

## **Pd( NHC)PEPPSI- diazonium salts: An efficient blend for decarboxylative Sonogashira cross coupling reaction**

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Jeevan Manohar Bhojane<sup>a</sup>, Vilas Gangadhar Jadhav<sup>a</sup> and Jayashree Milind Nagarkar<sup>a\*</sup>

Department of Chemistry, Institute of Chemical Technology (Deemed University), Nathalal Parekh Marg, Matunga (E), Mumbai - 400 019, India; Email: [jm.nagarkar@ictmumbai.edu.in](mailto:jm.nagarkar@ictmumbai.edu.in); [jayashreenagarkar@yahoo.co.in](mailto:jayashreenagarkar@yahoo.co.in); Tel.: +91 22 33611111/2222; fax: +91 22 33611020.

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**General:** All chemicals were purchased from Loba chemi, Avra, S.D Fine Chemical, Spectrochem Ltd and used without further purifications. The progress of reaction was monitored by GC analysis performed on PerkinElmer Clarus 480. GC equipped with flame ionized detector with capillary column (Elite- 1701, 30m X 0.32 X 0.25). The GC-MS-QP 2010 instrument (Rtx-17, 30 m\_25 mm ID, film thickness 0.25  $\mu$ m, column flow: 2 mLmin<sup>-1</sup>, 80–240 °C at 10 °Cmin<sup>-1</sup> rise). <sup>1</sup>H NMR Spectroscopic data of compound were recorded on a Agilent- 400 spectrometer using CDCl<sub>3</sub> as a solvent and TMS as internal standard. The products were purified by column chromatography using (60-120 mesh) silica gel with pet ether and ethyl acetate (90:10) as eluent. All aryl diazonium salts and Pd(NHC) complexes were prepared by reported procedures<sup>[1–3]</sup>.

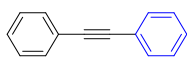
#### **General procedure for Unsymmetrical Sonogashira cross coupling reaction**

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged phenyl propylic acid (1 mmol), arenediazonium salt (1.2 mmol), Cat. C (5mol%), K<sub>2</sub>CO<sub>3</sub> (3 mmol) and TBAI (1.4 mmol) followed by anhydrous DMSO (2 mL). Reaction mixture was heated in an oil bath at 120°C and was stirred for 12 h. The reaction was monitored by GC and TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and the reaction mass was diluted with ethyl acetate and filtered through plug of celite. The resulting filtrate was washed with HCl(1N) and 20% brine solutions. The organic layer was separated and dried over anhydrous sodium sulphate. The solvent was removed under vacuum to get the crude product, which was purified by column chromatography on silica gel eluting with the mixture of pet ether / EtOAc (90:10) mixture to afford the pure product. The purity and identity of known products are conformed by <sup>1</sup>H NMR and GC-MS Spectroscopic techniques.

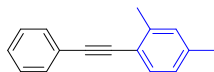
#### **General procedure for Symmetrical Sonogashira cross coupling reaction**

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged propylic acid (1.0mmol), arenediazonium salt (2.2 mmol), Cat. C3(5mol%), DBU (3 mmol) and TBAI (2.4 mmol) followed by anhydrous DMSO (2 mL). Reaction mixture was heated in an oil bath at 90°C and was stirred for 12 h. The reaction was monitored by GC and TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and the reaction mass was diluted with ethyl acetate and filtered through plug of celite. The resulting filtrate was washed with HCl(1N) and 20% brine solutions. The organic layer was separated and dried over anhydrous sodium sulphate. The solvent was removed under vacuum to get the crude product, which was purified by column chromatography on silica gel eluting with the mixture of pet ether / EtOAc (90:10) mixture to afford the pure product. The purity and identity of known products are conformed by <sup>1</sup>H NMR and GC-MS Spectroscopic techniques.

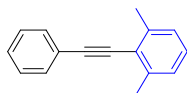
## Selected spectral data



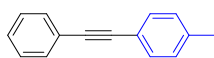
1. **Diphenylethyne (3a)**: White solid; yield: 0.15 g (85%); mp 61-63°C;  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  7.53 (d,  $J = 4.8$  Hz, 4H), 7.34 (d,  $J = 5.0$  Hz, 6H); **GC-MS m/z** (% relative intensity): 178(M+, 100), 152(8), 89(15), 76(16)



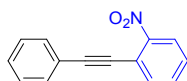
2. **2,4-dimethyl-1-(phenylethynyl)benzene (3d)**: Light yellow solid; yield: 0.146 g (71%); mp 38-40°C;  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  7.56 – 7.49 (m, 2H), 7.38 (d,  $J = 7.8$  Hz, 1H), 7.33 (d,  $J = 7.0$  Hz, 3H), 7.05 (s, 1H), 6.97 (d,  $J = 7.7$  Hz, 1H), 2.47 (s, 3H), 2.33 (s, 3H); **GC-MS m/z** (% relative intensity): 206(M+, 100), 191(75), 189(20), 165(17), 128(20), 91(18)



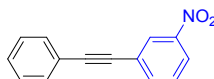
3. **1,3-dimethyl-2-(phenylethynyl)benzene (3e)**: Yellow liquid; yield: 0.148 g (72%);  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  7.57 (d,  $J = 6.2$  Hz, 2H), 7.37 (d,  $J = 6.8$  Hz, 3H), 7.20 – 7.12 (m, 1H), 7.09 (d,  $J = 7.0$  Hz, 2H), 2.54 (s, 6H). **GC-MS m/z** (% relative intensity): 206(M+, 100), 191(67), 101(13), 95(11), 89(16)



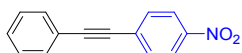
4. **1-methyl-4-(phenylethynyl)benzene (3f)**: Off white solid; yield: 0.151 g (79%); mp 68-70°C;  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  7.56 – 7.48 (m, 2H), 7.43 (d,  $J = 7.9$  Hz, 2H), 7.33 (d,  $J = 6.2$  Hz, 3H), 7.15 (d,  $J = 7.8$  Hz, 2H), 2.37 (s, 3H); **GC-MS m/z** (% relative intensity): 192(M+, 100), 165(16)



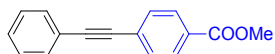
5. **1-nitro-2-(phenylethynyl)benzene (3g)**: Yellow solid; yield: 0.153 g (69%); mp 50-52°C;  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  8.07 (d,  $J = 8.2$  Hz, 1H), 7.71 (d,  $J = 7.7$  Hz, 1H), 7.59 (d,  $J = 4.1$  Hz, 3H), 7.45 (t,  $J = 7.8$  Hz, 1H), 7.37 (dd,  $J = 8.2$ , 5.1 Hz, 3H)



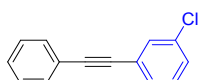
6. **1-nitro-3-(phenylethynyl)benzene (3h)**: Yellow solid; yield: 0.162 g (73%); mp 65-67°C;  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  8.37 (s, 1H), 8.17 (d,  $J = 8.4$  Hz, 1H), 7.82 (d,  $J = 7.7$  Hz, 1H), 7.53 (dd,  $J = 10.6$ , 5.5 Hz, 3H), 7.42 – 7.33 (m, 3H); **GC-MS m/z** (% relative intensity): 223(M+, 100), 176 (49), 165 (18), 151(15), 88(11)



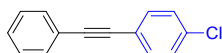
- 7 1-nitro-4-(phenylethynyl)benzene (3i):** Yellow solid; yield: 0.172 g (77%); mp 112-114°C; <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>) δ 8.21 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.48 (m, 2H), 7.38 (d, *J* = 4.2 Hz, 3H); **GC-MS m/z** (% relative intensity): 223(M+, 100), 193(40), 176(62), 177(58), 165(47), 151(22), 88(34)



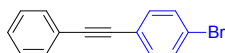
- 8 methyl 4-(phenylethynyl)benzoate (3j):** Yellow solid; yield: 0.184 g (78%); mp 116-117°C; <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 3.5 Hz, 2H), 7.36 (d, *J* = 2.8 Hz, 3H), 3.92 (s, 3H).



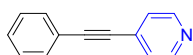
- 9 1-chloro-3-(phenylethynyl)benzene (3l):** Colourless liquid; yield: 0.166 g (78%); <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>) δ 7.52 (s, 3H), 7.40 (d, *J* = 6.1 Hz, 1H), 7.35 (d, *J* = 3.2 Hz, 3H), 7.29 (dd, *J* = 10.6, 8.1 Hz, 2H); **GC-MS m/z** (% relative intensity): 212(M+, 100), 176 (36), 150(10), 106 (12), 88 (15)



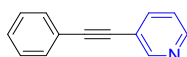
- 10 1-chloro-4-(phenylethynyl)benzene (3m):** Off white solid; yield: 0.168 g (79%); mp 81-82°C; <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>) δ 7.52 (d, *J* = 3.5 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.33 (dd, *J* = 10.9, 5.8 Hz, 5H); **GC-MS m/z** (% relative intensity): 212(M+, 100), 176 (36), 150(10), 106 (12), 88 (15)



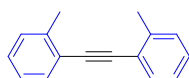
- 11 1-bromo-4-(phenylethynyl)benzene (3n):** White solid; yield: 0.21 g (81%); mp 82-84°C; <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>) δ 7.52 (s, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.35 (s, 3H); **GC-MS m/z** (% relative intensity): 256(M+, 100), 257(16), 258(98), 178(9), 177(62), 176(65), 151(20), 128(12), 88(49), 75(18)



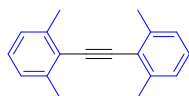
- 12 4-(phenylethynyl)pyridine (3o):** Off white solid; yield: 0.141 g (79%); mp 93-94°C; <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>) δ 8.58 (d, *J* = 4.6 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.41 – 7.29 (m, 5H); **GC-MS m/z** (% relative intensity): 179(M+, 100), 152 (13), 151(17), 76(14)



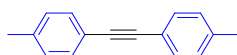
- 13 3-(phenylethynyl)pyridine (3p):** Yellow solid; yield: 0.144 g (81%); mp 47-49°C; <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>) δ 8.76 (s, 1H), 8.53 (d, *J* = 4.0 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.44 (m, 2H), 7.40 – 7.32 (m, 3H), 7.26 (dd, *J* = 7.7, 4.9 Hz, 1H); **GC-MS m/z** (% relative intensity): 179(M+, 100), 152 (13), 151(17), 76(14);



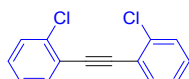
- 14 1,2-di-o-tolylethyne (5b):** Yellow liquid; yield: 0.157 g (76%);  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  7.51 (d,  $J = 7.5$  Hz, 2H), 7.24 (d,  $J = 3.9$  Hz, 4H), 7.18 (dd,  $J = 7.6, 4.6$  Hz, 2H), 2.53 (s, 6H); **GC-MS m/z** (% relative intensity): 206( $\text{M}^+$ , 100), 207(16.2), 191(20), 189(10), 178(14), 101(11), 91(30).



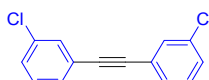
- 15 1,2-bis(2,6-dimethylphenyl)ethyne (5c):** Off white solid; yield: 0.168 g (72%); mp 112-114°C;  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  7.10 (s, 6H), 2.55 (s, 12H); **GC-MS m/z** (% relative intensity): 234( $\text{M}^+$ , 100), 235(22), 219(86), 218(12), 217(10), 204(33), 203(17), 202(13), 142(20), 141(20), 128(21), 105(52), 91(18).



- 16 1,2-di-p-tolylethyne (5d):** Off white solid; yield: 0.161 g (78%); mp 131-133°C;  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  7.40 (d,  $J = 7.6$  Hz, 4H), 7.14 (d,  $J = 7.7$  Hz, 4H), 2.35 (s, 6H); **GC-MS m/z** (% relative intensity): 206( $\text{M}^+$ , 100), 205(20), 191(38), 189(12).



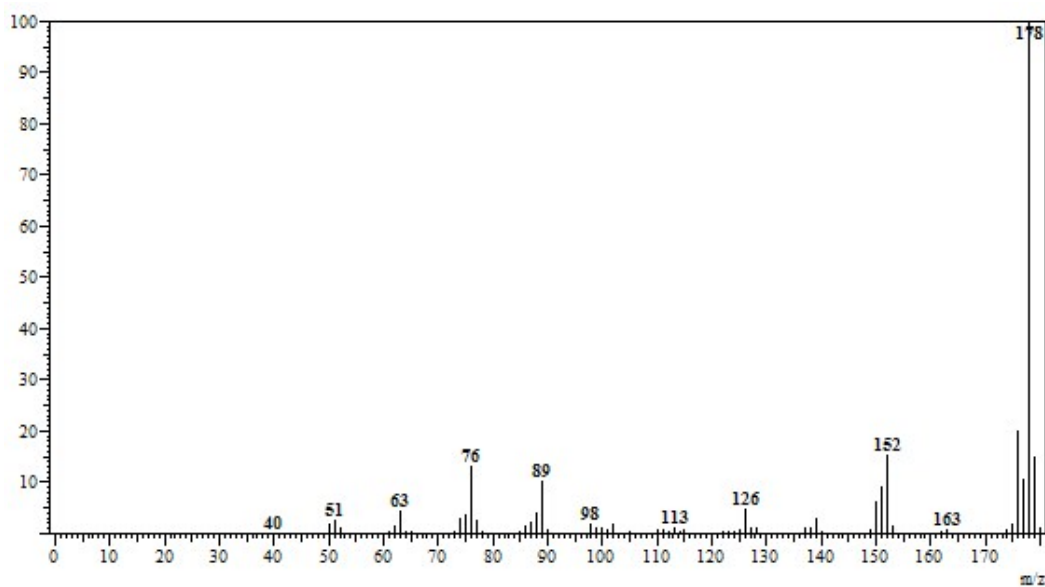
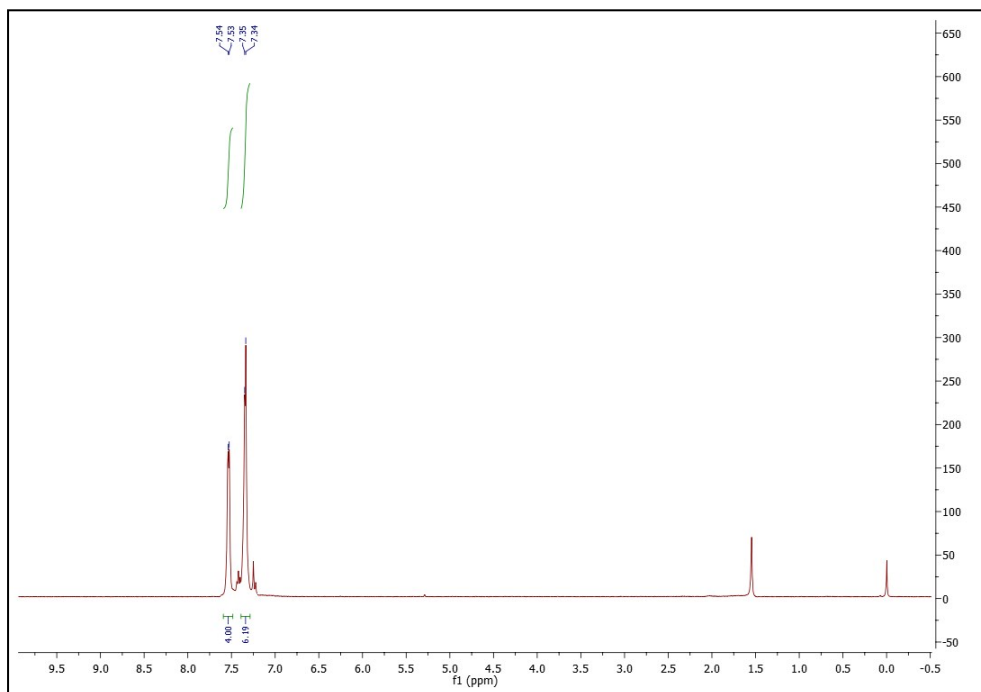
- 17 1,2-bis(2-chlorophenyl)ethyne (5e):** Light yellow solid; yield: 0.20 g (80%); mp 82-83°C; **GC-MS m/z** (% relative intensity): 246( $\text{M}^+$ , 100), 247(15), 248(62), 210(8), 211(9), 177(11), 176(79), 175(18), 150(7), 123(13)



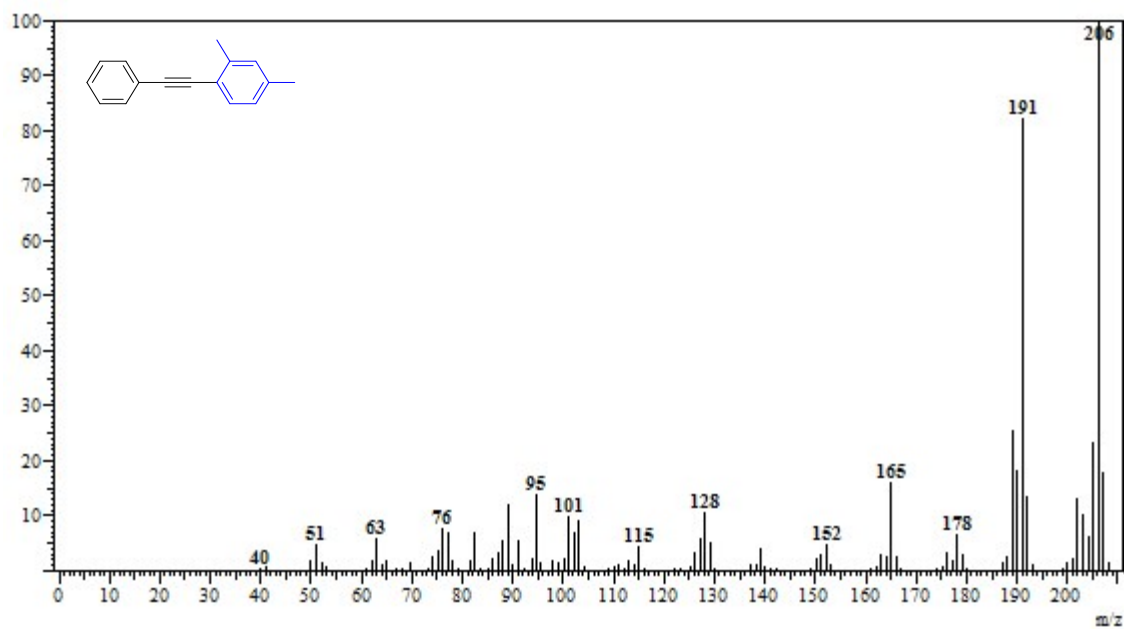
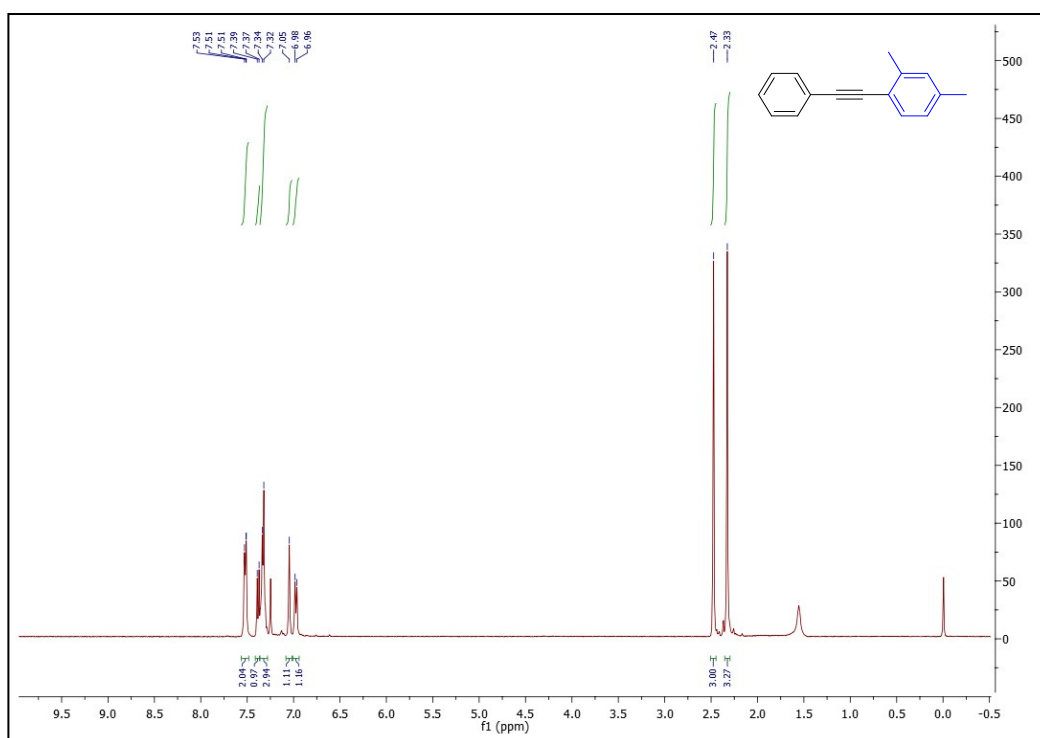
- 18 1,2-bis(3-chlorophenyl)ethyne (5f):** White solid; yield: 0.192 g (78%); mp 79-80°C;  $^1\text{H NMR}$  (400 MHz,  $\text{cdCl}_3$ )  $\delta$  7.48 (d,  $J = 8.3$  Hz, 4H), 7.37 (d,  $J = 8.3$  Hz, 4H); **GC-MS m/z** (% relative intensity): 246( $\text{M}^+$ , 100), 247(16), 248 (63), 176(52), 175(17), 174(18), 149(6), 150(9), 123(15), 87(20)

**<sup>1</sup>H NMR and GC-MS data of the products:**

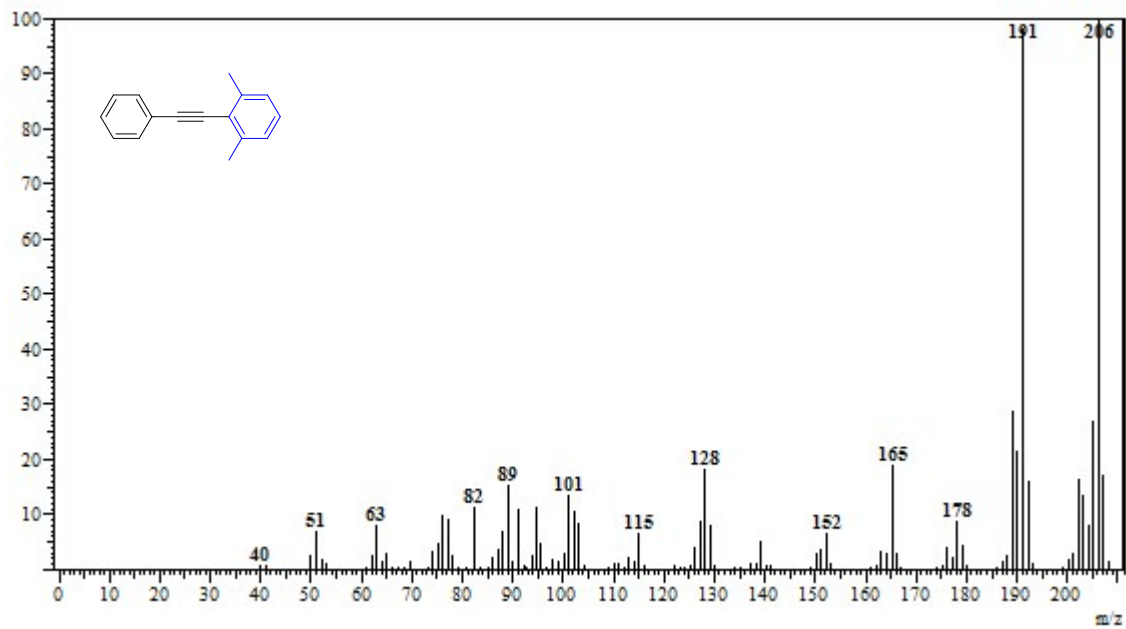
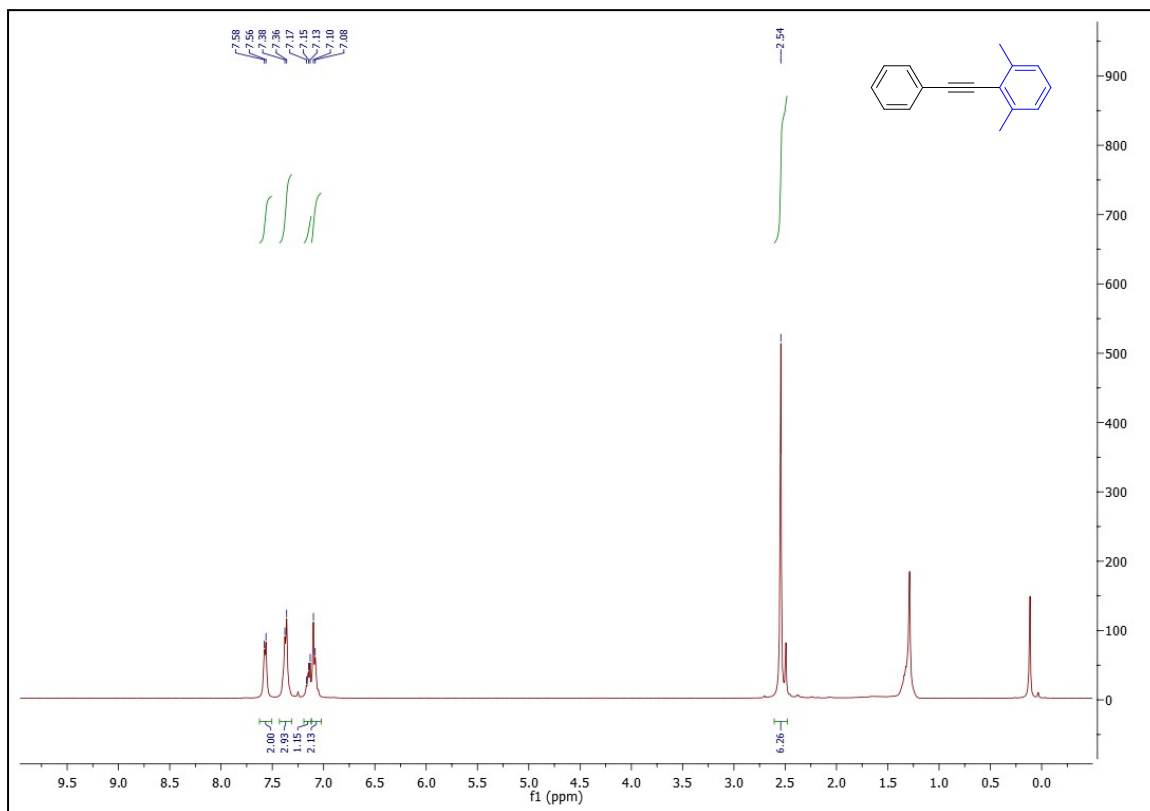
**Diphenylethyne (3a):**



2,4-dimethyl-1-(phenylethynyl)benzene (3d):

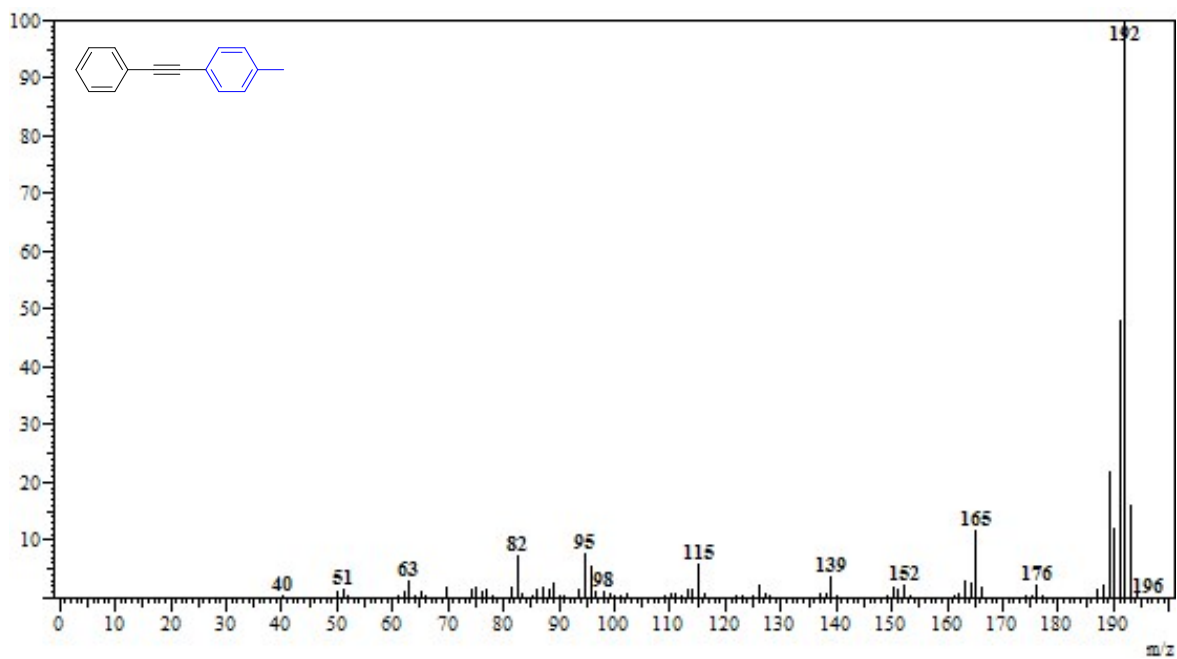
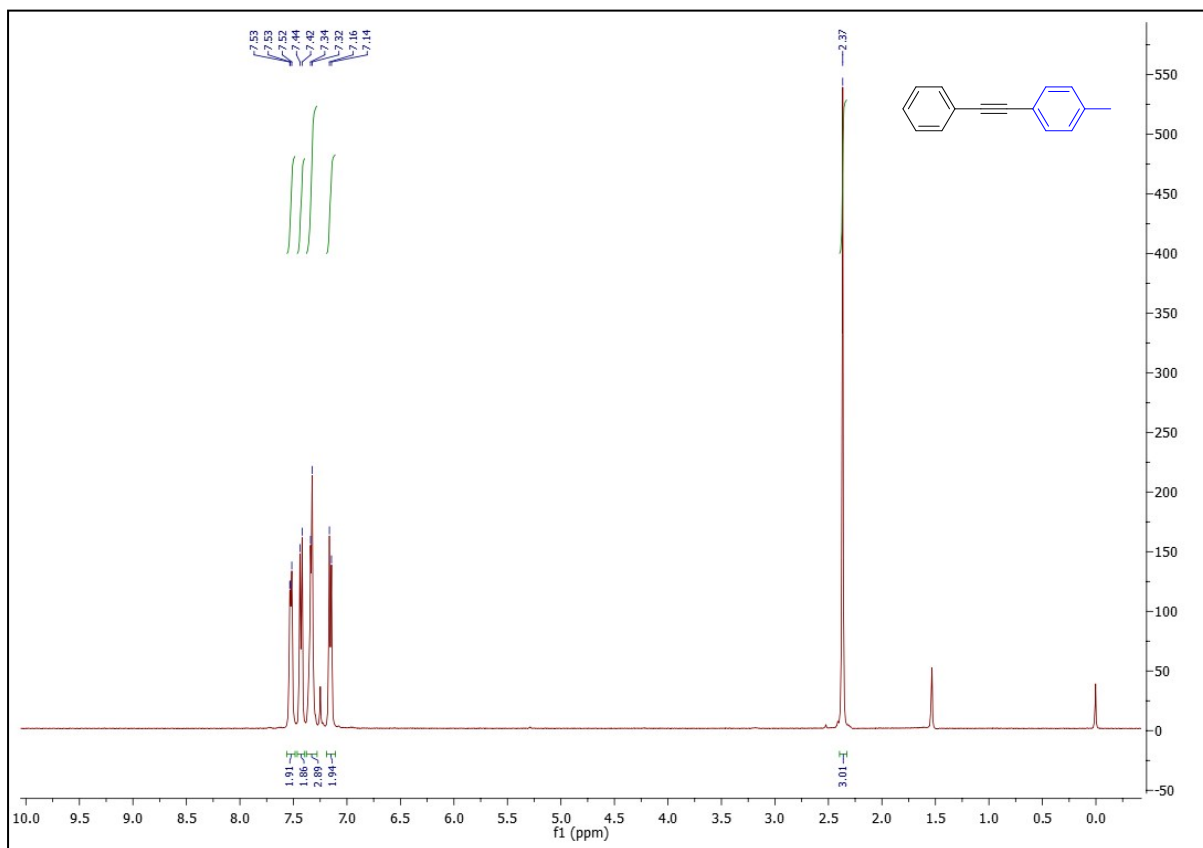


**1,3-dimethyl-2-(phenylethynyl)benzene (3e):**

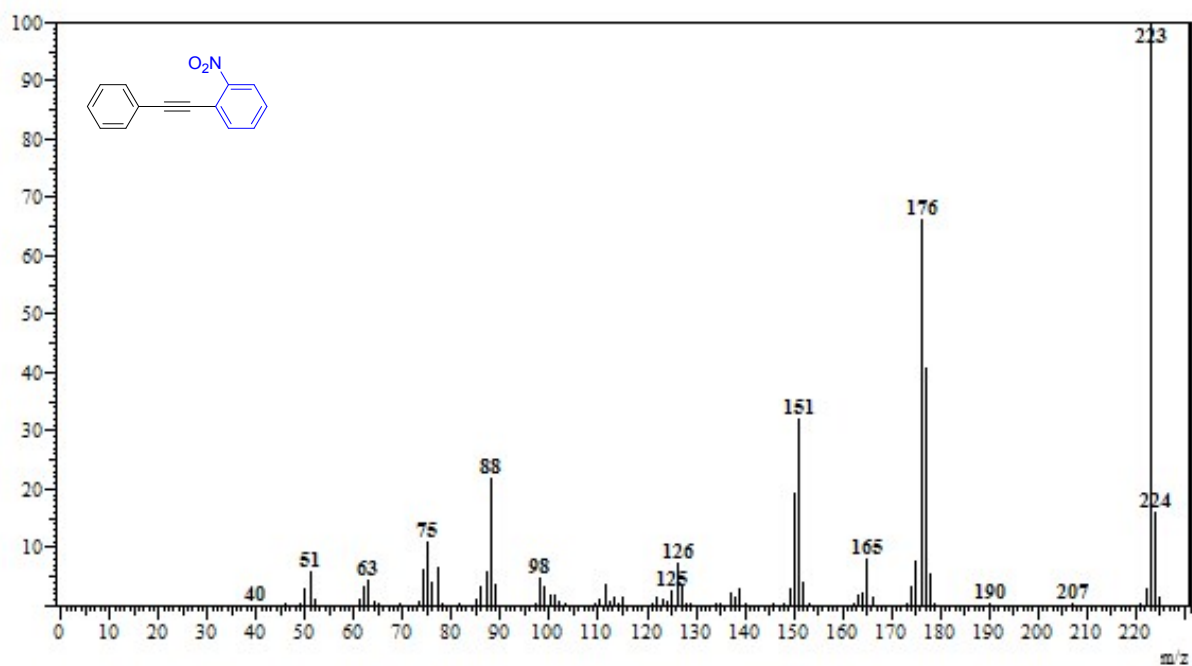
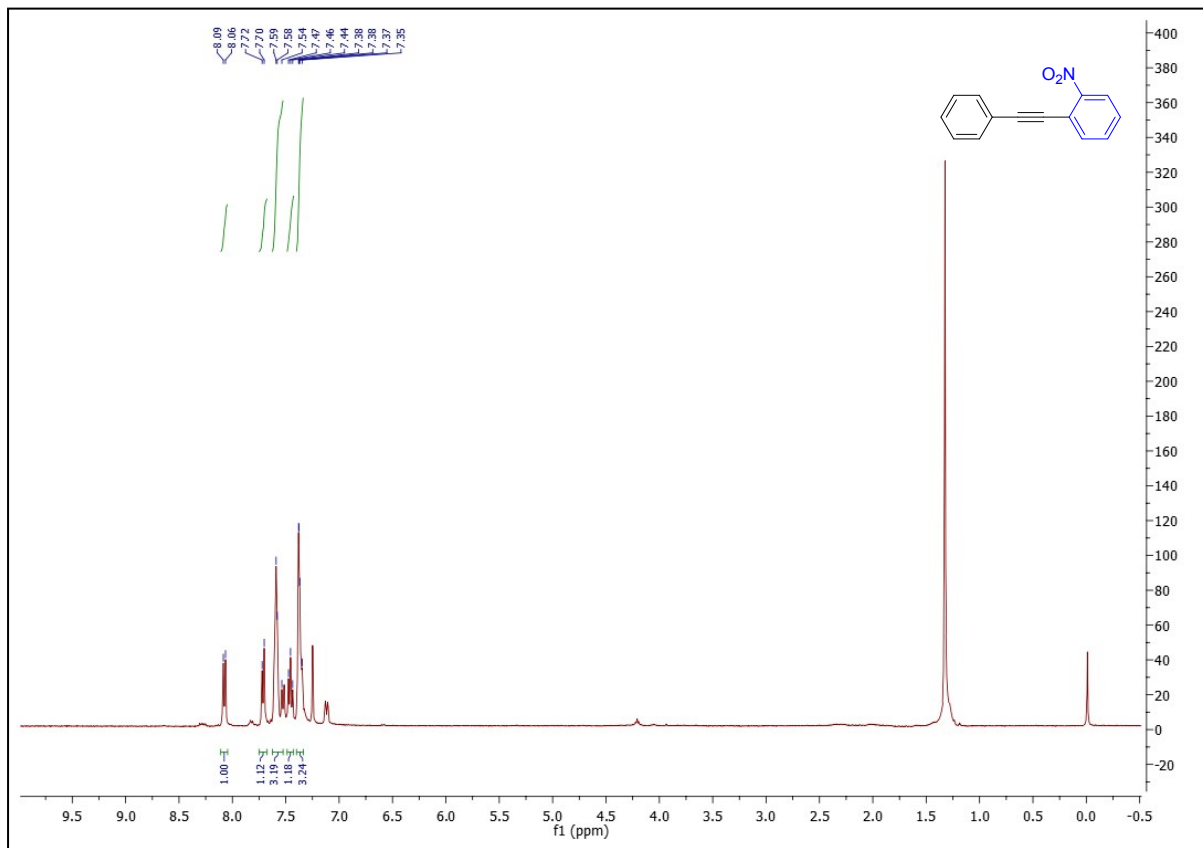




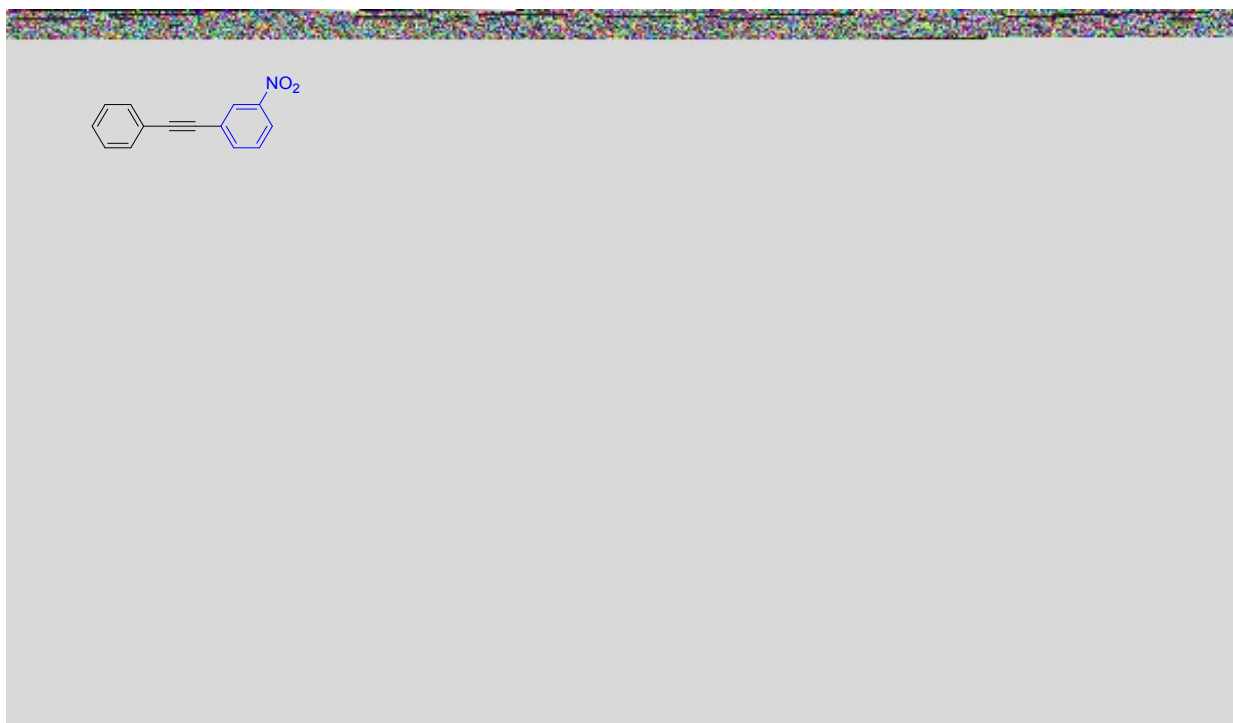
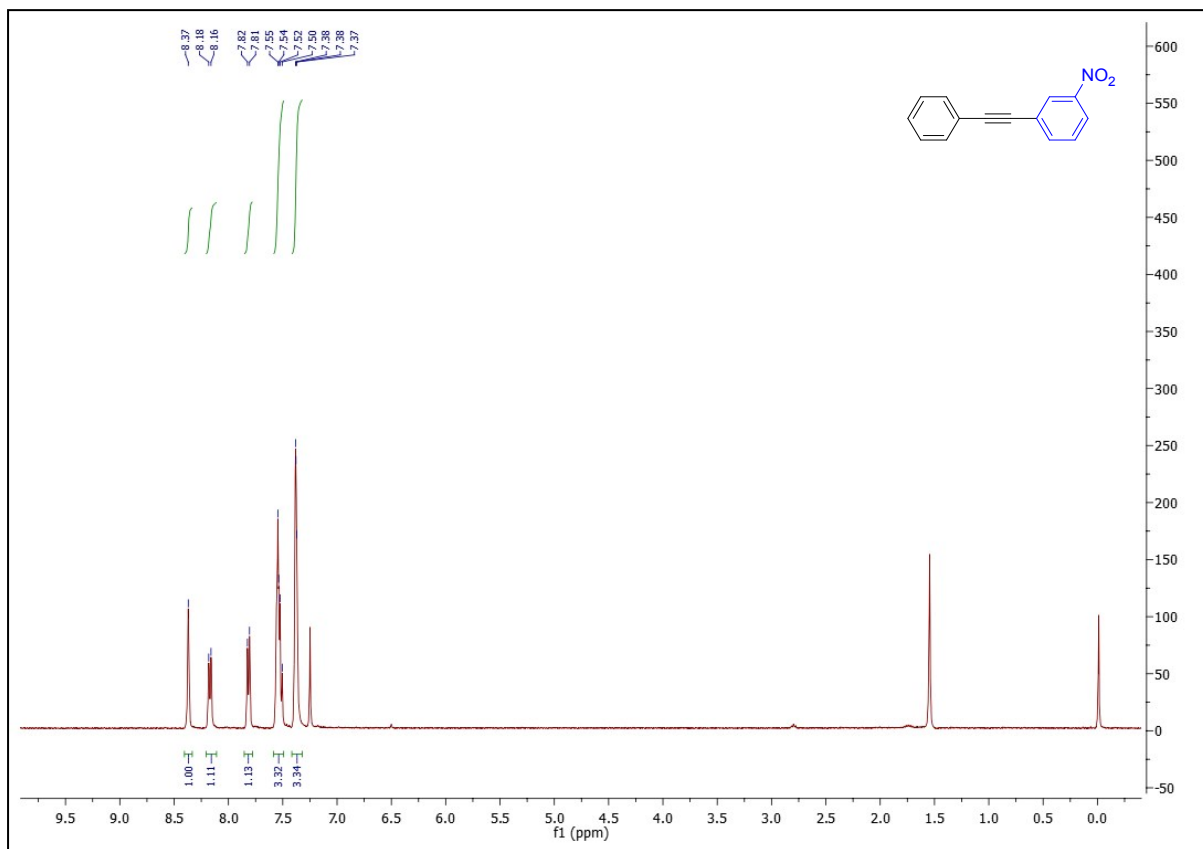
1-methyl-4-(phenylethynyl)benzene (3f):



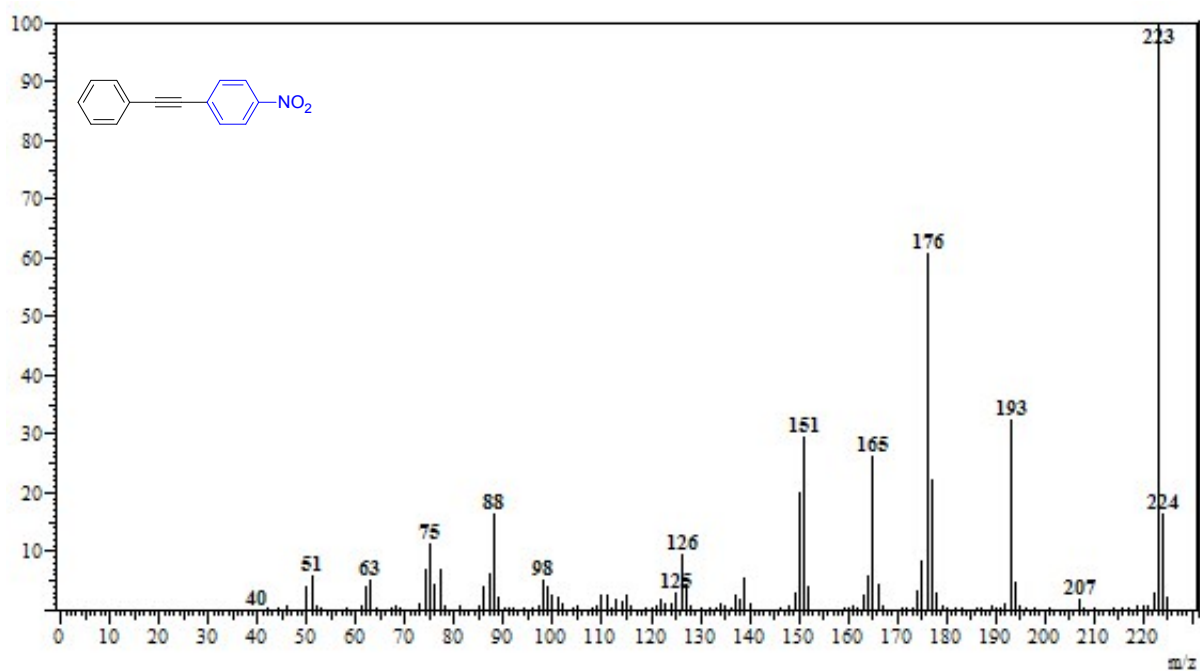
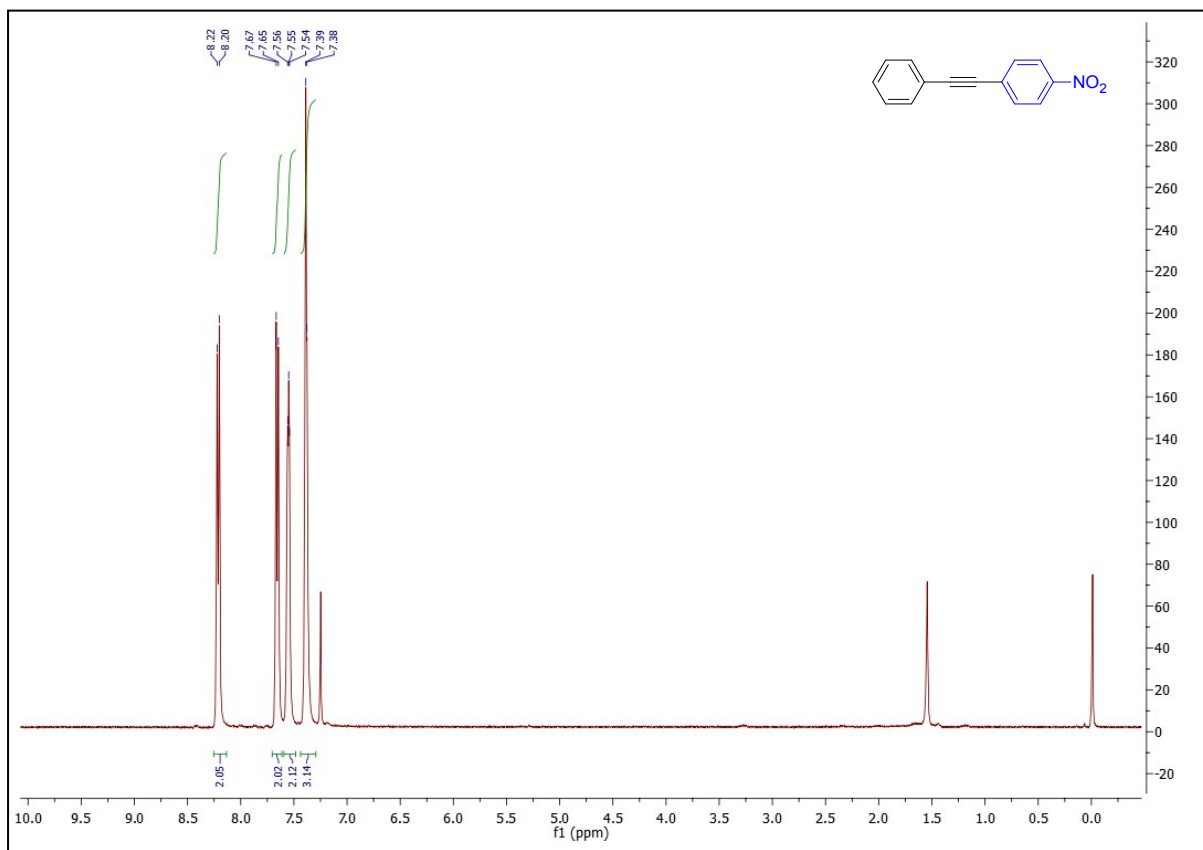
1-nitro-2-(phenylethynyl)benzene (3g):



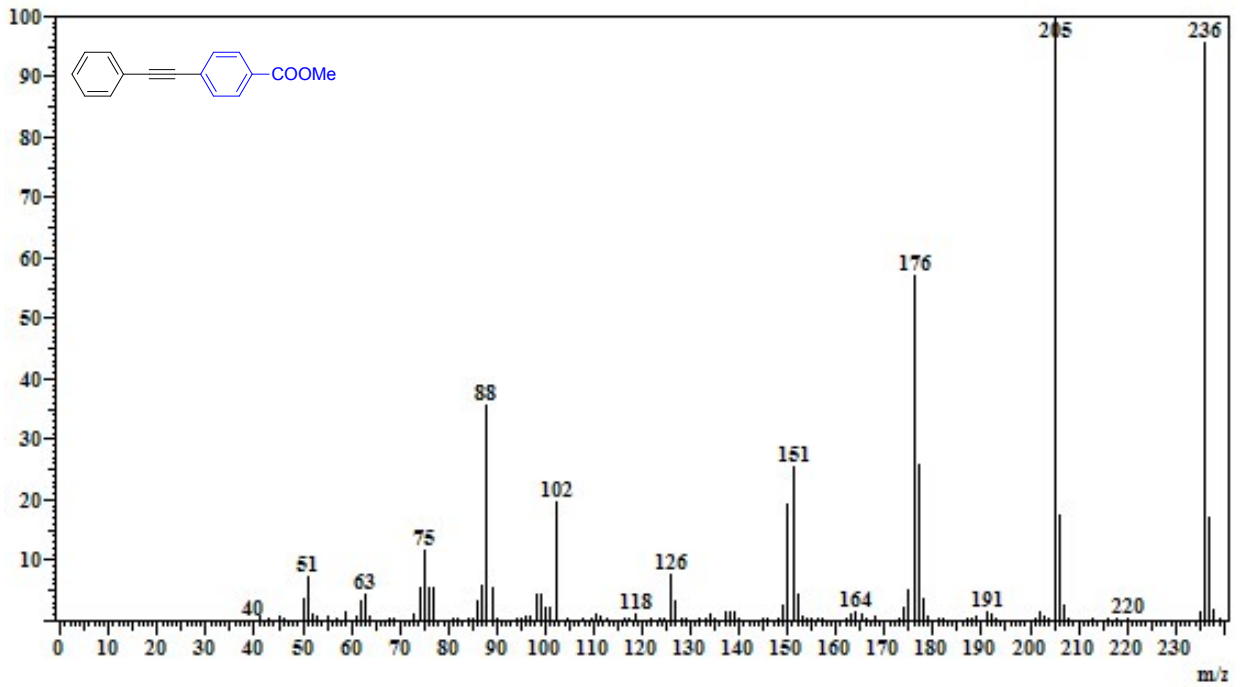
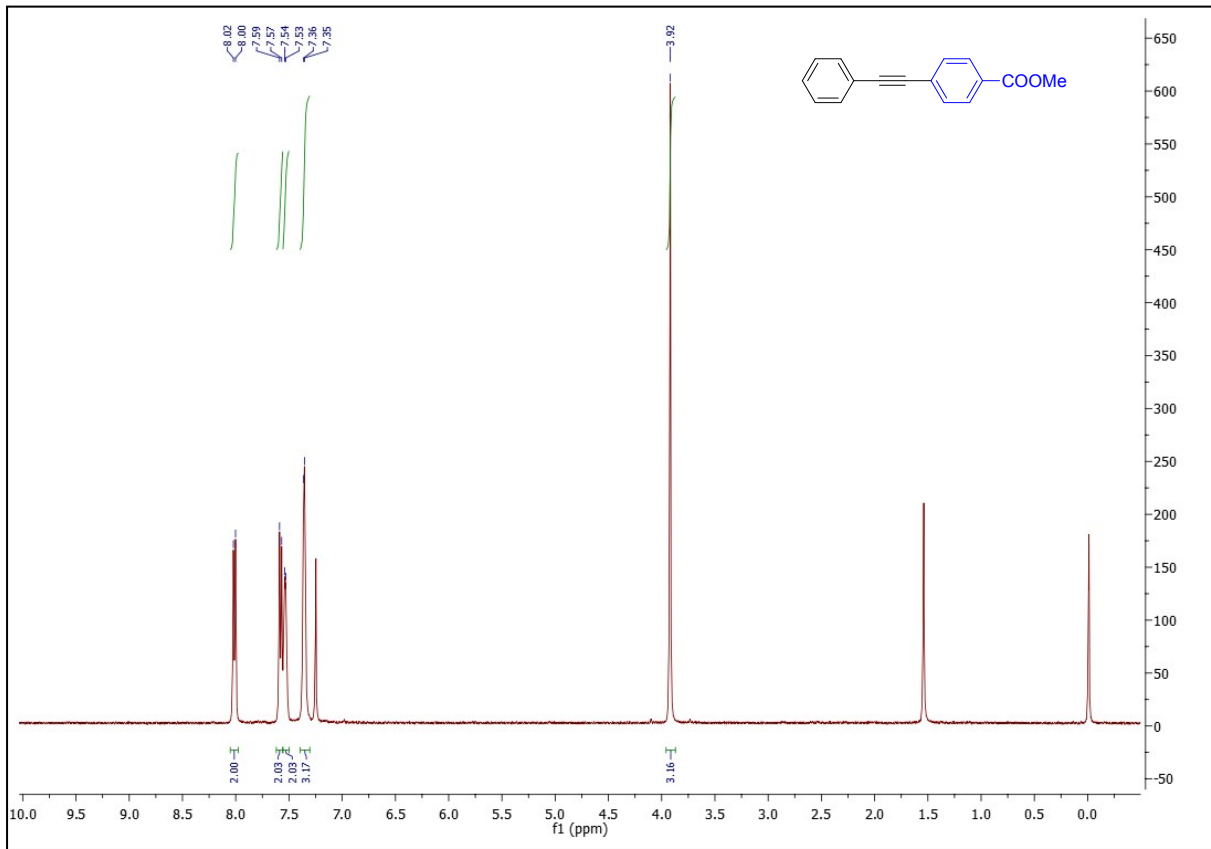
1-nitro-3-(phenylethynyl)benzene (3h):



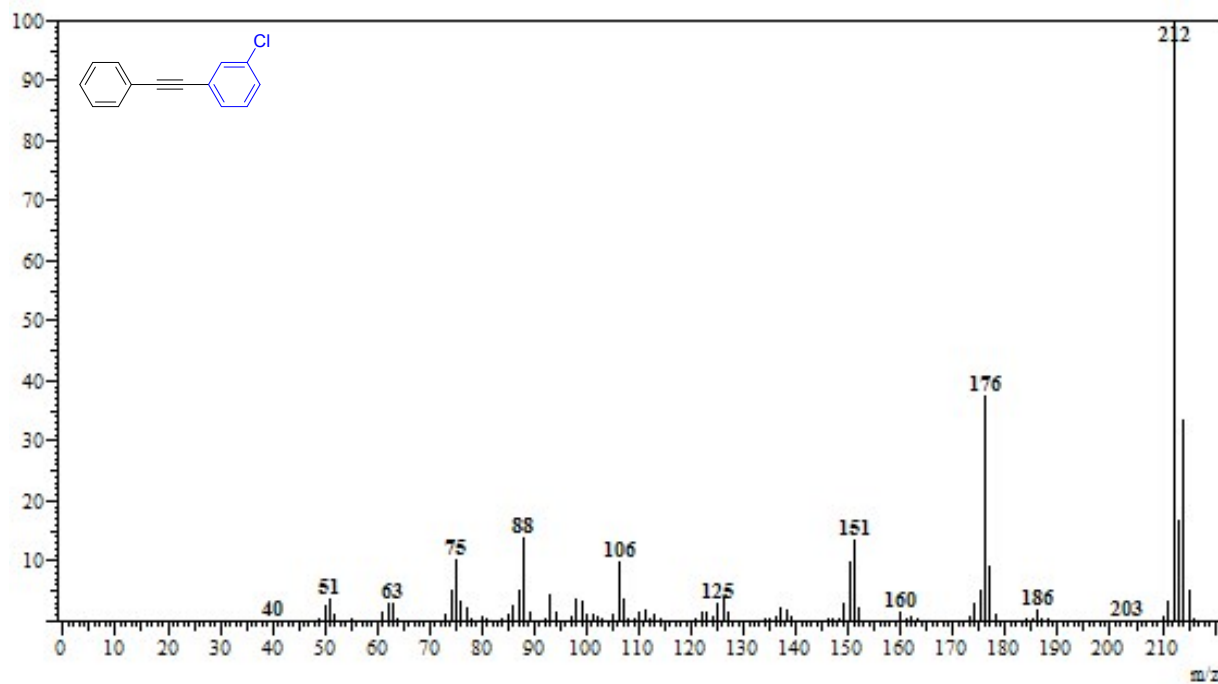
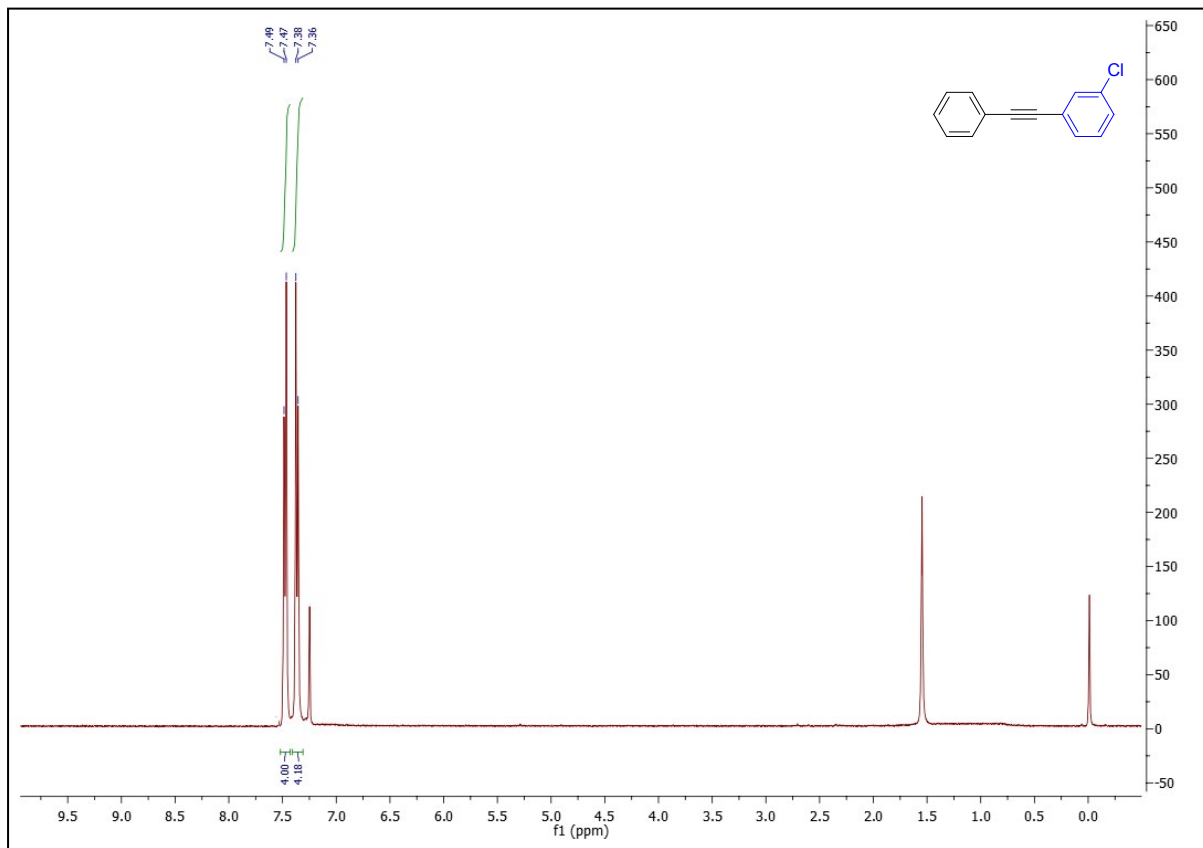
1-nitro-4-(phenylethynyl)benzene (3i):



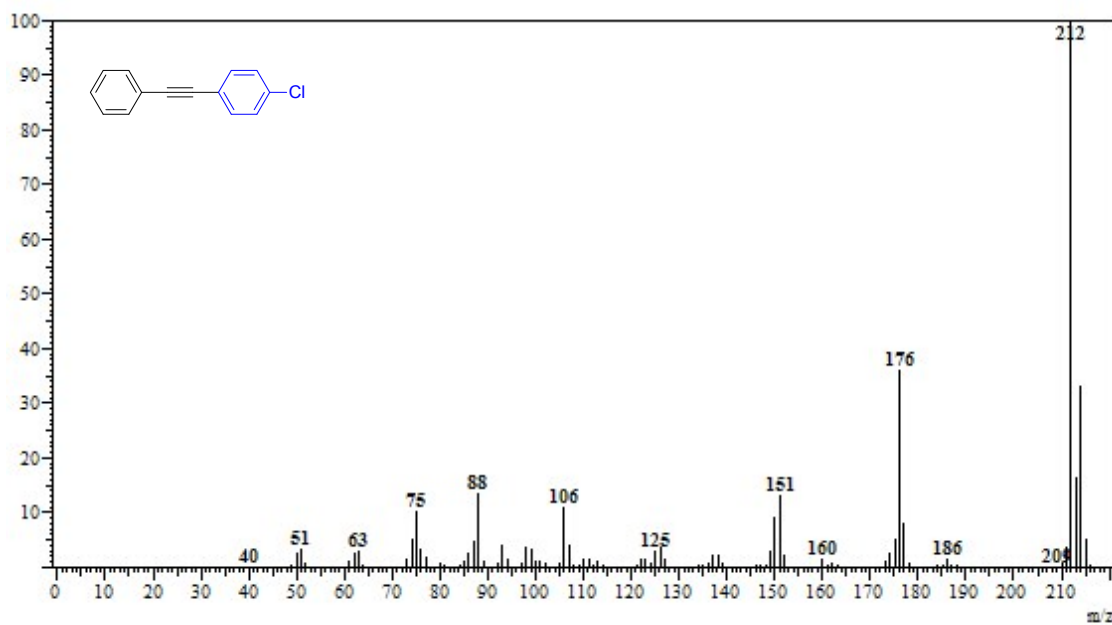
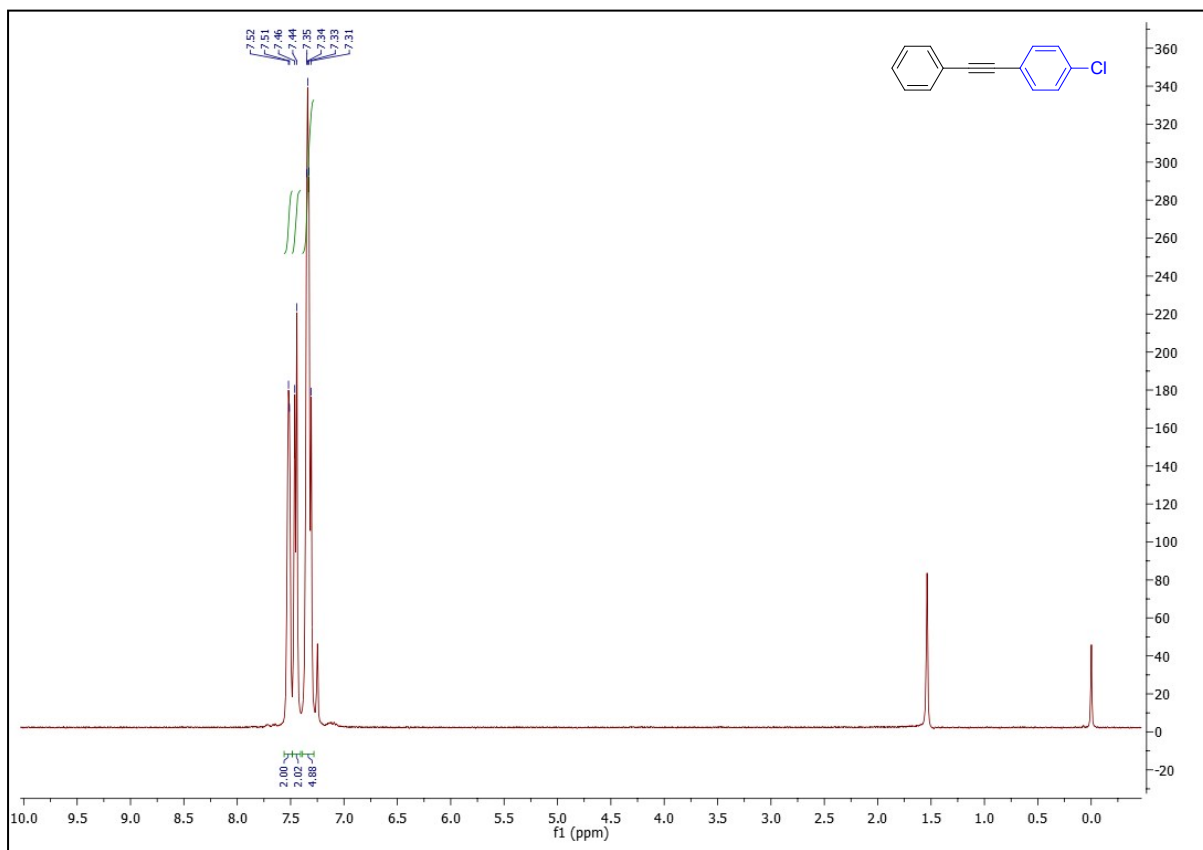
**methyl 4-(phenylethynyl)benzoate (3j):**



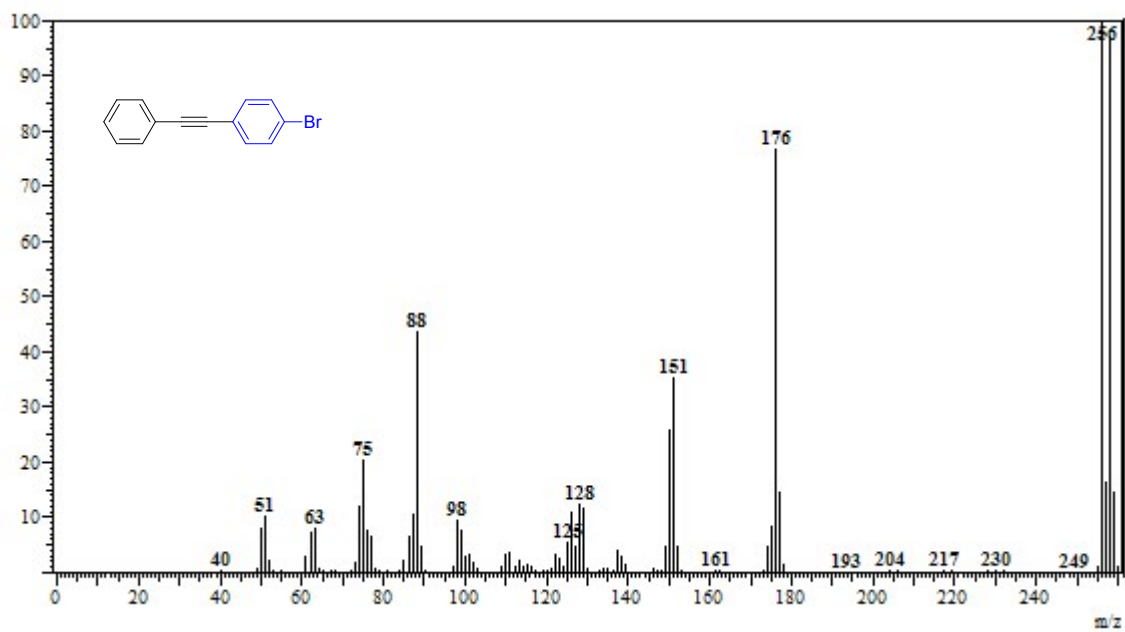
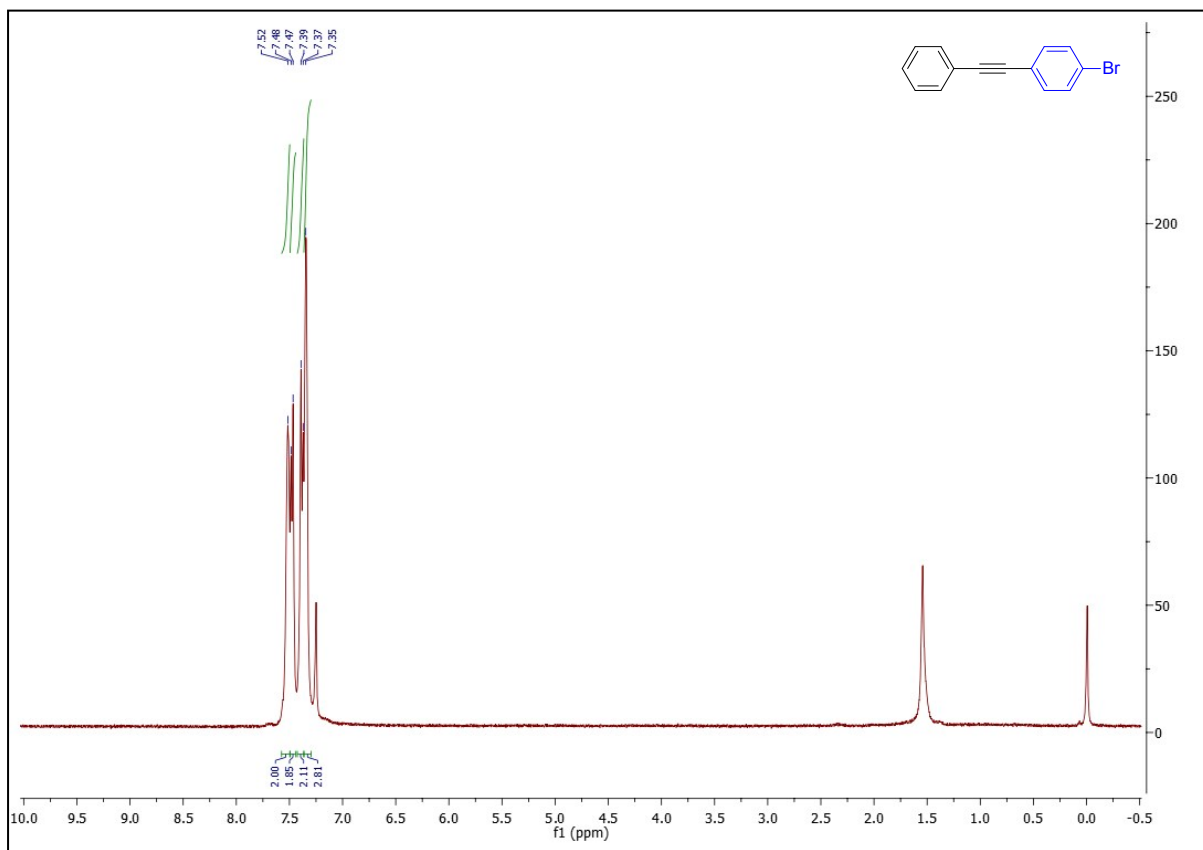
1-chloro-3-(phenylethynyl)benzene (31):



1-chloro-4-(phenylethynyl)benzene (3m):

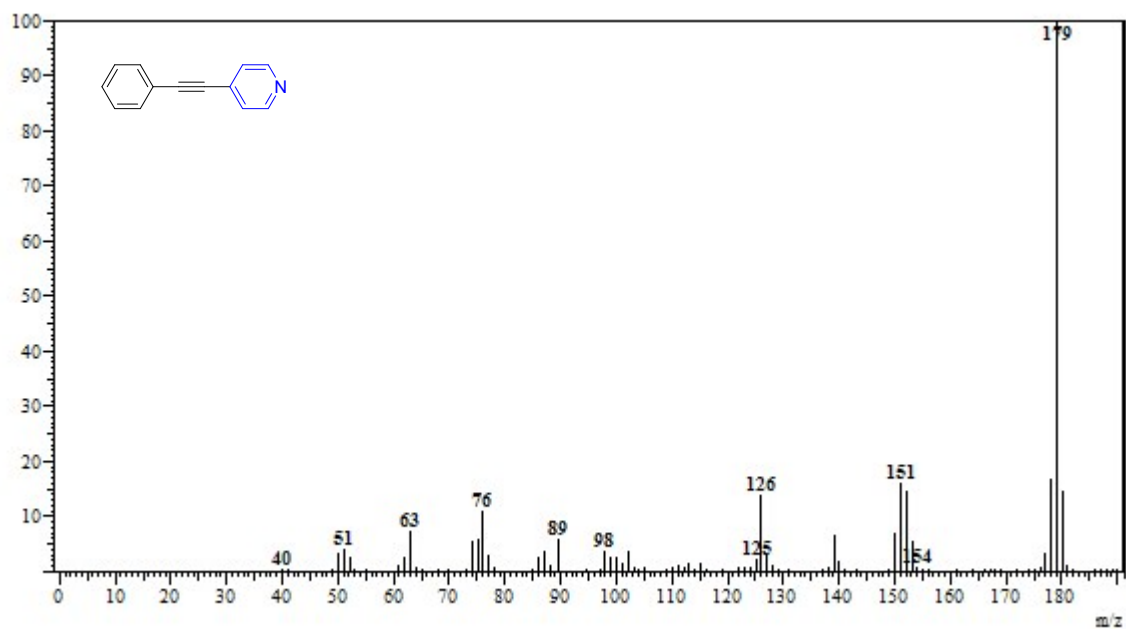
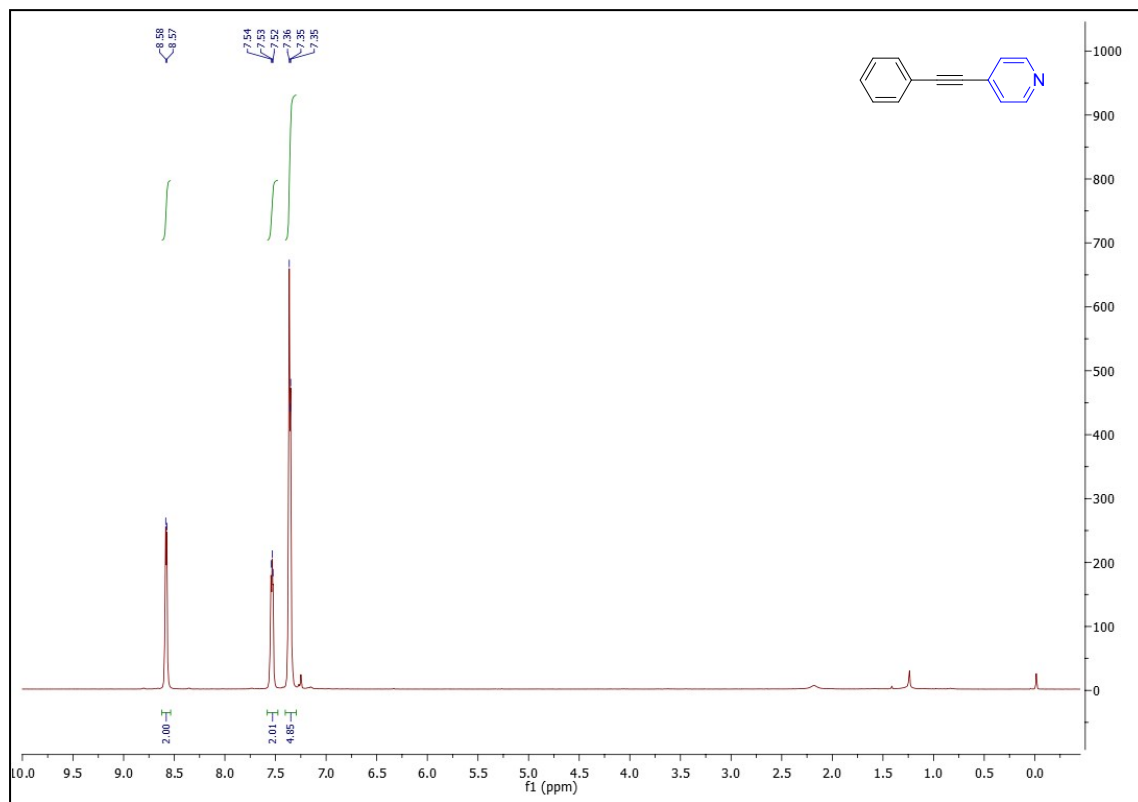


1-bromo-4-(phenylethynyl)benzene (3n):

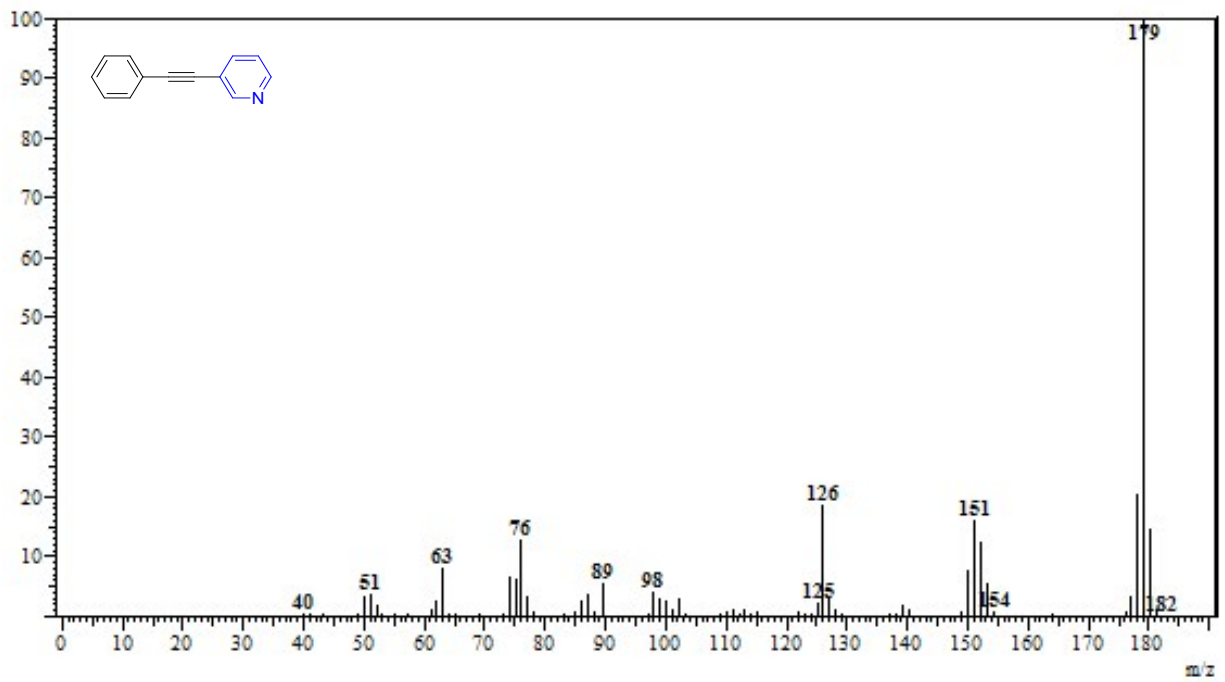
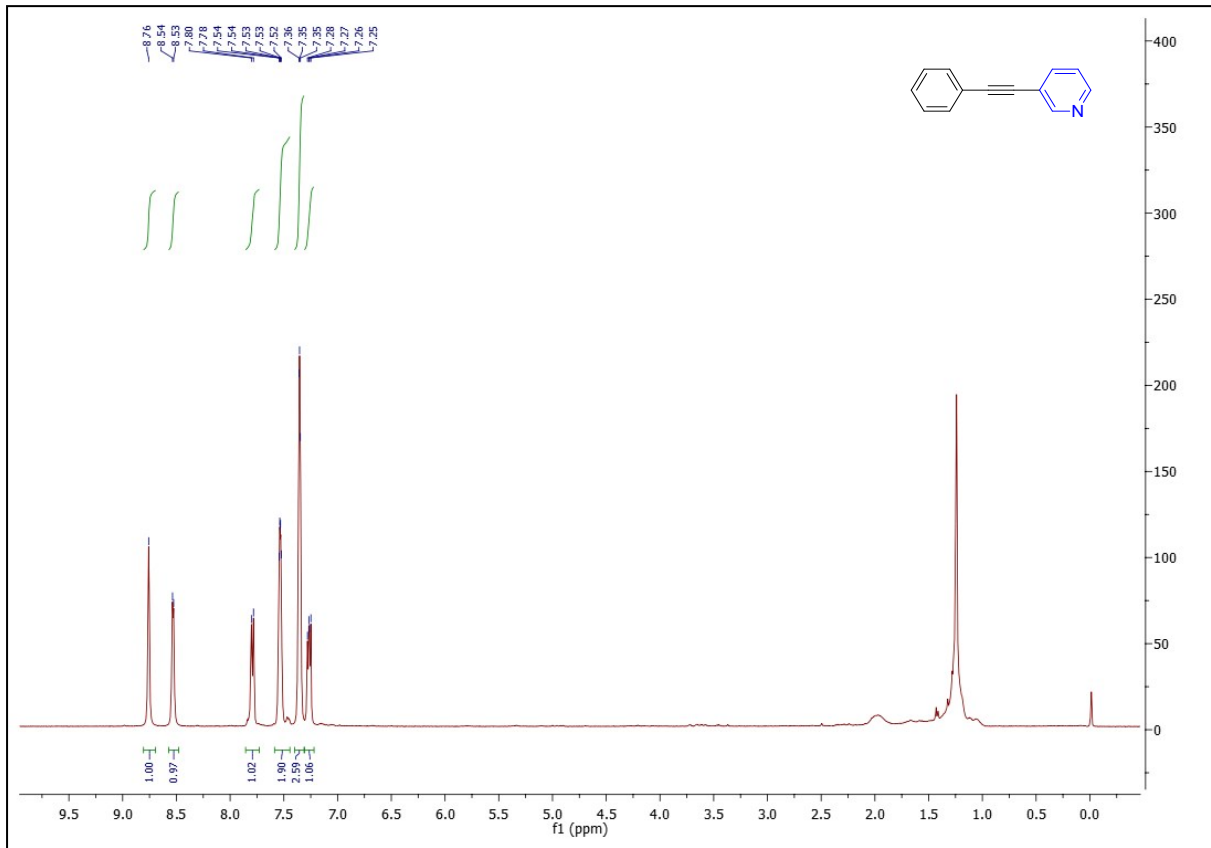




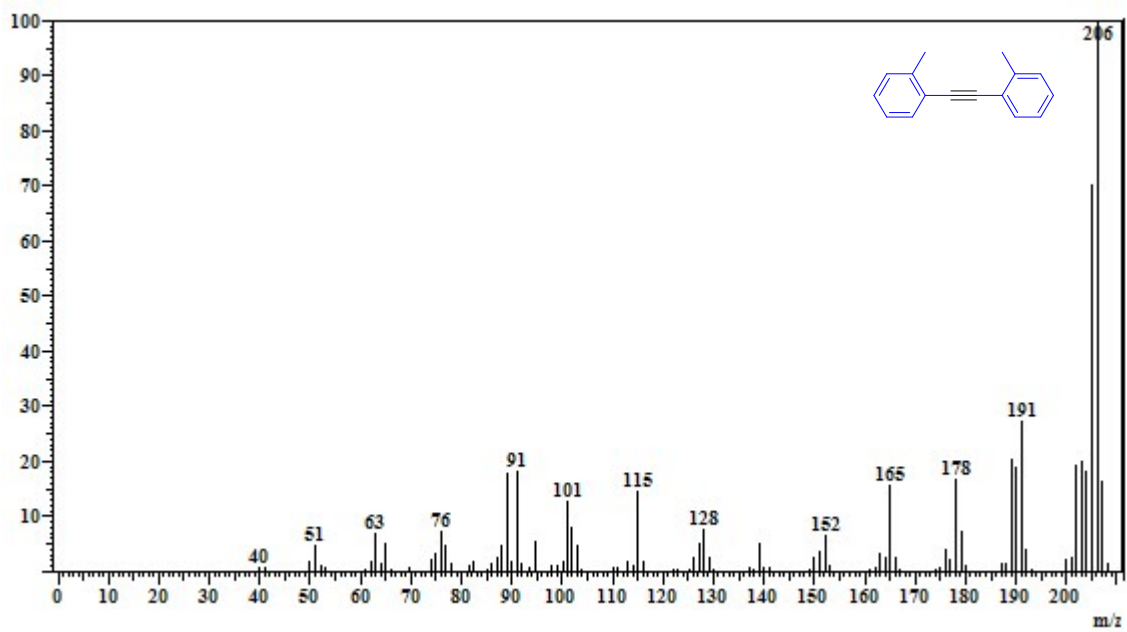
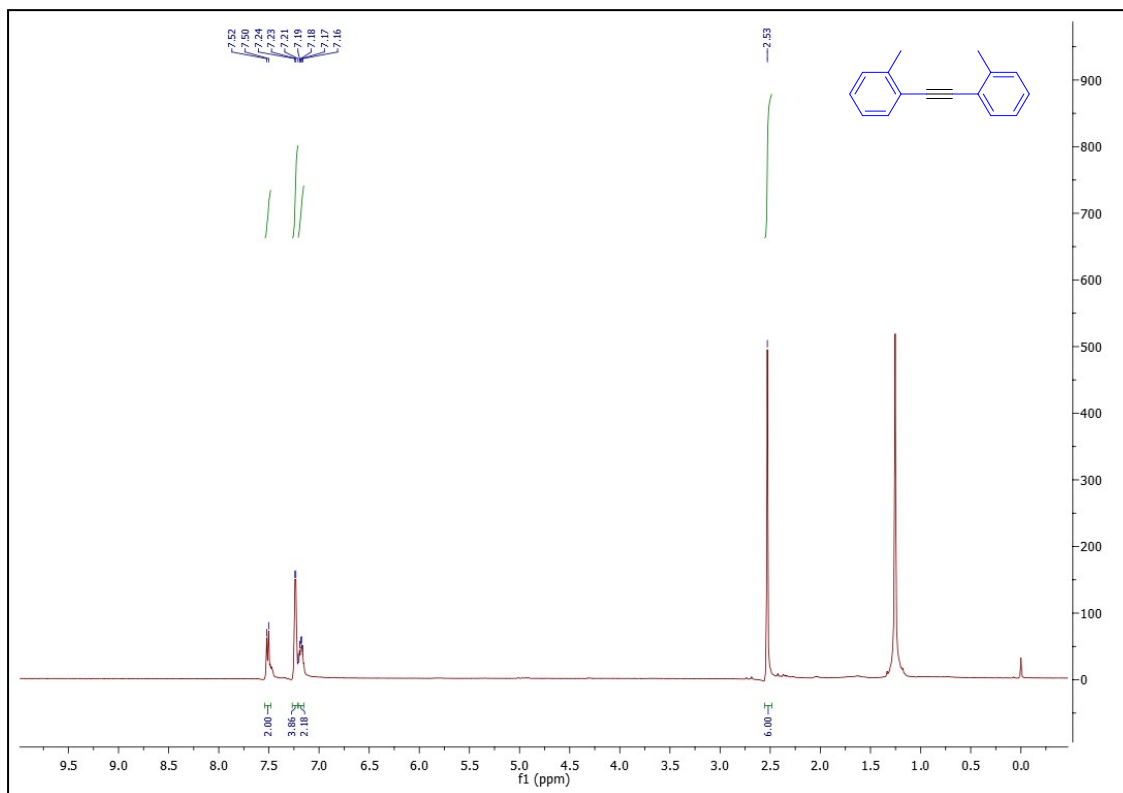
4-(phenylethynyl)pyridine (3o):



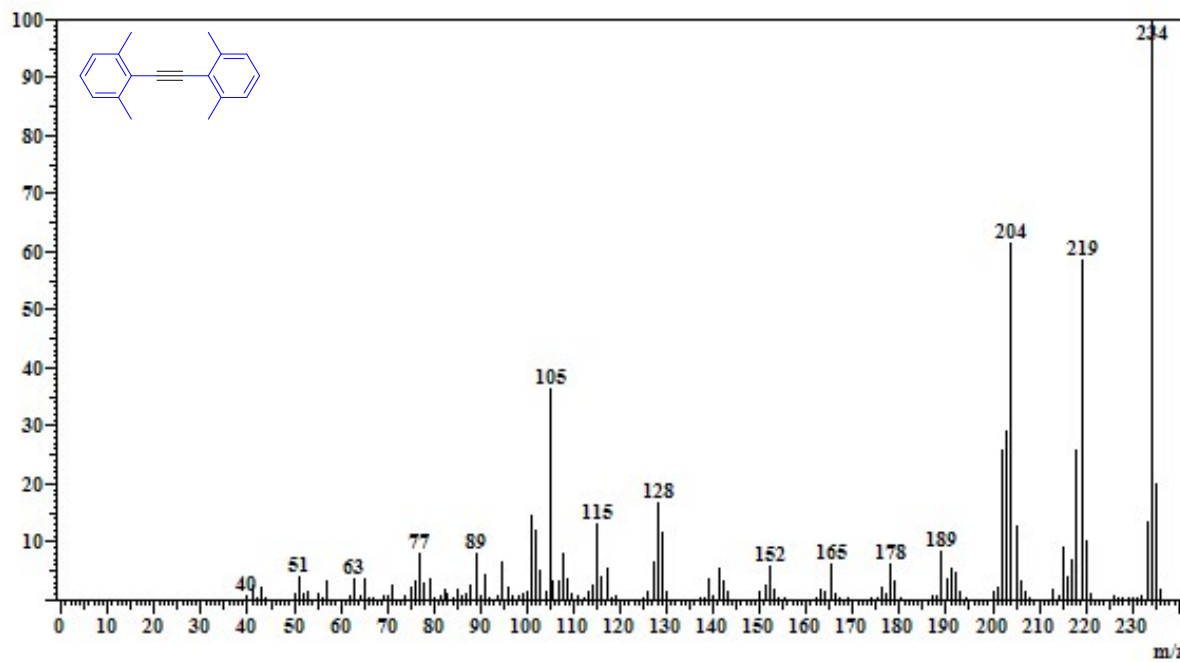
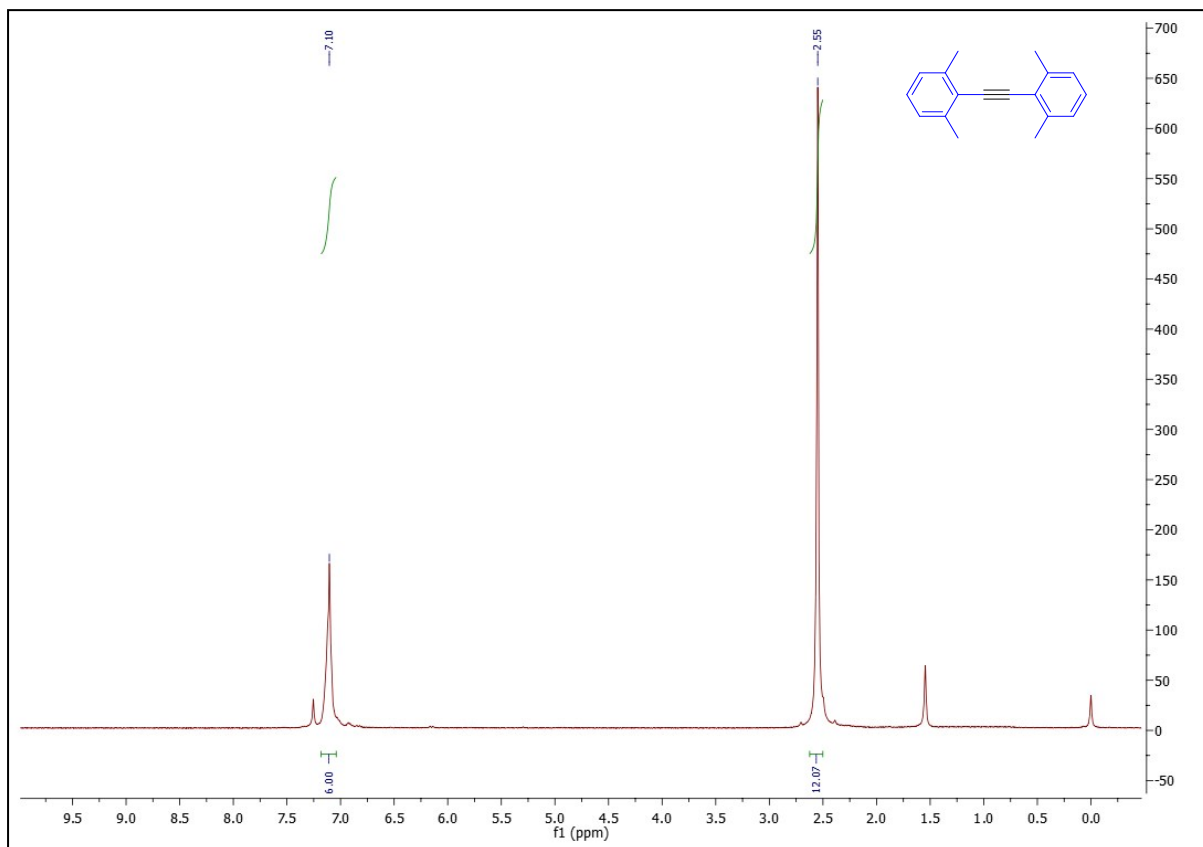
3-(phenylethynyl)pyridine (3p):



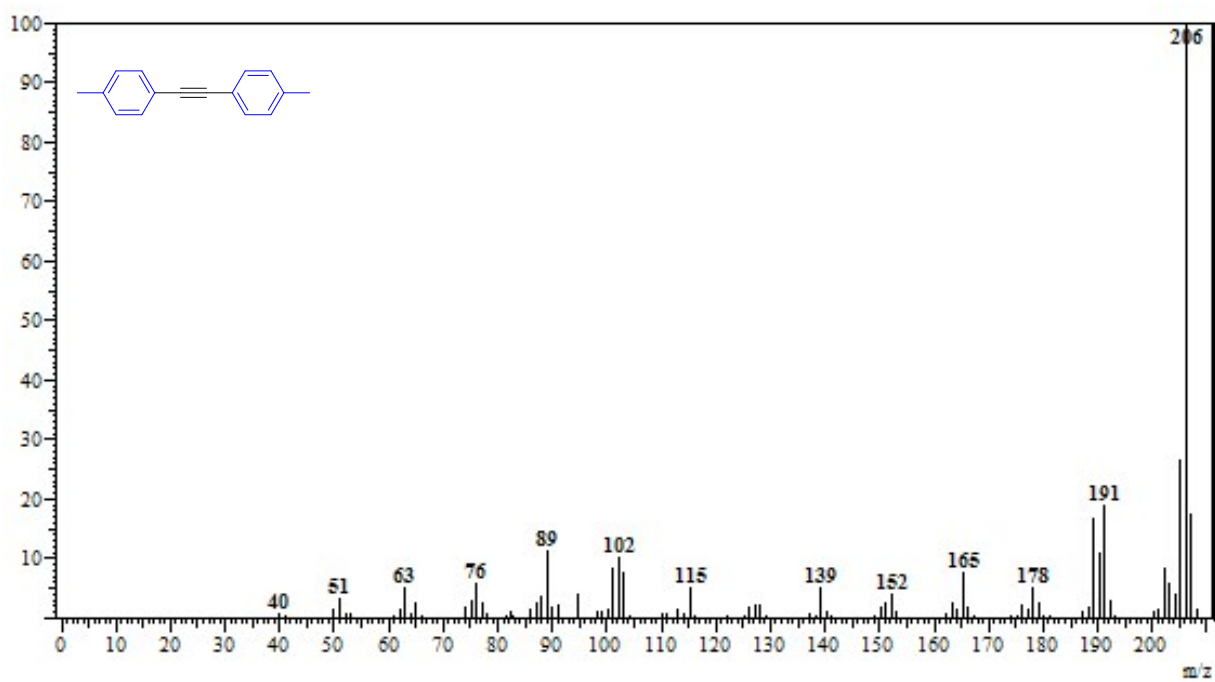
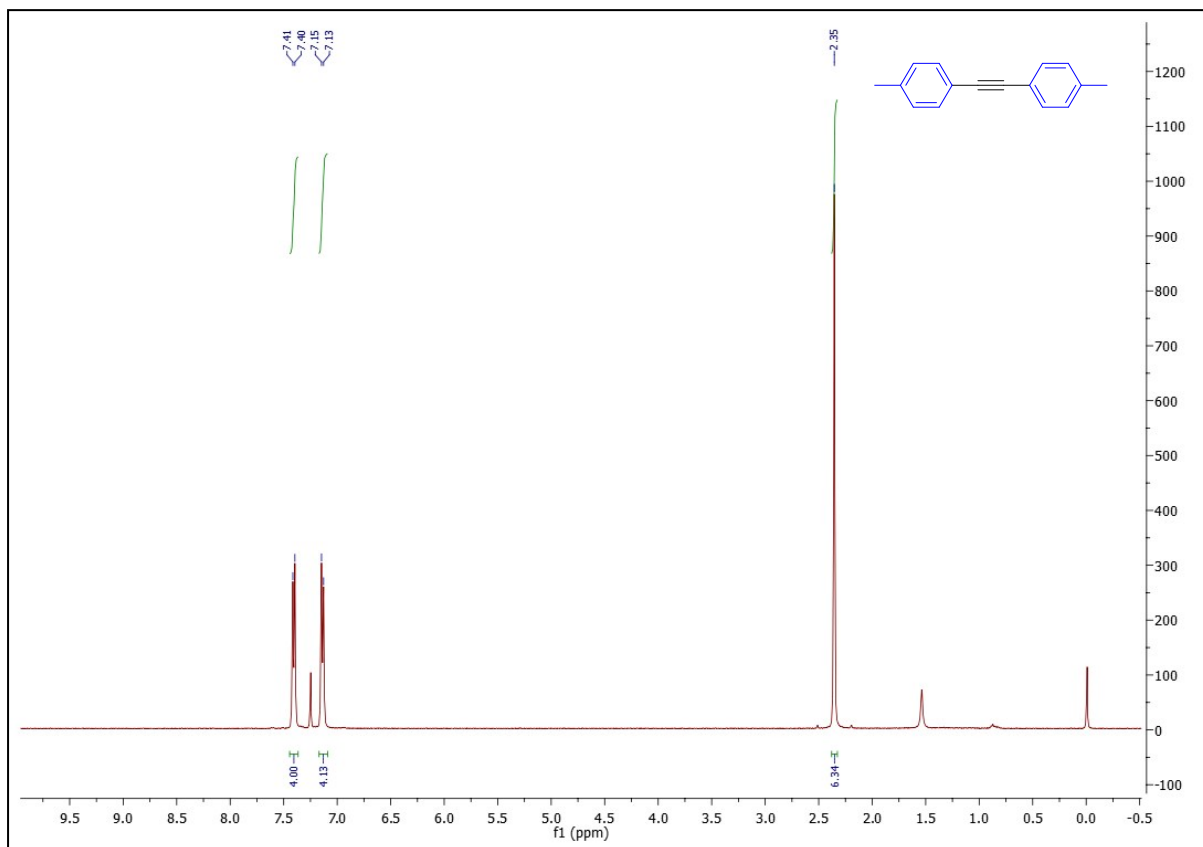
1,2-di-o-tolyne (5b):



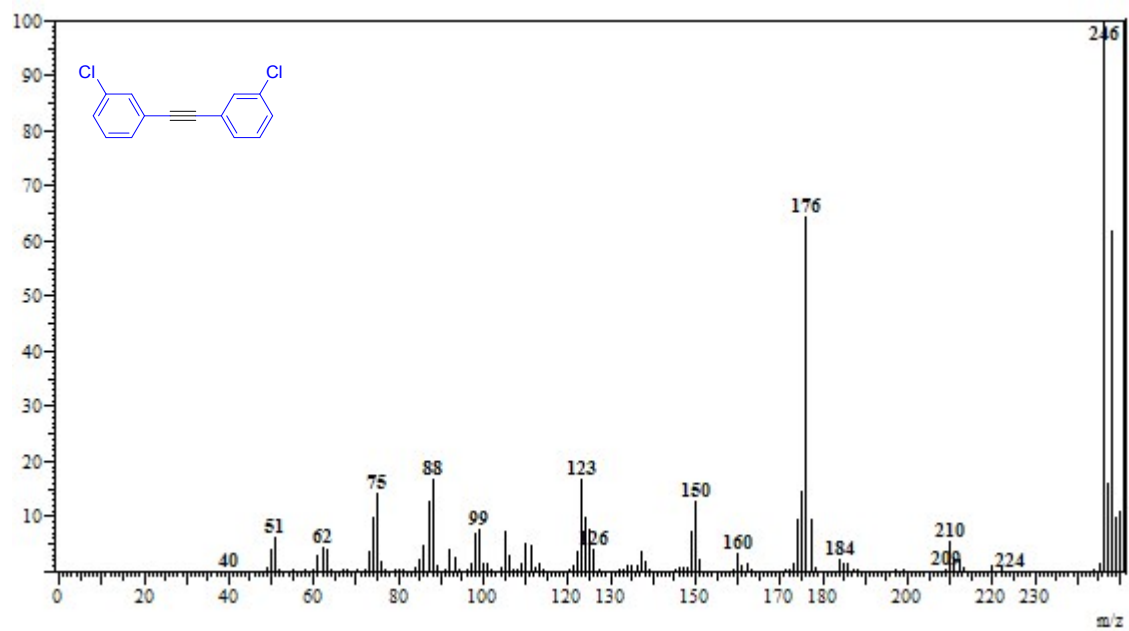
1,2-bis(2,6-dimethylphenyl)ethyne (5c):



1,2-di-p-tolylethyne (5d):



1,2-bis(3-chlorophenyl)ethyne (5f):



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