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Supporting Information

Rh-Catalyzed Regio-Switchable Cross-Coupling of *gem*-Difluorinated Cyclopropanes with Allylboronates to Structurally Diverse Fluorinated Dienes

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CONTENTS

1. General Information

All reactions were carried out under a nitrogen atmosphere. Anhydrous solvents were purchased from Energy Chemical or Adamas in AcroSeal glass bottle (extra dry over molecular sieve) and used directly. NMR spectra were recorded on a Bruker AMX 400 spectrometer, or a JEOL JNM-ECZ400S if noted (400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F, in which ^{19}F is H-decoupling in Bruker spectrometer and is not H-decoupling in JEOL) with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in δ ppm referenced to $CDCl_3$ (δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Gas chromatography mass spectrometry (GC-MS) analysis was performed on Agilent Technologies 5975C. HR-MS spectra was recorded on a Waters Q-TOF Premier. Flash column chromatography was performed with silica gel (200-300 mesh, Haiyang, Qingdao). Melting points were determined using a digital melting point apparatus (JHX-4).

2. Reagents and Substrates

Unless stated otherwise, commercially available reagents were used as supplied. $[Rh(C_2H_4)_2Cl]_2$, $[Rh(CO)_2Cl]_2$, BINAP, $(4\text{-}ClC_6H_4)_3P$, $(4\text{-}CF_3C_6H_4)_3P$ were purchased from Energy. $AgBF_4$ was purchased from Alfa Aesar.

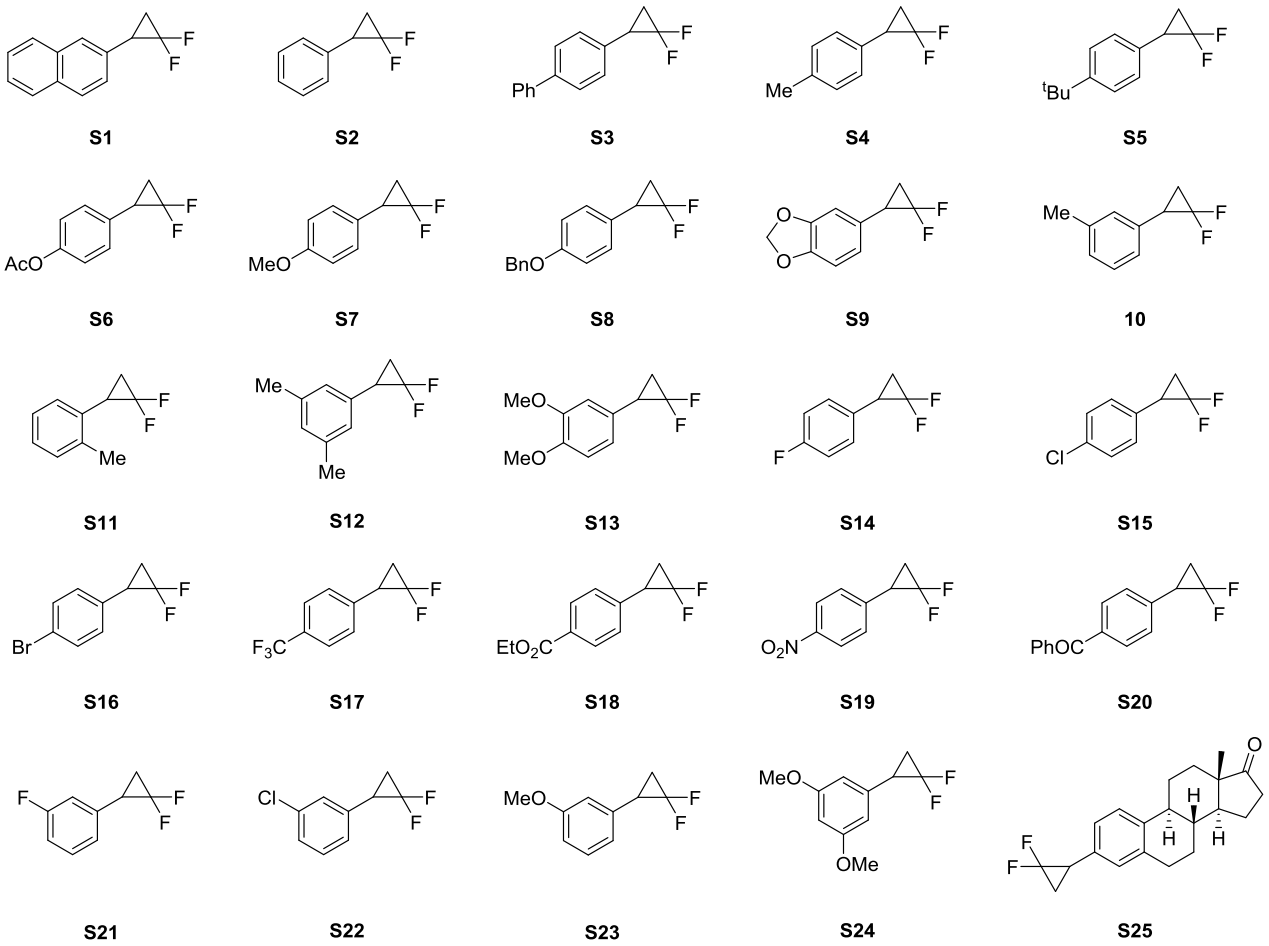
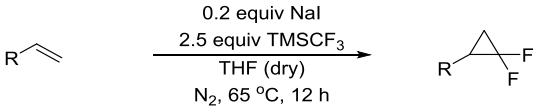


Fig. S1. *gem*-Difluorinated cyclopropanes used in this work

gem-Difluorinated cyclopropanes were prepared according to the known procedure[1-6] and the structure of these substrates are listed in **Fig. S1**. Allylboronates **S26** was commercially available and was used as supplied. **S27-S30** were prepared according to the known procedure.[7-8] The structure of these substrates is listed in **Fig. S2**.

<u>Synthesis of *gem*-Difluorinated Cyclopropanes</u>



To a flame-dried 100 mL three-necked flask equipped with a magnetic stir bar was added anhydrous NaI (0.3 g, 0.2 equiv), dry THF (20 mL), $TMSCF_3$ (3.7 mL, 2.5 equiv) and corresponding alkenes (10.0 mmol) under nitrogen atmosphere. The flask was sealed and stirred at 65 °C for 12 h. The reaction mixture was then cooled to room temperature, which was evaporated to dryness under reduce pressure and directly filtered through a pad of celite. The crude mixture was extracted with ethyl acetate (20 mL) and washed with saturated sodium sulfite solution (20 mL), brine (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated, which was purified by silica gel column chromatography to afford corresponding *gem*-difluorinated cyclopropanes. The spectral data matched the literature report.[1-6]

Synthesis of Allylboronates S27-S30

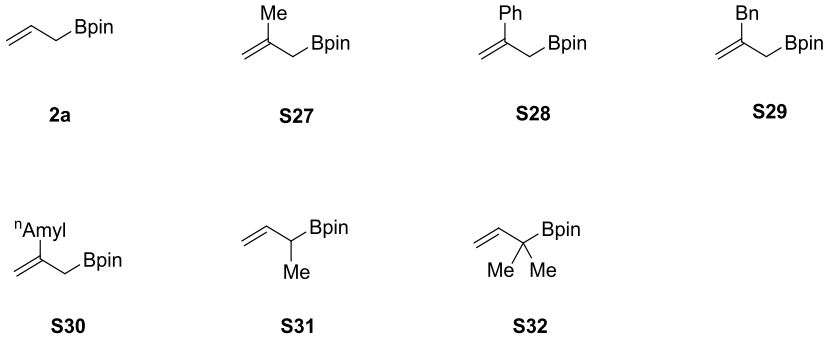
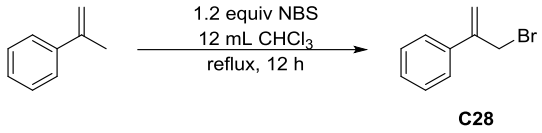
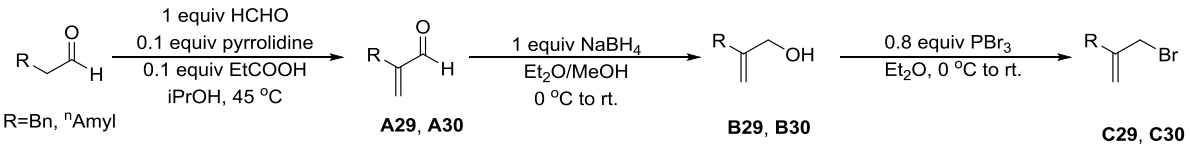


Fig. S2. Allylboronates used in this work

(3-bromoprop-1-en-2-yl) benzene C28:



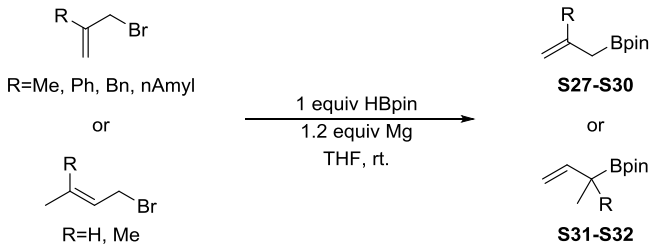
To a flame-dried 100 mL three-necked flask equipped with a magnetic stir bar was added anhydrous α-methylstyrene (10 mmol), N-Bromosuccinimide (1.2 equiv), $CHCl_3$ (40 mL). The flask was sealed and stirred to reflux for 12 h. The reaction mixture was then cooled to room temperature, which was directly filtered to remove insoluble residue through a pad of celite. The filtrate was concentrated under the reduce pressure to give the target product **C28** (1.49 g, 76% yield)**.**



To a 20 mL vial equipped with a magnetic stir bar was added aldehyde (10 mmol), iPrOH (1 mL), formaldehyde solution (37% in water, 750 μL, 10 mmol, 1.0 equiv), pyrrolidine (87.5 μL, 0.1 equiv) and propionic acid (75 μL, 0.1 equiv). After stirring at 45 °C for 4 h, the reaction mixture was quenched by addition of a saturated sodium hydrogen carbonate solution and extracted with EtOAc. The combined organic phase was dried over $MgSO_4$, filtered and concentrated, which was purified by silica gel column chromatography to give substituted acroleins **A29**-**A30**.

In a flame-dried 50 mL three-necked flask, the substituted acroleins (10 mmol) were dissolved in a solution of diethyl ether (8 mL) and methanol (2 mL). The resulting solution was stirred at 0 ºC and sodium borohydride (1 equiv) was added portionwise. After stirring for 1 h at 0 °C and 3-4 h for room temperature, the reaction mixture was diluted with MTBE and washed with water. The combined organic phase was dried over $MgSO_4$, filtered and concentrated to give substituted allyl alcohol **B29**-**B30**, which were used for the next step without further purification.

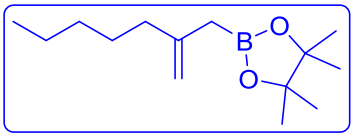
To a solution of substituted allyl alcohol **B29**-**B30** (10 mmol) in diethyl ether (8 mL) was added phosphorus tribromide (752 μL, 0.8 equiv) dropwise at 0 ºC. Then, the flask was stirred at room temperature overnight. The resulting mixture was cooled to 0 °C and quenched with ice water. The organic layer was sequentially washed with water, saturated sodium bicarbonate, and saturated brine solution. Subsequently, the organic phase was dried over $MgSO_4$, filtered and concentrated, which was purified by silica gel column chromatography to give substituted allyl bromide **C29-C30.**



A flame-dried 50 mL three-necked flask equipped with a magnetic stir bar was charged with magnesium turnings (291.7 mg, 1.2 equiv), dry THF (5 mL), and HBpin (1.27 g, 1.0 equiv). To this reaction mixture was added substituted allyl bromide (**C27-C30**, 1.0 equiv) dropwise over 5 min. After stirring for 0.5 h at room temperature, another substituted allyl bromide (1 equiv) was added. After the magnesium turinings were fully consumed, the reaction mixture was diluted with petroleum ether and quenched with aqueous HCl (0.1 M). The resulting solution was extracted with petroleum ether after stirring for 10 min. The combined organic phase was dried over $MgSO_4$, filtered and concentrated,

which was purified by neutral silica gel column chromatography to give allyl pinacol boronates **S27-S30.** The spectral data of **S7-S29** and **S31-S32** matched the literature reports.[7,8]

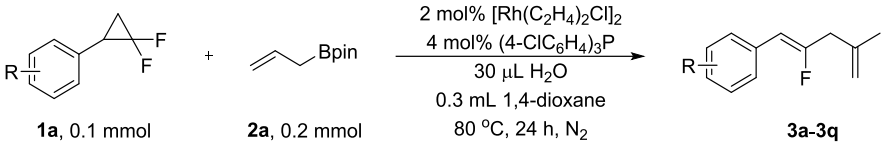
4,4,5,5-tetramethyl-2-(2-methyleneheptyl)-1,3,2-dioxaborolane (S30)



Isolated yield=76%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.7 (d, J = 3.8 Hz, 2H), 2.1 – 2.0 (m, 2H), 1.7 (s, 2H), 1.4 (m, 18H), 0.9 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 109.1, 83.2, 38.0, 31.6, 27.3, 24.7, 22.5, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.09.

3. Selective Synthesis of Fluorinated 1,4-Dienes

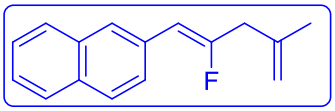
3.1 General Procedure A



In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_2)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), $(4\text{-}ClC_6H_4)_3P$ (1.5 mg, 0.004 mmol, 4 mol%), and 1,4-dioxane (0.3 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, *gem*-difluorinated cyclopropane (0.1 mmol), allylboronate **2a** (0.2 mmol) and H_2O (0.03 mL). Generally, several such type of reactions were carried out parallelly, thus the catalyst solution can be prepared in one vial together. The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 24 hours. The reaction mixture was cooled to room temperature and purified by chromatography on silica gel column to give the fluorinated 1,4-dienes.

3.2 Characterization Data of Products

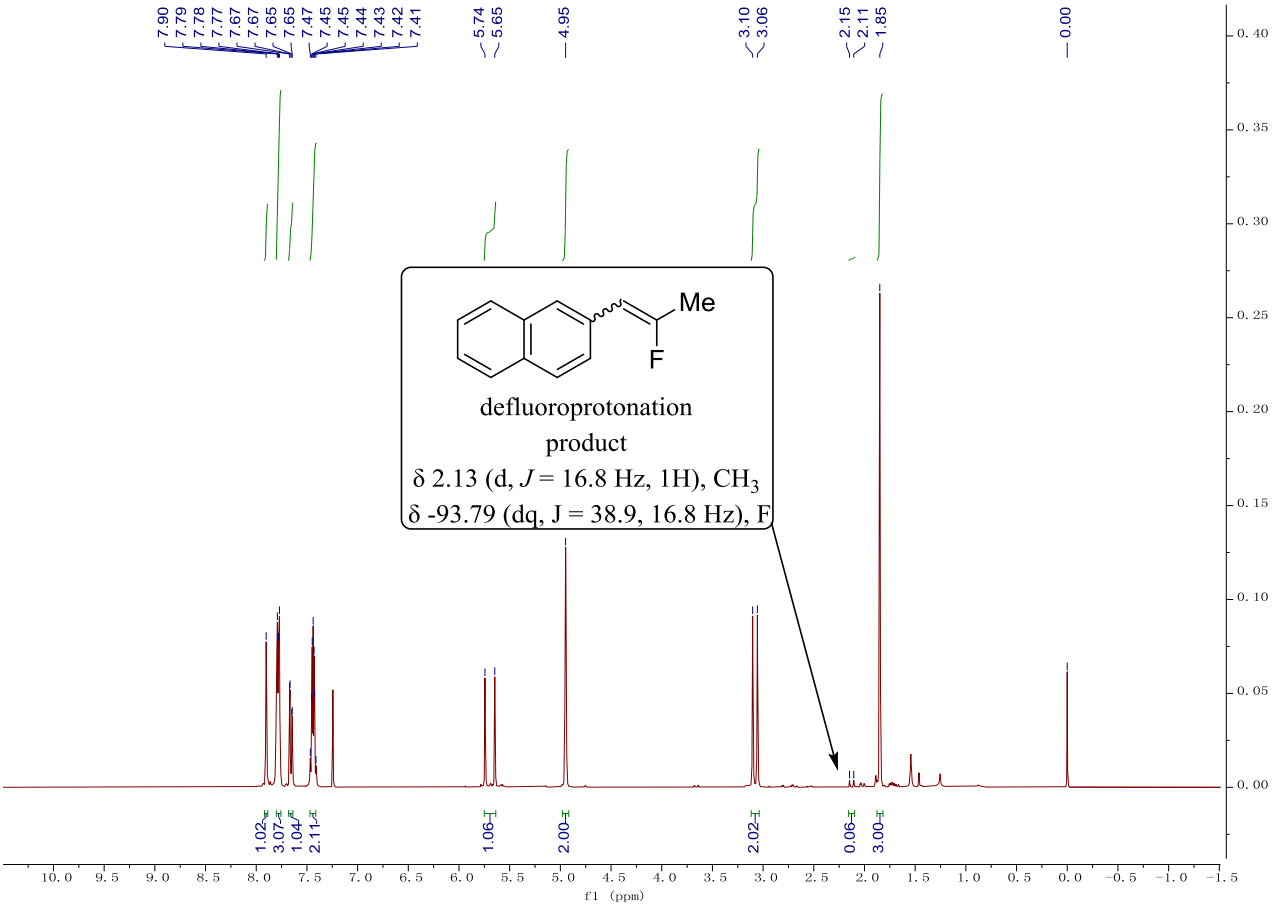
(Z)-2-(2-fluoro-4-methylpenta-1,4-dien-1-yl)naphthalene (3a)



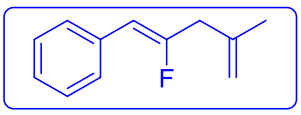
Following the general procedure A. Isolated yield = 88% (19.9 mg); White solid, m.p.: 61.3-62.1 °C; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.78 (dd, J = 7.3, 3.2 Hz, 3H), 7.65 (dd, J = 8.6, 1.8 Hz, 1H), 7.49 – 7.38 (m, 2H), 5.69 (d, J = 38.7 Hz, 1H), 4.94 (s, 2H), 3.08 (d, J = 18.7 Hz, 2H), 1.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$)

δ 158.9 (d, J = 268.3 Hz), 140.4, 133.5, 132.3, 131.2, 128.0, 127.9, 127.5, 127.2 (d, J = 7.6 Hz), 126.5 (d, J = 7.7 Hz), 126.1, 125.8, 113.8, 107.4 (d, J = 8.4 Hz), 42.0 (d, J = 27.5 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.51. **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{15}F$ $[M+H]^+$ 227.1231, found 227.1233.

Note: In this reaction, we can observe trace amount of ring-opening defluoroprotonation of **1a.** This product was generally inseparable with the corresponding fluorinated 1,4-diene due to their almost identical polarity. The defluoroprotonation product was also observed in some examples (e.g. **3a**, **3f**, **3g**, **3h**, **3i**, **3j**, **3k**, **3l**, **3o**, **3s**). The ratio of the 1,4-diene to the defluoroprotonation product was generally over 20:1 except example **3k** (13:1).



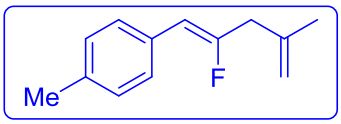
(Z)-(2-fluoro-4-methylpenta-1,4-dien-1-yl)benzene (3b)



Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 61% (10.8 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.36 – 7.27 (m, 2H), 7.26 – 7.16 (m, 1H), 5.54 (d, J = 38.8 Hz, 1H), 4.92 (d, J = 4.1 Hz, 2H), 3.03 (d, J = 18.9 Hz, 2H), 1.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6 (d, J = 267.7 Hz), 140.4, 133.7 (d, J = 2.7 Hz), 128.4, 128.3 (d, J = 7.4 Hz), 126.8 (d, J = 2.3 Hz), 113.7, 107.3 (d, J = 8.5 Hz), 41.9 (d, J = 27.7 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -

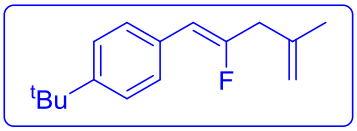
100.09. **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{13}F$ $[M+H]^+$ 177.1074, found 177.1078.

(Z)-1-(2-fluoro-4-methylpenta-1,4-dien-1-yl)-4-methylbenzene (3c)



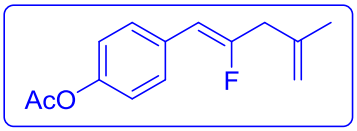
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 72% (13.7 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.50 (d, *J* = 39.0 Hz, 1H), 4.91 (s, 2H), 3.01 (d, *J* = 18.8 Hz, 2H), 2.33 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0 (d, *J* = 266.6 Hz), 140.6, 136.6 (d, *J* = 2.4 Hz), 130.8 (d, *J* = 2.7 Hz), 129.1, 128.2 (d, *J* = 7.3 Hz), 113.6, 107.2 (d, *J* = 8.7 Hz), 41.9 (d, *J* = 27.7 Hz), 22.0, 21.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.16. **HRMS** (ESI, *m/z*): calcd for $C_{13}H_{15}F$ $[M+H]^+$ 191.1231, found 191.1235.

(tert-butyl)-4-(2-fluoro-4-methylpenta-1,4-dien-1-yl)benzene (3d)



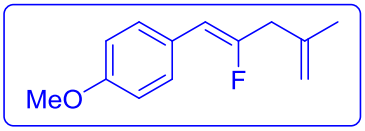
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 80% (18.6 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.38 – 7.32 (m, 2H), 5.52 (d, *J* = 39.0 Hz, 1H), 4.91 (s, 2H), 3.02 (d, *J* = 18.9 Hz, 2H), 1.80 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1 (d, *J* = 266.7 Hz), 149.8 (d, *J* = 2.4 Hz), 140.6, 130.8 (d, *J* = 2.7 Hz), 128.0 (d, *J* = 7.3 Hz), 125.3, 113.6, 107.1 (d, *J* = 8.8 Hz), 41.9 (d, *J* = 27.7 Hz), 34.5, 31.3, 21.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.06. **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{21}F$ $[M+H]^+$ 233.1700, found 233.1708.

(Z)-4-(2-fluoro-4-methylpenta-1,4-dien-1-yl)phenyl acetate (3e)



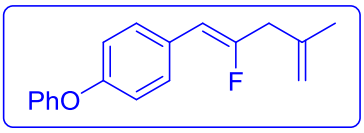
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 70% (16.4 mg); Pale yellow oil; R_f = 0.4 (PE:EA=20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 5.53 (d, *J* = 38.4 Hz, 1H), 4.92 (s, 1H), 4.90 (s, 1H), 3.02 (d, *J* = 18.8 Hz, 2H), 2.30 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 158.6 (d, *J* = 268.0 Hz), 149.2 (d, *J* = 3.0 Hz), 140.3, 131.4 (d, *J* = 2.5 Hz), 129.3 (d, *J* = 7.7 Hz), 121.5, 113.8, 106.5 (d, *J* = 8.4 Hz), 41.8 (d, *J* = 27.4 Hz), 22.0, 21.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.29 (dt, *J* = 38.4, 19.3 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{15}FO_2$ $[M+Na]^+$ 257.0948, found 257.0952.

(Z)-1-(2-fluoro-4-methylpenta-1,4-dien-1-yl)-4-methoxybenzene (3f)



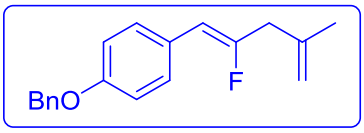
Following the general procedure A. Isolated yield = 90% (18.5 mg); Colorless oil; R_f = 0.5 (PE:EA=100:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.40 (d, *J* = 39.0 Hz, 1H), 4.83 (s, 2H), 3.73 (s, 3H), 2.93 (d, *J* = 18.9 Hz, 2H), 1.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4 (d, *J* = 2.8 Hz), 157.2 (d, *J* = 265.1 Hz), 140.7, 129.6 (d, *J* = 7.6 Hz), 126.4 (d, *J* = 2.8 Hz), 113.8, 113.5, 106.7 (d, *J* = 9.0 Hz), 55.2, 41.8 (d, *J* = 27.8 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.10. **HRMS** (ESI, *m/z*): calcd for $C_{13}H_{15}FO$ $[M+H]^+$ 207.1180, found 207.1186.

(Z)-1-(2-fluoro-4-methylpenta-1,4-dien-1-yl)-4-phenoxybenzene (3g)



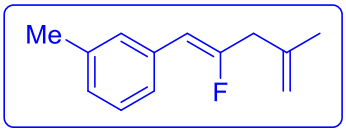
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 85% (22.8 mg); Colorless oil; R_f = 0.4 (PE:EA=100:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 6.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.51 (d, *J* = 38.7 Hz, 1H), 4.92 (d, *J* = 5.7 Hz, 2H), 3.02 (d, *J* = 18.8 Hz, 2H), 1.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9 (d, *J* = 266.6 Hz), 157.1, 155.9 (d, *J* = 2.8 Hz), 140.5, 129.7, 129.7 (d, *J* = 7.8 Hz), 128.8 (d, *J* = 2.8 Hz), 123.3, 118.9, 118.8, 113.7, 106.5 (d, *J* = 8.7 Hz), 41.8 (d, *J* = 27.5 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.53 (dt, *J* = 38.4, 19.2 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{17}FO$ $[M+Na]^+$ 269.1156, found 269.1163.

(Z)-1-(benzyloxy)-4-(2-fluoro-4-methylpenta-1,4-dien-1-yl)benzene (3h)



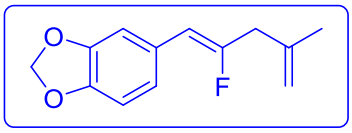
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 90% (25.4 mg); Colorless oil; R_f = 0.4 (PE:EA=100:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 6H), 7.31 (t, *J* = 7.1 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.47 (d, *J* = 39.1 Hz, 1H), 5.06 (s, 2H), 4.89 (s, 2H), 3.00 (d, *J* = 18.9 Hz, 2H), 1.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.6 (d, *J* = 2.9 Hz), 157.3 (d, *J* = 265.1 Hz), 140.6, 137.0, 129.5 (d, *J* = 7.5 Hz), 128.6, 127.9, 127.4, 126.6 (d, *J* = 2.7 Hz), 114.8, 113.5, 106.7 (d, *J* = 8.9 Hz), 70.0, 41.8 (d, *J* = 27.7 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.89. **HRMS** (ESI, *m/z*): calcd for $C_{19}H_{19}FO$ $[M+H]^+$ 283.1493, found 283.1502.

(Z)-1-(2-fluoro-4-methylpenta-1,4-dien-1-yl)-3-methylbenzene (3i)



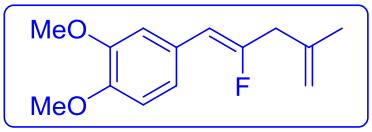
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 61% (11.6 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 9.3 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 5.50 (d, *J* = 38.9 Hz, 1H), 4.91 (d, *J* = 3.1 Hz, 2H), 3.02 (d, *J* = 18.8 Hz, 2H), 2.34 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4 (d, *J* = 267.5 Hz), 140.5, 137.9, 133.5 (d, *J* = 2.9 Hz), 129.0 (d, *J* = 7.3 Hz), 128.3, 127.6 (d, *J* = 2.3 Hz), 125.4 (d, *J* = 7.4 Hz), 113.7, 107.3 (d, *J* = 8.5 Hz), 41.9 (d, *J* = 27.6 Hz), 22.0, 21.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.16. **HRMS** (ESI, *m/z*): calcd for $C_{13}H_{15}F$ $[M+H]^+$ 191.1231, found 191.1237.

(Z)-5-(2-fluoro-4-methylpenta-1,4-dien-1-yl)benzo[d][1,3]dioxole (3j)



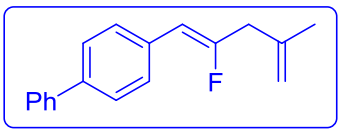
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 93% (20.5 mg); Colorless oil; R_f = 0.6 (PE:EA=100:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 1.8 Hz, 1H), 6.86 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 5.94 (s, 2H), 5.45 (d, *J* = 38.4 Hz, 1H), 4.91 (s, 1H), 4.89 (s, 1H), 2.99 (d, *J* = 18.9 Hz, 2H), 1.80 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.4 (d, *J* = 266.0 Hz), 147.7, 146.3 (d, *J* = 2.9 Hz), 140.5, 127.8 (d, *J* = 2.7 Hz), 122.2 (d, *J* = 6.0 Hz), 113.6, 108.6 (d, *J* = 10.0 Hz), 108.2, 107.0 (d, *J* = 8.5 Hz), 100.9, 41.8 (d, *J* = 27.7 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.12. **HRMS** (ESI, *m/z*): calcd for $C_{13}H_{13}FO_2$ $[M+H]^+$ 221.0972, found 257.0981.

(Z)-4-(2-fluoro-4-methylpenta-1,4-dien-1-yl)-1,2-dimethoxybenzene (3k)



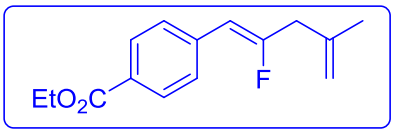
Following the general procedure A (except the reaction was carried out at 100 °C). The internal selective product 3k and the defluoroprotonation product were inseparable and isolated together (15.6 mg, 13:1), in which the adjusted yield is 62% (14.6 mg); Pale yellow oil; R_f = 0.4 (PE:EA=20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.47 (d, *J* = 38.8 Hz, 1H), 4.92 (d, *J* = 4.9 Hz, 2H), 3.88 (s, 3H), 3.88 (s, 4H), 3.01 (d, *J* = 18.9 Hz, 2H), 1.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 265.4 Hz), 148.6, 147.9 (d, *J* = 2.9 Hz), 140.5, 126.6 (d, *J* = 2.7 Hz), 121.0 (d, *J* = 6.7 Hz), 113.6, 111.2 (d, *J* = 9.2 Hz), 110.8, 106.9 (d, *J* = 8.6 Hz), 55.8, 55.7, 41.8 (d, *J* = 27.7 Hz), 21.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.73. **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{17}FO_2$ $[M+Na]^+$ 259.1105, found 259.1114.

(Z)-4-(2-fluoro-4-methylpenta-1,4-dien-1-yl)-1,1'-biphenyl (3l)



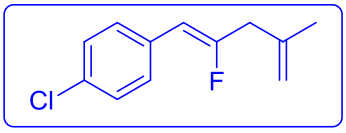
Following the general procedure A. (except the reaction was carried out at 100 °C). Isolated yield = 78% (19.7 mg); White solid, m.p.: 64.3-65.6 °C; R_f = 0.4 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.56 (s, 4H), 7.46 – 7.41 (m, 2H), 7.36 – 7.30 (m, 1H), 5.58 (d, *J* = 38.8 Hz, 1H), 4.93 (s, 2H), 3.05 (d, *J* = 18.7 Hz, 2H), 1.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8 (d, *J* = 268.1 Hz), 140.7, 140.4, 139.5 (d, *J* = 2.5 Hz), 132.7 (d, *J* = 2.9 Hz), 128.8, 128.7, 127.2, 127.1, 126.9, 113.8, 107.0 (d, *J* = 8.5 Hz), 41.9 (d, *J* = 27.6 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.46. **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{17}F$ $[M+H]^+$ 253.1387, found 253.1391.

ethyl (Z)-4-(2-fluoro-4-methylpenta-1,4-dien-1-yl)benzoate (3m)



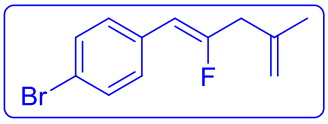
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 76% (18.8 mg); Pale yellow oil; R_f = 0.5 (PE:EA=20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 5.59 (d, *J* = 38.2 Hz, 1H), 4.93 (d, *J* = 10.7 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.05 (d, *J* = 18.5 Hz, 2H), 1.83 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 160.4 (d, *J* = 271.5 Hz), 140.0, 138.1 (d, *J* = 2.9 Hz), 129.7, 128.5 (d, *J* = 2.4 Hz), 128.1 (d, *J* = 7.8 Hz), 114.1, 106.8 (d, *J* = 8.1 Hz), 60.9, 41.9 (d, *J* = 27.1 Hz), 22.0, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.02. **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{17}FO_2$ $[M+H]^+$ 249.1285, found 249.1294.

(Z)-1-chloro-4-(2-fluoro-4-methylpenta-1,4-dien-1-yl)benzene (3n)



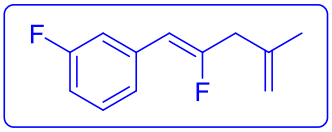
Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 72% (15.1 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 5.50 (d, *J* = 38.3 Hz, 1H), 4.92 (d, *J* = 9.8 Hz, 2H), 3.02 (d, *J* = 18.7 Hz, 2H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1 (d, *J* = 268.6 Hz), 140.2, 132.4 (d, *J* = 3.5 Hz), 132.1 (d, *J* = 2.7 Hz), 129.5 (d, *J* = 7.7 Hz), 128.5, 113.9, 106.3 (d, *J* = 8.5 Hz), 41.8 (d, *J* = 27.4 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.10. **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}FCl$ $[M+H]^+$ 211.0684, found 211.0691.

(Z)-1-bromo-4-(2-fluoro-4-methylpenta-1,4-dien-1-yl)benzene (3o)



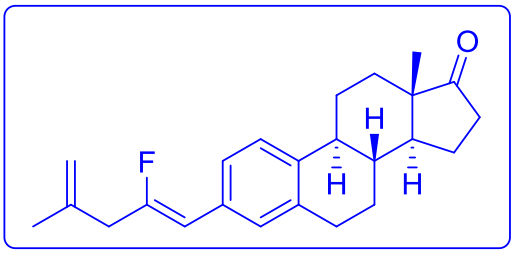
Following the general procedure A (except the reaction was carried out in the presence of 4 mol% $Rh(C_2H_4)_2Cl]_2$ and 8 mol% $(4\text{-}ClC_6H_4)_3P$ at 100 °C). Isolated yield = 69% (17.5 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 5.48 (d, *J* = 38.2 Hz, 1H), 4.92 (d, *J* = 10.3 Hz, 2H), 3.01 (d, *J* = 18.7 Hz, 2H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2 (d, *J* = 268.9 Hz), 140.1, 132.5 (d, *J* = 2.6 Hz), 131.5, 129.9 (d, *J* = 7.7 Hz), 120.5 (d, *J* = 3.4 Hz), 113.9, 106.3 (d, *J* = 8.5 Hz), 41.8 (d, *J* = 27.2 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.67. **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}FBr$ $[M+H]^+$ 255.0179, found 255.0176.

(Z)-1-fluoro-3-(2-fluoro-4-methylpenta-1,4-dien-1-yl)benzene (3p)



Following the general procedure A (except the reaction was carried out at 100 °C). Isolated yield = 76% (14.7 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 0H), 6.91 (td, *J* = 8.3, 2.4 Hz, 1H), 5.52 (d, *J* = 37.9 Hz, 1H), 4.92 (d, *J* = 10.3 Hz, 1H), 3.03 (d, *J* = 18.7 Hz, 1H), 1.82 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 244.4 Hz), 159.6 (d, *J* = 269.6 Hz), 140.1, 135.7 (dd, *J* = 8.3, 2.1 Hz), 129.7 (d, *J* = 8.4 Hz), 124.0 (dd, *J* = 6.6, 2.7 Hz), 114.0, 113.8 (d, *J* = 2.2 Hz), 113.6 (d, *J* = 2.2 Hz), 106.5 (dd, *J* = 8.2, 2.5 Hz), 41.8 (d, *J* = 27.4 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.84, -113.51. **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{13}F_2$ $[M+H]^+$ 195.0980, found 195.0987.

(8R,9S,13S,14S)-3-((Z)-2-fluoro-4-methylpenta-1,4-dien-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3q)

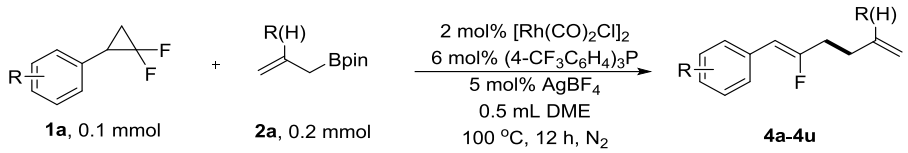


Following the general procedure A (except the reaction was carried out at 110 °C). Isolated yield = 82% (28.9 mg); Pale yellow solid, m.p.: 129.1-130.5 °C; R_f = 0.4 (PE:EA=10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 3H), 5.49 (d, *J* = 39.1 Hz, 1H), 4.91 (d, *J* = 5.2 Hz, 2H), 3.01 (d, *J* = 18.9 Hz, 2H), 2.91 (dd, *J* = 8.8, 3.9 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.29 (td, *J* = 10.5, 4.1 Hz, 1H), 2.20 – 2.12 (m, 1H), 2.11 – 2.03 (m, 2H), 1.99 – 1.94 (m, 1H), 1.80 (s, 3H), 1.64 – 1.43 (m, 6H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.1, 158.2 (d, *J* = 266.9 Hz), 140.5, 138.5, 136.4, 131.2 (d, *J* = 2.5 Hz), 128.8 (d, *J* = 7.2 Hz), 125.8 (d, *J* = 7.1 Hz), 125.4, 113.6, 107.0 (d, *J* = 8.6 Hz), 50.4, 48.0, 44.4, 41.9 (d, *J* = 27.6 Hz), 38.1, 35.8, 31.5, 29.4, 26.5, 25.6, 21.9, 21.5, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -

100.59 (dt, J = 38.4, 19.0 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{24}H_{29}FO$ $[M+Na]^+$ 375.2095, found 375.2095.

4. Selective Synthesis of Fluorinated 1,5-Dienes

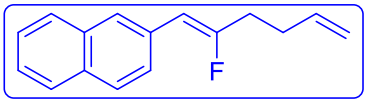
4.1 General Procedure B



In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(CO)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), $(4\text{-}CF_3C_6H_4)_3P$ (2.8 mg, 0.006 mmol, 6 mol%), and DME (0.5 mL). The mixture was stirred for about 10 min, which afforded a yellow homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, $AgBF_4$ (1 mg, 0.005 mmol), *gem*-difluorinated cyclopropane (0.1 mmol) and allylboronate (33.6 mg, 0.2 mmol). Generally, several such type of reactions were carried out parallelly, thus the catalyst solution can be prepared in one vial together. The 4 mL vial was sealed and removed from the glove box and stirred at 100 °C for 12 hours. The reaction mixture was cooled to room temperature and purified by chromatography on silica gel column to give the fluorinated 1,5-dienes.

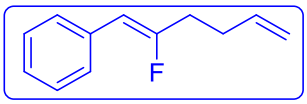
4.2 Characterization Data of Products

(Z)-2-(2-fluorohexa-1,5-dien-1-yl)naphthalene (4a)



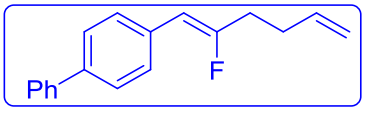
Following the general procedure B. Isolated yield = 72% (16.3 mg); White solid, m.p.: 60.1-60.8 °C; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.78 (td, J = 6.0, 5.6, 2.7 Hz, 3H), 7.64 (dd, J = 8.6, 1.8 Hz, 1H), 7.43 (td, J = 6.8, 6.1, 3.7 Hz, 2H), 5.88 (ddt, J = 16.6, 10.2, 6.4 Hz, 1H), 5.63 (d, J = 39.4 Hz, 1H), 5.12 (dd, J = 17.1, 1.7 Hz, 1H), 5.05 (d, J = 10.3 Hz, 1H), 2.55 – 2.36 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6 (d, J = 267.1 Hz), 136.8, 133.5, 132.2, 131.3 (d, J = 2.6 Hz), 127.9, 127.9, 127.5, 127.0 (d, J = 7.4 Hz), 126.5 (d, J = 7.5 Hz), 126.0, 125.7, 115.7, 106.3 (d, J = 8.4 Hz), 32.7 (d, J = 26.6 Hz), 30.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.76. The NMR data match with the reported literature.[9]

(Z)-(2-fluorohexa-1,5-dien-1-yl)benzene (4b)



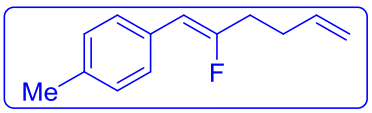
Following the general procedure B. Isolated yield = 67% (11.5 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.86 (ddt, *J* = 16.7, 10.3, 6.2 Hz, 1H), 5.48 (d, *J* = 39.5 Hz, 1H), 5.10 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 2.49 – 2.31 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.3 (d, *J* = 266.5 Hz), 136.8, 133.7 (d, *J* = 2.5 Hz), 128.4, 128.3 (d, *J* = 7.3 Hz), 126.7 (d, *J* = 2.3 Hz), 115.6, 106.1 (d, *J* = 8.5 Hz), 32.6 (d, *J* = 26.8 Hz), 30.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.38. The HRMS was not satisfied, and the result of LRMS was obtained for this compound. **LRMS** (EI) m/z: 176 (M+, 25), 147 (10), 135 (100), 115 (70), 109 (15).

(Z)-4-(2-fluorohexa-1,5-dien-1-yl)-1,1'-biphenyl (4c)



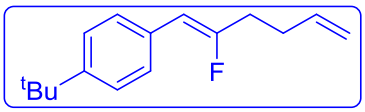
Following the general procedure B. Isolated yield = 68% (17.1 mg); White solid, m.p.: 65.3-66.6 °C; R_f = 0.4 (PE). **^{1}H NMR** (400 MHz, CDCl3) δ 7.63 – 7.51 (m, 6H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 5.87 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.52 (d, *J* = 39.4 Hz, 1H), 5.11 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.04 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.76 – 2.12 (m, 4H). **^{13}C NMR** (101 MHz, CDCl3) δ 160.5 (d, *J* = 266.9 Hz), 140.8, 139.4 (d, *J* = 2.3 Hz), 136.8, 132.8, 128.8, 128.7 (d, *J* = 7.5 Hz), 127.2, 127.1, 126.9, 115.7, 105.8 (d, *J* = 8.6 Hz), 32.6, 30.5. **^{19}F NMR** (376 MHz, CDCl3) δ -100.75. The NMR data match with the reported literature.[9]

(Z)-1-(2-fluorohexa-1,5-dien-1-yl)-4-methylbenzene (4d)



Following the general procedure B. Isolated yield = 70% (13.3 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.85 (ddt, *J* = 16.5, 10.3, 6.2 Hz, 1H), 5.44 (d, *J* = 39.7 Hz, 1H), 5.09 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.02 (d, *J* = 10.2 Hz, 1H), 2.47 – 2.34 (m, 4H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 265.4 Hz), 137.0, 136.4 (d, *J* = 2.4 Hz), 130.9 (d, *J* = 2.5 Hz), 129.1, 128.2 (d, *J* = 7.3 Hz), 115.6, 106.0 (d, *J* = 8.8 Hz), 32.6 (d, *J* = 26.8 Hz), 30.6, 21.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.41. The HRMS was not satisfied, and the result of LRMS was obtained for this compound. **LRMS** (EI) m/z: 190 (M+, 20), 161 (5), 149 (100), 133 (25), 129 (50), 77(5).

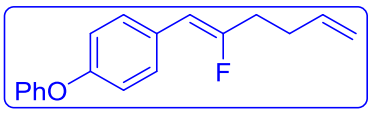
(Z)-1-(tert-butyl)-4-(2-fluorohexa-1,5-dien-1-yl)benzene (4e)



Following the general procedure B. Isolated yield = 68% (15.8 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* =

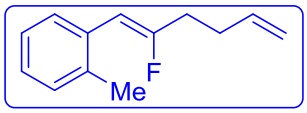
8.7 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 5.85 (ddt, *J* = 16.6, 10.3, 6.2 Hz, 1H), 5.46 (d, *J* = 39.7 Hz, 1H), 5.09 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.02 (d, *J* = 10.1 Hz, 1H), 2.40 (dq, *J* = 25.8, 6.4 Hz, 4H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 265.5 Hz), 149.7 (d, *J* = 2.2 Hz), 136.9, 130.9 (d, *J* = 2.4 Hz), 128.0 (d, *J* = 7.2 Hz), 125.3, 115.6, 105.9 (d, *J* = 8.8 Hz), 34.5, 32.6 (d, *J* = 26.8 Hz), 31.3, 30.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.36. The NMR data match with the reported literature.[9]

(Z)-1-(2-fluorohexa-1,5-dien-1-yl)-4-phenoxybenzene (4f)



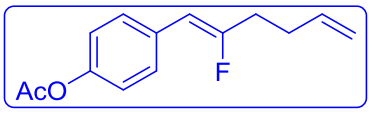
Following the general procedure B. Isolated yield = 59% (15.8 mg); White solid, m.p.: 72.5-73.8 °C; R_f = 0.3 (PE:EA=100:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.36 – 7.30 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.98 – 6.93 (m, 2H), 5.86 (ddt, *J* = 16.6, 10.1, 6.2 Hz, 1H), 5.46 (d, *J* = 39.5 Hz, 1H), 5.10 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.03 (dt, *J* = 10.2, 1.5 Hz, 1H), 2.47 – 2.32 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 265.3 Hz), 157.1, 155.8 (d, *J* = 3.2 Hz), 136.8, 129.7, 129.6, 128.9, 123.2, 118.8, 118.8, 115.7, 105.4 (d, *J* = 9.0 Hz), 32.5 (d, *J* = 26.6 Hz), 30.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.90. **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{17}O$ $[M+H]^+$ 269.1336, found 269.1339.

(Z)-1-(2-fluorohexa-1,5-dien-1-yl)-2-methylbenzene (4g)



Following the general procedure B (except the reaction was carried out at 120 °C). Isolated yield = 69% (13.1 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.19 – 7.11 (m, 3H), 5.87 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.59 (d, *J* = 38.5 Hz, 1H), 5.11 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.05 (d, *J* = 9.4 Hz, 1H), 2.50 – 2.34 (m, 4H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 265.1 Hz), 136.9, 135.4, 132.2 (d, *J* = 1.3 Hz), 129.9, 129.2 (d, *J* = 9.3 Hz), 126.8, 125.8, 115.7, 103.6 (d, *J* = 9.9 Hz), 32.6 (d, *J* = 27.0 Hz), 30.6, 20.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.77. The NMR data match with the reported literature.[9]

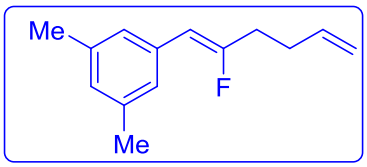
(Z)-4-(2-fluorohexa-1,5-dien-1-yl)phenyl acetate (4h)



Following the general procedure B. Isolated yield = 80% (18.7 mg); Pale yellow oil; R_f = 0.4 (PE:EA=20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 5.85 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.46 (d, *J* = 39.1 Hz, 1H), 5.09 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.03 (dd, *J* = 10.3, 1.6 Hz, 1H), 2.48 – 2.32 (m, 4H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 160.3 (d, *J* = 266.6 Hz), 149.1, 136.7, 131.5 (d, *J*

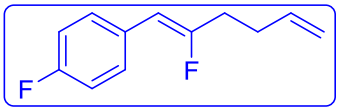
= 2.4 Hz), 129.3 (d, *J* = 7.5 Hz), 121.4, 115.7, 105.3 (d, *J* = 8.7 Hz), 32.6 (d, *J* = 26.5 Hz), 30.5, 21.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.70. **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{15}FO_2$ $[M+Na]^+$ 257.0948, found 257.0949.

(Z)-1-(2-fluorohexa-1,5-dien-1-yl)-3,5-dimethylbenzene (4i)



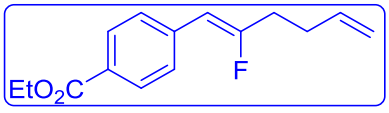
Following the general procedure B. Isolated yield = 65% (13.3 mg); Colorless oil; R_f = 0.4 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (s, 2H), 6.85 (s, 1H), 5.85 (ddt, *J* = 16.3, 10.5, 6.1 Hz, 1H), 5.41 (d, *J* = 39.8 Hz, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 5.02 (d, *J* = 10.2 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.39 – 2.33 (m, 3H), 2.29 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 266.0 Hz), 137.8, 136.9, 133.5 (d, *J* = 2.6 Hz), 128.4 (d, *J* = 2.2 Hz), 126.1 (d, *J* = 7.1 Hz), 115.6, 106.2 (d, *J* = 8.4 Hz), 32.6 (d, *J* = 26.6 Hz), 30.5, 21.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.51. **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{17}F$ $[M+H]^+$ 205.1387, found 205.1390.

(Z)-1-fluoro-4-(2-fluorohexa-1,5-dien-1-yl)benzene (4j)



Following the general procedure B (except the reaction was carried out in the presence of 3 mol% $[Rh(CO)_2Cl]_2$, 9 mol% $(4\text{-}CF_3C_6H_4)_3P$, and 7.5 mol% $AgBF_4$). Isolated yield = 57% (11.1 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.04 – 6.95 (m, 2H), 5.85 (ddt, *J* = 16.3, 10.0, 6.1 Hz, 1H), 5.44 (d, *J* = 39.1 Hz, 1H), 5.09 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.05 – 5.01 (m, 1H), 2.47 – 2.30 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4 (dd, *J* = 246.2, 3.4 Hz), 159.9 (dd, *J* = 265.9, 2.5 Hz), 136.8, 129.8 (t, *J* = 7.7 Hz), 115.7, 115.4, 115.1, 105.1 (d, *J* = 8.7 Hz), 32.5 (d, *J* = 26.6 Hz). 30.5 (*d*, *J* = 1.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.5 (dt, *J* = 38.8, 16.9 Hz), -114.9 (td, *J* = 8.9, 5.0 Hz). The NMR data match with the reported literature.[9]

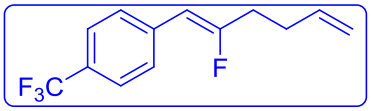
ethyl (Z)-4-(2-fluorohexa-1,5-dien-1-yl)benzoate (4k)



Following the general procedure B. Isolated yield = 71% (17.6 mg); Pale yellow oil; R_f = 0.4 (PE:EA=20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 5.85 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.54 (d, *J* = 38.9 Hz, 1H), 5.11 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.04 (d, *J* = 10.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.51 – 2.32 (m, 4H). 1.39 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 162.0 (d, *J* = 270.3 Hz), 138.2 (d, *J* = 2.6 Hz), 136.6, 129.7, 128.4 (d, *J* = 2.4 Hz), 128.1 (d, *J* = 7.8 Hz), 115.8, 105.7 (d,

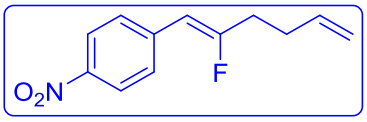
J = 8.2 Hz), 60.8, 32.7 (d, J = 26.3 Hz), 30.4 (d, J = 1.4 Hz), 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.30. **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{17}FO_2$ $[M+Na]^+$ 271.1105, found 271.1105.

(Z)-1-(2-fluorohexa-1,5-dien-1-yl)-4-(trifluoromethyl)benzene (4l)



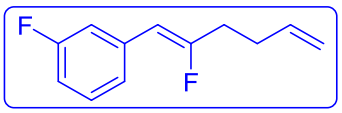
Following the general procedure B (except the reaction was carried out in the presence of 4 mol% $[Rh(CO)_2Cl]_2$, 12 mol% $(4\text{-}CF_3C_6H_4)_3P$, and 10 mol% $AgBF_4$). Isolated yield = 52% (12.7 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (s, 4H), 5.85 (ddt, J = 16.6, 10.2, 6.4 Hz, 1H), 5.53 (d, J = 38.6 Hz, 1H), 5.11 (dd, J = 17.1, 1.4 Hz, 1H), 5.05 (dd, J = 10.2, 0.9 Hz, 1H), 2.51 – 2.33 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1 (d, J = 269.8 Hz), 137.2, 136.5, 128.4 (d, J = 7.8 Hz), 125.3 (q, J = 3.8 Hz), 124.2 (d, J = 272.1 Hz), 115.9, 105.3 (d, J = 8.2 Hz), 32.6 (d, J = 26.3 Hz), 30.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.40, -97.78 (dt, J = 38.7, 17.1 Hz). The NMR data match with the reported literature.[9]

(Z)-1-(2-fluorohexa-1,5-dien-1-yl)-4-nitrobenzene (4m)



Following the general procedure B (except the reaction was carried out in the presence of 4 mol% $[Rh(CO)_2Cl]_2$, 12 mol% $(4\text{-}CF_3C_6H_4)_3P$, and 10 mol% $AgBF_4$). Isolated yield = 57% (12.6 mg); Yellow oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 2H), 7.60 (d, J = 8.9 Hz, 2H), 5.85 (ddt, J = 16.7, 10.2, 6.2 Hz, 1H), 5.60 (d, J = 38.1 Hz, 1H), 5.12 (dq, J = 17.1, 1.6 Hz, 1H), 5.06 (dq, J = 10.2, 1.3 Hz, 1H), 2.54 – 2.44 (m, 2H), 2.43 – 2.35 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5 (d, J = 273.2 Hz), 146.0, 140.4 (d, J = 2.5 Hz), 136.3, 128.7 (d, J = 8.2 Hz), 123.7, 116.1, 105.0 (d, J = 7.9 Hz), 32.7 (d, J = 25.8 Hz), 30.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.91 (dt, J = 37.7, 17.8 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}FNO_2$ $[M+Na]^+$ 244.0744, found 244.0745.

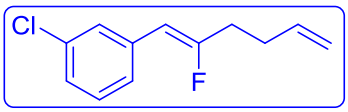
(Z)-1-fluoro-3-(2-fluorohexa-1,5-dien-1-yl)benzene (4n)



Following the general procedure B (except the reaction was carried out in the presence of 3 mol% $[Rh(CO)_2Cl]_2$, 9 mol% $(4\text{-}CF_3C_6H_4)_3P$, and 7.5 mol% $AgBF_4$). Isolated yield = 70% (13.6 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.17 (d, J = 7.8 Hz, 1H), 6.95 – 6.86 (m, 1H), 5.85 (ddt, J = 16.7, 10.3, 6.3 Hz, 1H), 5.47 (d, J = 38.6 Hz, 1H), 5.10 (dd, J = 17.1, 1.7 Hz, 1H), 5.04 (dd, J = 10.2, 1.6 Hz, 1H), 2.48 – 2.34 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8 (d, J = 244.2 Hz), 161.2 (d, J = 268.4 Hz), 136.6, 135.8 (dd, J = 8.5, 2.3 Hz), 129.7 (d, J = 8.4 Hz), 124.0 (dd, J = 6.6, 2.7 Hz), 115.8, 114.9 (dd,

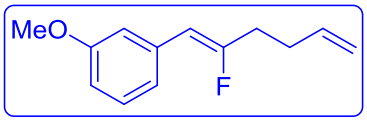
J = 22.5, 8.9 Hz), 113.6 (dd, J = 21.5, 2.1 Hz), 105.4 (dd, J = 8.2, 2.7 Hz), 32.6 (d, J = 26.2 Hz), 30.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.06 (dt, J = 38.1, 16.9 Hz), -113.42 (dd, J = 15.7, 9.7 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}F_2$ $[M+H]^+$ 195.0980, found 195.0982.

(Z)-1-chloro-3-(2-fluorohexa-1,5-dien-1-yl)benzene (4o)



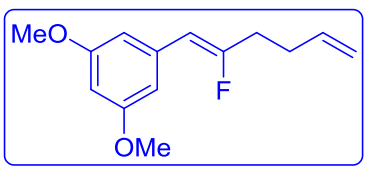
Following the general procedure B (except the reaction was carried out in the presence of 4 mol% $[Rh(CO)_2Cl]_2$, 12 mol% $(4\text{-}CF_3C_6H_4)_3P$, and 10 mol% $AgBF_4$). Isolated yield = 65% (13.7 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.31 (d, J = 7.7 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.18 (dd, J = 8.0, 1.8 Hz, 1H), 5.84 (ddt, J = 16.6, 9.9, 6.3 Hz, 1H), 5.10 (dd, J = 17.1, 1.7 Hz, 1H), 5.04 (dd, J = 10.3, 1.7 Hz, 1H), 2.49 – 2.31 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.3 (d, J = 268.5 Hz), 136.6, 135.4 (d, J = 2.6 Hz), 134.2, 129.6, 128.2 (d, J = 8.3 Hz), 126.7 (d, J = 2.2 Hz), 126.4 (d, J = 7.2 Hz), 115.8, 105.2 (d, J = 8.3 Hz), 32.5 (d, J = 26.3 Hz), 30.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.91 (dt, J = 39.1, 17.4 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}FCl$ $[M+H]^+$ 211.0684, found 211.0683.

(Z)-1-(2-fluorohexa-1,5-dien-1-yl)-3-methoxybenzene (4p)



Following the general procedure B. Isolated yield = 72% (14.8 mg); Colorless oil; R_f = 0.5 (PE:EA=100:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, J = 8.0 Hz, 1H), 7.08 – 7.01 (m, 2H), 6.77 (dd, J = 8.2, 2.7 Hz, 1H), 5.85 (ddt, J = 16.6, 10.4, 6.2 Hz, 1H), 5.46 (d, J = 39.0 Hz, 1H), 5.10 (dd, J = 17.1, 1.6 Hz, 1H), 5.03 (dd, J = 10.3, 1.6 Hz, 1H), 3.80 (s, 3H), 2.48 – 2.32 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5 (d, J = 267.1 Hz), 159.5, 136.8, 135.0 (d, J = 2.4 Hz), 129.3, 115.7, 113.6 (d, J = 8.1 Hz), 112.5, 106.1 (d, J = 8.3 Hz), 55.1, 32.6 (d, J = 26.6 Hz), 30.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.51. **HRMS** (ESI, *m/z*): calcd for $C_{13}H_{15}F_2O$ $[M+H]^+$ 207.1180, found 207.1181.

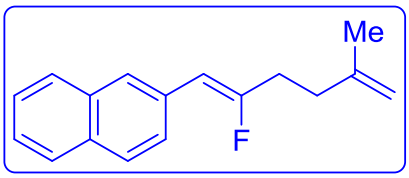
(Z)-1-(2-fluorohexa-1,5-dien-1-yl)-3,5-dimethoxybenzene (4q)



Following the general procedure B. Isolated yield = 72% (17.0 mg); Colorless oil; R_f = 0.5 (PE:EA=20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.65 (d, J = 2.3 Hz, 2H), 6.35 (t, J = 2.3 Hz, 1H), 5.85 (ddt, J = 16.4, 10.1, 6.2 Hz, 1H), 5.42 (d, J = 38.9 Hz, 1H), 5.10 (dq, J = 17.1, 1.6 Hz, 1H), 5.03 (dd, J = 10.2, 1.0 Hz, 1H), 3.79 (s, 6H), 2.47 – 2.41 (m, 1H), 2.40 – 2.32 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6 (d, J = 267.5 Hz), 160.6, 136.8, 135.4 (d, J = 2.6 Hz), 115.7, 106.3 (d, J = 7.7 Hz), 106.2 (d, J = 8.0

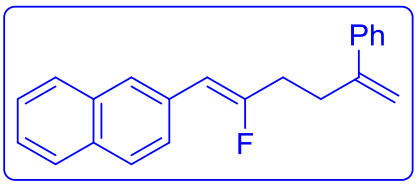
Hz), 99.2 (d, J = 1.8 Hz), 55.3, 32.6 (d, J = 26.5 Hz), 30.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.71 (dt, J = 39.3, 17.4 H z). **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{17}FO_2$ $[M+H]^+$ 237.1285, found 237.1286.

(Z)-2-(2-fluoro-5-methylhexa-1,5-dien-1-yl)naphthalene (4r)



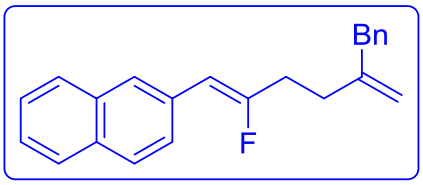
Following the general procedure B. Isolated yield = 92% (22.1 mg); White solid, m.p.: 60.0-60.9 °C; R_f = 0.4 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.78 (td, J = 6.1, 2.7 Hz, 3H), 7.64 (dd, J = 8.6, 1.6 Hz, 1H), 7.49 – 7.37 (m, 2H), 5.64 (d, J = 39.5 Hz, 1H), 4.79 (d, J = 7.5 Hz, 2H), 2.52 (ddd, J = 17.3, 9.3, 6.2 Hz, 2H), 2.41 – 2.31 (m, 2H), 1.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0 (d, J = 267.1 Hz), 144.1, 133.5, 132.2, 131.3 (d, J = 2.7 Hz), 127.9, 127.8, 127.5, 127.0 (d, J = 7.5 Hz), 126.5 (d, J = 7.5 Hz), 126.0, 125.7, 110.9, 106.1 (d, J = 8.6 Hz), 34.5, 31.7 (d, J = 26.7 Hz), 22.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.52. The NMR data match with the reported literature.[9]

(Z)-2-(2-fluoro-5-phenylhexa-1,5-dien-1-yl)naphthalene (5s)



Following the general procedure C. Isolated yield = 80% (24.2 mg); White solid, m.p.: 70.3-71.0 °C; R_f = 0.3 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.83 (dd, J = 7.8, 5.3 Hz, 3H), 7.67 (dd, J = 8.6, 1.8 Hz, 1H), 7.53 – 7.46 (m, 4H), 7.45 – 7.38 (m, 2H), 7.38 – 7.32 (m, 1H), 5.62 (d, J = 39.4 Hz, 1H), 5.39 (d, J = 1.2 Hz, 1H), 5.21 (d, J = 1.3 Hz, 1H), 2.91 (ddd, J = 9.1, 6.0, 1.2 Hz, 2H), 2.57 (ddd, J = 18.1, 8.9, 6.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5 (d, J = 267.0 Hz), 146.8, 140.6, 133.5, 132.2 (d, J = 1.8 Hz), 131.3 (d, J = 2.6 Hz), 128.4, 127.9, 127.8, 127.6, 127.5, 127.0 (d, J = 7.3 Hz), 126.5 (d, J = 7.5 Hz), 126.1, 126.0, 125.7, 113.4, 106.4 (d, J = 8.4 Hz), 32.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.26. The NMR data match with the reported literature.[9]

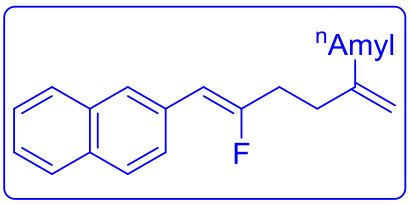
(Z)-2-(5-benzyl-2-fluorohexa-1,5-dien-1-yl)naphthalene (5t)



Following the general procedure B. Isolated yield = 83% (26.2 mg); White solid, m.p.: 79.0-80.3 °C; R_f = 0.3 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.84 – 7.79 (m, 3H), 7.66 (dd, J = 8.6, 1.7 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.30 – 7.24 (m, 3H), 5.62 (d, J = 39.5 Hz, 1H), 4.98 (s, 1H), 4.91 (s, 1H), 3.45 (s, 2H), 2.55 (ddd, J = 17.2, 9.2, 6.2 Hz, 2H), 2.41 – 2.32 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7 (d, J = 267.0 Hz), 147.2, 139.3, 133.5, 132.2 (d, J = 1.8 Hz), 131.3 (d, J = 2.7 Hz), 129.0, 128.4, 127.9, 127.8, 127.5, 127.0, 127.0, 126.6, 126.5, 126.2, 126.0, 125.7,

112.1, 106.1 (d, J = 8.5 Hz), 43.2, 32.0, 31.6 (d, J = 26.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.44. The NMR data match with the reported literature.[9]

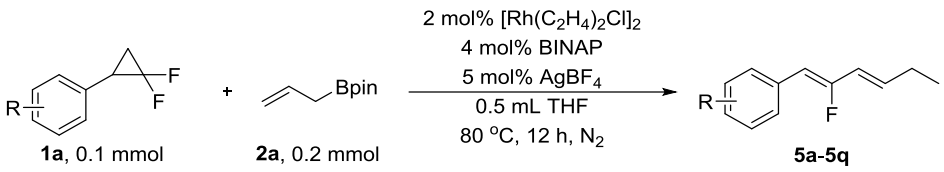
(Z)-2-(2-fluoro-5-methyleneundec-1-en-1-yl)naphthalene (5u)



Following the general procedure B. Isolated yield = 84% (24.9 mg); Colorless oil; R_f = 0.3 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.78 (td, J = 6.1, 5.7, 2.8 Hz, 3H), 7.64 (dd, J = 8.6, 1.7 Hz, 1H), 7.49 – 7.37 (m, 2H), 5.63 (d, J = 39.5 Hz, 1H), 4.80 (s, 2H), 2.51 (ddd, J = 17.1, 9.5, 6.1 Hz, 2H), 2.35 (dd, J = 9.5, 6.1 Hz, 2H), 2.06 (t, J = 7.7 Hz, 2H), 1.52 – 1.40 (m, 2H), 1.32 (dddt, J = 12.6, 9.5, 6.9, 3.5 Hz, 4H), 0.90 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1 (d, J = 267.0 Hz), 148.3, 133.5, 132.2 (d, J = 1.8 Hz), 131.4 (d, J = 2.6 Hz), 127.9, 127.8, 127.5, 127.0 (d, J = 7.5 Hz), 126.5 (d, J = 7.5 Hz), 126.0, 125.7, 109.6, 106.0 (d, J = 8.6 Hz), 36.1, 32.7 (d, J = 1.3 Hz), 31.8 (d, J = 26.5 Hz), 31.6, 27.4, 22.6, 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.36. **HRMS** (ESI, *m/z*): calcd for $C_{21}H_{26}F$ $[M+H]^+$ 297.2013, found 297.2013.

5. Selective Synthesis of Fluorinated 1,3-Dienes

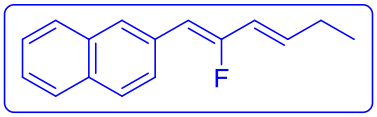
5.1 General Procedure C



In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), BINAP (2.5 mg, 0.004 mmol, 4 mol%), and THF (0.5 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, $AgBF_4$ (1 mg, 0.005 mmol), allylboronate **2a** (33.6 mg, 0.2 mmol), and *gem*-difluorinated cyclopropane (0.1 mmol). Generally, several such type of reactions were carried out parallelly, thus the catalyst solution can be prepared in one vial together. The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 12 hours. The reaction mixture was then cooled to room temperature and purified by chromatography on silica gel column to give the fluorinated 1,3-dienes.

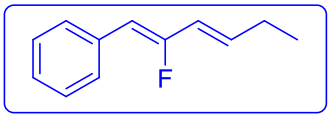
5.2 Characterization Data of Products

2-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)naphthalene (5a)



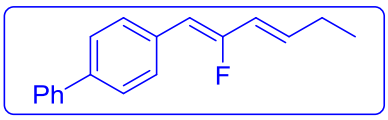
Following the general procedure C. Isolated yield = 68% (15.4 mg); White solid, m.p.: 83.1-84.0 °C; R_f = 0.6 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.81 – 7.75 (m, 3H), 7.68 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.46 – 7.40 (m, 2H), 6.24 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.96 (ddt, *J* = 25.8, 15.5, 1.6 Hz, 1H), 5.70 (d, *J* = 38.7 Hz, 1H), 2.26 – 2.18 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 260.4 Hz), 134.7 (d, *J* = 3.8 Hz), 133.5, 132.3, 131.7 (d, *J* = 3.1 Hz), 128.0, 127.9, 127.6, 127.5, 126.7 (d, *J* = 7.8 Hz), 126.1, 125.9, 121.9 (d, *J* = 23.0 Hz), 108.0 (d, *J* = 9.6 Hz), 25.5, 13.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.34 (dd, *J* = 38.4, 25.6 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{15}F$ $[M+H]^+$ 227.1231, found 227.1238.

((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)benzene (5b)



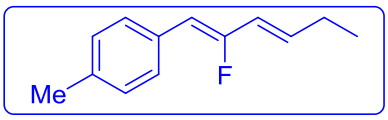
Following the general procedure C. Isolated yield = 51% (8.8 mg); Colorless oil; R_f = 0.6 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.18 (m, 1H), 6.20 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.92 (ddt, *J* = 25.7, 15.6, 1.6 Hz, 1H), 5.56 (d, *J* = 38.7 Hz, 1H), 2.25 – 2.16 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.0 (d, *J* = 260.2 Hz), 134.5 (d, *J* = 3.7 Hz), 134.0 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 7.6 Hz), 128.5, 126.9 (d, *J* = 2.3 Hz), 121.8 (d, *J* = 23.1 Hz), 107.8 (d, *J* = 9.7 Hz), 25.5, 13.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.83 (dd, *J* = 38.7, 25.3 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{13}F$ $[M+H]^+$ 177.1074, found 177.1076.

4-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)-1,1'-biphenyl (5c)



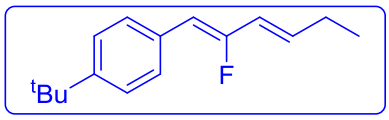
Following the general procedure C. Isolated yield = 59% (14.9 mg); White solid, m.p.: 77.5-79.0 °C; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 6H), 7.44 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.37 – 7.32 (m, 1H), 6.22 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.95 (ddt, *J* = 25.8, 15.6, 1.6 Hz, 1H), 5.60 (d, *J* = 38.7 Hz, 1H), 2.27 – 2.18 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1 (d, *J* = 260.5 Hz), 140.7, 139.5, 134.6 (d, *J* = 3.6 Hz), 133.2 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 7.7 Hz), 128.8, 127.3, 127.1, 126.9, 121.8 (d, *J* = 22.8 Hz), 107.5 (d, *J* = 9.8 Hz), 25.5, 13.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.34 (dd, *J* = 39.0, 26.3 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{17}F$ $[M+H]^+$ 253.1387, found 253.1394.

1-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)-4-methylbenzene (5d)



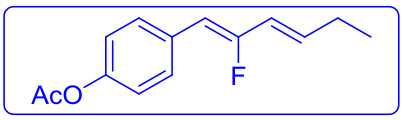
Following the general procedure C. Isolated yield = 38% (7.3 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.15 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.90 (ddt, *J* = 25.8, 15.5, 1.5 Hz, 1H), 5.52 (d, *J* = 39.0 Hz, 1H), 2.33 (s, 3H), 2.24 – 2.15 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5 (d, *J* = 259.1 Hz), 136.8 (d, *J* = 2.2 Hz), 133.9 (d, *J* = 3.8 Hz), 131.2 (d, *J* = 2.9 Hz), 129.2, 128.5 (d, *J* = 7.6 Hz), 121.9 (d, *J* = 23.1 Hz), 107.8 (d, *J* = 10.0 Hz), 25.5, 21.2, 13.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.64 (dd, *J* = 38.7, 25.4 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{13}H_{15}F$ $[M+H]^+$ 191.1231, found 191.1233.

1-(tert-butyl)-4-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)benzene (5e)



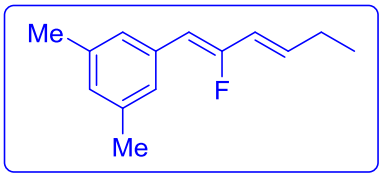
Following the general procedure C. Isolated yield = 55% (12.8 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.16 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.91 (ddt, *J* = 25.8, 15.6, 1.5 Hz, 1H), 5.54 (d, *J* = 39.0 Hz, 1H), 2.25 – 2.16 (m, 2H), 1.31 (s, 9H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6 (d, *J* = 258.7 Hz), 150.0, 134.0 (d, *J* = 3.7 Hz), 131.2, 128.4 (d, *J* = 7.5 Hz), 125.4, 121.9 (d, *J* = 23.2 Hz), 107.6 (d, *J* = 10.1 Hz), 34.6, 31.2, 25.5, 13.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.73 (dd, *J* = 38.6, 25.6 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{21}F$ $[M+H]^+$ 233.1700, found 233.1703.

4-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)phenyl acetate (5f)



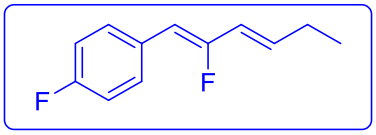
Following the general procedure C. Isolated yield = 85% (19.9 mg); Colorless oil; R_f = 0.4 (PE:EA=20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.19 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.91 (ddt, *J* = 25.8, 15.6, 1.6 Hz, 1H), 5.54 (d, *J* = 38.3 Hz, 1H), 2.29 (s, 3H), 2.25 – 2.16 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 156.9 (d, *J* = 260.1 Hz), 149.3, 134.7 (d, *J* = 3.7 Hz), 131.9, 129.6 (d, *J* = 7.9 Hz), 121.8, 121.6, 106.9 (d, *J* = 9.7 Hz), 25.5, 21.1, 13.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.27 (dd, *J* = 38.2, 26.1 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{15}FO_2$ $[M+Na]^+$ 257.0948, found 257.0951.

1-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)-3,5-dimethylbenzene (5g)



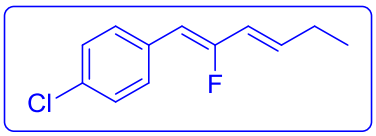
Following the general procedure C. Isolated yield = 54% (11.1 mg); Colorless oil; R_f = 0.4 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (s, 2H), 6.86 (s, 1H), 6.16 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.99 – 5.82 (m, 1H), 5.49 (d, *J* = 39.0 Hz, 1H), 2.30 (s, 6H), 2.20 (p, *J* = 7.2, 6.8 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.7 (d, *J* = 259.6 Hz), 137.8, 134.1 (d, *J* = 3.7 Hz), 133.8 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 2.4 Hz), 126.4 (d, *J* = 7.3 Hz), 121.9 (d, *J* = 23.1 Hz), 108.0 (d, *J* = 9.6 Hz), 25.5, 21.3, 13.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.89 (dd, *J* = 38.9, 25.5 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{17}F$ $[M+H]^+$ 205.1387, found 205.1391.

1-fluoro-4-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)benzene (5h)



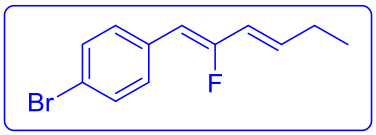
Following the general procedure C. Isolated yield = 72% (14.0 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.00 (t, *J* = 8.8 Hz, 2H), 6.18 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.89 (ddt, *J* = 25.9, 15.6, 1.6 Hz, 1H), 5.51 (d, *J* = 38.4 Hz, 1H), 2.25 – 2.16 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6 (dd, *J* = 247.3, 3.6 Hz), 156.6 (dd, *J* = 259.2, 2.5 Hz), 134.6 (d, *J* = 3.8 Hz), 130.2 (d, *J* = 15.8 Hz), 130.2, 121.6 (d, *J* = 23.0 Hz), 115.4 (d, *J* = 21.4 Hz), 106.7 (d, *J* = 9.9 Hz), 25.5, 13.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.32 (tt, *J* = 9.1, 5.5 Hz), -118.07 (dd, *J* = 38.1, 26.1 Hz). The HRMS was not satisfied, and the result of LRMS was obtained for this compound. **LRMS** (EI) m/z: 194 (M+, 60), 179 (30), 165 (100), 159 (30), 133 (30), 109 (15).

1-chloro-4-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)benzene (5i)



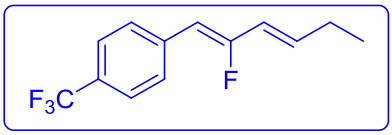
Following the general procedure C. Isolated yield = 78% (16.4 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.21 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.90 (ddt, *J* = 25.9, 15.5, 1.5 Hz, 1H), 5.51 (d, *J* = 38.3 Hz, 1H), 2.25 – 2.16 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 260.9 Hz), 135.2 (d, *J* = 3.8 Hz), 132.5 (d, *J* = 3.1 Hz), 132.4 (d, *J* = 3.6 Hz), 129.8 (d, *J* = 7.7 Hz), 128.6, 121.5 (d, *J* = 22.7 Hz), 106.6 (d, *J* = 9.6 Hz), 25.5, 13.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.13 (dd, *J* = 38.3, 25.9 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}FCl$ $[M+H]^+$ 211.0684, found 211.0687.

1-bromo-4-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)benzene (5j)



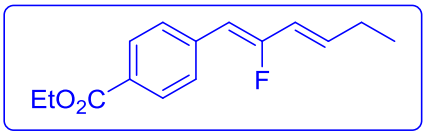
Following the general procedure C. Isolated yield = 73% (18.4 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 6.22 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.90 (ddd, *J* = 25.9, 15.6, 1.1 Hz, 1H), 5.49 (d, *J* = 38.2 Hz, 1H), 2.25 – 2.16 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.4 (d, *J* = 261.1 Hz), 135.3 (d, *J* = 3.8 Hz), 133.0 (d, *J* = 3.0 Hz), 131.6, 130.1 (d, *J* = 8.1 Hz), 121.5 (d, *J* = 22.8 Hz), 120.6 (d, *J* = 3.5 Hz), 106.7 (d, *J* = 9.7 Hz), 25.5, 13.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.19 (dd, *J* = 38.1, 25.8 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}FBr$ $[M+H]^+$ 255.0179, found 255.0182.

1-bromo-4-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)benzene (5k)



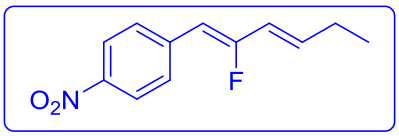
Following the general procedure C. Isolated yield = 68% (16.6 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 6.27 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.92 (ddt, *J* = 25.7, 15.5, 1.6 Hz, 1H), 5.58 (d, *J* = 37.9 Hz, 1H), 2.26 – 2.17 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.33 (d, *J* = 262.8 Hz), 137.60, 136.37 (d, *J* = 4.0 Hz), 128.61 (d, *J* = 8.0 Hz), 125.35 (q, *J* = 3.9 Hz), 124.20 (q, *J* = 271.9 Hz), 121.52, 121.29, 106.52 (d, *J* = 9.3 Hz), 25.53, 12.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.41, -113.97 (dd, *J* = 38.0, 25.9 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{13}H_{12}F_4$ $[M+H]^+$ 245.0948, found 245.0956.

ethyl 4-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)benzoate (5l)



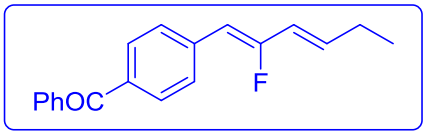
Following the general procedure C. Isolated yield = 88% (21.8 mg); Pale yellow oil; R_f = 0.4 (PE:EA=100:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 6.28 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.94 (ddd, *J* = 25.7, 15.6, 1.5 Hz, 1H), 5.60 (d, *J* = 38.2 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.23 (dt, *J* = 14.8, 7.3 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 158.3 (d, *J* = 263.3 Hz), 138.6 (d, *J* = 2.6 Hz), 136.2 (d, *J* = 3.9 Hz), 129.7, 128.4 (d, *J* = 2.6 Hz), 128.3 (d, *J* = 8.1 Hz), 121.5 (d, *J* = 22.8 Hz), 107.1 (d, *J* = 9.3 Hz), 60.9, 25.5, 14.3, 13.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.45 (dd, *J* = 38.5, 25.6 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{17}FO_2$ $[M+H]^+$ 249.1285, found 249.1290.

1-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)-4-nitrobenzene (5m)



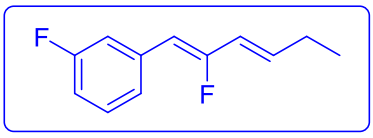
Following the general procedure C. Isolated yield = 88% (19.5 mg); Yellow oil; R_f = 0.4 (PE:EA=10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 2H), 6.36 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.96 (ddt, *J* = 25.8, 15.6, 1.7 Hz, 1H), 5.64 (d, *J* = 37.4 Hz, 1H), 2.25 (dtd, *J* = 14.6, 7.4, 1.6 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4 (d, *J* = 266.0 Hz), 145.9, 140.8 (d, *J* = 3.1 Hz), 138.0 (d, *J* = 4.0 Hz), 128.9 (d, *J* = 8.5 Hz), 123.8, 121.2 (d, *J* = 22.3 Hz), 106.0 (d, *J* = 9.2 Hz), 25.6, 12.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.63 (dd, *J* = 37.4, 25.5 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}FNO_2$ $[M+Na]^+$ 244.0744, found 244.0750.

1-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)-4-nitrobenzene (5n)



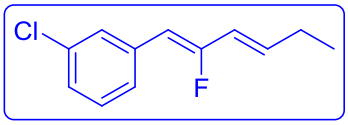
Following the general procedure C. Isolated yield = 68% (19.0 mg); Pale yellow oil; R_f = 0.3 (PE:EA=100:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (ddd, *J* = 8.6, 3.5, 1.6 Hz, 4H), 7.63 – 7.57 (m, 3H), 7.51 – 7.46 (m, 2H), 6.30 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.96 (ddt, *J* = 25.8, 15.6, 1.6 Hz, 1H), 5.64 (d, *J* = 38.2 Hz, 1H), 2.28 – 2.19 (m, 2H), 1.09 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.1, 158.5 (d, *J* = 263.8 Hz), 138.4 (d, *J* = 3.3 Hz), 137.8, 136.4 (d, *J* = 3.9 Hz), 135.4 (d, *J* = 2.4 Hz), 132.3, 130.5, 129.9, 128.3, 128.2, 121.5 (d, *J* = 22.7 Hz), 107.0 (d, *J* = 9.2 Hz), 25.6, 13.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.20 (dd, *J* = 37.5, 25.5 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{19}H_{17}FO$ $[M+Na]^+$ 303.1156, found 303.1166.

1-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)-4-nitrobenzene (5o)



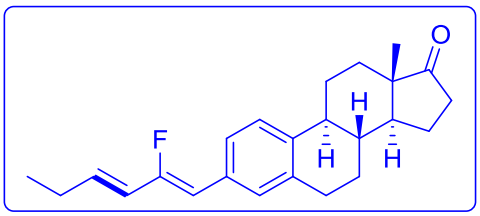
Following the general procedure C. Isolated yield = 73% (14.2 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (td, *J* = 13.9, 13.1, 8.0 Hz, 3H), 6.90 (td, *J* = 7.5, 2.1 Hz, 1H), 6.23 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.90 (ddt, *J* = 25.8, 15.6, 1.6 Hz, 1H), 5.52 (d, *J* = 37.9 Hz, 1H), 2.25 – 2.16 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 244.2 Hz), 157.8 (d, *J* = 261.5 Hz), 136.2 (dd, *J* = 8.6, 3.1 Hz), 135.7 (d, *J* = 3.8 Hz), 129.9 (d, *J* = 8.6 Hz), 124.5 (dd, *J* = 6.8, 2.9 Hz), 121.6 (d, *J* = 22.8 Hz), 115.2 (dd, *J* = 22.6, 9.2 Hz), 113.9 (dd, *J* = 21.3, 2.3 Hz), 106.9 (dd, *J* = 9.4, 2.8 Hz), 25.6, 13.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.32 (q, *J* = 9.1, 8.6 Hz), -115.05 (dd, *J* = 37.7, 25.8 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}F_2$ $[M+H]^+$ 195.0980, found 195.0982.

1-chloro-3-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)benzene (5p)



Following the general procedure C. Isolated yield = 77% (16.2 mg); Colorless oil; R_f = 0.5 (PE). **^{1}H NMR** (400 MHz, CDCl3) δ 7.51 (s, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.19 – 7.15 (m, 1H), 6.23 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.90 (ddt, *J* = 25.8, 15.6, 1.6 Hz, 1H), 5.49 (d, *J* = 38.0 Hz, 1H), 2.25 – 2.16 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7 (d, *J* = 261.9 Hz), 135.8 (d, *J* = 2.9 Hz), 135.7 (d, *J* = 3.9 Hz), 134.3, 129.6, 128.4 (d, *J* = 8.5 Hz), 126.8 (d, *J* = 2.2 Hz), 126.7 (d, *J* = 7.6 Hz), 121.4 (d, *J* = 22.7 Hz), 106.5 (d, *J* = 9.6 Hz), 25.5, 13.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.88 (dd, *J* = 38.0, 26.0 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{12}FCl$ $[M+H]^+$ 211.0684, found 211.0684.

(8R,9S,13S,14S)-3-((1Z,3E)-2-fluorohexa-1,3-dien-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5q)

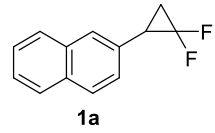


Following the general procedure C. Isolated yield = 52% (18.3 mg); Pale yellow solid, m.p.: 118.6-119.3 °C; R_f = 0.4 (PE). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 2H), 6.16 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.91 (dd, *J* = 25.9, 15.6 Hz, 1H), 5.50 (d, *J* = 39.0 Hz, 1H), 2.91 (dd, *J* = 8.7, 4.0 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.45 – 2.40 (m, 1H), 2.31 (dd, *J* = 10.1, 3.8 Hz, 1H), 2.20 (ddd, *J* = 12.0, 6.5, 5.0 Hz, 2H), 2.16 – 2.07 (m, 1H), 2.07 – 2.00 (m, 2H), 1.99 – 1.94 (m, 1H), 1.64 – 1.40 (m, 6H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.91 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.40 (dd, *J* = 39.1, 25.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.1, 156.7 (d, *J* = 259.4 Hz), 138.7 (d, *J* = 1.8 Hz), 136.5, 134.1 (d, *J* = 3.5 Hz), 131.6 (d, *J* = 2.8 Hz), 129.1 (d, *J* = 7.3 Hz), 126.1 (d, *J* = 7.5 Hz), 125.5, 121.8 (d, *J* = 22.9 Hz), 107.5 (d, *J* = 9.8 Hz), 50.4, 48.0, 44.4, 38.1, 35.8, 31.5, 29.4, 26.5, 25.6, 25.5, 21.5, 13.8, 13.1. **HRMS** (ESI, *m/z*): calcd for $C_{24}H_{29}FO$ $[M+Na]^+$ 375.2095, found 375.2104.

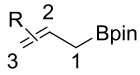
6. The Reactivity of Substituted Allylboronates

We tested the reactivity of other allylboronates such as 1-, 2-, and 3-substituted allyl-Bpin under the three reaction conditions (Table S1). 3-Substituted allyl-Bpin and 1,1-disubsituted allyl-Bpin were not reactive under all the three reaction conditions, probably due to the increasing steric hindrance. The 2-substituted allyl-Bpin with methyl, phenyl, benzyl, or n-amyl groups could undergo smoothly this transformation to afford the corresponding fluorinated 1,5-dienes in excellent yields.

Table S1 The reactivity of allylboronates



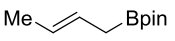
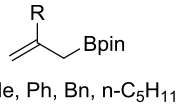
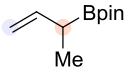
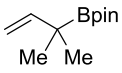
1a



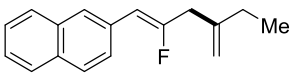
2

Procedure A, B, or C → **Flourinated 1,n-dienes**

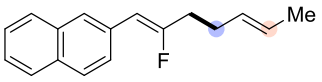
Allylboronates

				
		R=Me, Ph, Bn, n-C_5H_{11}		
Procedure A internal selectivity (1,4-dienes)	trace	—	**3r**, 20% yield	n.d.
Procedure B terminal selectivity (1,5-dienes)	trace	**4r-4u** 82%-92% yield	58% yield **4v**:**4v'** 3.3 :1	trace
Procedure C isomerized terminal selectivity (1,3-dienes)	trace	50% yield **13a:13b:13c** **1.5:1:4**	10% yield a mixture of **4v** and **4v'** 1,3-diene was not detected	trace

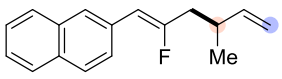
Flourinated 1,n-dienes



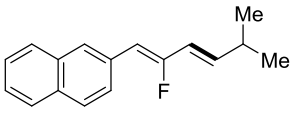
3r



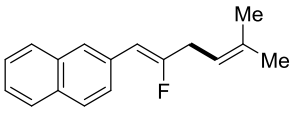
4v, linear-linear product



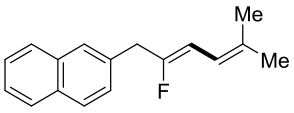
4v', linear-branched product



13a



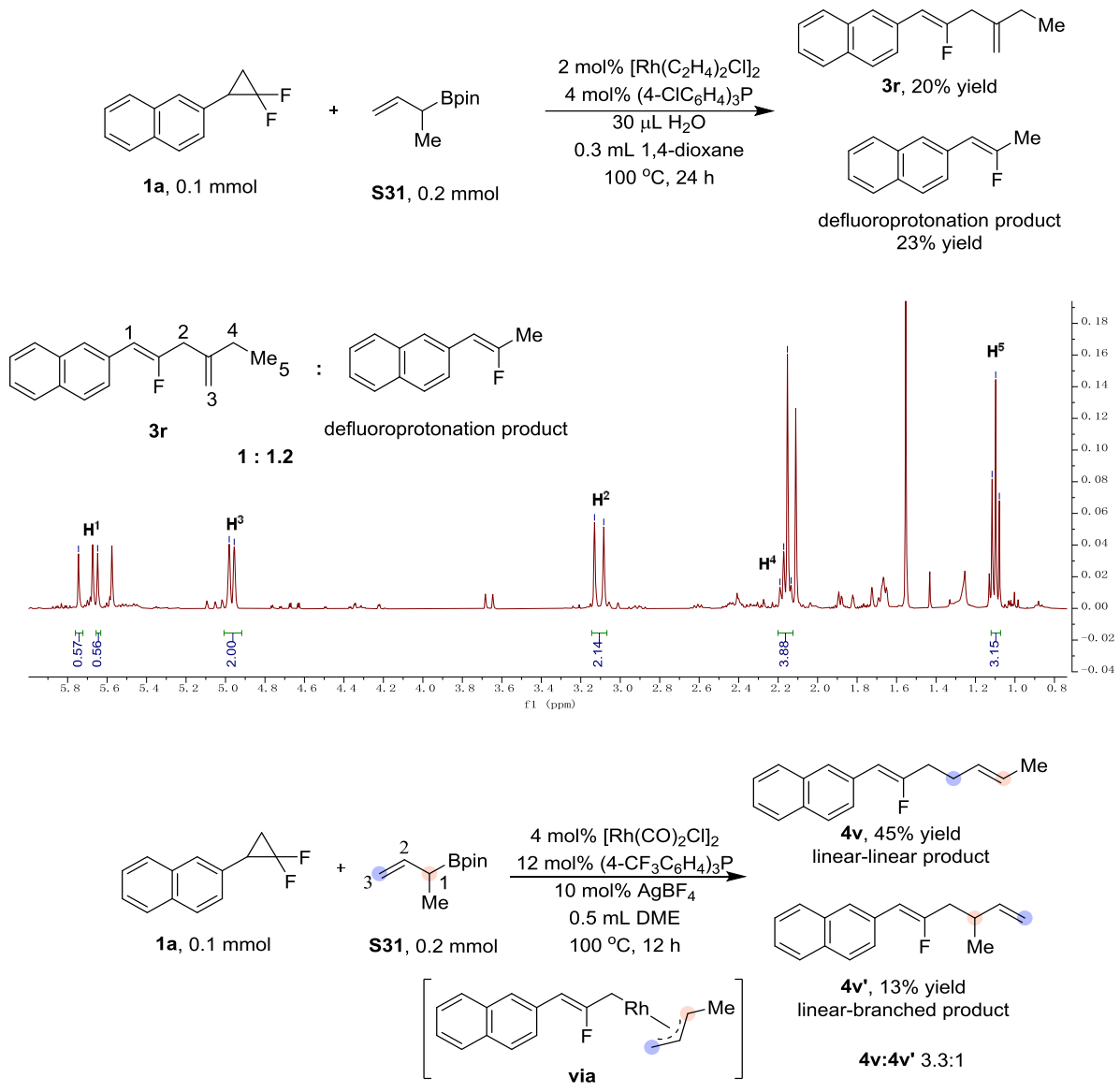
13b



13c

Next, the reactions of 1-methyl-substituted allyl-Bpin **S31** with *gem*-difluorinated cyclopropane **1a** were studied extensively under the three types of reaction conditions. Following the general procedure A, the 1,4-diene **3r** and defluoroprotonation product were inseparable and isolated together. We recognized **3r** as the desired 1,4-diene product based on the typical coupling pattern in the ^{1}H NMR spectrum and ^{19}F NMR of the mixture: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.70 (d, *J* = 38.8 Hz, 1H), 4.97 (d, *J* = 10.1 Hz, 2H), 3.11 (d, *J* = 18.8 Hz, 2H), 2.16 (q, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.28 (dt, *J* = 38.4, 18.9 Hz). In this reaction, we can observe the

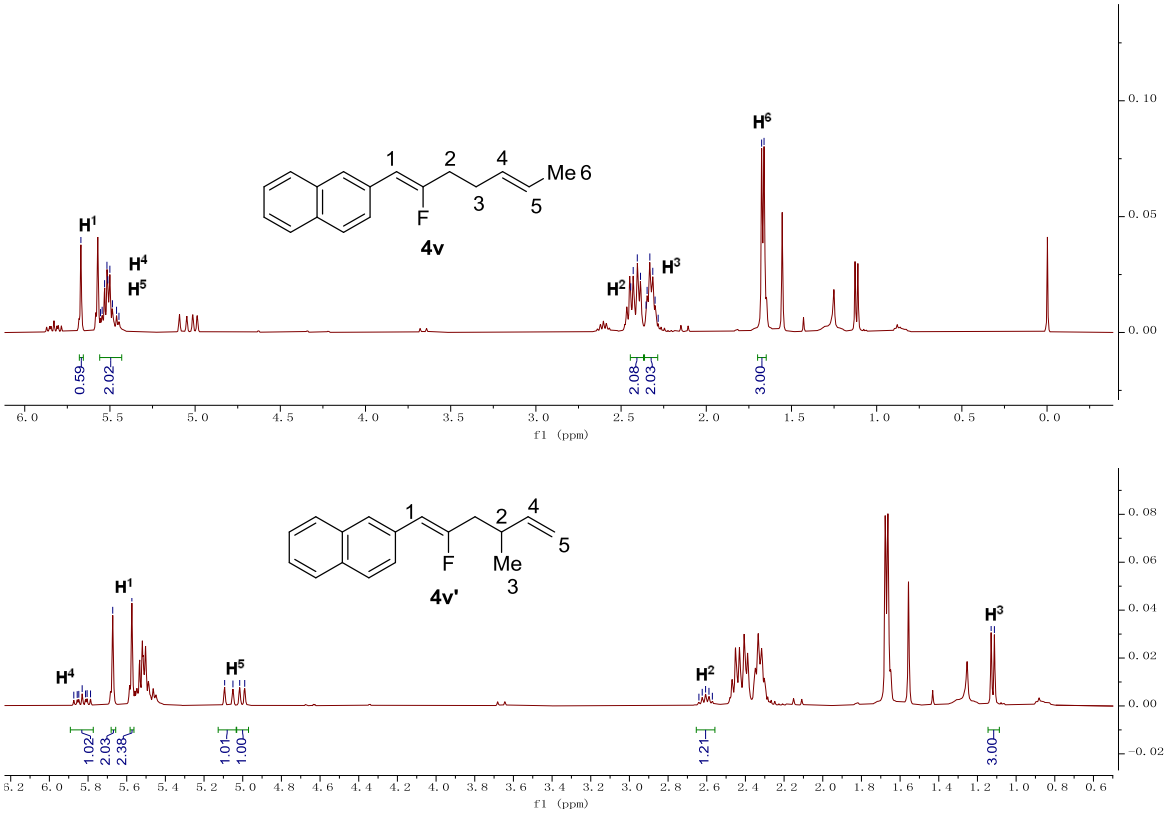
defluoroprotonation product in 23% yield and the adjusted yield of **3r** is 20% yield.



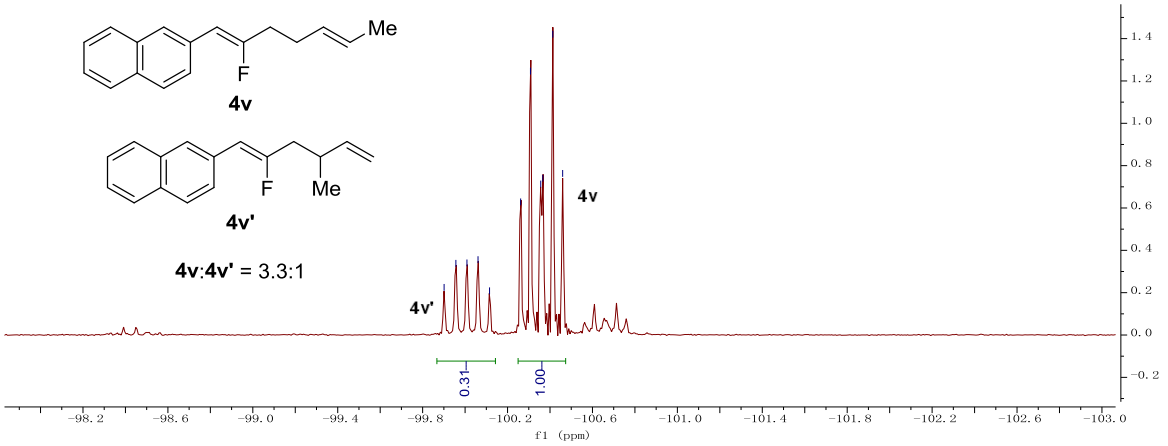
Following the general procedure B (except the reaction was carried out in the presence of 4 mol% $[Rh(CO)_2Cl]_2$, 12 mol% $(4\text{-}CF_3C_6H_4)_3P$, and 10 mol% $AgBF_4$), the linear-linear product **4v** and linear-branched product **4v'** were inseparable and isolated together in 58% combined yields with 3.3:1 site-selectivity, which were based on the typical coupling pattern of terminal olefin and methyl moiety in the ^1H NMR spectrum of the mixture: 1,5-diene **4v**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.62 (H^1, d, J = 39.6 Hz, 1H), 5.56 – 5.43 (m, 2H), 2.45 – 2.38 (m, 2H), 2.32 (dt, J = 12.6, 6.8 Hz, 2H), 1.67 (d, J = 5.6 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.36 (dt, J = 38.9, 17.5 Hz); 1,5-diene **4v'** :**^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.83 (ddd, J = 17.3, 10.3, 7.1 Hz, 1H), 5.62 (d, J = 39.6 Hz, 1H), 5.07 (d, J = 17.2 Hz, 1H), 5.00 (d, J = 10.3 Hz, 1H), 2.61 (dt, J = 14.0, 7.0 Hz, 1H), 1.12 (d, J = 6.7 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.01 (dt, J = 40.0, 20.6 Hz). This result indicates that the formation of

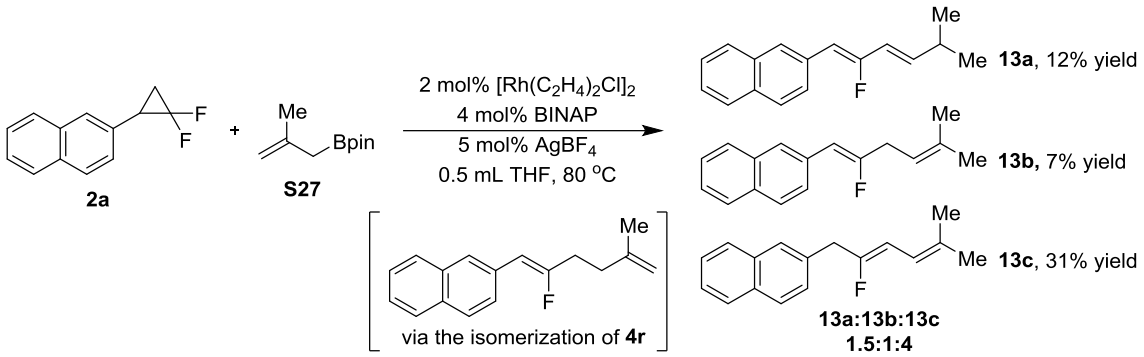
the (η^3-allyl)Rh species from allyl-Bpin in these reactions was involved, where the reductive elimination prefers to occur at sterically less hindered site of the allyl moiety. In the presence of cationic rhodium/BINAP (Procedure C for 1,3-dienes), the reaction gave 1,5-diene **4v** and **4v'** in 10% combined yields, which could not undergo alkene migration to give 1,3-diene. The possible reason was the increasing steric hindrance form the methyl group, resulting in that the formation of the π-allyl species is difficult via C–H bond activation at the allylic position.

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4v and 4v' (With JEOL)

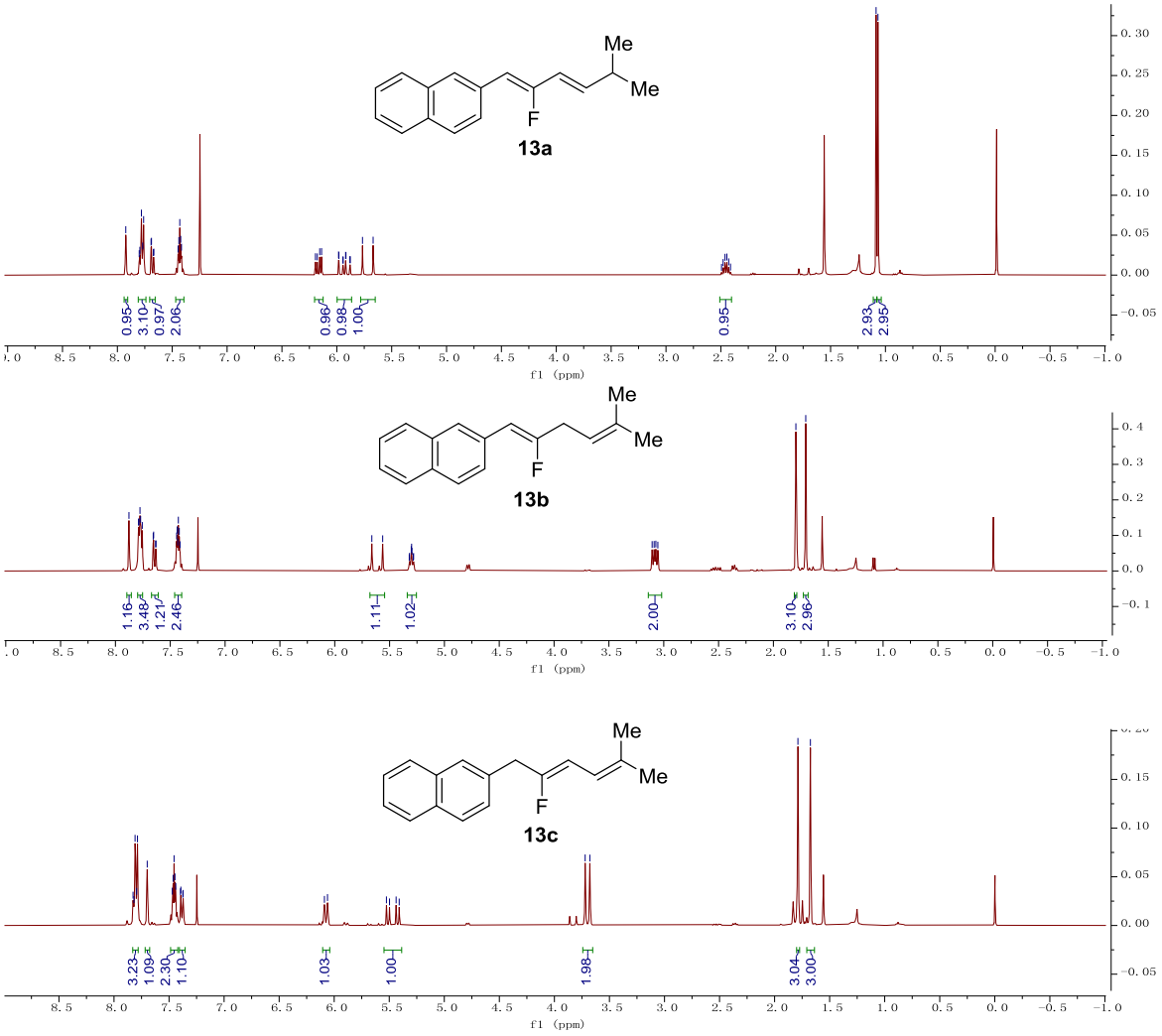


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4v and 4v' (With JEOL)



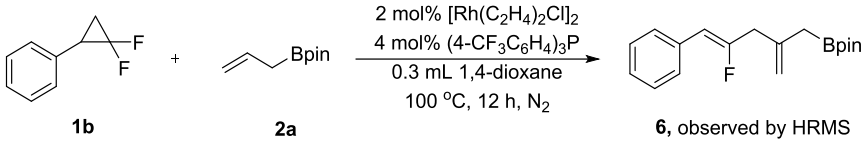


Following the general procedure C, three different products were obtained in the ratio of 1.5:1:4. The 1,3-diene **13a** and 1,4-diene **13b** were produced by two allylic isomerization processes and one allylic isomerization process via a π-allyl pathway, respectively. The 1,4-diene **13b** undergo a second migratory process in the direction of disubstituted alkene to give another conjugate 1,3-diene **13c**.



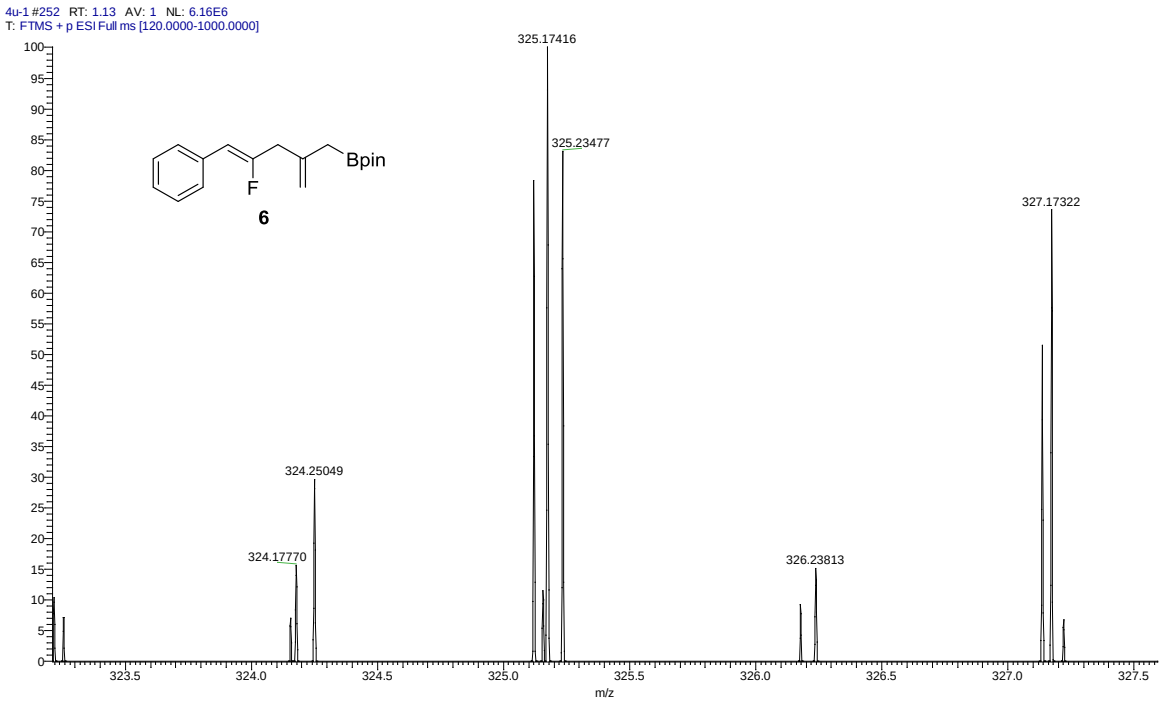
7. Mechanistic Investigations

Experiment A

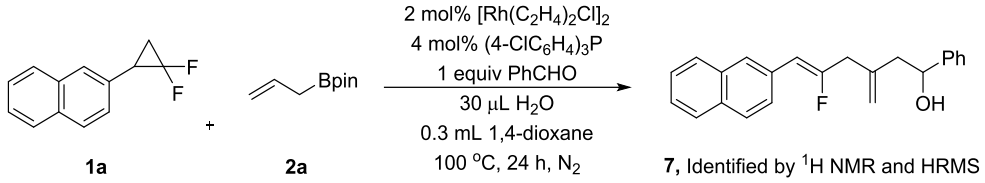


1b **2a** **6,** observed by HRMS

In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_2)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), $(4\text{-}CF_3C_6H_4)_3P$ (1.8 mg, 0.004 mmol, 4 mol%), and 1,4-dioxane (0.3 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, *gem*-difluorinated cyclopropane (0.1 mmol) and allylboronate (0.2 mmol). The 4 mL vial was sealed and removed from the glove box and stirred at 100 °C for 12 hours. After completion of the reaction, the dienyl-Bpin **6** can be detected by GC-MS analysis, which was further supported by HRMS. **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{24}BFO_2$ $[M+Na]^+$ 325.1746, found 325.1742. In addition, we have tried to employ extra bases to trap the by-product HF, whether it can promote the formation of the product **6**. However, with the addition of extra base, the reactions were suppressed to a great extent and the product **3a** and product **6** were not detected. Many kinds of bases, such as ^{t}BuOK, MeONa, KOH, K_2CO_3, Et_3N, were not compatible in this transformation.



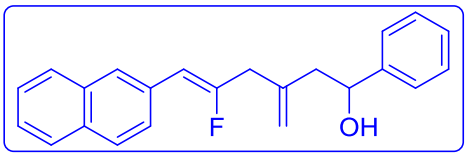
Experiment B



1a **2a** **7,** Identified by ^{1}H NMR and HRMS

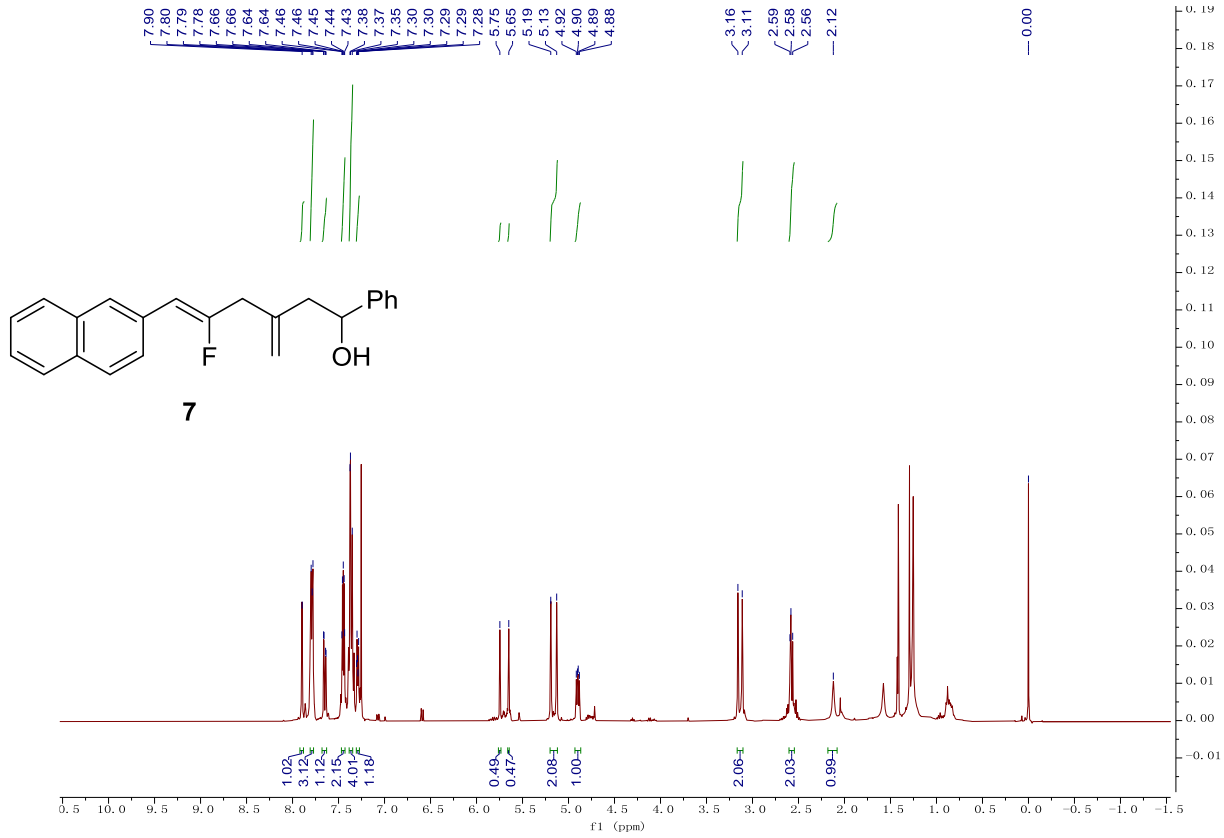
In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_2)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), $(4\text{-}ClC_6H_4)_3P$ (1.5 mg, 0.004 mmol, 4 mol%), and 1,4-dioxane (0.3 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, *gem*-difluorinated cyclopropane (0.1 mmol), allylboronate (0.2 mmol), PhCHO (10.6 mg, 0.1 mmol), and H_2O (0.03 mL). The 4 mL vial was sealed and removed from the glove box and stirred at 100 °C for 24 hours. The reaction mixture was cooled to room temperature and purified by chromatography on silica gel column to give the allylation product **7**, which was analyzed by ^{1}H NMR and HRMS to ensure the structure (there are other unknown products were inseparable with **7**).

(Z)-5-fluoro-3-methylene-6-(naphthalen-2-yl)-1-phenylhex-5-en-1-ol (7)

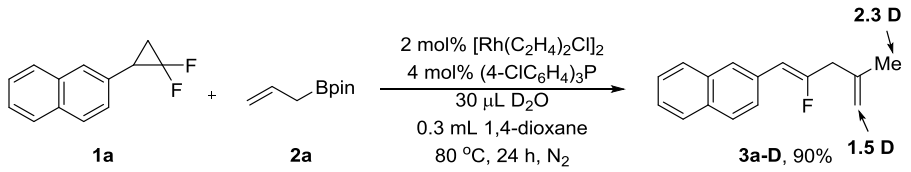


R_f = 0.2 (PE:EA=10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.85 – 7.76 (m, 3H), 7.65 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.39 – 7.34 (m, 4H), 7.31 – 7.28 (m, 1H), 5.70 (d, *J* = 38.7 Hz, 1H), 5.16 (d, *J* = 25.7 Hz, 2H), 4.90 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.14 (d, *J* = 18.9 Hz, 2H), 2.60 – 2.56 (m, 2H), 2.12 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.70 (dt, *J* = 37.7, 18.6 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{23}H_{21}FO$ $[M+Na]^+$ 355.1469, found 355.1468.

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7 (With JEOL)

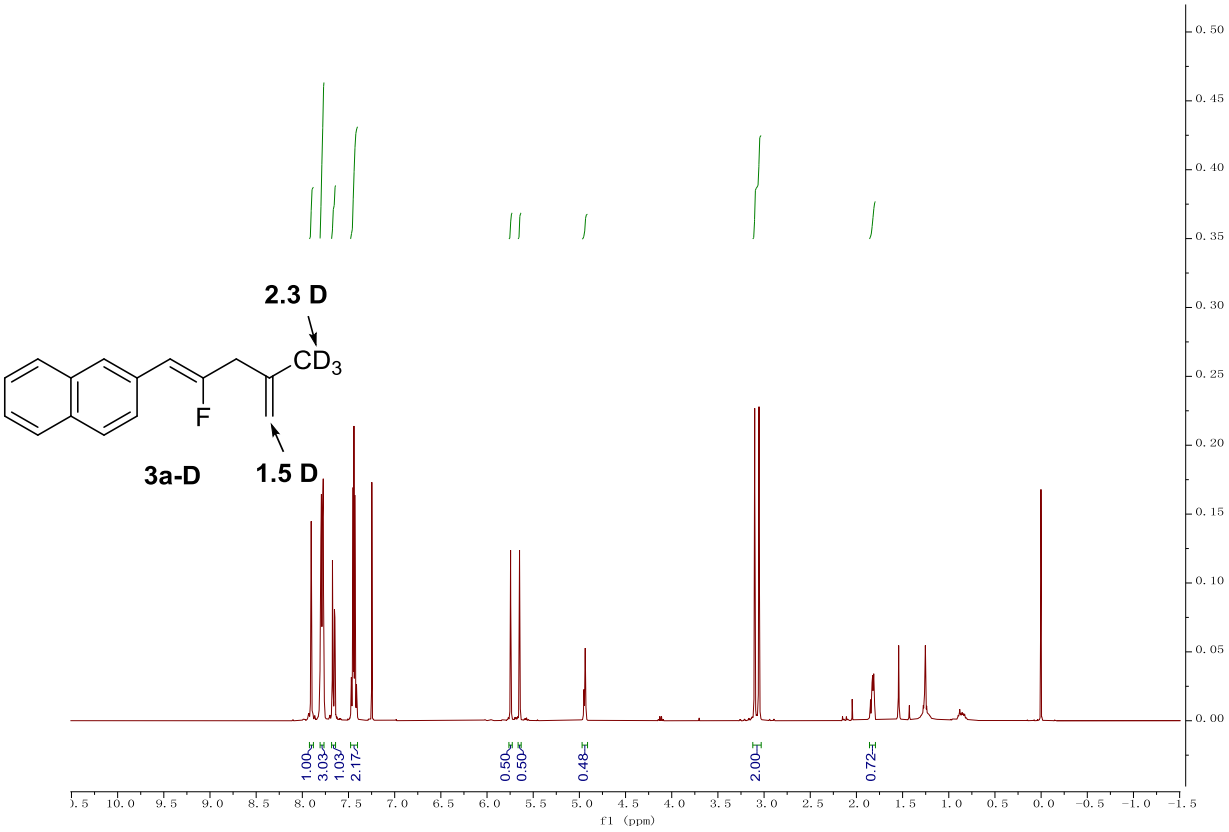


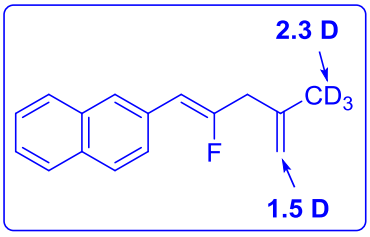
Experiment C



In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_2)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), $(4\text{-}ClC_6H_4)_3P$ (1.5 mg, 0.004 mmol, 4 mol%), and 1,4-dioxane (0.3 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, *gem*-difluorinated cyclopropane (0.1 mmol), allylboronate (0.2 mmol), and D_2O (0.03 mL). The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 24 hours. The reaction mixture was cooled to room temperature and purified by chromatography on silica gel column to give the desired product **3a-D** in 90% yield.

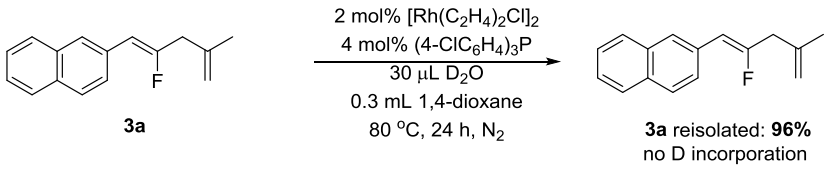
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a-D (With JEOL)





^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.79 (dd, J = 7.1, 3.3 Hz, 3H), 7.66 (dd, J = 8.6, 1.8 Hz, 1H), 7.47 – 7.41 (m, 2H), 5.69 (d, J = 38.8 Hz, 1H), 4.94 (d, J = 5.6 Hz, 0.48H), 3.08 (d, J = 18.7 Hz, 2H), 1.86 – 1.79 (m, 0.72H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.40 (dt, *J* = 37.8, 18.7 Hz).

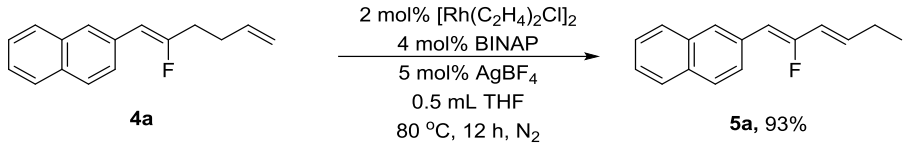
Experiment D



In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_2)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), $(4\text{-}ClC_6H_4)_3P$ (1.5 mg, 0.004 mmol, 4 mol%), and 1,4-dioxane (0.3 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, **3a** (22.6 mg, 0.1 mmol) and D_2O (0.03 mL). The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 24 hours. The reaction mixture was cooled to room temperature and purified by chromatography on silica

gel column to give the desired product **3a**, which was analyzed by ^{1}H NMR indicating no D incorporation.

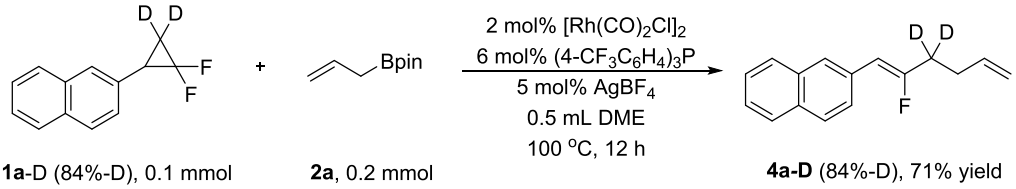
Experiment E



4a **5a,** 93%

In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), BINAP (2.5 mg, 0.004 mmol, 4 mol%), and THF (0.5 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, $AgBF_4$ (1 mg, 0.005 mmol) and **4a** (22.6 mg, 0.1 mmol). The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 12 hours. The reaction mixture was then cooled to room temperature and purified by chromatography on silica gel column to give product **5a** in 93% yield and 100% conversion.

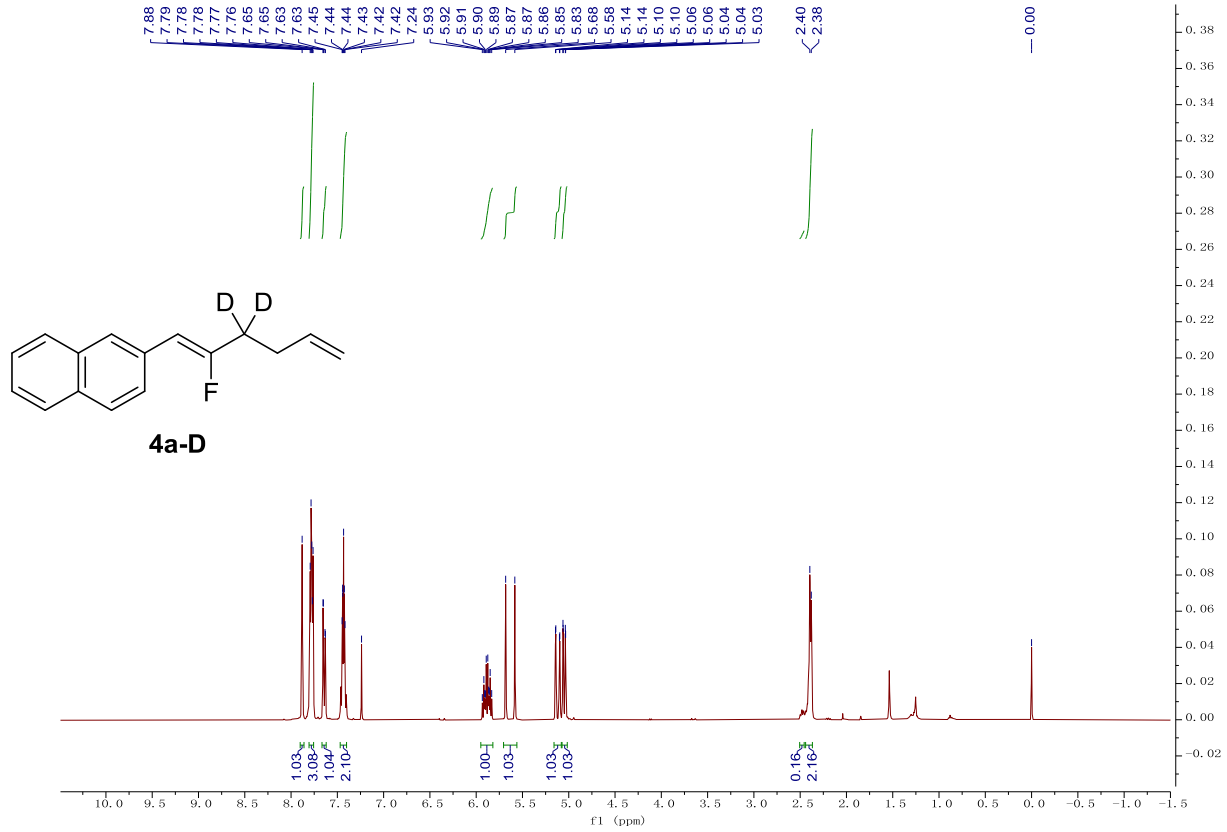
Experiment F: Deuterium Labelling Experiments

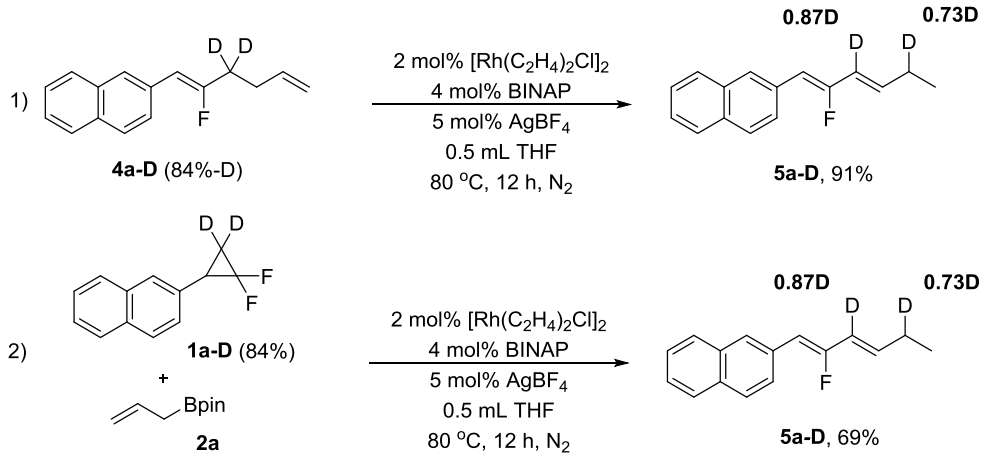


1a-D (84%-D), 0.1 mmol **2a**, 0.2 mmol **4a-D** (84%-D), 71% yield

In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(CO)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), $(4\text{-}CF_3C_6H_4)_3P$ (2.8 mg, 0.006 mmol, 6 mol%), and DME (0.5 mL). The mixture was stirred for about 10 min, which afforded a yellow homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, $AgBF_4$ (1 mg, 0.005 mmol), *gem*-difluorinated cyclopropane **1a-D** (0.1 mmol) and allylboronate **2a** (33.6 mg, 0.2 mmol). The 4 mL vial was sealed and removed from the glove box and stirred at 100 °C for 12 hours. The reaction mixture was cooled to room temperature and purified by chromatography on silica gel column to give the fluorinated 1,5-dienes **4a**-D in 71% yield.

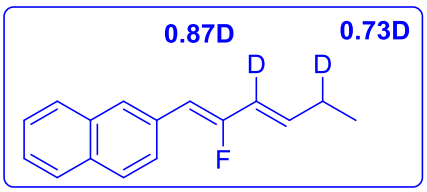
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4a-D (With JEOL)





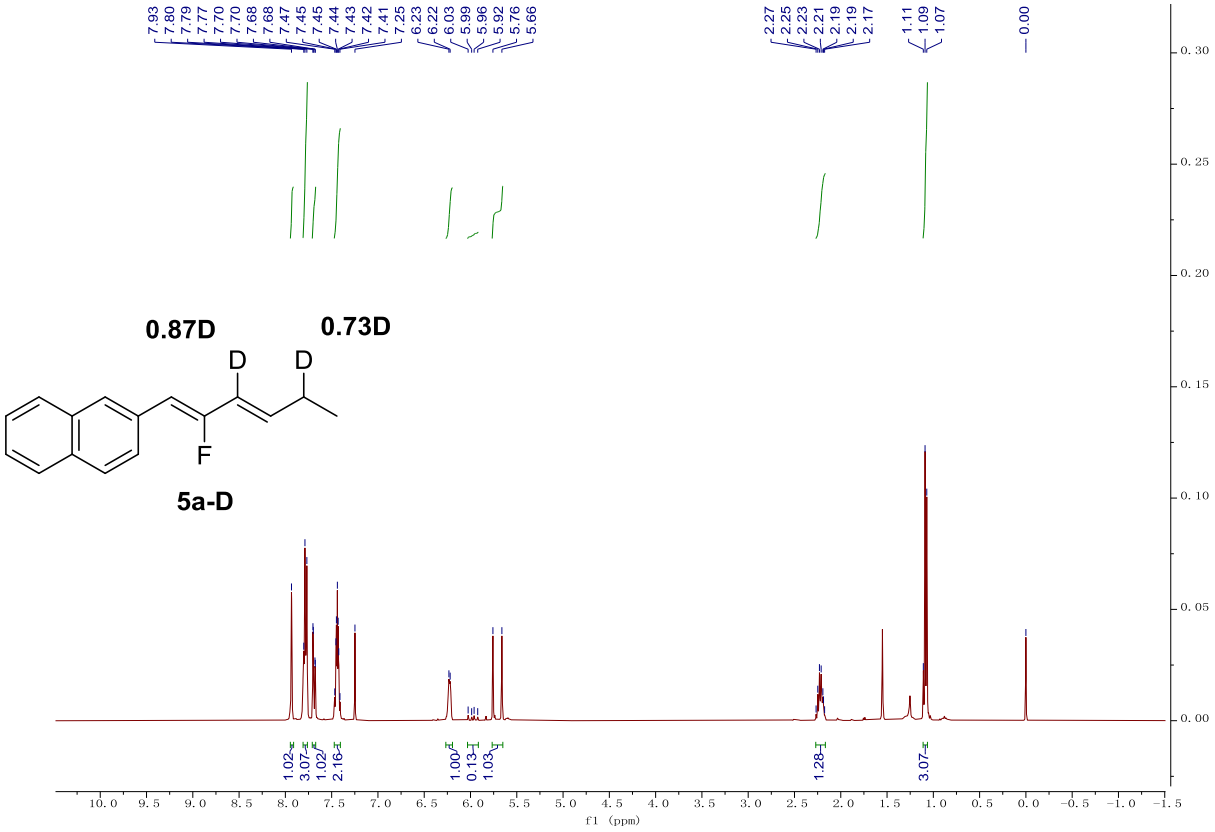
In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.8 mg, 0.002 mmol, 2 mol%), BINAP (2.5 mg, 0.004 mmol, 4 mol%), and THF (0.5 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, $AgBF_4$ (1 mg, 0.005 mmol) and **4a-D** (22.8 mg, 0.1 mmol). The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 12 hours. The reaction mixture was then cooled to room temperature and purified by chromatography on silica gel column to give product **5a-D** in 91% yield, which was analyzed by ^{1}H NMR indicating the presence of a 1,3-deuterium shift process. This result is matched with the reaction

using **1a**-D and **2a** as starting substrates (eq. 2).

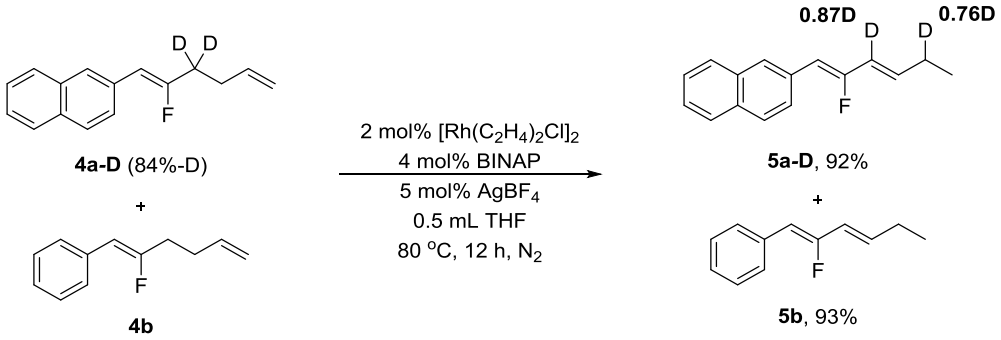


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.83 – 7.74 (m, 3H), 7.69 (dd, J = 8.6, 1.4 Hz, 1H), 7.48 – 7.40 (m, 2H), 6.23 (d, J = 5.3 Hz, 1H), 5.97 (dd, J = 26.0, 15.4 Hz, 0.13H), 5.71 (d, J = 38.8 Hz, 1H), 2.23 (p, J = 7.3 Hz, 1.28H), 1.09 (t, J = 7.4 Hz, 3H).

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5a-D (With JEOL)



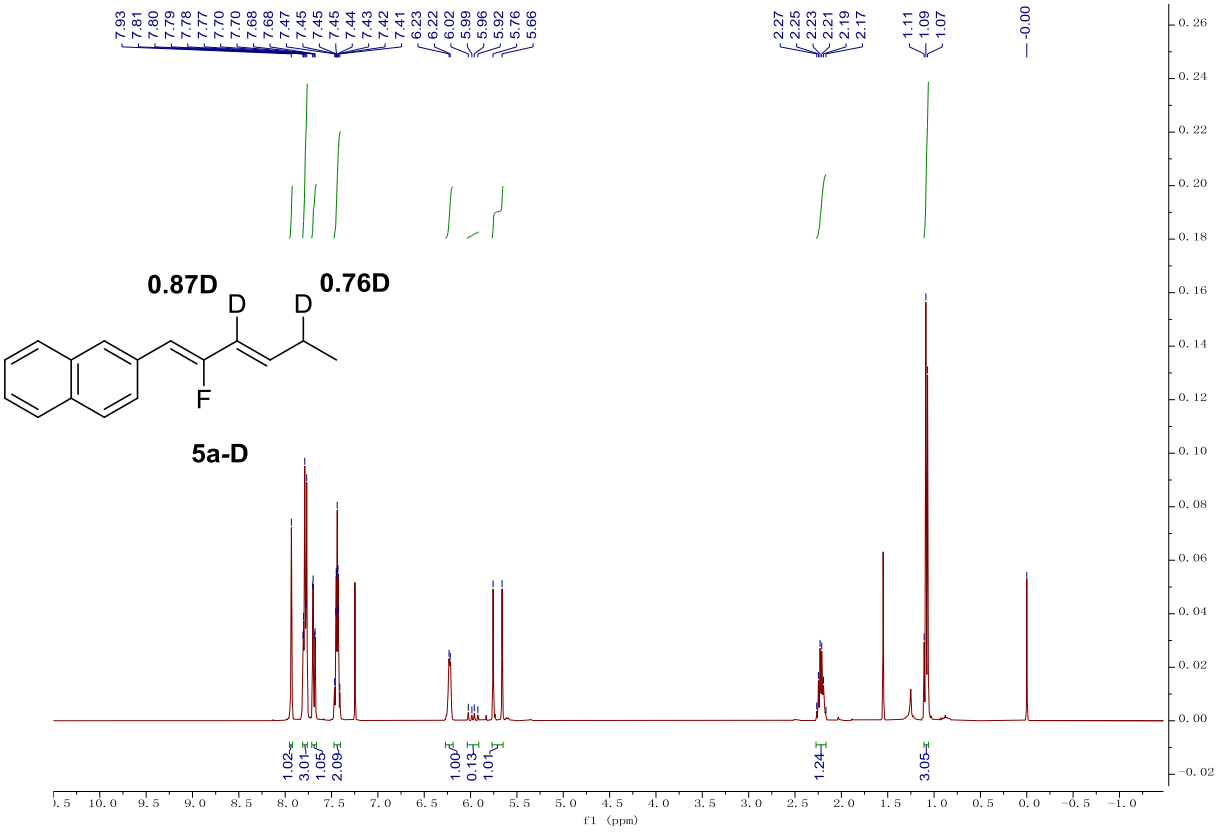
Experiments G: H/D Crossover Experiment

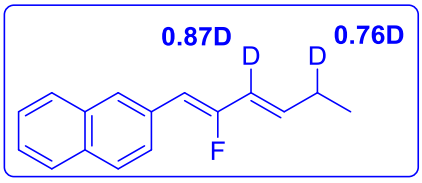


In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_4)_2Cl]_2$ (1.6 mg, 0.004 mmol, 2 mol%), BINAP (5.0 mg, 0.008 mmol, 4 mol%), and THF (1.0 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then

transferred the catalyst solution into another vial with stir bar, $AgBF_4$ (2 mg, 0.01 mmol), **4a-D** (22.8 mg, 0.1 mmol) and **4b** (17.6 mg, 0.1 mmol). The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 12 hours. The reaction mixture was then cooled to room temperature and purified by chromatography on silica gel column to give product **5a-D** in 92% yield and **5b** in 93% yield. This experiment result showed no intermolecular H/D exchange, which strongly supported the π-allyl mechanism.

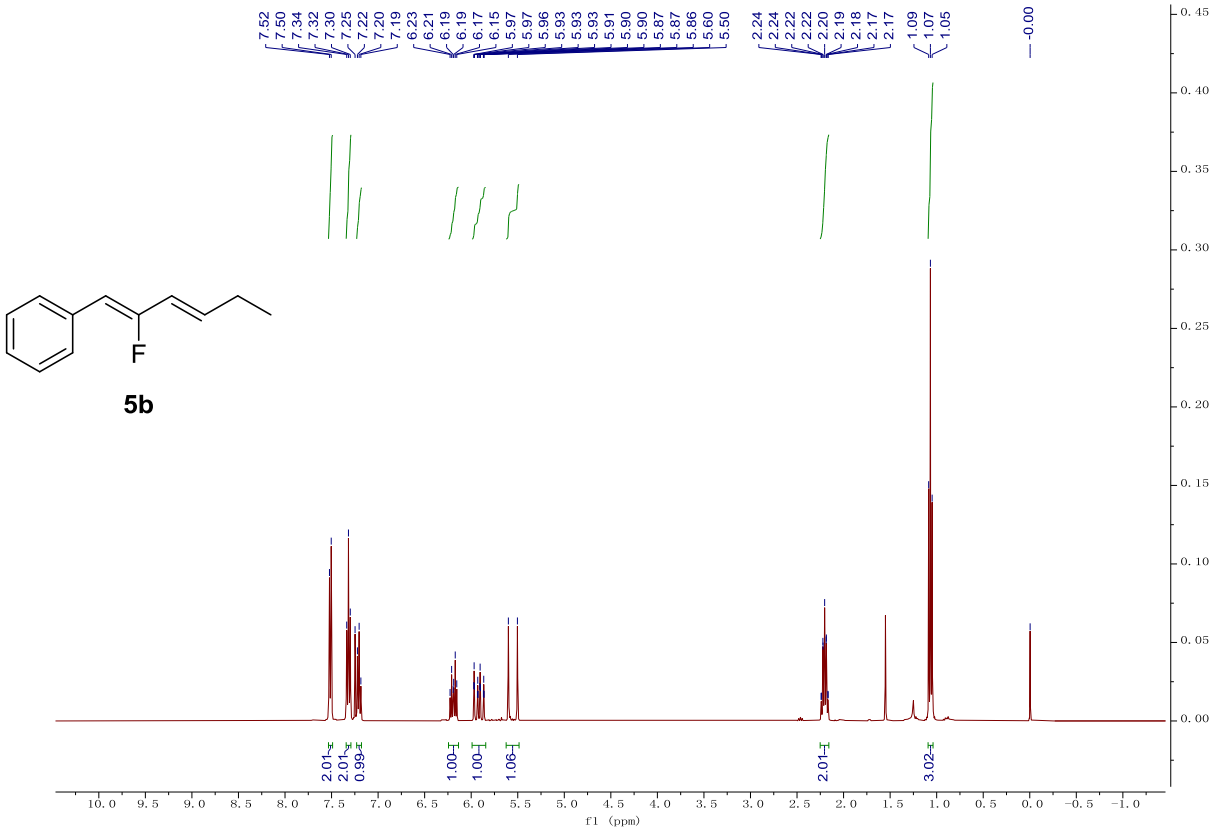
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5a-D (With JEOL)

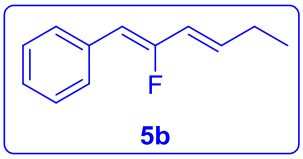




^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.82 – 7.75 (m, 3H), 7.69 (dd, J = 8.6, 1.5 Hz, 1H), 7.49 – 7.39 (m, 2H), 6.23 (d, J = 5.4 Hz, 1H), 5.97 (dd, J = 25.8, 15.5 Hz, 0.13H), 5.71 (d, J = 38.8 Hz, 1H), 2.23 (p, J = 7.4 Hz, 1.24H), 1.09 (t, J = 7.4 Hz, 3H).

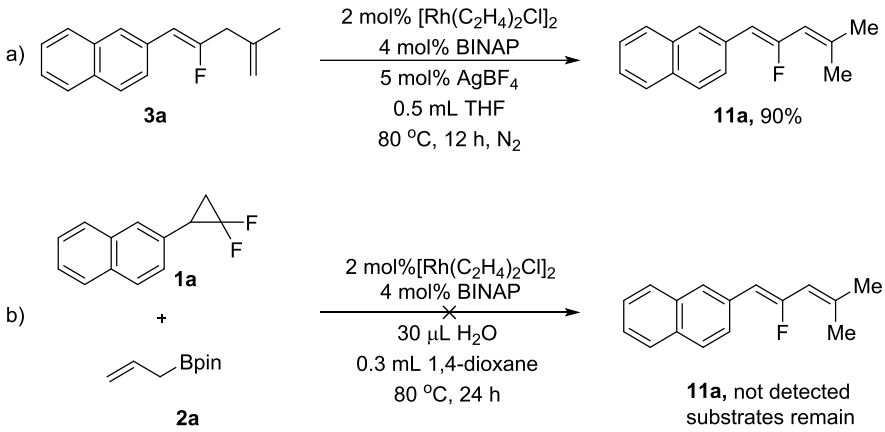
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5b (With JEOL)





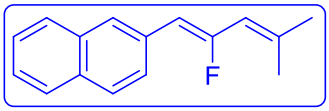
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.19 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.92 (ddt, *J* = 25.8, 15.5, 1.5 Hz, 1H), 5.55 (d, *J* = 38.8 Hz, 1H), 2.26 – 2.16 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

Experiment H



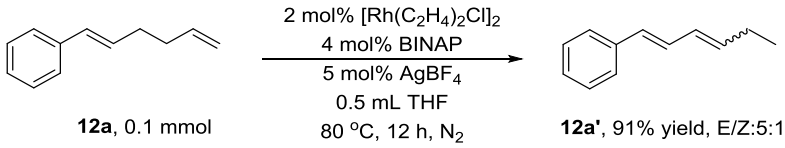
In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.8 mg, 0.004 mmol, 2 mol%), BINAP (2.5 mg, 0.004 mmol, 4 mol%), and THF (0.5 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then

transferred the catalyst solution into another vial with stir bar, $AgBF_4$ (1 mg, 0.005 mmol) and **3a** (22.6 mg, 0.1 mmol). The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 12 hours. The reaction mixture was then cooled to room temperature and purified by chromatography on silica gel column to give 1,3-diene **11a** in 90% yield. However, replacing the ligand from $(4\text{-}ClC_6H_4)_3P$ with BINAP could not give 1,3-diene **11a**. Thus, the cationic Rh/BINAP catalyst system is crucial for the alkene migration but unable to give the internal-selective product. Furthermore, we have tested many kinds of bidentate phosphine ligands, such as dppm, dppp, dppf, XantPhos, rac-SegPhos, R-SDP, R-SynPhos, where only BINAP and rac-SegPhos could promote the alkene migration.

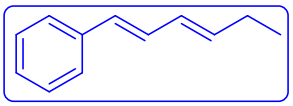


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.80 – 7.74 (m, 3H), 7.66 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.46 – 7.39 (m, 2H), 5.72 (d, *J* = 28.3 Hz, 1H), 5.68 (d, *J* = 38.4 Hz, 1H), 2.03 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5 (d, J = 263.2 Hz), 139.5 (d, J = 1.9 Hz), 133.5, 132.2 (d, J = 1.8 Hz), 131.9 (d, J = 3.2 Hz), 128.0, 127.9, 127.5, 127.2 (d, J = 8.3 Hz), 126.6 (d, J = 8.1 Hz), 126.1, 125.7, 117.7 (d, J = 22.2 Hz), 108.9 (d, J = 10.5 Hz), 27.7, 20.1 (d, J = 9.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.20 (dd, *J* = 38.4, 28.4 Hz). **LRMS (EI)** m/z: 226 (M+, 50), 211 (100), 196 (75), 183 (19), 165 (20), 128 (20).

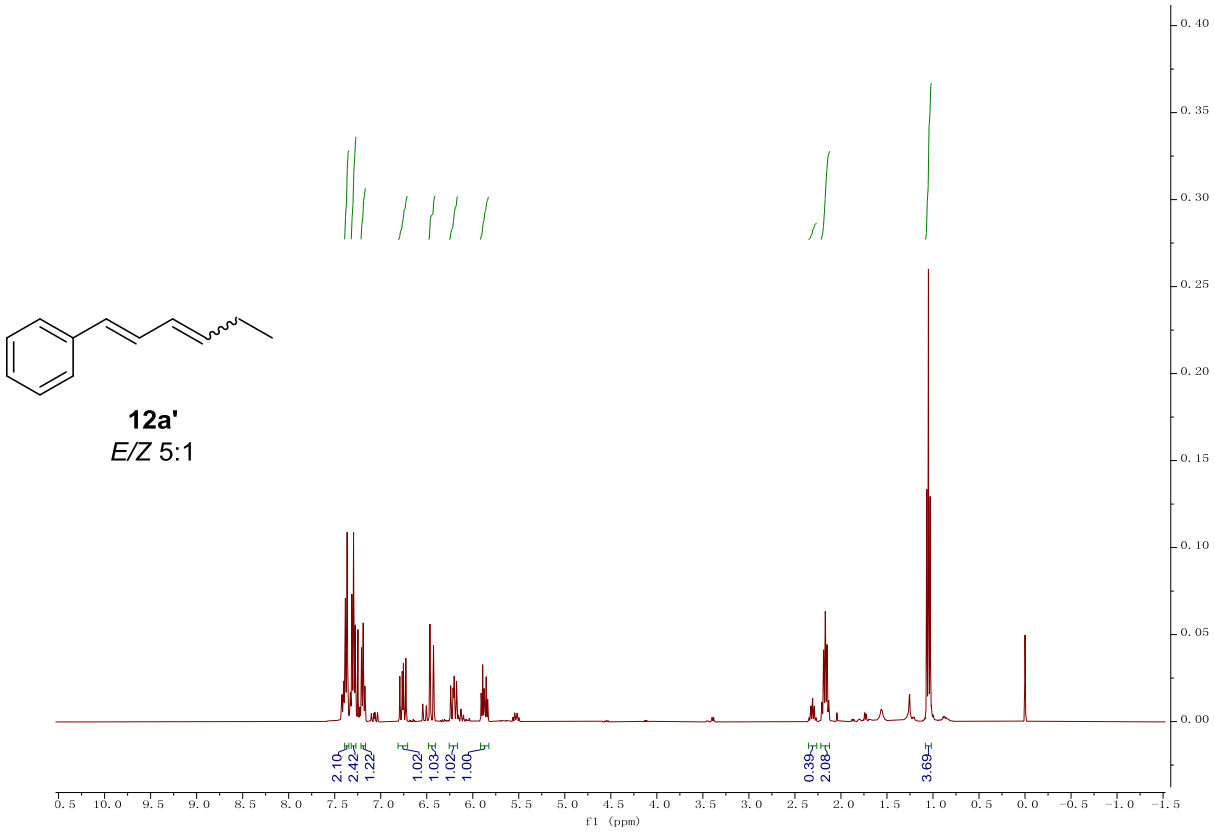
Experiment I



In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.8 mg, 0.004 mmol, 2 mol%), BINAP (2.5 mg, 0.004 mmol, 4 mol%), and THF (0.5 mL). The mixture was stirred for about 10 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, $AgBF_4$ (1 mg, 0.005 mmol) and **12a** (17.6 mg, 0.1 mmol). The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 12 hours. The reaction mixture was then cooled to room temperature and purified by chromatography on silica gel column to give product **12a'** in 91% yield with 5:1 *E/Z* selectivity. Comparing with the reaction using fluorinated 1,5-diene as substrate, this result indicated that the presence of fluorine atom is beneficial to maintain a high *E/Z* selectivity in this double bond migration process.

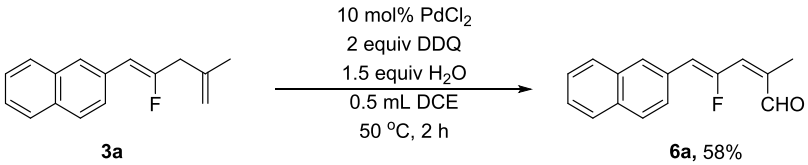


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 6.76 (dd, J = 15.7, 10.4 Hz, 1H), 6.45 (d, J = 15.7 Hz, 1H), 6.21 (dd, J = 15.2, 10.4 Hz, 1H), 5.87 (dt, J = 15.0, 6.6 Hz, 1H), 2.17 (p, J = 7.4, 7.0 Hz, 2H), 1.05 (t, J = 7.5 Hz, 3H). **LRMS (EI)** m/z: 158 (M+, 10), 141 (5), 129 (10), 117 (100), 91 (20), 75 (5).



8. Synthetic Applications

Oxygenation

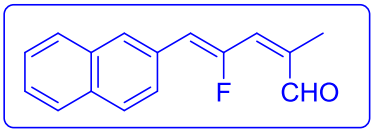


3a **6a,** 58%

Following the Fu's procedure[10], to a 4 mL vial was added $PdCl_2$ (1.8 mg, 0.01 mmol), **3a** (22.6 mg, 0.1 mmol), DDQ (45.4 mg, 0.2 mmol), and DCE (0.5 mL, dry). To solution was added H_2O (2.7 mg, 0.15 mmol) at room temperature. The vial was stirred for 2 h at 50 °C. After the reaction was completed, the reaction mixture was cooled to room temperature and concentrated in vacuum. The resulting residue was purified by column chromatography on silica gel to afford the desired product

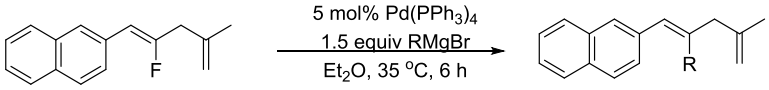
8a (13.8 mg, 58% yield).

(2Z,4Z)-4-fluoro-2-methyl-5-(naphthalen-2-yl)penta-2,4-dienal (8a)



Isolated yield = 58% (13.9 mg); Yellow oil; R_f = 0.4 (PE:EA=100:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.07 (s, 1H), 7.88 – 7.80 (m, 3H), 7.76 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.54 – 7.48 (m, 2H), 6.66 (dd, *J* = 29.8, 1.4 Hz, 1H), 6.29 (d, *J* = 35.8 Hz, 1H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.1, 156.9 (d, *J* = 262.9 Hz), 140.0, 139.7, 138.2 (d, *J* = 6.0 Hz), 133.3, 133.2 (d, *J* = 2.1 Hz), 130.2 (d, *J* = 4.2 Hz), 129.7 (d, *J* = 8.7 Hz), 128.4 (d, *J* = 2.9 Hz), 127.6, 127.0, 126.6, 126.6 (d, *J* = 8.4 Hz), 119.2 (d, *J* = 9.6 Hz), 10.5 (d, *J* = 8.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.69 (dd, *J* = 35.9, 29.8 Hz). The HRMS was not satisfied, and the result of LRMS was obtained for this compound. **LRMS** (EI) m/z: 240 (M+, 95), 211 (45), 196 (100), 191 (35), 178 (35), 165 (30), 128 (30).

Kumada Coupling Reaction

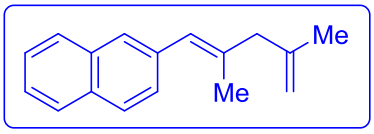


3a

8b, R=Me, 80%
8c, R=Ph, 82%

Following the Cao's procedure[11], to a 4 mL vial was added $Pd(PPh_3)_4$ (5.8mg, 0.005 mmol), fluorinated dienes (0.1 mmol), and Et_2O (0.2 mL, dry) in the glove box. To solution was added a Et_2O solution of PhMgBr (0.015 mL, 3.0 M, 0.15 mmol) at room temperature. The vial was removed from the glove box and stirred for 6 h at 35 °C. After completion of the reaction, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (2 mL) and extracted with ethyl acetate (3 × 3 mL). The combined organic layer was washed with water and brine, then dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel afforded the desired product **8a** (17.8 mg, 80% yield).

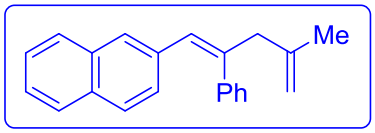
(E)-2-(2,4-dimethylpenta-1,4-dien-1-yl)naphthalene (8b)



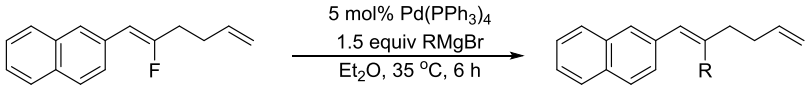
Following the Cao's procedure[11]; Isolated yield = 94% (20.8 mg); Colorless oil; R_f = 0.4 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (t, *J* = 7.7 Hz, 3H), 7.70 (s, 1H), 7.49 – 7.38 (m, 3H), 6.47 (s, 1H), 4.85 (d, *J* = 14.8 Hz, 2H), 2.92 (s, 2H), 1.90 (s, 3H), 1.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.71, 137.29, 135.94, 133.33, 131.85,

127.77, 127.53, 127.50, 127.42, 127.18, 126.78, 125.93, 125.43, 112.34, 49.66, 21.91, 17.42. **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{18}$ $[M+H]^+$ 223.1481, found 248.1481.

(Z)-2-(4-methyl-2-phenylpenta-1,4-dien-1-yl)naphthalene (8c)



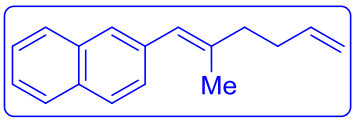
Following the Cao's procedure[11]; Isolated yield = 82% (23.4 mg); Colorless oil; R_f = 0.3 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 1H), 7.63 – 7.59 (m, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.27 – 7.23 (m, 3H), 7.21 – 7.18 (m, 2H), 6.99 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.64 (s, 1H), 4.82 (s, 1H), 4.77 (s, 1H), 3.24 (s, 2H), 1.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 141.0, 140.8, 135.0, 133.2, 132.0, 128.7, 128.4, 128.1, 128.1, 127.8, 127.4, 127.1, 127.0, 125.8, 125.5, 113.2, 49.0, 22.2. **HRMS** (ESI, *m/z*): calcd for $C_{22}H_{20}$ $[M+H]^+$ 265.1638, found 265.1639.



4a

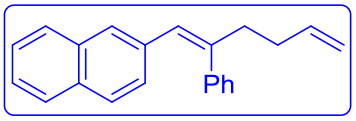
9b, R=Me, 90%
9c, R=Ph, 90%

(E)-2-(2-methylhexa-1,5-dien-1-yl)naphthalene (9b)



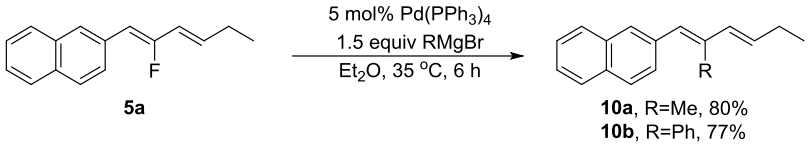
Following the Cao's procedure[11]; Isolated yield = 90% (20.0 mg); Colorless oil; R_f = 0.4 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 8.4 Hz, 3H), 7.67 (s, 1H), 7.43 (td, *J* = 5.3, 2.5 Hz, 2H), 7.37 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.43 (s, 1H), 5.97 – 5.84 (m, 1H), 5.09 (dd, *J* = 16.9, 2.0 Hz, 1H), 5.01 (dd, *J* = 9.8, 2.0 Hz, 1H), 2.32 (d, *J* = 3.2 Hz, 4H), 1.94 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 139.0, 138.3, 136.0, 133.3, 131.8, 127.8, 127.6, 127.5, 127.4, 127.2, 125.9, 125.4, 125.2, 114.7, 40.1, 32.4, 17.9. **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{18}$ $[M+H]^+$ 223.1481, found 223.1480.

(Z)-2-(2-phenylhexa-1,5-dien-1-yl)naphthalene (9c)



Following the Cao's procedure[11]; Isolated yield = 90% (25.7 mg); Pale yellow oil; R_f = 0.4 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 1H), 7.62 – 7.57 (m, 1H), 7.44 (s, 1H), 7.37 – 7.33 (m, 2H), 7.28 (dt, *J* = 6.4, 2.0 Hz, 2H), 7.19 (dd, *J* = 7.7, 1.9 Hz, 2H), 6.95 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.61 (s, 1H), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.03 (dq, *J* = 18.4, 1.6 Hz, 1H), 4.99 (dq, *J* = 18.4, 1.6 Hz, 1H), 2.64 (td, *J* = 7.6, 1.3 Hz, 2H), 2.24 – 2.16 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 141.0, 138.1, 135.0, 133.2, 131.9, 128.7, 128.6,

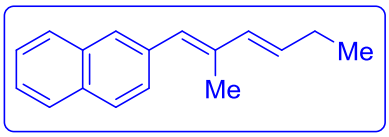
128.0, 127.8, 127.4, 127.1, 127.0, 127.0, 126.6, 125.8, 125.5, 114.9, 40.0, 32.2. **HRMS** (ESI, *m/z*): calcd for $C_{22}H_{20}$ $[M+H]^+$ 285.1638, found 285.1639



5a

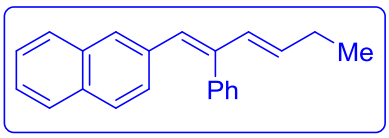
10a, R=Me, 80%
10b, R=Ph, 77%

2-((1E,3E)-2-methylhexa-1,3-dien-1-yl)naphthalene (10a)



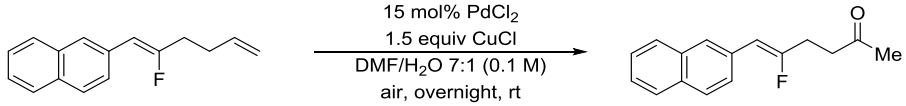
Following the Cao's procedure[11]; Isolated yield = 80% (17.8 mg); Colorless oil; R_f = 0.4 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 3H), 7.72 (s, 1H), 7.47 – 7.40 (m, 3H), 6.58 (s, 1H), 6.30 (d, *J* = 15.6 Hz, 1H), 5.88 (dt, *J* = 15.5, 6.6 Hz, 1H), 2.26 – 2.17 (m, 2H), 2.08 (d, *J* = 1.3 Hz, 3H), 1.08 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.4, 135.7, 134.2, 133.3, 132.2, 131.9, 129.2, 127.9, 127.7, 127.5, 127.4, 126.0, 125.6, 26.0, 14.1, 13.9. The HRMS was not satisfied, and the result of LRMS was obtained for this compound. **LRMS** (EI) m/z: 222 (M+, 25), 207 (10), 193 (100), 178 (70), 165 (20), 152 (10).

2-((1Z,3E)-2-phenylhexa-1,3-dien-1-yl)naphthalene (10b)



Following the Cao's procedure[11]; Isolated yield = 77% (22.0 mg); Colorless oil; R_f = 0.4 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 1H), 7.59 – 7.53 (m, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.43 – 7.33 (m, 6H), 7.26 – 7.19 (m, 2H), 6.93 – 6.87 (m, 1H), 6.68 (s, 1H), 6.49 (d, *J* = 15.4 Hz, 1H), 5.44 (dt, *J* = 15.5, 6.6 Hz, 1H), 2.21 – 2.11 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 138.9, 136.0, 134.8, 134.3, 133.2, 132.0, 129.7, 129.0, 128.7, 128.5, 127.9, 127.3, 127.2, 127.0, 125.8, 125.6, 26.0, 13.5. The HRMS was not satisfied, and the result of LRMS was obtained for this compound. **LRMS** (EI) m/z: 284 (M+, 25), 255 (100), 239 (20), 226 (10), 178 (10), 141 (15).

<u>Wacker Oxidation</u>



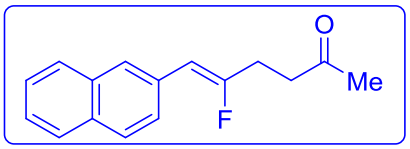
4a, 0.2 mmol

9a, 68%

Following the standard Wacker oxidation procedure[12], a 4 mL vial equipped with stir bar was charged with **4a** (22.6 mg, 0.1 mmol), $PdCl_2$ (2.7 mg, 0.015 mmol, 15 mol%), CuCl (14.9 mg, 0.15,

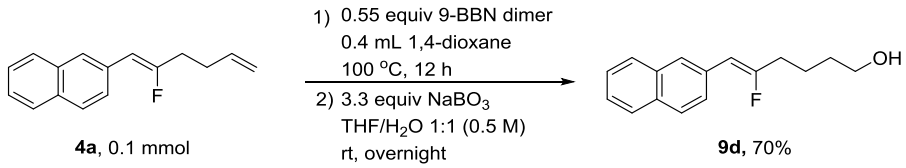
1.5 equiv), and DMF:H_2O (1 mL, 7:1, 0.1 M). The reaction mixture was stirred at room temperature under air atmosphere overnight. The crude mixture was diluted with H_2O and extracted with MTBE. The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel afforded the desired product **9a** (16.5 mg, 68% yield).

(Z)-5-fluoro-6-(naphthalen-2-yl)hex-5-en-2-one (9a)



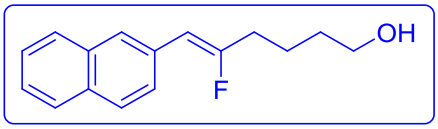
Isolated yield = 68% (16.5 mg); White solid, m.p.: 90.0-90.8 °C; R_f = 0.4 (PE:EA=50:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.81 – 7.75 (m, 3H), 7.62 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.48 – 7.40 (m, 2H), 5.67 (d, *J* = 39.4 Hz, 1H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.72 – 2.61 (m, 2H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.8, 159.7 (d, *J* = 266.2 Hz), 133.4, 132.2, 131.0 (d, *J* = 2.8 Hz), 127.9, 127.9, 127.5, 127.2 (d, *J* = 7.4 Hz), 126.4 (d, *J* = 7.7 Hz), 126.1, 125.8, 106.7 (d, *J* = 8.4 Hz), 40.1, 30.0, 27.3 (d, *J* = 27.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.10 (dt, *J* = 38.8, 19.3 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{15}FO$ $[M+Na]^+$ 265.0999, found 265.1000.

Hydroboration and Oxidation



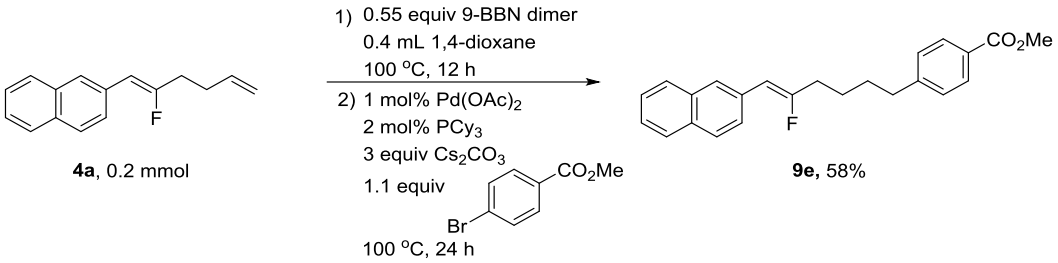
In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with **4a** (22.6 mg, 0.1 mmol), 9-BBN dimer (13.4 mg, 0.55 mmol, 0.55 equiv), and 1,4-dioxane (0.4 mL). The vial was removed from the glove box and stirred for 12 h at 100 °C. The solvent was removed under reduced pressure. To the resulting mixture was added $NaBO_3$·H_2O (32.9 mg, 0.33 mmol, 3.3 equiv), THF (0.1 mL), and H_2O (0.1 mL). After stirring at room temperature overnight, the reaction mixture was diluted with water and extracted with MTBE. The organic phase was dried with $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired product **9d** (17.0 mg, 70% yield).[13]

(Z)-5-fluoro-6-(naphthalen-2-yl)hex-5-en-1-ol (9d)



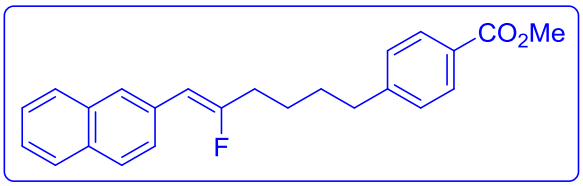
Isolated yield = 70% (17.1 mg); Colorless oil; R_f = 0.2 (PE:EA=10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.78 (dd, *J* = 7.8, 4.6 Hz, 3H), 7.64 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.44 (td, *J* = 7.0, 6.2, 3.8 Hz, 2H), 5.63 (d, *J* = 39.5 Hz, 1H), 3.70 (t, *J* = 6.0 Hz, 2H), 2.41 (dt, *J* = 18.2, 6.9 Hz, 2H), 1.80 – 1.63 (m, 4H), 1.51 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 267.3 Hz), 133.4, 132.1, 131.3 (d, *J* = 2.9 Hz), 127.9, 127.8, 127.5, 127.0 (d, *J* = 7.5 Hz), 126.5 (d, *J* = 7.6 Hz), 126.0, 125.7, 106.1 (d, *J* = 8.4 Hz), 62.5, 32.9 (d, *J* = 26.6 Hz), 31.8, 22.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.48 (dt, *J* = 38.8, 18.3 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{17}FO$ $[M+Na]^+$ 267.1156, found 267.1154.

Hydroboration and Suzuki-Miyaura Coupling Reaction



In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with **4a** (45.2 mg, 0.2 mmol), 9-BBN dimer (26.8 mg, 0.11 mmol, 0.55 equiv), and 1,4-dioxane (0.5 mL). The vial was removed from the glove box and stirred for 12 h at 100 °C. To this solution was added $Pd(OAc)_2$ (0.5 mg, 0.002, 1 mol%), PCy_3 (1.12 mg, 0.004 mmol, 2 mol%), Cs_2CO_3 (195.5 mg, 0.6 mmol, 3 equiv), and 4-bromo-methylbenzoate (47.3 mg, 0.22 mmol, 1.1 equiv). The reaction mixture was stirred at 100 °C for 24h. The reaction mixture was diluted with EtOAc and filtered through a pad of celite. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired product **9e** (42.1 mg, 58% yield).[14]

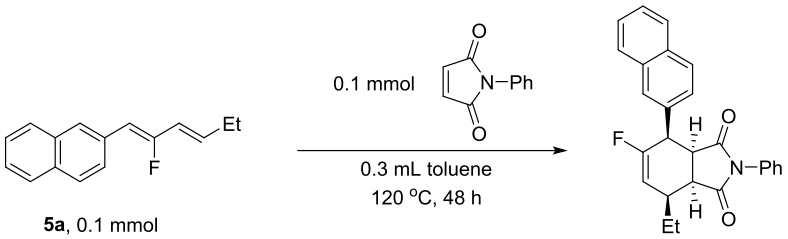
methyl (Z)-4-(5-fluoro-6-(naphthalen-2-yl)hex-5-en-1-yl)benzoate (9e)



Isolated yield = 58% (21.0 mg); White solid, m.p.: 80.5-81.4 °C; R_f = 0.4 (PE:EA=20:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.86 (s, 1H), 7.77 (dd, *J* = 7.7, 4.6 Hz, 3H), 7.63 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 5.59 (d, *J* = 39.5 Hz, 1H), 3.89 (s, 3H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.39 (dt, *J* = 18.4, 7.1 Hz, 2H),

1.79 – 1.62 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 161.0 (d, *J* = 267.2 Hz), 147.7, 133.4, 132.1, 131.2 (d, *J* = 2.6 Hz), 129.7, 128.4, 127.9, 127.8, 127.7, 127.5, 126.9 (d, *J* = 7.4 Hz), 126.5 (d, *J* = 7.6 Hz), 126.0, 125.7, 106.1 (d, *J* = 8.5 Hz), 52.0, 35.6, 33.0 (d, *J* = 26.6 Hz), 30.3, 25.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.10 (dt, *J* = 39.1, 18.9 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{24}H_{23}FO_2$ $[M+Na]^+$ 385.1574, found 385.1570.

Diels−Alder Reaction

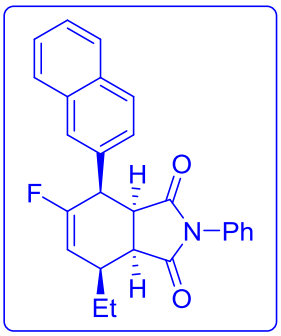


5a, 0.1 mmol

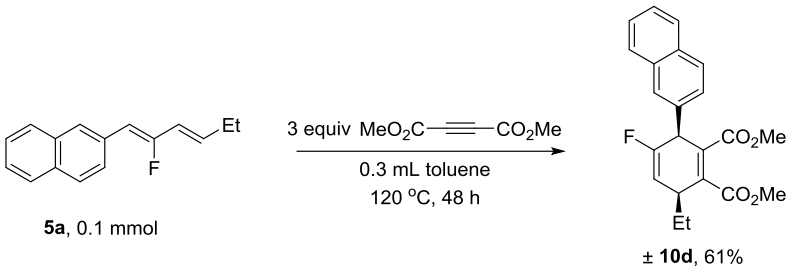
± **10c**, 56%

To a 4 mL via equipped with a magnetic stir bar was added **5a** (22.6 mg, 0.1 mmol), 1-phenyl-1H-pyrrole-2,5-dione (17.3 mg, 0.1 mmol, 1 equiv), and toluene (0.3 mL). The vial was sealed and stirred at 120 °C for 48 h. After the reaction was completed, purification by column chromatography on silica gel to afford the desired product **10c** (22.3 mg, 56% yield).

(3aR,4S,7S,7aR)-7-ethyl-5-fluoro-4-(naphthalen-2-yl)-2-phenyl-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione (10c)



Isolated yield = 56% (22.3 mg); Pale yellow solid, m.p.: 142.1-142.9 °C; R_f = 0.2 (PE:EA=5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 4H), 7.46 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.34 (d, *J* = 6.6 Hz, 1H), 7.13 – 7.06 (m, 1H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.25 (d, *J* = 8.3 Hz, 2H), 5.70 (dd, *J* = 16.5, 3.0 Hz, 1H), 4.26 (t, *J* = 7.1 Hz, 1H), 3.73 (t, *J* = 8.2 Hz, 1H), 3.37 (t, *J* = 7.7 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.41 (dp, *J* = 14.3, 7.4 Hz, 1H), 1.97 (dp, *J* = 15.1, 7.5 Hz, 1H), 1.18 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.2, 174.5 (d, *J* = 2.2 Hz), 156.7 (d, *J* = 258.6 Hz), 133.1, 133.0, 132.3 (d, *J* = 1.5 Hz), 130.8, 128.9, 128.5, 128.2, 128.1, 128.0, 127.5, 127.2, 126.4, 126.4, 125.8, 107.8 (d, *J* = 15.3 Hz), 46.4 (d, *J* = 5.9 Hz), 42.0 (d, *J* = 25.9 Hz), 41.0, 35.9 (d, *J* = 6.3 Hz), 25.4, 12.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.24 (dt, *J* = 16.1, 5.6 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{26}H_{22}FNO_2$ $[M+Na]^+$ 422.1527, found 422.1533.

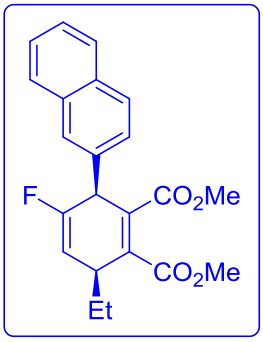


5a, 0.1 mmol

± **10d**, 61%

To a 4 mL via equipped with a magnetic stir bar was added **5a** (22.6 mg, 0.1 mmol), dimethyl but-2-ynedioate (42.6 mg, 0.3 mmol, 3 equiv), and toluene (0.3 mL). The vial was sealed and stirred at 120 °C for 48 h. After the reaction was completed, purification by column chromatography on silica gel to afford the desired product **10d** (22.4 mg, 61% yield).

dimethyl 6-ethyl-4-fluoro-3-(naphthalen-2-yl)cyclohexa-1,4-diene-1,2-dicarboxylate (10d)



Isolated yield = 61% (22.5 mg); Colorless oil; R_f = 0.6 (PE:EA=5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 3H), 7.75 (s, 1H), 7.50 – 7.45 (m, 2H), 7.42 (dd, *J* = 8.6, 1.8 Hz, 1H), 5.36 (dd, *J* = 15.7, 4.2 Hz, 1H), 4.68 (t, *J* = 5.3 Hz, 1H), 3.85 (s, 3H), 3.53 (s, 3H), 3.40 (dq, *J* = 13.8, 4.8, 4.3 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.69 (dt, *J* = 13.8, 7.0 Hz, 1H), 1.09 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 157.6 (d, *J* = 255.3 Hz), 141.9 (d, *J* = 2.4 Hz), 135.8 (d, *J* = 2.4 Hz), 133.5, 132.9, 130.7 (d, *J* = 9.4 Hz), 128.5, 128.0, 127.8, 127.7, 126.3, 126.3, 126.1, 102.2 (d, *J* = 16.4 Hz), 52.6, 52.4, 44.3 (d, *J* = 28.3 Hz), 40.3 (d, *J* = 7.3 Hz), 28.1, 11.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.7 (dt, *J* = 16.2, 5.0 Hz). **HRMS** (ESI, *m/z*): calcd for $C_{22}H_{21}FNO_4$ $[M+Na]^+$ 391.1316, found 391.1320.

9. References

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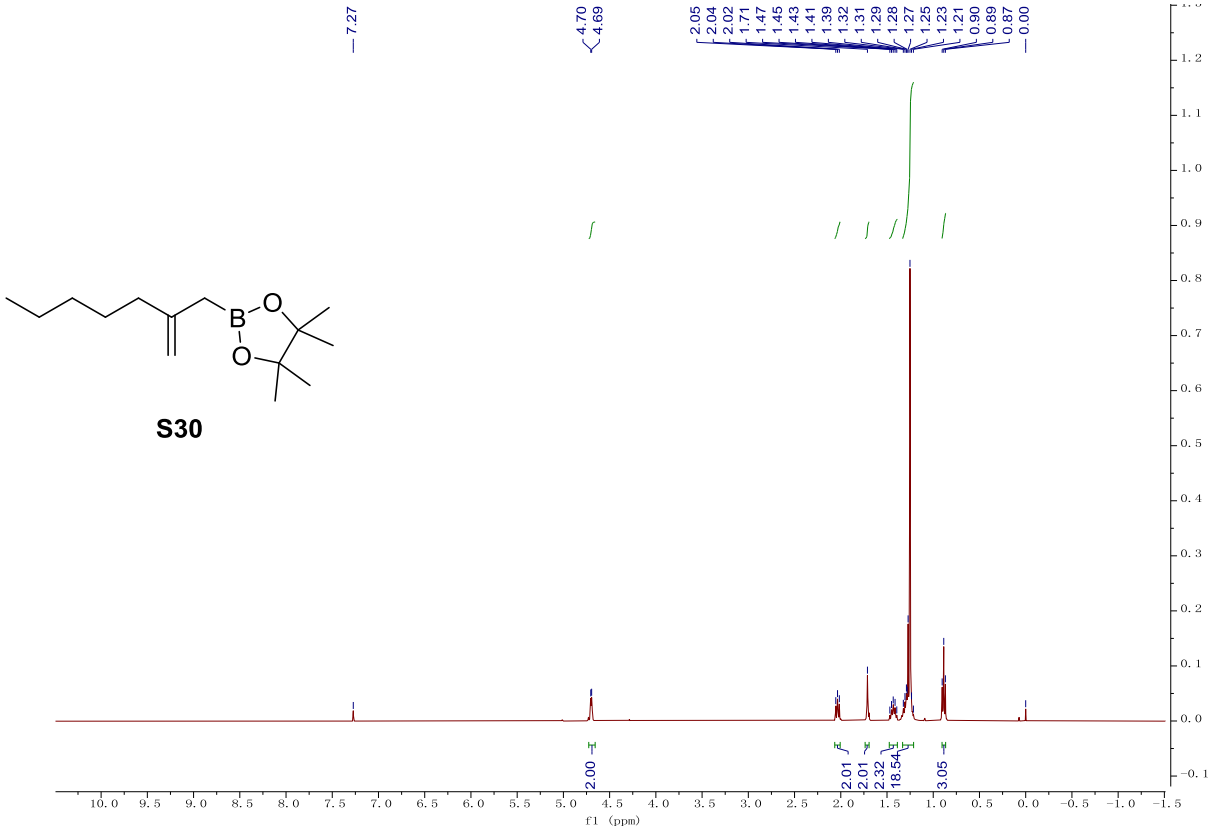
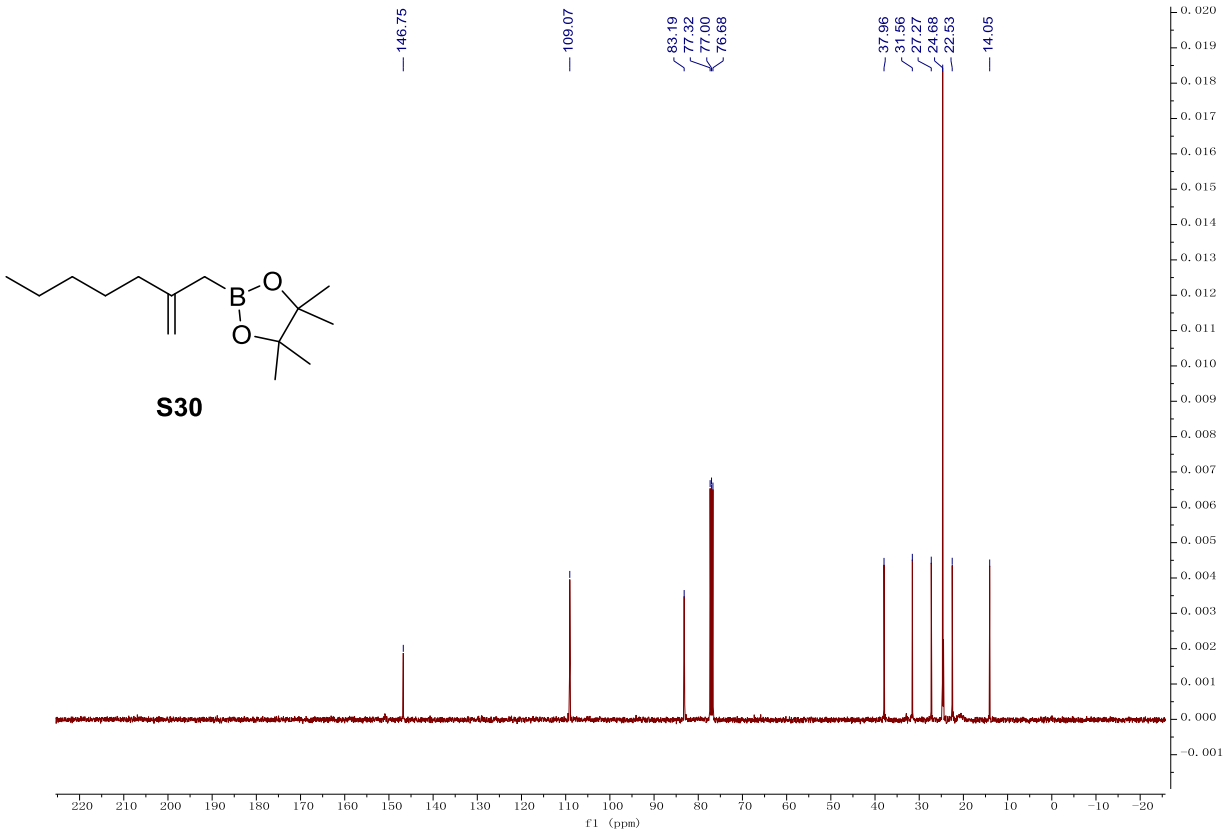
10.NMR Spectra

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S30 (With JEOL)



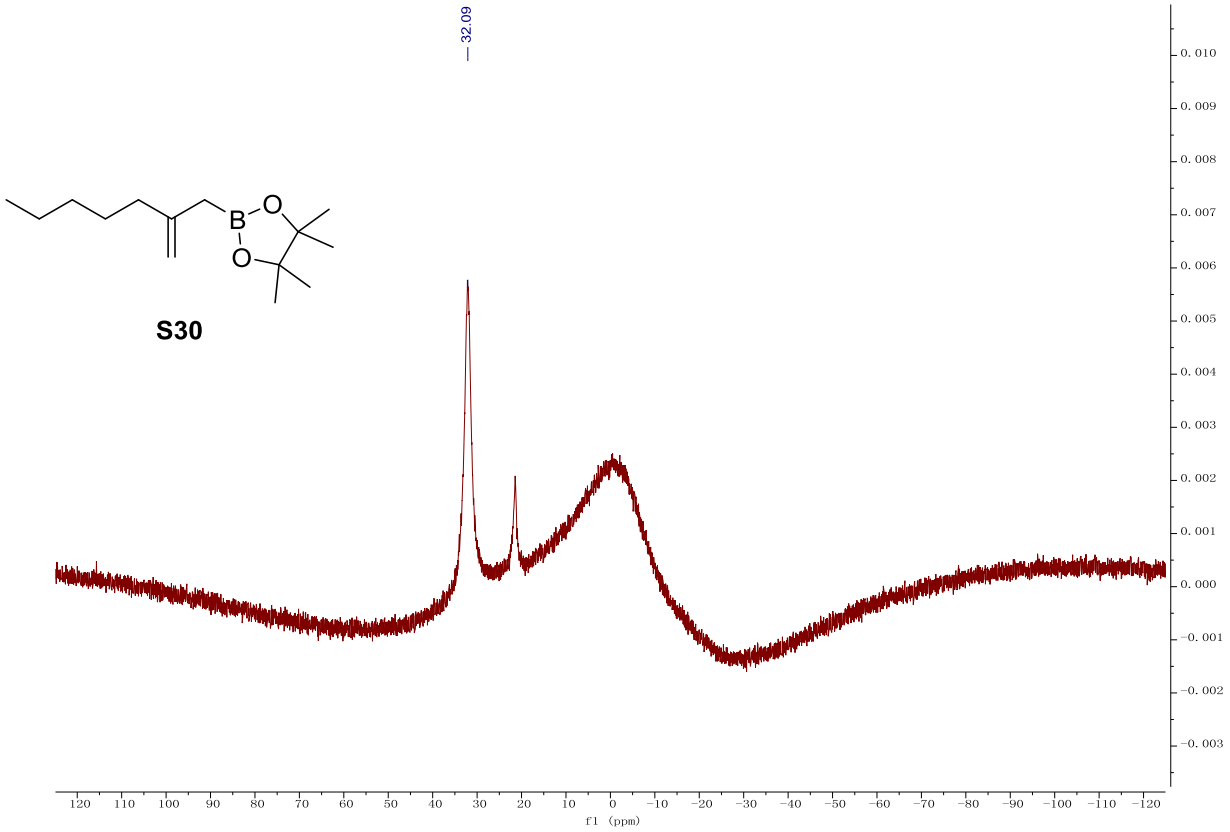
S30

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S30 (With JEOL)

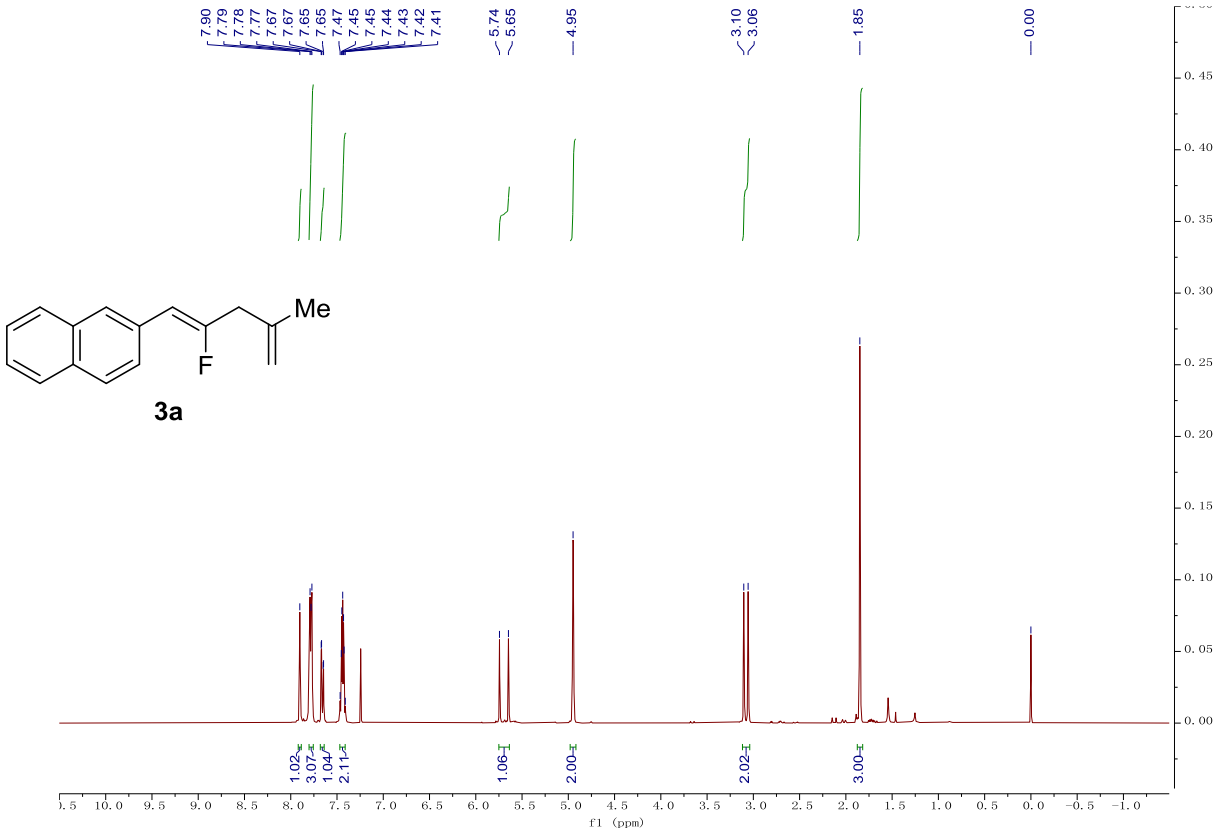


S30

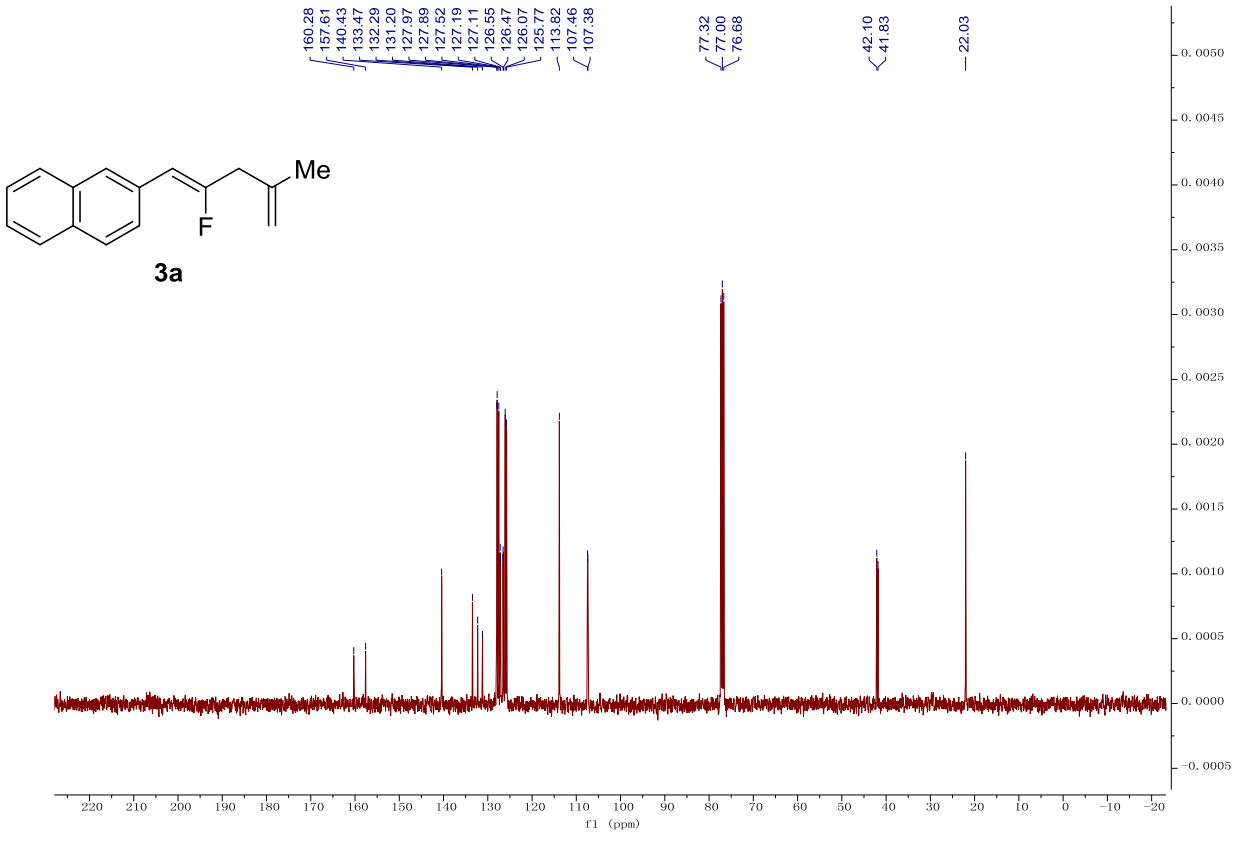
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of S30 (With JEOL)



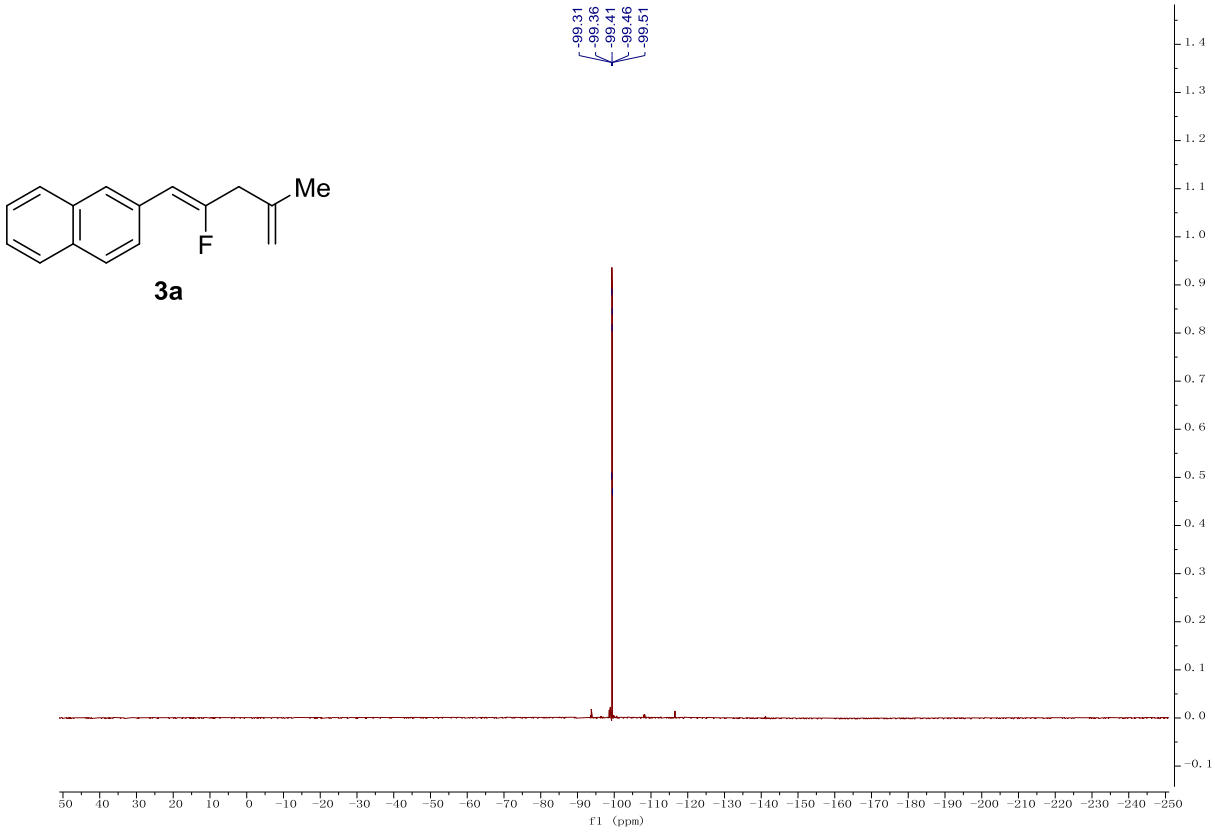
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a (With JEOL)



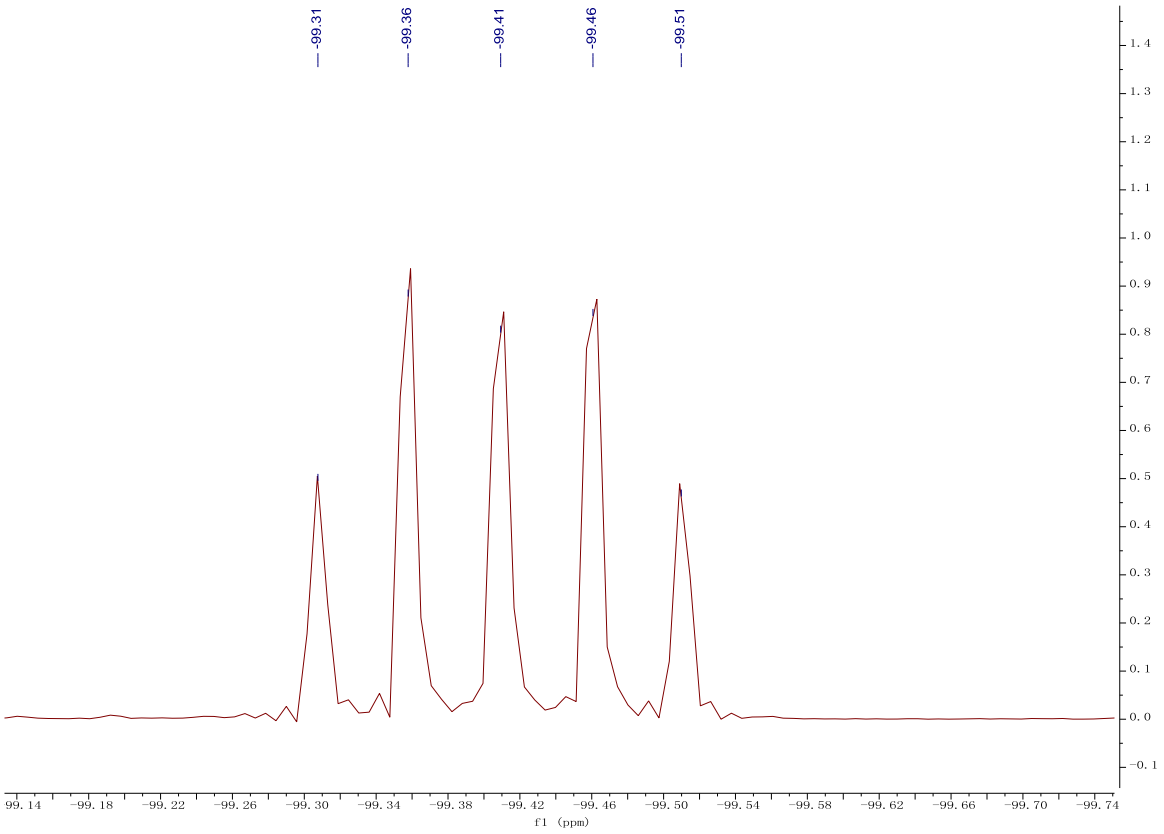
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3a



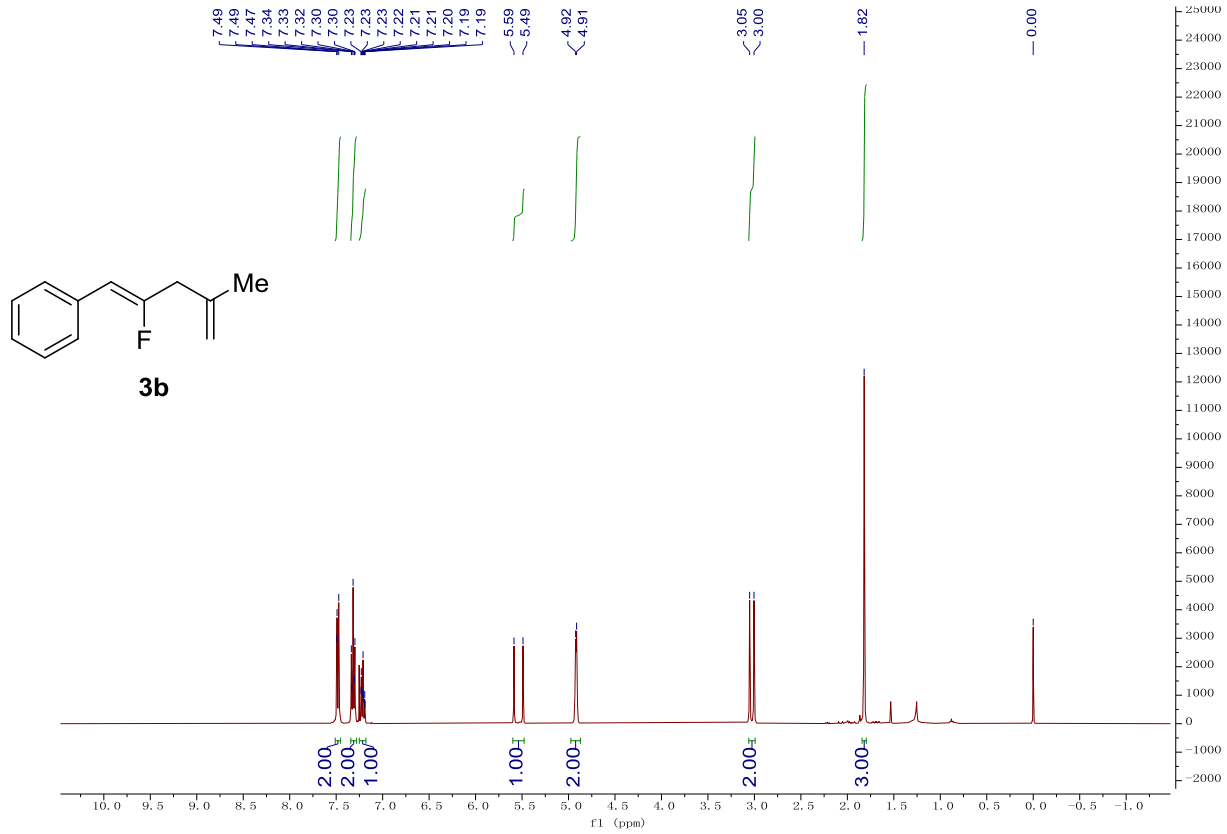
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3a



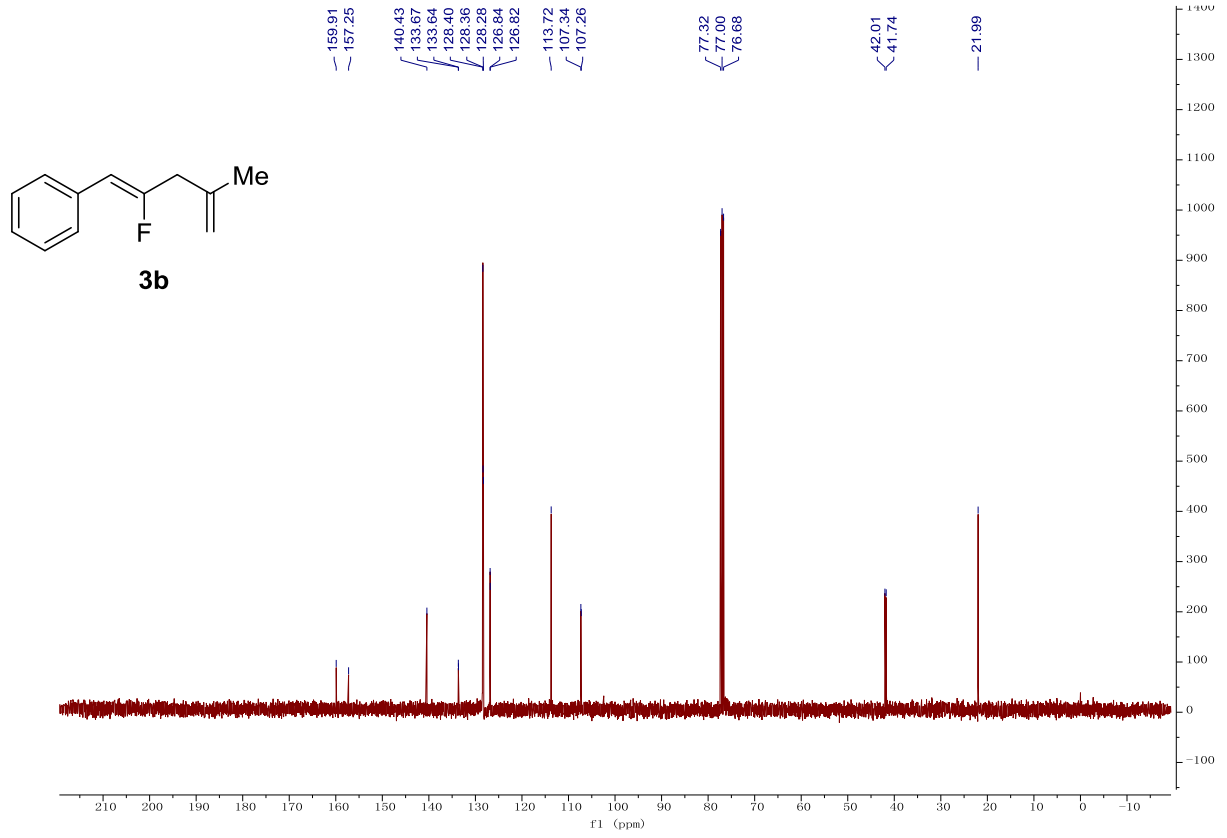
3a



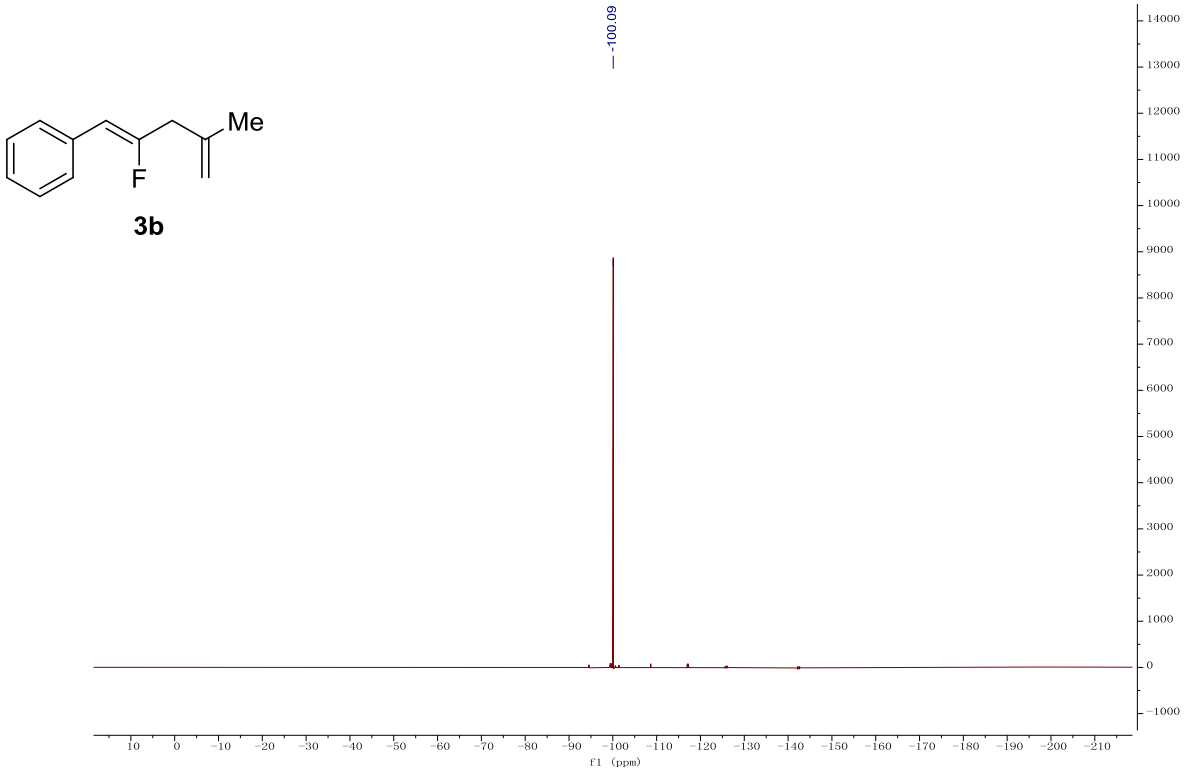
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b



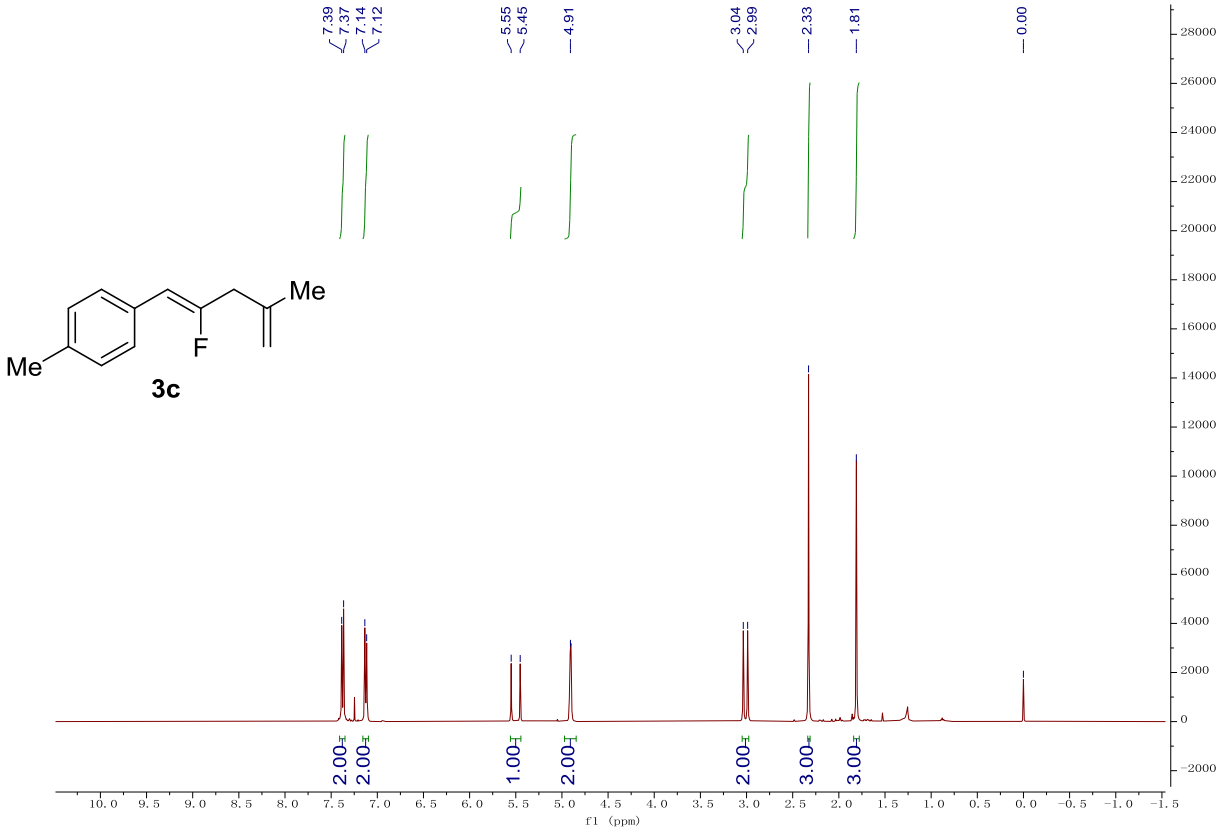
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3b



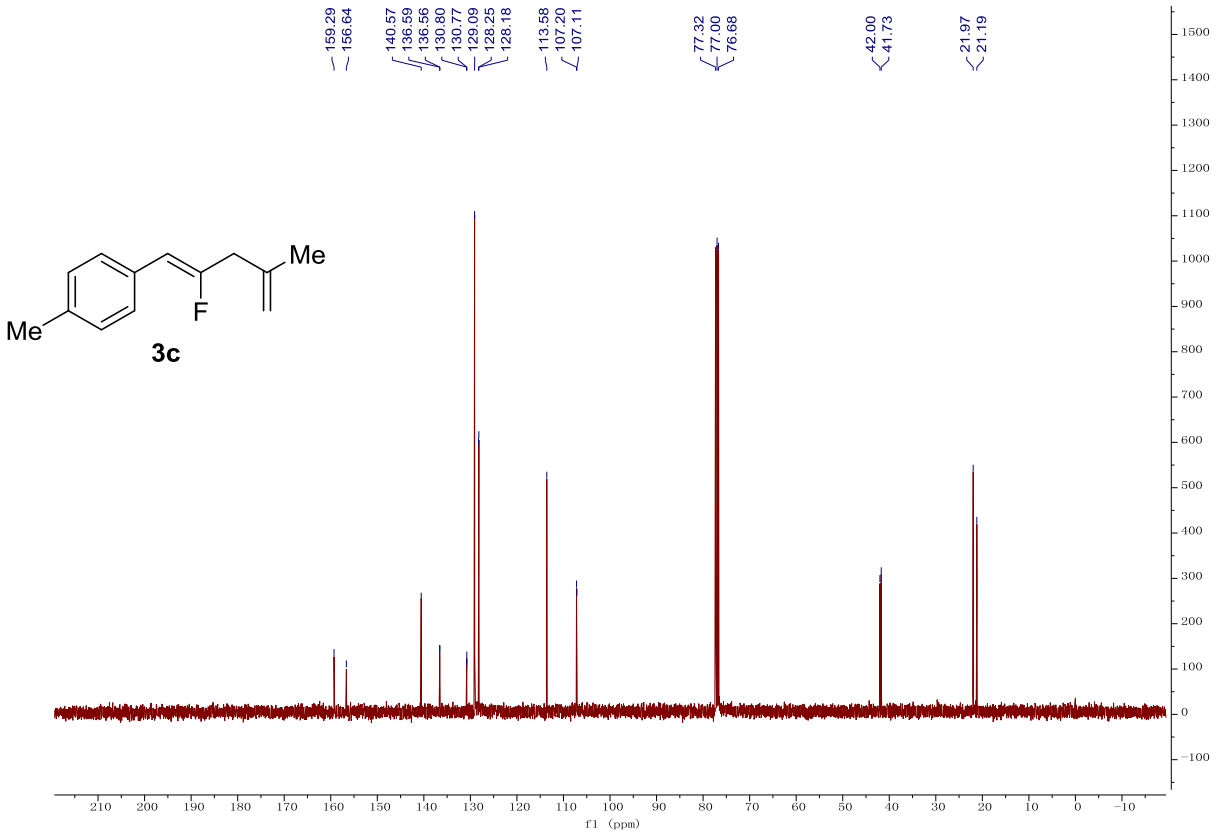
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3b



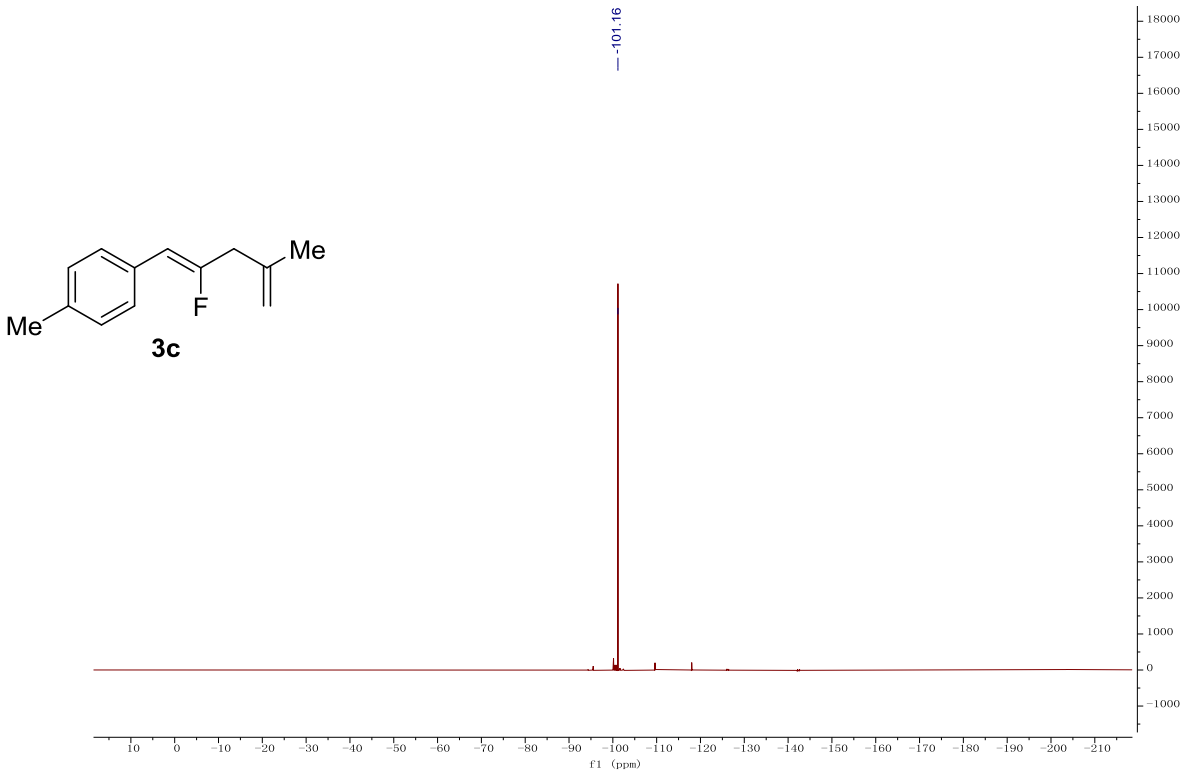
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c



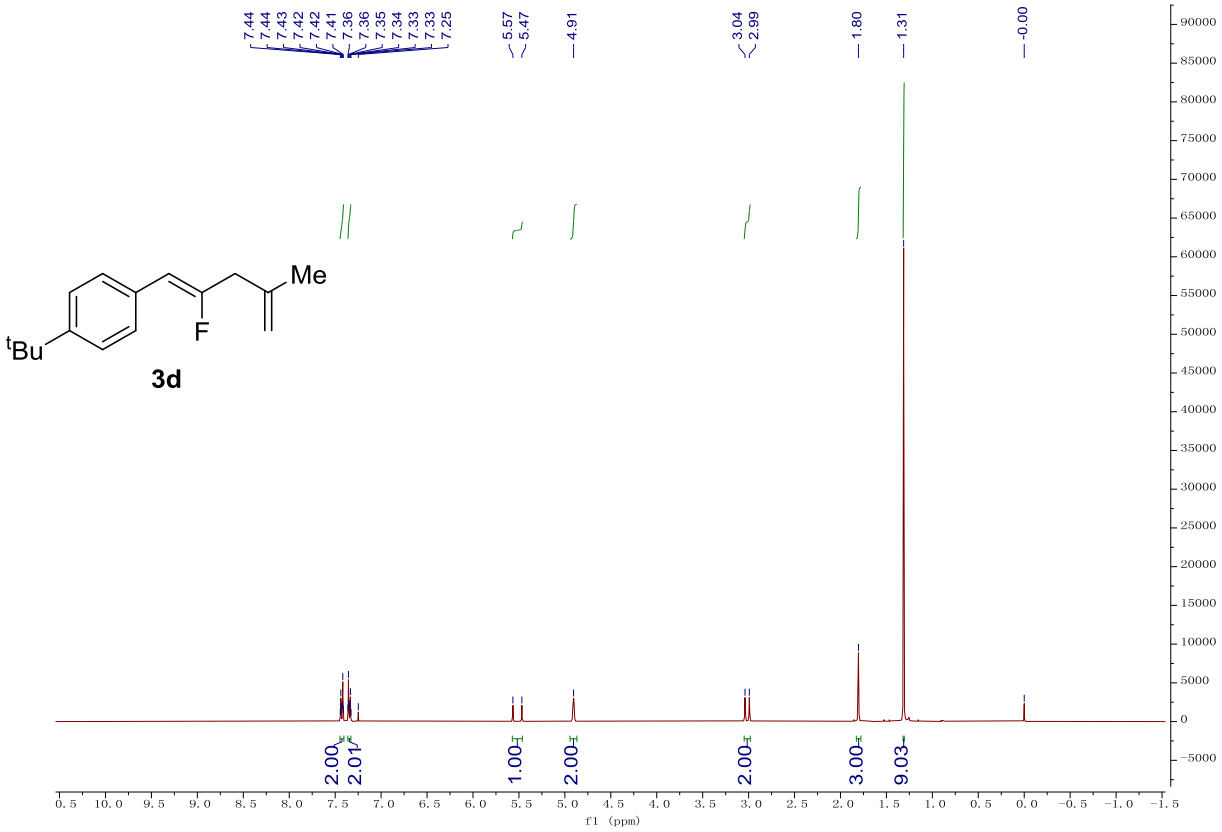
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3c



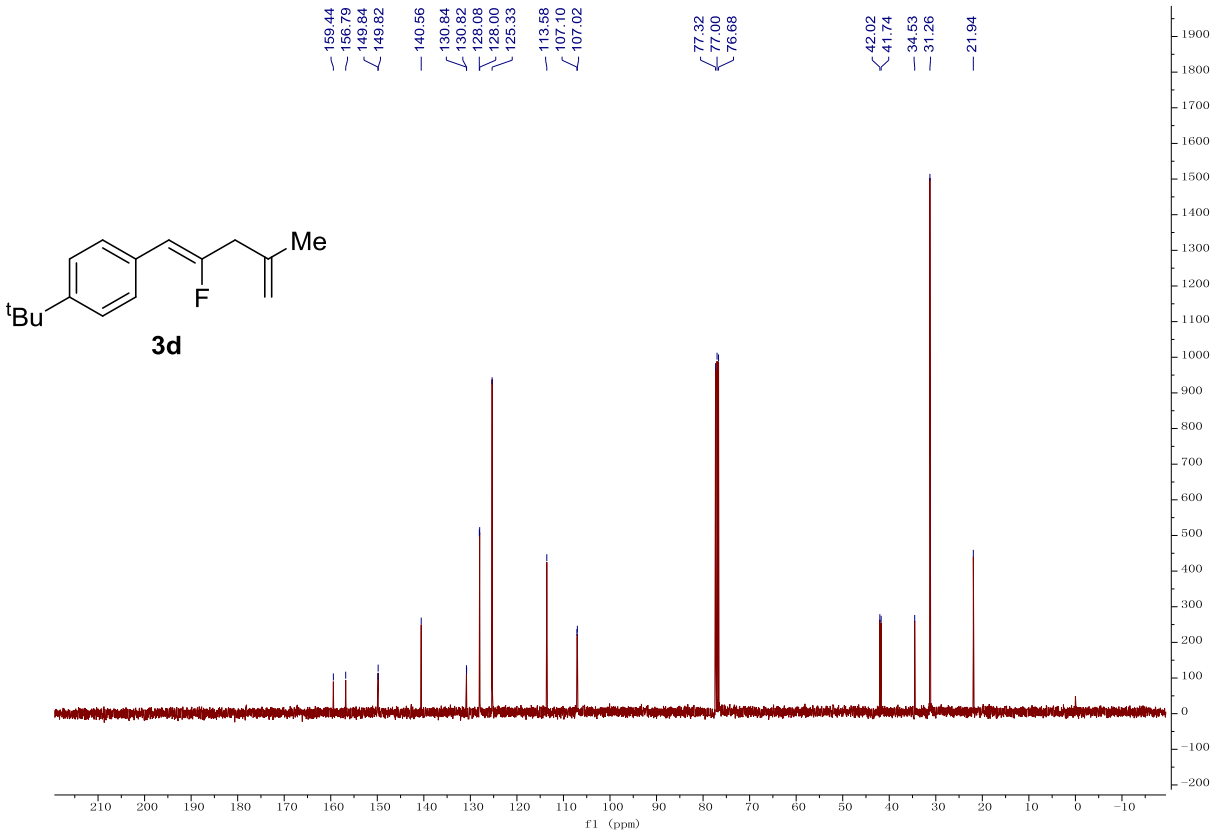
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3c



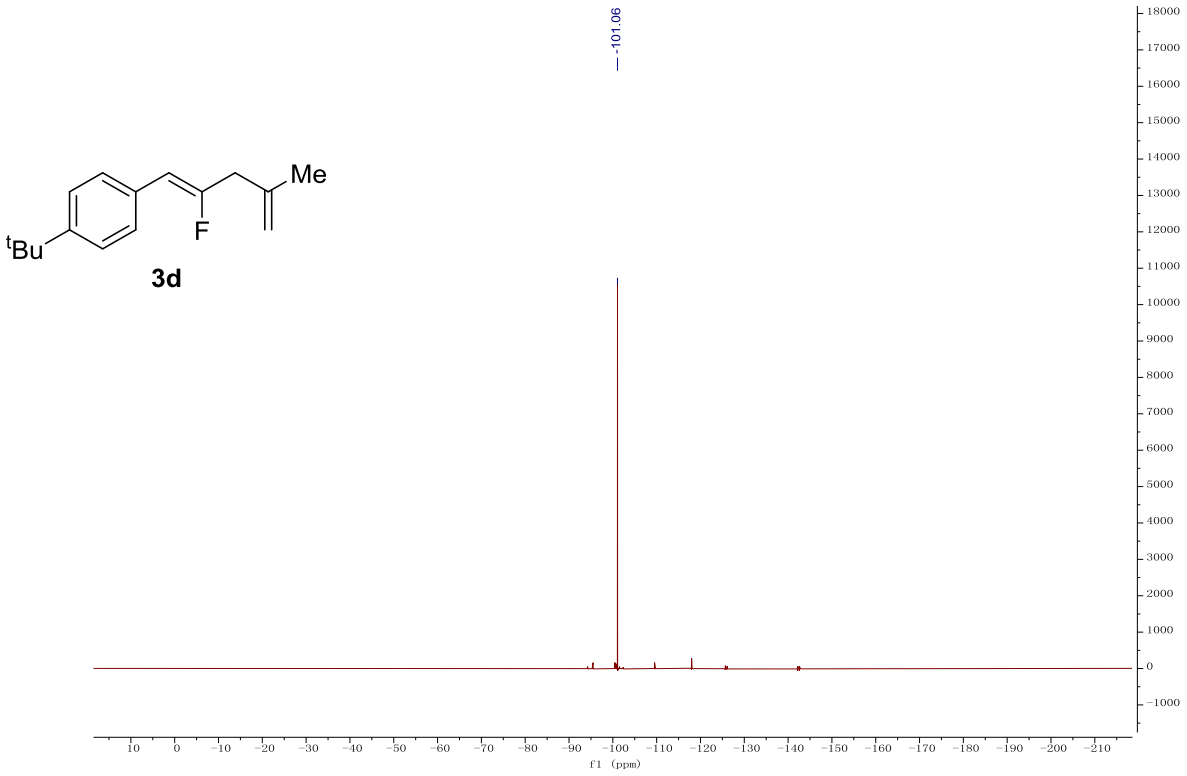
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3d



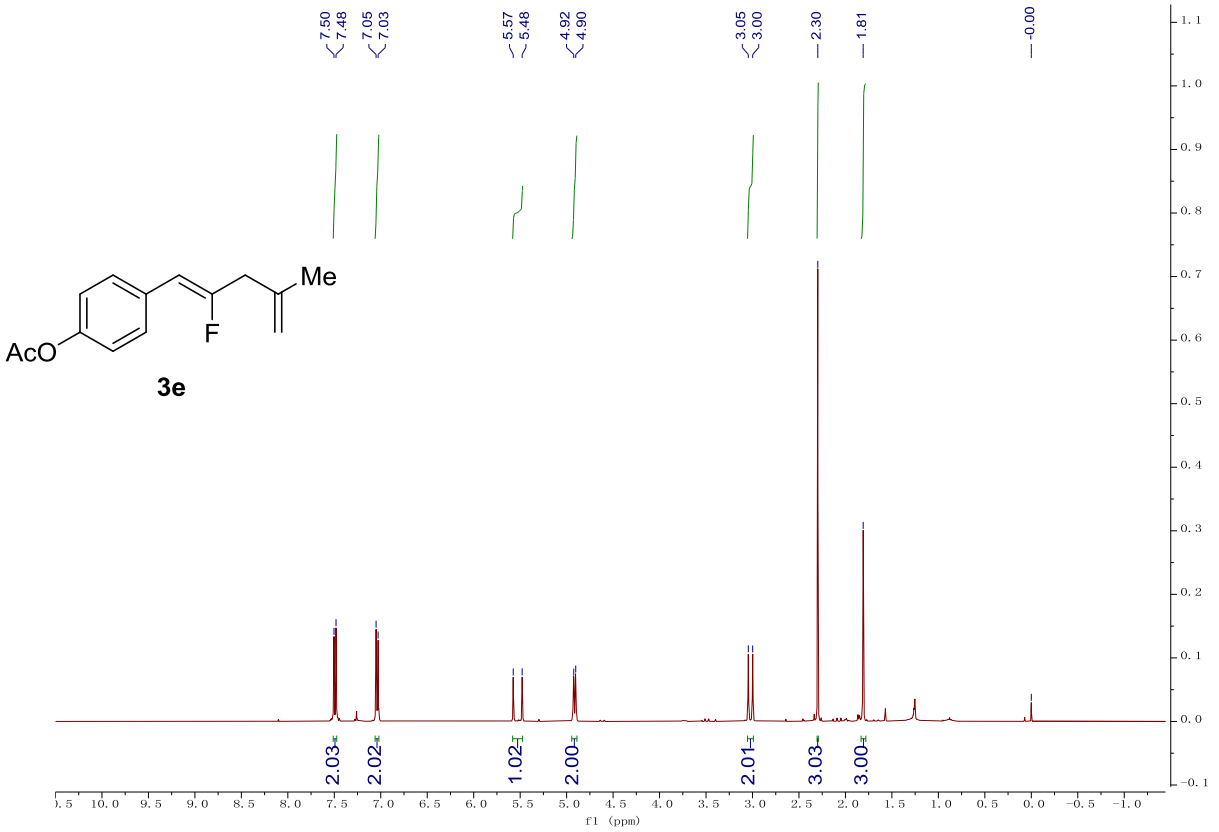
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3d



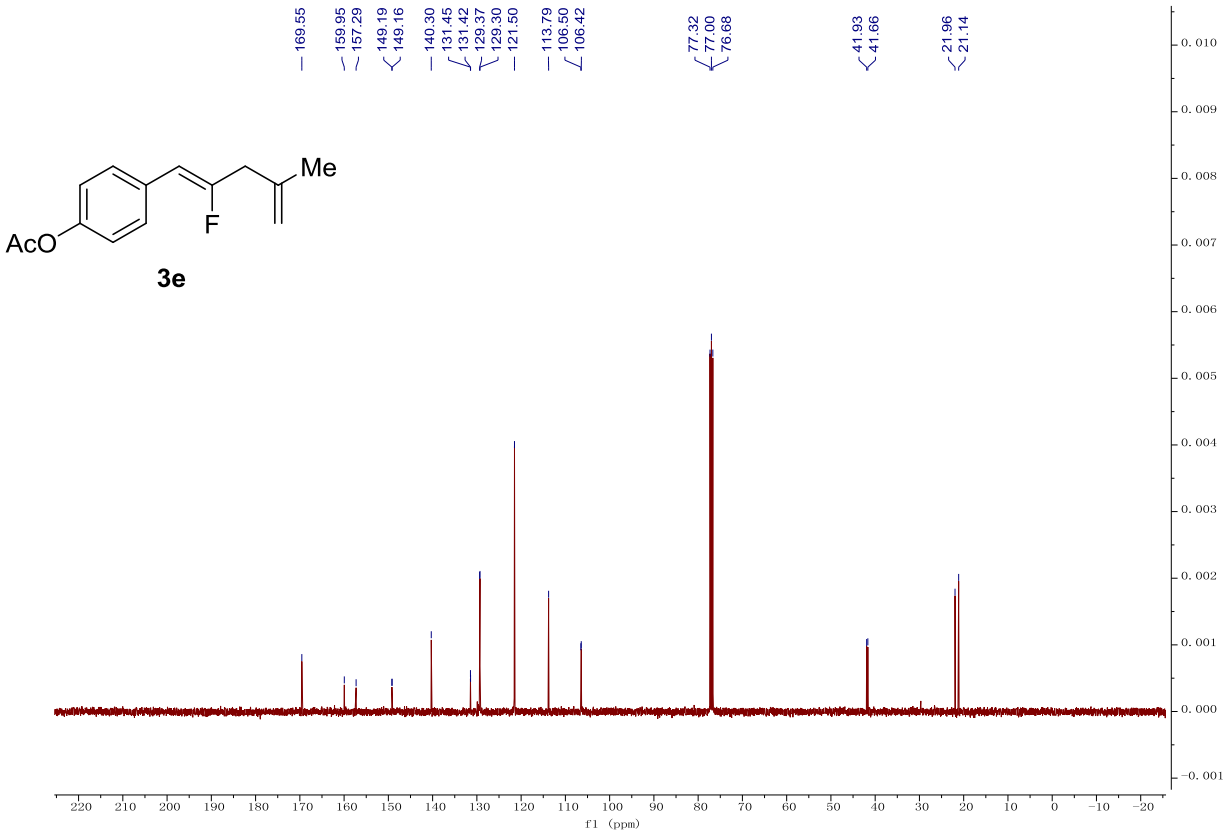
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3d



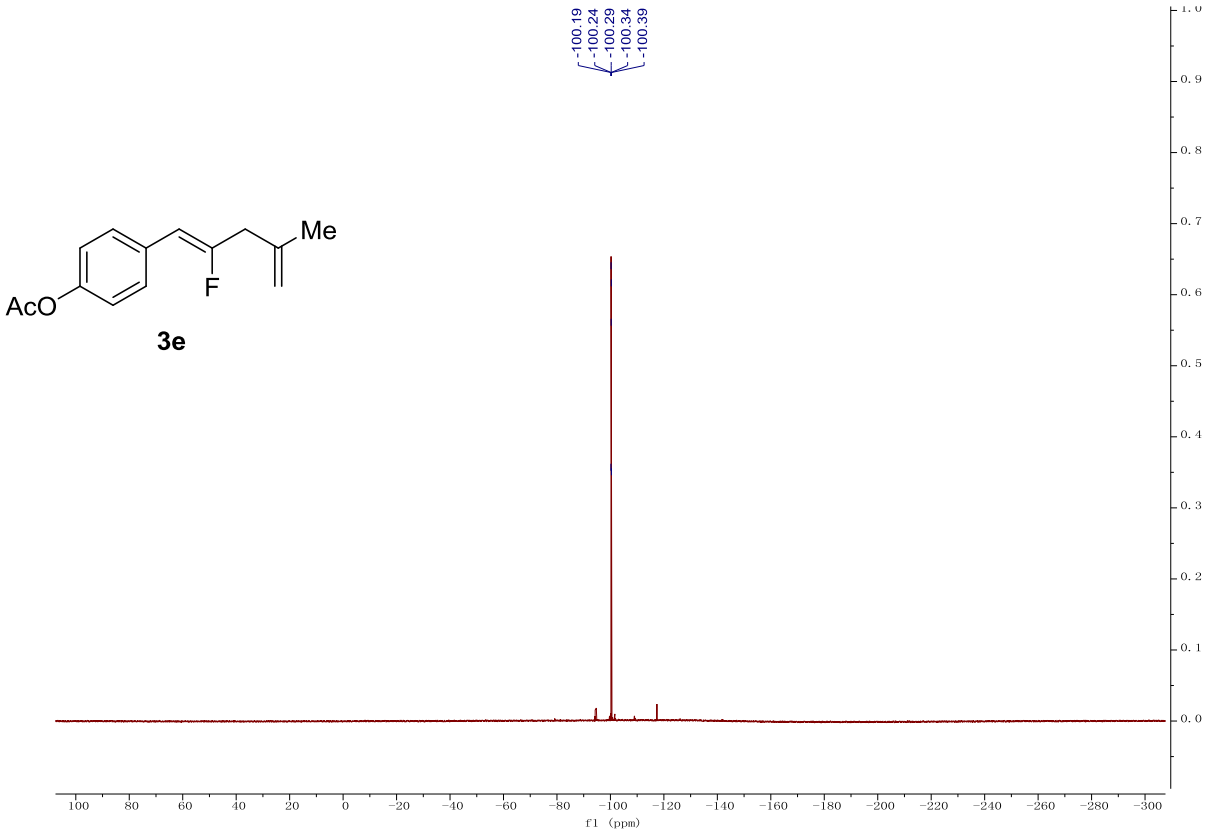
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3e (With JEOL)

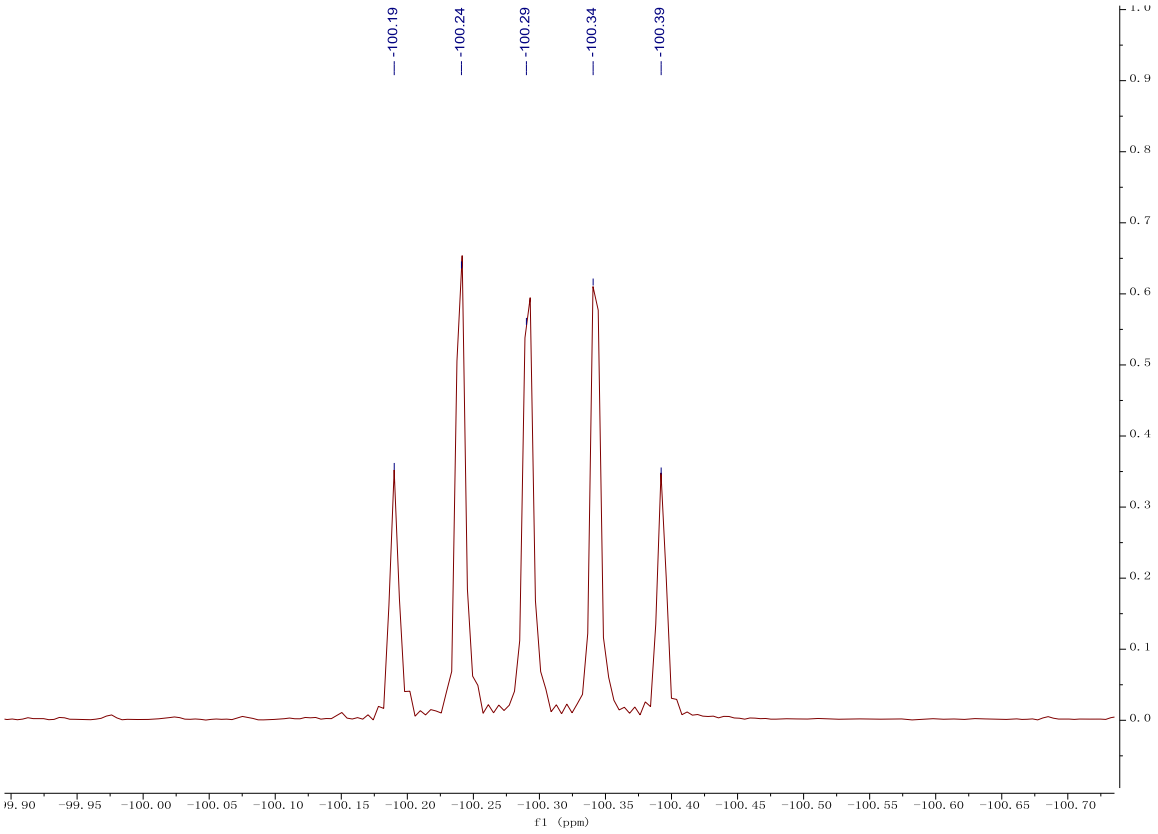


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3e (With JEOL)

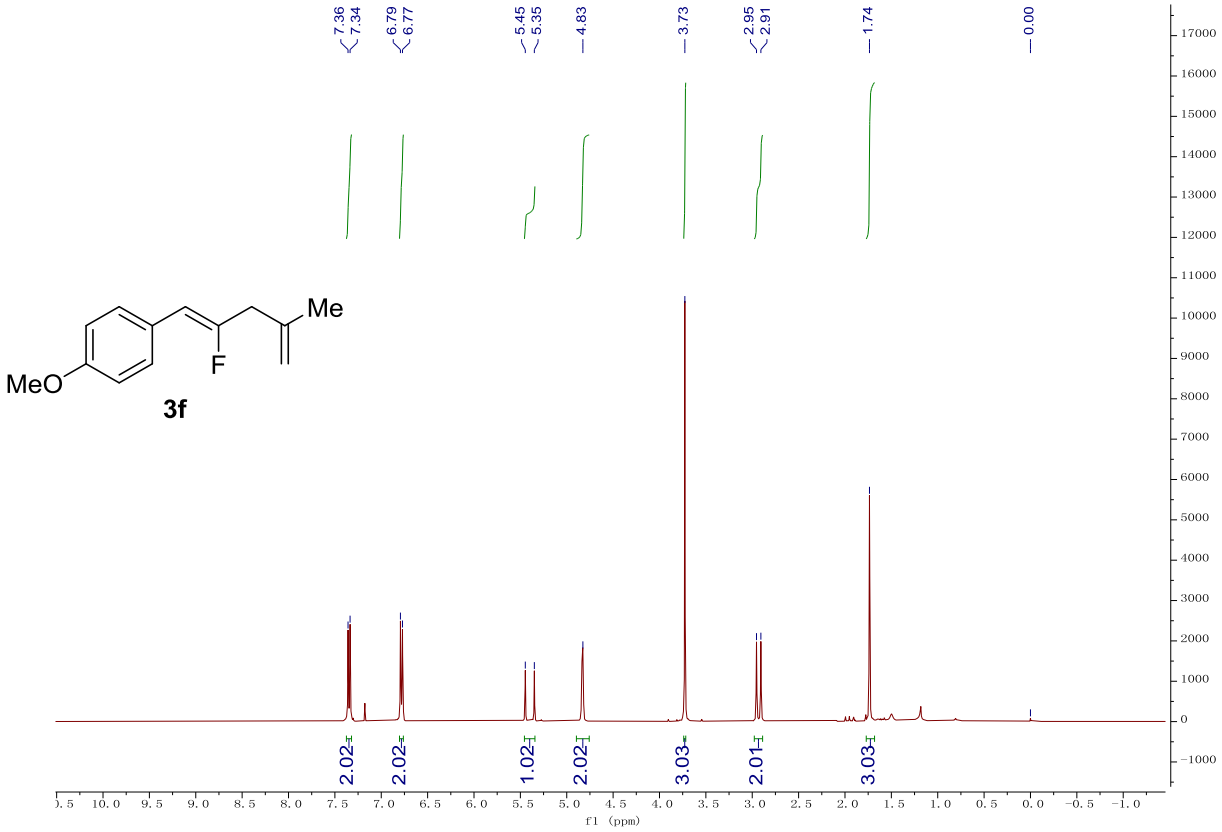


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3e (With JEOL)

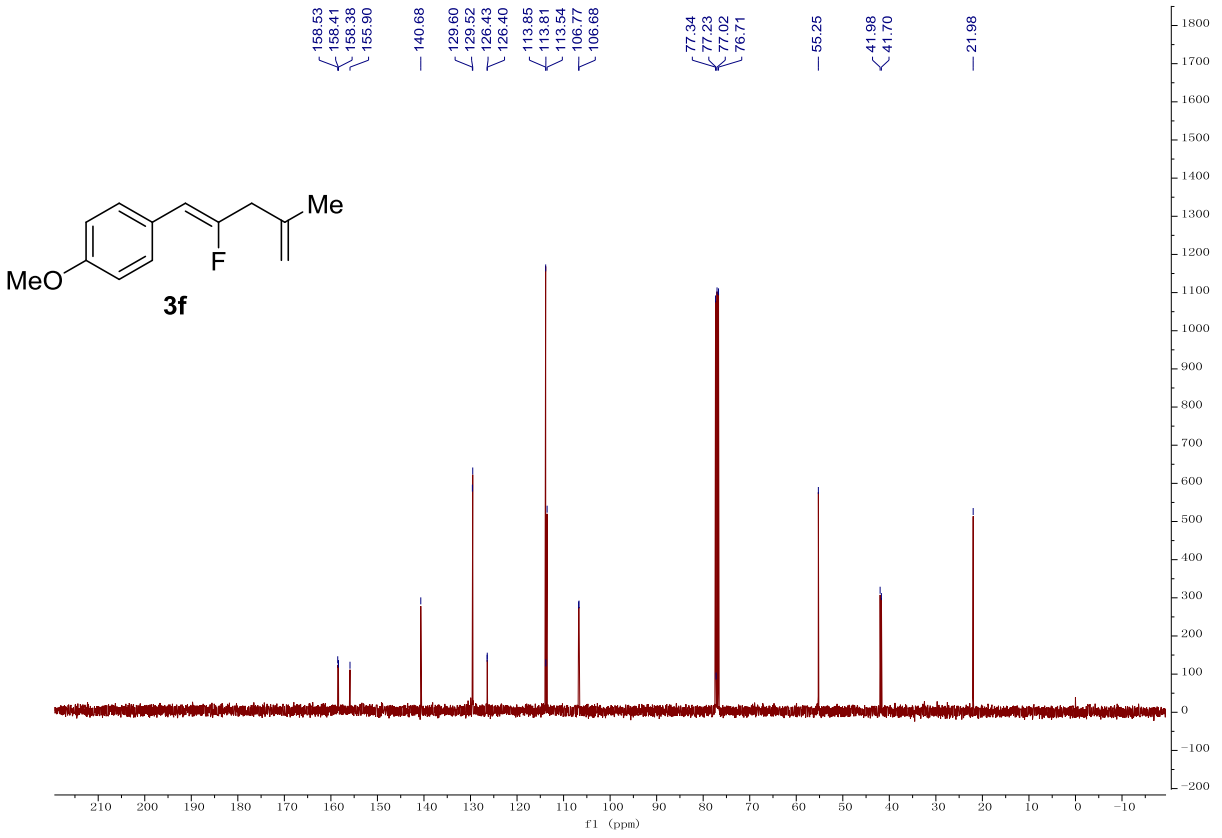




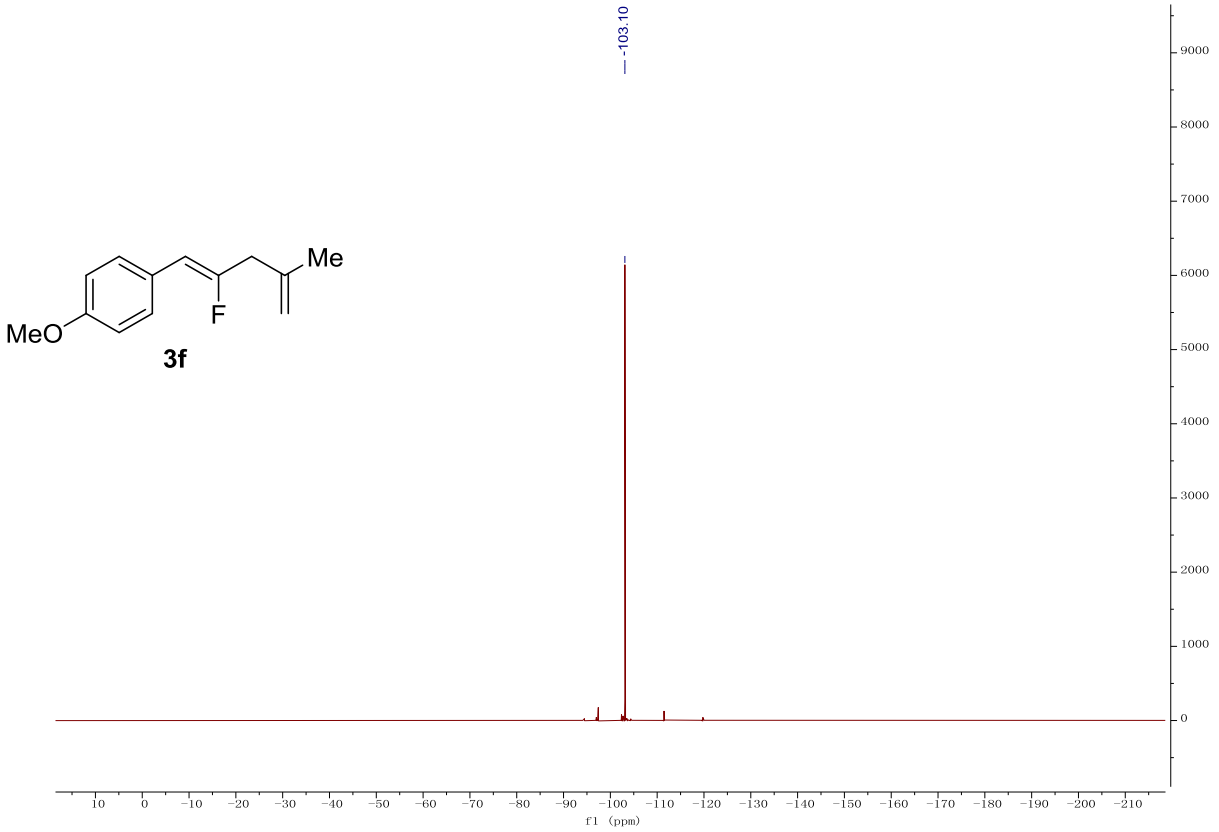
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3f



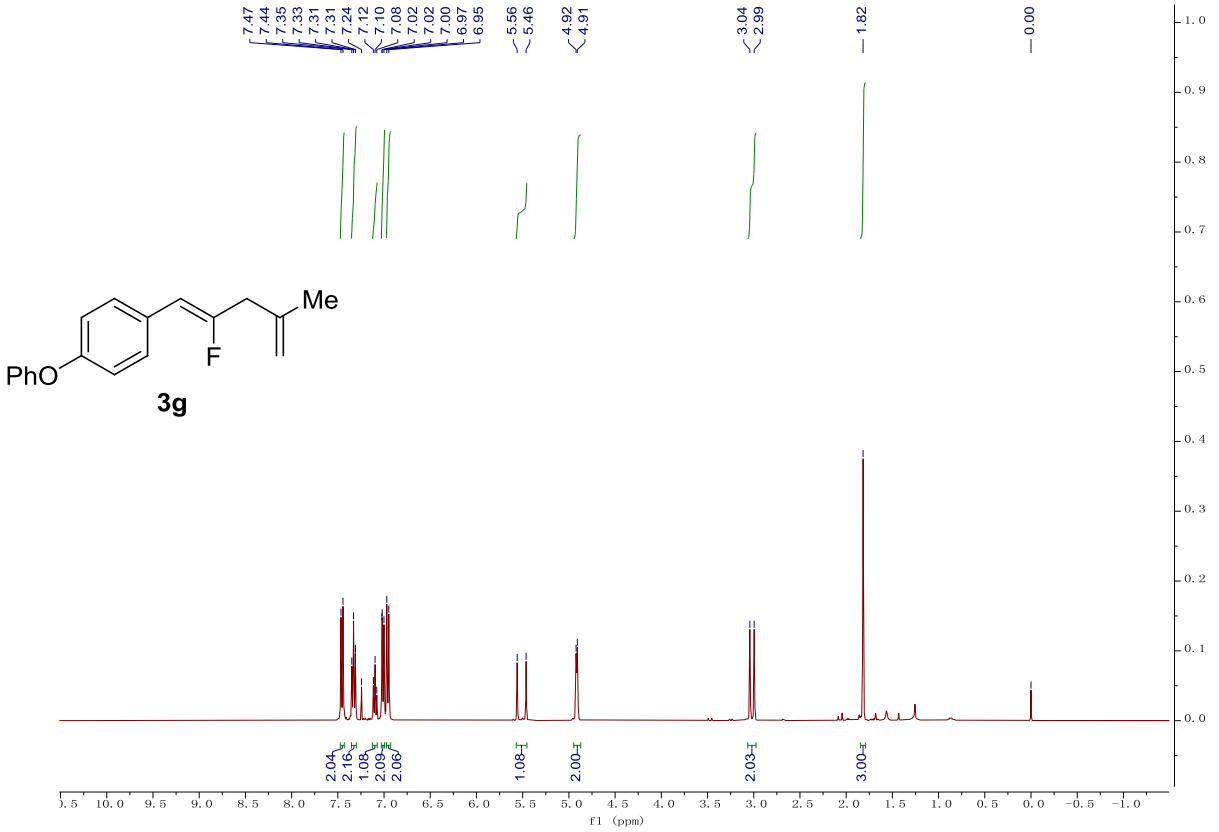
^{13}C NMR (101 MHz, CDCl3) spectrum of 3f



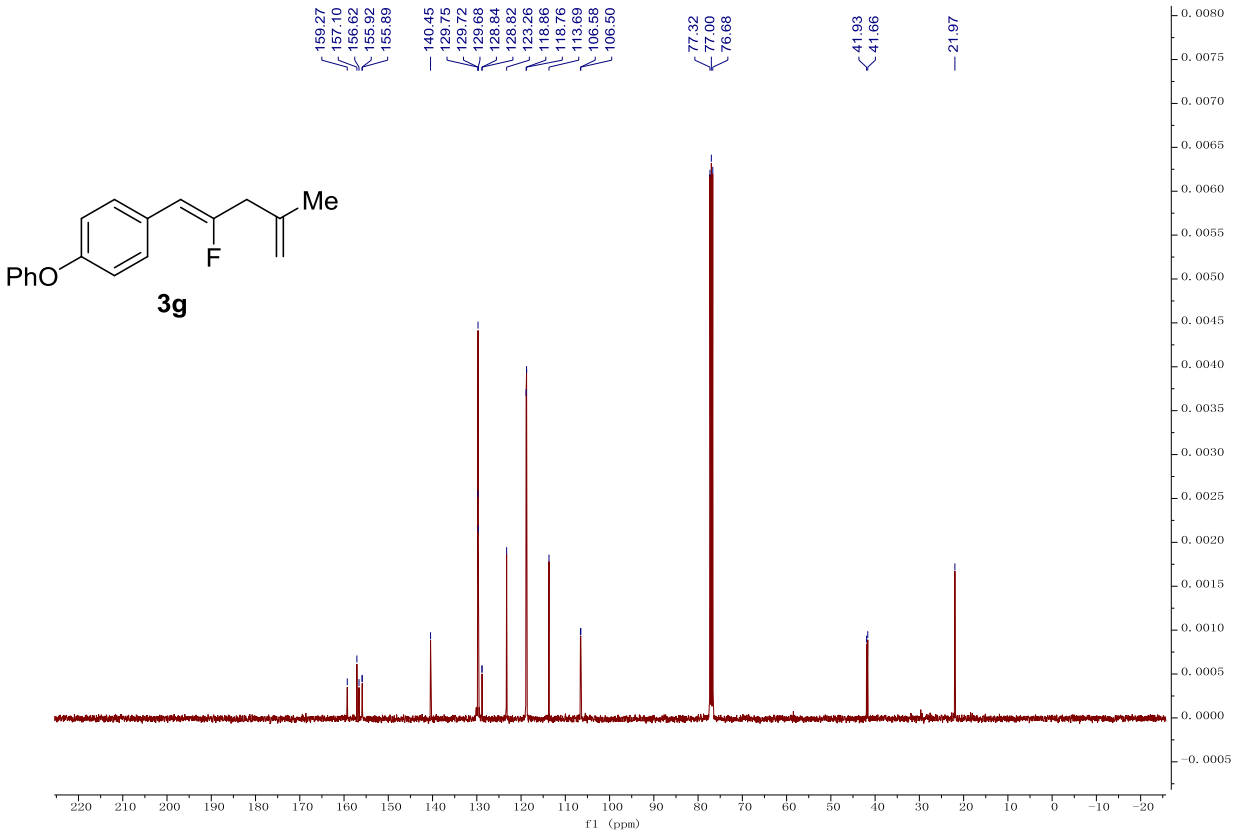
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3f



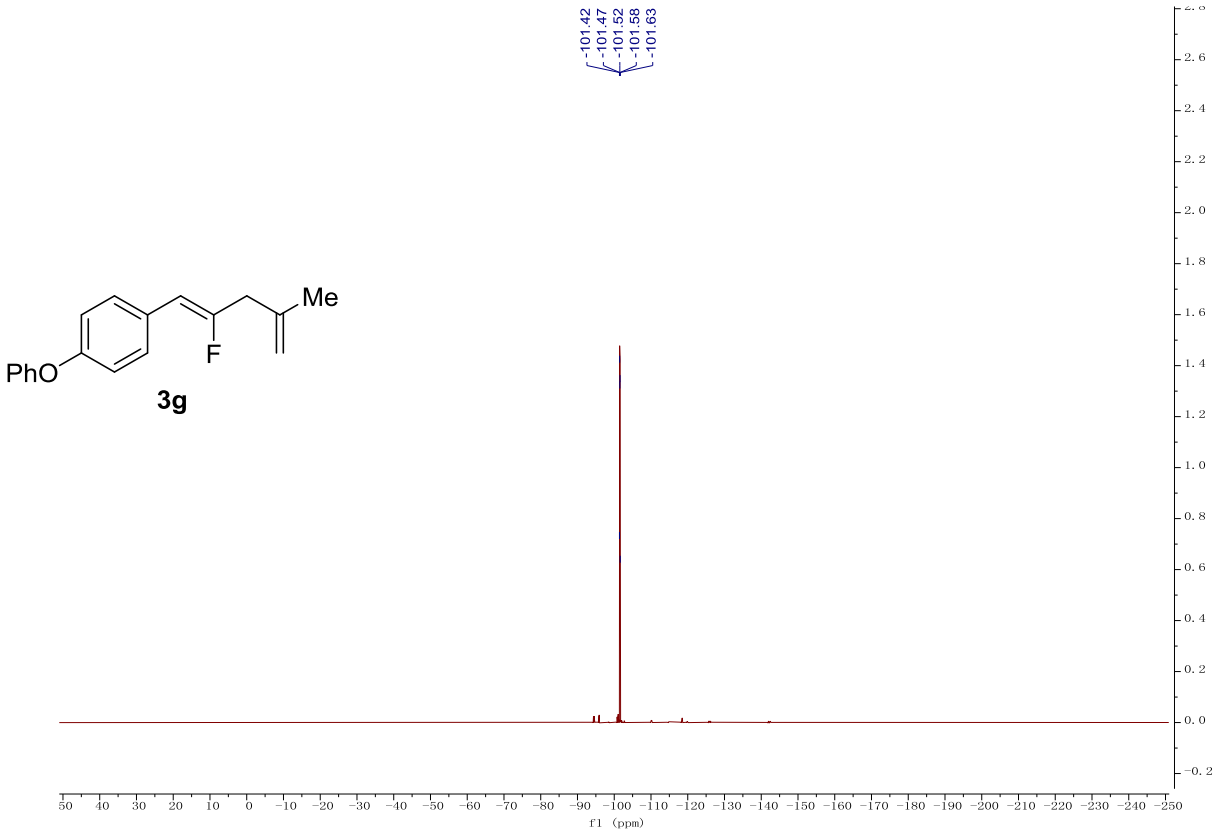
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3g (With JEOL)

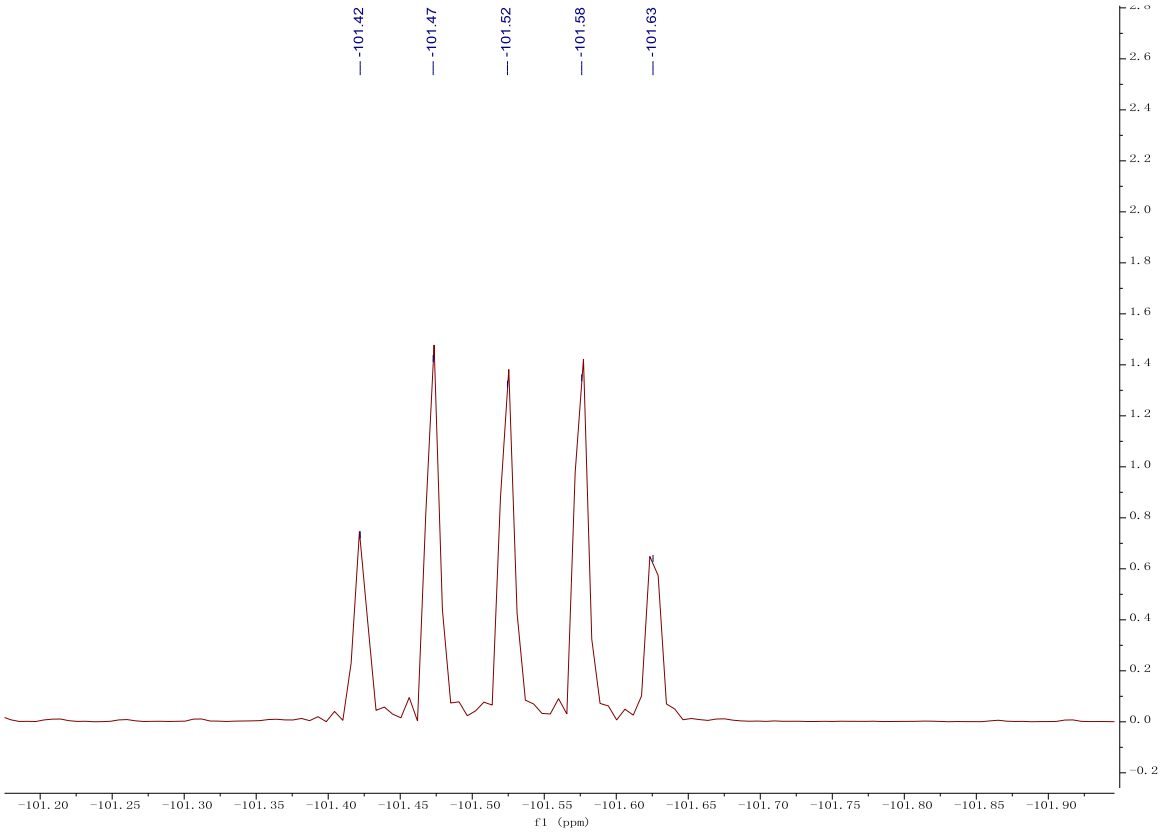


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3g (With JEOL)

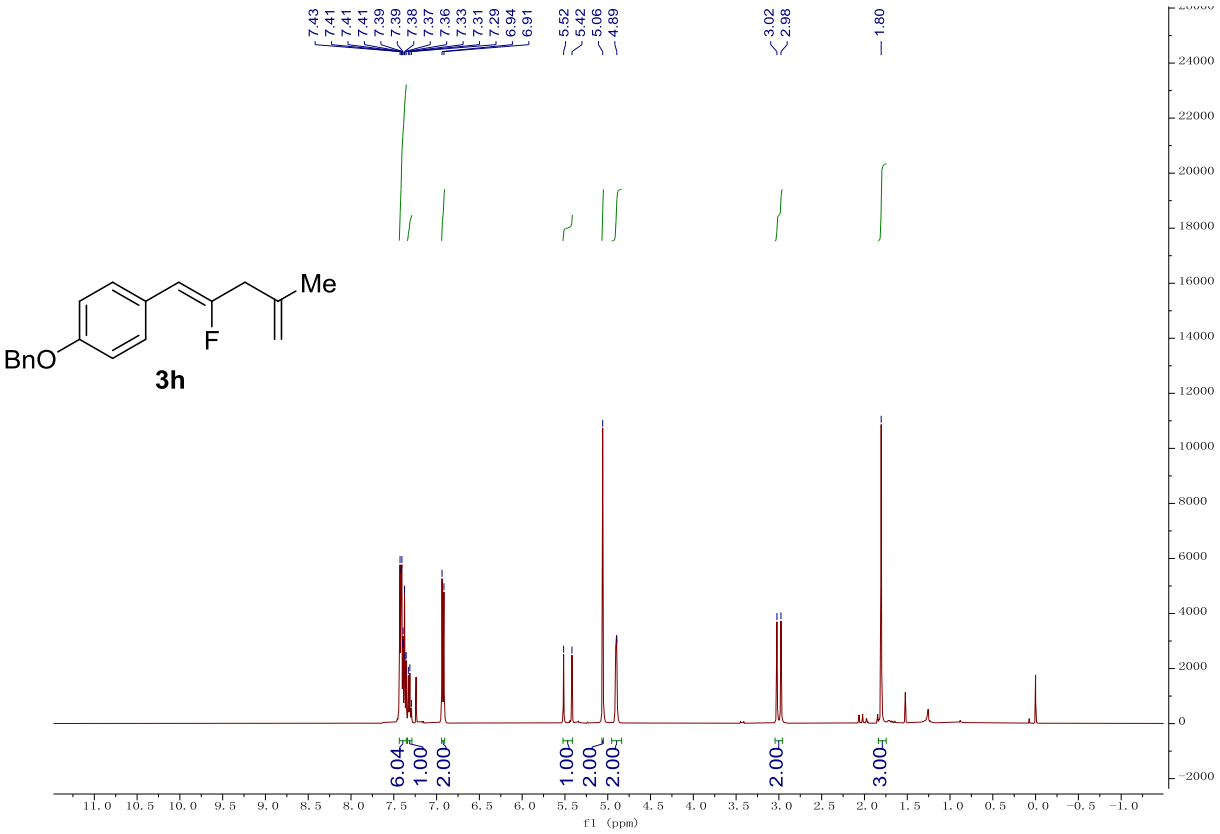


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3g (With JEOL)

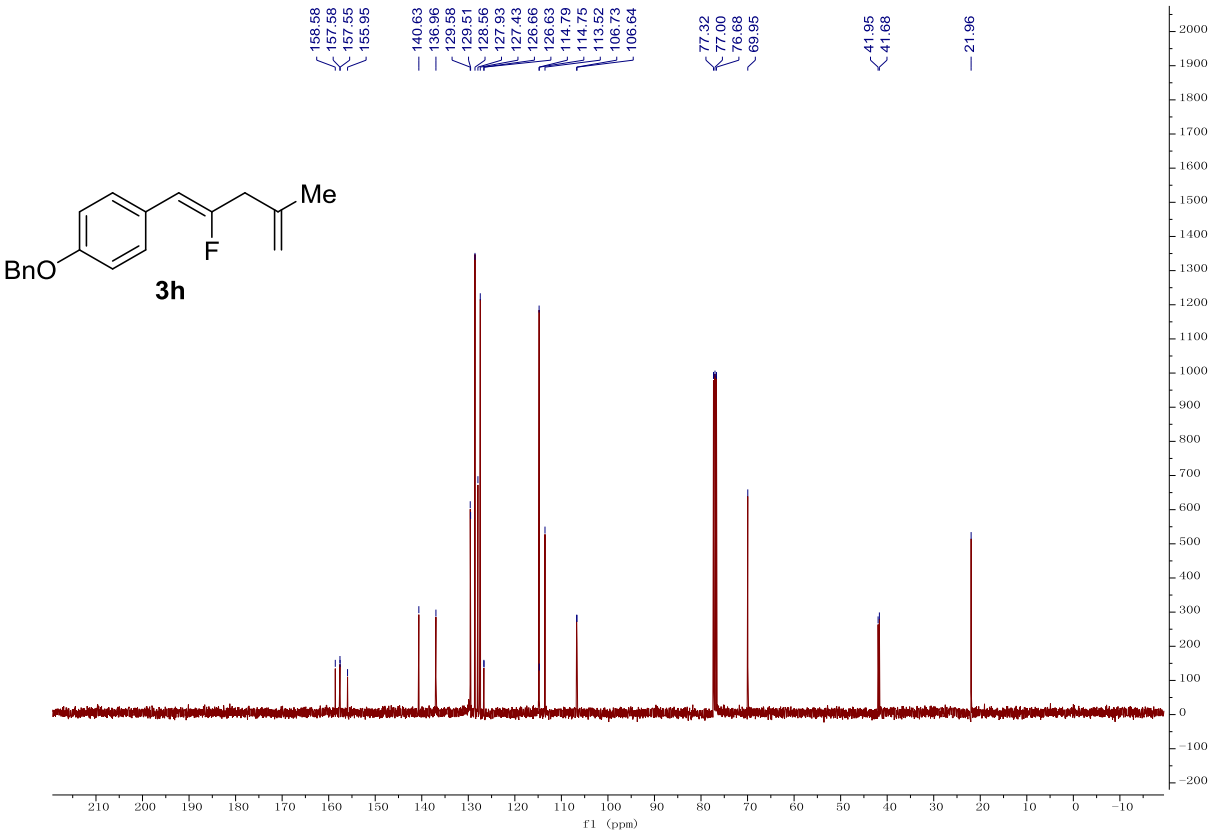




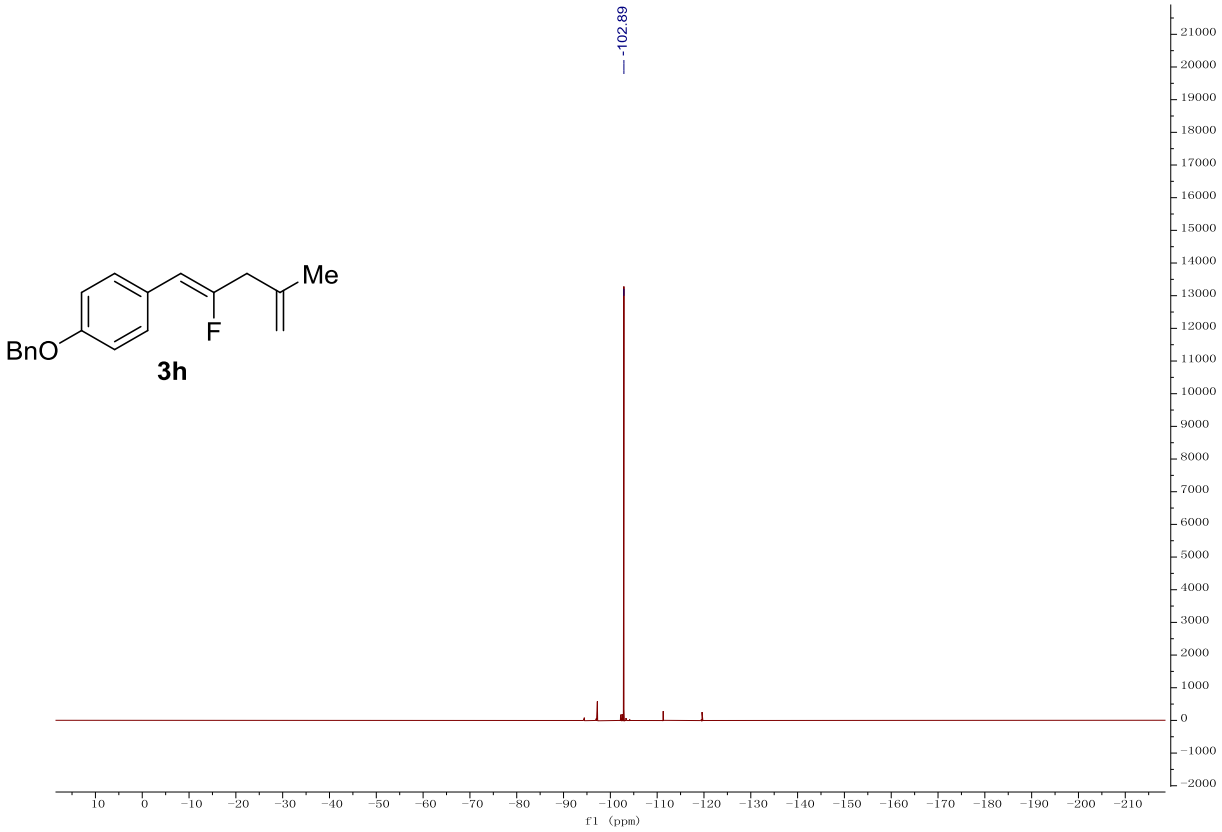
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3h



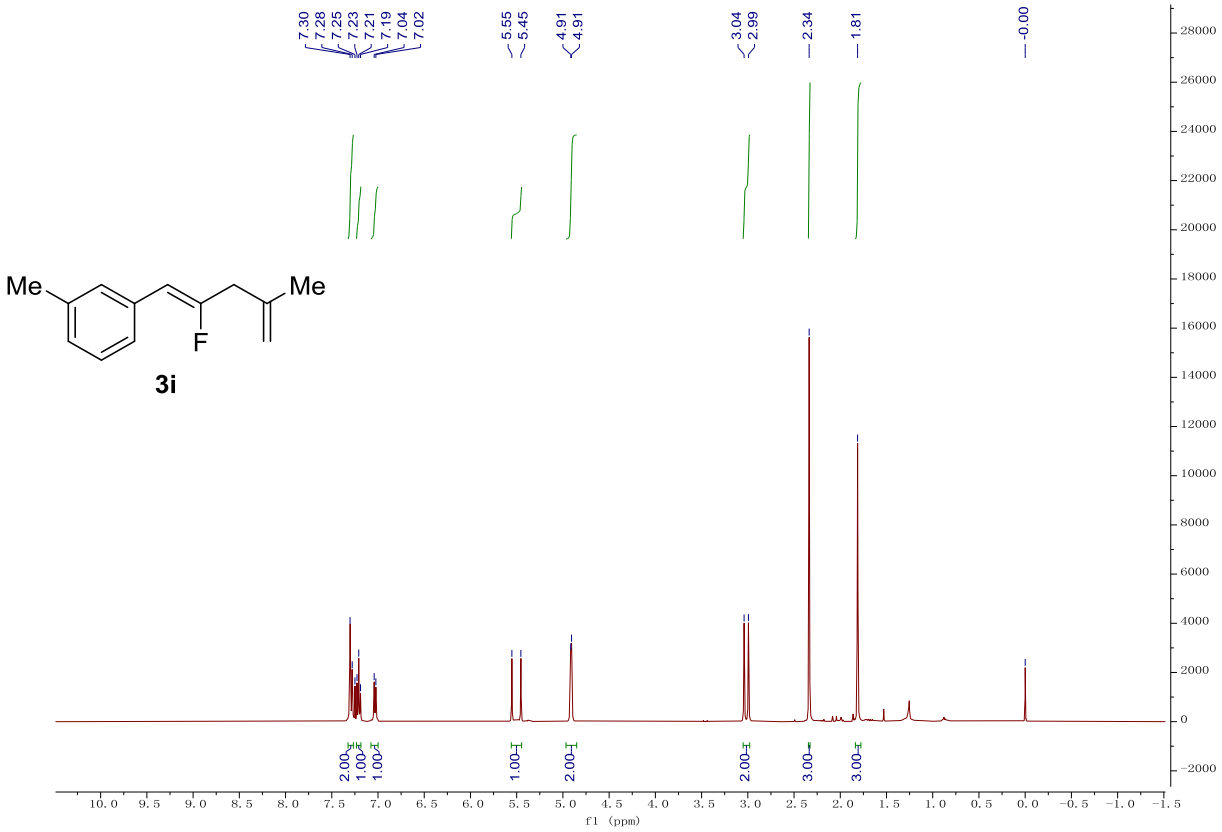
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3h



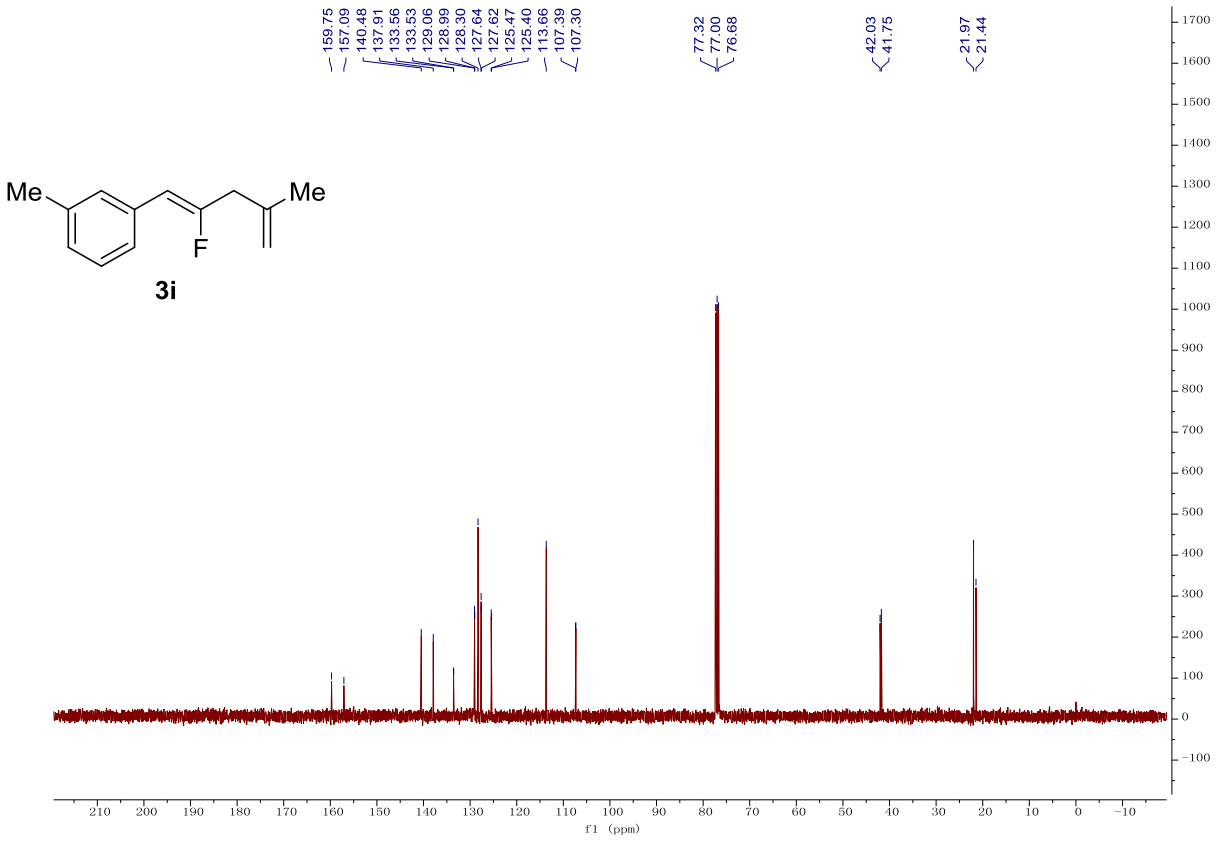
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3h



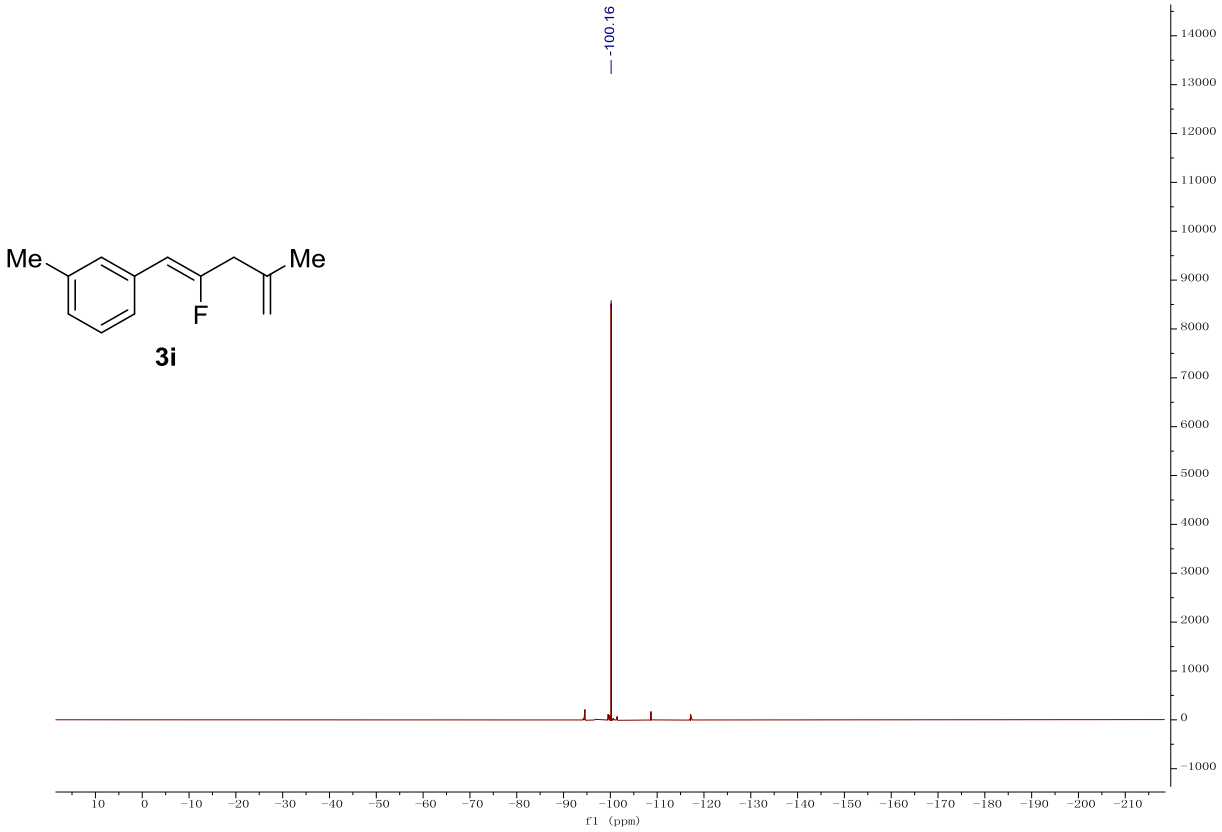
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3i



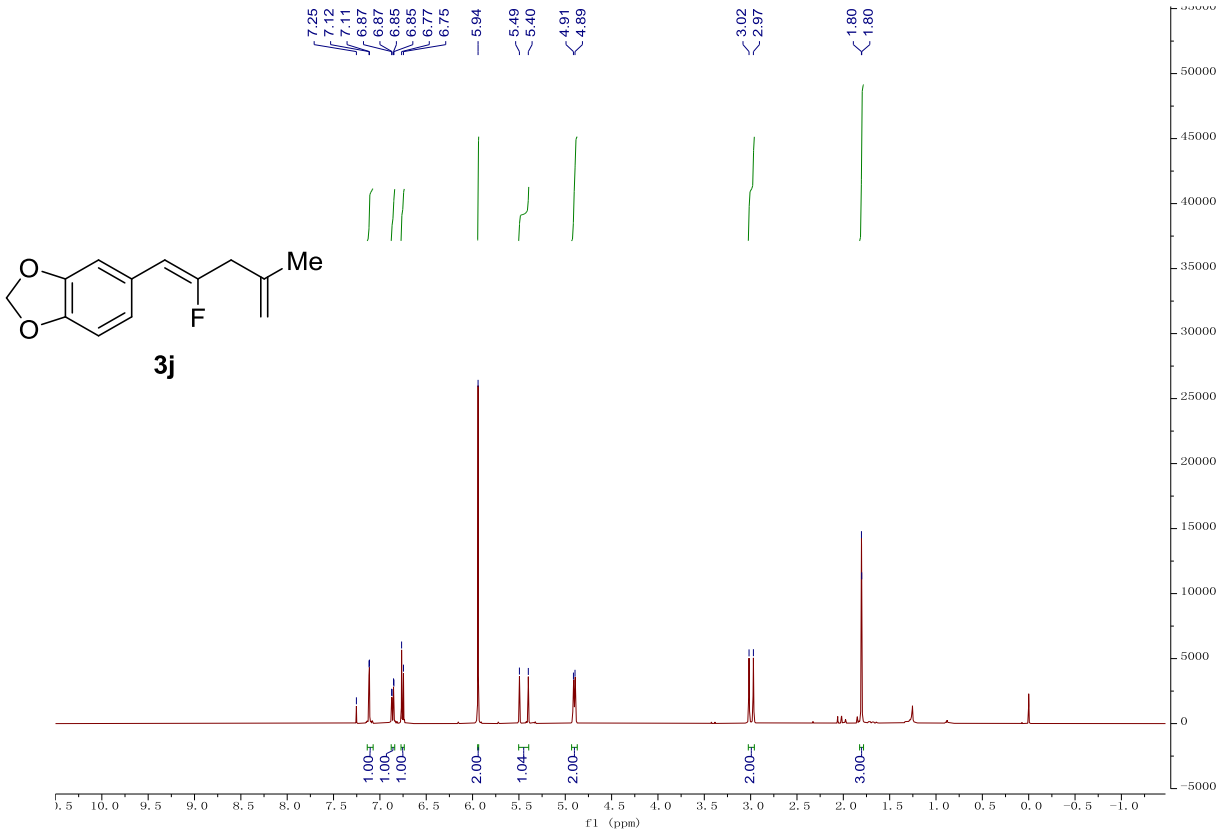
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3i



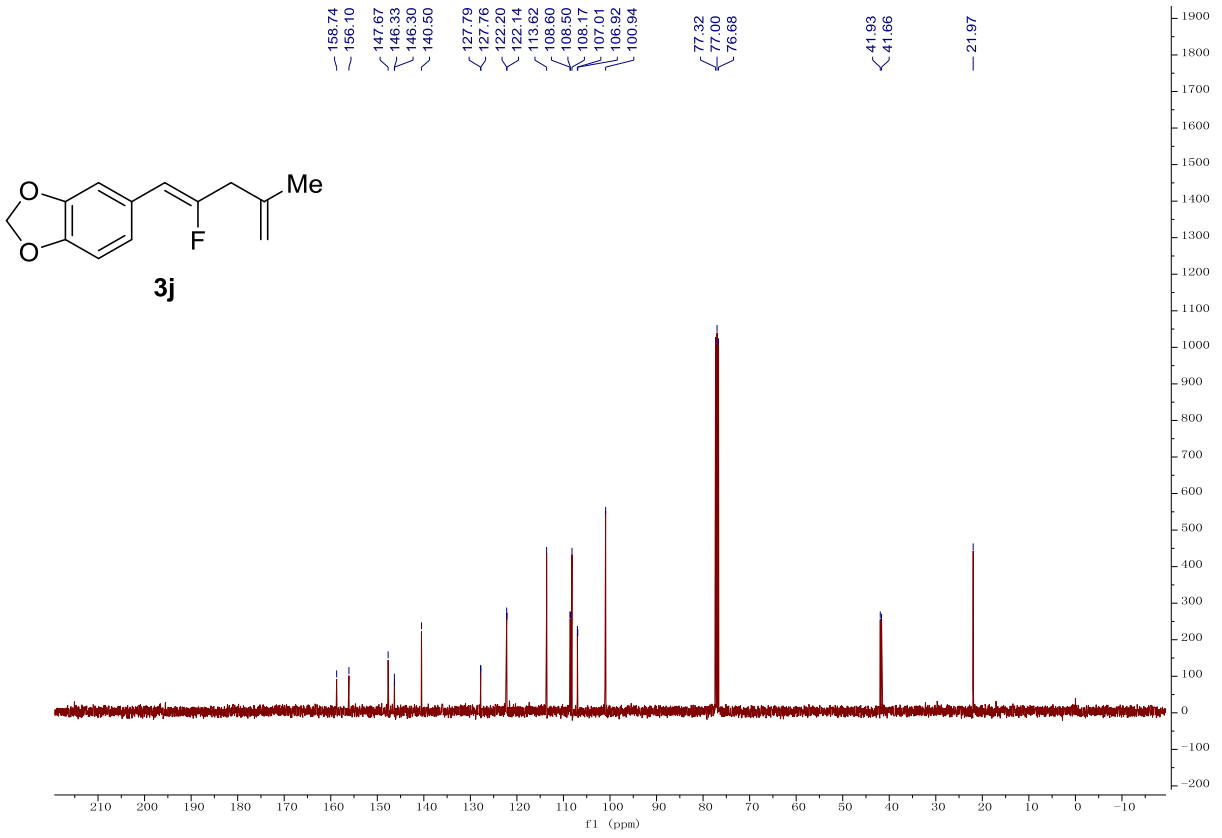
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3i



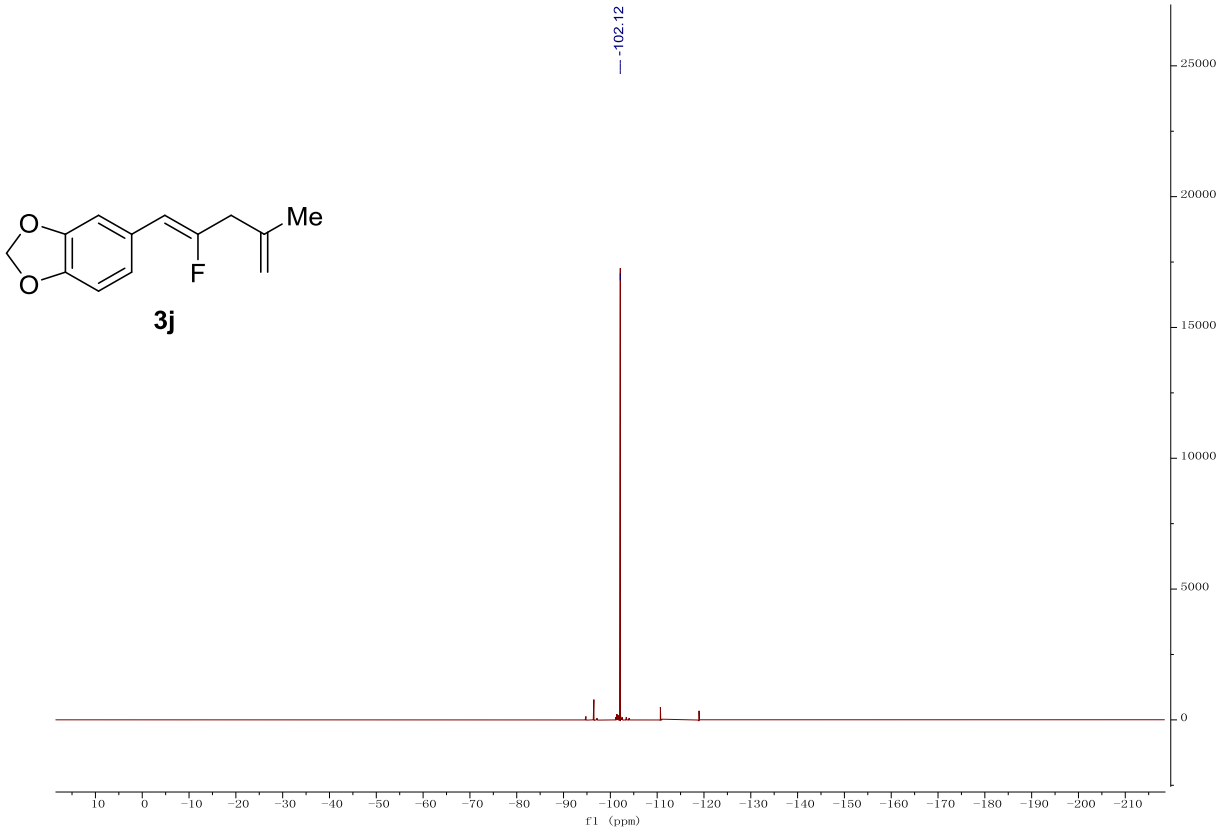
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3j



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3j

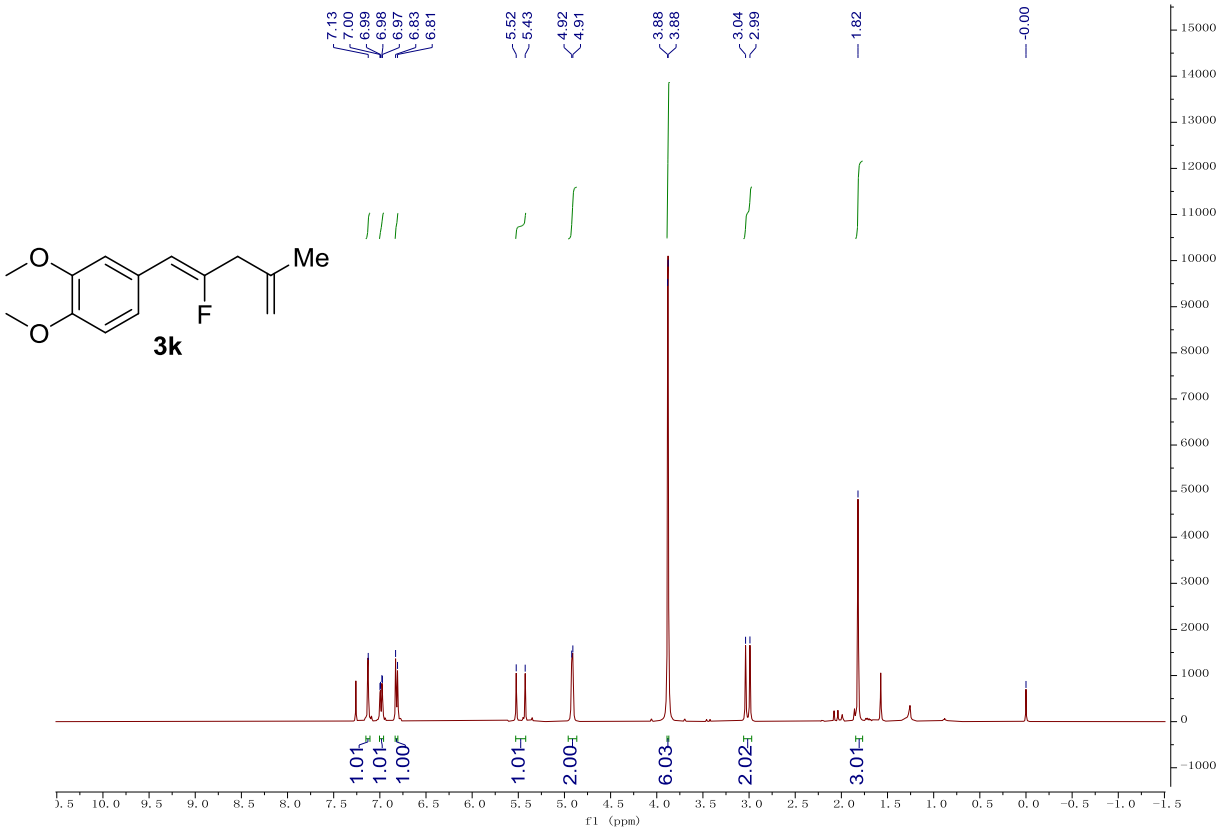


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3j

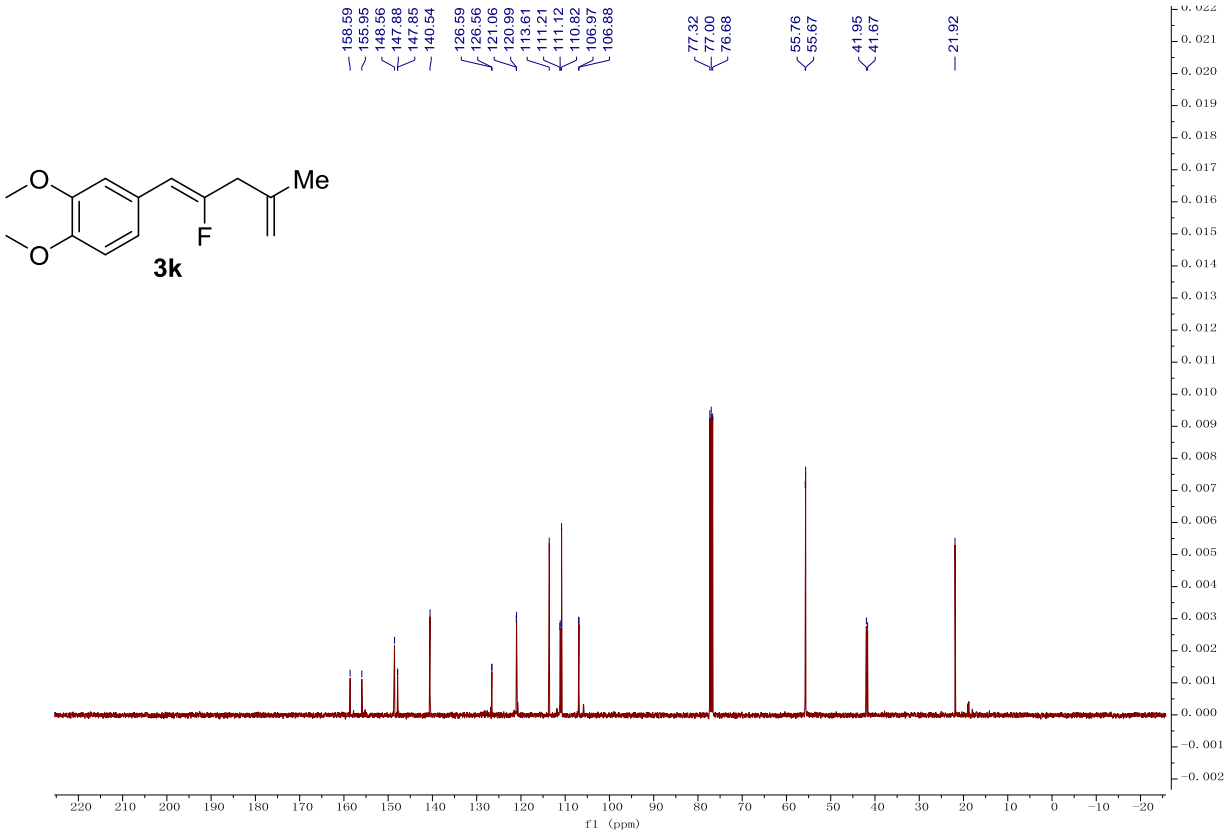


3j

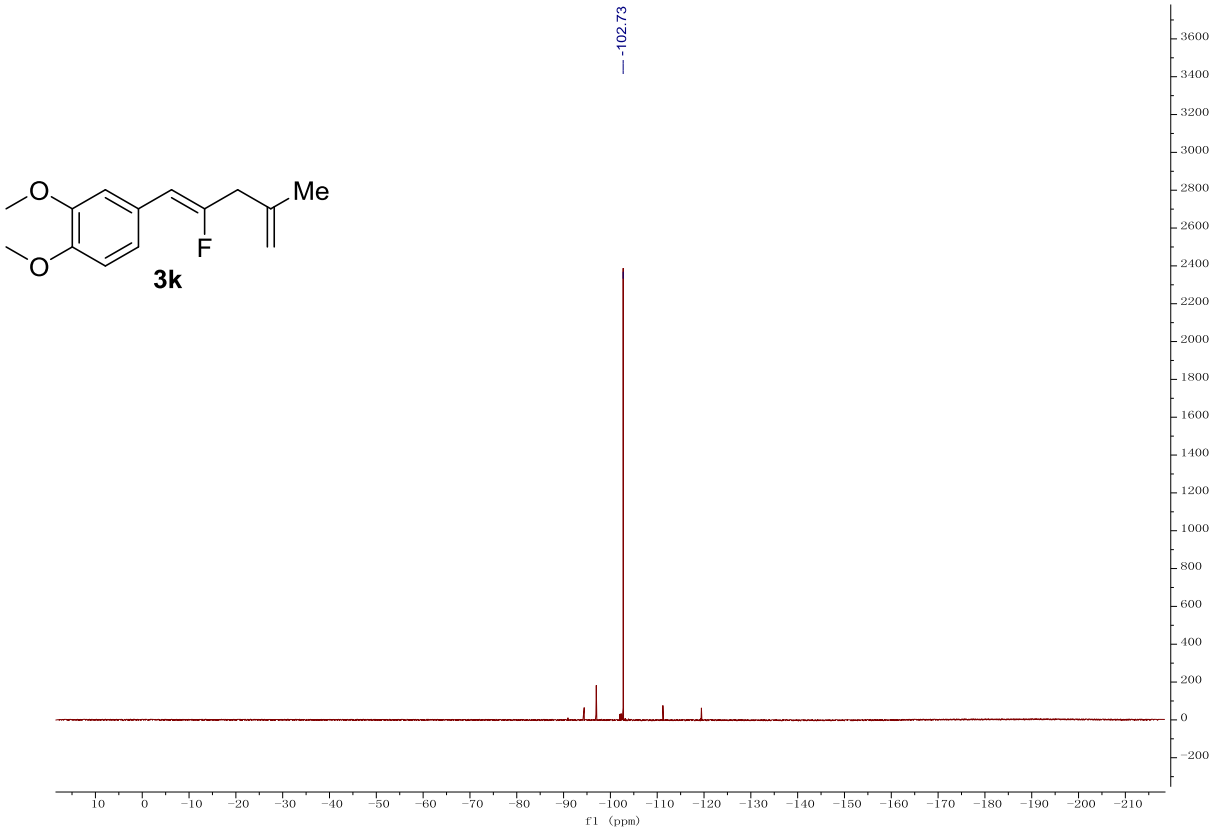
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3k



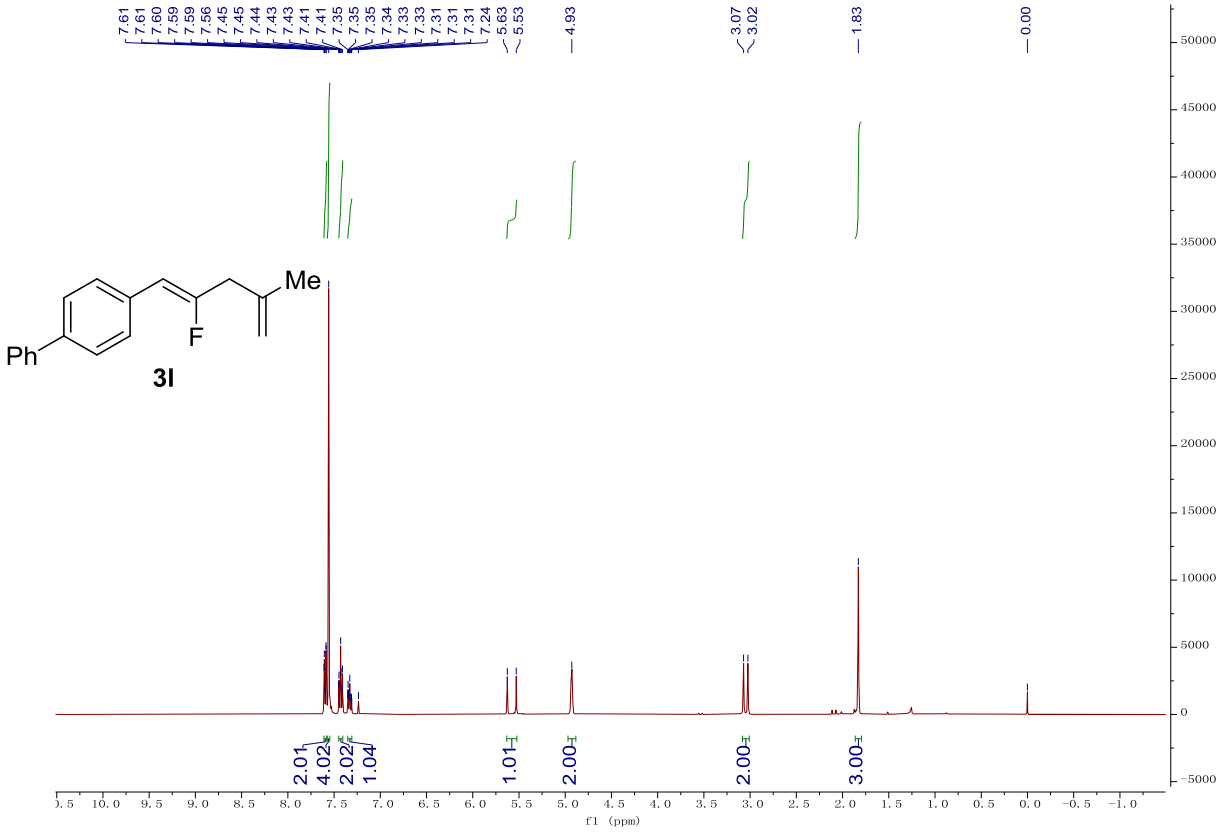
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3k



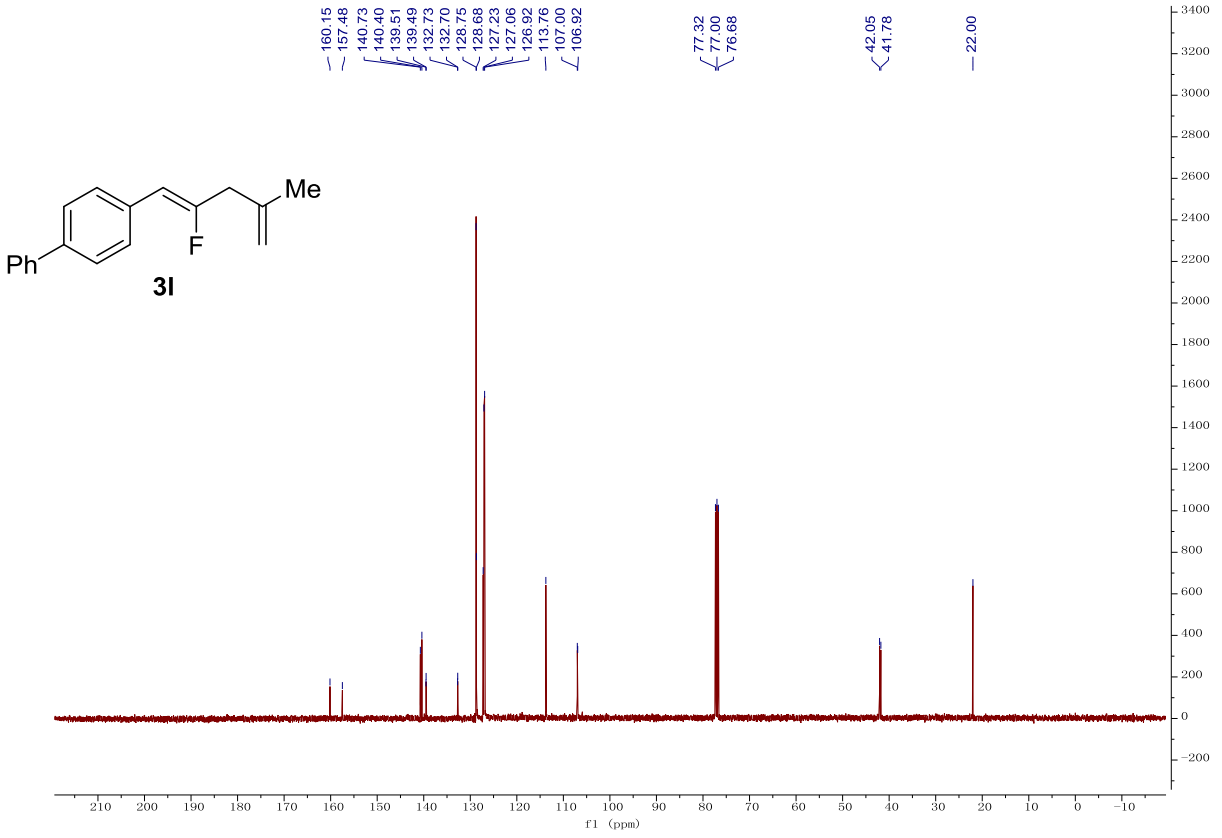
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3k



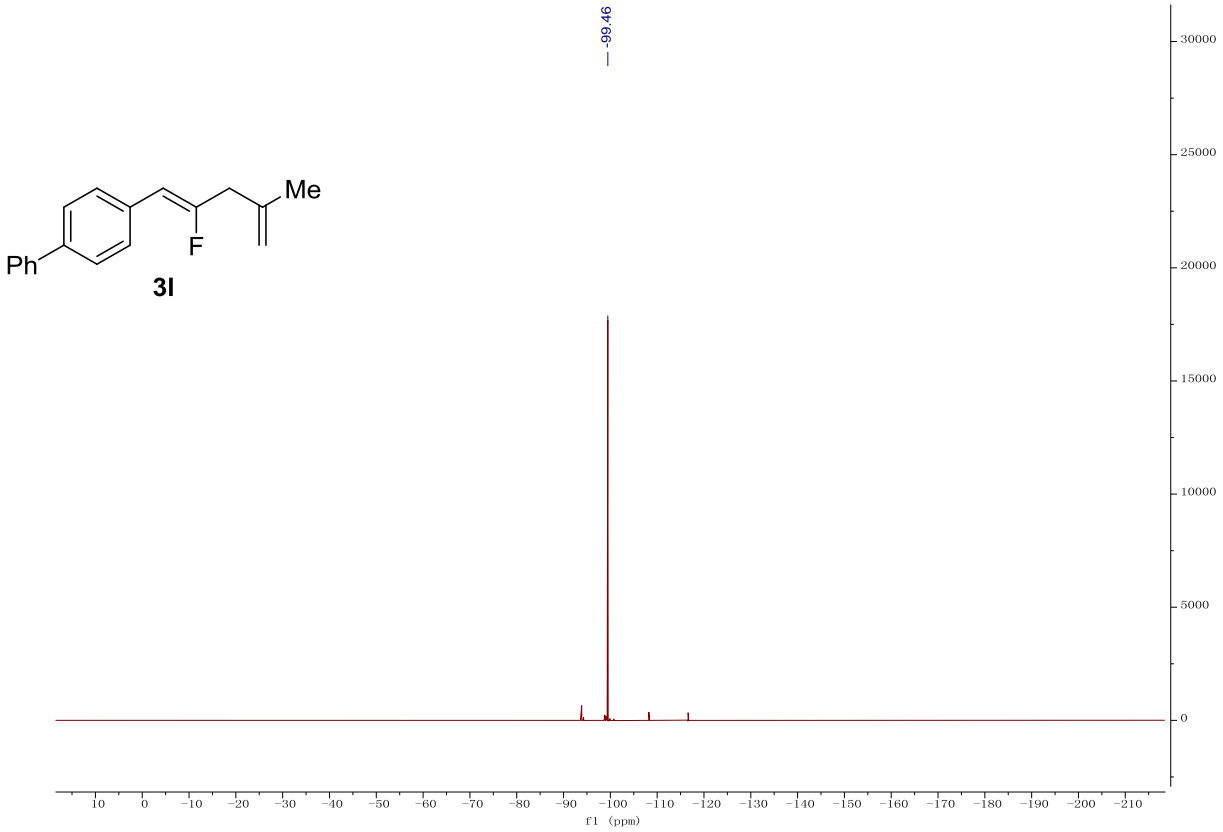
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3l



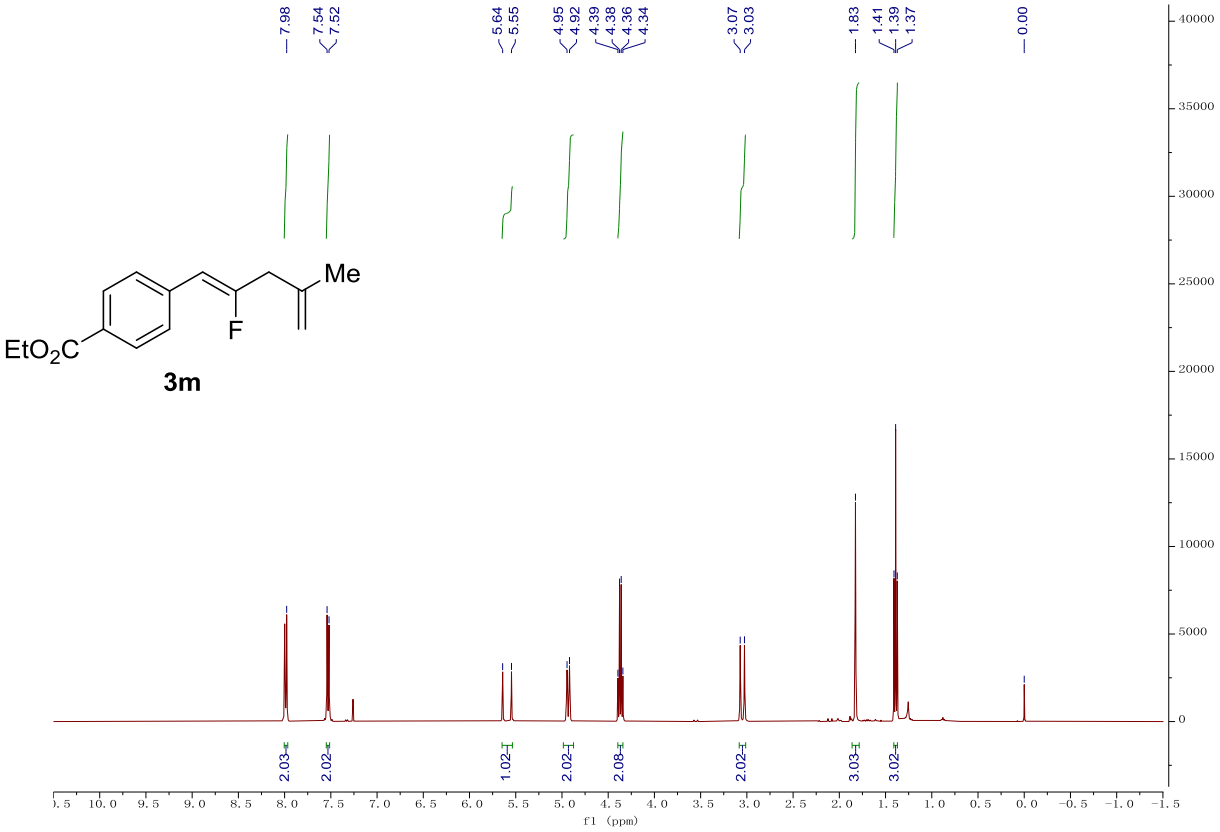
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3l



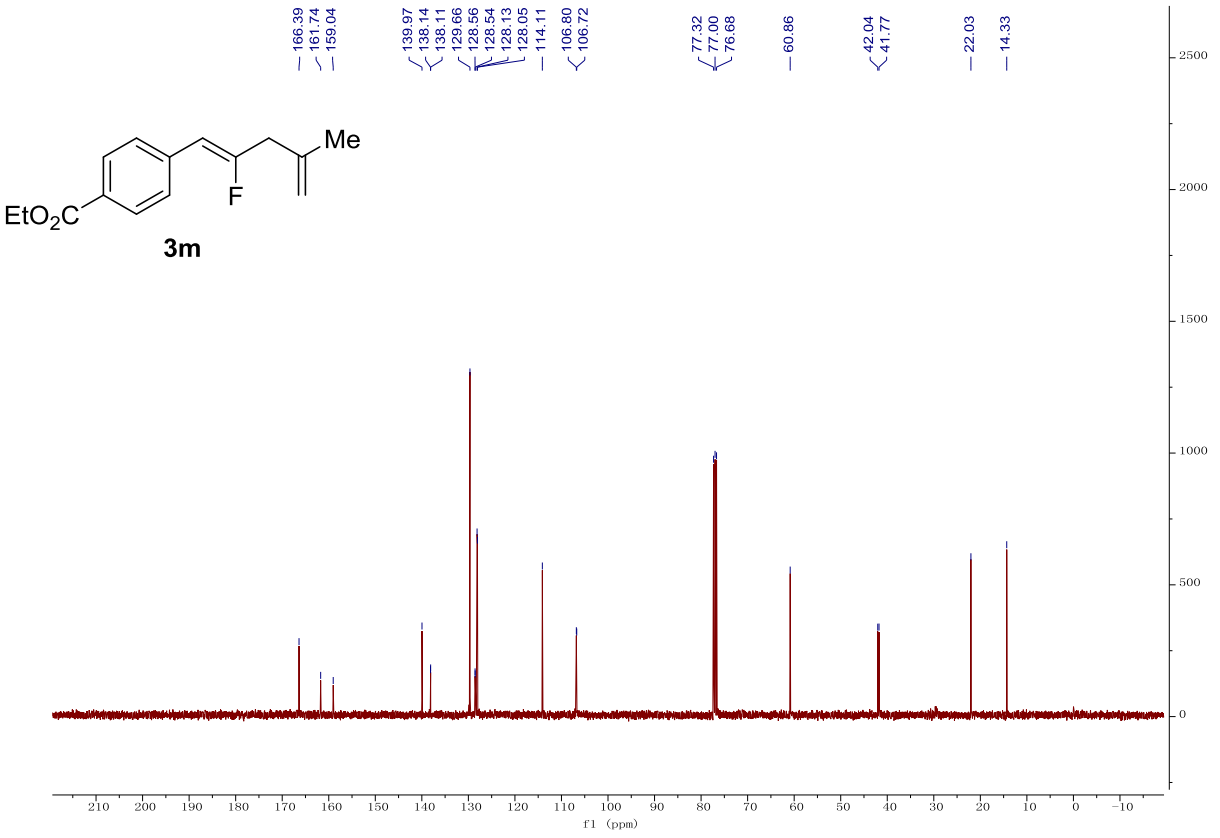
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3l



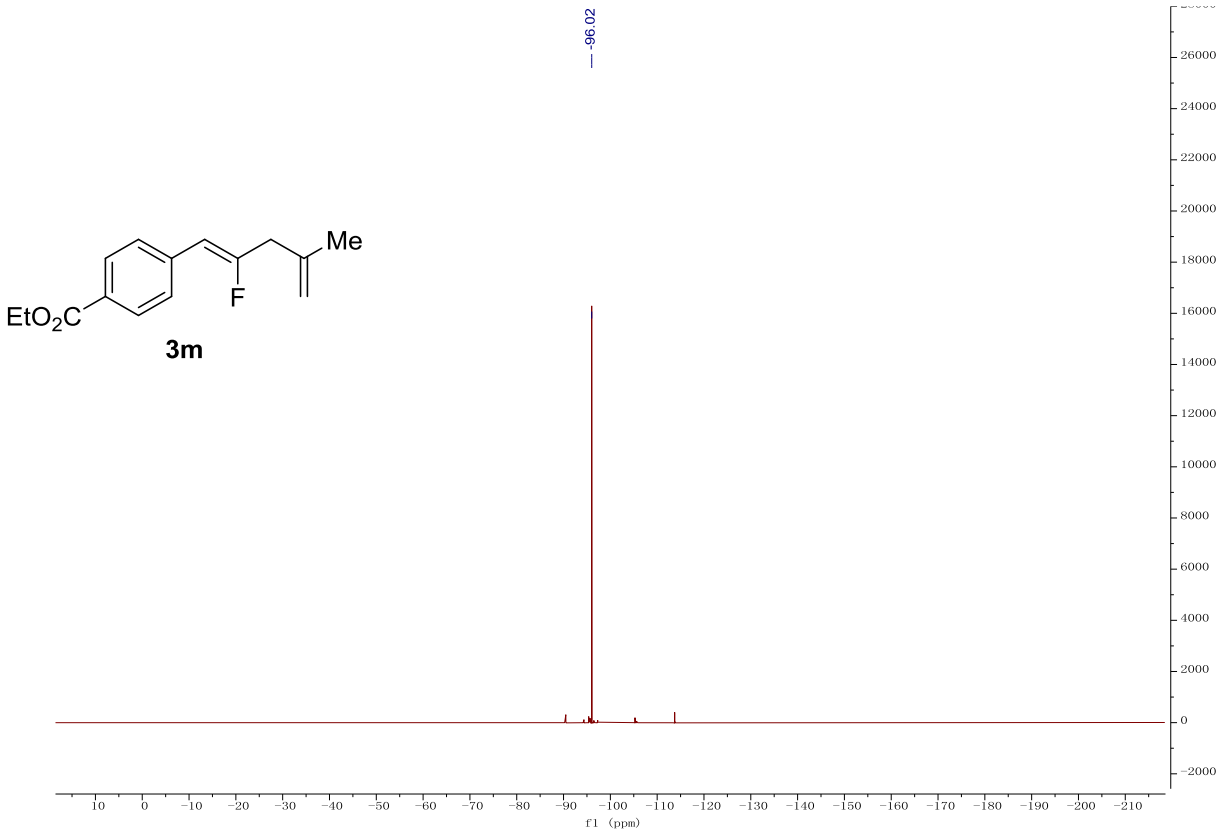
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3m



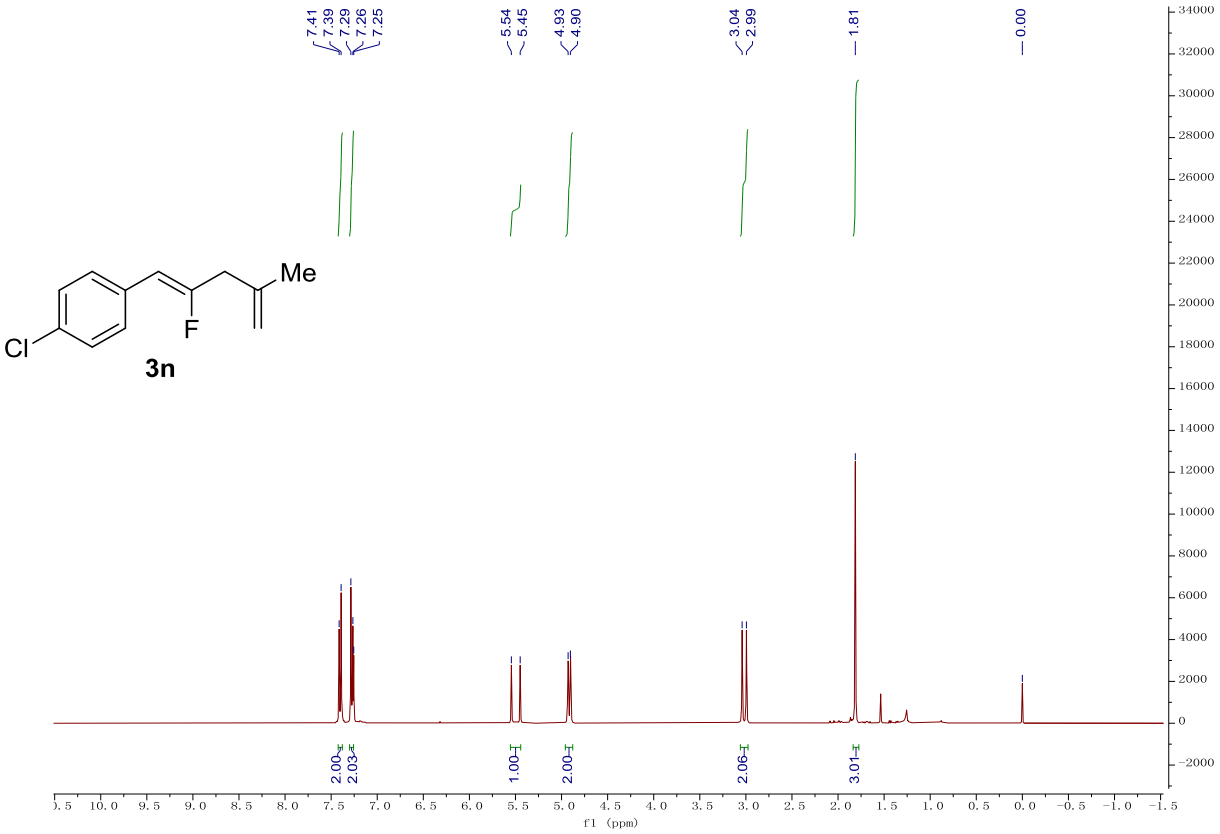
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3m



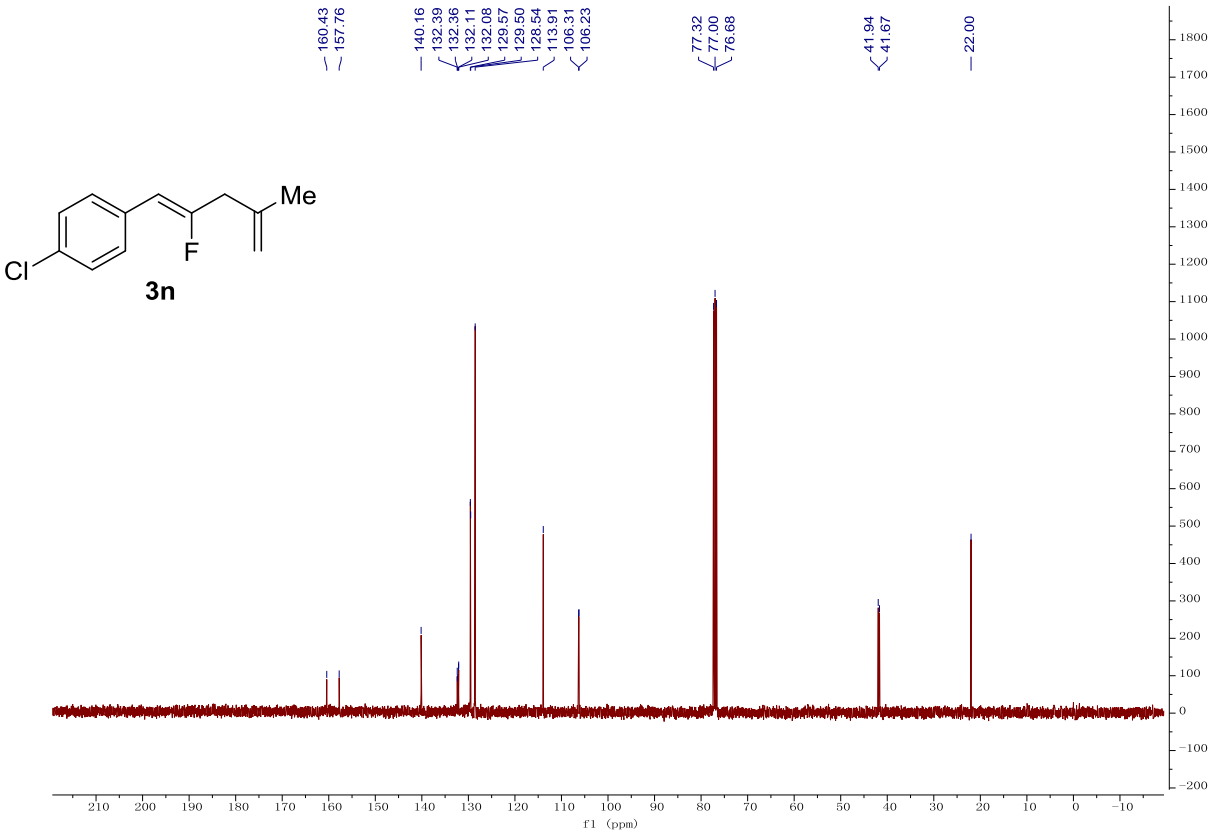
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3m



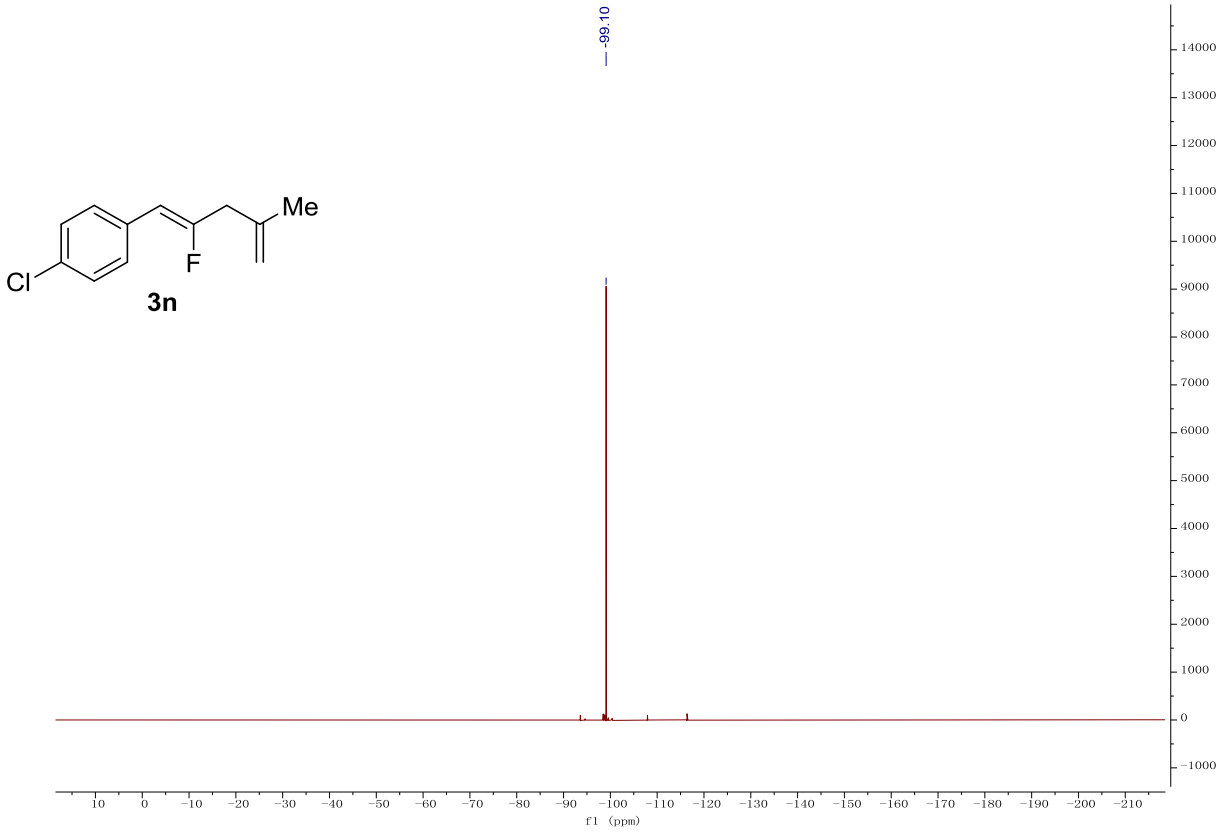
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3n



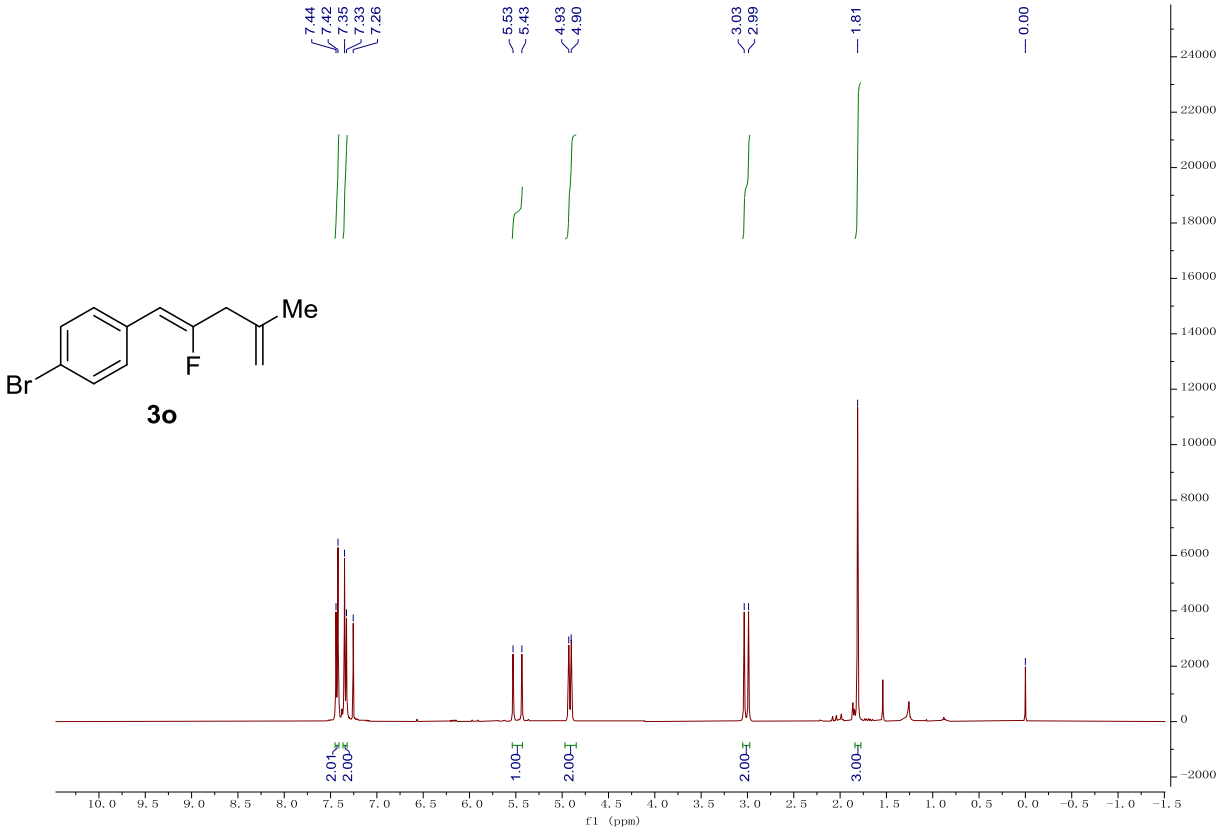
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3n



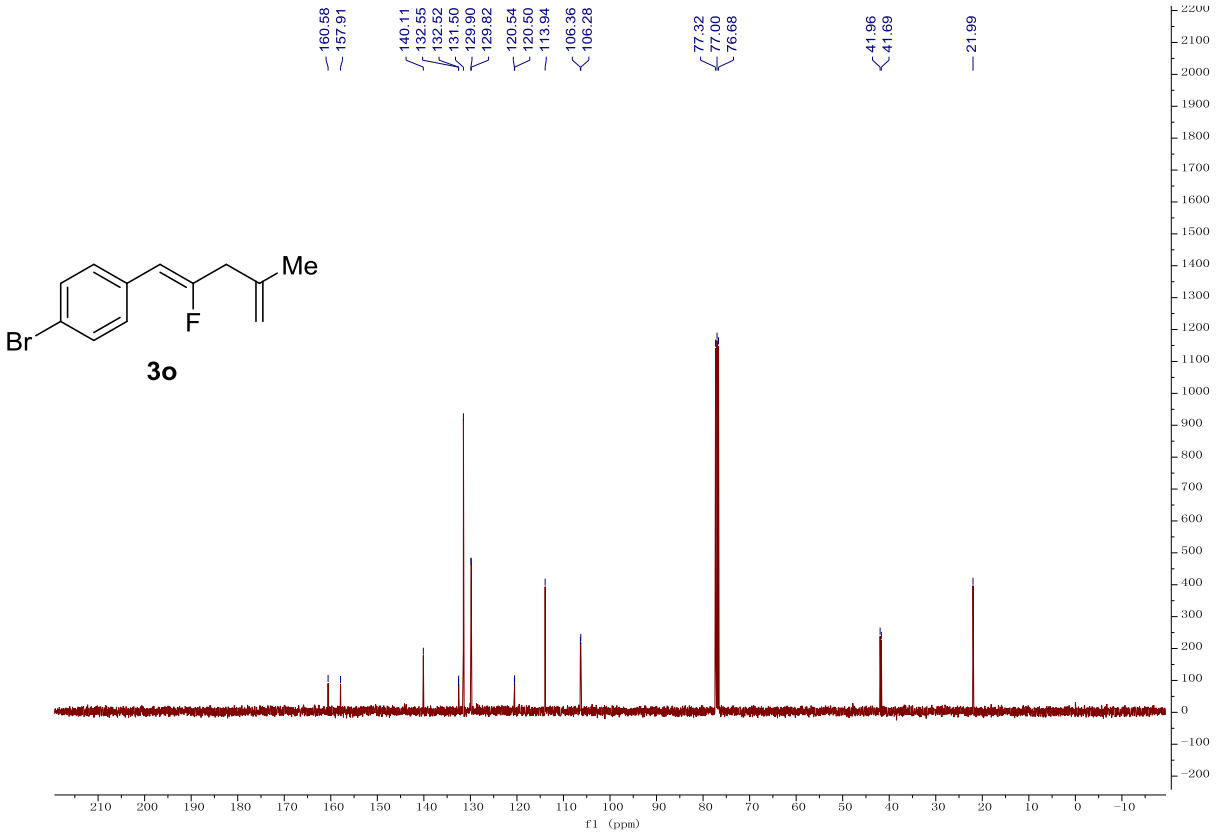
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3n



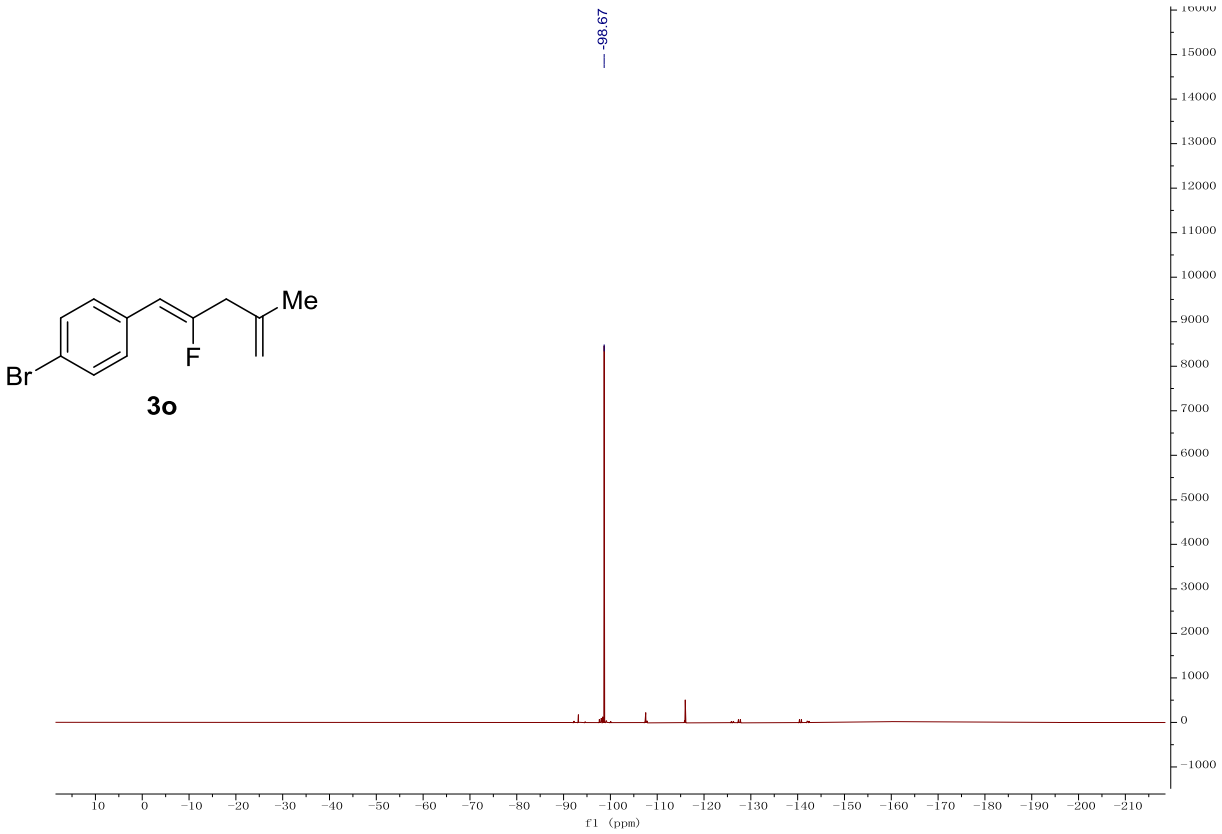
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3o



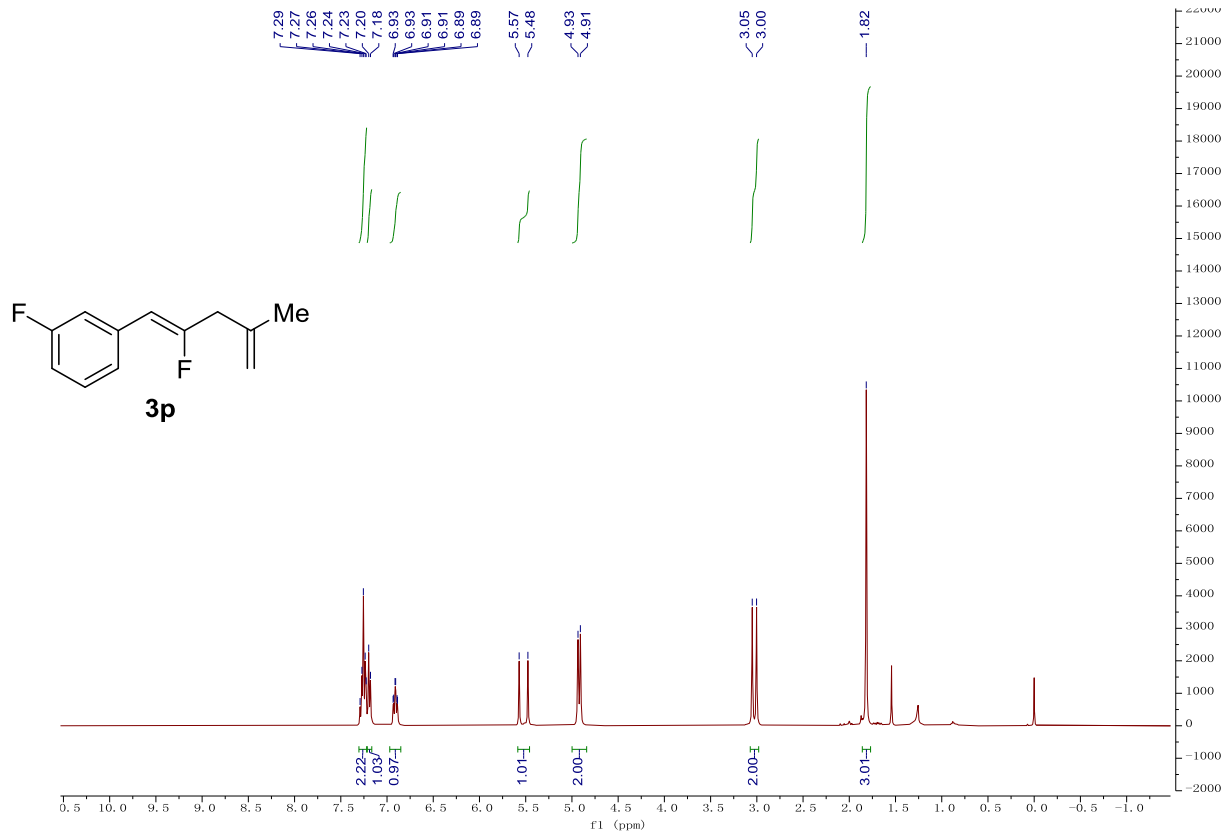
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3o



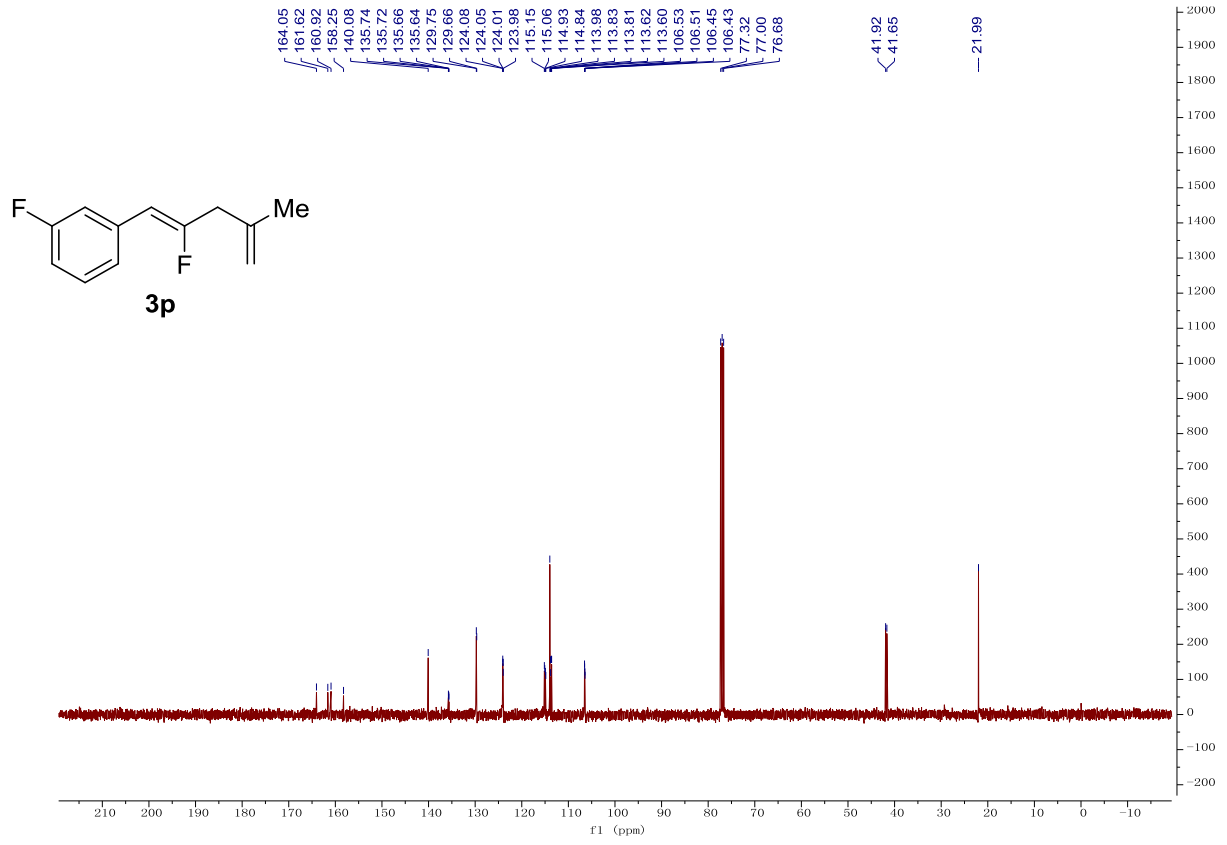
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3o



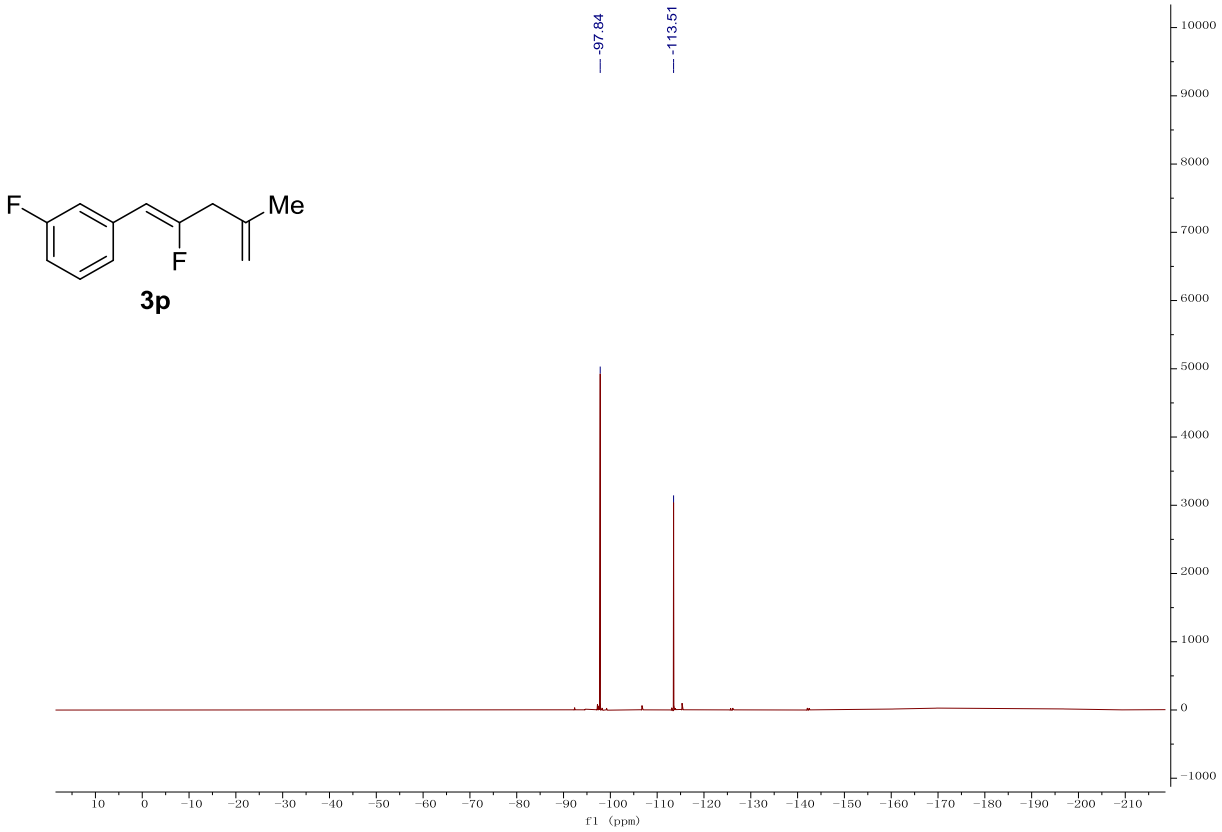
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3p



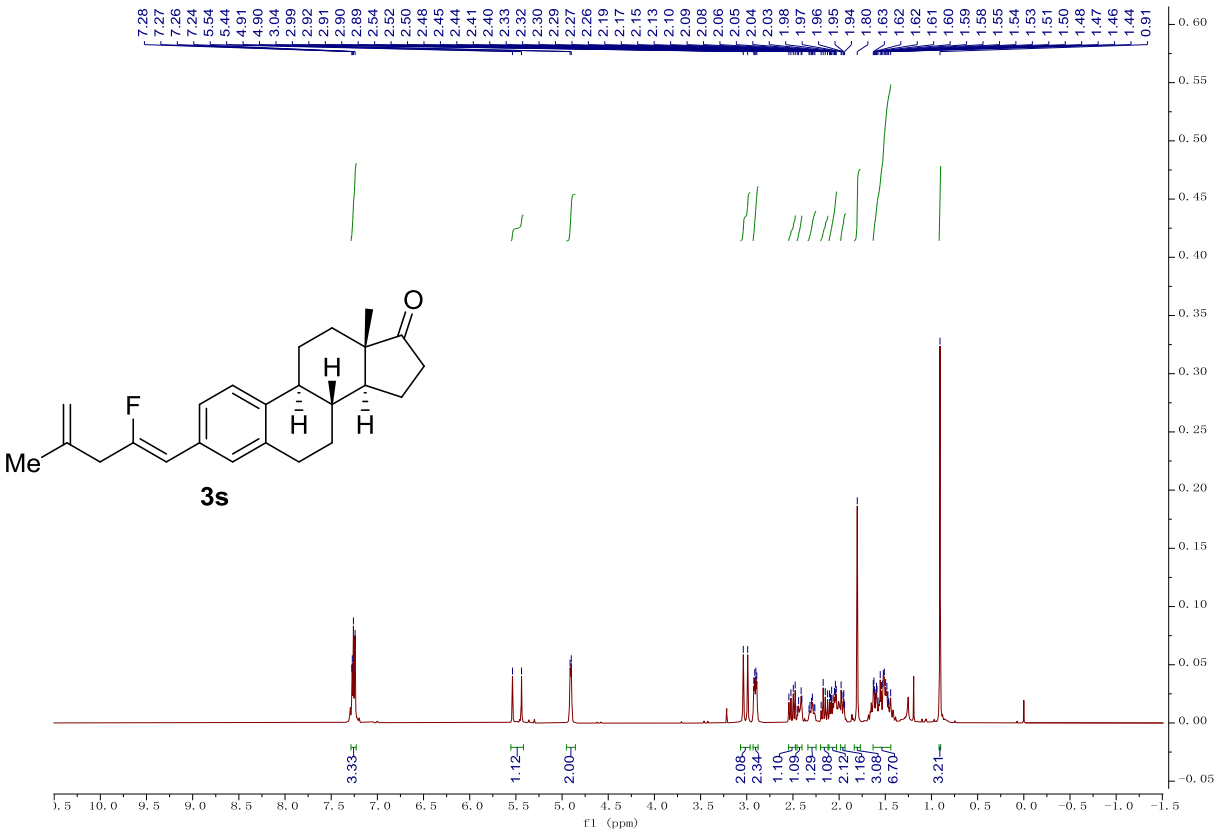
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3p



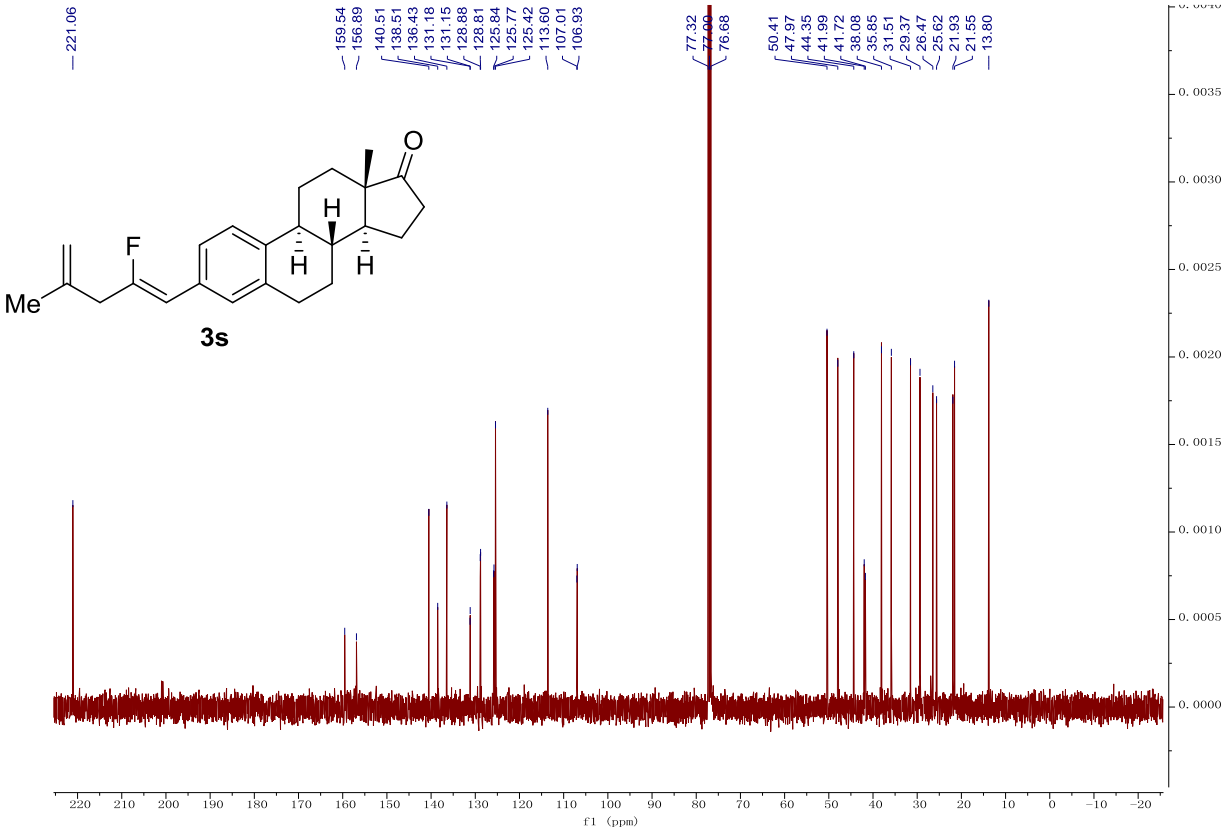
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3p



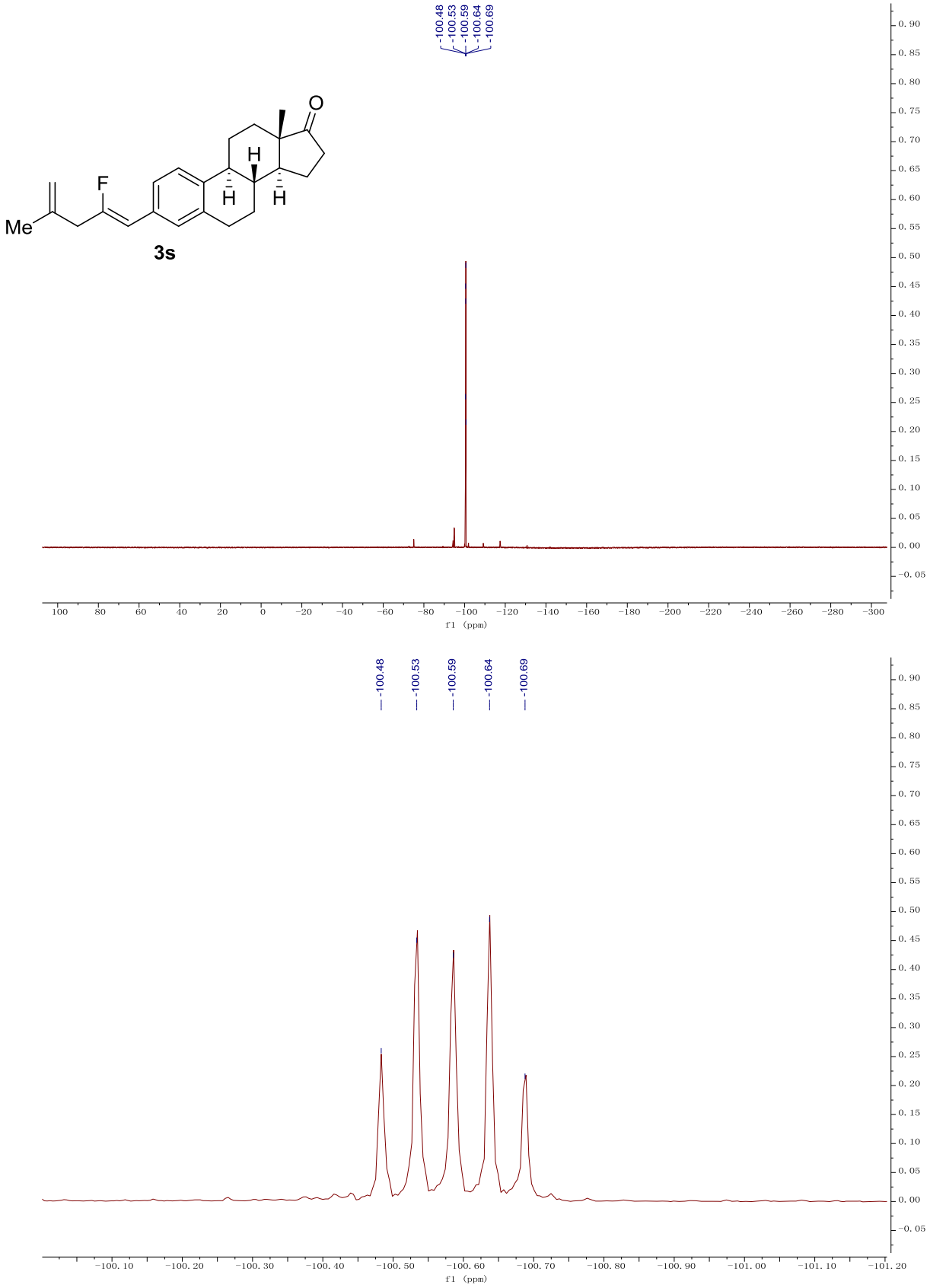
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3q (With JEOL)



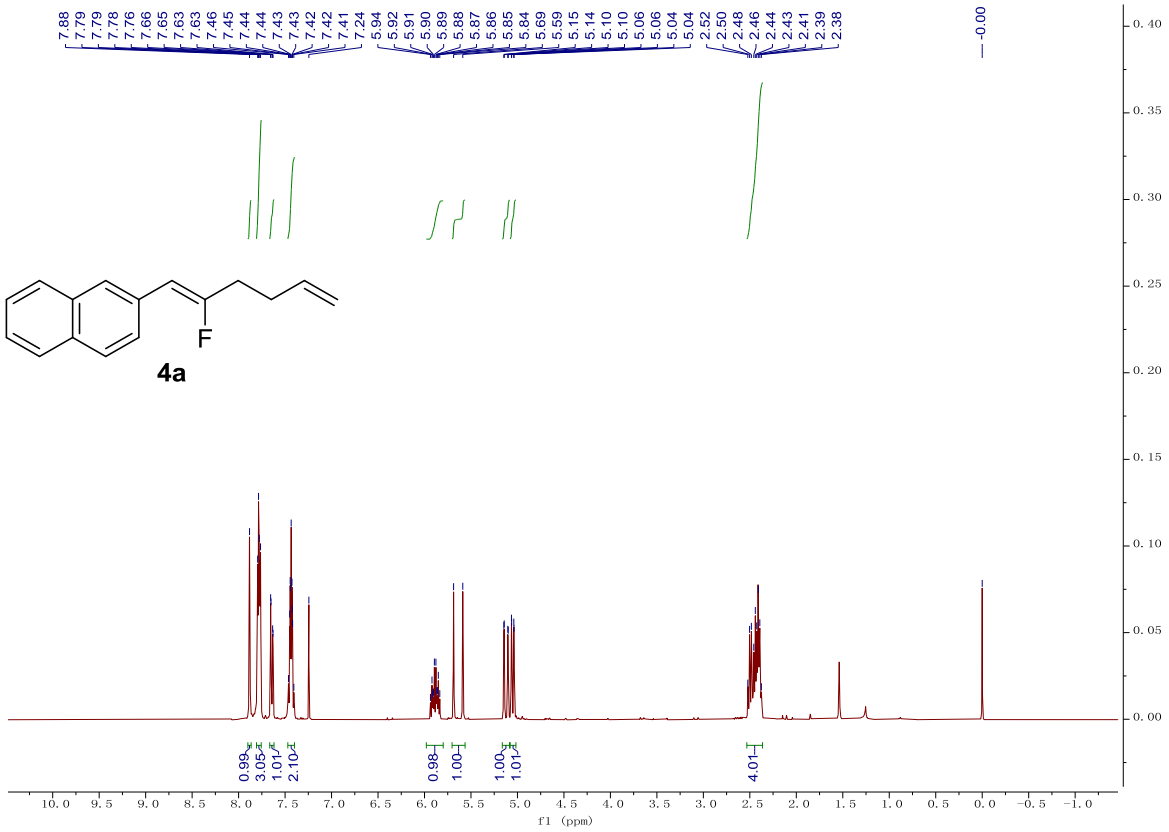
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3q (With JEOL)



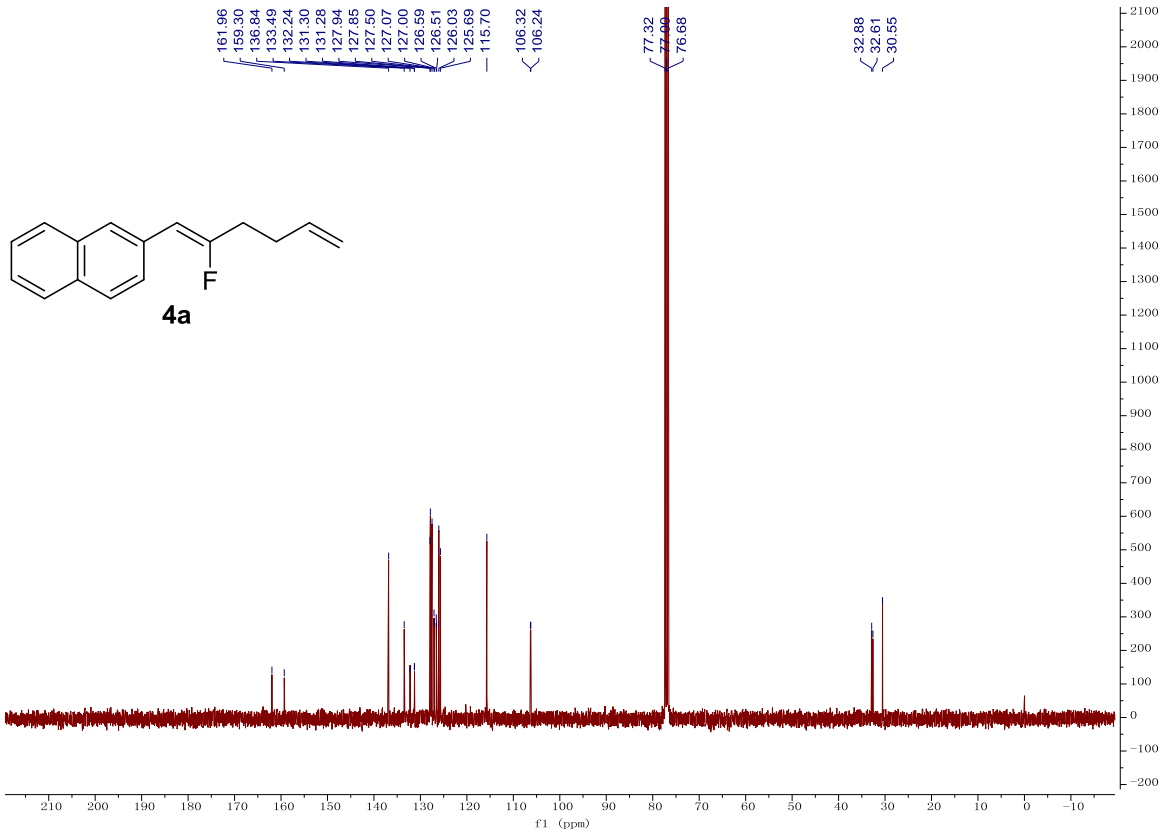
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3q (With JEOL)



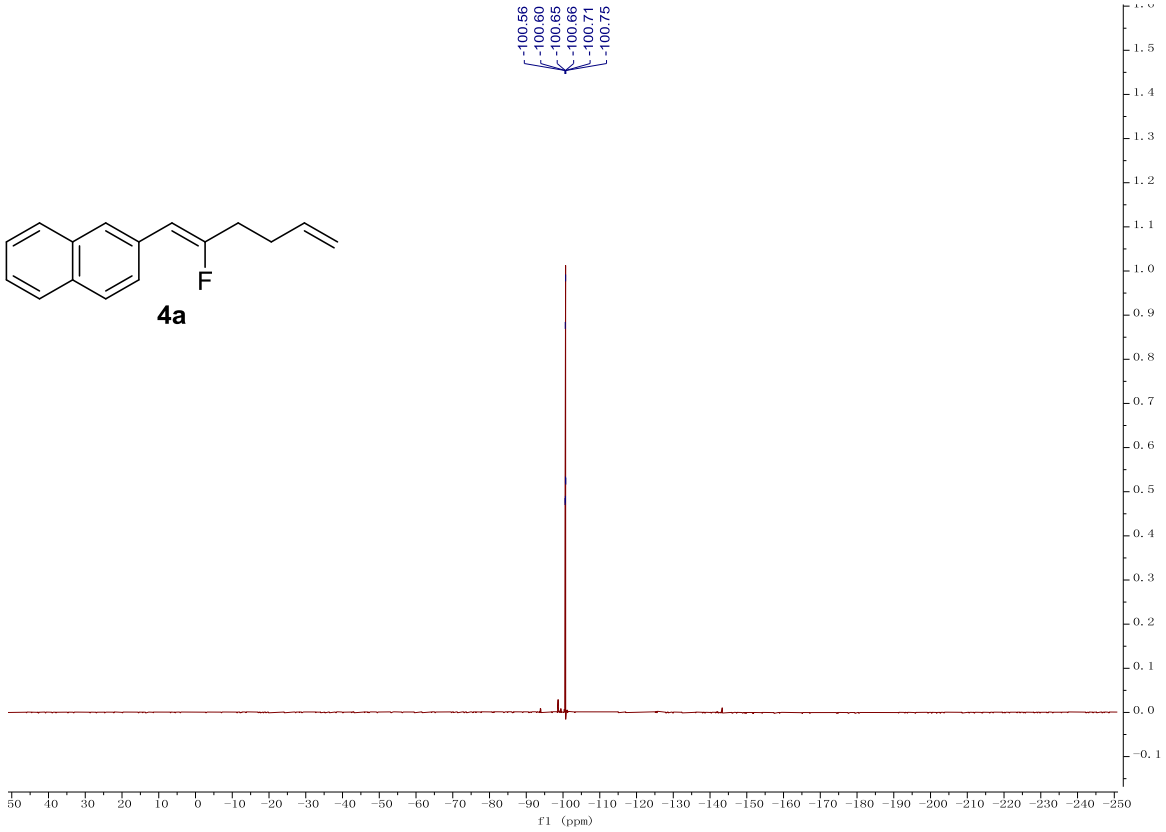
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4a (With JEOL)

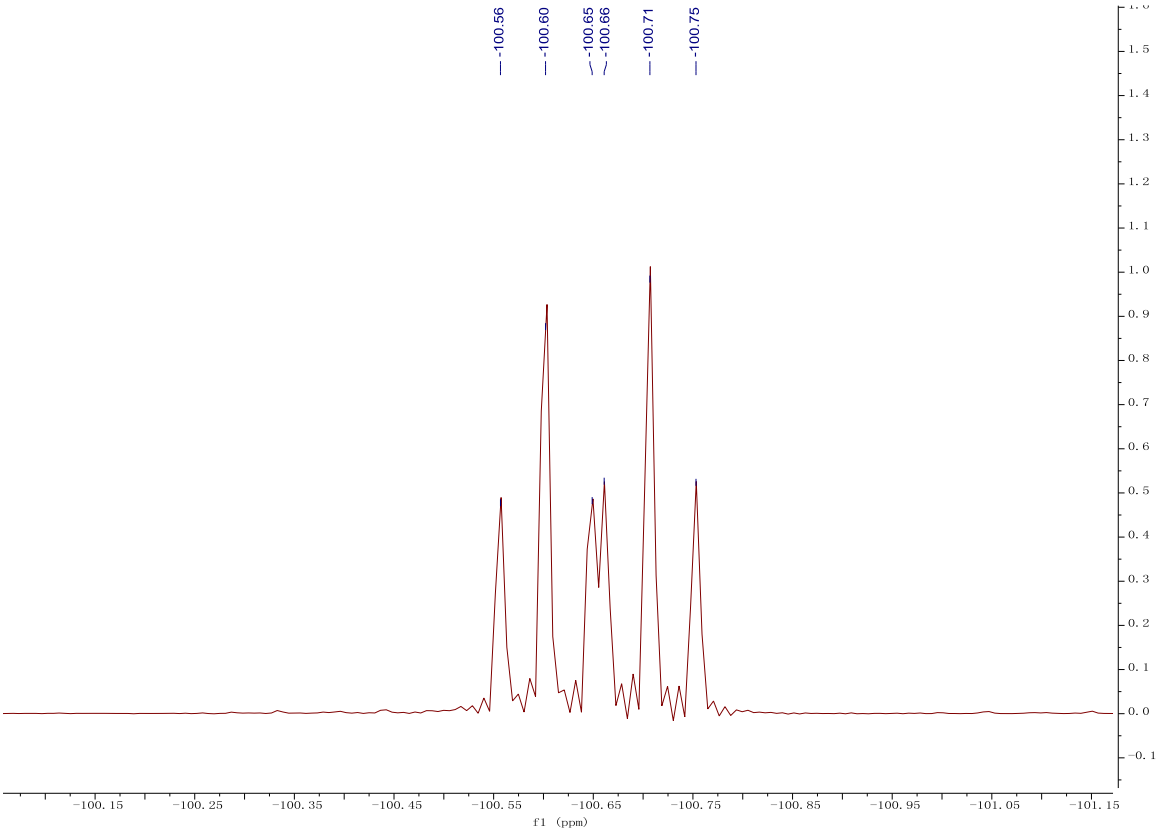


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4a

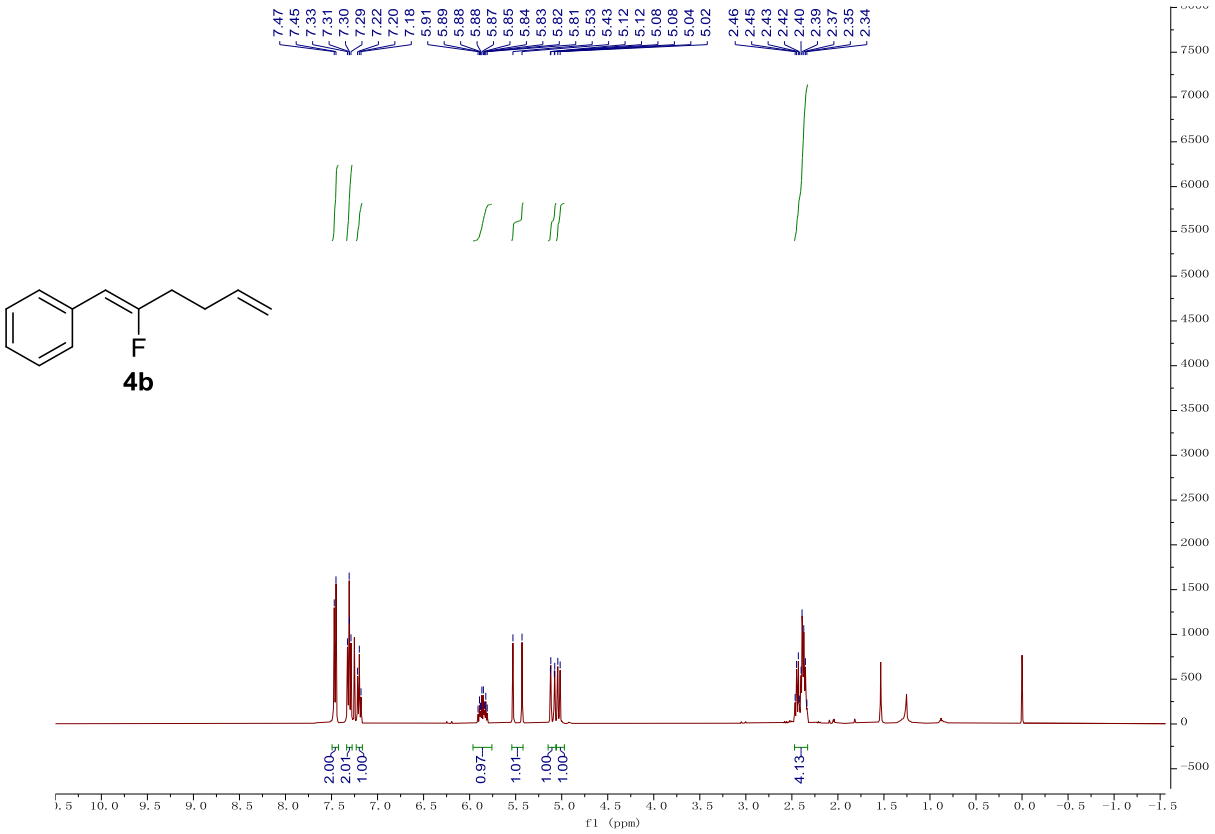


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4a (With JEOL)

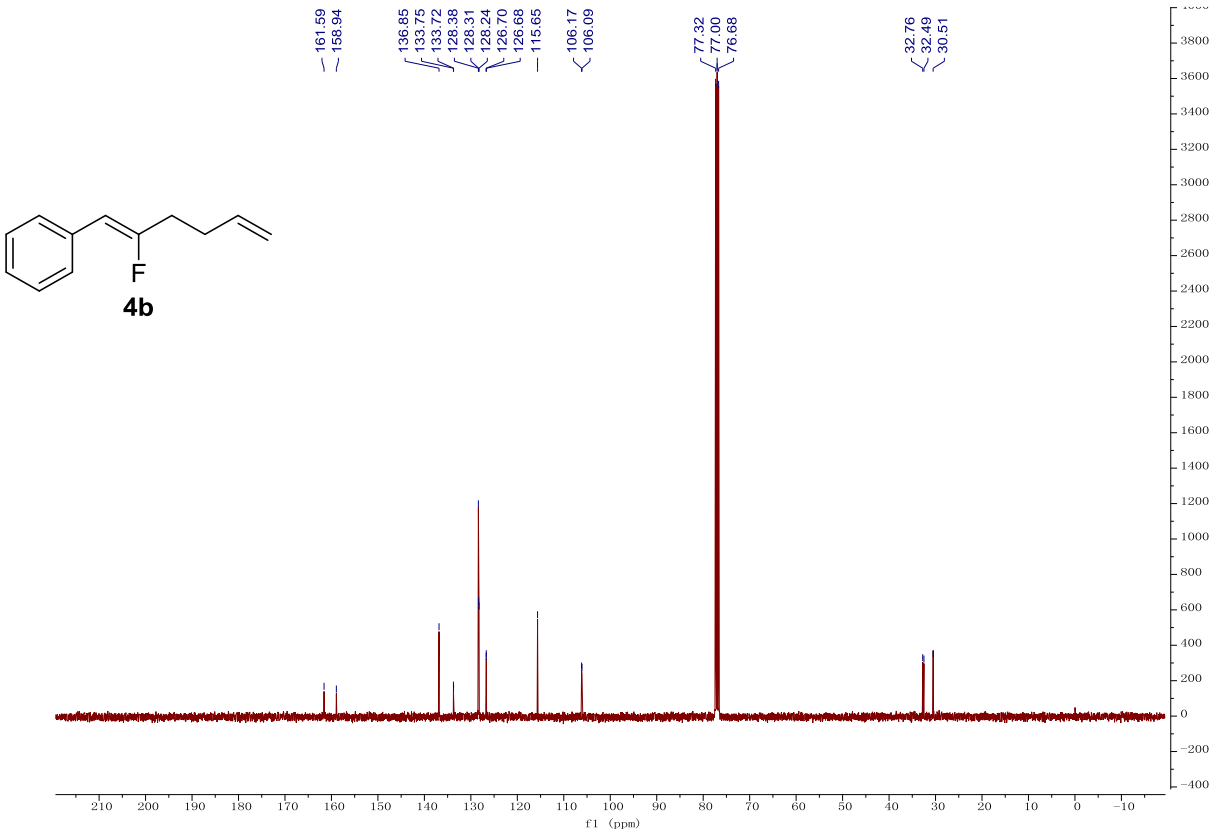




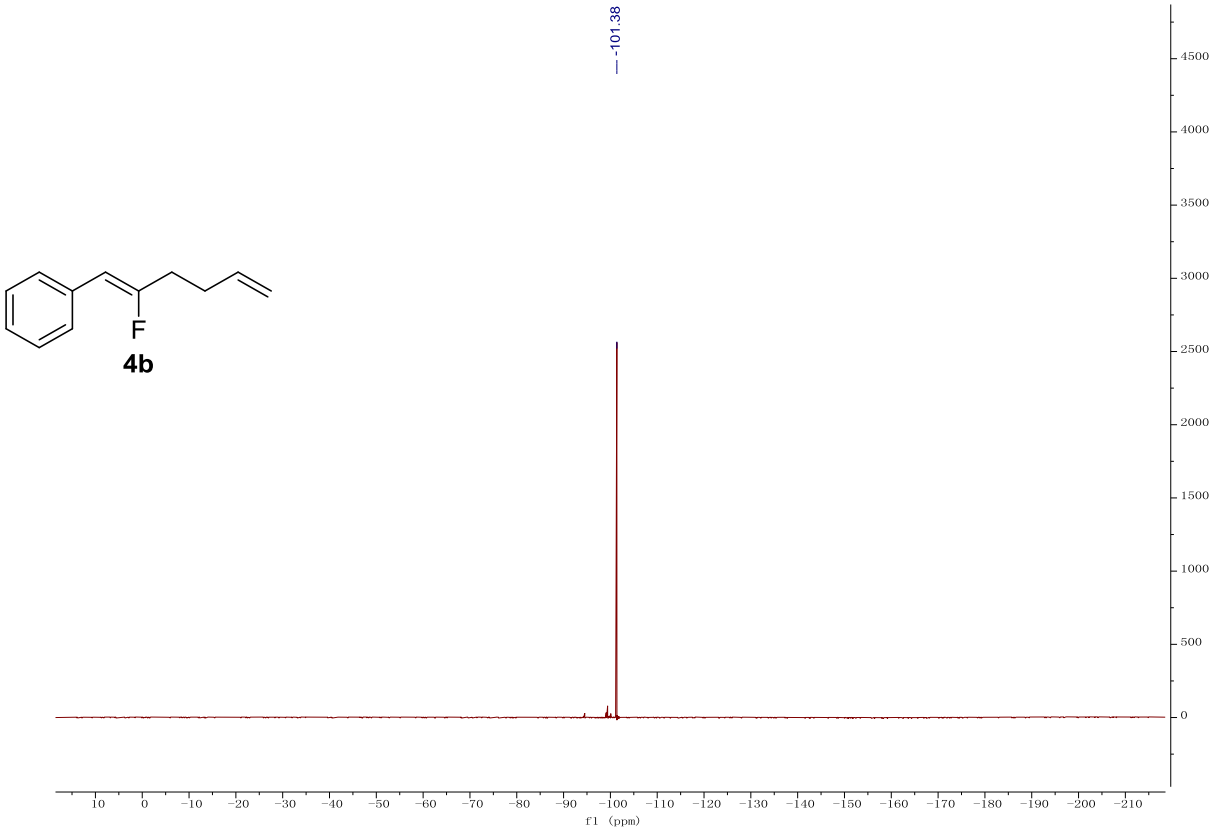
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4b



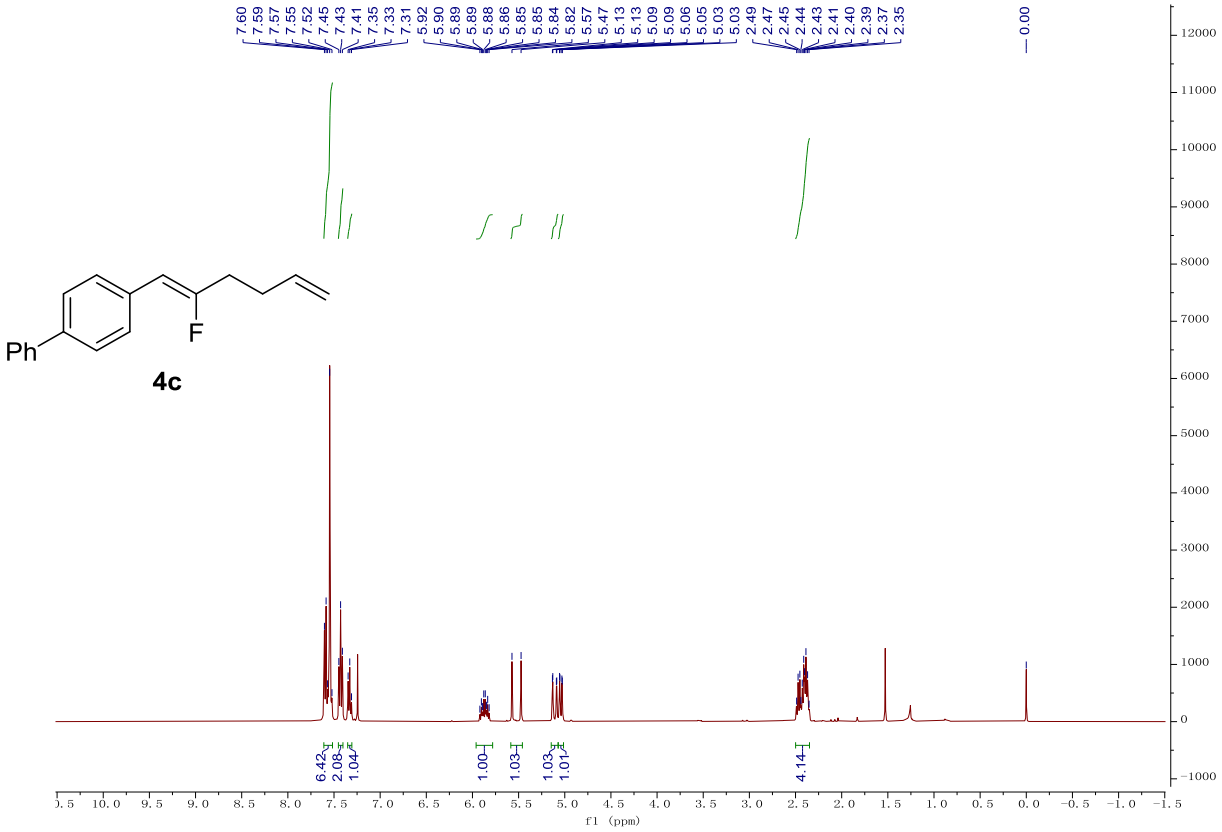
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4b



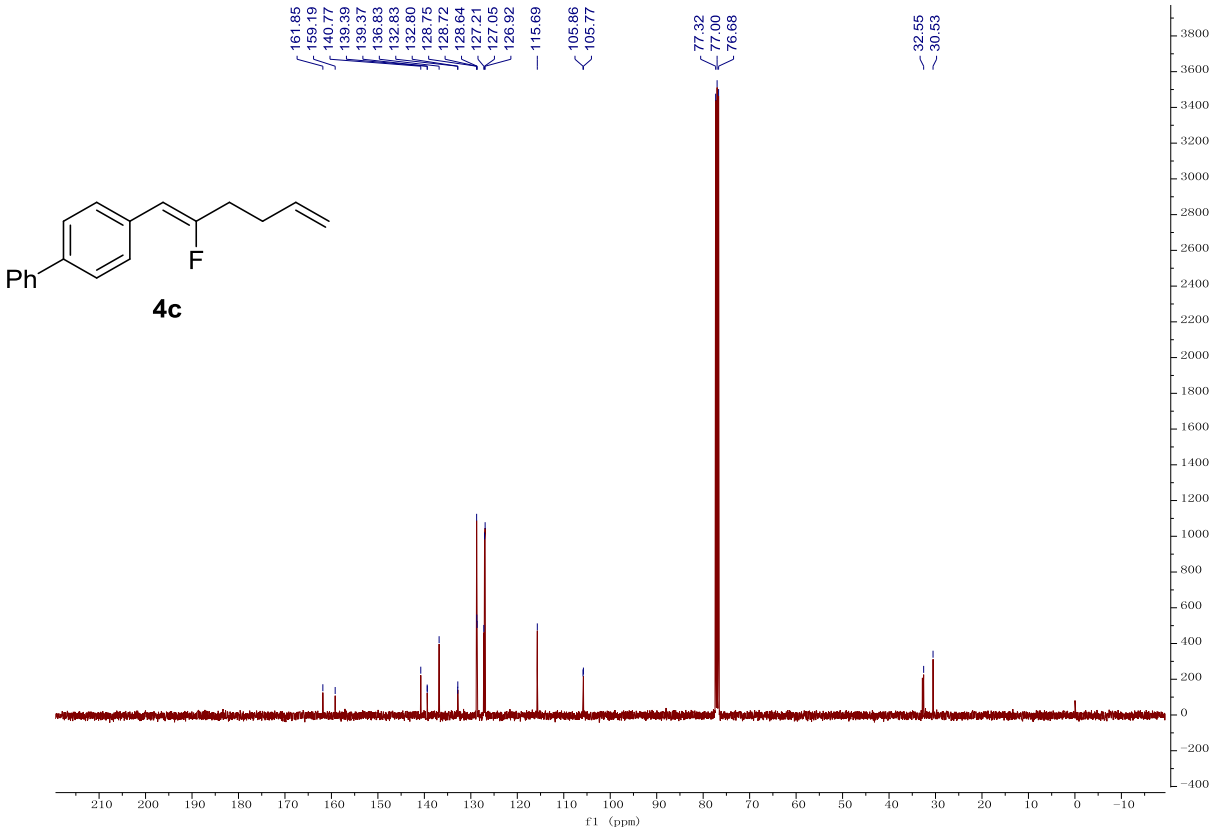
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4b



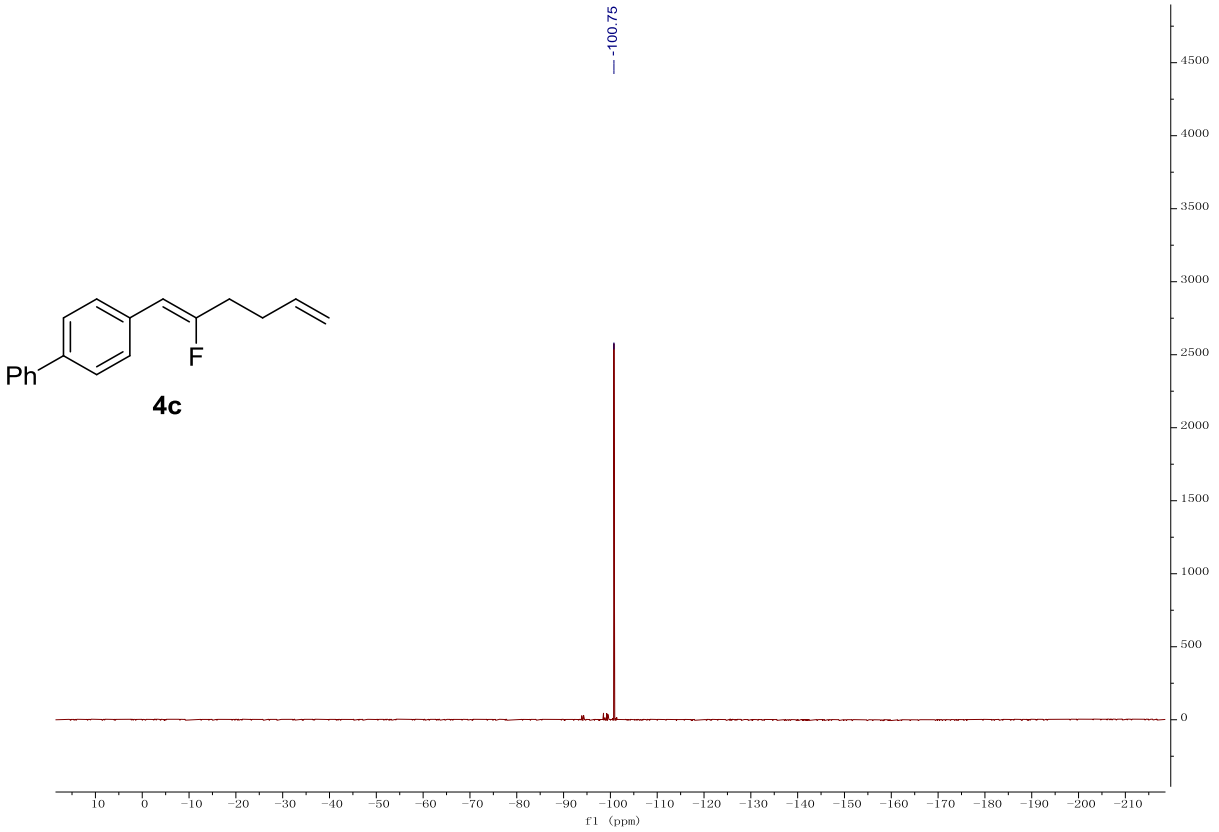
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4c



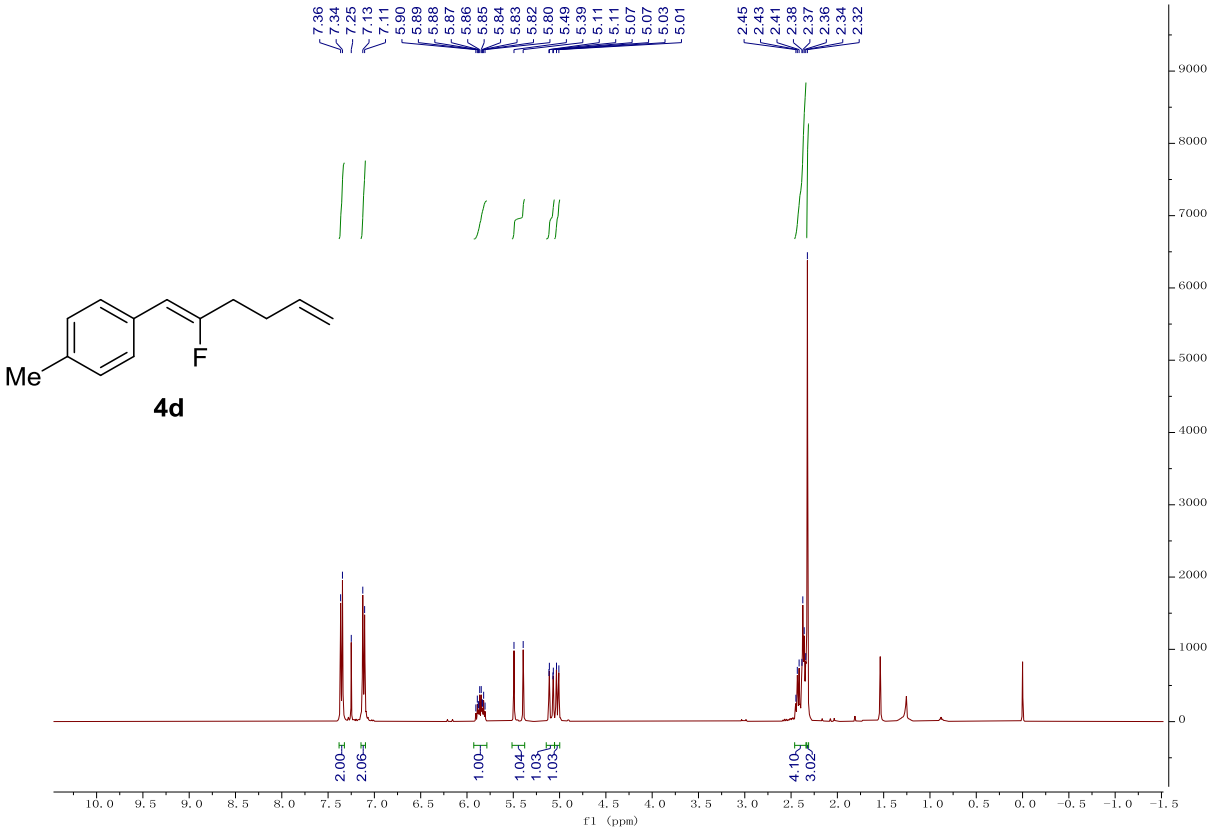
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4c



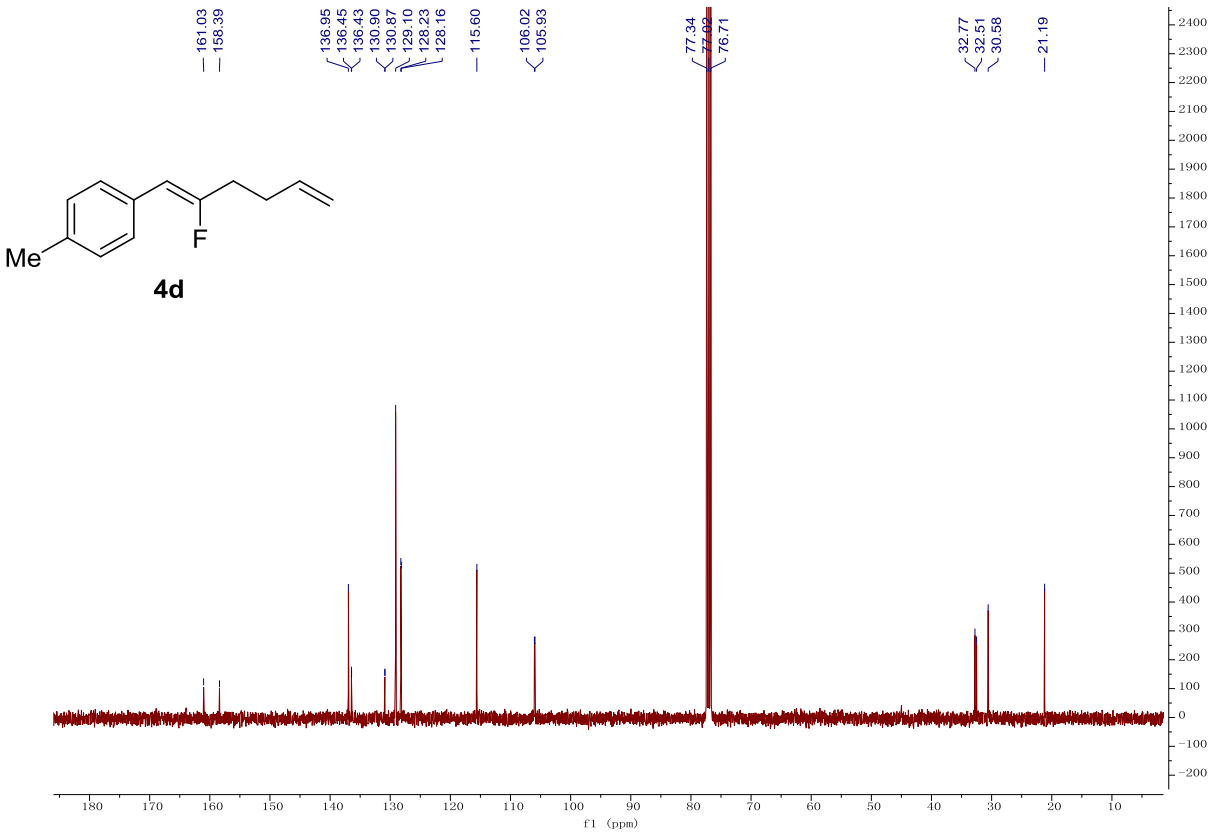
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4c



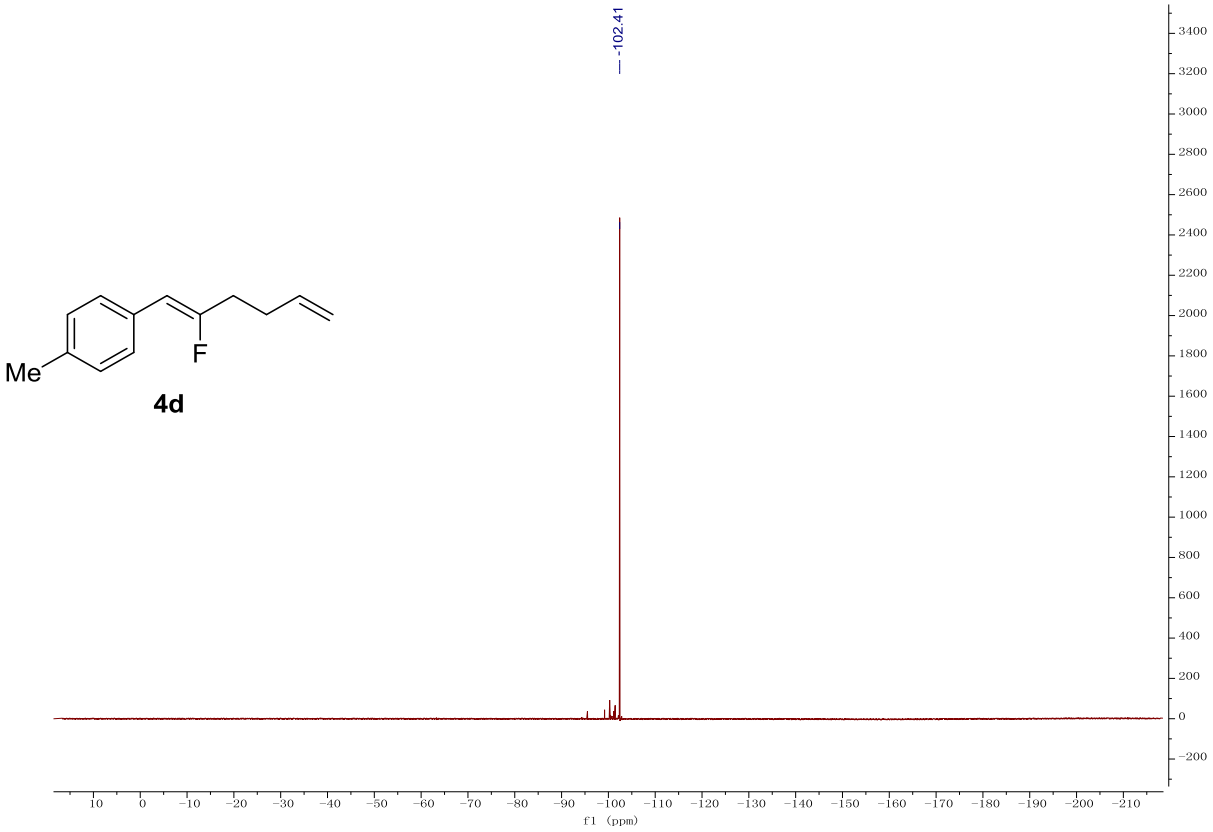
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4d



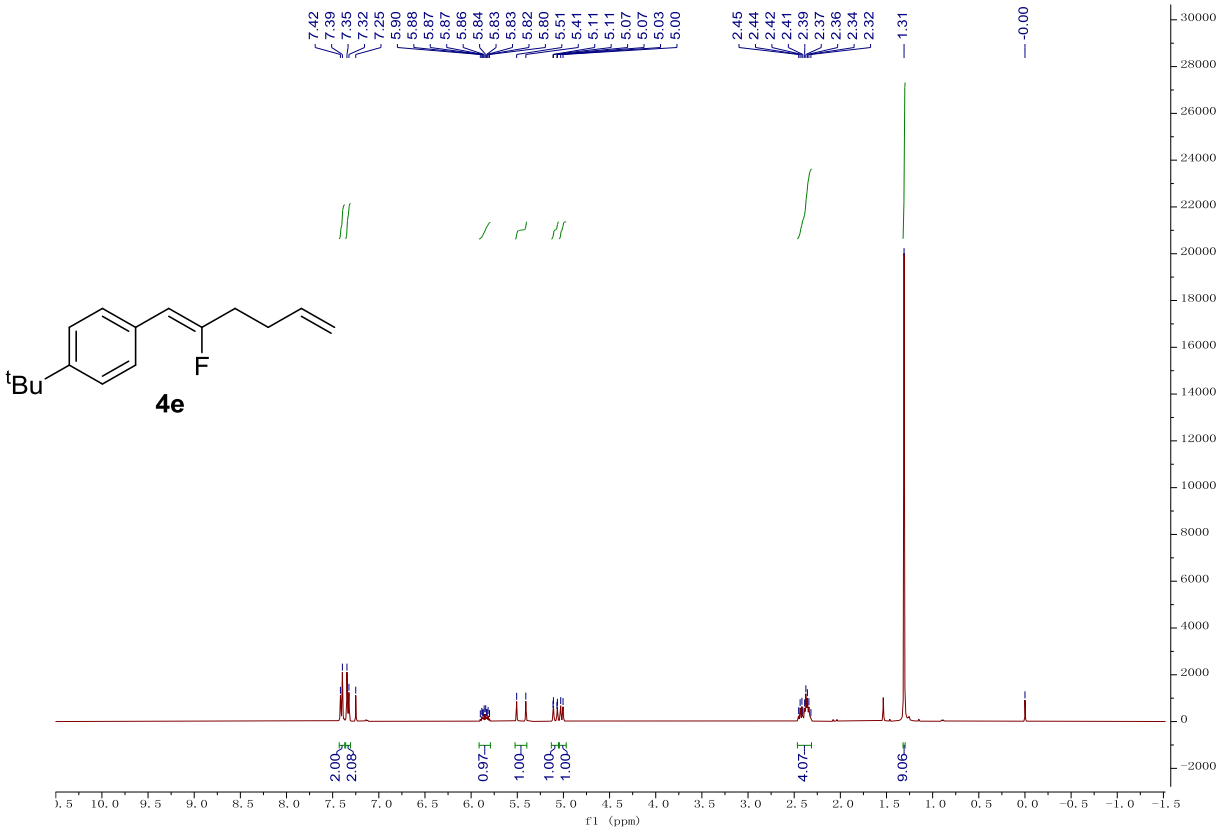
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4d



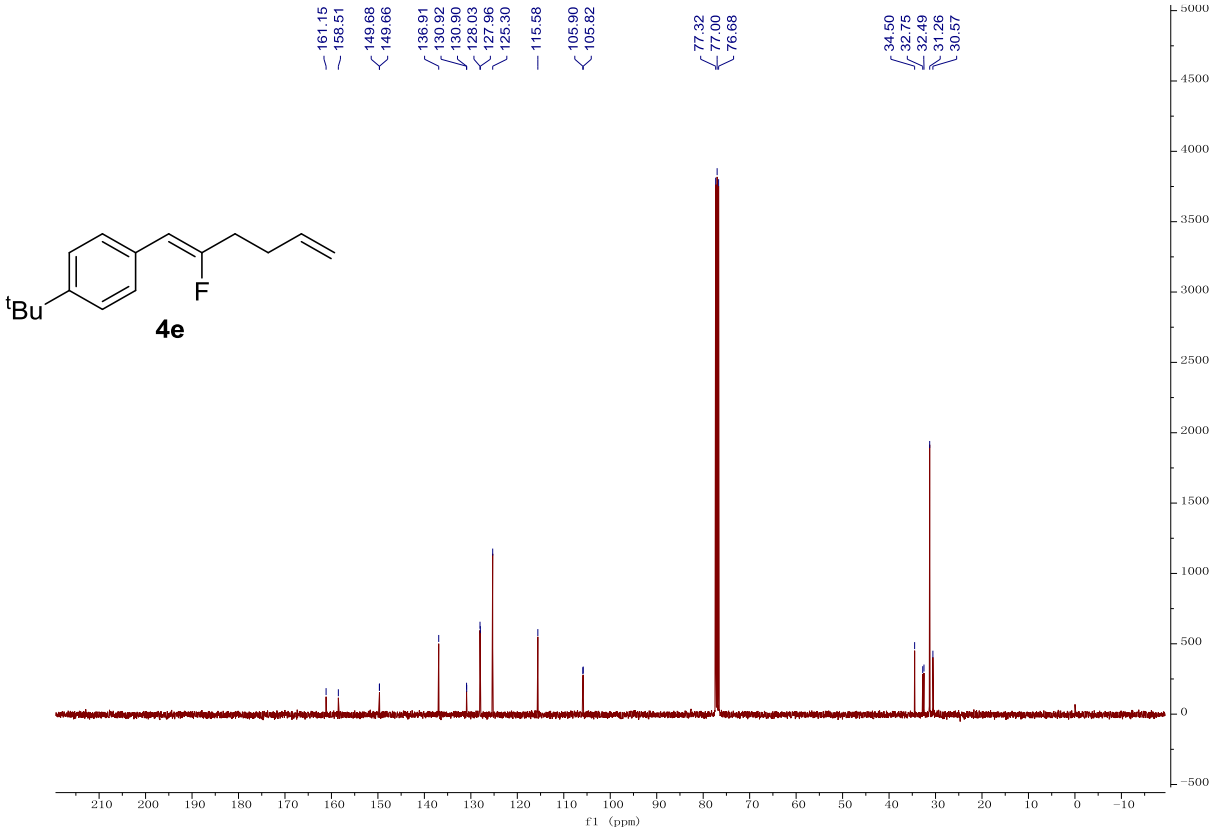
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4d



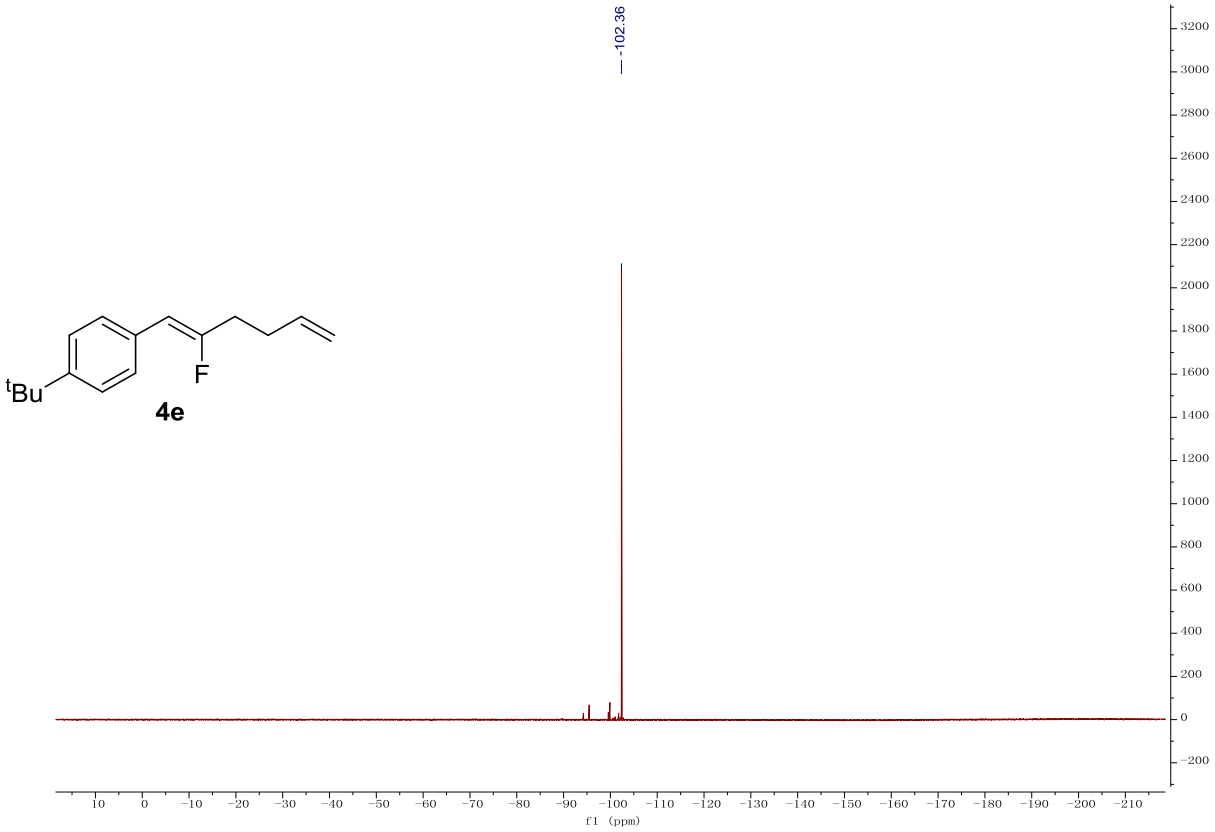
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4e



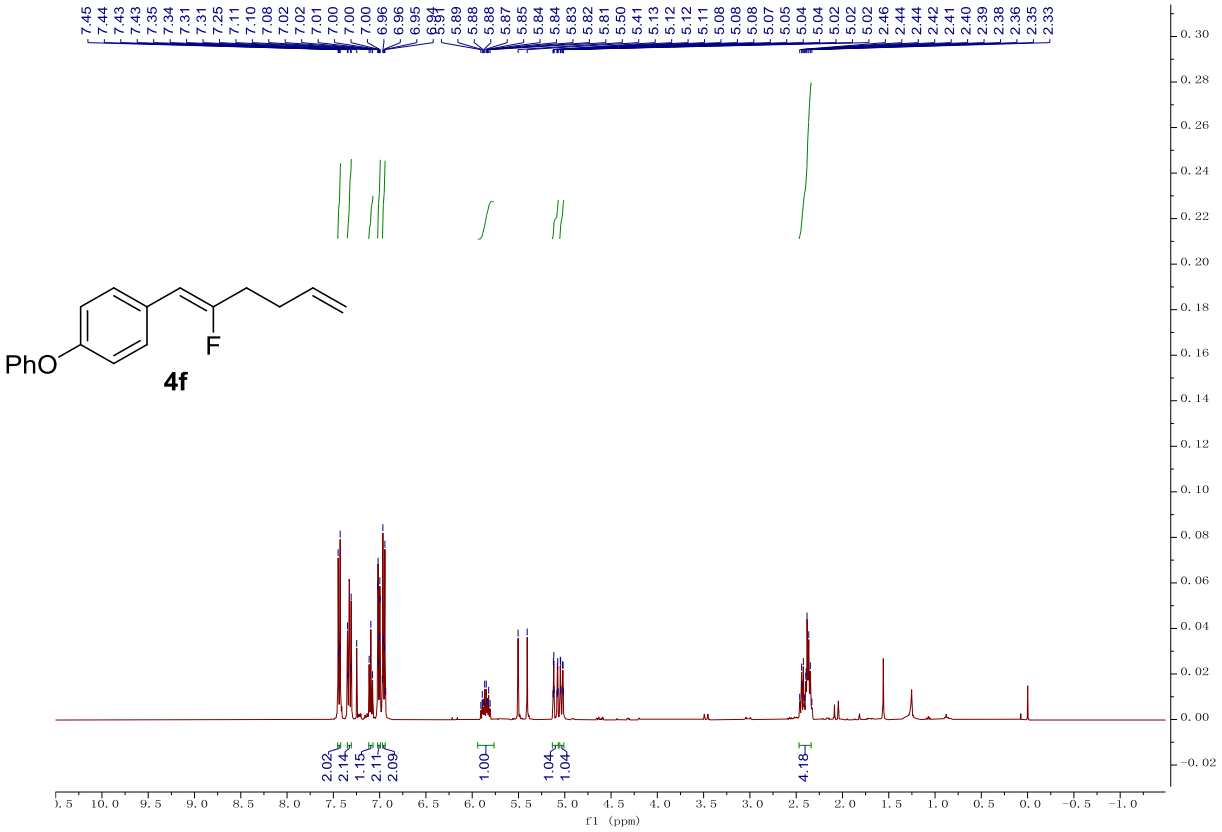
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4e



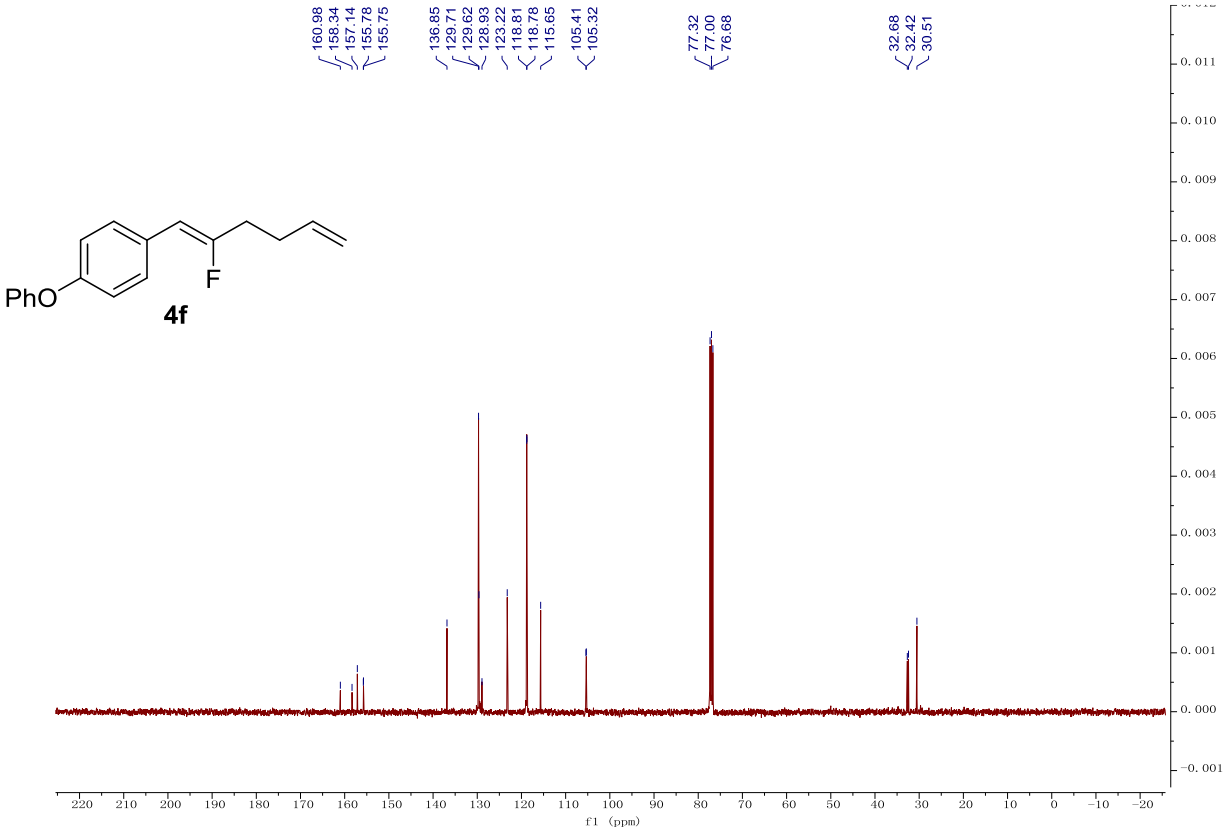
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4e



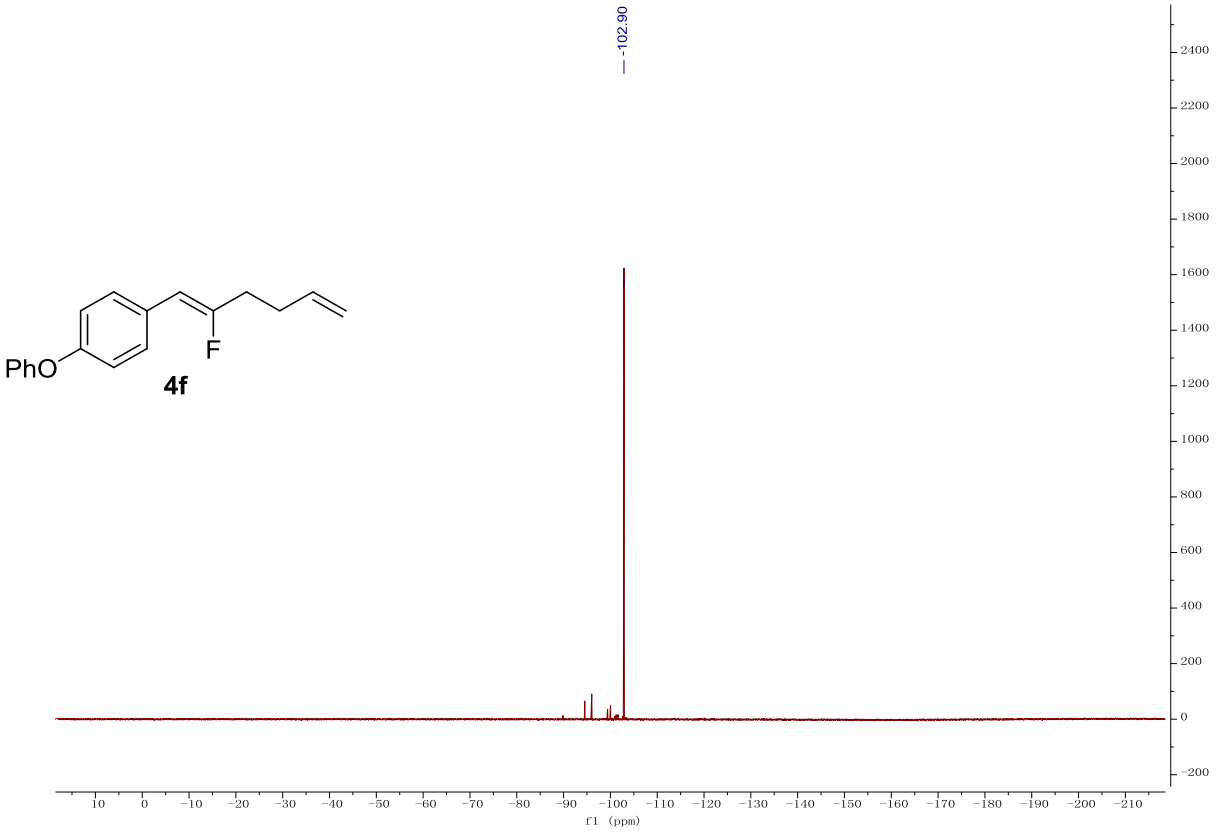
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4f



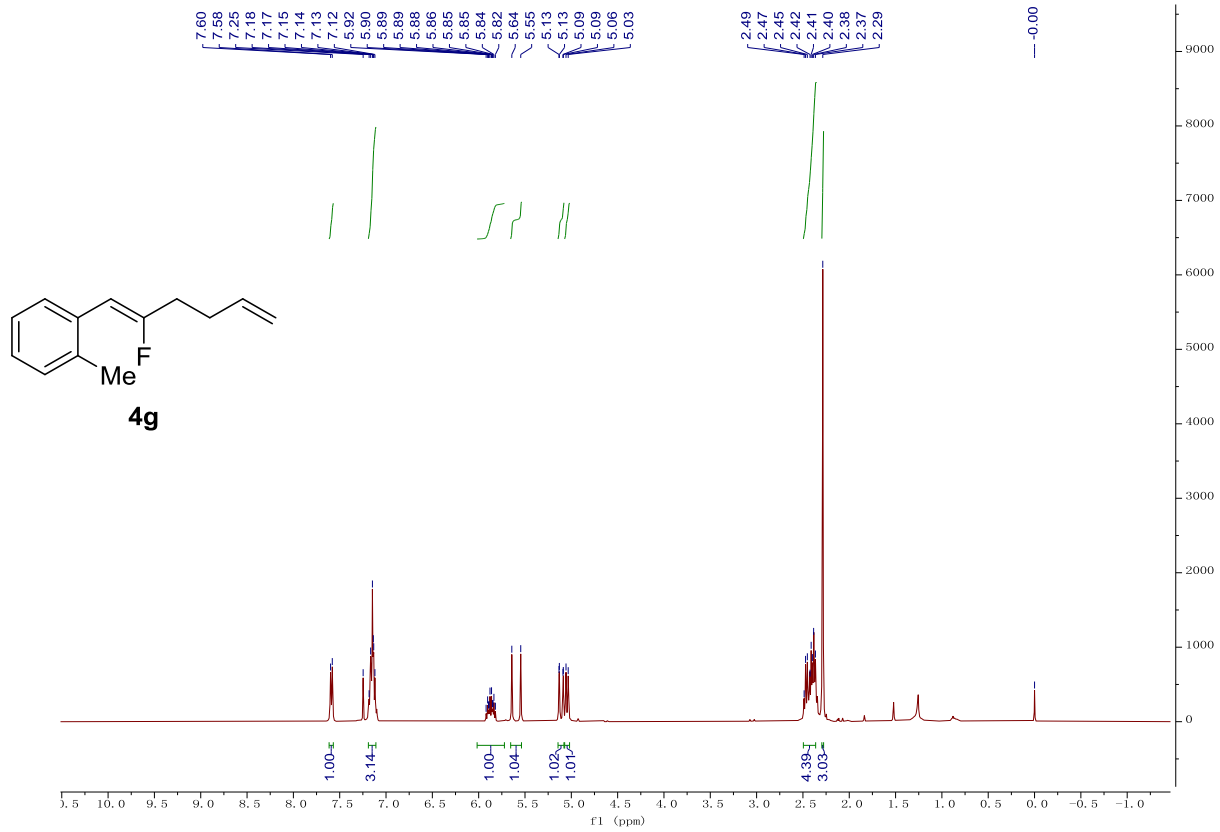
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4f



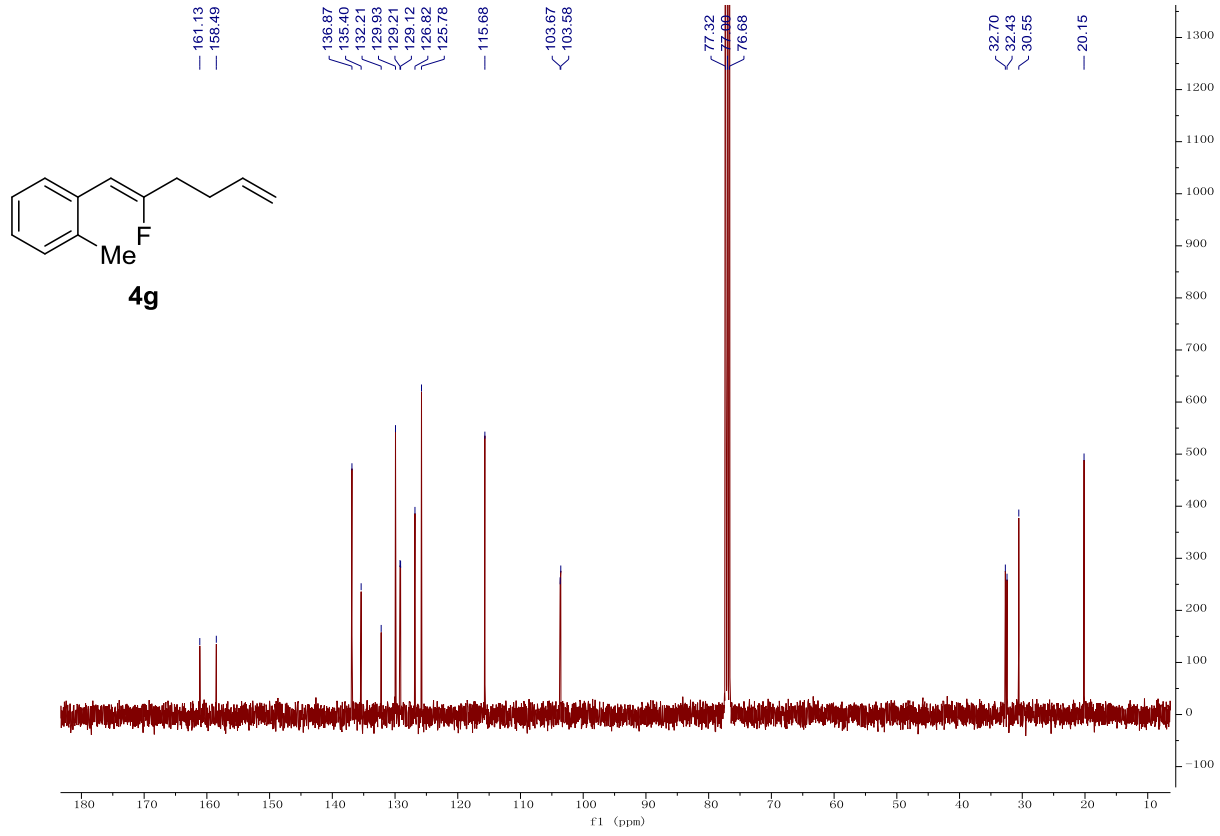
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4f



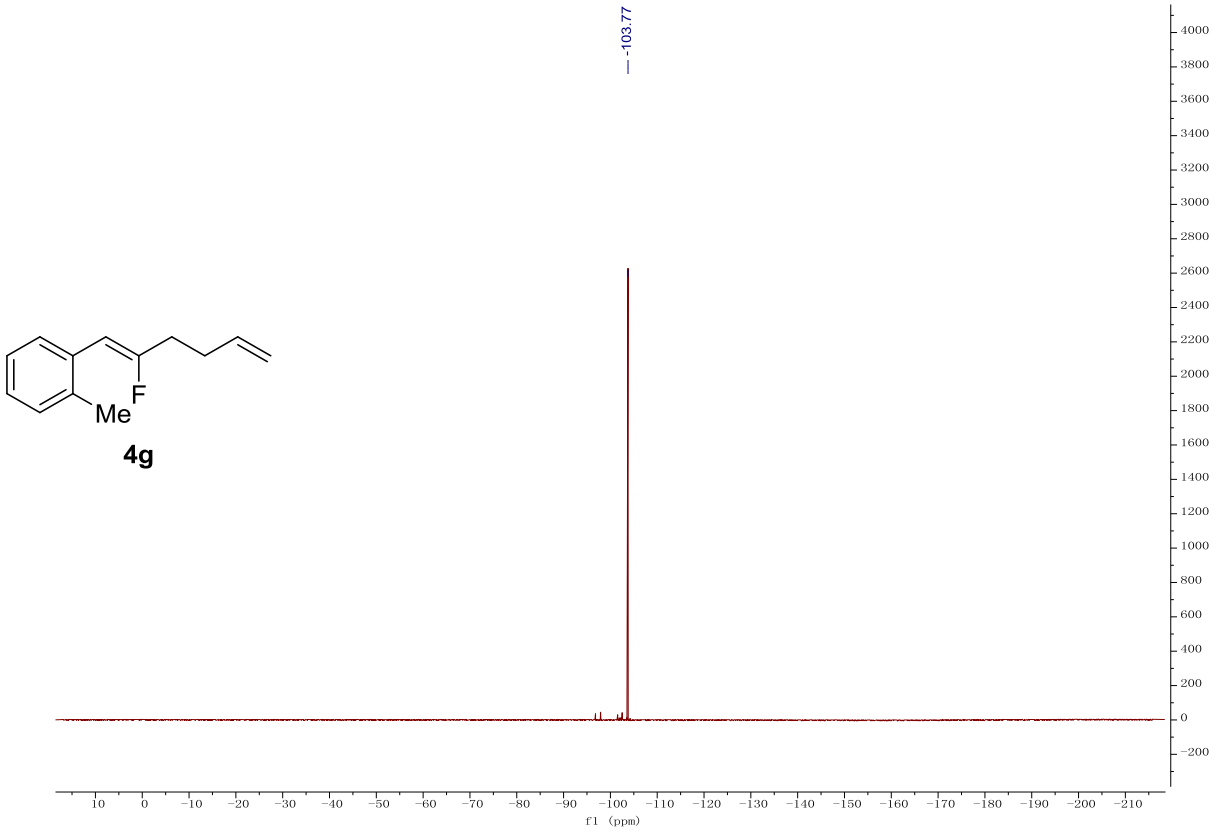
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4g



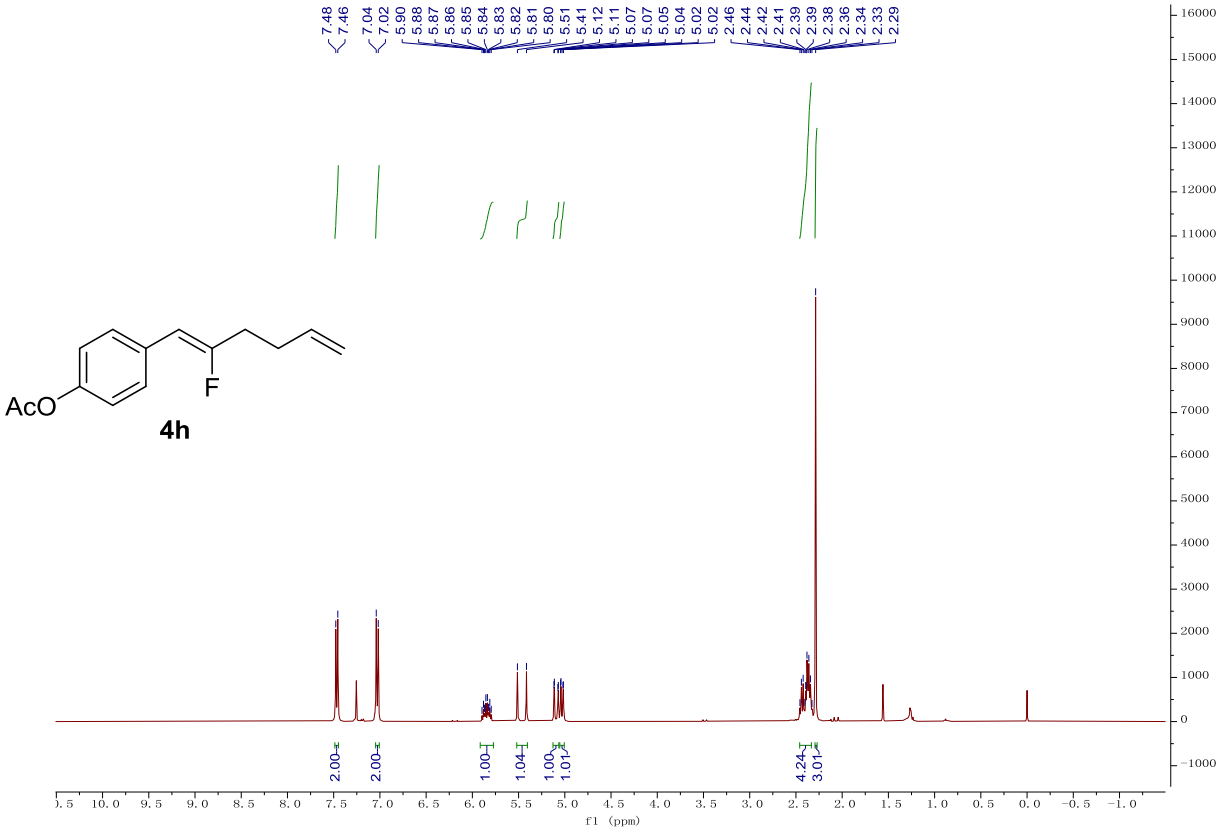
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4g



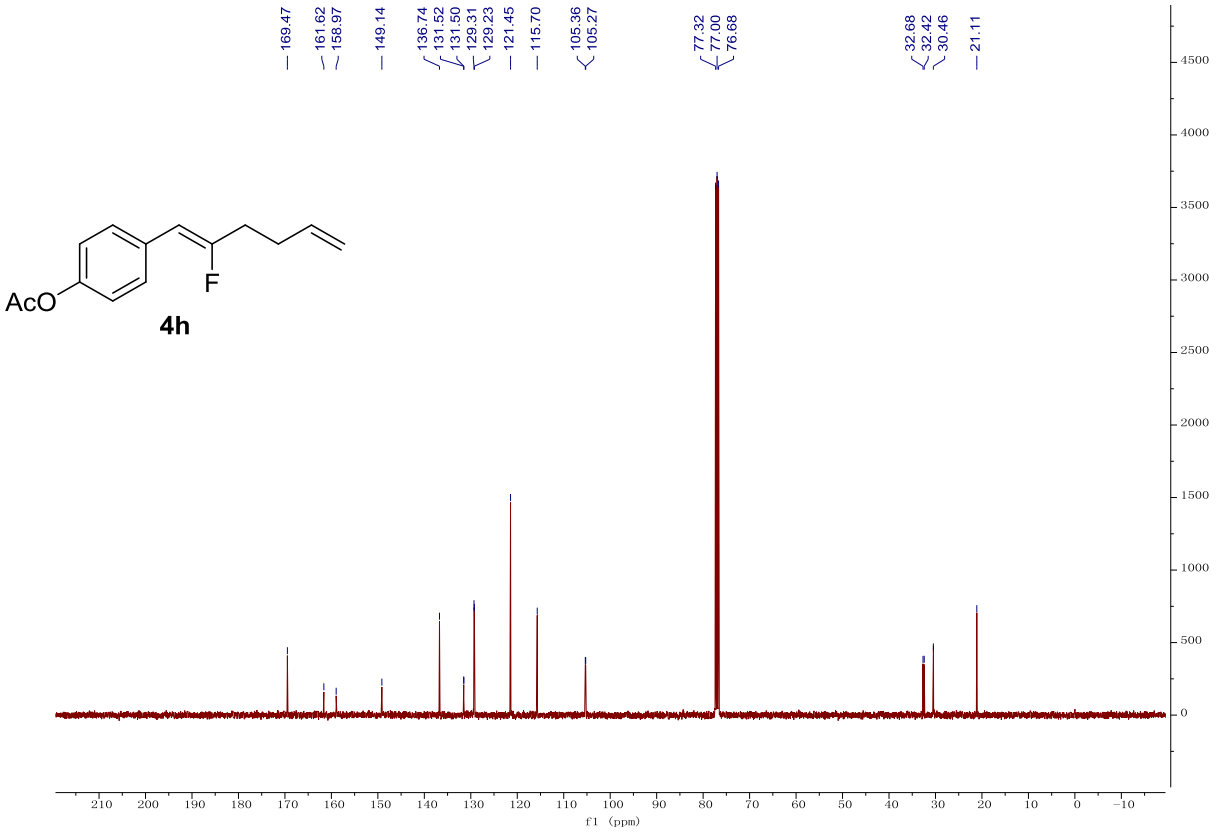
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4g



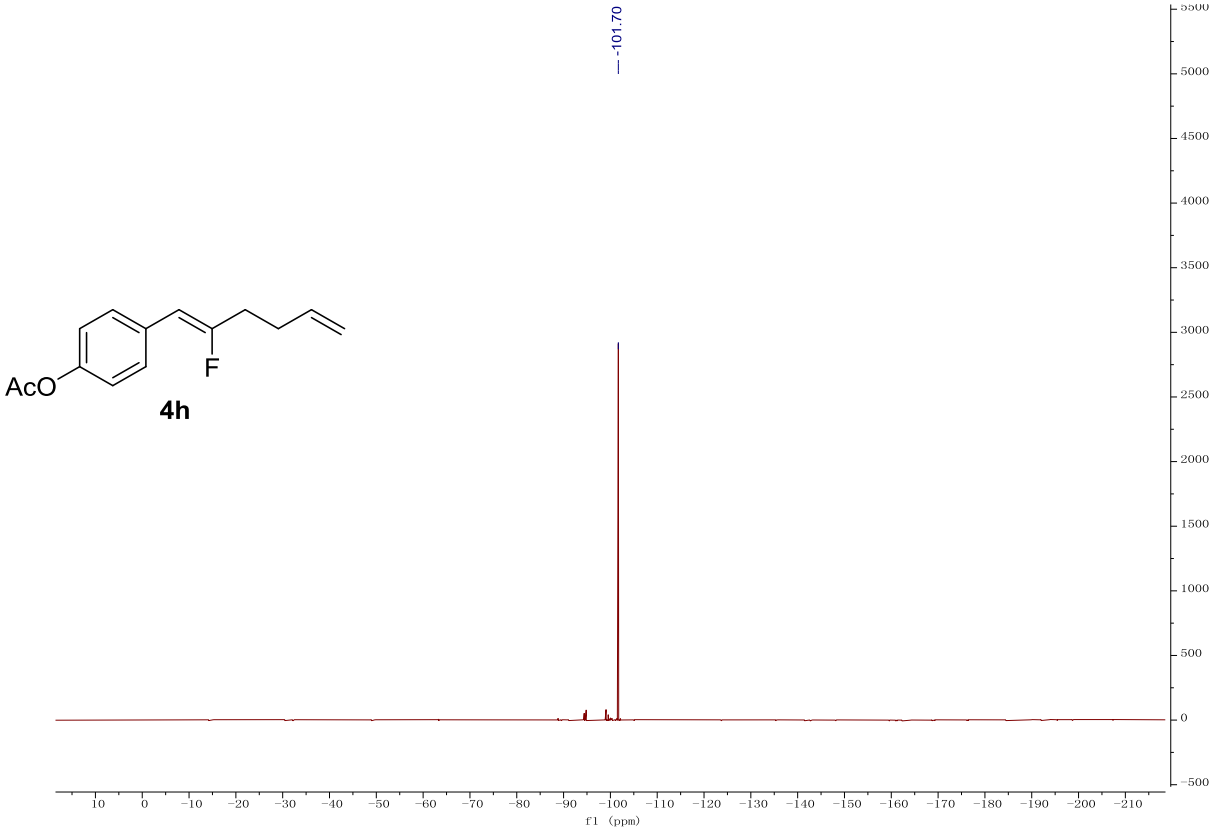
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4h



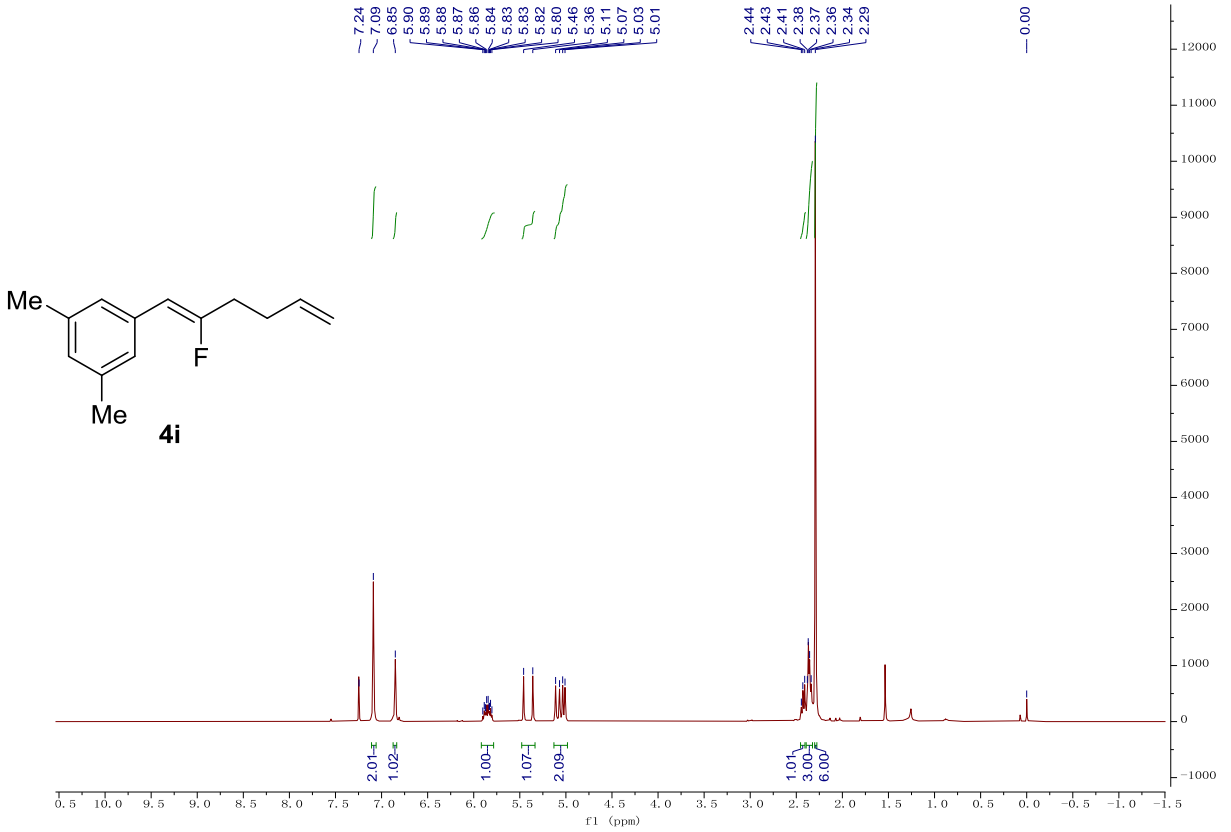
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4h



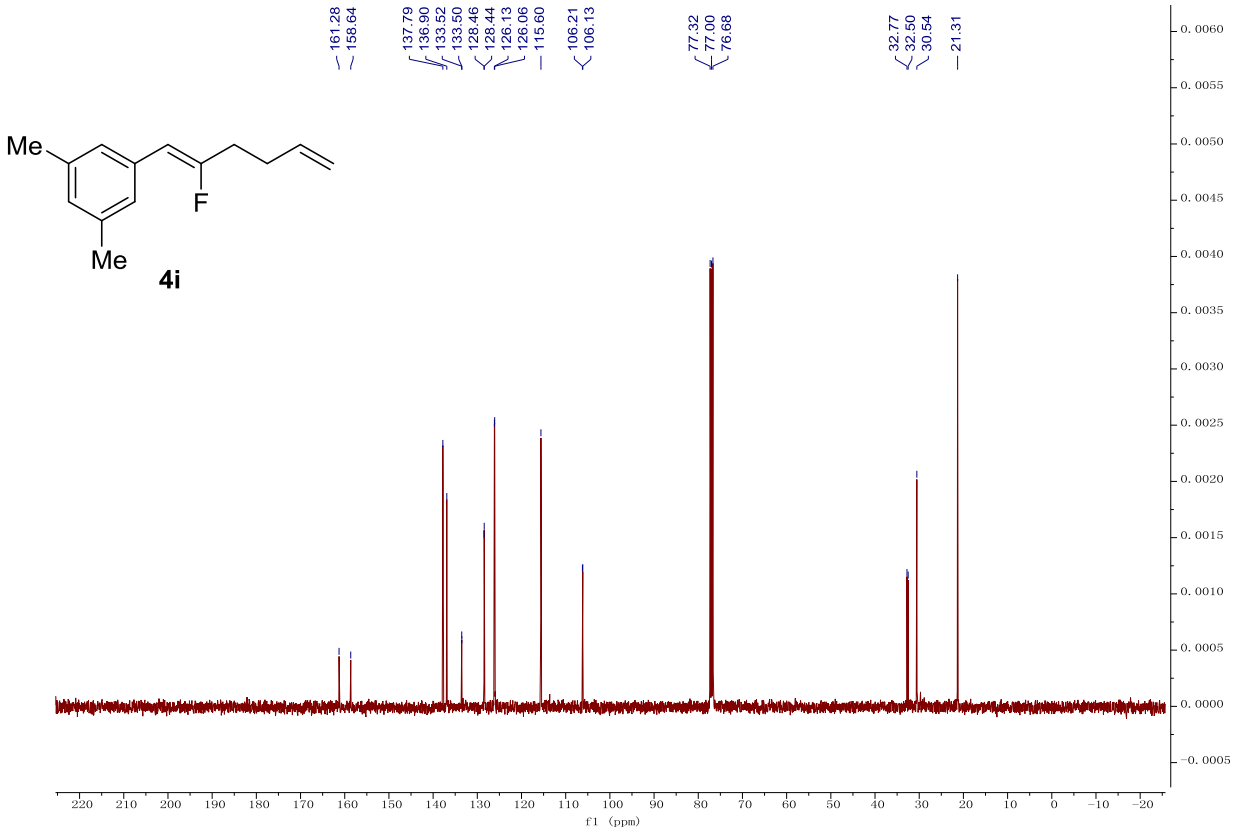
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4h



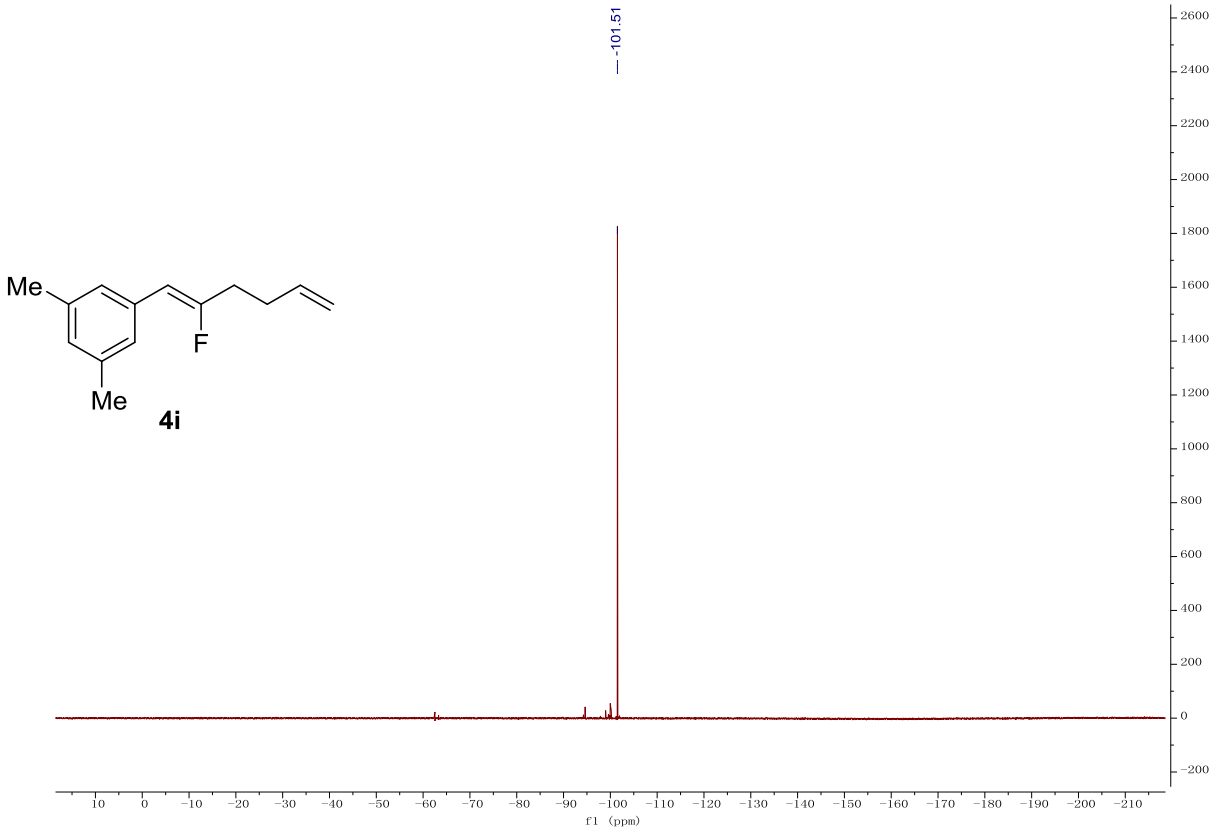
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4i



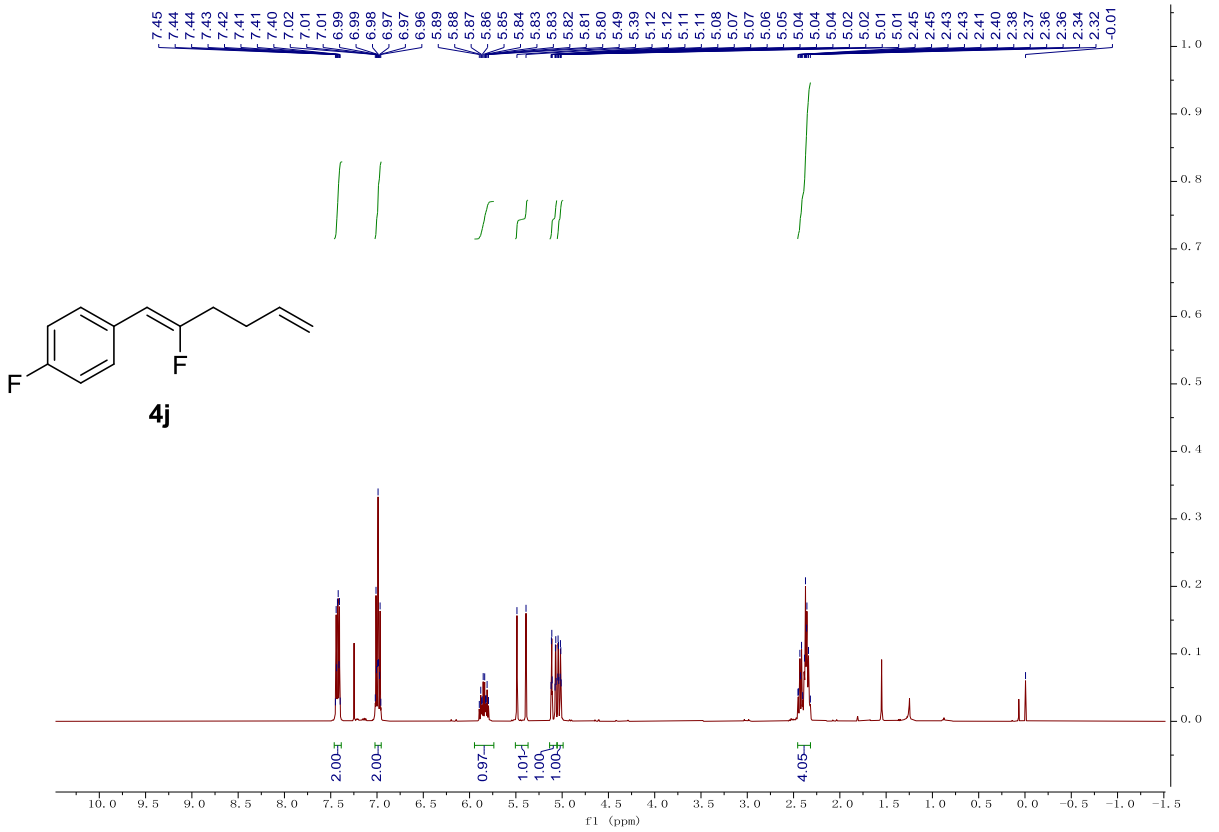
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4i



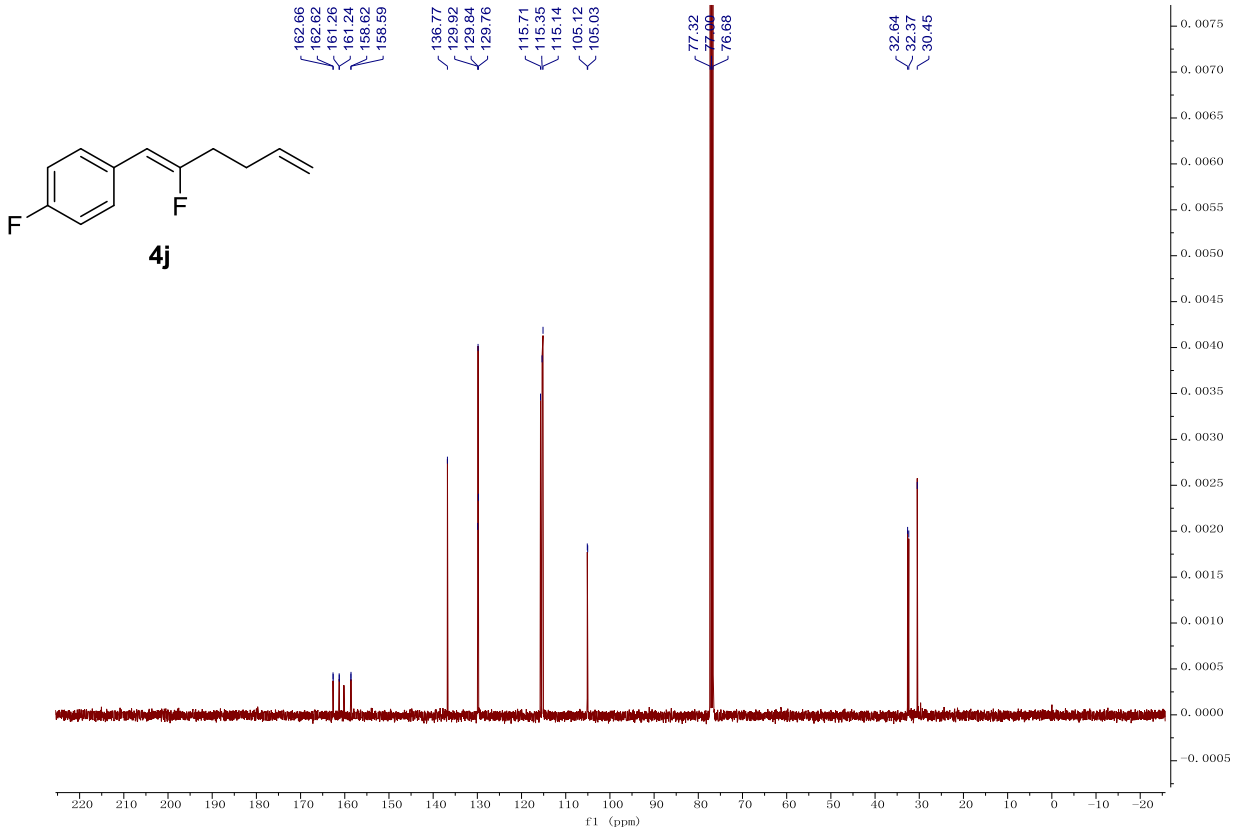
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4i



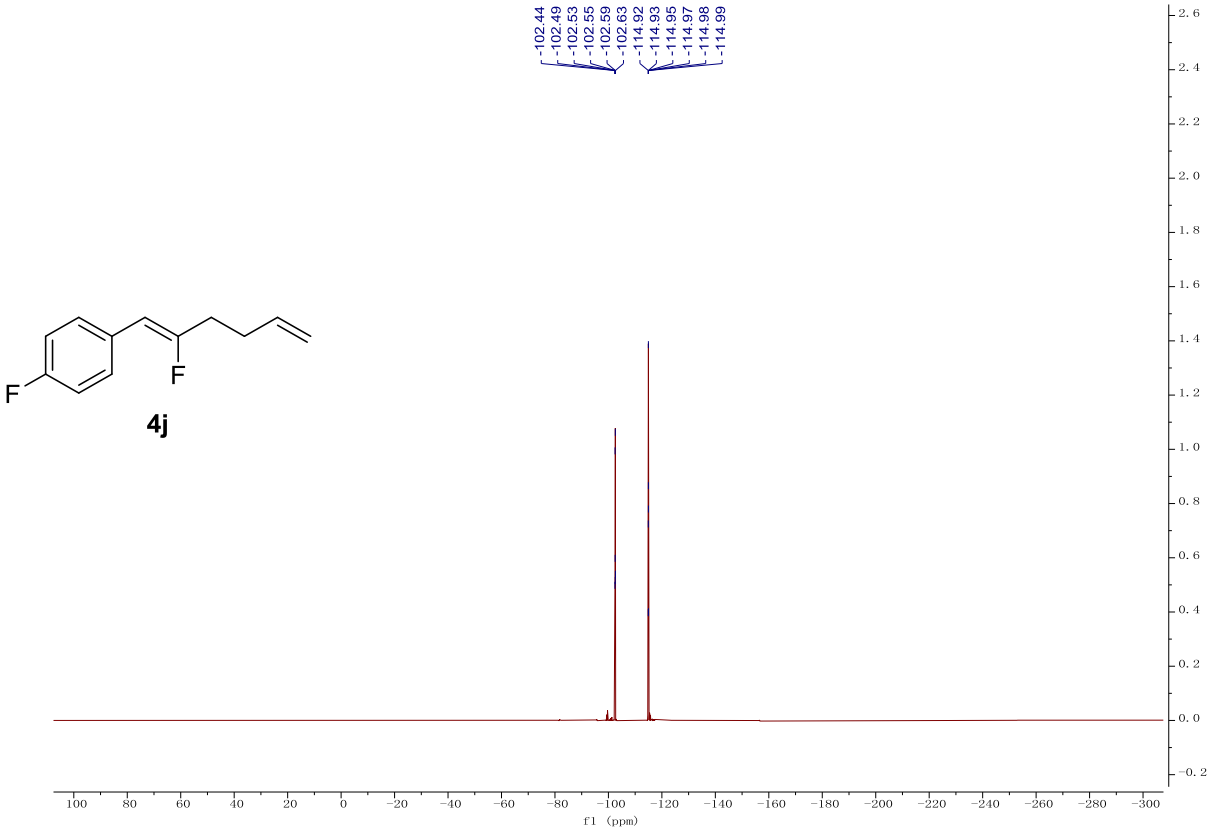
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4j (With JEOL)

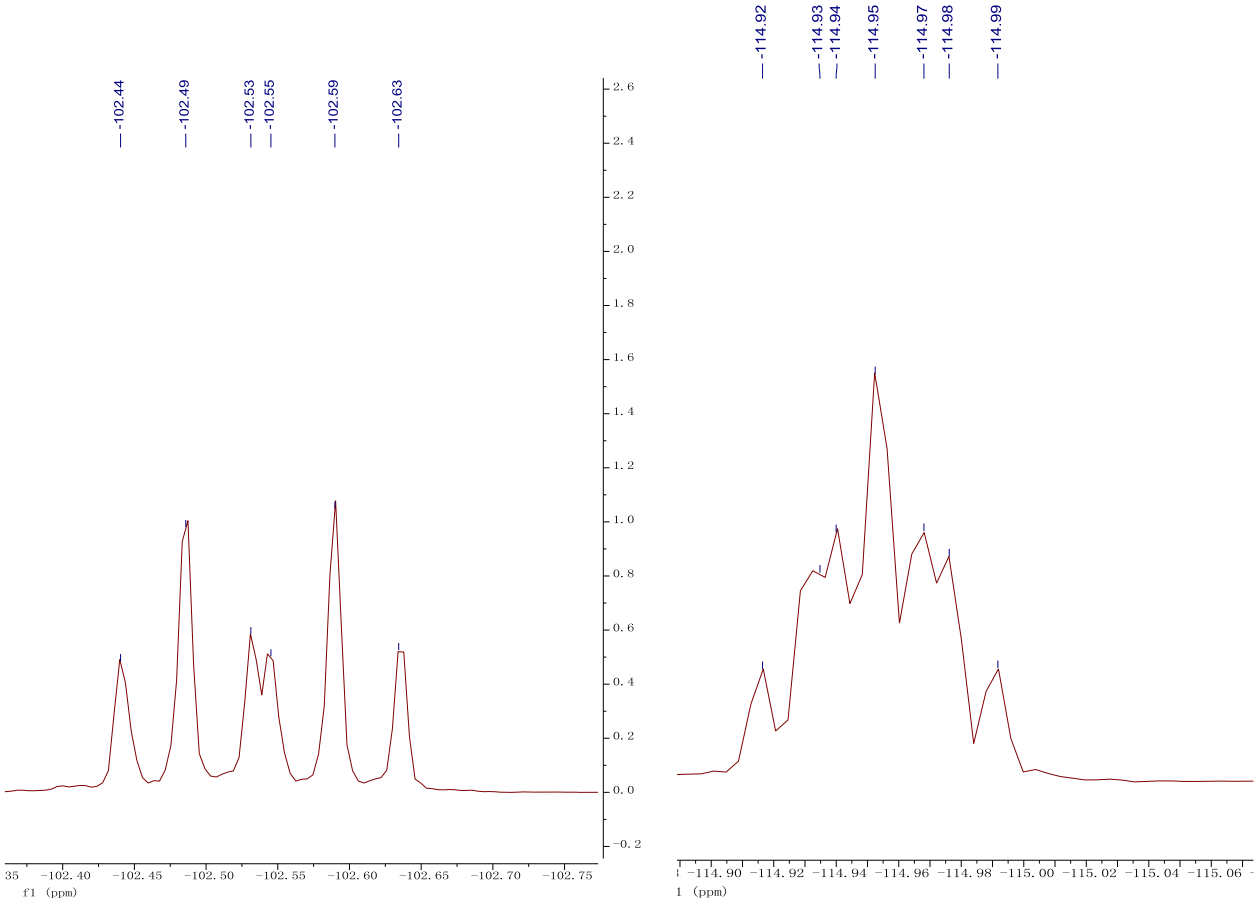


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4j (With JEOL)

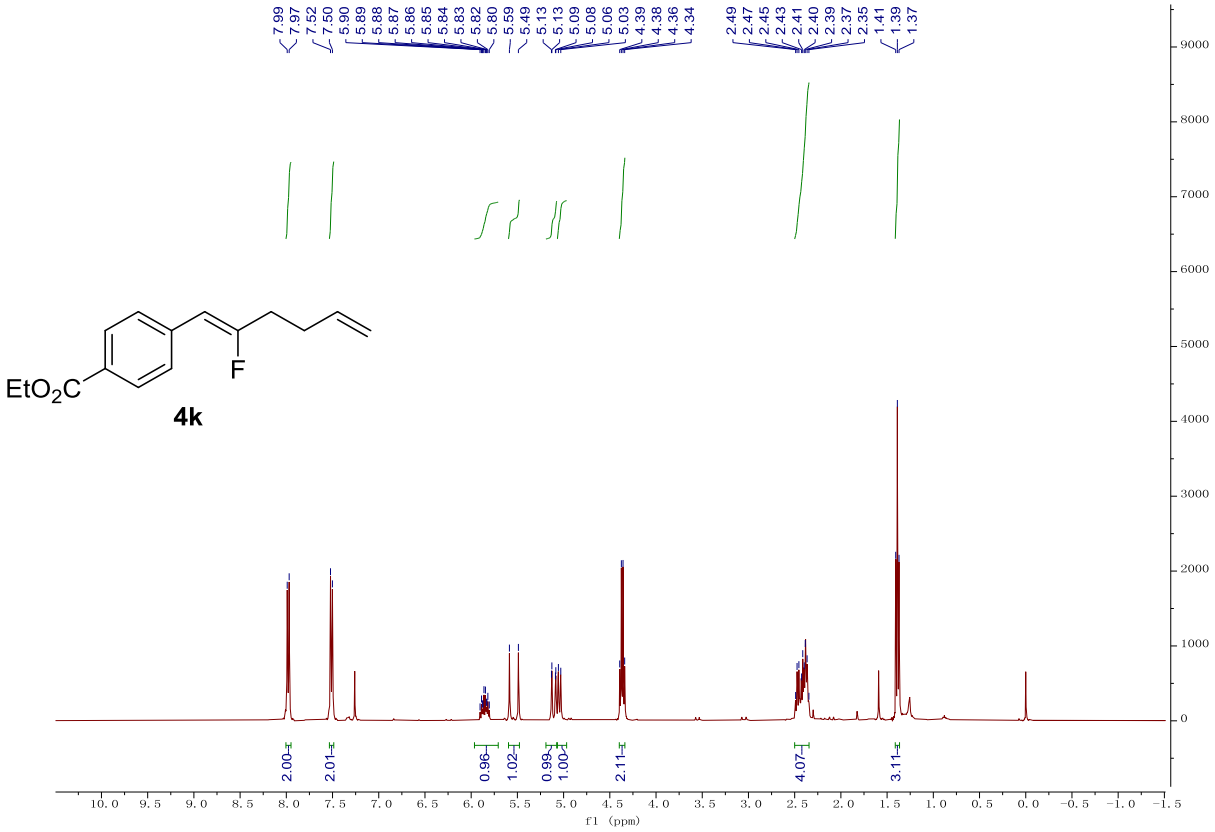


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4j (With JEOL)

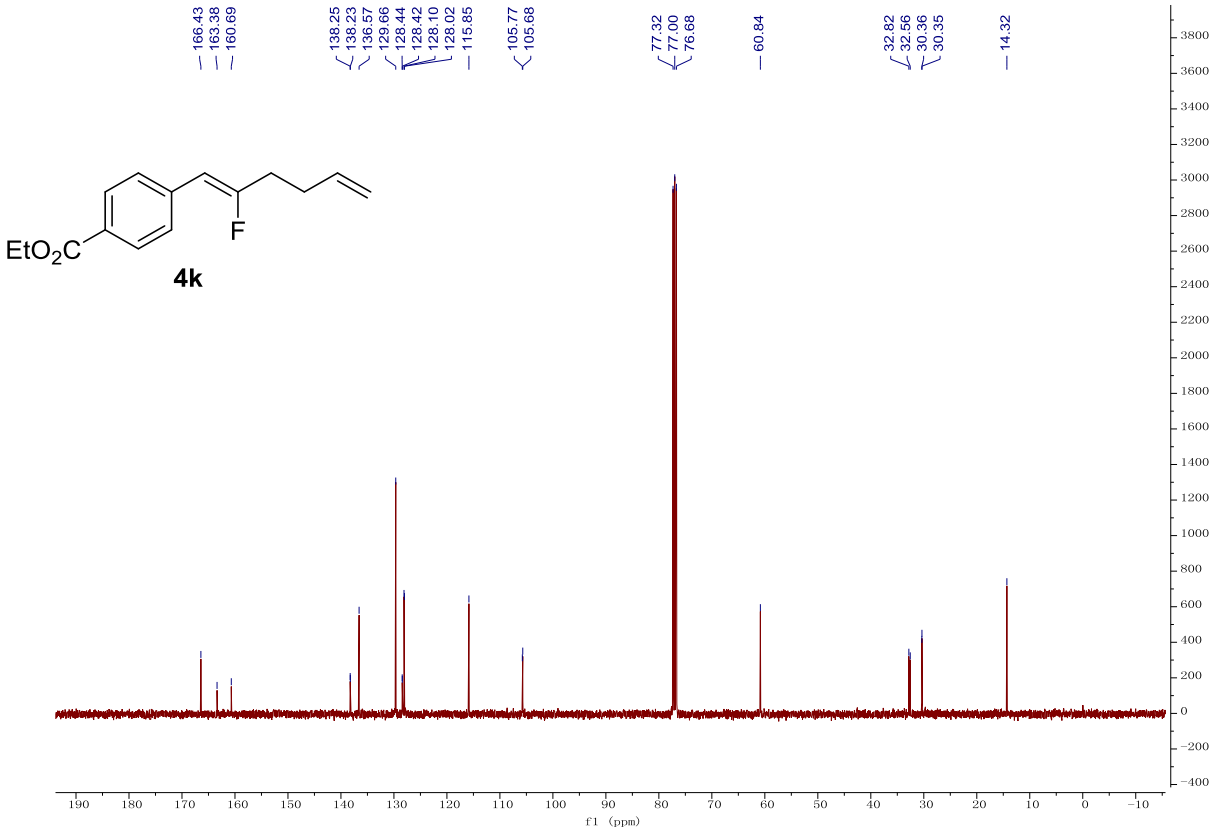




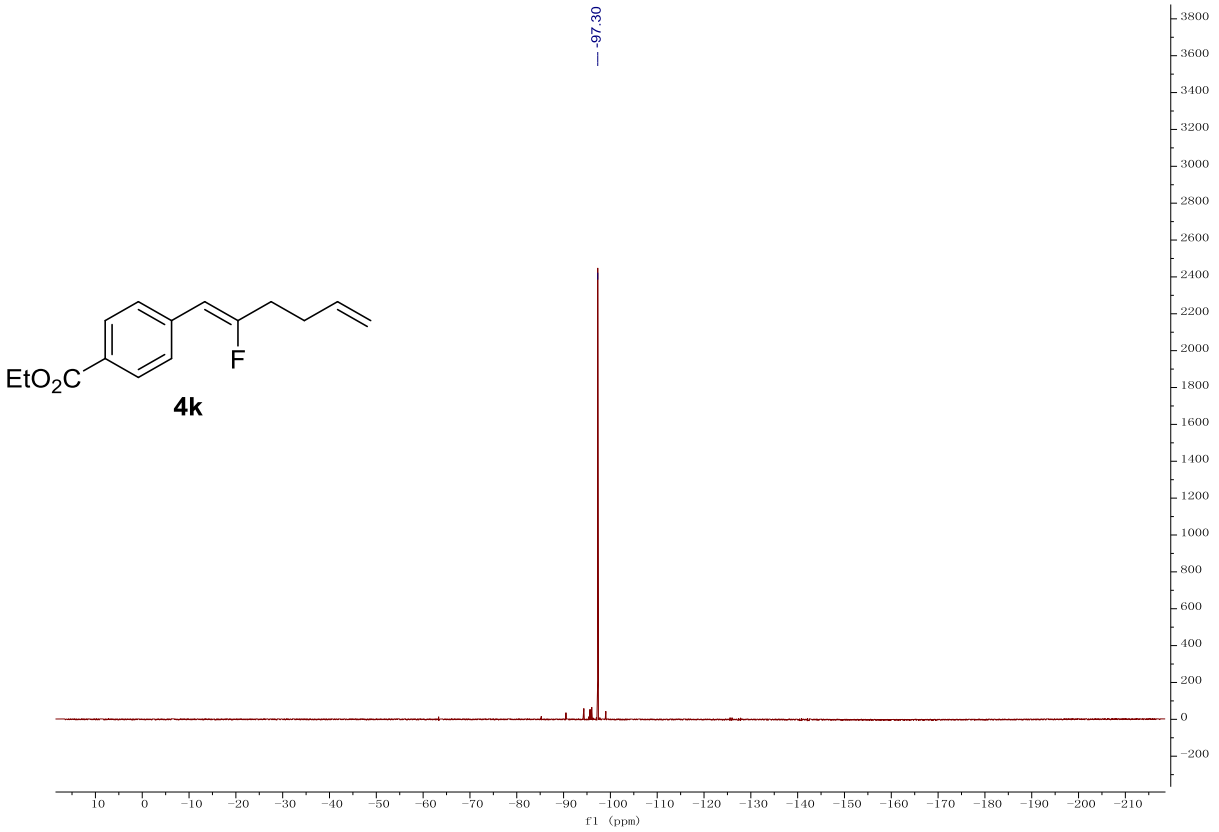
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4k



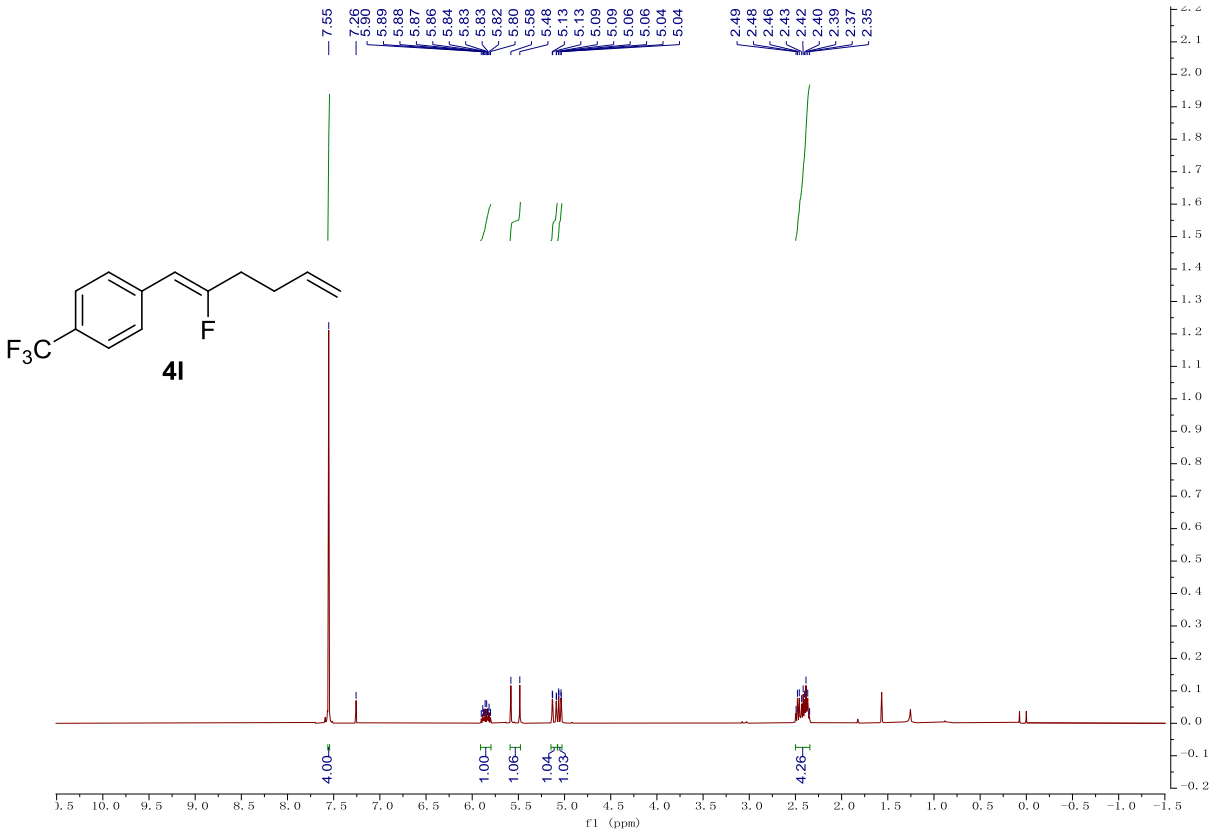
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4k



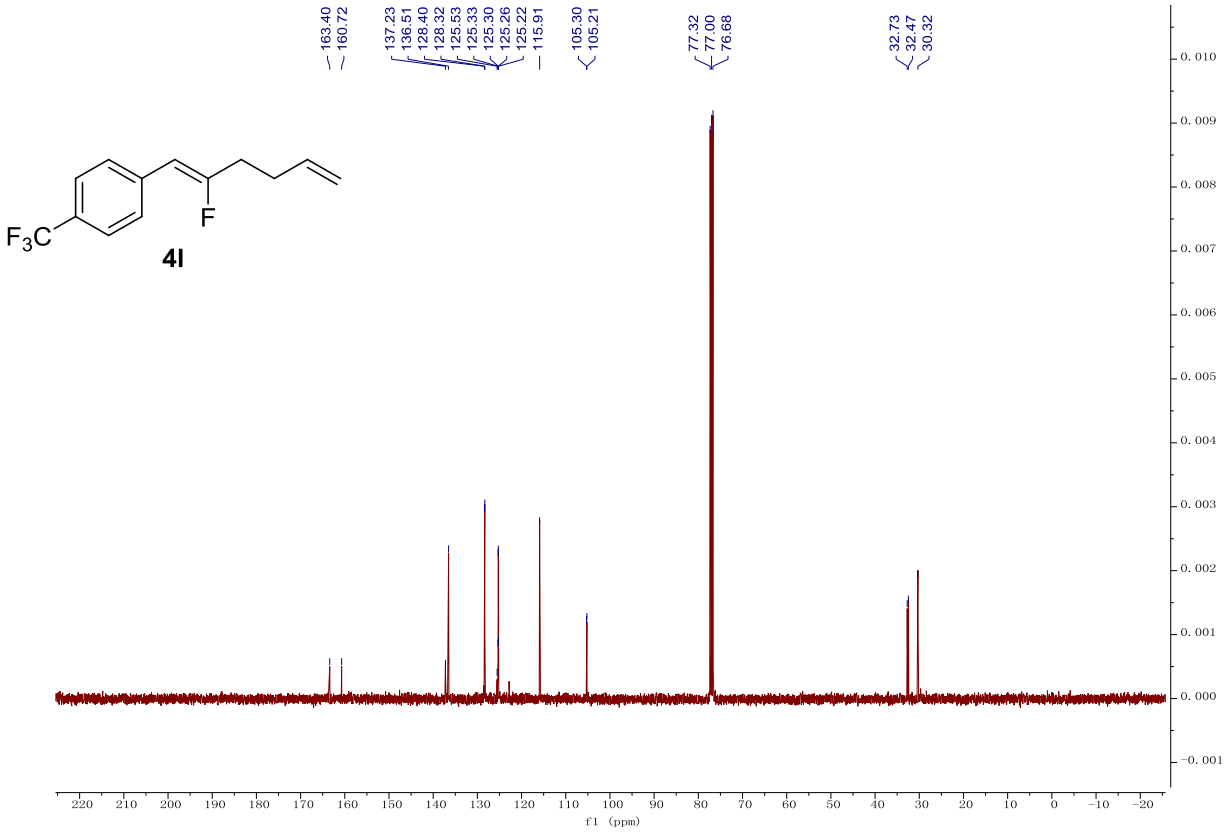
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4k



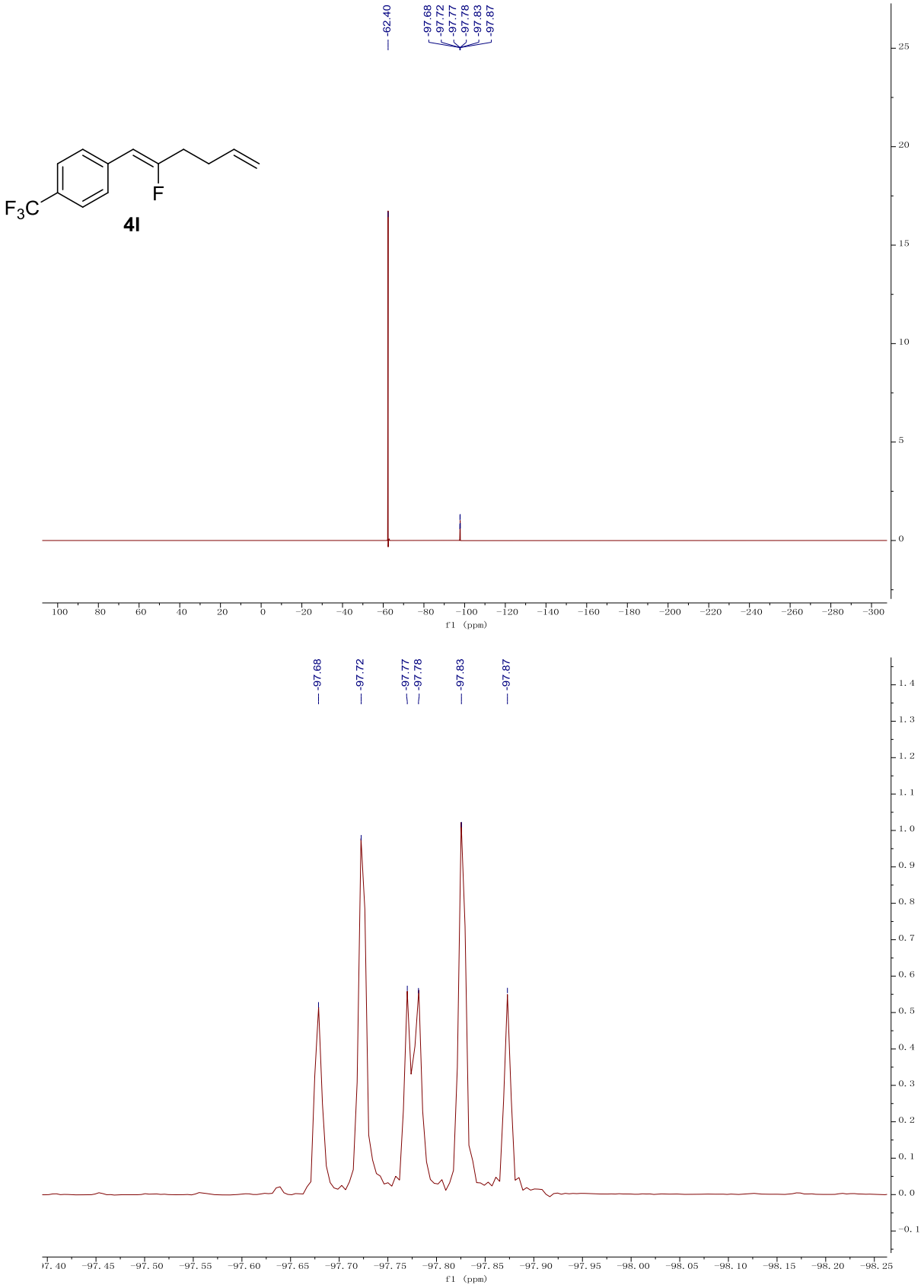
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4l (With JEOL)



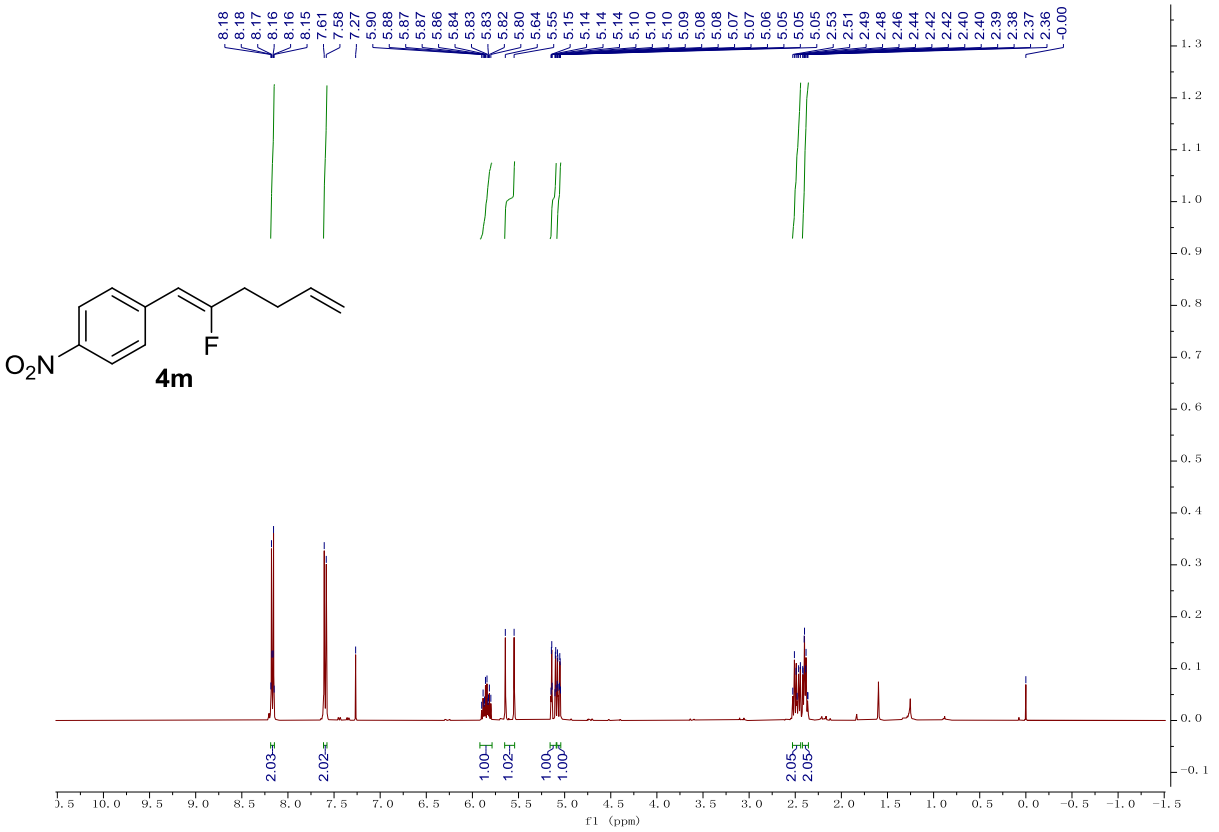
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4l (With JEOL)



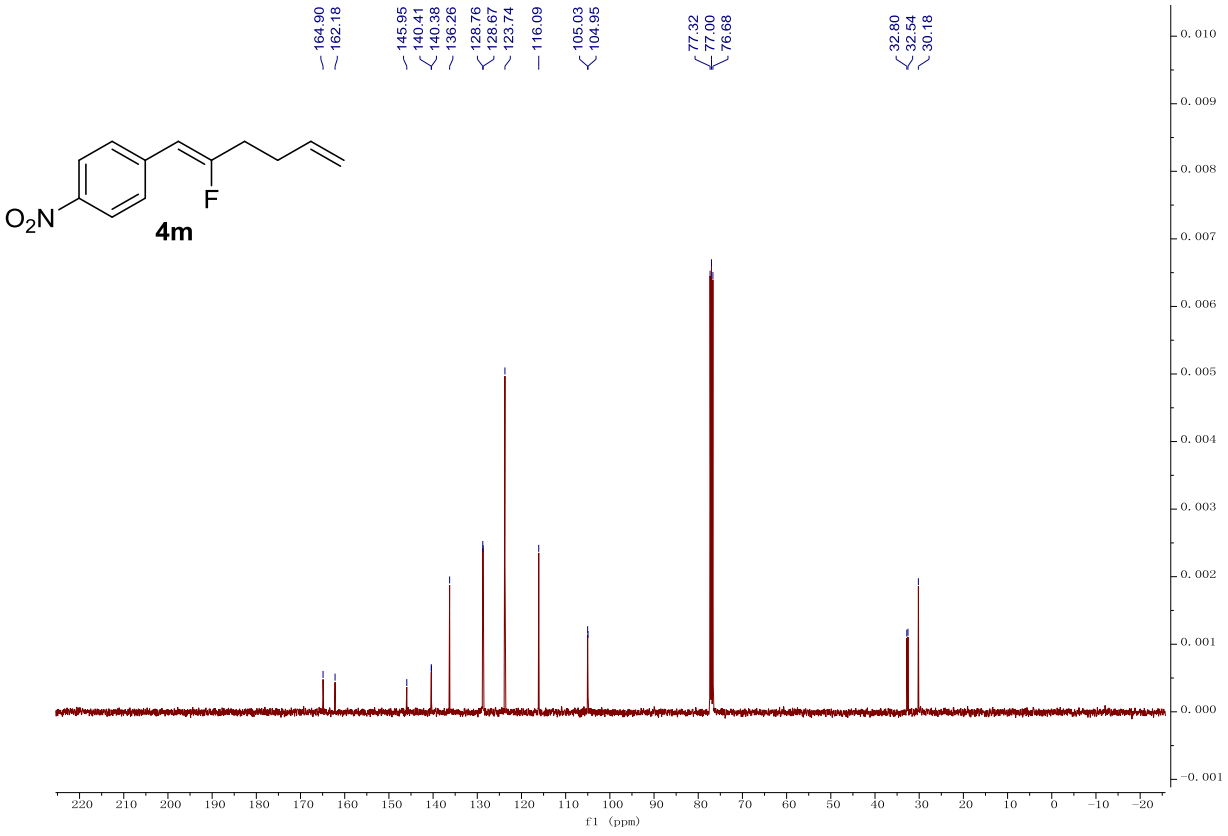
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4l (With JEOL)



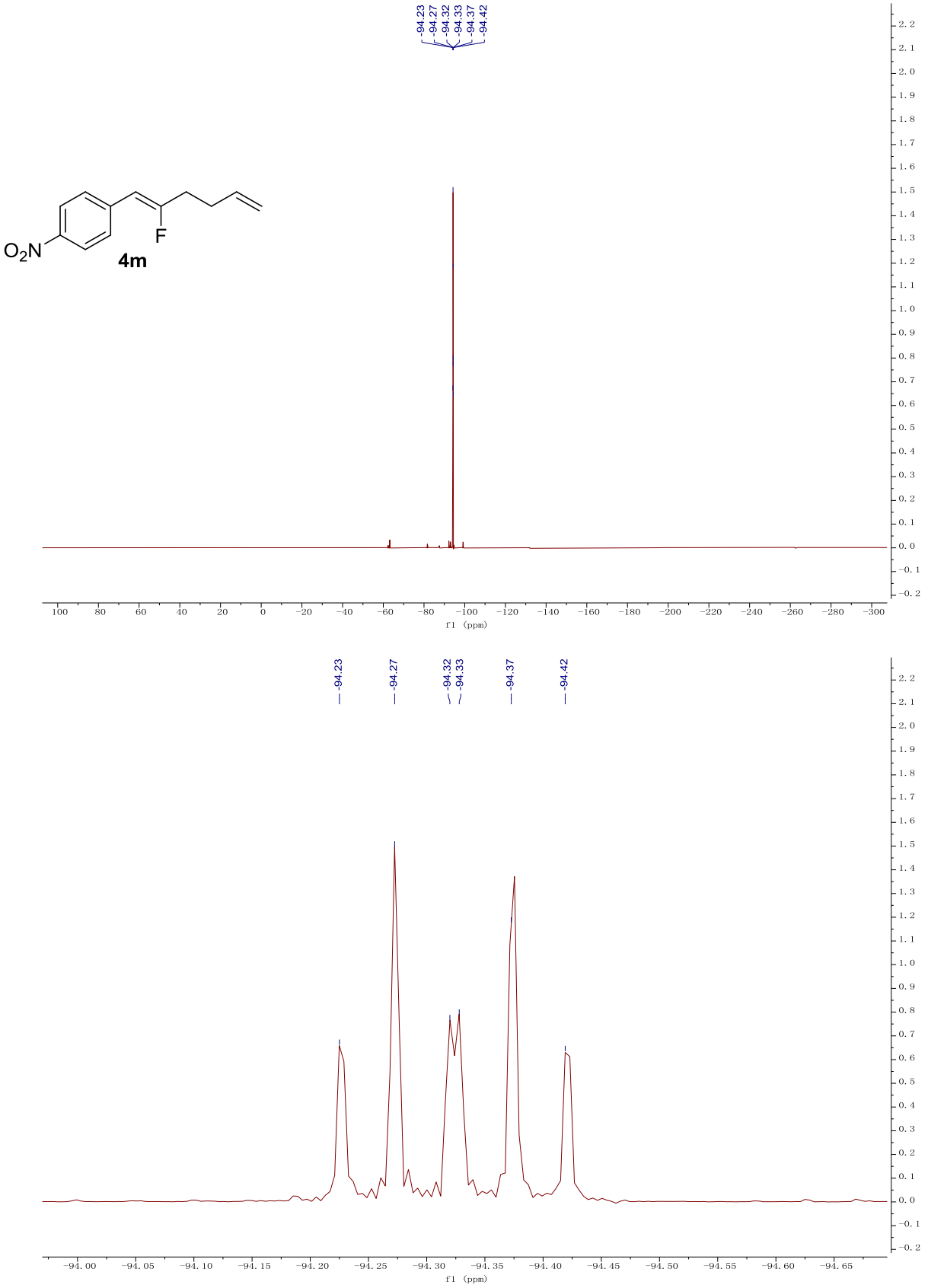
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4m (With JEOL)



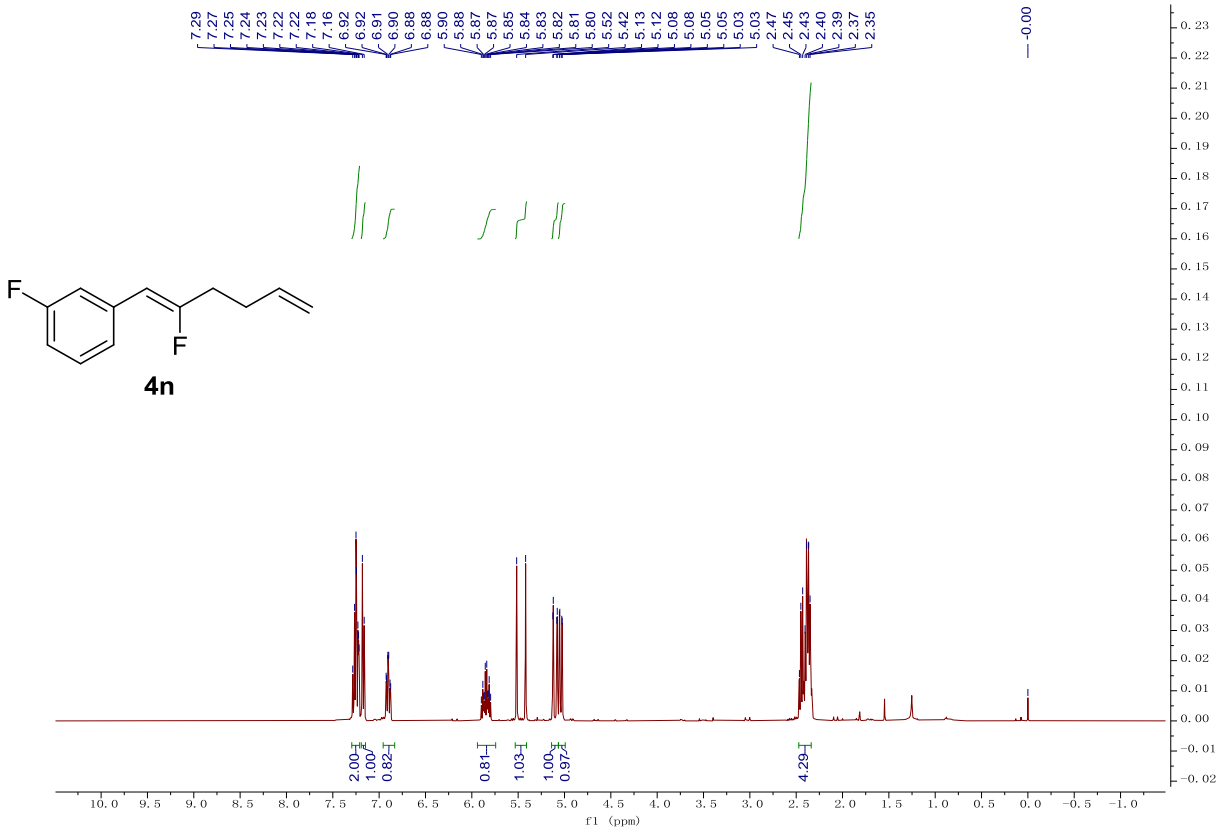
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4m (With JEOL)



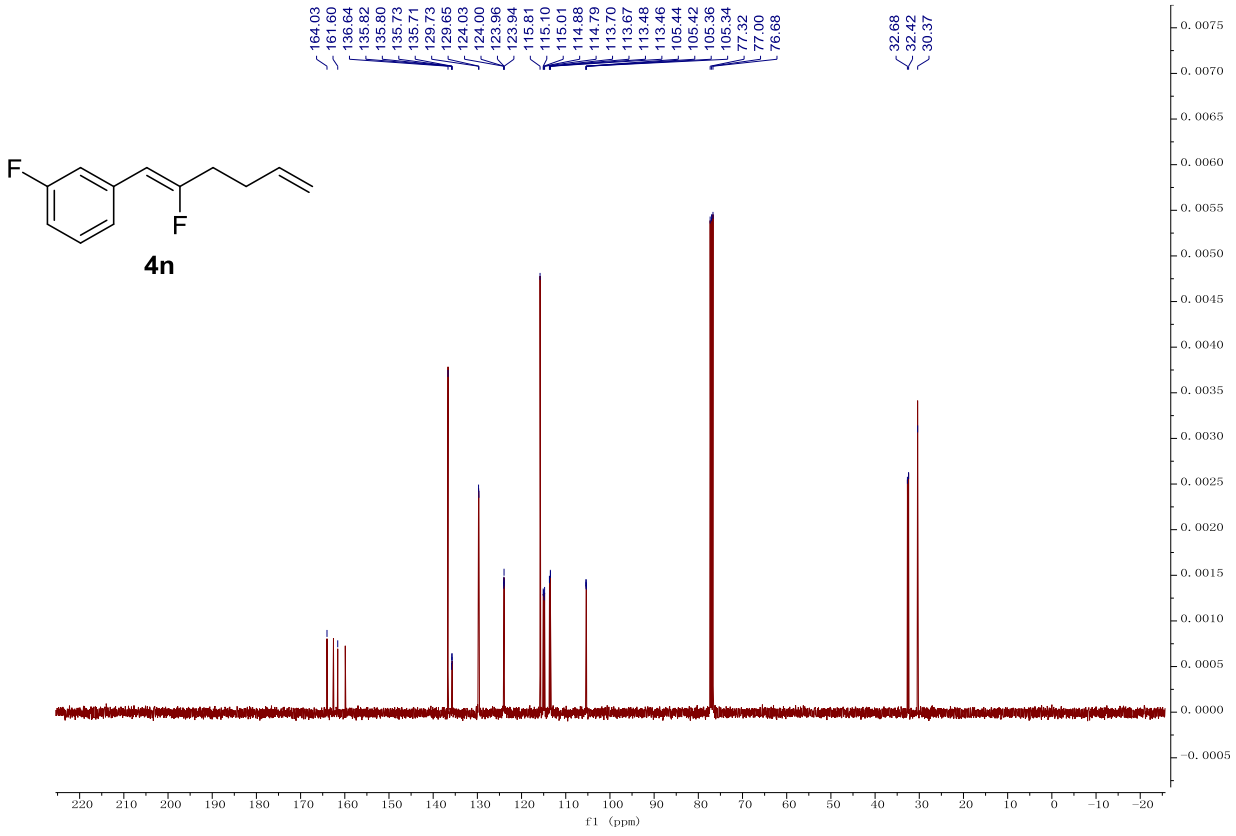
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4m (With JEOL)



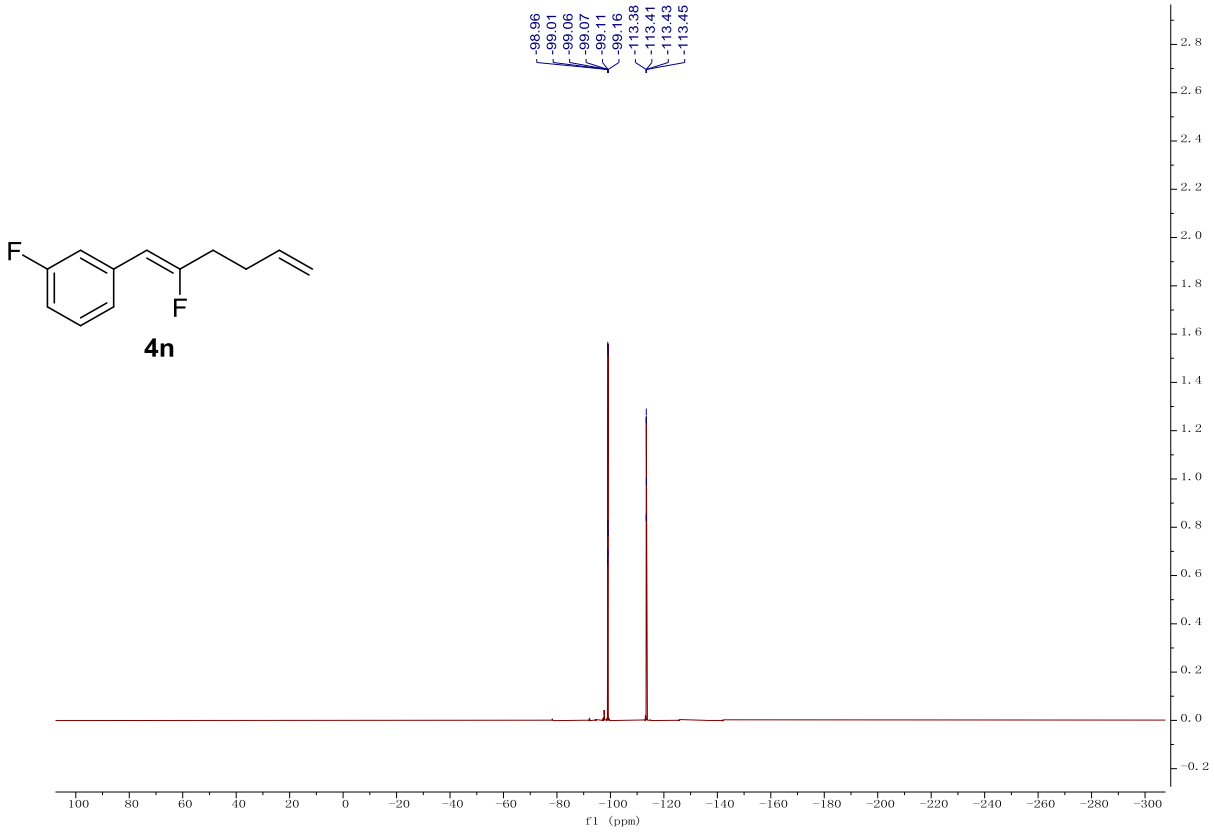
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4n (With JEOL)

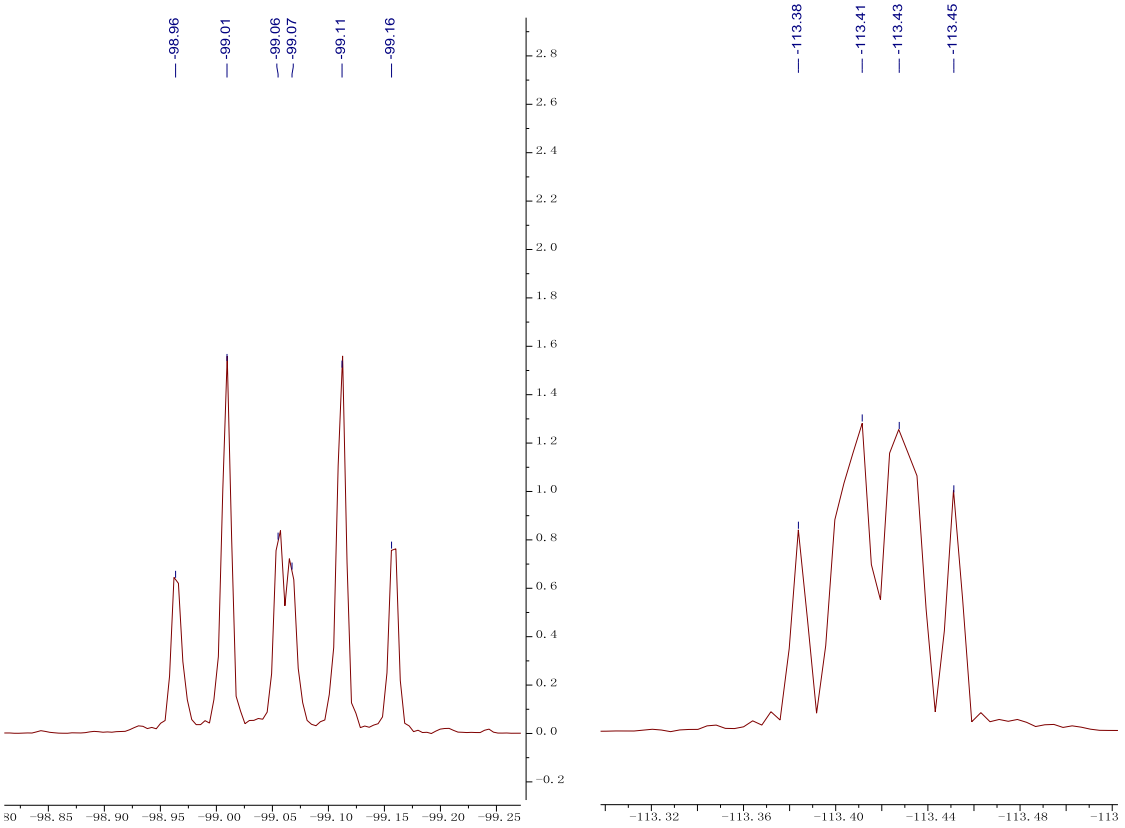


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4n (With JEOL)

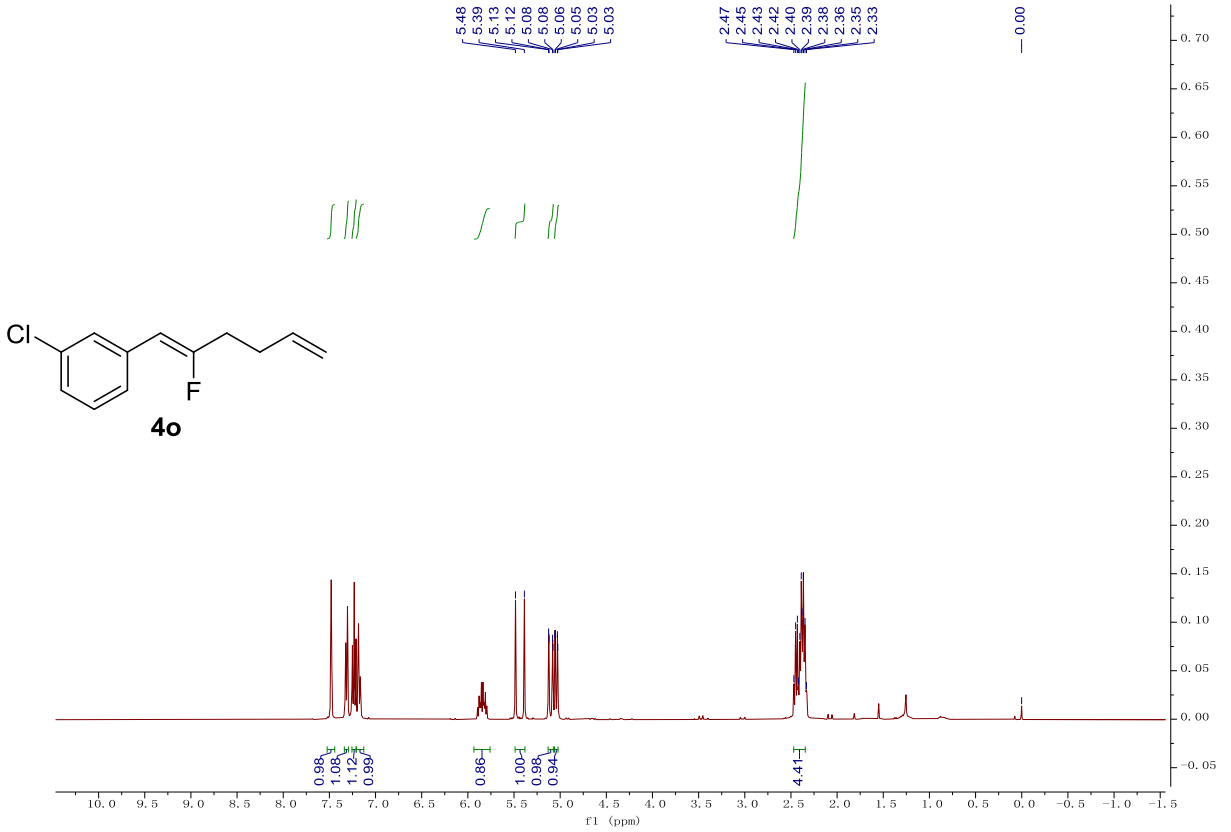


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4n (With JEOL)

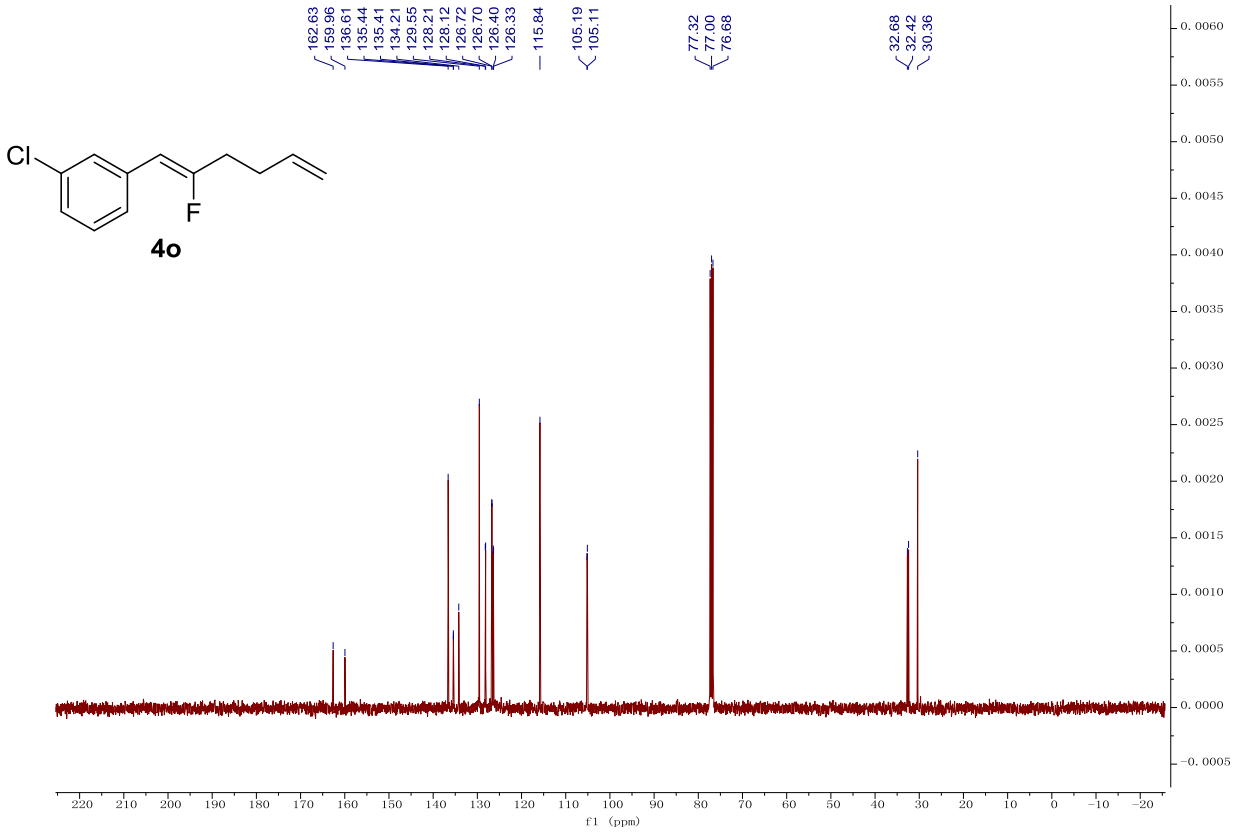




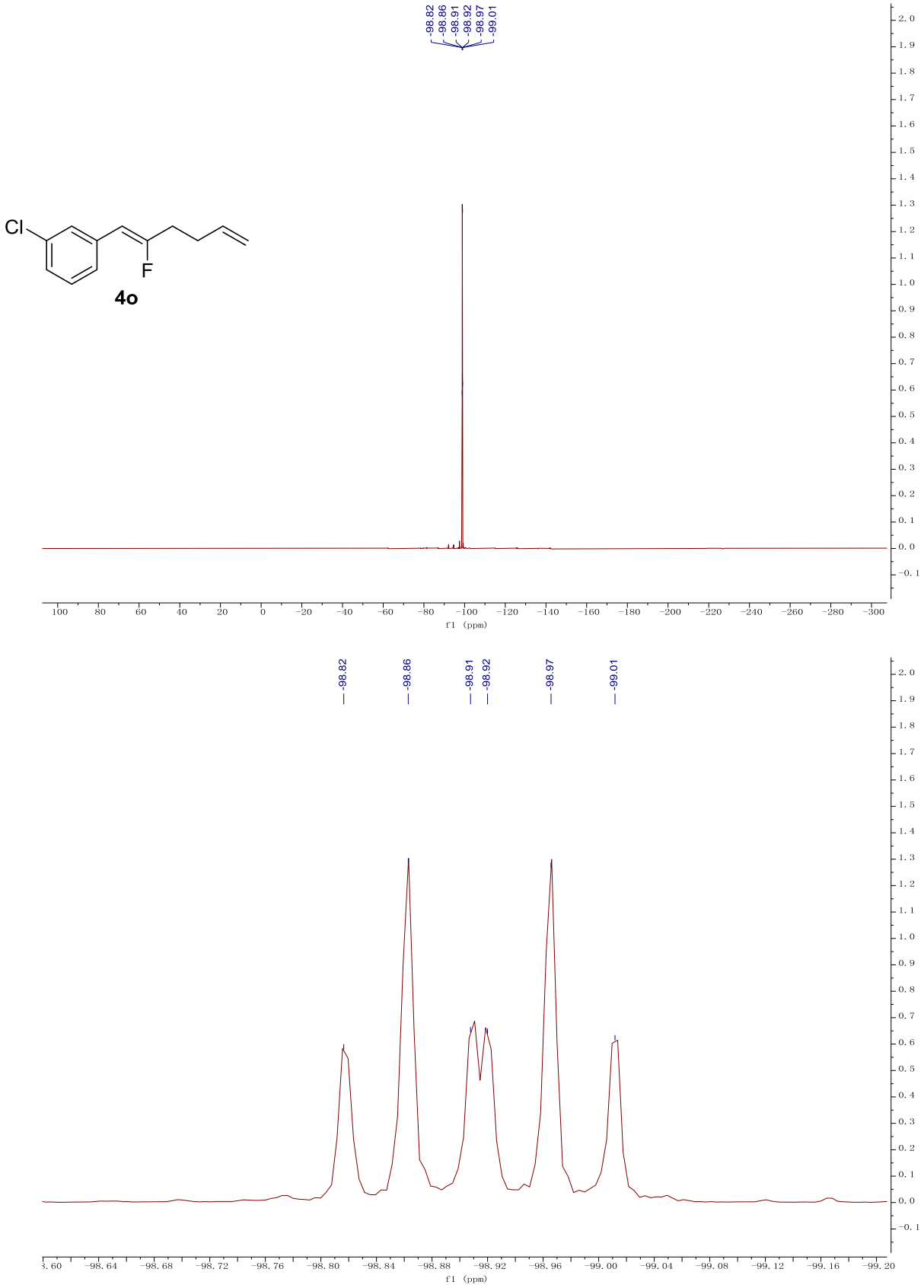
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4o (With JEOL)



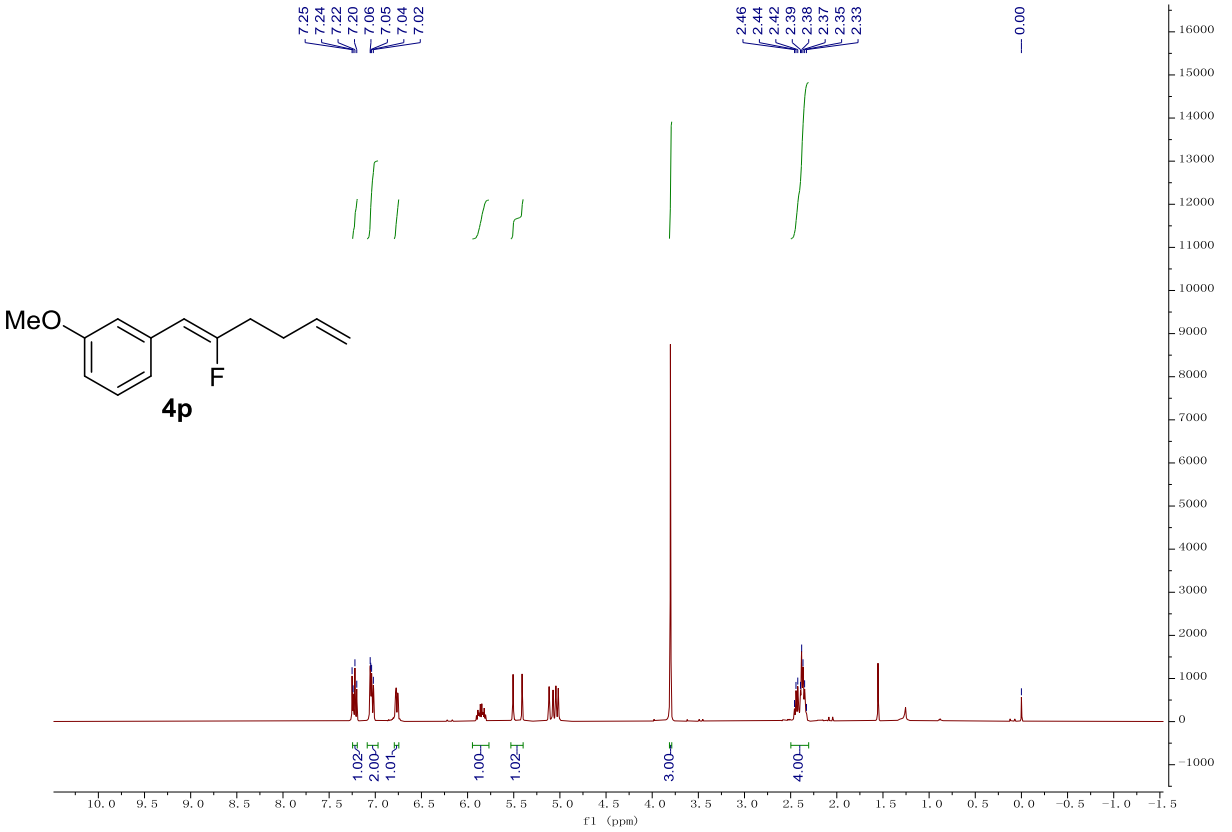
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4o (With JEOL)



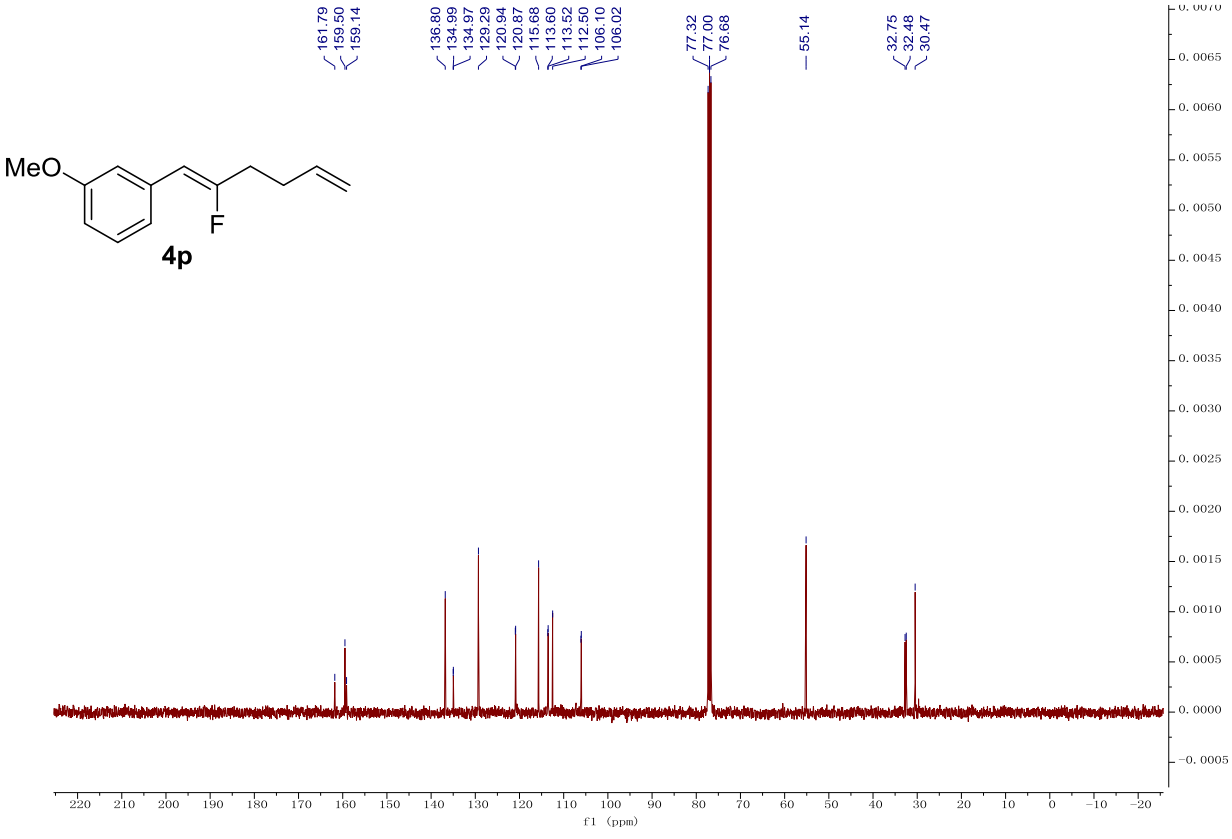
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4o (With JEOL)



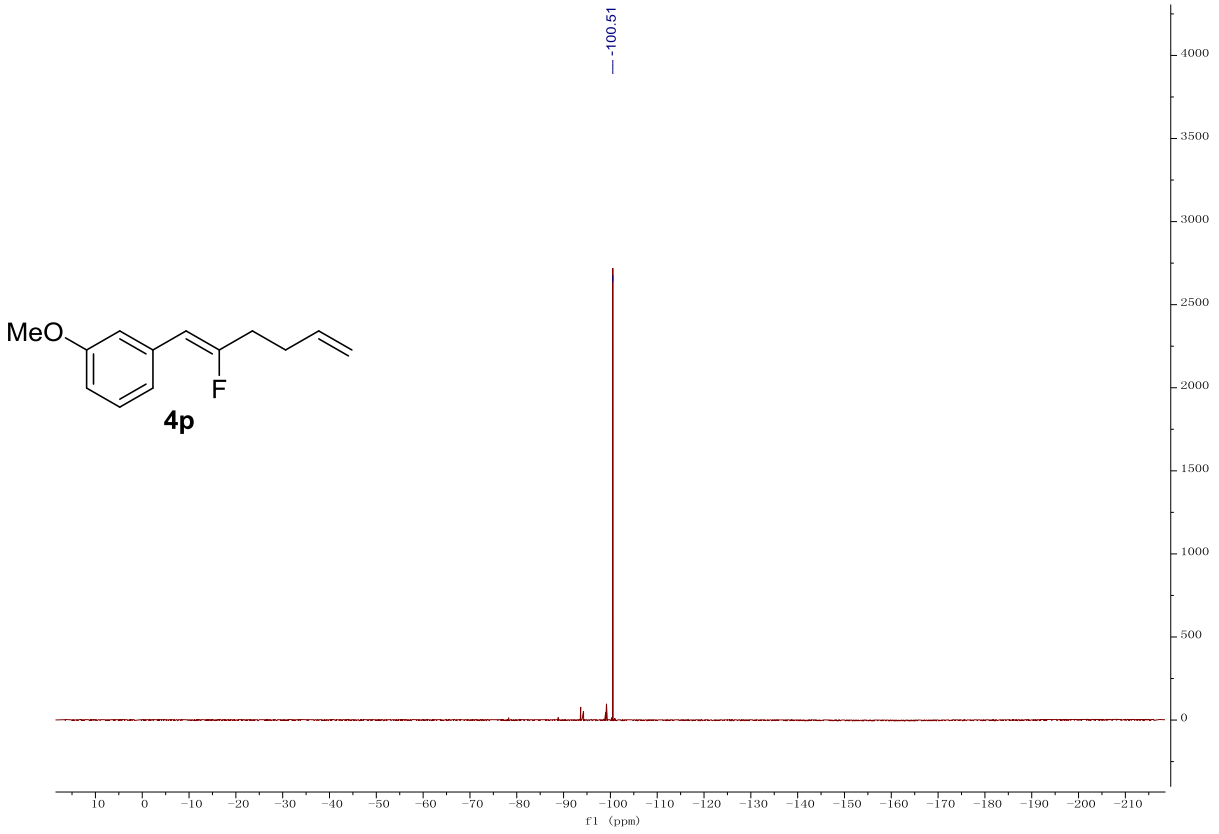
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4p



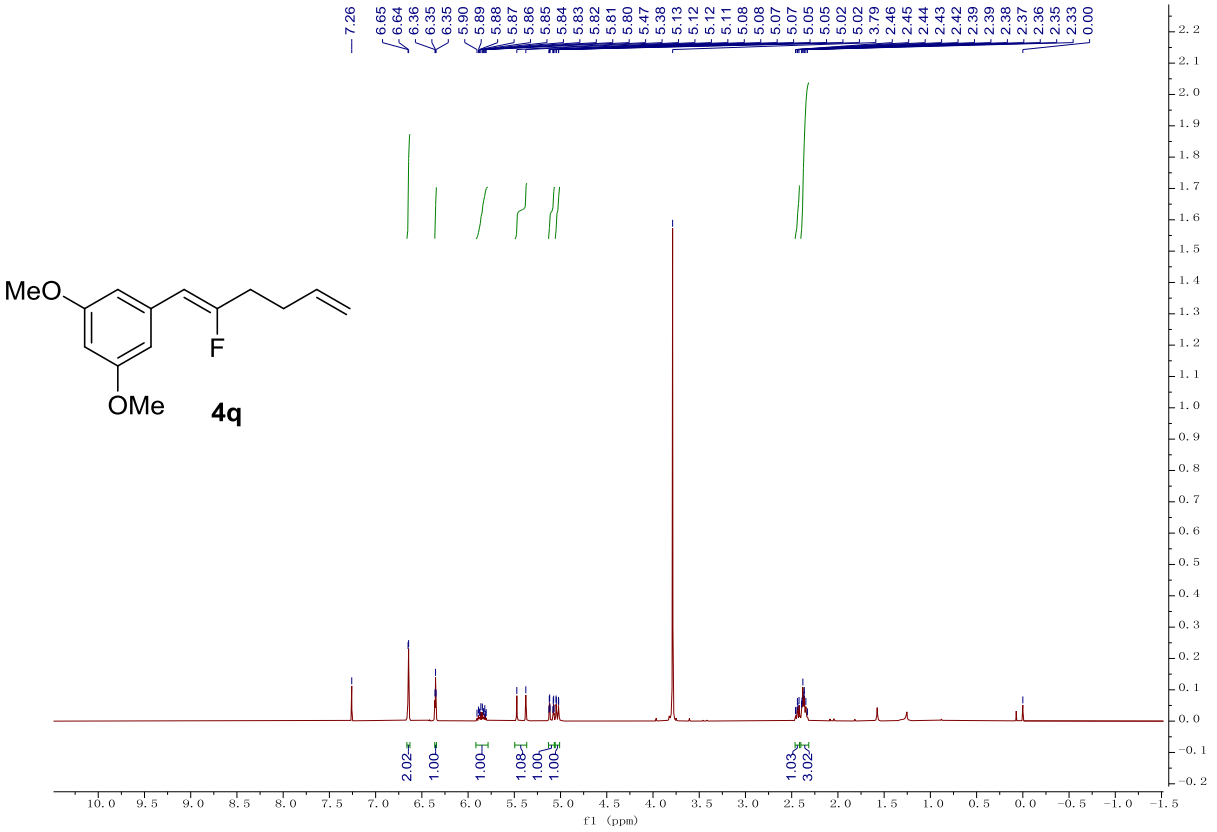
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4p



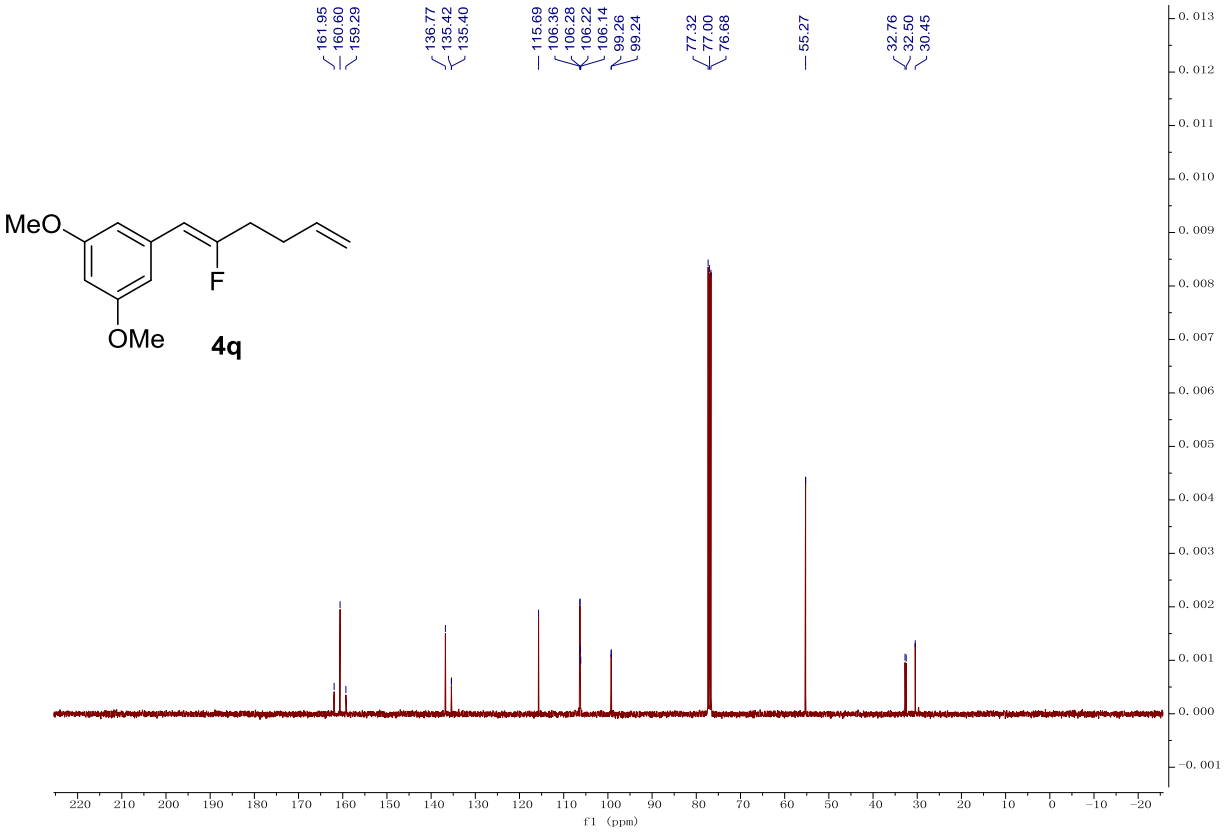
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4p



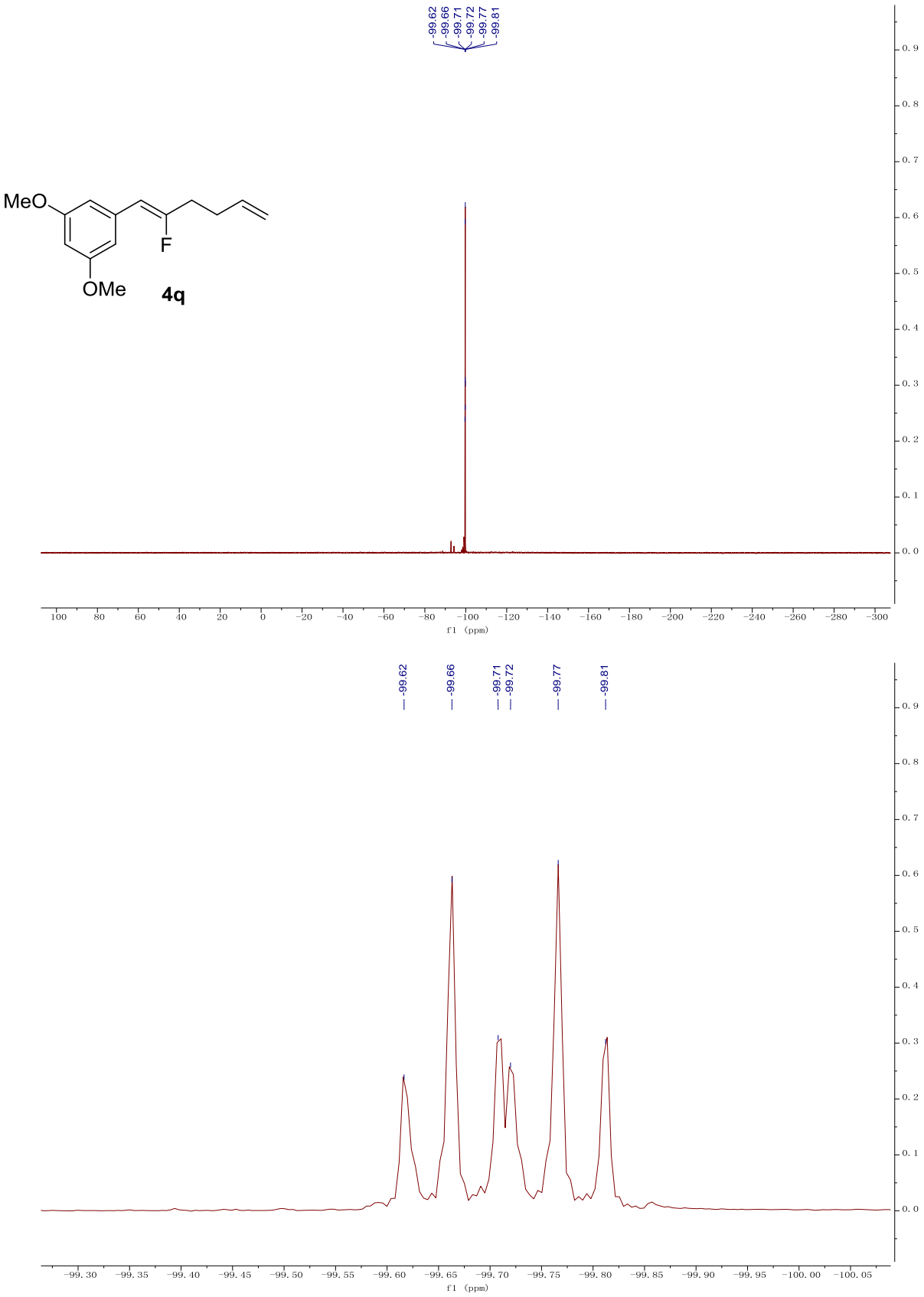
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4q (With JEOL)



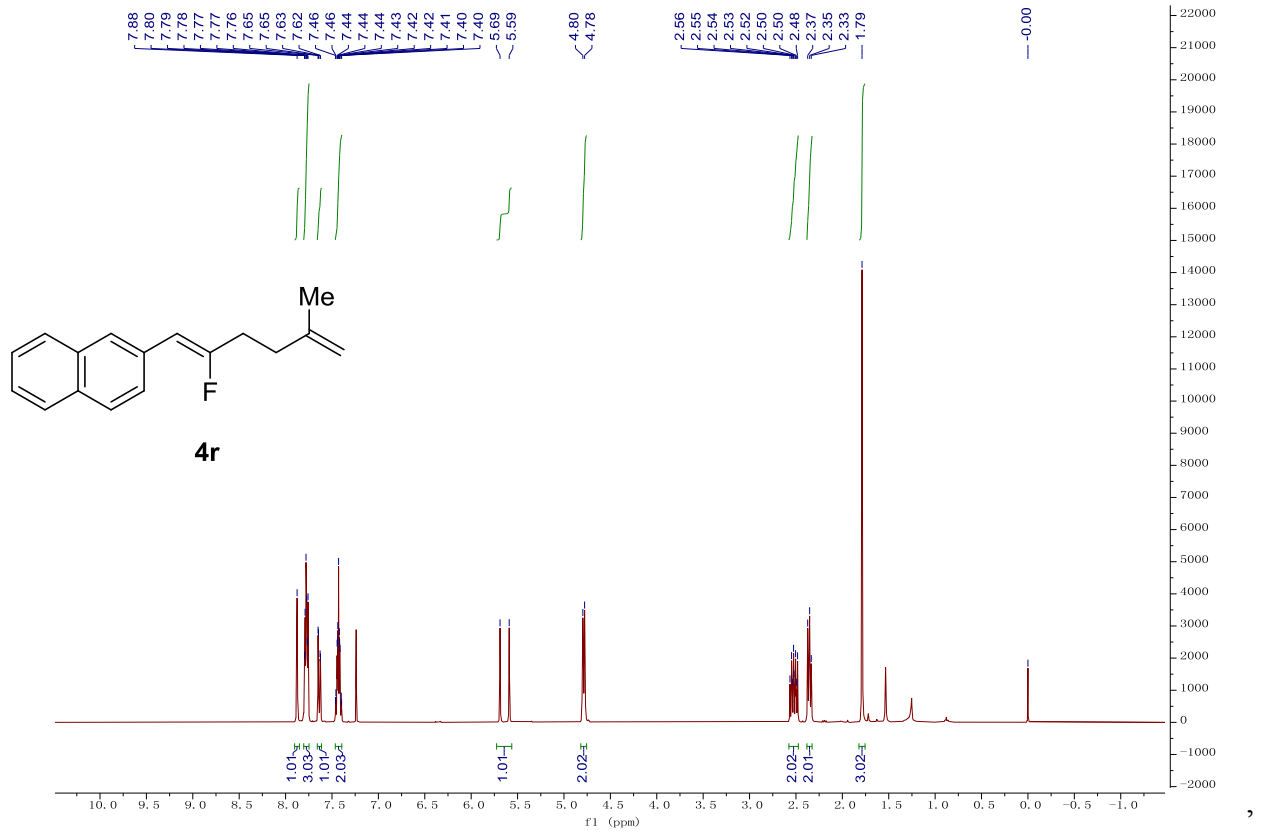
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4q (With JEOL)



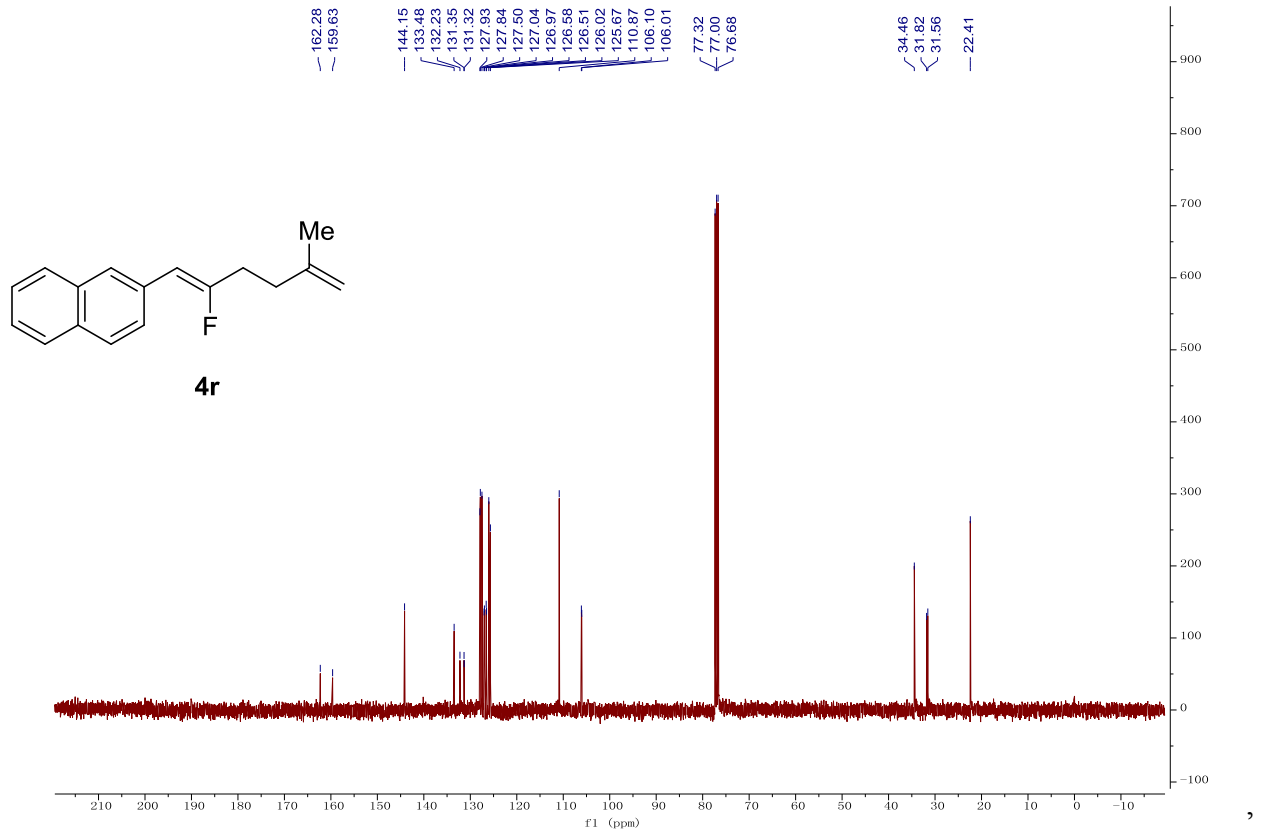
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4q (With JEOL)



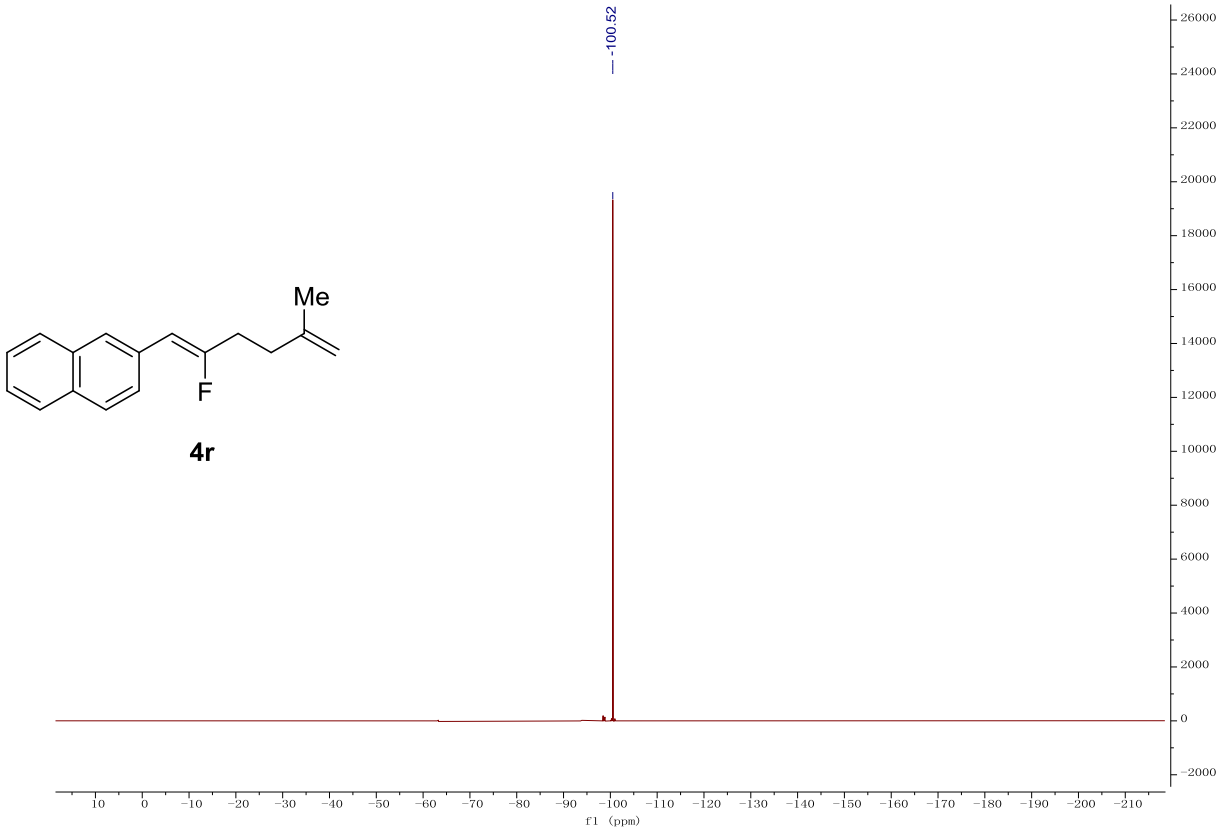
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4r



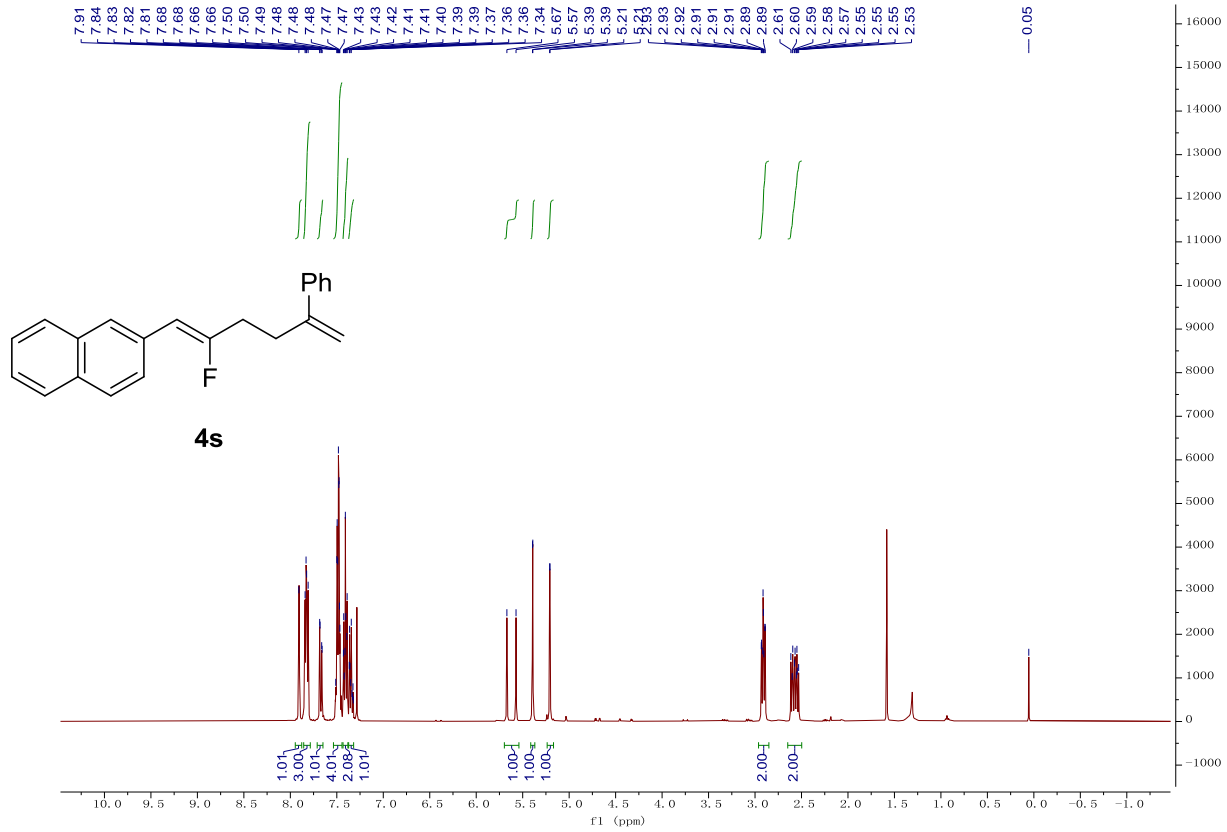
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4r



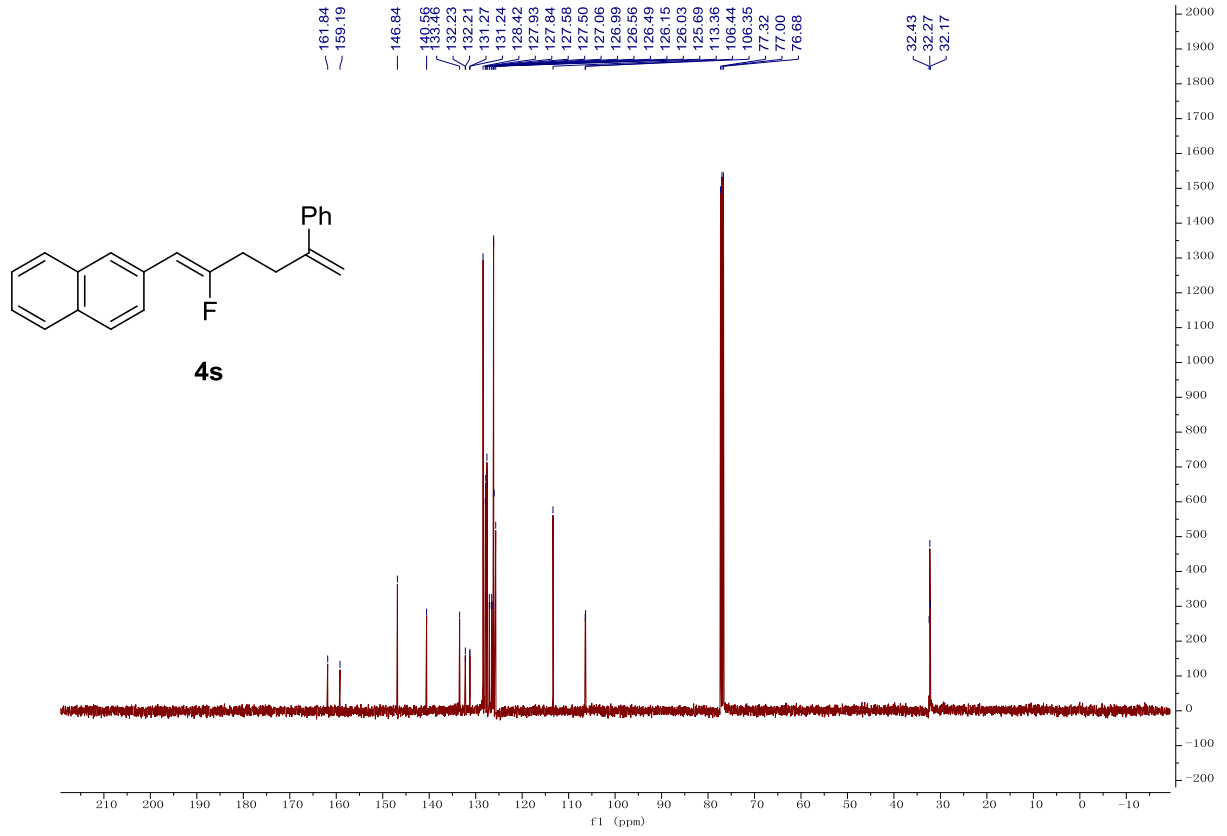
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4r



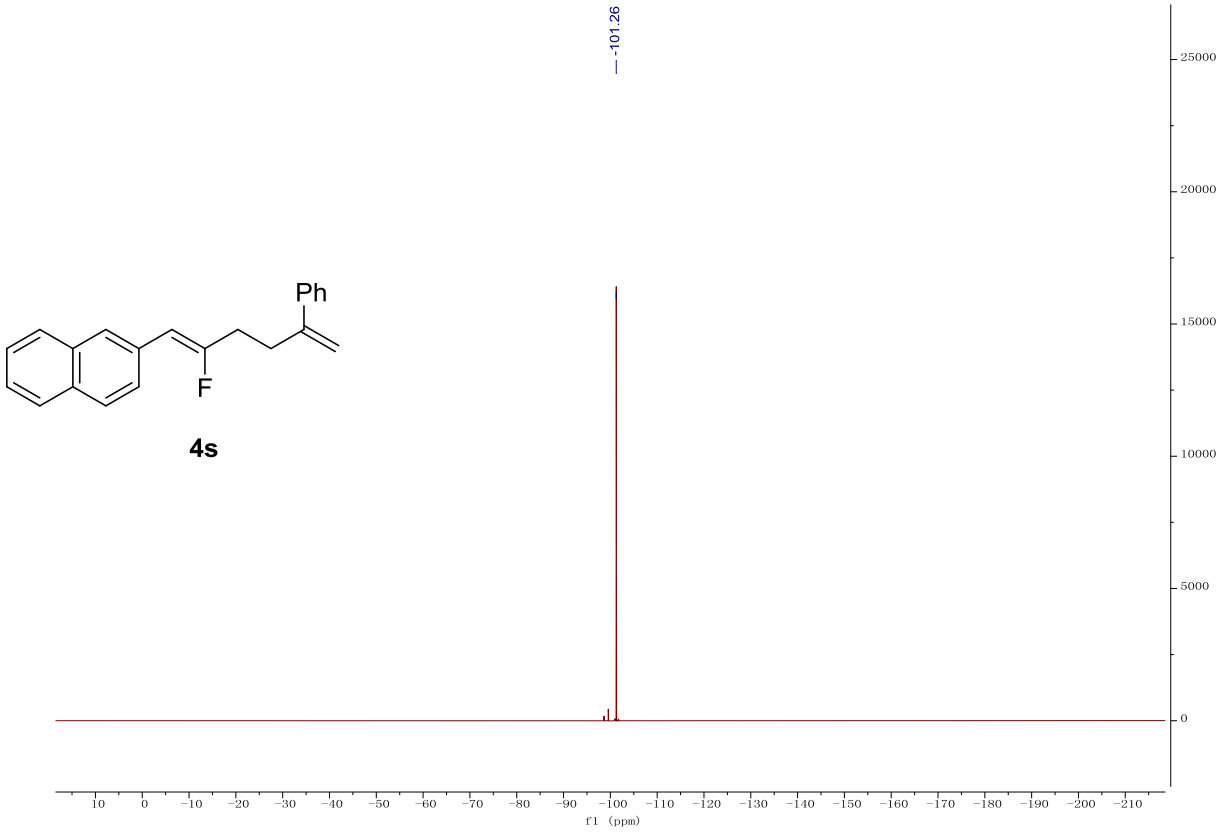
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4s



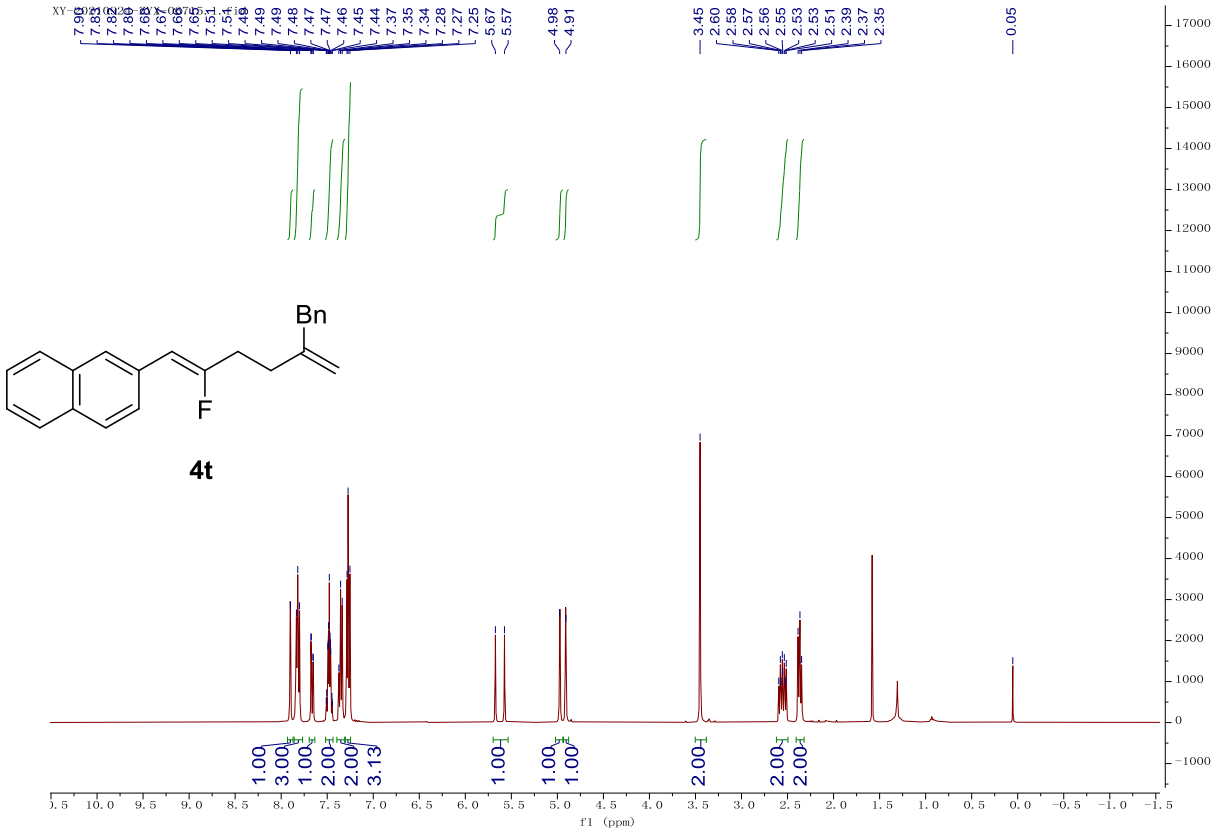
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4s



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4s



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4t



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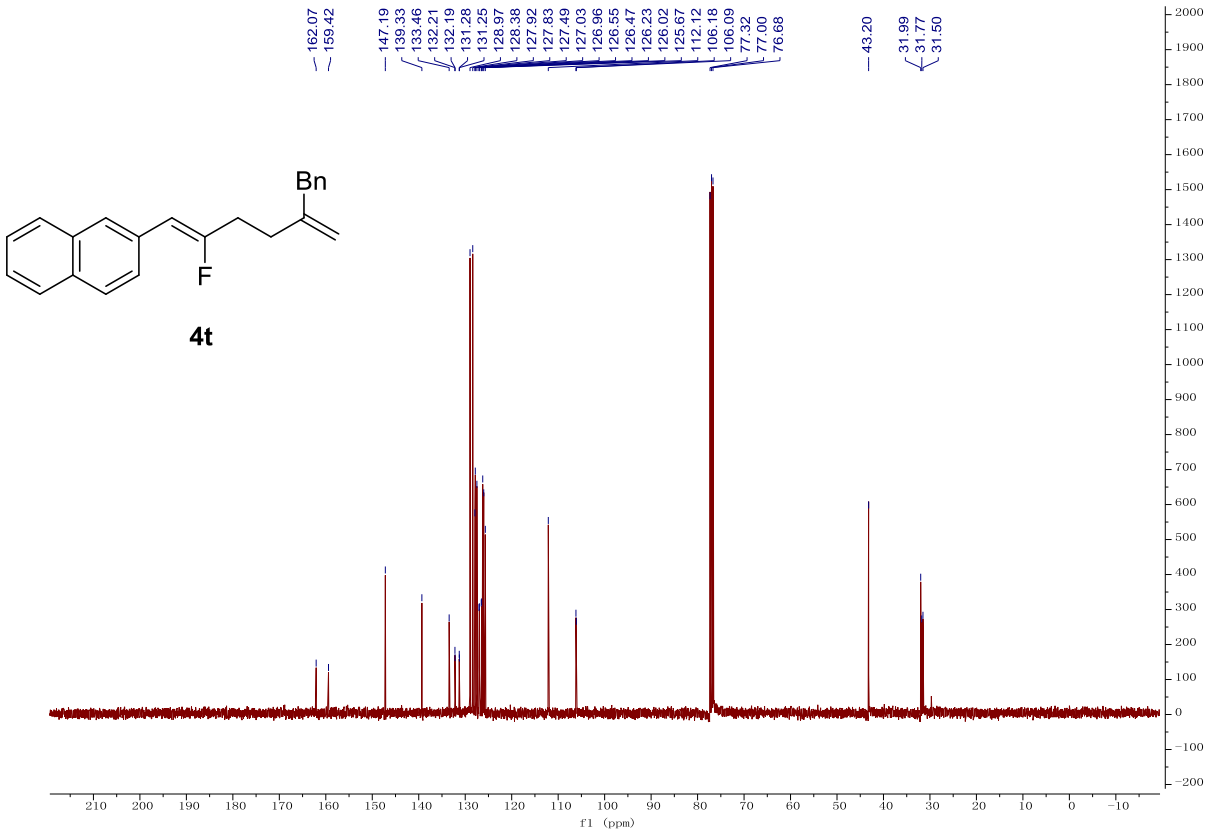
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4t



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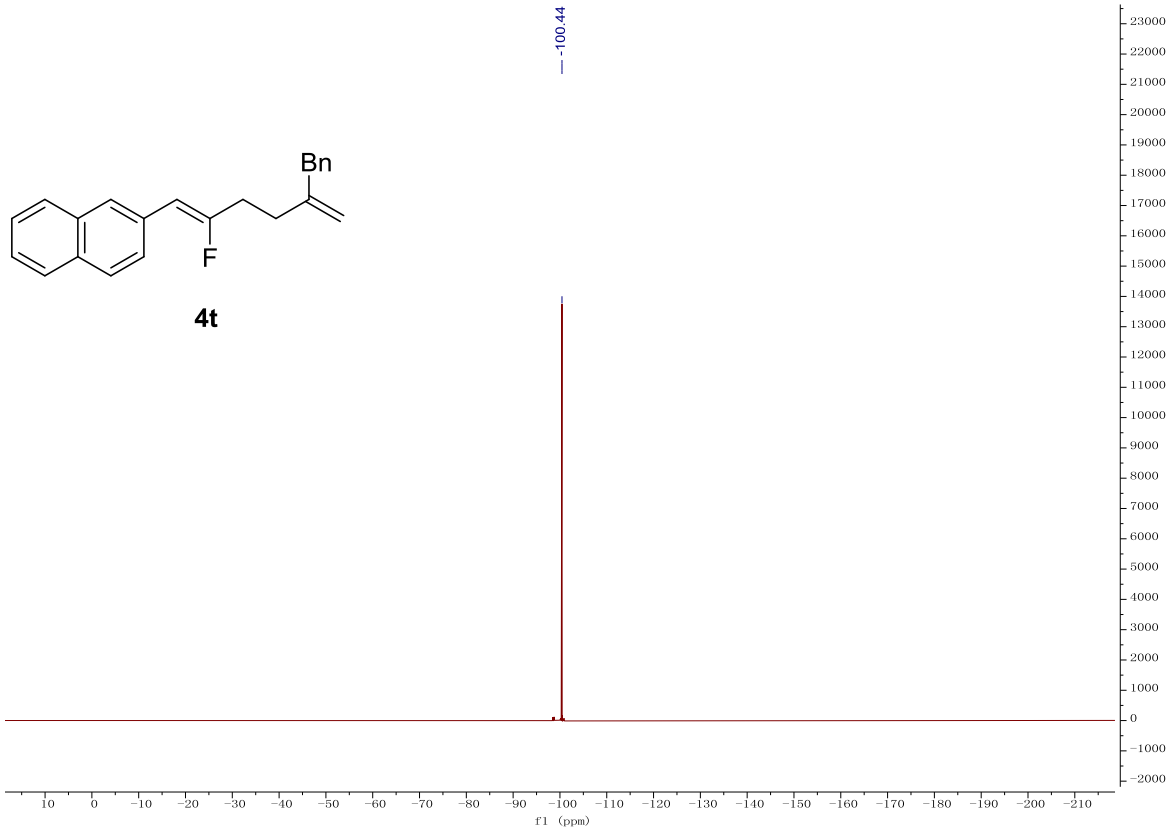
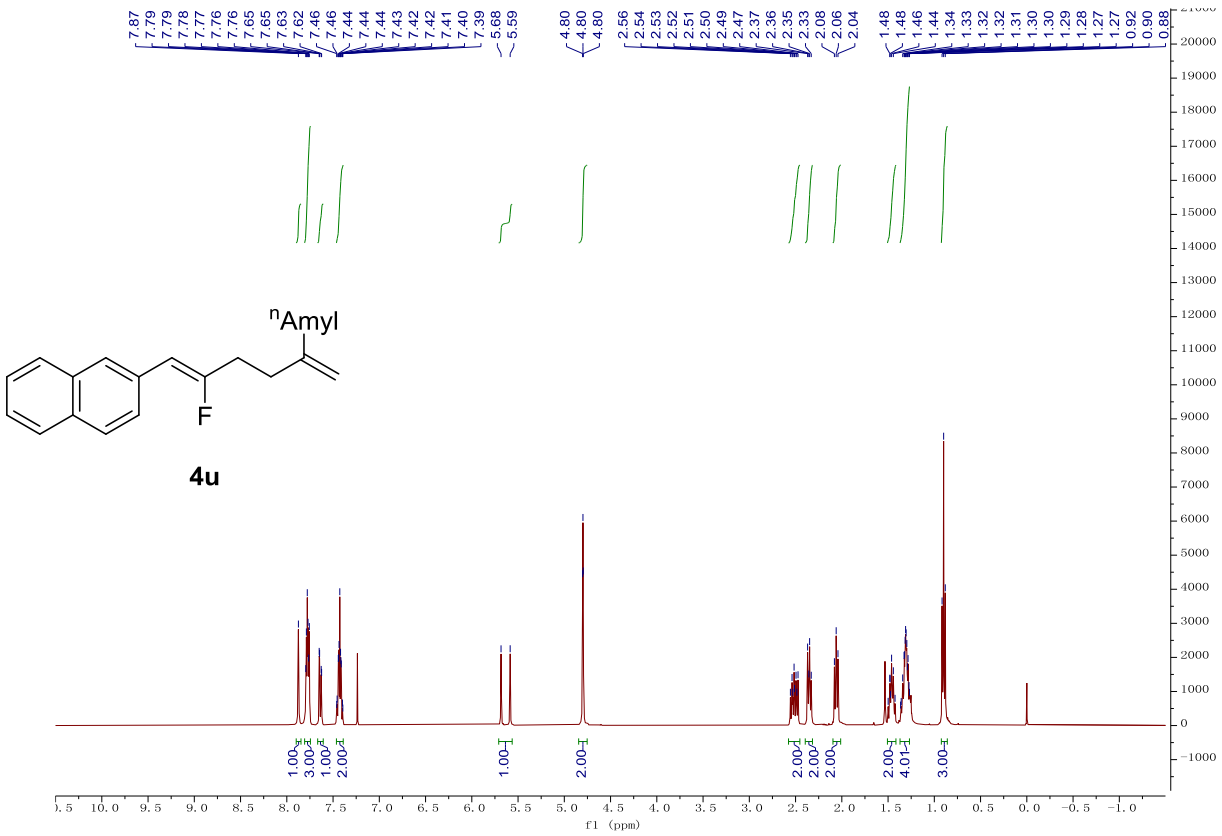
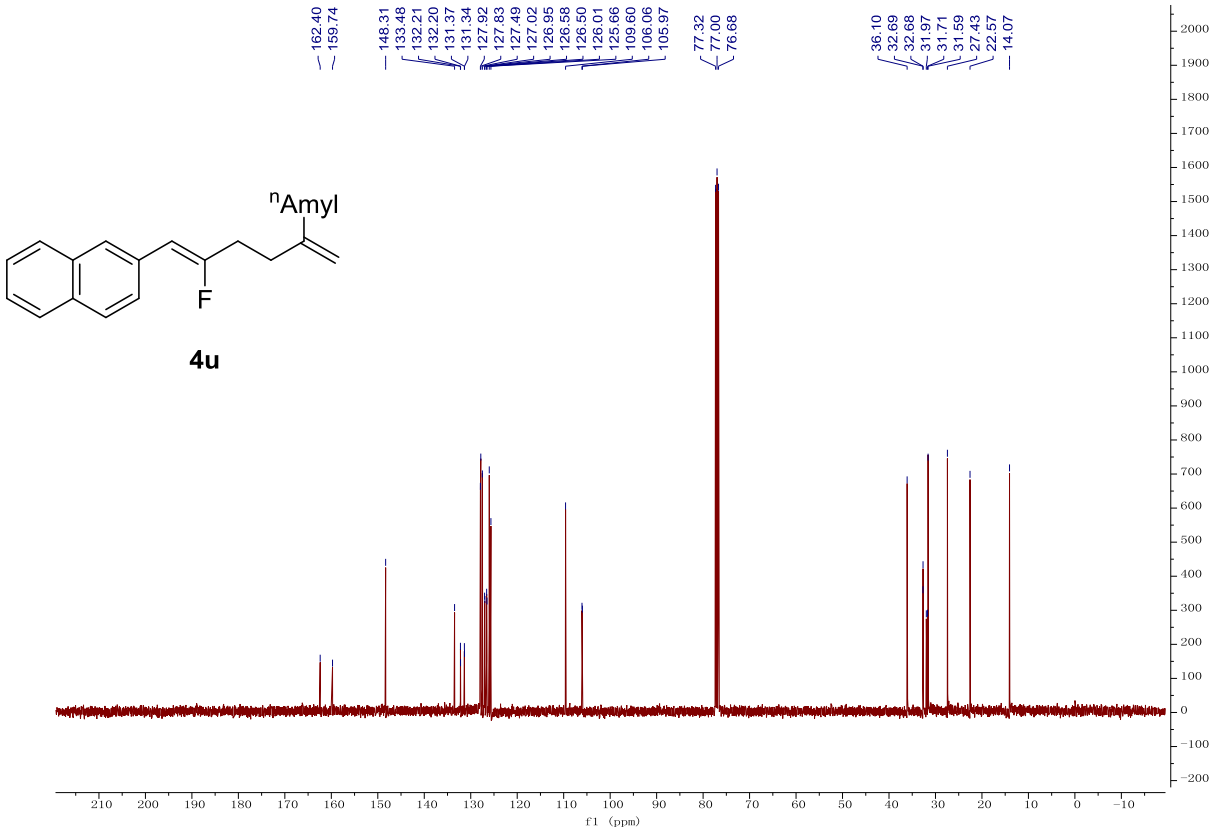
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4t



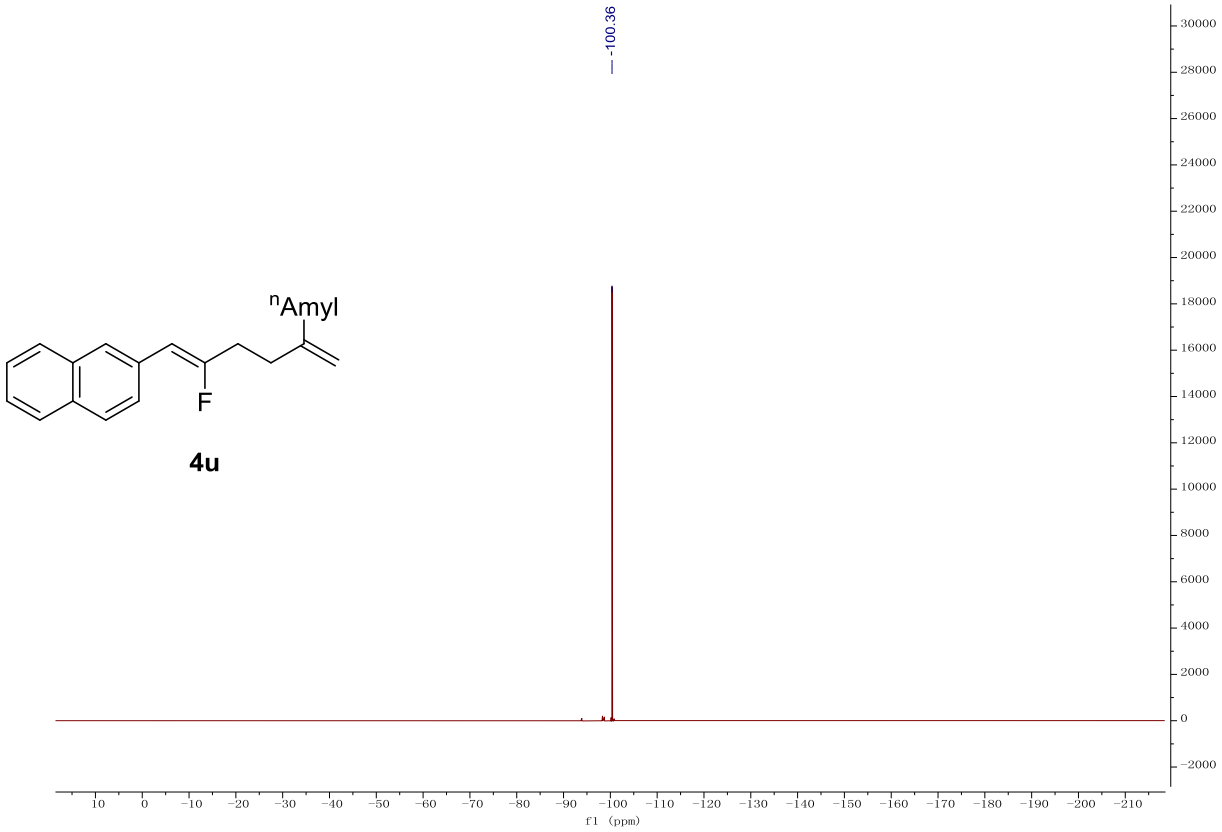
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4u



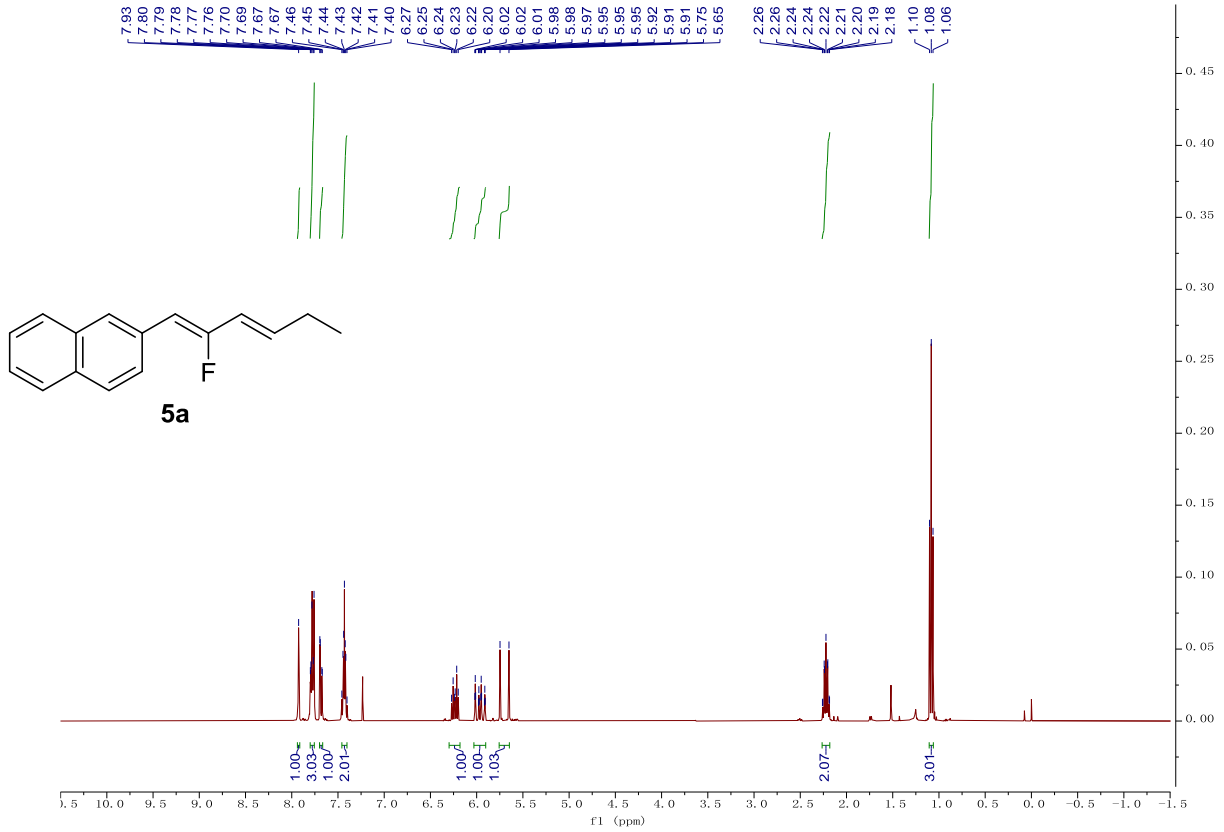
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4u



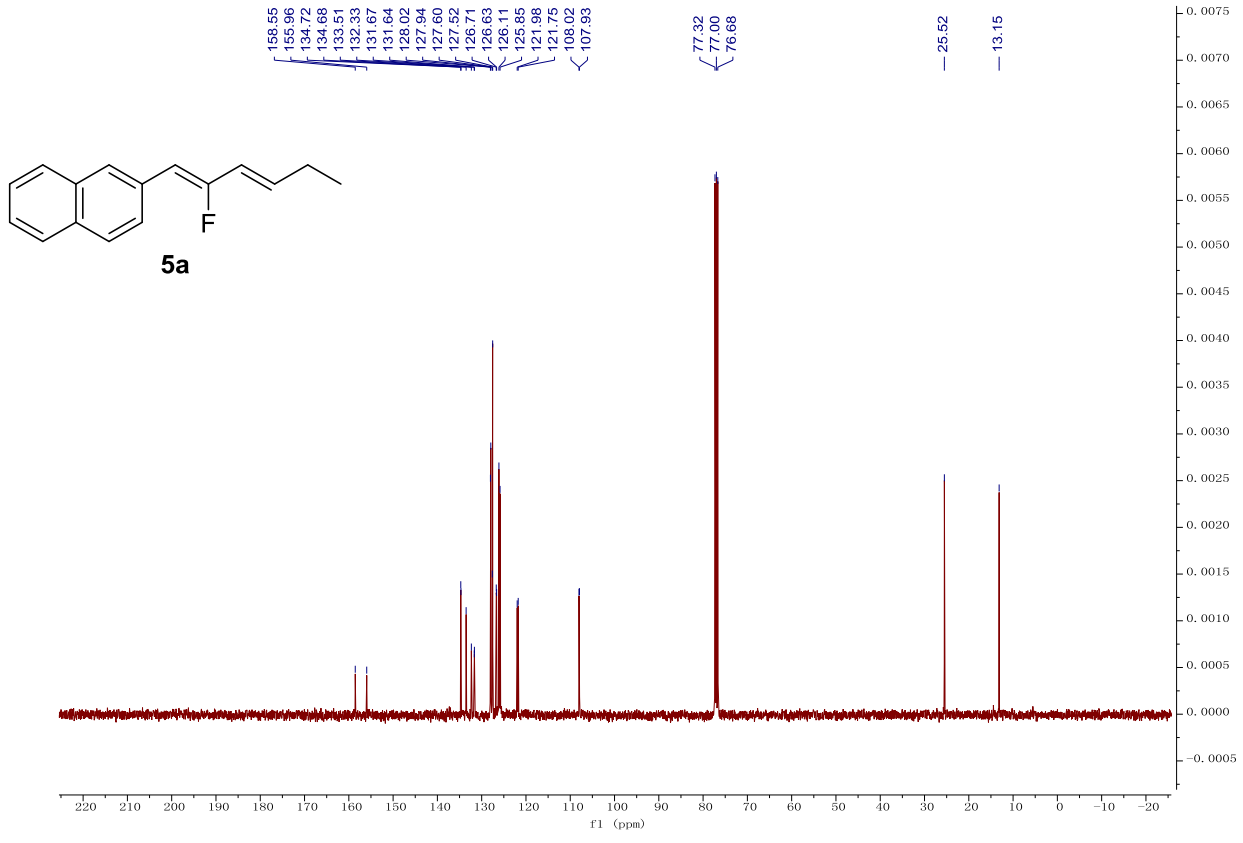
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4u



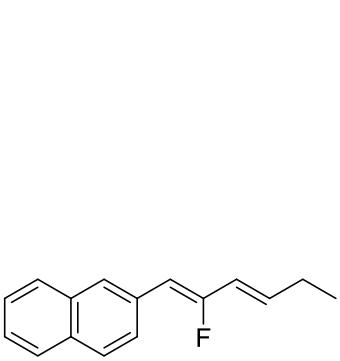
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5a (With JEOL)



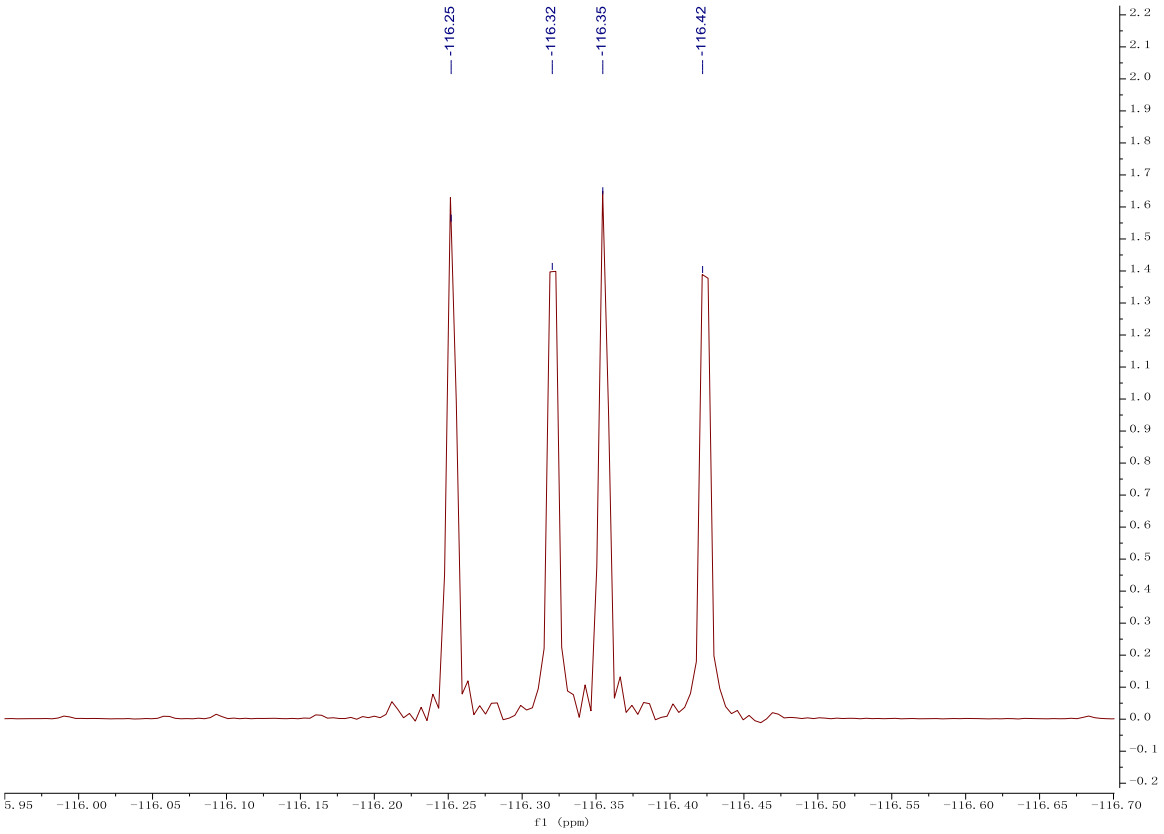
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5a (With JEOL)



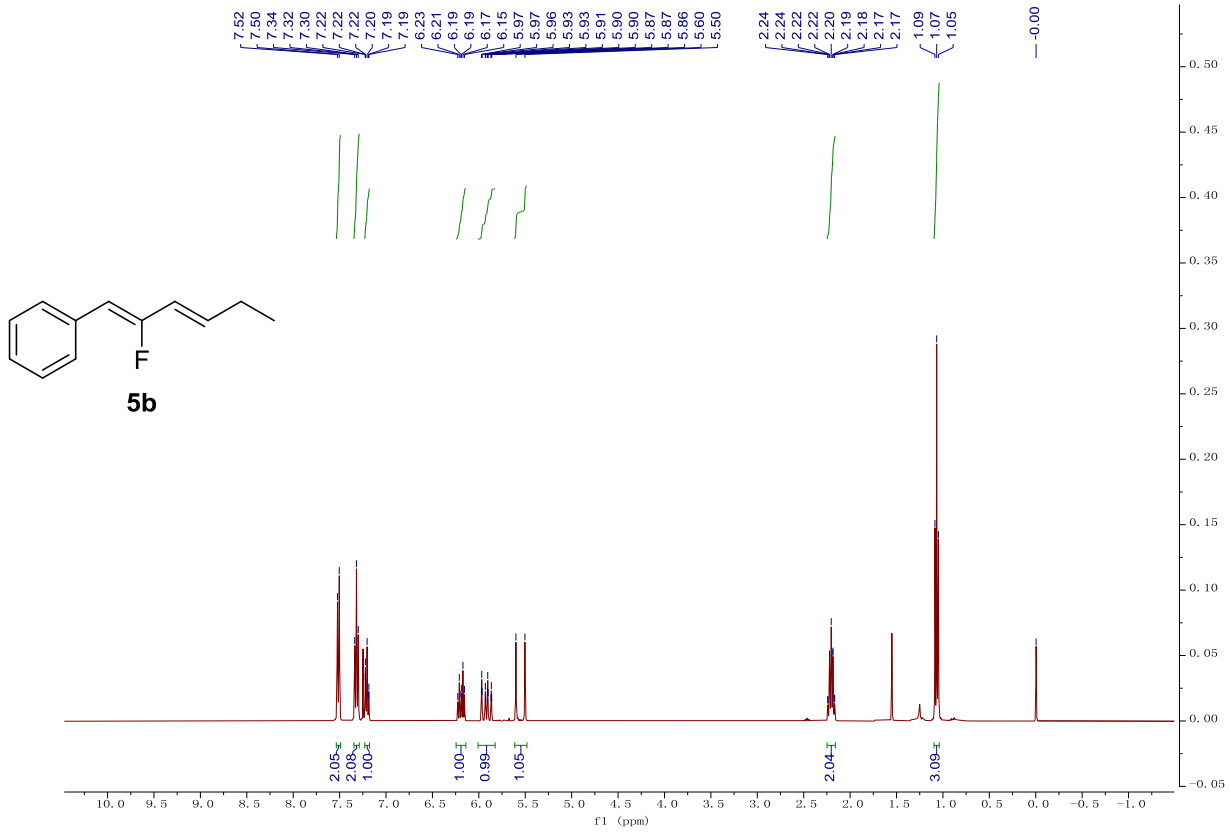
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5a (With JEOL)



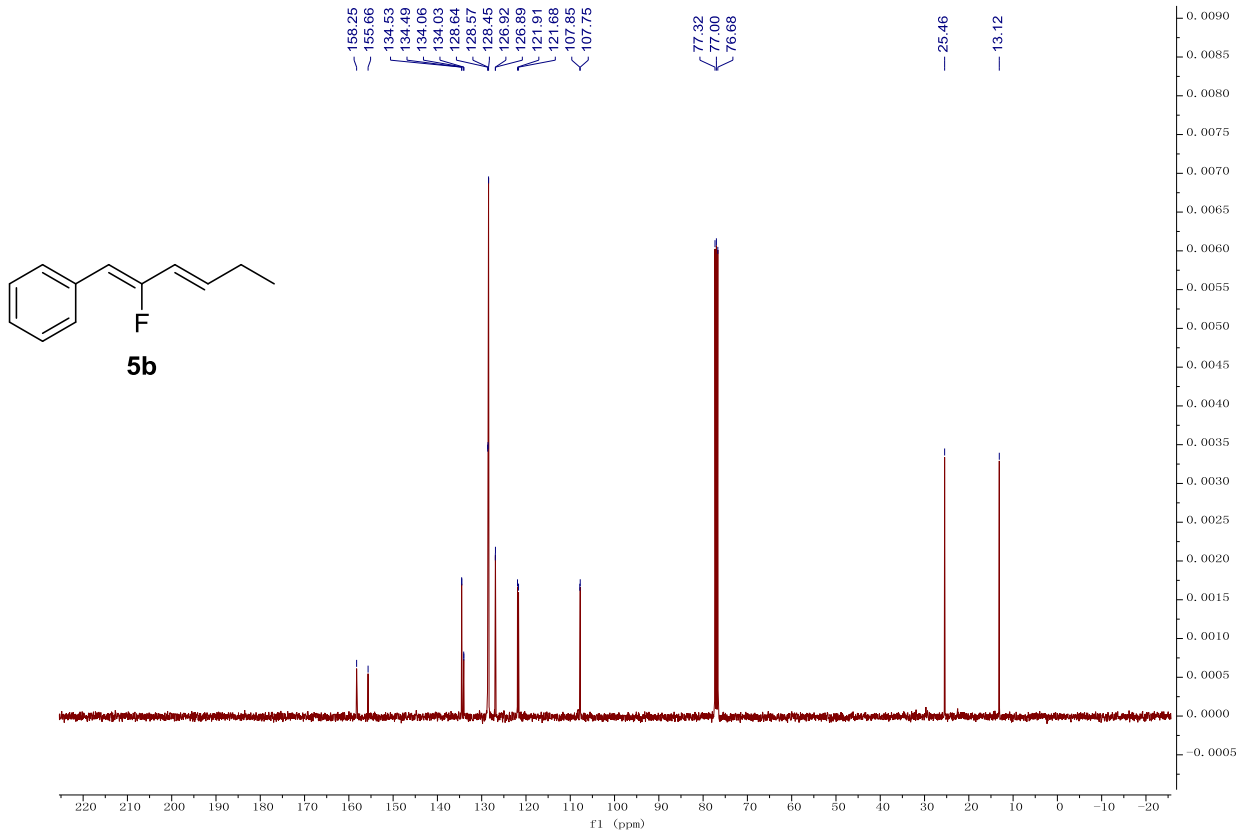
5a



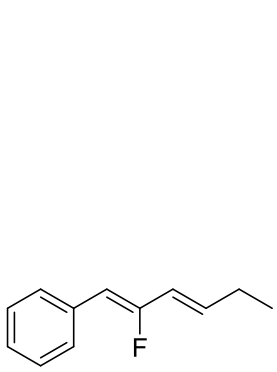
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5b (With JEOL)



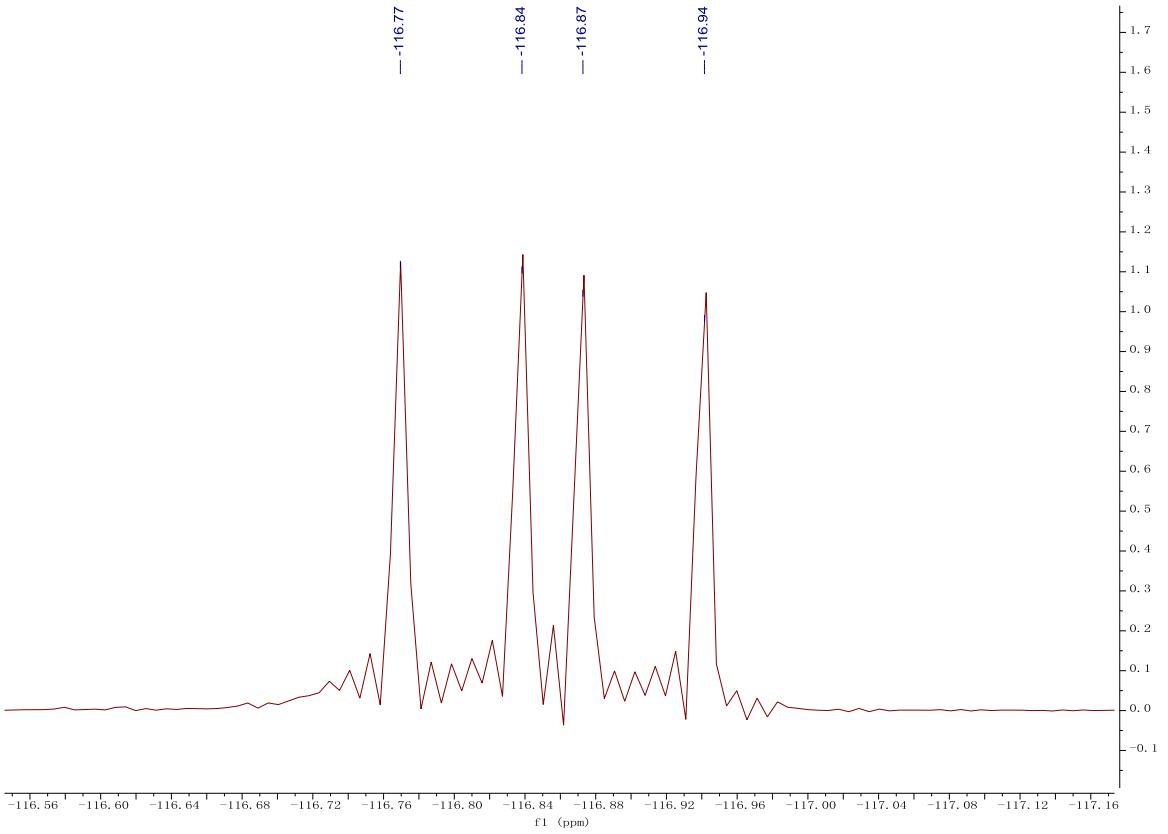
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5b (With JEOL)



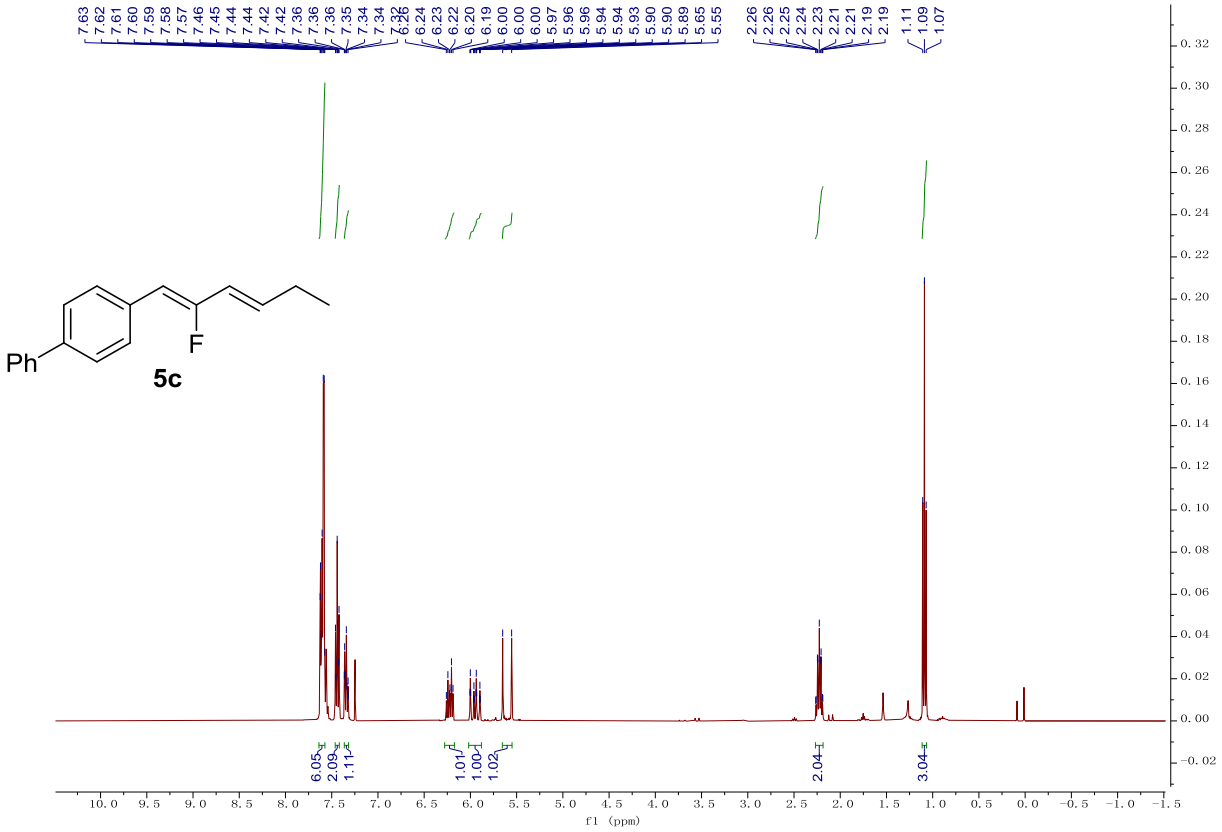
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5b (With JEOL)



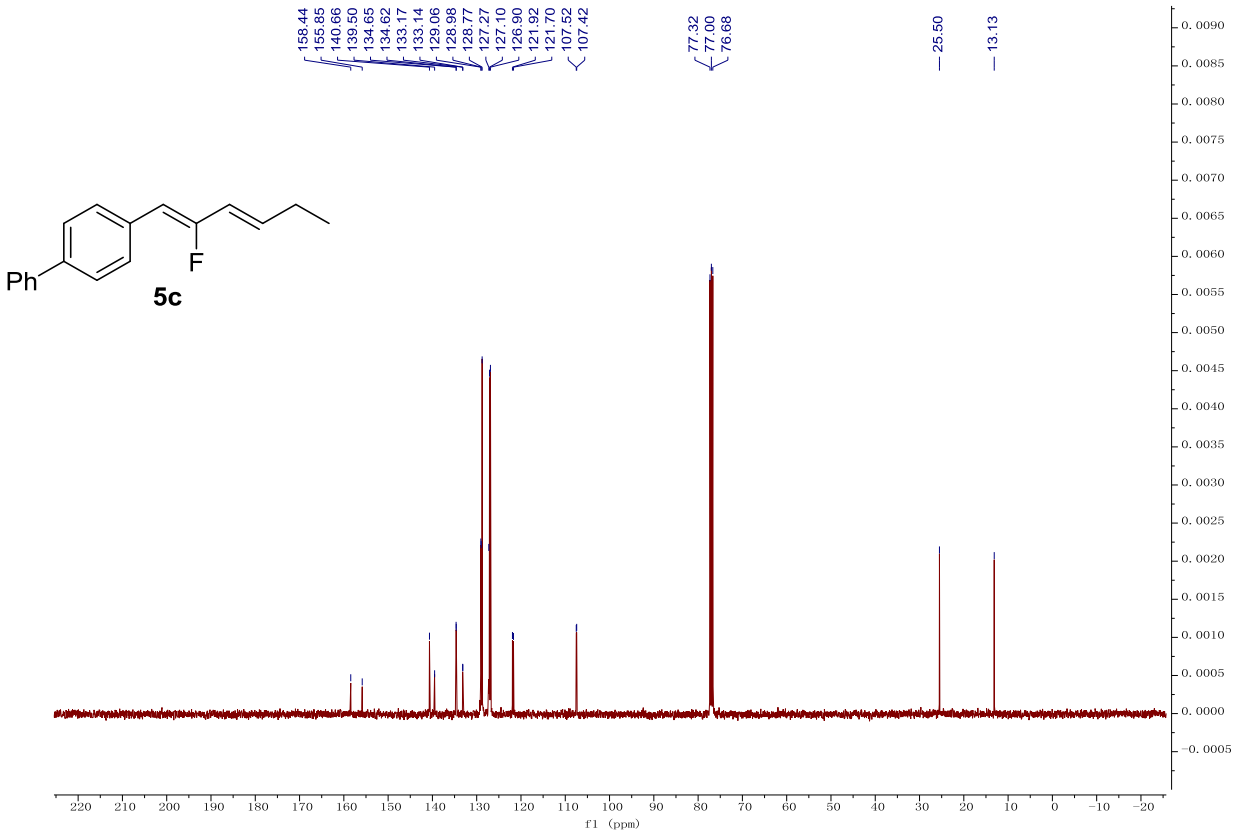
5b



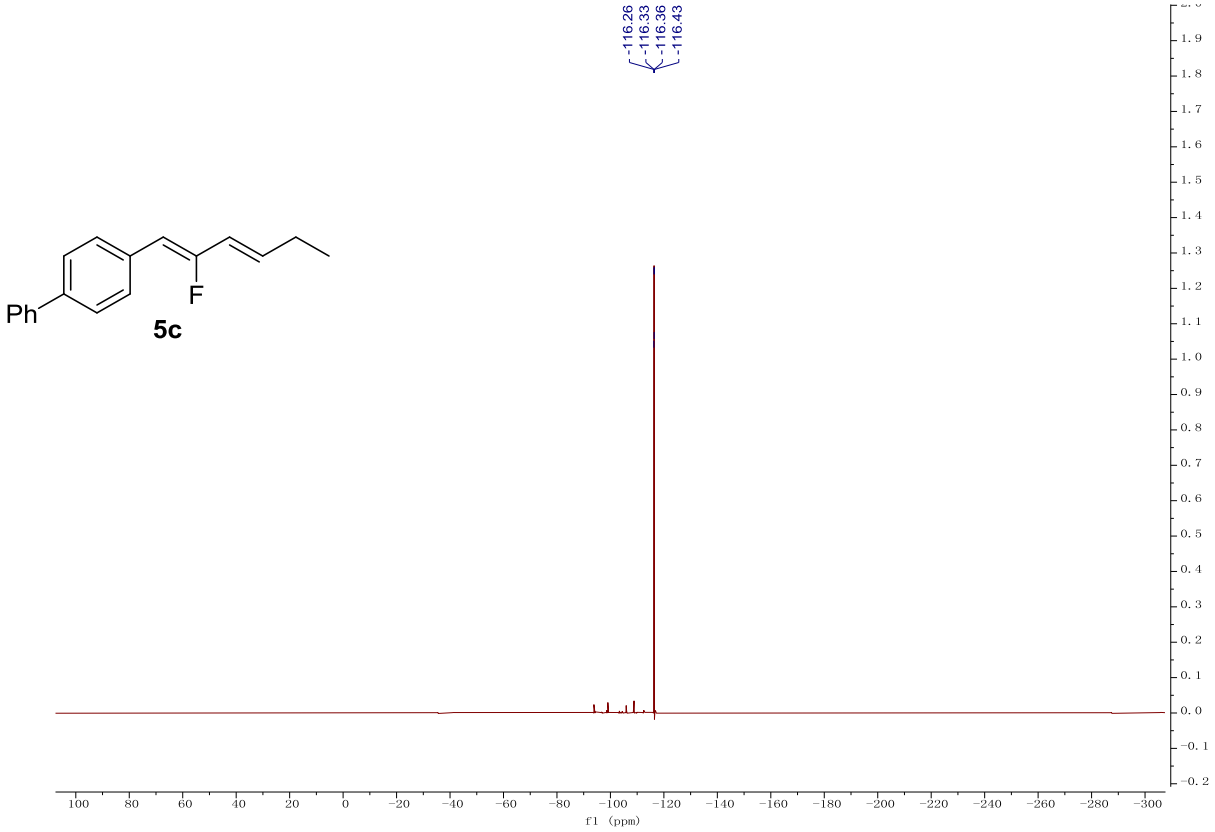
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5c (With JEOL)

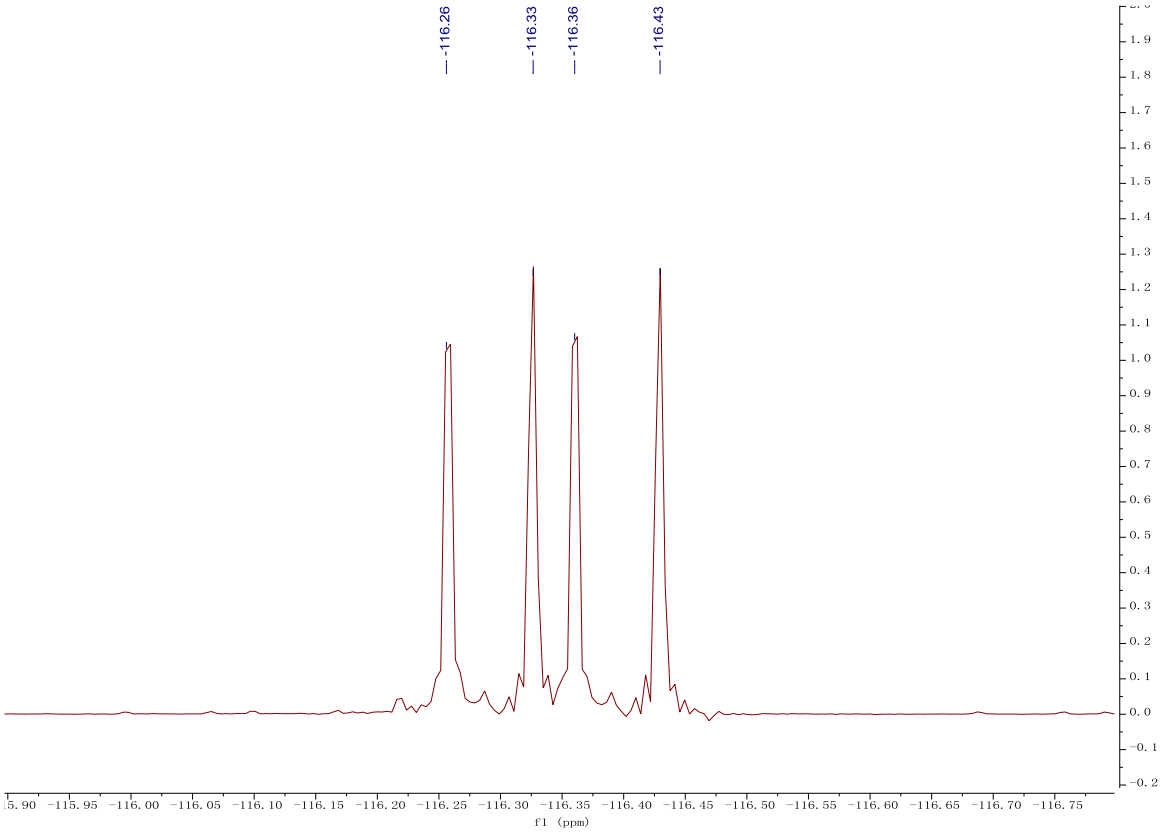


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5c (With JEOL)

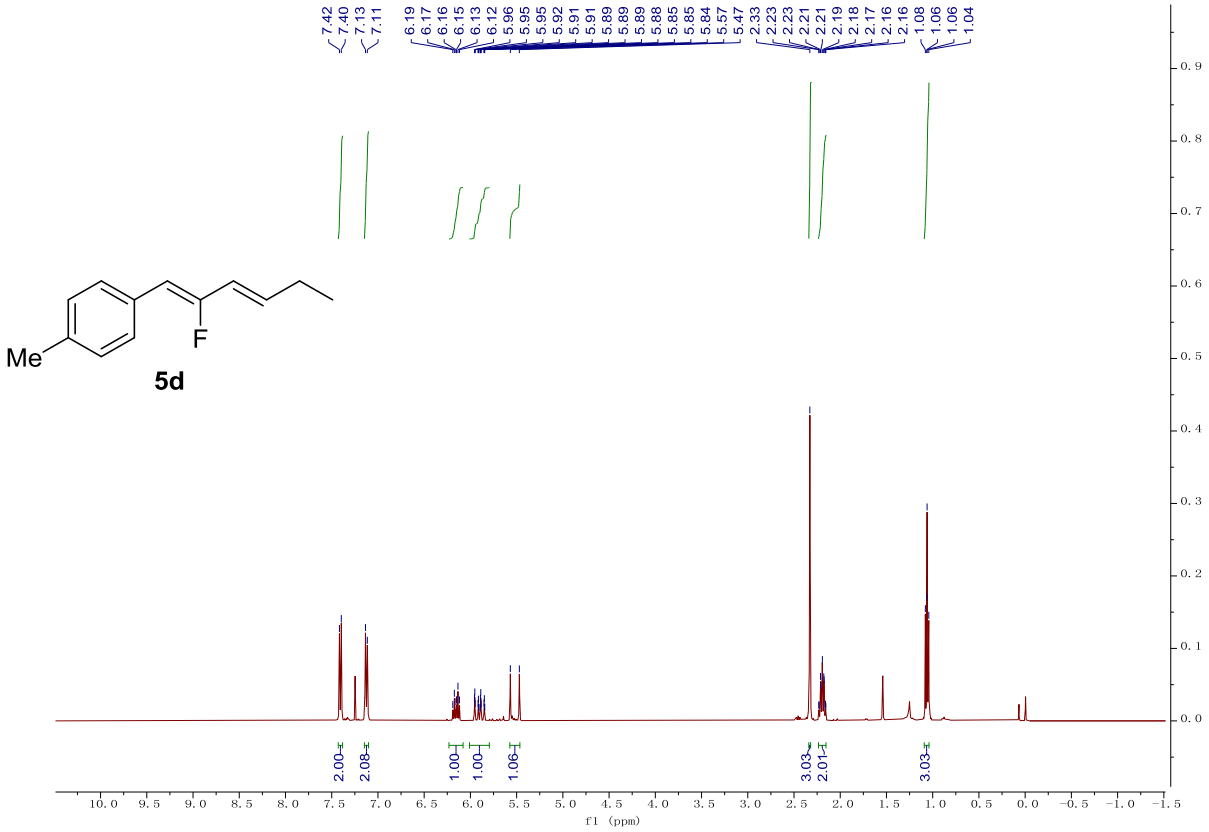


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5c (With JEOL)

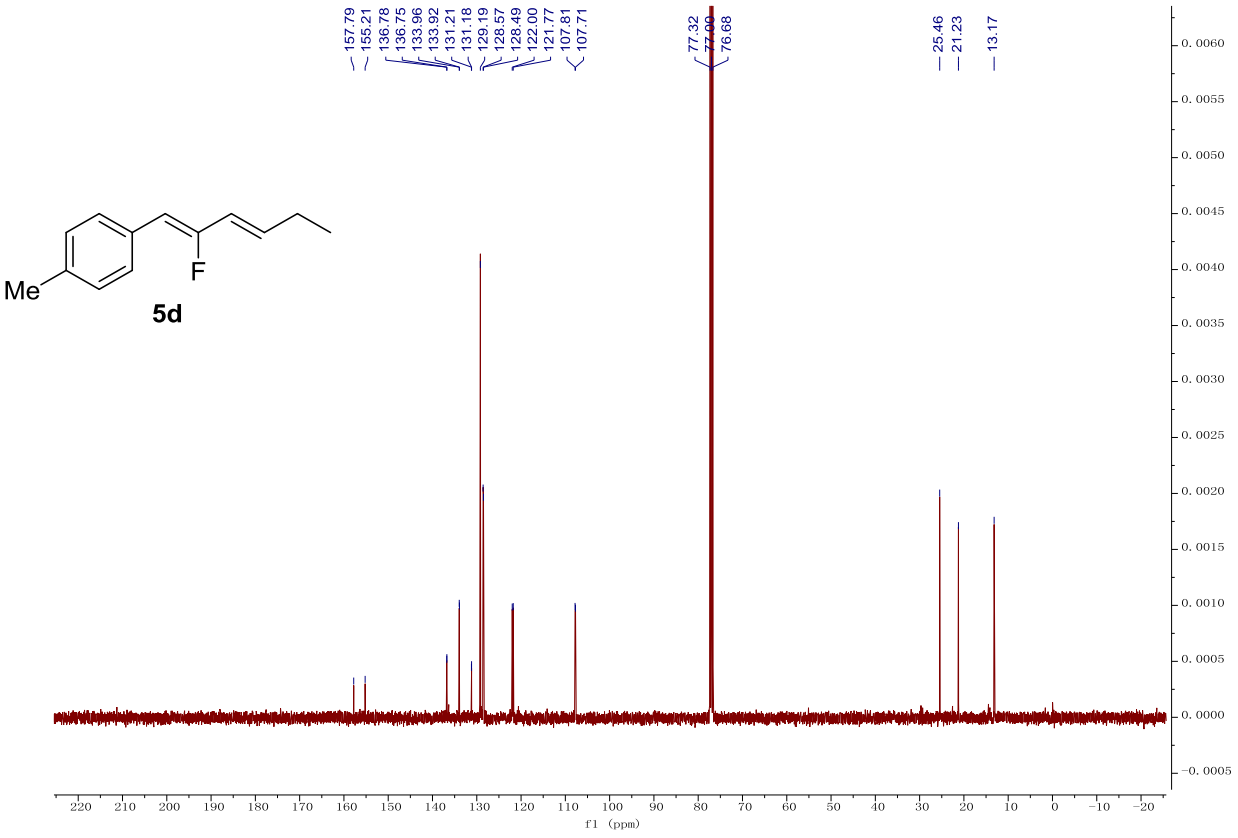




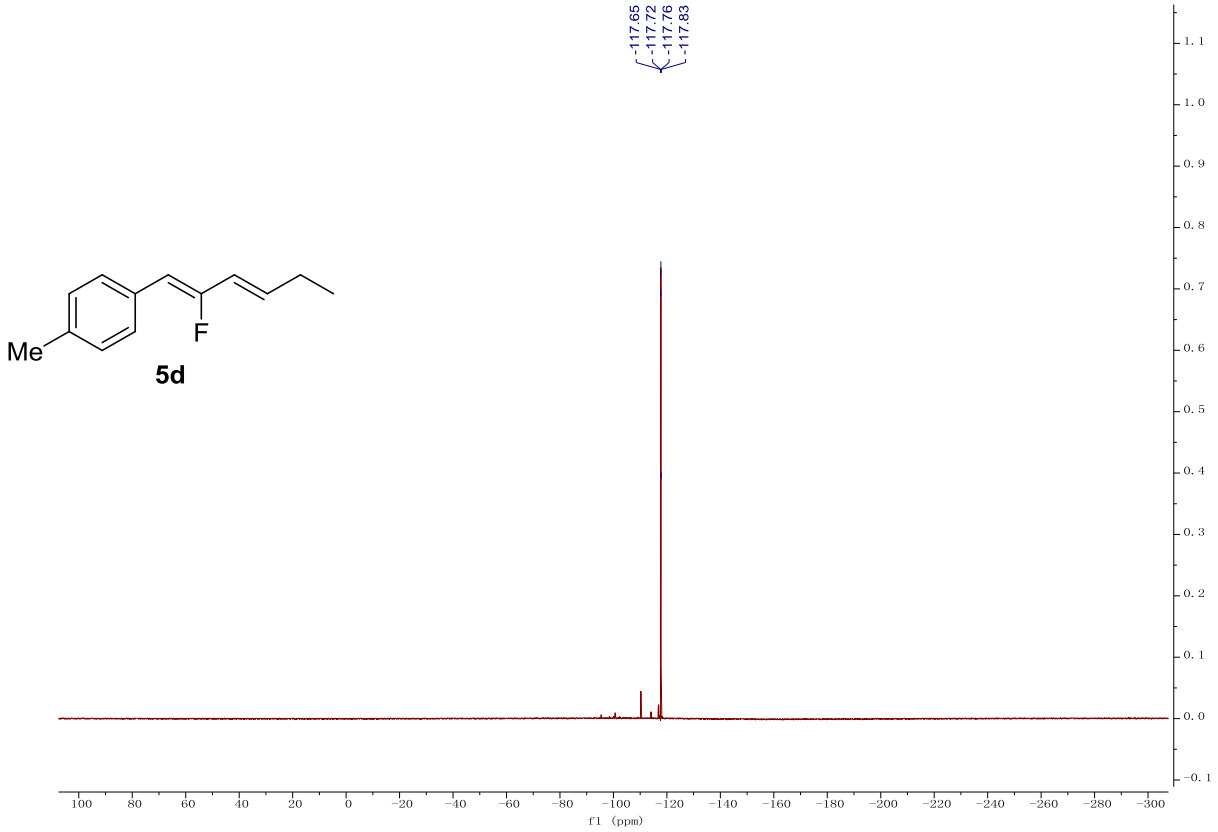
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5d (With JEOL)

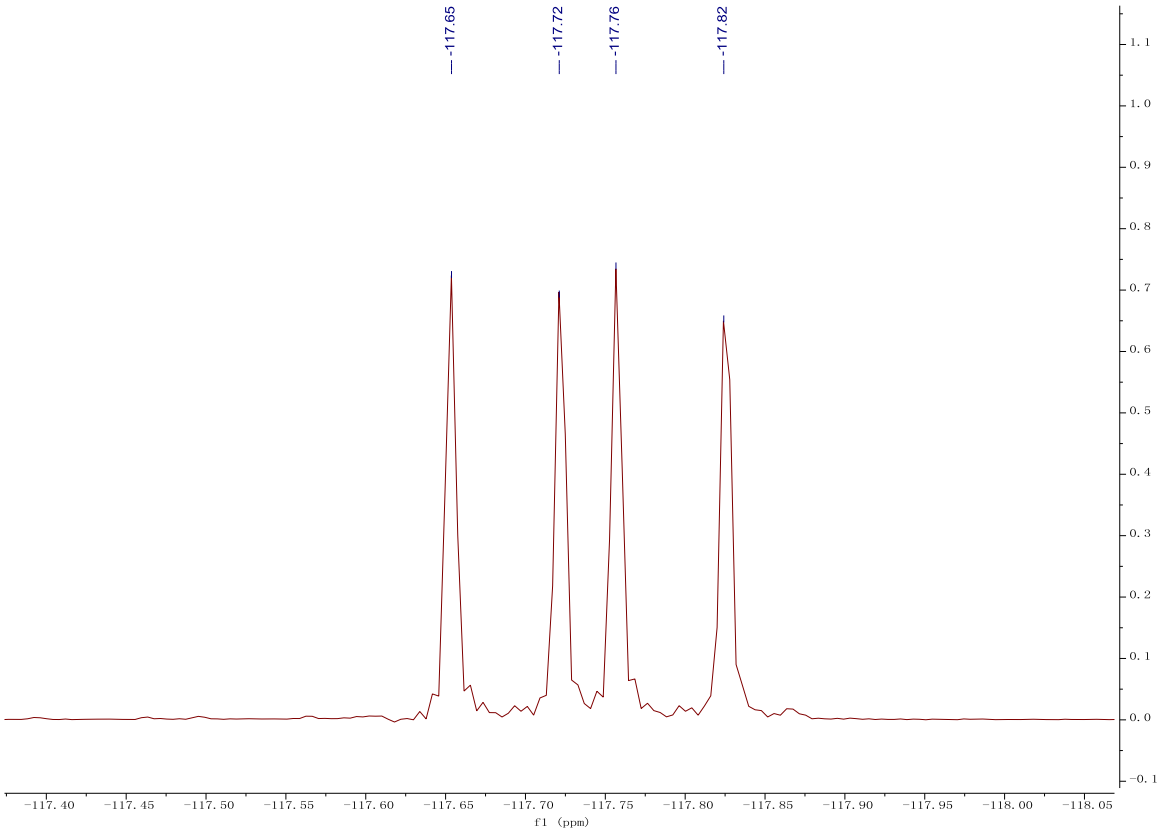


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5d (With JEOL)

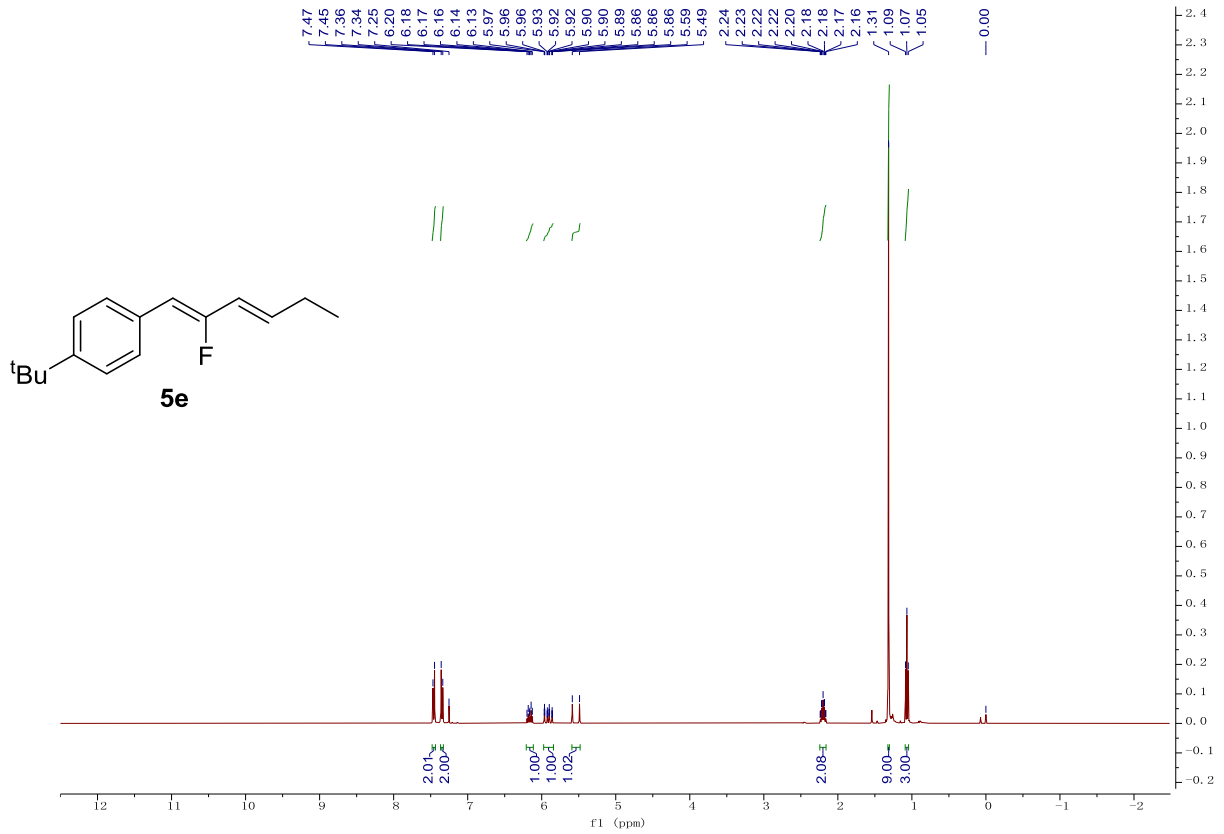


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5d (With JEOL)

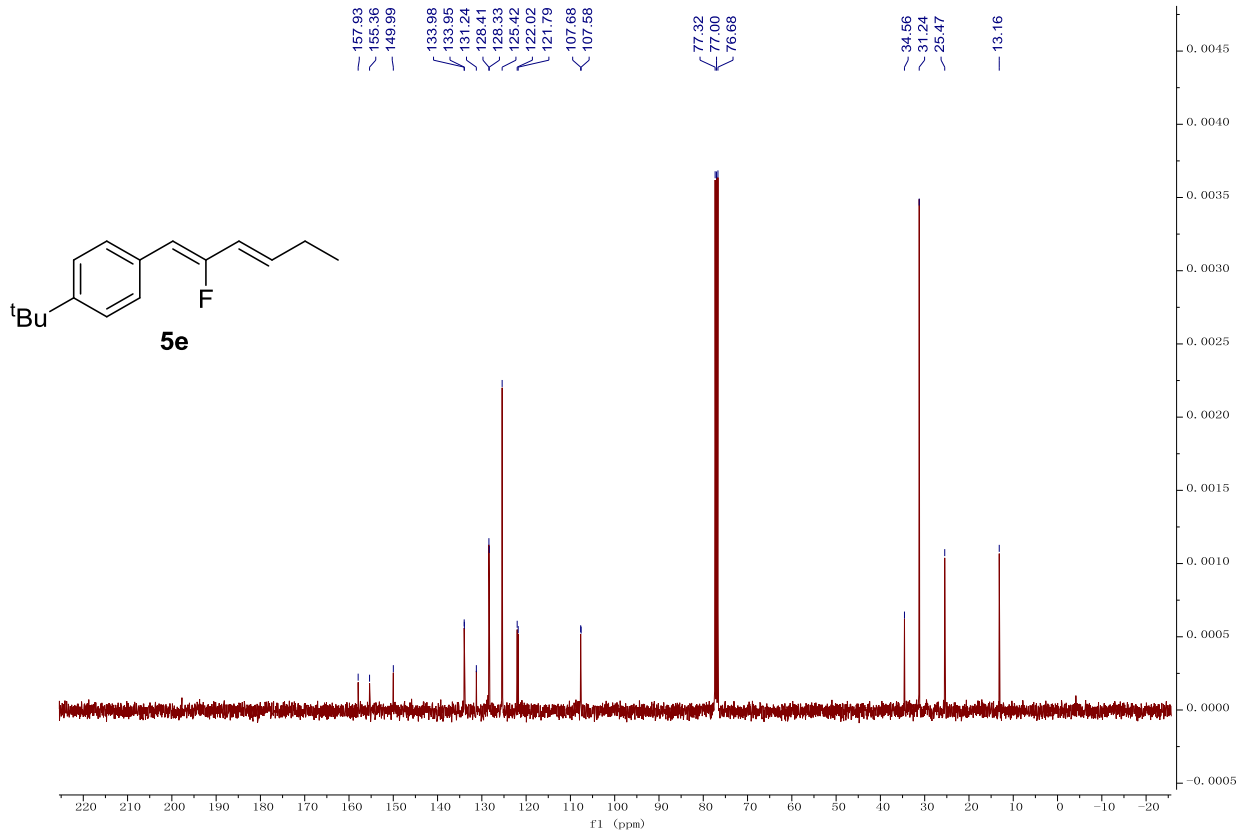




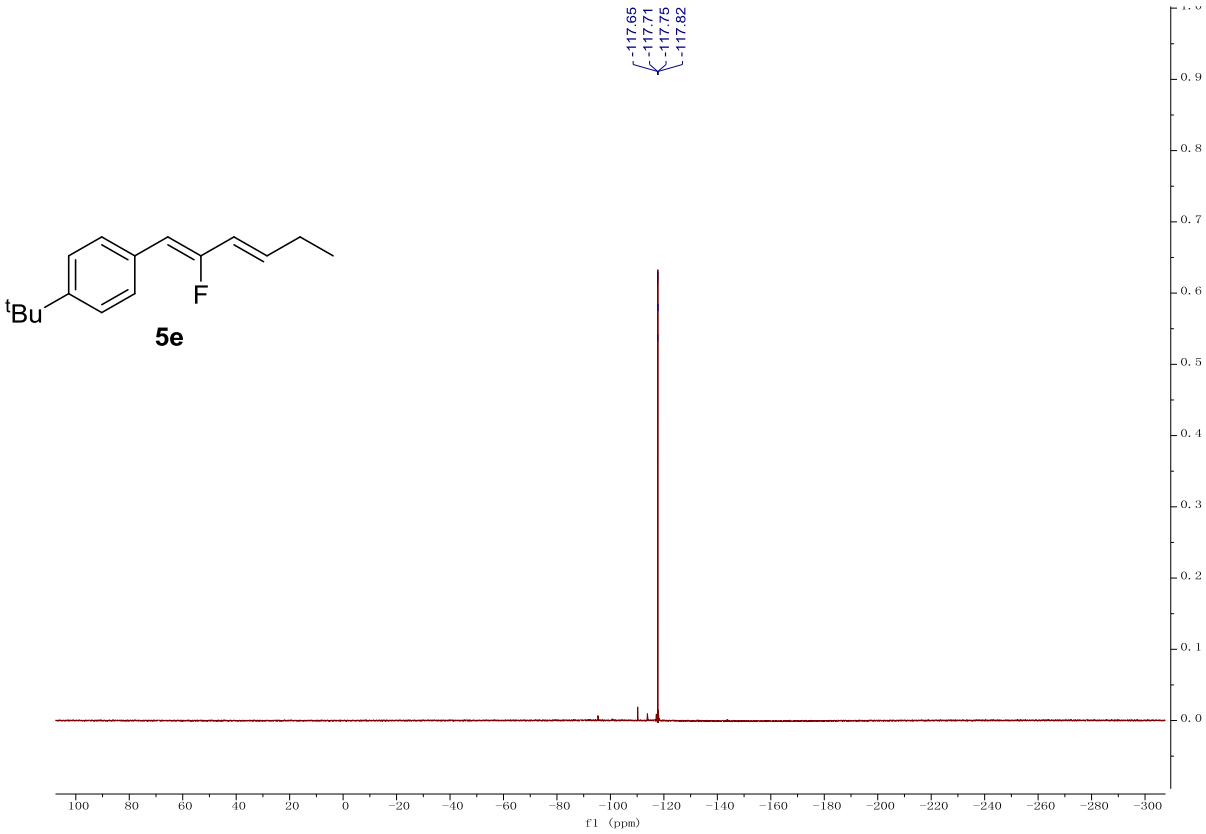
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5e (With JEOL)

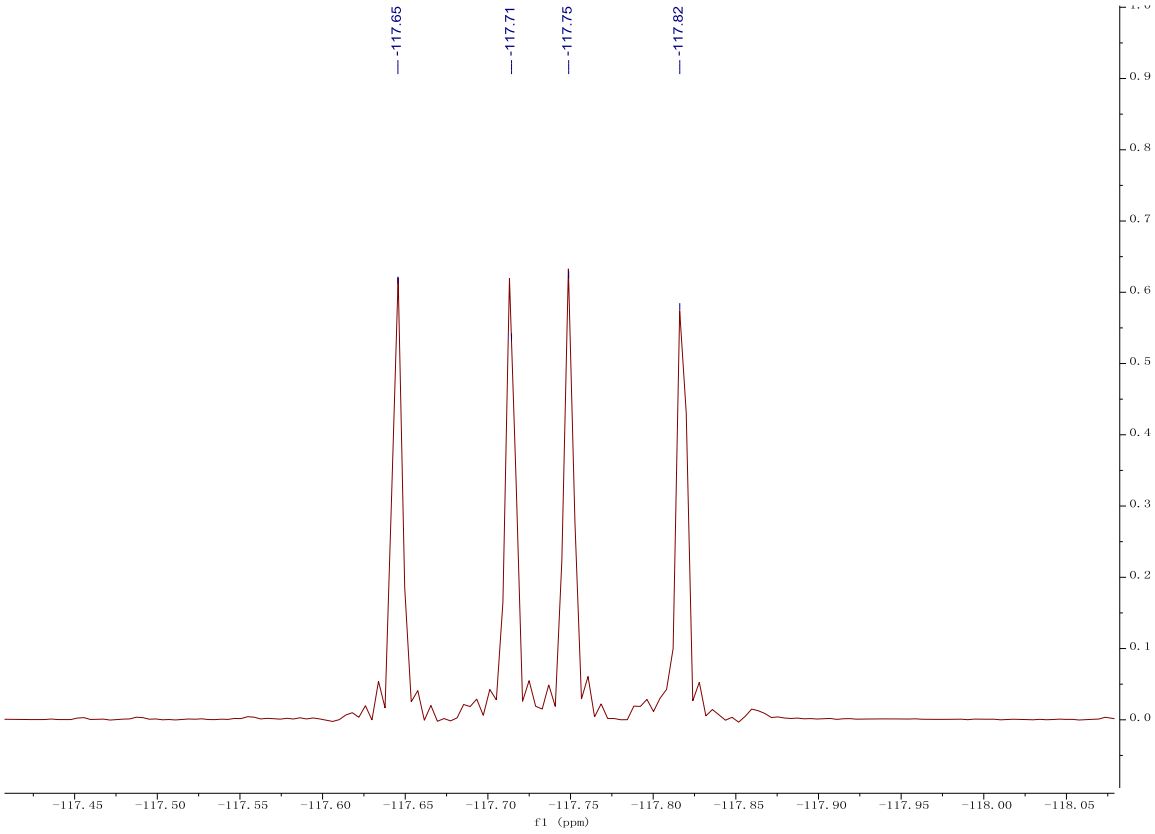


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5e (With JEOL)

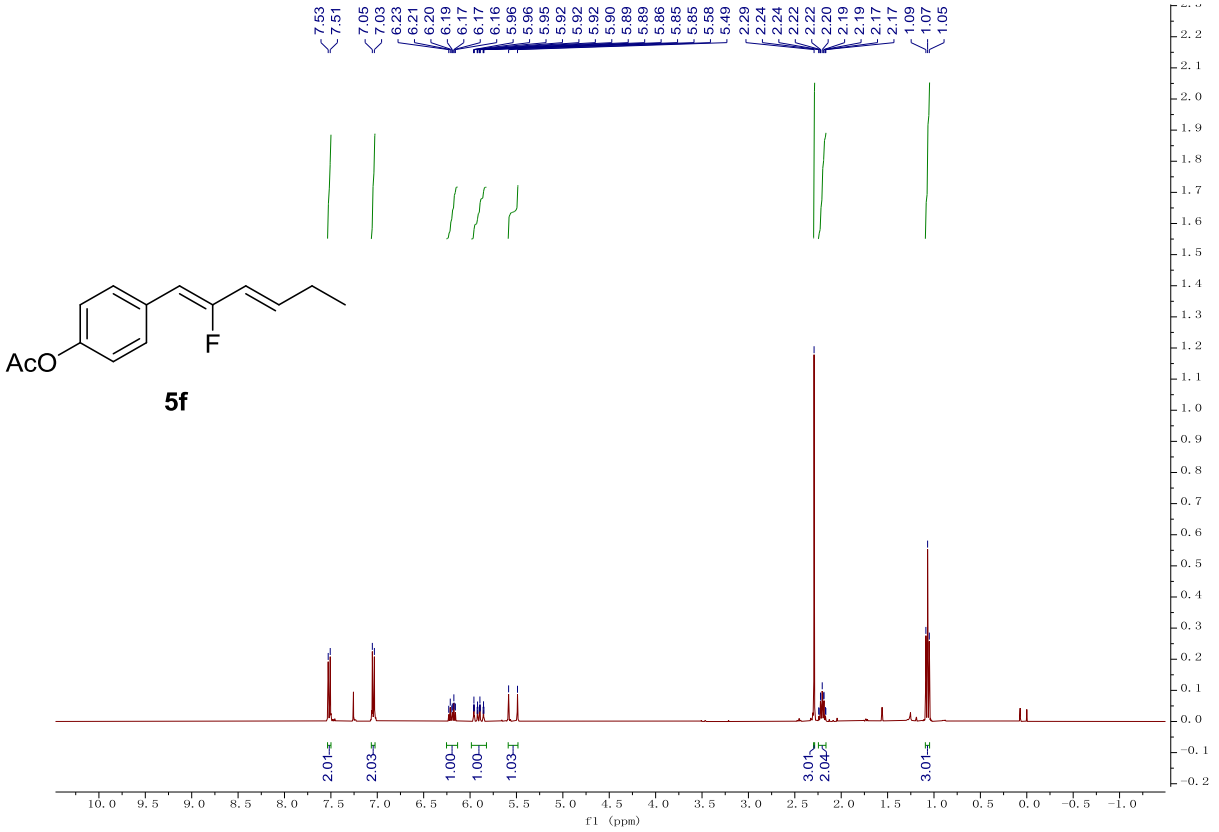


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5e (With JEOL)

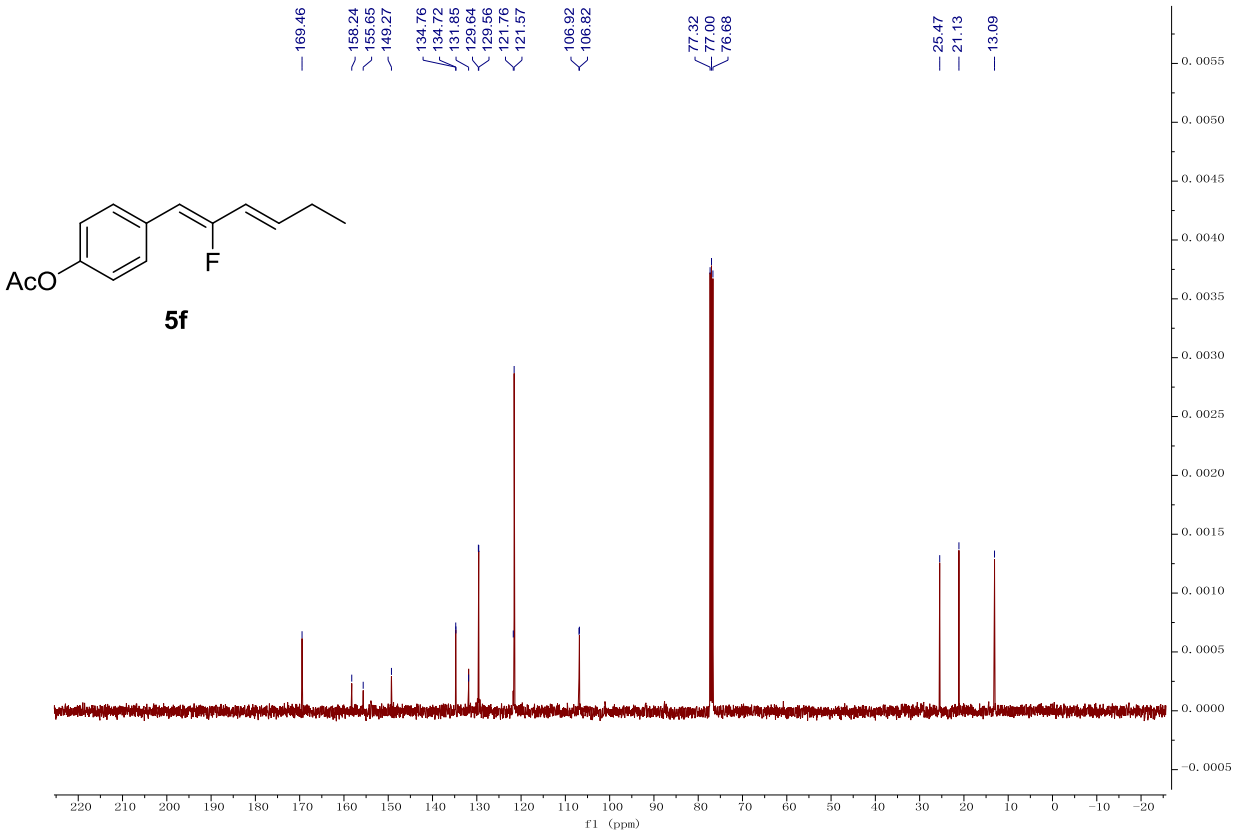




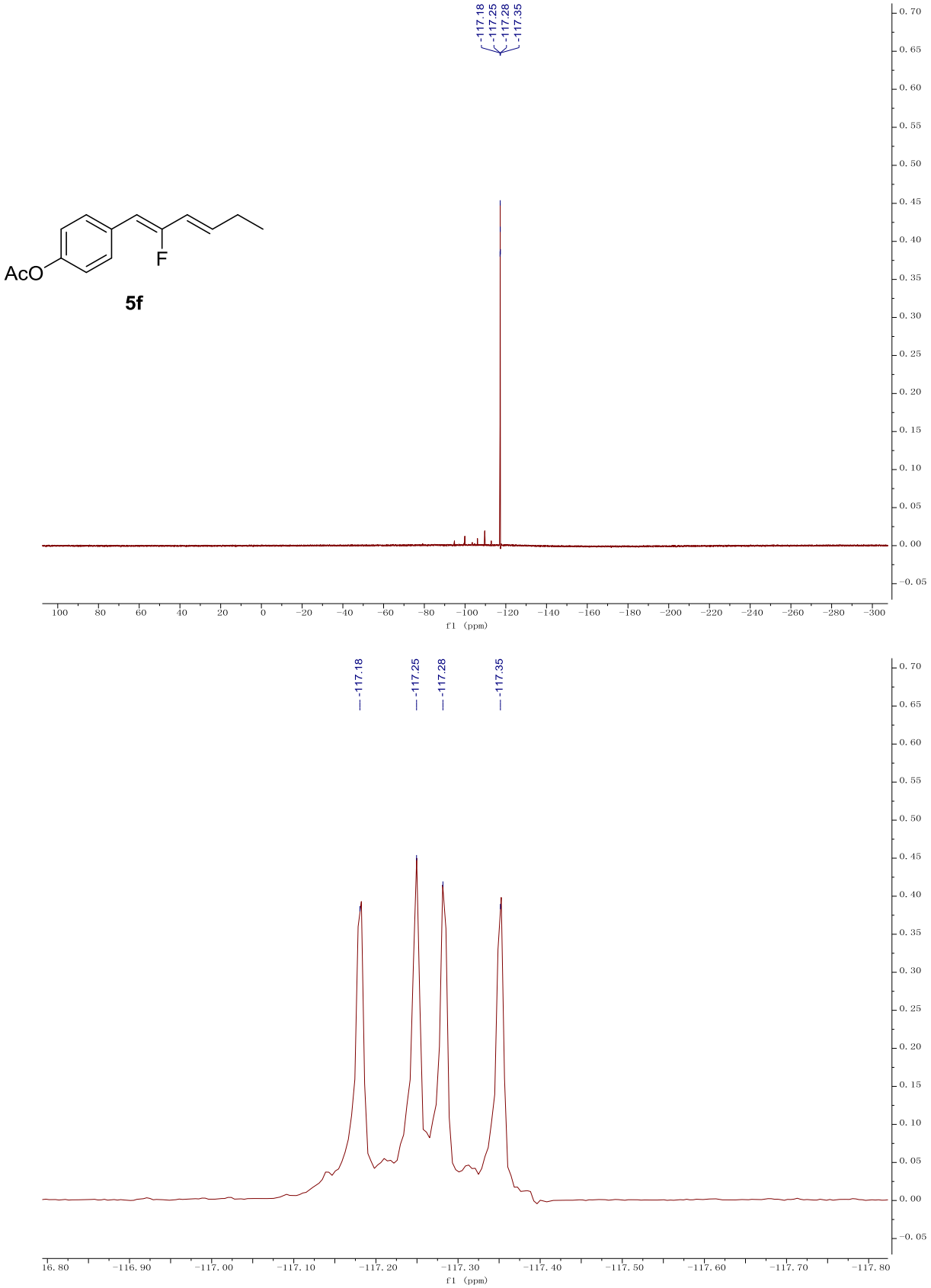
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5f (With JEOL)



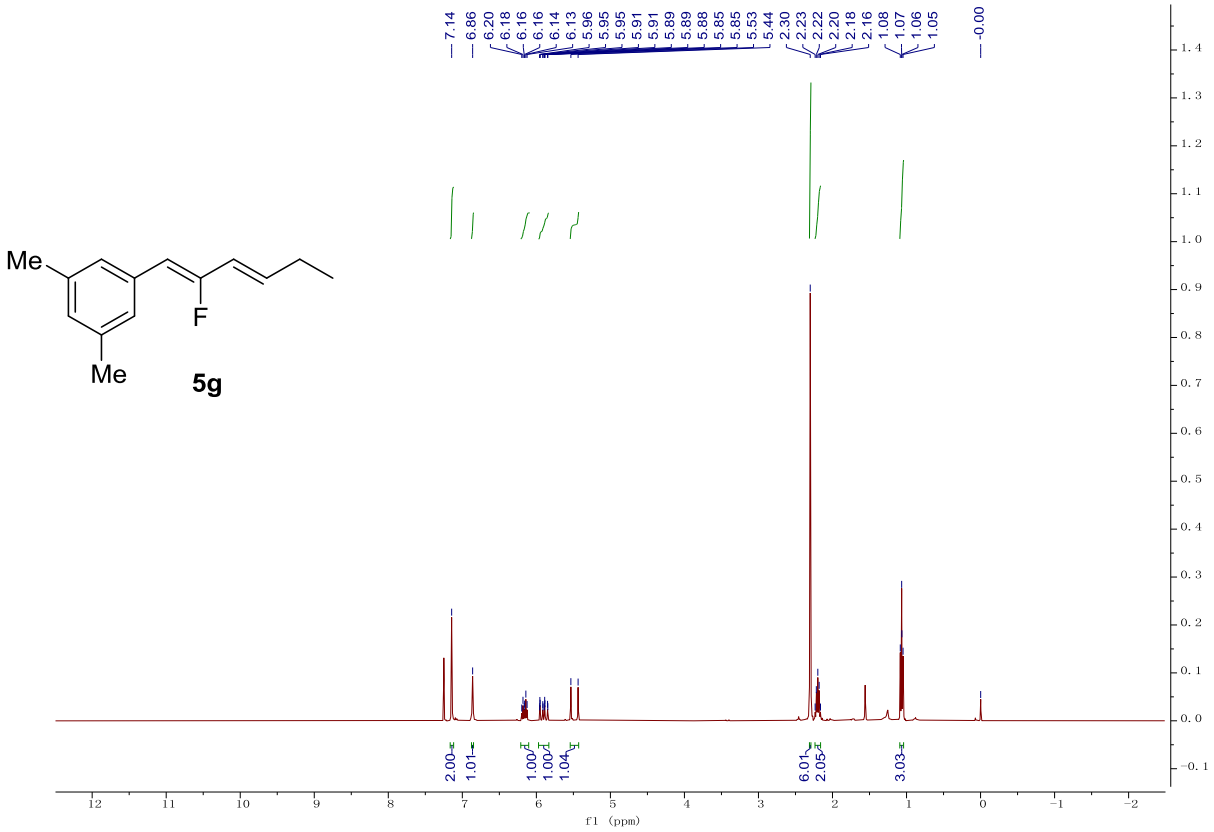
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5f (With JEOL)



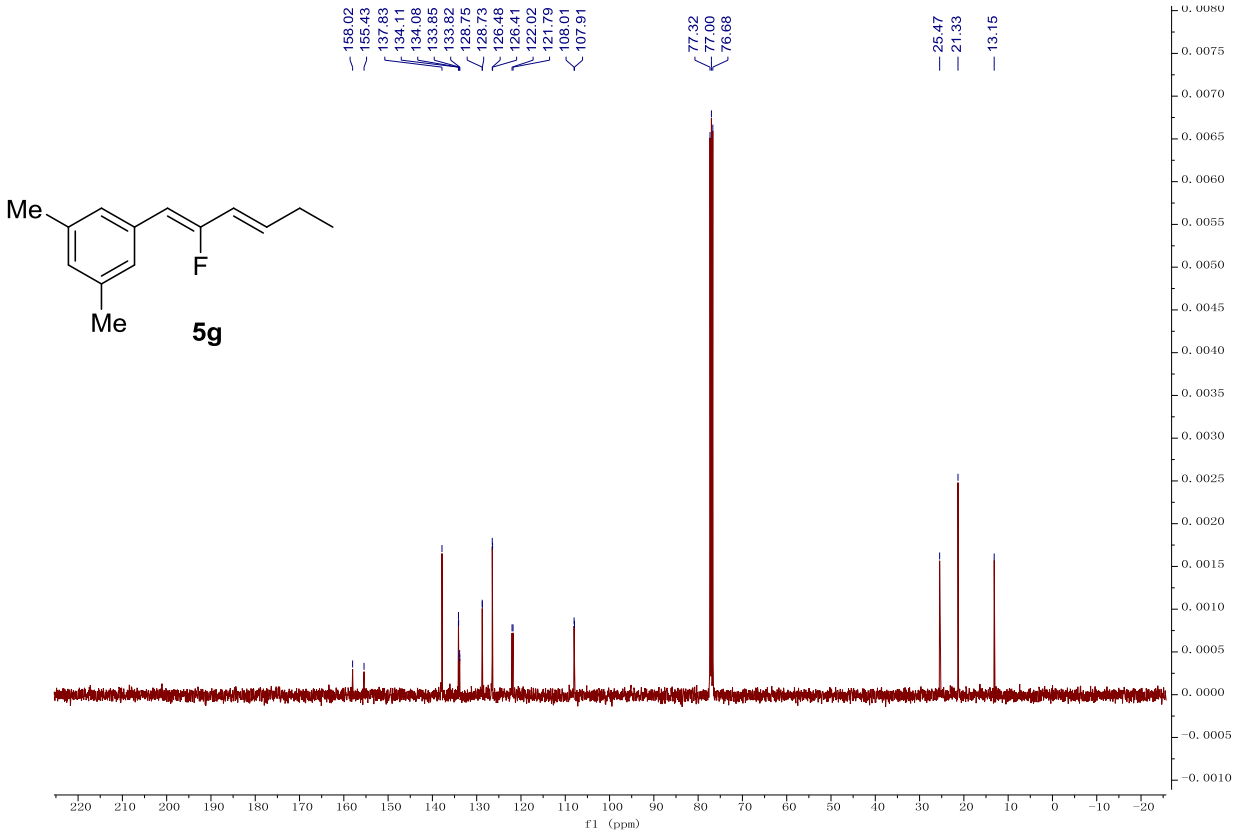
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5f (With JEOL)



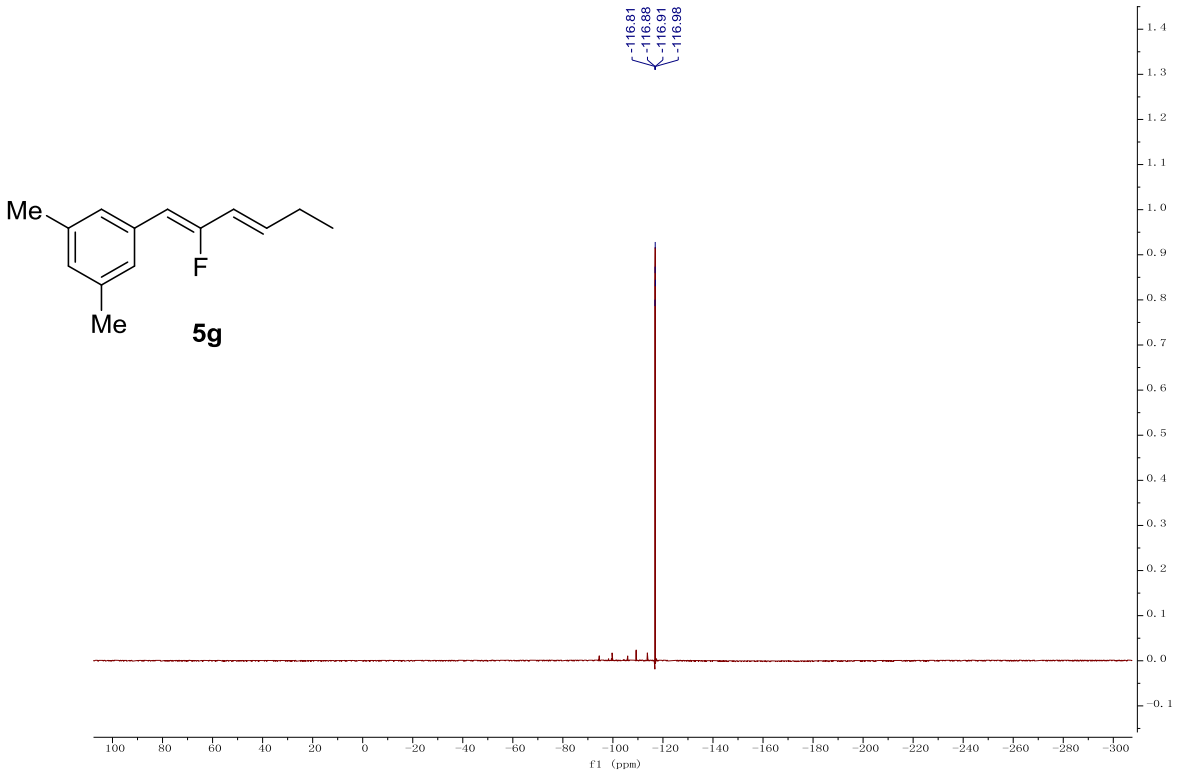
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5g (With JEOL)

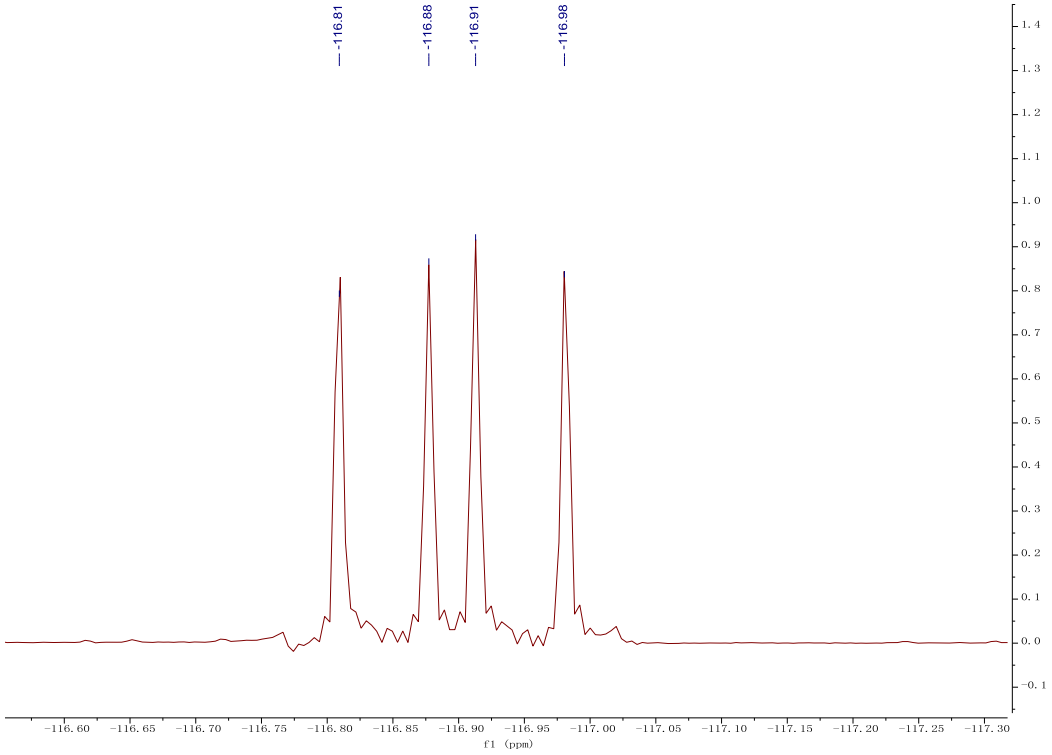


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5g (With JEOL)

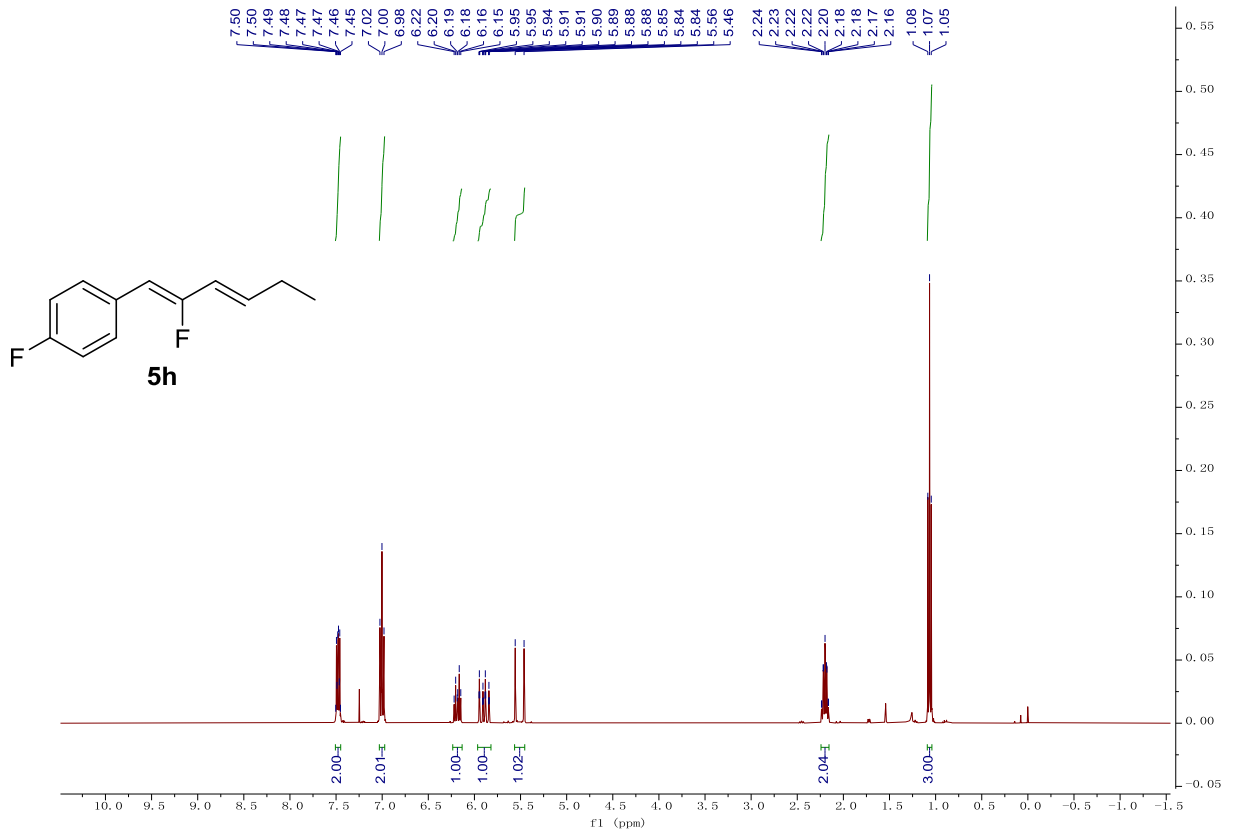


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5g (With JEOL)

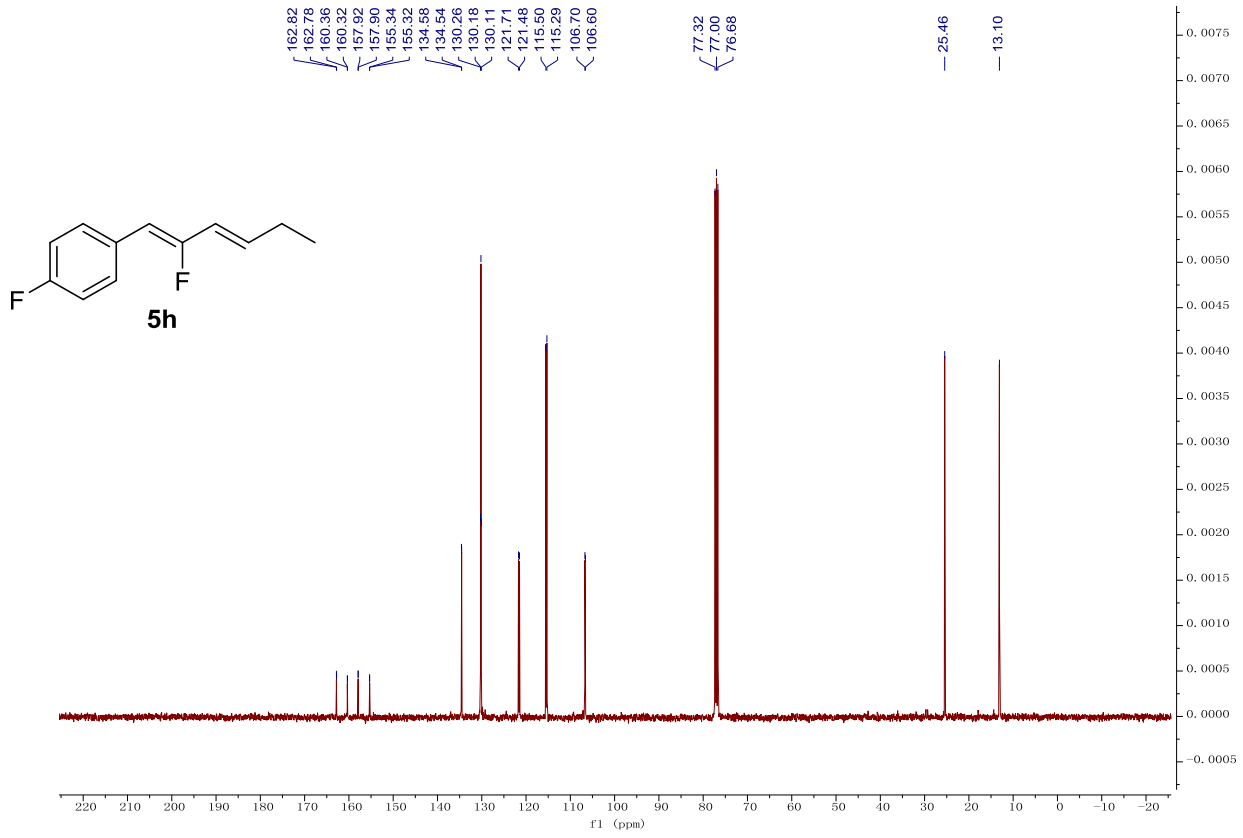




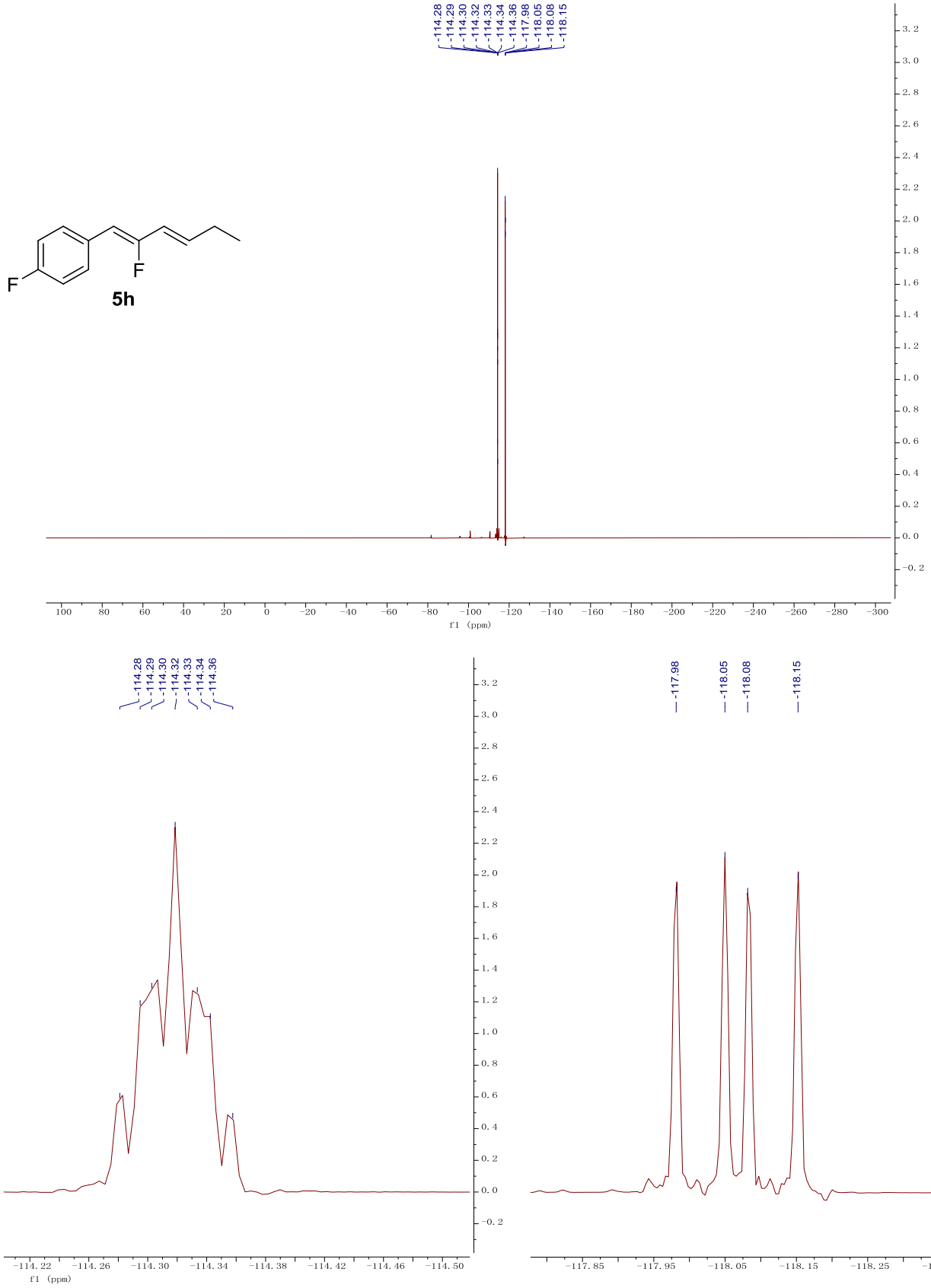
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5h (With JEOL)



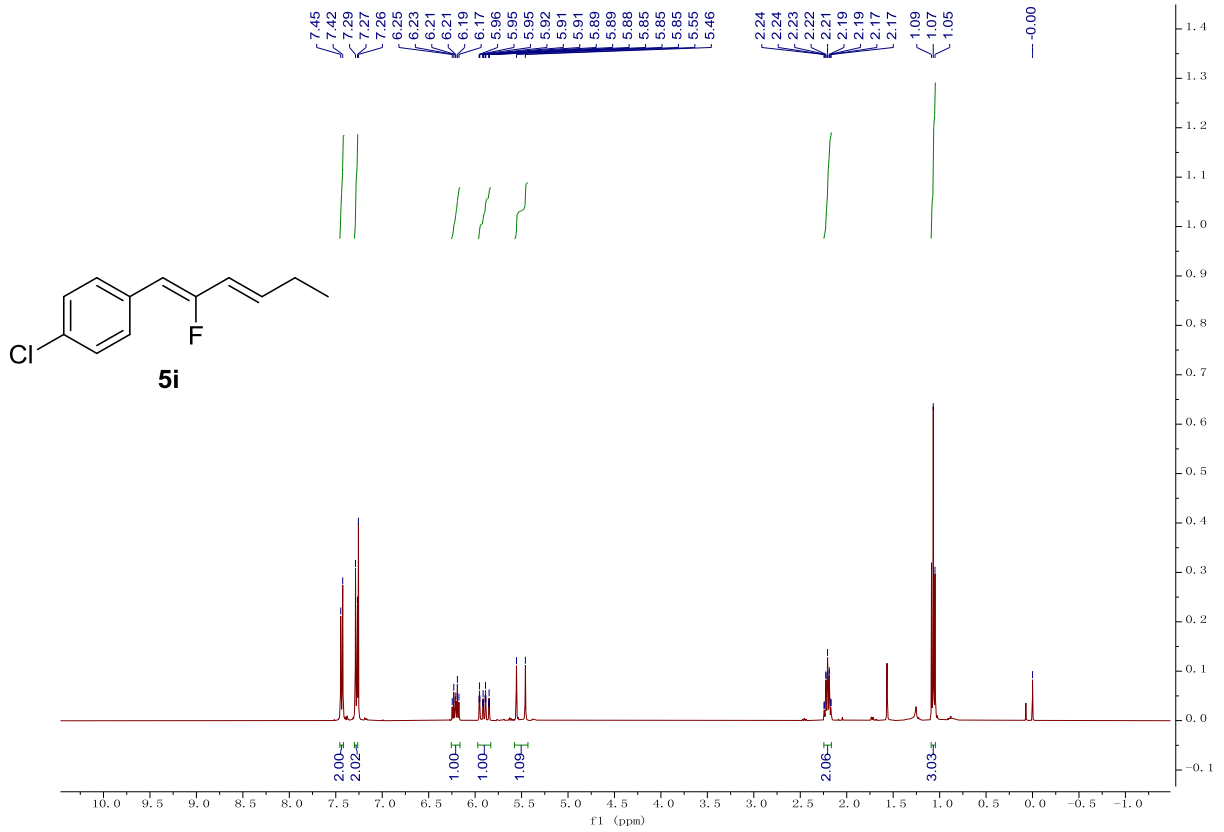
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5h (With JEOL)



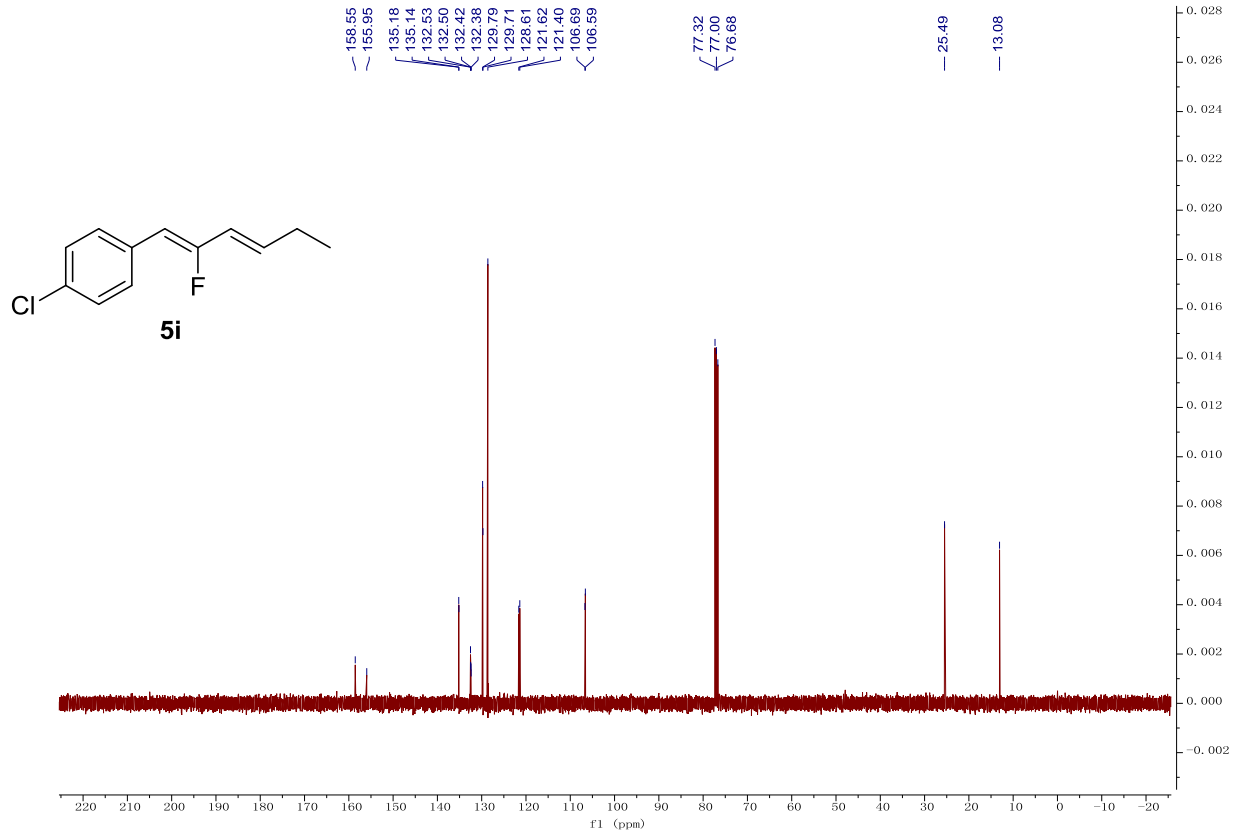
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5h (With JEOL)



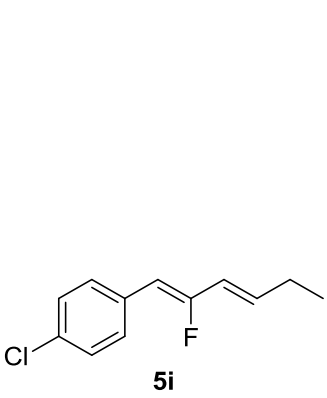
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5i (With JEOL)



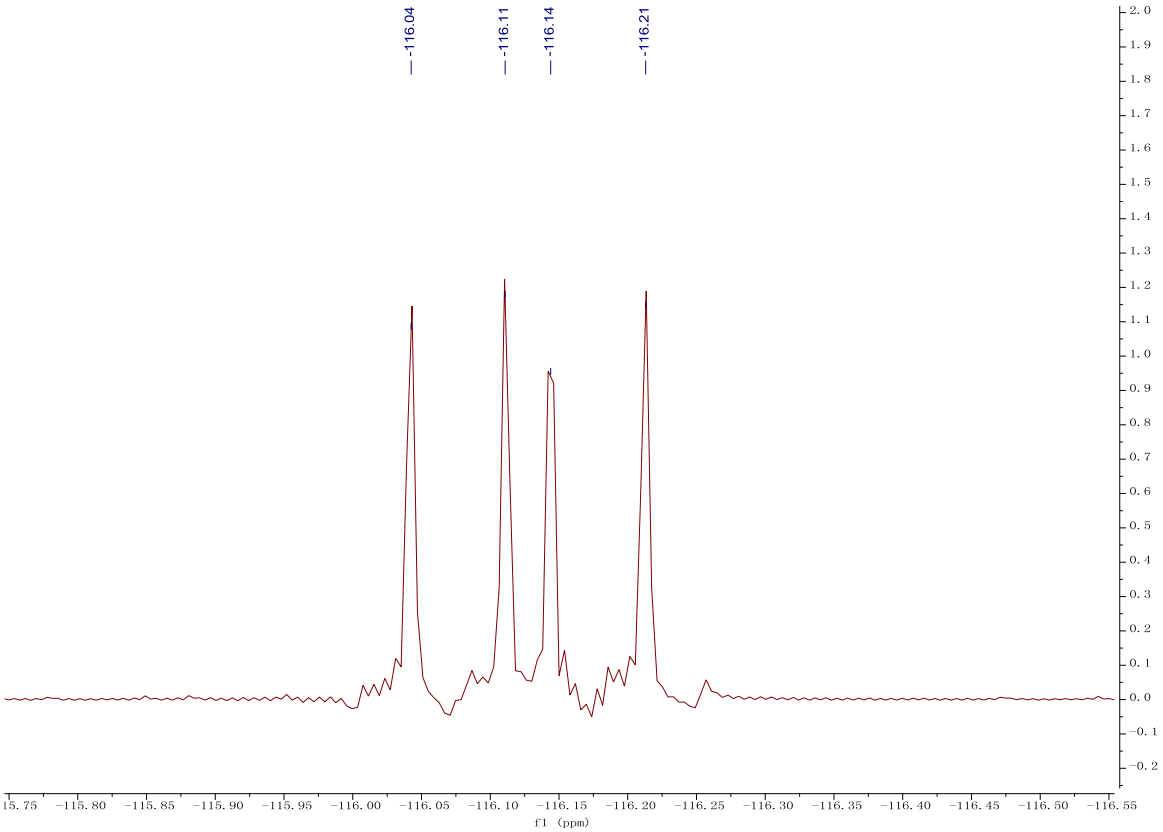
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5i (With JEOL)



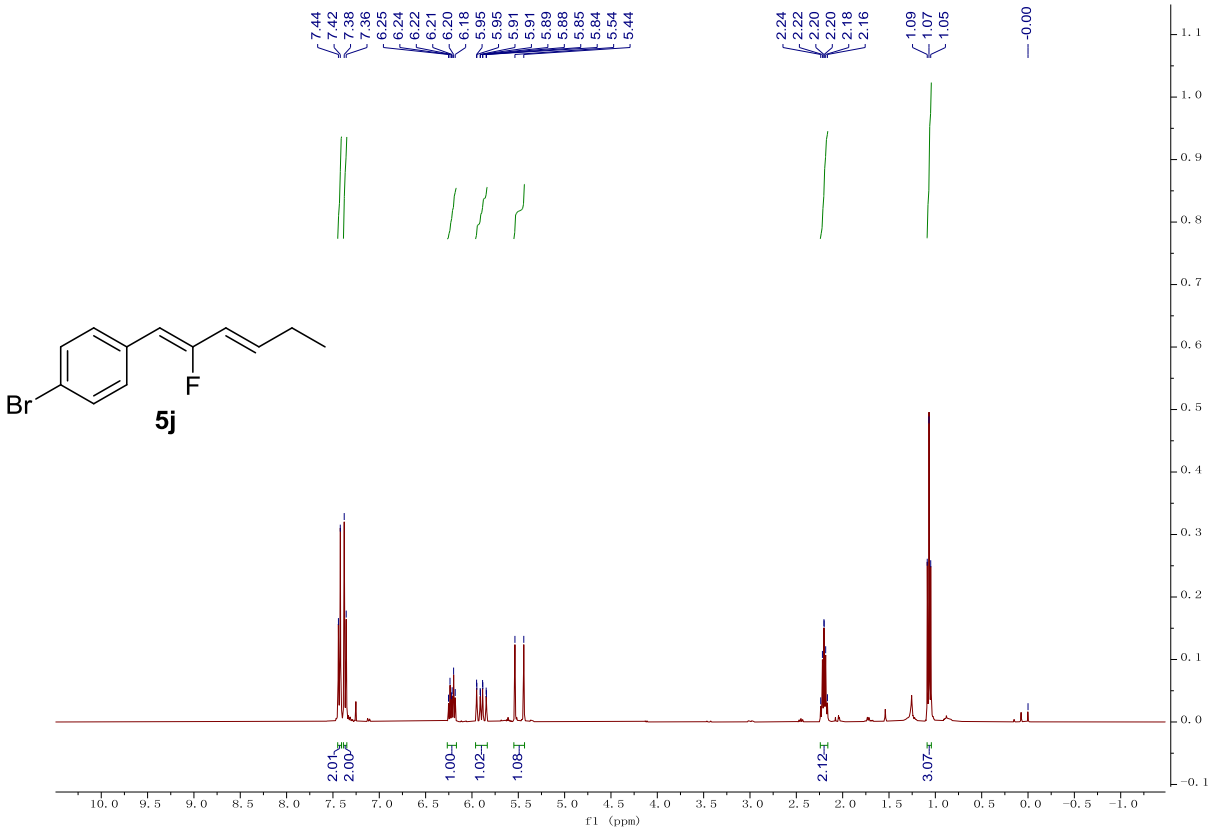
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5i (With JEOL)



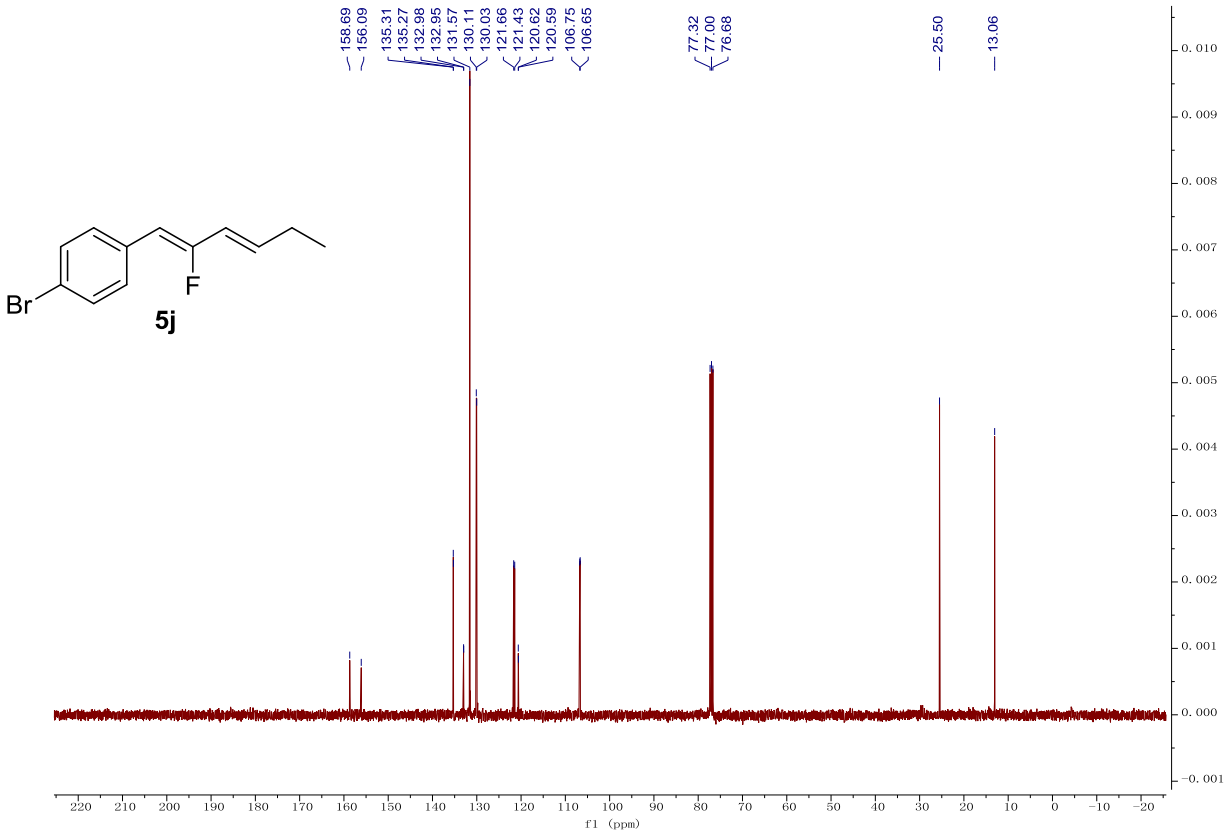
5i



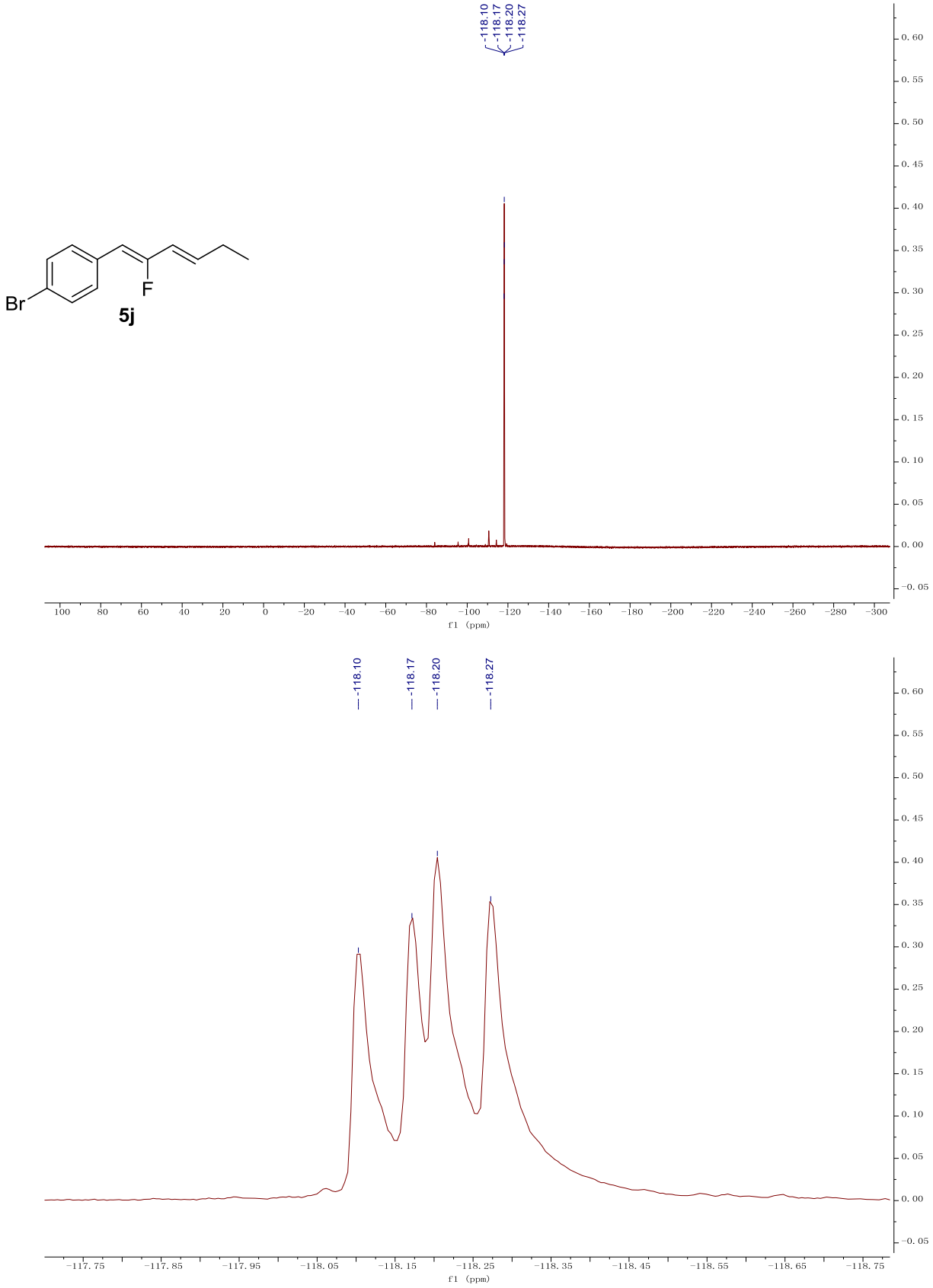
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5j (With JEOL)



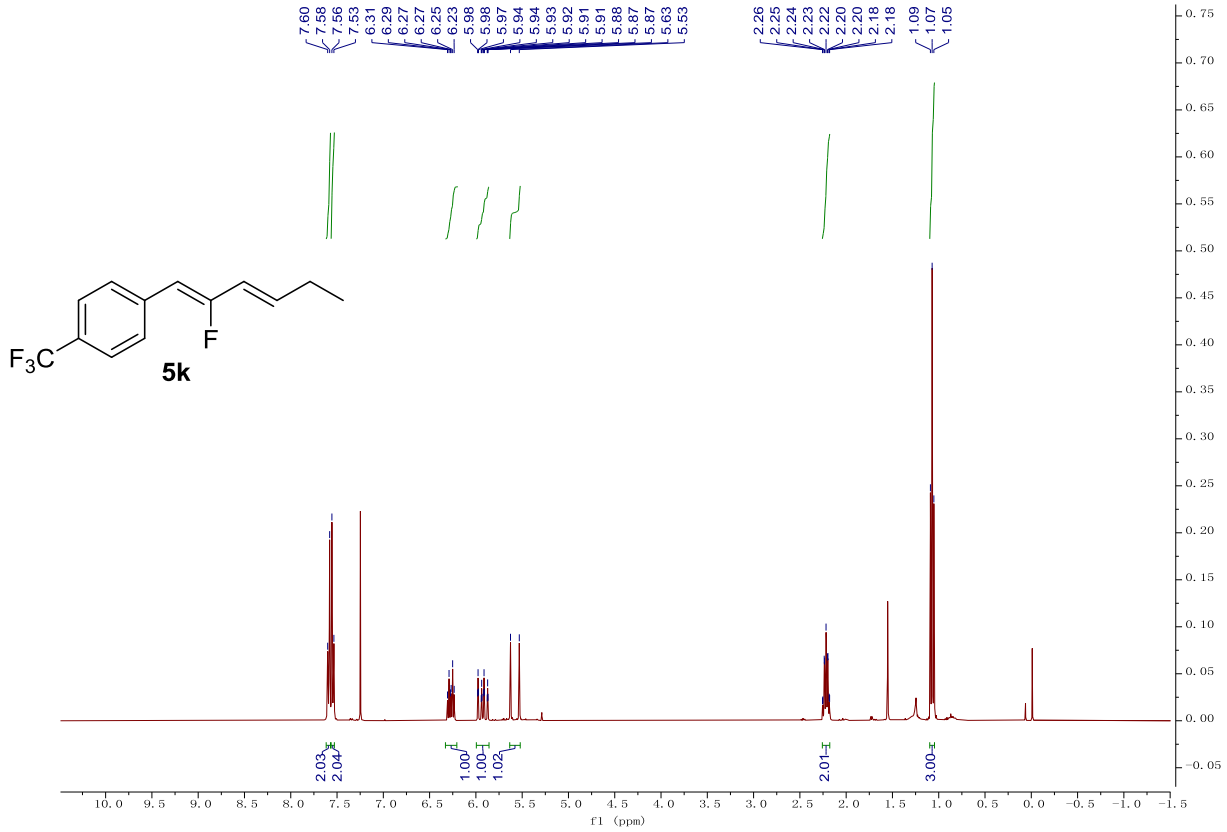
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5j (With JEOL)



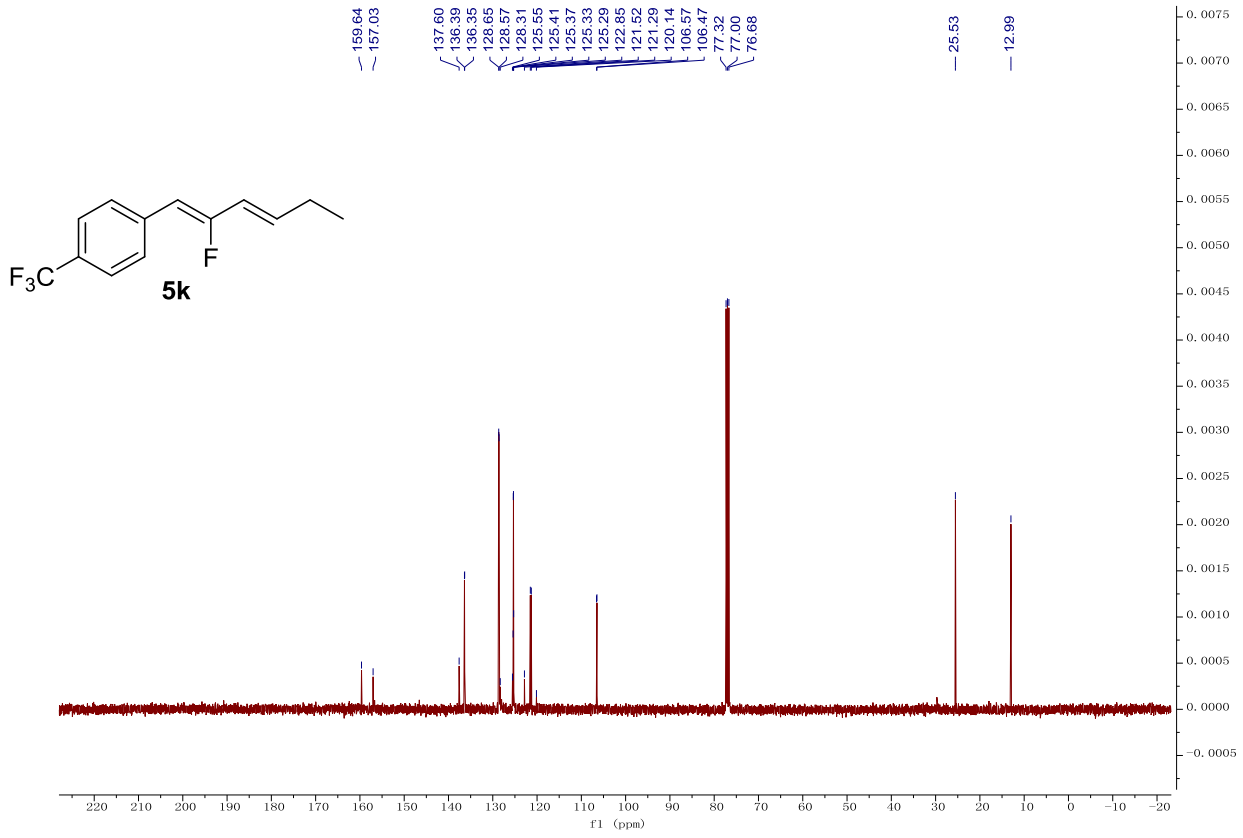
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5j (With JEOL)



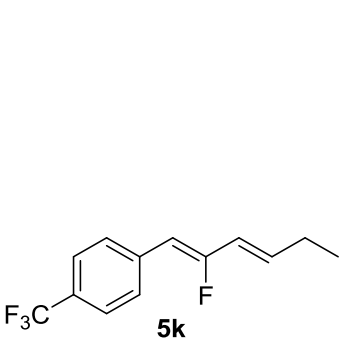
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5k (With JEOL)

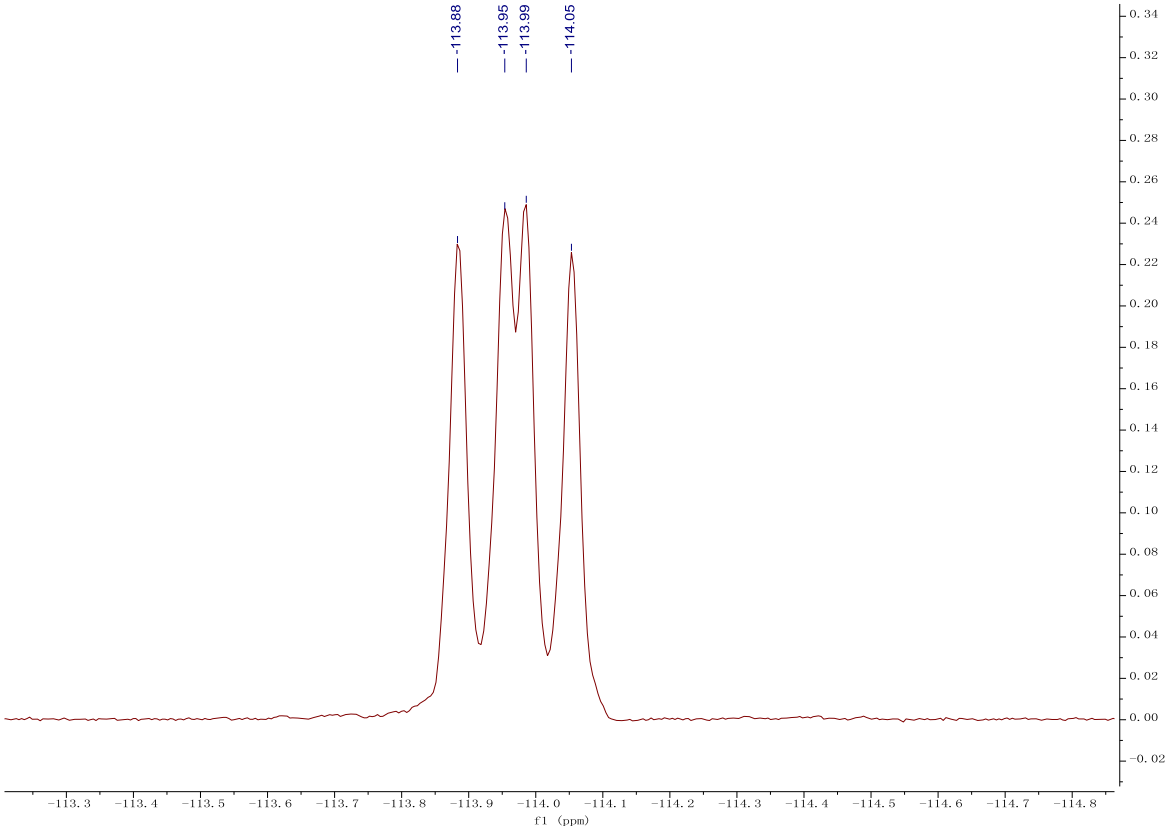


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5k (With JEOL)

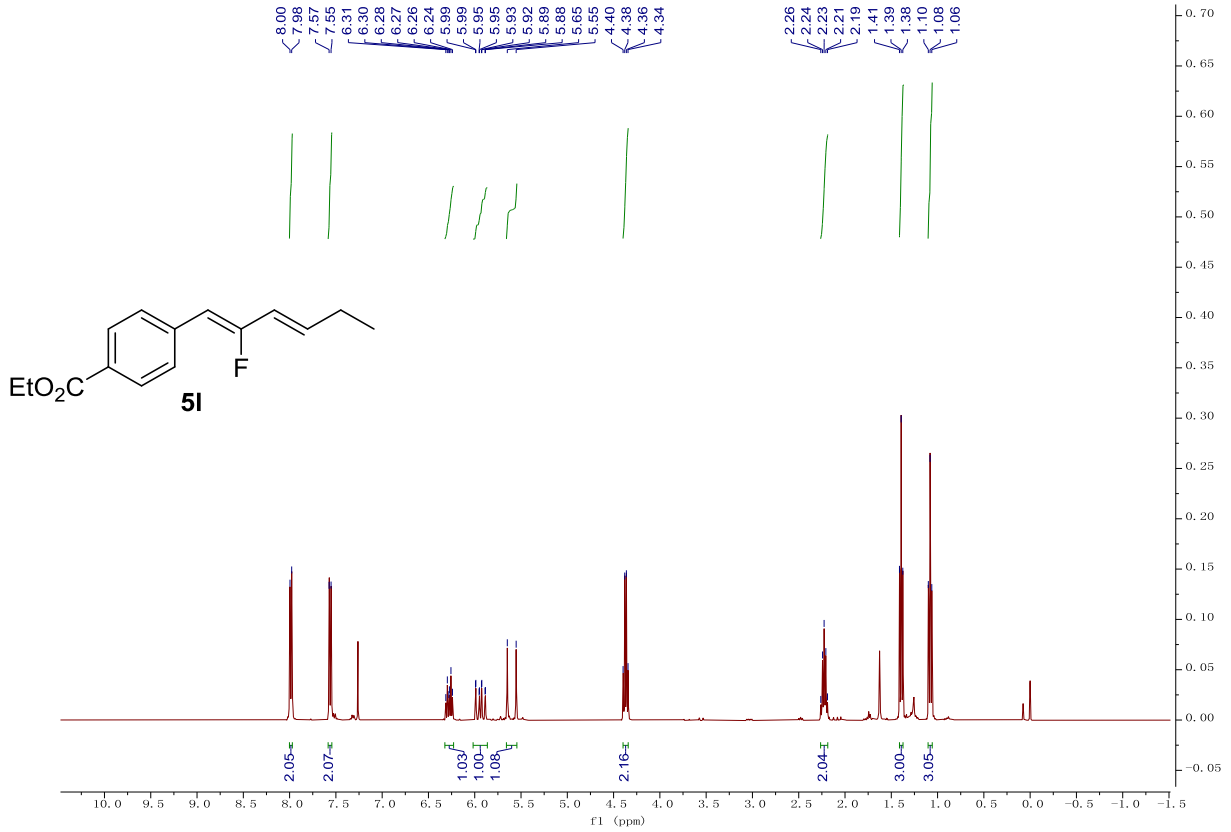


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5k (With JEOL)

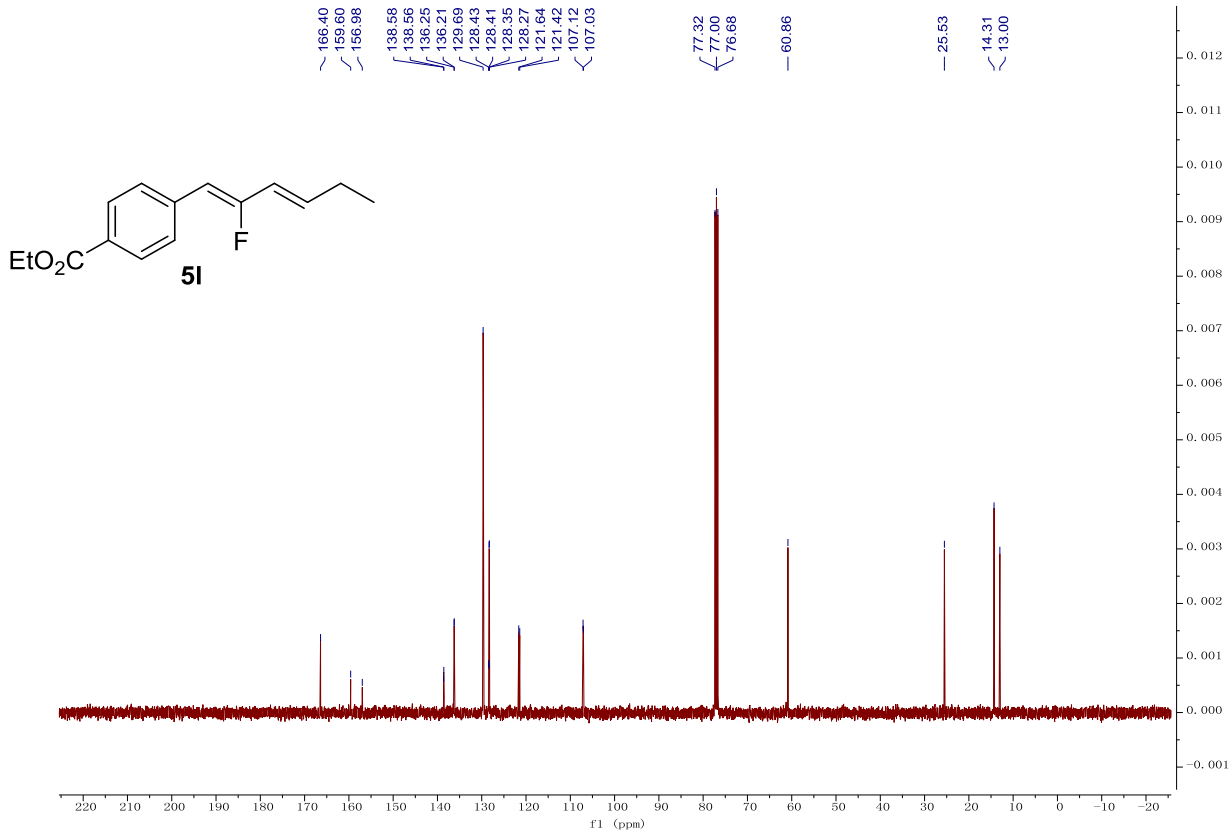




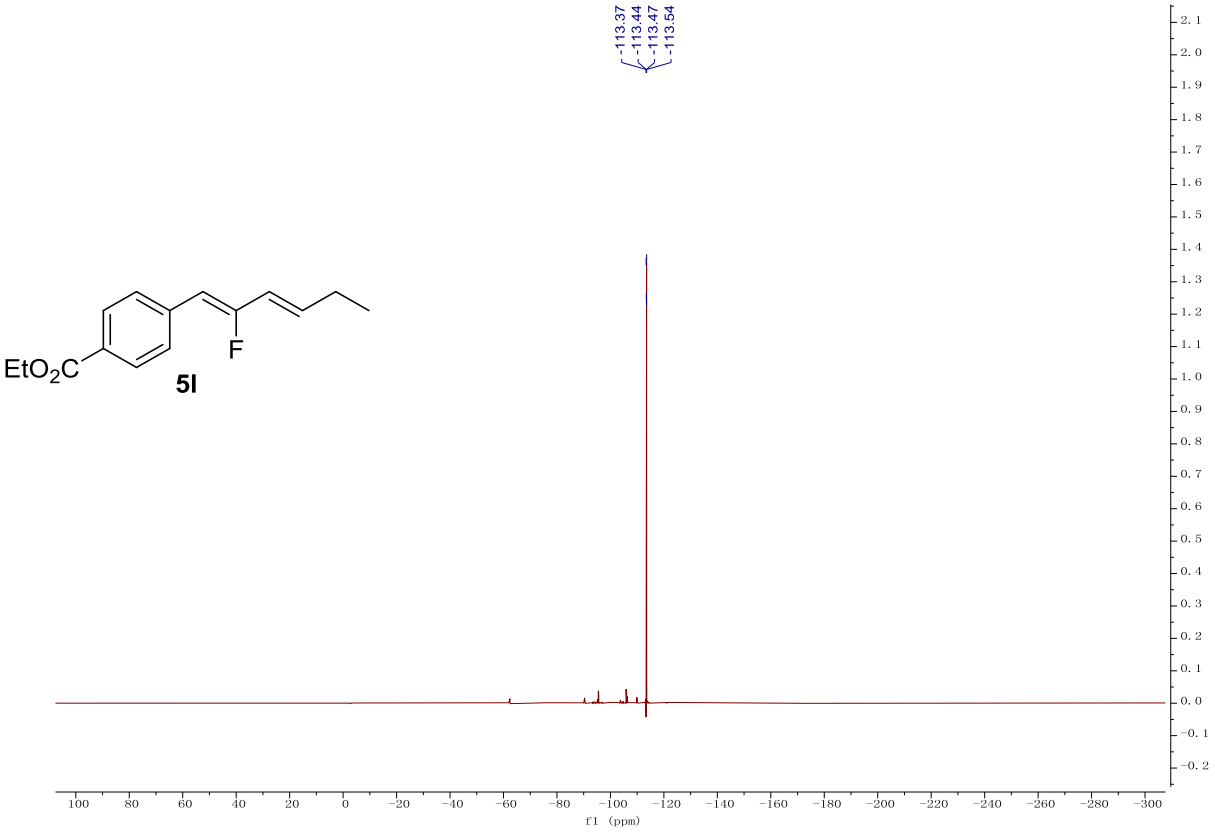
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5l (With JEOL)

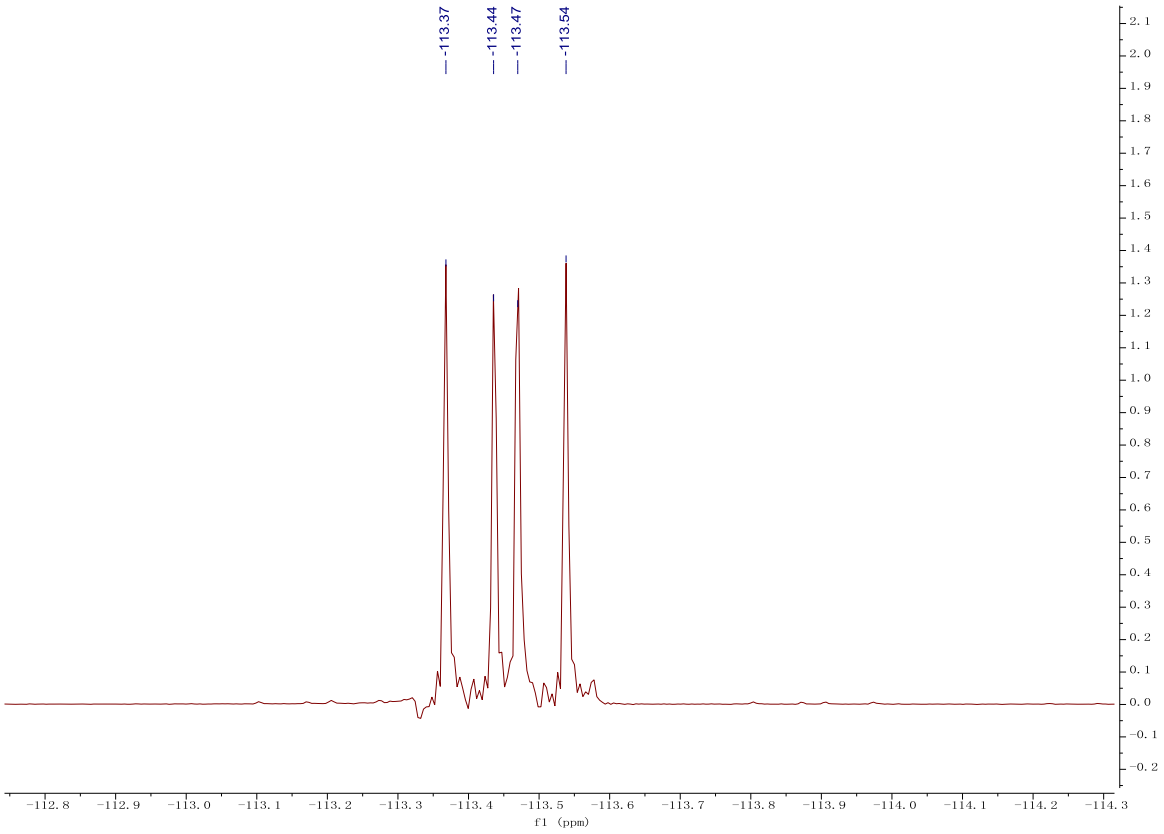


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5l (With JEOL)

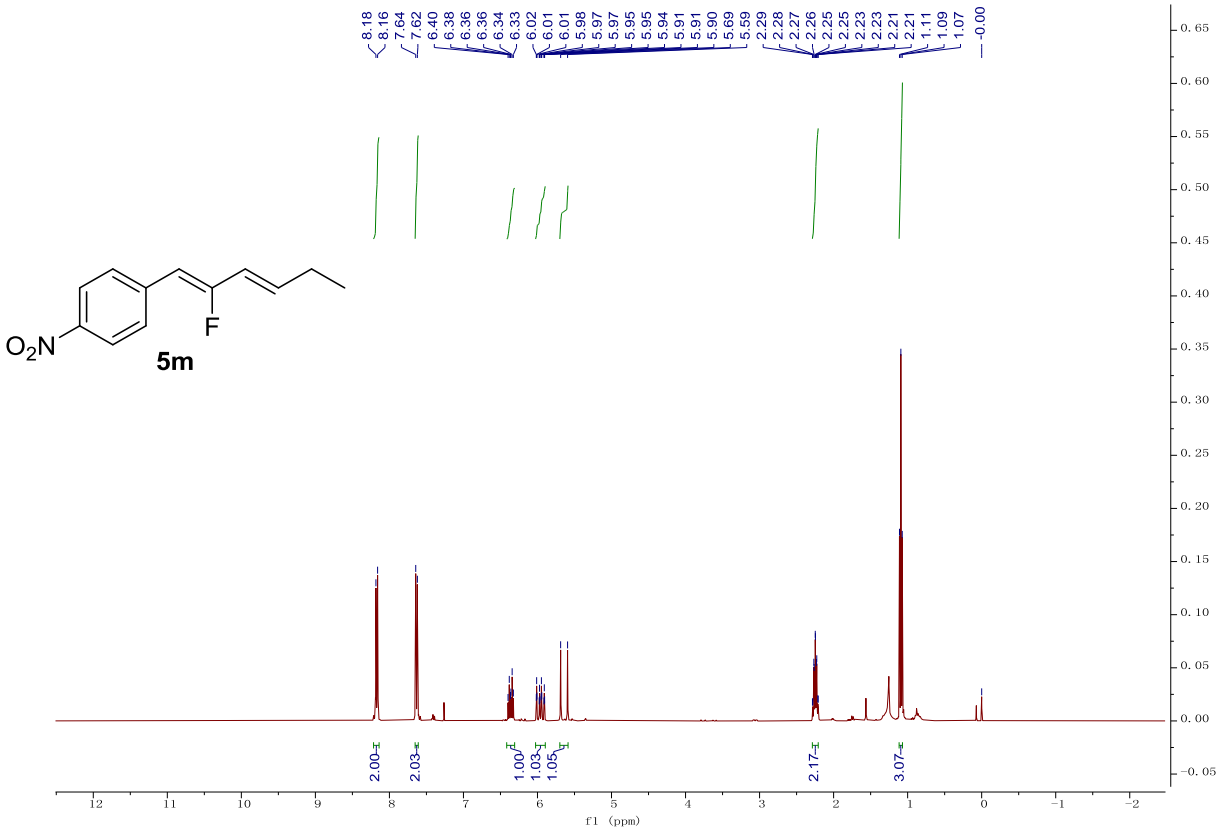


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5l (With JEOL)

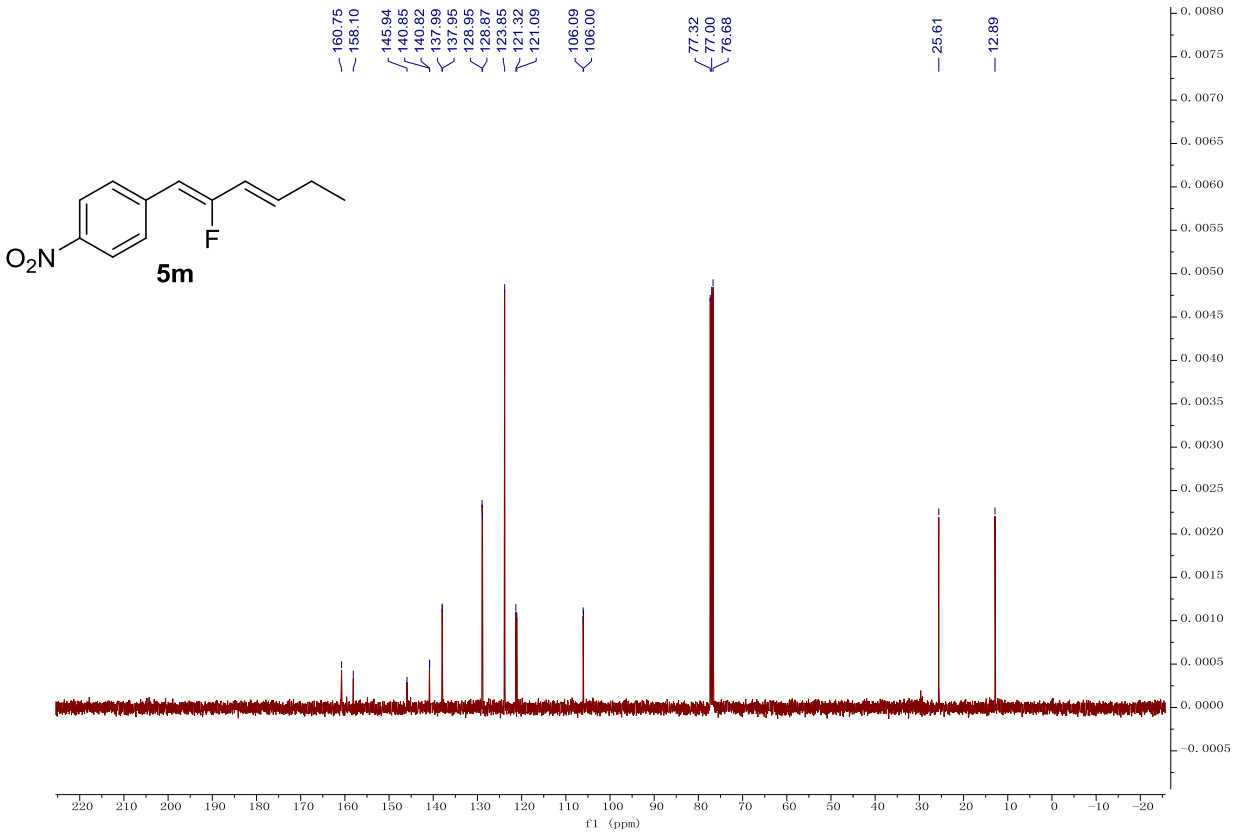




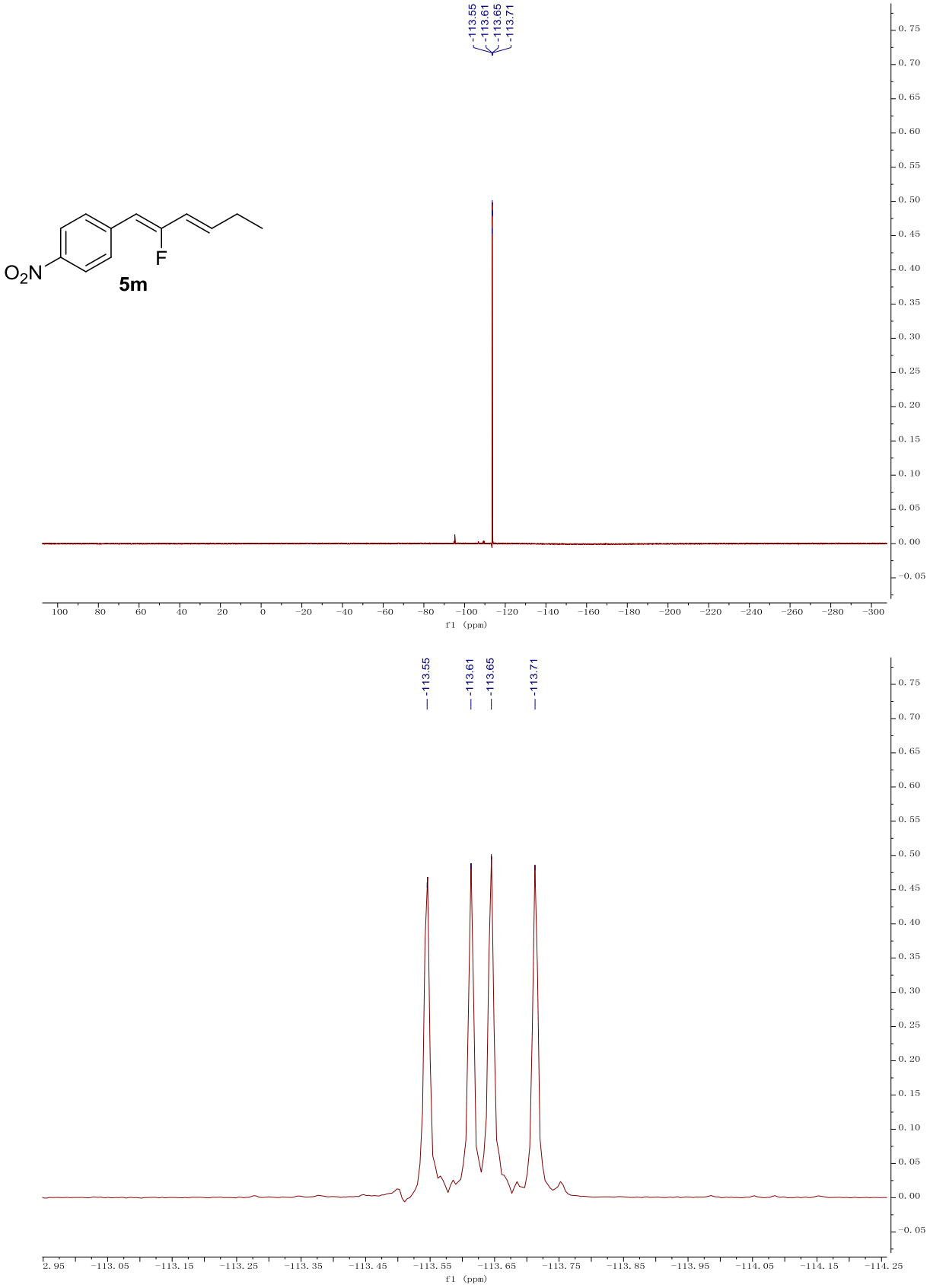
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5m (With JEOL)



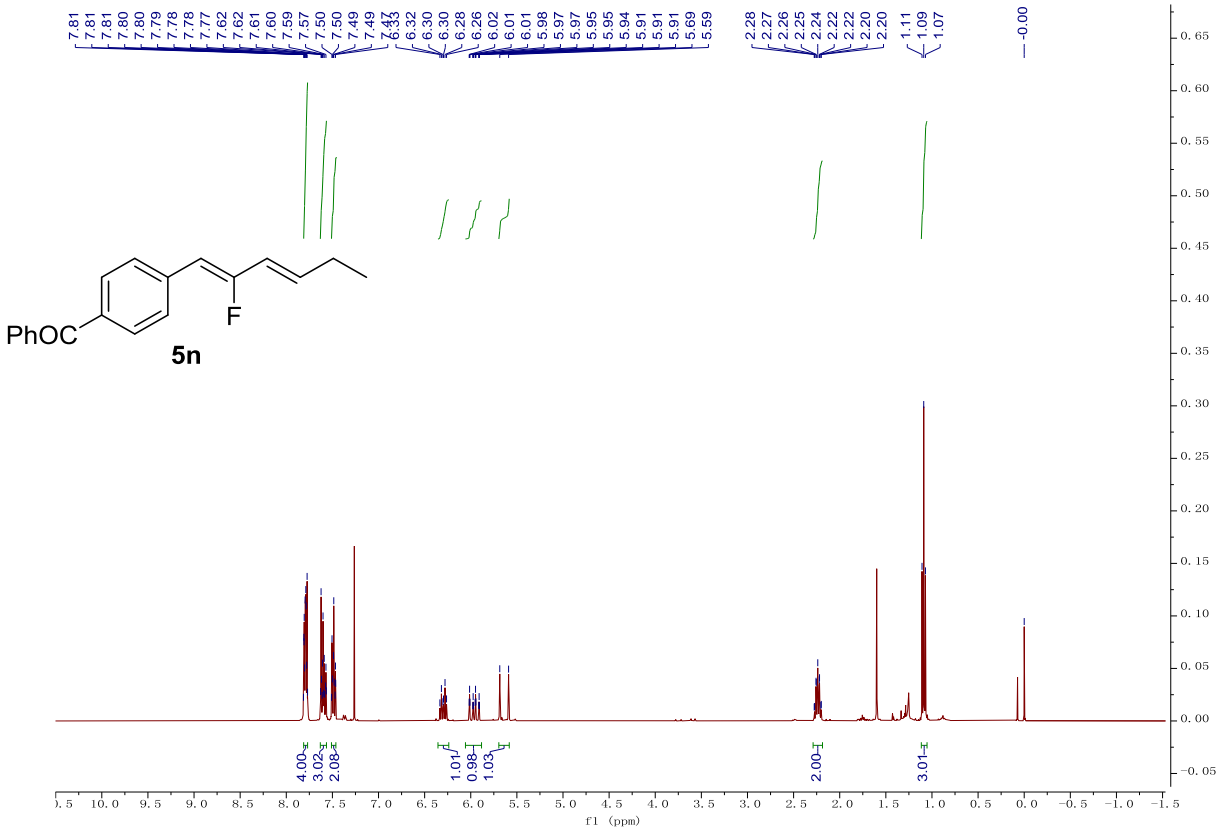
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5m (With JEOL)



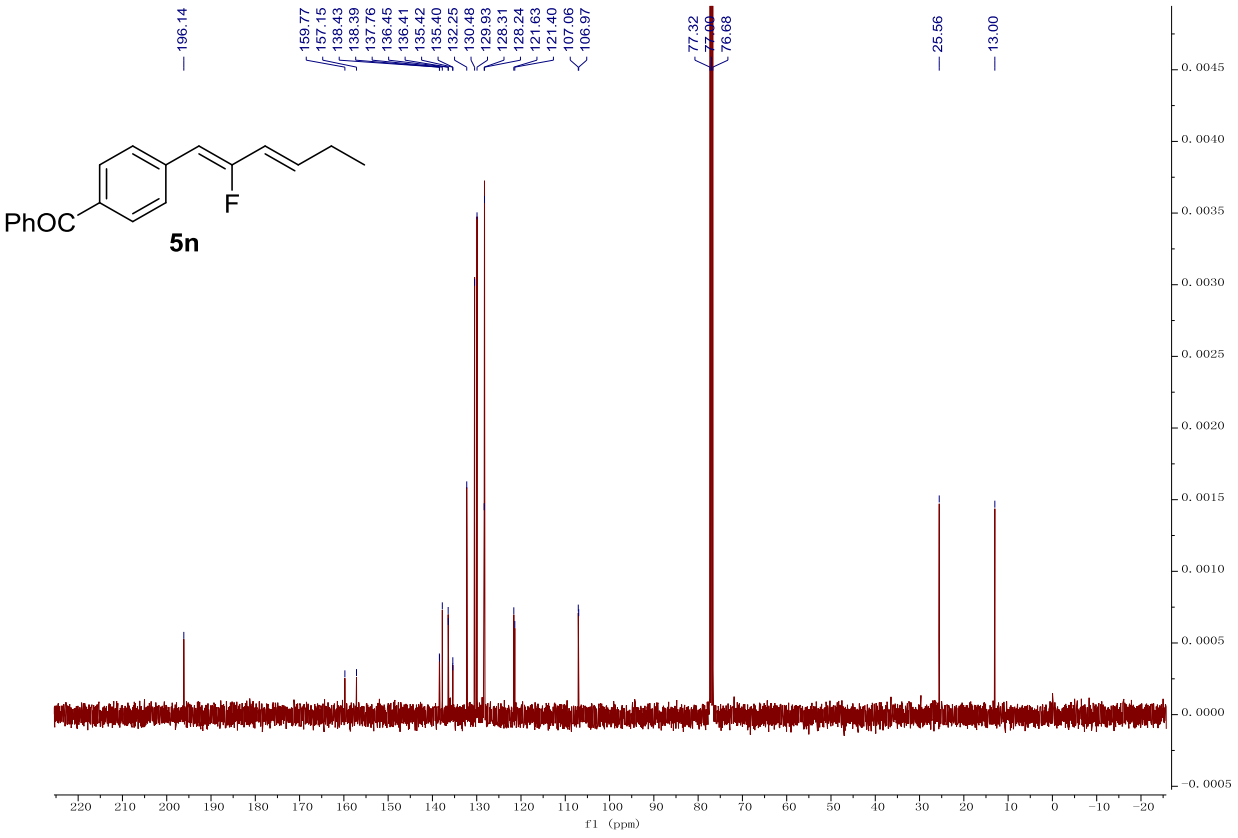
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5m (With JEOL)



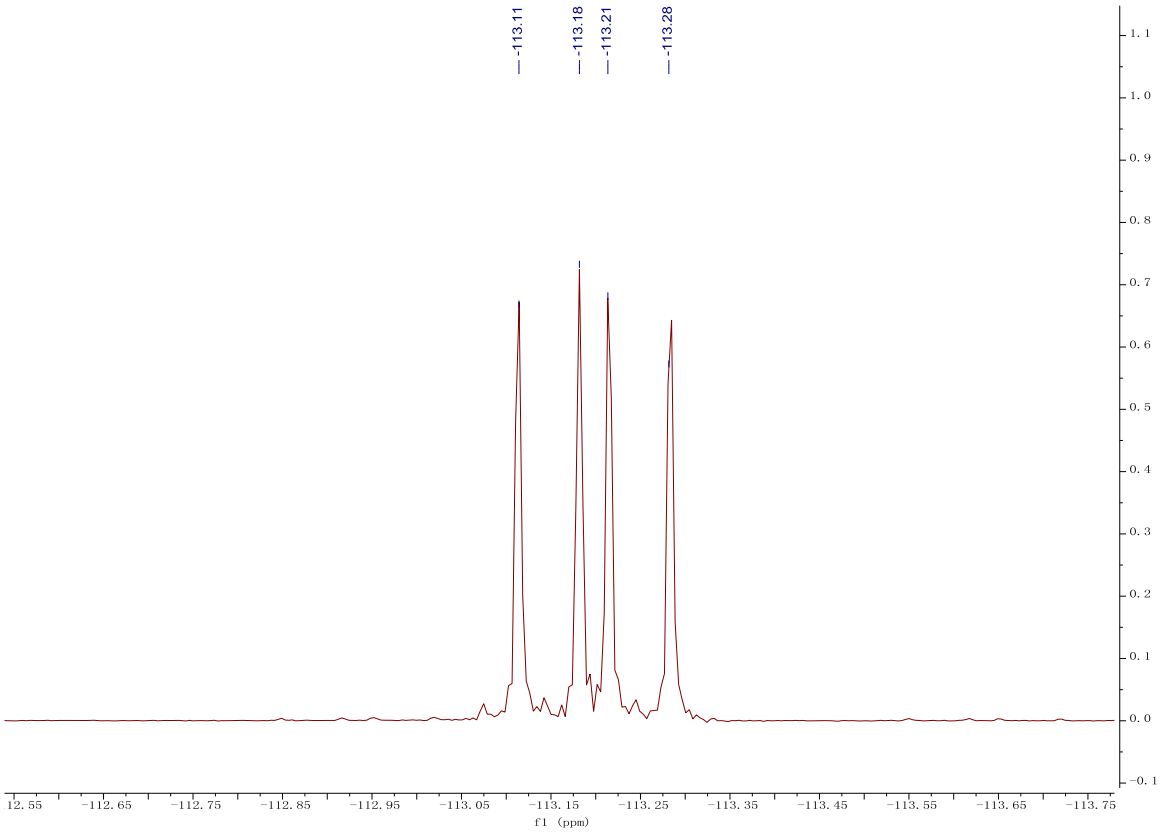
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5n (With JEOL)



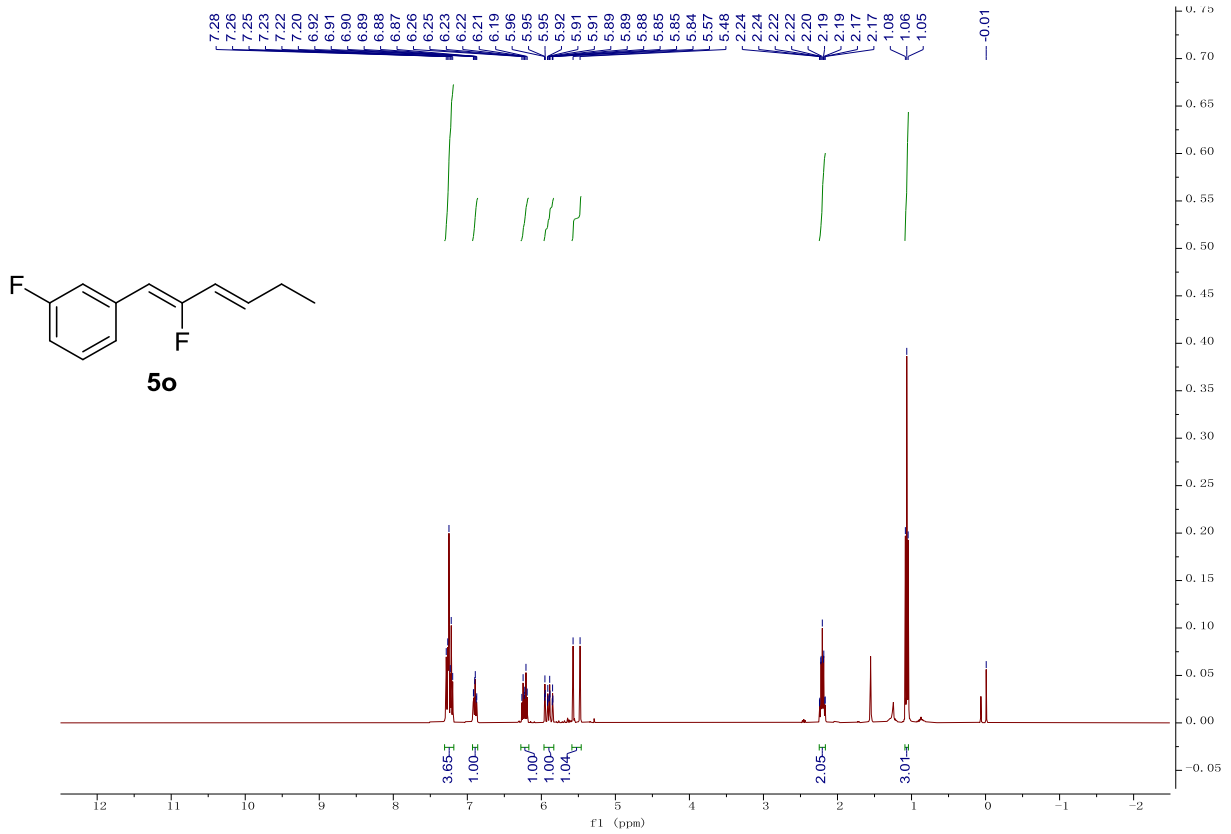
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5n (With JEOL)



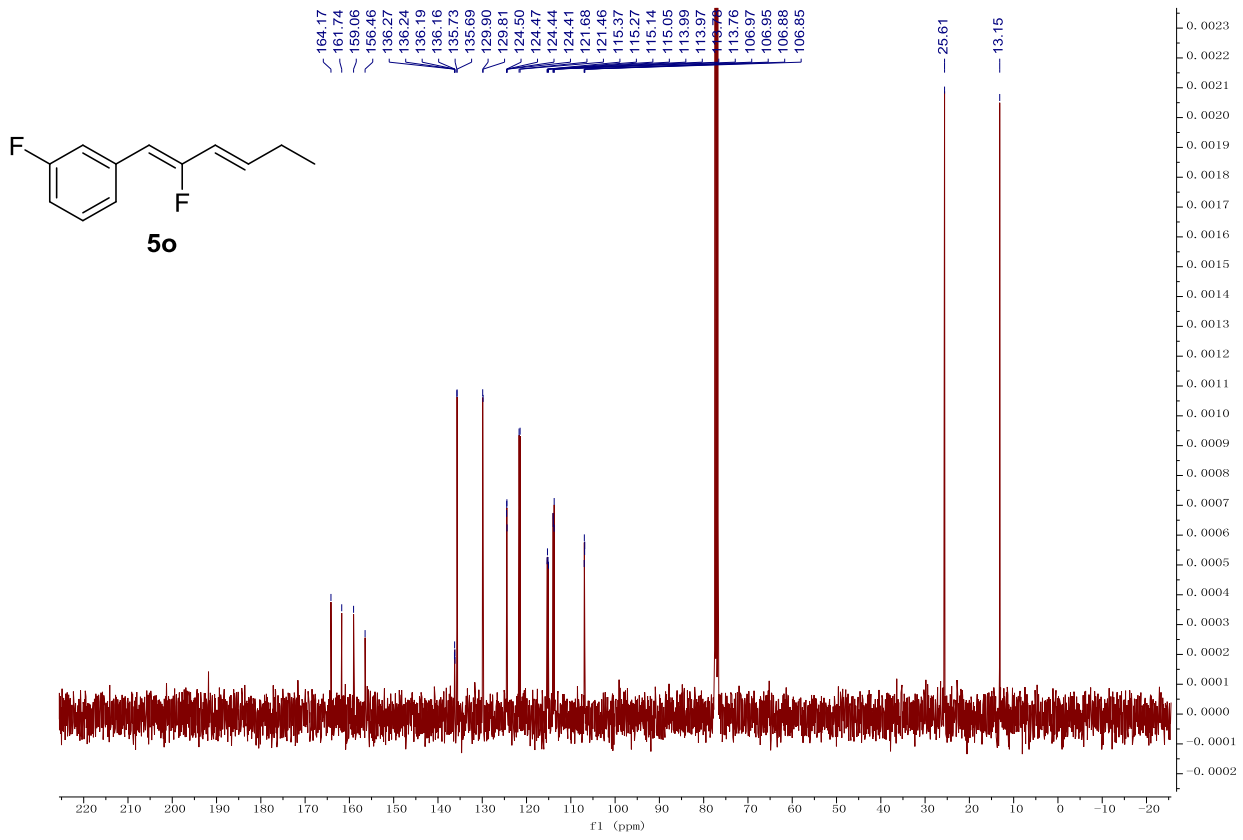
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5n (With JEOL)



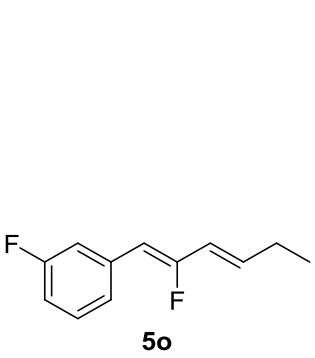
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5o (With JEOL)



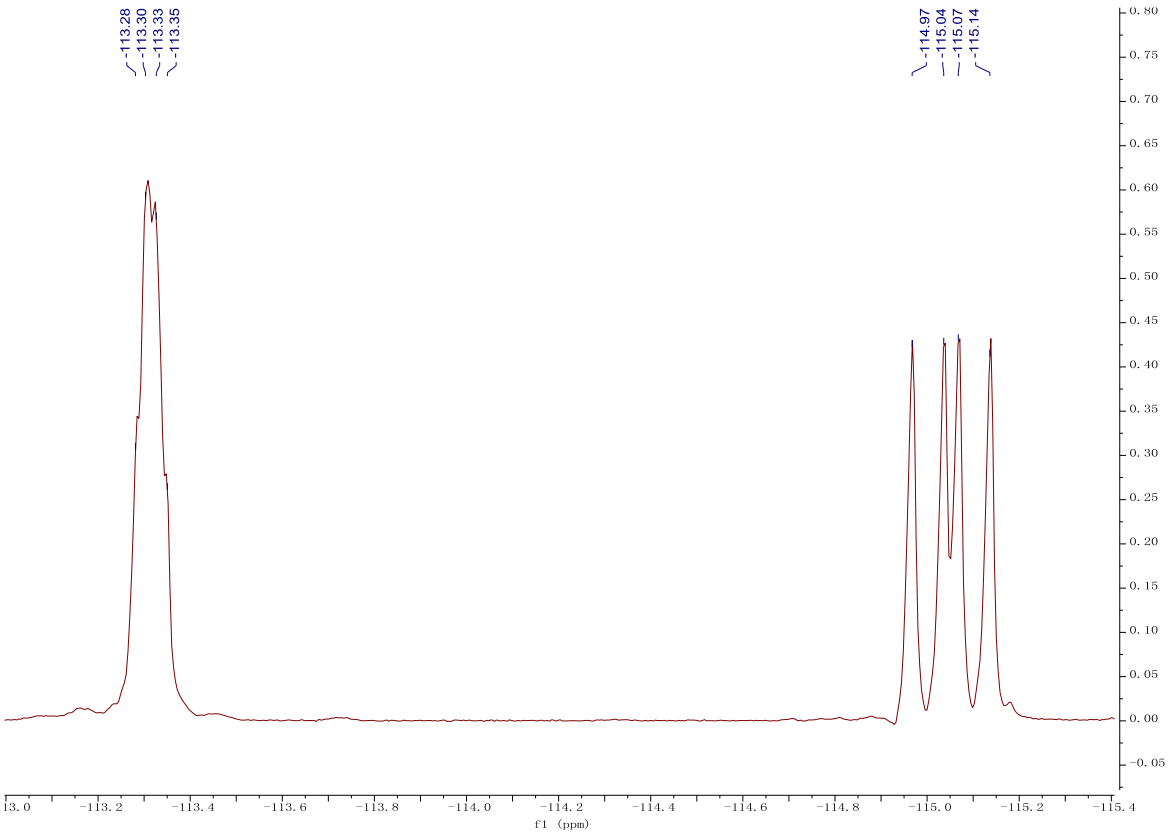
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5o (With JEOL)



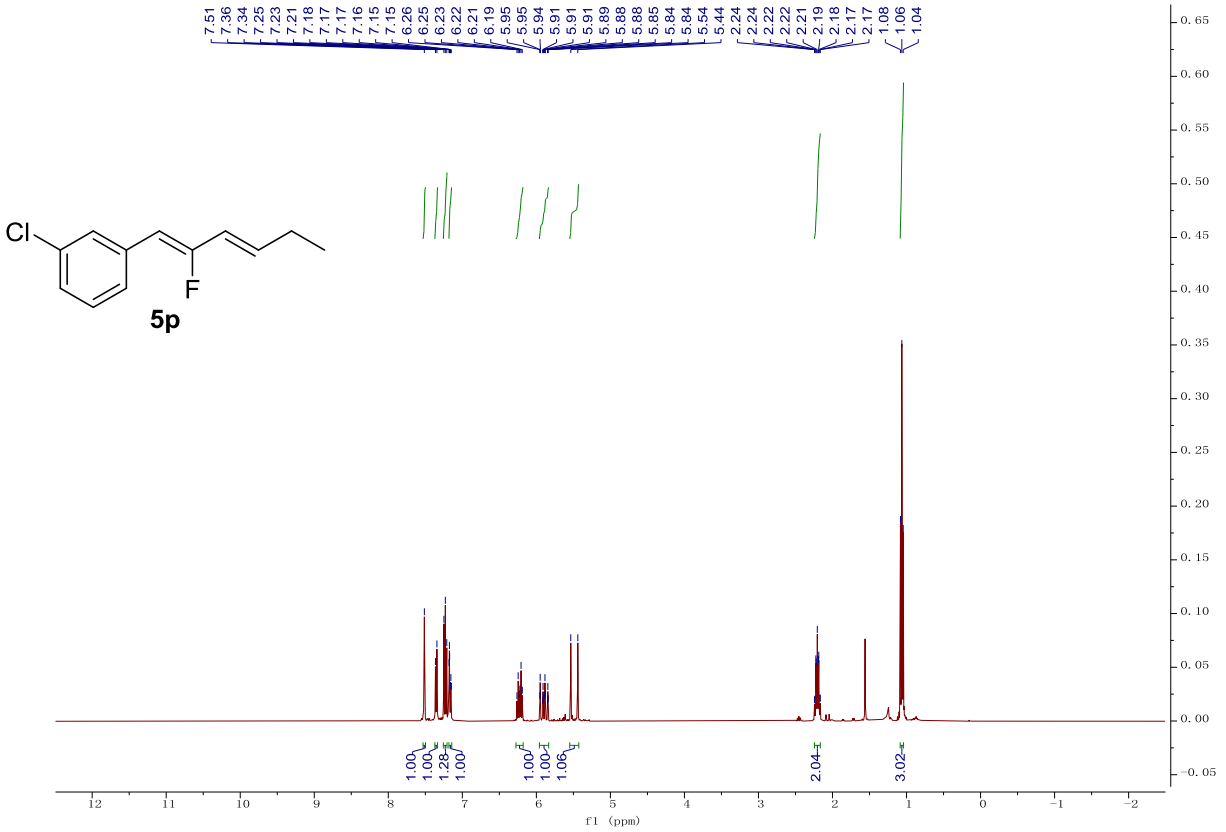
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5o (With JEOL)



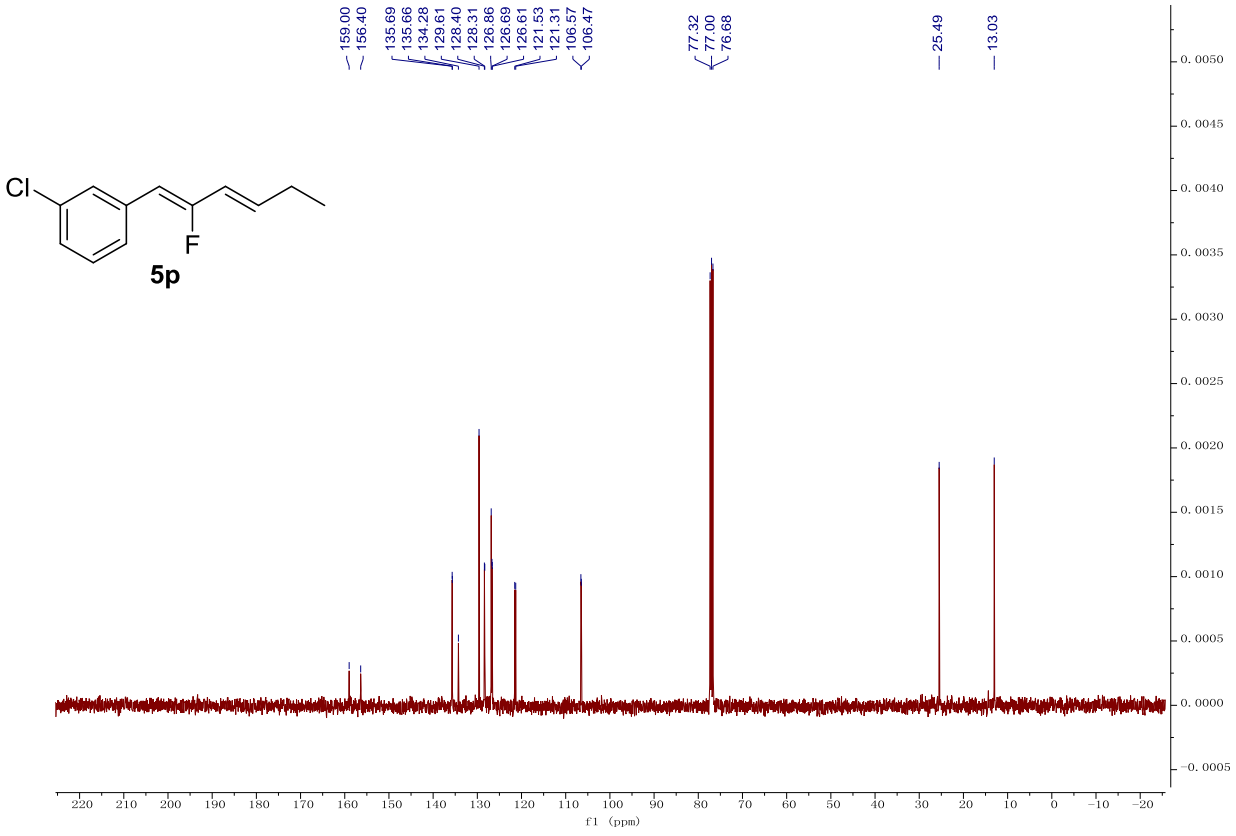
5o



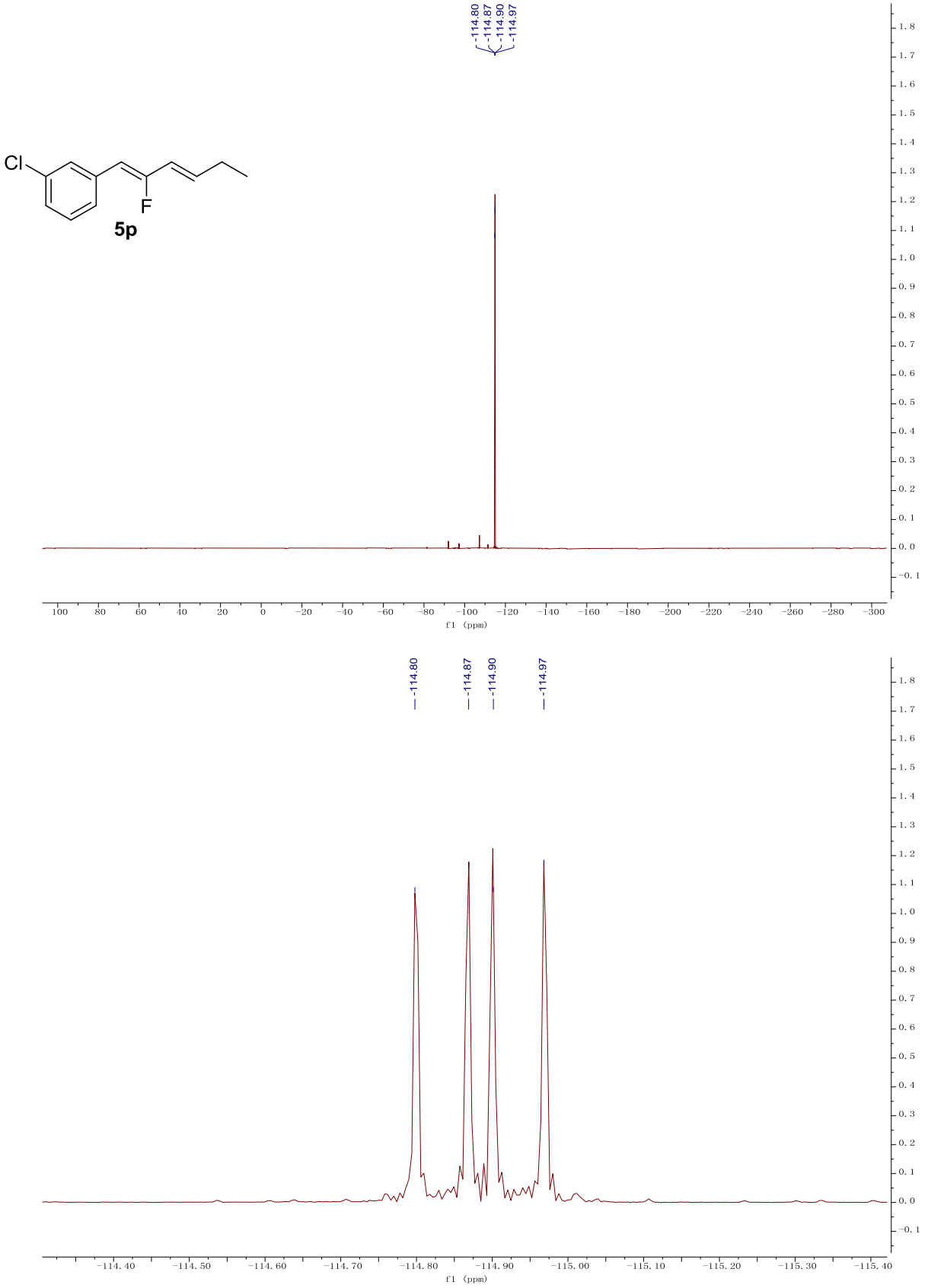
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5p (With JEOL)



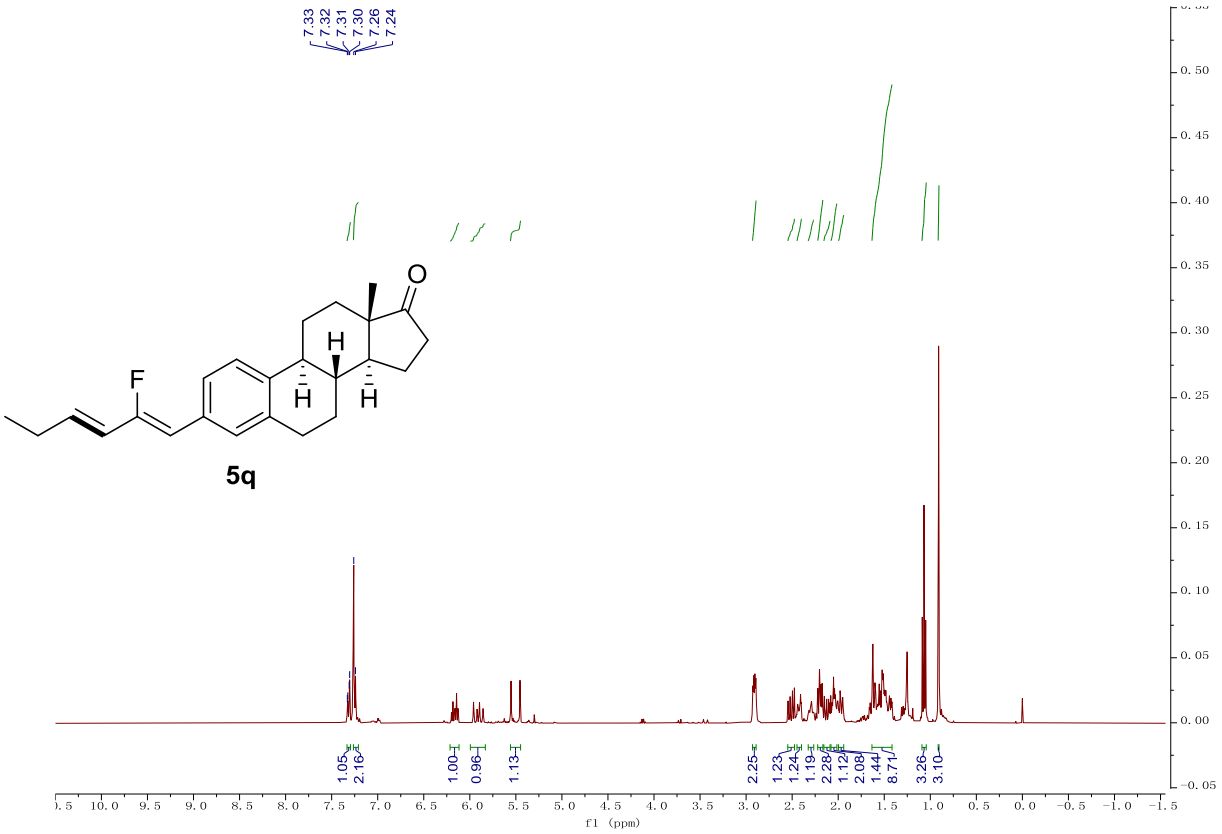
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5p (With JEOL)



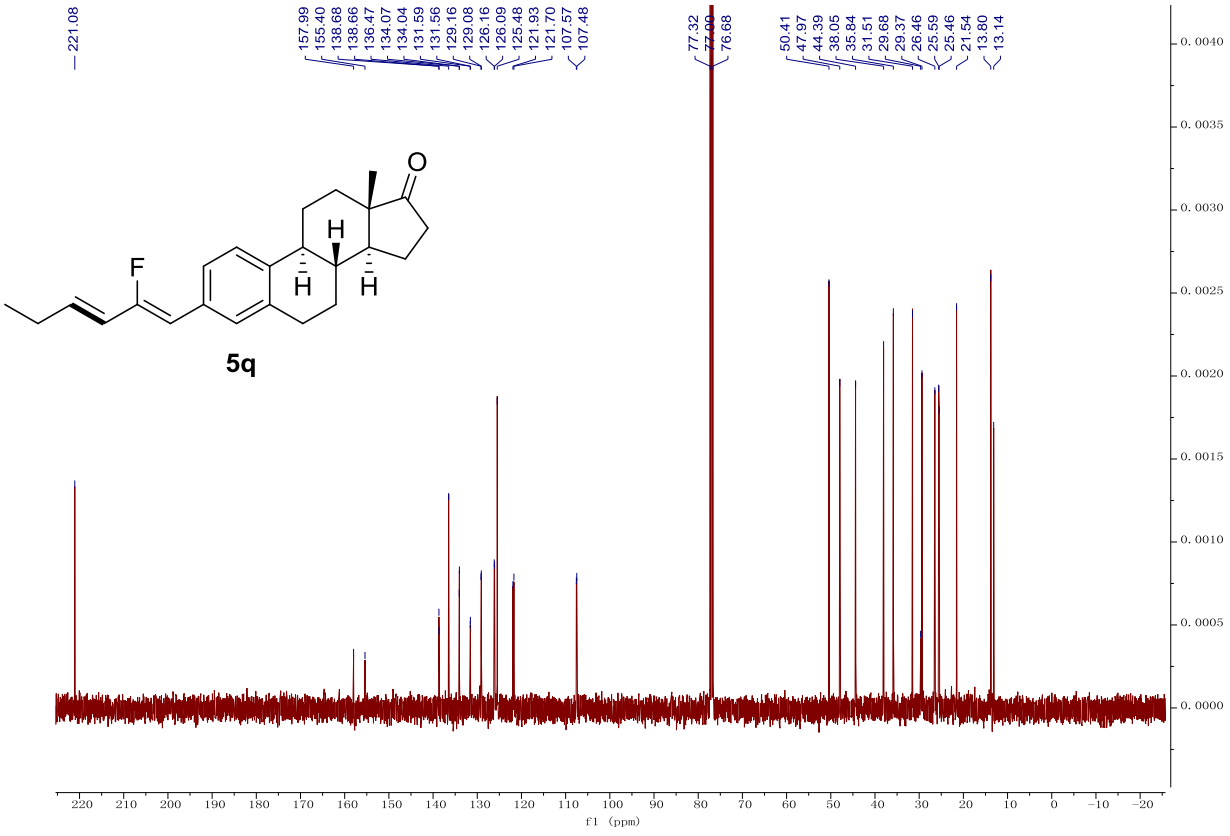
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5p (With JEOL)



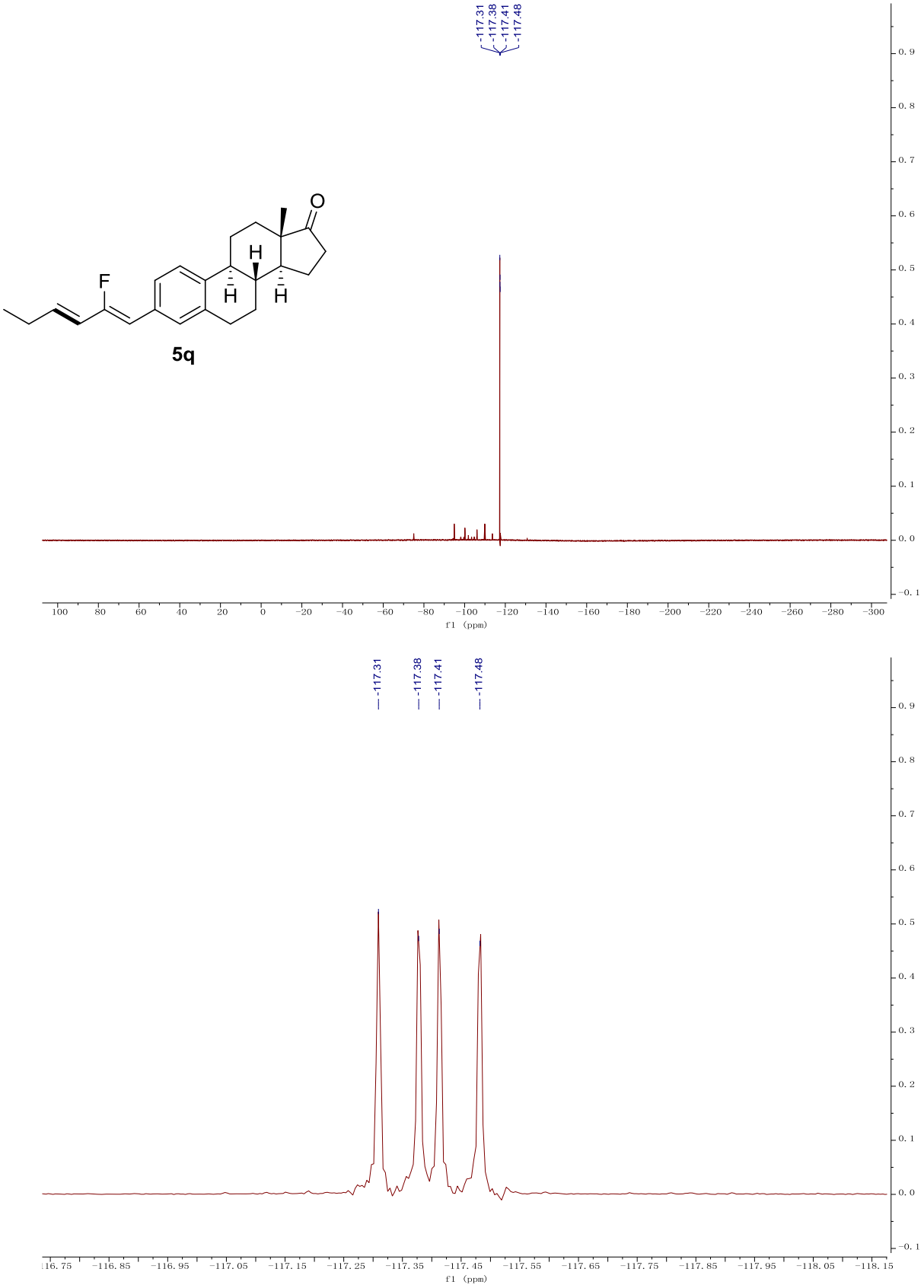
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5q (With JEOL)



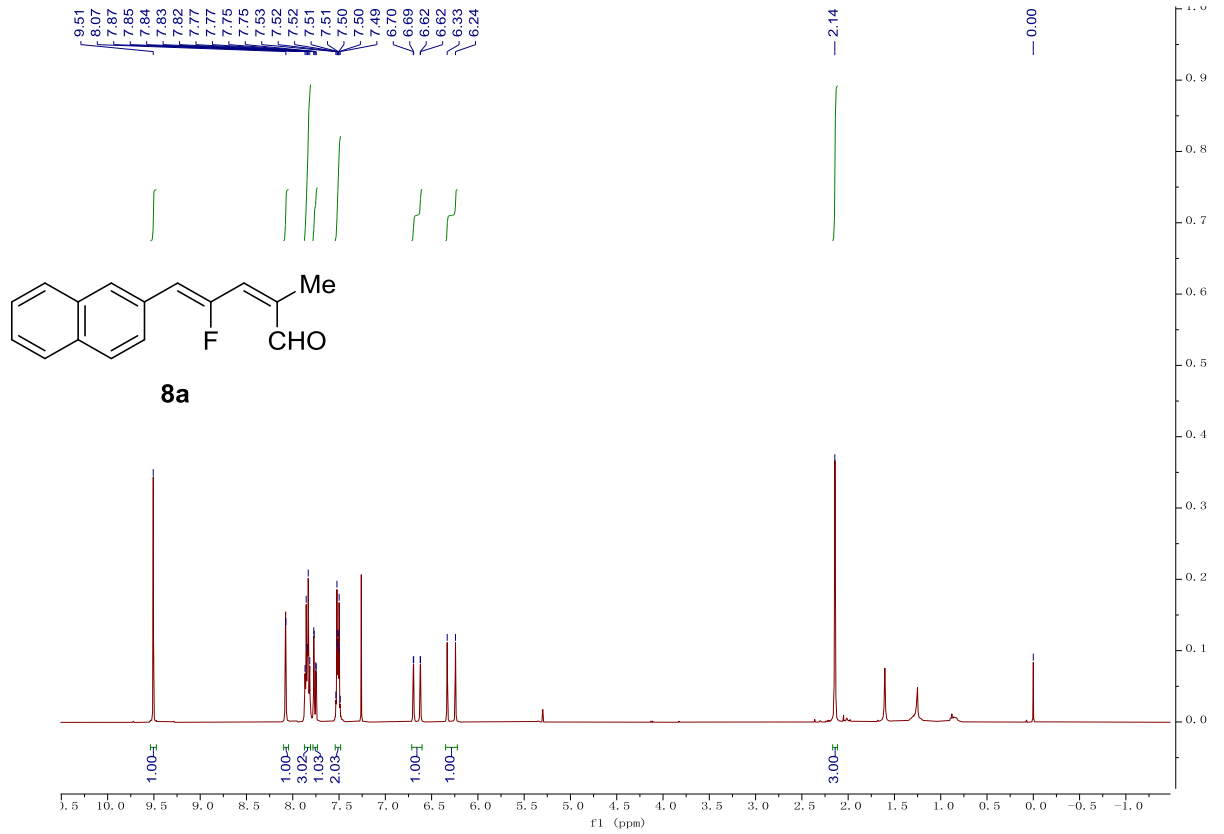
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5q (With JEOL)



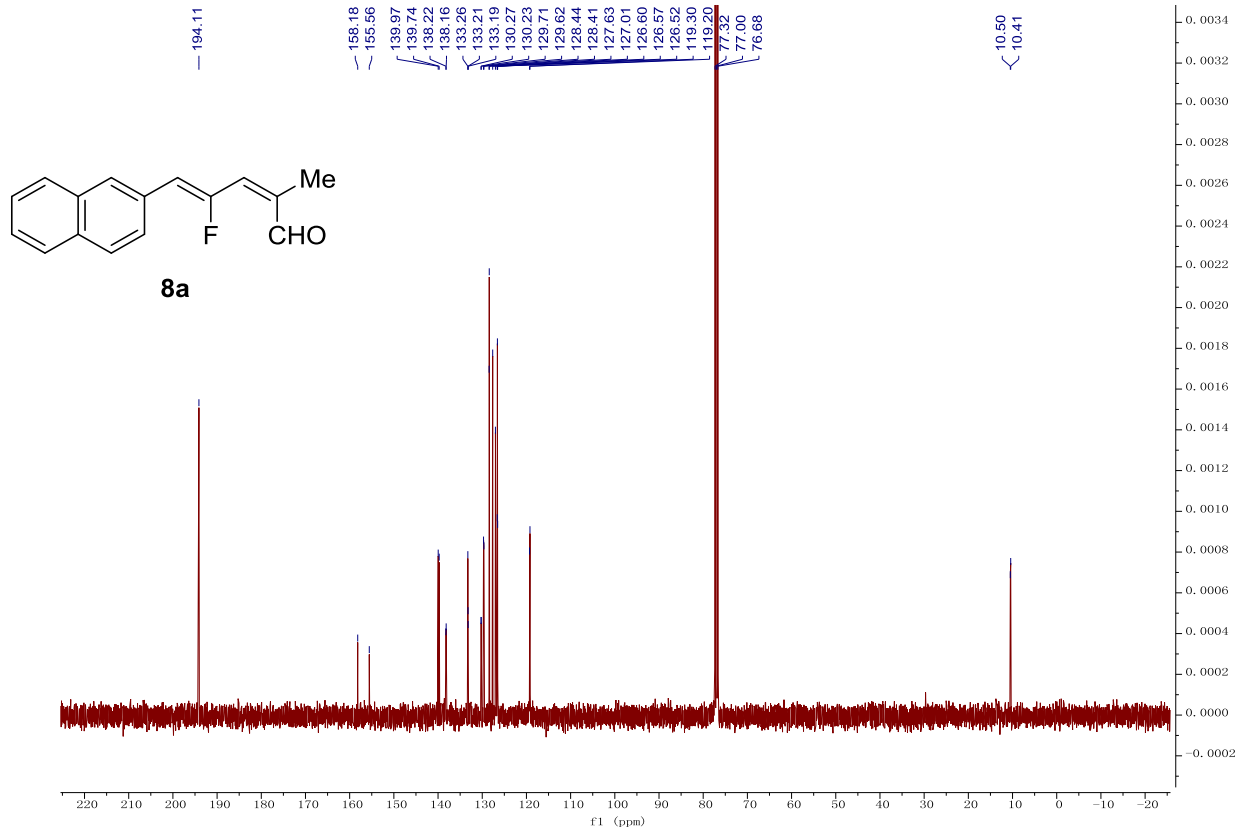
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5q (With JEOL)



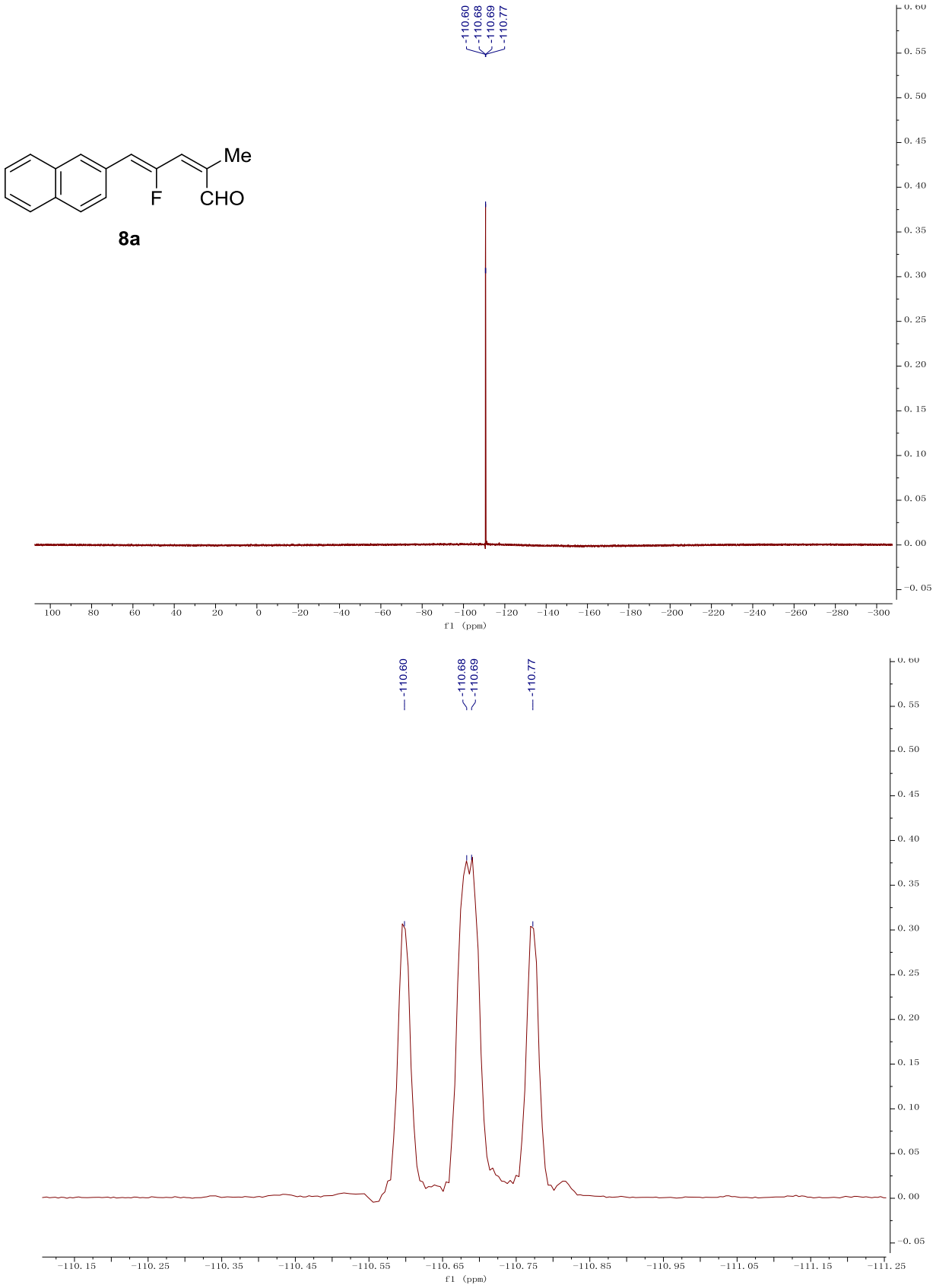
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8a (With JEOL)



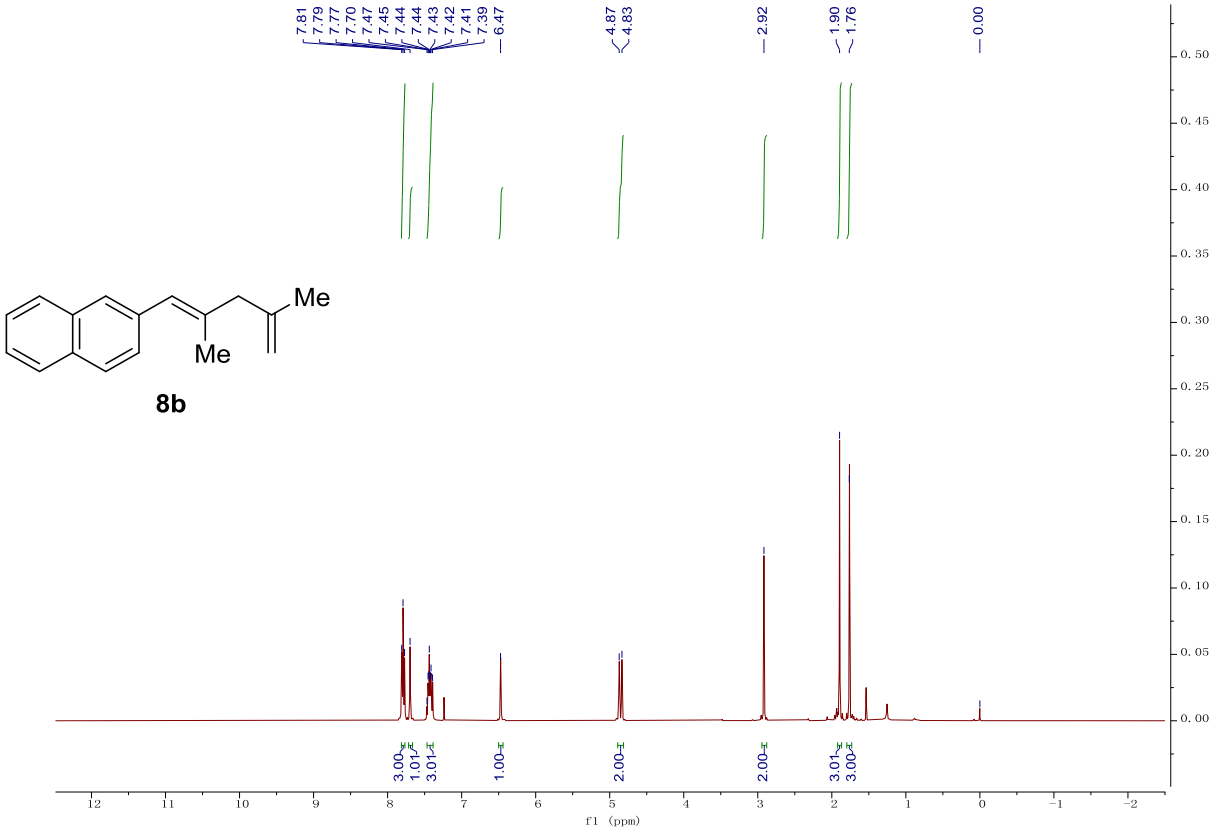
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 8a (With JEOL)



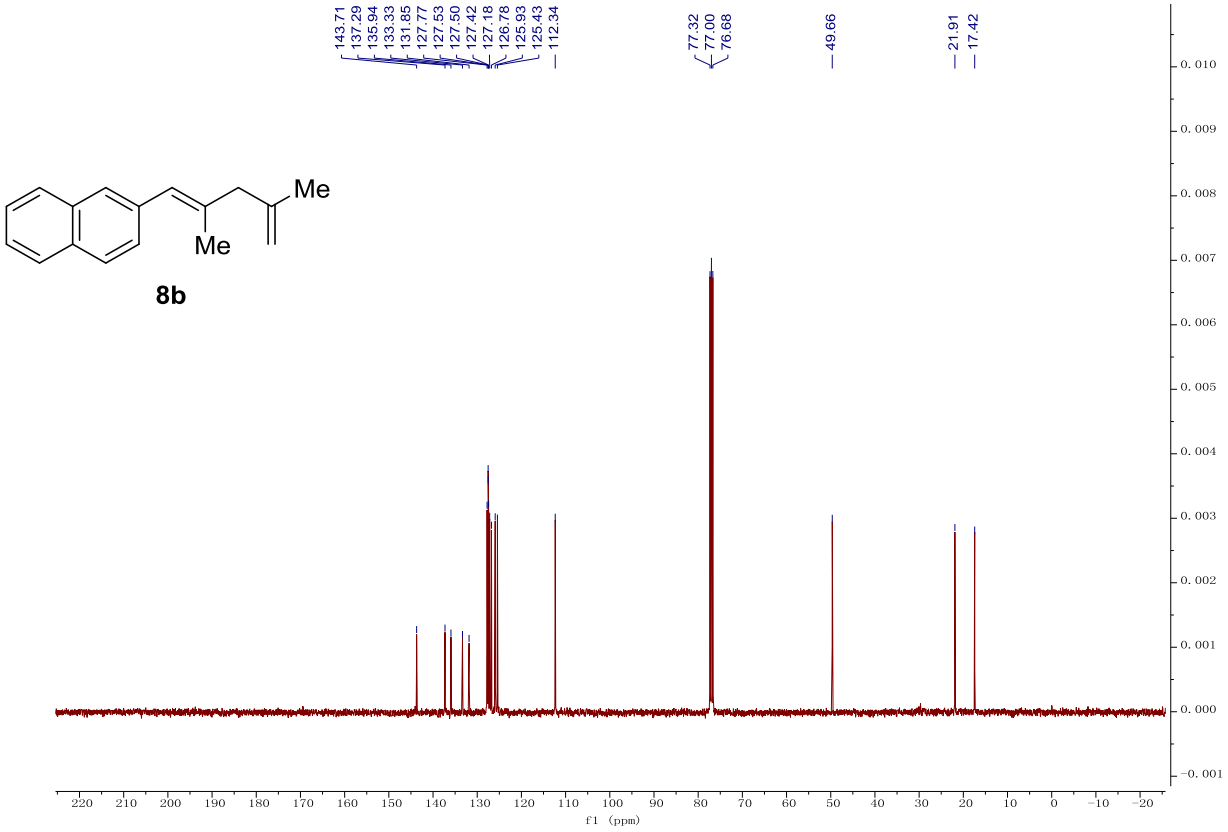
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 8a (With JEOL)



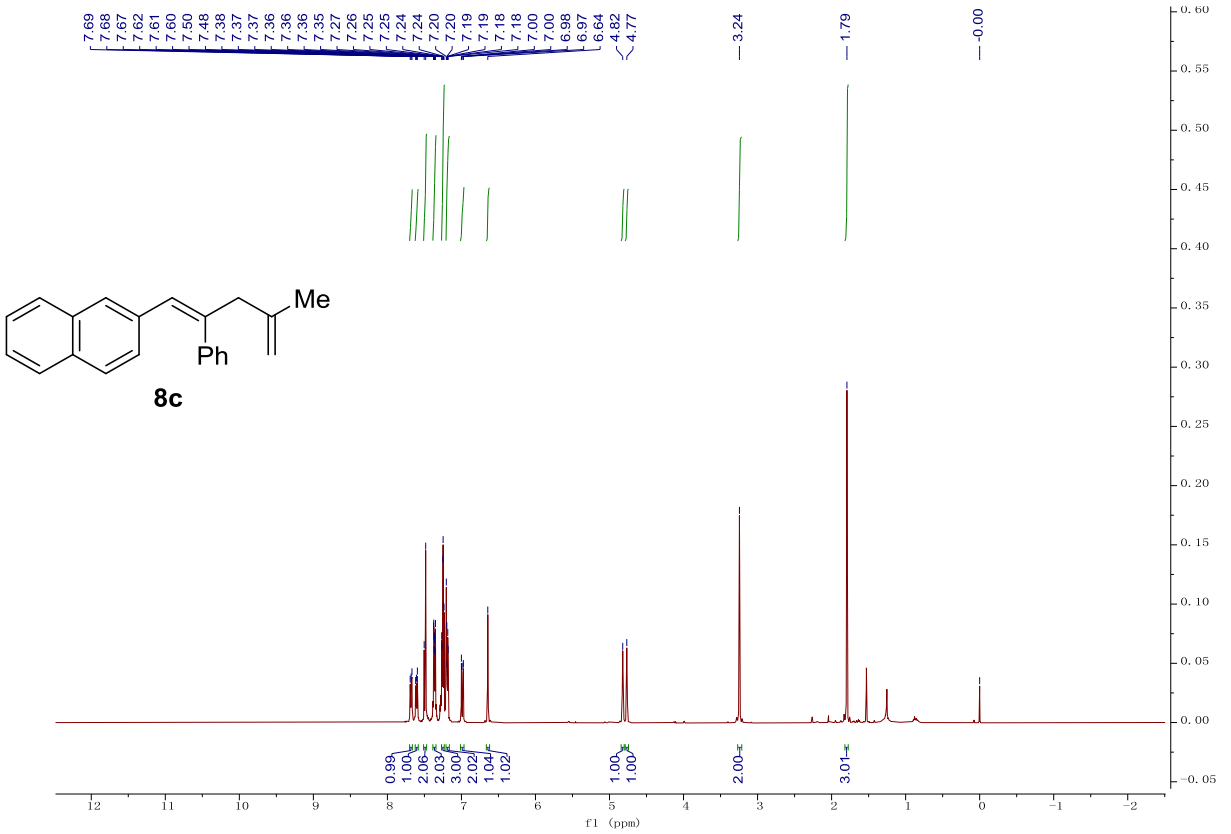
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8b (With JEOL)



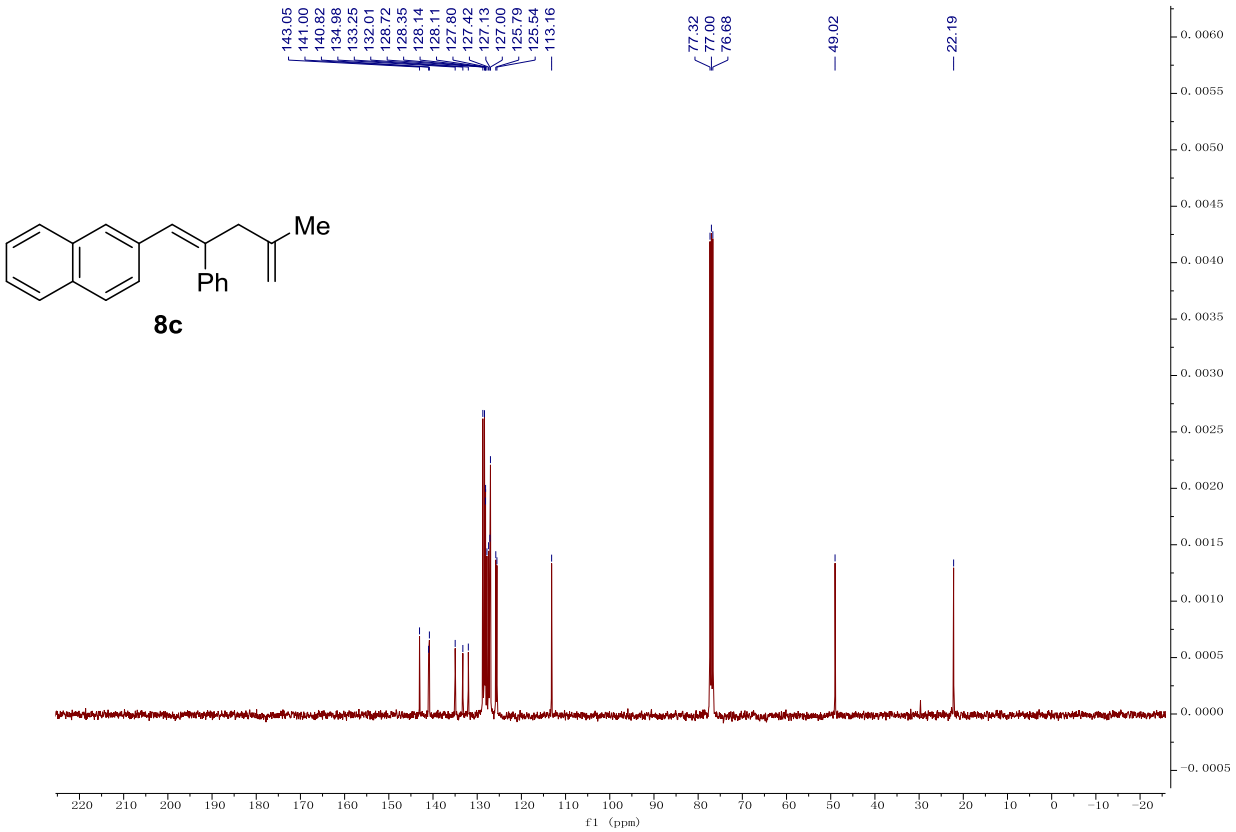
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 8b (With JEOL)



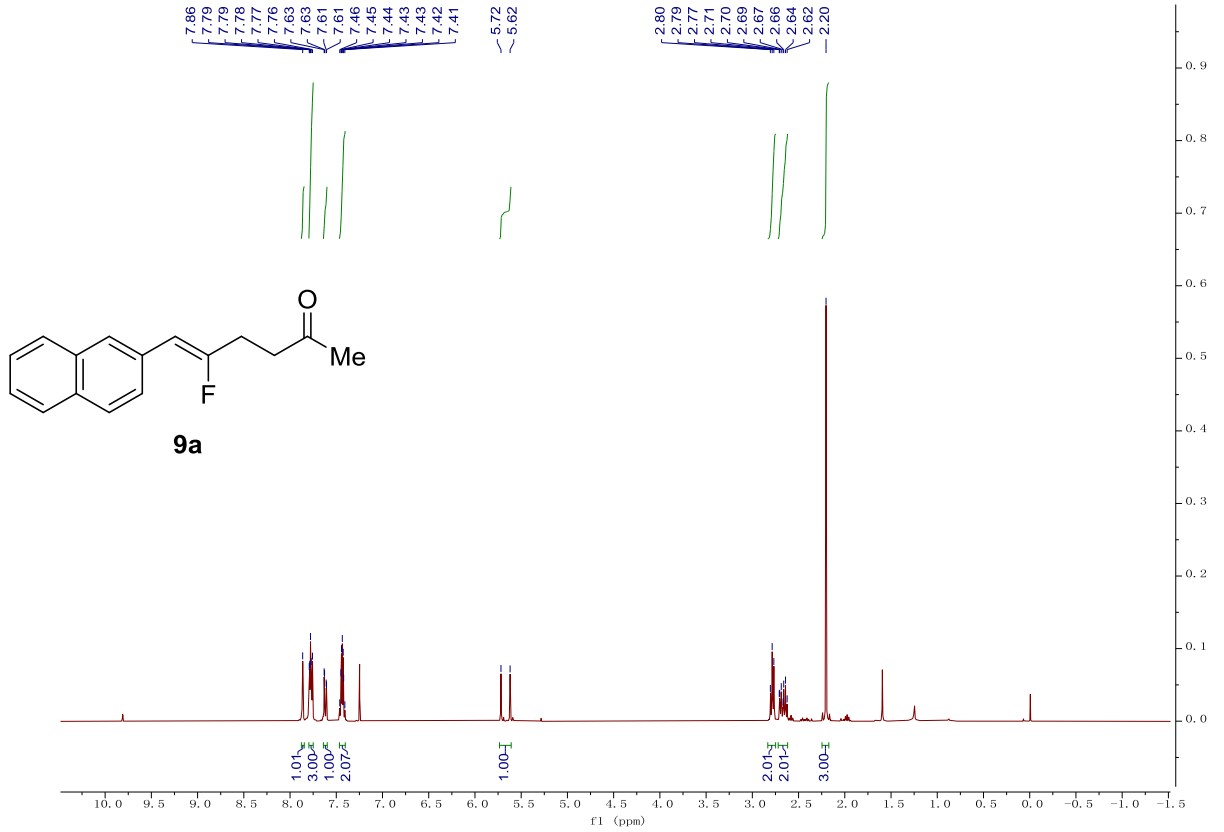
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8c (With JEOL)



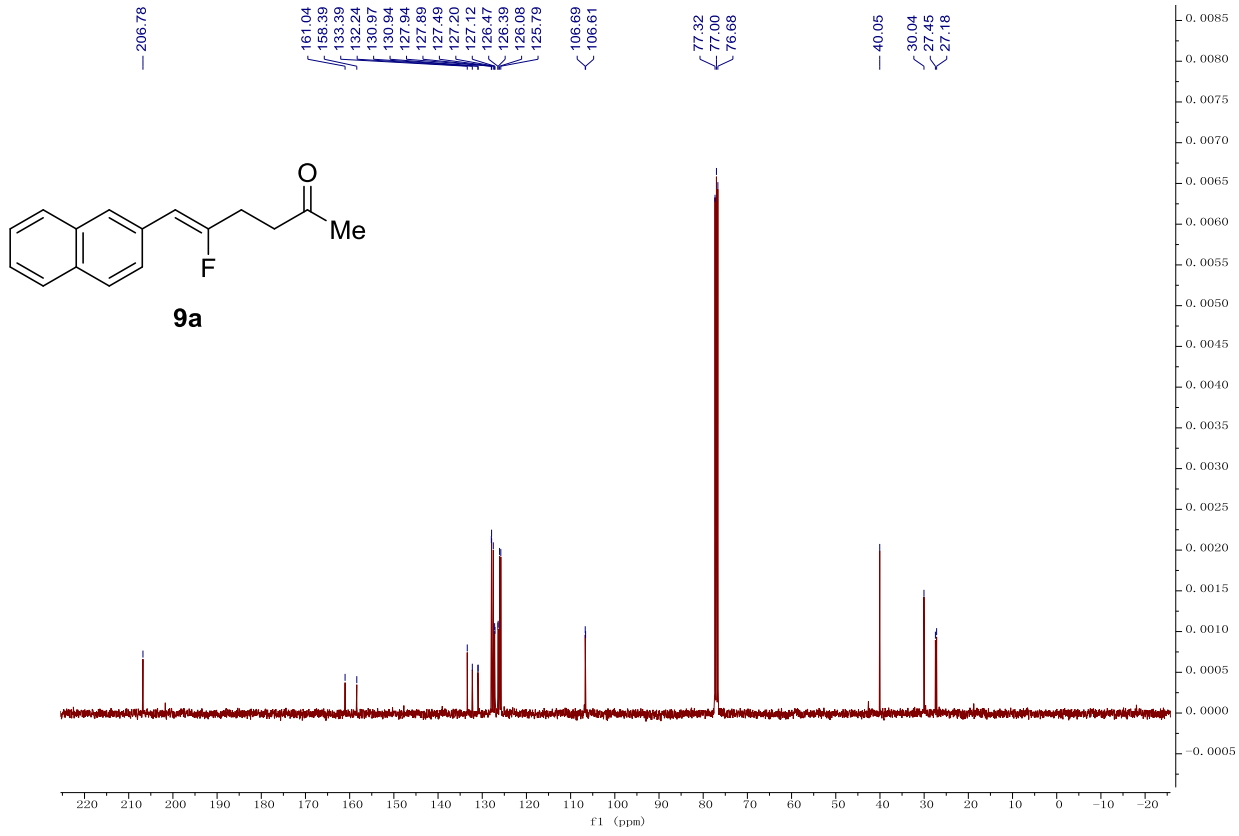
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 8c (With JEOL)



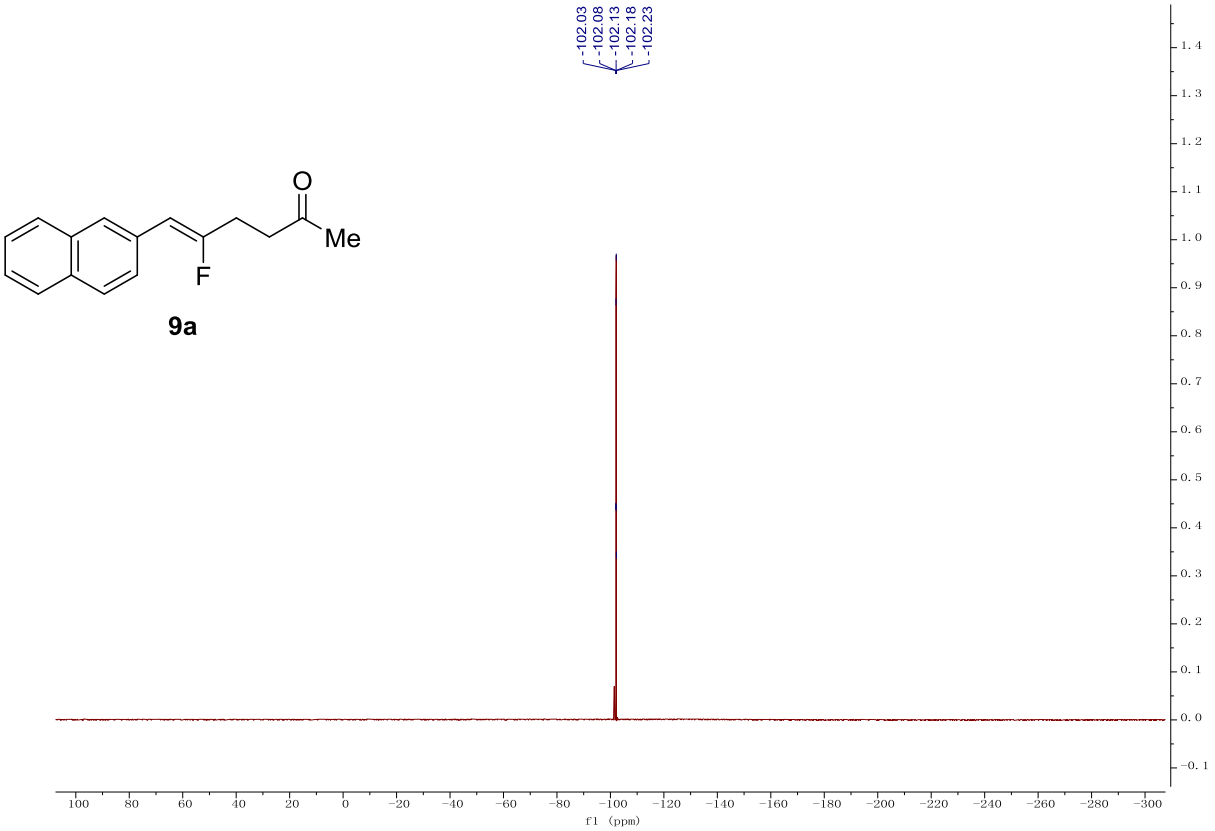
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 9a (With JEOL)



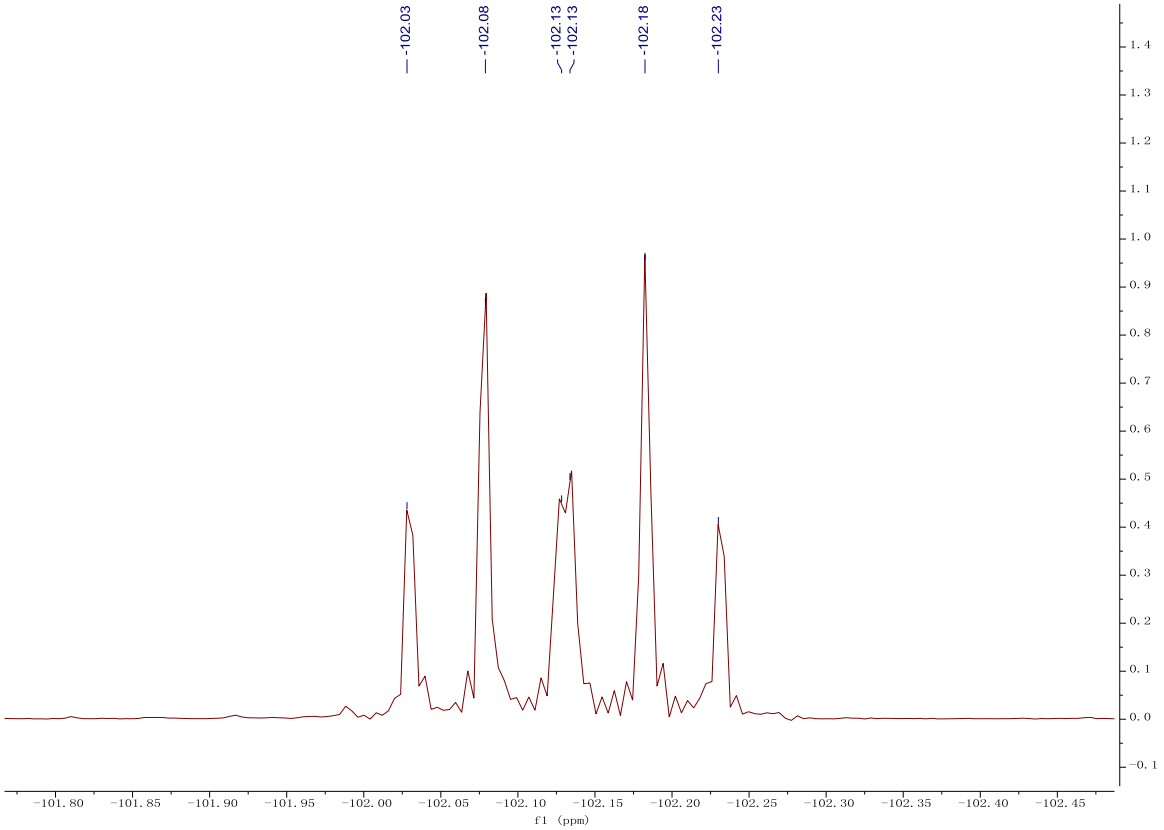
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 9a (With JEOL)



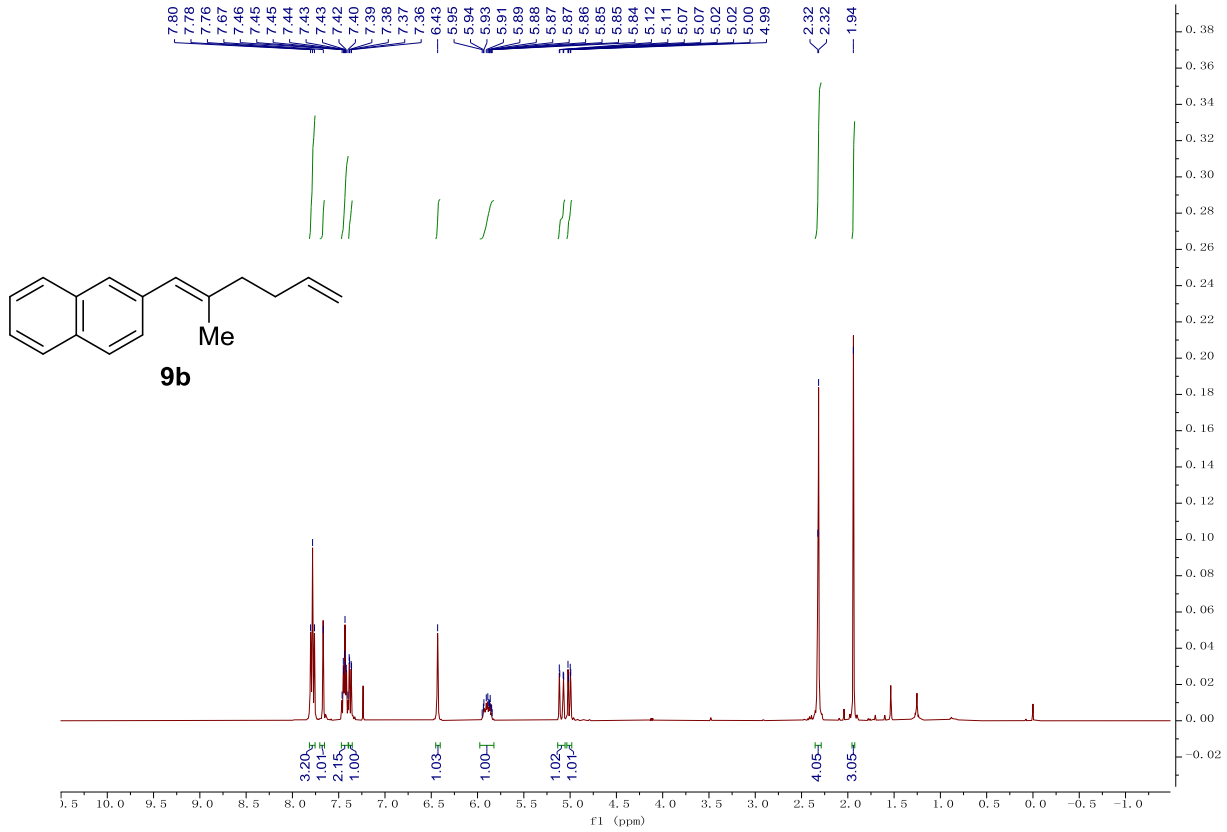
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 9a (With JEOL)



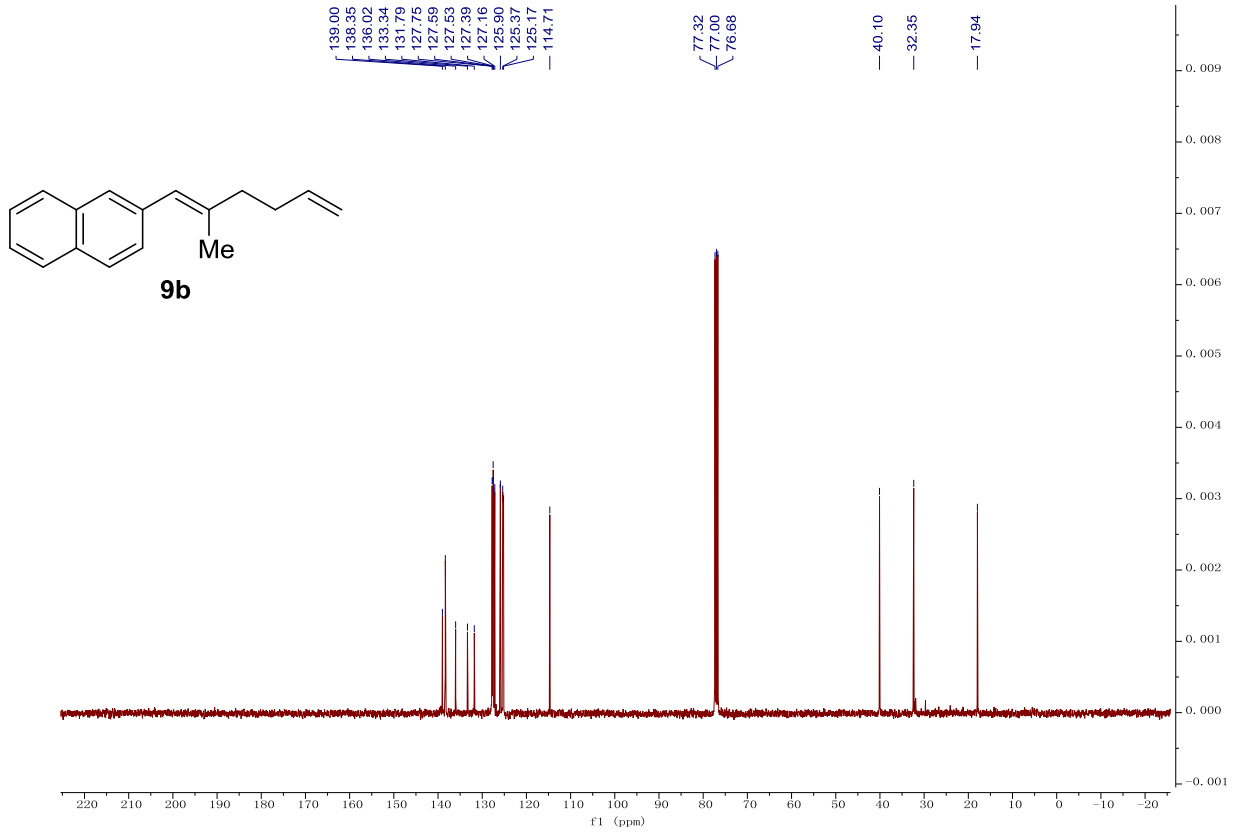
9a



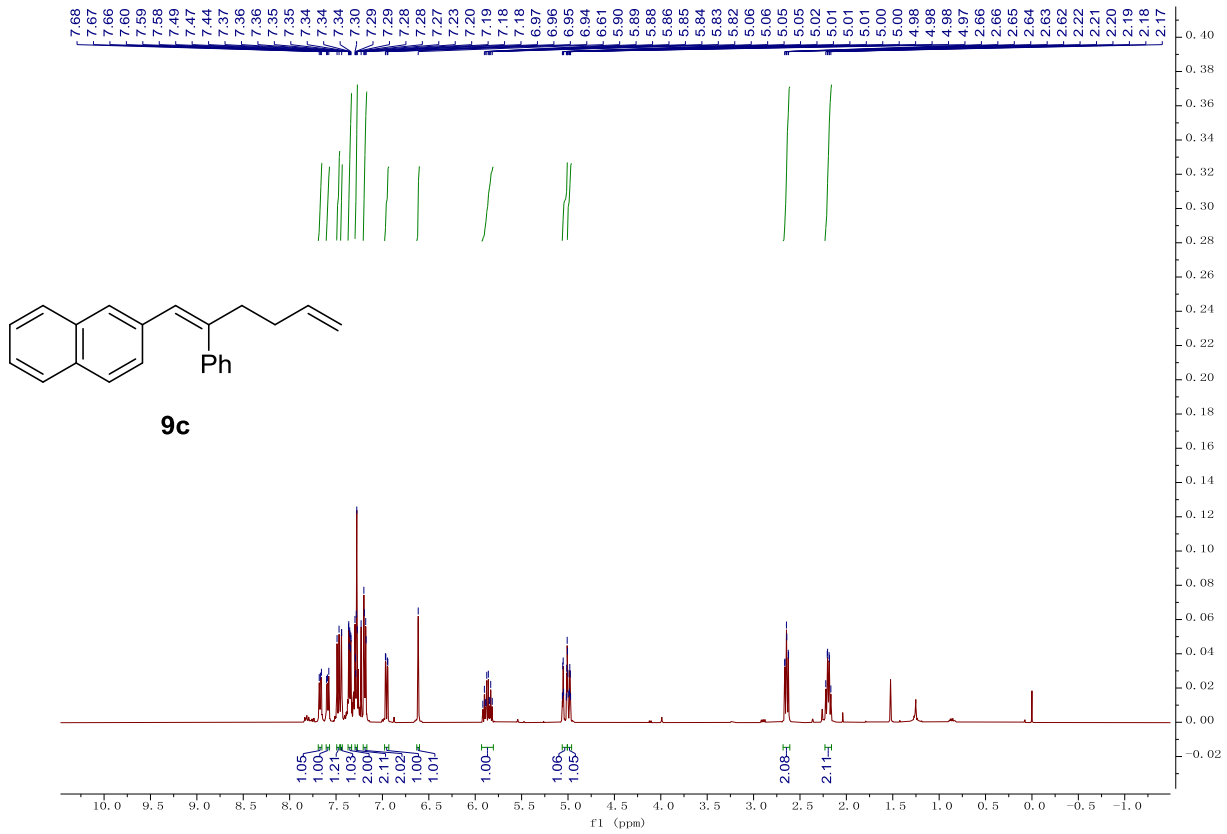
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 9b (With JEOL)



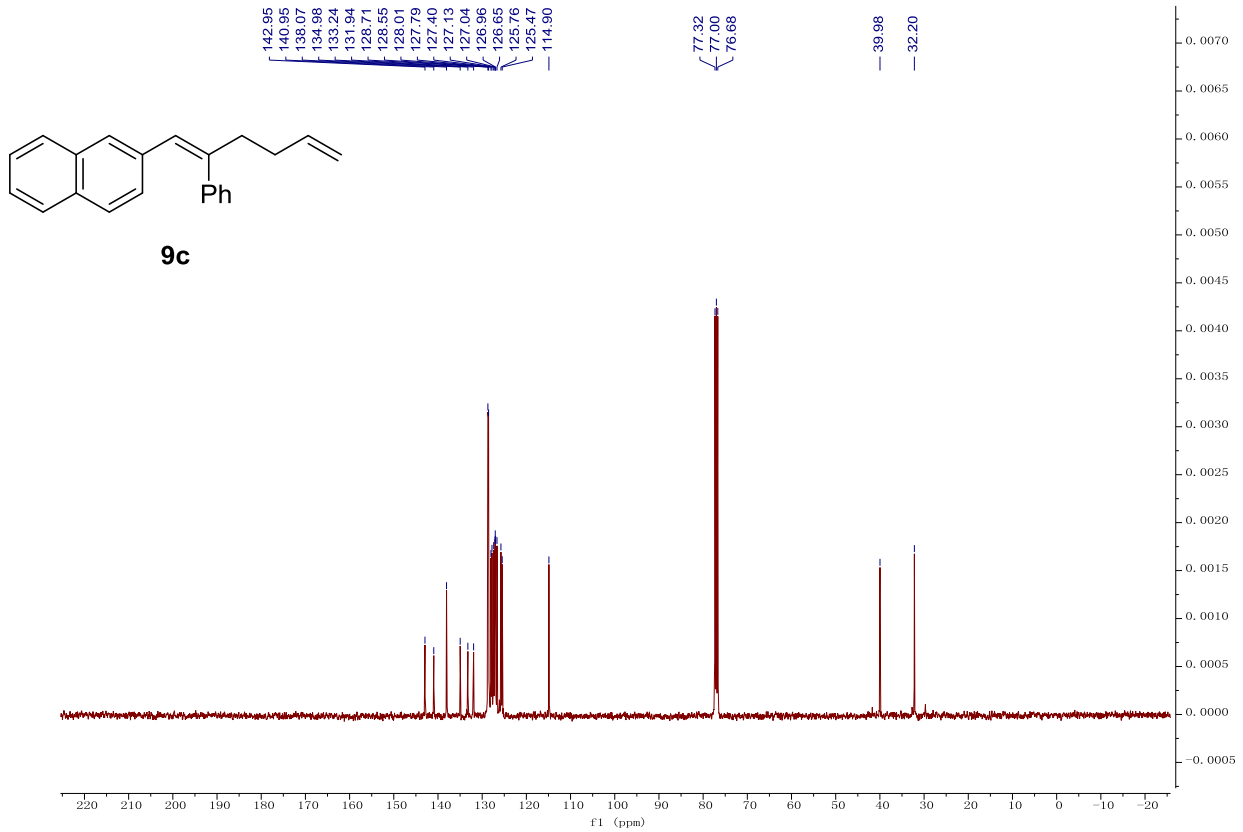
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 9b (With JEOL)



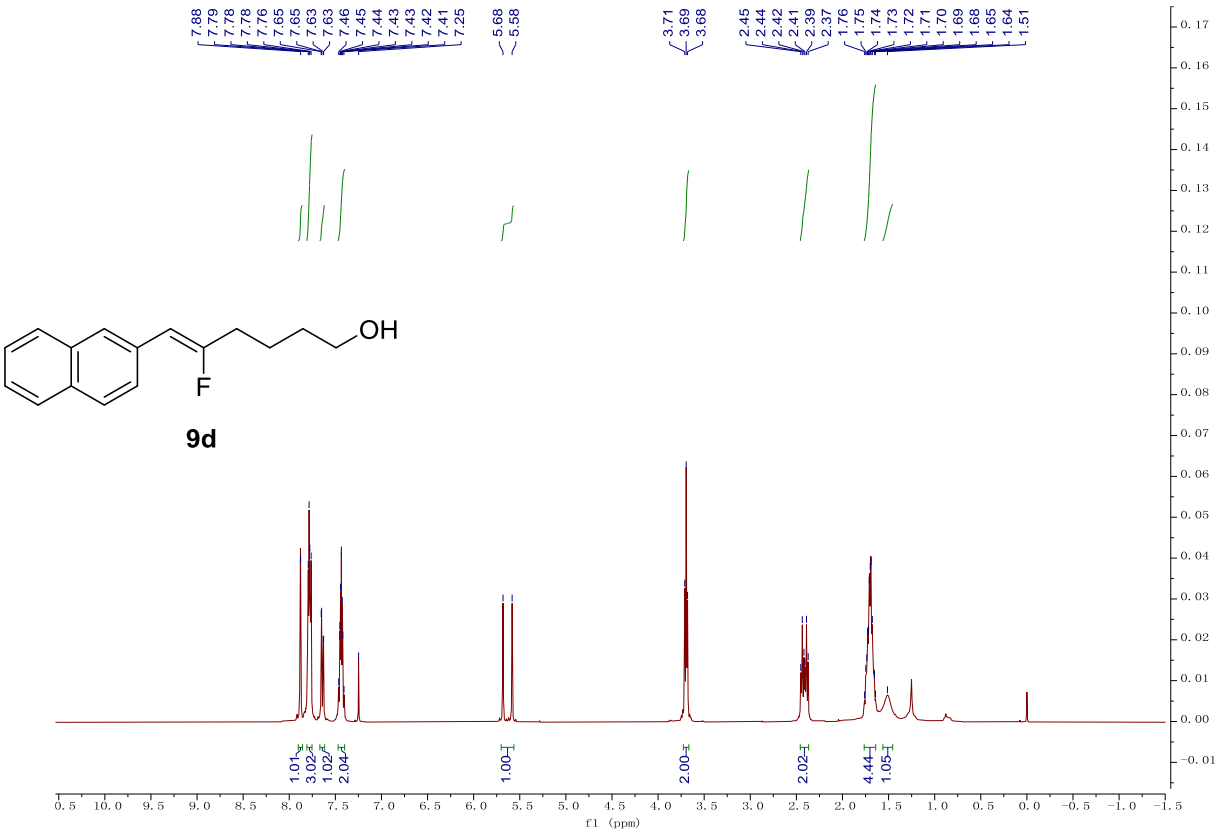
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 9c (With JEOL)



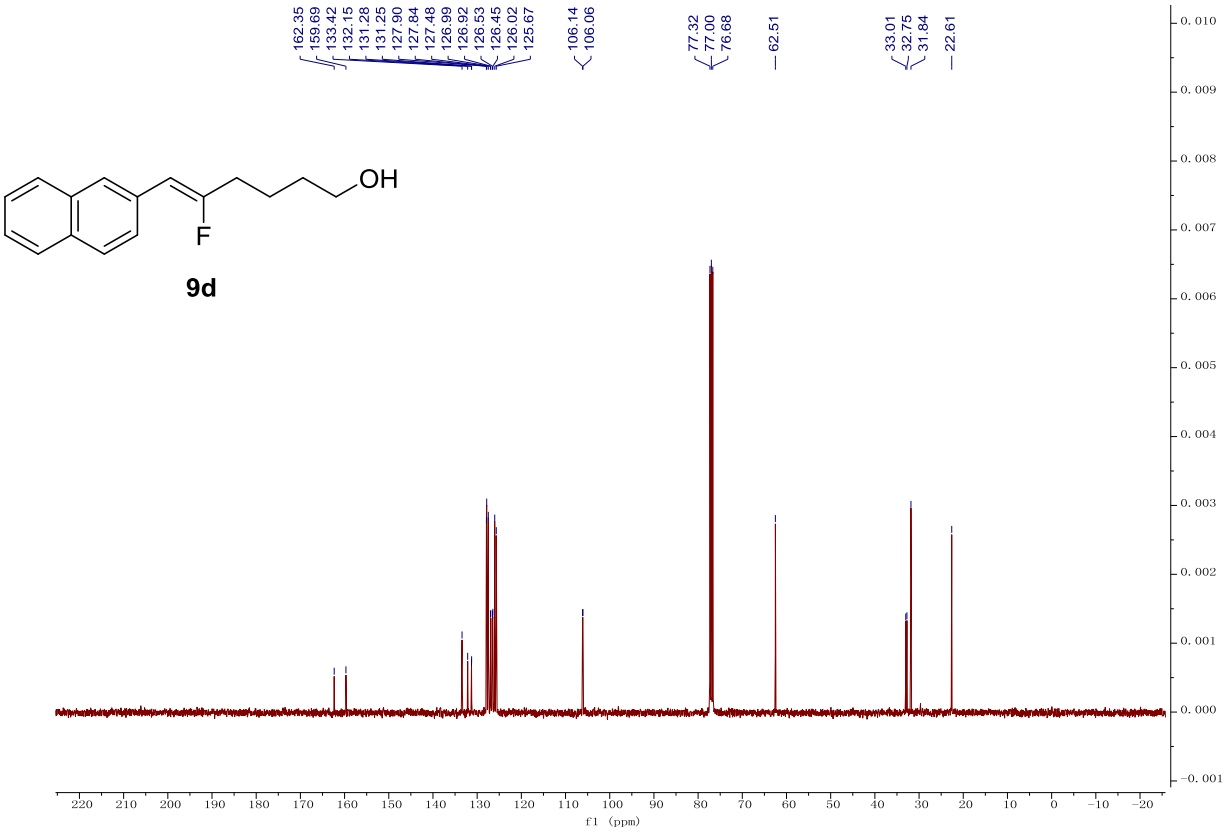
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 9c (With JEOL)



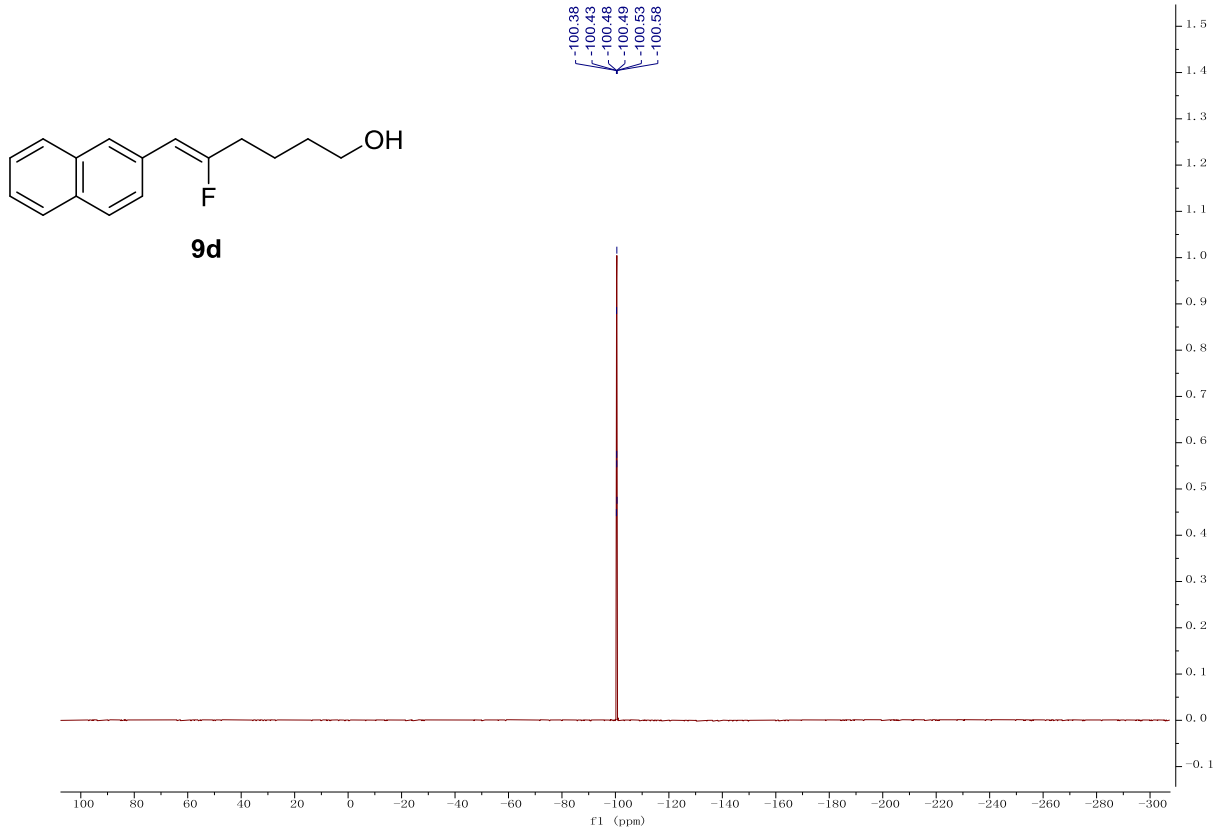
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 9d (With JEOL)

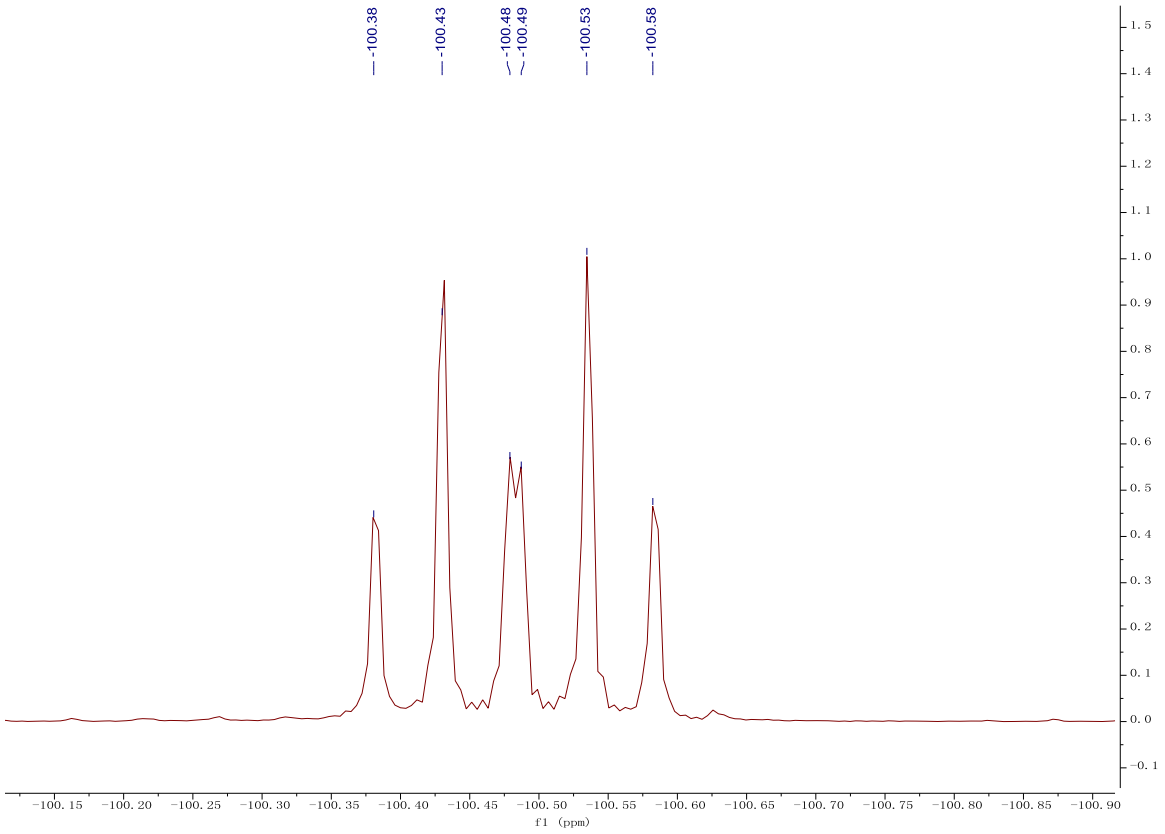


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 9d (With JEOL)

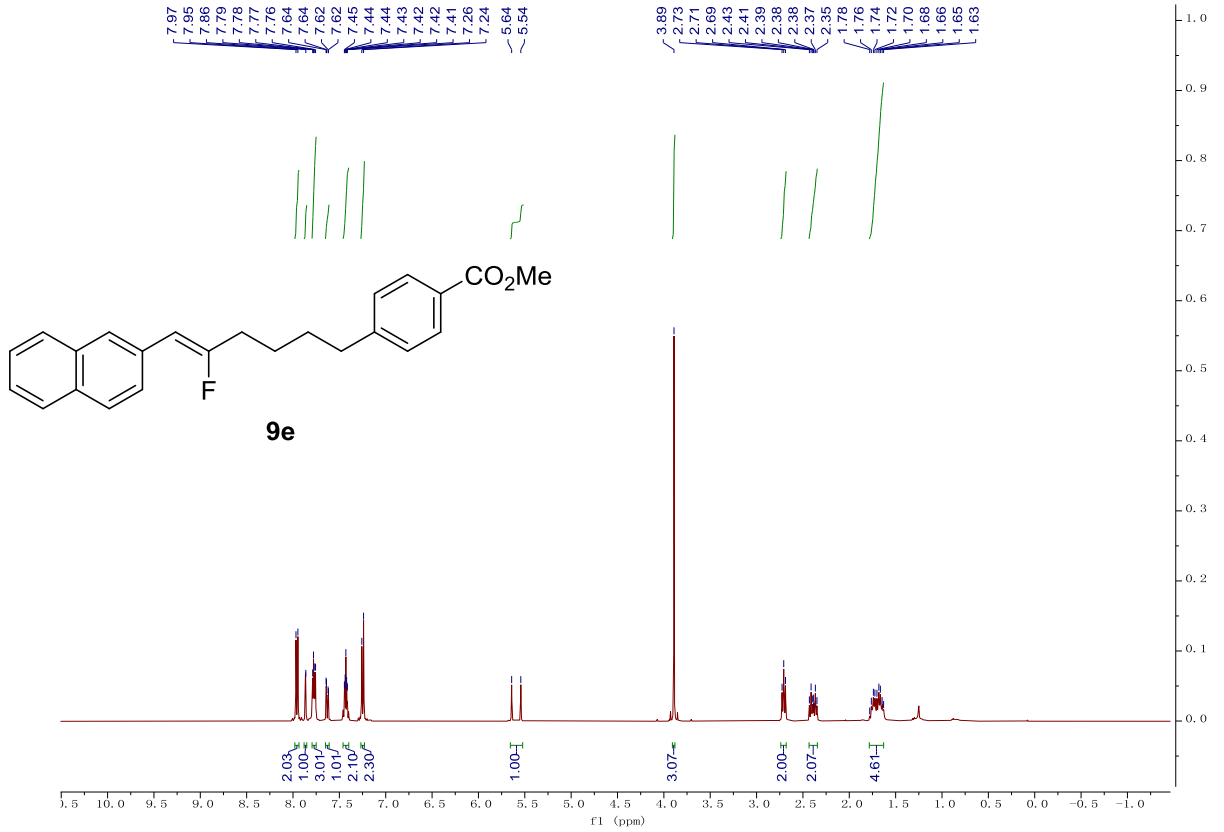


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 9d (With JEOL)

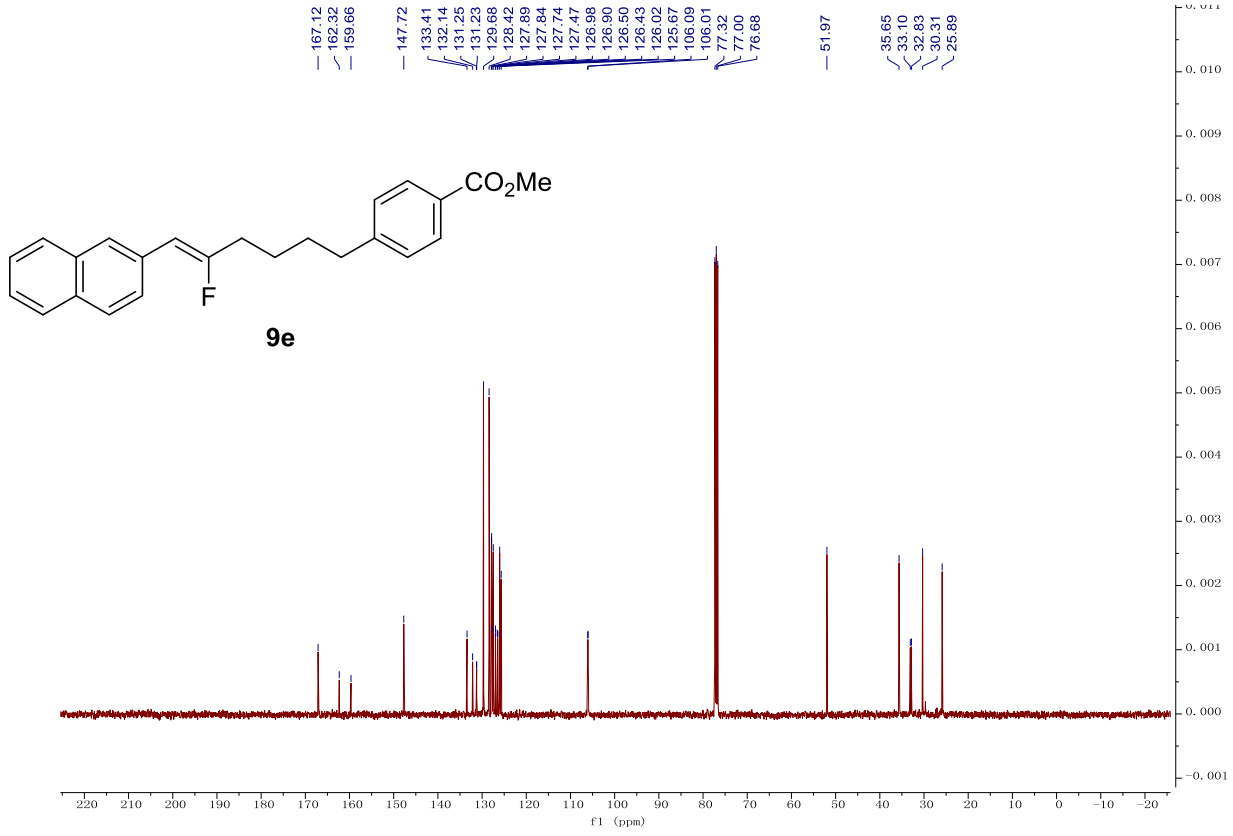




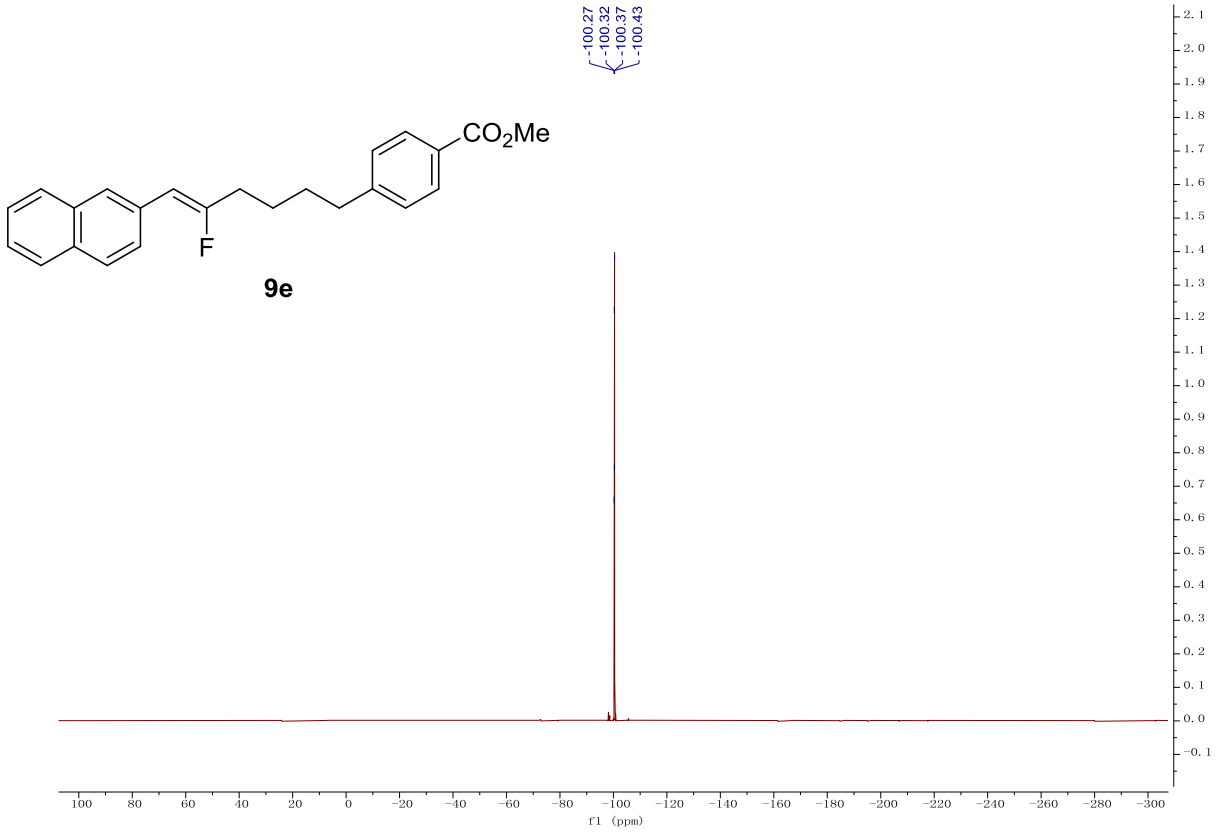
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 9e (With JEOL)

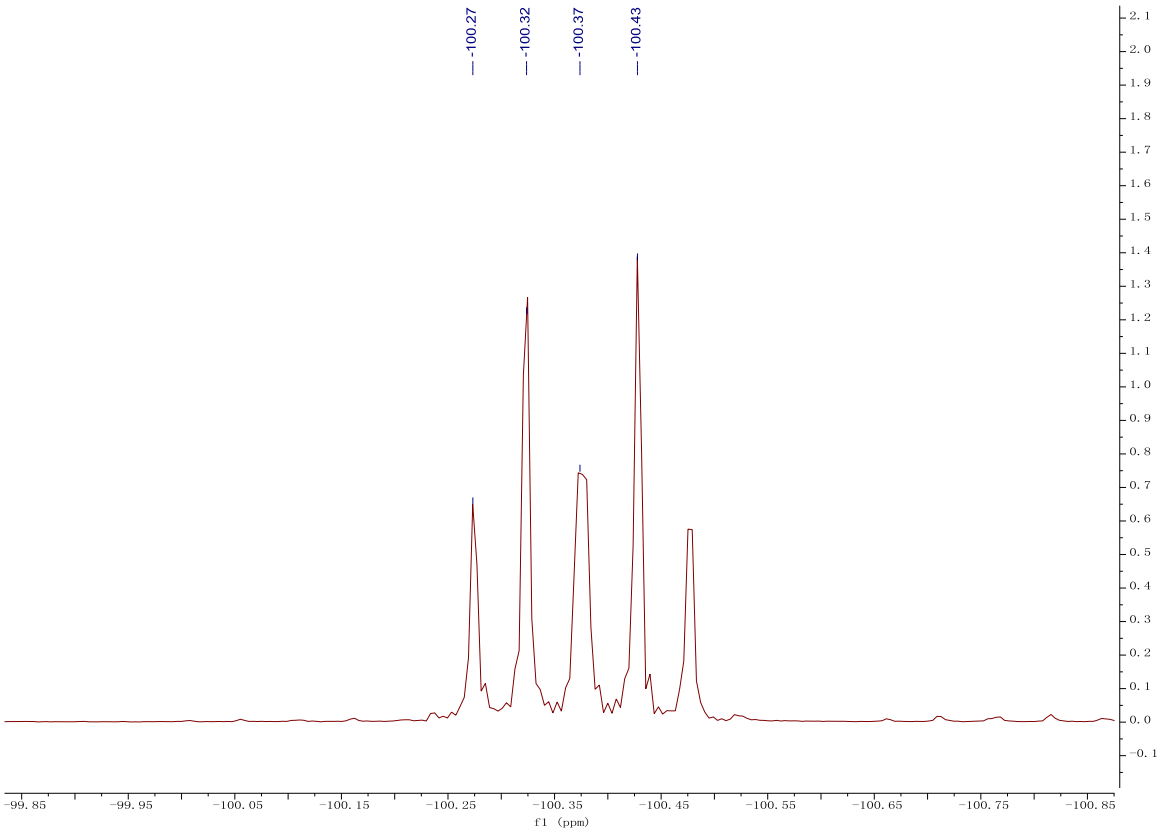


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 9e (With JEOL)

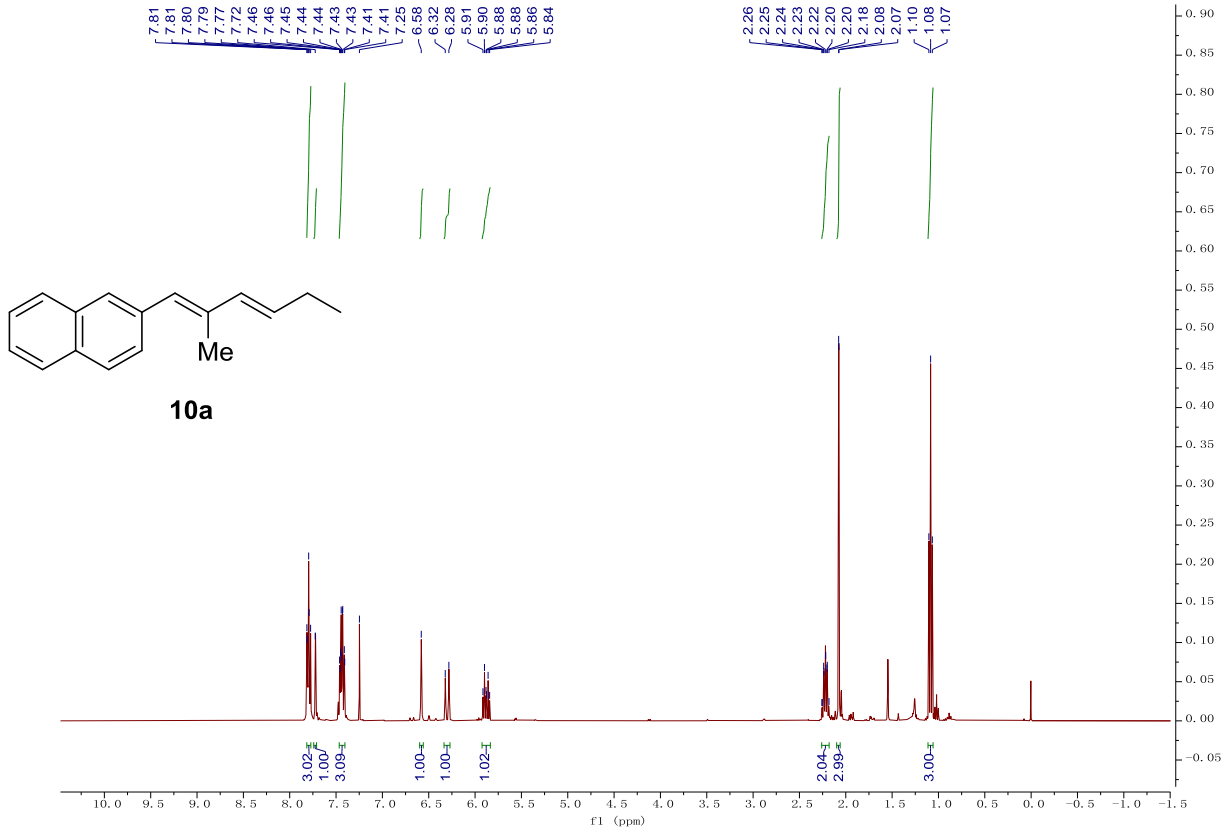


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 9e (With JEOL)

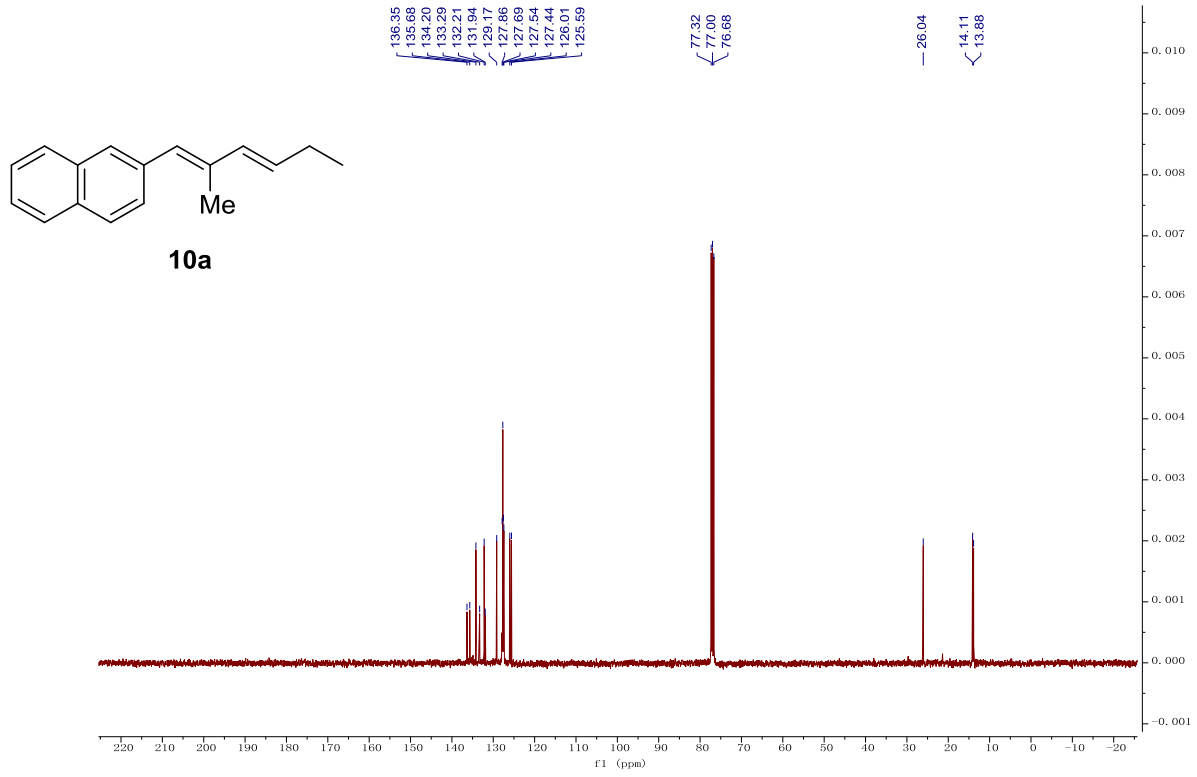




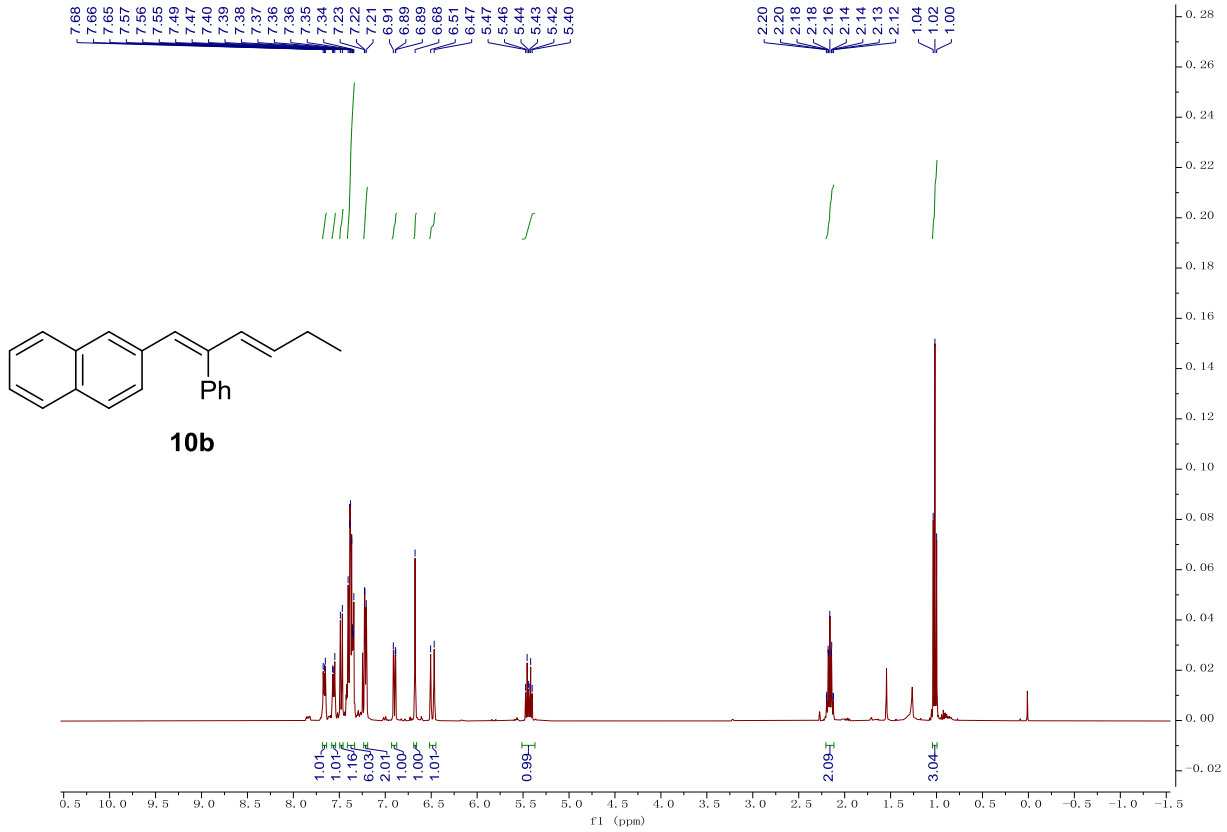
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 10a (With JEOL)



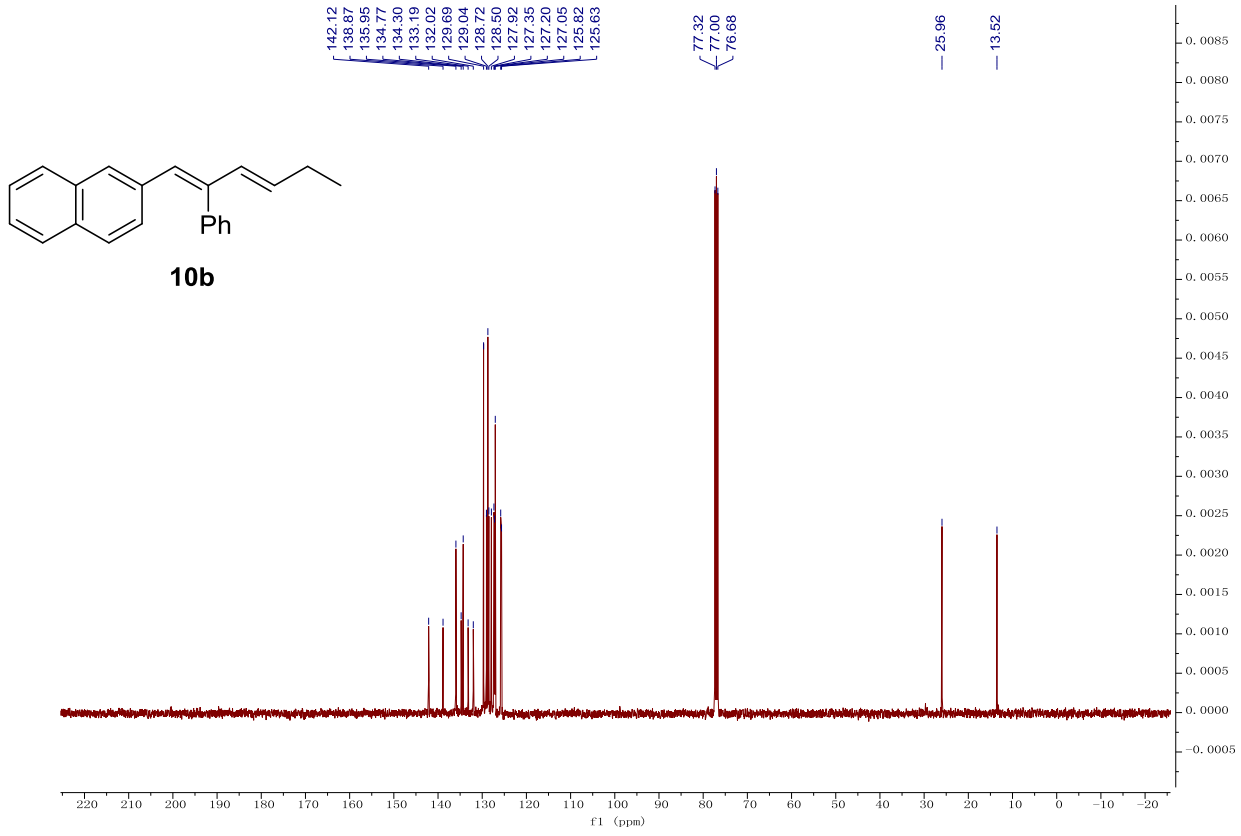
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 10a (With JEOL)



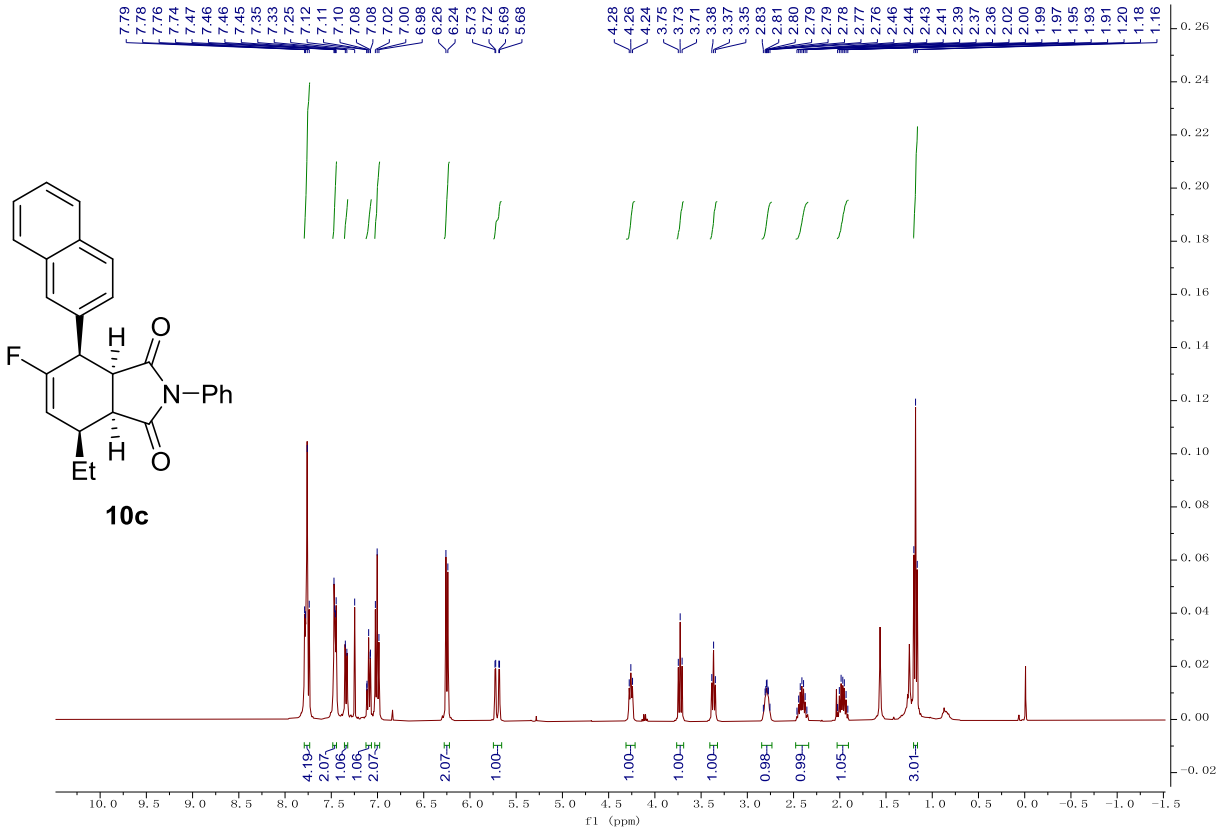
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 10b (With JEOL)



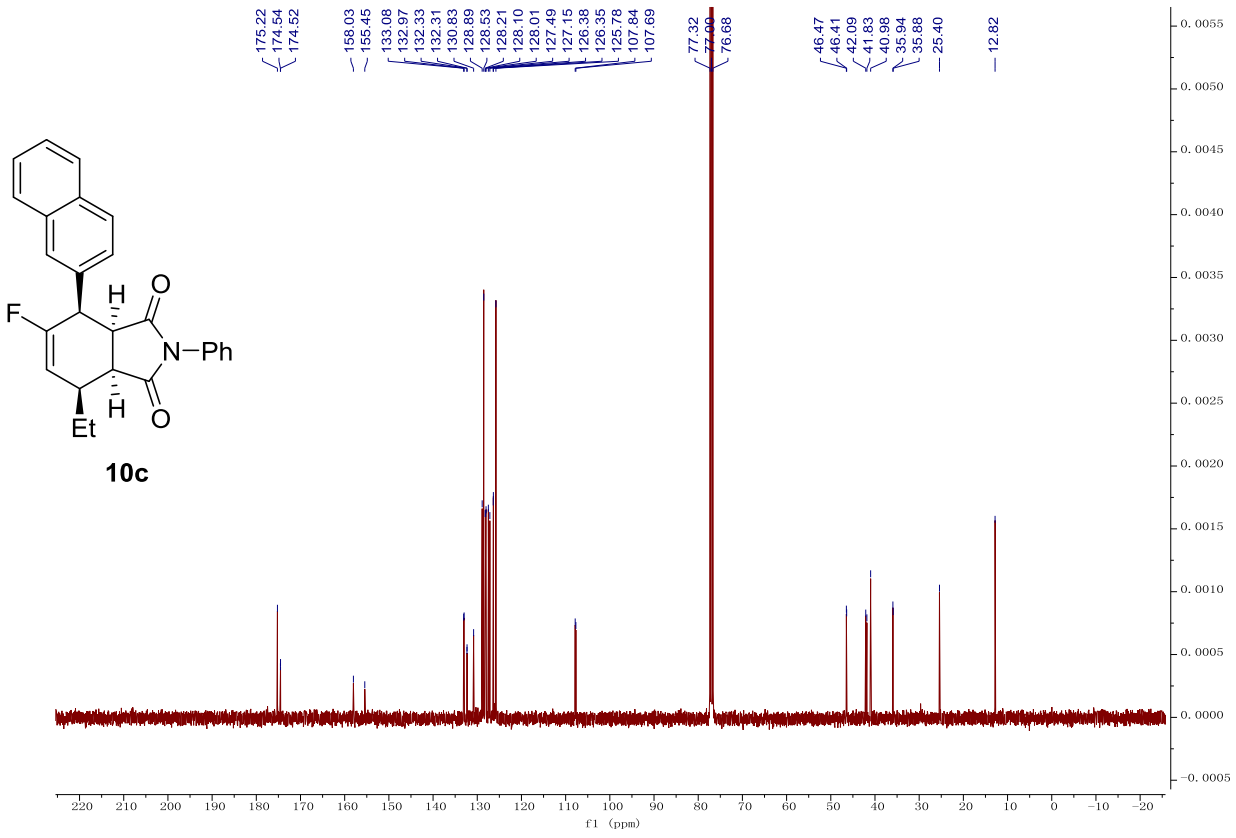
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 10b (With JEOL)



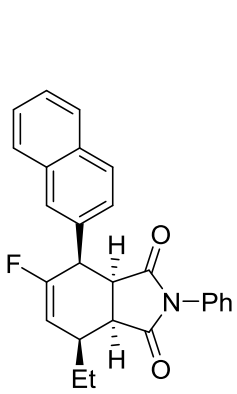
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 10c (With JEOL)



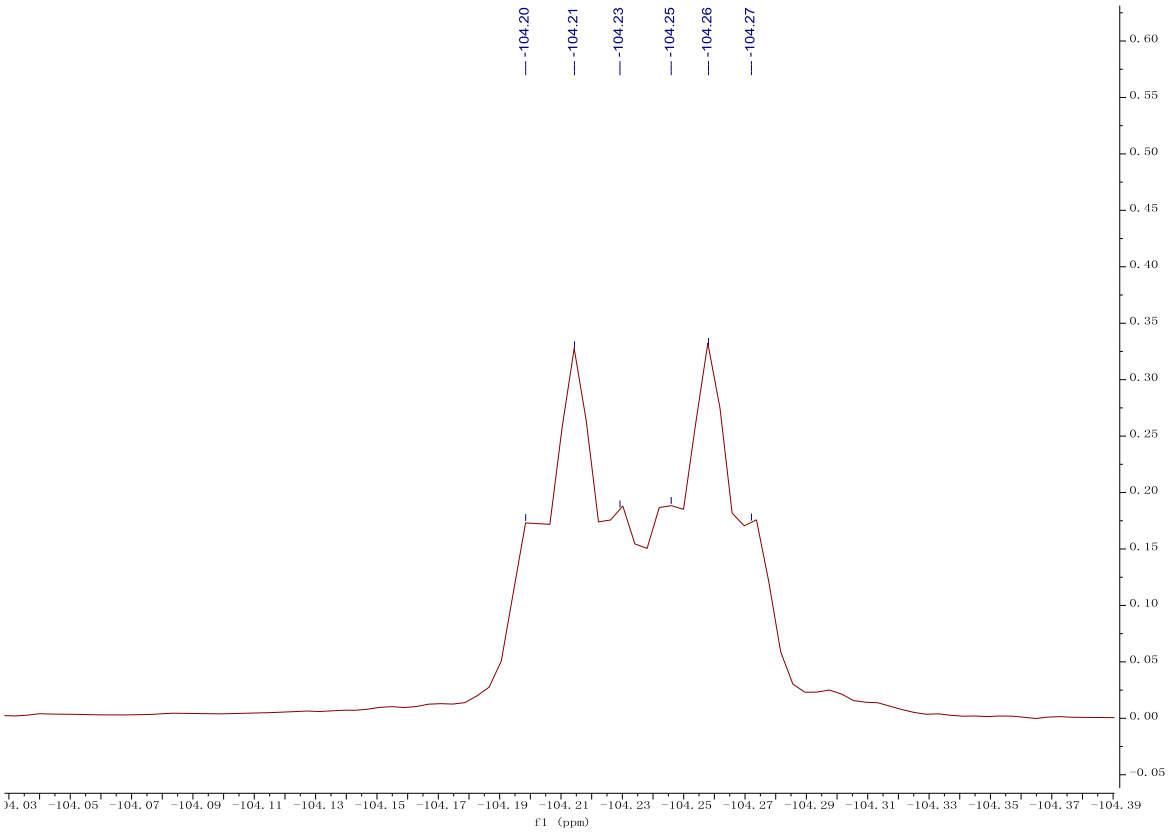
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 10c (With JEOL)



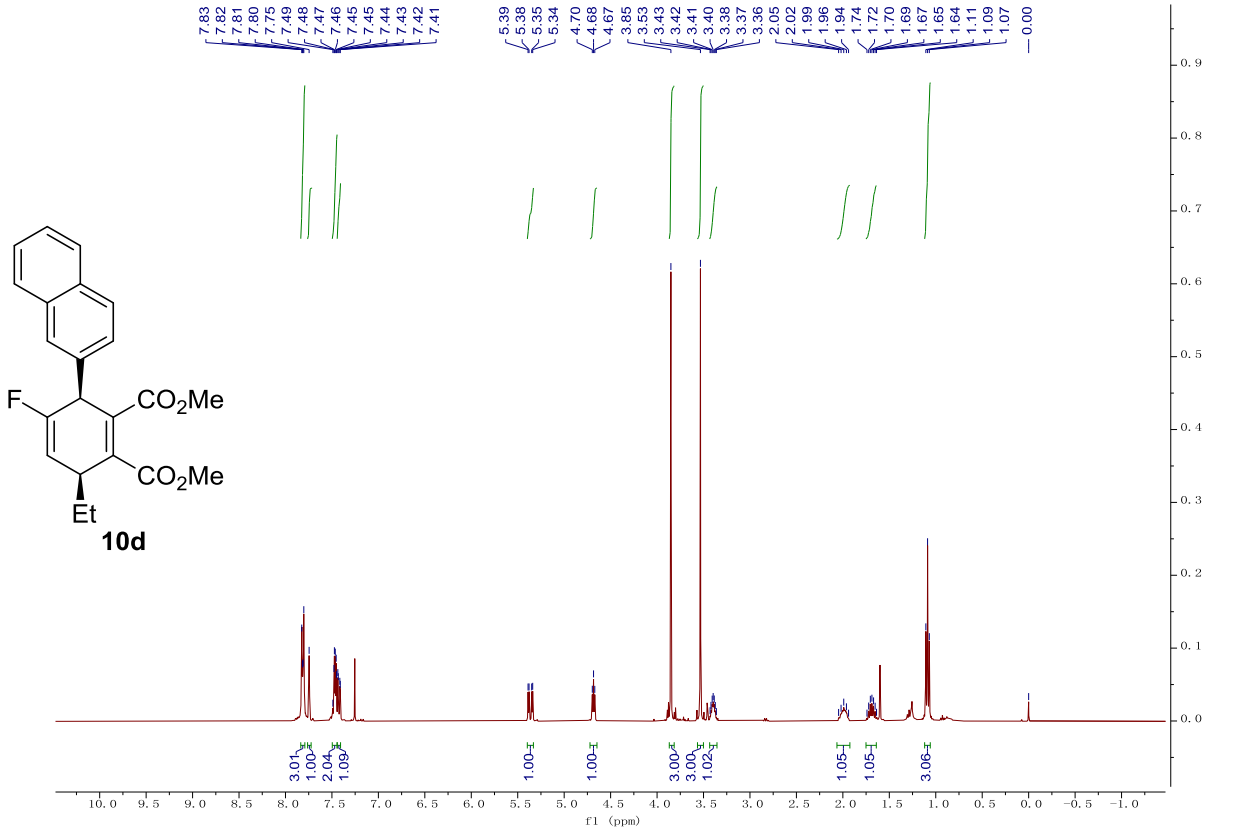
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 10c (With JEOL)



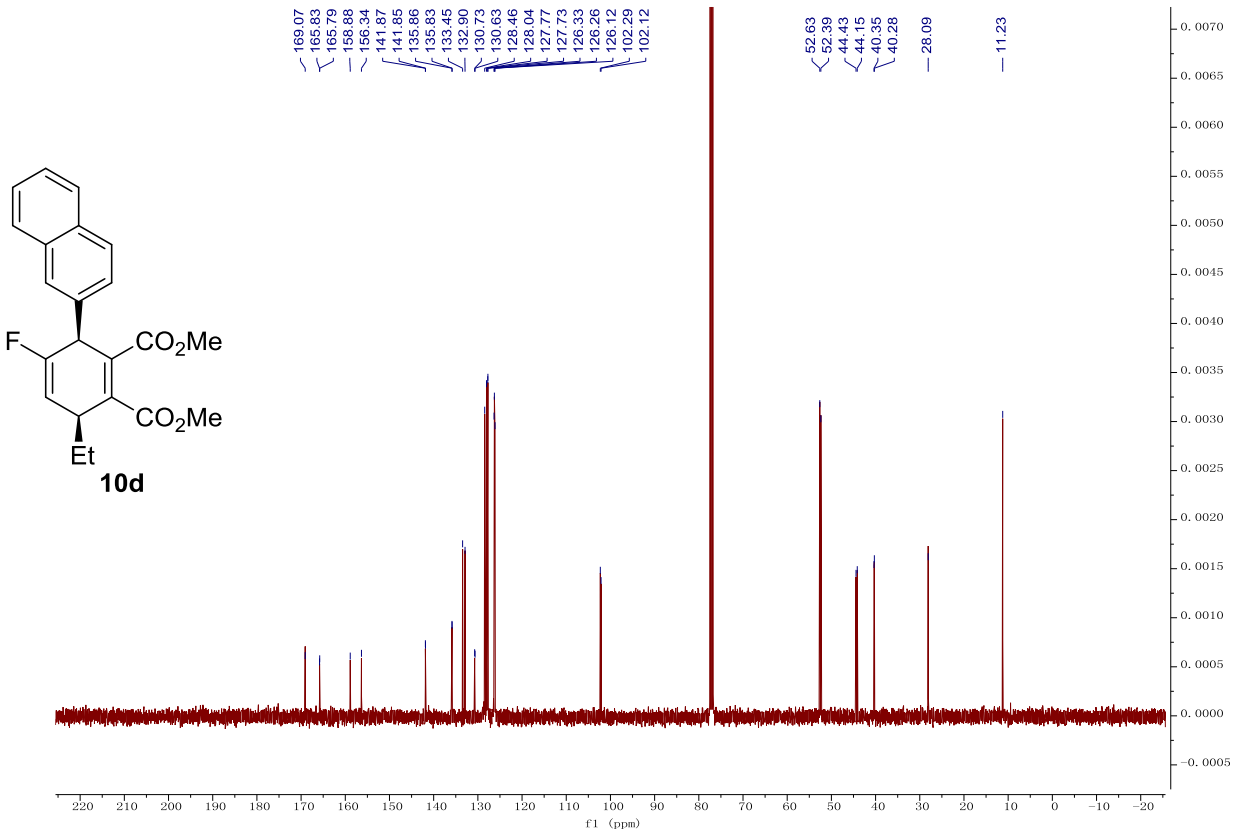
10c



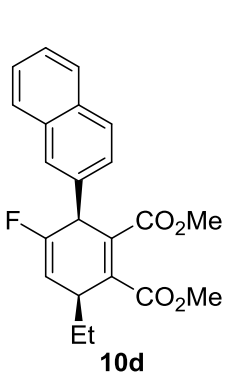
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 10d (With JEOL)



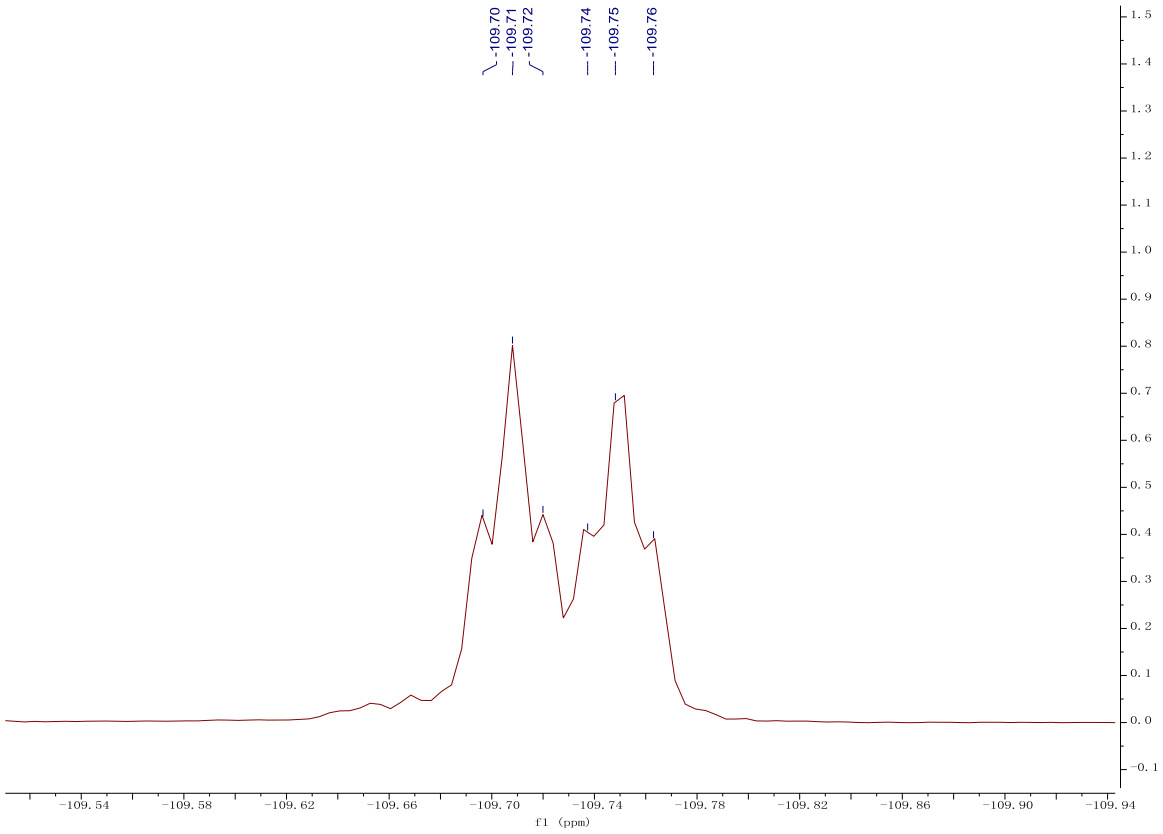
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 10d (With JEOL)



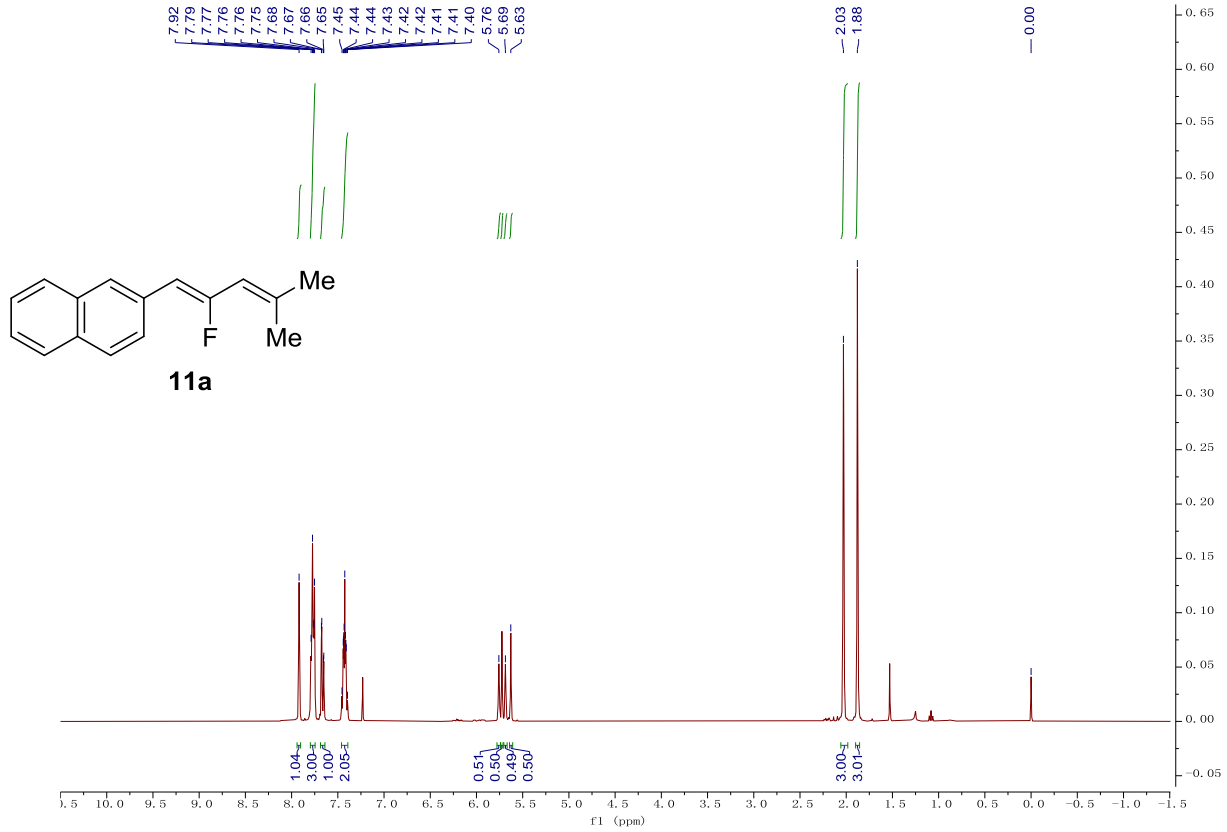
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 10d (With JEOL)



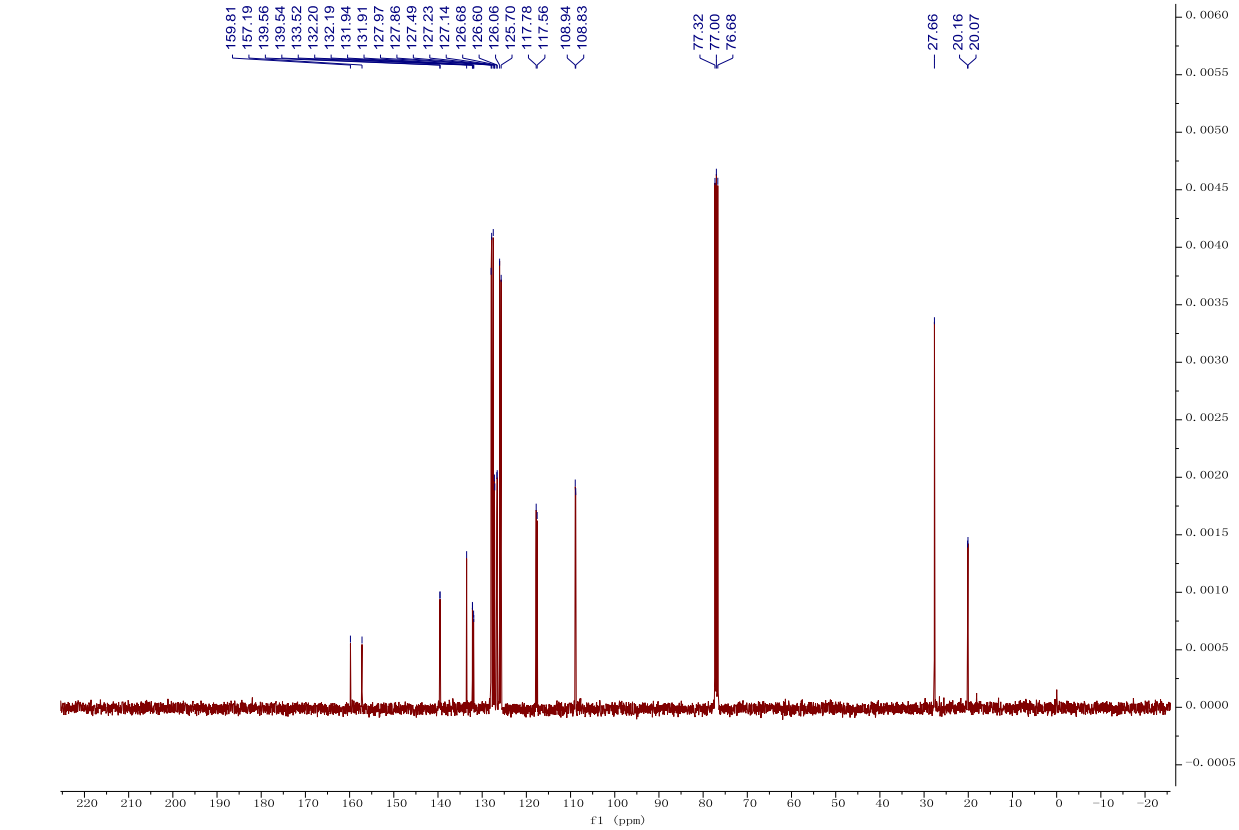
10d



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 11a (With JEOL)



^{13}C NMR (400 MHz, $CDCl_3$) spectrum of 11a (With JEOL)



^{19}F NMR (400 MHz, $CDCl_3$) spectrum of 11a (With JEOL)