Electronic Supplementary Material (ESI) for ChemComm.

Cu-catalyzed Intramolecular Aryl-etherification Reactions of Alkoxide Alkynes with Diaryliodonium Salts via the Cleavage of a Stable C-O Bond

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1. General Comments

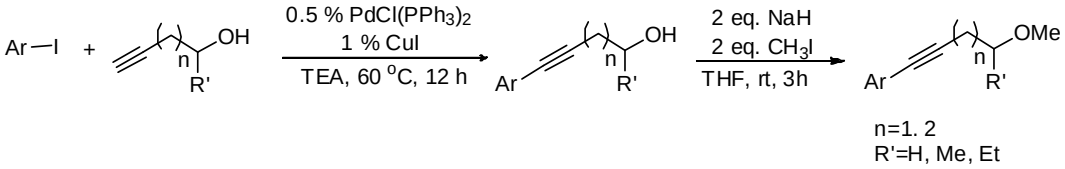
All the reactions were carried out using pre-dried screw capped tube with a Teflon-lined septum under N_2 atmosphere. Ph_2IPF_6 was obtained from Alfa-aesar. Diaryliodonium reagents except Ph_2IPF_6 were synthesized according to the literatures [1]. All of the solvents were fresh distilled. Column chromatography was performed using silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^1H NMR and ^{13}C NMR spectra were recorded using JEOL AL-300MHz or AL-400MHz spectrometer at ambient temperature with $CDCl_3$ or D-DMSO as the solvents. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26) or D-DMSO (2.54), to the carbon resonance of $CDCl_3$ (77.16) or D-DMSO (40.45). Coupling constants (*J*) were given in Hertz (Hz). The term m, dq, q, t, d, s referred to multiplet, doublet quartet, quartet, triplet, doublet, and singlet. Mass spectra were obtained on a Bruker Esquire ion trap mass spectrometer in positive mode. The reaction progress was monitored by GC-MS if applicable.

2. Experimental Section

Starting diaryliodonium salts

Diaryliodonium salts were synthesized according to the literature procedures [1].

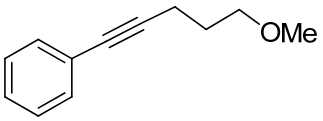
1) General procedure for the preparation of (4-methoxybut-1-yn-1-yl) benzene and (5-methoxypent-1-yn-1-yl) benzene[2].



Take the preparation of (5-methoxypent-1-yn-1-yl) benzene as example

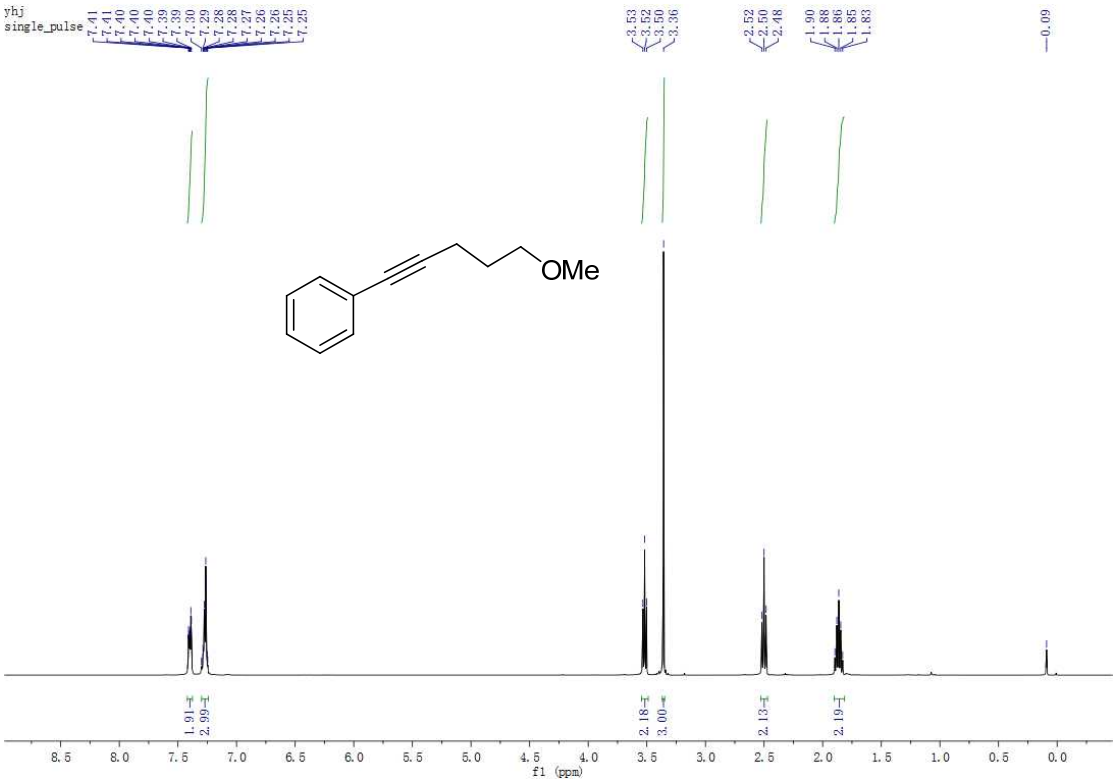
To a 100 mL sealed tube, under N_2, was added $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol), CuI (22.8 mg, 0.12 mmol), PhI (1.61 ml, 14.4 mmol) and anhydrous TEA (20 ml). The mixture was stirred at room temperature for 1 min and then alcohol (1.10 ml, 12 mmol) was added. The tube was sealed and the mixture was allowed to stir at 60℃ for 12 h. After completion, the mixture was cooled to room temperature, the H_2O (25 mL) was added and the mixture was extracted with EtOAc (25 mL x 3), dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (using 20% EtOAc/Hexane as eluent) provided 5-phenylpent-4-yn-1-ol as yellow oil.

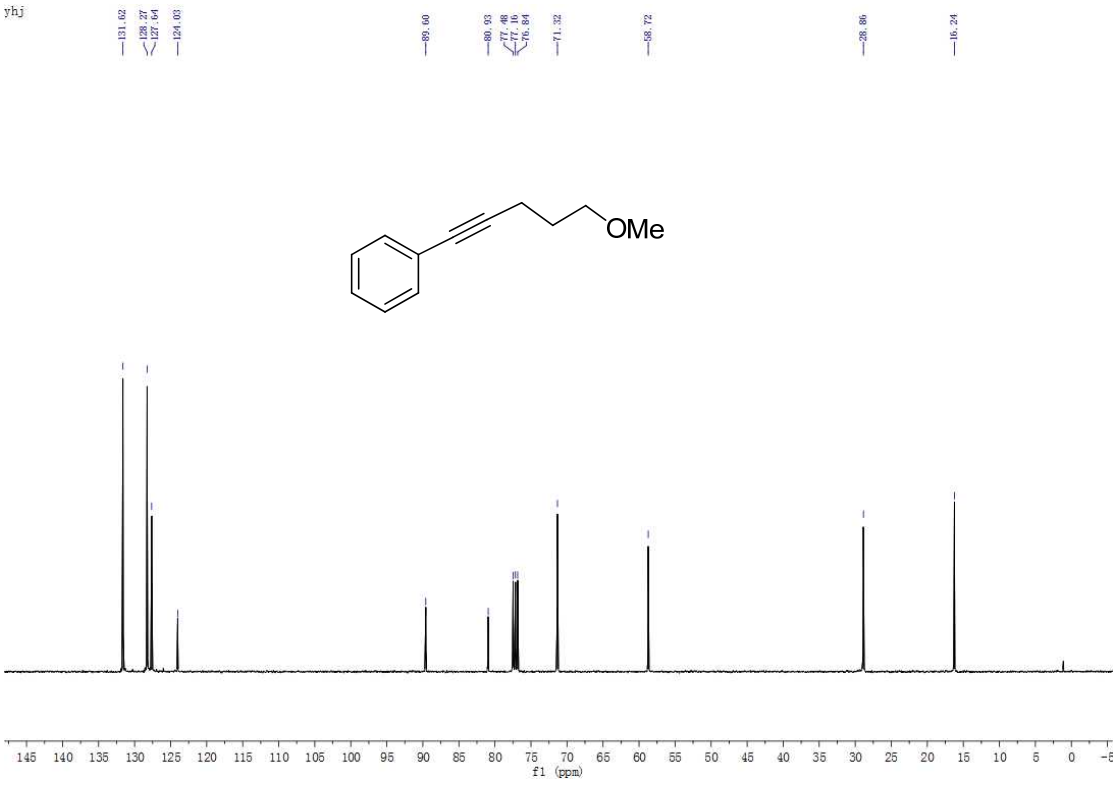
5-phenylpent-4-yn-1-ol (1.6 g, 10mmol), NaH (0.8 g, 20 mmol, 60% dispersion in mineral oil), CH_3I (1.01 mL, 20 mmol) and freshly distilled THF (20 mL) were used to afford the desired product as a yellow liquid. Purification of crude product was conducted by filtered over a short silica pad followed by flash column chromatography on silica gel using EtOAc/Hexane 1:50 as eluent.



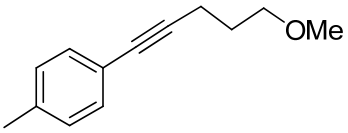
(5-methoxypent-1-yn-1-yl) benzene 2a: yellow oil, yield: 80%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.43 – 7.34 (m, 2H), 7.32 – 7.20 (m, 3H), 3.52 (t, *J* = 6.2 Hz, 2H), 3.36 (s, 3H), 2.50 (t, *J* = 7.0 Hz, 2H), 1.86 (p, *J* = 6.6 Hz, 2H);

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.67, 128.31, 127.69, 124.05, 89.63, 80.96, 71.39, 58.80, 28.89, 16.29. GC-MS m/z calcd for $C_{12}H_{14}O$: 174; found: 174





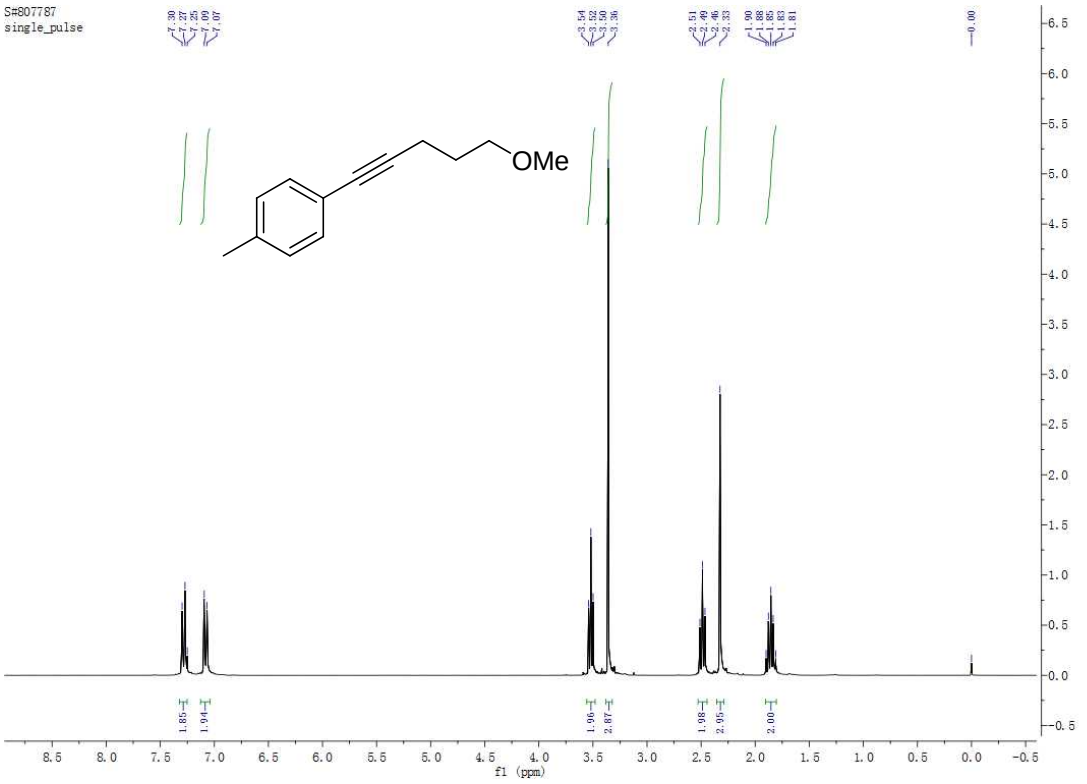
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

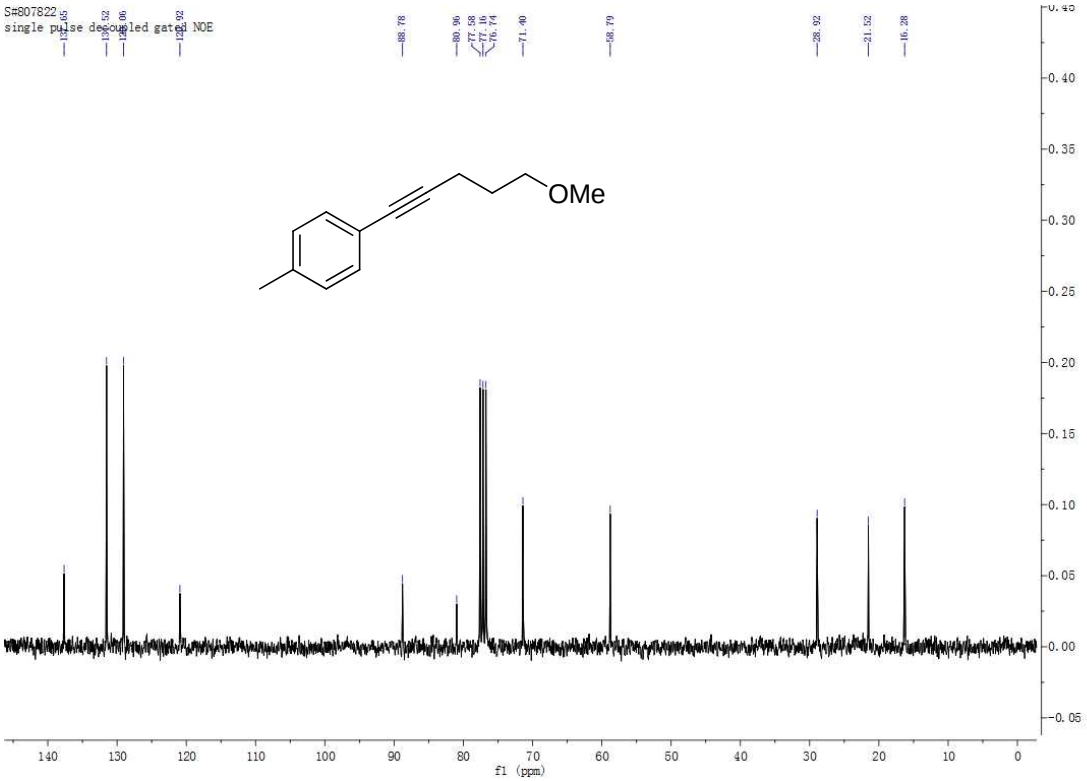


1-(5-methoxypent-1-yn-1-yl)-4-methylbenzene 2b: pale yellow-green oil, yield: 82%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.28 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 3.52 (t, J = 6.3 Hz, 2H), 3.36 (s, 3H), 2.49 (t, J = 7.0 Hz, 2H), 2.33 (s, 3H), 1.90 – 1.80 (m, 2H);

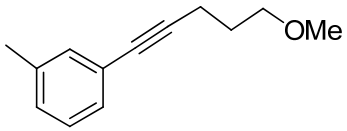
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 137.65, 131.52, 129.06, 120.92, 88.78, 80.96, 71.40, 58.79, 28.92, 21.52, 16.28.

GC-MS m/z calcd for $C_{13}H_{16}O$: 188; found: 188.





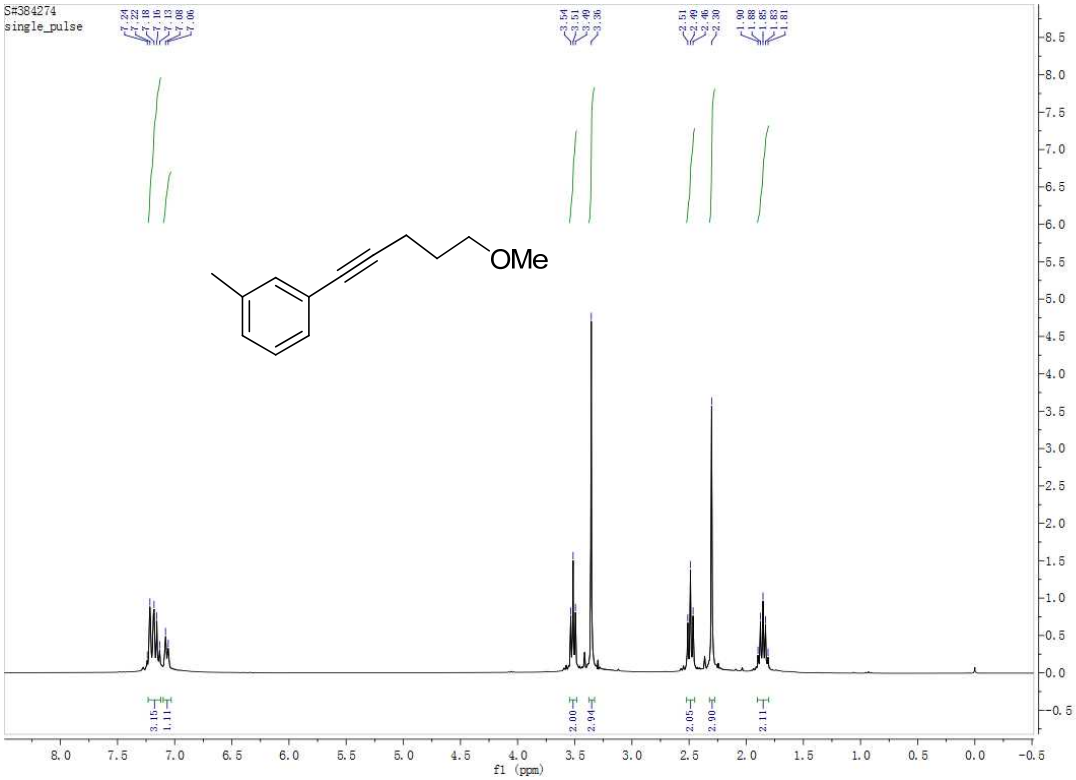
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

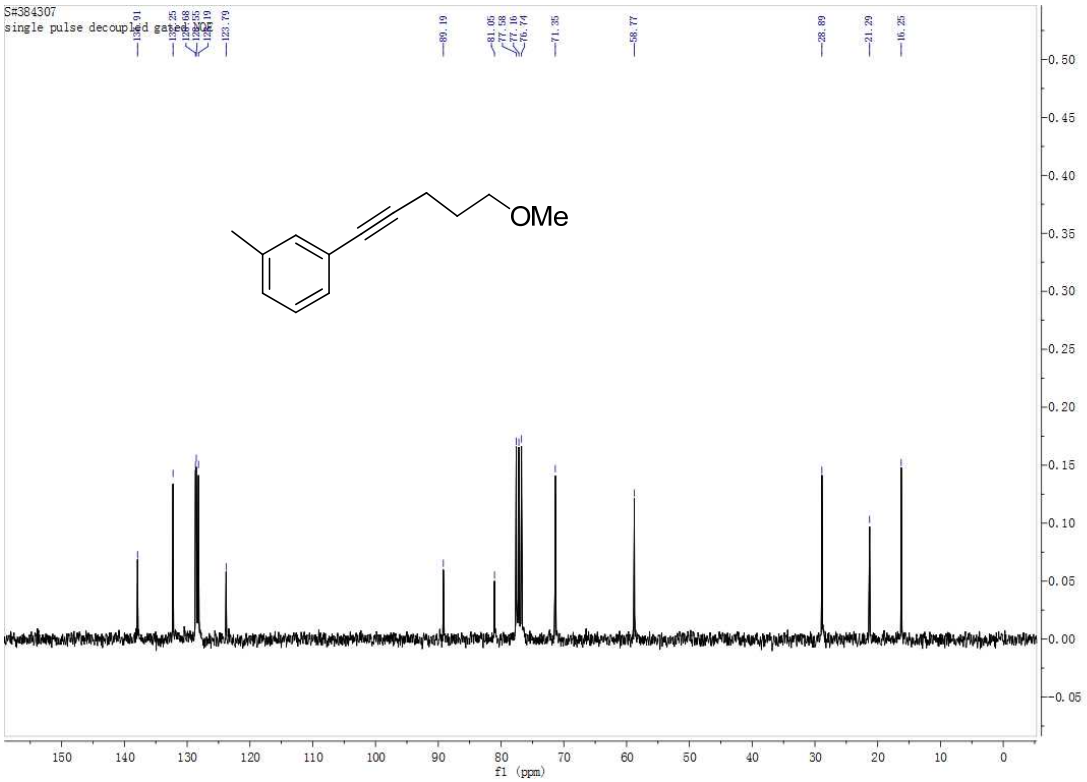


1-(5-methoxypent-1-yn-1-yl)-3-methylbenzene 2c: yellow oil, yield: 83%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.17 (dd, *J* = 16.5, 9.2 Hz, 3H), 7.07 (d, *J* = 7.0 Hz, 1H), 3.51 (t, *J* = 6.2 Hz, 2H), 3.36 (s, 3H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 1.90 – 1.80 (m, 2H);

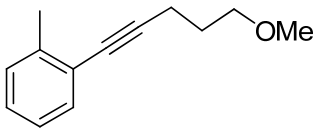
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 137.91, 132.25, 128.62, 128.55, 128.19, 123.79, 89.19, 81.05, 71.35, 58.77, 28.89, 21.29, 16.25.

GC-MS m/z calcd for $C_{13}H_{16}O$: 188; found: 188.



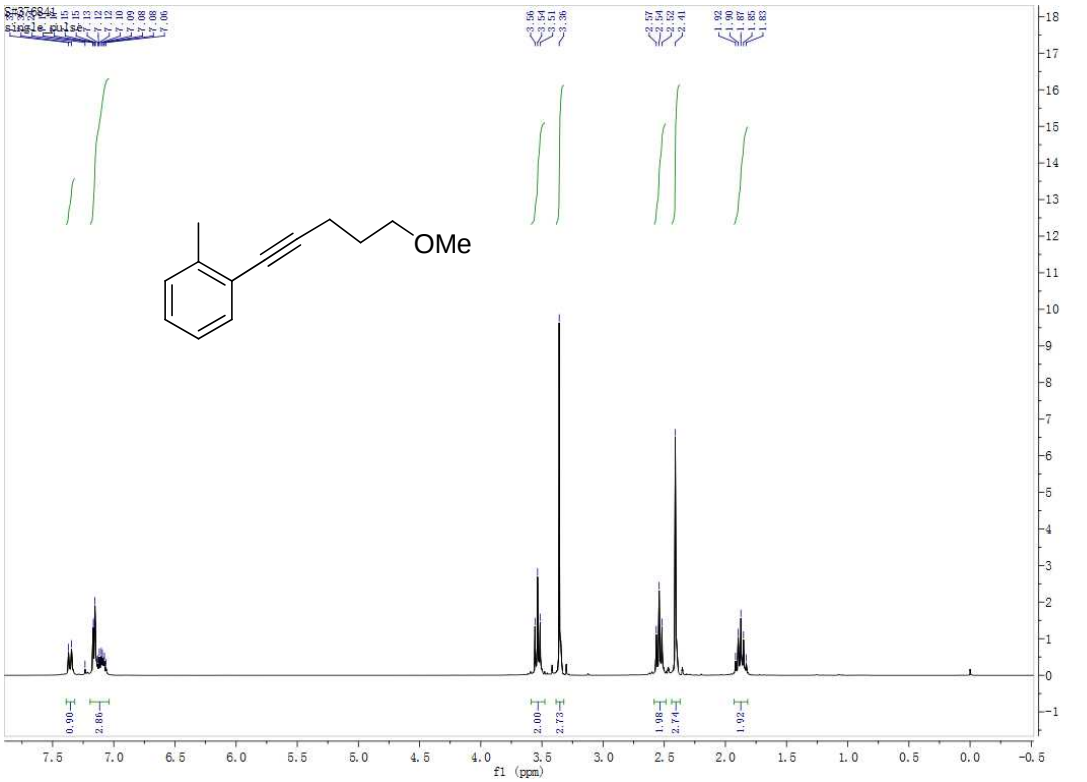


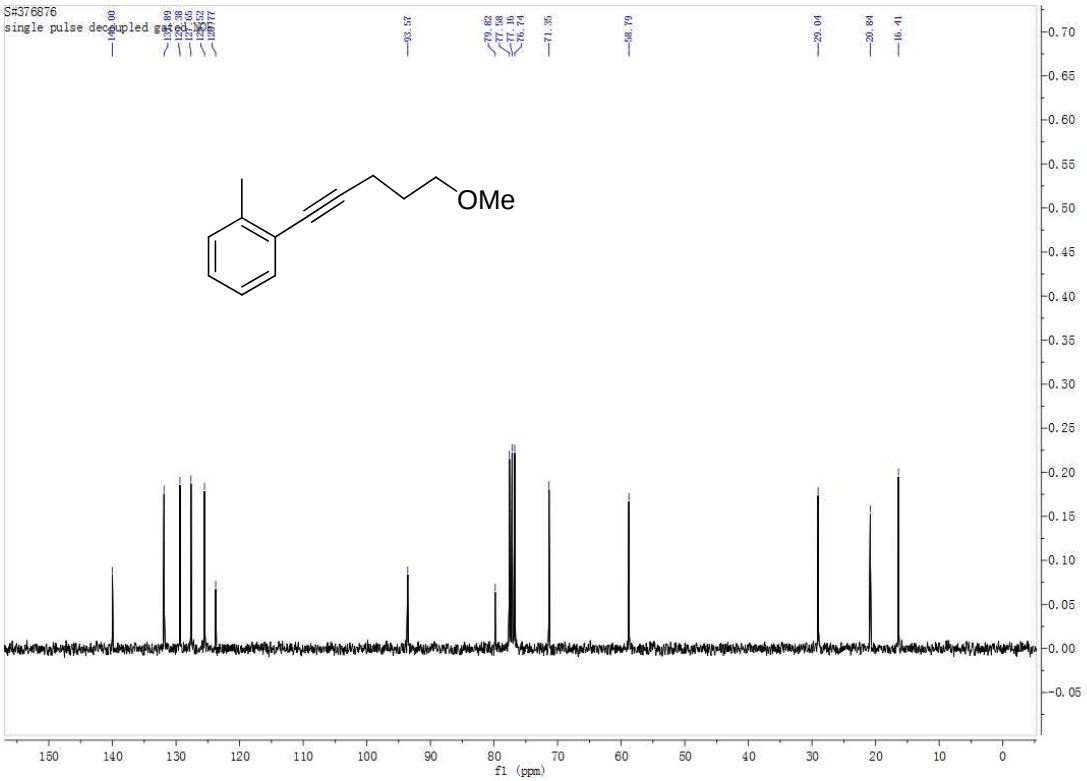
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)



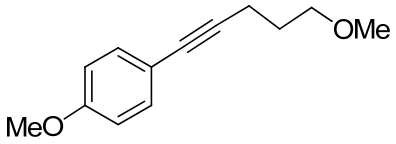
1-(5-methoxypent-1-yn-1-yl)-2-methylbenzene 2d: yellow oil, yield: 82%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.36 (d, *J* = 7.2 Hz, 1H), 7.19 – 7.04 (m, 3H), 3.54 (t, *J* = 6.3 Hz, 2H), 3.36 (s, 3H), 2.54 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.93 – 1.82 (m, 2H);

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 140.00, 131.89, 129.38, 127.65, 125.52, 123.77, 93.57, 79.82, 71.35, 58.79, 29.04, 20.84, 16.41. GC-MS m/z calcd for $C_{13}H_{16}O$: 188; found: 188.





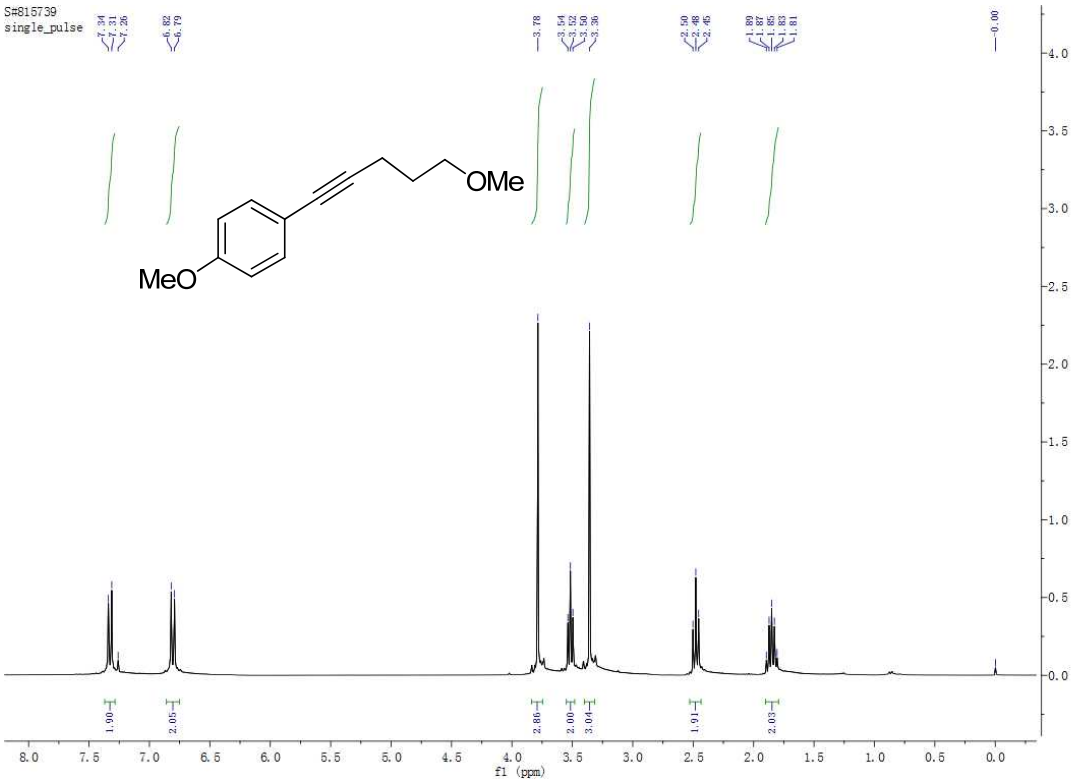
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

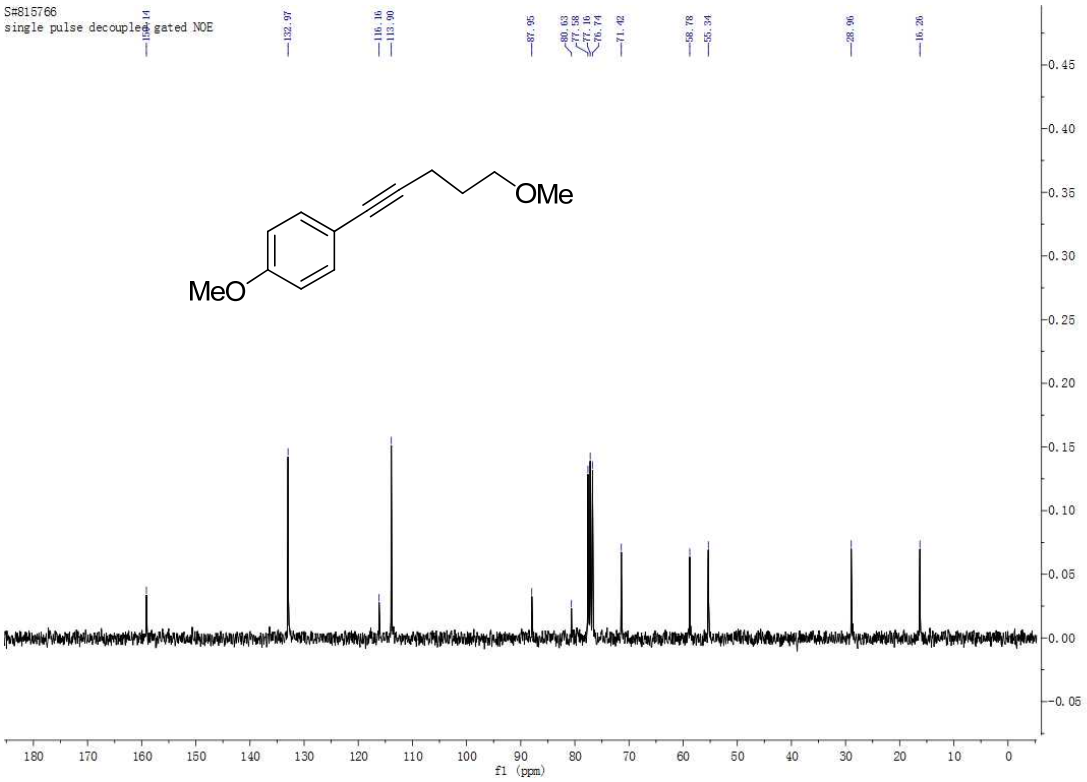


1-methoxy-4-(5-methoxypent-1-yn-1-yl) benzene 2e: colorless oil, yield: 84%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.33 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.3 Hz, 2H), 3.78 (s, 3H), 3.52 (t, J = 6.3 Hz, 2H), 3.36 (s, 3H), 2.48 (t, J = 7.1 Hz, 2H), 1.90 – 1.79 (m, 2H);

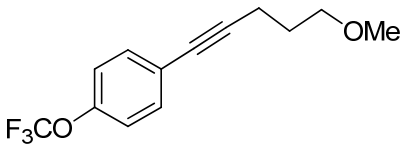
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 159.14, 132.97, 116.16, 113.90, 87.95, 80.63, 71.42, 58.78, 55.34, 28.96, 16.26.

GC-MS m/z calcd for $C_{13}H_{16}O_2$: 204; found: 204.





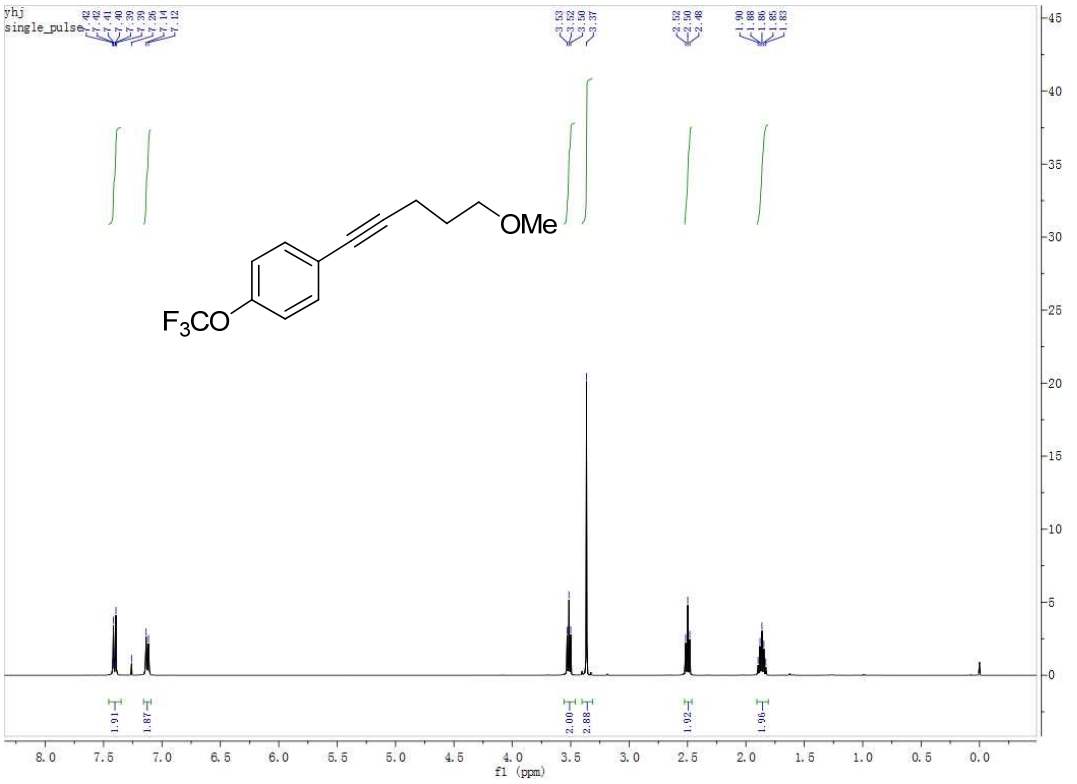
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

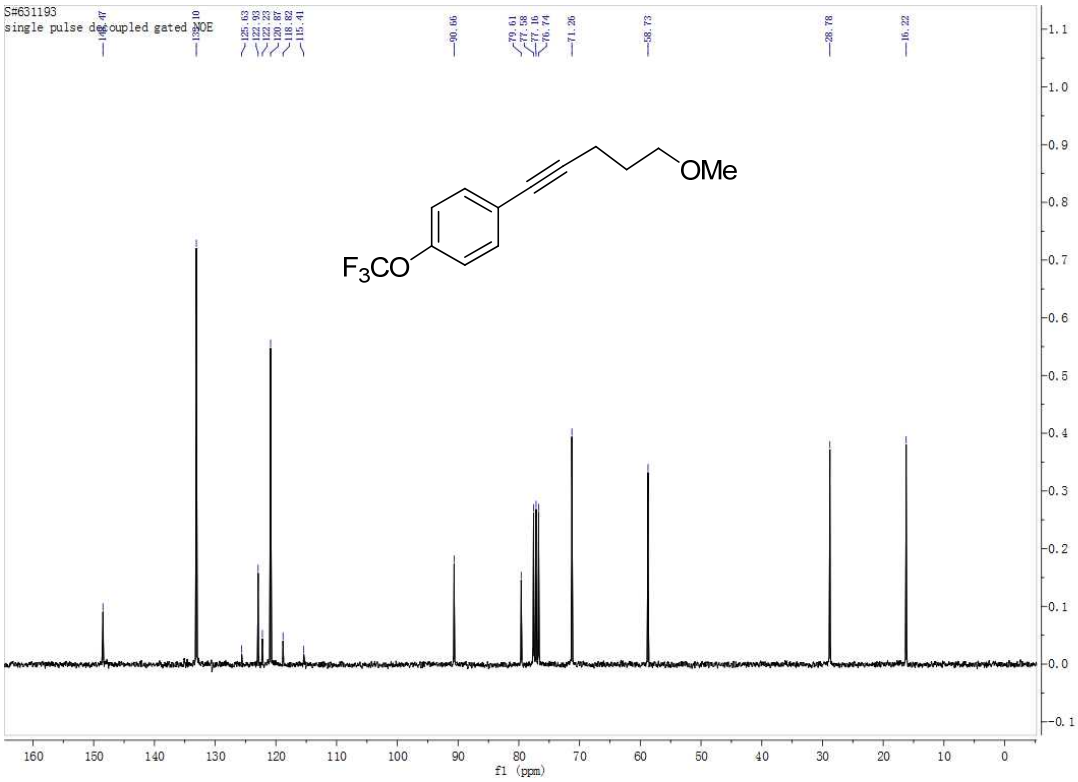


1-(5-methoxypent-1-yn-1-yl)-4-(trifluoromethoxy) benzene 2f: yellow oil, yield: 86%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.46 – 7.35 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.52 (t, J = 6.2 Hz, 2H), 3.37 (s, 3H), 2.50 (t, J = 7.1 Hz, 2H), 1.86 (p, J = 6.7 Hz, 2H);

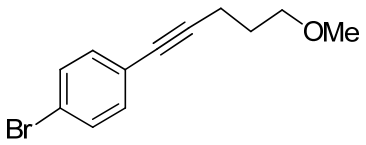
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 148.47, 133.10, 122.93, 120.87,120.52 (q, J = 259.2), 90.66, 79.61, 71.26, 58.73, 28.78, 16.22.

GC-MS m/z calcd for $C_{13}H_{13}F_3O_2$: 258; found: 258.





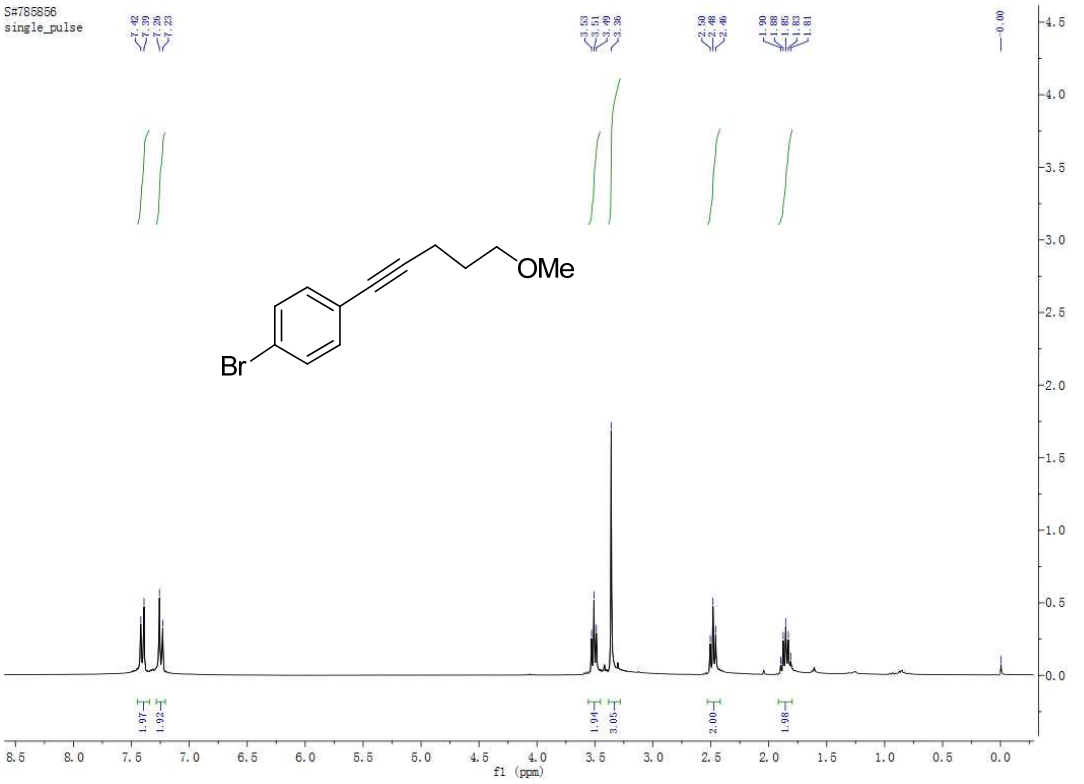
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

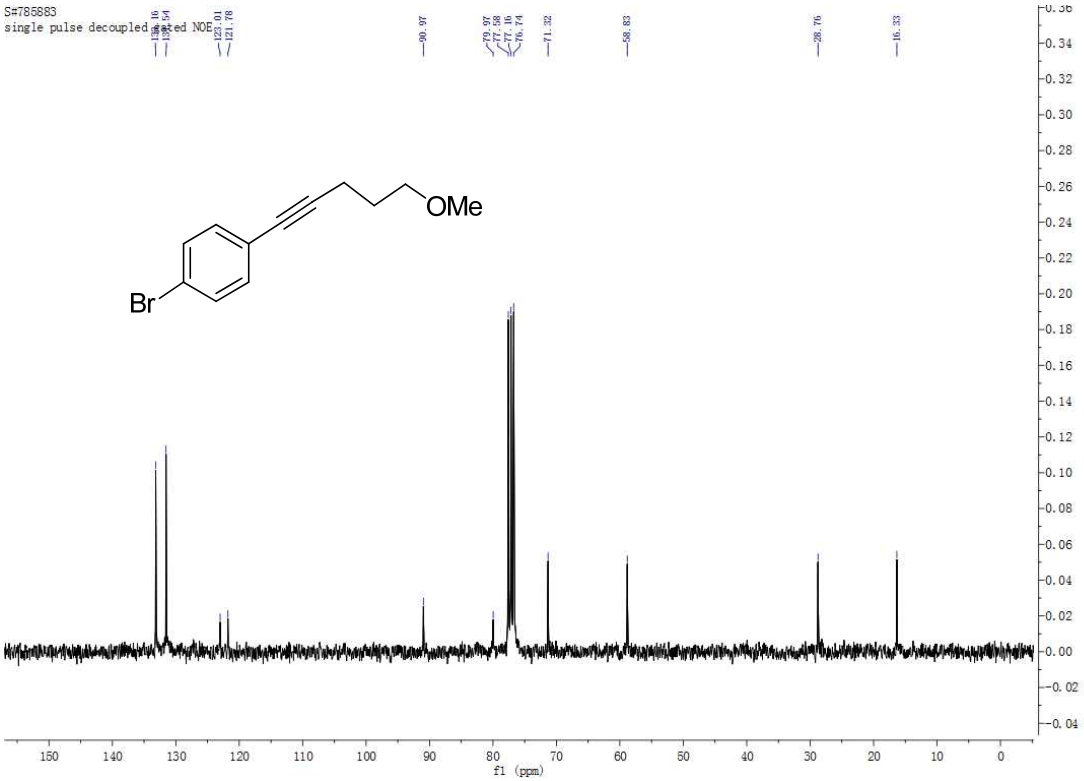


1-bromo-4-(5-methoxypent-1-yn-1-yl) benzene 2g: yellow-green oil, yield: 85%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 3.51 (t, *J* = 6.2 Hz, 2H), 3.36 (s, 3H), 2.48 (t, *J* = 7.1 Hz, 2H), 1.92 – 1.80 (m, 2H);

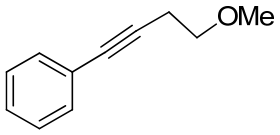
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 133.16, 131.54, 123.01, 121.78, 90.97, 79.97, 71.32, 58.83, 28.76, 16.33.

GC-MS m/z calcd for $C_{12}H_{13}BrO$: 252; found: 252.





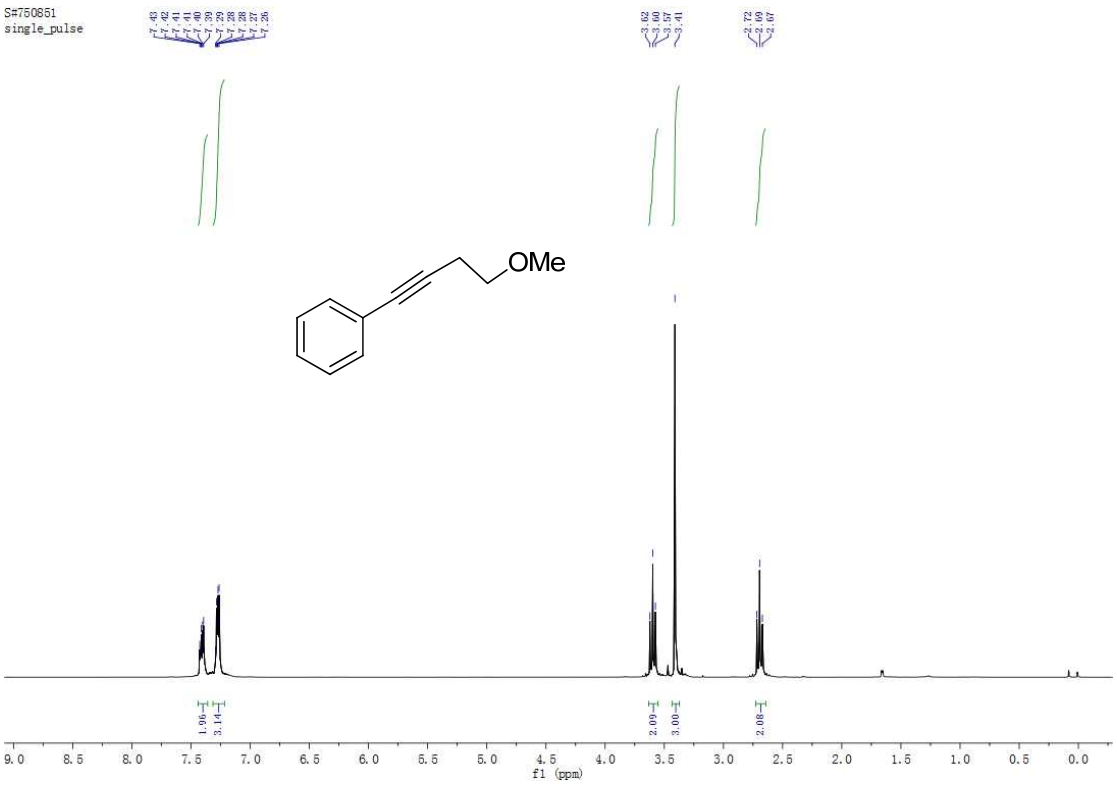
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

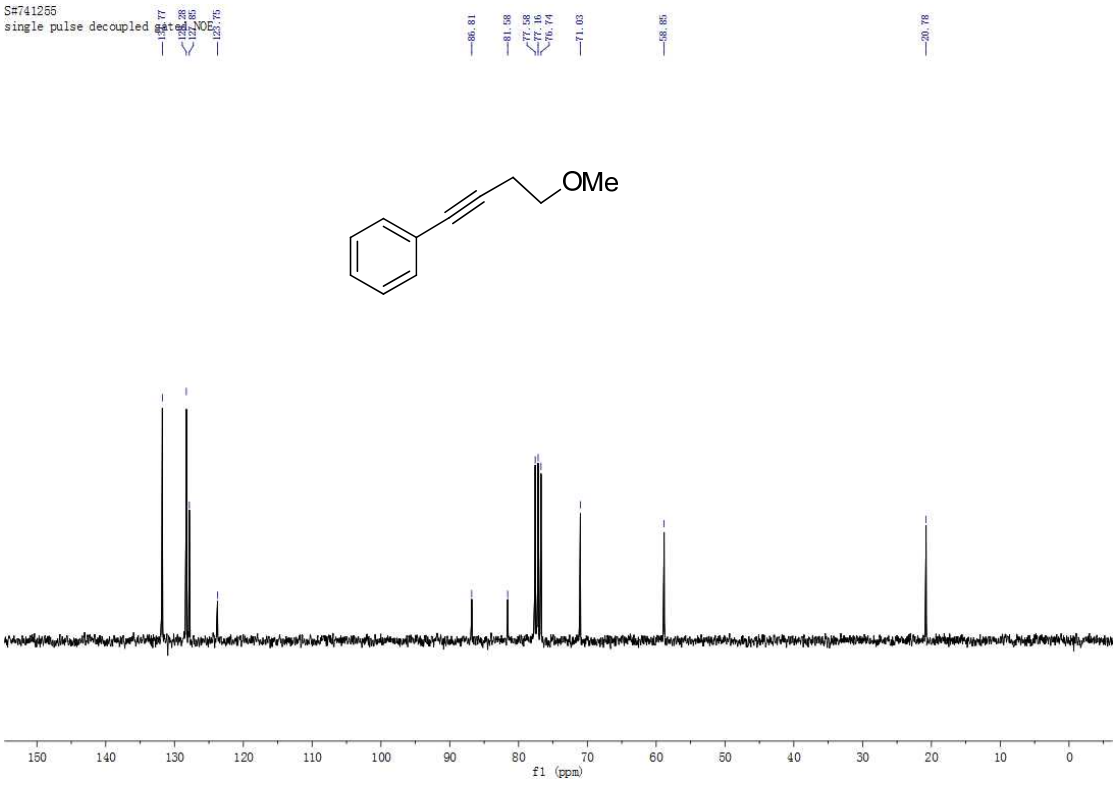


(4-methoxybut-1-yn-1-yl)benzene 4a: yellow oil, yield: 83%.^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.43 – 7.36 (m, 2H), 7.26 (dd, *J* = 5.3, 2.4 Hz, 3H), 3.59 (t, *J* = 7.0 Hz, 2H), 3.40 (s, 3H), 2.69 (t, *J* = 7.0 Hz, 2H);

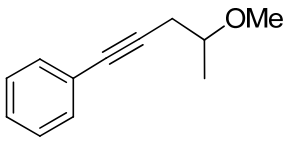
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.77, 128.29, 127.85, 123.76, 86.81, 81.58, 71.03, 58.85, 20.78.

GC-MS m/z calcd for $C_{11}H_{12}O$:160 ; found: 160.





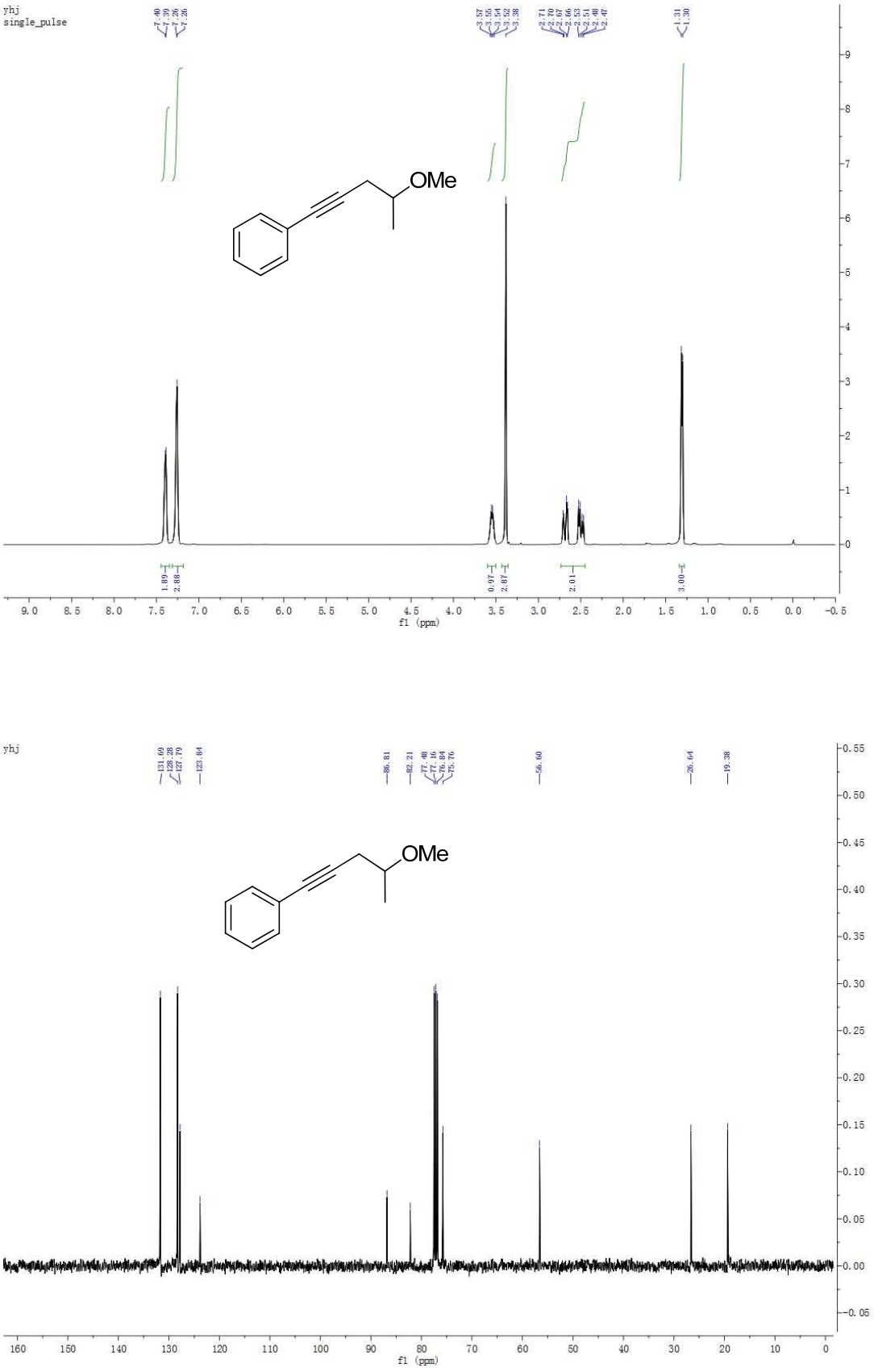
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)



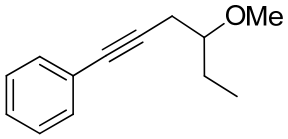
(4-methoxypent-1-yn-1-yl)benzene 4b: yellow oil, yield: 79%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 (d, *J* = 3.3 Hz, 2H), 7.26 (d, *J* = 2.6 Hz, 3H), 3.54 (dd, *J* = 11.5, 5.6 Hz, 1H), 3.38 (s, 3H), 2.59 (ddd, *J* = 23.8, 16.6, 5.8 Hz, 2H), 1.31 (d, *J* = 6.0 Hz, 3H);

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.69, 128.28, 127.79, 123.84, 86.81, 82.21, 75.76, 56.60, 26.64, 19.38.

GC-MS m/z calcd for $C_{12}H_{14}O$:174 ; found: 174.



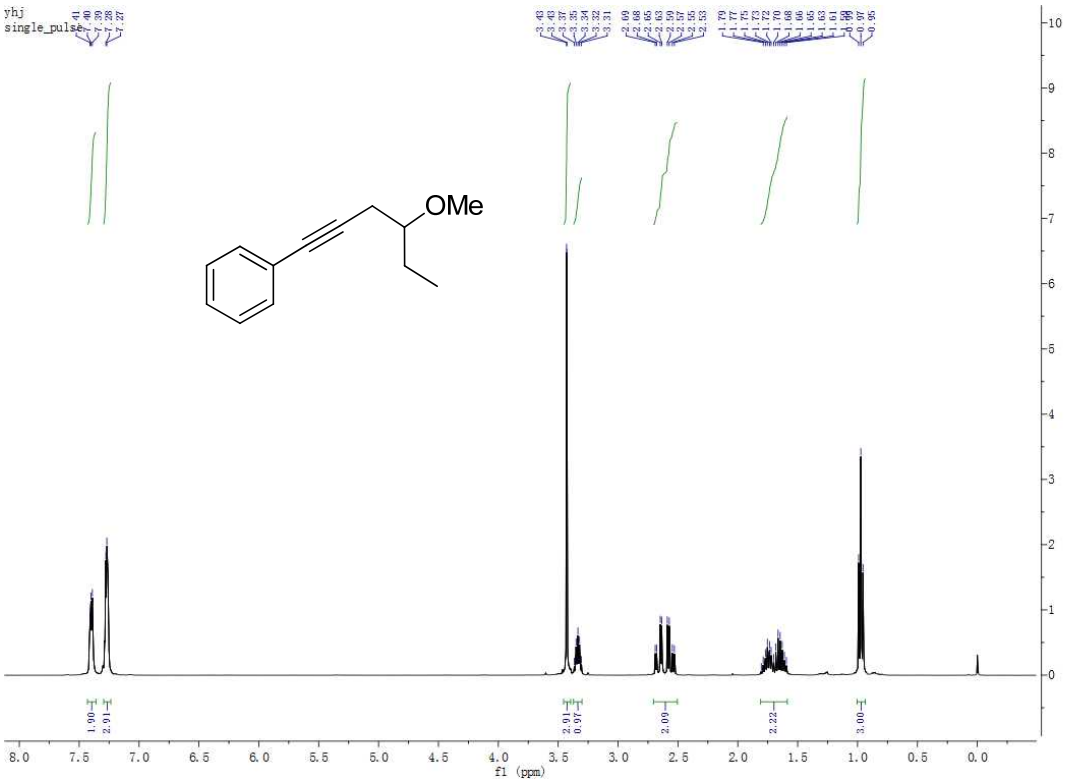
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

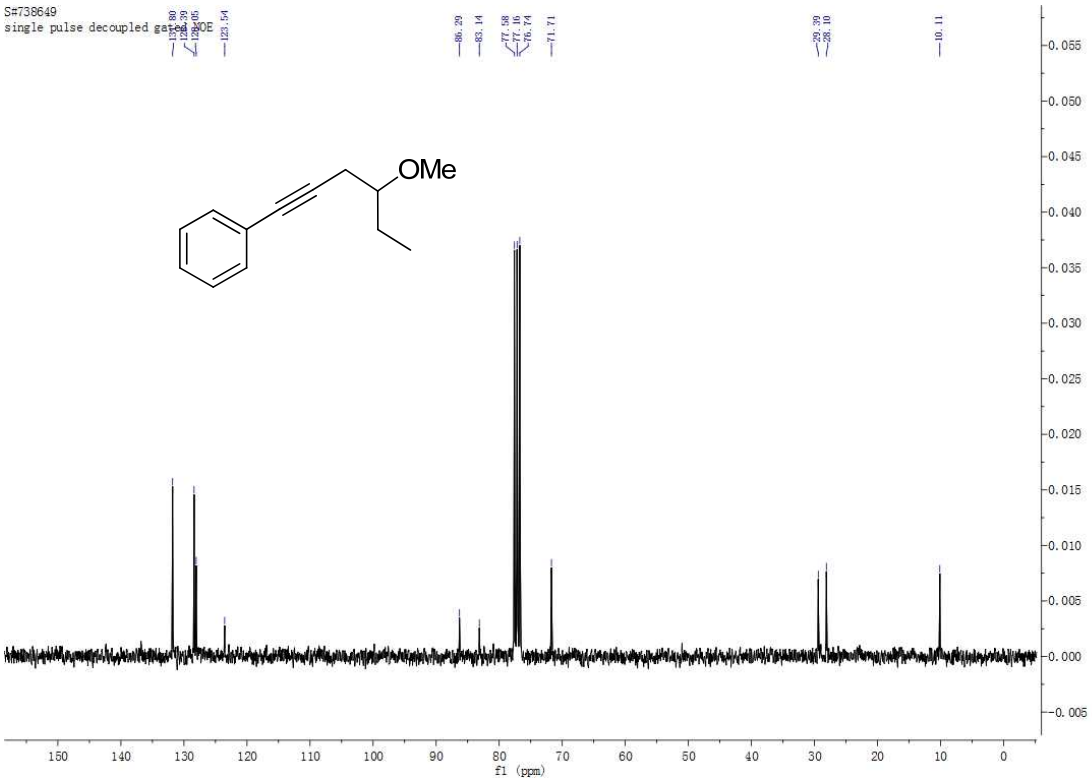


(4-methoxyhex-1-yn-1-yl)benzene 4c: yellow oil, yield: 82%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.43 – 7.36 (m, 2H), 7.27 (d, *J* = 3.5 Hz, 3H), 3.43 (d, *J* = 0.7 Hz, 3H), 3.37 – 3.30 (m, 1H), 2.61 (ddd, *J* = 23.6, 16.9, 5.9 Hz, 2H), 1.81 – 1.59 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.80, 128.39, 128.05, 123.54, 86.29, 83.14, 71.71, 29.39, 28.10, 10.11.

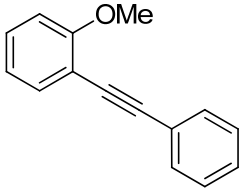
GC-MS m/z calcd for $C_{13}H_{16}O$:188 ; found: 188.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

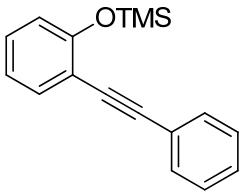
2) General procedure for the preparation of other Alkoxide Alkynes



1-methoxy-2-(phenylethynyl)benzene 4d[3]: yellow oil, yield: 83%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.55-7.57 (m, 2H), 7.50 (d, J = 7.2 Hz, 1H), 7.29-7.33 (m, 4H), 6.93 (t, J=7.6 Hz, 1H), 6.89 (d, J=8.4 Hz, 1H), 3.90 (s, 3H);

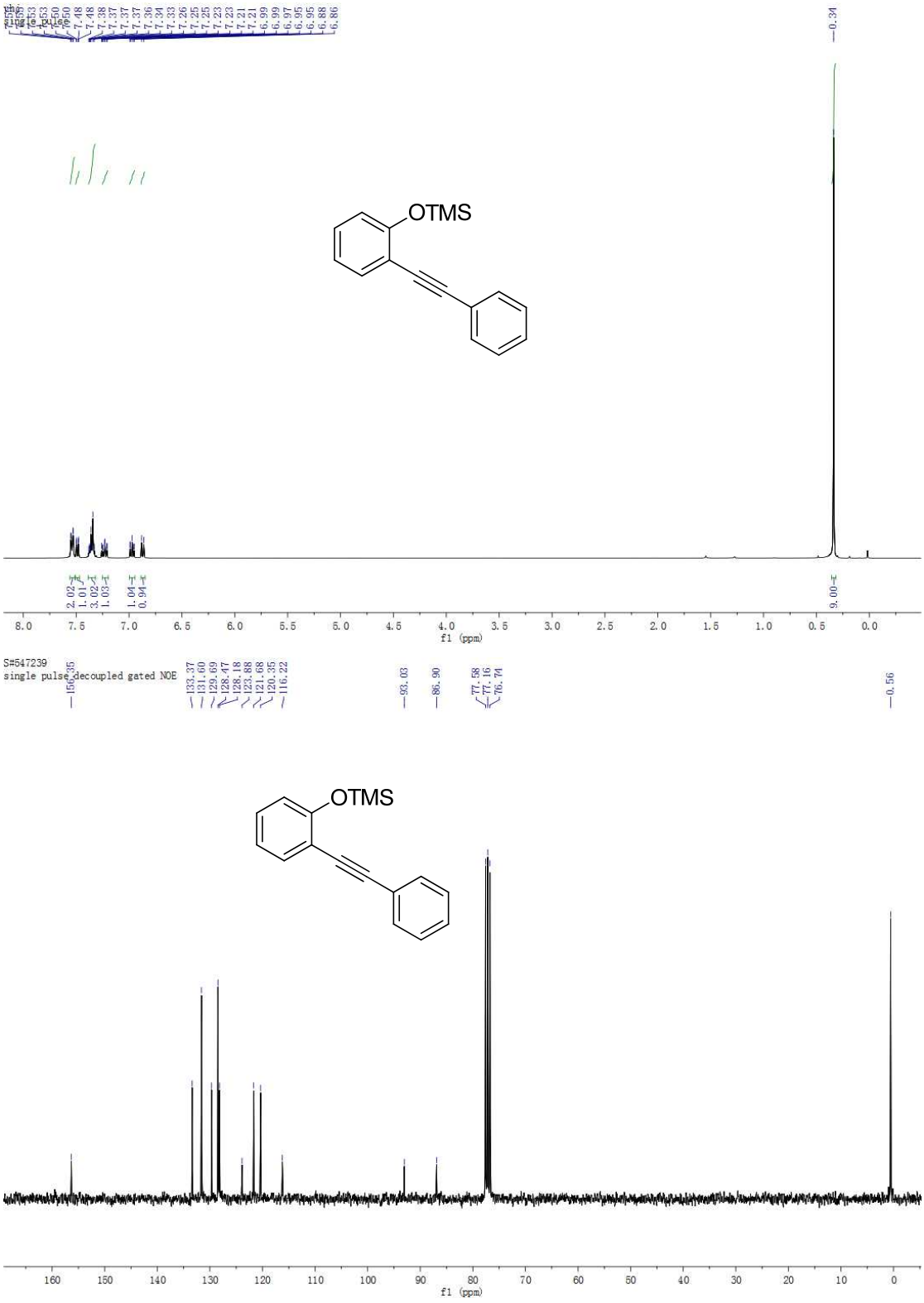
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 160.1, 133.7, 131.8, 129.9, 128.3, 128.2, 123.7, 120.7, 112.6, 110.9, 93.6, 85.9, 56.0. GC-MS m/z calcd for $C_{15}H_{12}O$:208 ; found: 208.

3) General procedure for the preparation of TMS-protected phenol



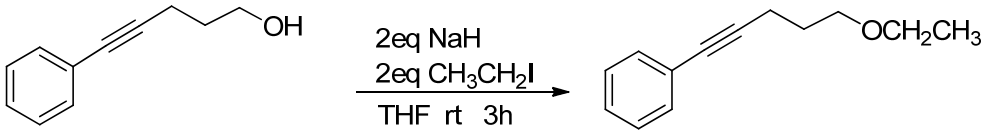
Trimethyl(2-(phenylethynyl)phenoxy)silane 4f[4][5]: yellow solid, yield: 76%, mp = 53.8-54.3 ^{o}C ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.54 (dd, J = 7.7, 1.7 Hz, 2H), 7.49 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.23 (td, J = 7.8, 1.6 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.87 (d, J = 8.3 Hz, 1H), 0.34 (s, 9H).
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 156.35, 133.37, 131.60, 129.69, 128.47, 128.18, 123.88, 121.68, 120.35, 116.22, 93.03, 86.90, 0.56.

GC-MS m/z calcd for $C_{17}H1_{8}OSi$:266 ; found: 266.

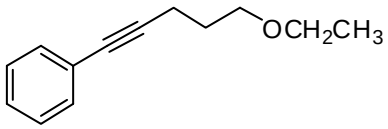


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

4) General procedure for the preparation of (5-ethoxypent-1-yn-1-yl)benzene

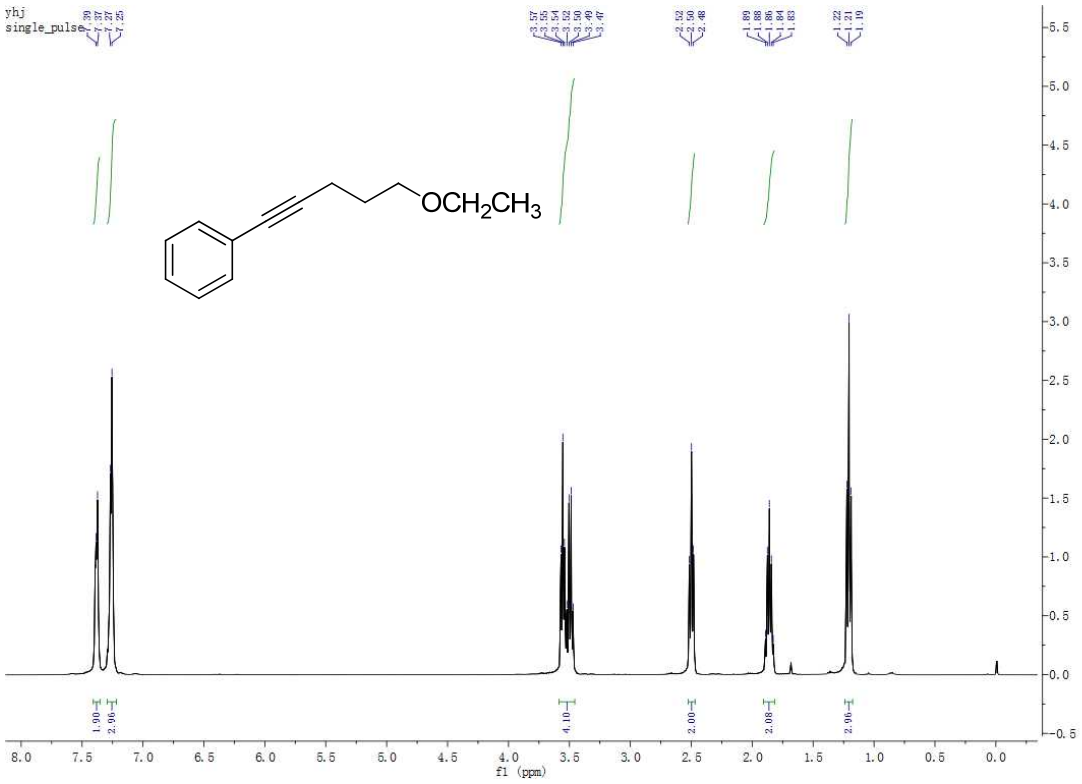


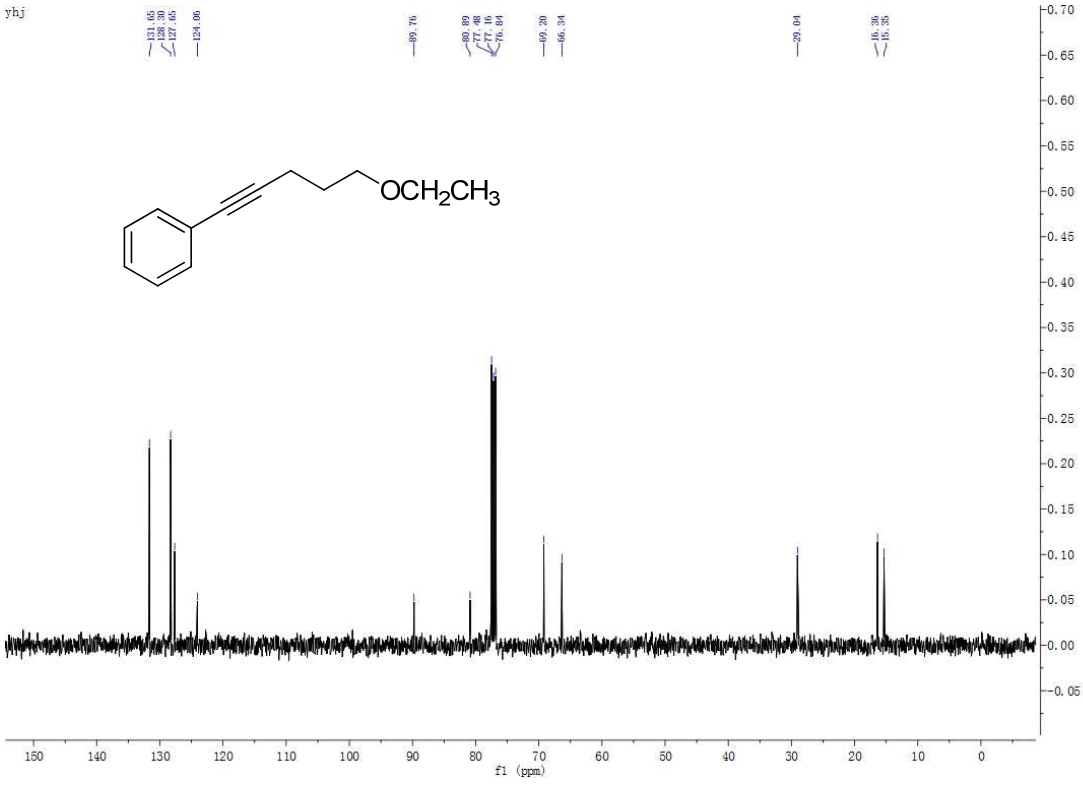
To a solution of 5-phenylpent-4-yn-1-ol (1.28 g, 8 mmol) in freshly distilled THF (15 mL) at 0℃ was added NaH (0.64 g, 16 mmol, 60% dispersion in mineral oil). After stirring at room temperature for 30 min, CH_3CH_2I (1.3 mL, 16 mmol) was added, and the solution stirred for 3 hour at room temperature. The reaction was quenched by the addition of H_2O at 0℃， and stirred for 30 min. the aqueous phase was extracted with EtOAc. The combined organic extracts were dried with magnesium sulfate, filtered and concentrated in vacuo. The crude product was purified by column chromatograph (EtOAc/Hexane 1:50) .



(5-ethoxypent-1-yn-1-yl)benzene: yellow solid, yield: 70%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.38 (d, *J* = 5.0 Hz, 2H), 7.26 (d, *J* = 5.1 Hz, 3H), 3.58 – 3.46 (m, 4H), 2.50 (t, *J* = 6.7 Hz, 2H), 1.86 (p, *J* = 6.2 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.65, 128.30, 127.65, 124.06, 89.76, 80.89, 69.20, 66.34, 29.04, 16.36, 15.35.

GC-MS m/z calcd for $C_{13}H_{16}O$: 188; found: 188.

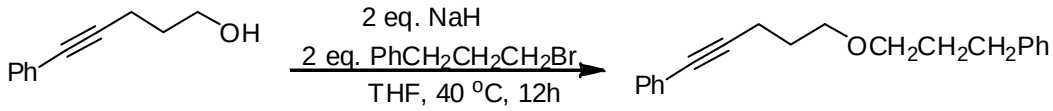




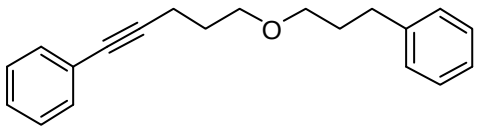
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

5) General procedure for the preparation of

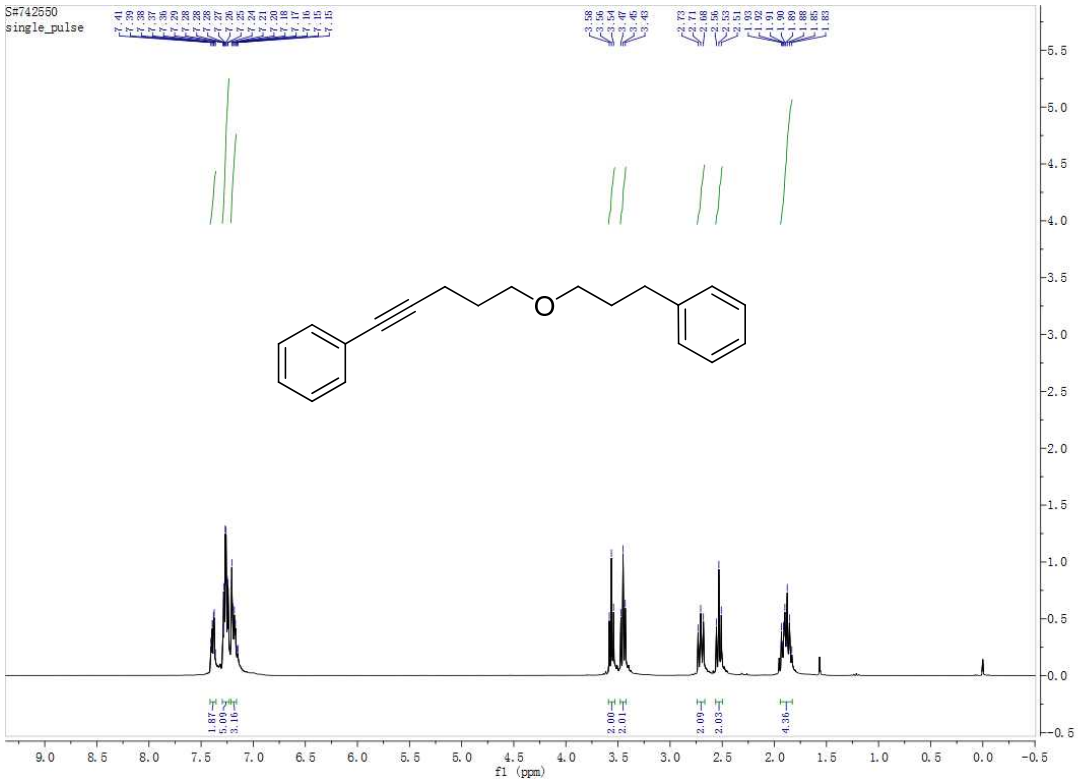
(3-((5-phenylpent-4-yn-1-yl)oxy)propyl)benzene

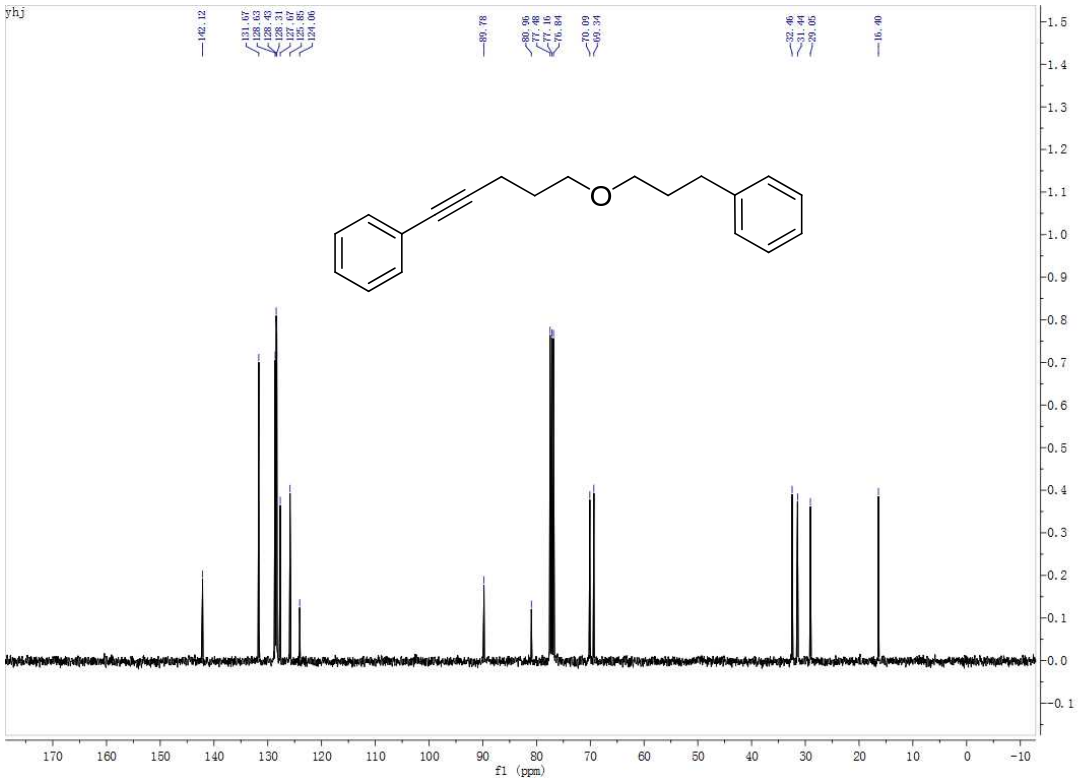


To a solution of 5-phenylpent-4-yn-1-ol (1.28 g, 8 mmol) in freshly distilled THF (15 mL) at 0℃ was added NaH (0.64 g, 16 mmol, 60% dispersion in mineral oil). After stirring at room temperature for 30 min, $PhCH_2CH_2CH_2Br$ (2.43 mL, 16 mmol) was added, and the solution stirred for 12 hour at 40℃. The reaction was quenched by the addition of H_2O at 0℃， and stirred for 30 min. The aqueous phase was extracted with EtOAc. The combined organic extracts were dried with magnesium sulfate, filtered and concentrated in vacuo. The crude product was purified by column chromatograph (EtOAc/Hexane 1:50).



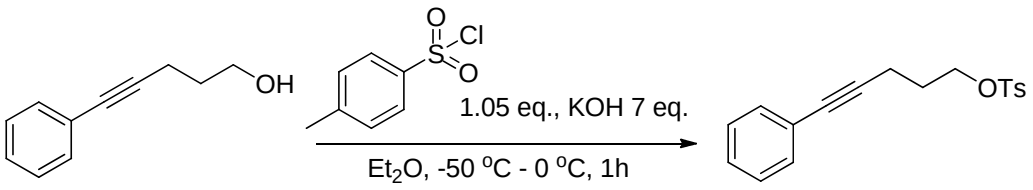
(3-((5-phenylpent-4-yn-1-yl)oxy)propyl)benzene: yellow solid, yield: 68%.^{1}H NMR (300 MHz, CHLOROFORM-D) δ 7.41 – 7.36 (m, 2H), 7.27 (ddd, *J* = 8.1, 4.5, 2.0 Hz, 5H), 7.21 – 7.16 (m, 3H), 3.56 (t, *J* = 6.2 Hz, 2H), 3.45 (t, *J* = 6.4 Hz, 2H), 2.74 – 2.67 (m, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 1.89 (ddd, *J* = 17.5, 9.8, 5.1 Hz, 4H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 142.12, 131.67, 128.63, 128.43, 128.31, 127.67, 125.85, 124.06, 89.78, 80.96, 70.09, 69.34, 32.46, 31.44, 29.05, 16.40. GC-MS m/z calcd for $C_{13}H_{16}O$: 278; found: 278.



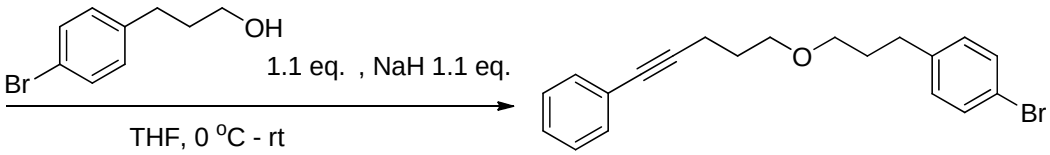


^{1}H NMR (300 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

6) General procedure for the preparation of 2x

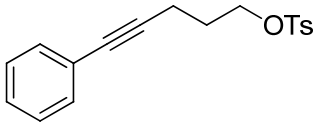


Step 1



Step 2

Step 1:



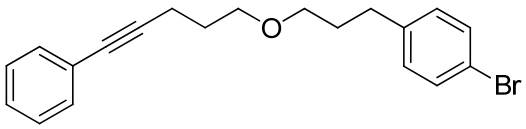
5-phenylpent-4-yn-1-yl 4-methylbenzenesulfonate[6]: To a solution of 5-phenylpent-4-yn-1-ol (1 equiv.) and tosyl chloride (1.05 equiv.) in diethyl ether (0.5-1.0 M) was added slowly freshly powered KOH (6-7 equiv) in -50 °C. The reaction was allowed to rise to warm to 0 °C and stirered for 0.5 h, after which time the mixture was poured into water and diluted with ether. The combined orgnic layer was dried over $MgSO_4$ and concentracted under reduced pressure to afford the crude product. Purification via flashed column chromatography afford product as a white solid in 92% yield.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.81 (d, J = 8.2 Hz, 2H), 7.28 (dd, J = 11.8, 7.4 Hz, 7H), 4.20 (t, J = 6.0 Hz, 2H), 2.48 (t, J = 6.8 Hz, 2H), 2.38 (s, 3H), 1.97 – 1.89 (m, 2H)；

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 132.95, 131.61, 129.93, 128.27, 128.03, 127.88，68.98, 27.99, 21.69, 15.72.

GC-MS m/z calcd for $C_{18}H_{18}O_3S$: 314; found: 314

Step 2:

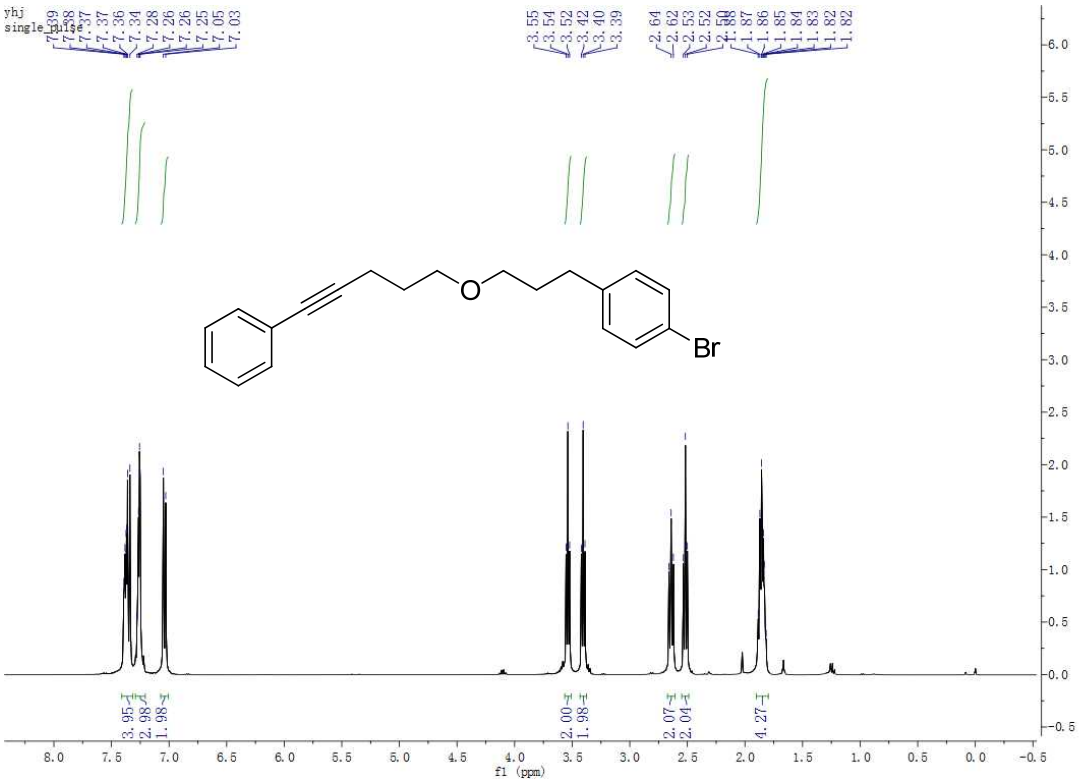


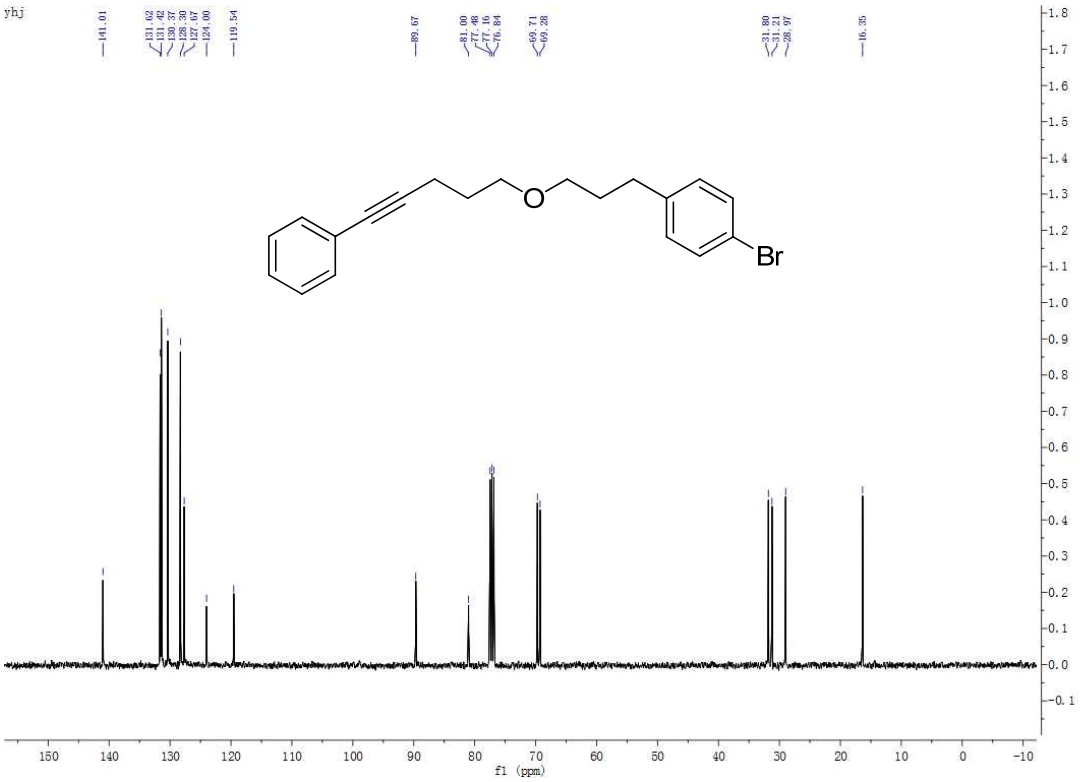
1-bromo-4-(3-((5-phenylpent-4-yn-1-yl)oxy)propyl)benzene 2x[7]: To a solution of 3-(4-bromophenyl)propan-1-ol (0.36 g, 1.68 mmol) in freshly distilled THF (3 mL) at 0℃ was added NaH (67.2 mg, 1.68 mmol, 60% dispersion in mineral oil). After stirring at room temperature for 1 hour, 5-phenylpent-4-yn-1-yl 4-methylbenzenesulfonate (0.471 g, 1.5 mmol) in THF 2 mL was added at 0 ℃, the solution refluxed for 3 hour and stirred for 18 hour at room temperature. The reaction was quenched by the addition of H_2O at 0℃， and stirred for 30 min. The aqueous phase was extracted with EtOAc. The combined organic extracts were dried with magnesium sulfate, filtered and concentrated in vacuo. Purification of crude product was conducted by filtered over a short silica pad followed by flash column chromatography on silica gel using EtOAc/Hexane 1:50 as eluent to afford 34% product as yellow oil.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.41 – 7.32 (m, 4H), 7.26 (dd, J = 6.9, 3.5 Hz, 3H), 7.04 (d, J = 8.2 Hz, 2H), 3.54 (t, J = 6.1 Hz, 2H), 3.40 (t, J = 6.3 Hz, 2H), 2.67 – 2.61 (m, 2H), 2.52 (t, J = 7.0 Hz, 2H), 1.90 – 1.80 (m, 4H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 141.01, 131.62, 131.42, 130.37, 128.30, 127.67, 124.00, 119.54, 89.67, 81.00, 69.71, 69.28, 31.80, 31.21, 28.97, 16.35.

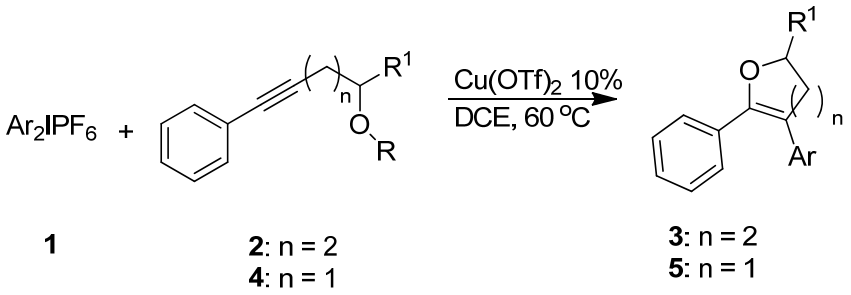
GC-MS m/z calcd for $C_{20}H_{21}BrO$: 356; found: 356.





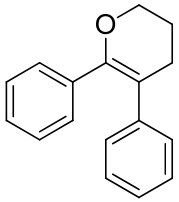
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

3. Experimental Section for products 3 and 5.



1 **2**: n = 2 **4**: n = 1 **3**: n = 2 **5**: n = 1

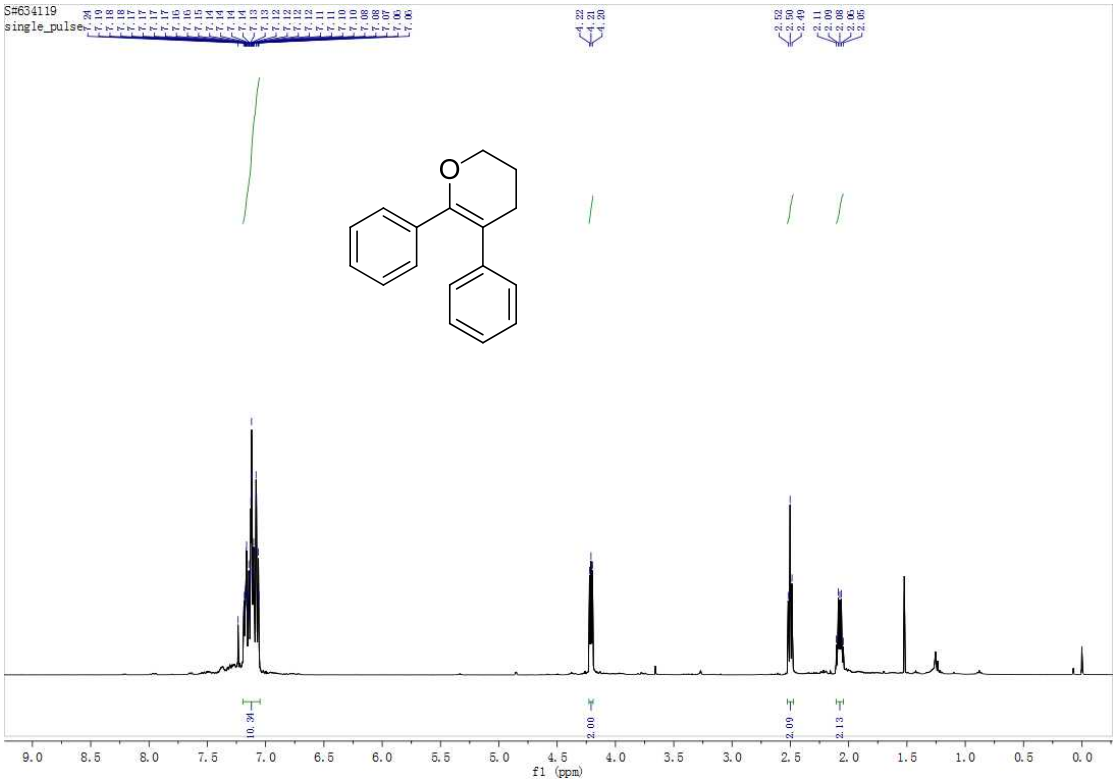
A sealed tube was charged with the mixture of diaryliodonium salt **1** (0.36 mmol) and $Cu(OTf)_2$ (0.03 mmol, 10.8 mg). The tube was evacuated and recharged with N_2 for 3 times. After appropriate Phenyl Alkyne (0.3 mmol) and dichloroethane (3 mL) were added, the tube was sealed and the mixture was allowed to stir at 60 °C for 12-24 h. After completion, the mixture was cooled to room temperature, then saturated K_2CO_3 aq. (5 mL) was added and the mixture was extracted with EA (5 mL × 3), dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (PE/EA/TEA: 200/4/1) provided the corresponding product as a yellow liquid or yellow solid.

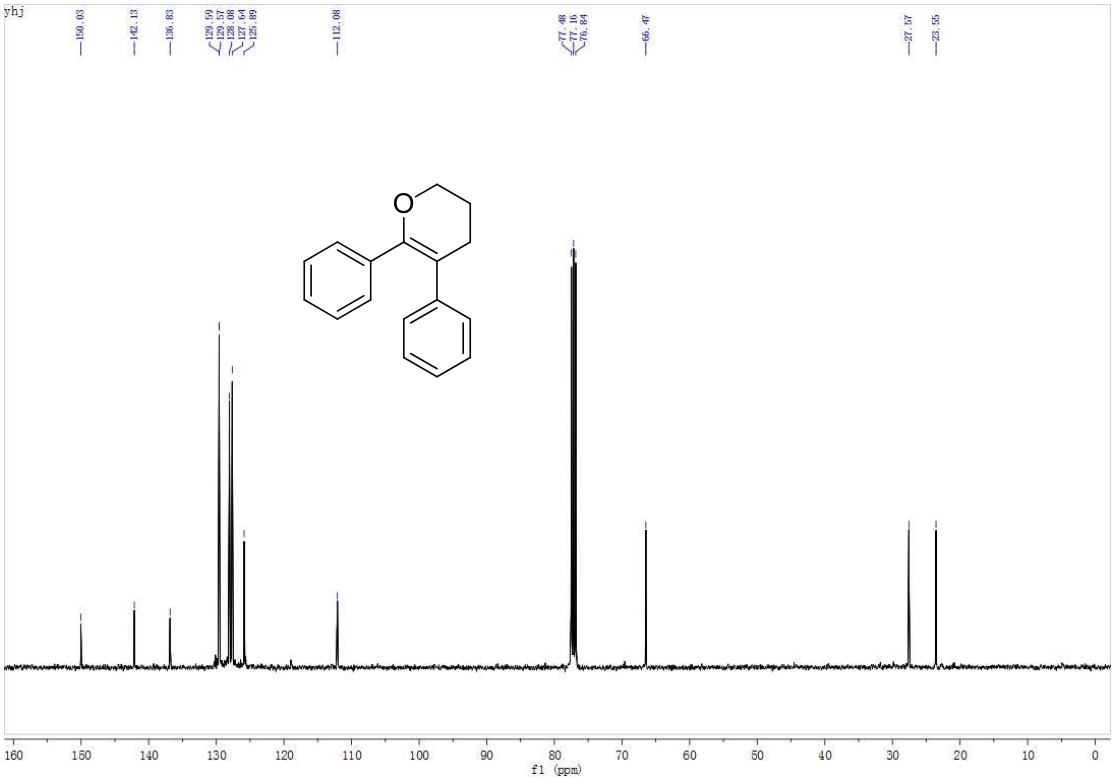


5,6-diphenyl-3,4-dihydro-2H-pyran 3aa: yellow liquid, yield: 92%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.20 – 7.05 (m, 10H), 4.23 – 4.19 (m, 2H), 2.50 (t, J = 6.6 Hz, 2H), 2.11 – 2.04 (m, 2H).

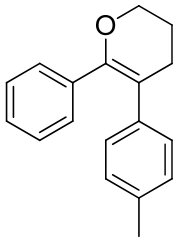
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.03, 142.13, 136.83, 129.59, 129.57, 128.08, 127.64(×2C), 125.89, 112.08, 66.47, 27.57, 23.55.

GC-MS: m/z calcd for $C_{16}H_{17}O$: 236; found: 236.





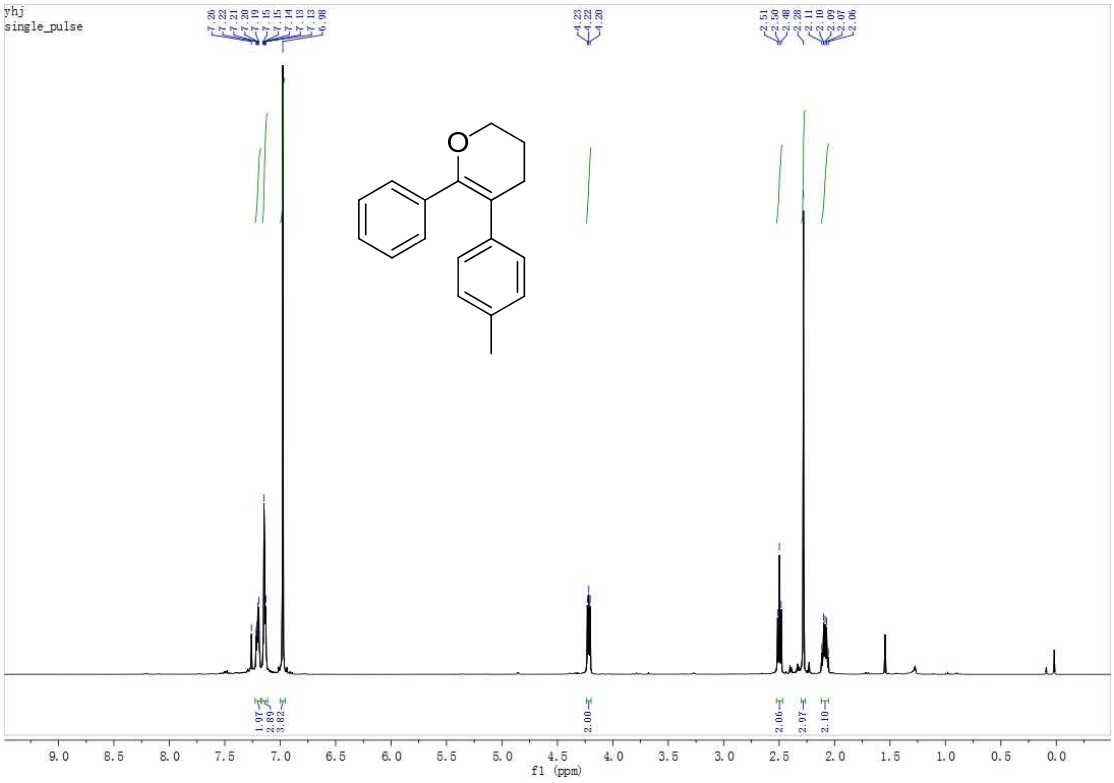
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

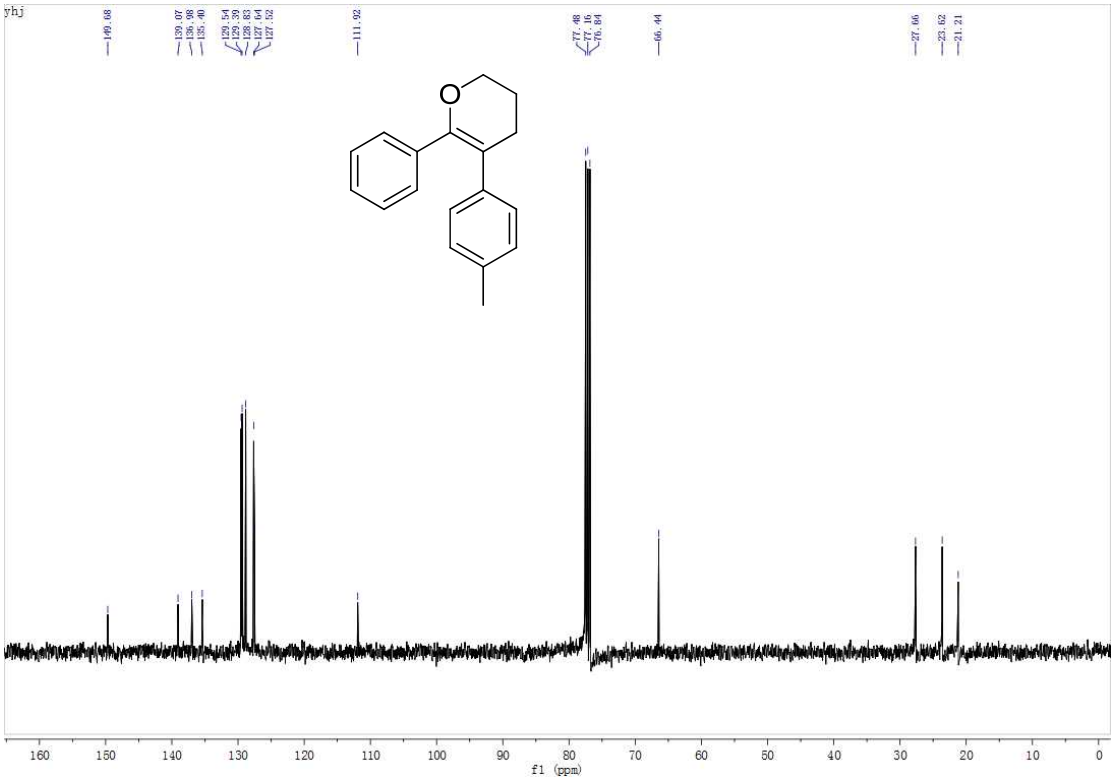


6-phenyl-5-(p-tolyl)-3,4-dihydro-2H-pyran 3ba: yellow liquid, yield: 86%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.19 (dd, J = 6.8, 3.1 Hz, 2H), 7.14 – 7.09 (m, 3H), 6.96 (s, 4H), 4.22 – 4.18 (m, 2H), 2.48 (t, J = 6.6 Hz, 2H), 2.26 (s, 3H), 2.10 – 2.03 (m, 2H).

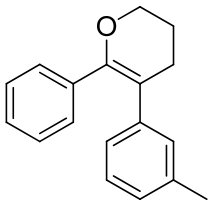
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 149.68, 139.07, 136.98, 135.40, 129.54, 129.39, 128.83, 127.64, 127.52, 111.92, 66.44, 27.66, 23.62, 21.21.

GC-MS: m/z calcd for $C_{18}H_{18}O$: 250; found: 250.





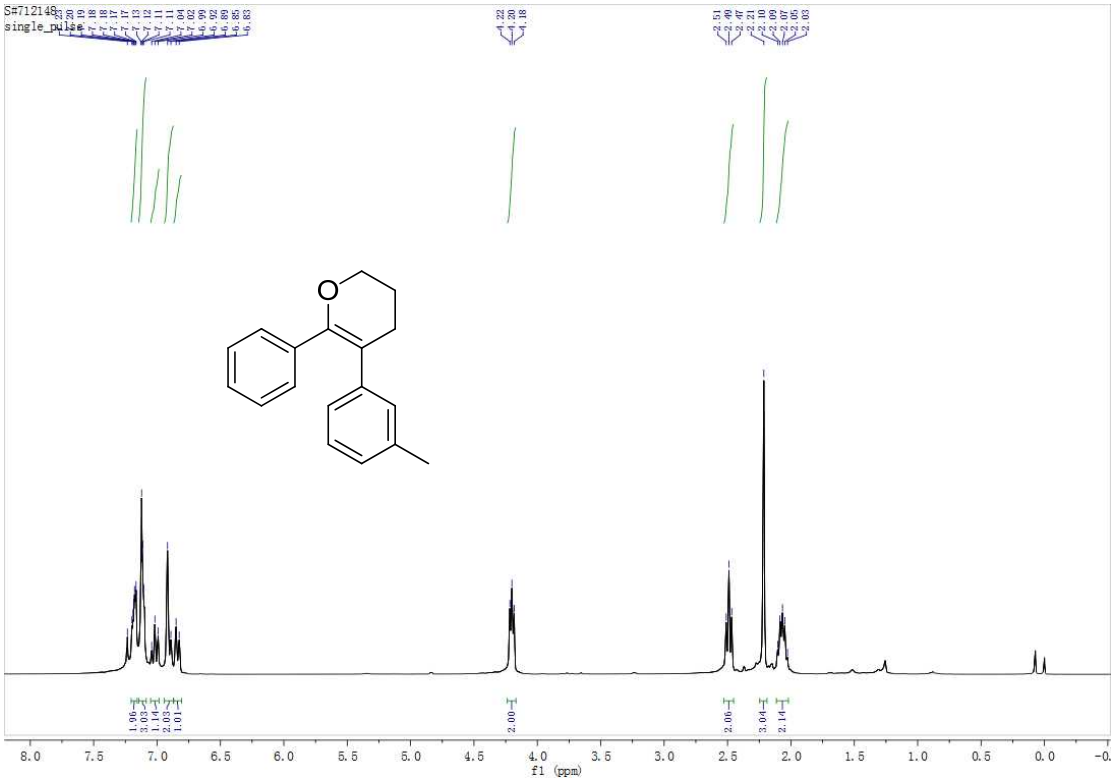
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

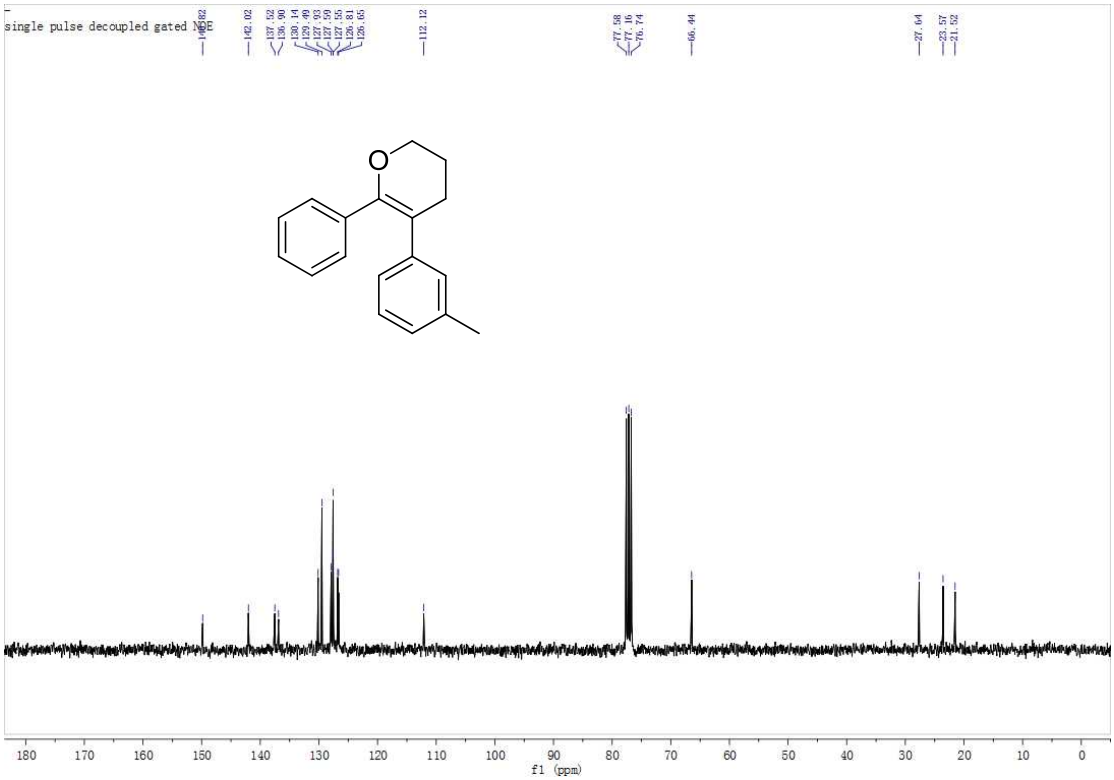


6-phenyl-5-(m-tolyl)-3,4-dihydro-2H-pyran 3ca: yellow liquid, yield: 68%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.20 – 7.16 (m, 2H), 7.12 (dd, J = 4.5, 1.9 Hz, 3H), 7.02 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.9 Hz, 2H), 6.84 (d, J = 7.4 Hz, 1H), 4.24 – 4.17 (m, 2H), 2.49 (t, J = 6.6 Hz, 2H), 2.21 (s, 3H), 2.11 – 2.02 (m, 2H).

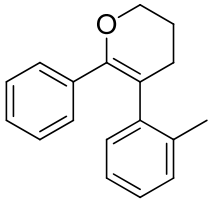
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 149.82, 142.02, 137.52, 136.90, 130.14, 129.49, 127.93, 127.59, 127.55, 126.81, 126.65, 112.12, 66.44, 27.64, 23.57, 21.52.

GC-MS: m/z calcd for $C_{18}H_{18}O$: 250; found: 250.





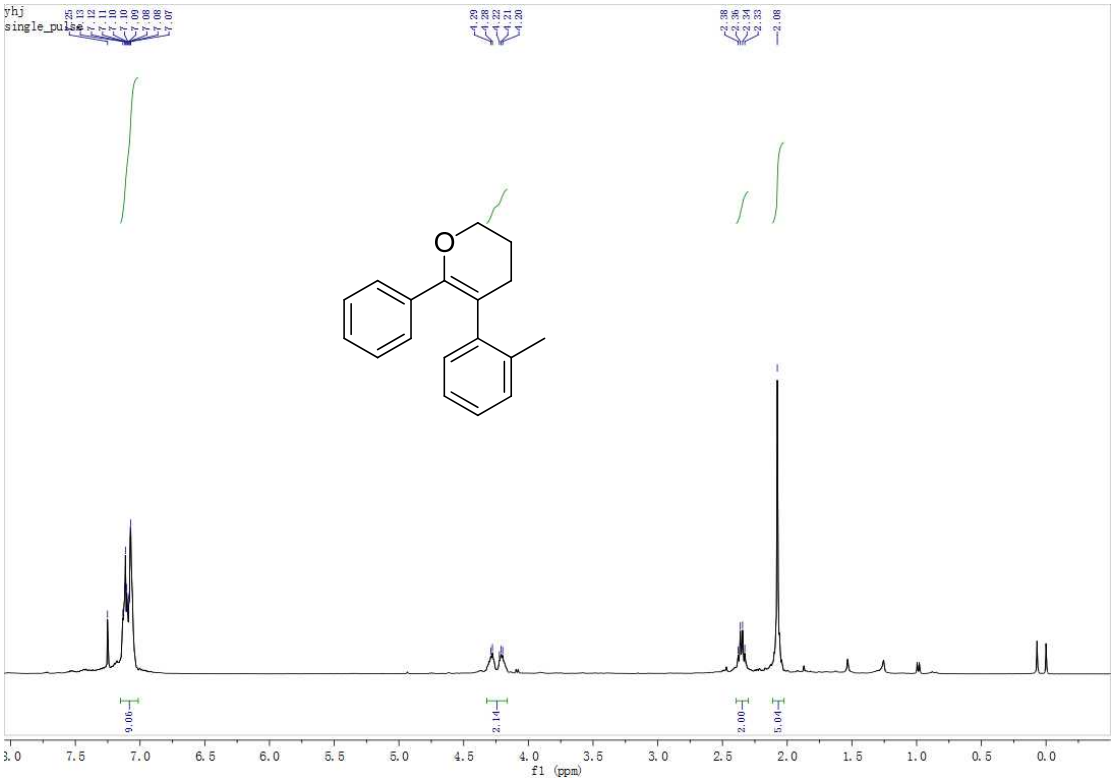
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

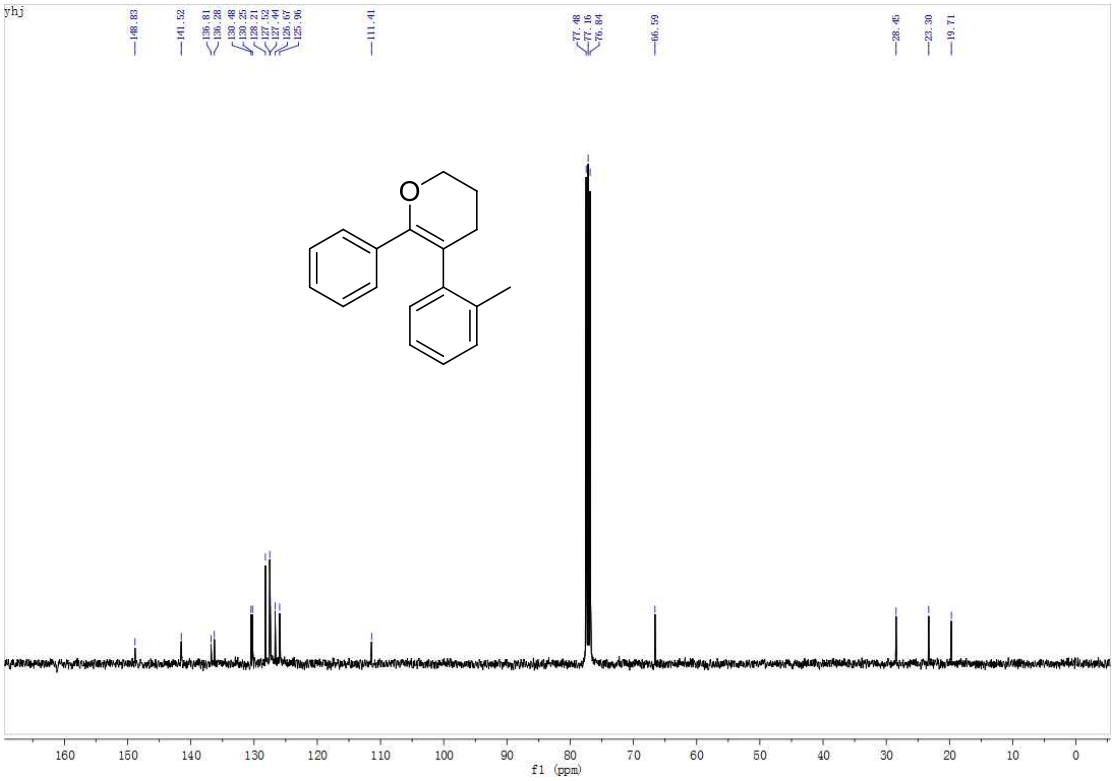


6-phenyl-5-(o-tolyl)-3,4-dihydro-2H-pyran 3da: yellow liquid, yield: 43%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.15 – 7.01 (m, 9H), 4.32 – 4.16 (m, 2H), 2.35 (dd, J = 13.9, 6.8 Hz, 2H), 2.11 – 2.02 (m, 5H).

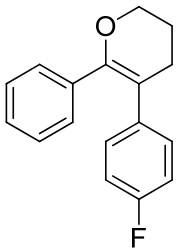
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 141.52, 136.81, 136.28, 130.48, 130.25, 128.21, 127.52, 127.44, 126.67, 125.96, 111.41, 66.59, 28.45, 23.30, 19.71.

GC-MS: m/z calcd for $C_{18}H_{18}O$: 250; found: 250.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

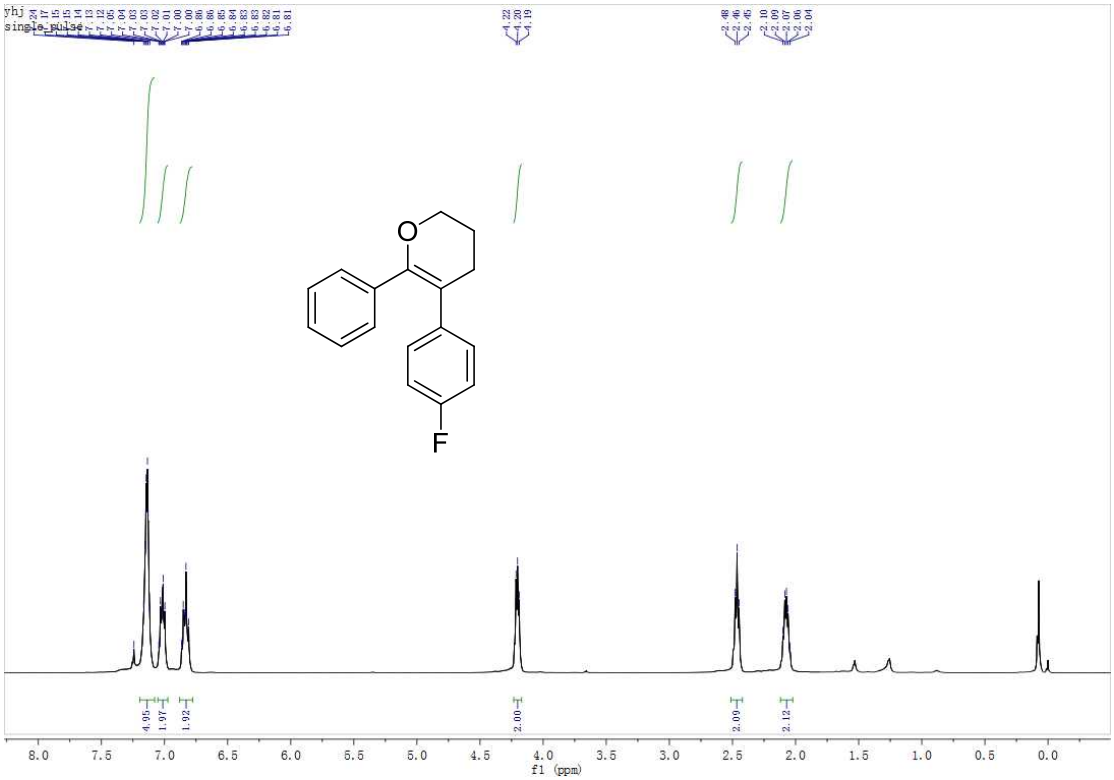


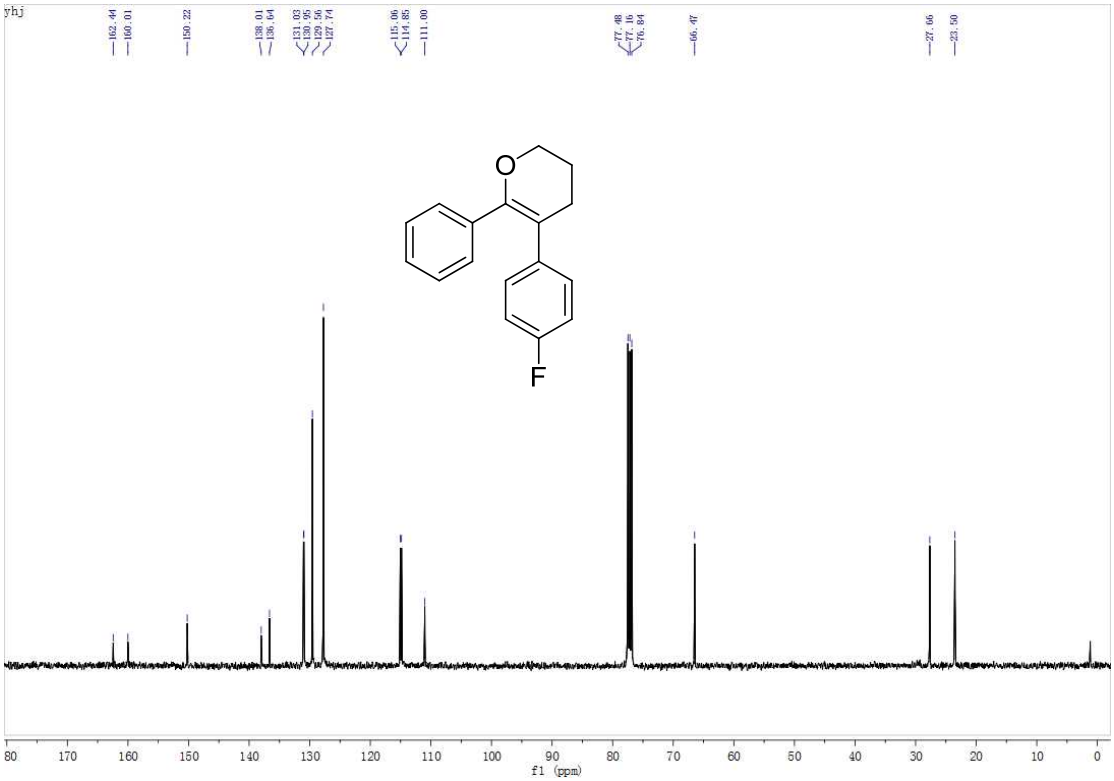
5-(4-fluorophenyl)-6-phenyl-3,4-dihydro-2H-pyran 3ea: yellow liquid, yield: 84%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.14 (td, J = 7.7, 5.0 Hz, 5H), 7.02 (ddd, J = 8.7, 5.3, 2.3 Hz, 2H), 6.88 – 6.78 (m, 2H), 4.23 – 4.17 (m, 2H), 2.46 (t, J = 6.2 Hz, 2H), 2.12 – 2.02 (m, 2H).

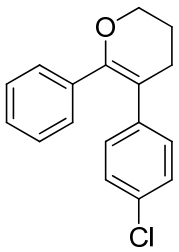
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 161.22 (d, J = 244.6 Hz), 150.22, 138.01, 136.64, 130.99 (d, J = 7.7 Hz), 129.56, 127.74(×2C), 114.95 (d, J = 21.1 Hz), 111.00, 66.47, 27.66, 23.50.

GC-MS: m/z calcd for $C_{17}H_{15}FO$: 254; found: 254.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

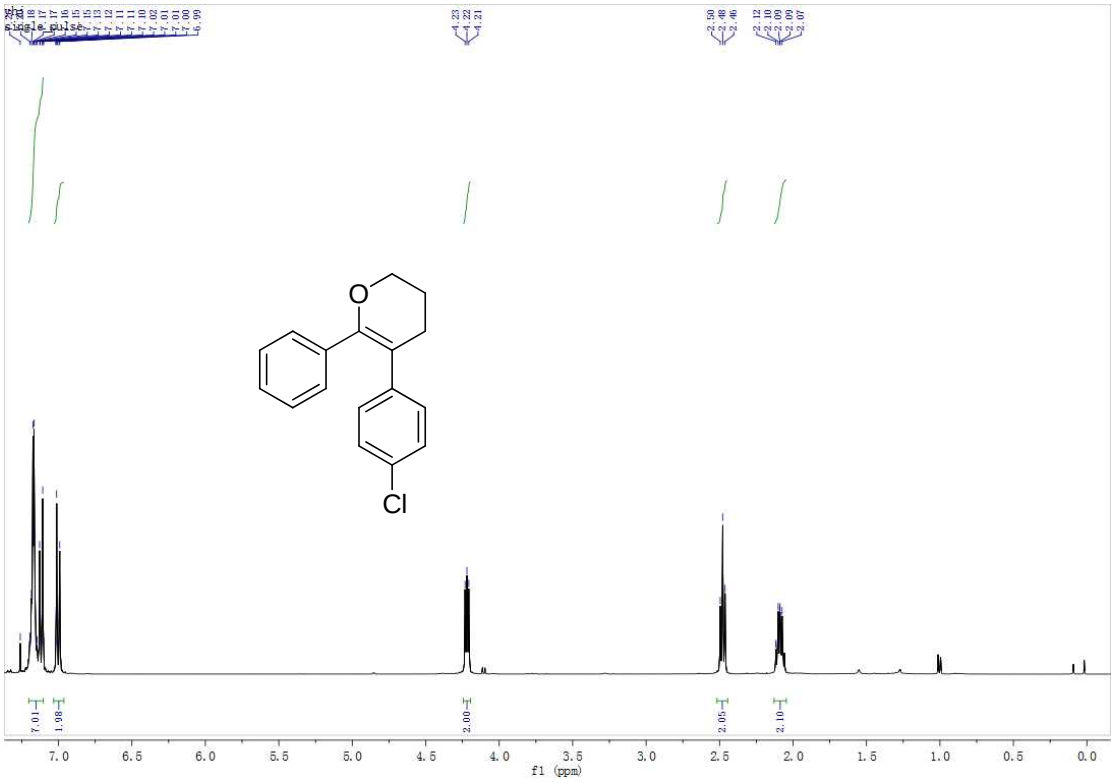


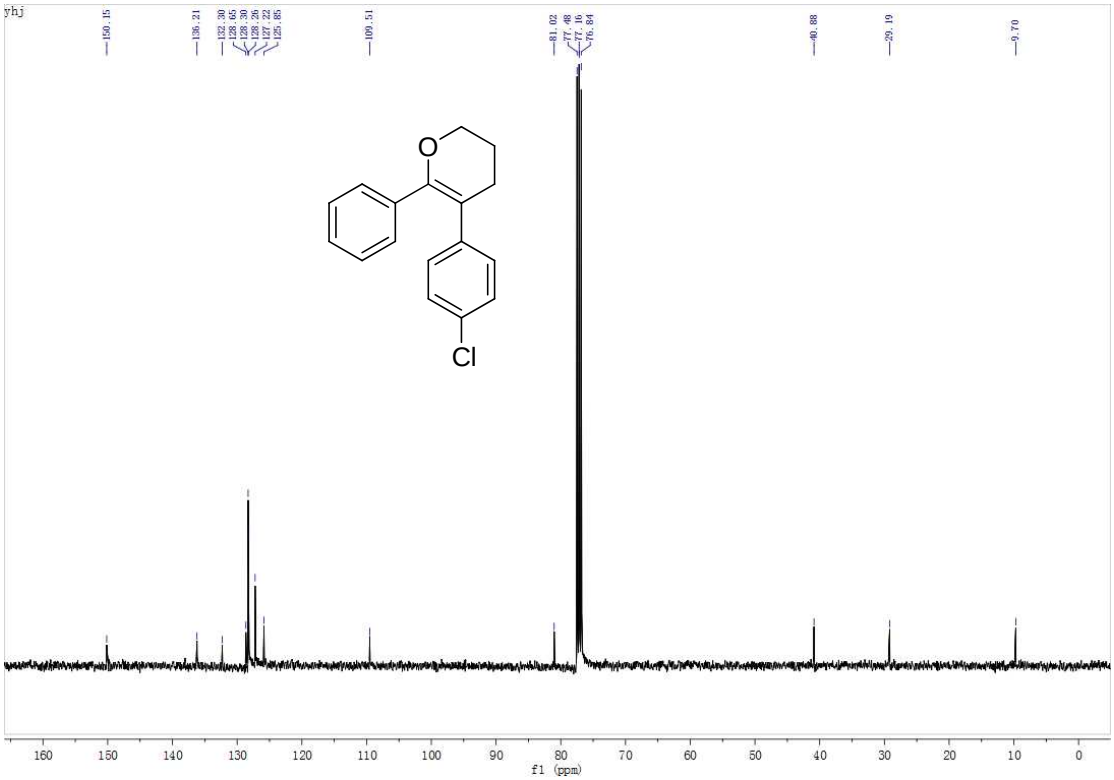
5-(4-chlorophenyl)-6-phenyl-3,4-dihydro-2H-pyran 3fa: yellow liquid, yield: 77%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.20 – 7.10 (m, 7H), 7.03 – 6.96 (m, 2H), 4.24 – 4.19 (m, 2H), 2.48 (t, J = 6.6 Hz, 2H), 2.13 – 2.05 (m, 2H).

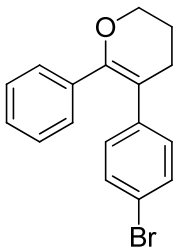
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 136.21, 128.65, 128.30, 128.26, 127.22, 125.85, 109.51, 81.02, 40.88, 29.19, 9.70.

GC-MS: m/z calcd for $C_{17}H_{15}ClO$: 270; found: 270.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

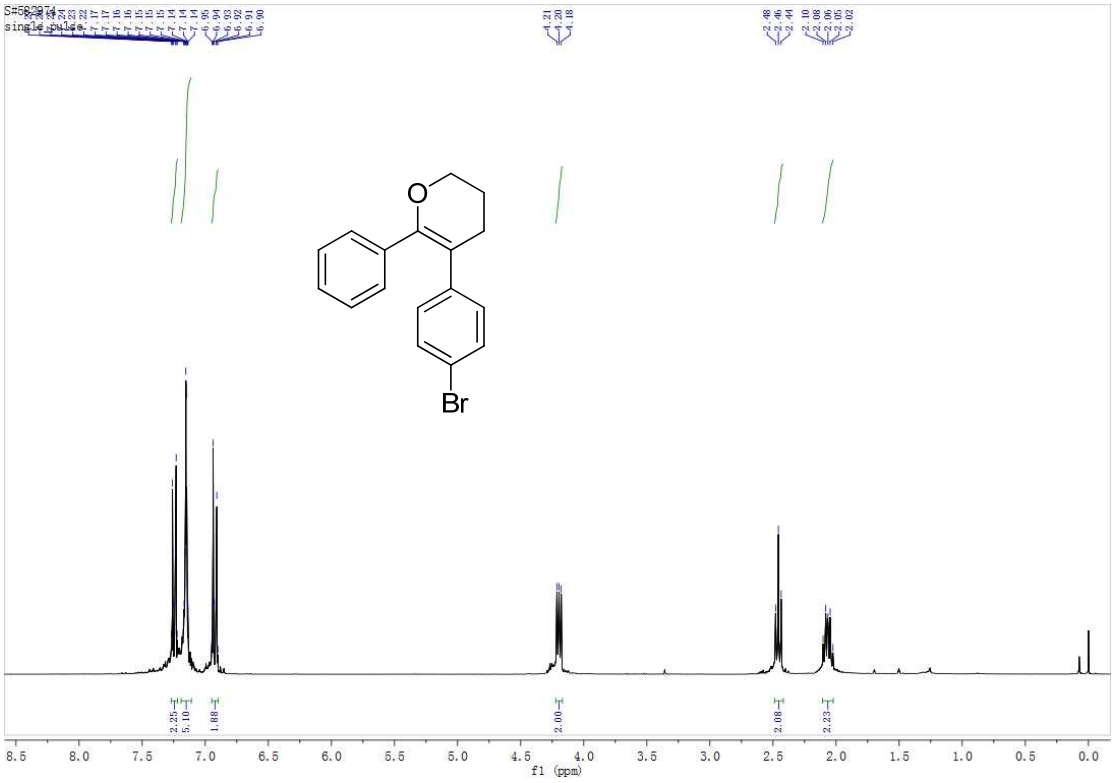


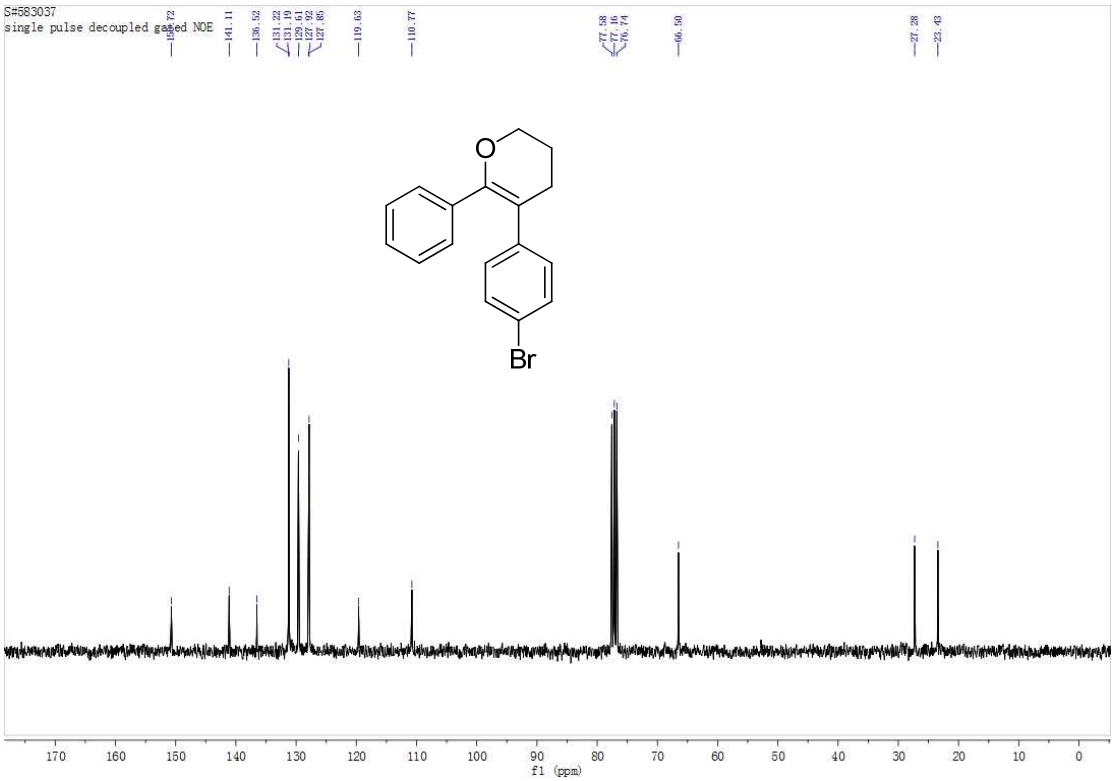
5-(4-bromophenyl)-6-phenyl-3,4-dihydro-2H-pyran 3ga: yellow liquid, yield: 92%.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.27 – 7.22 (m, 2H), 7.19 – 7.11 (m, 5H), 6.95 – 6.90 (m, 2H), 4.22 – 4.17 (m, 2H), 2.46 (t, J = 6.6 Hz, 2H), 2.11 – 2.02 (m, 2H).

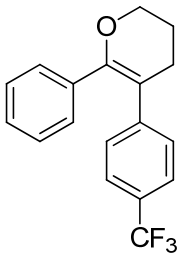
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 150.72, 141.11, 136.52, 131.22, 131.19, 129.61, 127.92, 127.85, 119.63, 110.77, 66.50, 27.28, 23.43.

GC-MS: m/z calcd for $C_{17}H_{15}BrO$: 314; found: 314.





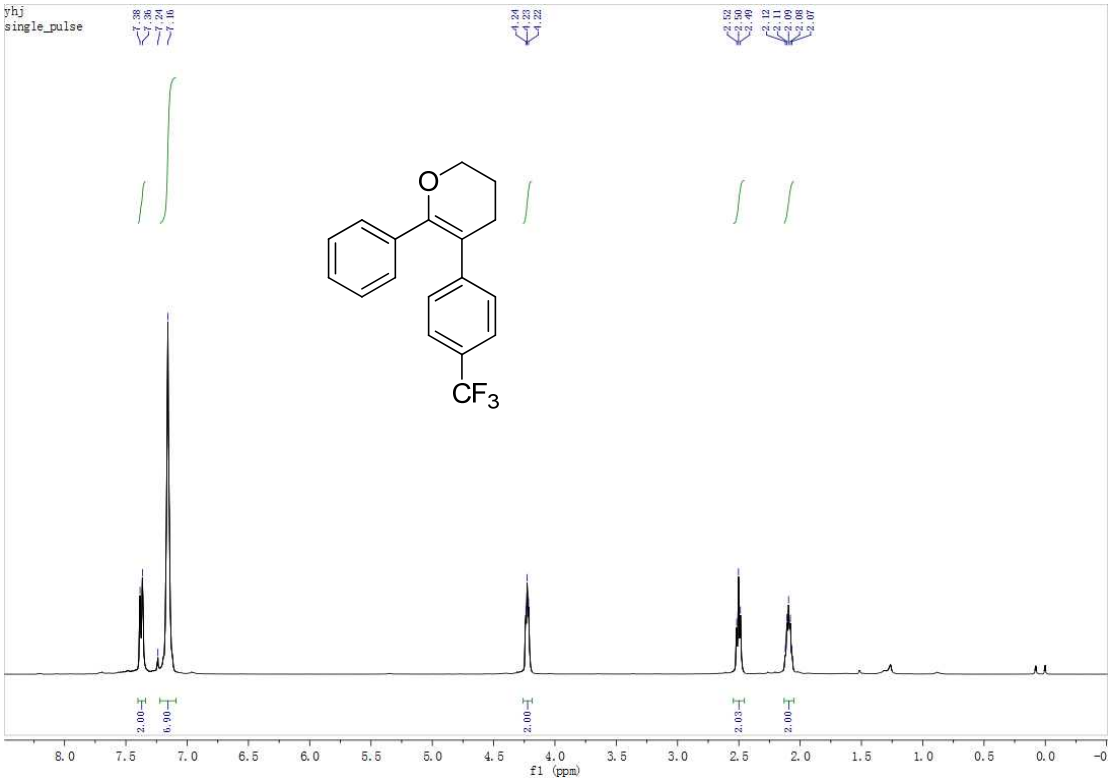
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

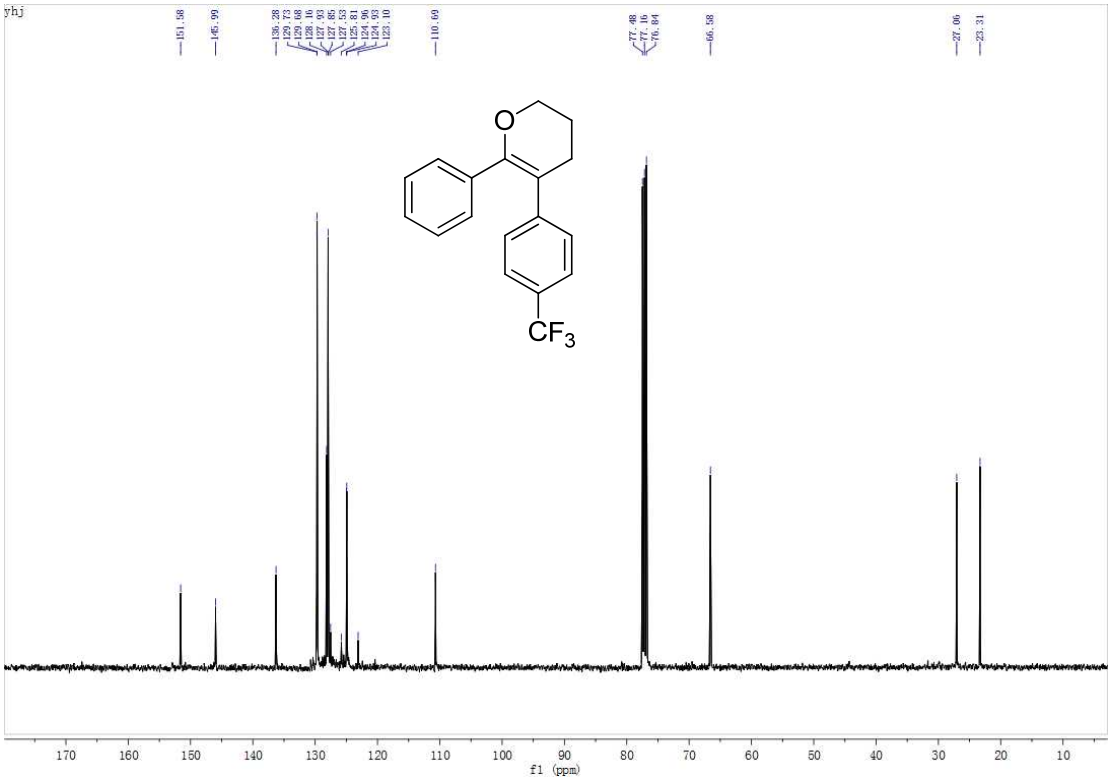


6-phenyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyran 3ha: yellow liquid, yield: 88%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.37 (d, J = 7.6 Hz, 2H), 7.16 (s, 7H), 4.26 – 4.19 (m, 2H), 2.50 (t, J = 6.0 Hz, 2H), 2.13 – 2.05 (m, 2H).

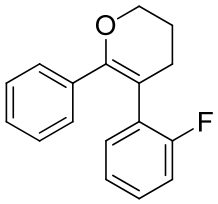
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 151.58, 145.99, 136.28, 129.73, 129.68, 128.16, 127.93, 127.69 (q, J = 32.3 Hz), 124.95 (q, J = 3.7 Hz), 124.46 (q, J = 273.7 Hz), 110.69, 66.58, 27.06, 23.31.

GC-MS: m/z calcd for $C_{18}H_{15}F_3O$: 304; found: 304.





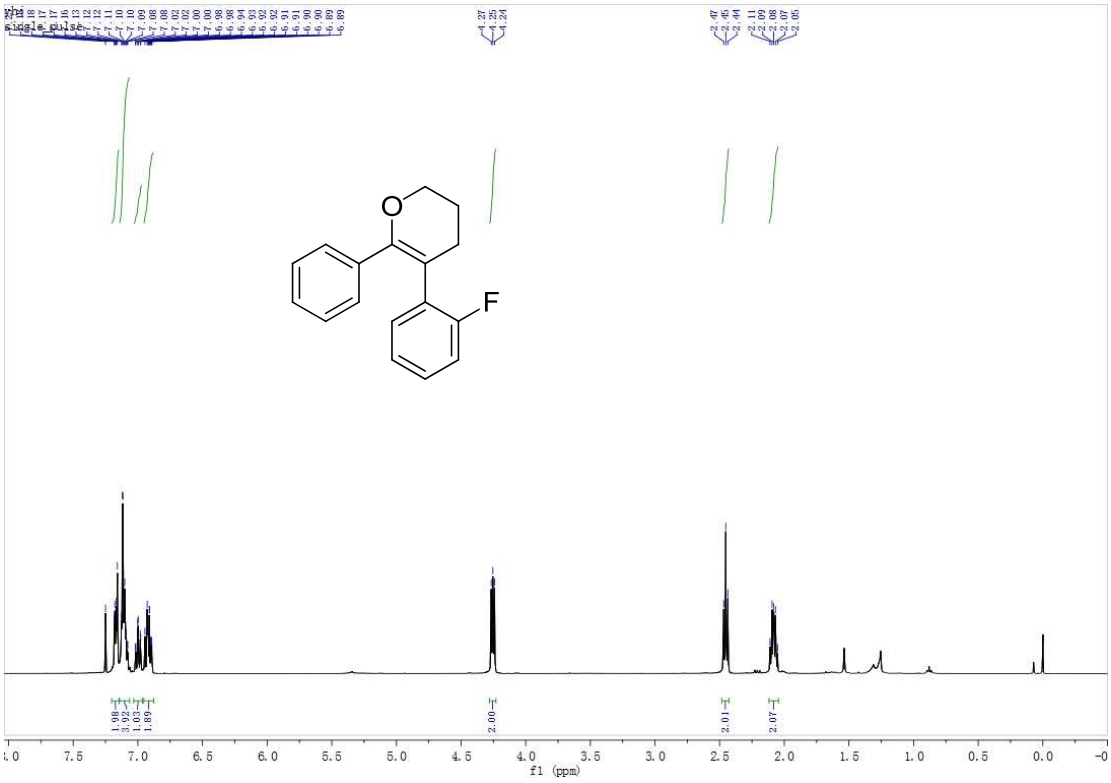
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

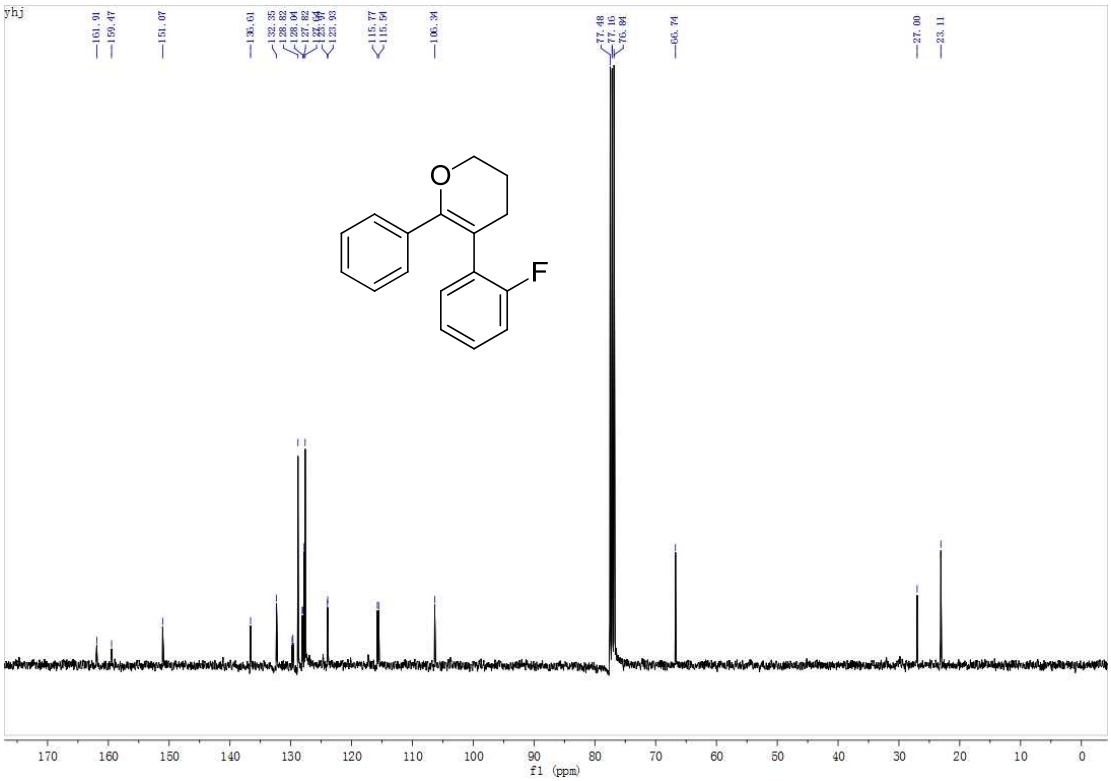


5-(2-fluorophenyl)-6-phenyl-3,4-dihydro-2H-pyran 3ia: yellow liquid, yield: 85%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.20 – 7.15 (m, 2H), 7.14 – 7.06 (m, 4H), 7.00 (td, J = 7.6, 1.7 Hz, 1H), 6.95 – 6.88 (m, 2H), 4.28 – 4.23 (m, 2H), 2.45 (t, J = 6.5 Hz, 2H), 2.12 – 2.05 (m, 2H).

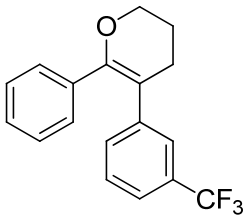
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 160.69 (d, J = 245.3 Hz), 151.07, 136.61, 132.37 (d, J = 4.0 Hz), 129.72 (d, J = 15.3 Hz), 128.82, 128.08 (d, J = 7.9 Hz), 127.82, 127.64, 123.95 (d, J = 3.3 Hz), 115.65 (d, J = 22.8 Hz), 106.34, 66.74, 27.00, 23.11.

GC-MS: m/z calcd for $C_{17}H_{15}FO$: 254; found: 254.





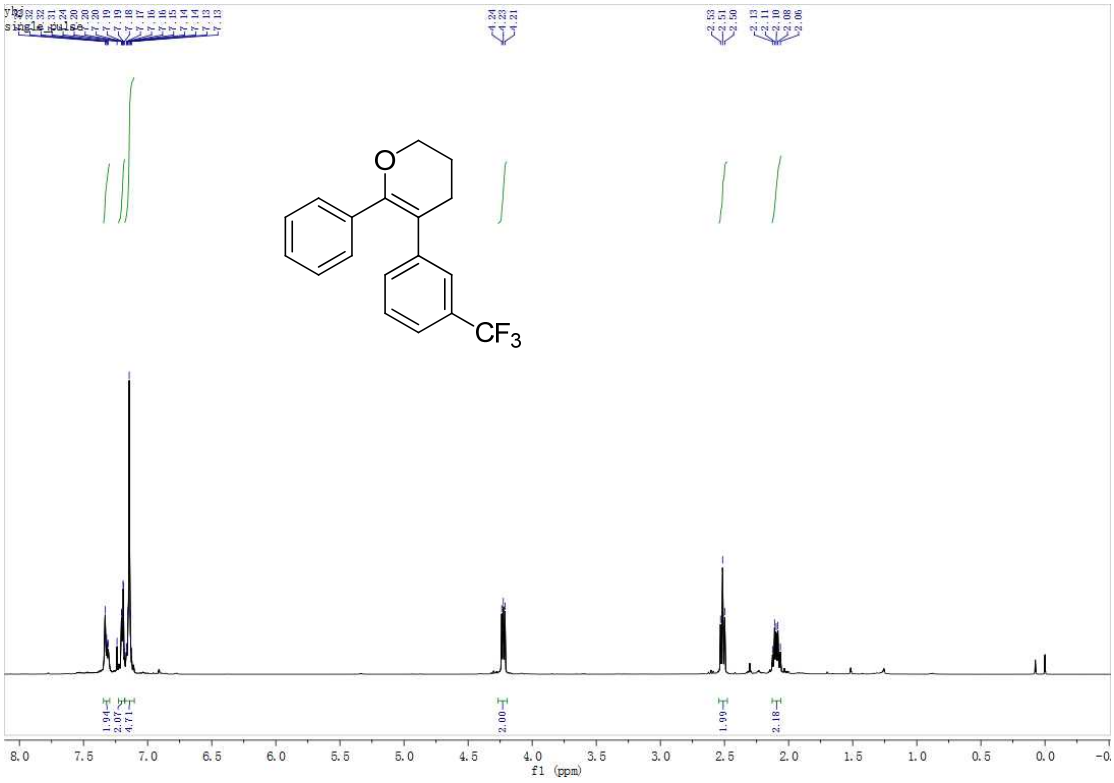
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

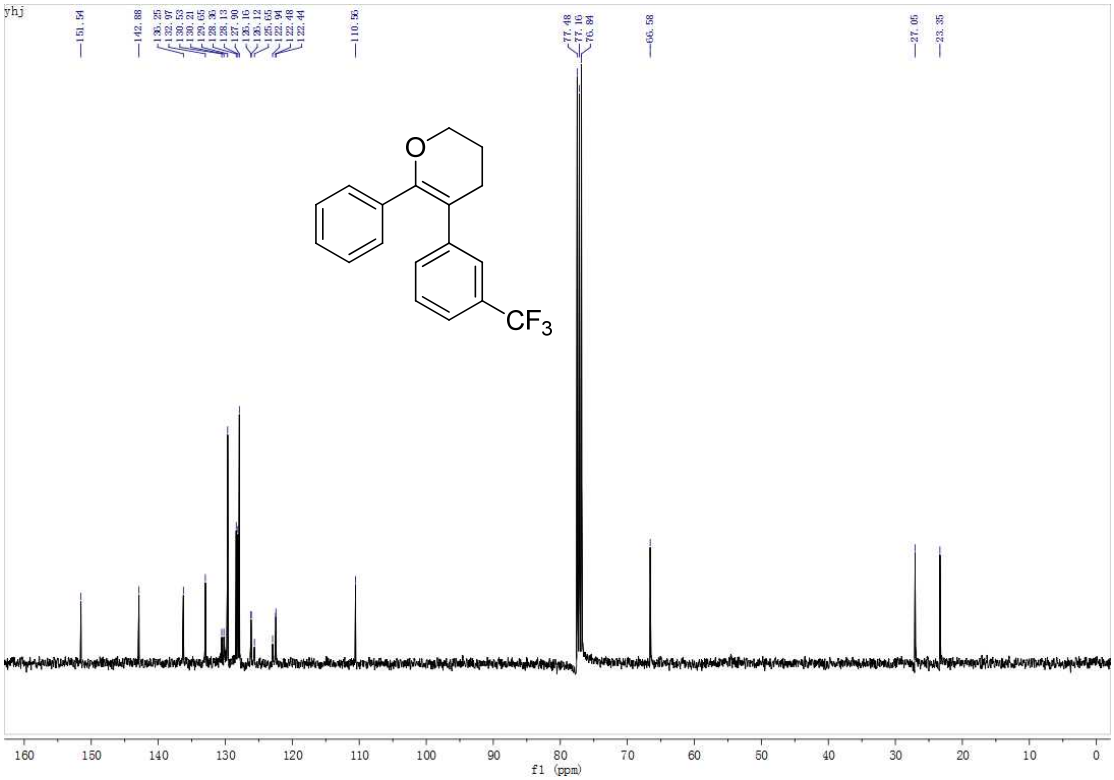


6-phenyl-5-(3-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyran 3ja: yellow liquid, yield: 65%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.32 (dd, J = 5.4, 4.2 Hz, 2H), 7.19 (dt, J = 6.1, 2.2 Hz, 2H), 7.18 – 7.10 (m, 5H), 4.27 – 4.19 (m, 2H), 2.51 (t, J = 6.6 Hz, 2H), 2.13 – 2.06 (m, 2H).

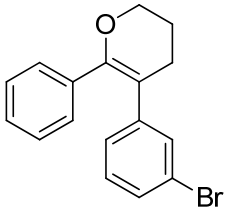
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 151.54, 142.88, 136.25, 132,97, 130.37 (q, J = 32.1 Hz), 129.65, 128.36, 128.13, 127.90, 126.14 (q, J = 3.83 Hz), 124.29 (q, J = 272.4 Hz), 122.46 (q, J = 3.9 Hz), 110.56, 66.58, 27.05, 23.35.

GC-MS: m/z calcd for $C_{18}H_{15}F_3O$: 304; found: 304.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

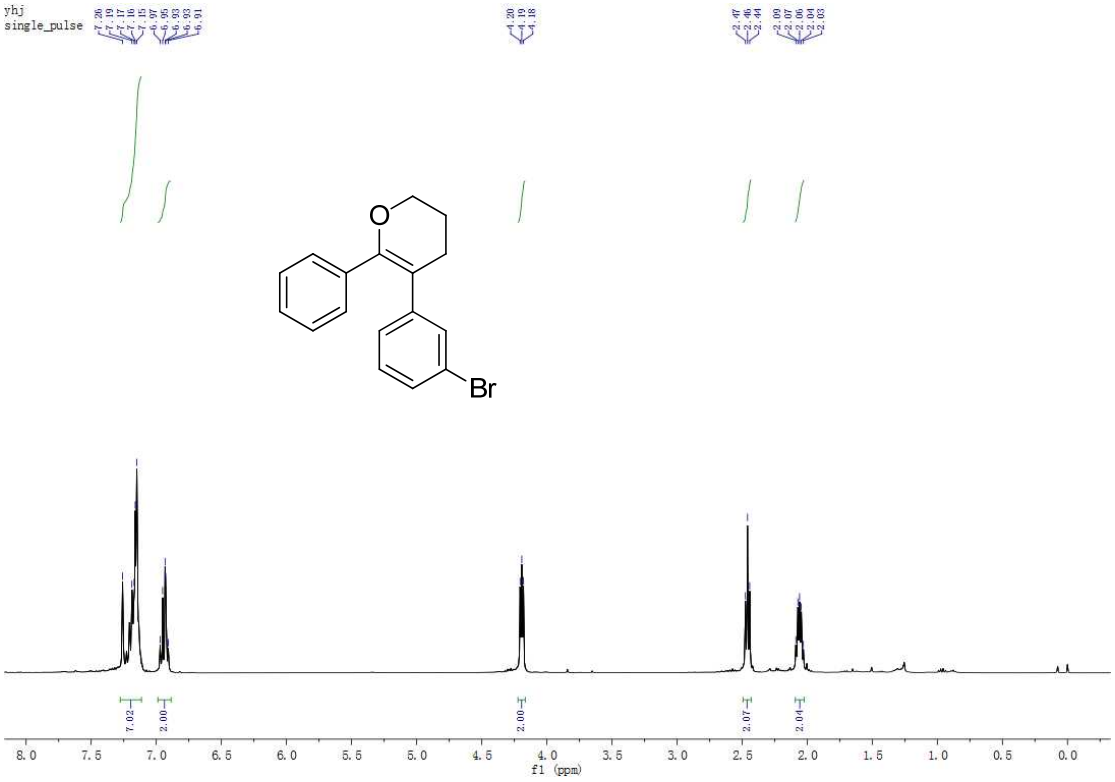


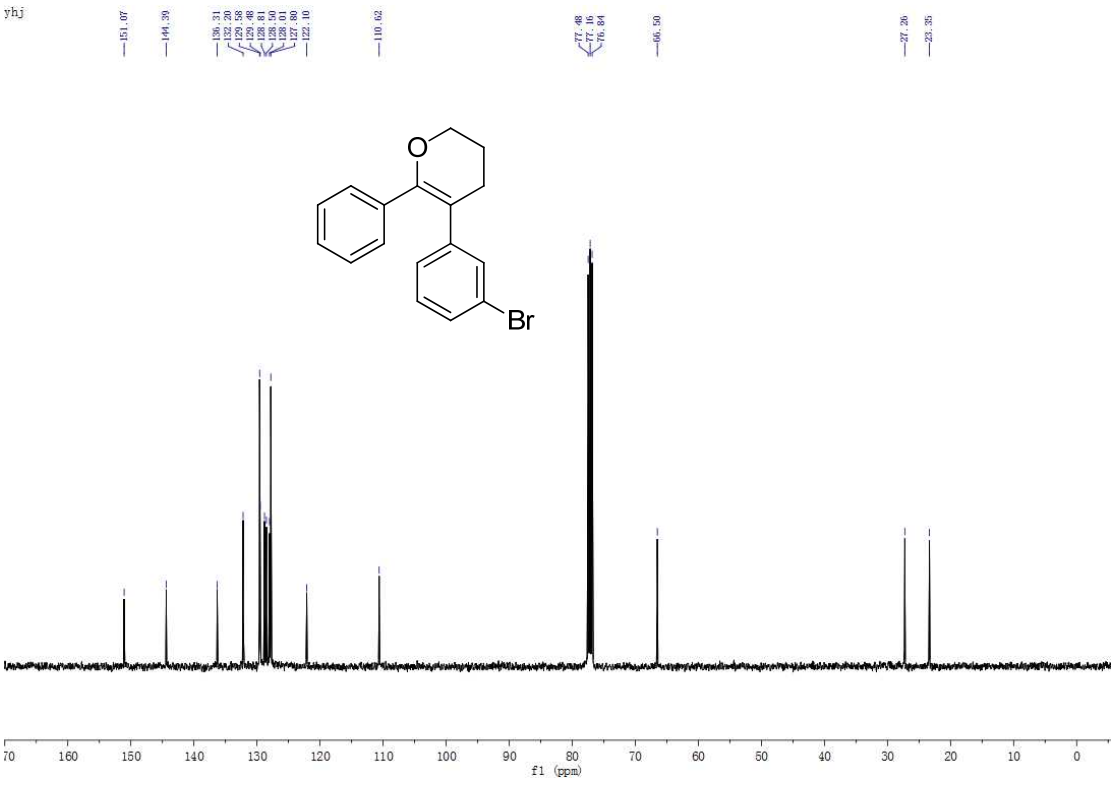
5-(3-bromophenyl)-6-phenyl-3,4-dihydro-2H-pyran 3ka: yellow liquid, yield: 89%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.28 – 7.11 (m, 7H), 6.99 – 6.89 (m, 2H), 4.22 – 4.17 (m, 2H), 2.46 (t, J = 6.6 Hz, 2H), 2.09 – 2.02 (m, 2H).

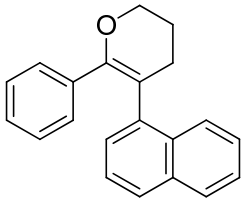
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 151.07, 144.39, 136.31, 132.20, 129.58, 129.48, 128.81, 128.50, 128.01, 127.80, 122.10, 110.62, 66.50, 27.26, 23.35.

GC-MS: m/z calcd for $C_{17}H_{15}BrO$: 314; found: 314.





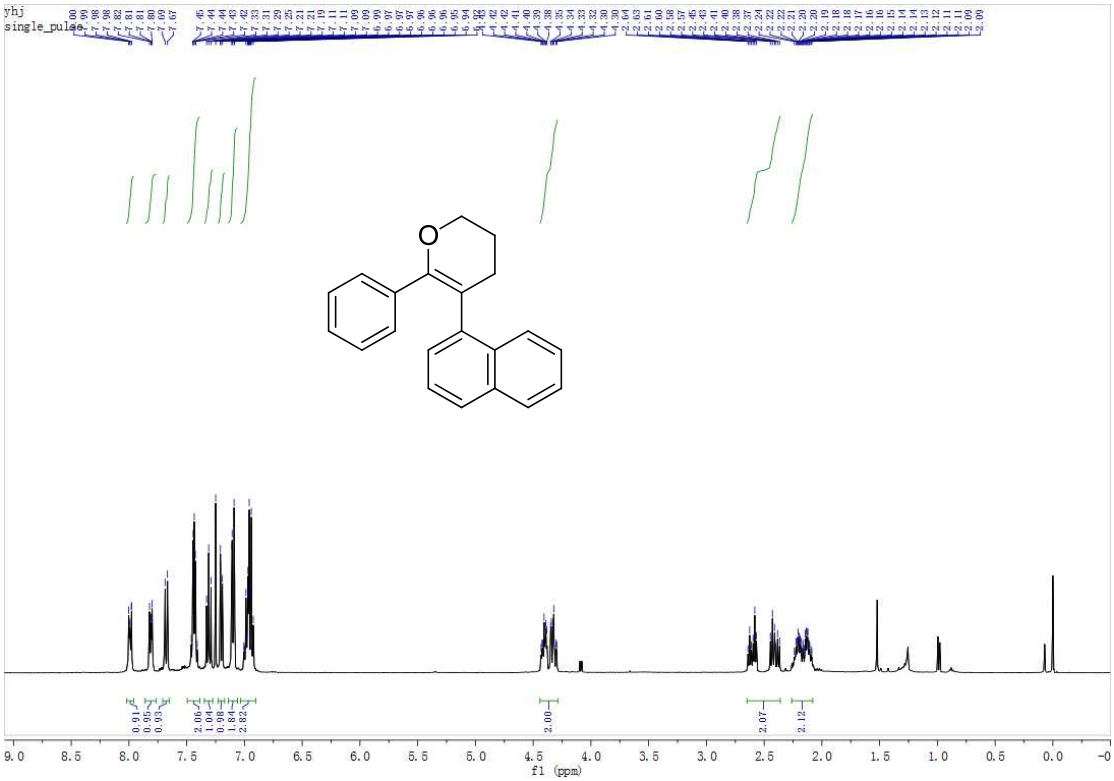
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

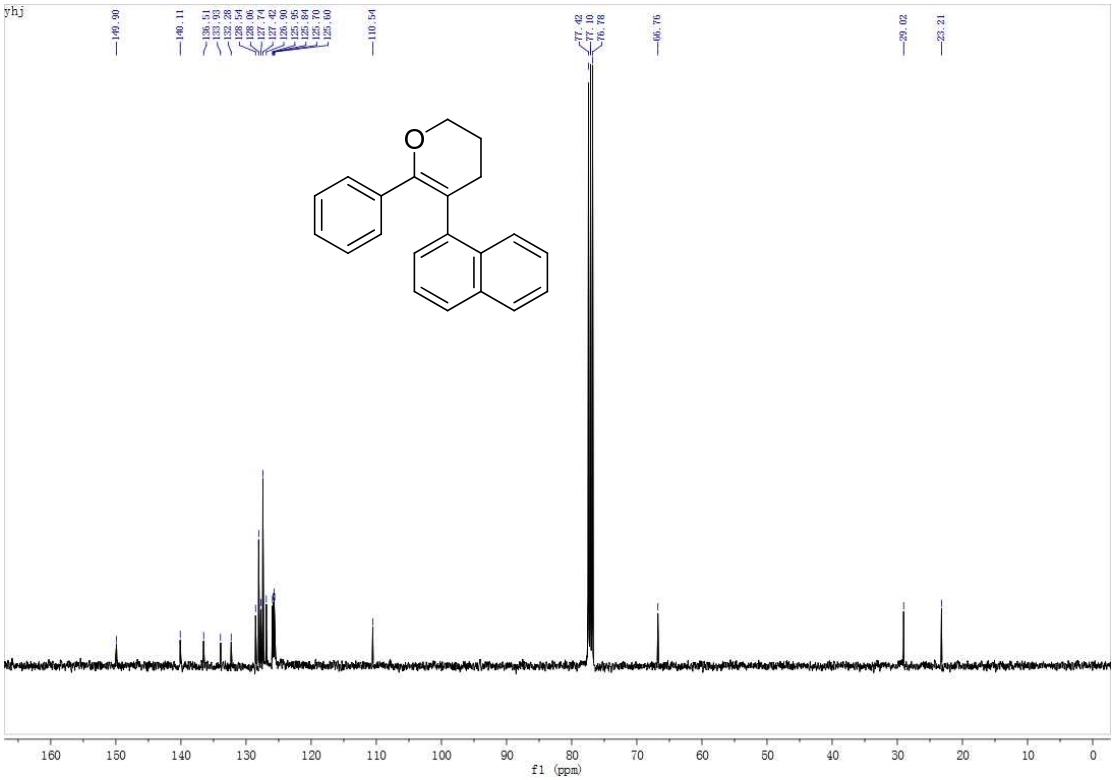


5-(naphthalen-1-yl)-6-phenyl-3,4-dihydro-2H-pyran 3la: yellow solid, mp = 98.4 – 99.8 ^{o}C, yield: 31%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.99 (dd, J = 7.6, 1.9 Hz, 1H), 7.81 (dd, J = 5.3, 4.0 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.10 (dd, J = 8.0, 1.4 Hz, 2H), 7.03 – 6.90 (m, 3H), 4.44 – 4.29 (m, 2H), 2.65 – 2.36 (m, 2H), 2.26 – 2.08 (m, 2H).

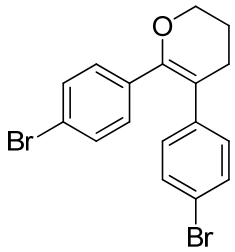
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 149.96, 140.17, 136.57, 133.98, 132.34, 128.60, 128.12, 127.80, 127.48, 126.96, 126.01, 125.90, 125.76, 125.66, 110.60, 66.82, 29.07, 23.27.

GC-MS: m/z calcd for $C_{21}H_{18}O$: 286; found: 286.





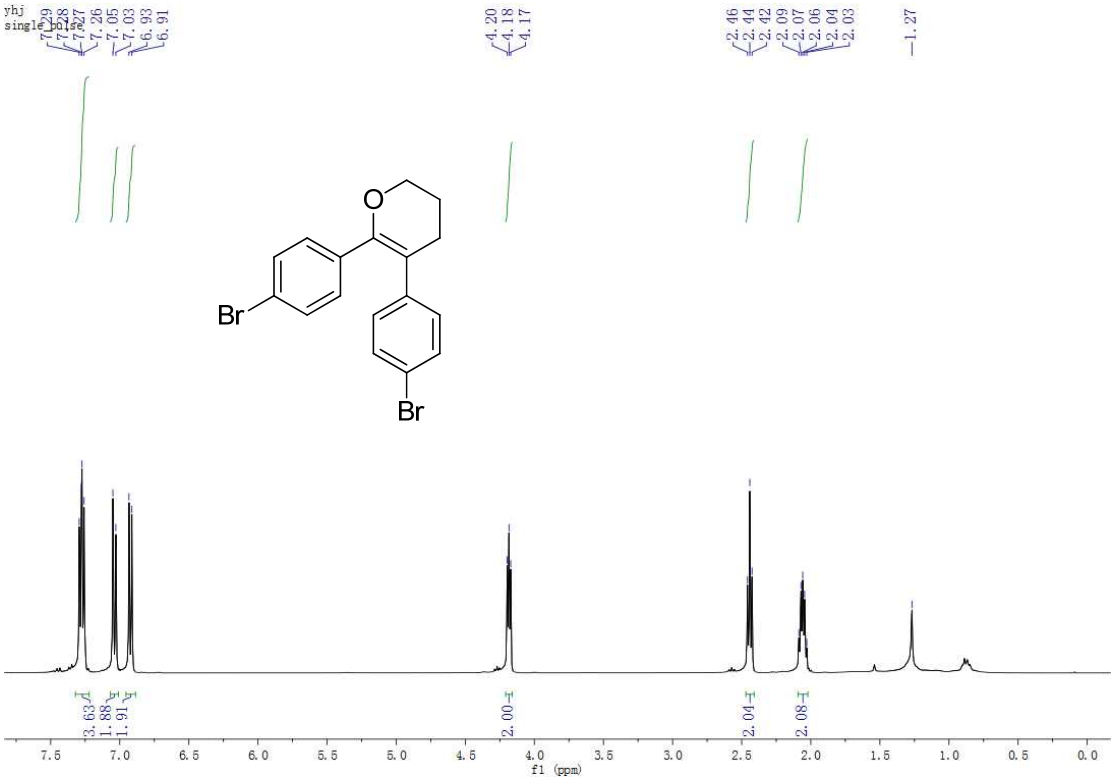
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

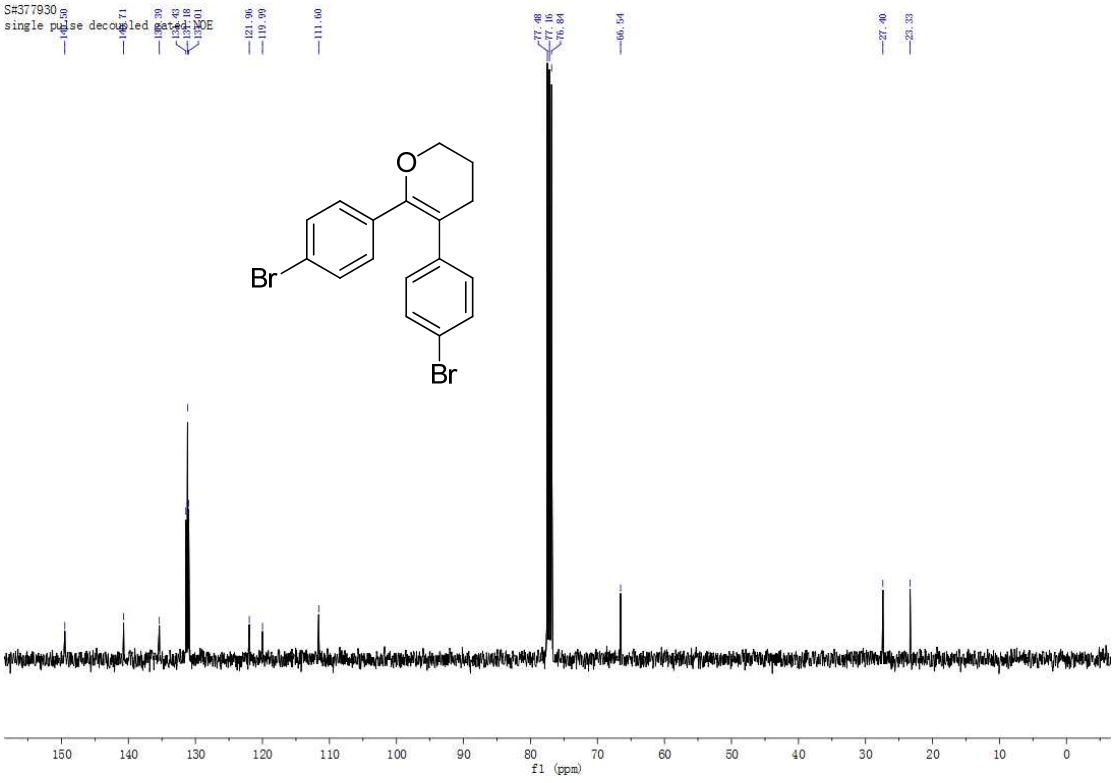


5,6-bis(4-bromophenyl)-3,4-dihydro-2H-pyran 3gg:white solid, mp = 103.0-103.8 ^{o}C, yield: 96%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.28 (dd, J = 8.0, 6.3 Hz, 4H), 7.04 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.21 – 4.16 (m, 2H), 2.44 (t, J = 6.5 Hz, 2H), 2.09 – 2.02 (m, 2H).

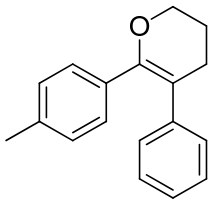
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 149.50, 140.71, 135.39, 131.43, 131.18 (×2C), 121.96, 119.99, 111.60, 66.54, 27.40, 23.33.

GC-MS: m/z calcd for $C_{17}H_{14}Br_2O$: 394; found: 394.





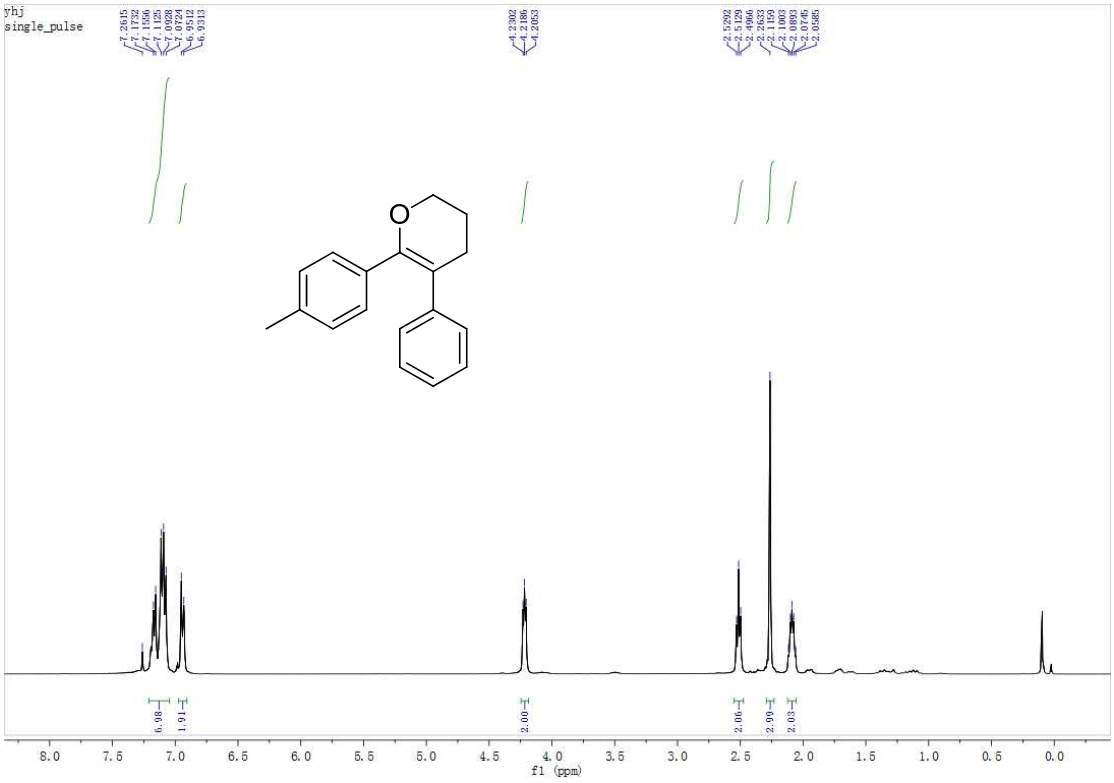
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

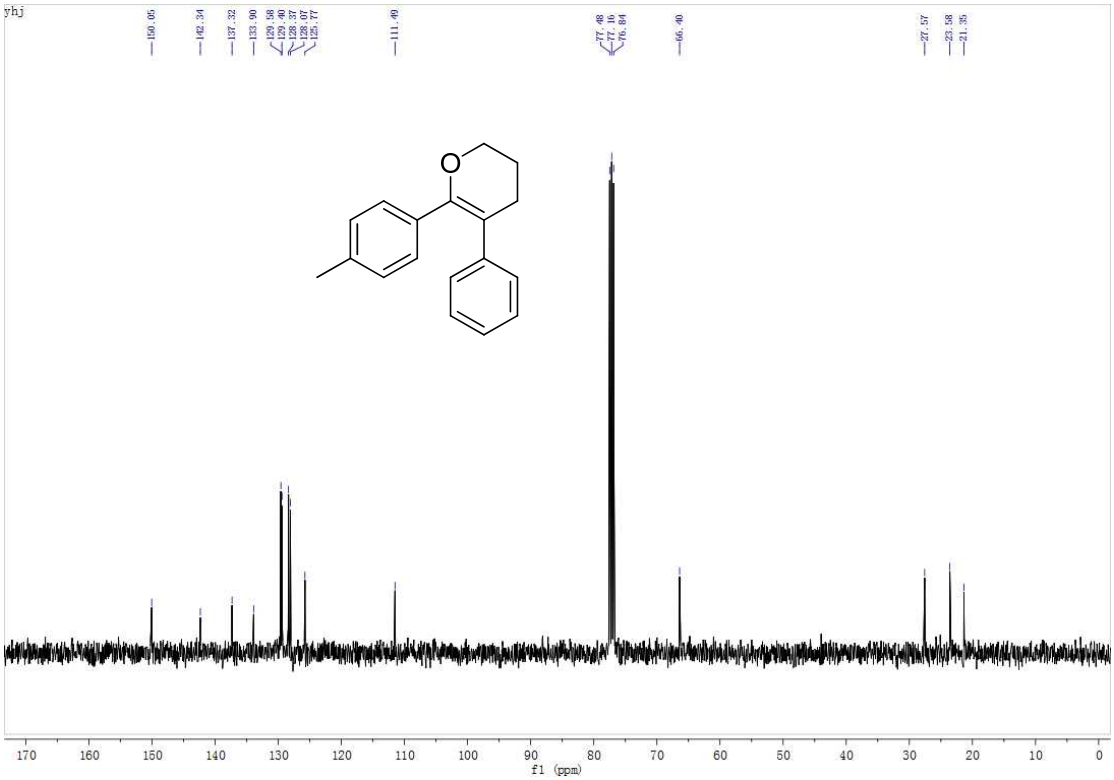


5-phenyl-6-(p-tolyl)-3,4-dihydro-2H-pyran 3ab: yellow solid, mp = 63.2 - 64.5 ^{o}C, yield: 88%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.21 – 7.04 (m, 7H), 6.94 (d, J = 7.9 Hz, 2H), 4.25 – 4.19 (m, 2H), 2.51 (t, J = 6.5 Hz, 2H), 2.26 (s, 3H), 2.09 (dt, J = 12.3, 6.3 Hz, 2H).

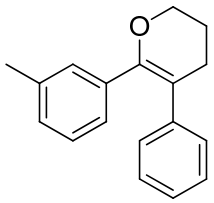
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.05, 142.34, 137.32, 133.90, 129.58, 129.40, 128.37, 128.07, 125.77, 111.49, 66.40, 27.57, 23.58, 21.35.

GC-MS: m/z calcd for $C_{18}H_{18}O$: 250; found: 250.





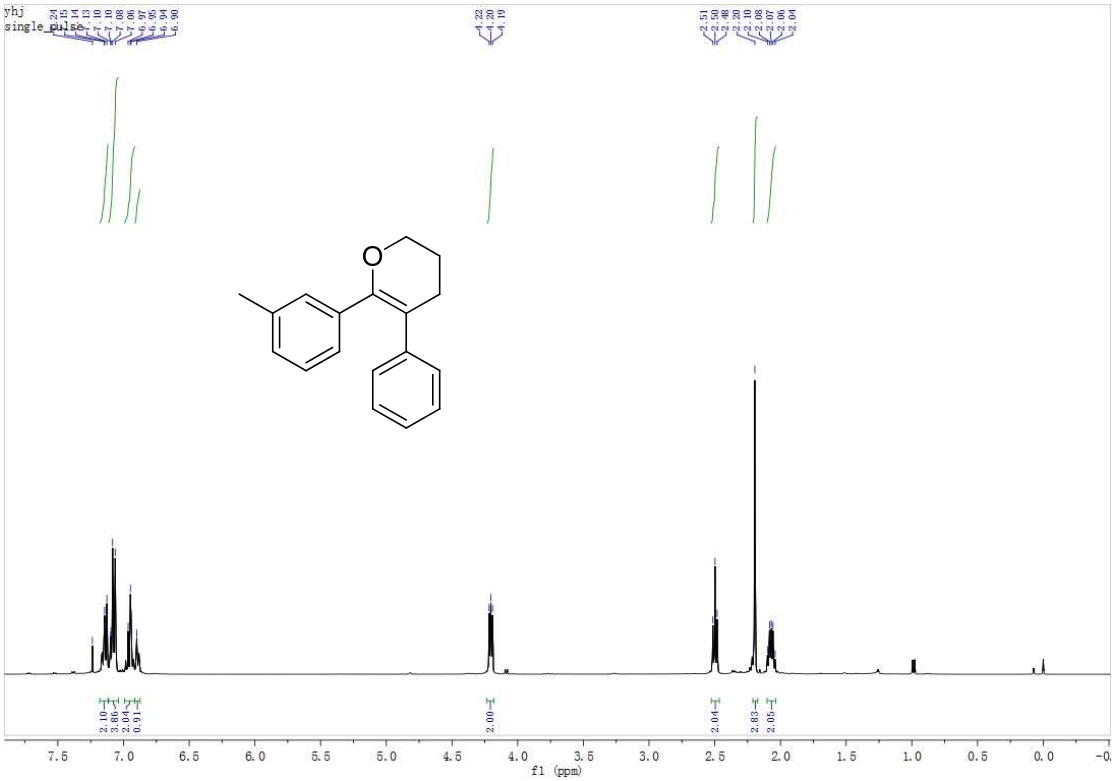
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

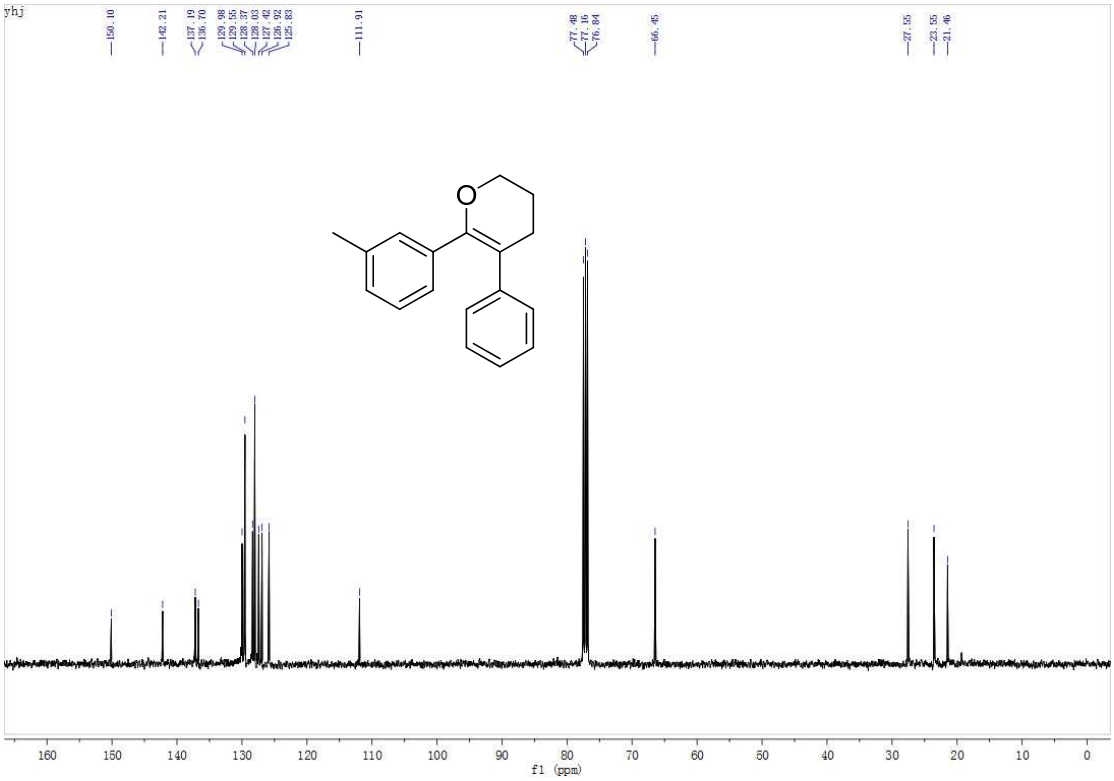


5-phenyl-6-(m-tolyl)-3,4-dihydro-2H-pyran 3ac: yellow liquid, yield: 70%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.18 – 7.12 (m, 2H), 7.09 (dd, J = 9.5, 4.5 Hz, 4H), 6.95 (t, J = 4.5 Hz, 2H), 6.90 (s, 1H), 4.23 – 4.18 (m, 2H), 2.50 (t, J = 6.6 Hz, 2H), 2.20 (s, 3H), 2.10 – 2.04 (m, 2H).

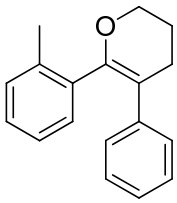
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.10, 142.21, 137.19, 136.70, 129.98, 129.55, 128.37, 128.03, 127.42, 126.92, 125.83, 111.91, 66.45, 27.55, 23.55, 21.46.

GC-MS: m/z calcd for $C_{18}H_{18}O$: 250; found: 250.





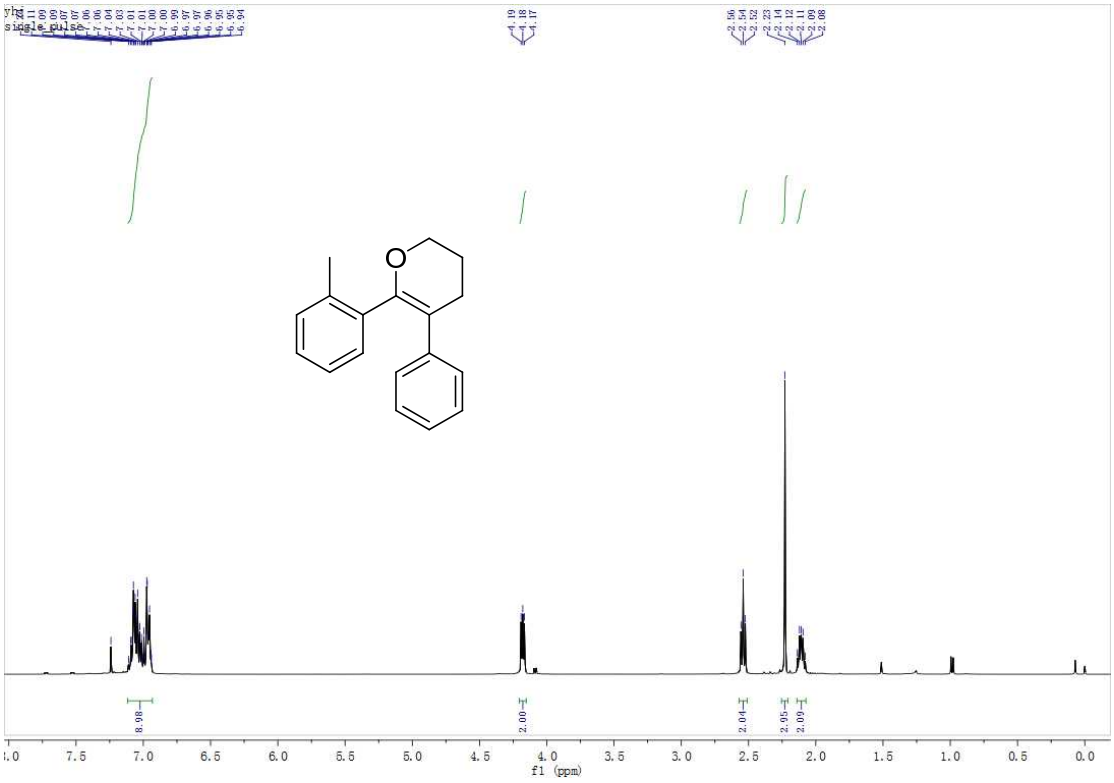
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

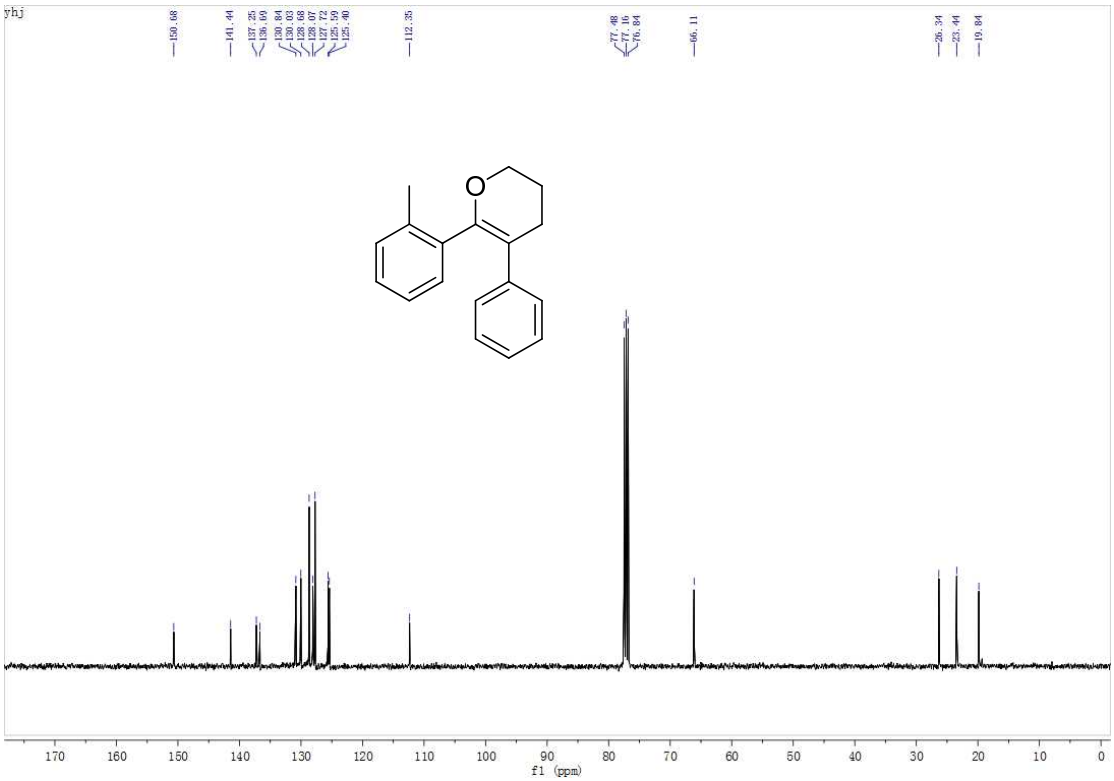


5-phenyl-6-(o-tolyl)-3,4-dihydro-2H-pyran 3ad: yellow liquid, yield: 72%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.12 – 6.93 (m, 9H), 4.20 – 4.15 (m, 2H), 2.54 (t, J = 6.5 Hz, 2H), 2.23 (s, 3H), 2.14 – 2.07 (m, 2H).

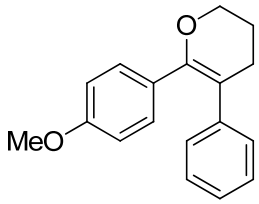
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.68, 141.44, 137.25, 136.69, 130.84, 130.03, 128.68, 128.07, 127.72, 125.59, 125.40, 112.35, 66.11, 26.34, 23.44, 19.84.

GC-MS: m/z calcd for $C_{18}H_{18}O$: 250; found: 250.





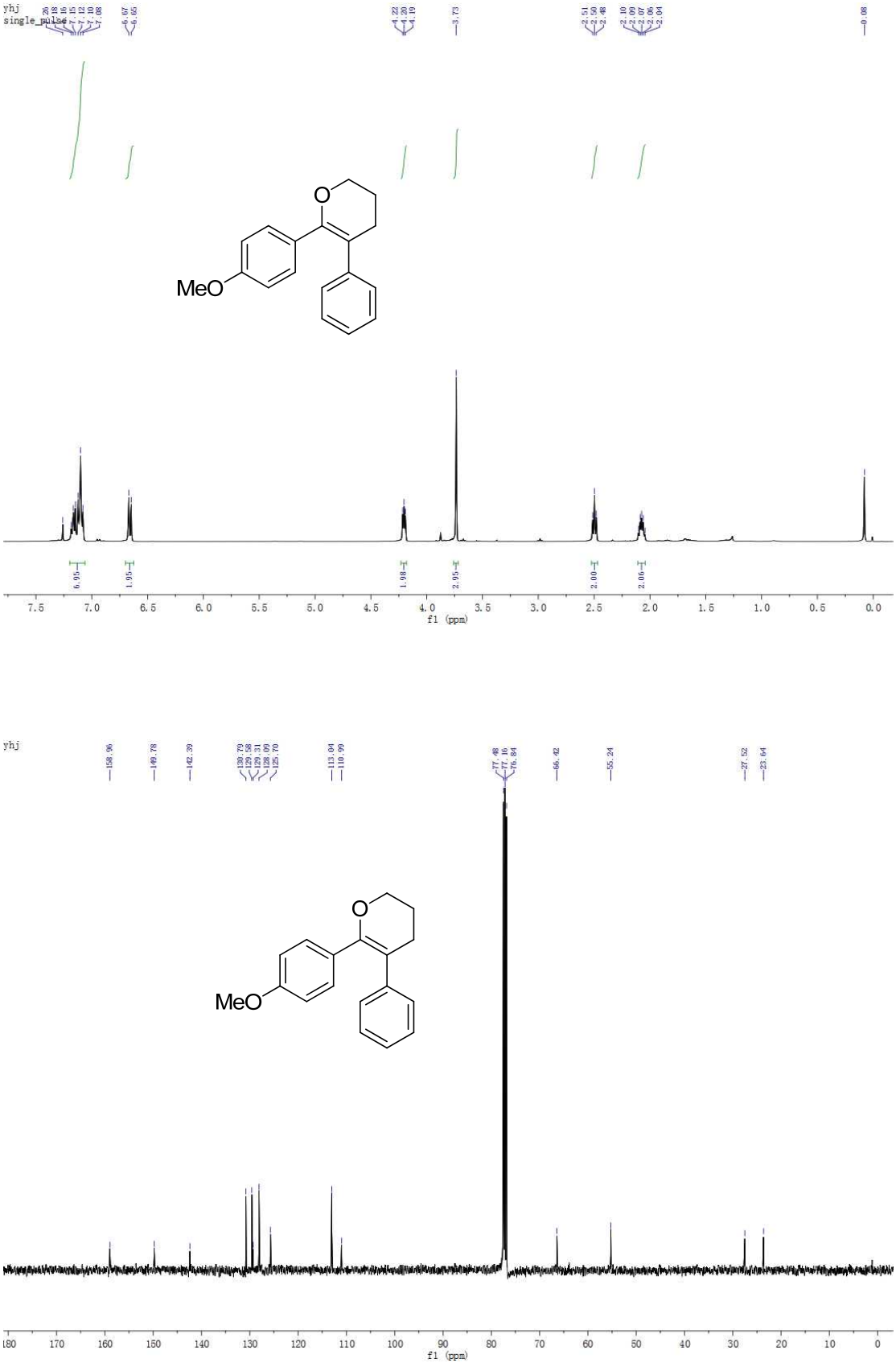
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



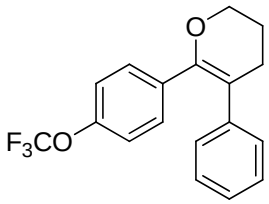
6-(4-methoxyphenyl)-5-phenyl-3,4-dihydro-2H-pyran 3ae: white solid, mp = 63.5 – 65.6 °C, yield: 62%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.13 (dt, J = 17.3, 8.0 Hz, 7H), 6.66 (d, J = 8.7 Hz, 2H), 4.23 – 4.18 (m, 2H), 3.73 (s, 3H), 2.50 (t, J = 6.6 Hz, 2H), 2.11 – 2.04 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 158.96, 149.78, 142.39, 130.79, 129.58, 129.31, 128.09, 125.70, 113.04, 110.99, 66.42, 55.24, 27.52, 23.64.

GC-MS: m/z calcd for $C_{18}H_{18}O_2$: 266; found: 266.



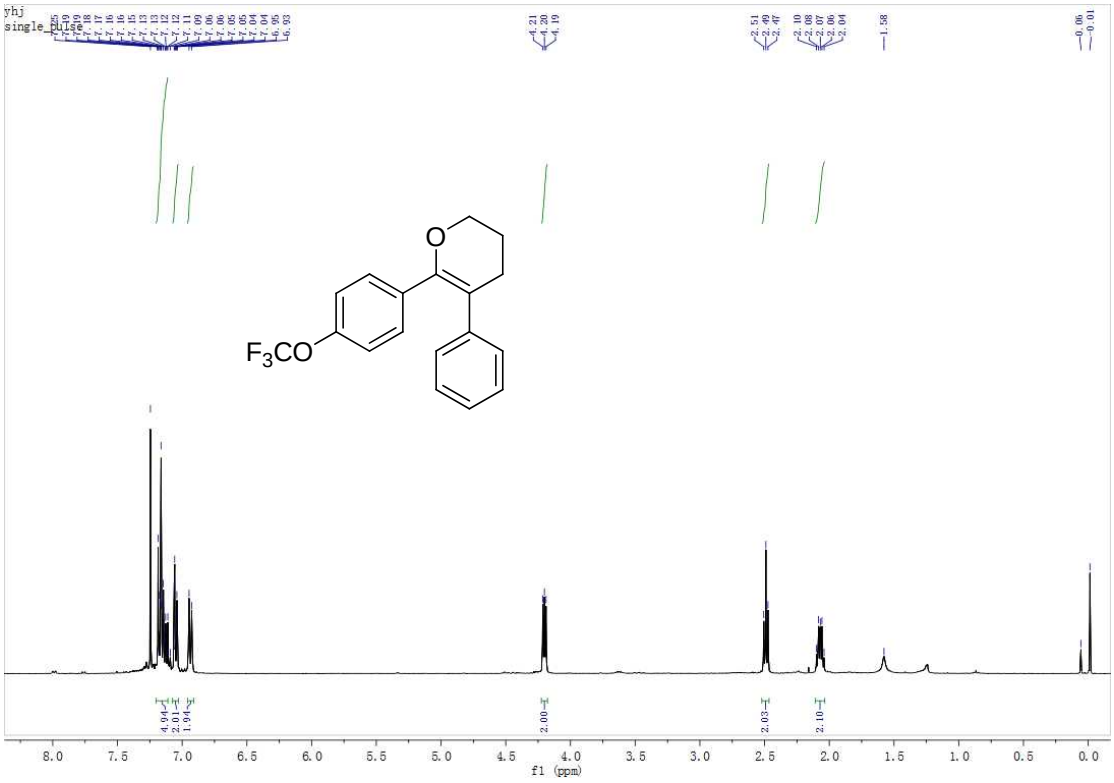
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

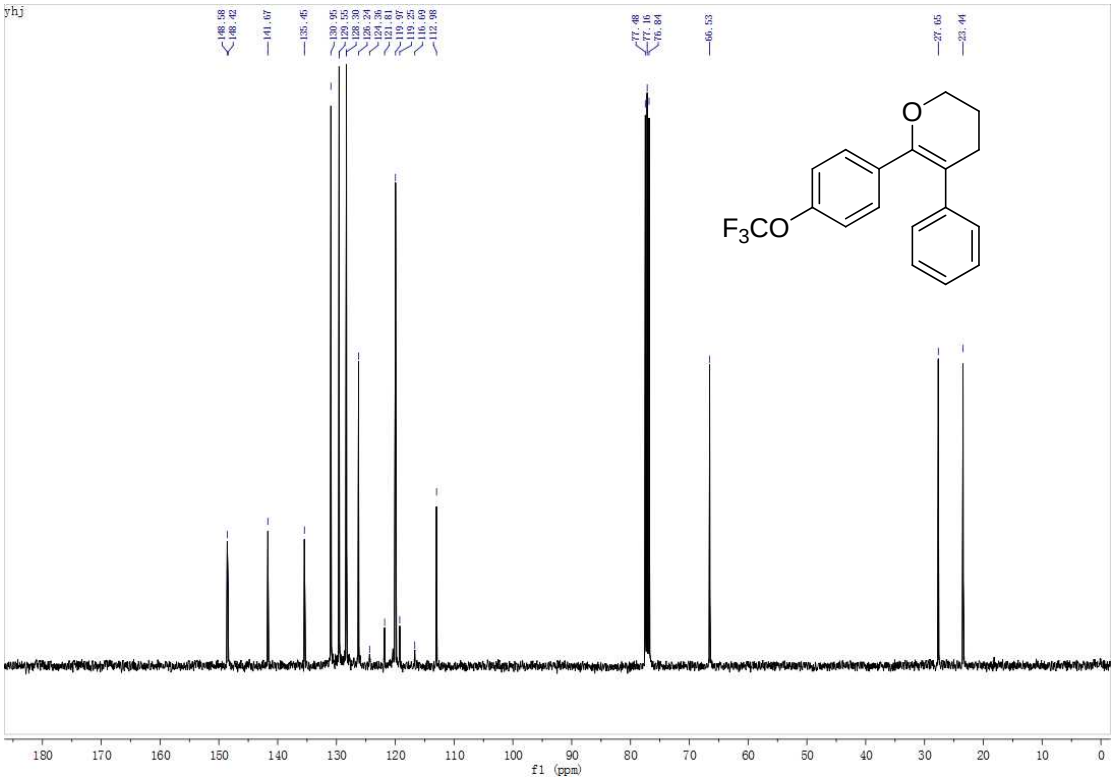


5-phenyl-6-(4-(trifluoromethoxy)phenyl)-3,4-dihydro-2H-pyran 3af: yellow liquid, yield: 67%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.20 – 7.11 (m, 5H), 7.07 – 7.03 (m, 2H), 6.94 (d, J = 8.2 Hz, 2H), 4.22 – 4.18 (m, 2H), 2.49 (t, J = 6.6 Hz, 2H), 2.11 – 2.03 (m, 2H).

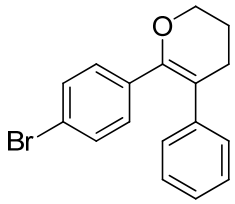
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 148.58, 148.42, 141.67, 135.45, 130.95, 129.55, 128.30, 126.24, 120.53 (q, J = 1024), 119.97, 112.98, 66.53, 27.65, 23.44.

GC-MS: m/z calcd for $C_{18}H_{15}F_3O_2$: 320; found: 320.





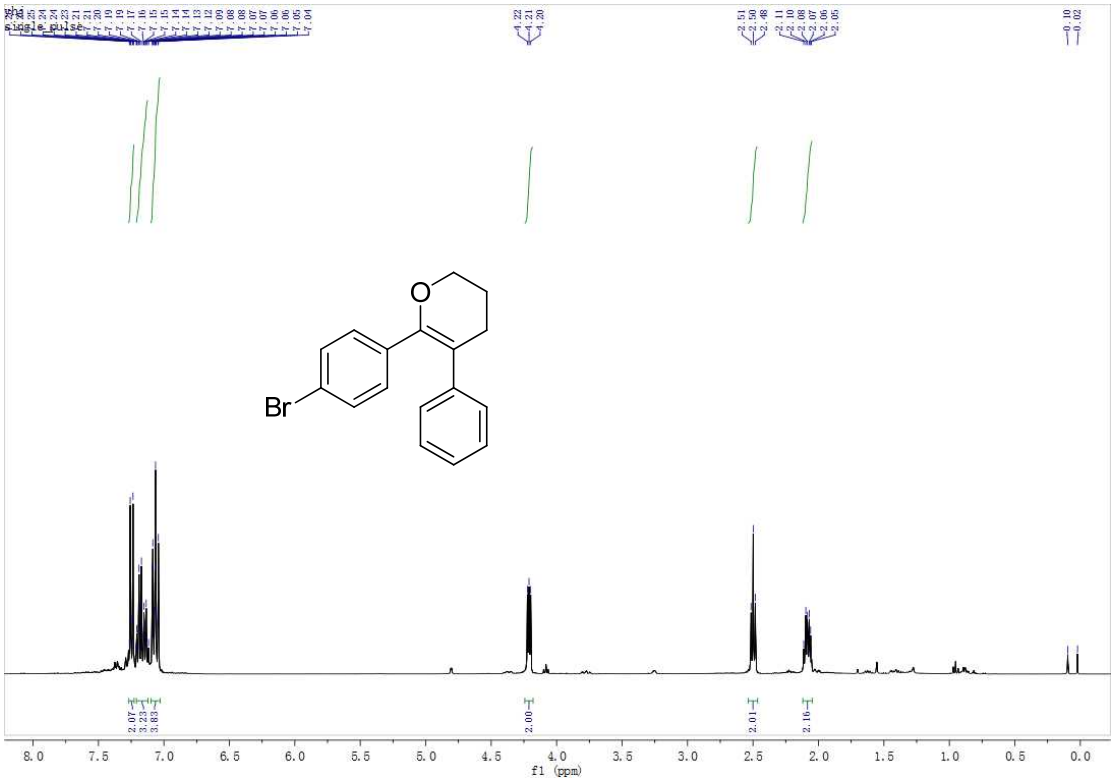
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

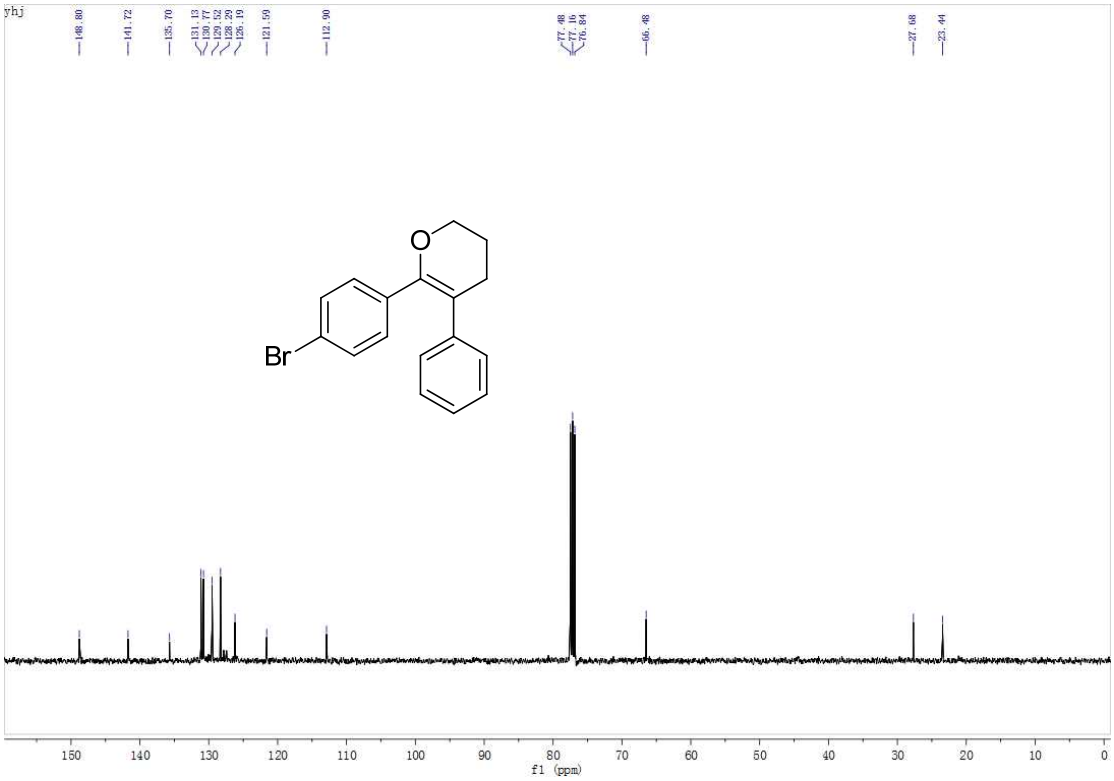


6-(4-bromophenyl)-5-phenyl-3,4-dihydro-2H-pyran 3ag: yellow solid, mp = 92.8-94.1 ^{o}C, yield: 92%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.27 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 7.10 – 7.03 (m, 4H), 4.24 – 4.18 (m, 2H), 2.50 (t, J = 6.6 Hz, 2H), 2.08 (dt, J = 6.5, 4.4 Hz, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 148.80, 141.72, 135.70, 131.13, 130.77, 129.52, 128.29, 126.19, 121.59, 112.90, 66.48, 27.68, 23.44.

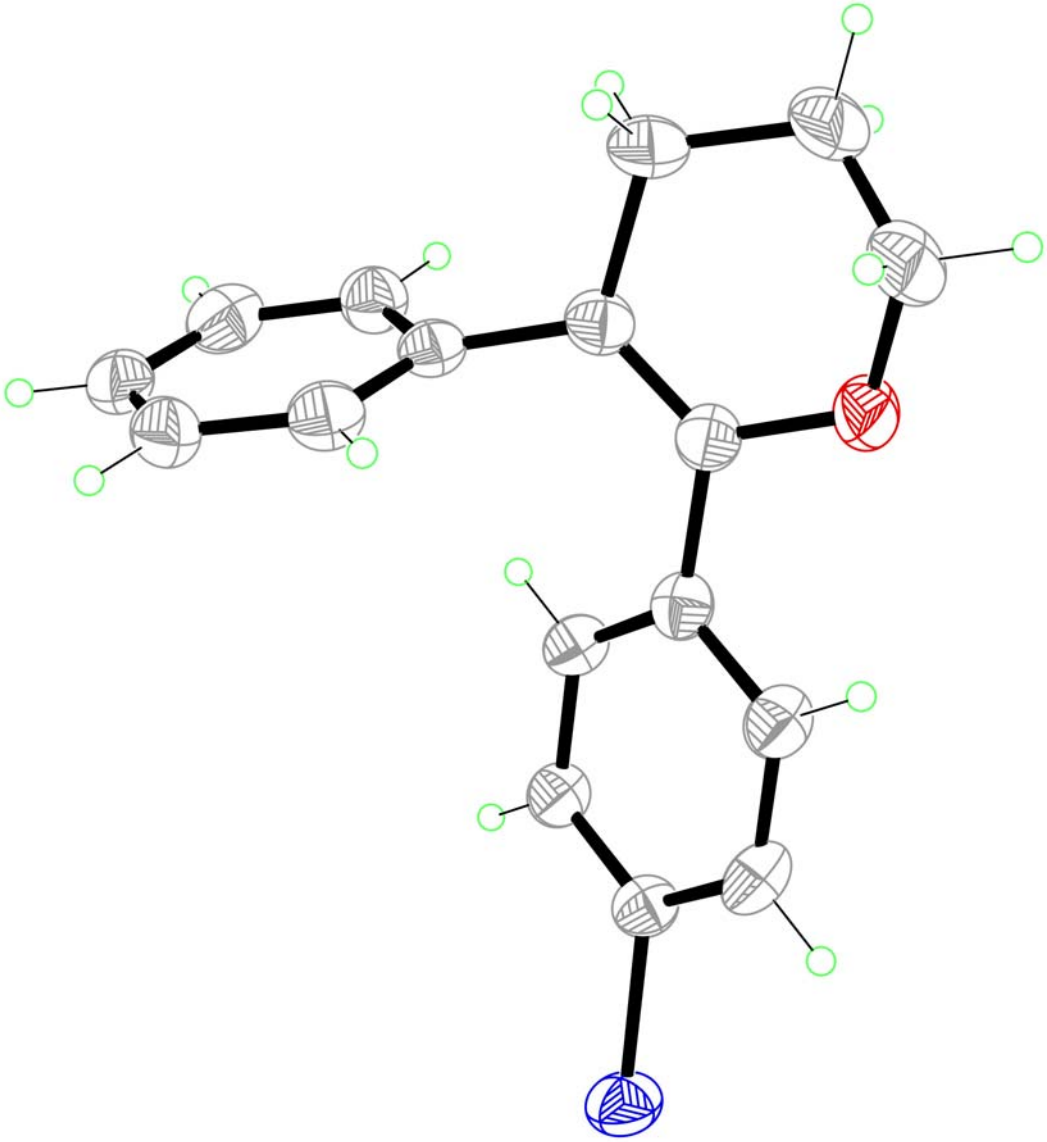
GC-MS: m/z calcd for $C_{17}H_{15}BrO$: 314; found: 314.

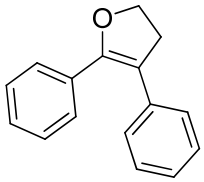




^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

X-ray crystal structure analysis of compound : Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in n-hexane. Formula: $C_{17}H_{15}BrO$, M = 315.20, yellow prism, 0.2 × 0.3 × 0.5 mm, a = 5.7276(19), b = 18.038(7), c = 13.687(5) Å, α = 90.00°, β = 100.05(3) °, γ = 90.00° , V = 1392.4(9) Å^3, ρ_{calc} = 1.504 gcm^{-3}, μ = 2.941 mm^{-1}, Z = 4, Monoclinic, space group $P21/c$, λ = 0.71073 Å, T = 295 ± 2K. Data completeness = 0.999, Theta (max) = 25.500, R (reflections) = 0.0636(1682), wR2 (reflections) = 0.1390(2542).

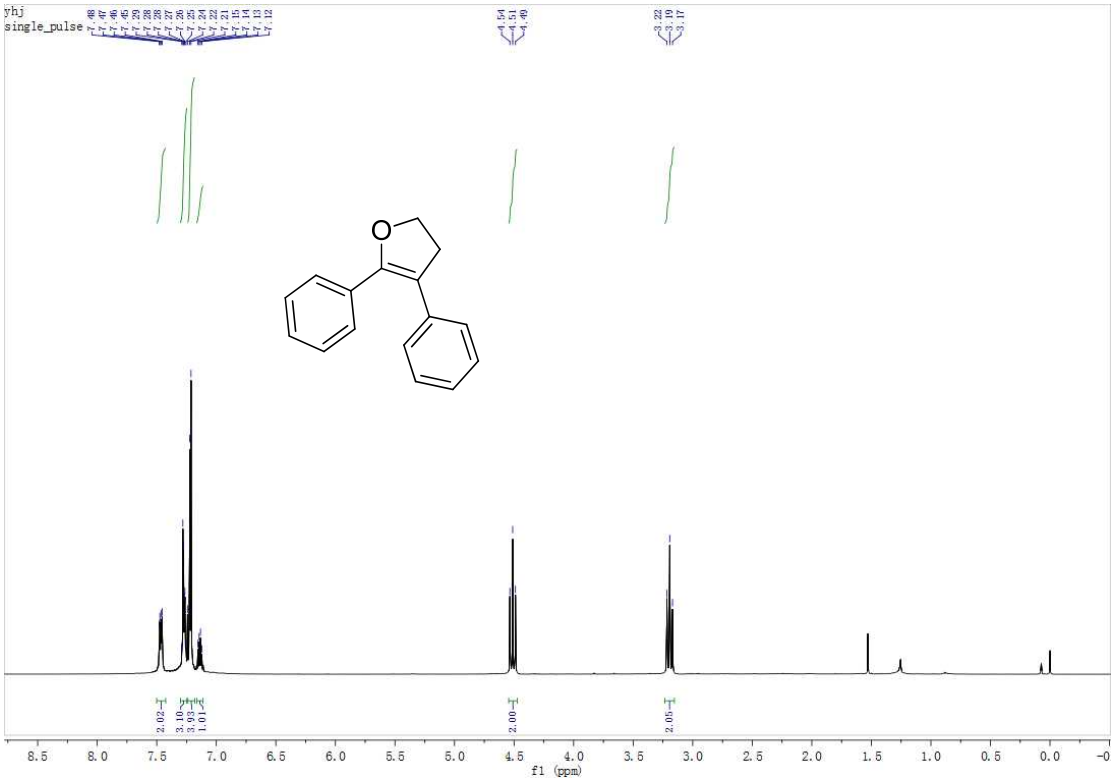


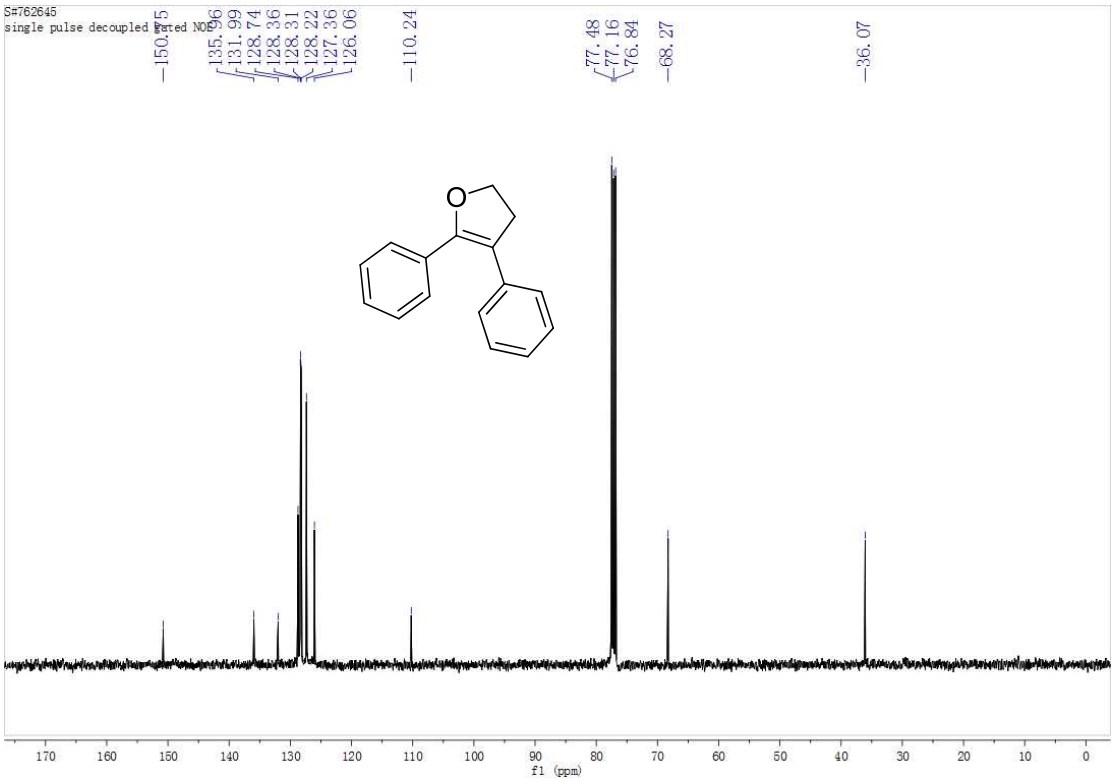


4,5-diphenyl-2,3-dihydrofuran 5aa: yellow liquid, yield: 62%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (dd, J = 6.7, 3.0 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.22 (d, J = 4.4 Hz, 4H), 7.14 (dd, J = 8.8, 4.4 Hz, 1H), 4.51 (t, J = 9.4 Hz, 2H), 3.19 (t, J = 9.4 Hz, 2H).

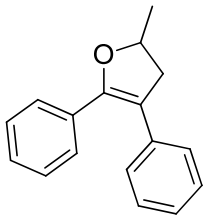
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.75, 135.96, 131.99, 128.74, 128.36, 128.31, 128.22, 127.36, 126.06, 110.24, 68.27, 36.07.

GC-MS: m/z calcd for $C_{16}H_{14}O$: 222; found: 222.





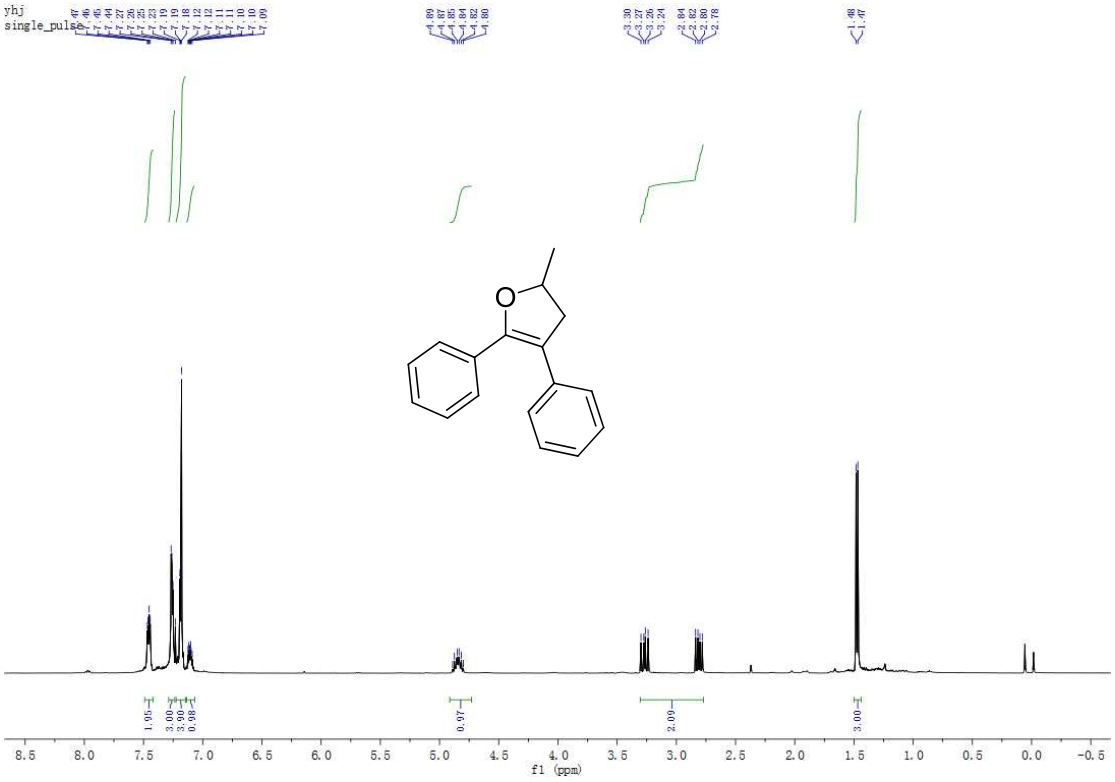
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

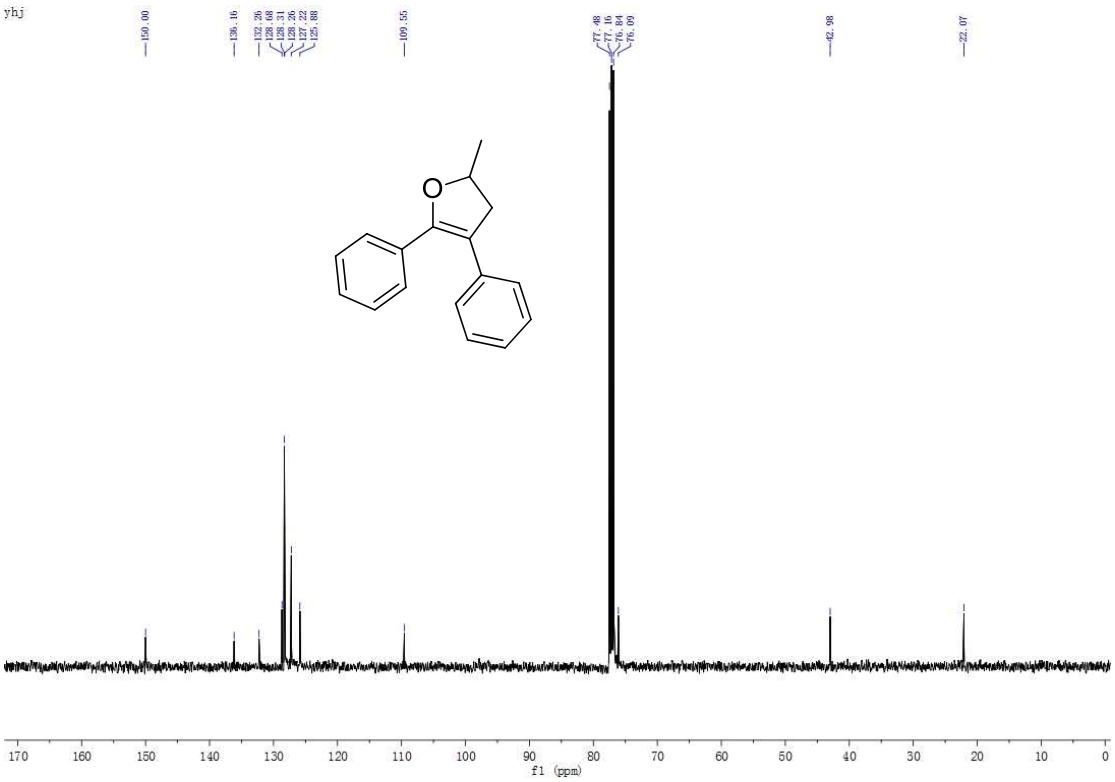


2-methyl-4,5-diphenyl-2,3-dihydrofuran 5ab: yellow liquid, yield: 57%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.46 (dd, J = 6.7, 3.0 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.22 – 7.15 (m, 4H), 7.14 – 7.07 (m, 1H), 4.91 – 4.73 (m, 1H), 3.04 (ddd, J = 22.6, 14.6, 8.8 Hz, 2H), 1.47 (d, J = 6.2 Hz, 3H).

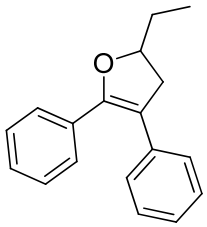
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.00, 136.16, 132.26, 128.68, 128.31 (×2C), 128.26, 127.22, 125.88, 109.55, 76.09, 42.98, 22.07.

GC-MS: m/z calcd for $C_{17}H_{16}O$: 236; found: 236.





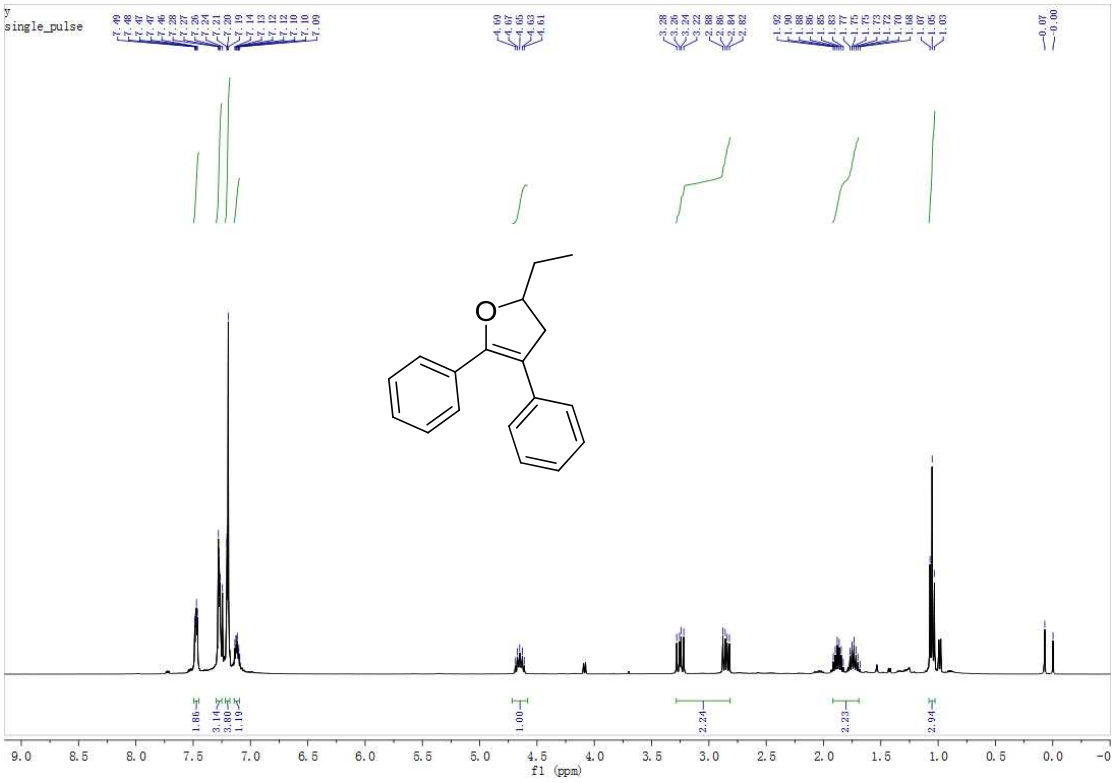
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

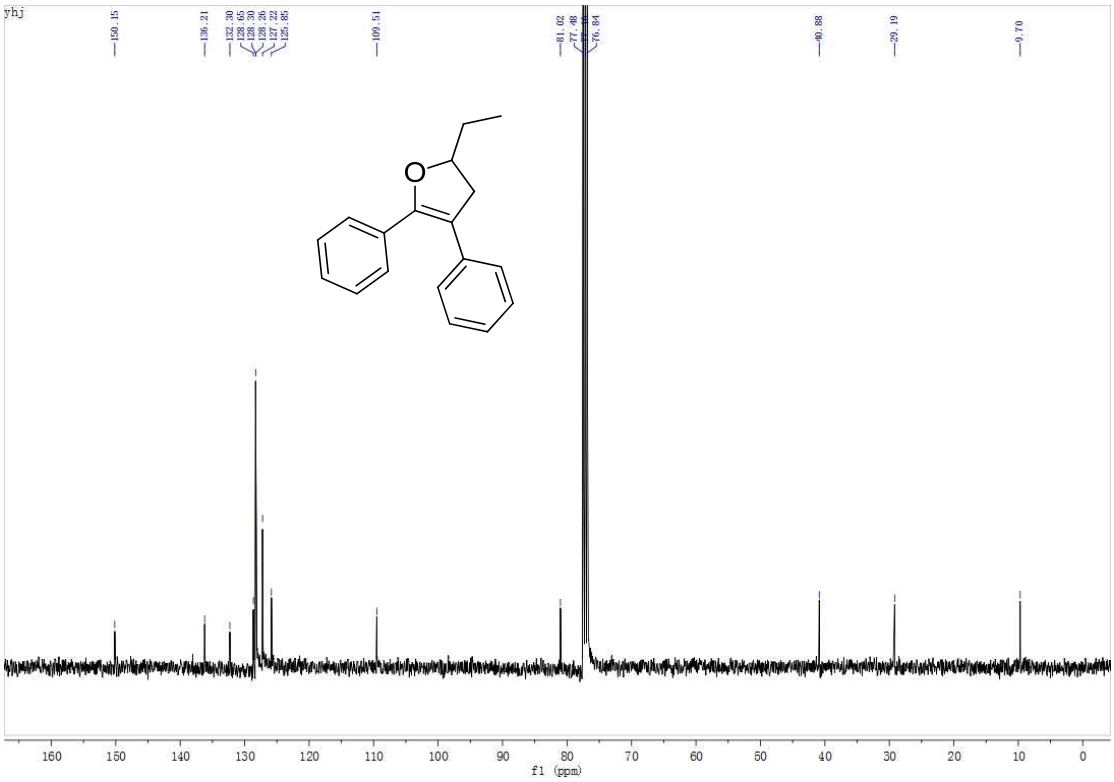


2-ethyl-4,5-diphenyl-2,3-dihydrofuran 5ac: yellow liquid, yield: 78%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.50 – 7.45 (m, 2H), 7.30 – 7.25 (m, 3H), 7.22 – 7.18 (m, 4H), 7.14 – 7.10 (m, 1H), 4.72 – 4.58 (m, 1H), 3.05 (ddd, J = 22.7, 14.7, 8.9 Hz, 2H), 1.80 (ddt, J = 20.9, 13.7, 6.6 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.15, 136.21, 132.30, 128.65, 128.30 (×2C), 128.26, 127.22, 125.85, 109.51, 81.02, 40.88, 29.19, 9.70.

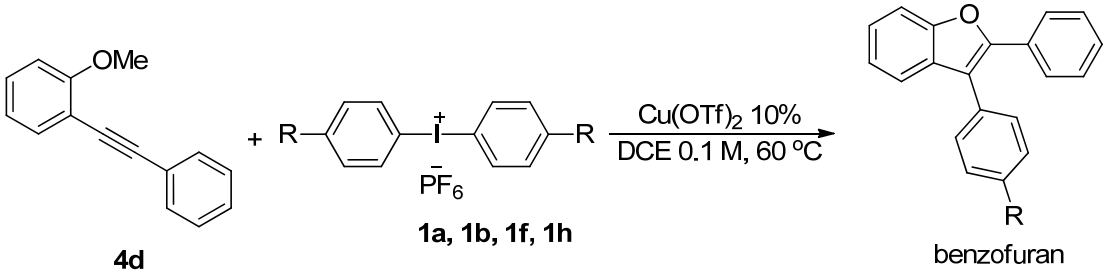
GC-MS: m/z calcd for $C_{18}H_{18}O$: 250; found: 250.



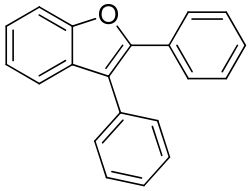


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

Experimental Section for products 5ad, 5bd, 5fd and 5hd



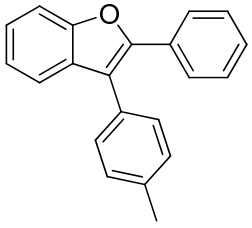
A sealed tube was charged with the mixture of diaryliodonium salt **1** (0.36 mmol) and $Cu(OTf)_2$ (0.03 mmol, 10.8 mg). The tube was evacuated and recharged with N_2 for 3 times. After 1-methoxy-2-(phenylethynyl)benzene **4d** (0.3 mmol) and dichloroethane (3 mL) were added, the tube was sealed and the mixture was allowed to stir at 60 °C for 12h. After completion, the mixture was cooled to room temperature, then saturated K_2CO_3 aq. (5 mL) was added and the mixture was extracted with EA (5 mL × 3), dried by anhydrous Na_2SO_4. Purification of crude product was conducted by filtered over a short silica pad followed by flash column chromatography on silica gel using Hexane as eluent.



2,3-diphenylbenzofuran 5ad[8]: white solid, yield: 37%.^{1}H NMR (400 MHz, DMSO-D6) δ 7.65 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 7.4 Hz, 2H), 7.50 – 7.40 (m, 6H), 7.38 – 7.30 (m, 4H), 7.25 (t, J = 7.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D6) δ 153.87, 150.43, 132.41, 130.37, 129.96, 129.96, 129.76, 129.39, 129.30, 128.55, 127.16, 125.74, 123.99, 120.30, 117.72, 111.79.

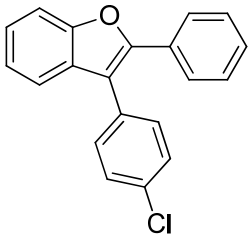
GC-MS: m/z calcd for $C_{20}H_{14}O$: 270; found: 270.



3-phenyl-2-(p-tolyl)benzofuran 5bd[8]: white solid, yield: 40%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.67 (dd, J = 7.4, 1.1 Hz, 2H), 7.53 (d, J = 8.2 Hz, 1H), 7.48 (d,

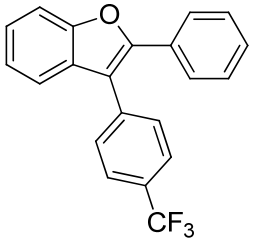
J = 7.7 Hz, 1H), 7.38 (d, J = 7.9 Hz, 2H), 7.32 – 7.20 (m, 7H), 2.41 (s, 3H).
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 154.12, 150.48, 137.46, 130.94, 130.27, 129.88, 129.83, 129.72, 128.52, 128.37, 127.11, 124.74, 122.97, 120.21, 117.60, 111.20, 21.48.

GC-MS: m/z calcd for $C_{21}H_{17}O$: 284; found: 284.



3-(4-chlorophenyl)-2-phenylbenzofuran 5fd[8]: white solid, yield: 27%. ^{1}H NMR (400 MHz, DMSO-D6) δ 7.66 (d, J = 8.2 Hz, 1H), 7.57 – 7.51 (m, 4H), 7.48 – 7.34 (m, 7H), 7.27 (t, J = 7.5 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-D6) δ 153.89, 150.78, 133.20, 131.81, 131.33, 130.12, 129.85, 129.61, 129.57, 129.41, 127.31, 125.86, 124.09, 120.20, 116.49, 111.86.

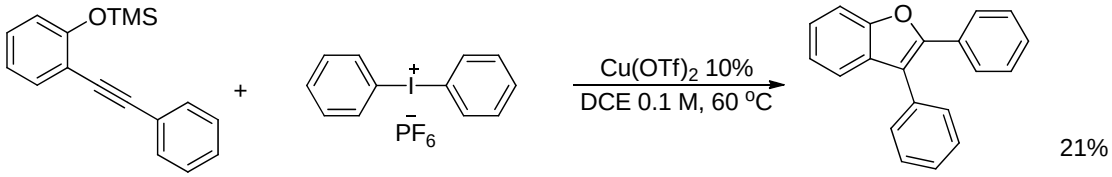
GC-MS: m/z calcd for $C_{20}H_{13}ClO$: 304; found: 304.



2-phenyl-3-(4-(trifluoromethyl)phenyl)benzofuran 5hd[8]: white solid, yield: 23%. ^{1}H NMR (400 MHz, DMSO-D6) δ 7.83 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.0 Hz, 3H), 7.53 (dd, J = 7.4, 1.6 Hz, 2H), 7.47 (d, J = 7.7 Hz, 1H), 7.41 – 7.34 (m, 4H), 7.28 (t, J = 7.5 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-D6) δ 153.97, 151.33, 136.92, 130.80, 129.93, 129.78, 129.47, 129.29, 128.79 (q, J = 32.3 Hz), 127.53, 126.60 (q, J = 4.0 Hz), 125.98, 124.77 (q, J = 272.7 Hz), 124.21, 120.17, 116.32, 111.94.

GC-MS: m/z calcd for $C_{21}H_{13}F_3O$: 338; found: 338

Experimental Section between TMS-protected phenol 4f and diaryliodonium salt

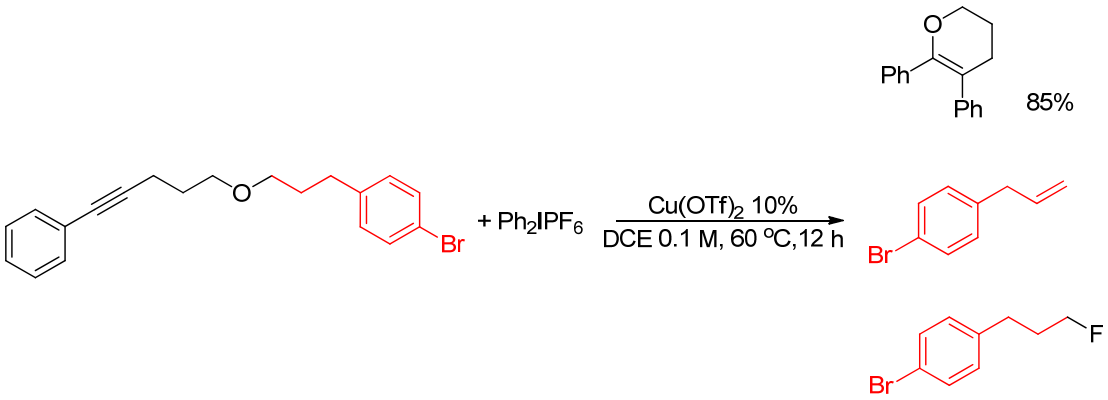


4f **1a** **5ad**

A sealed tube was charged with the mixture of diaryliodonium salt **1a** (0.36 mmol) and $Cu(OTf)_2$ (0.03 mmol, 10.8 mg). The tube was evacuated and recharged with N_2 for 3 times. After Trimethyl(2-(phenylethynyl)phenoxy)silane **4f** (0.3 mmol) and dichloroethane (3 mL) were added, the tube was sealed and the mixture was allowed to stir at 60 °C for 12h. After completion, the mixture was cooled to room temperature, then saturated K_2CO_3 aq. (5 mL) was added and the mixture was extracted with EA (5 mL × 3), dried by anhydrous Na_2SO_4. Purification of crude product was conducted by filtered over a short silica pad followed by flash column chromatography on silica gel using Hexane as eluent.

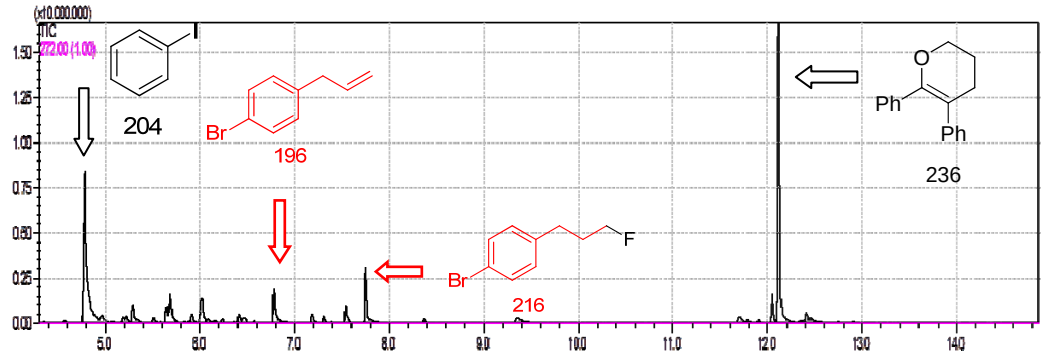
Under the standard conditions, the desired product **5ad** was obtained in 21% yield. We found that the TMS-protected phenol is not stable, a few side-reactions occurred and gave dimmers of the major product so that the yield was low.

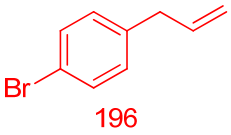
Mechanistic experiment



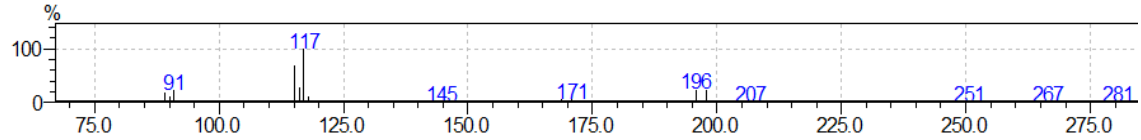
A sealed tube was charged with the mixture of diaryliodonium salt (0.24 mmol) and $Cu(OTf)_2$ (0.02 mmol, 7.2 mg). The tube was evacuated and recharged with N_2 for 3 times. After appropriate Phenyl Alkyne (0.2 mmol) and dichloroethane (2 mL) were added, the tube was sealed and the mixture was allowed to stir at 60 °C for 12 h. After completion, the mixture was cooled to room temperature, then saturated K_2CO_3 aq. (5 mL) was added and the mixture was extracted with EA (5 mL × 3), dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (PE/EA/TEA: 200/4/1) provided the corresponding product as a yellow liquid.

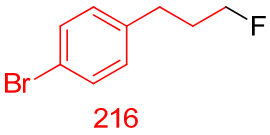
In the preparation of 5,6-diphenyl-3,4-dihydro-2H-pyran, compounds 1-allyl-4-bromobenzene and 1-bromo-4-(3-fluoropropyl)benzene were detected in the reaction mixture by GC-MS.


(x10,000,000)
TIC
272.00 (1.00)
204
Br
196
Br
F
216
O
Ph
Ph
236

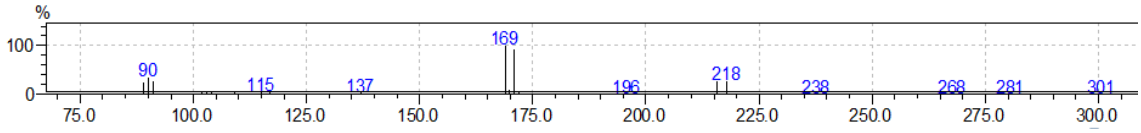

Br

196

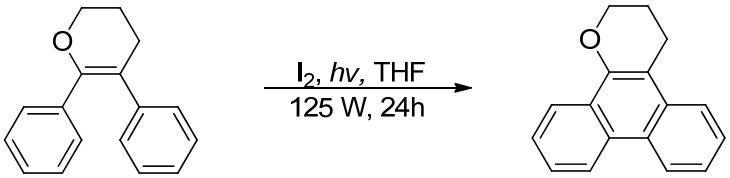

%
100
0
91
117
145
171
196
207
251
267
281
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0


Br
F

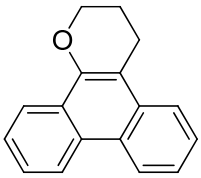
216


%
100
0
90
115
137
169
196
218
238
268
281
301
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0

Procedure for the preparation of phenanthrene derivative [9].



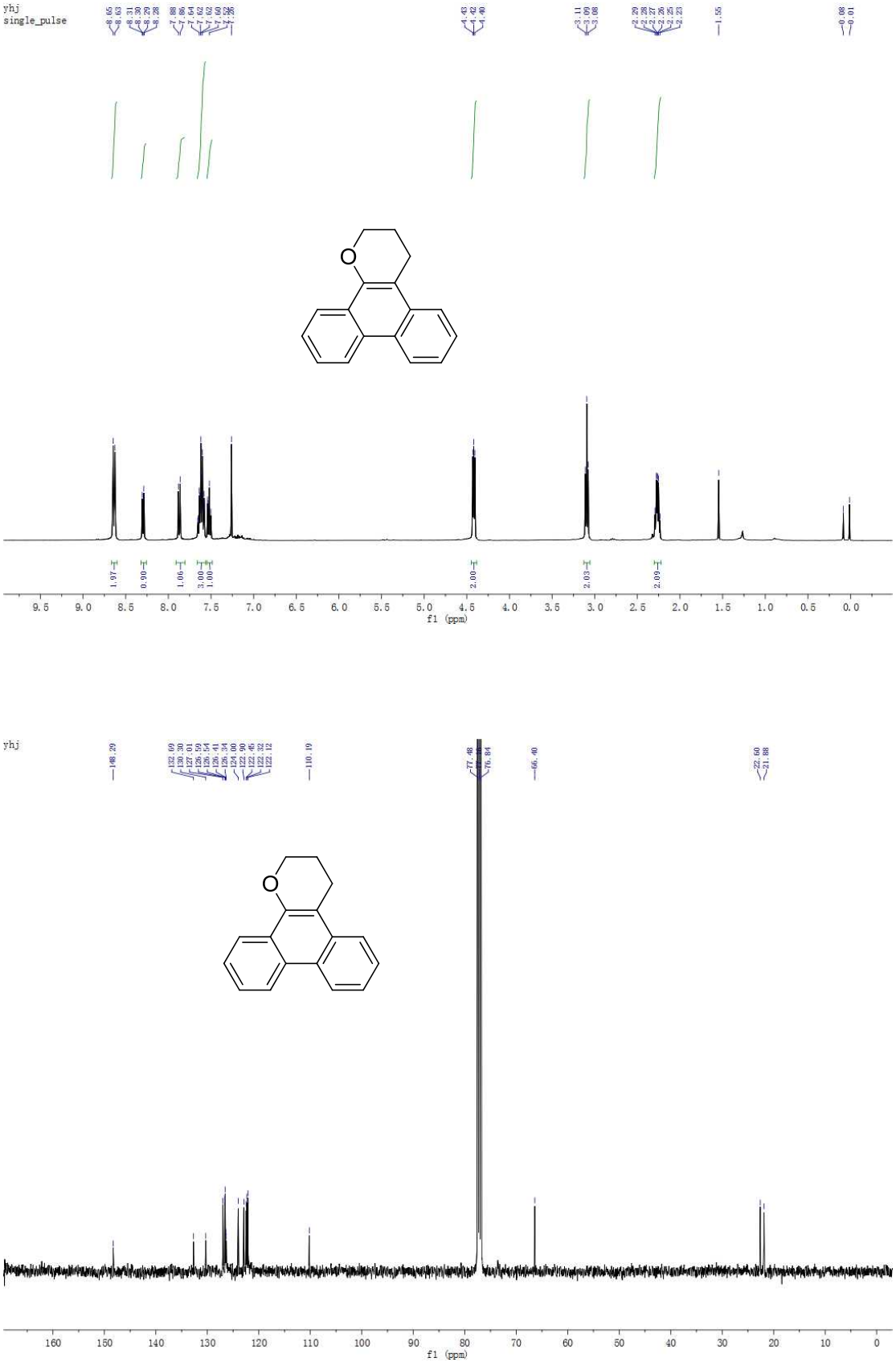
A solution of 5,6-diphenyl-3,4-dihydro-2H-pyran (47.2 mg, 0.2 mmol) and iodine (56 mg, 0.22 mmol) in tetrahydrofuran (0.5 mL) was irradiated in a standard immersion well photoreactor with 125-W high pressure mercury vapor lamp for 24 h. The reaction mixture was then treated with aqueous sodium thiosulfate, water, brine and dried over anhydrous sodium sulfate. The concentrated mixture was purified by column chromatograph to afford phenanthrene as yellow liquid.



3,4-dihydro-2H-dibenzo[f,h]chromene 6: yellow liquid, yield: 63%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.64 (d, J = 7.8 Hz, 2H), 8.30 (dd, J = 7.8, 1.6 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.66 – 7.56 (m, 3H), 7.52 (dd, J = 11.1, 4.1 Hz, 1H), 4.45 – 4.38 (m, 2H), 3.09 (t, J = 6.6 Hz, 2H), 2.30 – 2.22 (m, 2H).

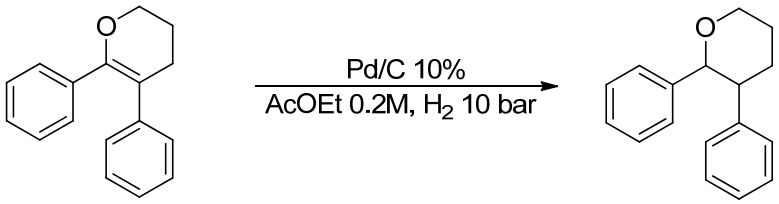
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 148.29, 132.69, 130.30, 127.01, 126.59, 126.54, 126.41, 126.34, 124.00, 122.90, 122.45, 122.32, 122.12, 110.19, 66.40, 22.60, 21.88.

GC-MS: m/z calcd for $C_{17}H_{14}O$: 234; found: 234.

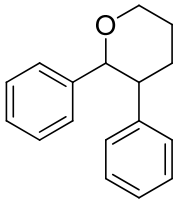


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

Procedure for the preparation of 2,3-diphenyltetrahydro-2H-pyran[10].



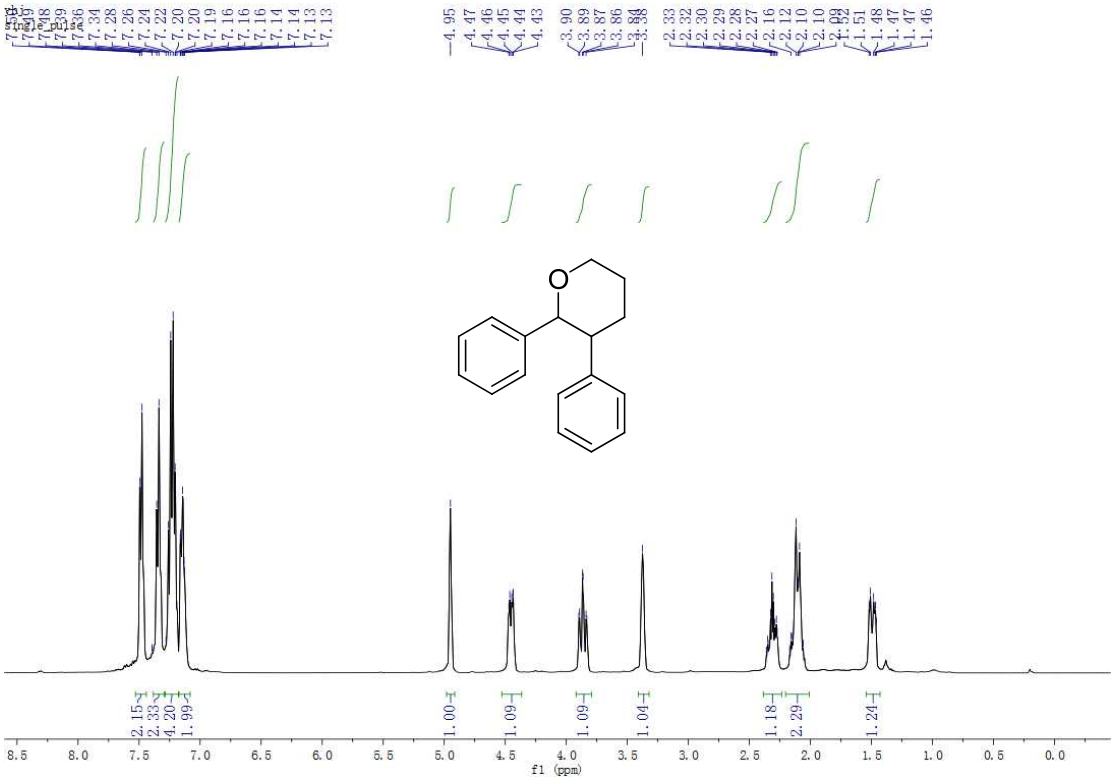
A high pressure reactor was filled with a ethyl acetate solution of 5,6-diphenyl-3,4-dihydro-2H-pyran (0.4 mmol) and palladium/activated carbon powder (0.04 mmol), then purged with hydrogen, and 10 bar of hydrogen was introduced. After stirring at room temperature for 12 h, the reaction was diluted with AcOEt, and filtered to remove Pd/C. The organic solvent was removed and then the residue was purified by flash chromatography on silica (10% EtOAc/ PE) to give 2,3-diphenyltetrahydro-2H-pyran as a white solid.

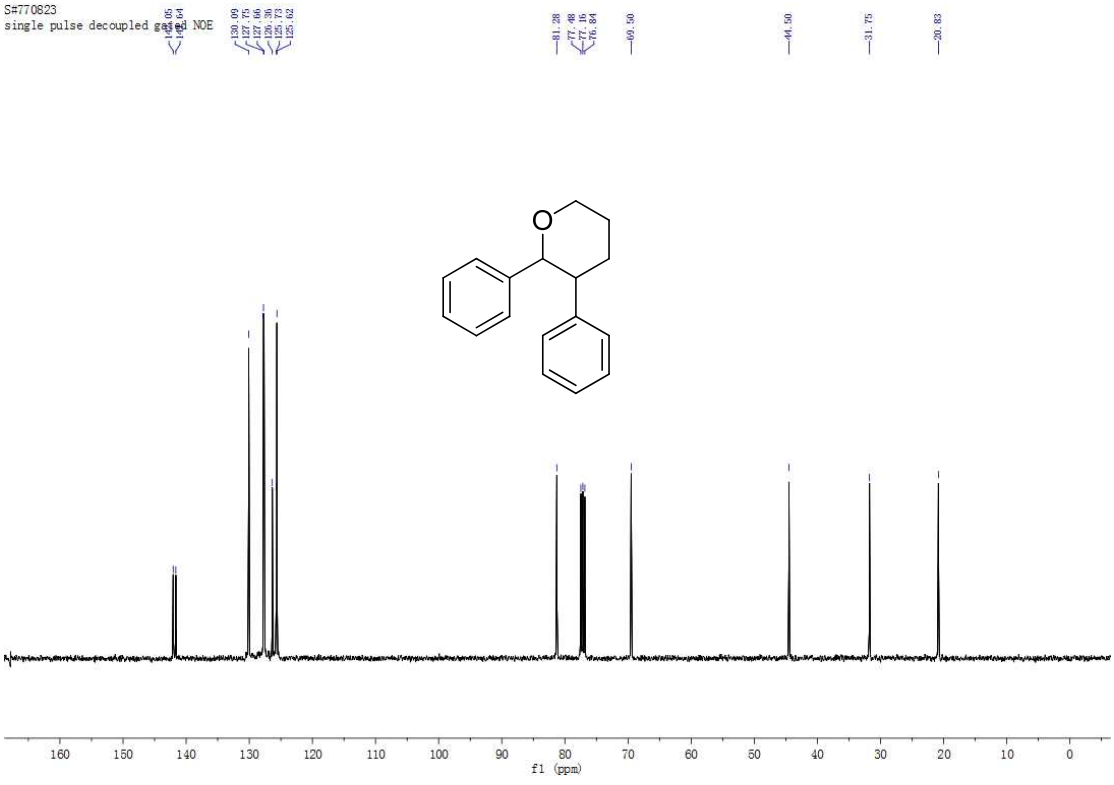


2,3-diphenyltetrahydro-2H-pyran 7: white solid, yield: 85%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.53 – 7.44 (m, 2H), 7.35 (d, J = 7.3 Hz, 2H), 7.29 – 7.18 (m, 4H), 7.17 – 7.08 (m, 2H), 4.95 (s, 1H), 4.53 – 4.37 (m, 1H), 3.92 – 3.79 (m, 1H), 3.38 (s, 1H), 2.39 – 2.23 (m, 1H), 2.20 – 2.01 (m, 2H), 1.54 – 1.43 (m, 1H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 142.05, 141.64, 130.09, 127.75, 127.66, 126.36, 125.73, 125.62, 81.28, 69.50, 44.50, 31.75, 20.83.

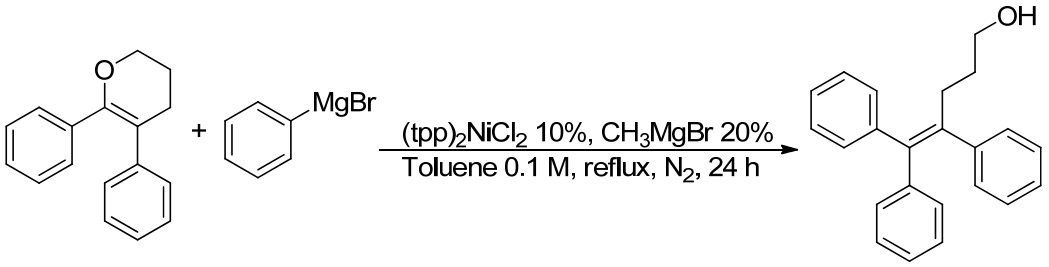
GC-MS: m/z calcd for $C_{17}H_{18}O$: 238; found: 238.



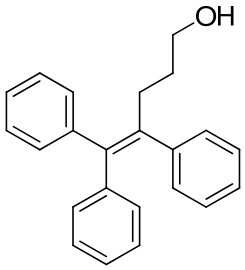


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

Procedure for the preparation of 4,5,5-triphenylpent-4-en-1-ol[11].



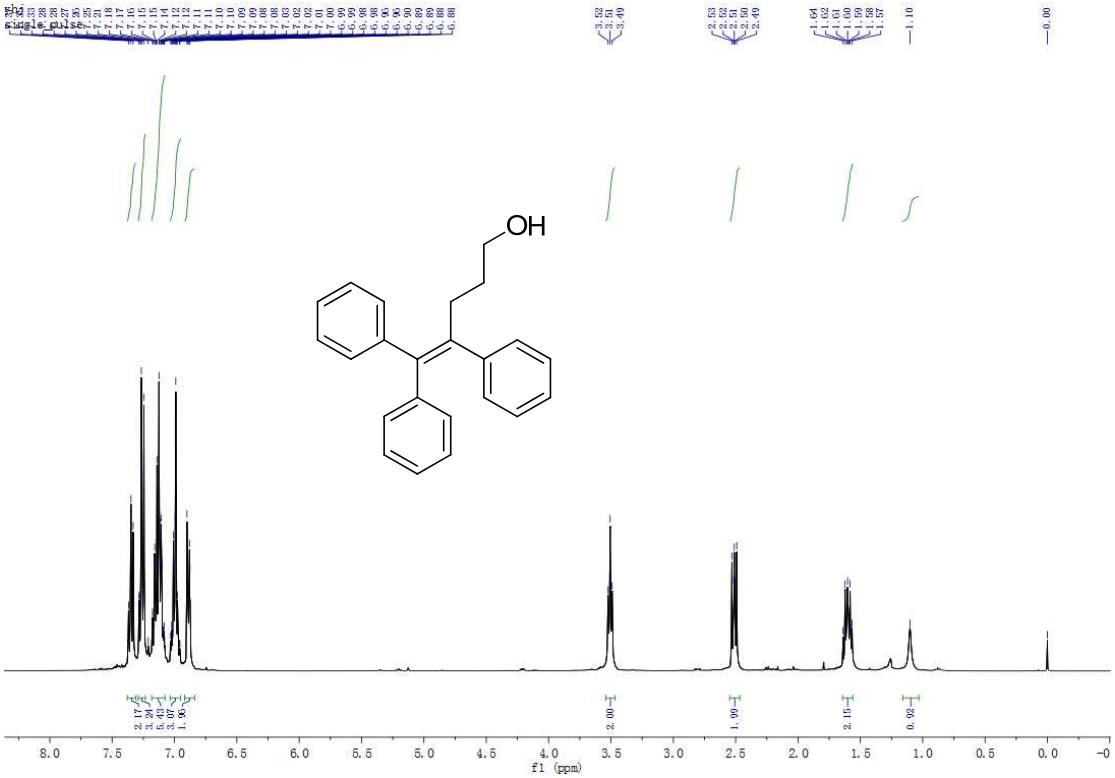
A ethereal solution of methylmagnesium bromide (0.04mmol) was added to a stirring suspension of 0.02 mmol of catalyst $(tpp)_2NiCl_2$ in 2 mL of dry toluene under N_2 and the stirring continued at room temperature for 15 min. At the end of this catalyst reduction the phenylmagnesium bromide 0.2 mmol was added and most of the ether removed by distillation and replaced by 1 mL of dry toluene. The oxygen-containing heterocycle, 0.2 mmol , was added and the solution refluxed under N_2 for 24 h. The cooled reaction mixture was washed with a saturated ammonium chloride solution and extracted with ether. The residue was purified by column chromatograph, providing white solid.

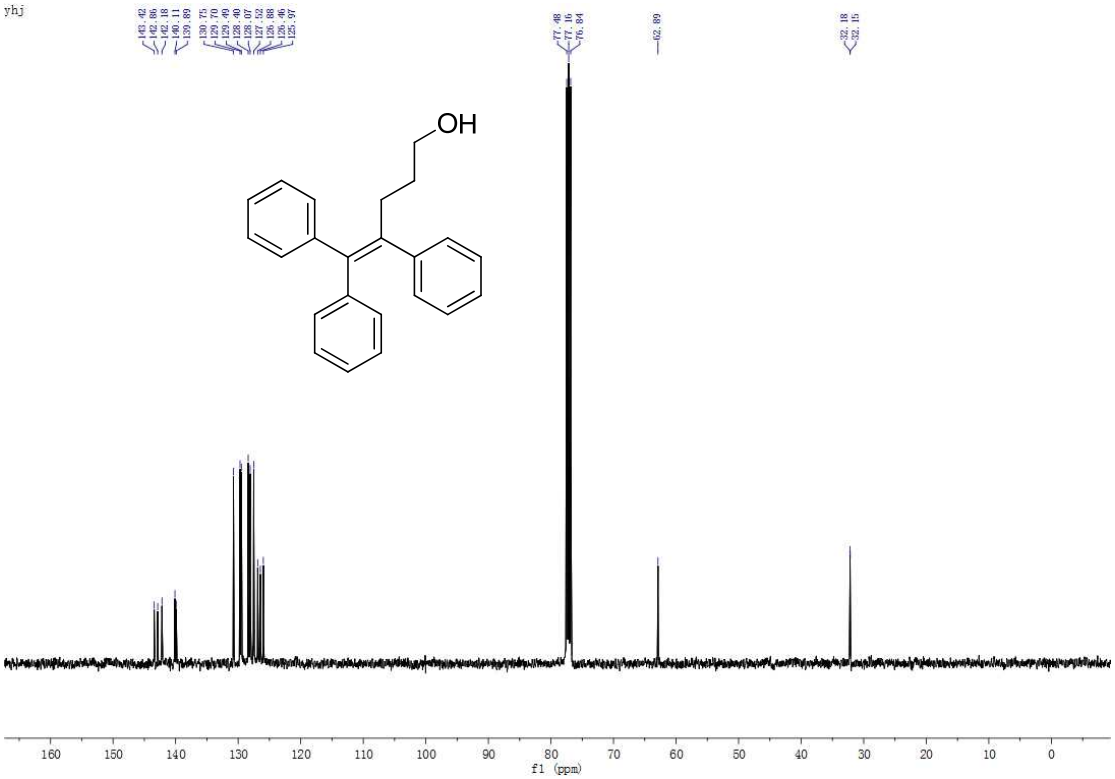


4,5,5-triphenylpent-4-en-1-ol 8: white solid, mp = 131.9 – 133.1 ^{o}C, yield: 76%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.35 (t, J = 7.3 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.18 – 7.08 (m, 5H), 7.04 – 6.95 (m, 3H), 6.92 – 6.84 (m, 2H), 3.51 (t, J = 6.6 Hz, 2H), 2.55 – 2.47 (m, 2H), 1.64 – 1.56 (m, 2H), 1.10 (s, 1H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 143.42, 142.86, 142.18, 140.11, 139.89, 130.75, 129.70, 129.49, 128.40, 128.07, 127.52, 126.88, 126.46, 125.97, 62.89, 32.18, 32.15.

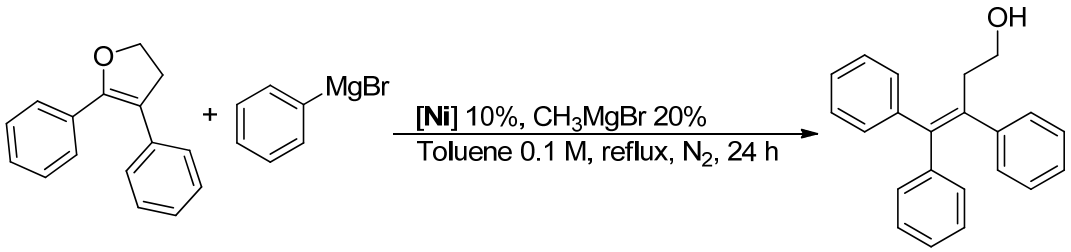
GC-MS: m/z calcd for $C_{23}H_{22}O$: 314; found: 314





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

Procedure for the ring opening Grignad coupling on the dihydrofurans.



$(tpp)_2NiCl_2$ 10% **NR**
$(dppp)_2NiCl_2$ 10% **NR**

A ethereal solution of methylmagnesium bromide (0.04mmol) was added to a stirring suspension of 0.02 mmol of catalyst $(tpp)_2NiCl_2$ or $(dppp)_2NiCl_2$ in 2 mL of dry toluene under N_2 and the stirring continued at room temperature for 15 min. At the end of this catalyst reduction the phenylmagnesium bromide 0.2 mmol was added and most of the ether removed by distillation and replaced by 1 mL of dry toluene. The oxygen-containing heterocycle, 0.2 mmol , was added and the solution refluxed under N_2 for 24 h. The cooled reaction mixture was washed with a saturated ammonium chloride solution and extracted with ether. The reaction was detected by TLC and GC-MS. No desired product was formed and 50% raw material was recovered.

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