Supporting Information

# Cu(II)@luviset clear as recyclable catalyst for the formation of C-C bond in homo-coupling of terminal alkynes

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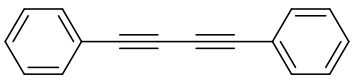
**General protocol for homo-coupling reactions of terminal alkynes:** A mixture of terminal alkyne (1 mmol), $Cu(NO_3)_2$ (4 mmol %,7.5 mg), **L1** (128 mg), and DMSO (2 mL) were put into a sealed Schlenk tube (10 mL), and then the mixture was stirred for desired time at 100 °C. The reaction was monitored by thin layer chromatography (TLC). Afterward, the reaction mixture was cooled to room temperature. The combined organic layer was dried by anhydrous sodium sulfate, and the crude product was purified by column chromatography on silica gel. NMR spectra were recorded in $CDCl_3$ on a Varian Inova-400 MHz NMR spectrometer with TMS as internal reference. Products were characterized by comparing $^1H$ NMR and $^{13}C$ NMR data with those in the literature.

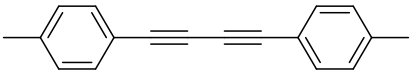
**$^1H$ NMR, $^{13}C$ NMR, and mass spectral data of the products from homo-coupling reactions:** From 2a-2k are those of known compounds.[1-6] The results of isolated products are summarized as follows:

**1,4-Diphenyl buta-1,3-diyne (2a)**: White solid; $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (t, 6H, J = 7.8 Hz), 7.53 (d, 4H, J = 7.6 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 73.91, 81.56, 121.79, 128.47, 129.24, 132.53. MS (EI): m/z 202.1.



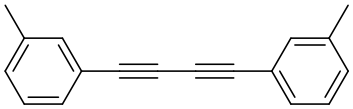
**2a**

**1,4-Bis(p-methylphenyl)buta-1,3-diyne (2b)**: White solid; $^1H$ NMR (400MHz, $CDCl_3$): δ (ppm) 2.36 (s, 6H), 7.14 (d, 4H, J = 8.0 Hz), 7.41 (d, 4H, J = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 29.66, 73.41, 81.49, 118.78, 129.15, 132.24, 139.43. MS (EI): m/z 230.1.



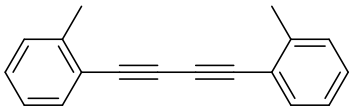
**2b**

**1,4-Bis(m-methylphenyl)buta-1,3-diyne (2c)**: White solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.34 (s, 6H), 7.17-7.24 (m, 4H), 7.34 (d, 3H, J = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 29.66, 73.61, 81.57, 121.62, 128.27, 129.56, 130.05, 132.93, 138.11. MS (EI): m/z 230.1.



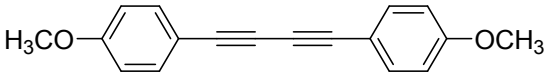
**2c**

**1,4-Bis(o-methylphenyl)buta-1,3-diyne (2d)**: White solid, $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.42 (s, 6H), 7.07-7.10 (m, 2H), 7.14-7.19 (m, 4H), 7.43 (d, 2H, J = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.72, 76.49, 80.11, 120.71, 124.64, 128.08, 128.55, 131.90, 140.63. MS (EI): m/z 230.1.



**2d**

**1,4-Bis(p-methoxyphenyl)buta-1,3-diyn (2e)**: White solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.80 (d, 6H, J = 7.2 Hz), 6.86 (t, 4H, J = 7.6 Hz), 7.46 (t, 4H, J = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 55.33, 72.90, 81.22, 114.11, 134.02, 160.21. MS (EI): m/z 262.1.

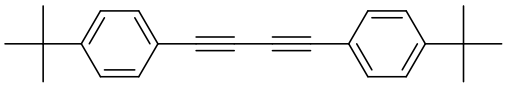



**2e**

**1,4-Bis(m-aminophenyl)buta-1,3-diyne (2f)**: Yellow liquid; 1H NMR (400 MHz, $CDCl_3$): δ (ppm), 3.70 (s, 4H), 6.67-6.69 (m, 2H), 6.82 (t, 2H, J =1.6 Hz), 6.92-6.94 (m, 2H), 7.09-7.13 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 73.34, 81.60, 116.20, 122.46, 122.92,129.32, 146.25. MS (EI): m/z 232.1.

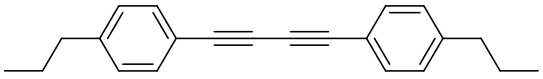

**2f**

**1,4-Bis(4-tert-butylphenyl)buta-1,3-diyne (2g)**: White solid; $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 1.32 (s, 18H), 7.35 (d, 4H, 8.0 Hz), 7.46 (d, 4H, J = 8.4 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): 31.11, 34.92, 73.46, 81.51, 118.83, 125.48, 132.26, 152.58. MS (EI): m/z 314.2.



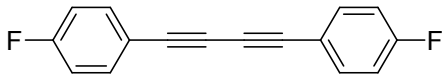
**2g**

**1,4-Bis(4-propylphenyl)buta-1,3-diyne (2h)**: Pale yellow solid; $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 0.94 (t, 6H, J = 7.4 Hz), 1.61-1.66 (m, 4H), 2.59 (t, 4H, J = 7.6 Hz), 7.14 (d, 4H, J = 8.0 Hz), 7.44 (d, 4H, J = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 13.76, 24.27, 38.05, 73.46, 81.58, 119.04, 128.63, 132.48, 144.24. MS (EI): m/z 286.1.



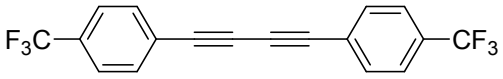
**2h**

**1,4-Bis(4-fluorophenyl)buta-1,3-diyne (2i):** White solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.04 (t, 4H, J = 8.6 Hz), 7.49-7.53 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 73.54, 80.44, 115.81, 116.03, 117.81, 117.85, 134.50, 134.59, 161.82, 164.32. MS (EI): m/z 238.1.



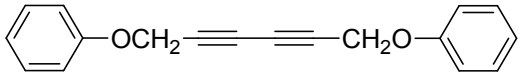

**2i**

**1,4-Bis(4-(trifluoromethyl)phenyl)buta-1,3-diyne (2j)**: White solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.66 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 75.63, 80.97, 125.26, 125.45, 125.49, 130.95, 131.27, 132.82. MS (EI): m/z 338.1.




**2j**

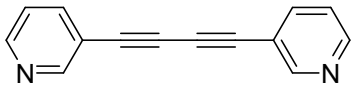
**1,6-Diphenoxy-2,4-hexadiyne (2k):** White solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.75 (s, 4H), 6.89-6.96 (m, 4H), 6.99-7.02(m, 2H), 7.25-7.32(m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 56.05, 70.92, 74.54, 114.75, 121.66, 129.45, 157.27. MS (EI): m/z 262.1.




**2k**

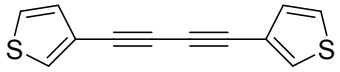
**1,4-Bis(3-pyridyl)buta-1,3-diyne (2l)**: White solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29-7.32 (m, 2H), 7.82 (d, 2H, J = 8.0 Hz), 8.60-8.61 (d, 2H, J = 3.6 Hz), 8.77-

8.78 (d, 2H, J = 1.2 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 76.62, 79.17, 118.87, 123.11, 139.41, 149.52,153.17. MS (EI): m/z 204.1.




**2l**

**1,4-Dithienyl buta-1,3-diyne (2m)**: White solid; $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 7. 17 (d, 2H, J = 4.8 Hz) 7.27-7.29 (m, 2H), 7.58 (d, 2H, J = 2.8 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 73.51, 76.56, 120.91, 125.61, 130.18, 131.24. MS (EI): m/z 213.1.




**2m**

## References

(1) X. Meng, C. Li, B. Han, T. Wang and B. Chen, *Tetrahedron.* 2010, **66**, 4029-4031.

(2) F. Alonso, T. Melkonian, Y. Moglie and M. Yus, *Eur. J. Org. Chem.* 2011, **2011**, 2524-2530.

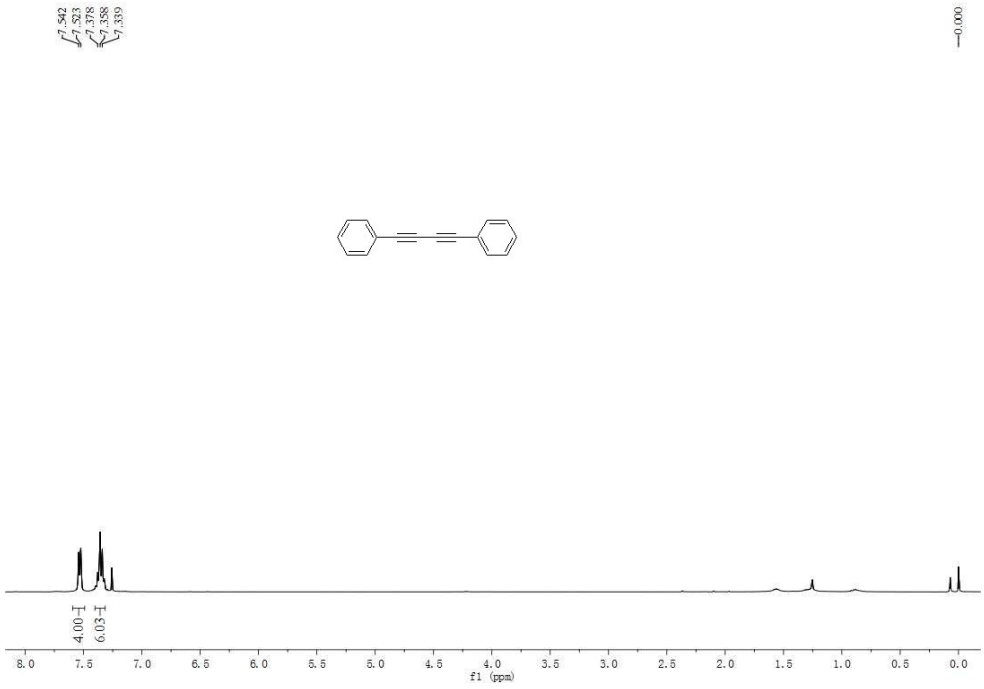
(3) D. Wang, J. Li, N. Li, T. Gao, S. Hou and B. Chen,b*Green Chem.* 2010, **12**, 45-48.

(4) W. Zhang, W. Xu, F. Zhang, H. Jin,Y. Wang and J. Li, *Res. Chem. Intermed.* 2014, **40**, 1337-1344.

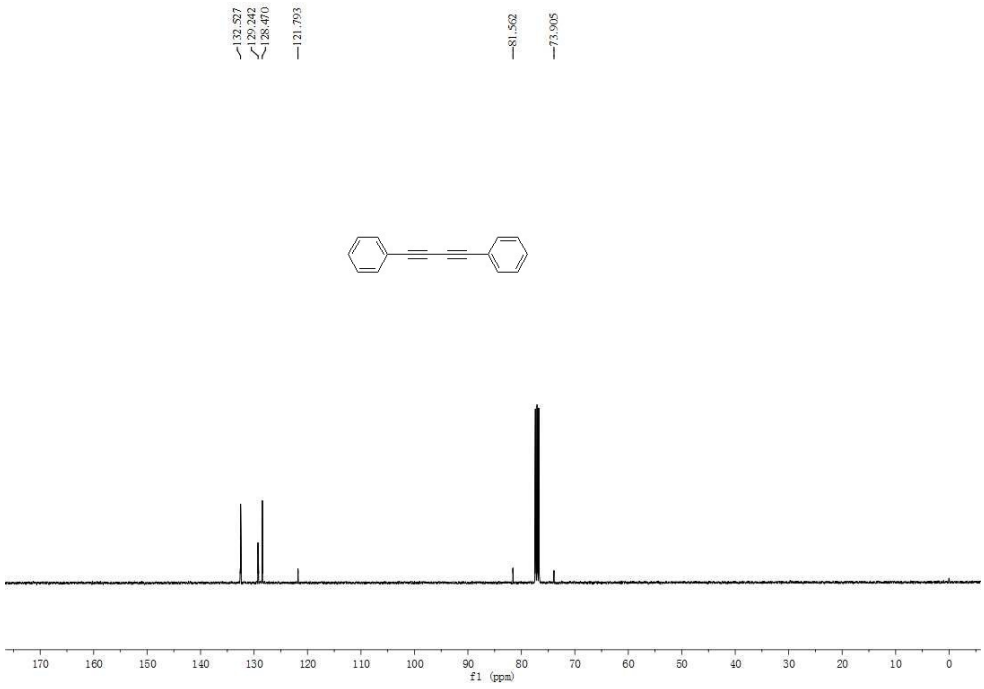
(5) T. Oishi, K, Yamaguchi and N. Mizuno, *ACS Catal.* 2011, **1**, 1351-1354.

(6) K. Yin, C. J. Li, J. Li and X. S. Jia, *Appl. Organomet. Chem.* 2011, **25**, 16-20.

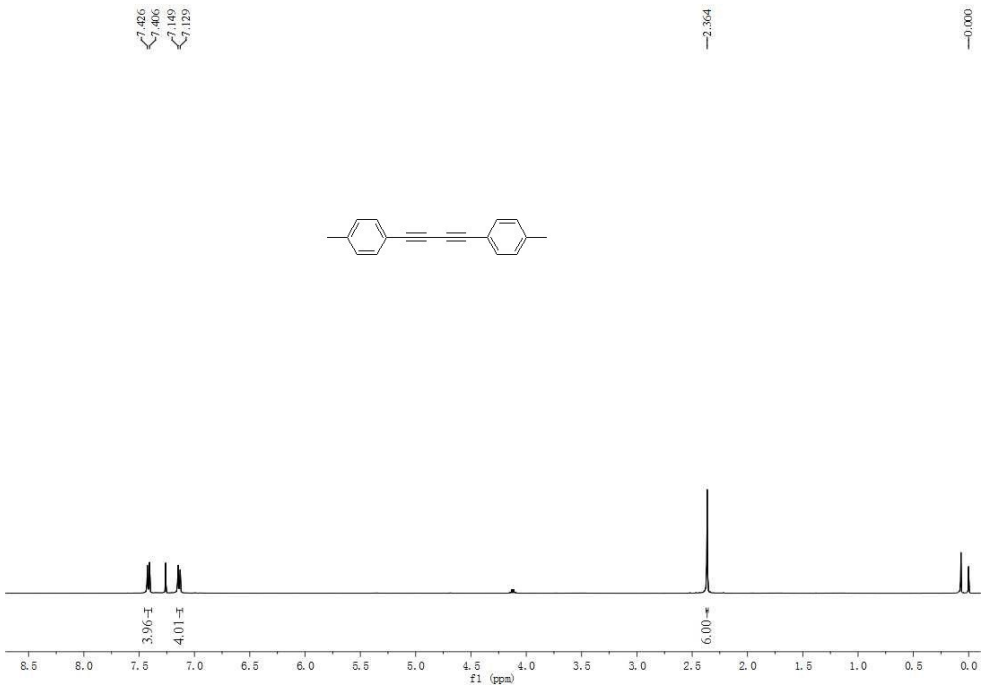
## $^{1}$H NMR, $^{13}$C NMR spectra of all compounds



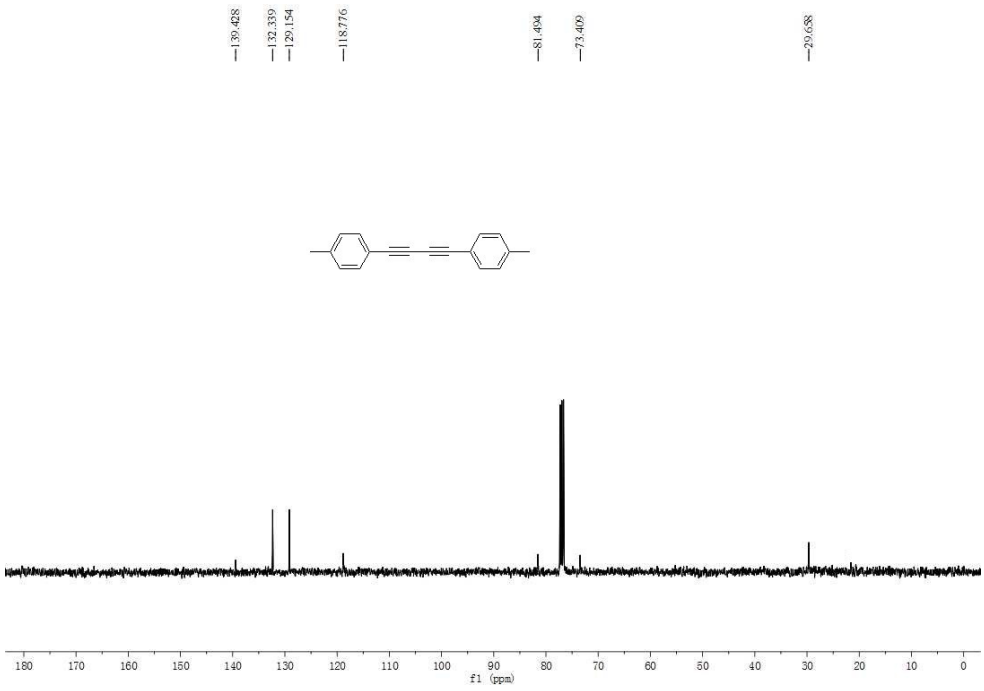

$^{1}$H NMR of **2a**



$^{13}$C NMR of **2a**




$^{1}$H NMR of **2b**

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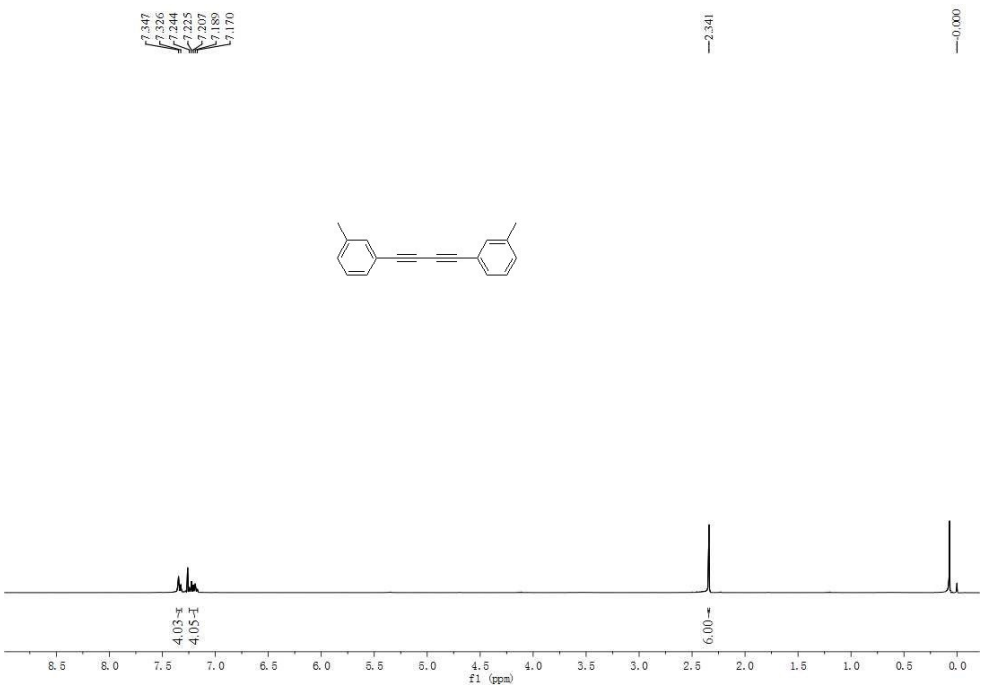
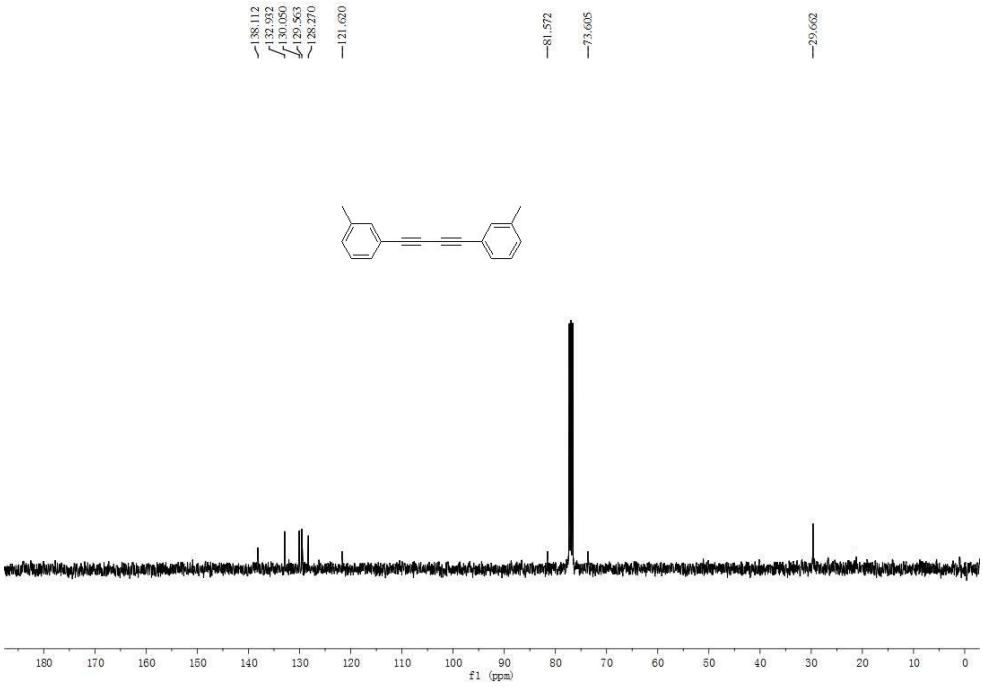
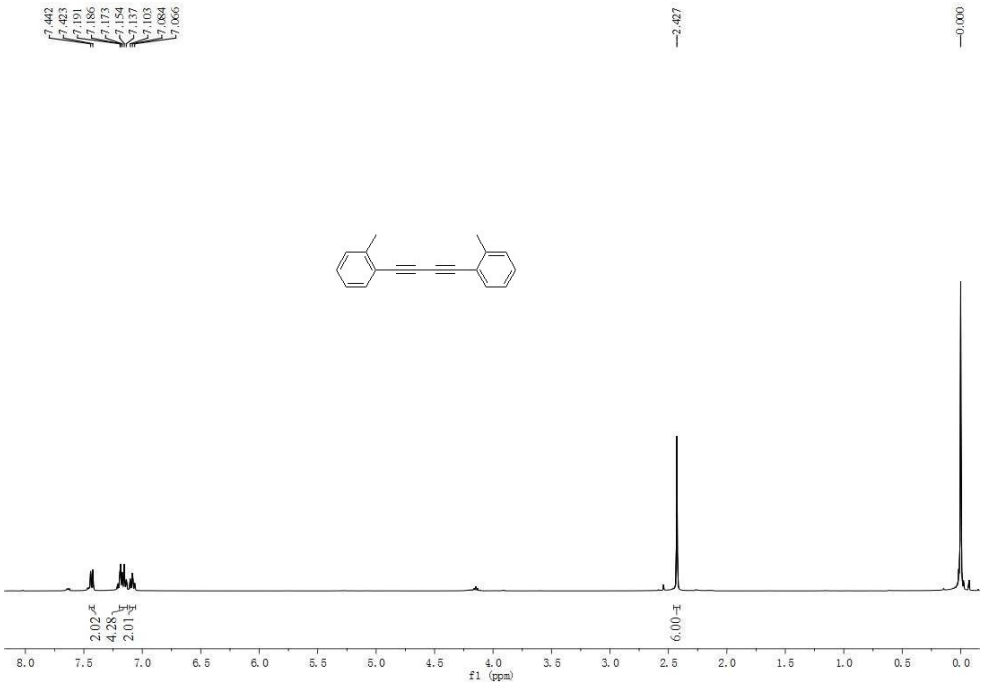

7.347
7.326
7.244
7.225
7.207
7.189
7.170
2.341
0.000
4.03
4.05
6.00
f1 (ppm)

$^{1}$H NMR of **2c**


138.112
132.932
130.050
129.563
128.270
121.620
81.572
73.605
29.662
f1 (ppm)

$^{13}$C NMR of **2c**

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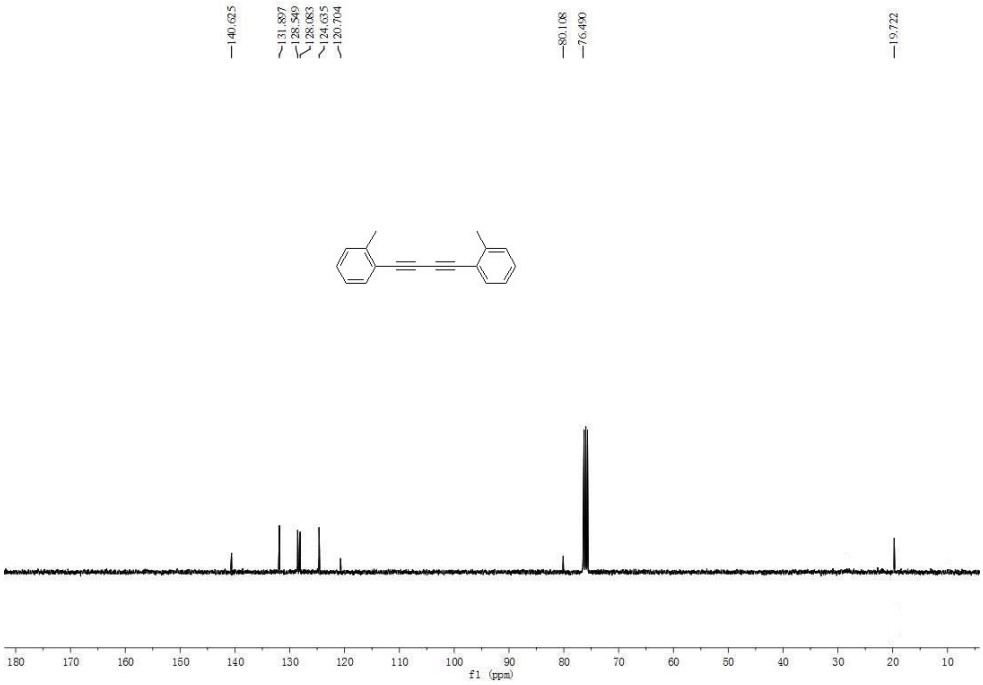


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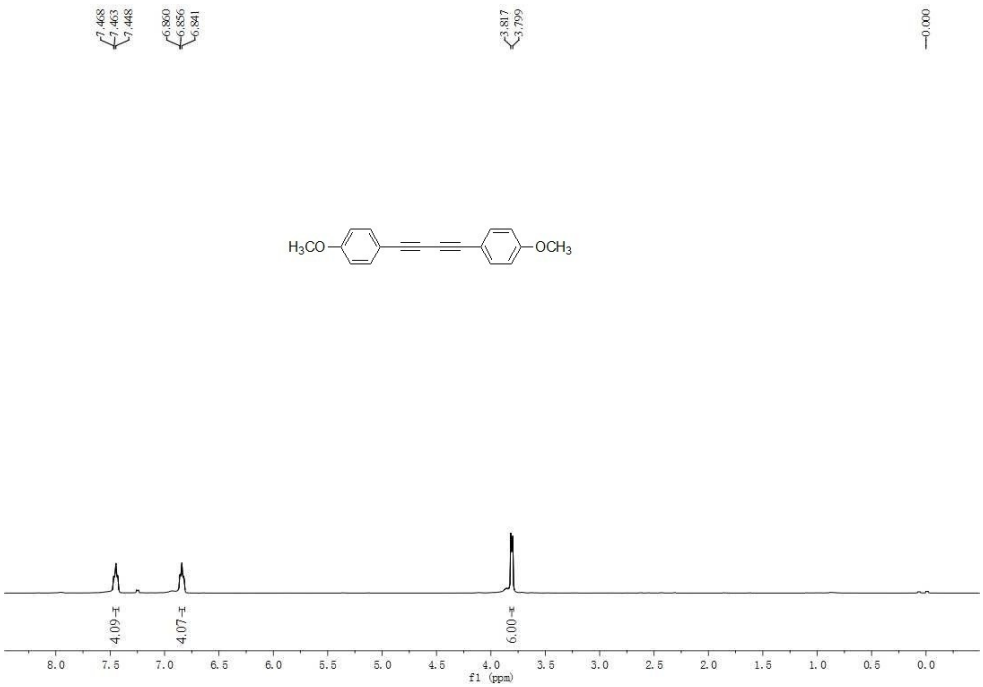


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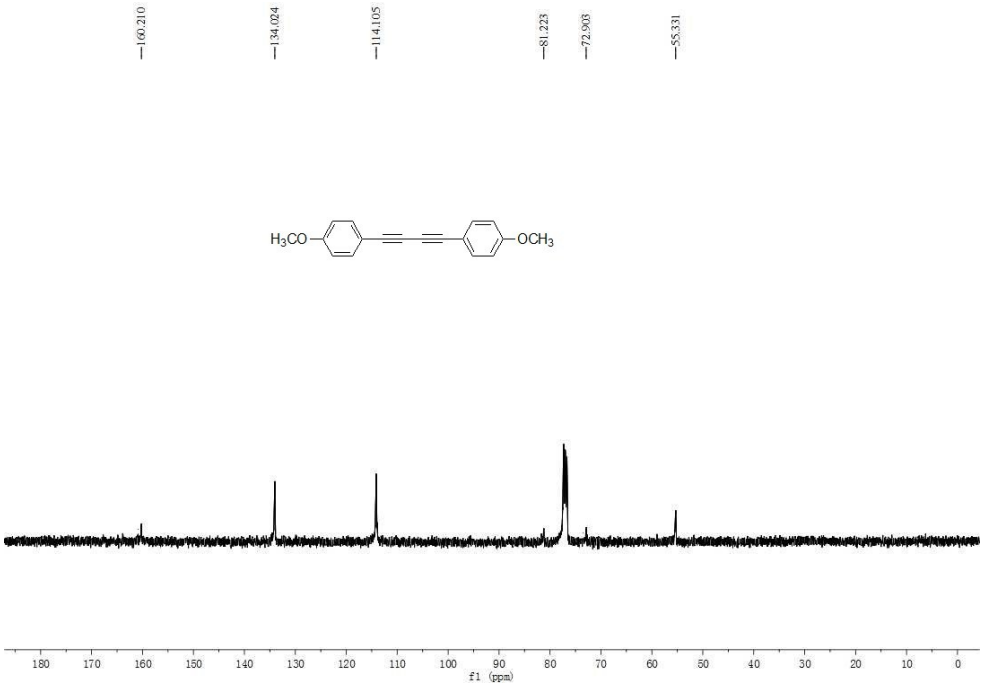


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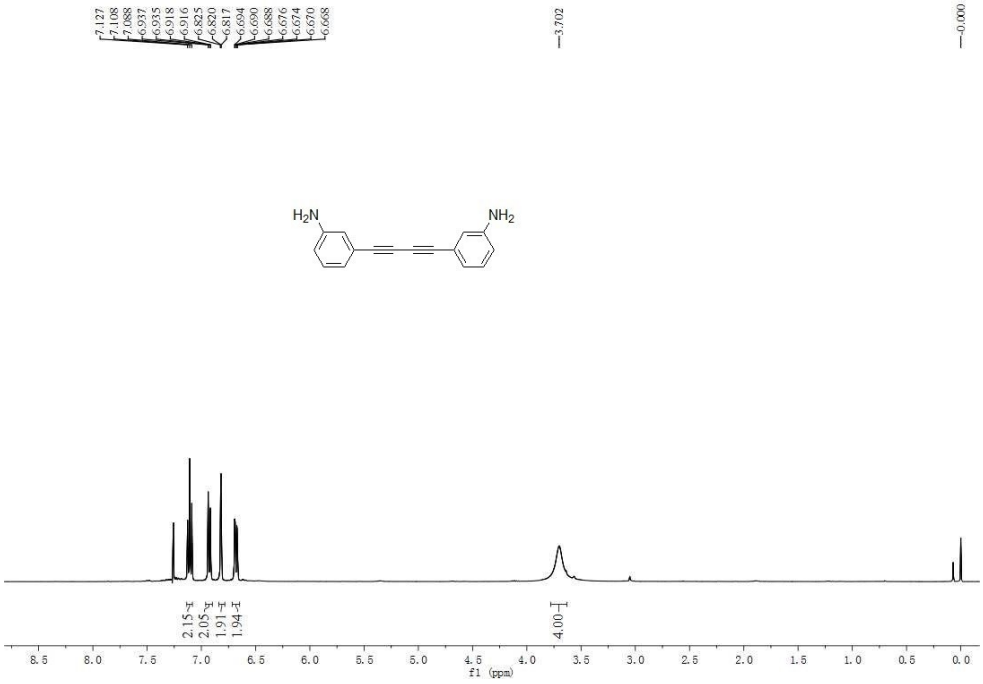
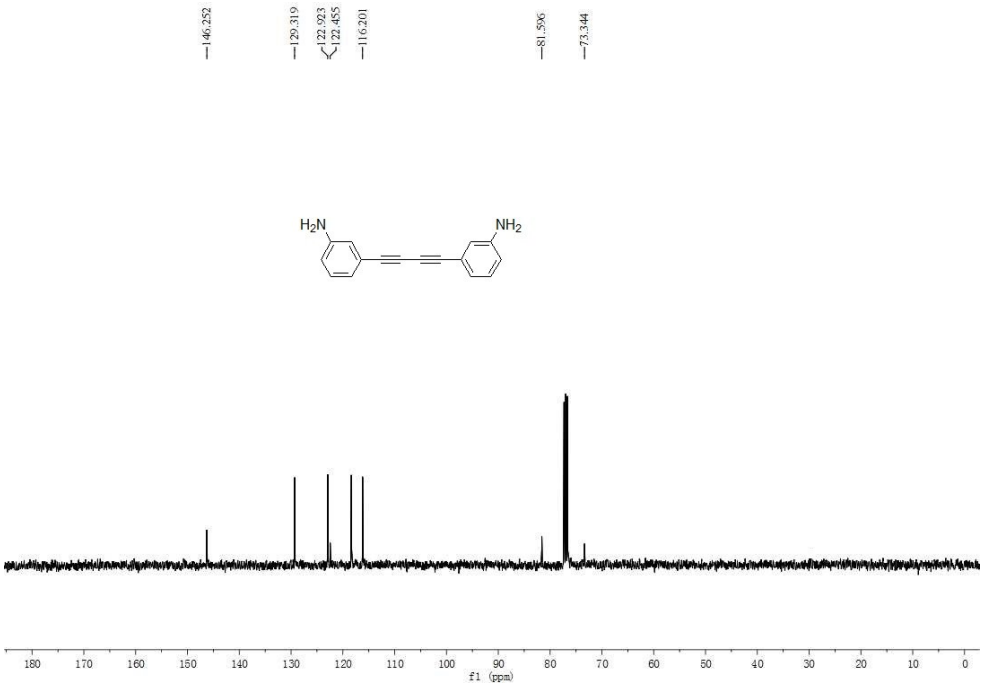



$^{1}$H NMR of **2f**

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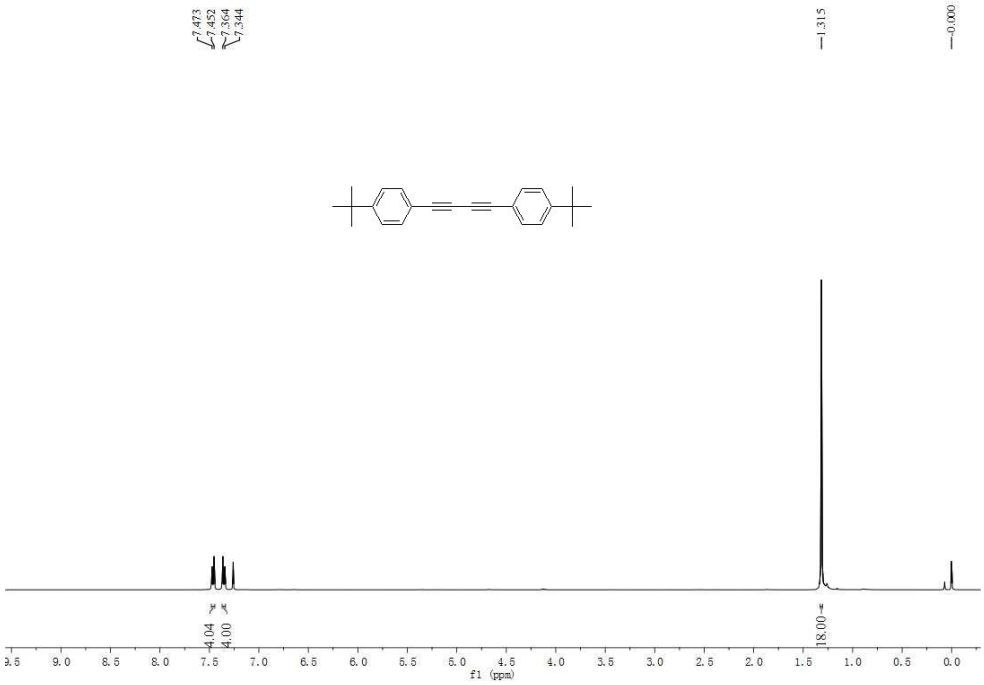
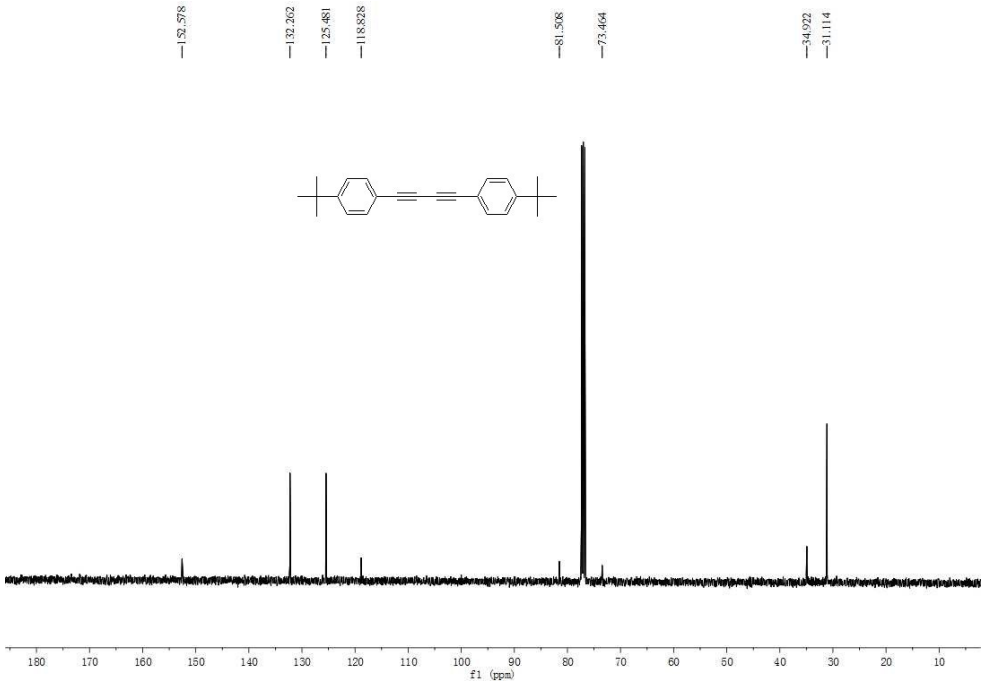



$^{1}$H NMR of **2g**

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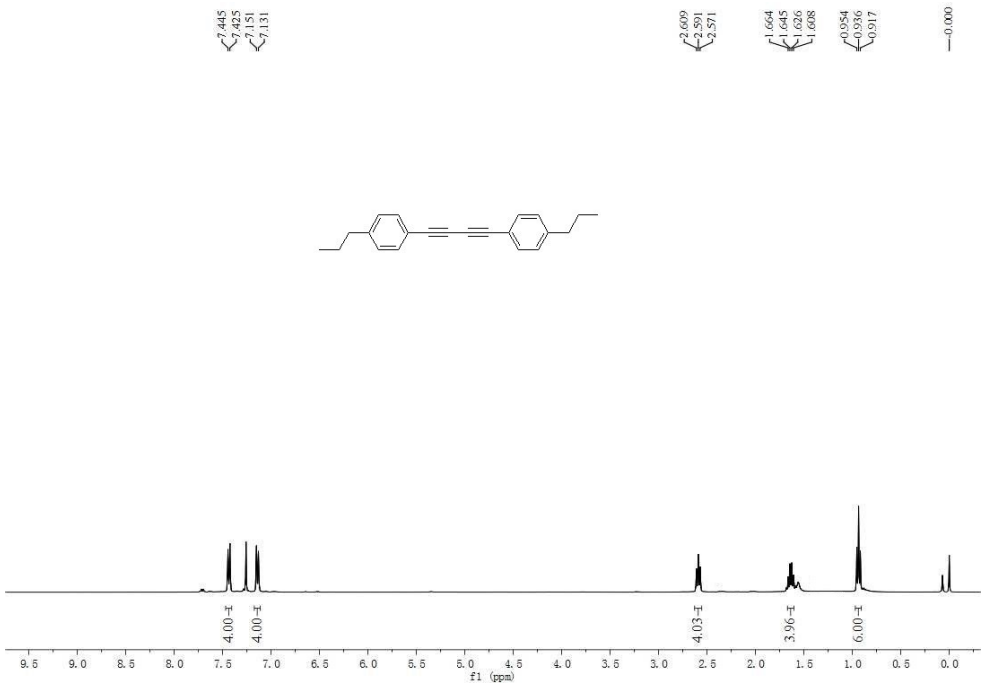


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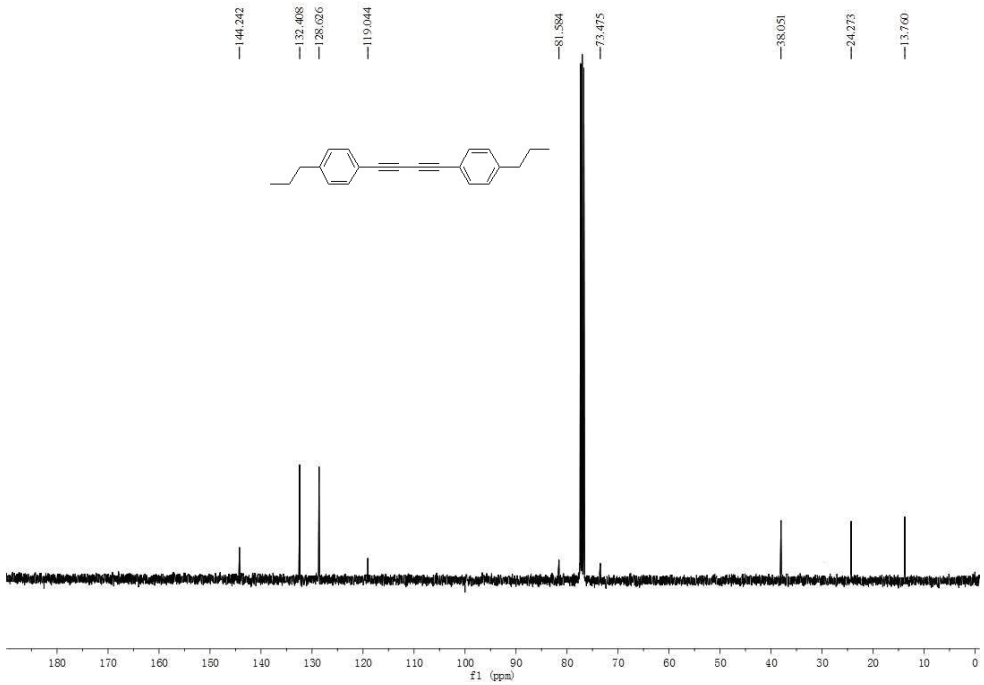


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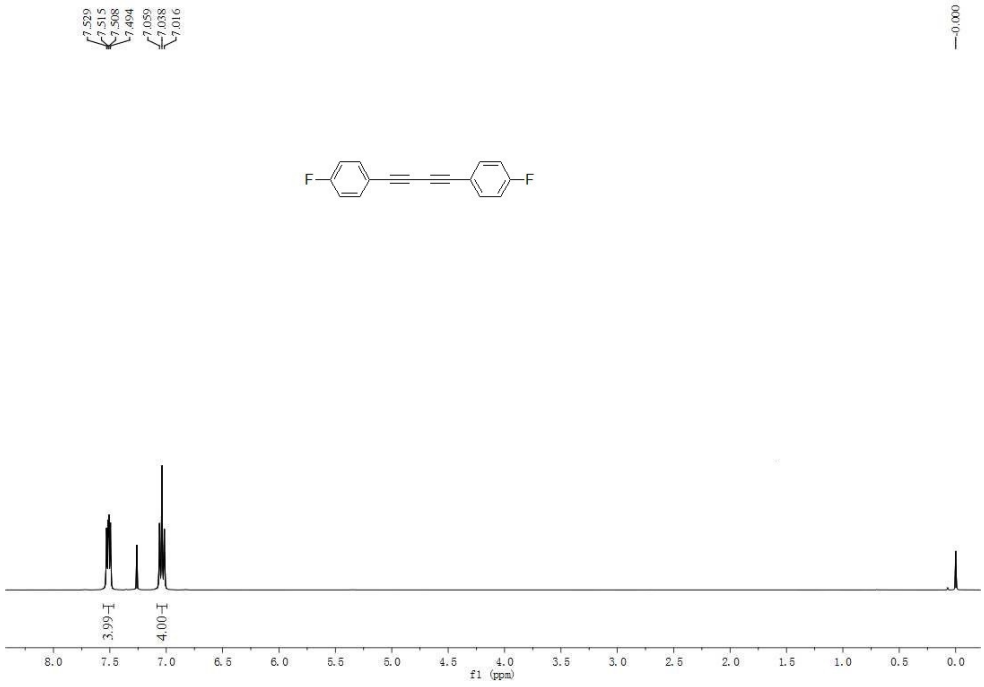


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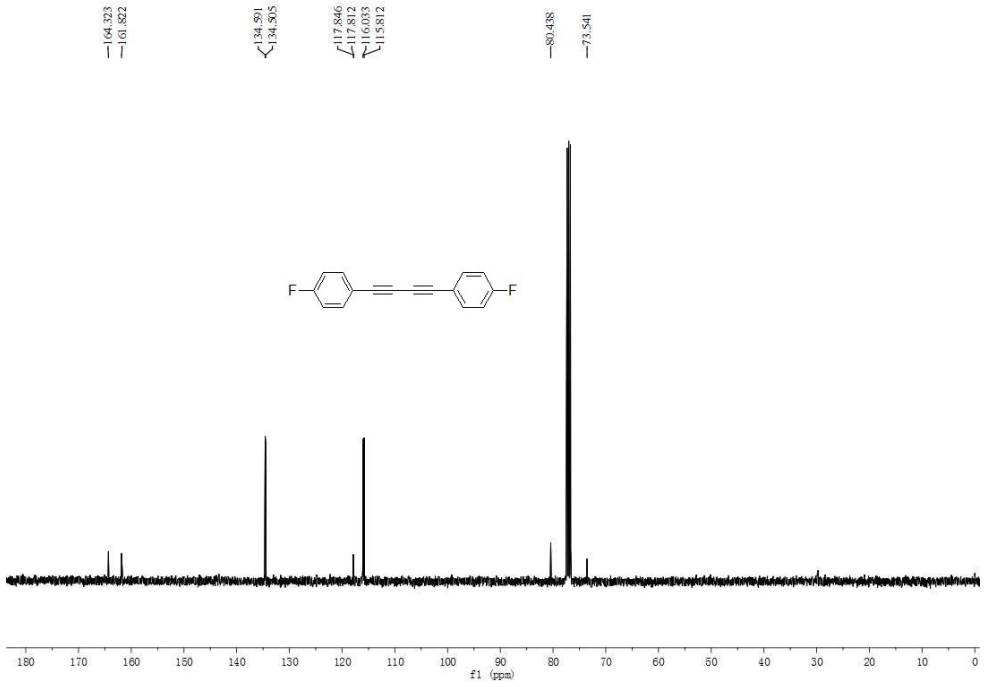


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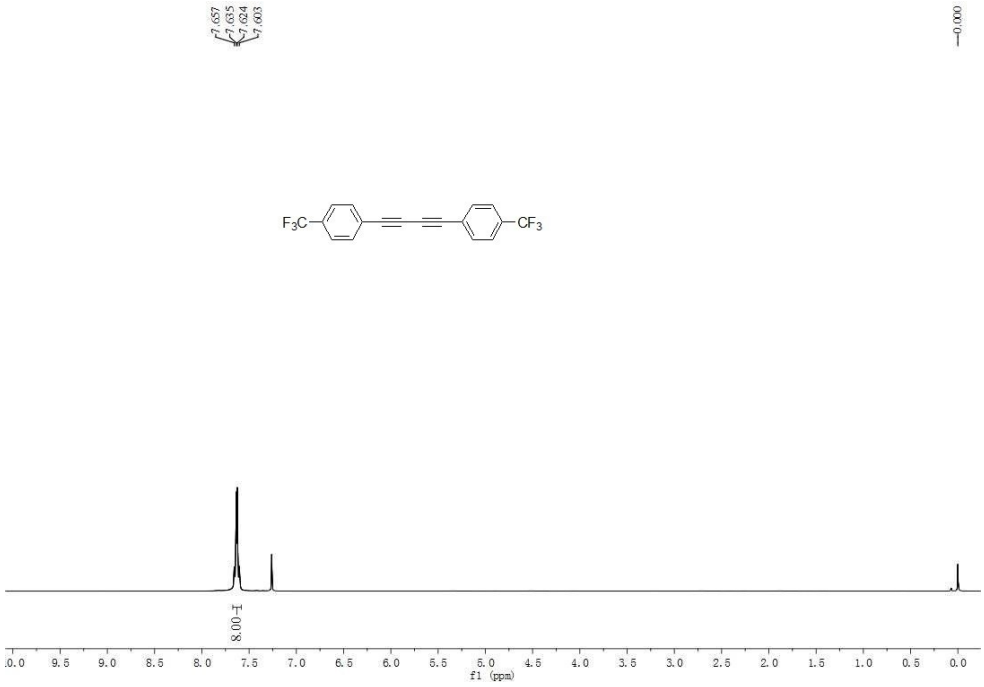


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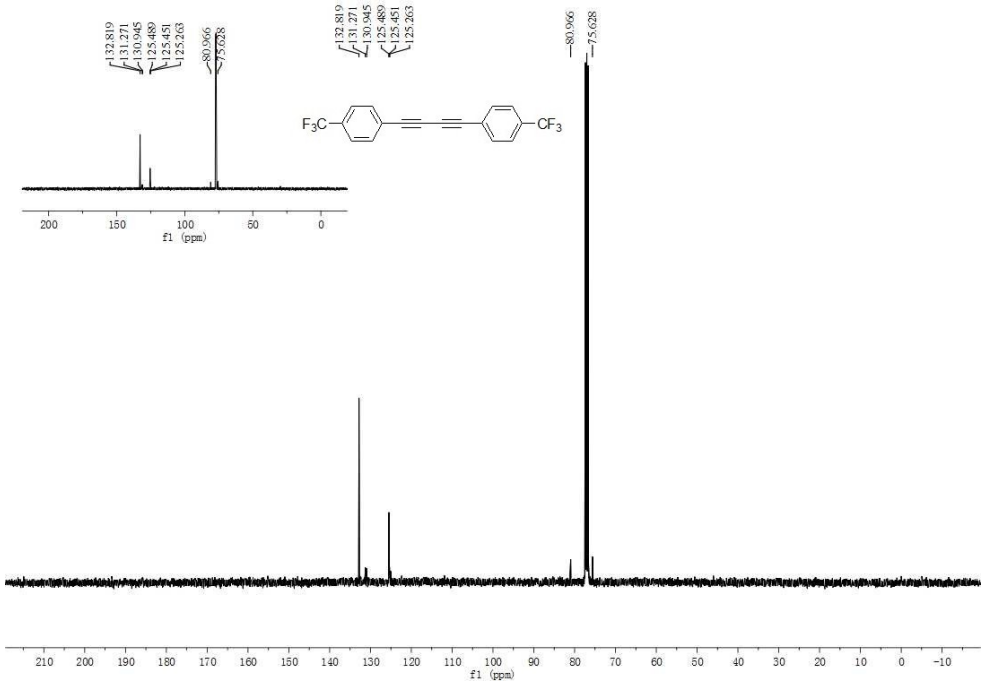


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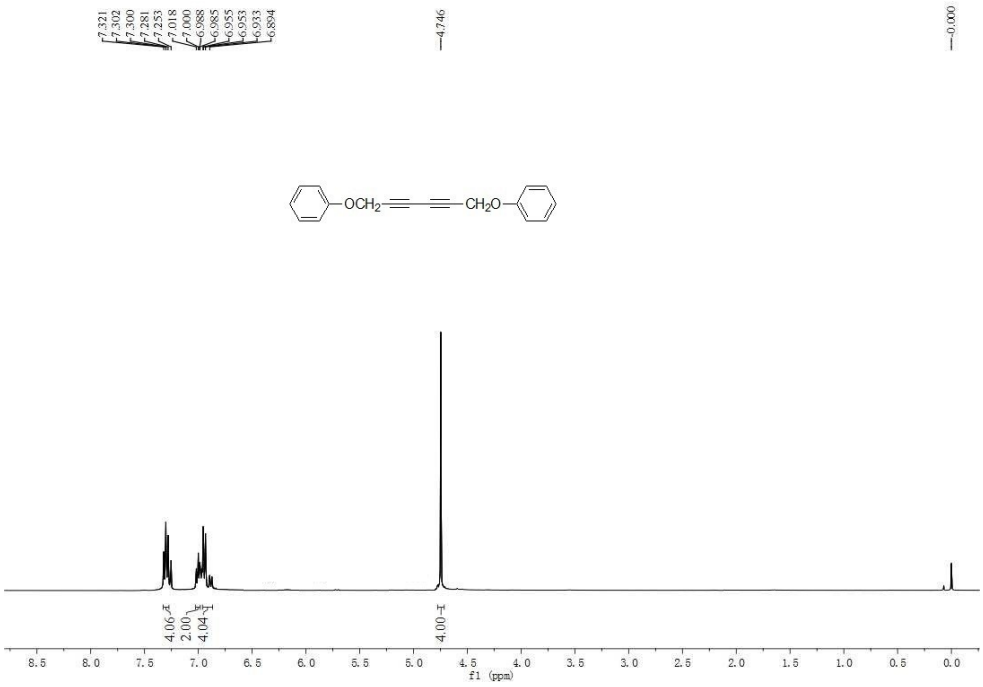


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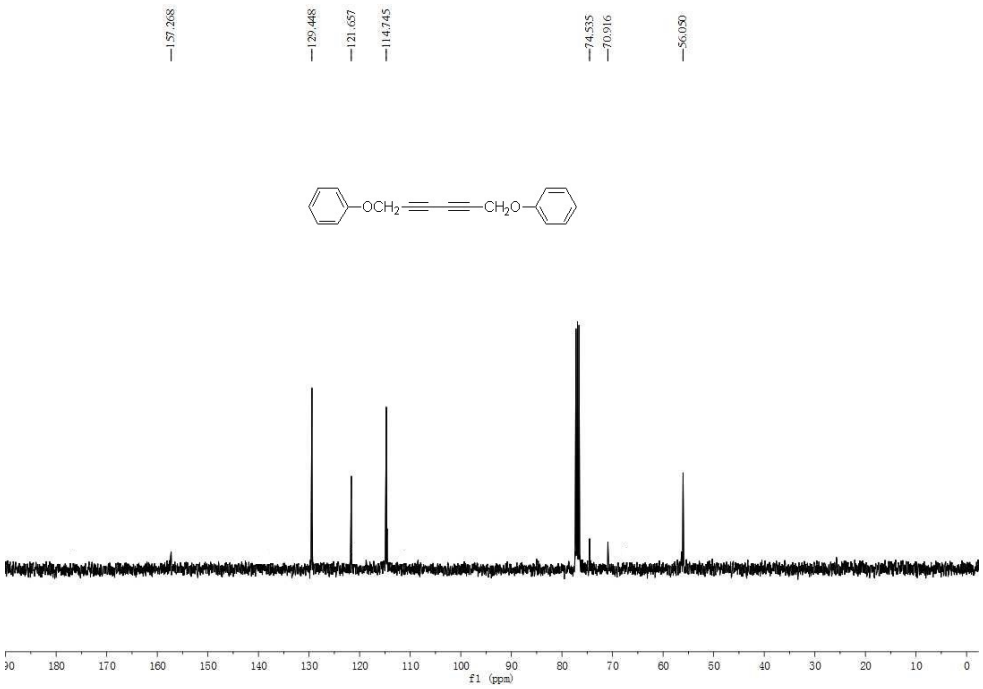


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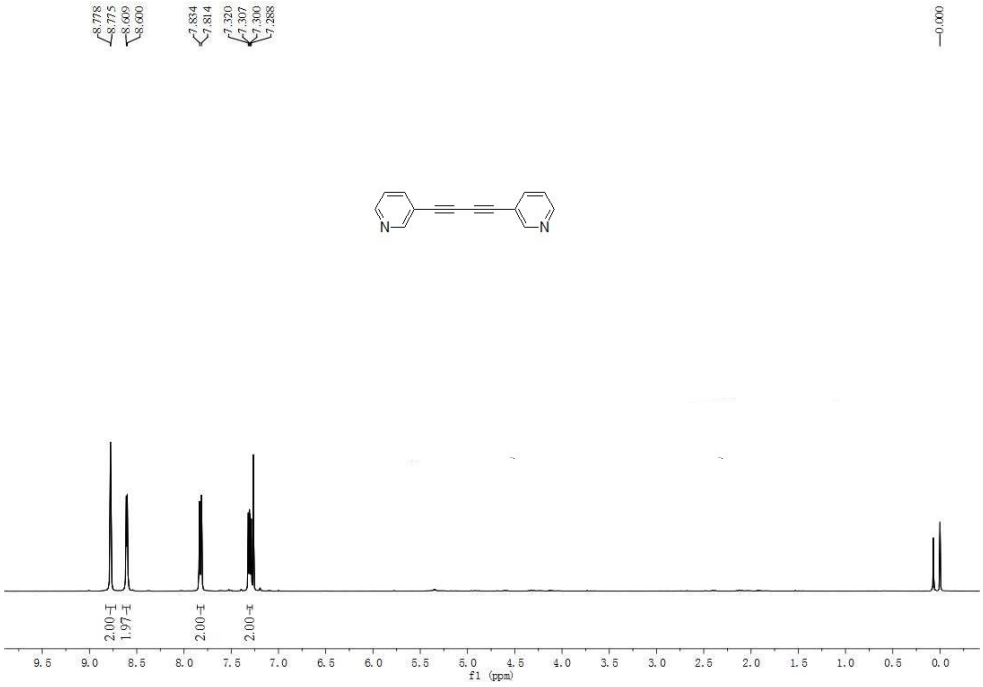


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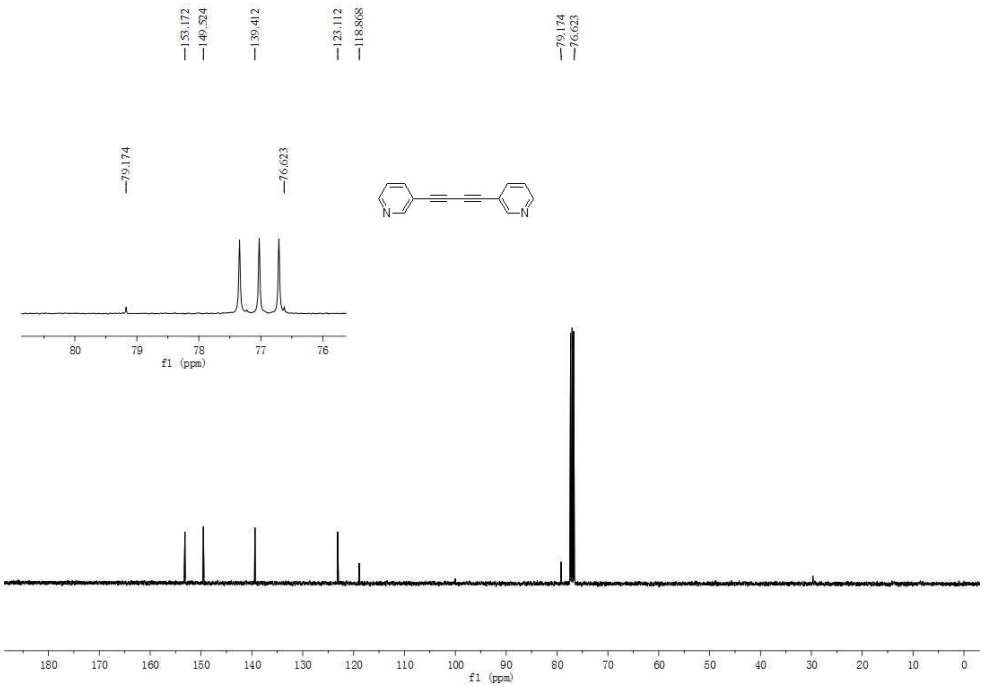
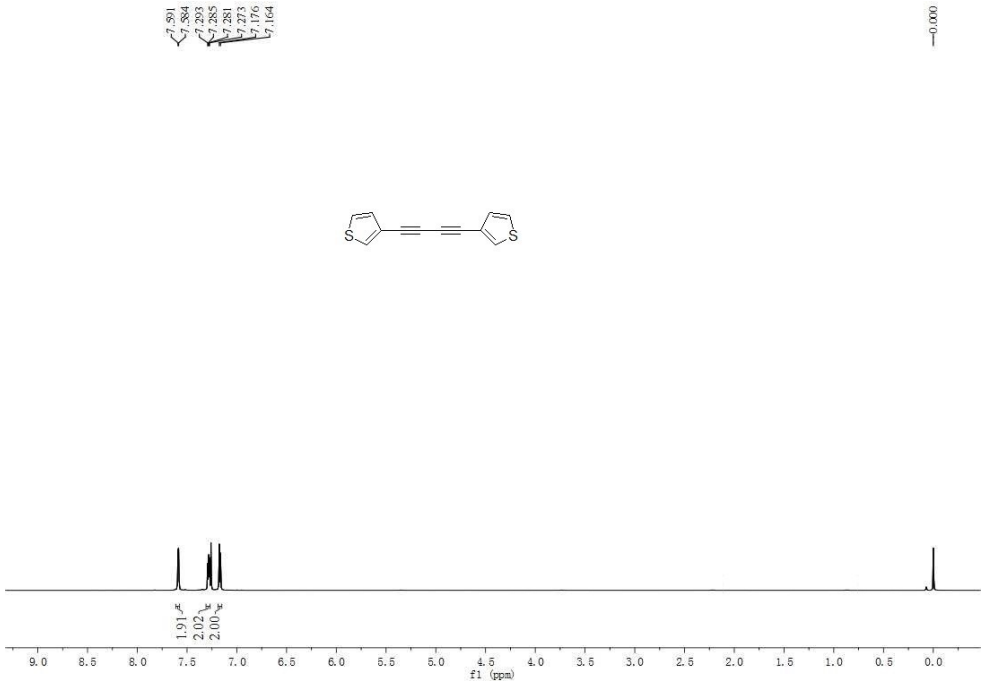
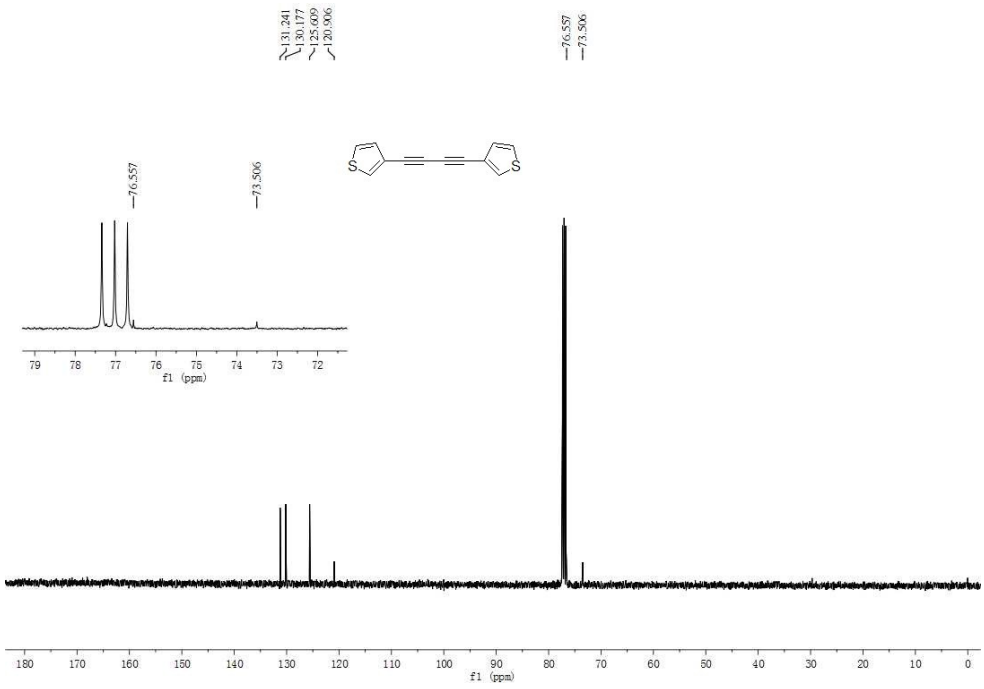



$^{13}$C NMR of **2l**




$^{1}$H NMR of **2m**




$^{13}$C NMR of **2m**