

Supporting Information

Visible-Light-Induced Defluorinative Carbonylative Coupling of Alkyl Iodides with α -Trifluoromethyl Substituted Styrenes

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1 General information

Reagents, solvents and analytical methods:

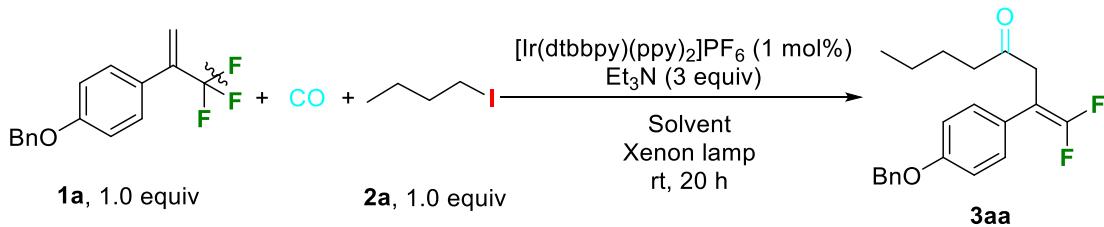
Unless otherwise noted, all reactions were carried out under a carbon monoxide or nitrogen atmosphere. All the α -trifluoromethyl substituted arylalkenes^[1] and some alkyl iodides^[2]: **2v**, **2w**, **2x**, **2y**, **2z** were synthesized by related references. All solvents were dried by standard techniques, and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (b. p. 30-60 °C) and ethyl acetate as eluent. ¹H, and ¹³C spectra were taken on Bruker AVANCE III 400 or 700 MHz spectrometers, ¹⁹F NMR was taken on Oxford instrument X-pulse 60 MHz and CDCl₃ (¹H NMR δ 7.26, ¹³C NMR δ 77.0) as solvent. All coupling constants (J) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quartet, m = multiplet, br = broad. Light source was from CEL-PE300L-3A (325w). Gas chromatography (GC) analyses were performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 μm film thickness) using argon as carrier gas. Gas chromatography mass spectrometer (GC-MS) analyses were performed on a Shimadzu QP2020 NX instrument. High resolution mass spectra (HRMS) were recorded on Agilent Q-TOF 6540. Because of the high toxicity of carbon monoxide, all of the reactions should be performed in an autoclave. The laboratory should well-equipped with a CO detector and alarm system.

[1] R.-Q. Pan, X.-X. Liu and M.-Z. Deng, *J. Fluorine Chem.* 1999, **95**, 167-170.

[2] J. E. Baldwin, L. Bischoff, T. D.W. Claridge, F. A. Heupel, D. R. Spring and R. C. Whitehead, *Tetrahedron* 1997, **53**, 2271-2290.

2. Optimization of reaction conditions

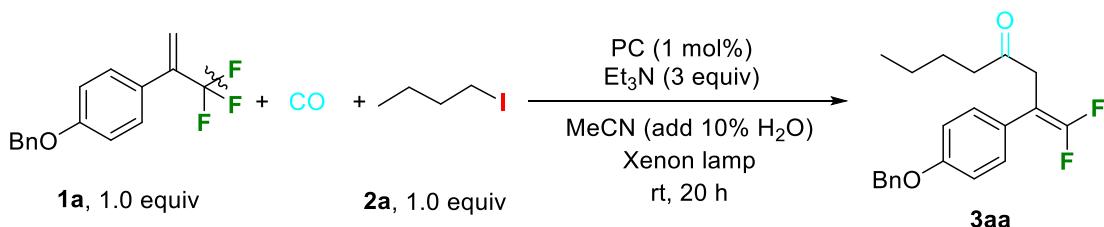
Screen for solvents^a



Entry	Solvent	Yield % ^b
1	MeCN	20
2	DCE	1
3	DMSO	0
4	EA	7
5	MeCN + 10% H ₂ O	35
6 ^c	MeCN + 10% H ₂ O	21

a) Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.10 mmol, 1.0 equiv), **[Ir(dtbbpy)(ppy)₂]PF₆** (1 mol%), **Et₃N** (0.30 mmol, 3.0 equiv), and **MeCN** (1.0 mL) under **CO** (60 bar) and stirred at **rt** for 20 h under **Xenon lamp** irradiation. b) The yields were determined by GC using hexadecane as the internal standard. c) **2a** (0.15 mmol).

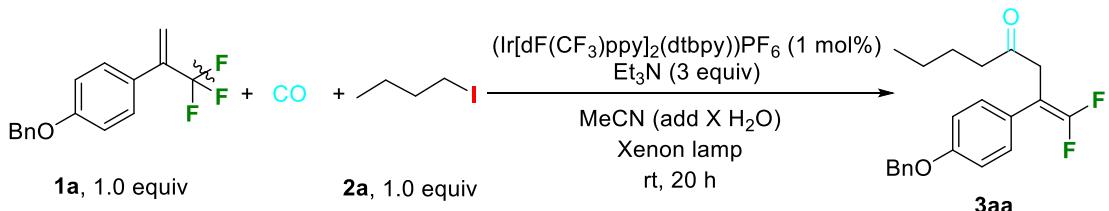
Screen for photocatalyst^a



Entry	Photocatalyst	Yield % ^b
1	<i>fac</i> -Ir(ppy) ₃	6
2	(Ir[DF(CF ₃)ppy] ₂ (dtbpy))PF ₆	47
3	Ru(bpy) ₂ (PF ₆) ₂	9
4 ^c	Phenol Red	0
5 ^c	Eosin Y	0
6 ^c	Rhodamine B	0
7 ^c	Methylene Blue	0

a) Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.10 mmol, 1.0 equiv), **PC** (1 mol%), **Et₃N** (0.30 mmol, 3.0 equiv), and **MeCN** (1.0 mL, add 10 % H₂O) under **CO** (60 bar) and stirred at **rt** for 20 h under **Xenon lamp** irradiation. b) The yields were determined by GC using hexadecane as the internal standard. c) photocatalyst (5 mol%).

Screen for the amount of water^a

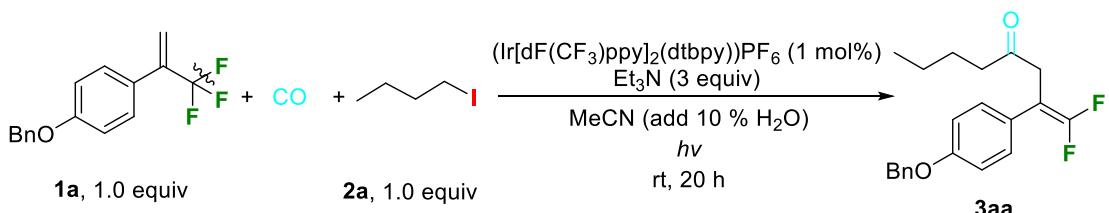


Entry	Addition of water	Yield % ^b
1	1 mL MeCN + 0.2 mL H ₂ O	38
2	1 mL MeCN + 0.4 mL H ₂ O	33
3	1 mL MeCN + 1.0 mL H ₂ O	28
4	0.5 mL MeCN + 1.0 mL H ₂ O	26
5	0.1 mL MeCN + 1.0 mL H ₂ O	7

a) Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.10 mmol, 1.0 equiv), (Ir[dF(CF₃)ppy]₂(dtbpy))PF₆ (1 mol%), Et₃N (0.30 mmol, 3.0 equiv) and solvent under CO (60 bar) and stirred at rt for 20 h under Xenon lamp irradiation.

b) The yields were determined by GC using hexadecane as the internal standard.

Screen for other factors^a

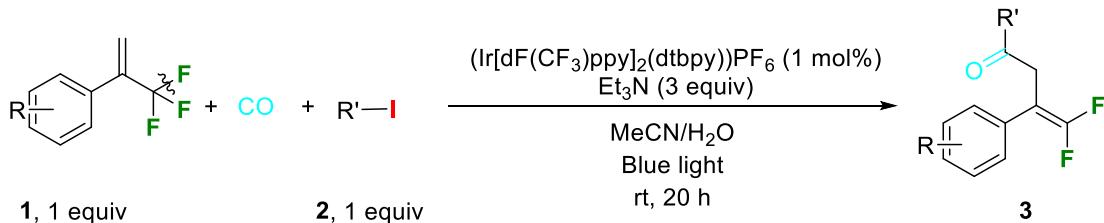


Entry	Light source	Yield % ^b
1	Blue light	13
2 ^d	Blue light	11
3 ^e	Blue light	53
4 ^f	Blue light	70
5 ^g	Blue light	75 (72 ^c)

a) Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.10 mmol, 1.0 equiv), (Ir[dF(CF₃)ppy]₂(dtbpy))PF₆ (1 mol %), Et₃N (0.30 mmol, 3.0 equiv) and MeCN (1.0 mL add 0.1 mL H₂O) under CO (60 bar) and stirred at rt for 20 h under blue light irradiation. b) The yields were determined by GC using hexadecane as the internal standard. c) Isolated yields. d) without water. e) 2.0 mL MeCN add 0.2 mL water. f) 3.0 mL MeCN add 0.3 mL water. g) 0.2 mmol scale reaction, 6.0 mL MeCN add 0.6 mL water.

3. General procedure

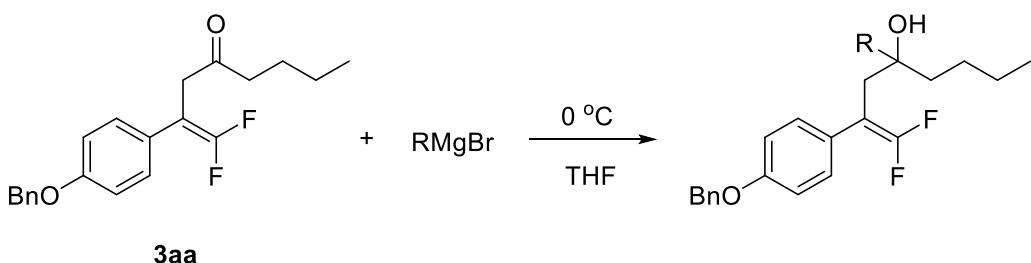
General procedure 1



A 10 mL screw-cap vial was charged with α -trifluoromethyl arylalkene (0.20 mmol), alkyl iodide (0.20 mmol), (Ir[dF(CF₃)ppy]₂(dtbpy))PF₆ (1 mol%, 2.3 mg), Et₃N (0.6 mmol, 121 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After MeCN (6.0 mL) and H₂O (0.6 mL) was added with a syringe under N₂ atmosphere, the vial was moved to an alloy plate and put into a perspective pressure reactor (500 mL) under N₂ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 60 bar CO. The autoclave was placed on a magnetic stirrer. The reaction was irradiated by blue light at room temperature for 20 h. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et₂O or EtOAc), concentrated, and purified by column chromatography.



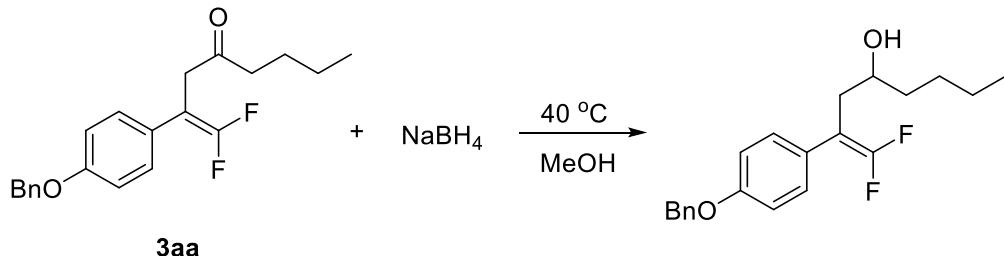
General procedure 2



A flame dried Schlenk tube was charged with 3aa (0.2 mmol, 69 mg) under nitrogen, and the compound was dissolved in dry THF (2.0 mL), resulting in a light yellow solution. The solution was stirred at 0 °C (ice bath). RMgBr (0.32 mmol, 0.32 mL of 1 M sol. in THF) was added dropwise over 10 min. The reaction mixture was stirred at room temperature and monitored by TLC until full conversion to the product was observed. The reaction mixture was quenched with aqueous saturated NH₄Cl and

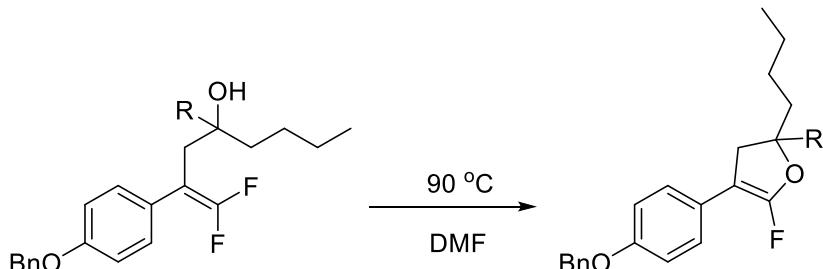
extracted with ethyl acetate (5.0 ml \times 3). The organic extracts are combined, concentrated and the residue was purified by silica gel column chromatography to afford the product.

General procedure 3



A flame dried Schlenk tube was charged with the requisite **3aa** (0.2 mmol, 69 mg), MeOH (10.0 mL) and NaBH₄ (0.4 mmol, 31 mg). The reaction mixture was stirred for 6 h at 40 °C. and monitored by TLC until full conversion to the product was observed. Then the reaction mixture was diluted with ethyl acetate, filtered and dried with NaSO₄, and concentrated in vacuo. The residue was chromatographed on silica gel to afford the product.

General procedure 4



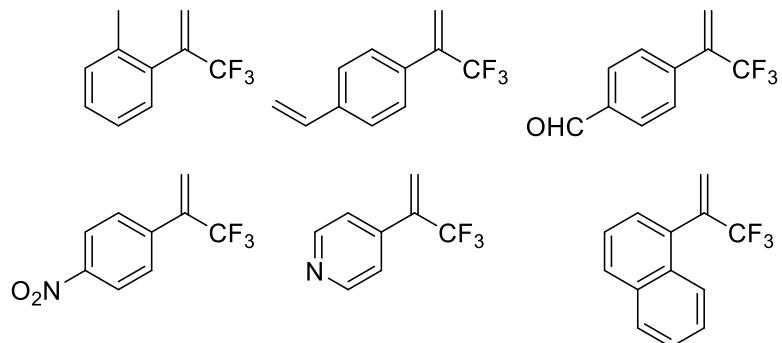
A separate flask is charged with the requisite γ,γ -difluoro allylic alcohols (0.2 mmol), DMF (2.0 mL) and NaH (7.2 mg, 0.3 mmol). The reaction mixture is then heated to 90 °C with stirring, and monitored by TLC until full conversion to the product was observed. The mixture is then cooled to room temperature, filtrated through celite, and concentrated. The residue chromatographed on silica gel to afford the product.

4. Failed examples

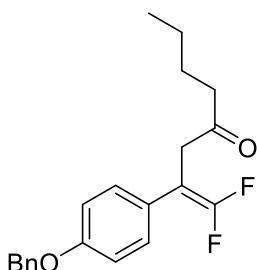
Alkyl Iodides



α -Trifluoromethyl Substituted Arylalkenes



5. Spectroscopic data of products



2-(4-(benzyloxy)phenyl)-1,1-difluorooct-1-en-4-one (3aa)

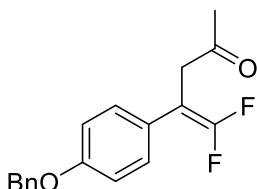
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 40:1) to give the product as a colorless oil (49 mg, 72%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.22 (m, 5H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 4.97 (s, 2H), 3.32 (s, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.45 (p, *J* = 7.4 Hz, 2H), 1.18 (q, *J* = 7.7 Hz, 2H), 0.79 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 207.0 (dd, *J* = 2.8, 3.0 Hz), 158.1, 154.6 (dd, *J* = 294.1, 290.7 Hz), 136.8, 130.1, 129.1 (t, *J* = 3.2 Hz), 128.6, 128.1, 127.5, 125.6 (t, *J* = 3.2 Hz), 115.0, 86.8 (dd, *J* = 21.8, 22.1 Hz), 70.0, 42.3 (d, *J* = 2.0 Hz), 41.7, 25.7, 22.2, 13.8.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -89.1 (d, *J* = 39.0 Hz), -90.2 (d, *J* = 39.0 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₁H₂₂F₂O₂ 345.1661; Found: 345.1660.



4-(4-(benzyloxy)phenyl)-5,5-difluoropent-4-en-2-one (3ab)

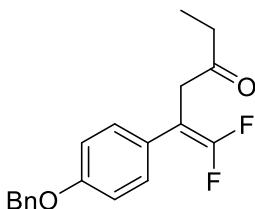
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and (iodomethyl)trimethylsilane (43 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 20:1) to give the product as a colorless oil (31 mg, 49%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 7.19 – 7.12 (m, 2H), 6.91 – 6.84 (m, 2H), 4.97 (s, 2H), 3.34 (t, *J* = 2.2 Hz, 2H), 2.07 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 204.7 (dd, *J* = 2.2, 3.7 Hz), 158.1, 154.6 (dd, *J* = 293.0, 293.0 Hz), 136.8, 129.1 (t, *J* = 3.3 Hz), 128.6, 128.1, 127.5, 125.4 (t, *J* = 4.4 Hz), 115.0, 86.8 (dd, *J* = 21.7, 22.0 Hz), 70.0, 43.1 (d, *J* = 2.0 Hz), 29.2.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.4 (d, *J* = 40.6 Hz), -89.7 (d, *J* = 37.4 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₁₆F₂O₂ 303.1191; Found: 303.1190.



5-(4-(benzyloxy)phenyl)-6,6-difluorohex-5-en-3-one (3ac)

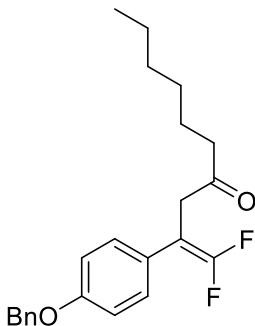
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and iodoethane (32 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 40:1) to give the product as a colorless oil (37 mg, 59%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 21.6, 7.6 Hz, 4H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.89 – 6.84 (m, 2H), 4.98 (s, 2H), 3.34 (s, 2H), 2.38 (q, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.3 (dd, *J* = 2.0, 3.4 Hz), 157.1, 154.4 (q, *J* = 290.2 Hz), 135.8, 129.0, 128.0 (t, *J* = 3.7 Hz), 127.6, 127.0, 126.4, 124.6 (t, *J* = 3.8 Hz), 85.8 (dd, *J* = 21.9, 22.3 Hz), 69.0, 40.9 (d, *J* = 2.0 Hz), 34.1, 6.6.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.7 (d, *J* = 38.2 Hz), -89.9 (d, *J* = 40.2 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₉H₁₈F₂O₂ 317.1348; Found: 317.1346.



2-(4-(benzyloxy)phenyl)-1,1-difluorodec-1-en-4-one (3ad)

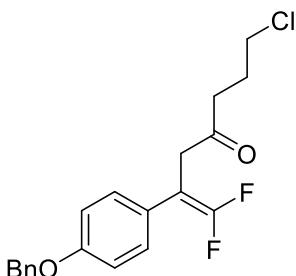
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 1-iodohexane (43 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 40:1) to give the product as a yellow oil (47 mg, 63%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.96 (s, 2H), 3.32 (s, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.45 (dd, *J* = 9.0, 5.5 Hz, 2H), 1.19 (td, *J* = 9.2, 8.4, 4.3 Hz, 2H), 1.15 (dt, *J* = 7.6, 3.6 Hz, 4H), 0.78 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 207.1 (dd, *J* = 2.9, 3.0 Hz), 158.1, 154.6 (dd, *J* = 292.1, 292.6 Hz), 136.8, 129.1 (t, *J* = 3.6 Hz), 128.6, 128.1, 127.5, 125.6 (t, *J* = 4.3 Hz), 115.0, 86.8 (dd, *J* = 22.3, 22.4 Hz), 70.0, 42.3 (d, *J* = 1.5 Hz), 42.0, 31.6, 28.8, 23.6, 22.5, 14.0.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.7 (d, *J* = 38.9 Hz), -90.0 (d, *J* = 38.9 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₂₆F₂O₂ 373.1974; Found: 373.1972.



2-(4-(benzyloxy)phenyl)-7-chloro-1,1-difluorohept-1-en-4-one (3ae)

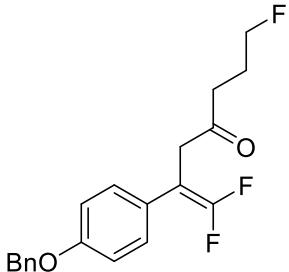
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 1-chloro-3-iodopropane (41 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (37 mg, 51%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 4H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.98 (s, 2H), 3.44 (t, *J* = 6.3 Hz, 2H), 3.37 (s, 2H), 2.56 (t, *J* = 7.0 Hz, 2H), 1.97 – 1.91 (m, 2H).

¹³C NMR (176 MHz, CDCl₃) δ 204.6 (dd, *J* = 2.8, 3.3 Hz), 157.1, 153.6 (dd, *J* = 292.8, 292.0 Hz), 135.7, 128.0 (t, *J* = 3.5 Hz), 127.6, 127.0, 126.4, 124.3 (t, *J* = 4.1 Hz), 114.0, 85.6 (dd, *J* = 21.9, 22.5 Hz), 69.0, 43.2, 41.4 (d, *J* = 1.7 Hz), 37.5, 25.1.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.3 (d, *J* = 40.0 Hz), -89.6 (d, *J* = 37.6 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₁₉ClF₂O₂ 365.1114; Found: 365.1111.



2-(4-(benzyloxy)phenyl)-1,1,7-trifluorohept-1-en-4-one (3af)

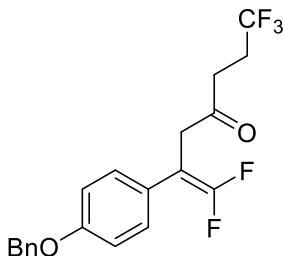
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 1-fluoro-3-iodopropane (38 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 20:1) to give the product as a colorless oil (50 mg, 72%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.30 (dd, *J* = 8.4, 6.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 4.35 (t, *J* = 5.8 Hz, 1H), 4.28 (t, *J* = 5.8 Hz, 1H), 3.36 (s, 2H), 2.51 (t, *J* = 7.1 Hz, 2H), 1.90 – 1.77 (m, 2H).

¹³C NMR (176 MHz, CDCl₃) δ 204.7 (dd, *J* = 2.9, 2.8 Hz), 157.1, 153.6 (dd, *J* = 292.2, 292.9 Hz), 135.7, 128.0 (t, *J* = 3.5 Hz), 127.6, 127.0, 126.4, 124.4 (t, *J* = 4.0 Hz), 114.0, 85.6 (dd, *J* = 22.0, 22.3 Hz), 81.9 (d, *J* = 165.0 Hz), 69.0, 41.3 (d, *J* = 1.7 Hz), 36.2 (d, *J* = 4.2 Hz), 23.3 (d, *J* = 21.1 Hz).

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.4 (d, *J* = 38.5 Hz), -89.6 (d, *J* = 38.5 Hz), -219.9 (m).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₁₉F₃O₂ 349.1410; Found: 349.1408.



2-(4-(benzyloxy)phenyl)-1,1,7,7,7-pentafluorohept-1-en-4-one (3ag)

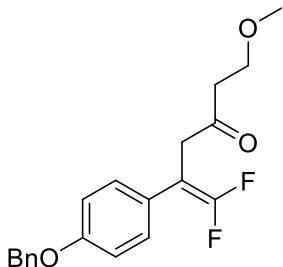
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 1,1,1-trifluoro-3-iodopropane (45 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 20:1) to give the product as a colorless oil (45 mg, 59%).

¹H NMR (700 MHz, Chloroform-d) δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 3.38 (s, 2H), 2.65 – 2.57 (m, 2H), 2.29 (tdd, *J* = 10.8, 7.8, 4.9 Hz, 2H).

¹³C NMR (176 MHz, CDCl₃) δ 203.1 (dd, *J* = 3.1, 3.0 Hz), 158.3, 154.7 (dd, *J* = 293.6, 292.3 Hz), 136.7, 129.0 (t, *J* = 3.7 Hz), 128.7, 128.1, 127.5, 125.1 (t, *J* = 4.0 Hz), 115.1, 86.3 (dd, *J* = 21.7, 22.3 Hz), 70.0, 42.2 (d, *J* = 2.1 Hz), 34.2 (d, *J* = 2.8 Hz), 27.9 (q, *J* = 30.1 Hz).

¹⁹F NMR (56 MHz, Chloroform-d) δ -66.2, -88.3 (d, *J* = 37.2 Hz), -89.3 (d, *J* = 36.4 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₁₇F₅O₂ 385.1221; Found: 385.1220.



5-(4-(benzyloxy)phenyl)-6,6-difluoro-1-methoxyhex-5-en-3-one (3ah)

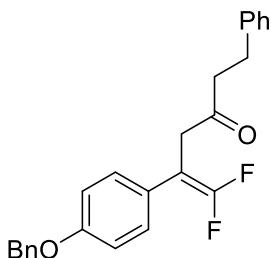
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 1-iodo-2-methoxyethane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 5:1) to give the product as a colorless oil (44 mg, 64%).

¹H NMR (700 MHz, Chloroform-d) δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.30 (dd, *J* = 8.6, 6.7 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.16 – 7.12 (m, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 3.53 (t, *J* = 6.2 Hz, 2H), 3.39 (s, 2H), 3.22 (s, 3H), 2.59 (t, *J* = 6.2 Hz, 2H).

¹³C NMR (176 MHz, CDCl₃) δ 205.1 (dd, *J* = 2.9, 3.2 Hz), 158.1, 154.6 (dd, *J* = 293.0, 293.0 Hz), 136.8, 129.1 (t, *J* = 3.6 Hz), 128.6, 128.1, 127.5, 125.5 (t, *J* = 3.8 Hz), 115.0, 86.5 (dd, *J* = 21.8, 22.4 Hz), 70.0, 67.5, 58.9, 42.9 (d, *J* = 1.8 Hz), 42.1.

¹⁹F NMR (56 MHz, Chloroform-d) δ -88.3 (d, *J* = 37.7 Hz), -89.6 (d, *J* = 38.6 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₂₀F₂O₃ 347.1453; Found: 347.1453.



5-(4-(benzyloxy)phenyl)-6,6-difluoro-1-phenylhex-5-en-3-one (3ai)

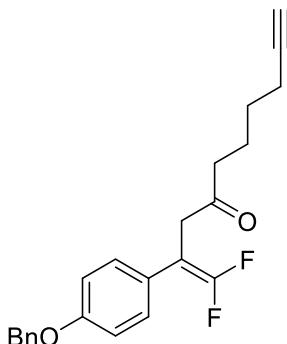
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and (2-iodoethyl)benzene (46 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 20:1) to give the product as a colorless oil (27 mg, 45%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.20 – 7.16 (m, 2H), 7.12 – 7.09 (m, 1H), 7.09 – 7.07 (m, 2H), 7.06 – 7.03 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.98 (s, 2H), 3.31 (d, *J* = 2.3 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H).

¹³C NMR (176 MHz, CDCl₃) δ 204.8 (dd, *J* = 2.1, 2.4 Hz), 157.0, 153.6 (dd, *J* = 292.4, 292.0 Hz), 139.7, 135.7, 128.0 (t, *J* = 4.2 Hz), 127.6, 127.5, 127.3, 127.0, 126.4, 125.2, 124.4 (t, *J* = 3.8 Hz), 113.9, 85.6 (dd, *J* = 22.1, 22.0 Hz), 69.0, 42.4, 41.5 (d, *J* = 1.7 Hz), 28.6.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.3 (d, *J* = 38.2 Hz), -89.6 (d, *J* = 38.2 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₅H₂₂F₂O₂ 393.1661; Found: 393.1659.



2-(4-(benzyloxy)phenyl)-1,1-difluorodec-1-en-9-yn-4-one (3aj)

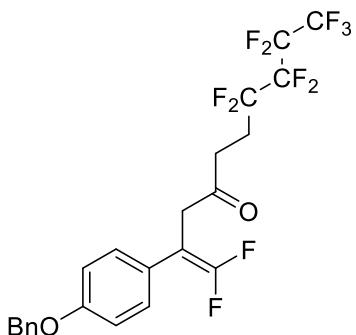
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 6-iodohex-1-yne (42 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (33 mg, 45%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.3 Hz, 2H), 7.31 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.15 – 7.11 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.98 (s, 2H), 3.34 (s, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 2.08 (td, *J* = 7.0, 2.7 Hz, 2H), 1.86 (s, 1H), 1.59 (p, *J* = 7.4 Hz, 2H), 1.43 – 1.36 (m, 2H).

¹³C NMR (176 MHz, CDCl₃) δ 205.4 (dd, *J* = 2.0, 3.6 Hz), 157.1, 153.6 (dd, *J* = 292.8, 292.5 Hz), 135.7, 128.0 (t, *J* = 4.0 Hz), 127.6, 127.0, 126.4, 124.5 (t, *J* = 4.1 Hz), 113.9, 85.7 (dd, *J* = 21.9, 21.9 Hz), 82.9, 69.0, 67.6, 41.2 (d, *J* = 1.6 Hz), 40.2, 26.7, 21.6, 17.2.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.5 (d, *J* = 39.1 Hz), -89.8 (d, *J* = 36.4 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₂₂F₂O₂ 369.1661; Found: 369.1660.



2-(4-(benzyloxy)phenyl)-1,1,7,7,8,8,9,9,10,10-undecafluorodec-1-en-4-one (3ak)

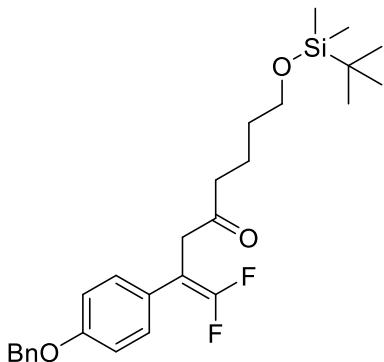
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodohexane (75 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (51 mg, 48%).

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.36 – 7.24 (m, 5H), 7.16 – 7.09 (m, 2H), 6.88 (d, J = 8.8 Hz, 2H), 4.97 (s, 2H), 3.40 (s, 2H), 2.66 (dd, J = 8.5, 6.6 Hz, 2H), 2.39 – 2.20 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl₃) δ 203.2 (dd, J = 3.0, 2.7 Hz), 158.3, 154.6 (dd, J = 292.9, 292.9 Hz), 136.7, 129.1 (t, J = 3.6 Hz), 128.6, 128.1, 127.5, 125.1 (t, J = 3.6 Hz), 115.1, 86.3 (dd, J = 22.0, 21.6 Hz), 70.0, 42.3 (d, J = 1.7 Hz), 32.5, 24.9 (t, J = 22.2 Hz).

$^{19}\text{F NMR}$ (56 MHz, Chloroform-*d*) δ -80.6 (s), -88.2 (d, J = 36.8 Hz), -89.3 (d, J = 38.0 Hz), -114.0 (s), -124.0 (s), -125.6 (s).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₁₇F₁₁O₂ 535.1126; Found: 535.1122.



2-(4-(benzyloxy)phenyl)-8-((tert-butyldimethylsilyl)oxy)-1,1-difluorooct-1-en-4-one (3al)

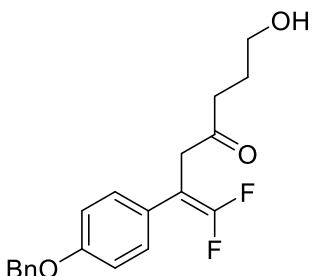
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and *tert*-butyl(4-iodobutoxy)dimethylsilane (63 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (45 mg, 47%).

$^1\text{H NMR}$ (700 MHz, Chloroform-*d*) δ 7.39 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.20 – 7.16 (m, 2H), 6.94 – 6.87 (m, 2H), 5.02 (s, 2H), 3.54 (t, J = 6.3 Hz, 2H), 3.38 (t, J = 2.3 Hz, 2H), 2.43 (t, J = 7.4 Hz, 2H), 1.57 (q, J = 7.6 Hz, 2H), 1.46 – 1.41 (m, 2H), 0.85 (s, 9H), 0.00 (s, 6H).

$^{13}\text{C NMR}$ (176 MHz, CDCl₃) δ 205.7 (dd, J = 2.6, 2.9 Hz), 153.6 (dd, J = 293.3, 291.7 Hz), 151.9, 135.8, 128.0 (t, J = 3.3 Hz), 127.6, 127.0, 126.4, 124.6 (t, J = 4.8 Hz), 113.9, 85.7 (dd, J = 22.5, 21.9 Hz), 69.0, 61.7, 41.2 (d, J = 1.9 Hz), 40.7, 31.0, 24.9, 19.1, 17.3, -6.4.

$^{19}\text{F NMR}$ (56 MHz, Chloroform-*d*) δ -88.6 (d, J = 39.5 Hz), -89.9 (d, J = 38.6 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₇H₃₆F₂O₃Si 475.2475; Found: 475.2474.



2-(4-(benzyloxy)phenyl)-1,1-difluoro-7-hydroxyhept-1-en-4-one (3am)

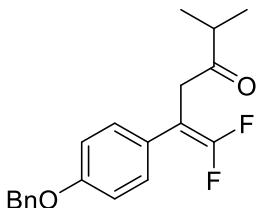
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 3-iodopropan-1-ol (38 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 2:1) to give the product as a colorless oil (34 mg, 49%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.16 – 7.12 (m, 2H), 6.88 – 6.85 (m, 2H), 4.97 (s, 2H), 3.51 (t, *J* = 6.1 Hz, 2H), 3.37 (s, 2H), 2.50 (t, *J* = 6.9 Hz, 2H), 1.73 (t, *J* = 6.5 Hz, 2H), 1.58 (s, 1H).

¹³C NMR (176 MHz, CDCl₃) δ 207.2 (dd, *J* = 2.6, 2.9 Hz), 158.1, 154.6 (dd, *J* = 293.1, 293.1 Hz), 136.8, 129.1 (t, *J* = 3.4 Hz), 128.6, 128.1, 127.5, 125.5 (t, *J* = 4.1 Hz), 115.0, 86.7 (dd, *J* = 22.1, 22.0 Hz), 70.0, 62.0, 42.4 (d, *J* = 1.7 Hz), 38.6, 26.3.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -90.9 (d, *J* = 45.9 Hz), -92.3 (d, *J* = 41.8 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₂₀F₂O₃ 347.1453; Found: 347.1450.



5-(4-(benzyloxy)phenyl)-6,6-difluoro-2-methylhex-5-en-3-one (3an)

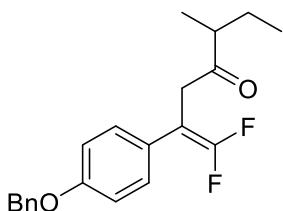
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 2-iodopropane (34 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (39 mg, 59%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 7.12 (dd, *J* = 8.9, 1.2 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 3.39 (t, *J* = 2.2 Hz, 2H), 2.59 (p, *J* = 6.9 Hz, 1H), 1.00 (d, *J* = 7.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 210.3 (dd, *J* = 2.6, 2.6 Hz), 158.1, 154.6 (dd, *J* = 292.7, 290.9 Hz), 136.8, 129.1 (t, *J* = 3.5 Hz), 128.6, 128.0, 127.5, 125.9 (t, *J* = 4.0 Hz), 114.9, 86.8 (dd, *J* = 22.0, 22.2 Hz), 70.0, 40.2, 40.1 (d, *J* = 2.2 Hz), 18.2.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -89.0 (d, *J* = 41.6 Hz), -90.2 (d, *J* = 39.1 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₂₀F₂O₂ 331.1504; Found: 331.1501.



2-(4-(benzyloxy)phenyl)-1,1-difluoro-5-methylhept-1-en-4-one (3ao)

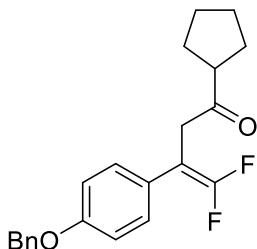
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 2-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 40:1) to give the product as a colorless oil (35 mg, 51%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.89 – 6.83 (m, 2H), 4.97 (s, 2H), 3.38 (s, 2H), 2.45 (q, *J* = 6.9 Hz, 1H), 1.58 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.30 (dp, *J* = 14.2, 7.1 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 209.3 (dd, *J* = 2.7, 3.0 Hz), 157.0, 153.6 (dd, *J* = 291.8, 290.9 Hz), 135.8, 128.1 (t, *J* = 3.5 Hz), 127.6, 127.0, 126.4, 124.8 (t, *J* = 3.9 Hz), 113.8, 85.6 (dd, *J* = 22.2, 22.0 Hz), 69.0, 46.0, 39.9 (d, *J* = 2.2 Hz), 24.9, 14.9, 10.5.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -89.0 (d, *J* = 40.3 Hz), -90.2 (d, *J* = 40.3 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₁H₂₂F₂O₂ 345.1661; Found: 345.1658.



3-(4-(benzyloxy)phenyl)-1-cyclopentyl-4,4-difluorobut-3-en-1-one (3ap)

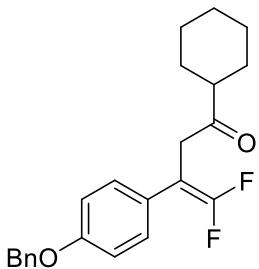
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and iodocyclopentane (39 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (37 mg, 52%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 5H), 7.27 – 7.22 (m, 1H), 7.16 – 7.11 (m, 2H), 6.88 – 6.83 (m, 2H), 4.96 (s, 2H), 3.39 (t, *J* = 2.2 Hz, 2H), 2.89 – 2.78 (m, 1H), 1.72 – 1.46 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 209.0 (dd, *J* = 2.7, 2.8 Hz), 158.0, 154.6 (dd, *J* = 292.2, 291.5 Hz), 136.8, 129.1 (t, *J* = 3.5 Hz), 128.6, 128.1, 127.5, 125.9 (t, *J* = 4.1 Hz), 114.9, 86.8 (dd, *J* = 22.2, 22.0 Hz), 70.0, 50.6, 41.5 (d, *J* = 2.2 Hz), 29.0, 26.0.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.8 (d, *J* = 37.9 Hz), -90.1 (d, *J* = 40.2 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₂H₂₂F₂O₂ 357.1661; Found: 357.1657.



3-(4-(benzyloxy)phenyl)-1-cyclohexyl-4,4-difluorobut-3-en-1-one (3aq)

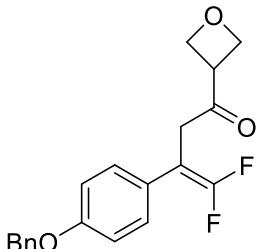
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and iodocyclohexane (42 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (43 mg, 58%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 4H), 7.27 – 7.21 (m, 1H), 7.14 – 7.08 (m, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.96 (s, 2H), 3.37 (s, 2H), 2.41 – 2.27 (m, 1H), 1.80 – 1.62 (m, 4H), 1.43 – 0.76 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 209.6 (dd, *J* = 2.1, 3.2 Hz), 158.0, 154.5 (dd, *J* = 291.9, 291.9 Hz), 136.8, 129.1 (t, *J* = 3.6 Hz), 128.6, 128.0, 127.5, 126.0 (t, *J* = 3.9 Hz), 114.9, 86.7 (dd, *J* = 22.4, 22.0 Hz), 70.0, 50.2, 40.3 (d, *J* = 2.1 Hz), 28.5, 25.8, 25.6.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -89.0 (d, *J* = 40.8 Hz), -90.2 (d, *J* = 40.8 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₂₄F₂O₂ 371.1817; Found: 371.1812.



3-(4-(benzyloxy)phenyl)-4,4-difluoro-1-(oxetan-3-yl)but-3-en-1-one (3ar)

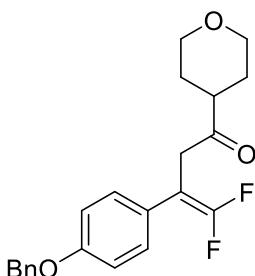
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 3-iodooxetane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 2:1) to give the product as a colorless oil (47 mg, 68%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.16 – 7.11 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.97 (s, 2H), 4.67 – 4.58 (m, 4H), 3.88 (p, *J* = 7.6 Hz, 1H), 3.35 (s, 2H).

¹³C NMR (176 MHz, CDCl₃) δ 204.1 (dd, *J* = 2.7, 3.2 Hz), 158.3, 154.6 (dd, *J* = 292.7, 293.8 Hz), 136.7, 129.0 (t, *J* = 3.5 Hz), 128.7, 128.1, 127.5, 125.0 (t, *J* = 3.8 Hz), 115.1, 86.1 (dd, *J* = 21.4, 21.6 Hz), 72.2, 70.1, 44.5, 40.8 (d, *J* = 1.9 Hz).

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.4 (d, *J* = 38.1 Hz), -89.5 (d, *J* = 38.5 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₁₈F₂O₃ 345.1297; Found: 345.1297.



3-(4-(benzyloxy)phenyl)-4,4-difluoro-1-(tetrahydro-2H-pyran-4-yl)but-3-en-1-one (3as)

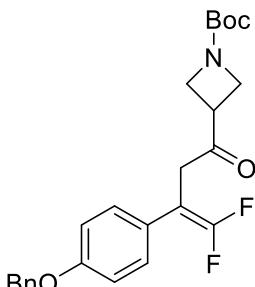
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 4-iodotetrahydro-2H-pyran (43 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 2:1) to give the product as a colorless oil (43 mg, 58%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 4H), 7.28 – 7.22 (m, 1H), 7.16 – 7.07 (m, 2H), 6.90 – 6.83 (m, 2H), 4.97 (s, 2H), 3.90 (dt, *J* = 11.5, 3.5 Hz, 2H), 3.39 (t, *J* = 2.2 Hz, 2H), 3.35 – 3.26 (m, 2H), 2.59 – 2.46 (m, 1H), 1.61 (ddd, *J* = 10.2, 7.2, 3.8 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 207.6 (dd, *J* = 2.6, 2.8 Hz), 158.1, 154.6 (dd, *J* = 292.6, 291.7 Hz), 136.8, 129.1 (t, *J* = 3.3 Hz), 128.6, 128.1, 127.5, 125.6 (t, *J* = 3.9 Hz), 115.0, 86.5 (dd, *J* = 22.3, 21.9 Hz), 70.0, 67.1, 46.9, 40.1 (d, *J* = 2.3 Hz), 28.1.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.7 (d, *J* = 40.8 Hz), -89.8 (d, *J* = 40.3 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₂H₂₂F₂O₃ 373.1610; Found: 373.1609.



tert-butyl 3-(3-(4-(benzyloxy)phenyl)-4,4-difluorobut-3-enoyl)azetidine-1-carboxylate (3at)

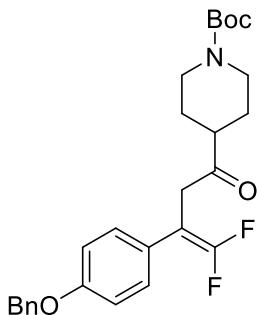
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and *tert*-butyl 3-iodoazetidine-1-carboxylate (57 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 2:1) to give the product as a colorless oil (56 mg, 63%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 7.16 – 7.10 (m, 2H), 6.90 – 6.85 (m, 2H), 5.20 (s, 1H), 4.97 (s, 2H), 3.88 (q, *J* = 8.3, 7.6 Hz, 4H), 3.36 (t, *J* = 2.2 Hz, 2H), 1.34 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 204.3 (dd, *J* = 2.9, 3.3 Hz), 158.3, 156.1, 154.6 (dd, *J* = 293.3, 293.5 Hz), 136.7, 129.0 (t, *J* = 3.5 Hz), 128.7, 128.1, 127.5, 125.0 (t, *J* = 4.0 Hz), 115.1, 86.1 (dd, *J* = 21.5, 21.9 Hz), 79.9, 70.1, 53.5, 40.7 (d, *J* = 2.1 Hz), 37.8, 28.3.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -87.9 (d, *J* = 37.4 Hz), -89.0 (d, *J* = 35.9 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₅H₂₇F₂NO₄ 444.1981; Found: 444.1980.



tert-butyl 4-(3-(4-(benzyloxy)phenyl)-4,4-difluorobut-3-enyl)piperidine-1-carboxylate (3au)

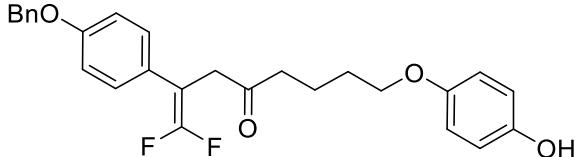
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and *tert*-butyl 4-iodopiperidine-1-carboxylate (62 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 2:1) to give the product as a colorless oil (52 mg, 55%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 12.5, 7.6, 6.4, 1.7 Hz, 4H), 7.27 – 7.21 (m, 1H), 7.14 – 7.08 (m, 2H), 6.88 – 6.83 (m, 2H), 4.97 (s, 2H), 4.00 (s, 2H), 3.40 (t, *J* = 2.3 Hz, 2H), 2.67 (t, *J* = 12.7 Hz, 2H), 2.45 (tt, *J* = 11.4, 3.7 Hz, 1H), 1.67 (d, *J* = 12.8 Hz, 2H), 1.49 – 1.39 (m, 2H), 1.37 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 207.9 (dd, *J* = 1.8, 3.2 Hz), 158.1, 154.6, 154.5 (dd, *J* = 291.6, 292.0 Hz), 136.8, 129.1 (t, *J* = 4.0 Hz), 128.6, 128.1, 127.5, 125.6 (t, *J* = 3.6 Hz), 115.0, 86.5 (dd, *J* = 21.9, 22.2 Hz), 79.7, 70.0, 47.9, 40.3 (d, *J* = 2.0 Hz), 28.4, 27.4.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.7 (d, *J* = 37.8 Hz), -89.9 (d, *J* = 37.8 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₇H₃₁F₂NO₄ 472.2294; Found: 472.2295.



2-(4-(benzyloxy)phenyl)-1,1-difluoro-8-(4-hydroxyphenoxy)oct-1-en-4-one (3av)

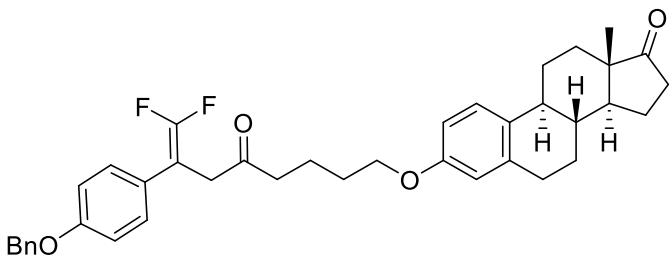
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 4-(4-iodobutoxy)phenol (59 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 5:1) to give the product as a colorless oil (44 mg, 49%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.64 (s, 4H), 4.95 (s, 2H), 4.90 (s, 1H), 3.75 (t, *J* = 5.9 Hz, 2H), 3.34 (s, 2H), 2.43 (t, *J* = 6.8 Hz, 2H), 1.62 (dq, *J* = 15.6, 6.2, 4.9 Hz, 4H).

¹³C NMR (176 MHz, CDCl₃) δ 207.1 (dd, *J* = 2.5, 3.1 Hz), 158.1, 154.6 (dd, *J* = 292.6, 291.6 Hz), 153.0, 149.6, 136.8, 129.1 (t, *J* = 3.1 Hz), 128.7, 128.1, 127.5, 125.5 (t, *J* = 3.8 Hz), 116.1, 115.6, 115.0, 86.7 (dd, *J* = 22.5, 22.5 Hz), 70.0, 68.2, 42.3 (d, *J* = 1.8 Hz), 41.5, 28.6, 20.3.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.6 (d, *J* = 37.1 Hz), -89.9 (d, *J* = 36.8 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₇H₂₆F₂O₄ 453.1872; Found: 453.1869.



(8R,9S,13S,14S)-3-((7-(4-(benzyloxy)phenyl)-8,8-difluoro-5-oxo-7-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3aw)

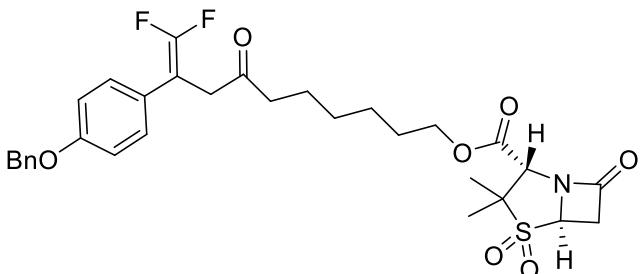
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and Estrone iodide (91 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 5:1) to give the product as a colorless oil (37 mg, 30%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.60 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.53 (d, *J* = 2.7 Hz, 1H), 4.96 (s, 2H), 3.81 (t, *J* = 5.6 Hz, 2H), 3.34 (s, 2H), 2.85 – 2.75 (m, 2H), 2.46 – 2.38 (m, 3H), 2.33 – 2.28 (m, 1H), 2.16 (td, *J* = 11.0, 4.3 Hz, 1H), 2.06 (dt, *J* = 18.7, 9.0 Hz, 1H), 1.99 – 1.94 (m, 1H), 1.91 (ddd, *J* = 11.4, 5.7, 2.7 Hz, 1H), 1.88 – 1.84 (m, 1H), 1.64 (dq, *J* = 6.1, 3.3, 2.7 Hz, 4H), 1.56 – 1.47 (m, 2H), 1.42 (ddd, *J* = 12.2, 6.2, 3.8 Hz, 2H), 1.39 – 1.30 (m, 2H), 0.82 (s, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.5 (dd, *J* = 2.5, 3.1 Hz), 158.1, 157.0, 154.6 (dd, *J* = 293.0, 293.0 Hz), 137.8, 136.8, 132.0, 129.1 (t, *J* = 2.7 Hz), 128.6, 128.1, 127.5, 126.3, 125.5 (t, *J* = 4.3 Hz), 115.0, 114.5, 112.1, 86.8 (dd, *J* = 22.1, 22.1 Hz), 70.0, 67.4, 50.4, 48.0, 44.0, 42.3 (d, *J* = 1.4 Hz), 41.5, 38.4, 35.9, 31.6, 29.7, 28.6, 26.9, 26.6, 25.9, 21.6, 20.3, 13.9.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.5 (d, *J* = 39.4 Hz), -89.8 (d, *J* = 39.4 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₉H₄₂F₂O₄ 613.3124; Found: 613.3122.



9-(4-(benzyloxy)phenyl)-10,10-difluoro-7-oxodec-9-en-1-yl

(2S,5R)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (3ax)

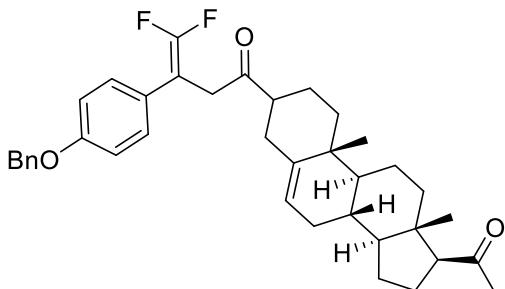
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and Sulbactam iodide (89 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 3:1) to give the product as a colorless oil (46 mg, 38%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.98 (s, 2H), 4.53 (dd, *J* = 4.4, 2.1 Hz, 1H), 4.30 (s, 1H), 4.10 (t, *J* = 6.8 Hz, 2H), 3.40 – 3.32 (m, 3H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.53 (s, 3H), 1.48 (p, *J* = 7.4 Hz, 2H), 1.33 (s, 3H), 1.23 (dq, *J* = 38.7, 8.2 Hz, 4H).

¹³C NMR (176 MHz, CDCl₃) δ 206.7 (dd, *J* = 2.3, 2.8 Hz), 170.8, 167.0, 158.1, 154.6 (dd, *J* = 293.5, 293.5 Hz), 136.8, 129.1 (t, *J* = 3.5 Hz), 128.6, 128.1, 127.5, 125.5 (t, *J* = 3.5 Hz), 115.0, 86.8 (dd, *J* = 22.0, 22.3 Hz), 70.0, 66.4, 63.3, 62.7, 61.1, 42.3 (d, *J* = 1.7 Hz), 41.6, 38.3, 28.5, 28.2, 25.7, 23.3, 20.4, 18.6.

¹⁹F NMR (56 MHz, Chloroform-d) δ -88.6 (d, *J* = 39.2 Hz), -89.9 (d, *J* = 39.2 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₁H₃₅F₂NO₇S 604.2175; Found: 604.2173.



1-((8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)-3-(4-(benzyloxy)phenyl)-4,4-difluorobut-3-en-1-one (3ay)

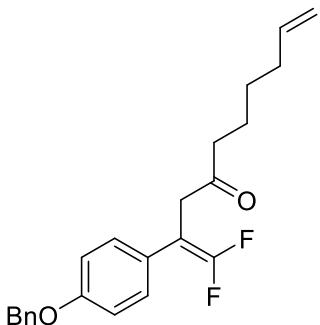
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and Pregnolenone iodide (85 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 10:1) to give the product as a colorless oil (47 mg, 40%).

¹H NMR (700 MHz, Chloroform-d) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.86 (t, *J* = 8.7 Hz, 2H), 5.26 (t, *J* = 6.4 Hz, 1H), 4.97 (s, 2H), 3.52 – 3.32 (m, 2H), 2.57 – 2.53 (m, 1H), 2.48 – 2.42 (m, 1H), 2.40 – 2.33 (m, 1H), 2.15 – 2.07 (m, 1H), 2.04 (d, *J* = 9.7 Hz, 3H), 2.00 – 1.87 (m, 3H), 1.62 – 1.49 (m, 5H), 1.36 (ddt, *J* = 22.1, 15.3, 6.3 Hz, 3H), 1.21 – 1.11 (m, 2H), 1.09 – 1.03 (m, 1H), 0.92 (d, *J* = 20.1 Hz, 4H), 0.83 – 0.71 (m, 1H), 0.55 (d, *J* = 10.7 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 209.6, 208.3 (dd, *J* = 3.0, 2.3 Hz), 158.0, 154.5 (dd, *J* = 291.8, 291.8 Hz), 141.1, 139.7, 136.8, 129.1 (t, *J* = 4.2 Hz), 128.6, 128.1, 127.5, 126.0 (t, *J* = 4.2 Hz), 121.7, 120.9, 114.9, 114.8, 86.7 (dd, *J* = 22.1, 22.8 Hz), 70.0, 63.7, 56.9, 51.3, 50.2, 49.9, 47.4, 44.0, 40.7, 40.0 (d, *J* = 1.7 Hz), 37.1, 37.0, 35.6, 34.3, 33.4, 31.8, 31.7, 31.7, 31.7, 31.6, 31.6, 26.9, 24.8, 24.5, 22.9, 22.8, 22.8, 20.9, 20.7, 19.4, 19.3, 13.2.

¹⁹F NMR (56 MHz, Chloroform-d) δ -88.9 (d, *J* = 44.4 Hz), -90.2 (d, *J* = 41.2 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₈H₄₄F₂O₃ 587.3331; Found: 587.3330.



2-(4-(benzyloxy)phenyl)-1,1-difluorodeca-1,9-dien-4-one (3az)

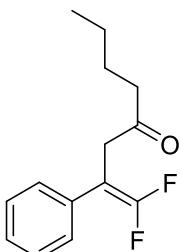
The title compound was prepared from 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (55 mg, 0.20 mmol) and 6-iodohex-1-ene (42 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (12 mg, 16%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.69 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.98 (s, 2H), 4.94 – 4.84 (m, 2H), 3.33 (s, 2H), 2.36 (q, *J* = 7.3 Hz, 2H), 1.95 (q, *J* = 7.2 Hz, 2H), 1.53 – 1.48 (m, 2H), 1.26 (p, *J* = 7.5 Hz, 2H).

¹³C NMR (176 MHz, CDCl₃) δ 206.8 (dd, *J* = 2.9, 2.9 Hz), 158.1, 154.5 (dd, *J* = 292.7, 292.9 Hz), 138.4, 136.8, 129.1 (t, *J* = 2.7 Hz), 128.6, 128.1, 127.5, 125.6 (t, *J* = 4.0 Hz), 115.0, 114.7, 86.8 (dd, *J* = 21.7, 22.2 Hz), 70.0, 42.3 (d, *J* = 2.0 Hz), 41.7, 33.5, 28.3, 23.1.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.6 (d, *J* = 38.9 Hz), -89.9 (d, *J* = 39.6 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₂₄F₂O₂ 371.1817; Found: 371.1815.



1,1-difluoro-2-phenyloct-1-en-4-one (3ba)

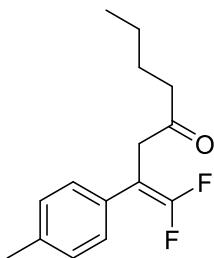
The title compound was prepared from (3,3,3-trifluoroprop-1-en-2-yl)benzene (35 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 40:1) to give the product as a colorless oil (39 mg, 82%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.25 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.19 (m, 2H), 7.19 – 7.16 (m, 1H), 3.36 (s, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.48 – 1.42 (m, 2H), 1.19 (q, *J* = 7.5 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.7 (dd, *J* = 2.8, 2.9 Hz), 154.8 (dd, *J* = 293.5, 293.5 Hz), 133.3 (t, *J* = 4.1 Hz), 128.6, 127.9 (t, *J* = 3.7 Hz), 127.5, 87.3 (dd, *J* = 22.2, 22.7 Hz), 42.2 (d, *J* = 2.0 Hz), 41.8, 25.7, 22.2, 13.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -87.7 (d, *J* = 36.5 Hz), -89.2 (d, *J* = 36.5 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₄H₁₆F₂O 239.1242; Found: 239.1239.



1,1-difluoro-2-(*p*-tolyl)oct-1-en-4-one (3ca)

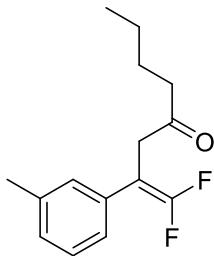
The title compound was prepared from 1-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (37 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (37 mg, 74%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.35 (s, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.25 (s, 3H), 1.45 (p, *J* = 7.5 Hz, 2H), 1.19 (h, *J* = 7.4 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.9 (dd, *J* = 3.0, 3.0 Hz), 154.7 (dd, *J* = 292.5, 292.8 Hz), 137.4, 130.2 (t, *J* = 4.5 Hz), 129.3, 127.7 (t, *J* = 3.9 Hz), 87.1 (dd, *J* = 21.7, 22.0 Hz), 42.2 (d, *J* = 2.0 Hz), 41.7, 25.7, 22.2, 21.1, 13.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.1 (d, *J* = 39.3 Hz), -89.5 (d, *J* = 39.3 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₈F₂O 253.1398; Found: 253.1398.



1,1-difluoro-2-(*m*-tolyl)oct-1-en-4-one (3da)

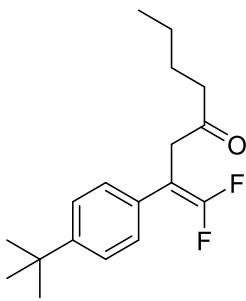
The title compound was prepared from 1-methyl-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (37 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (30 mg, 60%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.7 Hz, 1H), 7.13 – 7.05 (m, 3H), 3.43 (s, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 1.53 (p, *J* = 7.5 Hz, 2H), 1.31 – 1.22 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.8 (dd, *J* = 2.7, 3.0 Hz), 154.7 (dd, *J* = 293.1, 293.1 Hz), 138.2, 133.2 (t, *J* = 3.5 Hz), 128.6 (t, *J* = 4.2 Hz), 128.5, 128.3, 124.9 (t, *J* = 3.5 Hz), 87.3 (dd, *J* = 21.6, 21.6 Hz), 42.2 (d, *J* = 1.9 Hz), 41.8, 25.7, 22.2, 21.4, 13.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -87.8 (d, *J* = 38.4 Hz), -89.1 (d, *J* = 37.7 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₈F₂O 253.1398; Found: 253.1399.



2-(4-(*tert*-butyl)phenyl)-1,1-difluorooct-1-en-4-one (3ea)

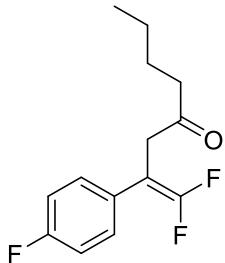
The title compound was prepared from 1-(*tert*-butyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (46 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (44 mg, 75%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.8 Hz, 2H), 7.27 – 7.20 (m, 2H), 3.46 (s, 2H), 2.47 (t, *J* = 7.9 Hz, 2H), 1.34 (s, 9H), 1.35 – 1.30 (m, 4H), 0.91 – 0.89 (m, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 207.0 (dd, *J* = 2.1, 3.2 Hz), 154.8 (dd, *J* = 294.0, 292.6 Hz), 150.5, 130.2 (t, *J* = 4.4 Hz), 127.4 (t, *J* = 3.8 Hz), 125.5, 87.1 (dd, *J* = 21.6, 21.9 Hz), 42.1 (d, *J* = 2.0 Hz), 41.7, 34.5, 31.2, 25.7, 22.2, 13.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -87.9 (d, *J* = 37.7 Hz), -89.2 (d, *J* = 37.7 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₄F₂O 295.1868; Found: 295.1863.



1,1-difluoro-2-(4-fluorophenyl)oct-1-en-4-one (3fa)

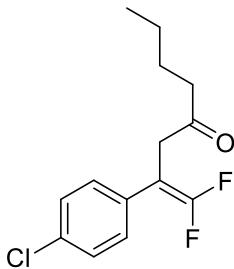
The title compound was prepared from 1-fluoro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (38 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (26 mg, 51%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.18 (ddd, *J* = 8.8, 5.1, 1.1 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 3.35 (s, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.46 (p, *J* = 7.5 Hz, 2H), 1.24 – 1.16 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.6 (dd, *J* = 2.6, 3.0 Hz), 162.0 (d, *J* = 248.5 Hz), 154.7 (dd, *J* = 293.7, 293.2 Hz), 129.7 (dt, *J* = 8.0, 7.5 Hz), 129.2 (q, *J* = 4.0 Hz), 115.6 (d, *J* = 21.7 Hz), 86.5 (dd, *J* = 22.4, 22.6 Hz), 42.2 (d, *J* = 1.8 Hz), 41.9, 25.7, 22.2, 13.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -87.9 (d, *J* = 35.3 Hz), -89.2 (d, *J* = 35.3 Hz), -113.7 (s).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₄H₁₅F₃O 257.1148; Found: 257.1144.



2-(4-chlorophenyl)-1,1-difluoroct-1-en-4-one (3ga)

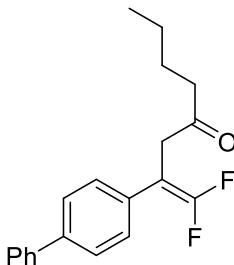
The title compound was prepared from 1-chloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (42 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (30 mg, 55%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 3.35 (s, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.46 (p, *J* = 7.5 Hz, 2H), 1.21 (dt, *J* = 15.1, 7.5 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.4 (dd, *J* = 2.6, 3.0 Hz), 154.8 (dd, *J* = 293.1, 294.1 Hz), 133.4, 129.2 (t, *J* = 3.8 Hz), 128.9, 128.8, 86.6 (dd, *J* = 23.2, 22.4 Hz), 42.0 (d, *J* = 1.8 Hz), 41.9, 25.7, 22.2, 13.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -87.0 (d, *J* = 36.6 Hz), -88.3 (d, *J* = 35.8 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₄H₁₅ClF₂O 273.0852; Found: 273.0848.



2-([1,1'-biphenyl]-4-yl)-1,1-difluoroct-1-en-4-one (3ha)

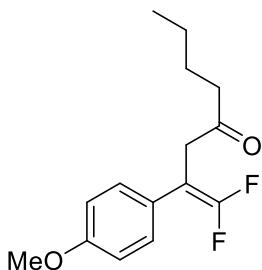
The title compound was prepared from 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (50 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (43 mg, 69%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.49 (td, *J* = 8.3, 4.0 Hz, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.23 (m, 3H), 3.40 (s, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 1.48 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.20 (dt, *J* = 14.7, 7.3 Hz, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.8 (dd, *J* = 2.9, 2.7 Hz), 154.9 (dd, *J* = 293.5, 294.4 Hz), 140.4, 140.3, 132.2 (t, *J* = 4.1 Hz), 128.8, 128.2 (t, *J* = 3.8 Hz), 127.5, 127.3, 127.0, 87.1 (dd, *J* = 21.8, 22.1 Hz), 42.1 (d, *J* = 1.5 Hz), 41.8, 25.8, 22.3, 13.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -87.1 (d, *J* = 34.8 Hz), -88.4 (d, *J* = 37.7 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₂₀F₂O 315.1555; Found: 315.1557.



1,1-difluoro-2-(4-methoxyphenyl)oct-1-en-4-one (3ia)

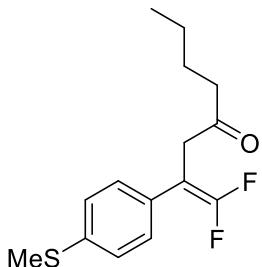
The title compound was prepared from 1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (41 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 40:1) to give the product as a colorless oil (33 mg, 62%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.72 (s, 3H), 3.34 (s, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.45 (p, *J* = 7.5 Hz, 2H), 1.22 – 1.18 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.0 (dd, *J* = 2.9, 3.3 Hz), 157.8, 153.5 (dd, *J* = 292.0, 292.0 Hz), 128.0 (t, *J* = 3.3 Hz), 124.3 (t, *J* = 3.9 Hz), 113.0, 85.8 (dd, *J* = 22.2, 21.6 Hz), 54.2, 41.3 (d, *J* = 2.0 Hz), 40.7, 24.7, 21.2, 12.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.8 (d, *J* = 39.6 Hz), -90.0 (d, *J* = 39.6 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₈F₂O₂ 269.1348; Found: 269.1347.



1,1-difluoro-2-(4-(methylthio)phenyl)oct-1-en-4-one (3ja)

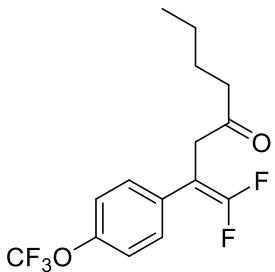
The title compound was prepared from methyl(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)sulfane (44 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (28 mg, 49%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.12–7.15 (m, 4H), 3.35 (s, 2H), 2.40 (s, 3H), 2.36 (t, *J* = 7.4 Hz, 2H), 1.46 (p, *J* = 7.5 Hz, 2H), 1.22 – 1.17 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.7 (dd, *J* = 2.6, 2.6 Hz), 154.7 (dd, *J* = 293.1, 293.4 Hz), 138.0, 129.8 (t, *J* = 4.3 Hz), 128.2 (t, *J* = 4.3 Hz), 126.5, 86.9 (dd, *J* = 22.3, 22.3 Hz), 42.0 (d, *J* = 1.9 Hz), 41.8, 25.7, 22.2, 15.6, 13.8.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -87.3 (d, *J* = 38.3 Hz), -88.6 (d, *J* = 39.6 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₈F₂OS 285.1119; Found: 285.1120.



1,1-difluoro-2-(4-(trifluoromethoxy)phenyl)oct-1-en-4-one (3ka)

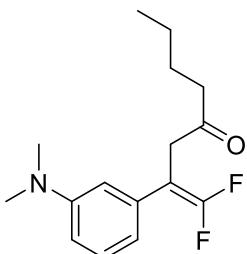
The title compound was prepared from 1-(trifluoromethoxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (51 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (32 mg, 50%).

$^1\text{H NMR}$ (700 MHz, Chloroform-*d*) δ 7.24 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 3.37 (s, 2H), 2.37 (t, J = 7.4 Hz, 2H), 1.47 (p, J = 7.4 Hz, 2H), 1.20 (h, J = 7.4 Hz, 2H), 0.81 (t, J = 7.4 Hz, 3H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 206.4 (dd, J = 2.8, 2.8 Hz), 154.8 (dd, J = 294.0, 293.4 Hz), 130.4, 129.4 (t, J = 4.0 Hz), 121.0, 120.3 (q, J = 257.2.0 Hz), 86.4 (dd, J = 22.9, 23.4 Hz), 42.0 (d, J = 2.0 Hz), 41.9, 25.7, 22.2, 13.8.

$^{19}\text{F NMR}$ (56 MHz, Chloroform-*d*) δ -57.5 (s), -86.9 (d, J = 36.0 Hz), -88.4 (d, J = 34.7 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for $\text{C}_{15}\text{H}_{15}\text{F}_5\text{O}_2$ 323.1065; Found: 323.1066.



2-(3-(dimethylamino)phenyl)-1,1-difluorooct-1-en-4-one (3la)

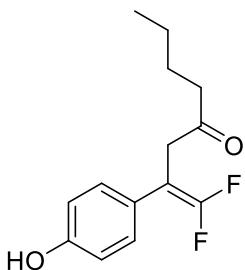
The title compound was prepared from *N,N*-dimethyl-3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (43 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 10:1) to give the product as a colorless oil (23 mg, 41%).

$^1\text{H NMR}$ (700 MHz, Chloroform-*d*) δ 7.12 (ddd, J = 8.5, 6.6, 1.8 Hz, 1H), 6.56 (q, J = 7.3 Hz, 3H), 3.35 (s, 2H), 2.86 (s, 6H), 2.36 (t, J = 7.4 Hz, 2H), 1.46 (p, J = 7.5 Hz, 2H), 1.24 – 1.17 (m, 2H), 0.80 (t, J = 7.4 Hz, 3H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 207.1 (dd, J = 2.5, 3.3 Hz), 154.7 (dd, J = 292.1, 292.4 Hz), 150.6, 134.0 (t, J = 4.0 Hz), 129.2, 116.1, 112.1, 111.9, 87.8 (dd, J = 22.3, 21.4 Hz), 42.5 (d, J = 1.8 Hz), 41.7, 40.5, 25.8, 22.2, 13.8.

$^{19}\text{F NMR}$ (56 MHz, Chloroform-*d*) δ -88.4.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for $\text{C}_{16}\text{H}_{21}\text{F}_2\text{NO}$ 282.1664; Found: 282.1667.



1,1-difluoro-2-(4-hydroxyphenyl)oct-1-en-4-one (3ma)

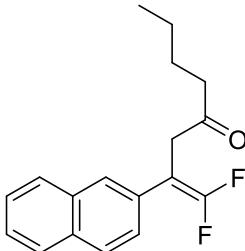
The title compound was prepared from 4-(3,3,3-trifluoroprop-1-en-2-yl)phenol (38 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 5:1) to give the product as a colorless oil (24 mg, 48%).

¹H NMR (400 MHz, Chloroform-d) δ 7.05 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 5.85 (s, 1H), 3.36 (s, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.46 (p, *J* = 7.4 Hz, 2H), 1.18 (dt, *J* = 14.5, 7.4 Hz, 2H), 0.79 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 208.7 (dd, *J* = 2.3, 3.1 Hz), 155.3, 154.6 (dd, *J* = 292.5, 292.5 Hz), 129.1 (t, *J* = 3.7 Hz), 124.9 (t, *J* = 3.9 Hz), 115.6, 86.8 (dd, *J* = 21.8, 22.0 Hz), 42.3 (d, *J* = 1.9 Hz), 41.7, 25.7, 22.2, 13.8.

¹⁹F NMR (56 MHz, Chloroform-d) δ -88.7 (d, *J* = 39.5 Hz), -89.9 (d, *J* = 39.5 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₄H₁₆F₂O₂ 255.1191; Found: 255.1188.



1,1-difluoro-2-(naphthalen-2-yl)oct-1-en-4-one (3na)

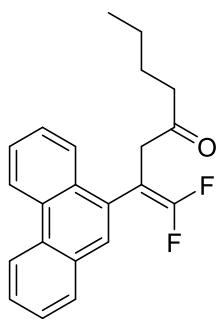
The title compound was prepared from 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (45 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (19 mg, 33%).

¹H NMR (700 MHz, Chloroform-d) δ 7.75 – 7.70 (m, 3H), 7.65 (d, *J* = 1.8 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.36 (dt, *J* = 8.5, 1.8 Hz, 1H), 3.47 (s, 2H), 2.41 – 2.31 (m, 2H), 1.46 (p, *J* = 7.5 Hz, 2H), 1.22 – 1.16 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 206.8 (dd, *J* = 2.8, 2.8 Hz), 155.0 (dd, *J* = 293.4, 293.7 Hz), 133.2, 132.5, 130.7 (t, *J* = 3.9 Hz), 128.3, 128.0, 127.6, 127.0 (t, *J* = 3.5 Hz), 126.4, 126.3, 125.6 (dd, *J* = 4.5, 4.5 Hz), 87.4 (dd, *J* = 21.7, 22.0 Hz), 42.3 (d, *J* = 1.7 Hz), 41.8, 25.8, 22.2, 13.8.

¹⁹F NMR (56 MHz, Chloroform-d) δ -87.1 (d, *J* = 35.8 Hz), -88.6 (d, *J* = 35.8 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₁₈F₂O 289.1398; Found: 289.1394.



1,1-difluoro-2-(phenanthren-9-yl)oct-1-en-4-one (3oa)

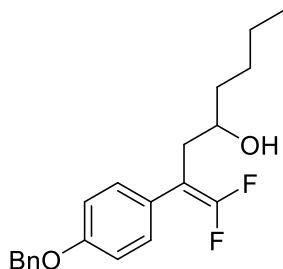
The title compound was prepared from 9-(3,3,3-trifluoroprop-1-en-2-yl)phenanthrene (55 mg, 0.20 mmol) and 1-iodobutane (37 mg, 0.20 mmol) according to general procedure 1. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (47 mg, 70%).

¹H NMR (700 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 8.2 Hz, 1H), 8.58 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.67 (s, 1H), 7.63 – 7.54 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 3.45 (d, *J* = 127.8 Hz, 2H), 2.29 (dt, *J* = 15.0, 6.9 Hz, 2H), 1.41 (p, *J* = 7.5 Hz, 2H), 1.14 (h, *J* = 7.5 Hz, 2H), 0.73 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 205.0 (dd, *J* = 3.0, 3.1 Hz), 154.0 (dd, *J* = 290.5, 290.3 Hz), 130.2, 129.7, 129.2, 129.0 (d, *J* = 2.8 Hz), 128.4 (d, *J* = 4.7 Hz), 128.0 (dd, *J* = 3.0, 2.7 Hz), 127.8, 126.1, 125.9, 125.8, 125.7, 124.4, 122.2, 121.4, 83.9 (t, *J* = 22.4 Hz), 41.9, 41.4, 24.7, 21.1, 12.7.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -86.4 (d, *J* = 35.6 Hz), -89.1 (d, *J* = 38.3 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₂H₂₀F₂O 339.1555; Found: 339.1556.



2-(4-(benzyloxy)phenyl)-1,1-difluoroct-1-en-4-ol (4a)

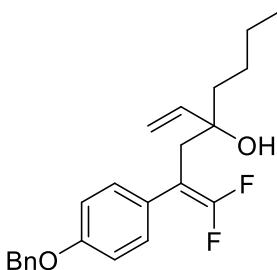
The title compound was prepared from **3aa** (69 mg, 0.20 mmol) general procedure 3. The crude residue was purified by flash chromatography (PE/EA = 10:1) to give the product as a colorless oil (69 mg, 99%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.05 (s, 2H), 3.61 – 3.53 (m, 1H), 2.50 (d, *J* = 5.6 Hz, 2H), 1.51 – 1.35 (m, 4H), 1.27 (ddt, *J* = 21.3, 14.2, 7.2 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 158.1, 154.3 (dd, *J* = 290.8, 290.1 Hz), 136.8, 129.5 (t, *J* = 3.3 Hz), 128.6, 128.1, 127.5, 125.8 (t, *J* = 4.0 Hz), 115.0, 89.4 (dd, *J* = 21.0, 21.5 Hz), 70.1, 69.9 (t, *J* = 2.5 Hz), 36.7, 36.0, 27.7, 22.7, 14.0.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -90.3.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₁H₂₄F₂O₂ 347.1817; Found: 347.1815.



2-(4-(benzyloxy)phenyl)-1,1-difluoro-4-vinyloct-1-en-4-ol (4b)

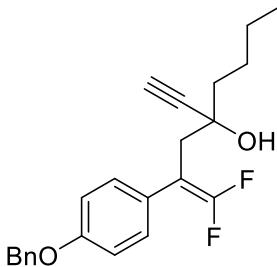
The title compound was prepared from **3aa** (69 mg, 0.20 mmol) general procedure 2. The crude residue was purified by flash chromatography (PE/EA = 20:1) to give the product as a colorless oil (49 mg, 66%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.64 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.04 (dd, *J* = 17.3, 1.4 Hz, 1H), 4.96 (d, *J* = 10.4 Hz, 3H), 2.54 (s, 2H), 1.43 (ddd, *J* = 13.3, 11.3, 4.1 Hz, 1H), 1.38 – 1.32 (m, 1H), 1.18 (s, 1H), 1.13 (dddd, *J* = 15.1, 9.7, 6.6, 2.3 Hz, 4H), 0.76 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 158.1, 154.5 (dd, *J* = 289.7, 289.9 Hz), 143.0, 136.9, 129.9 (t, *J* = 3.0 Hz), 128.6, 128.1, 127.5, 126.7 (dd, *J* = 4.3, 4.4 Hz), 114.9, 112.7, 88.6 (dd, *J* = 21.1, 21.5 Hz), 76.6 (t, *J* = 3.0 Hz), 70.1, 40.5, 39.4, 25.5, 23.0, 14.0.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -89.2 (d, *J* = 42.2 Hz), -91.2 (d, *J* = 42.3 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₂₆F₂O₂ 373.1974; Found: 373.1970.



2-(4-(benzyloxy)phenyl)-4-ethynyl-1,1-difluorooct-1-en-4-ol (4c)

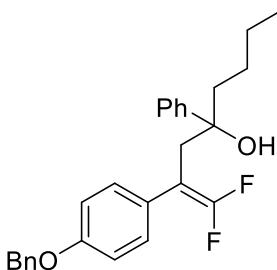
The title compound was prepared from **3aa** (69 mg, 0.20 mmol) general procedure 2. The crude residue was purified by flash chromatography (PE/EA = 20:1) to give the product as a colorless oil (47 mg, 64%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 4.97 (s, 2H), 2.81 – 2.59 (m, 2H), 2.26 (s, 1H), 1.73 (s, 1H), 1.51 (ddt, *J* = 11.6, 7.8, 4.5 Hz, 2H), 1.40 – 1.32 (m, 2H), 1.24 – 1.16 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 158.1, 154.9 (t, *J* = 289.2 Hz), 136.8, 130.0 (t, *J* = 2.5 Hz), 128.6, 128.1, 127.5, 126.4 (dd, *J* = 4.1, 4.4 Hz), 114.9, 88.4 (dd, *J* = 21.1, 20.9 Hz), 85.6, 73.2, 71.5 (t, *J* = 2.4 Hz), 70.0, 41.4, 40.3, 26.3, 22.7, 14.0.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -88.5 (d, *J* = 39.0 Hz), -90.2 (d, *J* = 37.1 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₂₄F₂O₂ 371.1817; Found: 371.1816.



2-(4-(benzyloxy)phenyl)-1,1-difluoro-4-phenyloct-1-en-4-ol (4d)

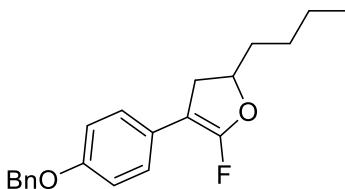
The title compound was prepared from **3aa** (69 mg, 0.20 mmol) general procedure 2. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (66 mg, 78%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.50 – 7.41 (m, 5H), 7.32 (s, 5H), 7.10 (d, *J* = 10.0 Hz, 2H), 6.94 (d, *J* = 9.2 Hz, 2H), 5.08 (s, 4H), 2.95 (t, *J* = 2.5 Hz, 3H), 1.60 (s, 1H), 0.83 – 0.81 (m, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 158.0, 154.4 (t, *J* = 288.6 Hz), 145.4, 136.9, 129.8 (t, *J* = 2.6 Hz), 128.6, 128.1, 127.9, 127.5, 126.5, 126.4 (t, *J* = 5.2 Hz), 125.3, 115.0, 88.7 (dd, *J* = 21.3, 21.1 Hz), 77.9 (t, *J* = 2.7 Hz), 70.0, 42.1, 41.5, 25.4, 23.0, 14.0.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -89.7 (d, *J* = 44.4 Hz), -91.2 (d, *J* = 37.9 Hz).

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₇H₂₈F₂O₂ 423.2130; Found: 423.2128.



4-(4-(benzyloxy)phenyl)-2-butyl-5-fluoro-2,3-dihydrofuran (4e)

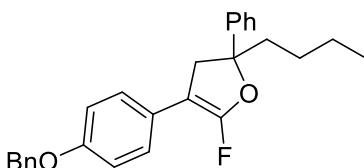
The title compound was prepared from **4a** (69 mg, 0.20 mmol) general procedure 4. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (40 mg, 62%).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.88 – 6.83 (m, 2H), 4.97 (s, 2H), 4.61 (dq, *J* = 9.0, 6.6 Hz, 1H), 2.99 (ddd, *J* = 13.2, 9.7, 3.7 Hz, 1H), 2.58 (ddd, *J* = 12.5, 7.3, 4.1 Hz, 1H), 1.76 (qd, *J* = 11.1, 9.1, 5.8 Hz, 1H), 1.59 (ddt, *J* = 14.2, 11.1, 5.0 Hz, 1H), 1.39 – 1.28 (m, 4H), 0.86 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 156.2 (d, *J* = 2.2 Hz), 155.4 (d, *J* = 277.8 Hz), 137.1, 128.6, 127.9, 127.5, 125.9 (d, *J* = 6.2 Hz), 125.7 (d, *J* = 5.6 Hz), 115.0, 80.3 (d, *J* = 11.3 Hz), 79.6 (d, *J* = 2.3 Hz), 70.1, 35.9, 35.2 (d, *J* = 3.0 Hz), 27.0, 22.5, 14.0.

¹⁹F NMR (56 MHz, Chloroform-*d*) δ -150.2.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₁H₂₃FO₂ 327.1755; Found: 327.1752.



4-(4-(benzyloxy)phenyl)-2-butyl-5-fluoro-2-phenyl-2,3-dihydrofuran (4f)

The title compound was prepared from **4d** (85 mg, 0.20 mmol) general procedure 4. The crude residue

was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (54 mg, 67%).

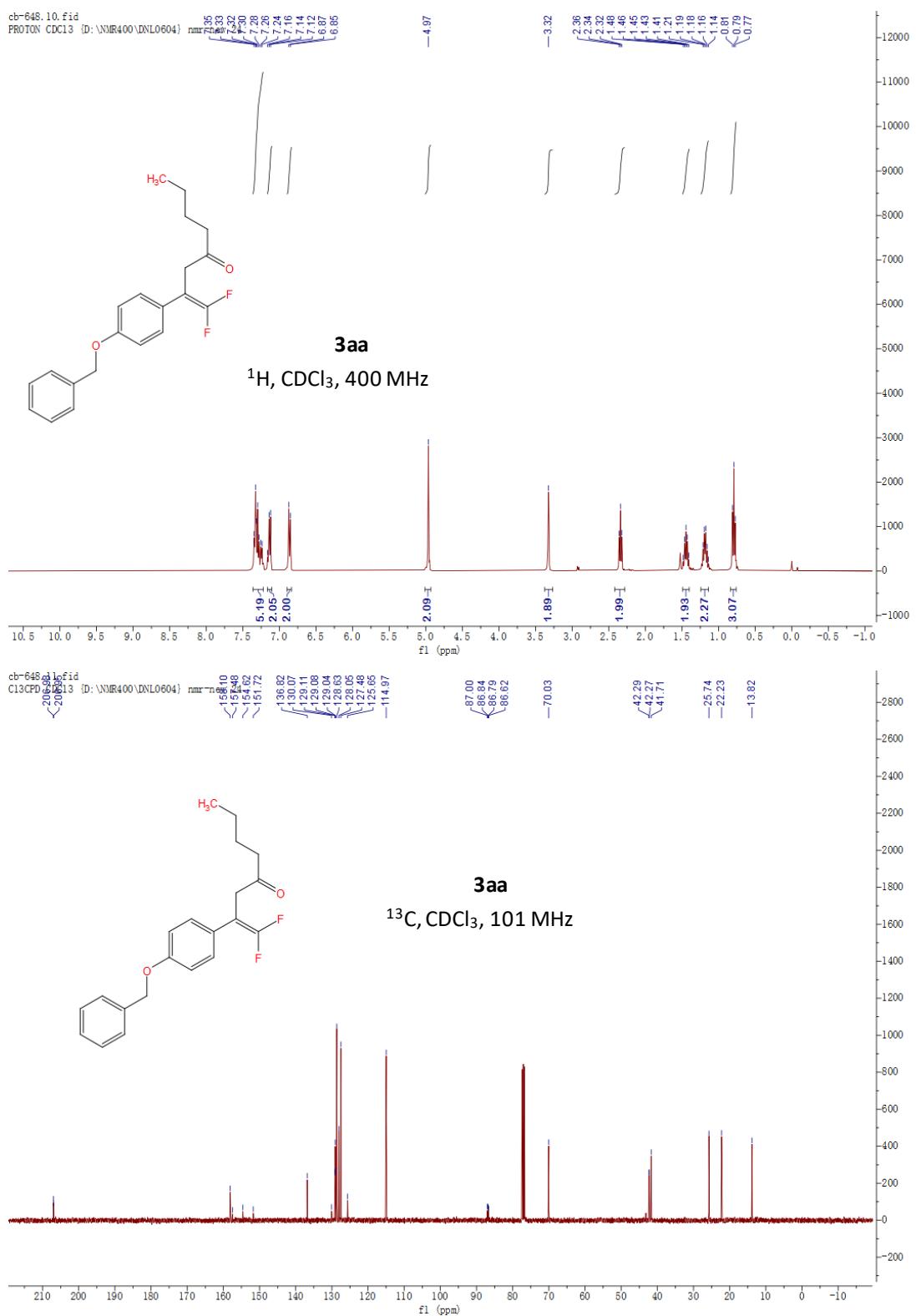
¹H NMR (700 MHz, Chloroform-d) δ 7.34 – 7.30 (m, 4H), 7.28 (td, *J* = 7.7, 2.1 Hz, 4H), 7.24 – 7.16 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.95 (s, 2H), 3.17 – 3.05 (m, 2H), 1.99 (ddd, *J* = 13.9, 11.7, 4.4 Hz, 1H), 1.88 (dddd, *J* = 13.9, 11.9, 4.5, 1.7 Hz, 1H), 1.33 – 1.26 (m, 1H), 1.23 – 1.15 (m, 2H), 1.11 – 1.01 (m, 1H), 0.76 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 155.2 (d, *J* = 1.8 Hz), 153.1 (d, *J* = 278.4 Hz), 144.1, 136.0, 127.5, 127.4, 126.9, 126.4, 126.1, 124.7 (d, *J* = 5.5 Hz), 124.5 (d, *J* = 6.4 Hz), 123.4, 114.0, 86.8, 79.2 (d, *J* = 10.9 Hz), 69.0, 42.4 (d, *J* = 2.7 Hz), 41.6, 24.6, 21.7, 12.9.

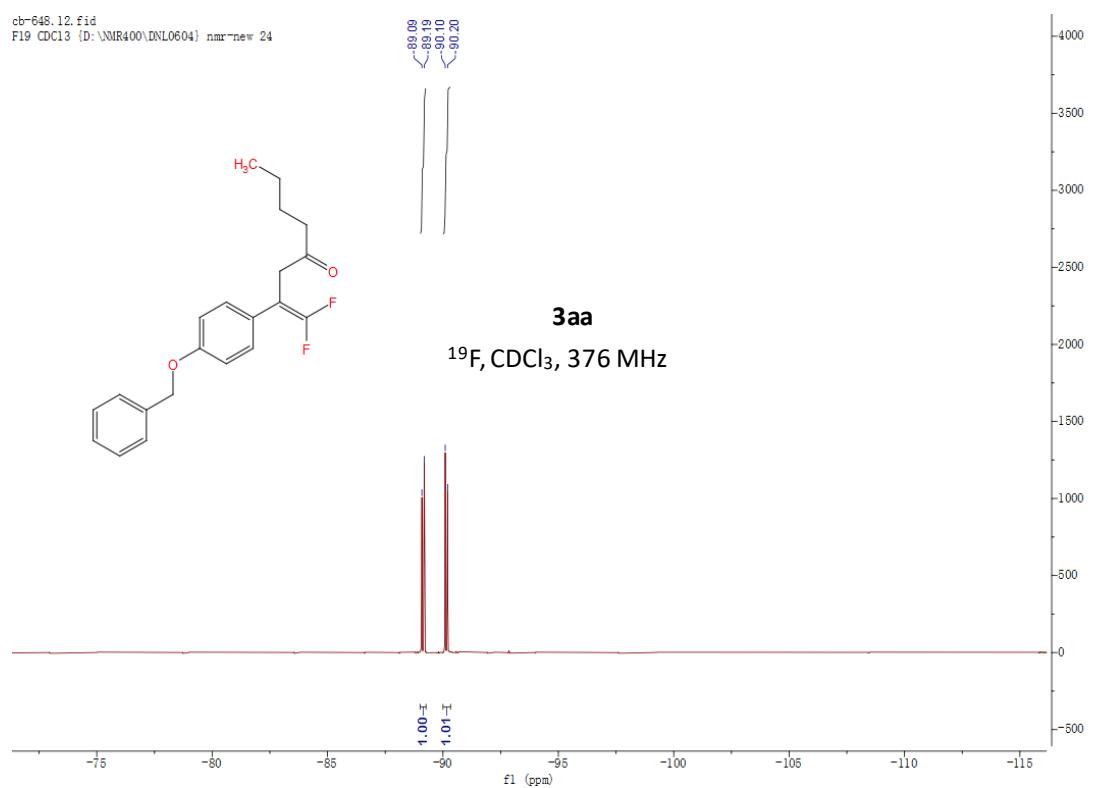
¹⁹F NMR (56 MHz, Chloroform-d) δ -149.2.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₇H₂₇FO₂ 403.2068; Found: 403.2066.

6. Copies of NMR spectra for compounds

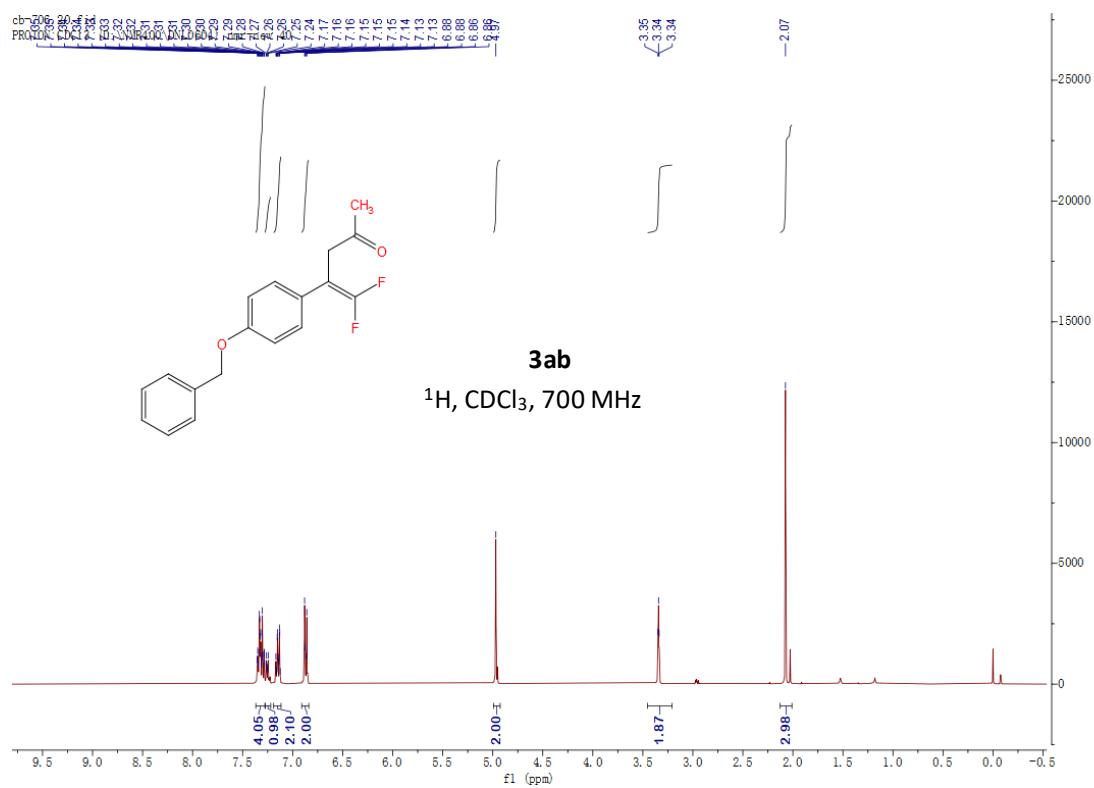


cb-648.12.fid
F19 CDCl₃ [D:\NMR400\DNL0604] nmr-new 24



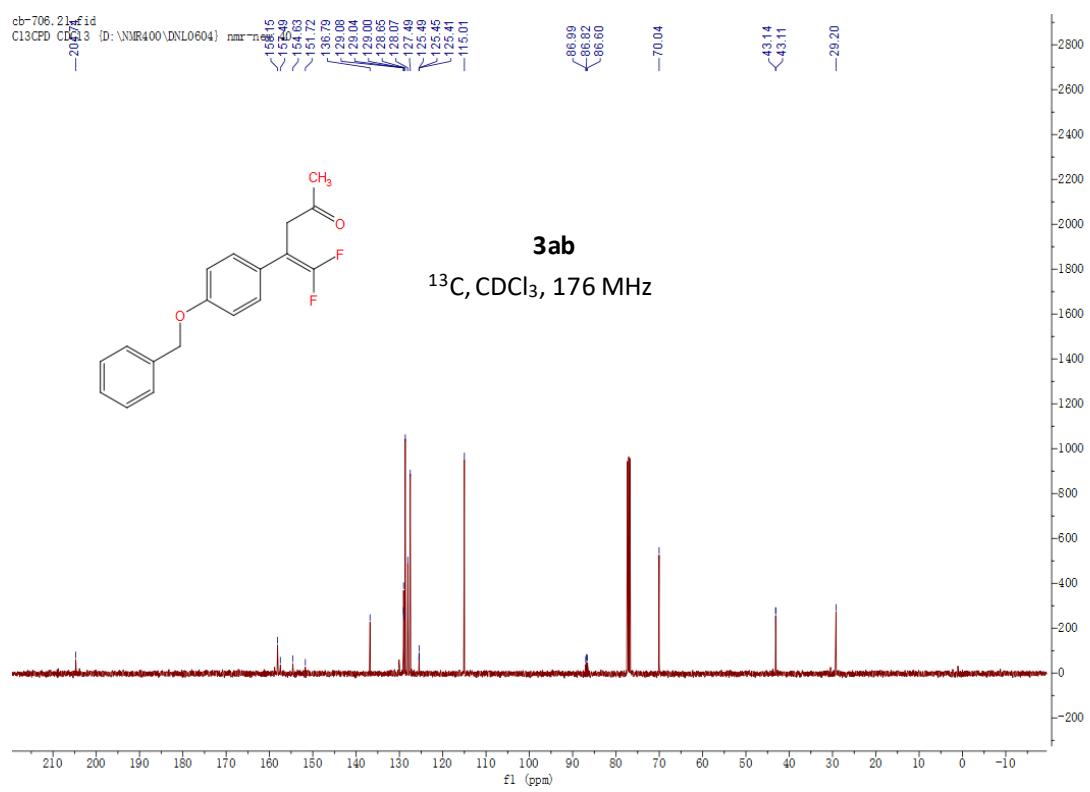
3aa

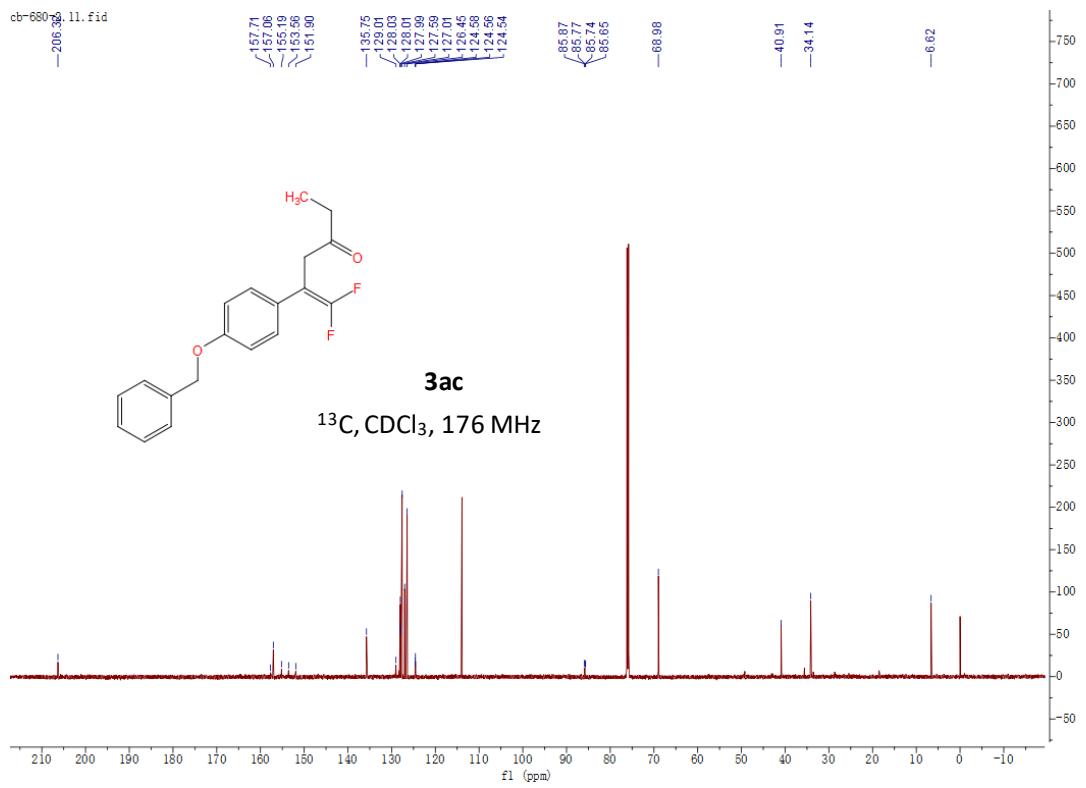
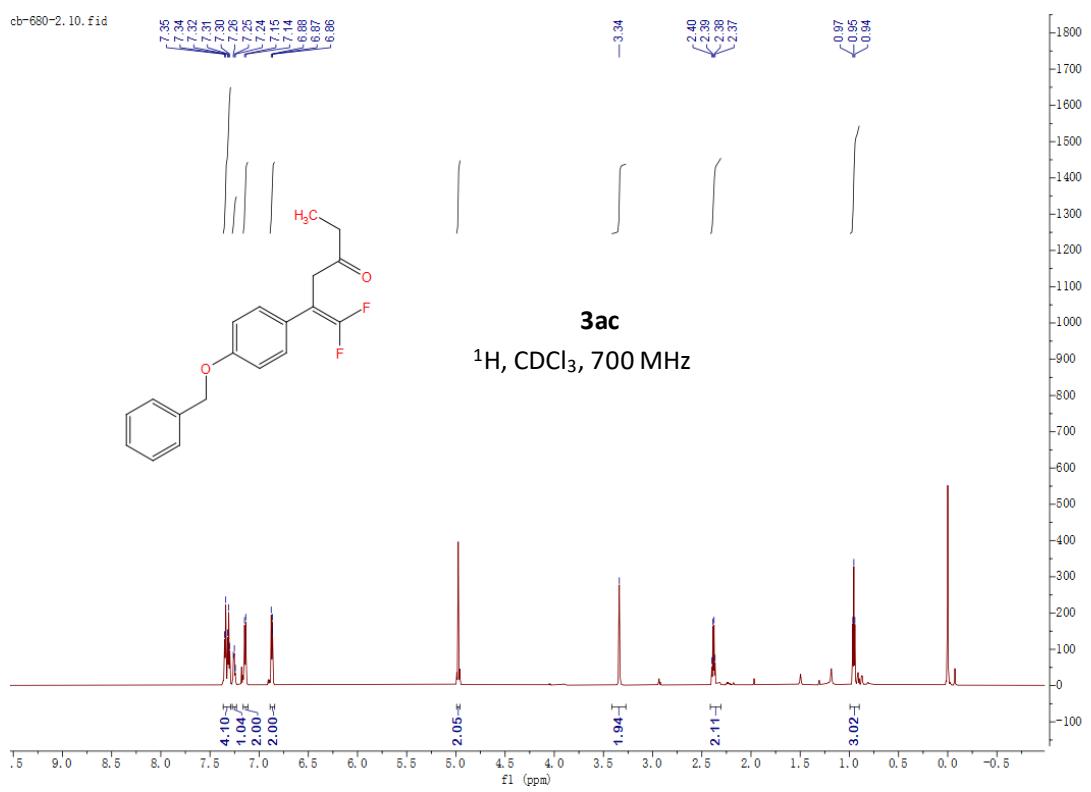
¹⁹F, CDCl₃, 376 MHz



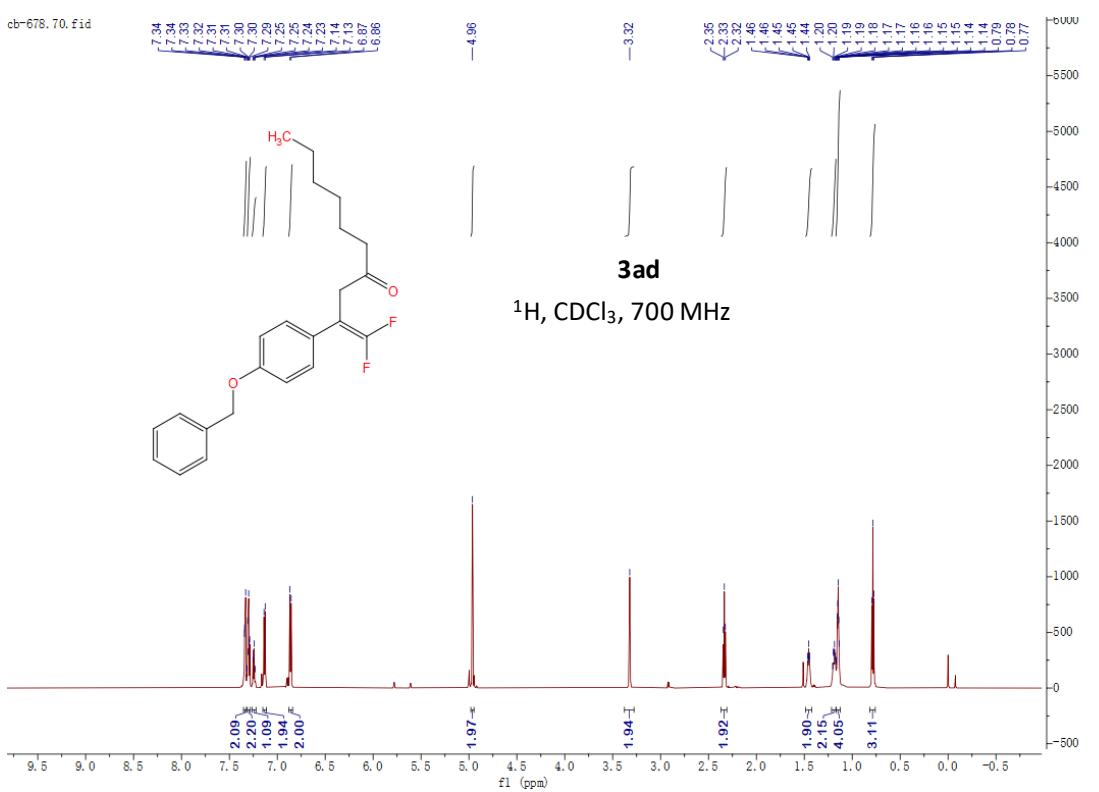
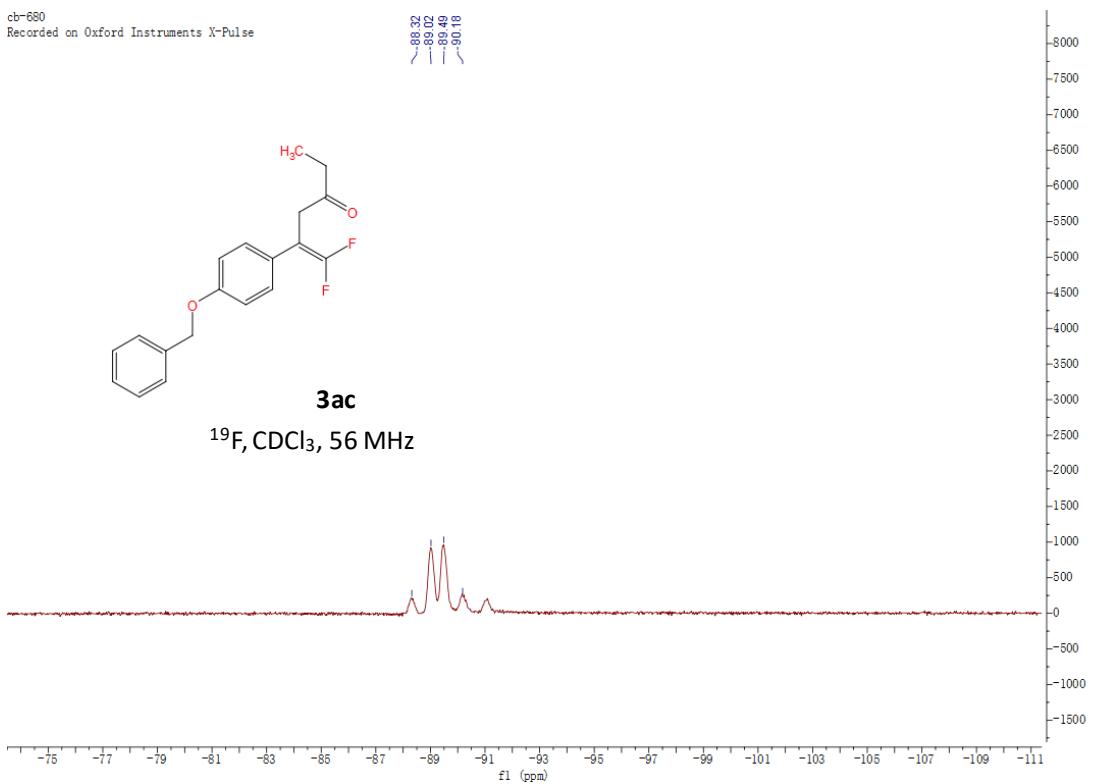
3ab

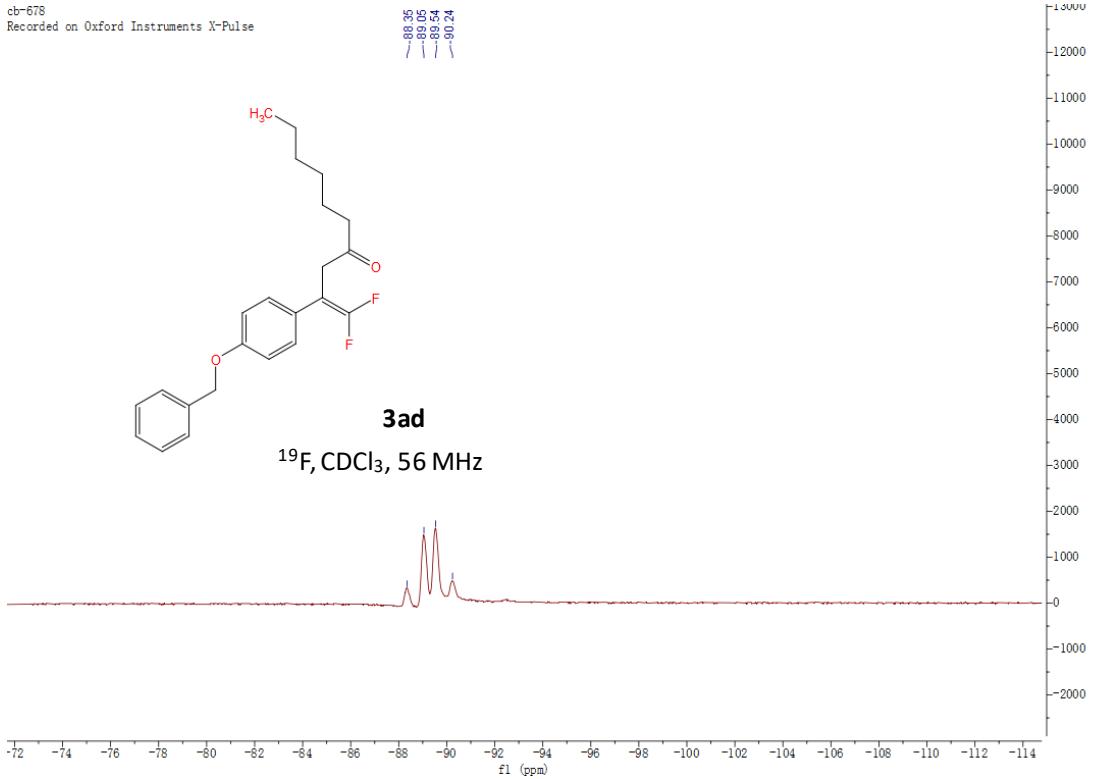
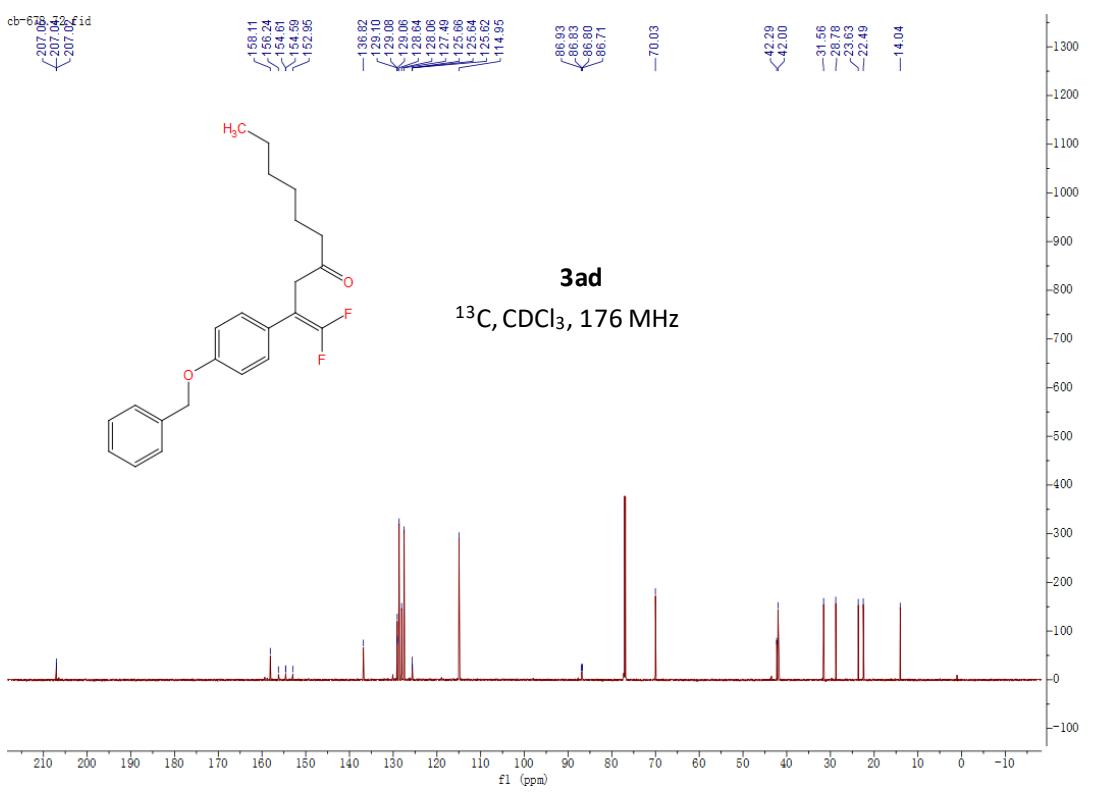
¹H, CDCl₃, 700 MHz

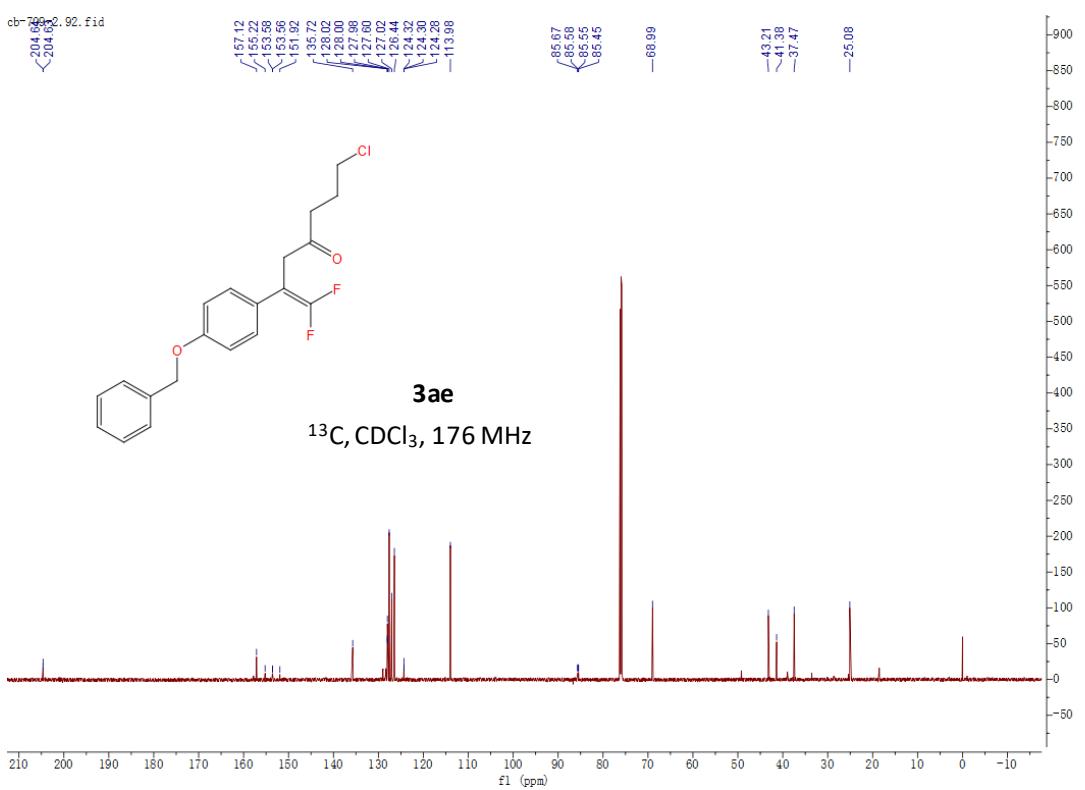
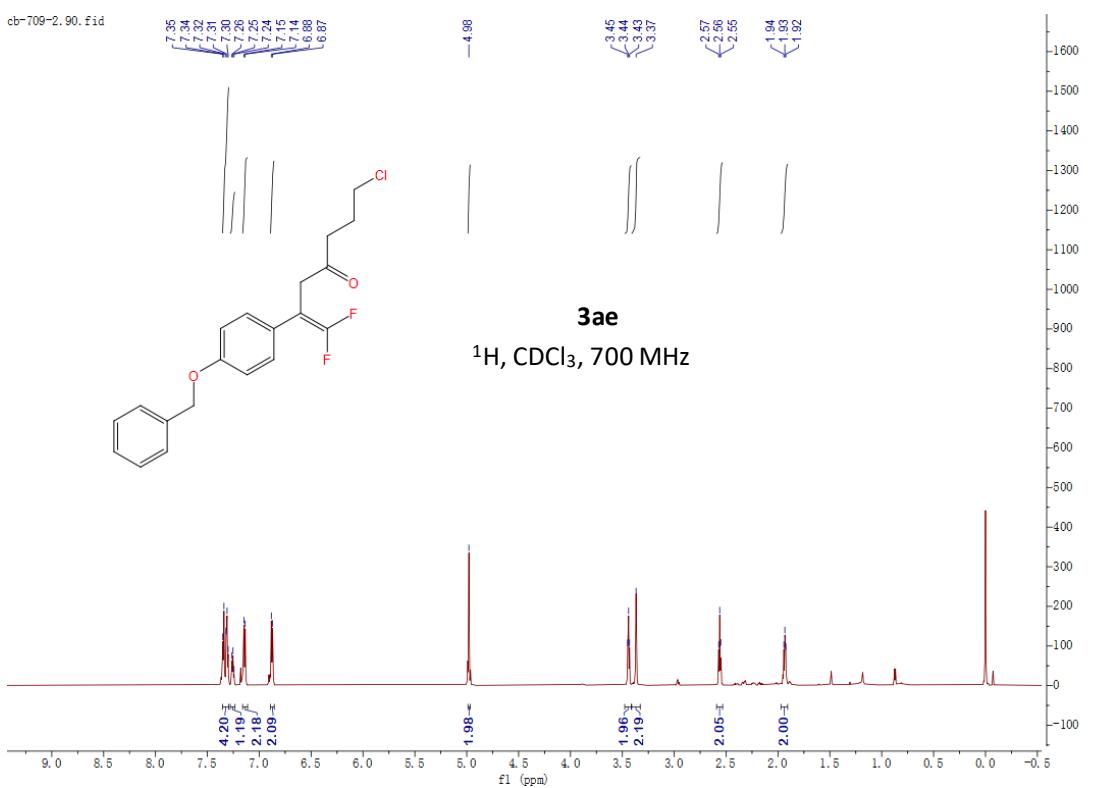




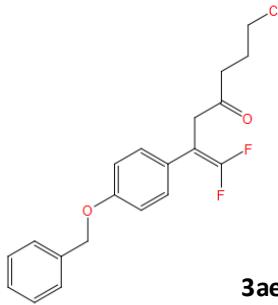
cb-680
Recorded on Oxford Instruments X-Pulse





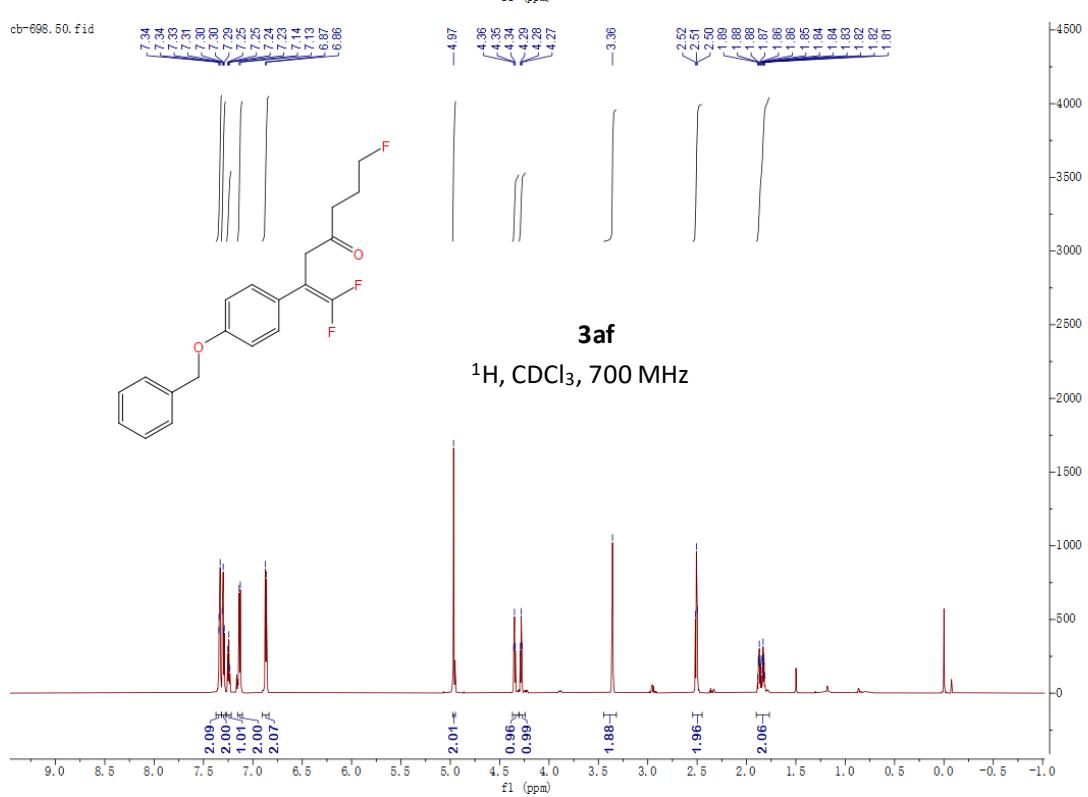


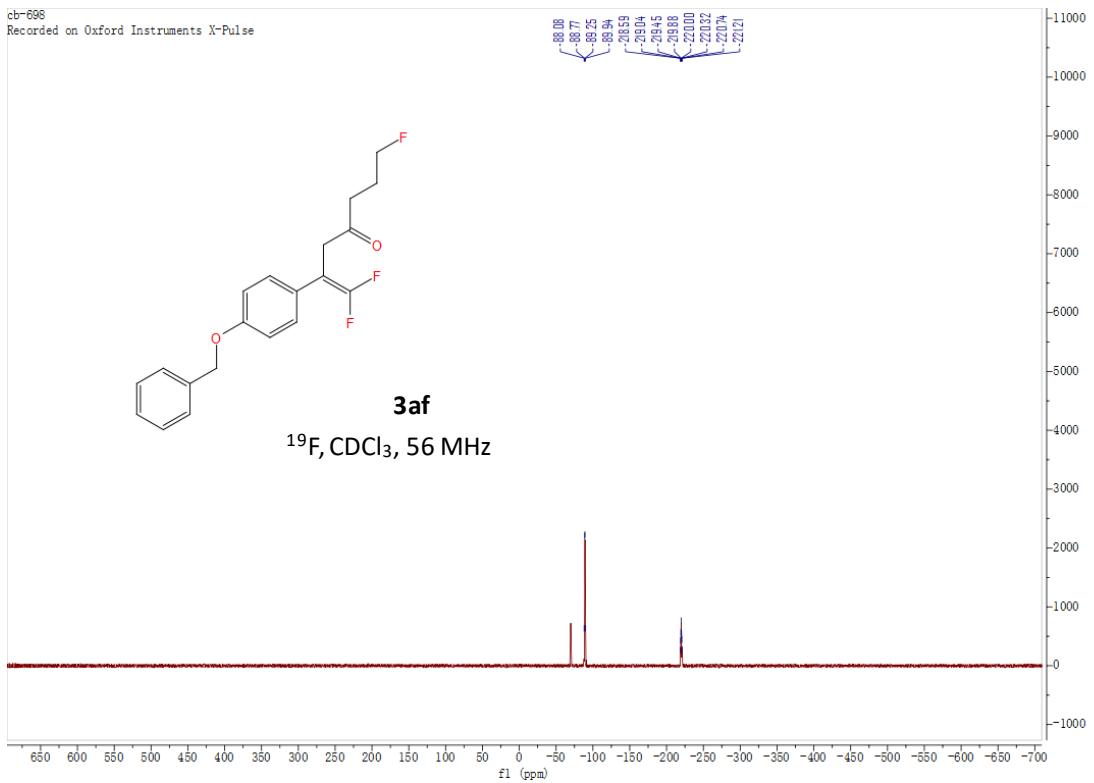
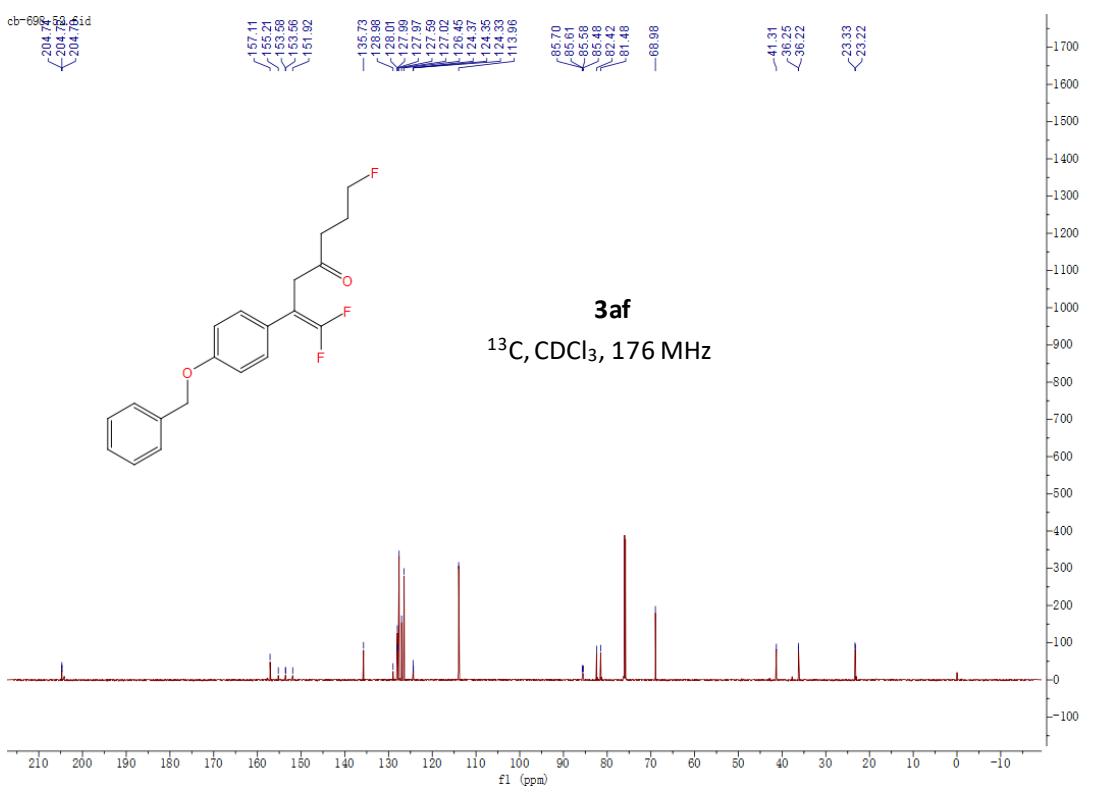
cb-709
Recorded on Oxford Instruments X-Pulse

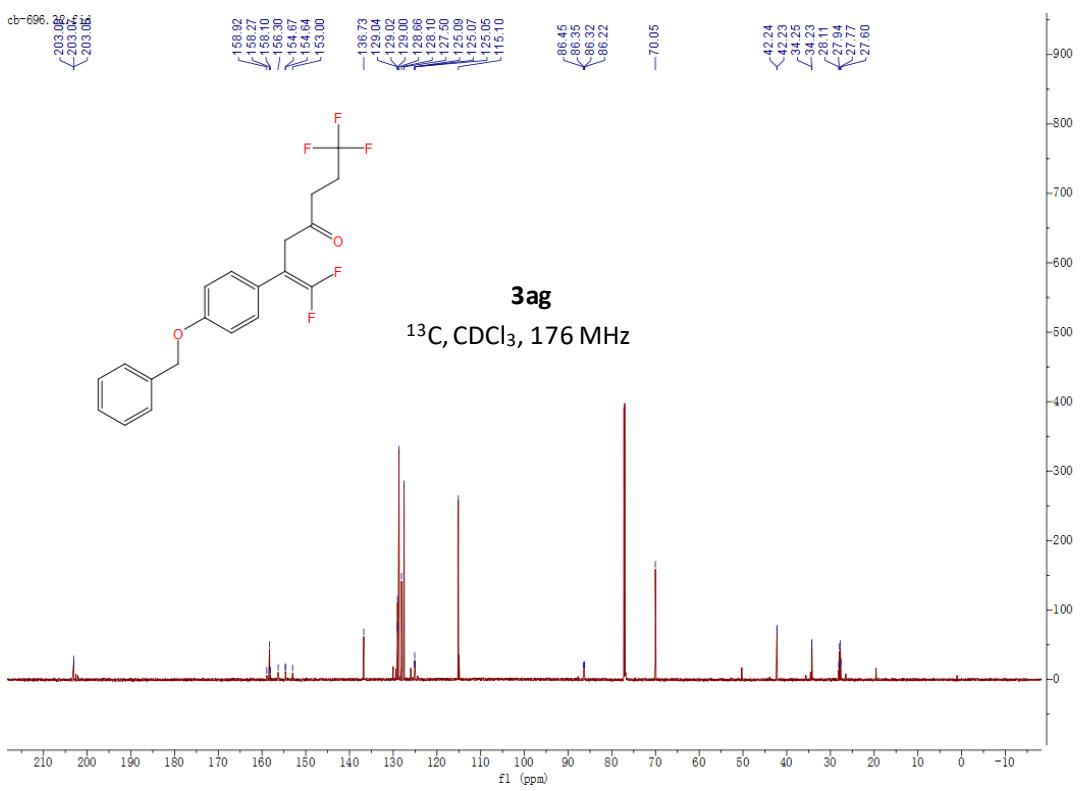
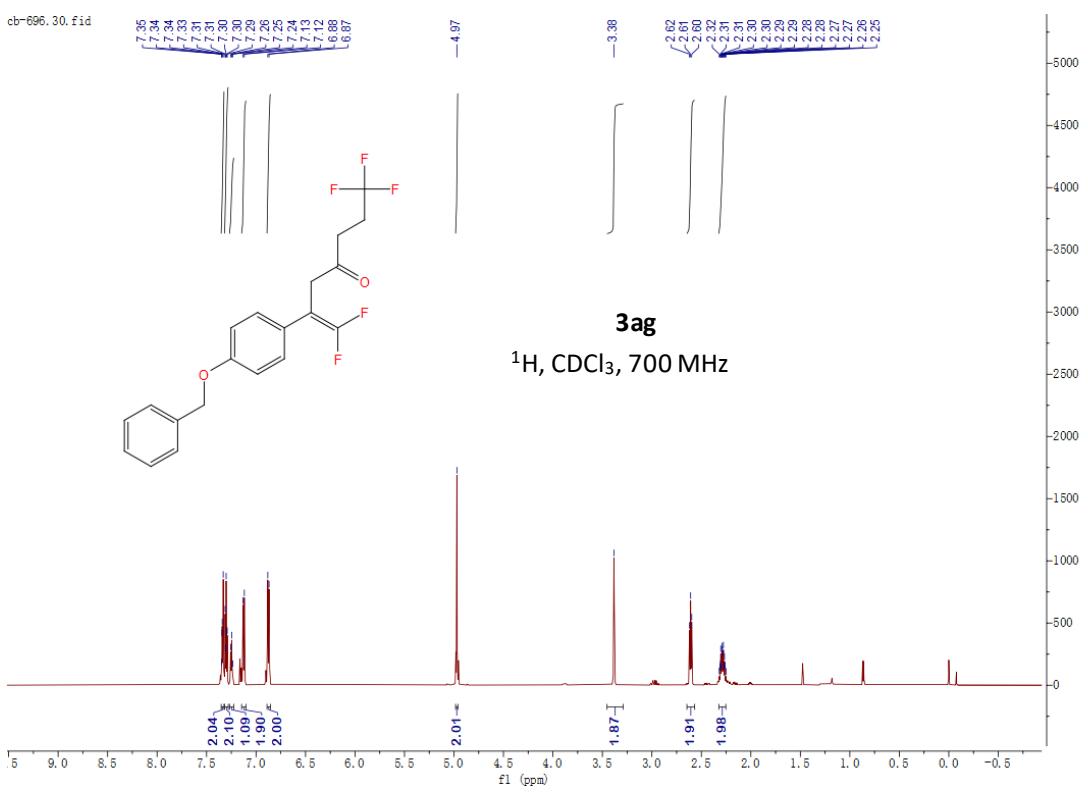


3ae

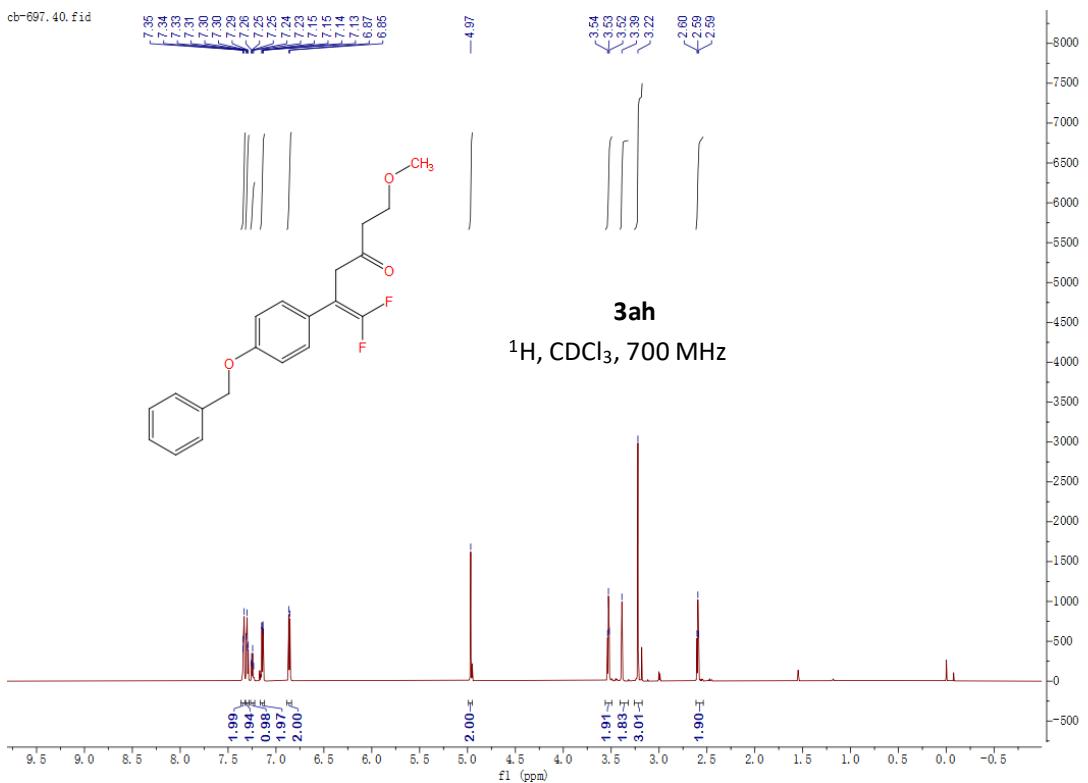
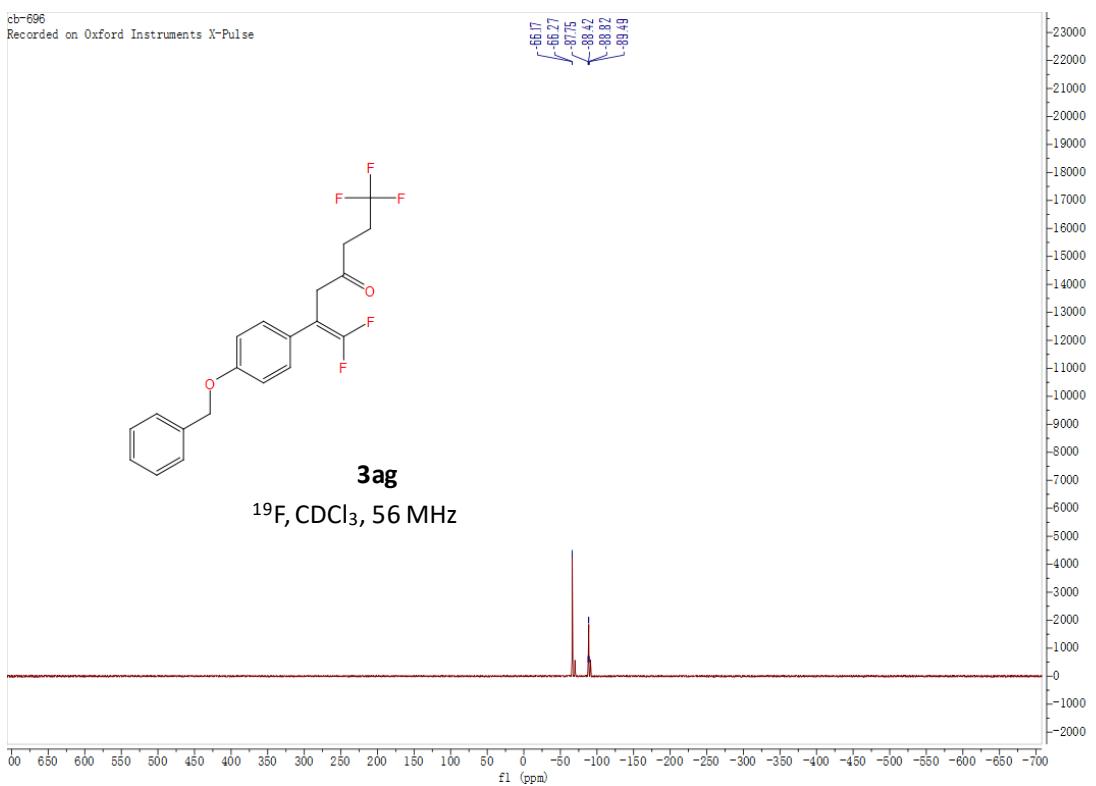
¹⁹F, CDCl₃, 56 MHz

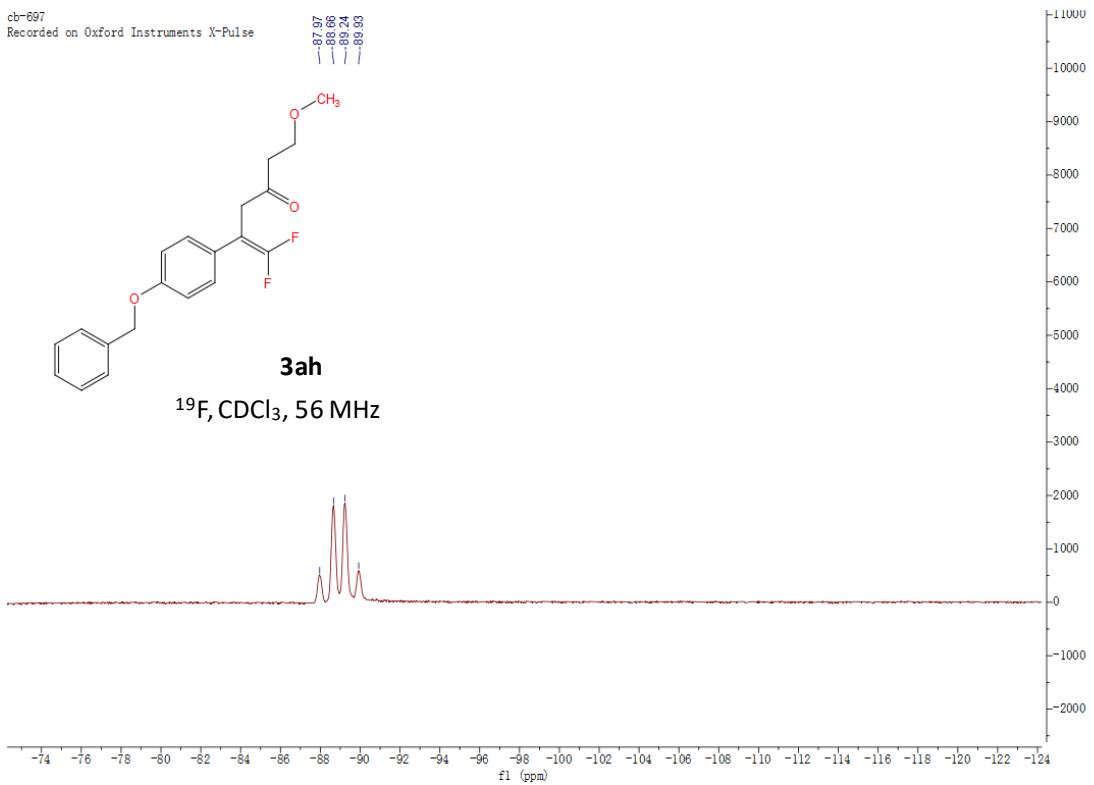
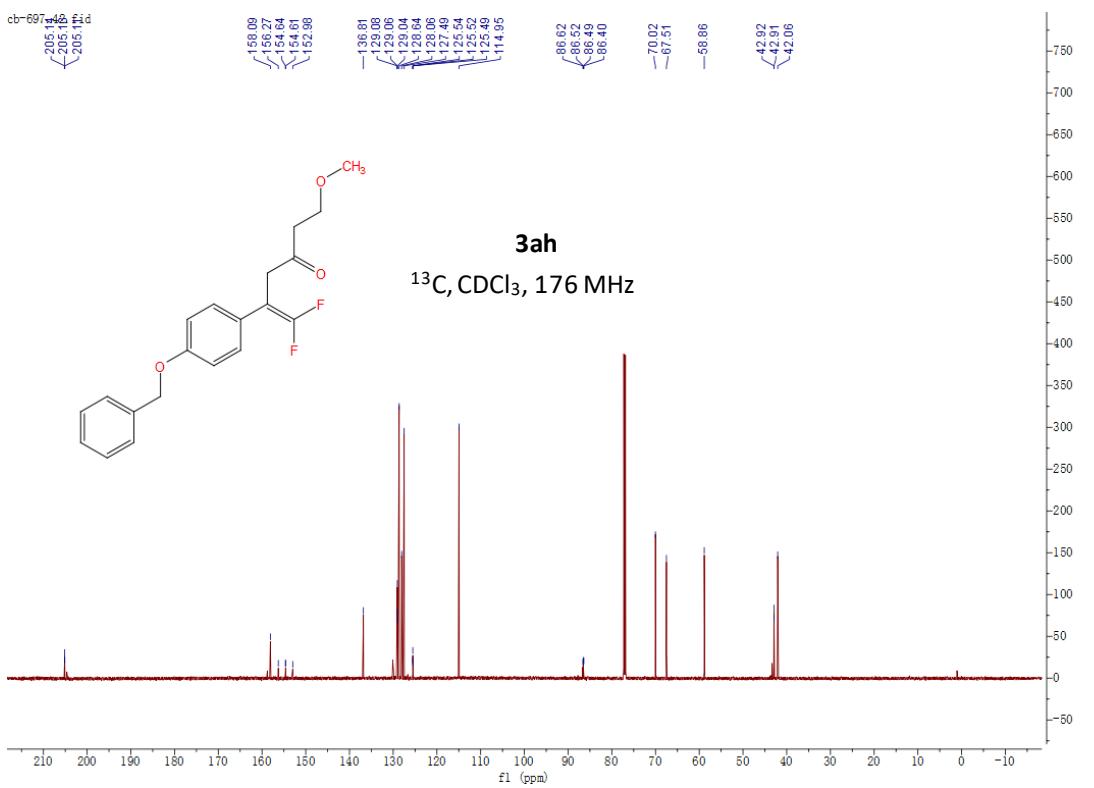


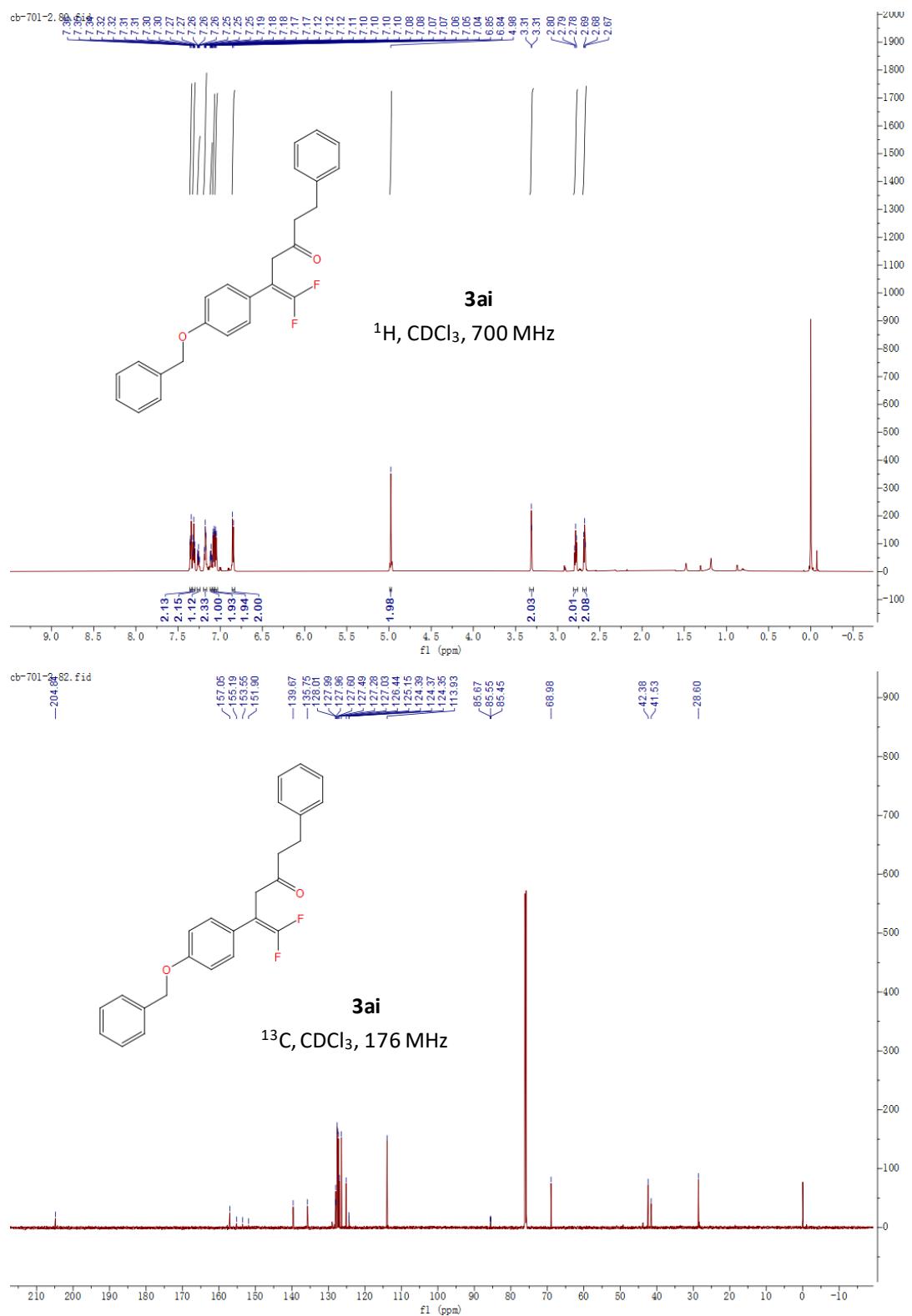




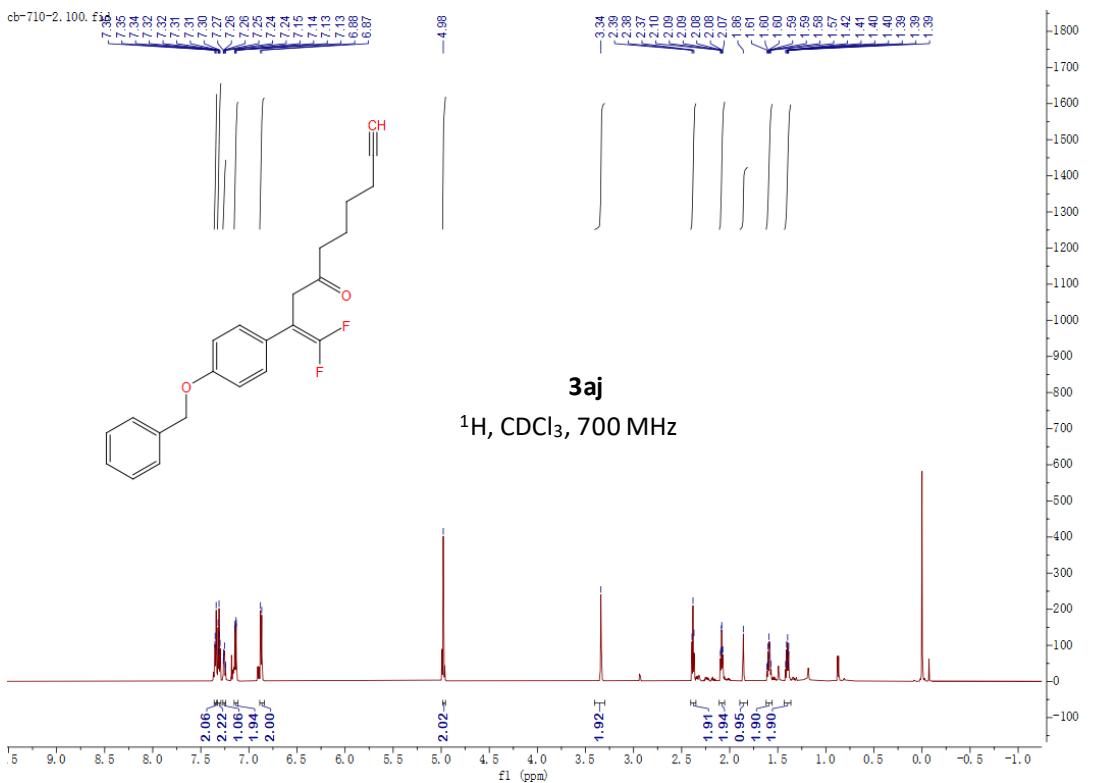
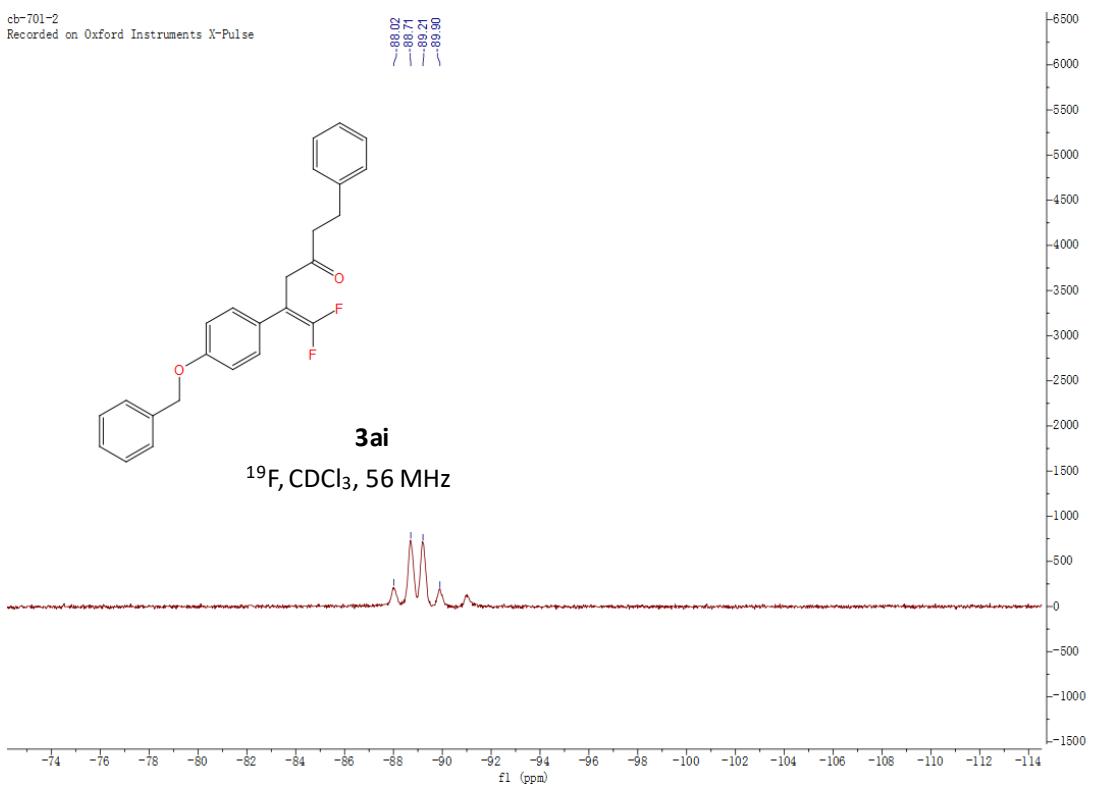
cb-696
Recorded on Oxford Instruments X-Pulse

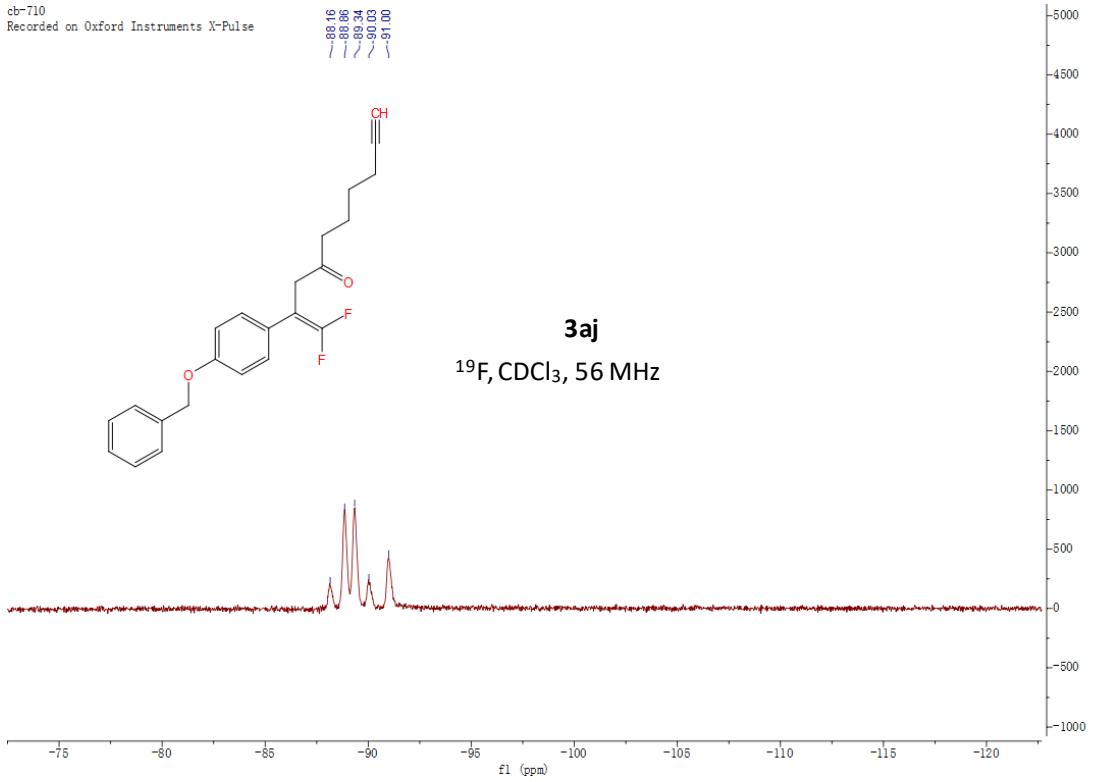
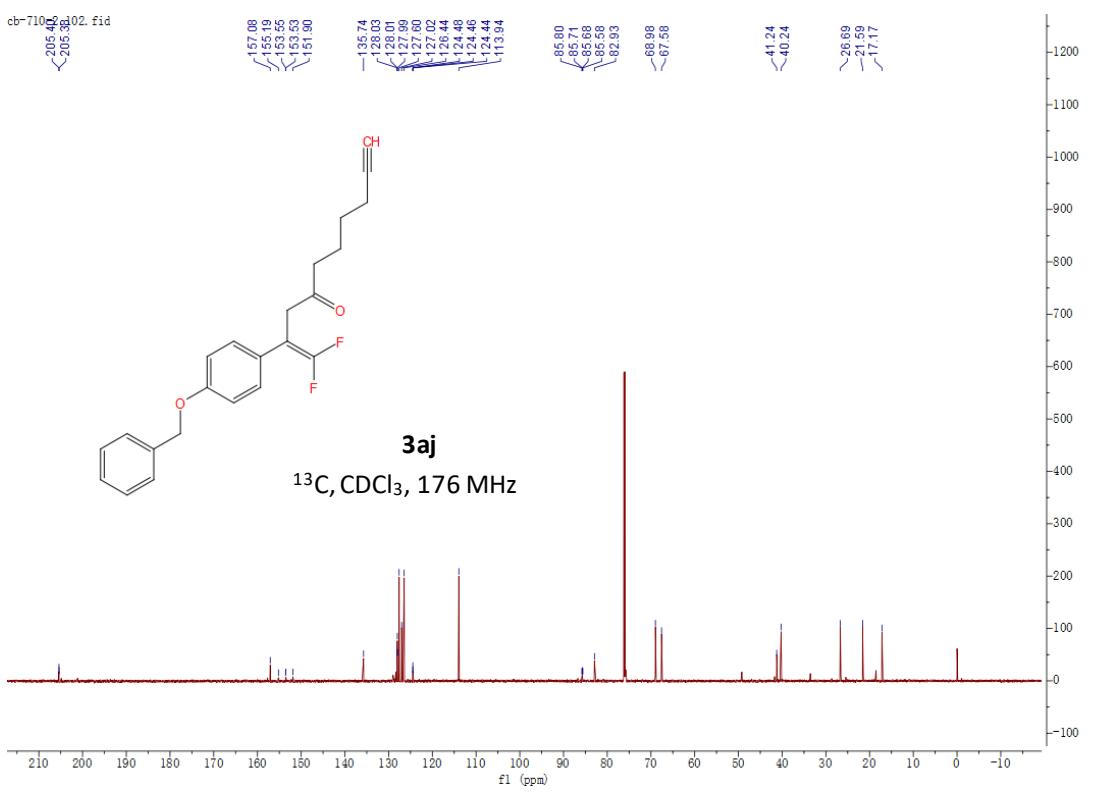


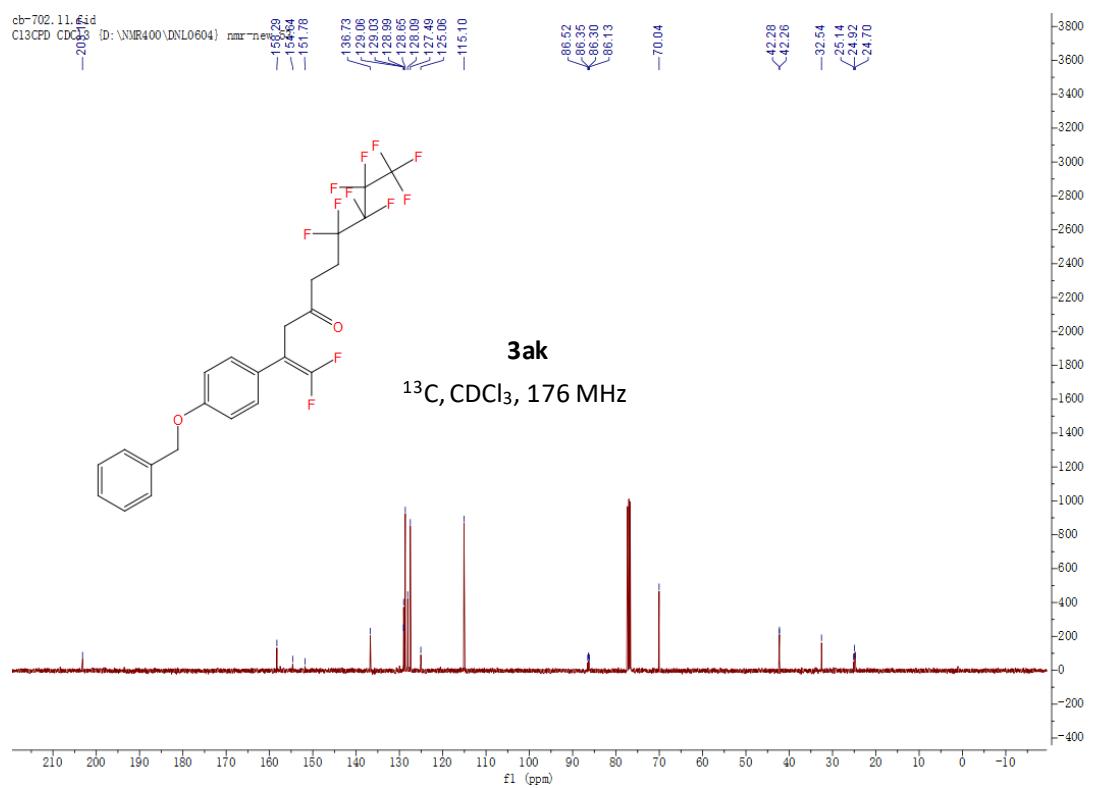
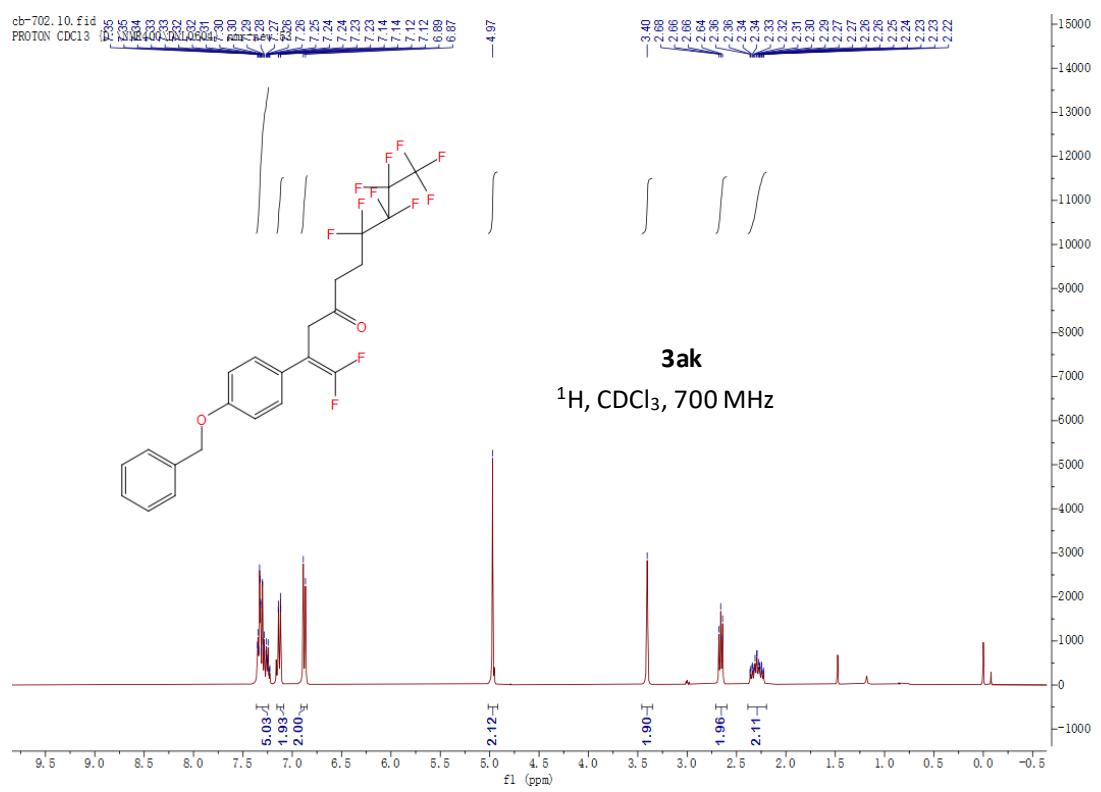




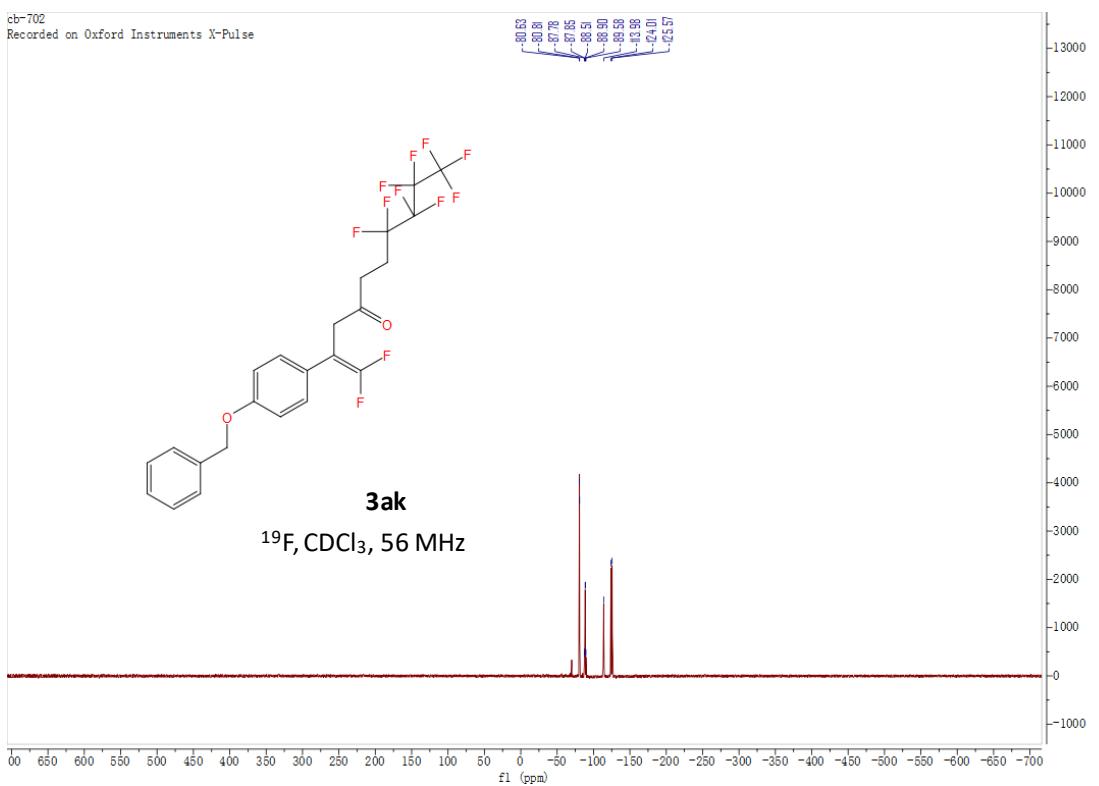
cb-701-2
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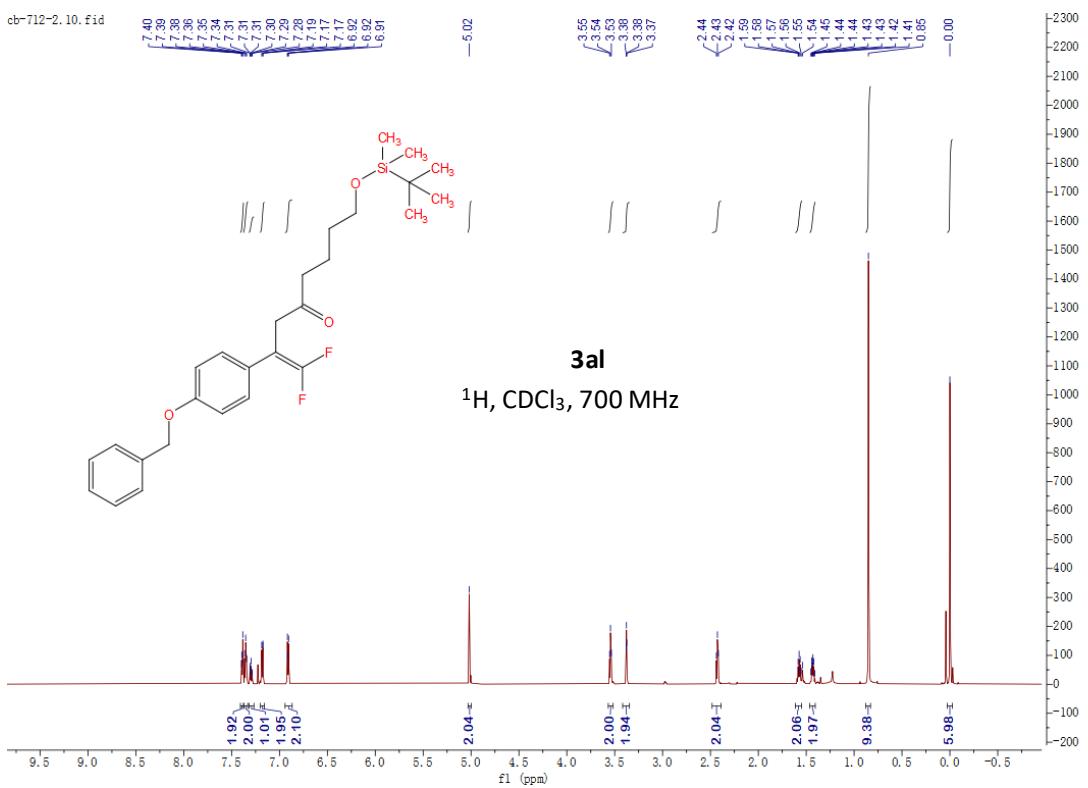




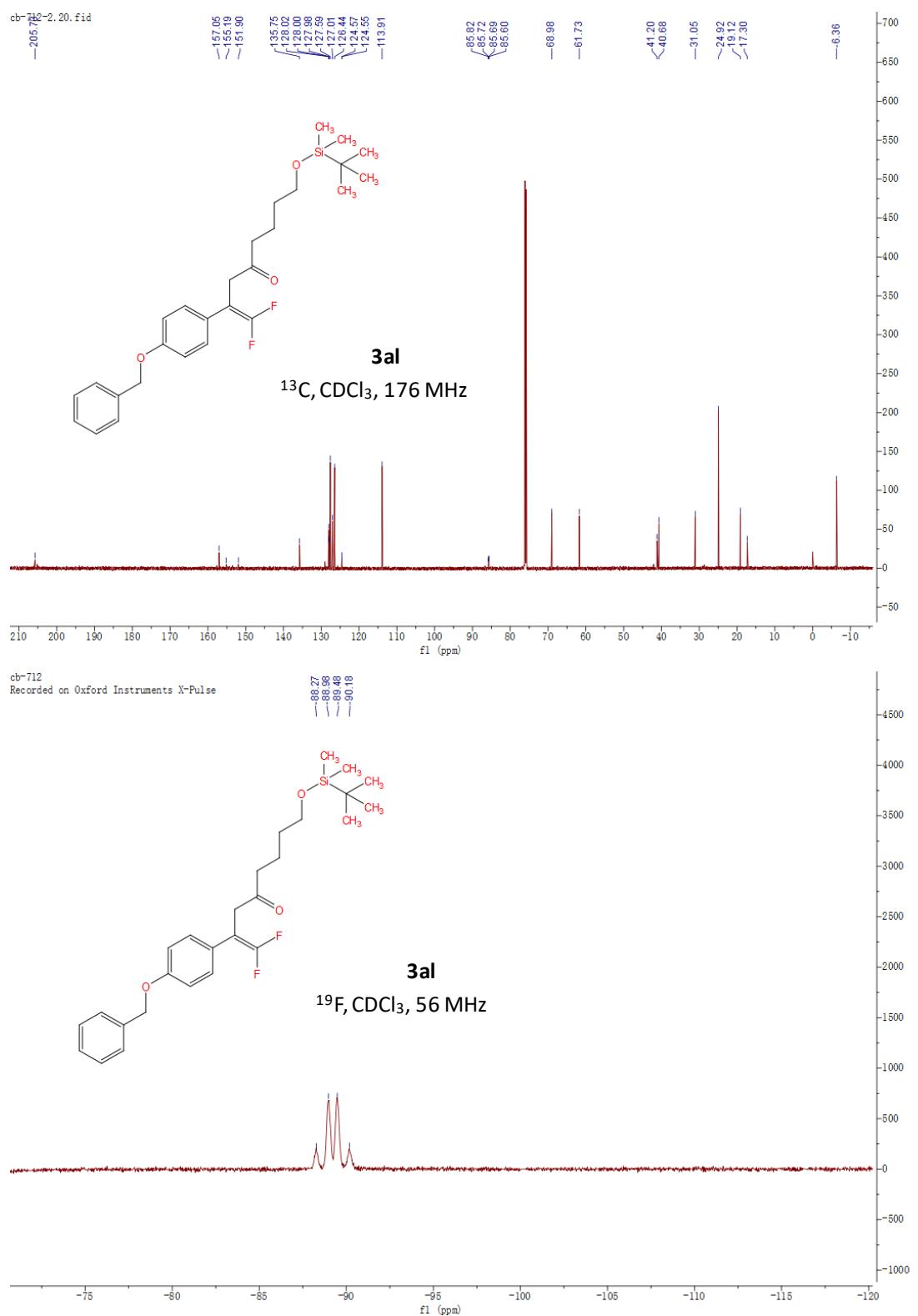
cb-702
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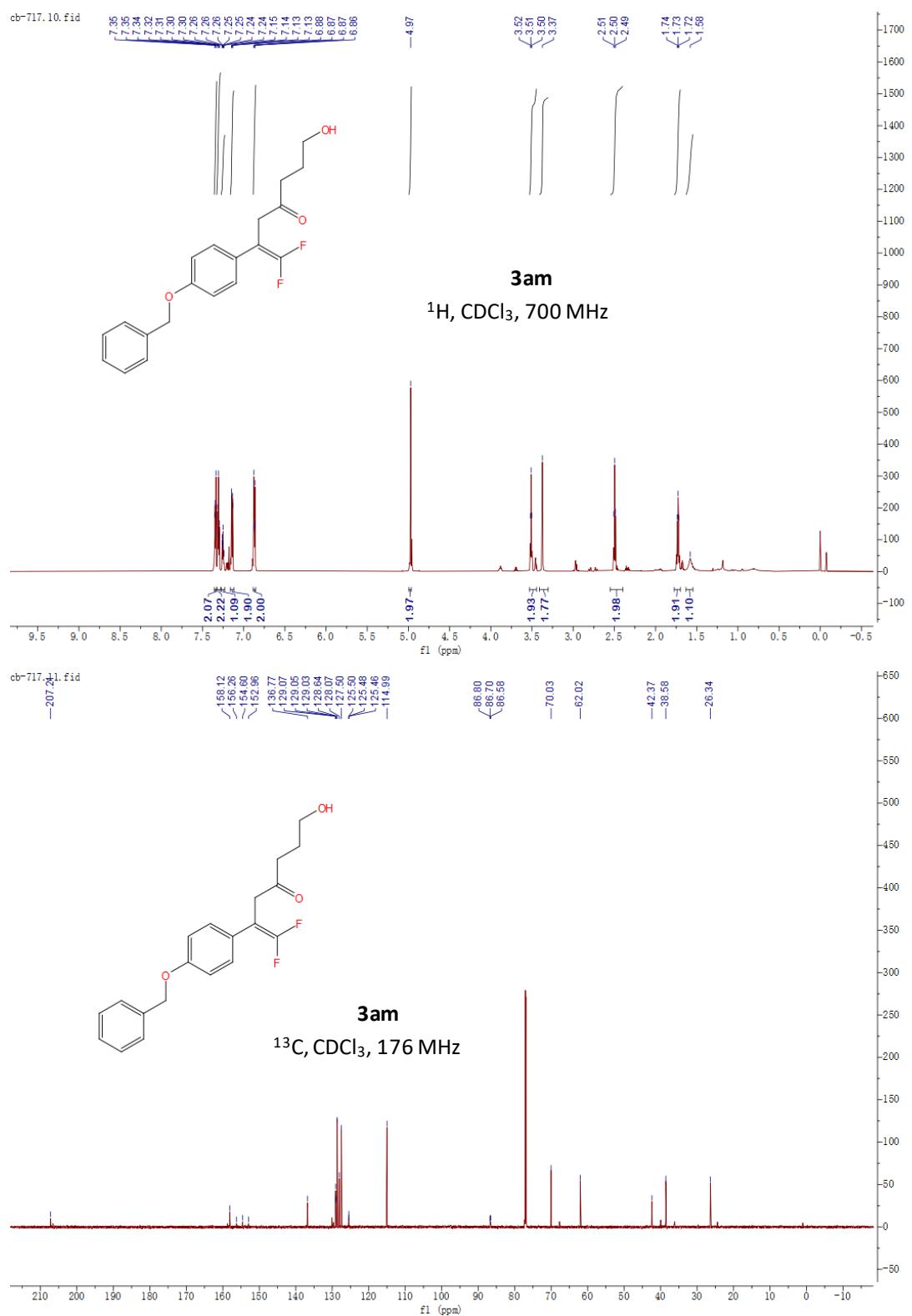


3ak
¹⁹F, CDCl₃, 56 MHz

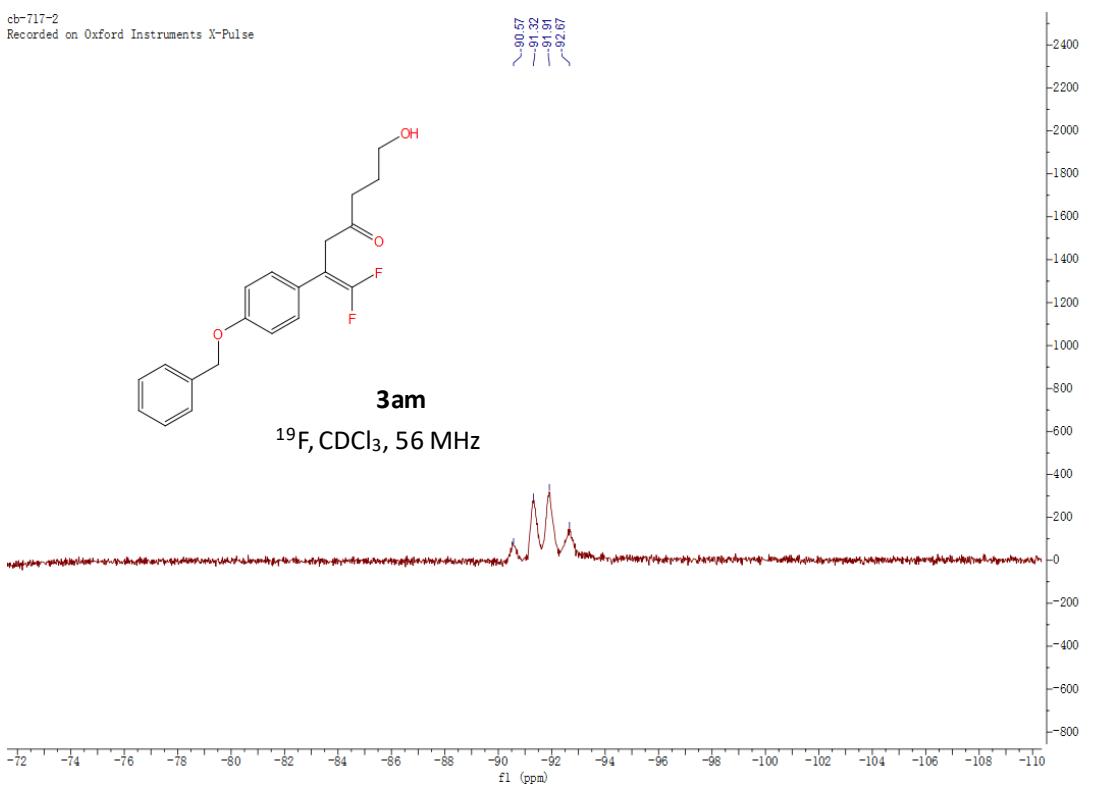


3al
¹H, CDCl₃, 700 MHz

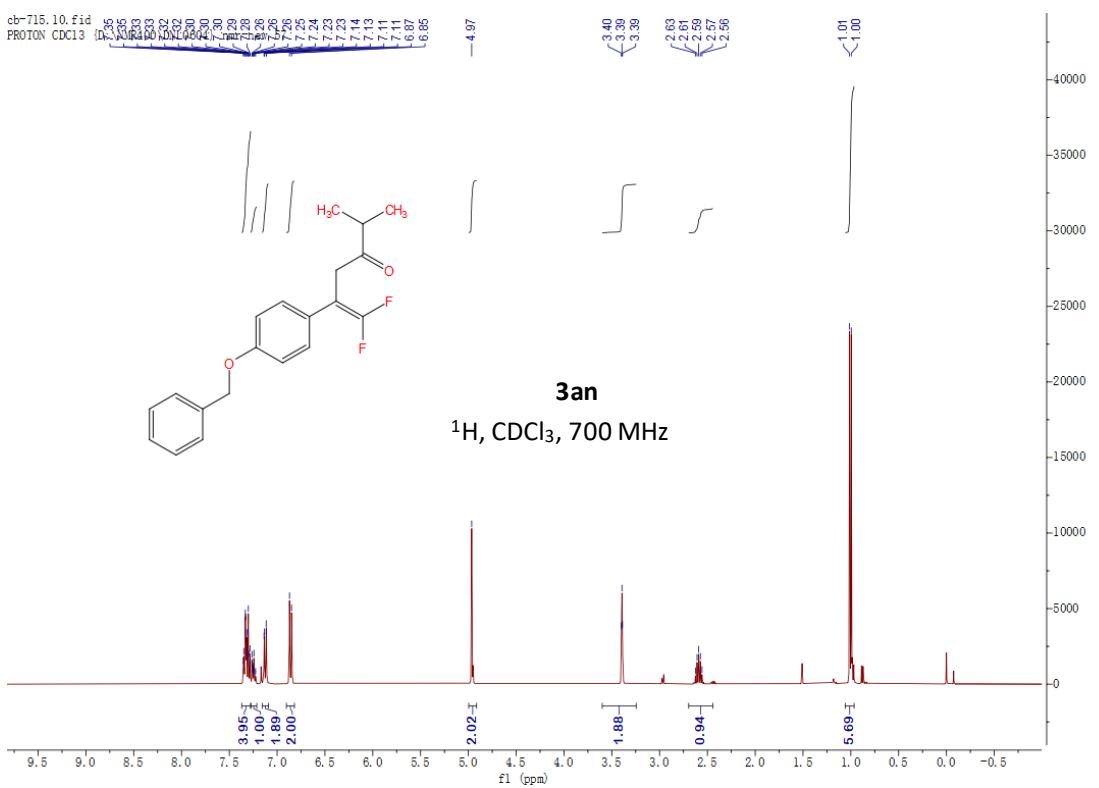


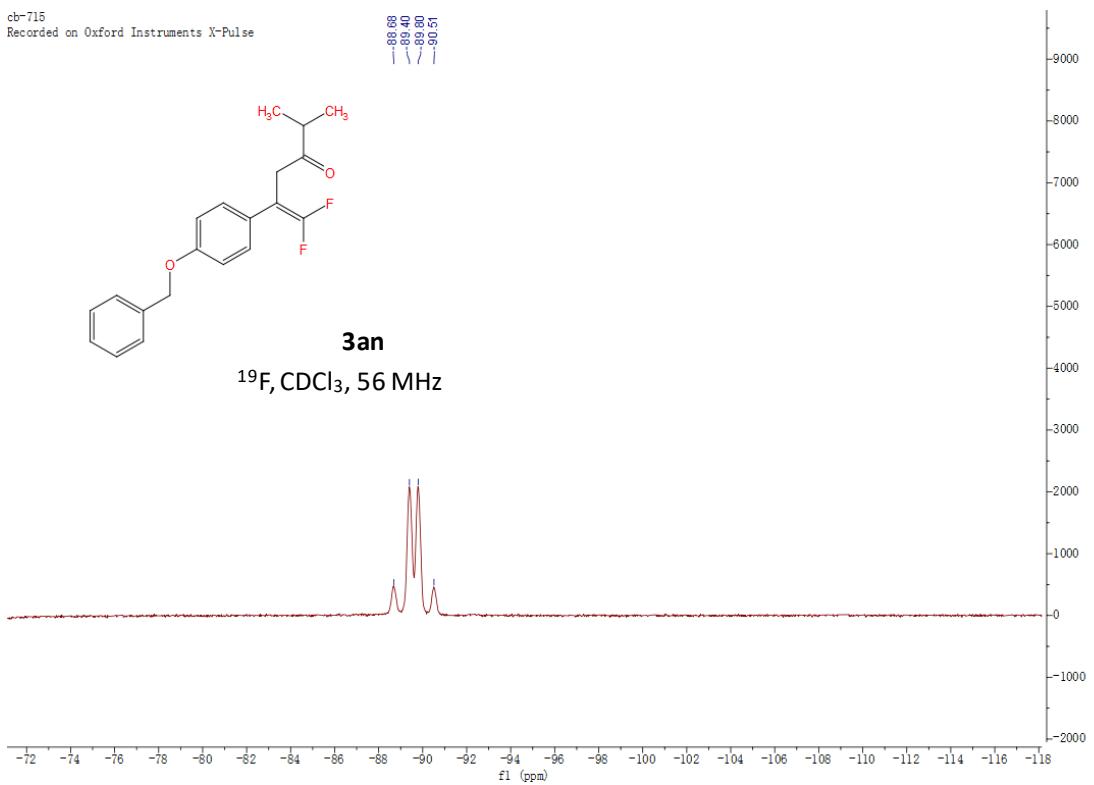
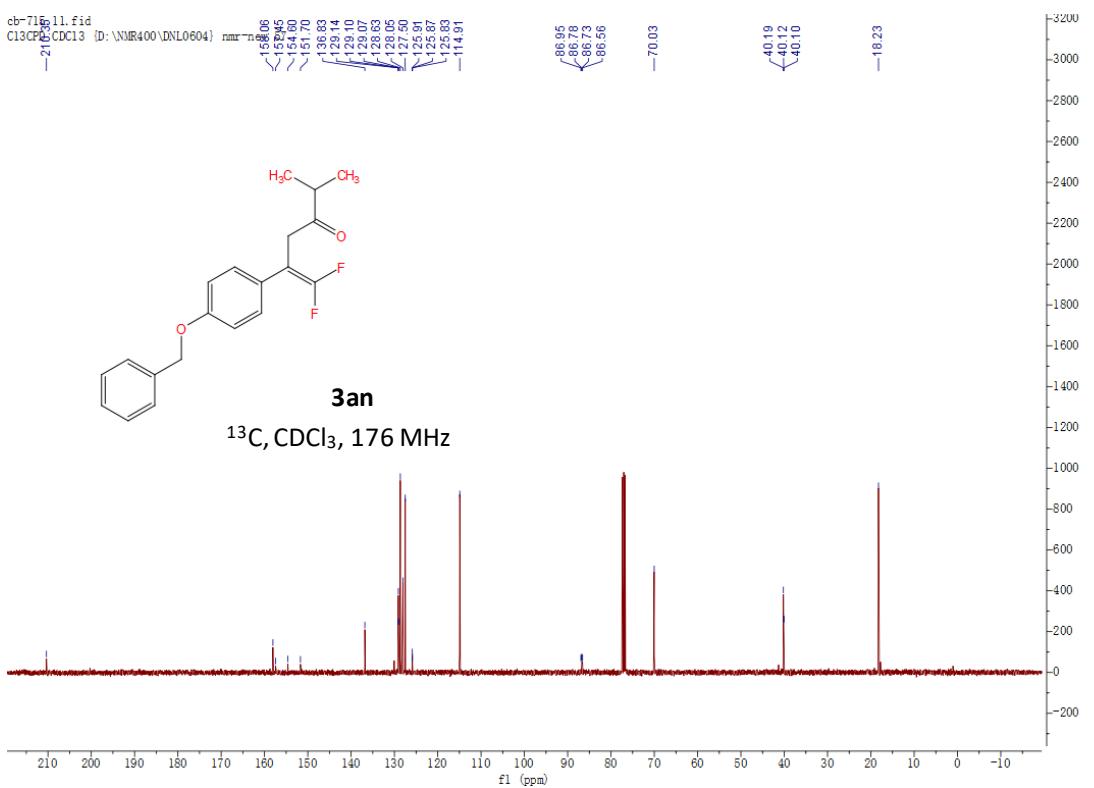


cb-717-2
Recorded on Oxford Instruments X-Pulse

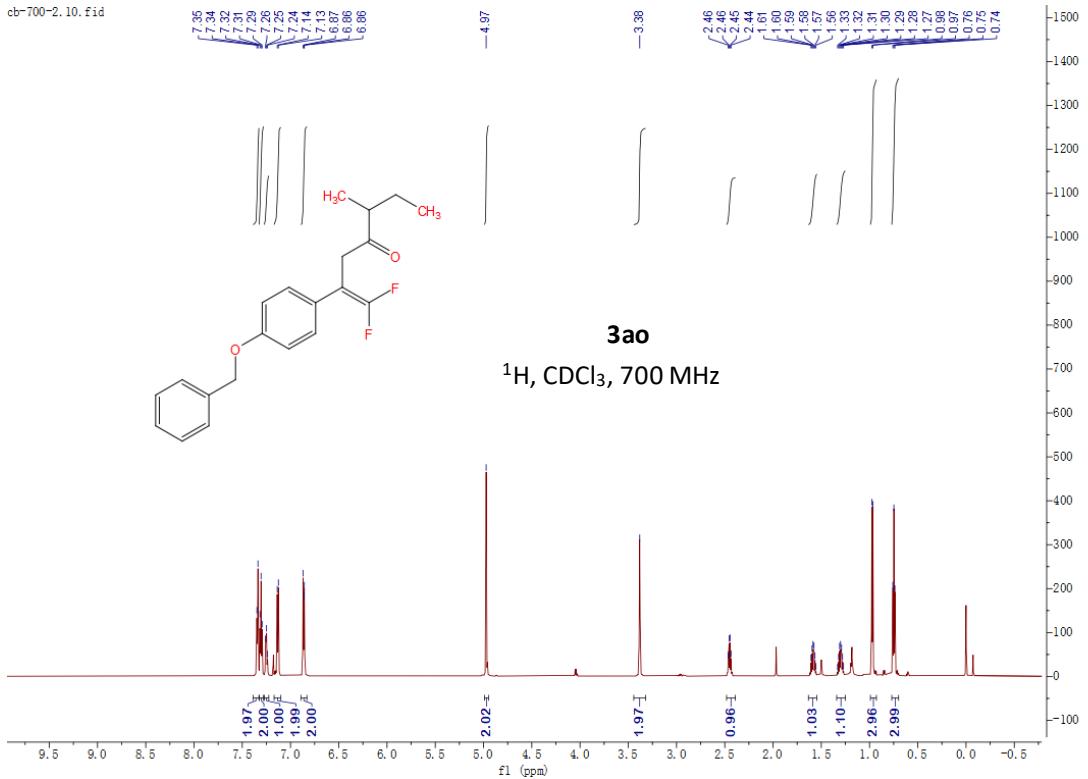


cb-715.10.fid
PROTON CDCl₃ [A-101435-DNL4804]





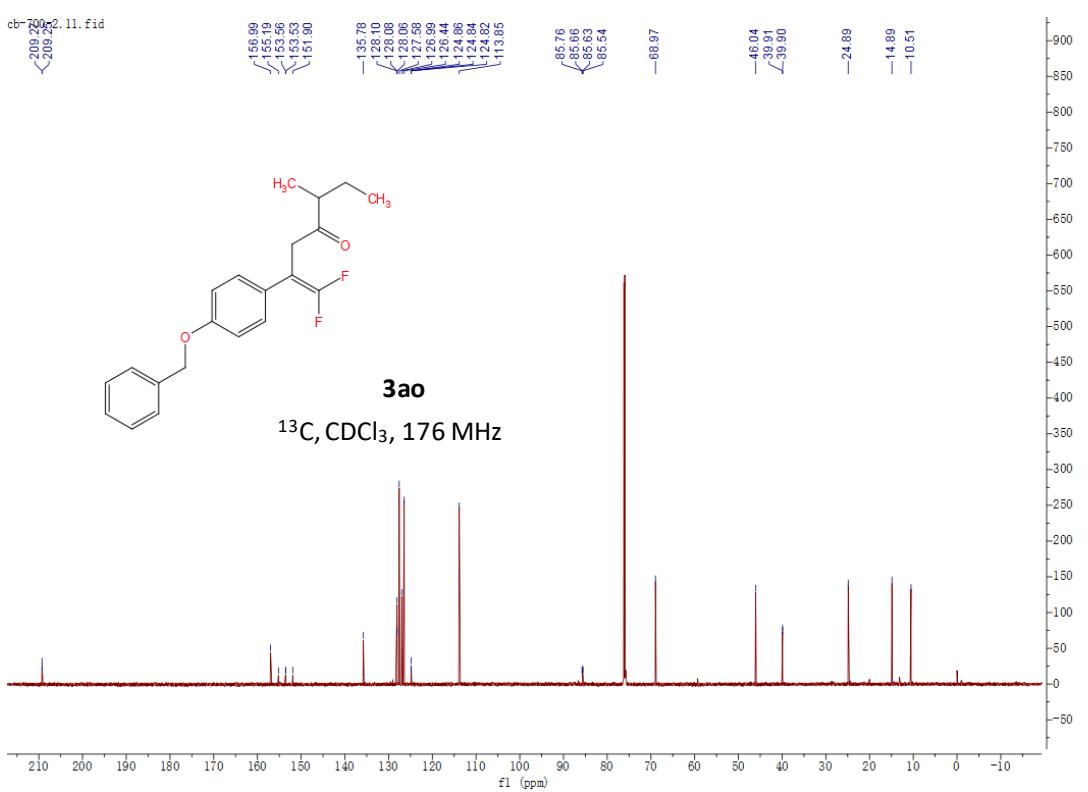
cb-700-2.10.fid



3ao

¹H, CDCl₃, 700 MHz

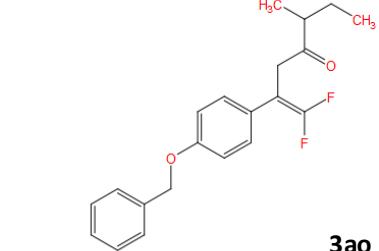
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<209 224



3ao

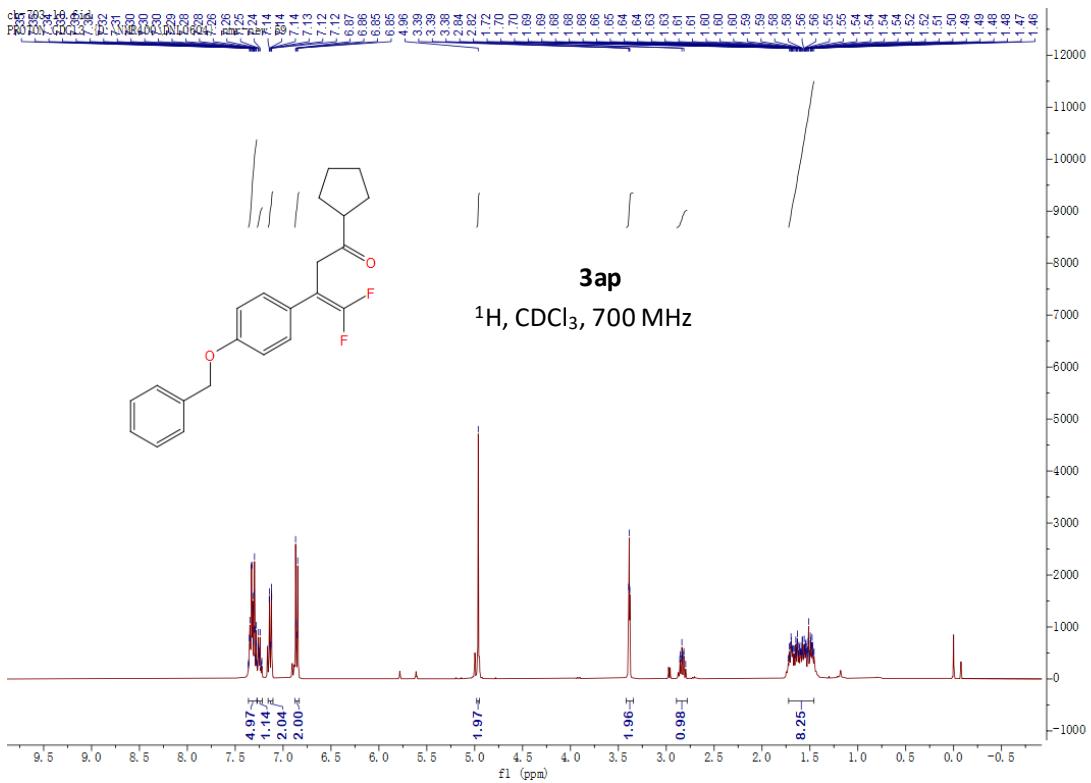
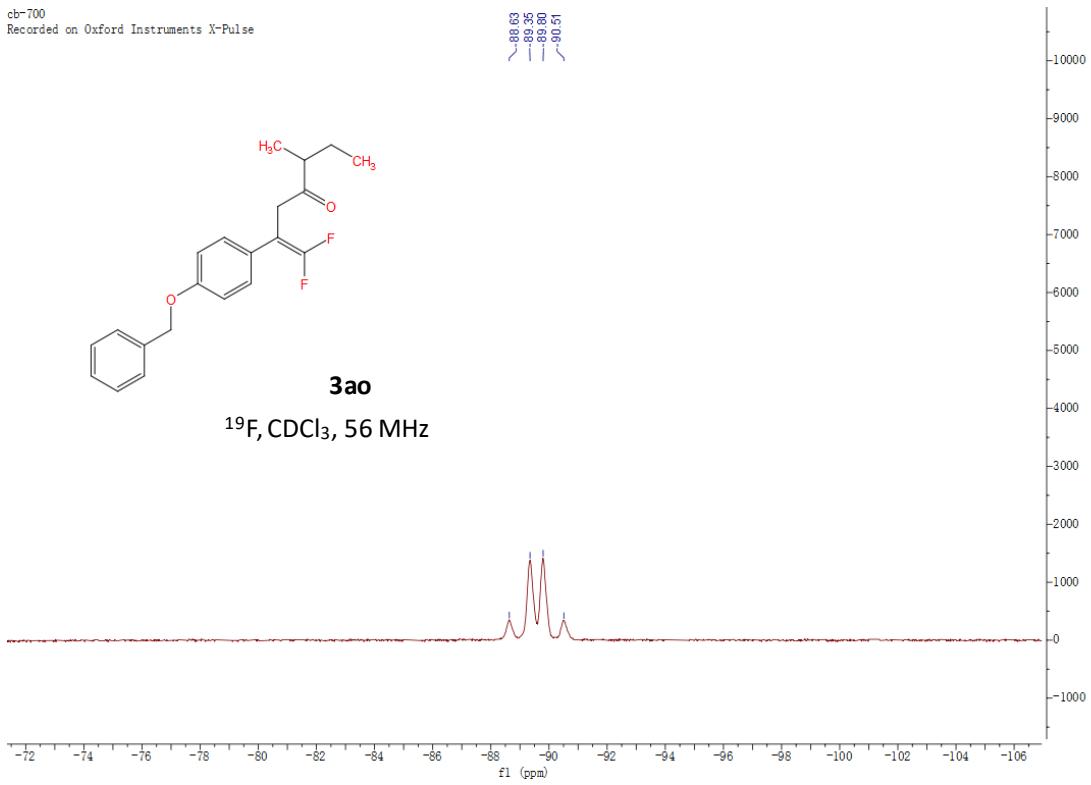
¹³C, CDCl₃, 176 MHz

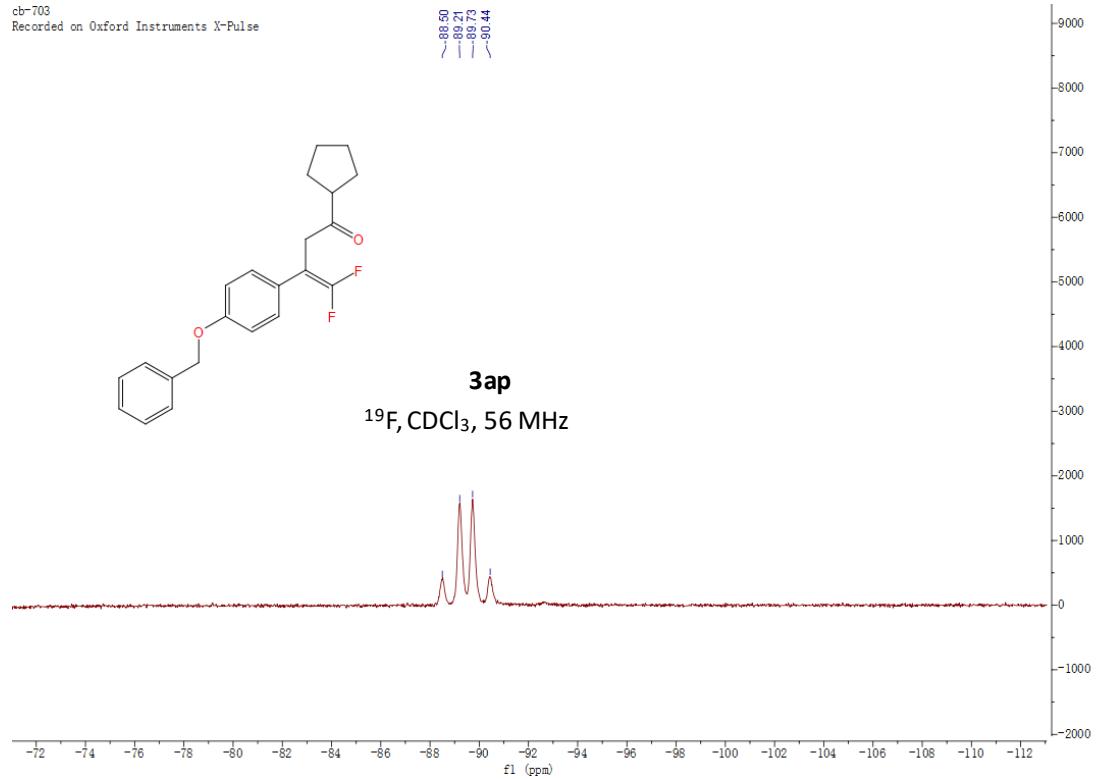
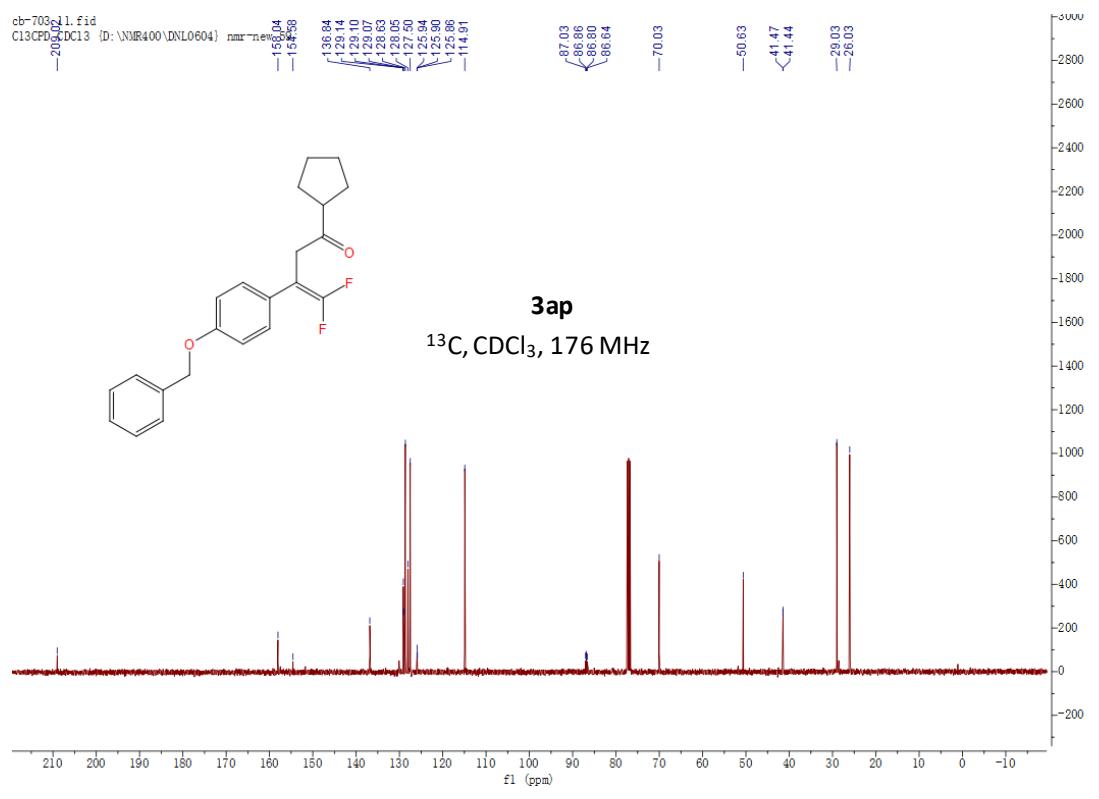
cb-700
Recorded on Oxford Instruments X-Pulse

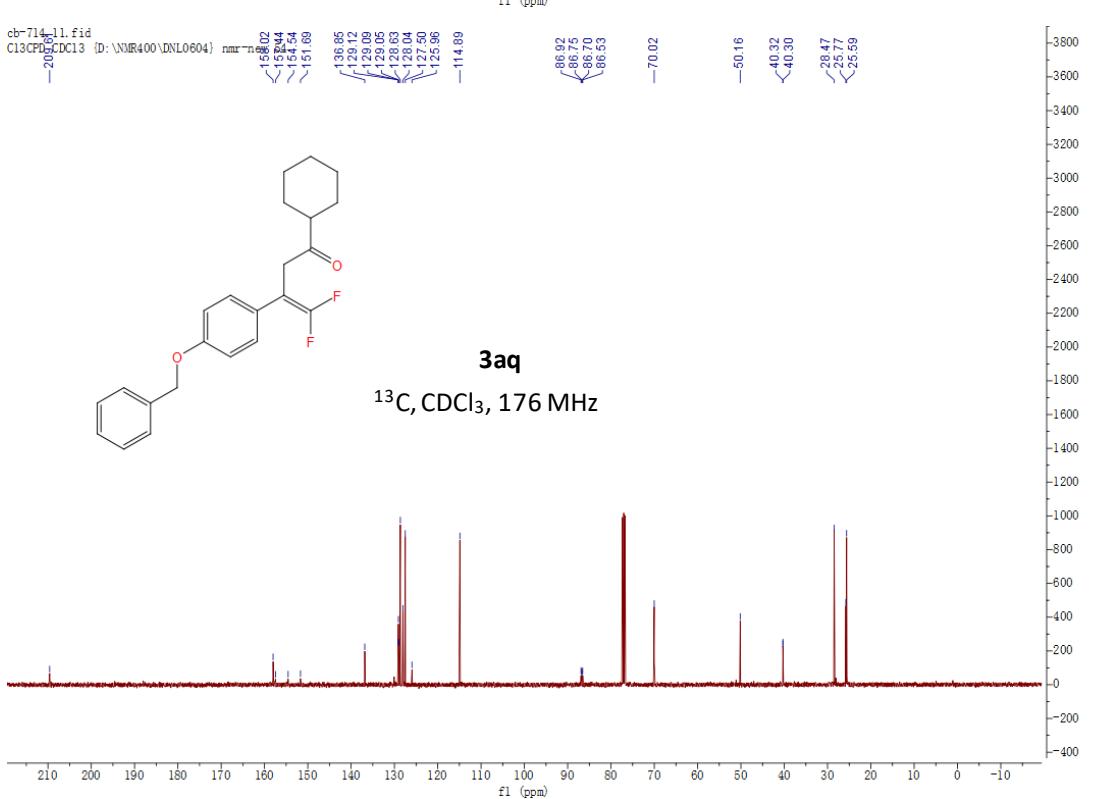
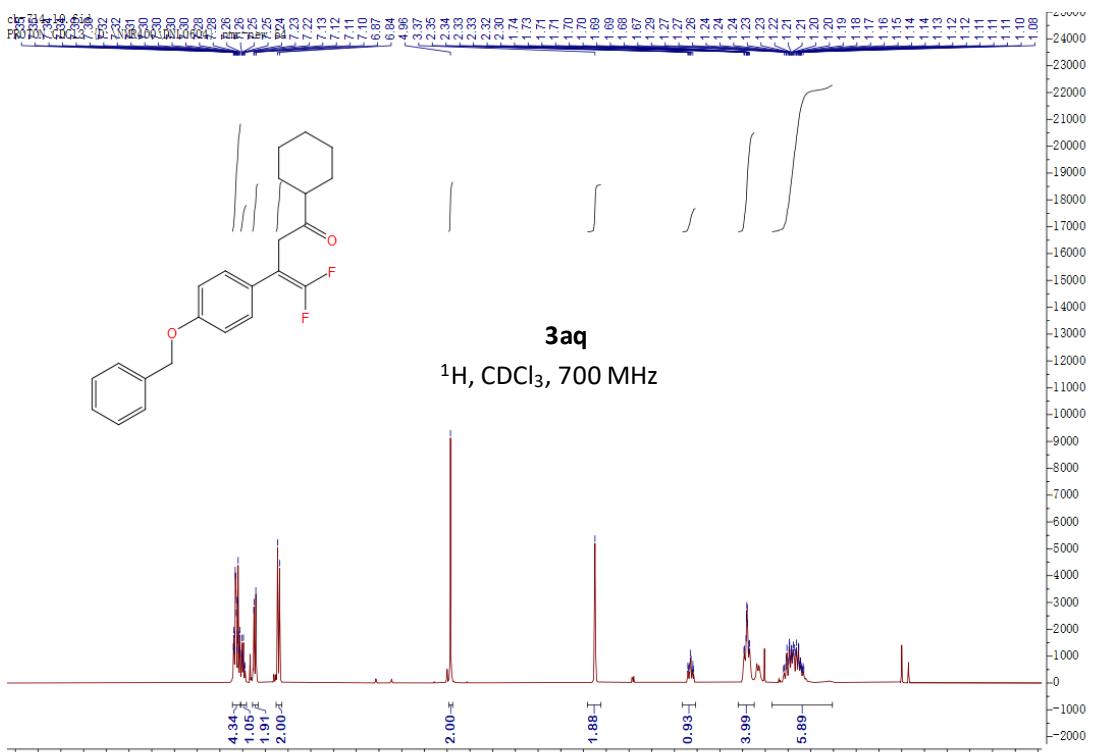


3ao

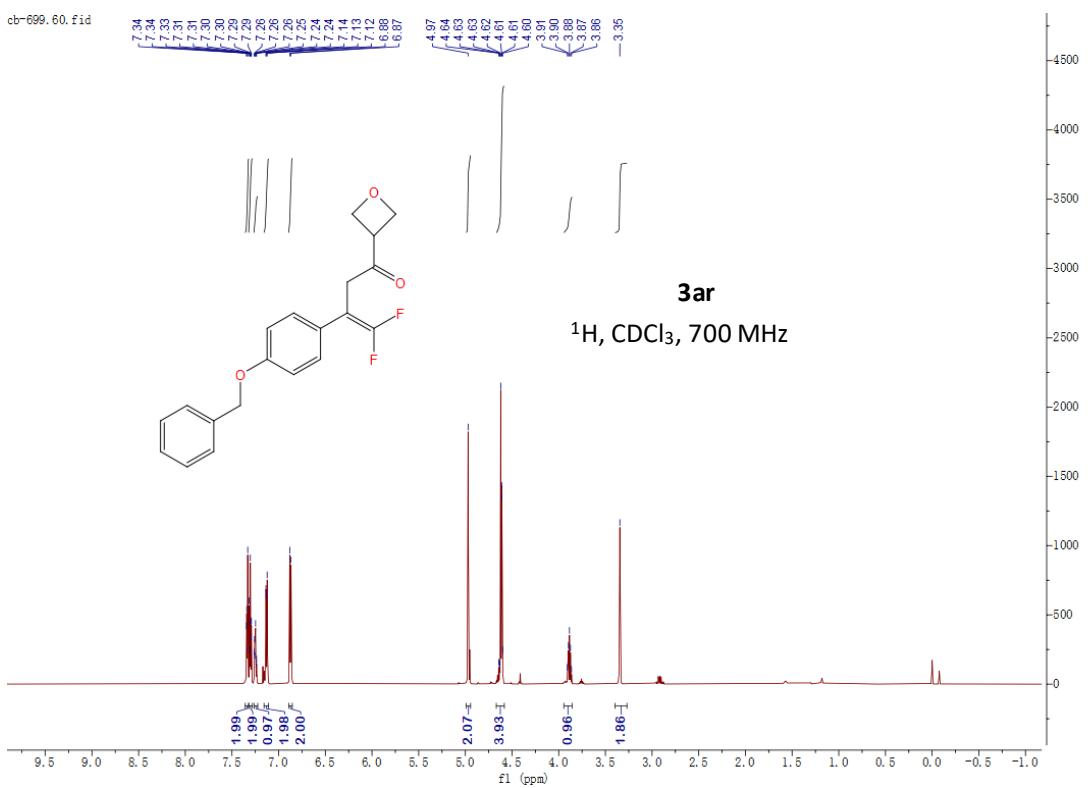
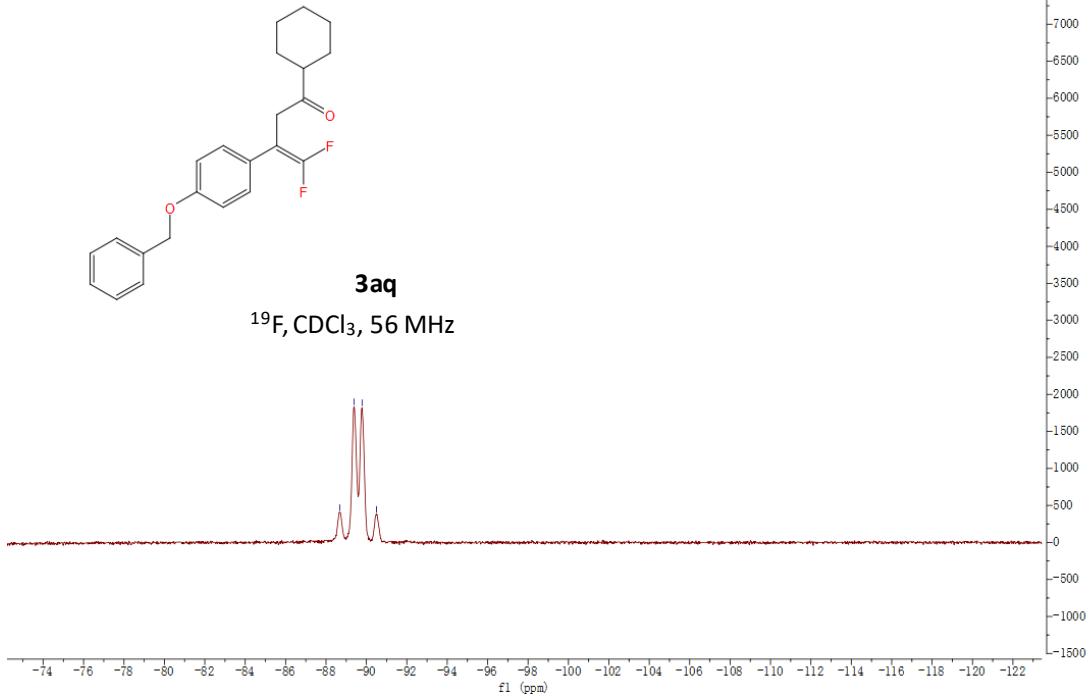
¹⁹F, CDCl₃, 56 MHz

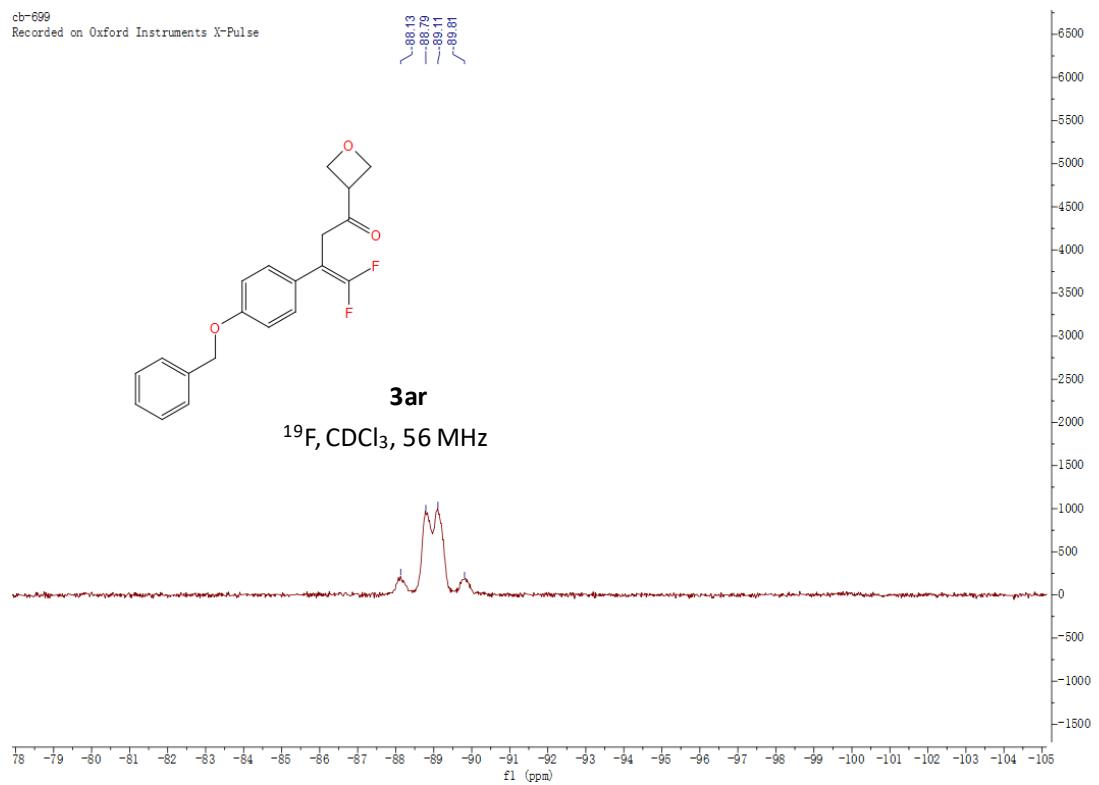
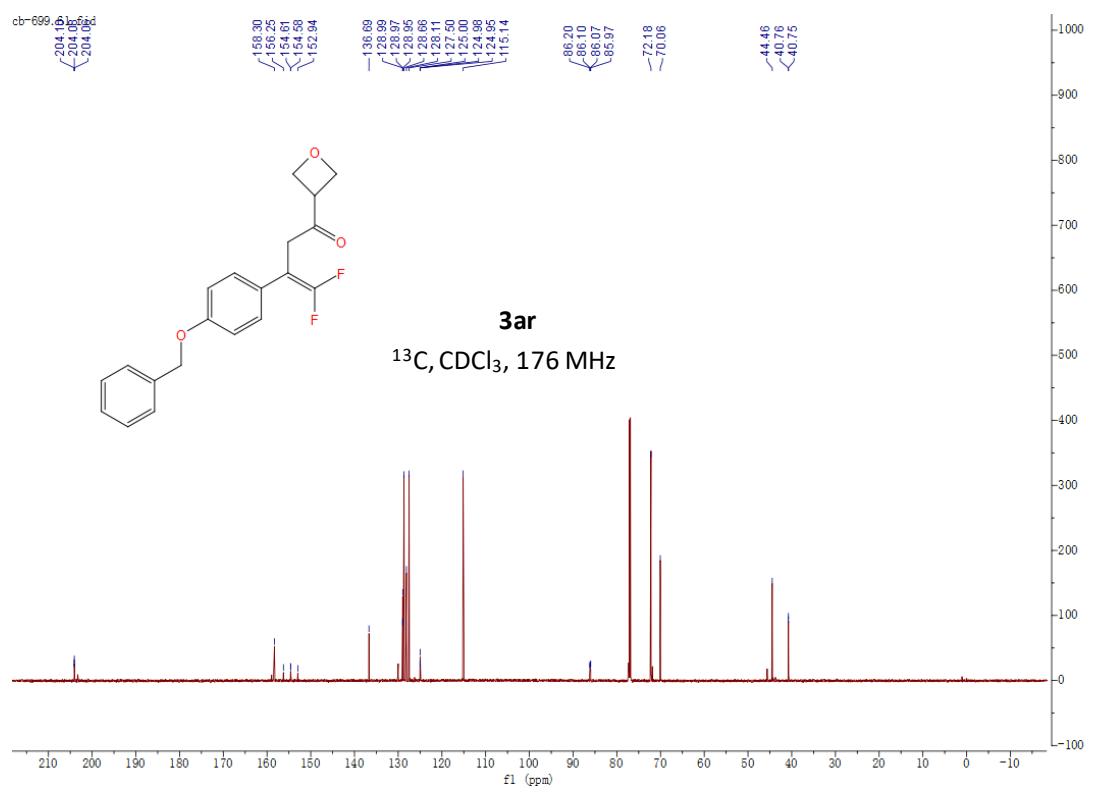


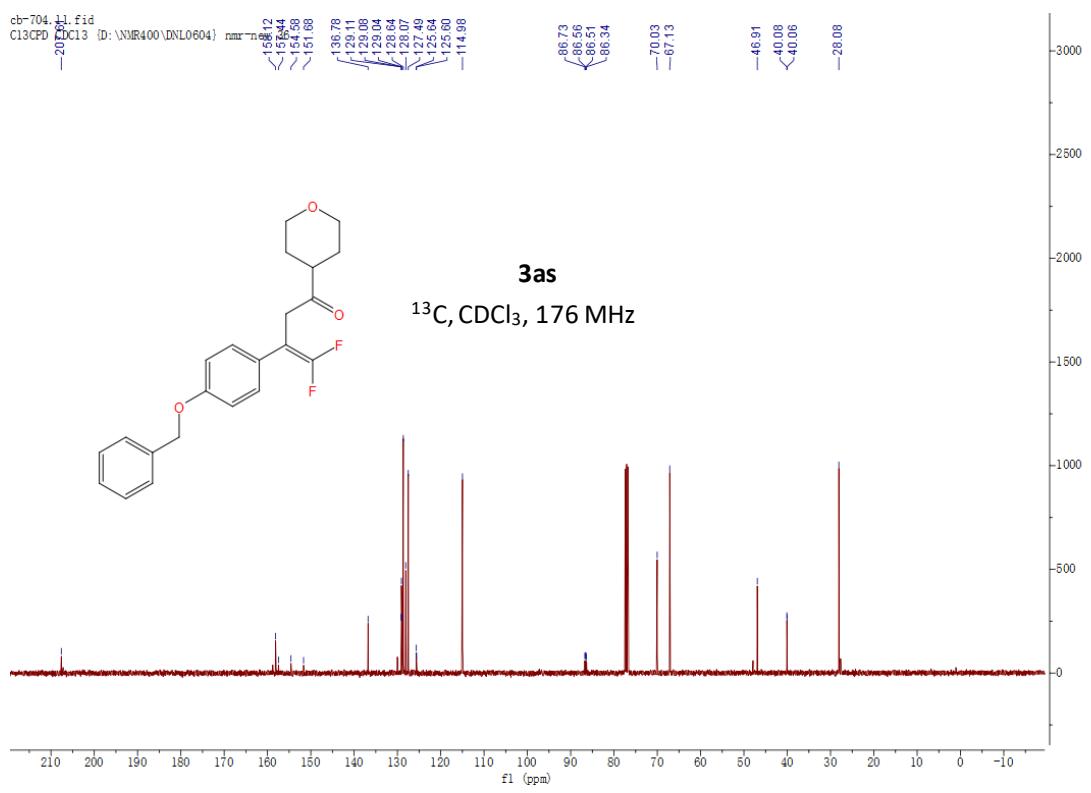
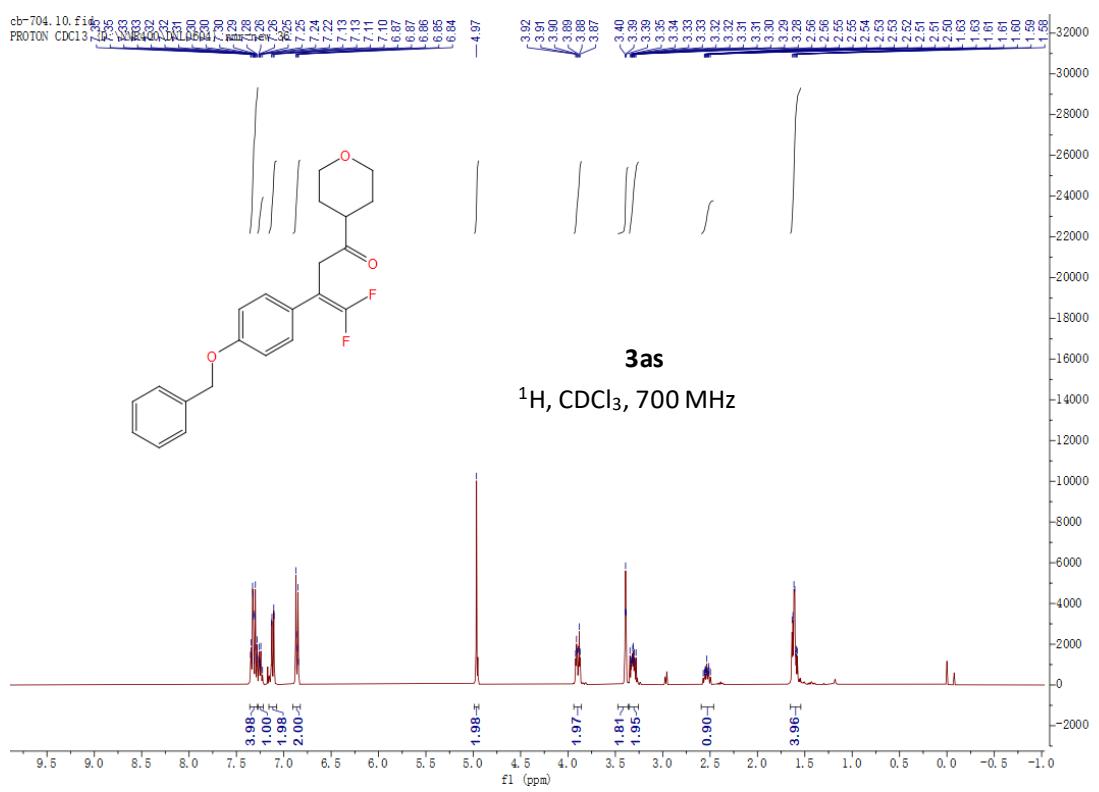




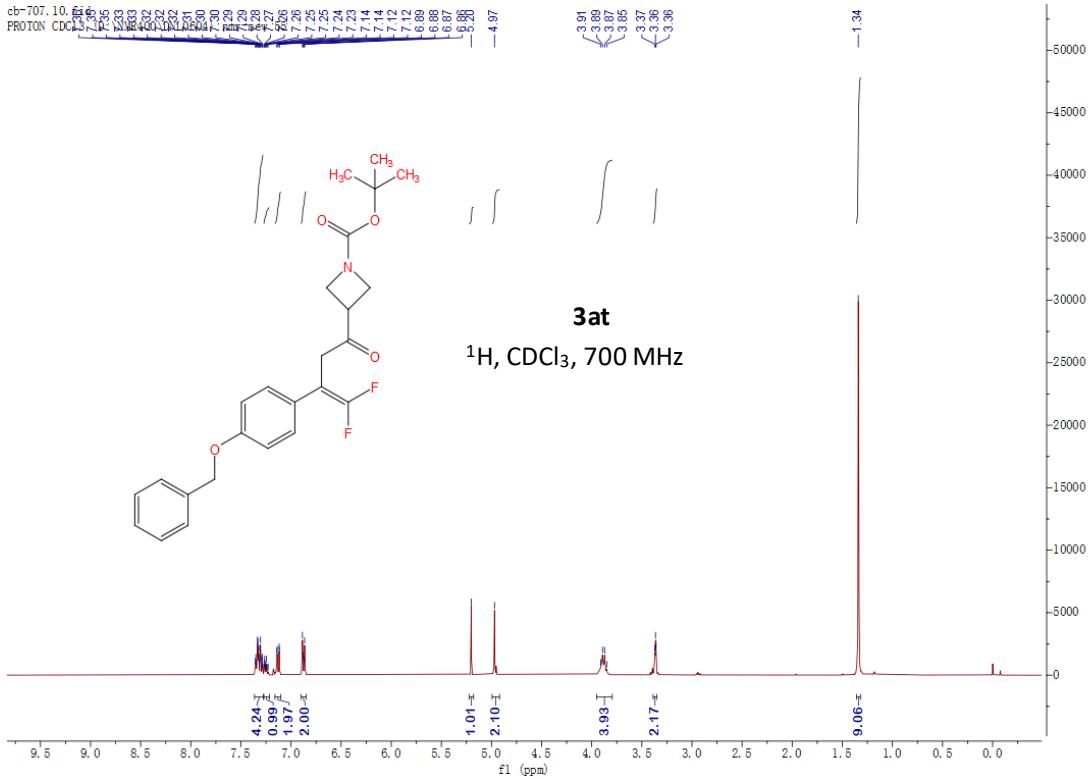
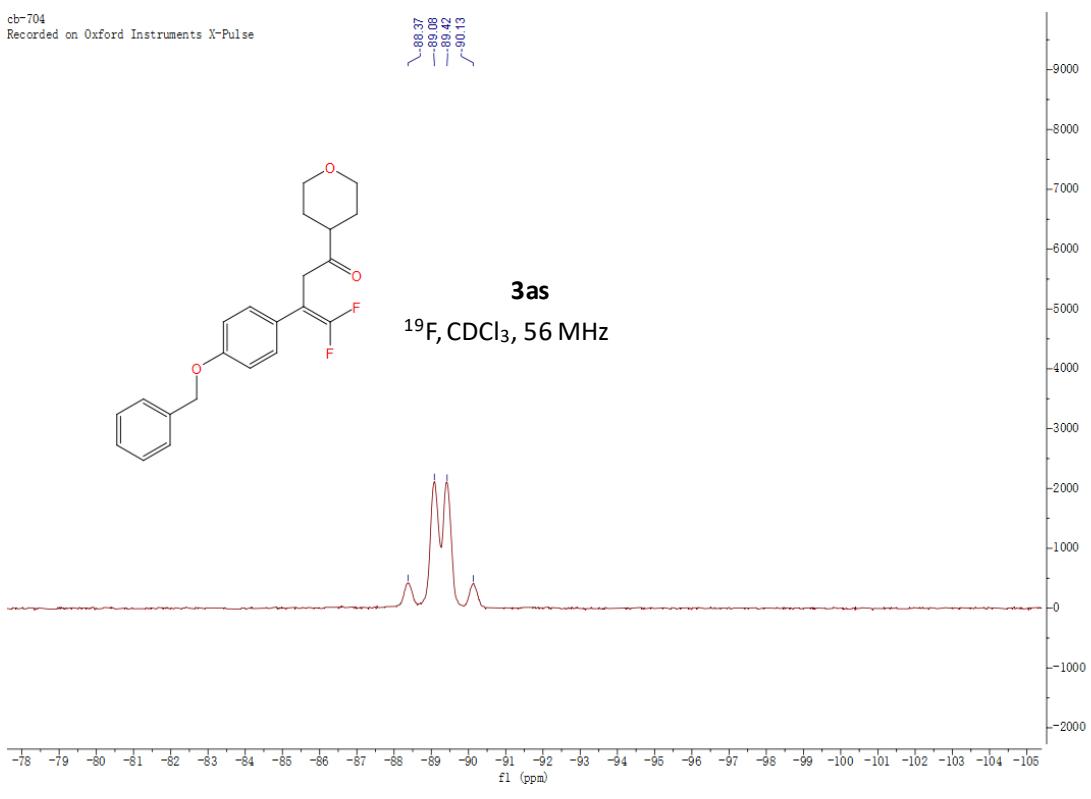
cb-714
Recorded on Oxford Instruments X-Pulse

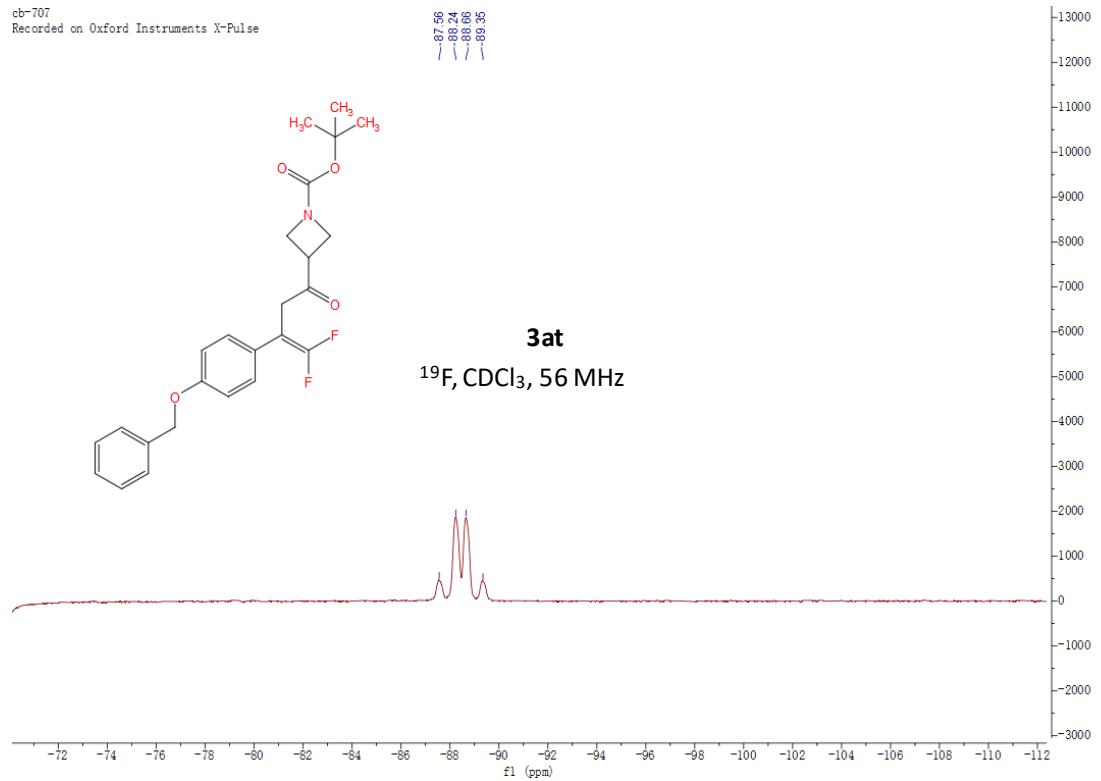
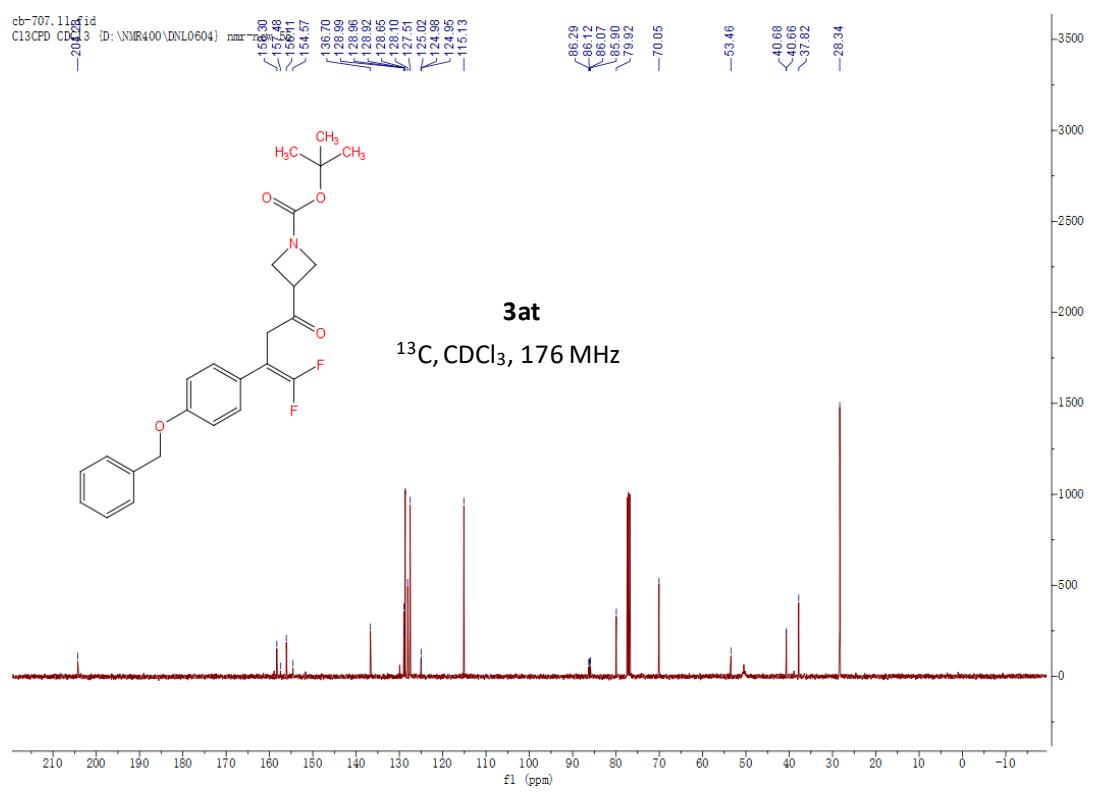


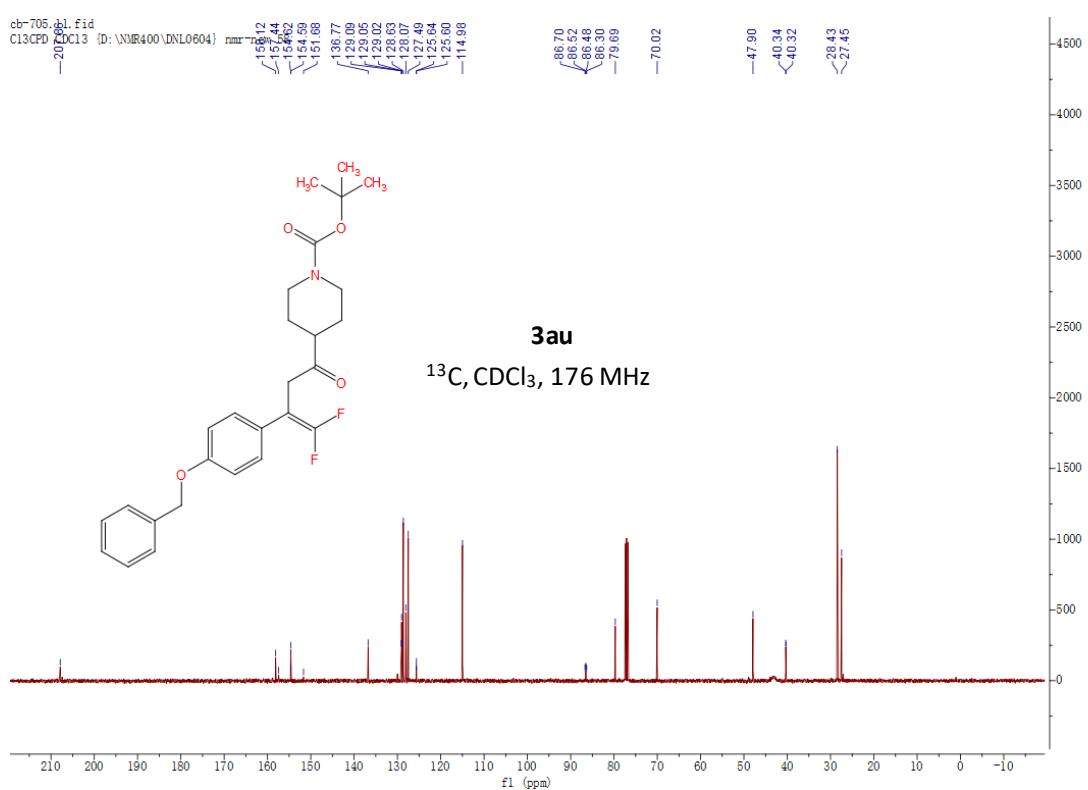
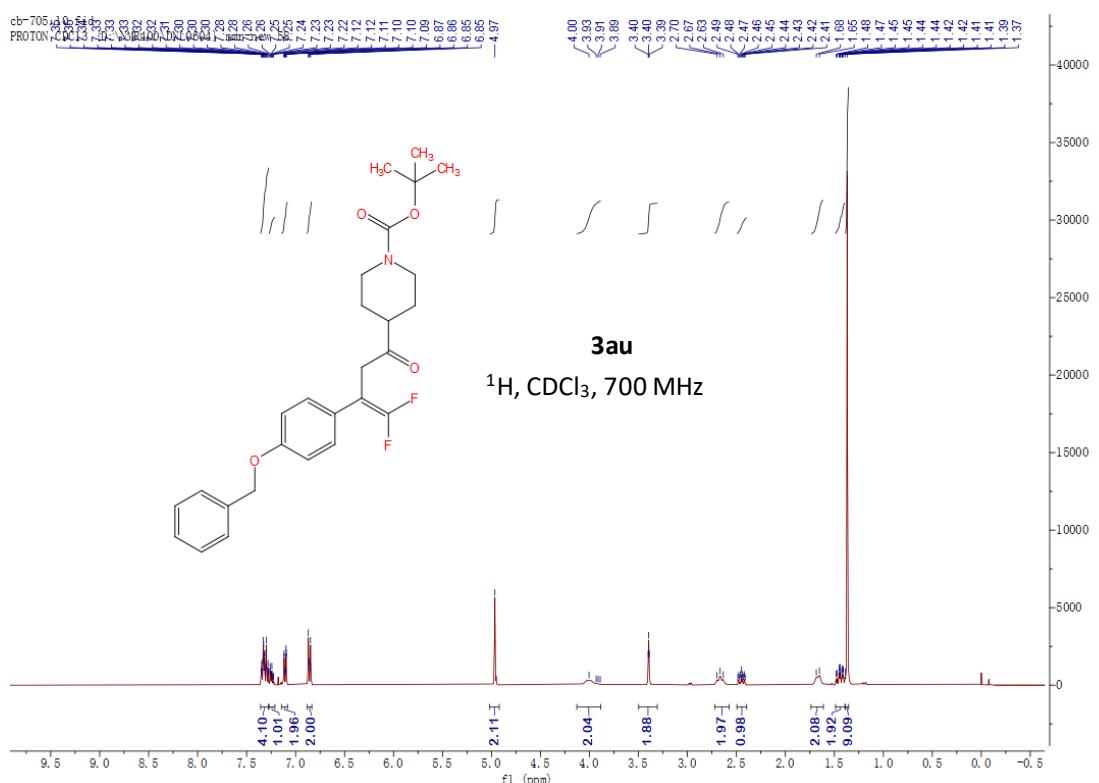




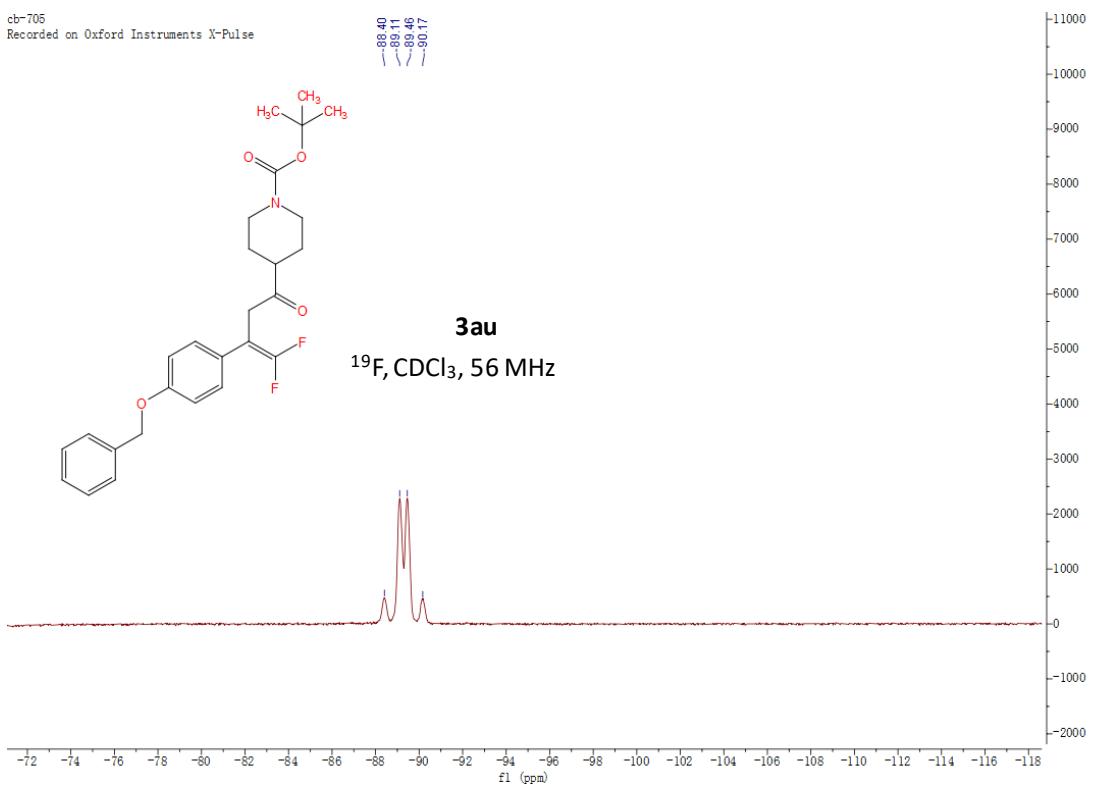
cb-704
Recorded on Oxford Instruments X-Pulse



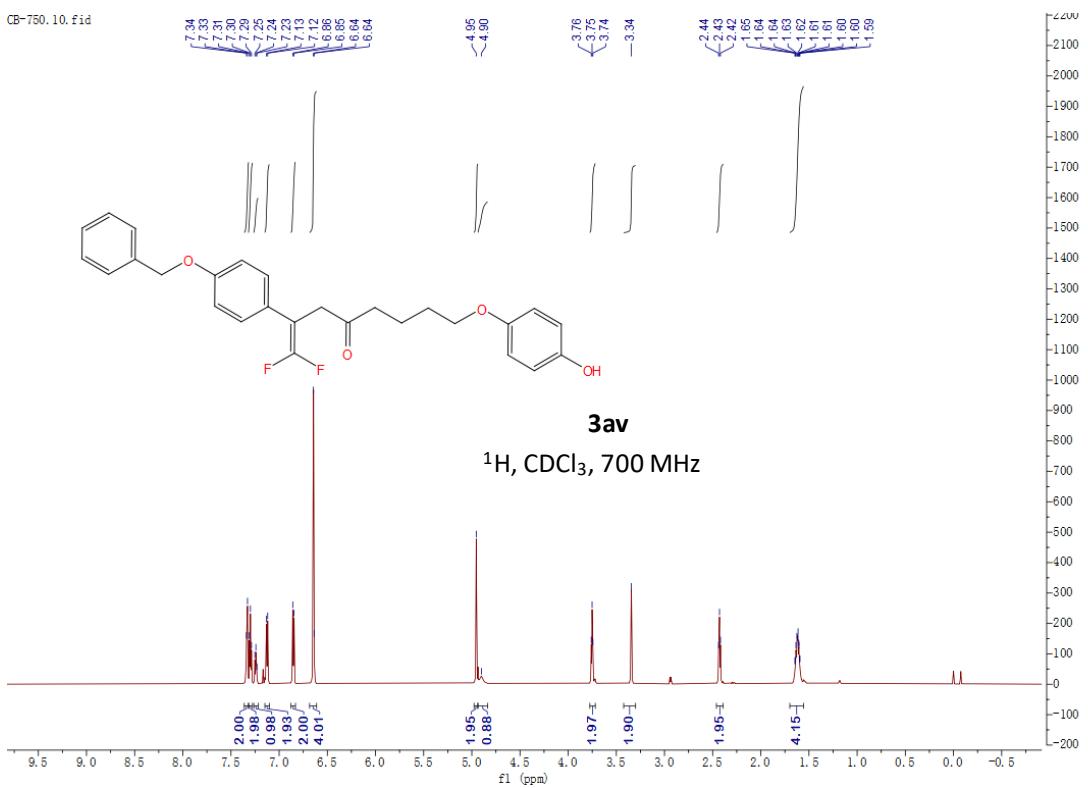


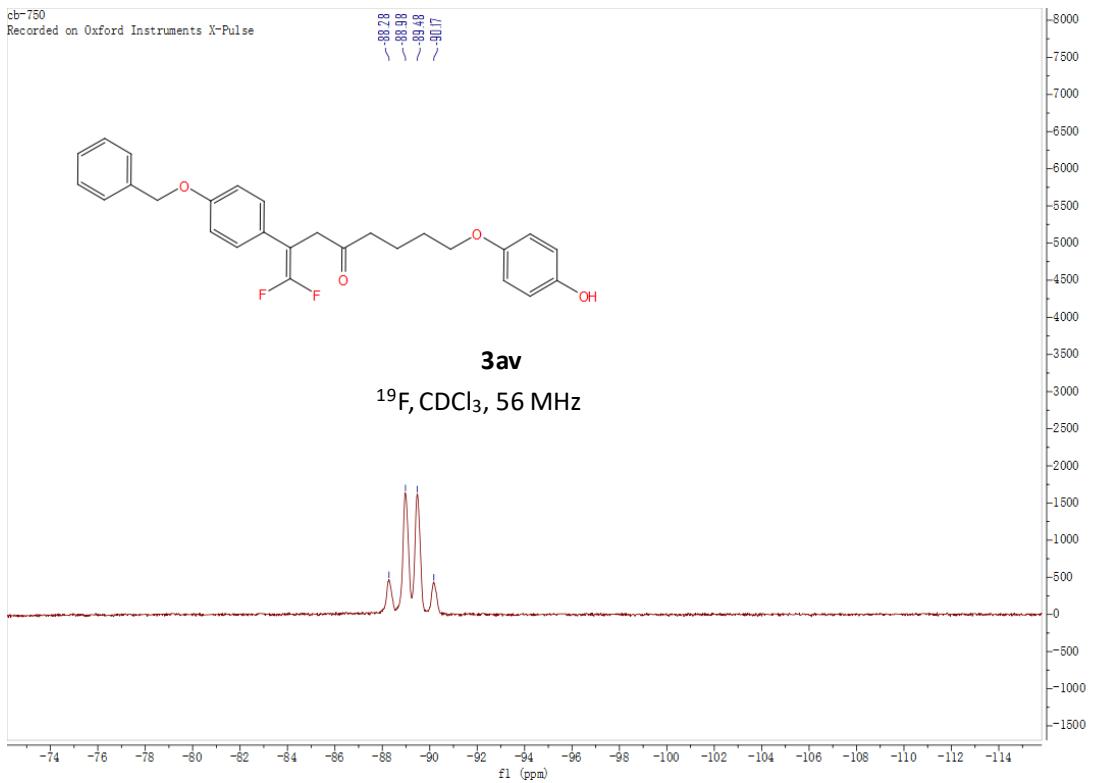
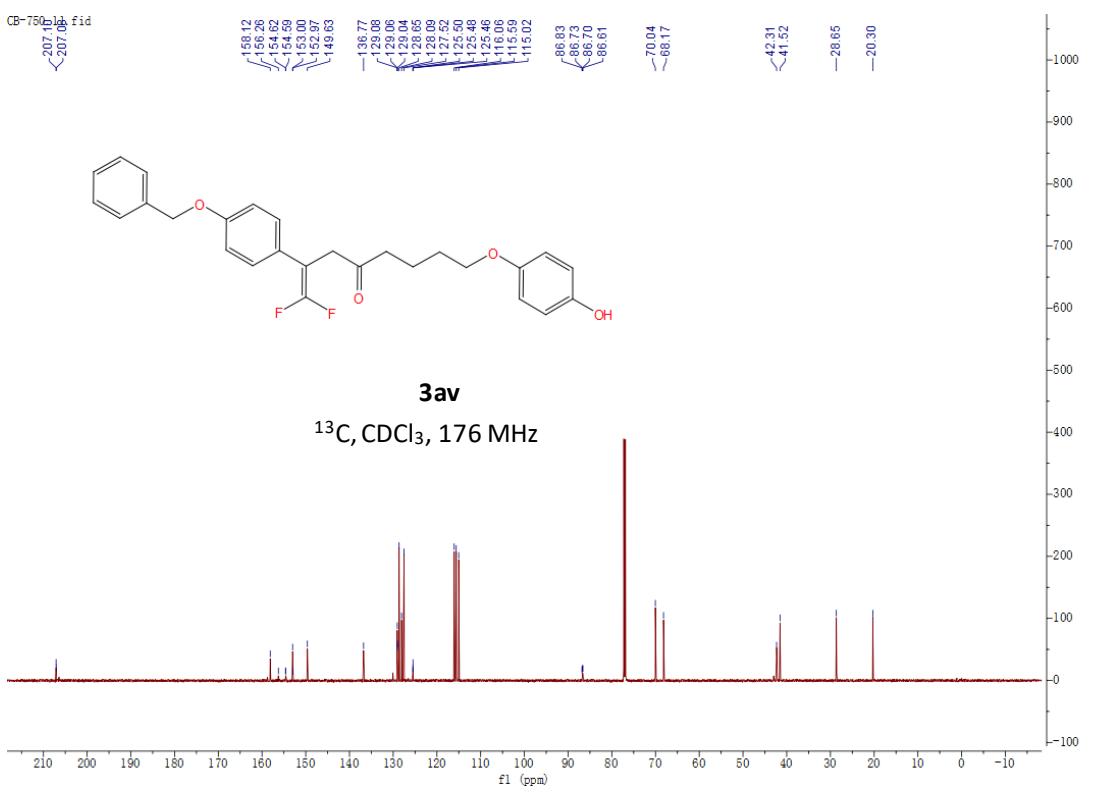


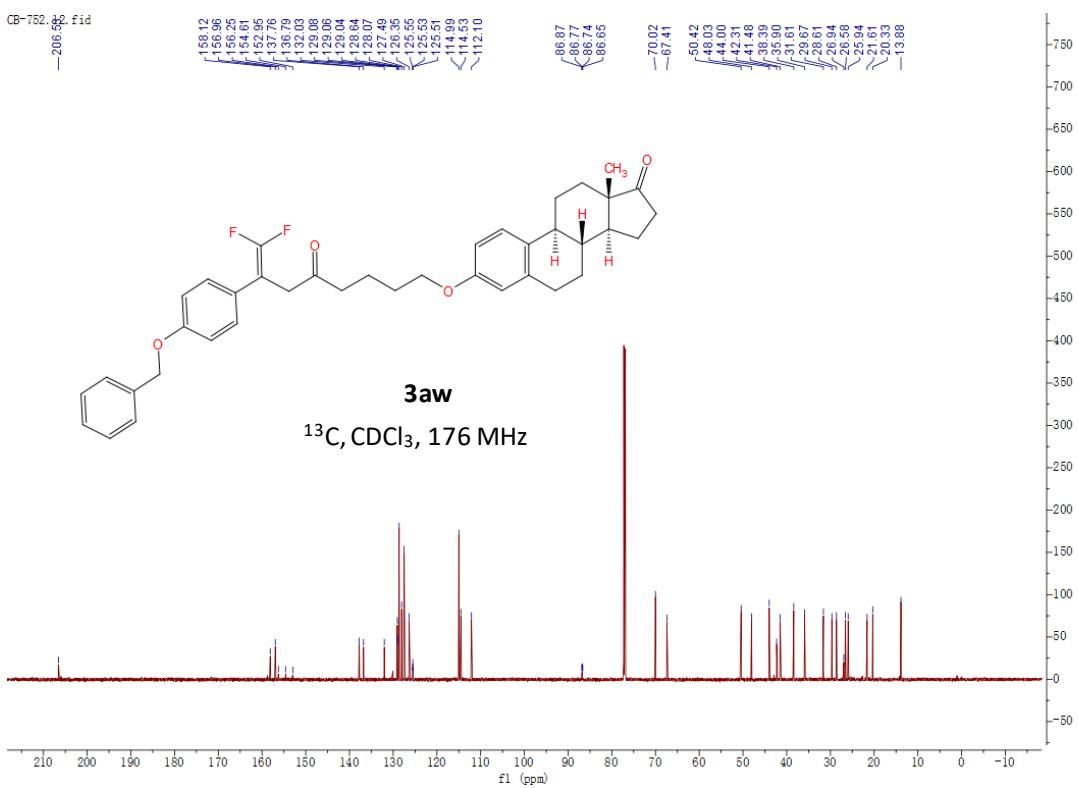
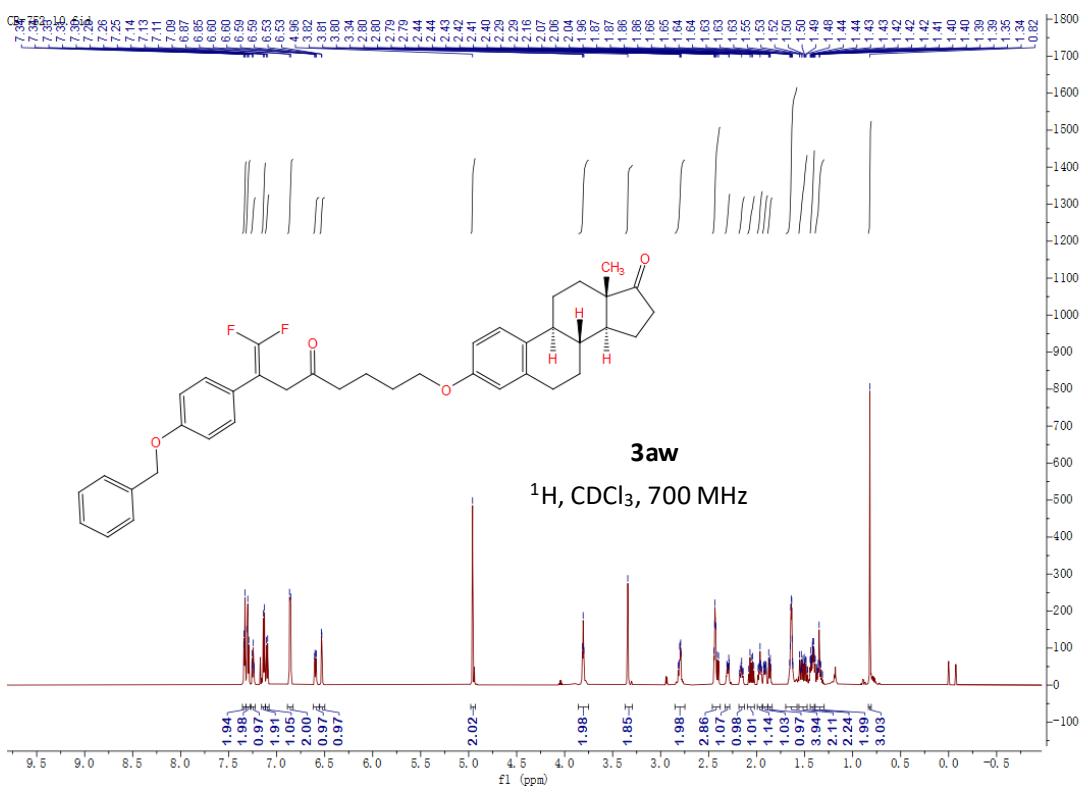
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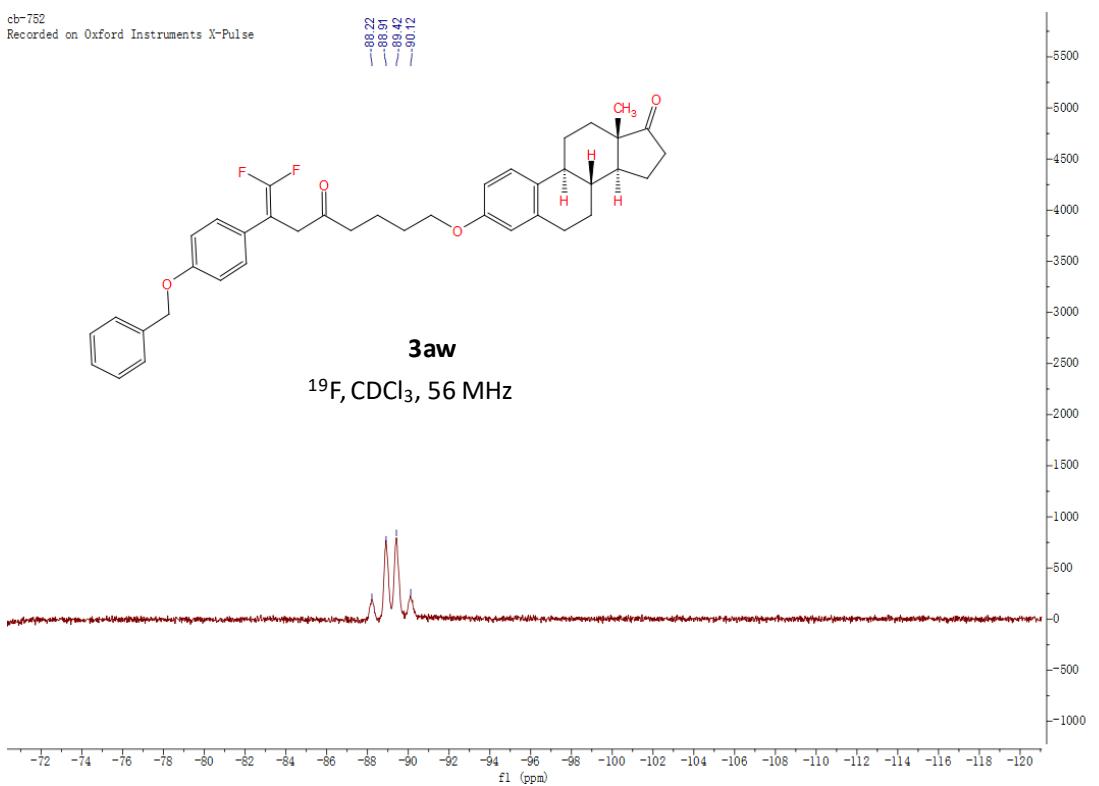
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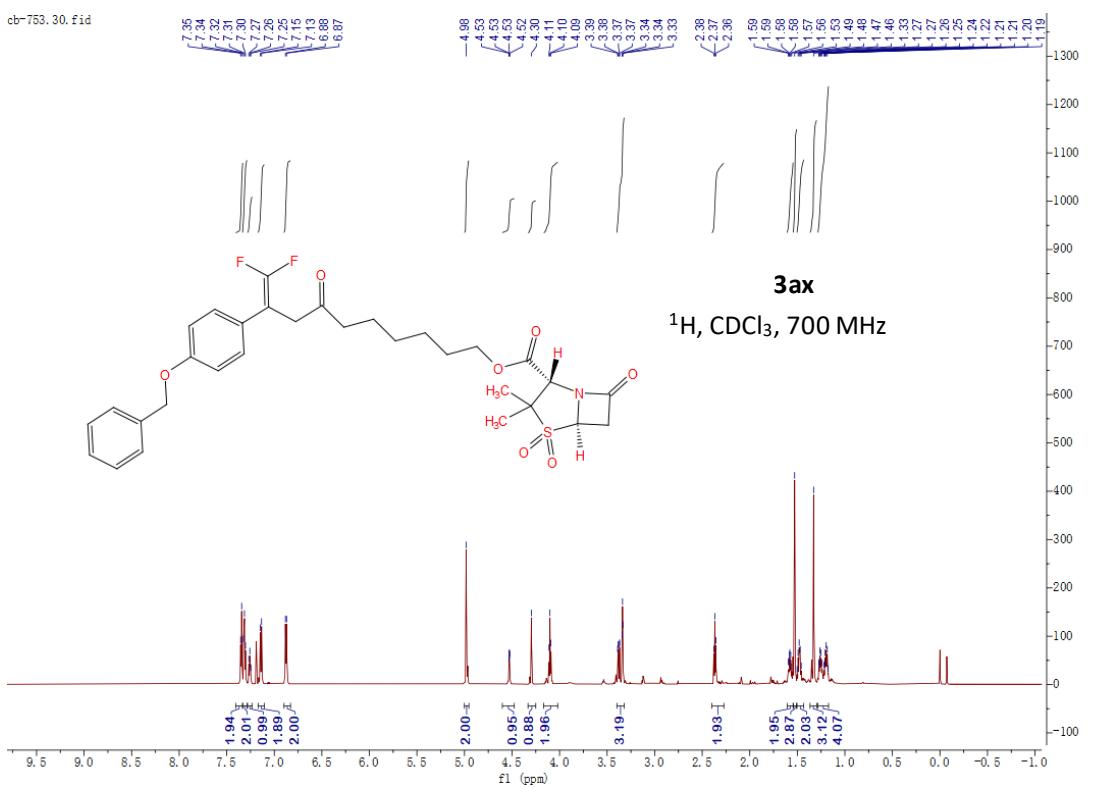




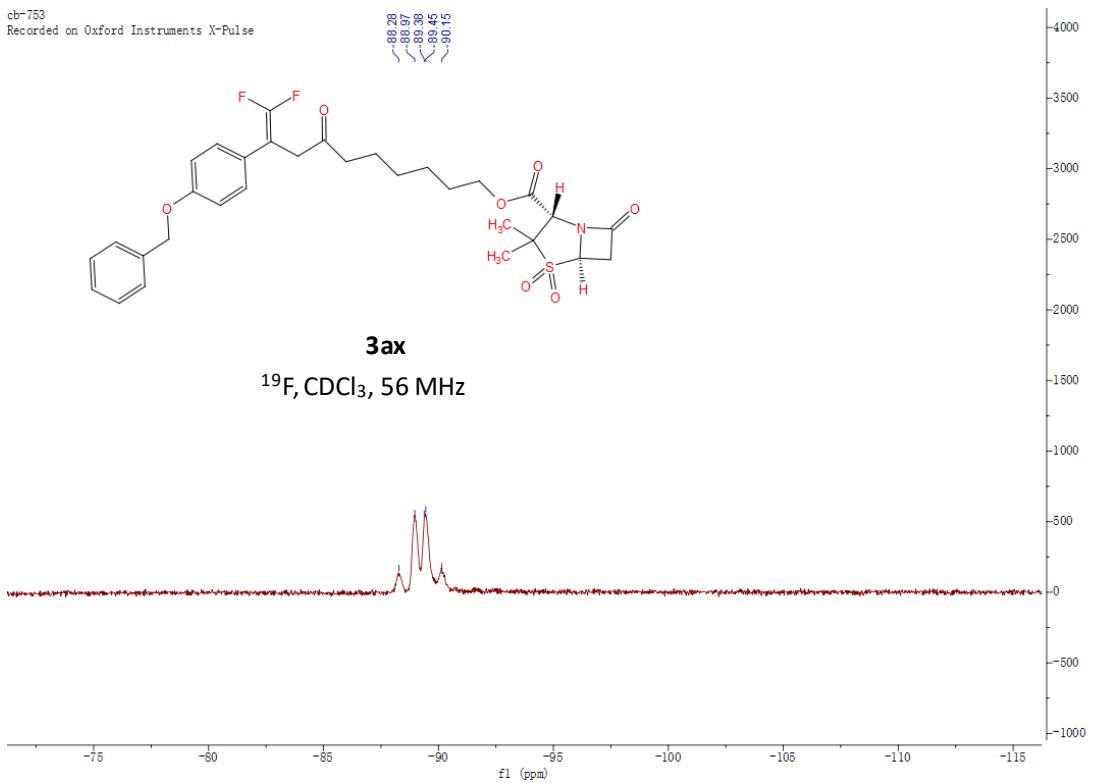
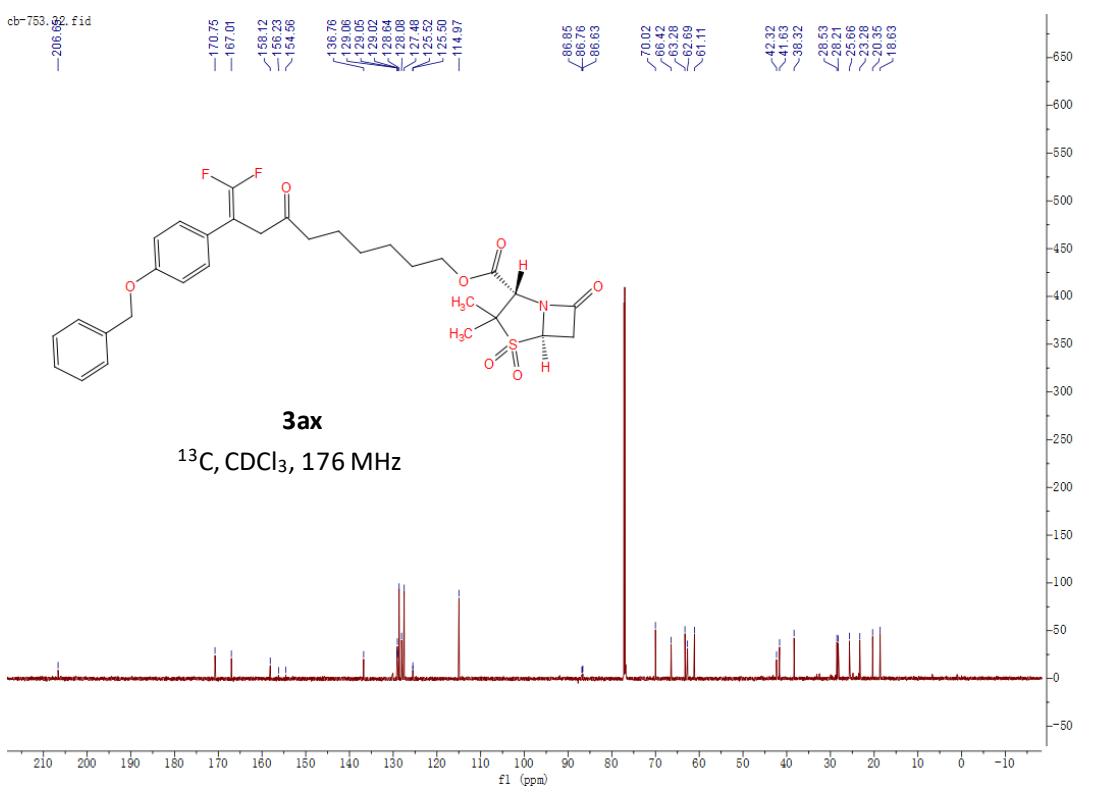
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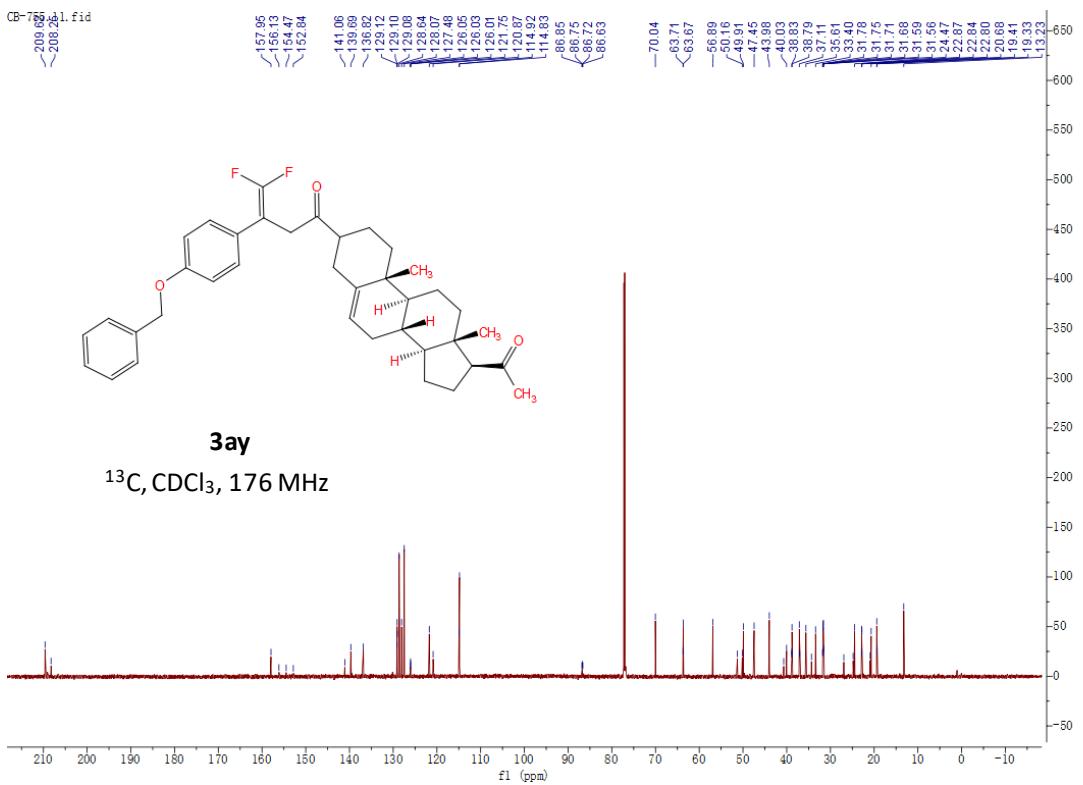
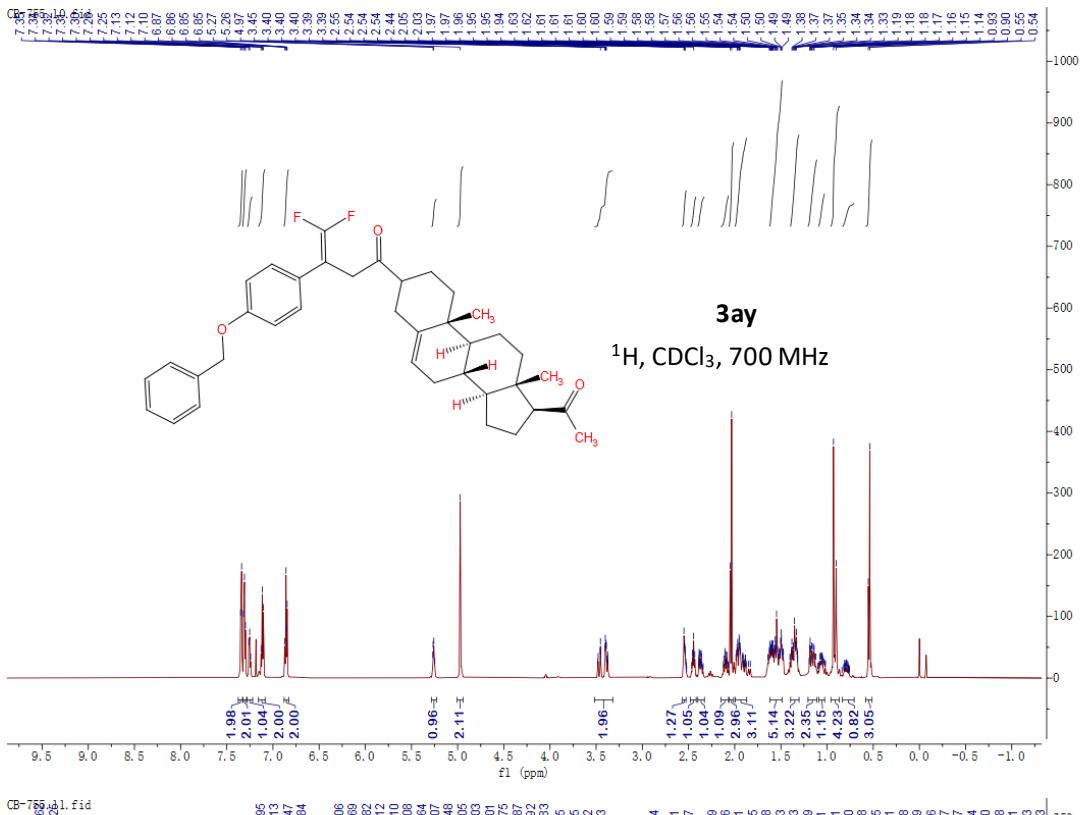


3aw
¹⁹F, CDCl₃, 56 MHz

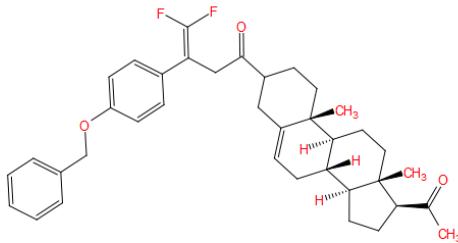


3ax
¹H, CDCl₃, 700 MHz



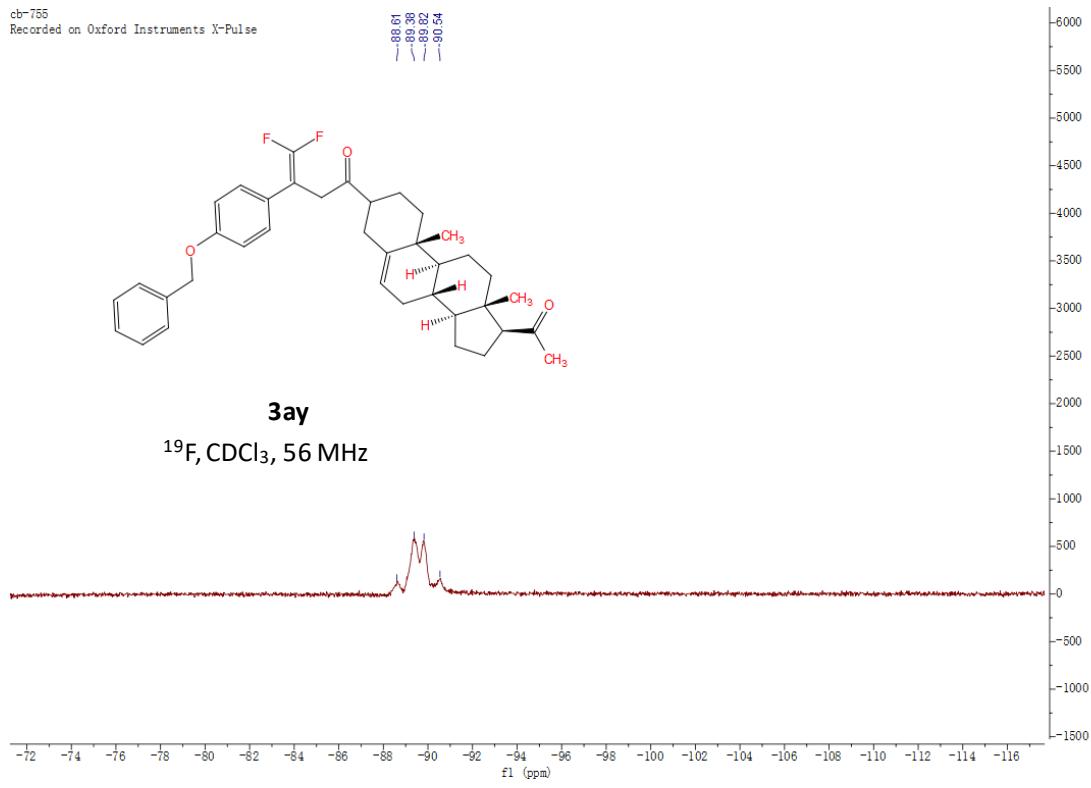


cb-755
Recorded on Oxford Instruments X-Pulse

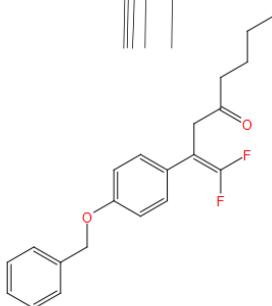


3ay

¹⁹F, CDCl₃, 56 MHz

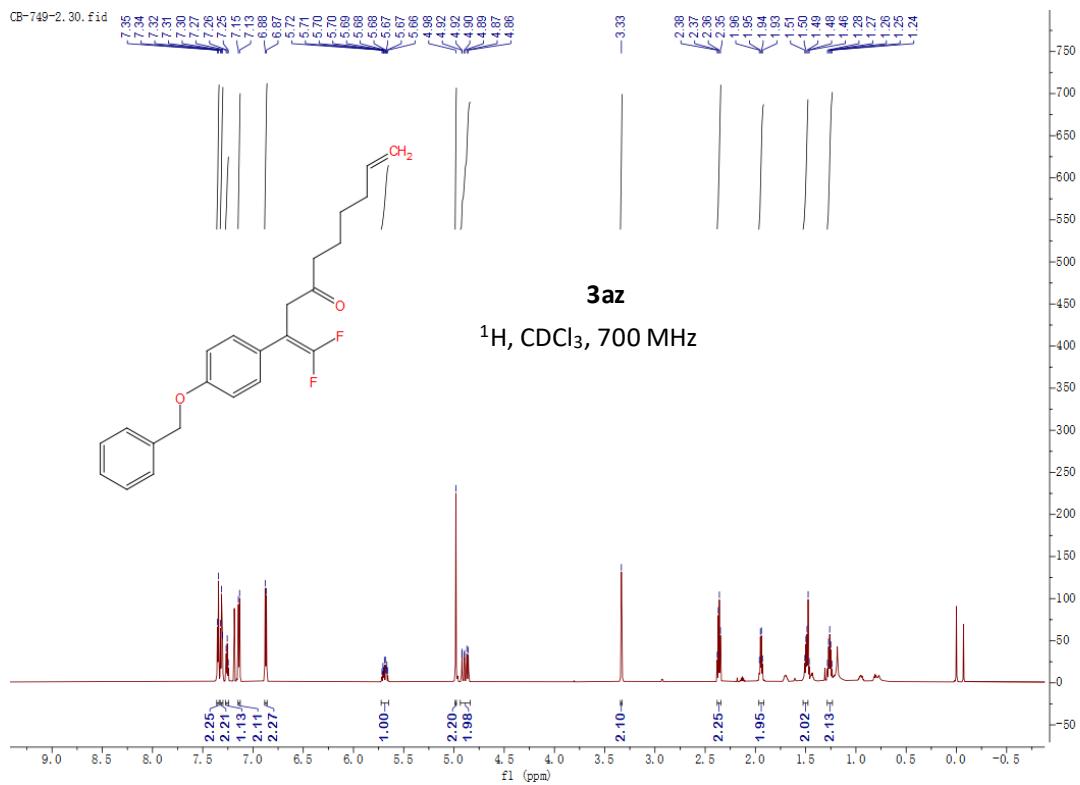


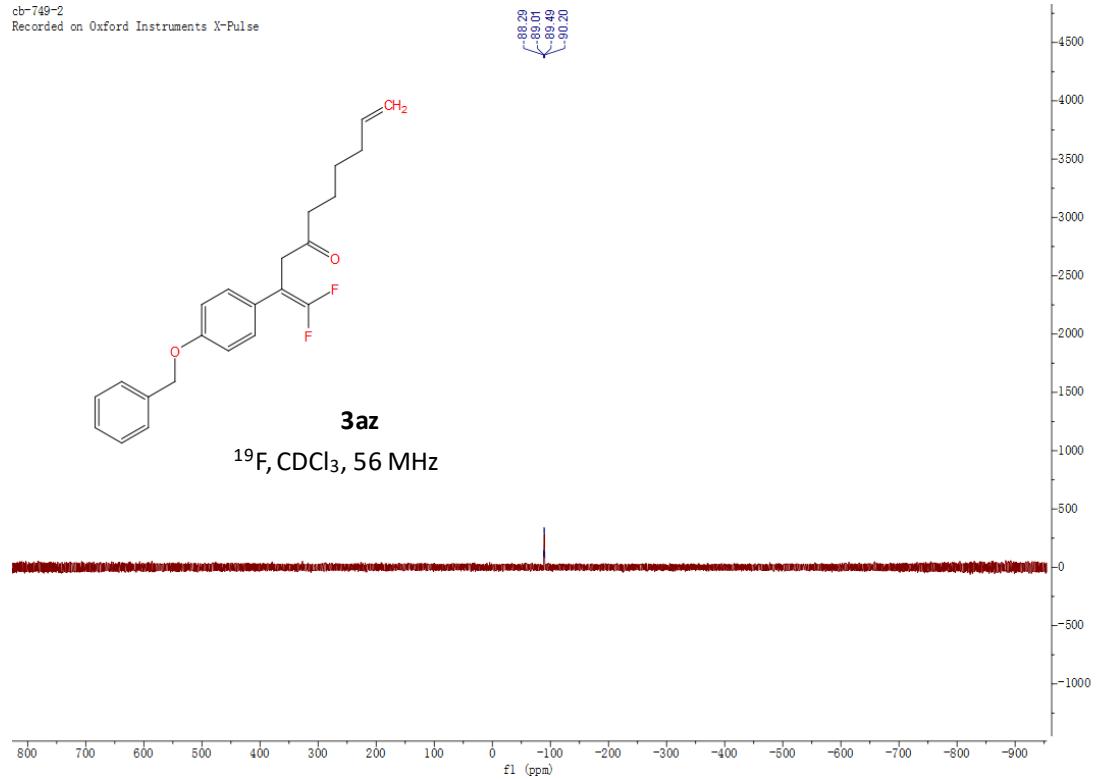
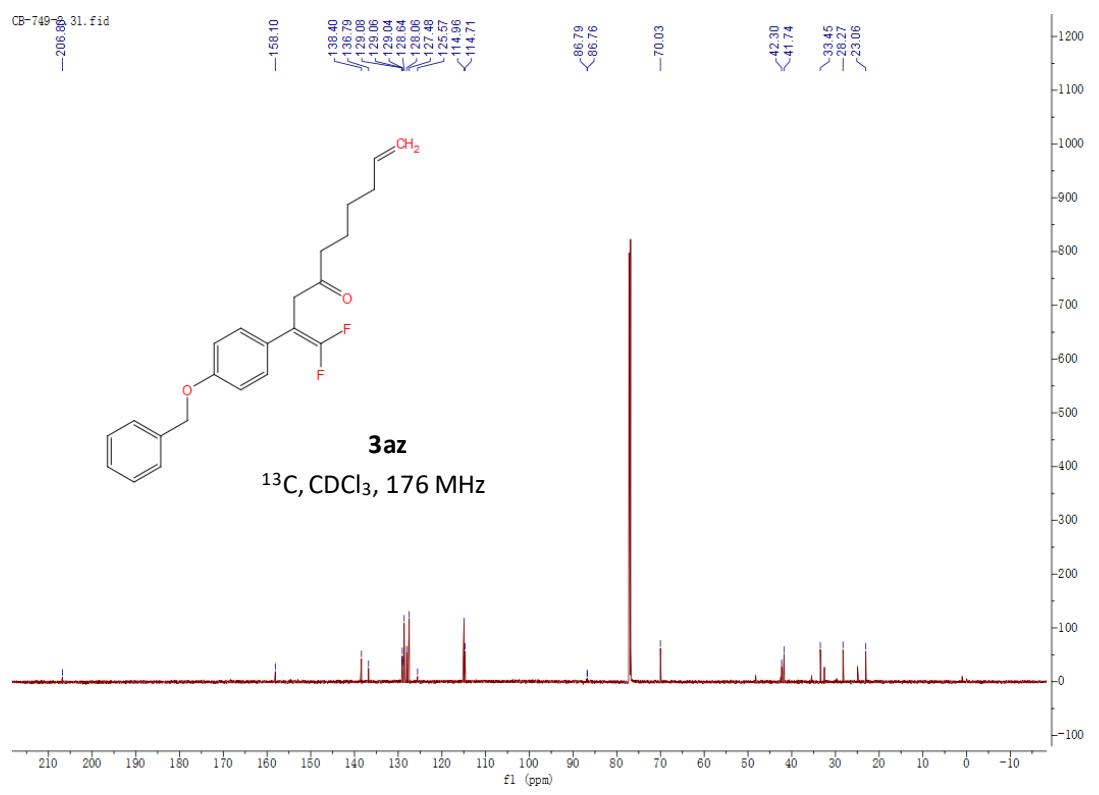
CB-749-2.30. f

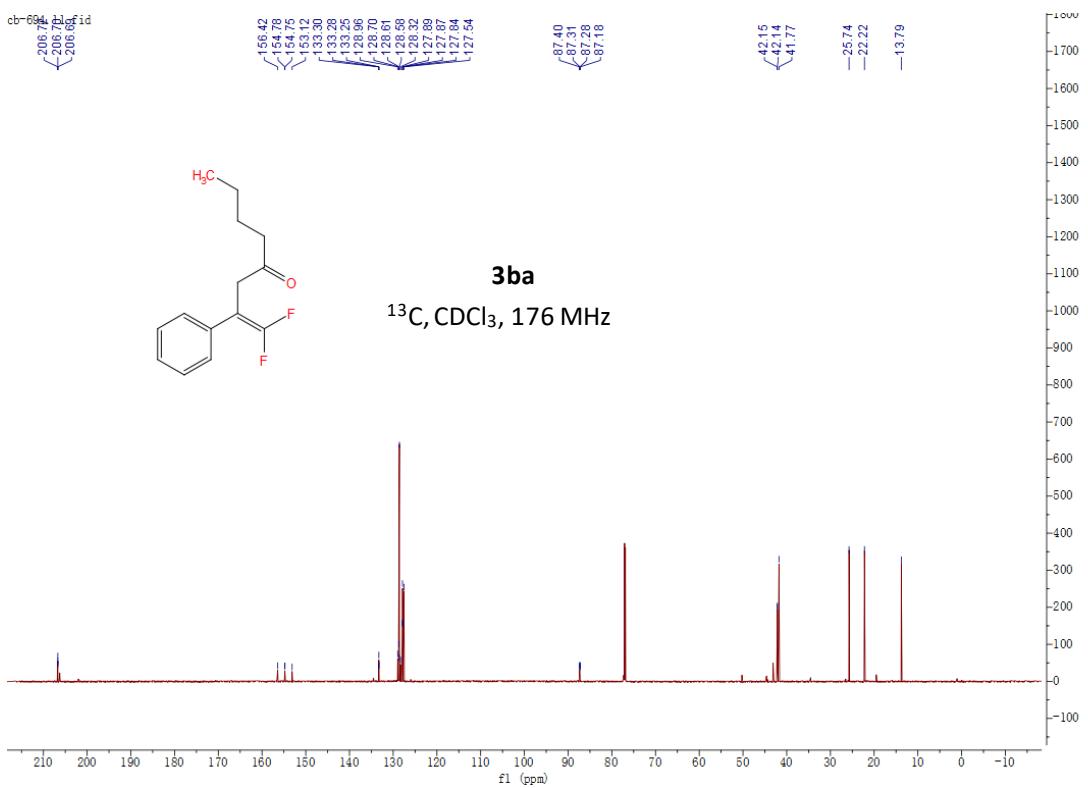
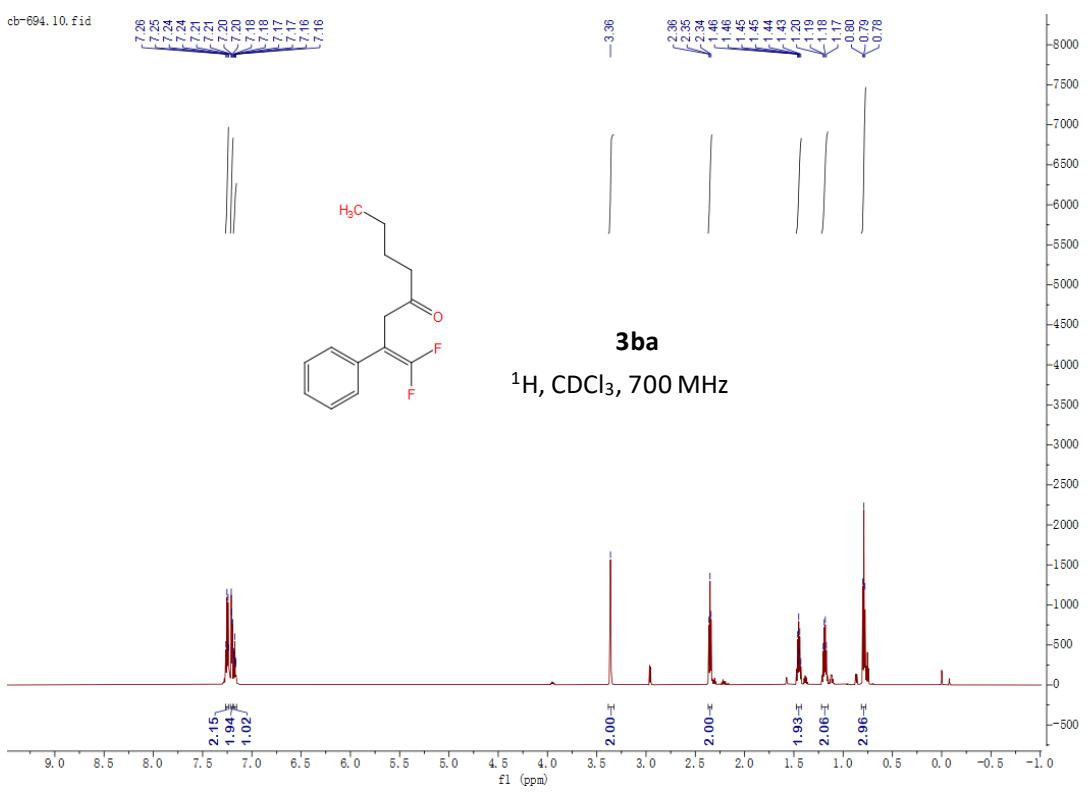


3az

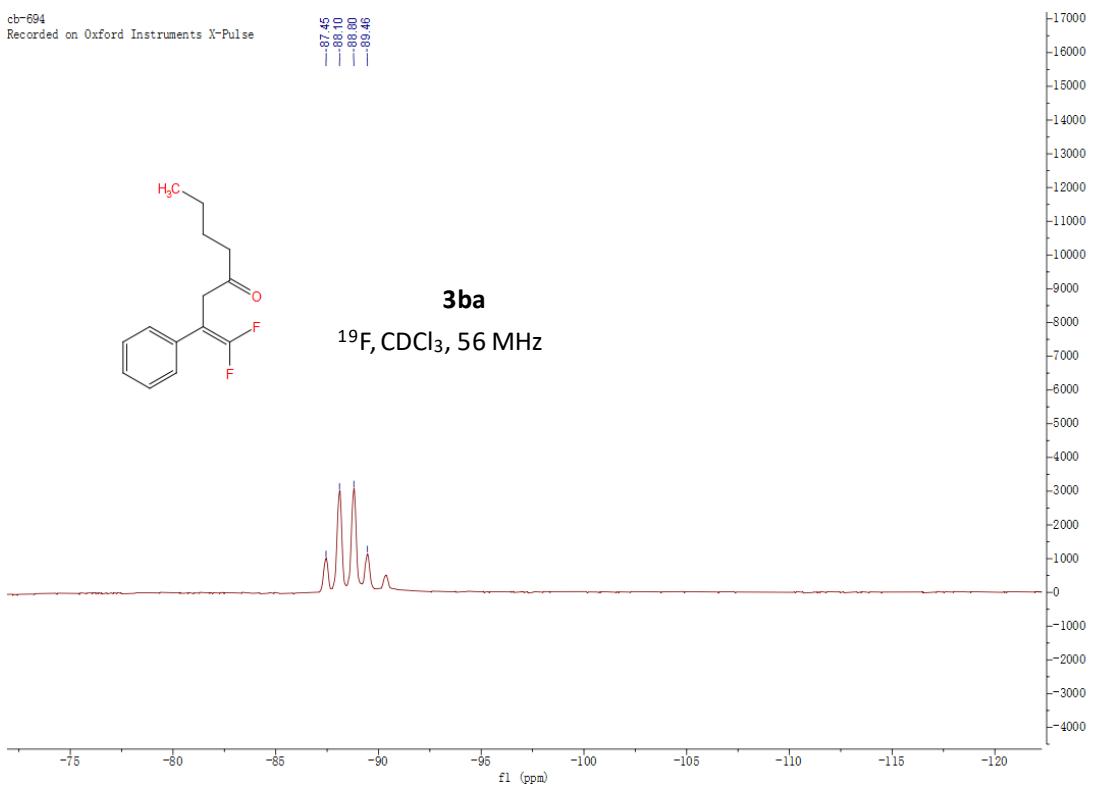
¹H, CDCl₃, 700 MHz



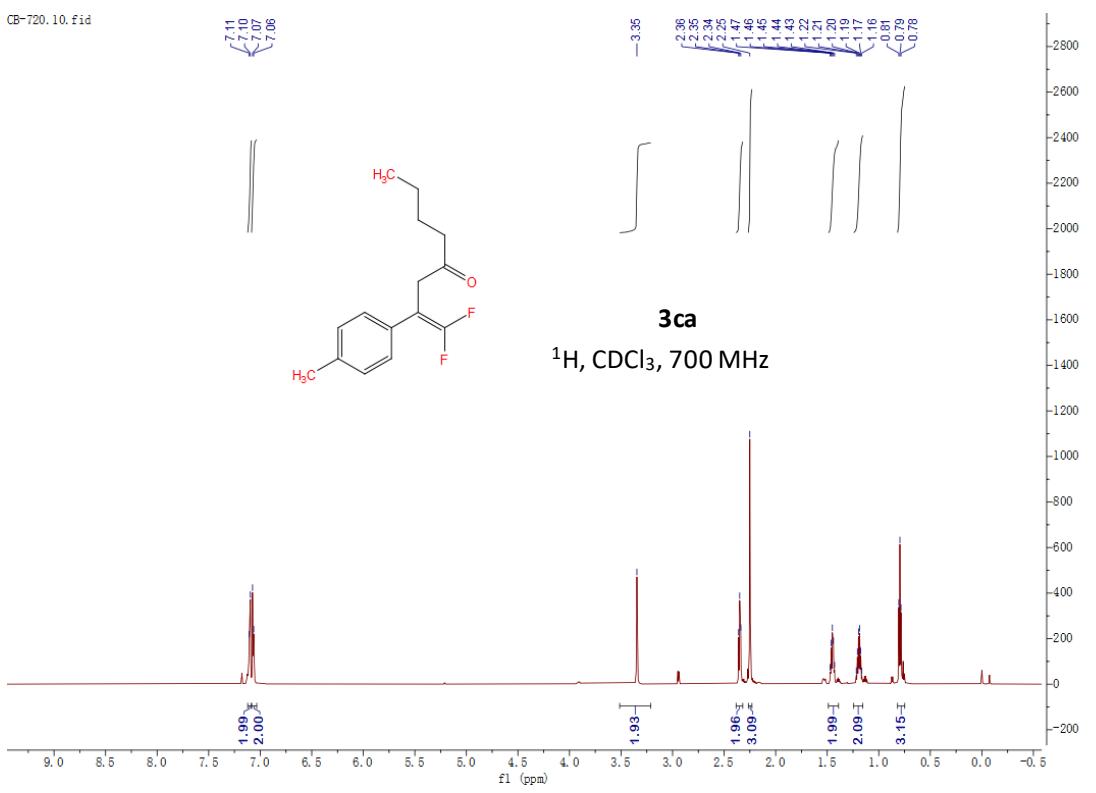


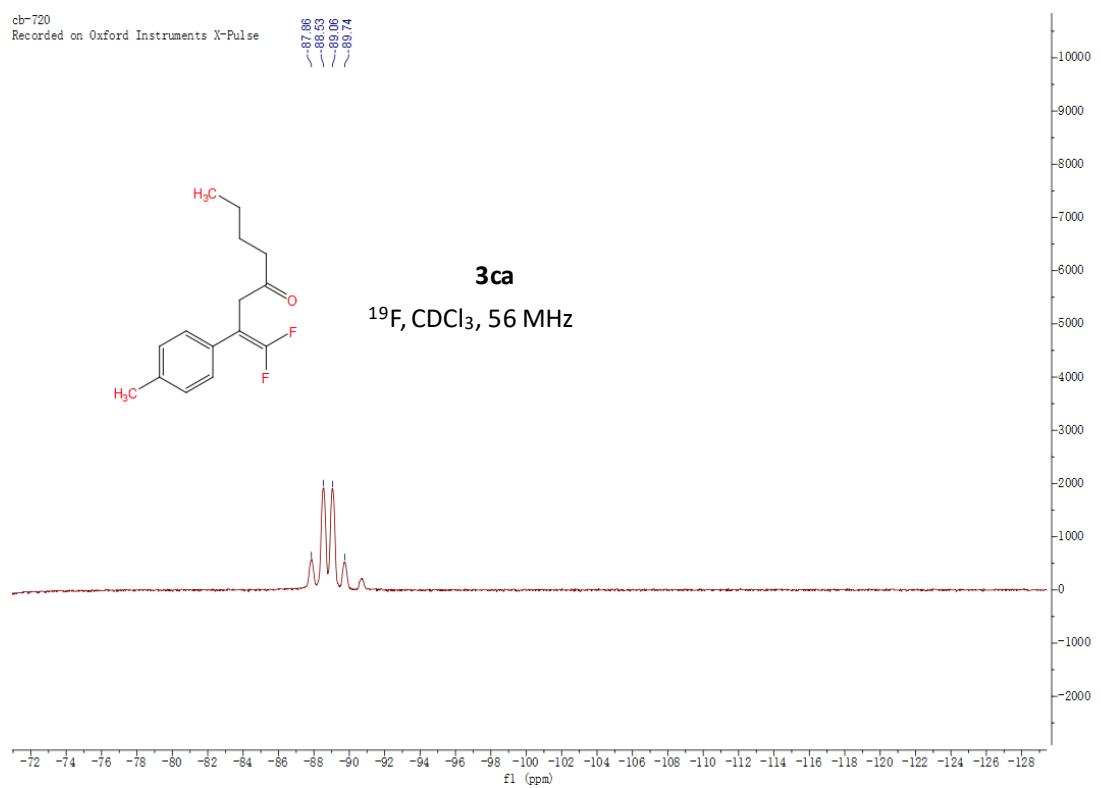
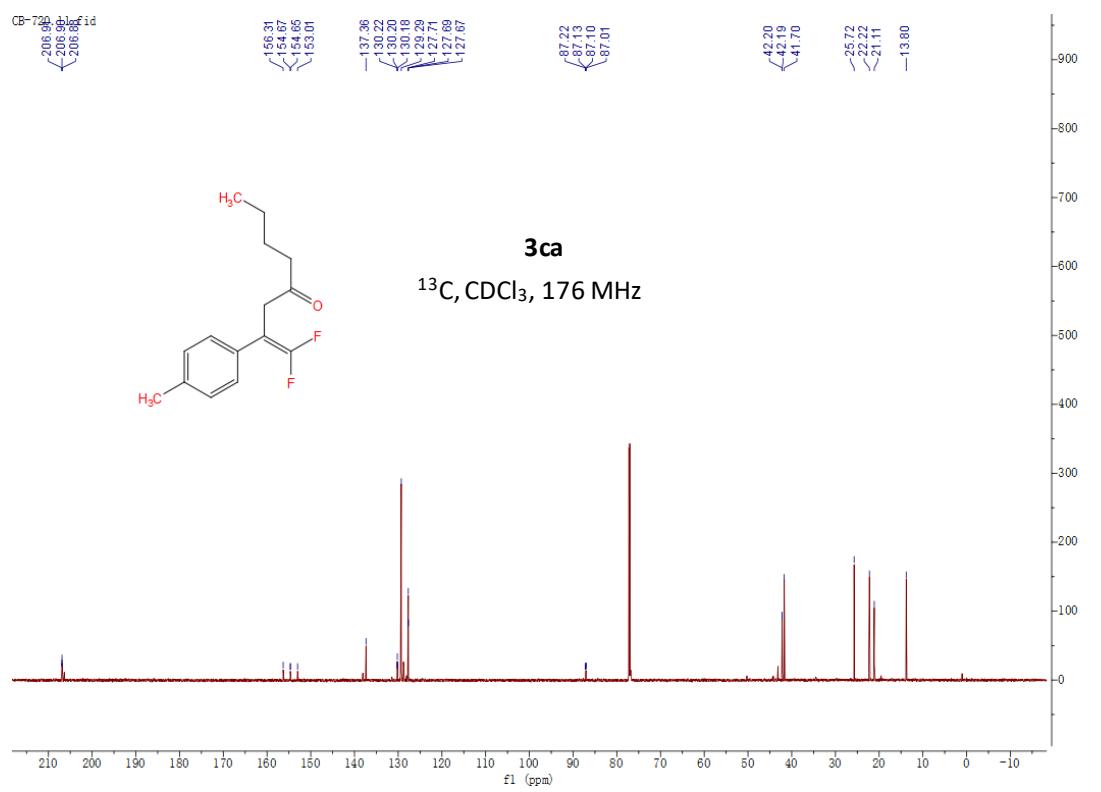


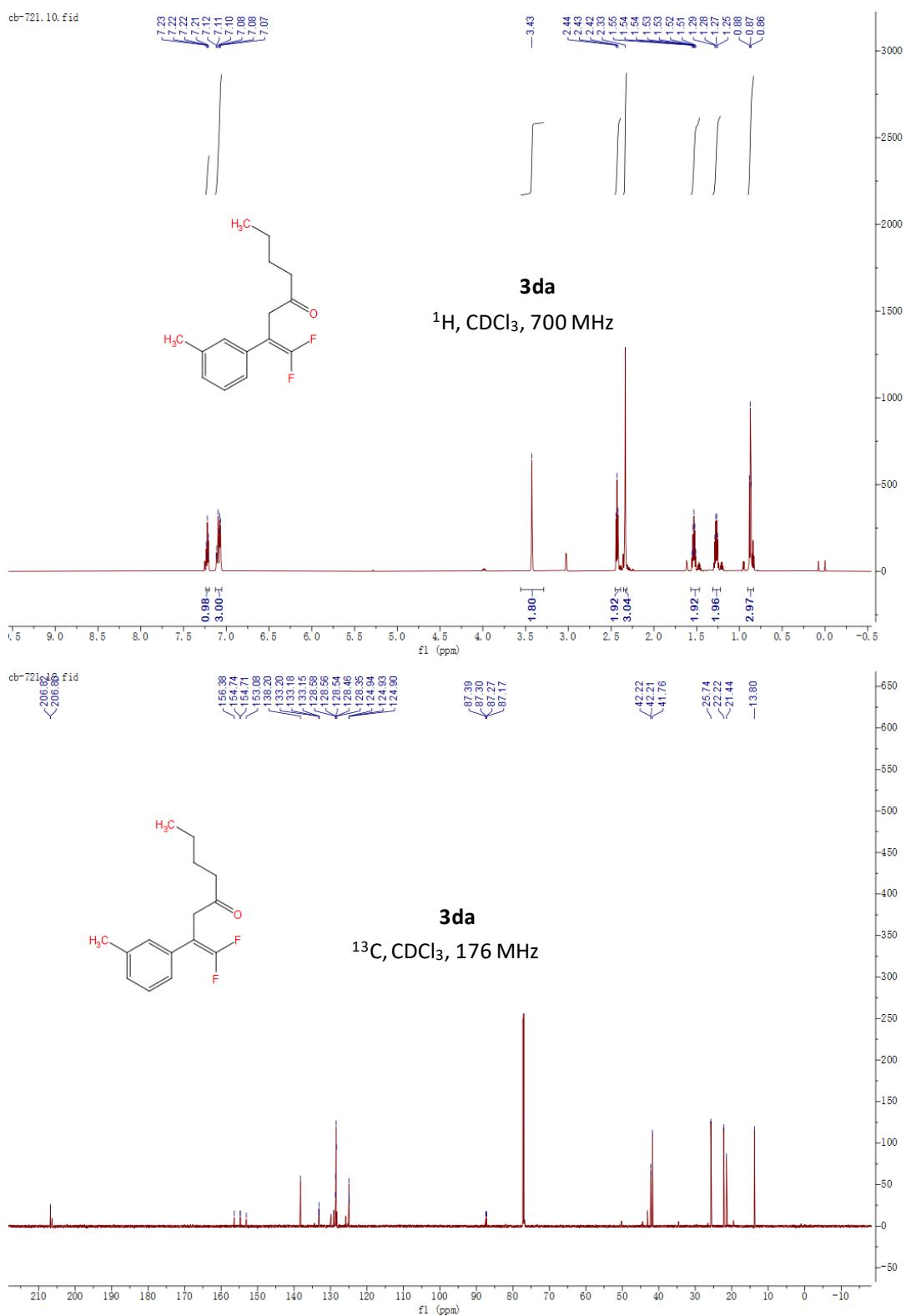
cb-694
Recorded on Oxford Instruments X-Pulse



CB-720.10.fid

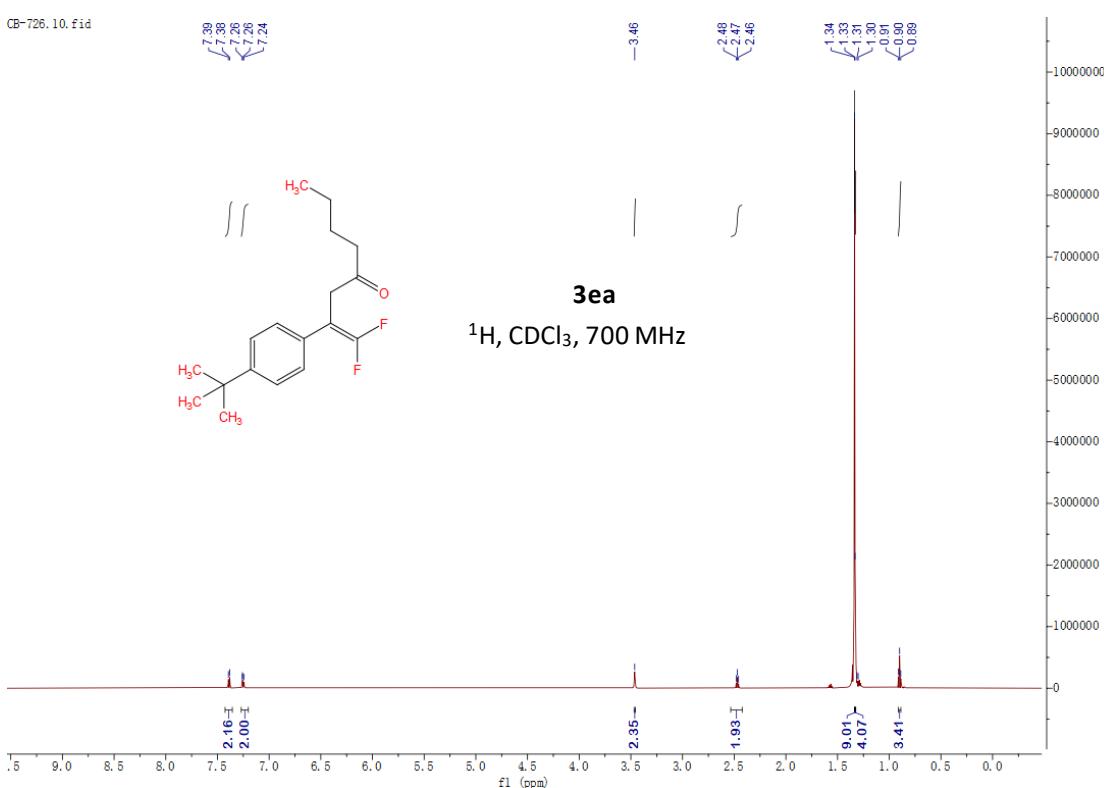
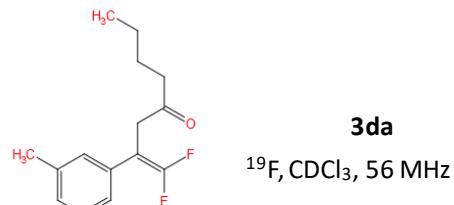


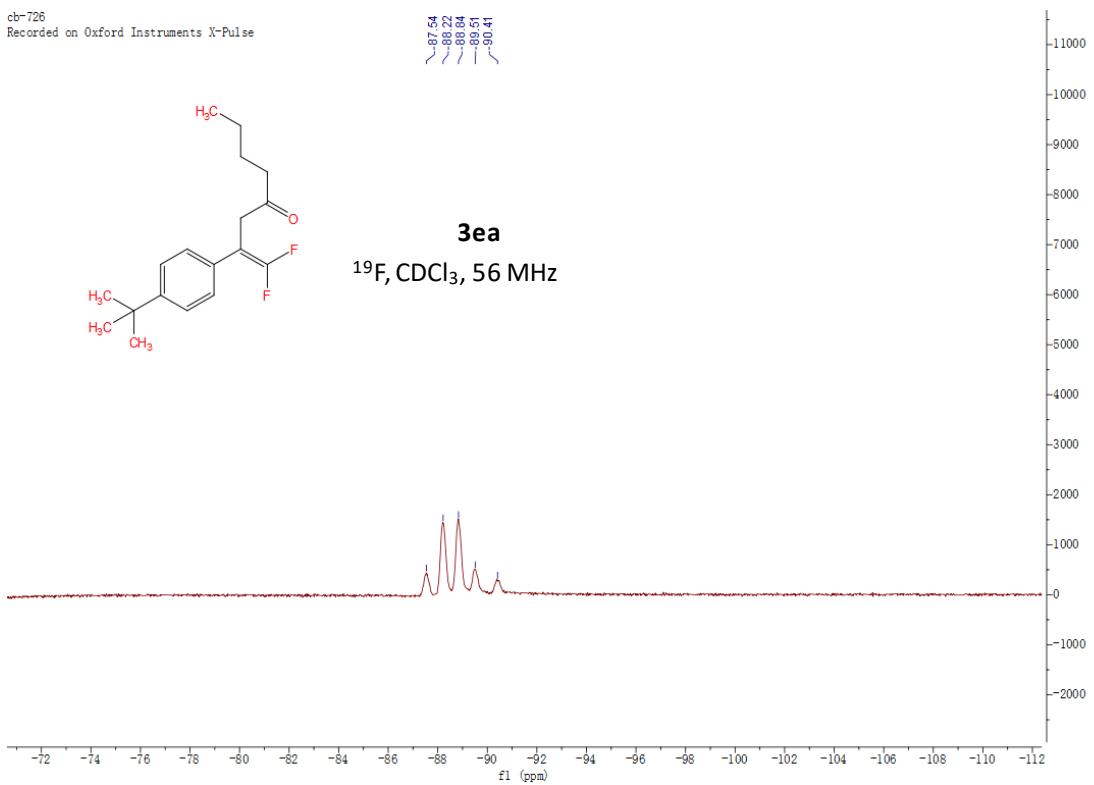
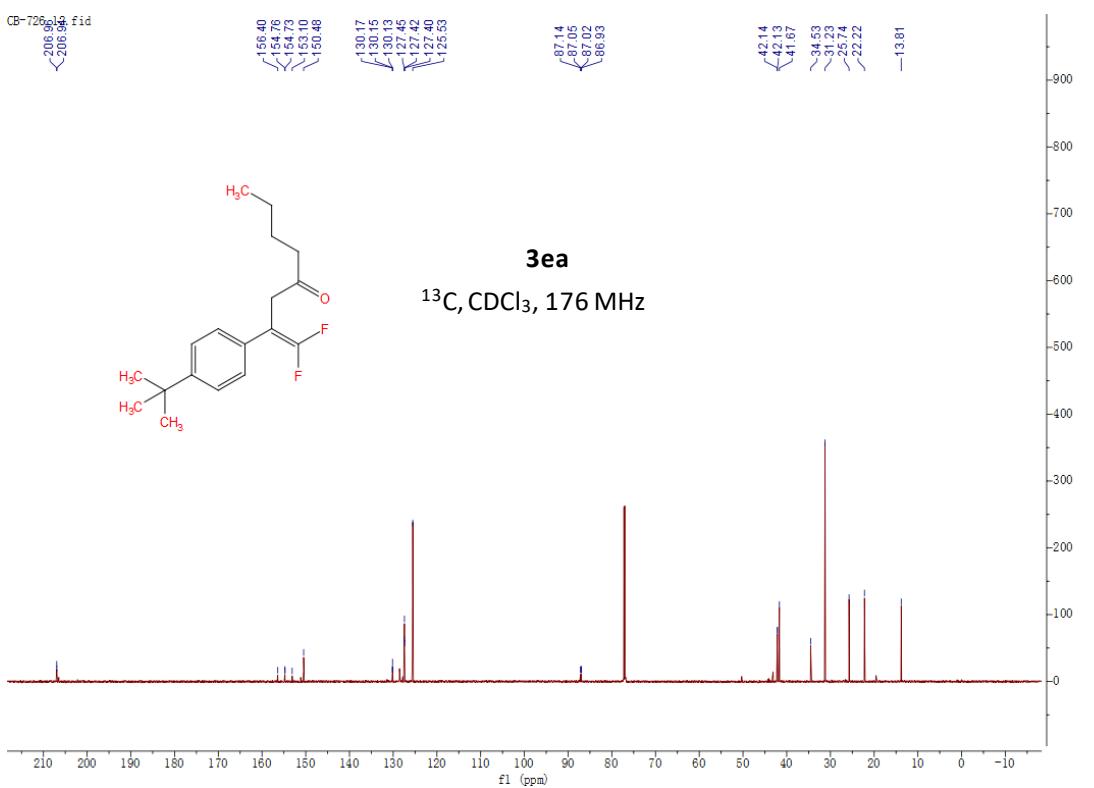


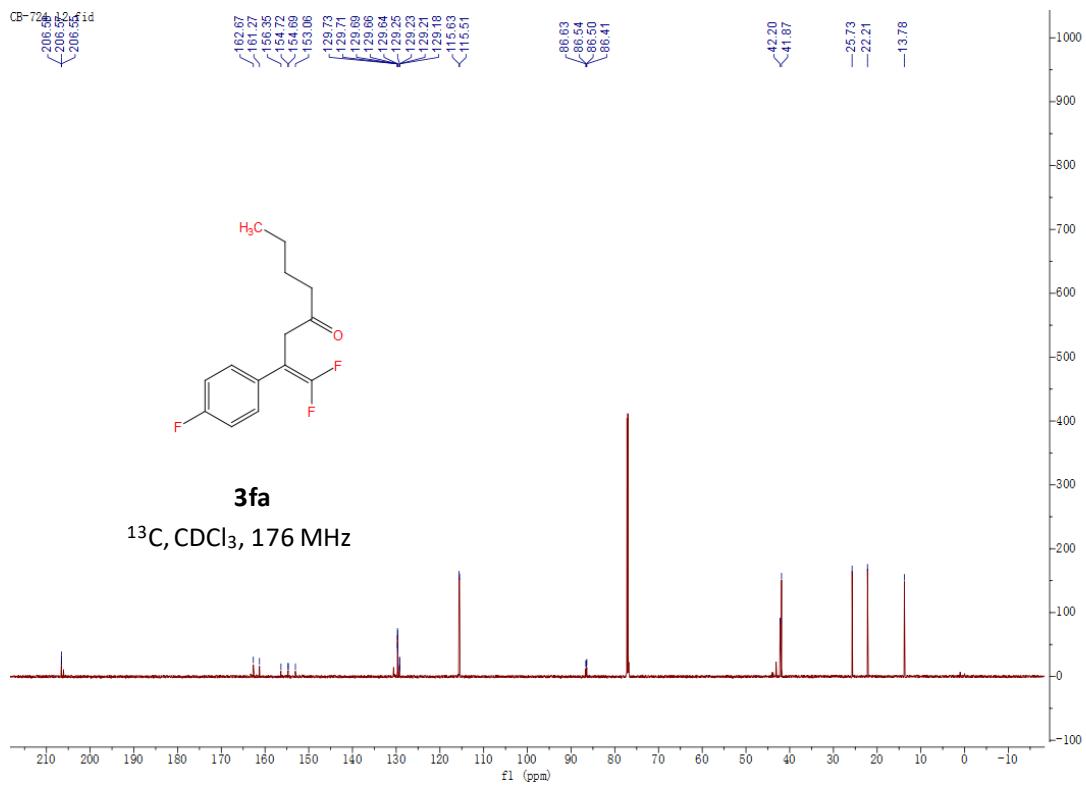
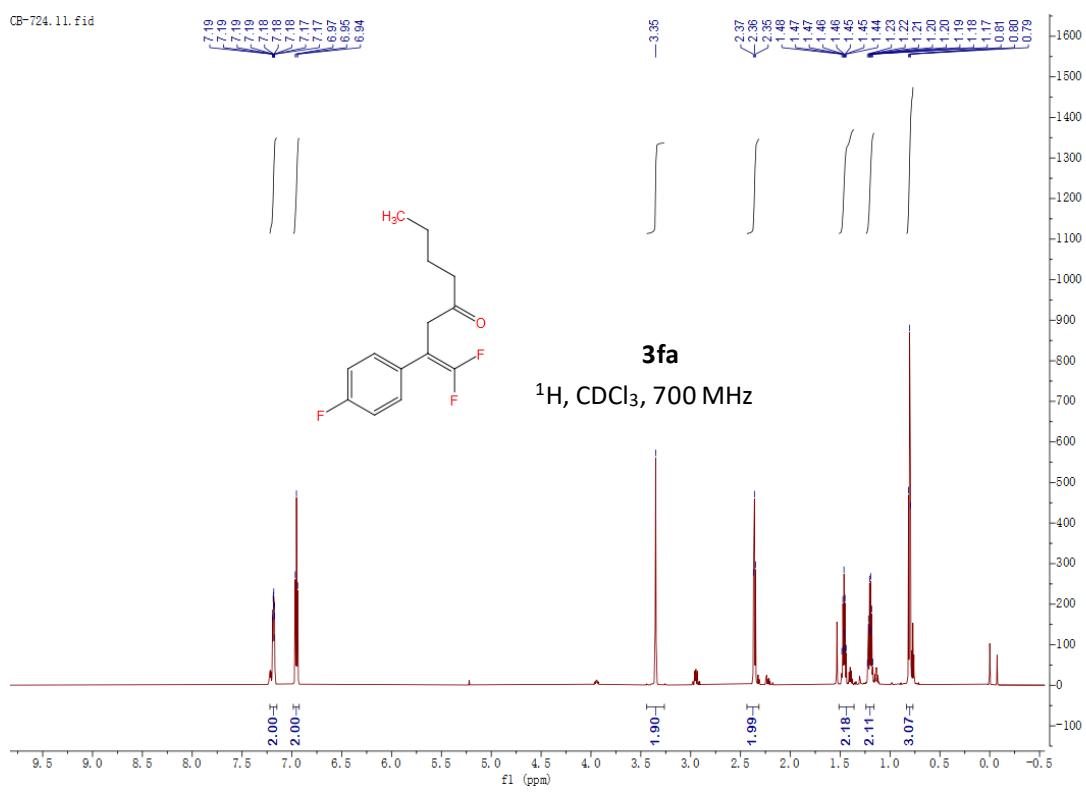


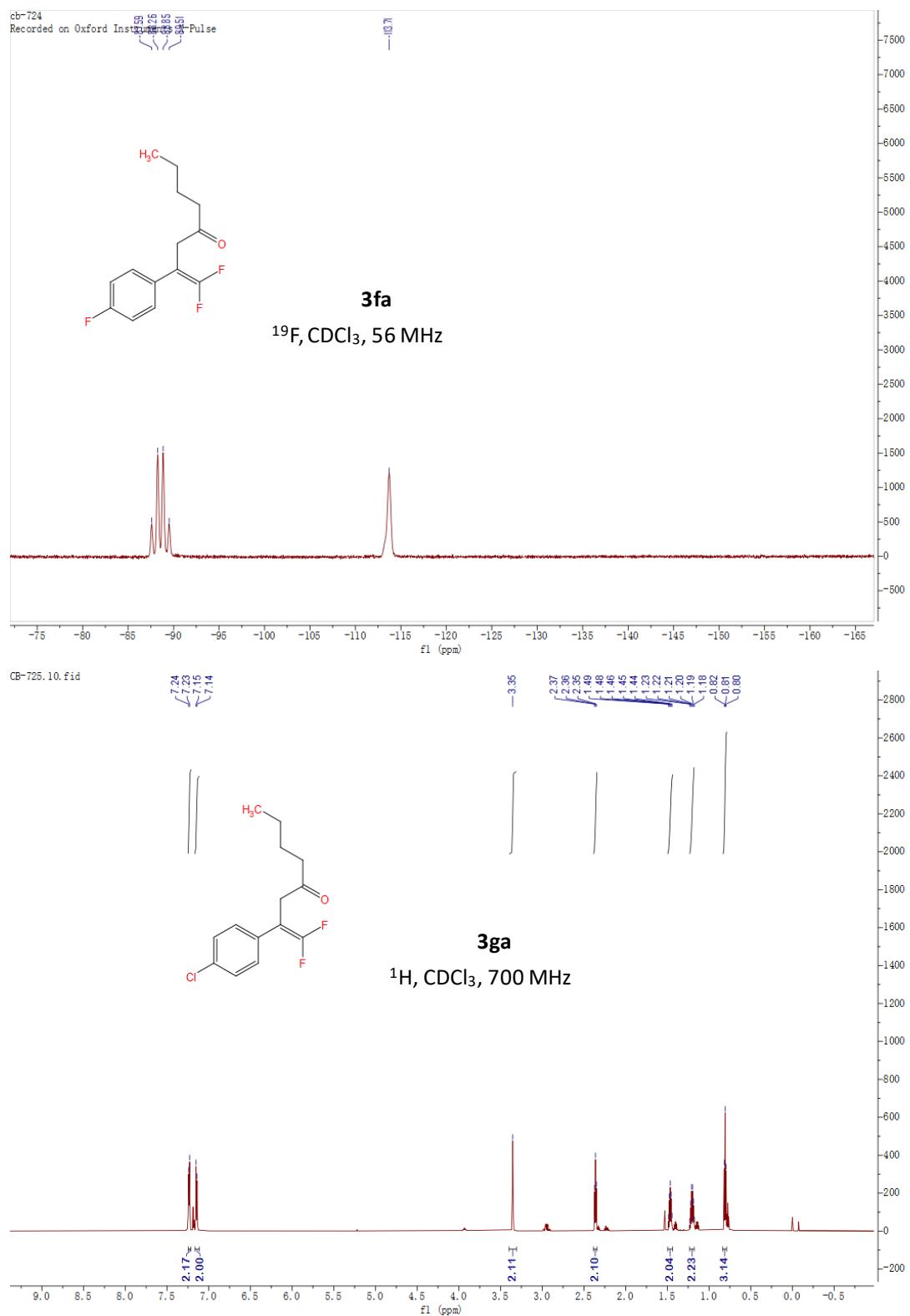
cb-721
Recorded on Oxford Instruments X-Pulse

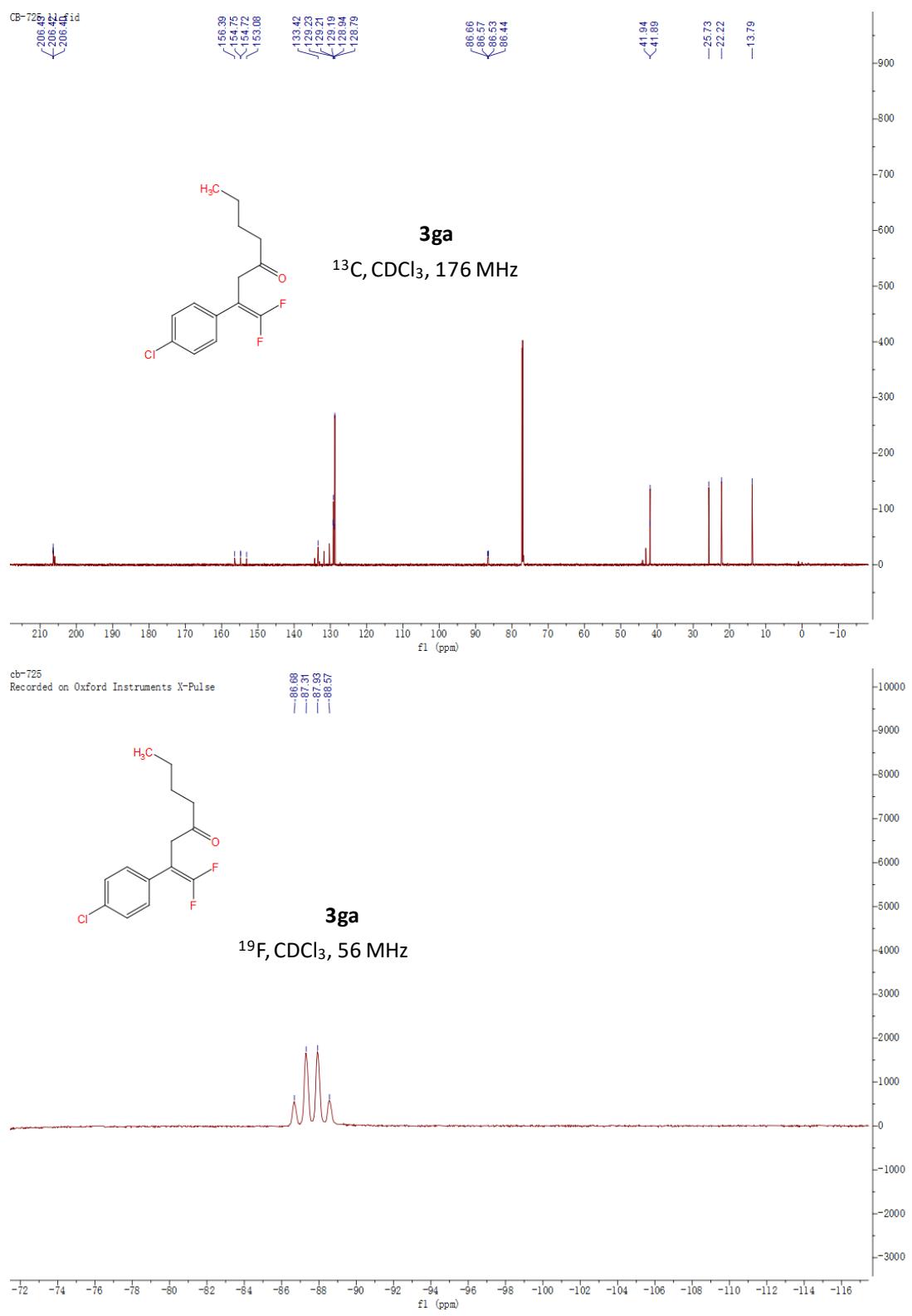
~87.56
~88.22
~88.79
~89.46

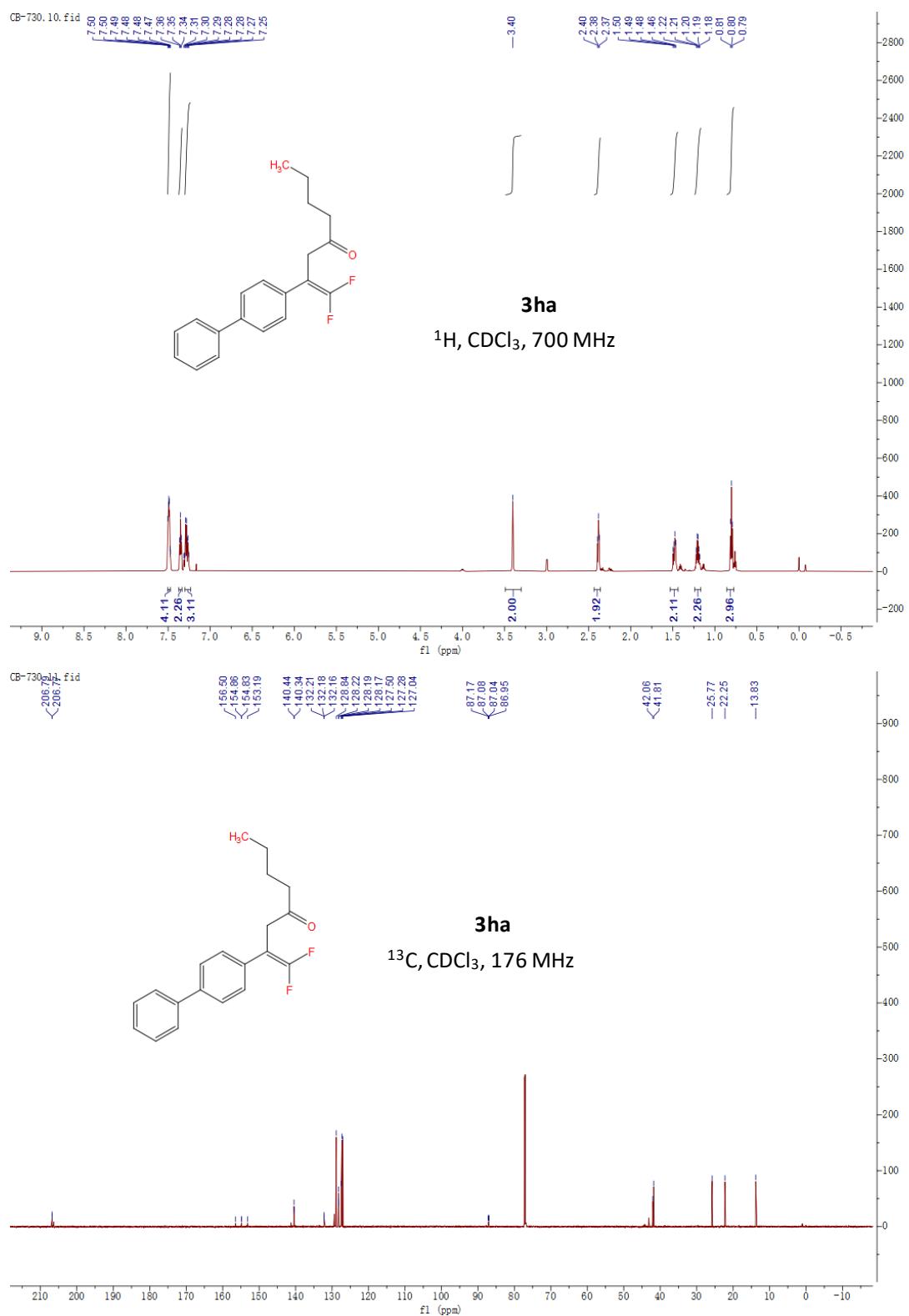




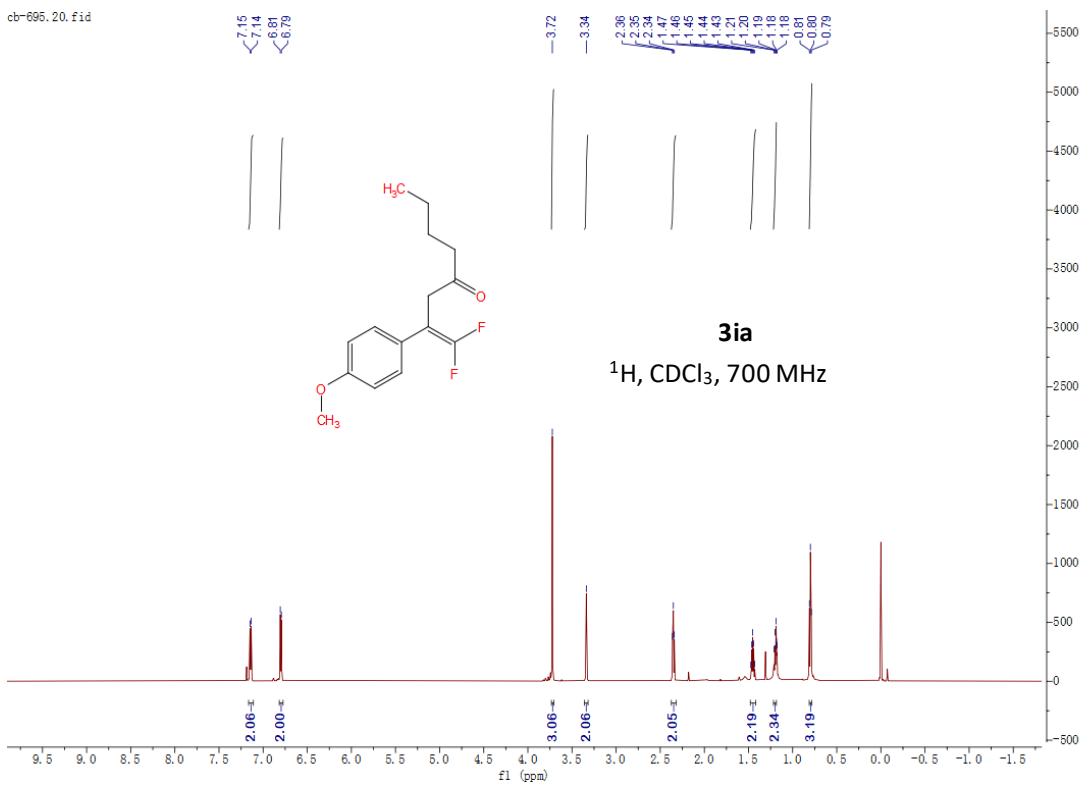
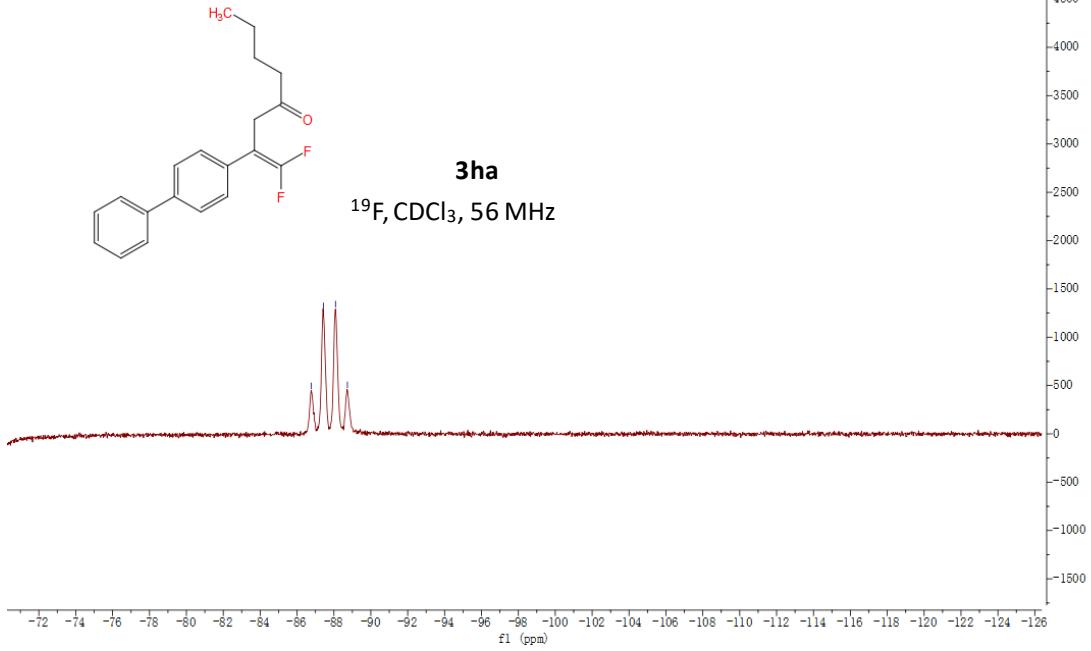


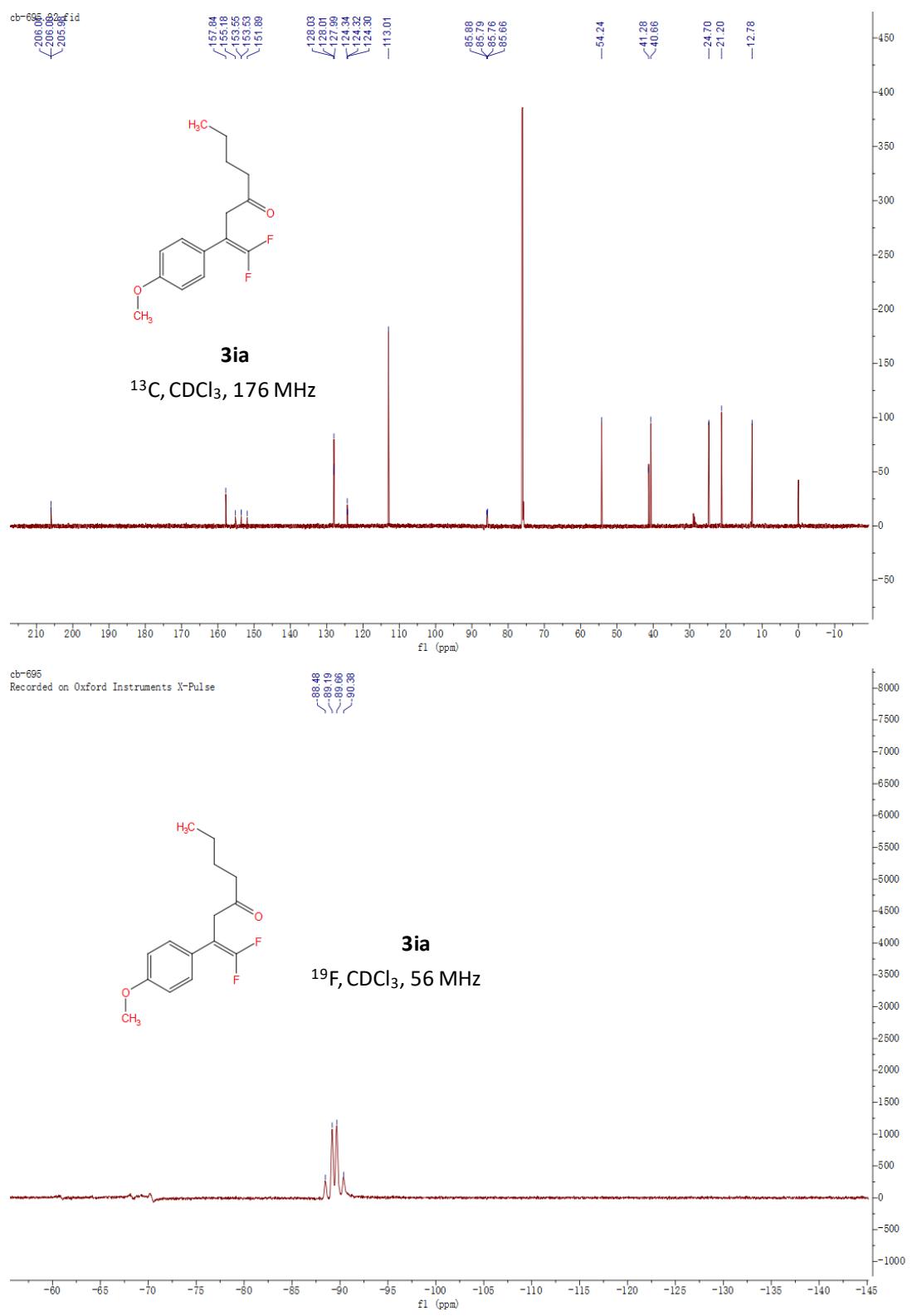


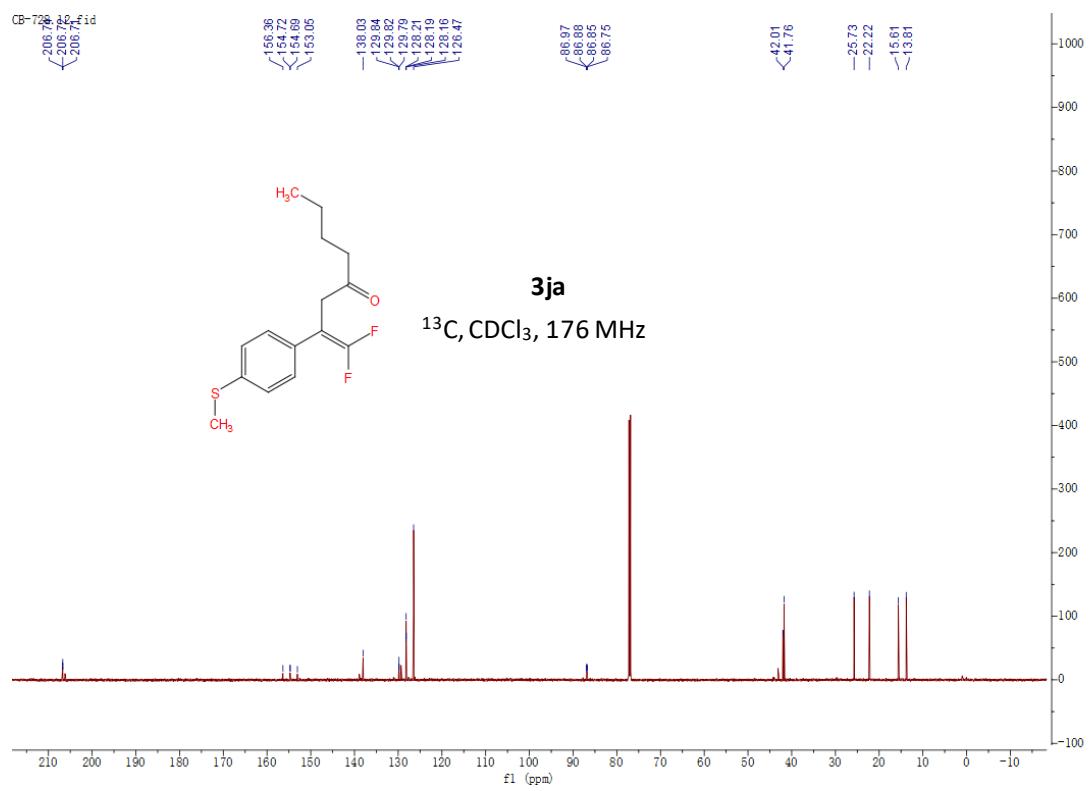
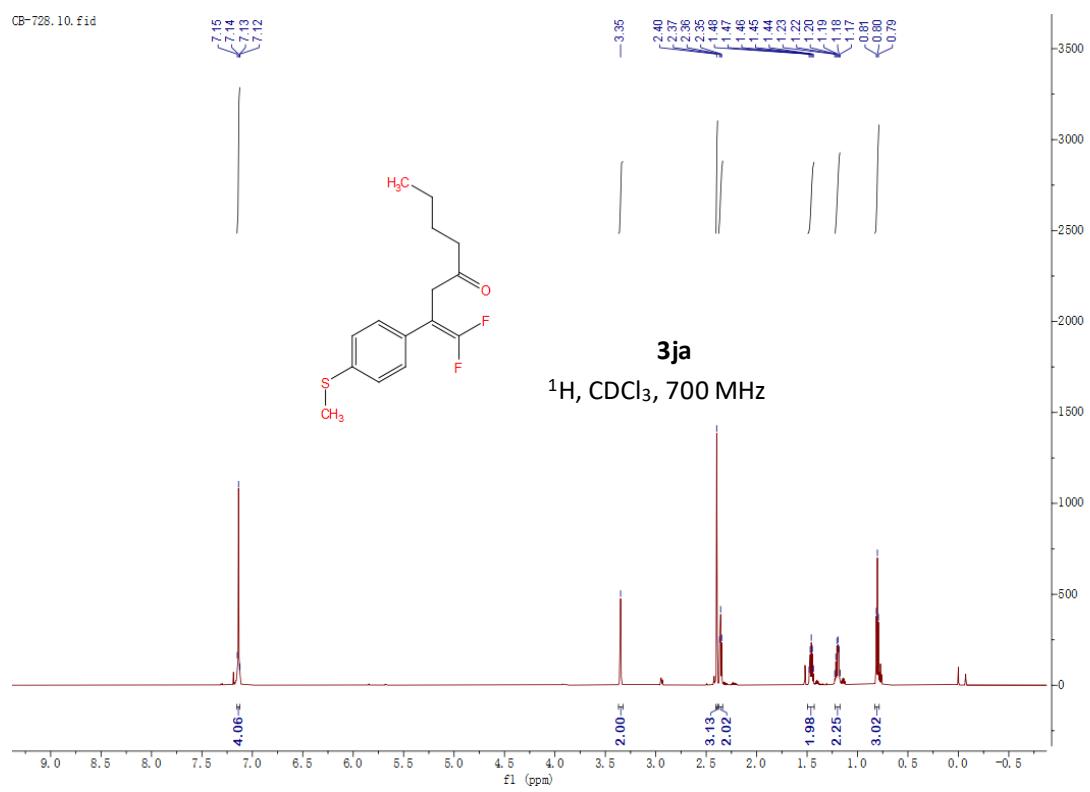




cb-730
Recorded on Oxford Instruments Y-Pulse

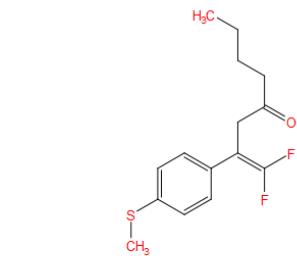






cb-728
Recorded on Oxford Instruments X-Pulse

~87.03
~86.69
~86.88



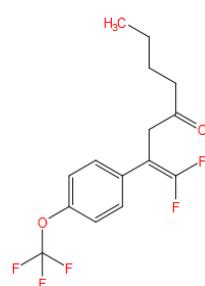
3ja

^{19}F , CDCl_3 , 56 MHz

CB-740.10.fid

7.25
7.12
7.11

-3.37
2.38
2.37
2.36
1.49
1.48
1.47
1.46
1.45
1.23
1.22
1.21
1.20
1.19
1.18
0.82
0.81
0.80



3ka

^1H , CDCl_3 , 700 MHz

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

1.89
2.15
2.16

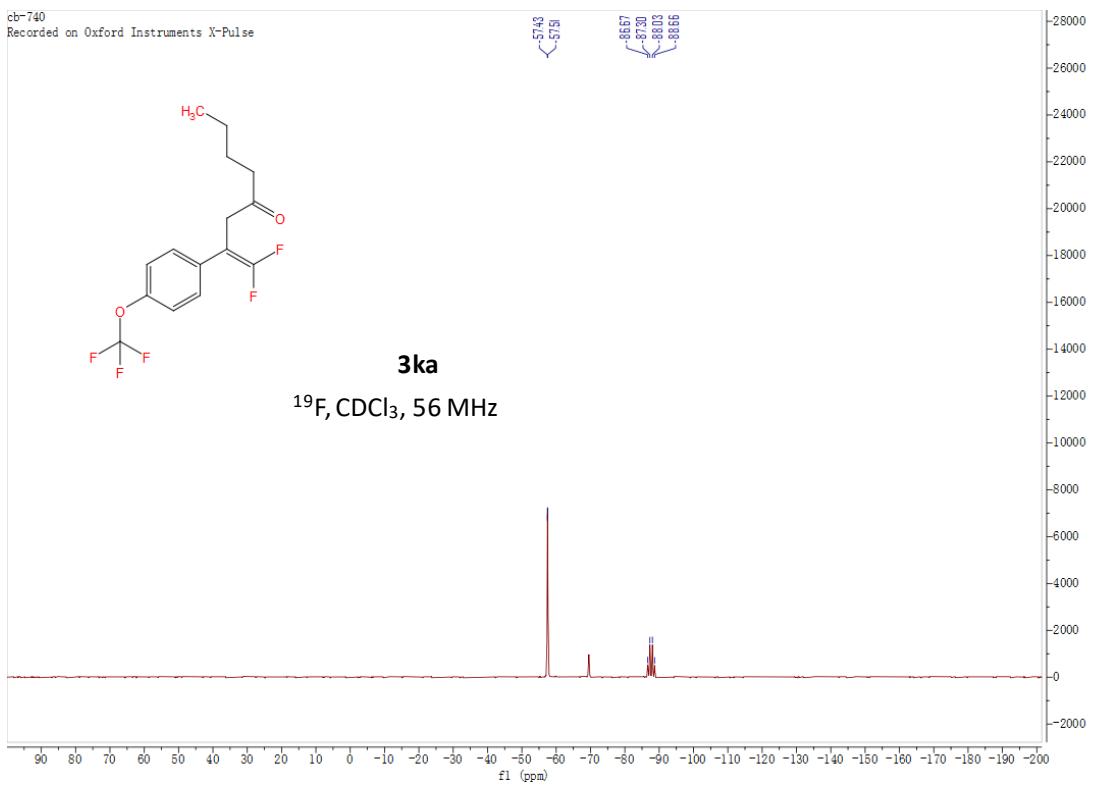
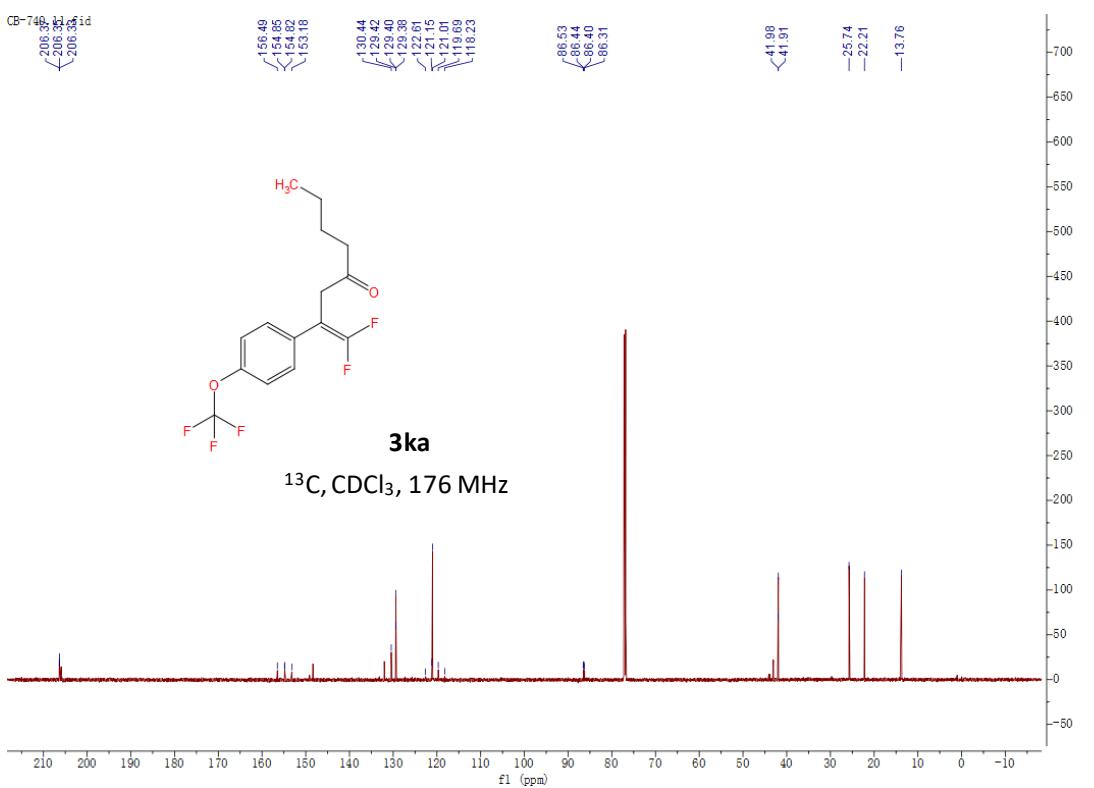
2.00^t

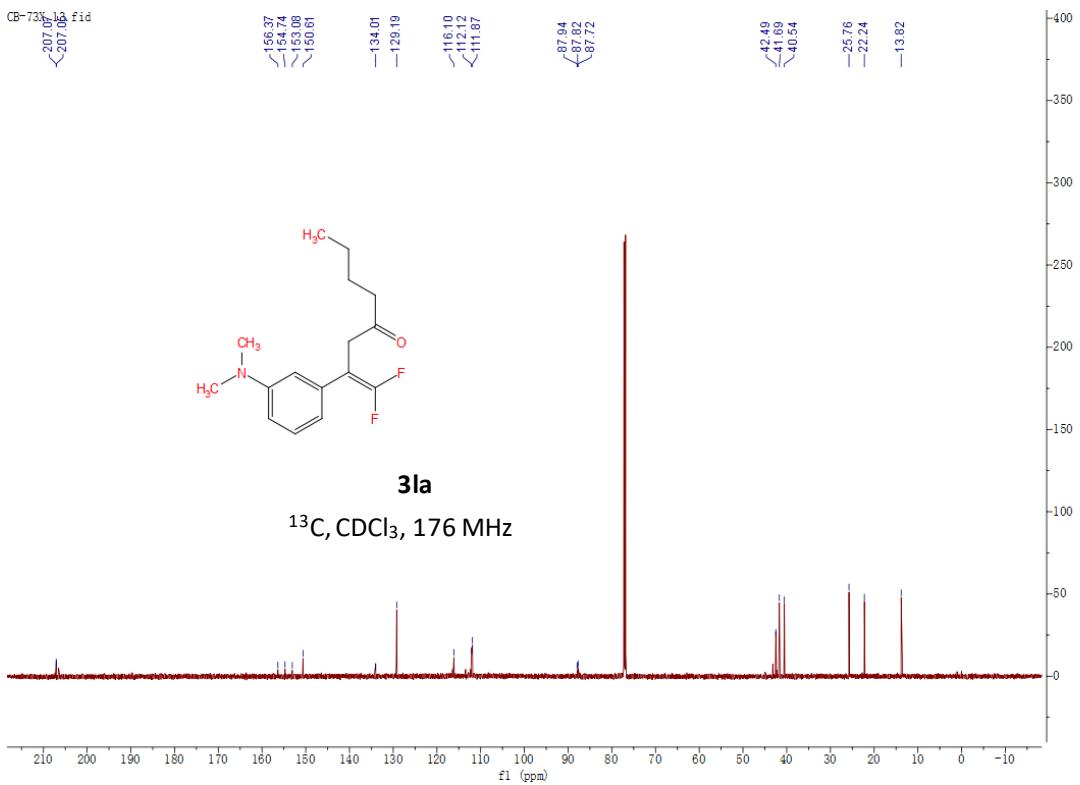
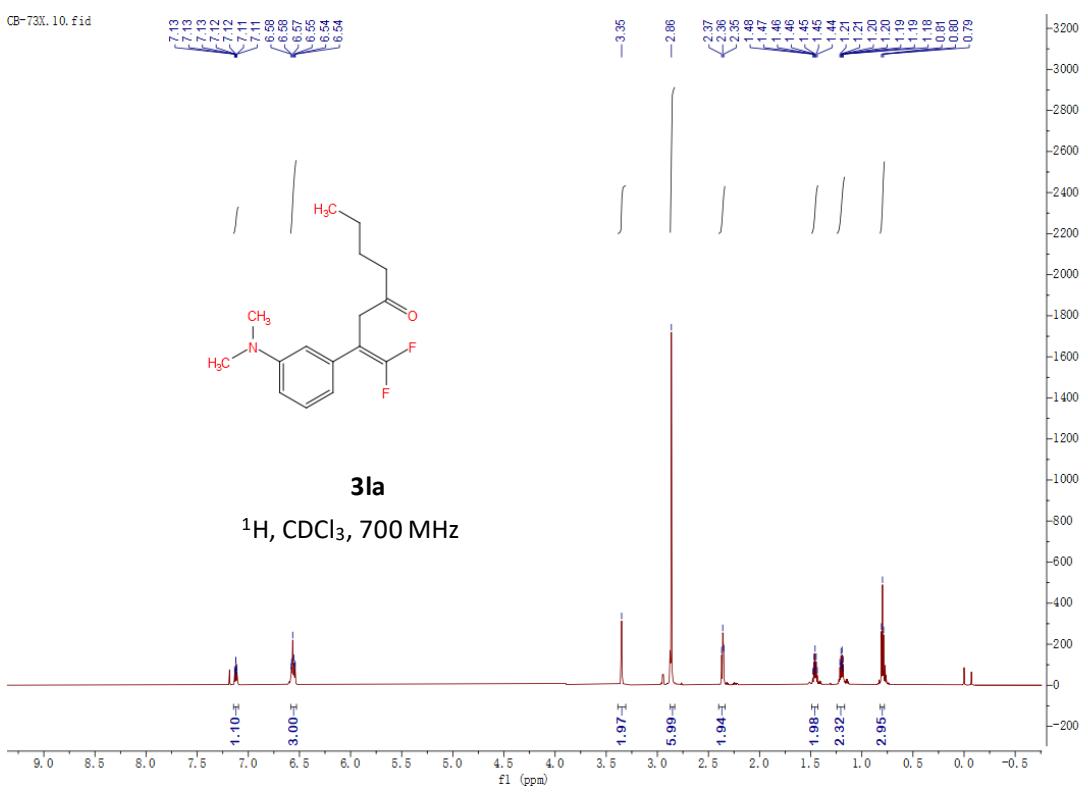
1.97^t

1.97^t

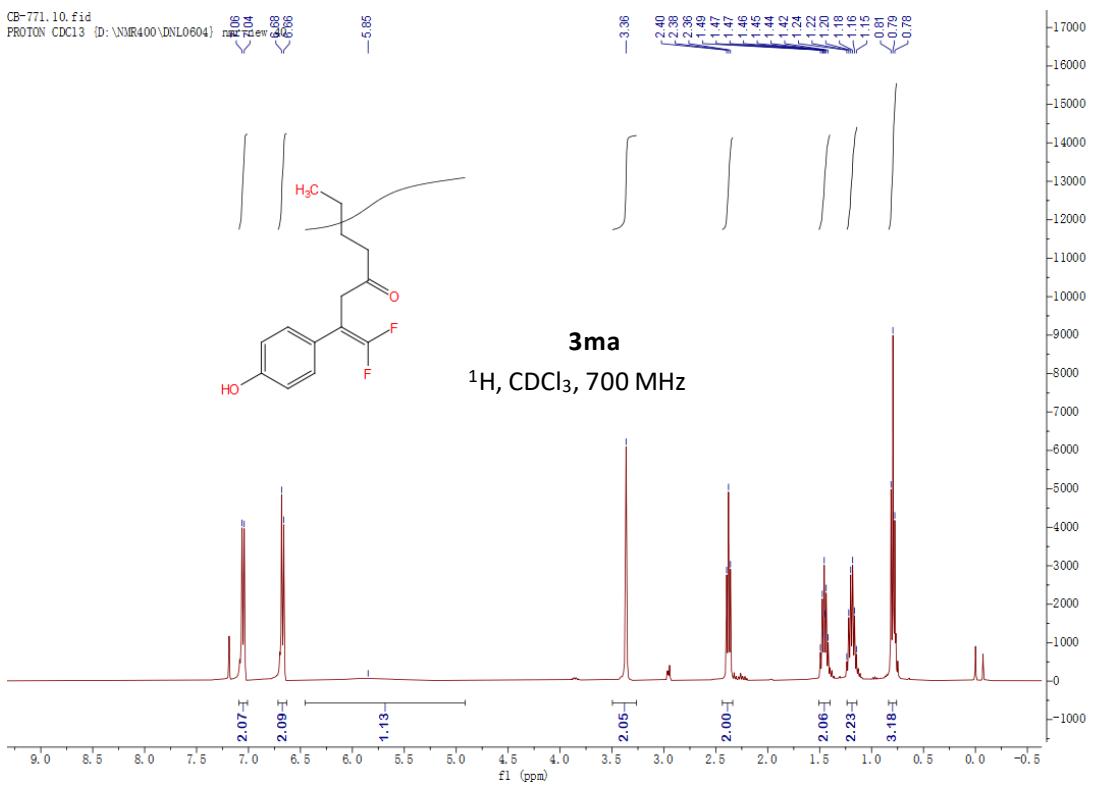
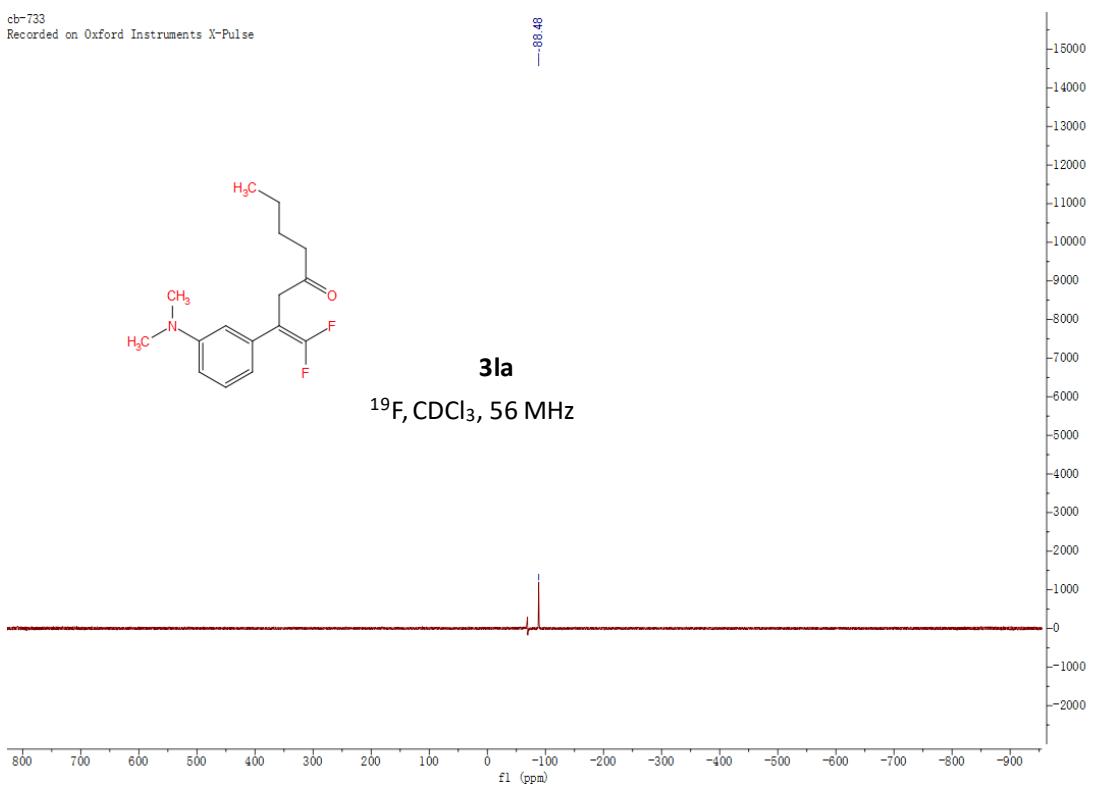
2.23^t

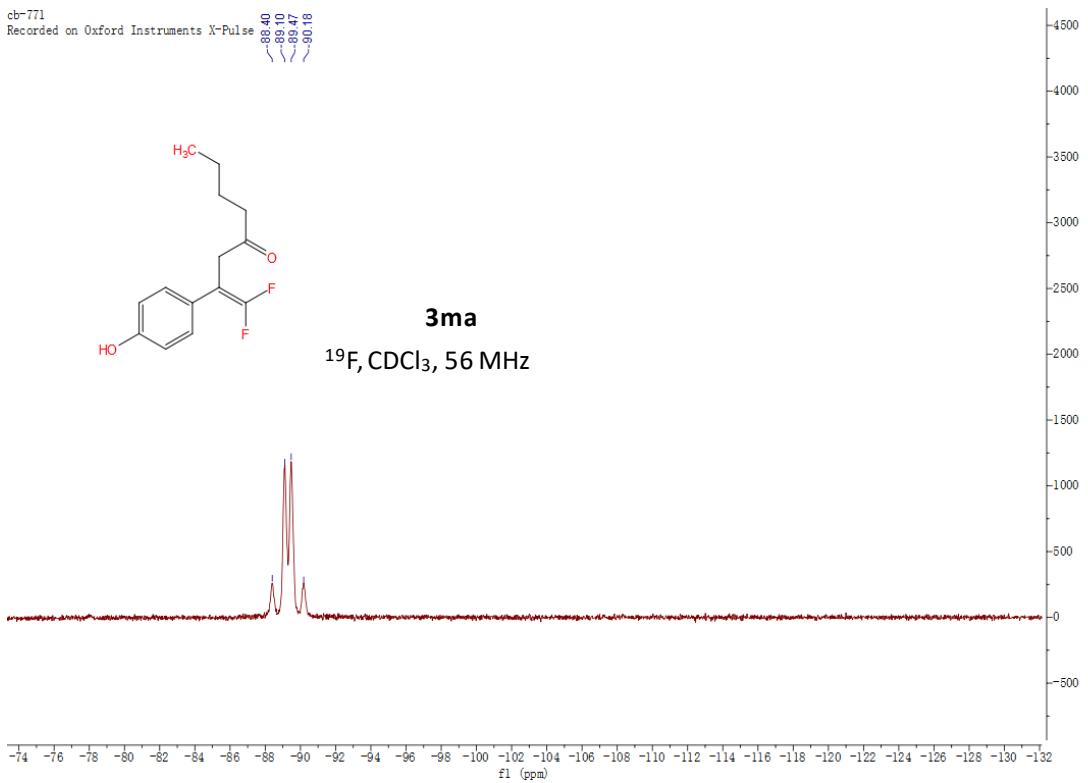
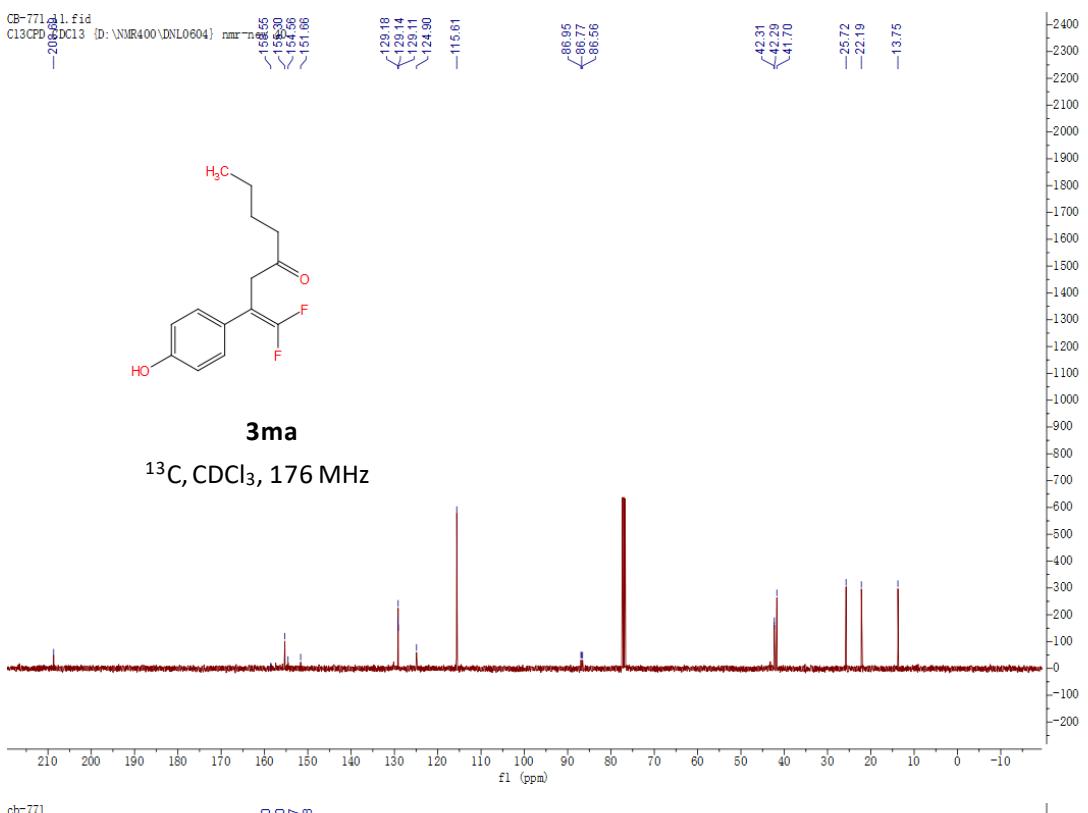
2.92^t

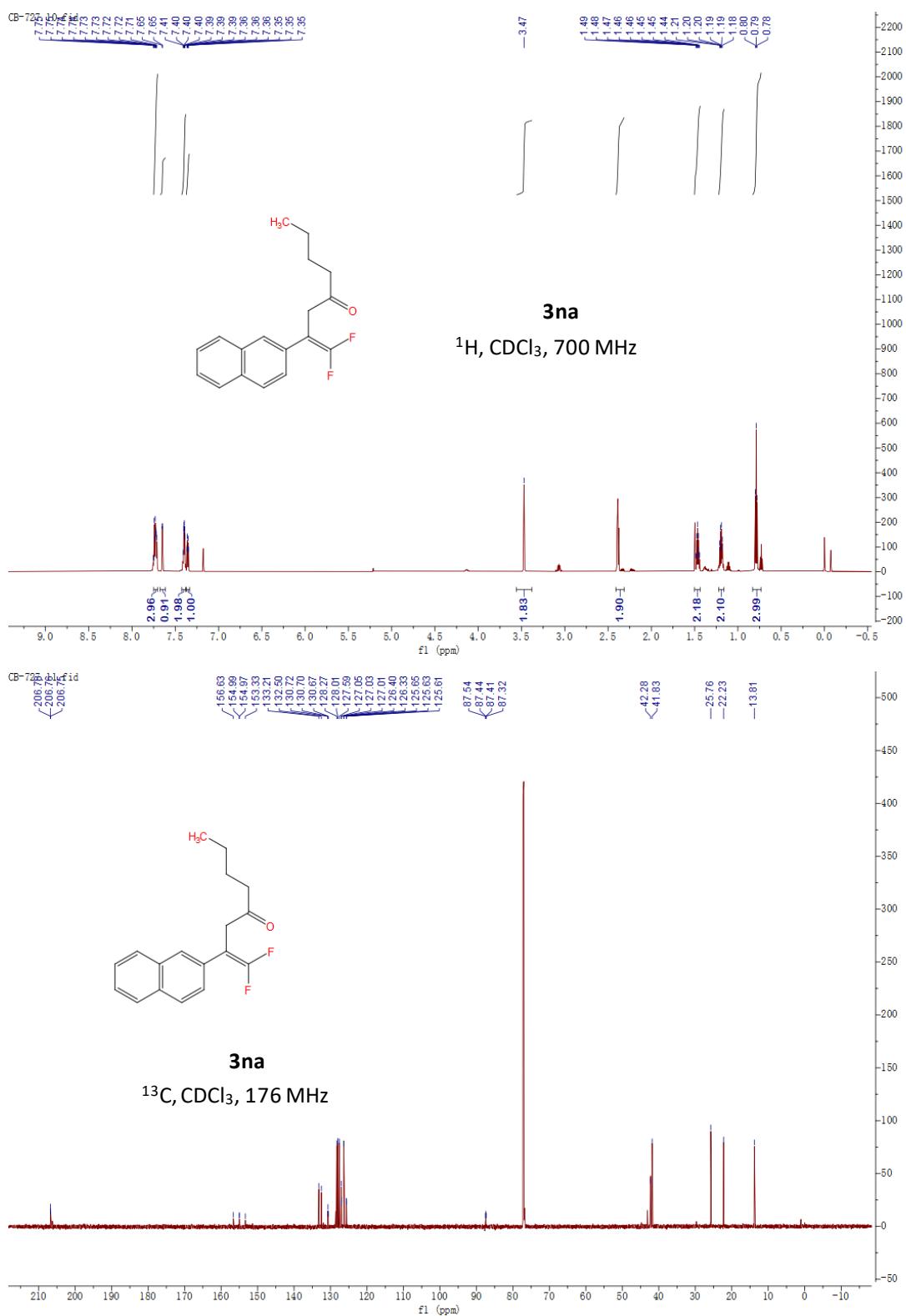




cb-733
Recorded on Oxford Instruments X-Pulse

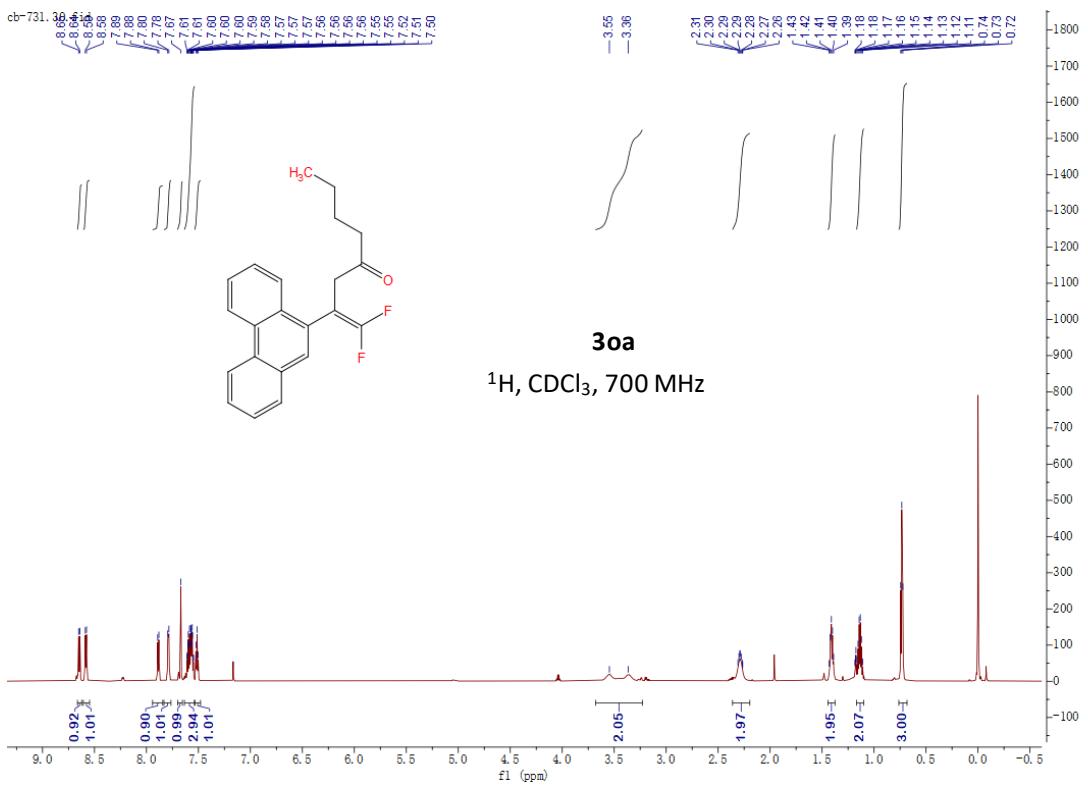
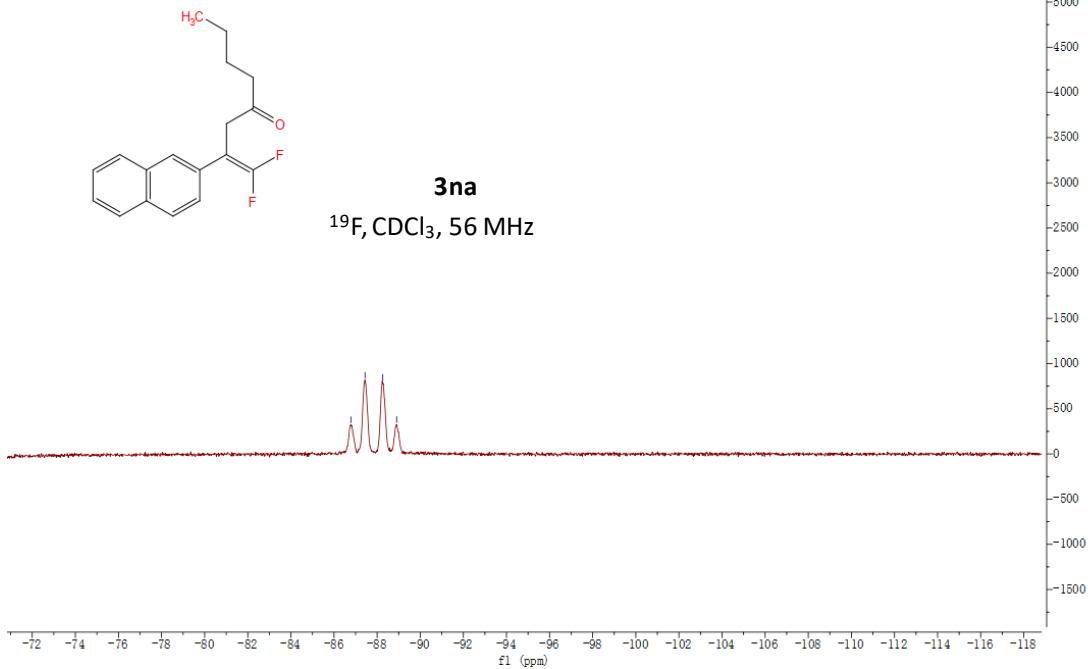


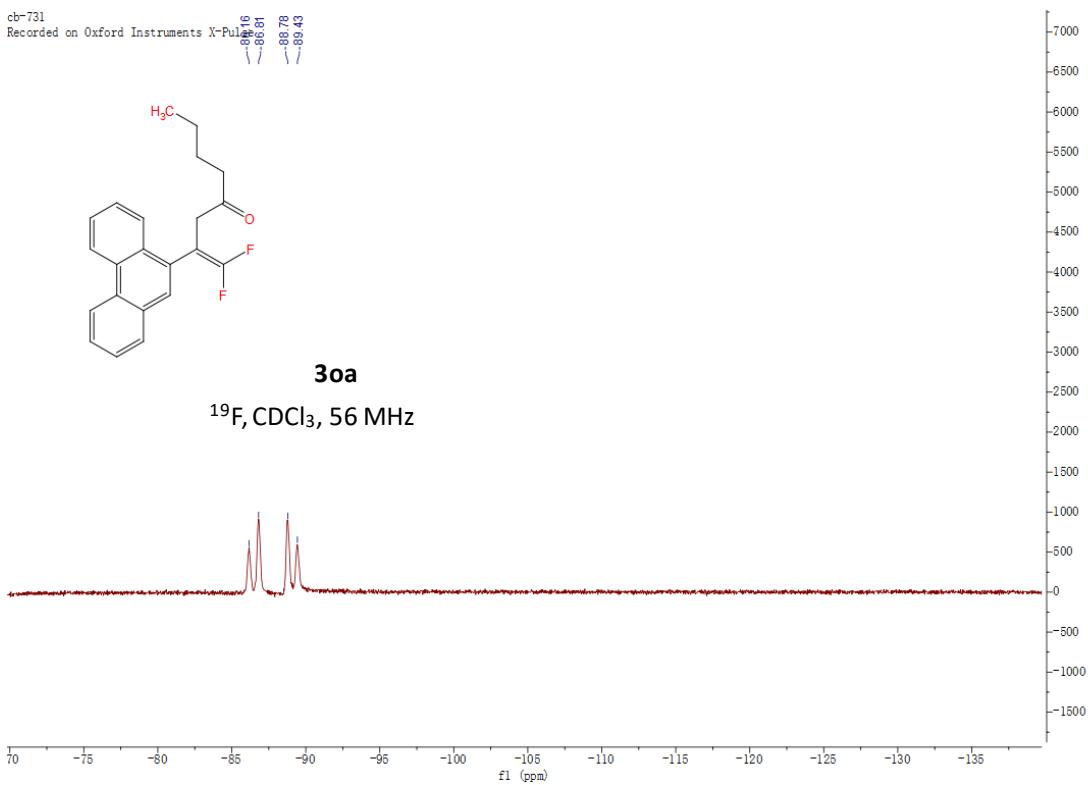
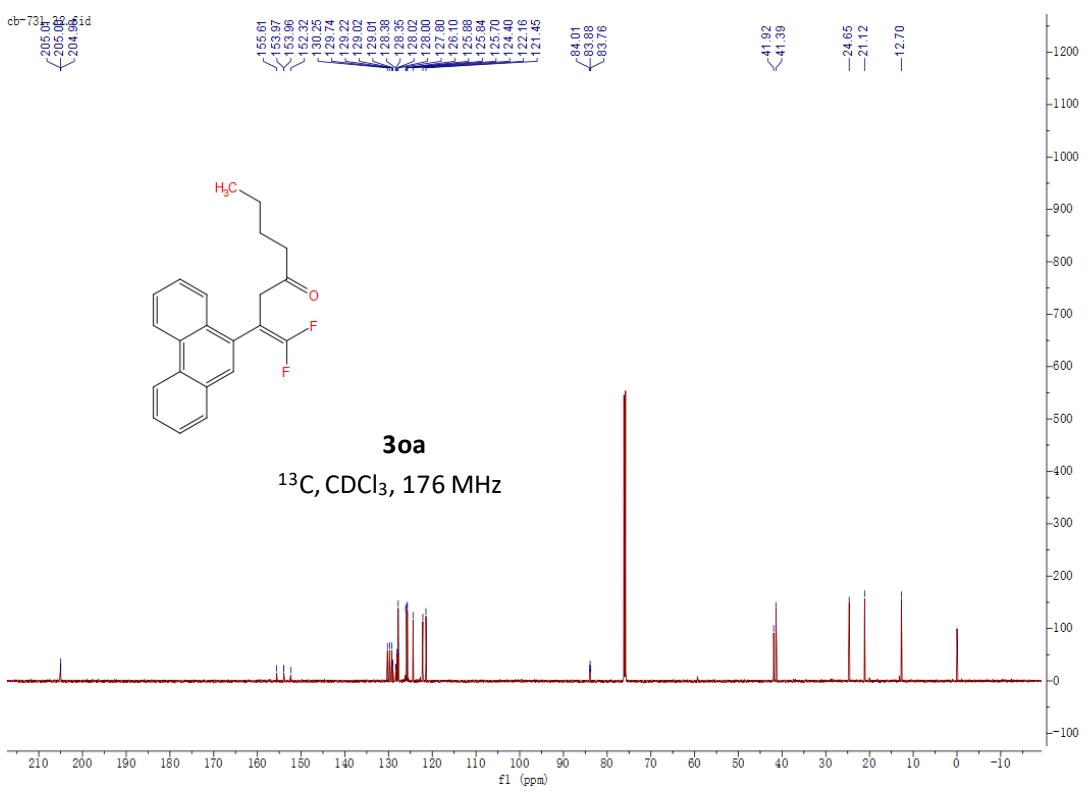


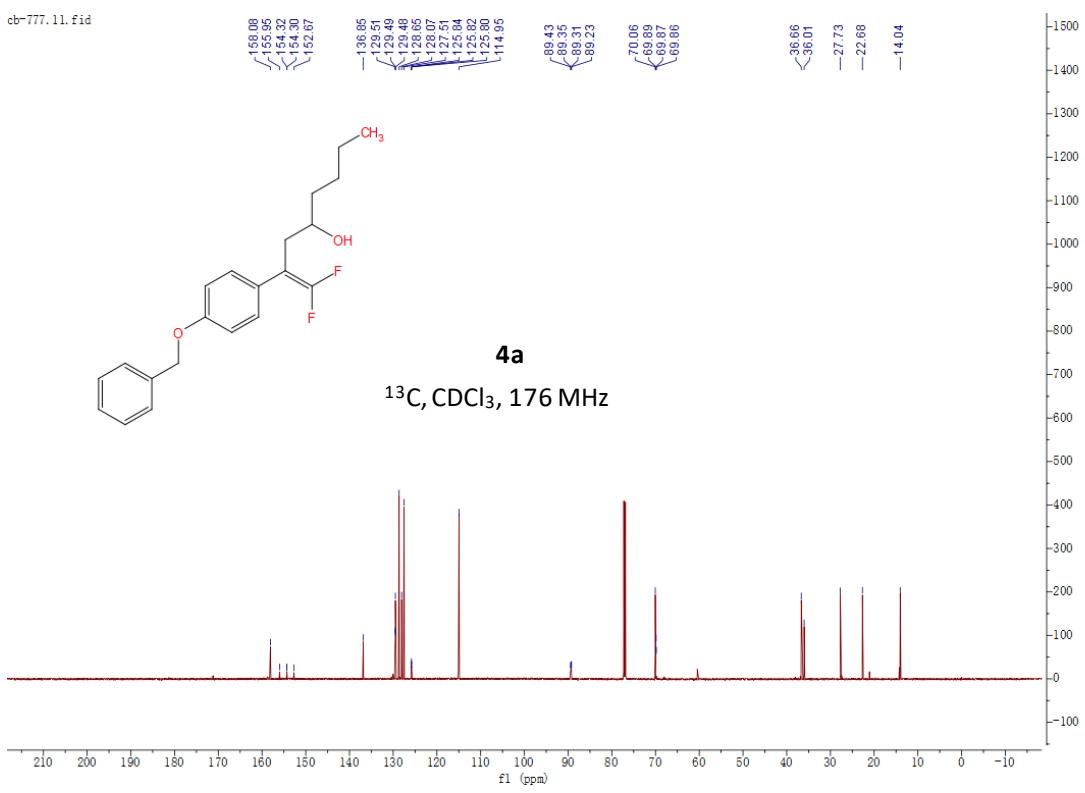
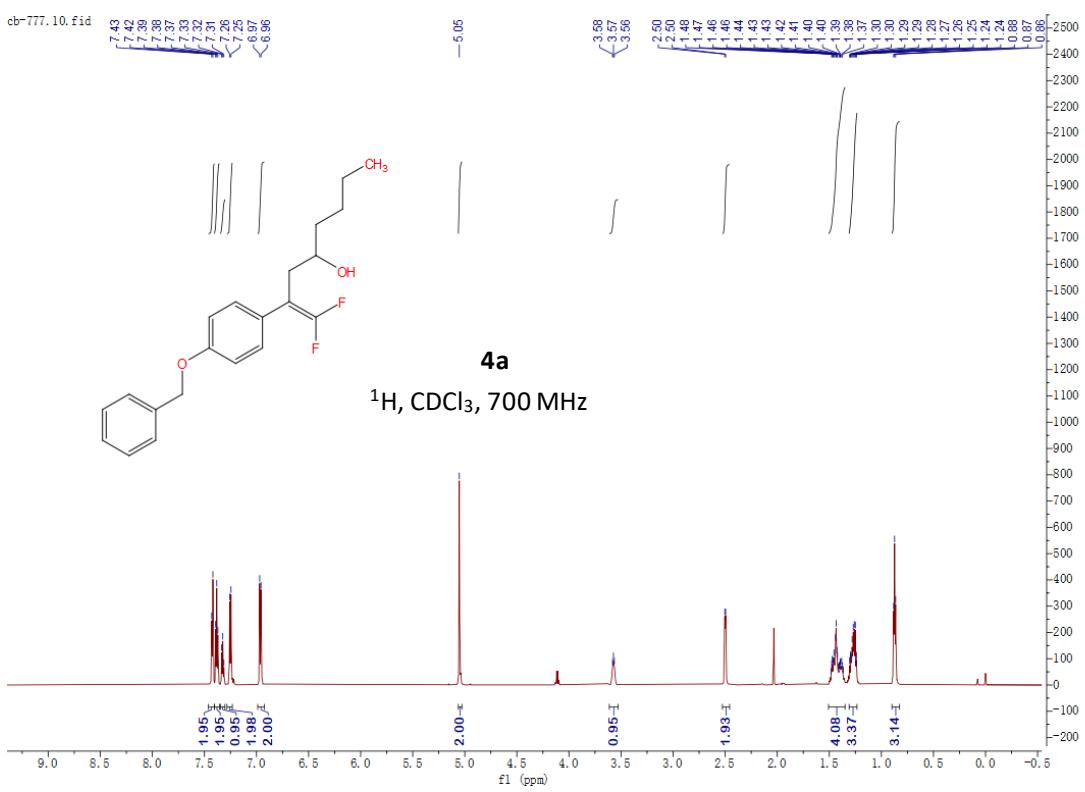


cb-727
Recorded on Oxford Instruments X-Pulse

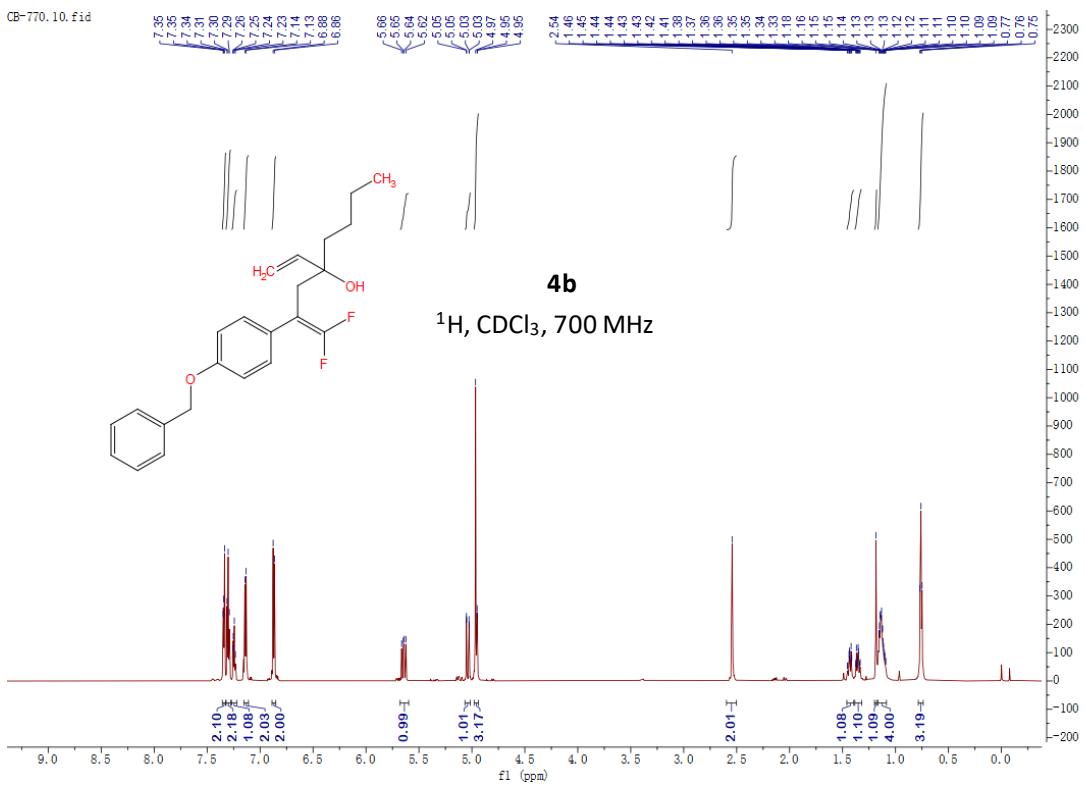
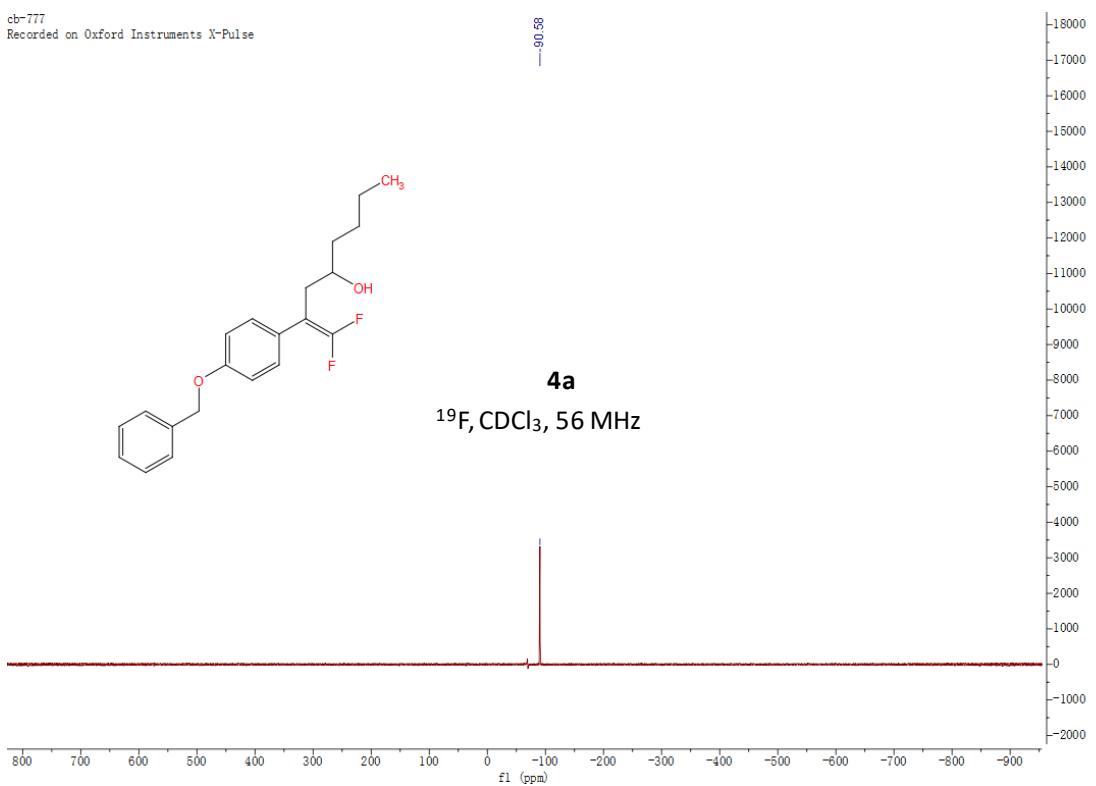
~ -86.78
~ -87.44
~ -88.28
~ -88.91

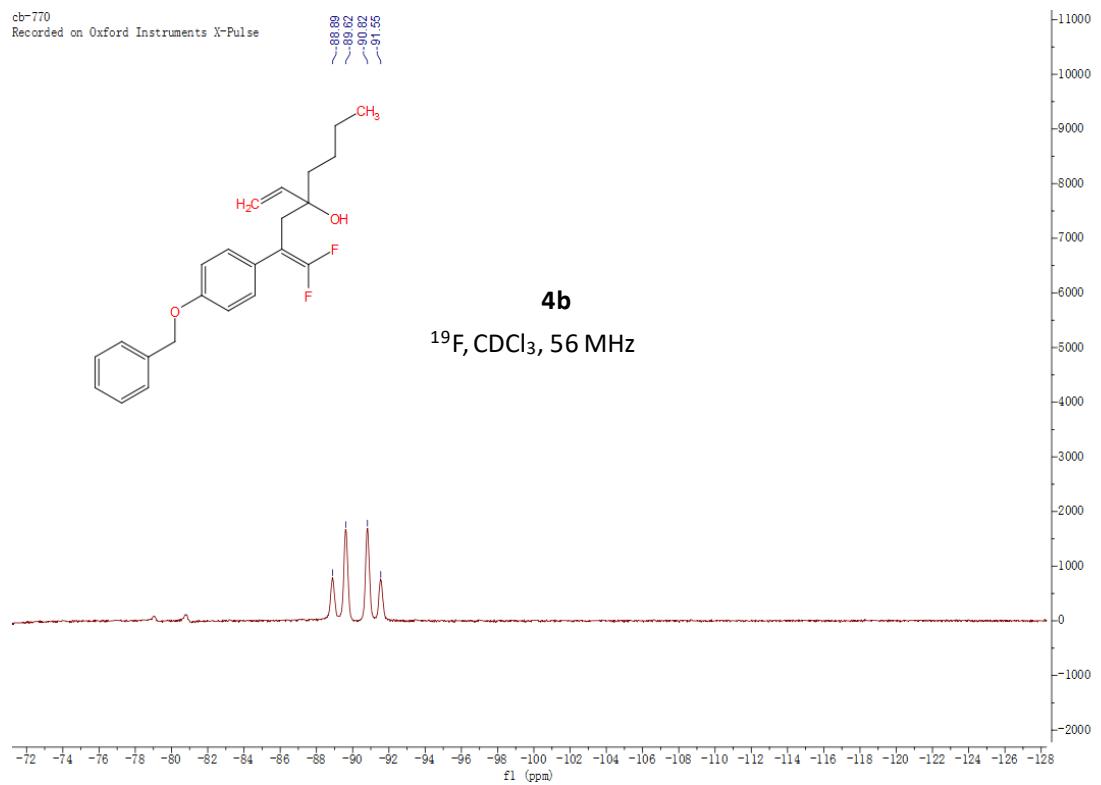
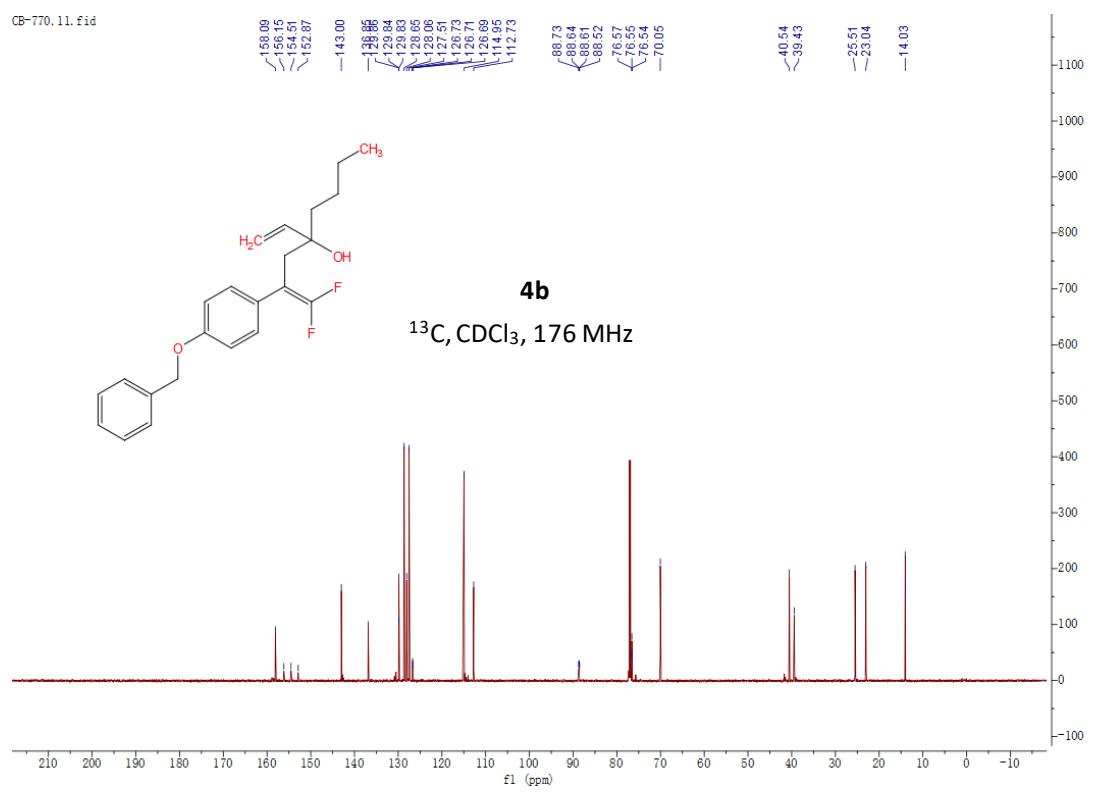


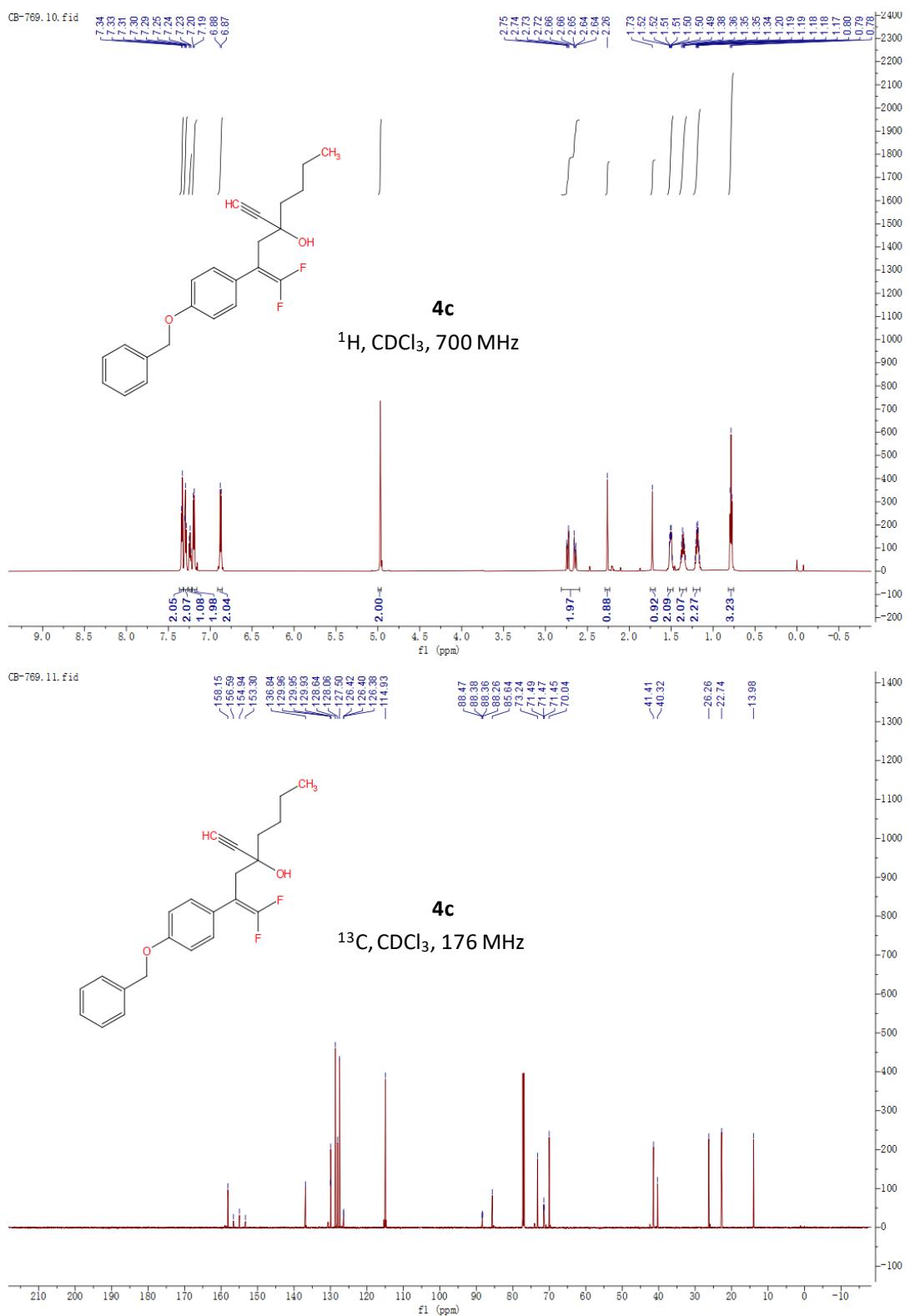




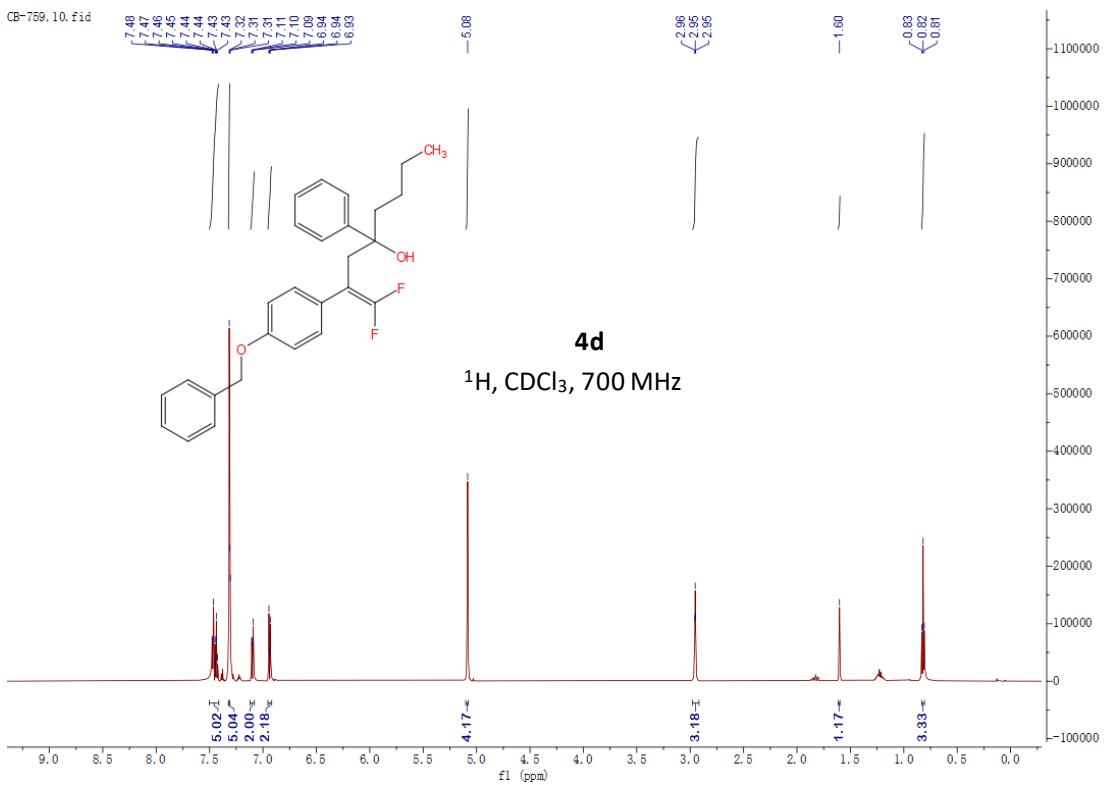
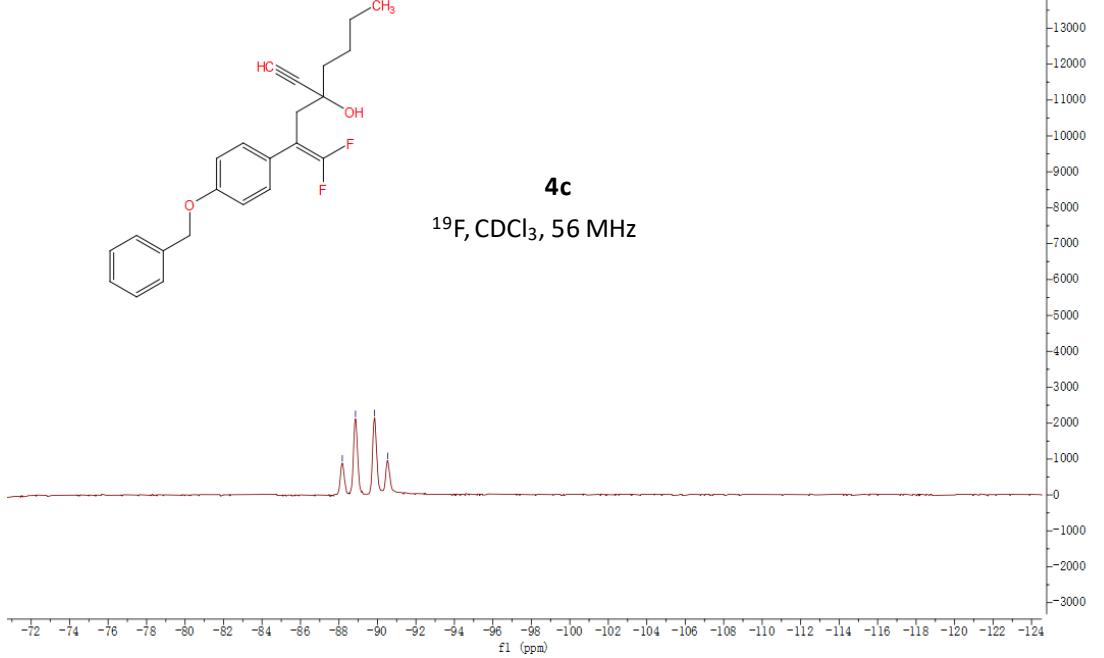
cb-777
Recorded on Oxford Instruments X-Pulse

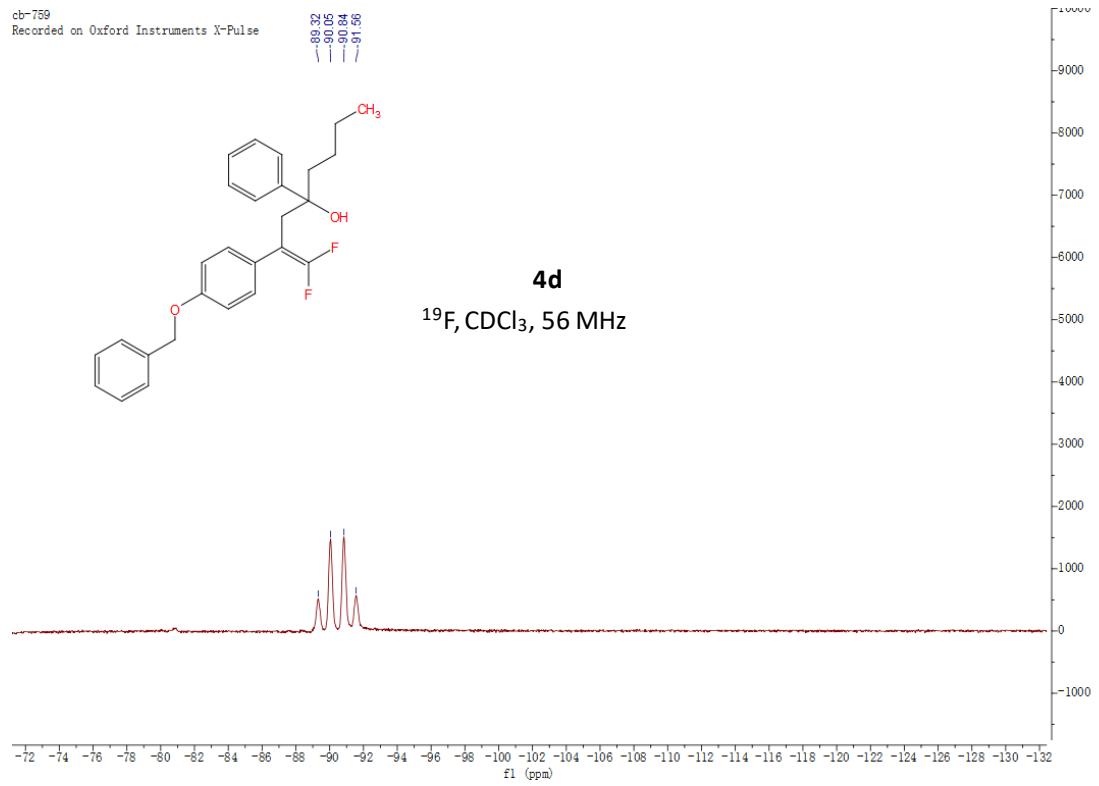
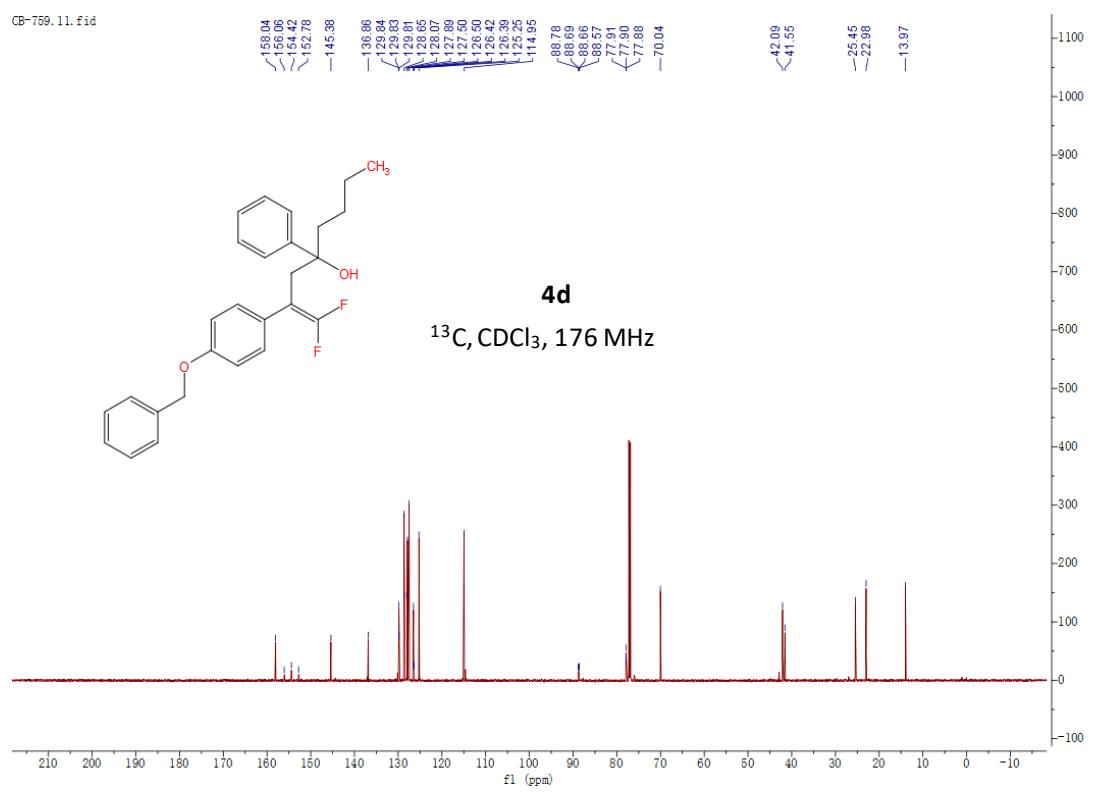


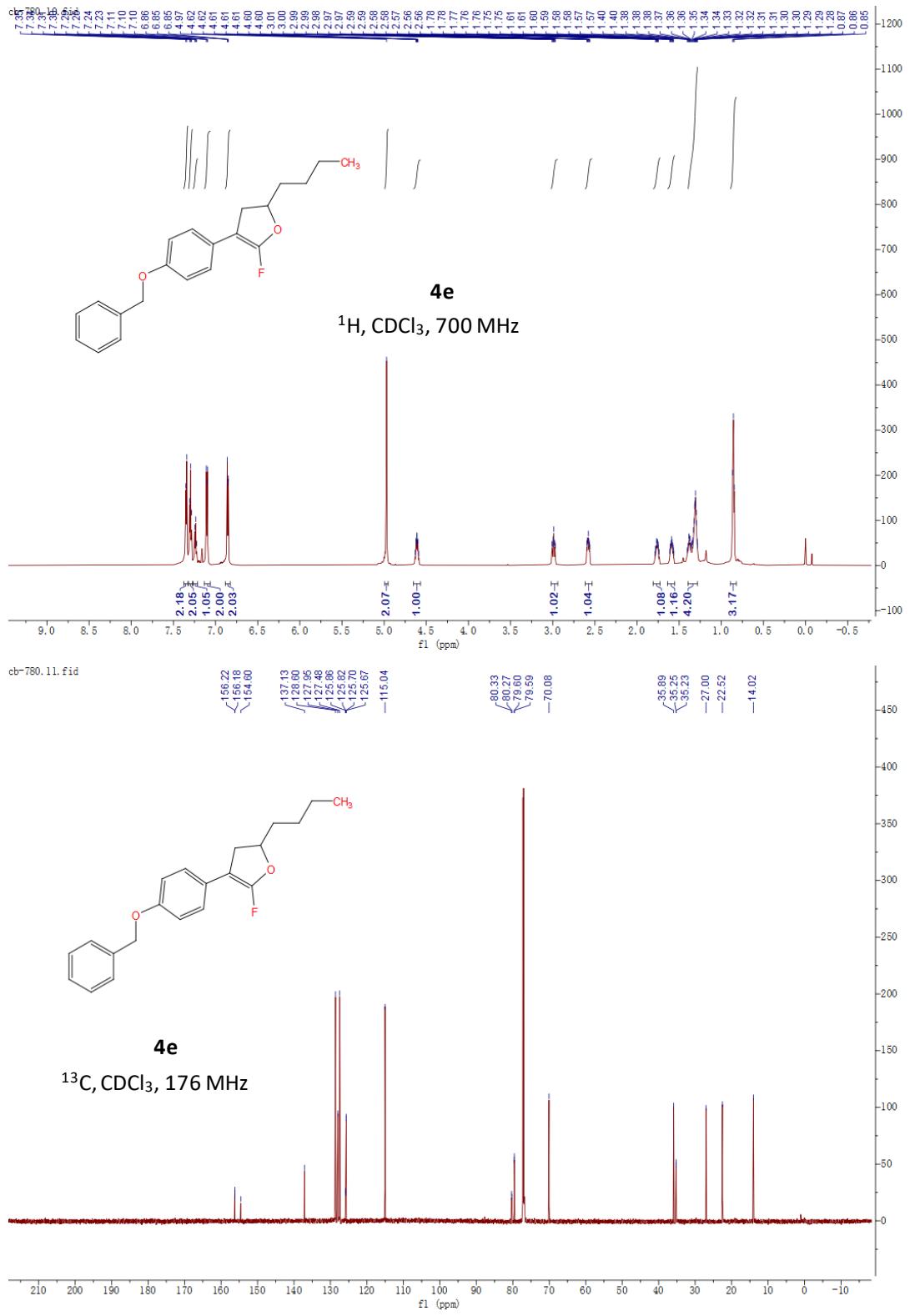




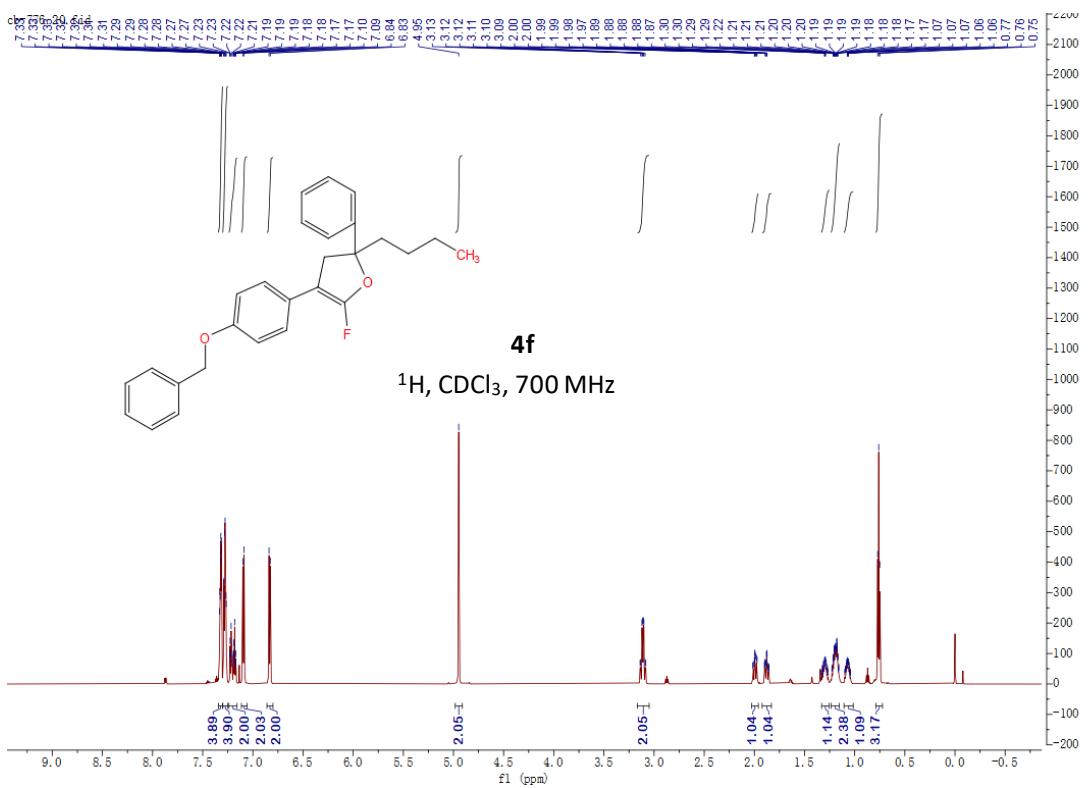
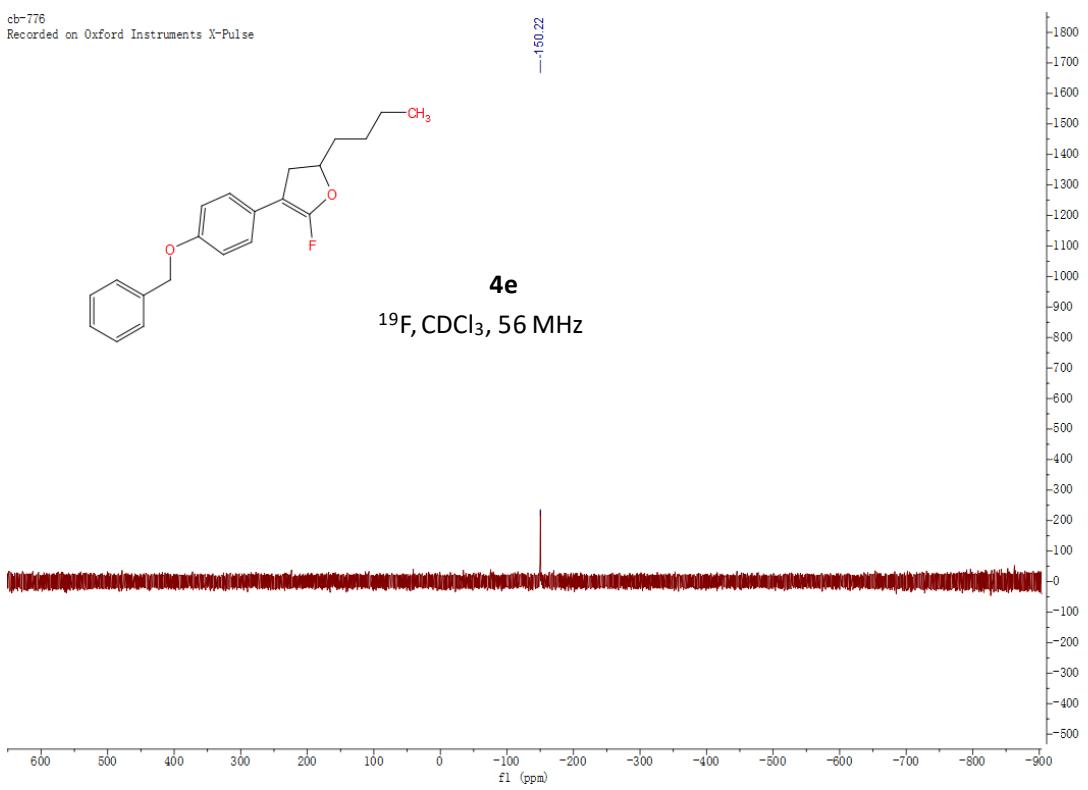
cb-769
Recorded on Oxford Instruments X-Pulse



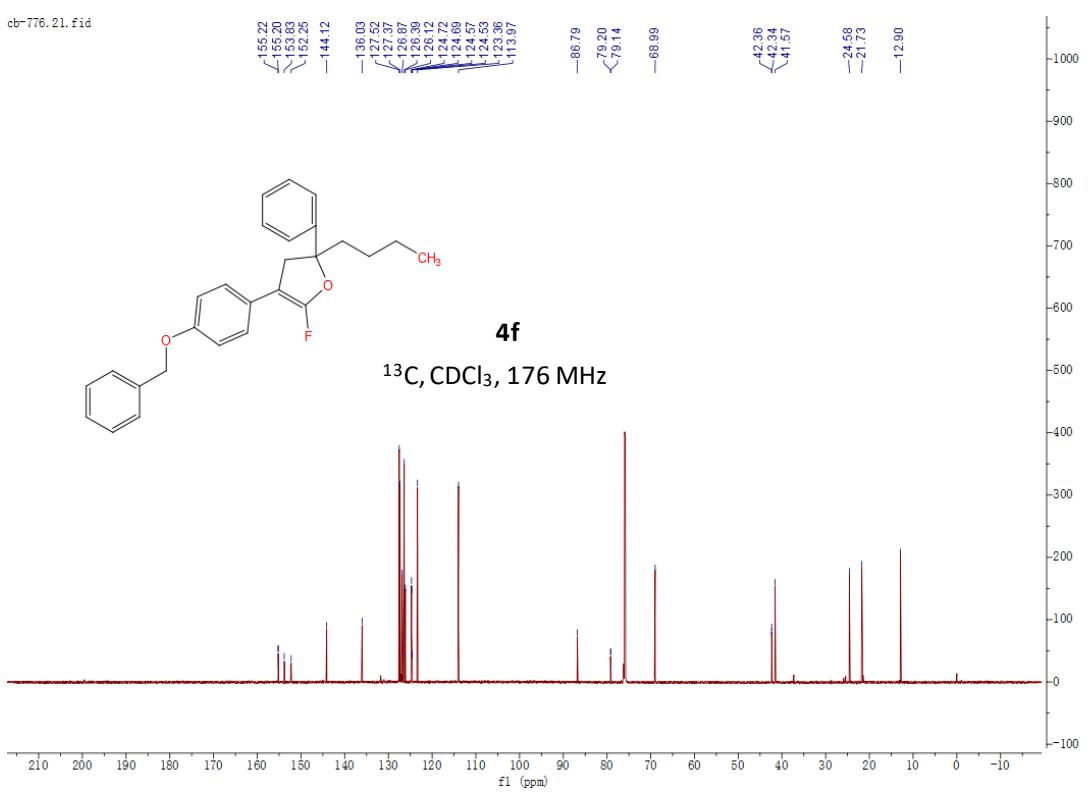




cb-776
Recorded on Oxford Instruments X-Pulse



cb-776.21.fid



cb-776
Recorded on Oxford Instruments X-Pulse

