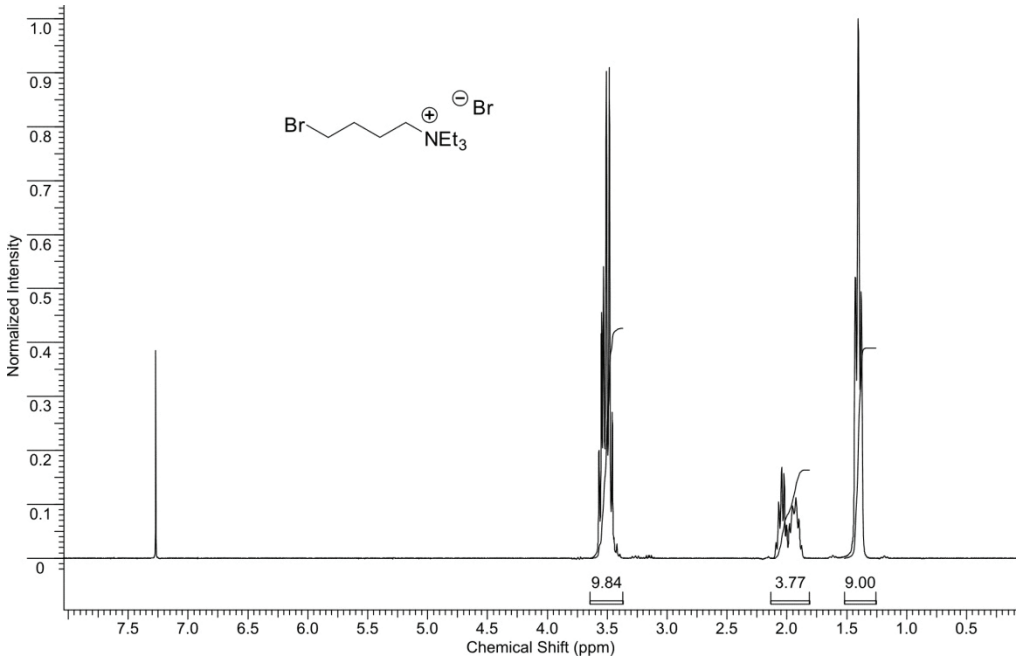
Supplementary Material (ESI) for Green Chemistry

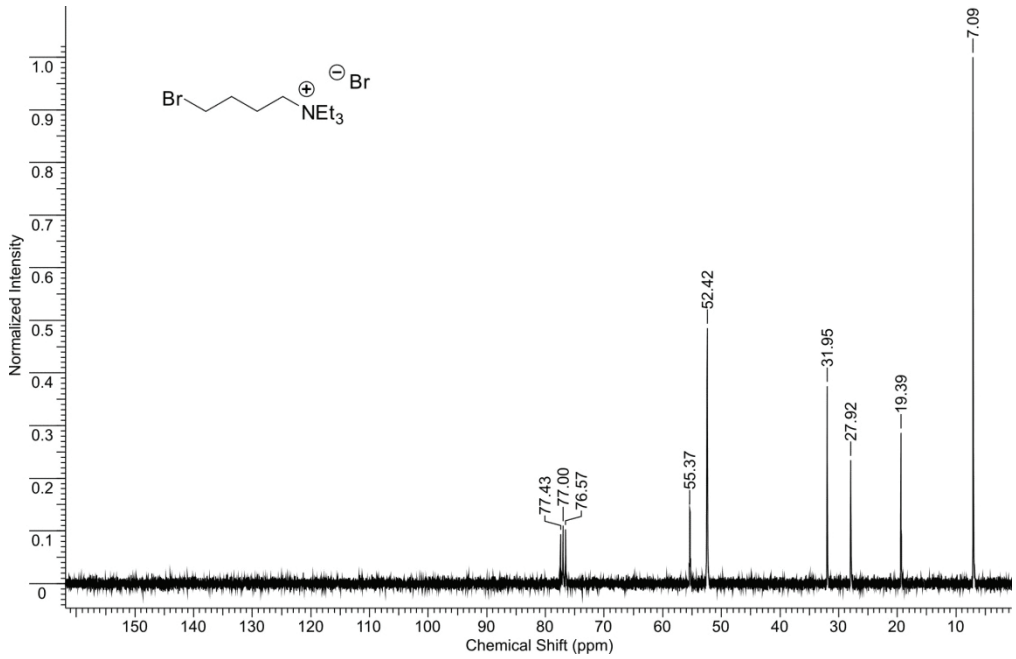
A Recyclable Triethylammonium Ion-Tagged Diphenylphosphine Palladium Complex for the Suzuki-Miyaura Reaction in Ionic Liquids

Marco Lombardo,* Michel Chiarucci and Claudio Trombini

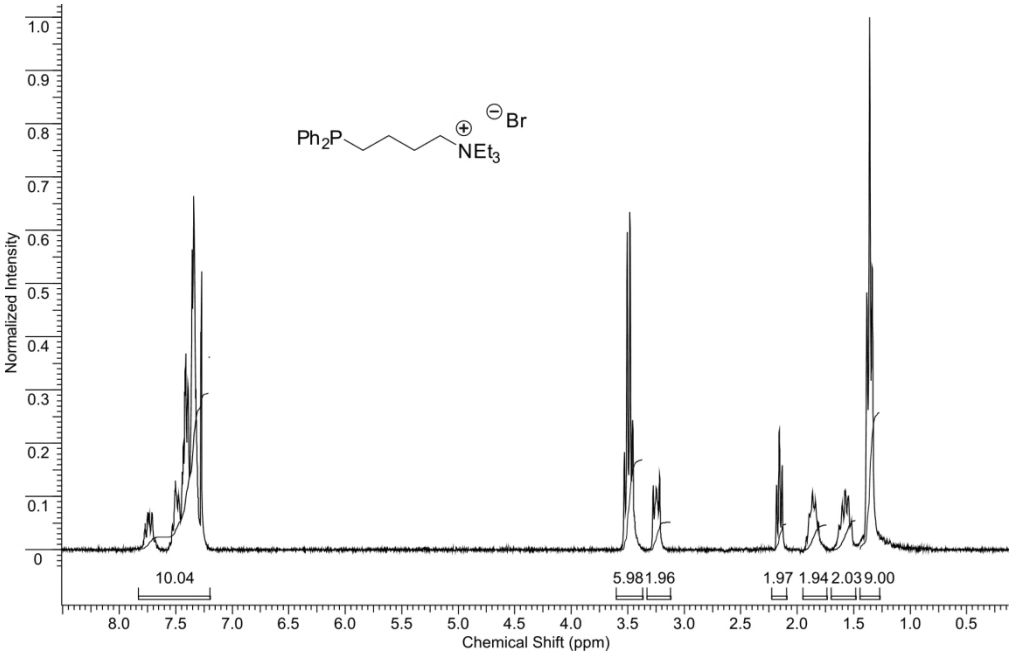
Synthesis of ligand 1

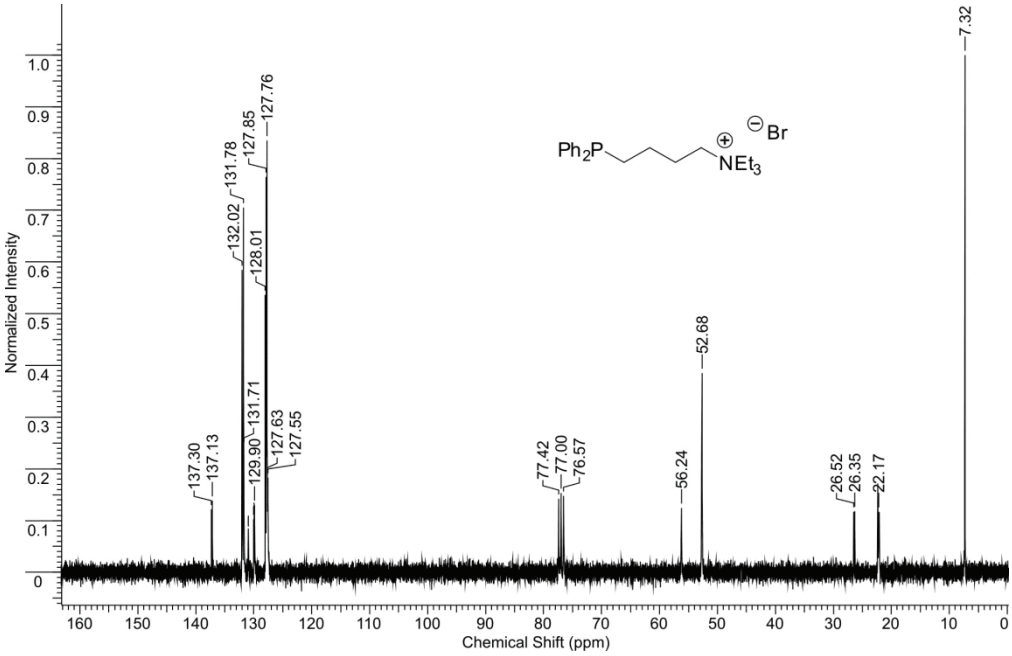
4-Bromobutyl-triethyl-ammonium bromide



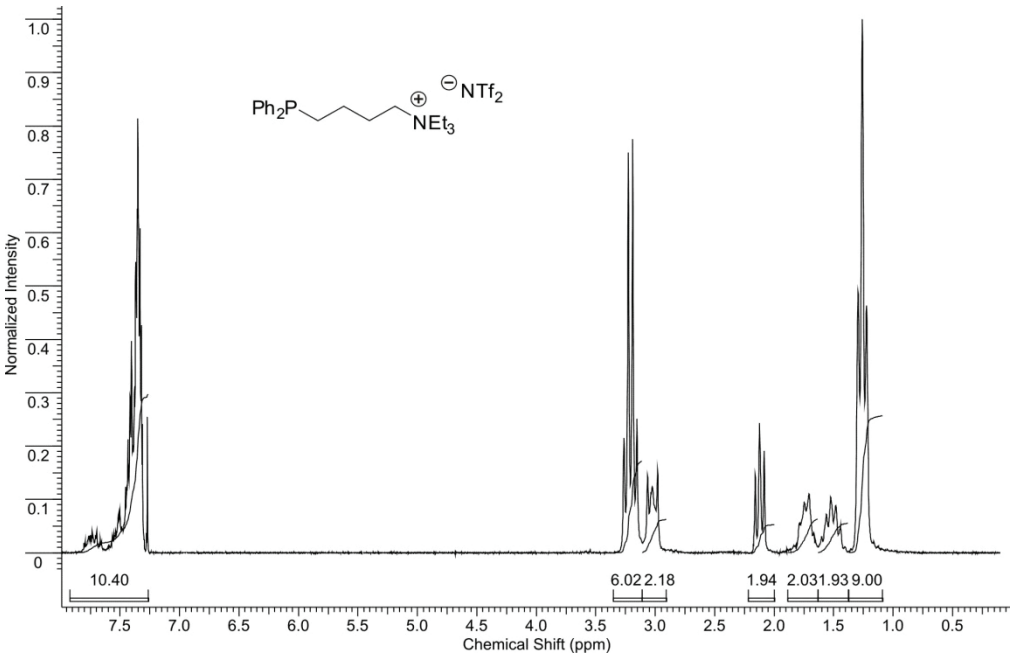


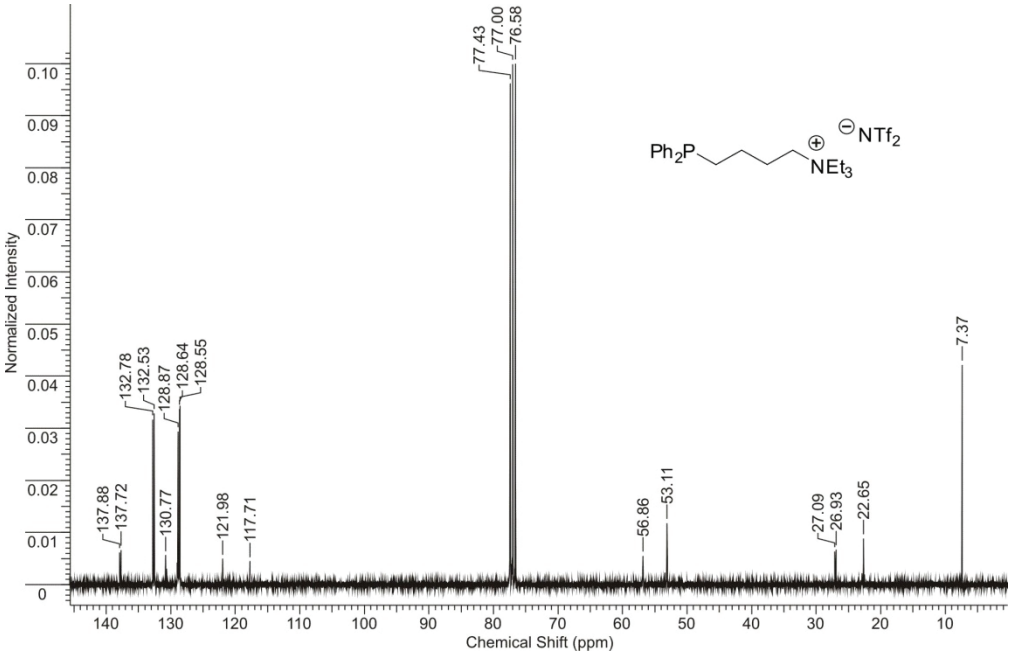
4- Diphenylphosphinobutyl-triethyl-ammonium bromide



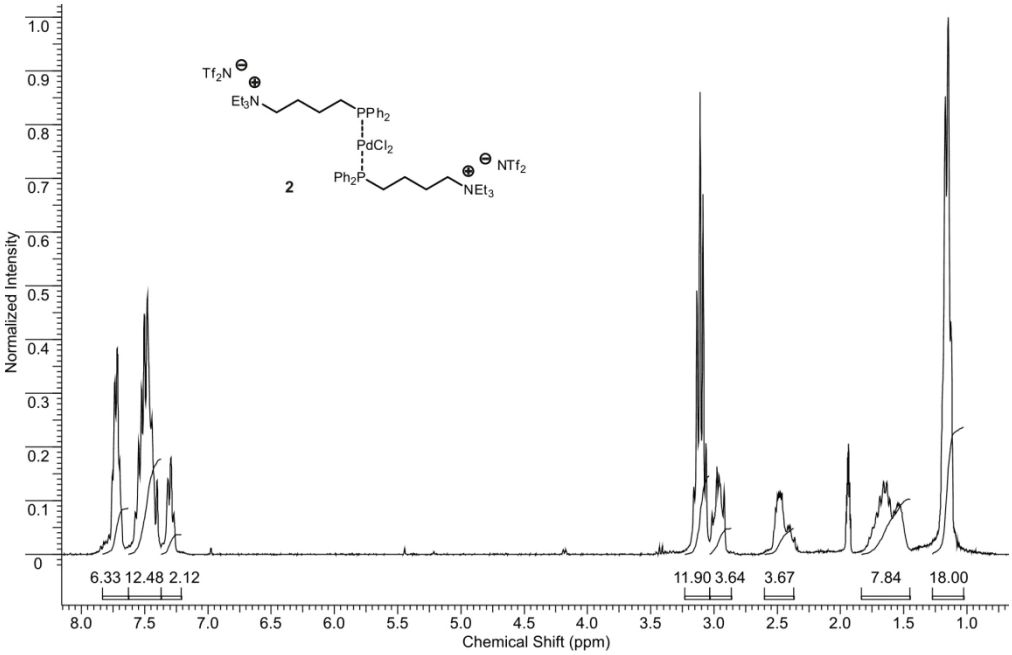


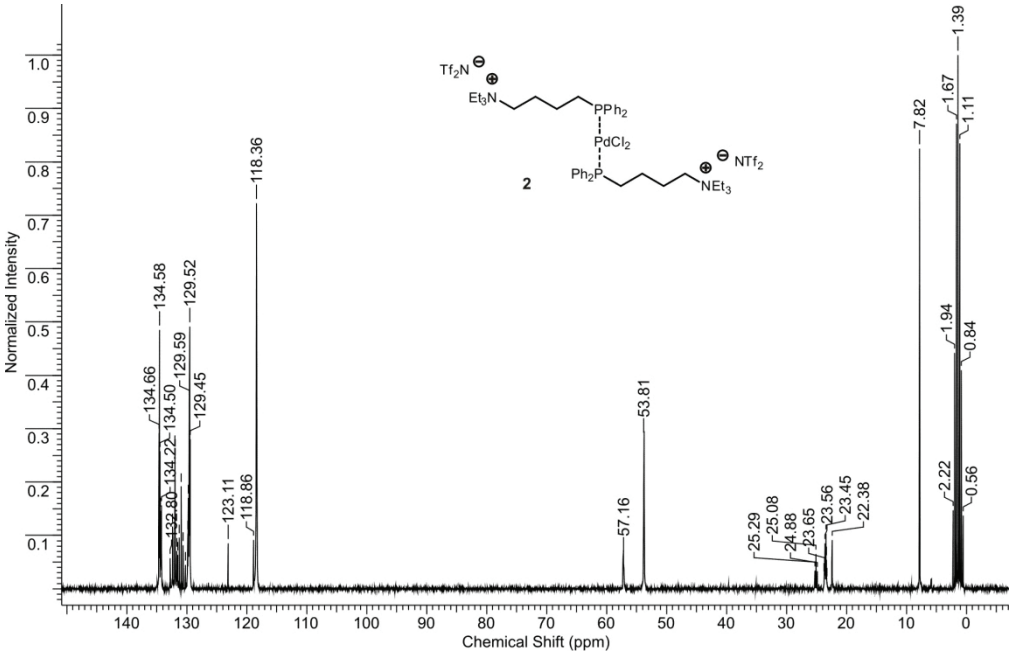
4-Diphenylphosphinobutyl-triethyl-ammonium bis(trifluoromethylsulfonyl) imide (1)



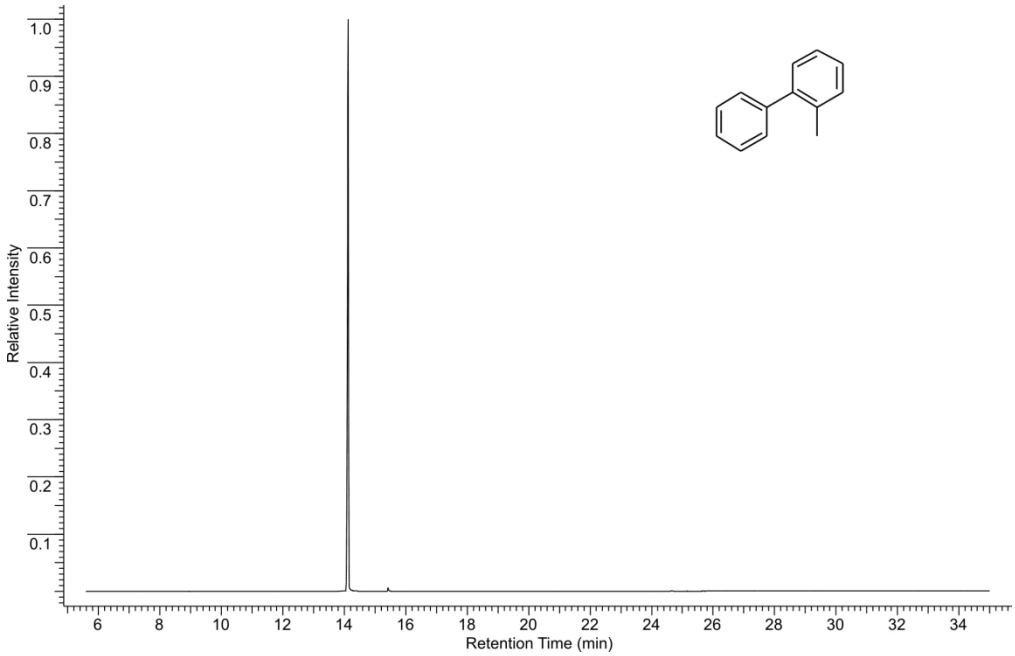


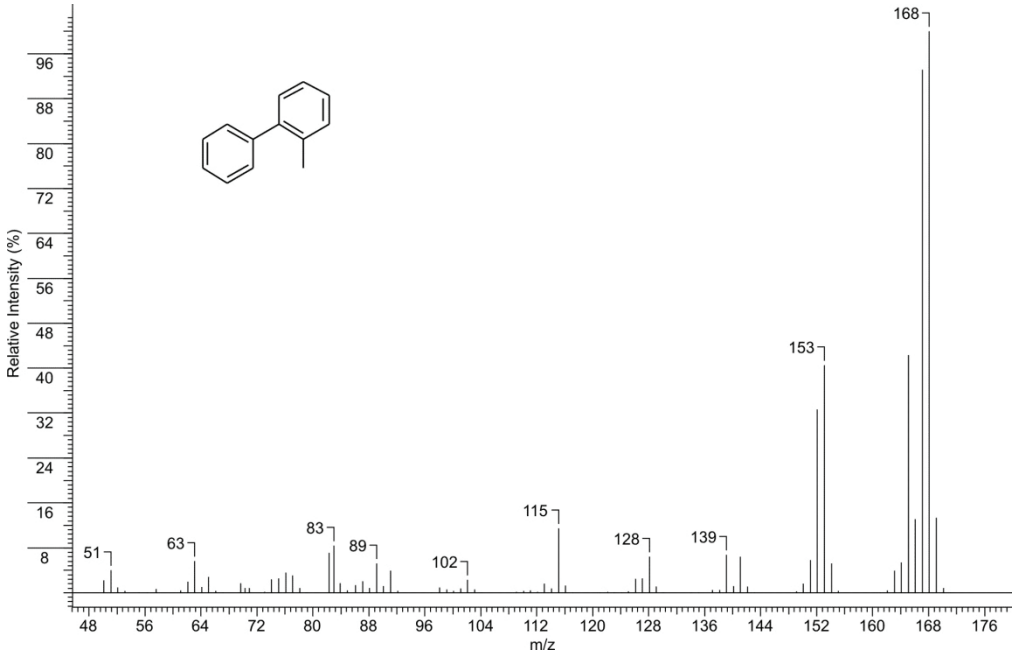
Synthesis of $L_2 \cdot PdCl_2$ (2)

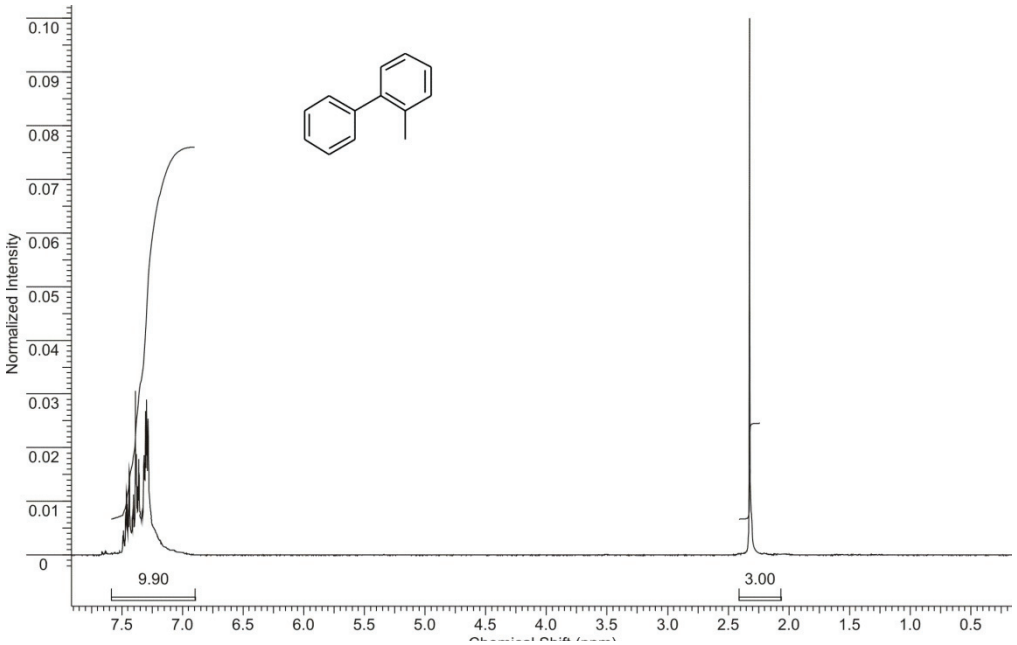


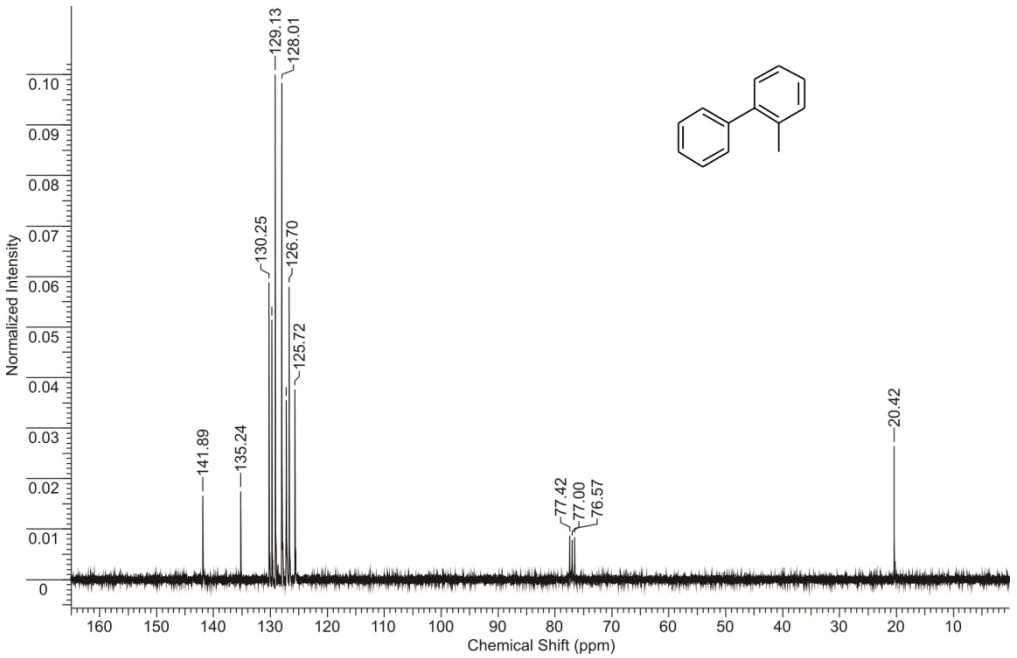


2-Methylbiphenyl (Table 1, Entry 1)









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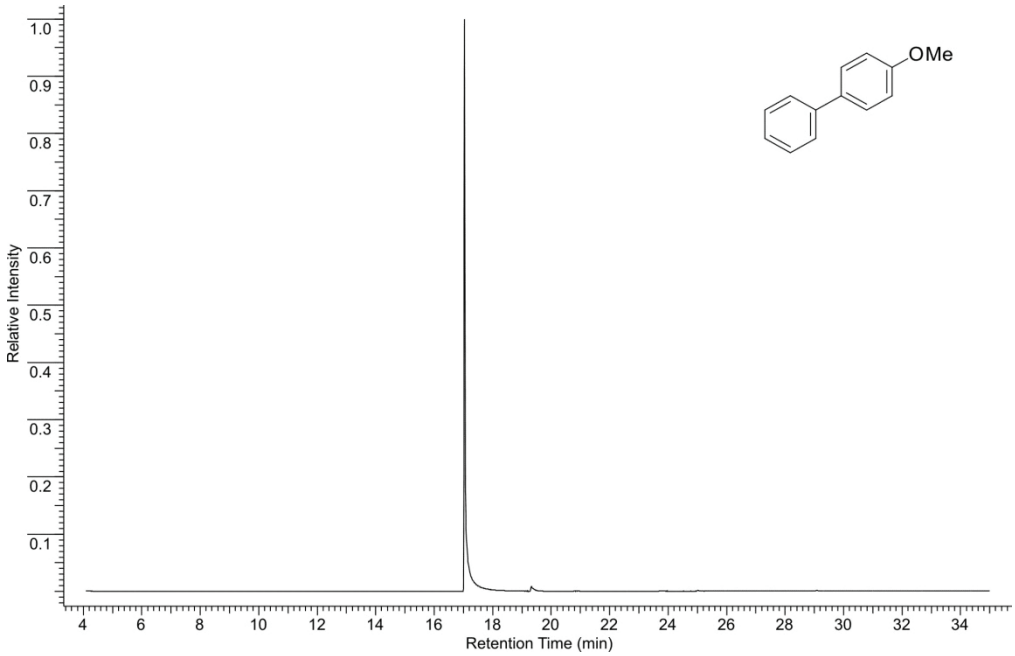
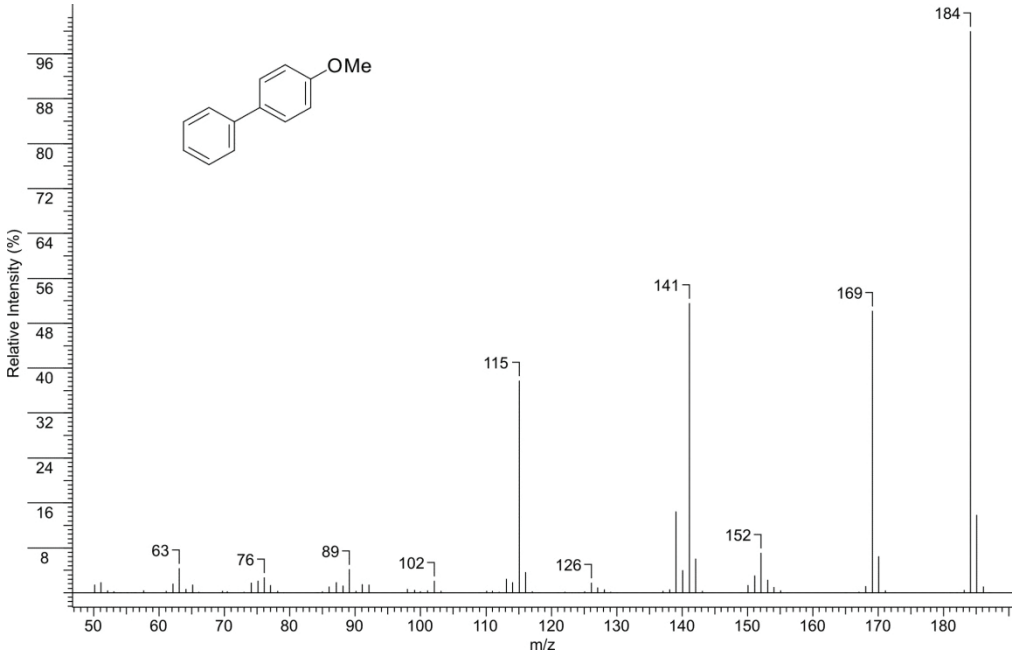
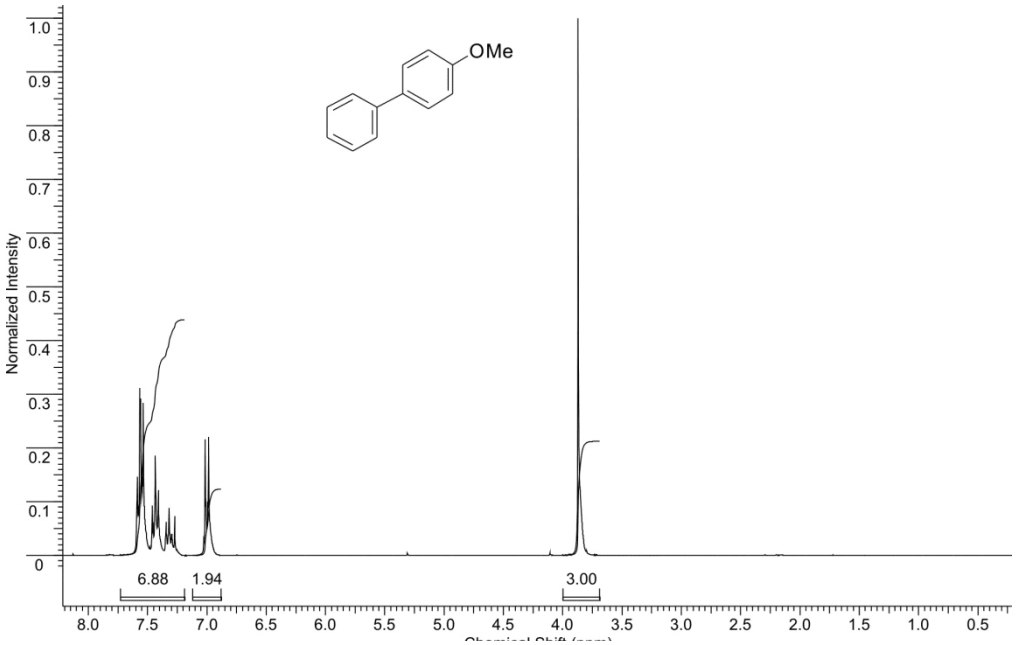
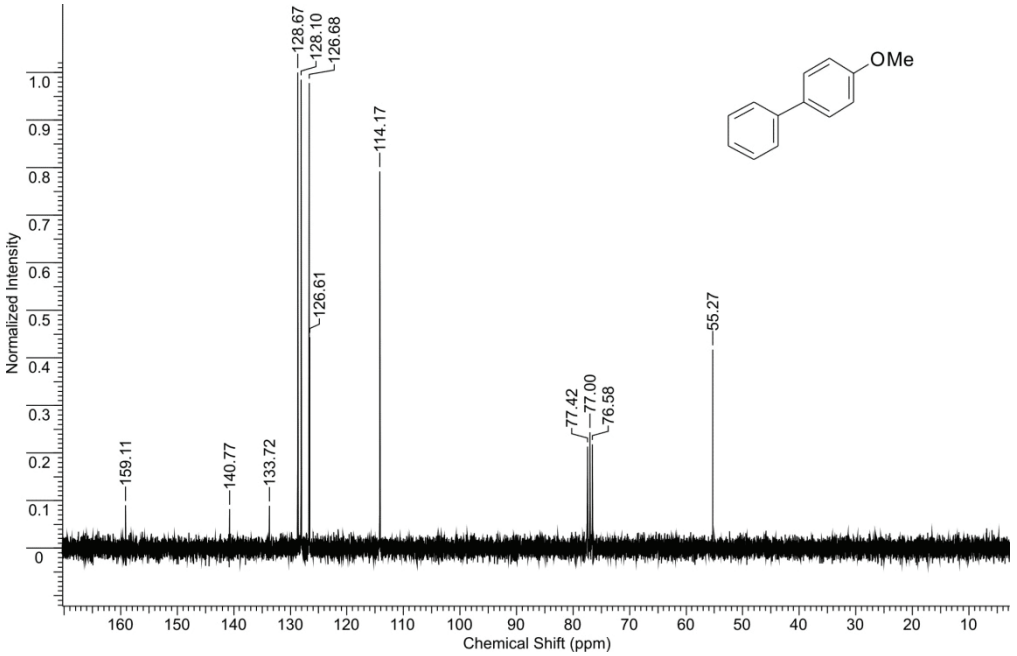
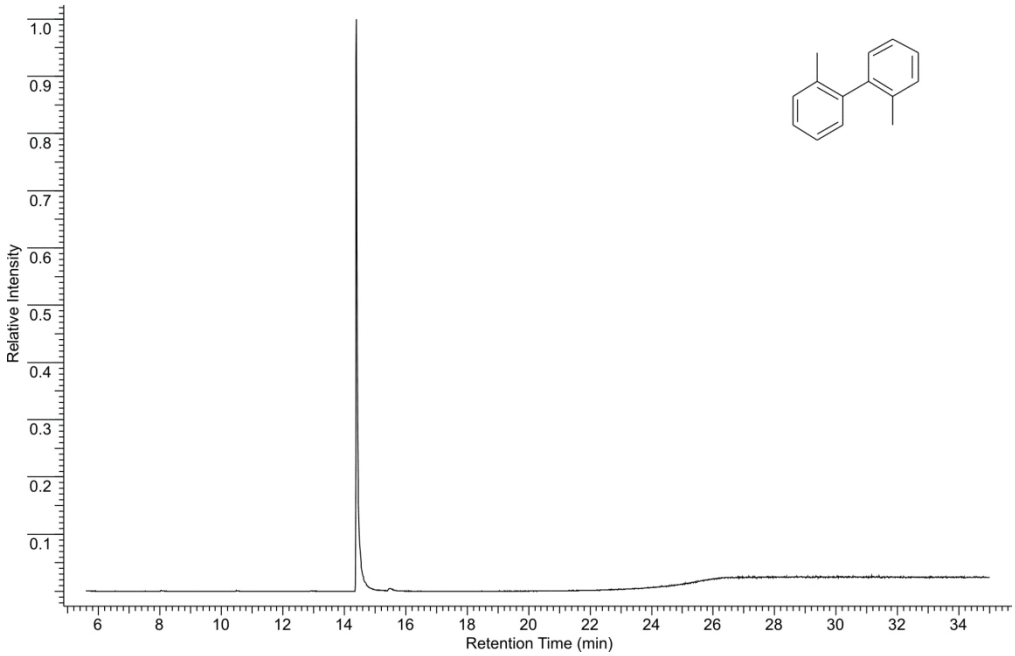


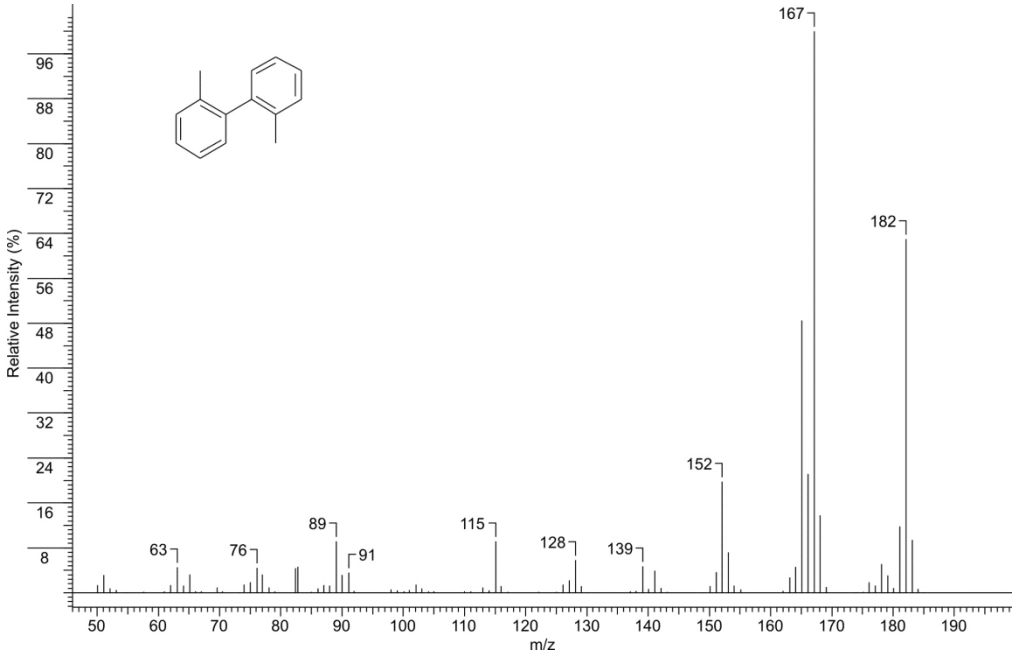


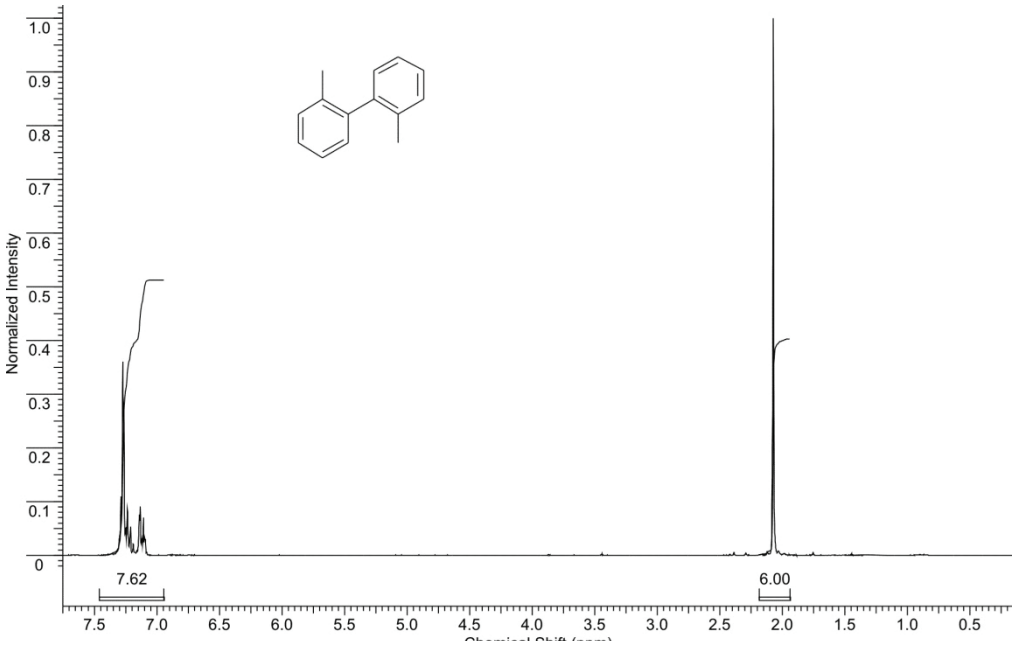


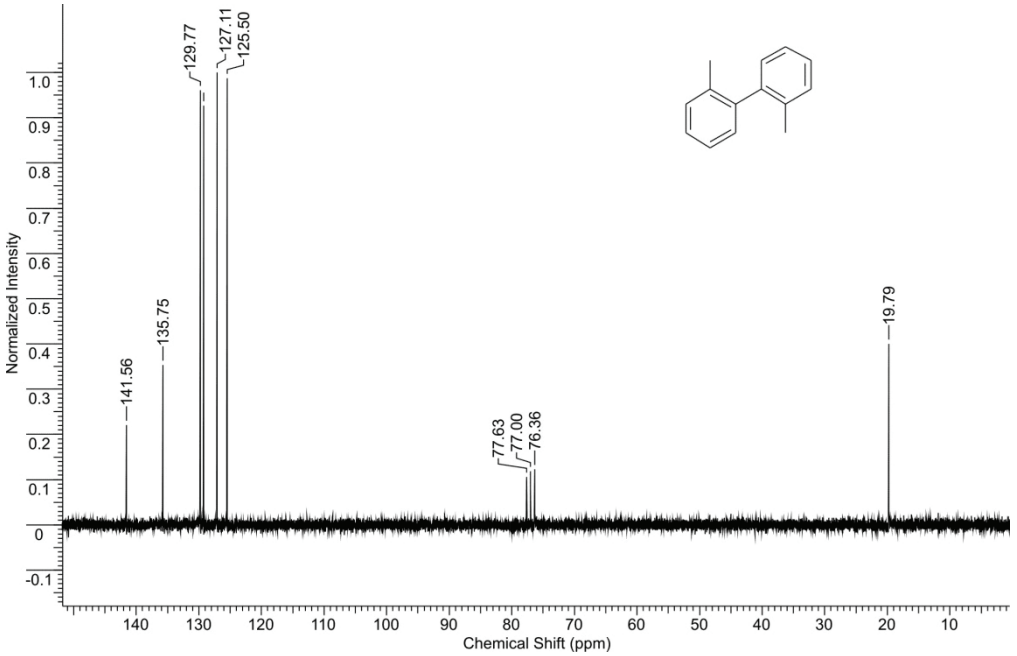


2,2'-Dimethylbiphenyl (Table 1, Entry 3)

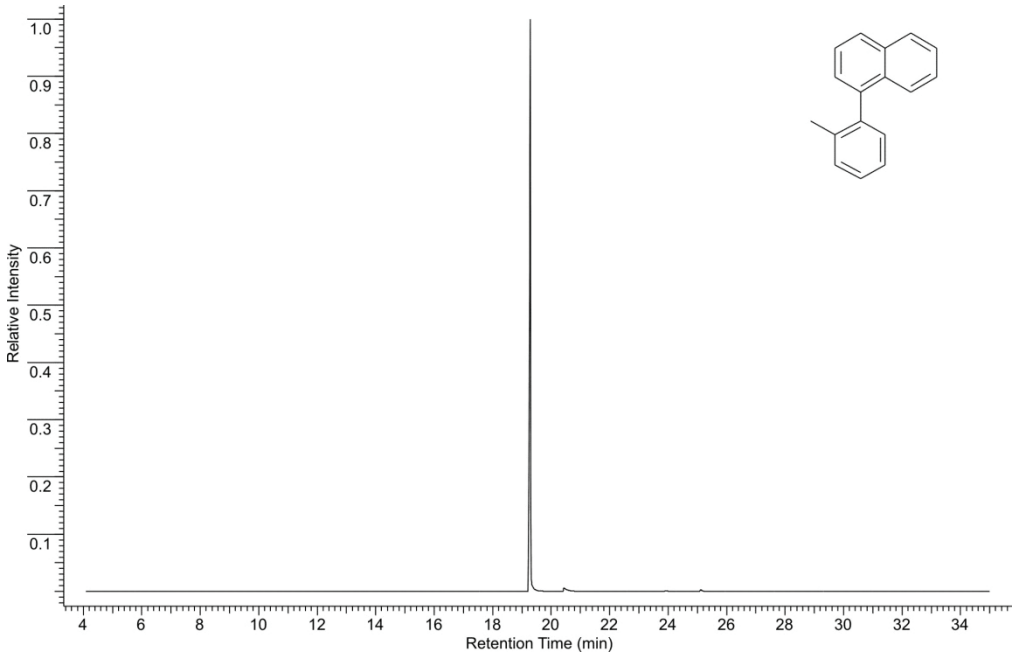


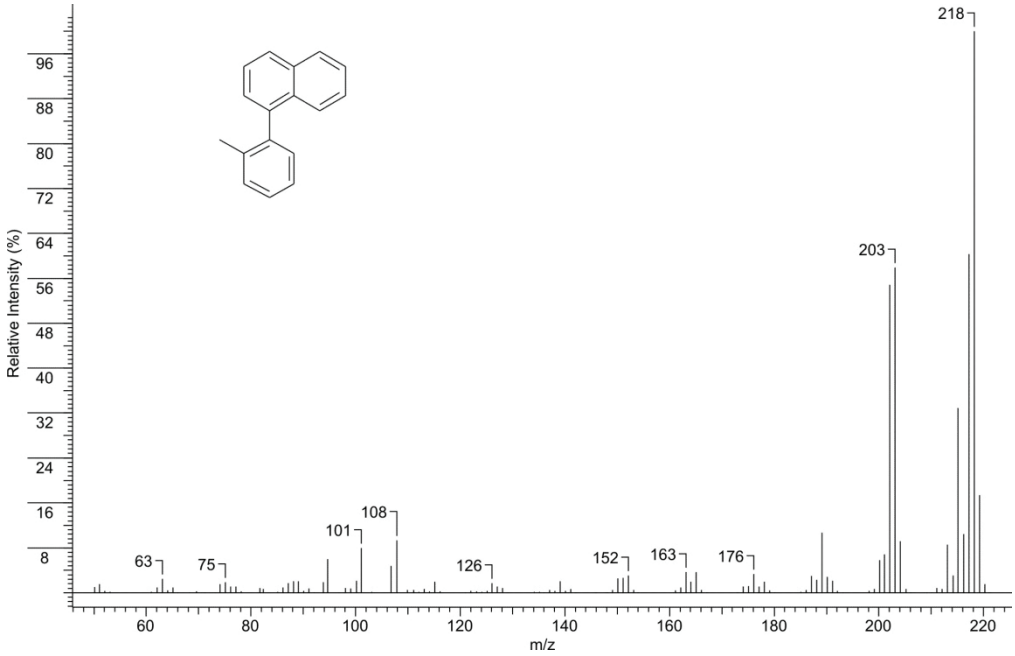


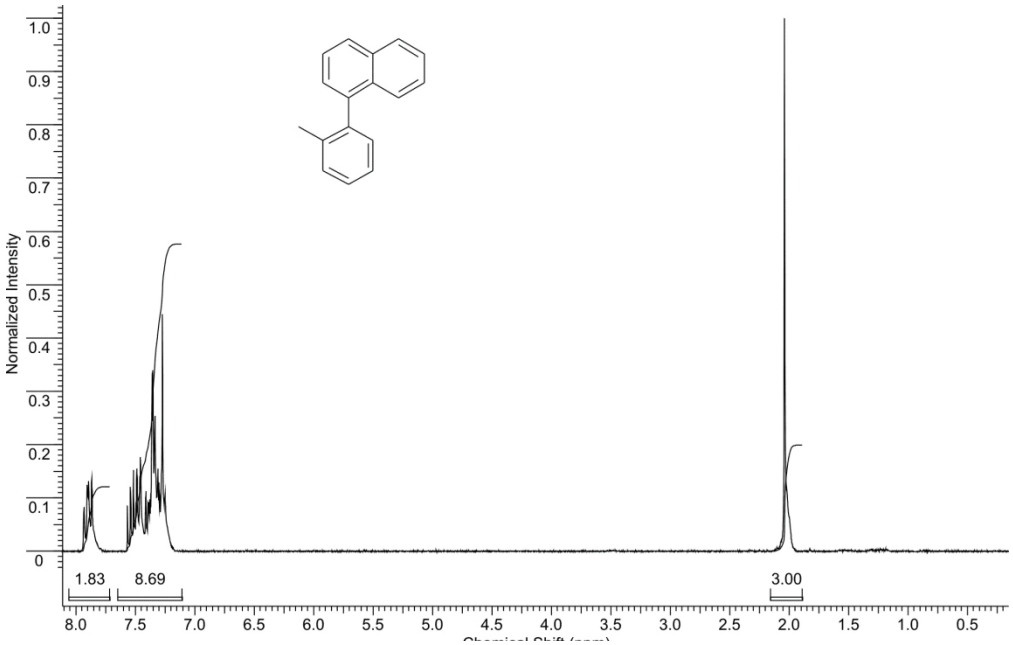


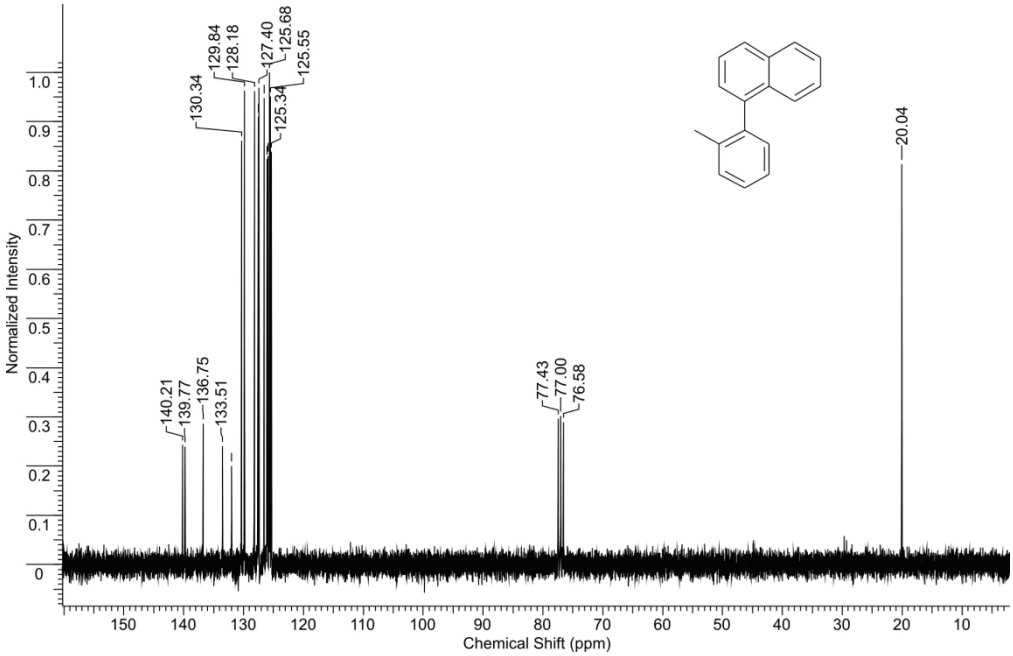


1-*o*-Tolylnaphthalene (Table 1, Entry 4)

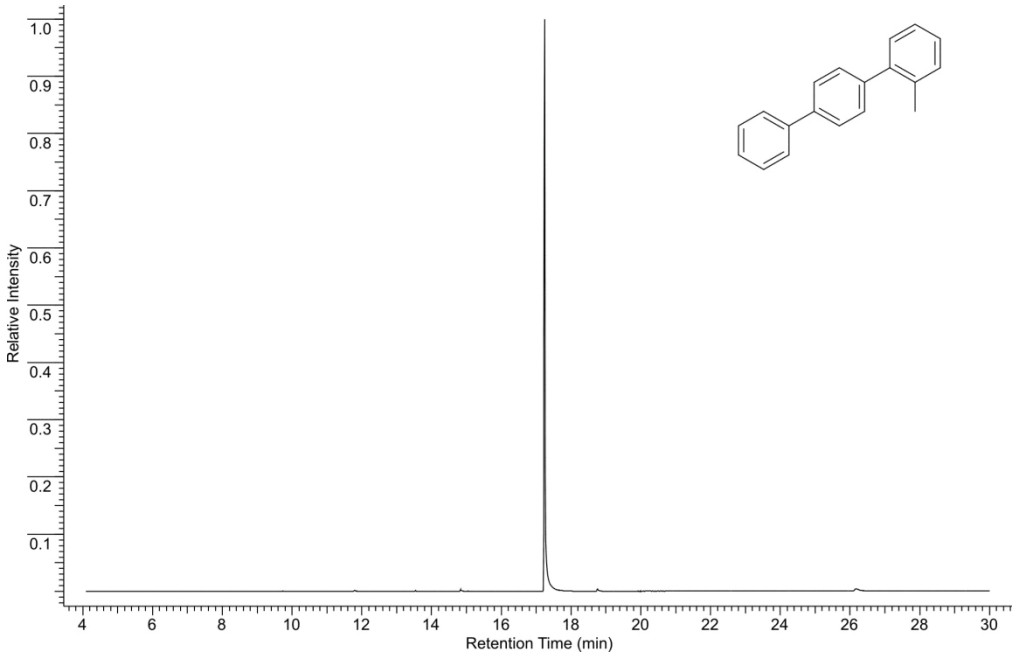


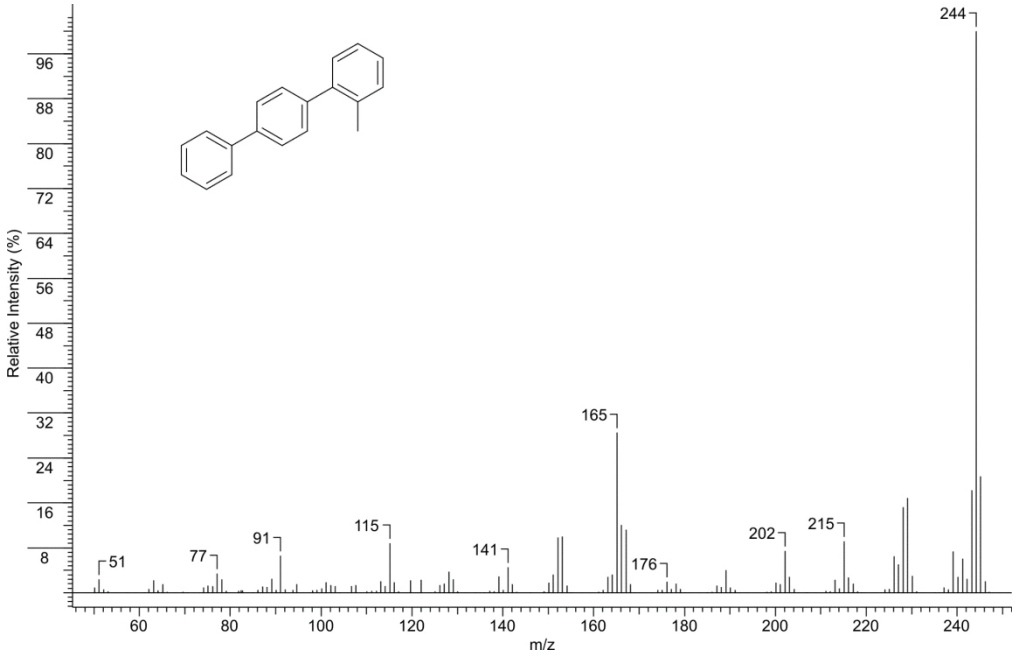


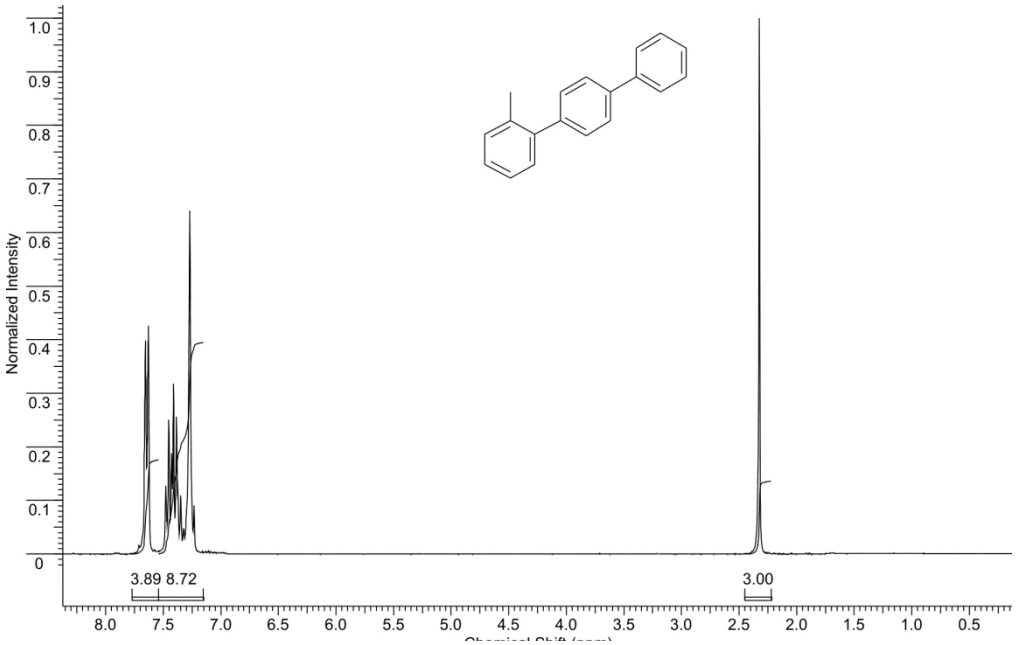


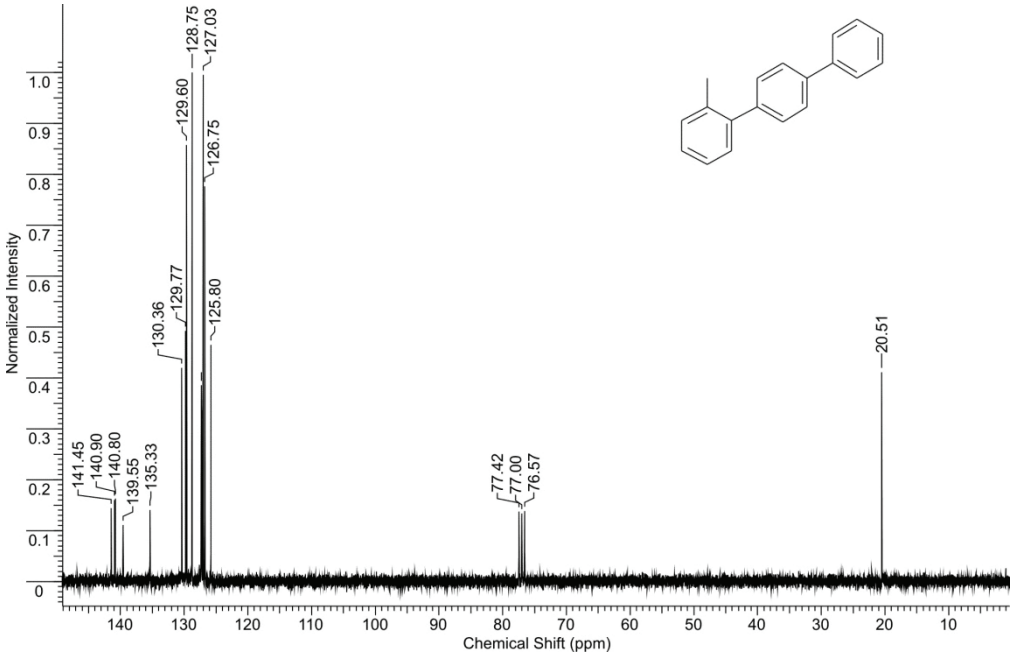


2-Methyl-4'-phenylbiphenyl (Table 1, Entry 5)

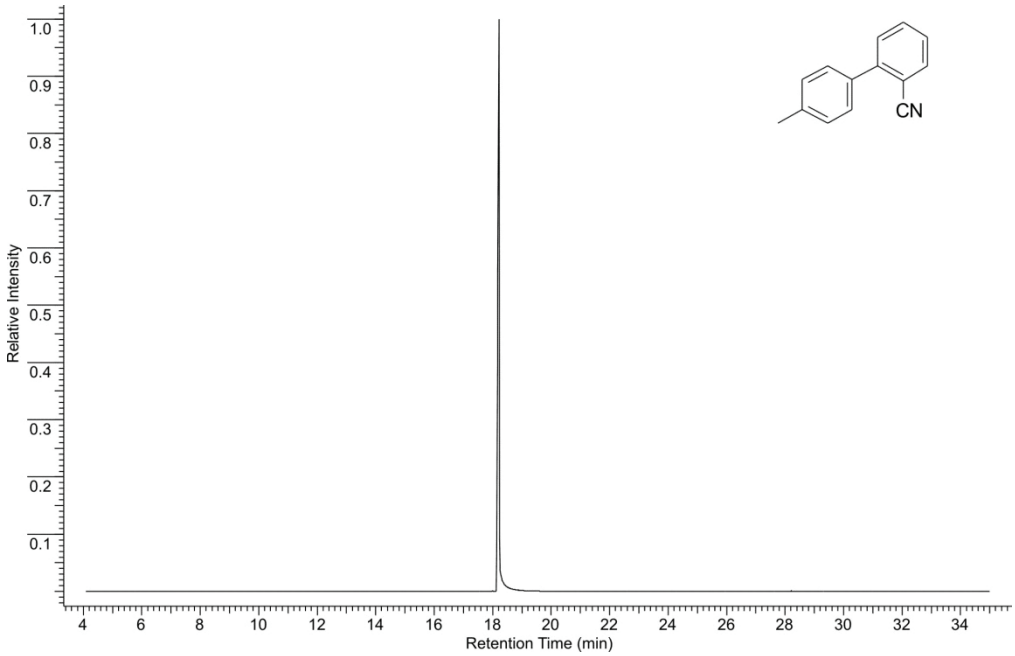


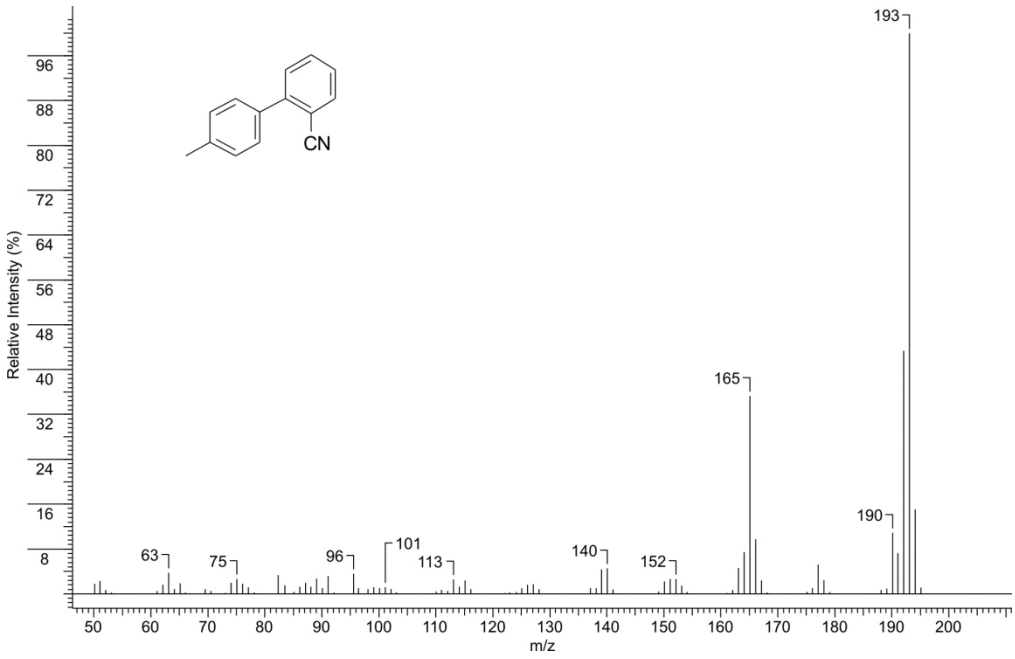


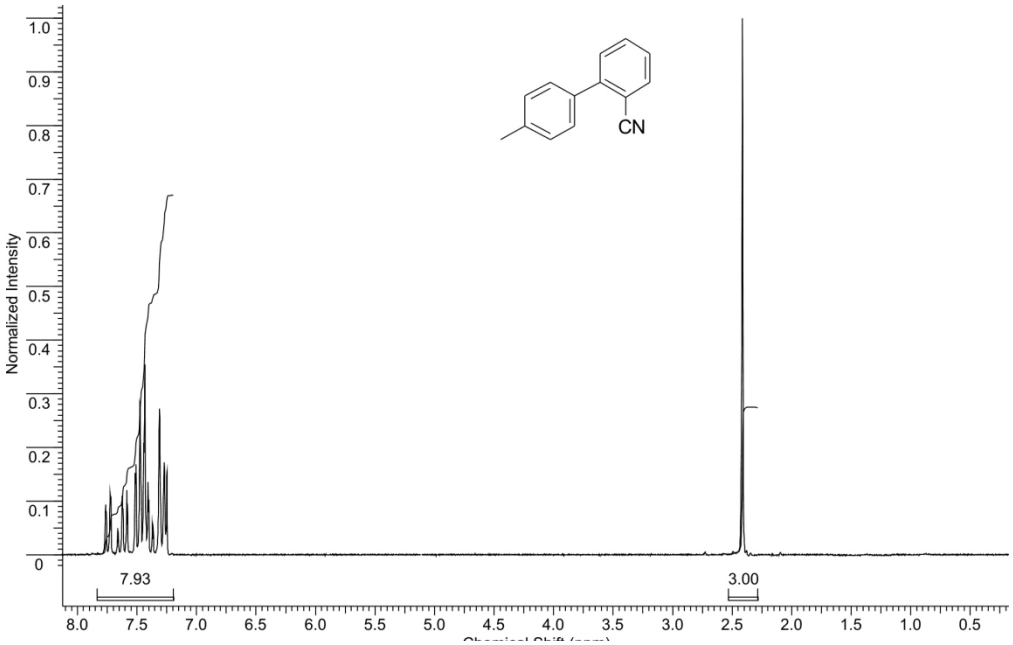


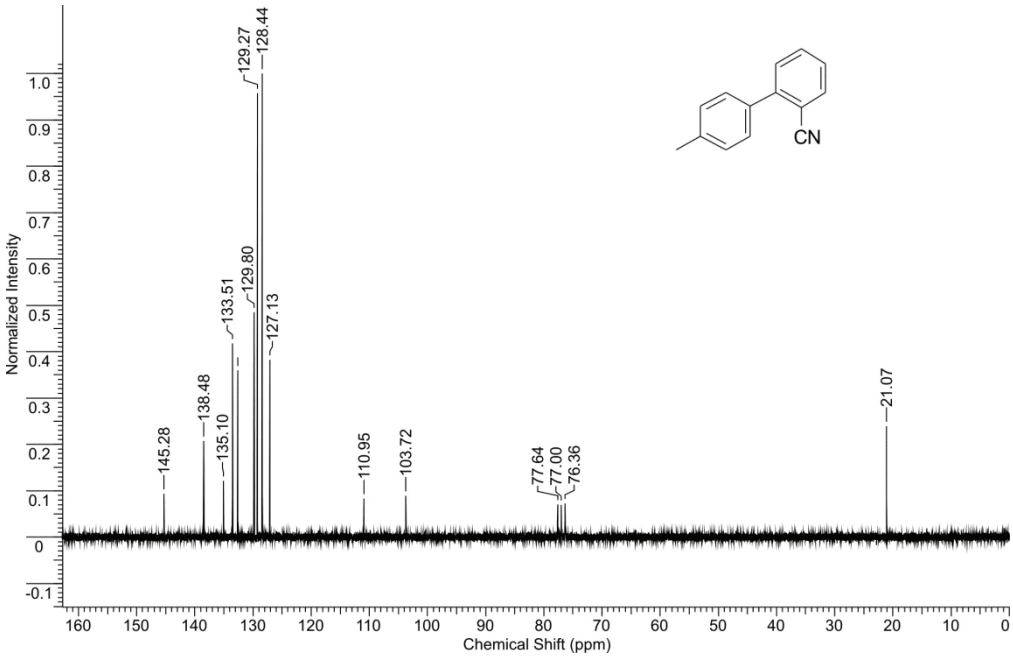


4'-Methylbiphenyl-2-carbonitrile (Table 1, Entry 6)

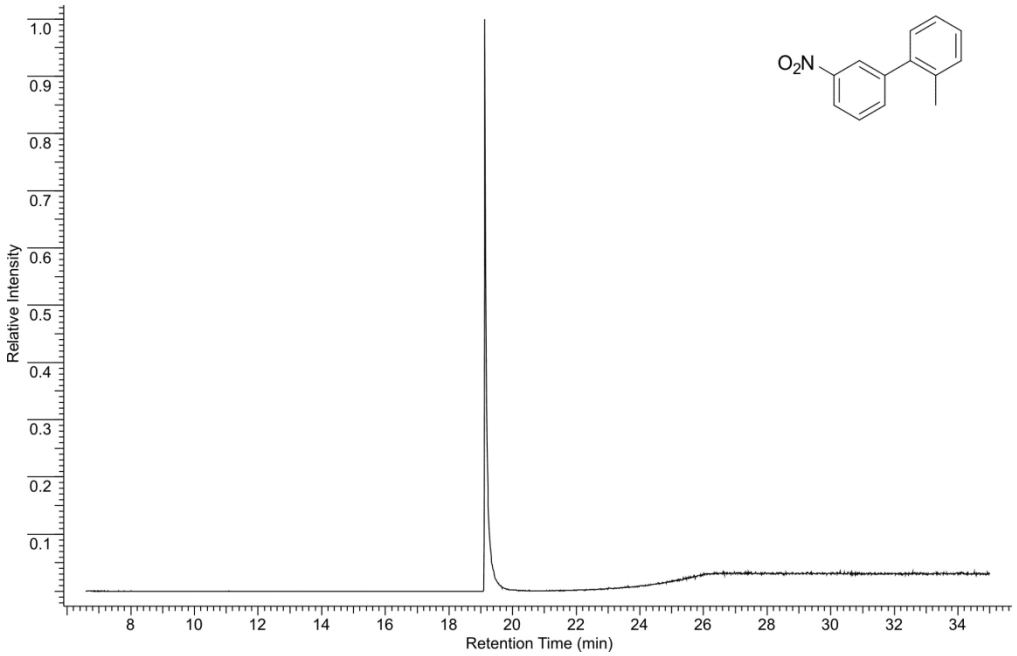


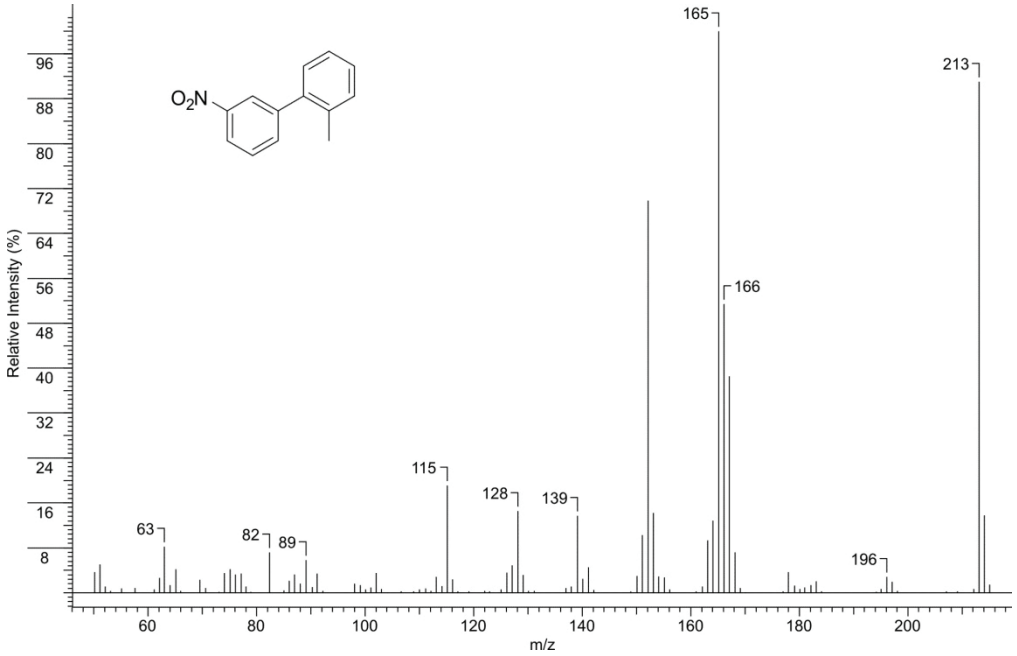


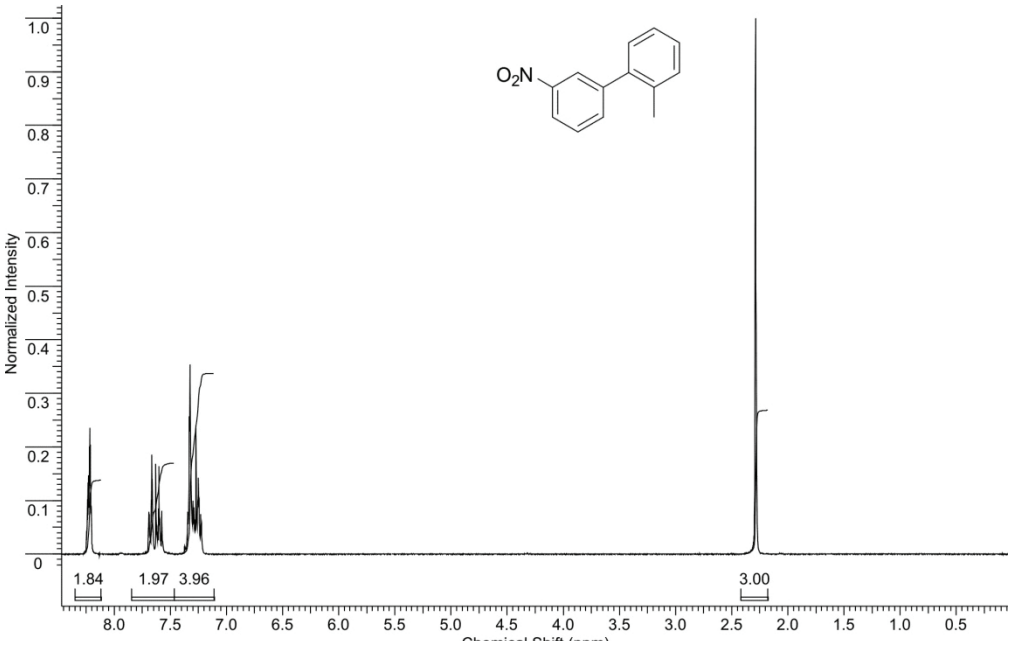


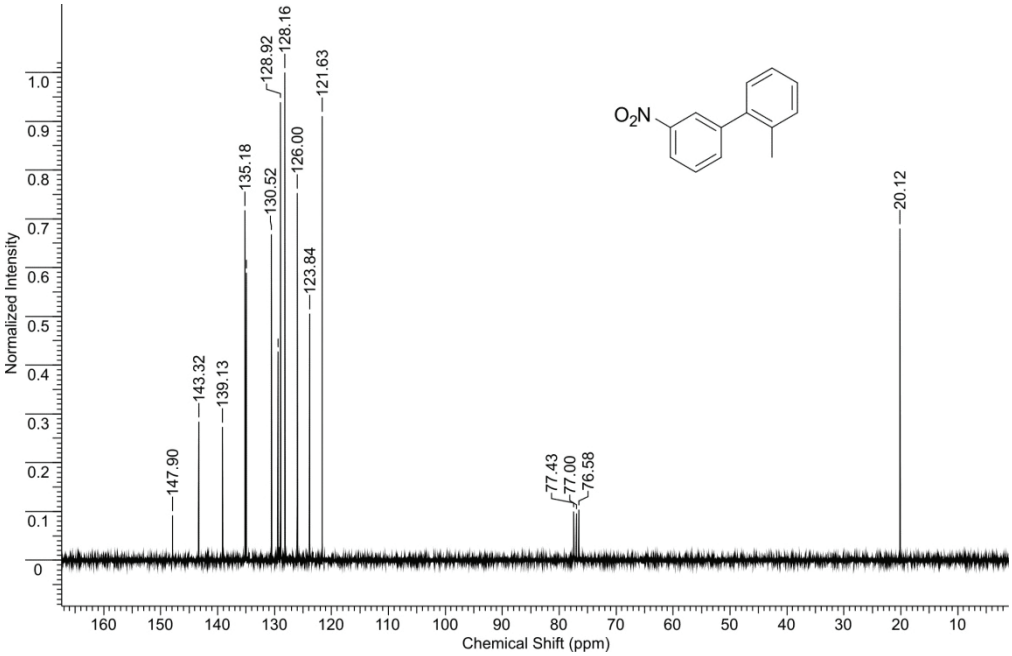


2-Methyl-3'-nitrobiphenyl (Table 1, Entry 7)

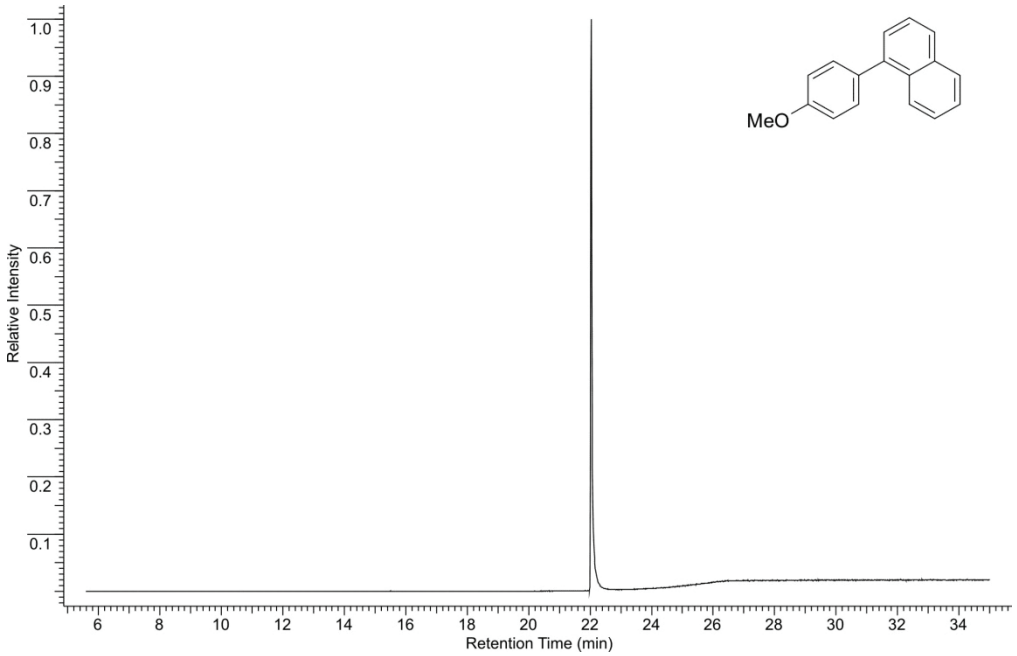


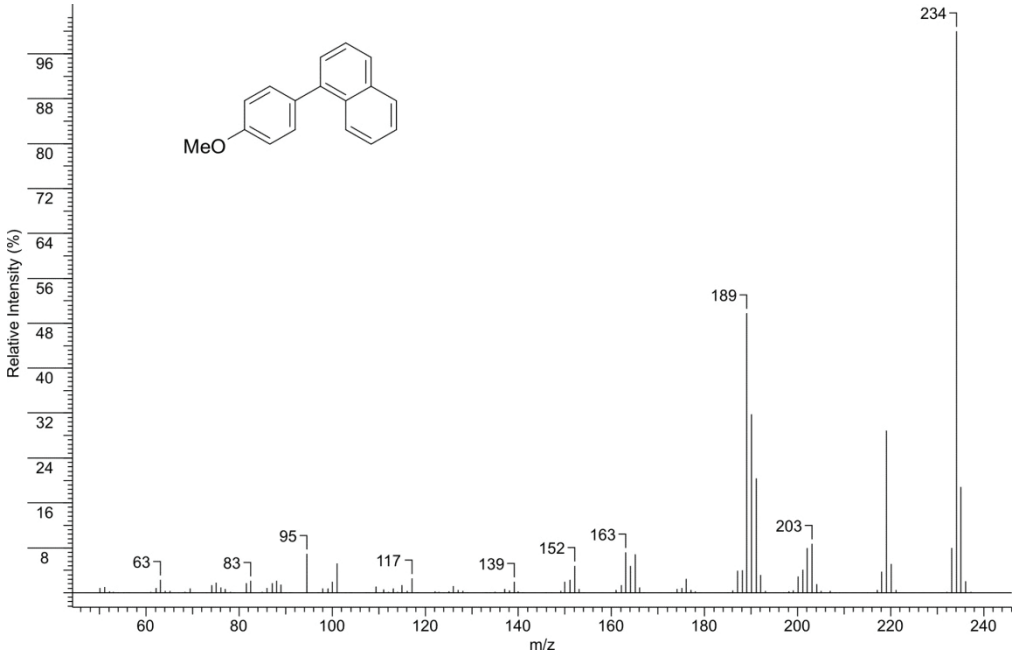


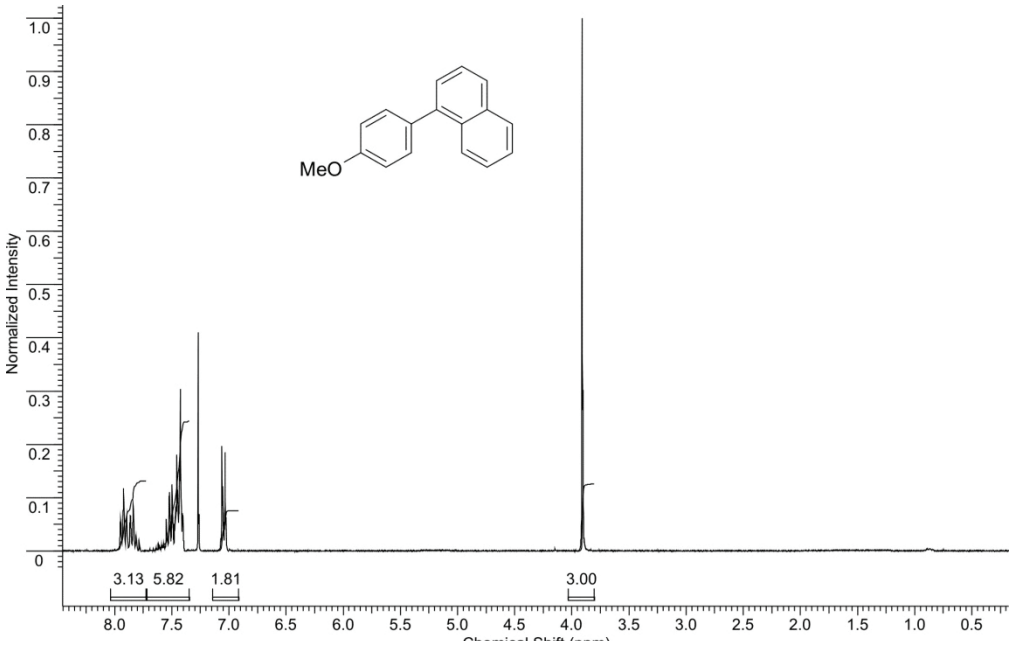


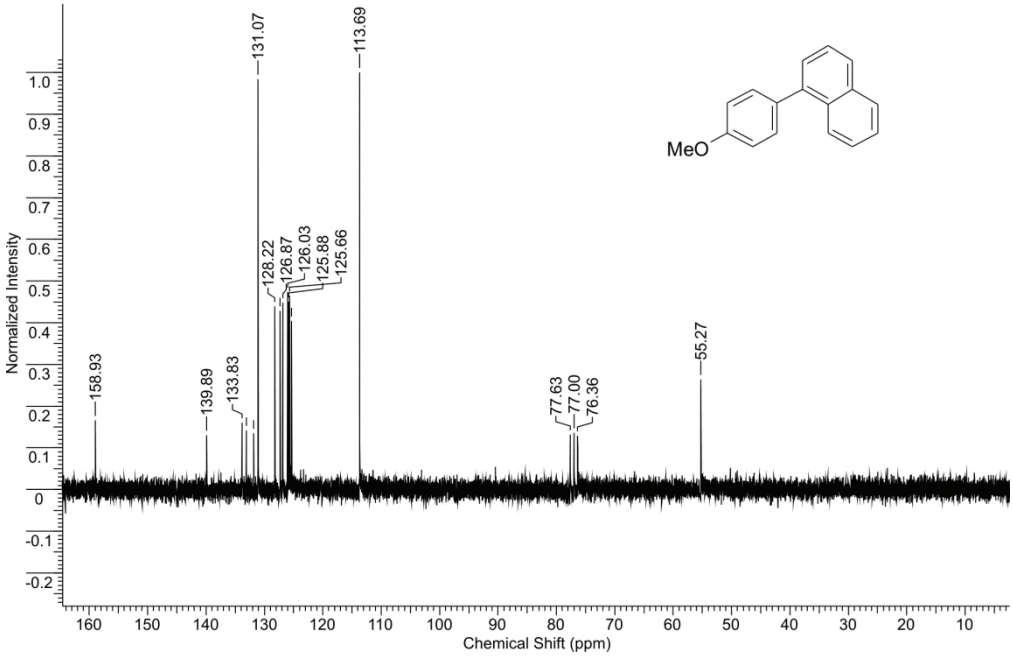


1-(4-Methoxyphenyl)naphthalene (Table 1, Entry 8)

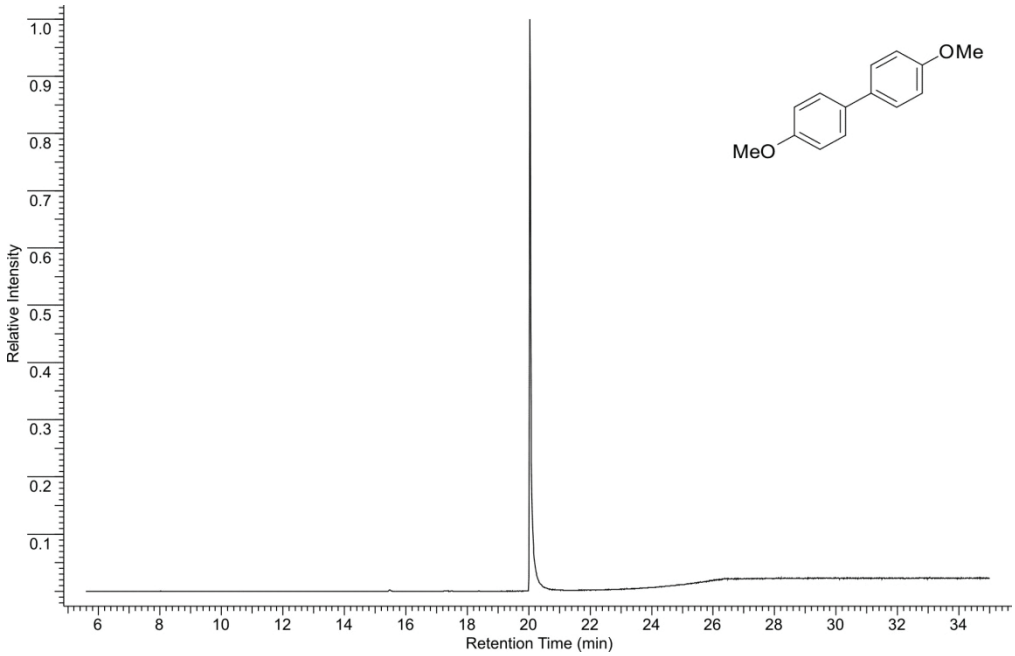


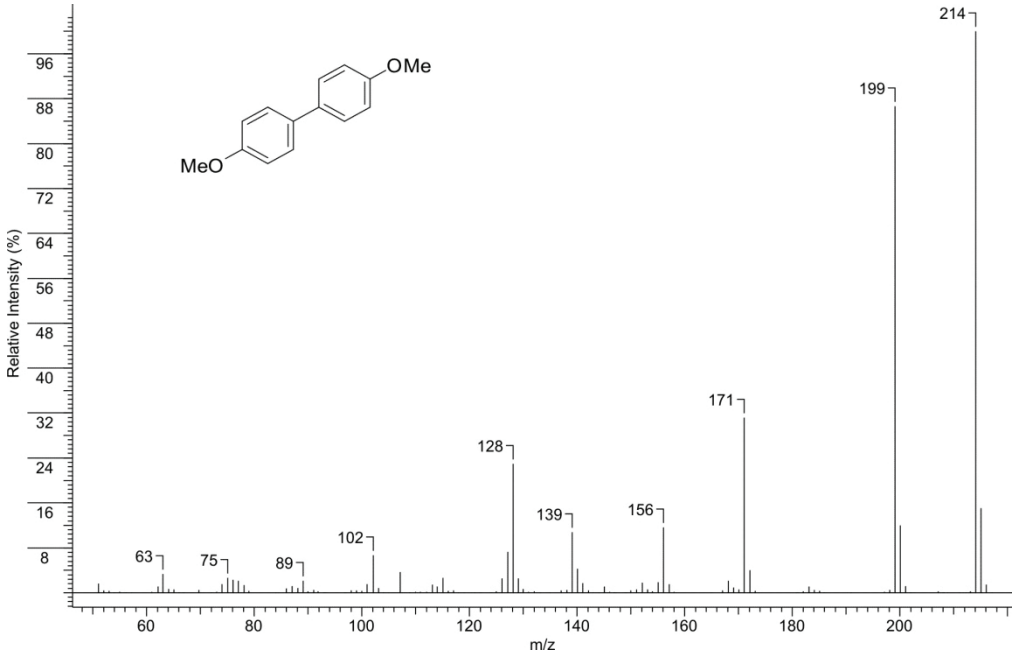


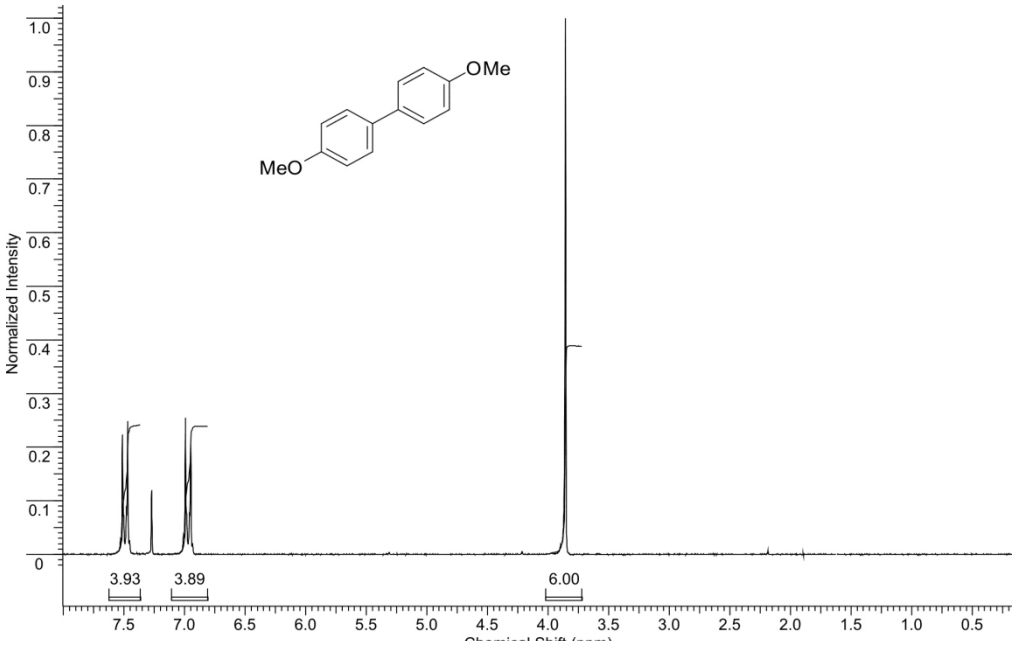


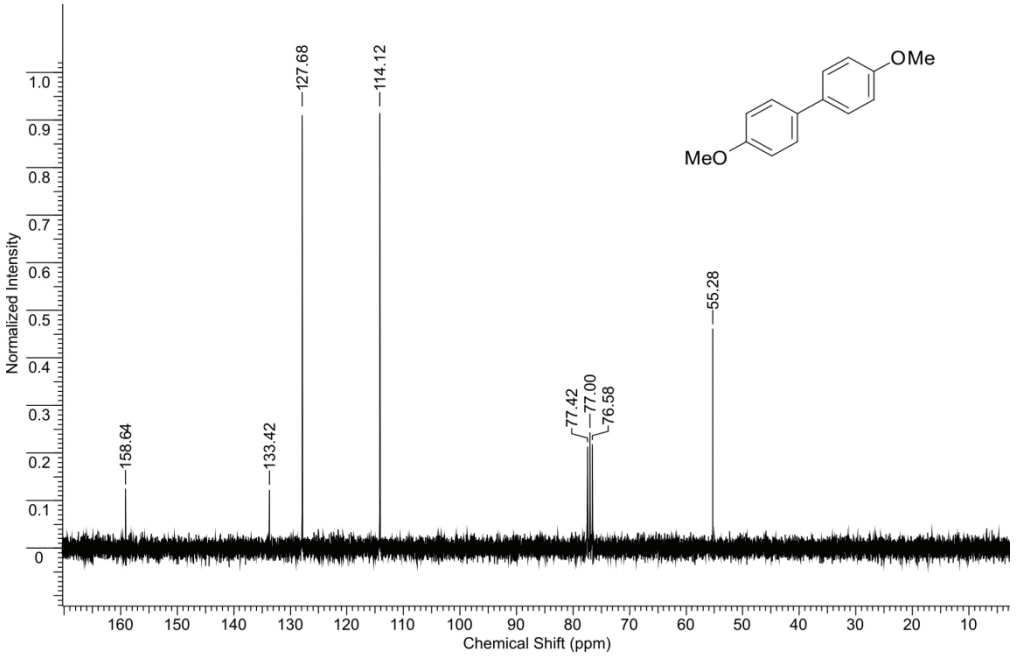


4,4'-dimethoxybiphenyl (Table 1, Entry 9)

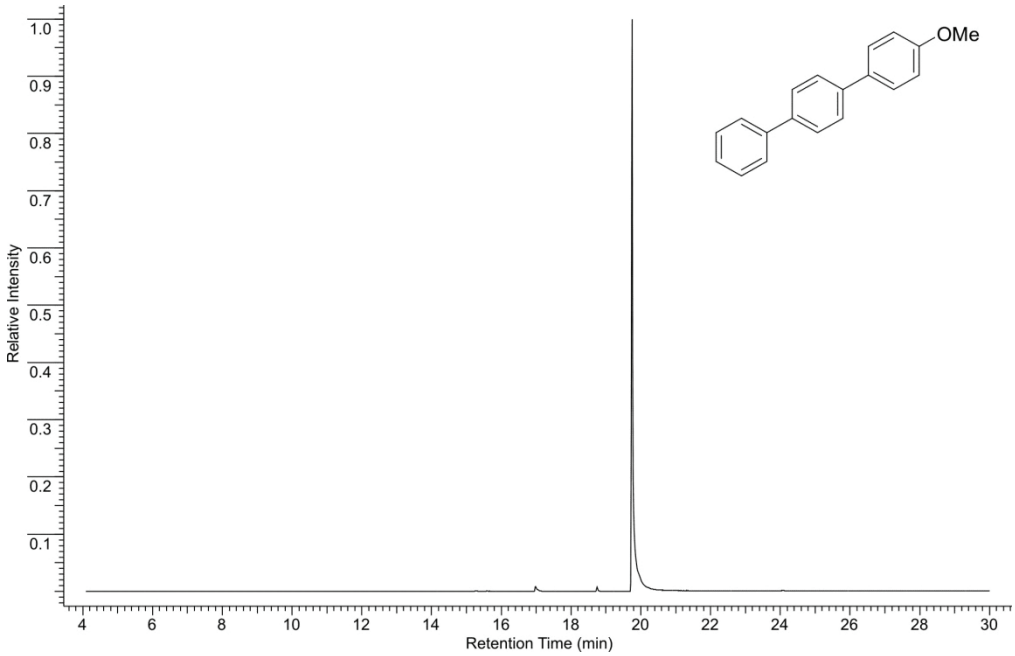


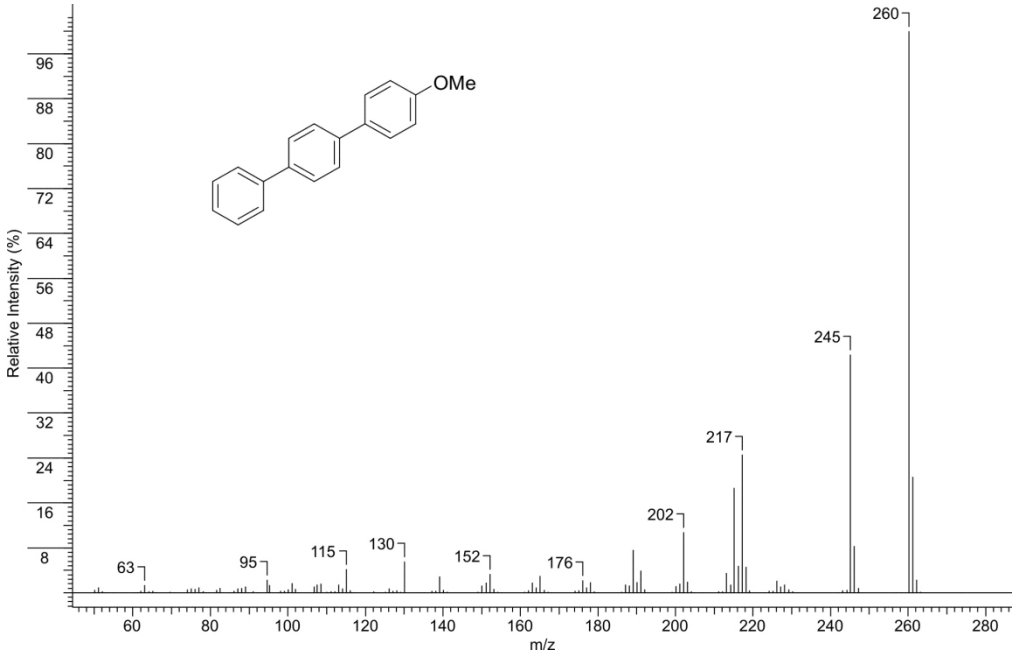


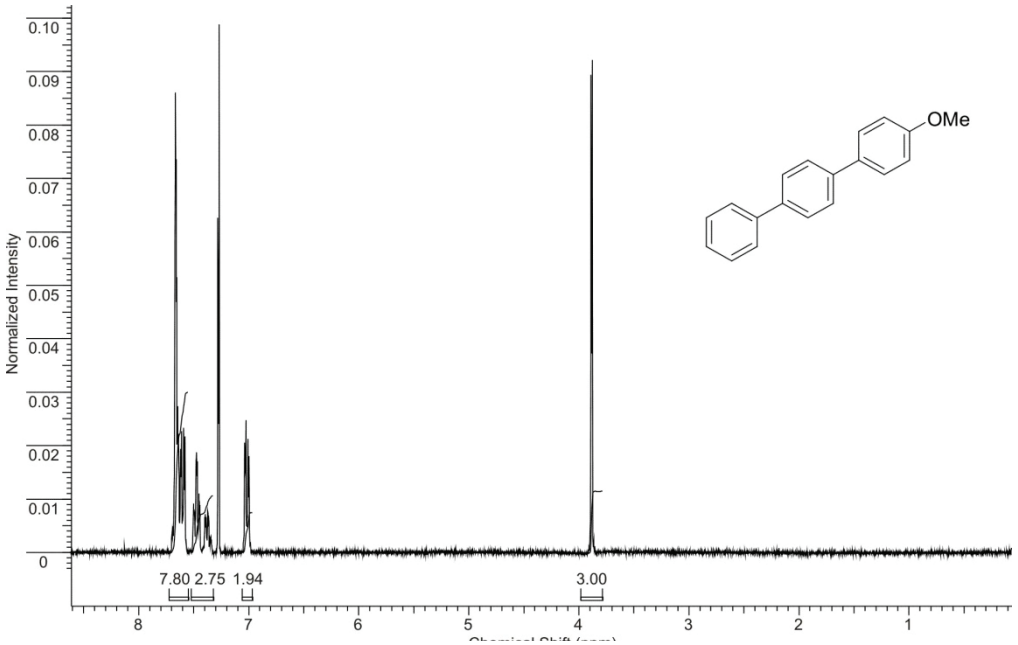


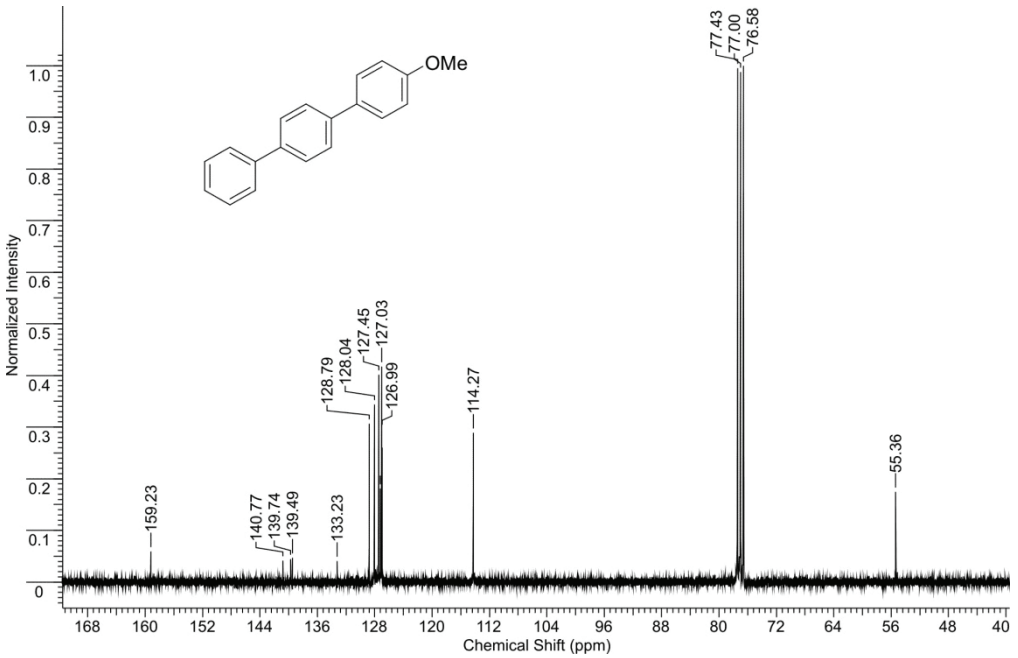


4-Methoxy-4'-phenylbiphenyl (Table 1, Entry 10)

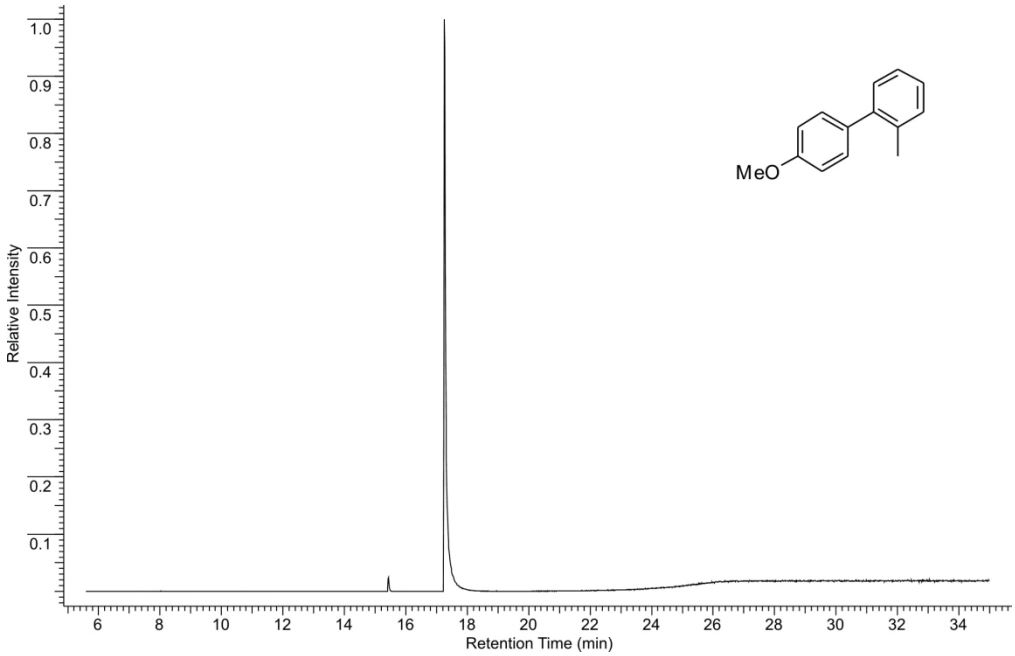


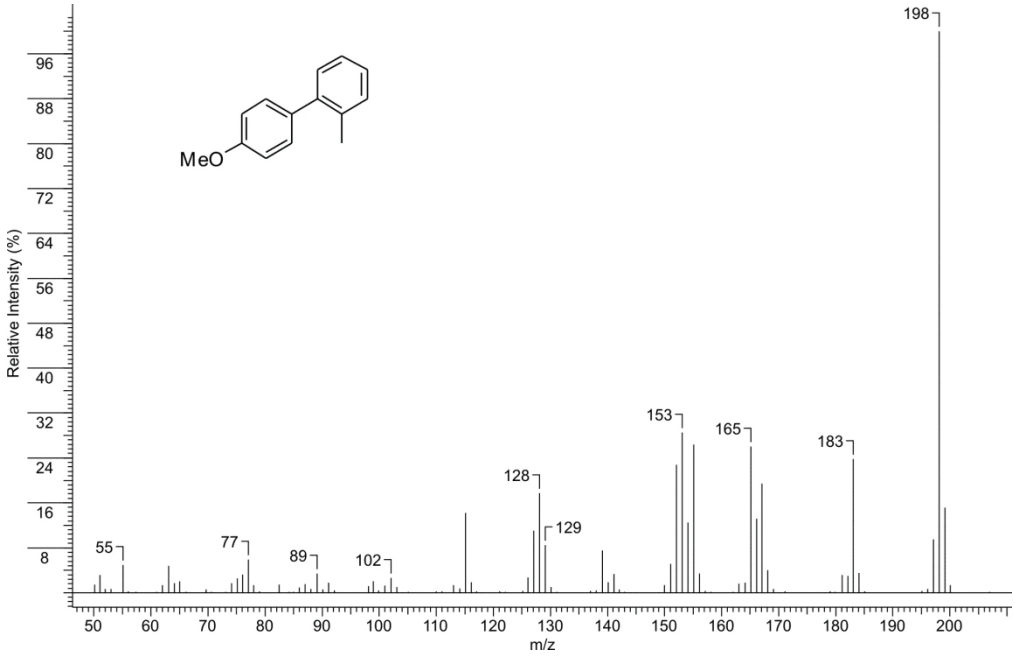


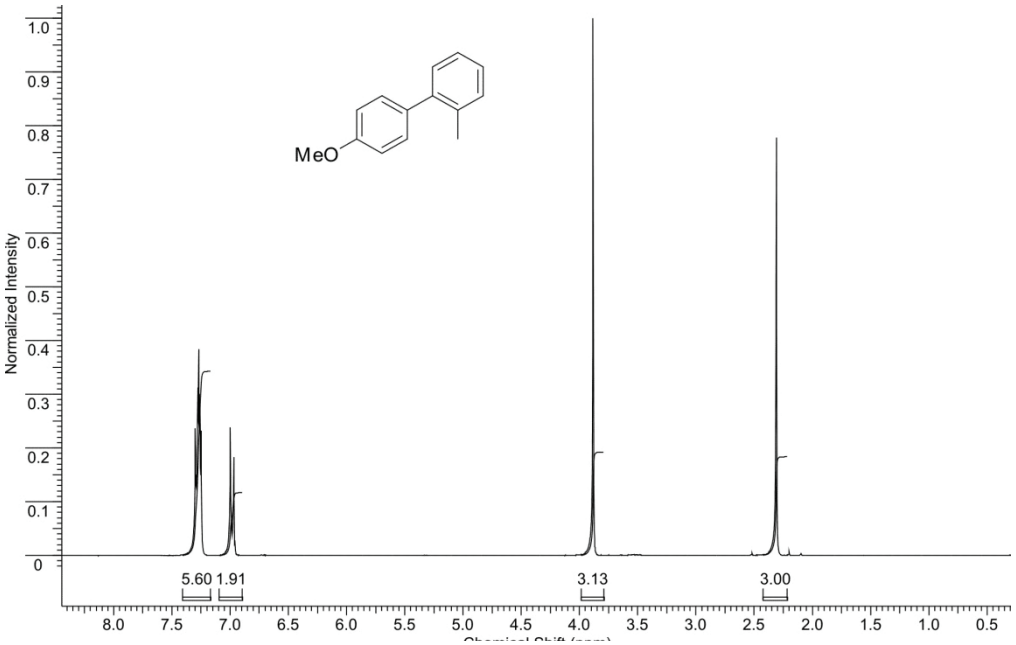


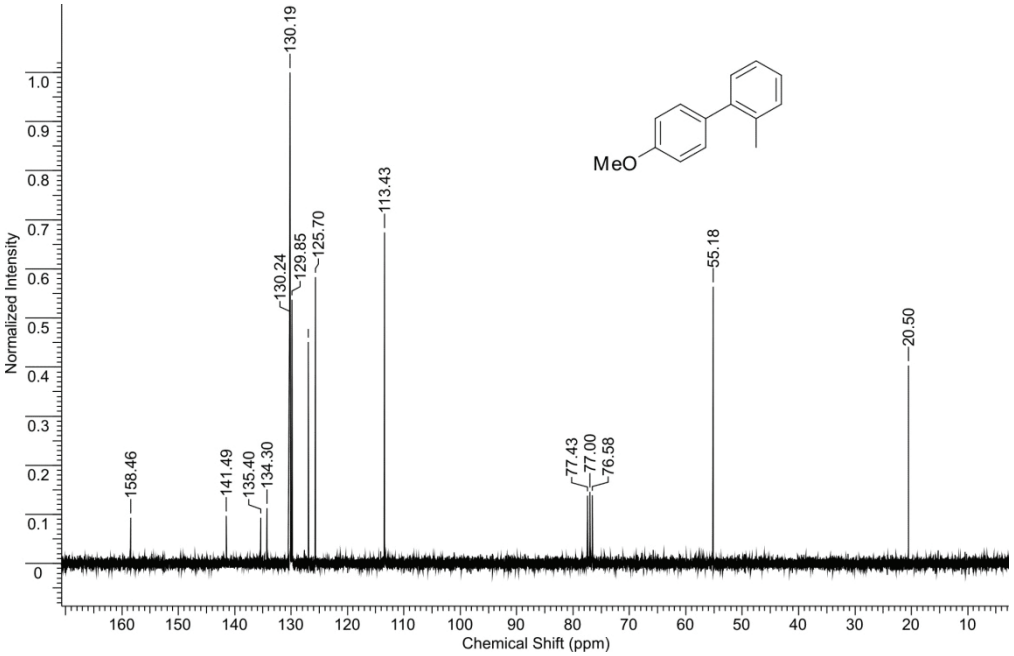


4'-Methoxy-2-methylbiphenyl (Table 1, Entry 11)

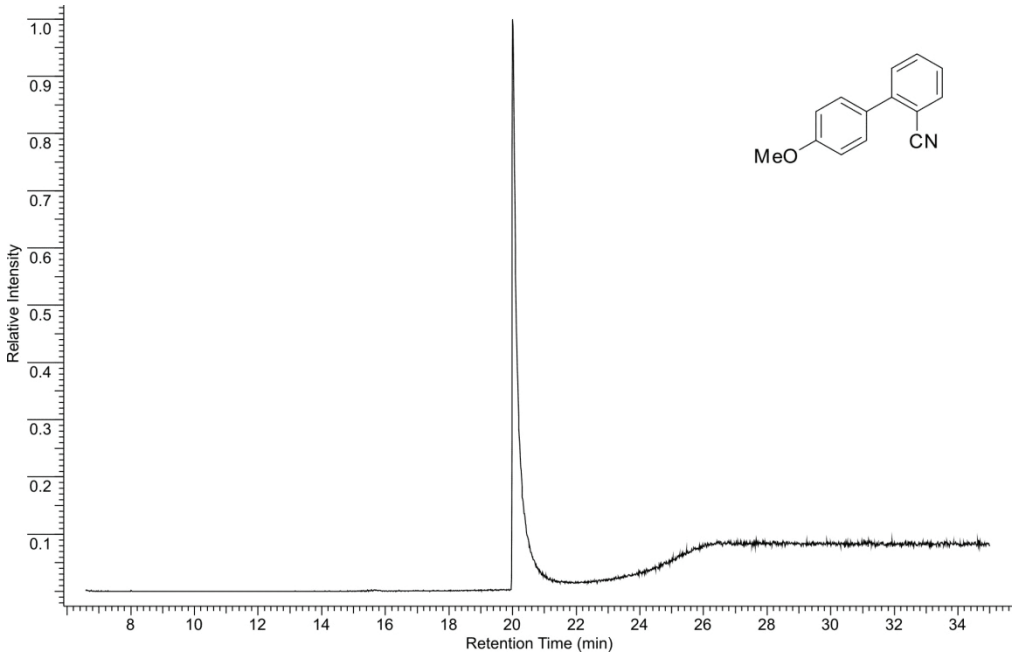


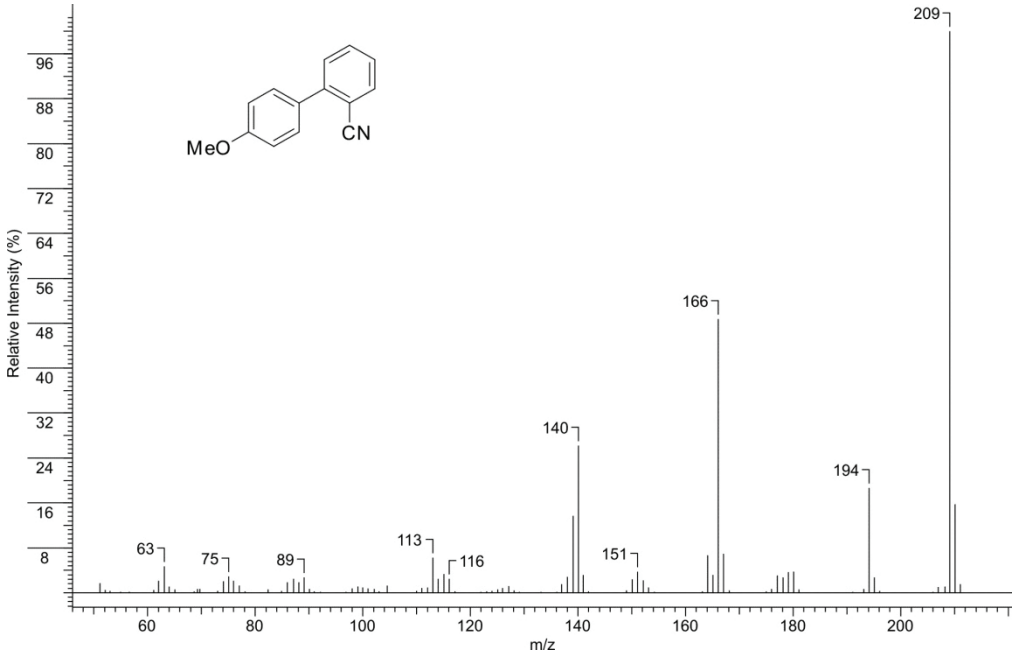


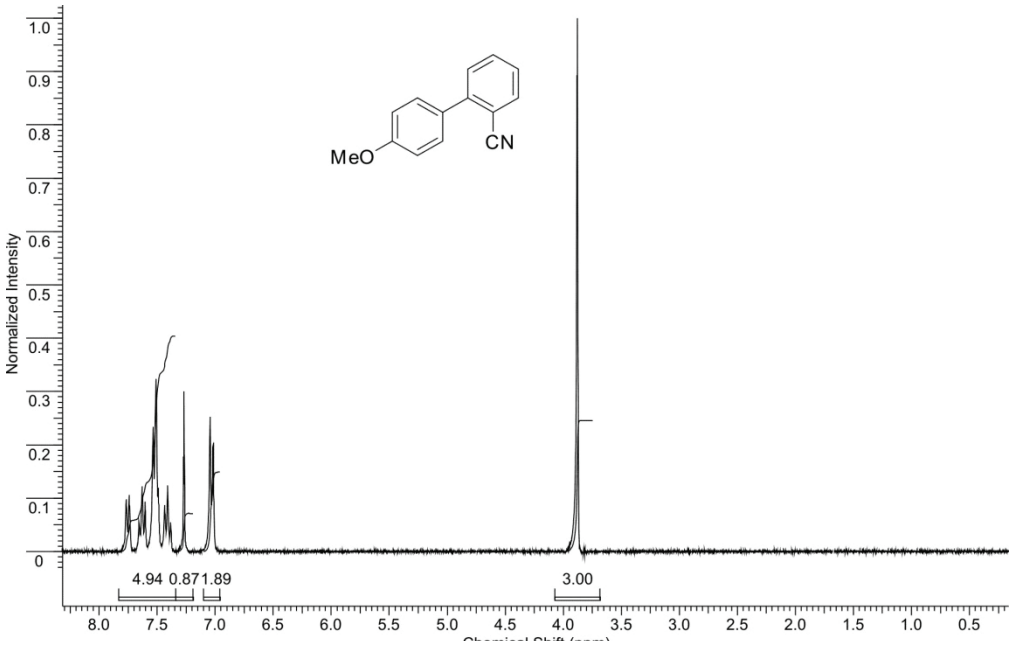


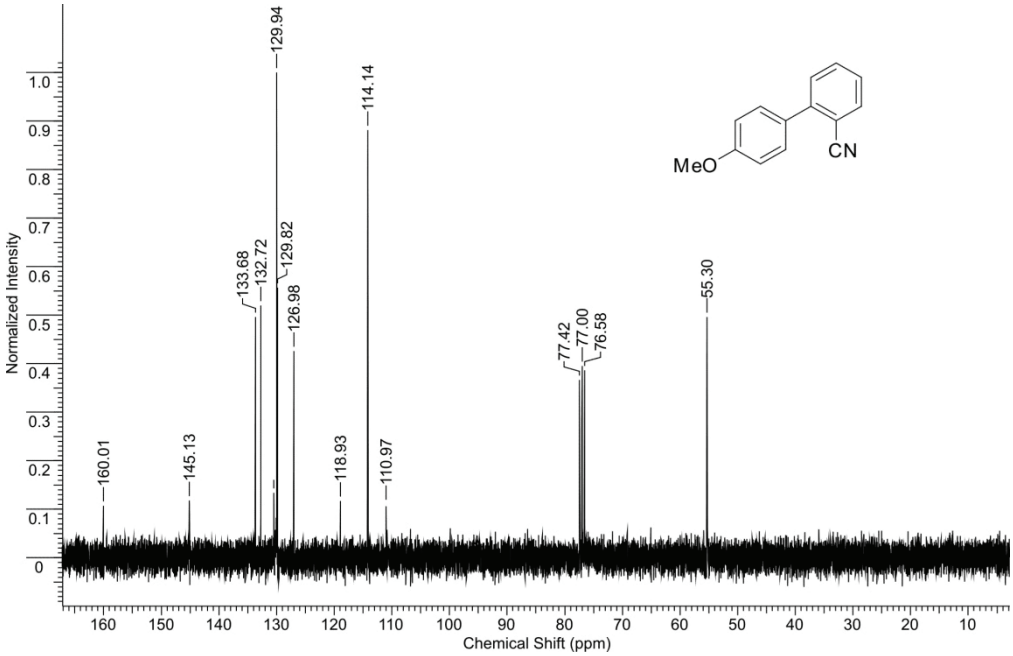


4'-Methoxybiphenyl-2-carbonitrile (Table 1, Entry 12)



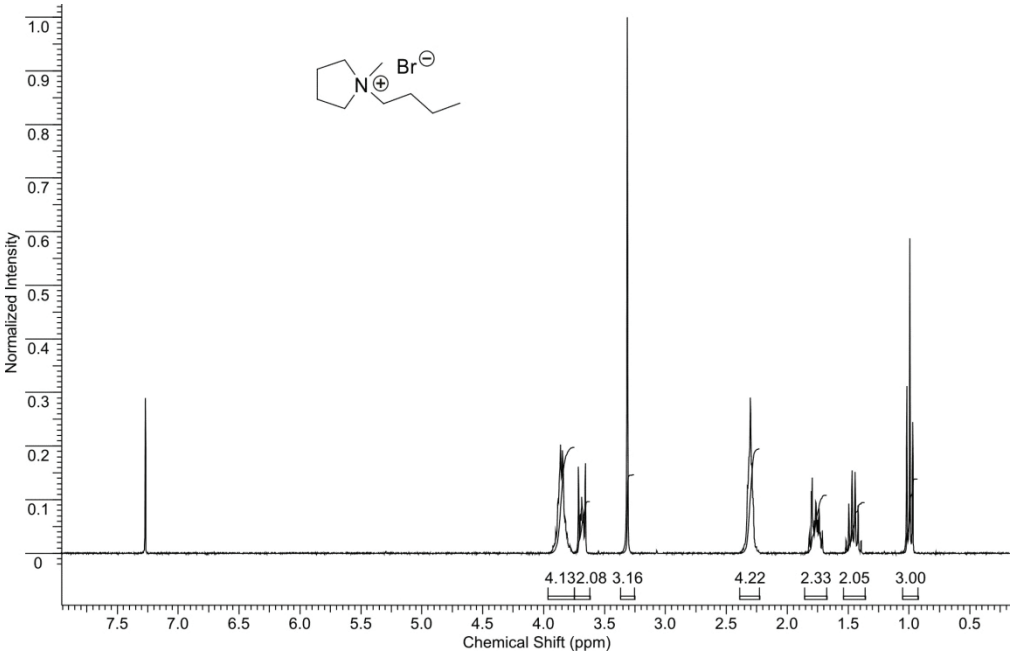


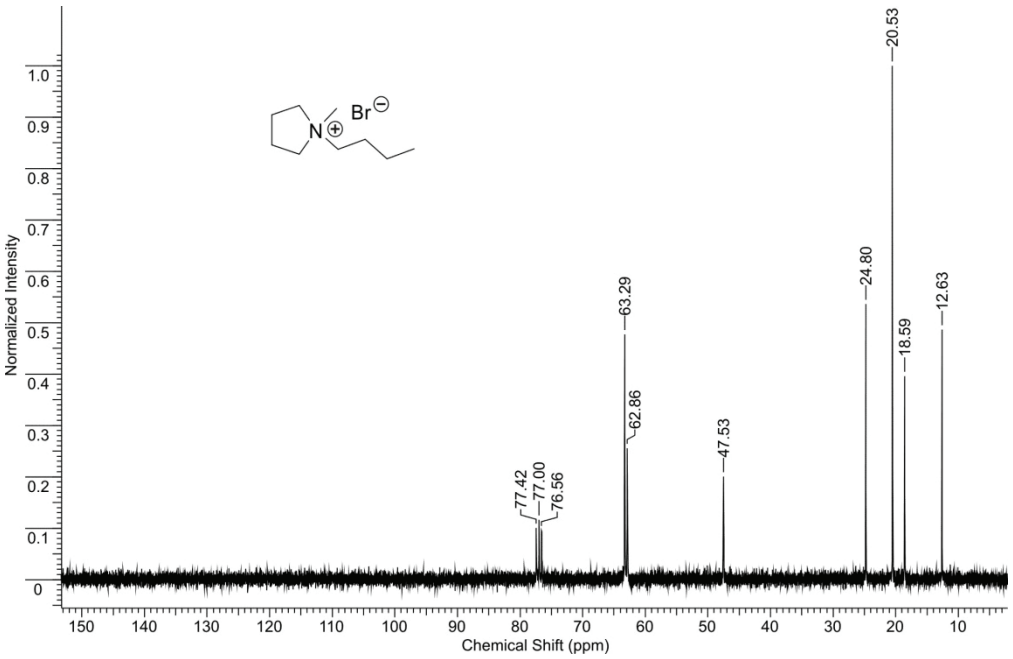




Synthesis of 1-butyl-1-methyl-pyrrolidinium bromide [bmpy][Br]

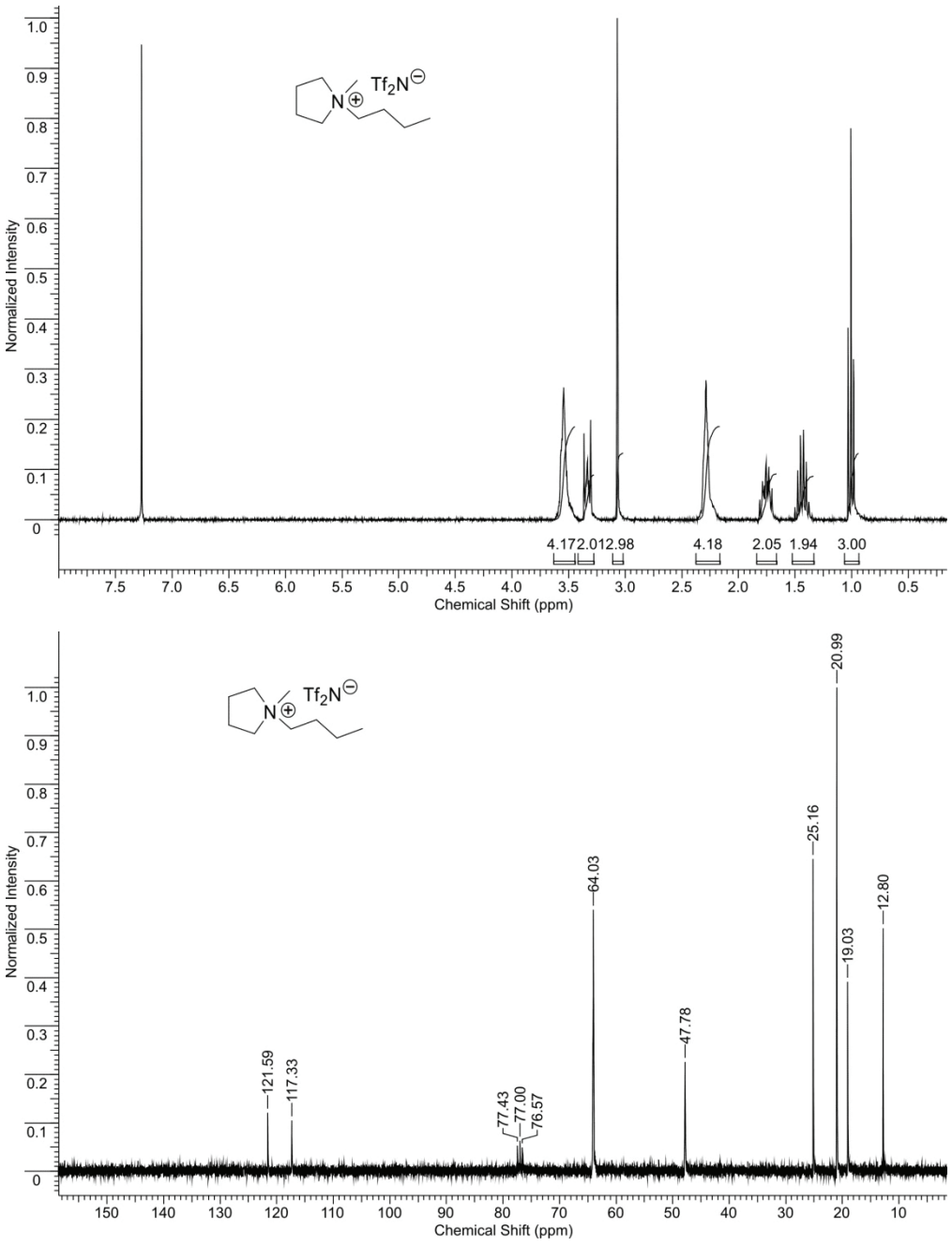
Bromobutane (15 mL, 140 mmol) is slowly added to a stirred solution of *N*-methylpyrrolidine (13.5 mL, 127 mmol) in CH_3CN (38 mL). The solution is stirred at room temperature for 12 h and then at 70 °C for 3 h. After cooling to room temperature, AcOEt is added to the solution and the precipitate is collected by filtration and dried under vacuum to afford 26.6 g (119 mmol, 94 %) of title compound as a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.99 (t, *J* = 7.4 Hz, 3 H), 1.46 (sxt, *J* = 7.4 Hz, 2 H), 1.69-1.84 (m, 2 H), 2.26-2.37 (m, 4 H), 3.31 (s, 3 H), 3.64-3.73 (m, 2 H), 3.79-3.93 (m, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 12.6, 18.6, 20.5, 24.8, 47.5, 62.9, 63.3. Anal. Calcd for $C_9H_{20}BrN$ (222.17): C, 48.66; H, 9.07; N, 6.30. Found: C, 48.71; H, 9.10; N, 6.32.



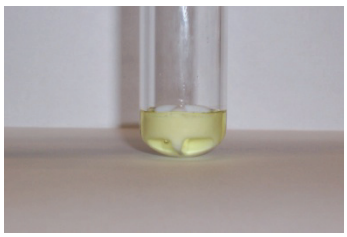


Synthesis of 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl) imide [bmpy][NTf_2]

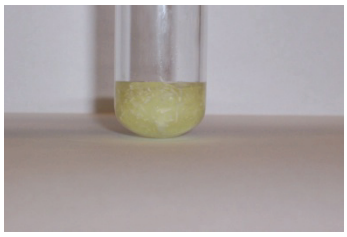
$LiNTf_2$ (15.8 g, 55 mmol) is added to a solution of *N*-butyl-*N*-methyl-pyrrolidinium bromide (11.1 g, 50 mmol) in water (15 mL) and the solution is vigorously stirred at room temperature for 12 h. The solution is extracted with CH_2Cl_2 and the combined organic phases are washed with water until no bromide is detected by $AgNO_3$ test. The combined organic phases are dried (Na_2SO_4) and CH_2Cl_2 is removed at reduced pressure to afford the title compound as a colorless liquid (20.1 g, 47.5 mmol, 95 %). The ionic liquid can be further purified by stirring for 12 h at 40 °C in the presence of decolorizing charcoal and filtering through a short pad of neutral alumina eluting with CH_2Cl_2. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.01 (t, *J* = 7.3 Hz, 3 H), 1.44 (sxt, *J* = 7.5 Hz, 2 H), 1.68-1.84 (m, 2 H), 2.23-2.36 (m, 4 H), 3.07 (s, 3 H), 3.28-3.38 (m, 2 H), 3.48-3.61 (m, 4 H). ^{13}C-NMR (300 MHz, $CDCl_3$) δ = 12.8, 19.0, 21.0, 25.2, 47.8, 64.0, 117.3, 121.6. Anal. Calcd for $C_{11}H_{20}F_6N_2O_4S_2$ (422.41): C, 31.28; H, 4.77; N, 6.63. Found: C, 31.31; H, 4.79; N, 6.60.



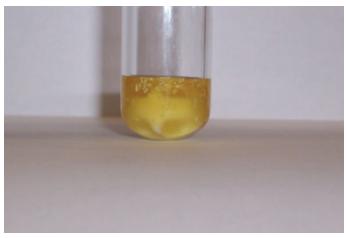
Precatalyst **2** dissolved in [bmpy][NTf_2]



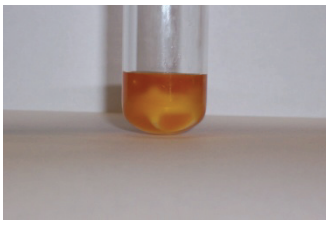
At the beginning of the reaction, salts are not completely dissolved in the IL



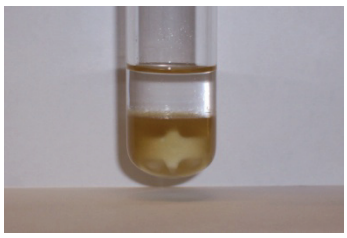
After a few minutes at 65 °C, salts begin to dissolve and the reaction mixture becomes slightly orange



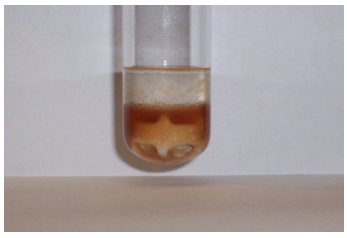
Finally the reaction mixture becomes completely homogeneous and dark orange



At the end of the reaction the product is extracted with pentane



The ionic liquid is washed with water



Finally the ionic liquid is dried under vacuum