

Electronic Supplementary Information

General and highly active catalyst for mono and double Hiyama coupling reactions of unreactive aryl chlorides in water

Dong-Hwan Lee, Ji-Young Jung, and Myung-Jong Jin*

School of Chemical Science and Engineering, Inha University, Incheon 402-751, Korea,

E-mail: mjjin@inha.ac.kr; Fax: 82-32-872-0959; Tel: 82-32-860-7469

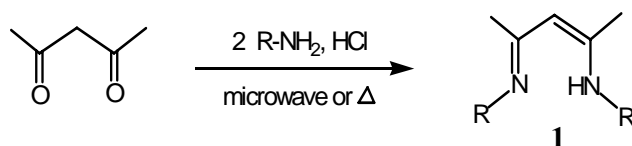
List of Contents for Experimental Section

1. General	S1
2. Synthesis of β -diketimines 1	S1
3. Synthesis of β -diketiminatophosphane palladium complexes 2	S2
4. General Procedure for the Hiyama coupling reaction	S4
5. General Procedure for double Hiyama coupling reaction	S4
6. General Procedure for double Hiyama-Heck coupling reaction	S4
7. References	S4
8. ^1H and ^{13}C NMR spectra of β -diketimines 1	S5
9. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra of palladium complexes 2	S9
10. NMR spectra of the coupling products	S18

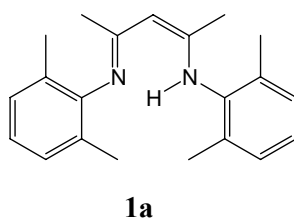
1. General information

Aryl(trialkoxo)silanes was prepared according to the literature procedures.¹ All other reagents were used as received from commercial source. All manipulations were conducted under an atmosphere of dry nitrogen. Microwave irradiation was performed with a Discover microwave synthesis system (CEM Co.). ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on a Varian Unity Inova (400 MHz) NMR spectrometer, Bruker AM 400 (400 MHz) and FT AM 300 (300MHz), respectively. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. ³¹P NMR spectra were referenced to external PPh₃ (0 ppm relative to free PPh₃). Elemental analyses (EA) were carried out using EA-110 (Thermo Finnigan, Italia). GC/GC-MS analyses were performed on an Agilent 6890N GC coupled to an Agilent 5975 Network Mass Selective Detector.

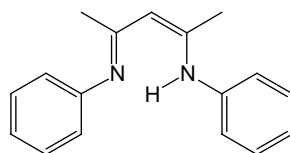
2. Synthesis of β-diketimines **1**



Acetylacetone (5.0 g, 50 mmol), amine (100 mmol), conc. HCl (5.0 g) and a magnetic stir bar were placed in a 100 mL round flask. The vessel was sealed with a septum and placed into the microwave cavity. The reaction temperature was raised from r.t. to 85 °C under microwave irradiation of 150 W. The power was maintained for 30 min. Alternatively, the reaction mixture was refluxed in ethanol for 3 days.³ The mixture was then cooled to room temperature and treated with water (100 ml) and Na₂CO₃ (8.0 g). The solution was extracted with methylene chloride (2 x 100 mL). The organic layers were dried (MgSO₄) and concentrated under reduced pressure. The solid product was washed with cold ethanol and dried under vacuum to give β-diketimines **1**.



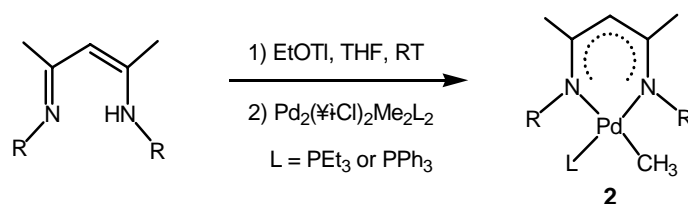
1a: White solid (13.0 g, 85 %). ^1H NMR (CDCl_3 , 400 MHz) δ 12.19 (br s, 1H), 7.03 (d, 4H, $J = 8.0$ Hz), 6.63 (dd, 2H, $J = 3.2$ Hz), 4.87 (s, 1H), 2.15 (s, 12H), 1.68 (s, 6H); ^{13}C NMR (C_6D_6 , 100 MHz) δ 160.81, 144.3, 132.3, 124.7, 94.3, 20.2, 18.5; Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2$ (306.44): C, 82.31; H, 8.51; N, 9.14. Found: C, 82.02; H, 8.54; N, 9.38.



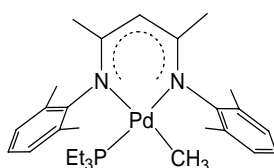
1b

1b: Light yellow solid (10.7 g, 86 %). ^1H NMR (CDCl_3 , 400 MHz) δ 13.17 (br s, 1H), 7.09 (m, 4H), 6.89 (m, 6H), 4.78 (s, 1H), 1.80 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.4, 145.7, 128.7, 123.1, 122.6, 97.3, 20.8; Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2$ (250.34): C, 81.56; H, 7.25; N, 11.19. Found: C, 81.24; H, 7.33; N, 11.16.

3. Synthesis of β -diketiminatophosphane palladium complexes **2**

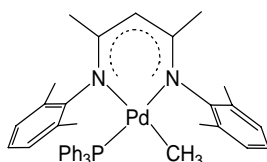


A solution of EtOTf (300 mg, 1.2 mmol) in THF (10 mL) was added dropwise at room temperature to a solution of β -diketimine **1** (1.0 mmol) in THF (10 mL). After 1 h, a solution of $\text{Pd}_2(\mu\text{-Cl})_2\text{Me}_2\text{L}_2^2$ ($\text{L} = \text{PPh}_3, \text{PEt}_3$) (0.6 mmol) in THF (5 mL) was added dropwise to the mixture. The mixture was stirred at room temperature for an additional 1 h. The solution was filtered through Celite and concentrated under reduced pressure. The residue was washed with cold hexane to afford **2** in 78~85% yields. When EtONa instead of EtOTf was used in the deprotonation of **1a**, product **2a** was obtained in 67% yield.



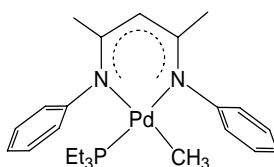
2a

2a: Light brown solid (0.46 g, 85 %). ^1H NMR (CDCl_3 , 400 MHz) δ 7.04 (d, 2H, $J = 7.2$ Hz), 7.01 (d, 2H, $J = 7.2$ Hz), 6.90 (t, 2H, $J = 15.6$ Hz), 4.72 (s, 1H), 2.33 (s, 6H), 2.22 (s, 6H), 1.56 (s, 3H), 1.46 (s, 3H), 0.94 (m, 6H), 0.850 (m, 9H), -0.62 (d, 3H, $J = 4.0$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.9, 149.9, 132.0, 131.8, 131.4, 130.9, 129.8, 128.4, 128.3, 127.8, 127.7, 97.9, 28.6, 26.1, 25.6, 18.6, 18.4, 18.3, 13.9, 8.4, 8.3, 8.1, 2.23; ^{31}P NMR (CDCl_3 , 162 MHz) δ 22.65; Anal. Calcd for $\text{C}_{28}\text{H}_{43}\text{N}_2\text{PPd}$ (545.05): C, 61.70; H, 7.95; N, 5.14. Found: C, 61.43; H, 7.91; N, 5.28.



2b

2b: Light brown solid (0.53 g, 78 %). ^1H NMR (CDCl_3 , 400 MHz) 7.68 (t, 2H, $J = 18.0$ Hz), 7.53 (d, 2H, $J = 8.0$ Hz), 7.44 ~ 7.05 (m, 15H), 6.60 (t, 2H, $J = 10.2$ Hz), 4.81 (s, 1H), 2.24 (s, 6H), 2.08 (s, 6H), 1.69 (s, 3H), 1.64 (s, 3H), -0.81 (d, 3H, $J = 4.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 179.3, 166.1, 154.4, 134.7, 134.6, 133.0, 132.1, 131.9, 131.8, 131.3, 130.8, 129.9, 129.8, 128.7, 128.4, 128.3, 128.1, 127.8, 125.3, 123.6, 93.8, 24.6, 23.2, 18.9, 18.7, 0.65; ^{31}P NMR (CDCl_3 , 162 MHz) δ 43.88; Anal. Calcd for $\text{C}_{40}\text{H}_{43}\text{N}_2\text{PPd}$ (689.18): C, 69.71; H, 6.29; N, 4.06. Found: C, 69.74; H, 6.38; N, 4.10.



2c

2c: Light brown solid (0.40 g, 82 %). ^1H NMR (CDCl_3 , 400 MHz) δ 7.26 (d, 3H, $J = 5.2$ Hz), 6.98 (m, 2H), 6.78 (m, 3H), 6.63 (d, 2H, $J = 6.0$ Hz), 4.70 (s, 1 H), 1.79 (s, 3 H), 1.72 (s, 3 H), 1.63 (m, 6H), 1.18 (m, 9H), -0.401 (d, 3H, $J = 4.0$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.3, 148.3, 135.9, 132.2, 131.2, 127.3, 127.1, 123.4, 123.3, 122.7, 96.5, 26.8, 25.4, 22.5, 22.4, 16.8, 16.5, 13.5, 8.4, 0.6; ^{31}P NMR (CDCl_3 , 162 MHz) δ 24.25; Anal. Calcd. For $\text{C}_{24}\text{H}_{35}\text{N}_2\text{PPd}$ (488.94) C, 58.96; H, 7.22; N, 5.73; Found C, 58.92; H, 7.06; N, 5.53.

4. General Procedure for Hiyama coupling reaction

Aryl chloride (1.0 mmol), arylsilane (1.3 mmol), NaOH (120 mg, 3.0 mmol), TBAB (161 mg, 0.5 mmol) and Pd complex **2** (2.7 mg, 0.5 mol%) were mixed in H_2O (2.0 mL). The reaction mixture was stirred at 60 °C and monitored by GC/GC-MS. The reaction mixture was extracted with diethyl ether (2 x 5 mL). The extract was dried (MgSO_4) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product.

5. General Procedure for double Hiyama coupling reaction

Aryl chloride (1.0 mmol), arylsilane (3.0 mmol), NaOH (240 mg, 6.0 mmol), TBAB (322 mg, 1.0 mmol) and Pd complex **2** (5.4 mg, 1.0 mol%) were mixed in H_2O (4.0 mL). The reaction mixture was stirred at 80 °C and monitored by GC/GC-MS. The reaction mixture was treated in the same workup manner as described above.

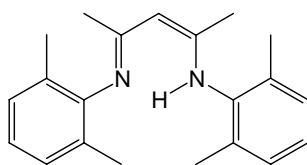
6. General Procedure for Hiyama-Heck double coupling reaction

The reaction was carried out by using a glass vial equipped with a Teflon screw cap. 1-chloro-2,4,6-trimethylbenzene (370 mg, 2.4 mmol), triethoxy(vinyl)silane (190 mg, 1.0 mmol), NaOH (160 mg, 4.0 mmol), TBAB (161 mg, 0.5 mmol) and catalyst **2a** (5.5 mg, 1.0 mol%) was mixed in H_2O (2.0 mL). The mixture was heated at 120 °C for 24 h. The reaction mixture was treated in the same workup manner as described above.

7. References

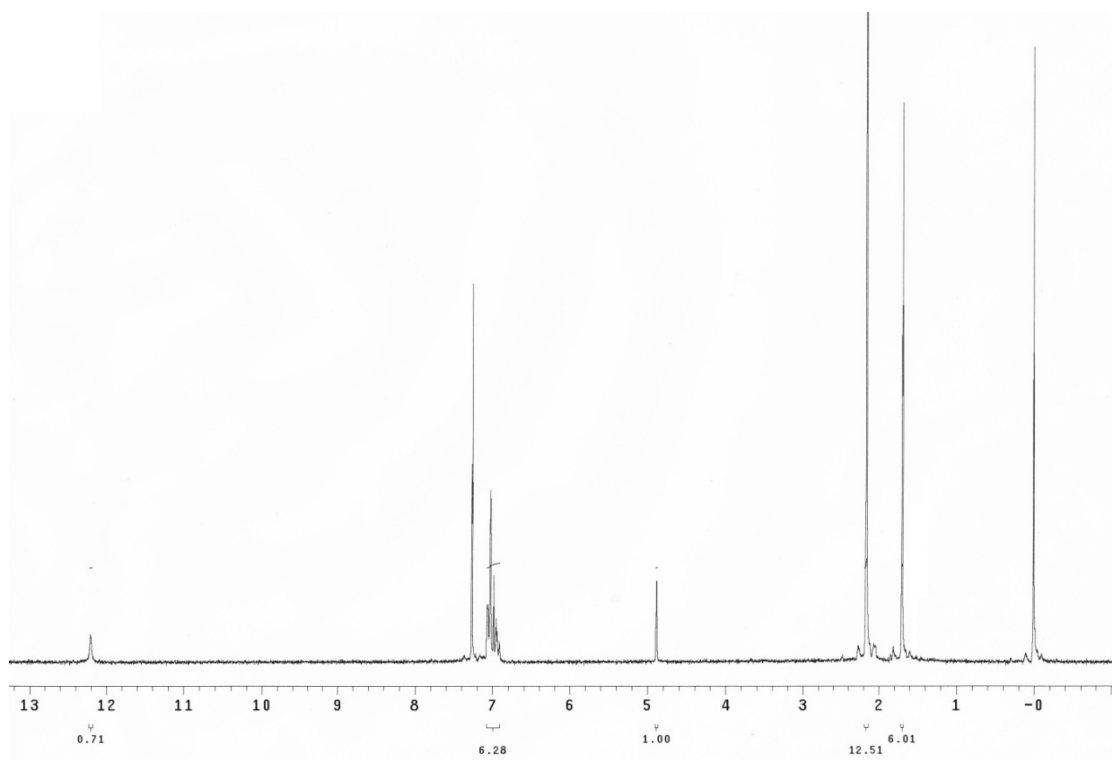
- (1) A. S. Manoso, C. Ahn, A. Soheili, C. J. Handy, R. Correia, W. M. Seganiash, P. DeShong, *J. Org. Chem.* **2004**, *69*, 8305.
- (2) Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303.

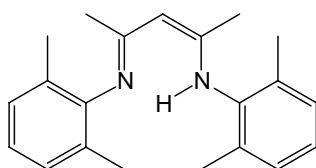
8. ^1H NMR and ^{13}C NMR spectra of β -diketimines **1**



1a

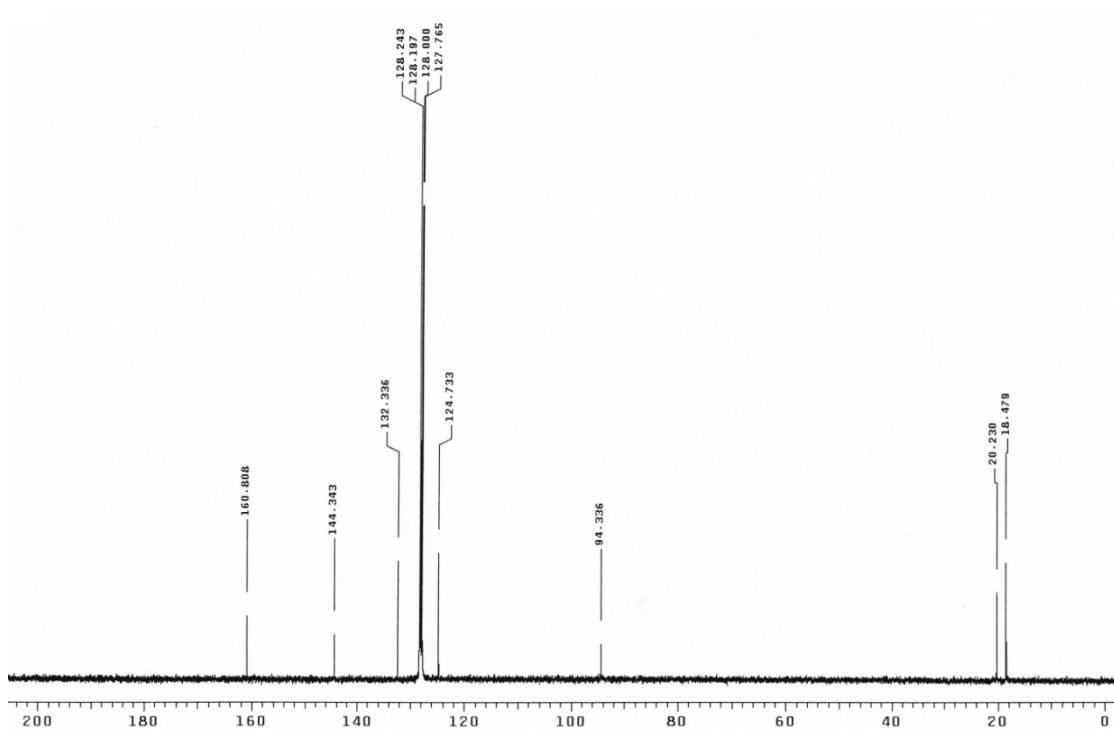
^1H NMR (CDCl_3 , 400 MHz)

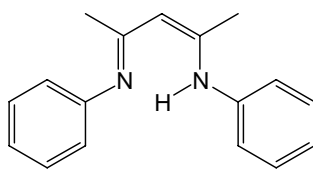




1a

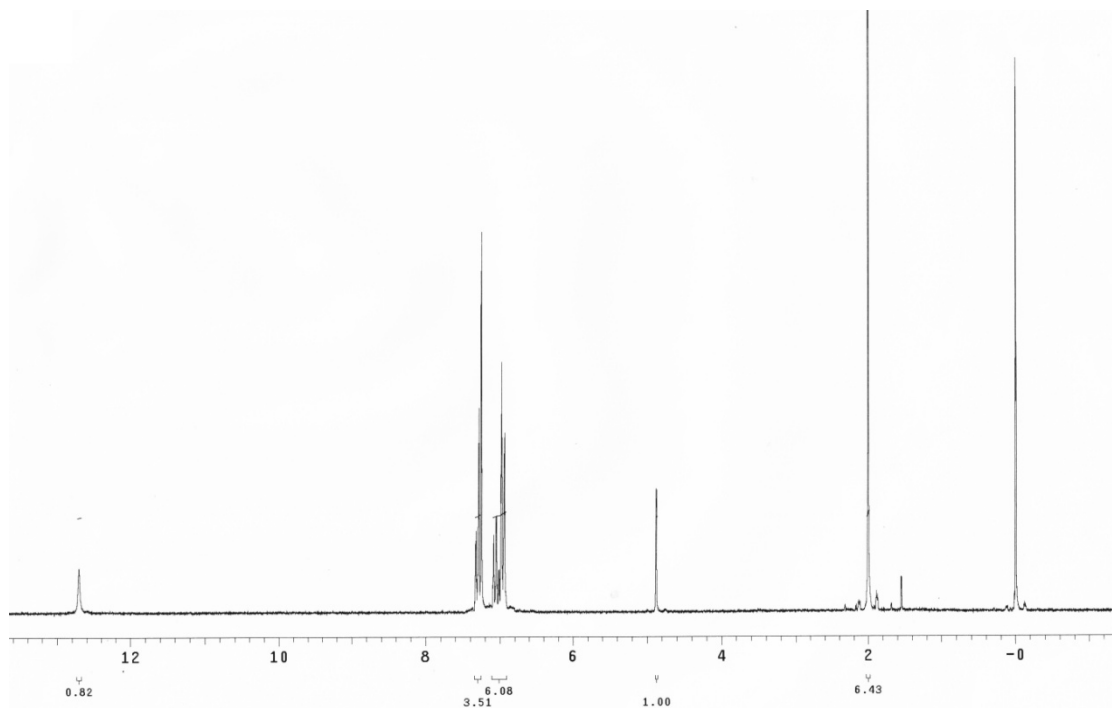
^{13}C NMR (C_6D_6 , 100 MHz)

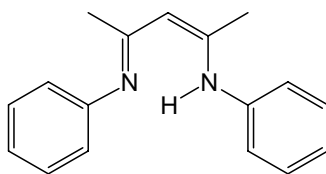




1b

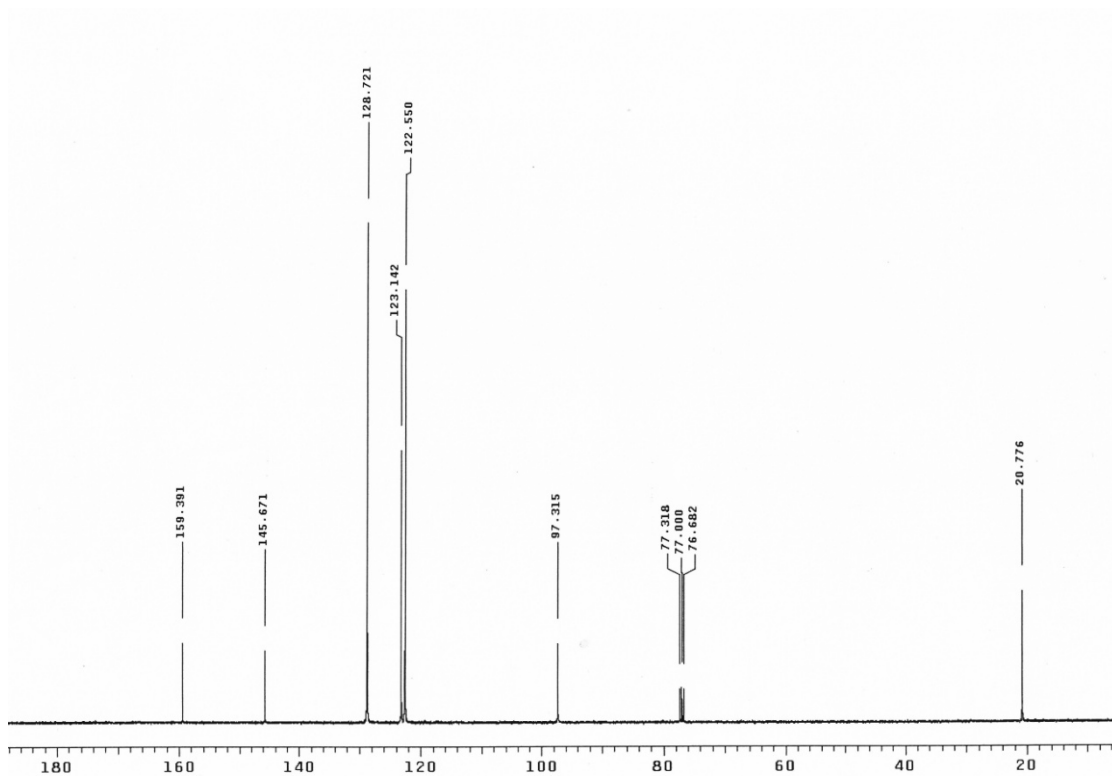
^1H NMR (CDCl_3 , 400 MHz)



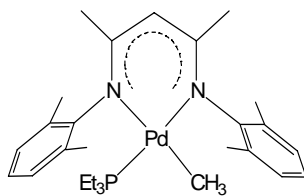


1b

^{13}C NMR (CDCl_3 , 100 MHz)

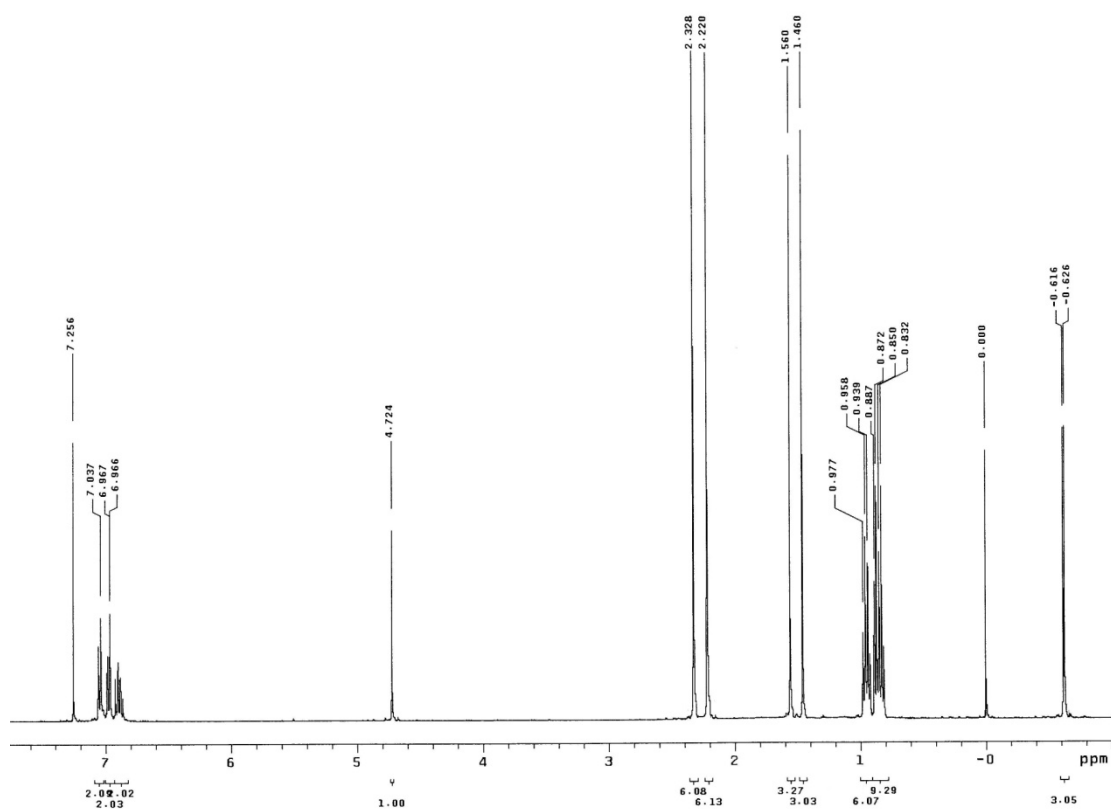


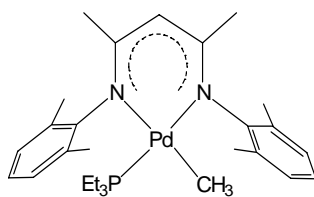
9. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra of palladium complexes 2



2a

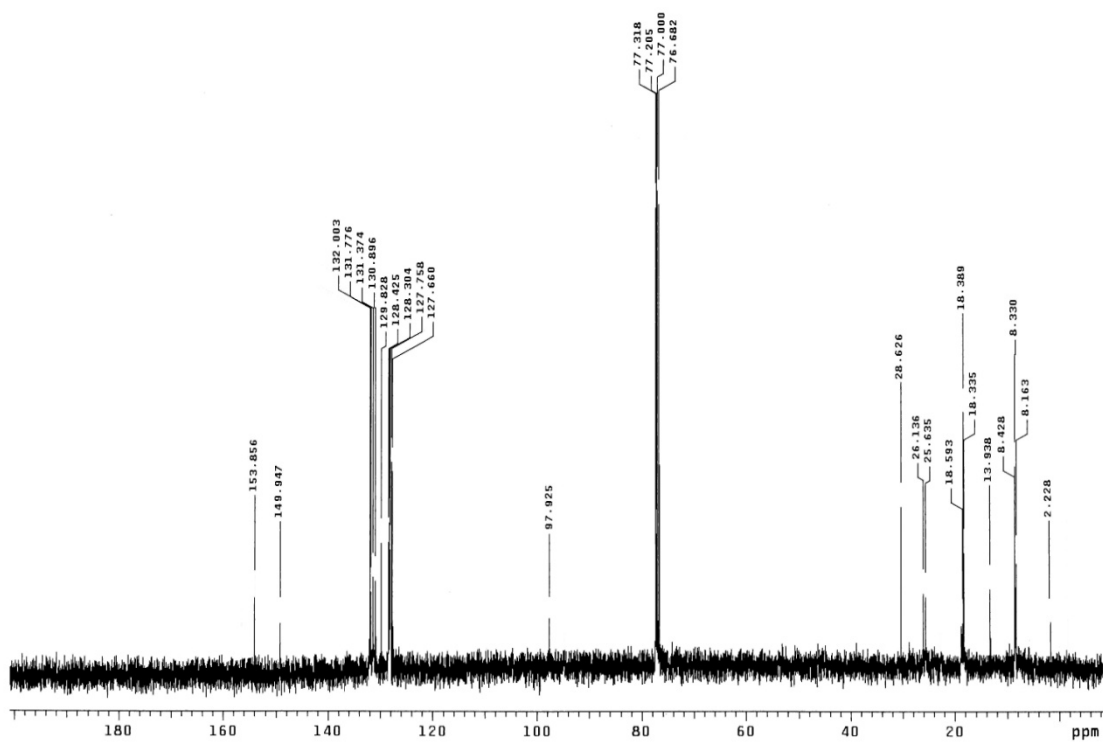
^1H NMR (CDCl_3 , 400 MHz)

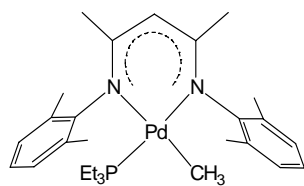




2a

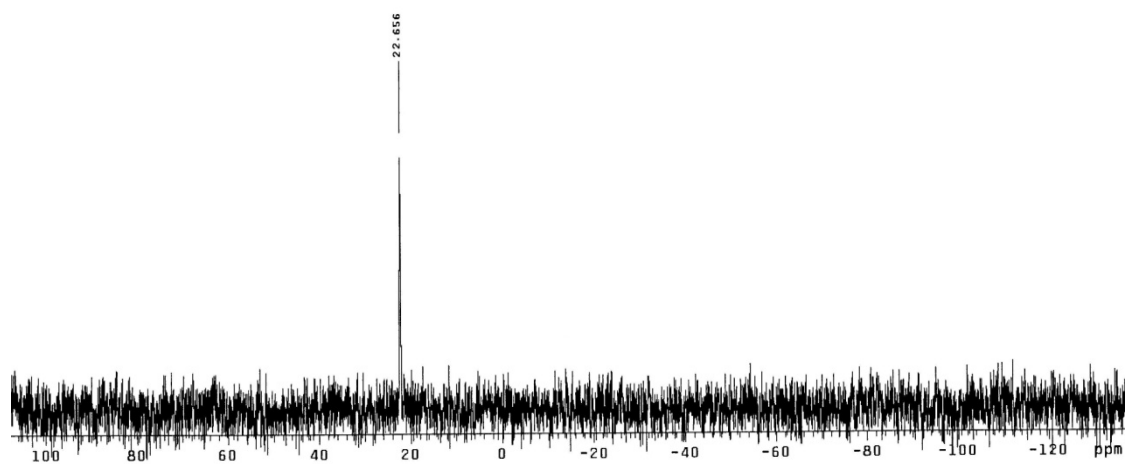
^{13}C NMR (CDCl_3 , 100 MHz)

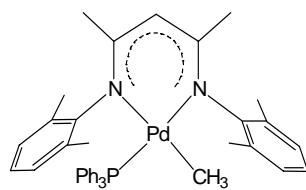




2a

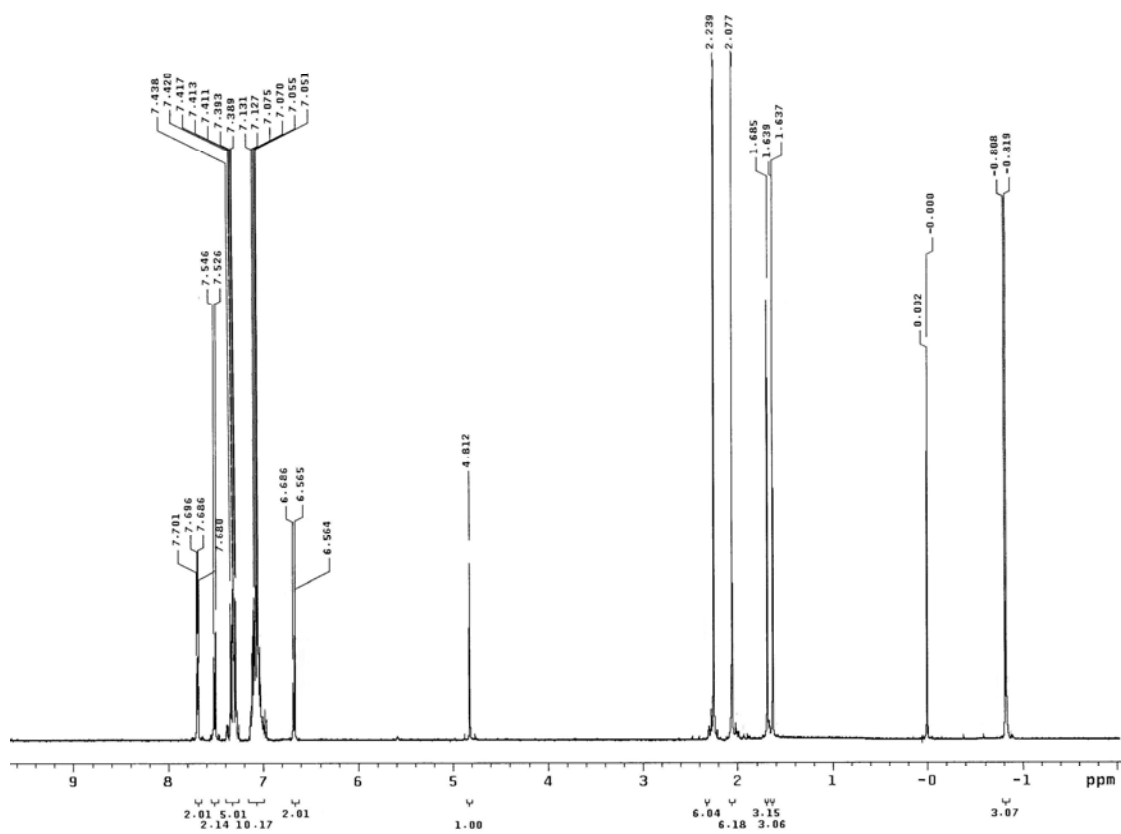
³¹P NMR (CDCl₃, 166 MHz)

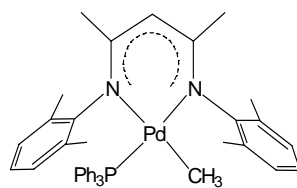




2b

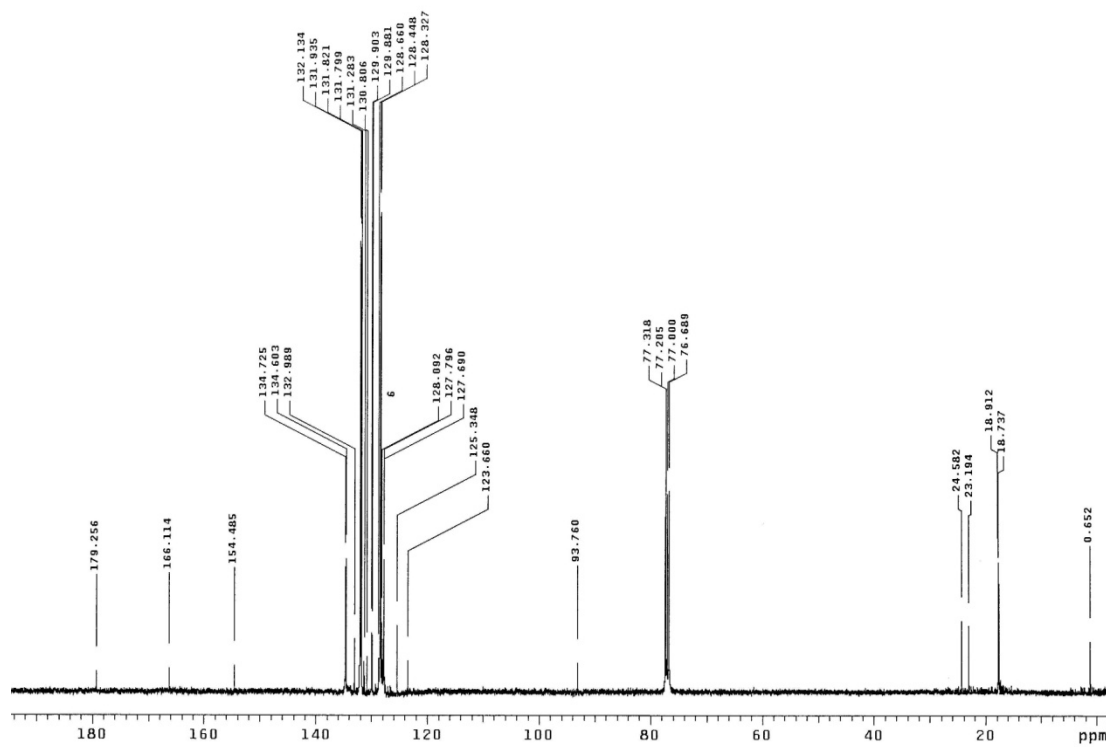
^1H NMR (CDCl_3 , 400 MHz)

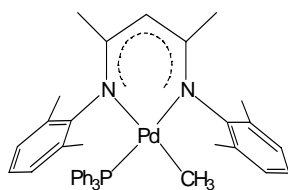




2b

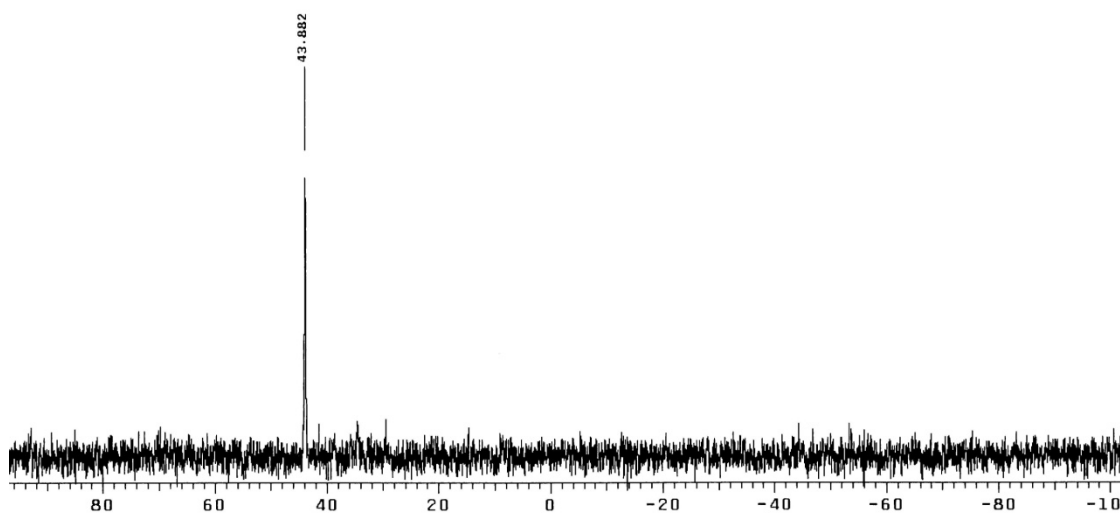
^{13}C NMR (CDCl_3 , 100 MHz)

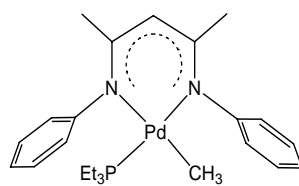




2b

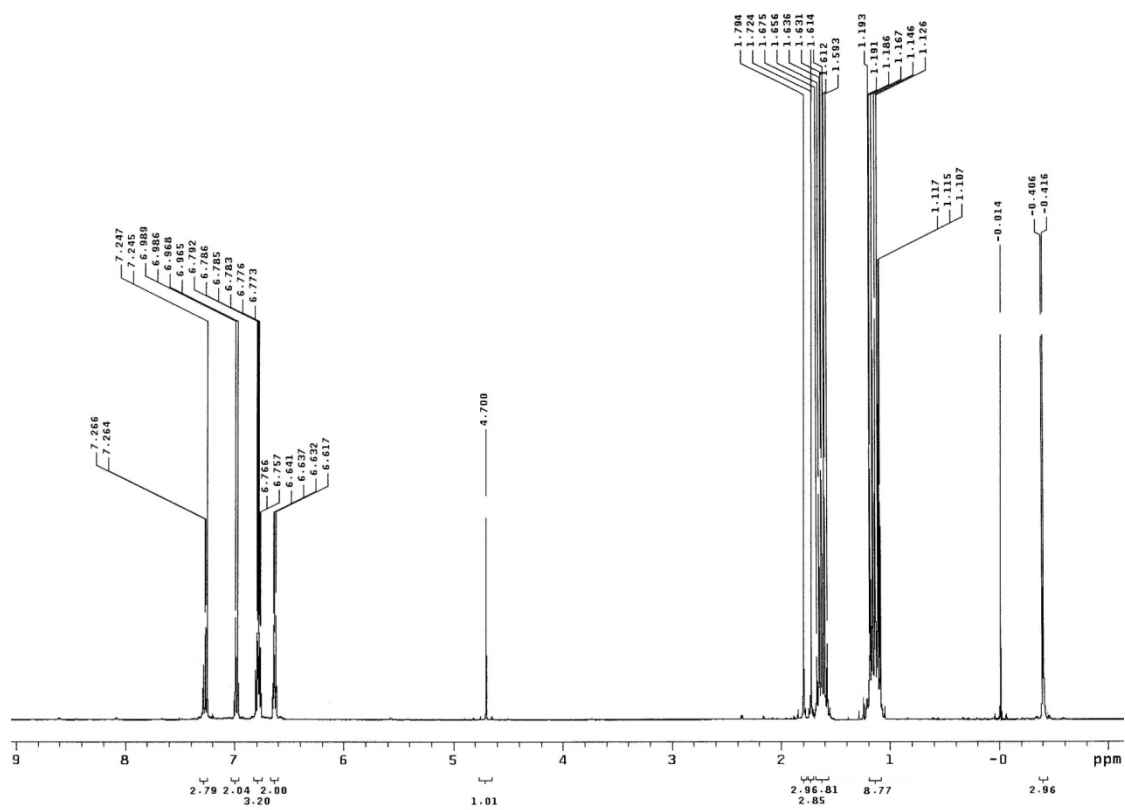
³¹P NMR (CDCl₃, 166 MHz)

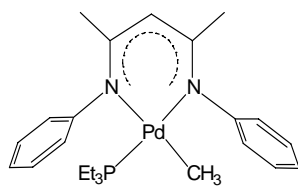




2c

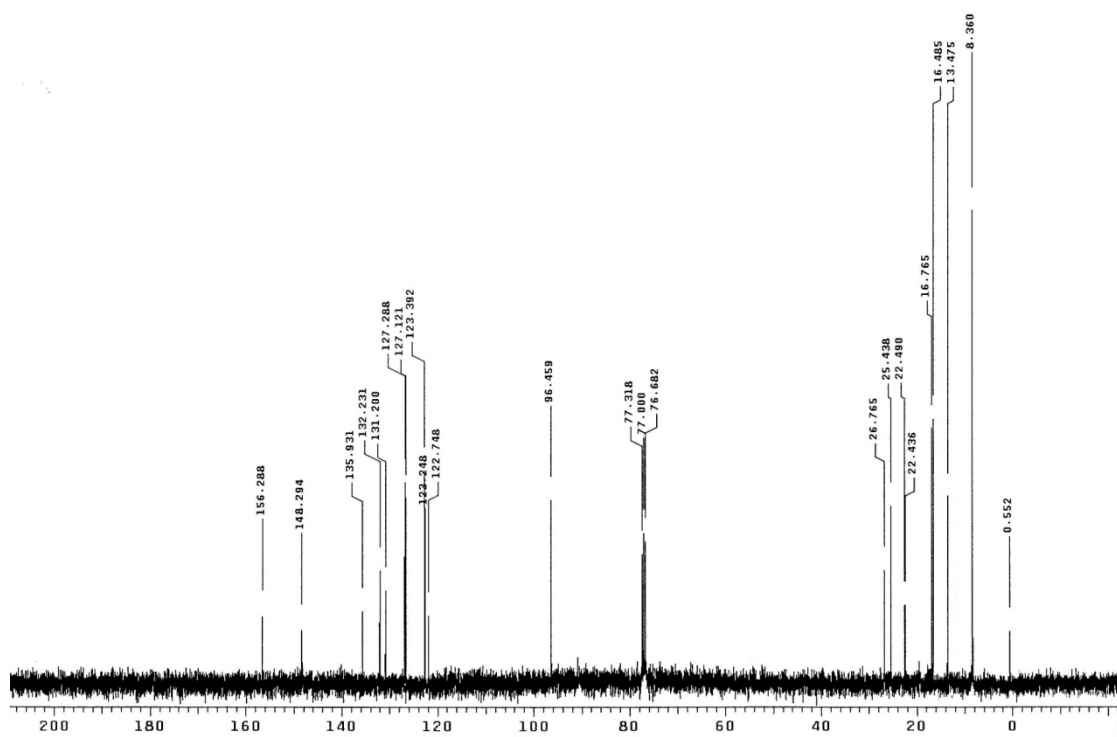
¹H NMR (CDCl₃, 400 MHz)

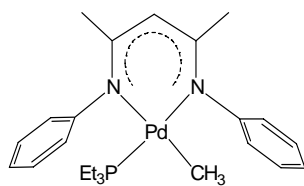




2c

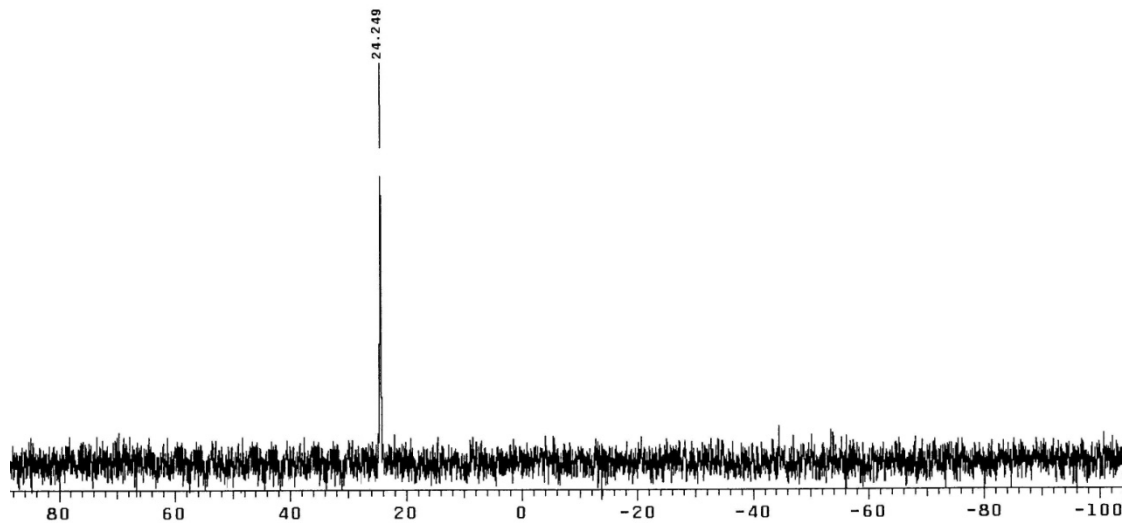
^{13}C NMR (CDCl_3 , 100 MHz)



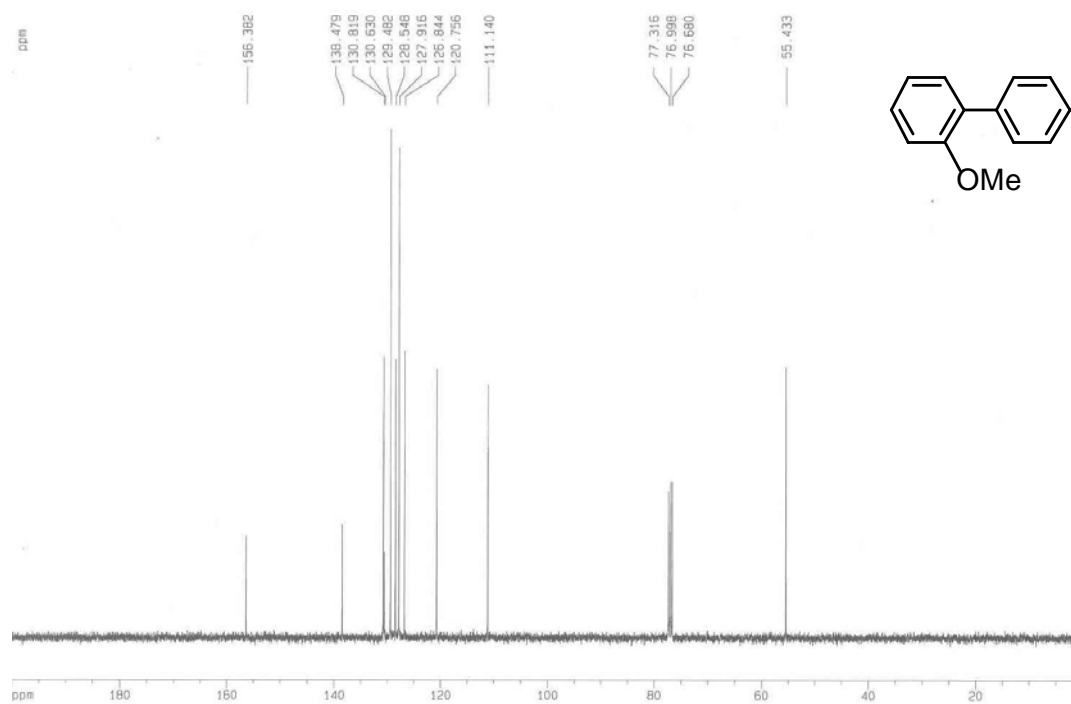
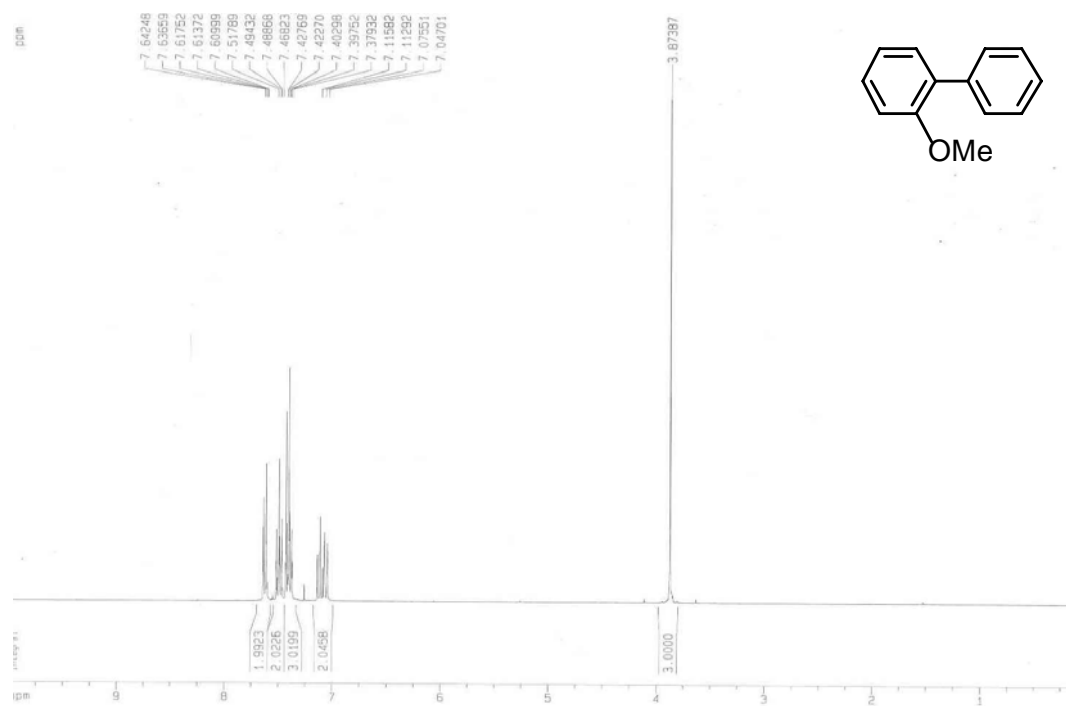


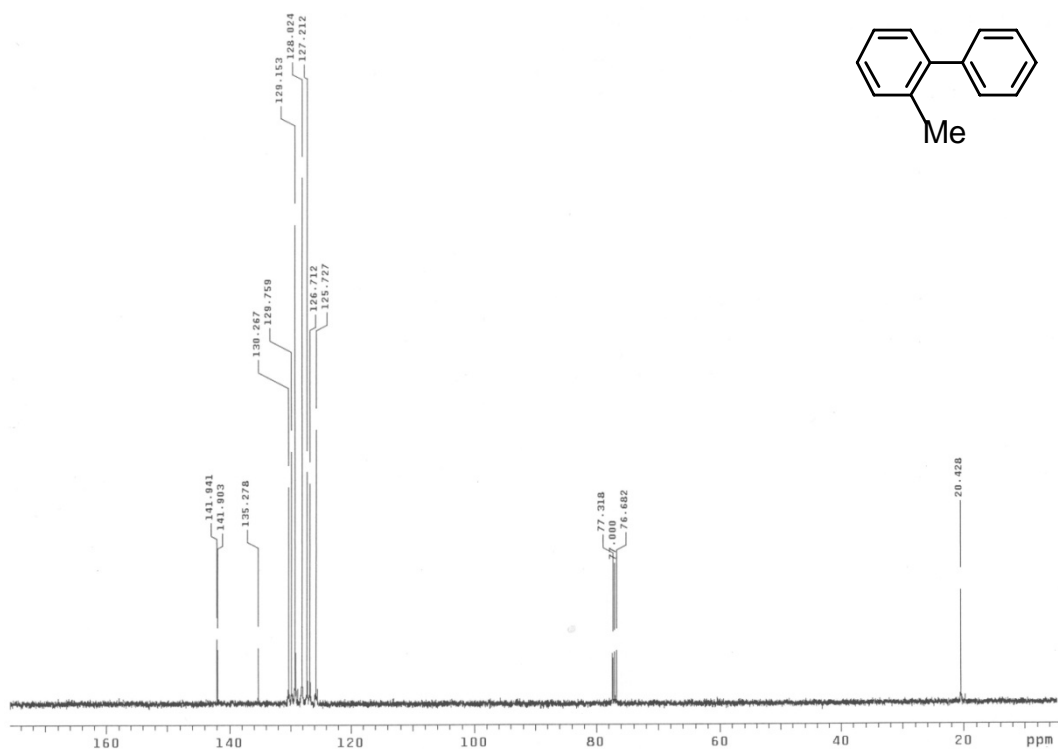
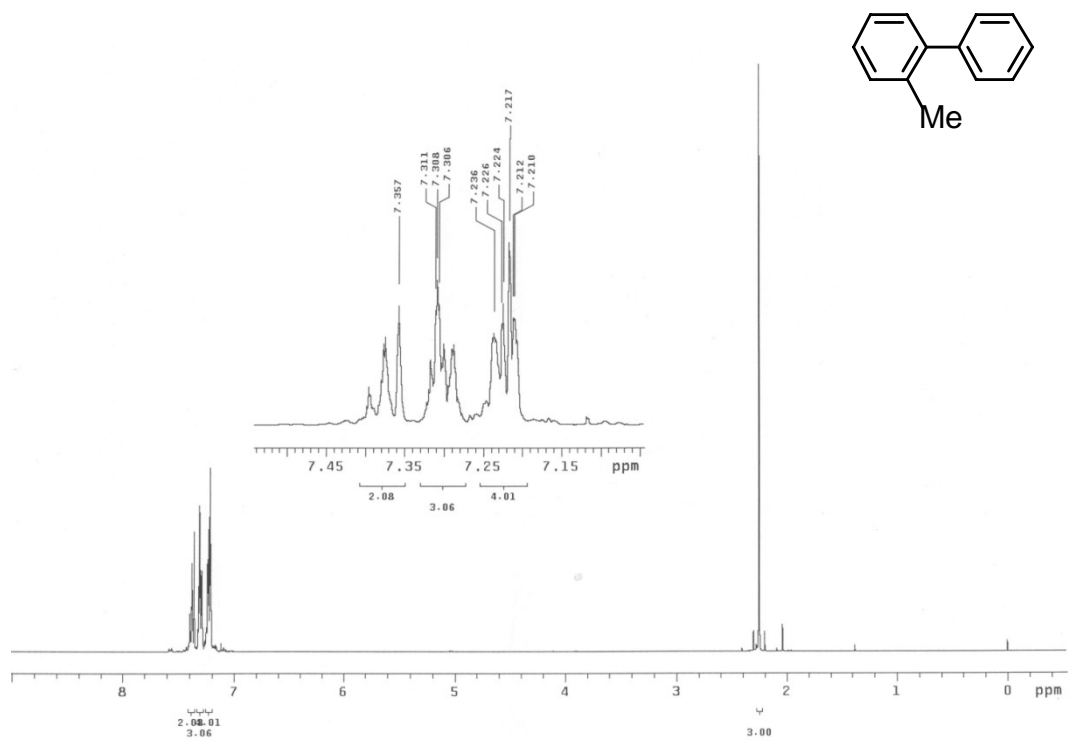
2c

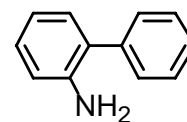
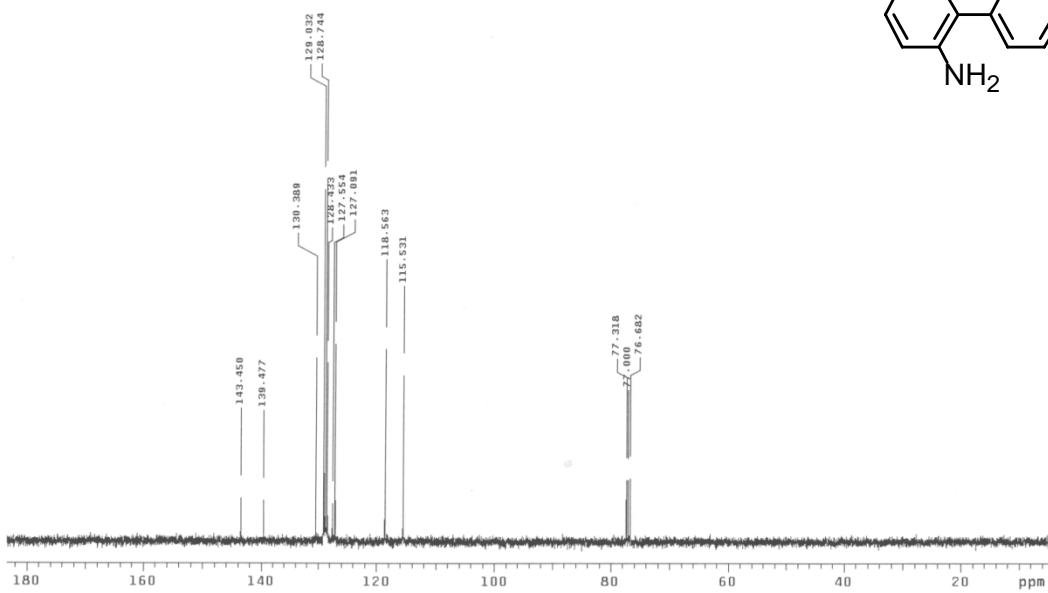
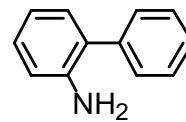
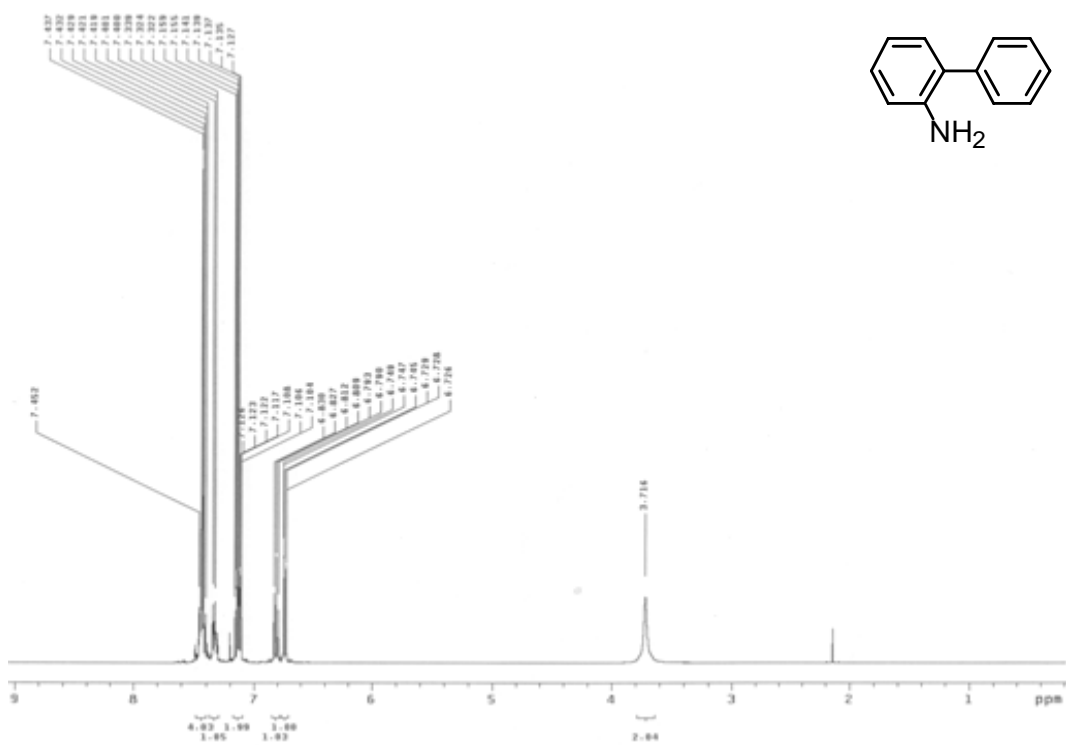
^{31}P NMR (CDCl_3 , 166 MHz)

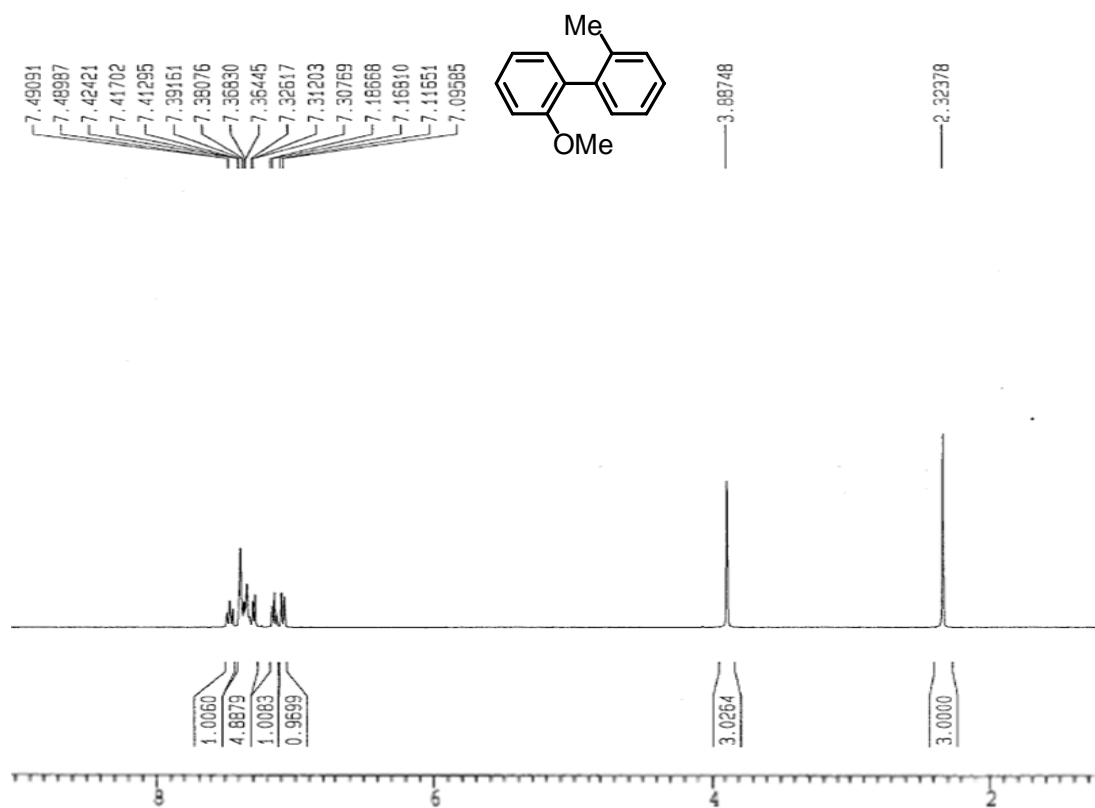


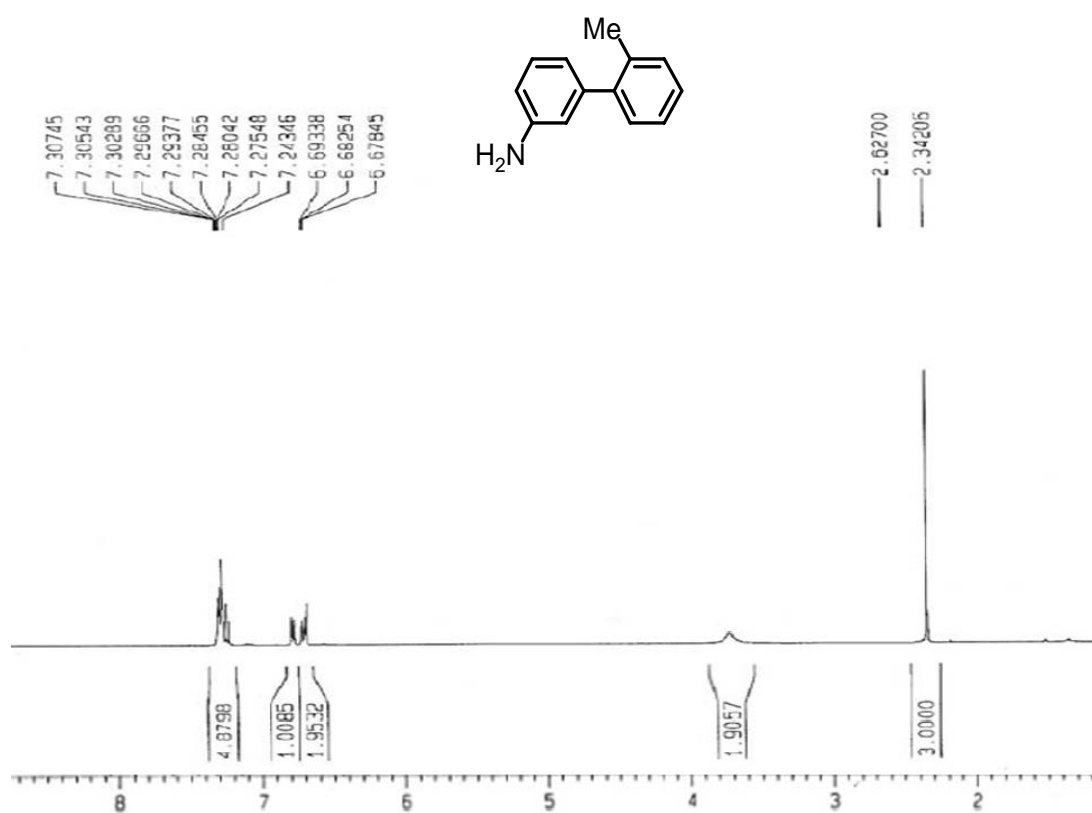
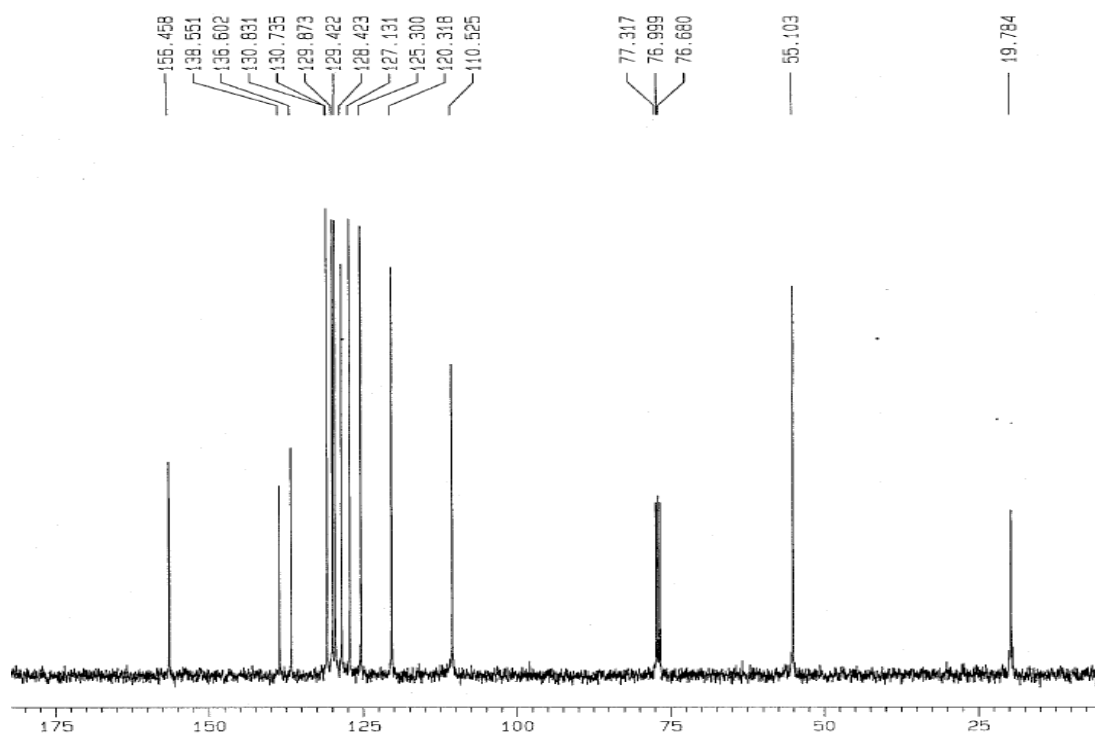
10. ^1H NMR and ^{13}C NMR spectra of the coupling products

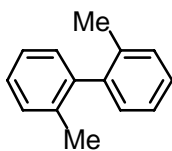
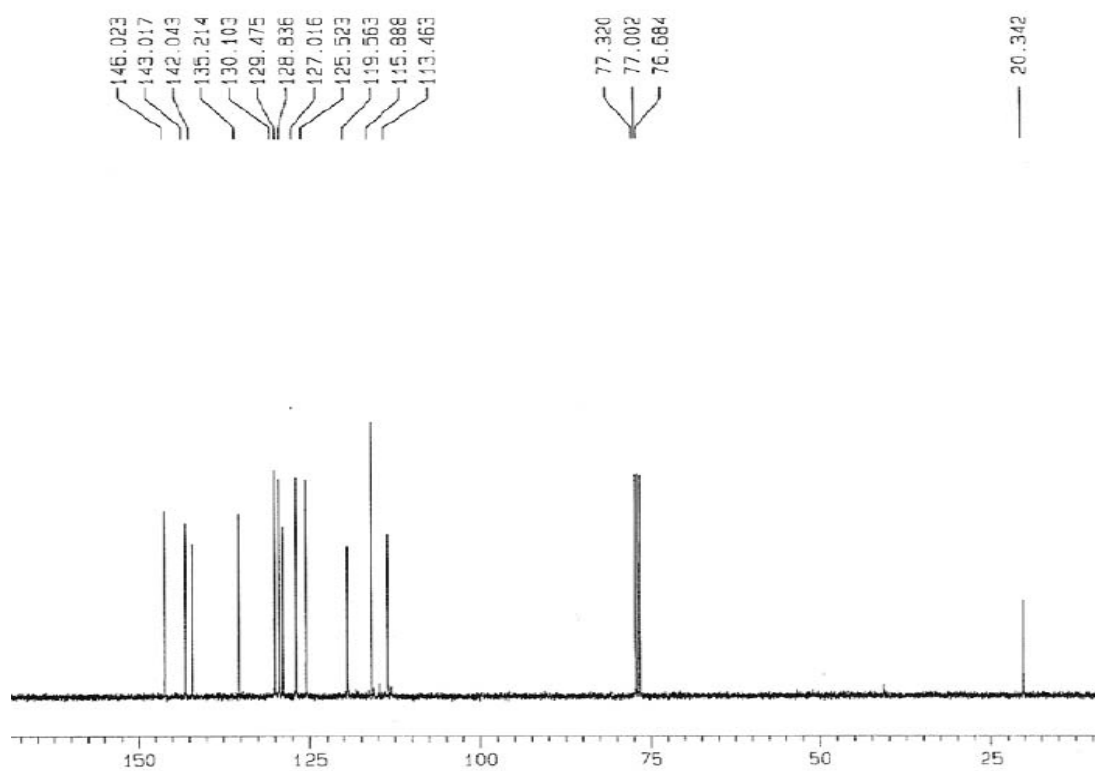


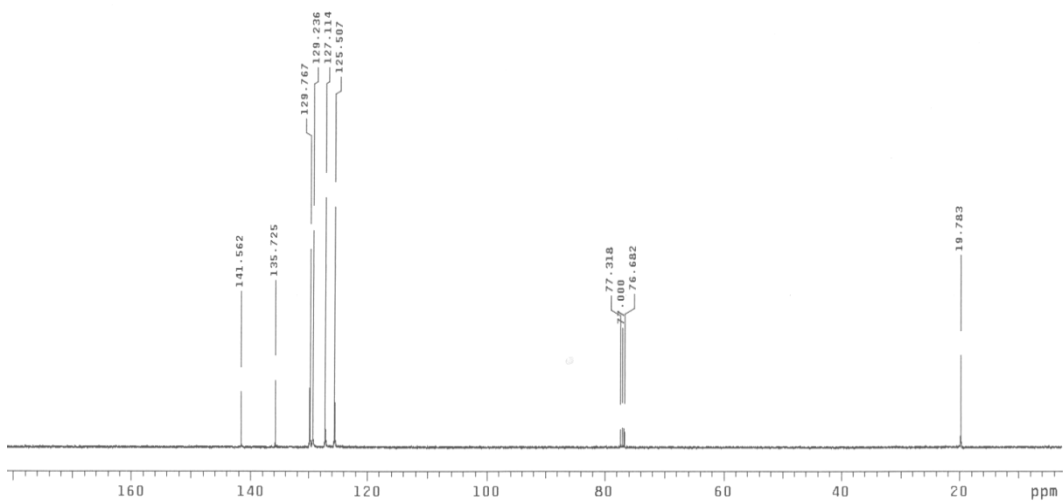
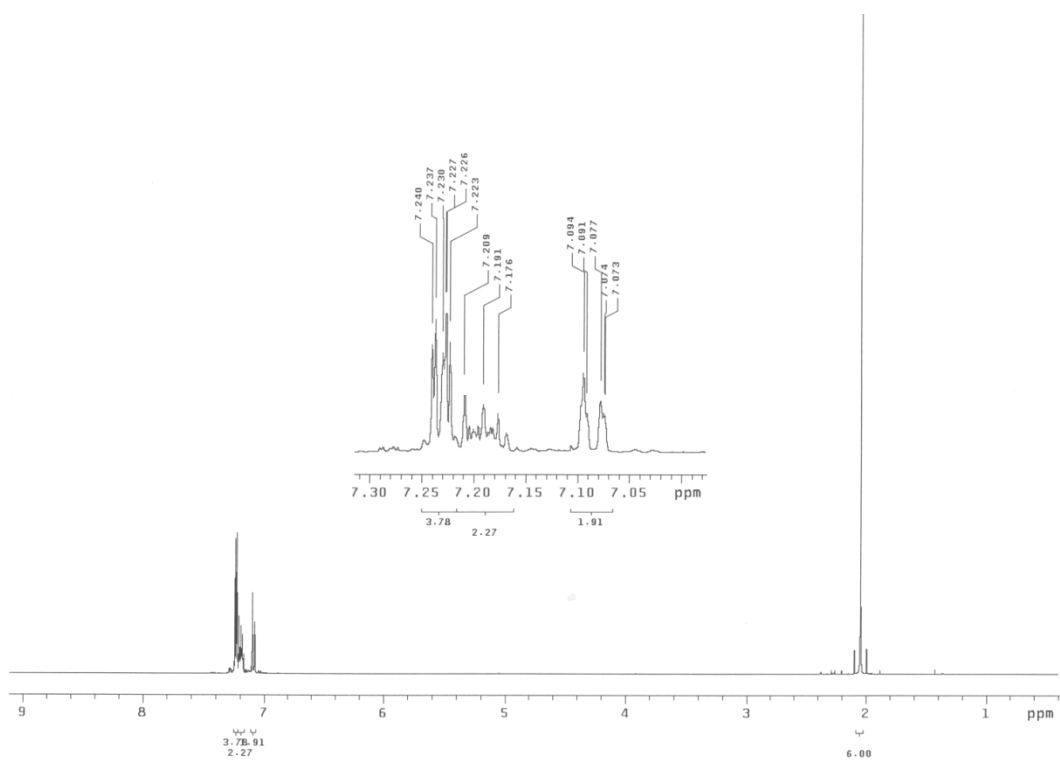


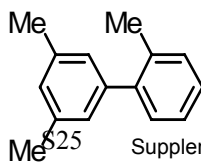
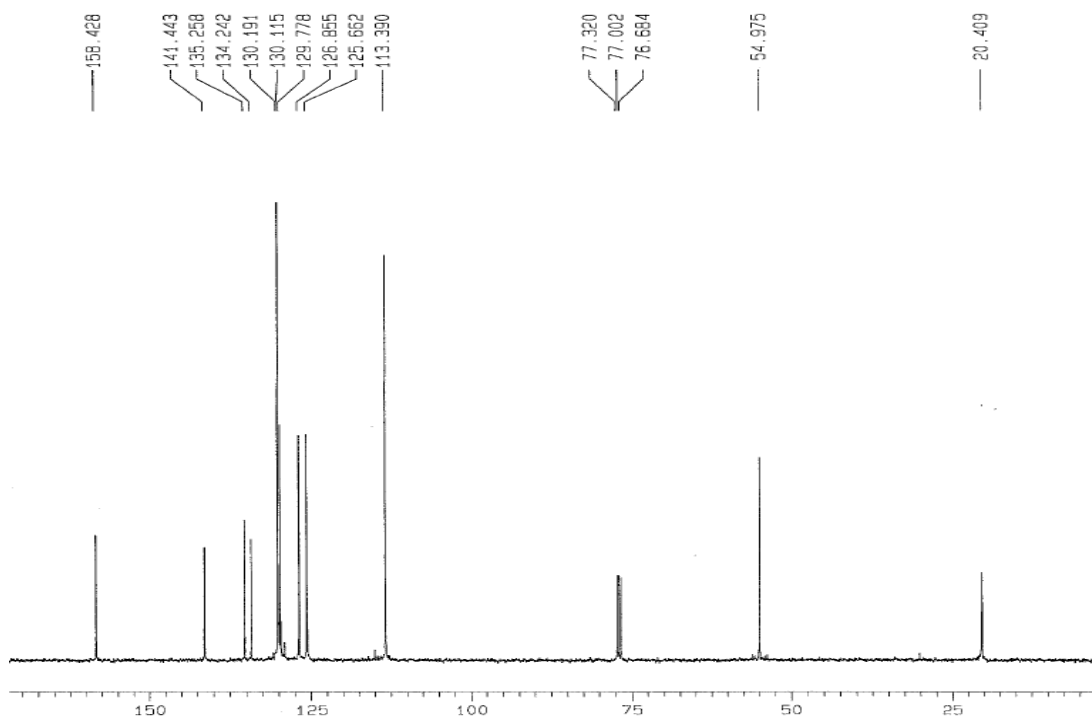
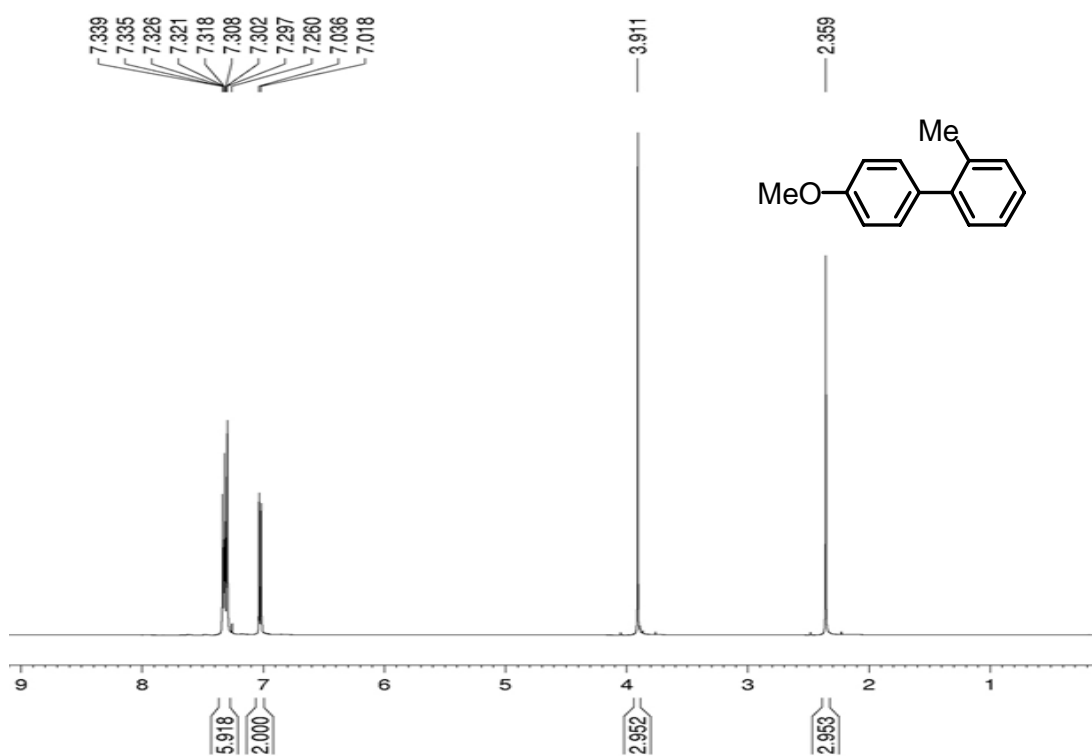


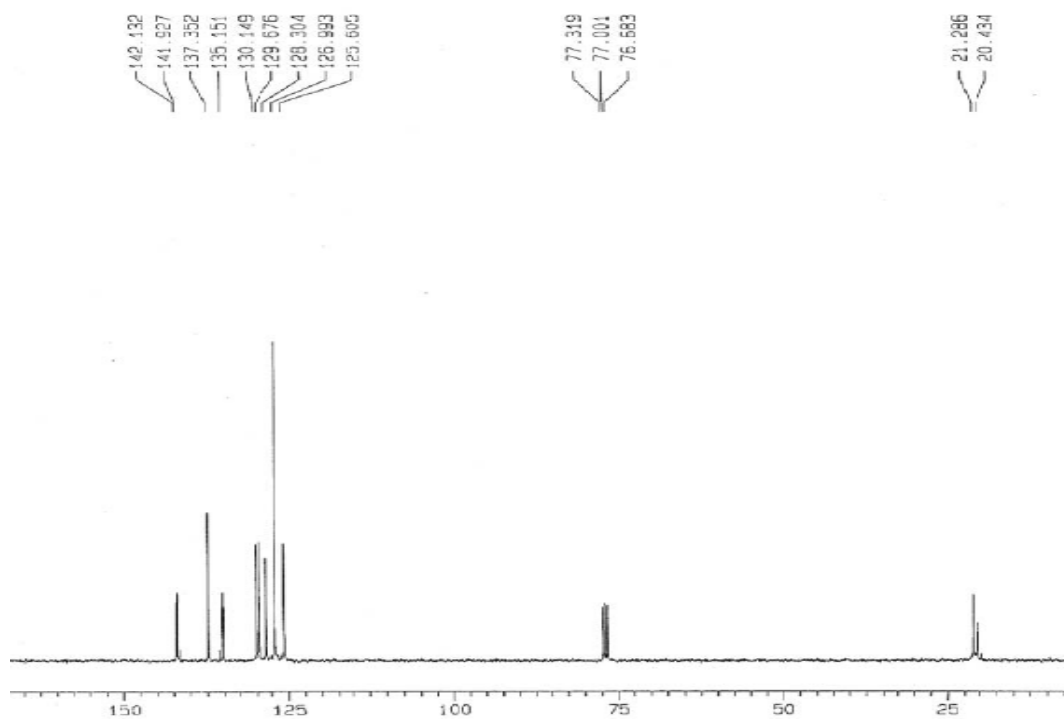
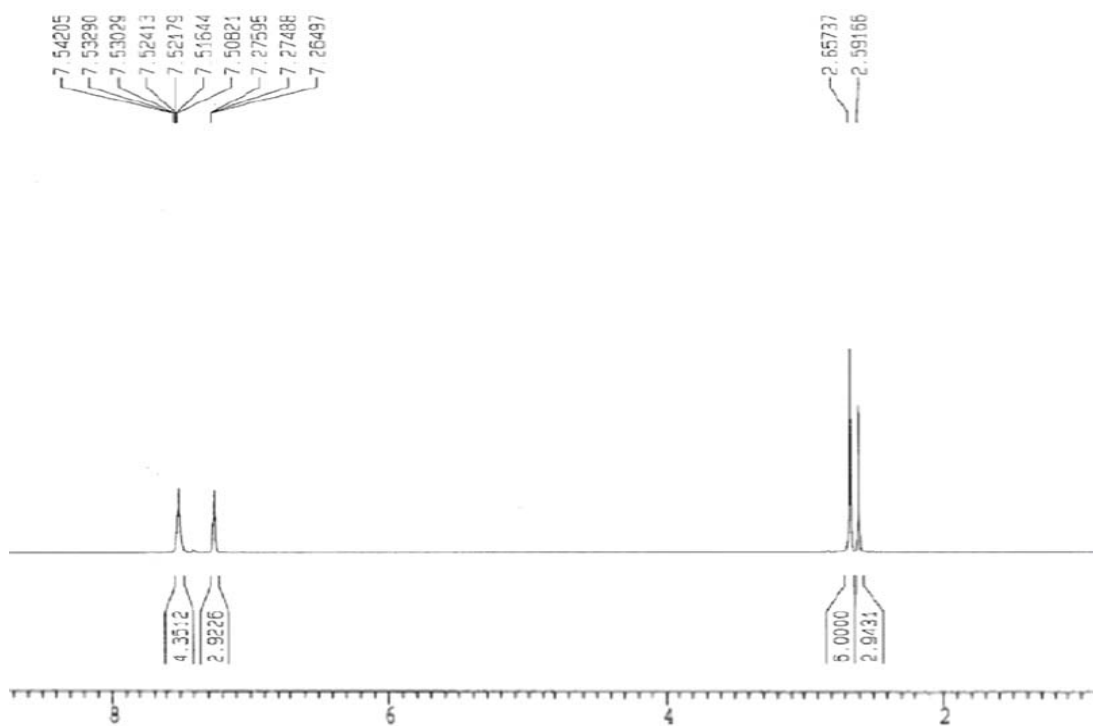


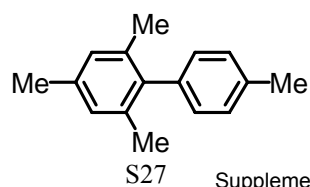
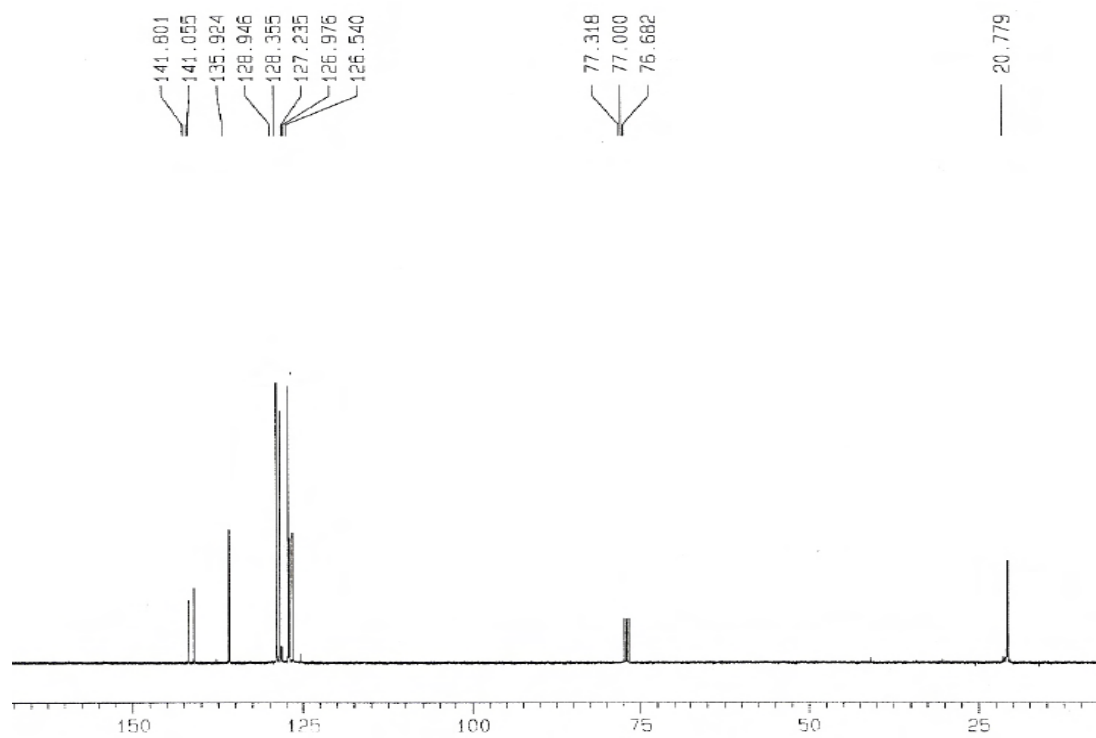
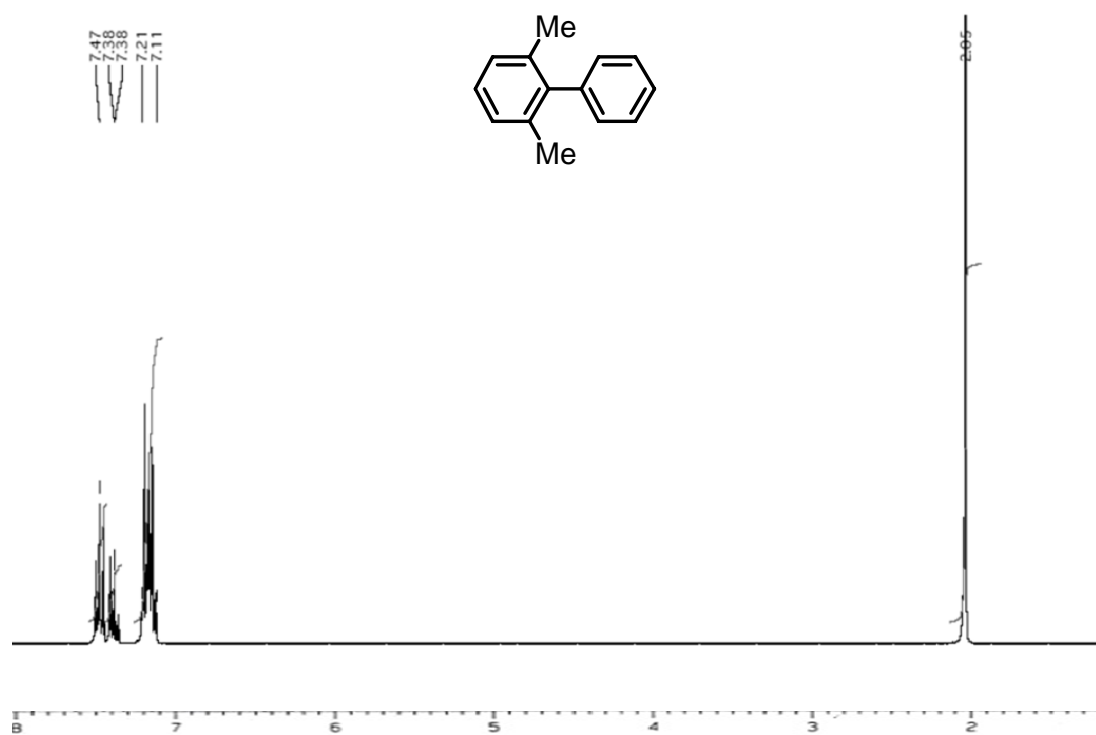


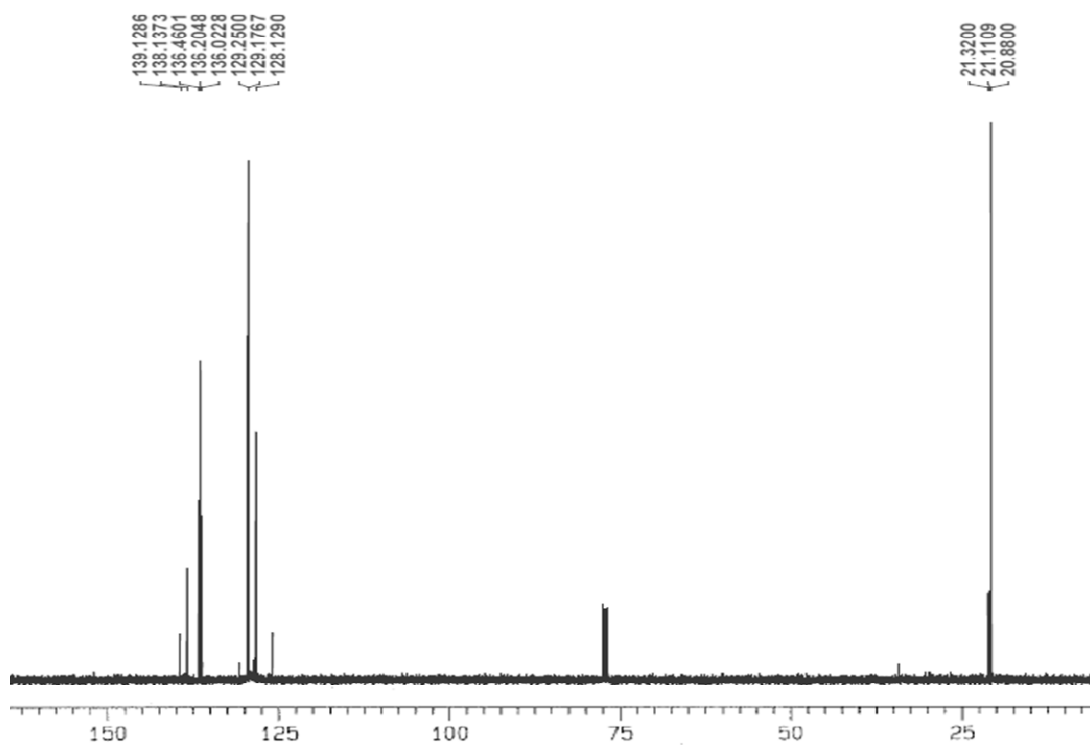
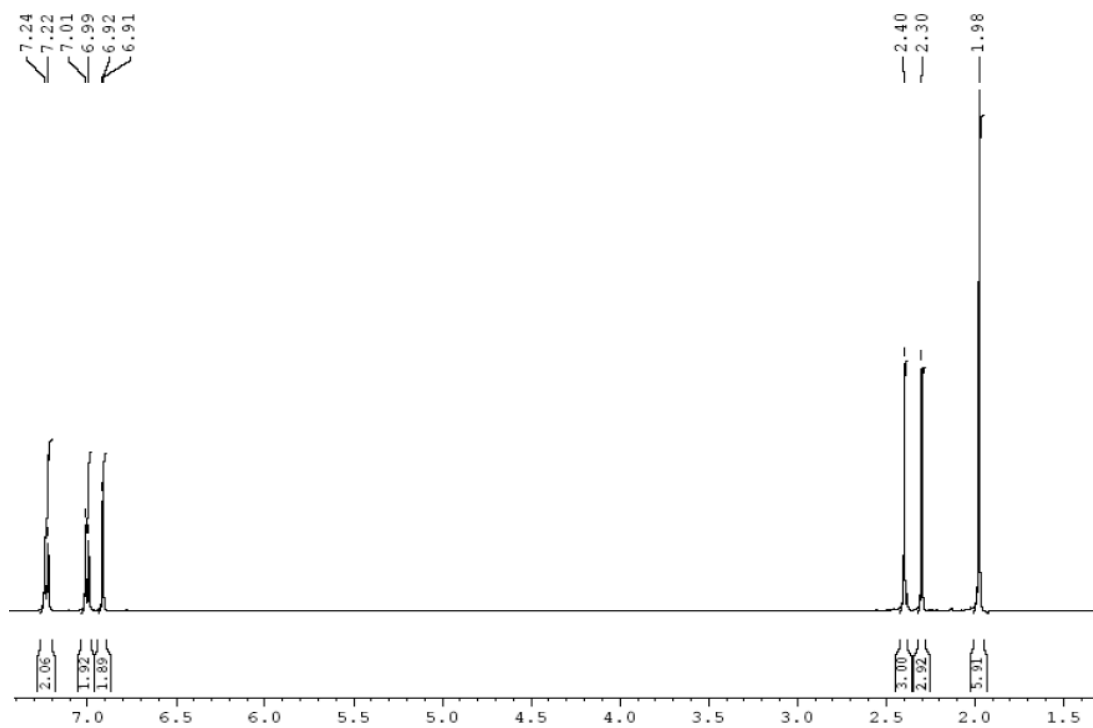


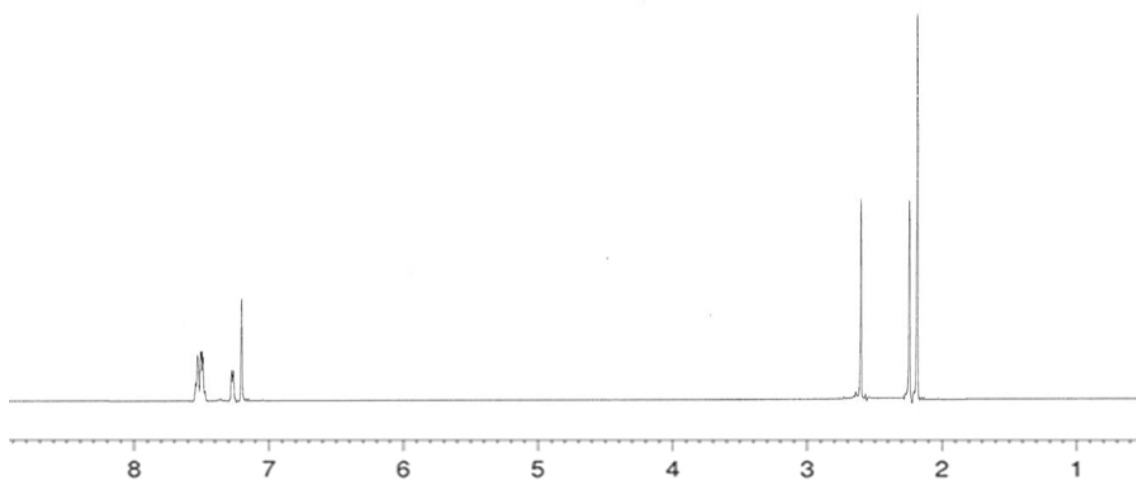
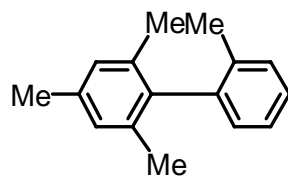


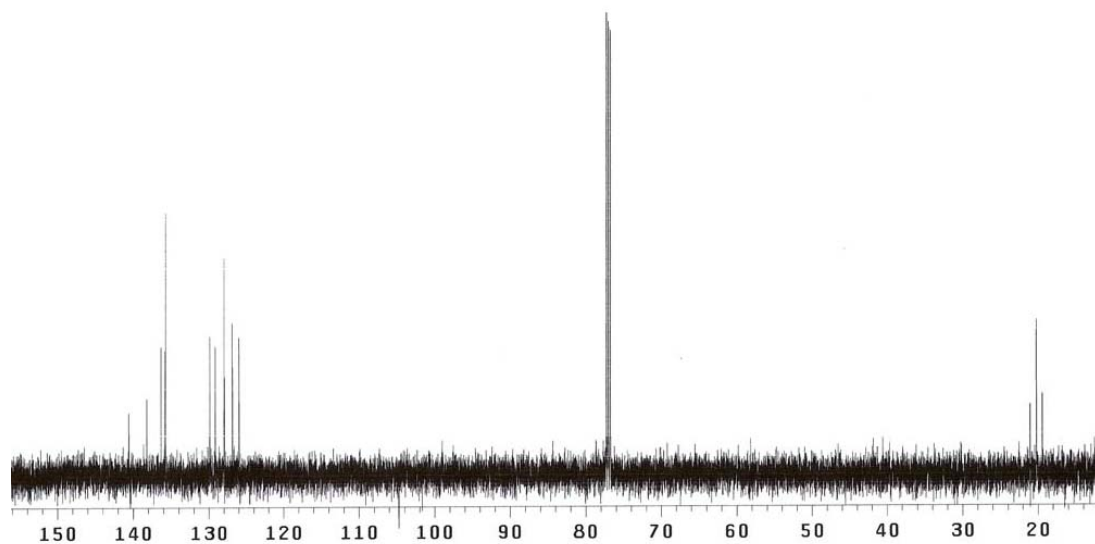












7.390
7.379
7.373
7.367
7.359
7.353
7.346
7.335
7.068
7.047
6.769
6.747

3.767

