Supporting Information

Iridium-Catalyzed Reductive Etherification of *α, β*-Unsaturated Ketones and Aldehydes with Alcohols

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A. General Methods

^{1}H and ^{13}C NMR spectra were recorded by using a Bruker DRX-400 spectrometer (400.0 MHz for ^{1}H; 100.0 MHz for ^{13}C), using $CDCl_3$ as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (7.26 ppm for 1H) or TMS (0 ppm for 1H) and $CDCl_3$ (77.0 ppm for ^{13}C). Data are reported as follows: Chemical shift (number of protons, multiplicity, coupling constants). Coupling constants were quoted to the nearest 0.1 Hz and multiplicity reported according to the following convention: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. GC analyses were performed on a GC-7900 chromatograph with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m).

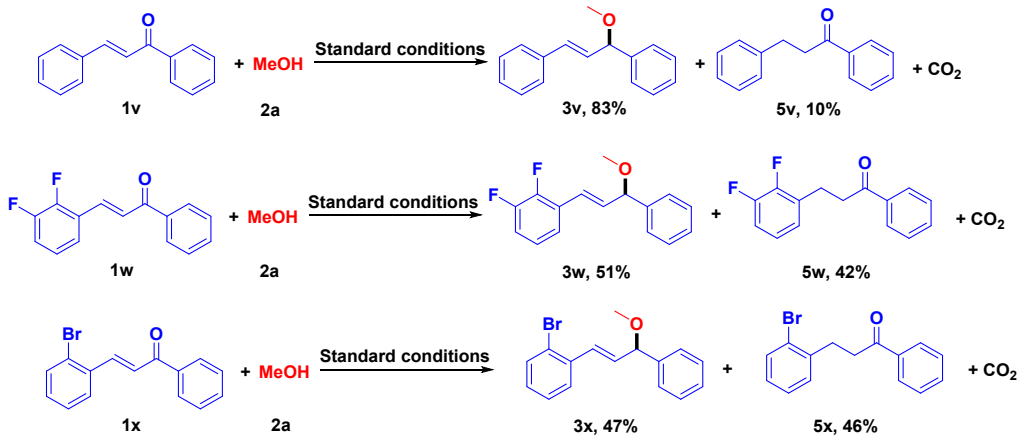
B. Procedure for the Preparation of 3

To a 25.0 mL dried Schlenk tube was added the mixture of *α, β*-unsaturated ketone (0.5 mmol), alcohols (1.0 mL), Ir catalyst (1.0 mol %), HCO_2H (10.0equiv), CF_3CO_2H (2.0equiv) in water (1.0 mL) successively. The mixture was stirred at 80 ^{o}C for 12 h under air. After the reaction was completed, the mixture was diluted with H_2O (15.0 mL), neutralized with $NaHCO_3$, and extracted with EtOAc (10.0 mL × 3). The organic extract was washed with brine (10.0 mL × 3) and dried over anhydrous $MgSO_4$. After removal of the EtOAc under vacuum, the crude product was purified by column chromatography on silica gel with hexanes or petroleum ether/ethyl acetate (10:1 to 50:1) to give the desired products.

C. Procedure for the Preparation of 5

To a 25 mL dried Schlenk tube was added the mixture of substituted chalcone (0.5 mmol), alcohols (1.0 mL), Ir catalyst (1.0 mol %), HCO_2H (10.0equiv), CF_3CO_2H (2.0equiv) in water (1.0 mL) successively. The mixture was stirred at 80 ^{o}C for 12 h under air. After the reaction was completed, the mixture was diluted with H_2O (15.0 mL), neutralized with $NaHCO_3$, and extracted with EtOAc (10.0 mL × 3). The organic extract was washed with brine (10.0 mL × 3) and dried over anhydrous $MgSO_4$. After removal of the EtOAc under vacuum, the crude product was purified by column chromatography on silica gel with hexanes or petroleum ether/ethyl acetate

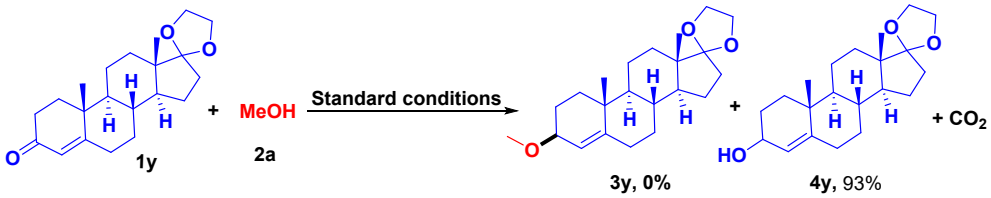
(10:1 to 50:1) to give the desired products (Scheme S1).



Scheme S1. General procedure for the synthesis of **5**.

D. Reductive etherification of 1y

To a 25.0 mL dried Schlenk tube was added the mixture of **1y** (0.5 mmol), alcohols (1 mL), Ir catalyst (1.0 mol %), HCO_2H (10.0 equiv), CF_3CO_2H (2.0 equiv) in water (1.0 mL) successively. The mixture was stirred at 80 °C for 12 h under air. After the reaction was completed, the mixture was diluted with H_2O (15.0 mL), neutralized with $NaHCO_3$, and extracted with EtOAc (10.0 mL × 3). The organic extract was washed with brine (10.0 mL × 3) and dried over anhydrous $MgSO_4$. After removal of the EtOAc under vacuum, the crude product was purified by column chromatography on silica gel with hexanes or petroleum ether/ethyl acetate (10:1 to 50:1) to give the desired products (Scheme S2).



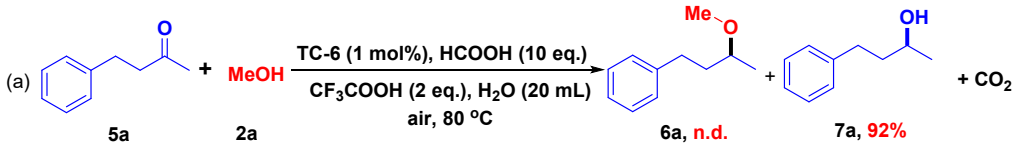
Scheme S2. General procedure for the synthesis of **4y**.

E. The kinetic isotope study of model reaction and control study

(1) control study

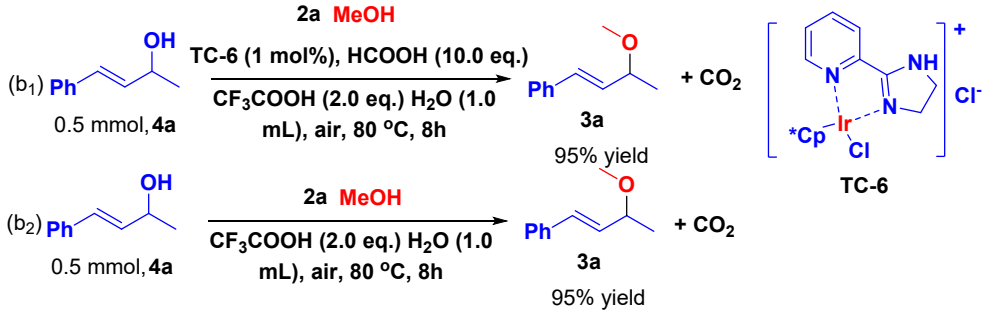
Preliminary control experiment was conducted to probe the mechanism of this reductive etherification (Scheme S3). For instance, no etherification product **6a** but reductive product

7a was formed when compound 4-phenyl-2-butanone (**5a**) was employed as the substrate under standard conditions.



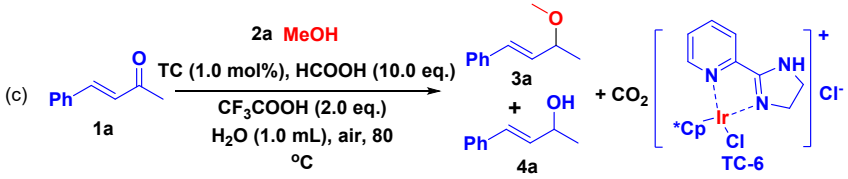
Scheme S3. Preliminary control studies.

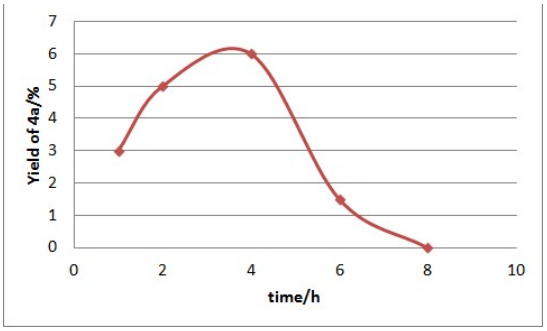
Besides, the reaction of allylic alcohol **4a** and MeOH as substrates was conducted under standard conditions. Indeed, the desired ether product of **3a** was provided in 95% yield after 4h (Scheme S4b$_1$). In fact, the corresponding product of **3a** was also formed even without iridium catalyst and HCO_2H by employing **4a** as material (Scheme S4b$_2$).



Scheme S4b. Allylic alcohol **4a** employed as substrate.

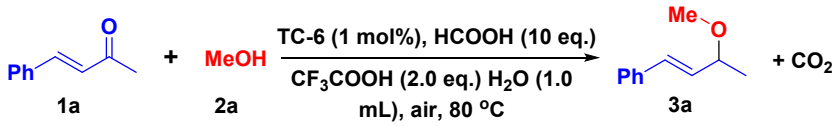
Base on above results, an additional experiment was performed to see whether the allylic alcohol was formed during the etherification and monitored its variation with time with model reaction. As expected, the allylic alcohol **4a** was observed by TLC or GC-MS. For instance, 3.0% of the allylic alcohol product **4a**determined by GC-MS was formed in 1h.The yield of **4a** was increased to 5% after 2 hours, which reached a peak of 6% about 4 hours. Nevertheless, only 1.5% of **4a** was detected after 6 hours, which was disappeared after 8 hours (Scheme S4c).





Scheme S4c. The yield of **4a** of the model reaction determined by GC-MS.

(2) The kinetic isotope study of model reaction



(a) DCO_2D as hydrogen donor

62% Deuterated product of **3a** was observed by using DCO_2D as hydrogen donor (Figure S1a) under standard conditions, which showed formic acid was directly involved in the reductive etherification process.

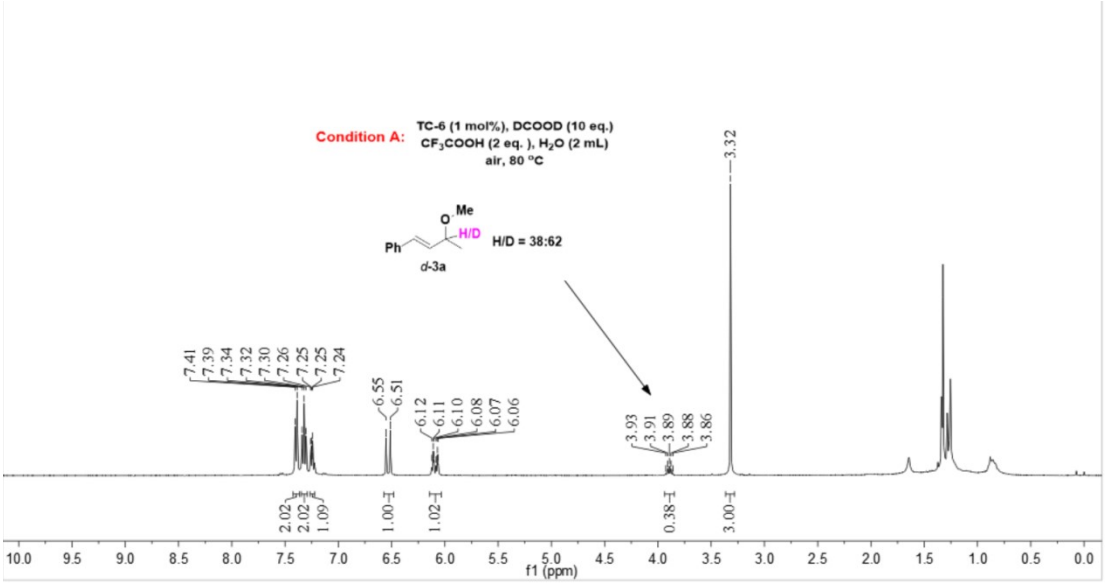


Figure S1a. DCO_2D as hydrogen donor.

(b) Instead CF_3CO_2H with CF_3CO_2D

No deuterated product of **3a** was formed instead CF_3CO_2H with CF_3CO_2D under standard conditions (Figure S1b), which indicated trifluoroacetic acid was only involved in the formation of the allyl carbocation intermediate.

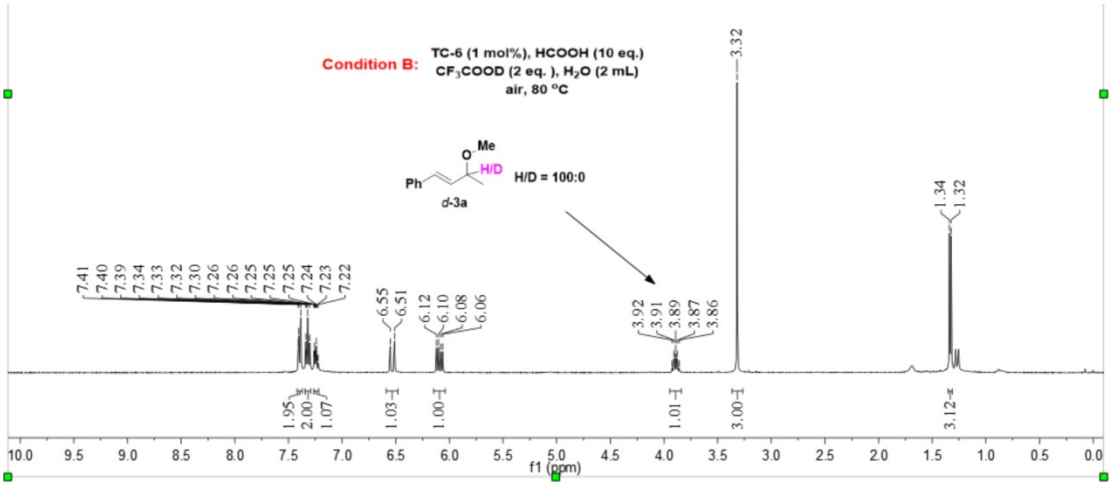


Figure S1b. Instead CF_3CO_2H with CF_3CO_2D.

(c) D_2O and DCO_2D were employed

Compared with Condition A, more deuterated product of **3a** (up to 82%) was achieved when D_2O was employed as solvent and DCO_2D was employed as hydrogen sources (Figure S1c), showing that water was also participated in the reductive etherification transformation.

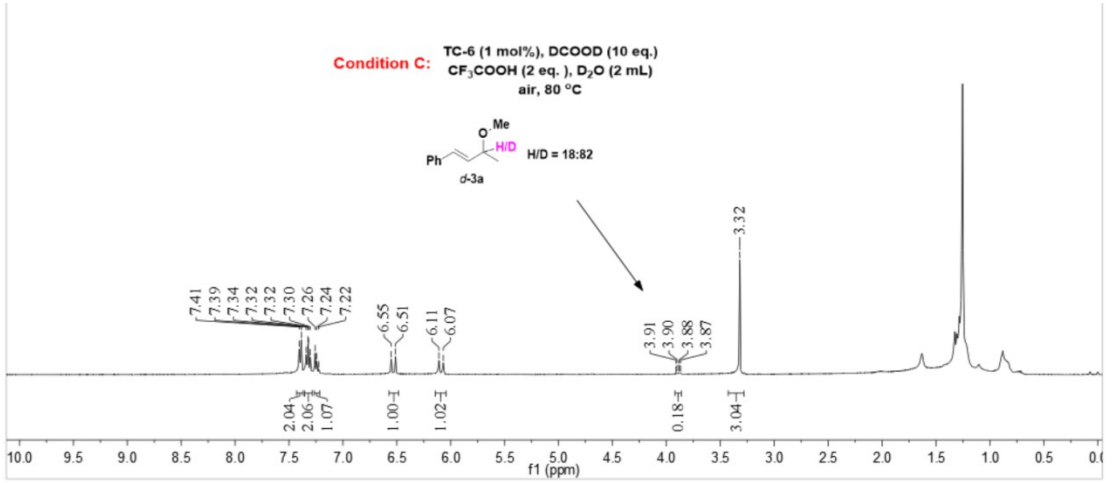


Figure S1c. D_2O and DCO_2D were employed.

(d) CF_3CO_2D and D_2O were employed

Compared with Condition B, deuterated product of **3a** (up to 18%) was achieved when D_2O was employed as solvent and CF_3CO_2D was employed (Figure S1d), showing that water was also participated in the reductive etherification transformation.

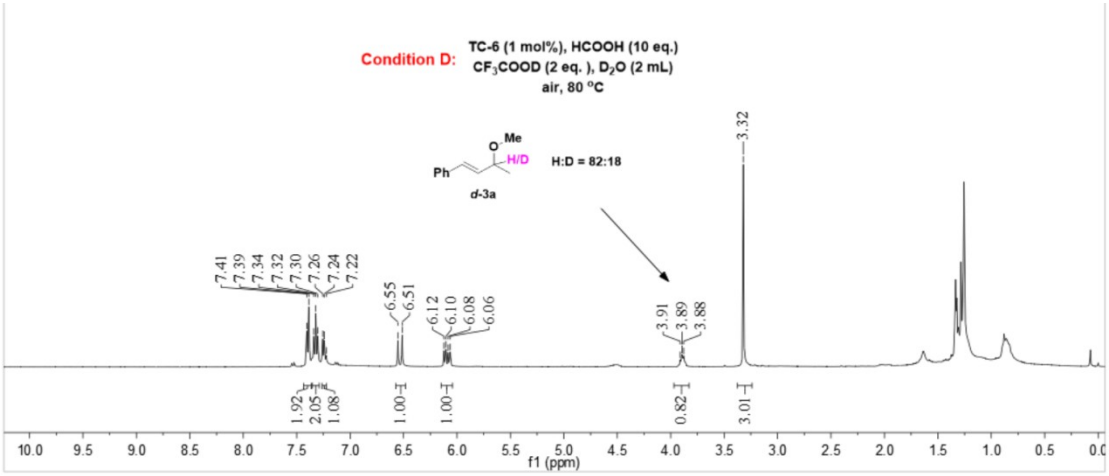


Figure S1d. CF_3CO_2D and D_2O were employed.

(e) CF_3CO_2D, D_2O and DCO_2D were employed

13% Non-deuterated **3a** was detected even CF_3CO_2D, DCO_2D and D_2O were employed (Figure S1e), which indirectly showcased that water, which came from air in this open system, was involved in the reductive etherification process. In this content, the hydrogen or deuterium incorporated product **3a** may be attributed to H-D exchange between [Ir]-H and D_2O or [Ir]-D and H_2O.

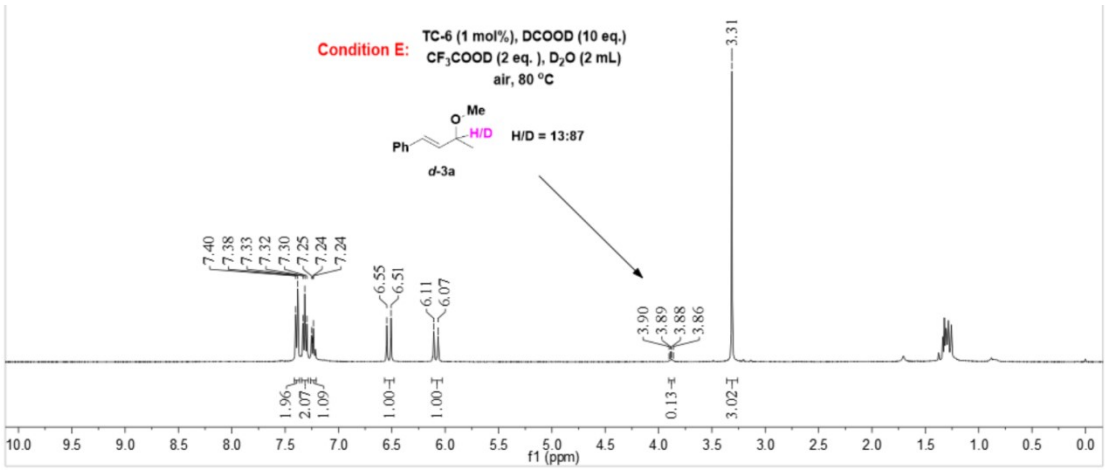


Figure S1e. CF_3CO_2D, D_2O and DCO_2D were employed.

F. Analytical Data

(3-methoxybut-1-en-1-yl)benzene (3a):[1]

Yield: 98% (79.5 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.15 (m, 5H), 6.46 (d, J = 15.9 Hz, 1H), 6.02 (dd, J = 15.9, 7.6 Hz, 1H), 3.98-3.70 (m, 1H), 3.25 (s, 3H), 1.26 (d, J = 6.2 Hz, 3H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 132.2, 130.8, 128.6, 127.6, 126. 5, 76.4, 63.6, 21.8, 15.5.

(3-ethoxybut-1-en-1-yl)benzene (3b):[2]

Yield: 96% (84.6 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.6 Hz, 2H), 7.24 (t, J = 7.3 Hz, 2H), 7.18-7.12 (m, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.05 (dd, J = 15.9, 7.5 Hz, 1H), 4.02-3.78 (m, 1H), 3.38 (dd, J = 15.4, 7.4 Hz, 1H), 3.23 (dd, J = 15.2, 7.3 Hz, 1H), 1.53 (dq, J = 14.0, 7.0 Hz, 2H), 1.25 (d, J = 6.3 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6, 127.6, 126. 5, 76.5, 70.2, 23.2, 21.7, 10.7.

(3-propoxybut-1-en-1-yl)benzene (3c):[3]

Yield: 95% (90.4 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 6.8 Hz, 3H), 6.52 (d, J = 15.9 Hz, 1H), 6.13 (dd, J = 15.9, 7.4 Hz, 1H), 4.11-3.87 (m, 1H), 3.46 (dd, J = 15.0, 7.5 Hz, 1H), 3.32 (dd, J = 14.6, 7.6 Hz, 1H), 1.63-1.57 (m, 2H), 1.36-1.32 (m, 3H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6, 127.6, 126.4, 76.4, 70.2, 23.2, 21.7, 10.7.

(3-butoxybut-1-en-1-yl)benzene (3d):[3]

Yield: 96% (98 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.1 Hz, 2H), 7.27 (d, J = 6.7 Hz, 1H), 6.54 (d, J = 15.9 Hz, 1H), 6.15 (dd, J = 15.9, 7.4 Hz, 1H), 4.11-3.91 (m, 1H), 3.53 (dd, J = 14.6, 7.4 Hz, 1H), 3.38 (dd, J = 14.5, 7.2 Hz, 1H), 1.63-1.56 (m, 2H), 1.41 (d, J = 7.3 Hz, 2H), 1.36 (d, J = 5.9 Hz, 3H), 0.95 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6, 127.6, 126.5, 76.5, 68.2, 32.1, 21.8, 19.5, 14.0

(3-(pentyloxy)but-1-en-1-yl)benzene (3e)：

Yield: 95% (103.7 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 7.5 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 6.12 (dd, J = 15.9, 7.5 Hz, 1H), 3.98 (p, J = 6.5 Hz, 1H), 3.49 (dt, J = 9.1, 6.9 Hz, 1H), 3.34 (dt, J = 9.1, 6.8 Hz, 1H), 1.58 (dd, J = 8.2, 5.7 Hz, 2H), 1.33 (d, J = 6.2 Hz, 7H), 0.90 (dd, J = 9.4, 4.5 Hz, 3H).. ^{13}C NMR

(100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6, 127.6, 126.5, 76.5, 68.6, 29.7, 28.4, 22.6, 21.7, 14.1.HRMS-ESI (m/z): calcd for $C_{15}H_{23}O$, [M+H]: 219.1749, found 219.1750.

(3-(heptyloxy)but-1-en-1-yl)benzene (3f):

Yield：97% (119.5 mg), light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.12 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.03-3.93 (m, 1H), 3.49 (dt, *J* = 9.2, 6.9 Hz, 1H), 3.34 (dt, *J* = 9.2, 6.7 Hz, 1H), 1.61-1.54 (m, 2H), 1.33 (s, 2H), 1.33-1.23 (m, 9H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6, 127.6, 126.4, 76.5, 68.6, 31.9, 30.0, 29.2, 26.2, 22.6, 21.7, 14.1. HRMS-ESI (m/z): calcd for $C_{15}H_{27}O$, [M+H]: 247.2062, found 247.2060.

(3-(isopentyloxy)but-1-en-1-yl)benzene (3g) :

Yield:94% (102.6 mg), light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.8, 7.4 Hz, 1H), 4.06-3.96 (m, 1H), 3.55 (dd, *J* = 14.7, 7.3 Hz, 1H), 3.40 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.73 (dt, *J* = 13.0, 6.4 Hz, 1H), 1.50 (dd, *J* = 12.9, 6.3 Hz, 2H), 1.35 (d, *J* = 5.9 Hz, 3H), 0.97-0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6, 127.5, 126.4, 76.5, 66.8, 38.8, 25.1, 22.8, 22.6, 21.7. HRMS-ESI (m/z): calcd for $C_{15}H_{23}O$, [M+H]: 219.1749, found 219.1748.

(3-(2-ethylbutoxy)but-1-en-1-yl)benzene (3h) :

Yield: 95% (110.4 mg), light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.12 (dd, *J* = 15.9, 7.4 Hz, 1H), 4.00-3.90 (m, 1H), 3.38 (dd, *J* = 9.3, 6.1 Hz, 1H), 3.23 (dd, *J* = 9.3, 5.7 Hz, 1H), 1.49-1.30 (m, 8H), 0.87 (td, *J* = 7.3, 3.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 132.5, 130.5, 128.6, 127.5, 126.4, 76.6, 71.0, 41.3, 23.4, 23.3, 21.7, 11.2, 11.0. HRMS-ESI (m/z): calcd for $C_{16}H_{25}O$, [M+H]: 233.1905, found 233.1909.

(3-(cyclopropylmethoxy)but-1-en-1-yl)benzene (3i) :

Yield: 84% (85.0 mg), light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.22 (m, 3H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.12 (dd, *J* = 16.0, 7.5 Hz, 1H), 3.98 (p, *J* = 6.5 Hz, 1H), 3.36 (dd, *J* = 8.8, 7.6 Hz, 1H), 3.22 (dd, *J* = 9.0, 7.2 Hz, 1H), 2.15 (dt, *J* = 14.9, 7.5 Hz, 1H), 1.74 (ddd, *J* = 12.2, 9.4, 6.0 Hz, 3H), 1.55 (dd, *J* = 12.2, 5.2 Hz, 4H), 1.33 (d, *J* = 6.4 Hz, 3H), 1.27 – 1.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 132.1, 130.8, 128.6, 127.6, 126.4, 76.2, 73.2, 21.8, 10.9, 3.2, 3.0. HRMS-ESI (m/z): calcd for $C_{14}H_{19}O$, [M+H]: 203.1436, found 203.1436.

(3-(cyclopropylmethoxy)but-1-en-1-yl)benzene (3j) :

Yield：83% (89.8 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 6.0 Hz, 2H), 7.34 (s, 2H), 7.27 (d, J = 6.3 Hz, 1H), 6.53 (d, J = 15.8 Hz, 1H), 6.14 (dd, J = 15.3, 5.7 Hz, 1H), 4.00 (s, 1H), 3.50 (t, J = 6.7 Hz, 1H), 3.36 (t, J = 6.3 Hz, 1H), 2.64-2.50 (m, 1H), 2.15-2.04 (m, 2H), 1.97-1.84 (m, 2H), 1.73 (s, 2H), 1.35 (d, J = 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6, 127.6, 126.4, 76.5, 73.3, 35.3, 25.3, 21.7, 18.6. HRMS-ESI (m/z): calcd for $C_{15}H_{21}O$, [M+H]: 217.1592, found 217.1598.

(3-(cyclopentylmethoxy)but-1-en-1-yl)benzene (3k) :

Yield：97% (111.7 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.4 Hz, 2H), 7.36-7.22 (m, 3H), 6.51 (d, J = 16.0 Hz, 1H), 6.12 (dd, J = 16.0, 7.5 Hz, 1H), 3.98 (dd, J = 13.3, 6.6 Hz, 1H), 3.36 (dd, J = 8.8, 7.6 Hz, 1H), 3.22 (dd, J = 9.0, 7.2 Hz, 1H), 2.15 (dt, J = 14.9, 7.5 Hz, 1H), 1.74 (ddd, J = 12.2, 9.4, 6.0 Hz, 3H), 1.55 (dd, J = 12.2, 5.2 Hz, 4H), 1.33 (d, J = 6.4 Hz, 3H), 1.27-1.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.4, 130.6, 128.6, 127.6, 126.5, 76.6, 73.2, 39.7, 29.8, 29.7, 25.4, 21.7. HRMS-ESI (m/z): calcd for $C_{16}H_{23}O$, [M+H]: 231.1749, found 231.1741.

(3-(cyclohexylmethoxy)but-1-en-1-yl)benzene (3l):

Yield: 92% (112.4 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.27 (d, J = 8.8 Hz, 1H), 6.53 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 7.3 Hz, 1H), 4.03-3.93 (m, 1H), 3.33 (dd, J = 15.6, 7.5 Hz, 1H), 3.18 (t, J = 7.7 Hz, 1H), 1.73 (dd, J = 31.2, 17.7 Hz, 6H), 1.34 (d, J = 6.2 Hz, 3H), 1.30-1.20 (m, 3H), 0.93 (dd, J = 24.0, 11.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 132.4, 130.5, 128.6, 127.5, 126.4, 76.5, 74.4, 38.3, 30.3, 30.3, 26.7, 25.9, 25.9, 21.7. HRMS-ESI (m/z): calcd for $C_{17}H_{25}O$, [M+H]: 245.1905, found 245.1907.

(3-(2-cyclopropylethoxy)but-1-en-1-yl)benzene (3m)：

Yield: 81% (87.6 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 6.9 Hz, 2H), 7.26 (s, 1H), 6.55 (d, J = 15.9 Hz, 1H), 6.15 (dd, J = 15.7, 7.3 Hz, 1H), 4.14 – 3.94 (m, 1H), 3.60 (dd, J = 15.4, 7.7 Hz, 1H), 3.45 (dd, J = 14.9, 7.5 Hz, 1H), 1.55 – 1.47 (m, 2H), 1.36 (d, J = 4.5 Hz, 3H), 0.81 – 0.71 (m, 1H), 0.44 (d, J = 6.6 Hz, 2H), 0.08 (d, J = 8.0 Hz, 2H). 0.08 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6,

127.6, 126.4, 76.5, 68.5, 35.1, 21.7, 7.9, 4.2, 4.2. HRMS-ESI (m/z): calcd for $C_{15}H_{21}O$, [M+H]: 217.1592, found 217.1586.

(3-(2-cyclohexylethoxy)but-1-en-1-yl)benzene (3n):[4]

Yield: 94% (121.5 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.32 (d, J = 5.5 Hz, 2H), 7.25 (s, 1H), 6.51 (d, J = 15.8 Hz, 1H), 6.21-6.00 (m, 1H), 3.98 (d, J = 5.0 Hz, 1H), 3.53 (d, J = 6.3 Hz, 1H), 3.44-3.30 (m, 1H), 1.65 (d, J = 28.1 Hz, 6H), 1.48 (s, 2H), 1.33 (s, 3H), 1.27-1.14 (m, 3H), 0.90 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.3, 130.7, 128.6, 127.6, 126.4, 76.5, 66.4, 37.4, 34.6, 33.5, 33.3, 26.6, 26.3, 21.8.

1-fluoro-4-(3-methoxybut-1-en-1-yl)benzene (3o) :

Yield: 71% (64.0 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.27 (m, 2H), 7.00 (t, J = 8.1 Hz, 2H), 6.49 (d, J = 15.9 Hz, 1H), 6.01 (dd, J = 15.9, 7.5 Hz, 1H), 4.07 – 3.71 (m, 1H), 3.32 (s, 3H), 1.32 (d, J = 6.2 Hz, 3H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 254 Hz), 132.8 (d, J = 3 Hz), 131.2 (d, J = 2 Hz), 130.2, 128.0 (d, J = 8 Hz), 115.5 (d, J = 22 Hz), 78.0, 56.1, 21.4. HRMS-ESI (m/z): calcd for $C_{11}H_{14}FO$, [M+H]: 181.1029, found 181.1024.

1-bromo-4-(3-methoxybut-1-en-1-yl)benzene (3p):[3]

Yield: 89% (107.3 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.7 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 6.49 (d, J = 15.9 Hz, 1H), 6.11 (dd, J = 15.9, 7.2 Hz, 1H), 3.97-3.84 (m, 1H), 3.34 (s, 3H), 1.34 (d, J = 6.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 132.3, 131.7, 130.1, 128.0, 121.4, 77.9, 56.2, 21.3.

1-chloro-2-(3-methoxybut-1-en-1-yl)benzene (3q):[3]

Yield: 76% (74.7 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.1 Hz, 1H), 7.35 (d, J = 7.3 Hz, 1H), 7.29 – 7.12 (m, 2H), 6.93 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9, 7.6 Hz, 1H), 3.94 (dt, J = 12.9, 6.3 Hz, 1H), 3.34 (s, 3H), 1.35 (d, J = 6.3 Hz, 3H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 134.3, 133.1, 129.7, 128.7, 127.6, 126.9, 126.9, 78.0, 56.2, 21.4.

1-(3-methoxybut-1-en-1-yl)-2,3-dimethylbenzene (3r):

Yield: 78% (74.2 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.08 (s, 2H), 6.82 (d, J = 15.7 Hz, 1H), 5.90 (dd, J = 15.7, 7.6 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.34 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H), 1.34 (d, J = 5.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.3, 134.0, 133.2, 130.3, 129.2, 125.6, 124.2, 78.3, 56.0, 21.6, 20.6 15.4. HRMS-ESI (m/z): calcd for $C_{13}H_{19}O$, [M+H]: 191.1436, found 191.1435.

2,4-difluoro-1-(3-methoxybut-1-en-1-yl)benzene (3s):

Yield: 60% (59.5 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.39 (m, 1H), 6.93 – 6.75 (m, 2H), 6.64 (d, *J* = 16.1 Hz, 1H), 6.12 (dd, *J* = 16.1, 7.4 Hz, 1H), 4.04 – 3.80 (m, 1H), 3.34 (s, 3H), 1.35 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 162.2 (dd, *J* = 12, 248 Hz), 160.2 (dd, *J* = 12, 251 Hz), 133.7, 128.2 (dd, *J* = 6, 9 Hz), 122.7, 120.8 (d, *J* = 13 Hz), 111.4 (dd, *J*= 4, 12 Hz), 104.0 (t, *J* = 26 Hz), 78.2, 56.2, 21.4. HRMS-ESI (m/z): calcd for $C_{11}H_{13}F_2O$, [M+H]: 199.0934, found 199.0944.

2-(3-methoxybut-1-en-1-yl)-1,4-dimethylbenzene (3t):

Yield：80% (76.1 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.29 (d, *J* = 10.9 Hz, 1H), 7.03 (dd, *J* = 24.0, 7.4 Hz, 2H), 6.74 (d, *J* = 15.8 Hz, 1H), 5.98 (dd, *J* = 15.7, 7.6 Hz, 1H), 4.00-3.85 (m, 1H), 3.36 (s, 3H), 2.34 (s, 6H), 1.37 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 135.5, 135.5, 132.5, 132.4, 130.2, 129.4, 128.3, 126.4, 78.4, 56.0, 21.7, 21.0, 19.4. HRMS-ESI (m/z): calcd for $C_{13}H_{19}O$, [M+H]: 191.1436, found 191.1435.

(3-methoxyhex-1-en-1-yl)benzene (3u):[5]

Yield: 83% (39.4 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28-7.23 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.04 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.69 (dd, *J* = 14.2, 6.7 Hz, 1H), 3.31 (s, 3H), 1.69-1.65 (m, 1H), 1.56-1.50 (m, 1H), 1.40 (dt, *J* = 9.0, 6.9 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 136.7, 132.2, 130.5, 128.6, 127.7, 126.5, 82.4, 56.3, 37.9, 18.7, 14.1.

(3-methoxyprop-1-ene-1,3-diyl)dibenzene (3v): [6]

Yield: 83% (93.1 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41 (s, 7H), 7.32 (s, 3H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.83 (d, *J* = 6.7 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 141.0, 136.6, 131.5, 130.1, 128.6, 127.8, 126.9, 126.6, 84.3, 56.5.

2,6-difluoro-3-(3-methoxy-3-phenylprop-1-en-1-yl)benzene (3w):

Yield: 51% (61.8 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.38 (s, 4H), 7.31 (d, *J* = 3.4 Hz, 1H), 7.12 (s, 1H), 7.03-6.93 (m, 1H), 6.88 (s, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.81 (d, *J* = 6.4 Hz, 1H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 157.3 (t, *J* = 243 Hz), 140.5, 133.9 (d, *J* = 4 Hz), 128.7, 127.9, 126.9, 122.6, 116.7 (dd, *J* = 9, 24 Hz), 115.3 (dd, *J* = 8, 24 Hz),113.3 (dd, *J* = 3, 24 Hz), 84.1, 56.6. HRMS-ESI (m/z): calcd for $C_{16}H_{15}F_2O$, [M+H]: 261.1091, found 261.1092.

1-bromo-2-(3-methoxy-3-phenylprop-1-en-1-yl)benzene (3x):

Yield: 47% (71.3 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.43-7.35 (m, 4H), 7.31 (d, J = 5.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 15.8 Hz, 1H), 6.22 (dd, J = 15.6, 6.3 Hz, 1H), 4.85 (d, J = 6.6 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.5, 133.0, 132.9, 130.3, 129.00, 128.6, 127.8, 127.4, 127.2, 126.9, 123.8, 84.1, 56.6. HRMS-ESI (m/z): calcd for $C_{16}H_{17}BrO$, [M+H]: 303.0385, found 303.0376.

(3-methoxyprop-1-en-1-yl)benzene (3aa):[8]

Yield: 78% (57.8 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (ddd, J = 30.4, 20.5, 7.3 Hz, 5H), 6.52 (t, J = 14.0 Hz, 1H), 6.28 – 6.05 (m, 1H), 4.05 – 3.78 (m, 2H), 3.47 – 3.03 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.5, 128.6, 127.7, 126.5, 126.0, 73.1, 58.0.

(3-ethoxyprop-1-en-1-yl)benzene(3ab):[8]

Yield: 63% (51.1 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 7.3 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.9, 6.0 Hz, 1H), 4.14 (d, J = 5.7 Hz, 2H), 3.55 (q, J = 7.0 Hz, 2H), 1.25 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.2, 128.6, 127.6, 126.5, 126.4, 71.3, 65.7, 15.3.

(3-butoxyprop-1-en-1-yl)benzene(3ac):[9]

Yield: 56% (53.3 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 7.0 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.8, 5.9 Hz, 1H), 4.13 (d, J = 5.9 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.40 (dd, J = 14.9, 7.4 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.1, 128.6, 127.6, 126.5, 71.4, 70.3, 31.9, 19.4, 14.0.

(3-(pentyloxy)prop-1-en-1-yl)benzene(3ad):[10]

Yield: 47% (48.0 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.24 (d, J = 7.7 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.7, 5.9 Hz, 1H), 4.13 (d, J = 5.9 Hz, 2H), 3.47 (t, J = 6.6 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.35 (s, 4H), 0.91 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.1, 128.5, 127.6, 126.5, 71.4, 70.6, 29.5, 28.4, 22.6, 14.1.

1-(3-methoxyprop-1-en-1-yl)-4-methylbenzene(3ae):[10]

Yield: 48% (38.9 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, J = 8.5 Hz, 2H), 7.12

(d, *J* = 7.4 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.29-6.16 (m, 1H), 4.08 (d, *J* = 5.9 Hz, 2H), 3.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.9, 132.5, 129.3, 126.4, 124.9, 73.2, 57.9, 21.2.

1-fluoro-4-(3-methoxyprop-1-en-1-yl)benzene(3af):

Yield: 54% (44.9 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.28 (m, 2H), 7.00 (t, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.8, 5.9 Hz, 1H), 4.07 (d, *J* = 5.9 Hz, 2H), 3.39 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 245 Hz), 132.9(d, *J* = 3 Hz), 131.3, 128.0(d, *J* = 8 Hz), 125.7(d, *J* = 2 Hz), 115.5 (d, *J* = 22 Hz), 73.0, 58.1. HRMS-ESI (m/z): calcd for $C_{10}H_{12}OF$, [M+H]: 167.0872, found 167.0876.

(3-methoxy-2-methylprop-1-en-1-yl)benzene(3ag):[11]

Yield: 38% (30.8 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.17 (m, 5H), 6.50 (s, 1H), 3.98 (s, 2H), 3.37 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137. 6, 135.1, 128.9, 128.1, 126.9, 126.5, 78.7, 57.8, 15.4.

(3-(2-methylbutoxy)prop-1-en-1-yl)benzene(3ah):

Yield: 42% (42.9 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.8, 5.9 Hz, 1H), 4.13 (d, *J* = 5.9 Hz, 2H), 3.34 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.29-3.22 (m, 1H), 1.68 (dd, *J* = 13.0, 6.5 Hz, 1H), 1.53-1.44 (m, 1H), 1.20-1.11 (m, 1H), 0.92 (dd, *J* = 6.7, 4.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.9, 128.5, 127.6, 126.7, 126.5, 75.8, 71.6, 35.1, 26.3, 16.7, 11.4. HRMS-ESI (m/z): calcd for $C_{14}H_{21}O$, [M+H]: 205.1592, found 205.1591.

2-(3-methoxybut-1-en-1-yl)naphthalene(3ai):

Yield：83% (42.9 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.60 (m, 4H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.41-7.30 (m, 2H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 15.9, 7.5 Hz, 1H), 3.93-3.78 (m, 1H), 3.27 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 133.6, 133.1, 131.9, 131.5, 128.3, 128.0, 127.7, 126.5, 126.3, 125.9, 123.6, 78.2, 56.2, 21.5. HRMS-ESI (m/z): calcd for $C_{15}H_{17}O$, [M+H]: 213.1279, found 213.1279.

(*E*)-(3-isopropoxyprop-1-en-1-yl)benzene (3aj):[12]

Yield：54% (23.8 mg), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.21 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.18 –

4.10 (m, 2H), 3.69 (dt, *J* = 12.2, 6.1 Hz, 1H), 1.21 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.91, 131.76, 128.51, 127.52, 126.91, 126.47, 70.97, 68.73, 22.17.

(*E*)-4-phenylbut-3-en-2-ol (4a):[7]

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.3 Hz, 1H), 4.52-4.41 (m, 1H), 1.36 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 136.7, 133.6, 129.4, 128.6, 128.4, 127.7, 126.5, 68.9, 23.4.

(8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (4y):

Yield: 93%, (127.4 mg), Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.28 (s, 1H), 4.19-4.10 (m, 1H), 3.93-3.83 (m, 4H), 2.24-2.13 (m, 1H), 2.06-1.94 (m, 3H), 1.81-1.67 (m, 4H), 1.52 (dd, *J* = 18.8, 7.0 Hz, 4H), 1.47-1.35 (m, 5H), 1.30-1.23 (m, 3H), 1.05 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 147.4, 123.5, 119.4, 67.9, 65.2, 64.5, 54.2, 50.0, 45.8, 37.4, 36.2, 35.4, 34.1, 32.4, 32.1, 30.6, 29.5, 22.7, 20.5, 19.0, 14.3.HR MS-ESI (m/z): calcd for $C_{21}H_{33}O_3$, [M+H]: 333.2430, found 333.2428.

1,3-diphenylpropan-1-one (5v):[13]

Yield: 10% (5.3 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.00 (d, J = 7.8 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.36-7.22 (m, 5H), 3.37-3.30 (m, 2H), 3.14-3.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 199.3, 141.3, 136.9, 133.1, 128.6, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.

3-(2,6-difluorophenyl)-1-phenylpropan-1-one (5w):

Yield: 42% (47.9 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.96 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.60-7.53 (m, 1H), 7.50-7.42 (m, 2H), 7.02-6.93 (m, 2H), 6.91-6.82 (m, 1H), 3.30 (dd, *J* = 9.7, 5.3 Hz, 2H), 3.07 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 198.6, 159.8, 159.8, 158.4, 158.4, 157.4, 156.0, 136.6, 133.3, 129.9, 129.8, 129.7, 129.6, 128.7, 128.0, 117.4, 117.3, 117.2, 117.1, 116.4, 116.3, 116.1, 116.0, 114.3, 114.2, 114.1, 114.0, 38.4, 23.8. HRMS-ESI (m/z): calcd for $C_{15}H_{13}F_2O$, [M+H]: 247.0934, found 247.0937.

3-(2-bromophenyl)-1-phenylpropan-1-one (5x):[14]

Yield：46% (66.5 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.98 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.32 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.25 (d, *J* = 7.0 Hz,

1H), 7.08 (td, J = 7.7, 1.6 Hz, 1H), 3.36-3.29 (m, 2H), 3.18 (dd, J = 9.2, 5.8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 140.6, 136.7, 133.2, 132.9, 130.8, 128.6, 128.1, 128.0, 127.7, 124.4, 38.6, 30.8.

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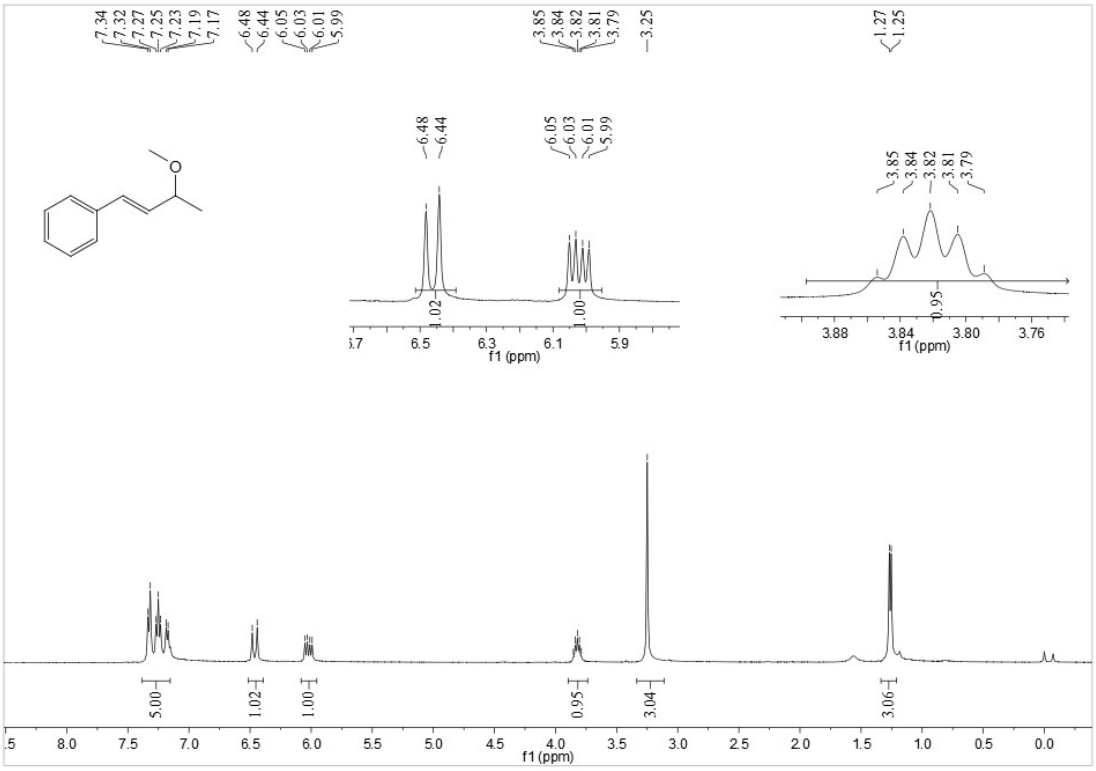
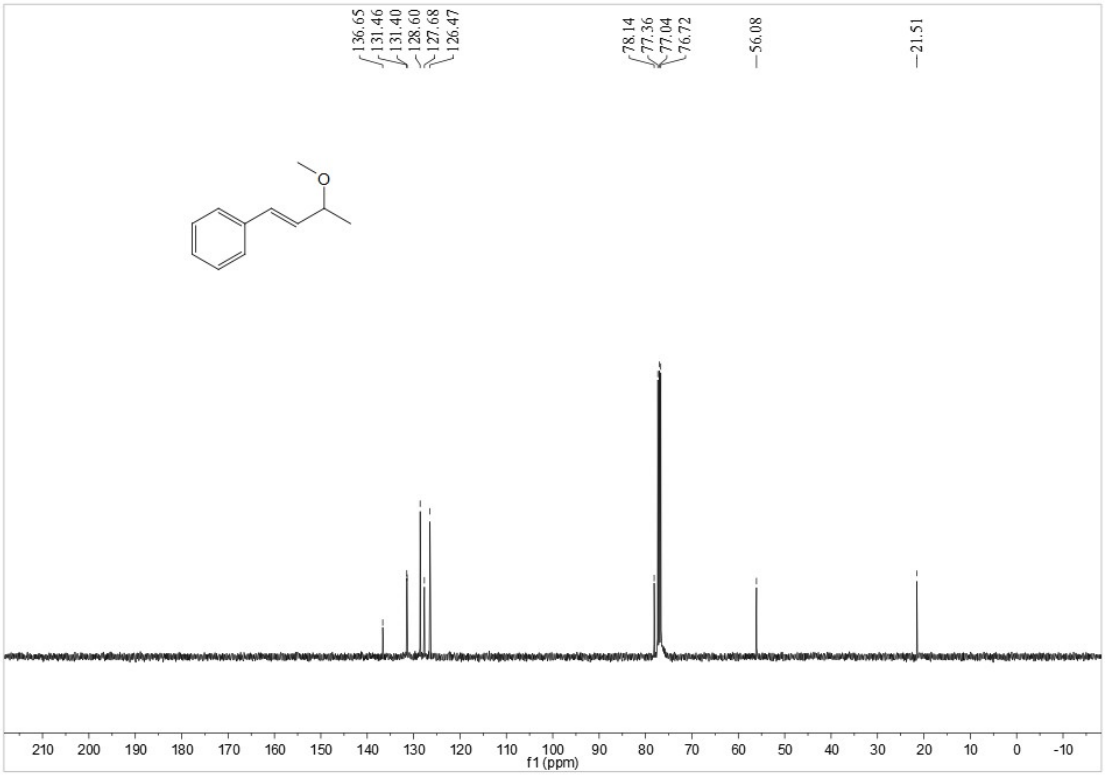
I. NMR Spectrum

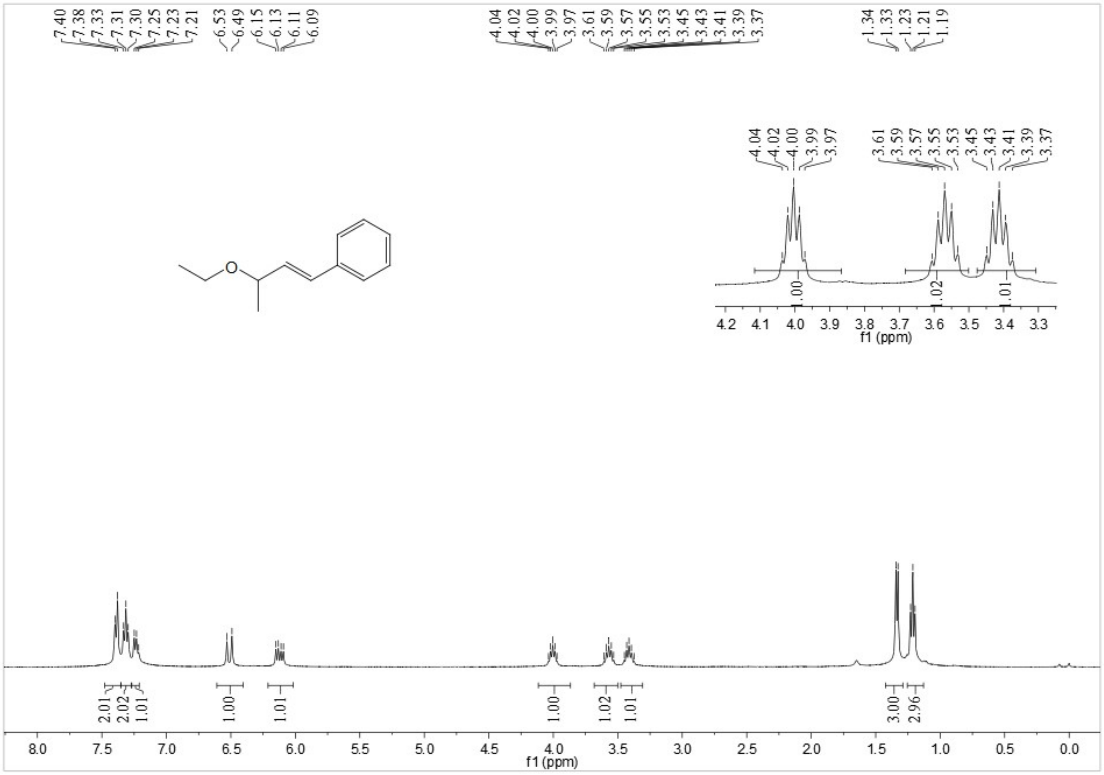
^{1}H NMR for (3-methoxybut-1-en-1-yl)benzene (3a)



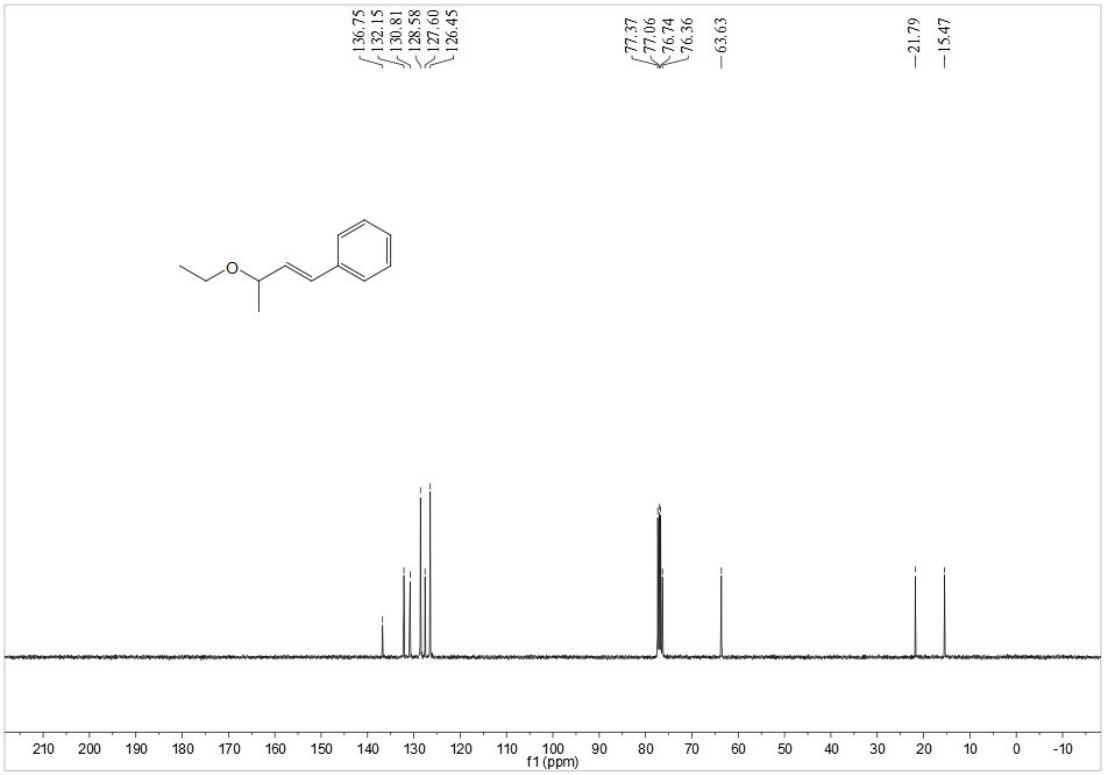
^{13}C NMR for (3-methoxybut-1-en-1-yl)benzene (3a)



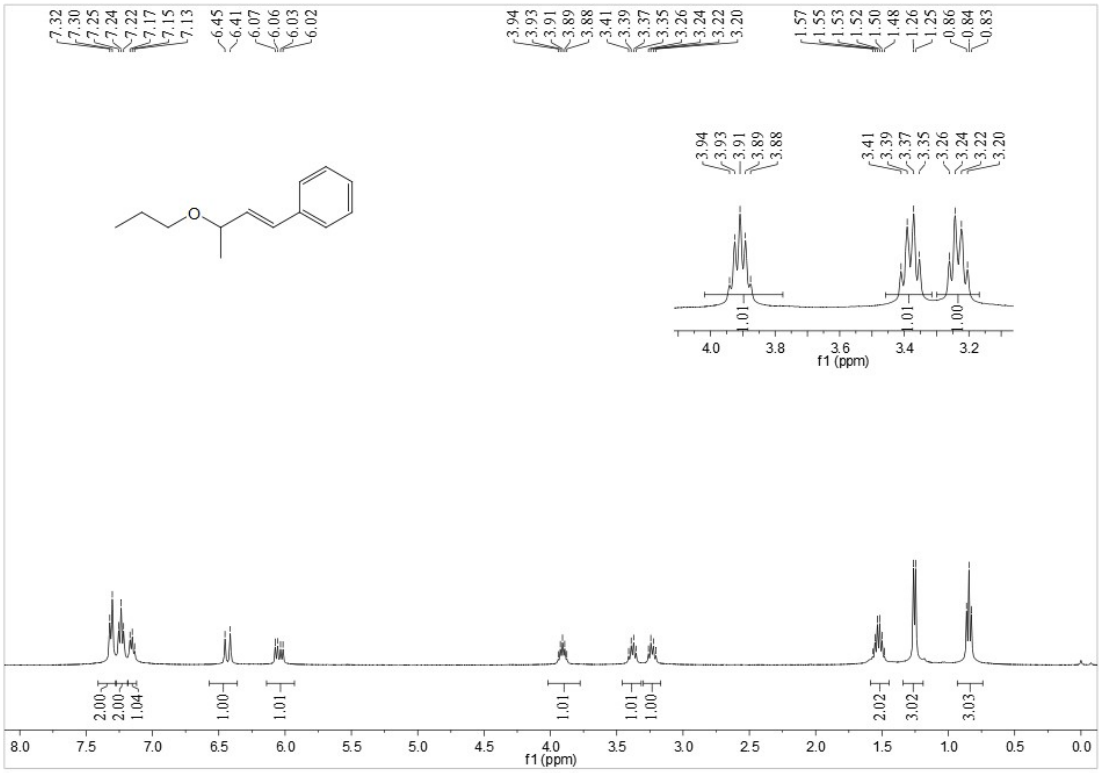
^{1}H NMR for (3-ethoxybut-1-en-1-yl)benzene (3b)



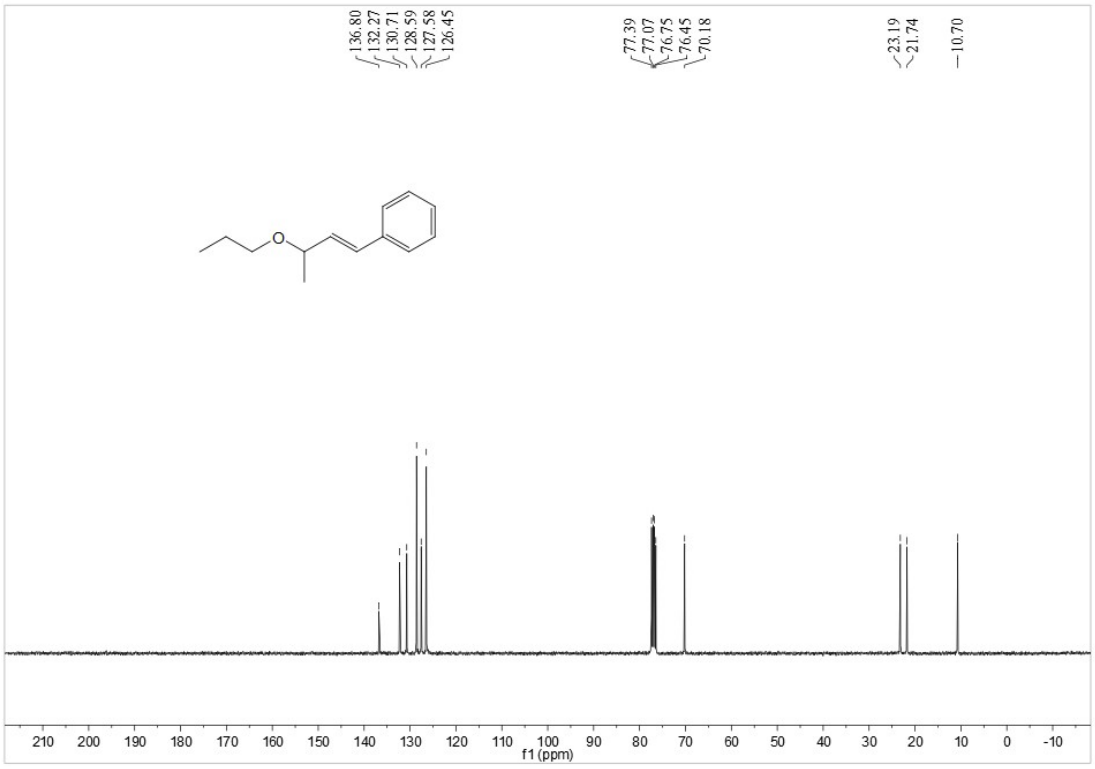
^{13}C NMR for (3-ethoxybut-1-en-1-yl)benzene (3b)



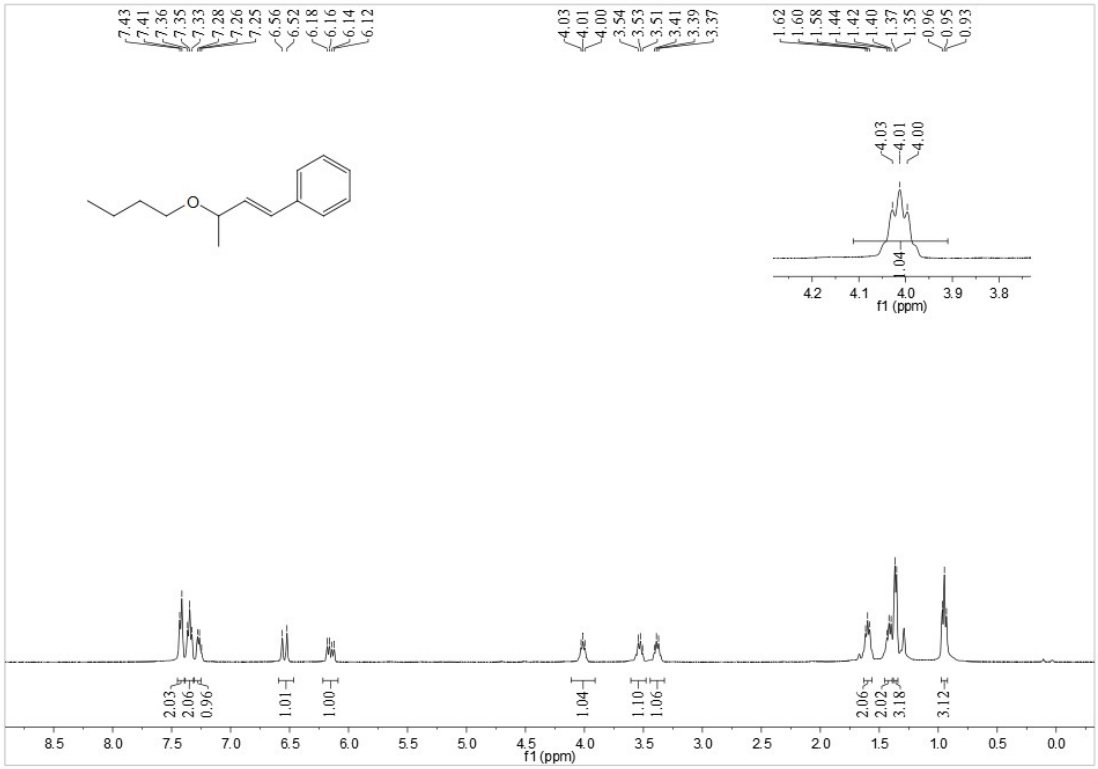
^{1}H NMR for (3-propoxybut-1-en-1-yl)benzene (3c)



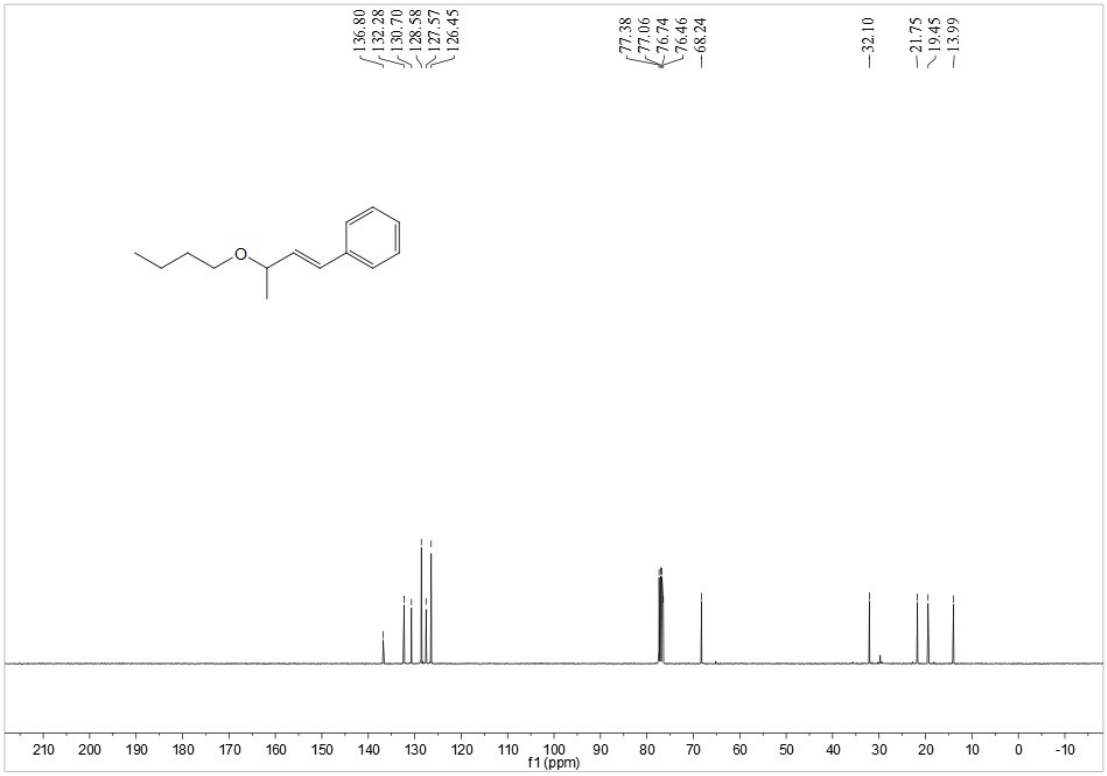
^{13}C NMR for (3-propoxybut-1-en-1-yl)benzene e (3c)



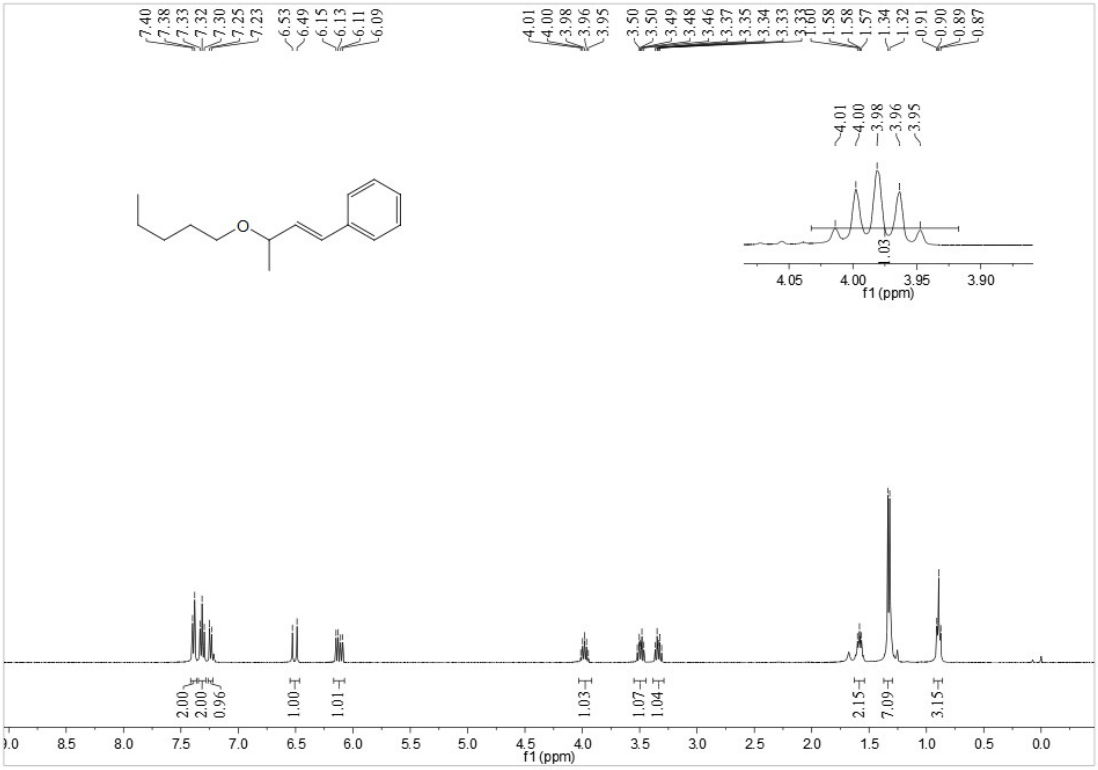
^{1}H NMR for (3-butoxybut-1-en-1-yl)benzene (3d)



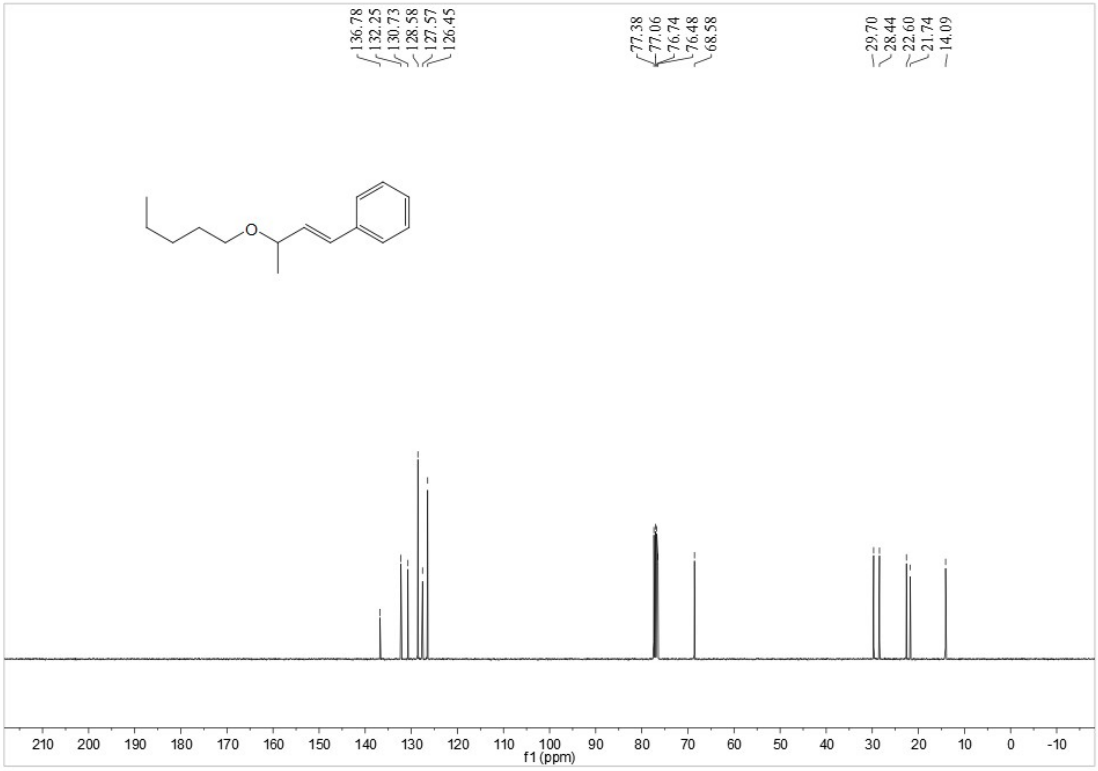
^{13}C NMR for (3-butoxybut-1-en-1-yl)benzene (3d)



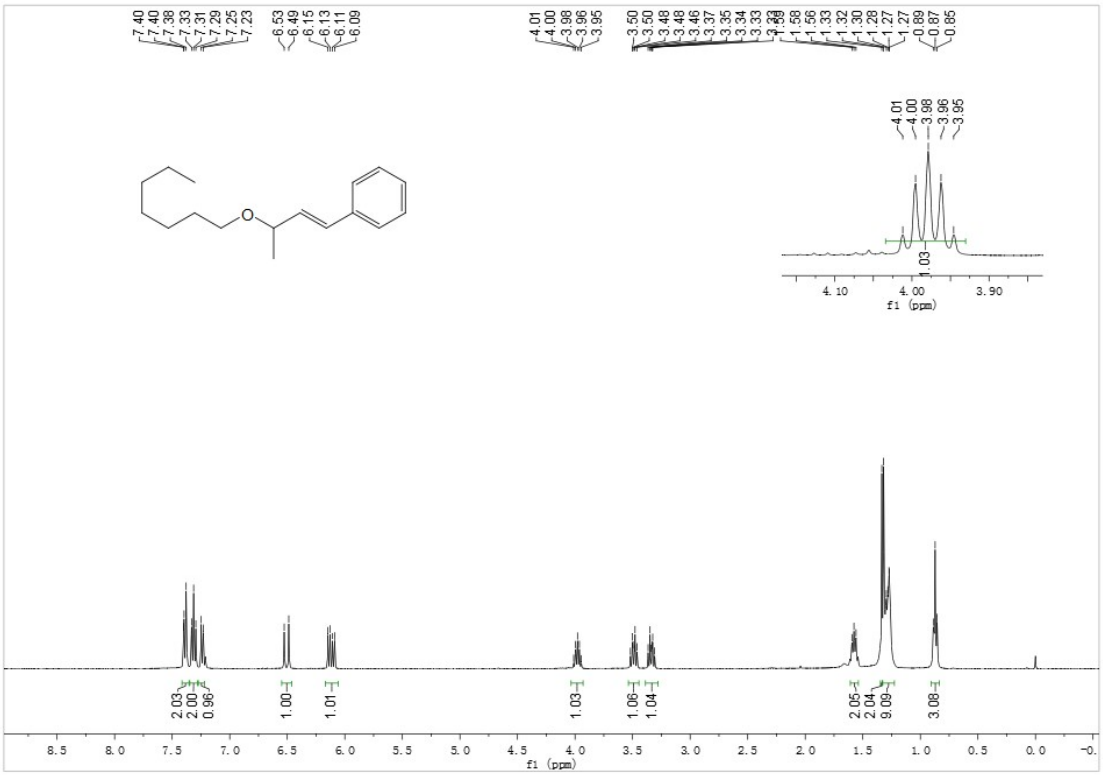
^{1}H NMR for (3-(pentyloxy)but-1-en-1-yl)benzene (3e)



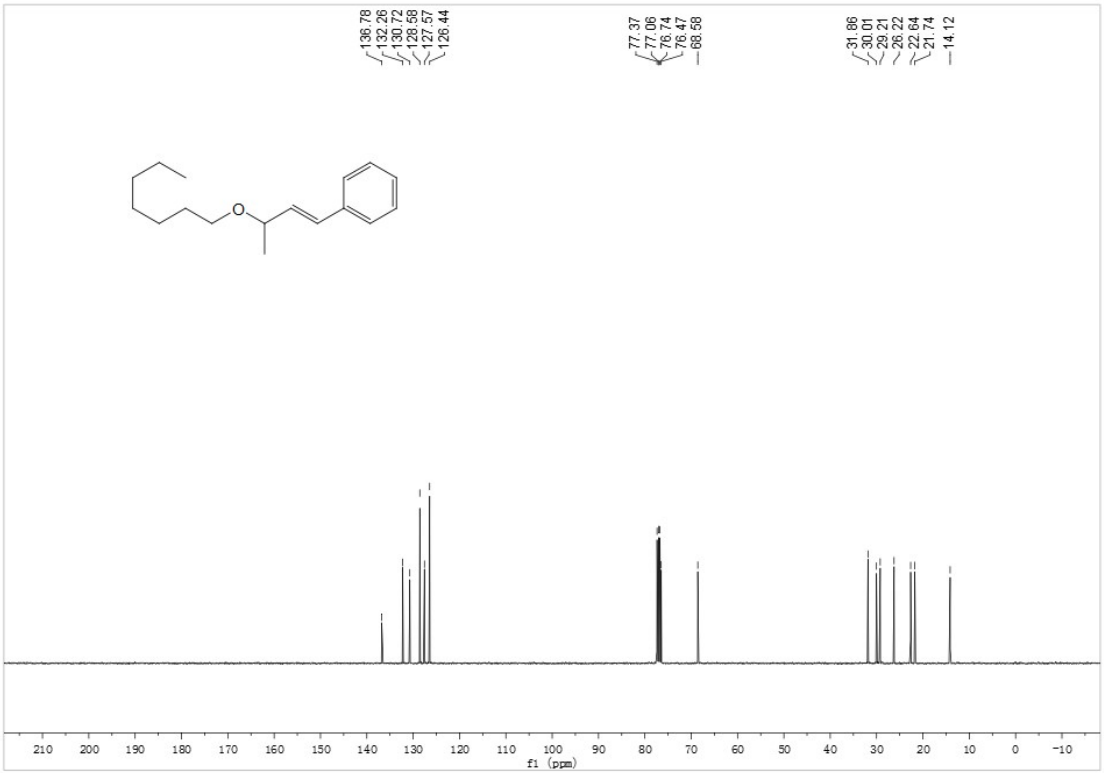
^{13}C NMR for (3-(pentyloxy)but-1-en-1-yl)benzene ene (3e)



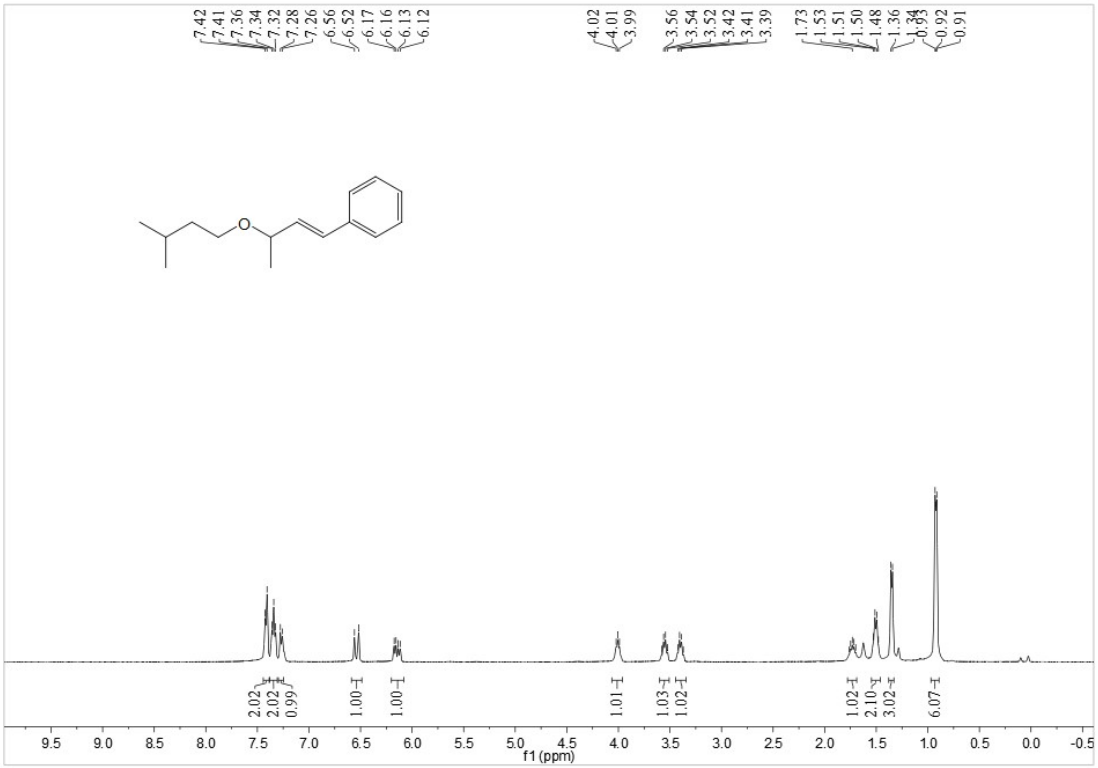
^{1}H NMR for (3-(heptyloxy)but-1-en-1-yl)benzene (3f)



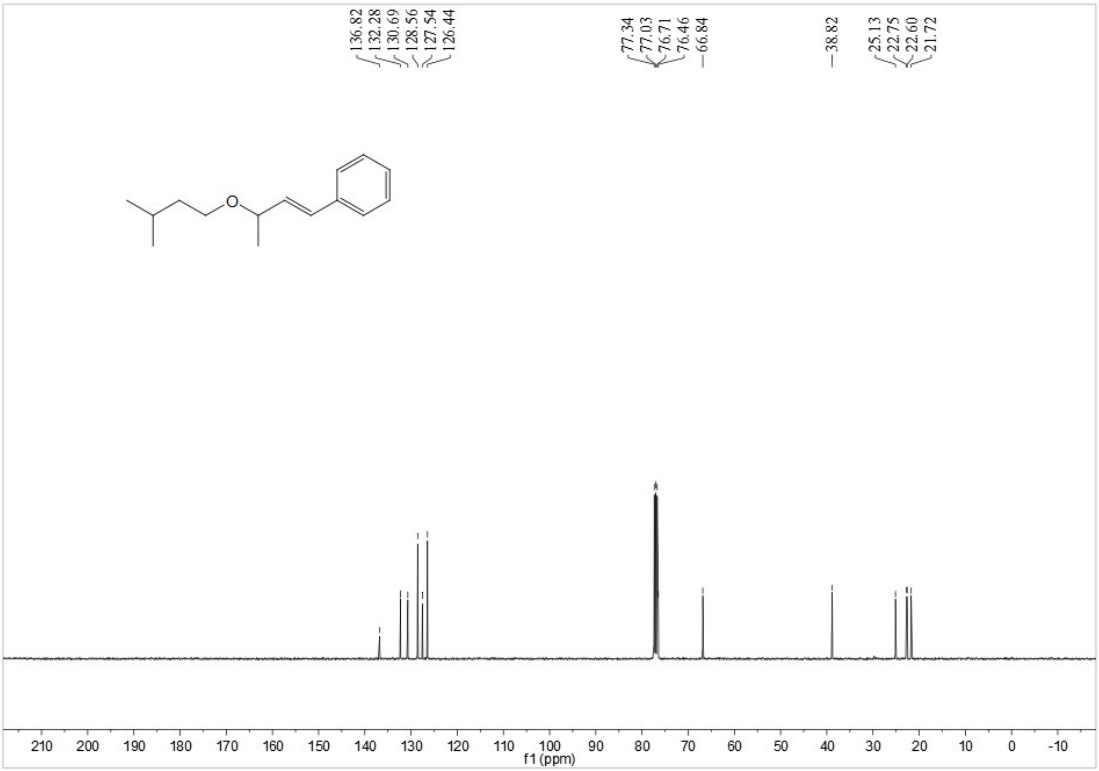
^{13}C NMR for (3-(heptyloxy)but-1-en-1-yl)benzene e (3f)



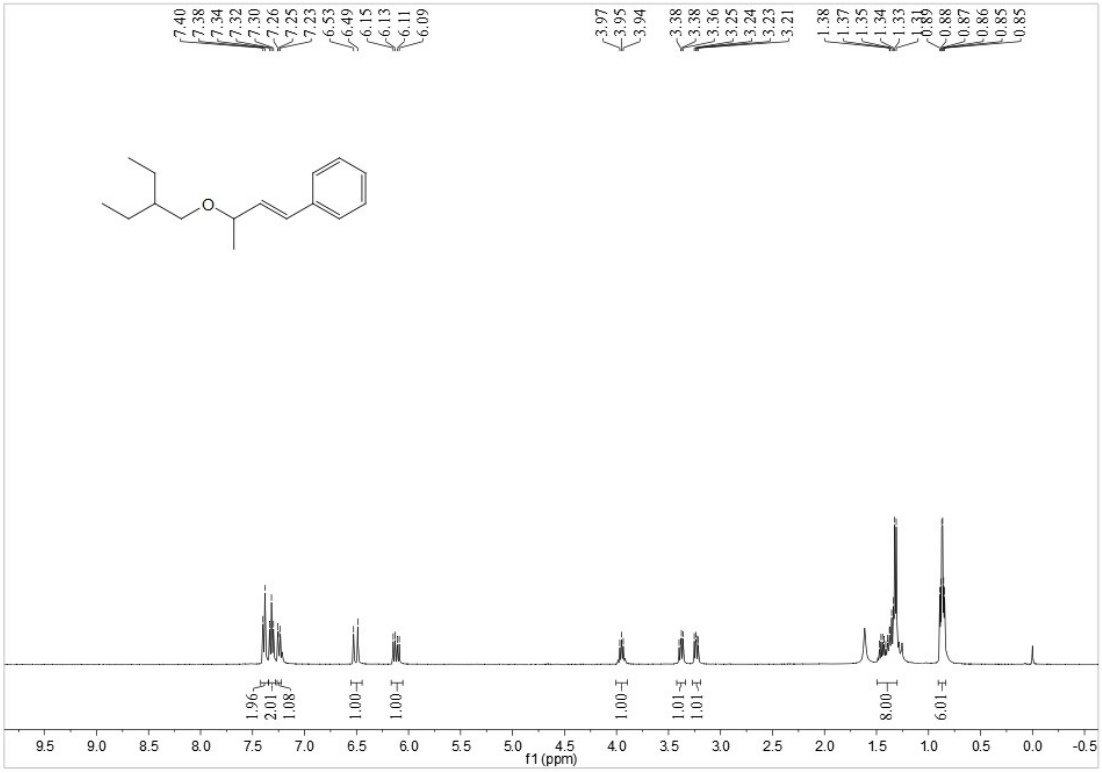
^{1}H NMR for (3-(isopentyloxy)but-1-en-1-yl)benzene (3g)



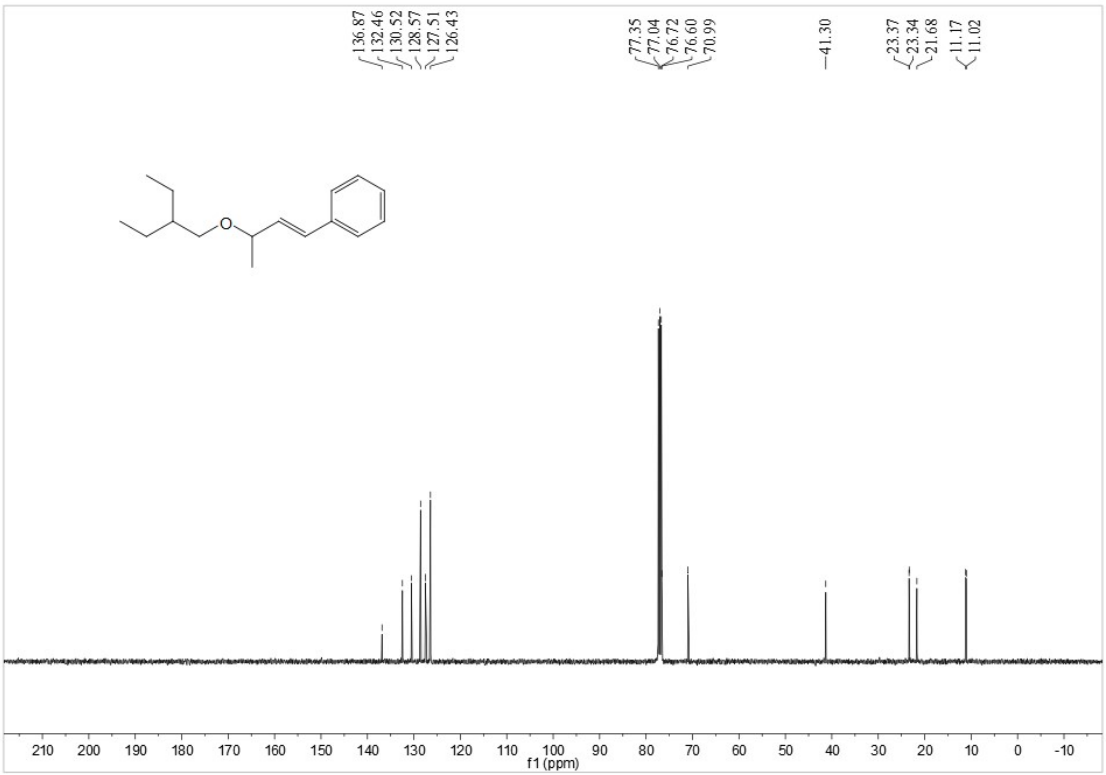
^{13}C NMR for (3-(isopentyloxy)but-1-en-1-yl)benzene (3g)



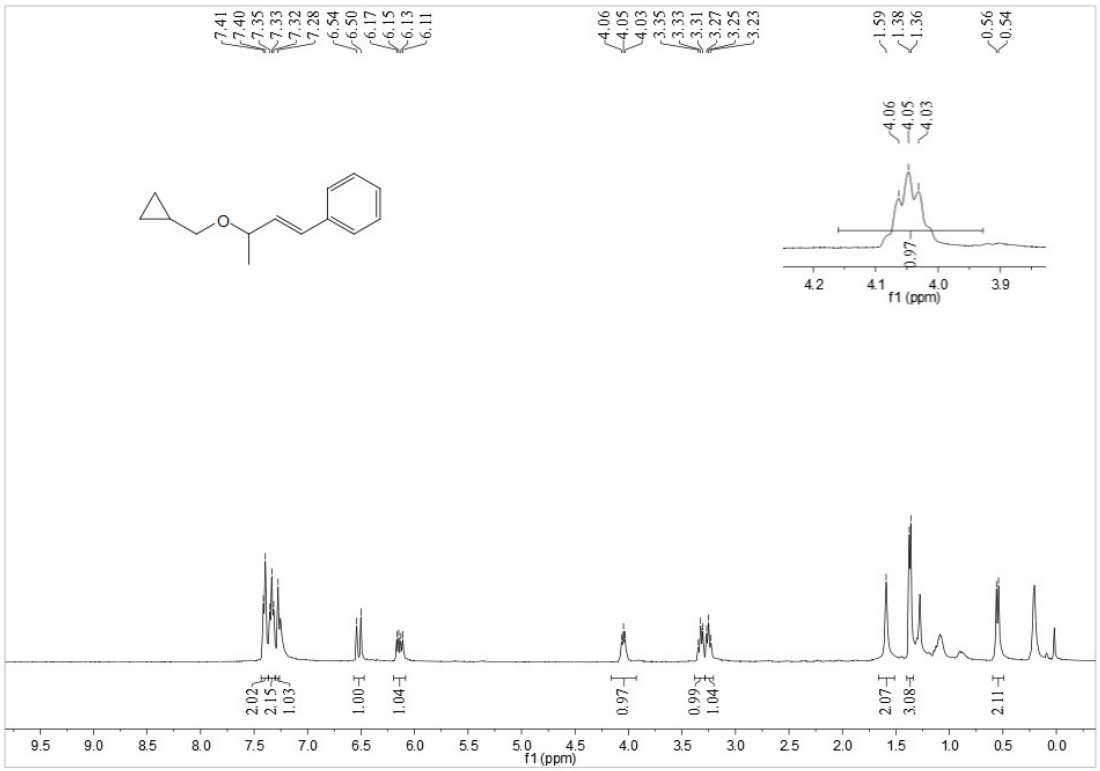
^{1}H NMR for (3-(2-ethylbutoxy)but-1-en-1-yl)benzene (3h)



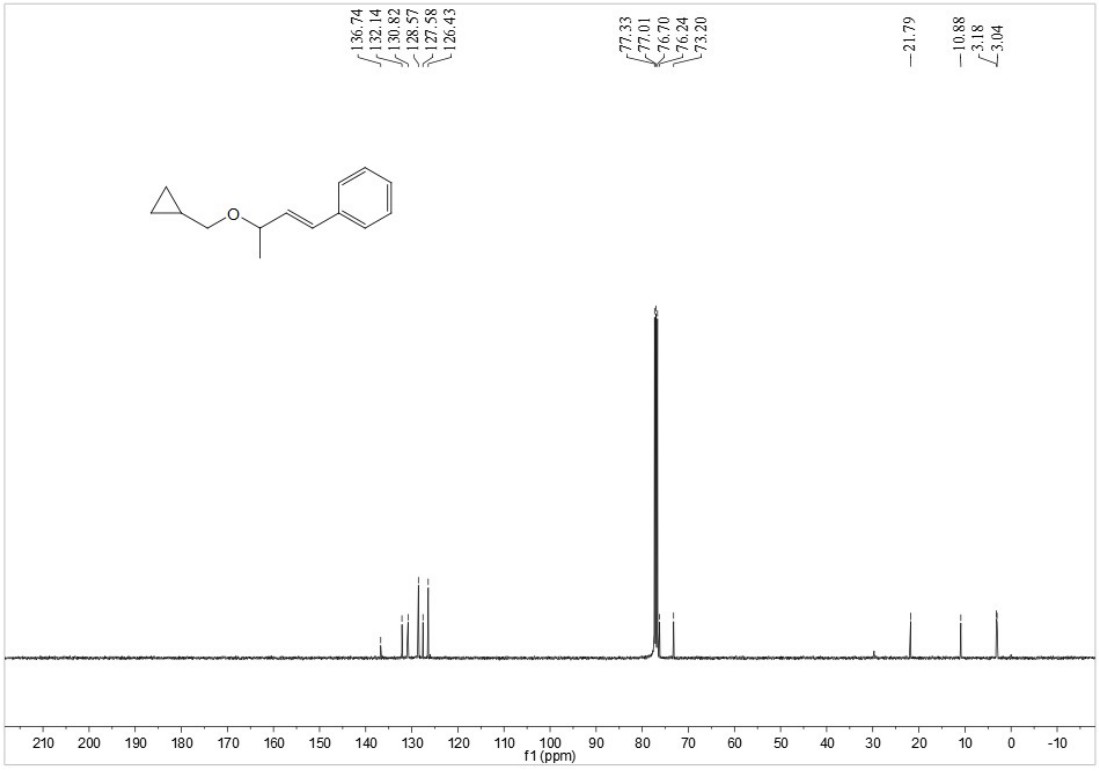
^{13}C NMR for (3-(2-ethylbutoxy)but-1-en-1-yl)benzene (3h)



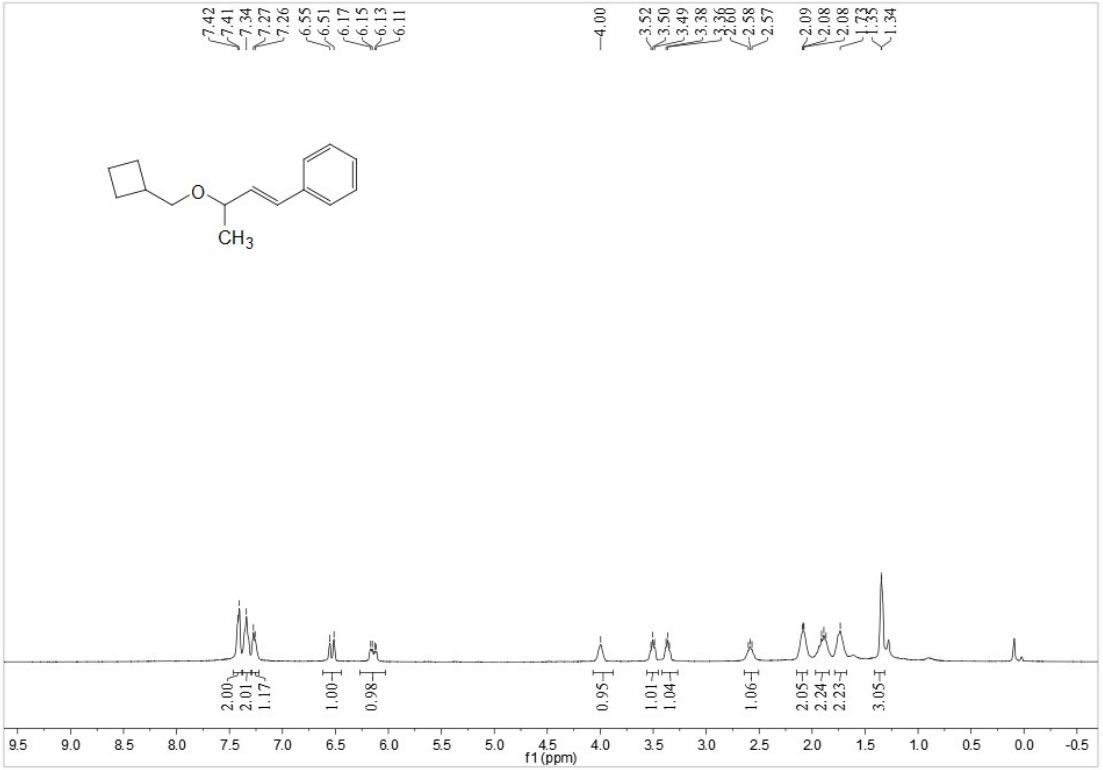
^{1}H NMR for (3-(cyclopropylmethoxy)but-1-en-1-yl)benzene (3i)



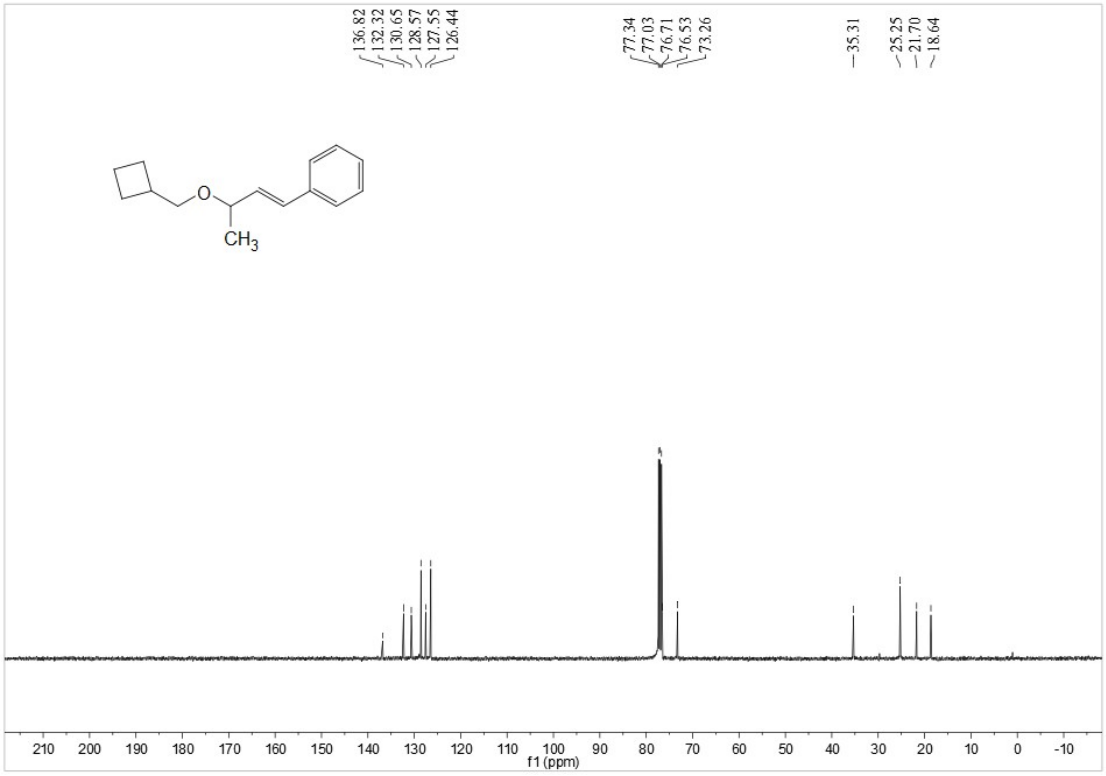
^{13}C NMR for (3-(cyclopropylmethoxy)but-1-en-1-yl)benzene (3i)



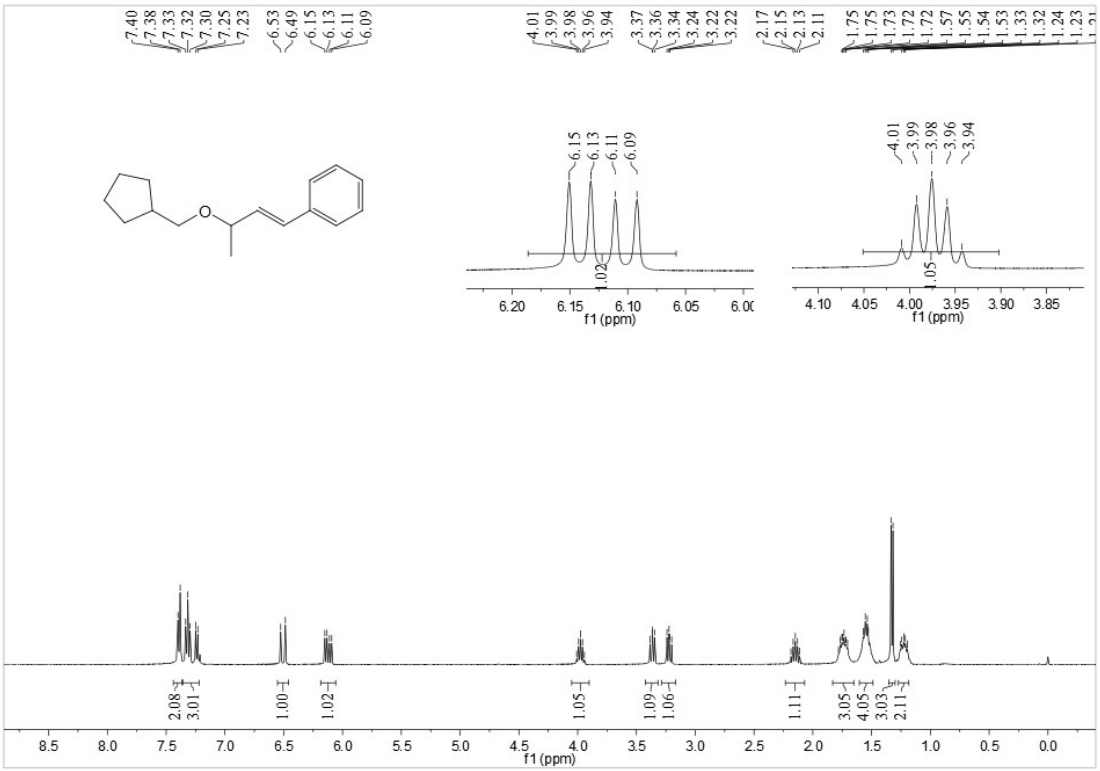
^{1}H NMR for (3-(cyclopropylmethoxy)but-1-en-1-yl)benzene (3j)



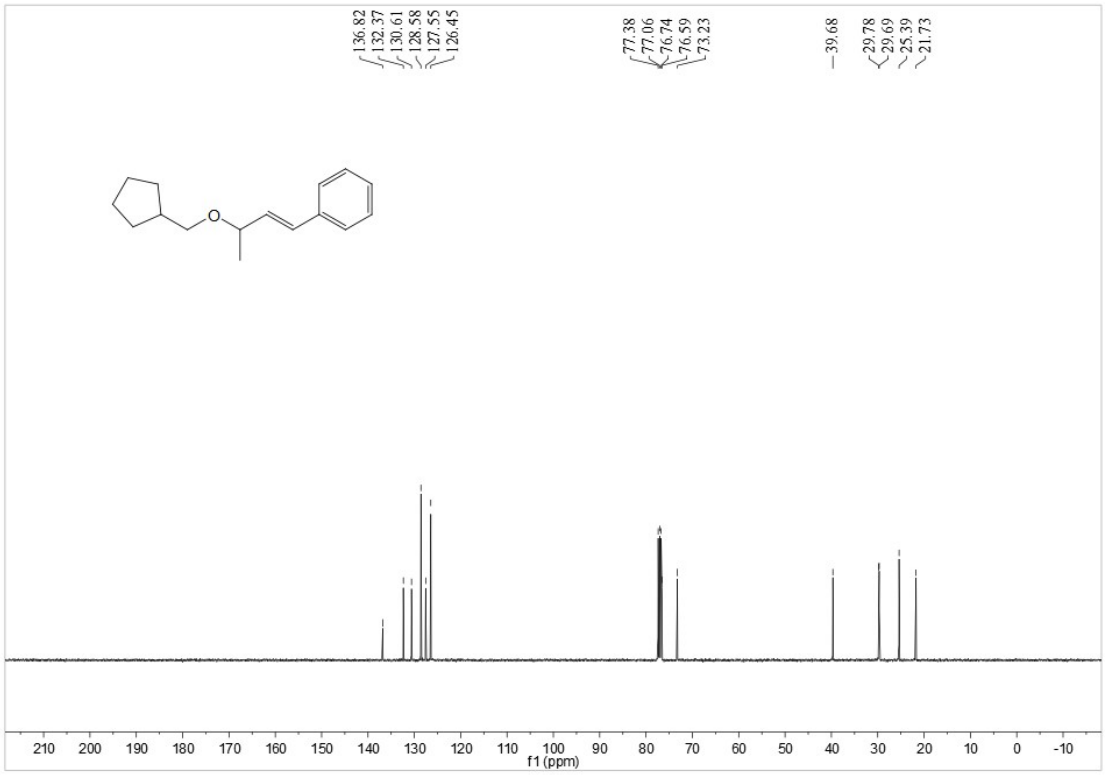
^{13}C NMR for (3-(cyclopropylmethoxy)but-1-en-1-yl)benzene (3j)



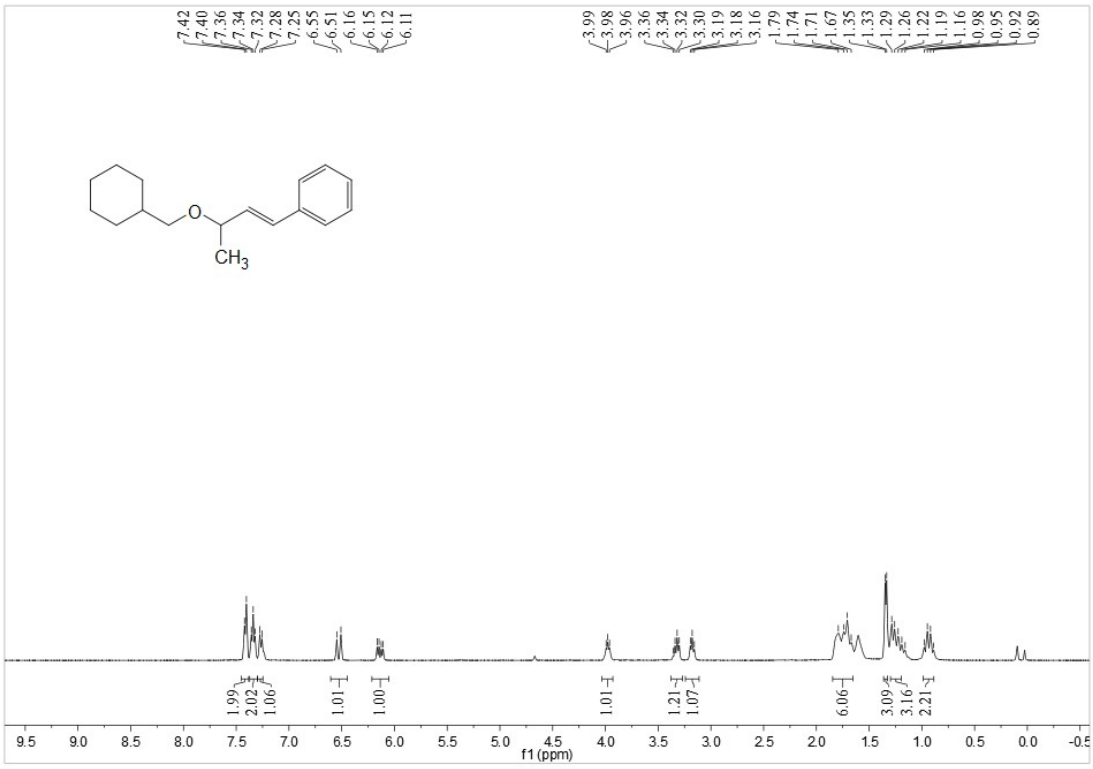
^{1}H NMR for (3-(cyclopentylmethoxy)but-1-en-1-yl)benzene (3k)



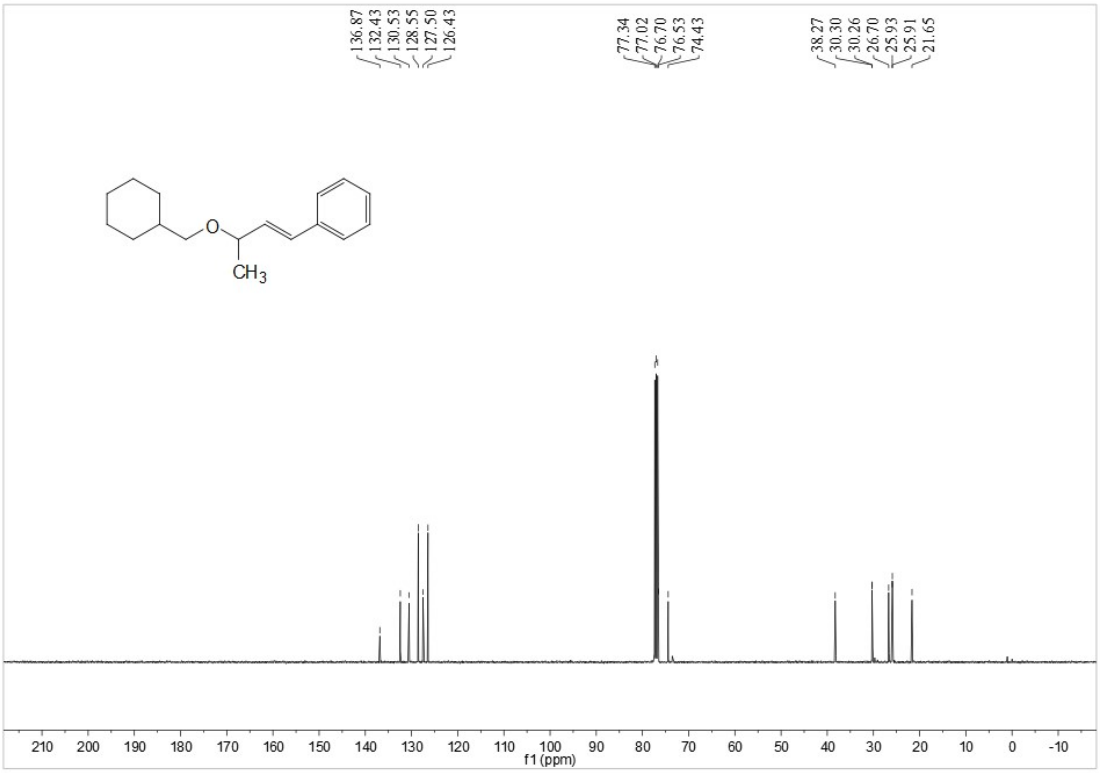
^{13}C NMR for (3-(cyclopentylmethoxy)but-1-en-1-yl)benzene (3k)



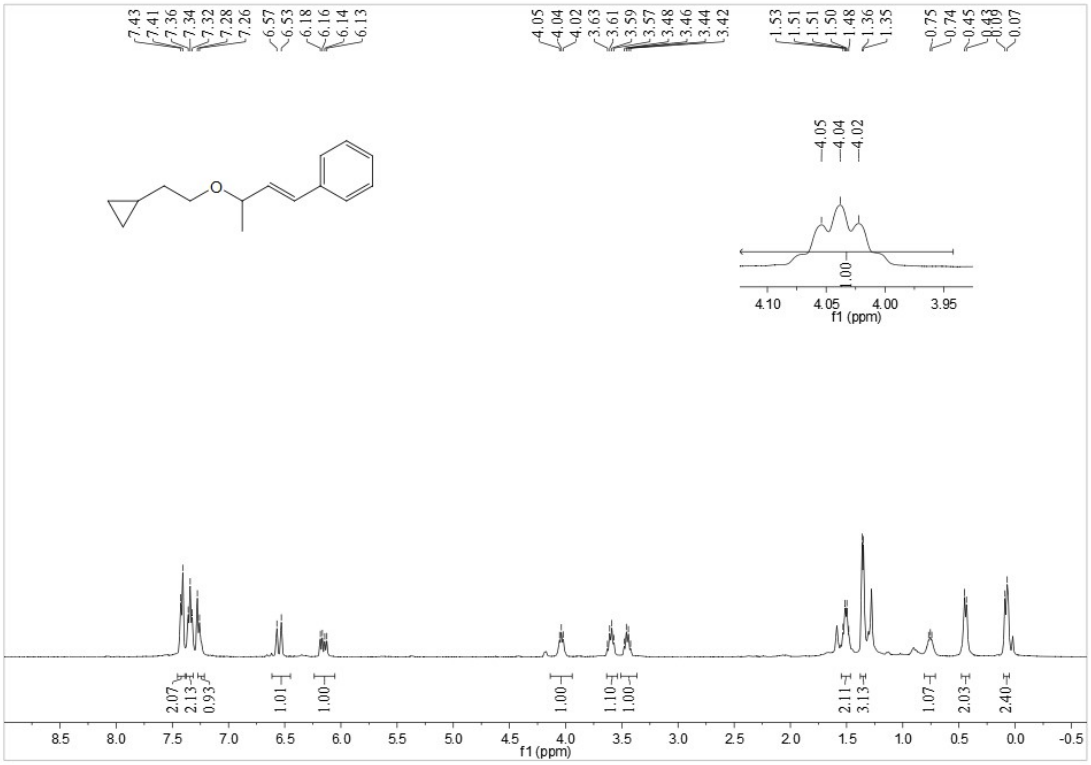
^{1}H NMR for (3-(cyclohexylmethoxy)but-1-en-1-yl)benzene (3l)



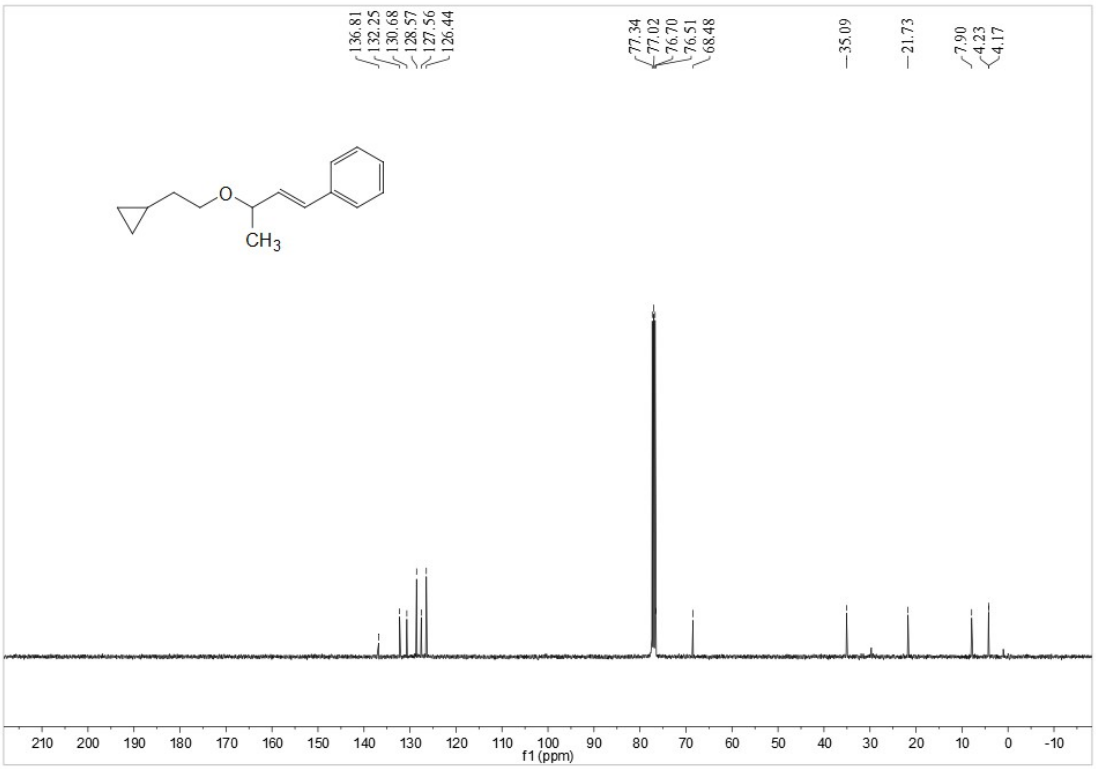
^{13}C NMR for (3-(cyclohexylmethoxy)but-1-en-1-yl)benzene (3l)



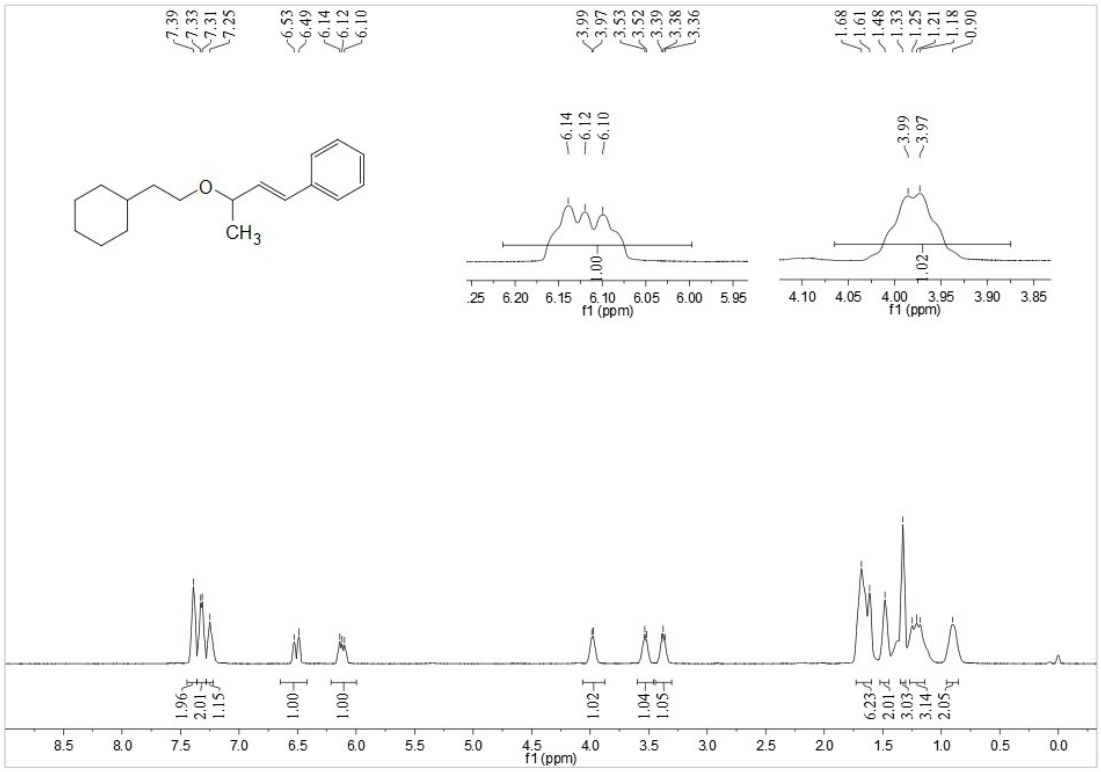
^{1}H NMR for (3-(2-cyclopropylethoxy)but-1-en-1-yl)benzene (3m)



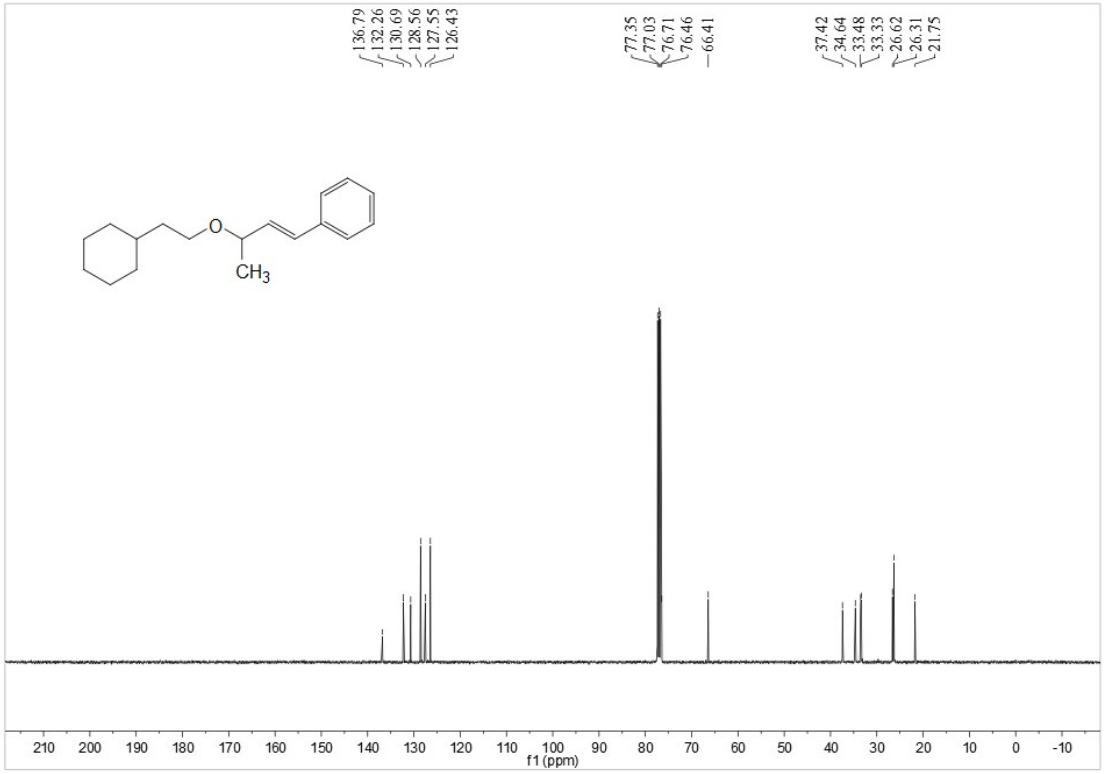
^{13}C NMR for (3-(2-cyclopropylethoxy)but-1-en-1-yl)benzene (3m)



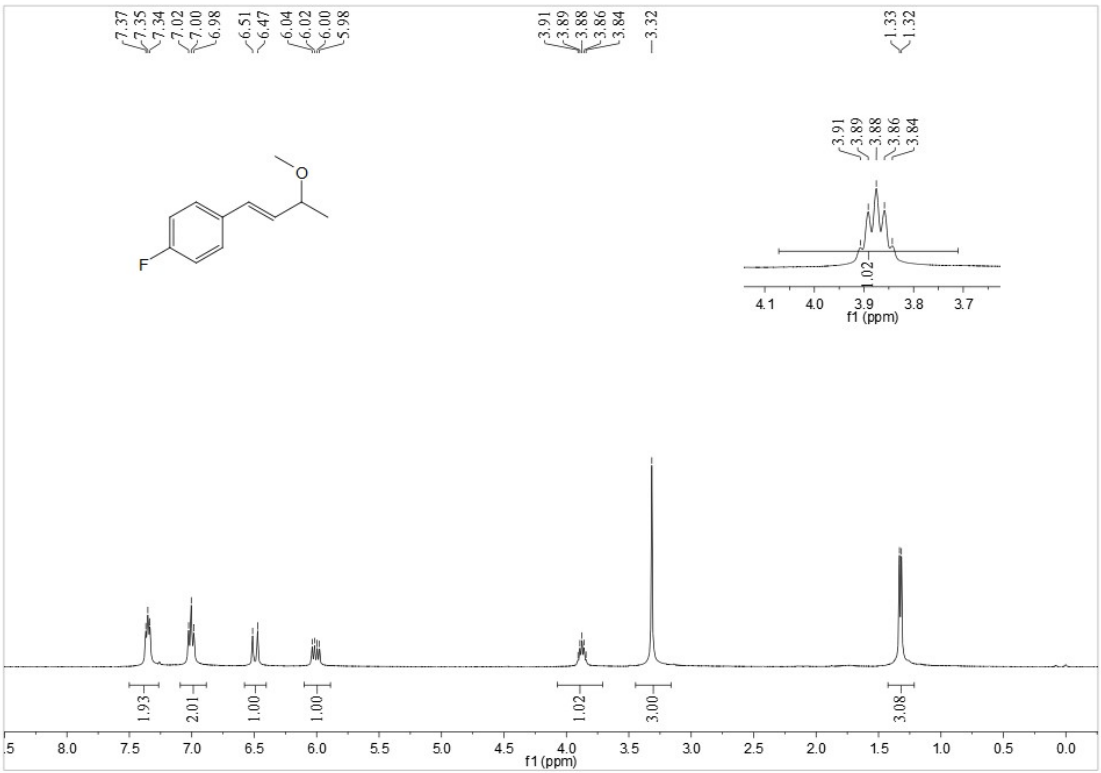
^{1}H NMR for (3-(2-cyclohexylethoxy)but-1-en-1-yl)benzene (3n)



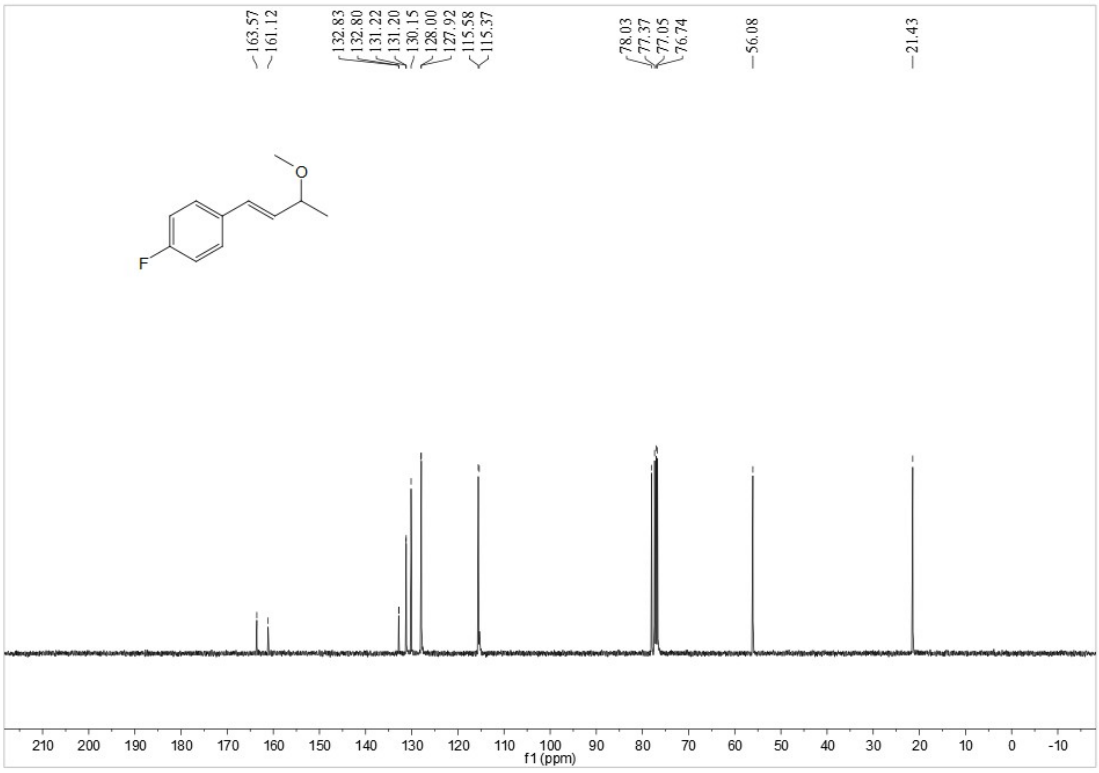
^{13}C NMR for (3-(2-cyclohexylethoxy)but-1-en-1-yl)benzene (3n)



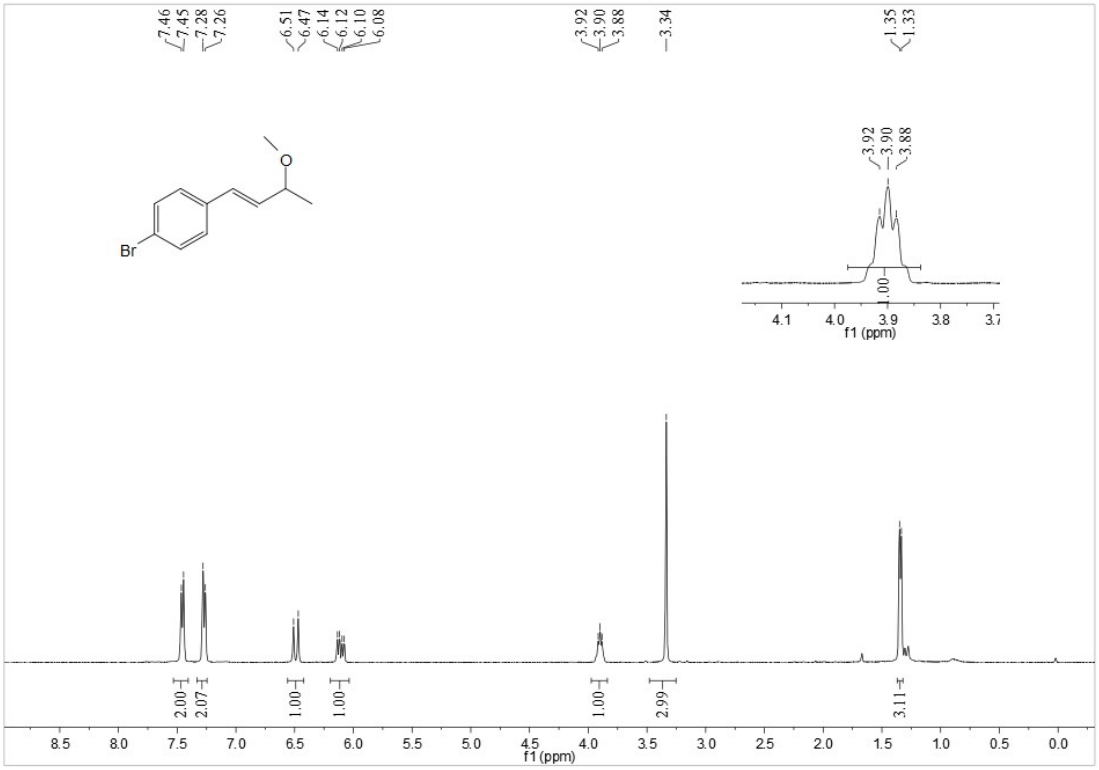
^{1}H NMR for 1-fluoro-4-(3-methoxybut-1-en-1-yl)benzene(3o)



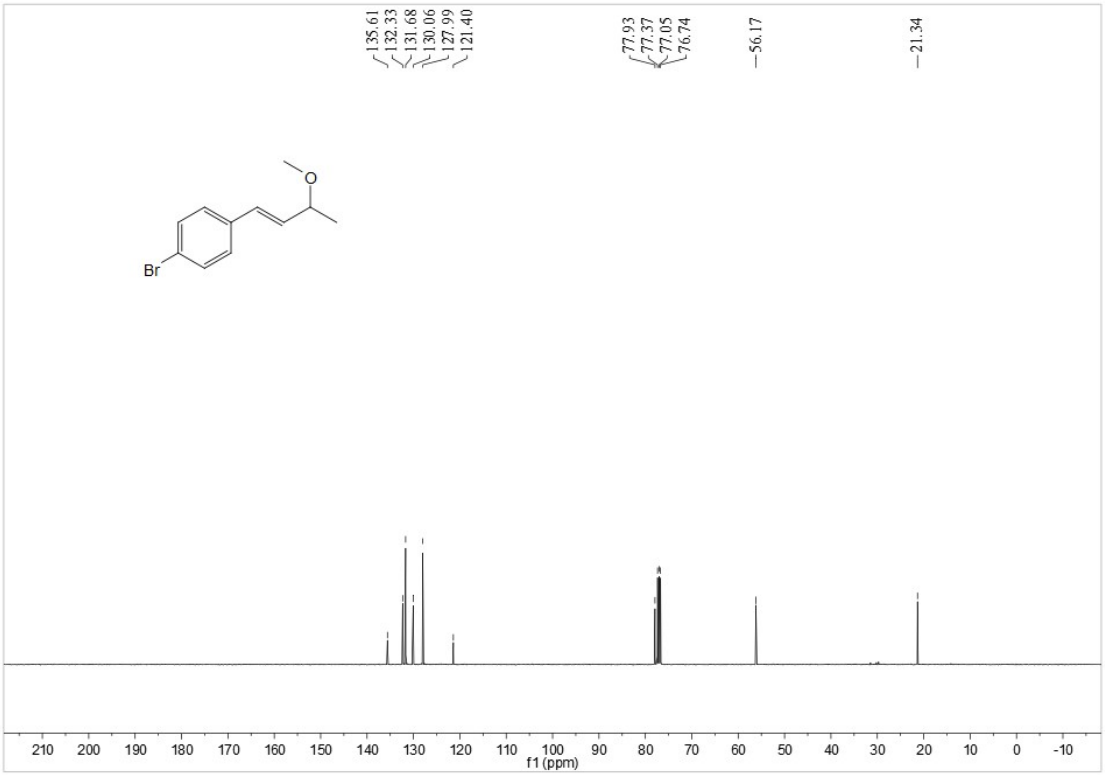
^{13}C NMR for 1-fluoro-4-(3-methoxybut-1-en-1-yl)benzene(3o)



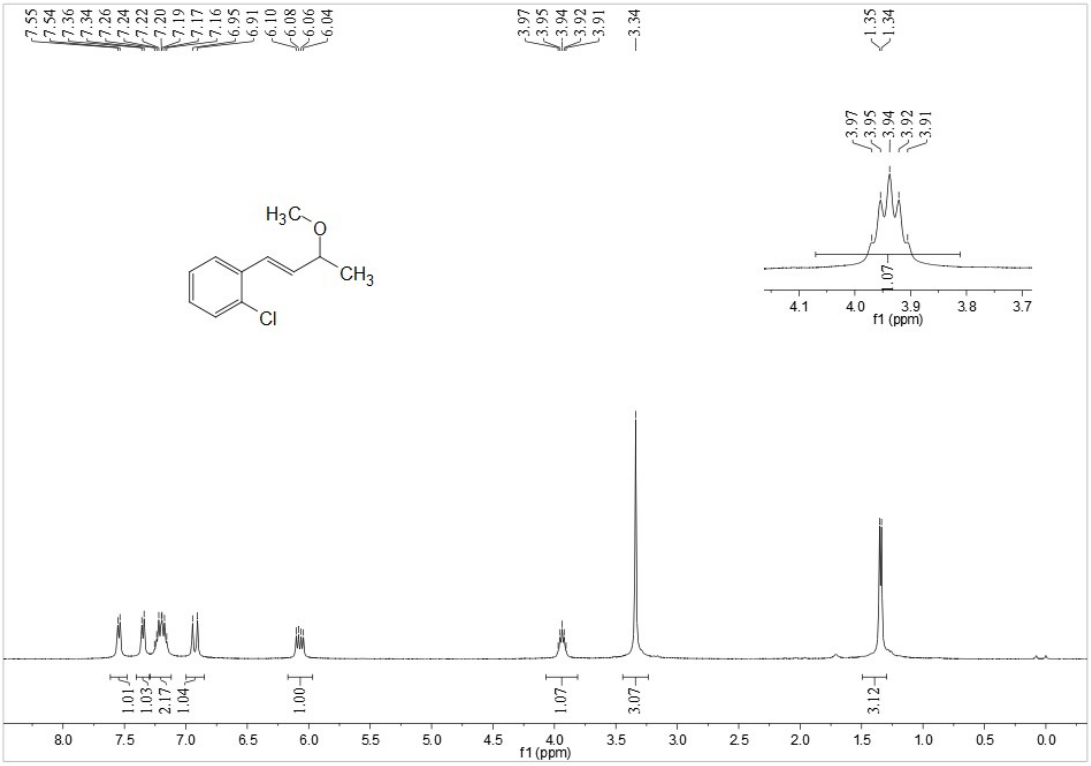
^{1}H NMR for 1-bromo-4-(3-methoxybut-1-en-1-yl)benzene(3p)



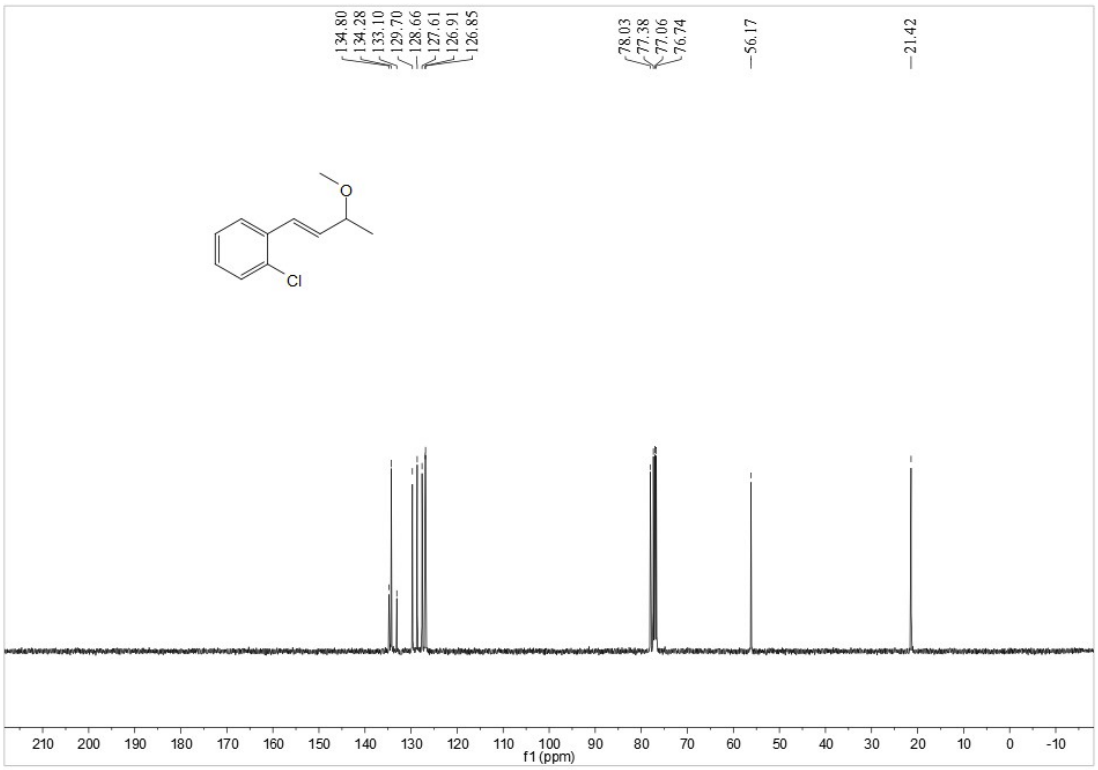
^{13}C NMR for 1-bromo-4-(3-methoxybut-1-en-1-yl)benzene(3p)



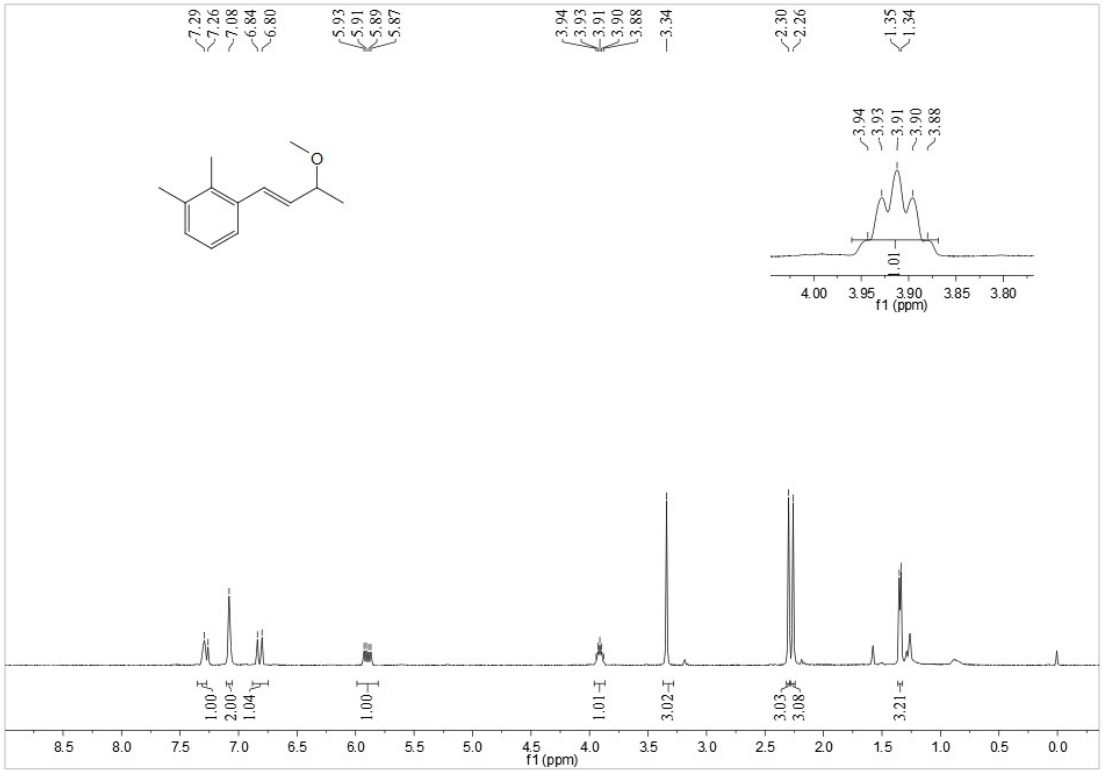
^{1}H NMR for 1-chloro-2-(3-methoxybut-1-en-1-yl)benzene (3q)



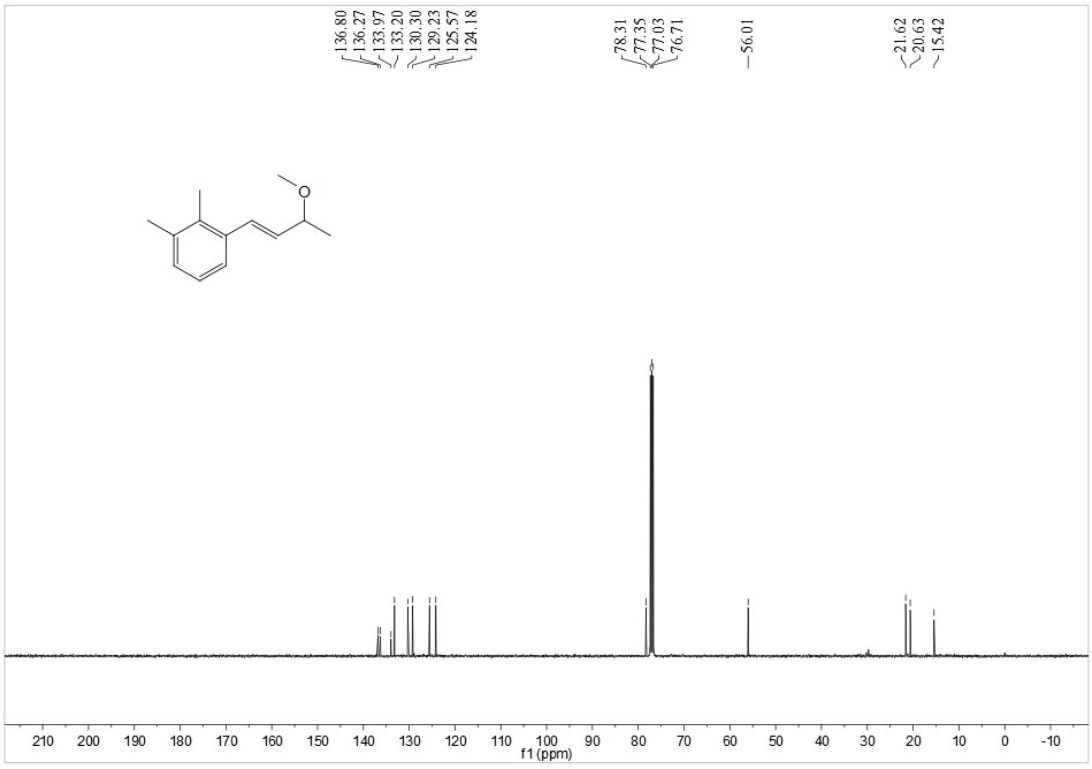
^{13}C NMR for 1-chloro-2-(3-methoxybut-1-en-1-yl)benzene(3q)



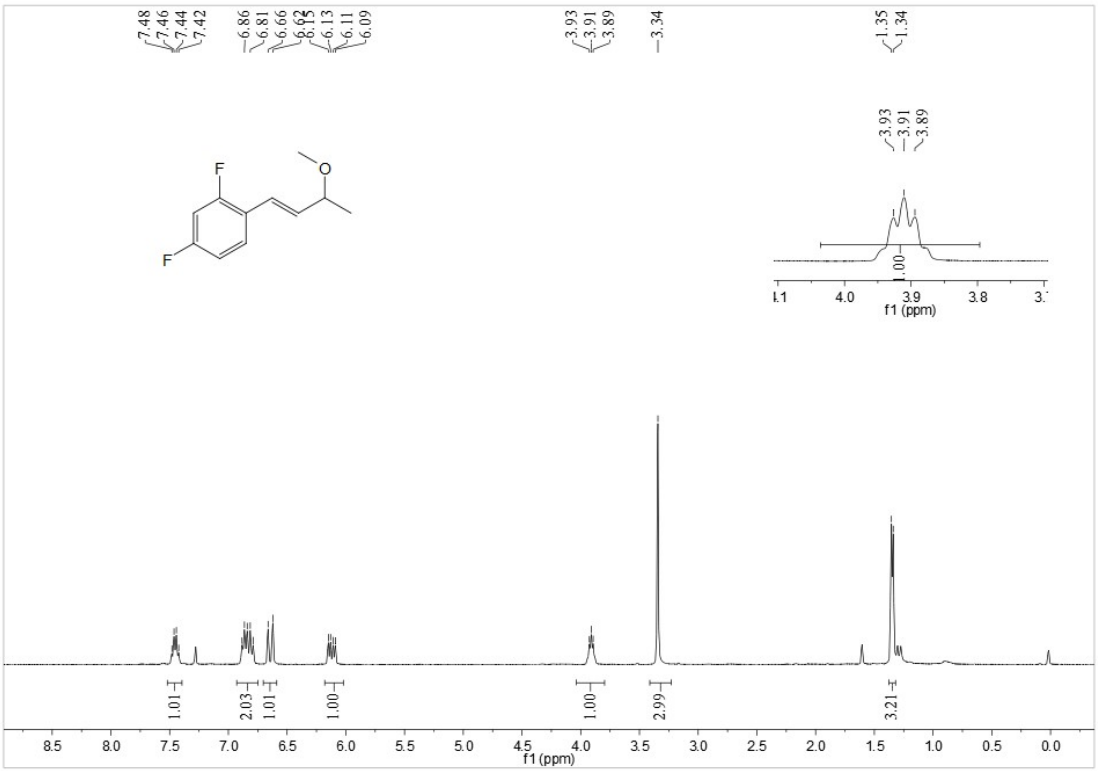
^{1}H NMR for 1-(3-methoxybut-1-en-1-yl)-2,3-dimethylbenzene (3r)



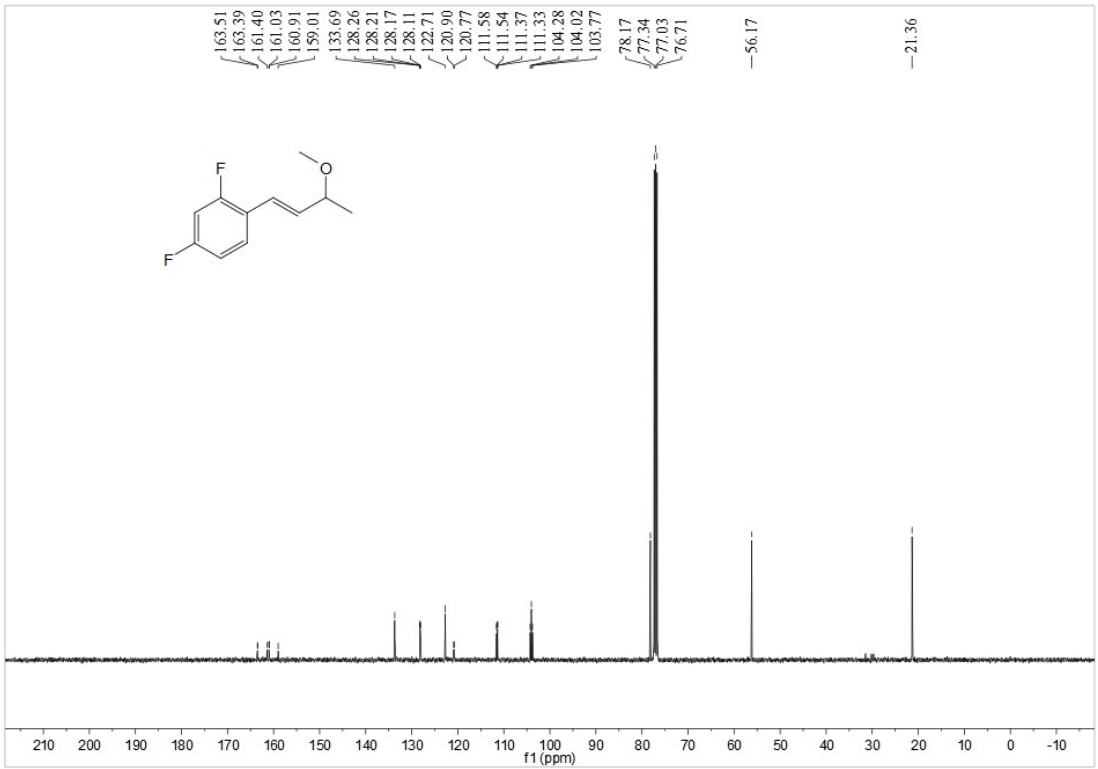
^{13}C NMR for 1-(3-methoxybut-1-en-1-yl)-2,3-dimethylbenzene (3r)



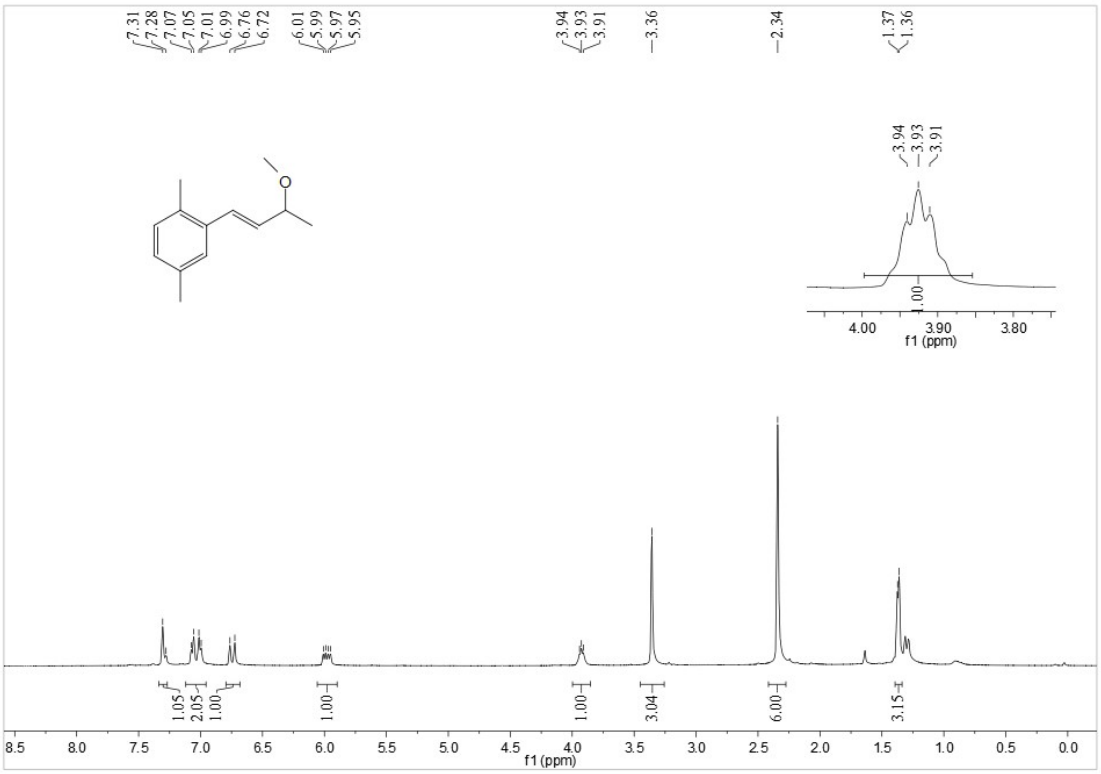
^{1}H NMR for 2,4-difluoro-1-(3-methoxybut-1-en-1-yl)benzene (3s)



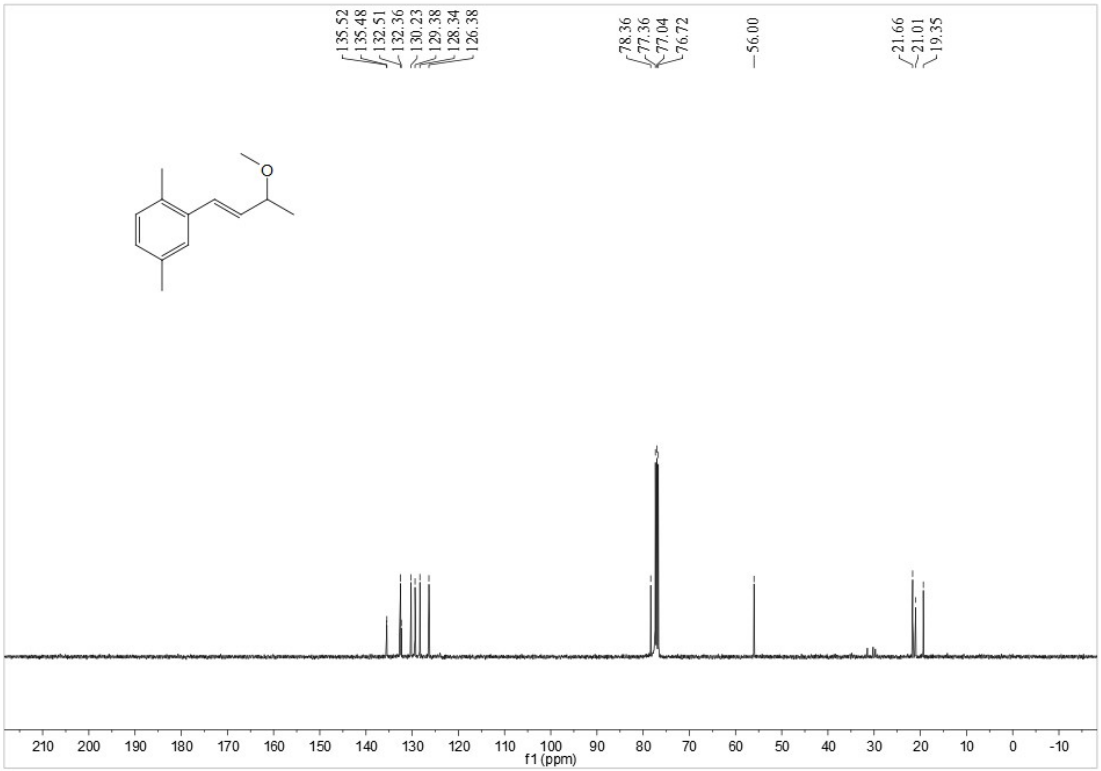
^{13}C NMR for 2,4-difluoro-1-(3-methoxybut-1-en-1-yl)benzene(3s)



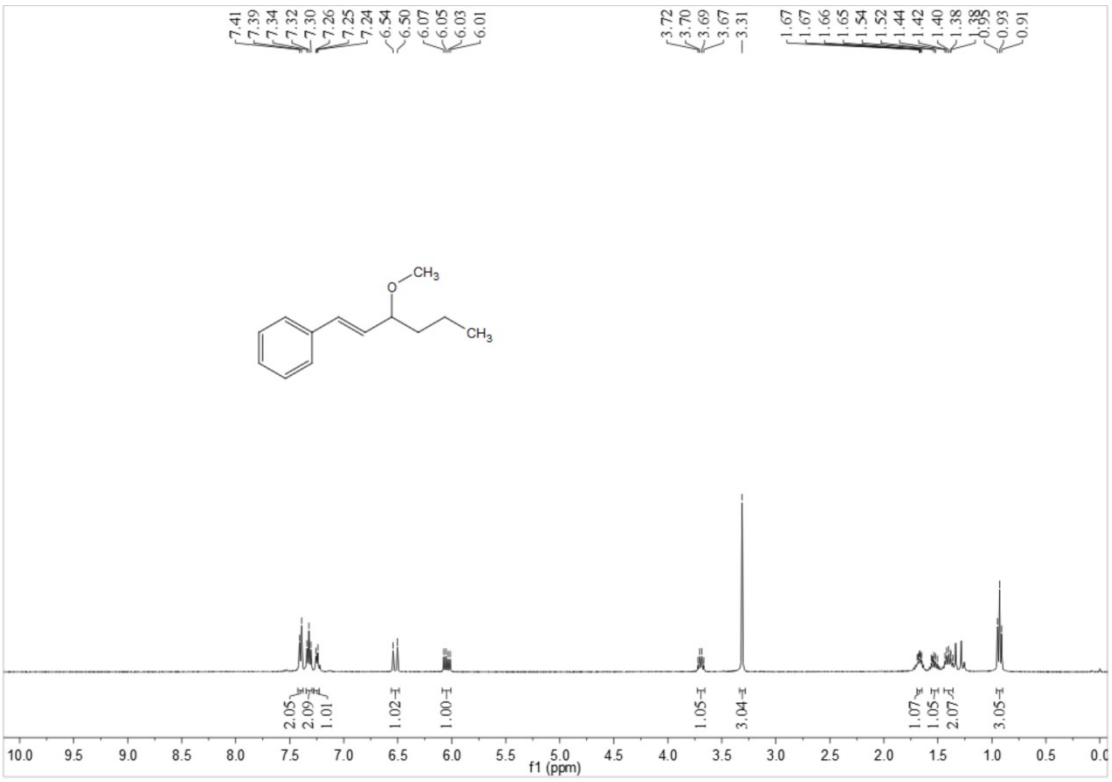
^{1}H NMR for 2-(3-methoxybut-1-en-1-yl)-1,4-dimethylbenzene (3t)



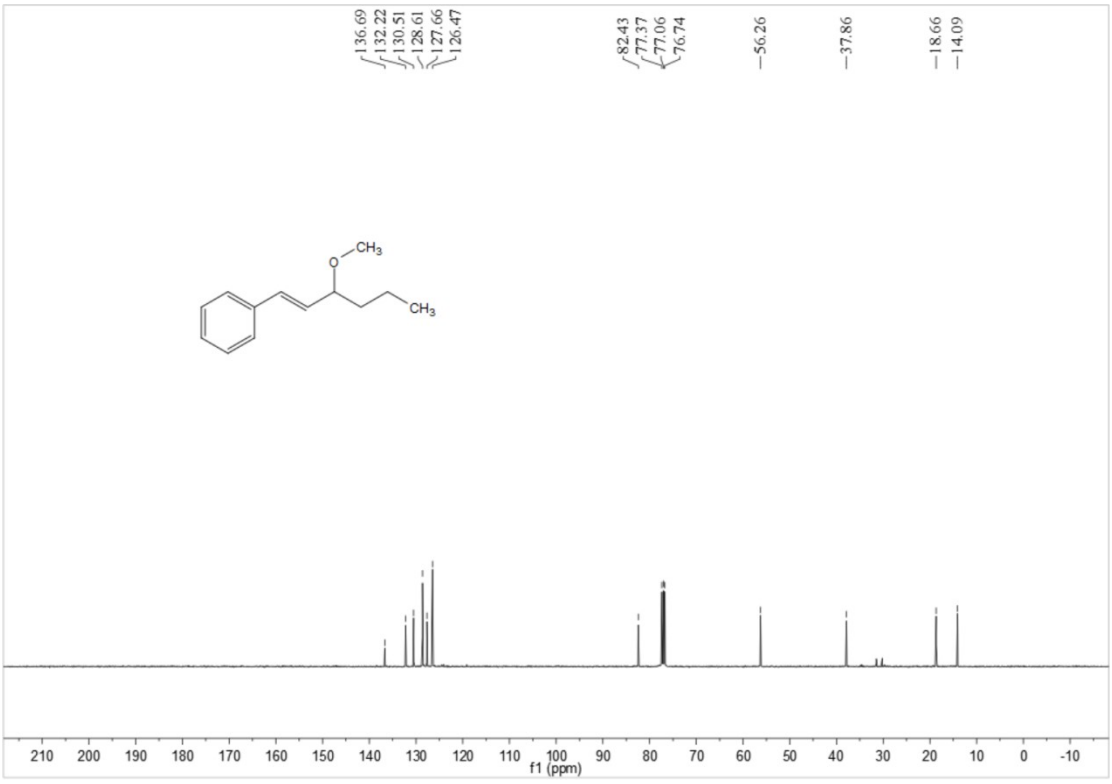
^{13}C NMR for 2-(3-methoxybut-1-en-1-yl)-1,4-dimethylbenzene (3t)



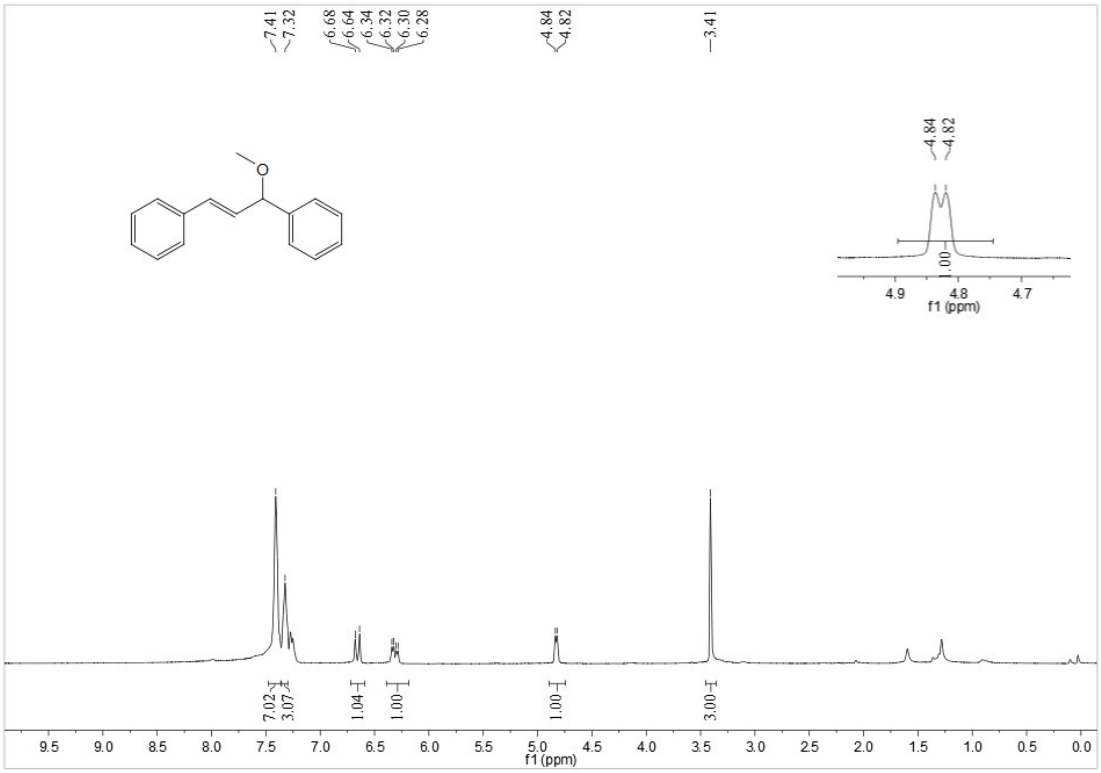
^{1}H NMR for(3-methoxyhex-1-en-1-yl)benzene (3u)



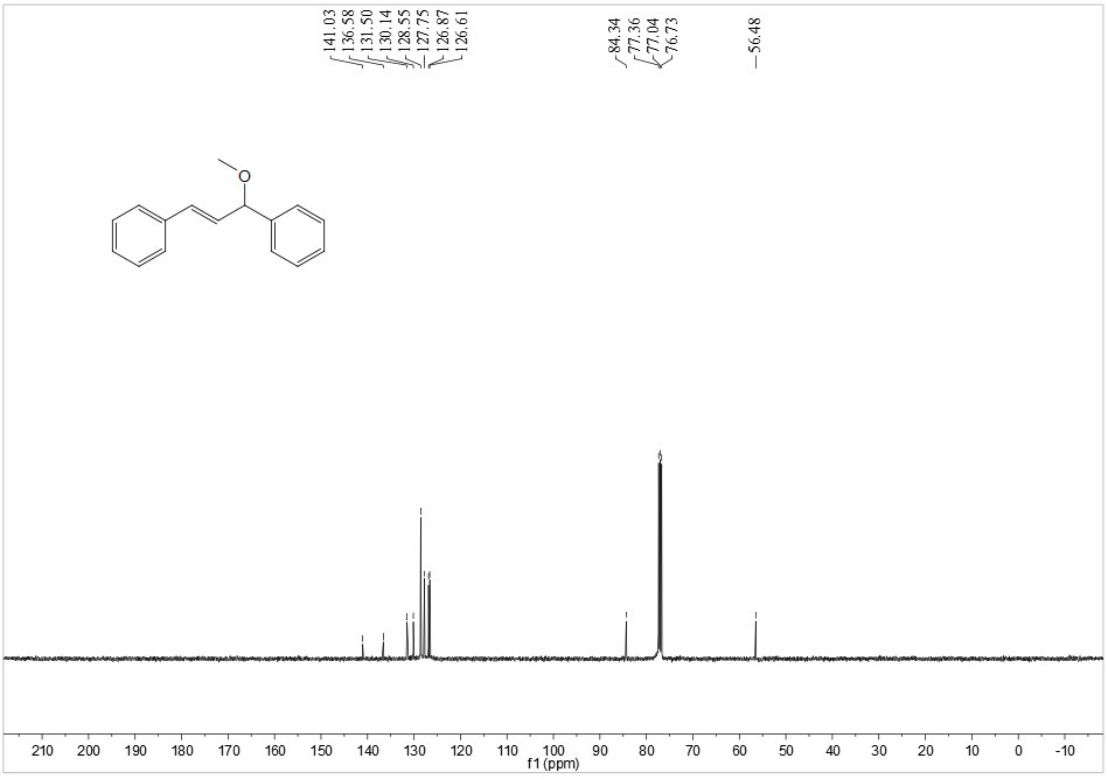
^{13}C NMR for(3-methoxyhex-1-en-1-yl)benzene (3u)



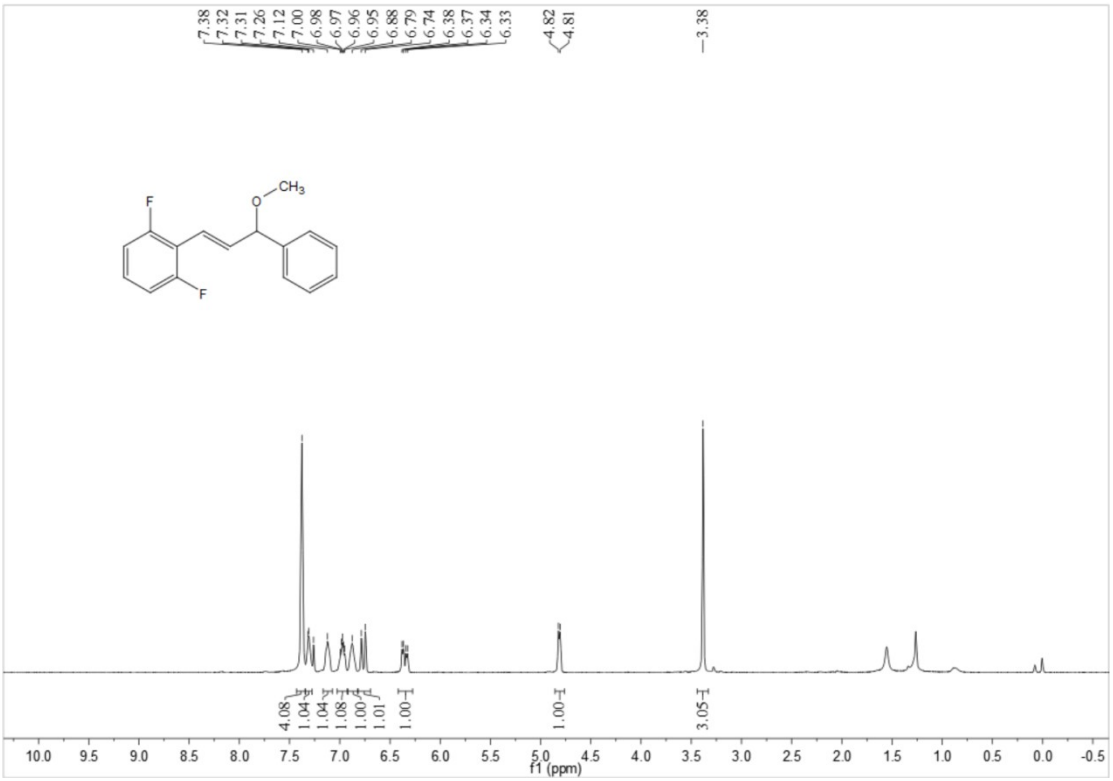
^{1}H NMR for (3-methoxyprop-1-ene-1,3-diyl)dibenzene (3v)



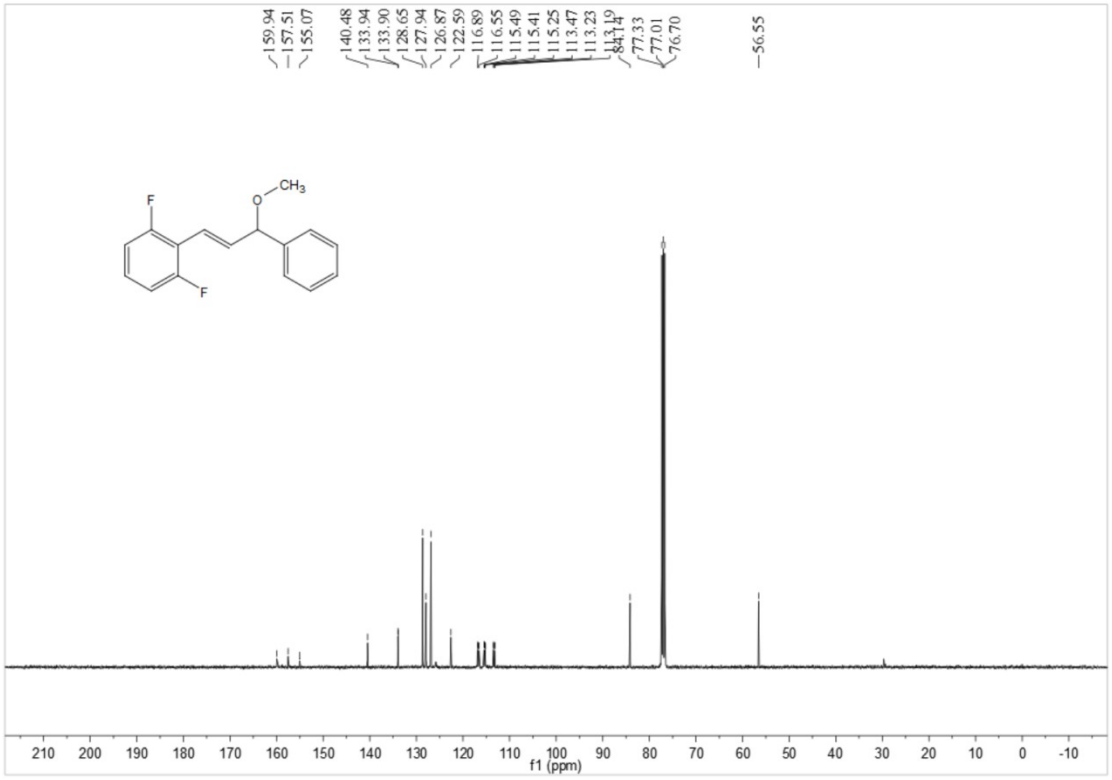
^{13}C NMR for (3-methoxyprop-1-ene-1,3-diyl)dibenzene(3v)



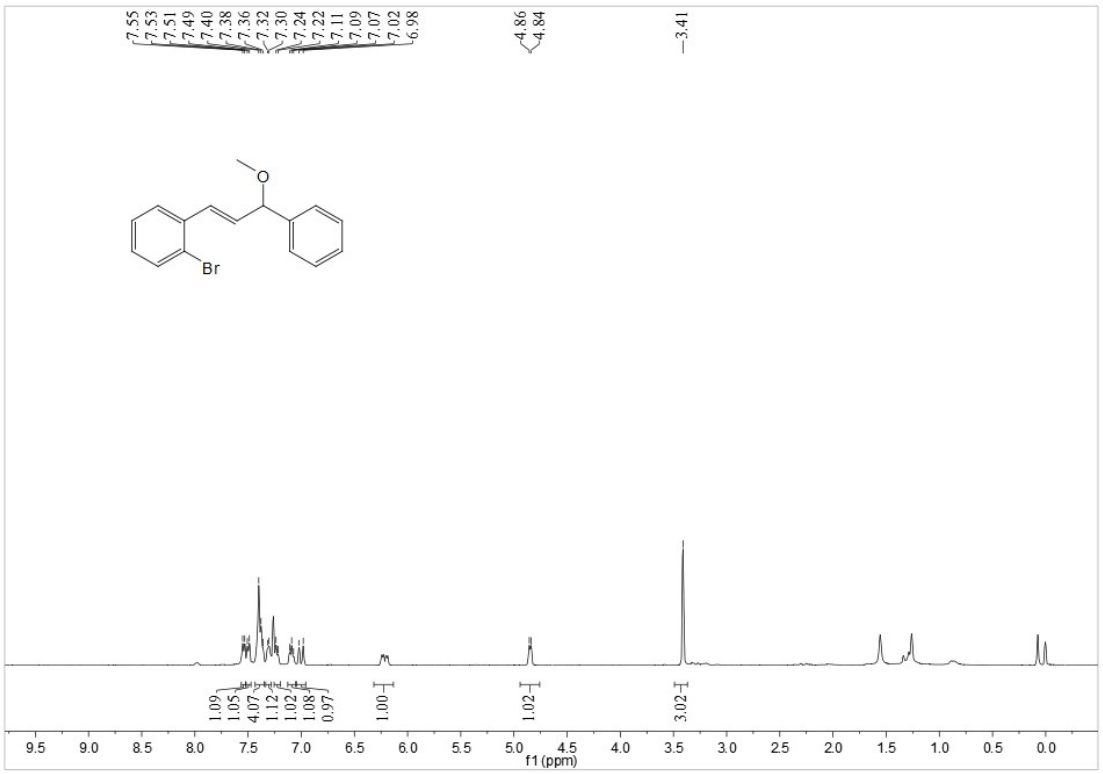
^{1}H NMR for 1,2-difluoro-3-(3-methoxy-3-phenylprop-1-en-1-yl)benzene (3w)



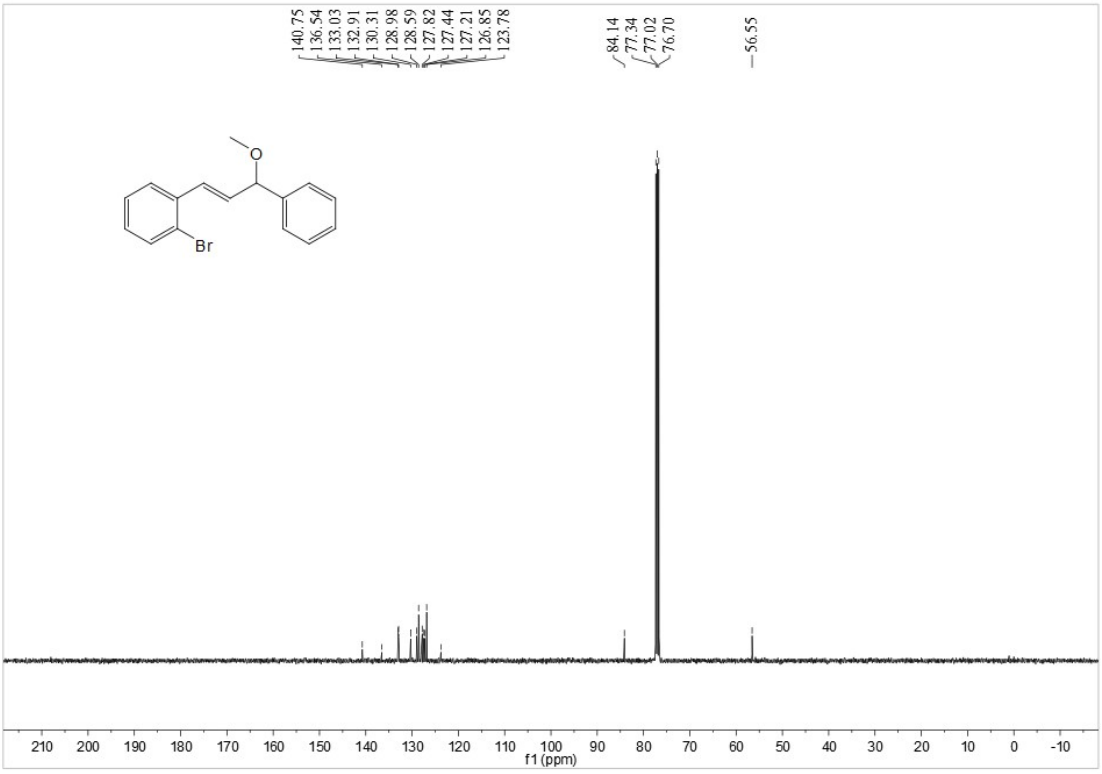
^{13}C NMR for 1,2-difluoro-3-(3-methoxy-3-phenylprop-1-en-1-yl)benzene (3w)



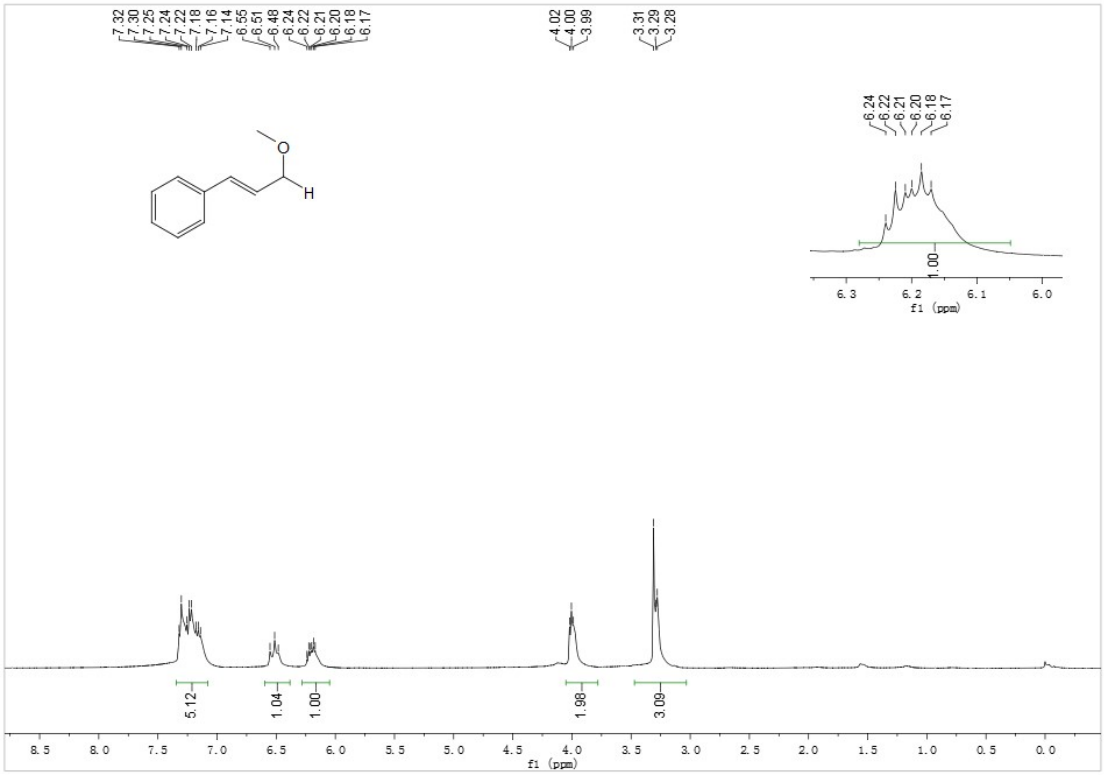
^{1}H NMR for 1-bromo-2-(3-methoxy-3-phenylprop-1-en-1-yl)benzene (3x)



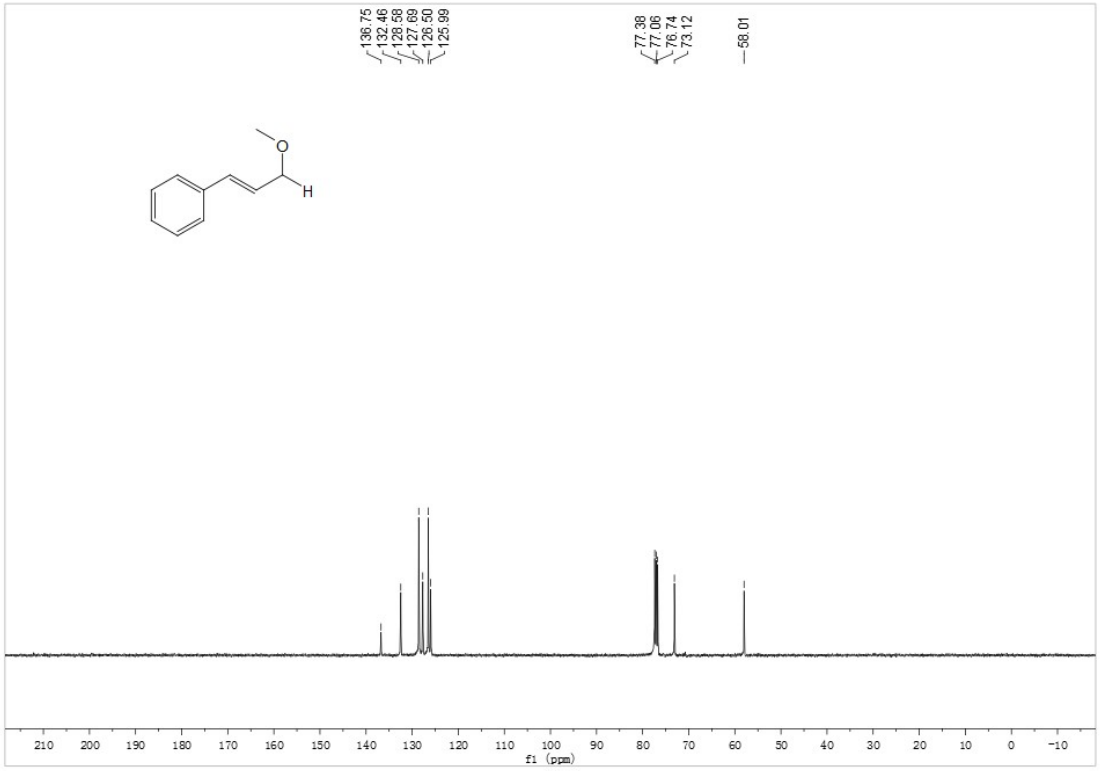
^{13}C NMR for 1-bromo-2-(3-methoxy-3-phenylprop-1-en-1-yl)benzene (3x)



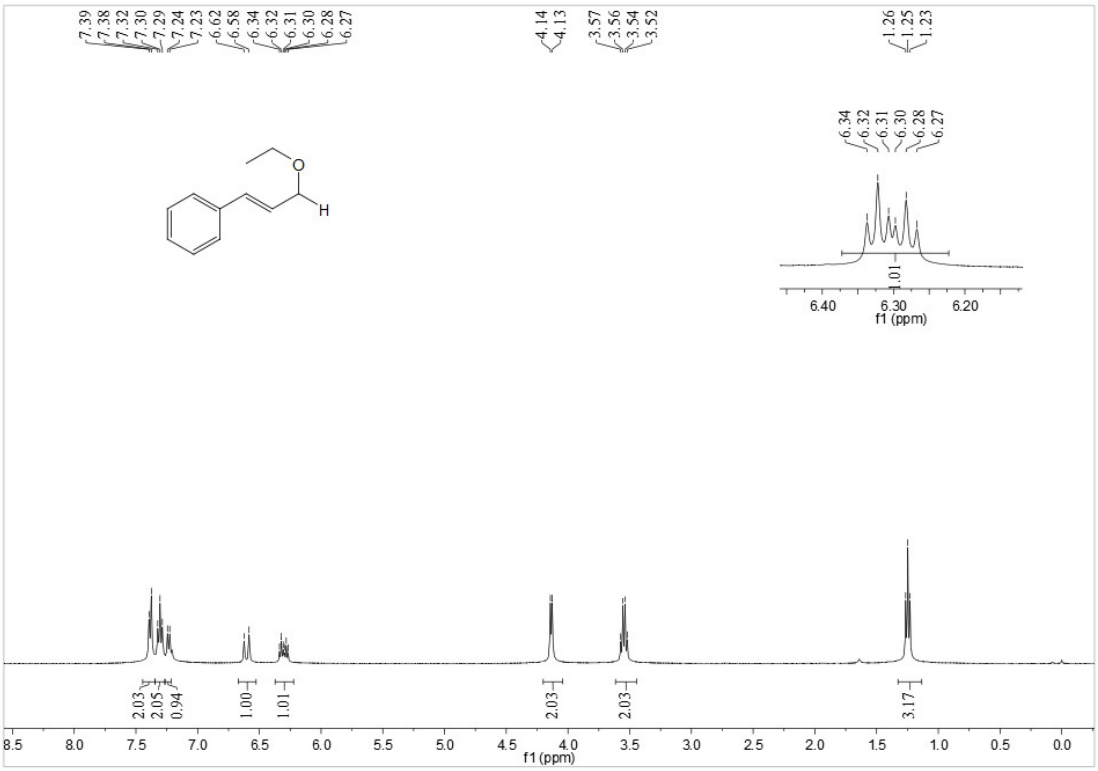
^{1}H NMR spectra of (3-methoxyprop-1-en-1-yl)benzene(3aa)



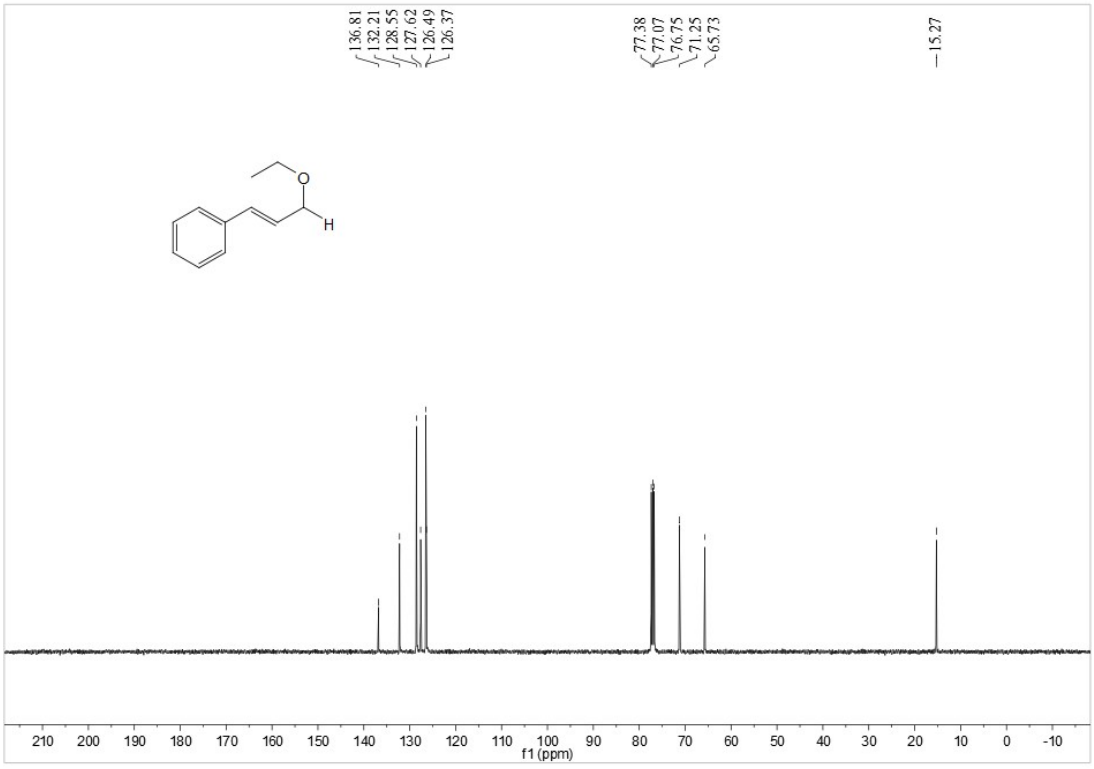
^{13}C NMR spectra of (3-methoxyprop-1-en-1-yl)benzene(3aa)



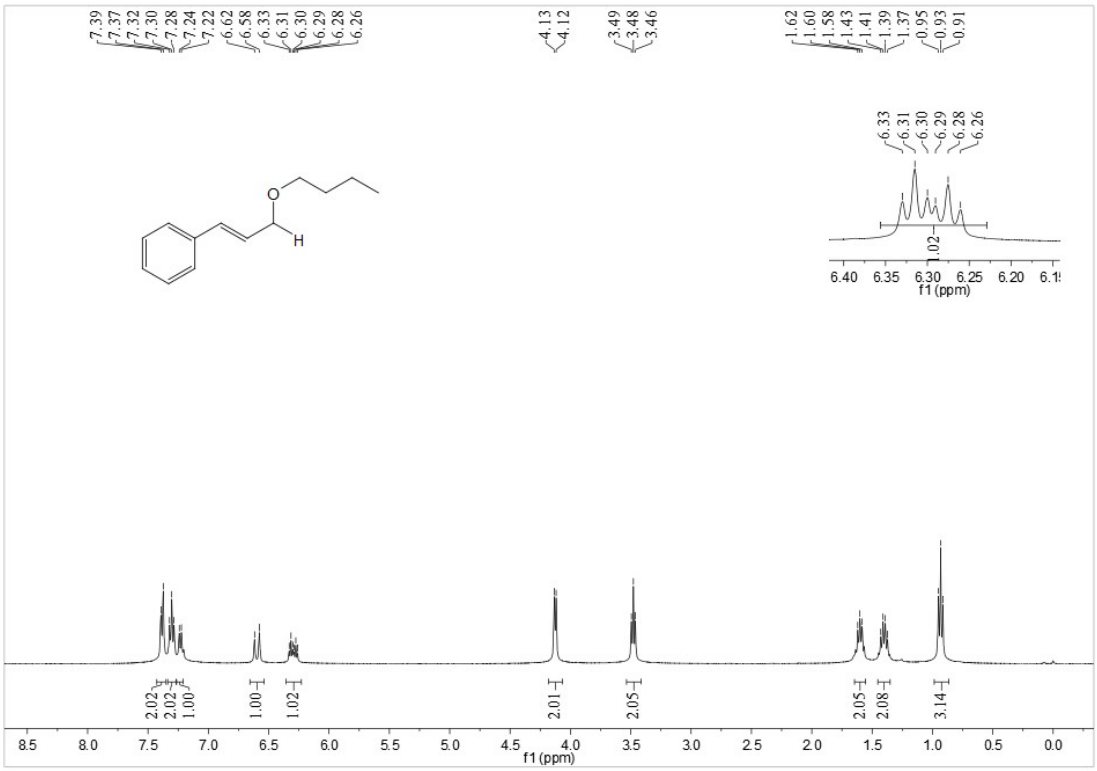
^{1}H NMR spectra of (3-ethoxyprop-1-en-1-yl)benzene(3ab)



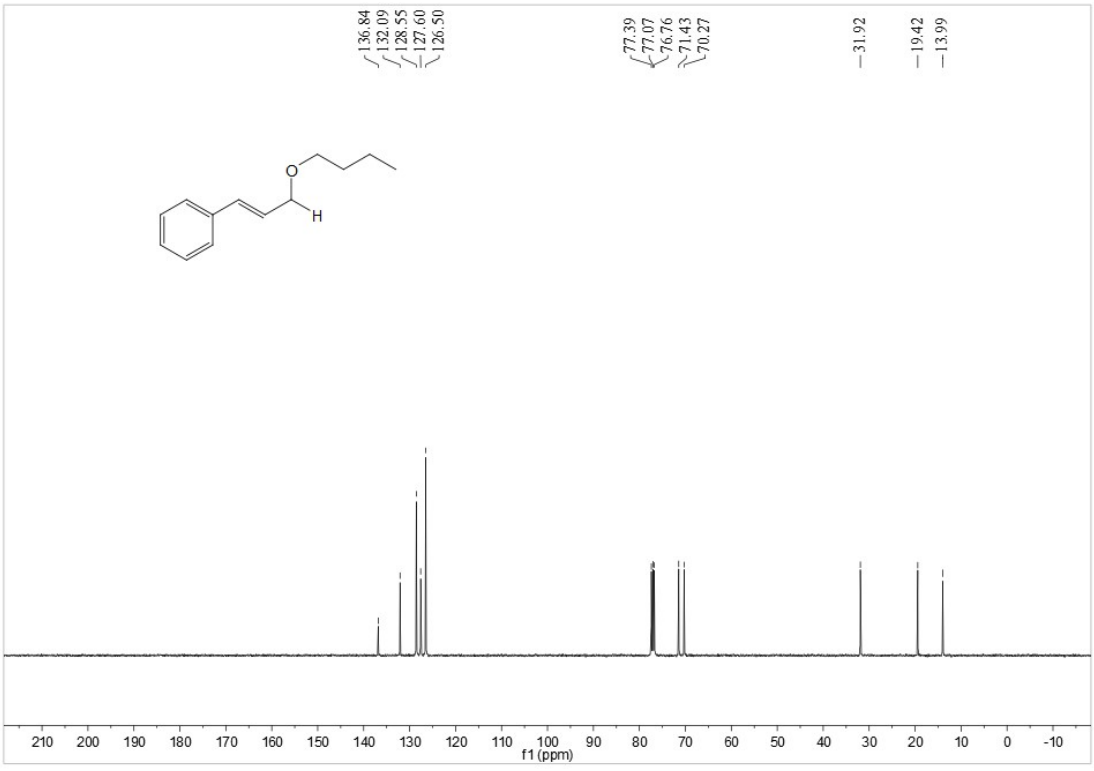
^{13}C NMR spectra of (3-ethoxyprop-1-en-1-yl)benzene(3ab)



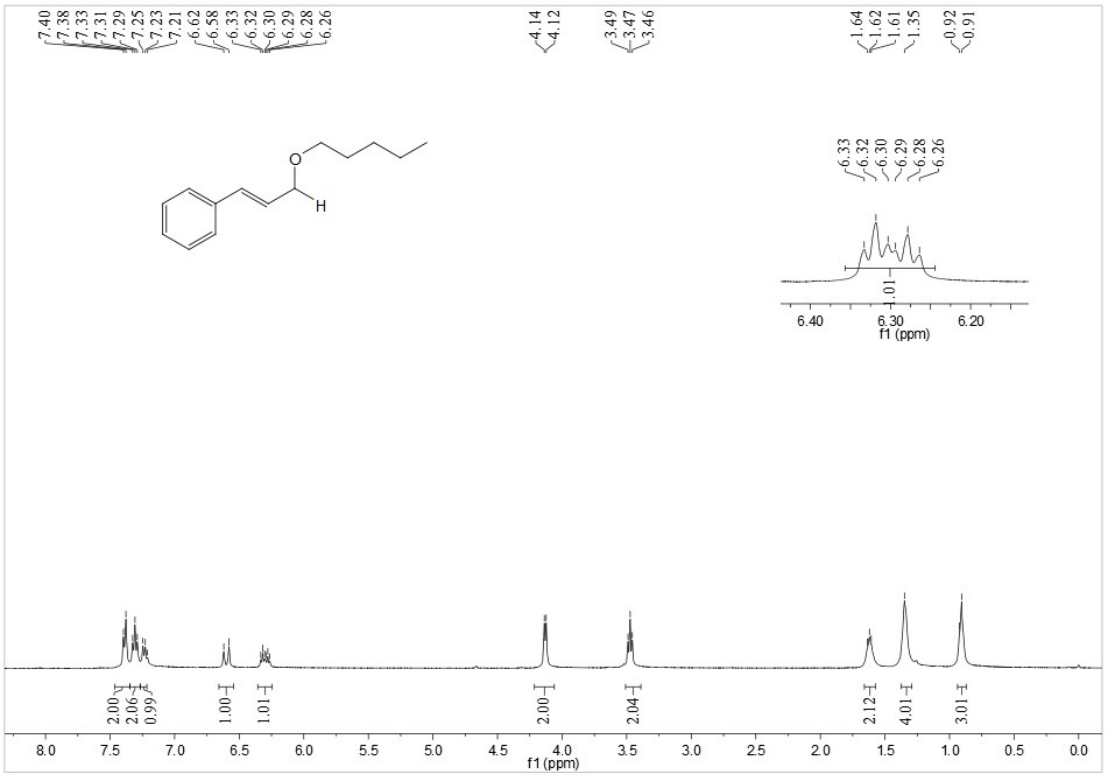
^{1}H NMR spectra of (3-butoxyprop-1-en-1-yl)benzene(3ac)



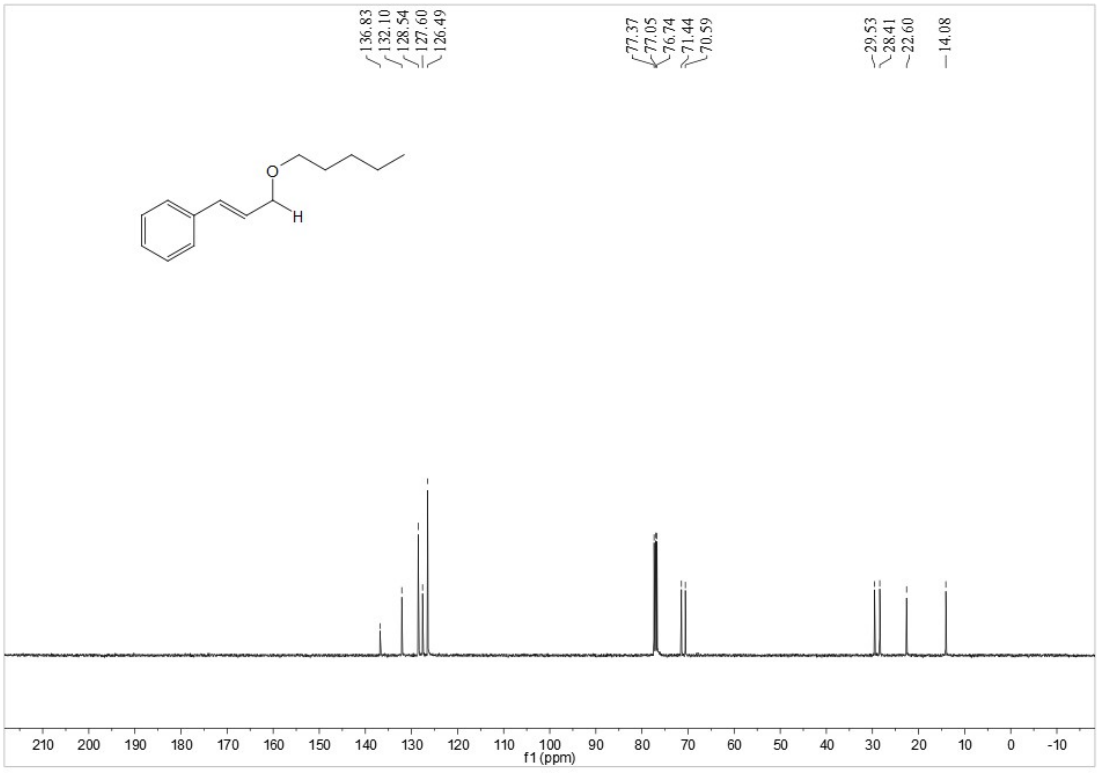
^{13}C NMR spectra of (3-butoxyprop-1-en-1-yl)benzene(3ac)



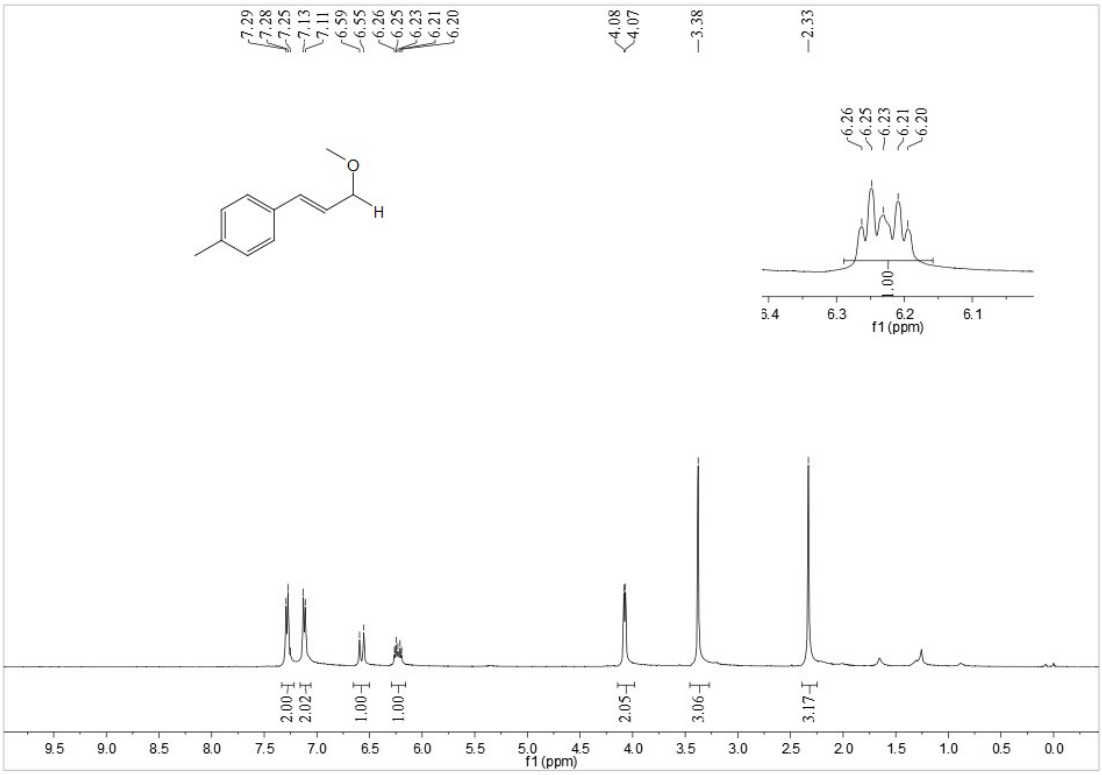
^{1}H NMR spectra of (3-(pentyloxy)prop-1-en-1-yl)benzene(3ad)



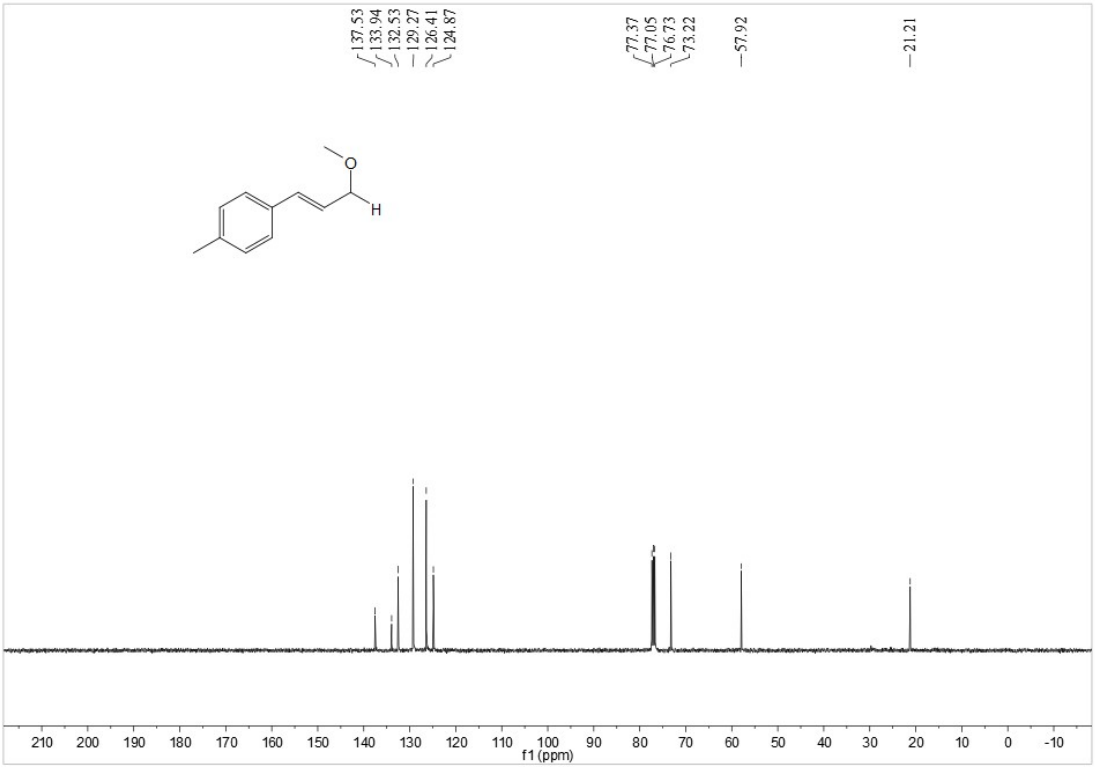
^{13}C NMR spectra of (3-(pentyloxy)prop-1-en-1-yl)benzene(3ad)



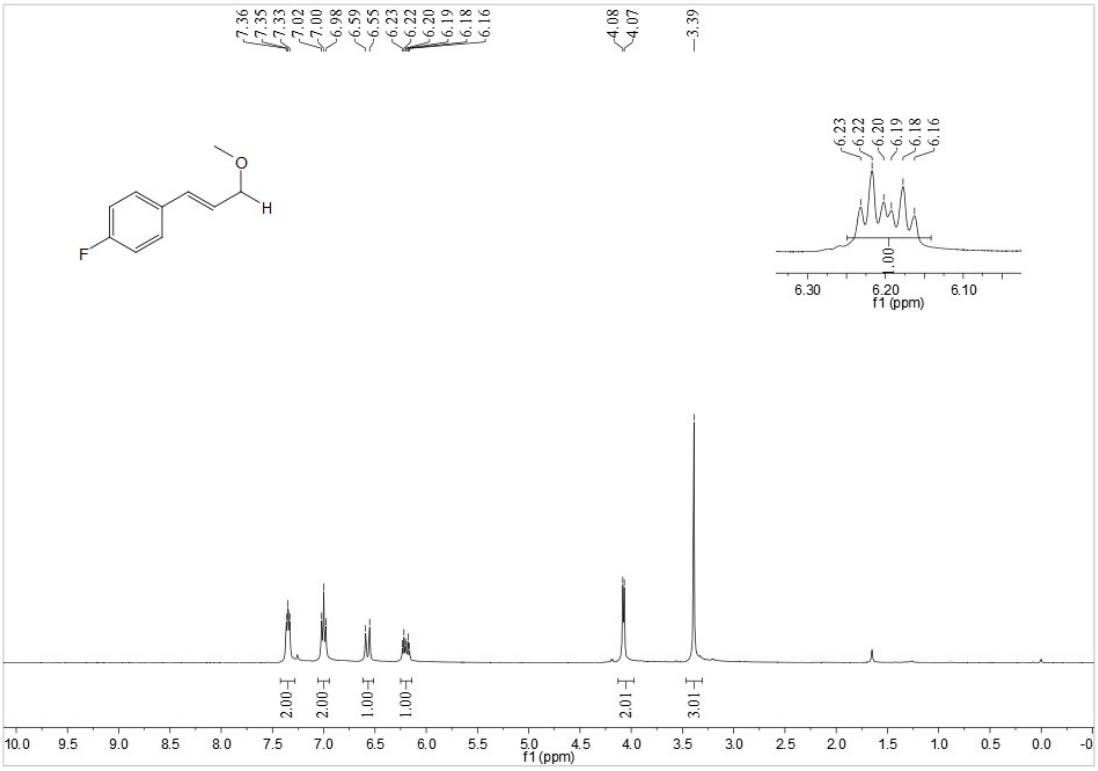
^{1}H NMR spectra of 1-(3-methoxyprop-1-en-1-yl)-4-methylbenzene(3ae)



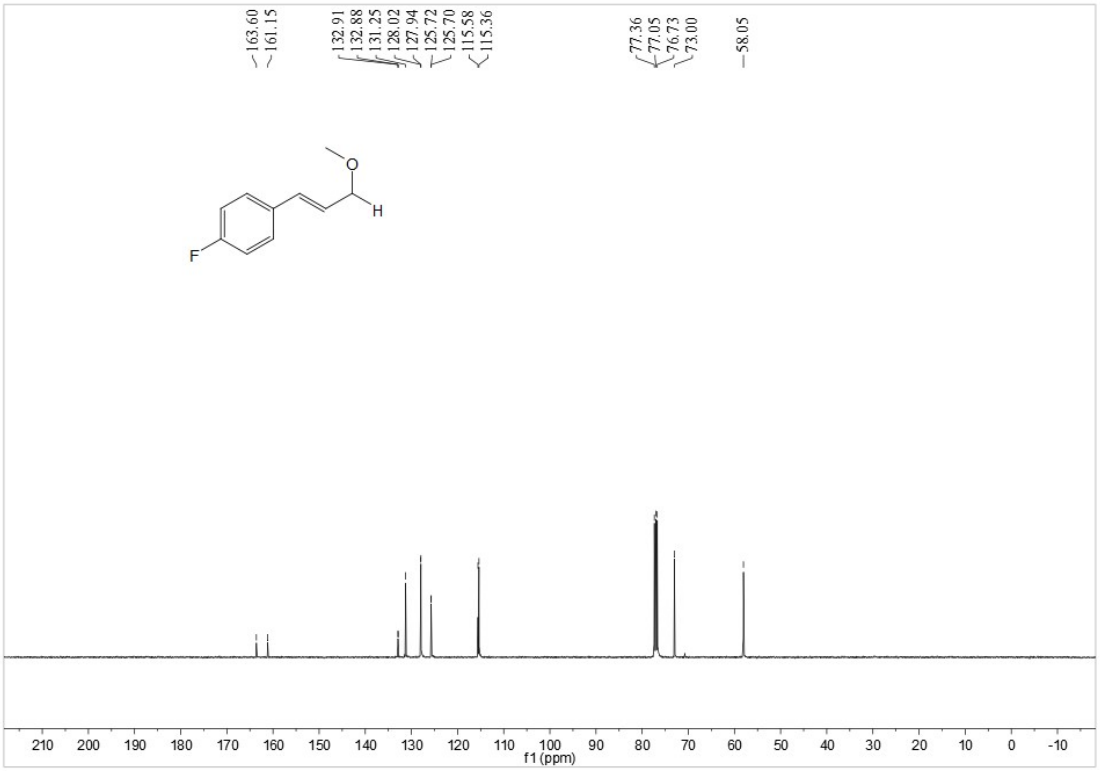
^{13}C NMR spectra of 1-(3-methoxyprop-1-en-1-yl)-4-methylbenzene(3ae)



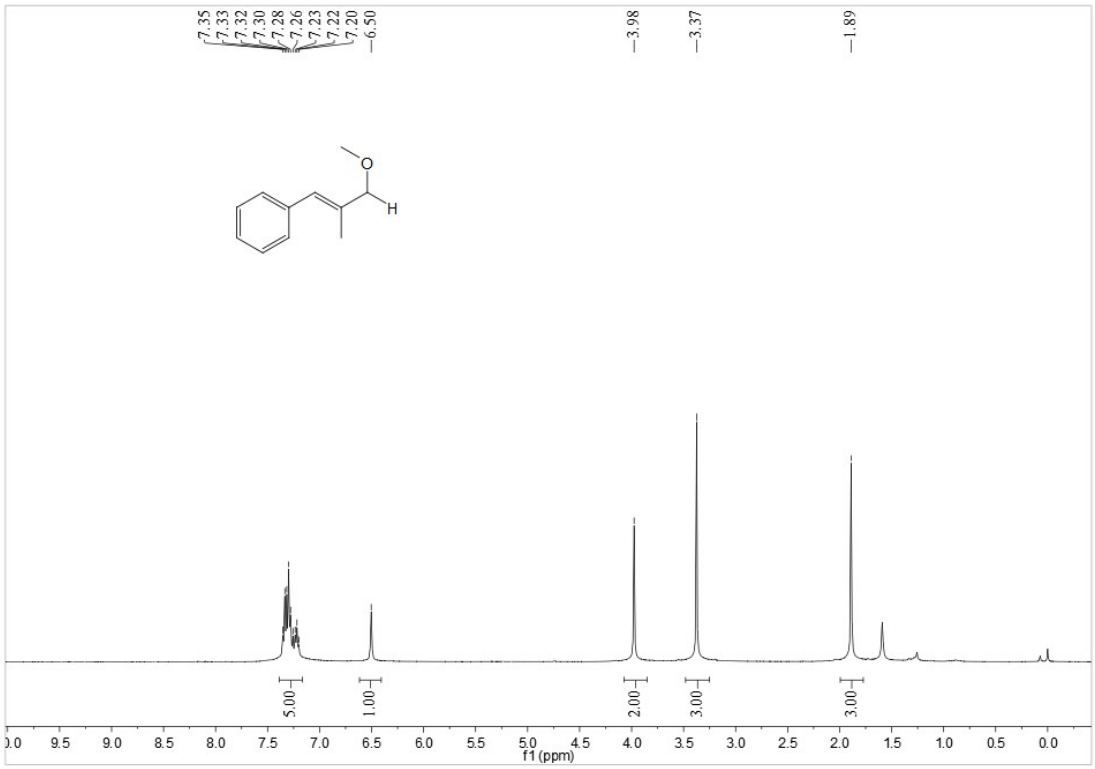
^{1}H NMR spectra of 1-fluoro-4-(3-methoxyprop-1-en-1-yl)benzene(3af)



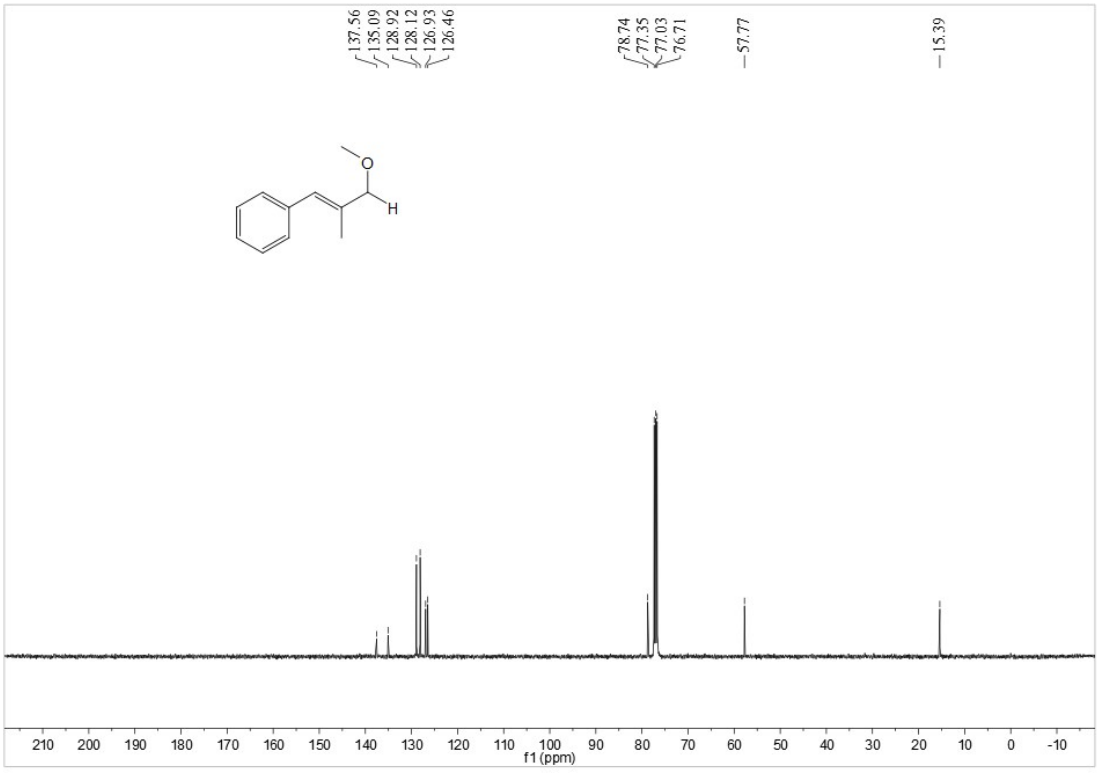
^{13}C NMR spectra of 1-fluoro-4-(3-methoxyprop-1-en-1-yl)benzene(3af)



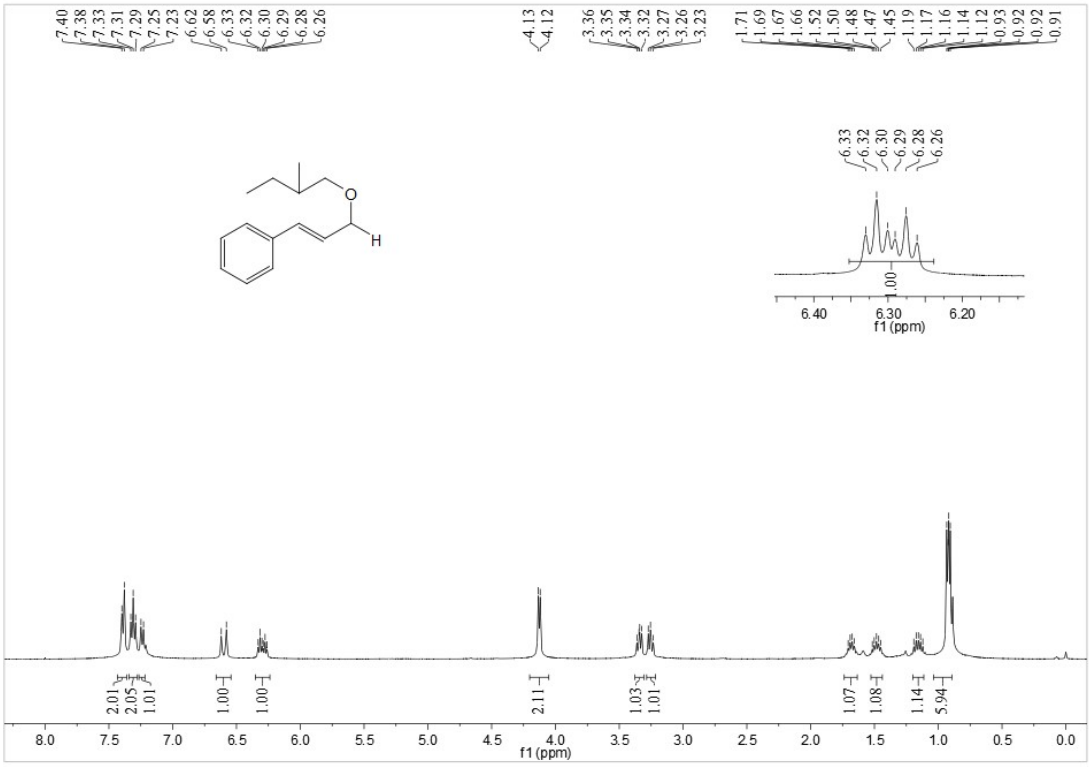
^{1}H NMR spectra of (3-methoxy-2-methylprop-1-en-1-yl)benzene(3ag)



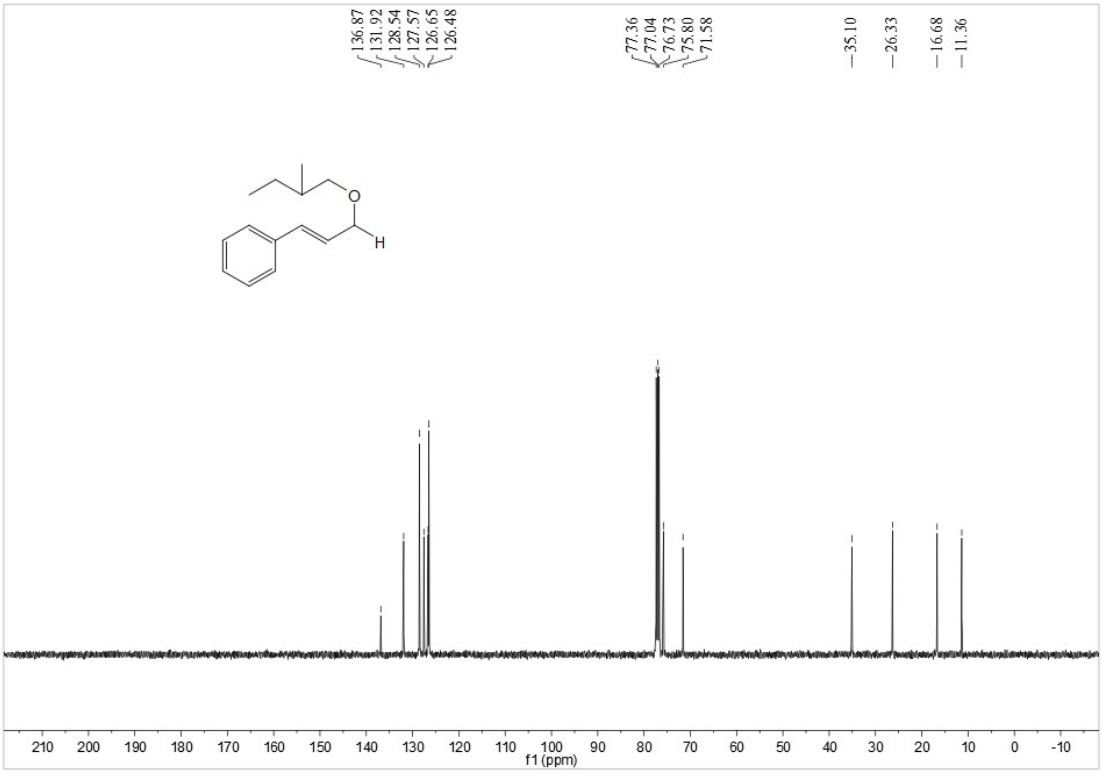
^{13}C NMR spectra of (3-methoxy-2-methylprop-1-en-1-yl)benzene(3ag)



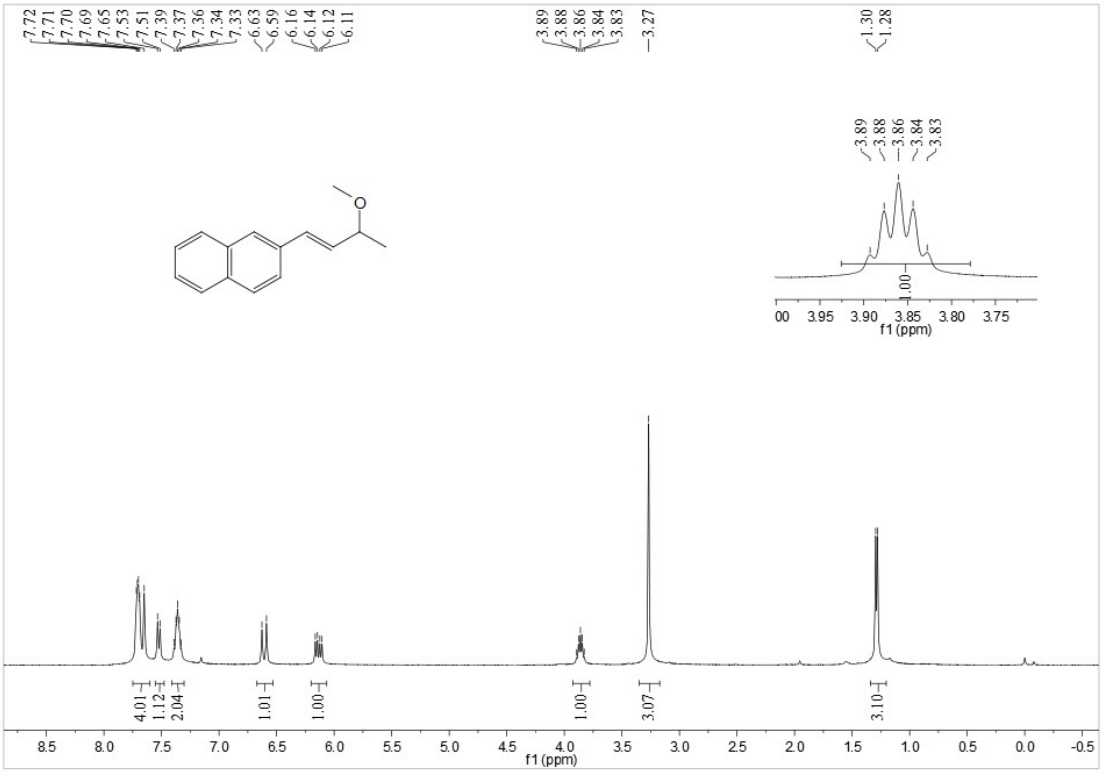
^{1}H NMR spectra of (3-(2-methylbutoxy)prop-1-en-1-yl)benzene(3ah)



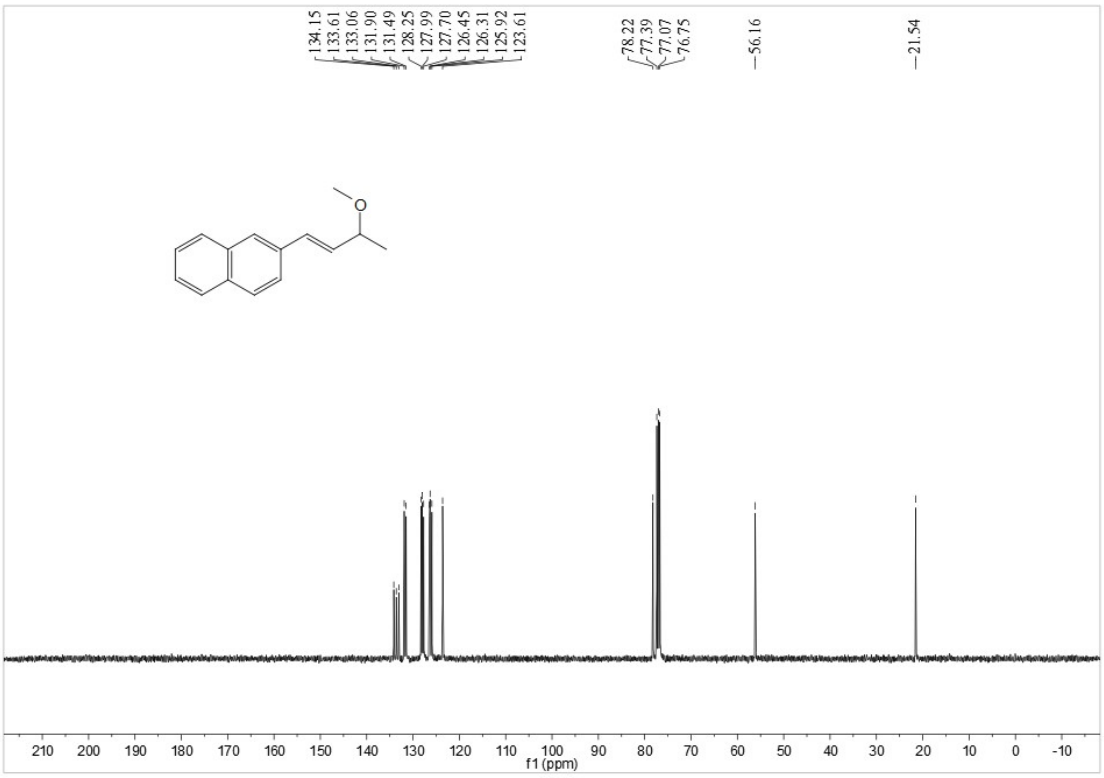
^{13}C NMR spectra of (3-(2-methylbutoxy)prop-1-en-1-yl)benzene(3ah)



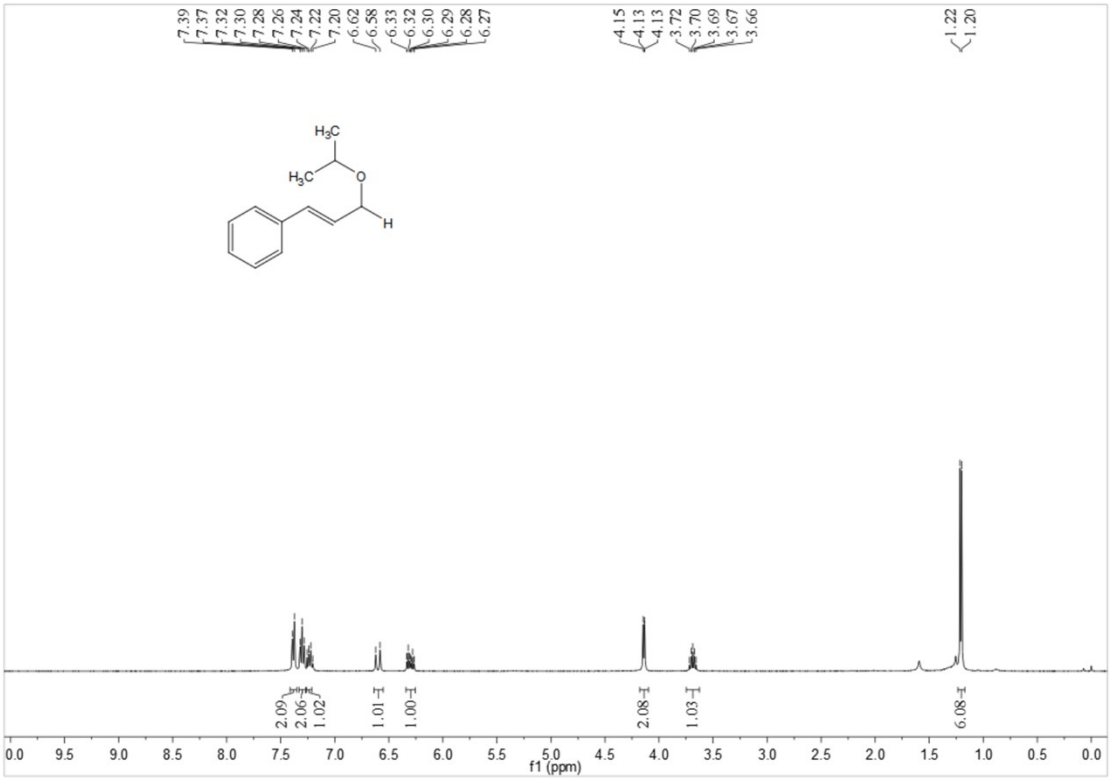
^{1}H NMR spectra of 2-(3-methoxybut-1-en-1-yl)naphthalene(3ai)



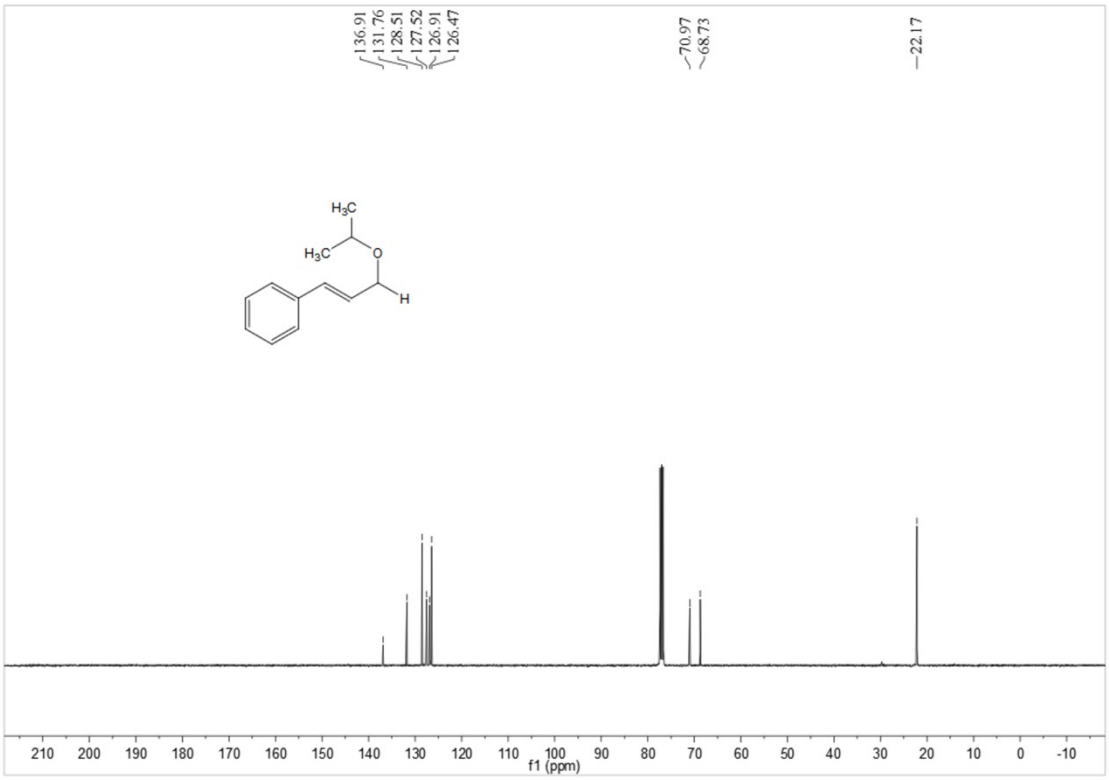
^{13}C NMR spectra of 2-(3-methoxybut-1-en-1-yl)naphthalene (3ai)



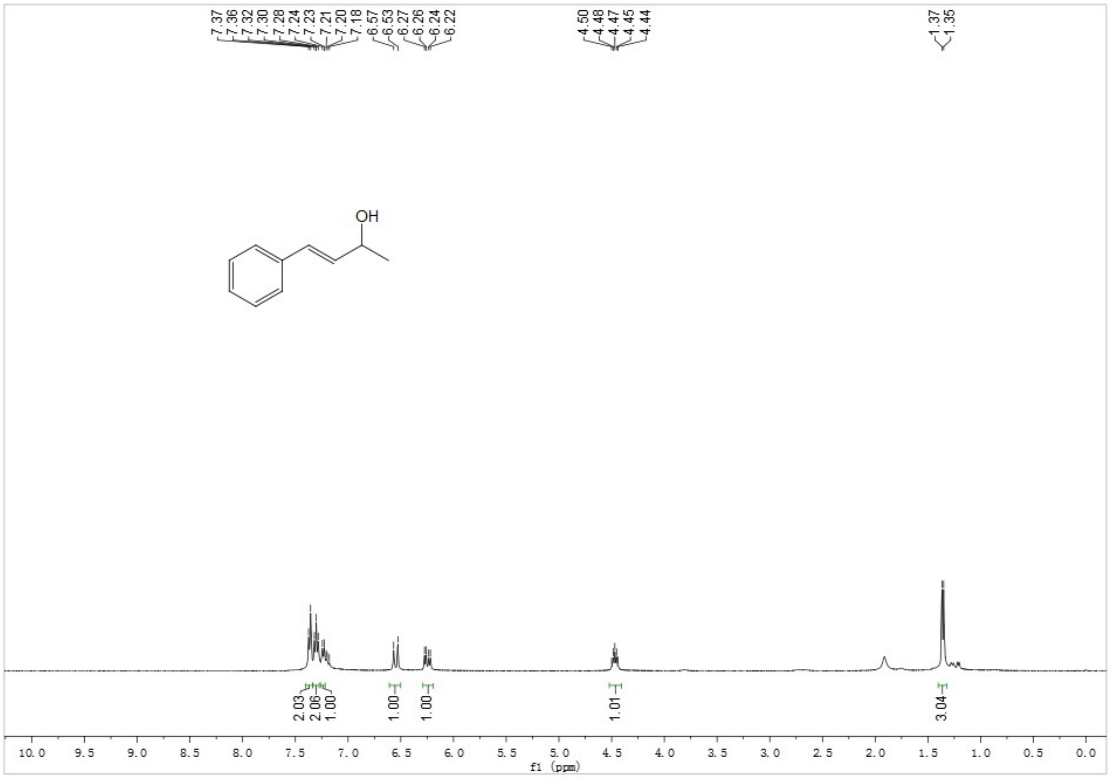
^{1}H NMR spectra of (*E*)-(3-isopropoxyprop-1-en-1-yl)benzene (3aj)



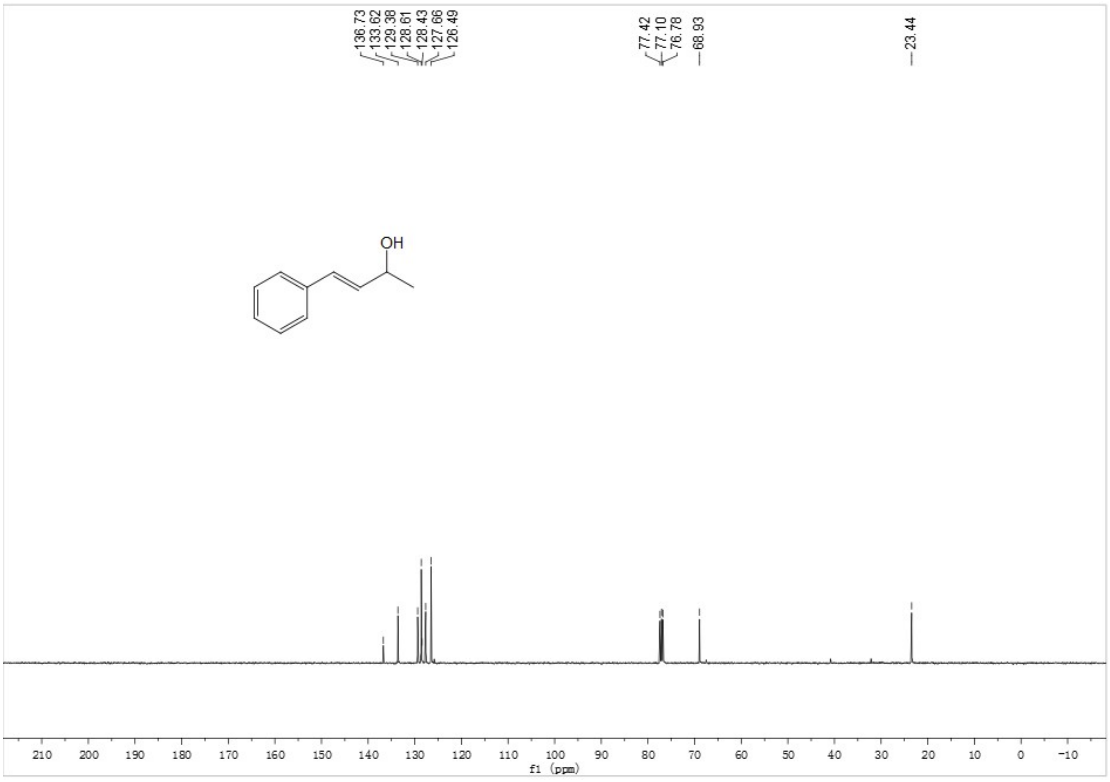
^{13}C NMR spectra of (*E*)-(3-isopropoxyprop-1-en-1-yl)benzene (3aj)



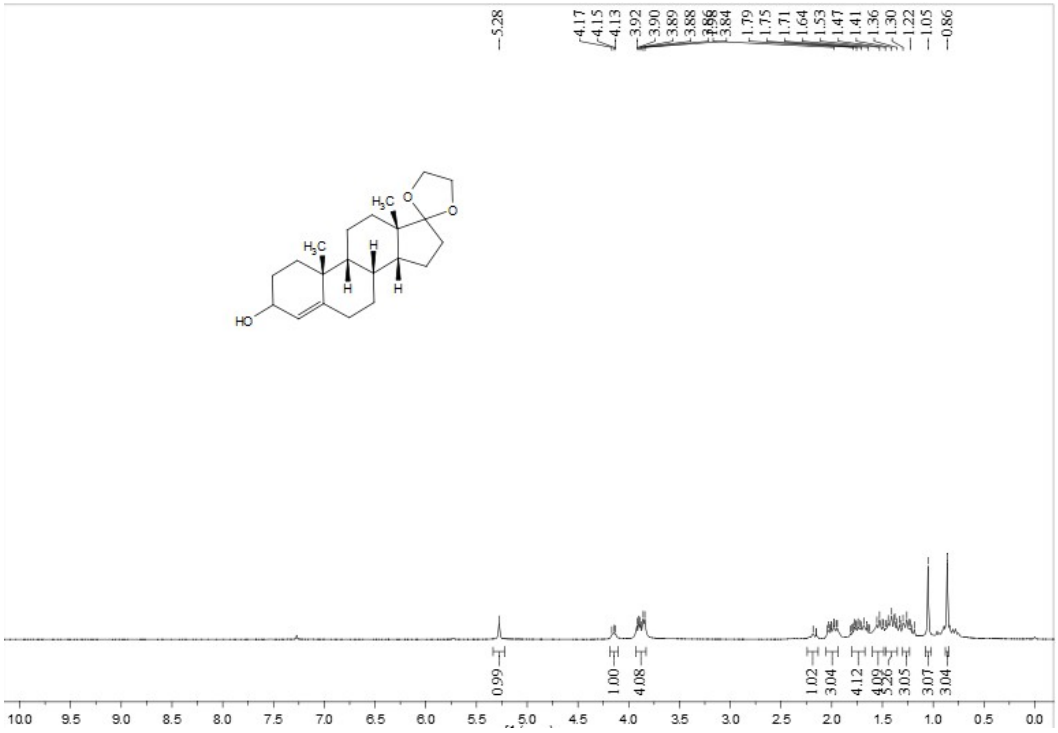
^{1}H NMR spectra of 4-phenylbutan-2-ol(4a)



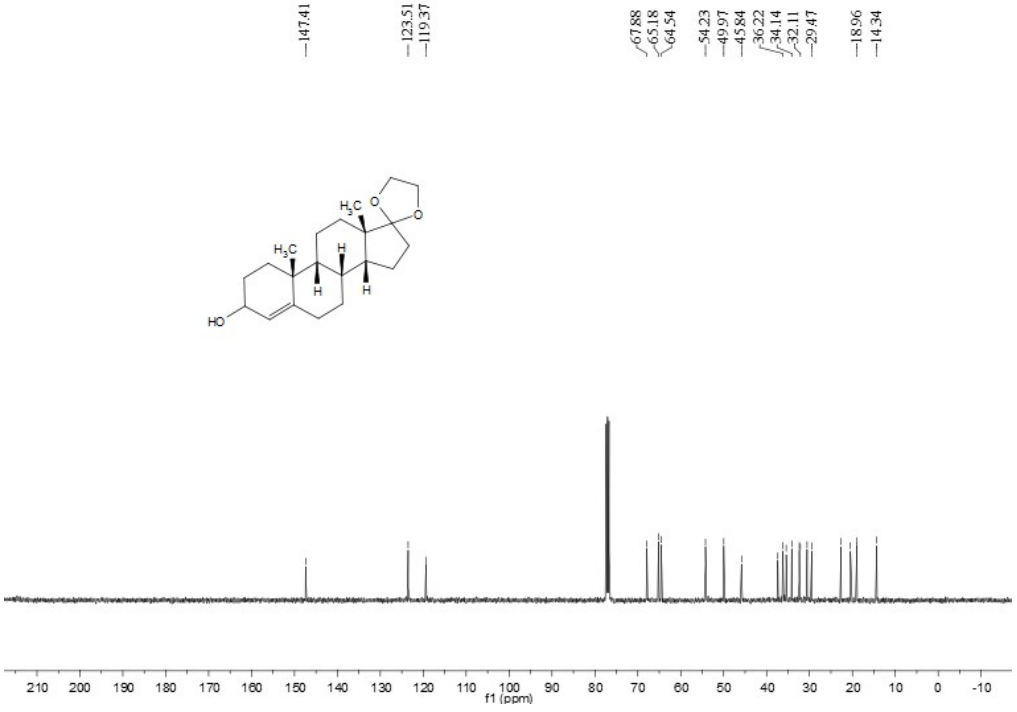
^{13}C NMR spectra of 4-phenylbutan-2-ol(4a)



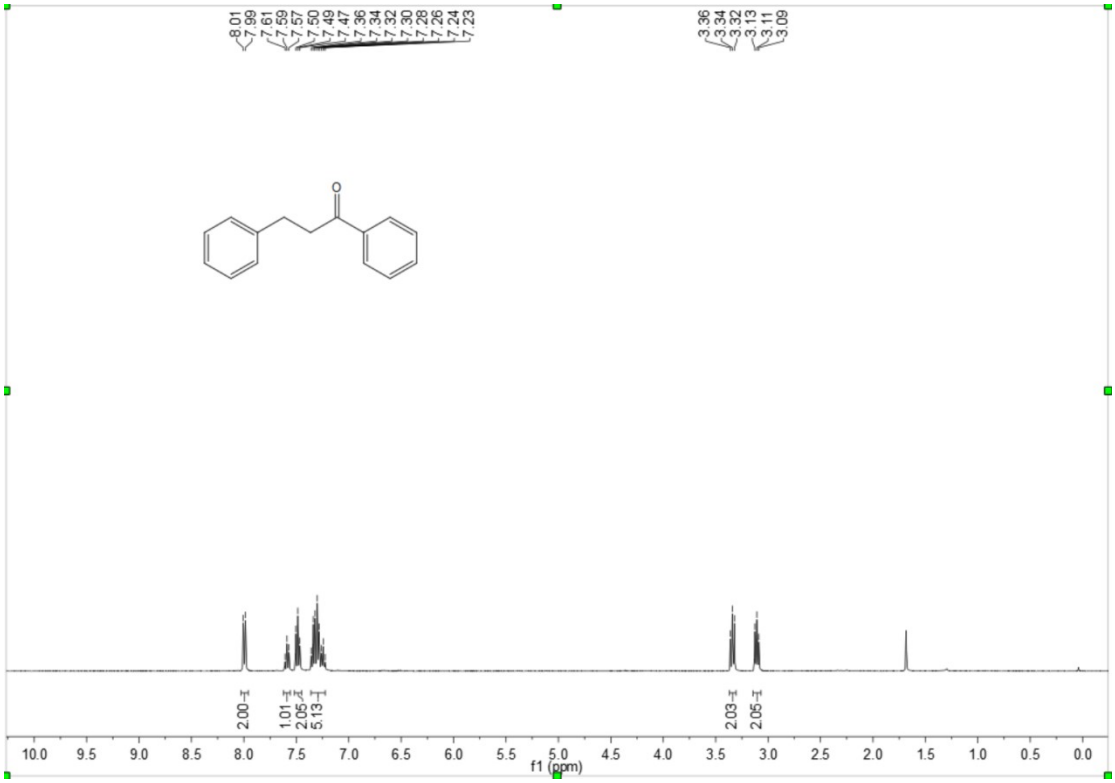
^{1}H NMR spectra of (8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol(4y)



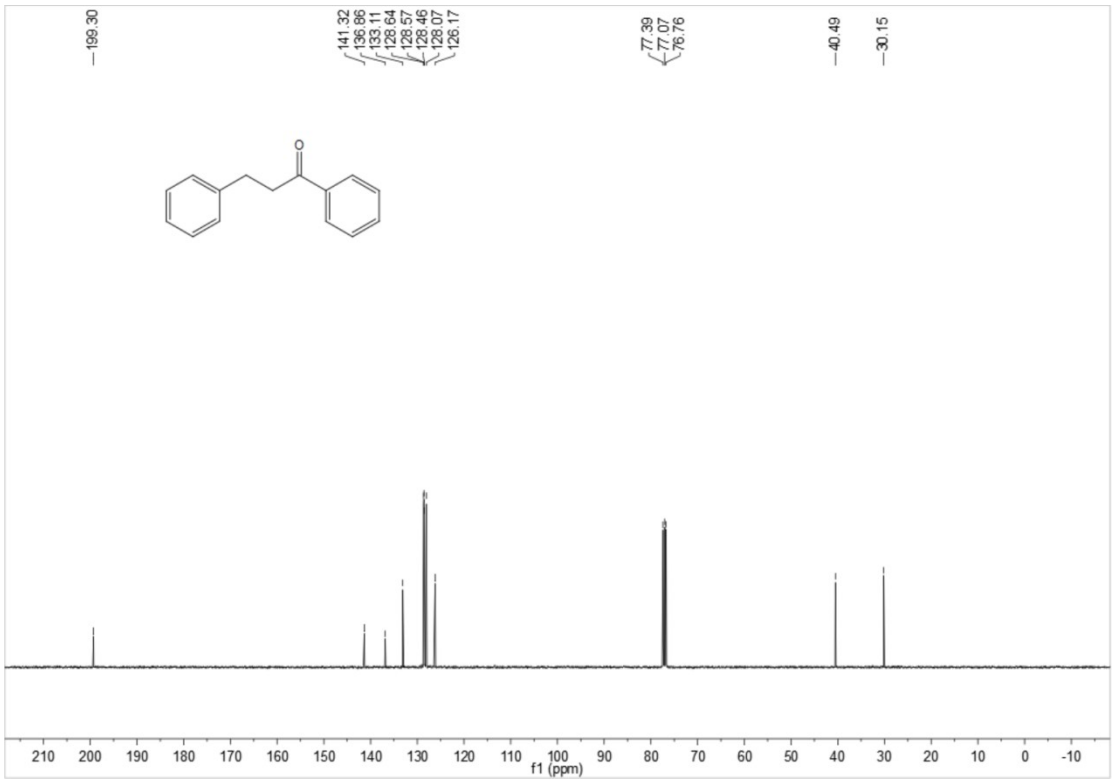
^{13}C NMR spectra of (8S,9S,10R,13S,14S)-10,13-dimethyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol(4y)



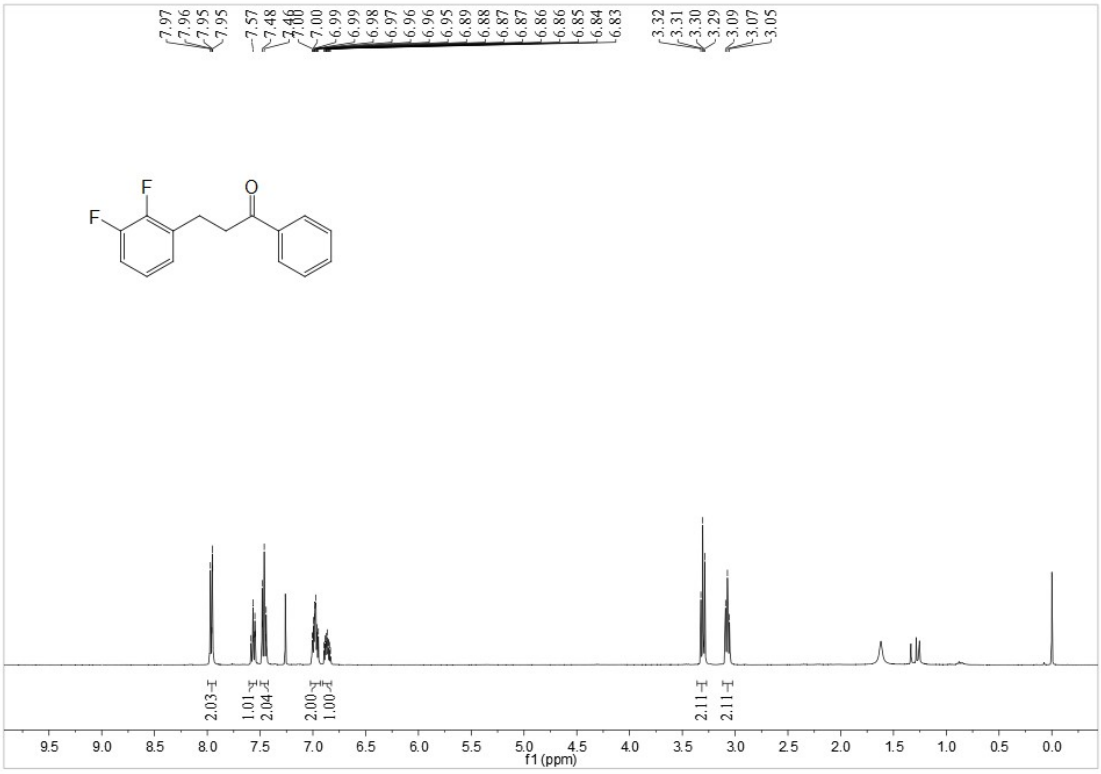
^{1}H NMR for 1,3-diphenylpropan-1-one (5v)



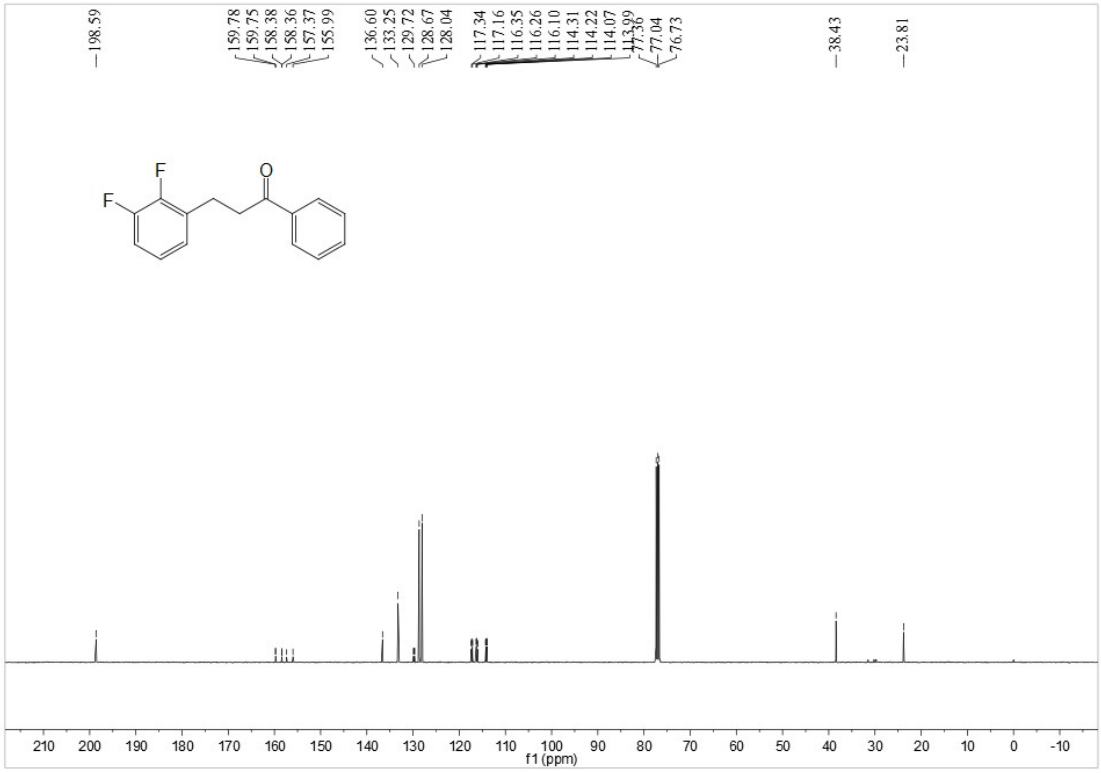
^{13}C NMR for 1,3-diphenylpropan-1-one (5v)



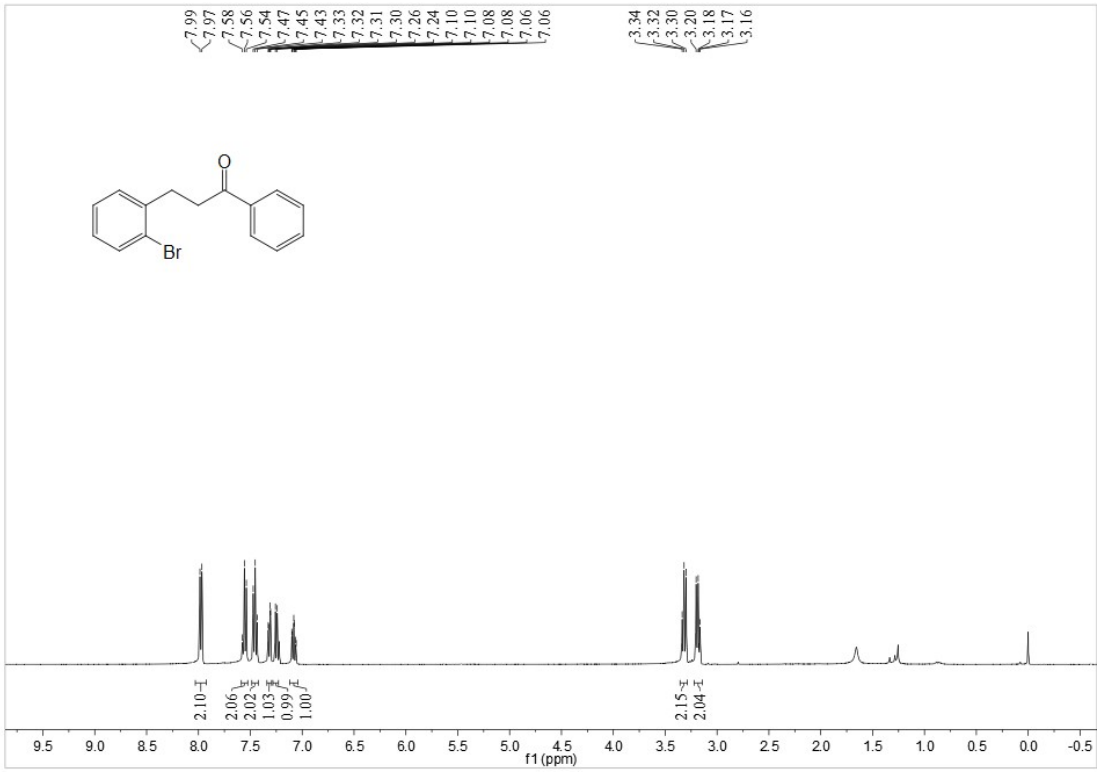
^{1}H NMR for 3-(2,3-difluorophenyl)-1-phenylpropan-1-one (5w)



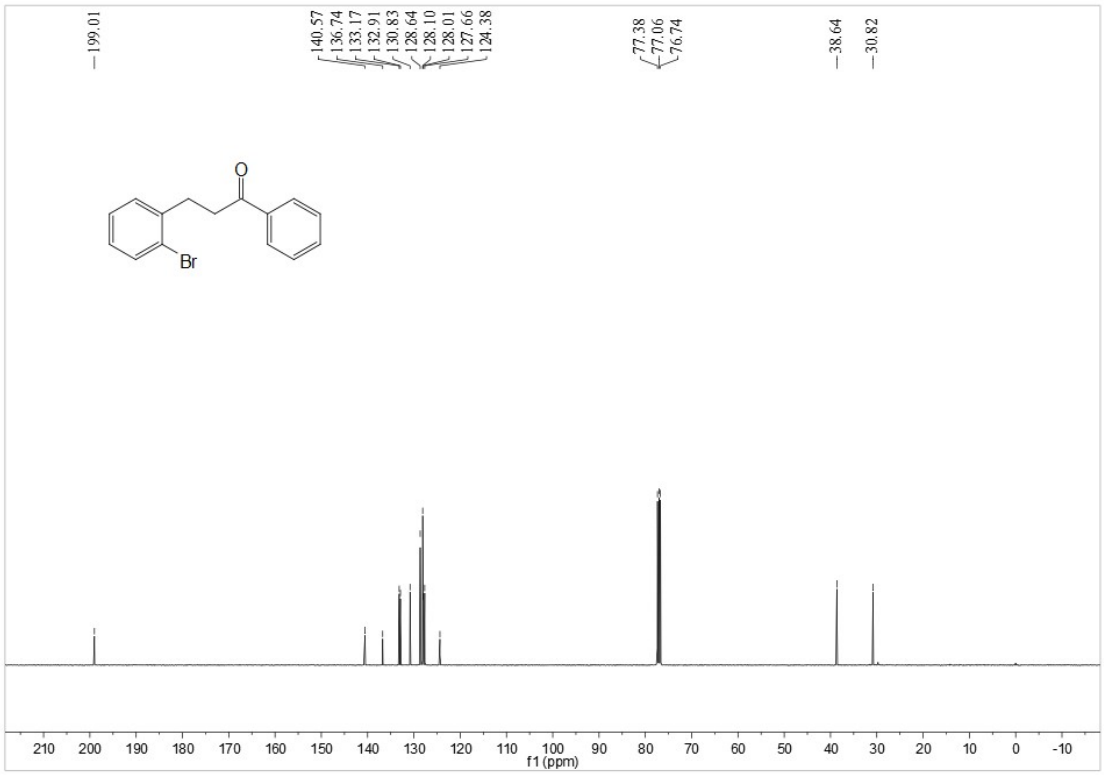
^{13}C NMR for 3-(2,3-difluorophenyl)-1-phenylpropan-1-one (5w)



^{1}H NMR for 3-(2-bromophenyl)-1-phenylpropan-1-one (5x)



^{13}C NMR for 3-(2-bromophenyl)-1-phenylpropan-1-one (5x)



J. ^{1}H NMR Spectrumof TC-6-H

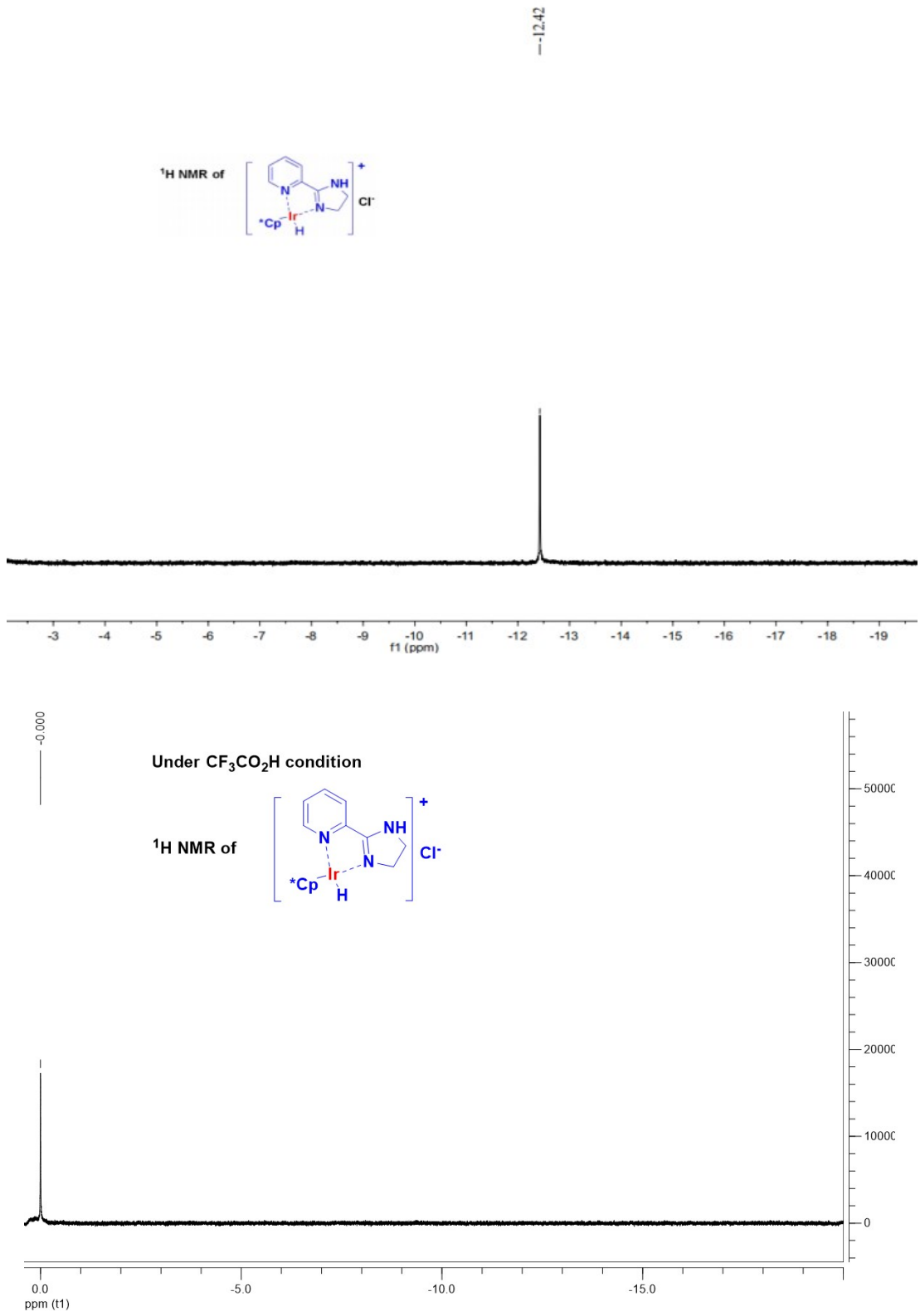


Figure S2. ^{1}H NMR of TC-6-H