Transition-Metal-Free Homocoupling of 1-Haloalkynes: a Facile Synthesis of Symmetrical 1,3-Diynes

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Supporting Information

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A. General method

^{1}H and ^{13}C NMR spectra were obtained on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a GC-MS spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m).

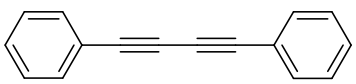
B. General procedure for the synthesis of symmetrical 1,3-diynes from 1-haloalkynes

The mixture of 1-haloalkyne (1 mmol) and KI (3 mmol) in DMF (2 mL) was stirred at 120 ^{o}C for 12 h in a 25 mL schlenk tube. Water (8 mL) was added after completion of the reaction, the aqueous solution was extracted with diethyl ether (3×5 mL) and the combined extract was dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was separated by column chromatography to give the pure sample.

C. General procedure for the synthesis of asymmetrical 1,3-diyne from 1-haloalkynes

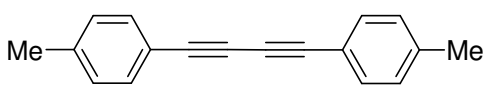
The mixture of phenylethynyl bromide (**1a**, 0.5 mmol), 4-methoxyphenylethynyl bromide (**1g**, 0.5 mmol) or iodide (**1h**, 0.5 mmol) and KI (3 mmol) in DMF (2 mL) was stirred at 120 ^{o}C for 12 h in a 25 mL schlenk tube. Water (8 mL) was added after completion of the reaction, the aqueous solution was extracted with diethyl ether (3×5 mL) and the combined extract was dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was separated by column chromatography to give the pure samples of symmetrical diynes and the cross-coupled product.

D. Analytical data



1,4-diphenylbuta-1,3-diyne (**2a**)

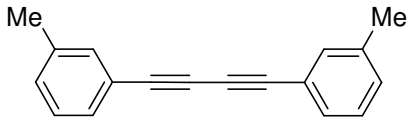
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.53 (m, 4H), 7.30-7.36 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.4, 129.1, 128.4, 121.7, 81.5, 75.8. MS (EI) m/z: 88, 101, 126, 150, 174, 202.



1,4-di*p*-tolylbuta-1,3-diyne (**2b**)

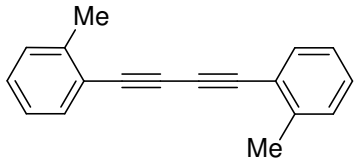
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.0 Hz, 4H), 7.12 (d, J = 8.0 Hz, 4H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 132.3, 129.1, 118.7, 81.5, 75.3, 73.3, 21.5. MS (EI) m/z: 88, 101,

115, 163, 189, 215, 230.



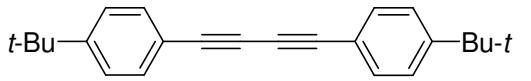
1,4-di*m*-tolylbuta-1,3-diyne (**2c**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.33 (m, 4H), 7.15-7.22 (m, 4H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 132.9, 130.0, 129.5, 128.2, 121.5, 81.5, 73.5, 21.1. MS (EI) m/z: 88, 101, 115, 163, 202, 215, 230.



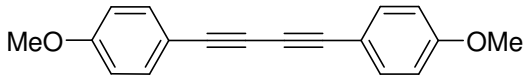
1,4-di*o*-tolylbuta-1,3-diyne (**2d**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.2 Hz, 2H), 7,20-7.27 (m, 4H), 7.13-7.17 (m, 2H), 2.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 132.9, 129.6, 129.1, 125.7, 121.7, 81.2, 77.5, 20.7. MS (EI) m/z: 89, 115, 189, 202, 215, 230.



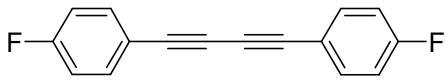
1,4-bis(4-tert-butylphenyl)buta-1,3-diyne (**2e**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 8.4 Hz, 4H), 1.30 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 132.2, 125.4, 118.7, 81.4, 73.4, 34.8, 31.0. MS (EI) m/z: 114, 142, 165, 215, 239, 271, 299, 314.



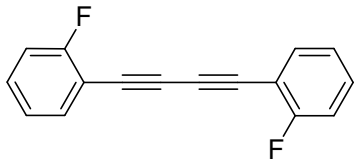
1,4-bis(4-methoxyphenyl)buta-1,3-diyne (**2f**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.8 Hz, 4H), 6.83 (d, J = 8.8 Hz, 4H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 133.9, 114.0, 113.8, 81.1, 72.8, 55.2. MS (EI) m/z: 110, 131, 176, 204, 219, 247, 262.



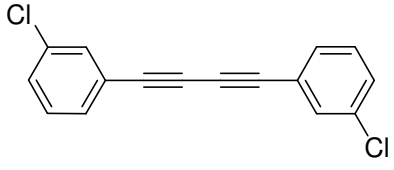
1,4-bis(4-fluorophenyl)buta-1,3-diyne (**2g**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.51 (m, 4H), 6.99-7.04 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2, 161.7, 134.5, 134.4, 117.7, 116.0, 115.7, 80.4, 73.4. MS (EI) m/z: 74, 119, 144, 168, 192, 218, 238.



1,4-bis(2-fluorophenyl)buta-1,3-diyne (**2h**)

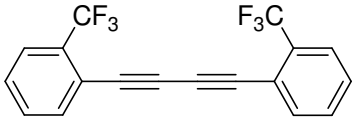
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.52 (m, 2H), 7.31-7.37 (m, 2H), 7.06-7.12 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 162.4, 134.2, 131.1, 131.0, 124.1, 124.1, 115.5, 115.5, 110.4, 110.2, 78.3, 75.8. MS (EI) m/z: 80, 106, 119, 135, 192, 207, 218, 238.



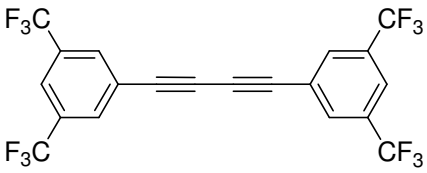
1,4-bis(3-chlorophenyl)buta-1,3-diyne (**2i**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (s, 2H), 7.38 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.23-7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.2, 132.2, 130.6, 129.6, 129.0, 123.1, 80.5, 74.6. MS (EI) m/z: 28, 32, 100, 135, 174,

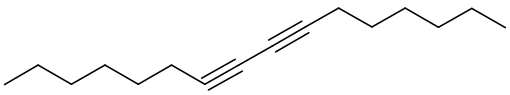
200, 270.



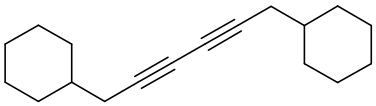
1,4-bis(2-(trifluoromethyl)phenyl)buta-1,3-diyne (**2j**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.70 (m, 4H), 7.43-7.53 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.6, 132.3, 132.0, 130.9, 128.6, 125.6, 125.5, 124.1, 121.4, 119.3, 78.2, 78.1. MS (EI) m/z: 135, 159, 269, 287, 319, 338.



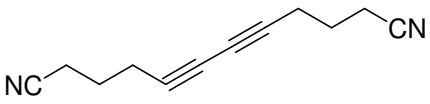
1,4-bis(3,5-bis(trifluoromethyl)phenyl)buta-1,3-diyne (**2k**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 4H), 7.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.0, 132.7, 132.5, 132.3, 132.0, 126.8, 124.1, 123.7, 123.1, 121.4, 118.7, 79.8, 76.2. MS (EI) m/z: 158, 168, 193, 203, 237, 285 355, 405, 474.



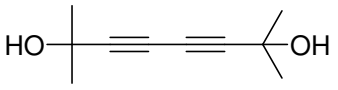
hexadeca-7,9-diyne (**2l**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (t, J = 6.8 Hz, 4H), 1.45-1.52 (m, 4H), 1.30-1.39 (m, 4H), 1.20-1.27 (m, 8H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 77.5, 65.1, 31.2, 28.5, 28.2, 22.4, 19.1, 14.0. MS (EI) m/z: 41, 67, 79, 91, 105, 119, 133, 147, 189, 203, 218.



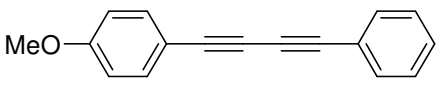
1,6-dicyclohexylhexa-2,4-diyne (**2m**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (d, J = 6.4 Hz, 4H), 1.74-1.78 (m, 4H), 1.66-1.70 (m, 4H), 1.59-1.63 (m, 2H), 1.41-1.49 (m, 2H), 1.05-1.26 (m, 6H), 0.90-1.00 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.3, 66.0, 37.2, 32.6, 26.9, 26.0, 26.0. MS (EI) m/z: 55, 83, 91, 117, 131, 145, 159, 199, 242. Anal. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 89.32; H, 10.76.



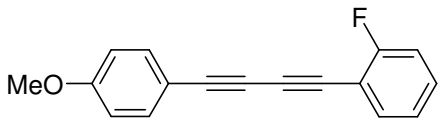
dodeca-5,7-diynedinitrile (**2n**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41-2.49 (m, 4H), 1.82-1.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.7, 75.1, 66.6, 24.1, 18.2, 16.1. MS (EI) m/z: 63, 77, 115, 143, 156, 183.



2,7-dimethylocta-3,5-diyne-2,7-diol (**2o**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.55 (s, 2H), 1.35 (s, 12H). ^{13}C NMR (100 MHz, DMSO): δ = 85.7, 65.0, 63.6, 31.0. MS (EI) m/z: 43, 69, 105, 133, 151, 166.

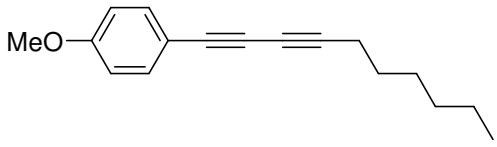


1-methoxy-4-(4-phenylbuta-1,3-diynyl)benzene (**2ah**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.51 (m, 4H), 7.29-7.36 (m, 3H), 6.84 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 134.1, 132.4, 129.0, 128.4, 122.0, 114.1, 113.7, 81.8 81.0, 74.2, 72.7, 55.3. MS (EI) m/z: 116, 163, 189, 217, 232.



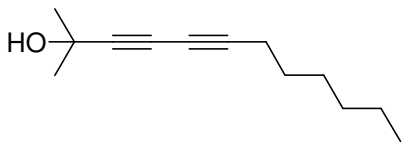
1-fluoro-2-(4-(4-methoxyphenyl)buta-1,3-diynyl)benzene (**2hl**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.49 (m, 3H), 7.29-7.34 (m, 1H), 7.04-7.11 (m, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1649, 162.4, 160.5, 134.2, 130.8, 130.7, 124.1, 124.1, 115.7, 115.5, 114.2, 113.4, 110.9, 110.7, 83.0, 79.0, 79.0, 74.2, 72.5, 55.3. MS (EI) m/z: 125, 157, 181, 207, 235, 250. Anal. Calcd for $C_{17}H_{11}FO$: C, 81.59; H, 4.43. Found: C, 81.40; H, 4.49.



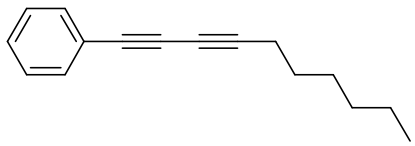
1-(deca-1,3-diynyl)-4-methoxybenzene (**2ht**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 2.32 (t, J = 6.8 Hz, 2H), 1.50-1.58 (m, 2H), 1.36-1.43 (m, 2H), 1.24-1.33 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 134.0, 114.0 114.0, 84.2, 74.8, 73.1, 65.2, 55.2, 31.3, 28.5, 28.3, 22.5, 19.6, 14.0. MS (EI) m/z: 126, 154, 169, 197, 211, 240.



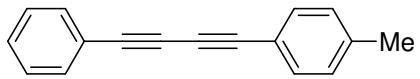
2-methyldodeca-3,5-diyn-2-ol (**2tx**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 1H), 2.22 (t, J = 6.8 Hz, 2H), 1.43-1.50 (m, 8H), 1.31-1.37 (m, 2H), 1.19-1.29 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 81.8, 79.8, 67.3, 65.4, 64.3, 31.2, 31.1, 28.4, 28.1, 22.4, 19.2, 14.0. MS (EI) m/z: 43, 77, 91, 135, 163, 177, 192.



1-(deca-1,3-diynyl)benzene (**2at**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.47 (m, 2H), 7.26-7.32 (m, 3H), 2.34 (t, J = 6.8 Hz, 2H), 1.52-1.60 (m, 2H), 1.38-1.45 (m, 2H), 1.26-1.35 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.5, 128.8, 128.3, 122.1, 84.9, 74.7, 74.4, 65.1, 31.3, 28.6, 28.2, 22.5, 19.6, 14.0. MS (EI) m/z: 91, 126, 139, 165, 181, 210.

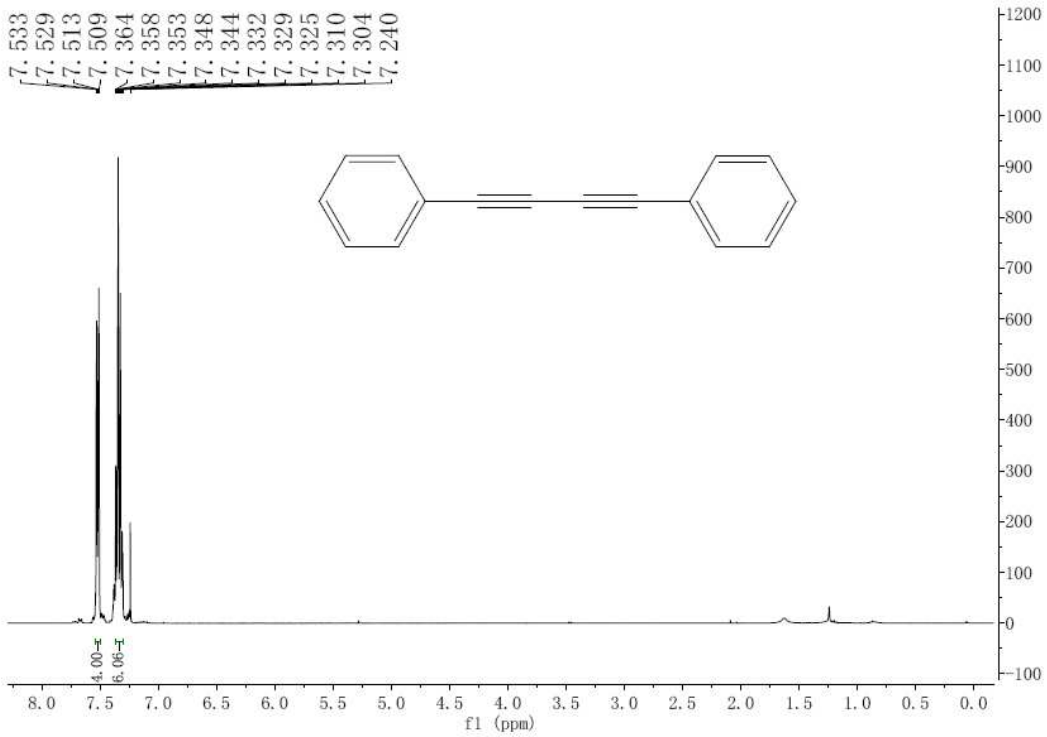


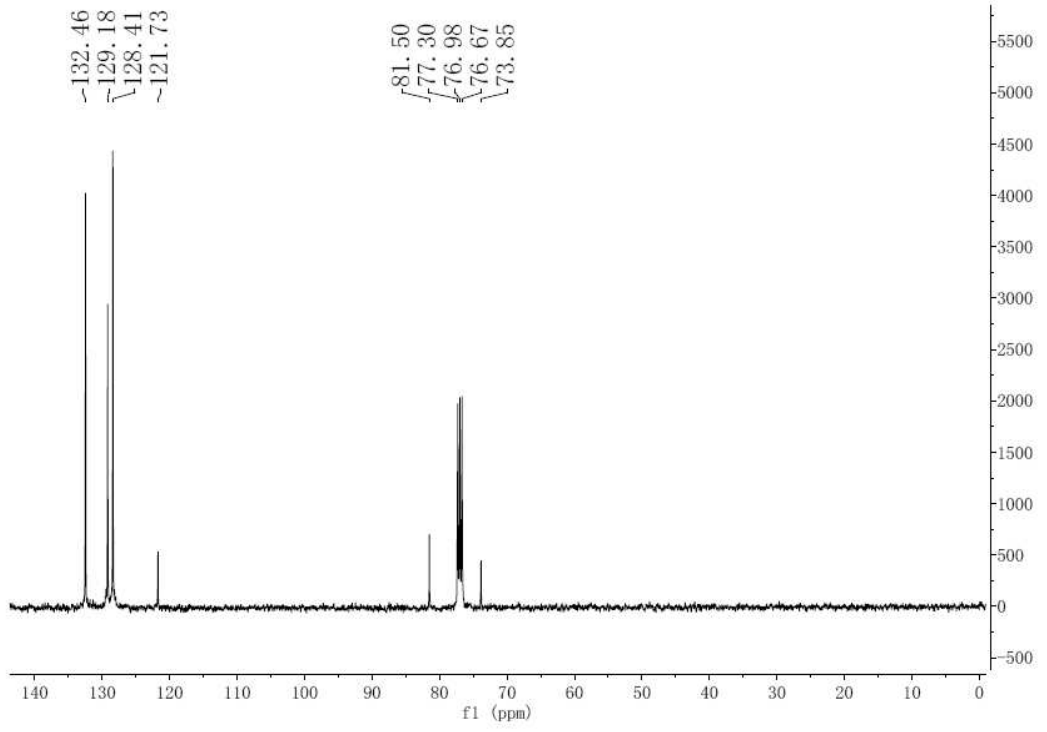
1-methyl-4-(4-phenylbuta-1,3-diynyl)benzene (**2ac**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.53 (m, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.31-7.34 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.6, 132.5, 132.4, 129.2, 129.1, 128.4, 121.9, 118.7, 81.9, 81.2, 74.1, 73.3, 21.6. MS (EI) m/z: 108, 139, 163, 189, 216.

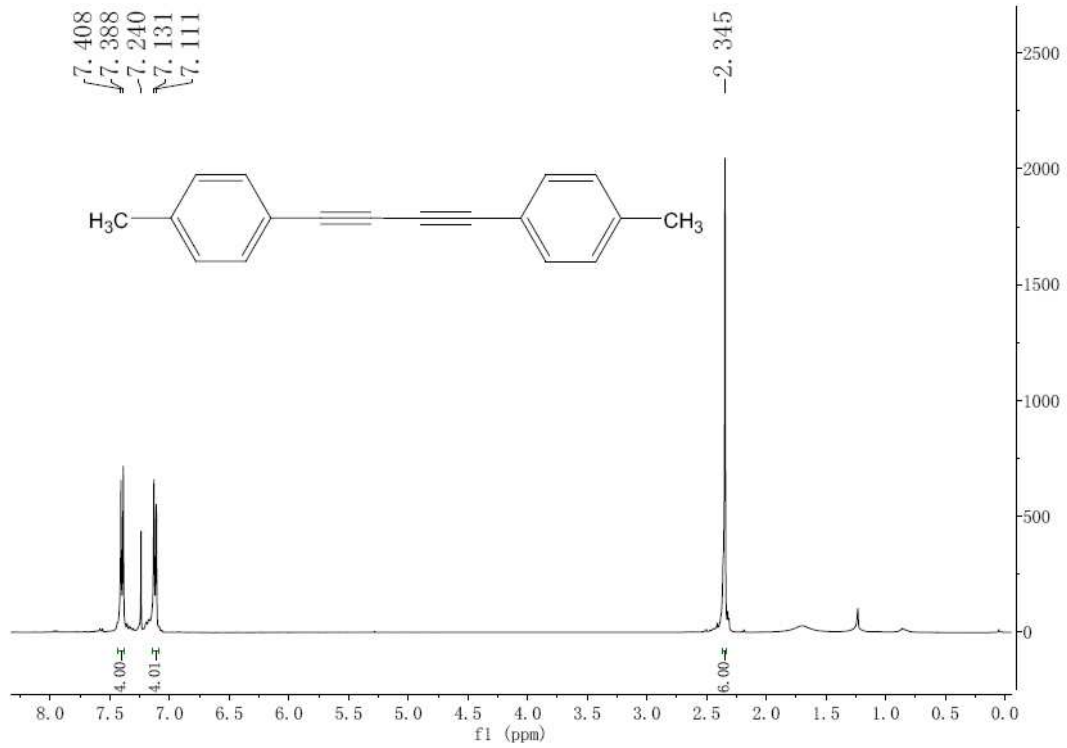
E. NMR Spectra

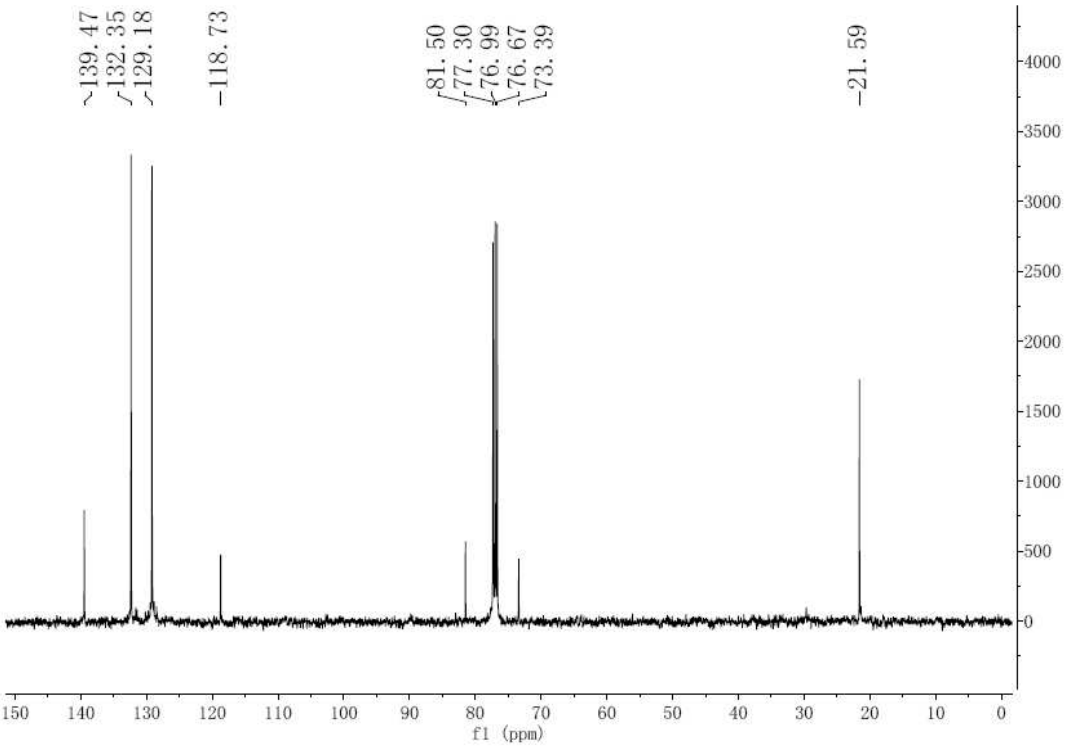
^{1}H NMR and ^{13}C NMR of 1,4-diphenylbuta-1,3-diyne (2a)



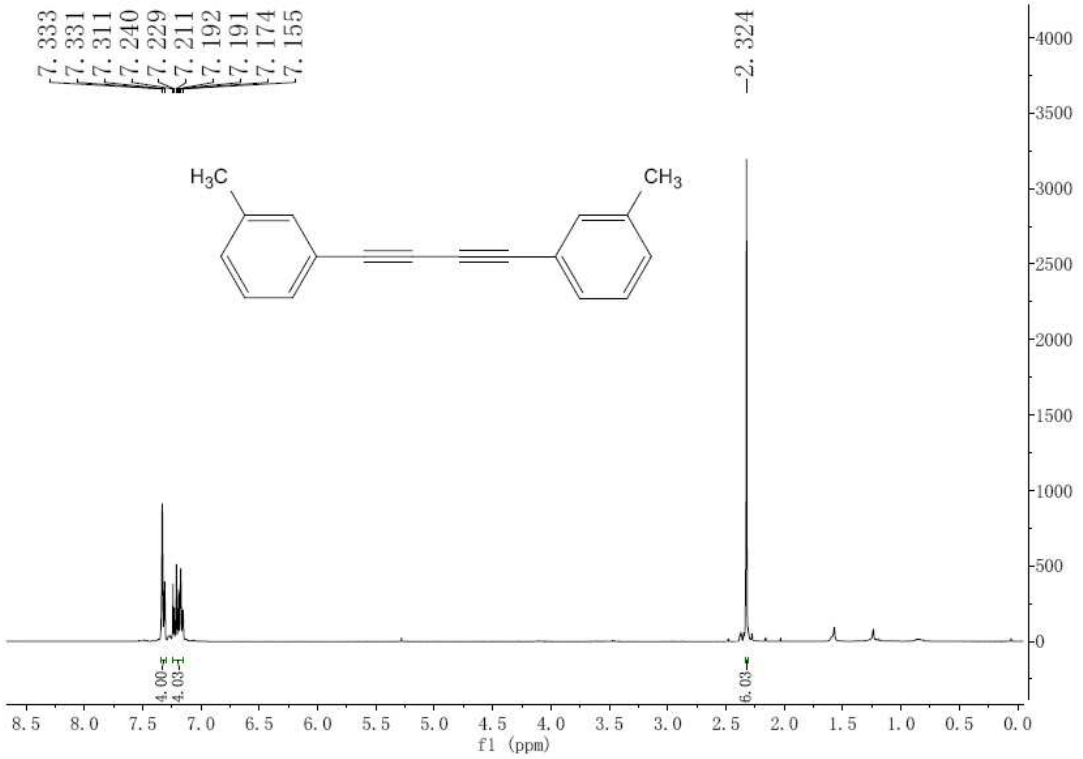


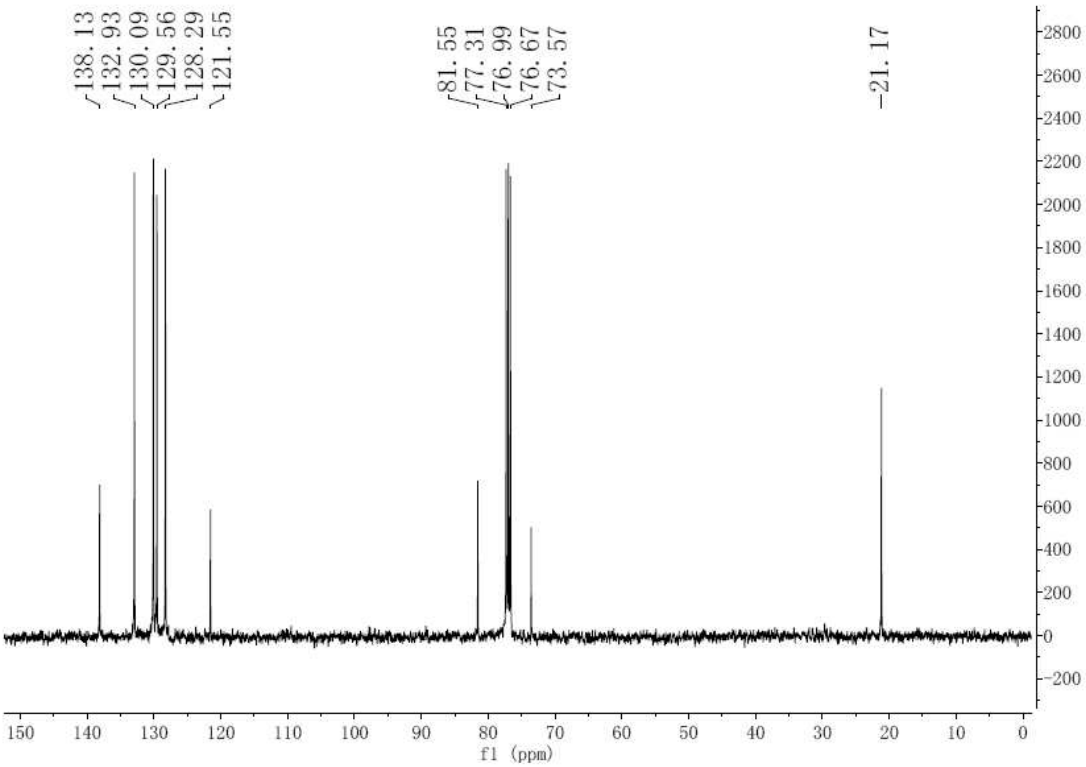
^{1}H NMR and ^{13}C NMR of 1,4-di*p*-tolylbuta-1,3-diyne (2b)



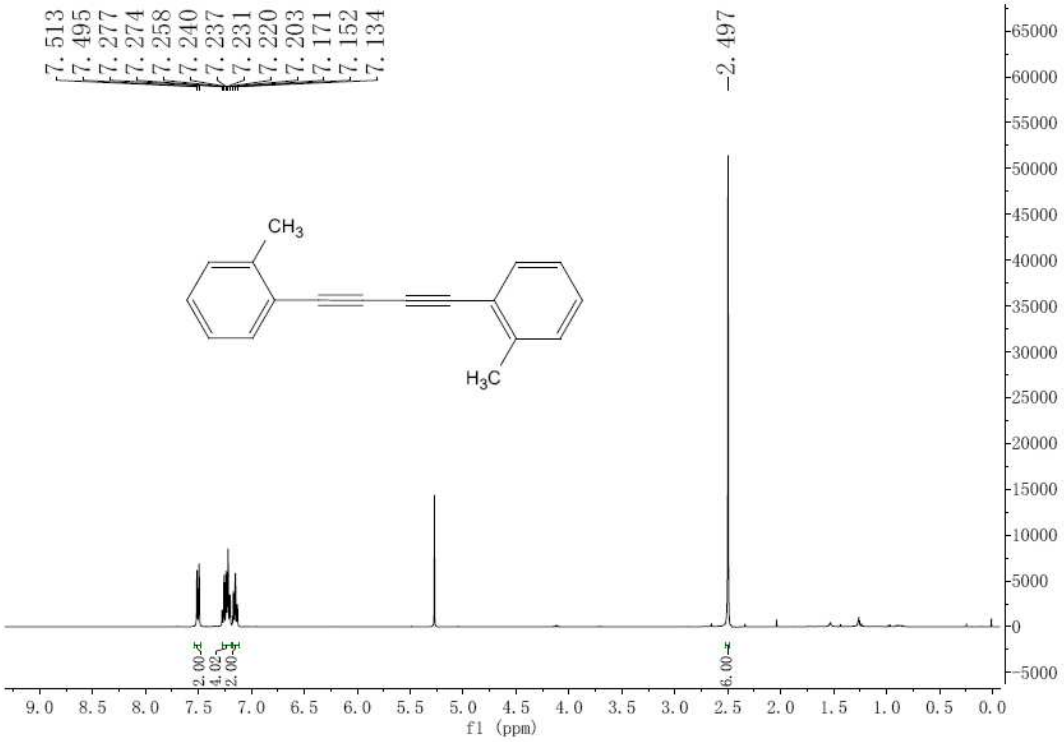


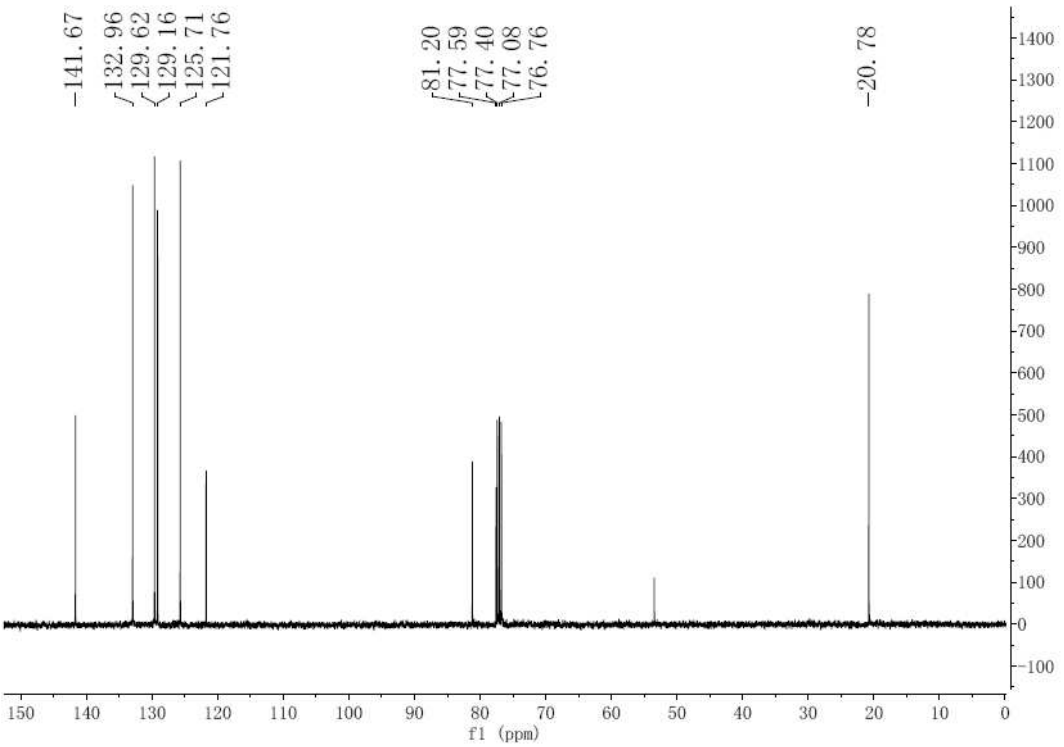
^{1}H NMR and ^{13}C NMR of 1,4-di*m*-tolylbuta-1,3-diyne (2c)



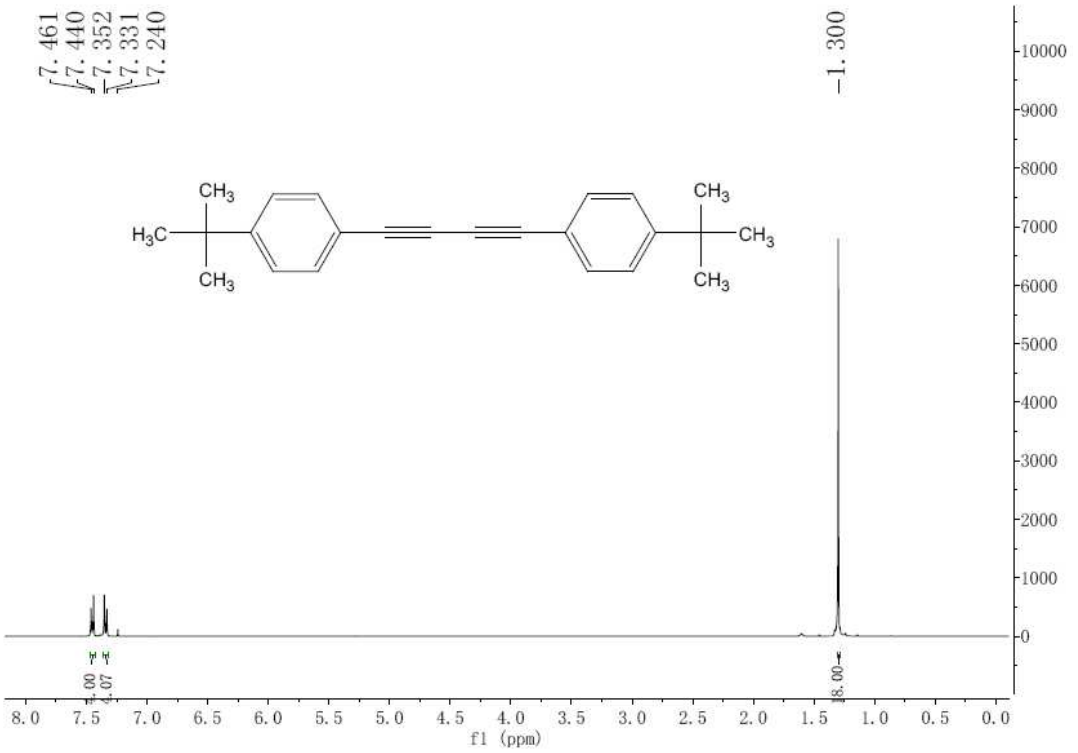


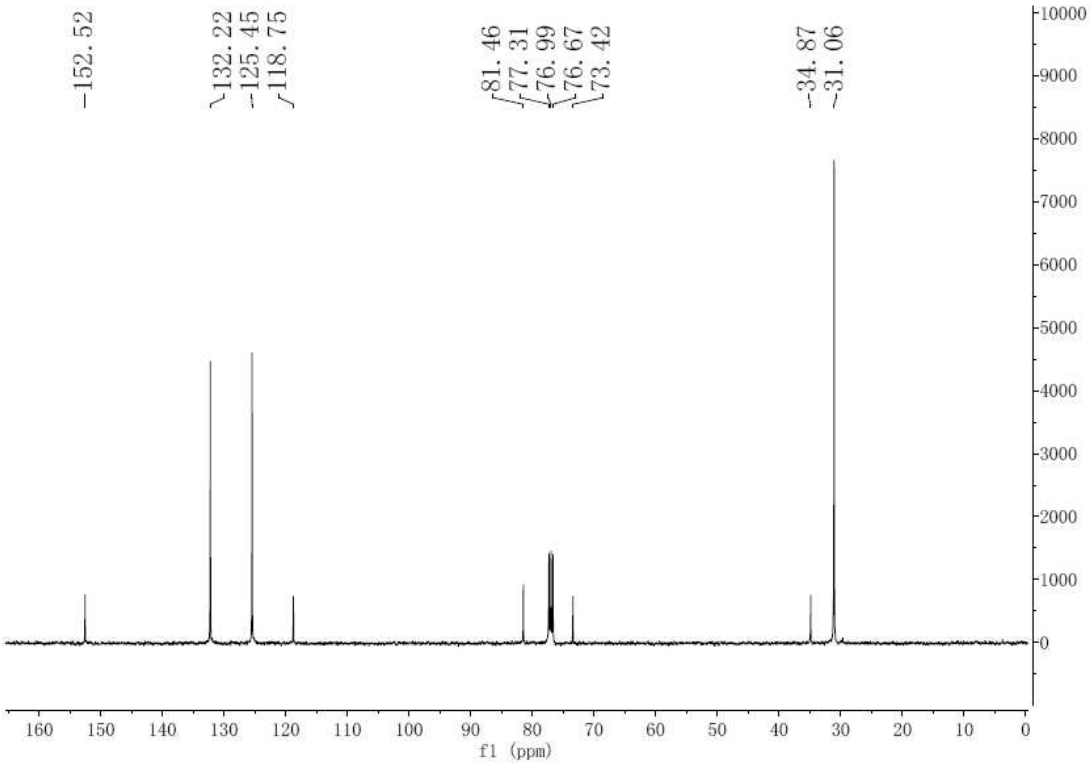
^{1}H NMR and ^{13}C NMR of 1,4-di*o*-tolylbuta-1,3-diyne (2d)



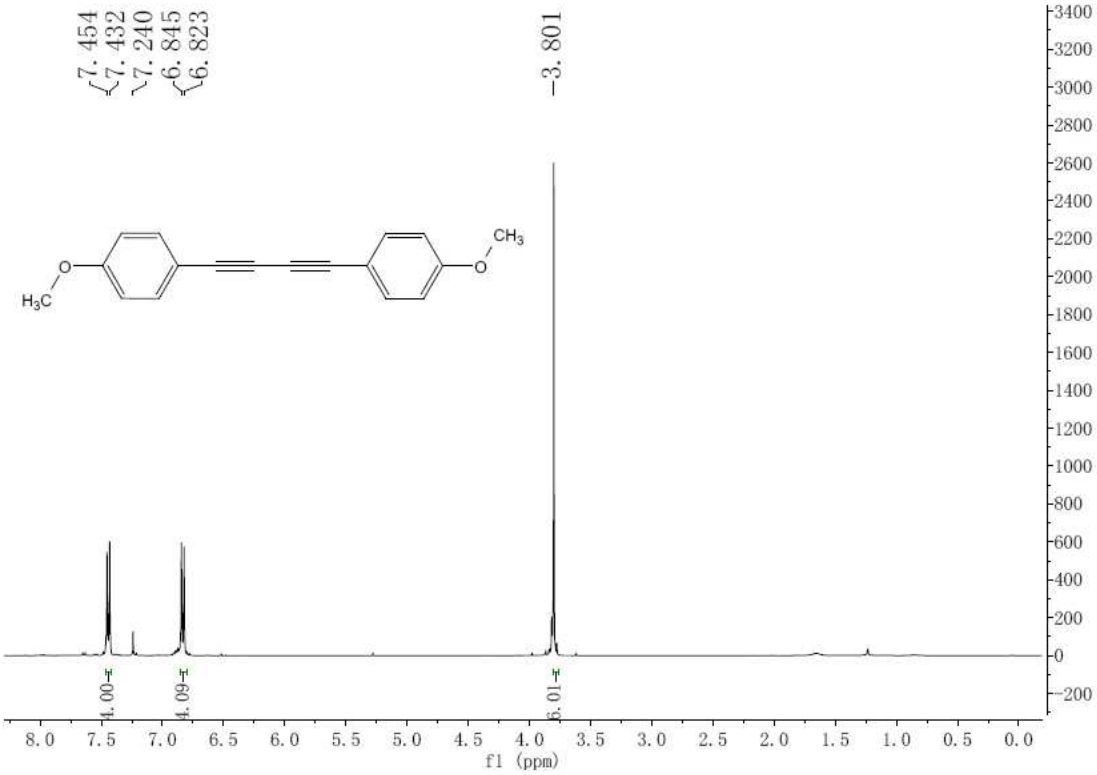


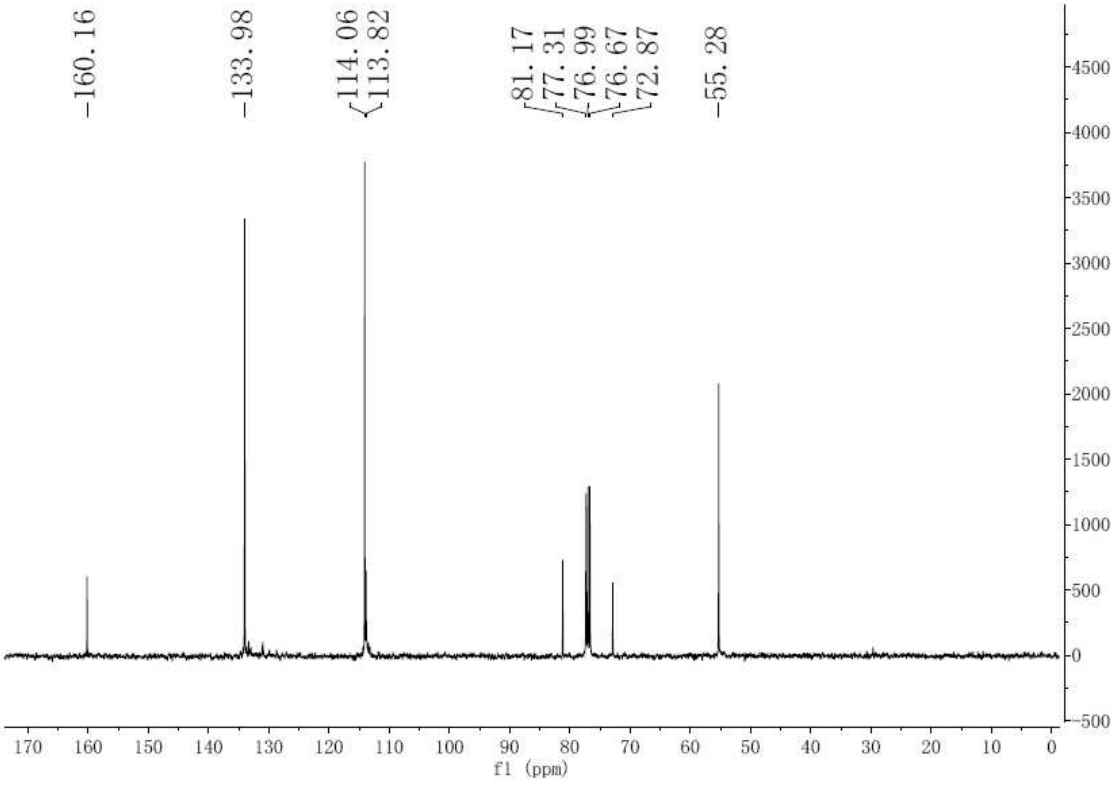
^{1}H NMR and ^{13}C NMR of 1,4-bis(4-tert-butylphenyl)buta-1,3-diyne (2e)



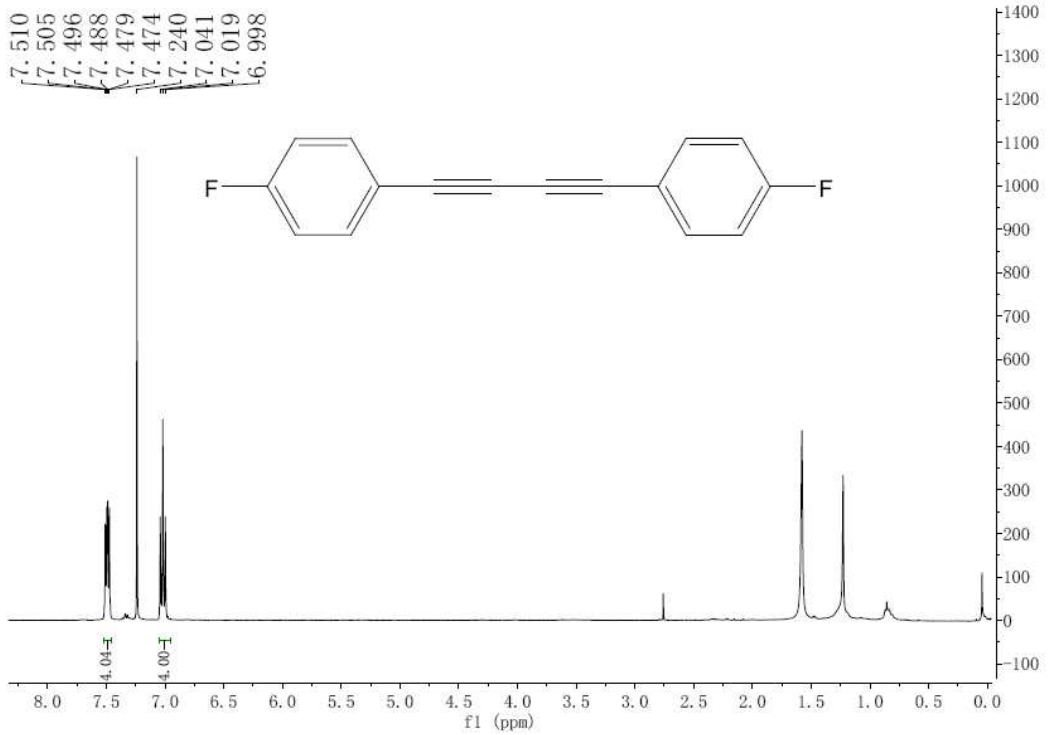


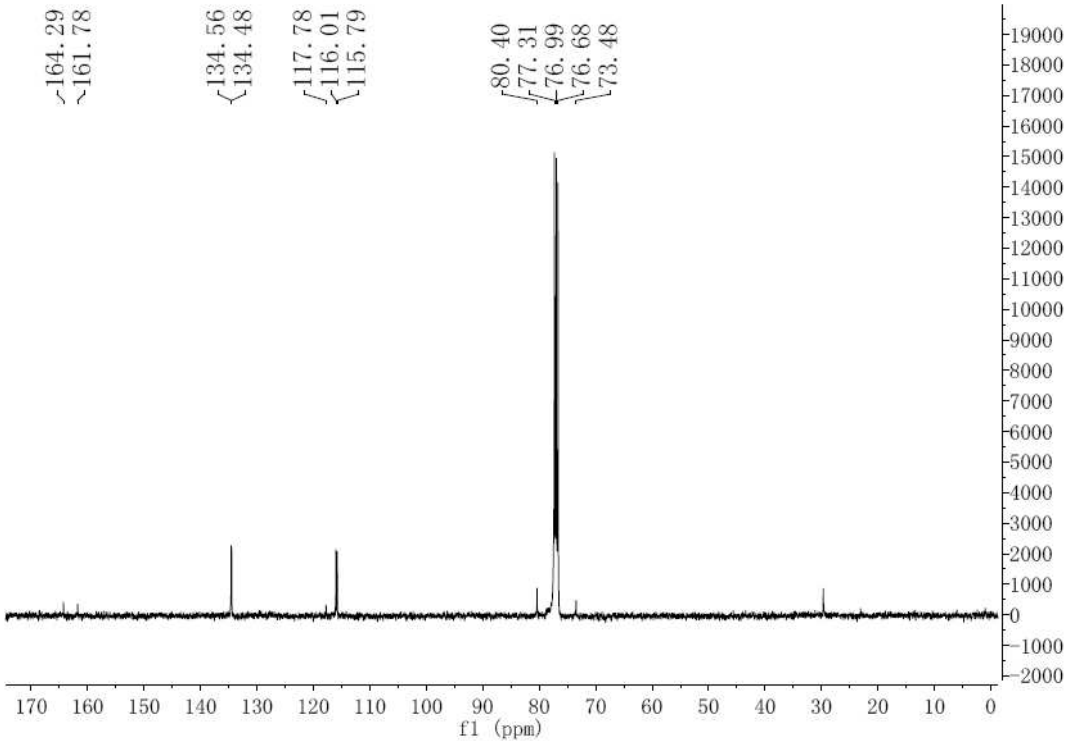
^{1}H NMR and ^{13}C NMR of 1,4-bis(4-methoxyphenyl)buta-1,3-diyne (2f)



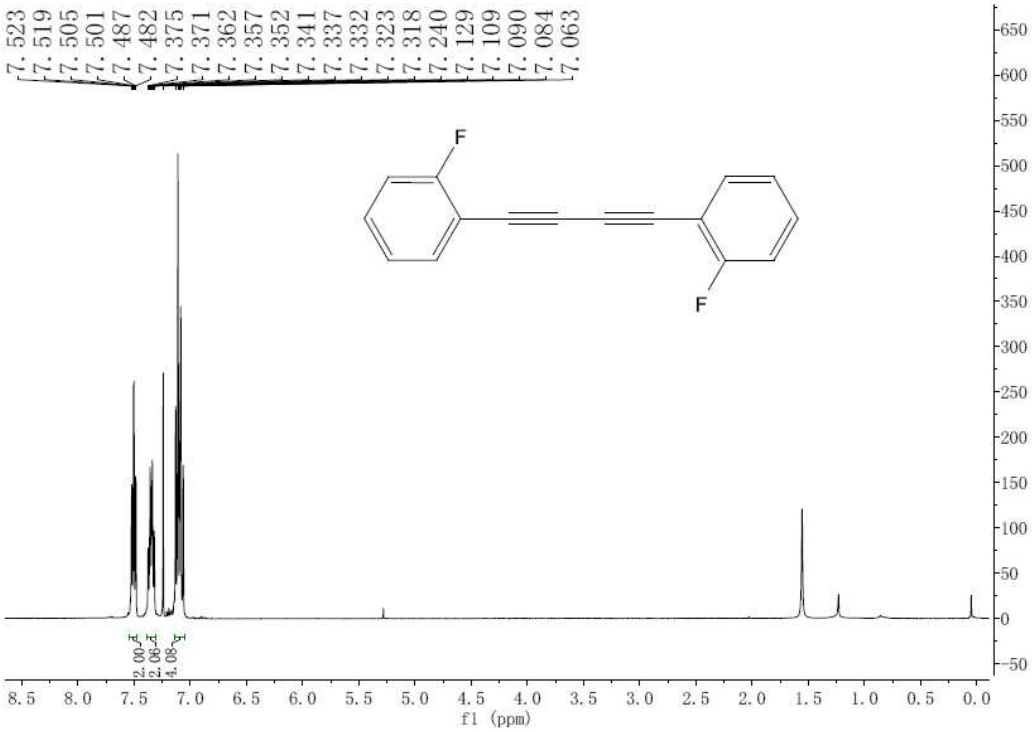


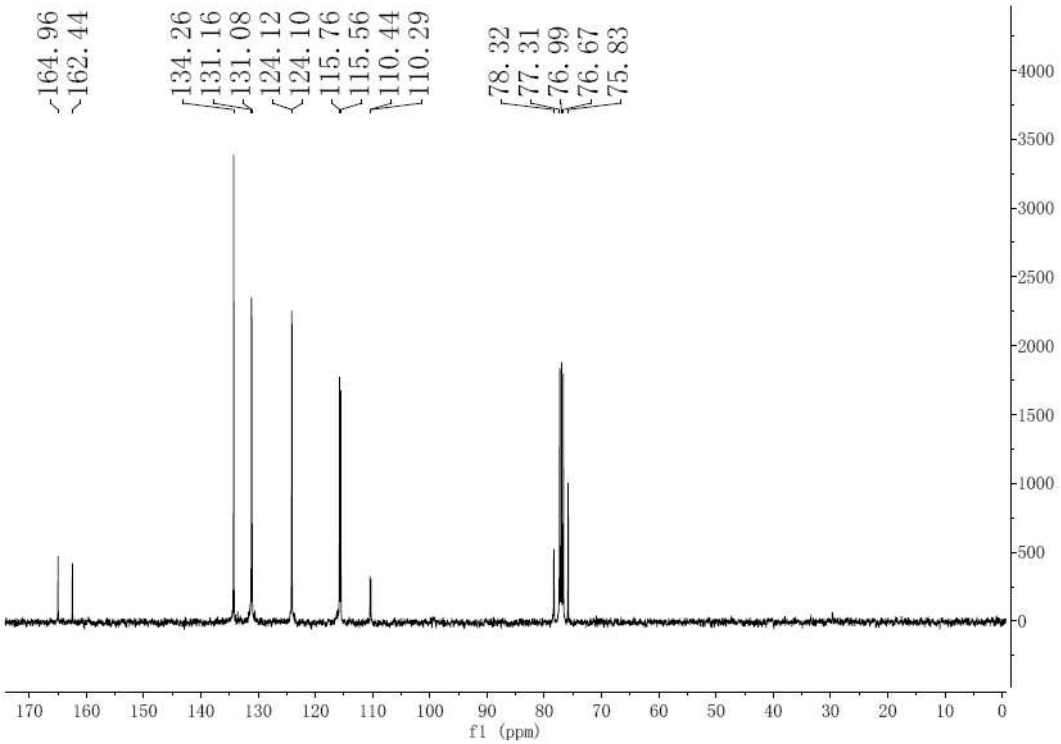
^{1}H NMR and ^{13}C NMR of 1,4-bis(4-fluorophenyl)buta-1,3-diyne (2g)



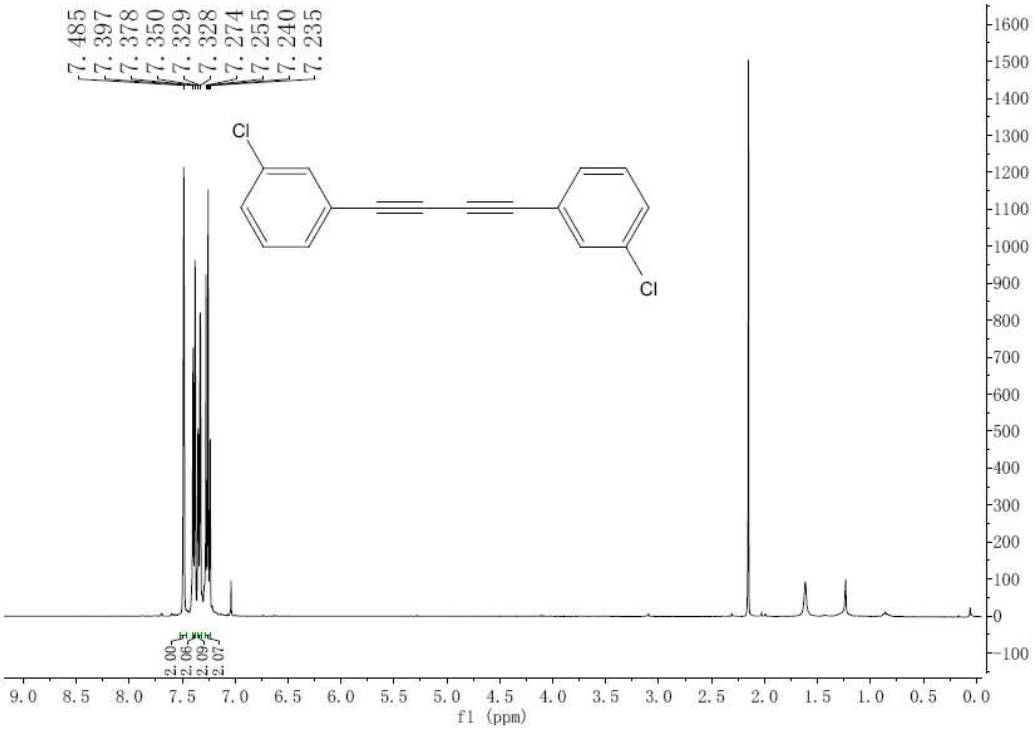


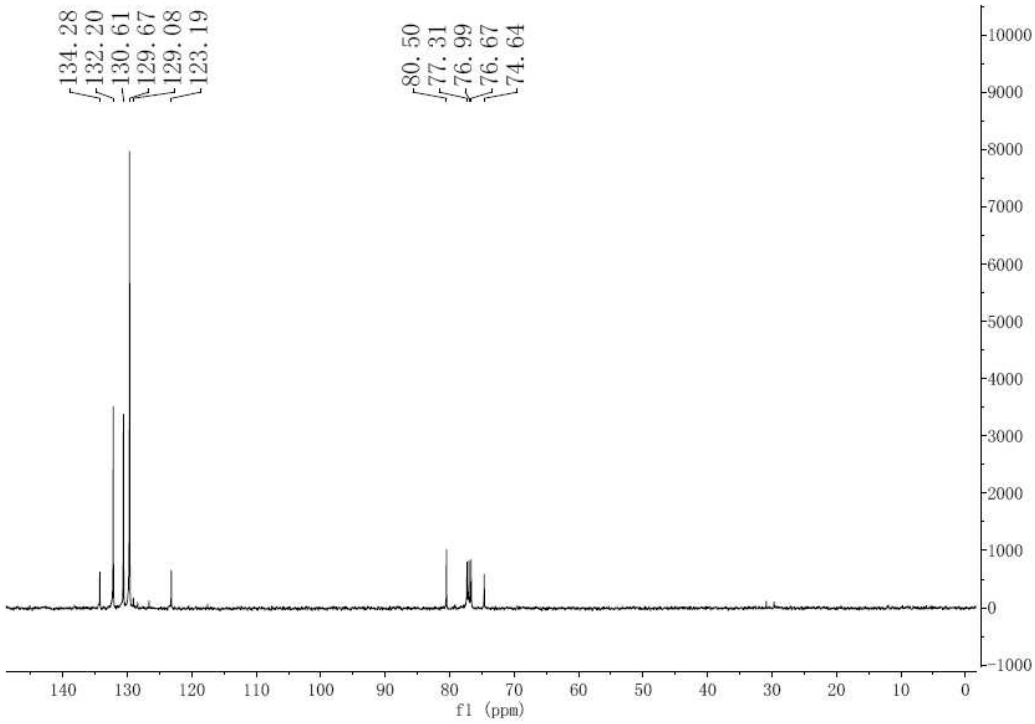
^{1}H NMR and ^{13}C NMR of 1,4-bis(2-fluorophenyl)buta-1,3-diyne (2h)



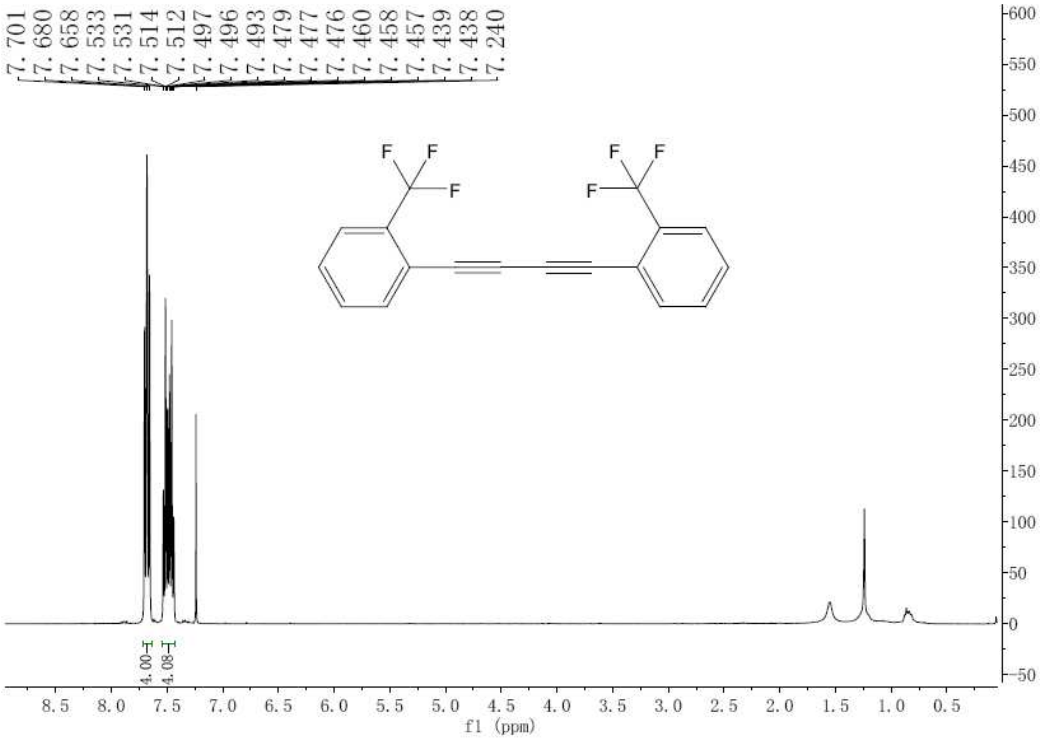


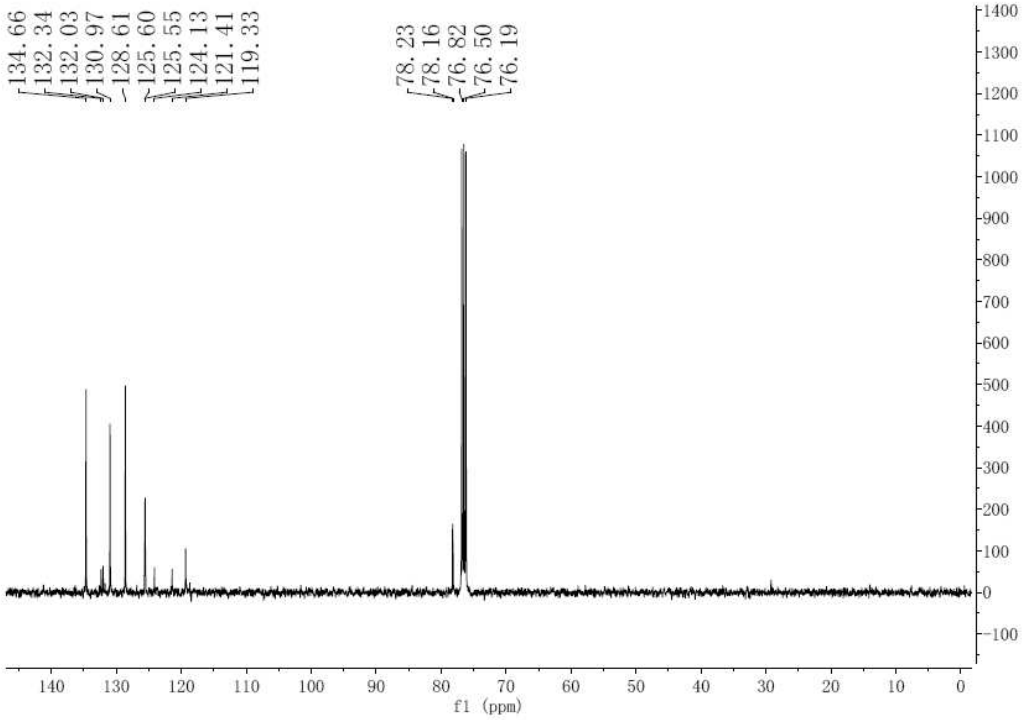
^{1}H NMR and ^{13}C NMR of 1,4-bis(3-chlorophenyl)buta-1,3-diyne (2i)



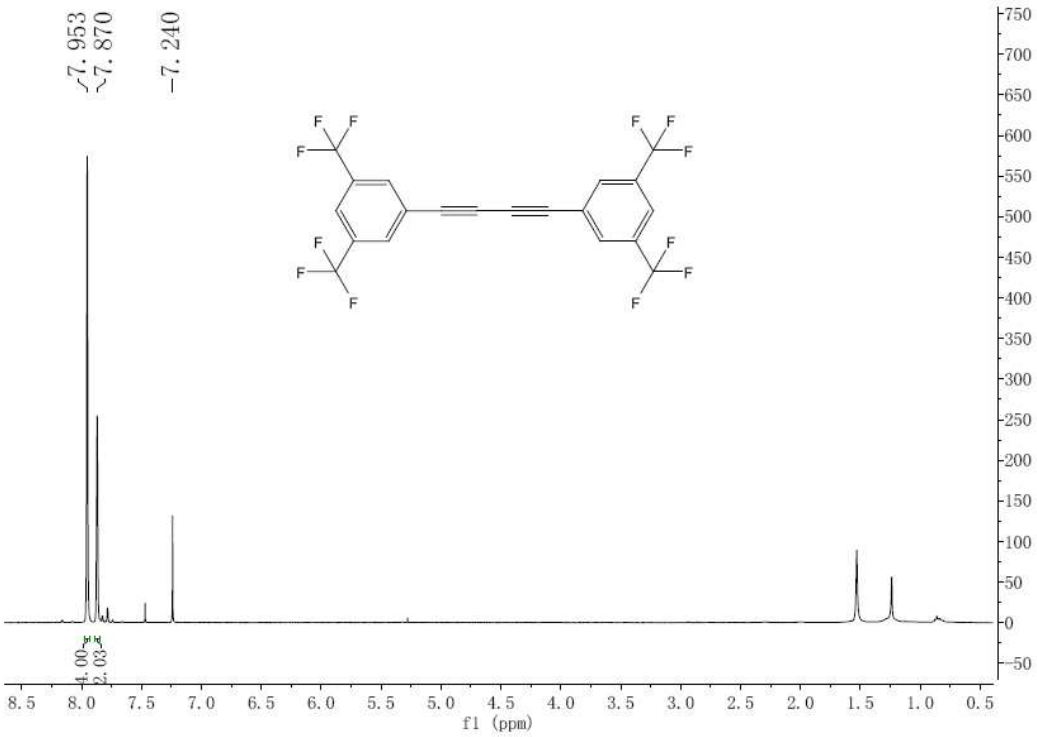


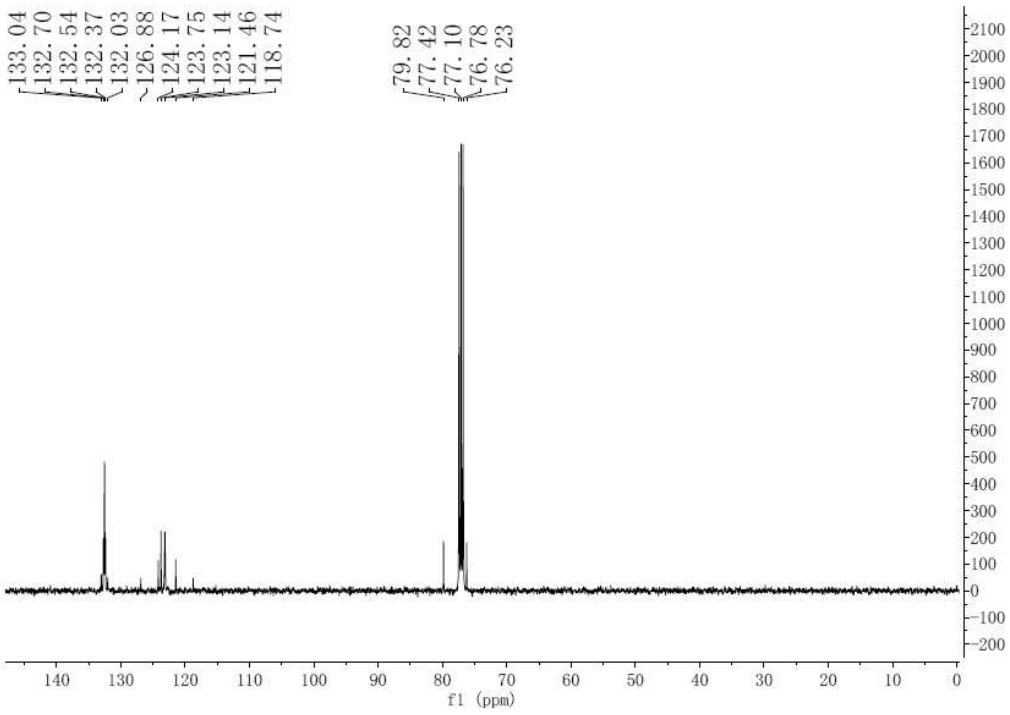
^{1}H NMR and ^{13}C NMR of 1,4-bis(2-(trifluoromethyl)phenyl)buta-1,3-diyne (2j)



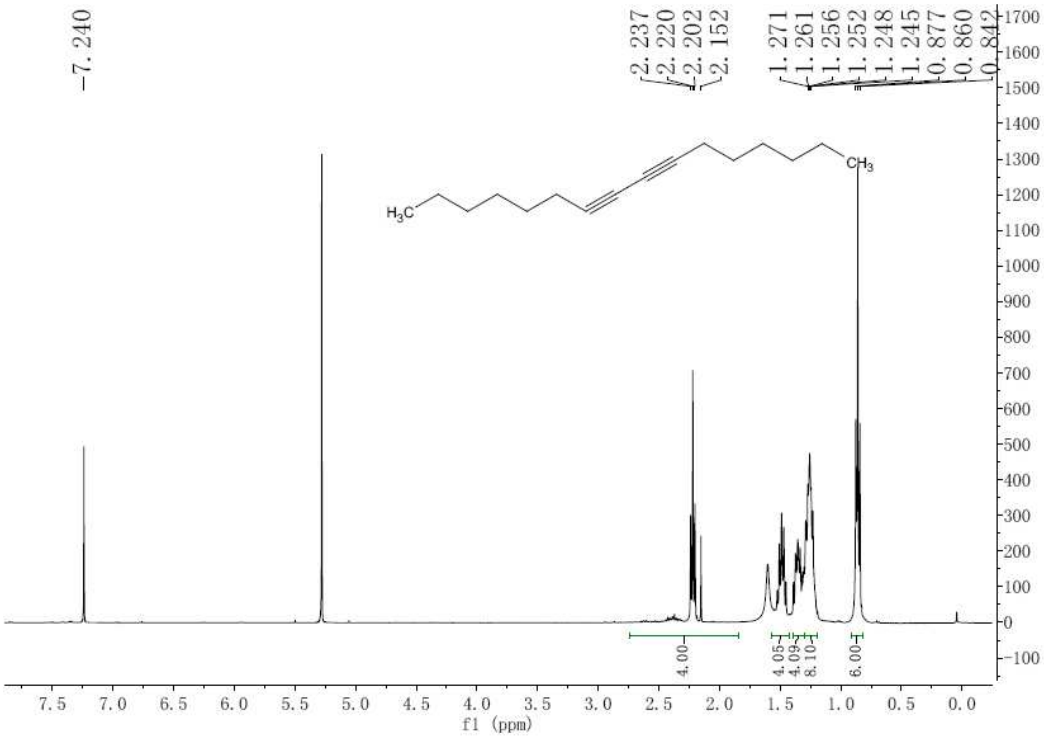


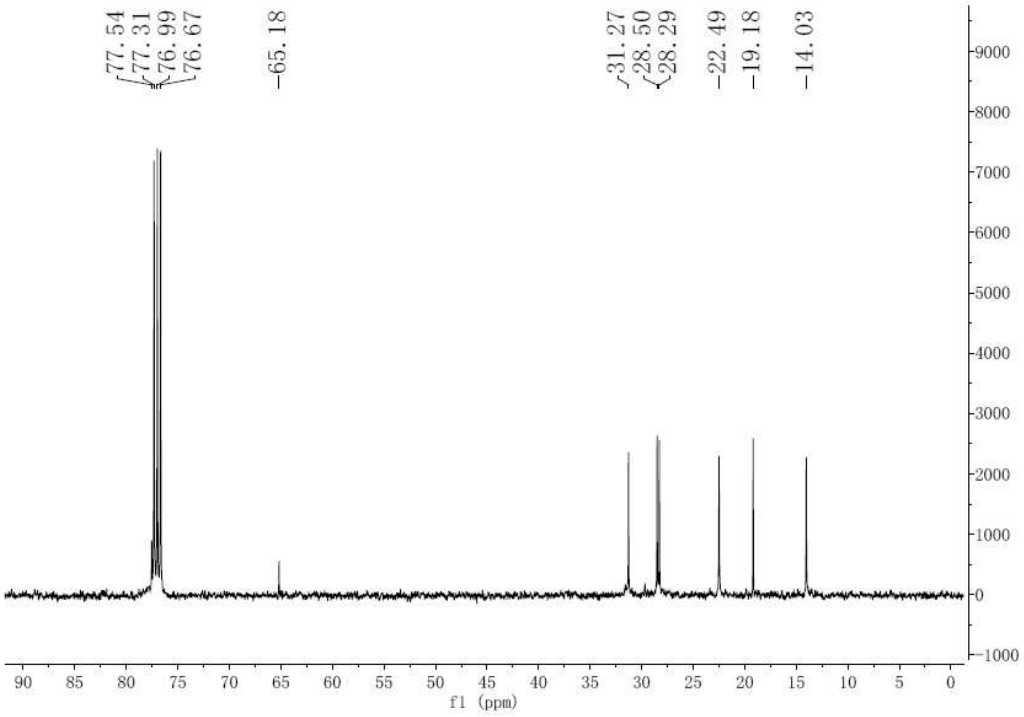
^{1}H NMR and ^{13}C NMR of 1,4-bis(3,5-bis(trifluoromethyl)phenyl)buta-1,3-diyne (2k)



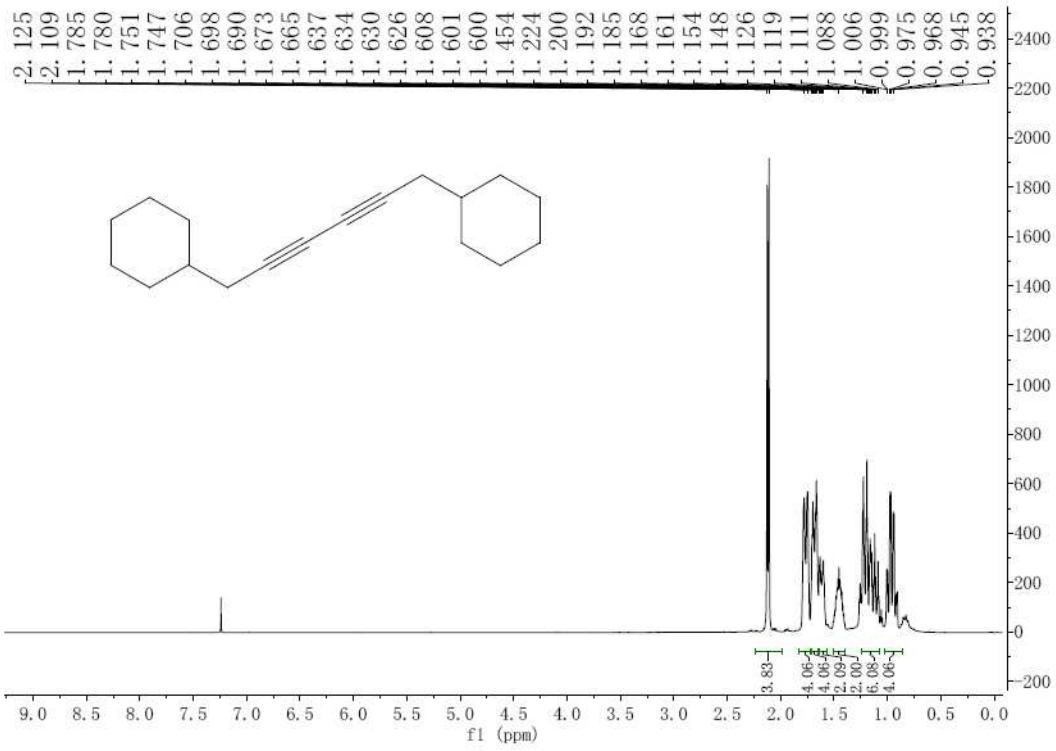


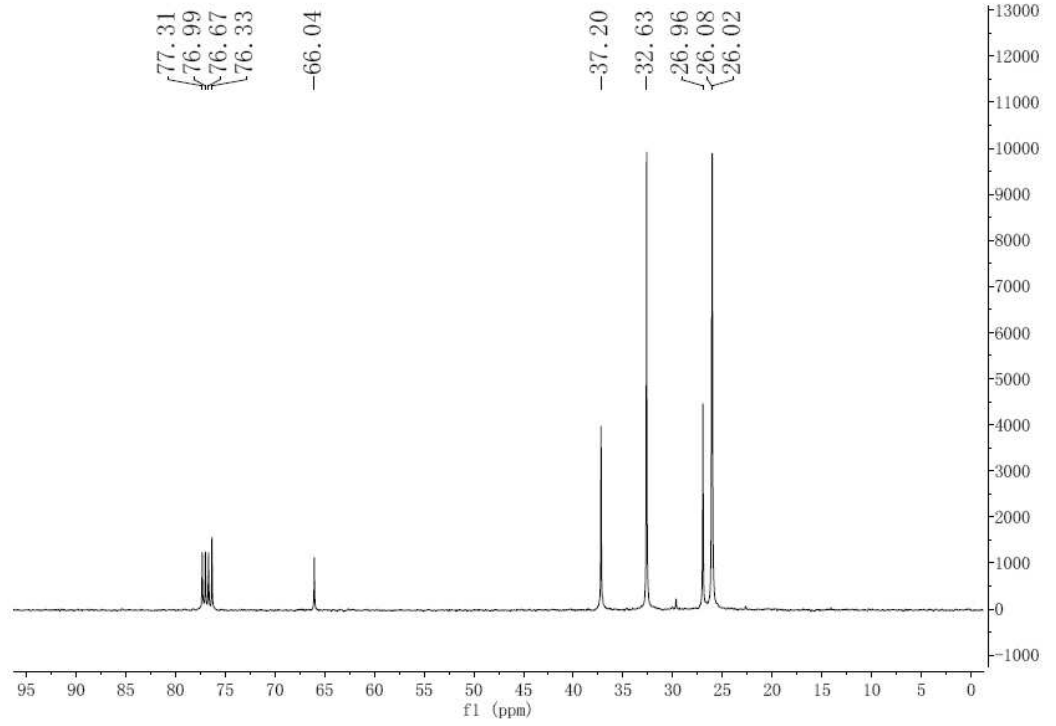
^{1}H NMR and ^{13}C NMR of hexadeca-7,9-diyne (2l)



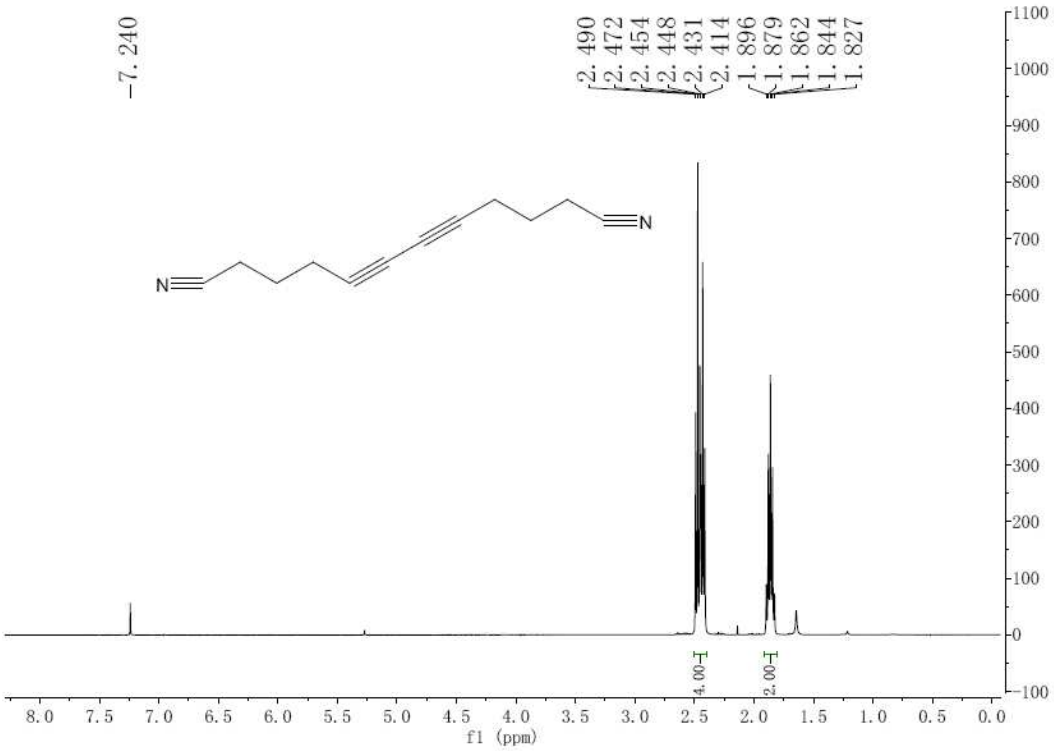


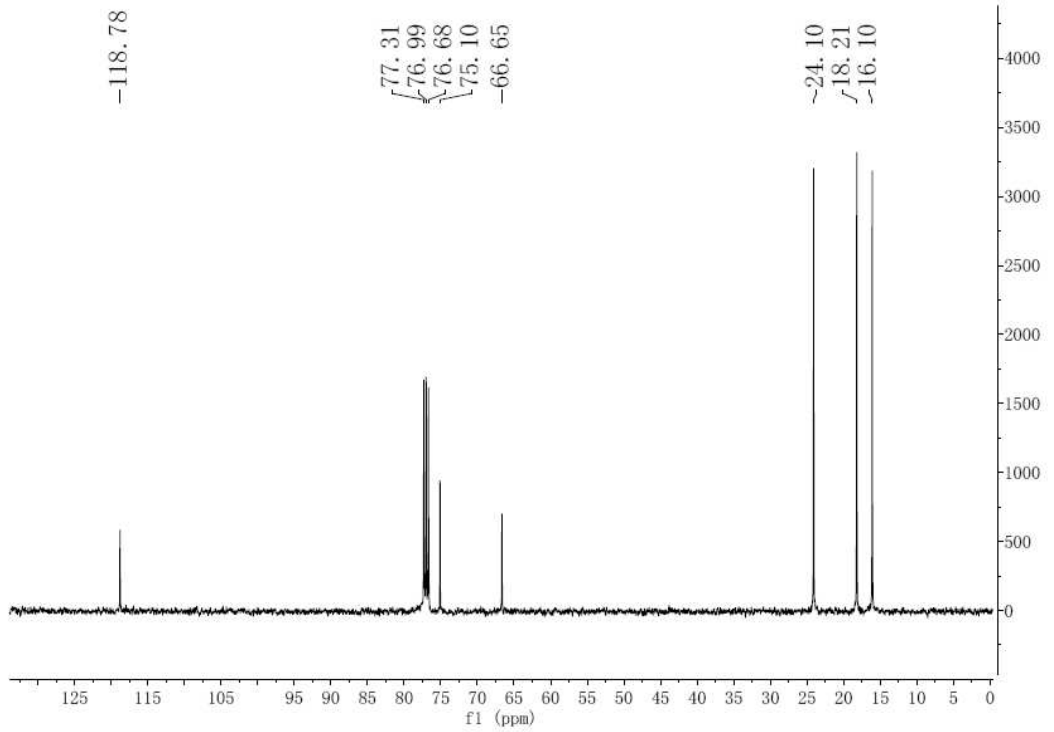
^{1}H NMR and ^{13}C NMR of 1,6-dicyclohexylhexa-2,4-diyne (2m)



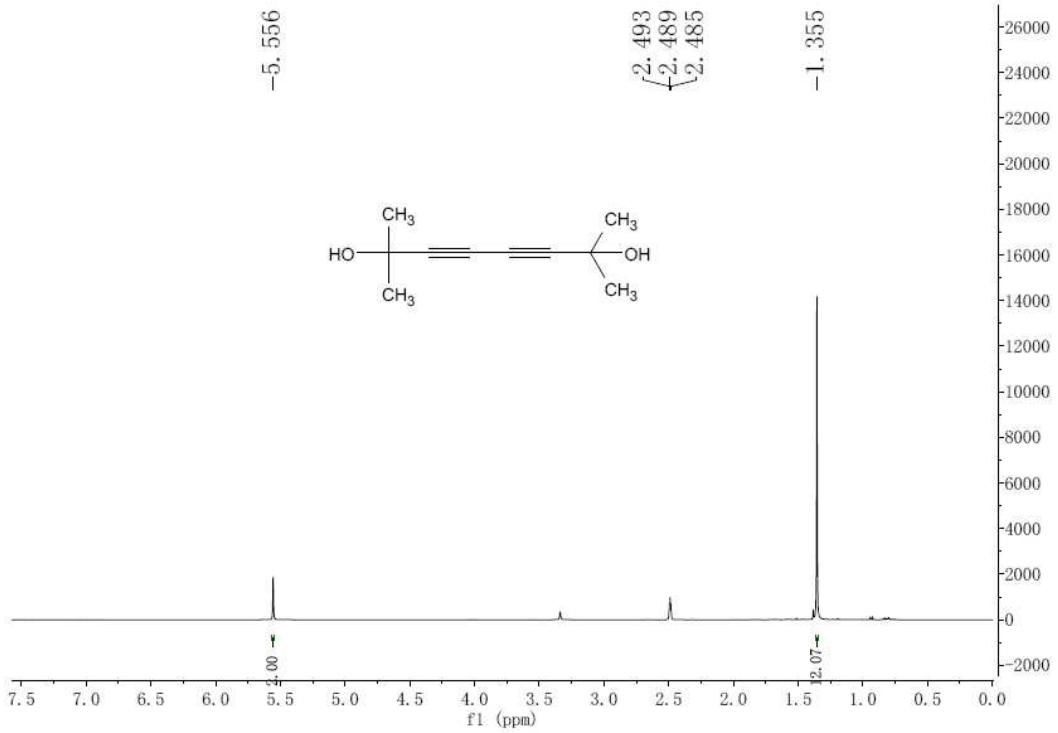


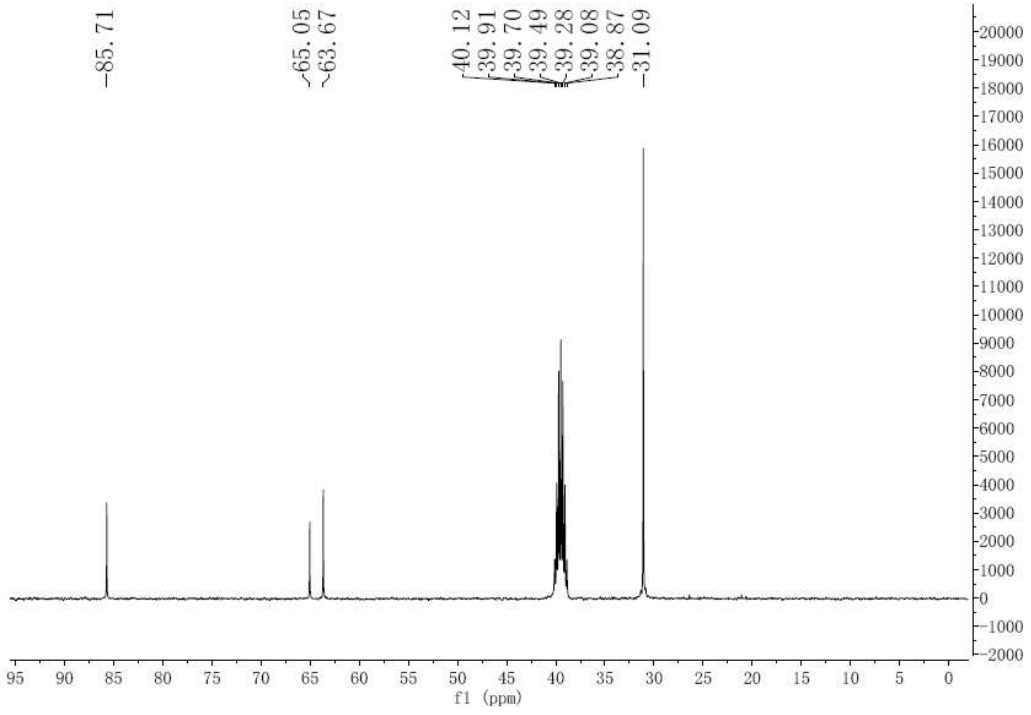
^{1}H NMR and ^{13}C NMR of dodeca-5,7-diynedinitrile (2n)



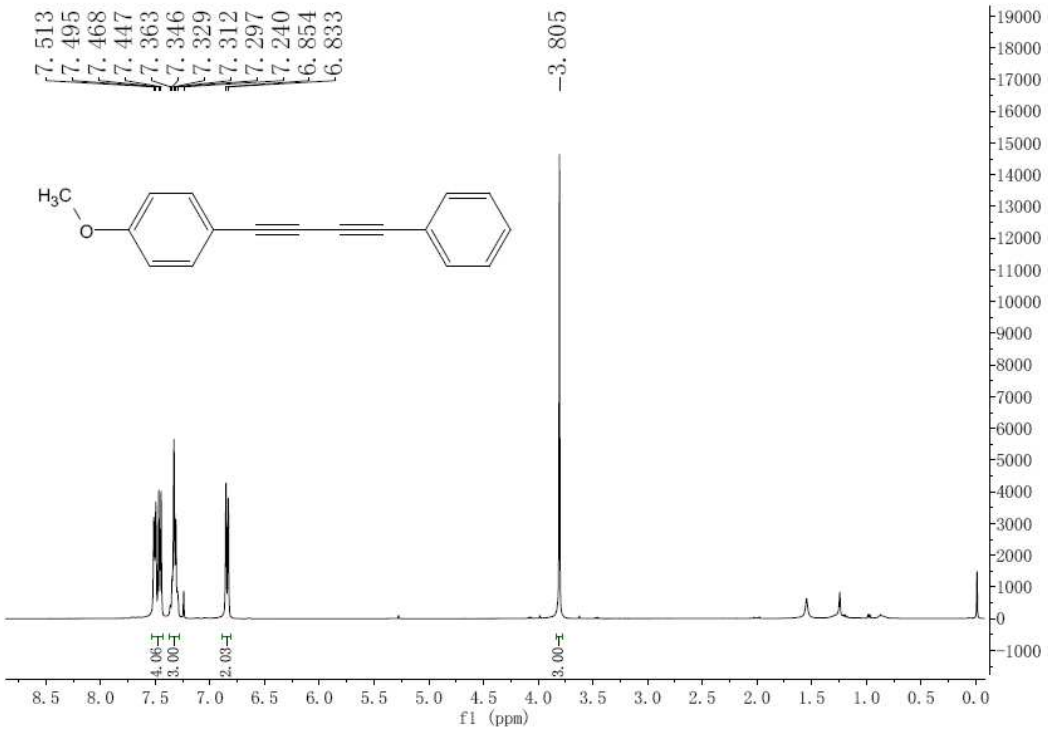


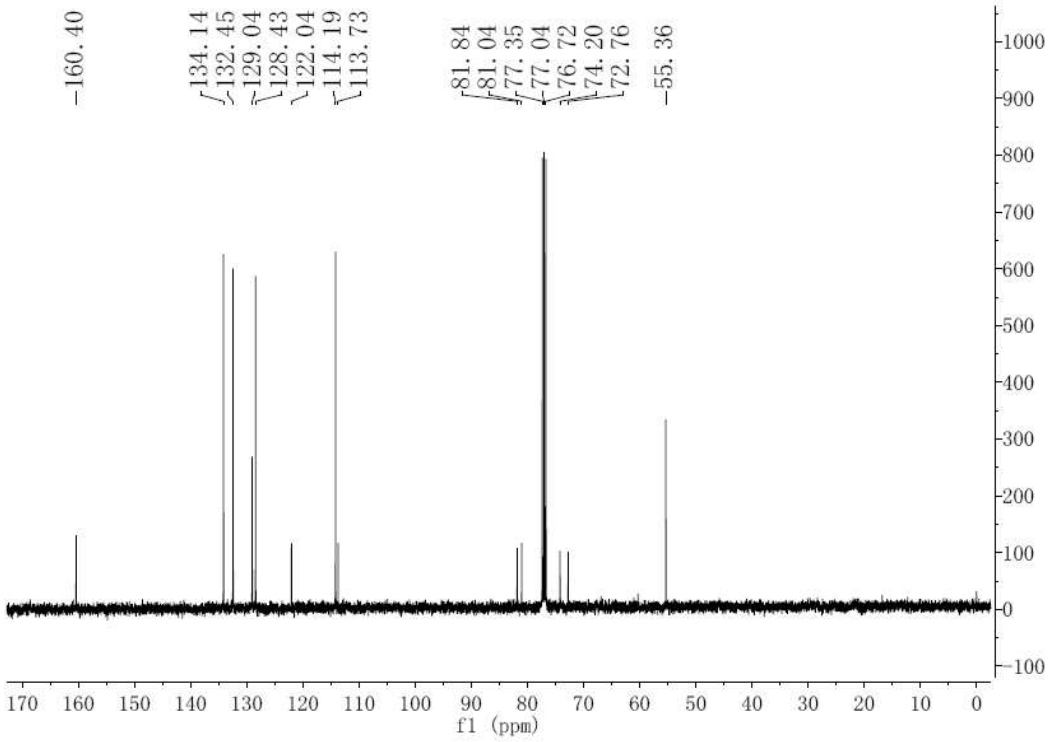
^{1}H NMR and ^{13}C NMR of 2,7-dimethylocta-3,5-diyne-2,7-diol (2o)



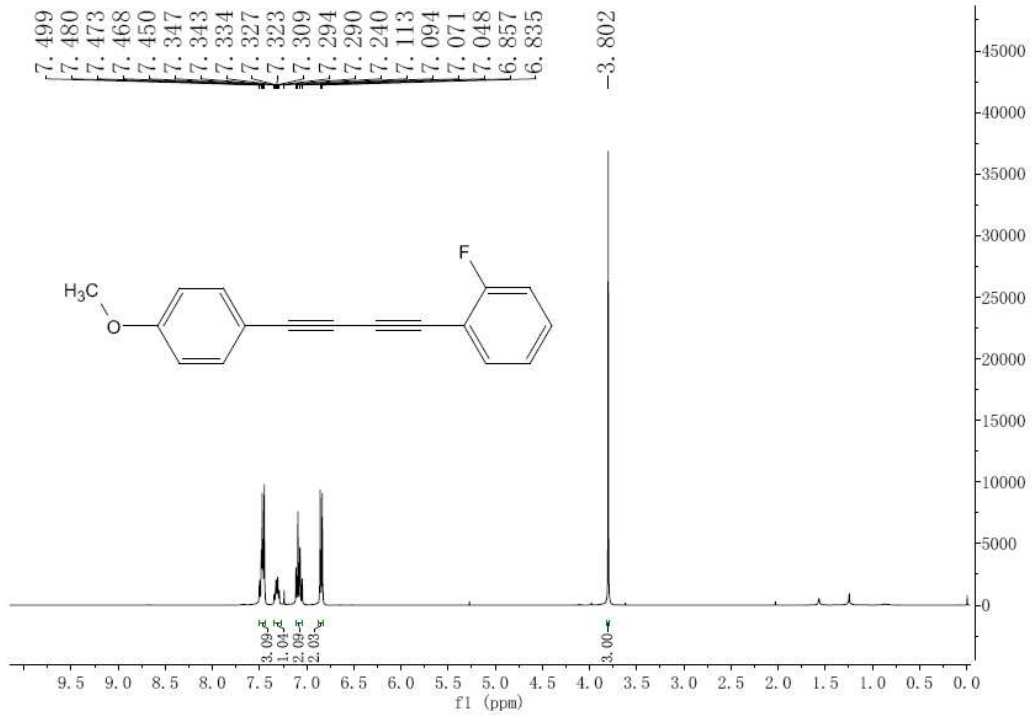


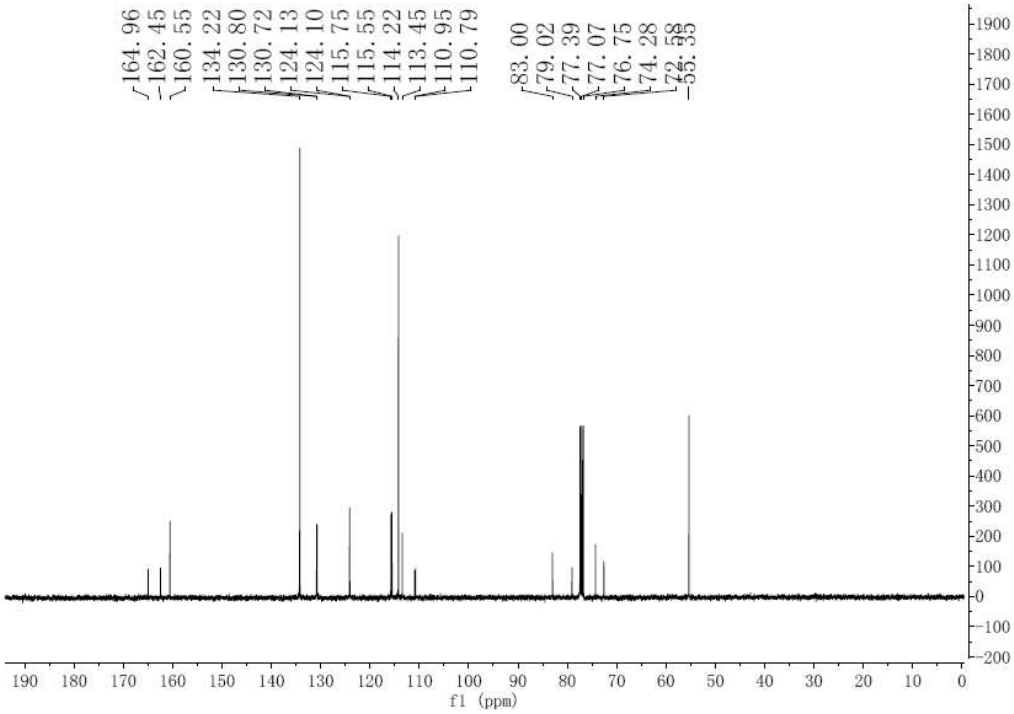
^{1}H NMR and ^{13}C NMR of 1-methoxy-4-(4-phenylbuta-1,3-diynyl)benzene (2ah)



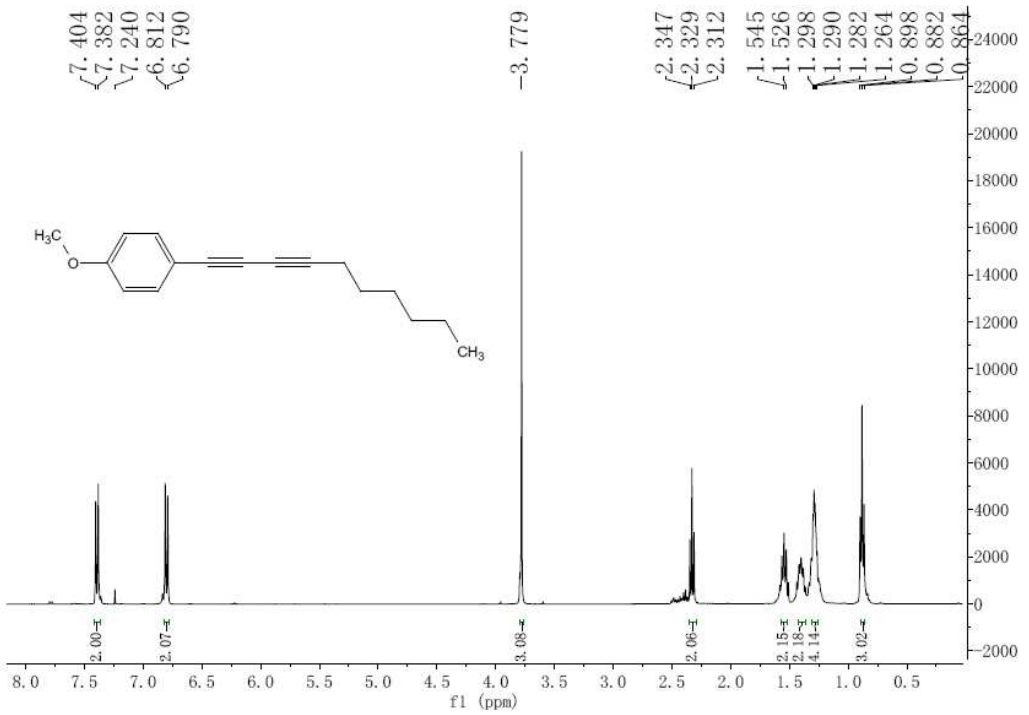


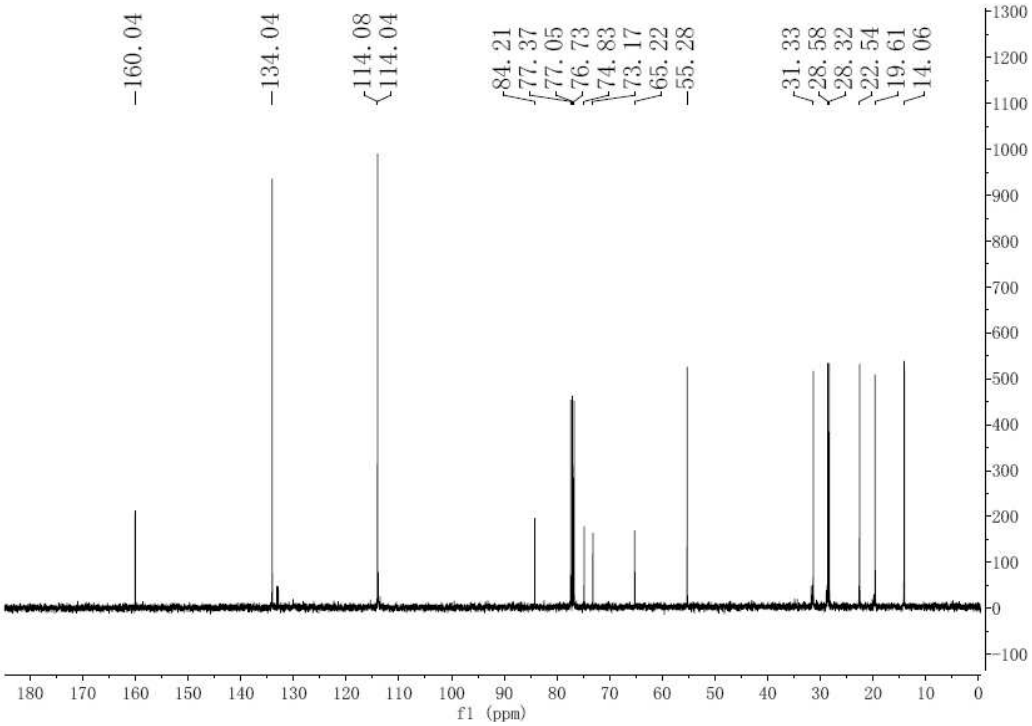
^{1}H NMR and ^{13}C NMR of 1-fluoro-2-(4-(4-methoxyphenyl)buta-1,3-diynyl)benzene (2hl)



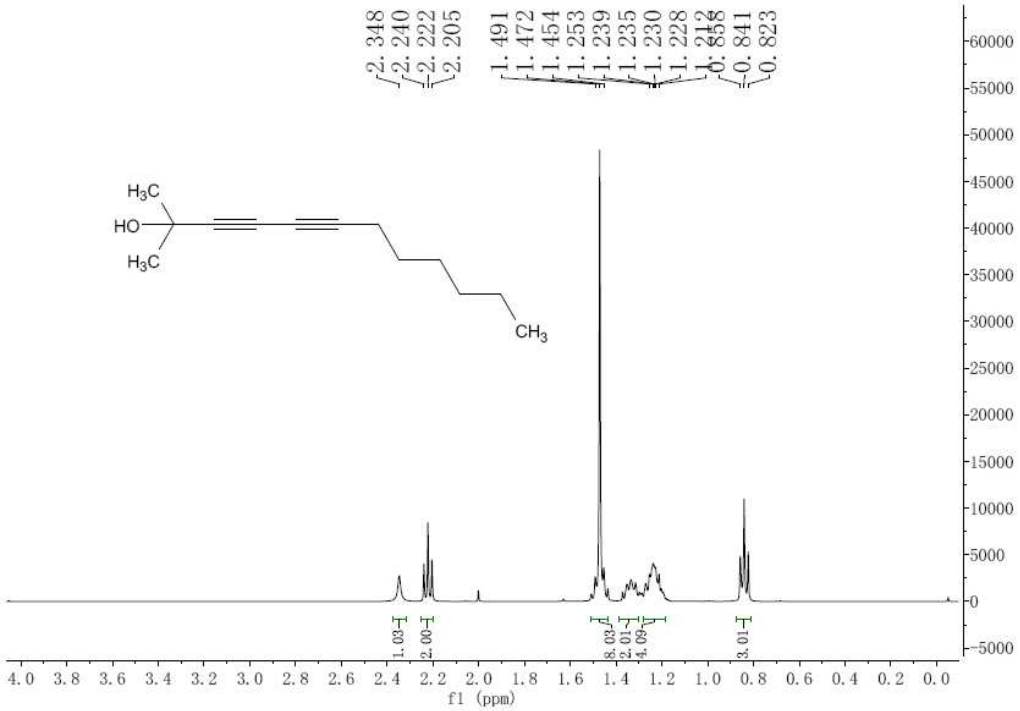


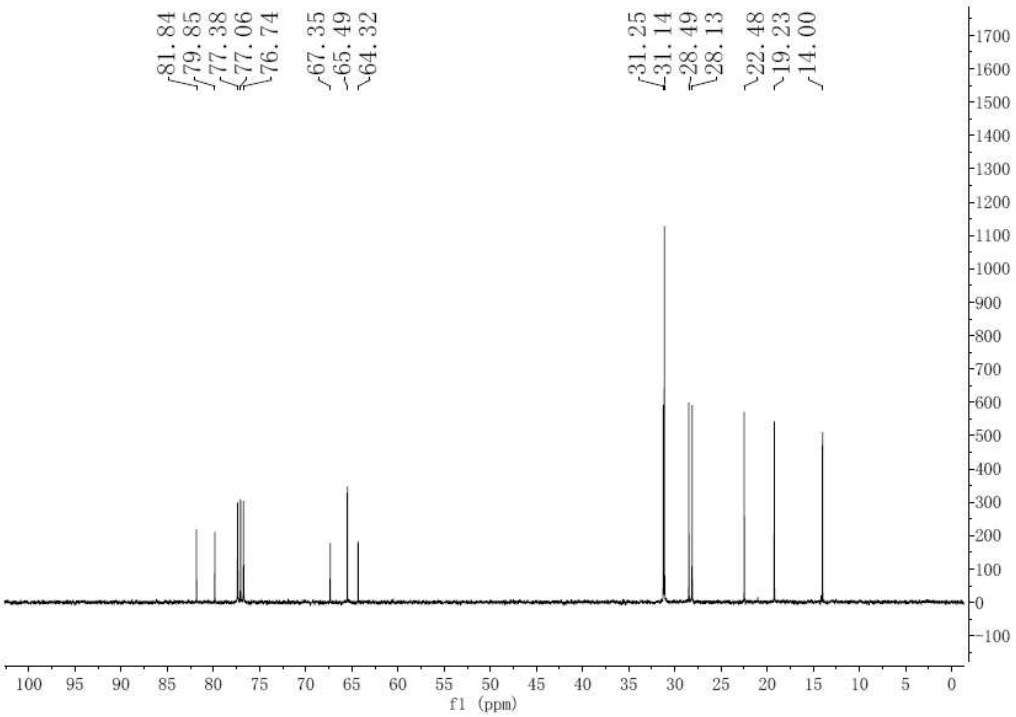
^{1}H NMR and ^{13}C NMR of 1-(deca-1,3-diynyl)-4-methoxybenzene (2ht)



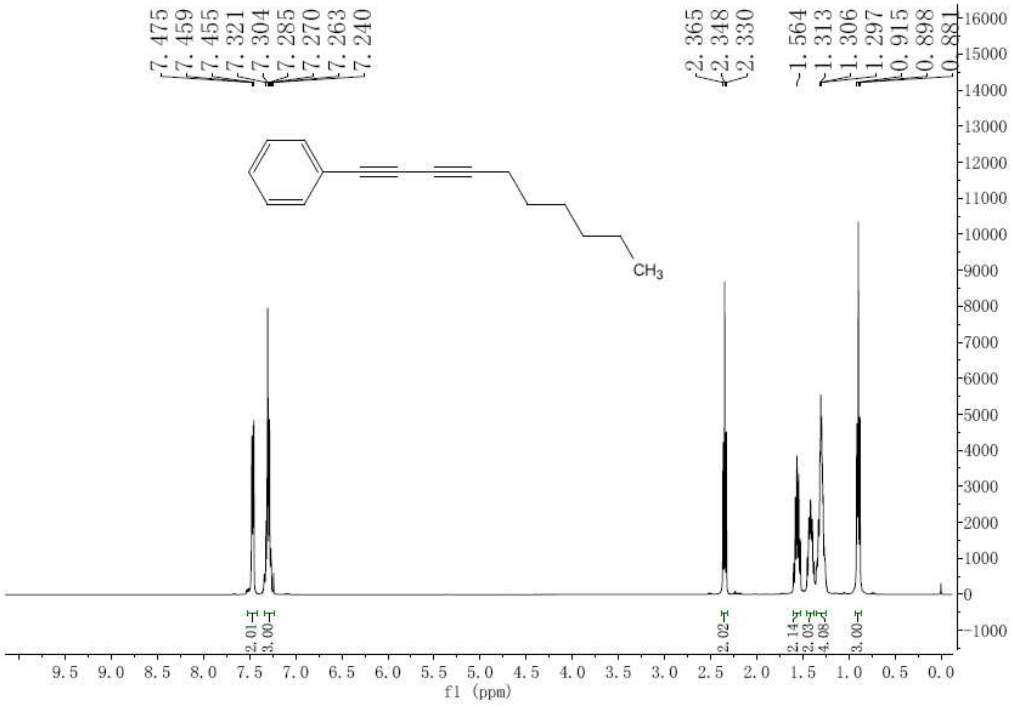


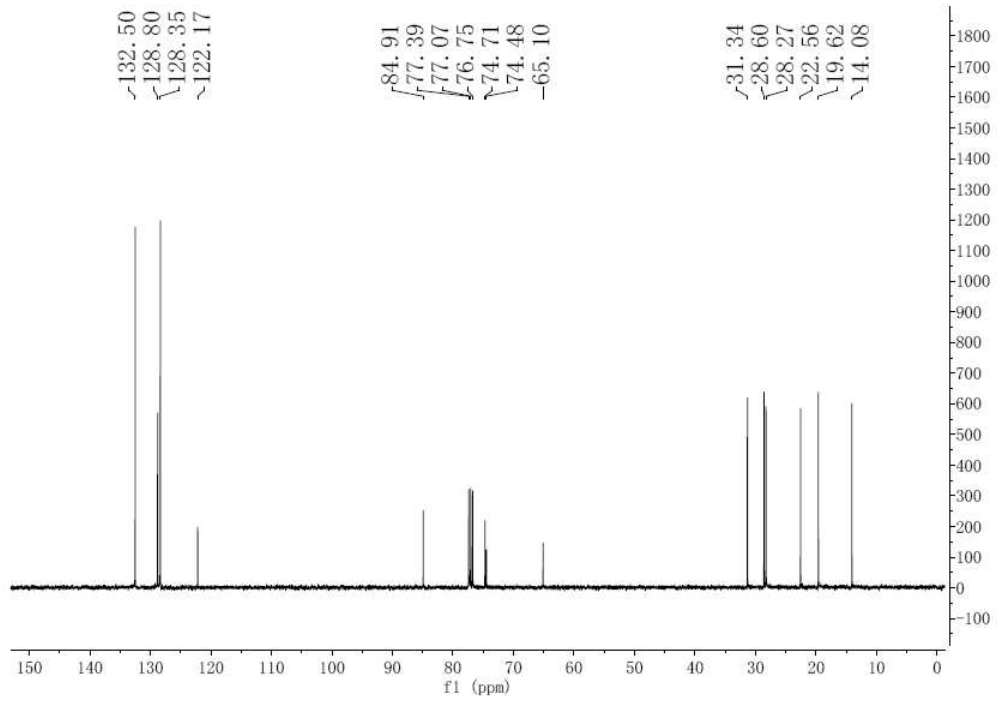
^{1}H NMR and ^{13}C NMR of 2-methyldodeca-3,5-diyn-2-ol (2tx)





^{1}H NMR and ^{13}C NMR of 1-(deca-1,3-diynyl)benzene (2at)





^{1}H NMR and ^{13}C NMR of 1-methyl-4-(4-phenylbuta-1,3-diynyl)benzene (2ac)