Supplementary Information

Palladium-Catalyzed Alkynylation of Allylic *gem*-Difluorides

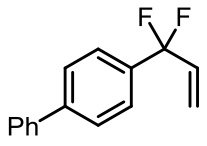
Supplementary Information

General Information

Unless noted otherwise, all the solvents and commercially available reagents were purchased and used directly. Benzene, 1,4-dioxane and tetrahydrofuran were distilled freshly over sodium, and carefully freeze-pump-thawed. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Reactions were monitored with thin layer chromatography (TLC) using silica gel 60 F-254 plates. TLC plates were normally visualized by UV irradiation (254 nm or 365 nm), stained with basic $KMnO_4$. Flash chromatography was performed using silica gel 60 (300−400 mesh). Vials (15 x 45 mm 1 dram (4 mL) / 17 x 60 mm 3 dram (7.5 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried or put in an oven overnight and cooled in a desiccator. Mass (HRMS) analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI). Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with Bruker AVANCE Ⅲ–300 (300 MHz, ^{1}H at 300 MHz, ^{13}C at 75 MHz) or 400 (400 MHz, ^{1}H at 400 MHz, ^{13}C at 101 MHz) or 600 (600 MHz, ^{1}H at 600 MHz, ^{13}C at 151 MHz).^{19}F NMR spectra were recorded on Bruker AVANCE Ⅲ–400.Unless otherwise noted, all spectra were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ = 7.26 ppm (^{1}H) and 77.00 ppm (^{13}C)). For ^{19}F NMR, $CFCl_3$ is used as the external standard. Coupling constants were reported in Hertz (Hz). Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All other materials were obtained from Energy Chemical and were used as received.

Syntheses of Allyl *gem*-difluoromethyl compounds

The Allyl gem-difluoromethyl compounds are prepared according to the previously reported literature.[1]



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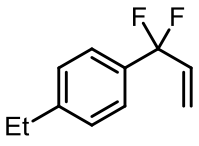

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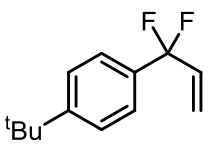

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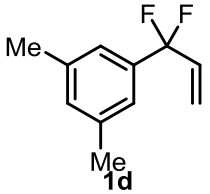

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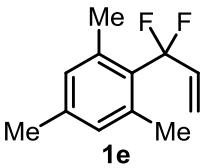

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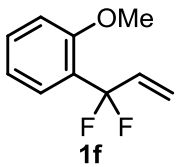

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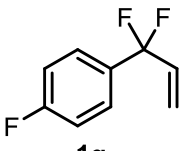

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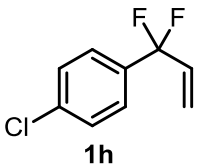

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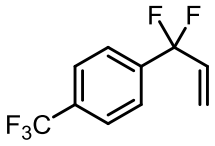

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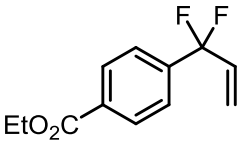

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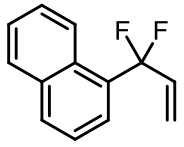

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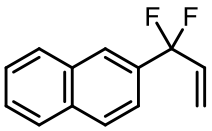

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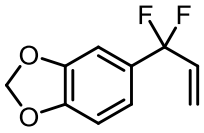

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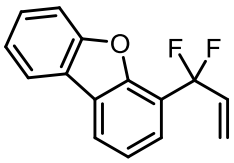

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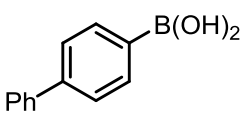
The compounds are commercially available and were used as recieved.



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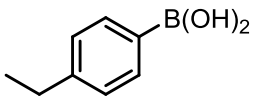

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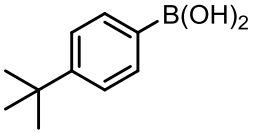

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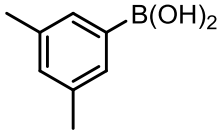

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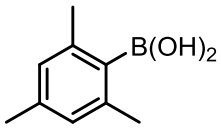

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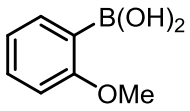

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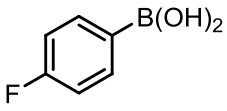

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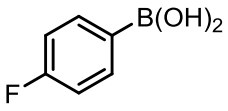

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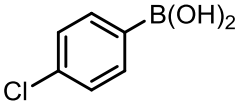

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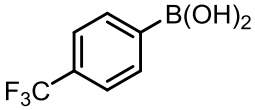

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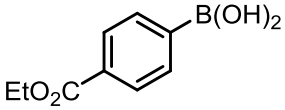

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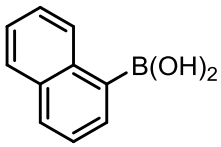

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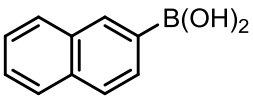

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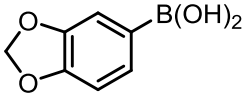

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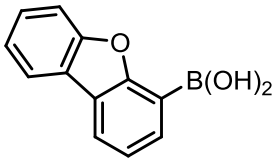

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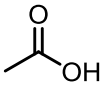

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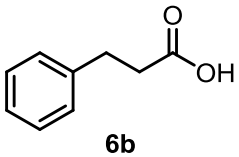

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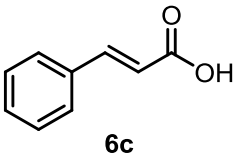

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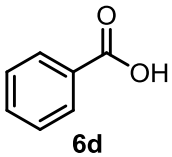

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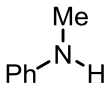

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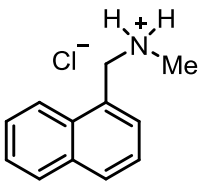

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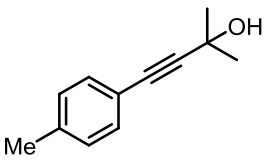
Syntheses of alkynol compounds

The alkynols are prepared according to the previously reported literature.[2]



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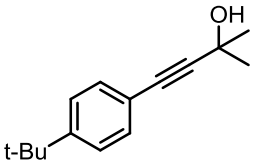

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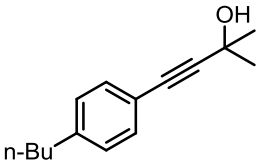

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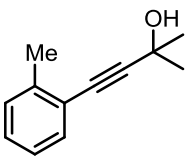

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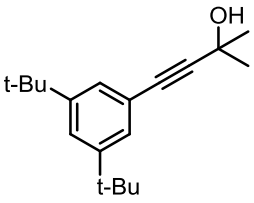

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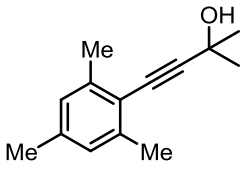

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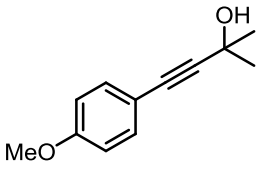

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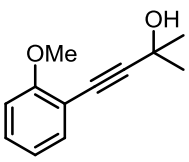

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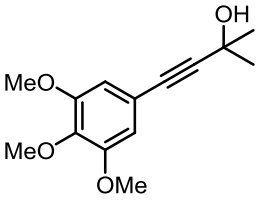

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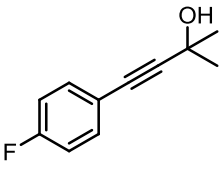

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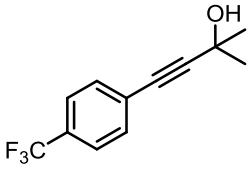

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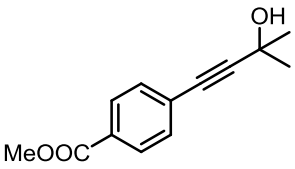

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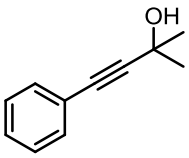

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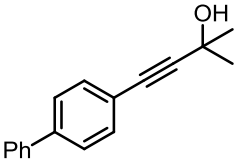

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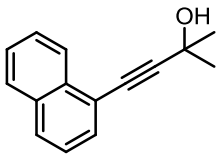

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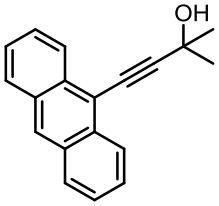

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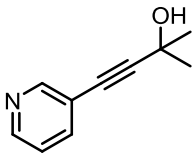

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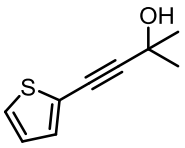

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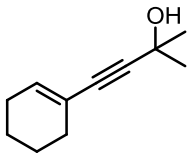

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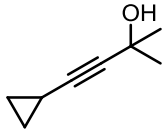
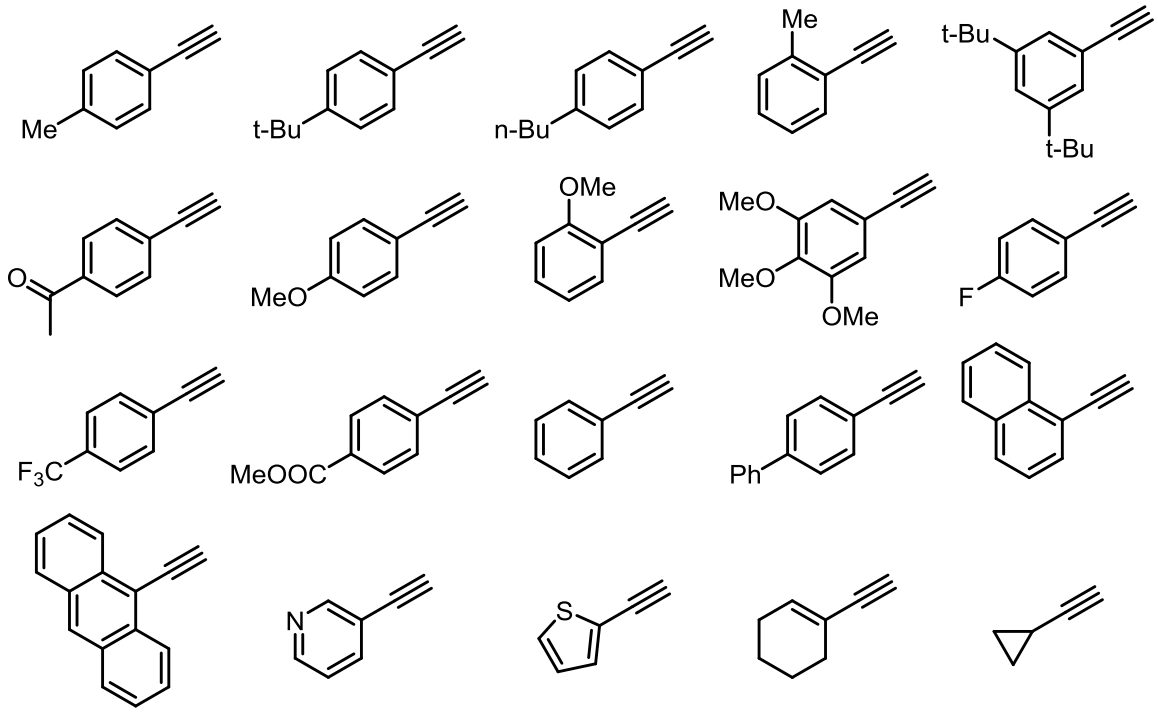


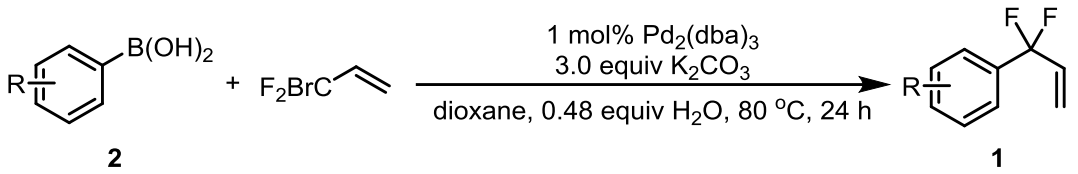
4t

These compounds are commercially available and were used as received.



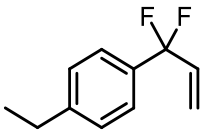
Experimental Section

General Procedure A



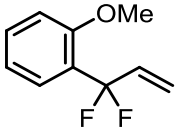
2 **1**

To a 25 mL of sealed tube were added phenylboronic acid **2** (2.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (0.02 mmol) and K_2CO_3 (829 mg, 6.0 mmol, 3 equiv) under air, followed by fresh distilled dioxane (10.0 mL) and H_2O (18 μl, 0.96 mmol, 0.48 equiv) with stirring. 3-Bromo-3,3-difluoropropene (330 μl, 3.0 mmol, 1.5 equiv) was added subsequently. The sealed tube was screw capped and heated to 80 °C (oil bath). After stirring for 24 h, the reaction mixture was cooled to room temperature and diluted with H_2O and ethyl acetate and the layers were separated. The aqueous layer was extracted with ethyl acetate, filtered through a pad of Na_2SO_4 and concentrated. The residue was purified with silica gel chromatography (petroleum ether) to provide pure product **1**.



1c

1-(1,1-difluoroallyl)-4-ethylbenzene (**1c**) was prepared from **2b** (300.2 mg, 2 mmol) as a colorless oil according to the General Procedure A (eluent for chromatography: petroleum ether) in 93% yield (169.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 4.0 Hz 2H), 6.15 (ddt, *J* = 17.2, 10.8, 9.6 Hz, 1H), 5.57 (dtd, *J* = 17.2, 2.8, 0.8 Hz, 1H), 5.46 (dd, *J* = 10.8, 0.8 Hz, 1H), 2.67 (q, *J* = 36.0 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.2, 133.9 (t, *J* = 30.4 Hz), 133.6 (t, *J* = 23.2 Hz), 127.9, 125.5 (t, *J* = 5.6 Hz), 119.5 (t, *J* = 9.2 Hz), 119.5 (t, *J* = 229.3 Hz), 28.63, 15.40. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -92.98. **HRMS (EI)** calcd for $C_{11}H_{12}F_2$ $[M]^+$: 182.0898, found 182.0902.

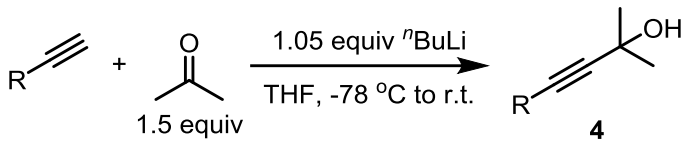


1h

1-(1,1-difluoroallyl)-2-methoxybenzene (**1h**) was prepared from **2f** (304.1 mg, 2 mmol) as a colorless oil

according to the General Procedure A (eluent for chromatography: petroleum ether) in 44% yield (162.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.41 (t, *J* = 16.0, 8.0 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 4.0 Hz, 1H), 6.37 (dq, *J* = 17.4, 10.8 Hz, 1H), 5.59 (dtd, *J* = 17.2, 2.8, 0.8 Hz, 1H), 5.40 (dd, *J* = 11.2, 1.2 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.9, 133.6 (t, *J* = 28.9 Hz), 131.5, 126.3 (t, *J* = 8.2 Hz), 124.6 (t, *J* = 26.7 Hz), 120.3, 118.6 (t, *J* = 9.6 Hz), 118.6 (t, *J* = 230.3 Hz), 111.8, 55.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -94.05. **HRMS (ESI)** calcd for Chemical Formula: $C_{10}H_{10}F_2O$ $[M+H]^+$: 223.0331, found 223.0334.

Preparation of alkynol[2]

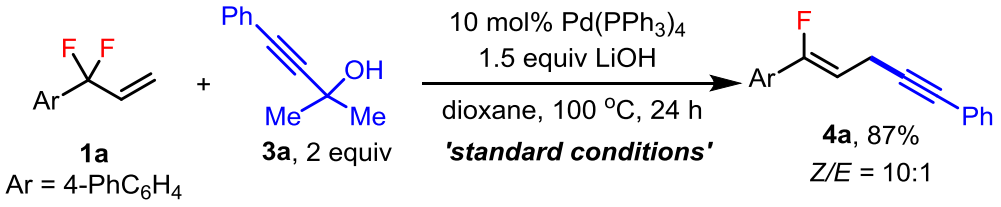


4

To a solution of ethynyl (10.0 mmol, 1.0 equiv) in tetrahydrofuran (10.0 mL), was added ^{n}BuLi (4.2 mL, 10.5 mmol, 1.05 equiv) slowly at -78 °C. After the reaction was stirred for 2 h, the propan-2-one (870 mg, 15.0 mmol, 1.5 equiv) was added slowly and the reaction was stirred for 20 min. Then the reaction was stirred for 5 h at room temperature. After quenched with NH_4Cl(aq) and the aqueous layer was extracted with ethyl acetate, and the organic layer was washed with brine. The organic layer was combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. Purification by column chromatography on silica gel eluting with petroleum ether: ethyl acetate = 5:1 gave the alkynol**.**

Reaction optimization[a,b]

Optimization of Reaction Conditions



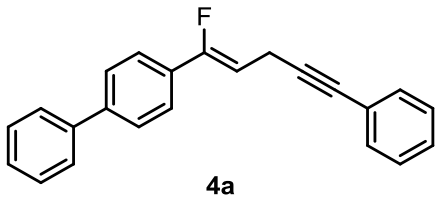
Entry	$Pd(PPh_3)_4$ (mol %)	Base	Solvent	T/°C	t/h	Yield (%) of **4a**[a,b]
1	10	LiOH	dioxane	80	24	71
2	5	LiOH	dioxane	80	24	67
3	**10**	**LiOH**	**dioxane**	**100**	**24**	**87**
4	10	Cs_2CO_3	dioxane	100	24	16
5	10	K_3PO_4	dioxane	100	24	19
6	10	NaOMe	dioxane	100	24	26
7	10	LiOH	THF	100	24	32
8	10	LiOH	DMF	100	24	26
9	10	LiOH	DMA	100	24	20
10	10	LiOH	MeCN	100	24	trace
11	10	LiOH	dioxane	100	12	38
12	10	LiOH	dioxane	100	6	24

[a]Each reaction was run on a 0.1 mmol scale in a sealed 4 mL vial for 24 h; *E*/*Z* ratios were determined by ^{19}F NMR. [b]Isolated yields.

General Procedure for the Palladium-Catalyzed Alkynylation, Esterification and Amination of Allylic gem-Difluorides

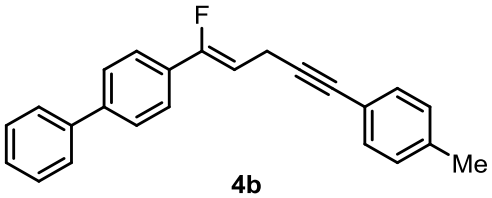
Method A: To a 4 mL of sealed tube were added 4-(1,1-difluoroallyl)-1,1'-biphenyl **1** (1.0 equiv), alkynol **2** (2.0 equiv), LiOH (1.5 equiv), then added $Pd(PPh_3)_4$ (10 mol %) under N_2 , followed by dioxane (1 mL). The sealed tube was screw capped and heated to 100 ºC. After stirring for 24 h, the reaction mixture was cooled to room temperature, filtered through a pad of Na_2SO_4 and concentrated. The residue was purified with silica gel chromatography to provide pure product.

Method B: To a 4 mL of sealed tube were added 4-(1,1-difluoroallyl)-1,1'-biphenyl **1** (1.0 equiv), acid or amine (2.0 equiv), LiOH (1.5 equiv), then added $Pd(PPh_3)_4$ (5 mol %) under N_2 , followed by dioxane (1 mL). The sealed tube was screw capped and heated to 80 ºC. After stirring for 24 h, the reaction mixture was cooled to room temperature, filtered through a pad of Na_2SO_4 and concentrated. The residue was purified with silica gel chromatography to provide pure product. *Note:^{19}F NMR confirms Z/E ratios are unchanged by separation.*



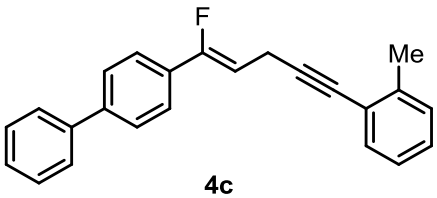
4a

(*Z*)-4-(1-fluoro-5-phenylpent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4a**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 87% yield (54.0 mg, *Z/E* = 10:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.61 (m, 6H), 7.49 – 7.44 (m, 4H), 7.37 (tt, *J* = 12.0, 4.0 Hz, 1H), 7.31 (dt, *J* = 4.4, 2.8 Hz, 3H), 5.59 (dt, *J* = 35.5, 7.1 Hz, 1H), 3.48 (dd, *J* = 7.1, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.1 (d, $J_{C\text{-}F}$ = 249.2 Hz), 141.7, 140.2, 131.6, 130.9 (d, $J_{C\text{-}F}$ = 28.7 Hz), 128.8, 128.2, 127.8, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.1 Hz), 127.0, 124.6 (d, $J_{C\text{-}F}$ = 7.0 Hz), 123.5, 87.12 (d, $J_{C\text{-}F}$ = 2.0 Hz), 80.5, 29.7, 15.1 (d, $J_{C\text{-}F}$ = 8.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -118.65. **HRMS (EI)** calcd for Chemical Formula: $C_{23}H_{17}F$ $[M]^+$: 312.1308, found 312.1309.



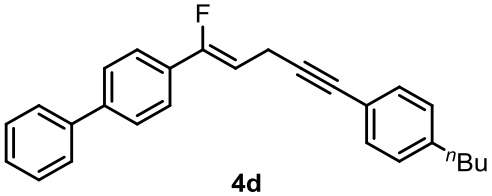
4b

(*Z*)-4-(1-fluoro-5-(p-tolyl)pent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4b**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 76% yield (49.6 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.54 – 7.51 (m, 6H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (td, J = 8.0, 4.0 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 5.50 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.38 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.0 (d, $J_{C\text{-}F}$ = 249.0 Hz), 141.6, 140.2, 137.8, 131.5, 130.9 (d, $J_{C\text{-}F}$ = 28.6 Hz), 129.0, 128.8, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 124.5 (d, $J_{C\text{-}F}$ = 7.0 Hz), 120.4, 101.4 (d, *J* = 16.7 Hz), 86.3 (d, $J_{C\text{-}F}$ = 2.2 Hz), 80.5, 21.4, 15.1 (d, $J_{C\text{-}F}$ = 8.2 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.81. **HRMS (EI)** calcd for Chemical Formula: $C_{24}H_{19}F$ $[M]^+$: 324.1465, found 324.1453.



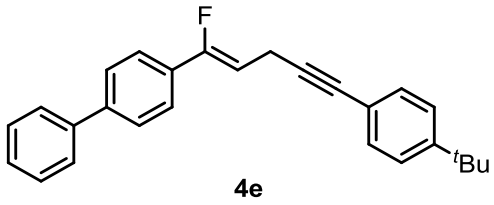
4c

(*Z*)-4-(1-fluoro-5-(o-tolyl)pent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4c**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 64% yield (41.7 mg, *Z/E* = 15:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.51 – 7.49 (m, 6H), 7.37 – 7.24 (m, 4H), 7.08 (d, *J* = 4.4 Hz, 2H), 7.02 (dq, *J* = 8.4, 4.4 Hz, 1H), 5.49 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.41 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.1 (d, $J_{C\text{-}F}$ = 249.0 Hz), 141.6, 140.2, 140.08, 131.9, 130.9 (d, $J_{C\text{-}F}$ = 28.6 Hz), 129.3, 128.8, 127.8, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 125.4, 124.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 123.3, 101.5 (d, $J_{C\text{-}F}$ = 16.8 Hz), 91.0 (d, $J_{C\text{-}F}$ = 2.0 Hz), 79.4, 20.7, 15.3 (d, $J_{C\text{-}F}$ = 8.3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.57. **HRMS (EI)** calcd for Chemical Formula: $C_{24}H_{19}F$ $[M]^+$: 324.1465, found 324.1462.



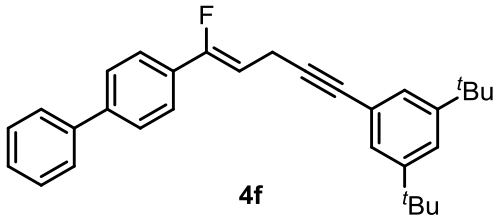
4d

(*Z*)-4-(5-(4-butylphenyl)-1-fluoropent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4d**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 71% yield (52.3 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.52 – 7.49 (m, 6H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 2H), 5.47 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.36 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.49 (t, *J* = 8.0 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.24 (dq, *J* = 14.8, 7.2 Hz, 2H), 0.82 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.0 (d, $J_{C\text{-}F}$ = 248.9 Hz), 142.8, 141.6, 140.2, 131.5, 130.9 (d, $J_{C\text{-}F}$ = 28.7 Hz), 128.8, 128.3, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 124.5 (d, $J_{C\text{-}F}$ = 6.9 Hz), 120.6, 101.4 (d, $J_{C\text{-}F}$ = 16.7 Hz), 86.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 80.6, 35.5, 33.4, 22.3, 15.1 (d, $J_{C\text{-}F}$ = 8.3 Hz), 13.9. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.78. **HRMS (EI)** calcd for Chemical Formula: $C_{27}H_{25}F$ $[M]^+$: 368.1935, found 368.1932.



4e

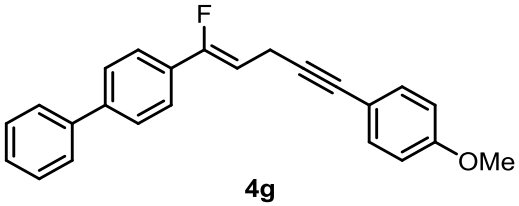
(*Z*)-4-(5-(4-(tert-butyl)phenyl)-1-fluoropent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4e**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 69% yield (50.8 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.54 – 7.51 (m, 6H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.22 (m, 5H), 5.50 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.38 (dd, *J* = 7.2, 1.6 Hz, 2H), 1.22 (s, 9H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.0 (d, $J_{C\text{-}F}$ = 249.0 Hz), 151.0, 141.6, 140.2, 131.3, 130.9 (d, $J_{C\text{-}F}$ = 28.8 Hz), 128.8, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.1 Hz), 127.0, 125.2, 124.5 (d, $J_{C\text{-}F}$ = 7.0 Hz), 120.5, 101.5 (d, $J_{C\text{-}F}$ = 16.8 Hz), 86.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 80.5, 34.7, 31.2, 15.2 (d, $J_{C\text{-}F}$ = 8.3 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.78. **HRMS (EI)** calcd for Chemical Formula: $C_{27}H_{25}F$ $[M]^+$: 368.1935, found 368.1928.



4f

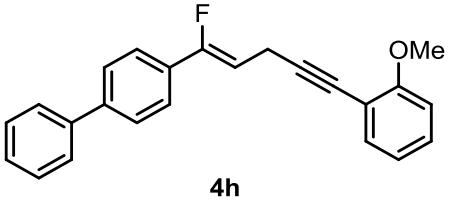
(*Z*)-4-(5-(3,5-di-tert-butylphenyl)-1-fluoropent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4f**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 76% yield (64.4 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.54

– 7.51 (m, 6H), 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 2H), 7.22 (d, J = 2.0 Hz, 2H), 5.52 (dt, J = 35.6, 7.2 Hz, 1H), 3.40 (dd, J = 7.2, 1.6 Hz, 2H), 1.23 (s, 18H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.0 (d, $J_{C\text{-}F}$ = 248.9 Hz), 150.7, 141.6, 140.3, 130.9 (d, $J_{C\text{-}F}$ = 28.7 Hz), 128.8, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.1 Hz), 127.0, 125.9, 124.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 122.4, 122.3, 101.5 (d, $J_{C\text{-}F}$ = 16.7 Hz), 85.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 81.5, 34.8, 31.3, 15.2 (d, $J_{C\text{-}F}$ = 8.3 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.87. **HRMS (EI)** calcd for Chemical Formula: $C_{31}H_{33}F$ $[M]^+$: 424.2561, found 424.2559.



4g

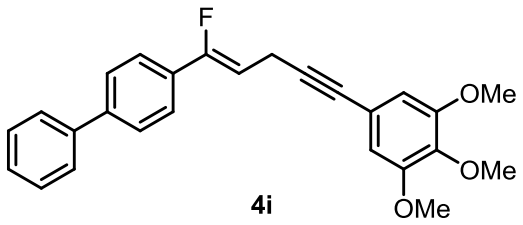
(*Z*)-4-(1-fluoro-5-(4-methoxyphenyl)pent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4g**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 71% yield (48.6 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.52 – 7.50 (m, 6H), 7.38 – 7.34 (m, 2H), 7.29 – 7.27 (m, 3H), 6.74 (dt, J = 12.0, 4.0 Hz, 2H), 5.48 (dt, J = 35.6, 7.2 Hz, 1H), 3.70 (s, 3H), 3.36 (dd, J = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.2, 157.0 (d, $J_{C\text{-}F}$ = 248.9 Hz), 141.6, 140.2, 133.0, 130.9 (d, $J_{C\text{-}F}$ = 28.7 Hz), 128.8, 127.6, 127.2,127.1, 127.0, 115.6, 113.8, 101.5 (d, $J_{C\text{-}F}$ = 16.7 Hz), 85.5 (d, $J_{C\text{-}F}$ = 2.1 Hz), 80.2, 55.2, 15.1 (d, $J_{C\text{-}F}$ = 8.3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.87. **HRMS (ESI)** calcd for Chemical Formula: $C_{24}H_{19}FO$ $[M+H]^+$: 343.1493, found 343.1490.



4h

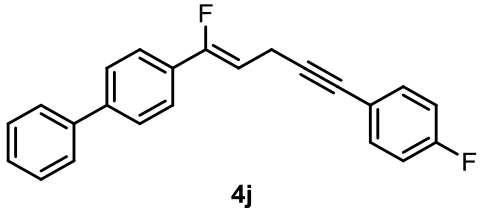
(*Z*)-4-(1-fluoro-5-(2-methoxyphenyl)pent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4h**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 61% yield (41.8 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.58 – 7.51 (m, 6H), 7.39 – 7.33 (m, 3H), 7.30 – 7.17 (m, 2H), 6.84 – 6.78 (m, 2H), 5.53 (dt, J = 35.6, 7.2 Hz, 1H), 3.82 (s, 3H), 3.47 (dd, J = 7.2, 1.6 Hz, 2H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.9, 157.0 (d, $J_{C\text{-}F}$ = 248.9 Hz), 141.6, 140.3, 133.8, 130.9 (d, $J_{C\text{-}F}$ = 28.7 Hz), 129.3, 128.8, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 124.6 (d, $J_{C\text{-}F}$ = 7.0 Hz), 120.4, 112.5, 110.5, 101.5 (d, $J_{C\text{-}F}$ = 16.7 Hz), 91.3, 76.6,

55.8, 15.5.**^{19}F NMR (376 MHz, $CDCl_3$)** δ -118.75. **HRMS (ESI)** calcd for Chemical Formula: $C_{24}H_{19}FO$ $[M+H]^+$: 343.1493, found 343.1495.



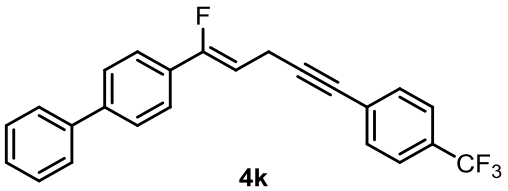
4i

(*Z*)-4-(1-fluoro-5-(3,4,5-trimethoxyphenyl)pent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4i**) **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 30:1) in 58% yield (46.6 mg, *Z/E* = 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.52 (m, 6H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 (tt, *J* = 12.0, 4.0 Hz, 1H), 6.60 (s, 2H), 5.50 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.77 (s, 9H), 3.39 (dd, J = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2 (d, $J_{C\text{-}F}$ = 250.48 Hz), 153.0, 141.7, 140.2, 138.4, 130.8 (d, $J_{C\text{-}F}$ = 33.3 Hz), 128.9, 127.7, 127.2, 127.1, 127.0, 124.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 118.5, 108.7, 101.1 (d, $J_{C\text{-}F}$ = 16.8 Hz), 86.2 (d, $J_{C\text{-}F}$ = 5.1 Hz), 60.9, 56.1, 15.07 (d, $J_{C\text{-}F}$ = 8.3 Hz).**^{19}F NMR (376 MHz, $CDCl_3$)** δ -118.66. **HRMS (ESI)** calcd for Chemical Formula: $C_{26}H_{23}FO_3$ $[M+H]^+$: 403.1704, found 403.1703.



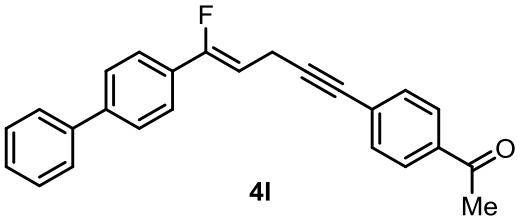
4j

(*Z*)-4-(1-fluoro-5-(4-fluorophenyl)pent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4j**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 73% yield (48.2 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.50 (m, 6H), 7.39 – 7.25 (m, 5H), 6.92 – 6.87 (m, 2H), 5.47 (dtd, *J* = 35.6, 7.2, 1.2 Hz, 1H), 3.36 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.2 (d, $J_{C\text{-}F}$ = 248.5 Hz), 157.2 (d, $J_{C\text{-}F}$ = 249.3 Hz), 141.7, 140.2, 133.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.8 (d, $J_{C\text{-}F}$ = 28.6 Hz), 128.8, 127.6, 127.2, 127.1, 127.0, 124.6 (d, $J_{C\text{-}F}$ = 7.0 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.0 Hz), 101.0 (d, $J_{C\text{-}F}$ = 16.7 Hz), 86.8, 79.4, 15.0 (d, $J_{C\text{-}F}$ = 8.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.66 – -111.69 (m), -118.54 (d, *J* = 4.2 Hz). **HRMS (EI)** calcd for Chemical Formula: $C_{23}H_{16}F_2$ $[M]^+$: 330.1215, found 330.1217.



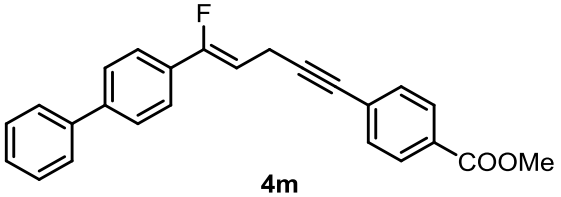
4k

(Z)-4-(1-fluoro-5-(4-(trifluoromethyl)phenyl)pent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4k**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 64% yield (48.6 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.53 – 7.50 (m, 6H), 7.45 (q, *J* = 8.0 Hz, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (tt, J = 8.0, 4.0 Hz, 1H), 5.47 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.39 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.5 (d, $J_{C\text{-}F}$ = 249.6 Hz), 141.8, 140.2, 131.9, 130.7 (d, $J_{C\text{-}F}$ = 28.5 Hz), 128.9, 127.7, 127.2, 127.1, 127.0, 125.2, 125.1, 124.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 124.0 (q, $J_{C\text{-}F}$ = 272.7 Hz), 100.5 (d, $J_{C\text{-}F}$ = 16.8 Hz), 89.9 (d, $J_{C\text{-}F}$ = 2.2 Hz), 79.4, 15.1 (d, $J_{C\text{-}F}$ = 8.4 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.13, -62.71. **HRMS (EI)** calcd for Chemical Formula: $C_{24}H_{16}F_4$ $[M]^+$: 380.1183, found 380.1179.



4l

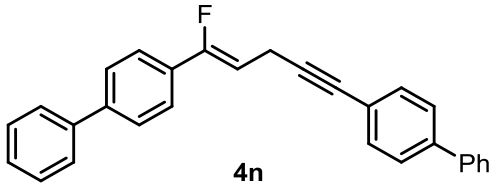
(*Z*)-1-(4-(5-([1,1'-biphenyl]-4-yl)-5-fluoropent-4-en-1-yn-1-yl)phenyl)ethan-1-one (**4l**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 30:1) in 57% yield (40.4 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.52 (m, 6H), 7.43 (d, J = 8.4 Hz, 2H), 7.38 (t, *J* = 4.0 Hz, 2H), 7.30 (tt, *J* = 12.0, 4.0 Hz, 1H), 5.49 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.42 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.51 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 197.4, 157.4 (d, $J_{C\text{-}F}$ = 249.6 Hz), 141.8, 140.2, 135.9, 131.7, 130.7 (d, $J_{C\text{-}F}$ = 28.4 Hz), 128.9, 128.2, 127.7, 127.2, 127.1, 127.0, 124.6 (d, $J_{C\text{-}F}$ = 7.0 Hz), 100.6 (d, $J_{C\text{-}F}$ = 16.7 Hz), 90.9, 79.9, 26.6, 15.2 (d, $J_{C\text{-}F}$ = 8.4 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.19. **HRMS (ESI)** calcd for Chemical Formula: $C_{26}H_{23}F$ $[M+H]^+$: 355.1493, found 355.1496.



4m

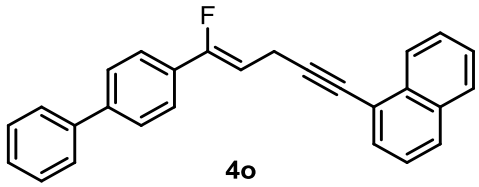
methyl (*Z*)-4-(5-([1,1'-biphenyl]-4-yl)-5-fluoropent-4-en-1-yn-1-yl)benzoate (**4m**) was prepared from

1a (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 45% yield (33.3 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.51 (m, 6H), 7.42 – 7.35 (m, 4H), 7.31 – 7.27 (m, 1H), 5.49 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.83 (s, 3H), 3.41 (dd, *J* = 7.2, 1.6 Hz, 2H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 166.6, 157.4 (d, $J_{C\text{-}F}$ = 249.7 Hz), 141.8, 140.2, 131.6, 130.7 (d, $J_{C\text{-}F}$ = 28.6 Hz), 129.4, 129.1, 128.8, 128.3, 127.7, 127.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 124.6 (d, $J_{C\text{-}F}$ = 7.1 Hz), 100.6 (d, $J_{C\text{-}F}$ = 16.8 Hz), 90.50 (d, $J_{C\text{-}F}$ = 2.0 Hz), 79.9, 52.2, 15.2 (d, $J_{C\text{-}F}$ = 8.3 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.23. **HRMS (ESI)** calcd for Chemical Formula: $C_{25}H_{19}FO_2$ $[M+MeOHH]^+$: 403.1704, found 403.1706.



4n

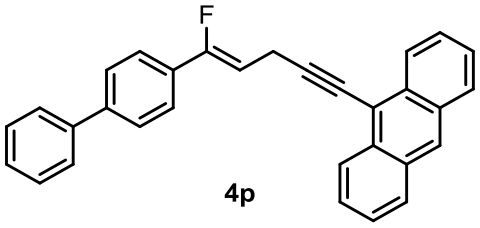
(*Z*)-4,4''-(1-fluoropent-1-en-4-yne-1,5-diyl)di-1,1'-biphenyl (**4n**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 62% yield (48.1 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.54 – 7.49 (m, 8H), 7.47 – 7.41 (m, 4H), 7.39 – 7.33 (m, 4H), 7.31 – 7.24 (m, 2H), 5.51 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.41 (dd, *J* = 7.2, 1.6 Hz, 2H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.2 (d, $J_{C\text{-}F}$ = 249.2 Hz), 141.7, 140.5, 140.4, 140.2, 132.0, 130.9 (d, $J_{C\text{-}F}$ = 28.6 Hz), 128.8, 128.8, 127.6, 127.5, 127.1 (d, $J_{C\text{-}F}$ = 2.1 Hz), 127.0, 126.9, 126.8, 124.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 122.4, 101.2 (d, $J_{C\text{-}F}$ = 16.9 Hz), 87.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 80.3, 15.2 (d, $J_{C\text{-}F}$ = 8.3 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.61. **HRMS (EI)** calcd for Chemical Formula: $C_{29}H_{21}F$ $[M]^+$: 388.1622, found 388.1619.



4o

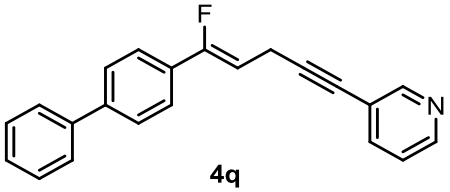
(*Z*)-1-(5-([1,1'-biphenyl]-4-yl)-5-fluoropent-4-en-1-yn-1-yl)naphthalene (**4o**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 55% yield (39.8 mg, *Z/E* = 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.73 (q, *J* = 16.0, 12.0 Hz, 2H), 7.59 – 7.46 (m, 8H), 7.44 – 7.25 (m, 5H), 5.58 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.54 (dd, *J* = 7.2, 1.6 Hz, 2H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.3 (d, $J_{C\text{-}F}$ = 249.3 Hz), 141.7, 140.2, 133.5, 133.1, 130.9 (d, $J_{C\text{-}F}$ = 28.6 Hz), 130.3, 128.8, 128.3, 128.2, 127.6, 127.2 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 126.6, 126.3, 126.2, 125.2, 124.6 (d, $J_{C\text{-}F}$ = 6.8 Hz), 121.2, 101.3 (d, $J_{C\text{-}F}$ = 16.7

Hz), 92.1 (d, J_{C-F} = 2.0 Hz), 78.6, 15.5 (d, J_{C-F} = 8.3 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.34. **HRMS (EI)** calcd for Chemical Formula: $C_{27}H_{19}F$ $[M]^+$:362.1465 , found 362.1468.



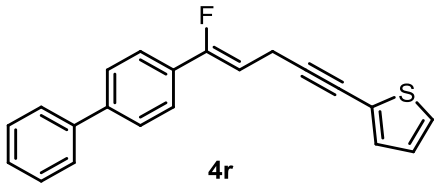
4p

(*Z*)-9-(5-([1,1'-biphenyl]-4-yl)-5-fluoropent-4-en-1-yn-1-yl)anthracene (**4p**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 49% yield (40.4 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.49 (d, *J* = 8.8 Hz, 2H), 8.30 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.47 (m, 8H), 7.38 (dt, *J* = 13.2, 7.6 Hz, 4H), 7.28 (t, *J* = 7.2 Hz, 1H), 5.68 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.73 (dd, *J* = 7.2, 1.6 Hz, 2H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.4 (d, J_{C-F} = 249.4 Hz), 141.8, 140.2, 132.7, 131.1, 130.9 (d, J_{C-F} = 28.6 Hz), 128.9, 128.6, 127.7, 127.3, 127.2, 127.1, 126.8, 126.4, 125.6, 124.7 (d, J_{C-F} = 7.0 Hz), 117.7, 101.3 (d, J_{C-F} = 16.7 Hz), 98.5 (d, J_{C-F} = 1.9 Hz), 77.2, 15.9 (d, J_{C-F} = 8.3 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.06. **HRMS (ESI)** calcd for Chemical Formula: $C_{31}H_{21}F$ $[M]^+$: 412.1622, found 412.1618.



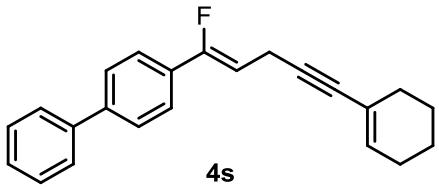
4q

(*Z*)-3-(5-([1,1'-biphenyl]-4-yl)-5-fluoropent-4-en-1-yn-1-yl)pyridine (**4q**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 47% yield (30.4 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.59 (dd, *J* = 2.0, 1.0 Hz, 1H), 8.42 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.63 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.53 – 7.51 (m, 6H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (tt, *J* = 8.0, 2.0 Hz, 1H), 7.17 – 7.13 (m, 1H), 5.48 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.40 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.4 (d, J_{C-F} = 249.9 Hz), 152.3, 148.1, 141.8, 140.2, 138.6, 130.6 (d, J_{C-F} = 28.5 Hz), 128.8, 127.6, 127.1 (d, J_{C-F} = 2.0 Hz), 127.0, 124.6 (d, J_{C-F} = 7.0 Hz), 122.9, 120.7, 100.5 (d, J_{C-F} = 16.7 Hz), 90.8 (d, J_{C-F} = 2.2 Hz), 77.2, 15.12 (d, J_{C-F} = 8.4 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.09. **HRMS (ESI)** calcd for Chemical Formula: $C_{22}H_{16}FN$ $[M+H]^+$: 314.1340, found 314.1341.



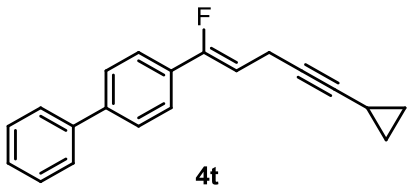
4r

(*Z*)-2-(5-([1,1'-biphenyl]-4-yl)-5-fluoropent-4-en-1-yn-1-yl)thiophene (**4r**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 58% yield (36.9 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.54 – 7.51 (m, 6H), 7.37 (t, J = 8.0 Hz, 2H), 7.29 (tt, *J* = 8.0, 2.0 Hz, 1H), 7.12 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.09 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.87 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.48 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.40 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.3 (d, $J_{C\text{-}F}$ = 249.4 Hz), 141.7, 140.2, 131.4, 130.7 (d, $J_{C\text{-}F}$ = 28.6 Hz), 128.8, 127.6, 127.2, 127.1, 126.8, 126.3, 124.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 123.56, 100.7 (d, $J_{C\text{-}F}$ = 16.6 Hz), 91.1 (d, $J_{C\text{-}F}$ = 2.1 Hz), 73.7, 15.4 (d, $J_{C\text{-}F}$ = 8.4 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.39. **HRMS (ESI)** calcd for Chemical Formula: $C_{21}H_{15}FS$ $[M+H]^+$: 319.0951, found 319.0948.



4s

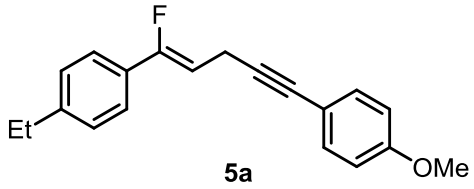
(*Z*)-4-(5-(cyclohex-1-en-1-yl)-1-fluoropent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4s**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 55% yield (34.8 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.53 – 7.51 (m, 6H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (tt, *J* = 8.0, 2.0 Hz, 1H), 6.00 (m, 1H), 5.42 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.27 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.09 – 1.94 (m, 4H), 1.62 – 1.42 (m, 4H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.9 (d, $J_{C\text{-}F}$ = 248.7 Hz), 141.6, 140.3, 134.1, 131.0 (d, $J_{C\text{-}F}$ = 28.6 Hz), 128.8, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 124.5 (d, $J_{C\text{-}F}$ = 6.9 Hz), 120.7, 101.8 (d, $J_{C\text{-}F}$ = 16.8 Hz), 84.2 (d, $J_{C\text{-}F}$ = 2.1 Hz), 82.2, 29.4, 25.6, 22.3, 21.5, 15.0 (d, $J_{C\text{-}F}$ = 8.3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -119.16. **HRMS (EI)** calcd for Chemical Formula: $C_{23}H_{21}F$ $[M]^+$: 317.1700, found 317.1703.



4t

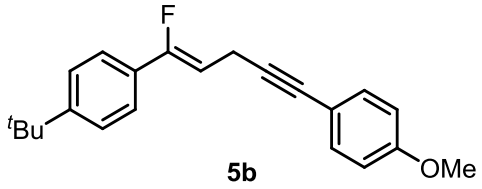
(*Z*)-4-(5-cyclopropyl-1-fluoropent-1-en-4-yn-1-yl)-1,1'-biphenyl (**4t**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 51%

yield (28.2 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.56 – 7.44 (m, 6H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.25 (m, 1H), 5.38 (dt, J = 35.7, 7.2 Hz, 1H), 3.11 (d, *J* = 7.2 Hz, 2H), 1.18 (m, 1H), 0.65 (dq, *J* = 8.1, 3.2, 2.6 Hz, 2H), 0.57 (tt, *J* = 5.1, 3.0 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.7 (d, $J_{C\text{-}F}$ = 248.5 Hz), 141.5, 140.3, 131.0 (d, $J_{C\text{-}F}$ = 28.7 Hz), 128.8, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 2.1 Hz), 127.0, 124.5 (d, $J_{C\text{-}F}$ = 6.8 Hz), 102.1 (d, $J_{C\text{-}F}$ = 16.8 Hz), 83.3, 72.7 (d, $J_{C\text{-}F}$ = 1.9 Hz), 14.4 (d, $J_{C\text{-}F}$ = 8.2 Hz), 7.9, 1.0. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -119.44. **HRMS (EI)** calcd for Chemical Formula: $C_{20}H_{17}F$ $[M]^+$: 276.1309, found 276.1305.



5a

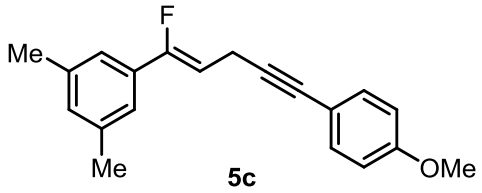
(*Z*)-1-ethyl-4-(1-fluoro-5-(4-methoxyphenyl)pent-1-en-4-yn-1-yl)benzene (5a) was prepared from **1b** (36.4 mg, 0.2 mmol) as a light oil according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 64% yield (37.7 mg, *Z/E* = 10:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 5.39 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.71 (s, 3H), 3.33 (d, *J* = 7.2 Hz, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.17 (d, *J* = 8.4 Hz, 3H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.2, 157.4 (d, $J_{C\text{-}F}$ = 275.0 Hz), 145.3, 133.0, 131.4, 128.3, 127.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 124.2 (d, $J_{C\text{-}F}$ = 6.9 Hz), 113.8, 100.5 (d, $J_{C\text{-}F}$ = 16.8 Hz), 85.7, 80.1, 55.2, 28.6, 15.4, 15.0 (d, $J_{C\text{-}F}$ = 8.4 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.55. **HRMS (EI)** calcd for Chemical Formula: $C_{20}H_{19}FO$ $[M]^+$: 294.1414, found 294.1415.



5b

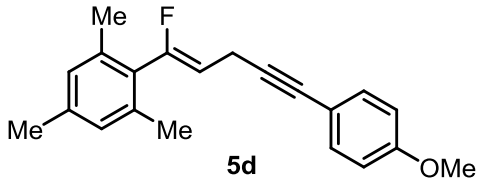
(*Z*)-1-(tert-butyl)-4-(1-fluoro-5-(4-methoxyphenyl)pent-1-en-4-yn-1-yl)benzene (5b) was prepared from **1c** (42.0 mg, 0.2 mmol) as a white oil according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 62% yield (40.0 mg, *Z/E* = 10:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.25 (m, 4H), 6.73 (d, *J* = 8.8 Hz, 2H), 5.39 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.70 (s, 3H), 3.33 (d, *J* = 7.2 Hz, 2H), 1.24 (s, 9H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.2, 157.3 (d, $J_{C\text{-}F}$ = 248.9 Hz), 152.1, 133.0, 129.9 (d, $J_{C\text{-}F}$ = 316.5 Hz), 125.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 123.9 (d, $J_{C\text{-}F}$ = 6.8 Hz), 115.7, 113.8, 100.6 (d, $J_{C\text{-}F}$ = 16.7 Hz), 85.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 80.1, 55.2, 34.7, 31.2, 15.0 (d, $J_{C\text{-}F}$ = 8.3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.72. **HRMS (EI)** calcd for Chemical

Formula: $C_{22}H_{23}FO$ $[M]^+$: 322.1727, found 322.1726.



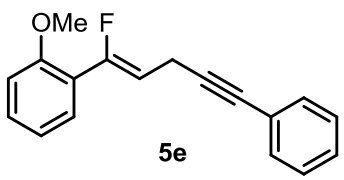
5c

(*Z*)-1-(1-fluoro-5-(4-methoxyphenyl)pent-1-en-4-yn-1-yl)-3,5-dimethylbenzene (5c) was prepared from **1d** (36.4 mg, 0.2 mmol) as a white oil according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 70% yield (41.2 mg, *Z/E* = 10:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.28 (d, *J* = 8.8 Hz, 1H), 7.08 (s, 2H), 6.89 (s, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.41 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.72 (s, 3H), 3.33 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.25 (s, 6H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.2, 157.5 (d, $J_{C\text{-}F}$ = 249.4 Hz), 138.0 (d, $J_{C\text{-}F}$ = 1.9 Hz), 133.0, 131.4, 130.6, 128.3, 122.0 (d, $J_{C\text{-}F}$ = 6.9 Hz), 115.7, 113.8, 101.1 (d, $J_{C\text{-}F}$ = 16.8 Hz), 85.7 (d, $J_{C\text{-}F}$ = 2.1 Hz), 80.1, 55.2, 21.3, 15.1 (d, $J_{C\text{-}F}$ = 8.4 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.38. **HRMS (EI)** calcd for Chemical Formula: $C_{20}H_{19}FO$ $[M]^+$: 294.1414, found 294.1411.



5d

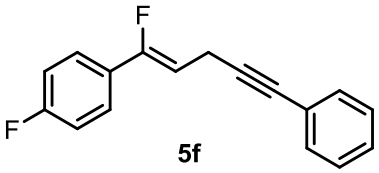
(*Z*)-2-(1-fluoro-5-(4-methoxyphenyl)pent-1-en-4-yn-1-yl)-1,3,5-trimethylbenzene (5d) was prepared from **1e** (39.2 mg, 0.2 mmol) as a white oil according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 84% yield (51.8 mg, *Z/E* = 3:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.26 (d, *J* = 8.8 Hz, 2H), 6.79 (s, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.85 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.70 (s, 3H), 3.33 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.24 (s, 6H), 2.20 (s, 3H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.2, 155.6 (d, $J_{C\text{-}F}$ = 256.4 Hz), 139.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 137.8, 132.9, 129.5 (d, $J_{C\text{-}F}$ = 25.0 Hz), 128.2 (d, $J_{C\text{-}F}$ = 1.7 Hz), 115.8, 113.8, 106.5 (d, $J_{C\text{-}F}$ = 18.2 Hz), 85.8 (d, $J_{C\text{-}F}$ = 2.1 Hz), 80.0, 55.2, 21.1, 19.9, 15.0 (d, $J_{C\text{-}F}$ = 5.8 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -96.07. **HRMS (EI)** calcd for Chemical Formula: $C_{21}H_{21}FO$ $[M]^+$: 308.1571, found 308.1570.



5e

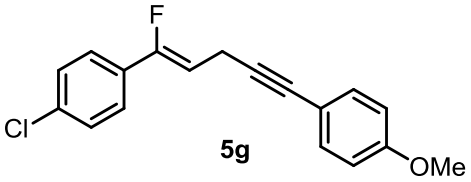
(*Z*)-1-(1-fluoro-5-phenylpent-1-en-4-yn-1-yl)-2-methoxybenzene (5e) was prepared from **1f** (36.8 mg,

0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 67% yield (35.7 mg, *Z/E* = 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.24 – 7.20 (m, 4H), 6.91 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.83 (dt, *J* = 38.0, 7.2 Hz, 1H), 3.83 (s, 3H), 3.40 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.0 (d, $J_{C\text{-}F}$ = 119.7 Hz), 153.0, 131.6, 129.8, 128.2, 127.7, 127.31(d, $J_{C\text{-}F}$ = 9.9 Hz), 123.7, 120.4, 111.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 106.2 (d, $J_{C\text{-}F}$ = 15.5 Hz), 87.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 80.1, 55.5, 15.4 (d, $J_{C\text{-}F}$ = 10.0 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -111.74. **HRMS (ESI)** calcd for Chemical Formula: $C_{18}H_{15}FO$ $[M+H]^+$: 267.1180, found 267.1181.



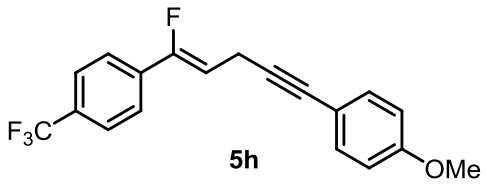
5f

(*Z*)-1-fluoro-4-(1-fluoro-5-phenylpent-1-en-4-yn-1-yl)benzene (5f) was prepared from **1g** (46.0 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 61% yield (31.0 mg, *Z/E* = 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.43 – 7.40 (m, 2H), 7.35 – 7.32 (m, 2H), 7.20 – 7.19 (m, 2H), 6.99 – 6.94 (m, 2H), 5.36 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.34 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.3, 159.8 (d, $J_{C\text{-}F}$ = 405.7 Hz), 155.3, 131.6, 128.2, 127.8, 126.1 (dd, $J_{C\text{-}F}$ = 8.3, 6.9 Hz), 123.5, 115.5 (dd, $J_{C\text{-}F}$ = 22.0, 1.9 Hz), 101.0 (dd, $J_{C\text{-}F}$ = 16.7, 2.0 Hz), 87.0 (d, $J_{C\text{-}F}$ = 2.1 Hz), 80.5, 15.0 (d, $J_{C\text{-}F}$ = 8.2 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -111.93, -117.63. **HRMS (EI)** calcd for Chemical Formula: $C_{17}H_{12}F_2$ $[M]^+$: 254.0902, found 254.0902.



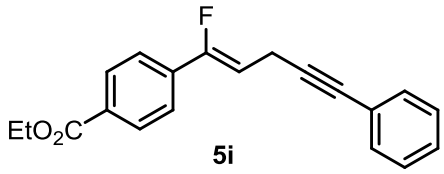
5g

(*Z*)-1-chloro-4-(1-fluoro-5-(4-methoxyphenyl)pent-1-en-4-yn-1-yl)benzene (5g) was prepared from **1h** (37.6 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 48% yield (28.8 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 (d, J = 8.6 Hz, 2H), 7.29 – 7.25 (m, 4H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.44 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.72 (s, 3H), 3.34 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.3, 156.3 (d, $J_{C\text{-}F}$ = 249.0 Hz), 133.0, 131.4, 128.7 (d, $J_{C\text{-}F}$ = 1.9 Hz), 128.3, 125.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 115.5, 113.8, 102.1 (d, $J_{C\text{-}F}$ = 16.7 Hz), 85.2, 80.3, 55.2, 15.1 (d, $J_{C\text{-}F}$ = 8.2 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.81. **HRMS (EI)** calcd for Chemical Formula: $C_{18}H_{14}ClFO$ $[M]^+$: 300.0712, found 300.0713.



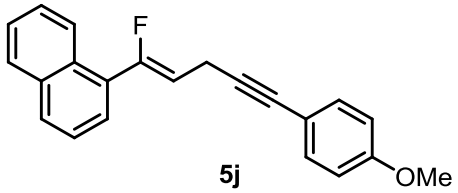
5h

(*Z*)-1-(5-fluoro-5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yn-1-yl)-4-methoxybenzene (5h) was prepared from **1i** (37.6 mg, 0.2 mmol) as a white oil according to the Method A (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 45% yield (30.0 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.56 (s, 3H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.19 (s, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.59 (dt, *J* = 35.2, 7.2 Hz, 1H), 3.73 (s, 3H), 3.38 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.3, 155.9 (d, $J_{C\text{-}F}$ = 249.4 Hz), 135.3 (d, $J_{C\text{-}F}$ = 28.8 Hz), 133.0, 131.4, 126.6 (q, $J_{C\text{-}F}$ = 232.3 Hz), 125.48 (dd, $J_{C\text{-}F}$ = 4.0, 2.3 Hz), 124.32 (d, $J_{C\text{-}F}$ = 7.1 Hz), 115.45, 113.86, 103.96 (d, $J_{C\text{-}F}$ = 16.4 Hz), 84.86 (d, $J_{C\text{-}F}$ = 2.1 Hz), 80.54, 55.18, 15.17 (d, $J_{C\text{-}F}$ = 8.0 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.74, -119.28. **HRMS (EI)** calcd for Chemical Formula: $C_{19}H_{14}F_4O$ $[M]^+$: 334.0975, found 334.0973.



5i

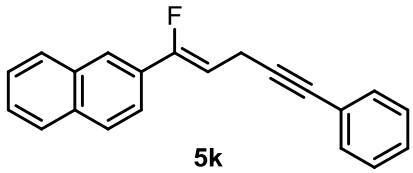
ethyl (*Z*)-4-(1-fluoro-5-phenylpent-1-en-4-yn-1-yl)benzoate (5i) was prepared from **1j** (45.2 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 54% yield (33.3 mg, *Z/E* = 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.22 – 7.21 (m, 3H), 5.60 (dt, *J* = 35.2, 7.2 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.39 (dd, *J* = 7.2, 1.6 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 166.0, 156.5 (d, $J_{C\text{-}F}$ = 249.7 Hz), 135.9 (d, $J_{C\text{-}F}$ = 28.3 Hz), 131.6, 130.7, 129.7 (d, $J_{C\text{-}F}$ = 2.2 Hz), 128.2, 127.9, 123.9 (d, $J_{C\text{-}F}$ = 7.2 Hz), 123.4, 103.7 (d, $J_{C\text{-}F}$ = 16.4 Hz), 86.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 80.7, 61.1, 15.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 14.3.**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.96. **HRMS (ESI)** calcd for Chemical Formula: $C_{20}H_{17}FO_2$ $[M+NH_4]^+$: 326.1151, found 326.1150.



5j

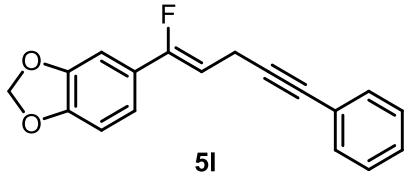
(*Z*)-1-(1-fluoro-5-(4-methoxyphenyl)pent-1-en-4-yn-1-yl)naphthalene (5j) was prepared from **1k** (40.8 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether)

in 60% yield (32.2 mg, *Z/E* = 6:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.10 (d, J = 7.2 Hz, 1H), 7.78 (dd, J = 7.9, 5.4 Hz, 2H), 7.50 (d, J = 7.1 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.35 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 5.28 (dt, J = 34.2, 7.1 Hz, 1H), 3.70 (s, 4H), 3.44 (dd, J = 7.1, 1.7 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.6 (d, $J_{C\text{-}F}$ = 278.3 Hz), 159.2, 133.5, 133.0, 130.1, 128.4, 127.4 (d, $J_{C\text{-}F}$ = 4.7 Hz), 126.7, 126.1, 125.5 (d, $J_{C\text{-}F}$ = 4.1 Hz), 125.0, 115.7, 113.8, 106.5 (d, $J_{C\text{-}F}$ = 17.1 Hz), 85.6 (d, $J_{C\text{-}F}$ = 2.1 Hz), 80.2, 55.2, 15.4 (d, $J_{C\text{-}F}$ = 6.7 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -99.52. **HRMS (EI)** calcd for Chemical Formula: $C_{22}H_{17}FO$ $[M]^+$: 316.1258, found 316.1255.



5k

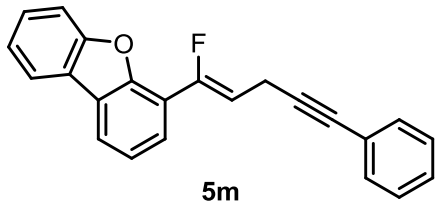
(*Z*)-2-(1-fluoro-5-phenylpent-1-en-4-yn-1-yl)naphthalene (5k) was prepared from **1l** (40.8 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 65% yield (37.2 mg, *Z/E* = 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.94 (s, 1H), 7.79 – 7.72 (m, 3H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.23 – 7.19 (m, 3H), 5.59 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.43 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.4 (d, $J_{C\text{-}F}$ = 249.2 Hz), 133.4, 133.0, 131.6, 129.2 (d, $J_{C\text{-}F}$ = 27.9 Hz), 128.5, 128.3, 128.2, 127.8, 127.7, 126.7, 126.6, 123.5, 123.4 (d, $J_{C\text{-}F}$ = 7.4 Hz), 121.7 (d, $J_{C\text{-}F}$ = 6.6 Hz), 101.8 (d, $J_{C\text{-}F}$ = 16.8 Hz), 87.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 80.5, 15.2 (d, $J_{C\text{-}F}$ = 8.5 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.69. **HRMS (EI)** calcd for Chemical Formula: $C_{21}H_{15}F$ $[M]^+$: 286.1152, found 286.1150.



5l

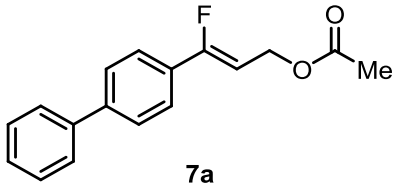
(*Z*)-5-(1-fluoro-5-phenylpent-1-en-4-yn-1-yl)benzo[d][1,3]dioxole (5l) was prepared from **1m** (39.6 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 75% yield (42.0 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.34 (d, *J* = 3.6 Hz, 1H), 7.21 (t, *J* = 3.2 Hz, 3H), 6.98 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 5.29 (dt, *J* = 35.6, 7.2 Hz, 1H), 3.34 (dd, J = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.1 (d, $J_{C\text{-}F}$ = 248.9 Hz), 148.3, 147.9 (d, $J_{C\text{-}F}$ = 2.6 Hz), 131.6, 128.2, 127.8, 126.2 (d, $J_{C\text{-}F}$ = 29.1 Hz), 123.5, 118.5 (d, $J_{C\text{-}F}$ = 7.4 Hz), 108.2 (d, $J_{C\text{-}F}$ = 1.8 Hz), 104.8 (d, $J_{C\text{-}F}$ = 7.5 Hz), 101.3, 99.8 (d, $J_{C\text{-}F}$ = 17.1 Hz), 87.3 (d, $J_{C\text{-}F}$ = 2.1 Hz), 80.4, 15.1 (d, $J_{C\text{-}F}$ = 8.4 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -116.62. **HRMS (EI)** calcd

for Chemical Formula: $C_{18}H_{13}FO_2$ $[M]^+$: 280.0894, found 280.0886.



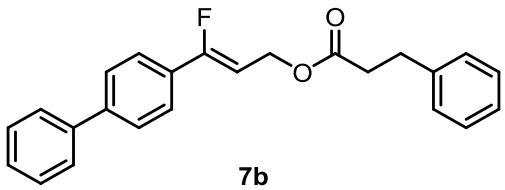
5m

(*Z*)-4-(1-fluoro-5-phenylpent-1-en-4-yn-1-yl)dibenzo[b,d]furan (5m) was prepared from **1n** (48.8 mg, 0.2 mmol) as a white solid according to the Method A (eluent for chromatography: petroleum ether) in 59% yield (38.5 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.83 (q, *J* = 12.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.39 – 7.37 (m, 3H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.18 (dm, 3H), 6.32 (dt, *J* = 37.6, 7.2 Hz, 1H), 3.51 (dd, *J* = 7.2, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.0, 153.0 (d, $J_{C\text{-}F}$ = 247.1 Hz), 131.7, 128.2, 127.8, 127.4, 124.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 123.6, 123.3, 123.2, 123.1, 122.7 (d, $J_{C\text{-}F}$ = 1.5 Hz), 120.9, 120.6, 117.1 (d, $J_{C\text{-}F}$ = 31.1 Hz), 111.9, 106.8, 106.6, 87.3 (d, $J_{C\text{-}F}$ = 2.2 Hz), 80.5, 15.4 (d, $J_{C\text{-}F}$ = 9.1 Hz).**^{19}F NMR (376 MHz, CDCl$_3$)** δ -117.78. **HRMS (ESI)** calcd for Chemical Formula: $C_{23}H_{15}FO$ $[M+H]^+$: 327.1180, found 327.1181.



7a

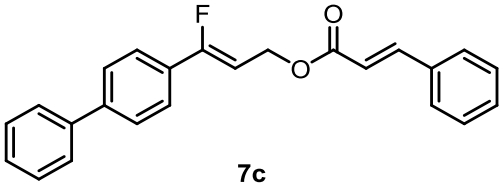
(*Z*)-3-([1,1'-biphenyl]-4-yl)-3-fluoroallyl acetate (**7a**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method B (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 67% yield (36.4 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.60 (m, 6H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (tt, *J* = 12.0, 8.0 Hz, 1H), 5.67 (dt, *J* = 35.2, 7.2 Hz, 1H), 4.88 (dd, *J* = 7.6, 2.0 Hz, 2H), 2.10 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.0, 159.5 (d, $J_{C\text{-}F}$ = 254.2 Hz), 142.4, 140.1, 130.2 (d, $J_{C\text{-}F}$ = 28.4 Hz), 128.9, 127.8, 127.2 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 125.0 (d, $J_{C\text{-}F}$ = 7.2 Hz), 100.0 (d, $J_{C\text{-}F}$ = 14.9 Hz), 57.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 20.9. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -115.07. **HRMS (ESI)** calcd for Chemical Formula: $C_{17}H_{15}FO_2$ $[M+H]^+$: 271.1129, found 271.1126.



7b

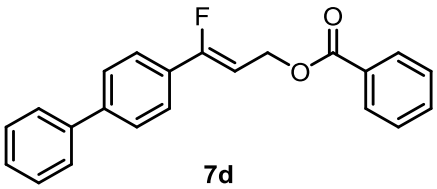
(*Z*)-3-([1,1'-biphenyl]-4-yl)-3-fluoroallyl 3-phenylpropanoate (**7b**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method B (eluent for chromatography: petroleum ether : ethyl

acetate = 20:1) in 68% yield (49.0 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (m, 6H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.21 – 7.18 (m, 2H), 7.13 – 7.11 (m, 3H), 5.53 (dt, *J* = 35.2, 7.2 Hz, 1H), 4.79 (dd, *J* = 7.6, 2.0 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 159.4 (d, $J_{C\text{-}F}$ = 254.1 Hz), 142.3, 140.4, 140.0, 128.9, 128.5, 128.3, 127.8, 127.2, 127.1, 127.0, 126.2, 125.0 (d, $J_{C\text{-}F}$ = 7.1 Hz), 100.0 (d, $J_{C\text{-}F}$ = 14.9 Hz), 57.73 (d, $J_{C\text{-}F}$ = 8.3 Hz), 35.8, 30.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.09. **HRMS (ESI)** calcd for Chemical Formula: $C_{24}H_{21}FO_2$ $[M+H]^+$:361.1598, found 361.1595.



7c

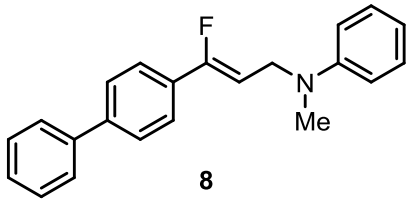
(*Z*)-3-([1,1'-biphenyl]-4-yl)-3-fluoroallyl cinnamate (**7c**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method B (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 66% yield (47.3 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.50 (m, 6H), 7.45 – 7.43 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 4H), 6.39 (d, *J* = 16.0 Hz, 1H), 5.66 (dt, *J* = 35.4, 7.6 Hz, 1H), 4.93 (dd, *J* = 7.6, 2.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 159.5 (d, $J_{C\text{-}F}$ = 254.0 Hz), 145.1, 142.3, 140.0, 134.3, 130.3, 128.9, 128.8, 128.1, 127.7, 127.2, 127.1, 127.0, 125.0 (d, $J_{C\text{-}F}$ = 7.2 Hz), 117.7, 100.1 (d, $J_{C\text{-}F}$ = 14.8 Hz), 57.8 (d, $J_{C\text{-}F}$ = 8.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.03. **HRMS (ESI)** calcd for Chemical Formula: $C_{24}H_{19}FO_2$ $[M+H]^+$: 359.1442, found 359.1444.



7d

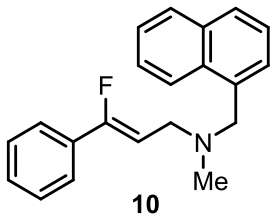
(*Z*)-3-([1,1'-biphenyl]-4-yl)-3-fluoroallyl benzoate (**7d**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method B (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 53% yield (35.7 mg, *Z/E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.68 – 7.59 (m, 6H), 7.56 (dt, *J* = 8.0, 4.0 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.39 (tt, *J* = 16.0, 8.0 Hz, 1H), 5.82 (dt, *J* = 35.2, 7.2 Hz, 1H), 5.16 (dd, *J* = 7.2, 2.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 160.83, 159.6 (d, $J_{C\text{-}F}$ = 255.5 Hz), 142.4, 140.1, 133.0, 130.2 (d, $J_{C\text{-}F}$ = 29.3 Hz), 130.1, 129.7, 128.9, 128.3, 127.8, 127.2, 127.1, 127.0, 125.0 (d, $J_{C\text{-}F}$ = 7.2 Hz), 100.1 (d, $J_{C\text{-}F}$ = 14.7 Hz), 58.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 29.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -114.86. **HRMS (ESI)** calcd for Chemical Formula:

$C_{22}H_{17}FO_2$ $[M+H]^+$: 333.1285, found 333.1288.



8

(*Z*)-*N*-(3-([1,1'-biphenyl]-4-yl)-3-fluoroallyl)-*N*-methylaniline (**8**) was prepared from **1a** (46.0 mg, 0.2 mmol) as a white solid according to the Method B (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 95% yield (60.5 mg, *Z*/*E* > 20:1 determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.49 (s, 6H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.21 – 7.16 (m, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.67 (t, *J* = 8.0 Hz, 1H), 5.46 (dt, *J* = 37.4, 6.8 Hz, 1H), 4.17 (dd, *J* = 6.8, 2.0 Hz, 2H), 2.91 (s, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.2 (d, $J_{C\text{-}F}$ = 248.3 Hz), 149.1, 141.7, 140.2, 130.7 (d, $J_{C\text{-}F}$ = 29.3 Hz), 129.3, 128.8, 127.6, 127.1, 127.0, 124.6 (d, $J_{C\text{-}F}$ = 7.1 Hz), 116.9, 113.0, 101.9 (d, $J_{C\text{-}F}$ = 16.4 Hz), 46.9 (d, $J_{C\text{-}F}$ = 6.3 Hz), 38.2. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.27. **HRMS (ESI)** calcd for Chemical Formula: $C_{22}H_{20}FN$ $[M+H]^+$: 318.1653, found 318.1656.



10

(*Z*)-3-fluoro-*N*-methyl-*N*-(naphthalen-2-ylmethyl)-3-phenylprop-2-en-1-amine (10) was prepared from **1p** (30.8 mg, 0.2 mmol) as a white solid according to the Method B (eluent for chromatography: petroleum ether : ethyl acetate = 20:1) in 80% yield (49.3 mg, *Z* only determined by ^{19}F NMR). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.20 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.70 (ddd, *J* = 27.6, 8.0, 1.2 Hz, 2H), 7.43 (dd, *J* = 7.6, 1.6 Hz, 3H), 7.39 (dd, *J* = 6.4, 1.6 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.28 – 7.21 (m, 3H), 5.52 (dt, *J* = 37.2, 7.2 Hz, 1H), 3.86 (s, 2H), 3.31 (dd, *J* = 7.6, 2.4 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.4 (d, $J_{C\text{-}F}$ = 249.3 Hz), 134.7, 133.8, 132.4, 132.1 (d, $J_{C\text{-}F}$ = 29.0 Hz), 128.8, 128.4, 128.0, 127.5, 125.9, 125.5, 125.1, 124.5, 124.2, 124.1, 102.9 (d, $J_{C\text{-}F}$ = 15.2 Hz), 60.0, 51.4 (d, $J_{C\text{-}F}$ = 4.5 Hz), 42.32.**^{19}F NMR (376 MHz, CDCl$_3$)** δ -117.77. **HRMS (ESI)** calcd for Chemical Formula: $C_{21}H_{20}FN$ $[M+H]^+$: 306.1653, found 306.1648.

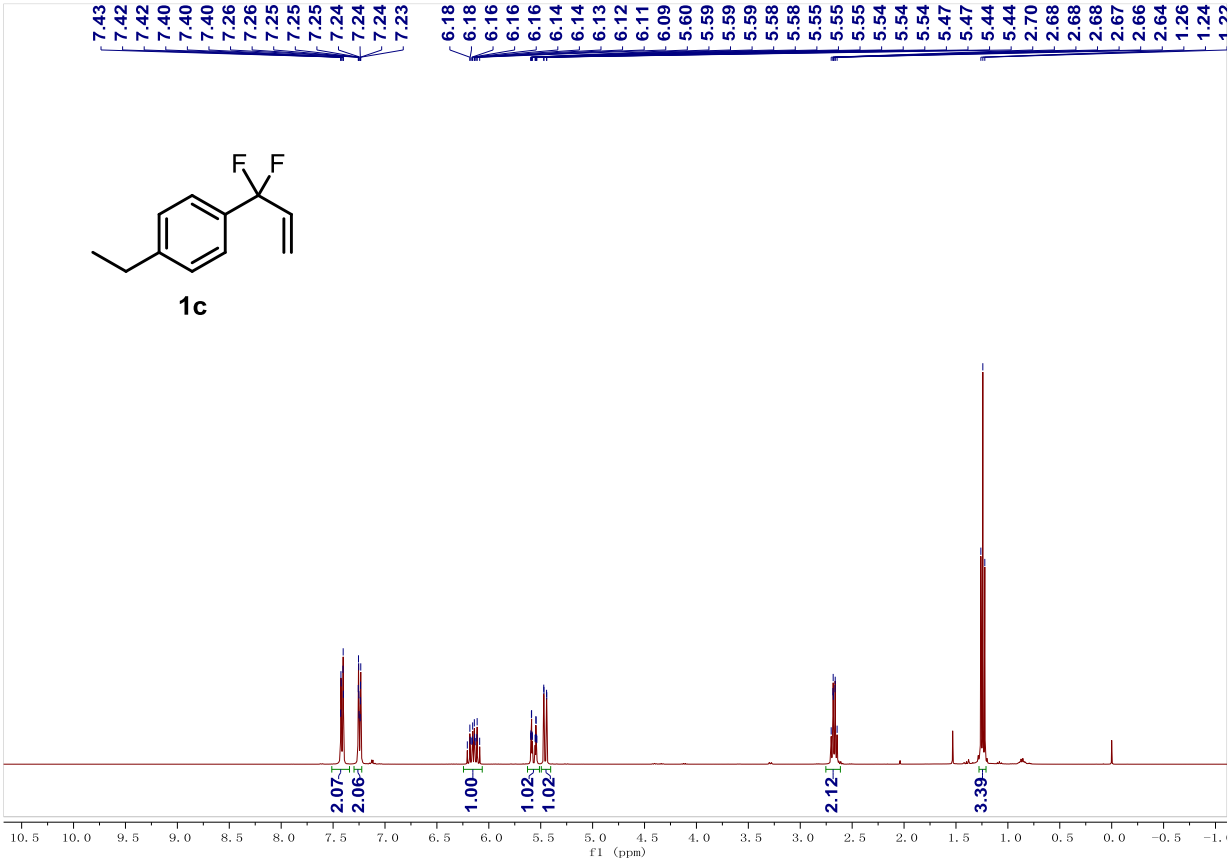
References

[1] Q.-Q. Min, Z.-S. Yin, Z. Feng, W.-H. Guo and X.-G. Zhang, *J. Am. Chem. Soc.* 2014, **136**, 1230.

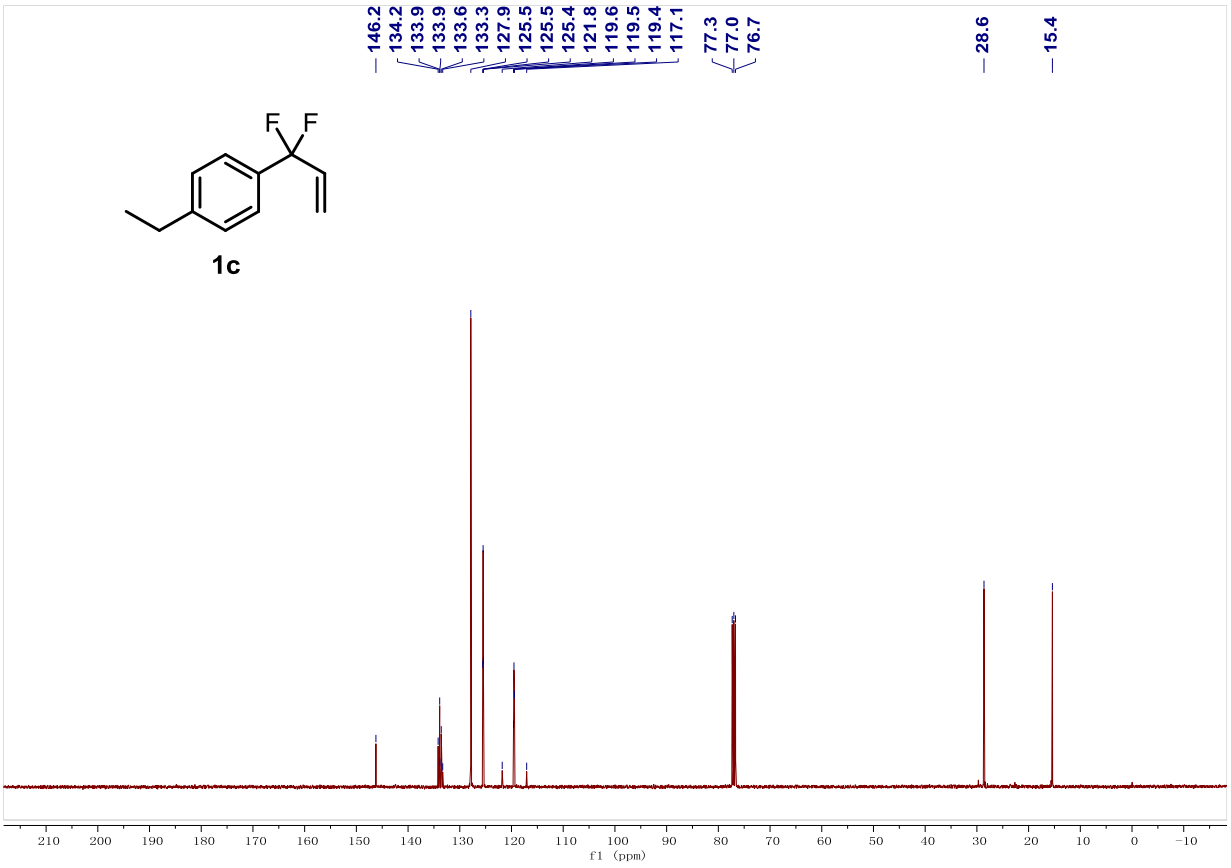
[2] X. Chen, M.-K. Li, Z.-P. Liu, C. Yang, H.-S. Xie, X.-W. Hu, S.-J. Su, H.-F. Jiang and W. Zeng, *Org. Lett.*, 2021, **23**, 6724.

NMR Spectra

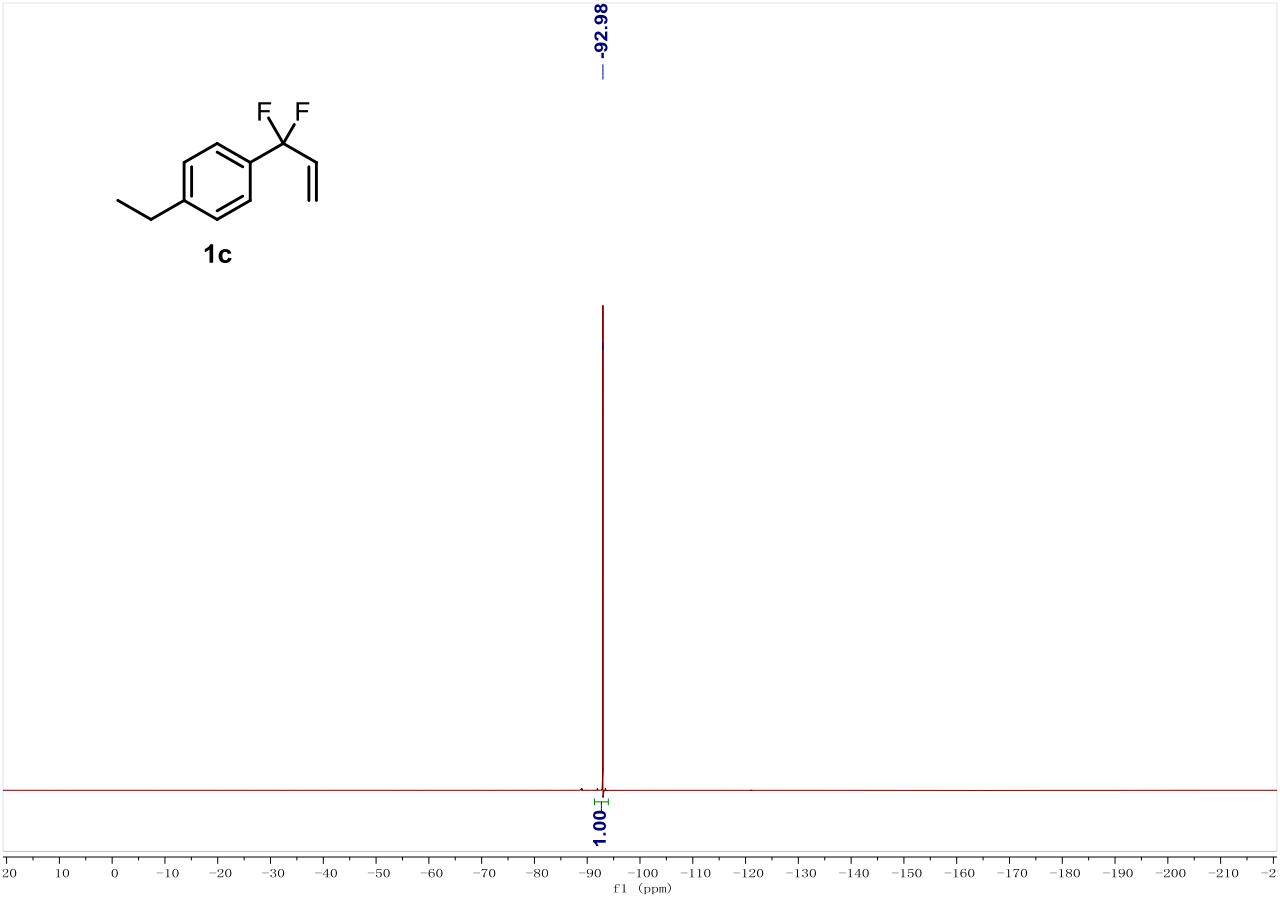
^{1}H NMR (400 MHz, $CDCl_3$)



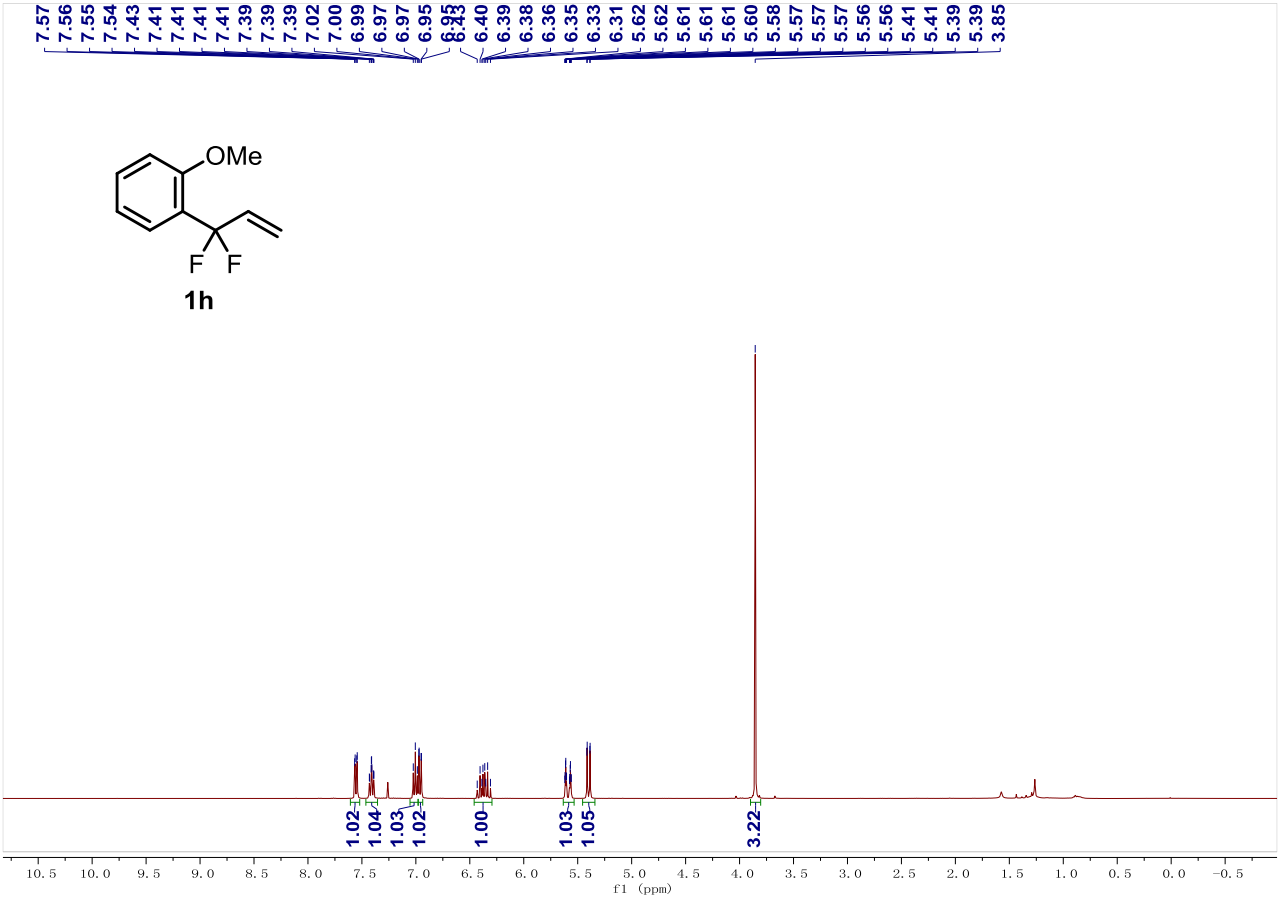
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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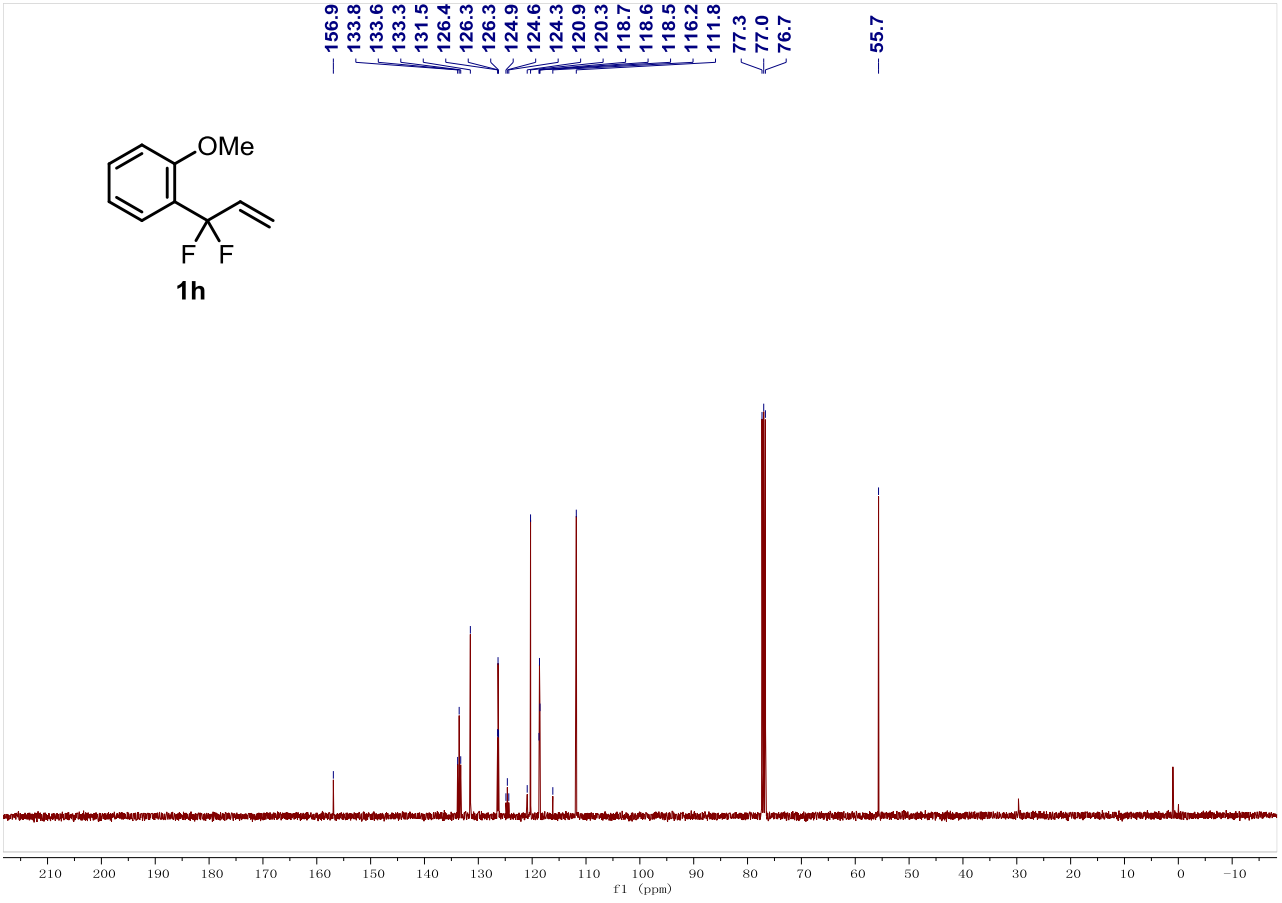

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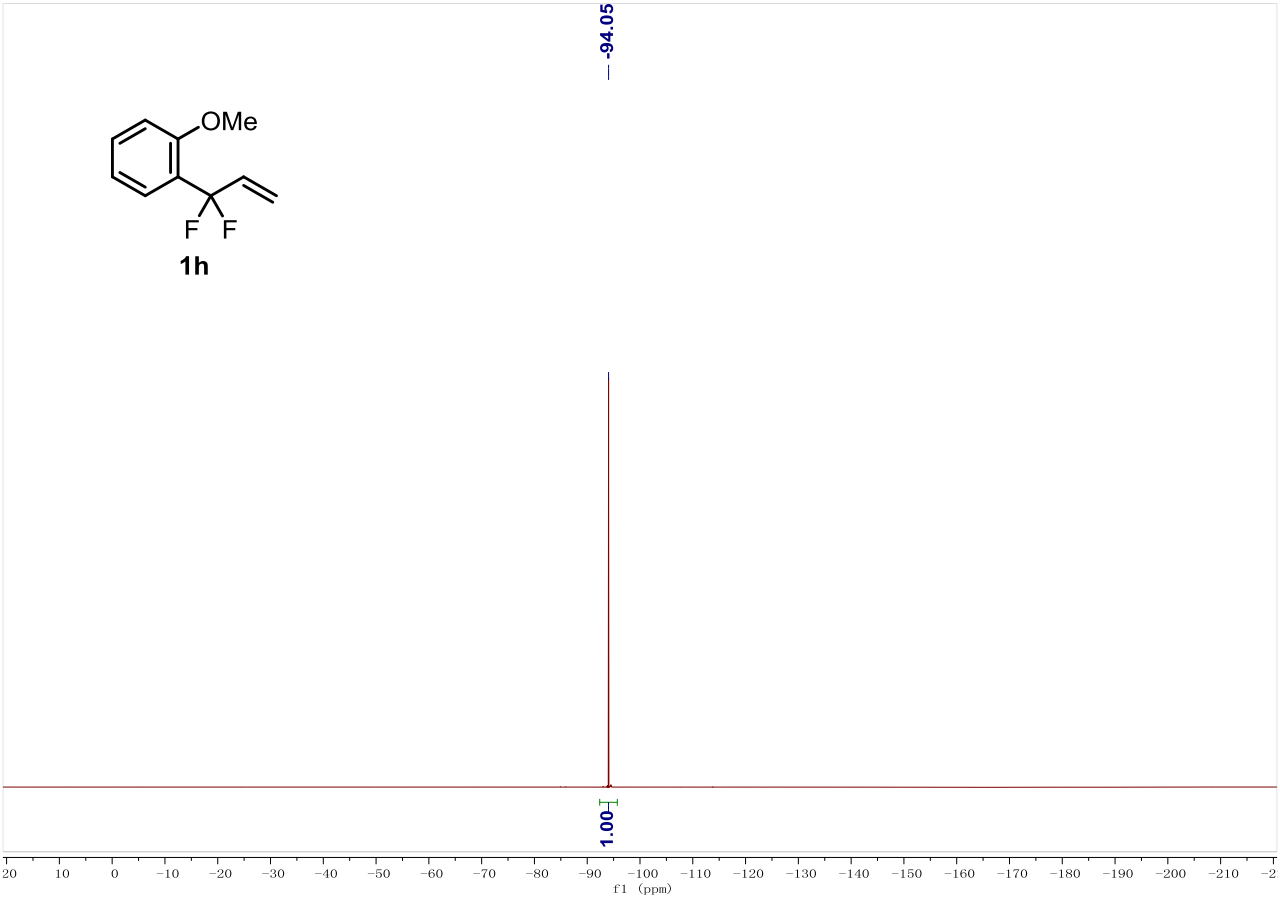

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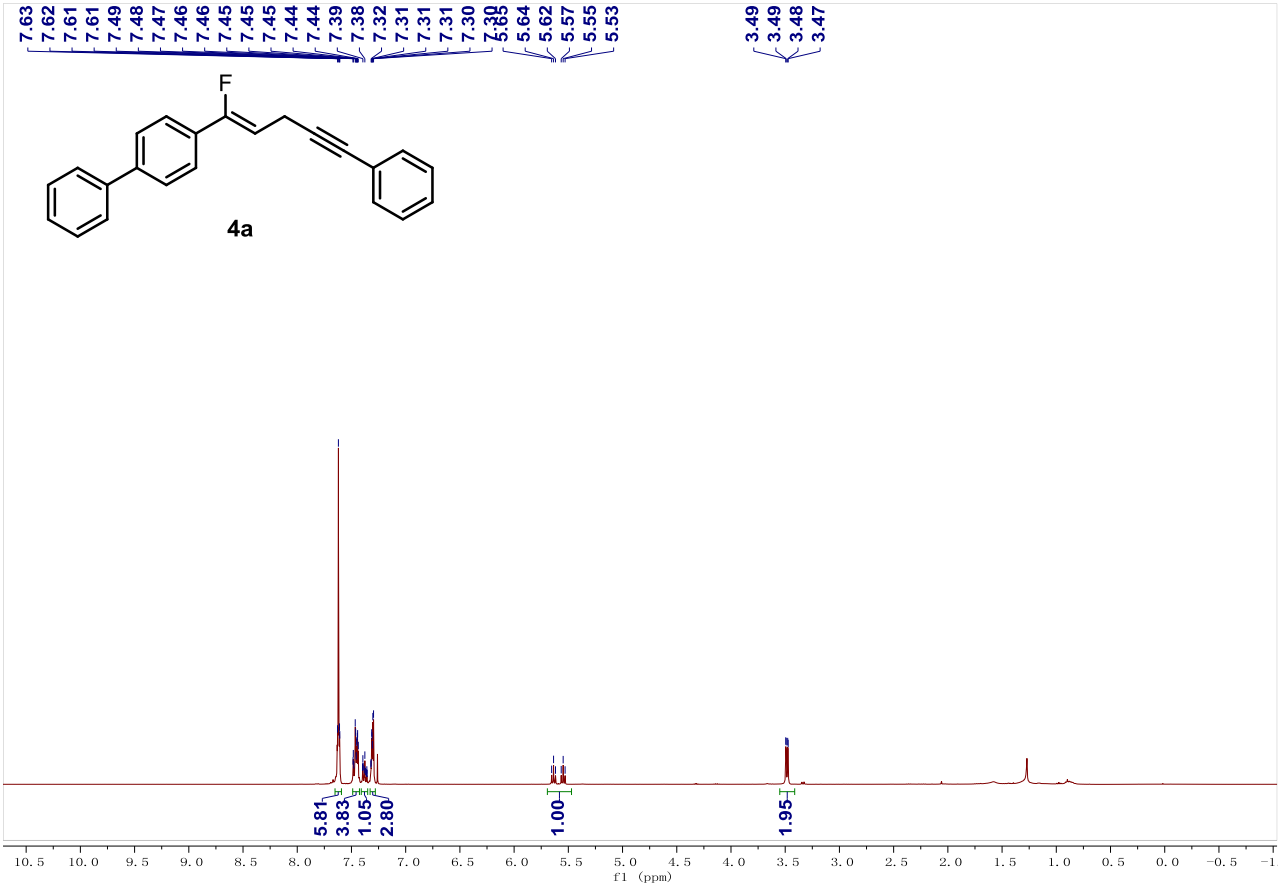

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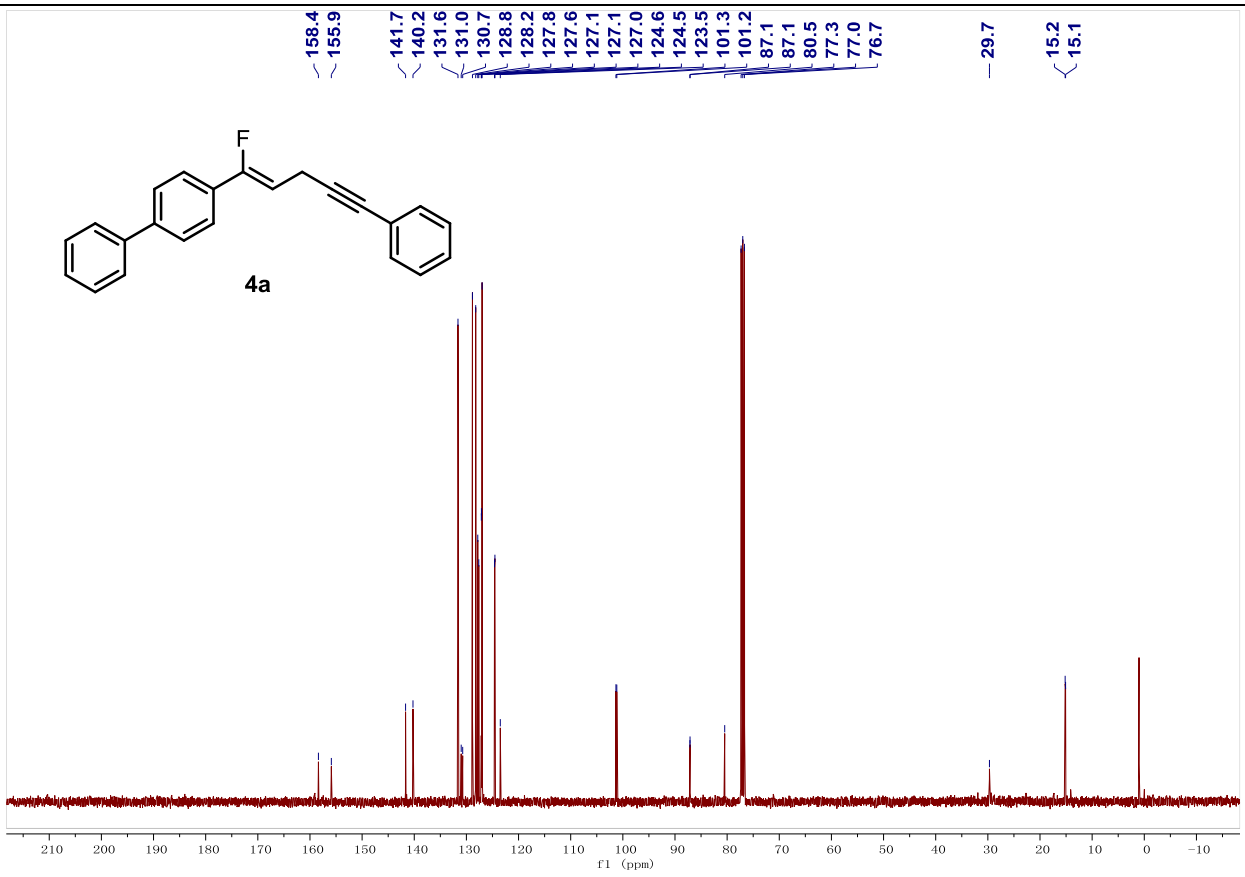

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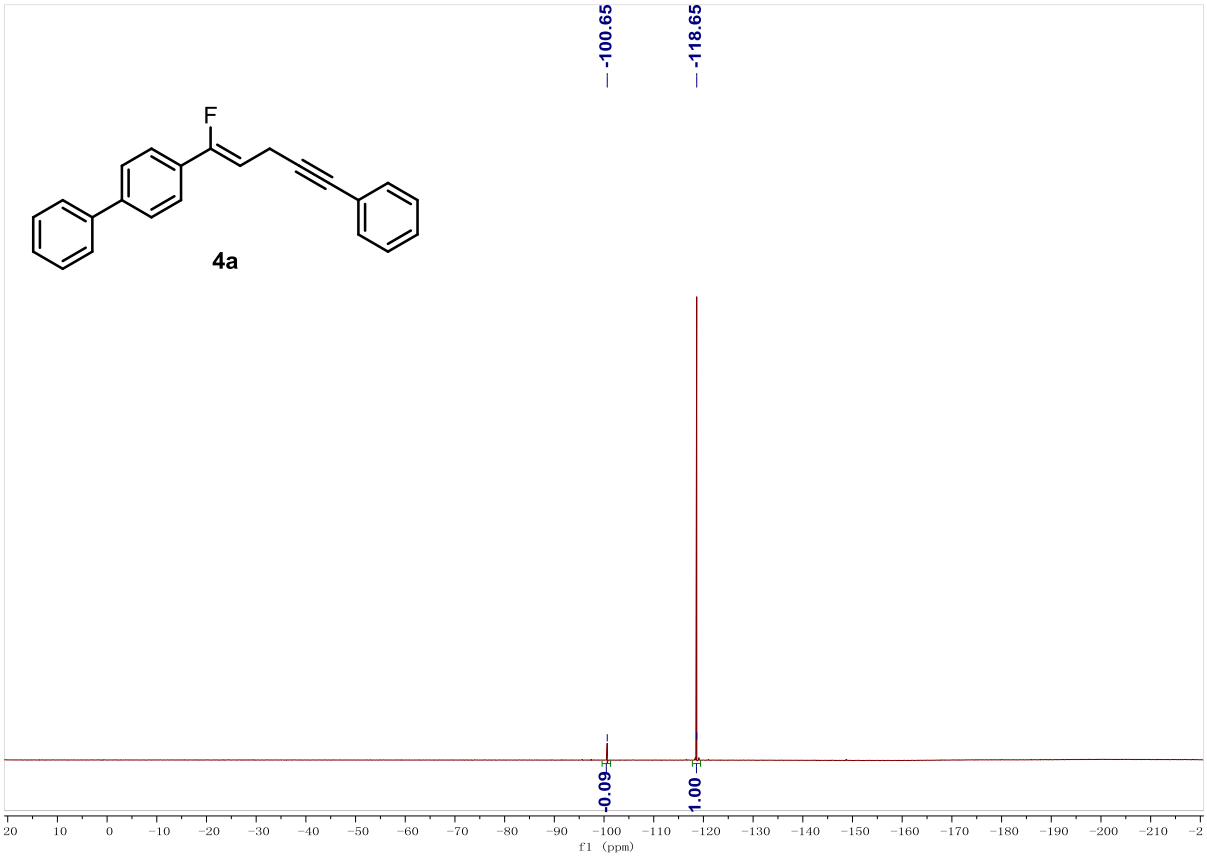

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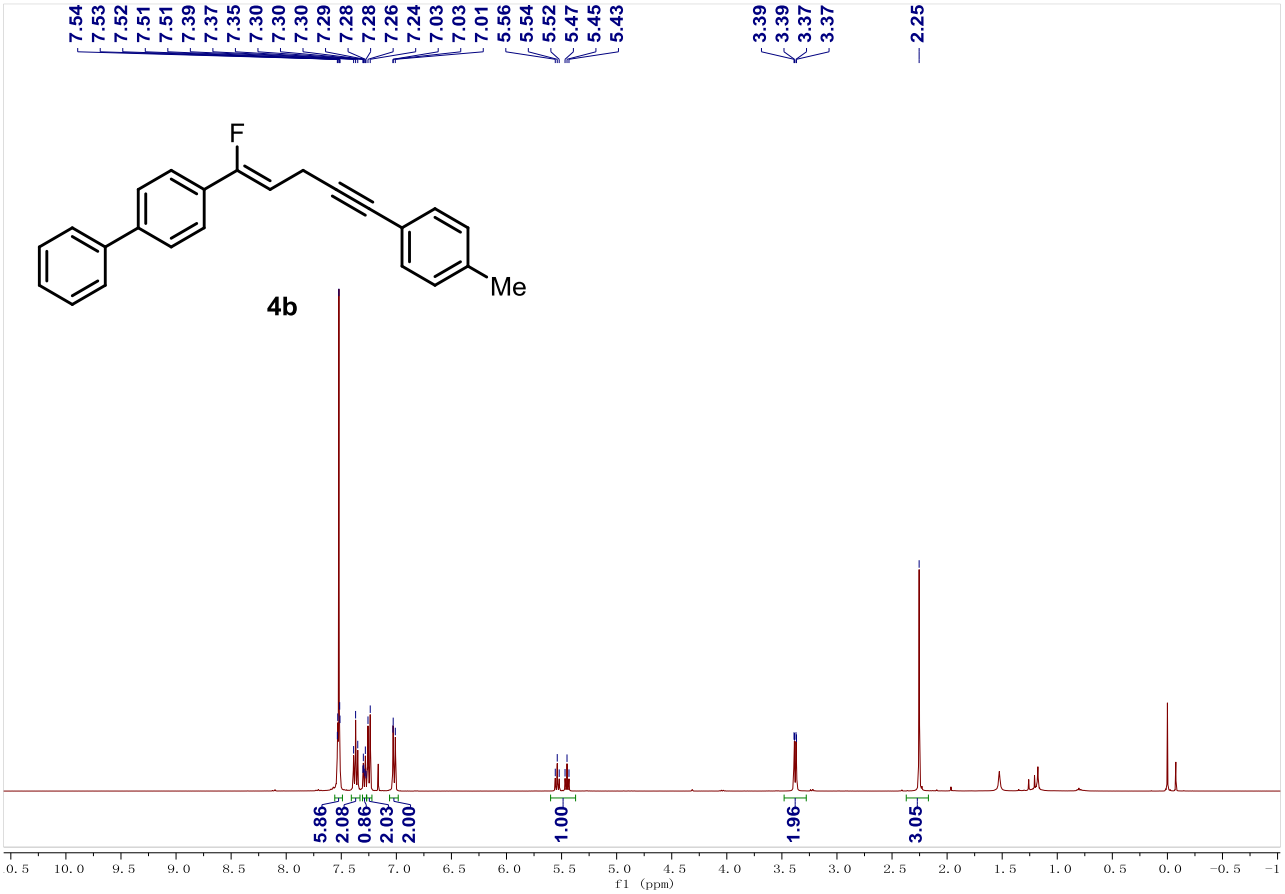

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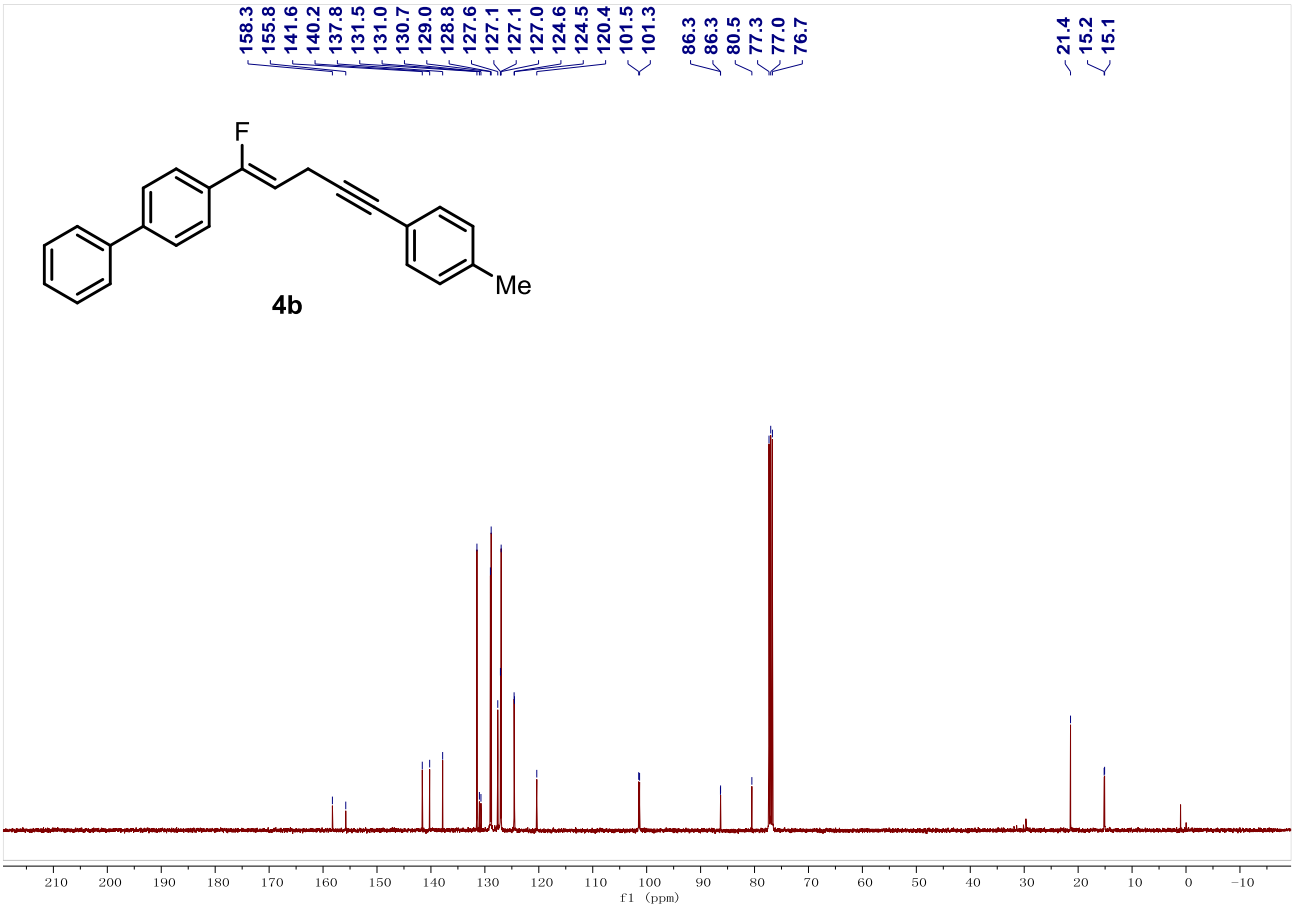

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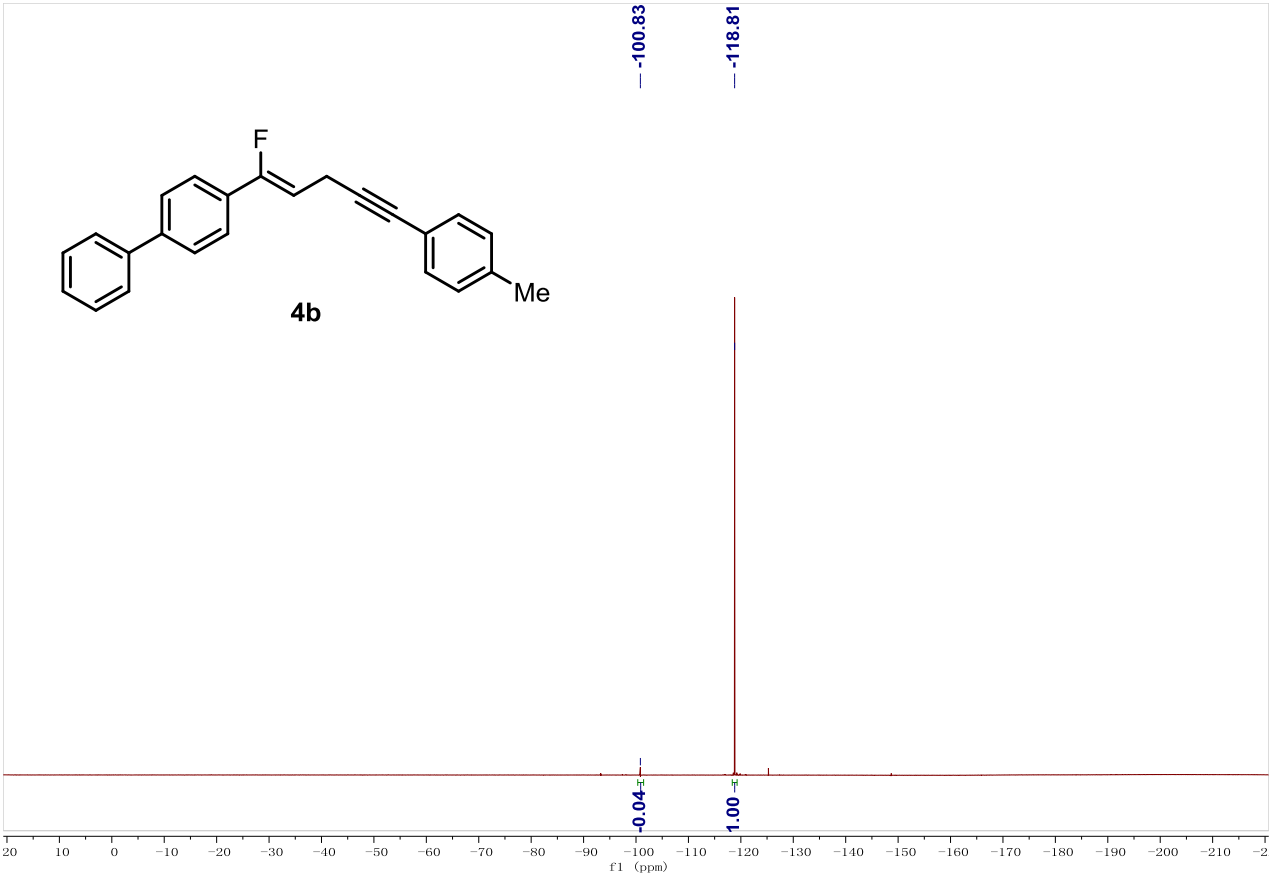

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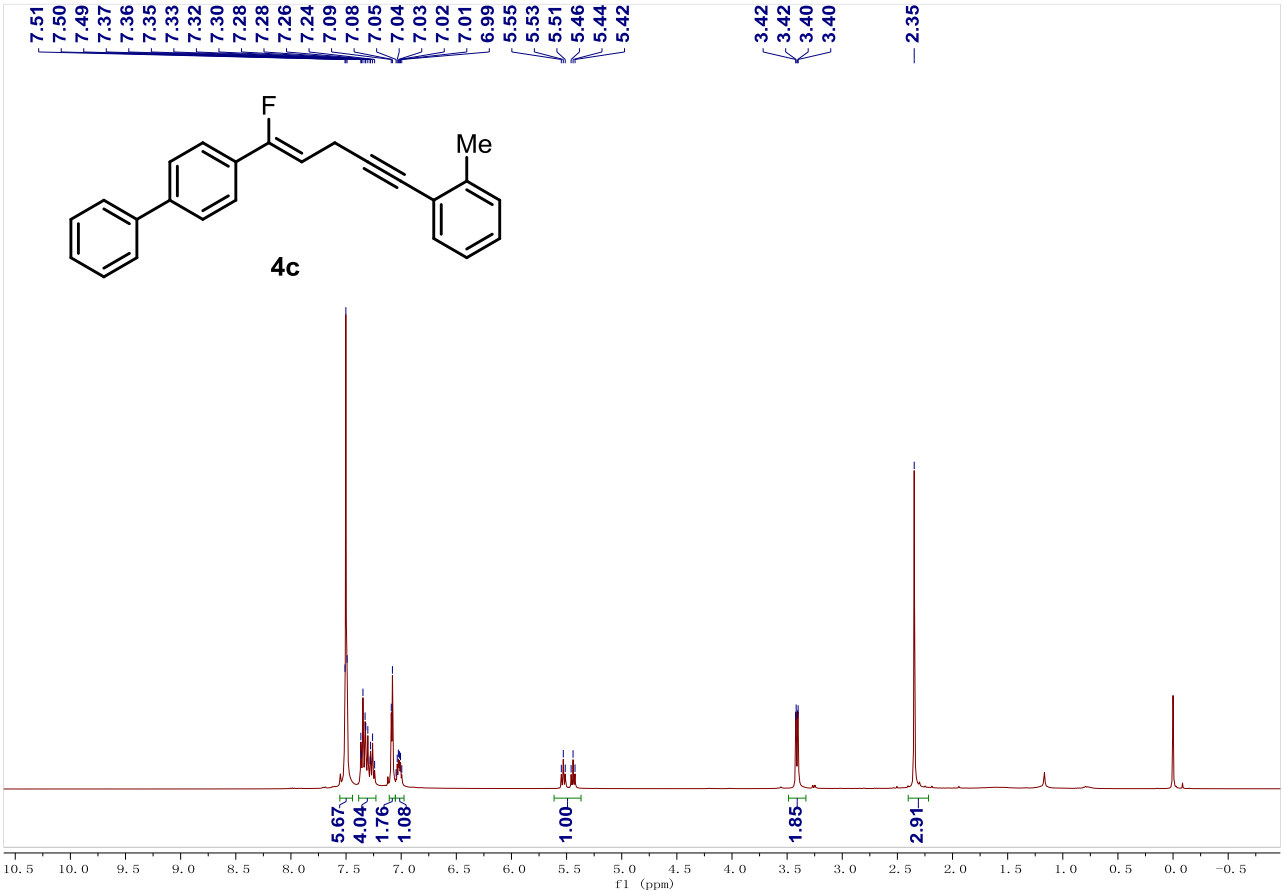

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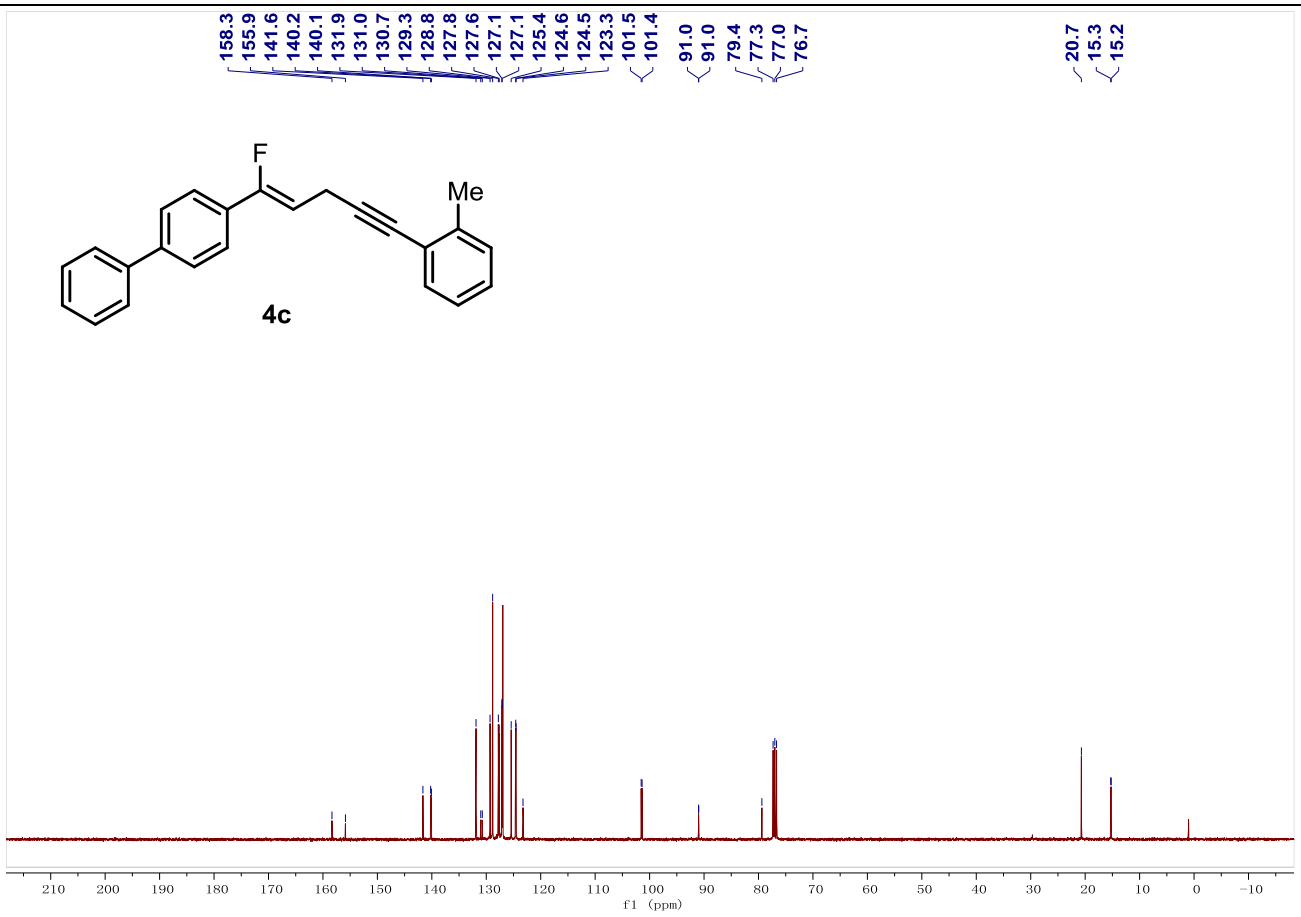

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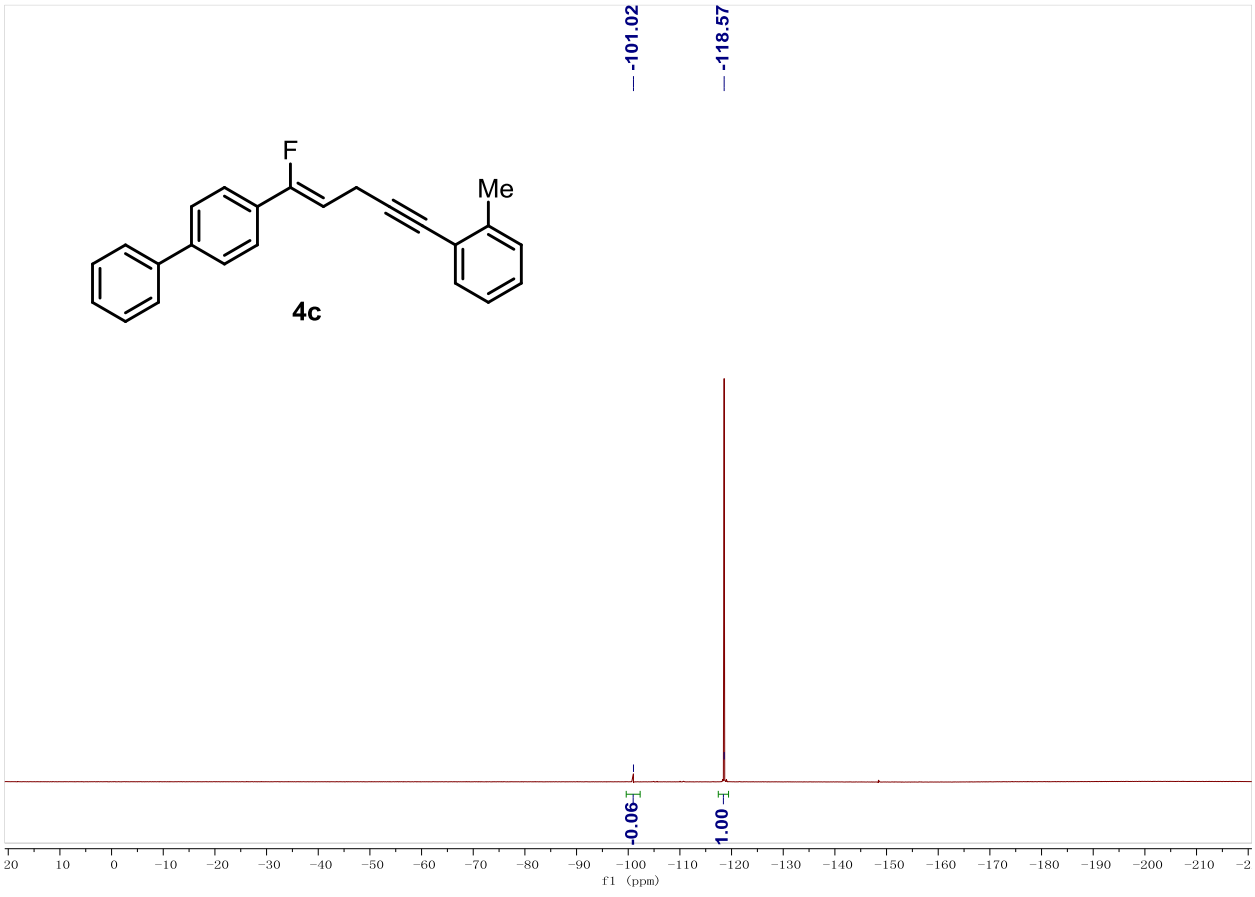

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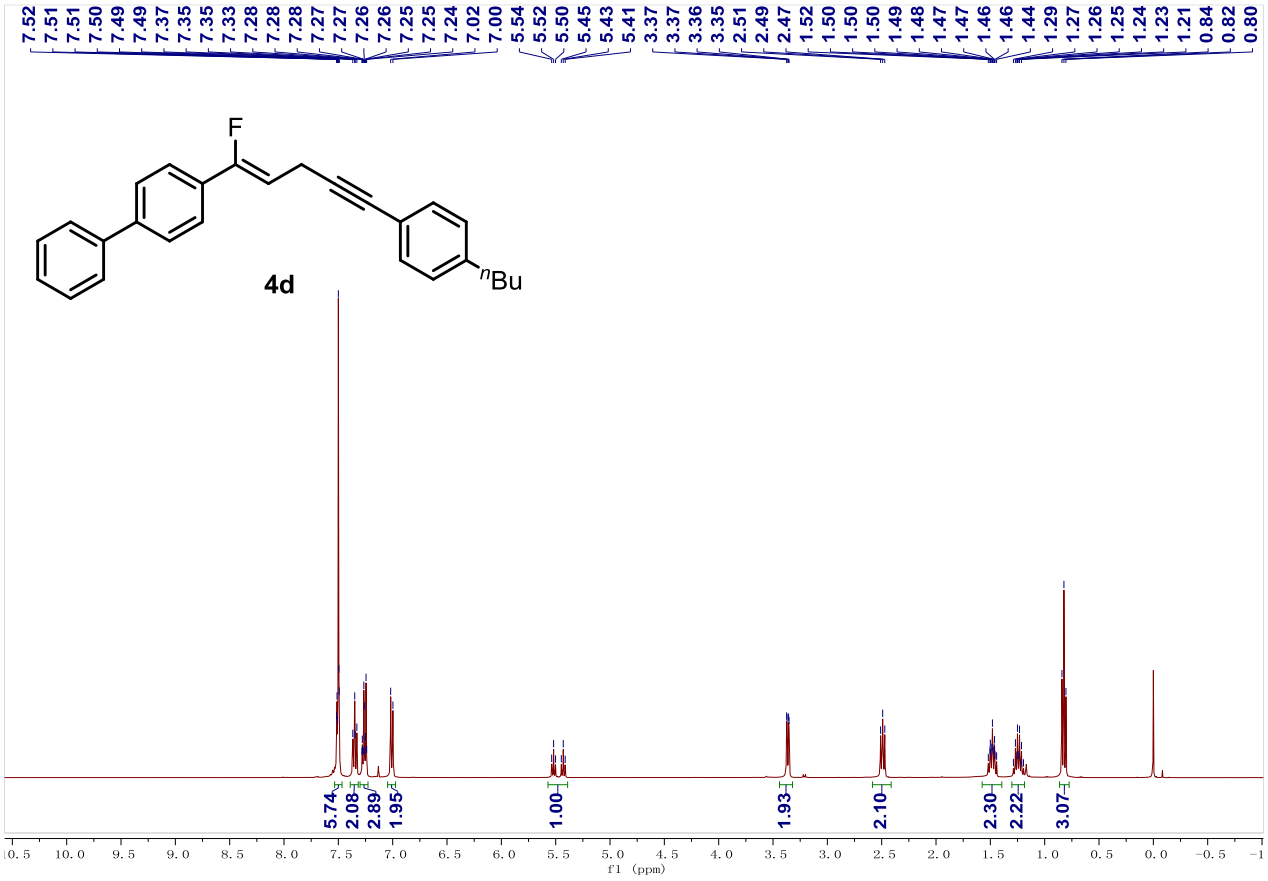

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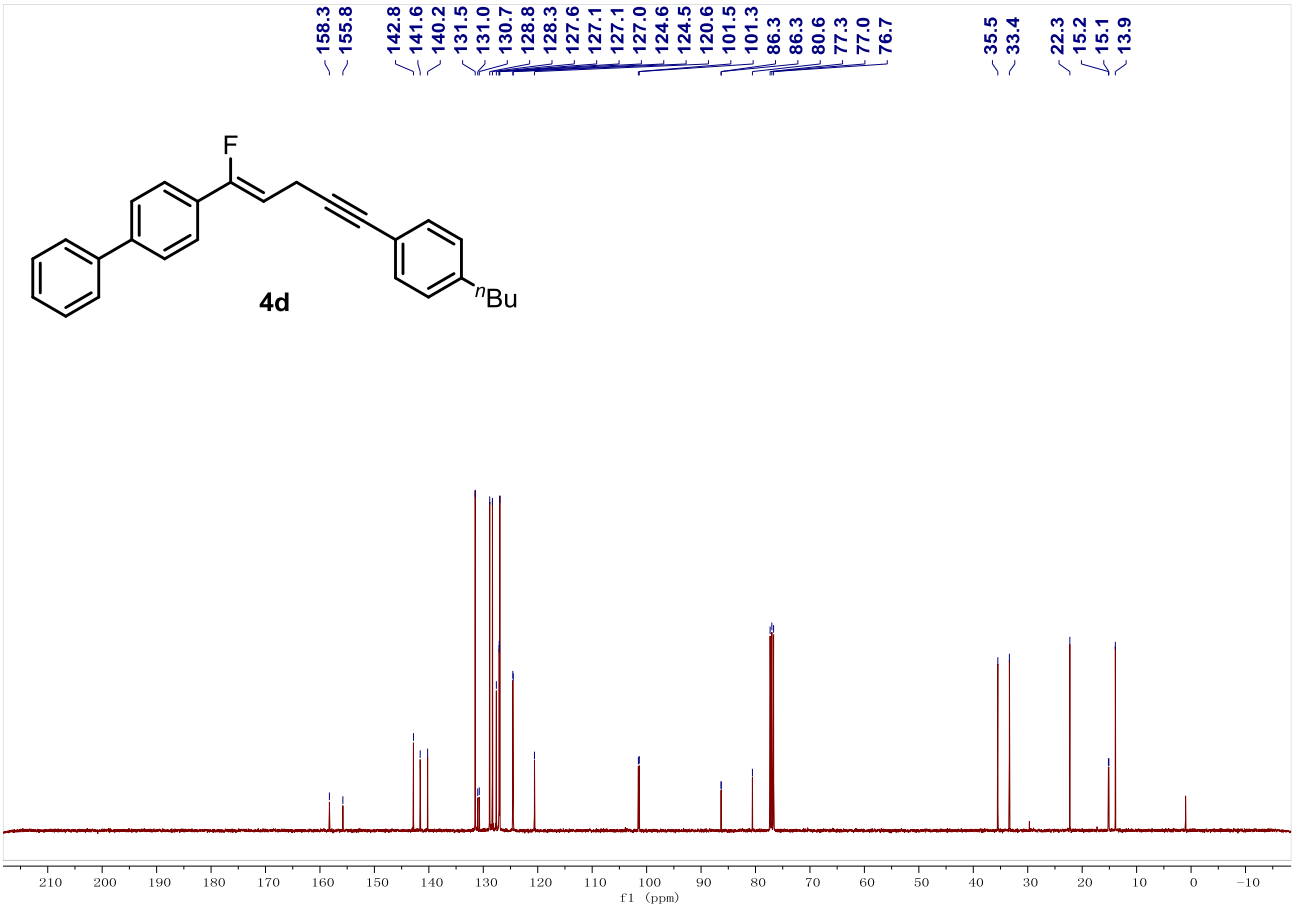

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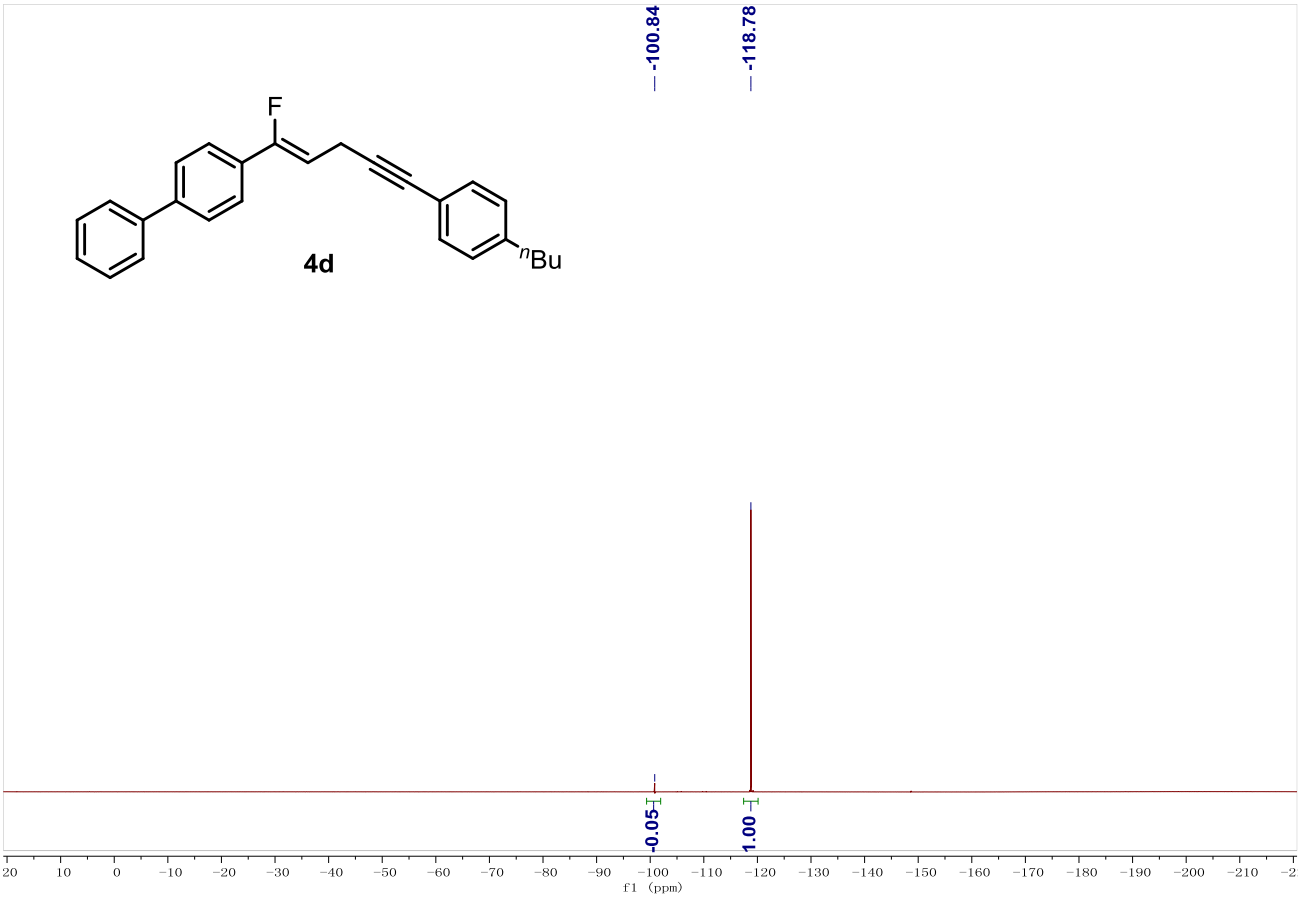

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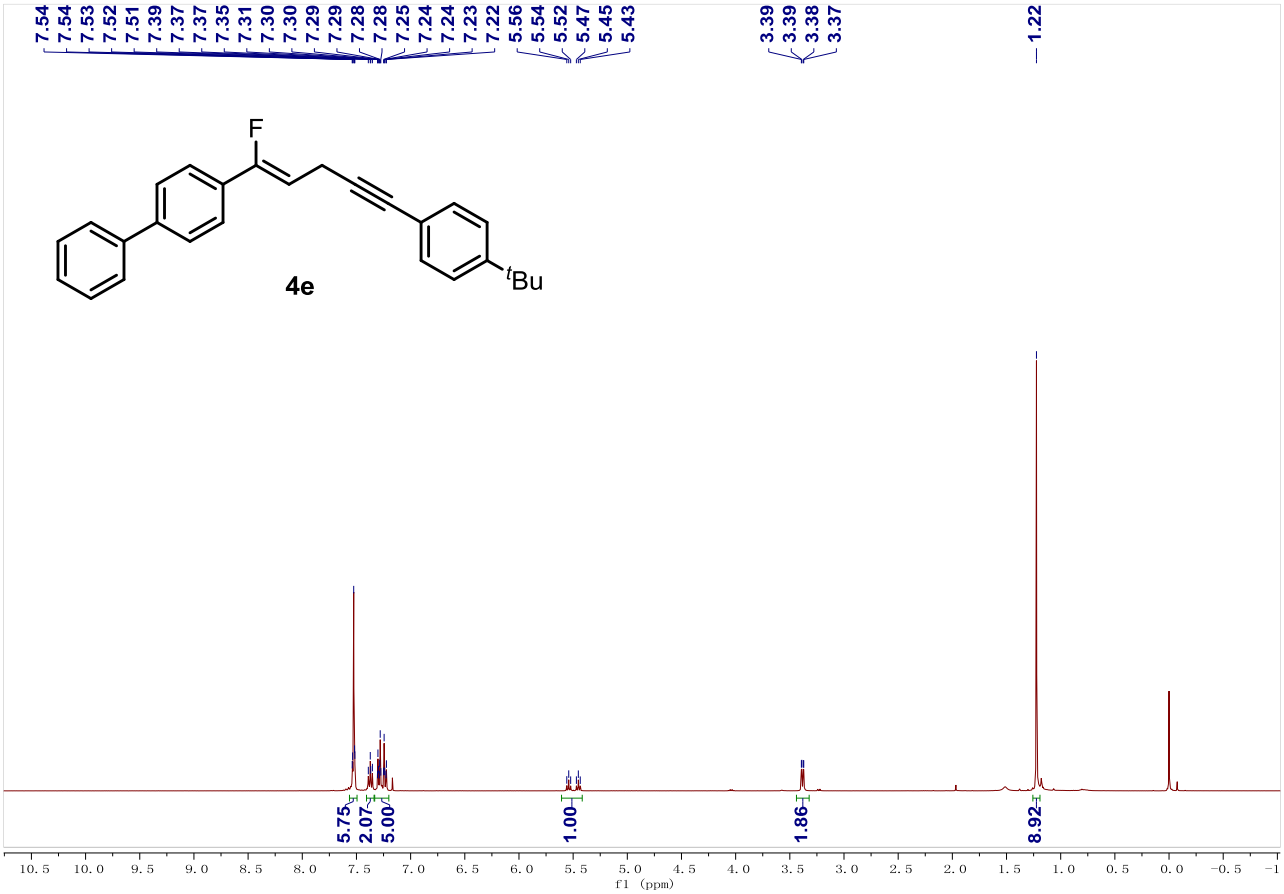

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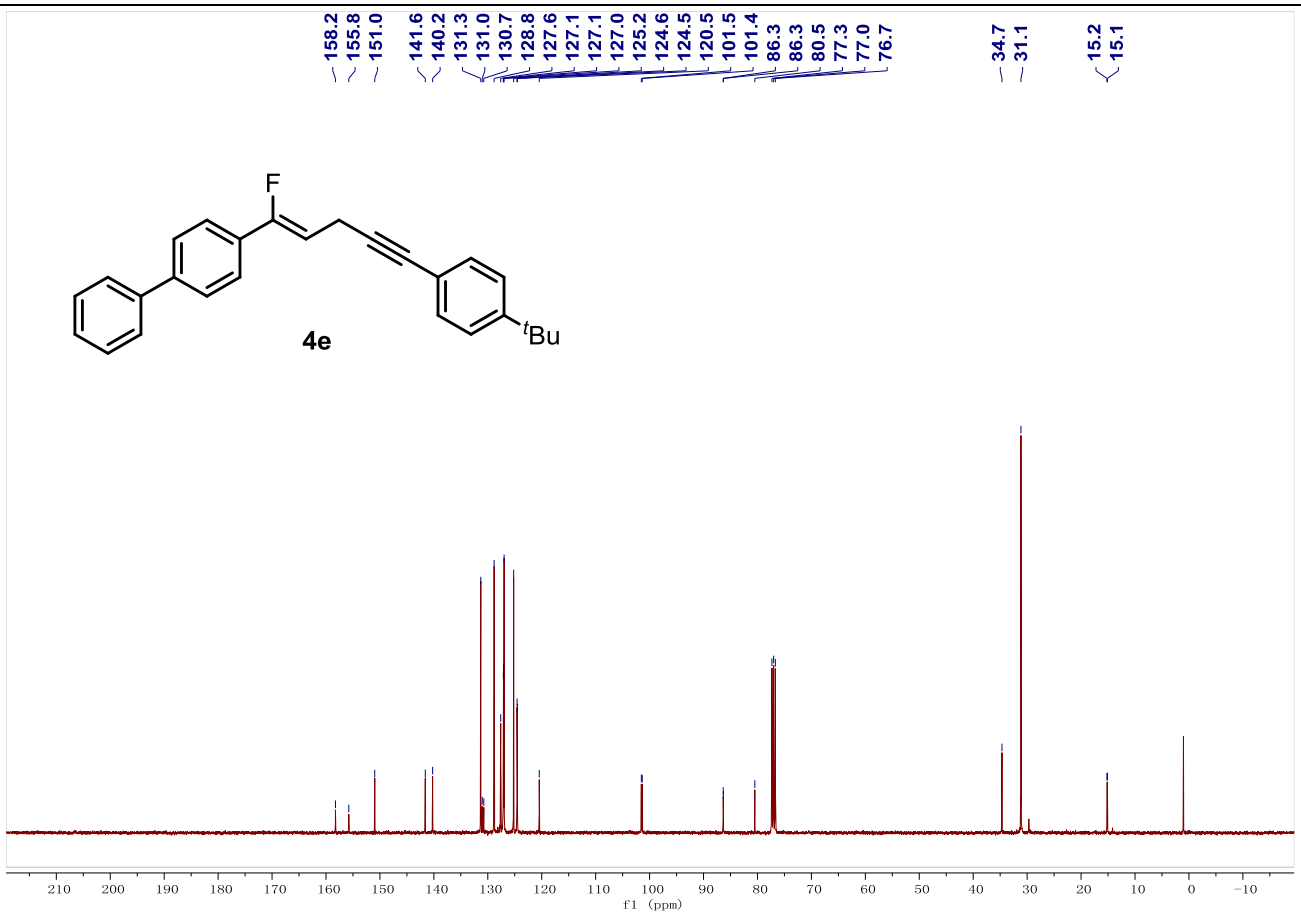

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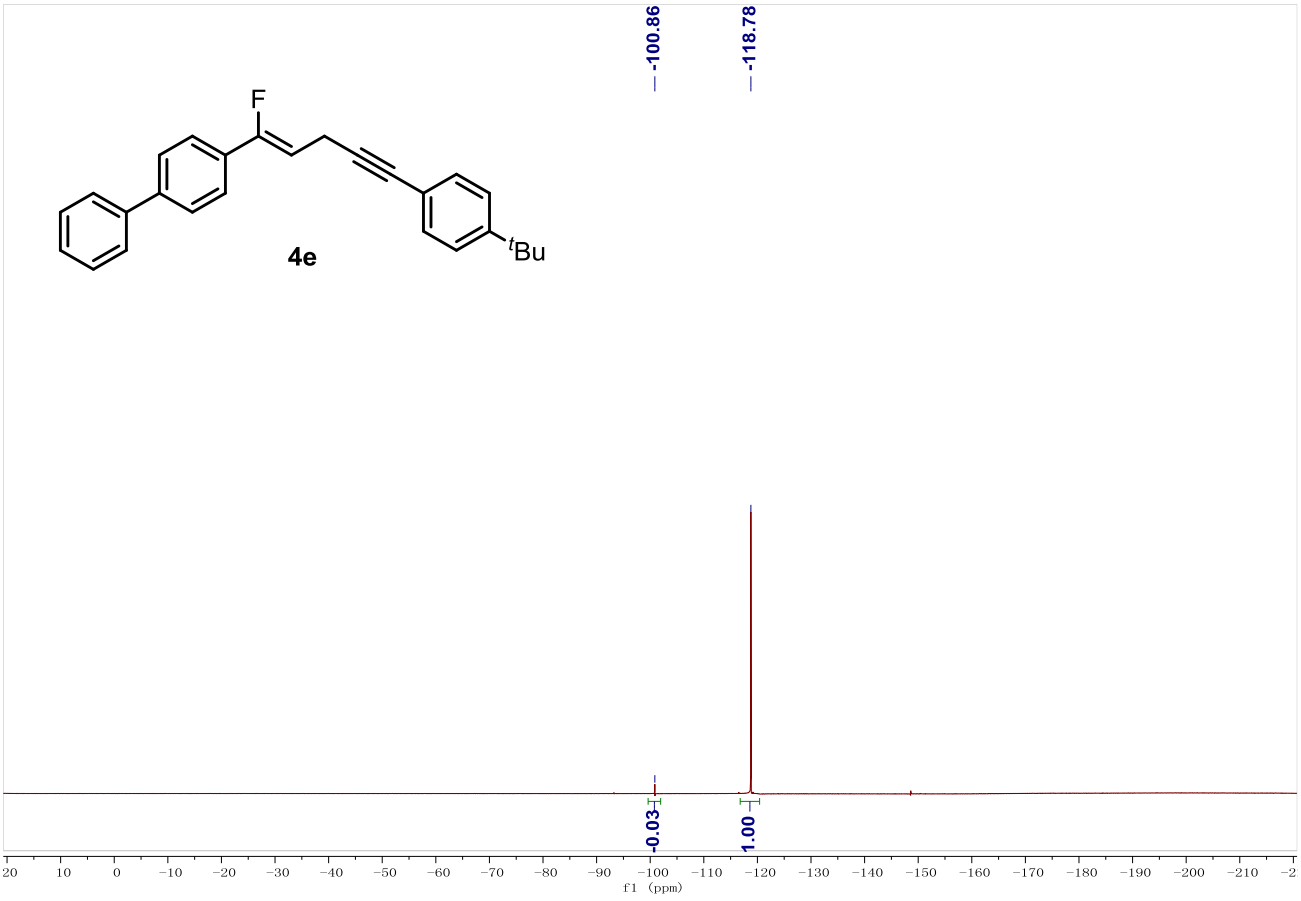

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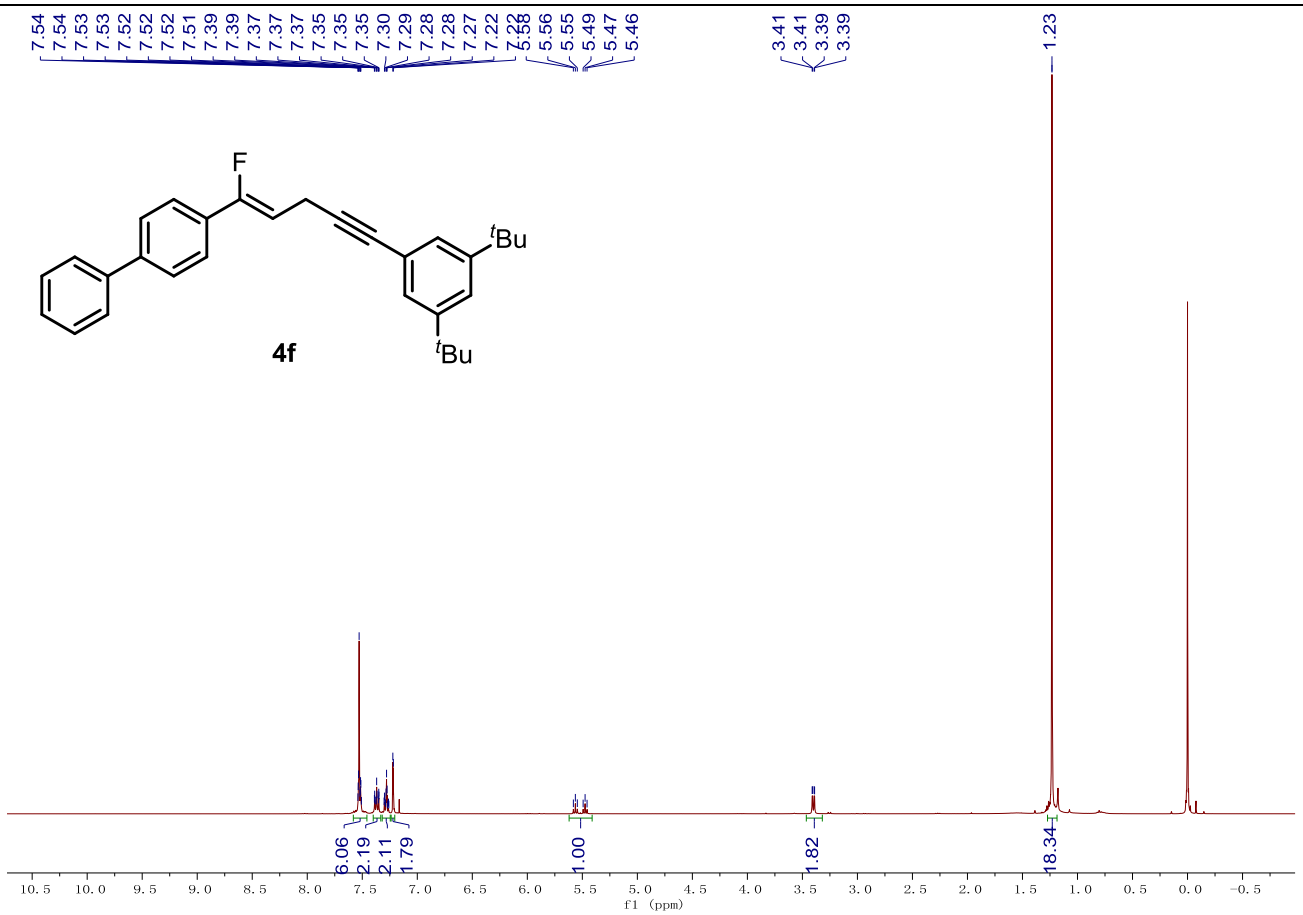

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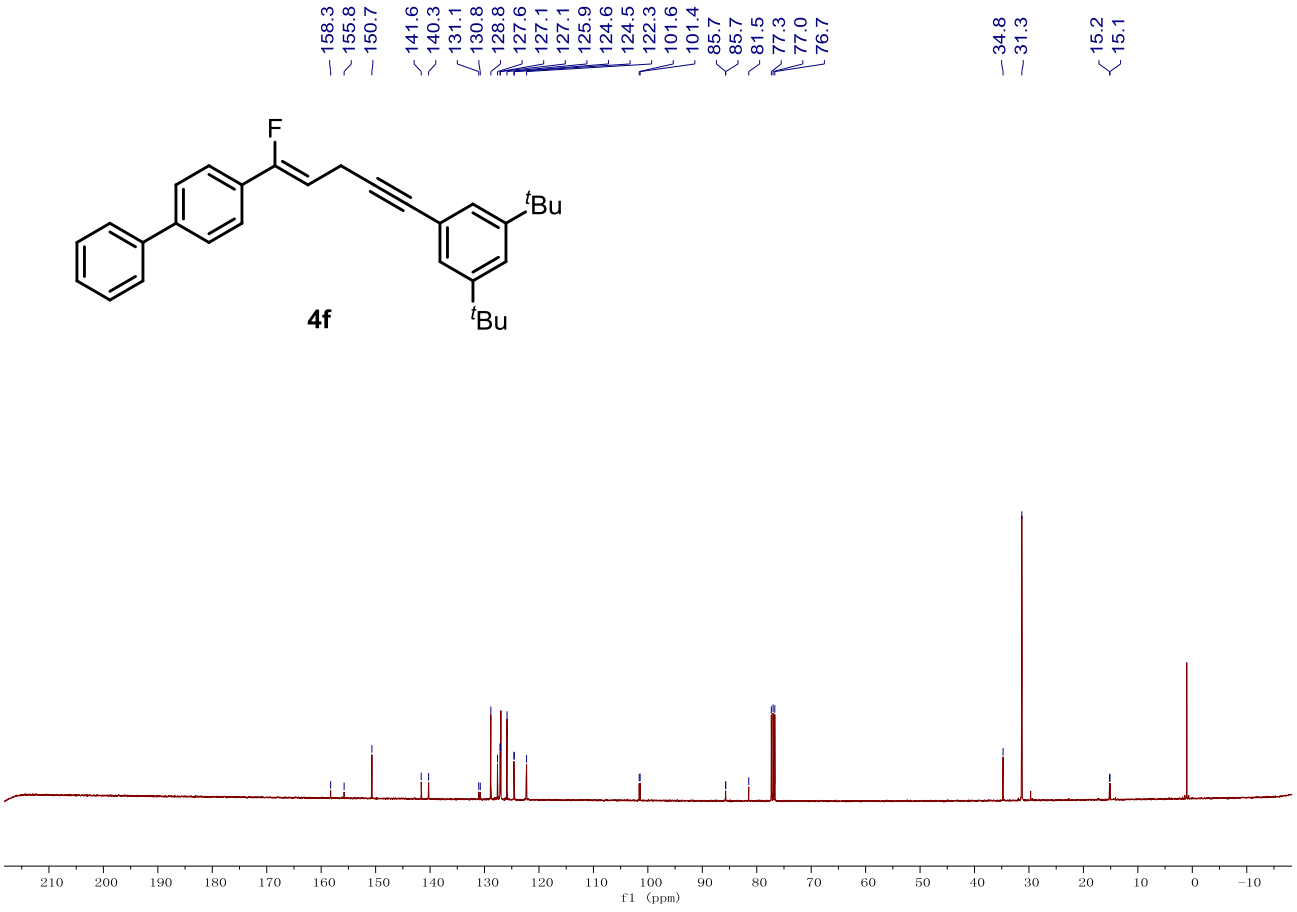

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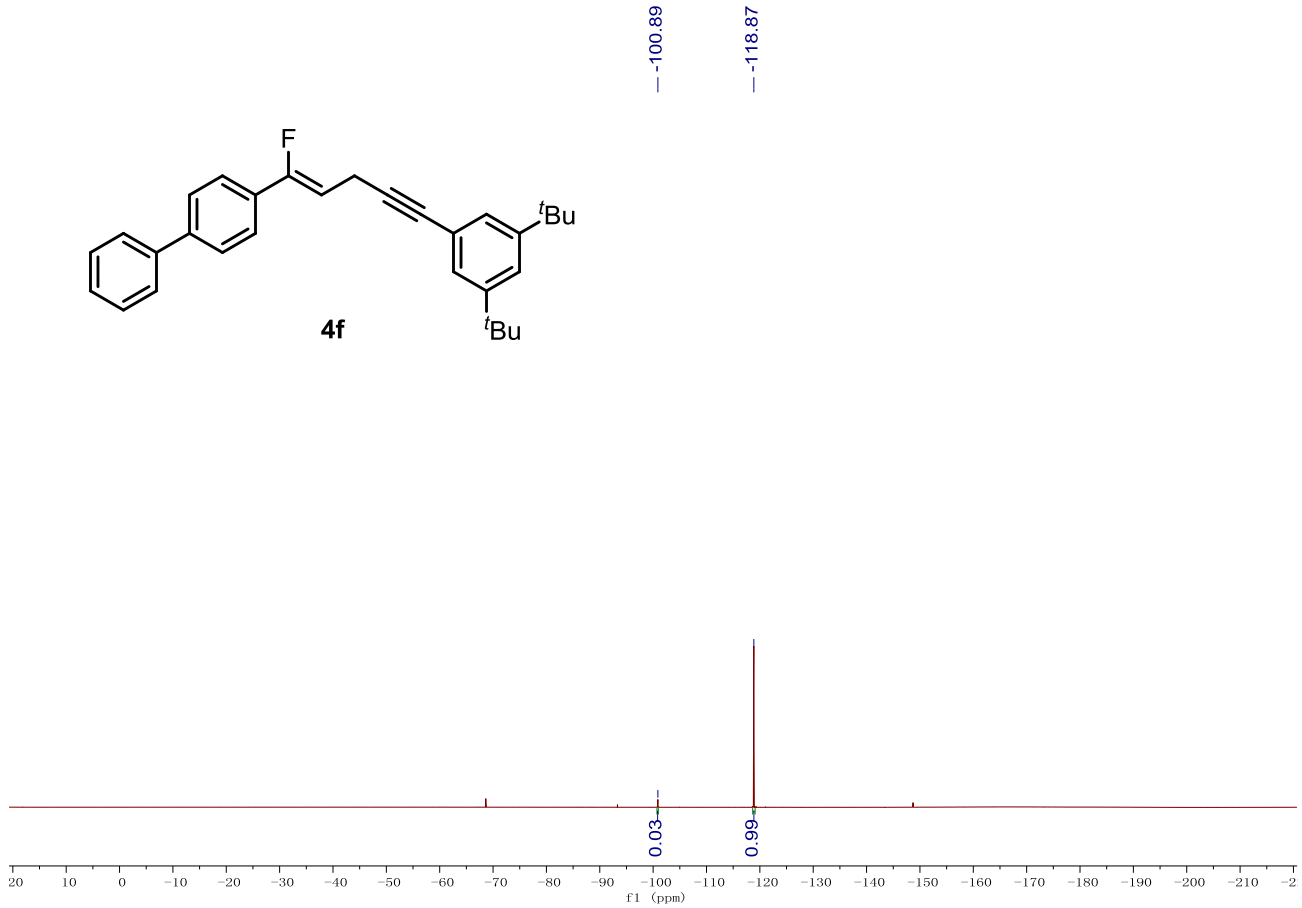
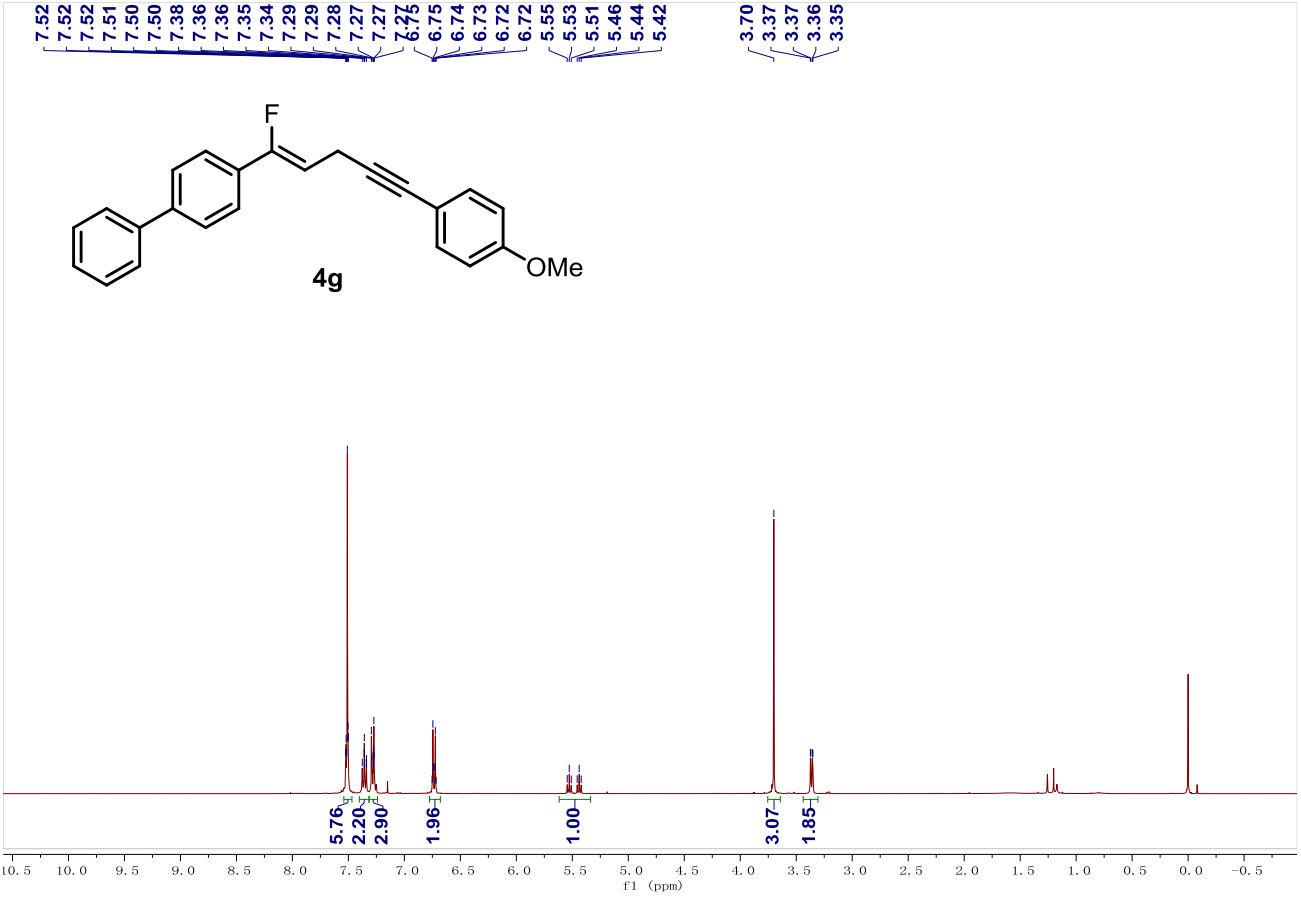
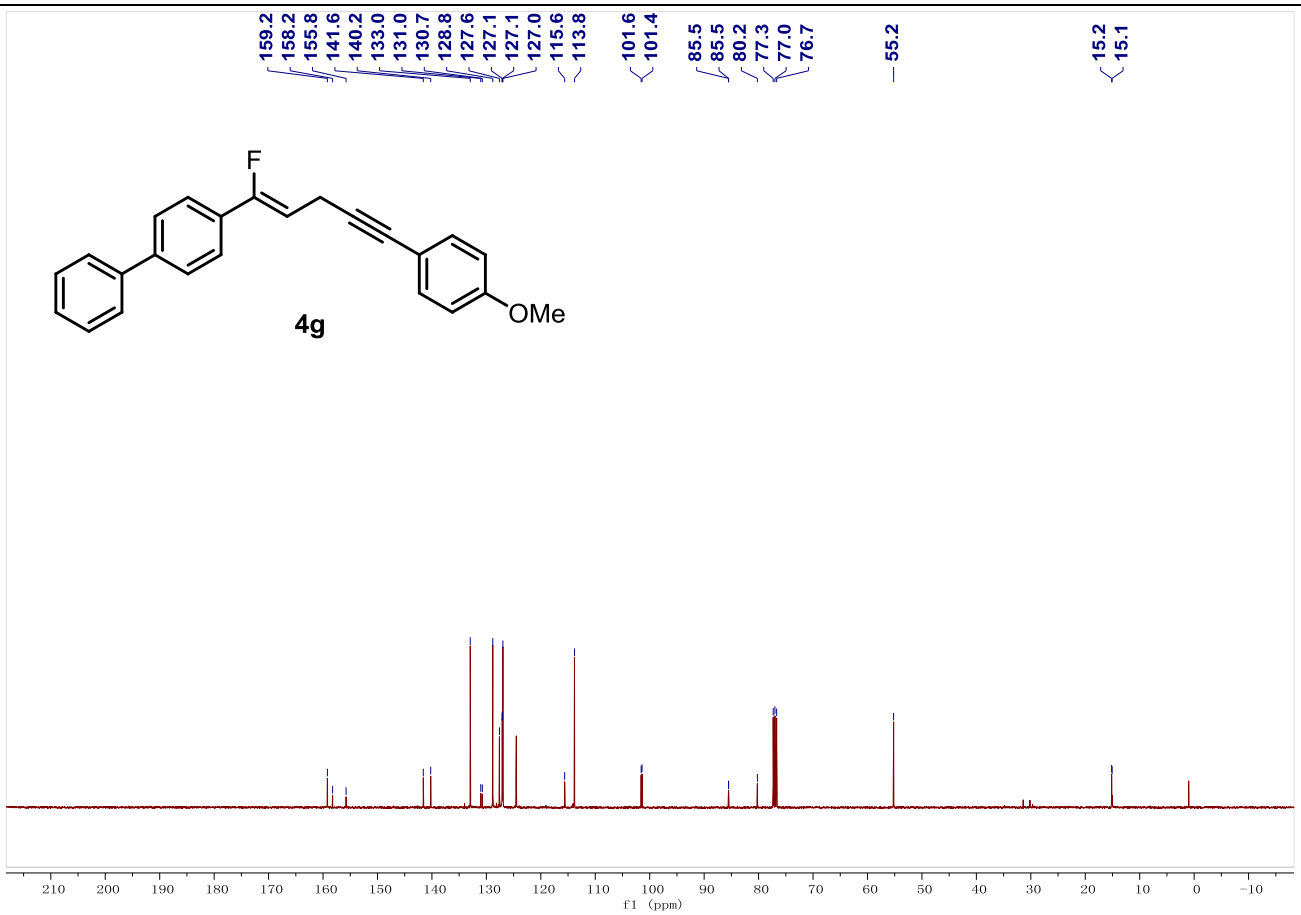


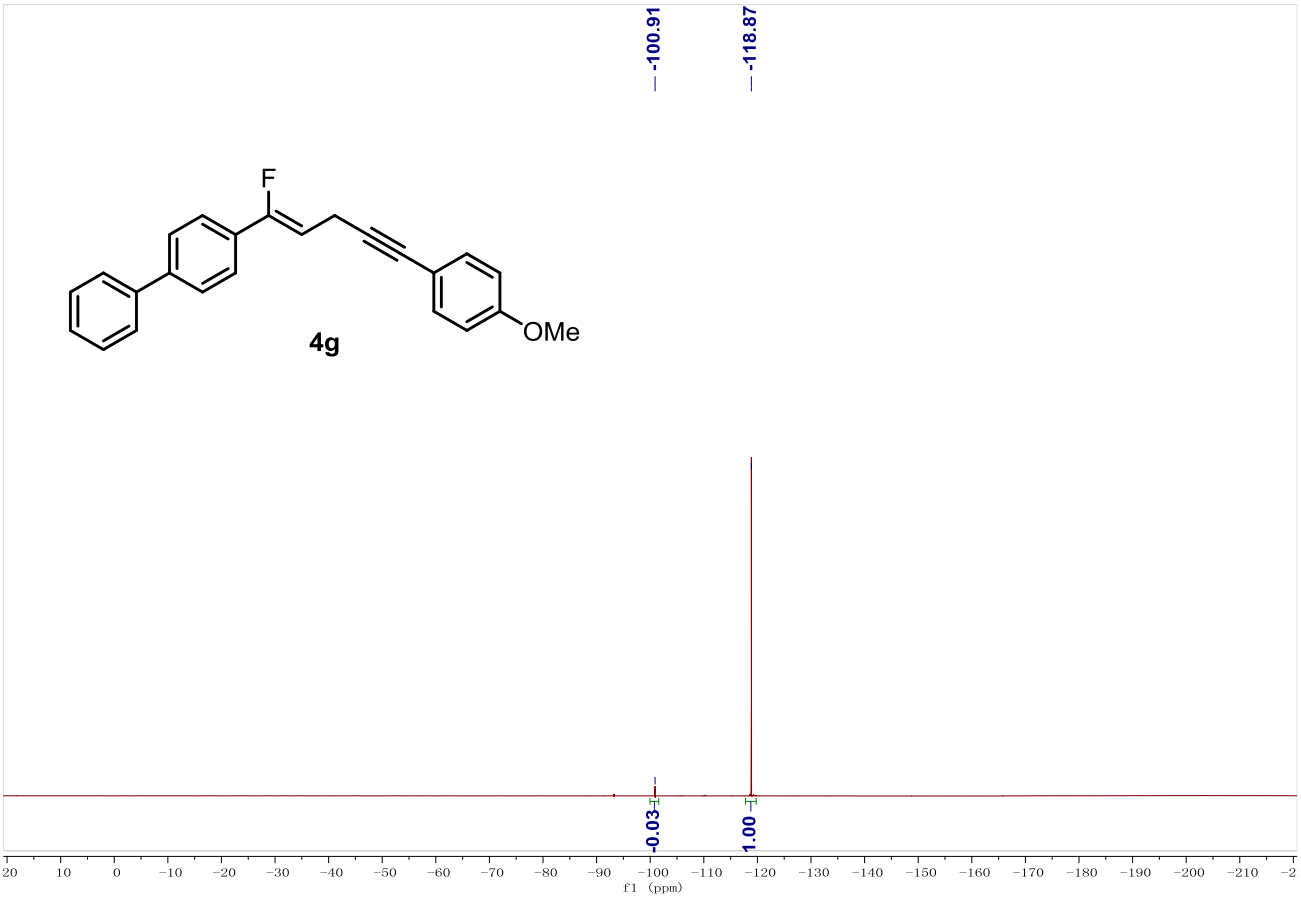
^{1}H NMR (400 MHz, $CDCl_3$)



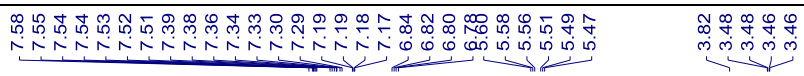
^{13}C NMR (101 MHz, $CDCl_3$)

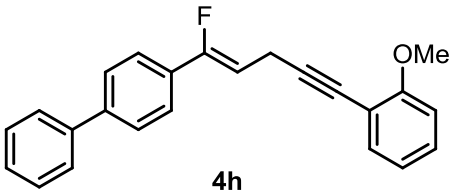


^{19}F NMR (376 MHz, $CDCl_3$)



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





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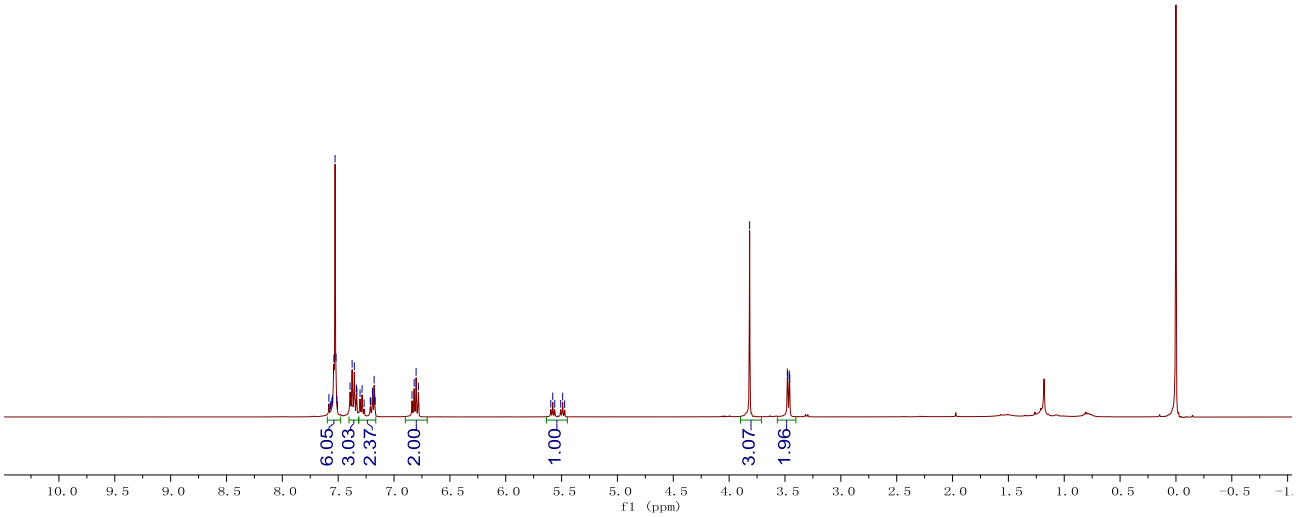
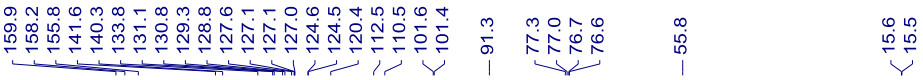
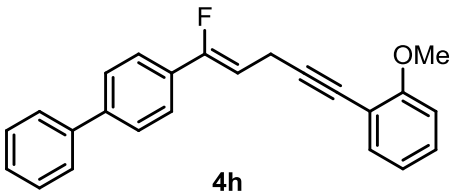


^{13}C NMR (101 MHz, $CDCl_3$)





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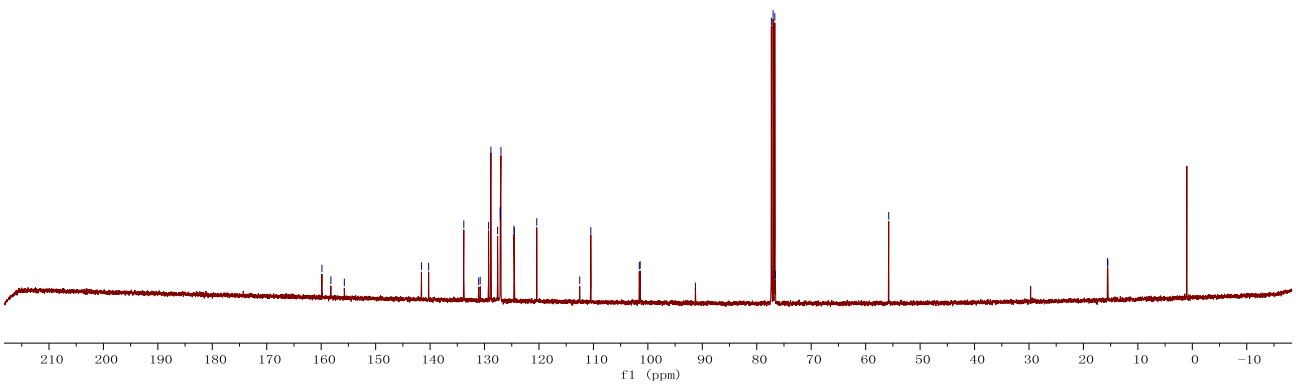
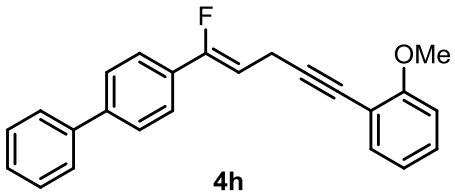


^{19}F NMR (376 MHz, $CDCl_3$)



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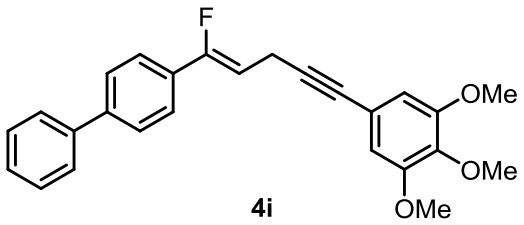
^{1}H NMR (400 MHz, $CDCl_3$)



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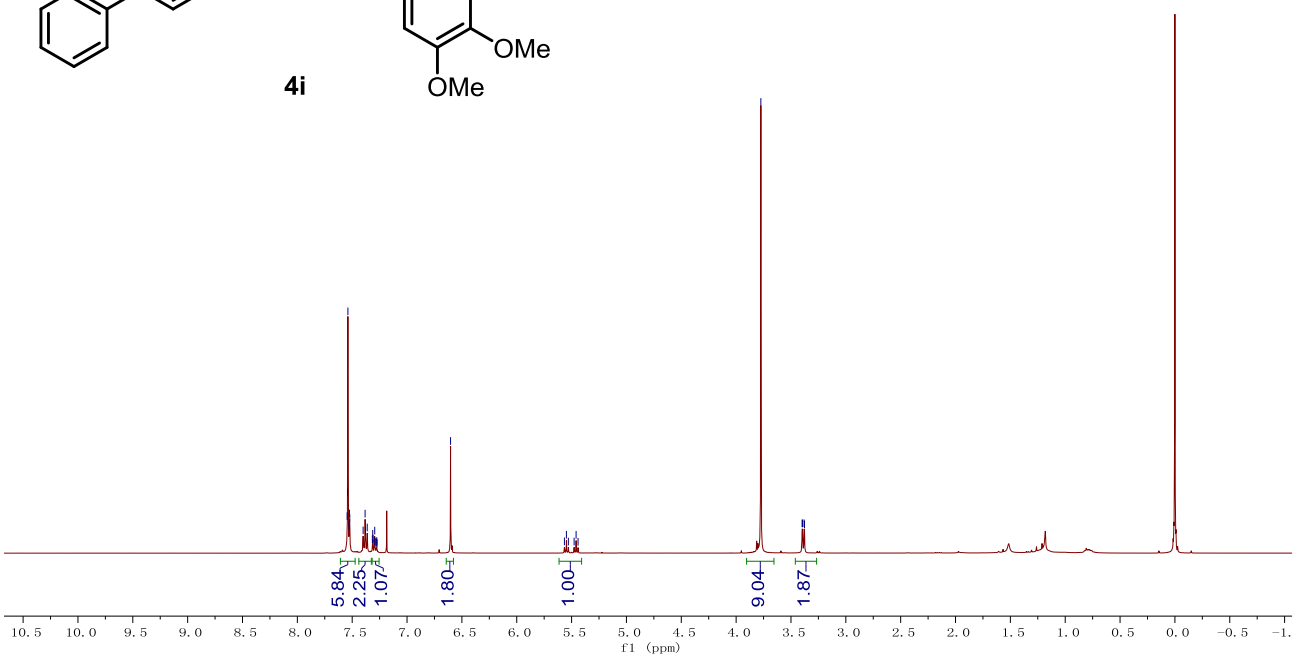
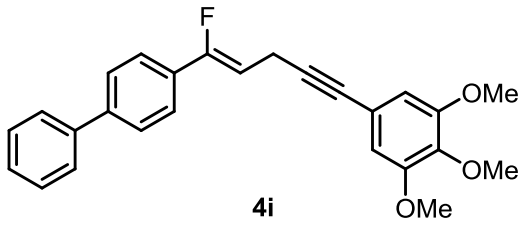


^{13}C NMR (101 MHz, $CDCl_3$)



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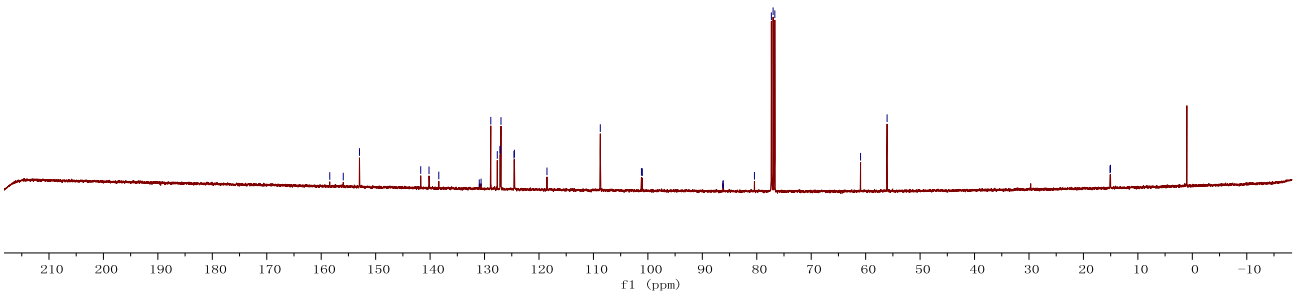
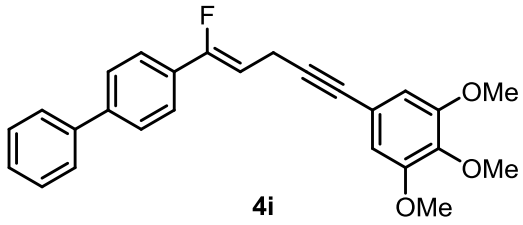


^{19}F NMR (376 MHz, $CDCl_3$)



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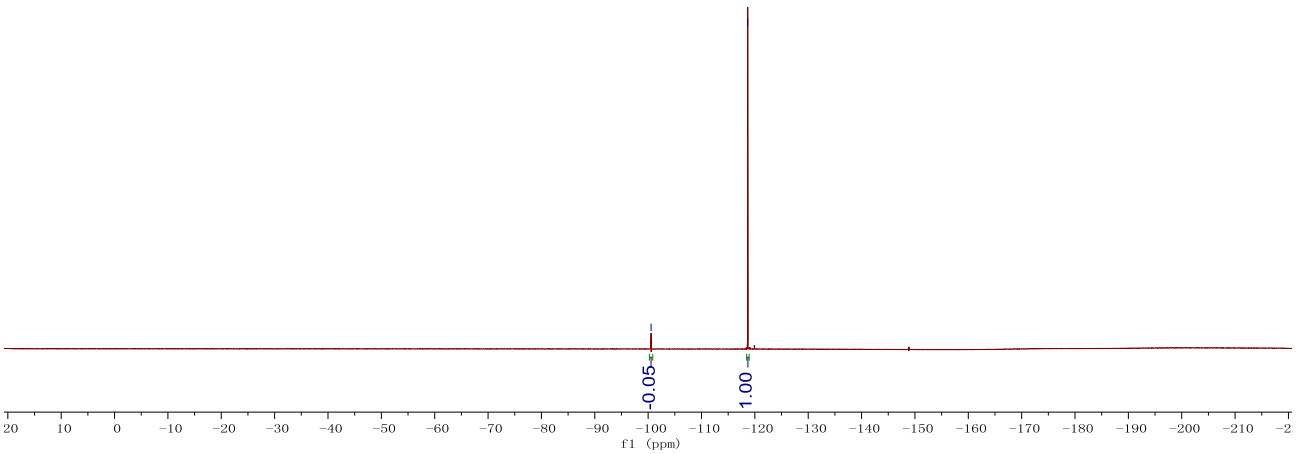
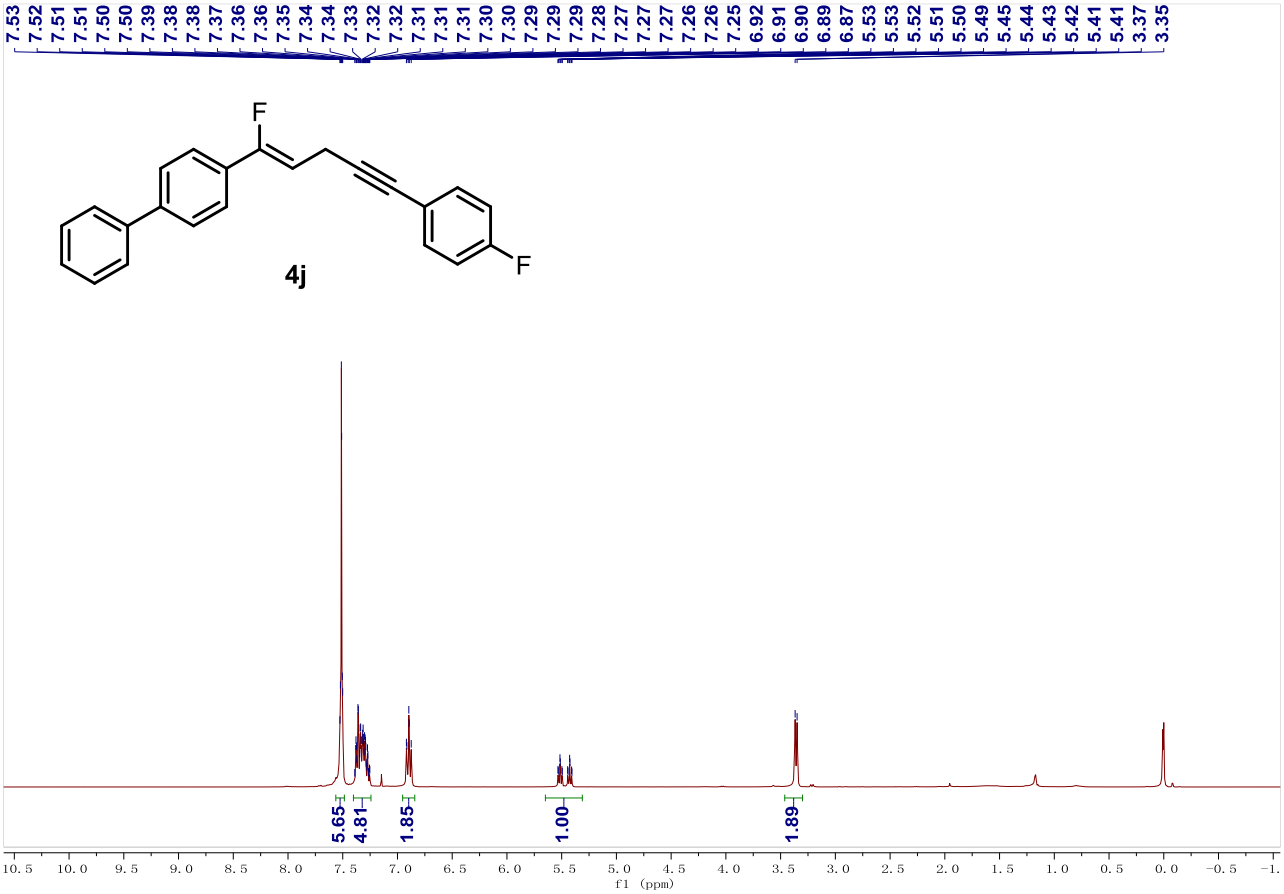
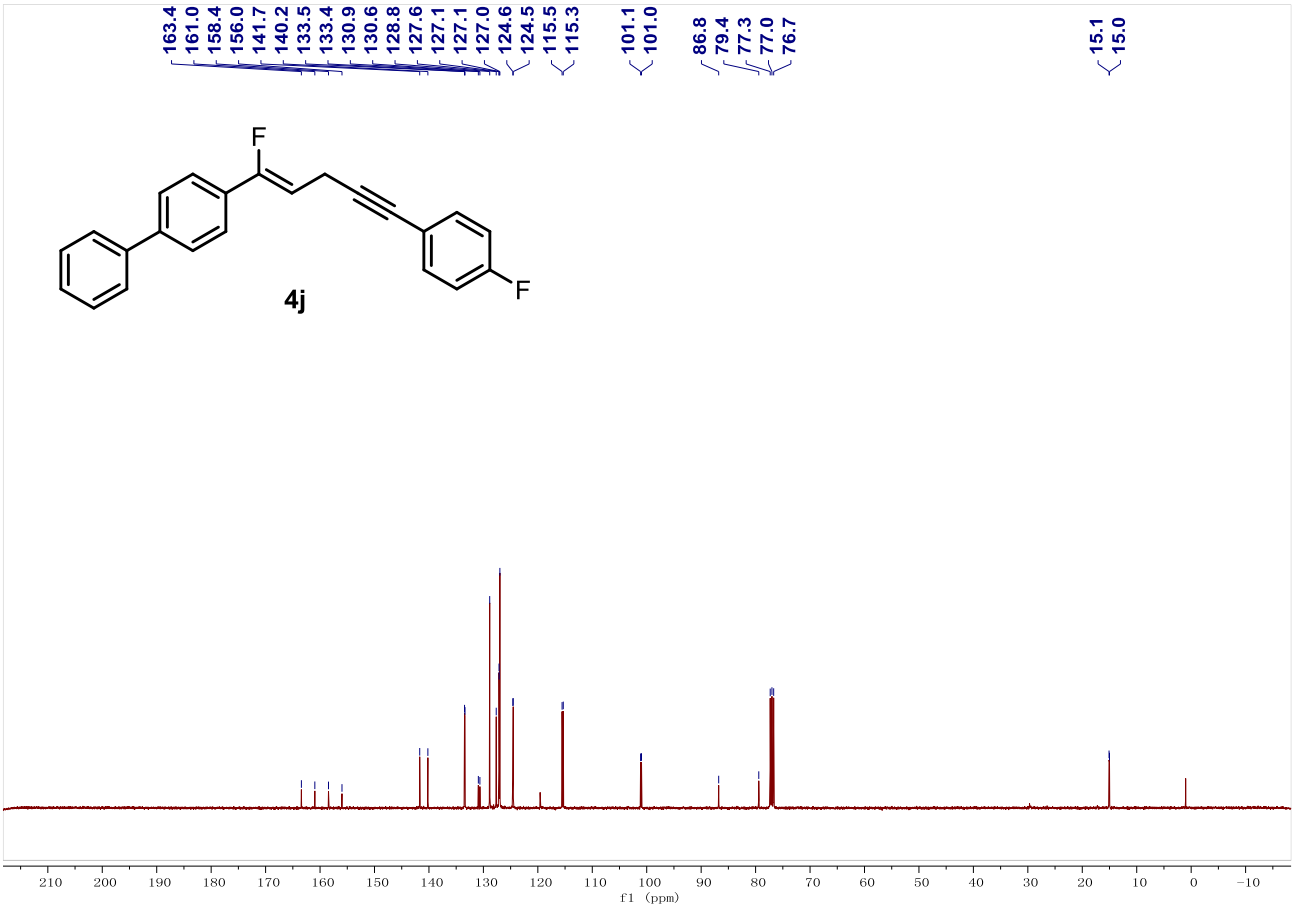


^{1}H NMR (400 MHz, $CDCl_3$)



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



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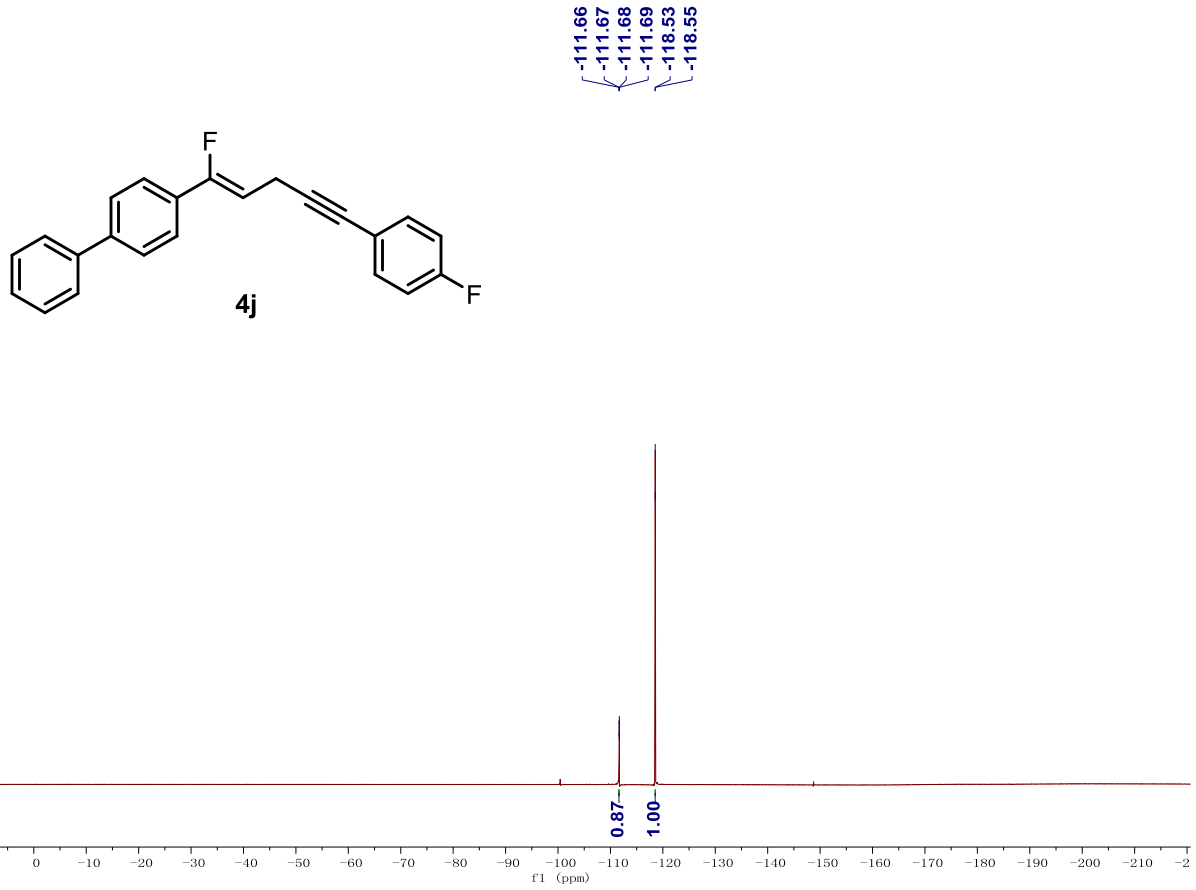

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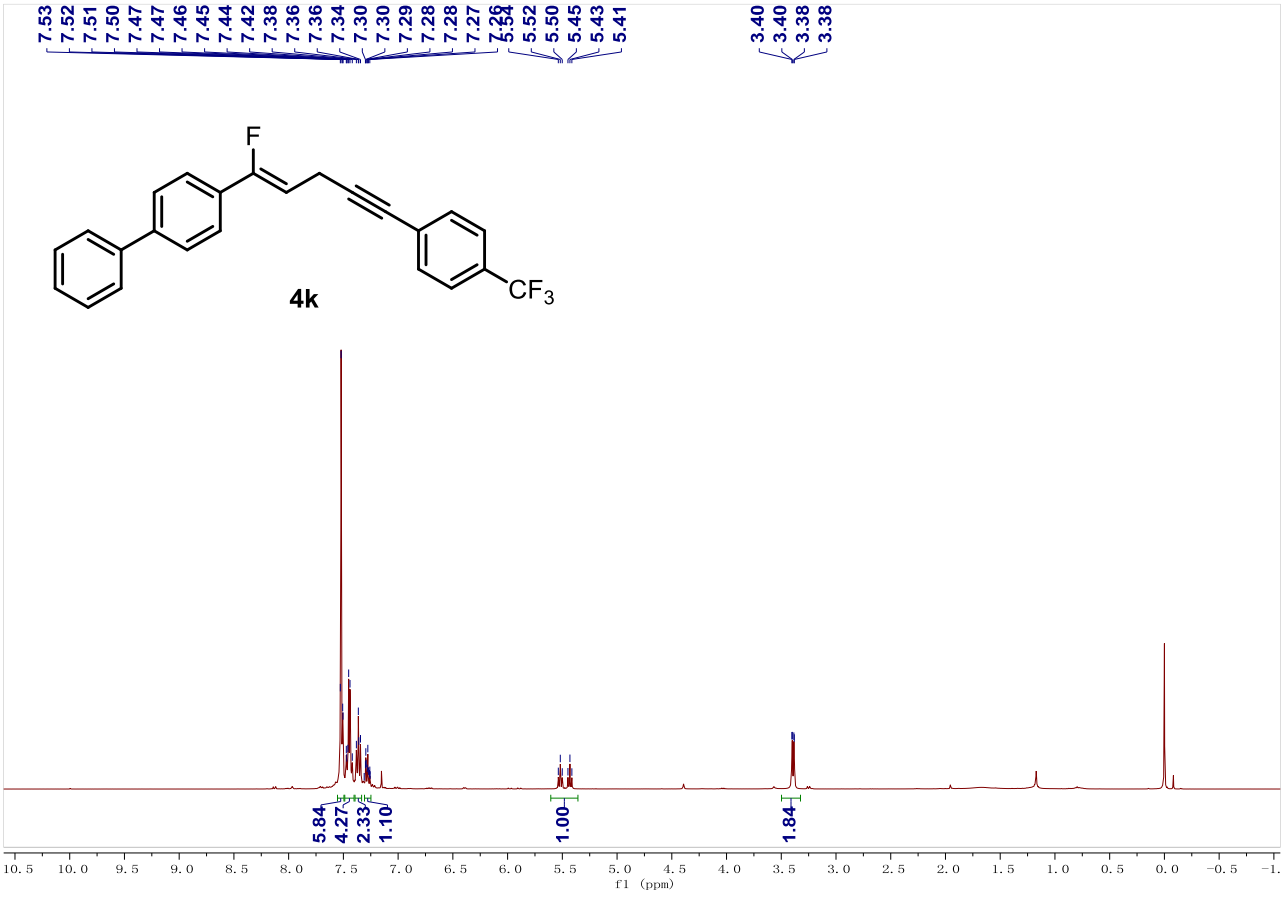

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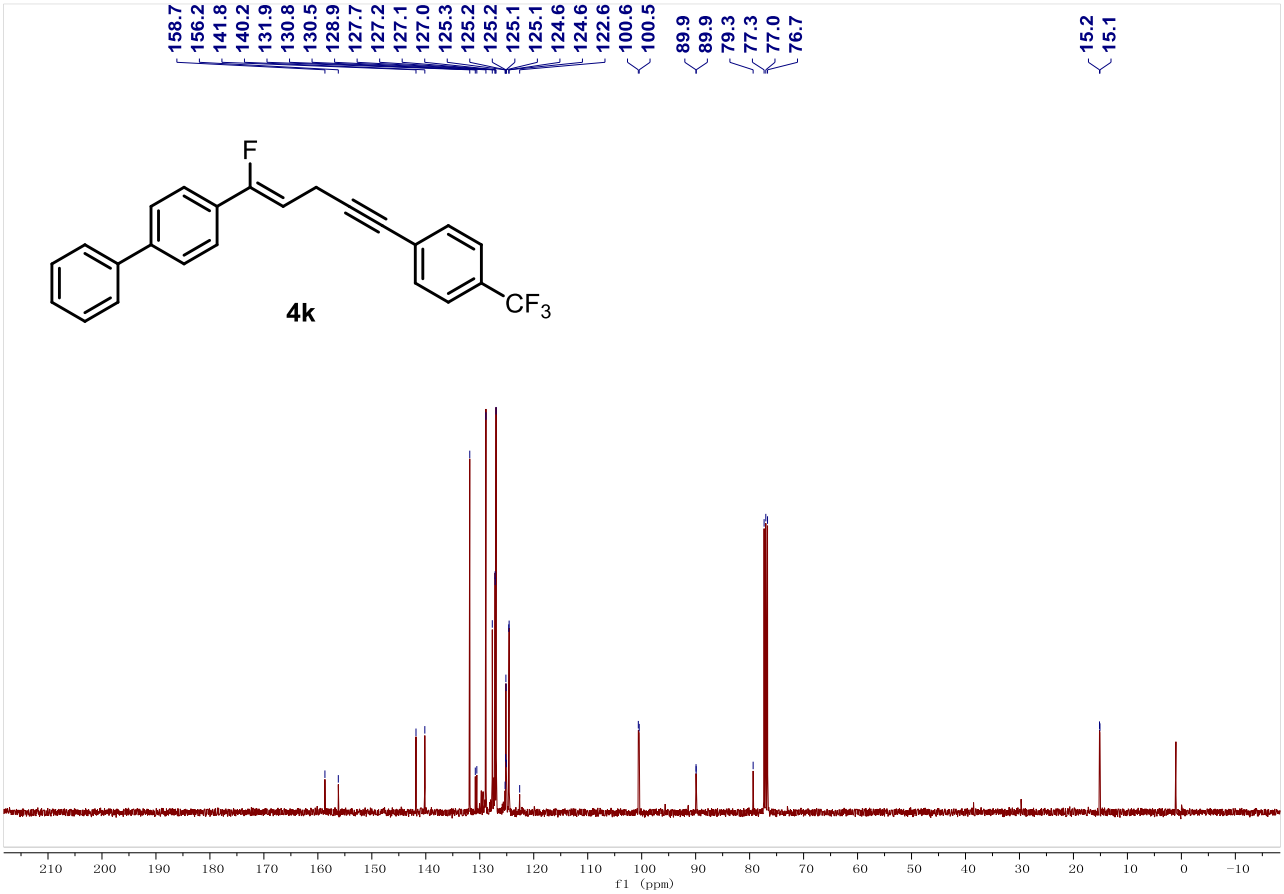

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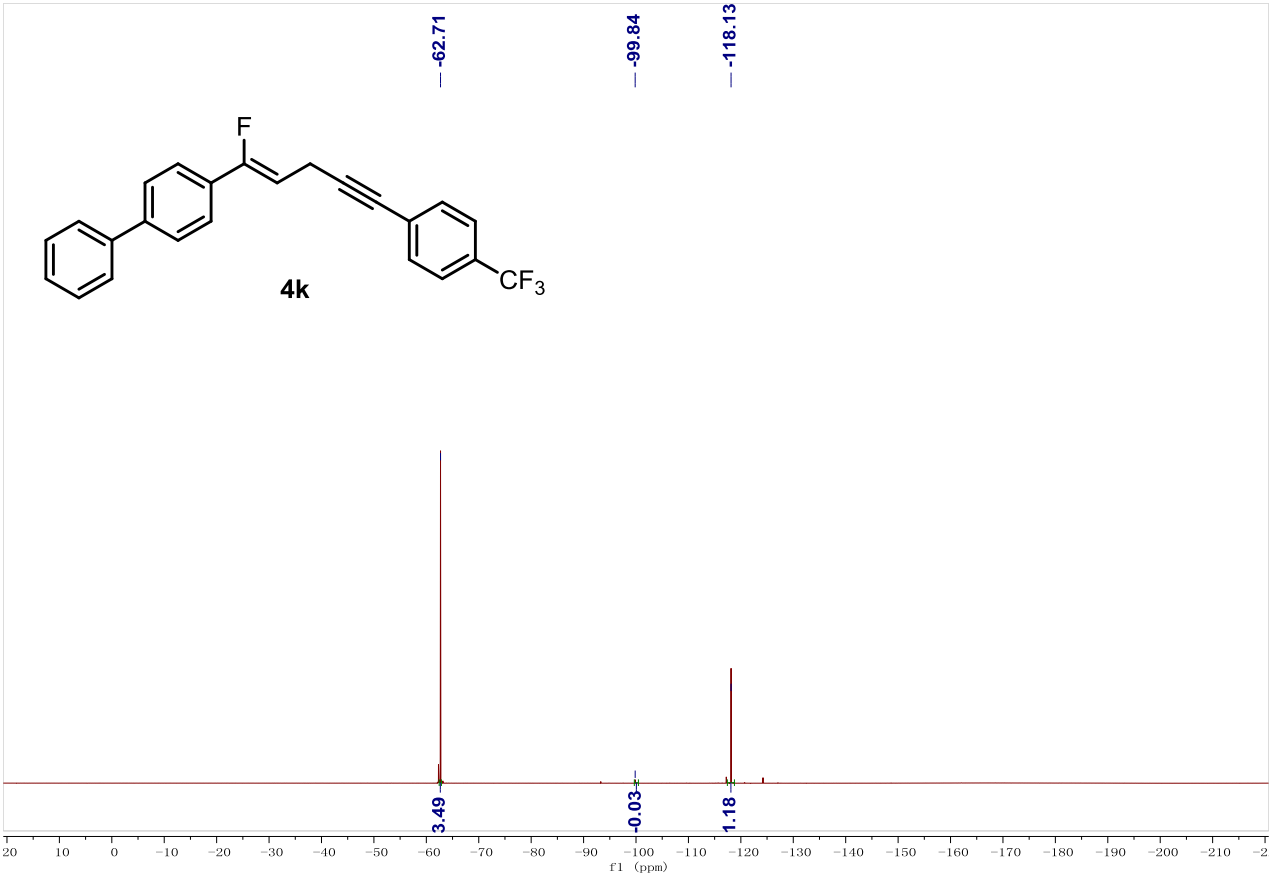

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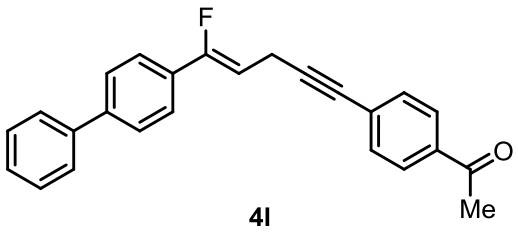

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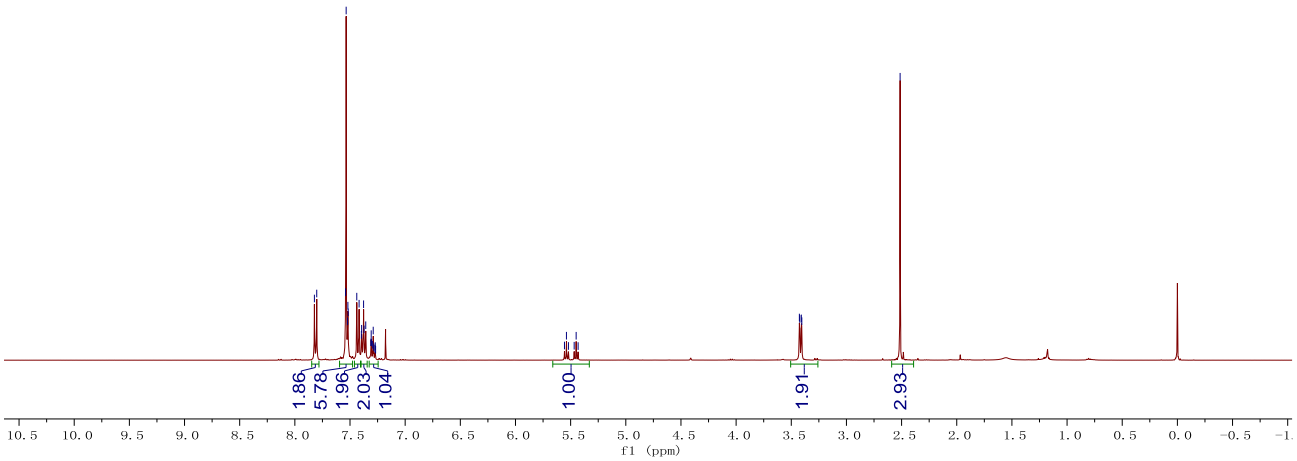
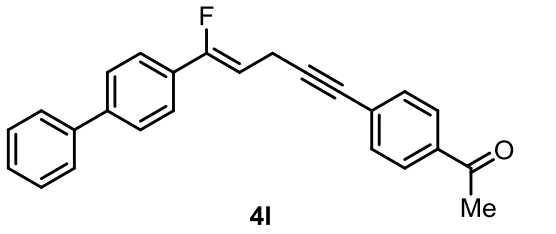


^{13}C NMR (101 MHz, $CDCl_3$)



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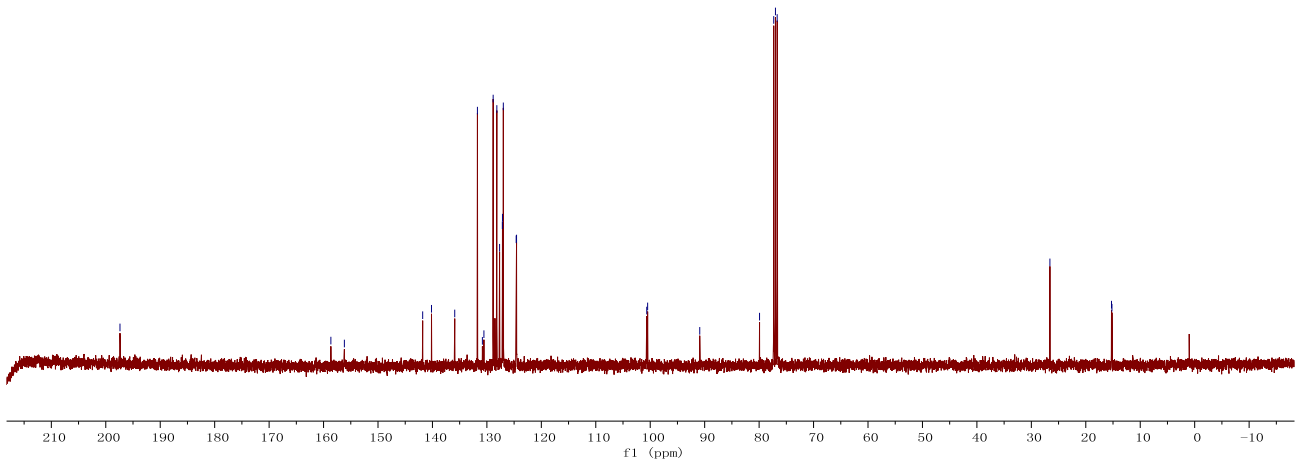

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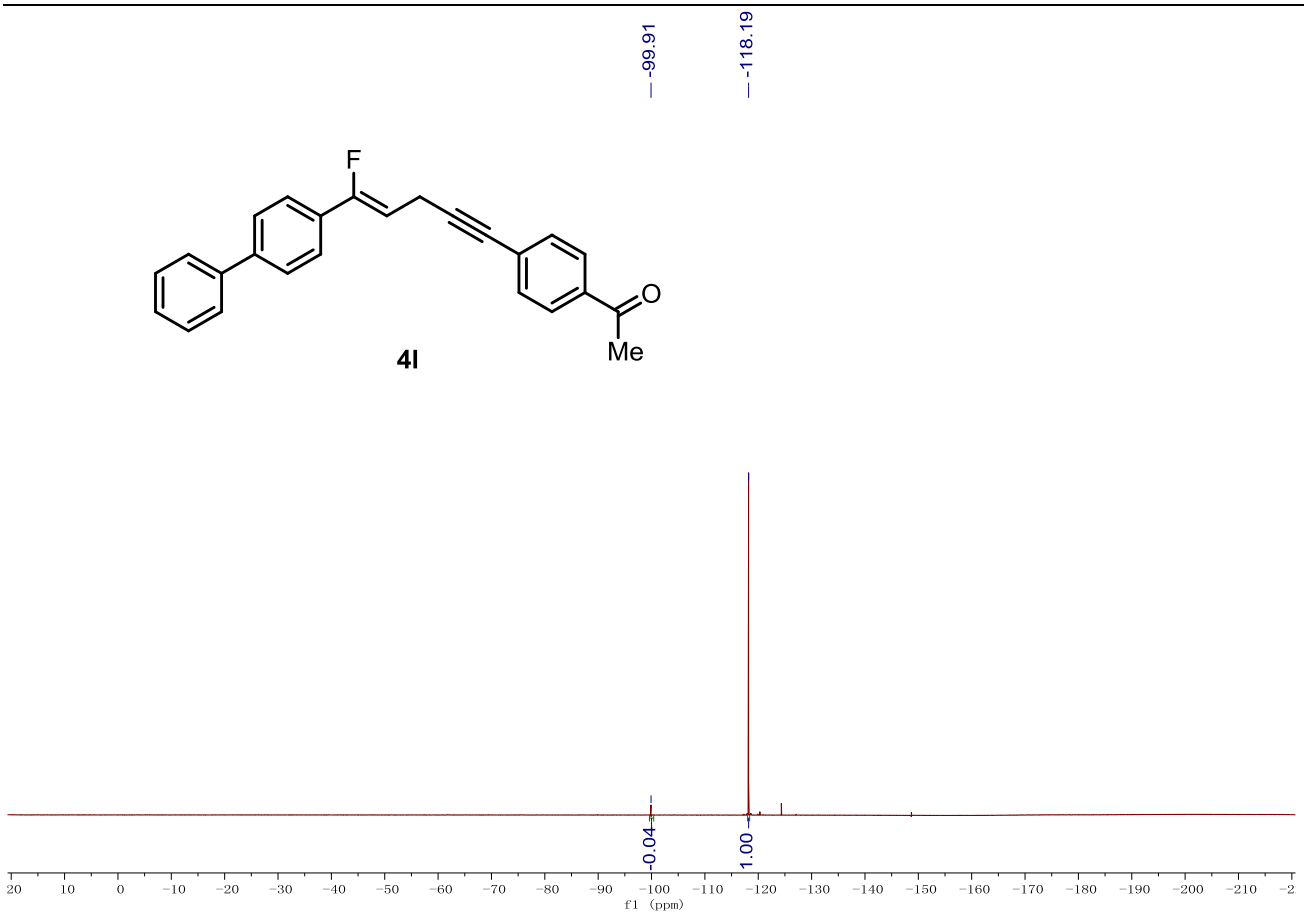

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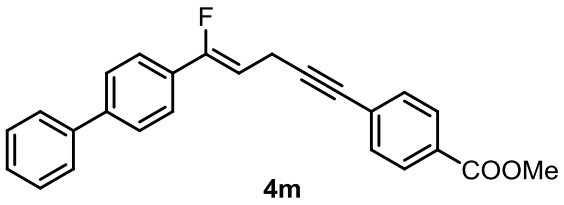

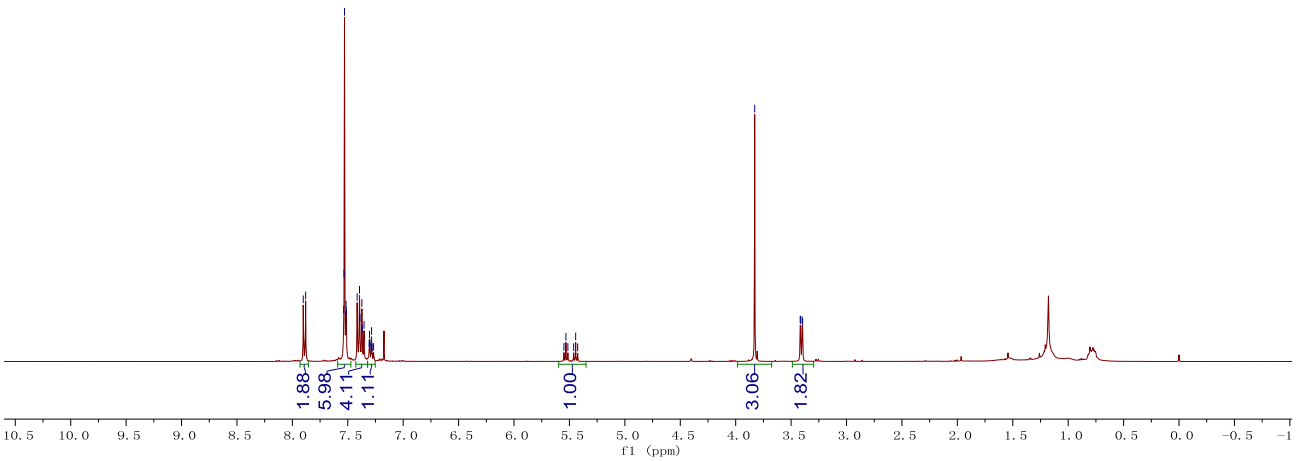

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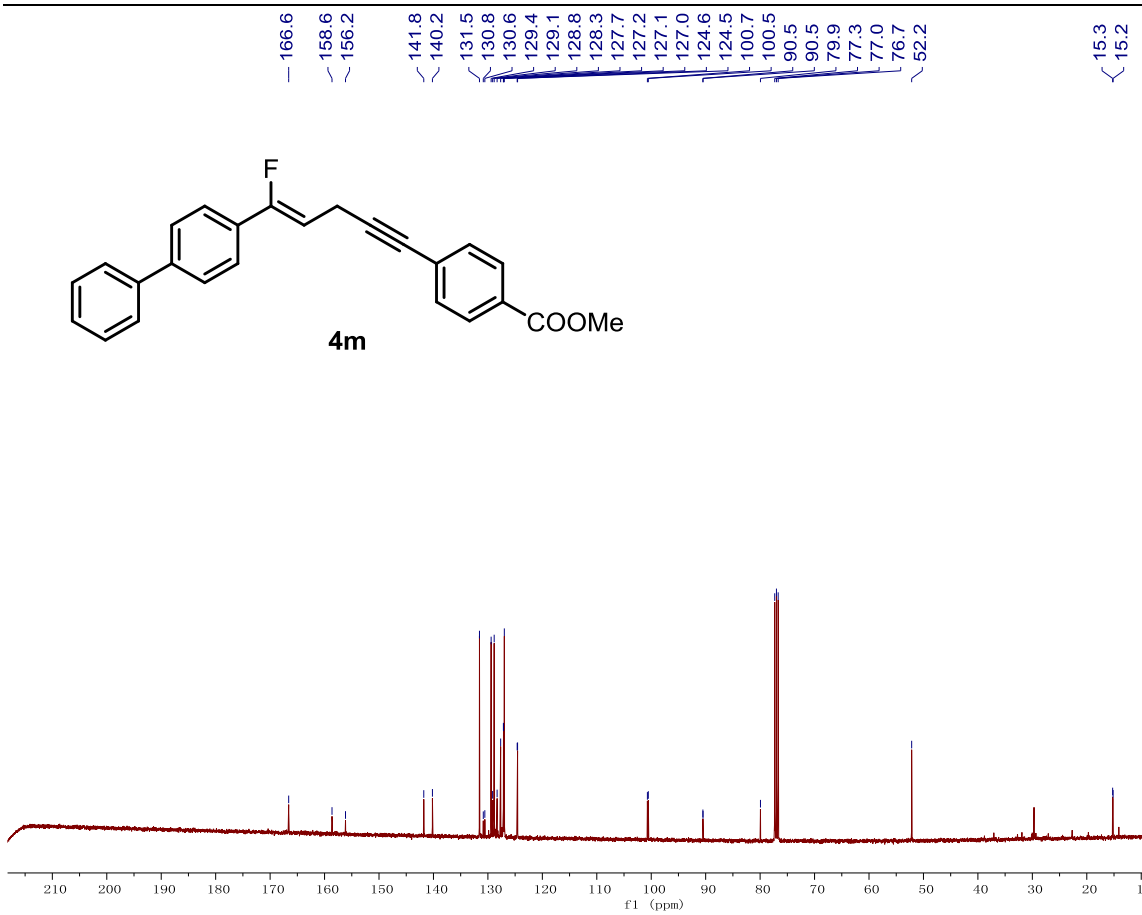

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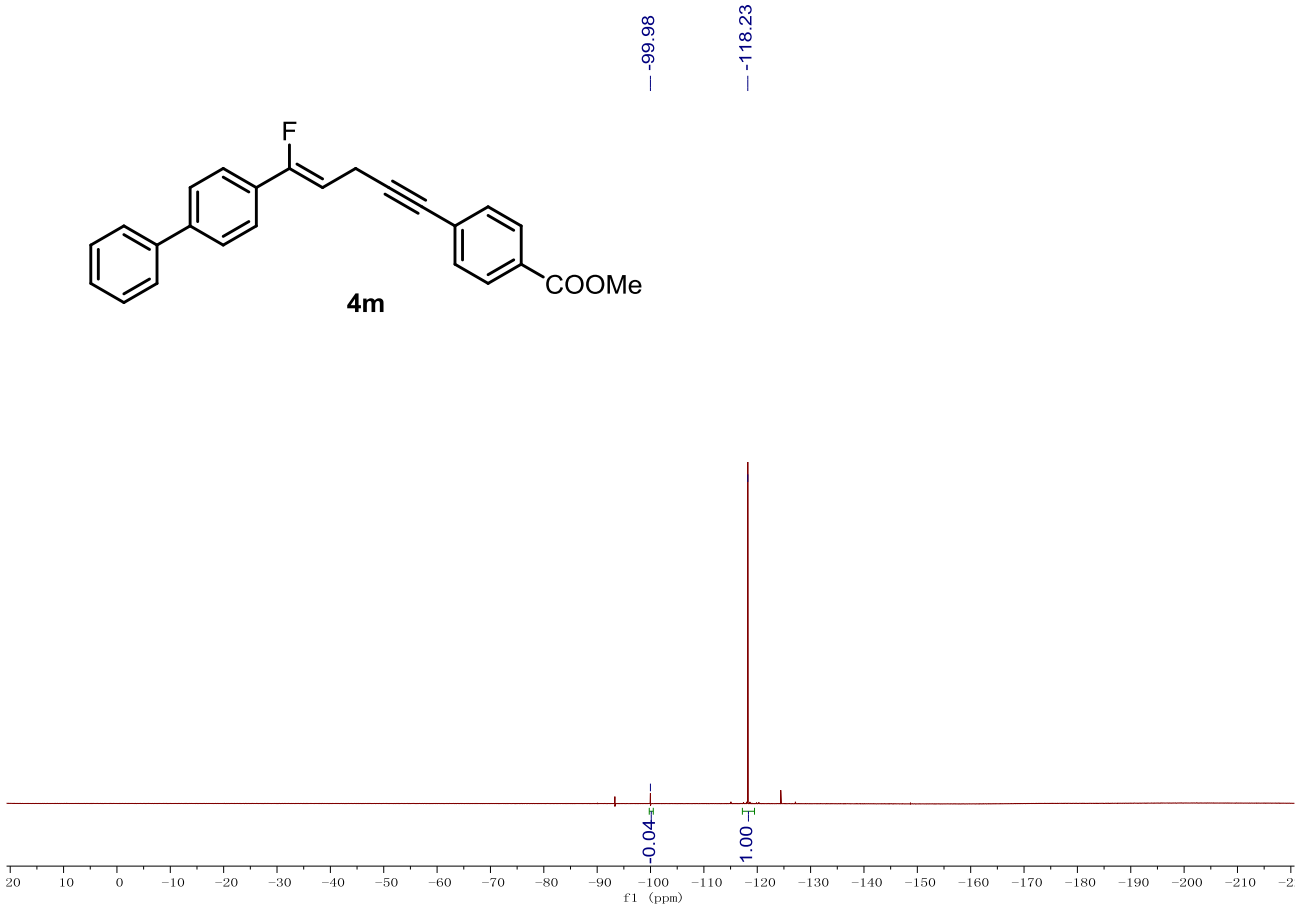

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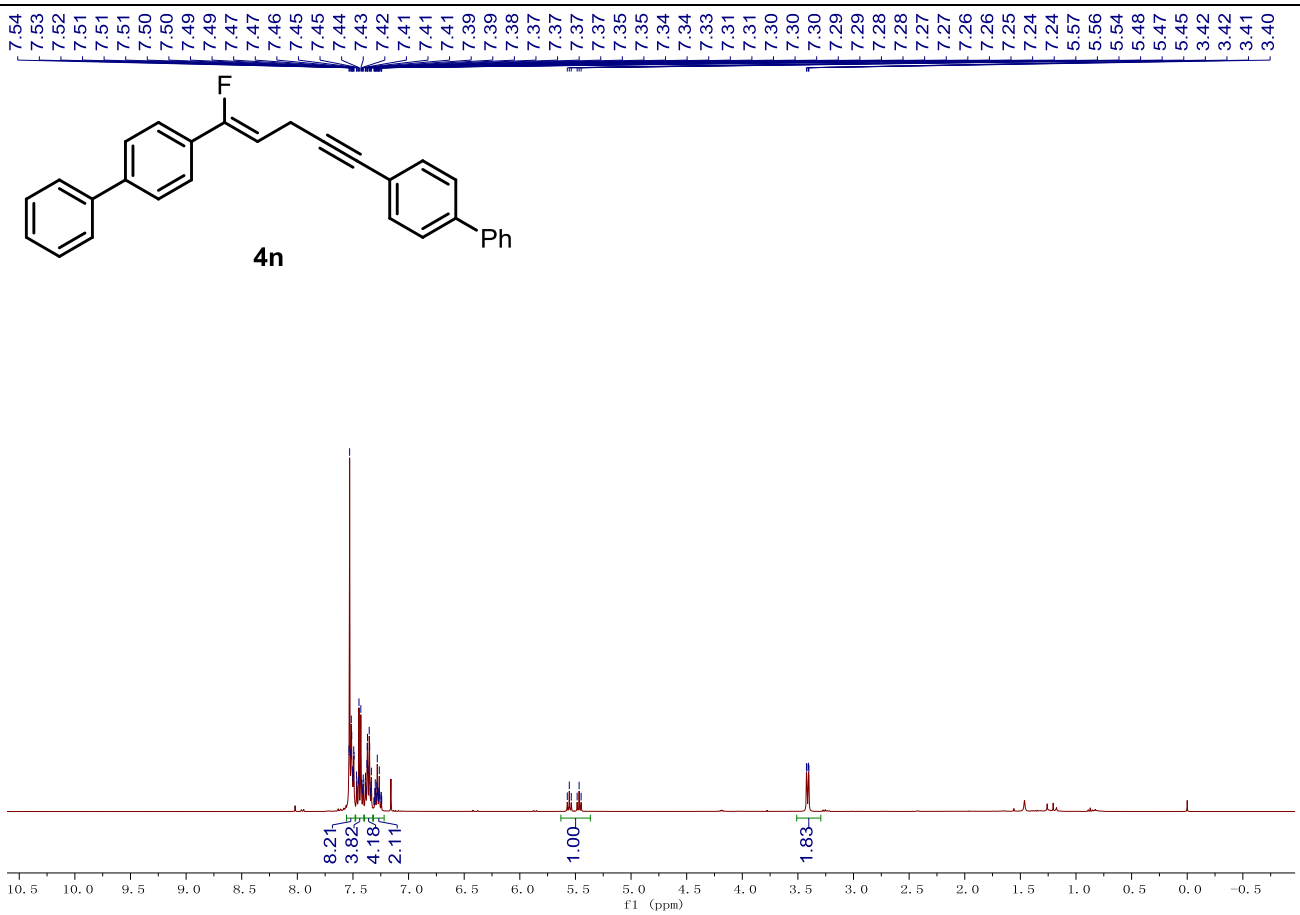

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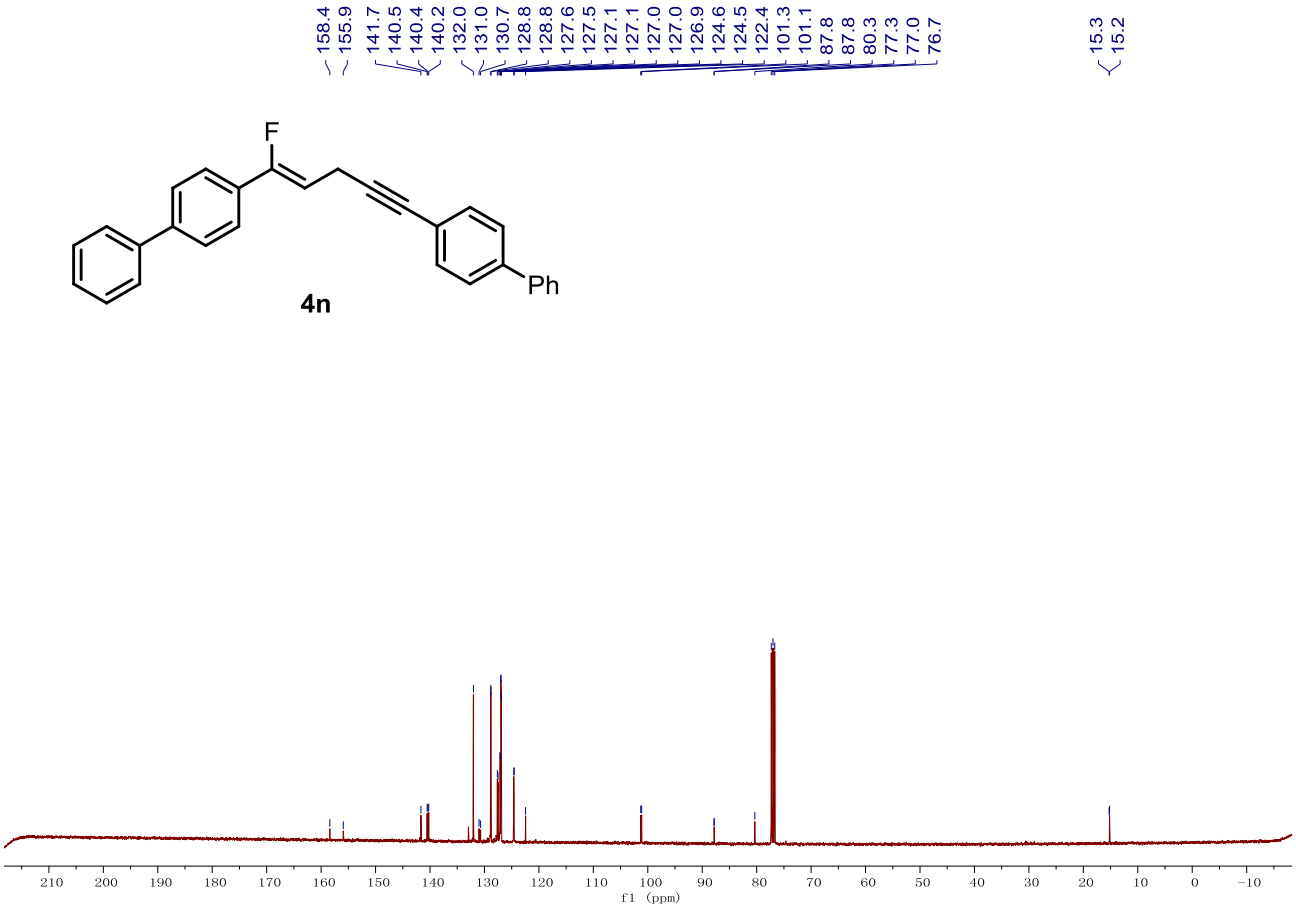

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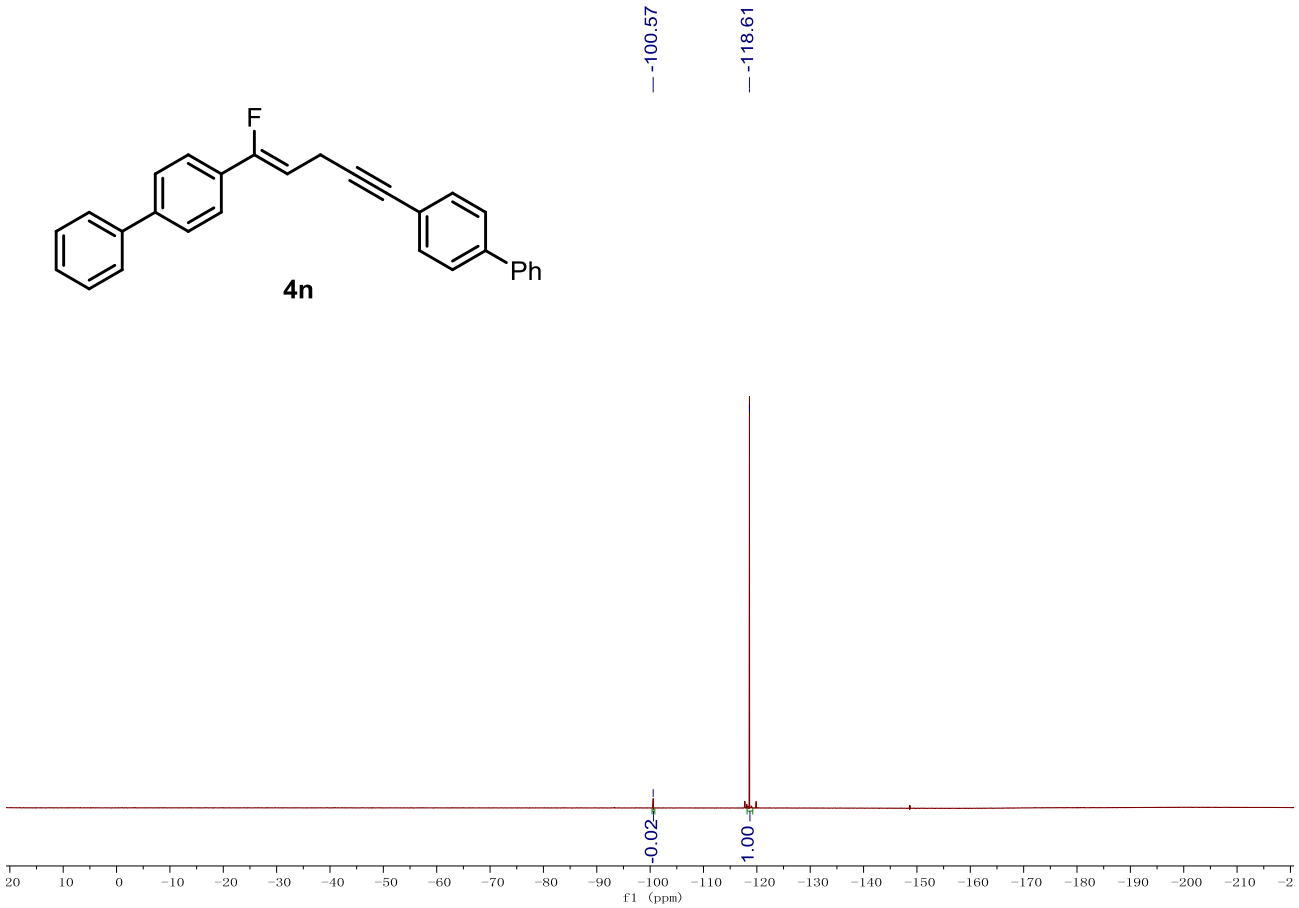

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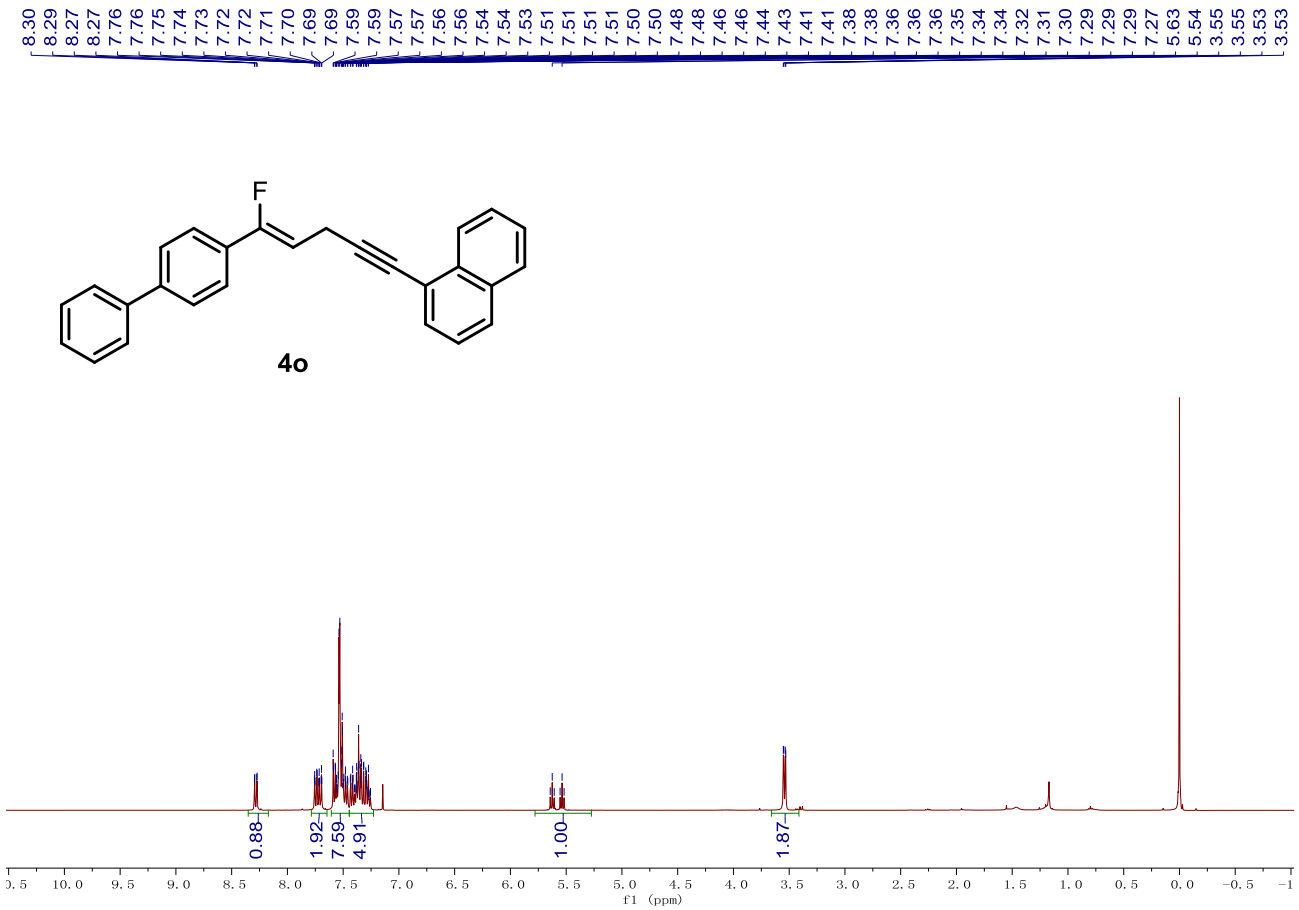

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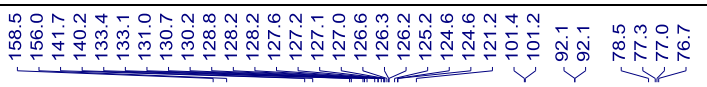

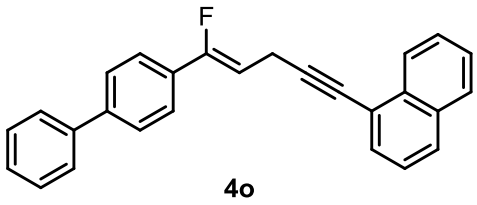

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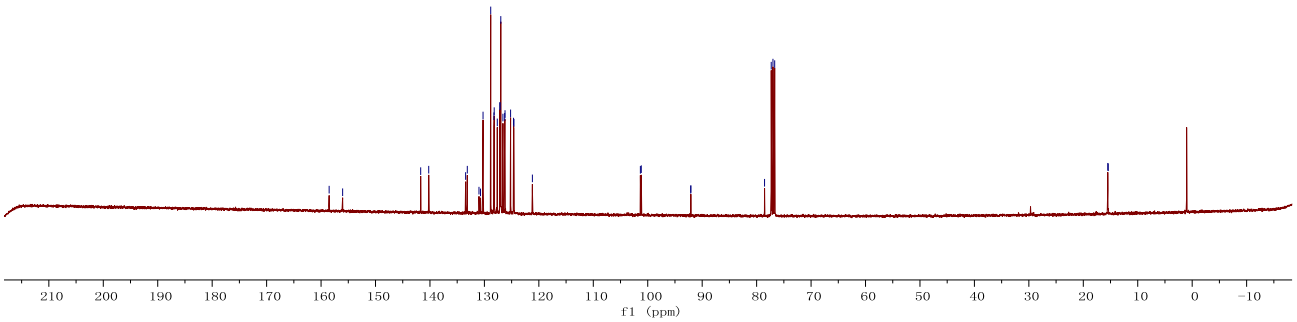
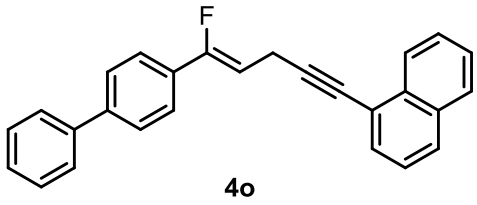


^{19}F NMR (376 MHz, CDCl$_3$)



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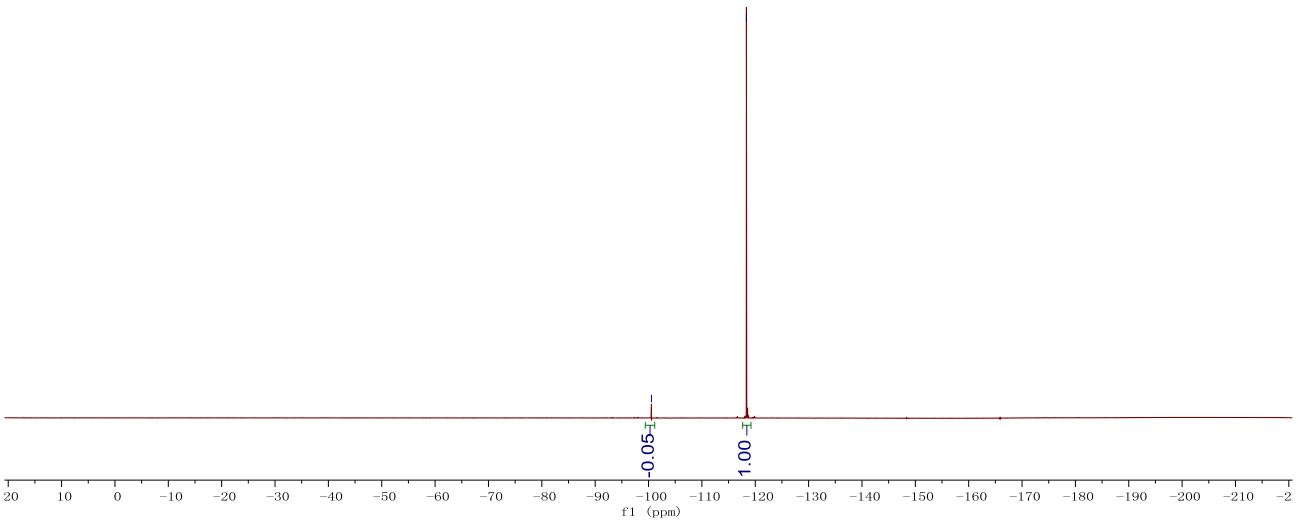
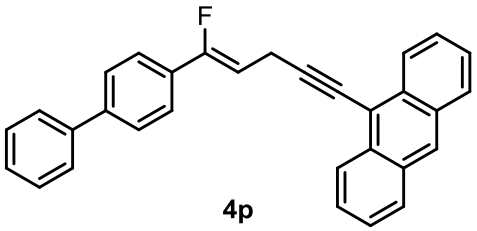


^{1}H NMR (400 MHz, CDCl$_3$)



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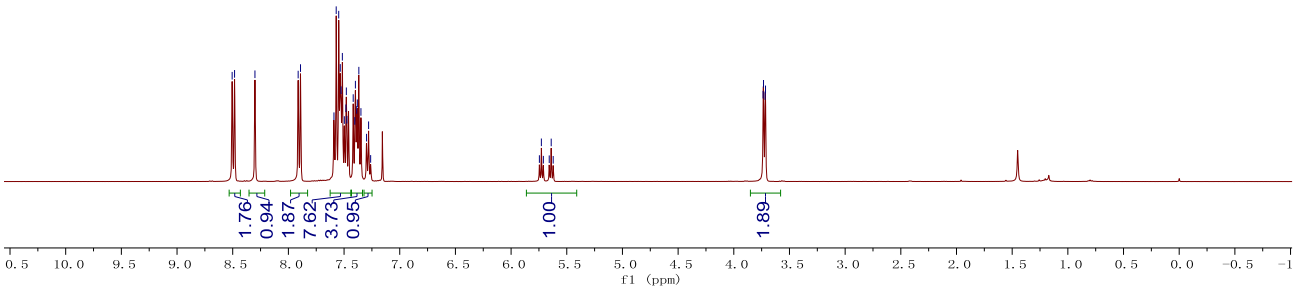
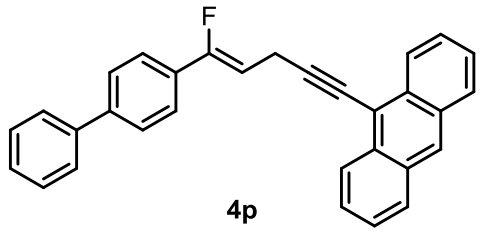


^{13}C NMR (101 MHz, $CDCl_3$)



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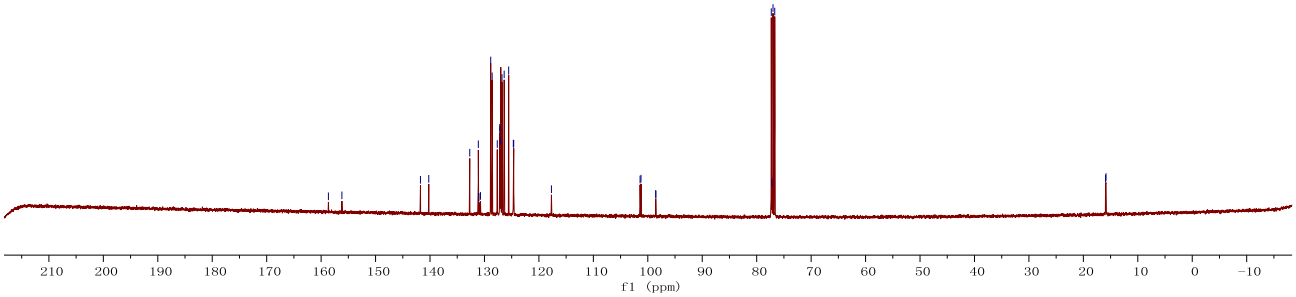

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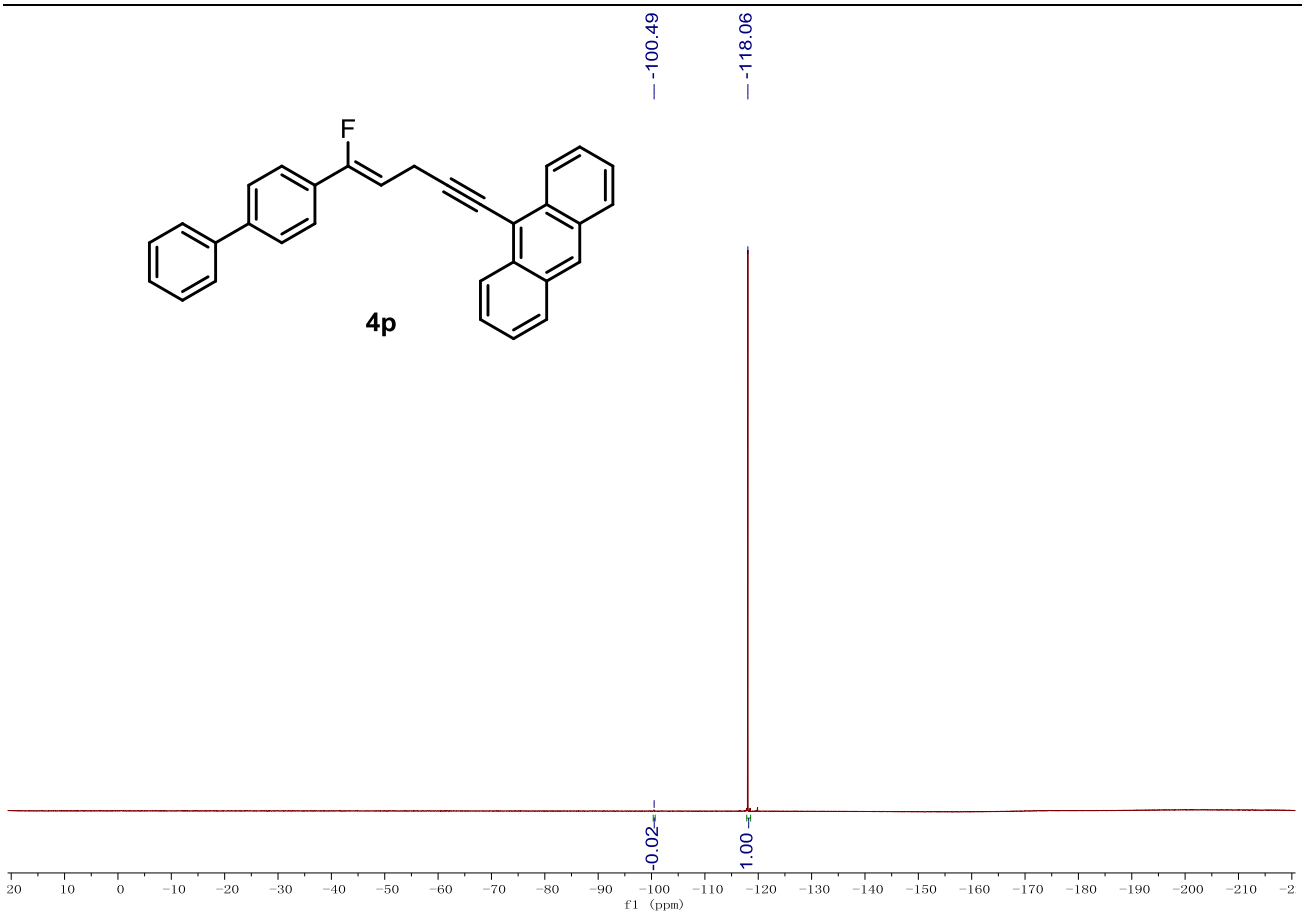
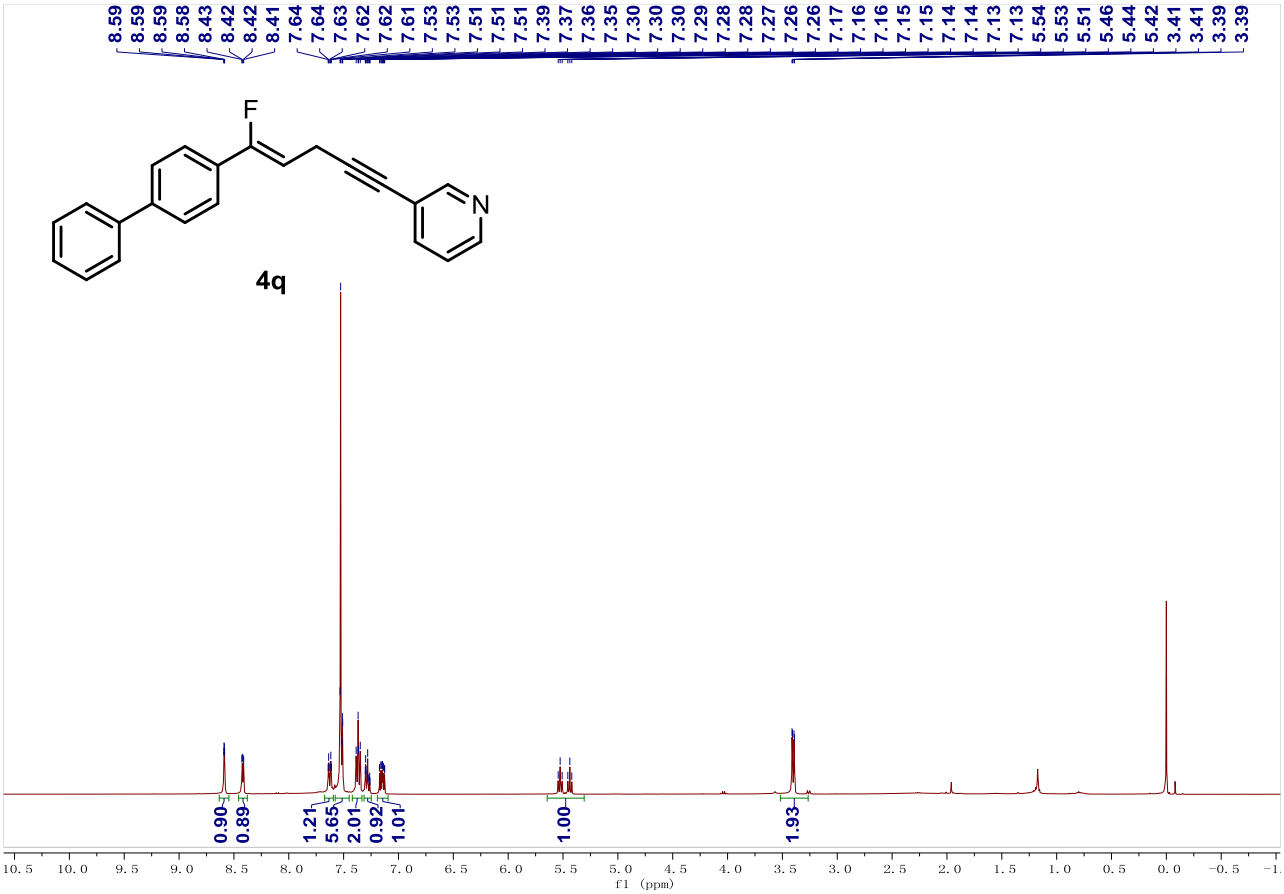


^{1}H NMR (400 MHz, $CDCl_3$)



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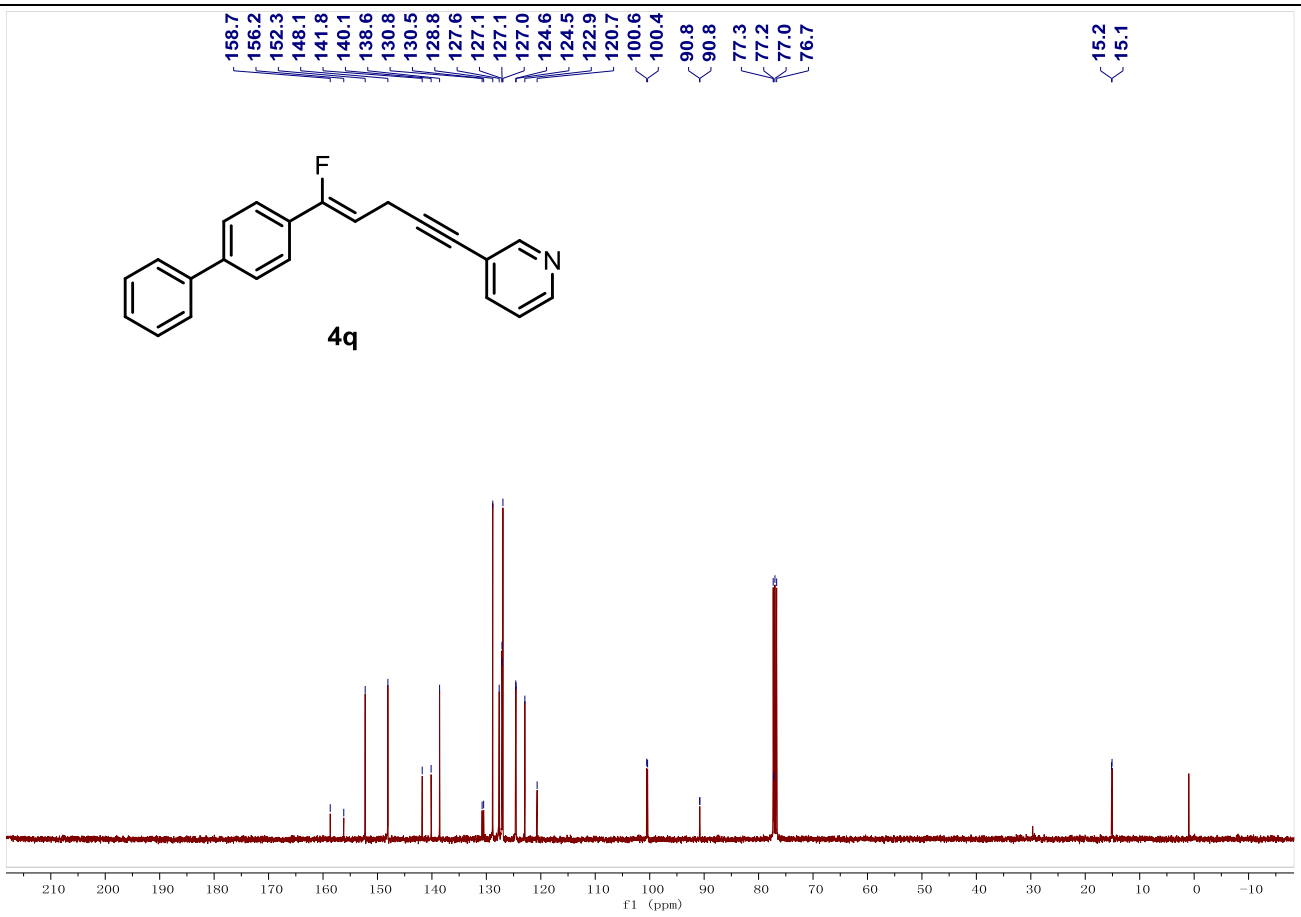

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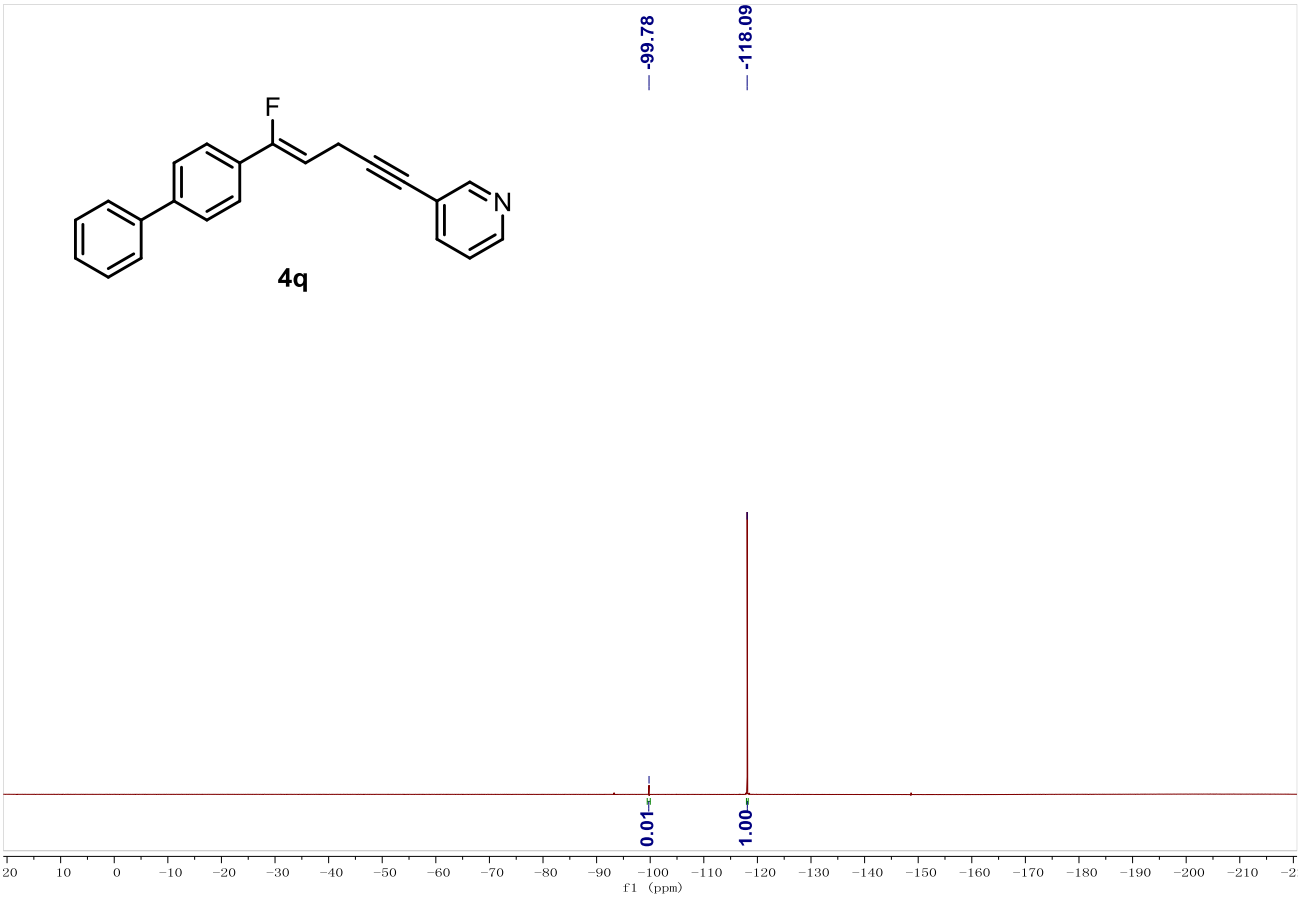
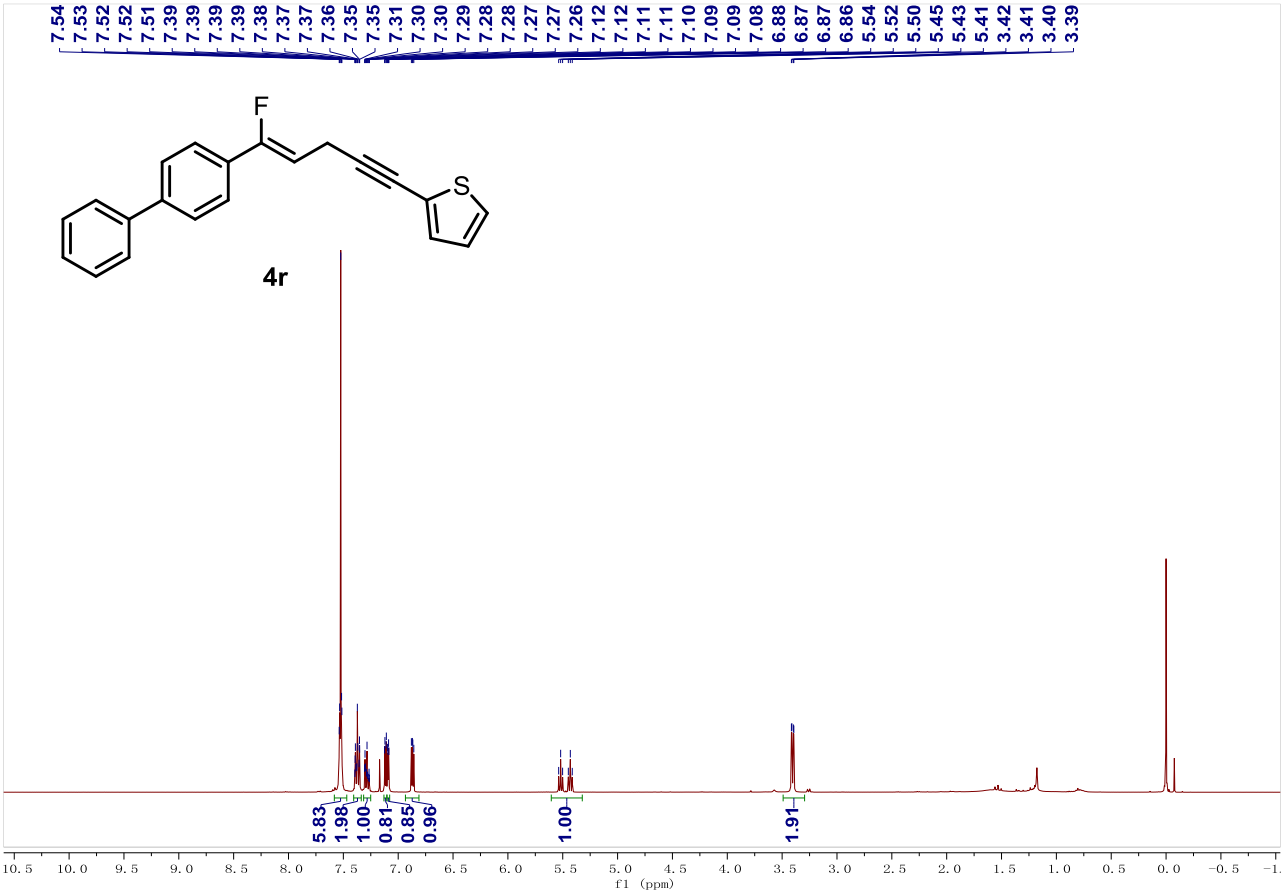


^{1}H NMR (400 MHz, $CDCl_3$)



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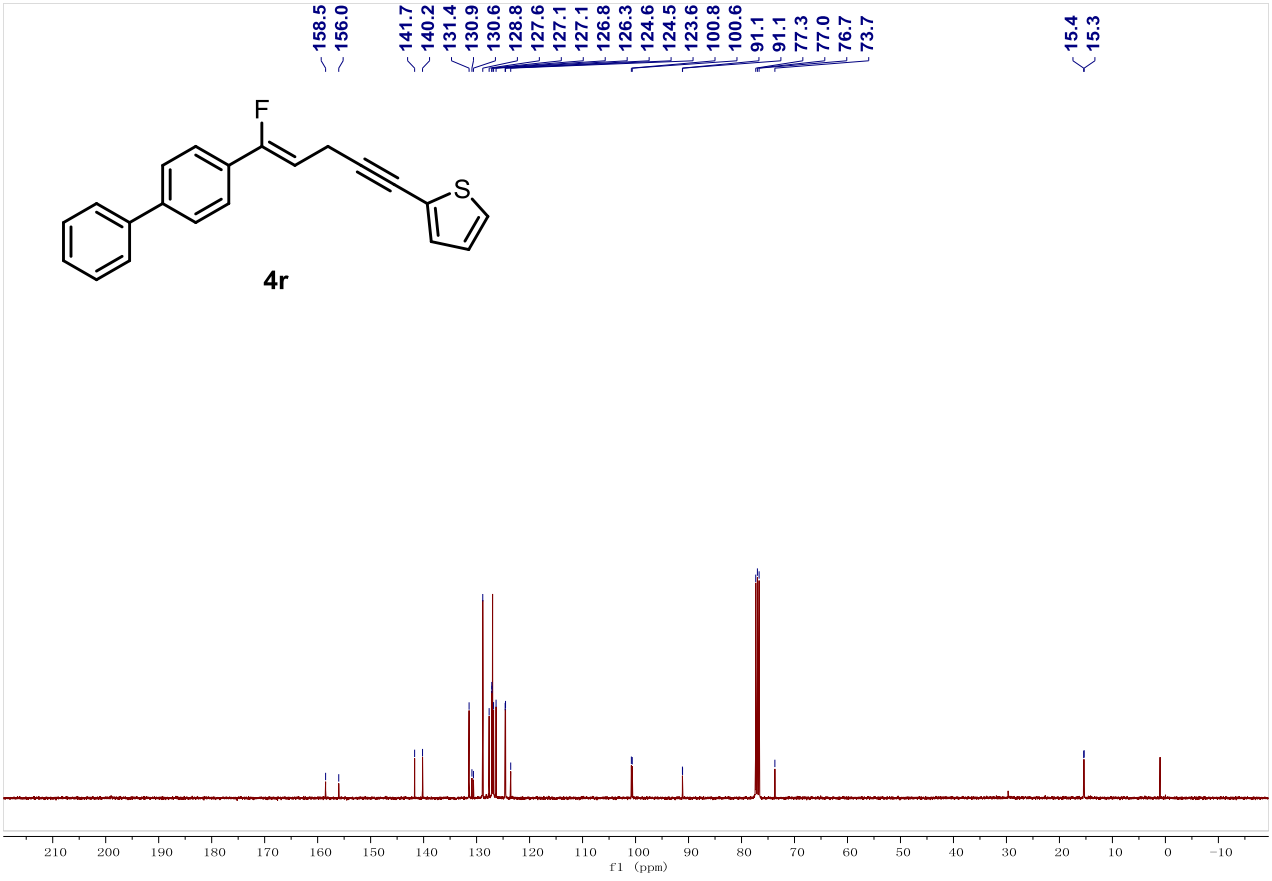

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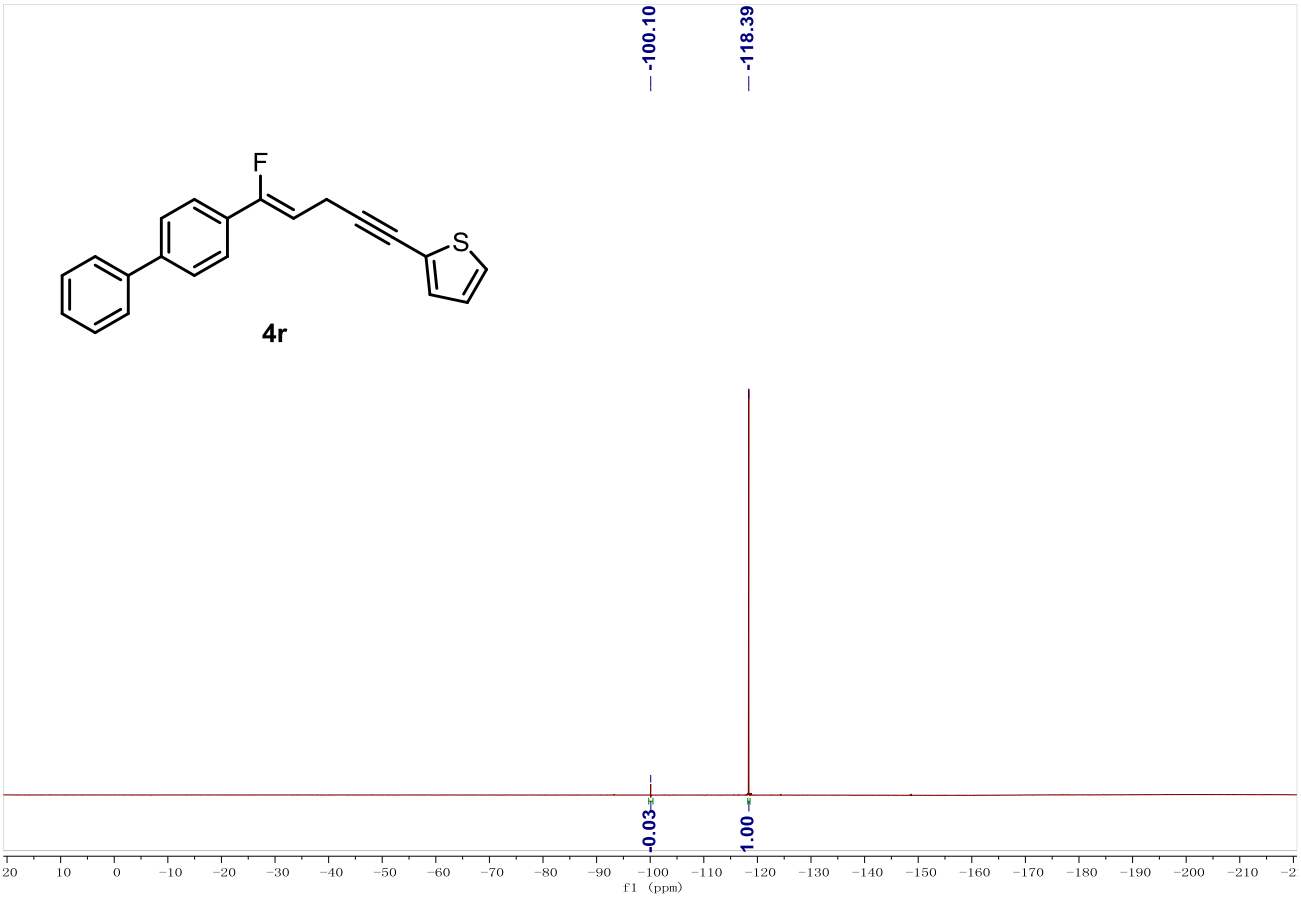

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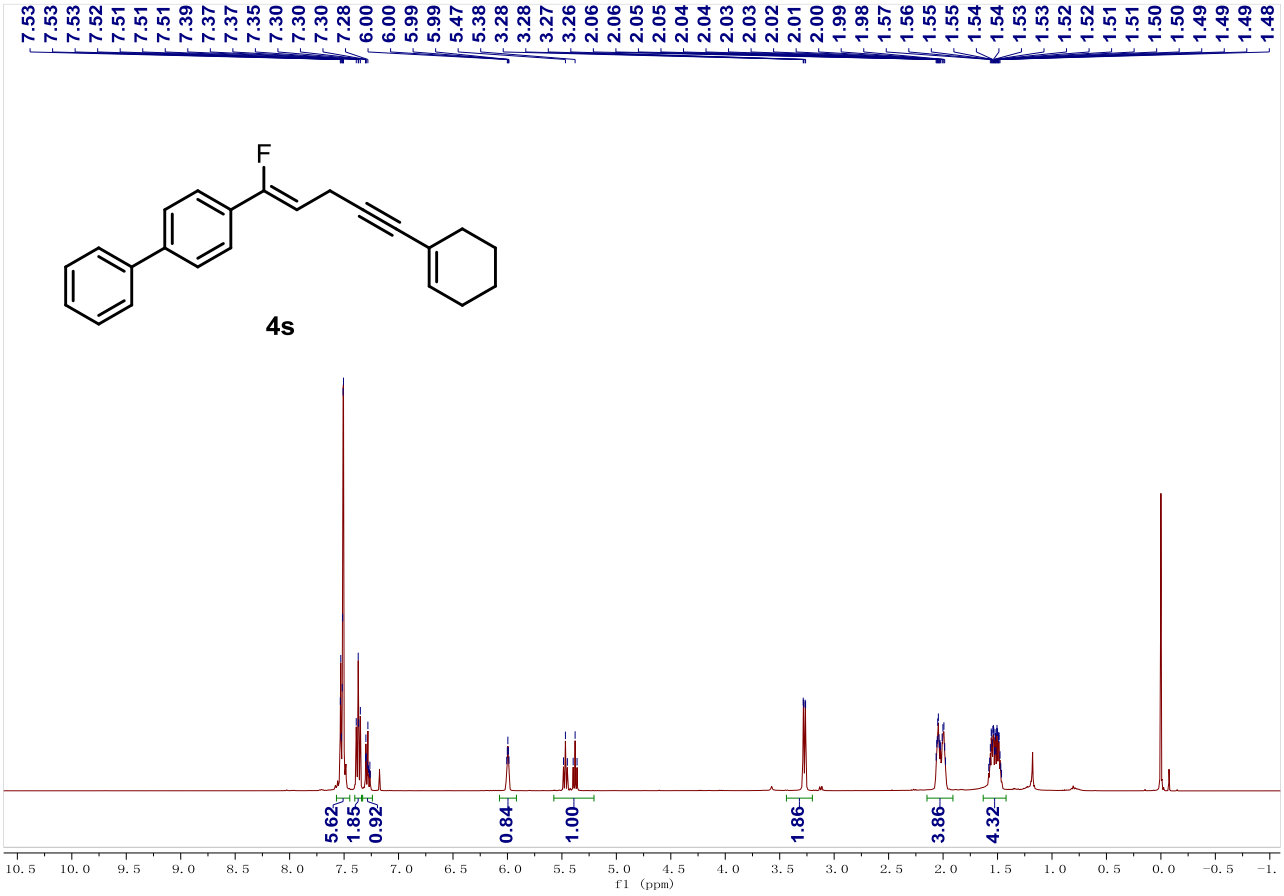

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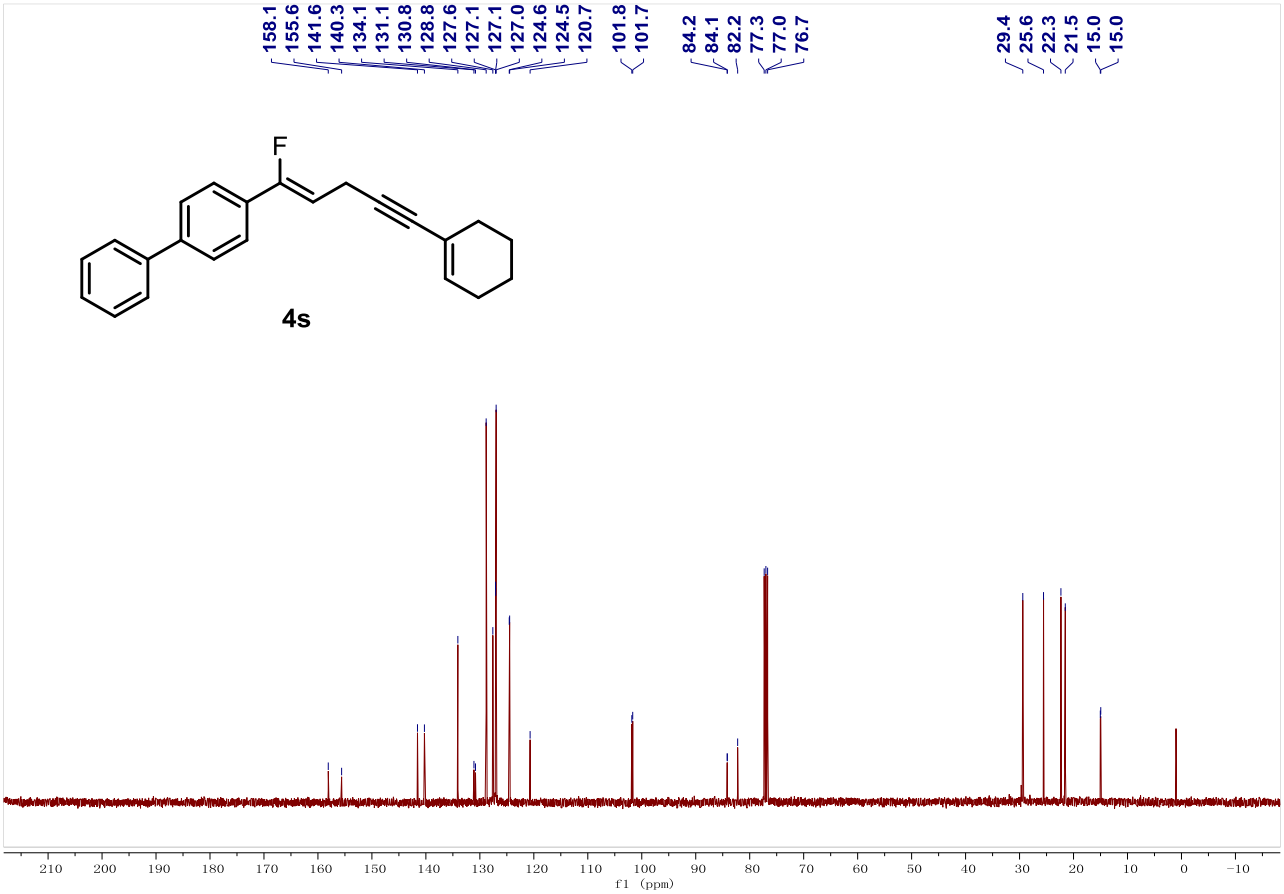

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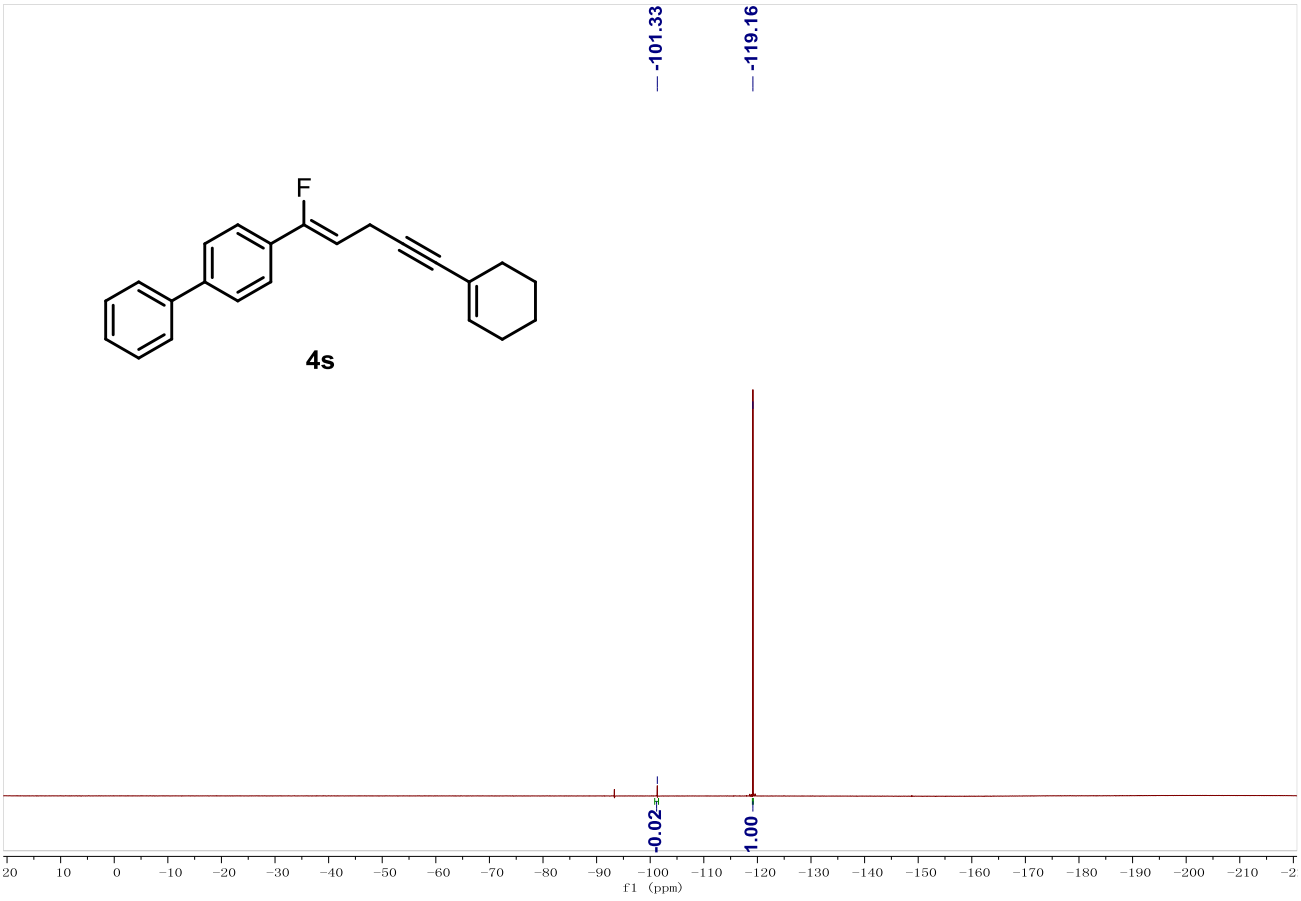

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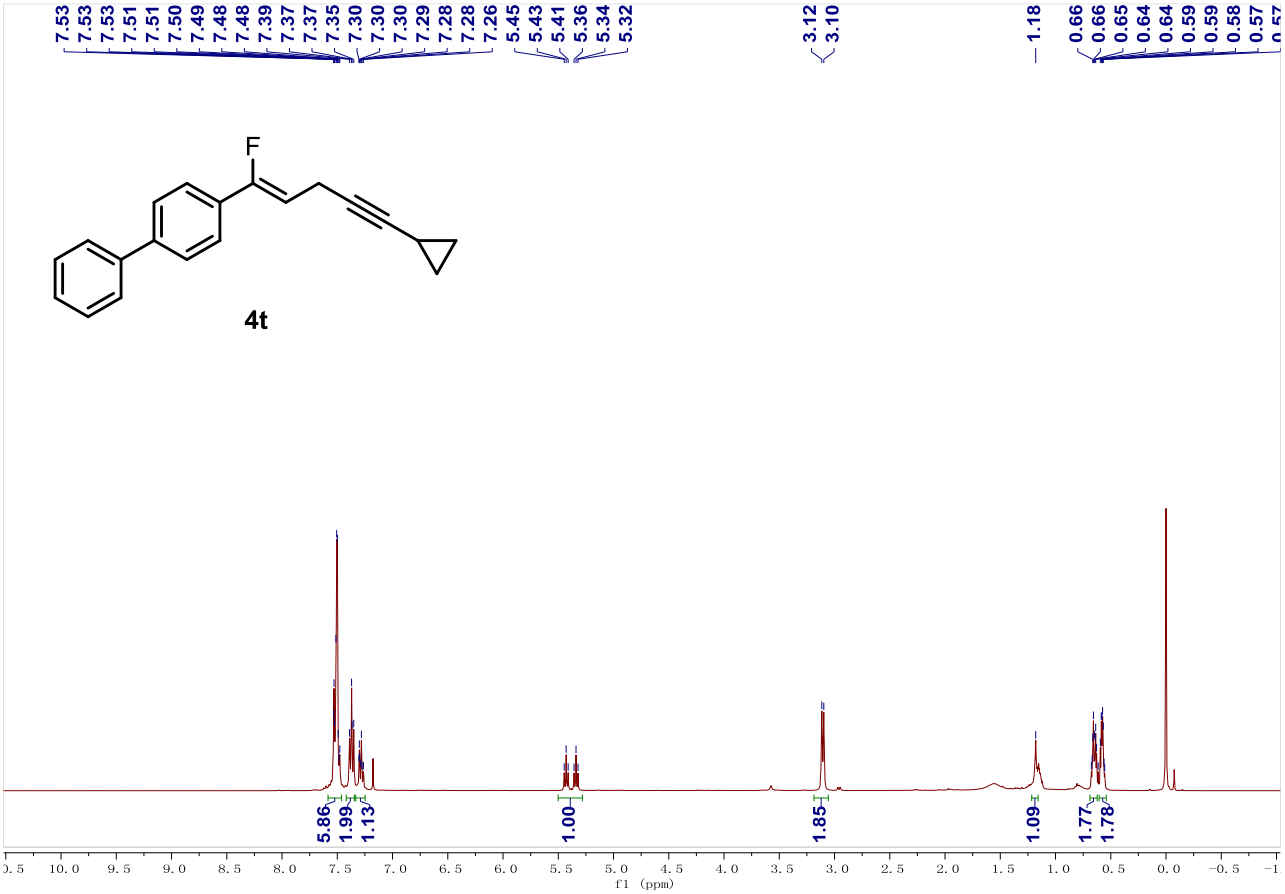

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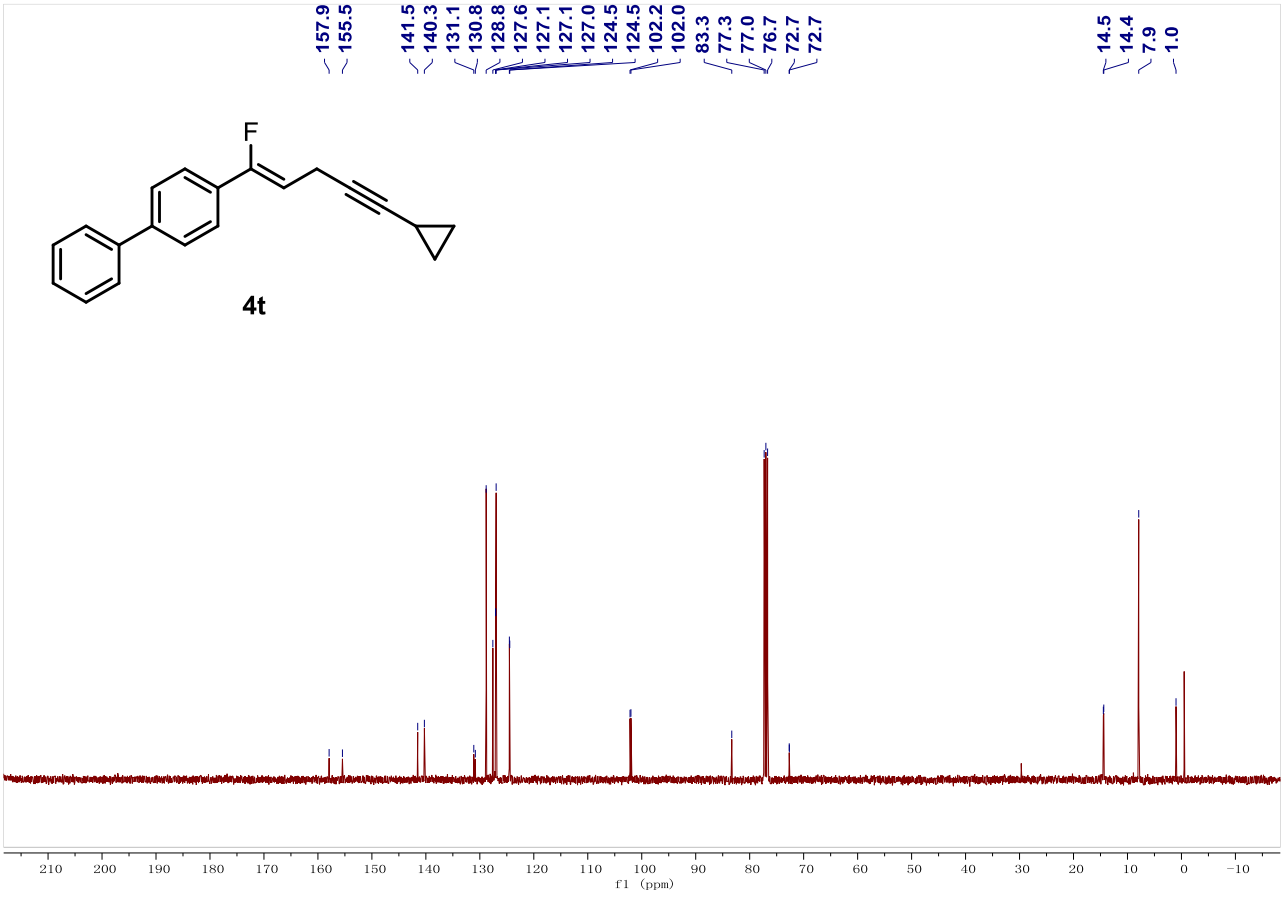
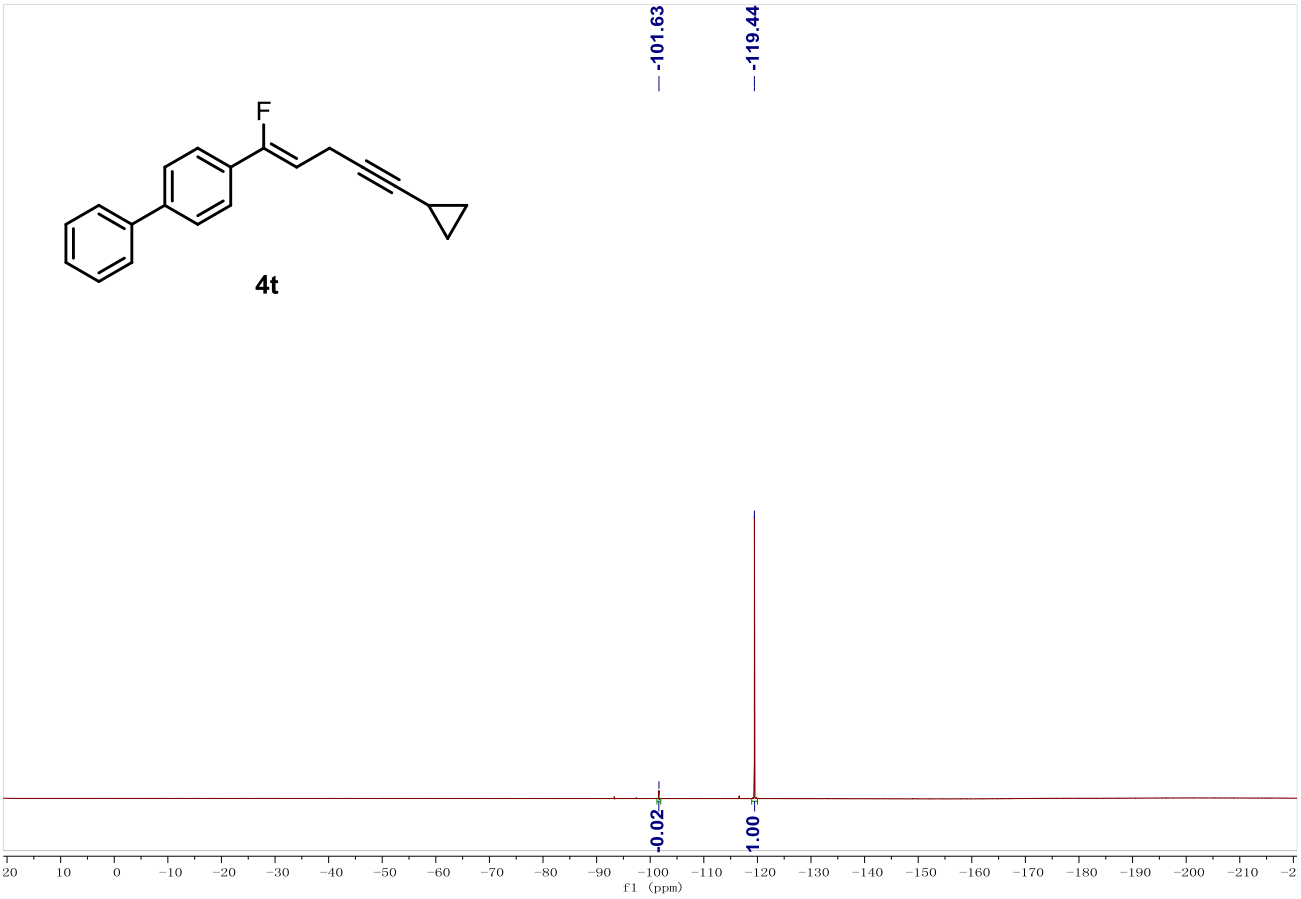
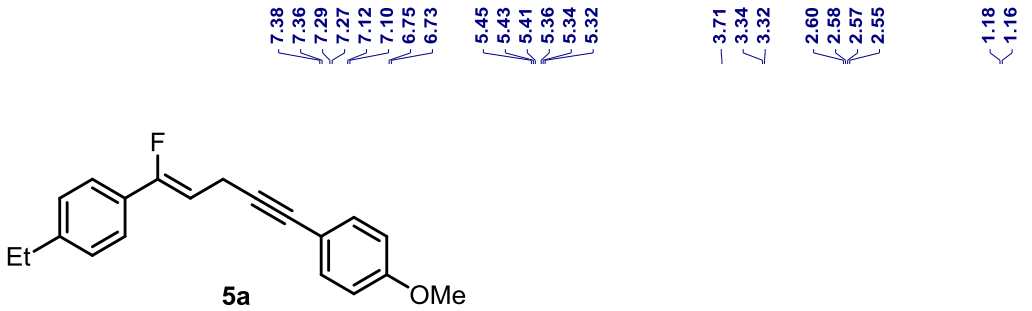
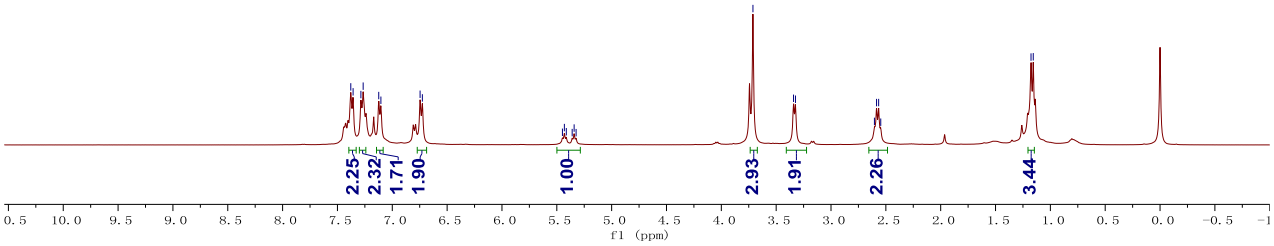


^{19}F NMR (376 MHz, $CDCl_3$)

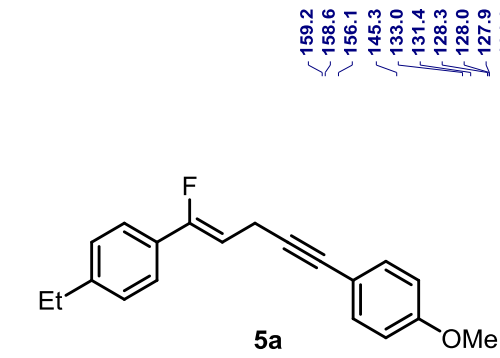


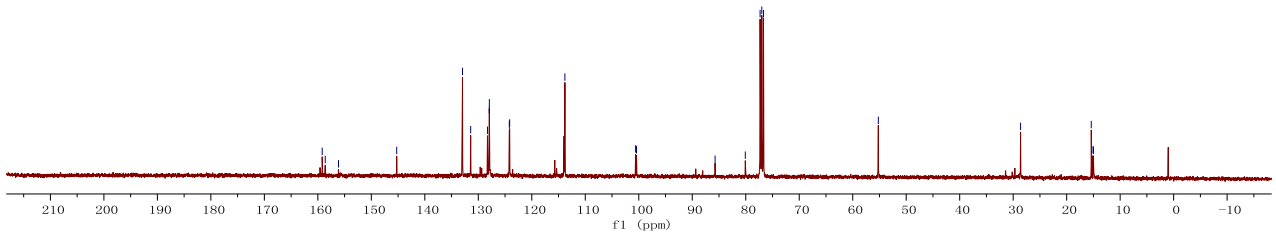
^{1}H NMR (400 MHz, $CDCl_3$)



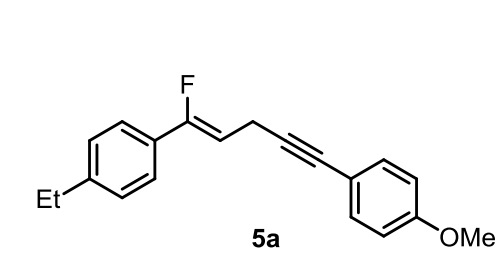


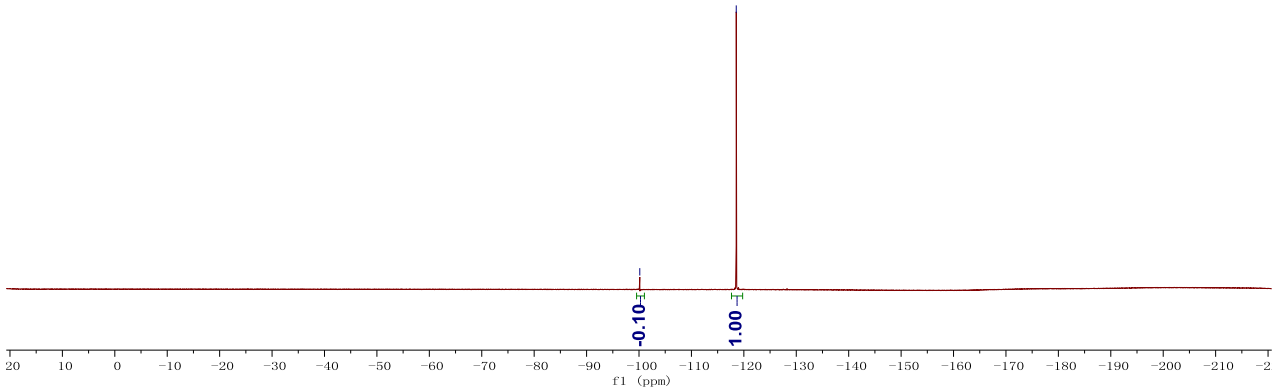
^{13}C NMR (101 MHz, $CDCl_3$)



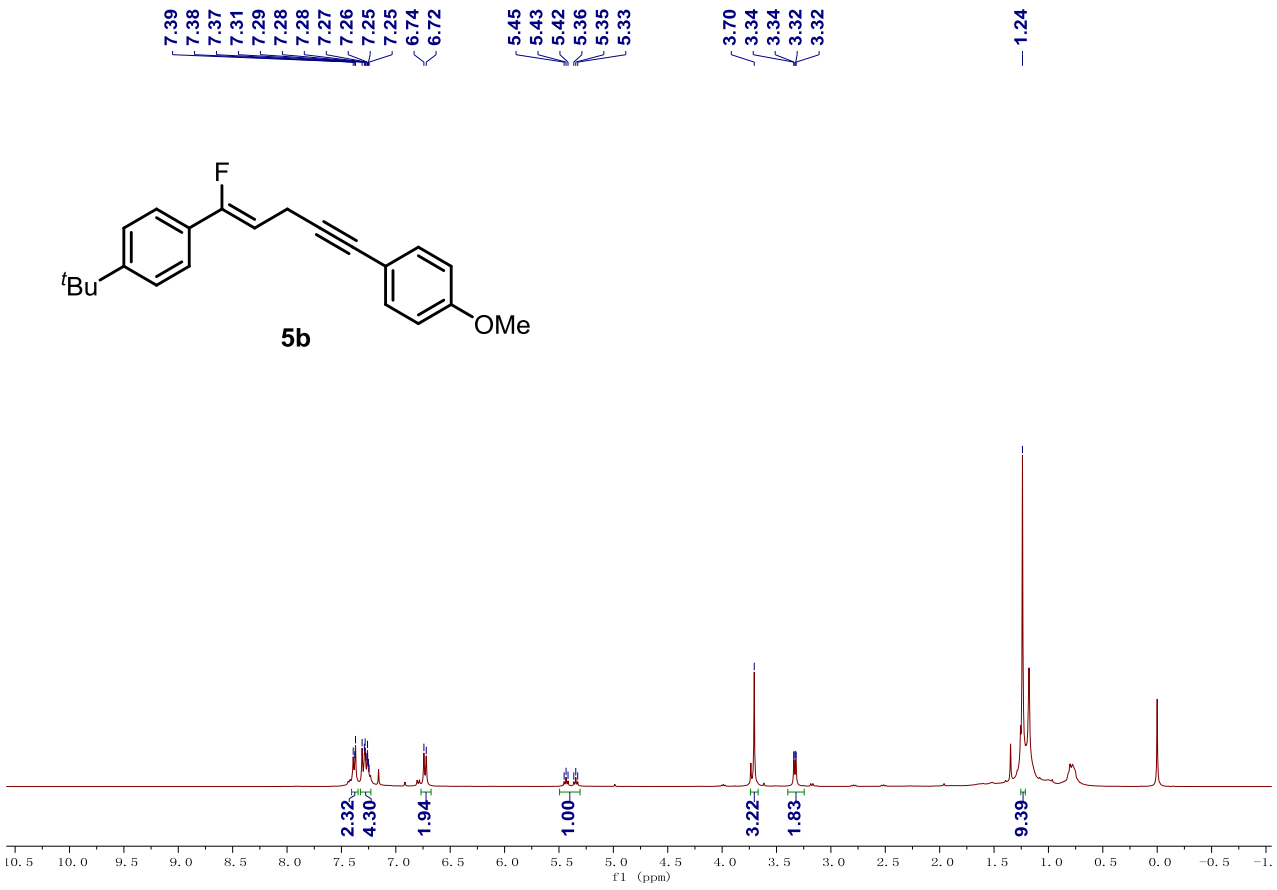


^{19}F NMR (376 MHz, $CDCl_3$)

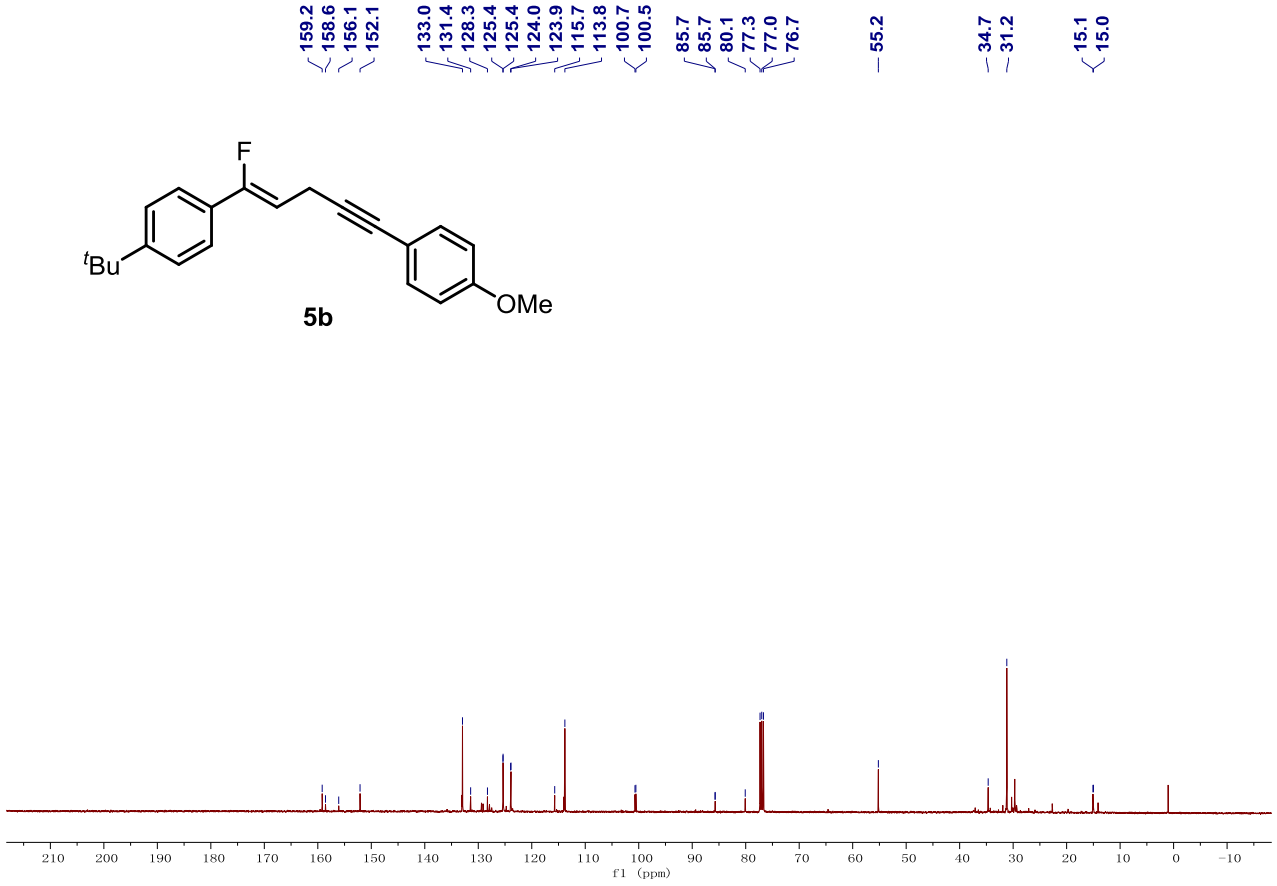




^{1}H NMR (400 MHz, $CDCl_3$)



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



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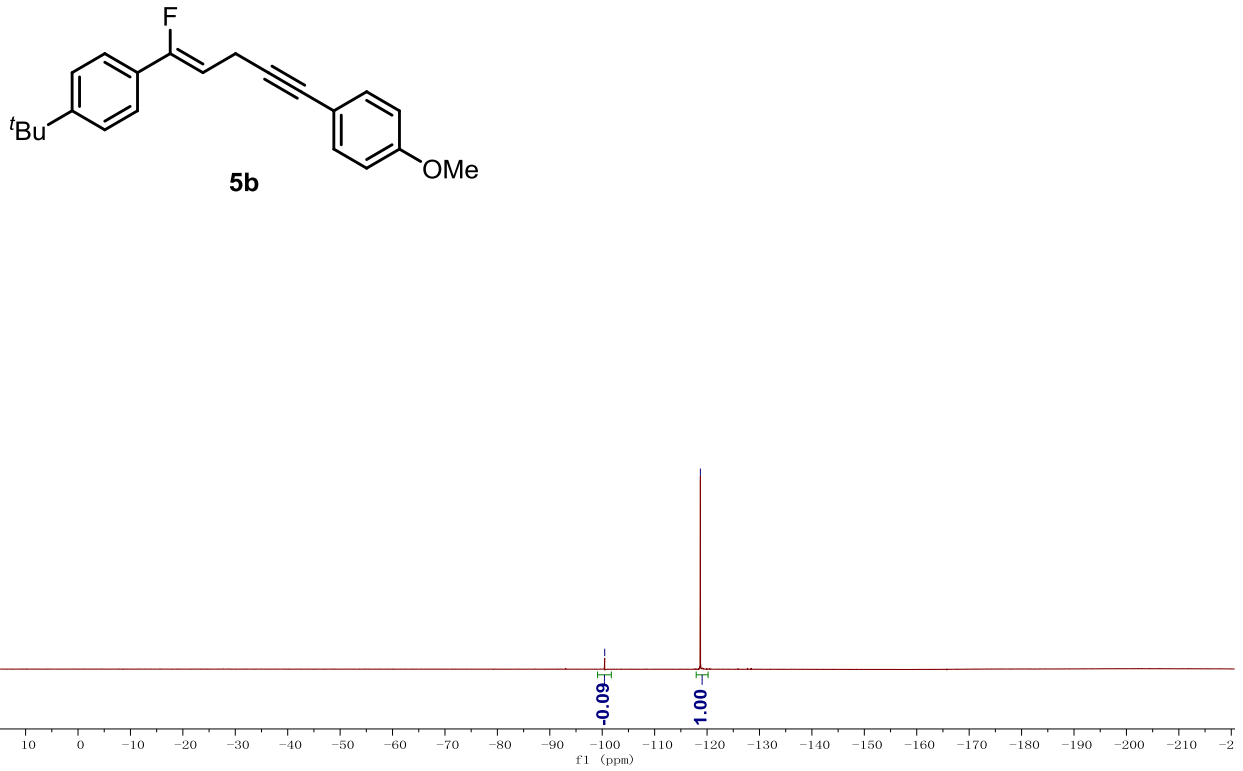

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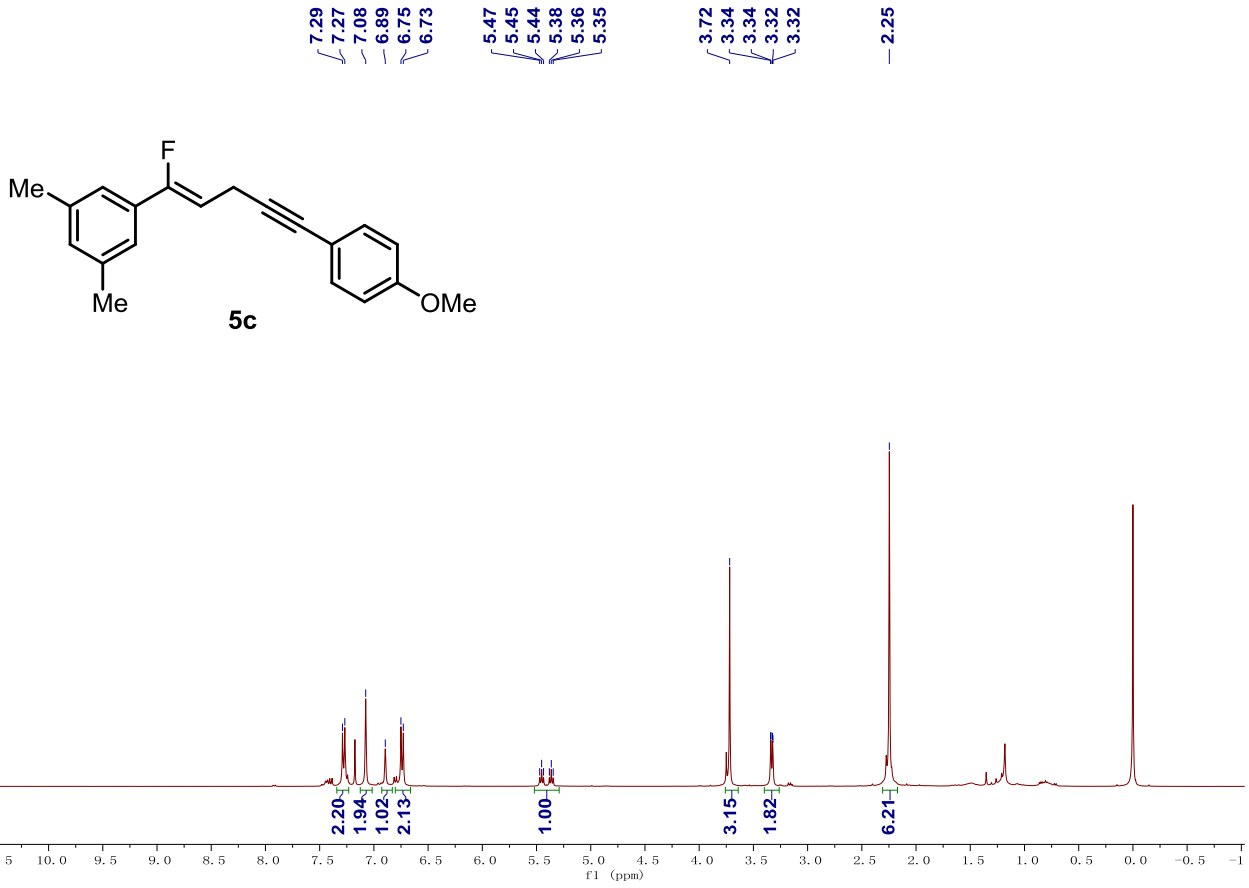

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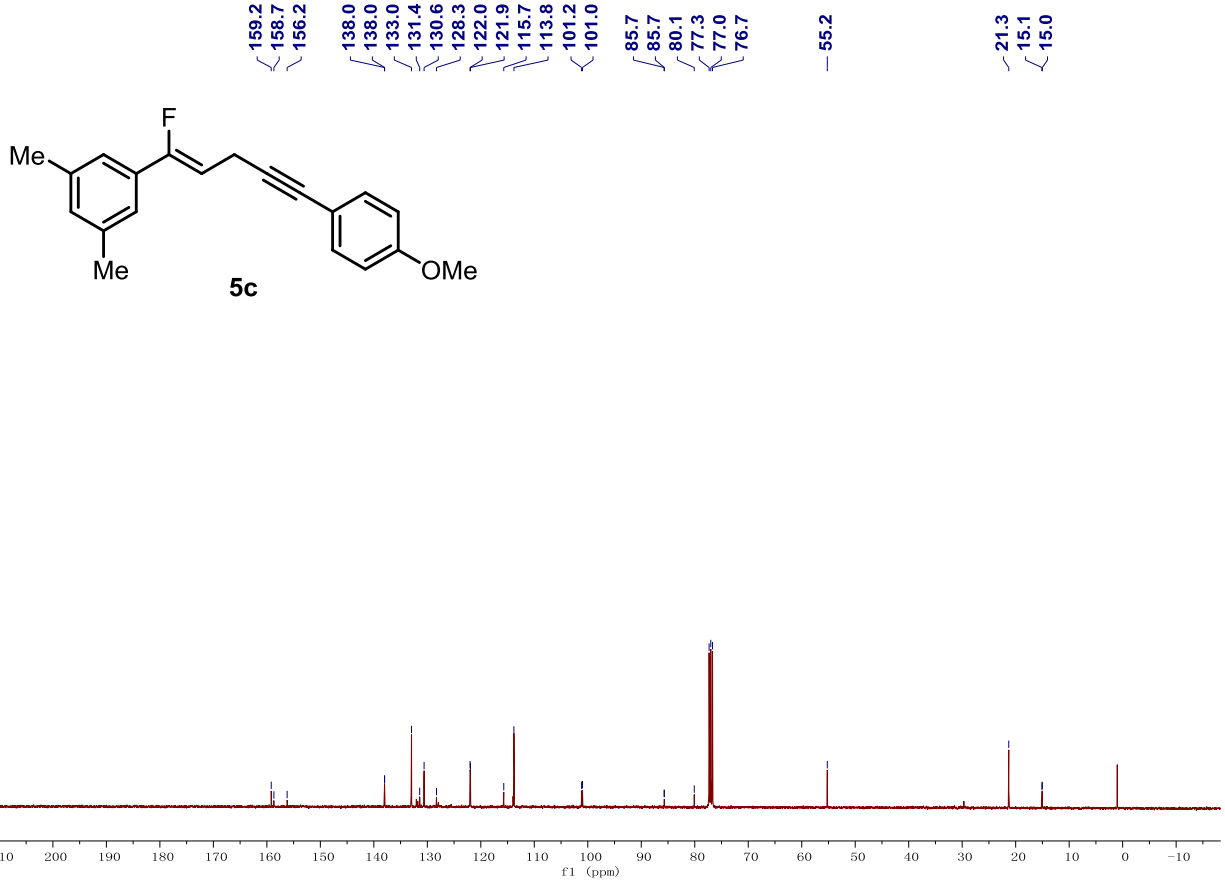

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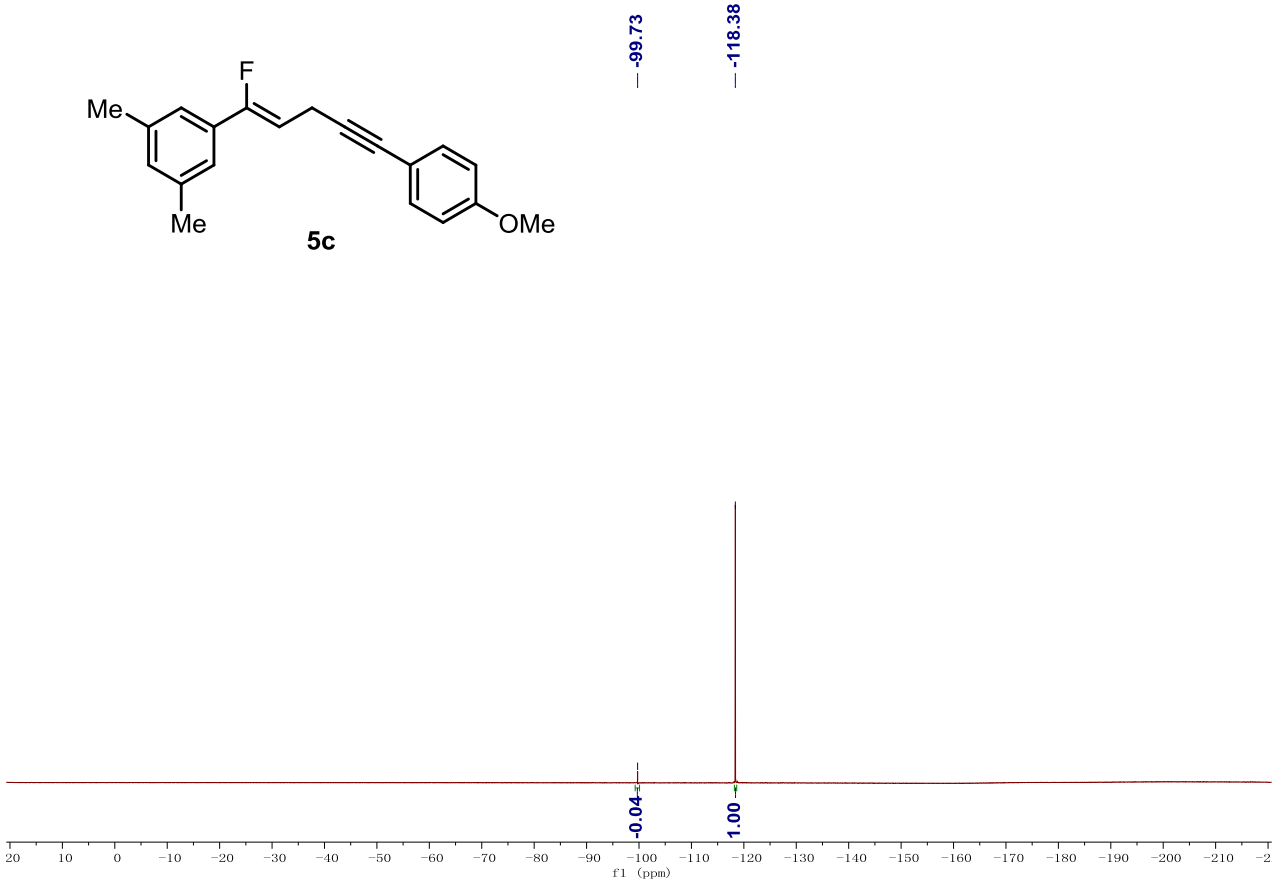

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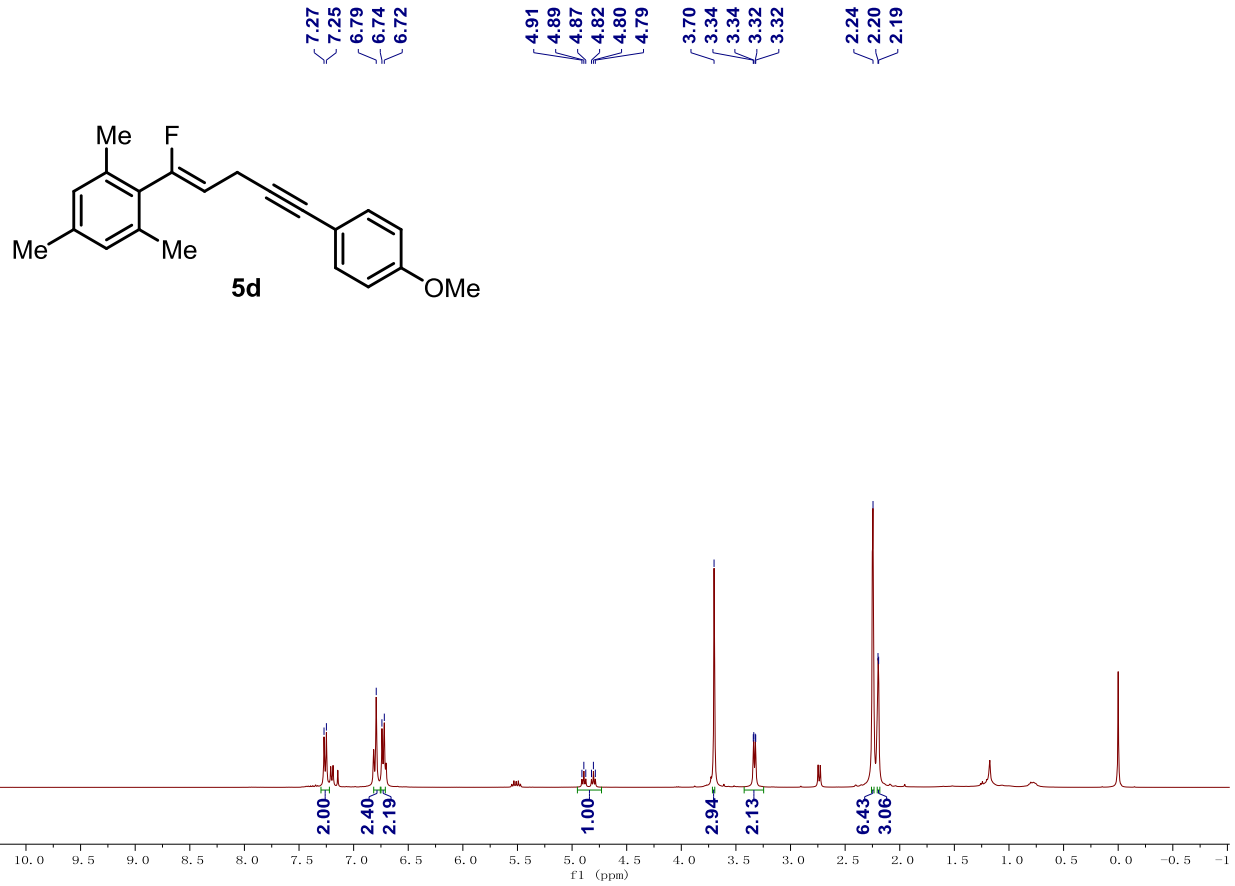

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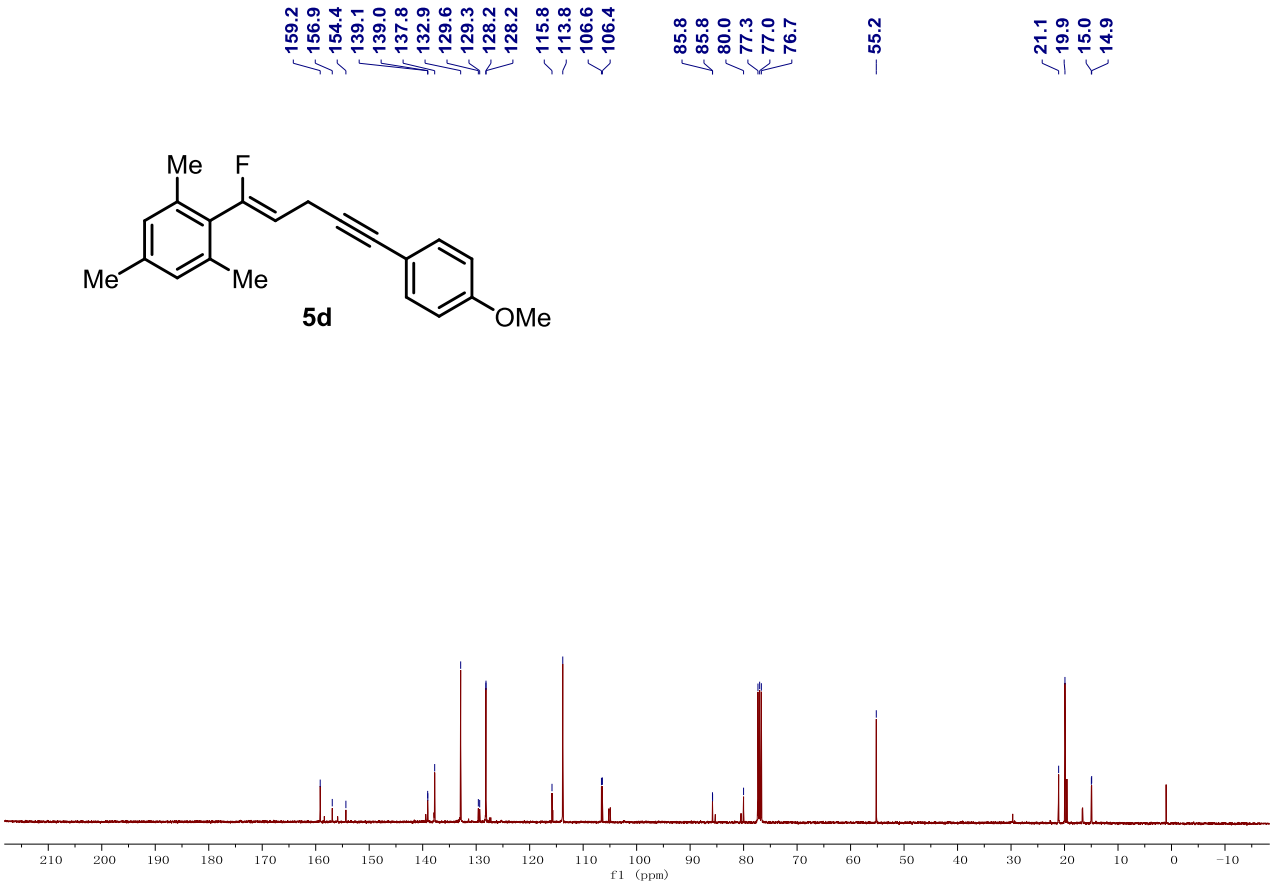

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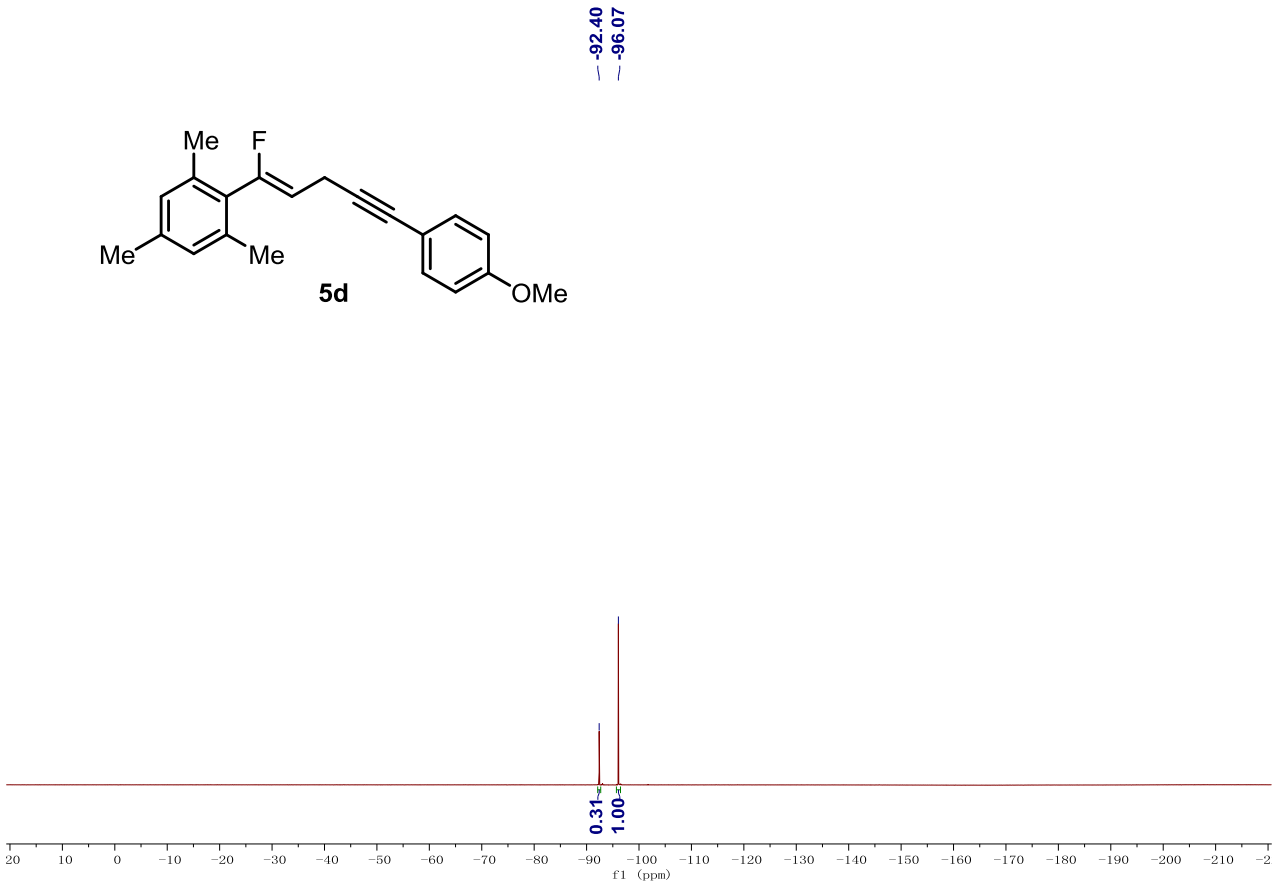

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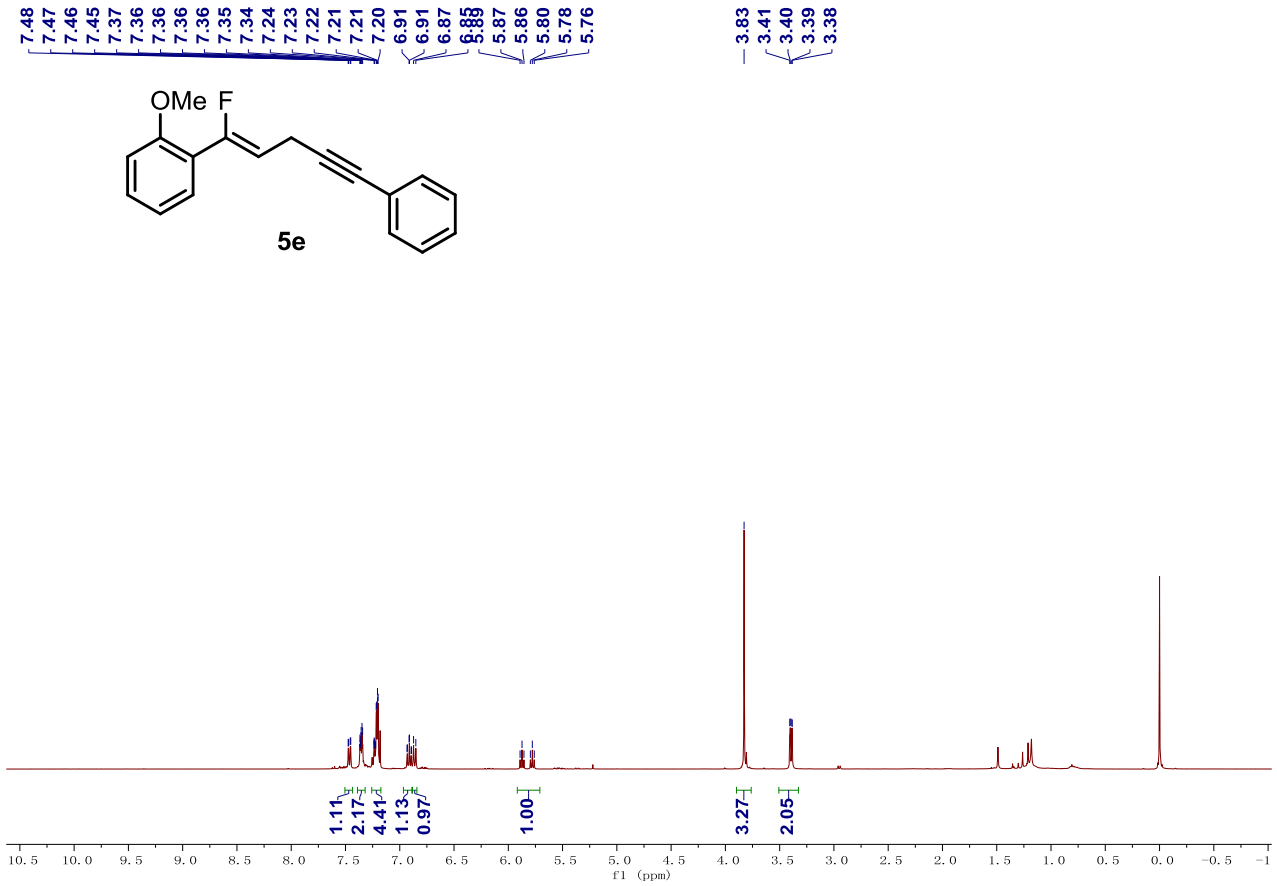

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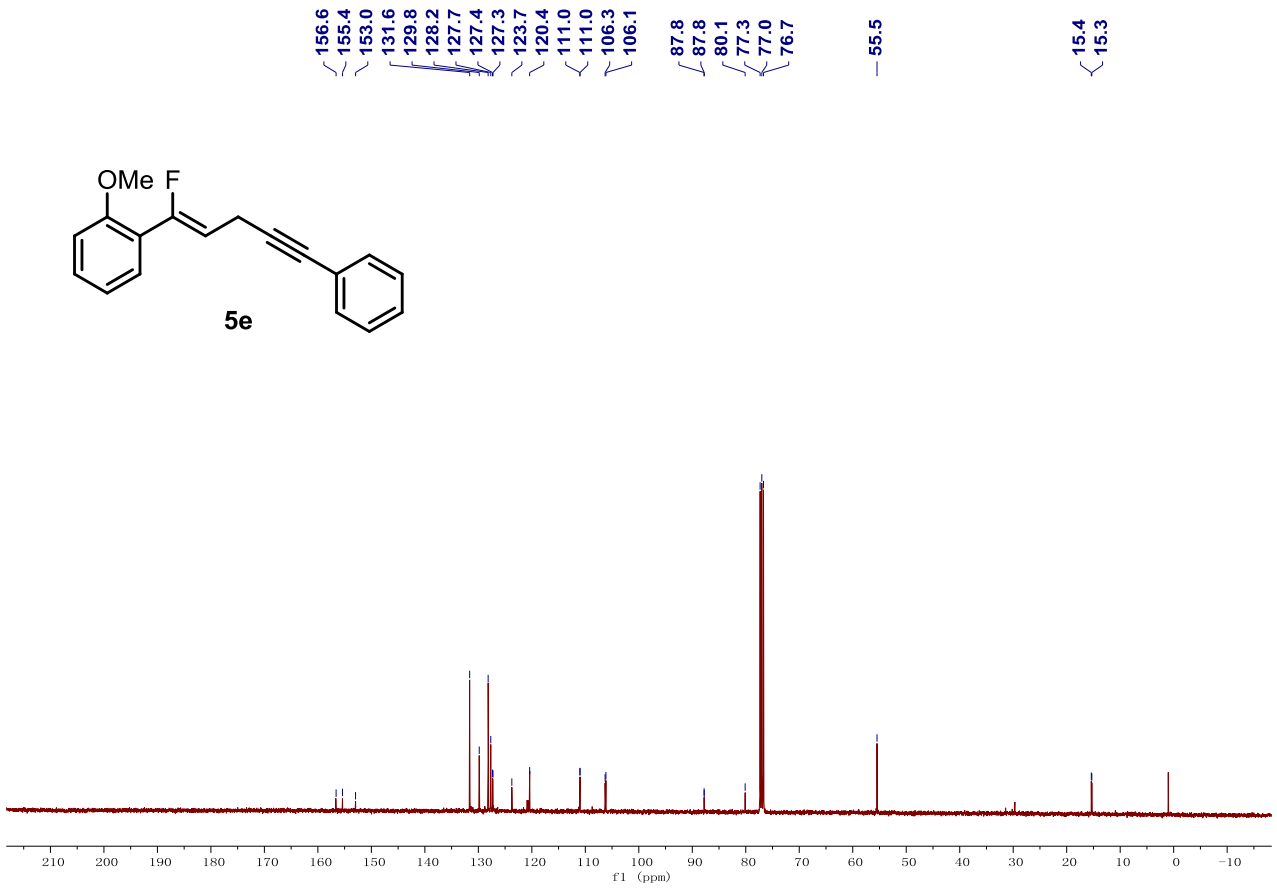

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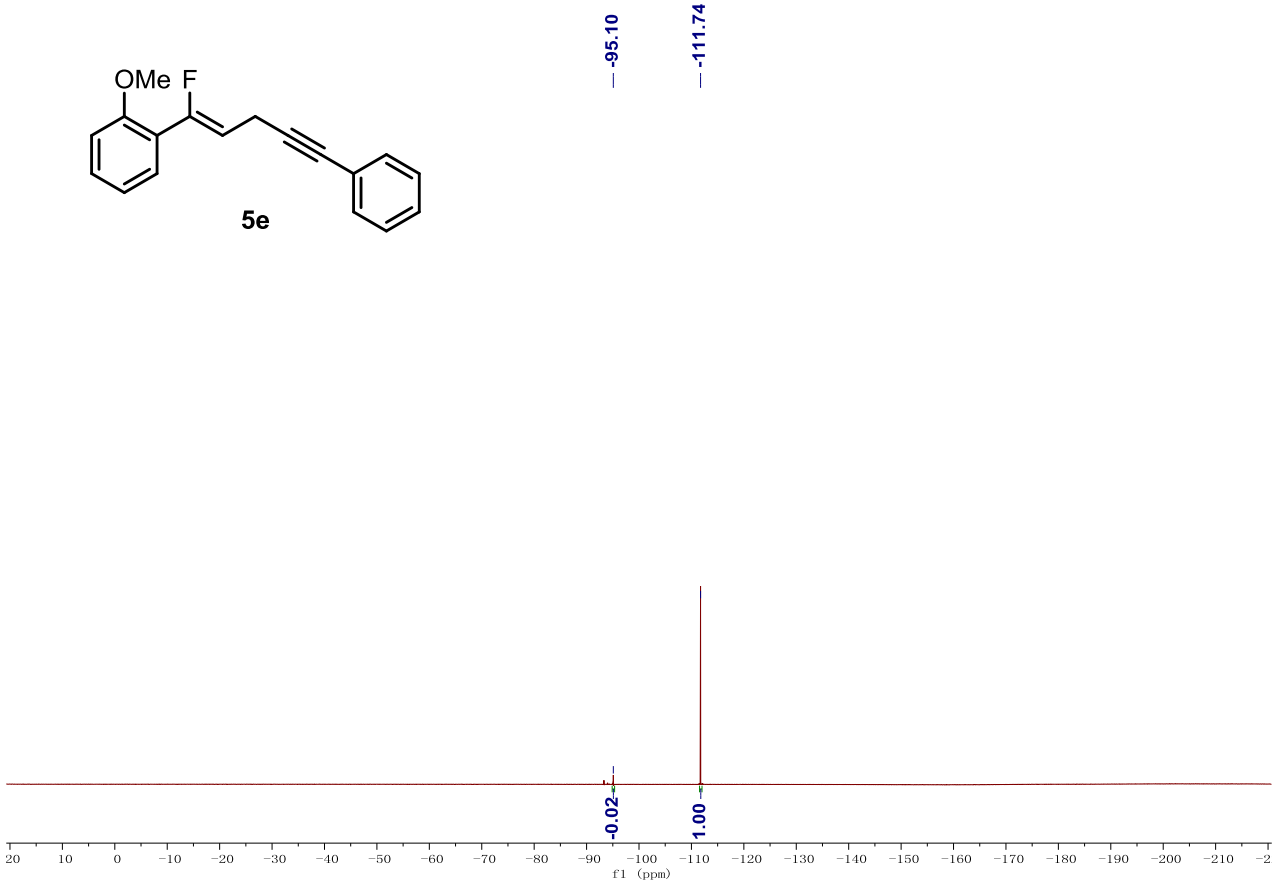

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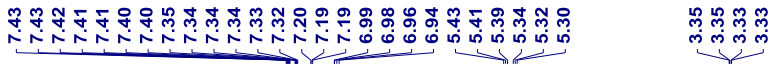

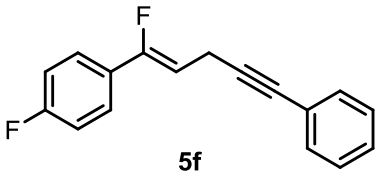

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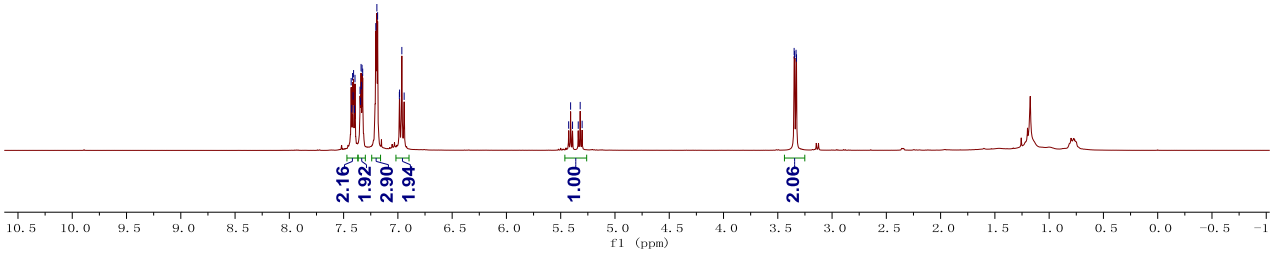

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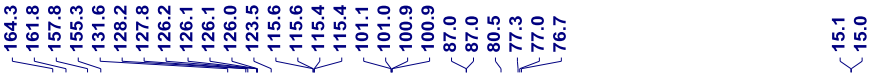

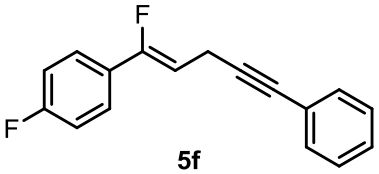

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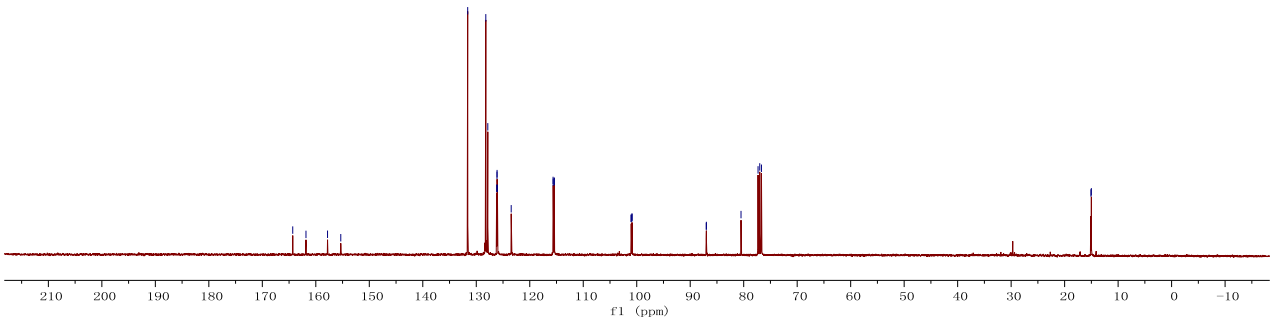
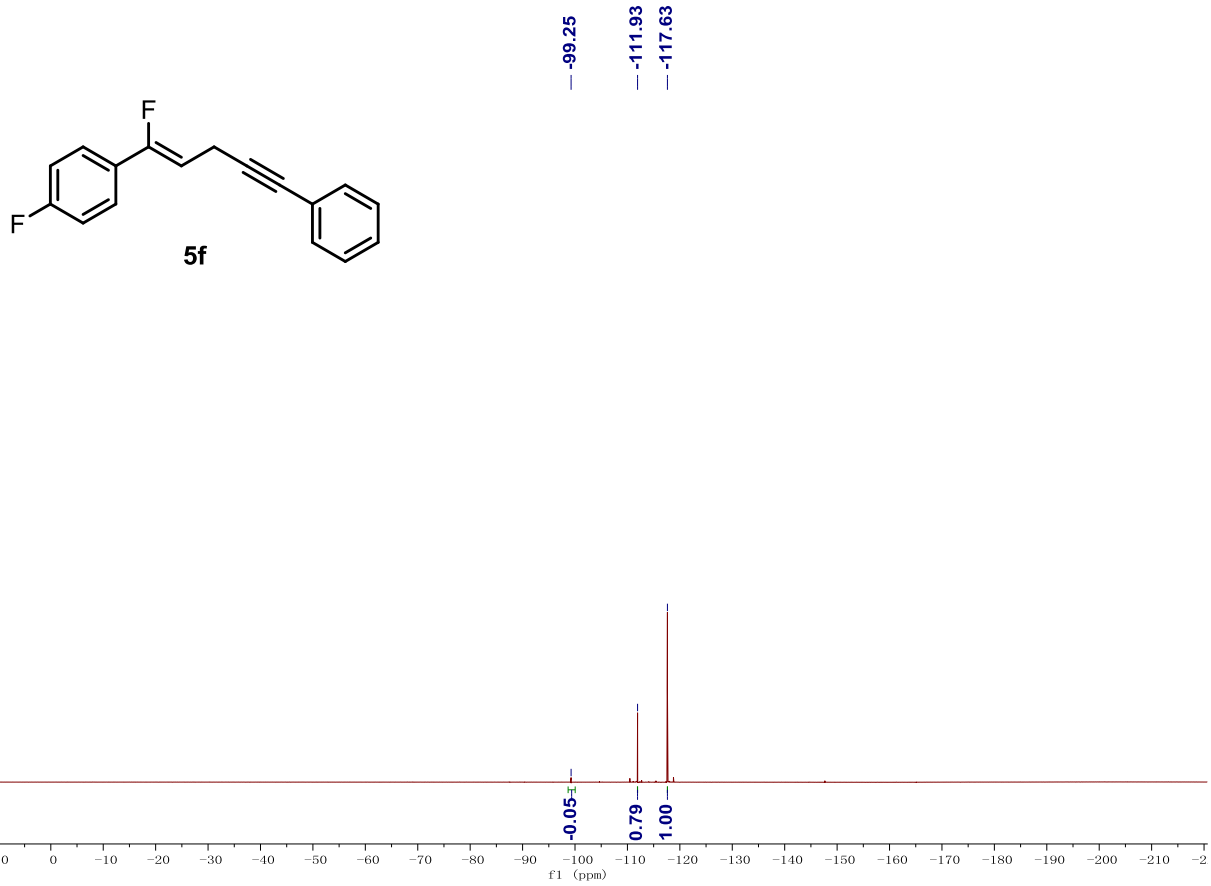


^{19}F NMR (376 MHz, $CDCl_3$)



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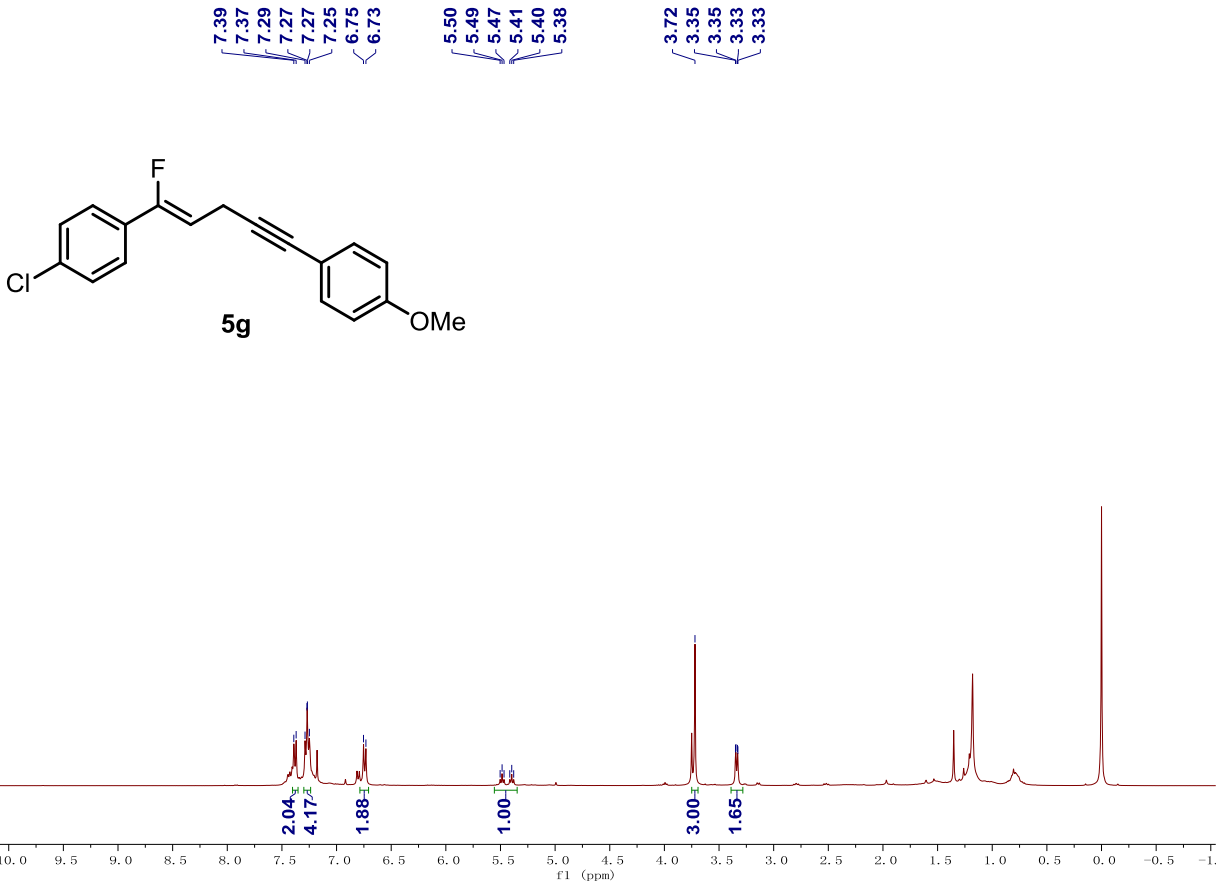
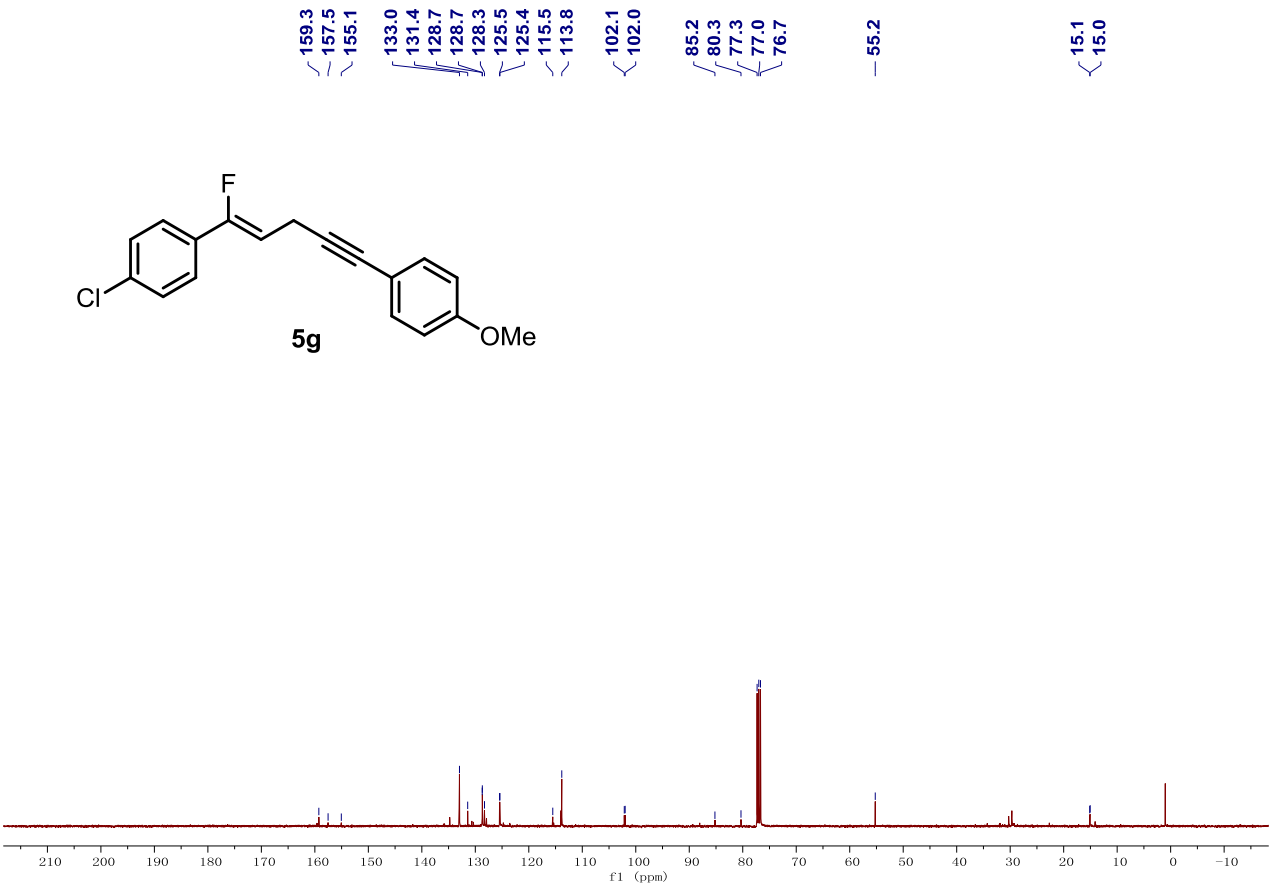
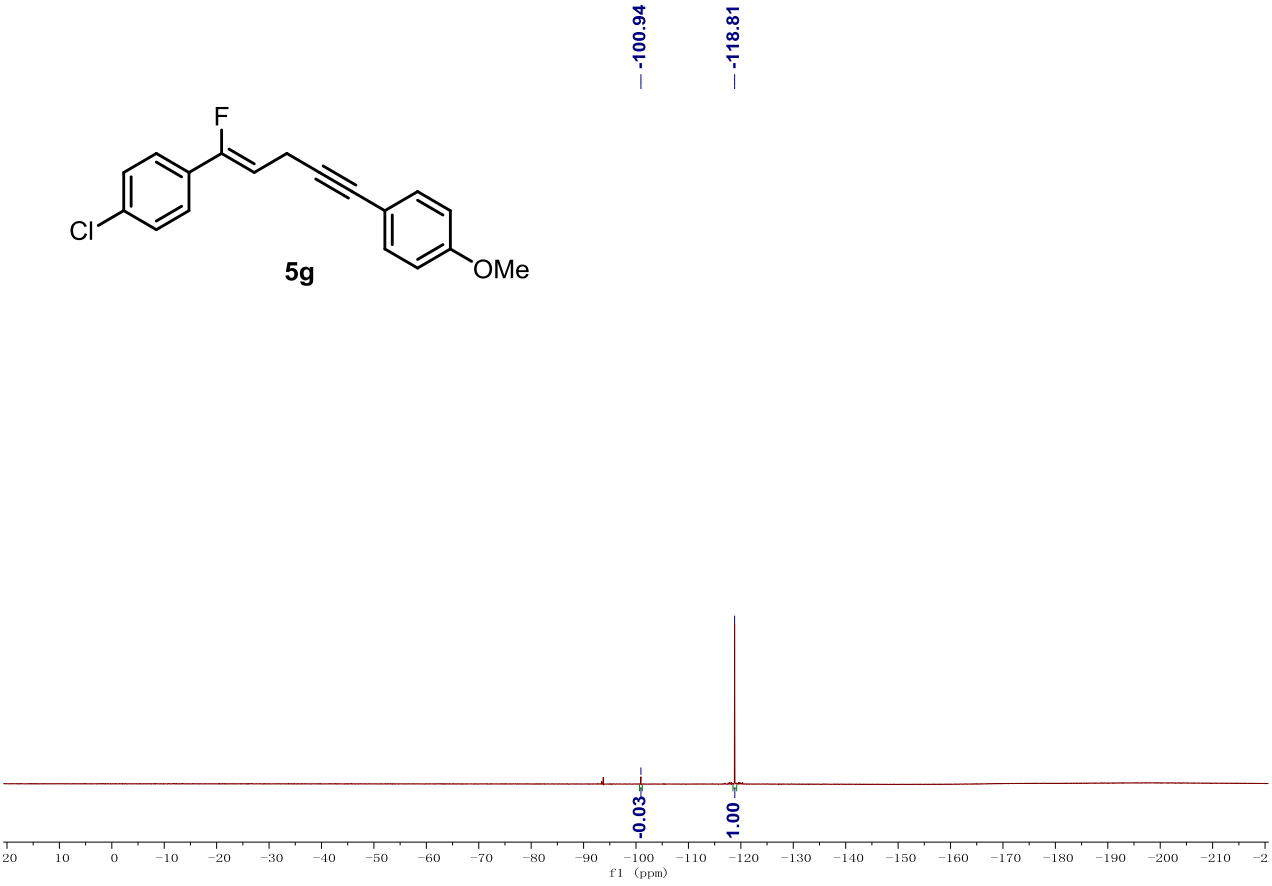


^{13}C NMR (101 MHz, $CDCl_3$)



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



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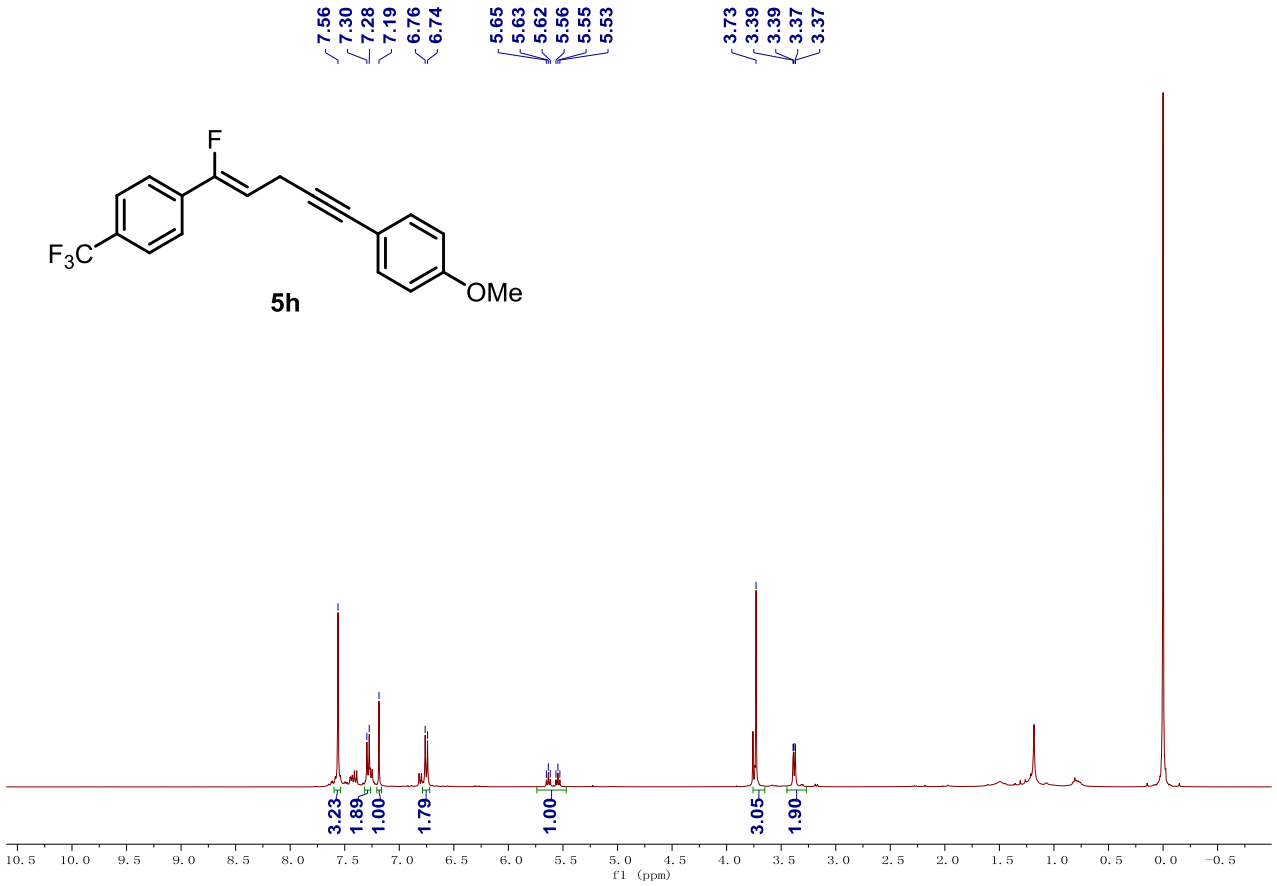

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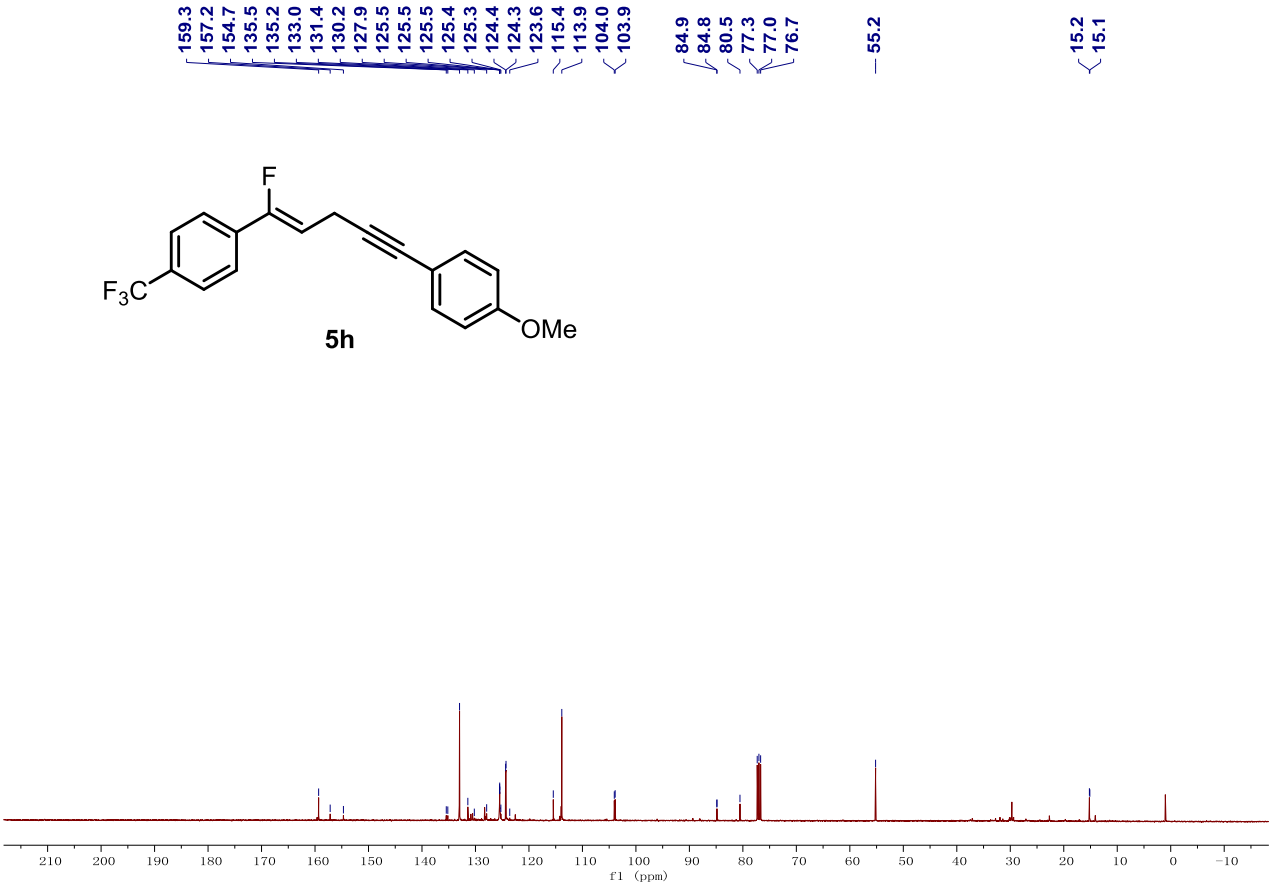

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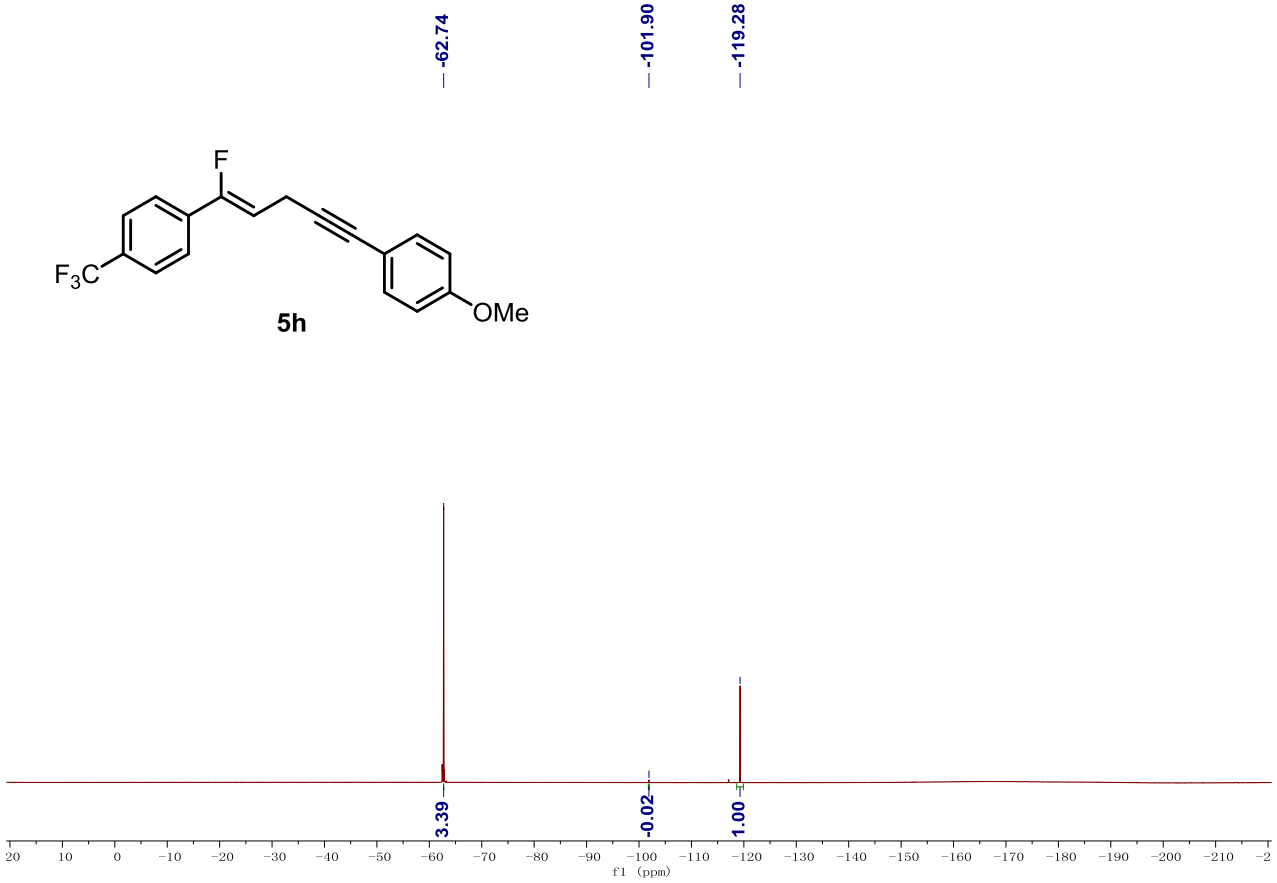

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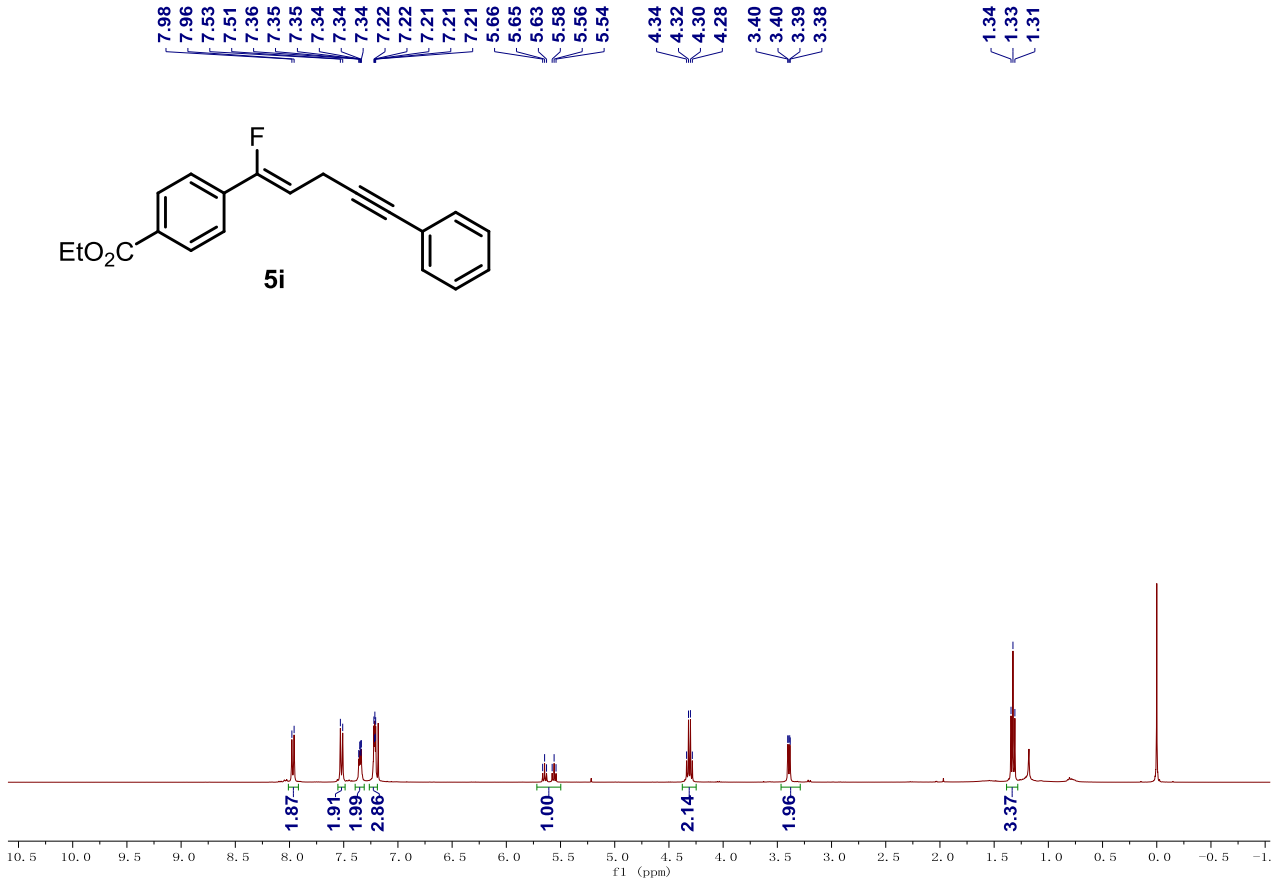

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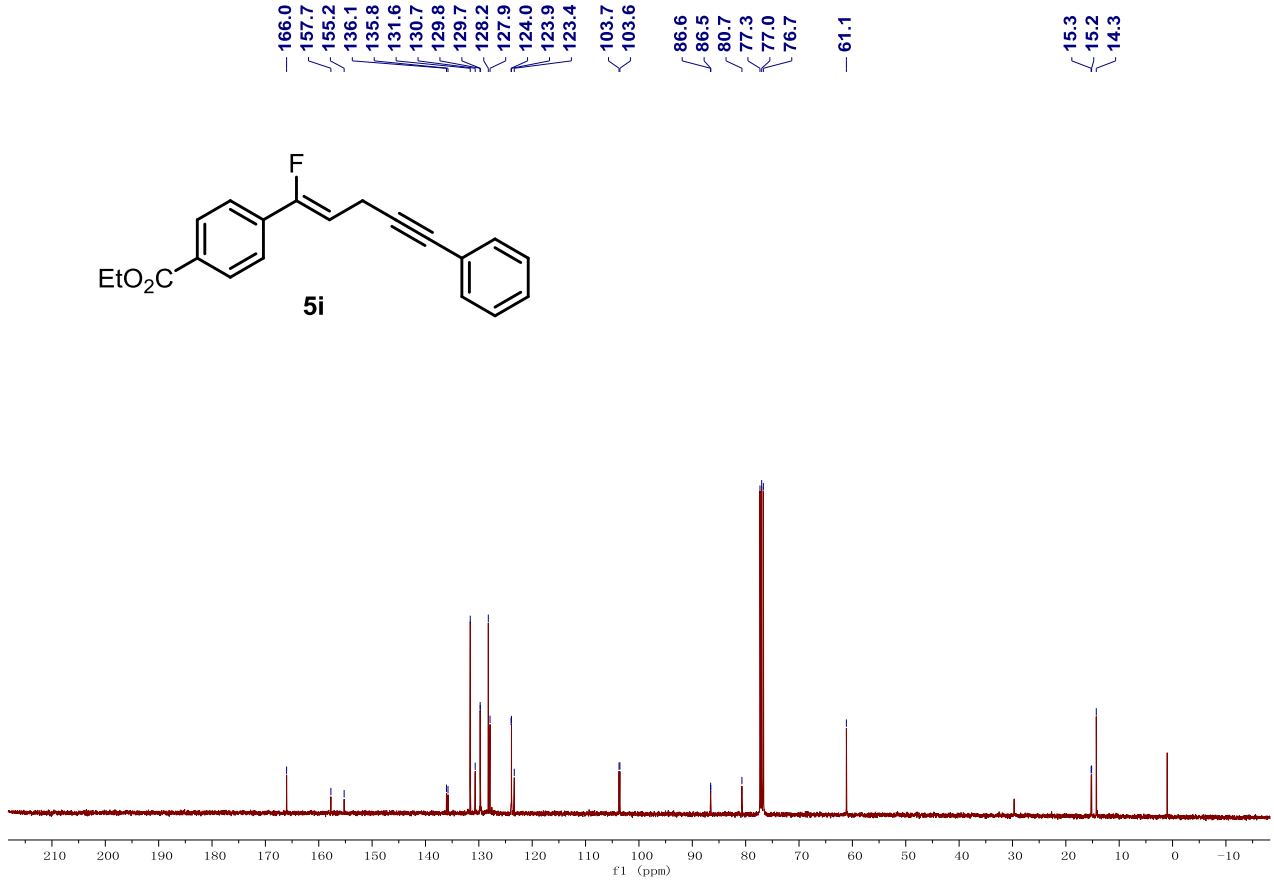

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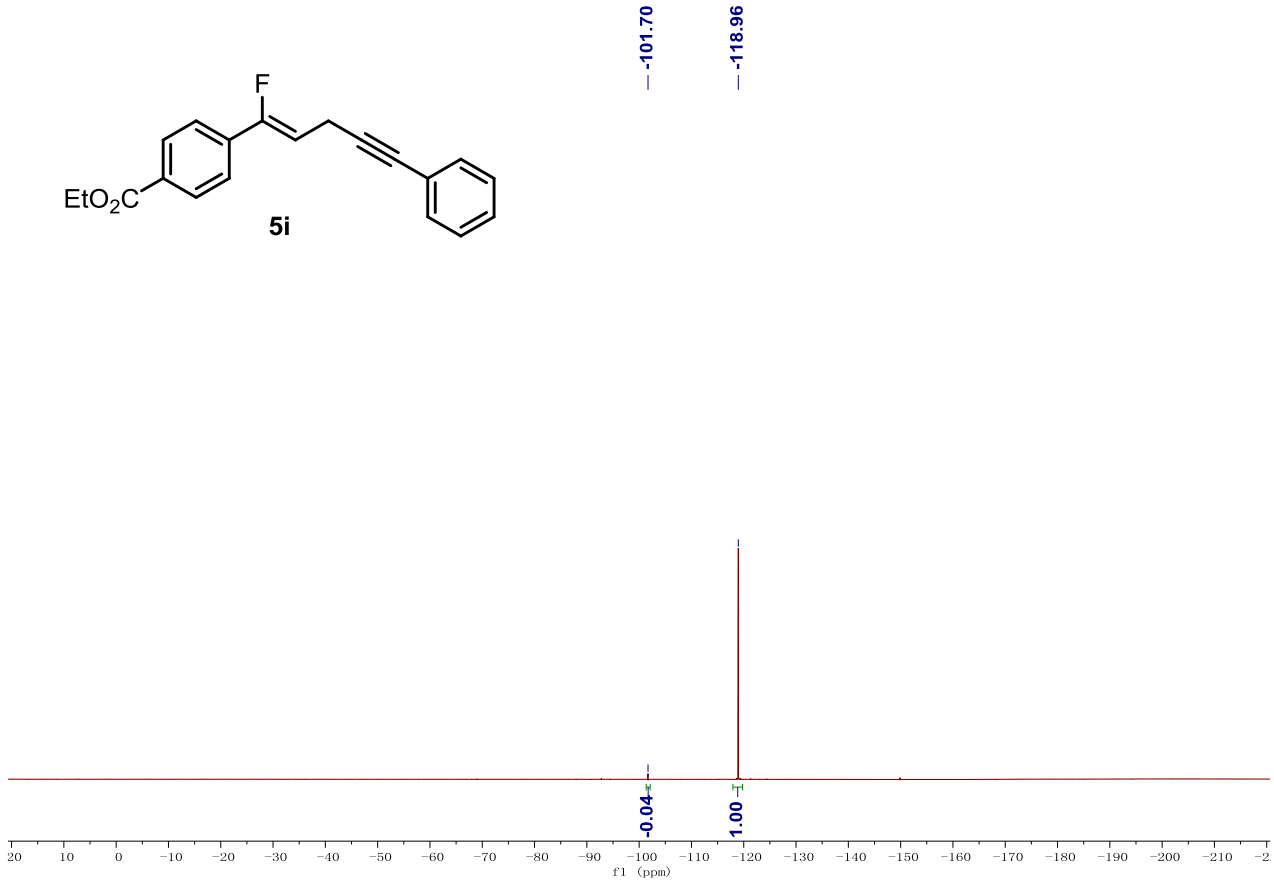

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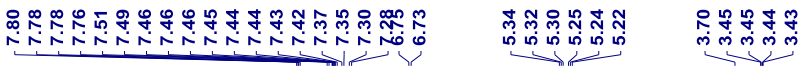

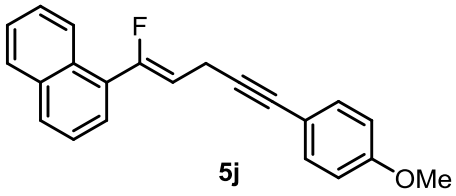

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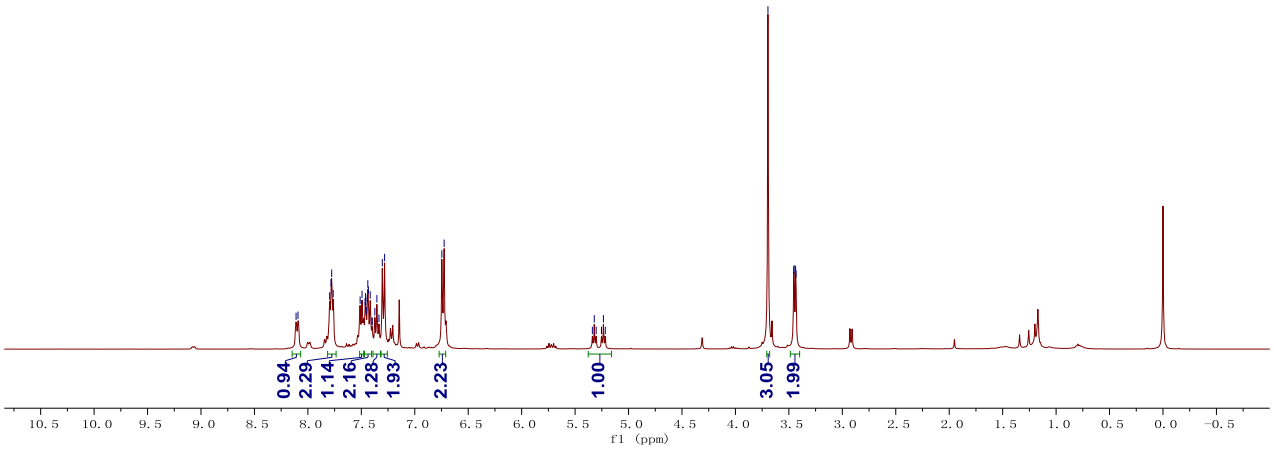
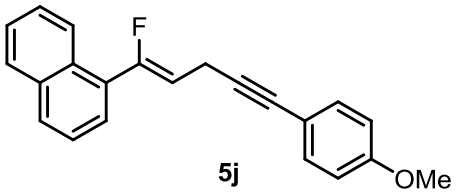


^{13}C NMR (101 MHz, $CDCl_3$)



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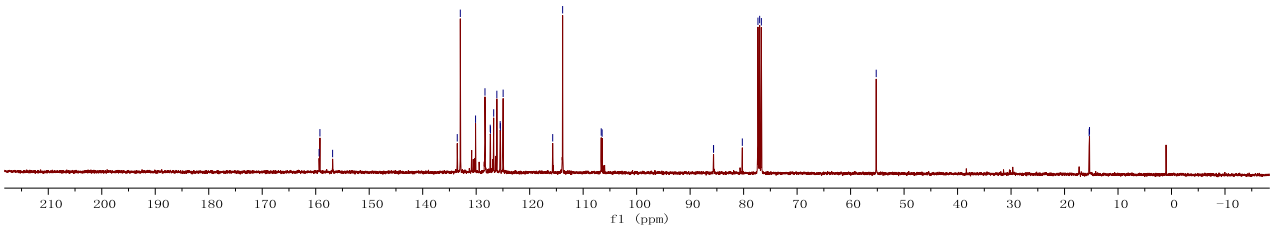
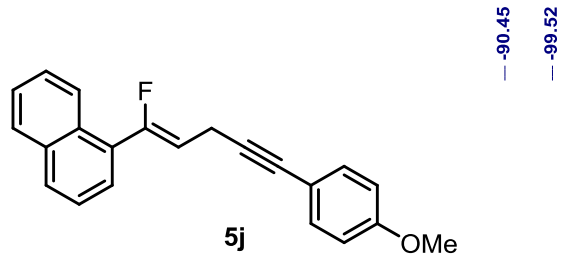


^{19}F NMR (376 MHz, $CDCl_3$)



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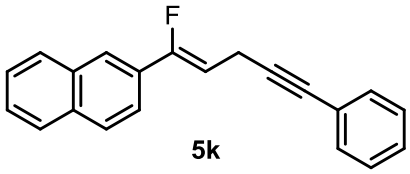

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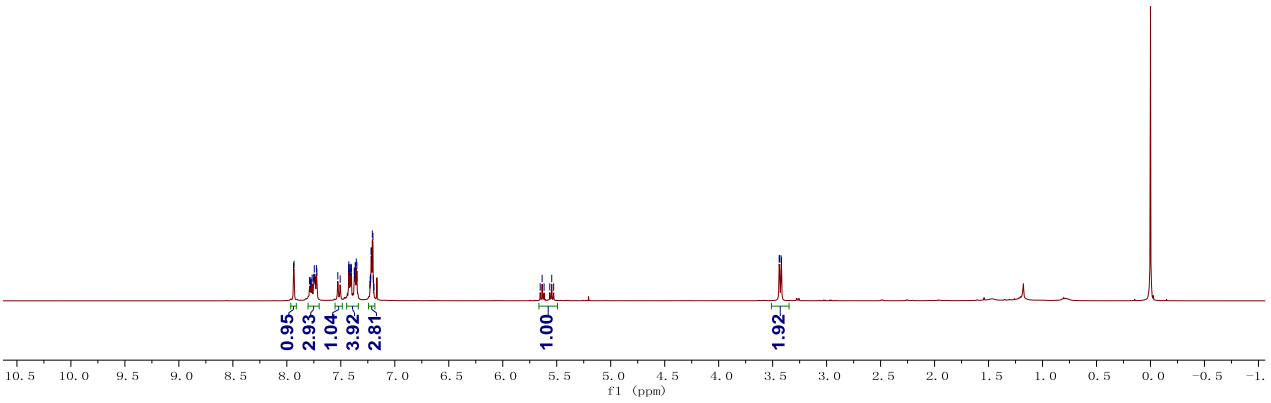
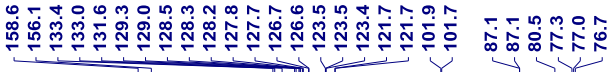
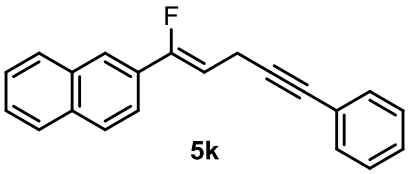
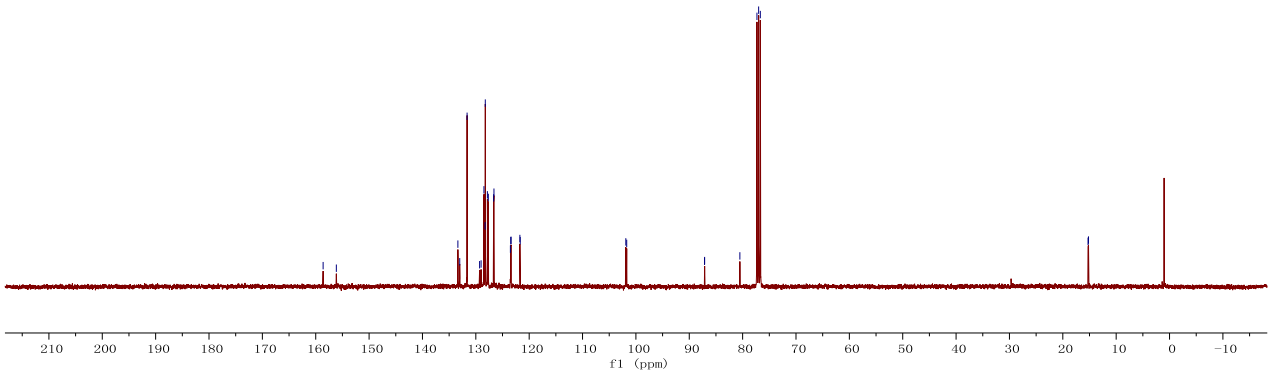


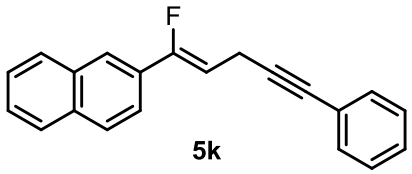
^{13}C NMR (101 MHz, $CDCl_3$)

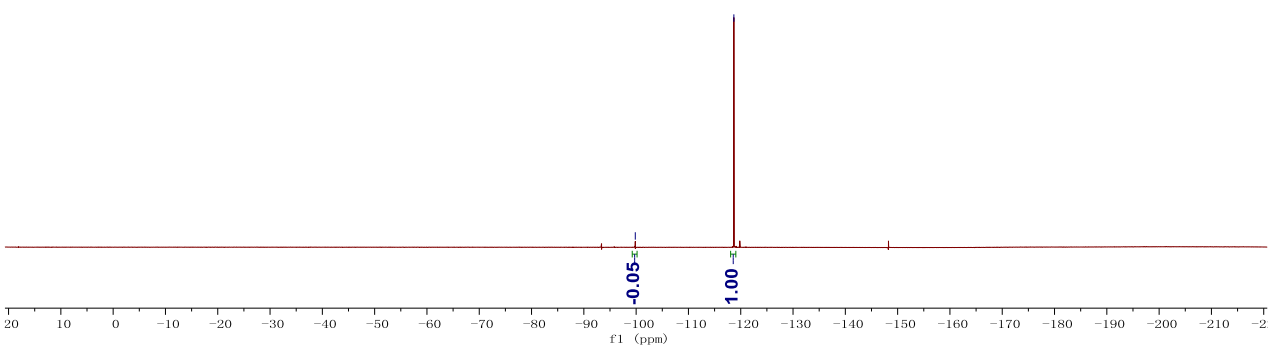




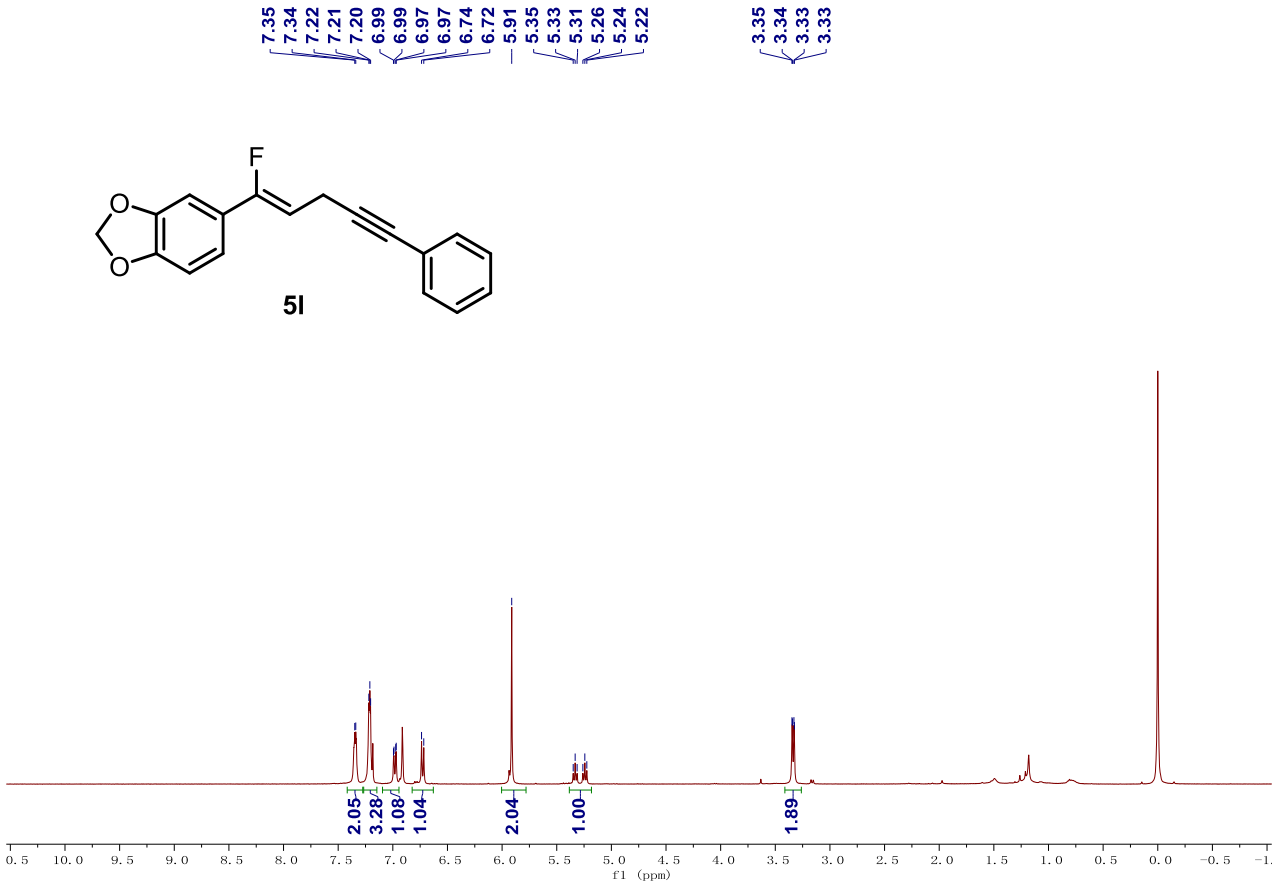


^{19}F NMR (376 MHz, $CDCl_3$)

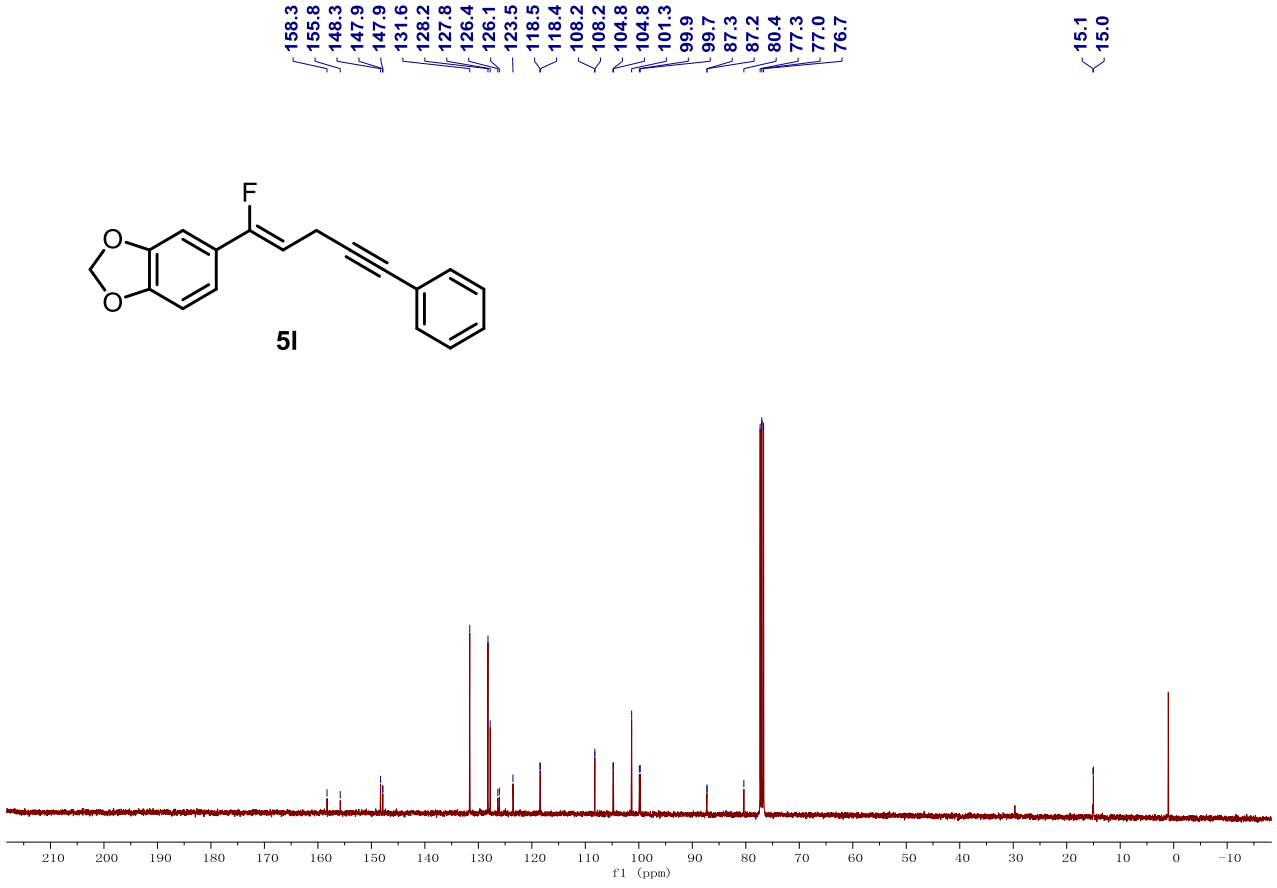




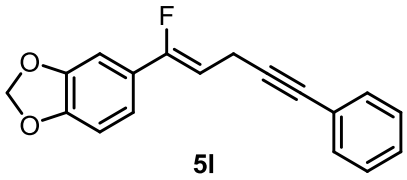
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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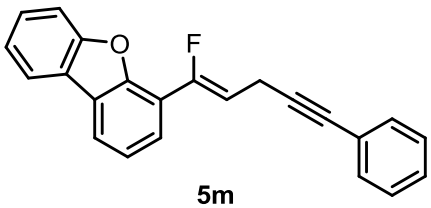

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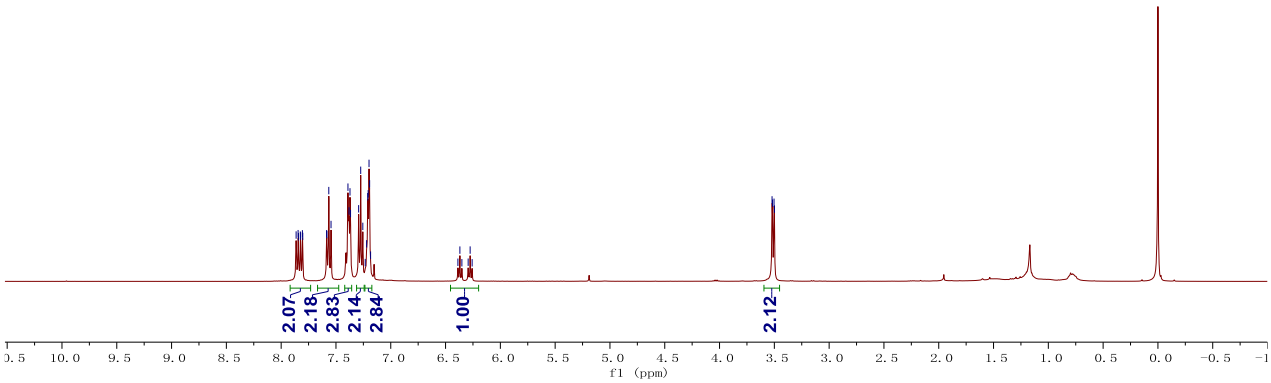
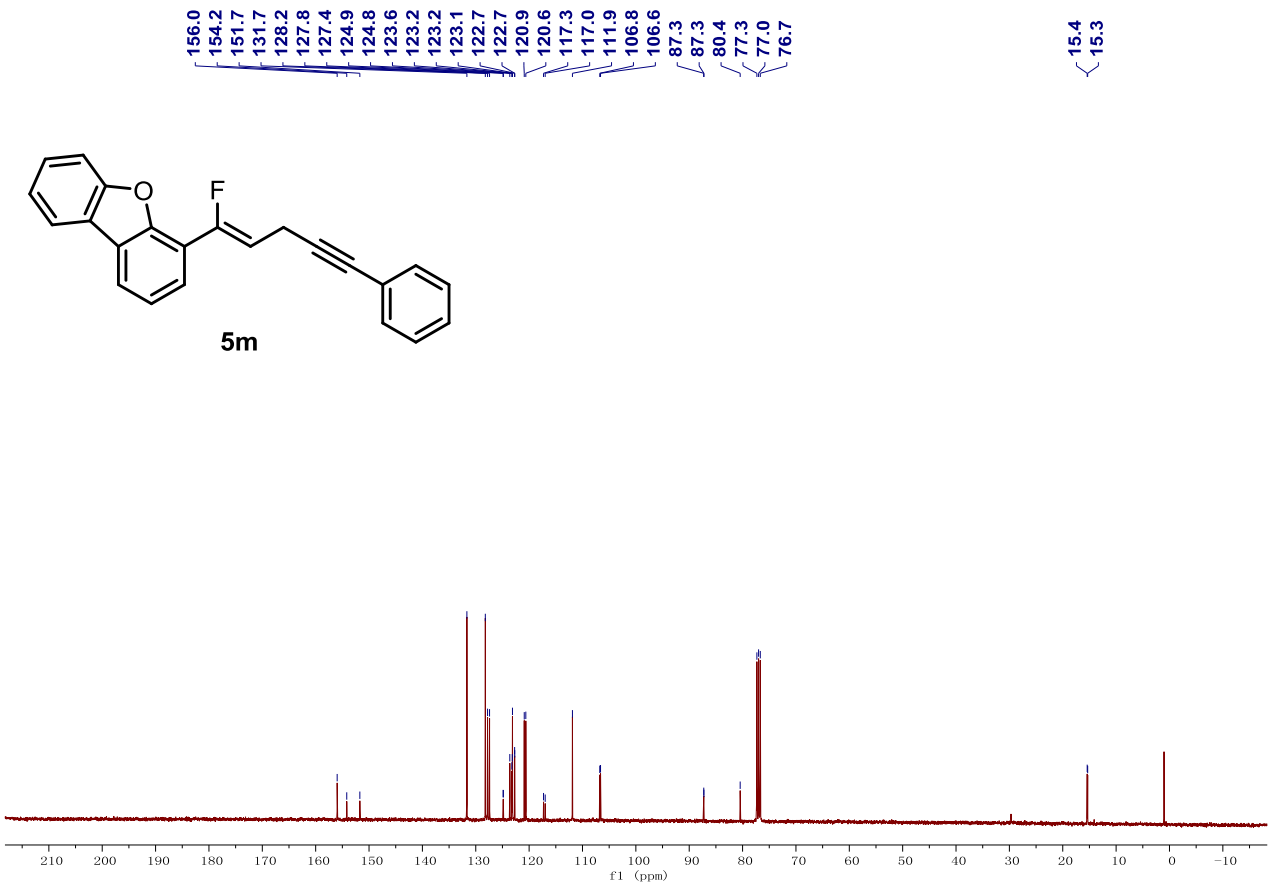


^{13}C NMR (101 MHz, $CDCl_3$)



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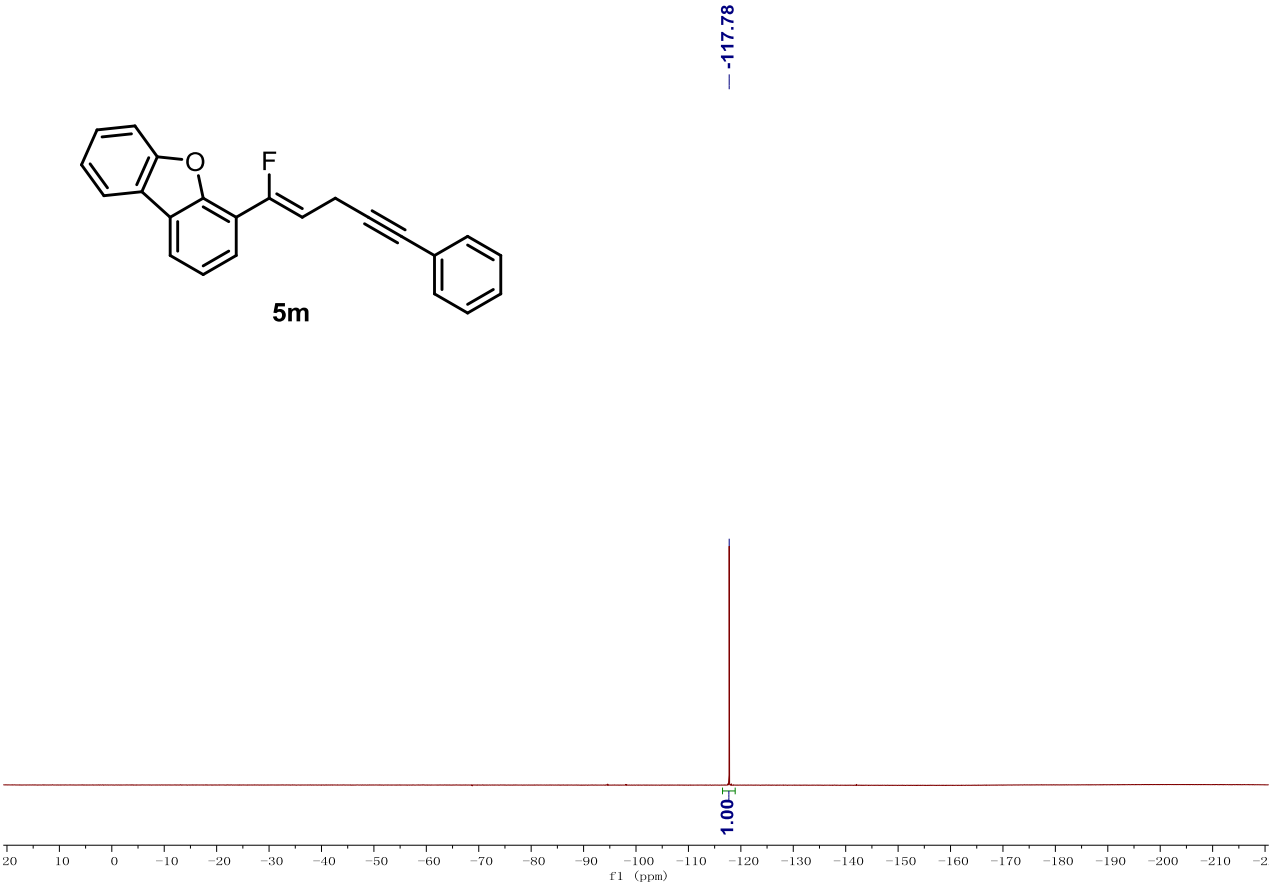

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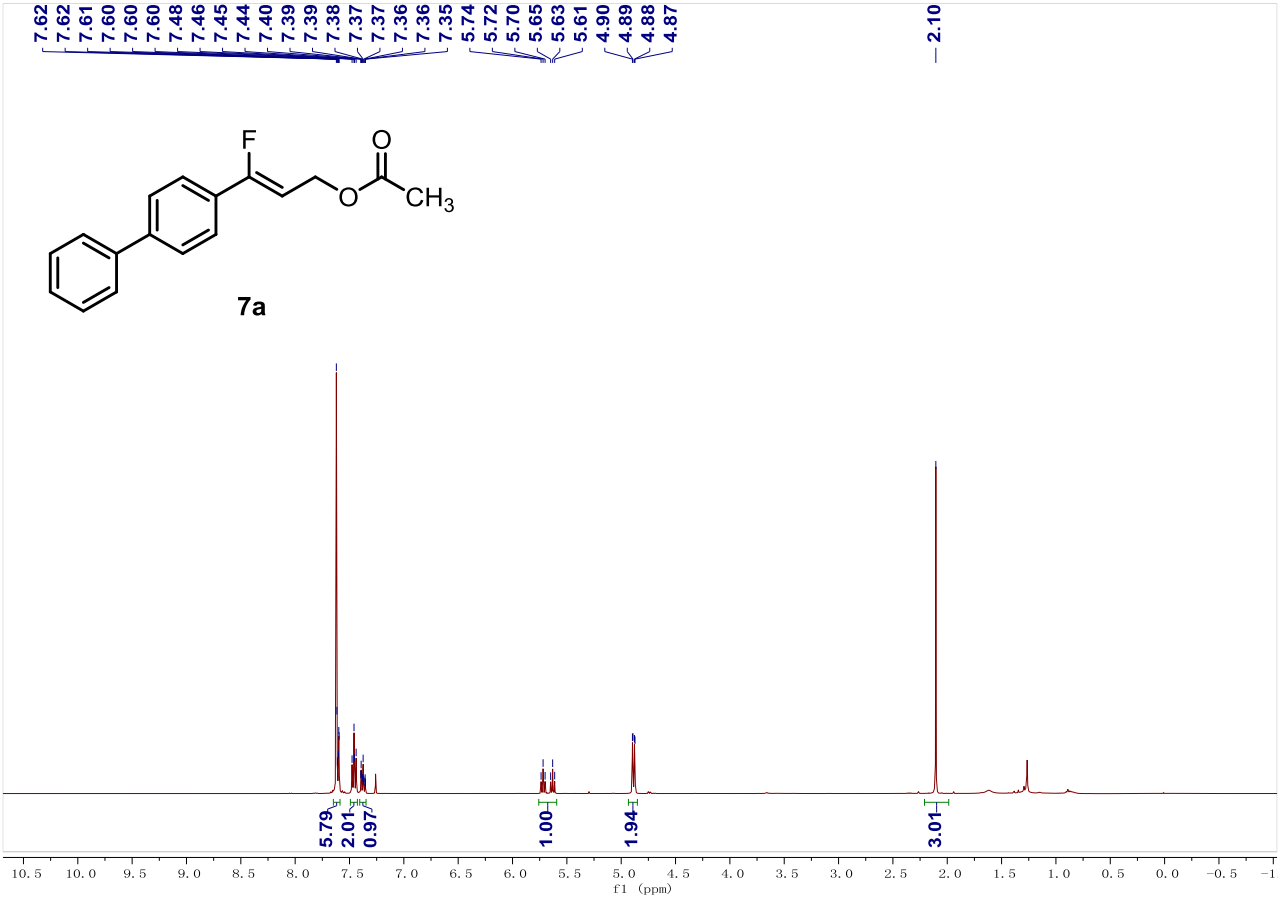
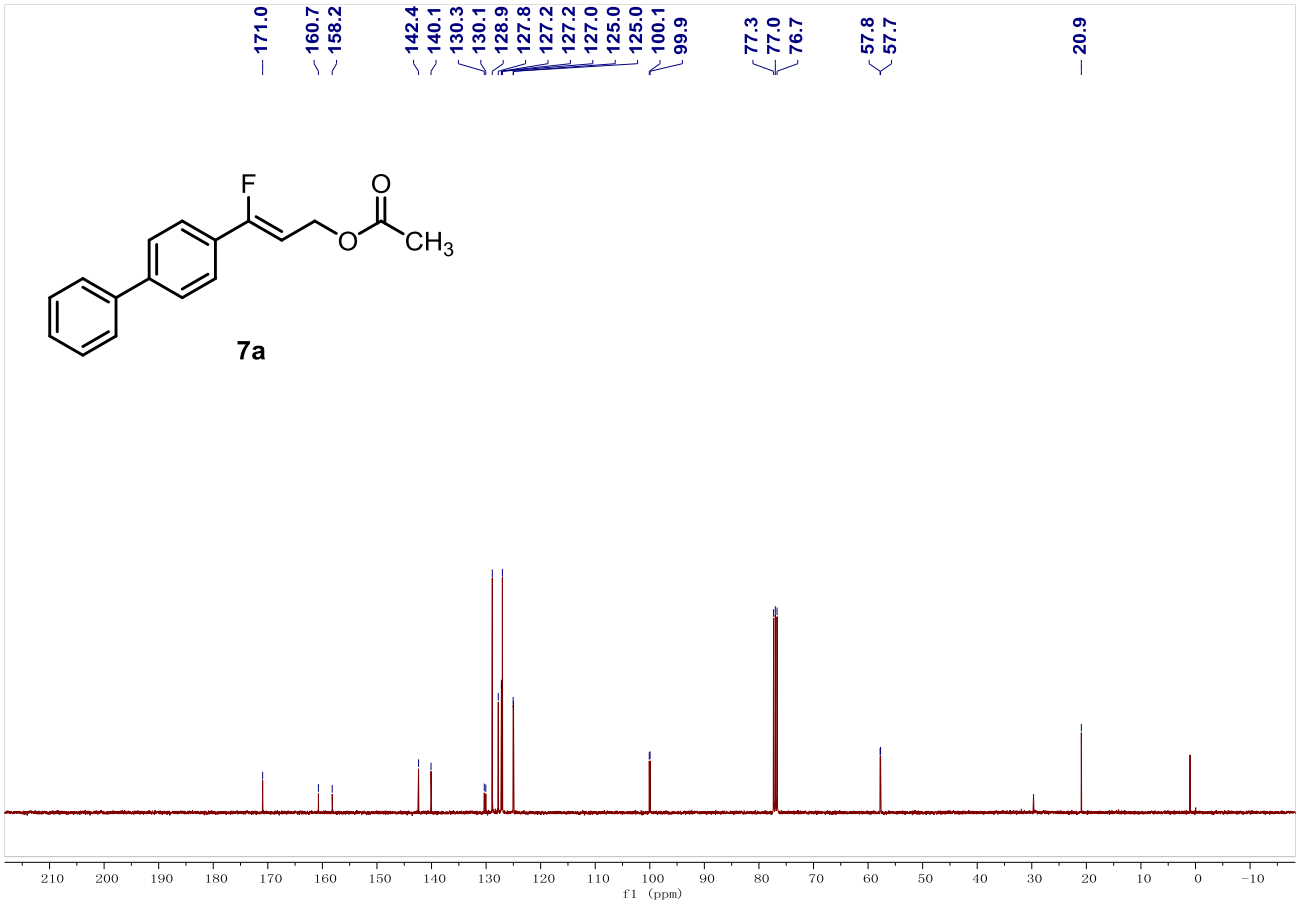
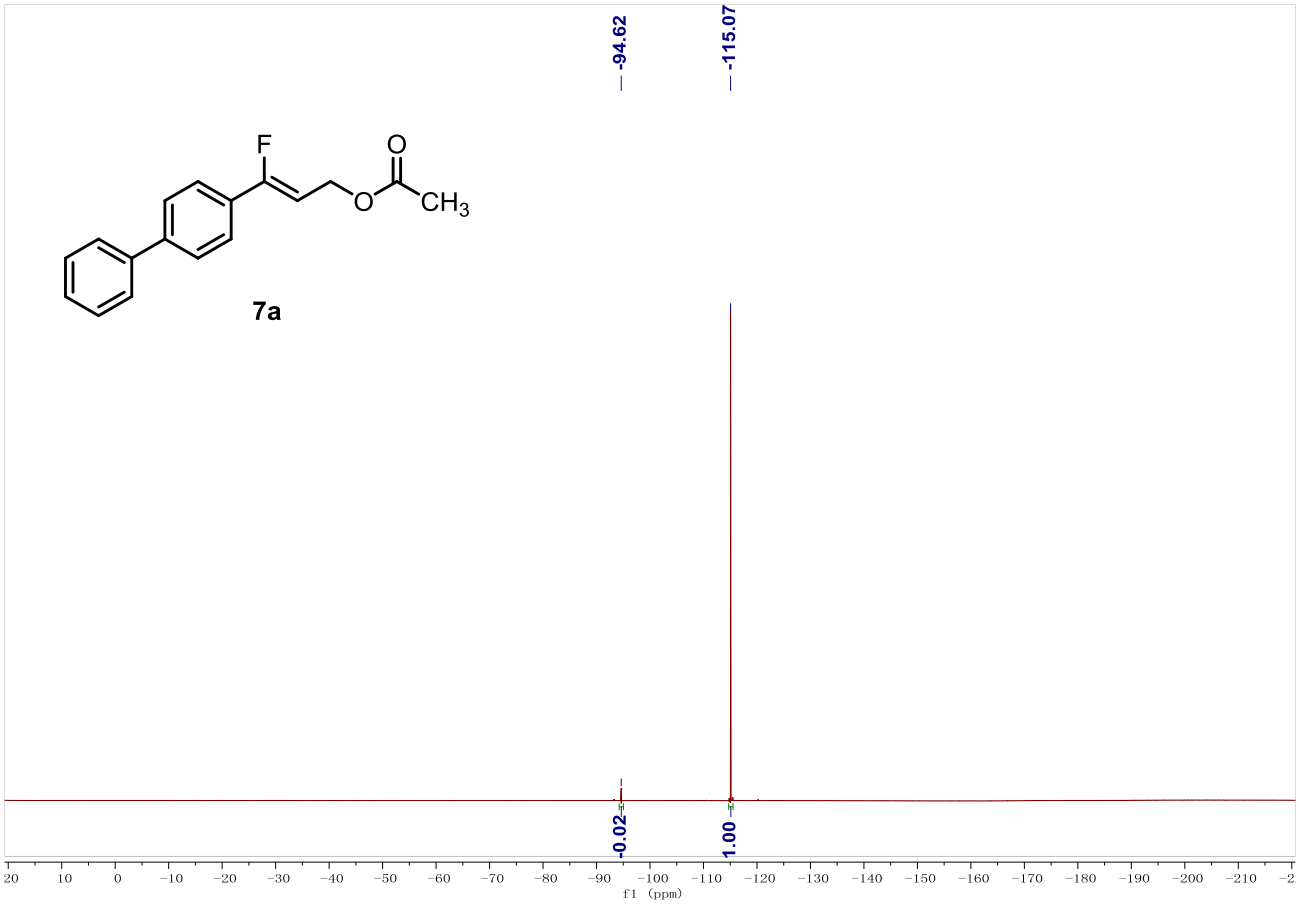


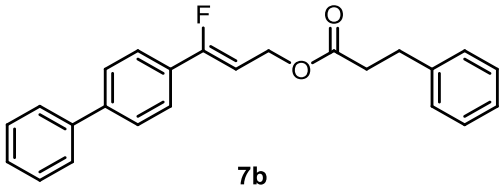
^{13}C NMR (101 MHz, $CDCl_3$)

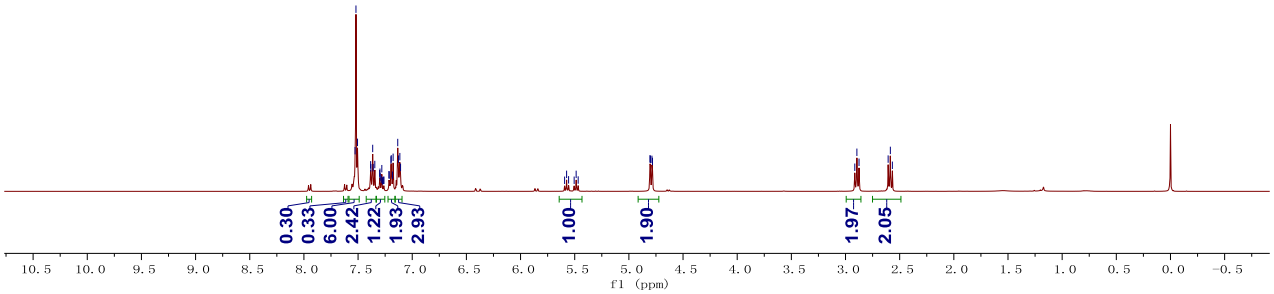


^{19}F NMR (376 MHz, $CDCl_3$)

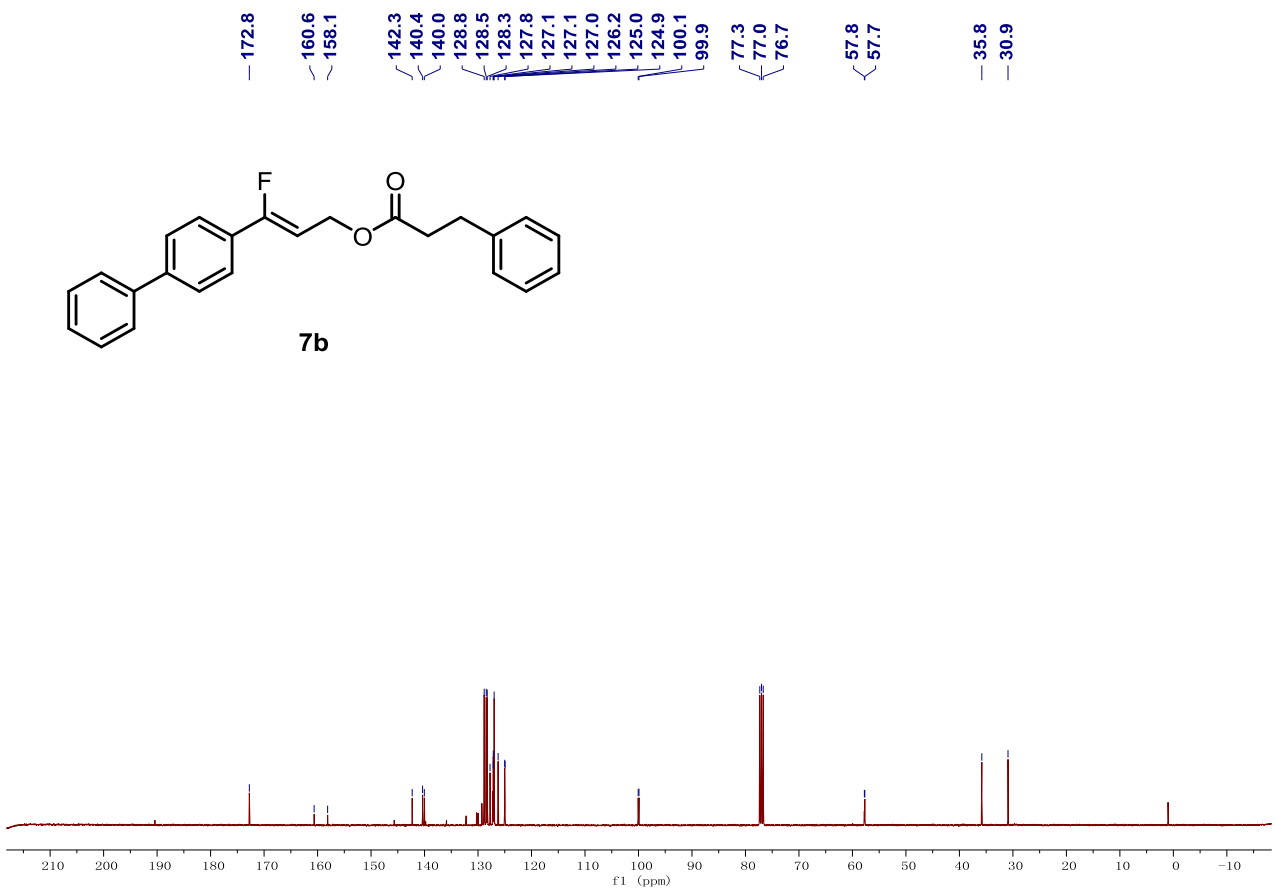


^{1}H NMR (400 MHz, $CDCl_3$)

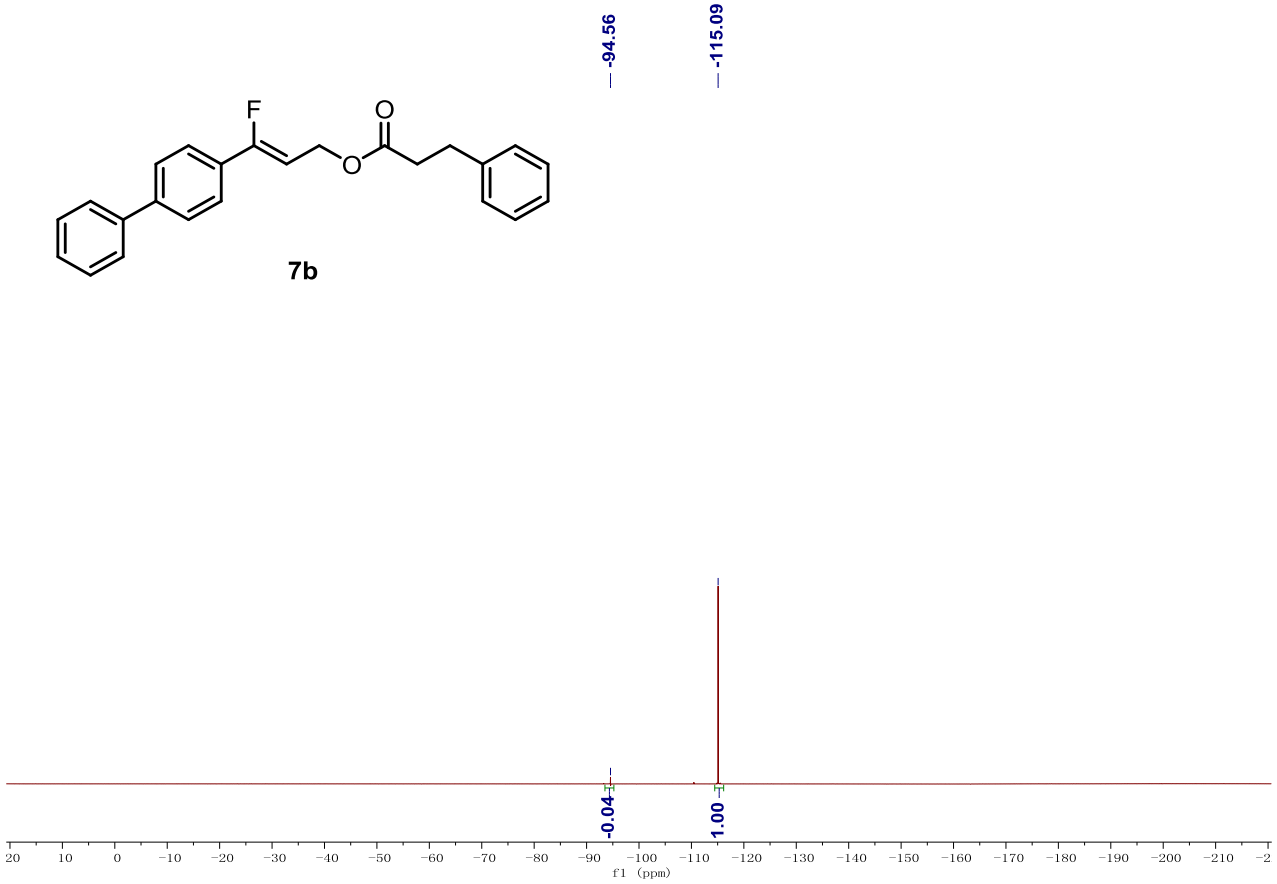




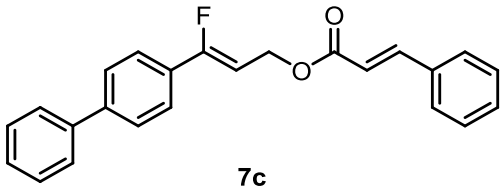
^{13}C NMR (101 MHz, $CDCl_3$)



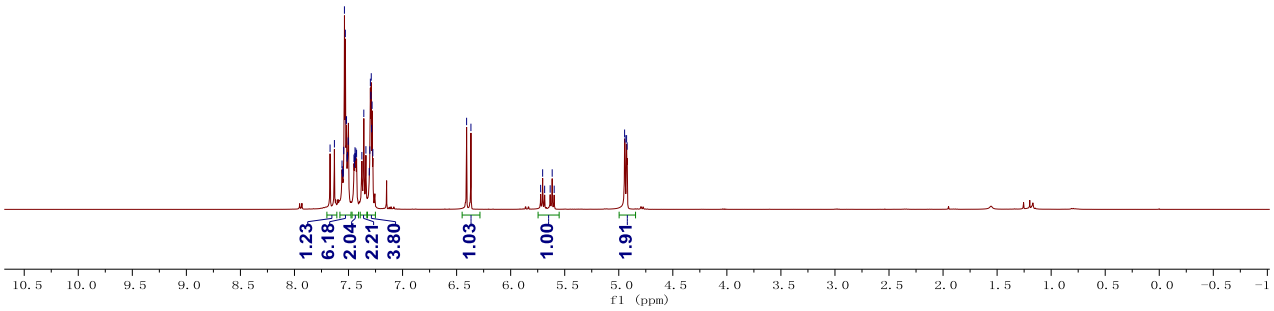
^{19}F NMR (376 MHz, $CDCl_3$)



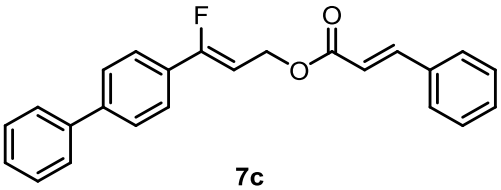
^{1}H NMR (400 MHz, $CDCl_3$)



7c



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



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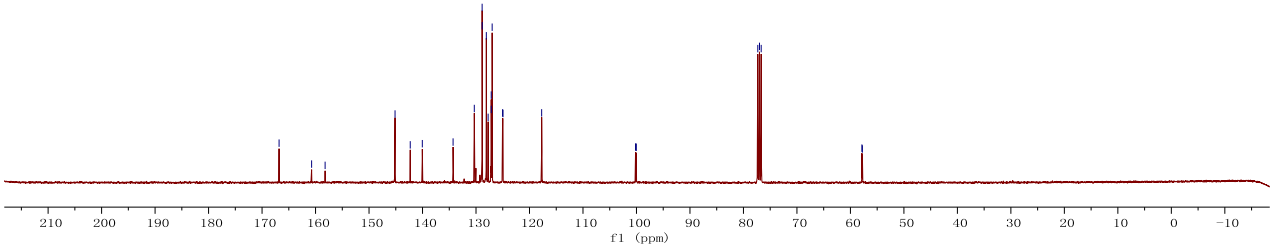
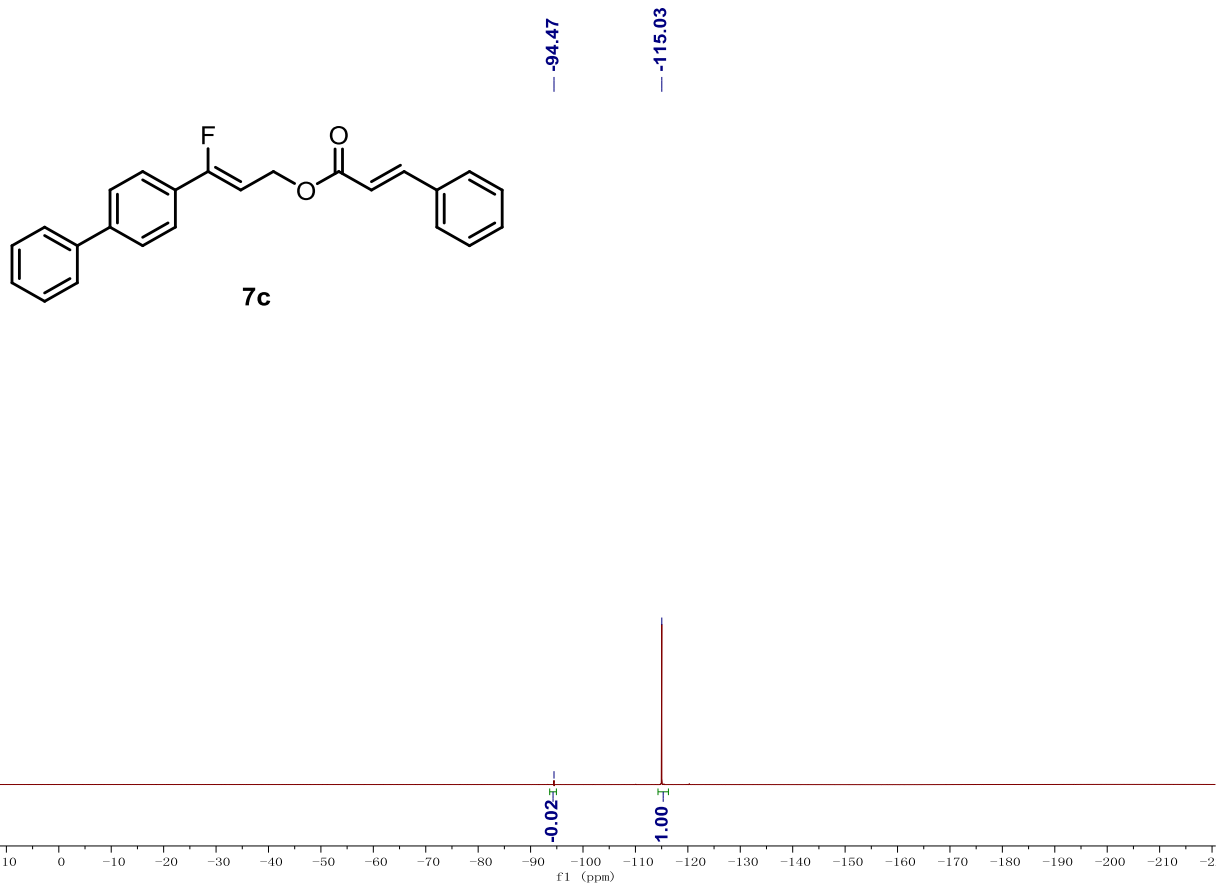
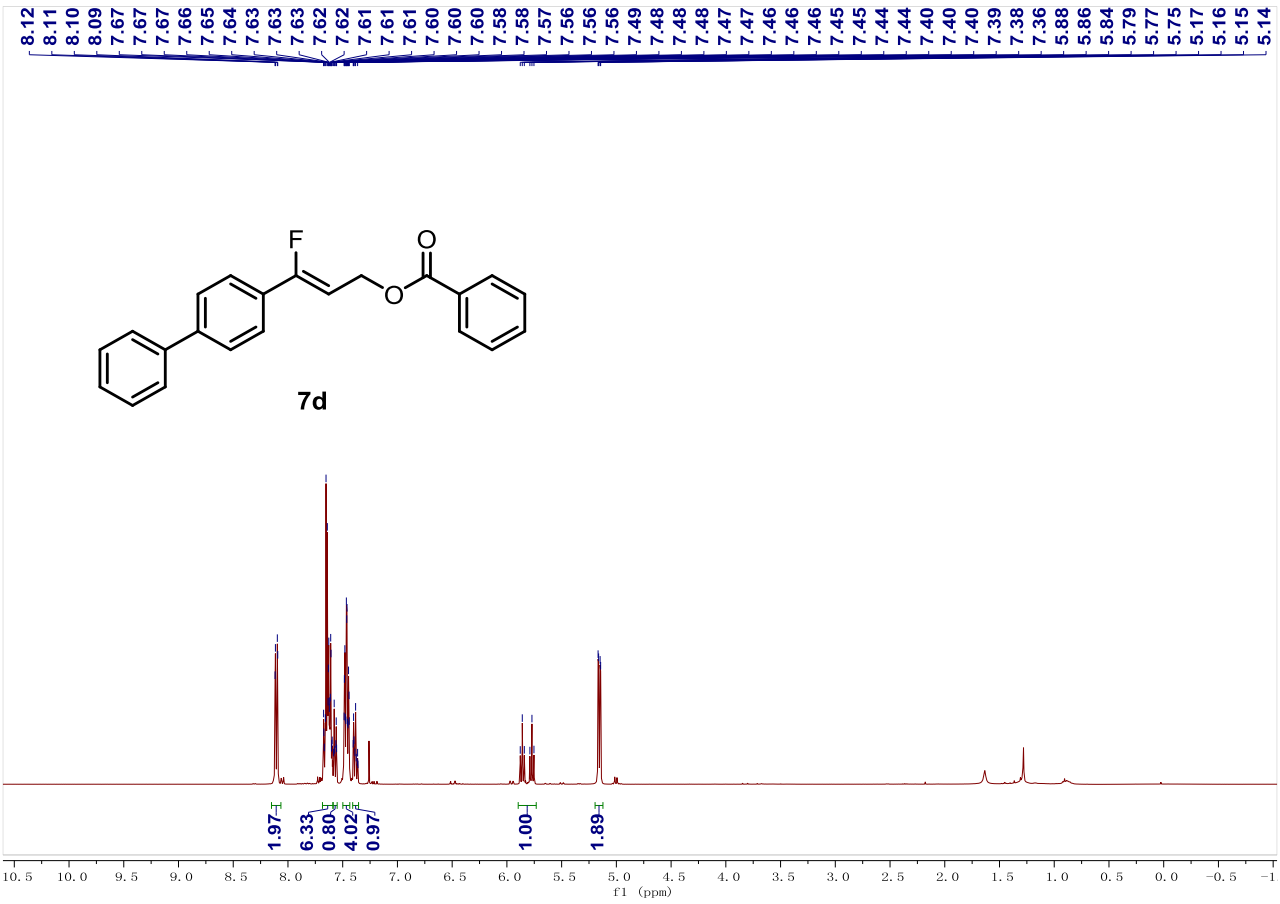


^{19}F NMR (376 MHz, $CDCl_3$)



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



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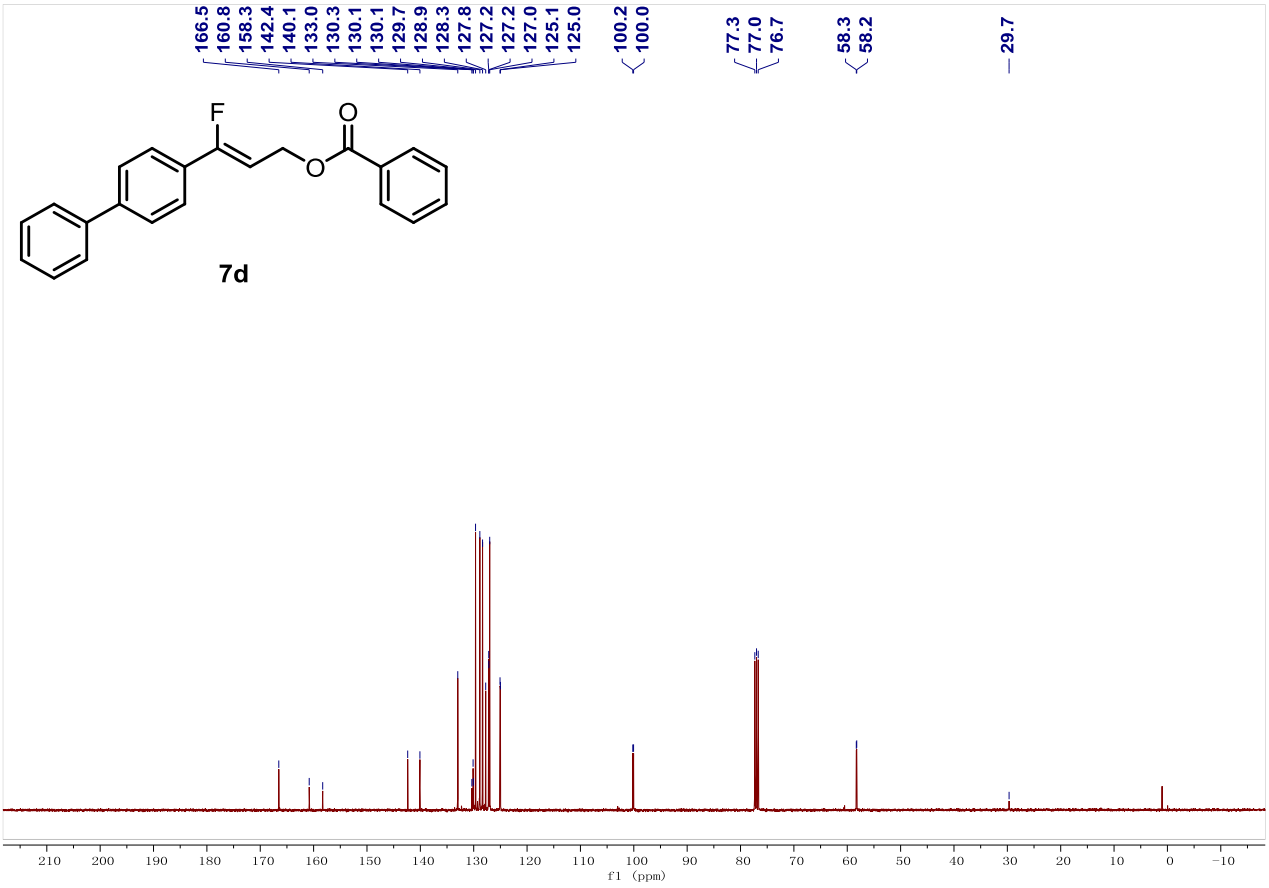
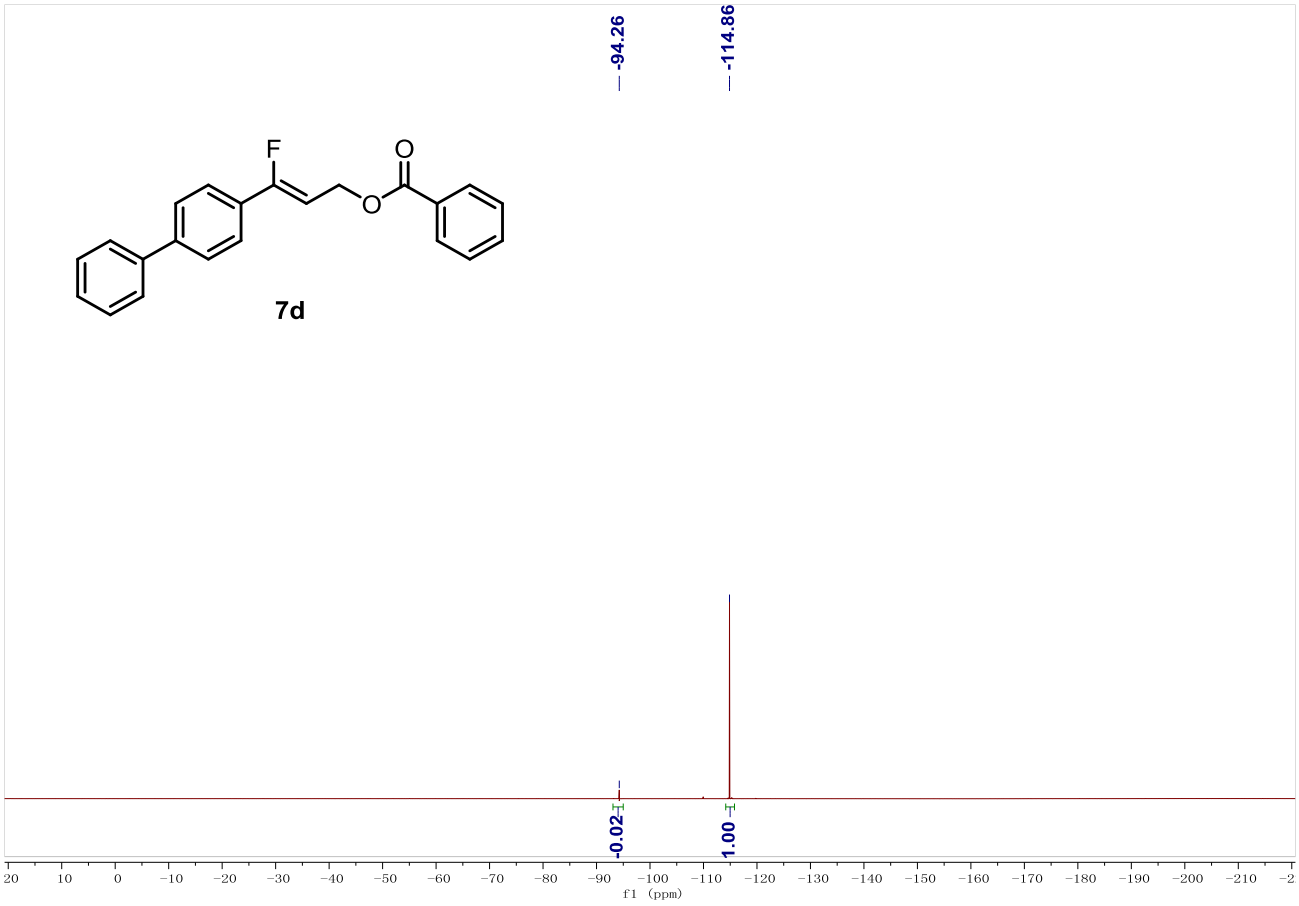


^{19}F NMR (376 MHz, $CDCl_3$)



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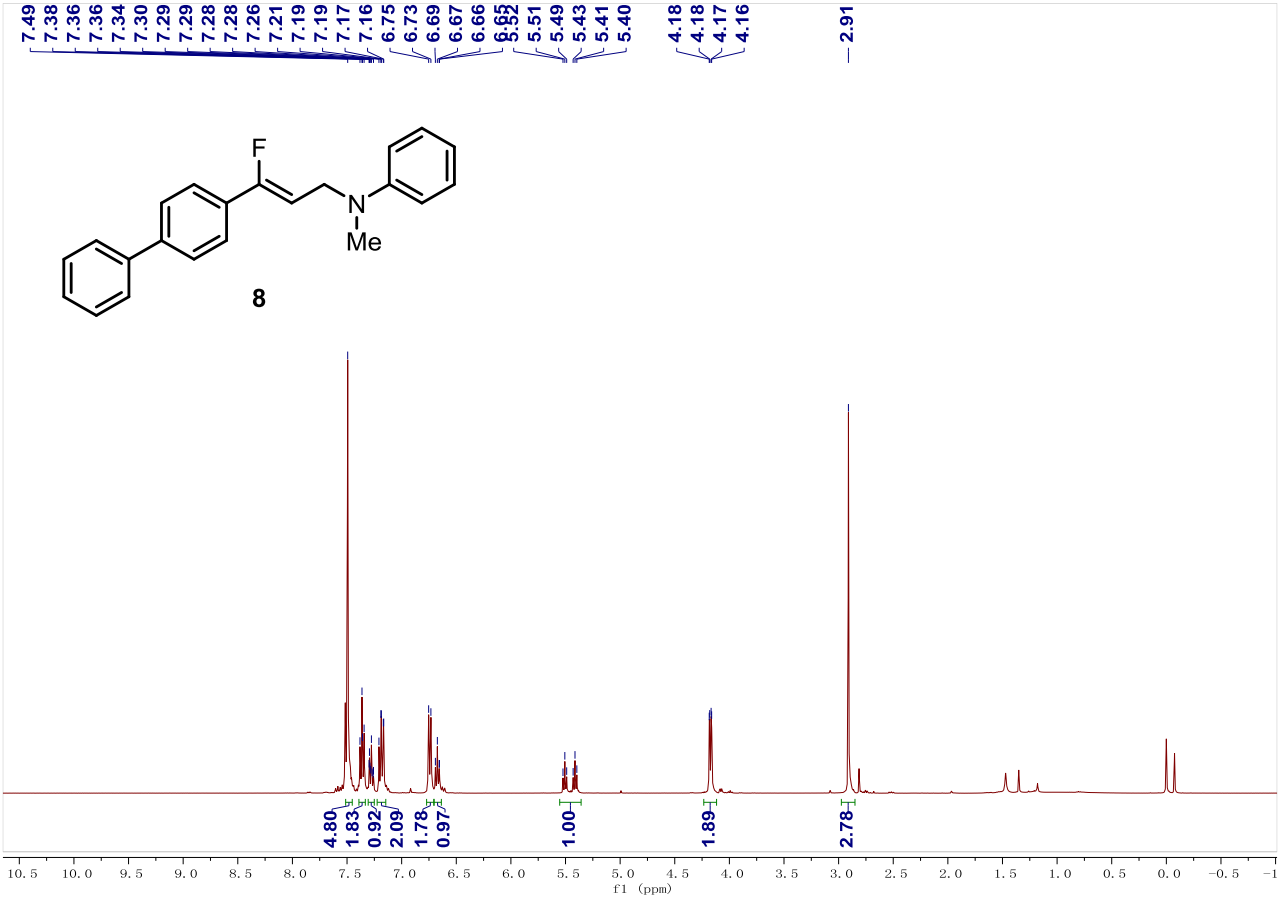
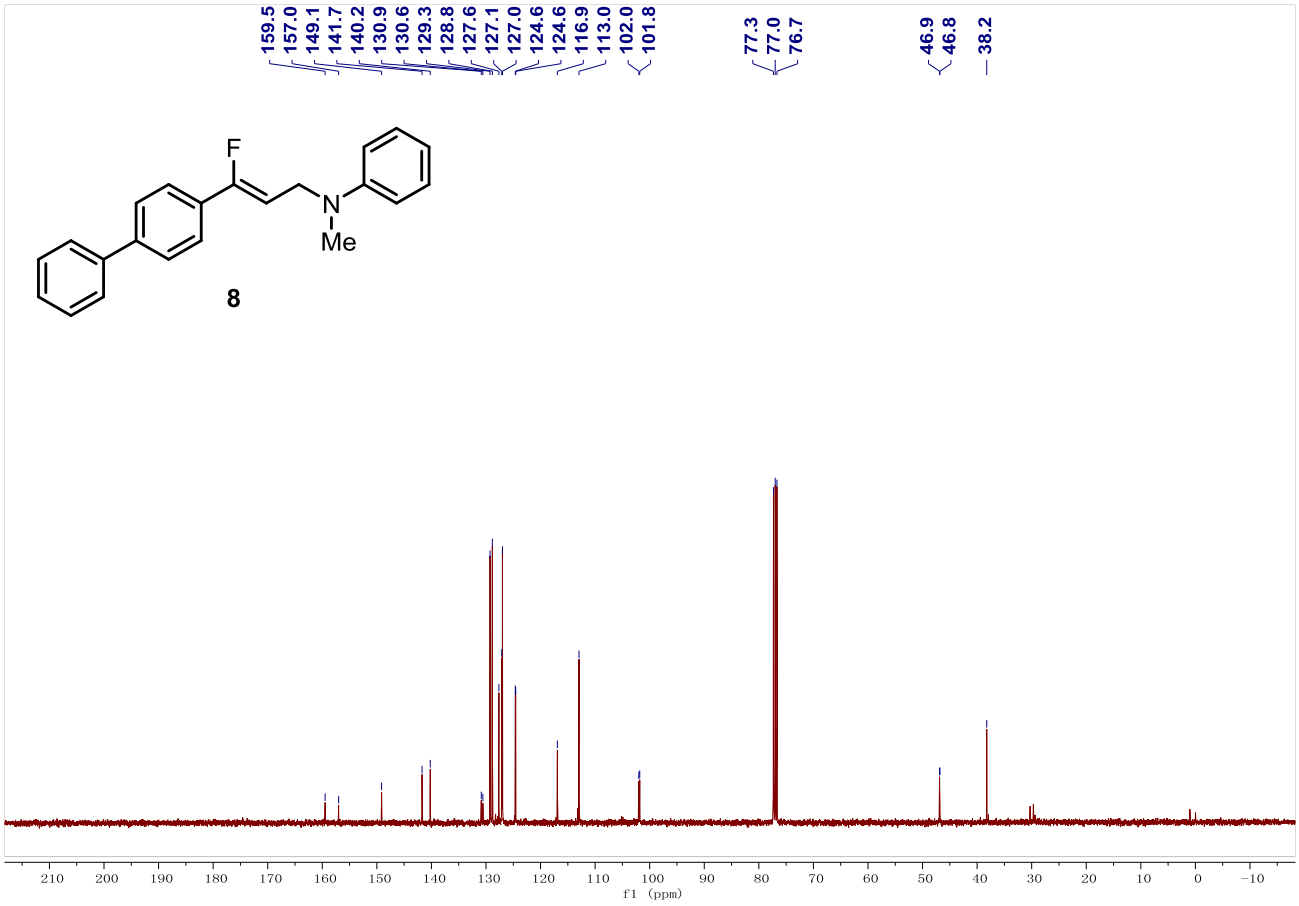
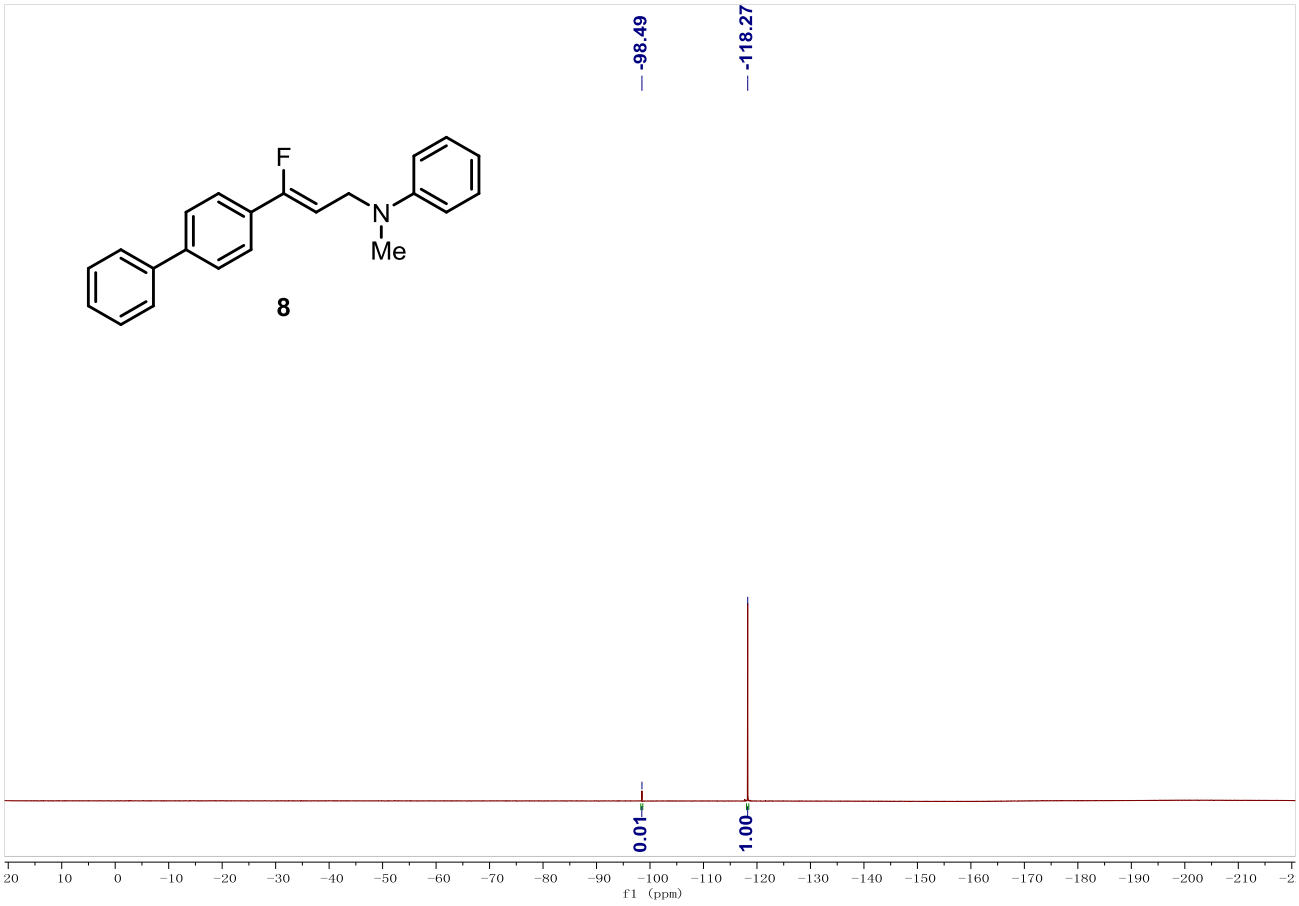


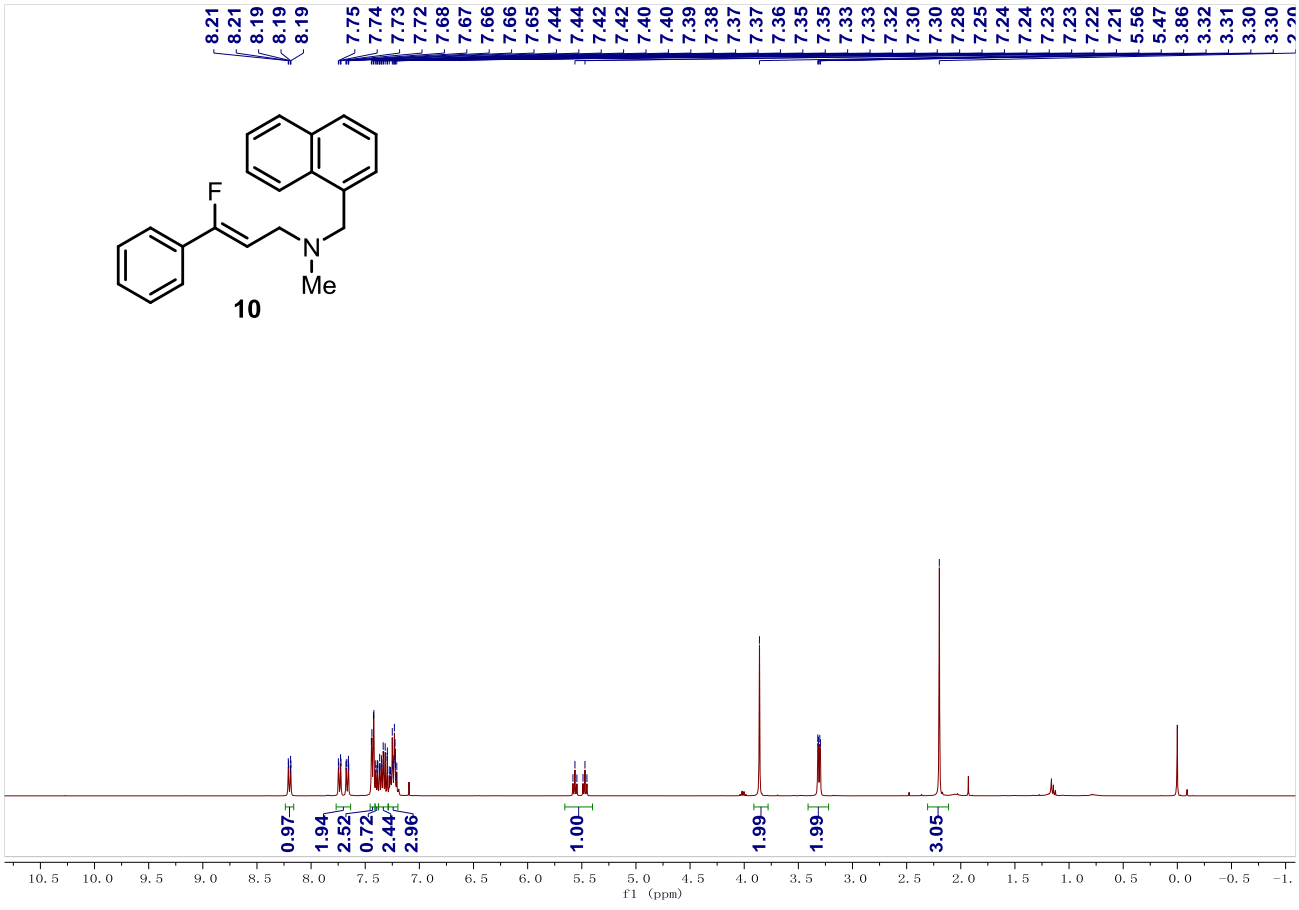
^{13}C NMR (101 MHz, $CDCl_3$)



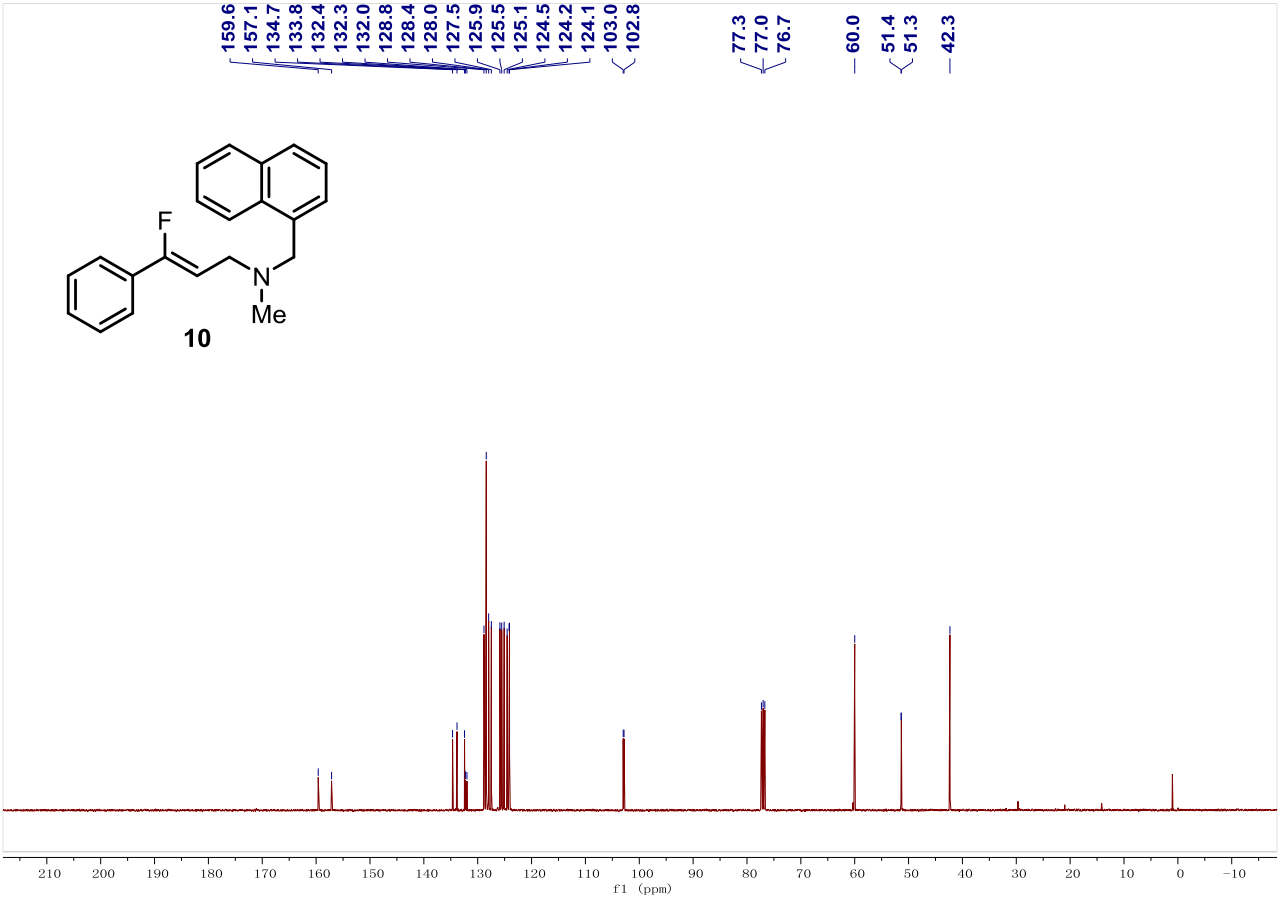
^{19}F NMR (376 MHz, $CDCl_3$)



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



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



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