

## Nickel-glycerol: An efficient, recyclable system for Suzuki cross coupling reaction using aryl diazonium salt

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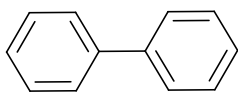
### Experimental section

General: All chemicals were purchased from Sigma Aldrich S.D Fine Chemical, Avra, Spectrochem Ltd, commercial suppliers and used without further purifications. The reaction was monitored by TLC and 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 product mass conformed by 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 to 240 °C at 10 °C/ min rise). The products were purified by column chromatography using (60-120 mesh) silica gel with pet ether as eluent. The pure product <sup>1</sup>H NMR Spectroscopic data of compounds was recorded on a Varian Mercury plus- 300 spectrometer using DMSO and CDCl<sub>3</sub> as a solvent and TMS as internal standard. NiCl<sub>2</sub>.glyme has been synthesized by known literature method<sup>1</sup>. Aryl diazonium tetraboroflourate are synthesis by known method<sup>2</sup>.

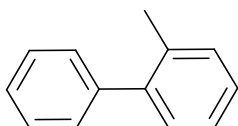
### General procedure for Suzuki coupling with aryl diazonium salt

To an oven-dried 25 ml schlenk tube equipped with a magnetic stirring bar was charged with arenediazonium salt (1.2mmol), phenyl boronic acid (1mmol), NiCl<sub>2</sub>.glyme (10 mol %), followed by anhydrous DMSO (0.5ml), glycerol (2 ml). Reaction mixture was stirred at 80°C for 12 h. The reaction was monitored by GC and TLC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate. The resulting ethyl acetate layer was washed with water and 20% brine solutions. The organic layer was 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 pet ether (100). 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. While glycerol layer contain catalyst which used for further reactions.

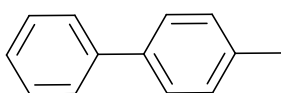
## Spectroscopic data:



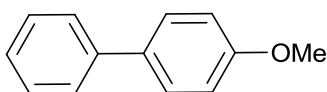
**Biphenyl (3a):** White solid; yield: 0.137 g (90%); mp 68-70°C. **GC-MS m/z** (% relative intensity): 154(M+, 30), 152 (100), 77(60),



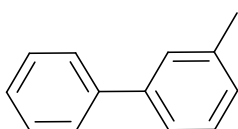
**2-methyl-1,1'-biphenyl (3b) :** Colourless liquid; yield: 0.121 g (73%). **GC-MS m/z** (% relative intensity): 168(M+, 100), 167 (73), 152(27), 128(6),115(14),102(4), 91(8), 82(10)



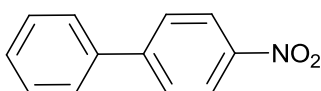
**4-methyl-1, 1'-biphenyl (3c):** Off white solid; yield: 0.142 g (84%); mp 46-47°C. **GC-MS m/z** (% relative intensity): 168(M+, 100), 153 (43), 128(7), 115(13), 102(3),91(6),89(8), 83(15).



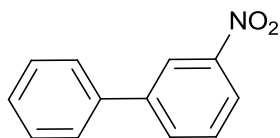
**4-methoxy-1, 1'-biphenyl (3d)**<sup>35</sup>: White solid; yield: 0.161 g (87%); mp 87-89°C. <sup>1</sup>H NMR : (300 MHz, d- DMSO, TMS):  $\delta$  7.61( d, 2H,Ar-H), 7.59( d, 2H,Ar-H),7.45(d, 1H, Ar-H),7.32(d,2H,Ar-H), 7.02(d, 2H,Ar-H), 3.81(s,3H,CH<sub>3</sub>),,GC-MS m/z (% relative intensity): 184(M+, 100), 169(56.39), 141(57.10),139(14),115(43), 92(5), 76(8)



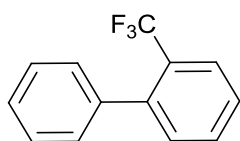
**3-methyl-1, 1'-biphenyl (3e):** Colourless liquid; yield: 0.125 g (75%).**GC-MS m/z** (% relative intensity): 168(M+, 100),167(62), 152 (25), 128(4), 115(8), 102(2),91(6),89(5), 83(10).



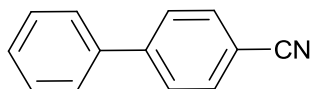
**4-nitro-1, 1'-biphenyl (3f)**<sup>36</sup>: Yellowish solid; yield: 0.150 g (76%); mp 110-112°C. <sup>1</sup>H NMR: (300 MHz, d- DMSO, TMS):  $\delta$  8.32(d,2H,Ar-H), 7.98(dd, 2H,Ar-H), 7.81(d, 2H,Ar-H), 7.58(d, 2H,Ar-H),7.45(m, 1H,Ar-H) GC-MS m/z (% relative intensity): 199(M+, 97), 152 (100), 127(9), 115(9), 102(5), 87(4), 76(20).



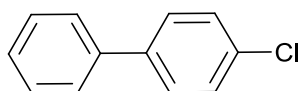
**3-nitro-1, 1'-biphenyl (3g):** Pale yellow solid; yield: 0.146 g (74%); mp 57-59°C.  $^1\text{H NMR}$ : (300 MHz, d- DMSO, TMS)  $\delta$  8.42(s, 1H, Ar-H), 8.25 (d, 1H, Ar-H), 7.79(t, 2H, Ar- H), 7.54(dd, 4H, Ar-H), 7.42(s, 1H, Ar-H). **GC-MS m/z** (% relative intensity): 199(M+, 100), 169(43), 152(96), 127(9), 115(15), 102(6), 87(3), 76(15)



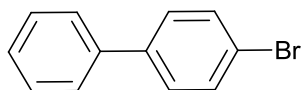
**2-(trifluoromethyl)-1, 1'-biphenyl (3h):** colourless liquid; yield: 0.156 g (71%); **GC-MS m/z** (% relative intensity): 222(M+, 100), 201(13), 183(3), 172(3), 154(24), 152(27), 125(3), 111(6.36), 85(4)



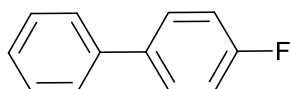
**[1, 1'-biphenyl]- 4- carbonitrile (3i):** White solid; yield: 0.136 g (77%); mp 84-86°C. **GC-MS m/z** (% relative intensity): 179(M+, 100), 151 (13), 126(5), 113(2), 100(3), 89(18), 73(10).



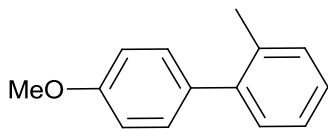
**4-chloro -1, 1'-biphenyl (3j):** White solid; yield: 0.147 g (79%); mp 70-72°C. **GC-MS m/z** (% relative intensity): 188(M+, 100), 153(33), 152(58), 76(27).



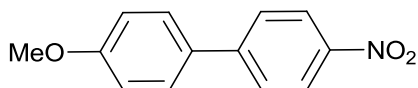
**4-bromo -1, 1'-biphenyl (3k):** Off white solid; yield: 0.190 g (82%); mp 89-90°C.  $^1\text{H NMR}$ : (300 MHz, d- DMSO, TMS):  $\delta$  7.64(m, 2H, Ar-H), 7.51(d, 2H, Ar-H), 7.55(m, 4H, Ar-H), 7.41(d, 1H, Ar-H). **GC-MS m/z** (% relative intensity): 232(M+, 77), 152 (100), 126(9), 116(5), 102(4), 87(3), 76(35).



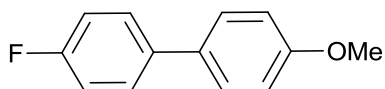
**4-fluoro -1, 1'-biphenyl (3l):**  $\delta$  7.91(m, 4H,Ar-H),7.75(d,2H,Ar-H), 7.49(m,3H,Ar-H).**GC-MS m/z** (% relative intensity): 172(M+, 100), 146 (3), 133(3), 120(2), 85(9), 83(15).



**4'- methoxy-2- methyl-1, 1'- biphenyl (3m):** Pale yellow solid; yield: 0.137 g (70%); mp 120-122°C. **GC-MS m/z** (% relative intensity): 198(M+, 100), 183 (16), 167(34),153(11), 128(4),115(6), 99(3), 89(3),77(6).



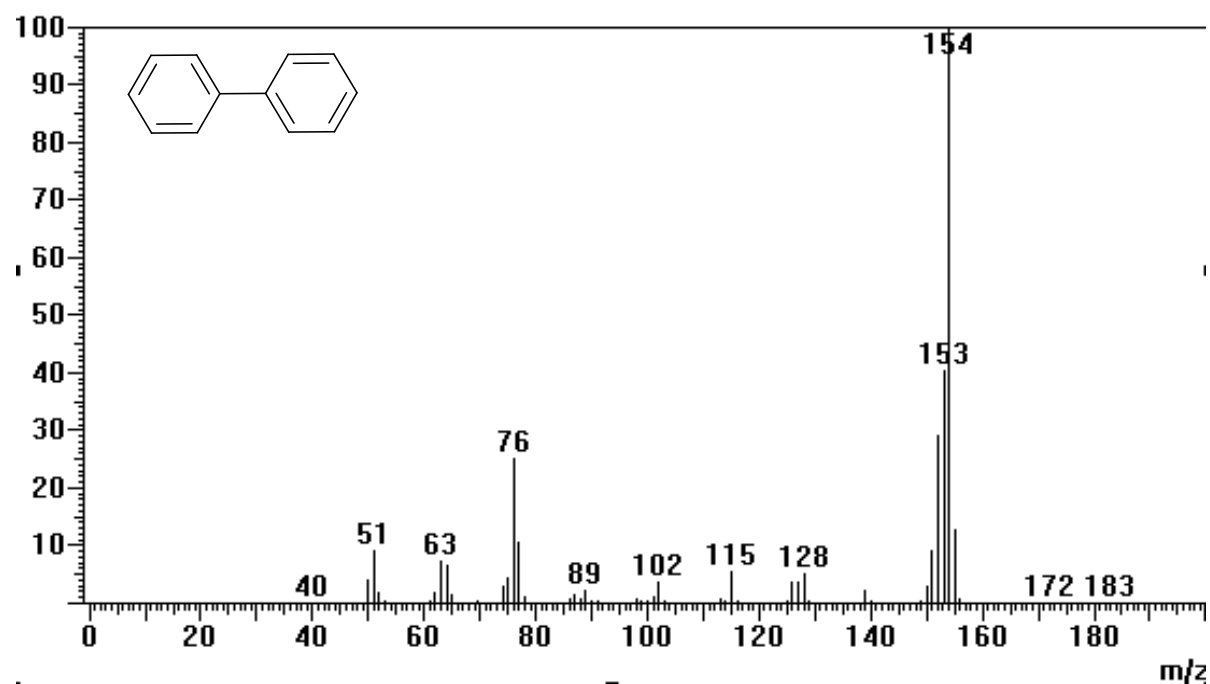
**4- methoxy-4'- nitro-1, 1'- biphenyl (3n):** Pale yellow solid: 0.174 g (76%); mp 108-110°C. **<sup>1</sup>H NMR:** (300 MHz, d- DMSO, TMS):  $\delta$ 8.28(d, 2H,Ar-H),7.91(d, 2H,Ar-H), 7.79(d, 2H,Ar-H), 7.10(d,2H,Ar-H), 3.82(s,3H, CH<sub>3</sub>), **GC-MS m/z** (% relative intensity): 229(M+, 100), 214 (2), 199(2), 183(7), 168(45), 156(3), 140(26), 139(64), 113(4), 102(6), 89(5), 75(3).



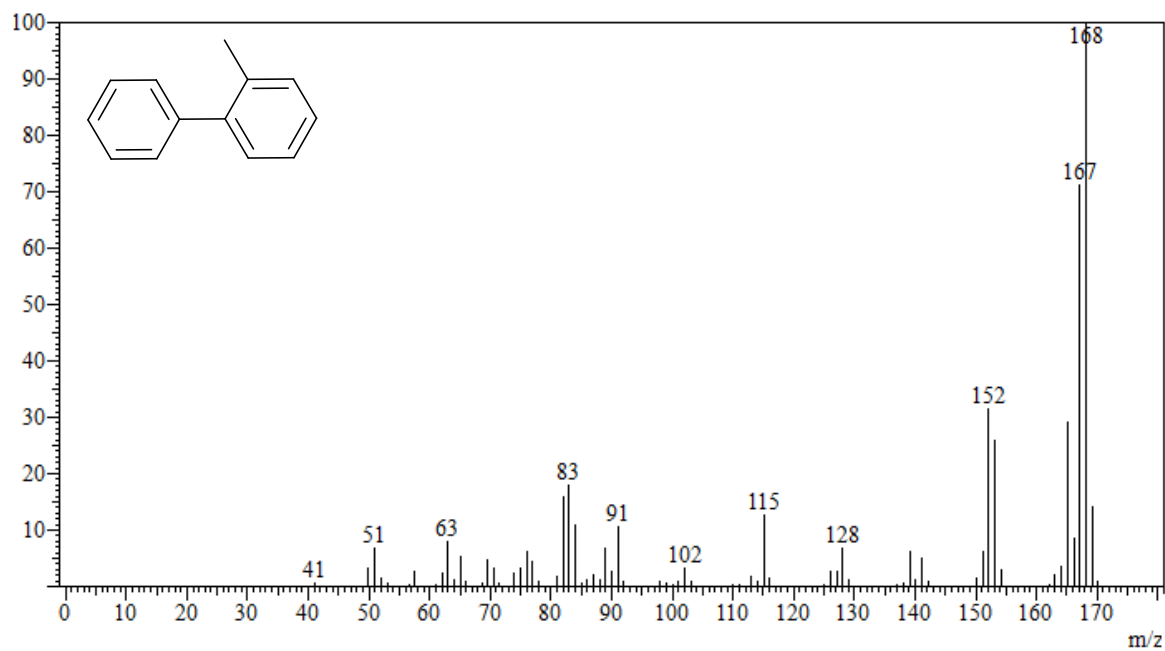
**4- fluoro- 4'- methoxy-1, 1'- biphenyl (3o):** White solid; yield: 0.155 g (77%); mp 85-86°C. **<sup>1</sup>H NMR:** (300 MHz, d- DMSO, TMS):  $\delta$ 7.63(d, 2H,Ar-H),7.58(m,2H, Ar-H), 7.26(d,2H, Ar-H), 7.02(d, 2H,Ar-H), 3.79(s,3H -OCH<sub>3</sub> ). **GC-MS m/z** (% relative intensity): 202(M+, 100), 187 (68),170( 6), 159(64), 144( 2) 133(47), 120(3), 101(7), 83(5)

# $^1\text{H}$ NMR and GC-MS data of the product:

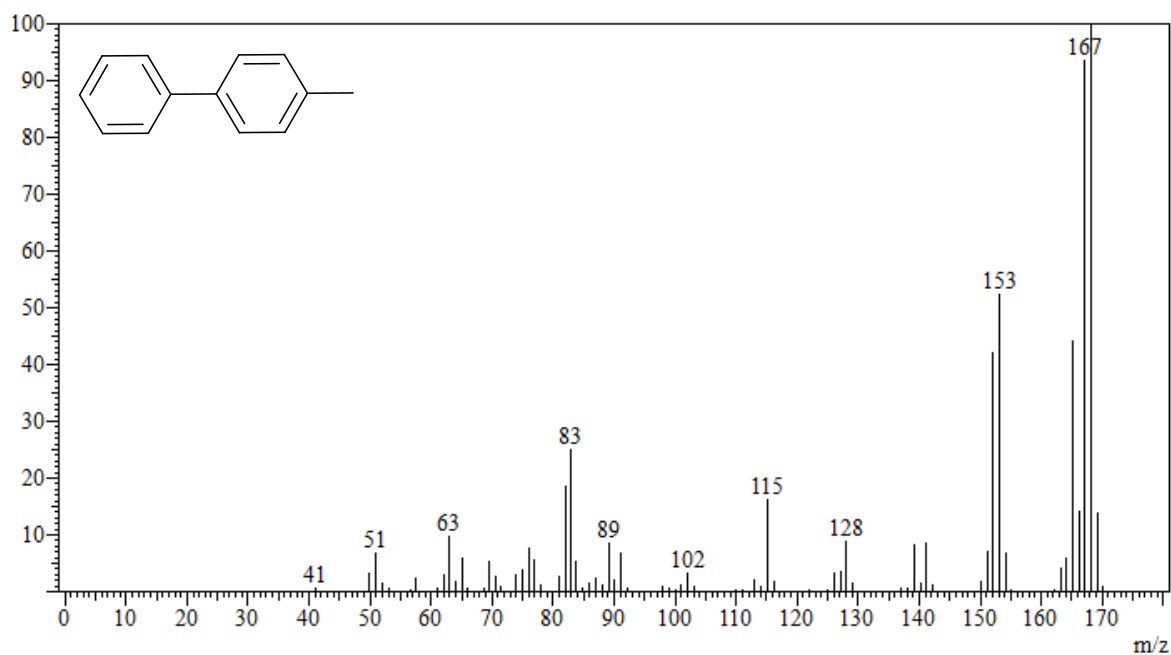
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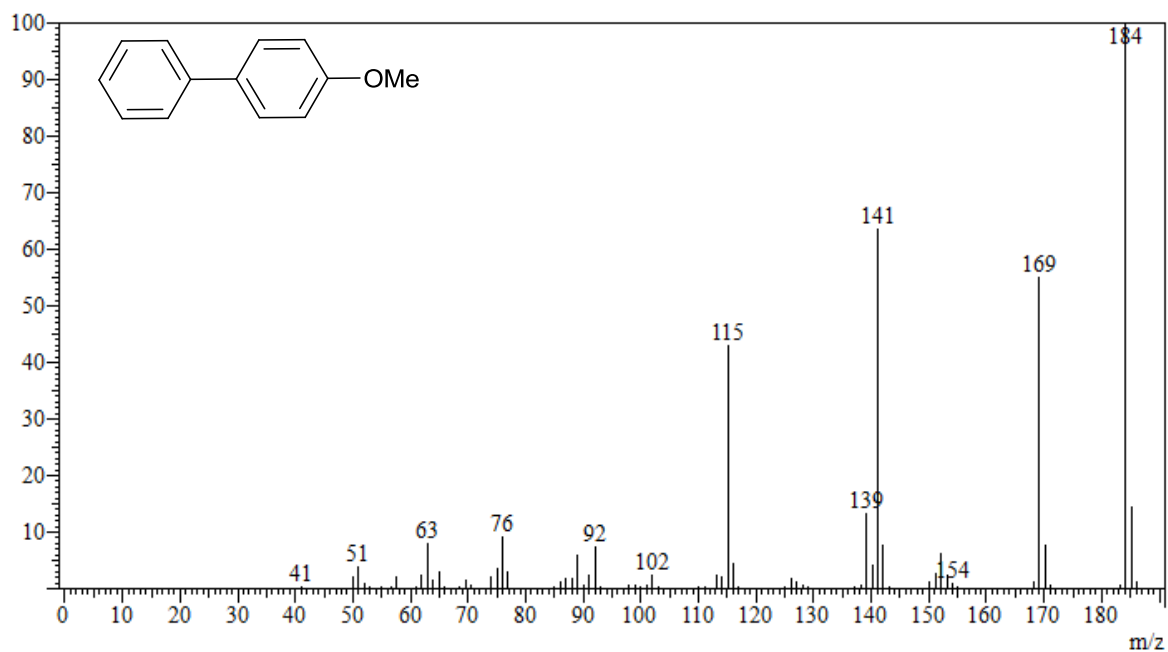
## 2-methyl-1,1'-biphenyl (3b):

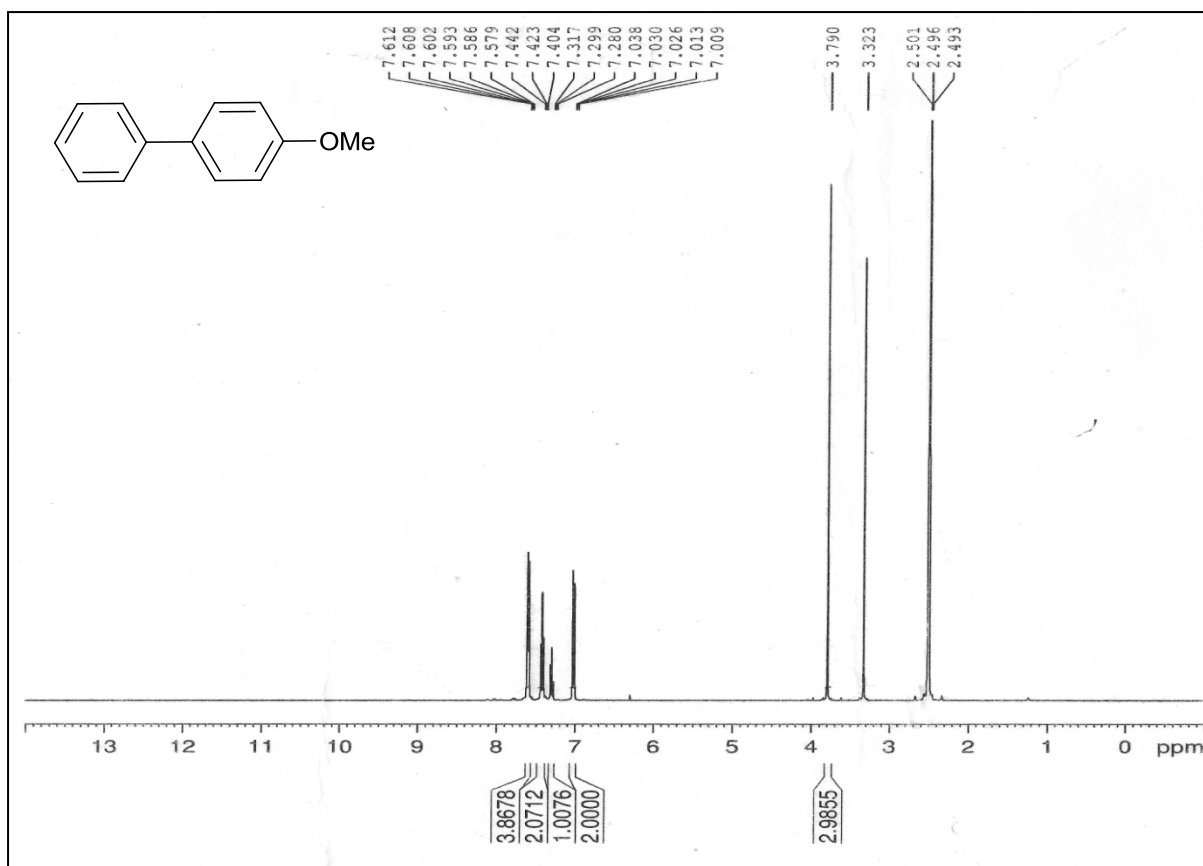


**4-methyl-1, 1'-biphenyl (3c):**

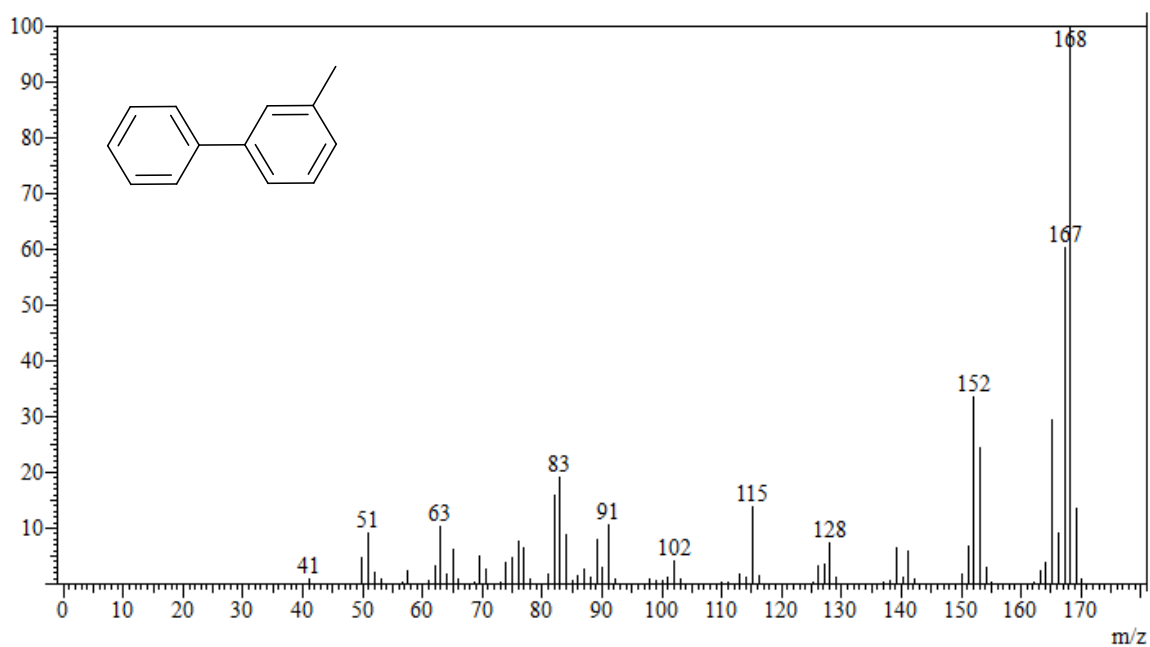


**4-methoxy-1, 1'-biphenyl (3d):**



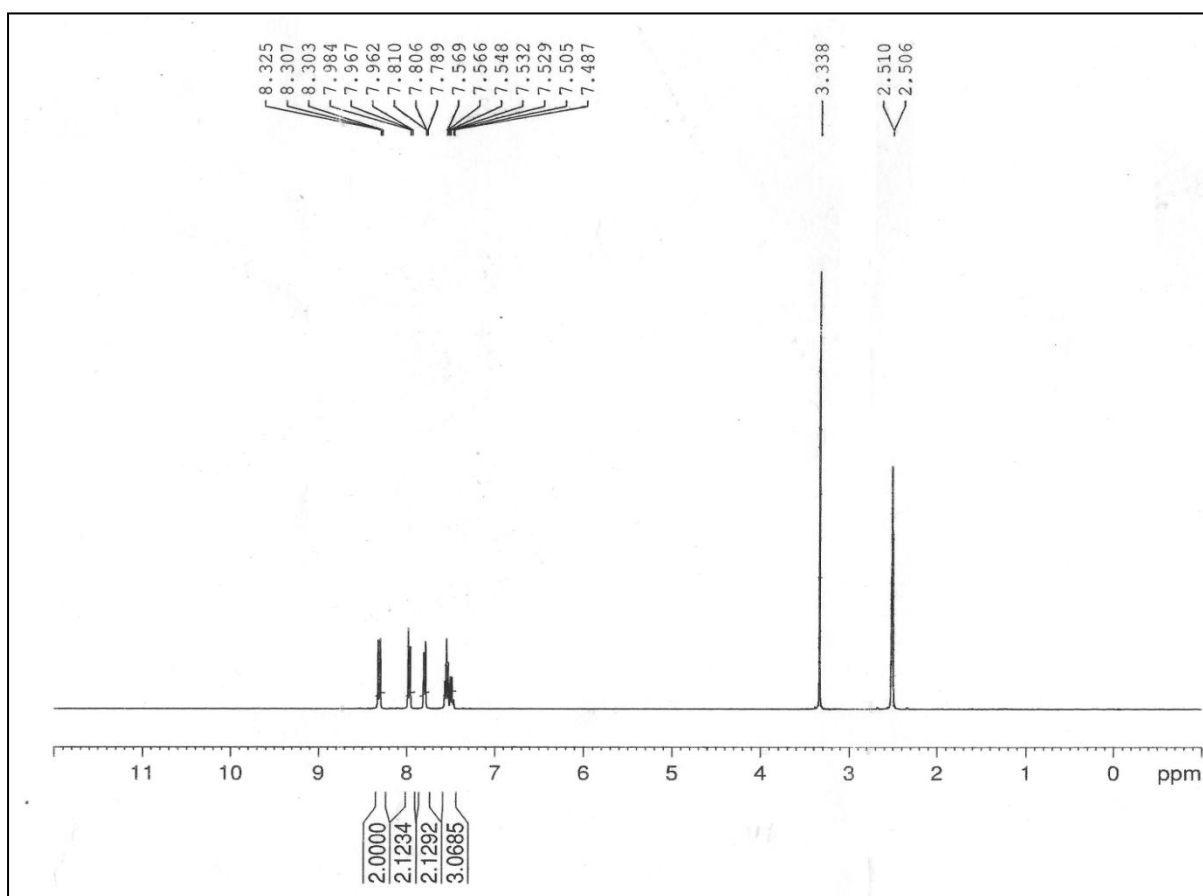
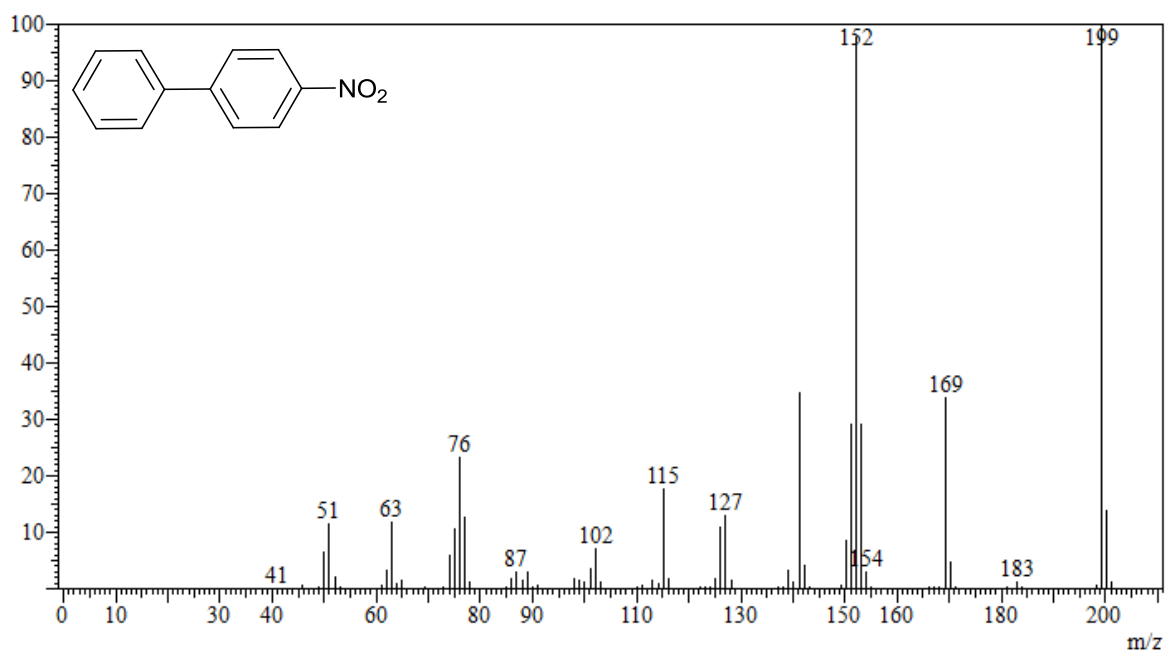


**3-methyl-1, 1'-biphenyl:**

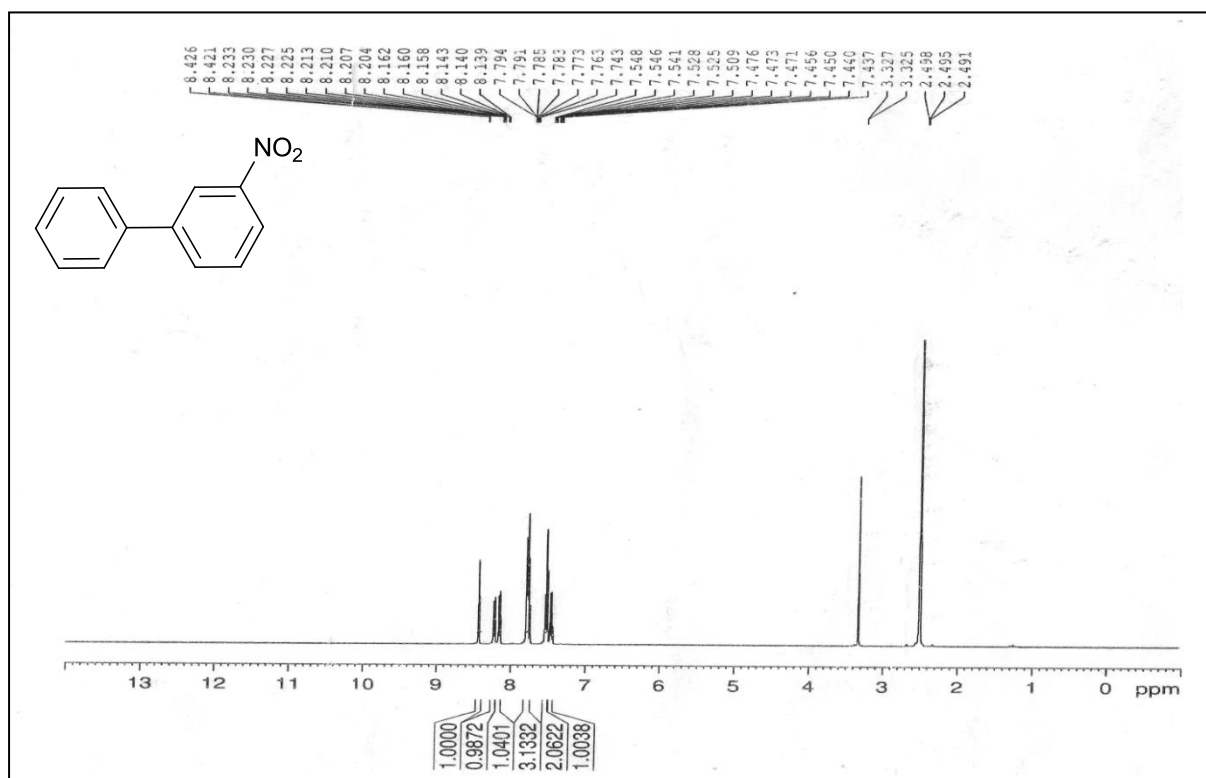
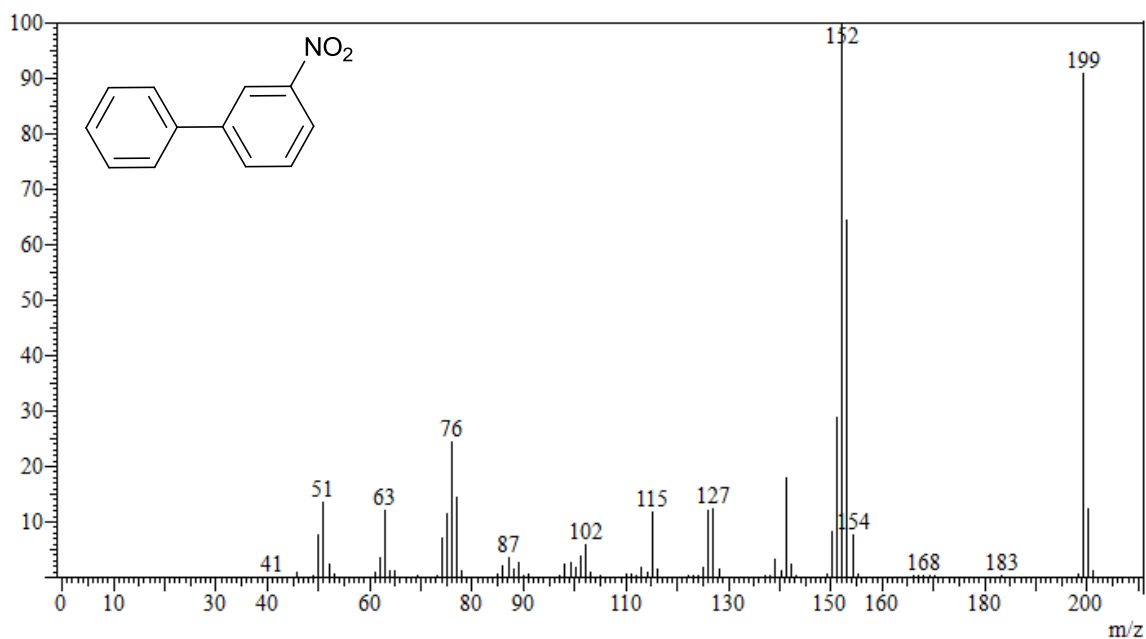




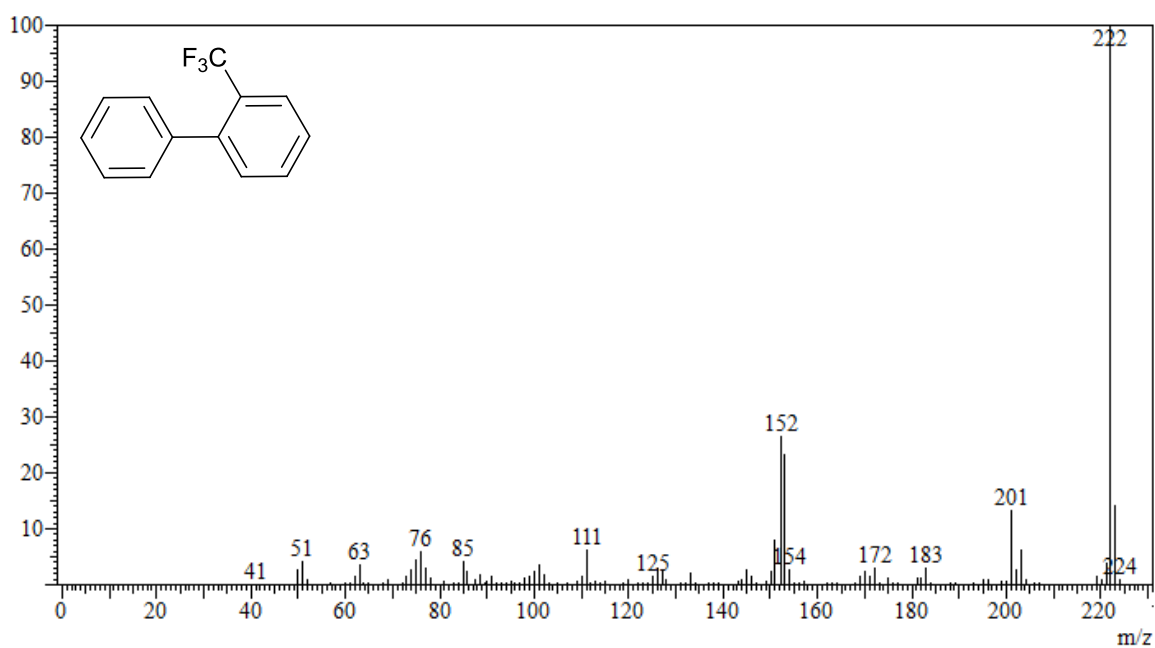
**4-nitro-1, 1'-biphenyl:**



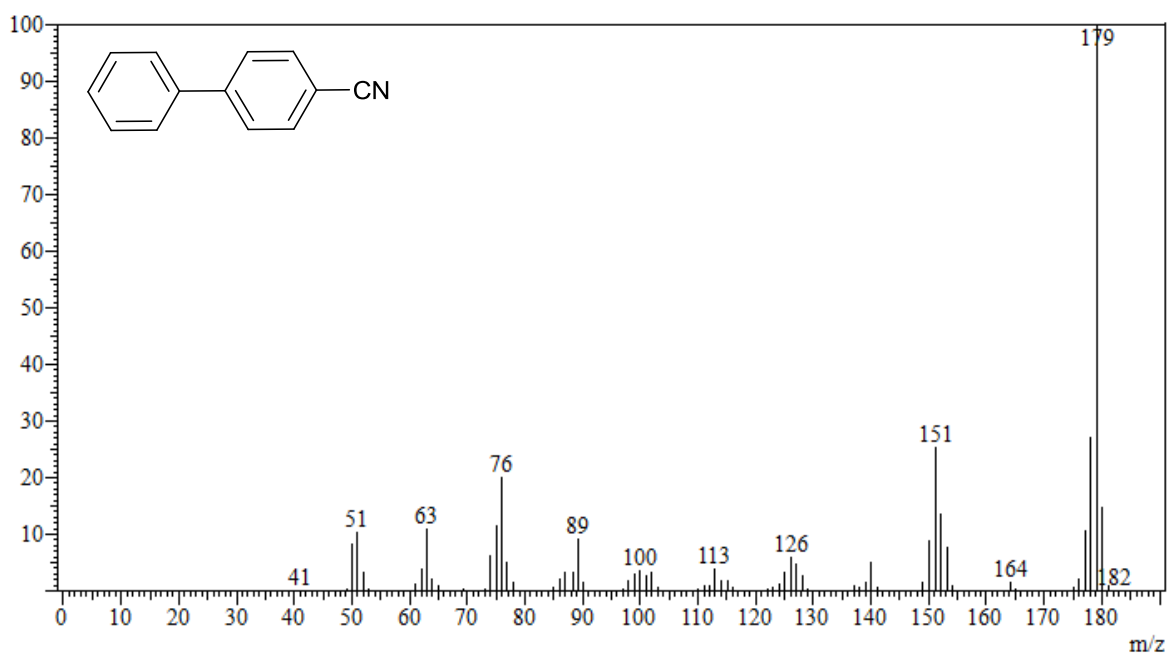
**3-nitro-1, 1'-biphenyl:**



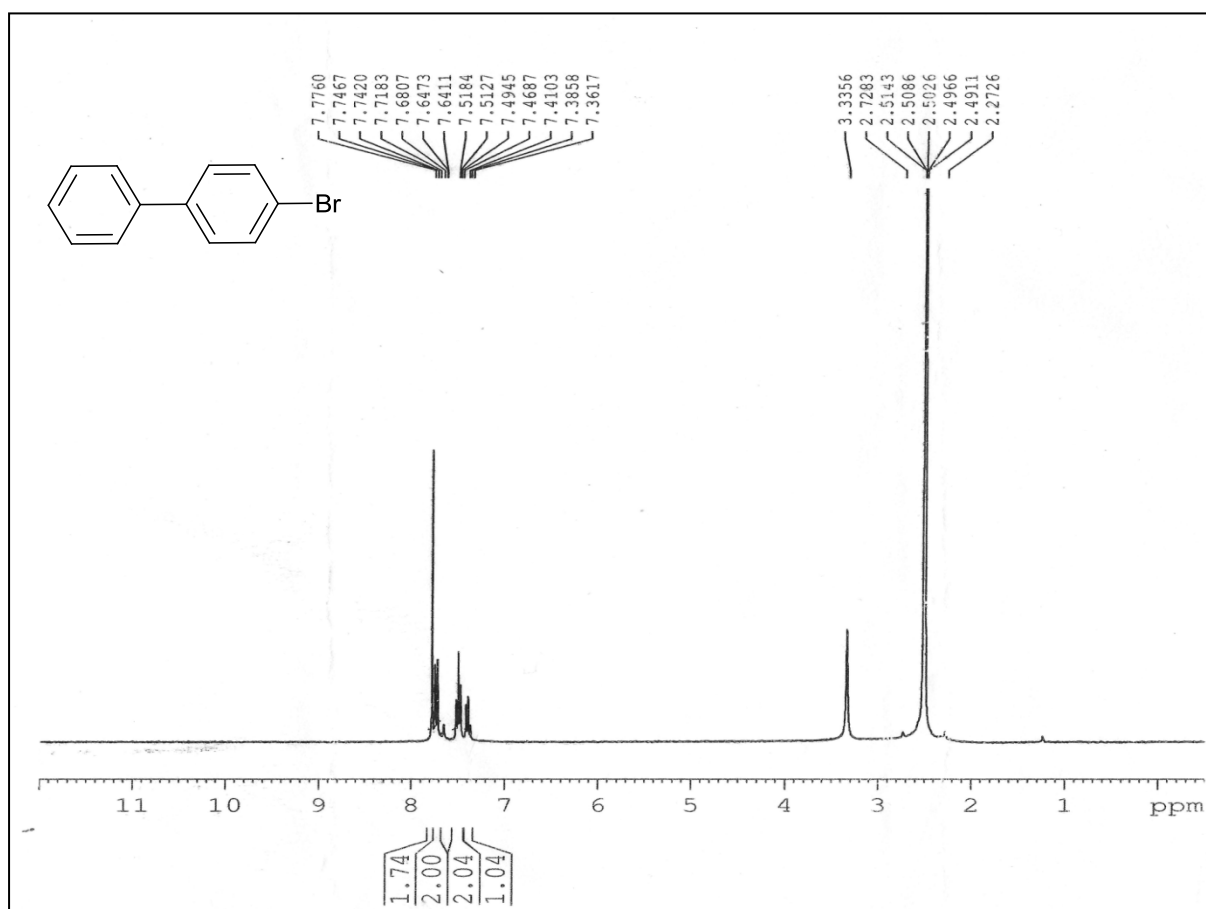
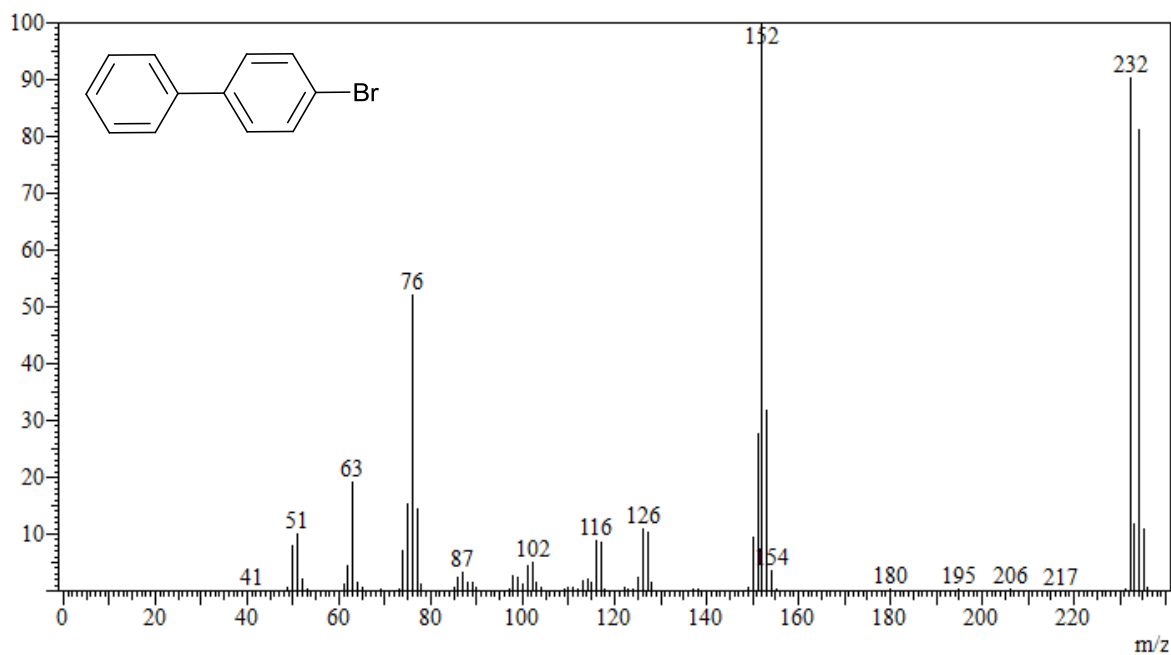
**2-(trifluoromethyl)-1, 1'-biphenyl (3h):**



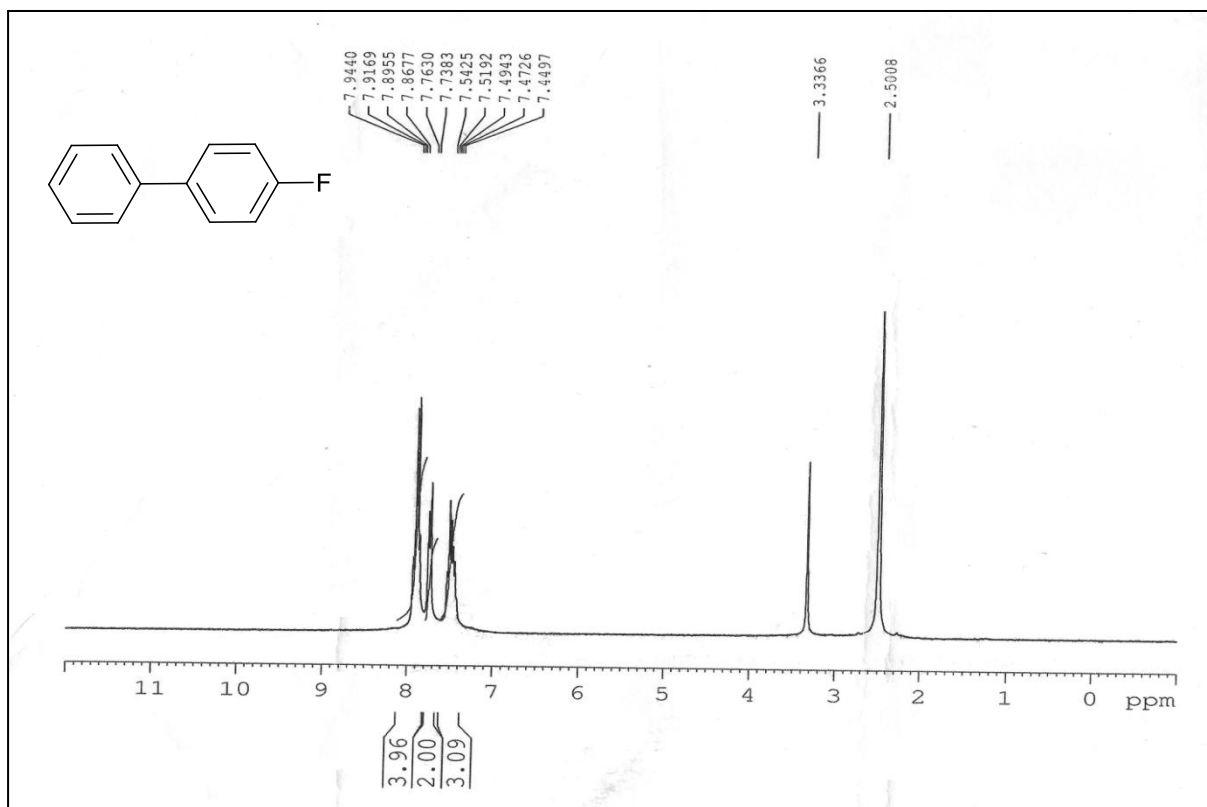
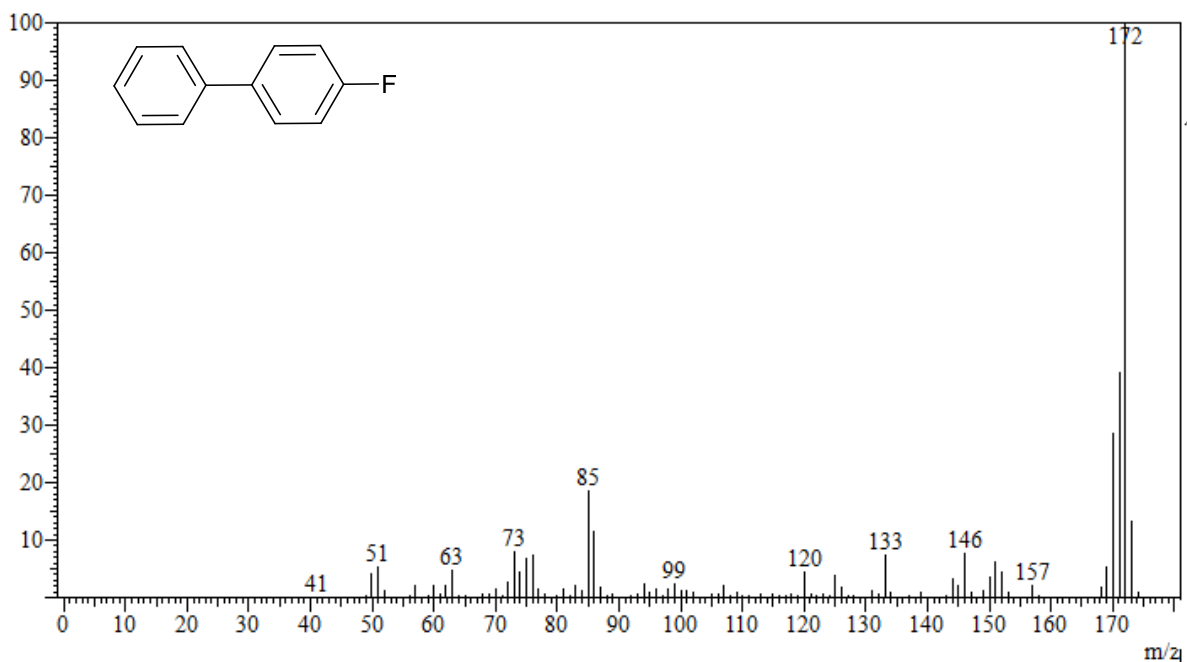
**[1, 1'-biphenyl]- 4- carbonitrile (3i):**



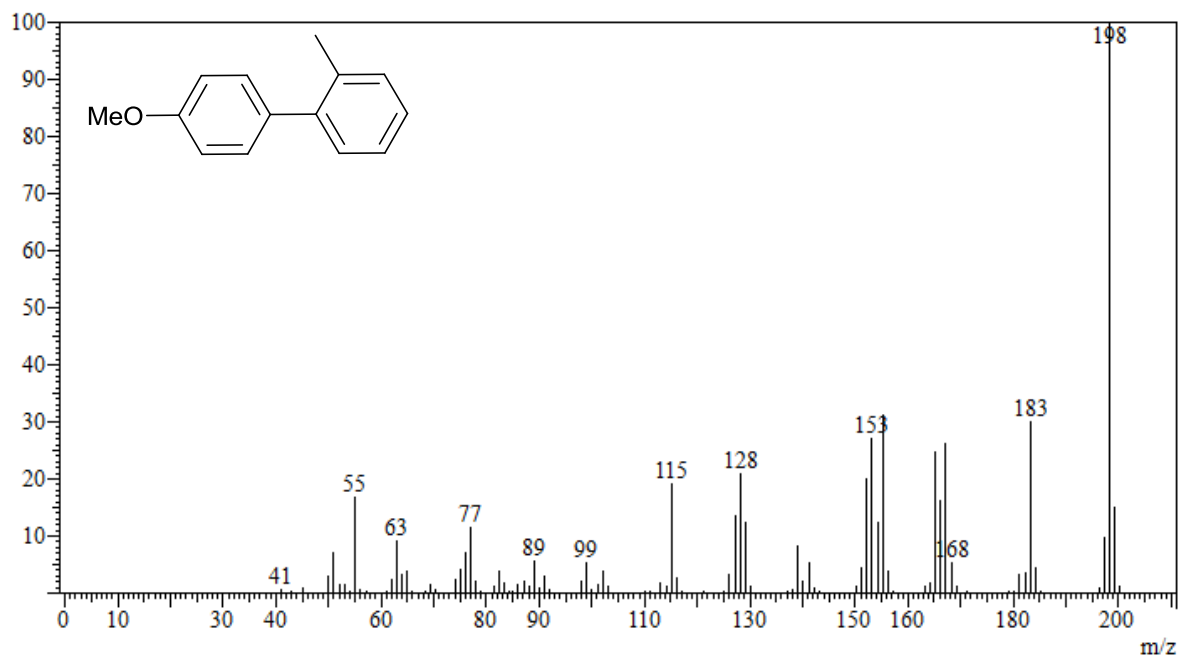
**4-bromo -1, 1'-biphenyl (3k):**



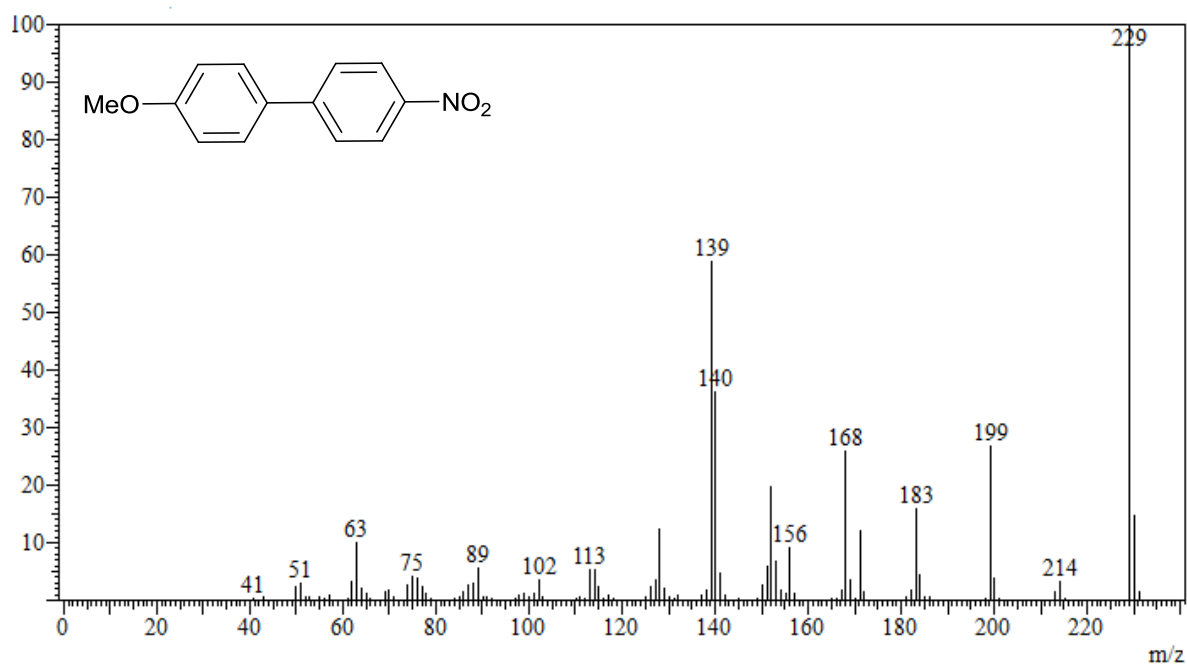
**4-fluoro -1, 1'-biphenyl (3l):**

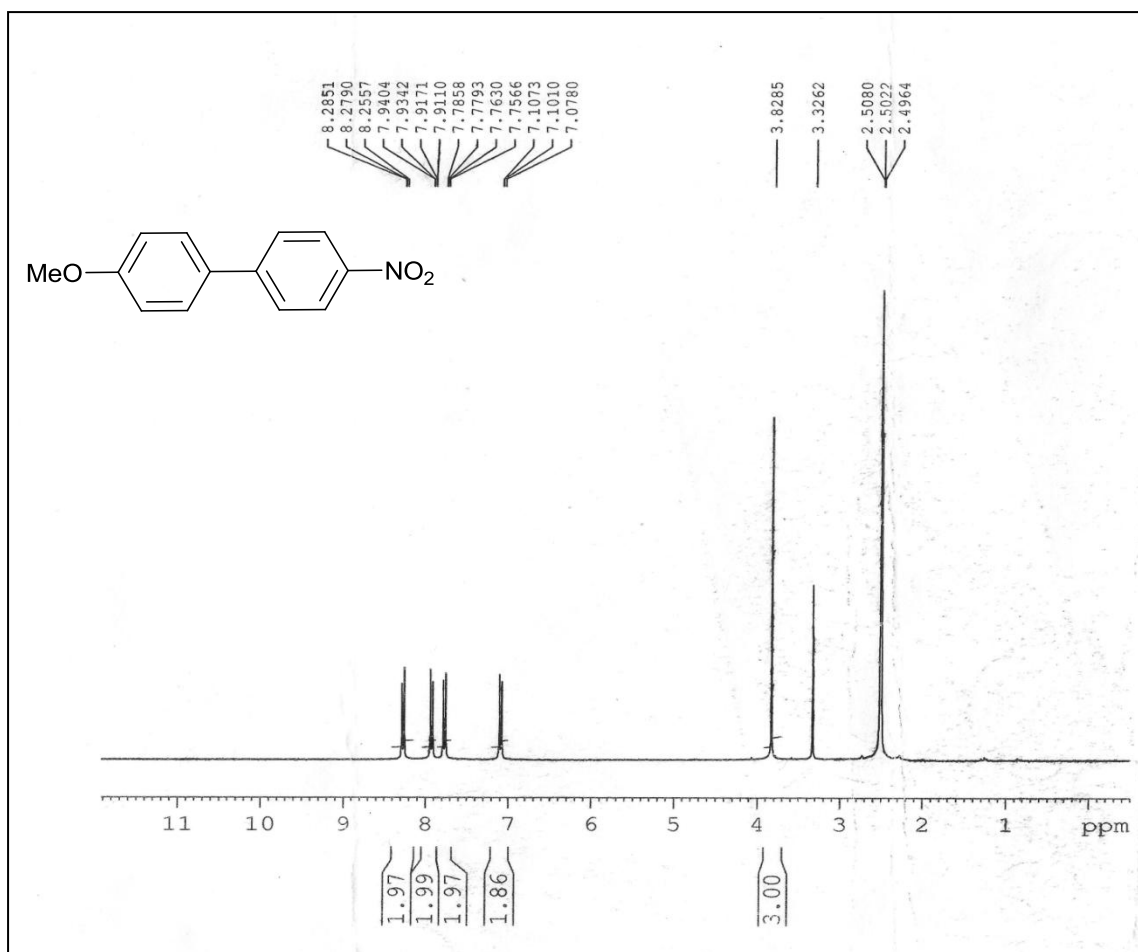


**4'- methoxy-2- methyl-1, 1'- biphenyl (3m):**

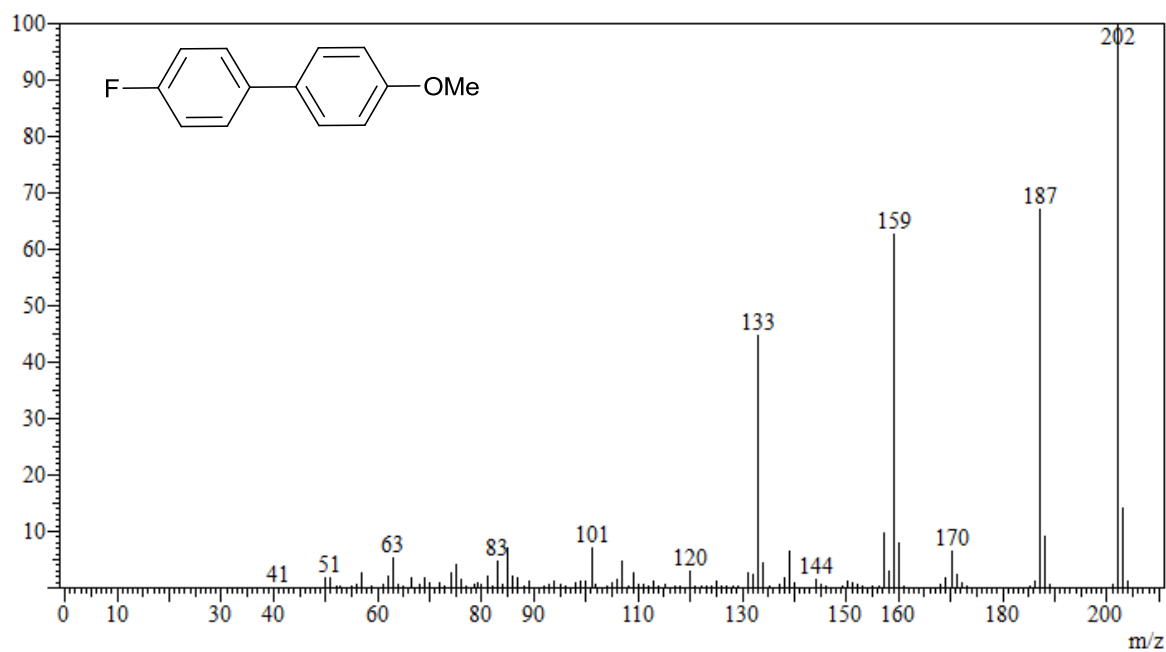


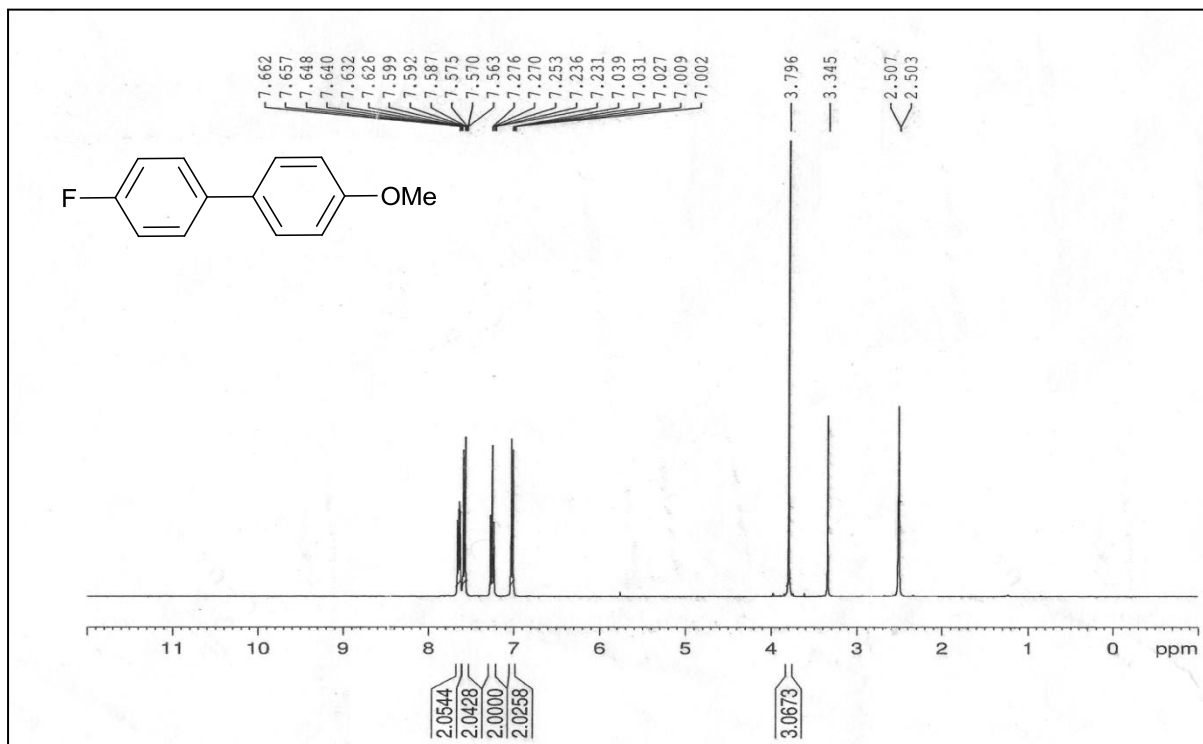
**4- methoxy-4'- nitro-1, 1'- biphenyl (3n):**





**4- fluoro- 4'- methoxy-1, 1'- biphenyl (3o):**







## References

- 1) A. Boudier, P. R. Breuil , L. Magna , H. Bourbigou ,P. Braunstein, *J. Organo. Chem.*2012, **718**, 31- 37
- 2) K. Cheng, C. Wang, Y. Ding, Q. Song, C. Qi, X. M. Zhang, *J. Org. Chem.* ,2011, **76**, 9261