Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Copper-Catalyzed Synthesis of Internal Alkynes *via* Domino Couplings between 1,1-Dihalo-1-alkenes and Arylboronic acids

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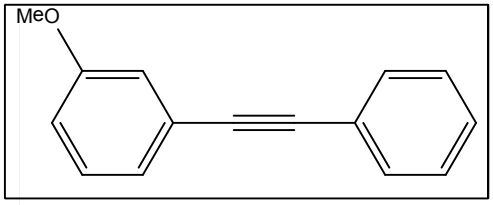
Experimental Section

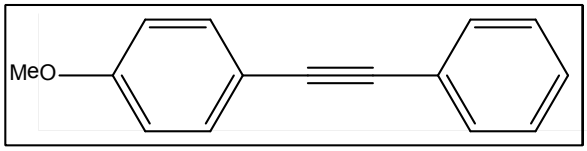
General experimental: All reactions were carried out under an argon atmosphere. Solvents were dried and degassed by the standard methods and all aryl halides were purchased from Aldrich or Alfa. Arylboronic acids and palladium catalysts were purchased from Aldrich, Acros or Alfa. 1,1-Dihalo-1-alkenes were prepared according to the reference. Flash column chromatography was performed using silica gel (300–400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in $CDCl_3$ on a Varian Inova-400 NMR spectrometer (400 or 300 MHz) with TMS as an internal reference. Products were characterized by comparison of ^{1}H NMR, ^{13}C NMR and TOF-MS data in the literatures.

General procedure for copper-catalyzed domino coupling between arylboronic acid and 1,1-dihalo-1-alkene: A schlenk tube was charged with arylboronic acid (if it is a solid) (0.6 mmol), base (if it is a solid) (1.0 mmol), copper catalyst and ligand. The tube was evacuated and filled with argon (3 times), *N*,*N*-dimethylformamide (2 mL), the corresponding 1,1-dihalo-1-alkene (if it is a liquid) (0.3 mmol) were added. The reaction mixture was stirred at 110 ◦C for 24 h. At the end of the reaction, the reaction mixture was cooled to room temperature and was diluted with diethylether and water was added. The combined organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford the desired product in high purity.

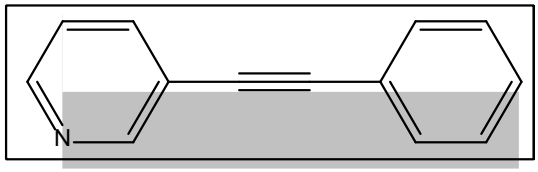
Characterization of the corresponding products:



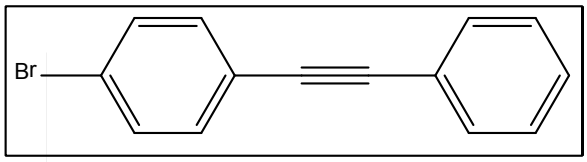
1-Methoxy-3-(2-phenylethynyl)benzene[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.52 (m, 2H, ArH), 7.37-7.33 (m, 3H, ArH), 7.24 (t, J = 8.0 Hz, 1H, ArH), 7.13 (d, J = 8.0 Hz, 1H, ArH), 7.07-7.06 (m, 1H, ArH), 6.90-6.87 (m, 1H, ArH), 3.81 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 131.6, 129.4, 128.3, 128.2, 124.2, 124.1, 123.1, 116.3, 114.9, 89.3, 89.2, 55.3; MS ($C_{15}H_{13}O$): 209.



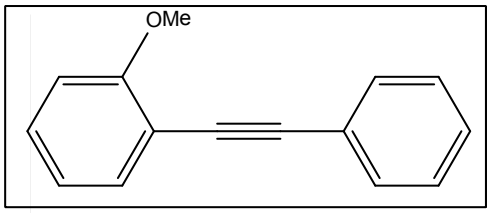
1-Methoxy-4-(2-phenylethynyl)benzene[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.46 (m, 4H, ArH), 7.35-7.28 (m, 3H, ArH), 6.87 (d, J = 8.0 Hz, 2H, ArH), 3.81 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.5, 133.0, 131.4, 128.3, 127.9, 123.6, 115.3, 113.9, 89.4, 88.0, 55.2; MS ($C_{15}H_{13}O$): 209.1.



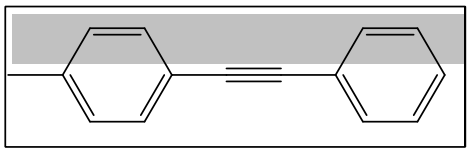
3-(2-Phenylethynyl)pyridine[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (s, 1H, ArH), 8.53 (s, 1H, ArH), 7.80 (d, J = 4.0 Hz, 1H, ArH), 7.54 (s, 2H, ArH), 7.36 (s, 3H, ArH), 7.26 (t, J = 6.0 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.1, 148.4, 138.3, 131.6, 128.7, 128.4, 122.9, 122.4, 120.4, 92.6, 85.9; MS ($C_{13}H_{10}N$): 180.



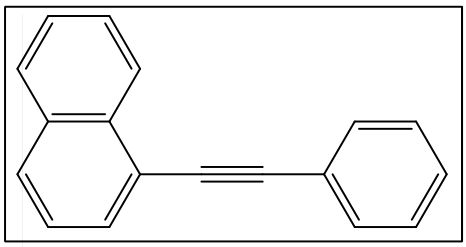
1-(2-(4-Bromophenyl)ethynyl)benzene[4]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.46 (m, 4H, ArH), 7.39-7.33 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.5, 133.0, 131.6, 128.5, 128.4, 122.9, 122.4, 122.2, 90.5, 88.3; MS ($C_{14}H_9Br$): 256.



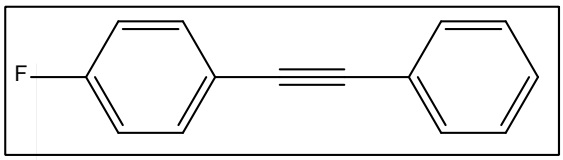
1-Methoxy-2-(2-phenylethynyl)benzene[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57-7.55 (m, 2H, ArH), 7.51-7.49 (m, 1H, ArH), 7.35-7.28 (m, 4H, ArH), 6.95-6.88 (m, 2H, ArH), 3.91 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.9, 133.5, 131.6, 129.7, 128.2, 128.1, 123.5, 120.4, 112.4, 110.6, 93.4, 85.7, 55.8; MS ($C_{15}H_{13}O$): 209.



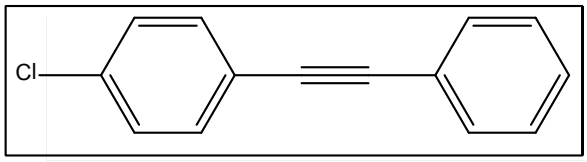
1-(2-*p*-Tolylethynyl)benzene[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.51 (m, 2H, ArH), 7.42 (d, J = 8.0 Hz, 2H, ArH), 7.32 (d, J = 8.0 Hz, 3H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 2.35 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.3, 131.5, 131.4, 129.1, 128.3, 128.0, 123.4, 120.1, 89.5, 88.7, 21.5.



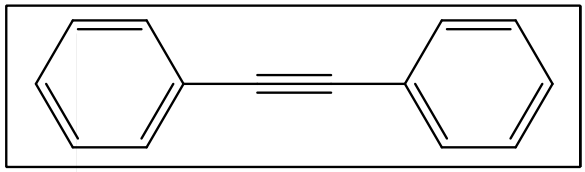
1-(2-Phenylethynyl)naphthalene[1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.45 (d, J = 9.0 Hz, 1H, ArH), 7.83 (t, J = 7.5 Hz, 2H, ArH), 7.76 (d, J = 9.0 Hz, 1H, ArH), 7.66-7.61 (m, 2H, ArH), 7.58-7.56 (m, 1H, ArH), 7.54-7.48 (m, 1H, ArH), 7.45 (d, J = 9.0 Hz, 1H, ArH), 7.41-7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.2, 133.1, 131.6, 130.3, 128.7, 128.5, 128.4, 128.3, 126.7, 126.4, 126.2, 125.2, 123.4, 120.9, 94.30, 87.5.



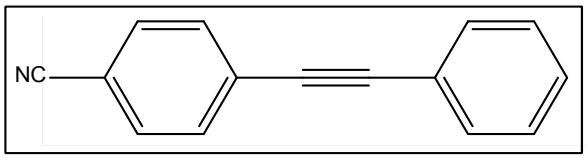
1-(2-(4-Fluorophenyl)ethynyl)benzene[4]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56-7.52 (m, 4H, ArH), 7.38-7.36 (m, 3H, ArH), 7.07 (t, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.5 (d, J = 248.0 Hz), 133.5 (d, J = 8.0 Hz), 131.5, 128.3 (d, J = 4.0 Hz), 123.1, 119.3, 115.6 (d, J = 22.0 Hz), 89.0, 88.3.



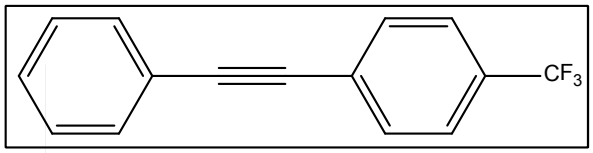
1-(2-(4-Chlorophenyl)ethynyl)benzene[4]: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53-7.49 (m, 2H, ArH), 7.46 (t, J = 3.0 Hz, 1H, ArH), 7.43 (t, J = 3.0 Hz, 1H, ArH), 7.36-7.31 (m, 4H, ArH), 7.29 (t, J = 3.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.2, 132.8, 131.6, 128.6, 128.4, 128.3, 122.9, 121.7, 90.3, 88.2.



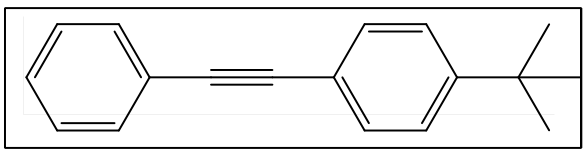
1,2-Diphenylethyne[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.52 (m, 4H, ArH), 7.36-7.32 (m, 6H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.6, 128.3, 128.2, 123.2, 89.4.



4-(2-Phenylethynyl)benzonitrile[1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.65-7.53 (m, 6H, ArH), 7.39-7.37 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 132.0, 131.7, 129.1, 128.5, 128.2, 122.2, 118.5, 111.4, 93.7, 87.7.



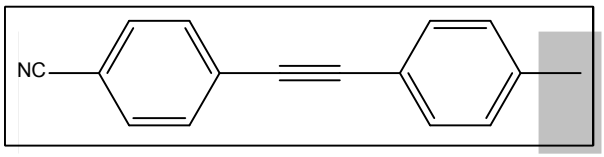
1-(2-(4-(Trifluoromethyl)phenyl)ethynyl)benzene[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62-7.59 (m, 4H, ArH), 7.55-7.54 (m, 2H, ArH), 7.38-7.36 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 131.8, 131.7, 129.9 (d, J = 33.0 Hz), 128.8, 128.5, 127.1, 125.3 (d, J = 3.0 Hz), 123.9 (d, J = 270.8 Hz), 122.5, 91.7, 87.9; Elem. Anal. Calcd for $C_{15}H_9F_3$: C, 73.17; H, 3.68; Found: C, 73.45; H, 3.73.



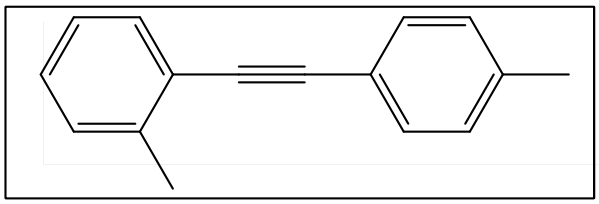
1-Tert-butyl-4-(2-phenylethynyl)benzene[6]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.52 (m, 2H, ArH), 7.48-7.46 (m, 2H, ArH), 7.38-7.32 (m, 5H, ArH), 1.32 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.5, 131.6, 131.4, 128.3, 128.1, 125.4,

123.5, 120.3, 89.6, 88.8, 34.8, 31.2.

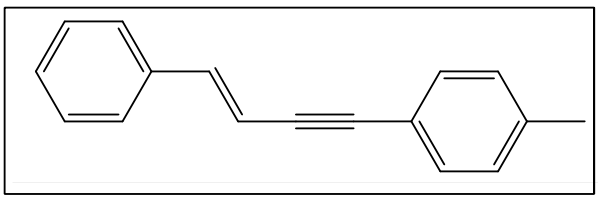
1,2-Di*p*-tolylethyne[6]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.40 (m, 4H, ArH), 7.15-7.13 (m, 4H, ArH), 2.35 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.0, 131.4, 129.1, 120.2, 88.9, 21.5.



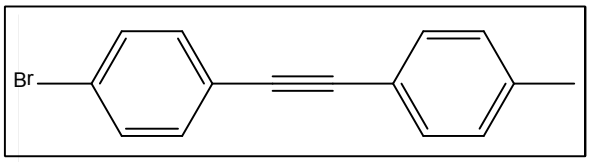
4-(2-*p*-Tolylethynyl)benzonitrile[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, J = 8.0 Hz, 2H, ArH), 7.59 (d, J = 8.0 Hz, 2H, ArH), 7.44 (d, J = 8.0 Hz, 2H, ArH), 7.18 (d, J = 8.0 Hz, 2H, ArH), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.4, 132.0, 131.9, 131.7, 129.2, 128.4, 119.1, 118.4, 111.2, 94.1, 87.0, 21.3; MS ($C_{16}H_{12}N$): 218.1.



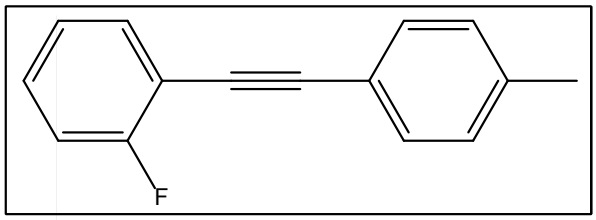
1-*o*-Tolyl-2-p-tolylethyne[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, J = 8.0 Hz, 1H, ArH), 7.43 (d, J = 8.0 Hz, 2H, ArH), 7.22 (d, J = 4.0 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 3H, ArH), 2.51 (s, 3H, CH_3), 2.36 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.0, 138.3, 131.7, 131.4, 129.4, 129.1, 128.1, 125.5, 123.2, 120.4, 93.5, 87.6, 21.5, 16.4.



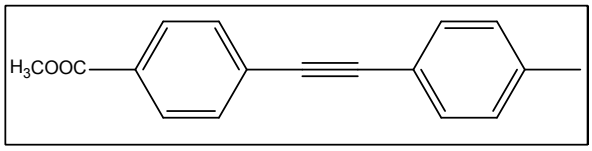
1-Methyl-4-((*E*)-4-phenylbut-3-en-1-ynyl)benzene[7]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, J = 8.0 Hz, 2H, ArH), 7.38-7.32 (m, 4H, ArH), 7.29 (d, J = 8.0 Hz, 1H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 7.02 (d, J = 16.0 Hz, 1H, CH), 6.38 (d, J = 16.0 Hz, 1H, CH), 2.36 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.9, 138.4, 136.4, 131.4, 129.1, 128.7, 128.5, 126.3, 120.3, 108.3, 92.0, 88.3, 21.5.



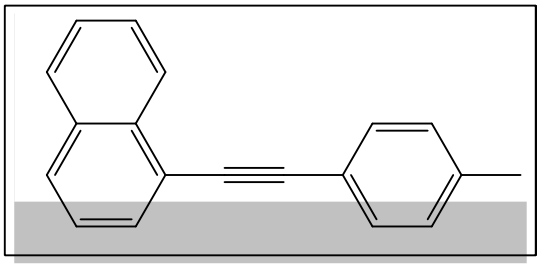
1-(2-(4-Bromophenyl)ethynyl)-4-methylbenzene[8]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J = 8.0 Hz, 2H, ArH), 7.41 (d, J = 8.0 Hz, 2H, Ar), 7.37 (d, J = 8.0 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 2H, Ar), 2.36 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.5, 132.9, 131.6, 131.5, 129.2, 122.4, 122.2, 119.8, 90.7, 87.7, 21.4; Elem. Anal. Calcd for $C_{15}H_{11}Br$: C, 66.44; H, 4.09; Found: C, 66.92; H, 4.29.



1-(2-(2-Fluorophenyl)ethynyl)-4-methylbenzene[8]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (t, J = 8.0 Hz, 1H, ArH), 7.48 (d, J = 8.0 Hz, 2H, ArH), 7.34-7.29 (m, 1H, ArH), 7.18 (d, J = 8.0 Hz, 2H, ArH), 7.15-7.09 (m, 2H, ArH), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.8 (d, J = 250.0 Hz), 139.0, 133.6, 131.8, 129.5 (d, J = 8.0 Hz), 129.3, 124.1 (d, J = 3.0 Hz), 120.0, 115.7 (d, J = 21.0 Hz), 112.3 (d, J = 15.0 Hz), 94.9, 82.2, 21.8; Elem. Anal. Calcd for $C_{15}H_{11}F$: C, 85.69; H, 5.27; Found: C, 85.59; H, 5.44.

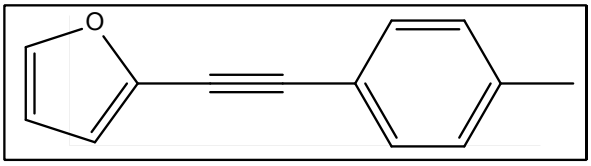


Methyl 4-(2-p-tolylethynyl)benzoate[9]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, J = 8.0 Hz, 2H, ArH), 7.60 (d, J = 8.0 Hz, 2H, ArH), 7.46 (d, J = 8.0 Hz, 2H, ArH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 3.95 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 138.9, 131.6, 131.4, 129.4, 129.2, 128.2, 119.5, 92.6, 88.0, 52.2, 21.5.

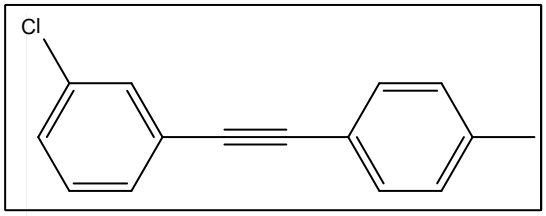


1-(2-*p*-Tolylethynyl)naphthalene[10]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (d, J = 8.0 Hz, 1H, ArH), 7.87-7.82 (m, 2H, ArH), 7.75 (d, J = 8.0 Hz, 1H, ArH), 7.61-7.51 (m,

4H, ArH), 7.45 (t, J = 8.0 Hz, 1H, ArH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 2.36 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.6, 133.3, 133.2, 131.6, 130.3, 129.3, 128.7, 128.4, 126.8, 126.5, 126.3, 125.4, 121.2, 120.4, 94.6, 87.0, 21.6.



2-(2-*p*-Tolylethynyl)furan[11]: ^1H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, J = 8.0 Hz, 3H, ArH), 7.15 (d, J = 8.0 Hz, 2H, ArH), 6.64 (d, J = 4.0 Hz, 1H, ArH), 6.42 (s, 1H, ArH), 2.36 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 138.9, 137.3, 131.3, 129.1, 119.1, 114.9, 111.0, 93.4, 78.7, 21.5; MS($C_{13}H_{11}O$): 183.1.



1-(2-(3-Chlorophenyl)ethynyl)-4-methylbenzene[12]: ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51 (s, 1H, ArH), 7.43-7.38 (t, J = 10.0 Hz, 3H, ArH), 7.29 (t, J = 4.0 Hz, 1H, ArH), 7.24 (t, J = 4.0 Hz, 1H, ArH), 7.16 (d, J = 8.0 Hz, 2H, ArH), 2.36 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8, 134.1, 131.5, 131.3, 129.6, 129.5, 129.1, 128.3, 125.2, 119.6, 90.7, 87.3, 21.5.

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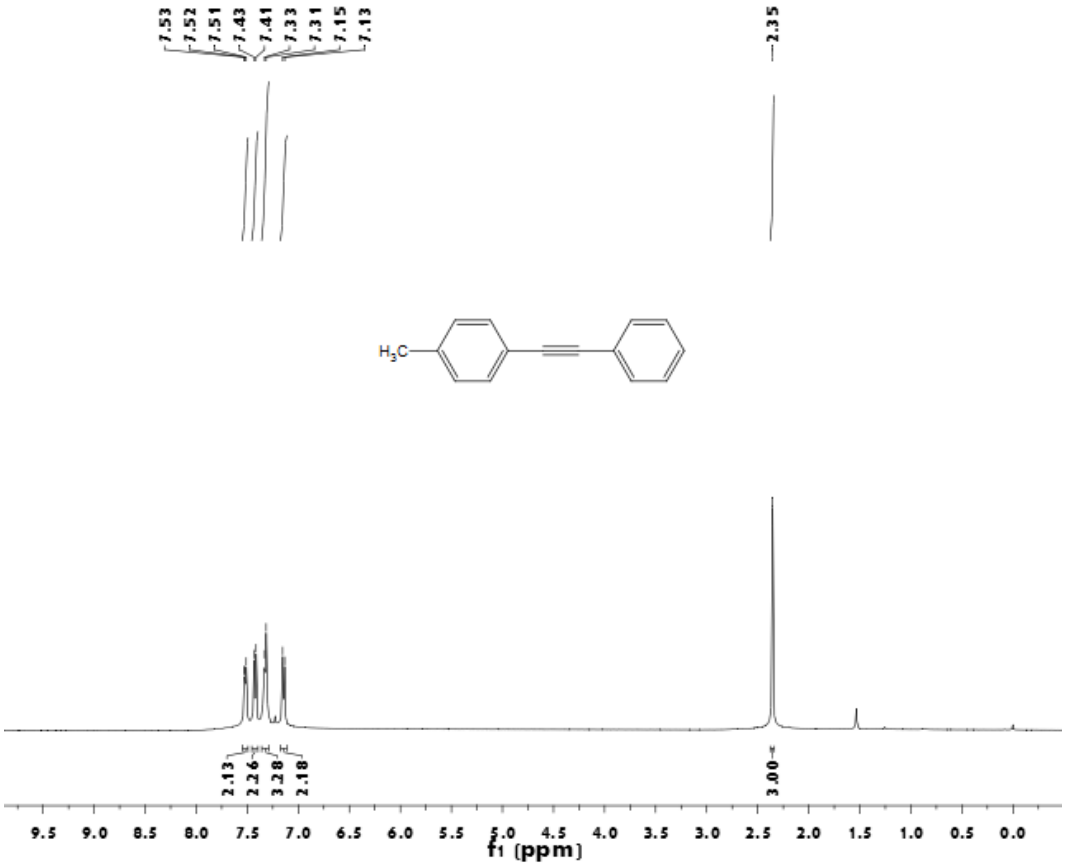
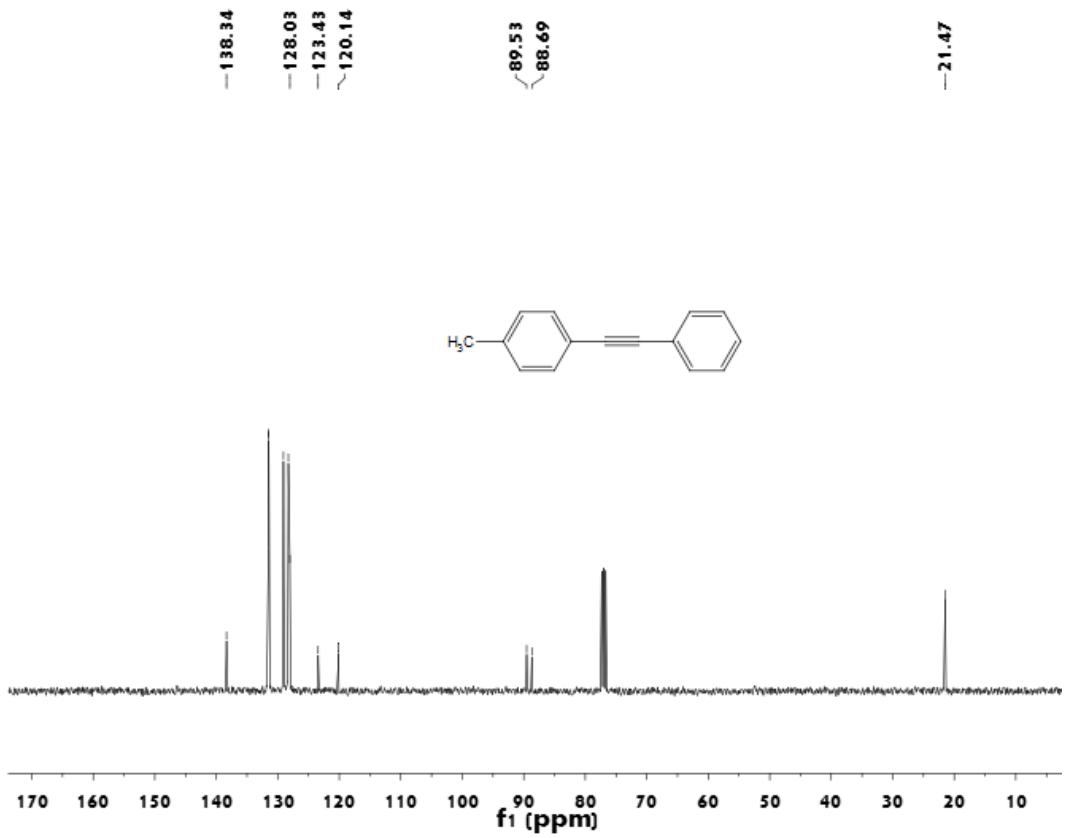
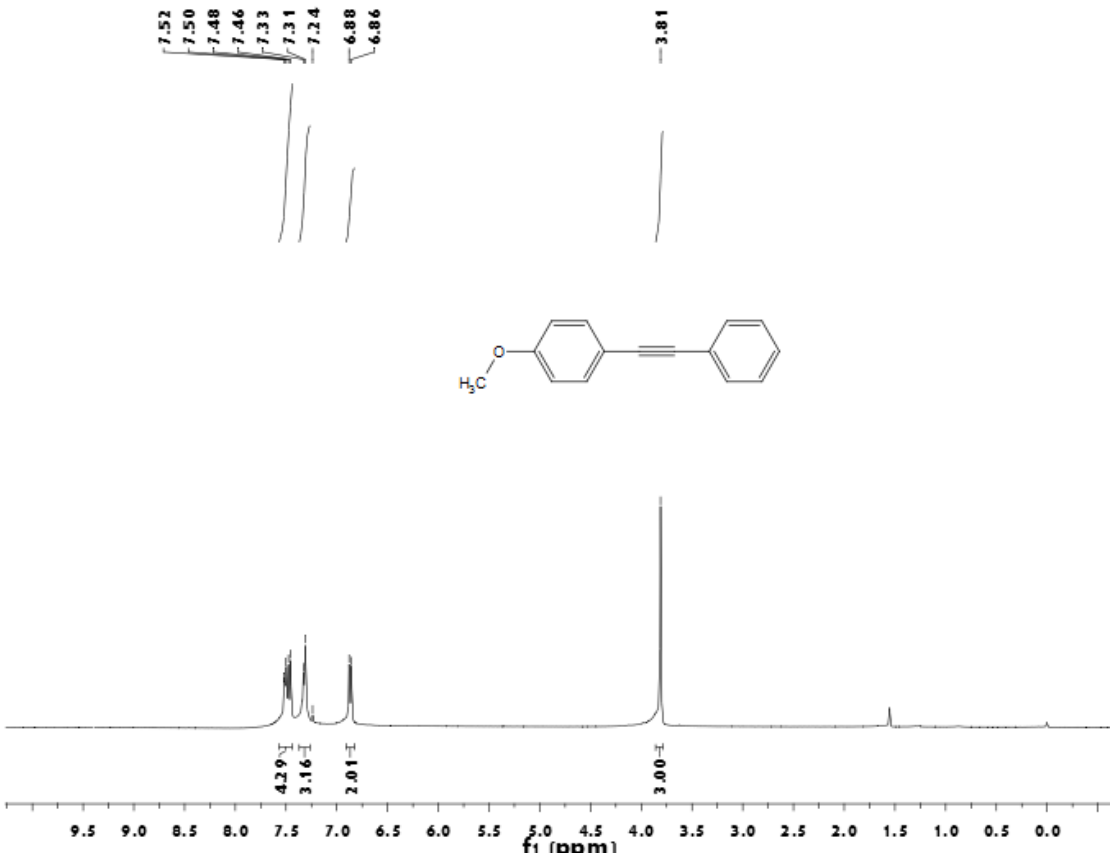
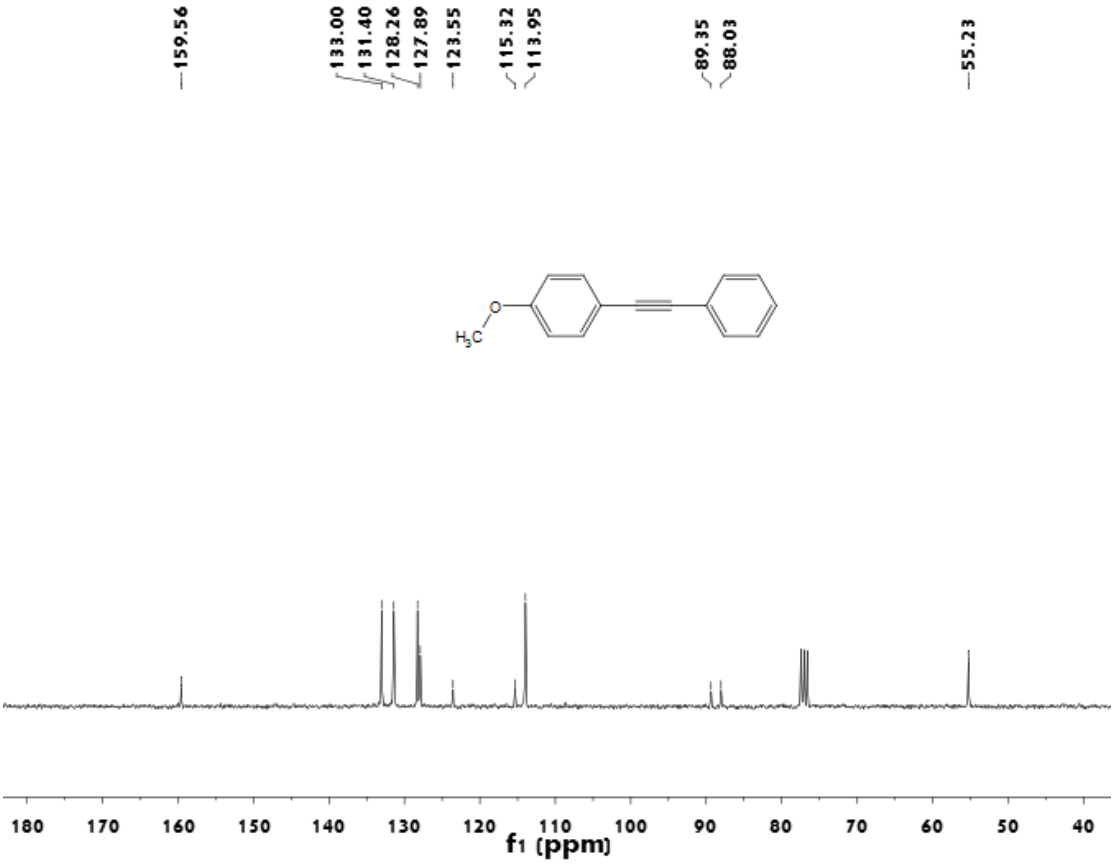
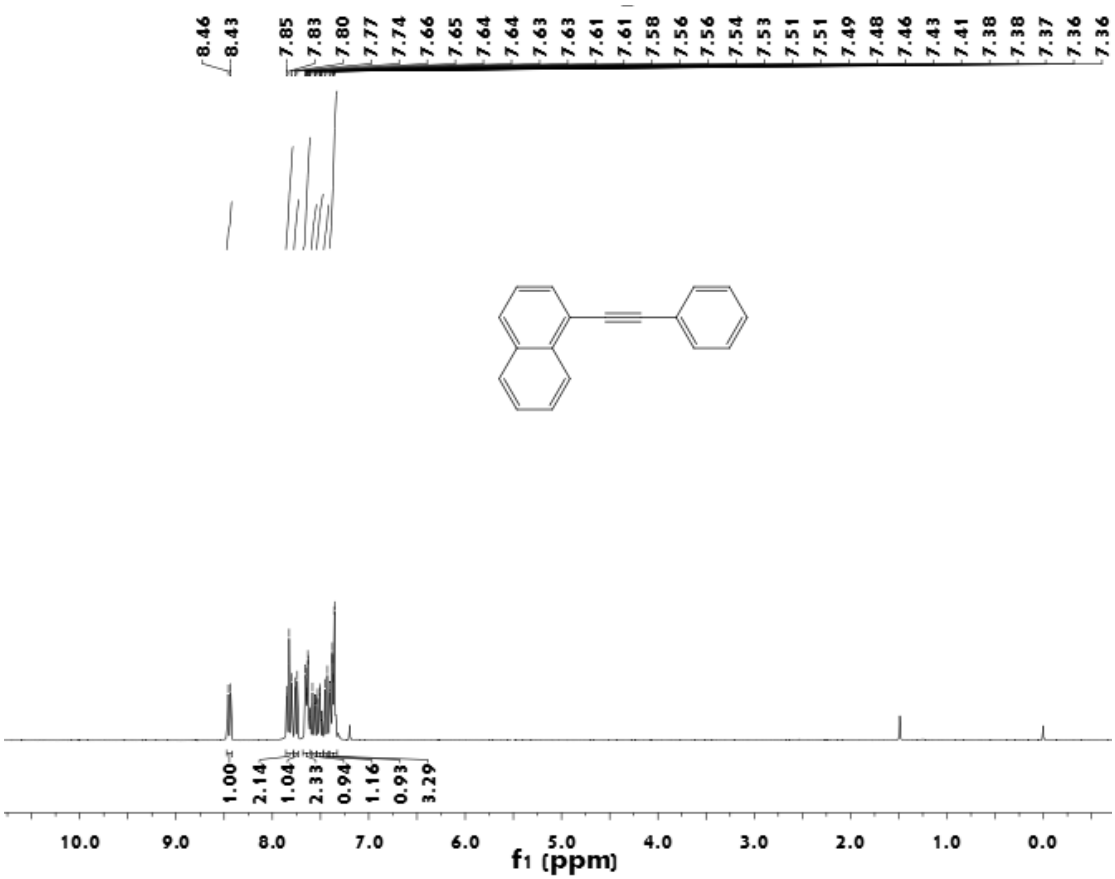
Copy of ^{1}H NMR and ^{13}C NMR Spectra for desired products:

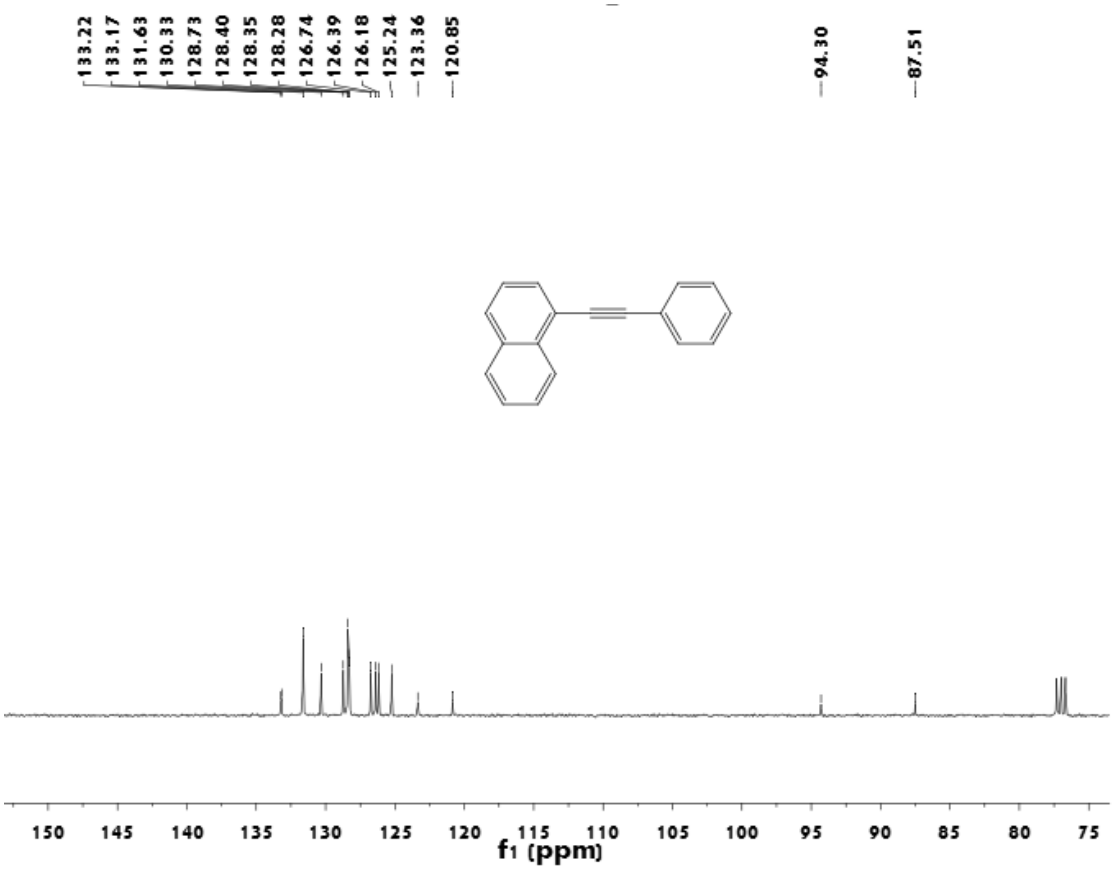


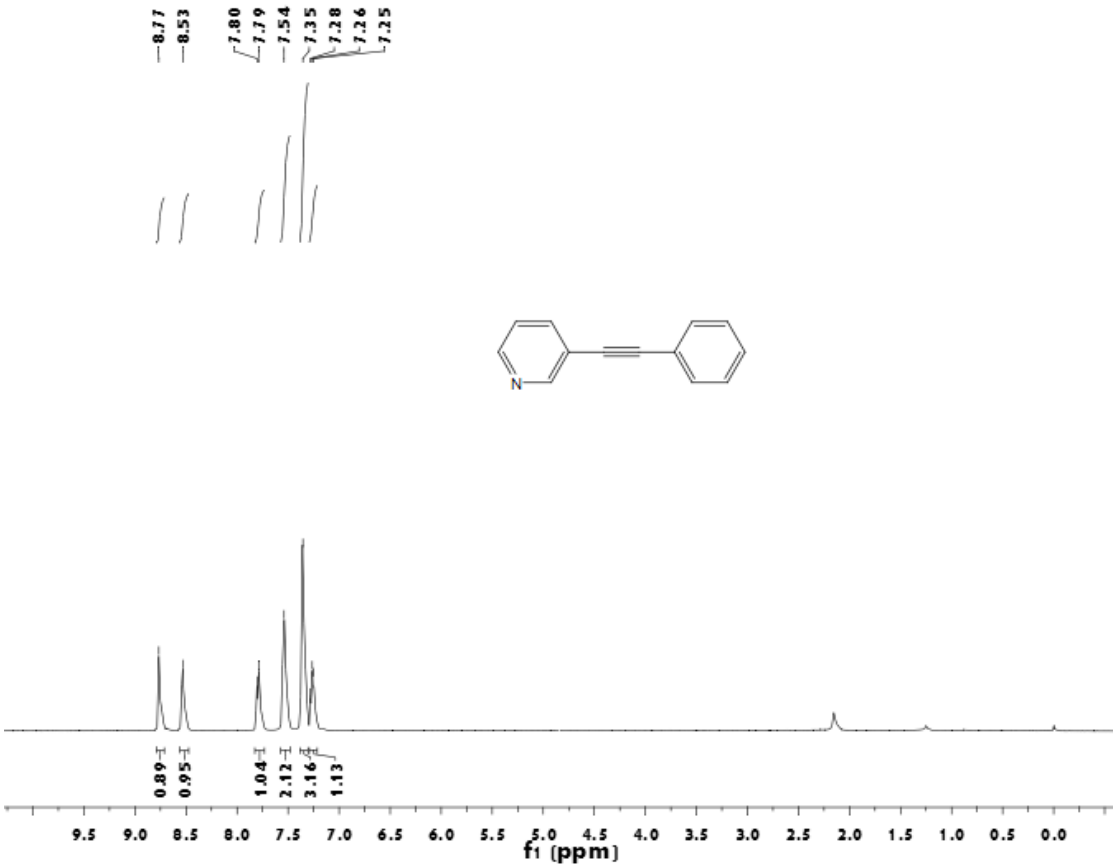


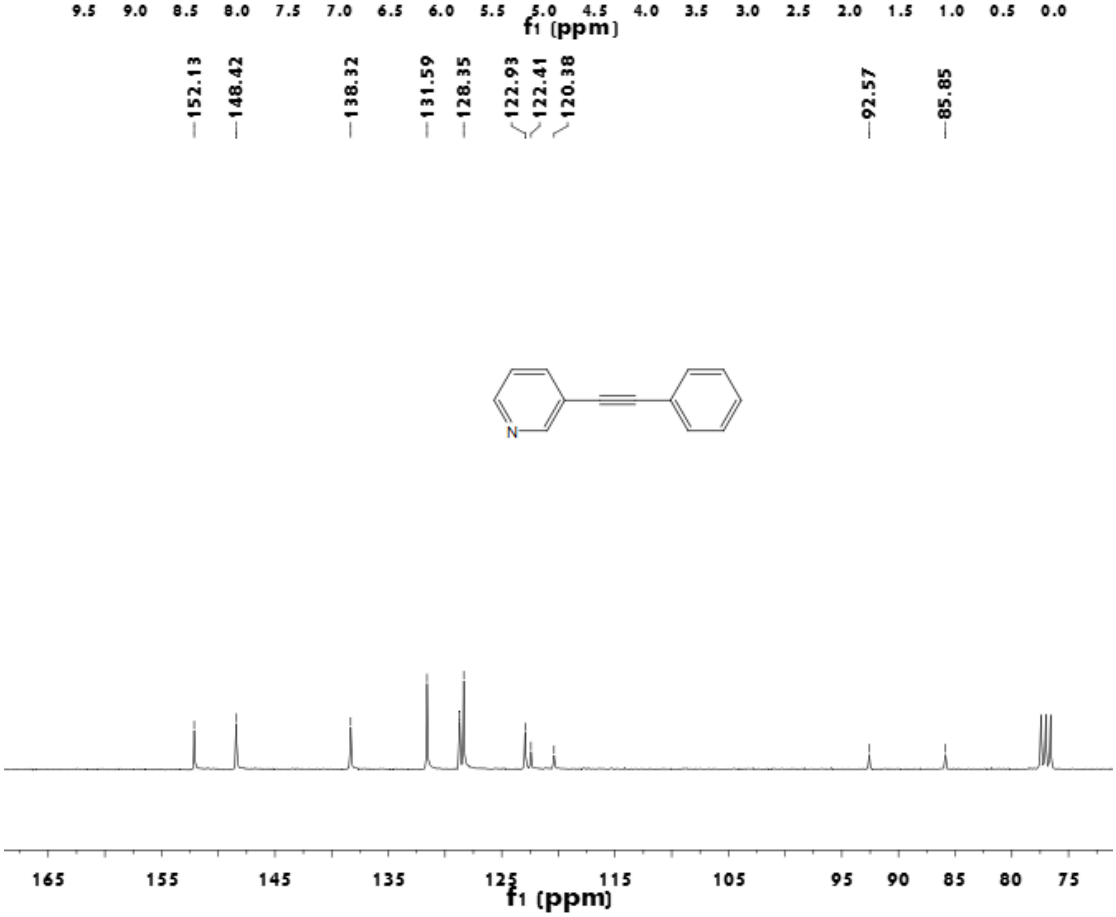


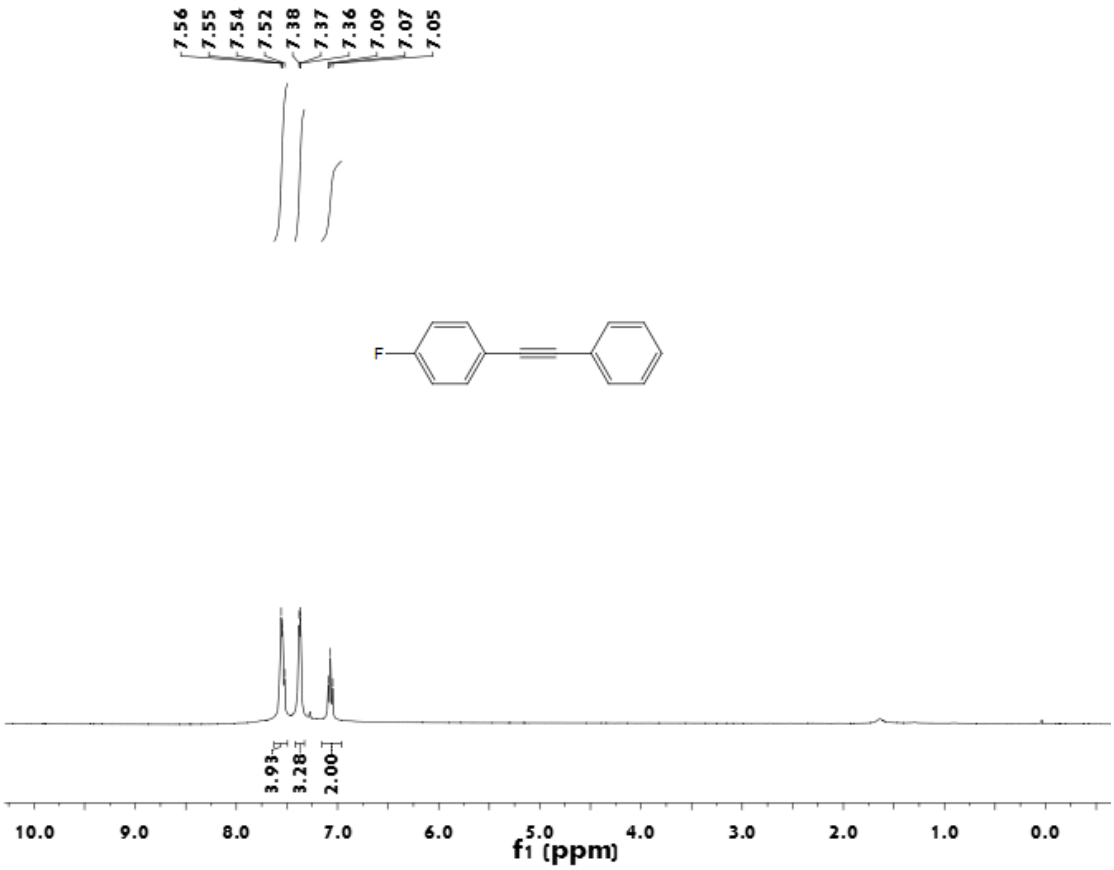


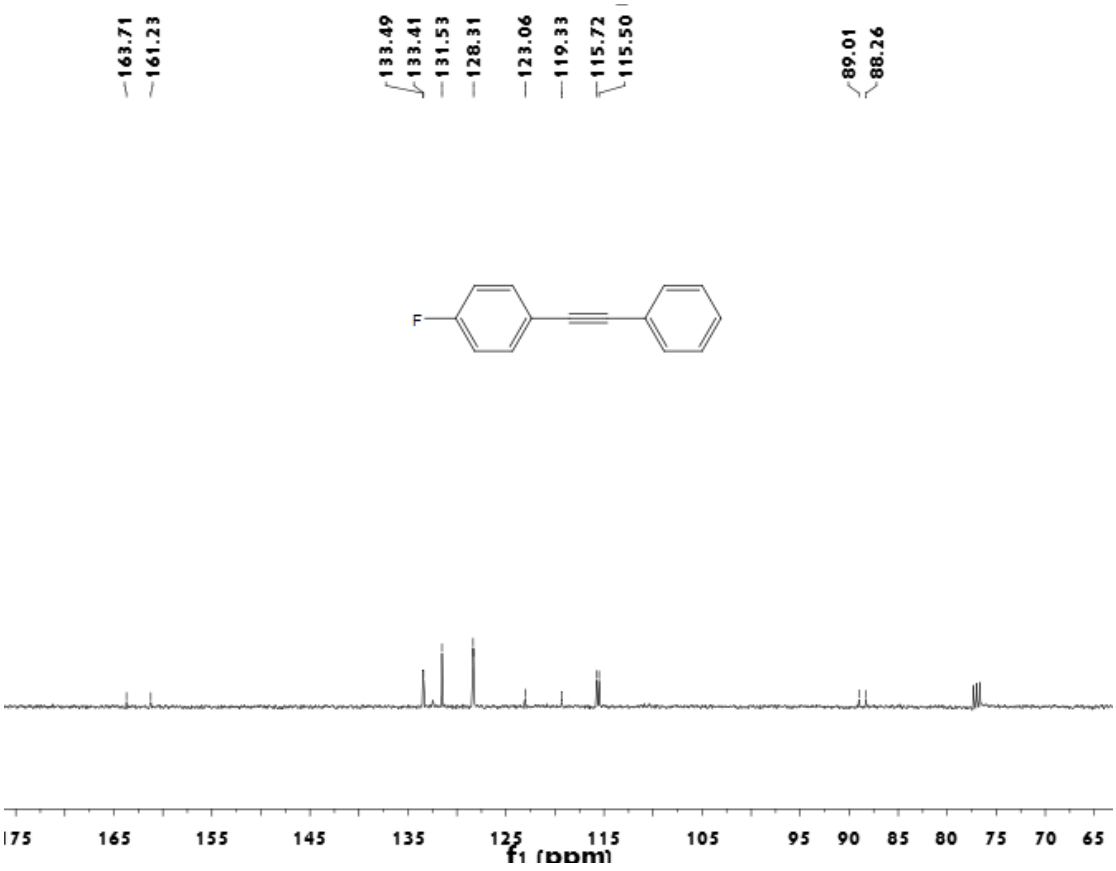


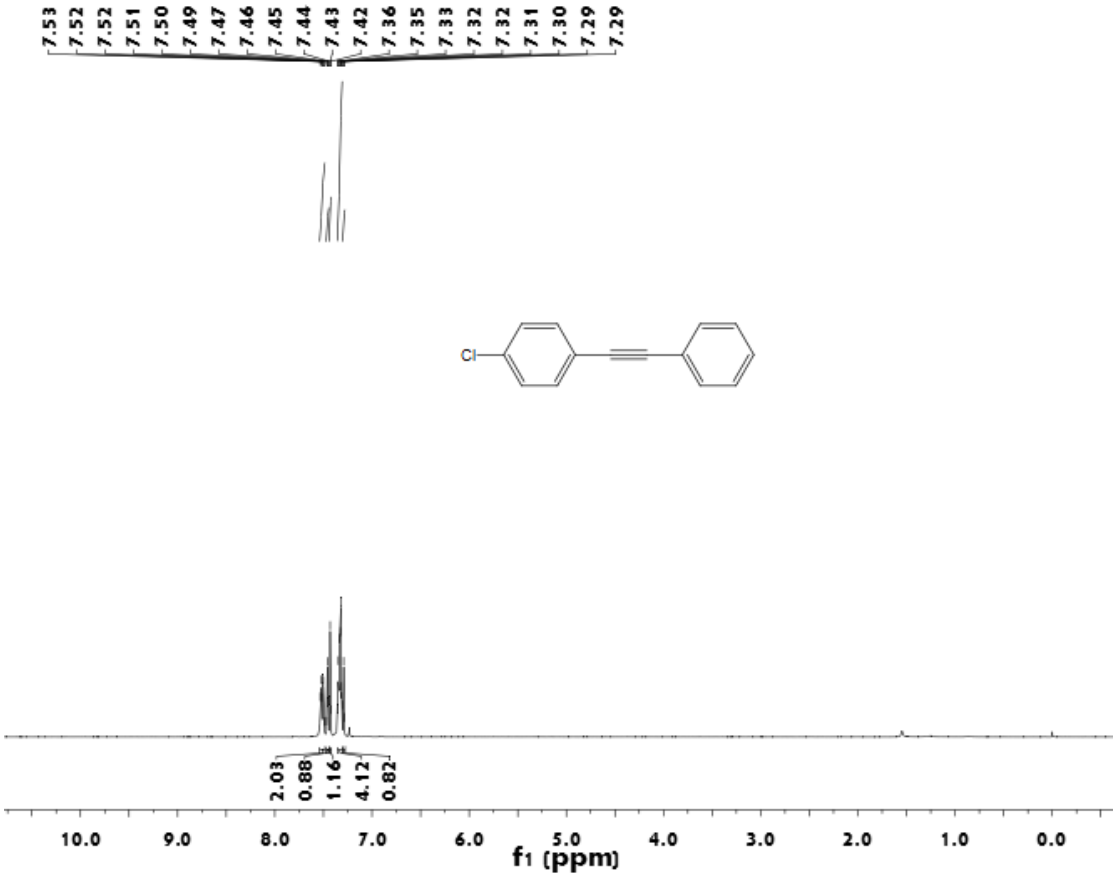


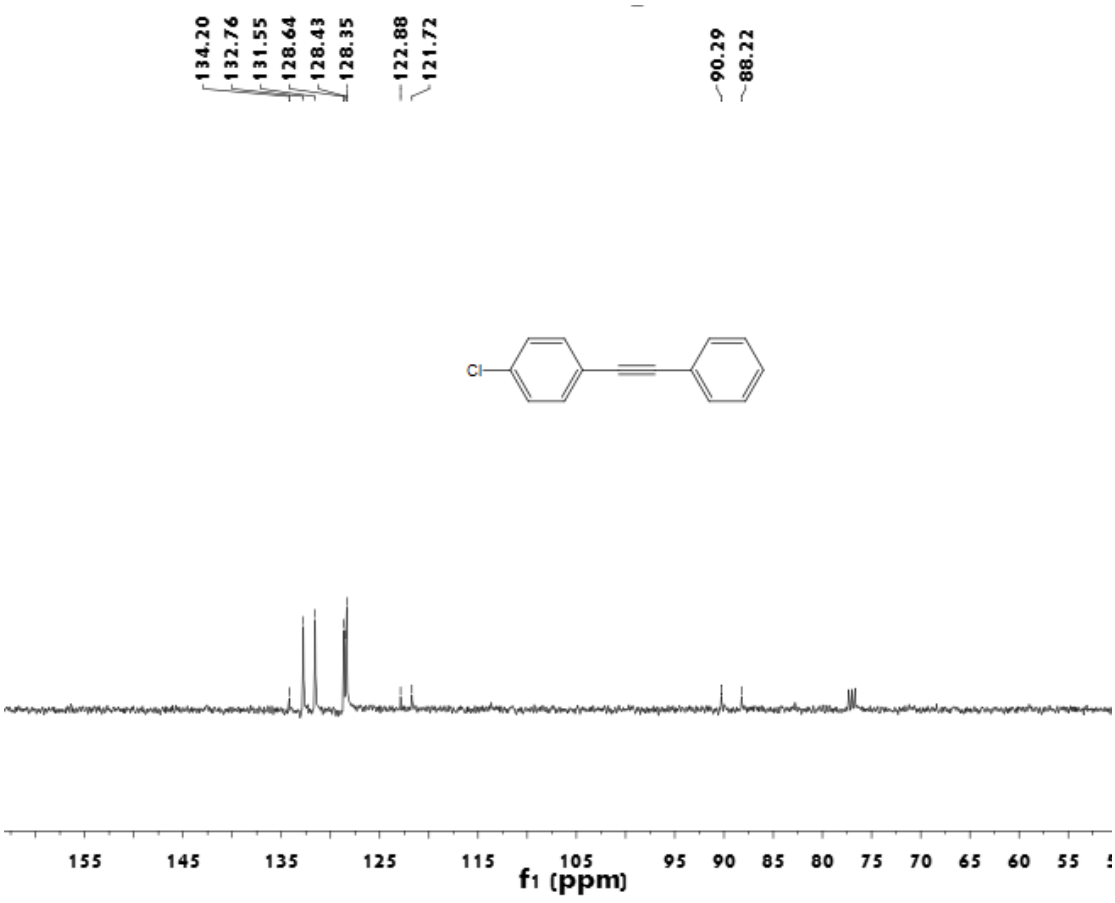


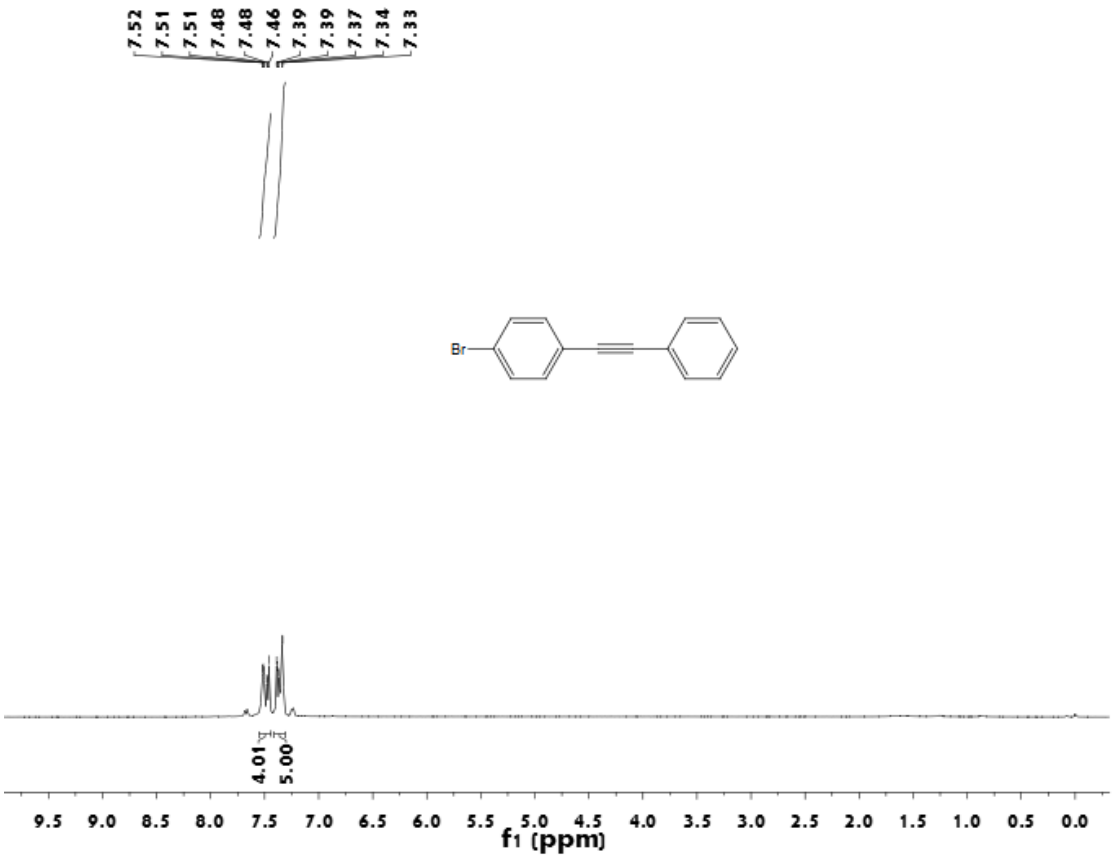


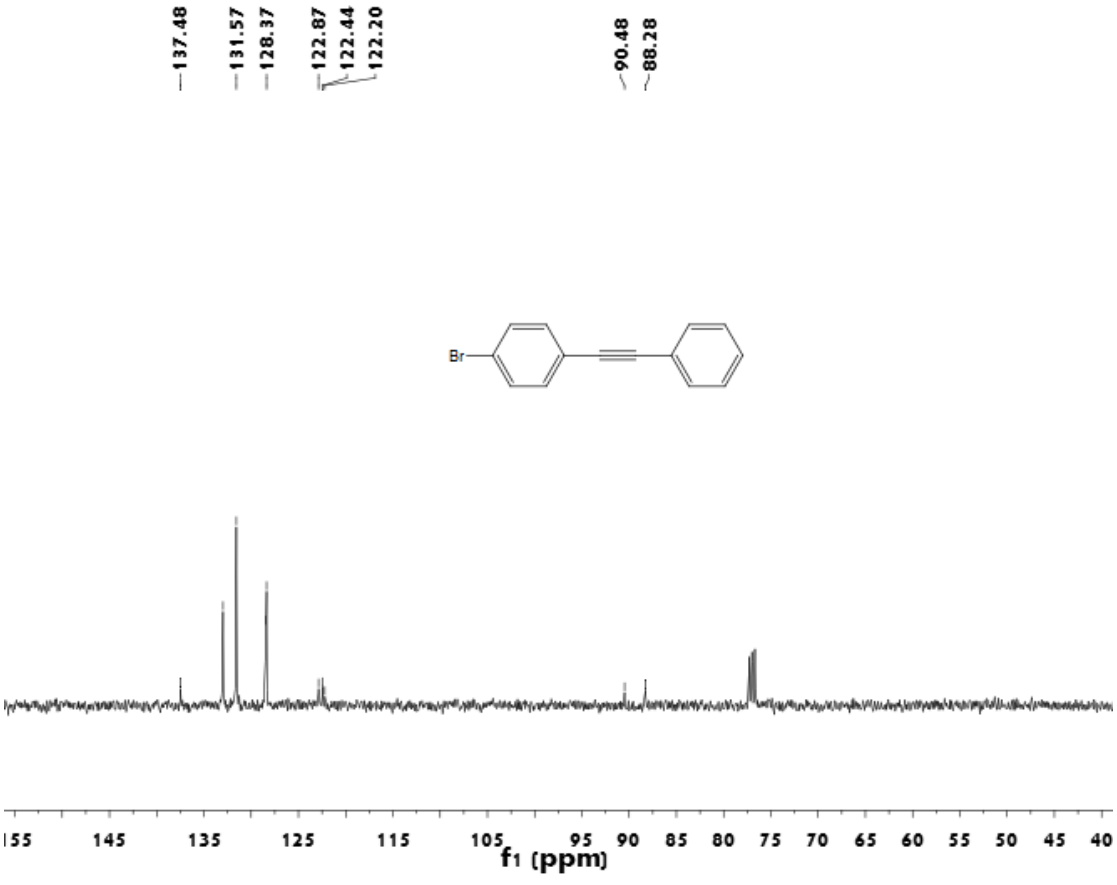


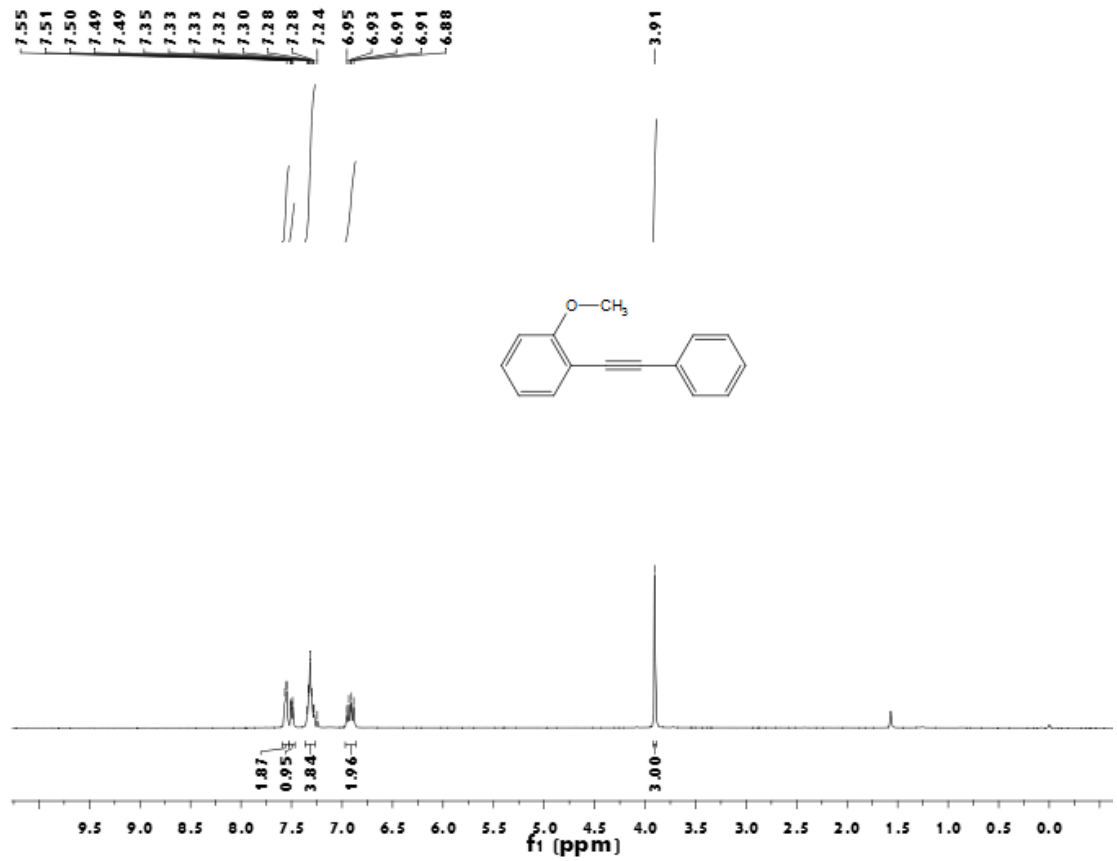


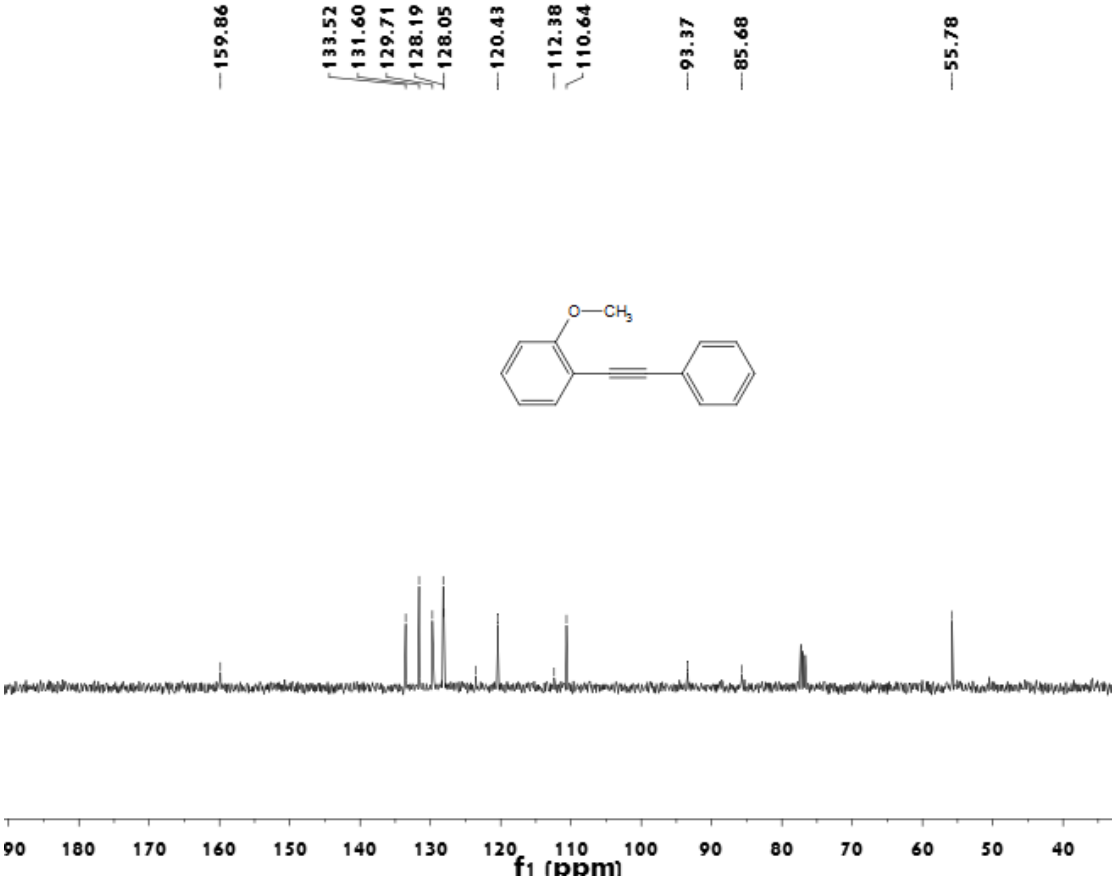


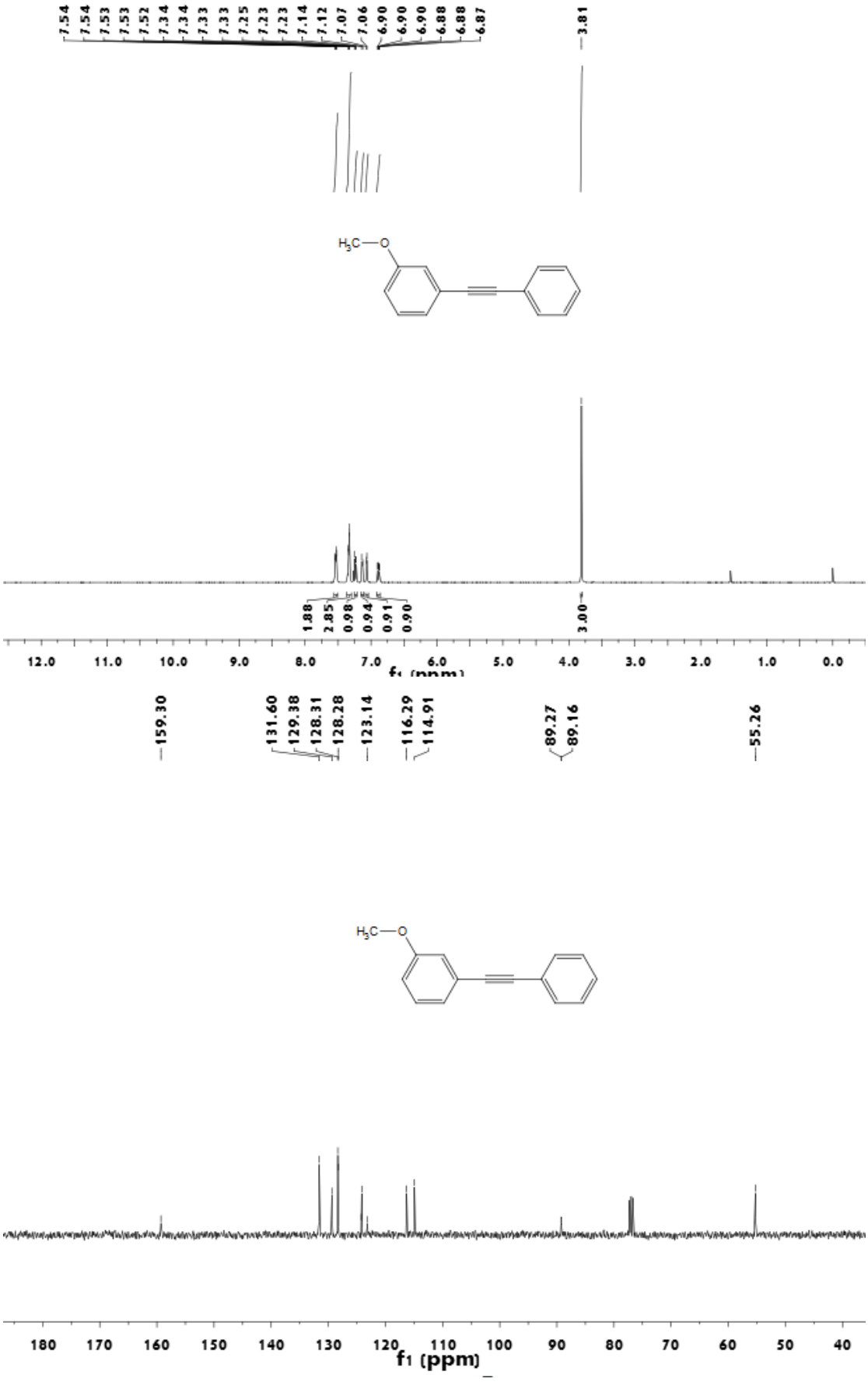


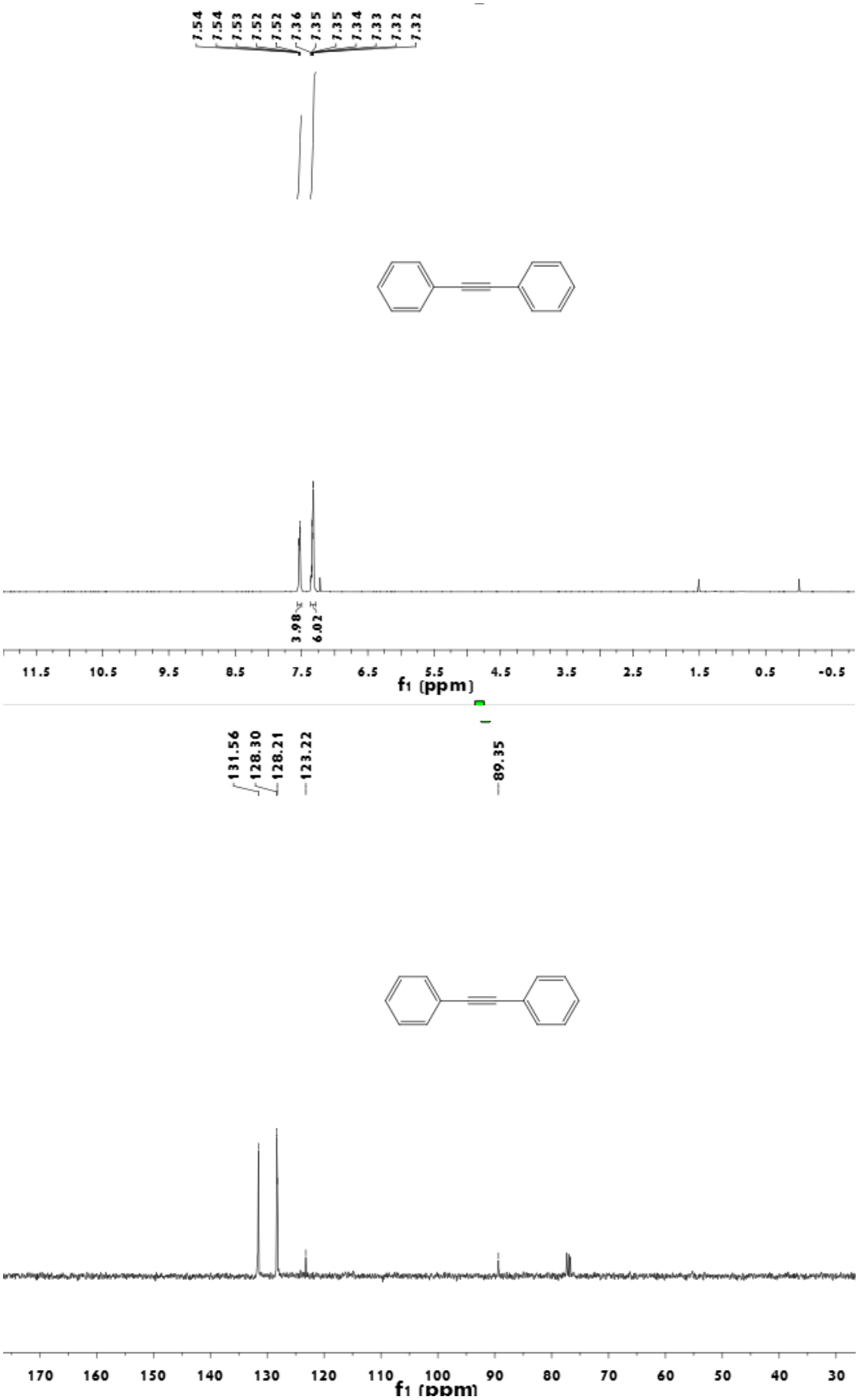








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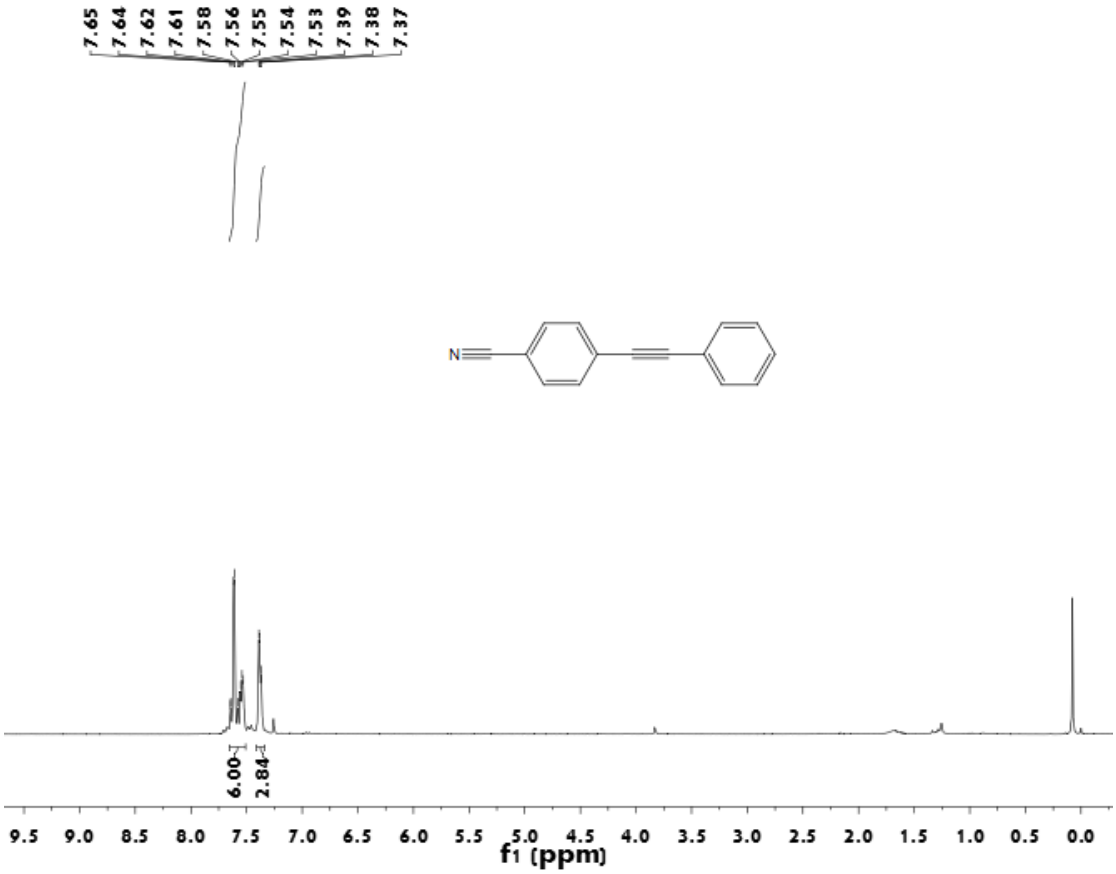

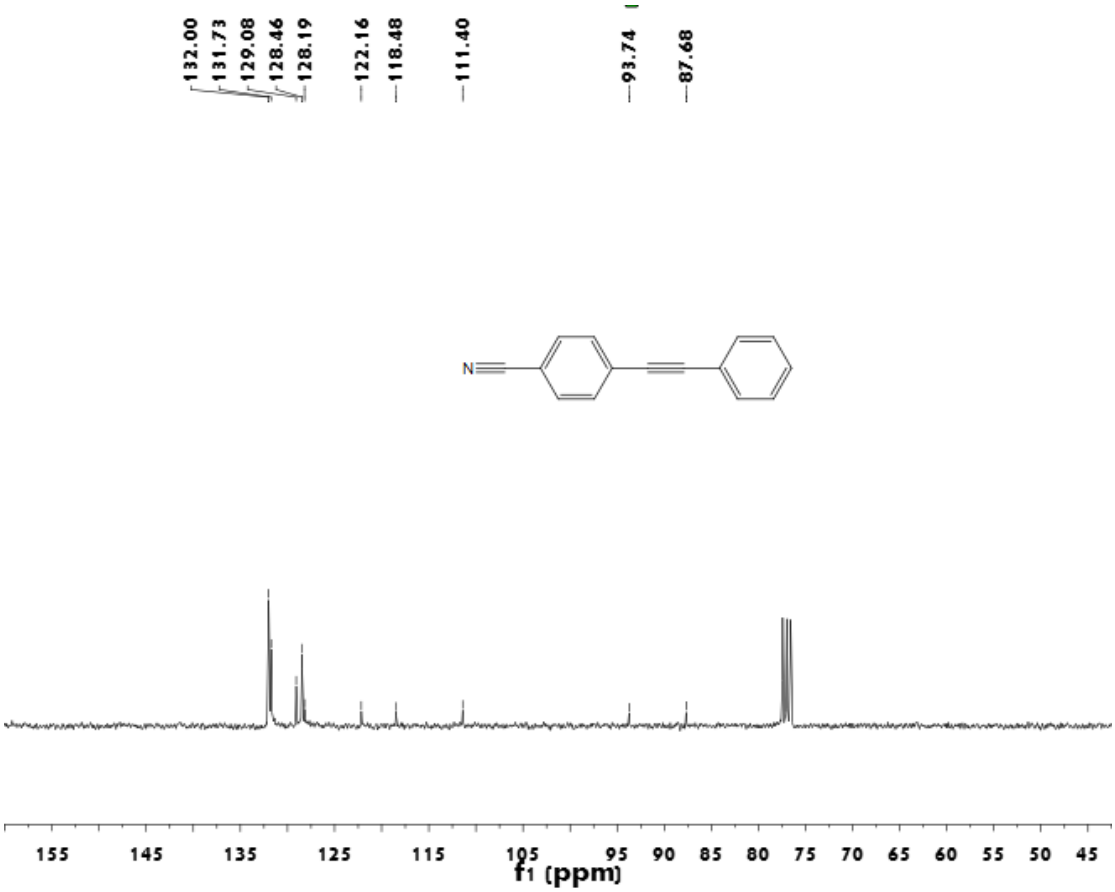

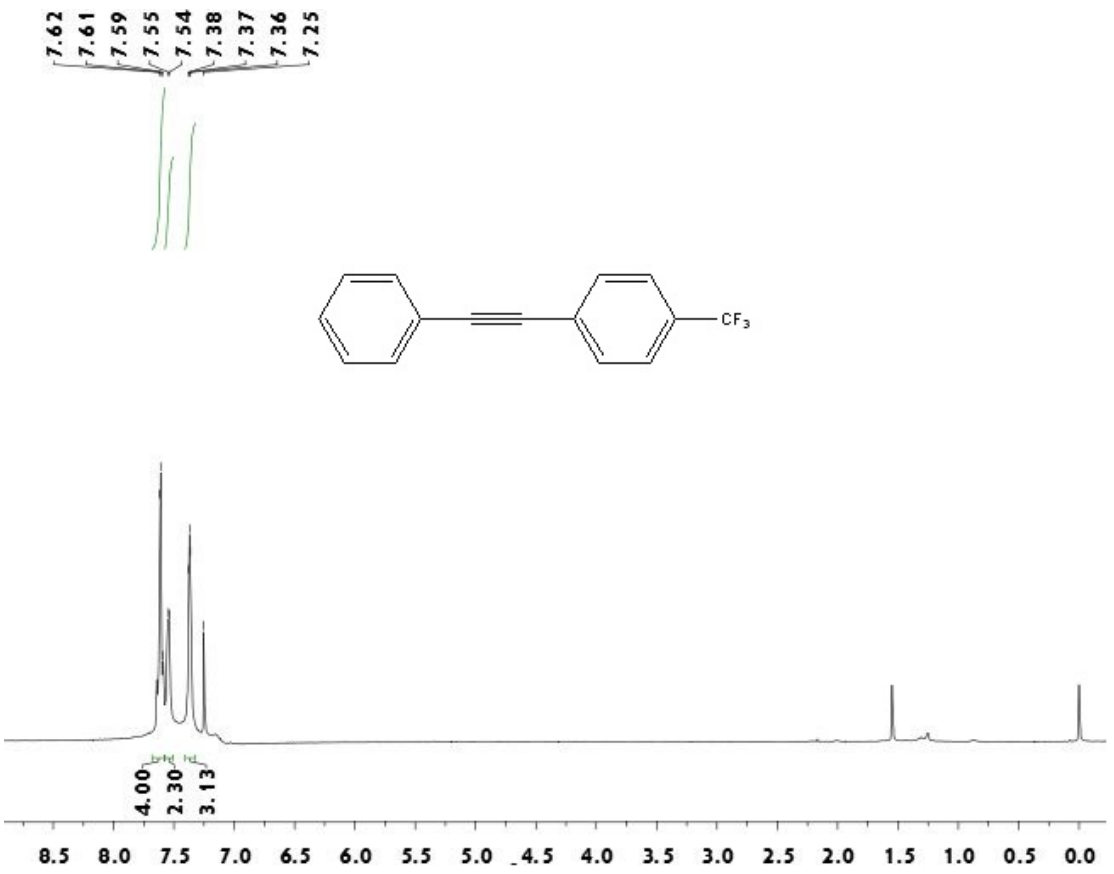

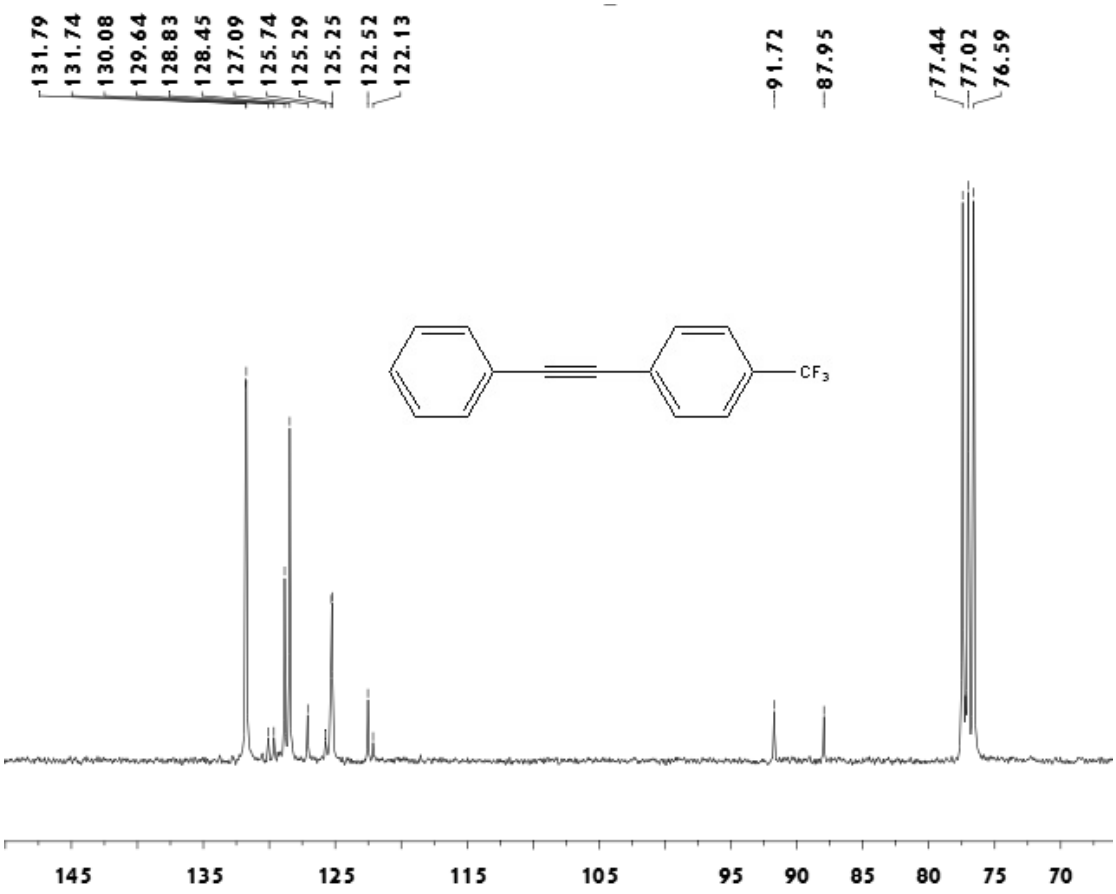

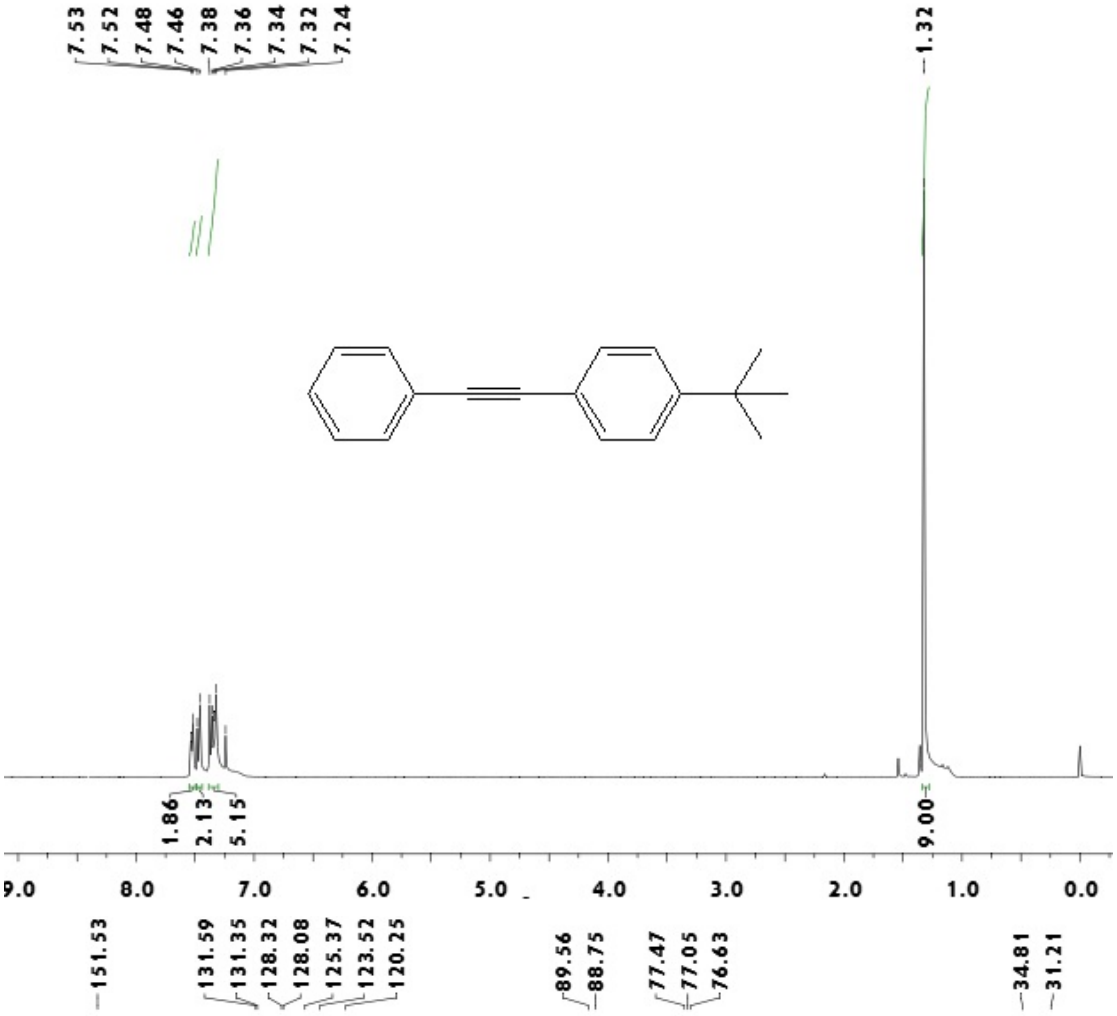

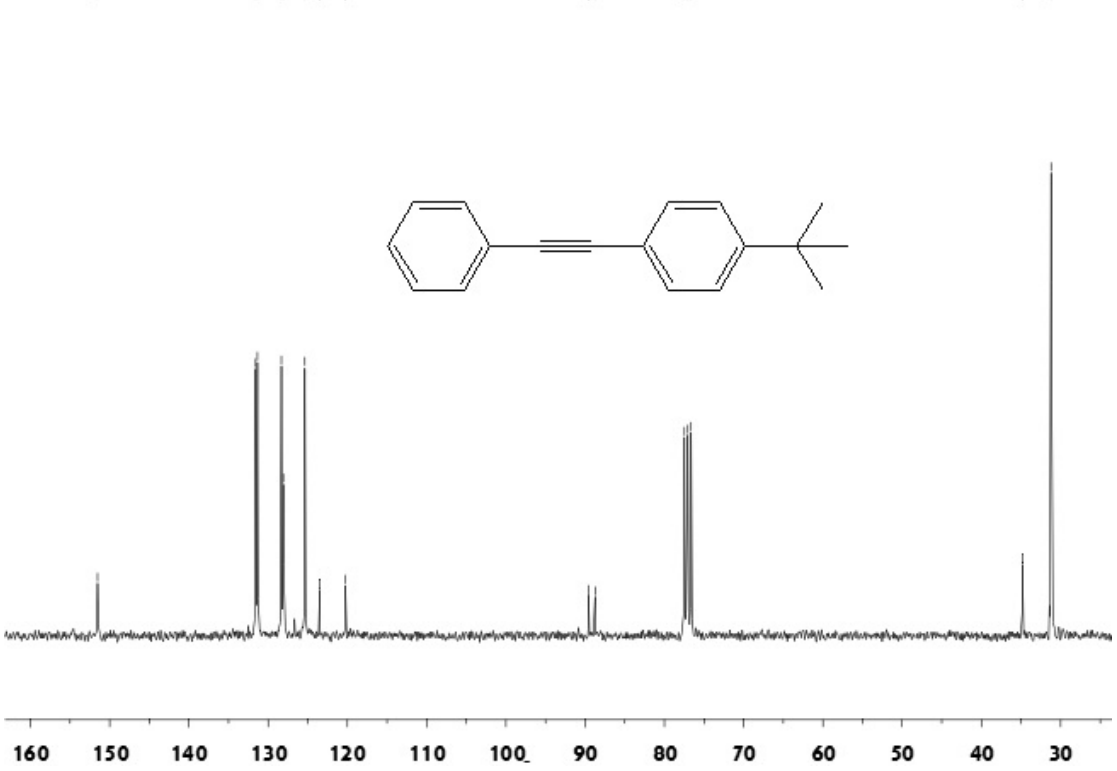

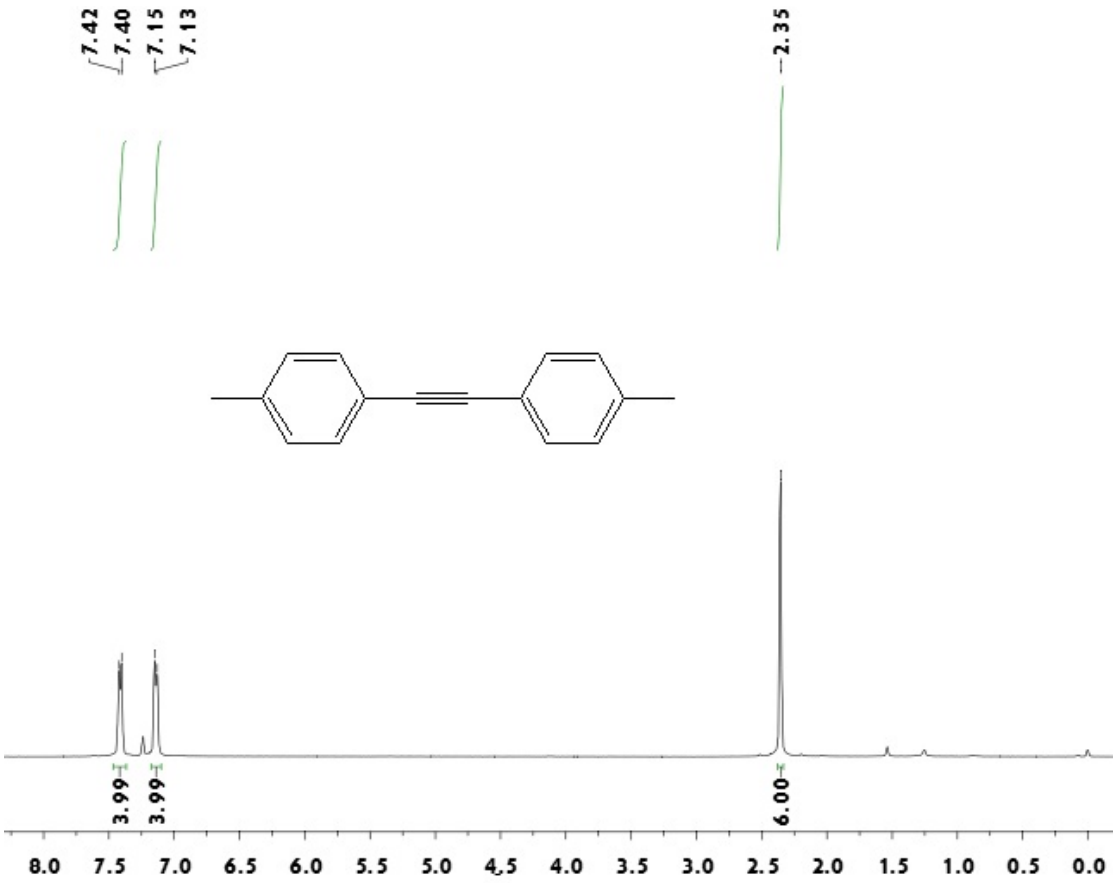

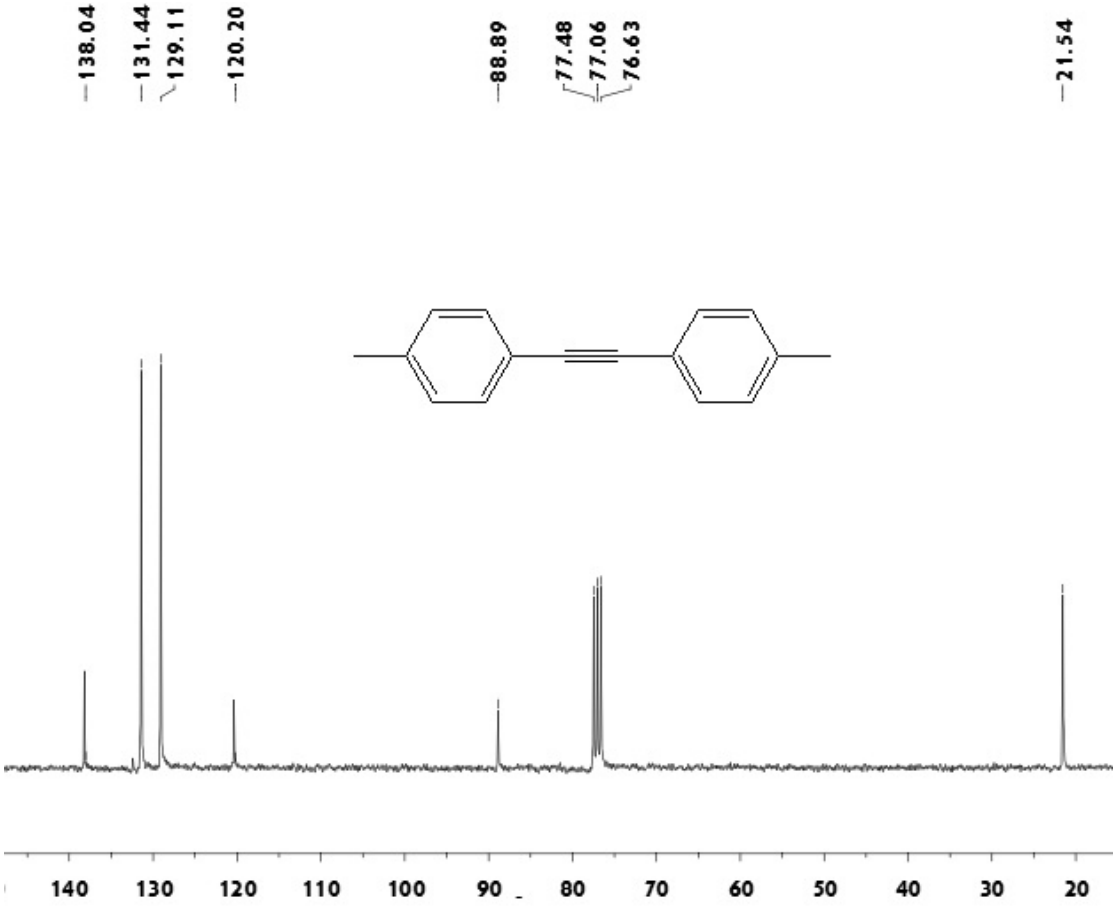

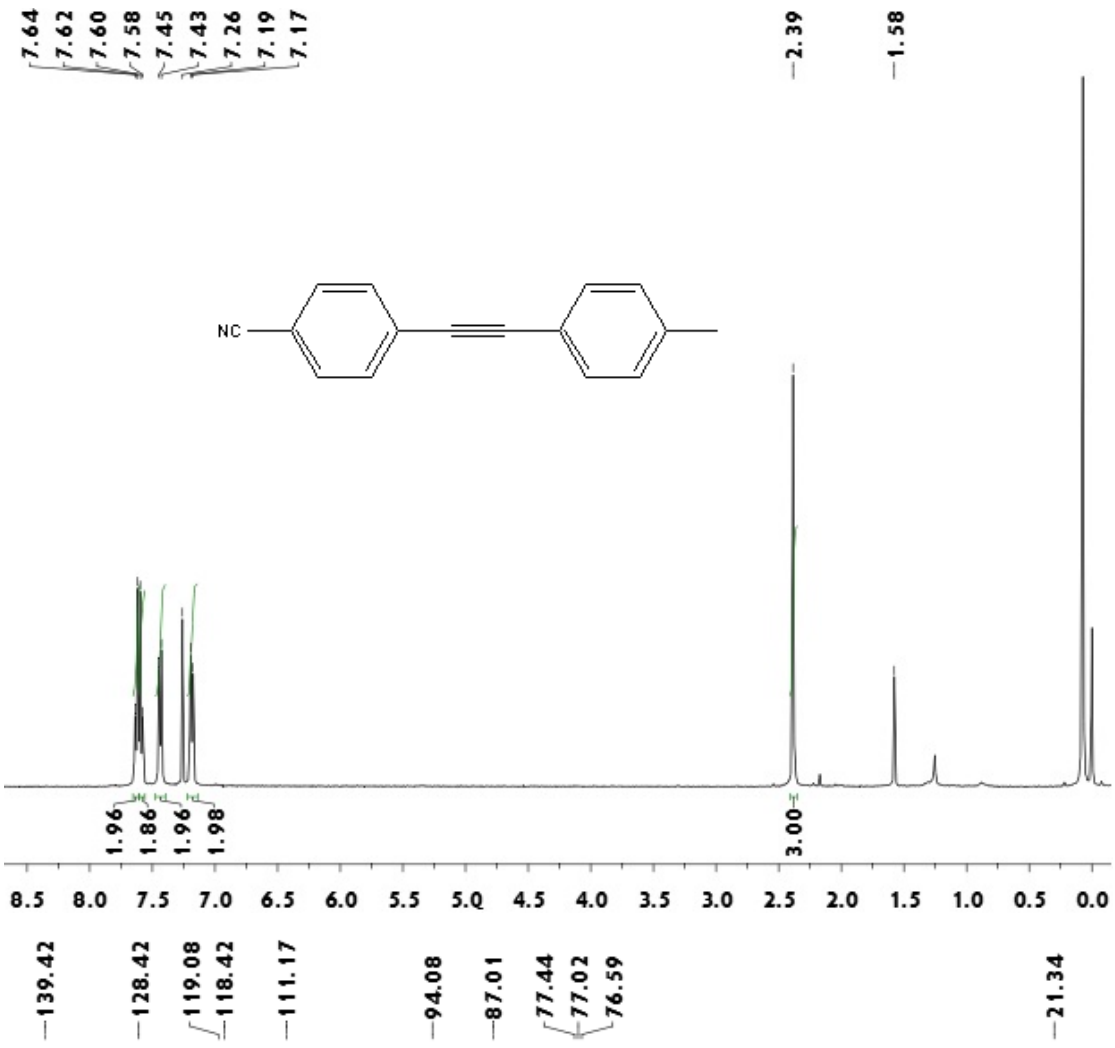

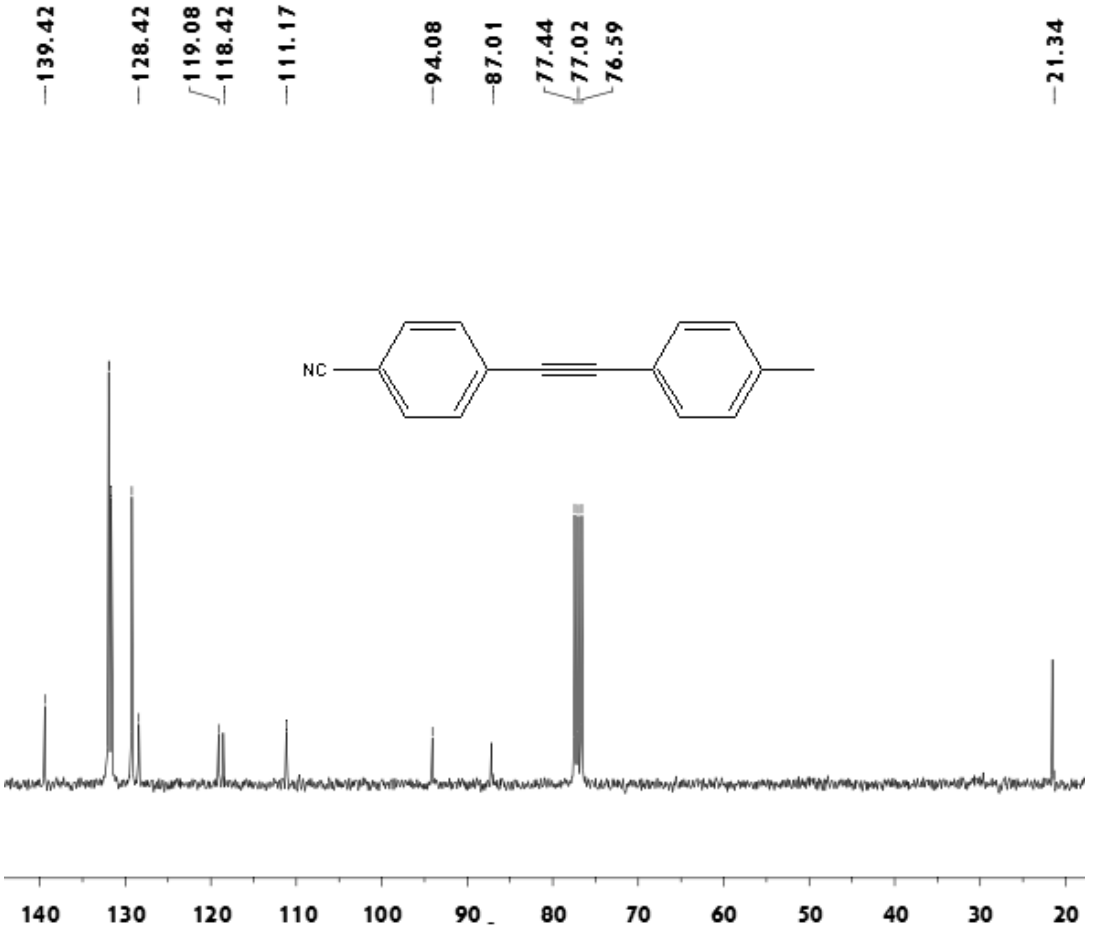

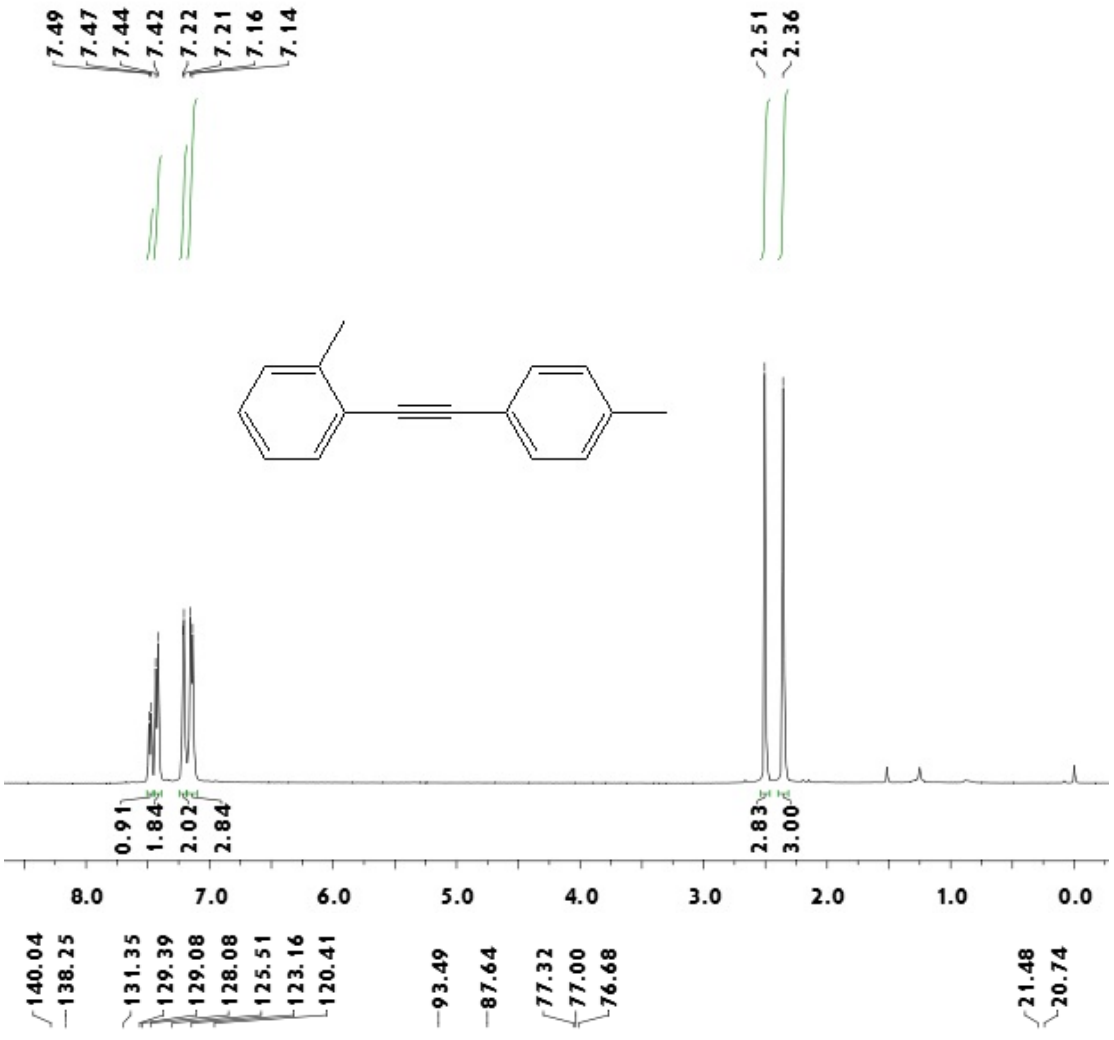

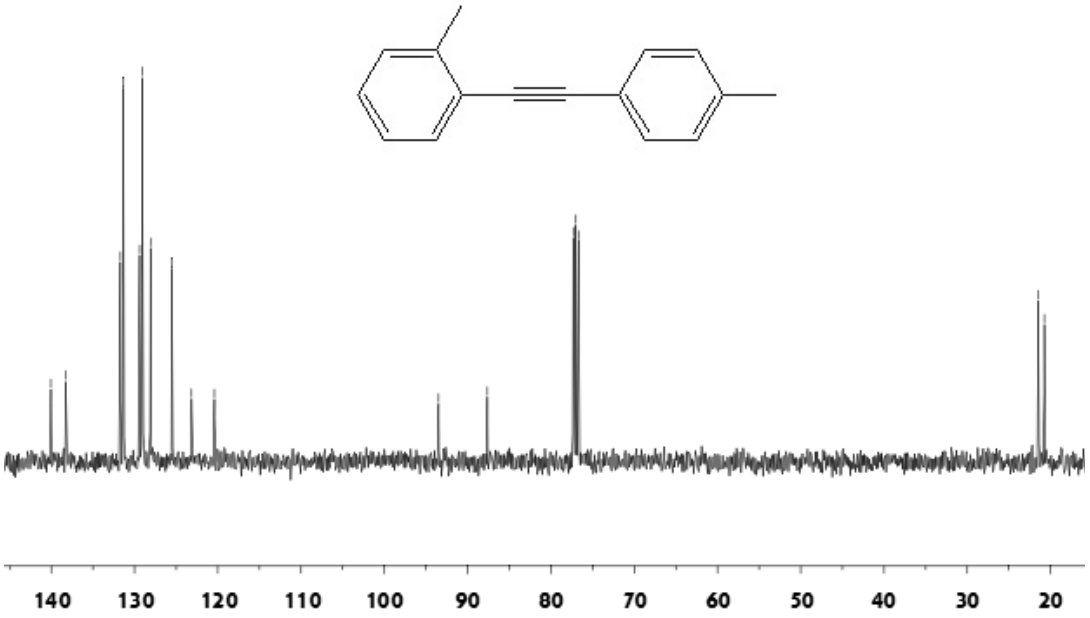

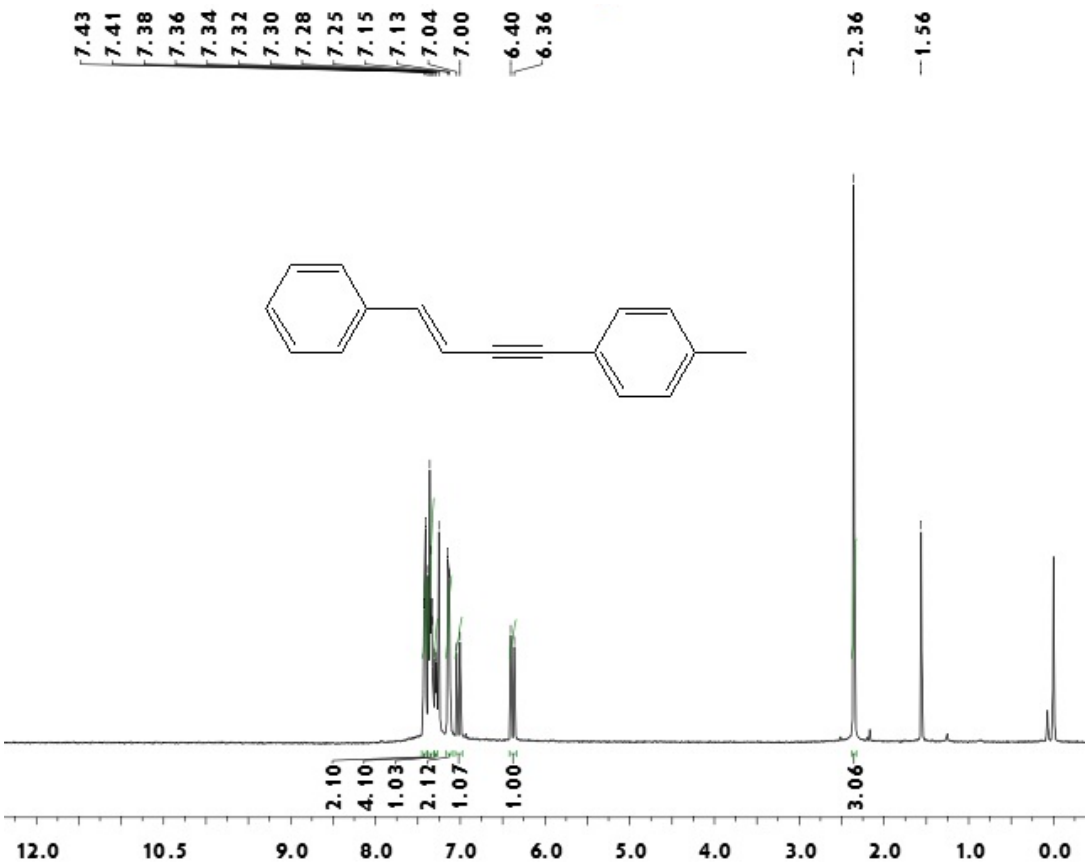

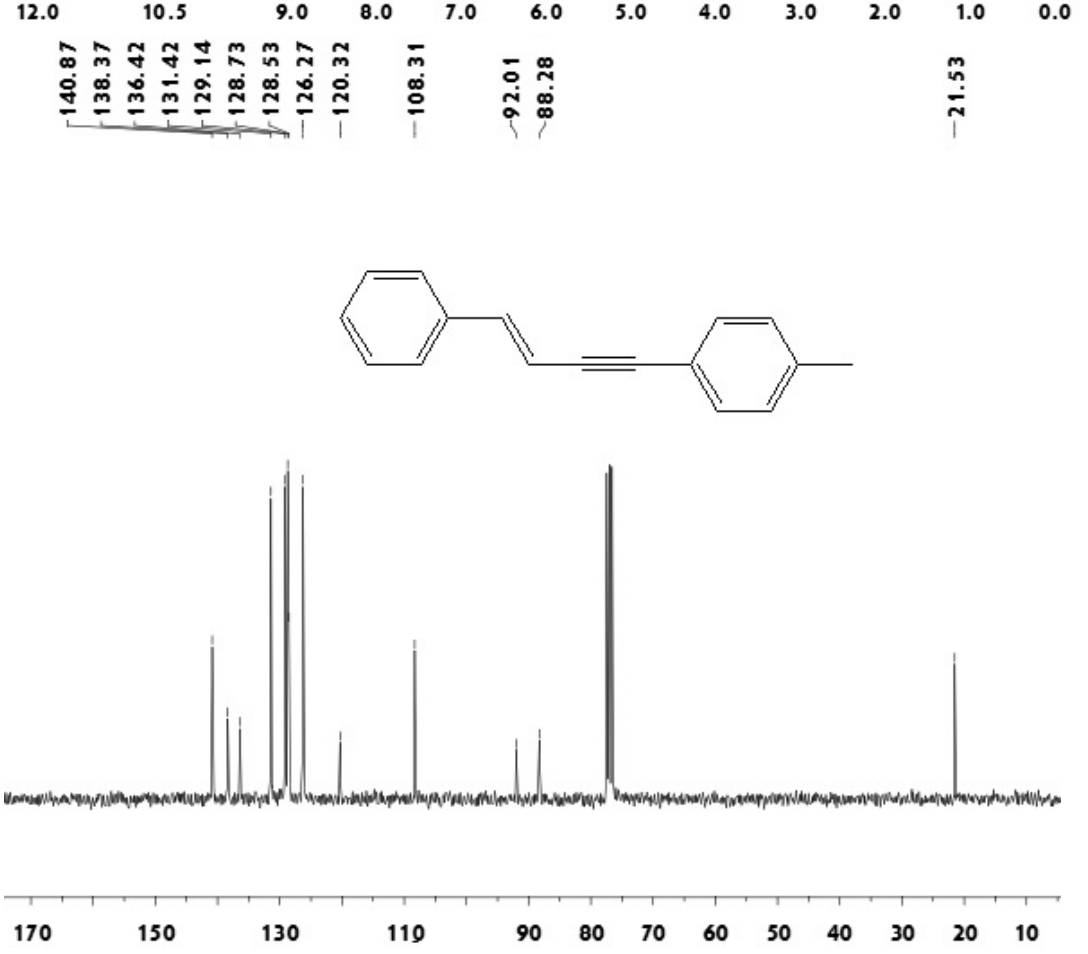

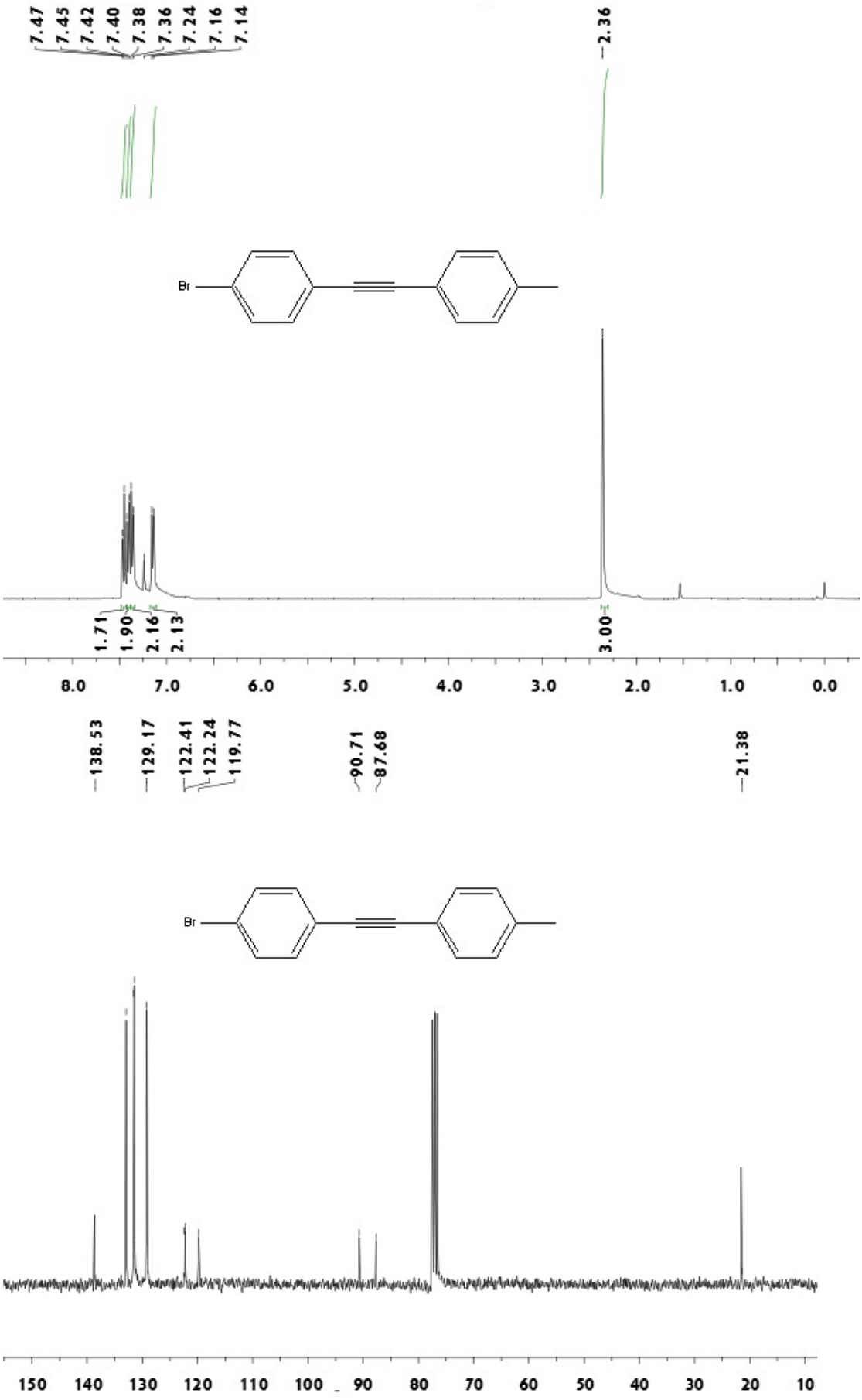

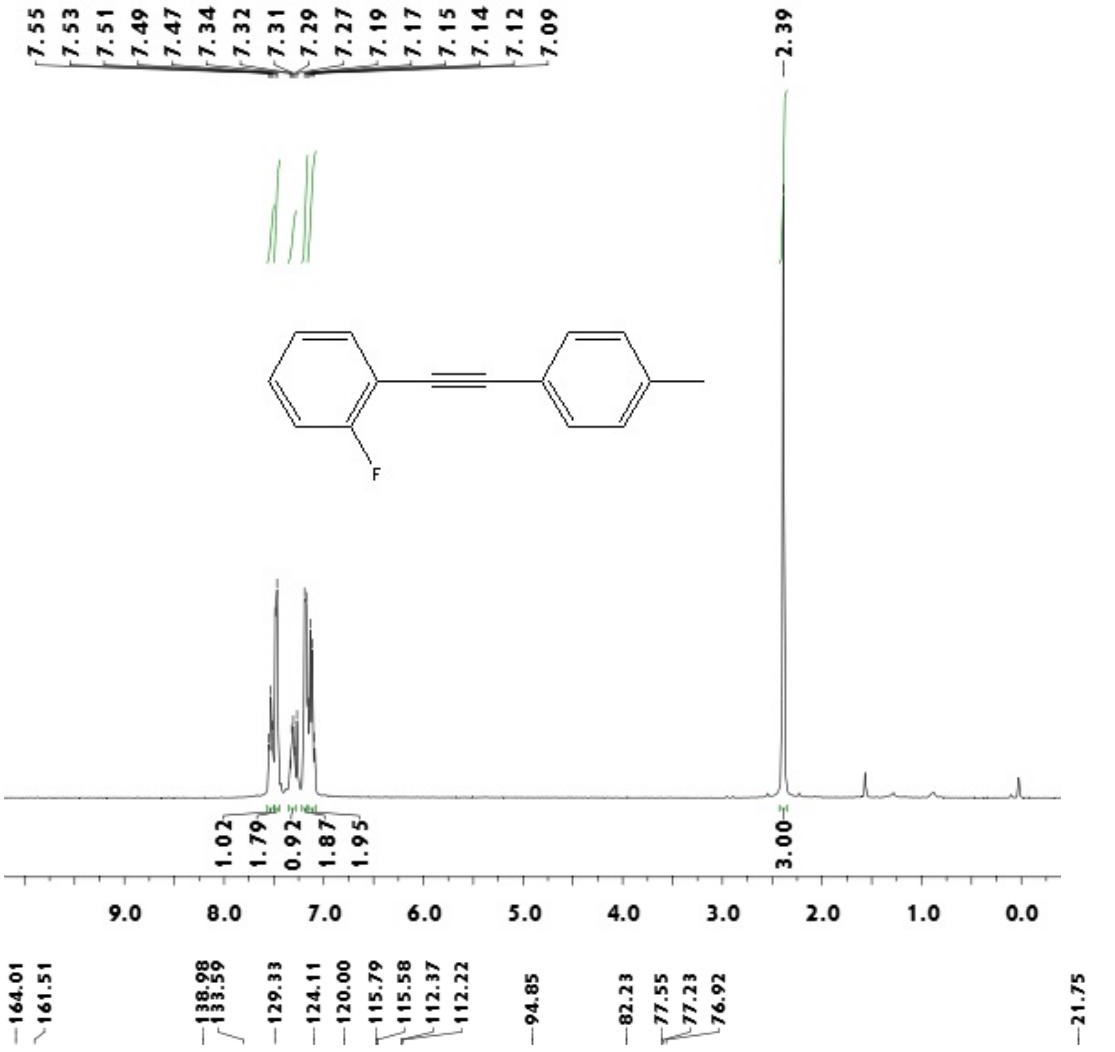
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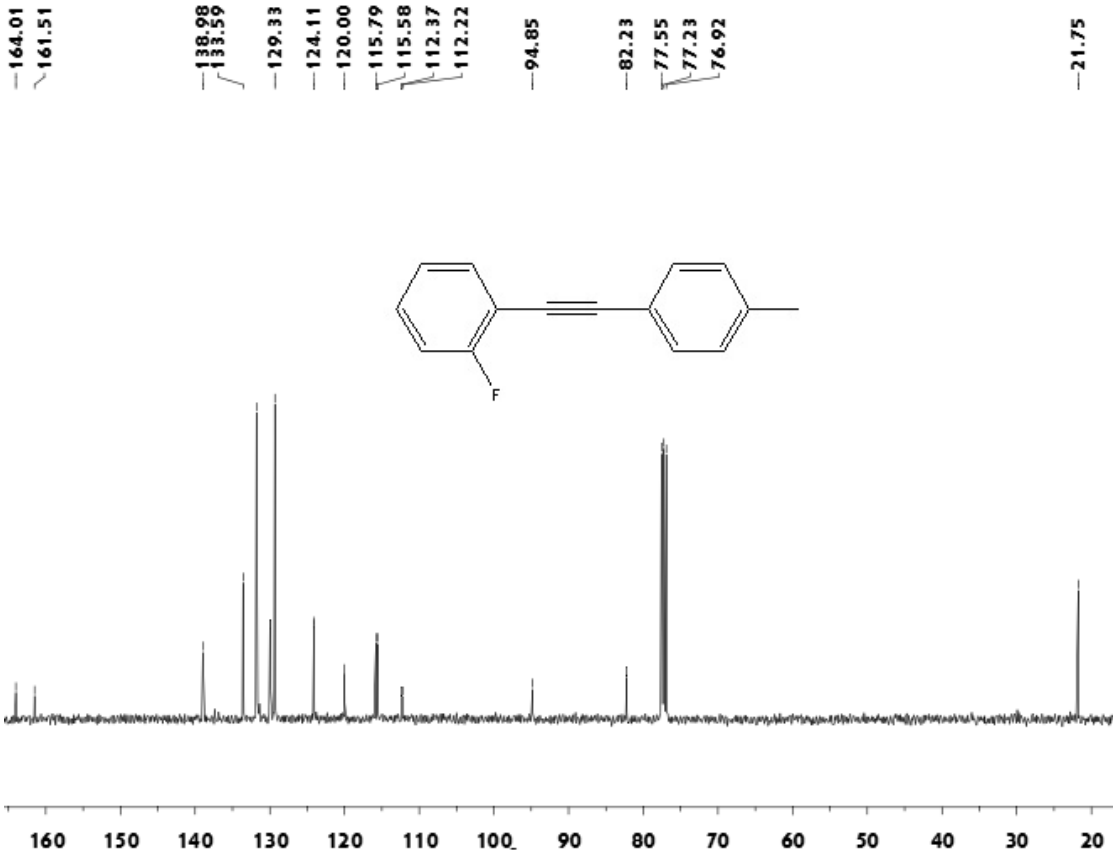
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