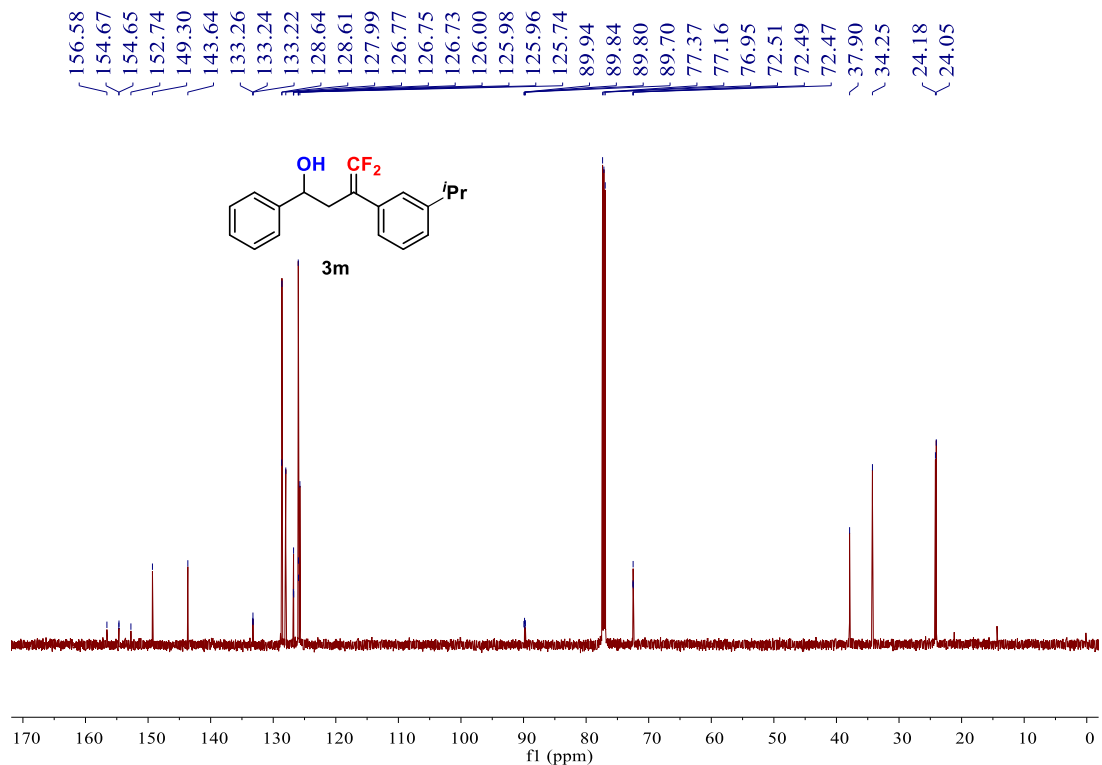
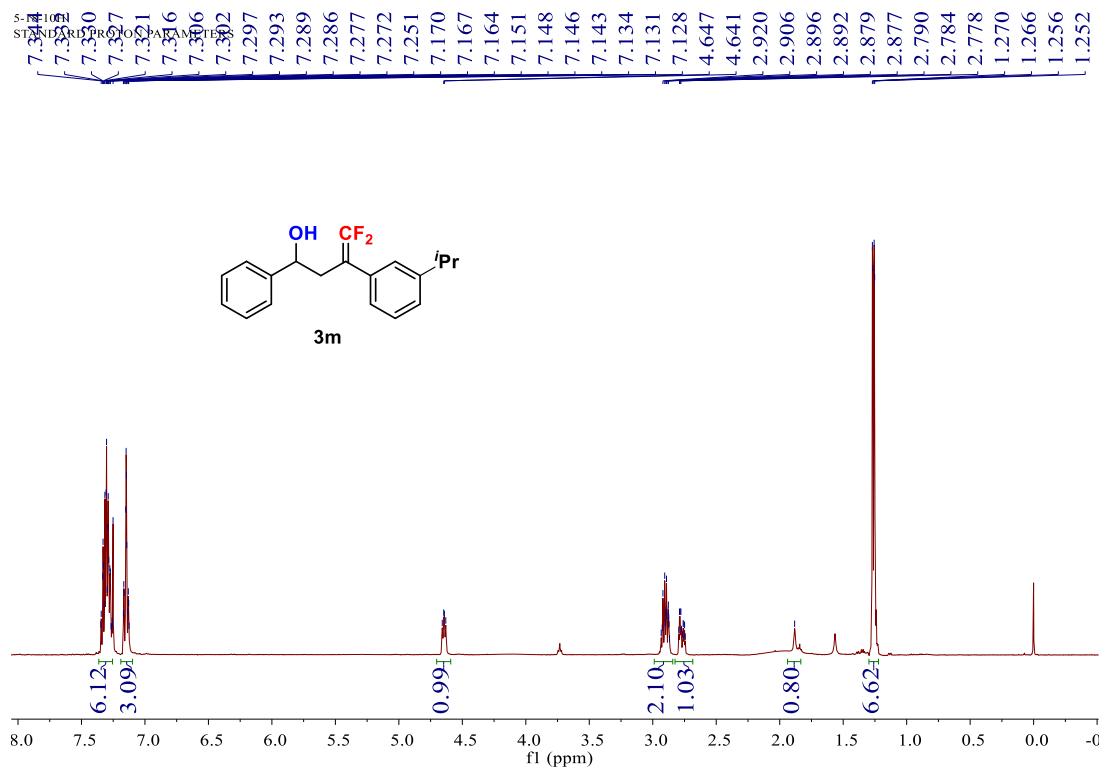


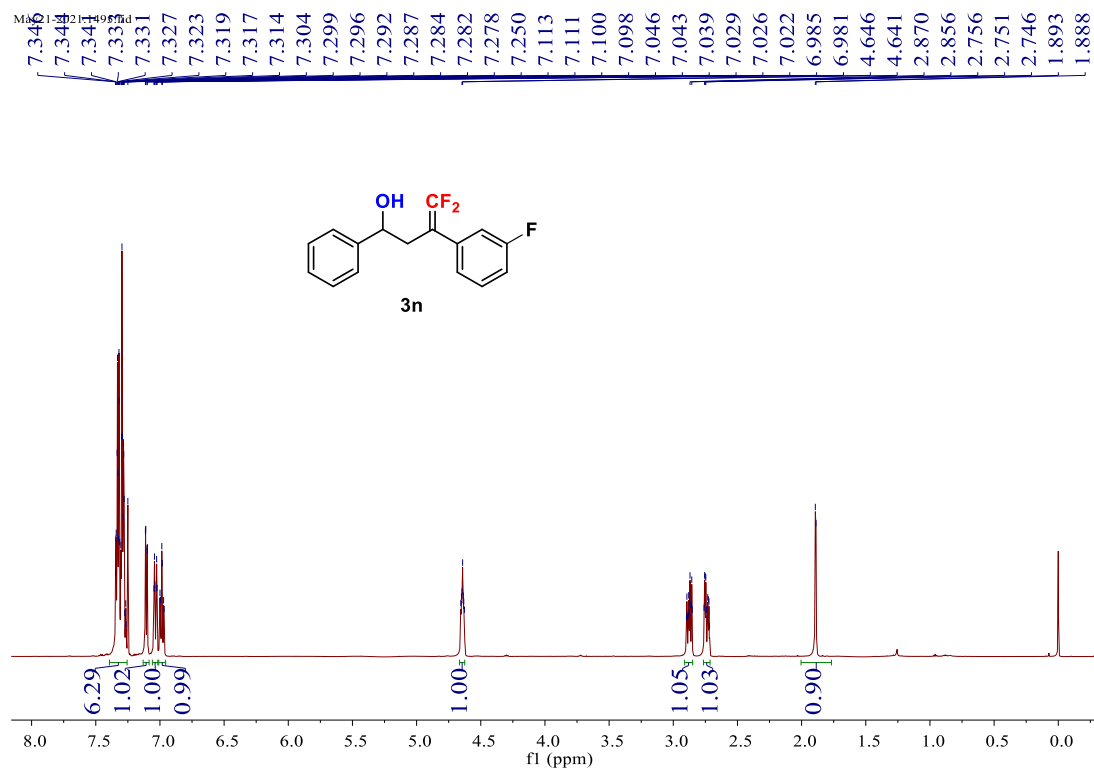
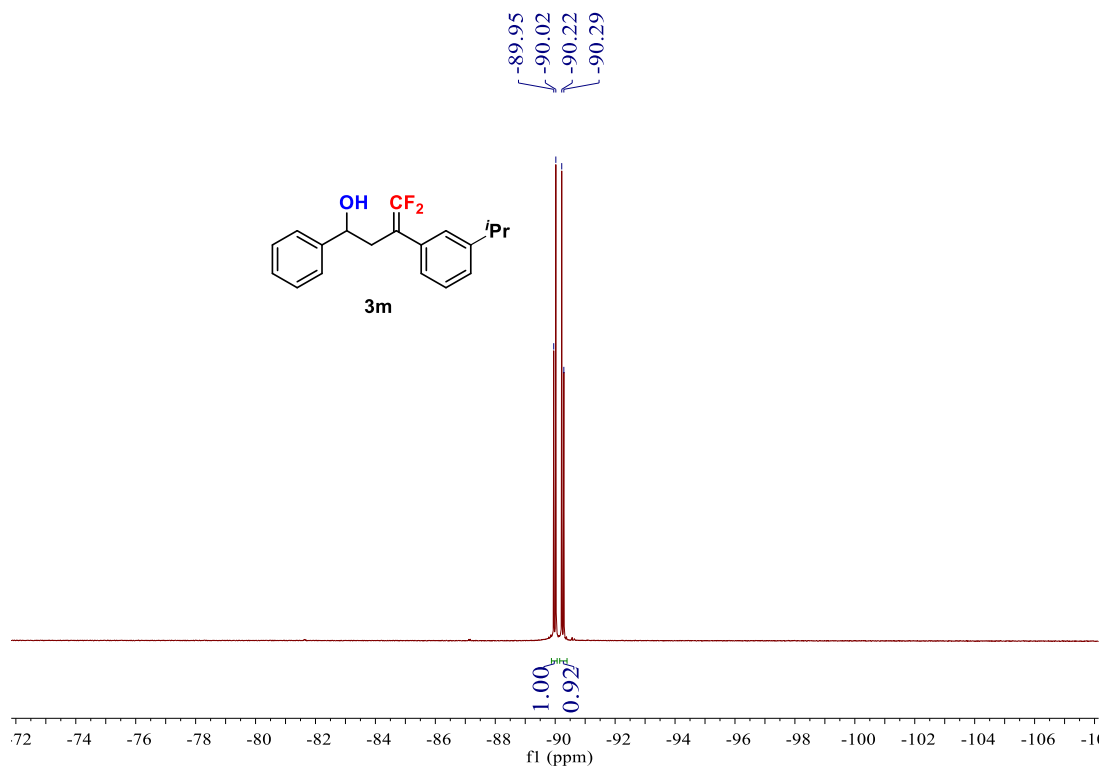


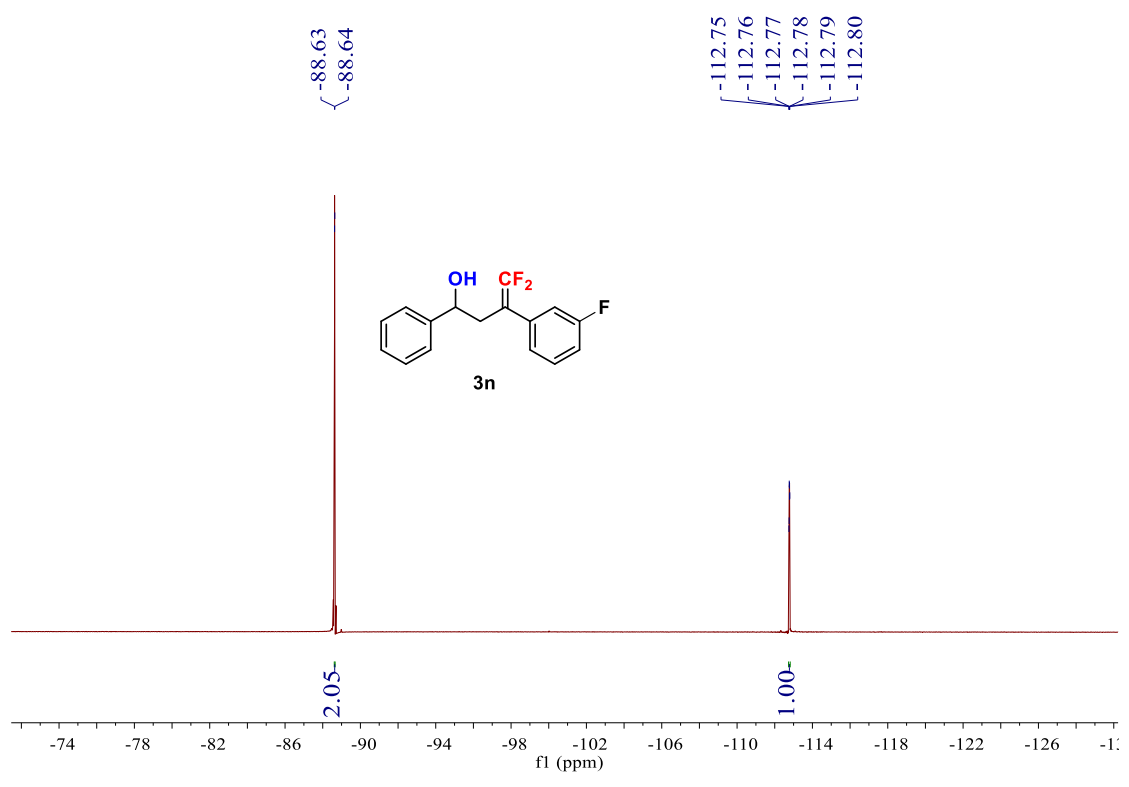
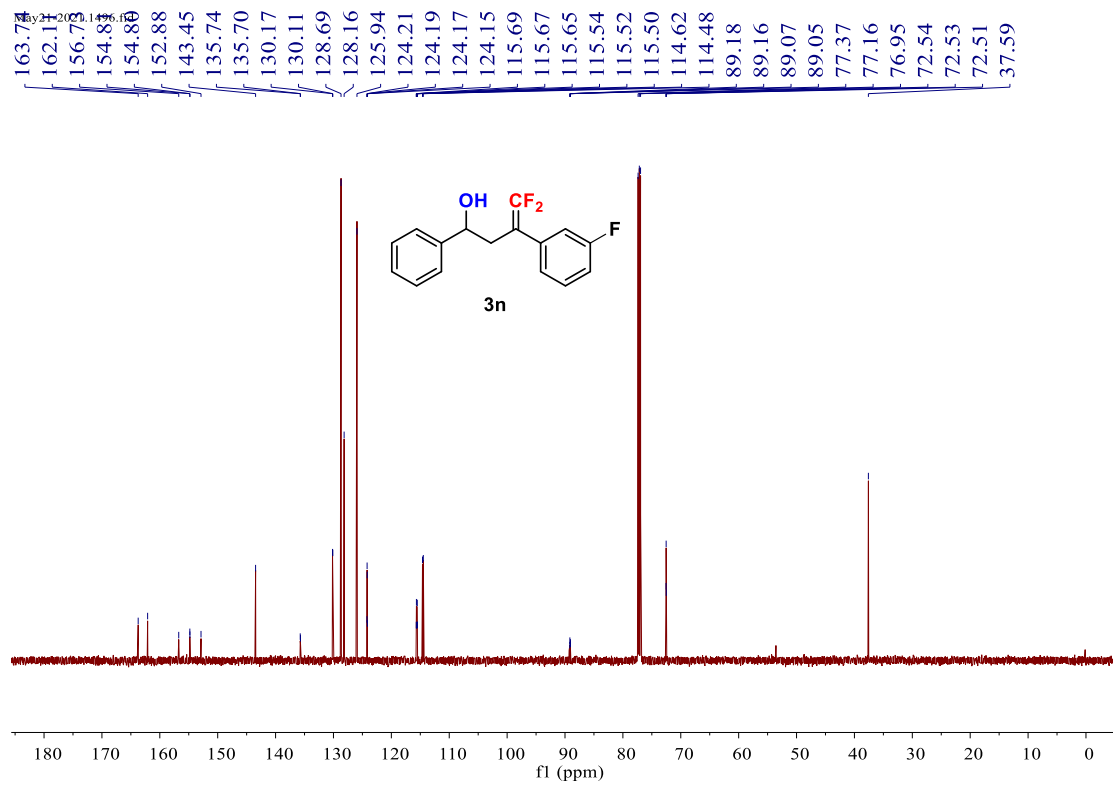


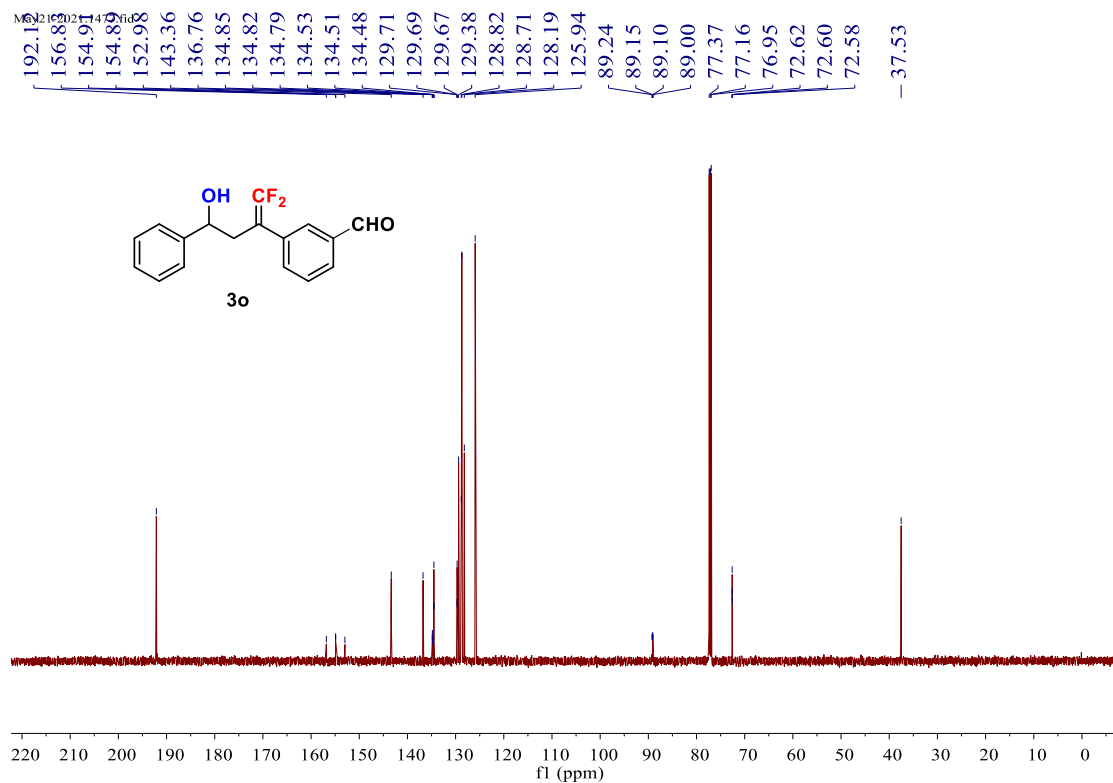
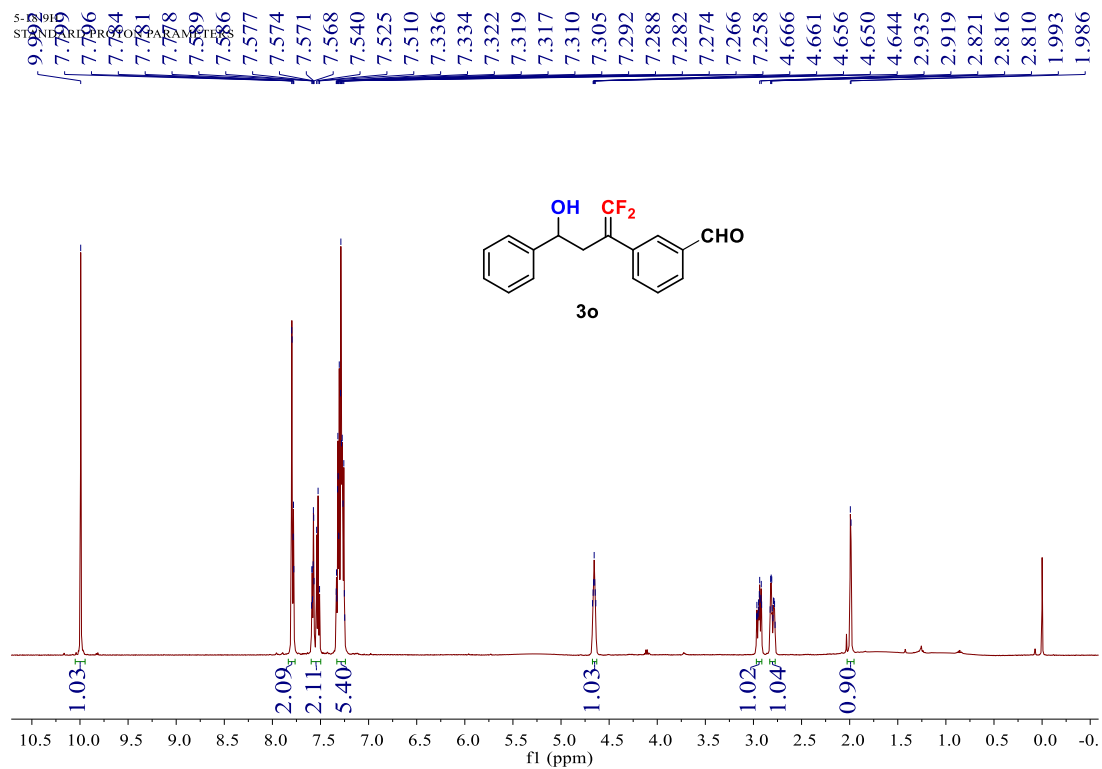


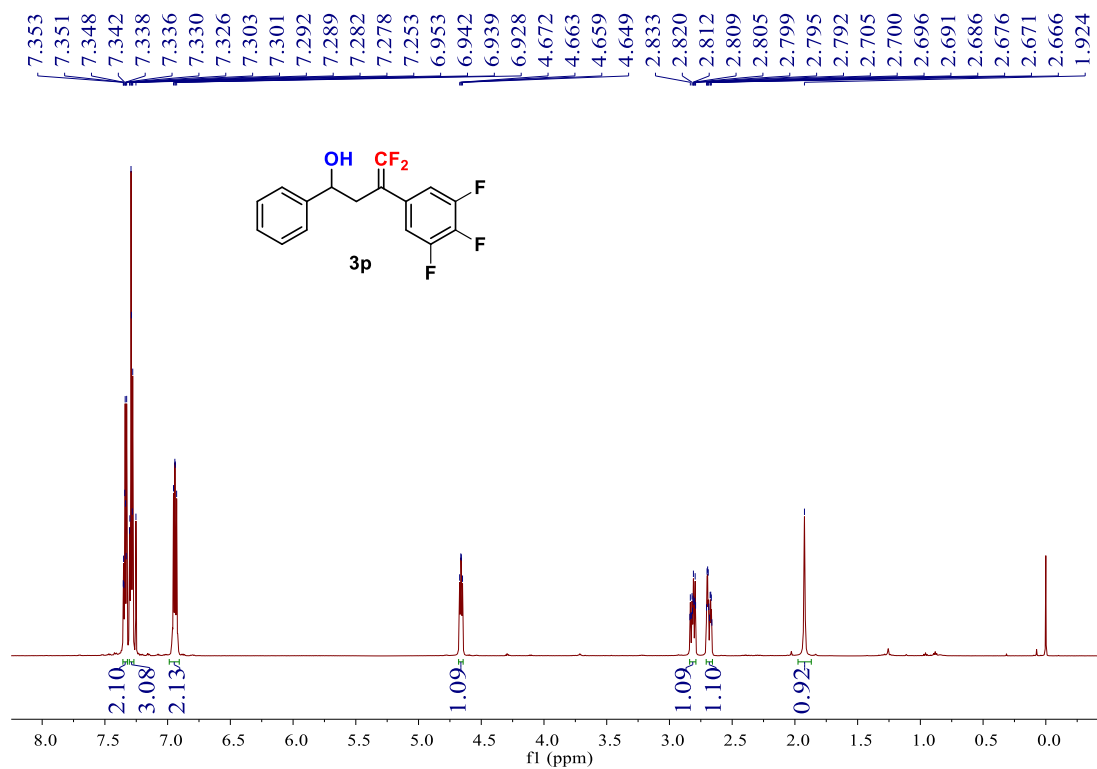
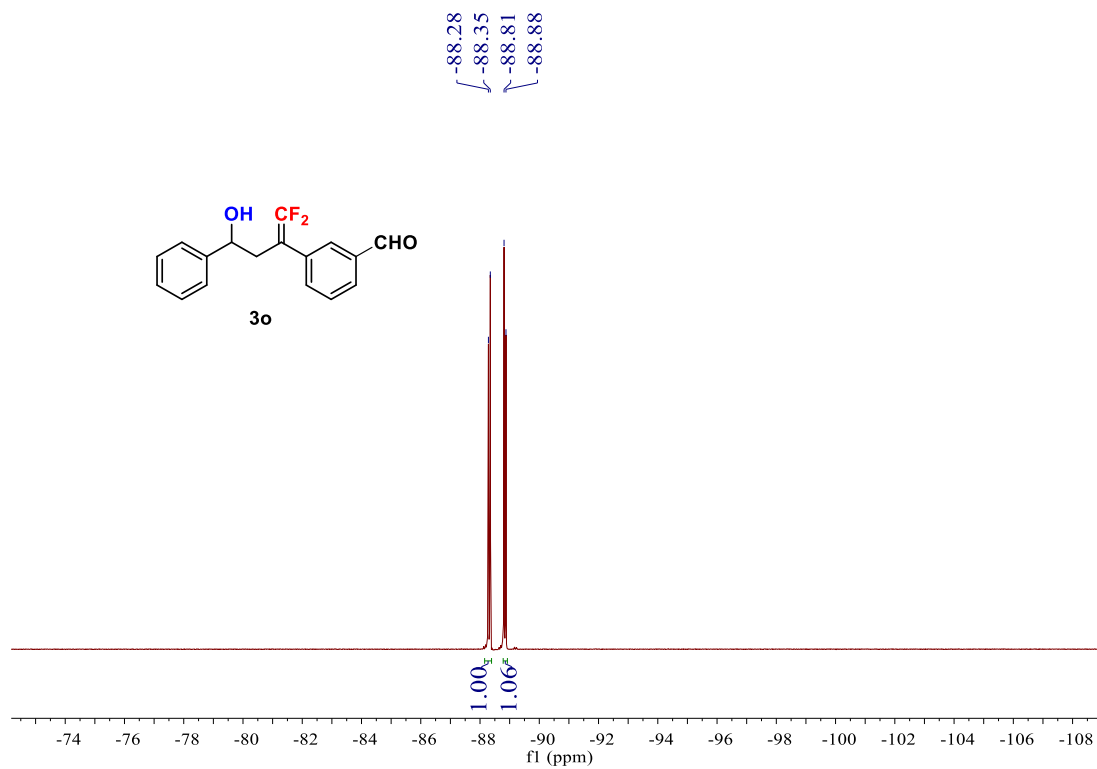


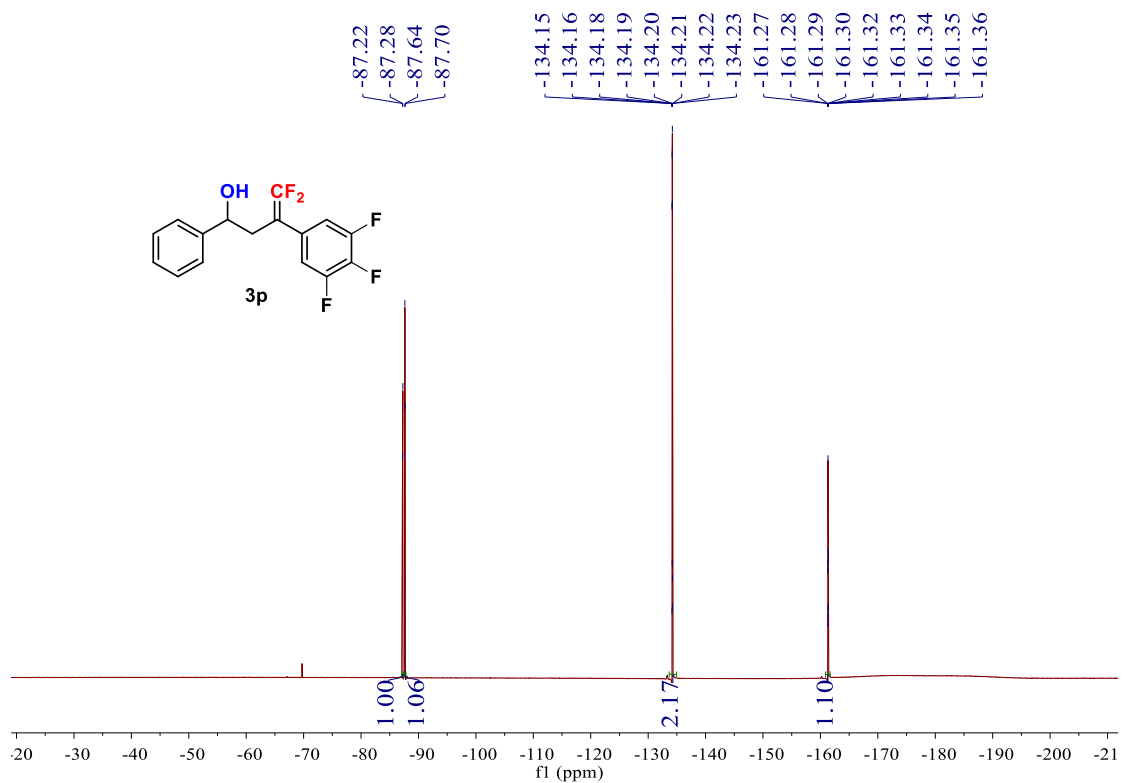
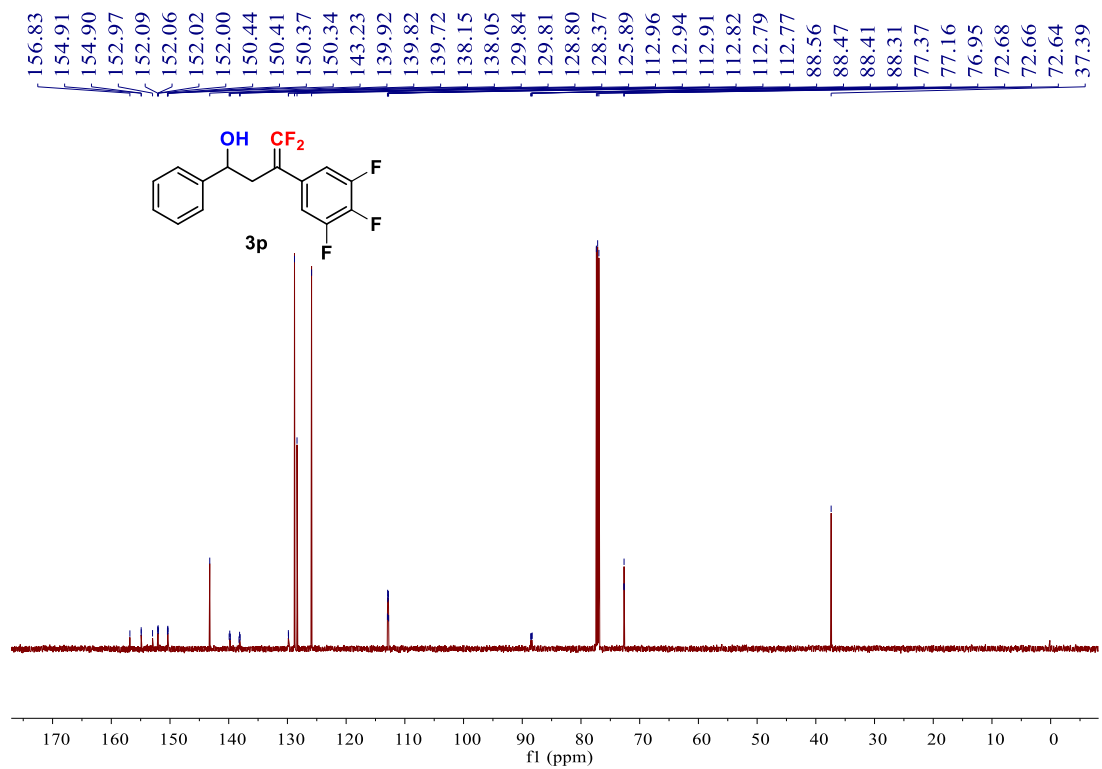


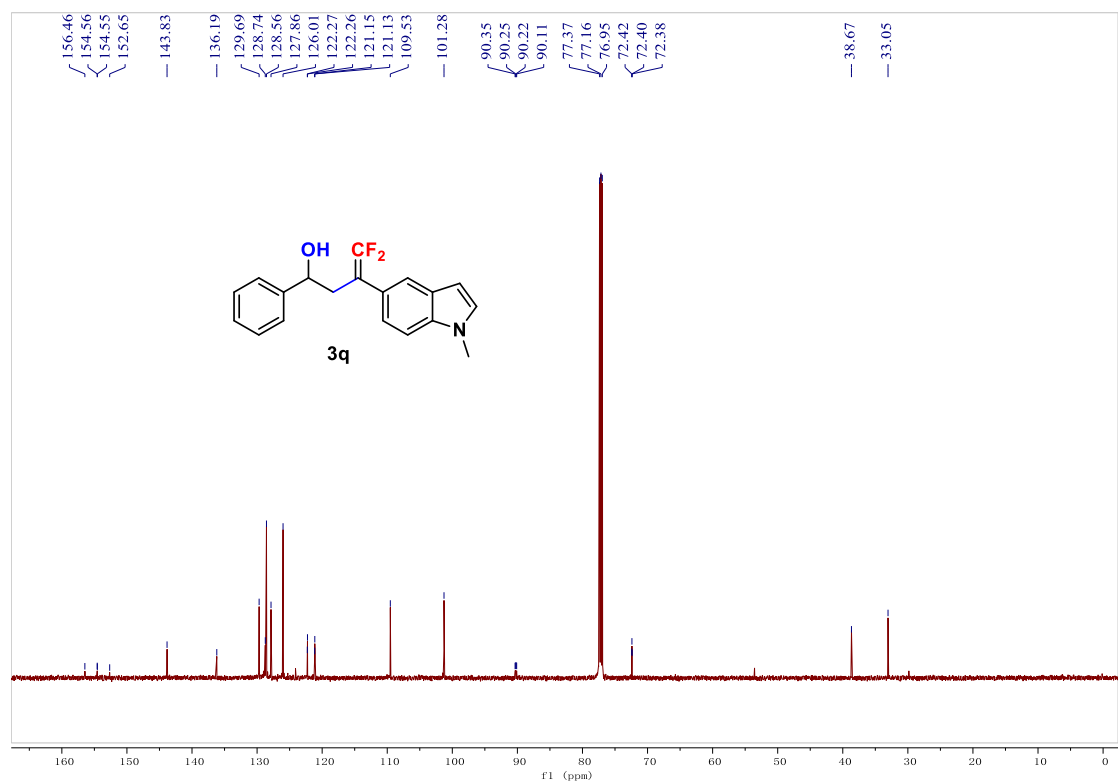
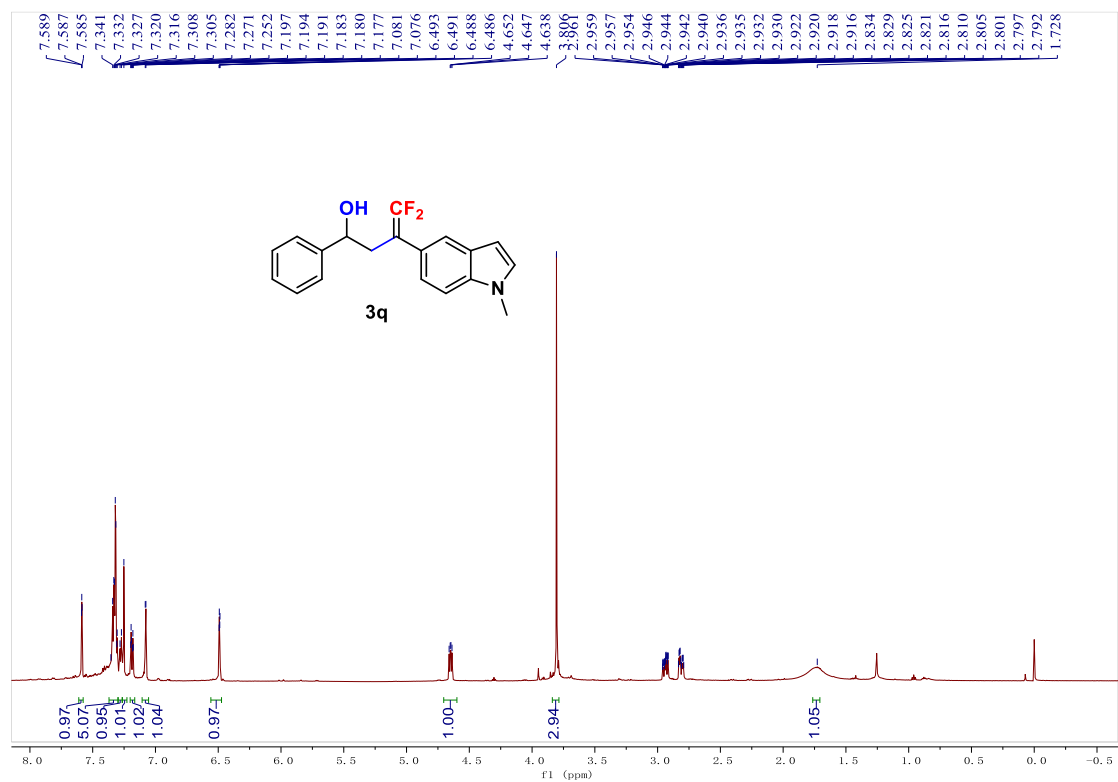


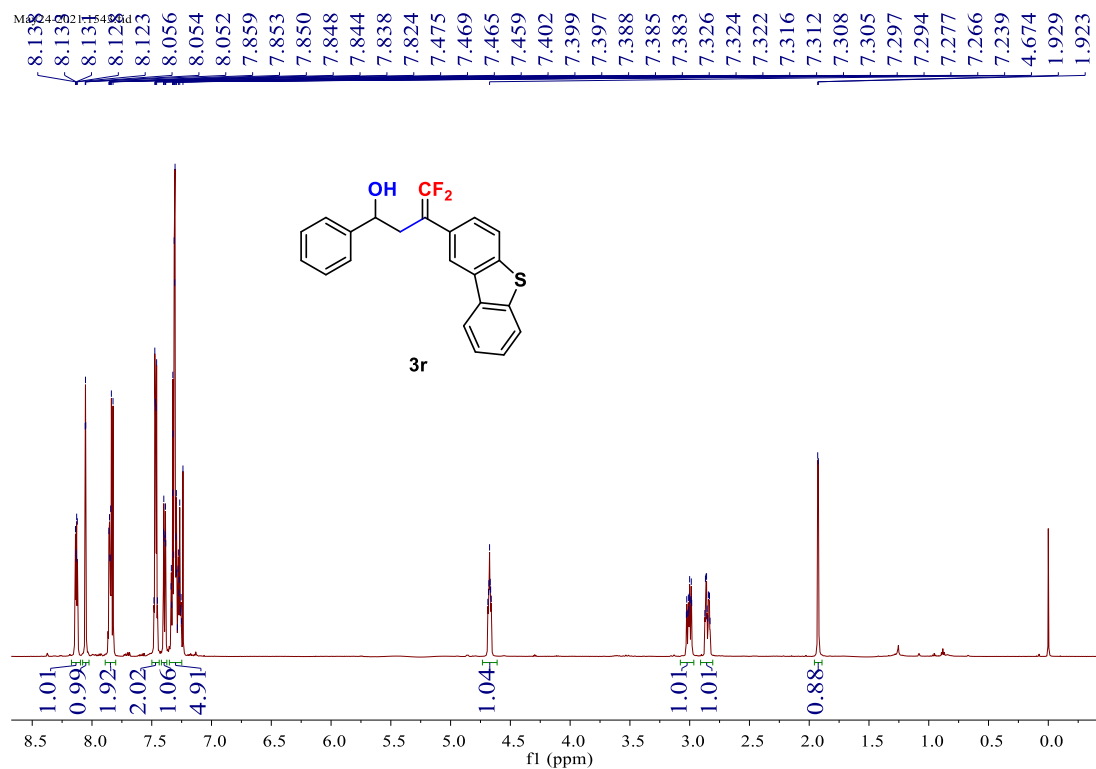
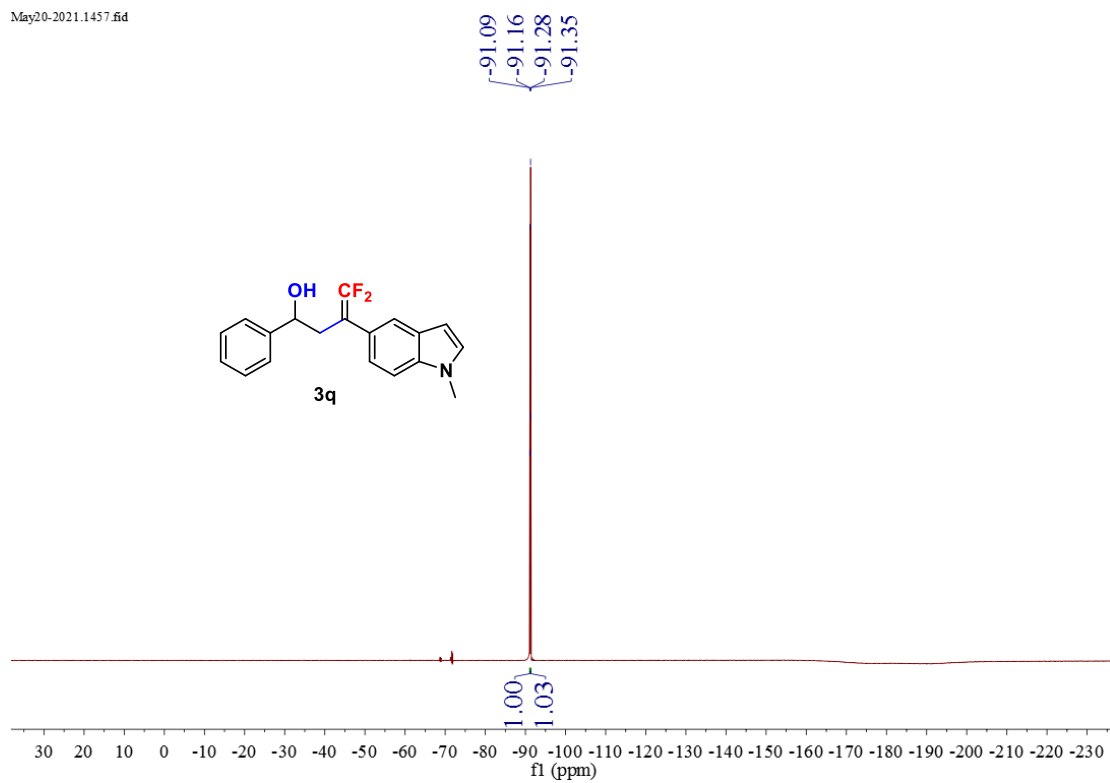


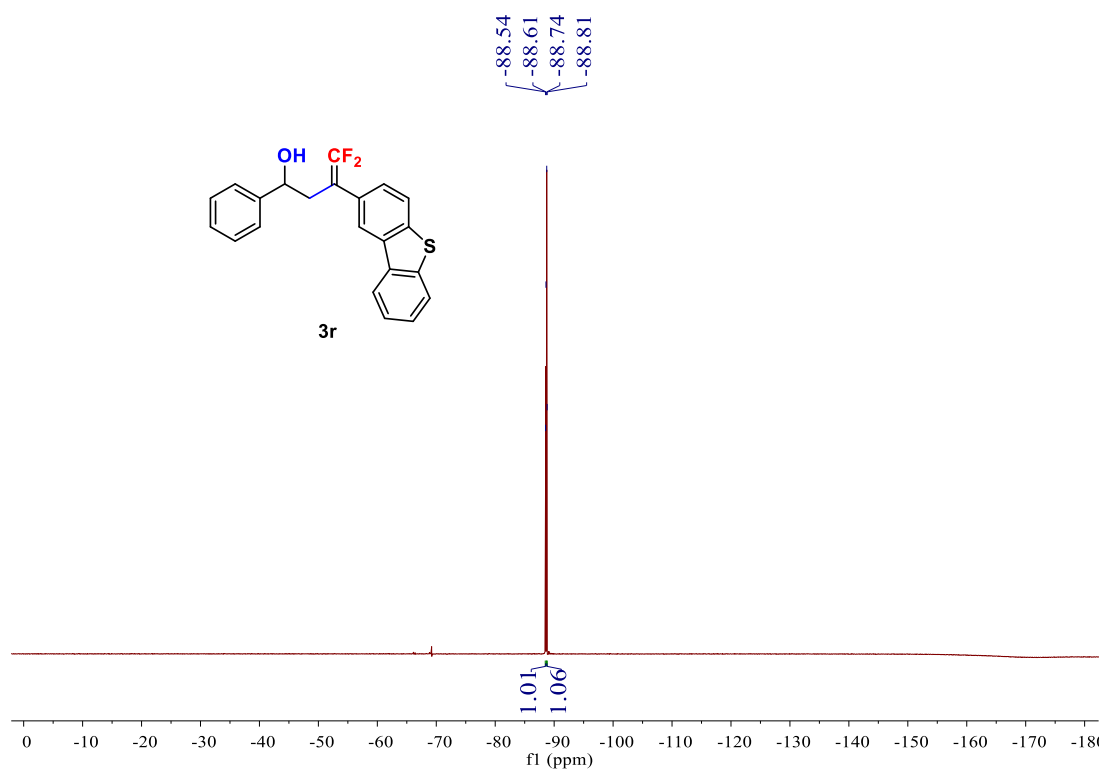
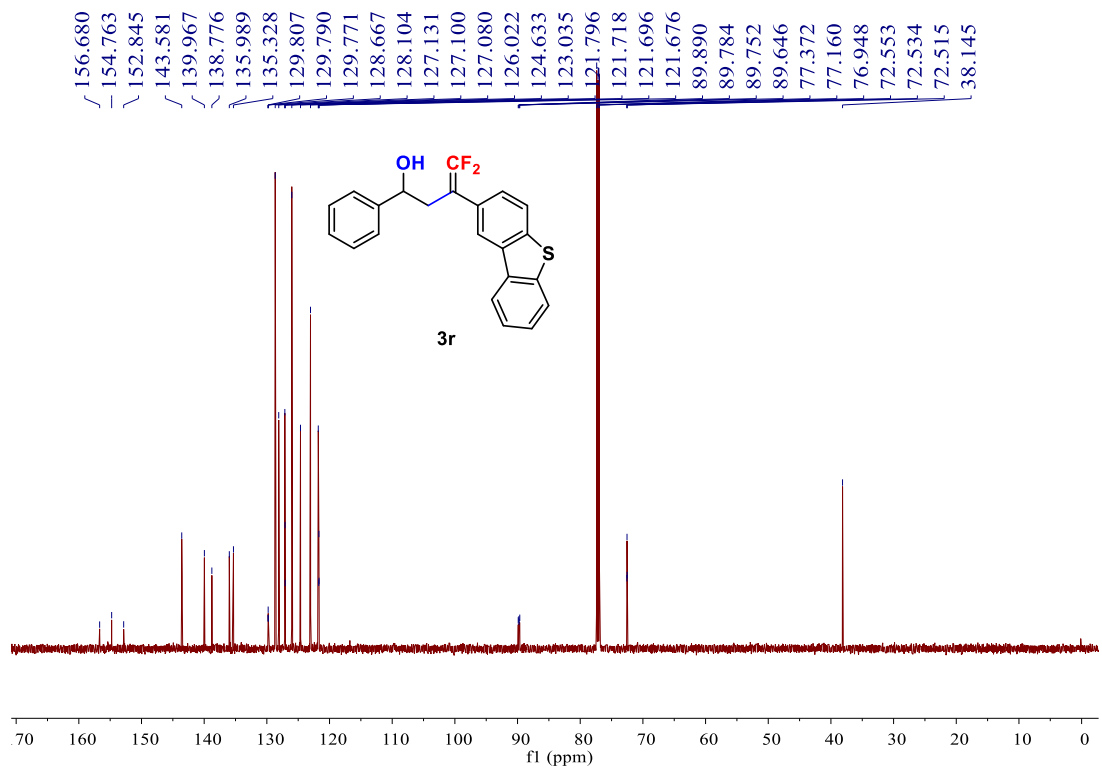


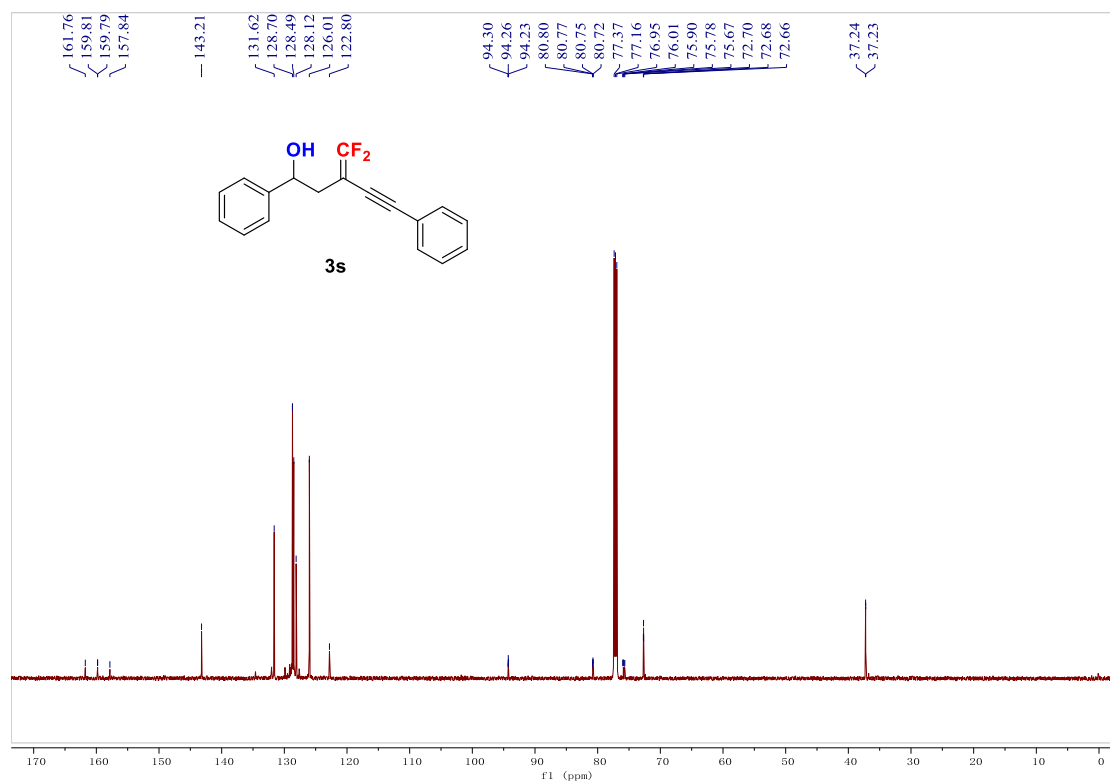
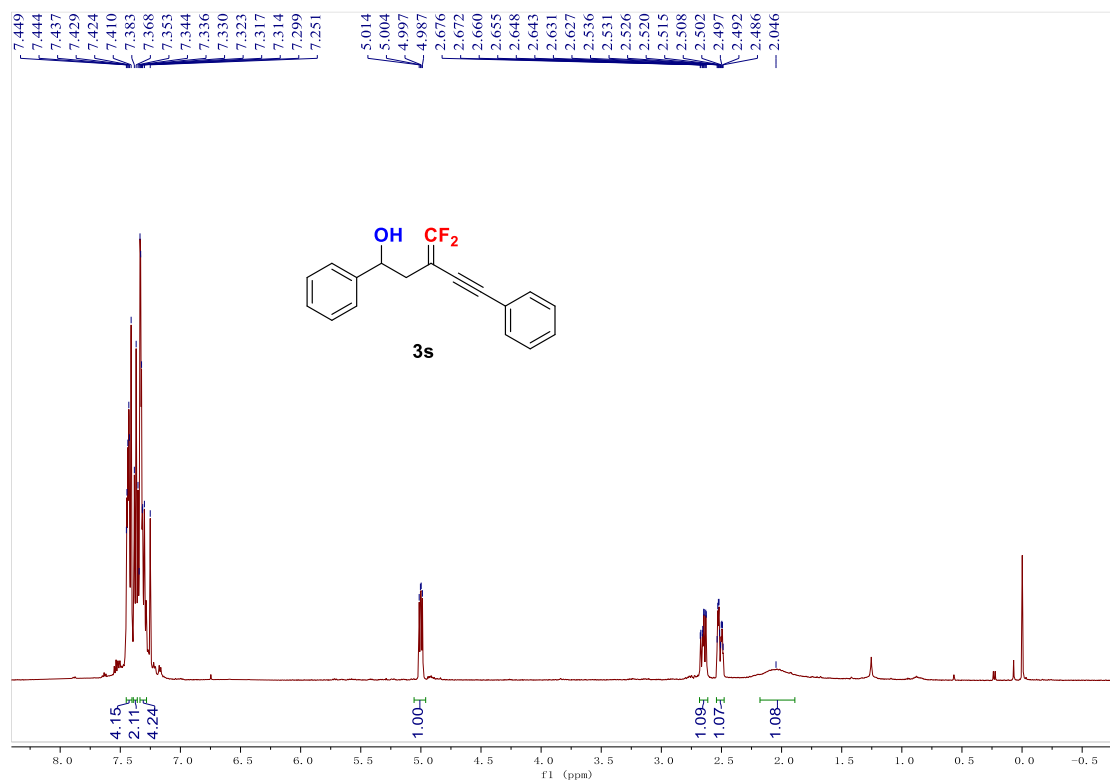


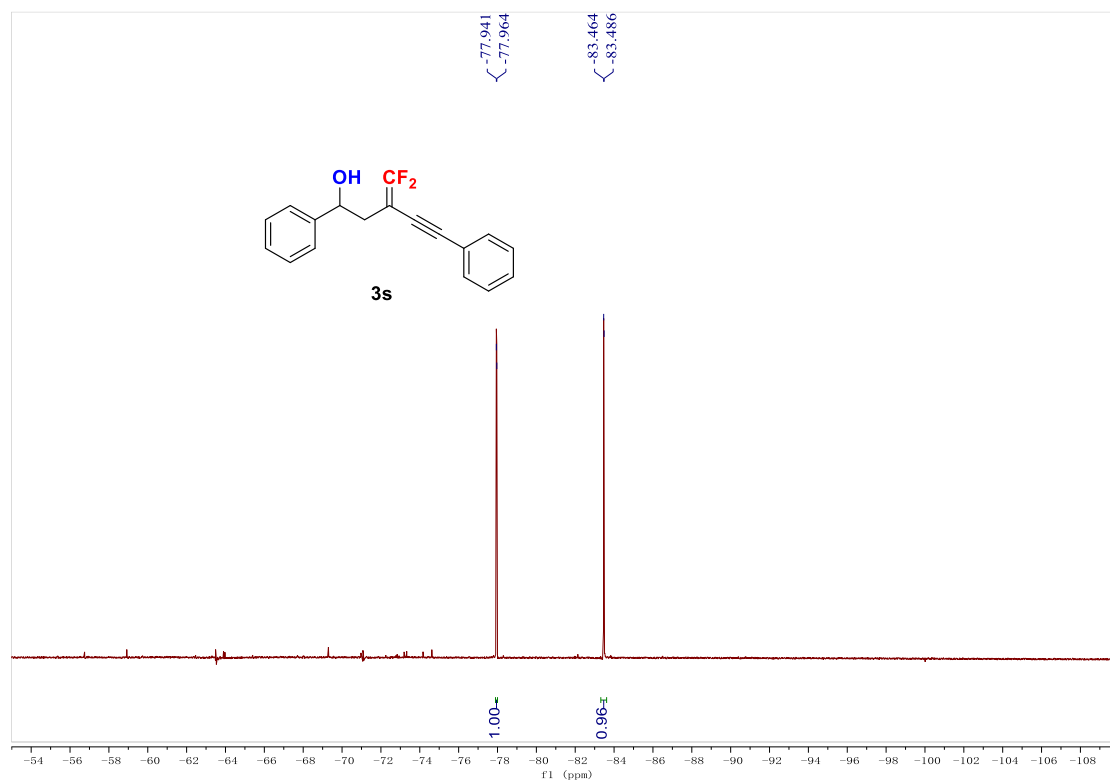






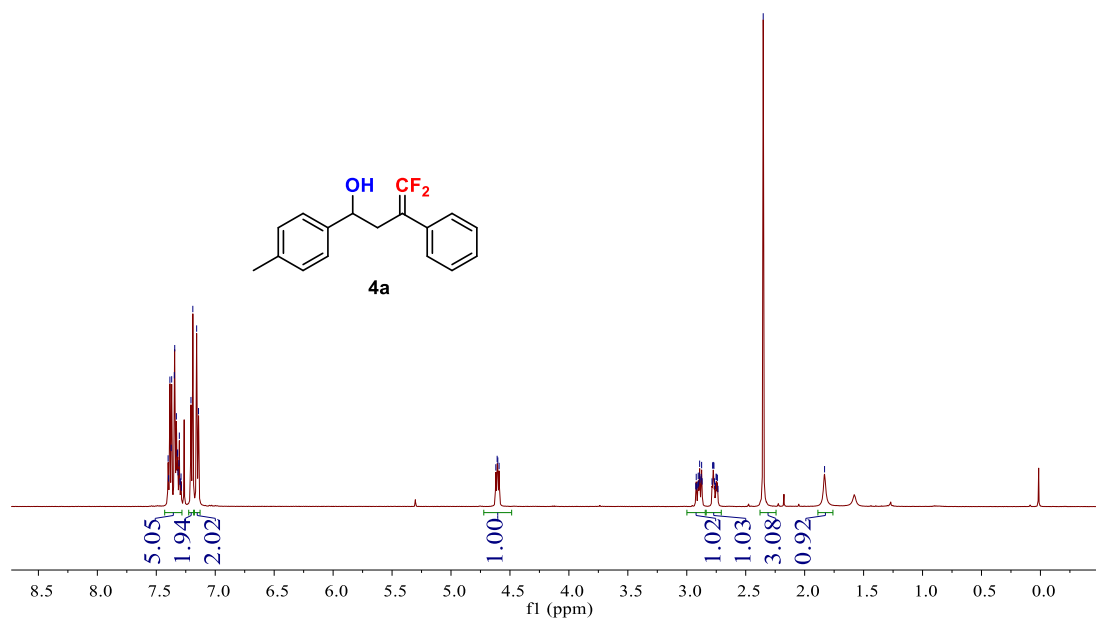


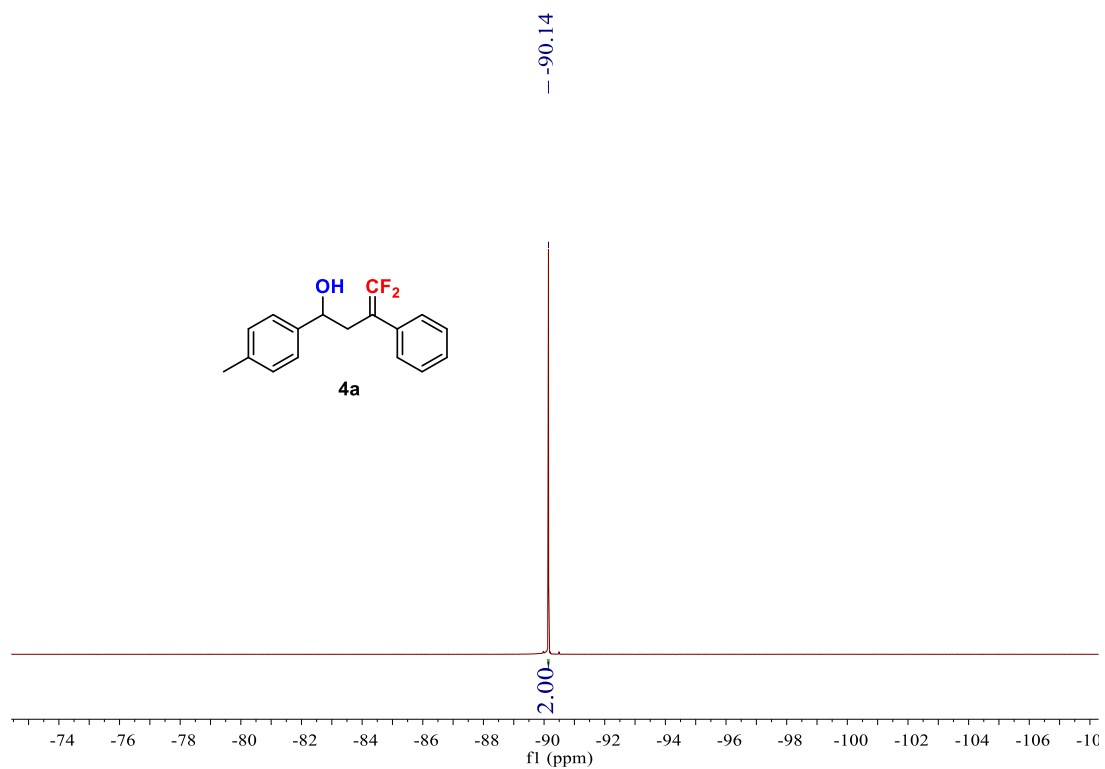
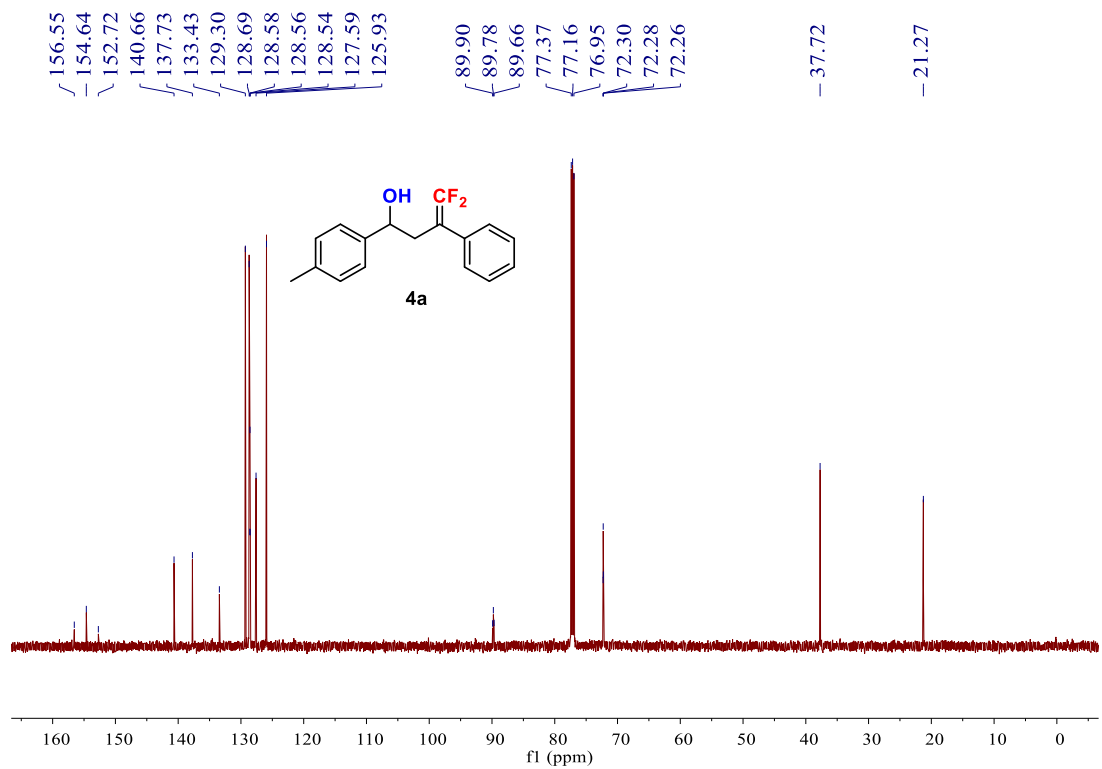


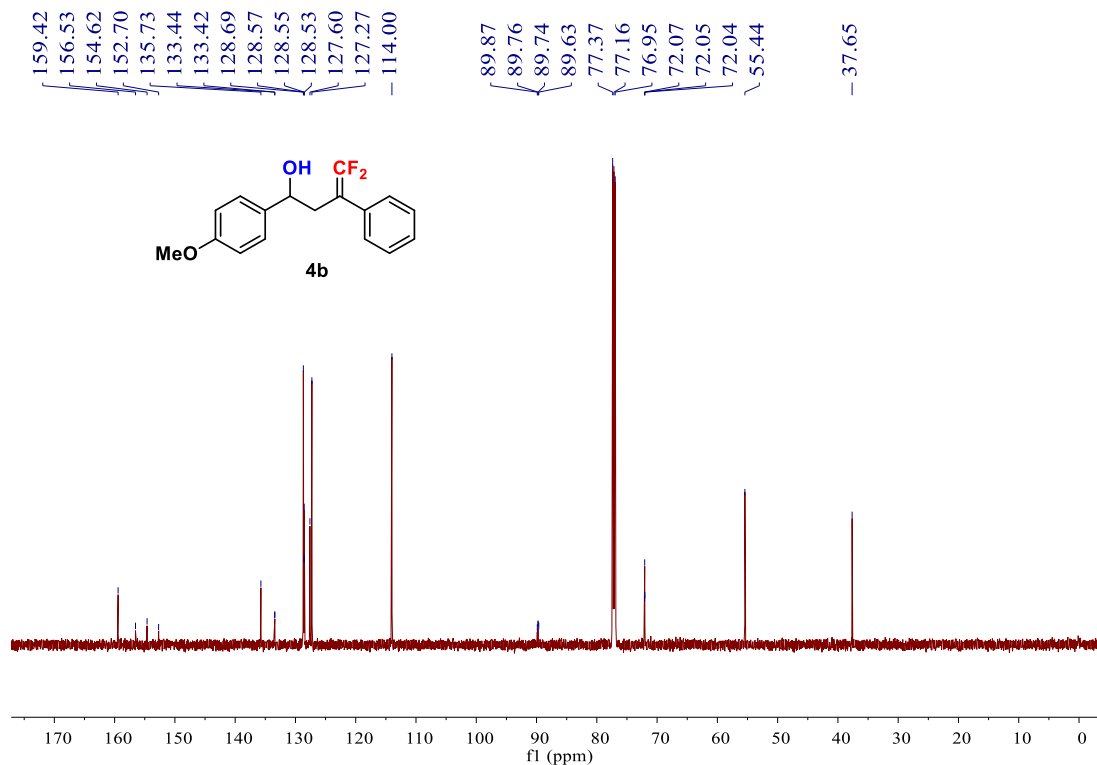
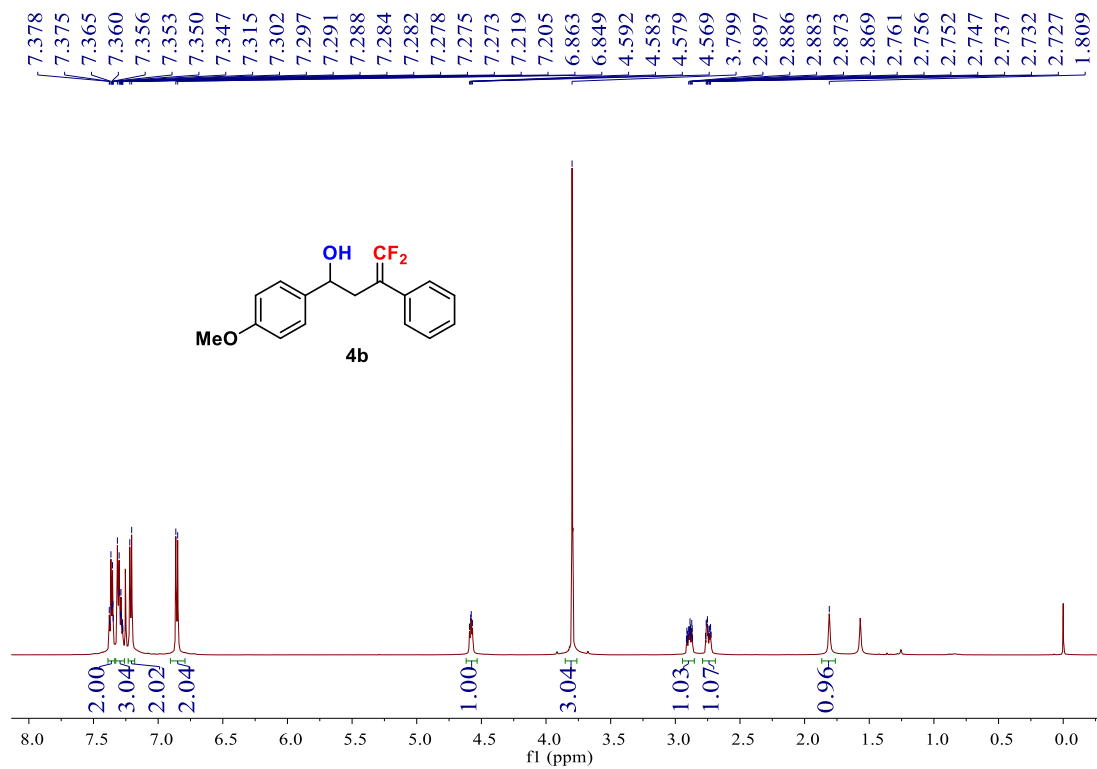


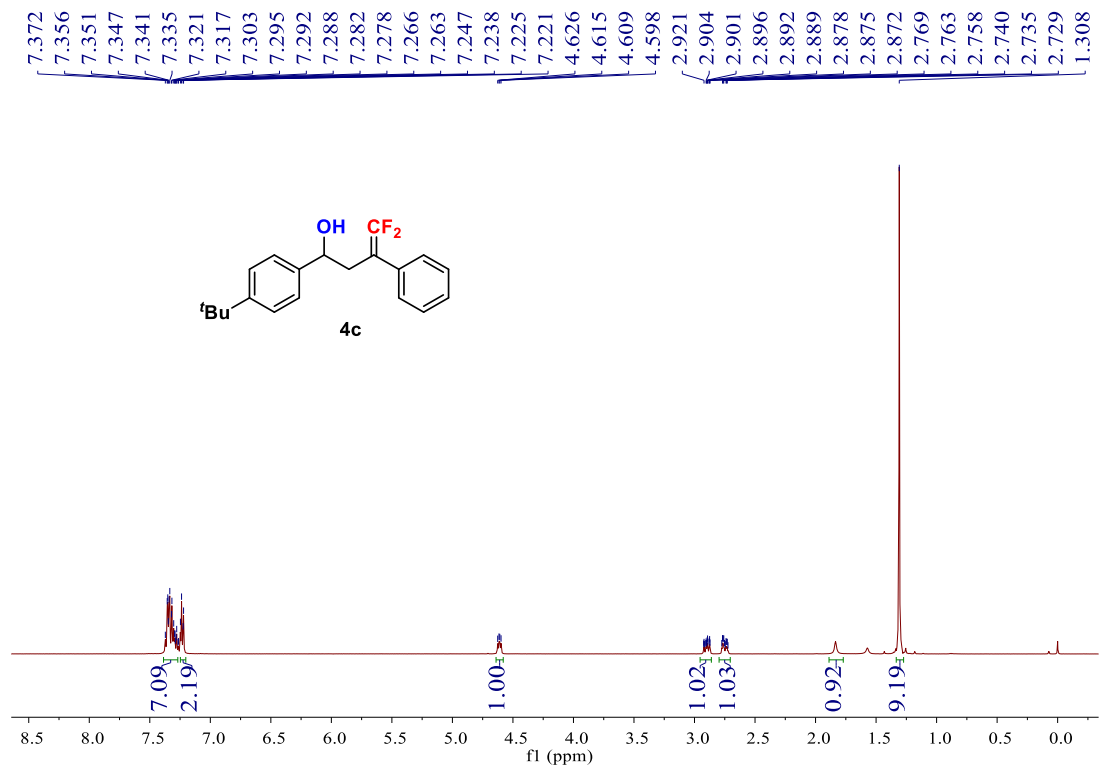
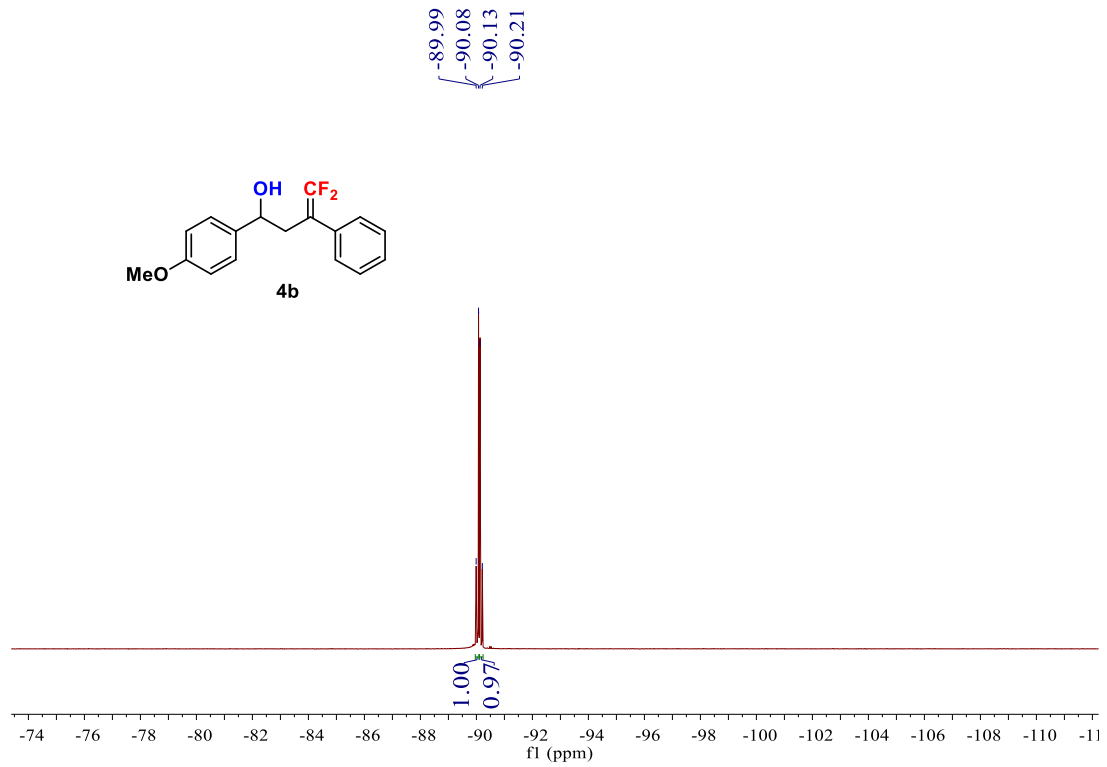
5-⁹H
STANDARD PROTON PARAMETERS

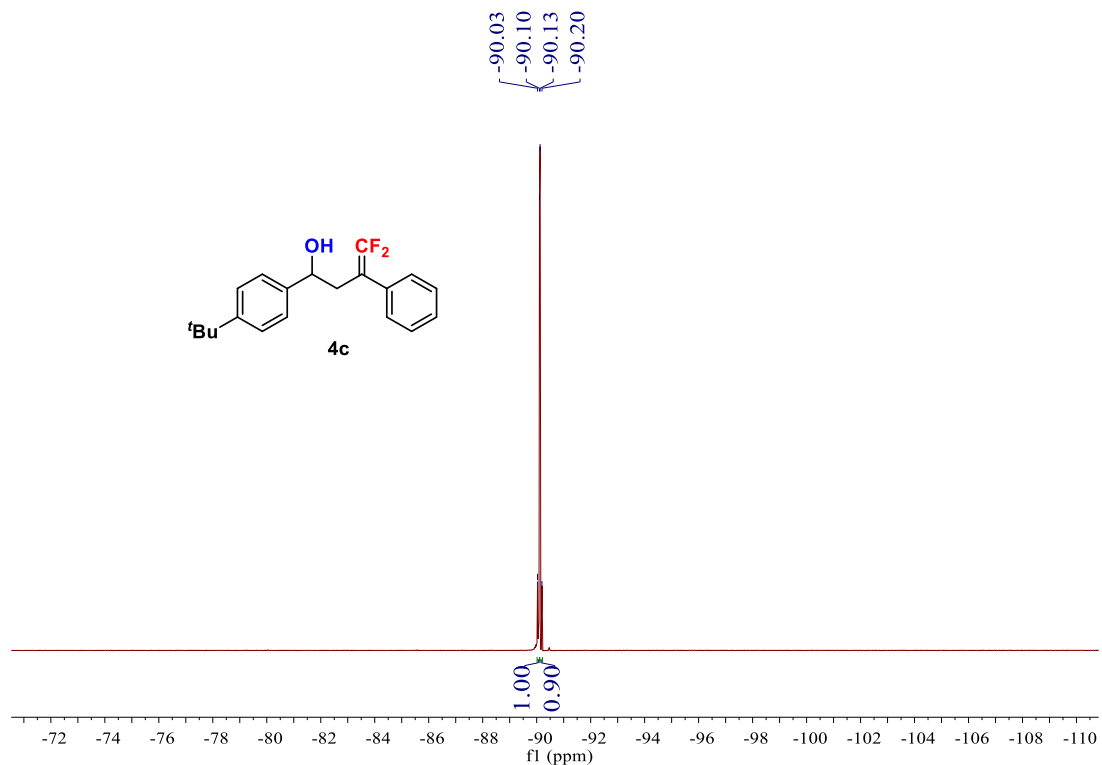
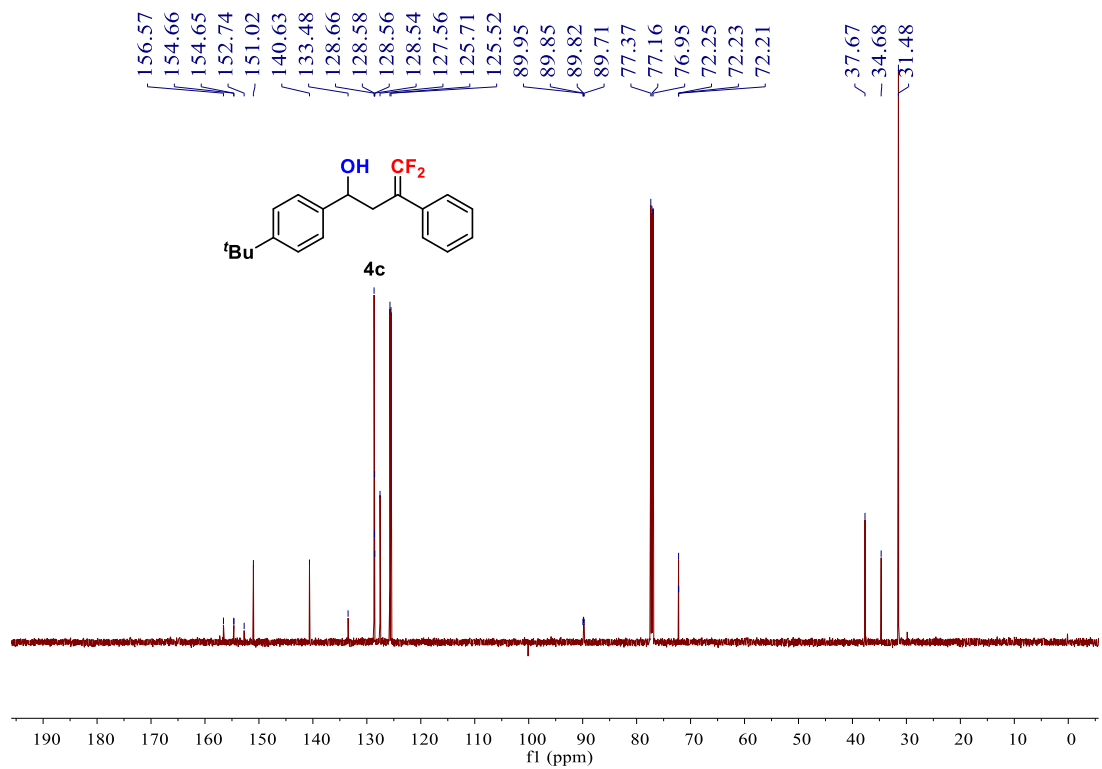
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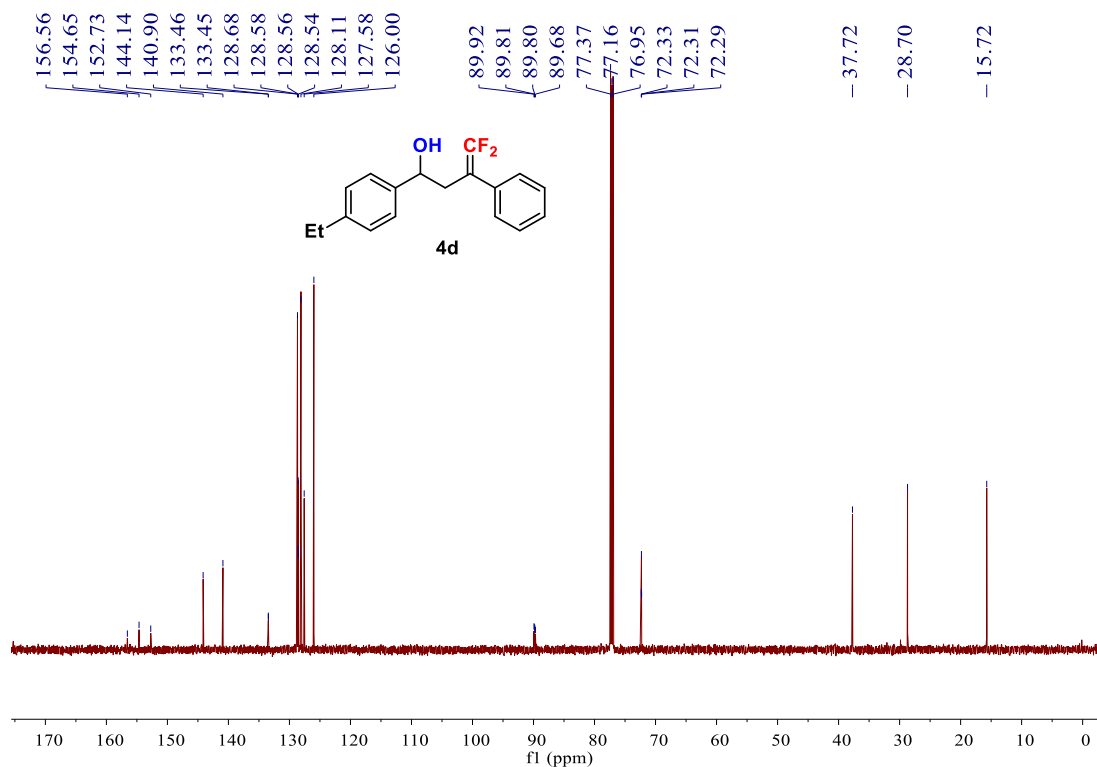
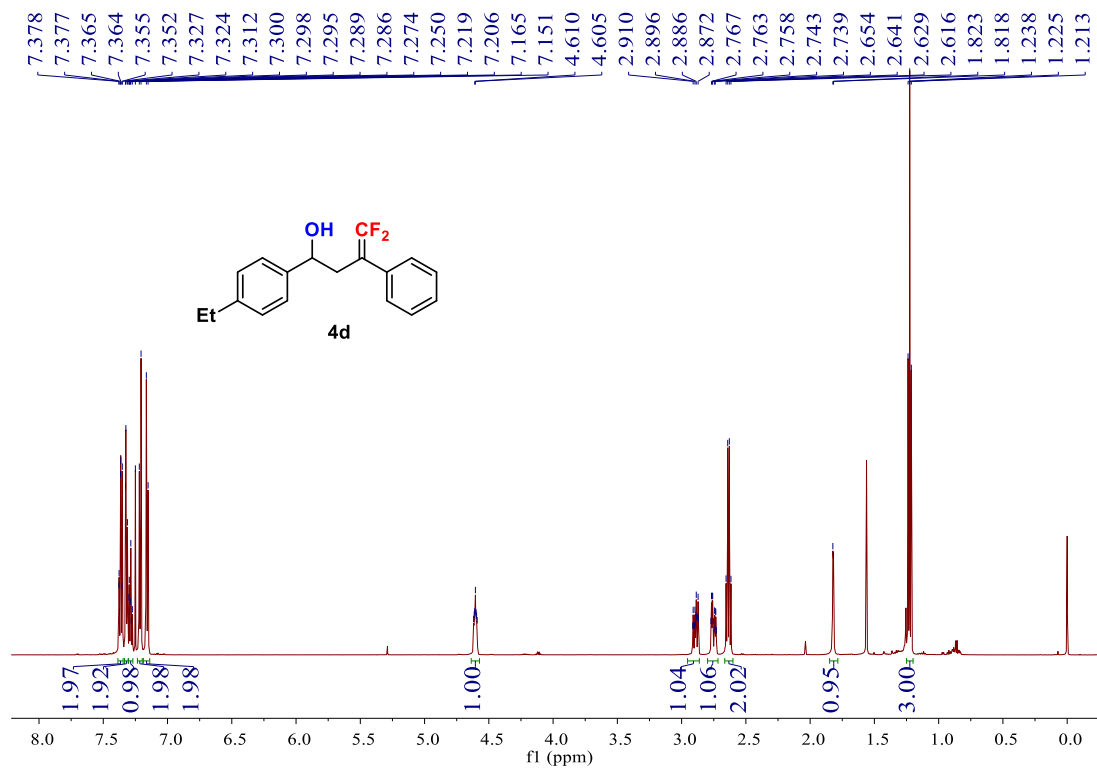


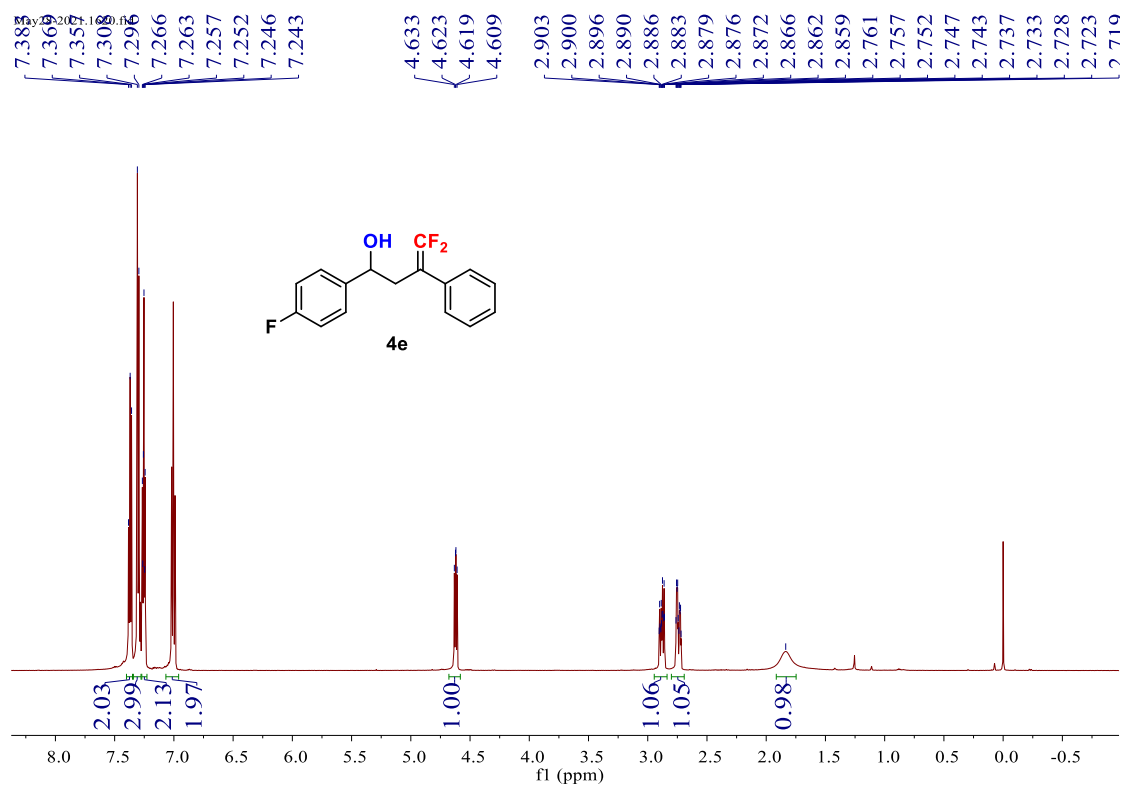
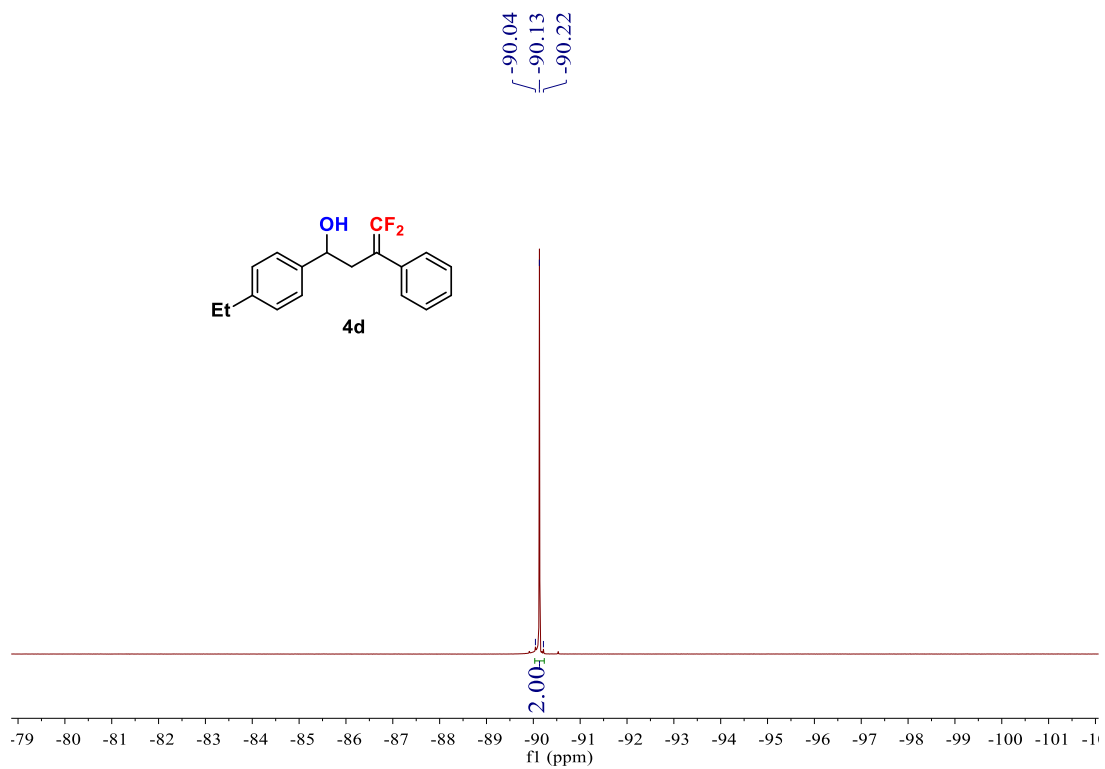


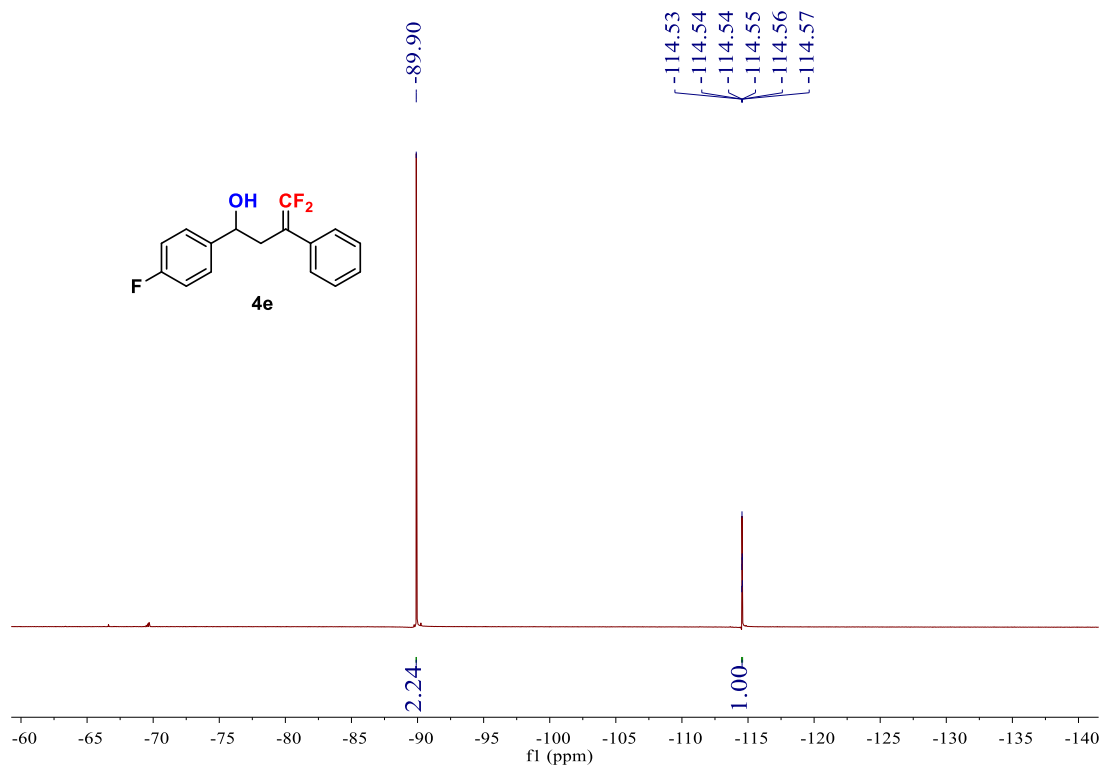
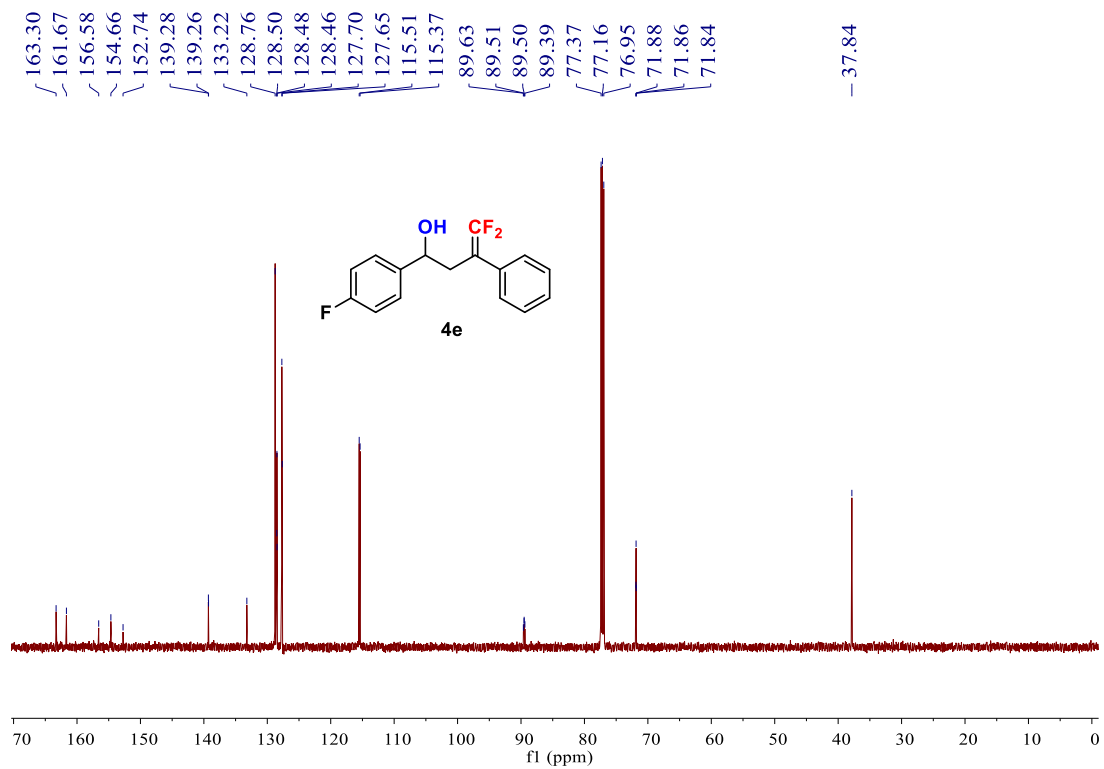


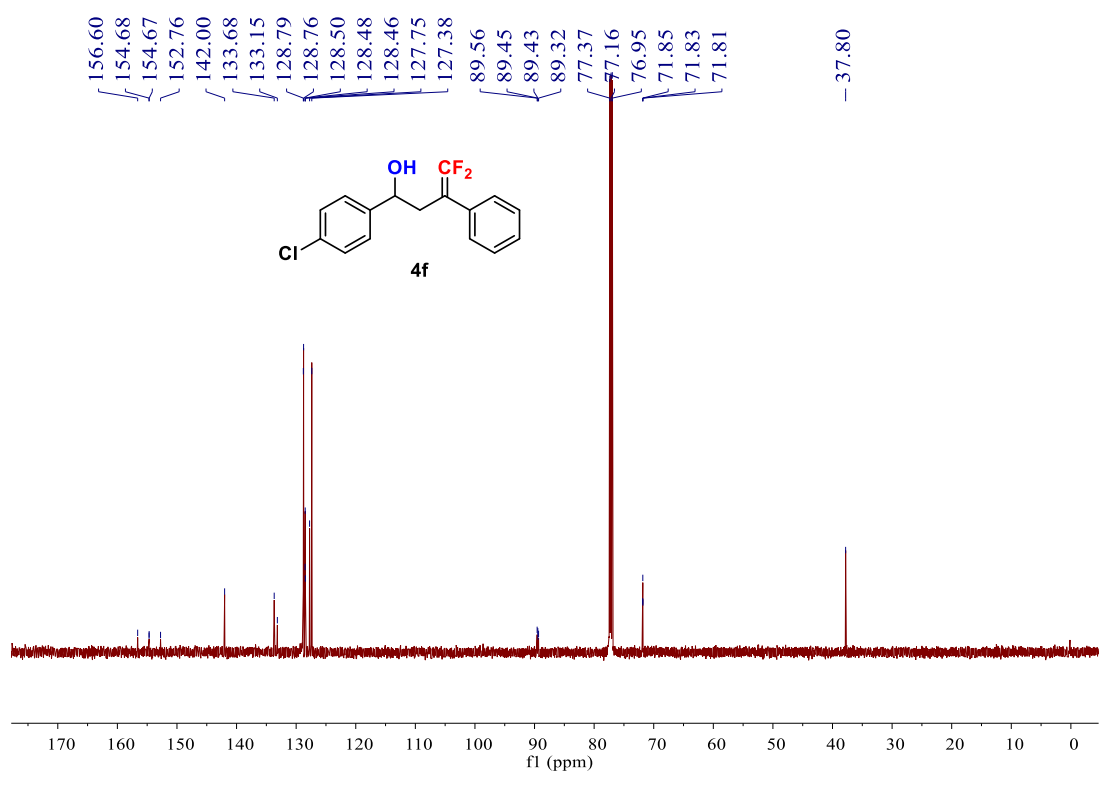
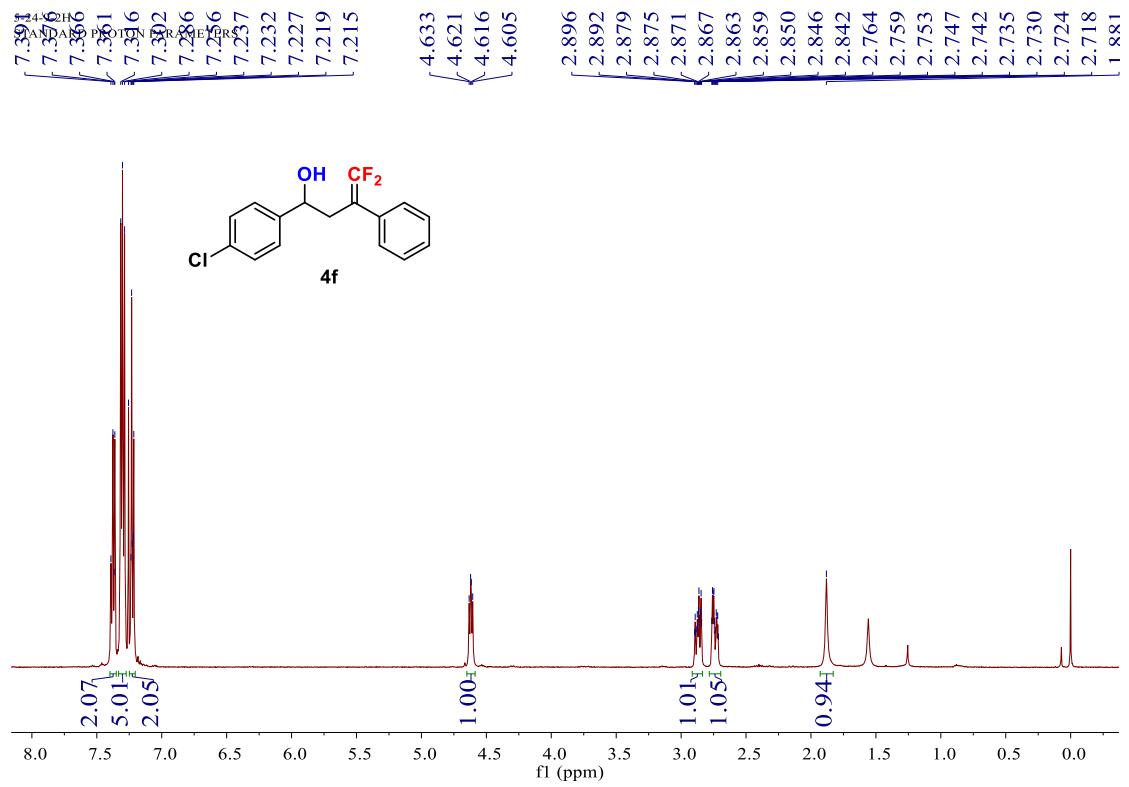


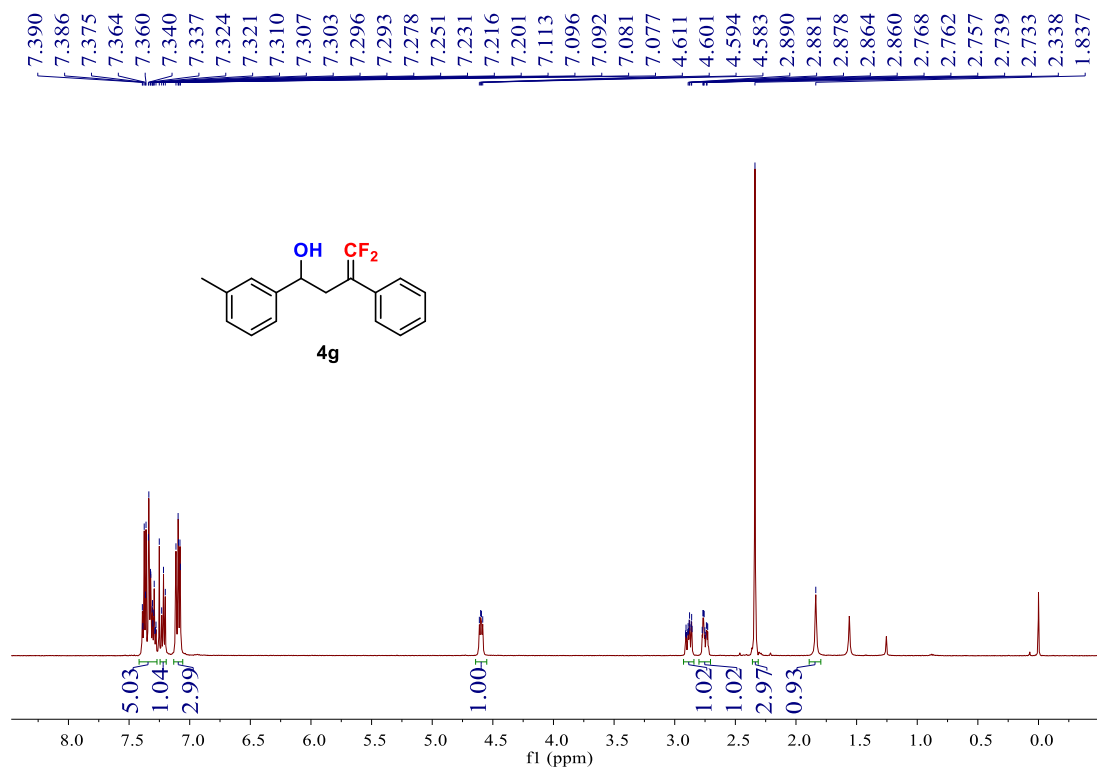
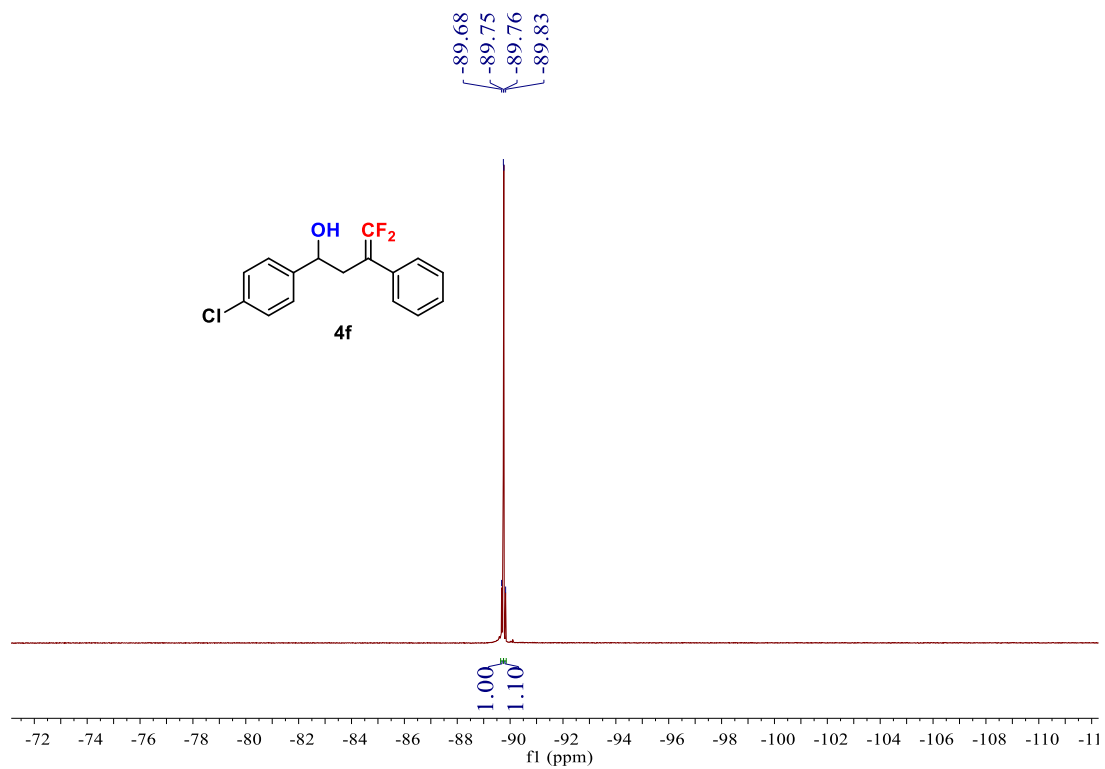


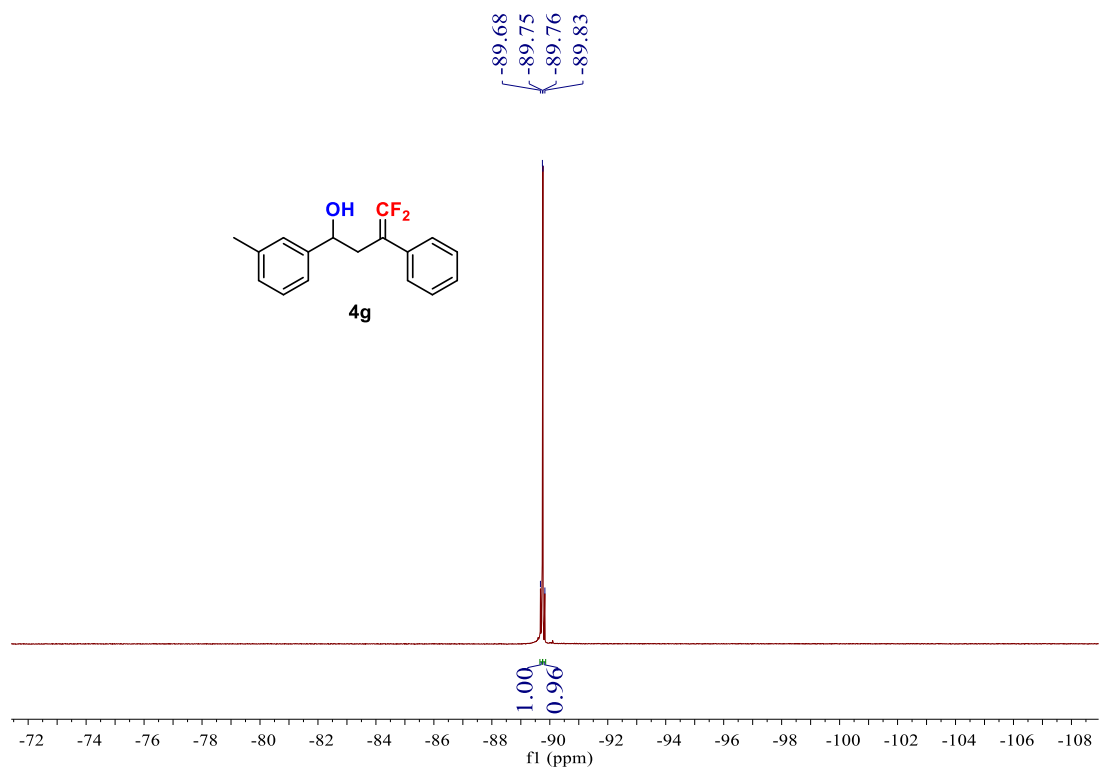
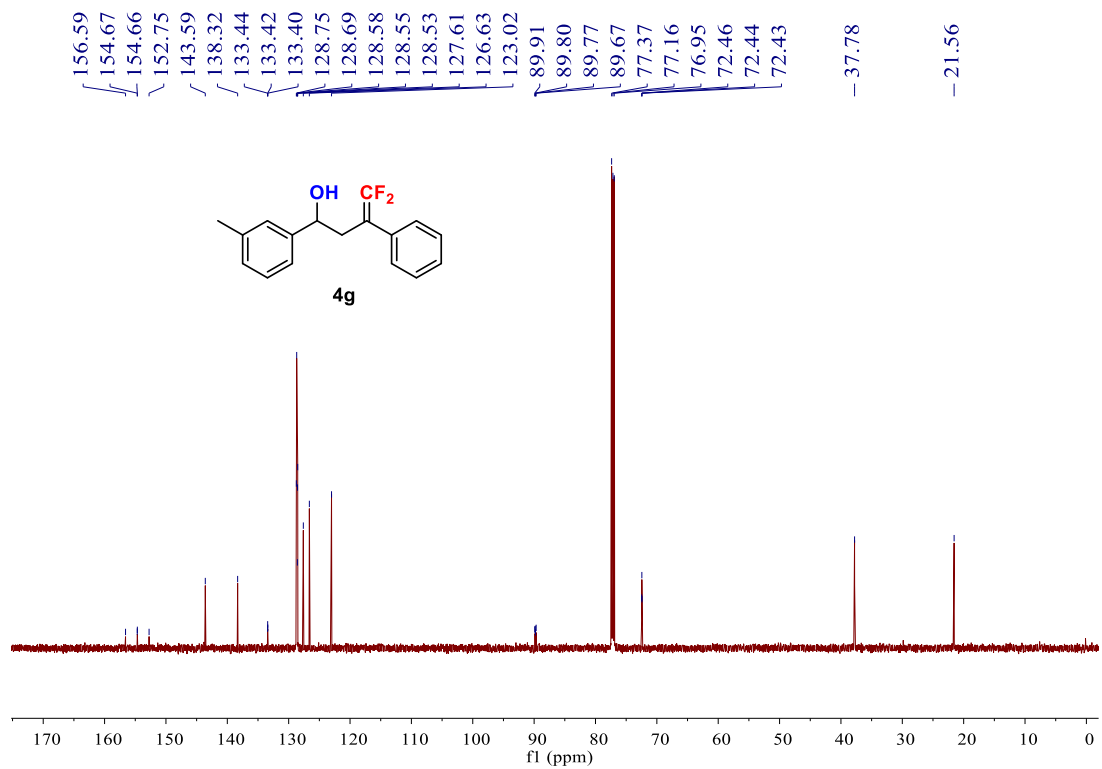


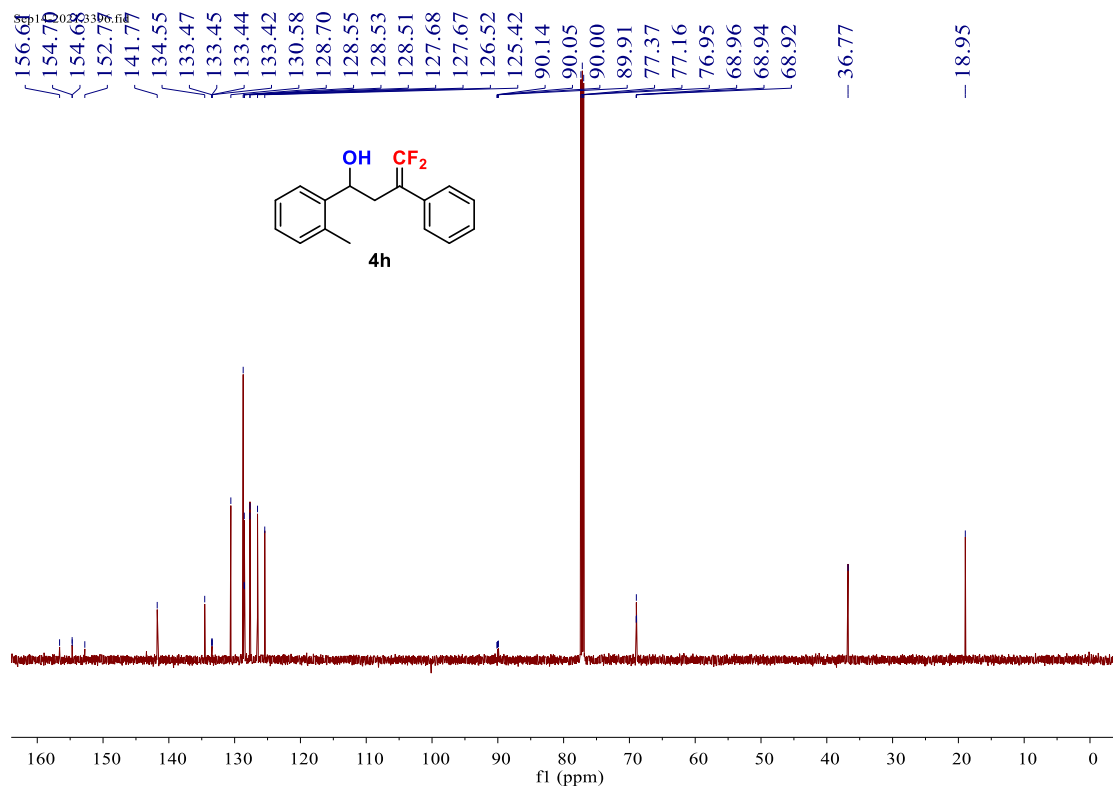
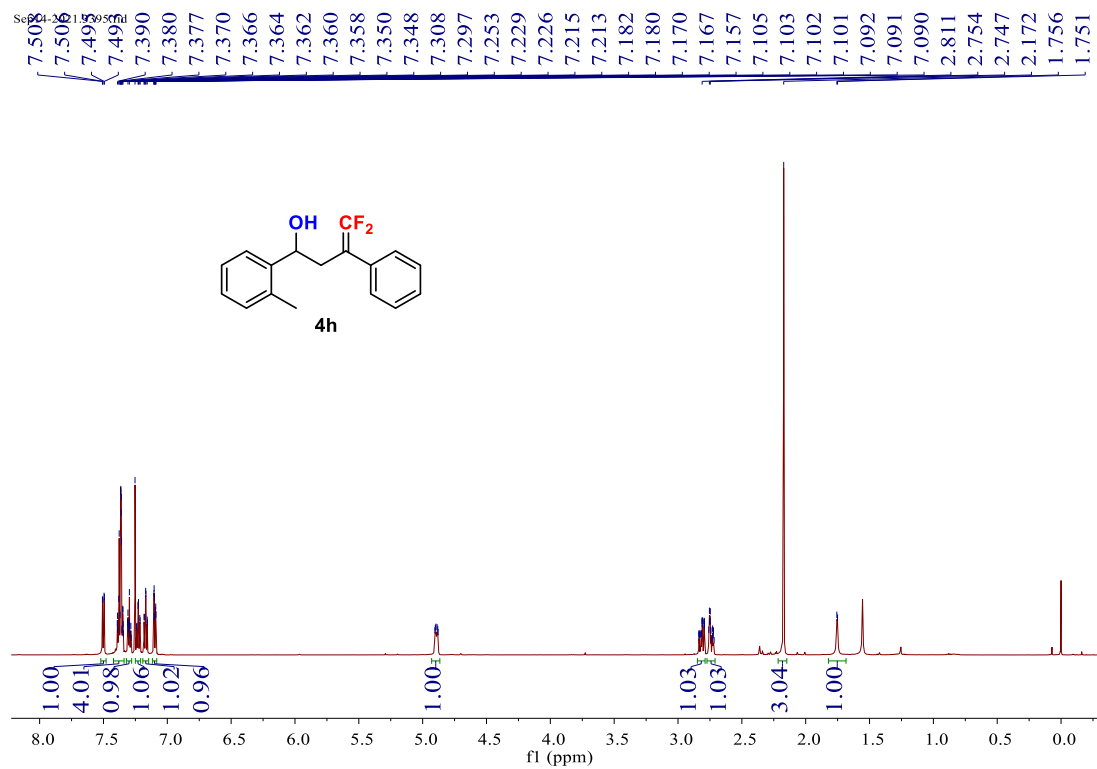


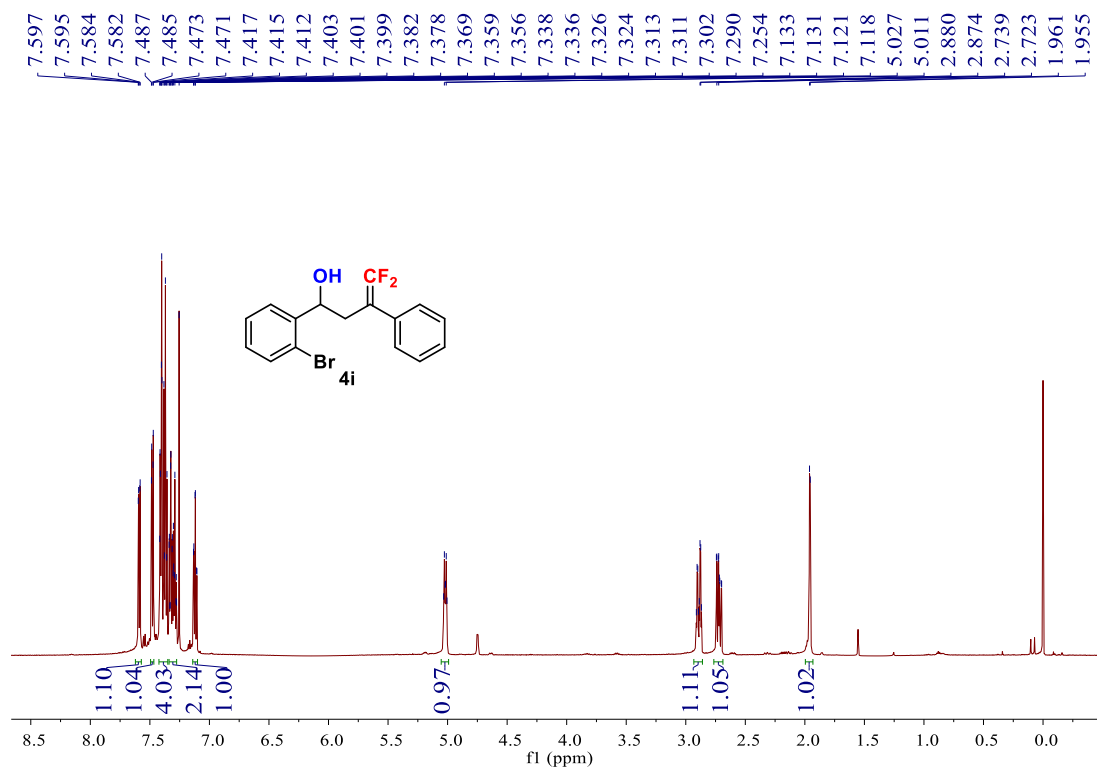
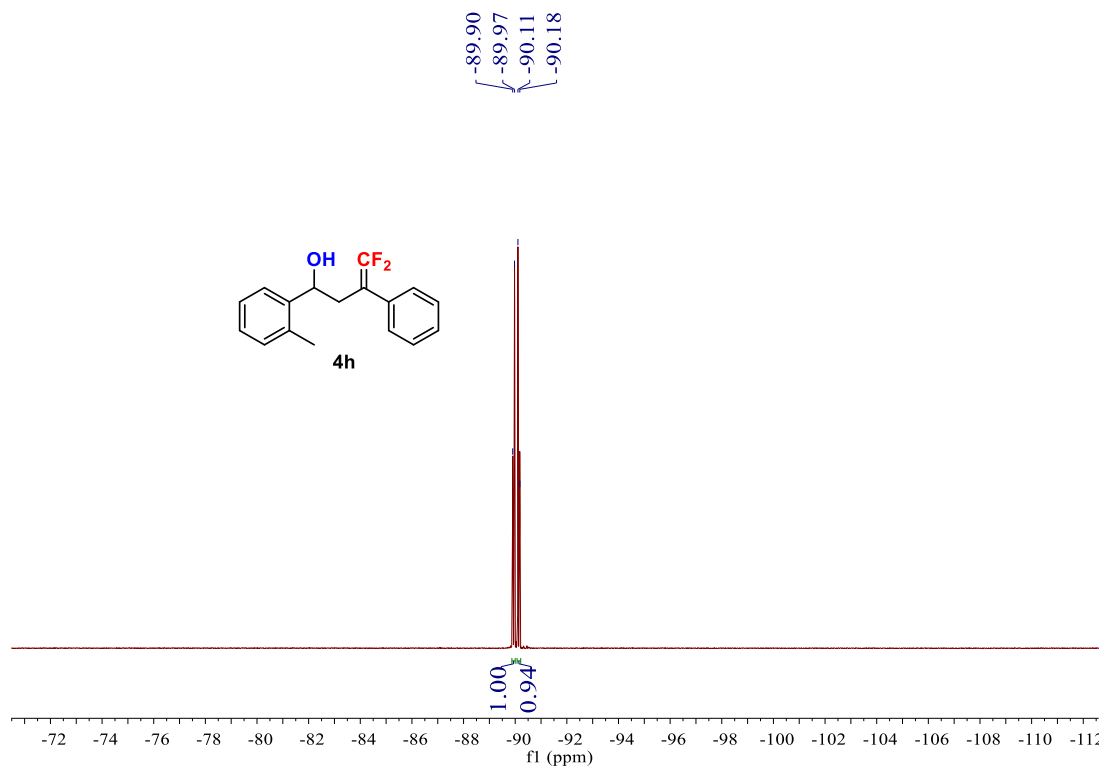


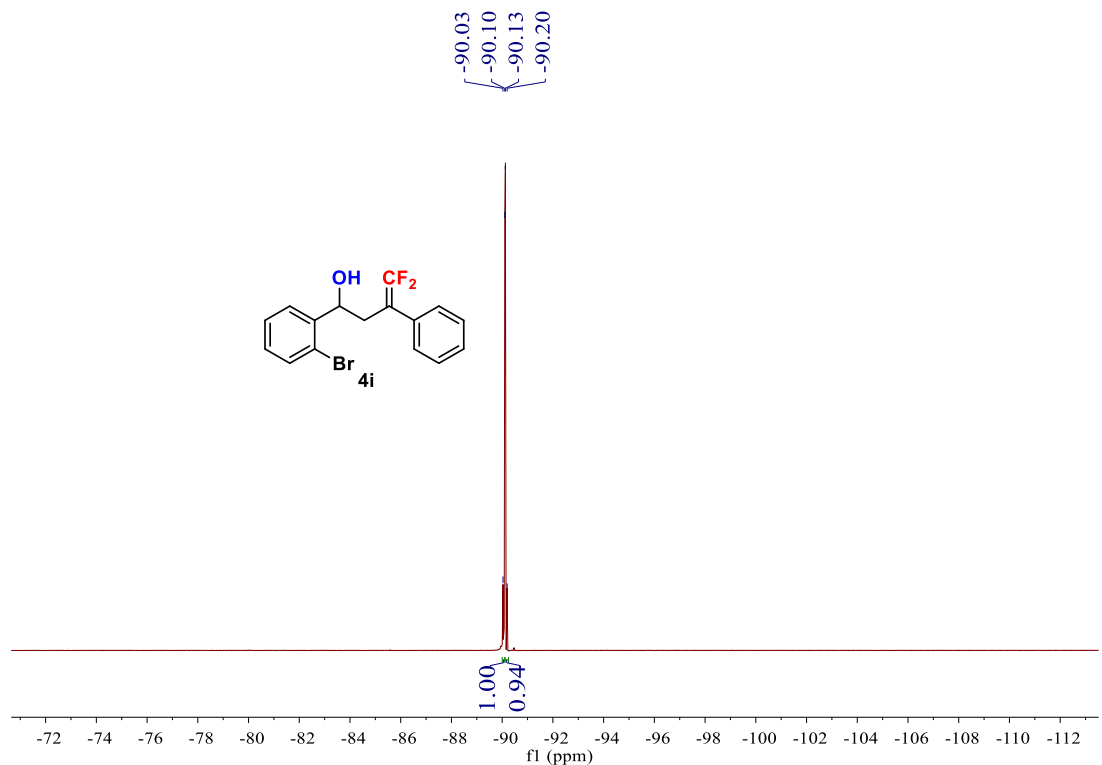
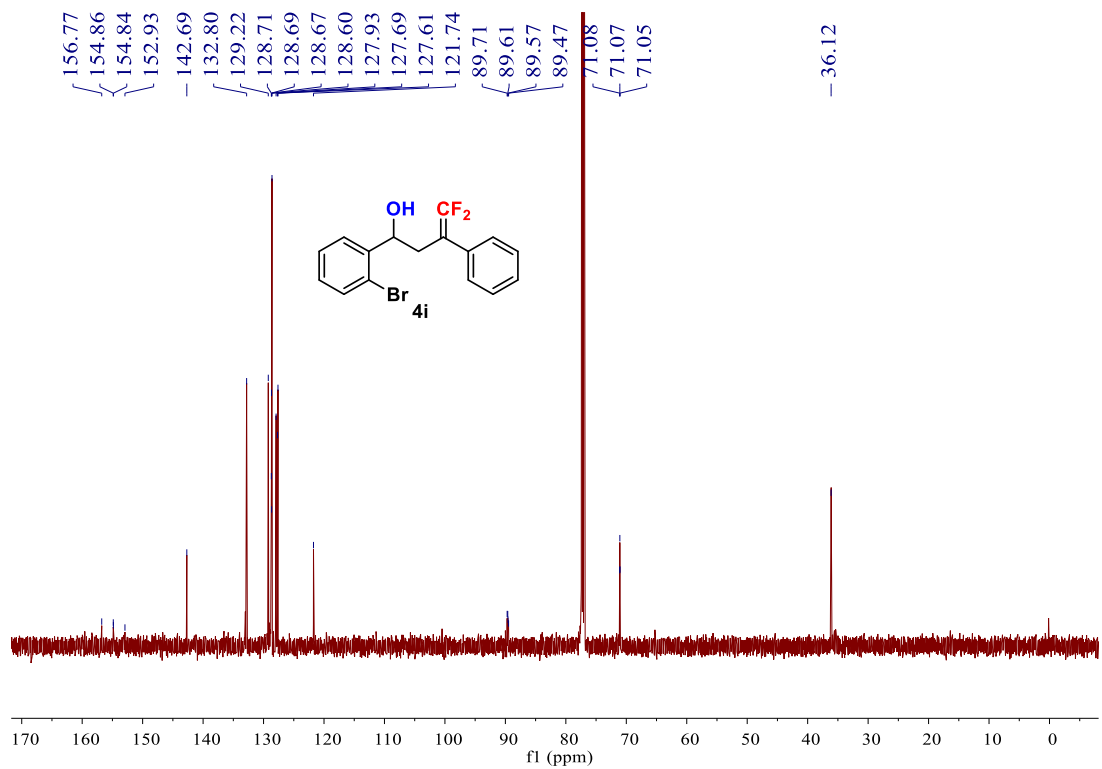


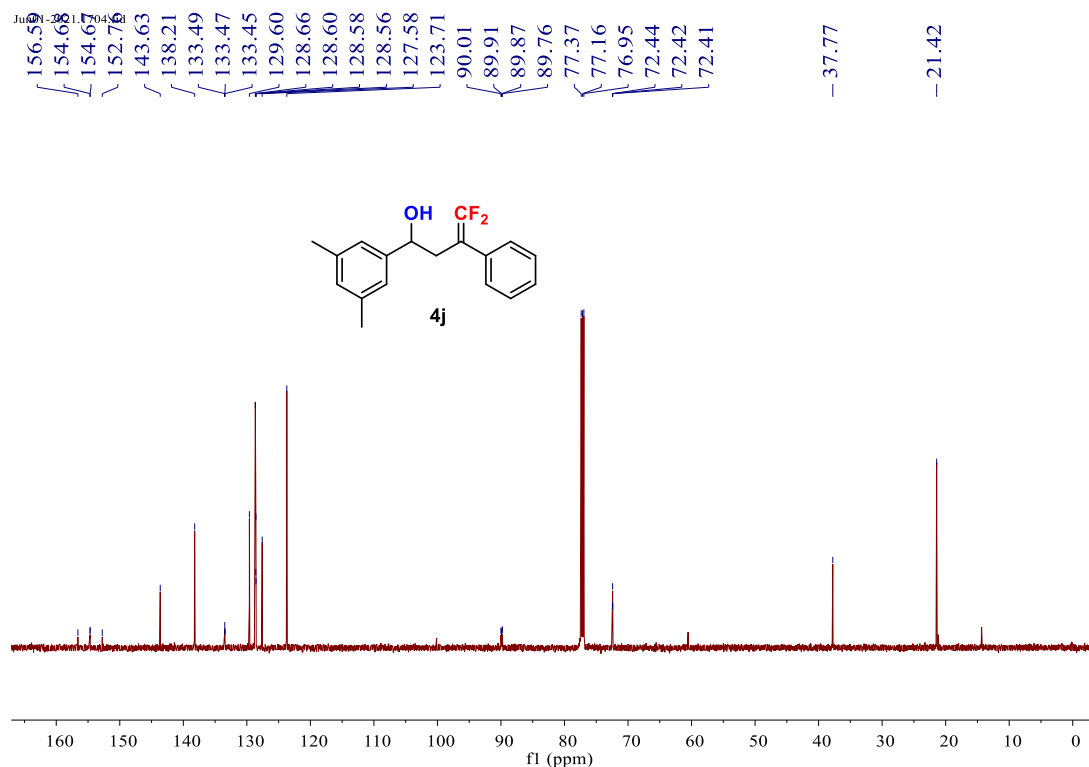
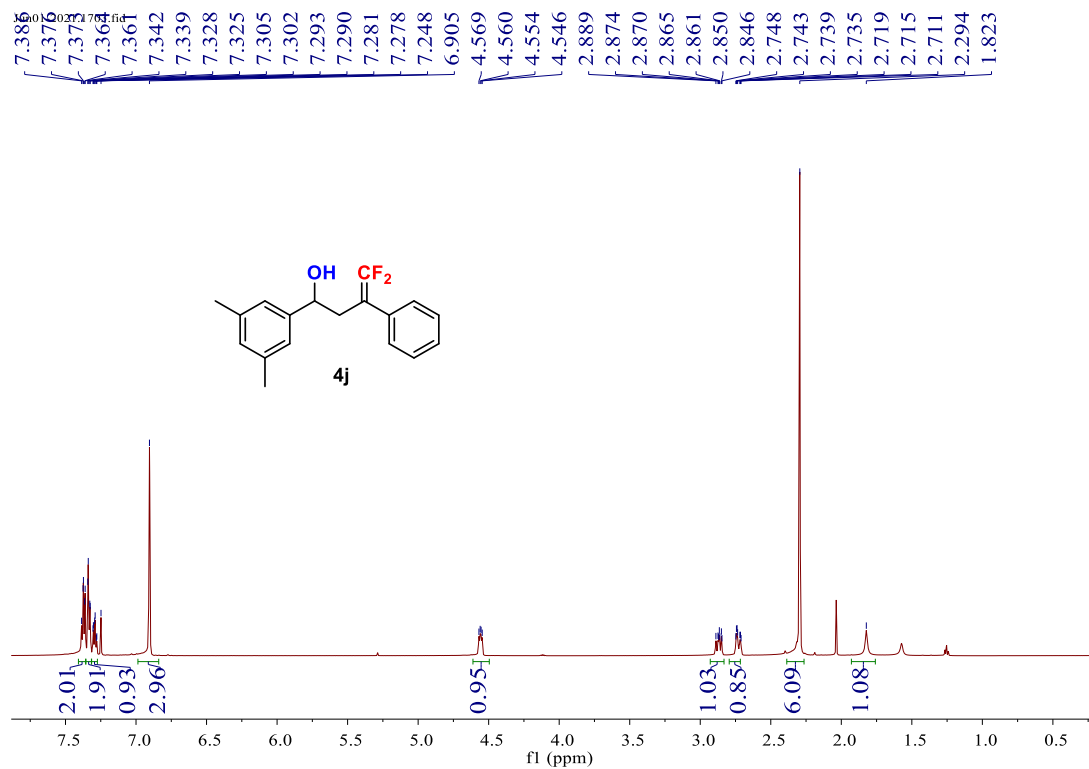


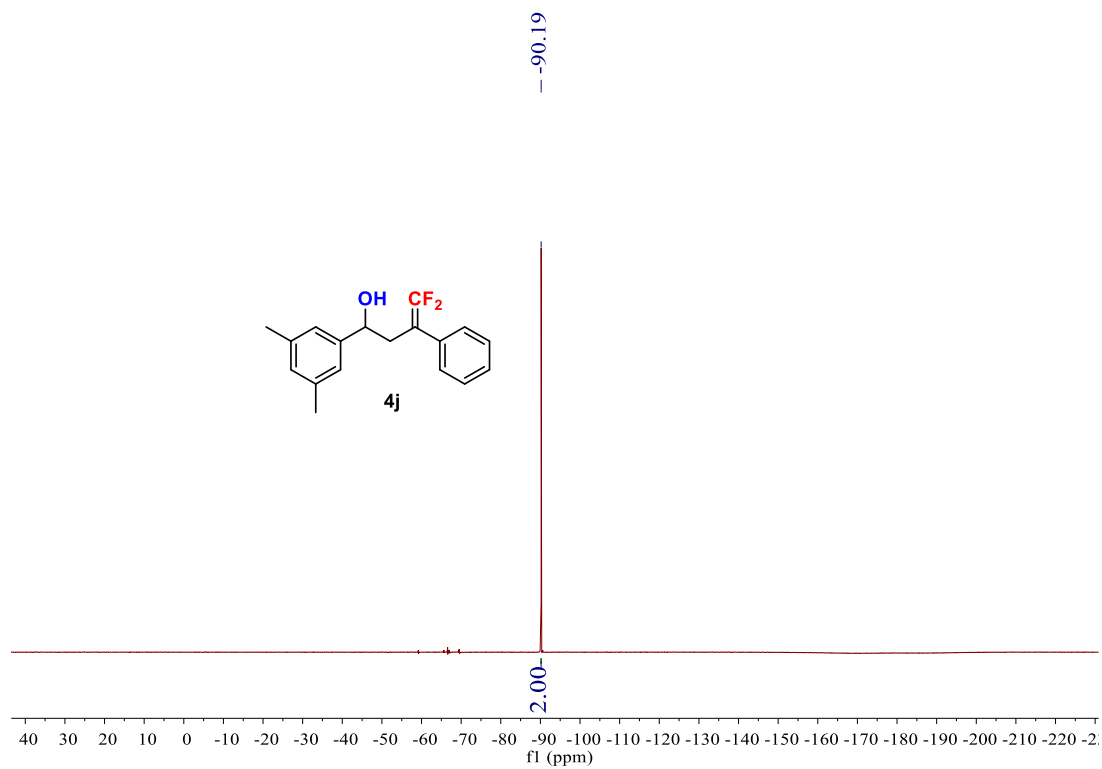




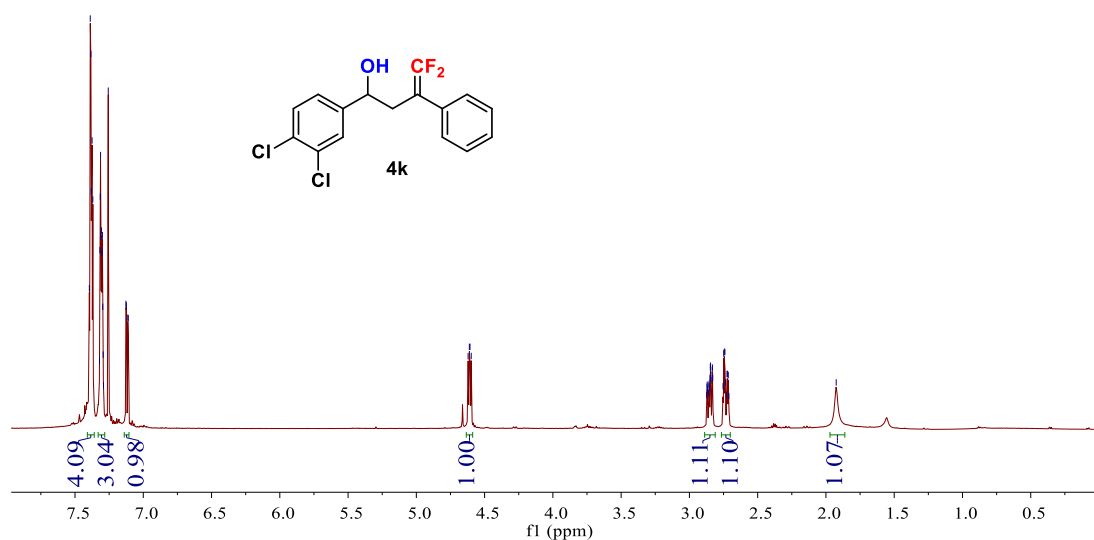


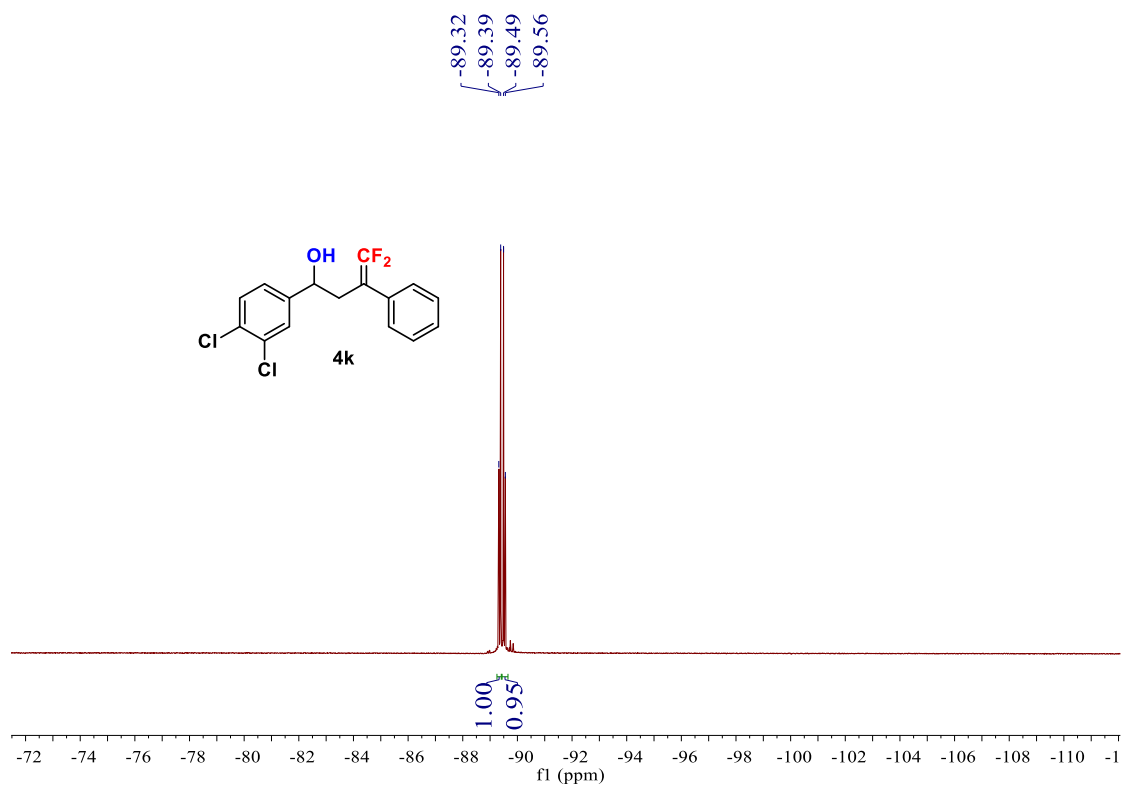
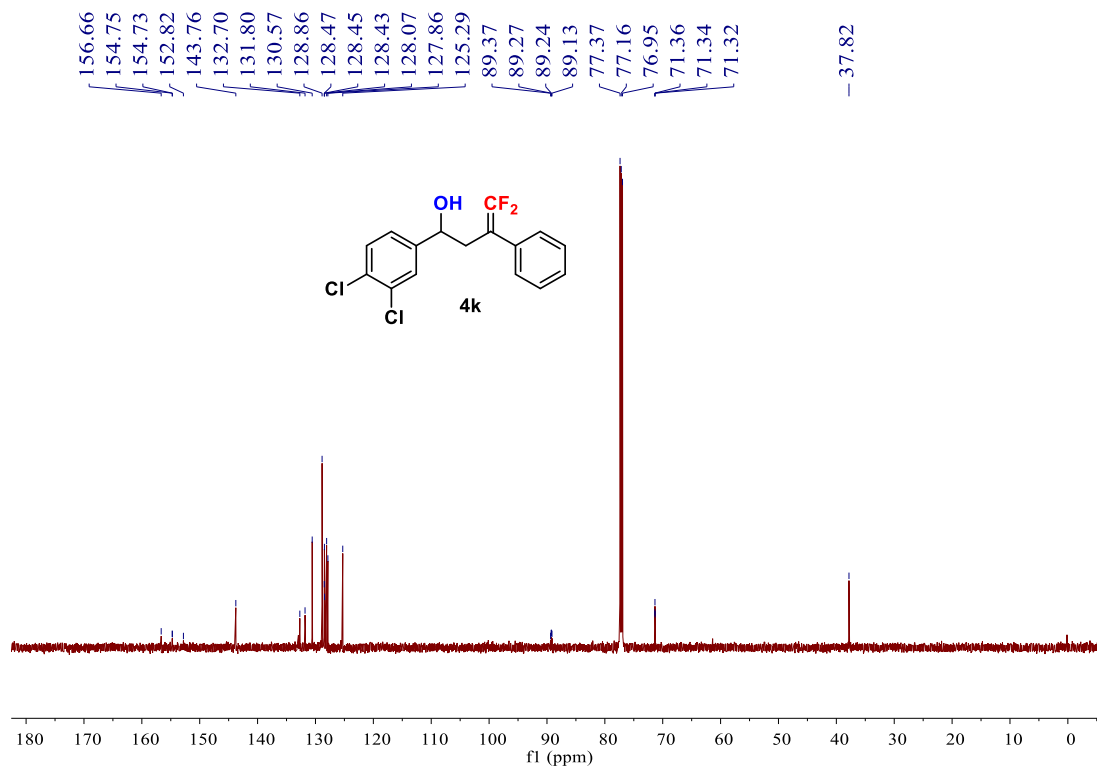


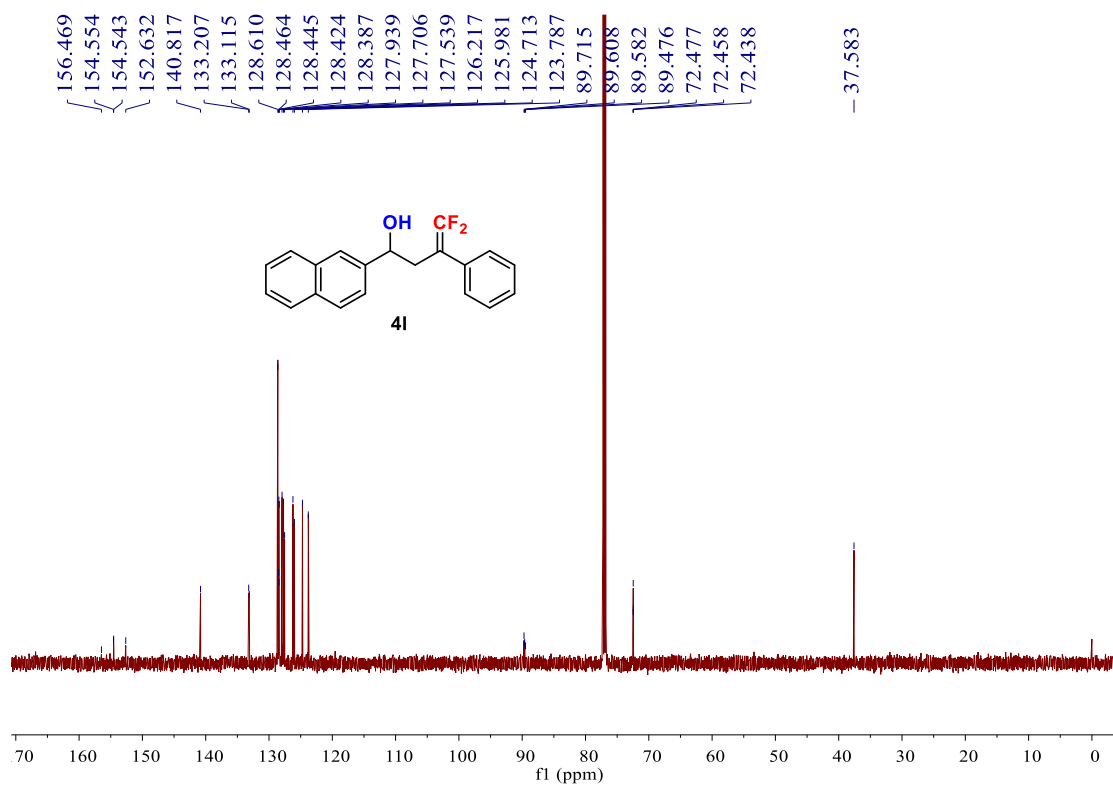
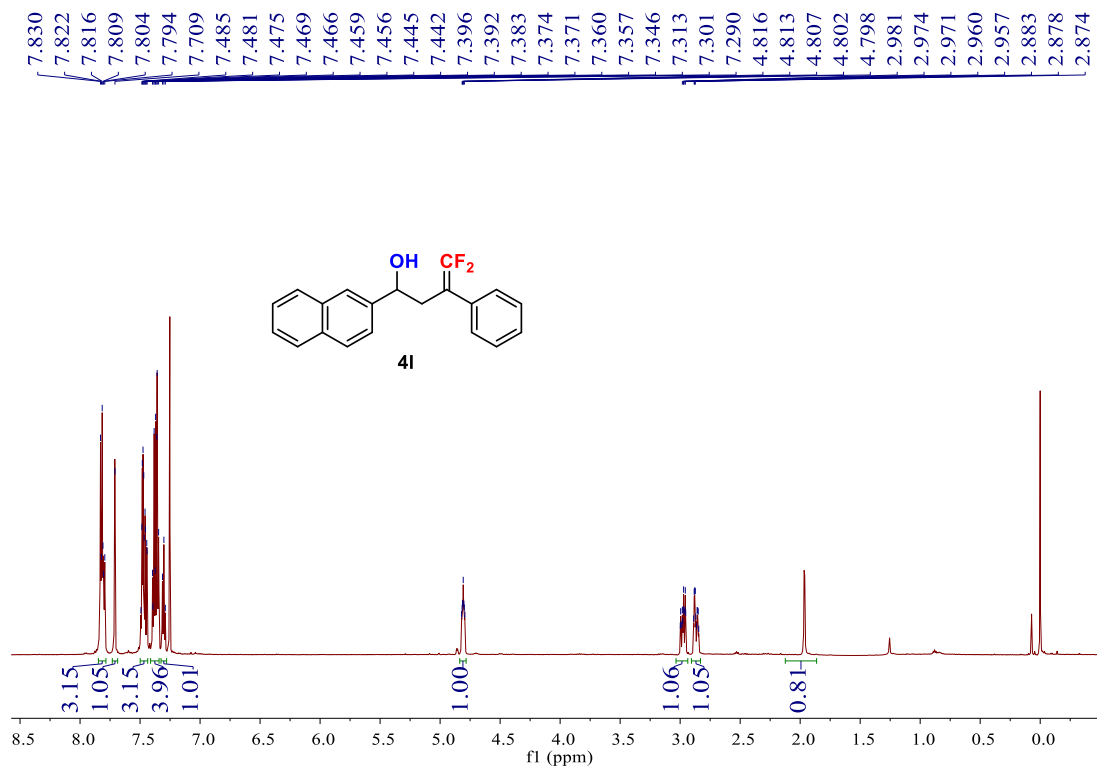


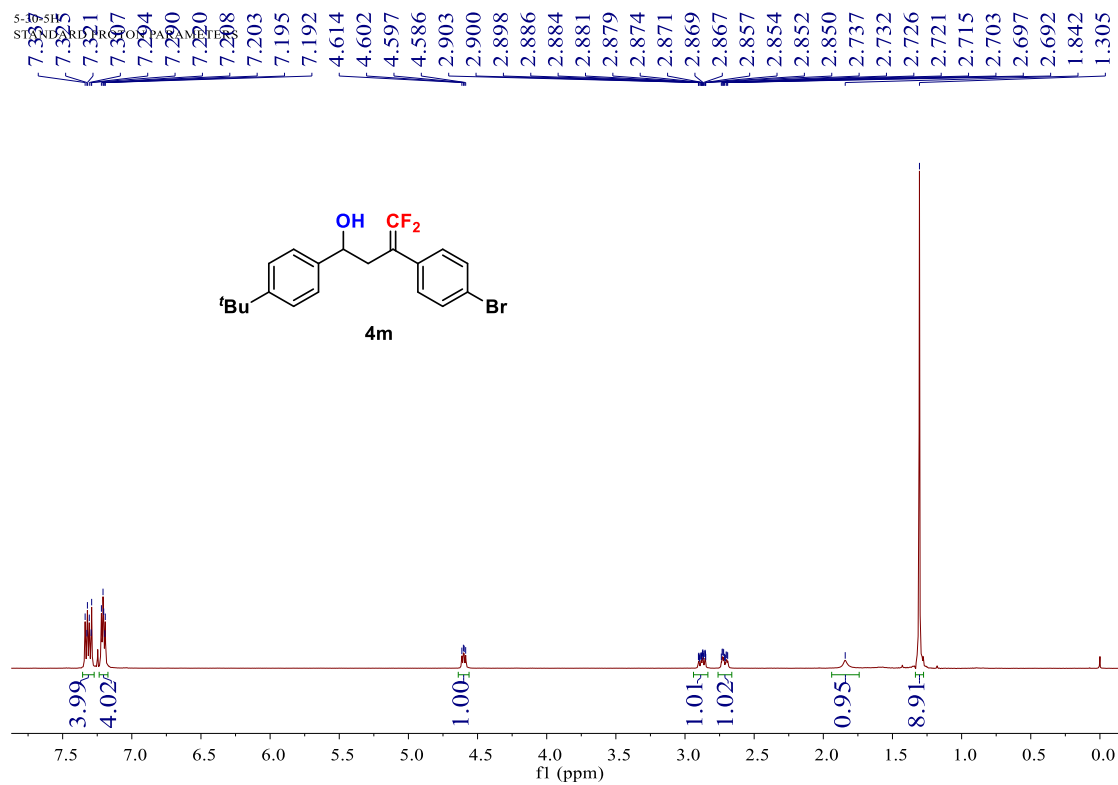
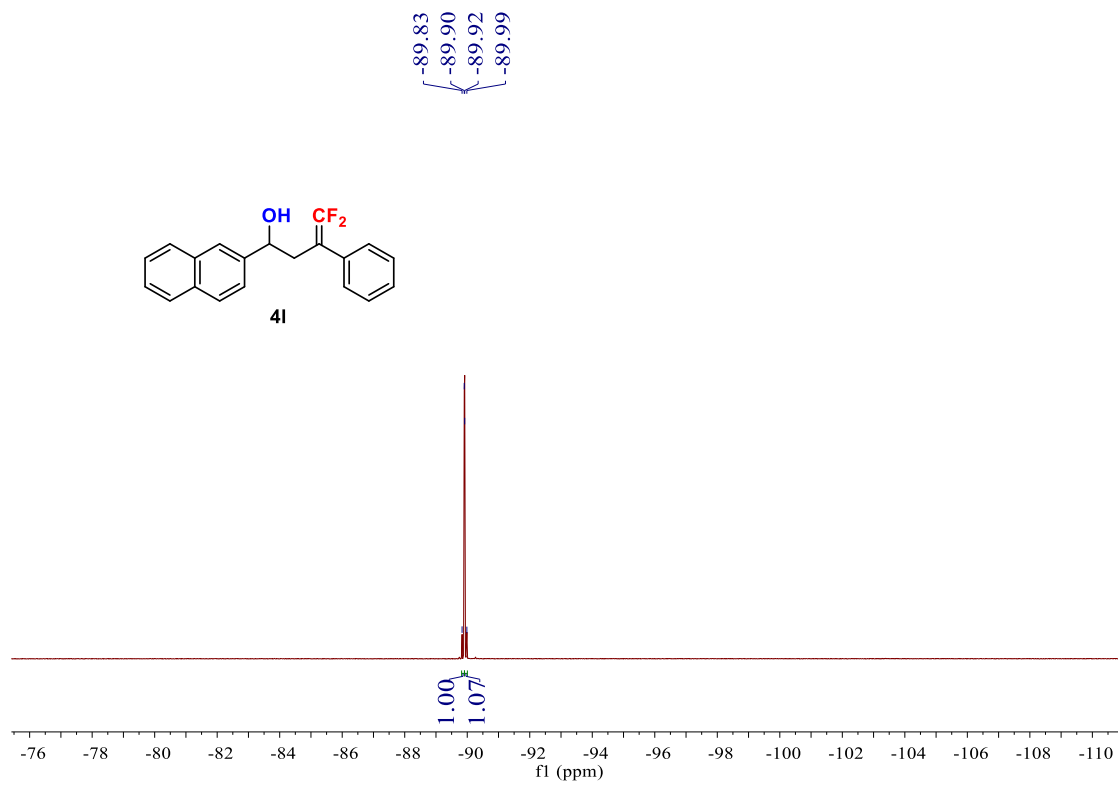


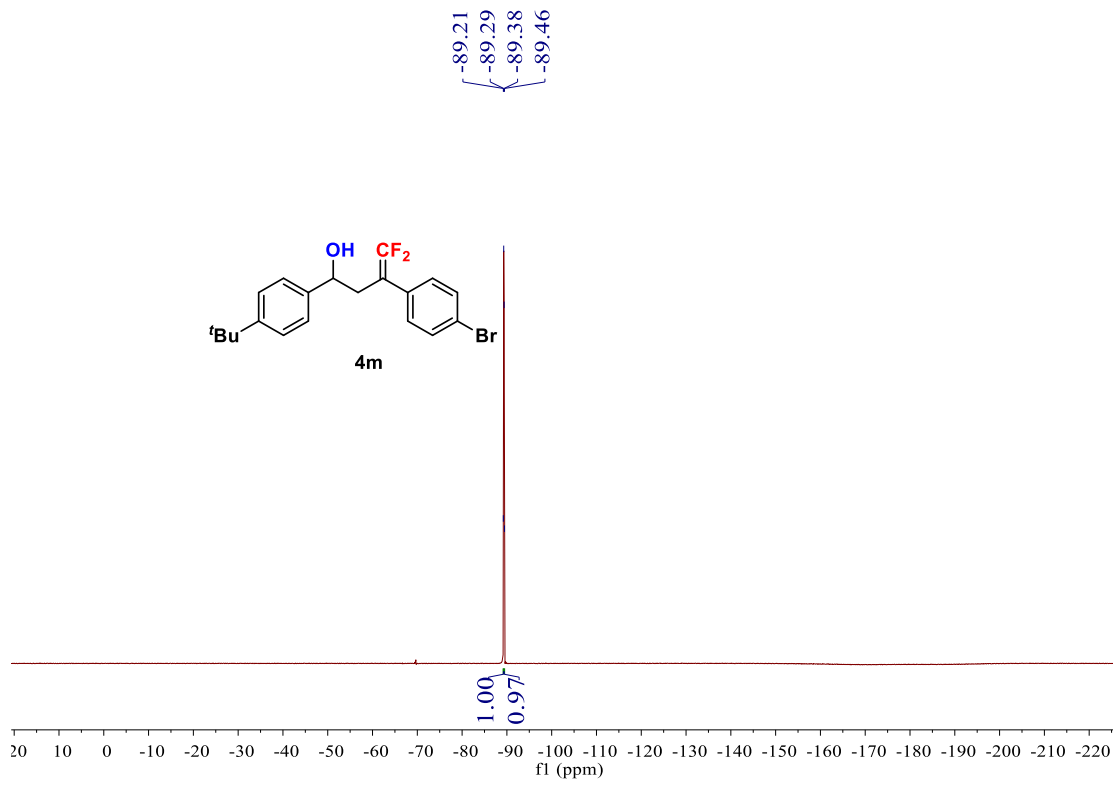
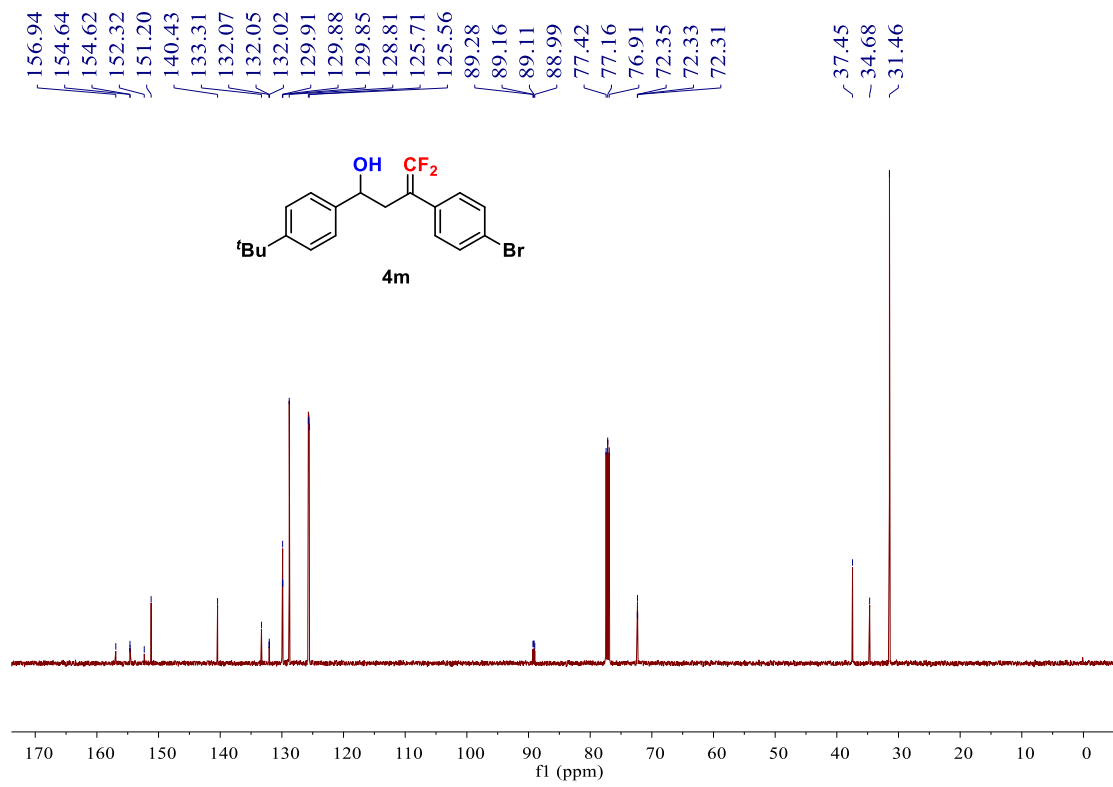
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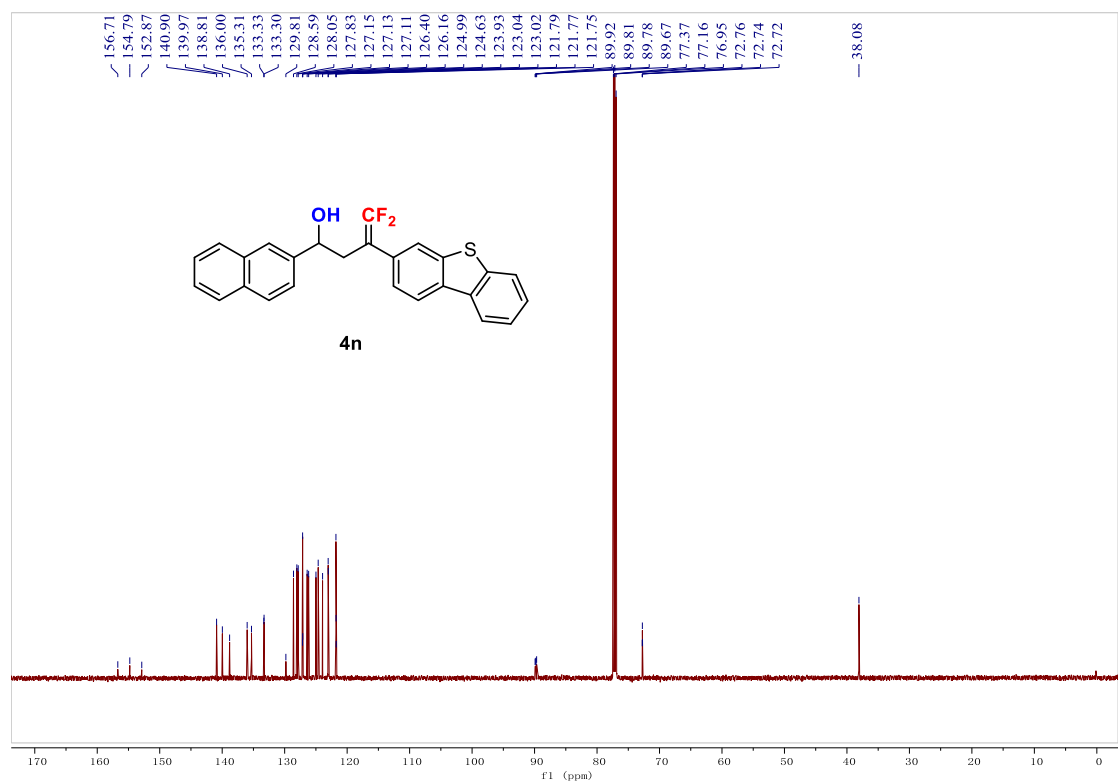
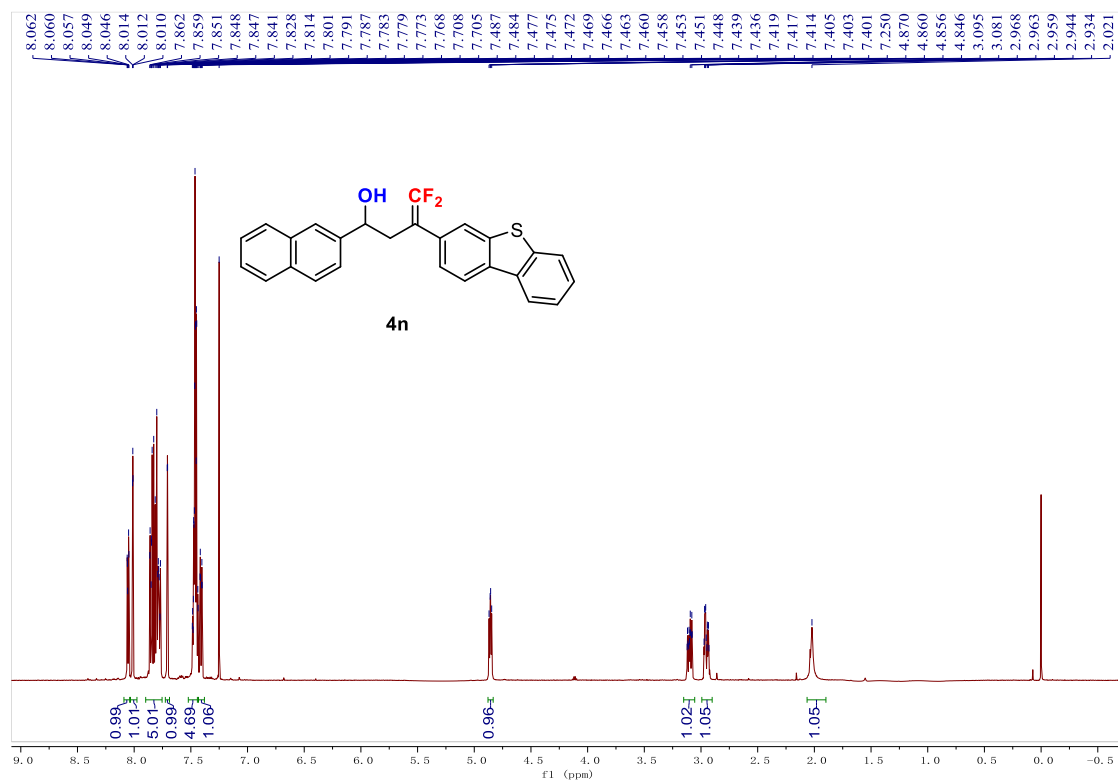


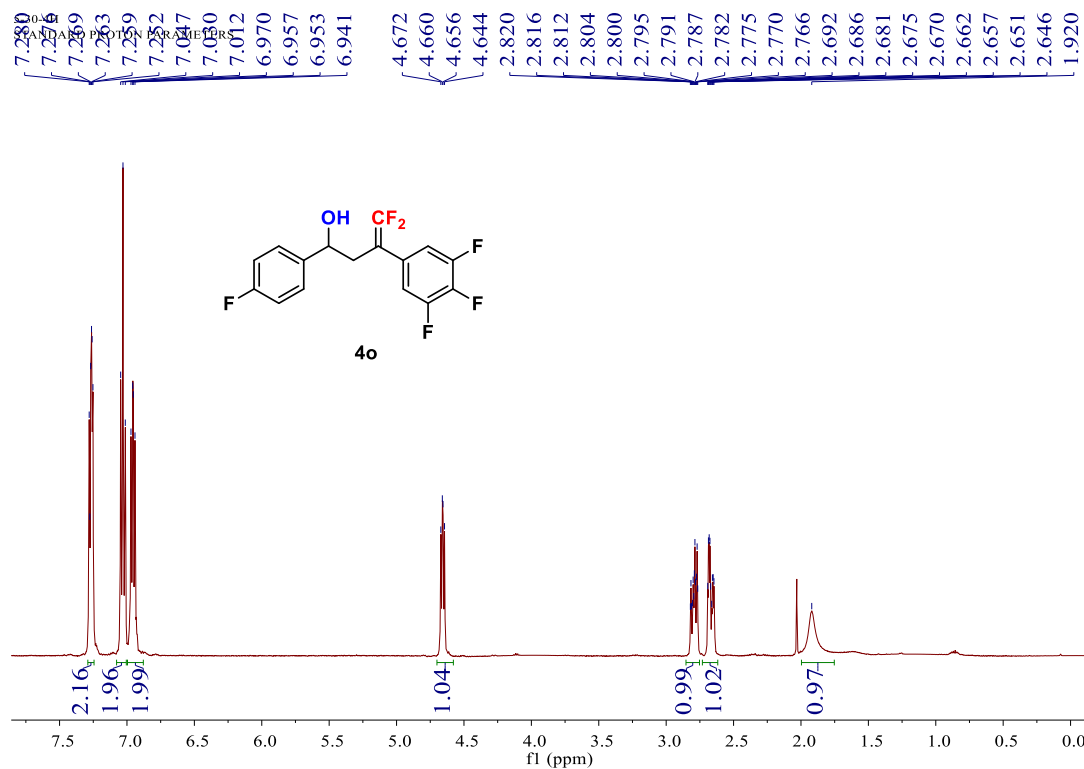
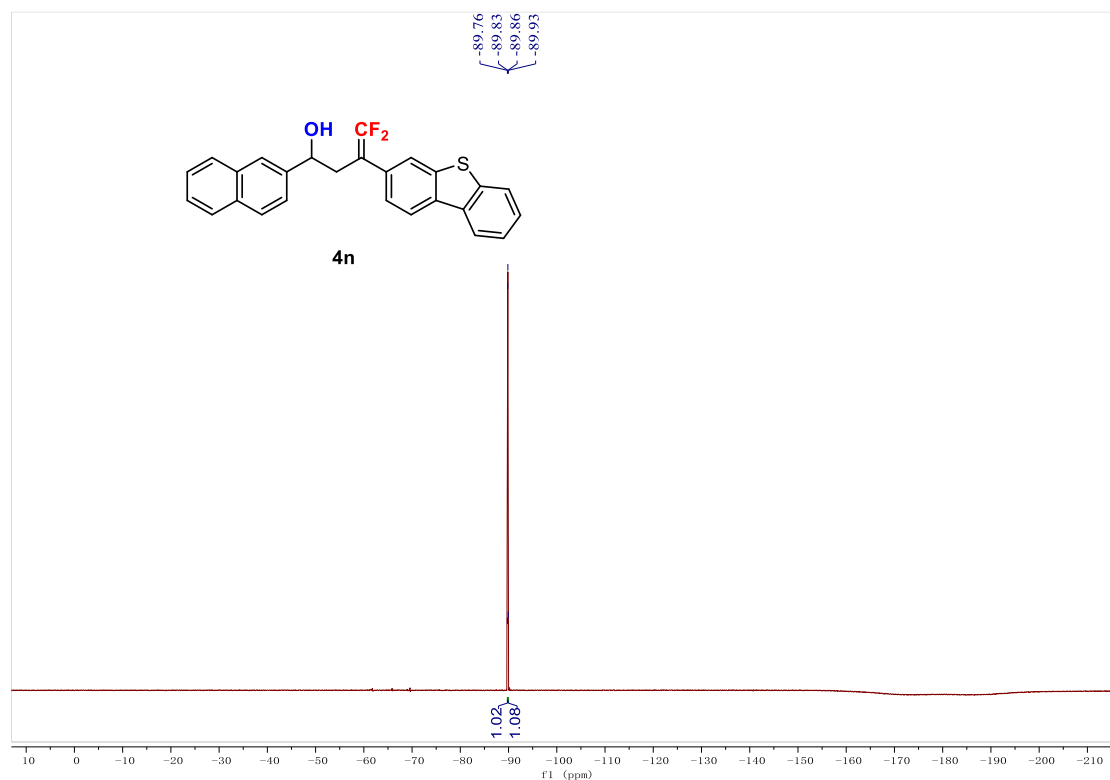


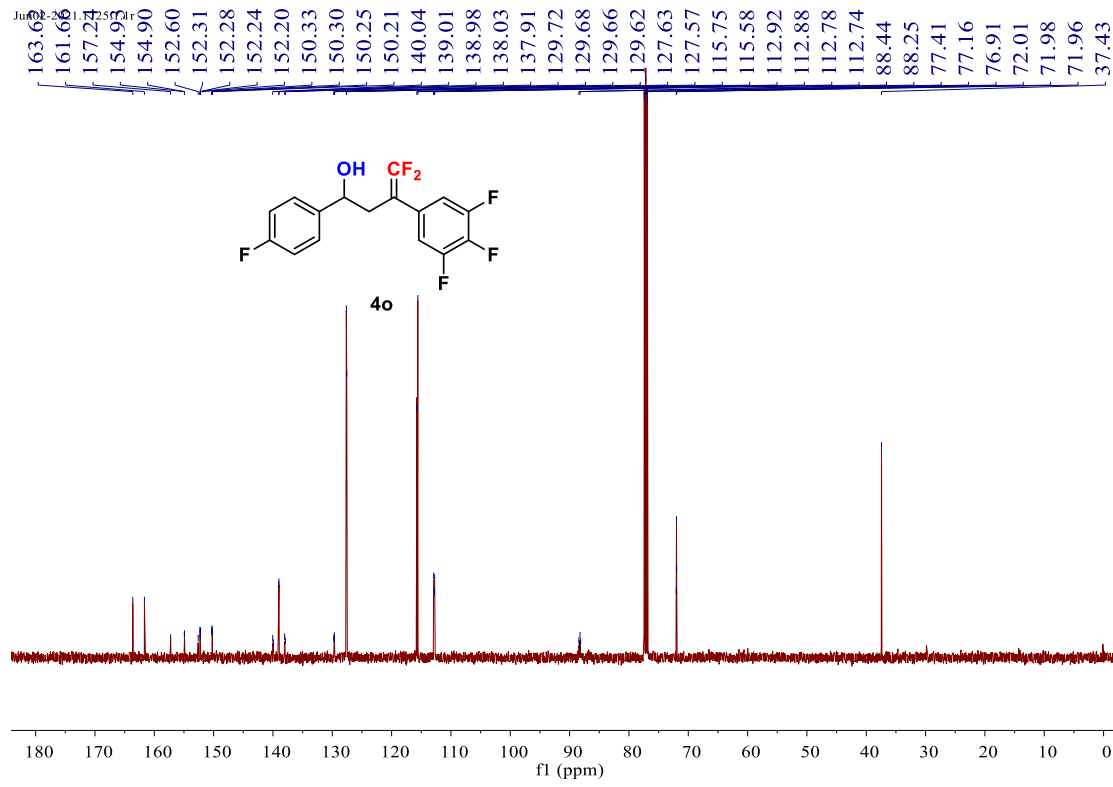
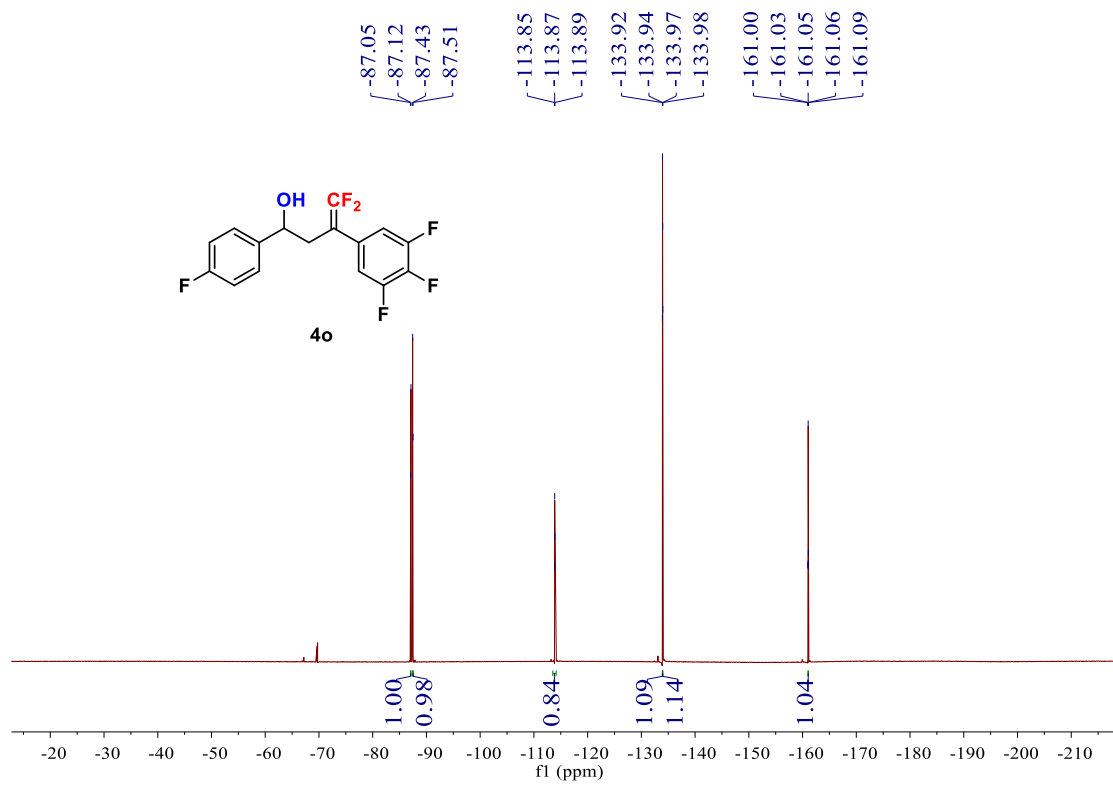


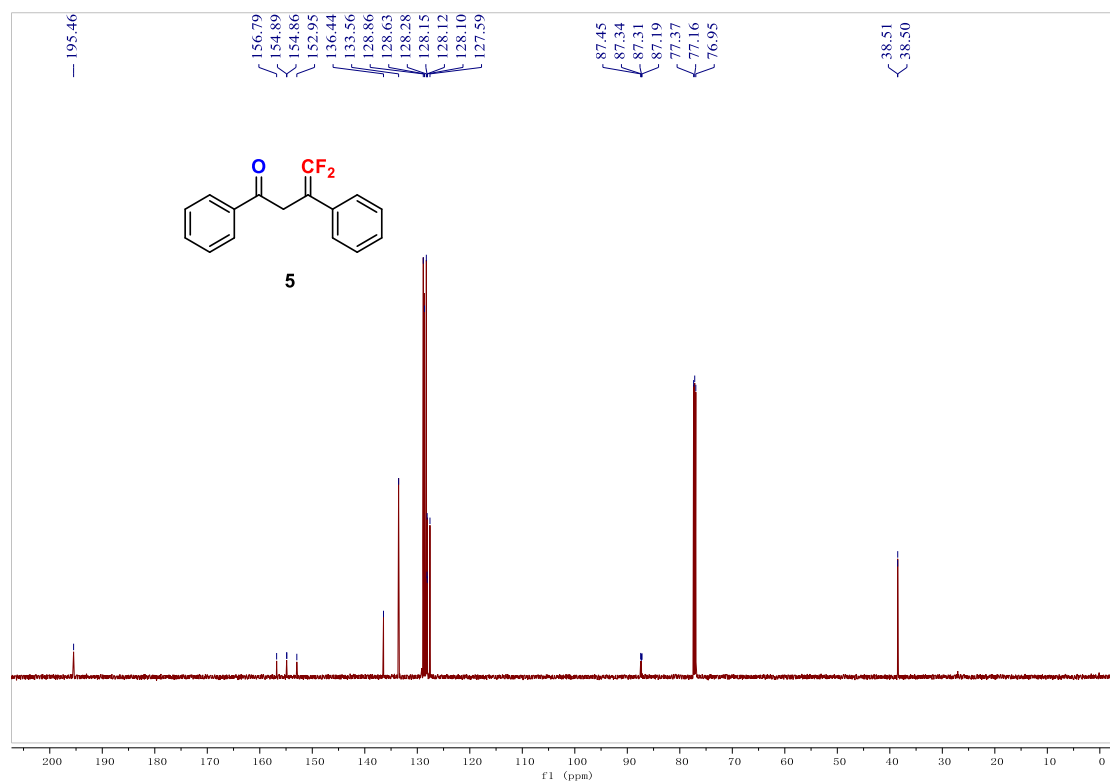
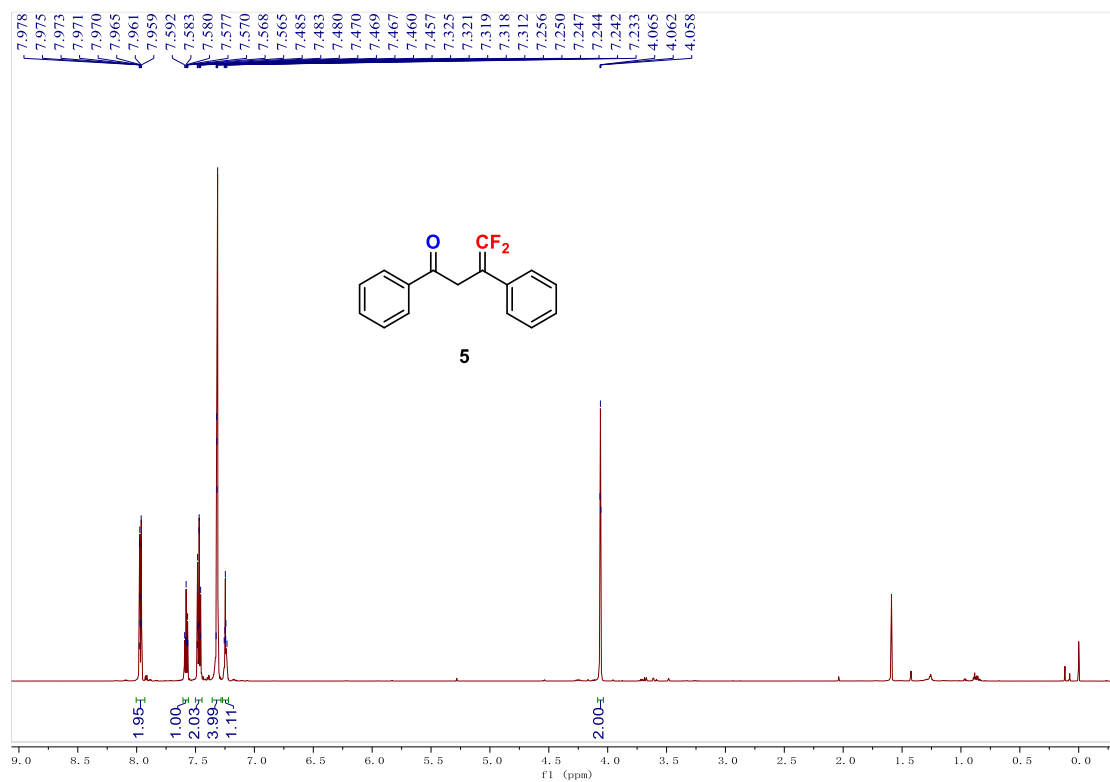


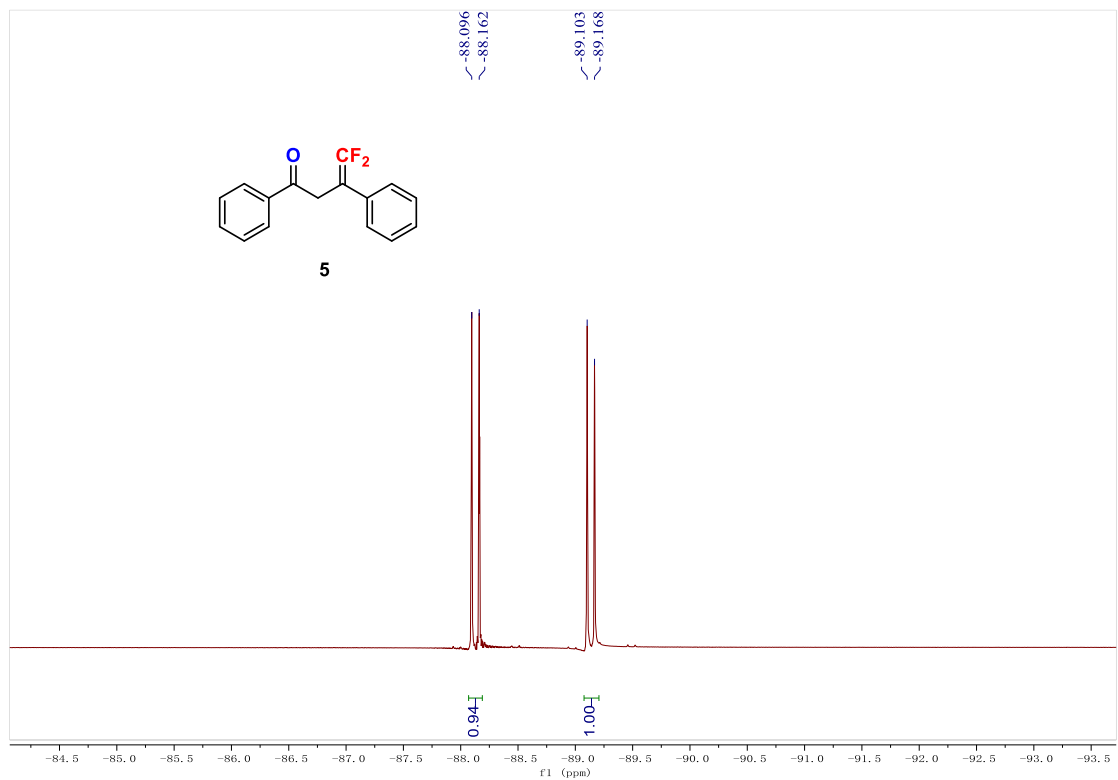




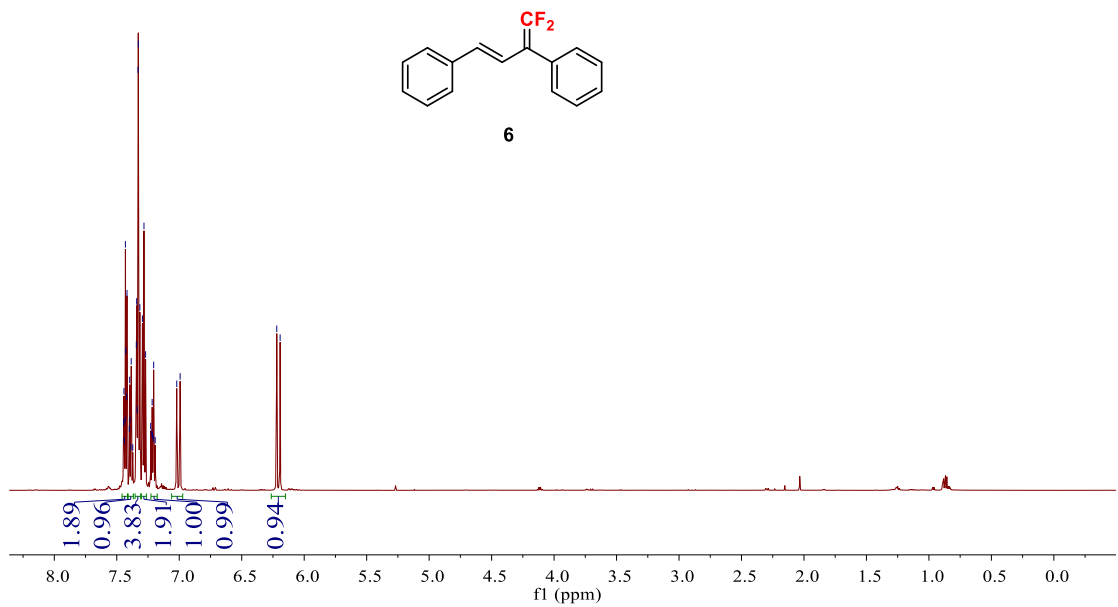








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