

Cu-Catalyzed Intramolecular Hydroarylation of Alkynes

Yun-Long Wang, Wen-Man Zhang, Jian-Jun Dai, Yi-Si Feng,* Hua-Jian Xu*

*School of Chemistry and Chemical Engineering, School of Medical Engineering, Hefei
University of Technology, Hefei 230009, P. R. China
E-mail: hjxu@hfut.edu.cn*

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I. General Information

a. Materials:

All reagents were used without further purification as obtained from commercial suppliers. Cu(OTf)₂ was purchased from J&K, and used without further purification. The anhydrous DCE was purchased from J&K. All others solvents were purchased from commercial sources without further purification.

b. Analytical Methods

¹H NMR spectra were acquired on a Bruker 400 MHz spectrometer. Chemical shifts of ¹⁹F NMR spectra were recorded with ¹H-coupling on a Bruker 376 MHz spectrometer. ¹³C-NMR spectra were recorded with ¹H-decoupling on a Bruker 100 MHz spectrometer. CDCl₃ was used as the solvent. Chemical shifts (δ) are quoted in ppm. Coupling constants (*J*) are quoted in Hz. Multiplicities are expressed by: s = singlet, d = doublet, t = triplet, q = quartet, m =

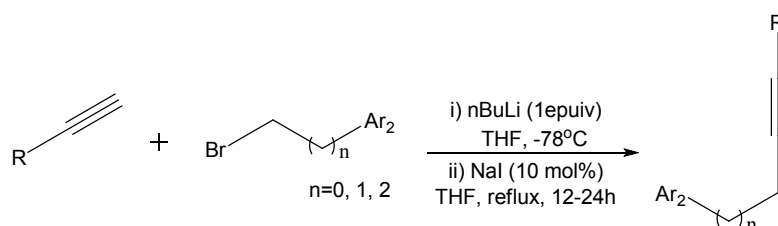
multiplet, br = broad. High-resolution mass experiments (EI) were recorded on a BRUKER VPEXII spectrometer. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. The products were accomplished by flash column chromatographic purification on silica gel (200-400 mesh).

II. Preparation of Substrates

1a-1f, 1m, 1p, 1q, 1t-1v, 1x was prepared according to this literature¹.

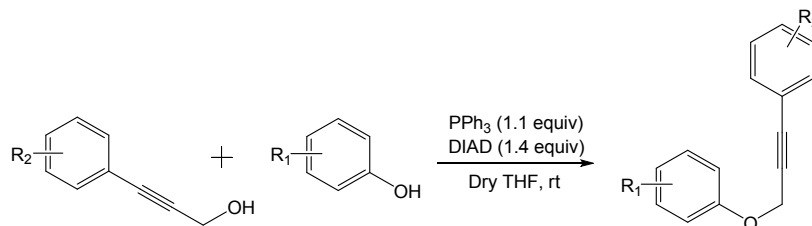
1g-1l, 1n, 1r, 1s was prepared according to this literature².

1.General Procedure A for the Synthesis of Alkynes¹ (1)



A solution of alkynes (1.0 equiv) in tetrahydrofuran (0.16 M) was cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of *n*-butyllithium (1.0 equiv, 1.6 M in hexanes) was added. The reaction mixture was allowed to warm to room temperature and sodium iodide (0.1 equiv) and the corresponding bromoethylbenzene (1.2 equiv) were added. The mixture was heated to reflux for the specified length of time. The reaction mixture was cooled to room temperature and quenched by addition of ammonium chloride solution. The aqueous layer was separated and extracted with diethyl ether. The combined organics were washed (brine), dried (MgSO_4) and the solvent removed in vacuo. The crude residue was purified by flash chromatography to yield the corresponding alkyne (1).

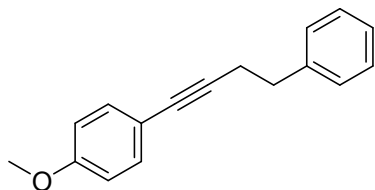
2. General Procedure B for the Synthesis of Alkynes² (1)



To a solution of aryl alkynyl alcohols (1 equiv), triphenylphosphine (1.1 equiv) and aryl phenol (5 mmol) in dry THF at $0\text{ }^{\circ}\text{C}$ was added Di-iso-propyl azodicarboxylate (1.4 equiv). The reaction was stirred at $0\text{ }^{\circ}\text{C}$ and then at room temperature for a further 3 h. The reaction mixture was diluted with diethyl ether, washed (brine) and dried (MgSO_4). The solvent was removed in vacuo and the residue purified by recrystallization from hot ethanol to give Alkynes (1).

3. Substrates Spectra Data

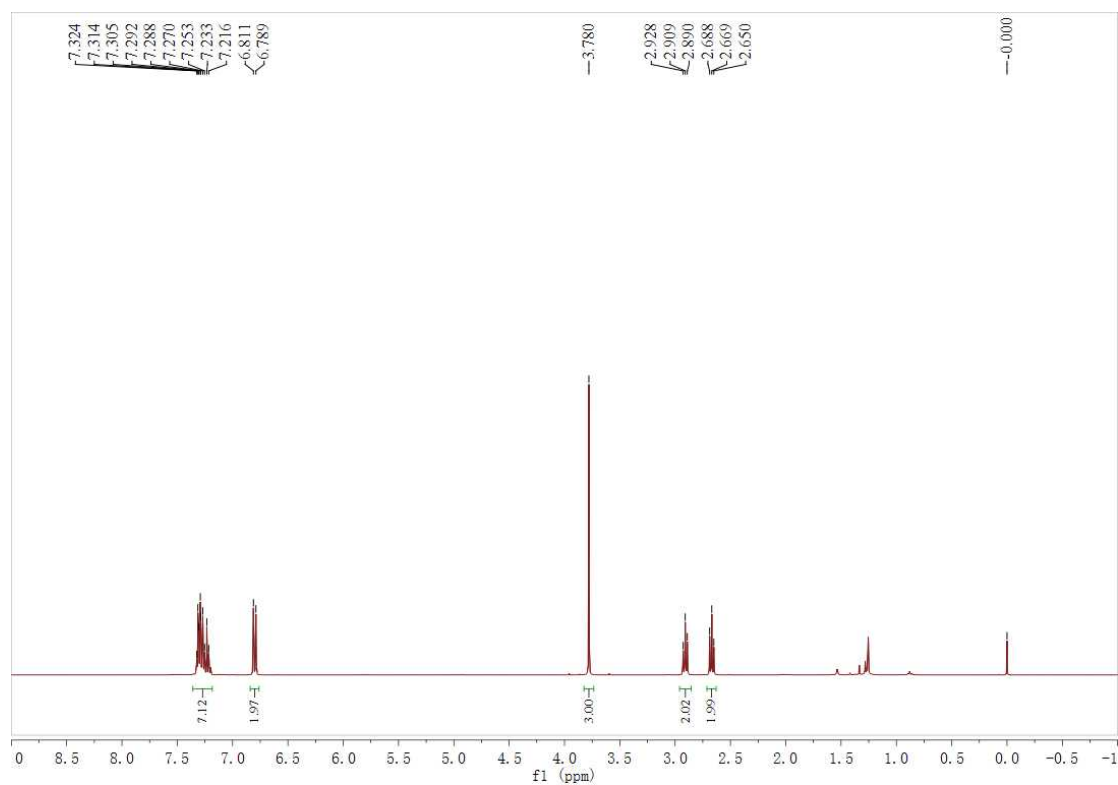
1-methoxy-4-(4-phenylbut-1-yn-1-yl)benzene(I)

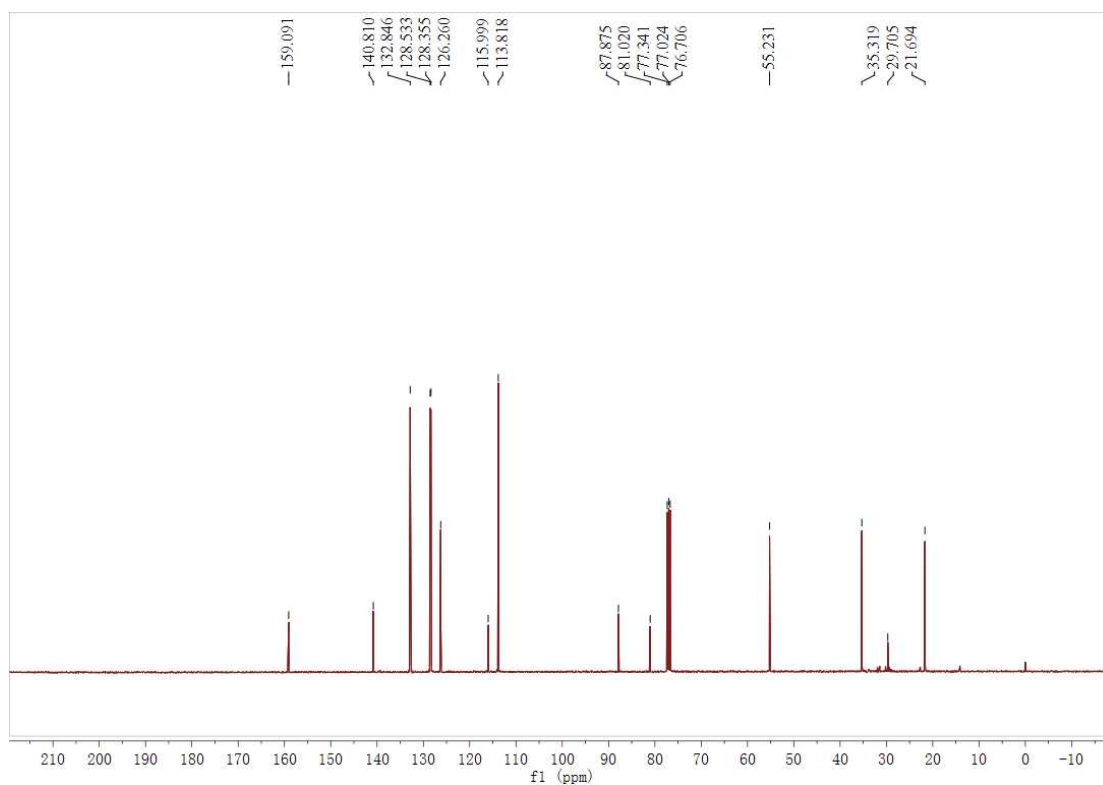


Prepared according to General Procedure A

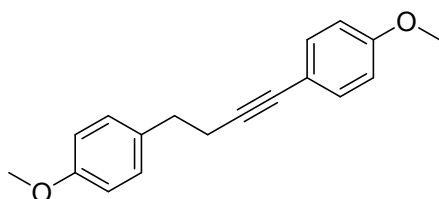
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.18 (m, 7H), 6.80 (d, $J = 8.9$ Hz, 2H), 3.78 (s, 3H), 2.91 (t, $J = 7.6$ Hz, 2H), 2.67 (t, $J = 7.6$ Hz, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.09, 140.81, 132.85, 128.533, 128.355, 126.26, 116.00, 113.82, 87.87, 81.02, 55.23, 35.32, 21.69.





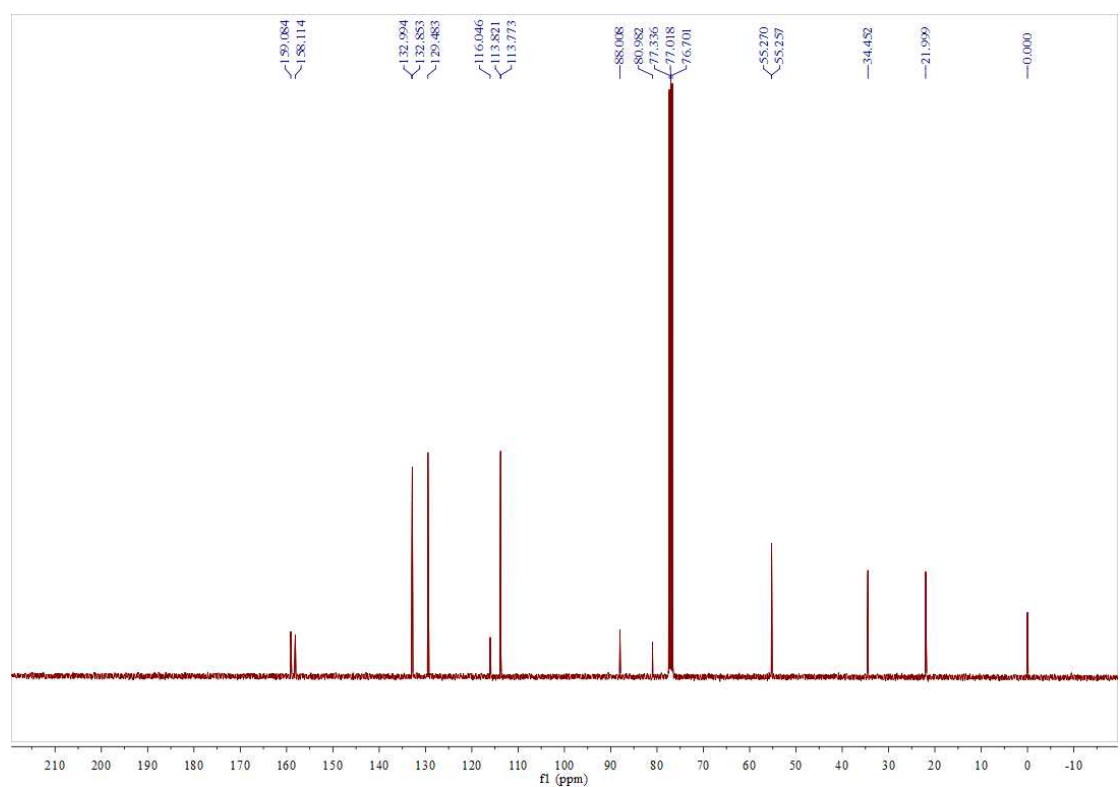
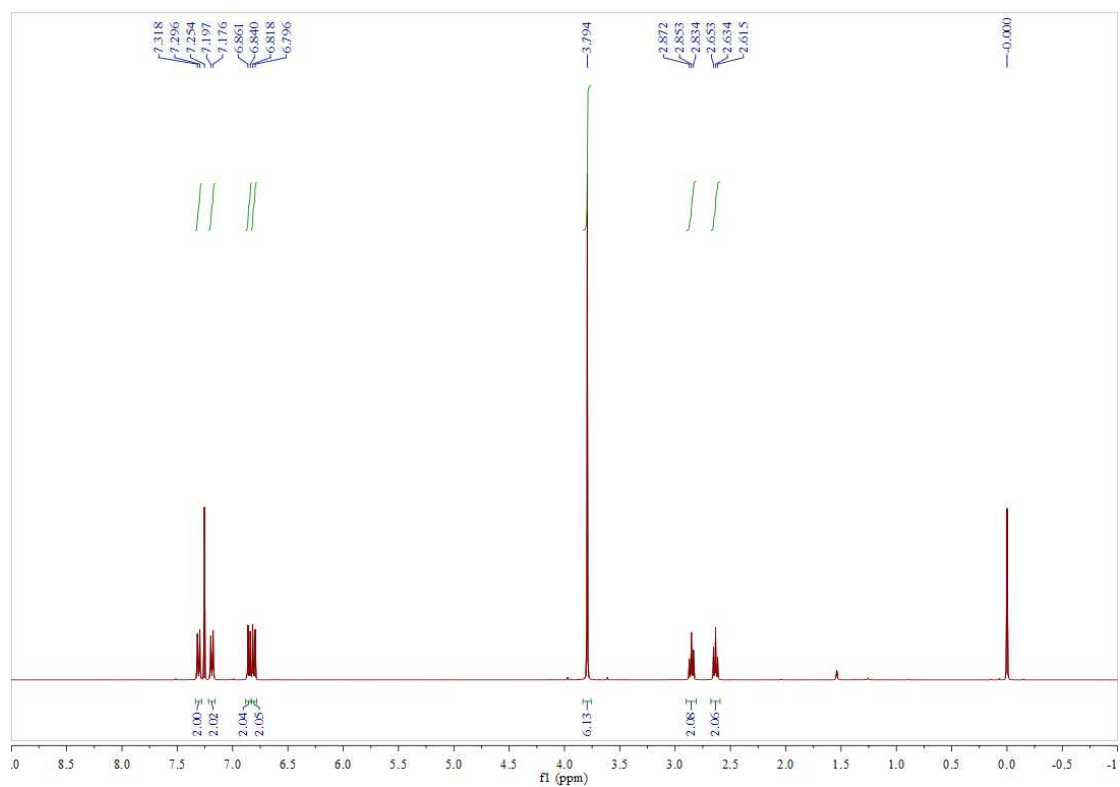
4,4'-(but-1-yne-1,4-diyl)bis(methoxybenzene)(1a)



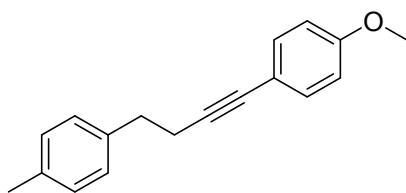
Prepared according to General Procedure A

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31 (d, $J = 8.7$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 3.79 (s, 6H), 2.85 (t, $J = 7.5$ Hz, 2H), 2.63 (t, $J = 7.5$ Hz, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.08, 158.11, 132.99, 132.85, 129.48, 116.05, 113.82, 113.77, 88.01, 80.98, 55.27, 55.25, 34.45, 22.00.



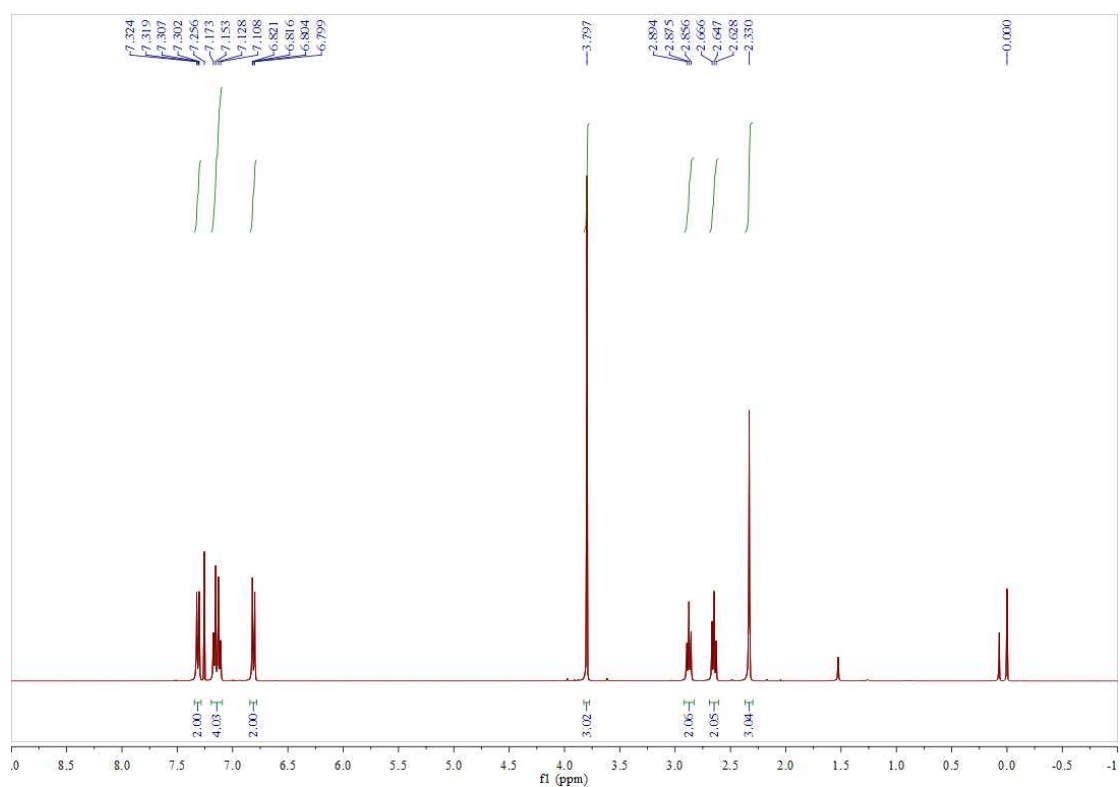
1-methoxy-4-(4-(p-tolyl)but-1-yn-1-yl)benzene(1b)

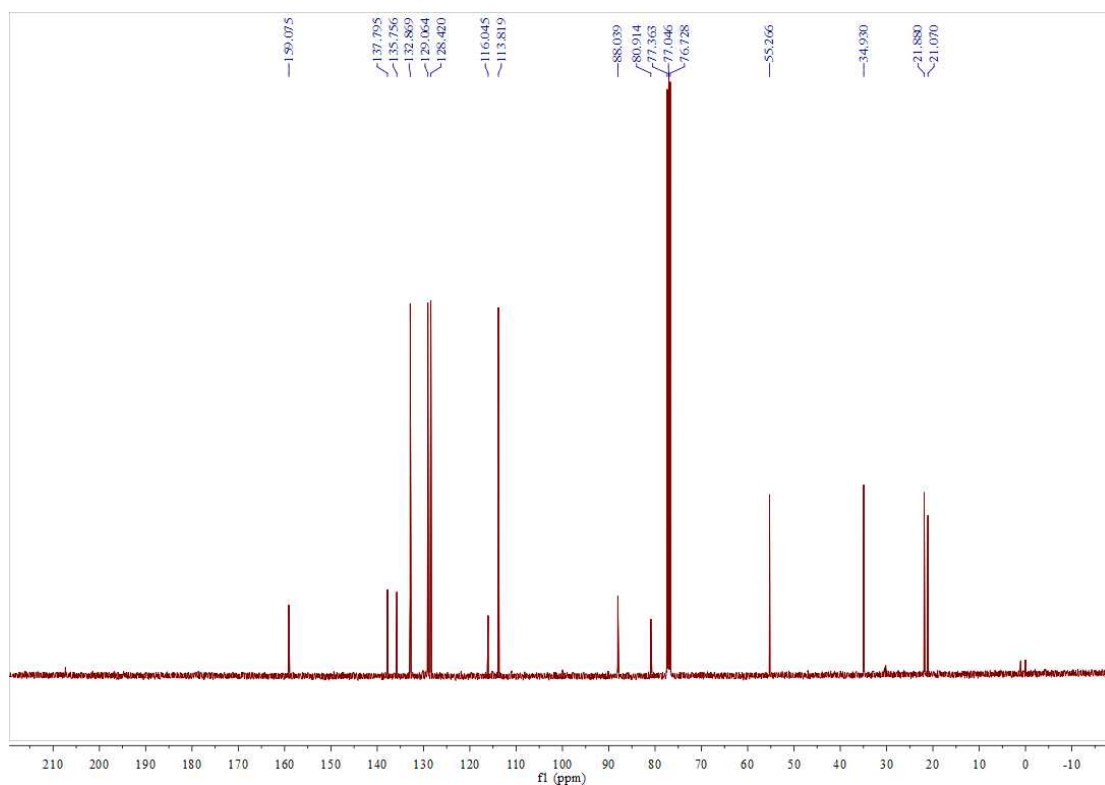


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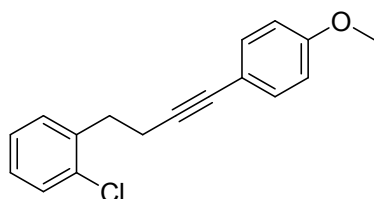
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.28 (m, 2H), 7.14 (dd, $J = 18.1, 8.0$ Hz, 4H), 6.84 – 6.78 (m, 2H), 3.80 (s, 3H), 2.88 (t, $J = 7.6$ Hz, 2H), 2.65 (t, $J = 7.6$ Hz, 2H), 2.33 (s, 3H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.08, 137.80, 135.76, 132.87, 129.06, 128.42, 116.04, 113.82, 88.04, 80.91, 55.27, 34.93, 21.88, 21.07.





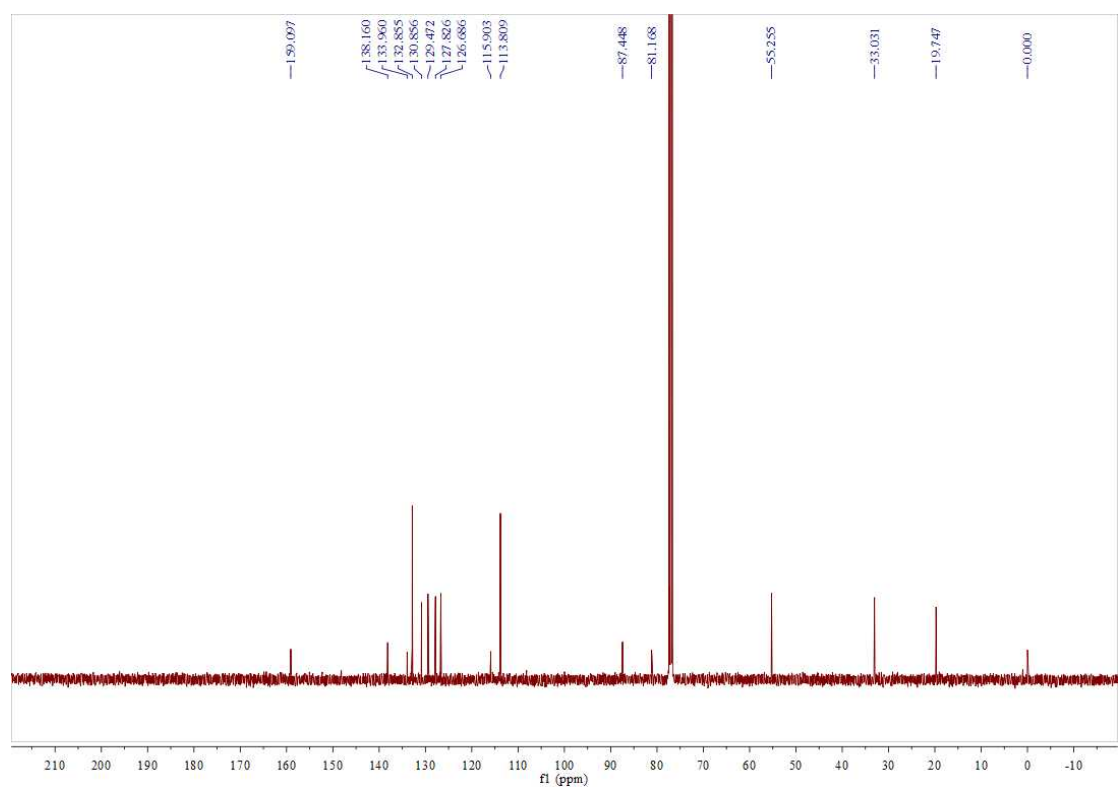
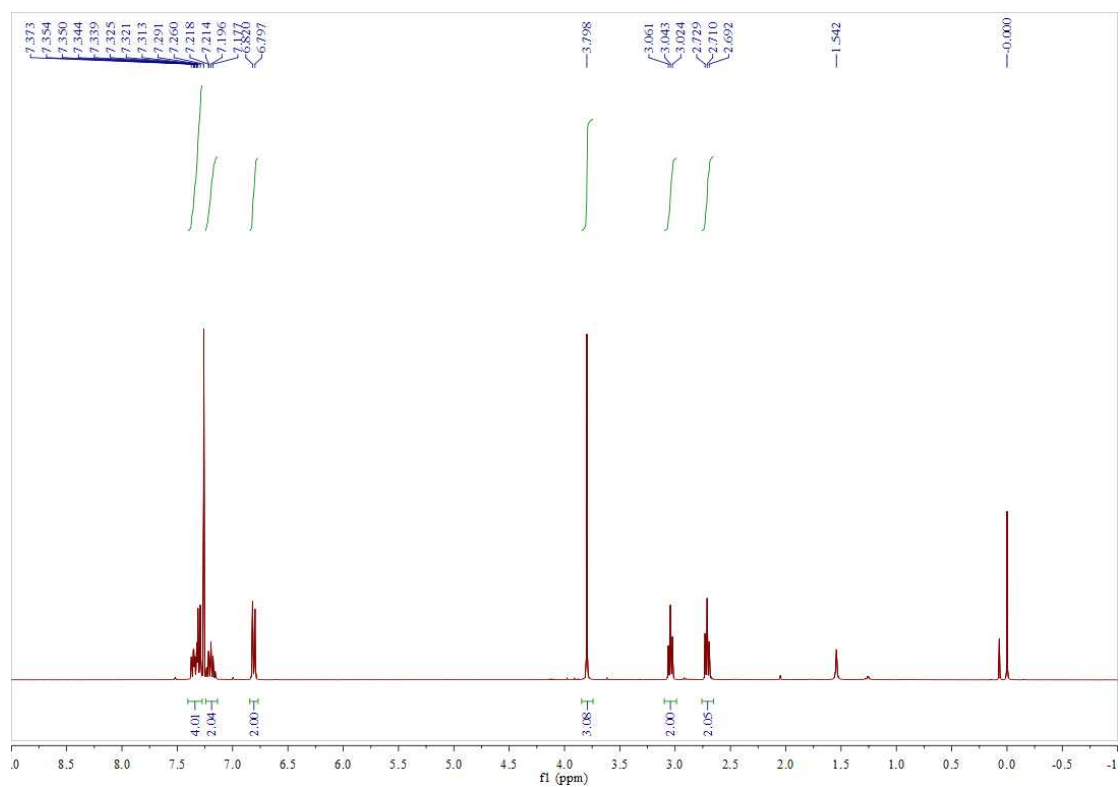
1-chloro-2-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene(1c)



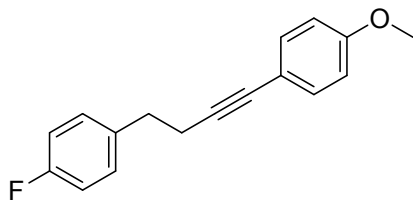
Prepared according to General Procedure A

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.27 (m, 4H), 7.24 – 7.14 (m, 2H), 6.84 – 6.77 (m, 2H), 3.80 (s, 3H), 3.04 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 159.10, 138.16, 133.96, 132.86, 130.86, 129.47, 127.83, 126.69, 115.90, 113.81, 87.45, 81.17, 55.25, 33.03, 19.75.



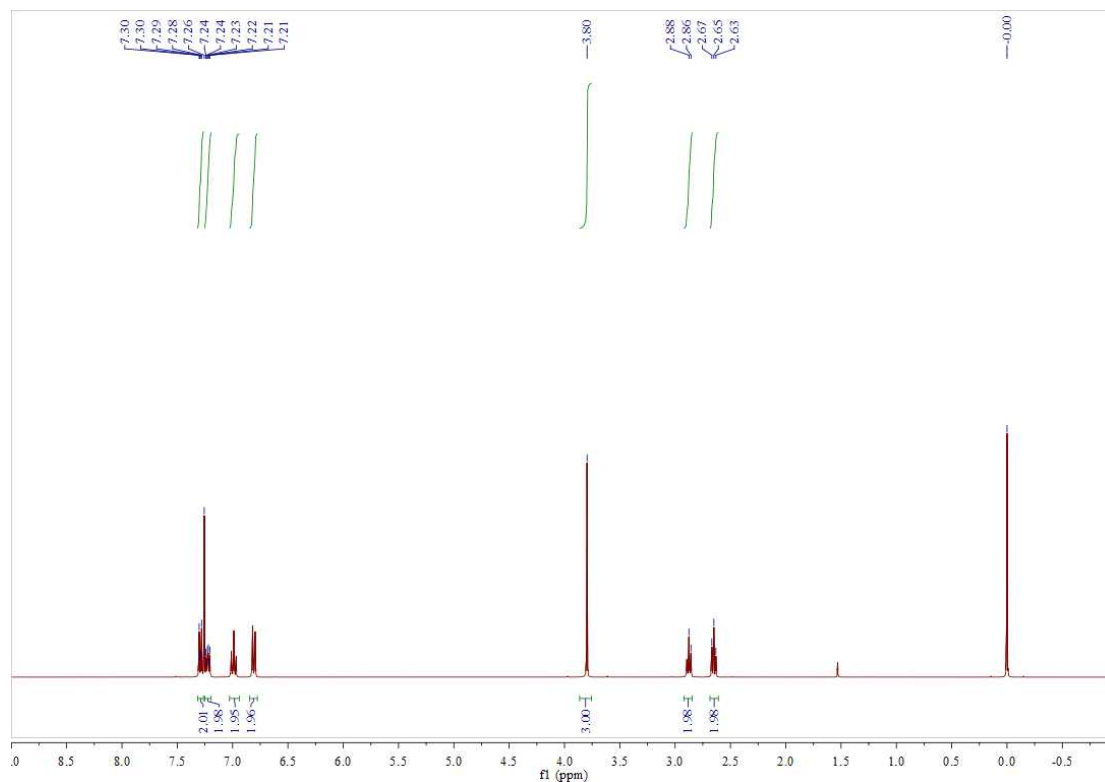
1-fluoro-4-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene(1d)

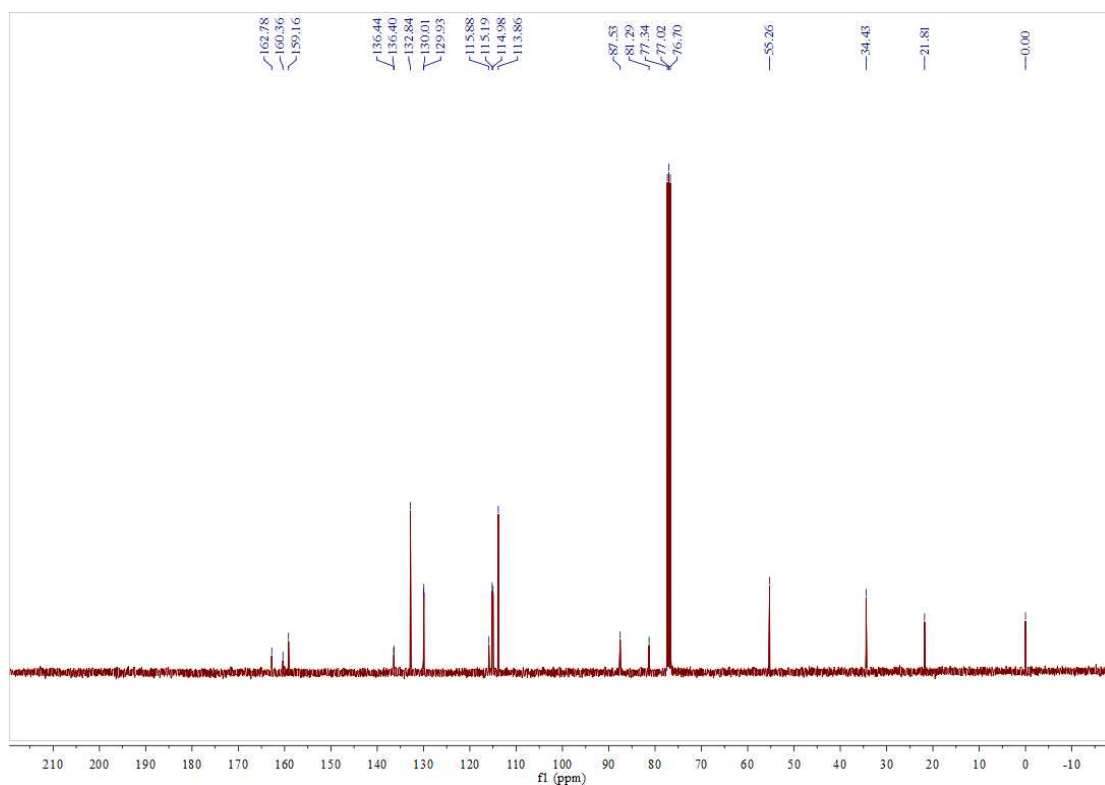


Prepared according to General Procedure A

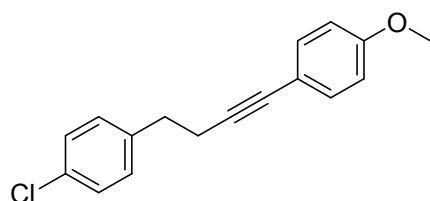
^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.26 (m, 2H), 7.25 – 7.19 (m, 2H), 6.88 – 6.71 (m, 2H), 6.95 – 6.64 (m, 2H), 3.80 (s, 3H), 2.87 (d, $J = 7.4$ Hz, 2H), 2.65 (t, $J = 7.4$ Hz, 2H);

^{13}C NMR (100 MHz, CDCl_3) δ 159.16, 132.84, 130.01, 129.93, 115.88, 115.19, 114.98, 113.86, 87.53, 81.29, 55.26, 34.43, 21.81.





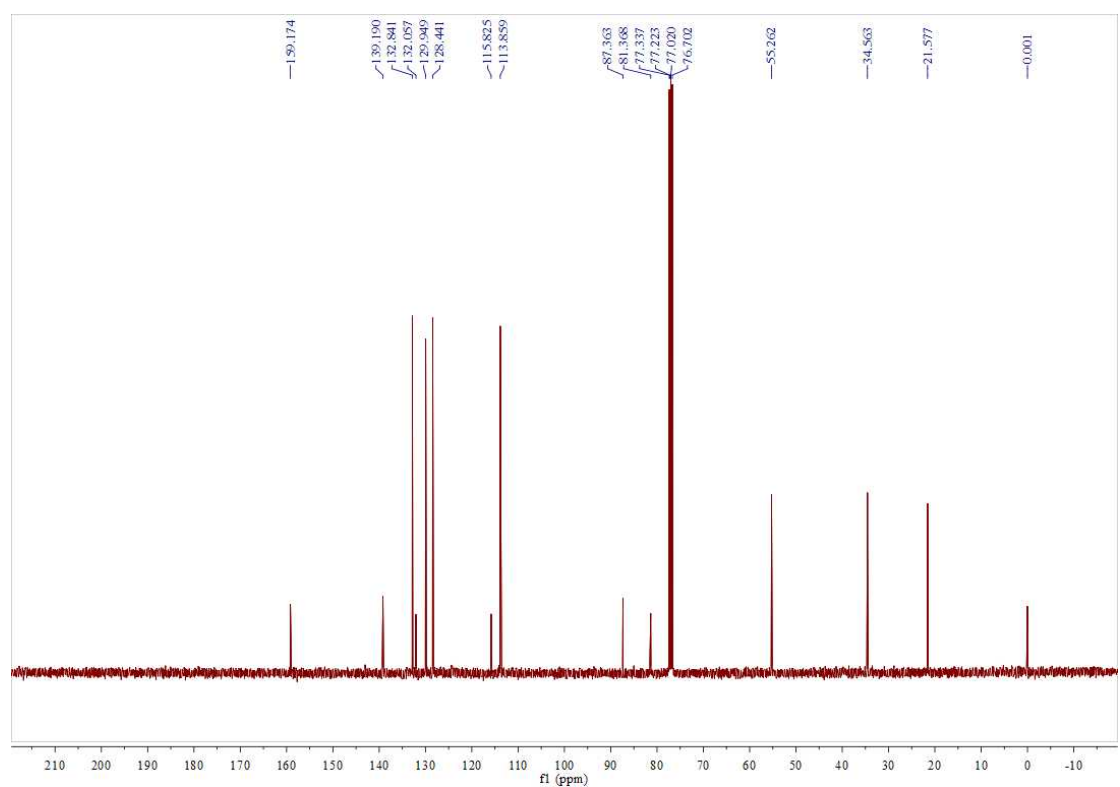
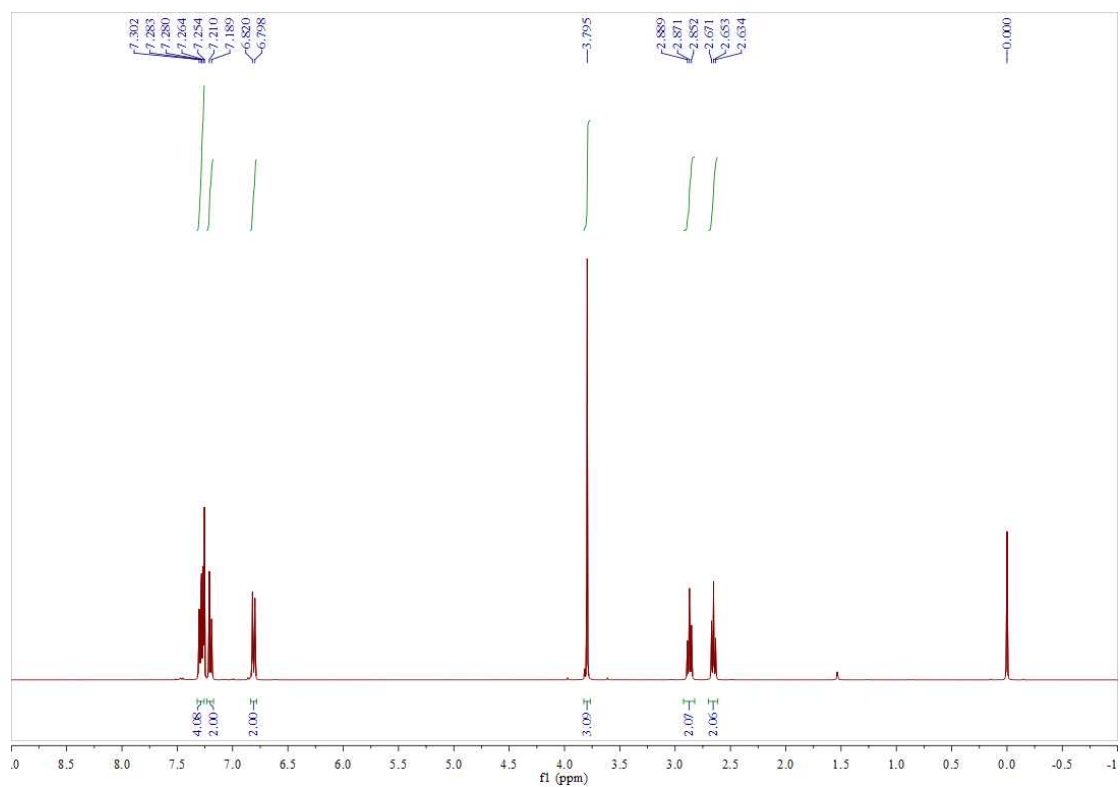
1-chloro-4-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene(1e)



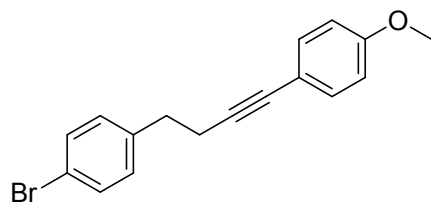
Prepared according to General Procedure A

¹H NMR (400 MHz, CDCl₃) δ 7.28 (dd, *J* = 8.3, 7.1 Hz, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 159.17, 139.19, 132.84, 132.06, 129.95, 128.44, 115.82, 113.86, 87.36, 81.37, 55.26, 34.56, 21.58.



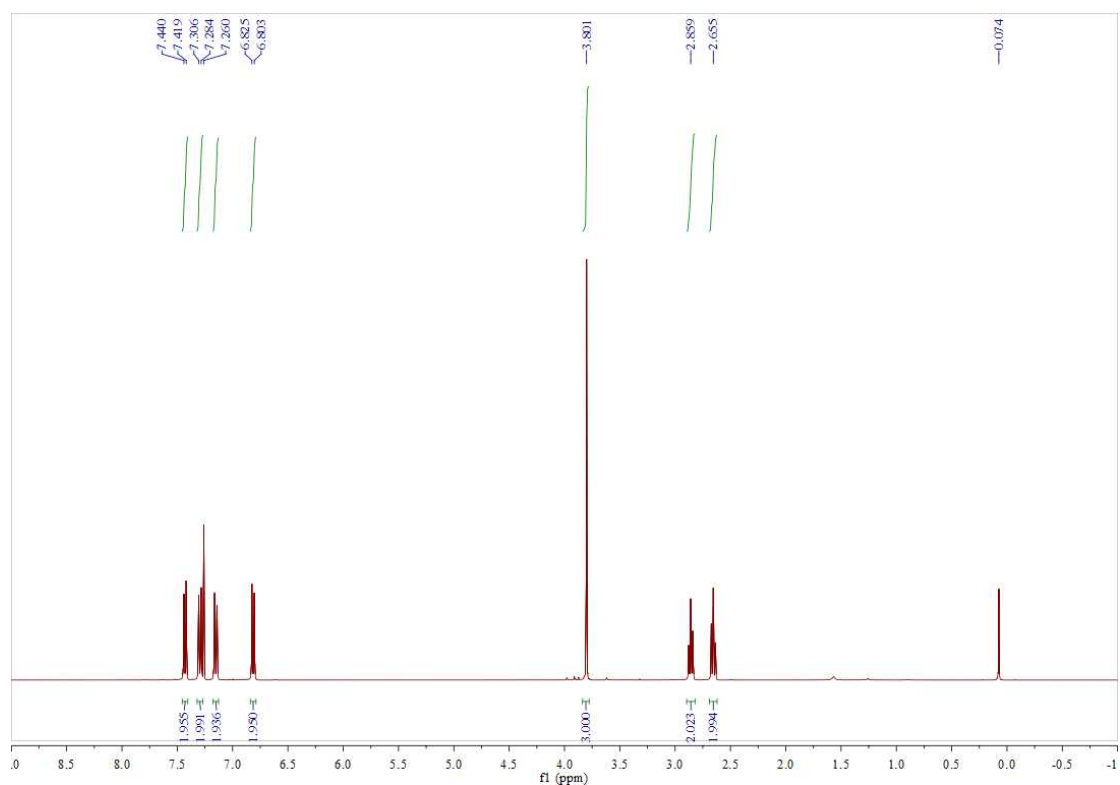
1-bromo-4-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene(1f)

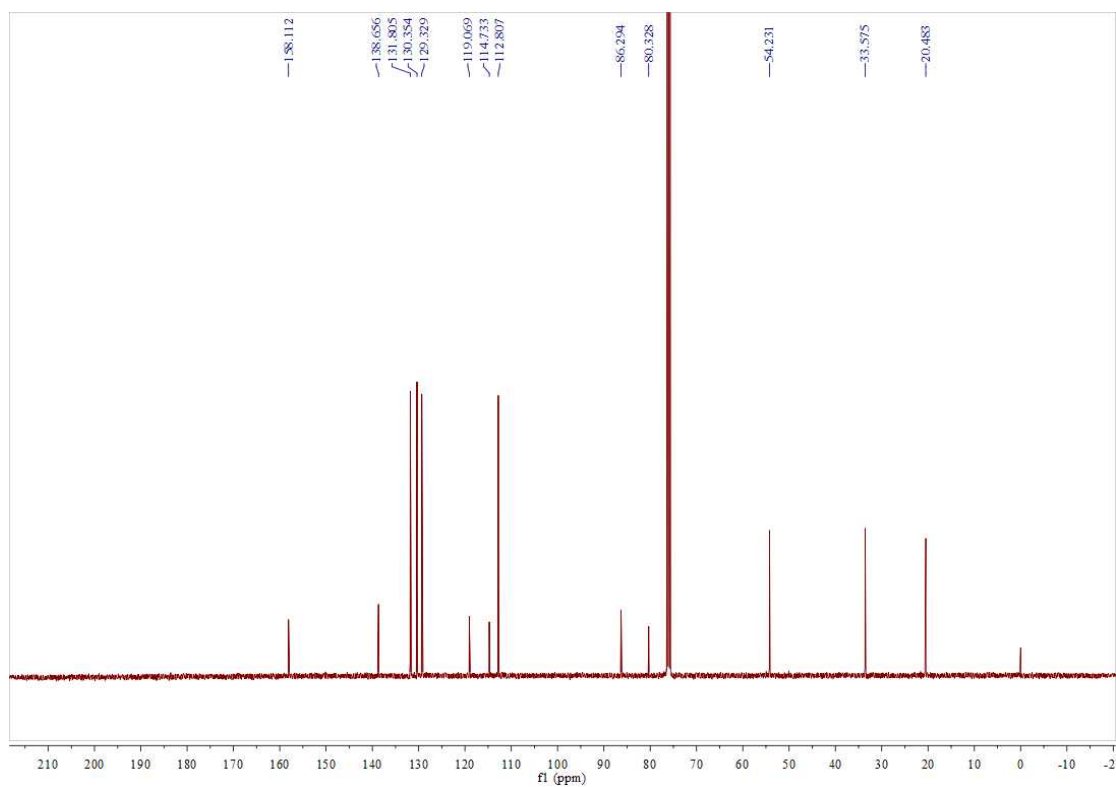


Prepared according to General Procedure A

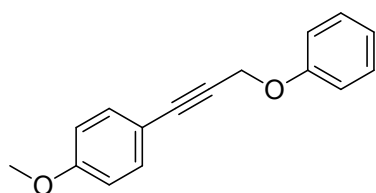
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.8$ Hz, 2H), 7.15 (d, $J = 8.3$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 3.80 (s, 3H), 2.86 (s, 2H), 2.65 (s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.11, 138.66, 131.80, 130.35, 129.33, 119.07, 114.73, 112.81, 86.29, 80.33, 54.23, 33.57, 20.48.





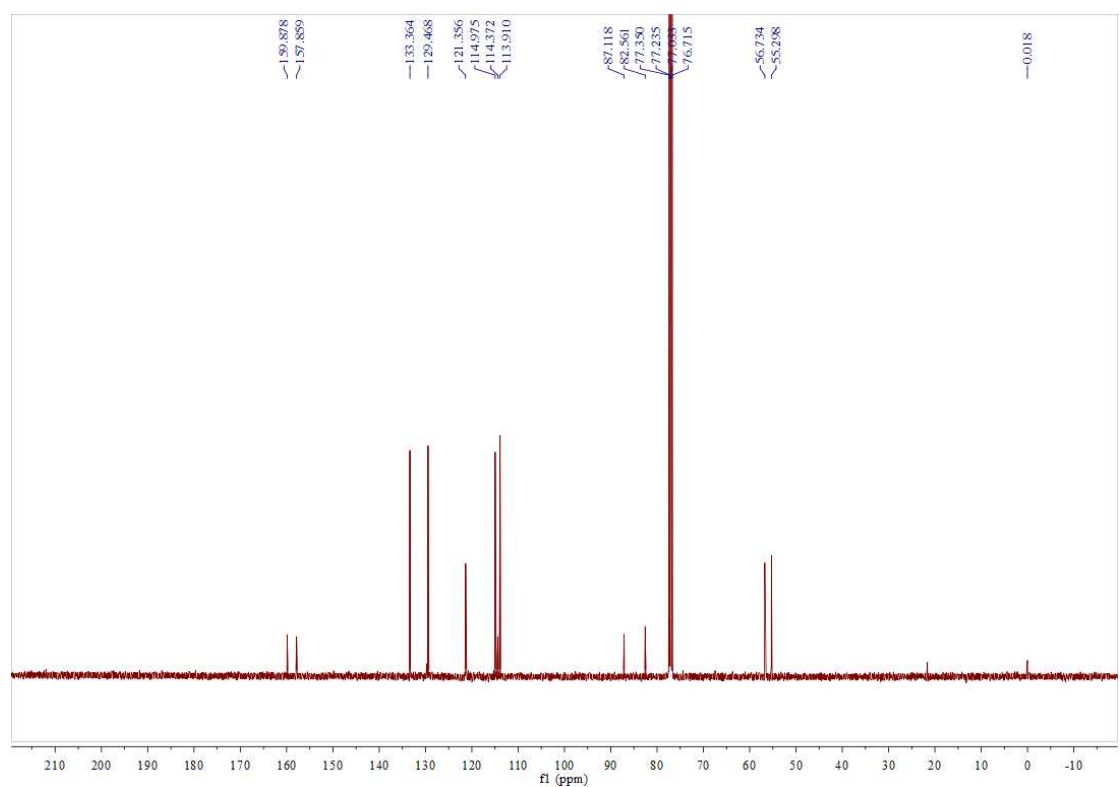
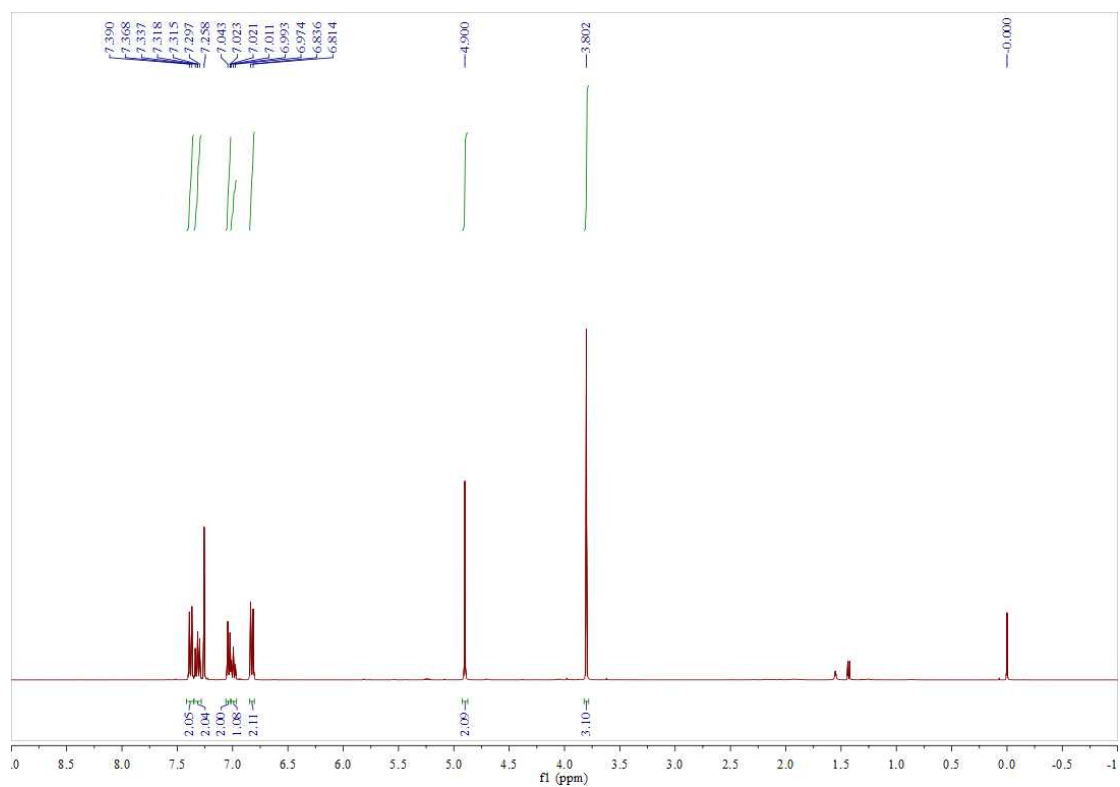
1-methoxy-4-(3-phenoxyprop-1-yn-1-yl)benzene(1g)



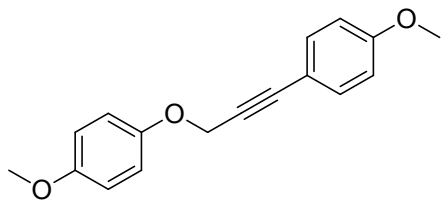
Prepared according to General Procedure **B**

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.35 (m, 2H), 7.32 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.03 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.02 – 6.96 (m, 1H), 6.85 – 6.80 (m, 2H), 4.90 (s, 2H), 3.80 (s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 159.88, 157.86, 133.36, 129.47, 121.36, 114.98, 114.37, 113.91, 87.12, 82.56, 56.73, 55.30.



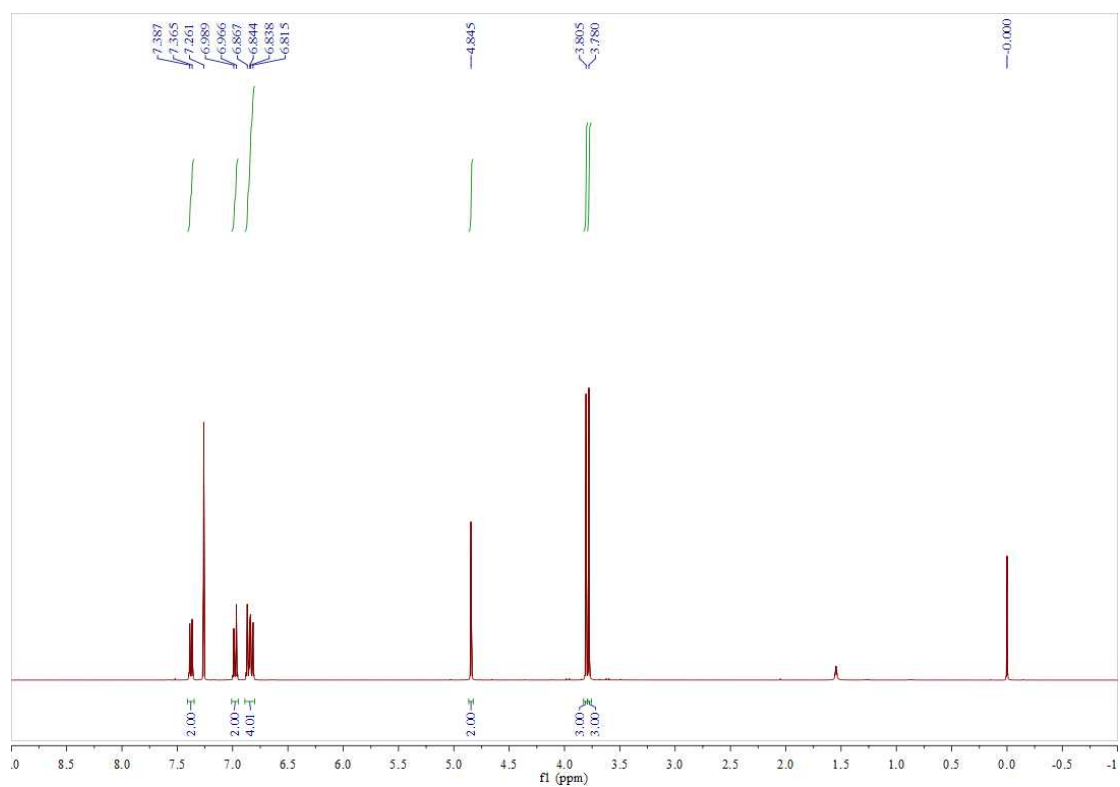
1-methoxy-4-(3-(4-methoxyphenoxy)prop-1-yn-1-yl)benzene(1h)

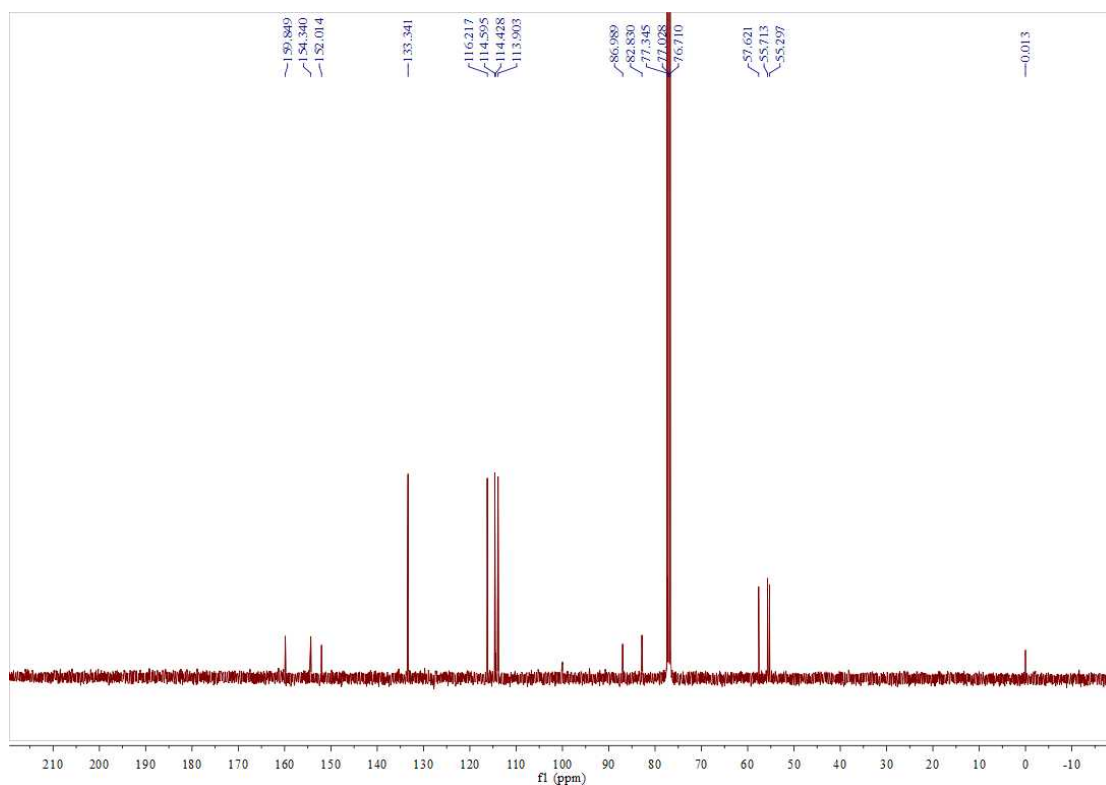


Prepared according to General Procedure **B**

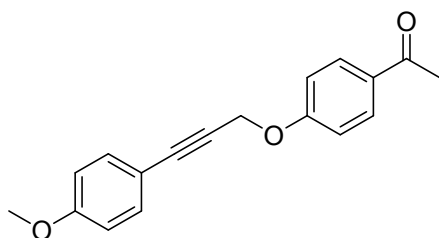
¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 9.1 Hz, 2H), 6.84 (dd, *J* = 11.6, 9.0 Hz, 4H), 4.84 (s, 2H), 3.81 (s, 3H), 3.78 (s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 159.85, 154.34, 152.01, 133.34, 116.22, 114.60, 114.43, 113.90, 86.99, 82.83, 57.62, 55.71, 55.30.





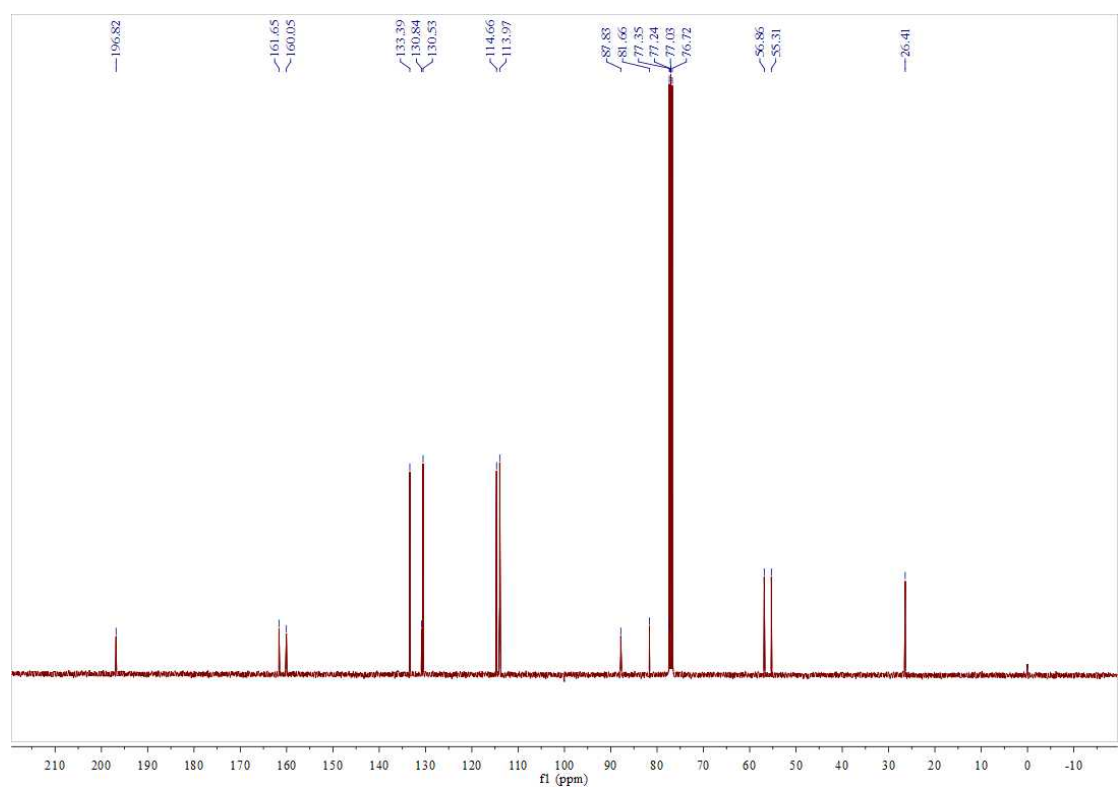
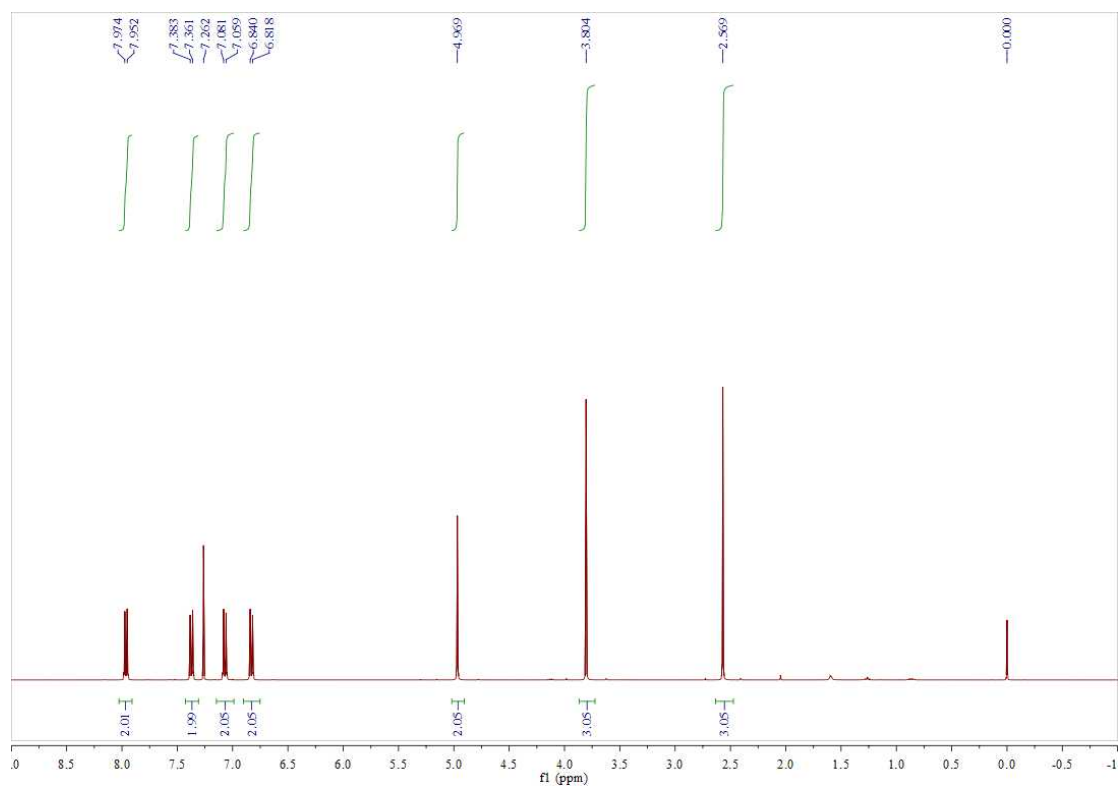
1-(4-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl)ethanone(1i)



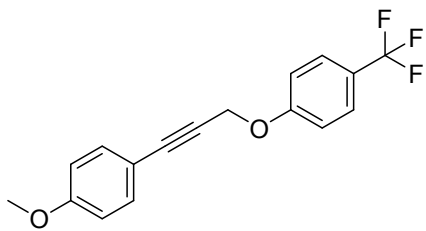
Prepared according to General Procedure **B**

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 3.80 (s, 3H), 2.57 (s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 196.82, 161.65, 160.05, 133.39, 130.84, 130.53, 114.66, 113.97, 87.83, 81.66, 56.86, 55.31, 26.41.



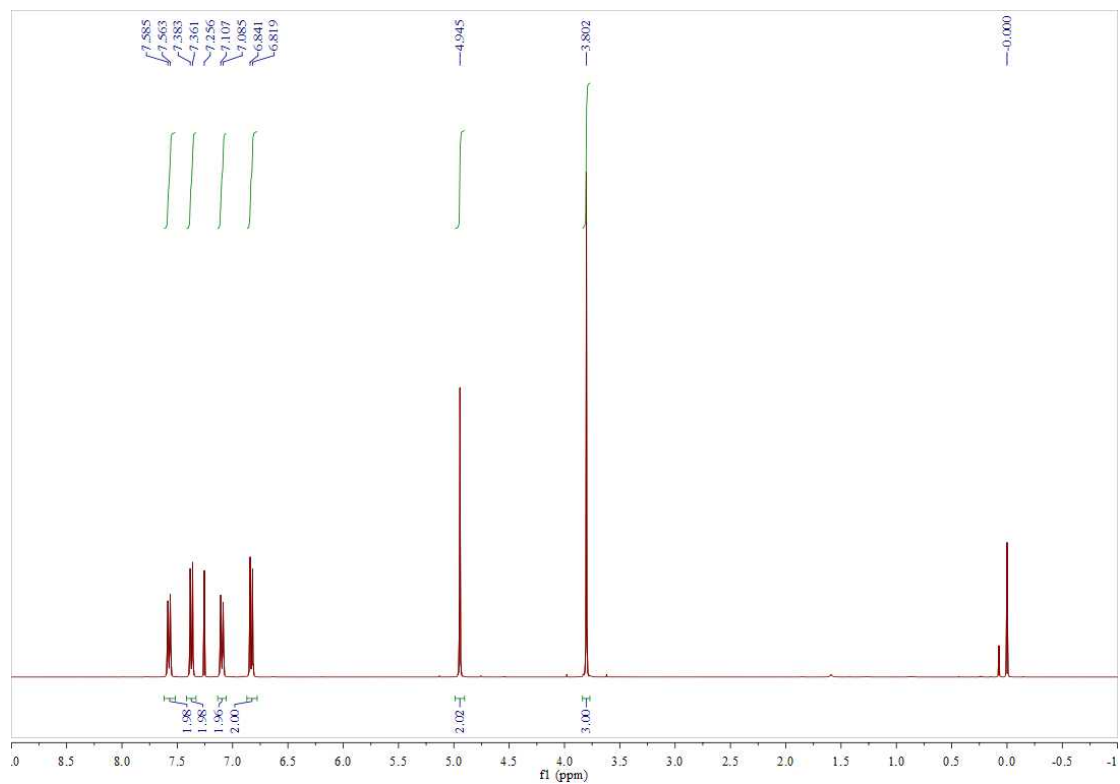
1-methoxy-4-(3-(4-(trifluoromethyl)phenoxy)prop-1-yn-1-yl)benzene(1j)

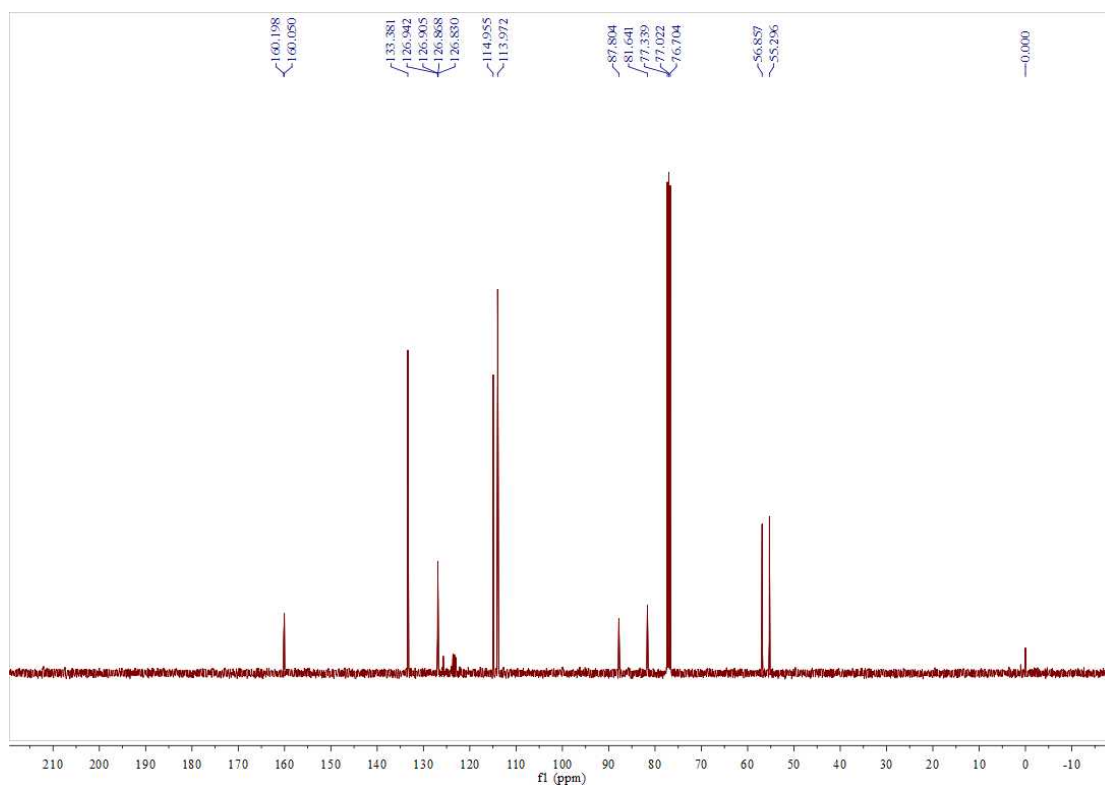


Prepared according to General Procedure **B**

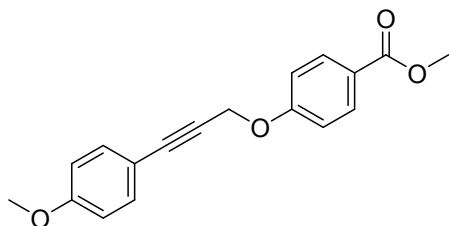
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.6$ Hz, 2H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.10 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.9$ Hz, 2H), 4.94 (s, 2H), 3.80 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.20, 160.05, 133.38, 126.89 (q, $J = 3.7$ Hz), 124.52 (q, $J = 244.8$ Hz), 123.63, 123.04, 114.95, 113.97, 87.80, 81.64, 56.86, 55.30.





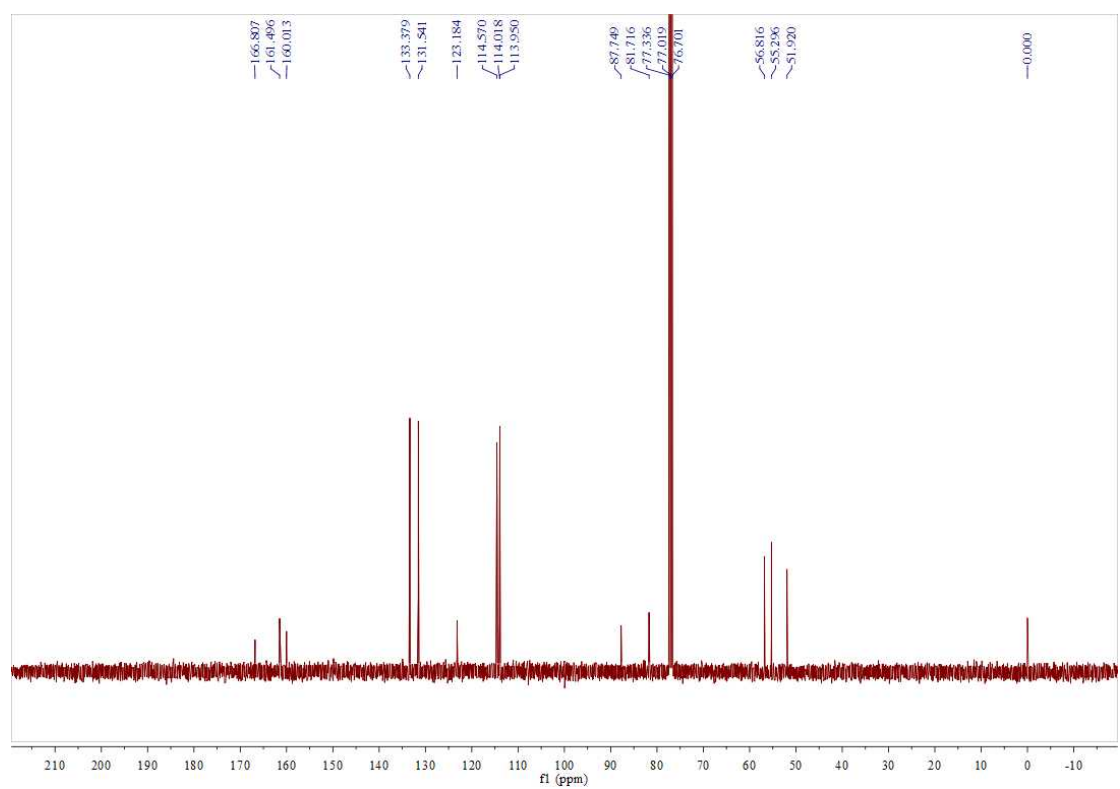
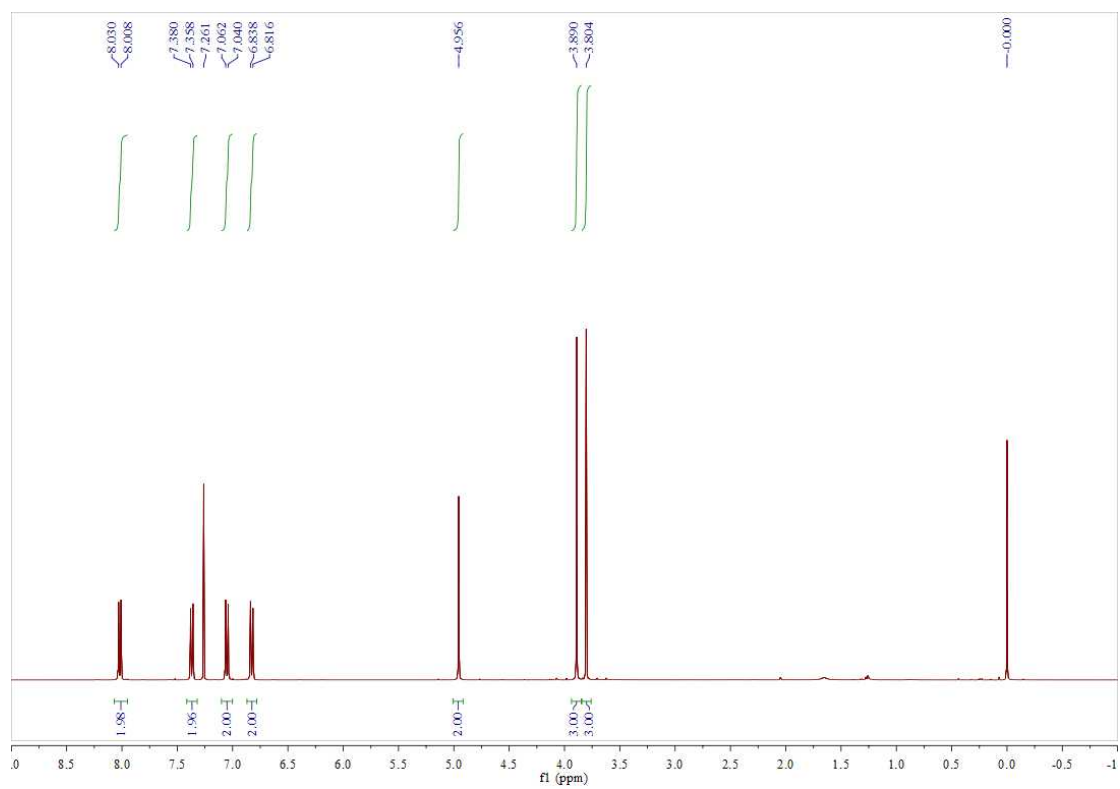
methyl 4-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzoate(1k)



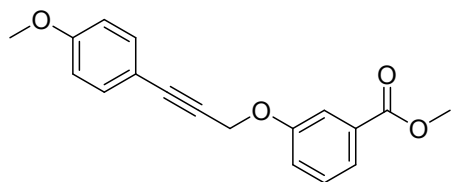
Prepared according to General Procedure **B**

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 4.96 (s, 2H), 3.89 (s, 3H), 3.80 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.81, 161.50, 160.01, 133.38, 131.54, 123.18, 114.57, 114.02, 113.95, 87.75, 81.72, 56.82, 55.30, 51.92.



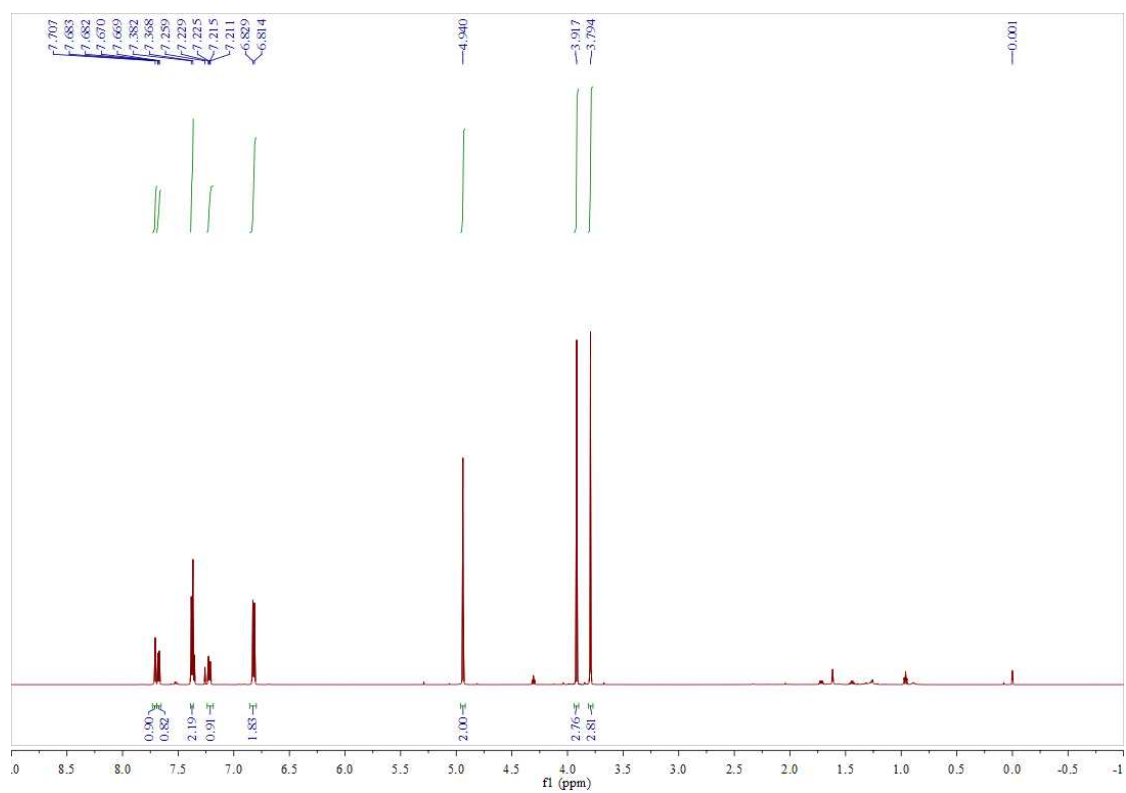
methyl 3-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzoate(11)

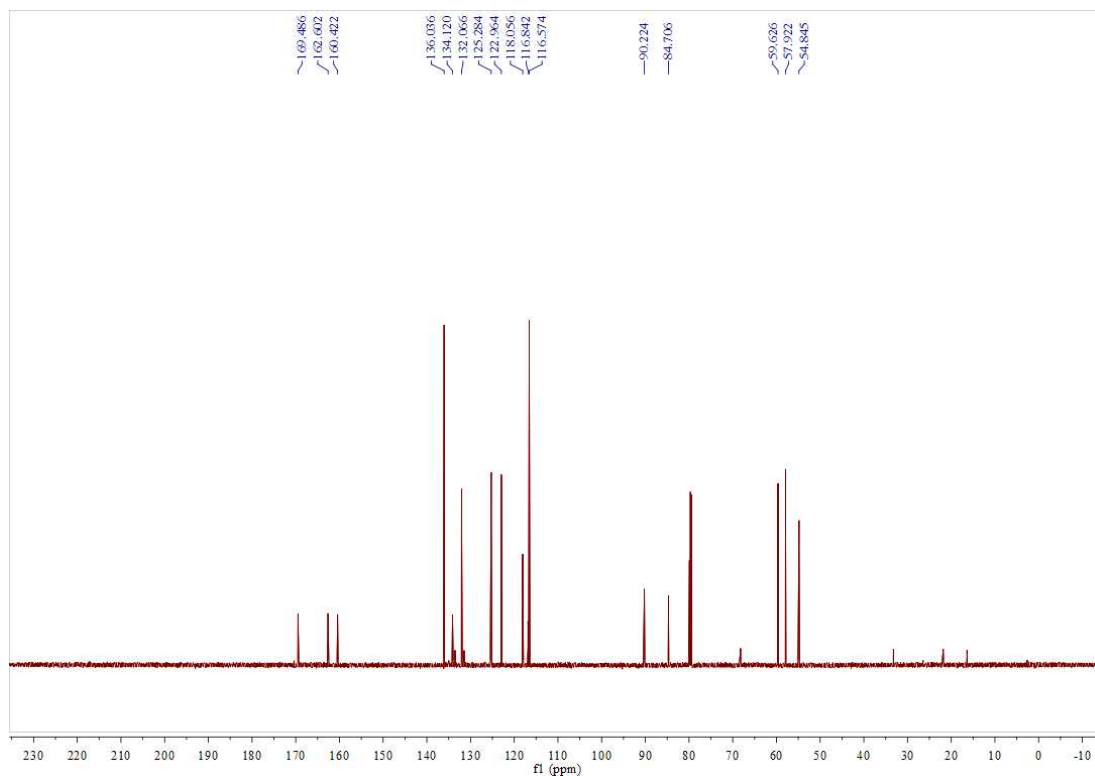


Prepared according to General Procedure B

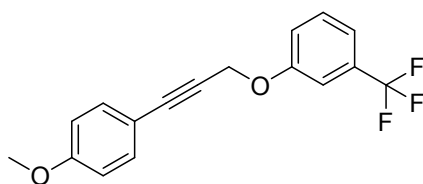
$^1\text{H NMR}$ (600 MHz, cdCl_3) δ 7.71 (s, 1H), 7.68 (dd, $J = 7.7, 0.6$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 2H), 7.22 (dd, $J = 8.2, 2.6$ Hz, 1H), 6.82 (d, $J = 8.5$ Hz, 2H), 4.94 (s, 2H), 3.92 (s, 3H), 3.79 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, cdCl_3) δ 169.49, 162.60, 160.42, 136.04, 134.12, 132.07, 125.28, 122.96, 118.06, 116.84, 116.57, 90.22, 84.71, 59.63, 57.92, 54.84.





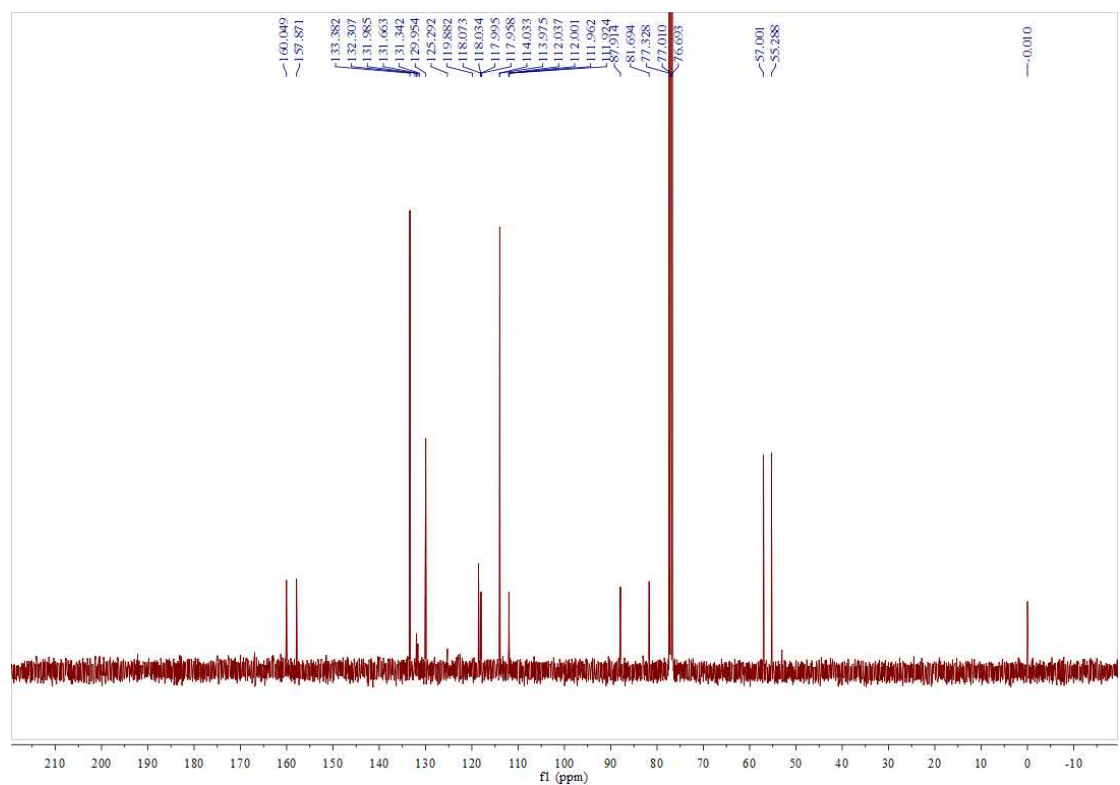
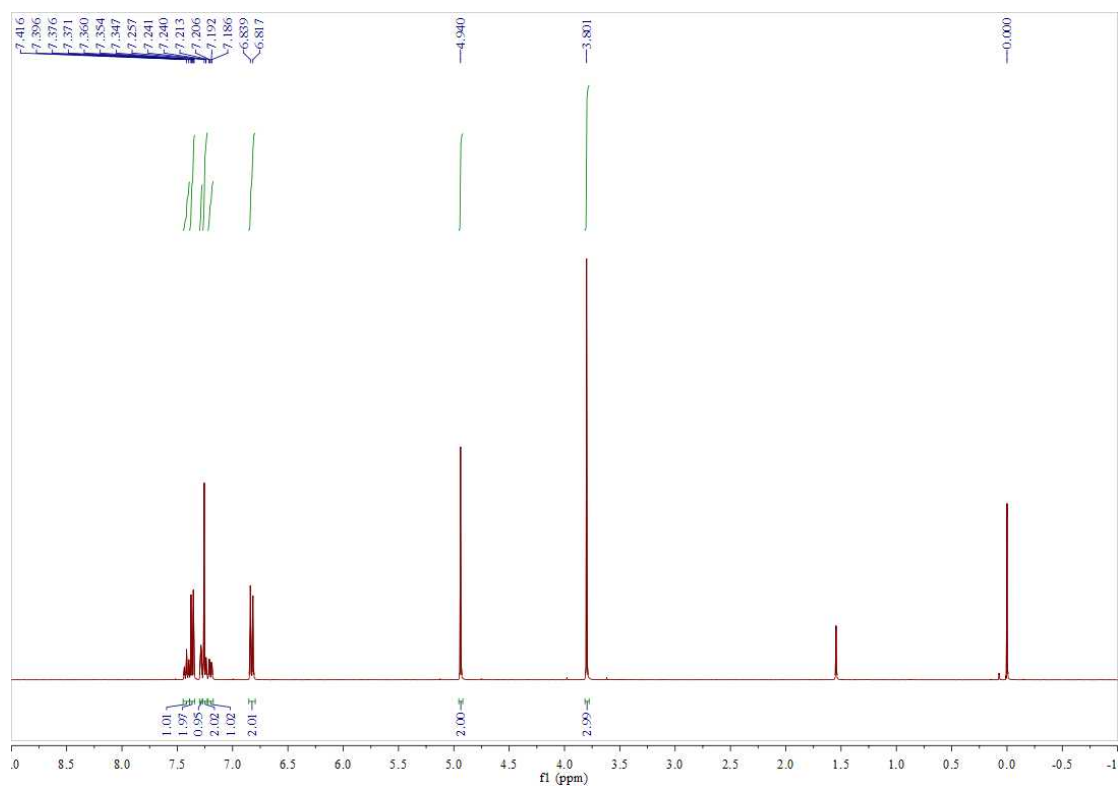
1-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)-3-(trifluoromethyl)benzene(1m)



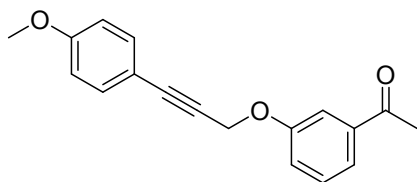
Prepared according to General Procedure **B**

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (d, $J = 8.0$ Hz, 1H), 7.39 - 7.34 (m, 2H), 7.29 (s, 1H), 7.27 - 7.23 (m, 1H), 7.20 (dd, $J = 8.3, 2.5$ Hz, 1H), 6.83 (d, $J = 8.9$ Hz, 2H), 4.94 (s, 2H), 3.80 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.05, 157.87, 133.38, 131.82 (q, $J = 32.3$ Hz), 129.95, 123.94 (q, $J = 272.0$ Hz), 118.56, 118.01 (q, $J = 3.8$ Hz), 114.03, 113.97, 111.98 (q, $J = 3.7$ Hz), 87.91, 81.69, 57.00, 55.29.



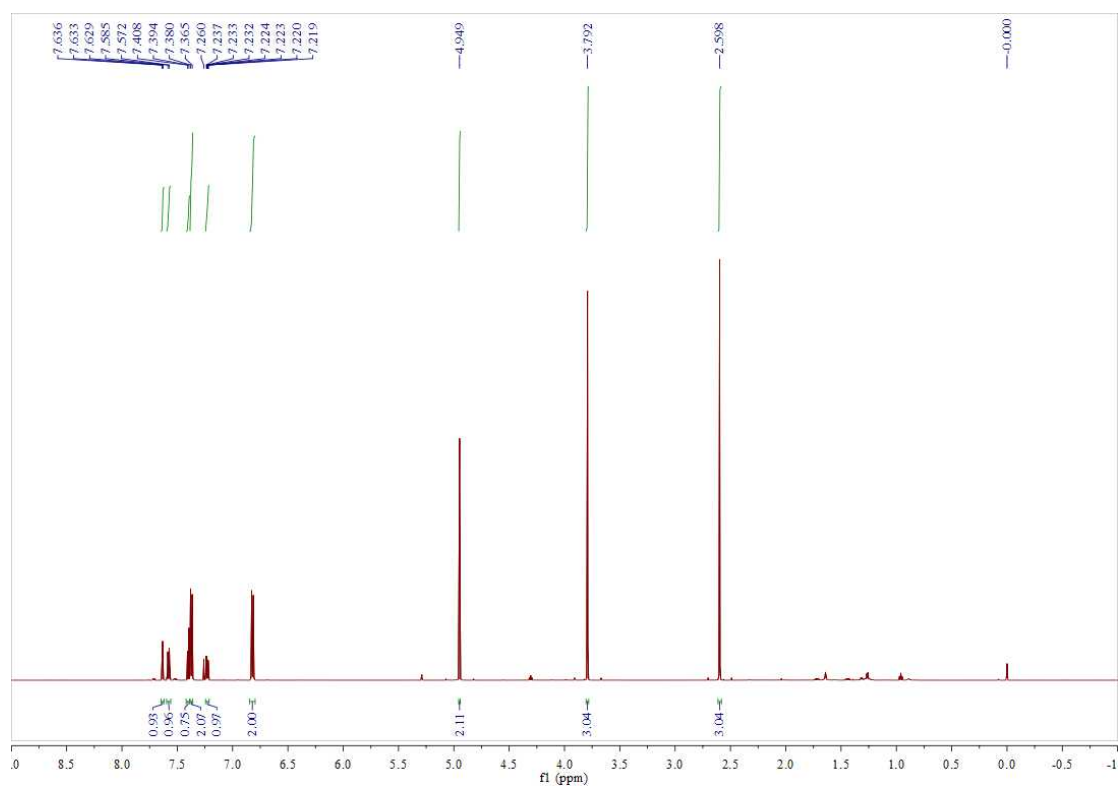
1-(3-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl)ethanone(1n)

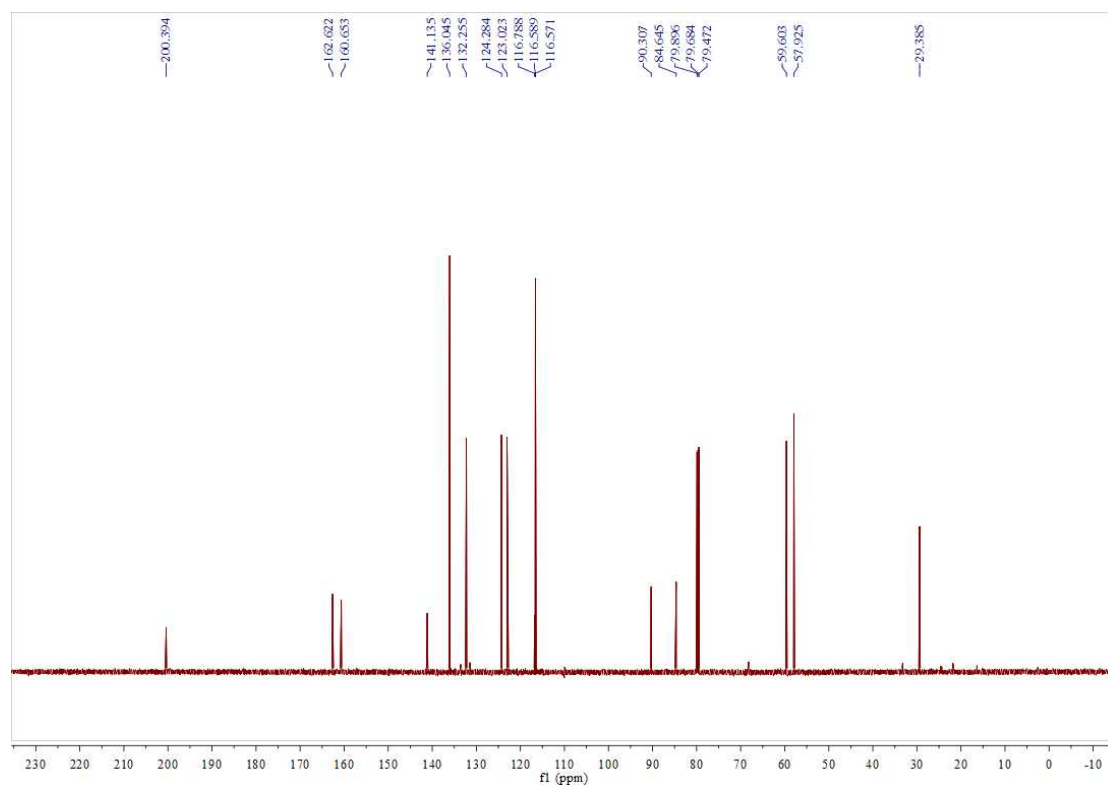


Prepared according to General Procedure B

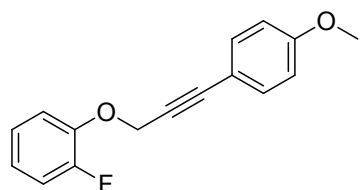
¹H NMR (600 MHz, cdcl₃) δ 7.65 – 7.62 (m, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.9 Hz, 2H), 7.24 – 7.21 (m, 1H), 6.85 – 6.80 (m, 2H), 4.95 (s, 2H), 3.79 (s, 3H), 2.60 (s, 3H).

¹³C NMR (150 MHz, cdcl₃) δ 200.39, 162.62, 160.65, 141.13, 136.05, 132.26, 124.28, 123.02, 116.79, 116.59, 116.57, 90.31, 84.64, 59.60, 57.93, 29.38 .





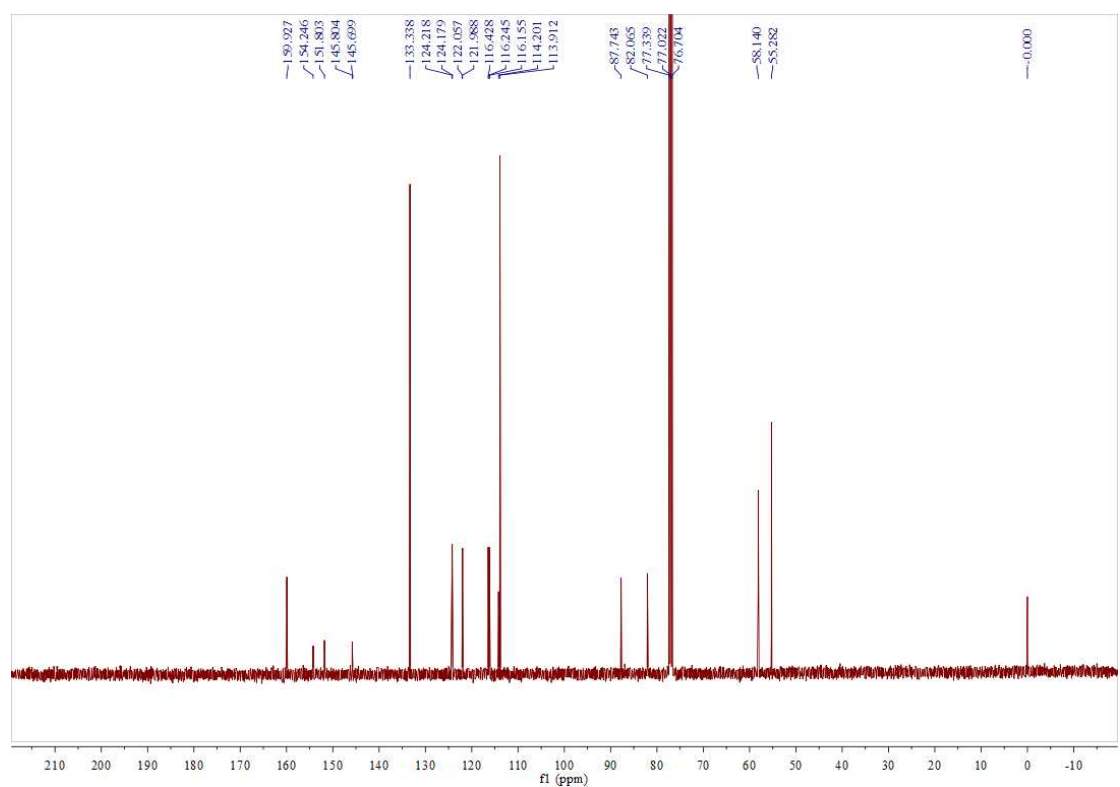
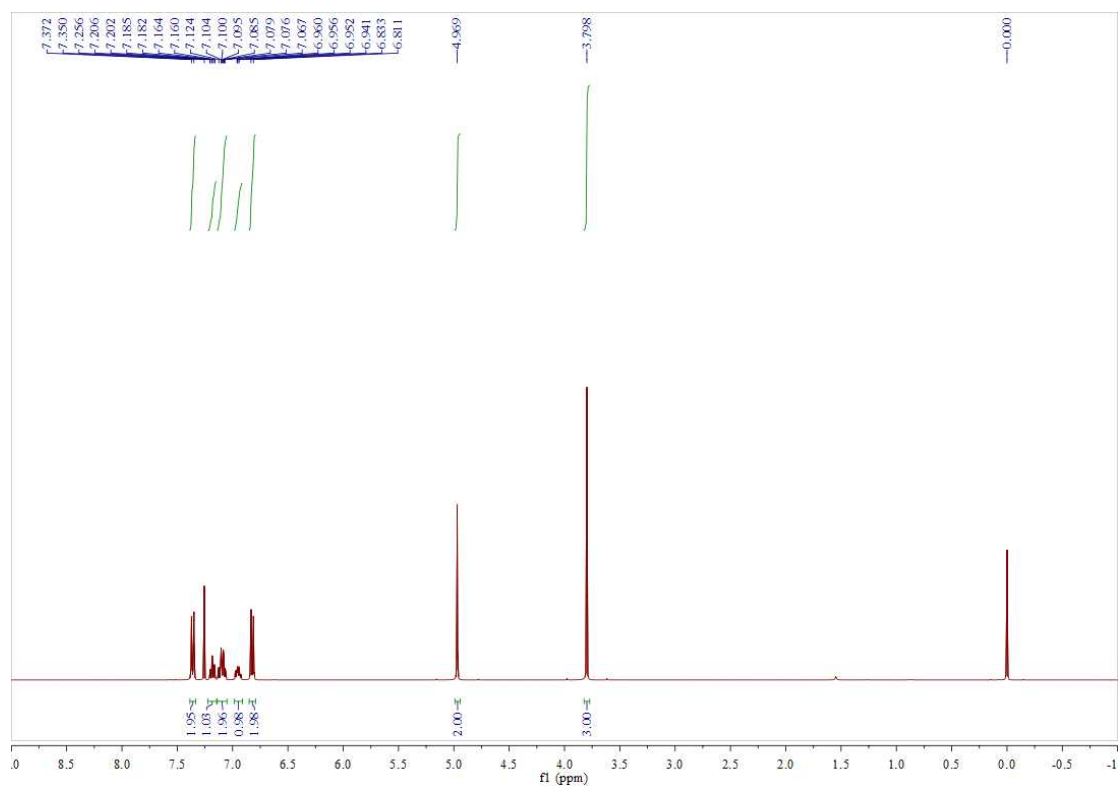
1-fluoro-2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzene(1o)



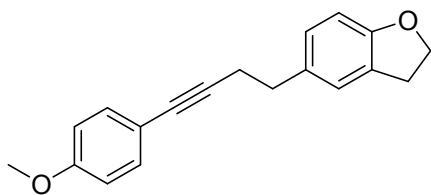
Prepared according to General Procedure **B**

¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.8 Hz, 2H), 7.18 (td, *J* = 8.4, 1.6 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.95 (dd, *J* = 4.6, 3.1 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 3.80 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.93, 153.02 (d, *J* = 245.9 Hz), 145.75 (d, *J* = 10.6 Hz), 133.34, 124.20 (d, *J* = 4.0 Hz), 122.02 (d, *J* = 7.0 Hz), 116.34 (d, *J* = 18.3 Hz), 116.15, 114.20, 113.91, 87.74, 82.07, 58.14, 55.28.



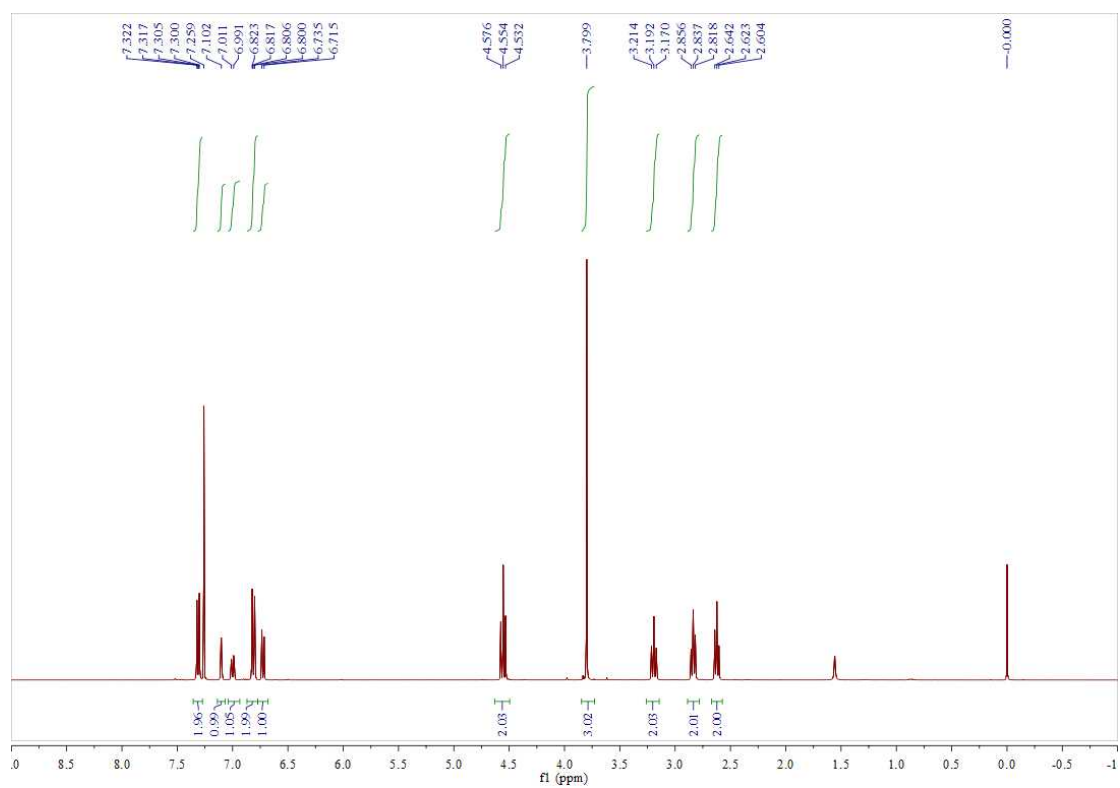
5-(4-(4-methoxyphenyl)but-3-yn-1-yl)-2,3-dihydrobenzofuran(1p)

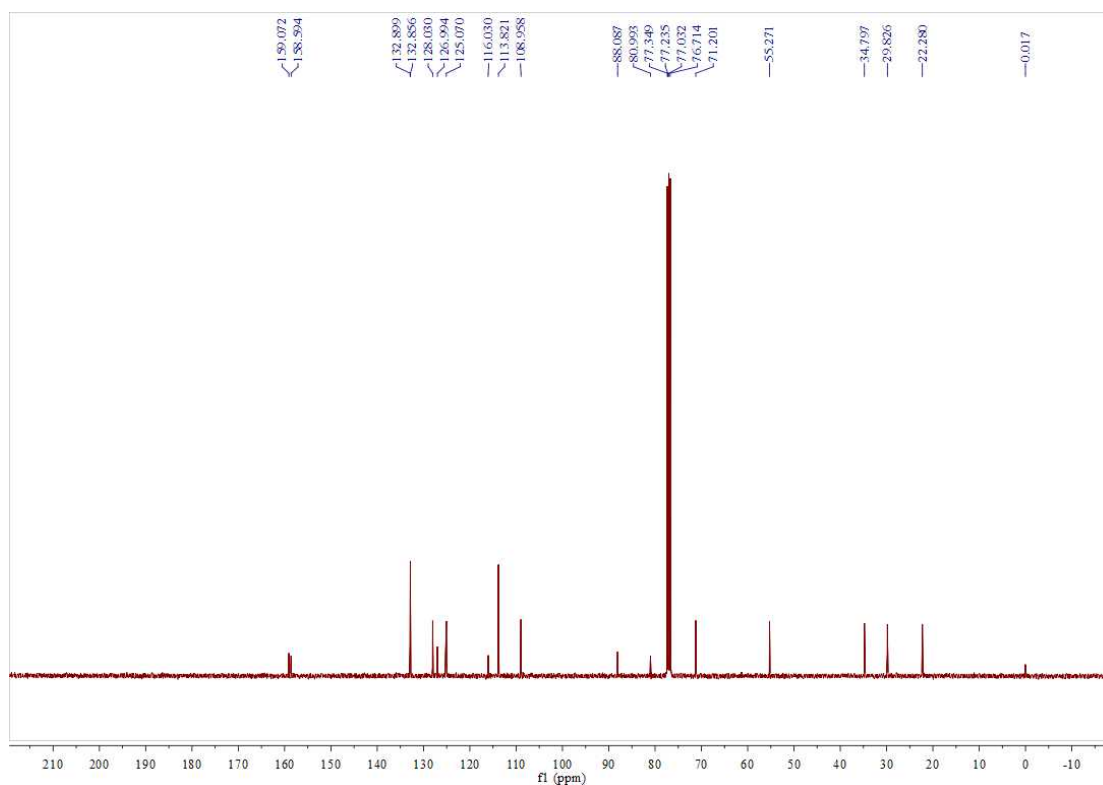


Prepared according to General Procedure A

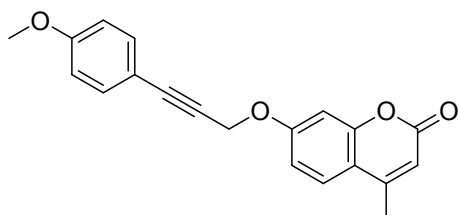
¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.27 (m, 2H), 7.10 (s, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.87 – 6.77 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 4.55 (t, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.19 (t, *J* = 8.7 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 159.07, 158.60, 132.90, 132.86, 128.03, 126.99, 125.07, 116.03, 113.82, 108.96, 88.09, 80.99, 71.20, 55.27, 34.80, 29.83, 22.28.





7-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)-4-methyl-2H-chromen-2-one(1q)

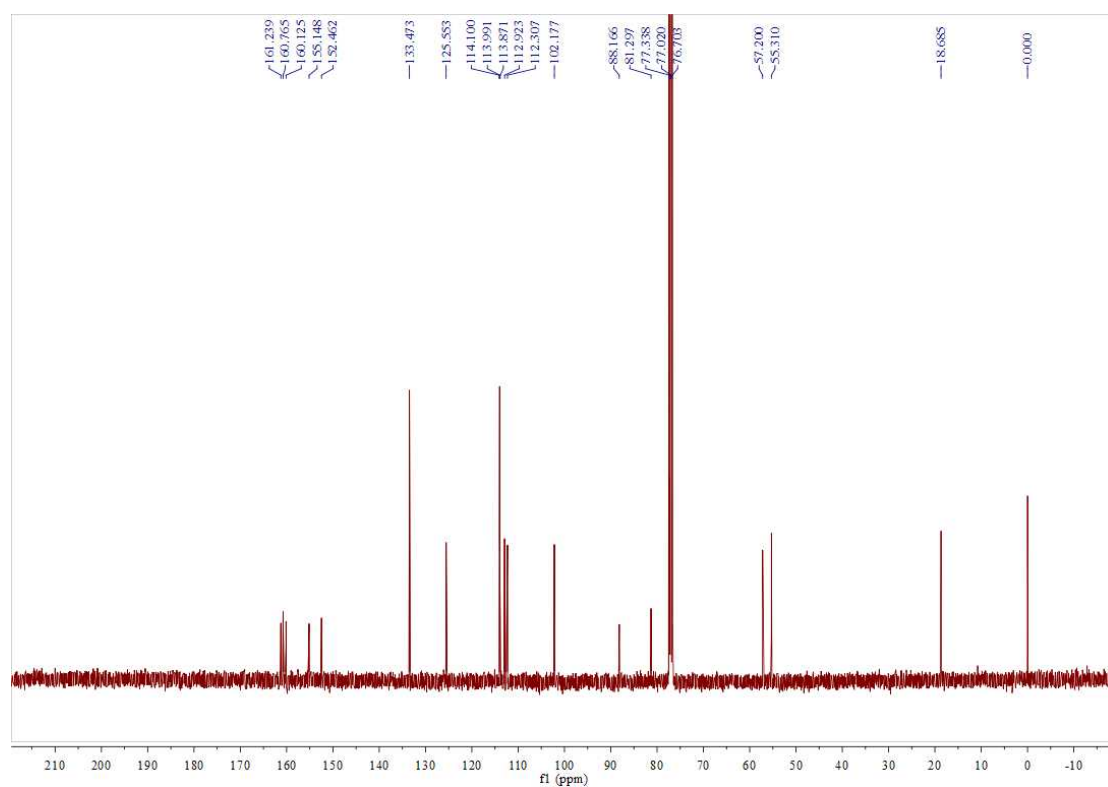
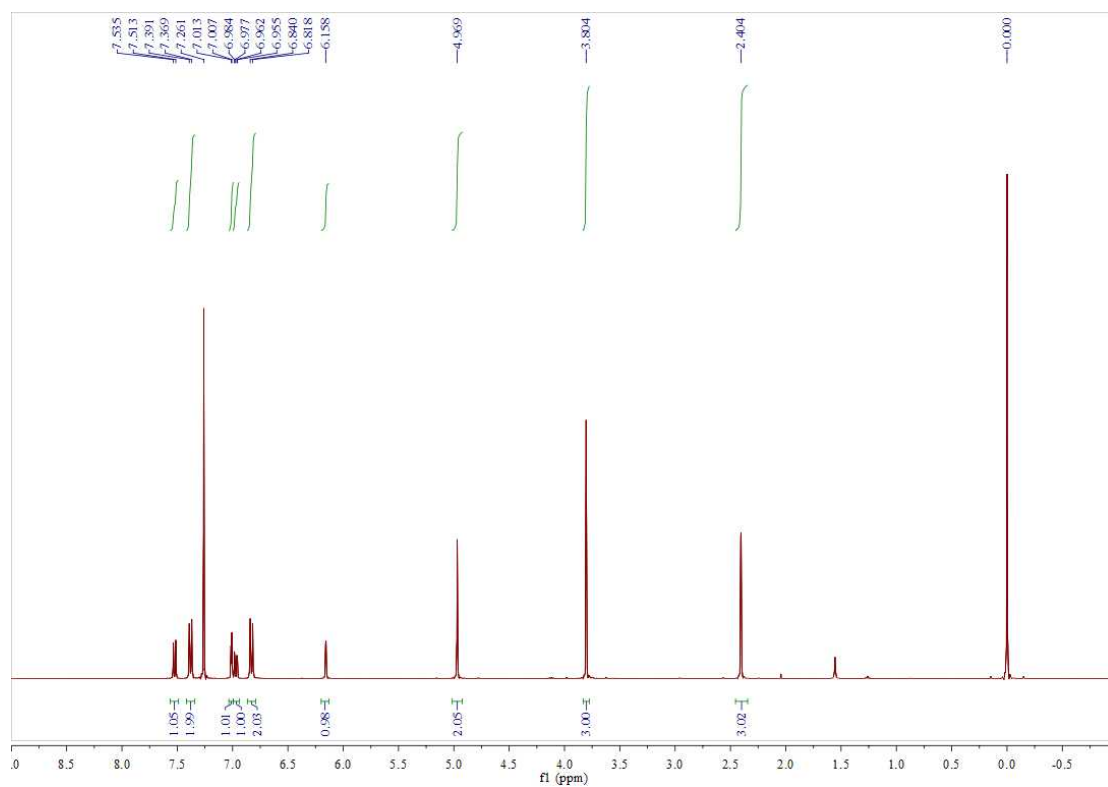


Prepared according to a procedure from E. J. Corey *et al.*³

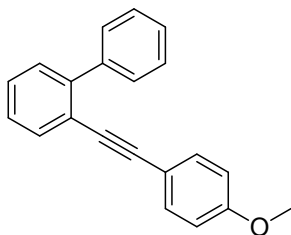
A round-bottomed flask was charged 7-hydroxy-4-methyl-2H-chromen-2-one (2 mmol, 352 mg), 1-(3-bromoprop-1-yn-1-yl)-4-methoxybenzene (2equiv, 900 mg), DMF (30 mL). NaH (2equiv, 96 mg) was added at 0 °C. The mixture returned to room temperature. The reaction was carried out at room temperature for 12 hours. The mixture was diluted with water and CH₂Cl₂. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (3×5 mL). The combined organic phase was dried (MgSO₄), filtered, and the solvent removed in vacuo to provide the crude product. And then the crude product was purified by column chromatography on silica gel eluting with petroleum ether/diethyl ether, and got **1n**.

¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.16 (s, 1H), 4.97 (s, 2H), 3.80 (s, 3H), 2.40 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 161.24, 160.77, 160.12, 155.15, 152.46, 133.47, 125.55, 114.10, 113.99, 113.87, 112.92, 112.31, 102.18, 88.17, 81.30, 57.20, 55.31, 18.68.



2-((4-methoxyphenyl)ethynyl)-1,1'-biphenyl(1r)

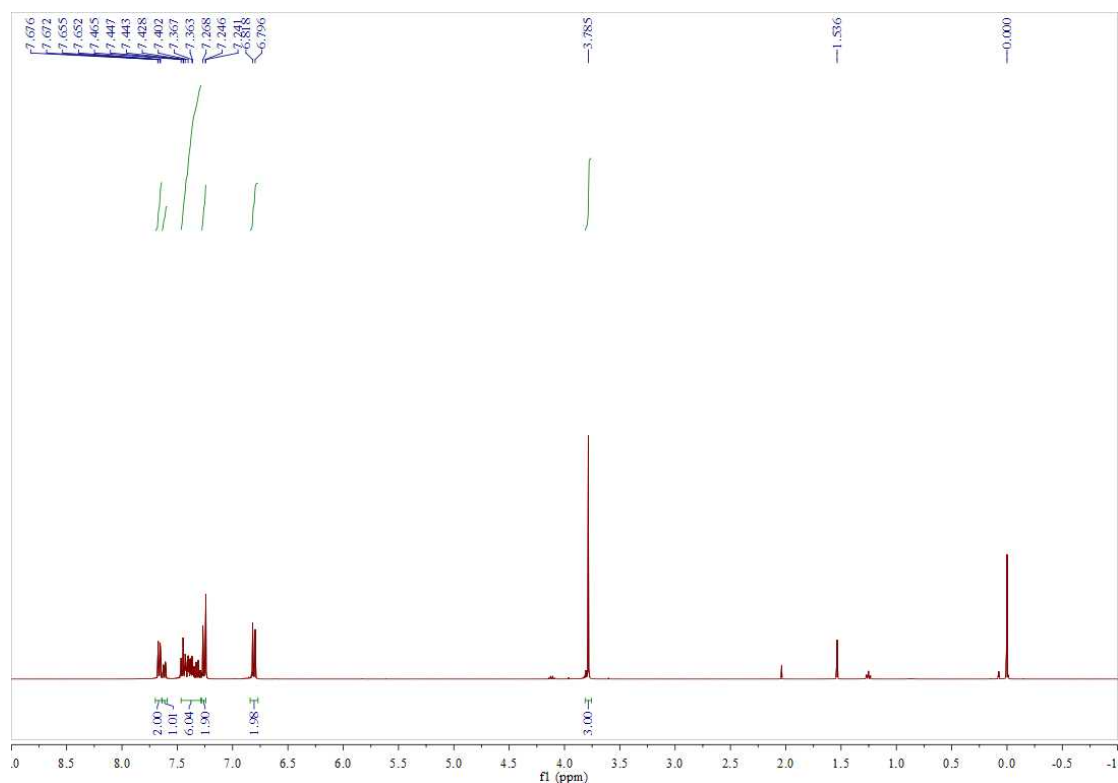


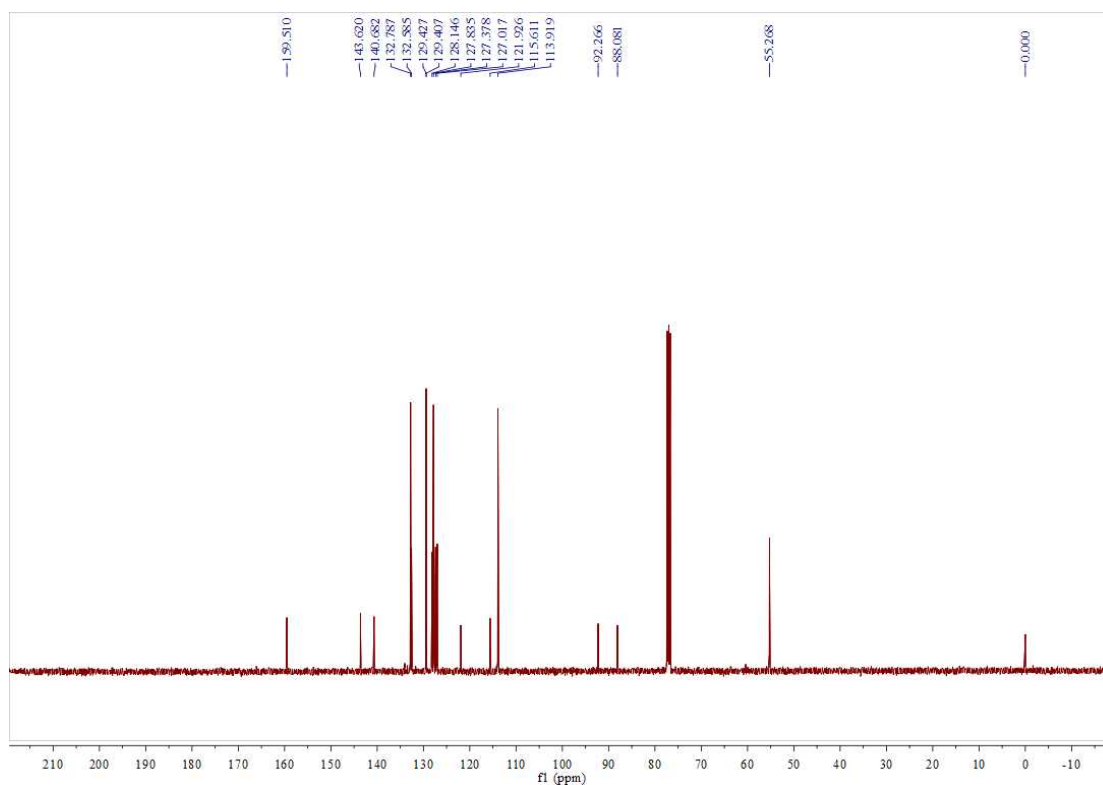
Prepared according to a procedure from R. C. Larock *et al.*⁴

To a solution of the 2-iodo-1,1'-biphenyl (1.0 mmol) and the 1-ethynyl-4-methoxybenzene (1.2 mmol, 1.2 equiv) in Et₃N (4 mL), were added PdCl₂(PPh₃)₂ (14 mg, 2 mol%) and CuI (2 mg, 1 mol%). The resulting mixture was then heated under Ar atmosphere at 55 °C for 3 h. The mixture was allowed to cool to room temperature, and the ammonium salt was removed by filtration. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the product **1o**.

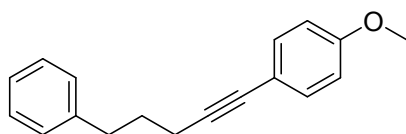
¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.64 (m, 2H), 7.64 – 7.59 (m, 1H), 7.47 – 7.29 (m, 6H), 7.26 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.51, 143.62, 140.68, 132.79, 132.59, 129.43, 129.41, 128.15, 127.83, 127.38, 127.02, 121.93, 115.61, 113.92, 92.27, 88.08, 55.27.





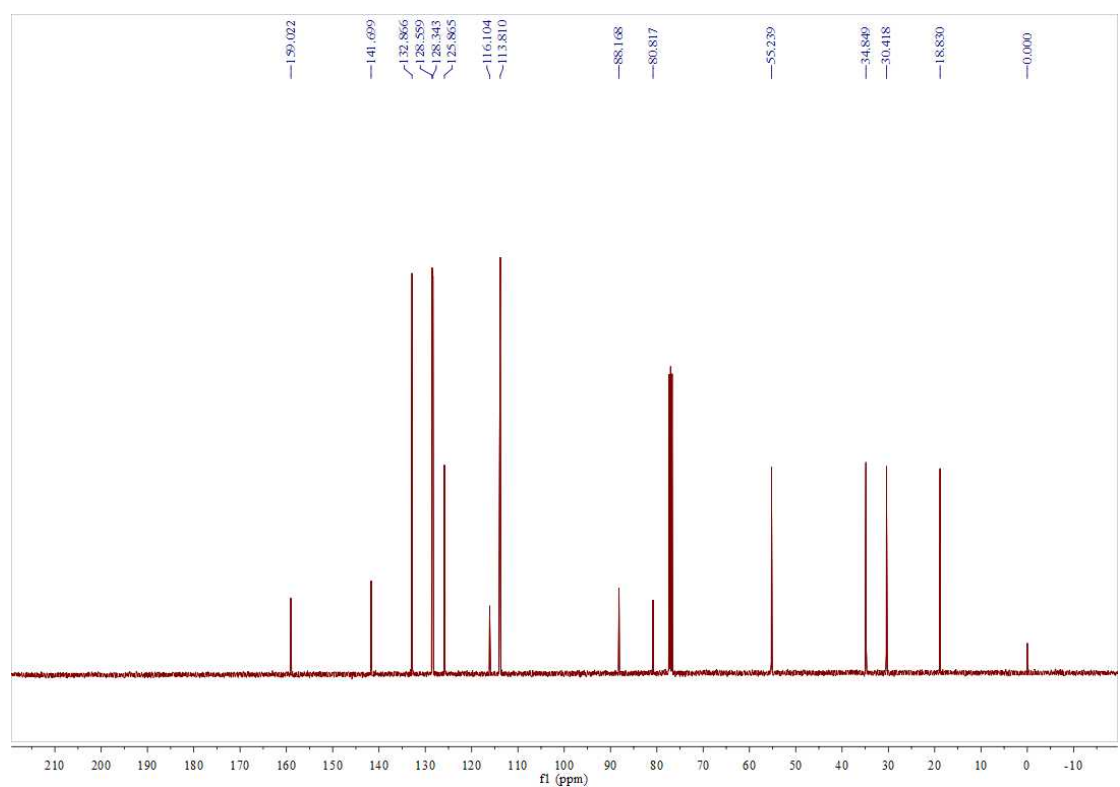
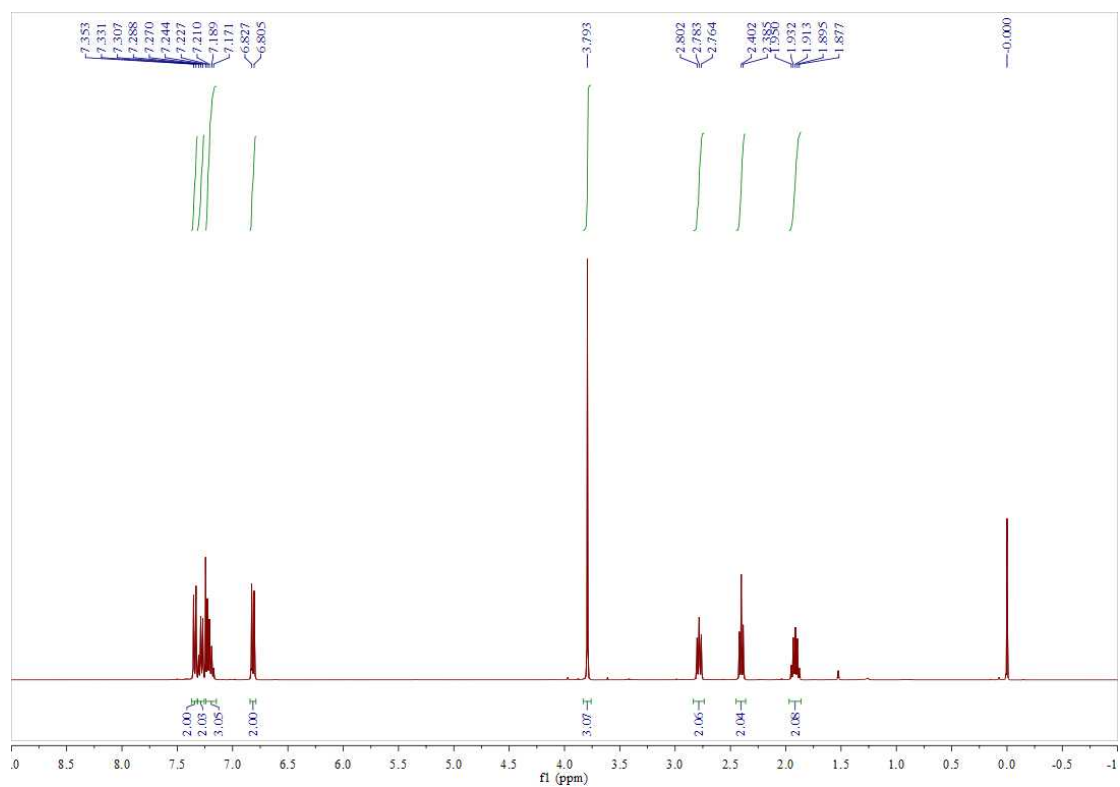
1-methoxy-4-(5-phenylpent-1-yn-1-yl)benzene(1s)



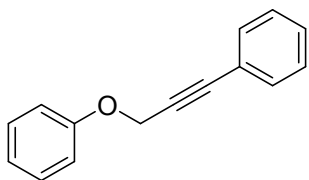
Prepared according to General Procedure A

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 2H), 7.20 (dd, *J* = 15.5, 7.1 Hz, 3H), 6.84 – 6.79 (m, 2H), 3.79 (s, 3H), 2.84 – 2.74 (m, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.97 – 1.86 (m, 2H);

¹³C NMR(100 MHz, CDCl₃) δ 159.02, 141.70, 132.87, 128.56, 128.34, 125.87, 116.10, 113.81, 88.17, 80.82, 55.24, 34.85, 30.42, 18.83.



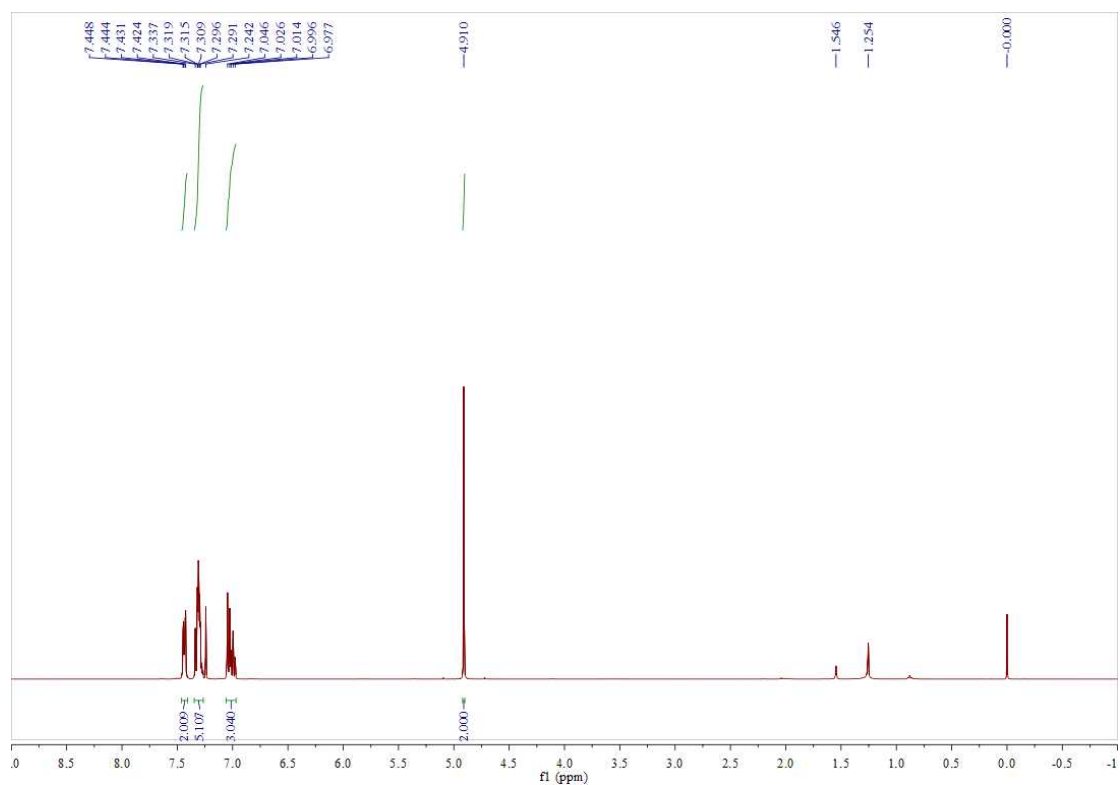
(3-phenoxyprop-1-yn-1-yl)benzene(1u)

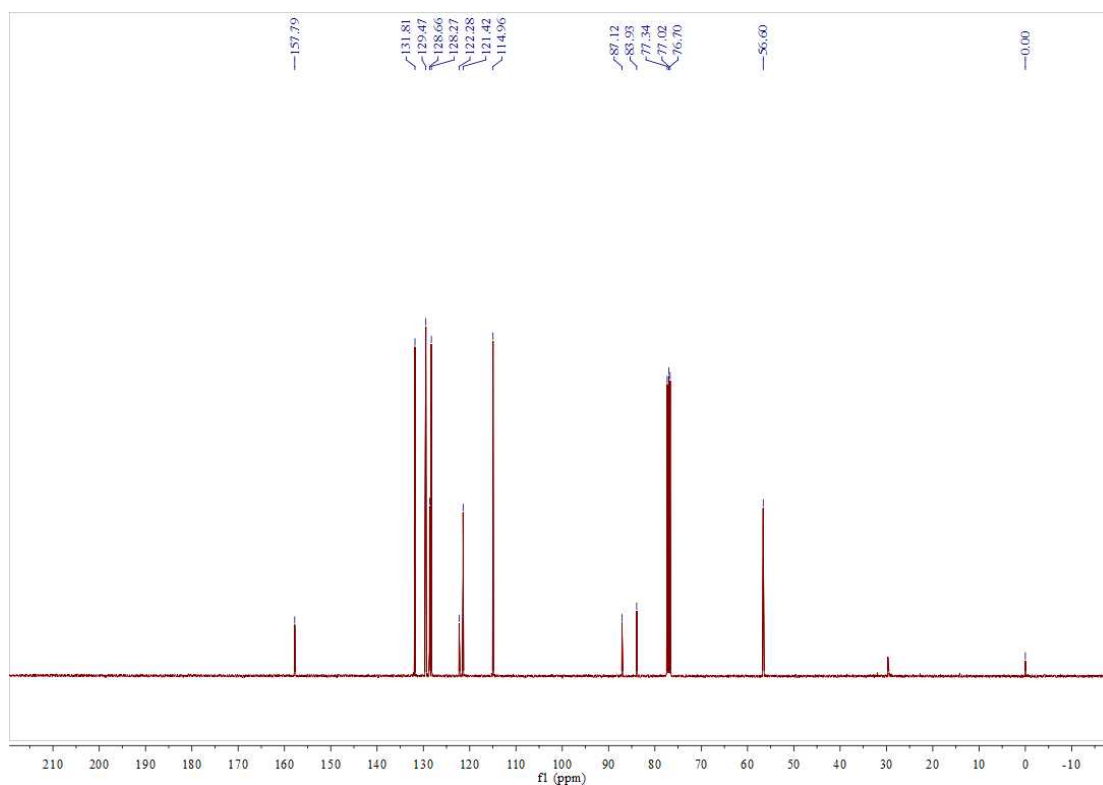


Prepared according to General Procedure B

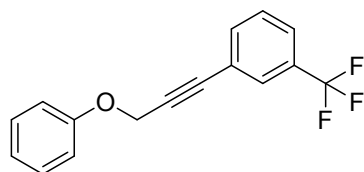
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 – 7.41 (m, 2H), 7.35 – 7.26 (m, 5H), 7.06 – 6.97 (m, 3H), 4.91 (s, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.79, 131.81, 129.47, 128.66, 128.27, 122.28, 121.42, 114.96, 87.12, 83.93, 56.60.





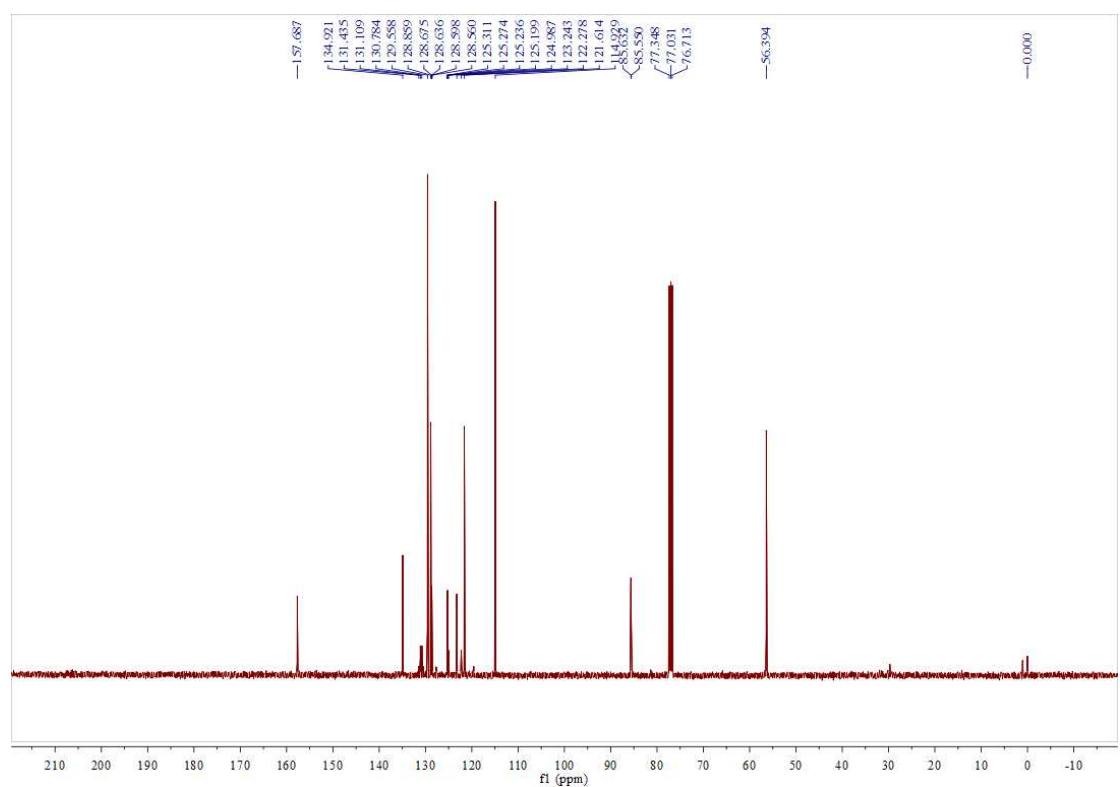
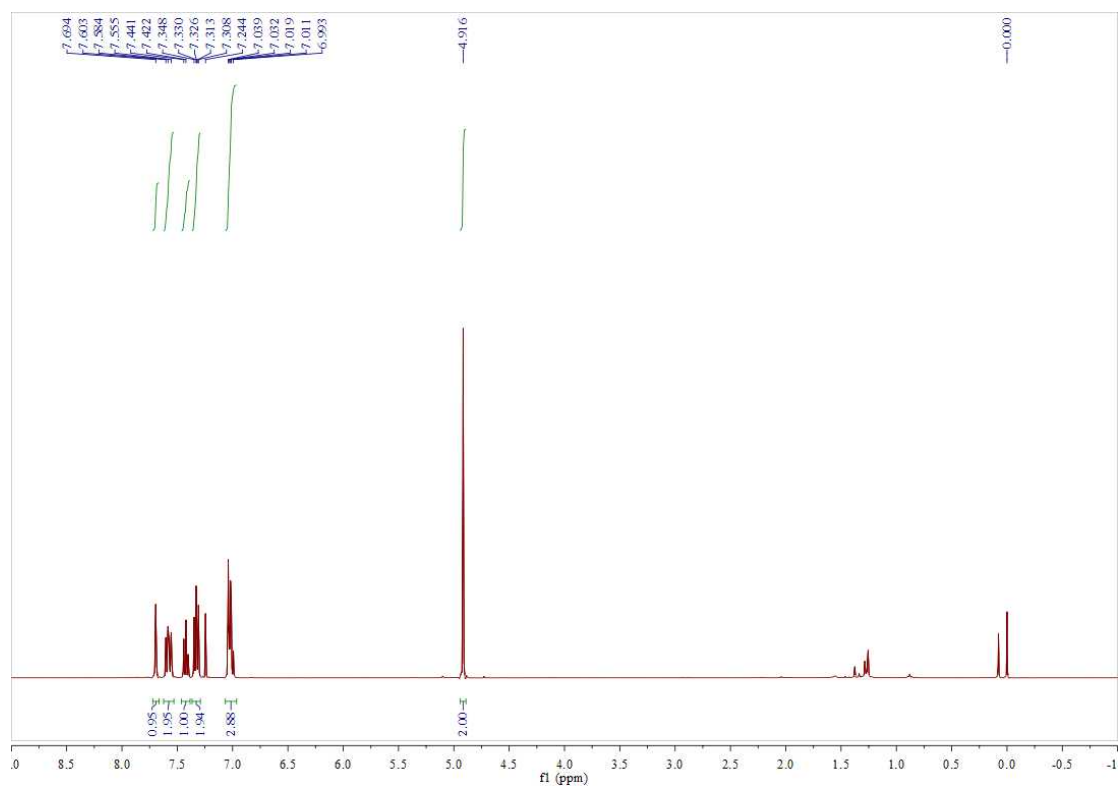
1-(3-phenoxyprop-1-yn-1-yl)-3-(trifluoromethyl)benzene(1v)



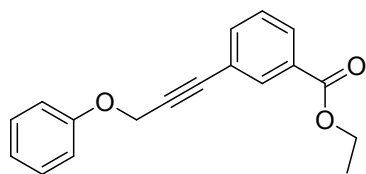
Prepared according to General Procedure **B**

¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 1H), 7.62 – 7.53 (m, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.07 – 6.96 (m, 3H), 4.92 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 157.69, 134.92, 130.95 (q, *J* = 32.8 Hz), 129.56, 128.86, 128.62 (q, *J* = 3.9 Hz), 125.26 (q, *J* = 3.7 Hz), 123.63 (q, *J* = 272.5 Hz), 123.24, 121.61, 114.93, 85.63, 85.55, 56.39.



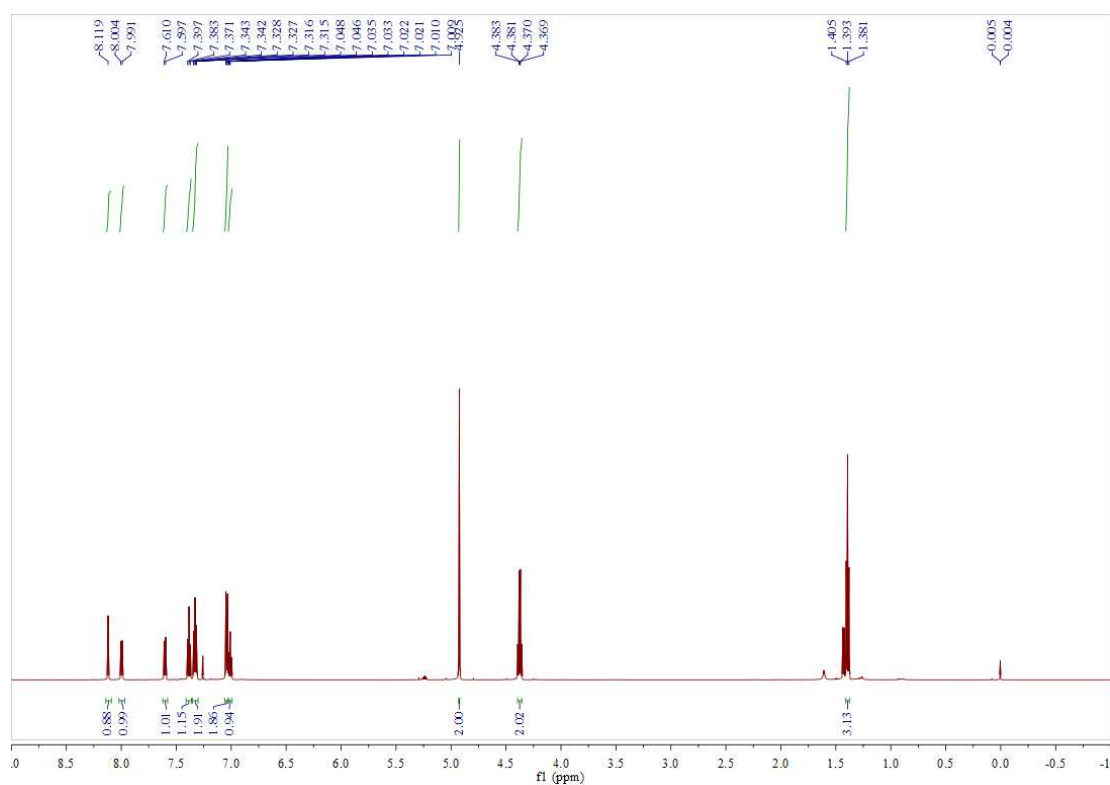
ethyl 3-(3-phenoxyprop-1-yn-1-yl)benzoate(1w)

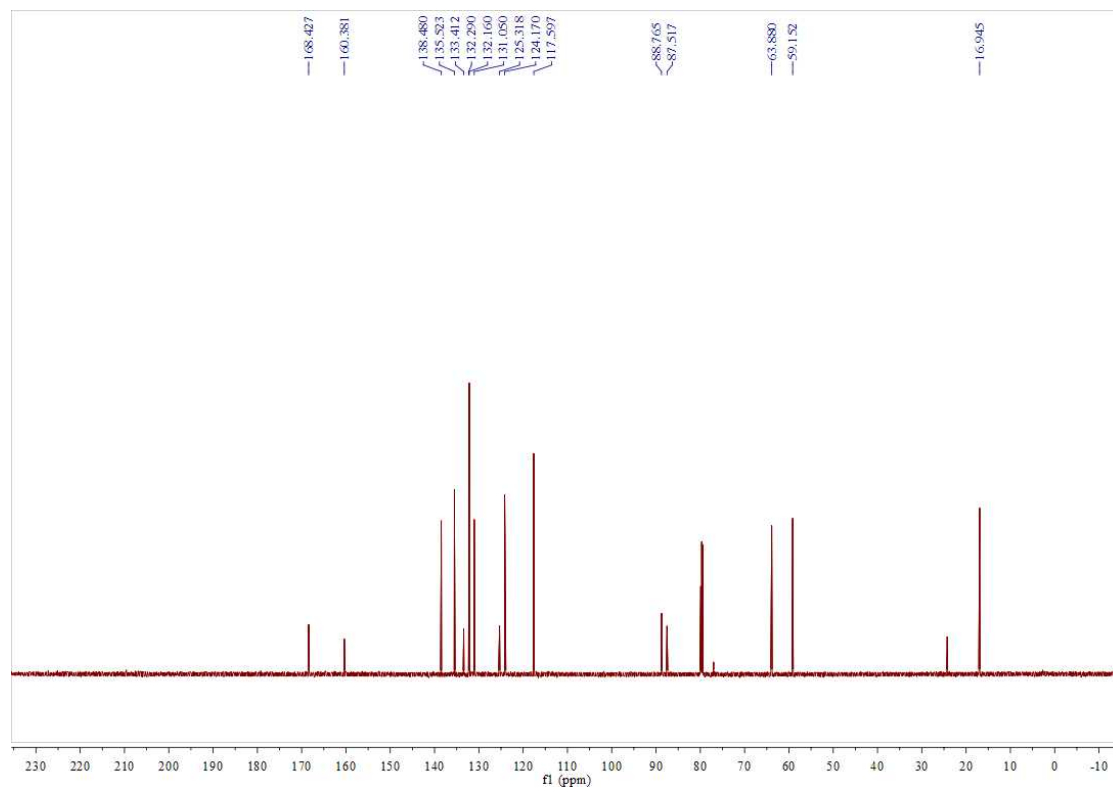


Prepared according to General Procedure B

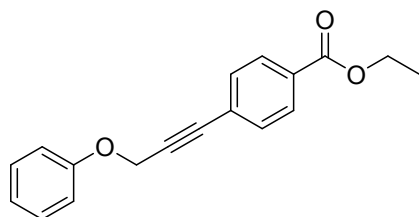
¹H NMR (600 MHz, $cdCl_3$) δ 8.12 (s, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.60 (d, $J = 7.7$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 7.35 – 7.30 (m, 2H), 7.04 (dd, $J = 7.9, 0.8$ Hz, 2H), 7.01 (td, $J = 7.4, 0.8$ Hz, 1H), 4.92 (s, 2H), 4.38 (dd, $J = 7.2, 0.7$ Hz, 2H), 1.39 (t, $J = 7.2$ Hz, 3H).

¹³C NMR (151 MHz, $cdCl_3$) δ 168.43, 160.38, 138.48, 135.52, 133.41, 132.29, 132.16, 131.05, 125.32, 124.17, 117.60, 88.76, 87.52, 63.88, 59.15, 16.94.





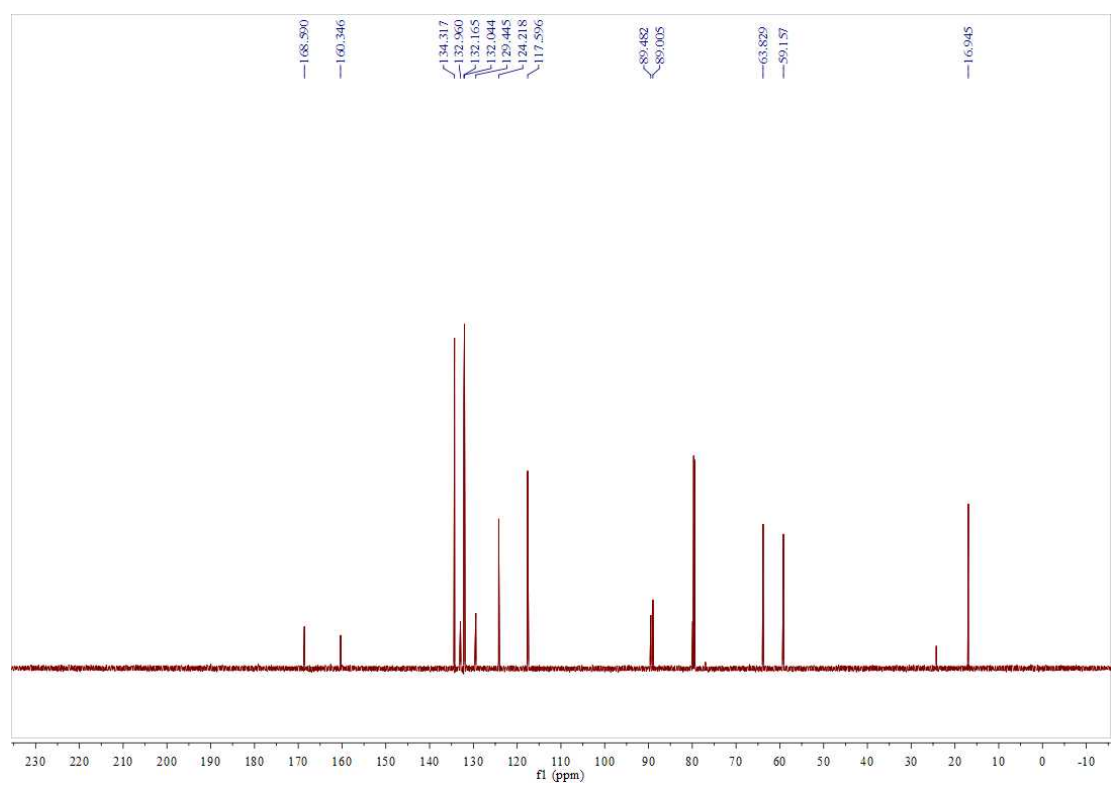
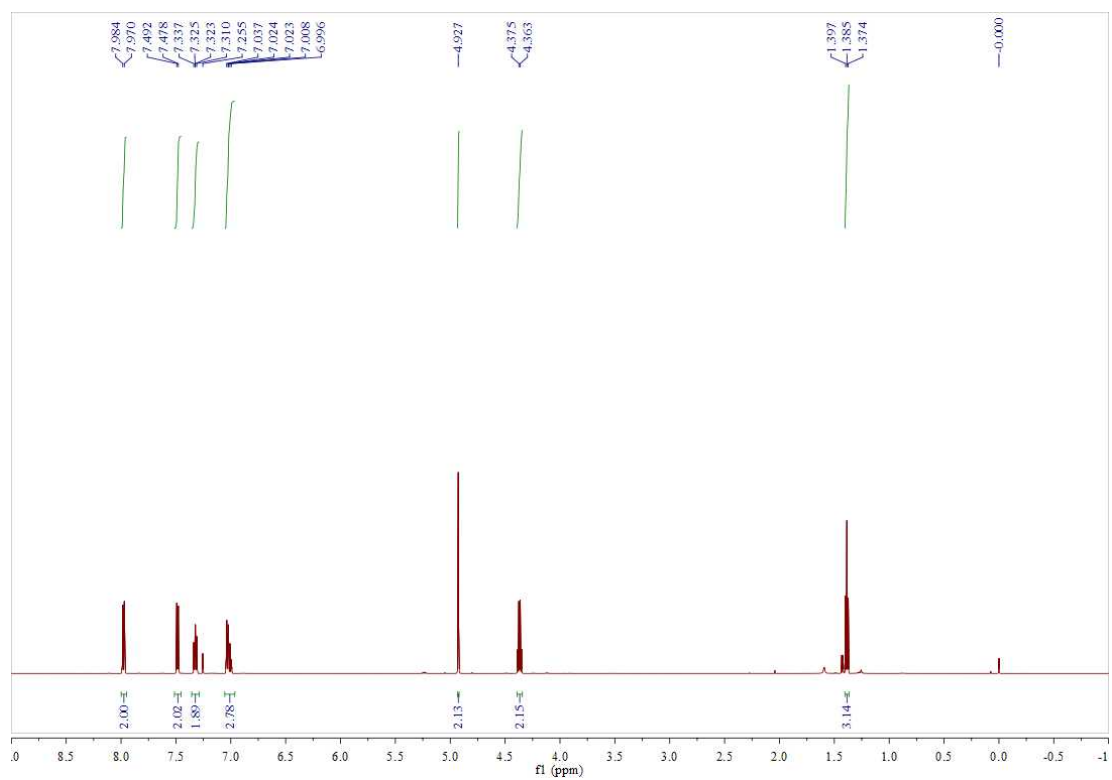
ethyl 4-(3-phenoxyprop-1-yn-1-yl)benzoate(1x)



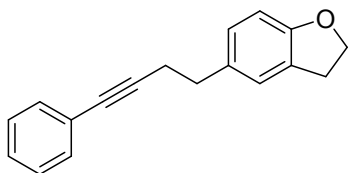
Prepared according to General Procedure **B**

¹H NMR (600 MHz, $cdCl_3$) δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.32 (dd, $J = 8.6, 7.4$ Hz, 2H), 7.05 – 6.96 (m, 3H), 4.93 (s, 2H), 4.37 (d, $J = 7.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (150 MHz, $cdCl_3$) δ 168.59, 160.35, 134.32, 132.96, 132.16, 132.04, 129.44, 124.22, 117.60, 89.48, 89.01, 63.83, 59.16, 16.95.



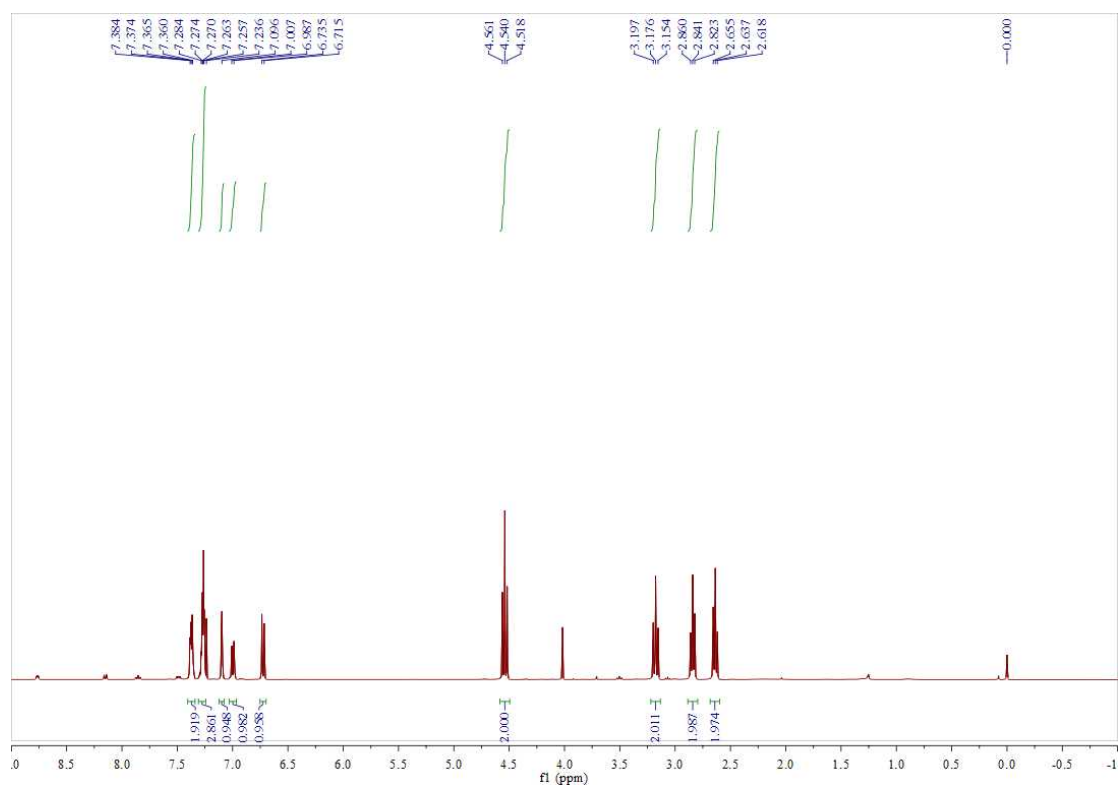
5-(4-phenylbut-3-yn-1-yl)-2,3-dihydrobenzofuran(1y)

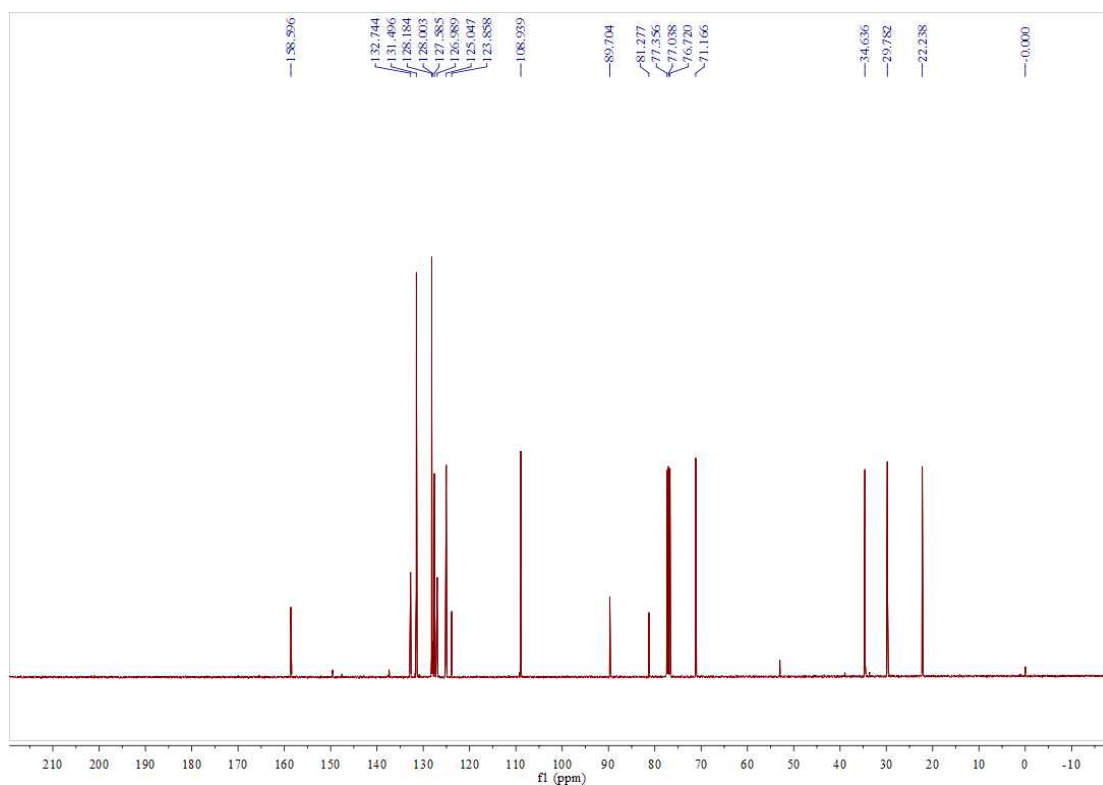


Prepared according to General Procedure A

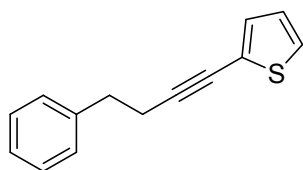
¹H NMR (400 MHz, CDCl₃) δ 7.37 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.10 (s, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.54 (t, *J* = 8.7 Hz, 2H), 3.18 (t, *J* = 8.7 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 158.60, 132.74, 131.50, 128.09, 127.59, 126.99, 125.05, 123.86, 108.94, 89.70, 81.28, 71.17, 34.64, 29.78, 22.24.





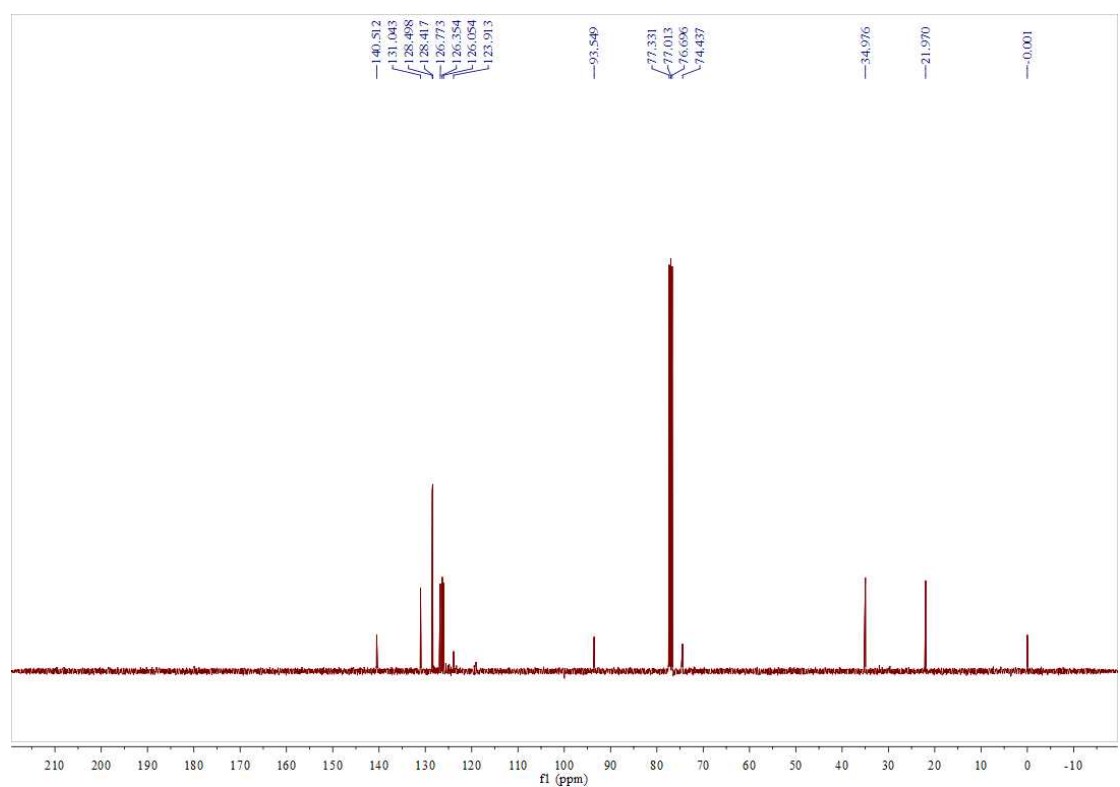
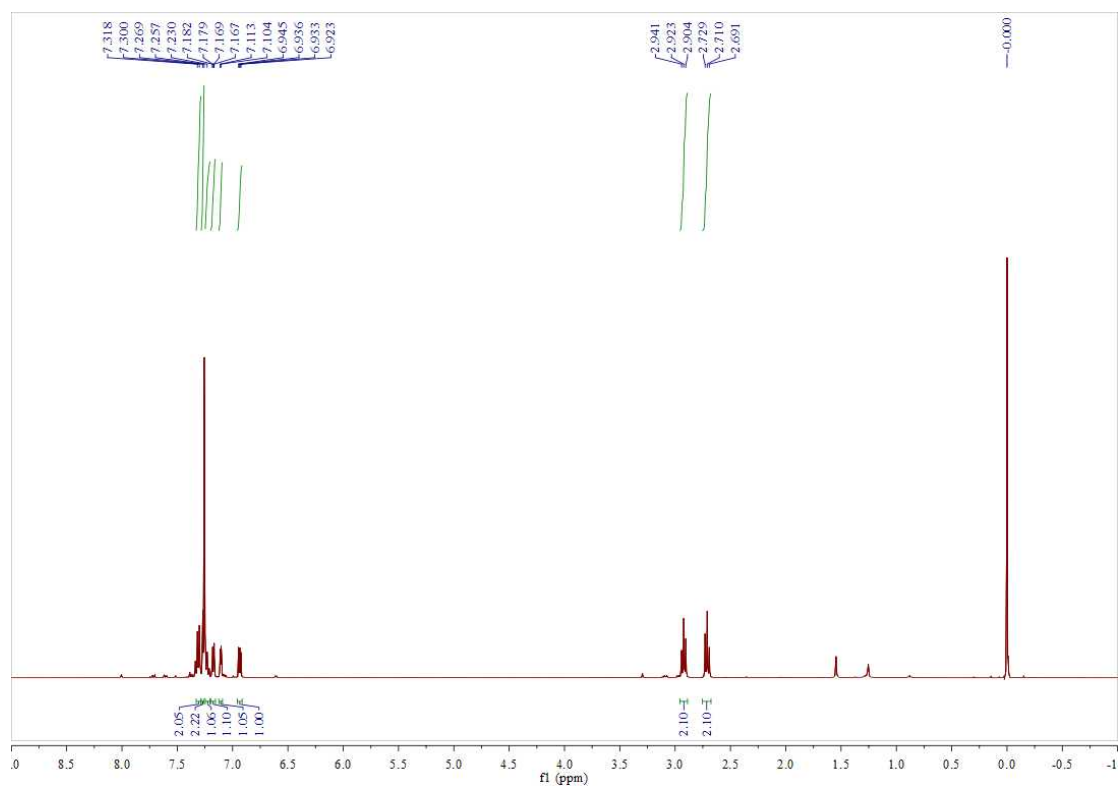
2-(4-phenylbut-1-yn-1-yl)thiophene(1z)



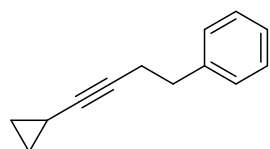
Prepared according to General Procedure A

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.29 (m, 2H), 7.27 (s, 2H), 7.23 (s, 1H), 7.17 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.12 – 7.09 (m, 1H), 6.93 (dd, *J* = 5.2, 3.6 Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 140.51, 131.04, 128.50, 128.42, 126.77, 126.35, 126.05, 123.91, 93.55, 74.44, 34.98, 21.97.



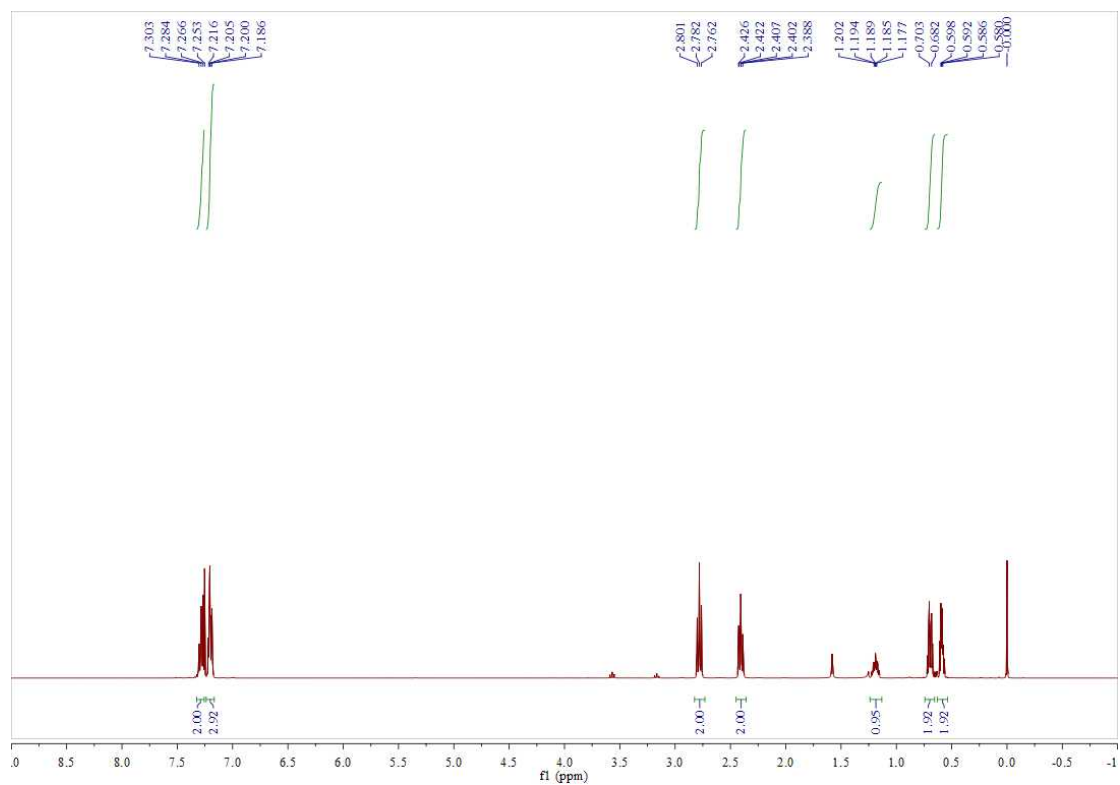
(4-cyclopropylbut-3-yn-1-yl)benzene(1aa)

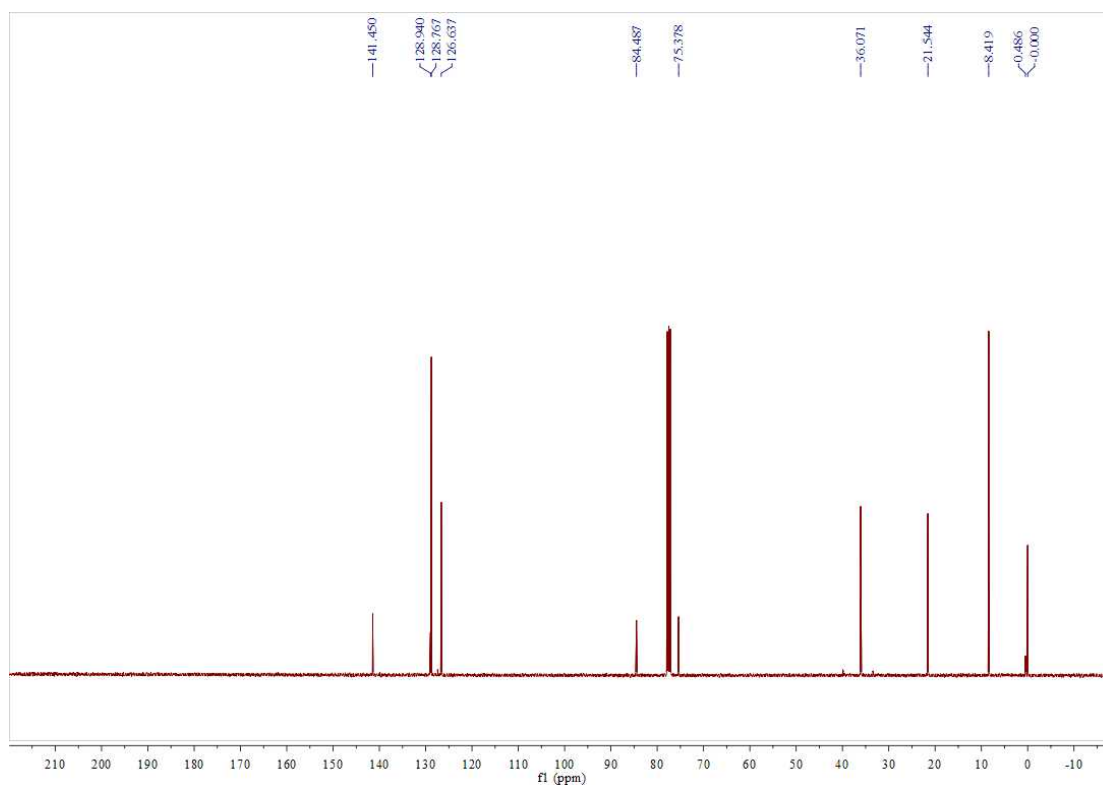


Prepared according to General Procedure A

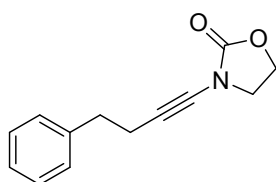
^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.26 (m, 2H), 7.20 (dd, $J = 7.1, 4.9$ Hz, 3H), 2.78 (t, $J = 7.7$ Hz, 2H), 2.40 (td, $J = 7.7, 1.9$ Hz, 2H), 1.24 – 1.13 (m, 1H), 0.74 – 0.65 (m, 2H), 0.59 (dt, $J = 7.1, 4.2$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 141.45, 128.94, 128.77, 126.64, 84.49, 75.38, 36.07, 21.54, 8.42, 0.49.





3-(4-phenylbut-1-yn-1-yl)oxazolidin-2-one(1ab)

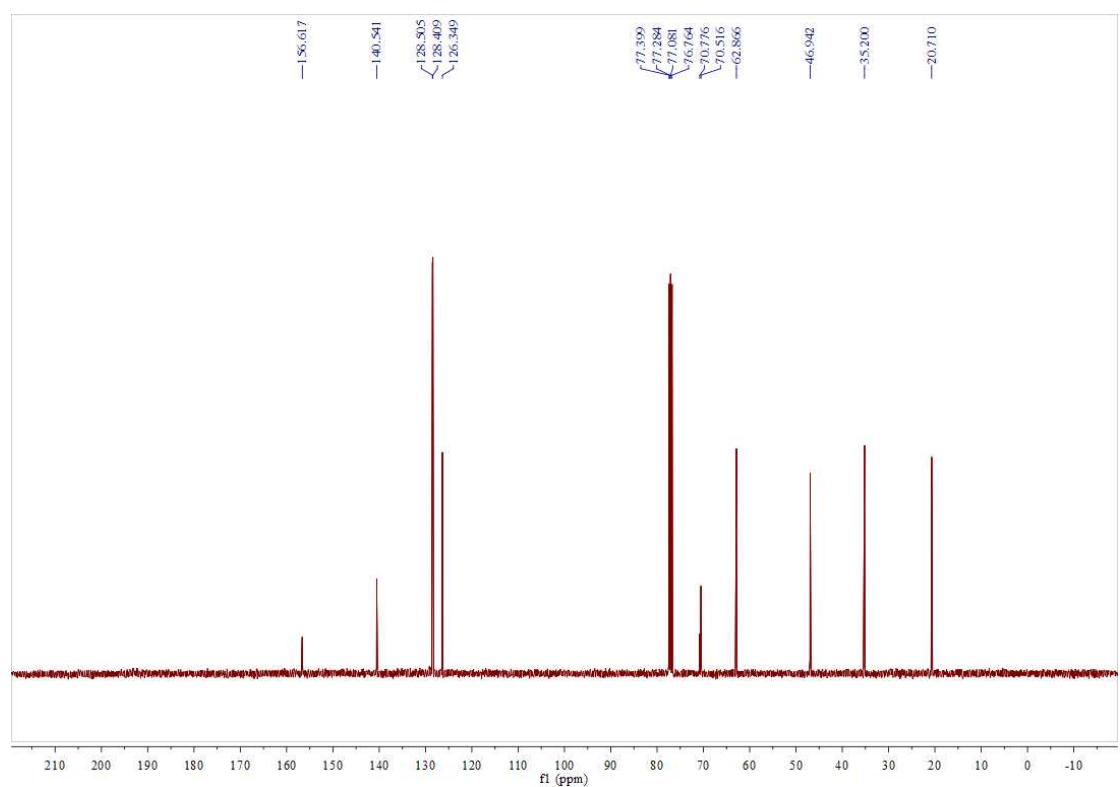
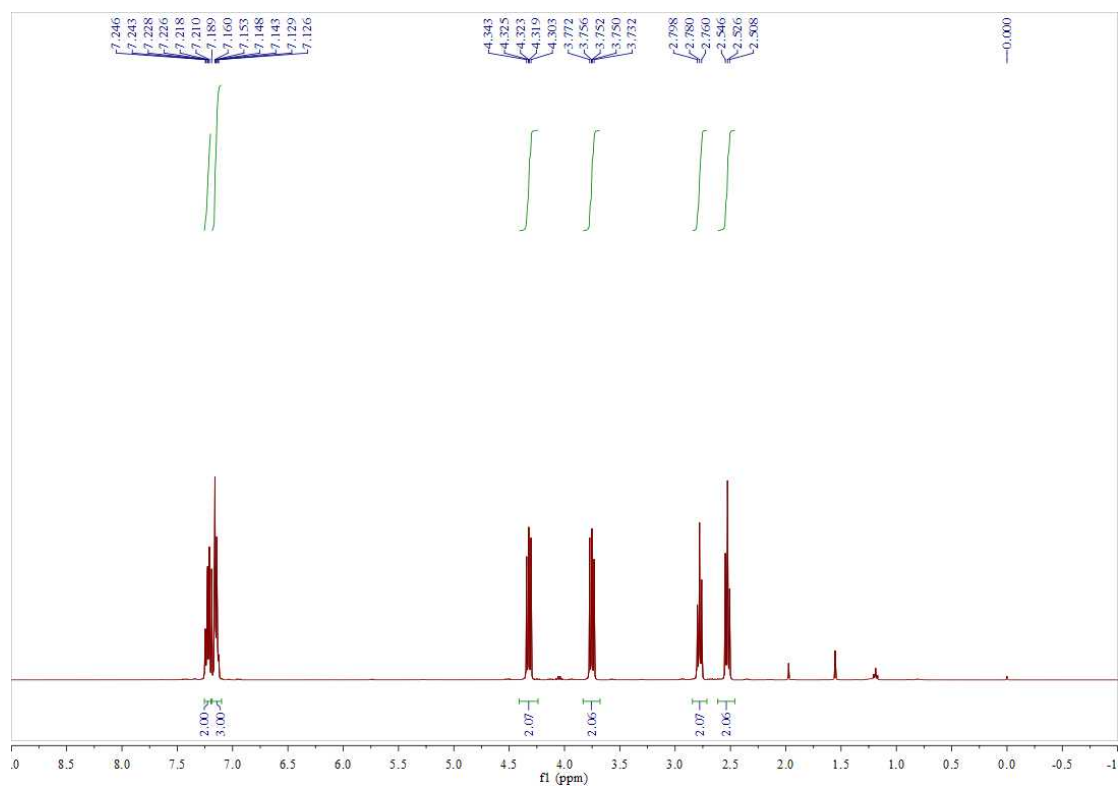


Prepared according to a procedure from S. S. Stahl *et al.*⁵

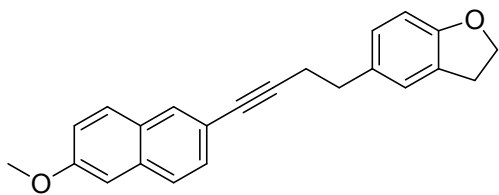
To a solution of oxazolidin-2-one (10 mmol), copper (II) chloride (0.4 mmol) and sodium carbonate (4 mmol) in toluene (20 mL) was added pyridine (4 mmol). Oxygen was bubbled through the reaction mixture (20 min). The reaction was heated to 70 °C under an atmosphere of oxygen. A solution of but-3-yn-1-ylbenzene (2 mmol) in toluene (20 mL) was added dropwise over 4 h, by use of a syringe pump. Once the addition was complete, the reaction mixture was stirred at 70 °C for a further 12 h. The reaction mixture was cooled to room temperature and filtered through a plug of celite, eluting with dichloromethane (3 × 25 mL). The solvent was removed *in vacuo* and the crude residue was purified by flash chromatography to give compound **1w** as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.20 (m, 2H), 7.19 – 7.10 (m, 3H), 4.41 – 4.24 (m, 2H), 3.83 – 3.68 (m, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 156.62, 140.54, 128.50, 128.41, 126.35, 70.78, 70.52, 62.87, 46.94, 35.20, 20.71.



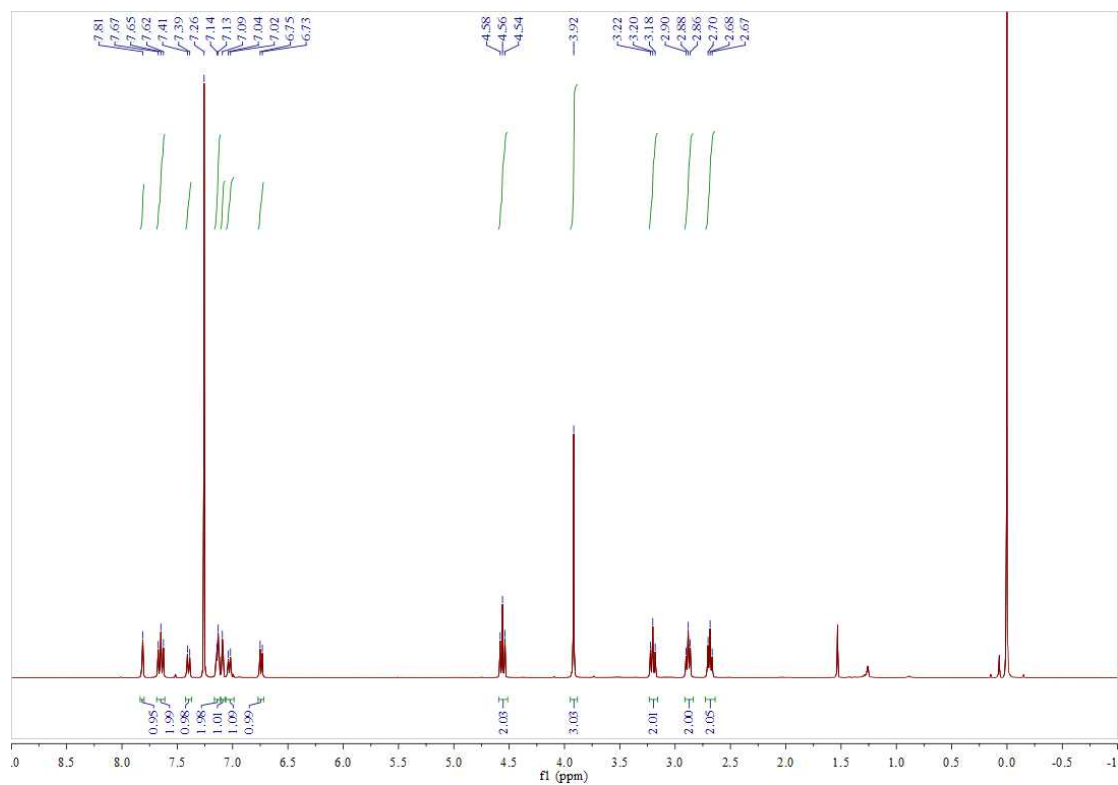
5-(4-(6-methoxynaphthalen-2-yl)but-3-yn-1-yl)-2,3-dihydrobenzofuran(1ac)

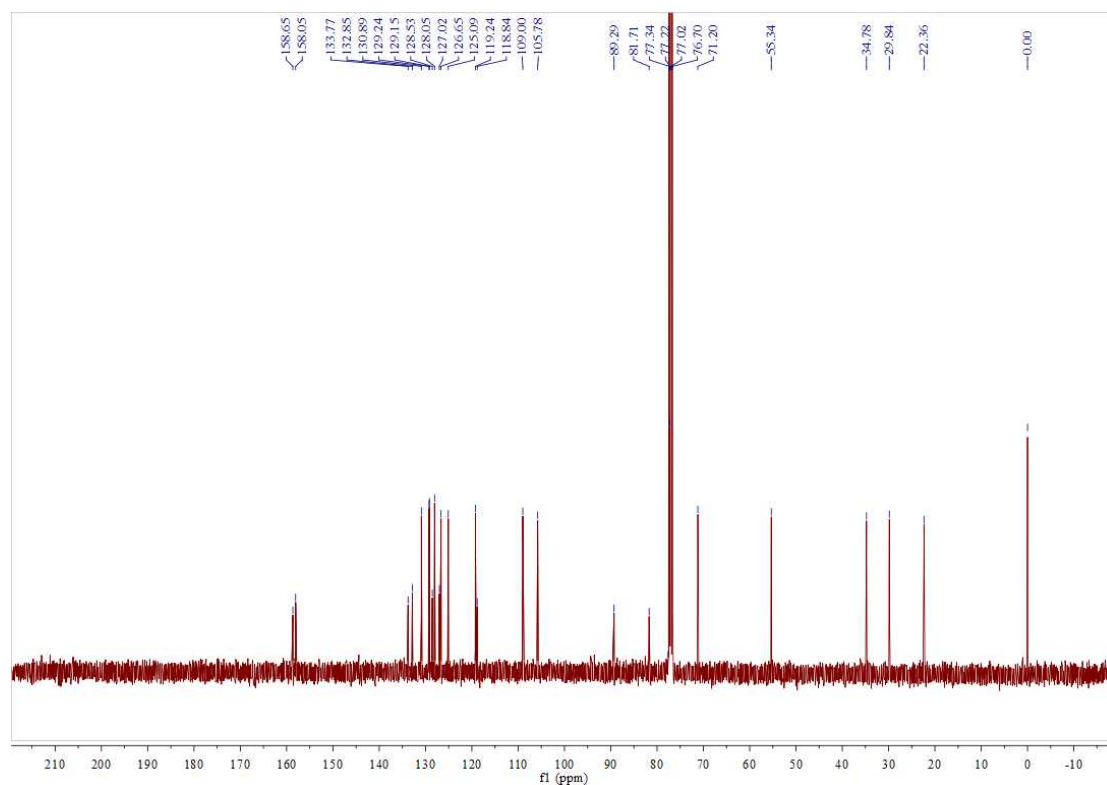


Prepared according to General Procedure A

¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.65 (t, *J* = 9.4 Hz, 2H), 7.40 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.17 – 6.97 (m, 4H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.56 (t, *J* = 8.7 Hz, 2H), 3.93 (s, 3H), 3.20 (t, *J* = 8.6 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 158.65, 158.05, 133.77, 132.85, 130.89, 129.24, 129.15, 128.53, 128.05, 127.02, 126.65, 125.09, 119.24, 118.84, 109.00, 105.78, 89.29, 81.71, 71.20, 55.34, 34.78, 29.84, 22.36.





Reference:

- [1] A. J. Walkinshaw, W.-S. Xu, M. G. Suero, M. J. Gaunt, *J. Am. Chem. Soc.*, 2013, **135**, 12532-12535.
- [2] S. J. Pastine, S.-W. Youn, D. Sames, *Org. Lett.*, 2003, **5**, 7.
- [3] W.-W. Qiu, K. Surendra, L. Yin, and E. J. Corey, *Org. Lett.*, 2011, **13**, 5893.
- [4] T.-L. Yao, M. A. Campo, R. C. Larock, *J. Org. Chem.*, 2005, **70**, 3511.
- [5] T. Hamada, X. Ye, S. S. Stahl, *J. Am. Chem. Soc.*, 2008, **130**, 833.

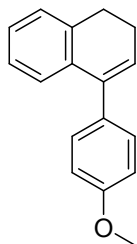
III. General Procedure for Cu-Catalyzed Intramolecular Hydroarylation of Alkynes

a. General procedure for the synthesis of the Products

A 10 mL over-dried Schlenk tube was charged with corresponding alkyne (0.1 mmol) (if solid), Cu(OTf)₂ (10 mol%, 3.62 mg). The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, corresponding alkyne (0.1 mmol) (if liquid) and solvent (1 mL) were added by syringe. The tube was sealed and the mixture was allowed to stir in a preheated oil bath at 60 °C for 4 h. The mixture was cooled to room temperature when the reaction was completed. Next, the organic solvent was concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate to give the product **2**.

b. Products Spectra data

4-(4-methoxyphenyl)-1,2-dihydronaphthalene(II)

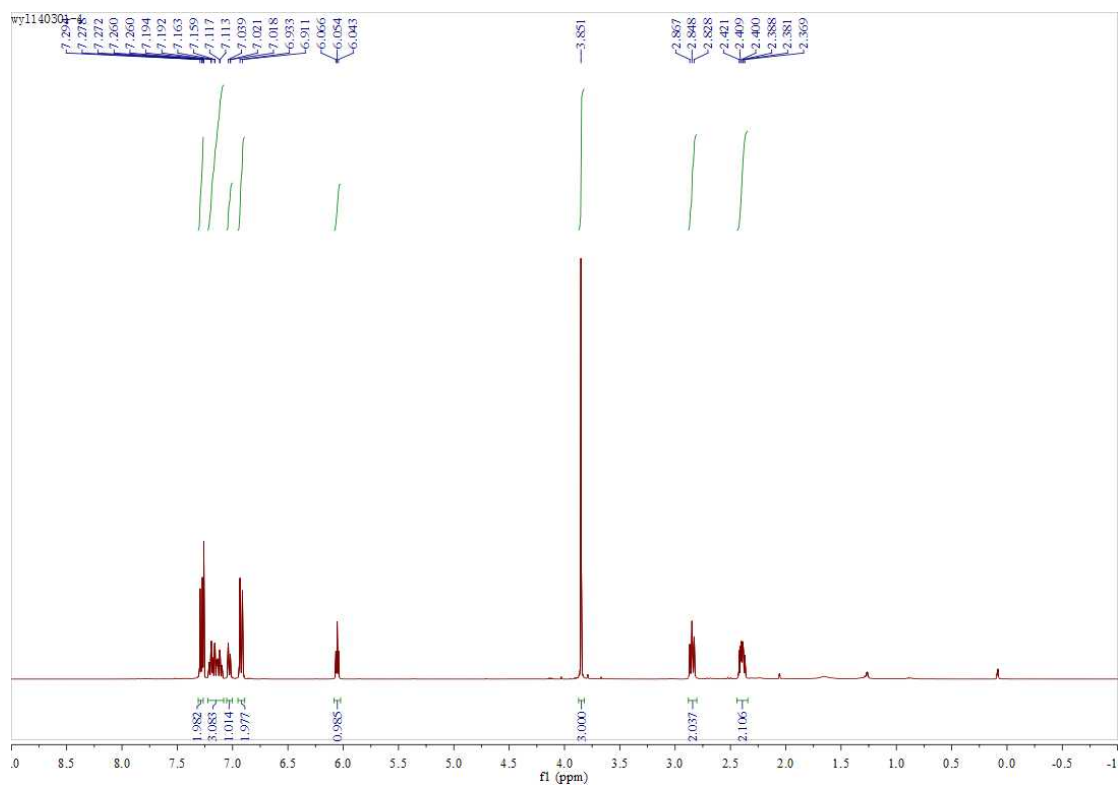


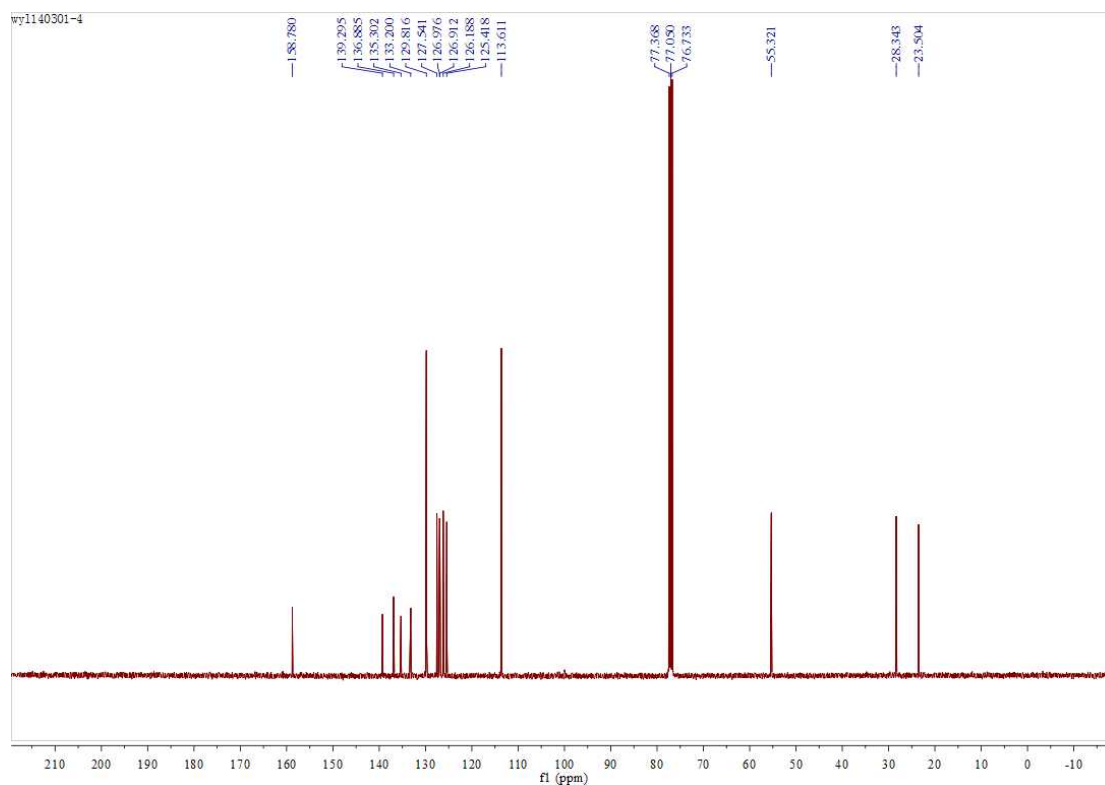
white solid (89%, 21mg). Mp: 79 – 80 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.08 (m, 3H), 7.05 – 7.00 (m, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.05 (t, *J* = 4.7 Hz, 1H), 3.85 (s, 3H), 2.85 (t, *J* = 7.9 Hz, 2H), 2.44 – 2.34 (m, 2H).

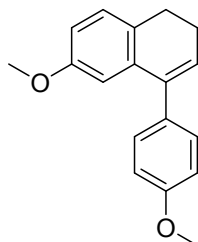
¹³C NMR (100 MHz, CDCl₃) δ 158.78, 139.30, 136.88, 135.30, 133.20, 129.82, 127.54, 126.98, 126.91, 126.19, 125.42, 113.61, 55.32, 28.34, 23.50.

HRMS calcd for C₁₇H₁₆O ([M]⁺): 236.1201; found 236.1198.





6-methoxy-4-(4-methoxyphenyl)-1,2-dihydronaphthalene(2a)

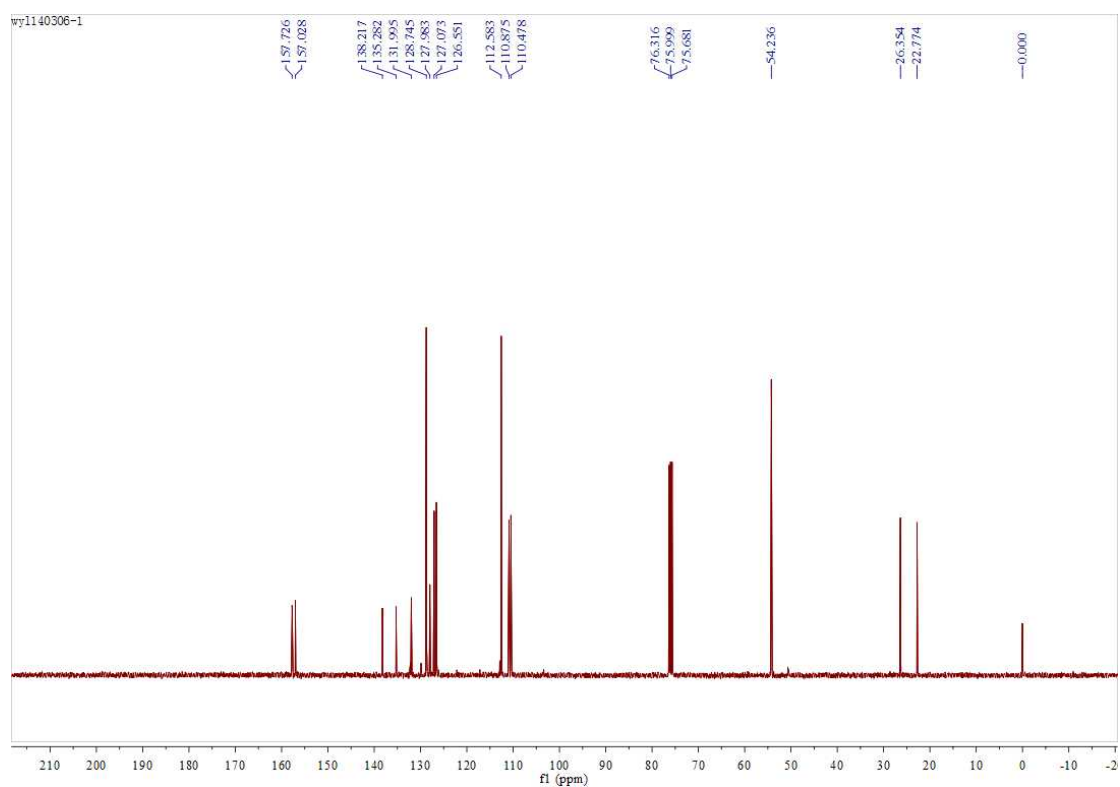
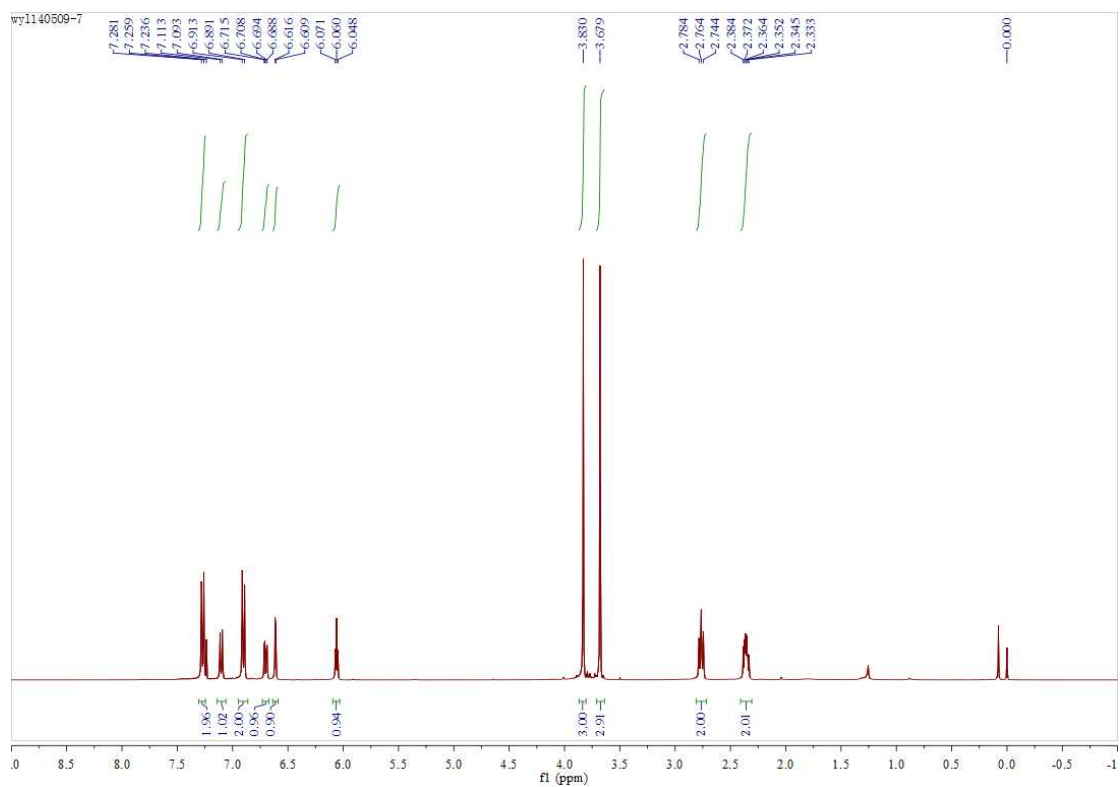


white solid (90%, 24mg). Mp: 80 – 81 °C.

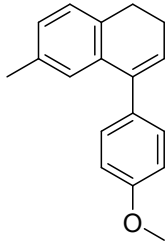
¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.70 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.61 (d, *J* = 2.6 Hz, 1H), 6.06 (t, *J* = 4.7 Hz, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 2.76 (t, *J* = 7.9 Hz, 2H), 2.36 (td, *J* = 7.9, 4.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 158.80, 158.10, 139.29, 136.36, 133.07, 129.82, 129.06, 128.15, 127.63, 113.66, 111.95, 111.55, 77.39, 77.07, 76.76, 55.31, 27.43, 23.85.

HRMS calcd for C₁₈H₁₈O₂ ([M]⁺): 266.1307; found 266.1301.



4-(4-methoxyphenyl)-6-methyl-1,2-dihydronaphthalene(2b)

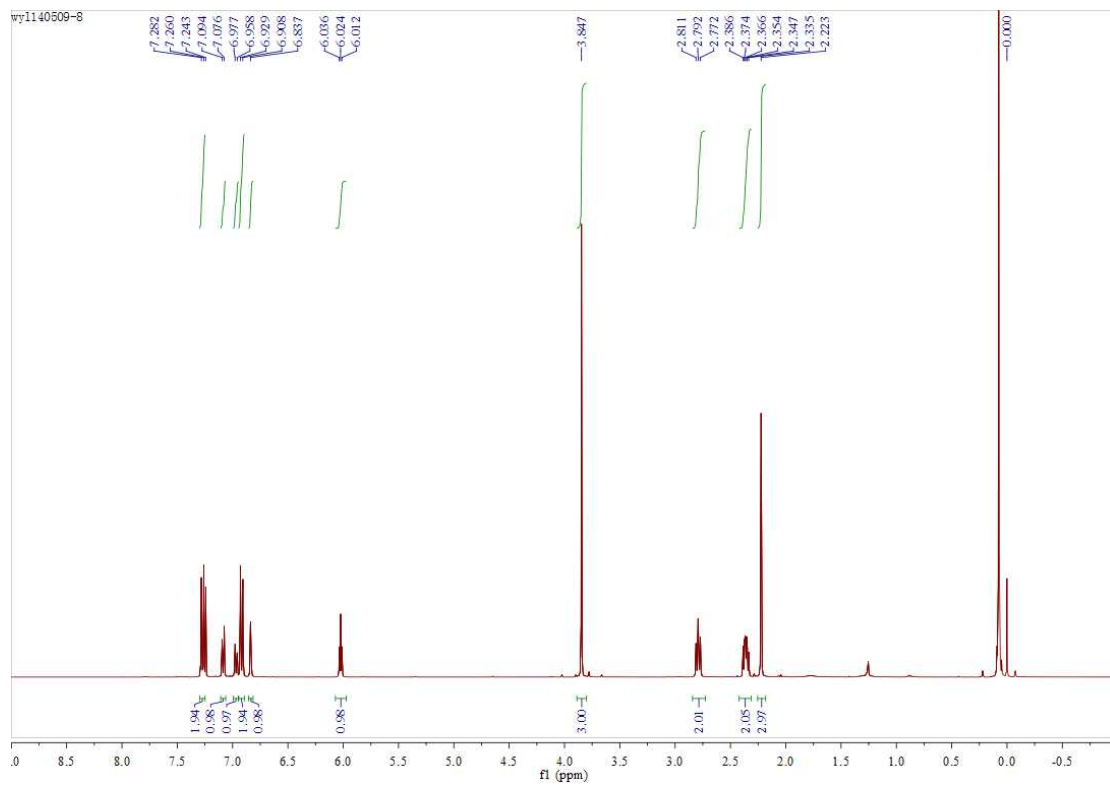


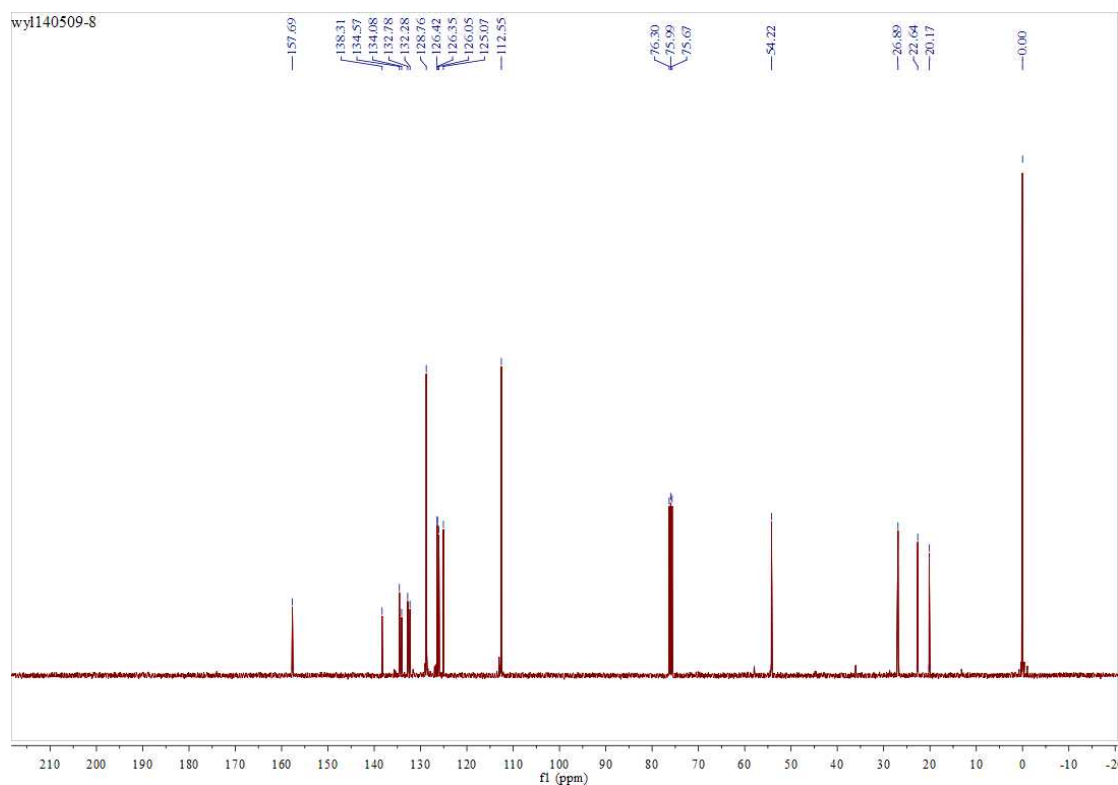
Colorless oil (89%, 22mg)

¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 1H), 6.02 (t, *J* = 4.7 Hz, 1H), 3.85 (s, 3H), 2.79 (t, *J* = 7.9 Hz, 2H), 2.42 – 2.31 (m, 2H), 2.22 (s, 3H).

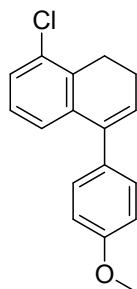
¹³C NMR (100 MHz, CDCl₃) δ 157.69, 138.31, 134.57, 134.08, 132.78, 132.28, 128.76, 126.42, 126.35, 126.05, 125.07, 112.55, 54.22, 26.89, 22.64, 20.17.

HRMS calcd for C₁₈H₁₈O([M]⁺): 250.1358; found 250.1355.





8-chloro-4-(4-methoxyphenyl)-1,2-dihydronaphthalene(2c)

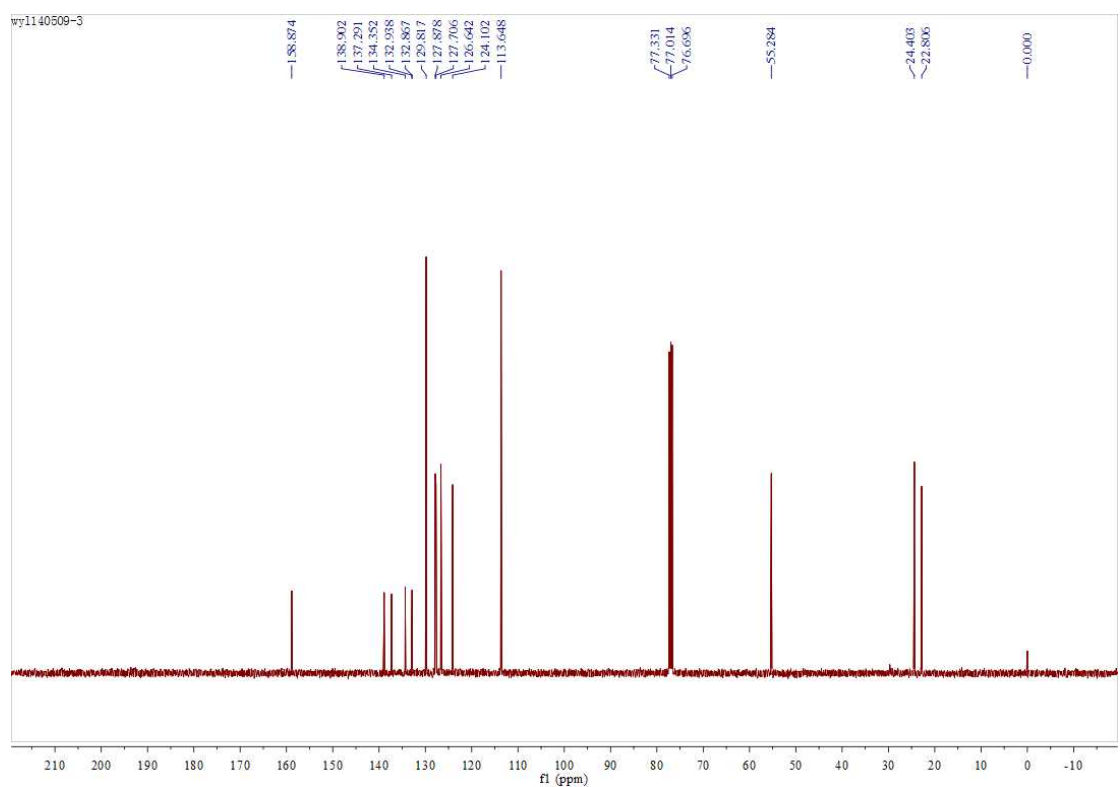
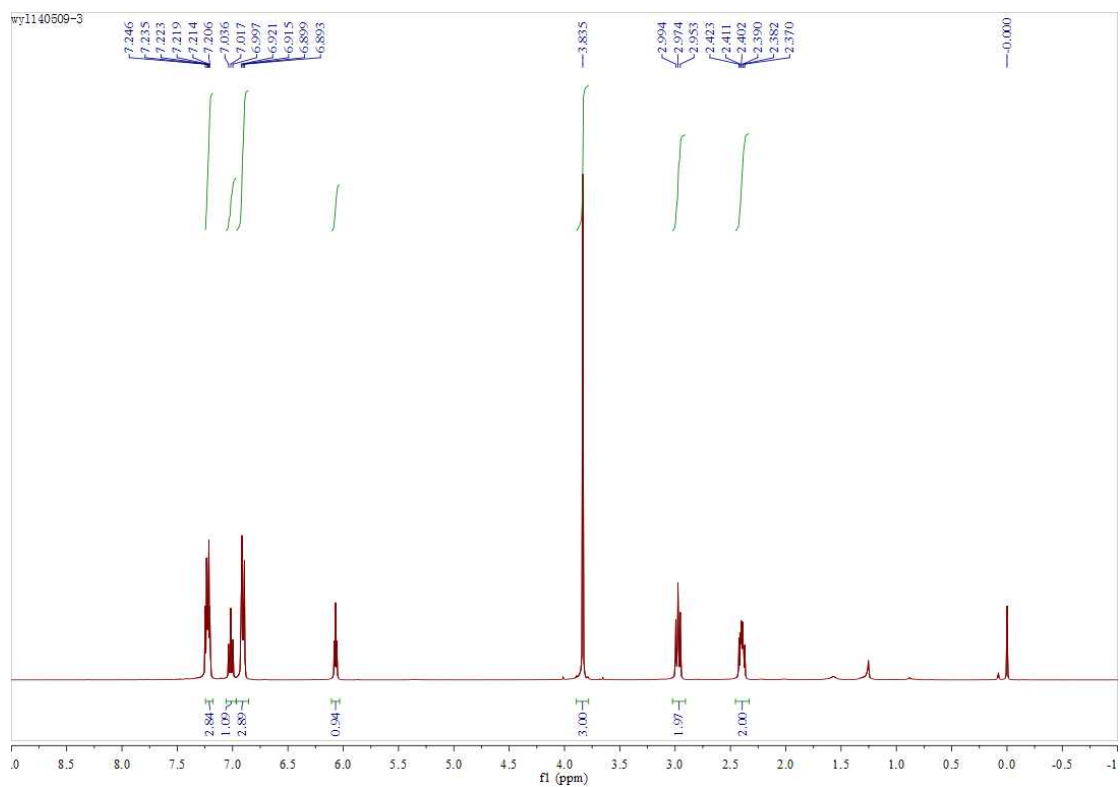


Colorless oil (75%, 20mg).

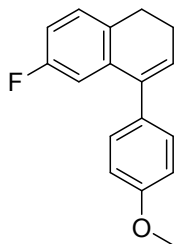
¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.18 (m, 3H), 7.02 (t, *J* = 7.9 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 3H), 6.07 (t, *J* = 4.7 Hz, 1H), 3.83 (s, 3H), 2.97 (t, *J* = 8.1 Hz, 2H), 2.40 (td, *J* = 8.1, 4.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 158.87, 138.90, 137.29, 134.35, 132.94, 132.87, 129.82, 127.88, 127.71, 126.64, 124.10, 113.65, 55.28, 24.40, 22.81.

HRMS calcd for C₁₇H₁₅ClO([M]⁺): 270.0811; found 270.0810.



6-fluoro-4-(4-methoxyphenyl)-1,2-dihydronaphthalene(2d)



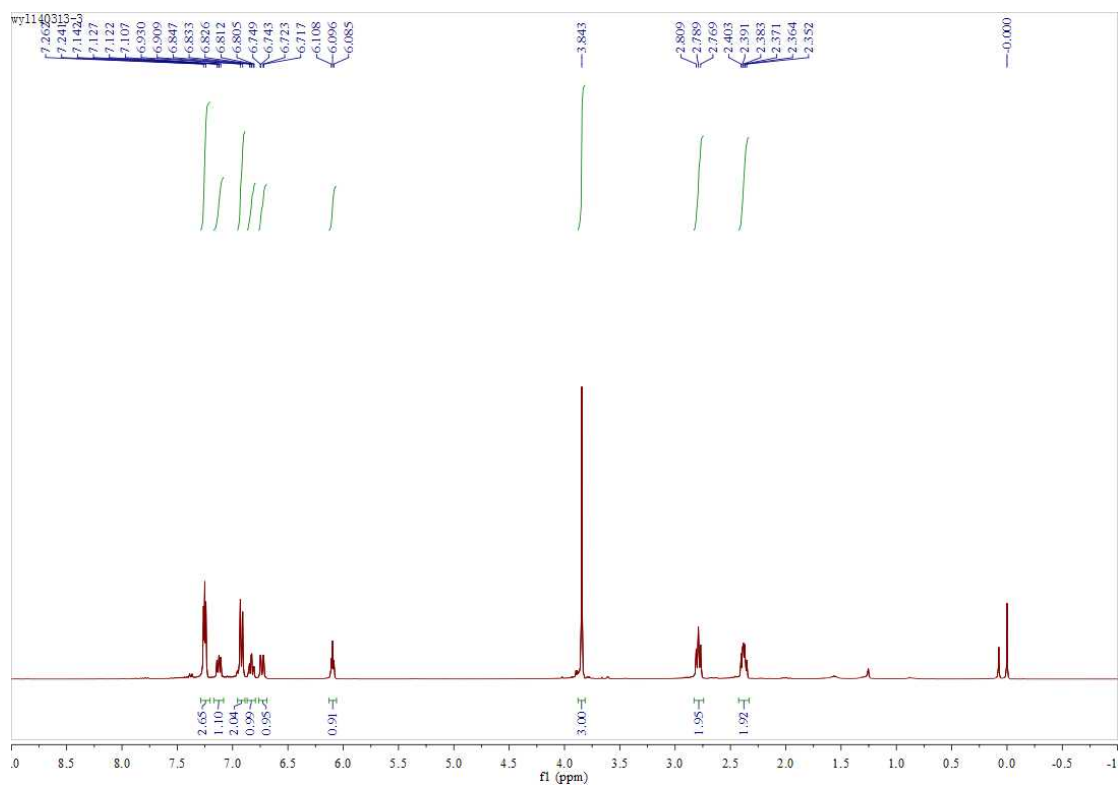
Colorless oil (83%, 21mg).

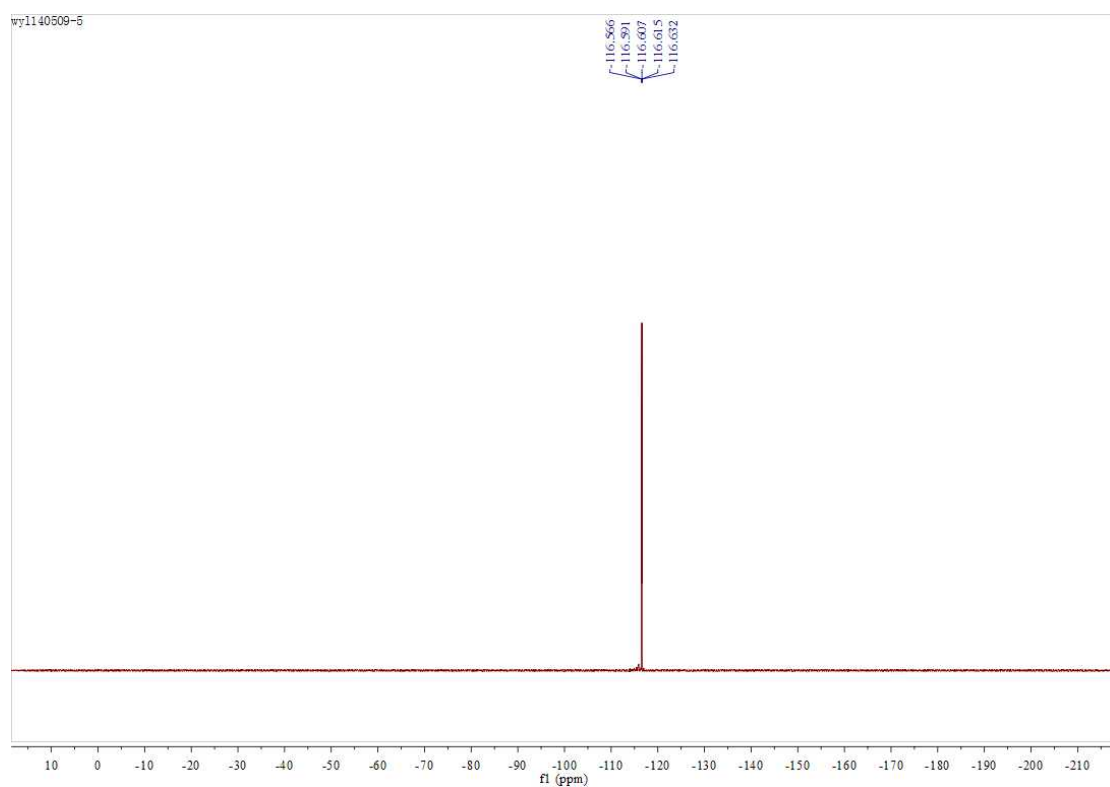
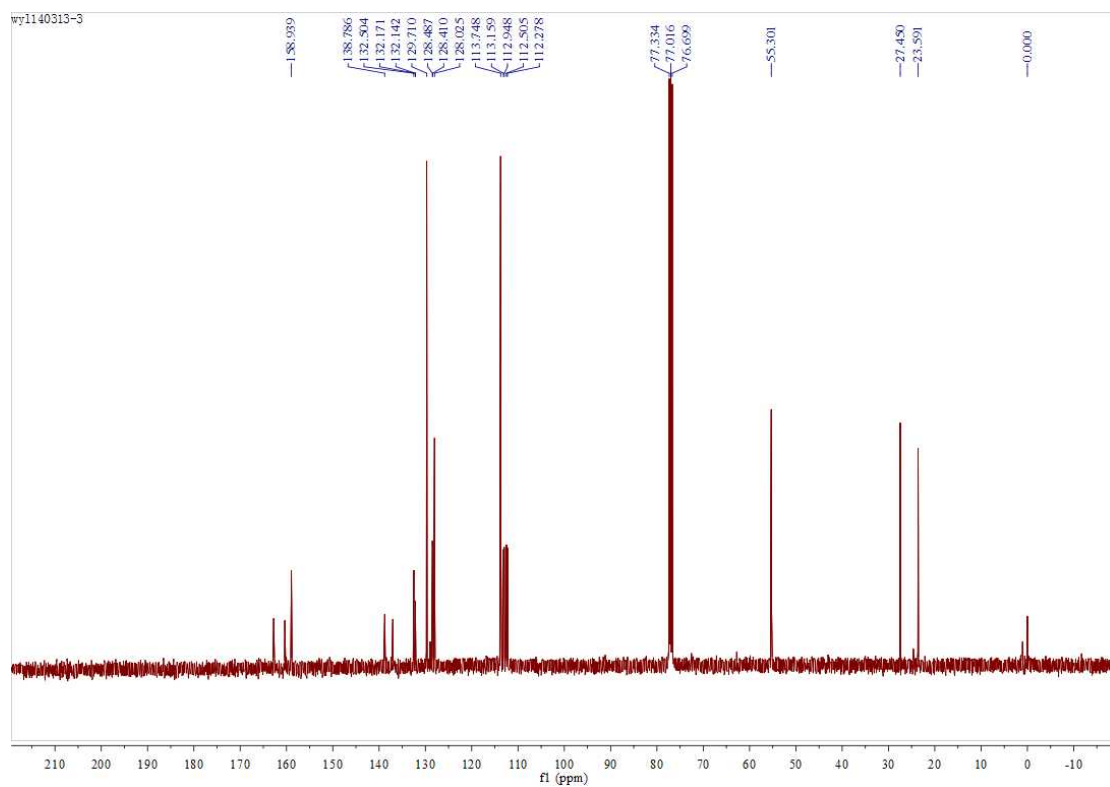
¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 8.7 Hz, 2H), 7.12 (dd, *J* = 7.9, 6.1 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.87 – 6.79 (m, 1H), 6.73 (dd, *J* = 10.4, 2.5 Hz, 1H), 6.10 (t, *J* = 4.6 Hz, 1H), 3.84 (s, 3H), 2.79 (t, *J* = 7.9 Hz, 2H), 2.38 (td, *J* = 7.9, 4.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 161.55 (d, *J* = 242.0 Hz) 158.94, 138.77(d, *J* = 2.1 Hz), 132.50, 132.16 (d, *J* = 3.0 Hz), 129.71, 128.45 (d, *J* = 7.8 Hz), 128.03, 113.75, 113.05(d, *J* = 21.2 Hz), 112.39(d, *J* = 22.8Hz), 55.30, 27.45, 23.59.

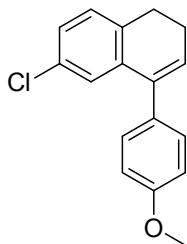
¹⁹F NMR (376 MHz, CDCl₃) δ -116.54 – -116.66 (m).

HRMS calcd for C₁₇H₁₅FO([M]⁺): 254.1107; found 254.1109.





6-chloro-4-(4-methoxyphenyl)-1,2-dihydronaphthalene(2e)

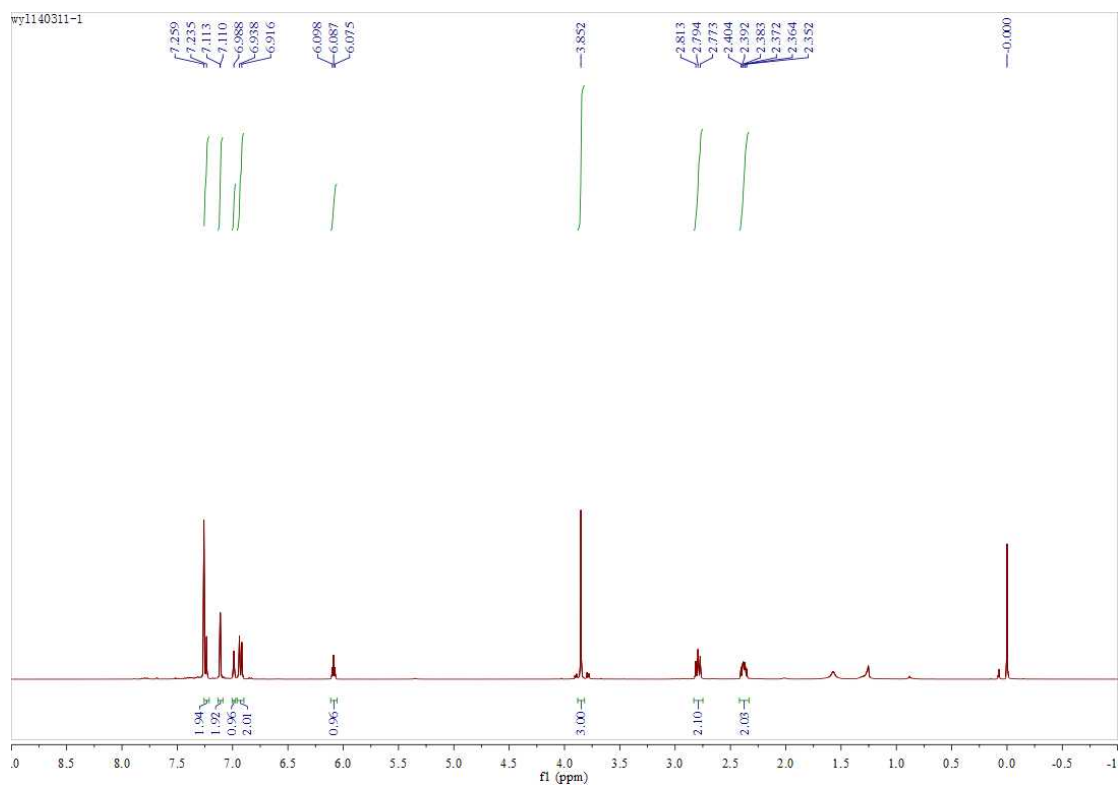


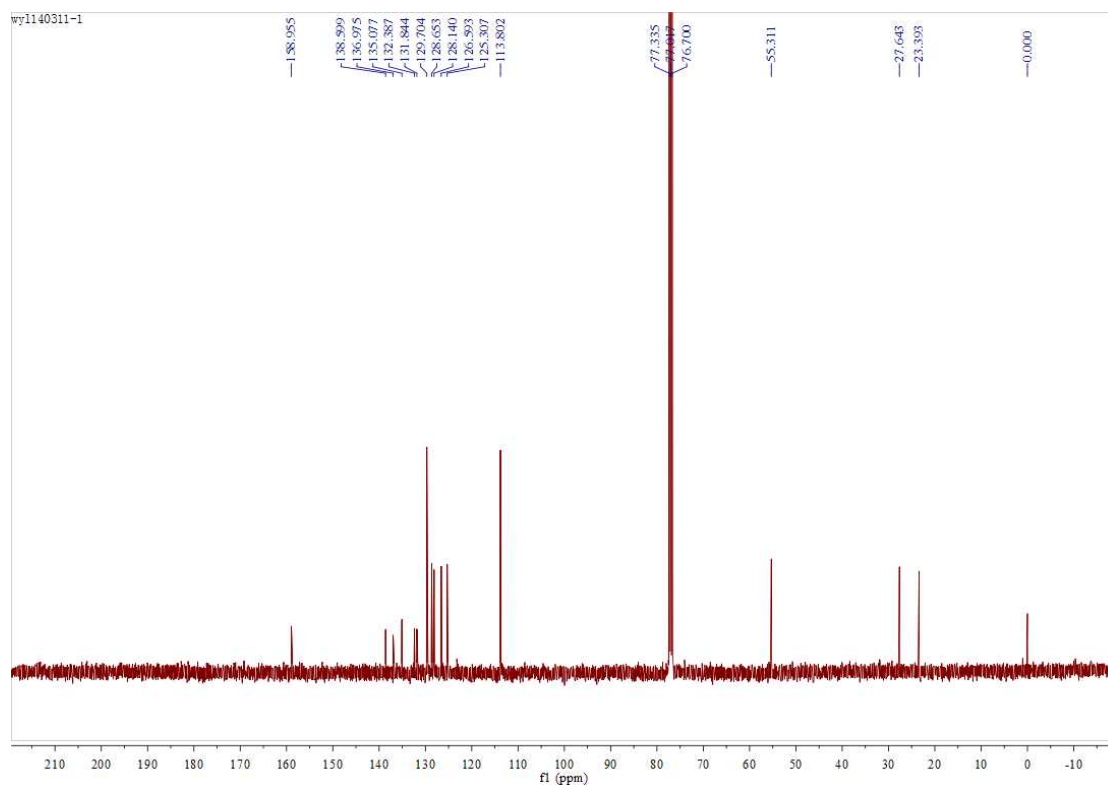
Colorless oil (80%, 22mg).

¹H NMR (400 MHz, CDCl₃) δ 7.23 (s, 2H), 7.11 (d, *J* = 1.0 Hz, 2H), 6.99 (s, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.09 (t, *J* = 4.7 Hz, 1H), 3.85 (s, 3H), 2.83 – 2.75 (m, 2H), 2.38 (td, *J* = 8.0, 4.8 Hz, 2H).

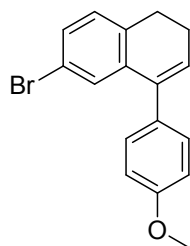
¹³C NMR (100 MHz, CDCl₃) δ 158.95, 138.60, 135.08, 132.39, 131.84, 129.70, 128.65, 128.14, 126.59, 125.31, 113.80, 55.31, 27.64, 23.39.

HRMS calcd for C₁₇H₁₅ClO([M]⁺): 270.0811; found 270.0811.





6-bromo-4-(4-methoxyphenyl)-1,2-dihydronaphthalene(2f)

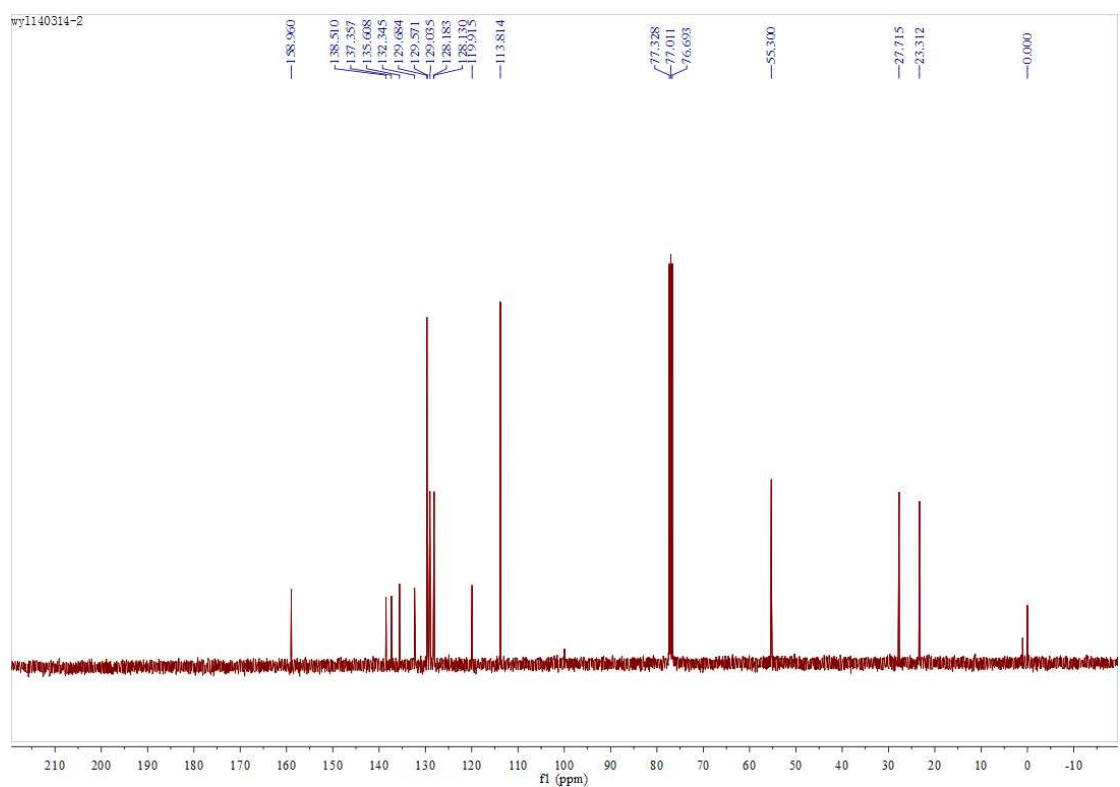
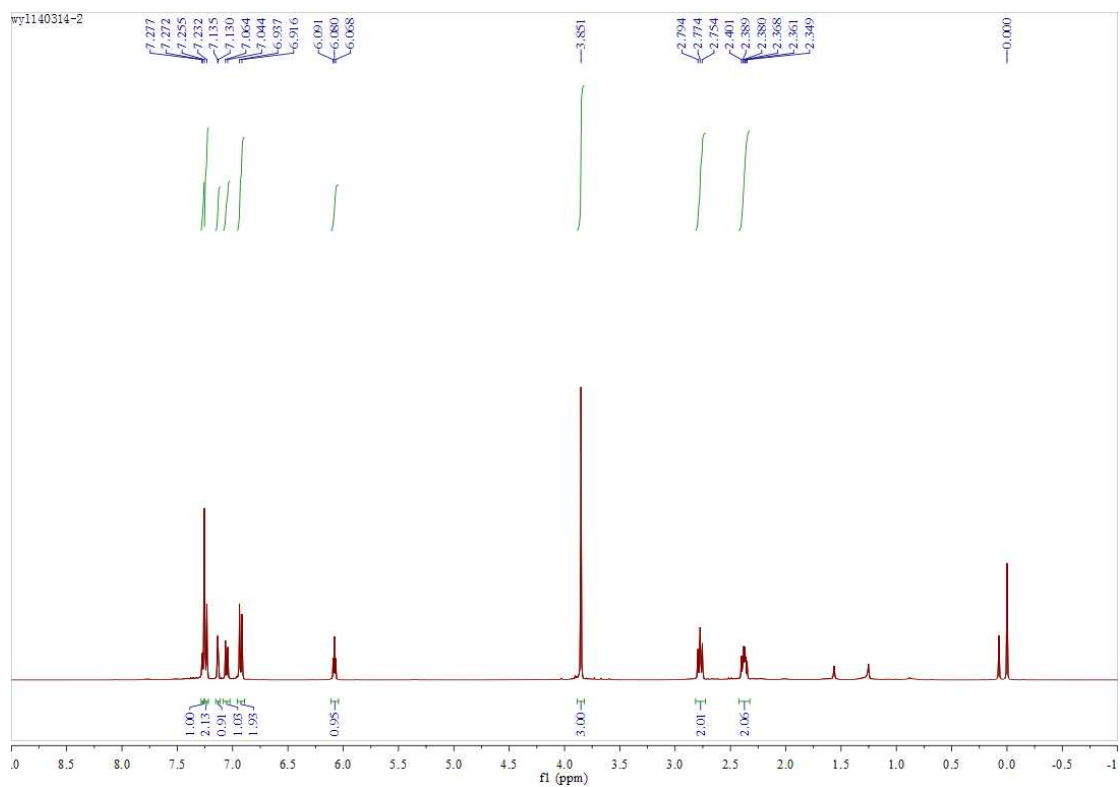


Colorless oil (92%, 29mg)

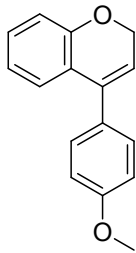
¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 2.0 Hz, 1H), 7.23 (s, 2H), 7.13 (d, *J* = 1.8 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.08 (t, *J* = 4.7 Hz, 1H), 3.85 (s, 3H), 2.77 (t, *J* = 7.9 Hz, 2H), 2.37 (td, *J* = 7.9, 4.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 158.96, 138.51, 137.36, 135.61, 132.34, 129.68, 129.57, 129.03, 128.18, 128.13, 119.92, 113.81, 55.30, 27.71, 23.31.

HRMS calcd for C₁₇H₁₅BrO([M]⁺): 314.0306; found 314.0299.



4-(4-methoxyphenyl)-2H-chromene(2g)

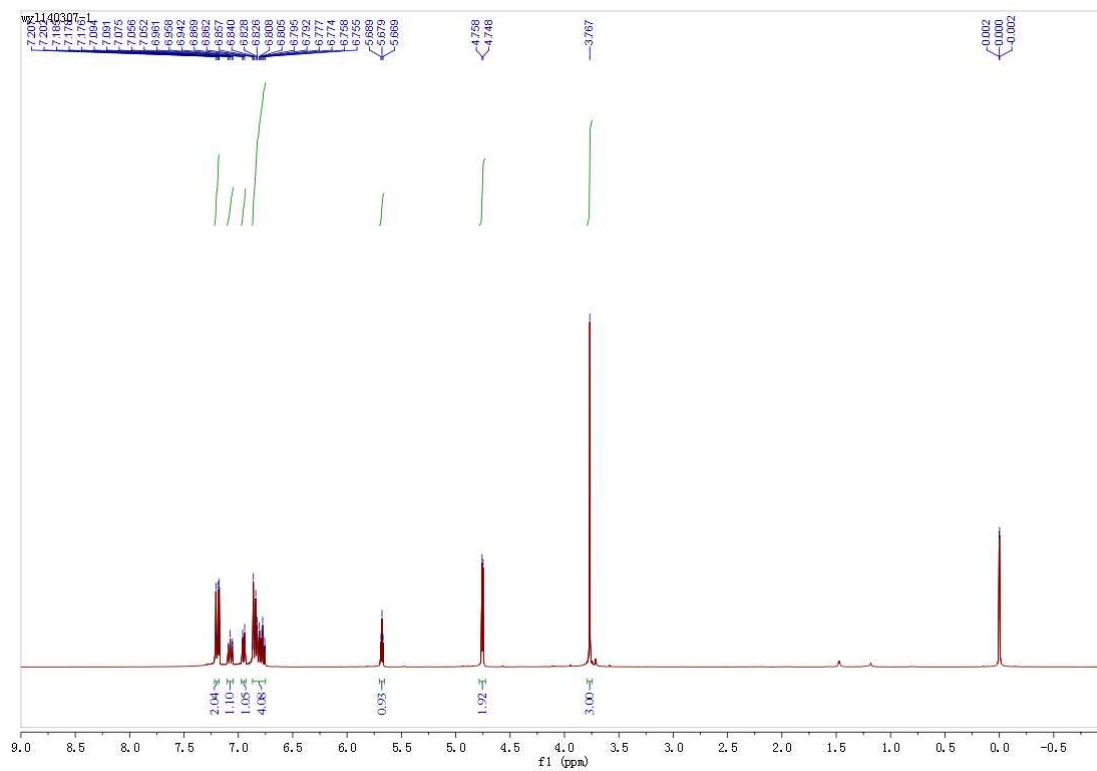


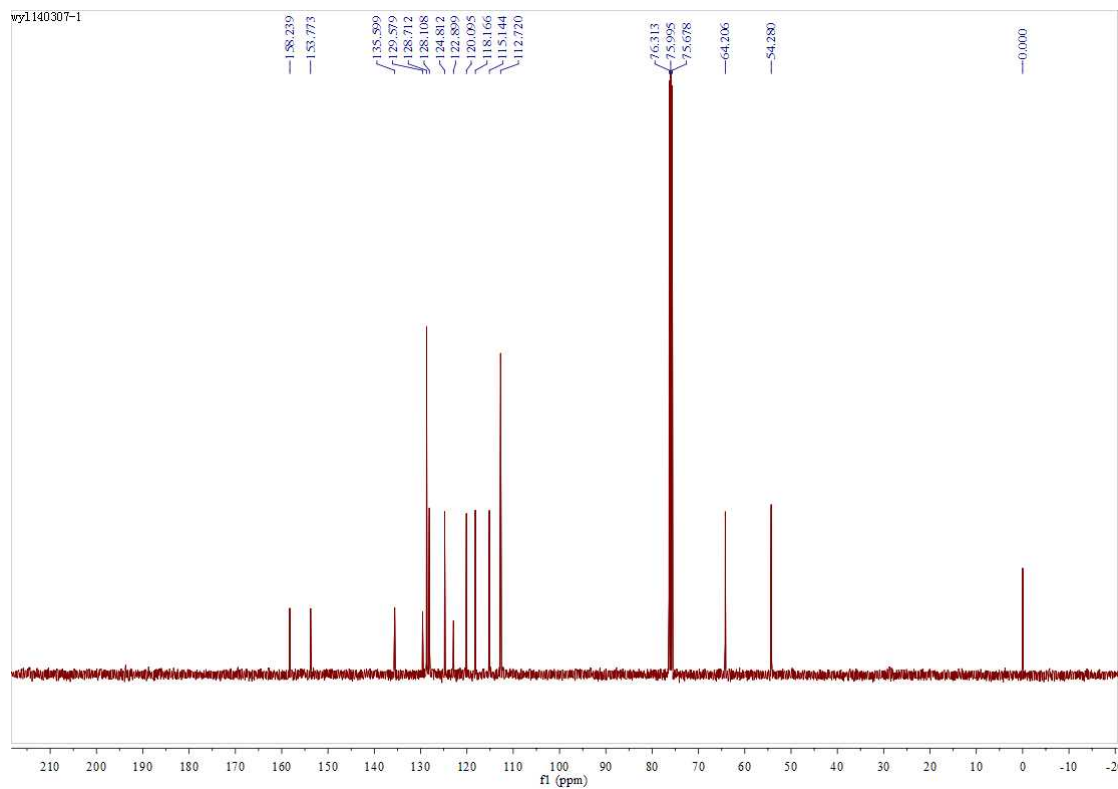
white solid (84%, 20mg). Mp: 92 – 93 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.18 (m, 2H), 7.10 – 7.05 (m, 1H), 6.97 – 6.93 (m, 1H), 6.87 – 6.75 (m, 4H), 5.68 (t, *J* = 4.0 Hz, 1H), 4.75 (d, *J* = 4.0 Hz, 2H), 3.77 (s, 3H).

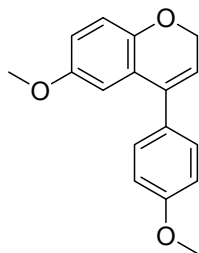
¹³C NMR (100 MHz, CDCl₃) δ 158.24, 153.77, 135.60, 129.58, 128.71, 128.11, 124.81, 122.90, 120.09, 118.17, 115.14, 112.72, 64.21, 54.28.

HRMS calcd for C₁₆H₁₄O₂([M]⁺): 238.0994; found 238.0989.





6-methoxy-4-(4-methoxyphenyl)-2H-chromene(2h)

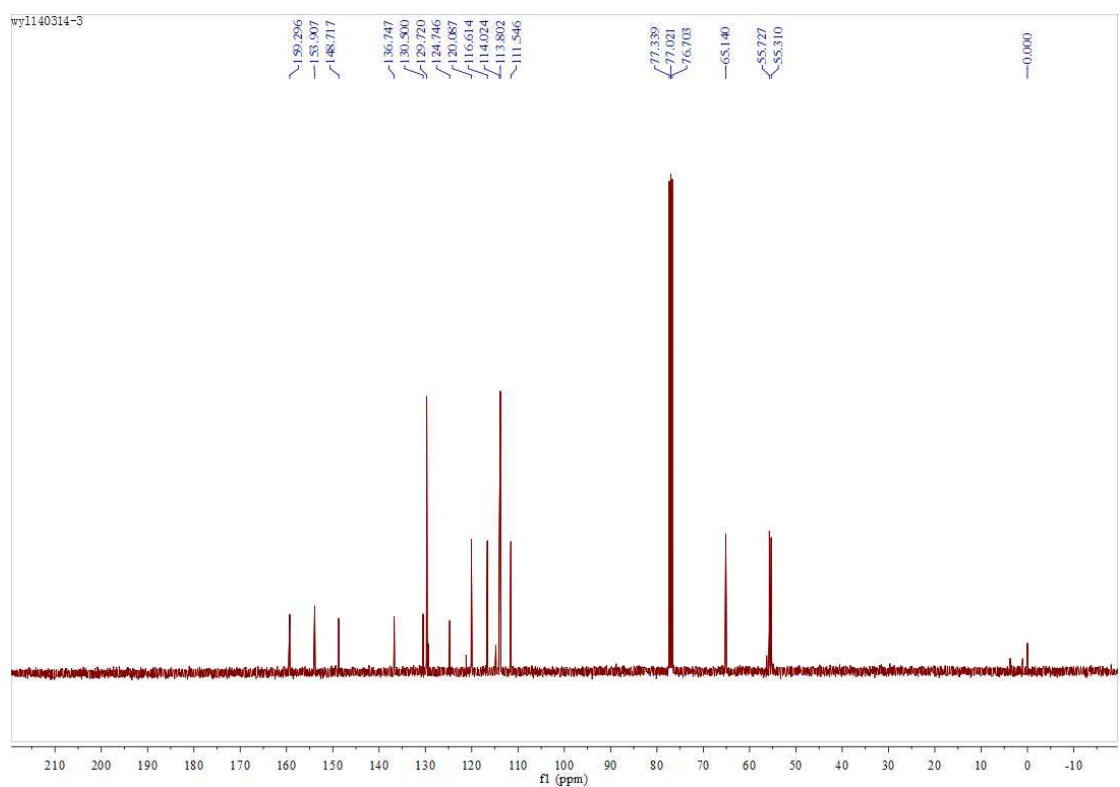
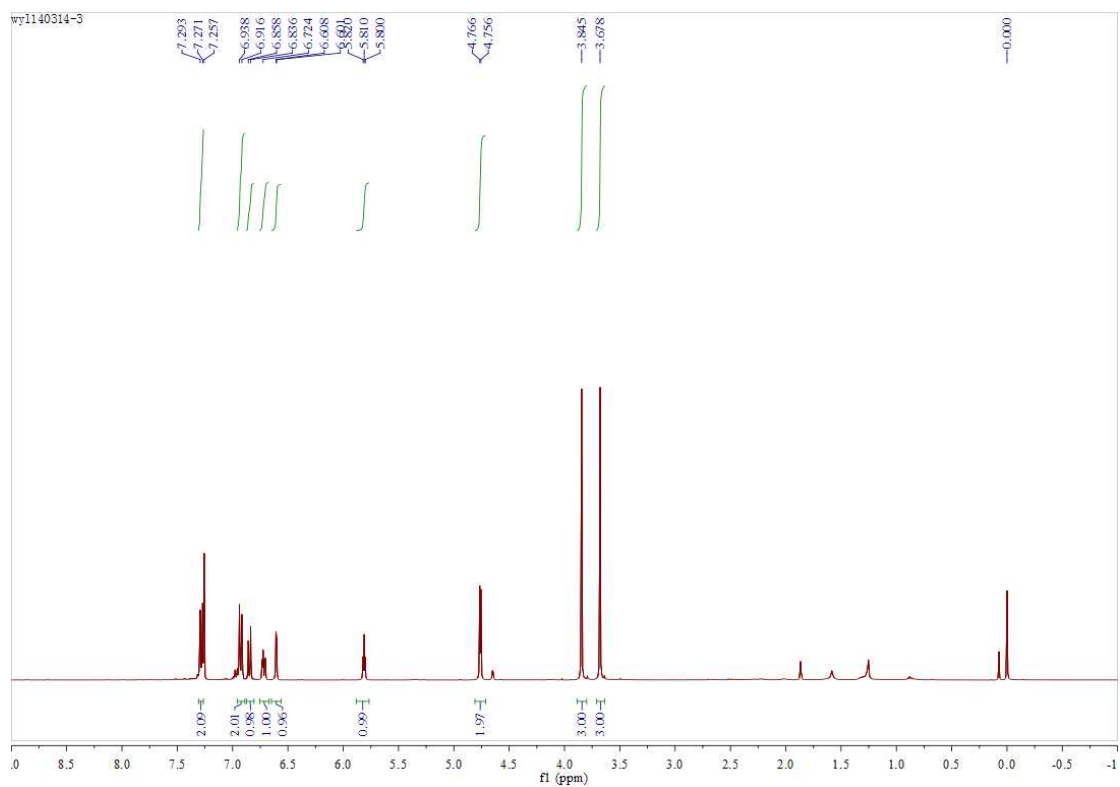


Colorless oil (79%, 21mg).

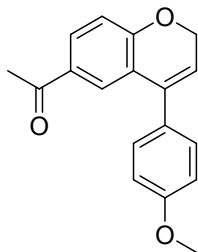
¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.72 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.60 (d, *J* = 3.0 Hz, 1H), 5.81 (s, 1H), 4.76 (d, *J* = 4.0 Hz, 2H), 3.85 (s, 3H), 3.68 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.32, 153.93, 148.74, 136.77, 130.52, 129.74, 124.77, 120.11, 116.64, 114.05, 113.83, 111.57, 65.16, 55.75, 55.33.

HRMS calcd for C₁₇H₁₆O₃([M]⁺): 268.1099; found 268.1091.



1-(4-(4-methoxyphenyl)-2H-chromen-6-yl)ethanone(2i)

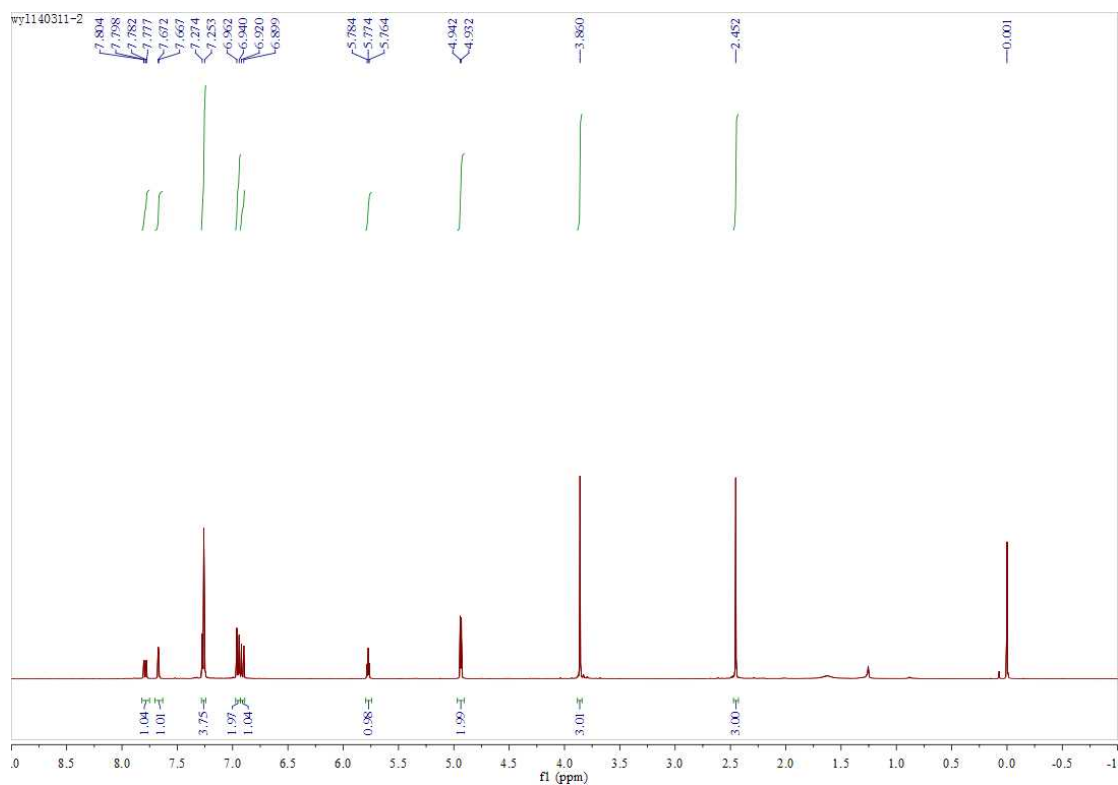


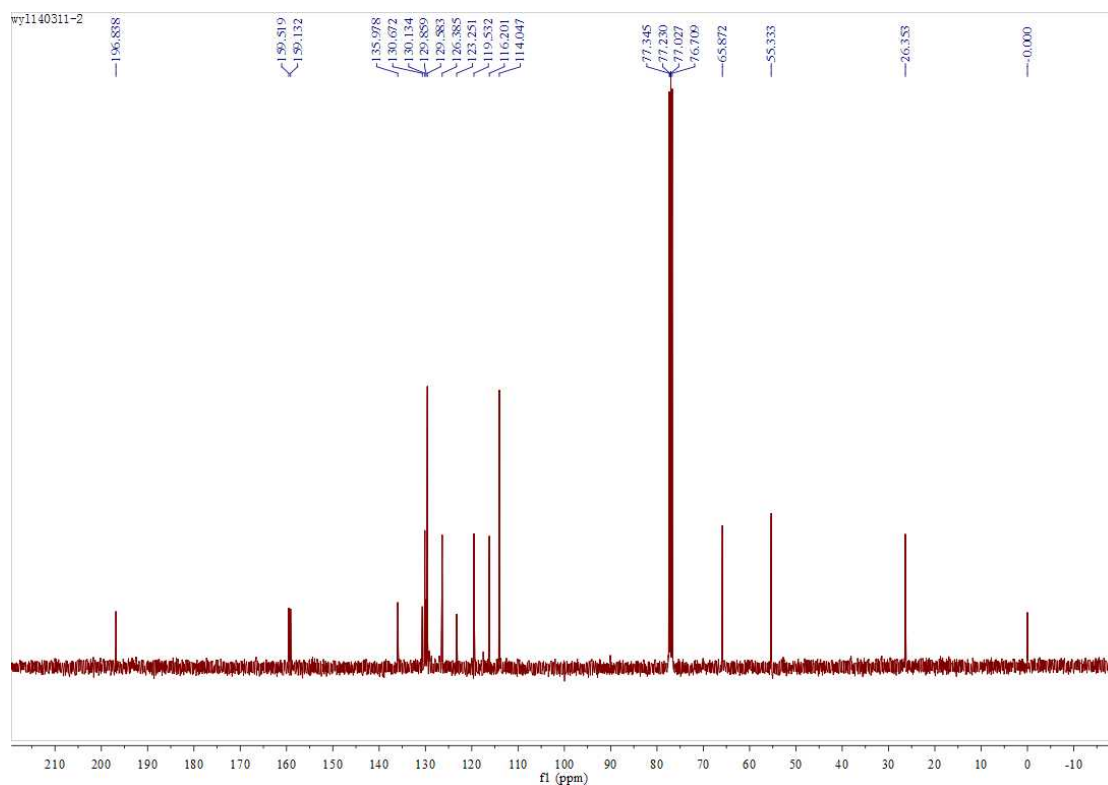
Colorless oil (78%, 22mg)

¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.77 (t, *J* = 3.9 Hz, 1H), 4.94 (d, *J* = 3.8 Hz, 2H), 3.86 (s, 3H), 2.45 (s, 3H).

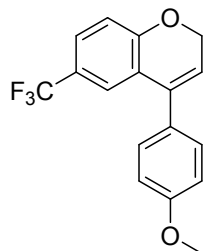
¹³C NMR (100 MHz, CDCl₃) δ 196.84, 159.52, 159.13, 135.98, 130.67, 130.13, 129.86, 129.58, 126.38, 123.25, 119.53, 116.20, 114.05, 65.87, 55.33, 26.35.

HRMS calcd for C₁₈H₁₆O₃[M]⁺: 280.1099; found 280.1098.





4-(4-methoxyphenyl)-6-(trifluoromethyl)-2H-chromene(2j)



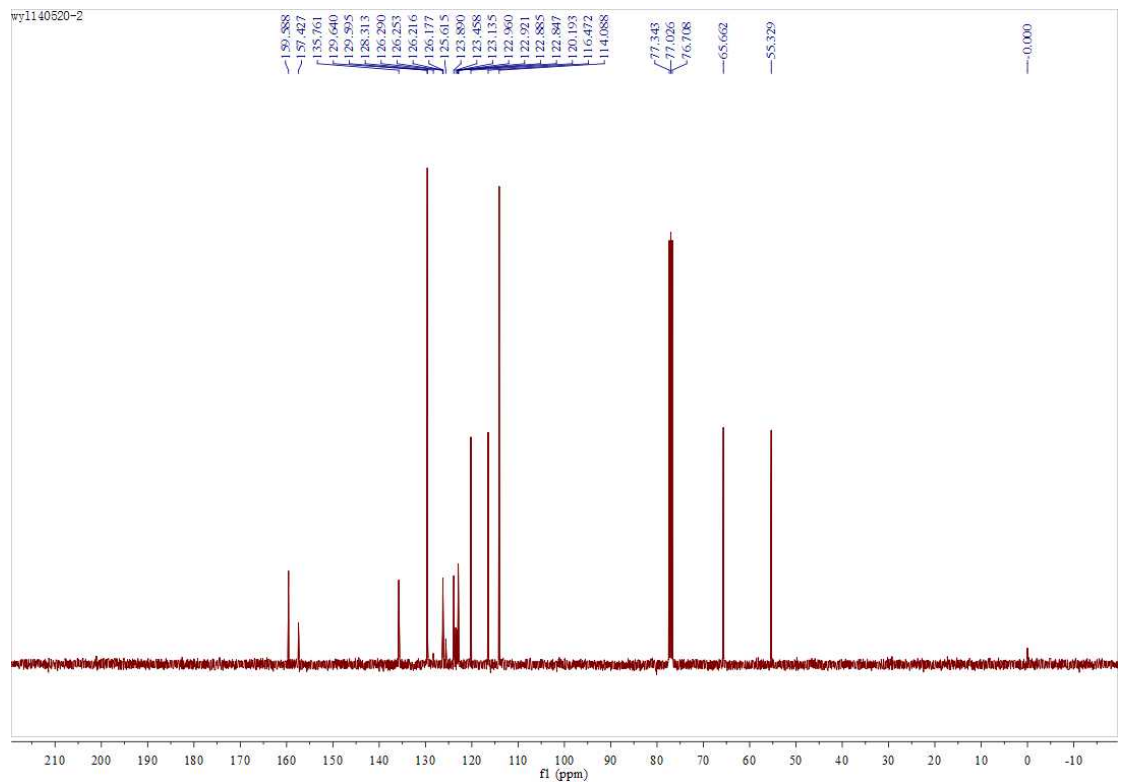
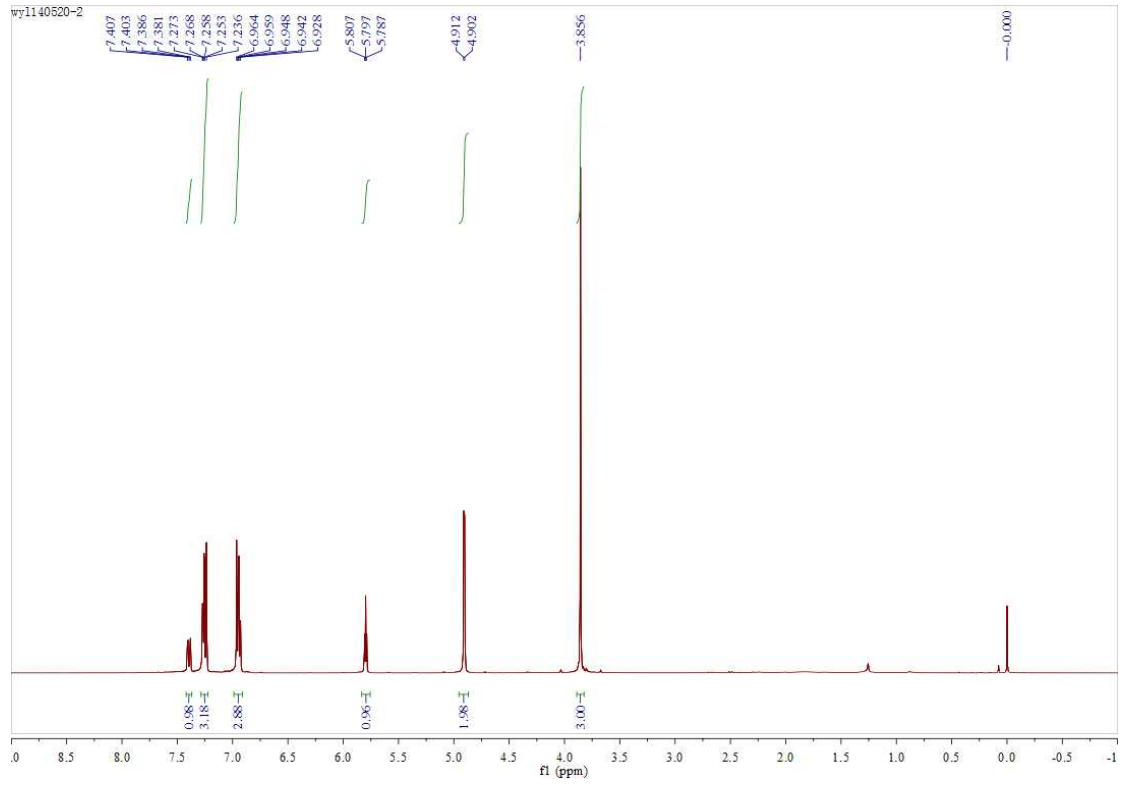
Colorless oil (73%, 22mg)

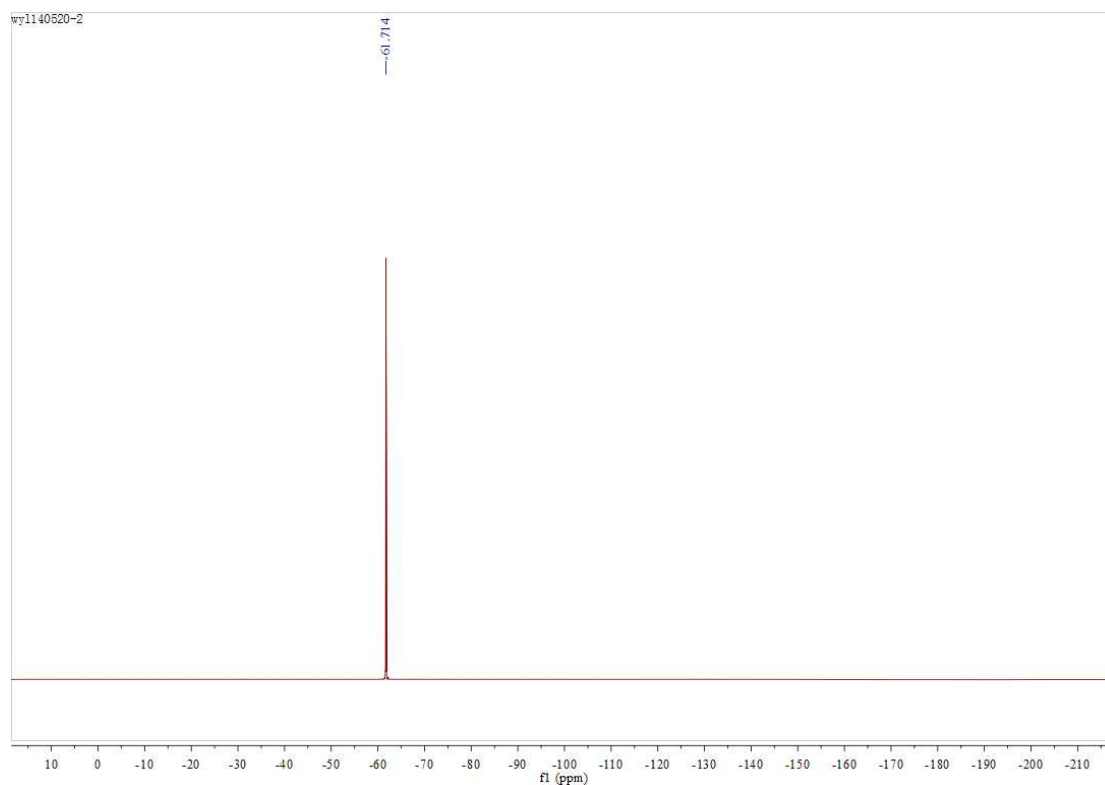
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.29 – 7.22 (m, 3H), 6.99 – 6.91 (m, 3H), 5.80 (t, $J = 3.9$ Hz, 1H), 4.91 (d, $J = 3.9$ Hz, 2H), 3.86 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.59, 157.43, 135.76, 129.64, 129.60, 126.23 (q, $J = 3.8$ Hz), 124.37 (q, $J = 249.6$ Hz), 123.89, 123.46, 122.90 (q, $J = 3.8$ Hz), 120.19, 116.47, 114.09, 65.66, 55.33 .

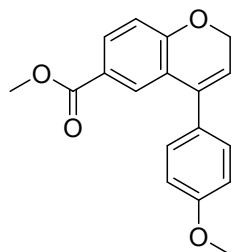
$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -61.71 (s).

HRMS calcd for $\text{C}_{17}\text{H}_{13}\text{F}_3\text{O}_2$ ($[\text{M}]^+$): 306.0868; found 306.0860.





methyl 4-(4-methoxyphenyl)-2H-chromene-6-carboxylate(2k)

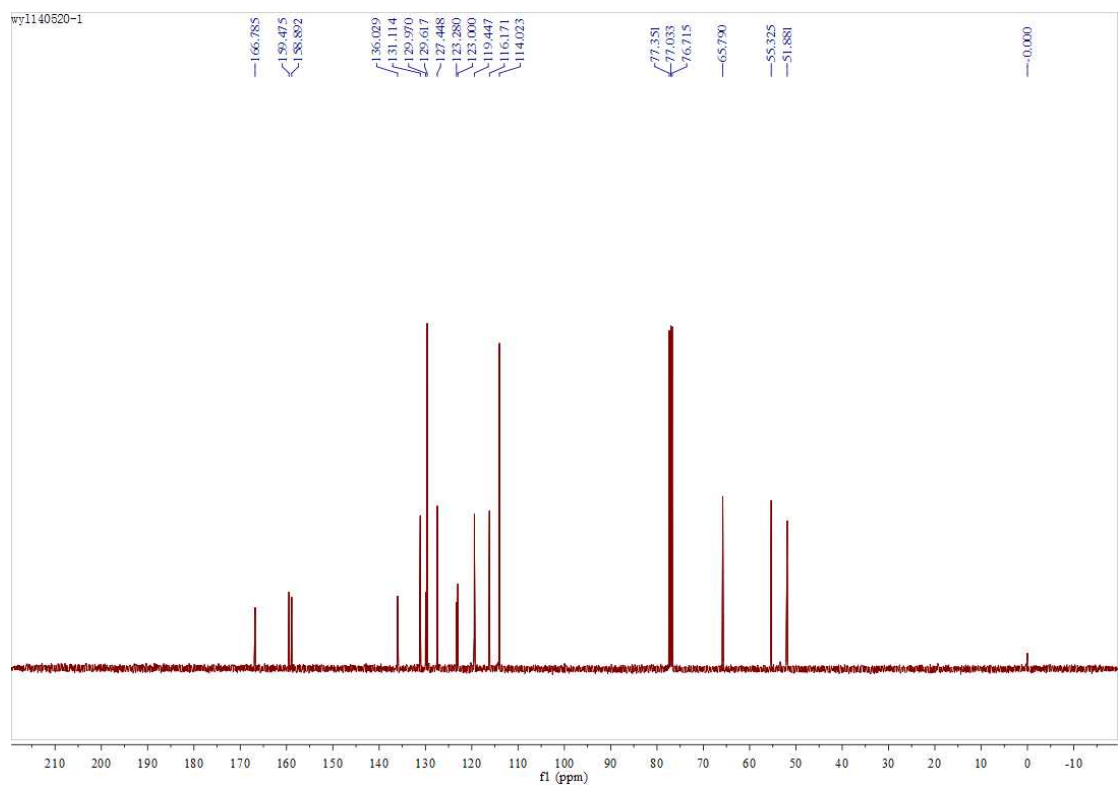
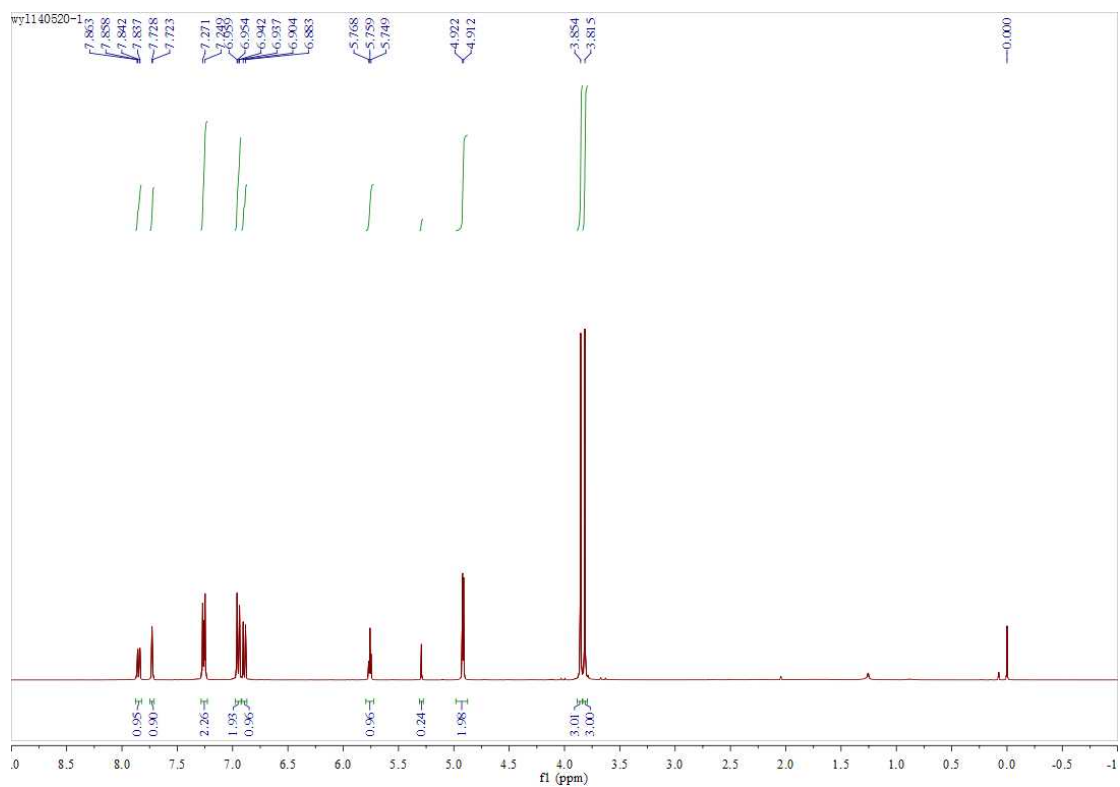


Colorless oil (82%, 24mg).

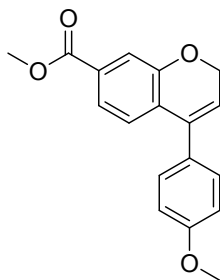
¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.73 (d, *J* = 2.1 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.98 – 6.92 (m, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.76 (t, *J* = 3.9 Hz, 1H), 5.29 (s, 1H), 4.92 (d, *J* = 3.9 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.78, 159.48, 158.89, 136.03, 131.11, 129.97, 129.62, 127.45, 123.28, 123.00, 119.45, 116.17, 114.02, 65.79, 55.33, 51.88.

HRMS calcd for C₁₈H₁₆O₄([M]⁺): 296.1049; found 296.1052.



methyl 4-(4-methoxyphenyl)-2H-chromene-7-carboxylate(2l)

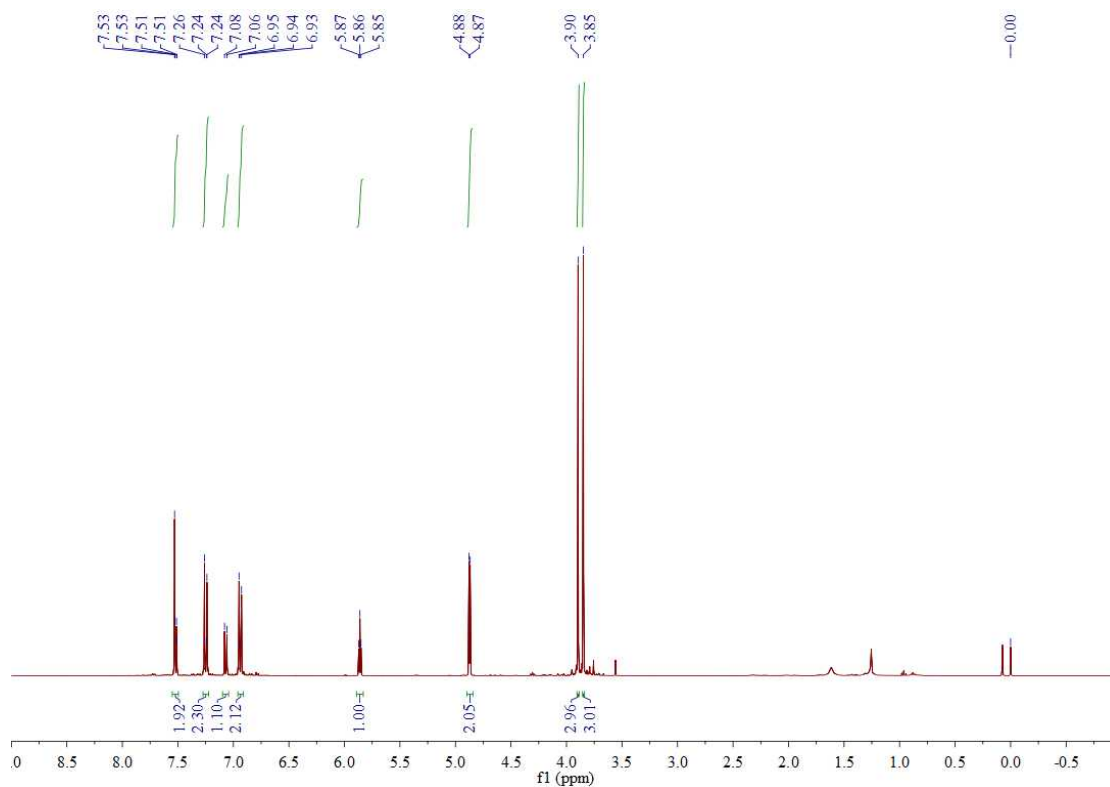


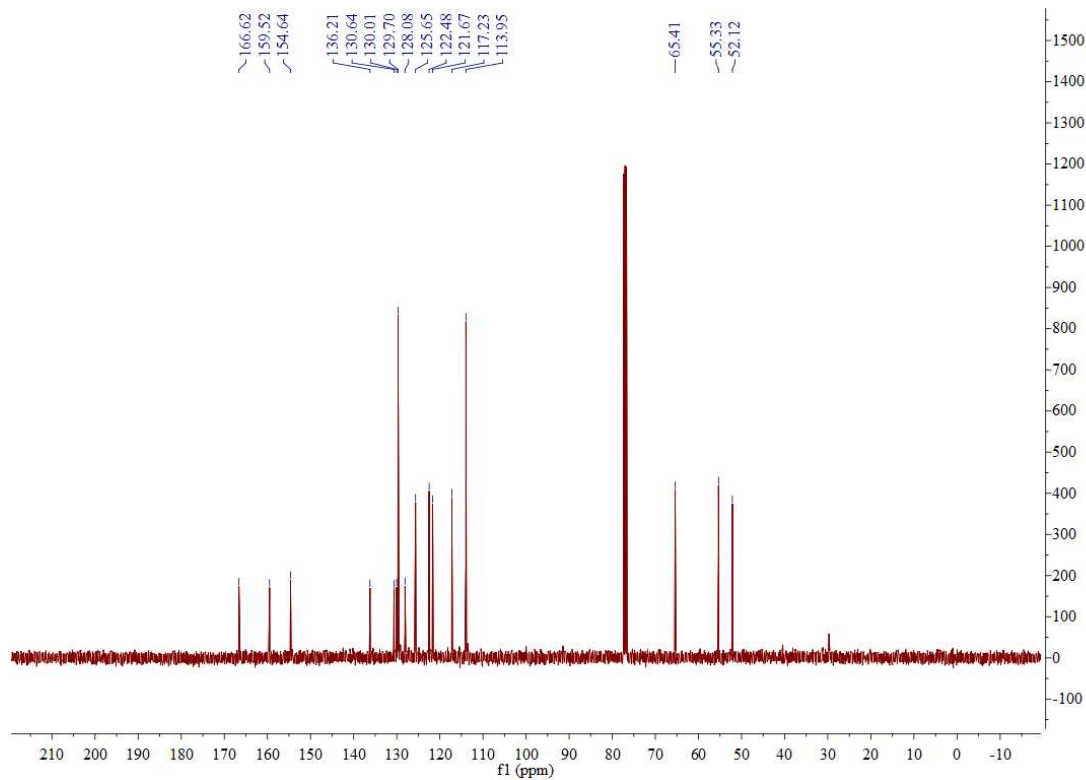
Colorless oil (26%, 7.6mg)

¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, *J* = 7.1, 1.6 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.96 – 6.91 (m, 2H), 5.86 (t, *J* = 4.0 Hz, 1H), 4.87 (d, *J* = 4.0 Hz, 2H), 3.90 (s, 3H), 3.85 (s, 3H).

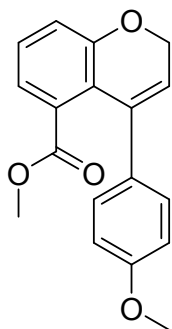
¹³C NMR (100MHz, CDCl₃) δ 166.62, 159.52, 154.64, 136.21, 130.64, 130.01, 129.70, 128.08, 125.65, 122.48, 121.67, 117.23, 113.95, 65.41, 55.33, 52.12

HRMS calcd for C₁₈H₁₆O₄([M]⁺): 296.1049; found 296.1046.





methyl 4-(4-methoxyphenyl)-2H-chromene-5-carboxylate(21')

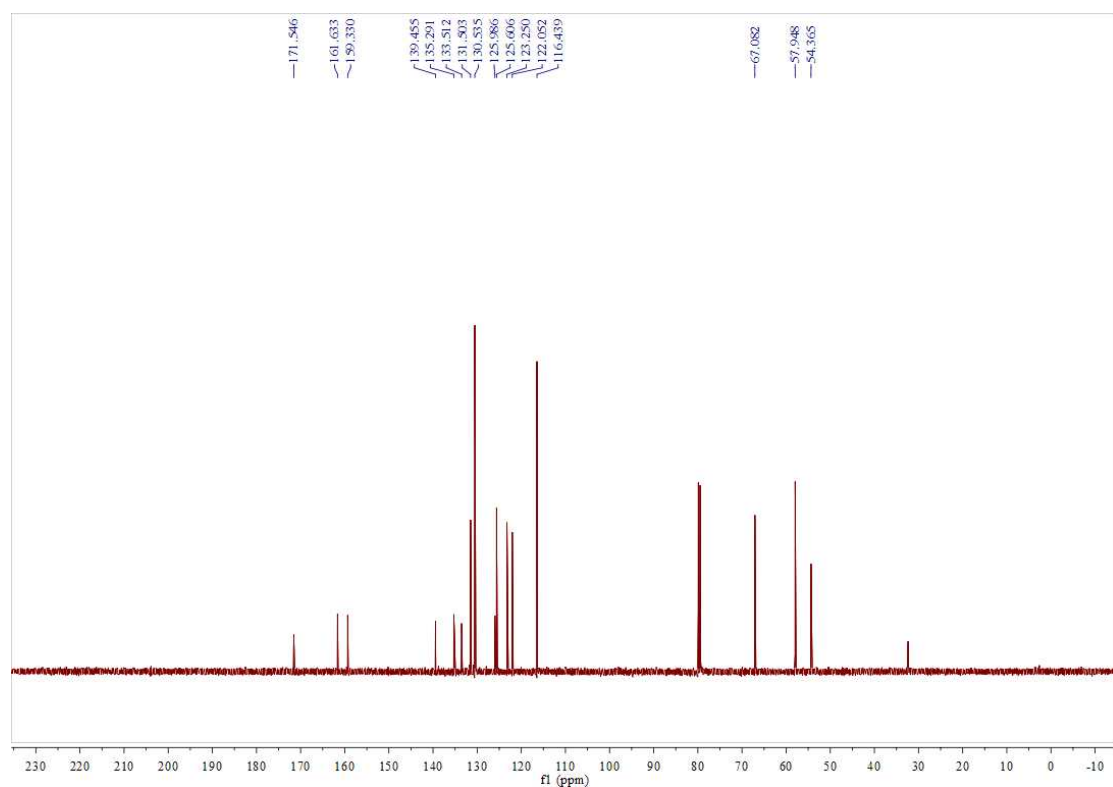
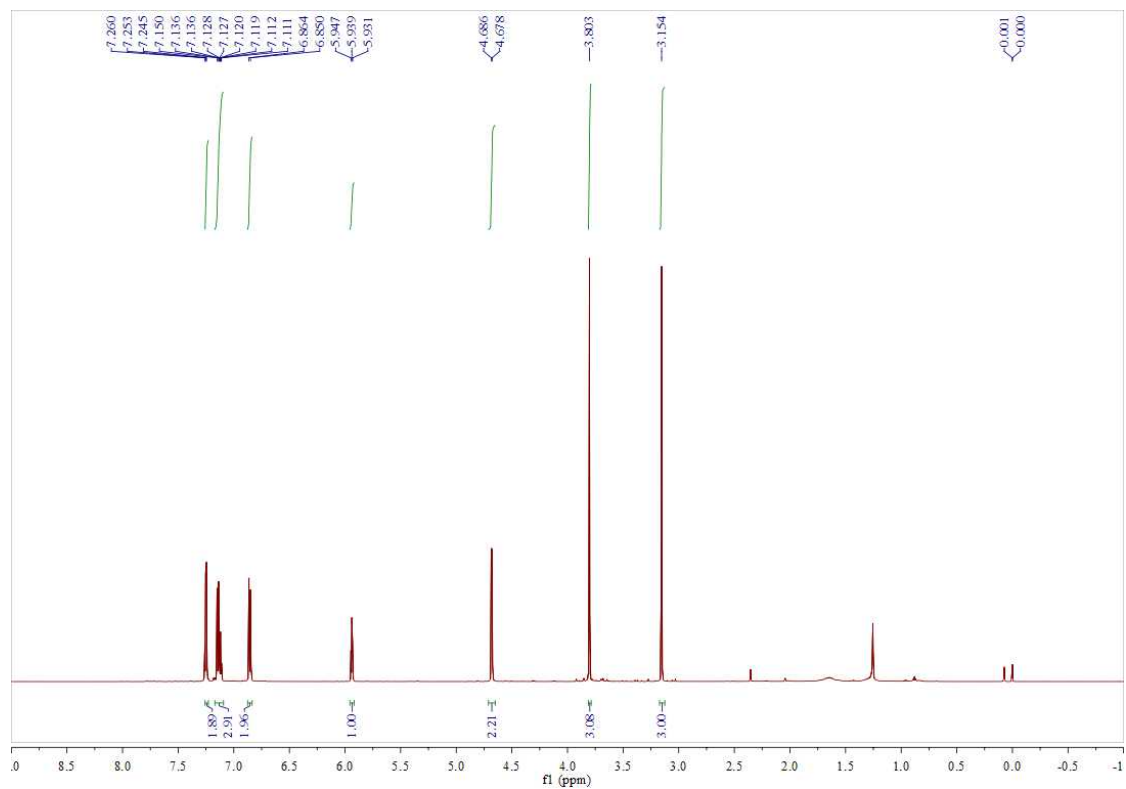


Colorless oil (59%, 17.5mg)

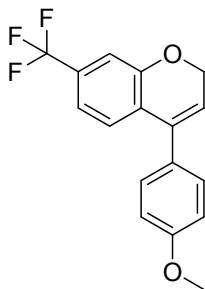
¹H NMR (600 MHz, cdcl₃) δ 7.25 (d, *J* = 4.7 Hz, 2H), 7.17 – 7.09 (m, 3H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.94 (t, *J* = 4.7 Hz, 1H), 4.68 (d, *J* = 4.7 Hz, 2H), 3.80 (s, 3H), 3.15 (s, 3H).

¹³C NMR (150 MHz, cdcl₃) δ 171.55 (s), 161.63, 159.33, 139.46, 135.29, 133.51, 131.50, 130.53, 125.99, 125.61, 123.25, 122.05, 116.44, 67.08, 57.95, 54.36.

HRMS calcd for C₁₈H₁₆O₄([M]⁺): 296.1049; found 296.1042.



4-(4-methoxyphenyl)-7-(trifluoromethyl)-2H-chromene(2m)

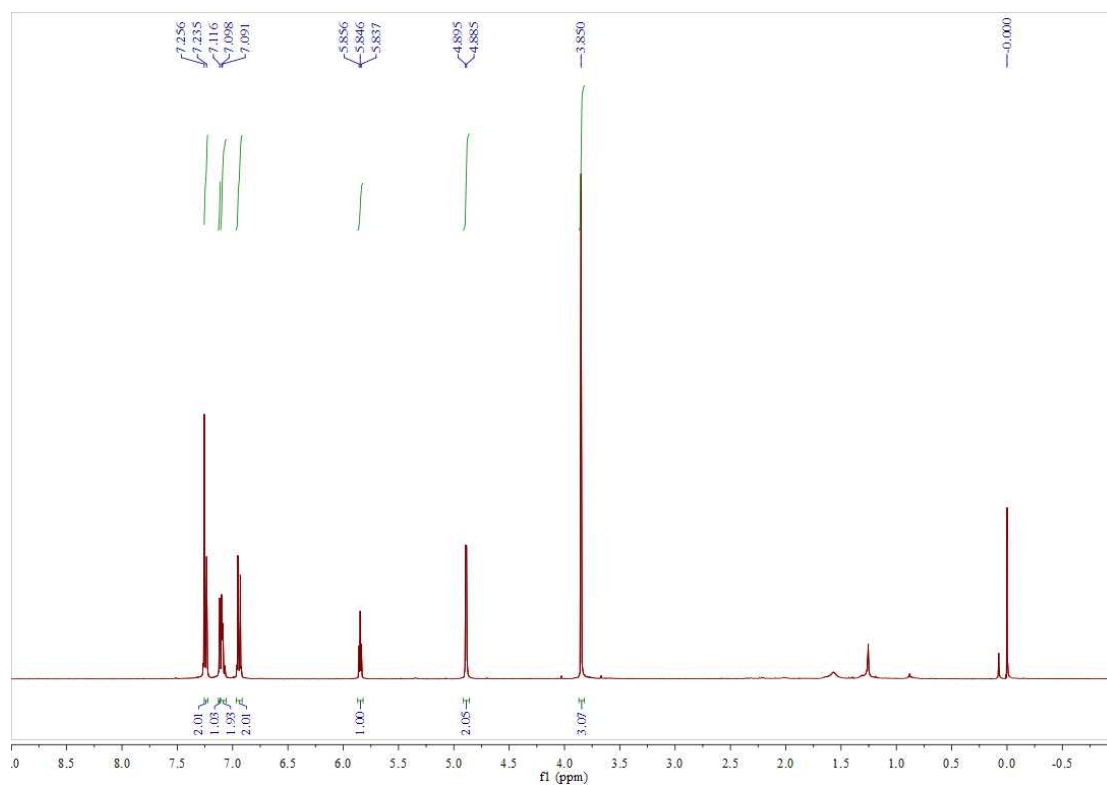


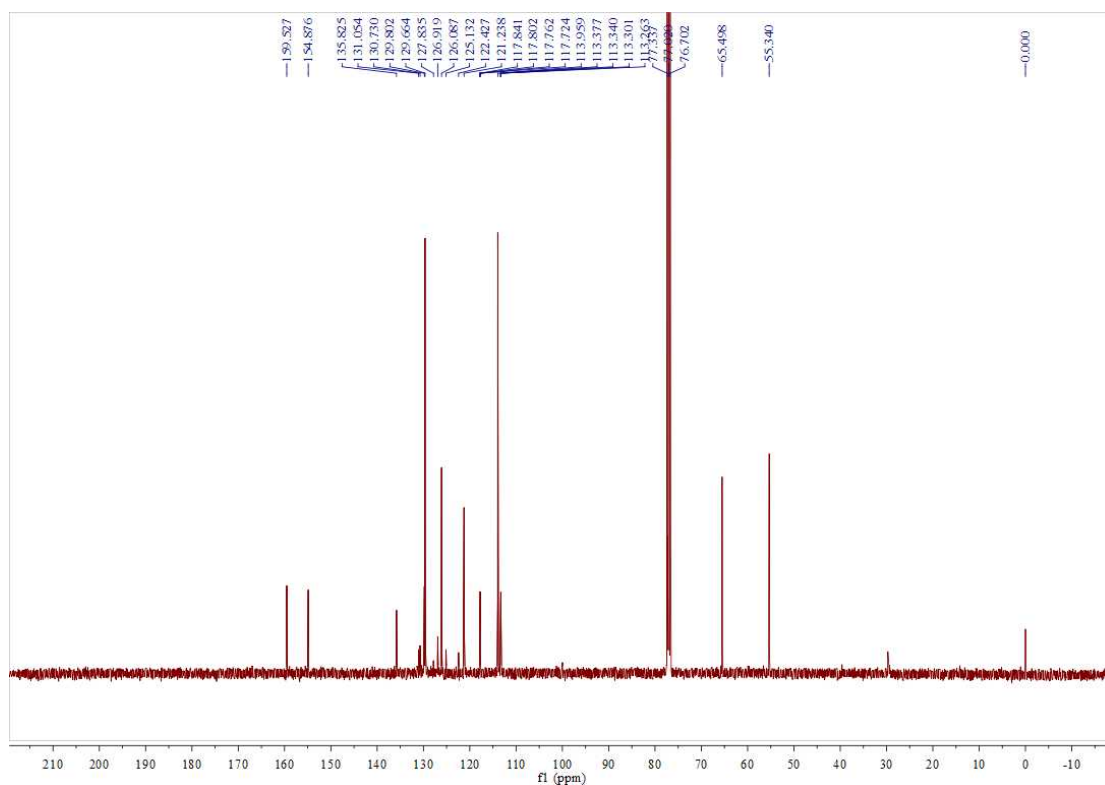
white solid (61%, 18mg). Mp: 102– 103 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 8.7 Hz, 2H), 7.12 (s, 1H), 7.09 (d, J = 2.8 Hz, 2H), 6.97 - 6.91 (m, 2H), 5.85 (t, J = 3.9 Hz, 1H), 4.89 (d, J = 3.9 Hz, 2H), 3.85 (s, 3H).

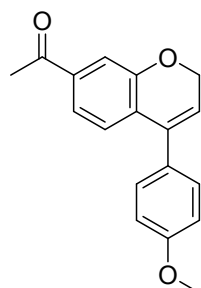
¹³C NMR (100 MHz, CDCl₃) δ 159.53, 154.88, 135.83, 130.89 (q, J = 32.8 Hz), 129.80, 129.66, 126.92, 126.09, 123.80 (q, J = 272.1 Hz), 121.24, 117.78 (q, J = 3.9 Hz), 113.96, 113.32 (q, J = 3.8 Hz), 65.50, 55.34.

HRMS calcd for C₁₇H₁₃F₃O₂ ([M]⁺): 306.0868; found 306.0860.





1-(4-(4-methoxyphenyl)-2H-chromen-7-yl)ethanone(2n)

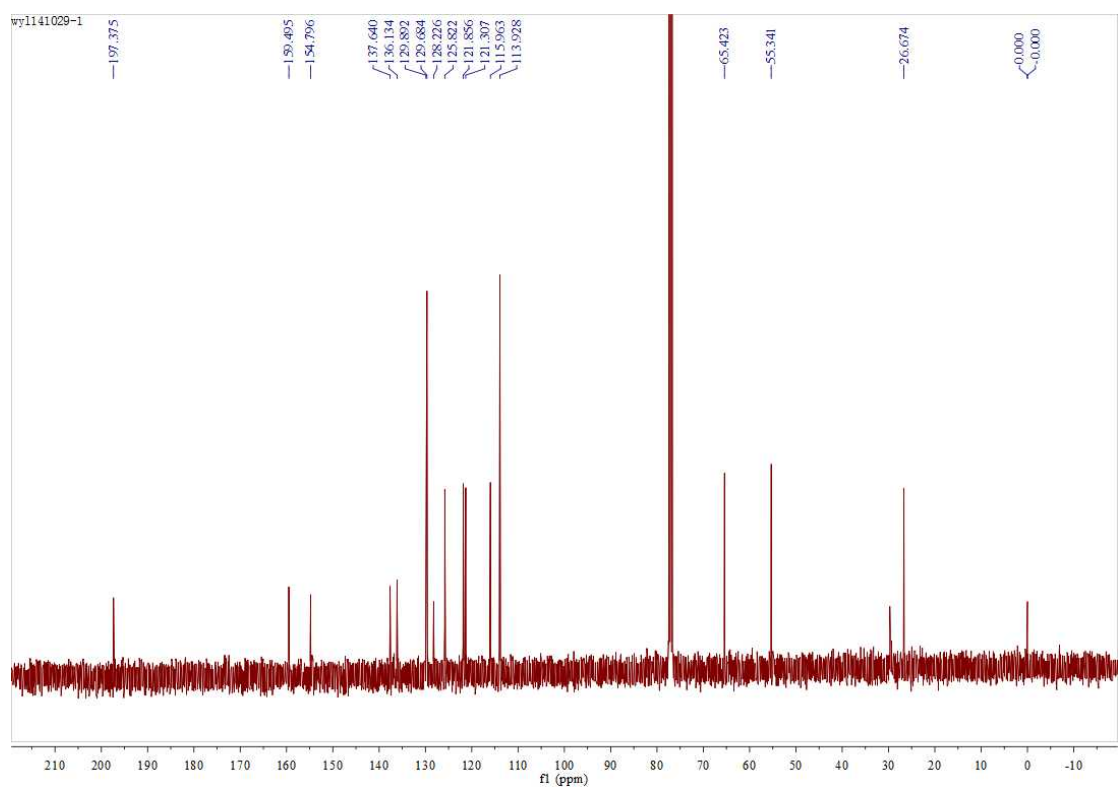
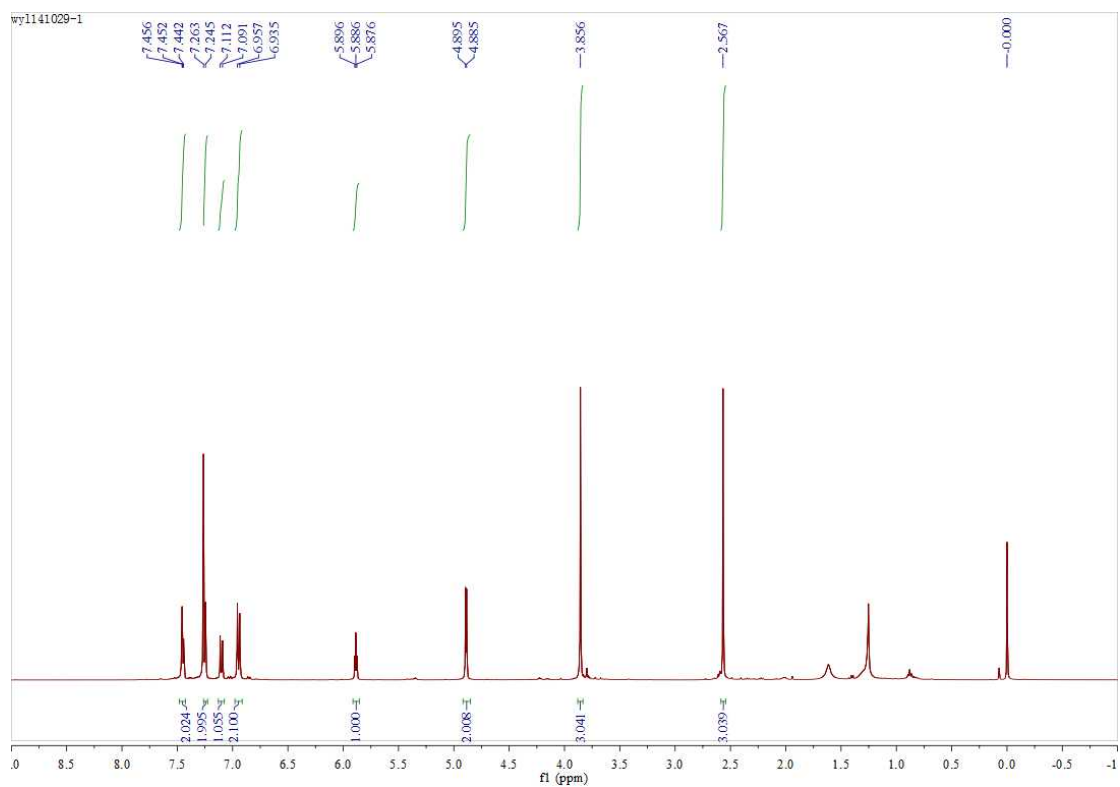


colorless oil (28%, 8mg)

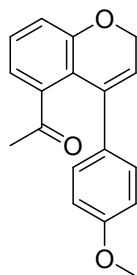
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 – 7.43 (m, 2H), 7.25 (s, 2H), 7.10 (d, $J = 8.4$ Hz, 1H), 6.95 (d, $J = 8.7$ Hz, 2H), 5.89 (t, $J = 3.9$ Hz, 1H), 4.89 (d, $J = 3.9$ Hz, 2H), 3.86 (s, 3H), 2.57 (s, 3H).

$^{13}\text{C NMR}$ (100MHz, CDCl_3) δ 197.37, 159.50, 154.80, 137.64, 136.13, 129.89, 129.68, 128.23, 125.82, 121.86, 121.31, 115.96, 113.93, 65.42, 55.34, 26.67.

HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{O}_3$ ($[\text{M}]^+$): 280.1099; found 280.1098.



1-(4-(4-methoxyphenyl)-2H-chromen-5-yl)ethanone(2n')

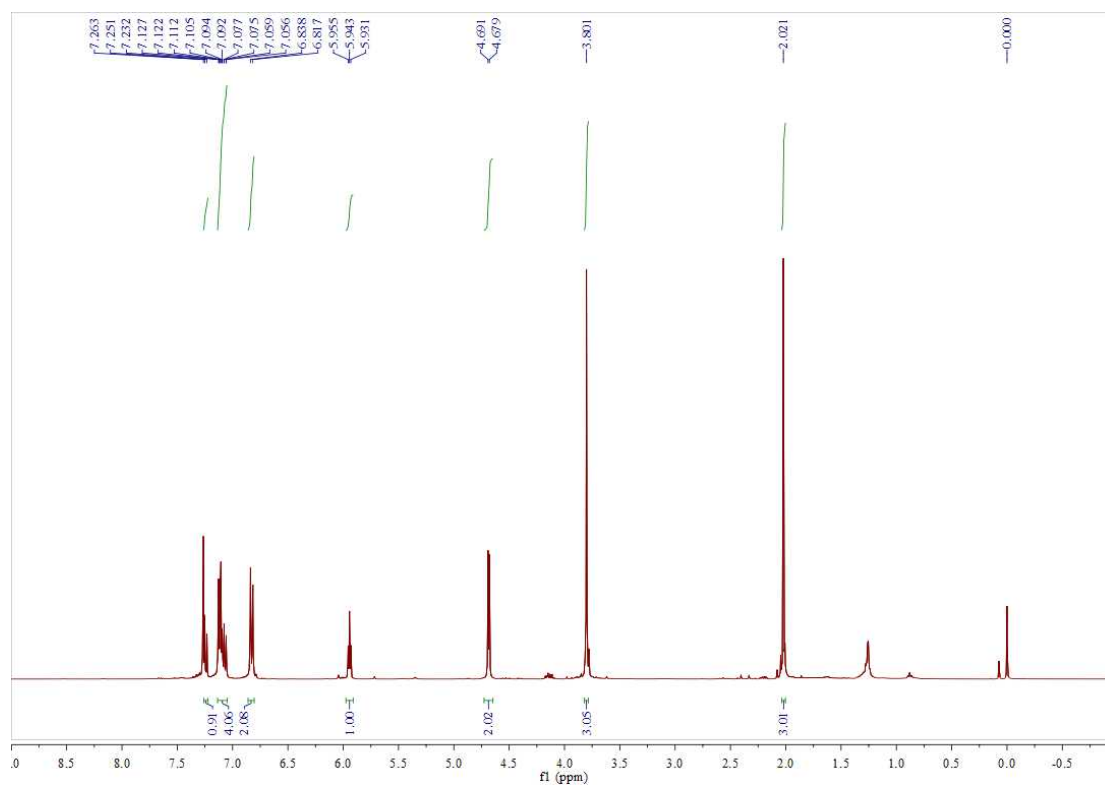


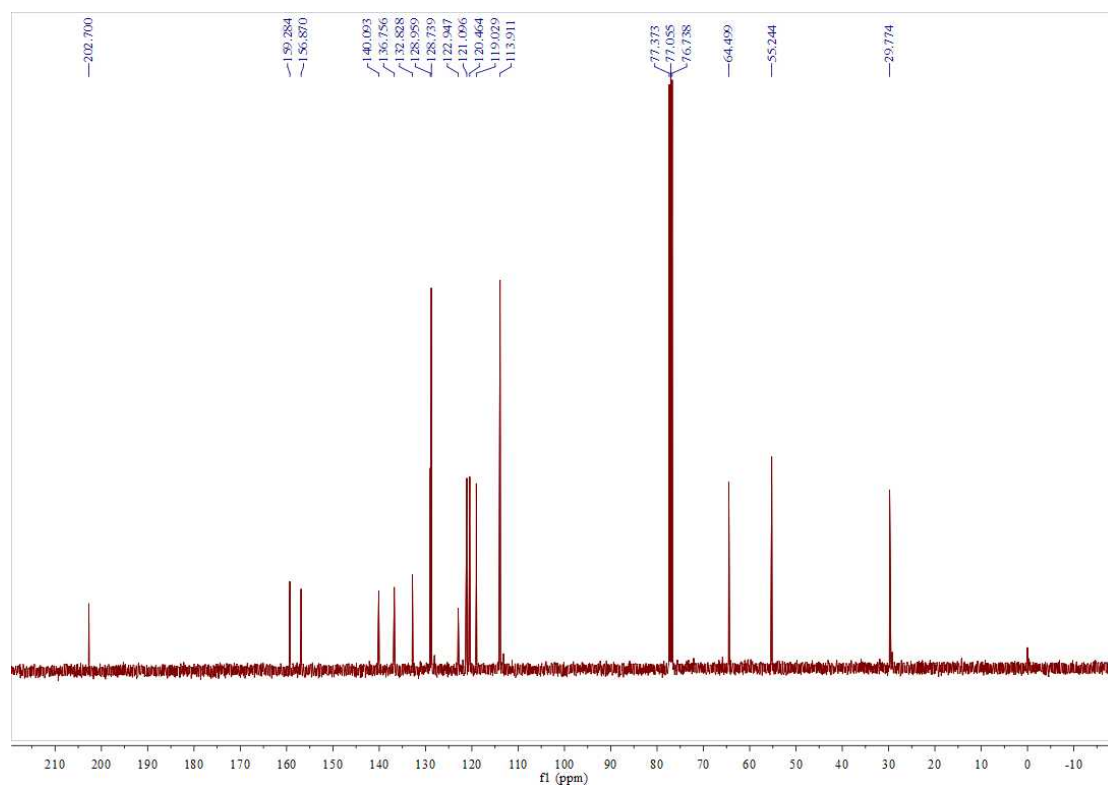
colorless oil (48%, 13mg)

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 7.8 Hz, 1H), 7.14 - 7.05 (m, 4H), 6.83 (d, J = 8.7 Hz, 2H), 5.94 (t, J = 4.8 Hz, 1H), 4.68 (d, J = 4.8 Hz, 2H), 3.80 (s, 3H), 2.02 (s, 3H).

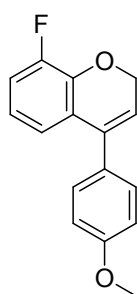
¹³C NMR (100 MHz, CDCl₃) δ 202.70, 159.28, 156.87, 140.09, 136.76, 132.83, 128.96, 128.74, 122.95, 121.10, 120.46, 119.03, 113.91, 64.50, 55.24, 29.77.

HRMS calcd for C₁₈H₁₆O₃([M]⁺): 280.1099; found 280.1095.





8-fluoro-4-(4-methoxyphenyl)-2H-chromene(2o)



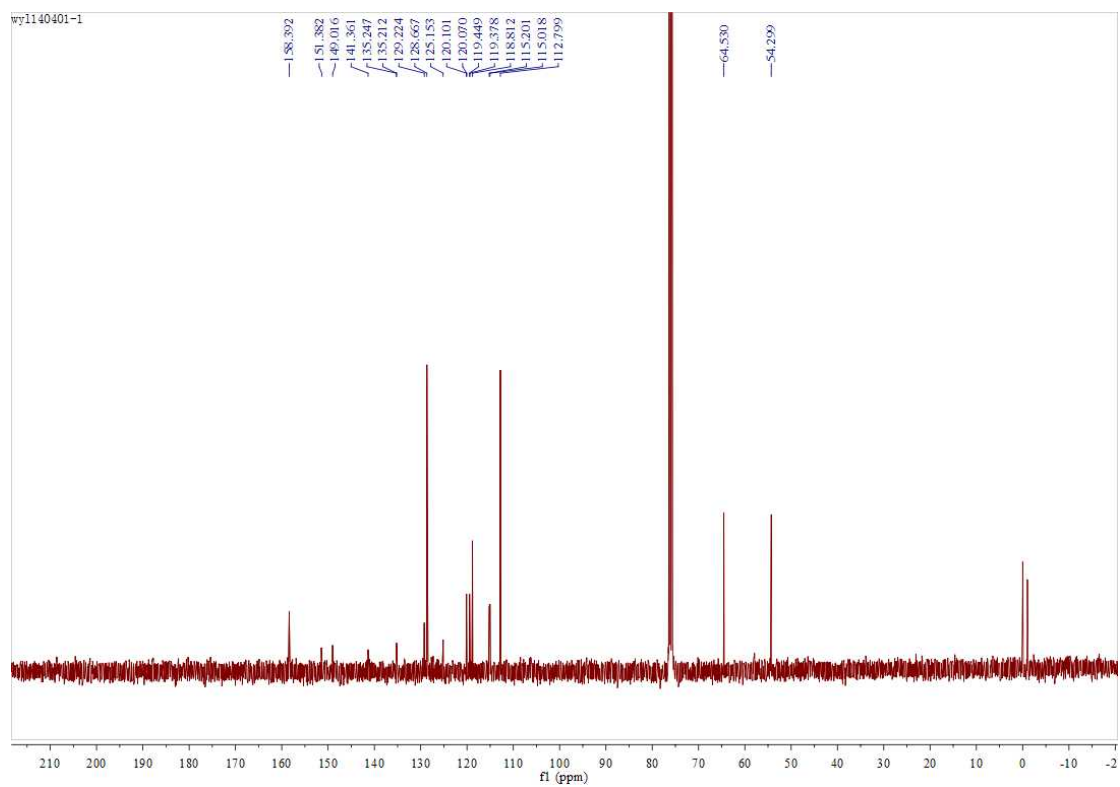
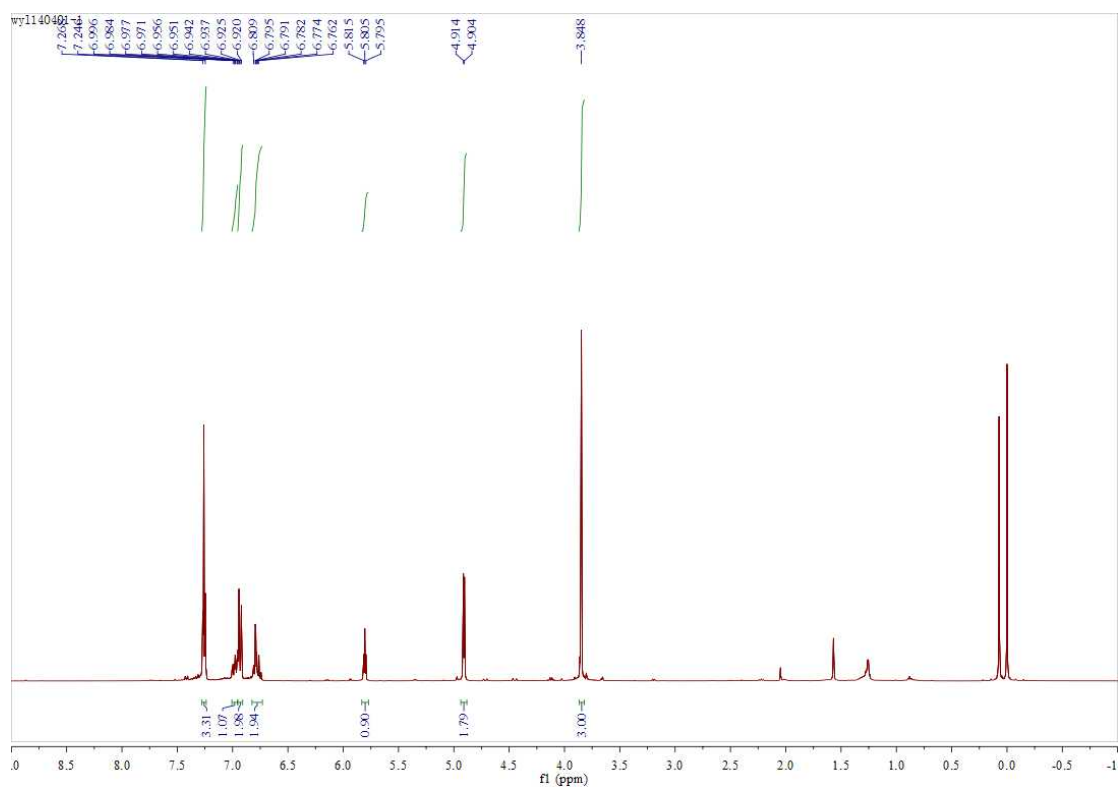
Colorless oil (68%, 17mg)

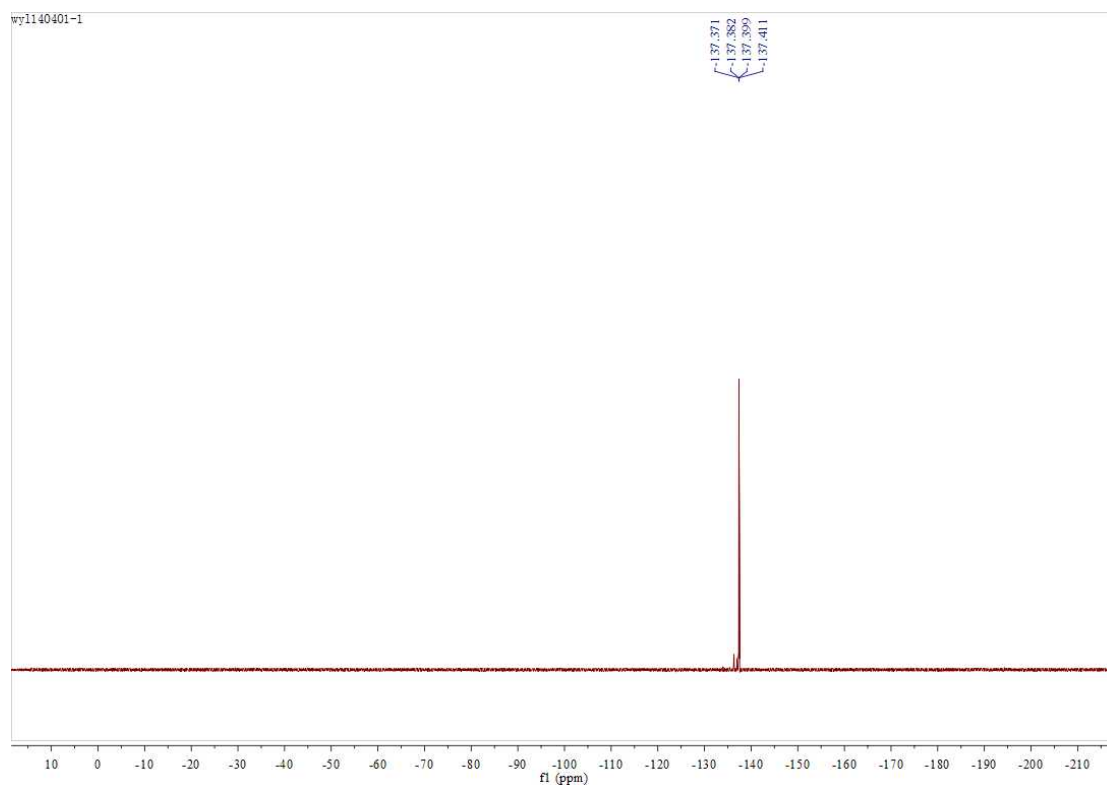
¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.7 Hz, 2H), 7.01 – 6.95 (m, 1H), 6.95 – 6.91 (m, 2H), 6.79 (dt, *J* = 7.8, 5.2 Hz, 2H), 5.80 (t, *J* = 3.9 Hz, 1H), 4.91 (d, *J* = 3.9 Hz, 2H), 3.85 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 158.39, 150.19(d, *J* = 244.4 Hz), 141.36, 135.23 (d, *J* = 3.5 Hz), 129.22, 128.67, 125.15, 120.09 (d, *J* = 3.2 Hz), 119.41 (d, *J* = 7.2 Hz), 118.81, 115.11 (d, *J* = 18.4 Hz), 112.80, 64.53, 54.30.

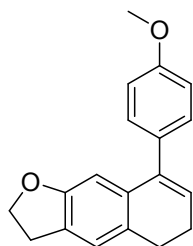
¹⁹F NMR (376 MHz, CDCl₃) δ -137.39 (dd, *J* = 10.6, 4.3 Hz).

HRMS calcd for C₁₆H₁₃FO₂([M]⁺): 256.0900; found 256.0894.





8-(4-methoxyphenyl)-2,3,5,6-tetrahydronaphtho[2,3-b]furan(2p)

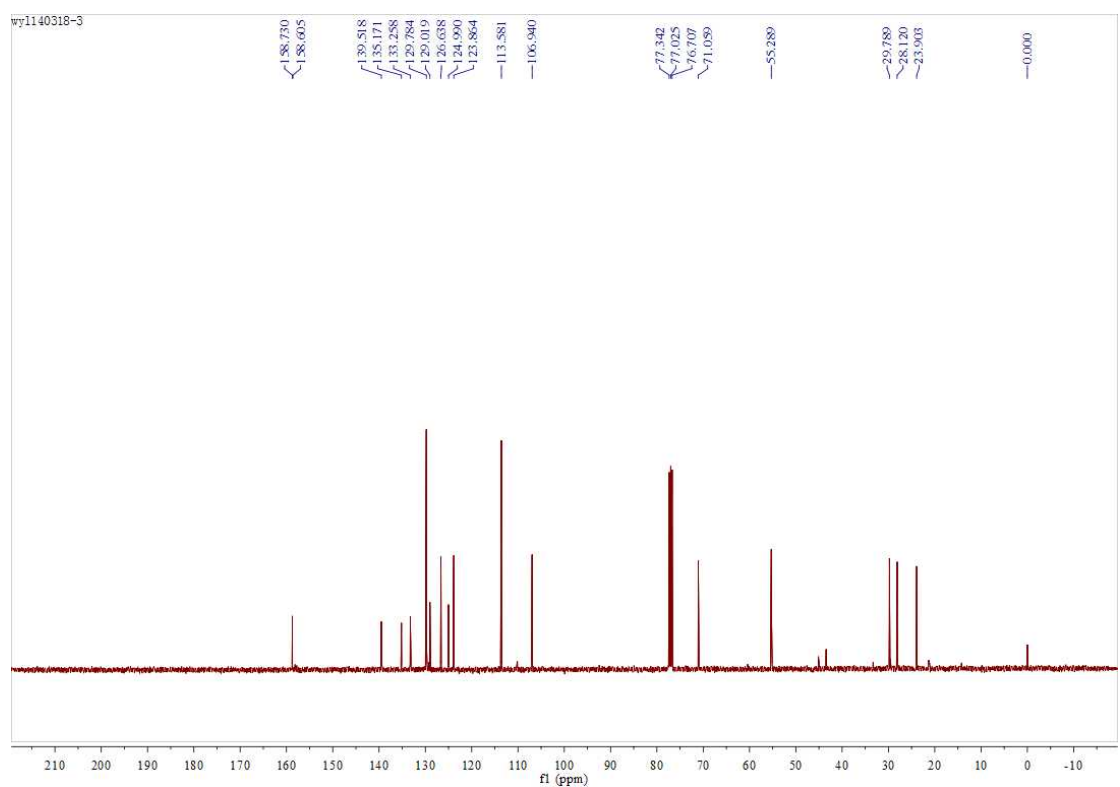
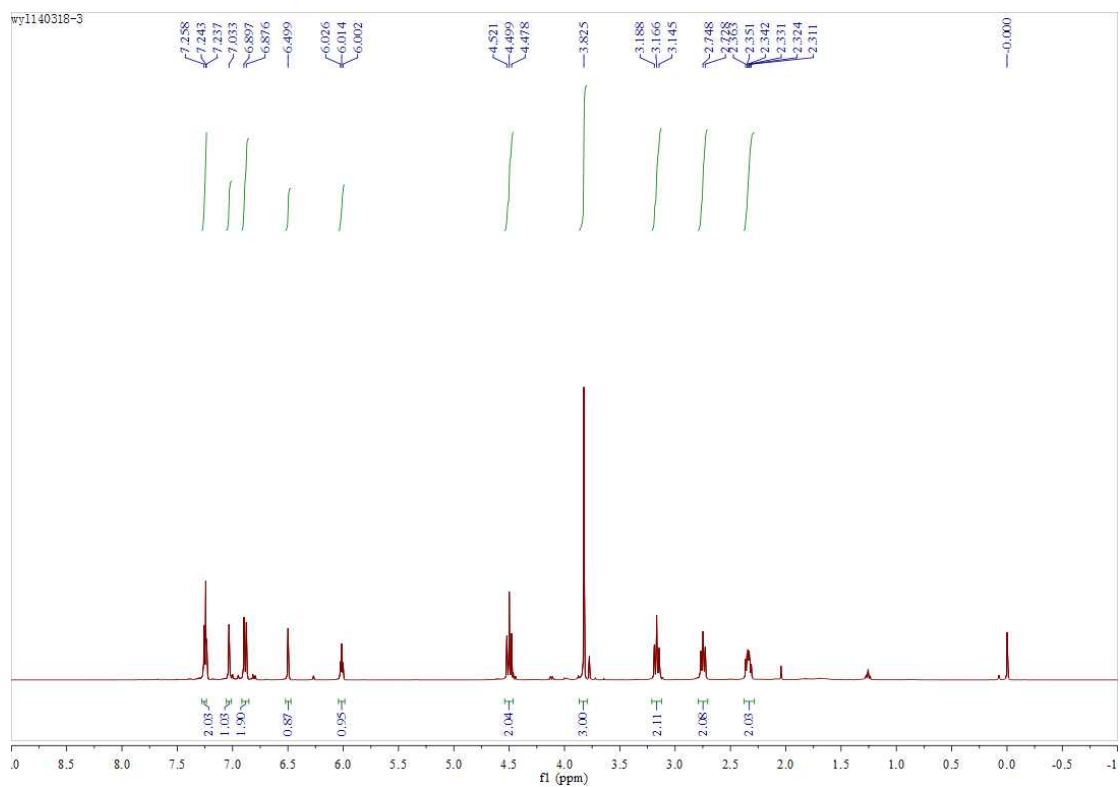


Colorless oil (77%, 21mg).

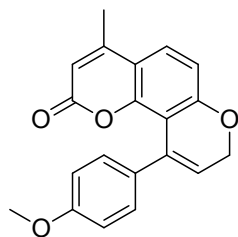
¹H NMR (400 MHz, CDCl₃) δ 7.25 (t, *J* = 4.3 Hz, 2H), 7.03 (s, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.50 (s, 1H), 6.01 (t, *J* = 4.7 Hz, 1H), 4.50 (t, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.17 (t, *J* = 8.6 Hz, 2H), 2.75 (t, *J* = 7.9 Hz, 2H), 2.34 (td, *J* = 7.9, 4.9 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 158.73, 158.61, 139.52, 135.17, 133.26, 129.78, 129.02, 126.64, 124.99, 123.86, 113.58, 106.94, 71.06, 55.29, 29.79, 28.12, 23.90.

HRMS calcd for C₁₉H₁₈O₂([M]⁺): 278.1307; found 278.1303.



10-(4-methoxyphenyl)-4-methylpyrano[2,3-f]chromen-2(8H)-one(2q)

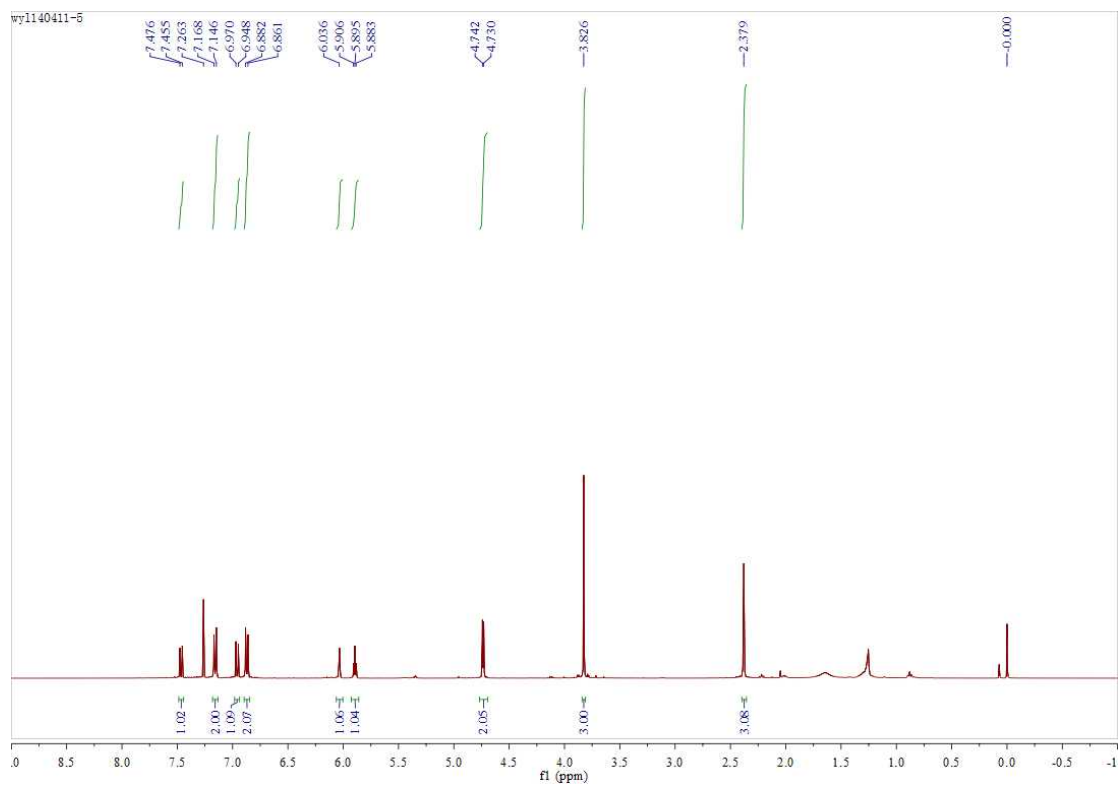


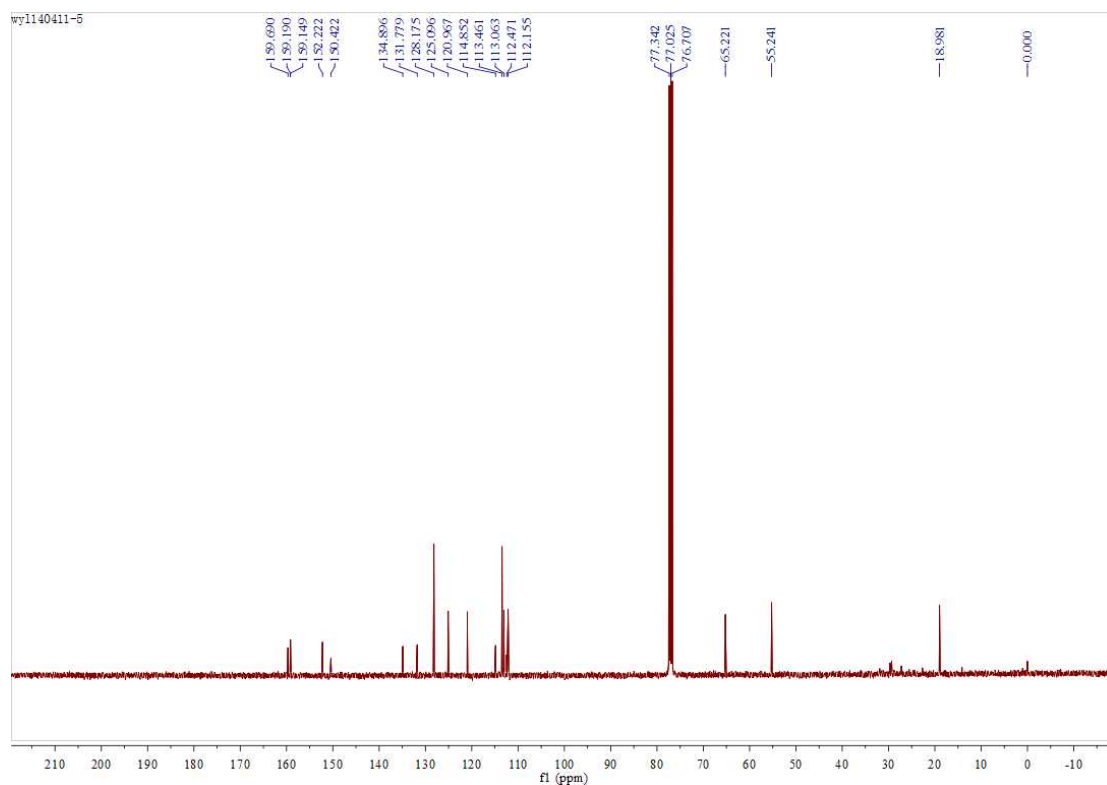
pale yellow solid (44%, 14mg). Mp: 125 – 127 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.7 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.04 (s, 1H), 5.89 (t, *J* = 4.6 Hz, 1H), 4.74 (d, *J* = 4.6 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H).

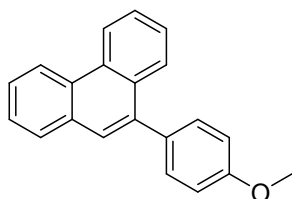
¹³C NMR (100 MHz, CDCl₃) δ 159.69, 159.19, 159.15, 152.22, 150.42, 134.90, 131.78, 128.17, 125.10, 120.97, 114.85, 113.46, 113.06, 112.47, 112.15, 65.22, 55.24, 18.98.

HRMS calcd for C₂₀H₁₆O₄([M]⁺): 320.1049; found 320.1039.





9-(4-methoxyphenyl)phenanthrene(2r)

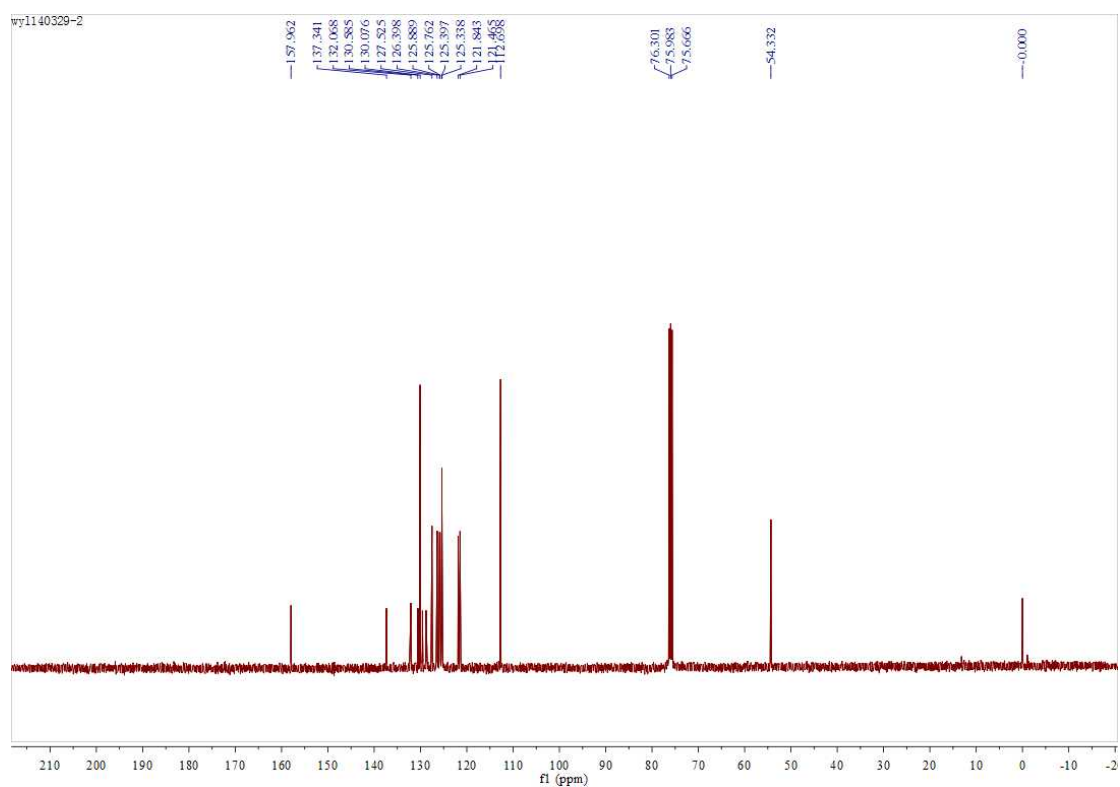
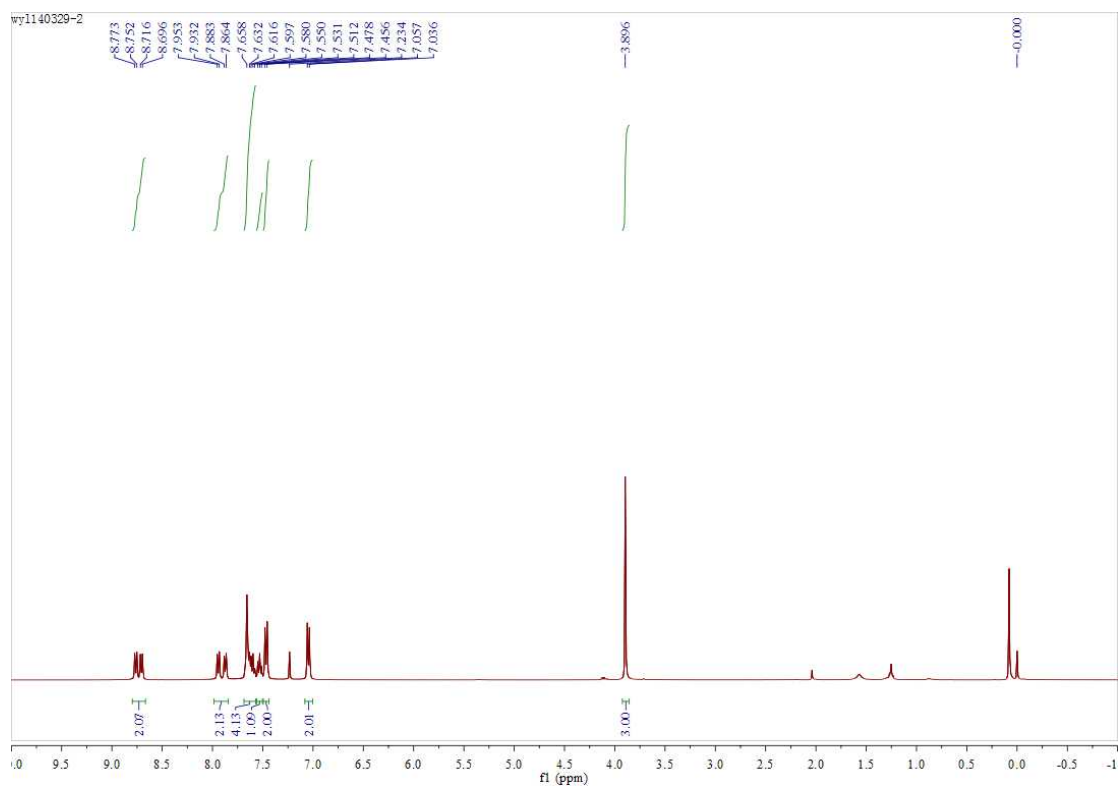


white solid (96%, 27mg). Mp: 94 – 95 °C.

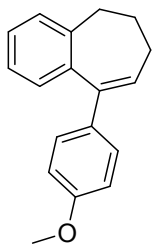
¹H NMR (400 MHz, CDCl₃) δ 8.73 (dd, *J* = 22.5, 8.2 Hz, 2H), 7.91 (dd, *J* = 27.6, 7.9 Hz, 2H), 7.69 – 7.57 (m, 4H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 157.96, 137.34, 132.07, 130.59, 130.33, 130.08, 129.59, 128.79, 127.53, 126.40, 125.89, 125.76, 125.40, 125.34, 121.84, 121.47, 112.70, 54.33.

HRMS calcd for C₂₁H₁₆O([M]⁺): 284.1201; found 284.1196.



9-(4-methoxyphenyl)-6,7-dihydro-5H-benzo[7]annulene(2s)

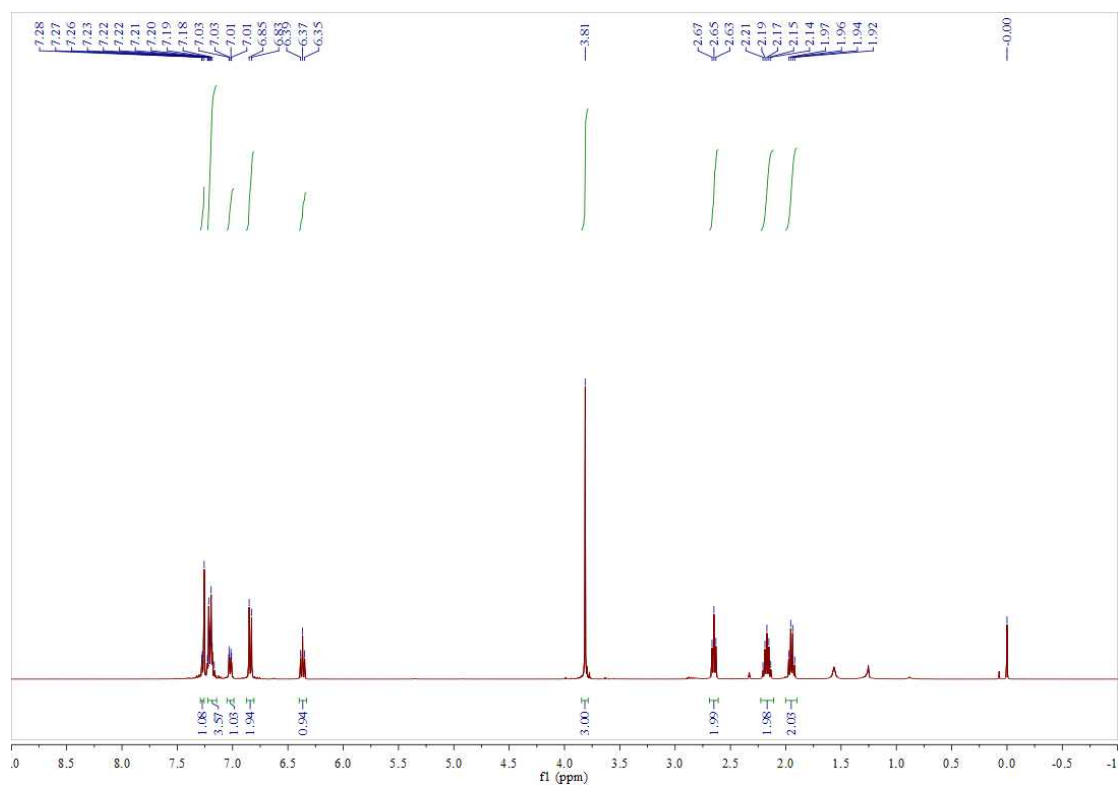


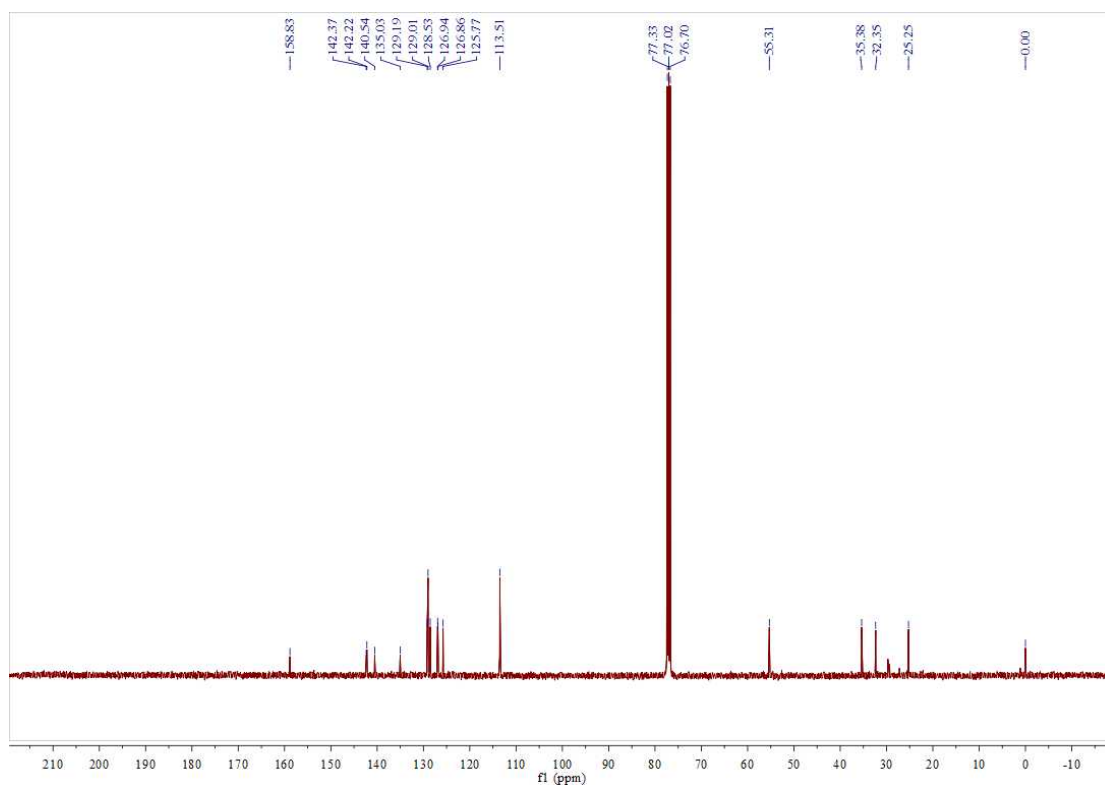
colorless oil (36%, 9mg)

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 2.1 Hz, 1H), 7.22 – 7.14 (m, 4H), 7.02 (dd, *J* = 7.2, 1.7 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.37 (t, *J* = 7.4 Hz, 1H), 3.81 (s, 3H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.17 (p, *J* = 7.1 Hz, 2H), 1.95 (q, *J* = 7.2 Hz, 2H).

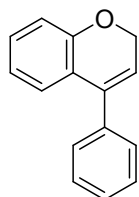
¹³C NMR (100 MHz, CDCl₃) δ 158.83, 142.37, 142.22, 140.54, 135.03, 129.19, 129.01, 128.53, 126.94, 126.86, 125.77, 113.51, 55.31, 35.38, 32.35, 25.25.

HRMS calcd for C₁₈H₁₈O([M]⁺): 250.1358; found 250.1350.





4-phenyl-2H-chromene(2u)

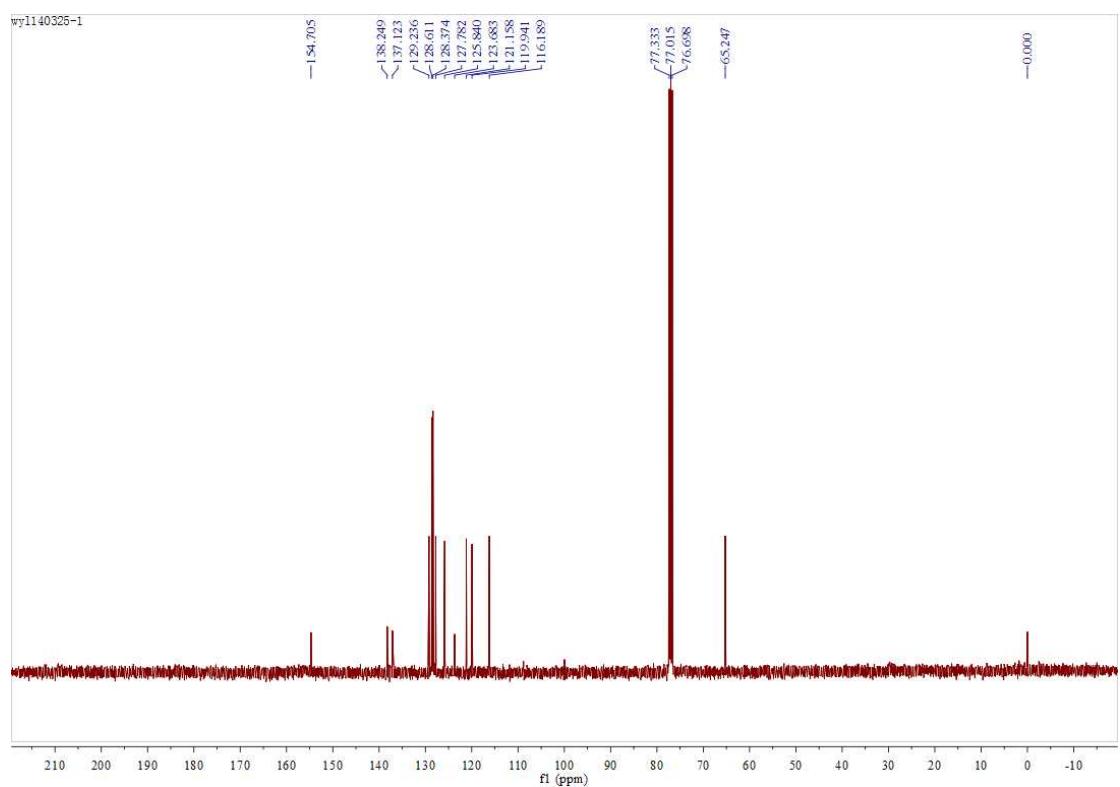
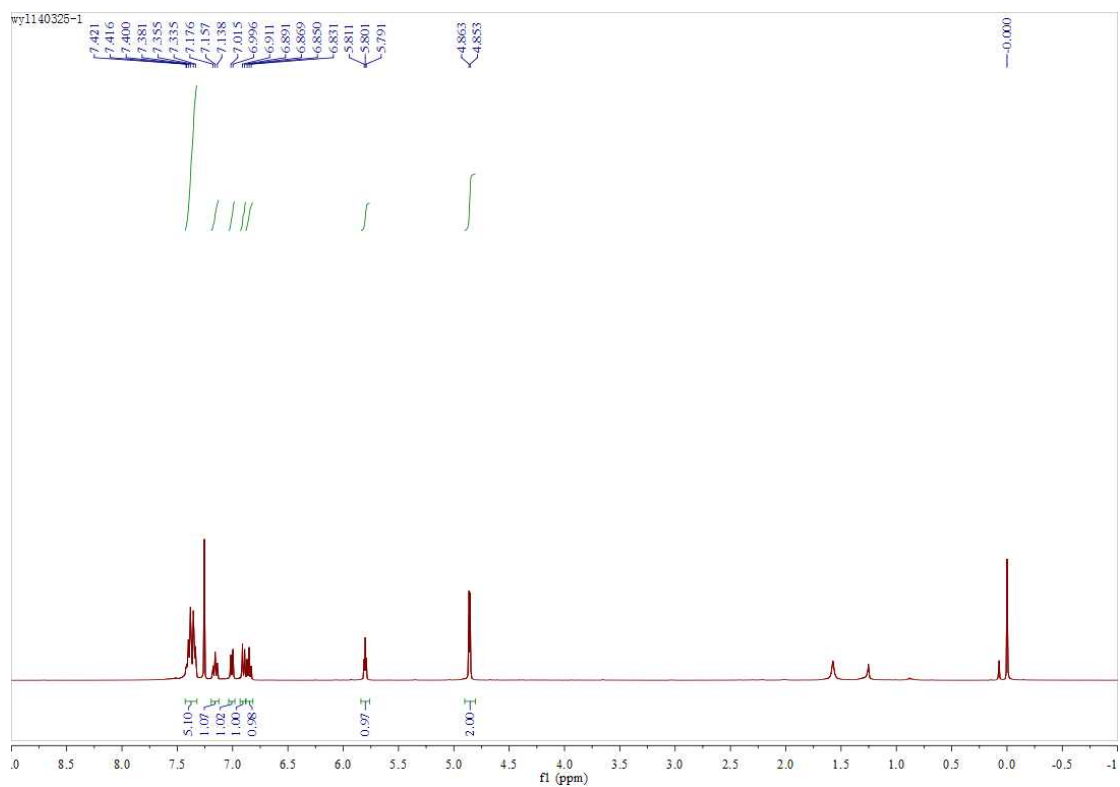


colorless oil (52%, 11mg).

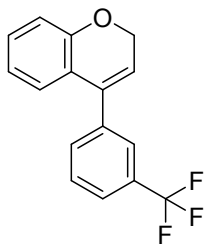
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 (dt, $J = 18.5, 5.0$ Hz, 5H), 7.16 (t, $J = 7.7$ Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 6.85 (t, $J = 7.5$ Hz, 1H), 5.80 (t, $J = 3.9$ Hz, 1H), 4.86 (d, $J = 3.9$ Hz, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 154.71, 138.25, 137.12, 129.24, 128.61, 128.37, 127.78, 125.84, 123.68, 121.16, 119.94, 116.19, 65.25.

HRMS calcd for $\text{C}_{15}\text{H}_{12}\text{O}([\text{M}]^+)$: 208.0888; found 208.0880.



4-(3-(trifluoromethyl)phenyl)-2H-chromene(2v)



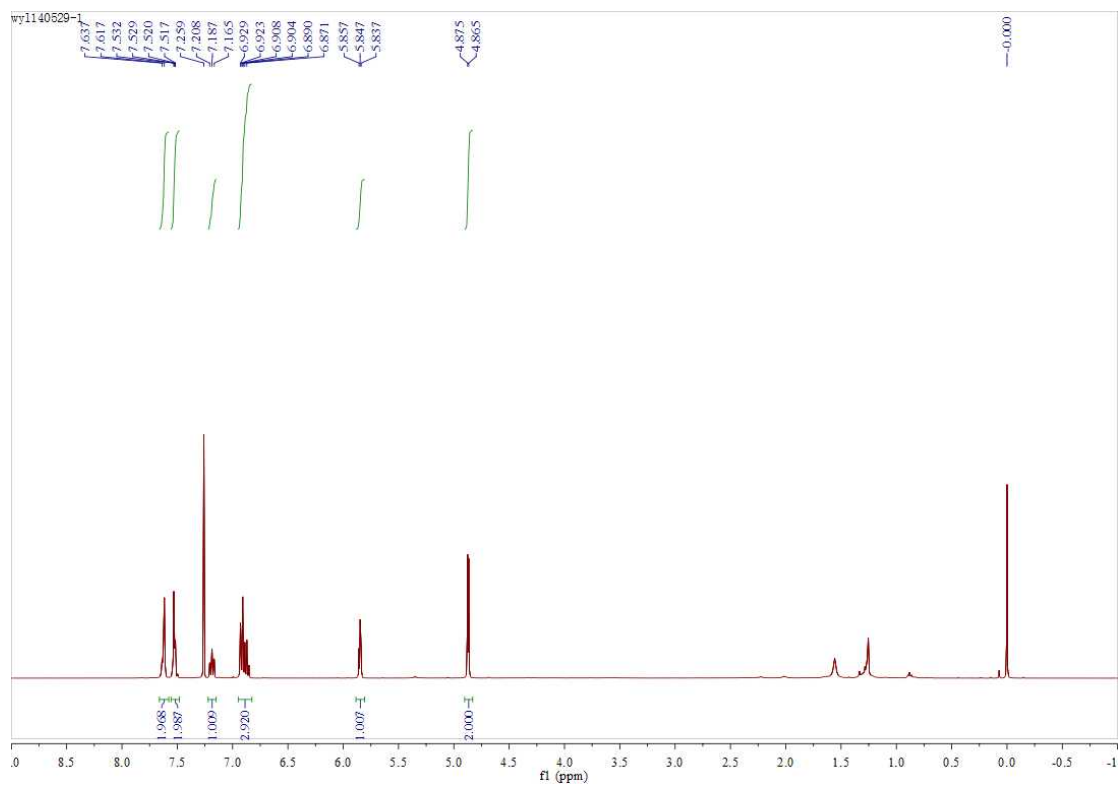
colorless oil (70%, 19mg).

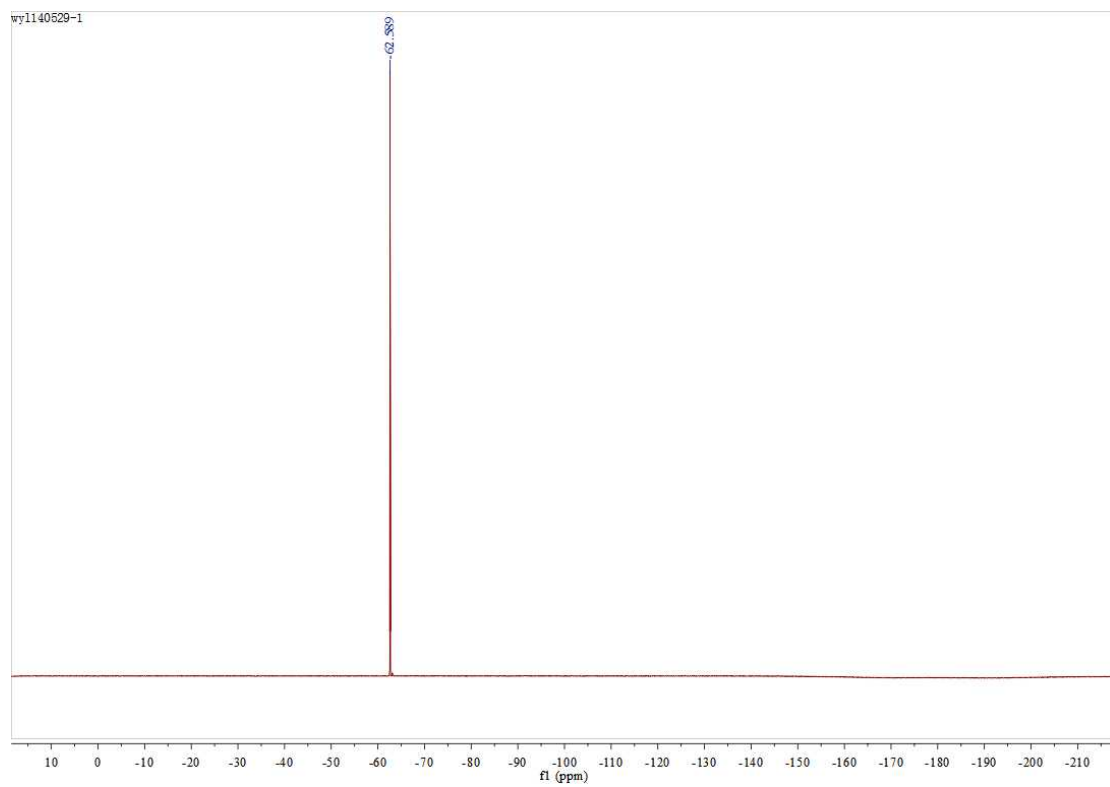
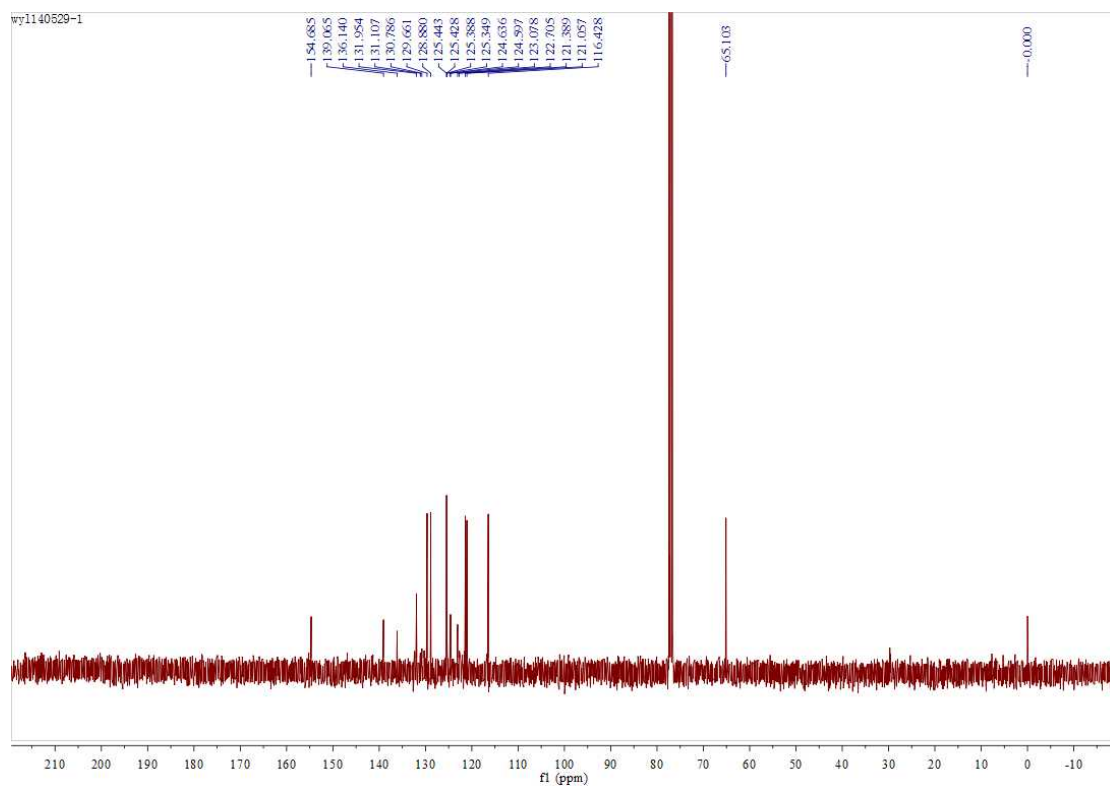
¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.52 (dd, *J* = 4.7, 1.2 Hz, 2H), 7.19 (t, *J* = 8.5 Hz, 1H), 6.95 – 6.83 (m, 3H), 5.85 (t, *J* = 3.9 Hz, 1H), 4.87 (d, *J* = 3.9 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 154.69, 139.07, 136.14, 131.95, 130.95 (q, *J* = 32.3 Hz), 129.66, 128.88, 125.44 (q, *J* = 1.54 Hz), 125.39, 124.62 (q, *J* = 3.9 Hz), 124.03 (q, *J* = 266.1), 123.08, 121.39, 121.06, 116.43, 65.10.

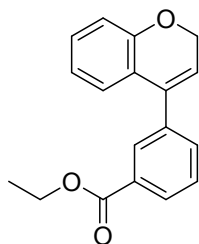
¹⁹F NMR (376 MHz, CDCl₃) δ -62.59 (s).

HRMS calcd for C₁₆H₁₁F₃O([M]⁺): 276.0762; found 276.0759.





ethyl 3-(2H-chromen-4-yl)benzoate(2w)

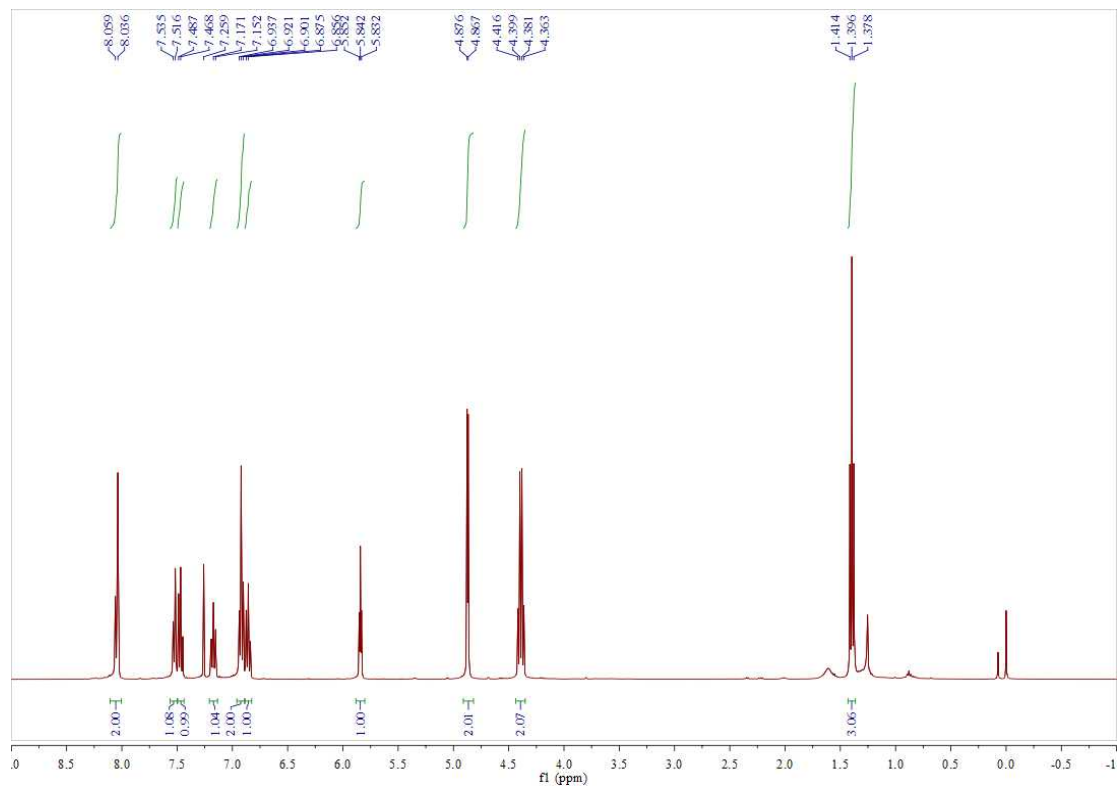


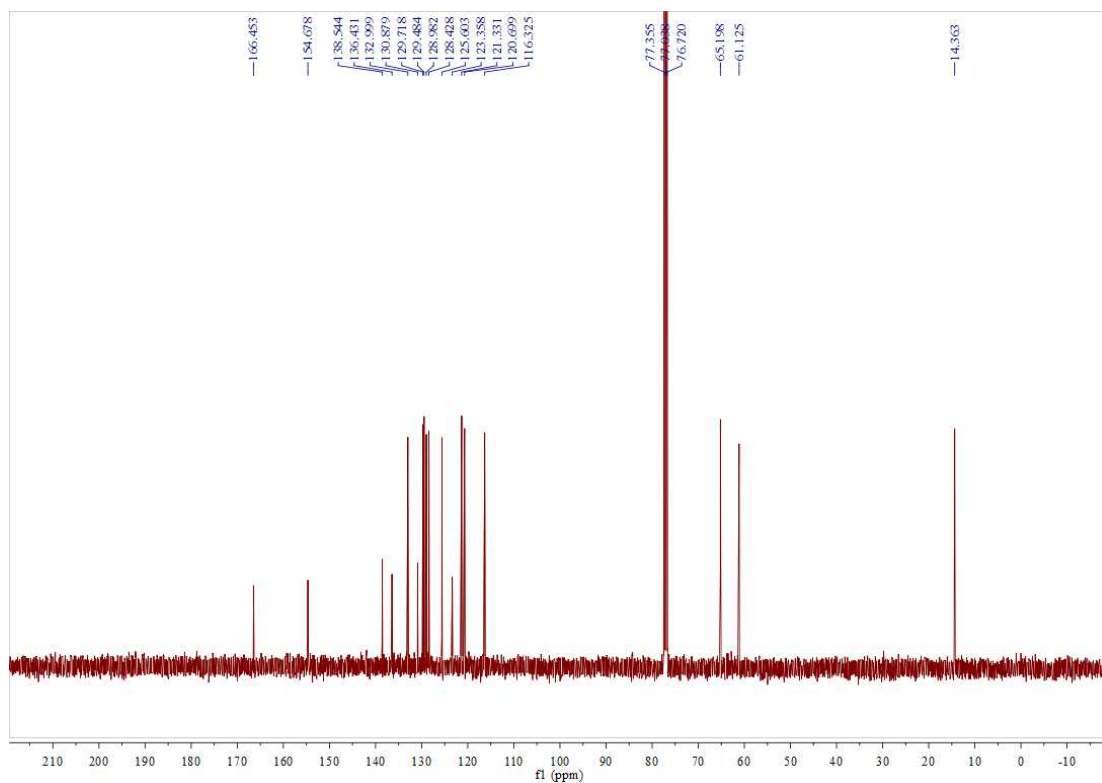
colorless oil (64%, 18mg)

¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 12.1, 4.6 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 5.84 (t, *J* = 3.9 Hz, 1H), 4.87 (d, *J* = 3.9 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

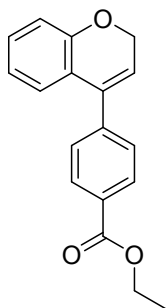
¹³C NMR (100 MHz, CDCl₃) δ 166.45, 154.68, 138.54, 136.43, 133.00, 130.88, 129.72, 129.48, 128.98, 128.43, 125.60, 123.36, 121.33, 120.70, 116.32, 65.20, 61.12, 14.36.

HRMS calcd for C₁₈H₁₆O₃([M]⁺): 280.1099; found 280.1095.





ethyl 4-(2H-chromen-4-yl)benzoate(2x)

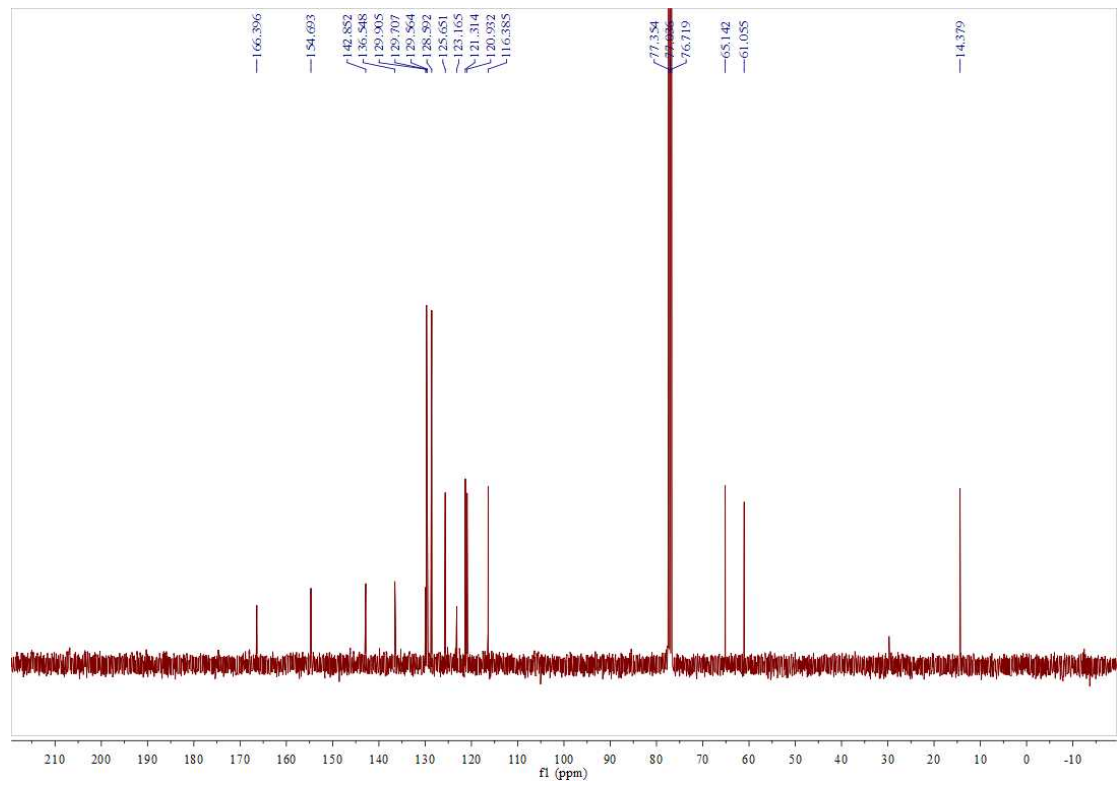
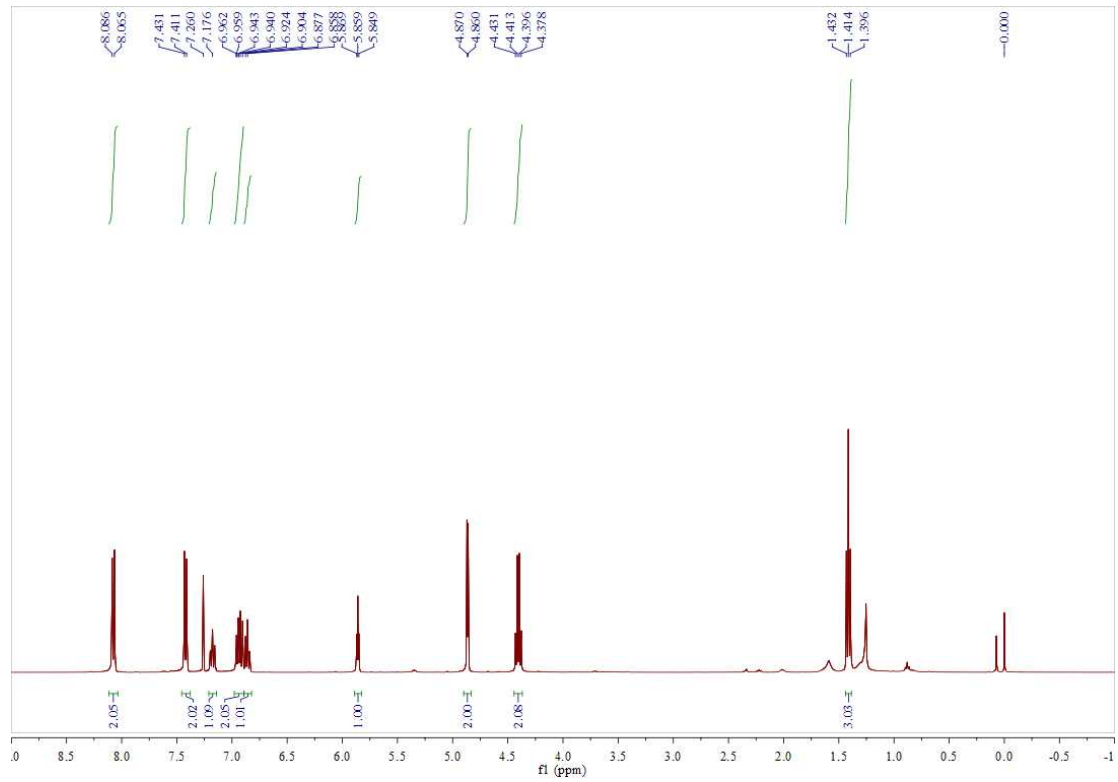


colorless oil (56%, 15mg)

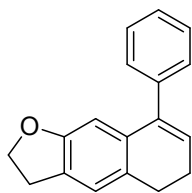
¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.14 (m, 1H), 6.98 – 6.89 (m, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 5.86 (t, *J* = 4.0 Hz, 1H), 4.87 (d, *J* = 4.0 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.40, 154.69, 142.85, 136.55, 129.91, 129.71, 129.56, 128.59, 125.65, 123.16, 121.31, 120.93, 116.38, 65.14, 61.05, 14.38.

HRMS calcd for C₁₈H₁₆O₃([M]⁺): 280.1099; found 280.1096.



8-phenyl-2,3,5,6-tetrahydro[2,3-b]furan(2y)

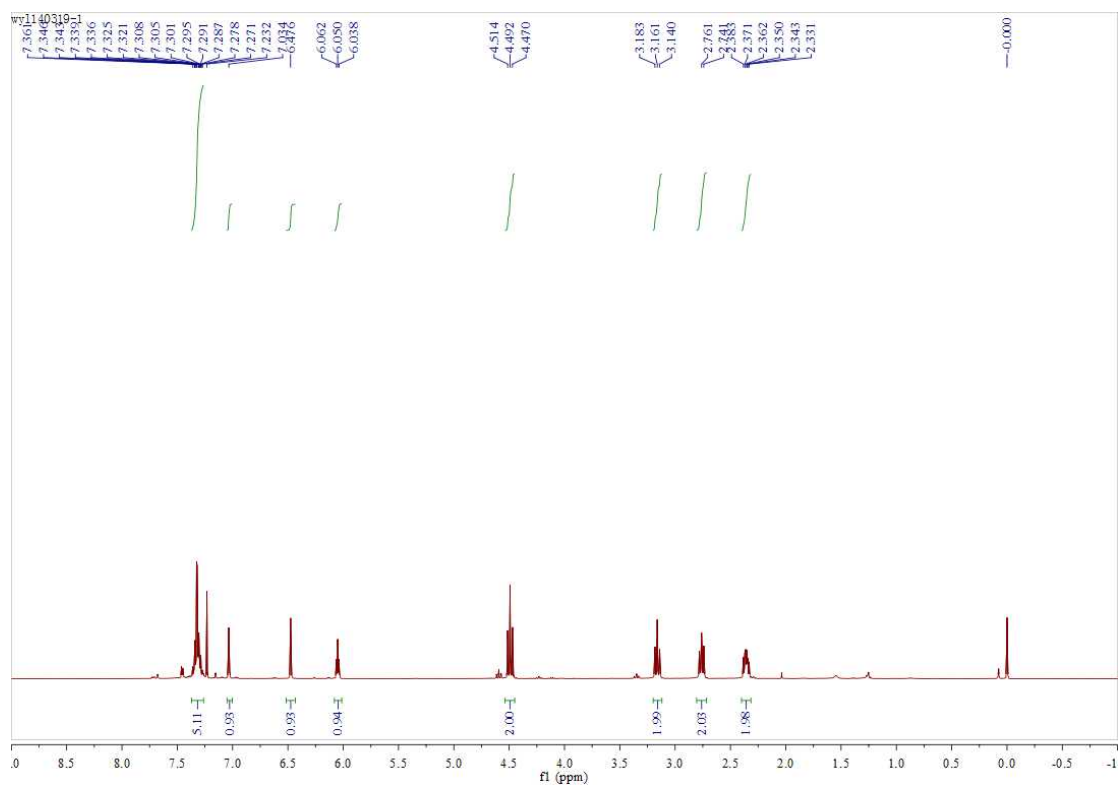


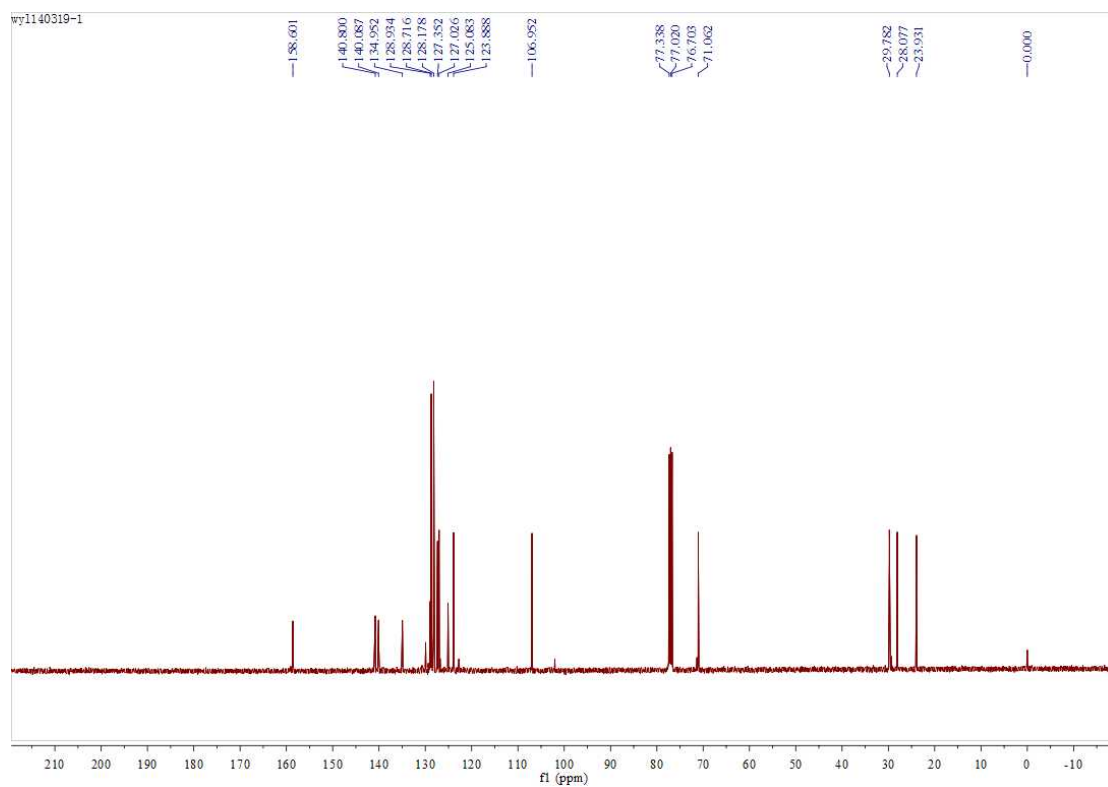
pale yellow oil (86%, 21 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.26 (m, 5H), 7.03 (s, 1H), 6.48 (s, 1H), 6.05 (t, *J* = 4.7 Hz, 1H), 4.49 (t, *J* = 8.6 Hz, 2H), 3.16 (t, *J* = 8.6 Hz, 2H), 2.76 (t, *J* = 7.9 Hz, 2H), 2.40 – 2.32 (m, 2H).

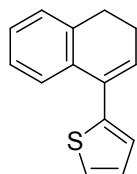
¹³C NMR (100 MHz, CDCl₃) δ 158.60, 140.80, 140.09, 134.95, 128.93, 128.71, 128.18, 127.35, 127.02, 125.08, 123.89, 106.95, 71.06, 29.78, 28.08, 23.93.

HRMS calcd for C₁₈H₁₆O([M]⁺): 248.1201; found 248.1197.





2-(3,4-dihydronaphthalen-1-yl)thiophene(2z)

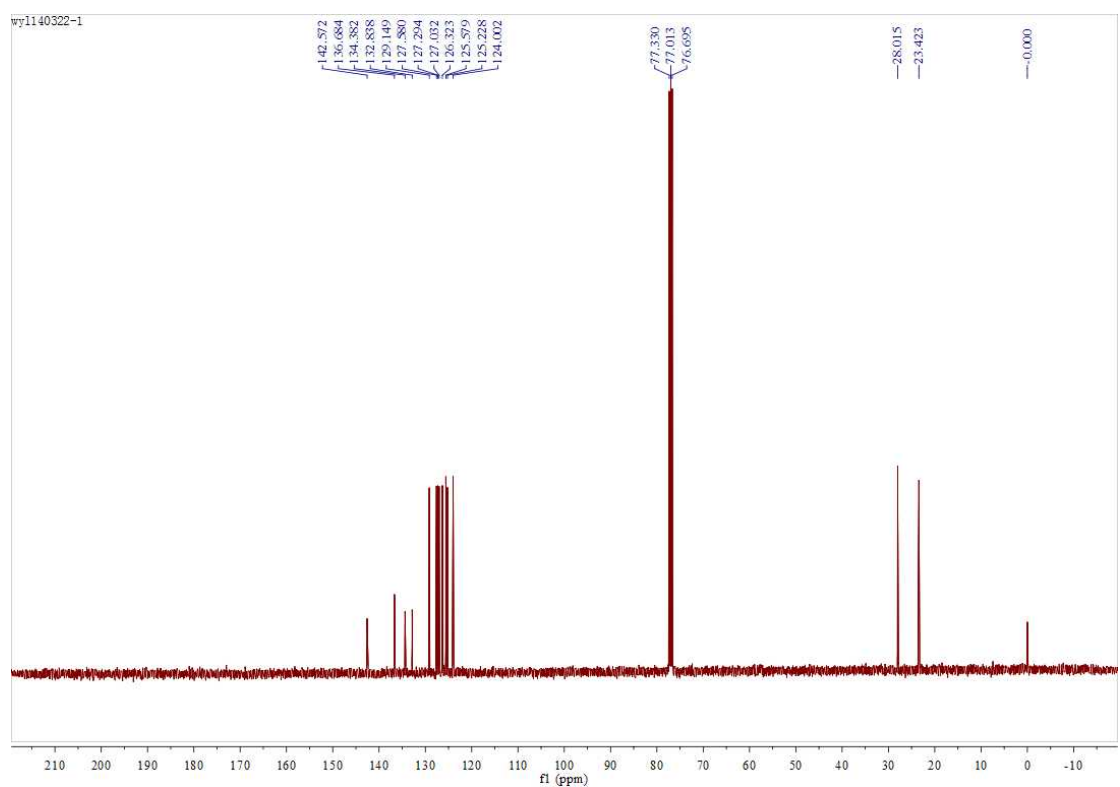
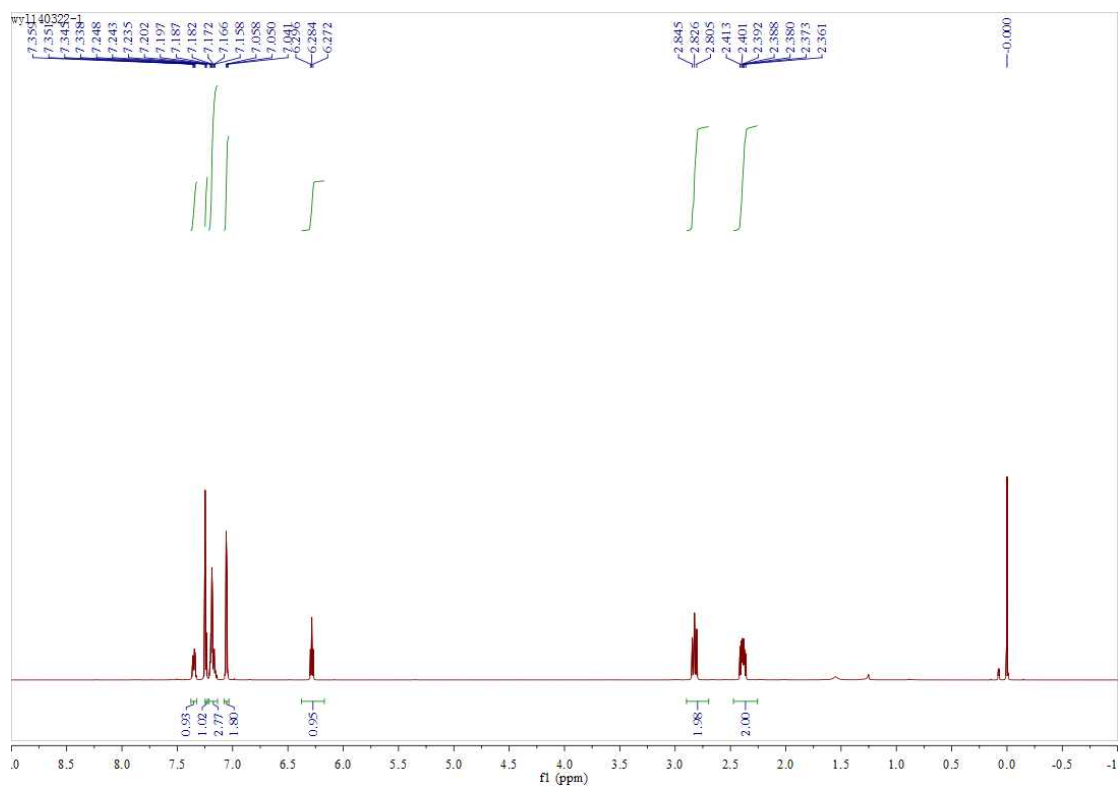


pale yellow solid (65%, 14mg). Mp: 81 – 82 °C.

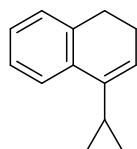
¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.32 (m, 1H), 7.24 (d, *J* = 3.2 Hz, 1H), 7.21 – 7.14 (m, 3H), 7.08 – 7.03 (m, 2H), 6.28 (t, *J* = 4.8 Hz, 1H), 2.90 – 2.70 (m, 2H), 2.47 – 2.26 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 142.57, 136.69, 134.38, 132.84, 129.15, 127.58, 127.30, 127.03, 126.32, 125.58, 125.23, 124.00, 28.02, 23.42.

HRMS calcd for C₁₄H₁₂S([M]⁺): 212.0660; found 212.0655.



4-cyclopropyl-1,2-dihydronaphthalene(2aa)

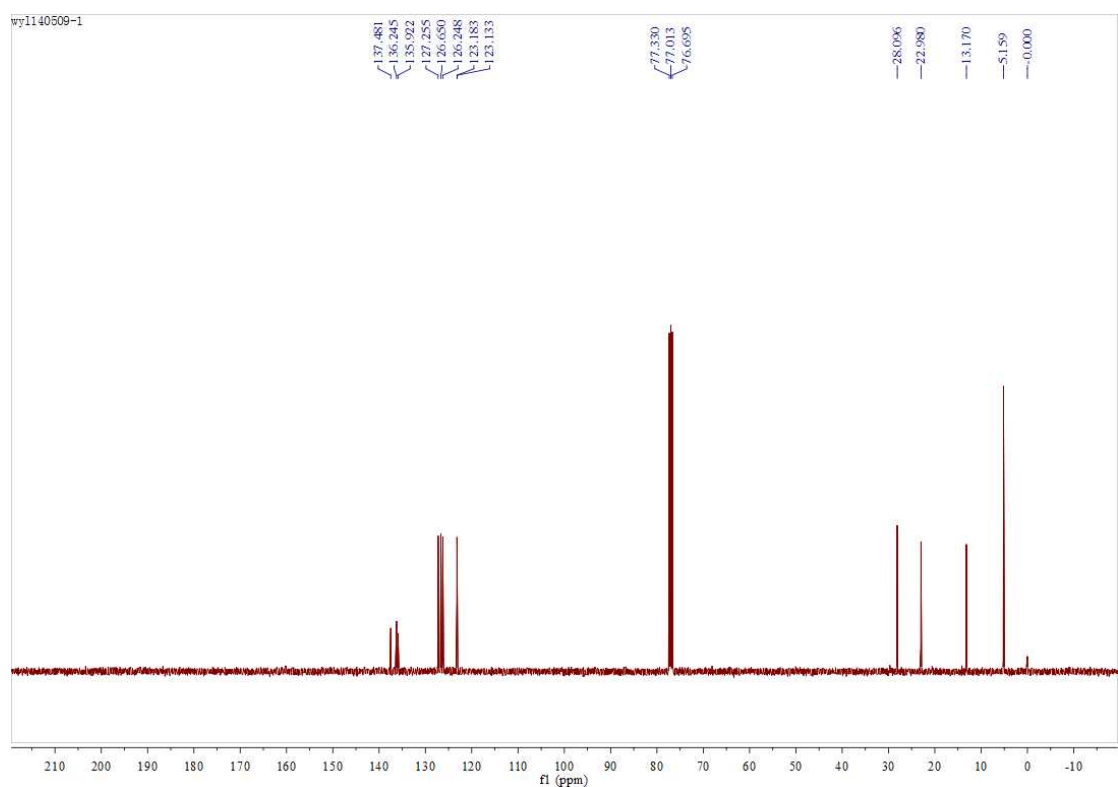
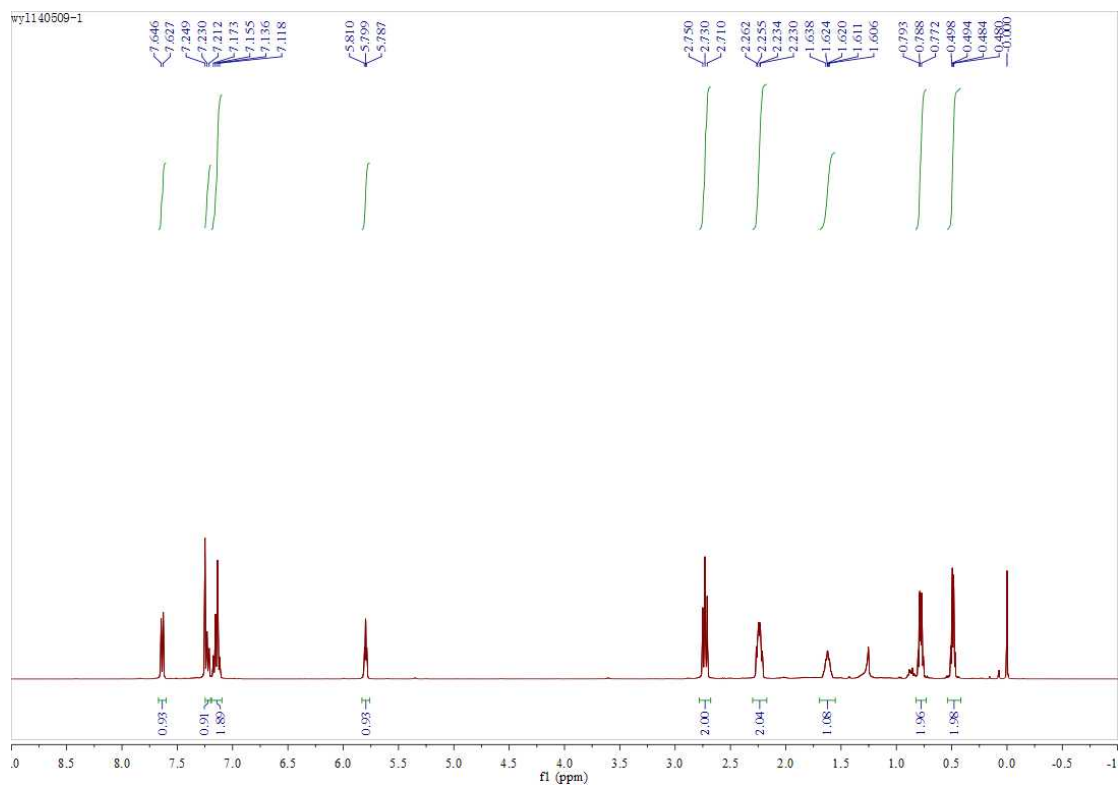


colorless oil (68%, 12mg).

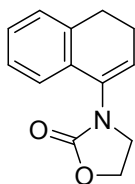
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (d, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 7.5$ Hz, 1H), 7.15 (q, $J = 7.4$ Hz, 2H), 5.80 (t, $J = 4.5$ Hz, 1H), 2.73 (t, $J = 8.0$ Hz, 2H), 2.30 – 2.17 (m, 2H), 1.69 – 1.55 (m, 1H), 0.82 – 0.73 (m, 2H), 0.54 – 0.42 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 137.48, 136.24, 135.92, 127.25, 126.65, 126.25, 123.18, 123.13, 28.10, 22.98, 13.17, 5.16.

HRMS calcd for $\text{C}_{13}\text{H}_{14}([\text{M}]^+)$: 170.1096; found 170.1088.



3-(3,4-dihydronaphthalen-1-yl)oxazolidin-2-one(2ab)

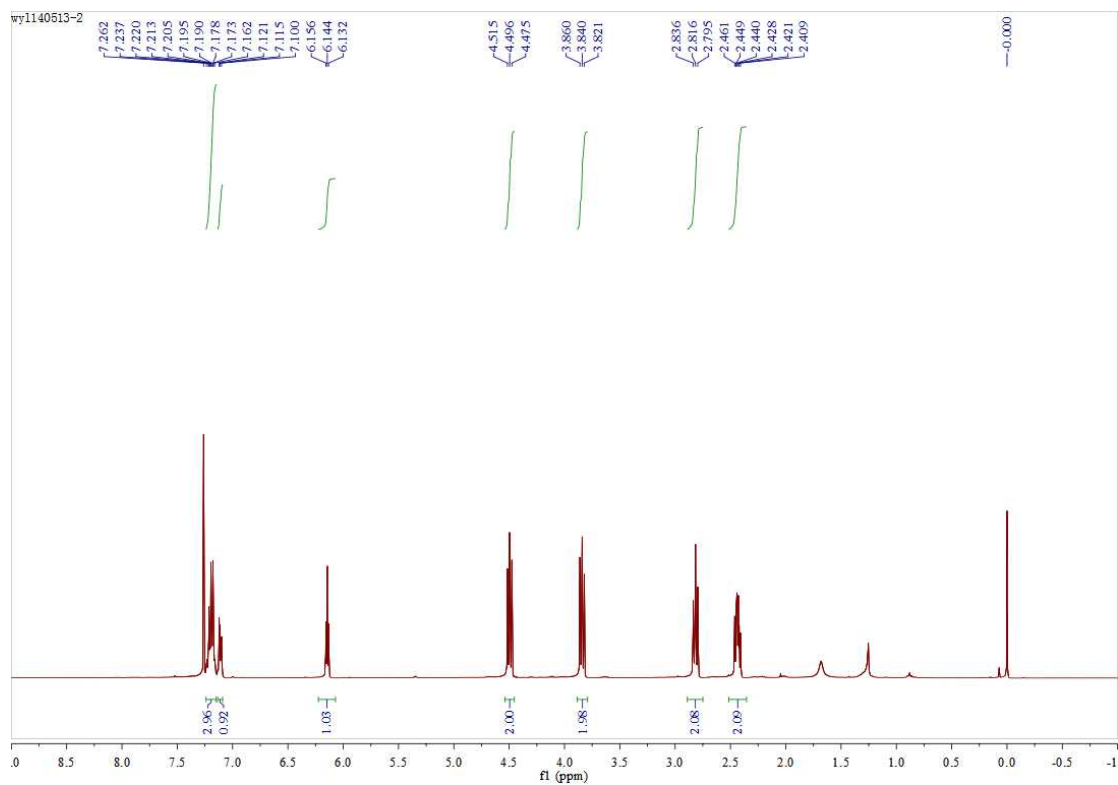


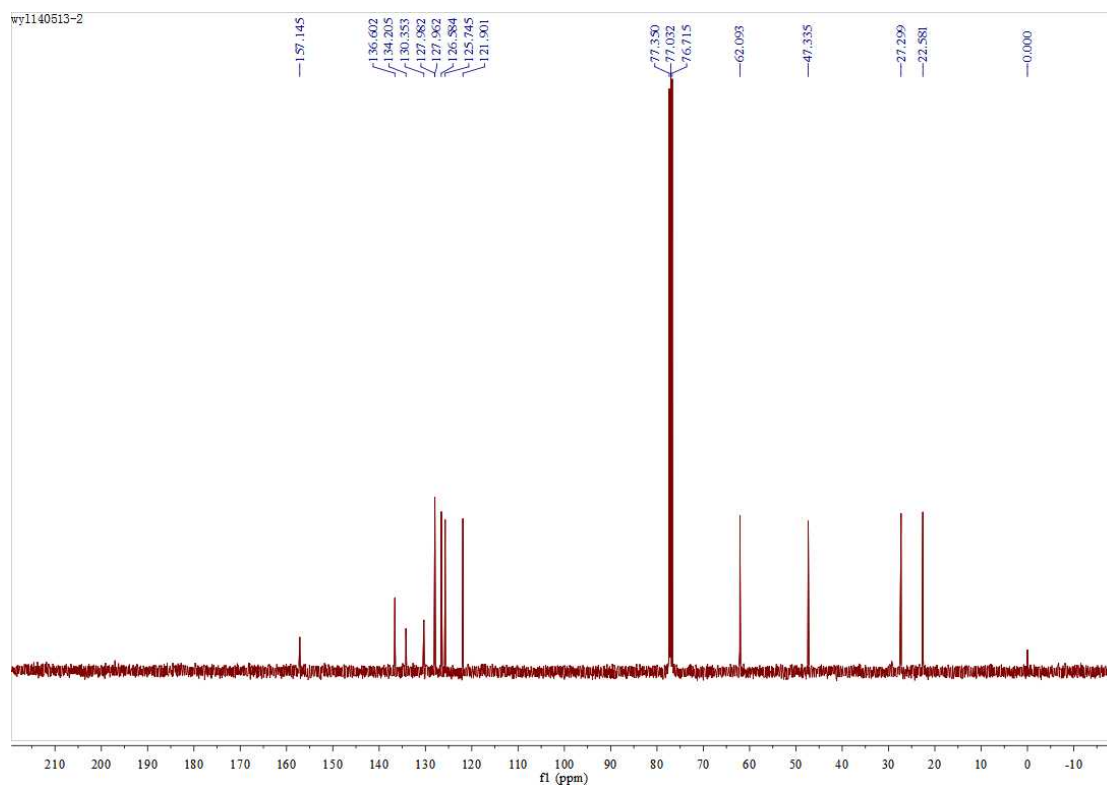
colorless oil (62%, 13mg).

¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.15 (m, 3H), 7.13 – 7.09 (m, 1H), 6.14 (t, *J* = 4.7 Hz, 1H), 4.54 – 4.45 (m, 2H), 3.88 – 3.79 (m, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.43 (td, *J* = 8.0, 4.8 Hz, 2H).

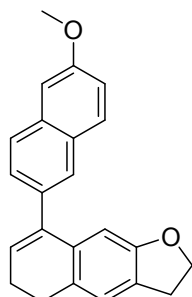
¹³C NMR (100 MHz, CDCl₃) δ 157.15, 136.60, 134.21, 130.35, 127.98, 127.96, 126.58, 125.75, 121.90, 62.09, 47.33, 27.30, 22.58.

HRMS calcd for C₁₃H₁₃NO₂([M]⁺): 215.0946; found 215.0938.





8-(6-methoxynaphthalen-2-yl)-2,3,5,6-tetrahydronaphtho[2,3-b]furan(2ac)

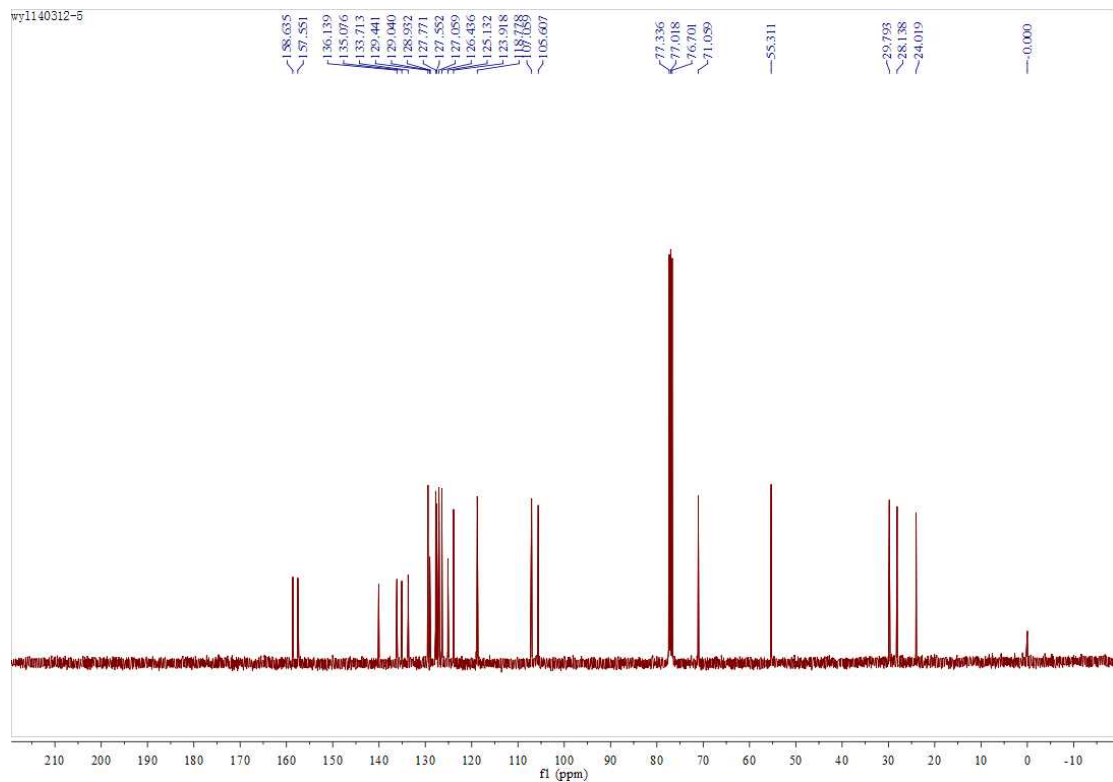
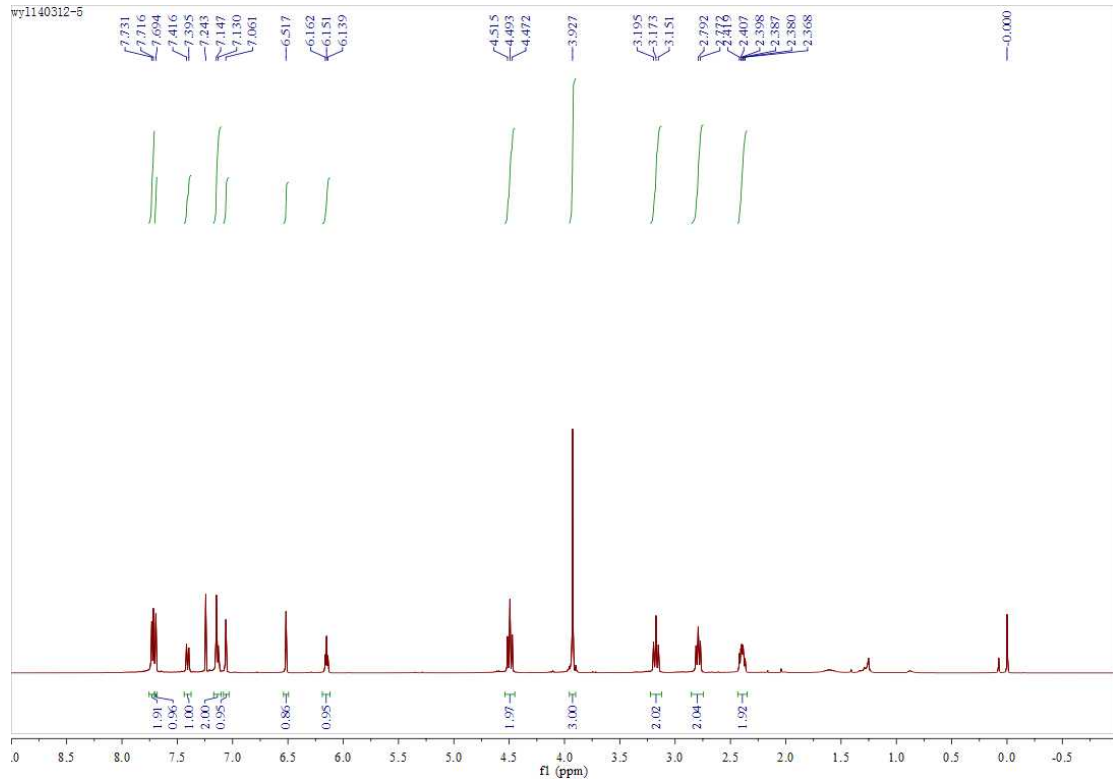


colorless oil (65%, 21mg).

¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 5.9 Hz, 2H), 7.69 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.14 (d, *J* = 6.8 Hz, 2H), 7.06 (s, 1H), 6.52 (s, 1H), 6.15 (t, *J* = 4.6 Hz, 1H), 4.49 (t, *J* = 8.6 Hz, 2H), 3.93 (s, 3H), 3.17 (t, *J* = 8.6 Hz, 2H), 2.79 (t, *J* = 7.9 Hz, 2H), 2.39 (td, *J* = 7.9, 5.0 Hz, 2H).

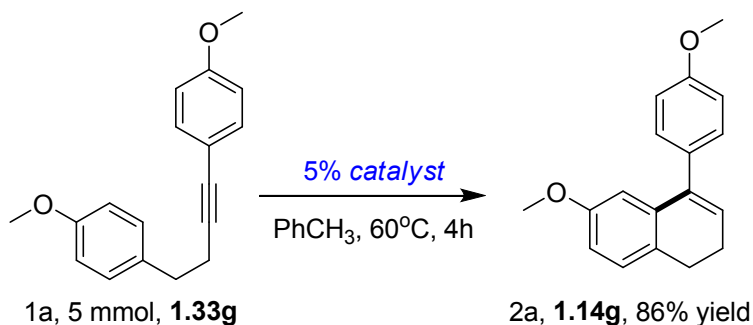
¹³C NMR (100 MHz, CDCl₃) δ 158.63, 157.55, 140.06, 136.14, 135.08, 133.71, 129.44, 129.04, 128.93, 127.77, 127.55, 127.06, 126.44, 125.13, 123.92, 118.78, 107.06, 105.61, 71.06, 55.31, 29.79, 28.14, 24.02.

HRMS calcd for C₂₃H₂₀O₂([M]⁺): 328.1463; found 328.1455.



IV. Synthetic Application

1. Representative Procedure for Gram-Scale Reaction

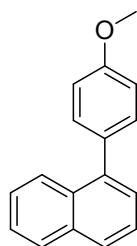


A 50 mL three-necked round bottom flask was charged with **1a** (5 mmol, 1.33g), Cu(OTf)₂ (5 mol%, 90.5 mg). The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, PhCH₃ (20 mL) were added by syringe. The flask was sealed and the mixture was allowed to stir in a preheated oil bath at 60 °C for 4 h. The mixture was cooled to room temperature when the reaction was completed. Next, the organic solvent was concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate to give the product **2a** with the yield of 86%.

2. Representative Procedure for Aromatization¹

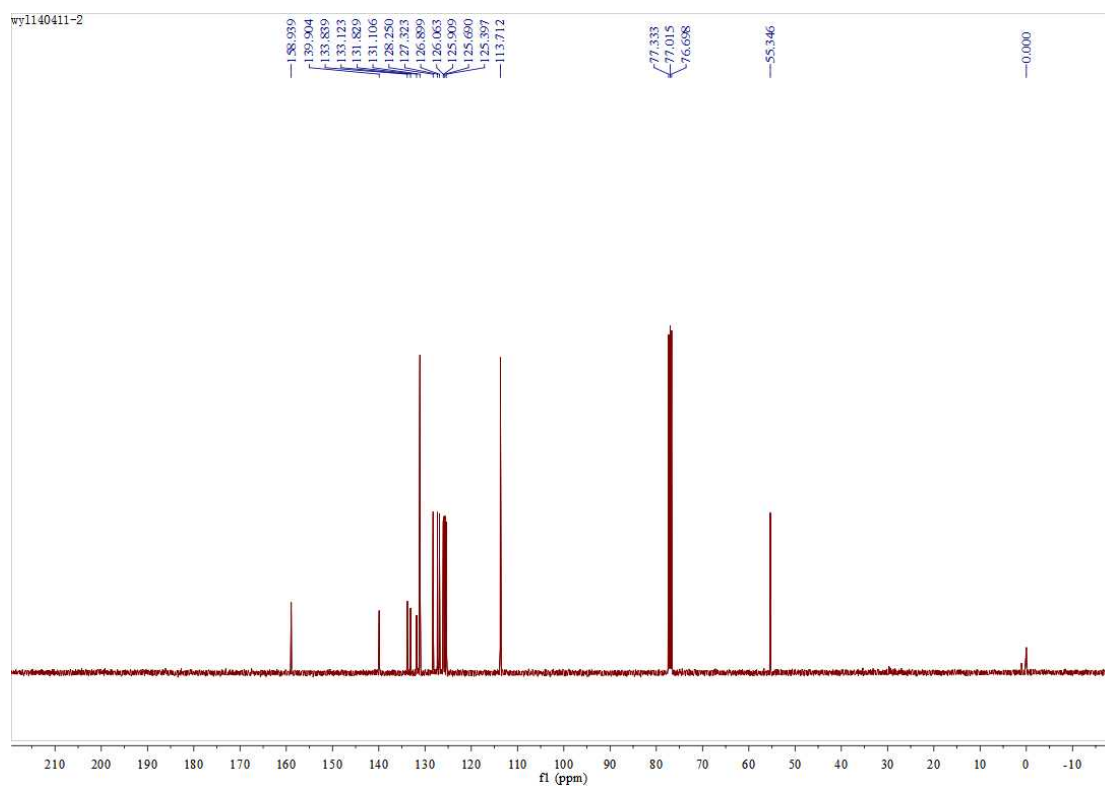
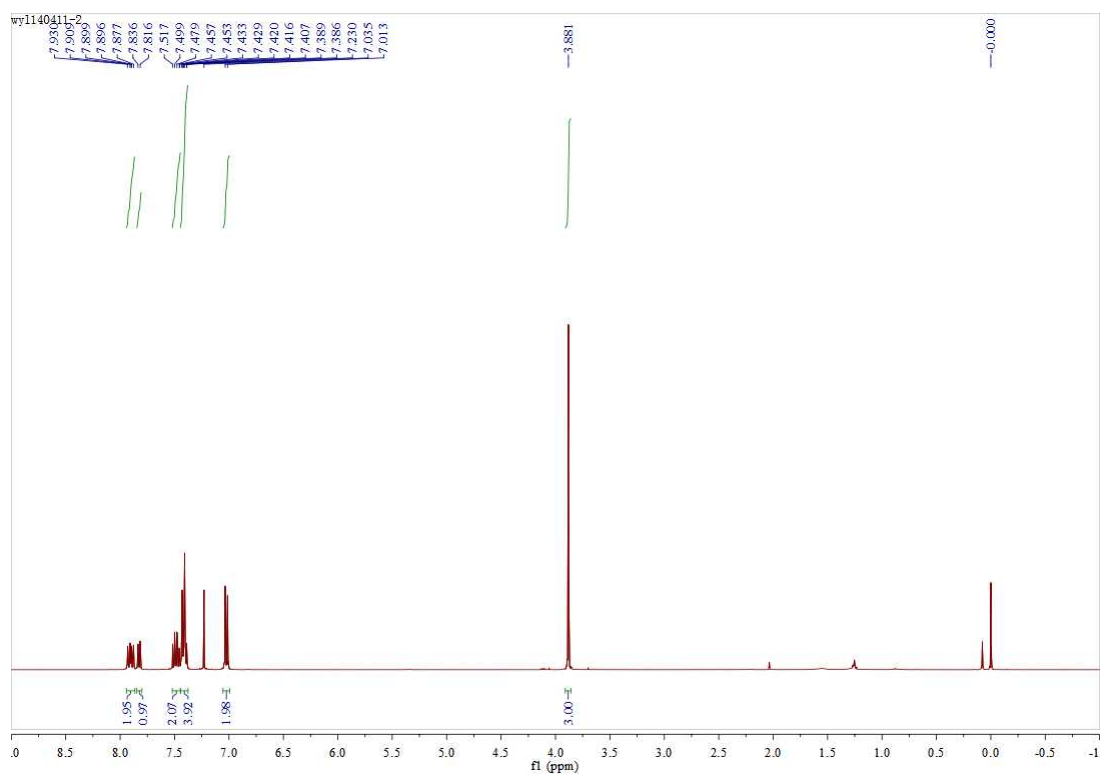
To a solution of 4-(4-methoxyphenyl)-1,2-dihydronaphthalene (**II**, 0.1 mmol) in toluene (2 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2 equiv) and the mixture heated to reflux for 16 h. The reaction mixture was cooled to room temperature and quenched by addition of NaHCO₃. The aqueous layer was separated and extracted with dichloromethane. The combined organics were washed with brine, dried (MgSO₄) and the solvent removed in vacuo. Purification by flash chromatography gave **III**.

1-(4-methoxyphenyl)naphthalene (**III**)



¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.86 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.38 (m, 4H), 7.02 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H).

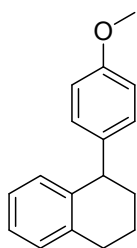
¹³C NMR (100 MHz, CDCl₃) δ 158.94, 139.90, 133.84, 133.12, 131.83, 131.11, 128.25, 127.32, 126.90, 126.06, 125.91, 125.69, 125.40, 113.71, 55.35.



3. Representative Procedure for Hydrogenation²

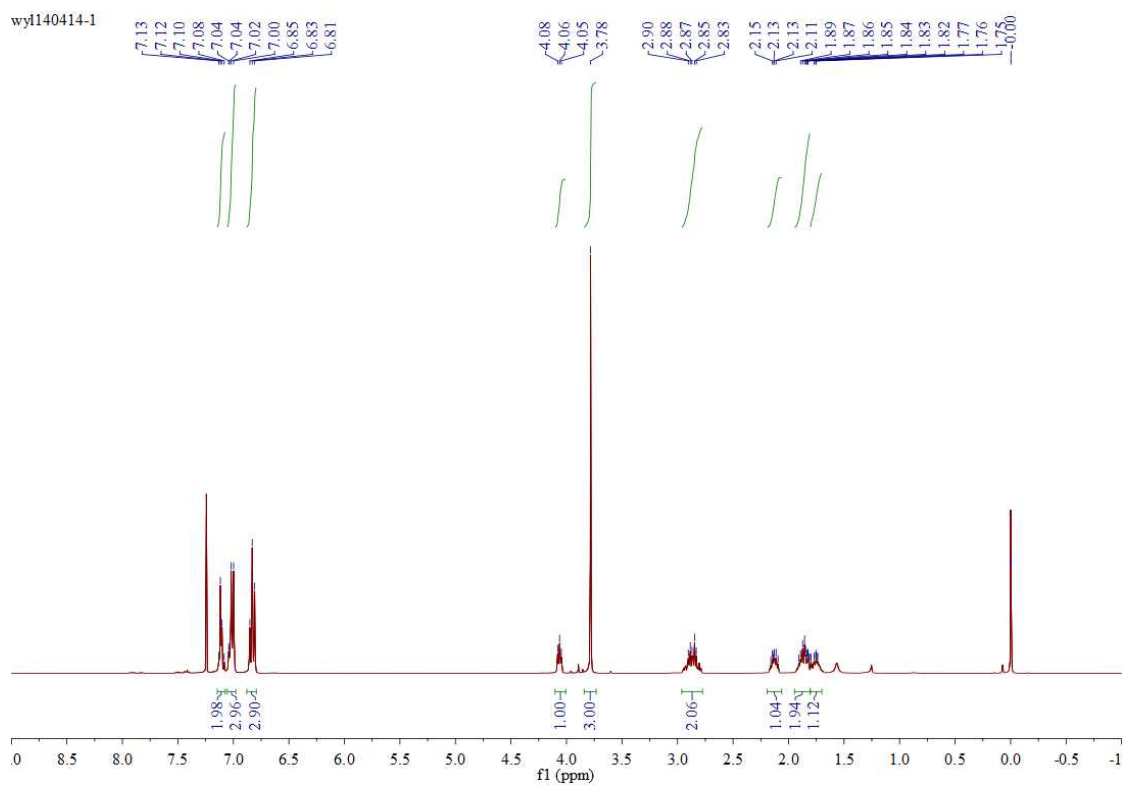
Combine 4-(4-methoxyphenyl)-1,2-dihydronaphthalene (**II**, 0.1 mmol), 5% Pd on carbon (0.08 mmol), and methanol (1 mL), degas, and add 345 kPa H₂ at room temperature. After 12 hours, filter off the Pd catalyst over celite eluting with ethyl acetate. Concentrate and flash chromatography gave **IV**.

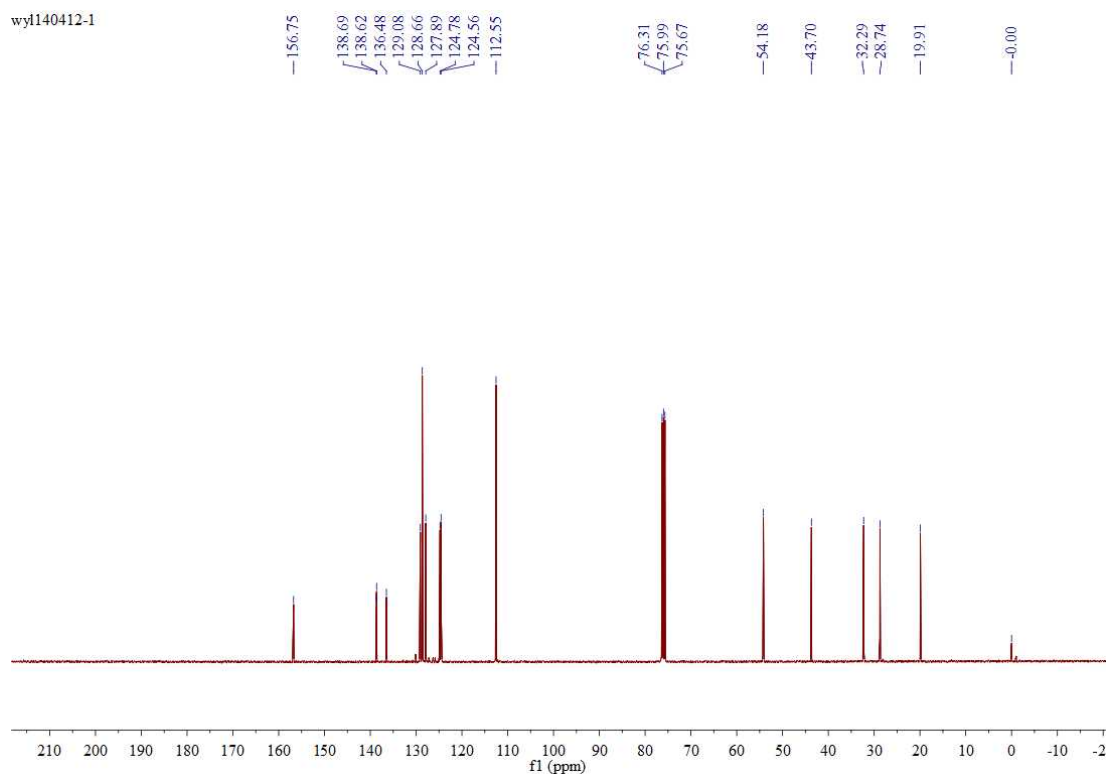
1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (IV)



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.15 – 7.07 (m, 2H), 7.02 (dd, $J = 12.0, 5.6$ Hz, 3H), 6.83 (t, $J = 8.6$ Hz, 3H), 4.06 (t, $J = 6.6$ Hz, 1H), 3.78 (s, 3H), 2.96 – 2.78 (m, 2H), 2.19 – 2.06 (m, 1H), 1.95 – 1.81 (m, 2H), 1.80 – 1.70 (m, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.75, 138.69, 138.62, 136.48, 129.08, 128.66, 127.89, 124.78, 124.56, 112.55, 76.31, 75.99, 75.67, 54.18, 43.70, 32.29, 28.74, 19.91.

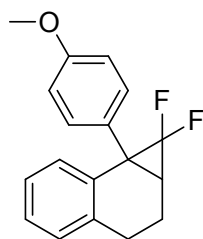




4. Representative Procedure for 1, 1- difluorocyclopropanation³

To a 10 mL pressure tube charged with a magnetic stir bar was added anhydrous NaI (0.02 mmol, 0.2 equiv), 1 mL of freshly distilled THF as solvent, and 4-(4-methoxyphenyl)-1,2-dihydronaphthalene (**II**, 0.1 mmol) in that order under Ar atmosphere. To this was added TMSCF₃ (0.25 mmol, 2.5 equiv). The reaction vessel was sealed and heated to 65 °C in an oil bath for a period of 2 hours. The reaction mixture was evaporated to dryness under reduced pressure to remove THF. The crude was extracted with ether (15 mL) and washed with water (15 mL), saturated sodium sulfite solution (15 mL), saturated sodium bicarbonate solution (15 mL), and water (15 mL), in that order. The organic layer was then collected and dried over anhydrous MgSO₄. Concentrate and flash chromatography gave **V**.

1,1-difluoro-7b-(4-methoxyphenyl)-1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalene (**V**)

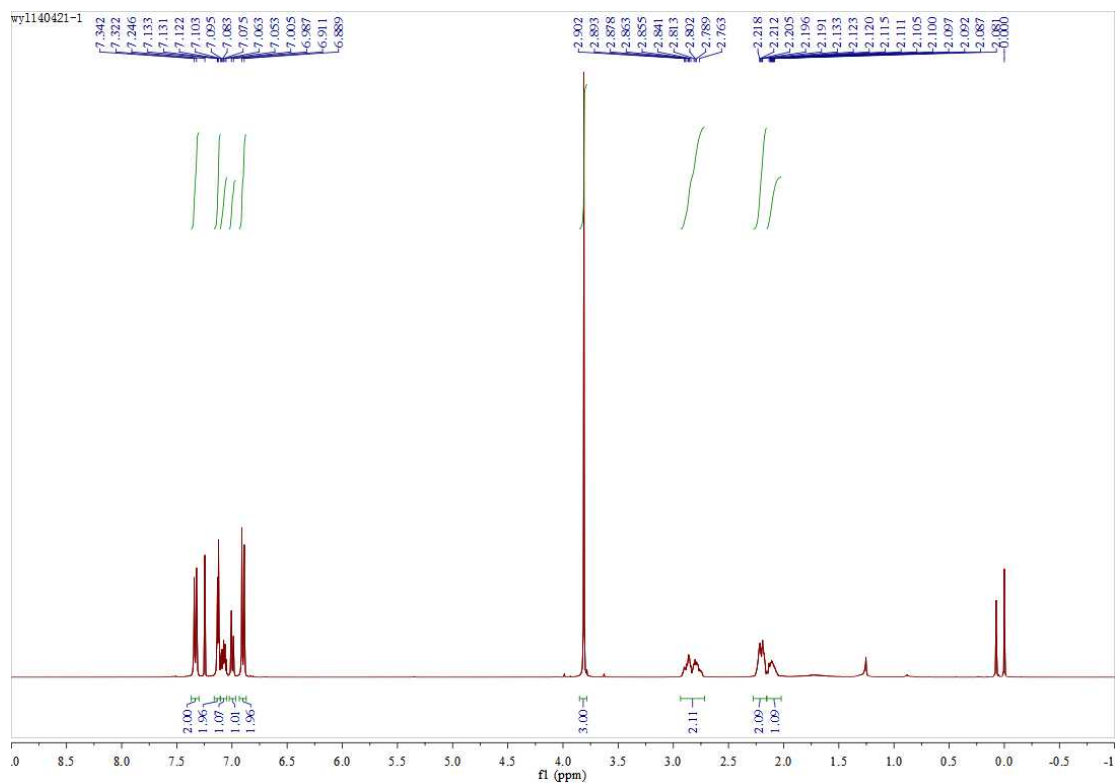


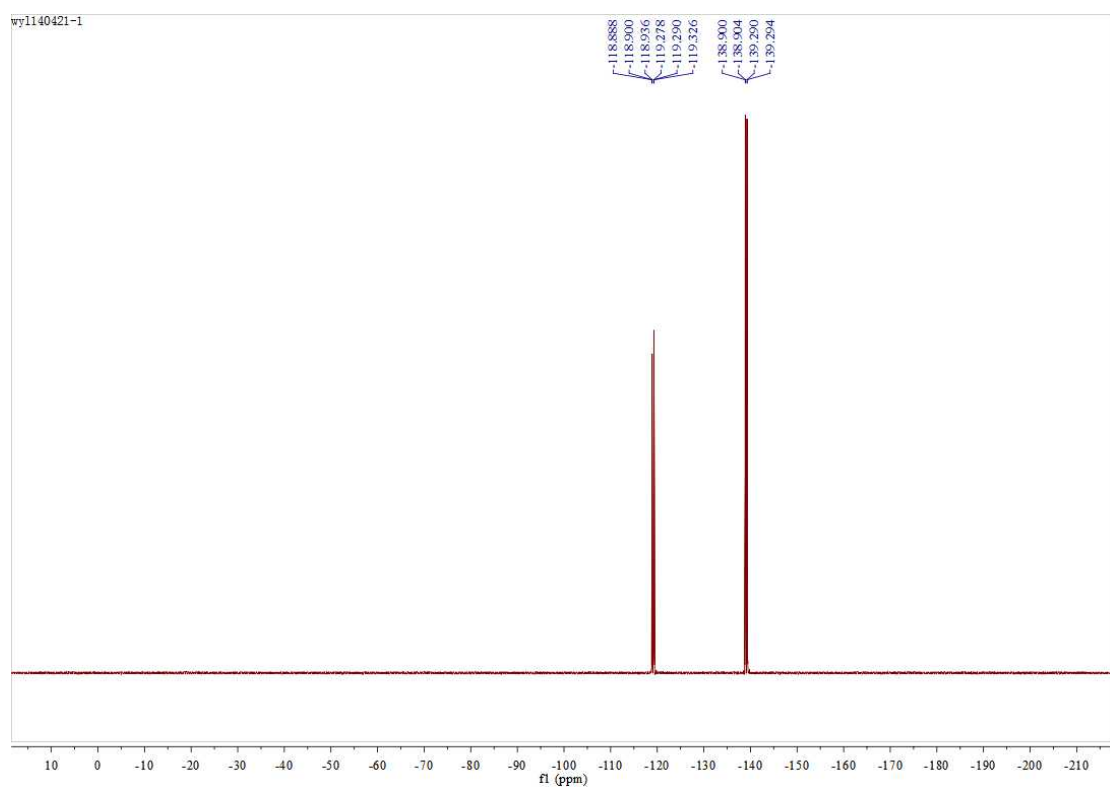
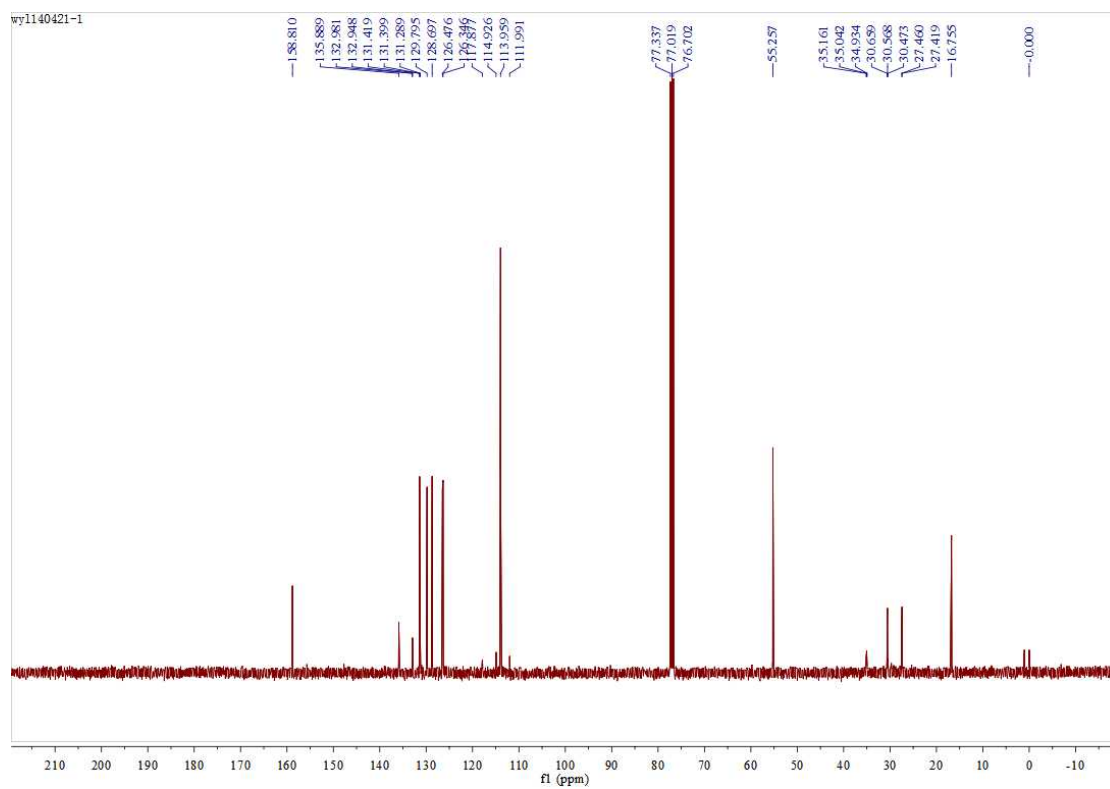
¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.11 (m, 2H), 7.08 (dt, *J* = 8.8, 3.7 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.93 – 2.72 (m,

2H), 2.27 – 2.15 (m, 2H), 2.15 – 2.02 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 158.81, 135.89, 132.95 (t, *J* = 3.3 Hz), 131.41 (d, *J* = 2.0 Hz), 131.29, 129.80, 128.70, 126.48, 126.35, 114.93 (t, *J* = 294.3 Hz), 113.96, 55.26, 35.05 (t, *J* = 11.5 Hz), 30.57 (t, *J* = 9.30 Hz), 27.44 (d, *J* = 4.1 Hz), 16.76.

¹⁹F NMR (376 MHz, CDCl₃) δ -118.84 – -118.99 (m), -119.21 – -119.38 (m), -138.90 (d, *J* = 1.6 Hz), -139.29 (d, *J* = 1.6 Hz).





Reference:

1. A. J. Walkinshaw, W.-S. Xu, M. G. Suero, M. J. Gaunt, *J. Am. Chem. Soc.*, 2013, **135**, 12532-12535.
2. D. L. J. Clive, J. Wang, *Angew. Chem. Int. Ed.*, 2003, **42**, 3406.
3. F. Wang, T. Luo, J.-B. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. Surya Prakash, G. A. Olah, *Angew. Chem. Int. Ed.*, 2011, **50**, 7153–7157.

V. Mechanistic Study

1. intramolecular isotope labeling experiments

A reaction tube was charged with $\text{Cu}(\text{OTf})_2$ (10 % mol, 3.62 mg) and **3** (0.1 mmol, 23.8 mg), the vessel was sealed before being evacuated and filled with argon (three times). Anhydrous DCE (1 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was kept for 3 h at 60°C. The mixture was cooled to room temperature when the reaction was completed. Next, the organic solvent was concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate to give the products **4** and **5**. The $K_{\text{H}}/K_{\text{D}}$ was determined by the analysis followed by Yu et al. The ratio **4** and **5** was analyzed by ^1H NMR. The yield of **5**, X, was determined by integration of the H_b signal of **5**, which appeared as a doublets approximately at 6.89 ppm. The total yield of **4** and **5**, Y was determined by integration of H_a of **4** and **5**, which appeared as d at 7.03 ppm. The yield of **4**, Z, could then be determined from the following formula: $Z = Y - X$. Then $K_{\text{H}}/K_{\text{D}} = Z/X = 0.49/0.51 = 0.96$.

