Supporting Information

Palladium complex with functionalized β-cyclodextrin: a promising catalyst featured by recognition ability for Suzuki-Miyaura coupling reaction in water

Guofu Zhang,[a] Yuxin Luan,[a] Xingwang Han,[a] Yong Wang,[a] Xin Wen,[a] Chengrong Ding,[*a] and Jianrong Gao[a]

[a] *College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, China.*

Fax: (+86)-571-8832-0147; Tel: (+86)-571-8832-0147; E-mail: dingcr2004@yahoo.com.cn

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General information

All reagents were commercially available and used without purification, unless otherwise noted. β-Cyclodextrin, 2-ethynylpyridine and palladium acetate were purchased from Sigma-Aldrich. The electrospray ionization mass spectra (MS-ESI) were recorded on an Agilent 6210 TOF LC-MS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode. NMR spectra were recorded on Bruker AVANCE III 500MHz instrument with TMS as internal standard. Coupling constants were reported in Hertz (Hz). The 2D-ROESY spectrum was measured on a Bruker AVANCE III 500MHz instrument with a relaxation delay of 2 s and a ROESY spinlock time of 800 ms. The FT-IR spectra were recorded from KBr pellets in the range of 4000-400 cm^{-1} on Nicolet 6700. The content of palladium was measured by inductively coupled plasma mass spectrometry (ICP-MS) on PerkinElmer Elan DRC-e ICP-MS.

Experimental sections

a) Synthesis and characterization of L_n@β-CD and PdL_n@β-CD

***Synthesis of 6-O-monotosyl-β-CD*:** β-cyclodextrin (39.6900 g, 35.0 mmol) and NaOH (20.0000 g, 500.0 mmol) were dissolved in 800.0 mL of water in a 2.0 L three-neck round-bottom flask equipped with a magnetic stirrer. The temperature was lowered to 0-5 °C. *p*-toluenesulfonyl chloride (TsCl, 26.6980 g, 140.0 mmol) was added, and the suspension was stirred vigorously for 4 h. The unreacted TsCl was removed by filtration. Then, the pH of the filtrate was adjusted to neutral by addition of hydrochloric acid, and the product was precipitated. Subsequently, the mixture was filtered, washed with water, dried in vacuum and recrystallized by water. The final pure 6-O-monotosyl-β-CD was dried overnight in vacuum at 60 °C. Yield: 10.9644 g (24.3%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 7.77-7.72(m, 2H), 7.45-7.40(m, 2H), 5.73(s, 14H), 4.85-4.77(m, 7H), 4.50-4.32(m, 6H), 3.67-3.53(m, 28H), 3.51-3.29(m, overlaps with HDO), 2.43(s, 3H).

***Synthesis of 6-monodeoxy-6-monoazido-β-CD*:** 6-O-monotosyl-β-CD (6.4459 g, 5.0 mmol) and sodium azide (0.6501 g, 10.0 mmol) were dissolved in anhydrous DMF. The mixture was stirred at 75 °C for 4 h, after which 20.0 mL of H_2O was added. Then, the product began to precipitate when a plenty of acetone was added. After that, the mixture was filtrated and washed with acetone twice (2×400.0 mL). The 6-monodeoxy-6-monoazido-β-CD was obtained after dried in vacuum at 60 °C overnight. Yield: 5.4288 g (93.6%). According to FT-IR spectra, the absorption band at 2105.5 cm^{-1} clearly indicates the successful attachment of azido group onto the β-cyclodextrin (Fig. S1). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 5.81-5.63(m, 14H), 4.88-4.83(m, 7H), 4.56-4.45(m, 6H), 3.77-3.56(m, 28H), 3.40-3.29(m, overlaps with HDO).

***Synthesis of L_n@β-CD*:** 6-monodeoxy-6-monoazido-β-CD (3.4800 g, 3.0 mmol), 2-ethynylpyridine (0.3712 g, 3.6 mmol), sodium ascorbate (0.1189 g, 0.6 mmol) and $CuSO_4$ (0.0479 g, 0.3 mmol) were added under nitrogen atmosphere into a Schlenk tube and dissolved in deaerated DMSO/H_2O (v/v, 1/1, 40.0 mL). The resulting mixture was stirred at room temperature for 24 h. After the reaction, 20.0 mL of water was added. Poured the mixed solution to acetone (400.0 mL) and the desired triazole functionalized β-CD (L_n@β-CD) precipitated. The crude product was obtained by filtration, washed with acetone until the copper content was beyond the detection limit of ICP-MS. L_n@β-CD was obtained as white solid powder. Yield: 3.4880 g (92.1%). The absorption band at 2105.5 cm^{-1} disappeared and the FT-IR showed a new band at

1604.8 cm^{-1}, which was assigned to the C=C vibration of the triazole ring and implied that the "click" process was completed (Fig. S2). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.59(d, *J* = 4.5 Hz, 1H), 8.56(s, 1H), 8.03(d, *J* = 7.5 Hz, 1H), 7.90(t, *J* = 8.5 Hz, 1H), 7.35(t, *J* = 6.0 Hz, 1H), 5.90-5.61(m, 14H), 4.93-4.71(m, 7H), 4.54-4.41(m, 6H), 3.94-3.57(m, 28H), 3.46-3.26(m, overlaps with HDO); ESI-MS: 1263.4 (The major ion was assigned to the $[L_n@\beta\text{-CD}+H]^+$ species).

***Synthesis of PdL$_n$@β-CD*:** $Pd(OAc)_2$ (0.0449 g, 0.20 mmol) was dissolved in anhydrous toluene (20.0 mL) and L_n@β-CD (0.7575 g, 0.60 mmol) was added. The solid-liquid mixture was stirred for 12 h at room temperature, after which the solid was filtered, washed thoroughly with large volume of acetone in order to remove any adsorbed palladium and finally dried at 30 ^{o}C under vacuum. The palladium complex was obtained as light yellow powder. The palladium content analyzed by ICP-MS was 0.1550 mmol/g. Yield: 0.6820 g. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 9.26(s, 1H), 8.27(d, *J* = 8.0 Hz, 1H), 8.13(d, *J* = 5.0 Hz, 1H), 8.07(t, *J* = 9.2 Hz, 1H), 7.68(t, *J* = 8.5 Hz, 1H), 5.96-5.70(m, 14H), 4.95-4.78(m, 7H), 4.52-4.44(m, 6H), 3.64-3.58(m, 28H), 3.43-3.09(m, overlaps with HDO).

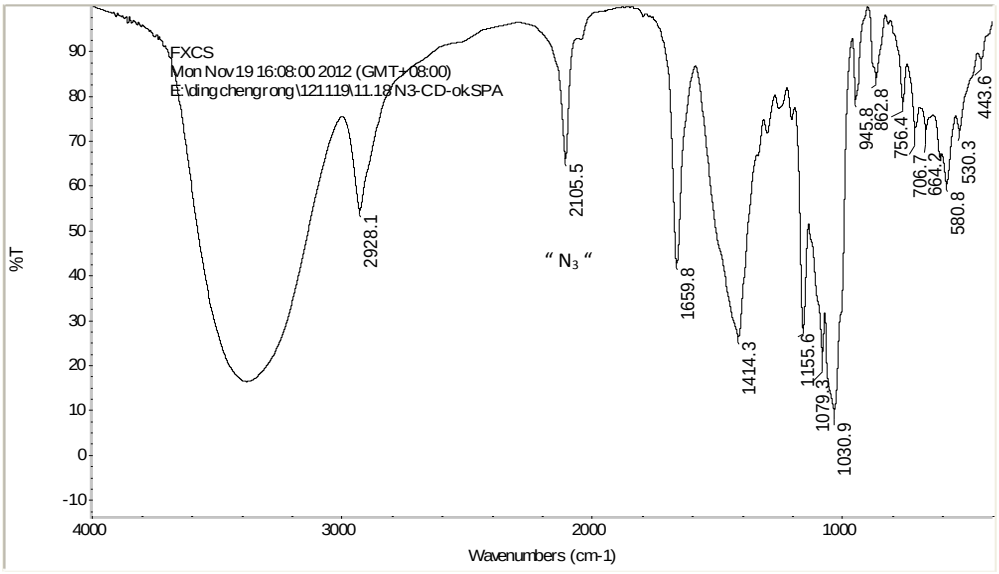


Figure S1. FT-IR spectrum of 6-monodeoxy-6-monoazido-β-CD.

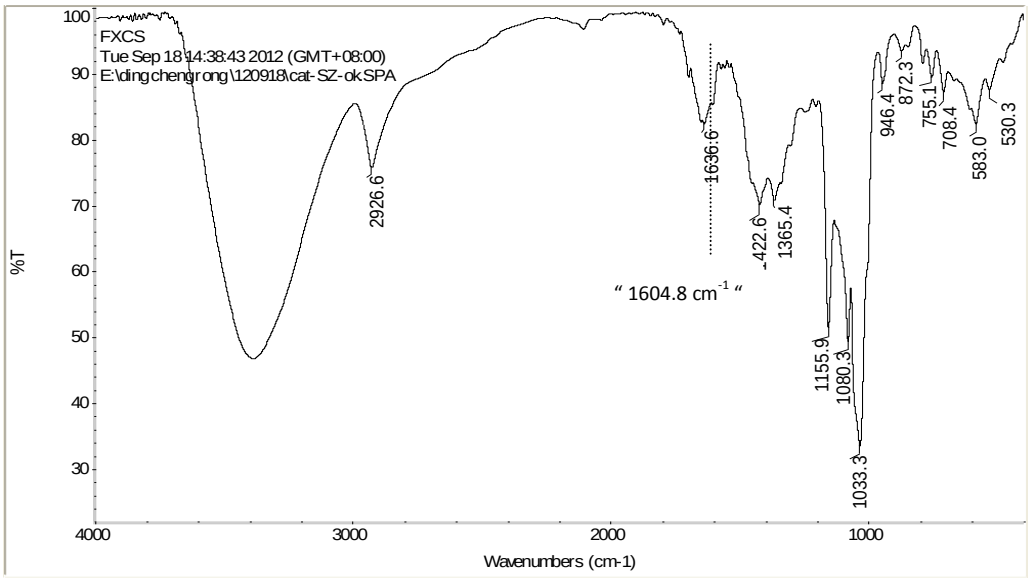


Figure S2. FT-IR spectrum of L_n@β-CD.

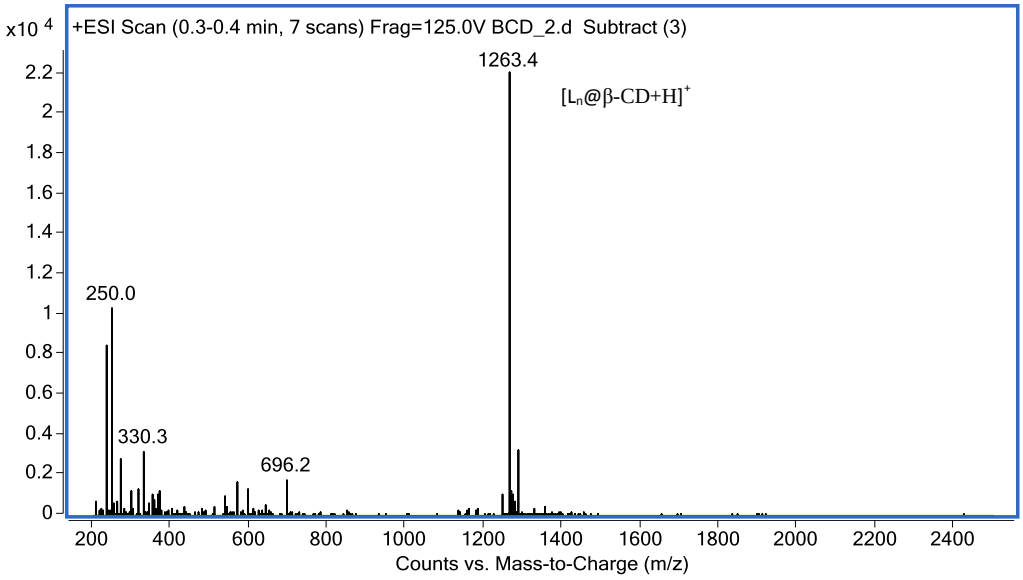


Figure S3. ESI-MS spectrum of L_n@β-CD.

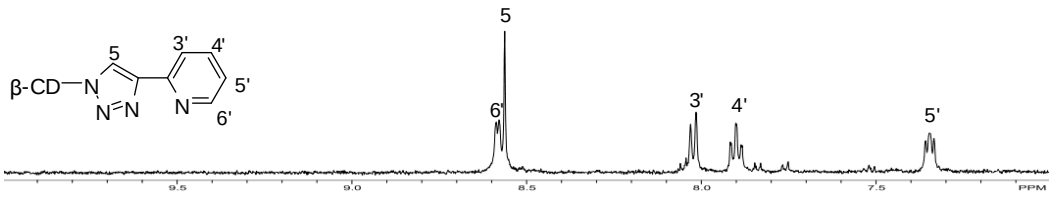


Figure S4. Partial ^{1}H NMR spectrum of L_n@β-CD.

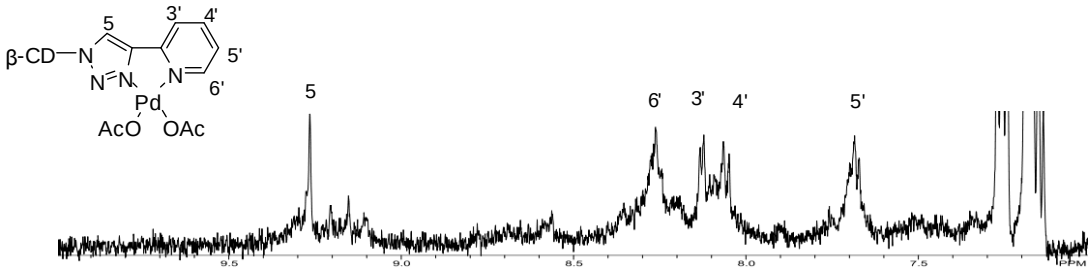


Figure S5. Partial ^{1}H NMR spectrum of PdL_n@β-CD.

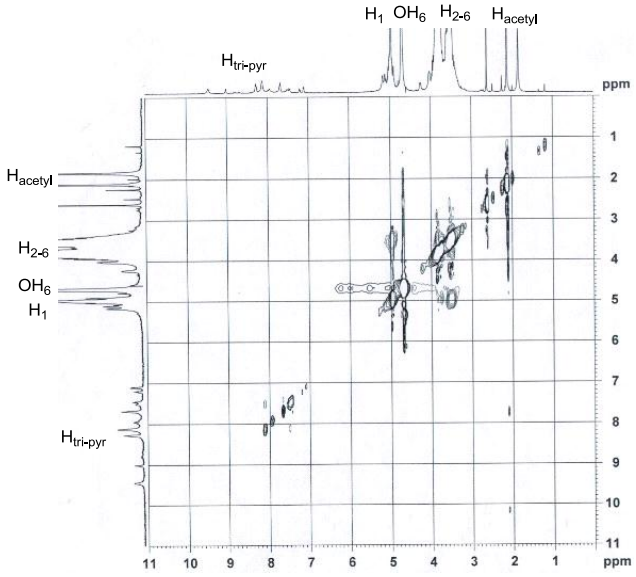


Figure S6. 2D ROESY NMR spectrum of saturated PdL_n@β-CD in D_2O (25 ^{o}C).

b) Synthesis of 1-methyl-4-(2'-pyridyl)-1,2,3-triazole (L'_n) and corresponding palladium complex ($PdL'_n(OAc)_2$)

1-methyl-4-(2'-pyridyl)-1,2,3-triazole (L'_n) and its corresponding palladium complex $PdL'_n(OAc)_2$ were prepared and characterized following the procedures in our previous work.[1]

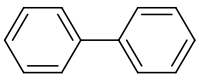
c) General procedure for Suzuki-Miyaura coupling reaction between aryl halides and arylboronic acid using PdL_n@β-CD

Aryl halide (1.0 mmol), arylboronic acid (1.5 mmol) and Na_2CO_3 (1.5 mmol) was added into a sealed tube, and 2.0 mL of water containing appropriate amount of catalyst was introduced. The reaction was stirred at reflux. After the reaction, the aqueous phase was extracted with CH_2Cl_2 for 4 times (4×1.5 mL). Then the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography (*n*-hexane/ethyl acetate 10:1) to afford the desired product.

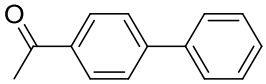
d) General procedure for Suzuki-Miyaura coupling reactions of aryl halides with phenylboronic acid using $Pd(OAc)_2$ or PdL'_n:

1.0 mL of CH_2Cl_2 containing appropriate amount of $Pd(OAc)_2$ or PdL'_n was introduced into a sealed tube. CH_2Cl_2 was evaporated under vacuum. Then aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), Na_2CO_3 (1.5 mmol) and water (2.0 mL) was added. The mixture was stirred at reflux. After the reaction, the aqueous phase was extracted with CH_2Cl_2 for 4 times (4×1.5 mL). Then the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography (*n*-hexane/ethyl acetate 10:1) to afford the desired product.

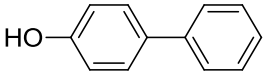
NMR Characterization Data and Figures



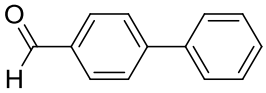
biphenyl (Table 2, entries 1 and 4) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.59(dd, *J* = 8.5, 2.0 Hz, 4H), 7.44(t, *J* = 8.0 Hz, 4H), 7.34(t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 141.3, 128.7, 127.2, 127.1.



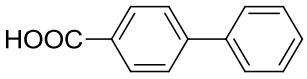
4-phenyl acetophenone (Table2, entries 2 and 6) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.05(dt, *J* = 10.0, 2.0 Hz, 2H), 7.70(dt, *J* = 9.0, 1.8 Hz, 2H), 7.64(dd, *J* = 9.0, 2.0 Hz, 2H), 7.49(t, *J* = 7.2 Hz, 2H), 7.42(tt, *J* = 7.5, 1.5 Hz, 1H), 2.66(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 197.7, 145.8, 139.9, 135.9, 128.9, 128.8, 128.2, 127.2, 127.1, 26.6.



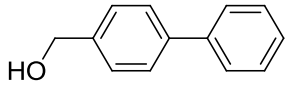
4-phenylphenol (Table2, entry 3) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.56(dd, *J* = 9.0, 1.5 Hz, 2H), 7.51(dt, *J* = 9.5, 2.5 Hz, 2H), 7.44(t, *J* = 7.5 Hz, 2H), 7.33(t, *J* = 7.5 Hz, 1H), 6.93(dt, *J* = 9.5, 3.0 Hz, 2H), 4.83(s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 157.1, 140.2, 130.9, 128.7, 127.7, 126.3, 125.9, 115.7.



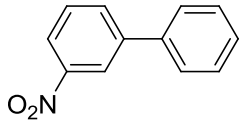
4-phenylbenzaldehyde (Table 2, entry 5) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 10.08(s, 1H), 7.97(dt, *J* = 8.0, 1.5 Hz, 2H), 7.77(dd, *J* = 7.0, 1.5 Hz, 2H), 7.65(dt, *J* = 8.5, 1.5 Hz, 2H), 7.52-7.48(m, 2H), 7.44(tt, *J* = 7.0, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 191.9, 147.2, 139.7, 135.2, 130.2, 128.9, 128.4, 127.7, 127.3.



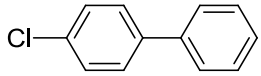
4-phenylbenzoic acid (Table 2, entry 7) ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.17(s, 1H), 8.03(d, *J* = 8.5 Hz, 2H), 7.79(d, *J* = 8.0 Hz, 2H), 7.74(t, *J* = 4.2 Hz, 2H), 7.51(t, *J* = 7.5 Hz, 2H), 7.42(t, *J* = 7.2 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 167.4, 143.8, 139.1, 130.5, 129.9, 129.0, 128.2, 126.9, 126.6.



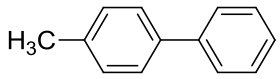
4-biphenylmethanol (Table 2, entry 8) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.59 (dt, *J* = 6.5, 2.0 Hz, 4H), 7.46-7.42(m, 4H), 7.37-7.33(m, 1H), 4.75(s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 140.9, 140.7, 139.9, 128.8, 127.5, 127.4, 127.3, 127.1, 65.1.



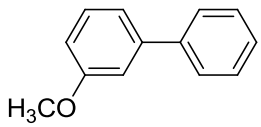
3-nitrobiphenyl (Table 2, entries 9a-9c, 12) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.44(t, *J* = 2.0 Hz, 1H), 8.20(dq, *J* = 8.0, 1.0 Hz, 1H), 7.91(dq, *J* = 7.5, 0.8 Hz, 1H), 7.64-7.58(m, 3H), 7.53-7.48(m, 2H), 7.45(tt, *J* = 4.0, 1.5 Hz, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 148.7, 142.8, 138.6, 133.0, 129.7, 129.2, 128.5, 127.1, 122.0, 121.8.



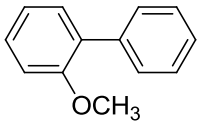
4-chlorobiphenyl (Table 2, entries 10a and 10b) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.58(dt, *J* = 8.5, 1.8 Hz, 2H), 7.55(dt, *J* = 9.0, 2.3 Hz, 2H), 7.50-7.46(m, 2H), 7.44(dt, *J* = 7.5, 2.8 Hz, 2H), 7.42-7.37(m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 140.0, 139.7, 133.4, 129.0, 128.9, 128.4, 127.6, 127.0.



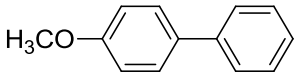
4-methylbiphenyl (Table 2, entries 11a and 11b) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.62(t, *J* = 4.2 Hz, 2H), 7.53(d, *J* = 8.0 Hz, 2H), 7.46(t, *J* = 7.5 Hz, 2H), 7.36(t, *J* = 11.5 Hz, 1H), 7.28(t, *J* = 5.8 Hz, 2H), 2.43(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 141.2, 138.5, 137.0, 129.5, 128.7, 127.0, 126.9, 21.1.



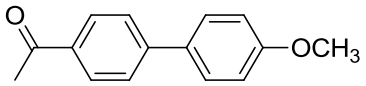
3-phenylanisol (Table 2, entry 13) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.76(dt, *J* = 8.5, 1.5 Hz, 2H), 7.58(t, *J* = 7.7 Hz, 2H), 7.52-7.48(m, 2H), 7.35(dd, *J* = 9.0, 1.0 Hz, 1H), 7.31(t, *J* = 2.0 Hz, 1H), 7.05(dd, *J* = 8.5, 2.0 Hz, 1H), 3.97(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.9, 142.7, 141.0, 129.7, 128.7, 127.3, 127.1, 119.6, 112.8, 112.6, 55.1.



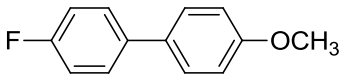
2-phenylanisol (Table 2, entries 14a, 14b) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.66(d, *J* = 7.0 Hz, 2H), 7.52(t, *J* = 7.5 Hz, 2H), 7.46-7.41(m, 3H), 7.14(t, *J* = 7.7 Hz, 1H), 7.09(d, *J* = 8.0 Hz, 1H), 3.90(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 156.5, 138.5, 130.8, 130.7, 129.5, 128.6, 127.9, 126.8, 120.9, 111.3, 55.5.



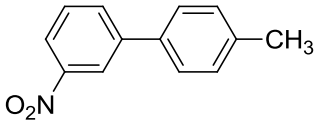
4-methoxybiphenyl (Table2, entry 15) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.59-7.53(m, 4H), 7.43(t, *J* = 7.8 Hz, 2H), 7.32(tt, *J* = 7.5, 3.0 Hz, 1H), 7.00(dt, *J* = 9.5, 3.0 Hz, 2H), 3.87(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.2, 140.9, 133.9, 128.7, 128.2, 126.8, 126.7, 114.2, 55.4.



4-acetyl-4'-methoxy-biphenyl (Table 2, entries 16a, 16b, 18) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.02(d, *J* = 8.5 Hz, 2H), 7.66(d, *J* = 8.0 Hz, 2H), 7.59(d, *J* = 9.5 Hz, 2H), 7.01(d, *J* = 9.0 Hz, 2H), 3.88(s, 3H), 2.64(s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 197.8, 159.9, 145.4, 135.3, 132.3, 128.9, 128.4, 126.6, 114.4, 55.4, 26.6.

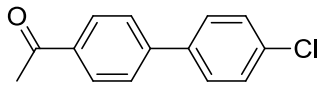


4-fluoro-4'-methoxy-biphenyl (Table 2, entry 17) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.52(dd, *J* = 5.0, 2.0 Hz, 2H), 7.49(d, *J* = 9.0 Hz, 2H), 7.12(t, *J* = 8.7 Hz, 2H), 6.99(d, *J* = 8.5 Hz, 2H), 3.87(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 162.1(d, *J* = 296.5 Hz), 159.2, 136.8, 132.9, 128.3, 128.0, 115.7, 114.3, 55.2.



3-nitro-4'-methyl-biphenyl (Table 2, entry 19) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.43(t, *J* = 1.7 Hz, 1H), 8.17(dq, *J* = 8.0, 1.0 Hz, 1H), 7.90(dq, *J* = 8.0, 1.0 Hz, 1H), 7.59(t, *J* = 8.0 Hz, 1H), 7.53(dt, *J* = 8.5, 2.0 Hz, 2H), 7.31(d, *J* = 7.5 Hz, 2H), 2.44(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 148.8,

142.7, 138.5, 135.6, 132.7, 129.8, 129.6, 126.9, 121.6, 121.5, 21.1.



3-acetyl-4'-chlorine-biphenyl (Table 2, entry 20) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.03(dt, *J* = 8.5, 2.0 Hz, 2H), 7.65(dt, *J* = 8.5, 2.0 Hz, 2H), 7.56(dt, *J* = 9.0, 2.5 Hz, 2H), 7.44(dt, *J* = 8.5, 3.0 Hz, 2H), 2.65(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 197.6, 144.4, 138.3, 136.1, 134.5, 129.1, 128.9, 128.5, 127.1, 26.6.

Figure 1. ^{1}H NMR spectrum of 6-O-monotosyl-β-CD.

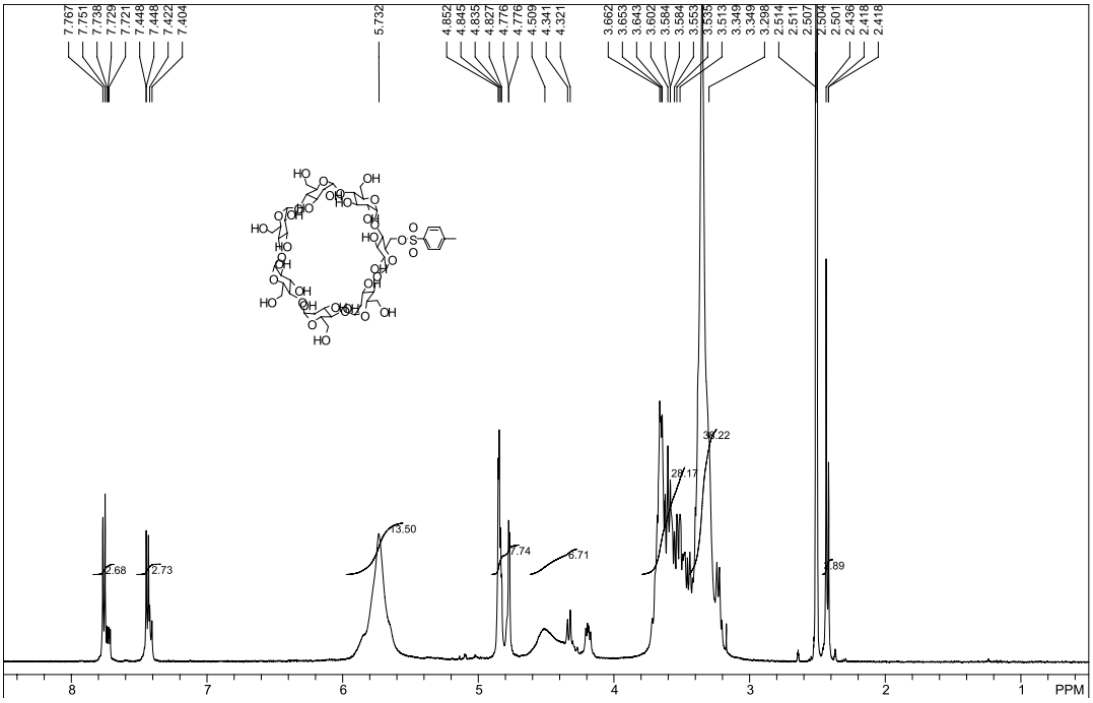


Figure 2. ^{1}H NMR spectrum of 6-monodeoxy-6-monoazido-β-CD.

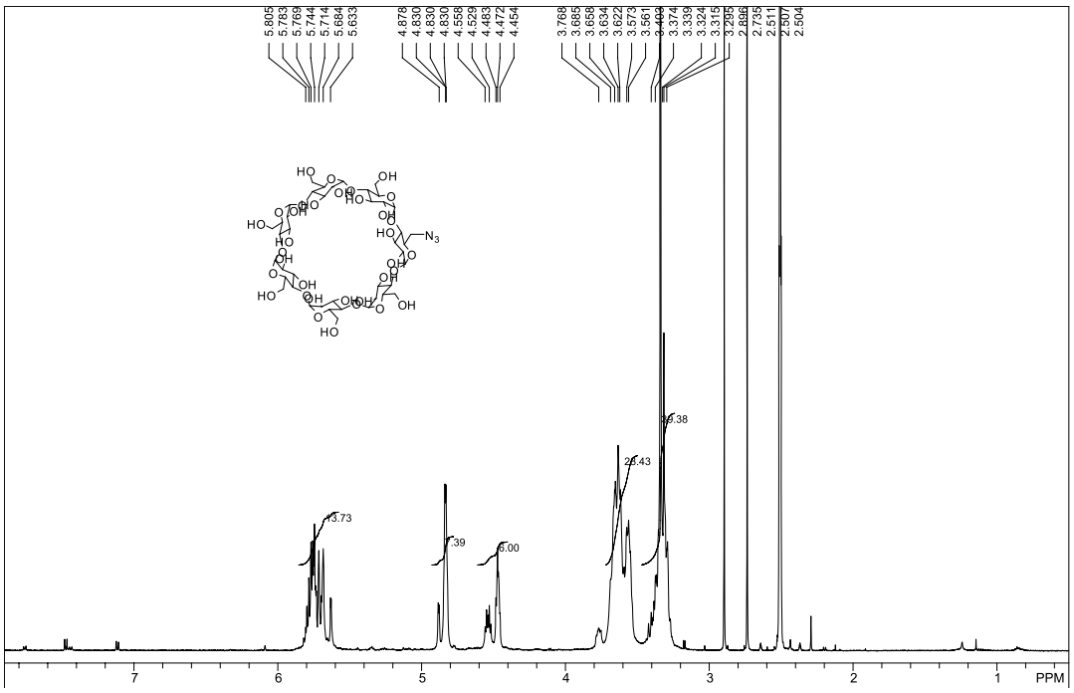
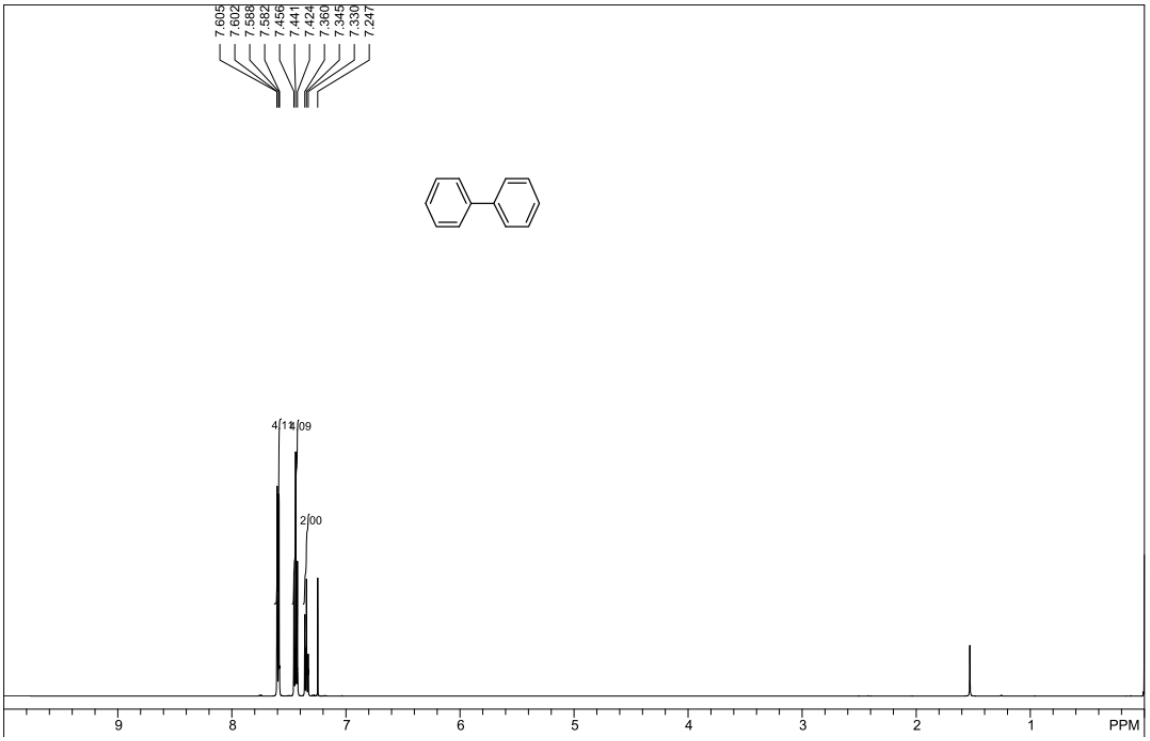


Figure 3. ^{1}H NMR and ^{13}C NMR spectrum of biphenyl.



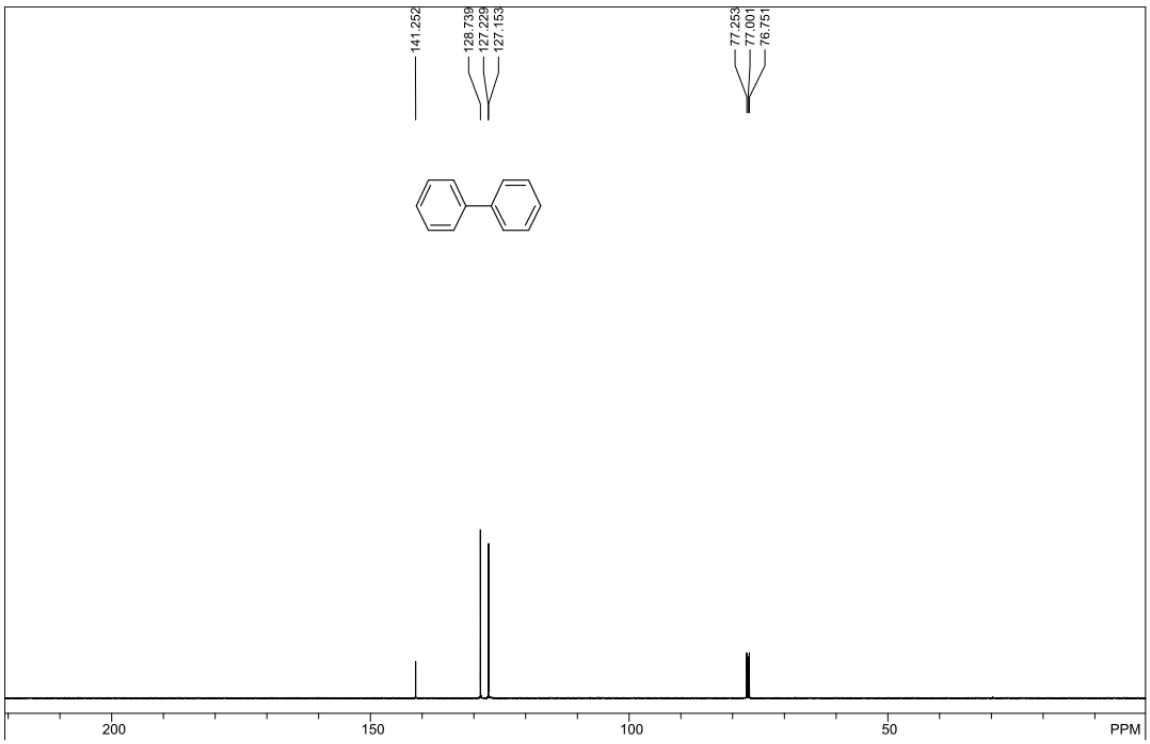
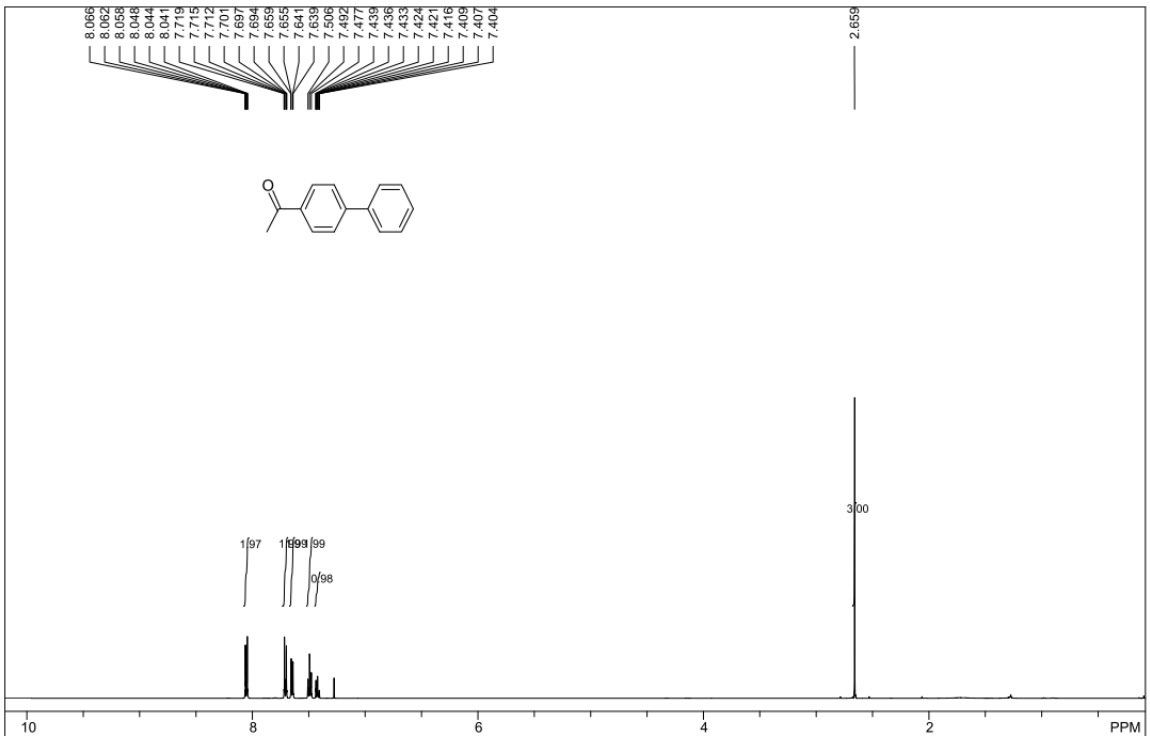


Figure 4. ^{1}H NMR and ^{13}C NMR spectrum of 4-acetylbiphenyl.



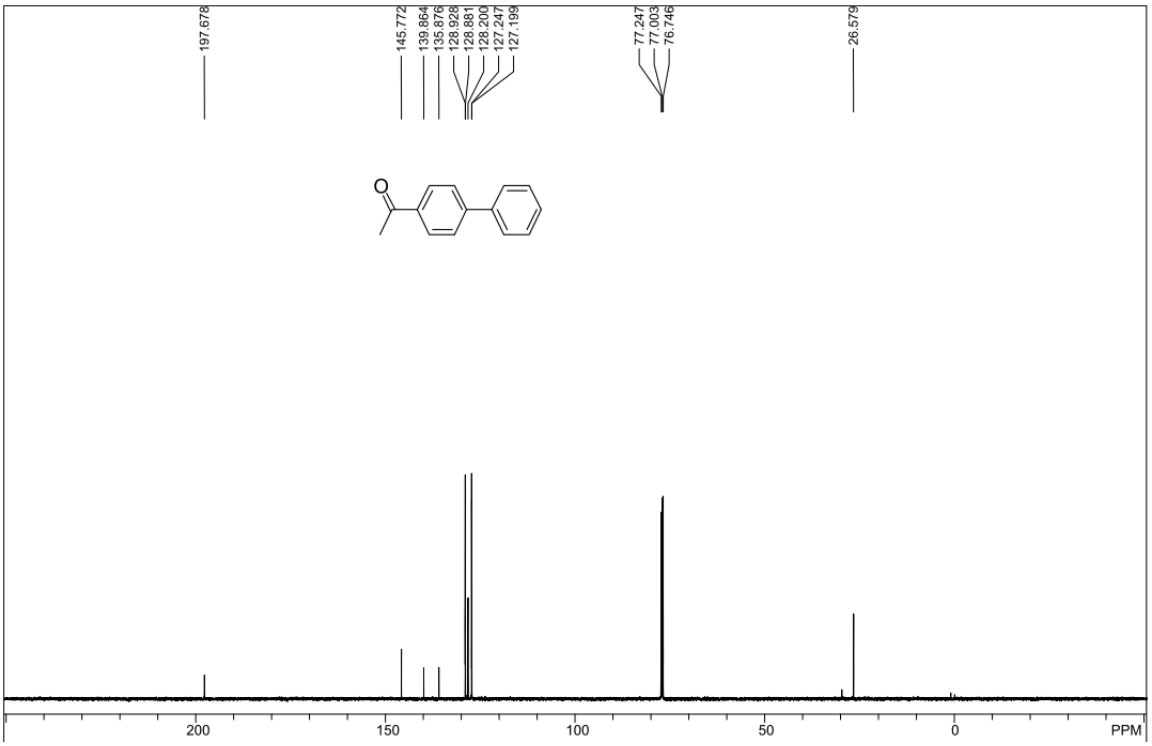
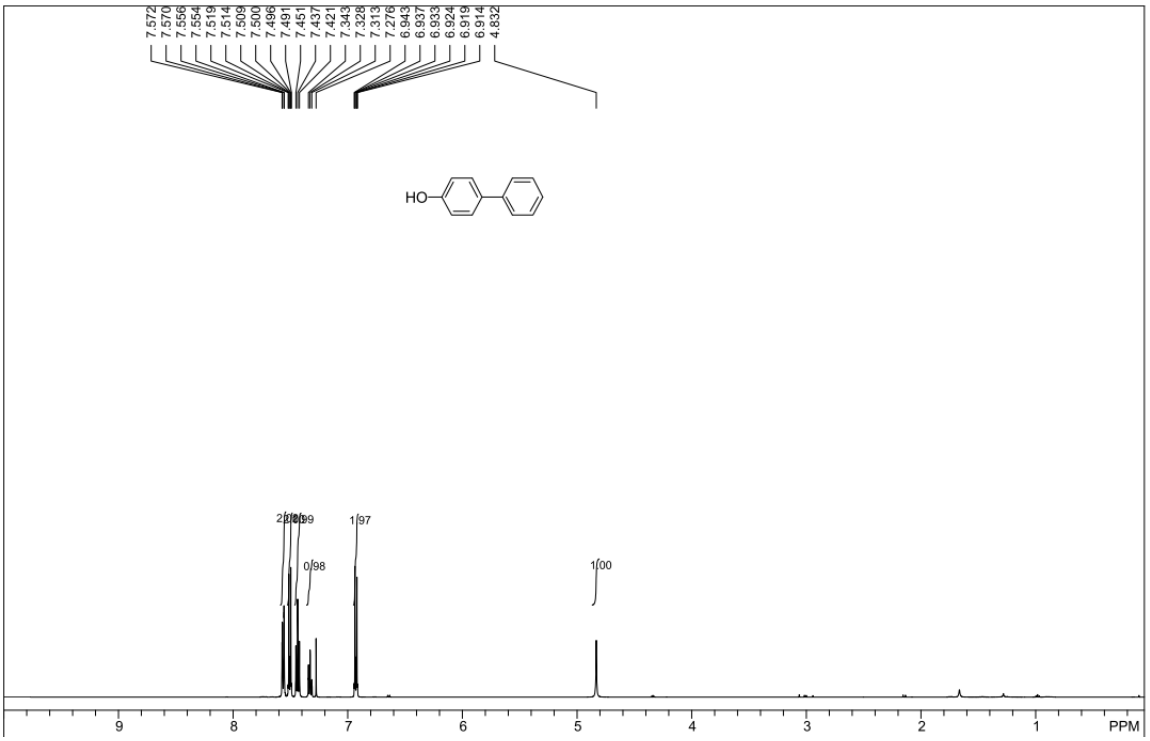


Figure 5. ^{1}H NMR and ^{13}C NMR spectrum of 4-hydroxybiphenyl.



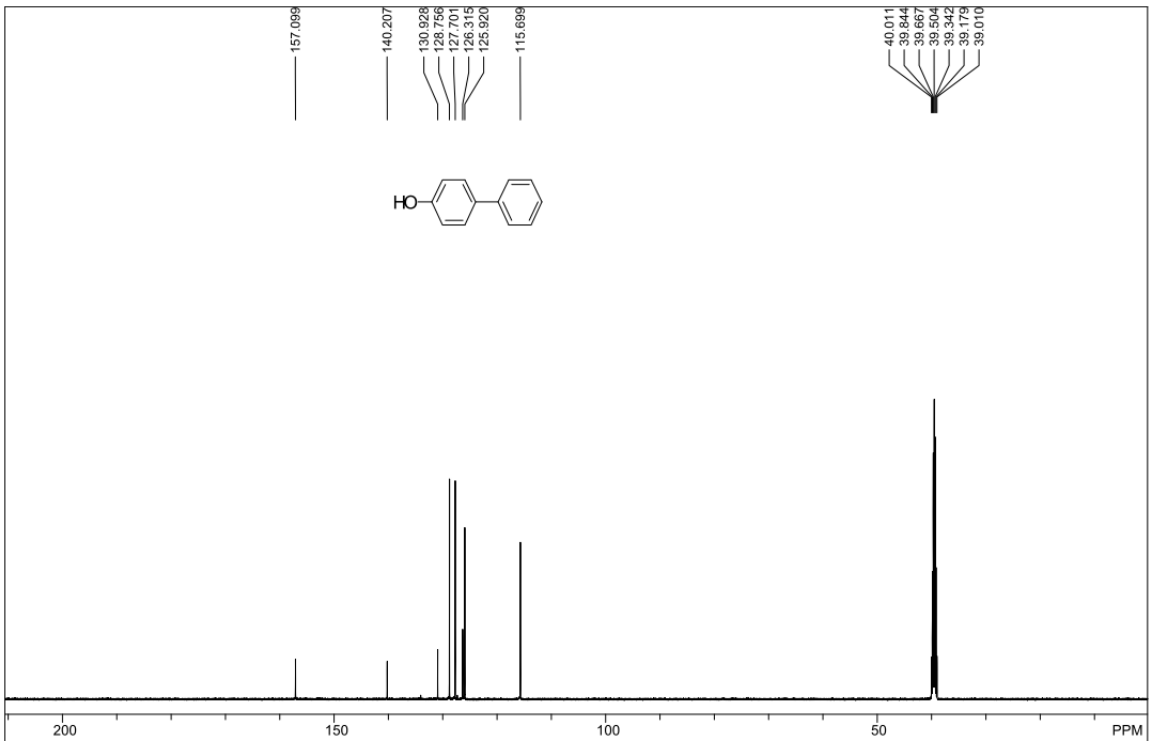
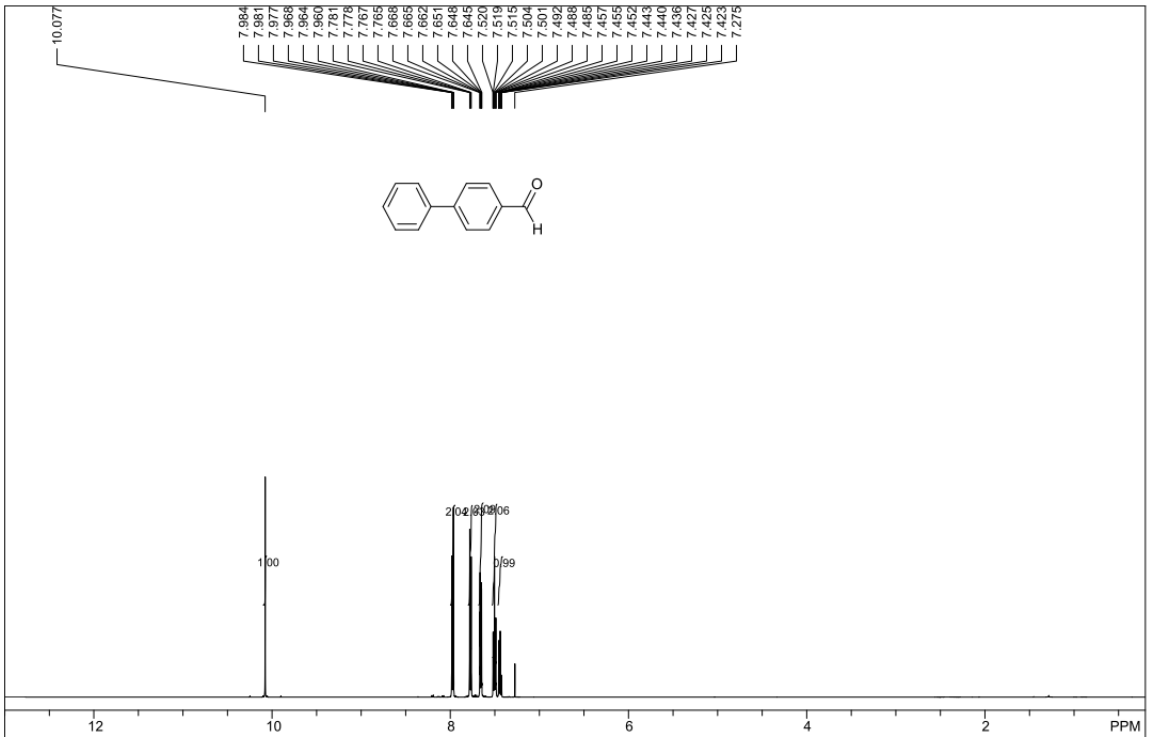


Figure 6. ^{1}H NMR and ^{13}C NMR spectrum of 4-phenylbenzaldehyde.



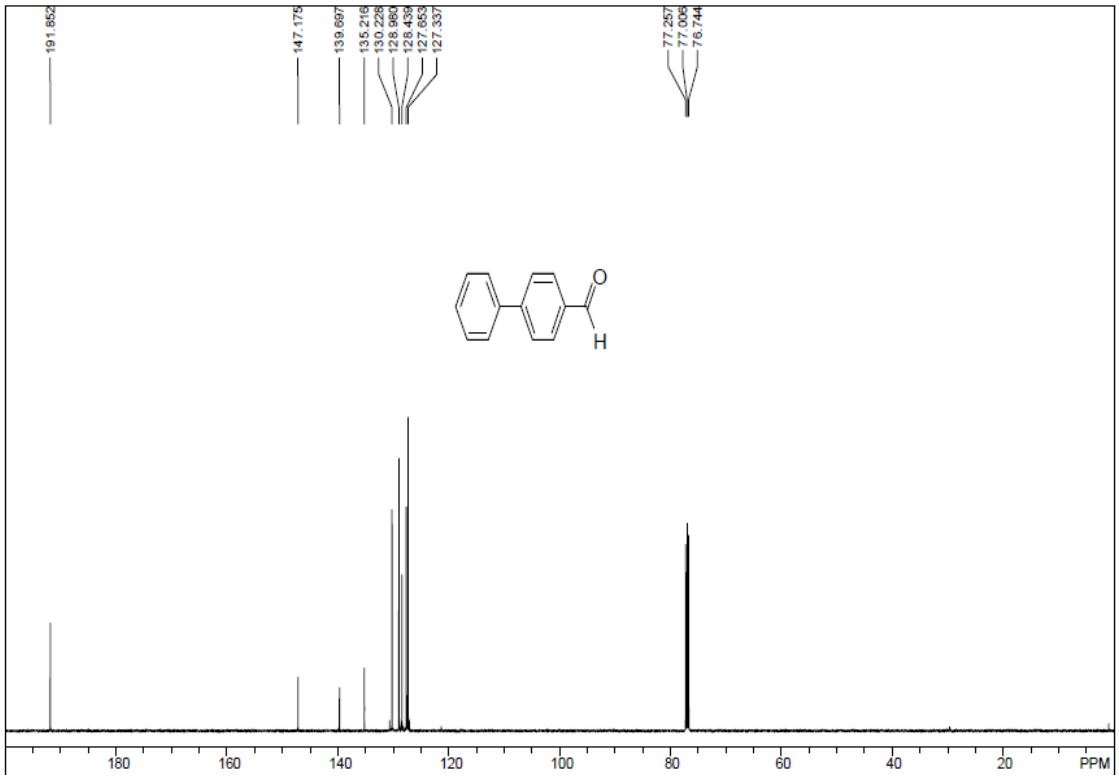
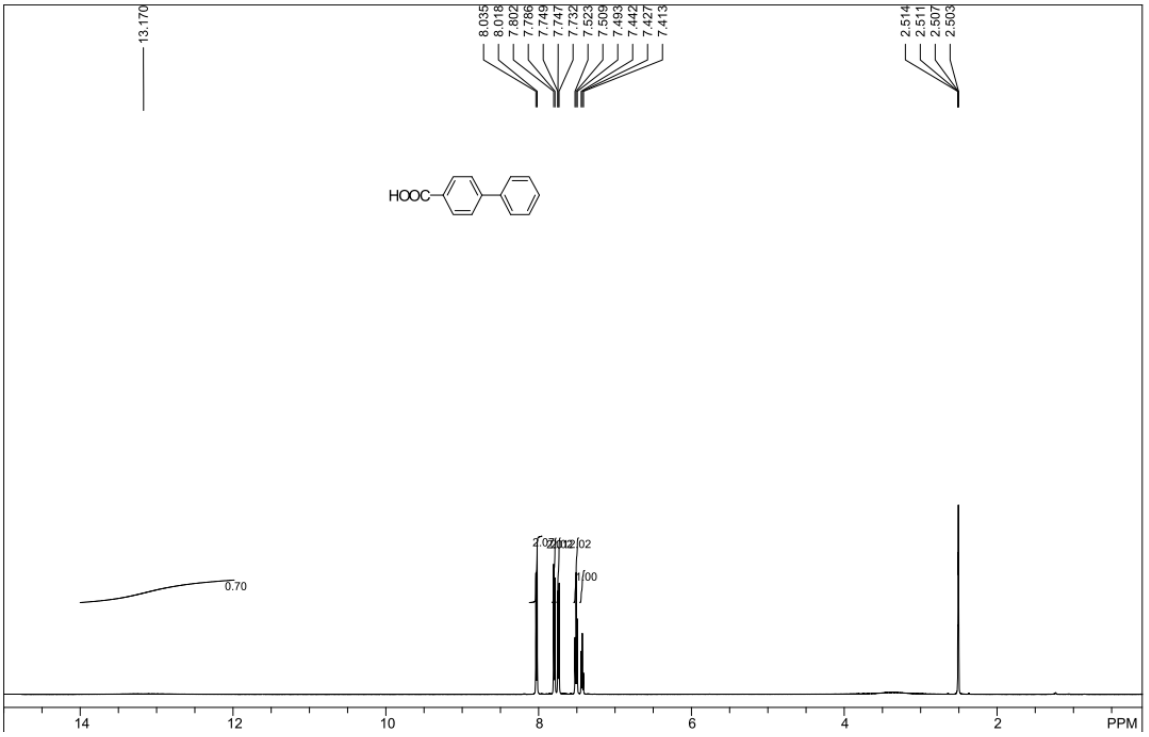


Figure 7. ^{1}H NMR and ^{13}C NMR spectrum of 4-carboxylbiphenyl.



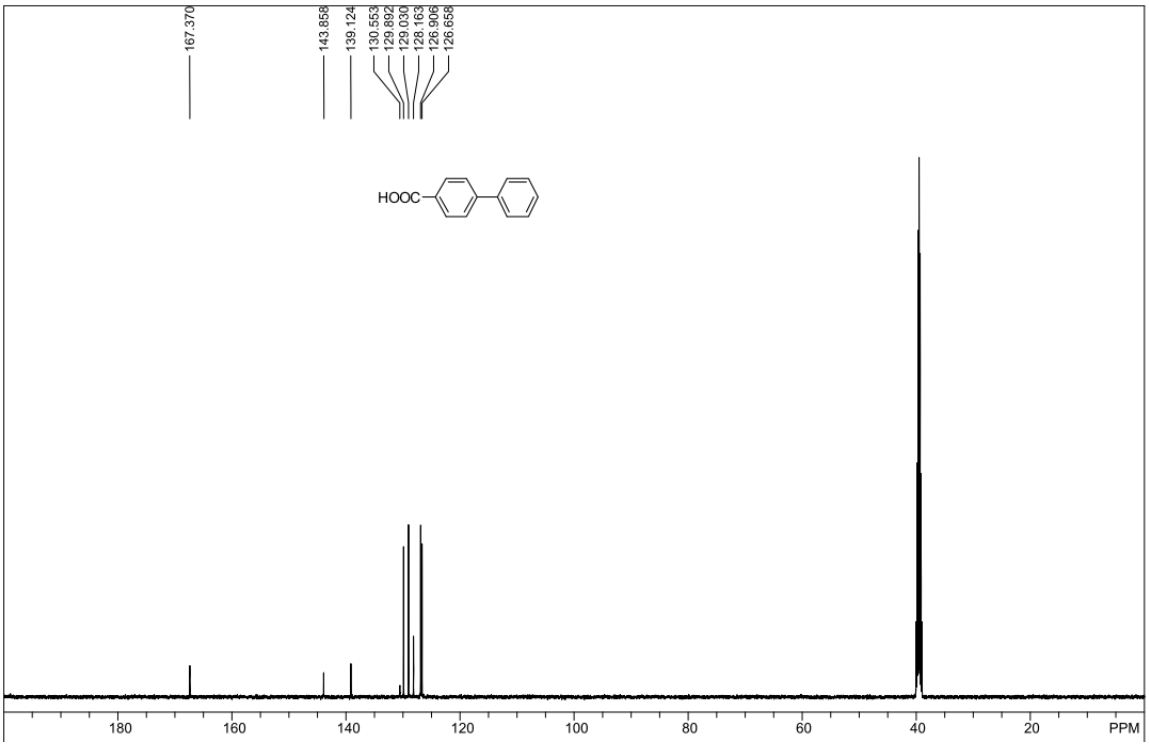
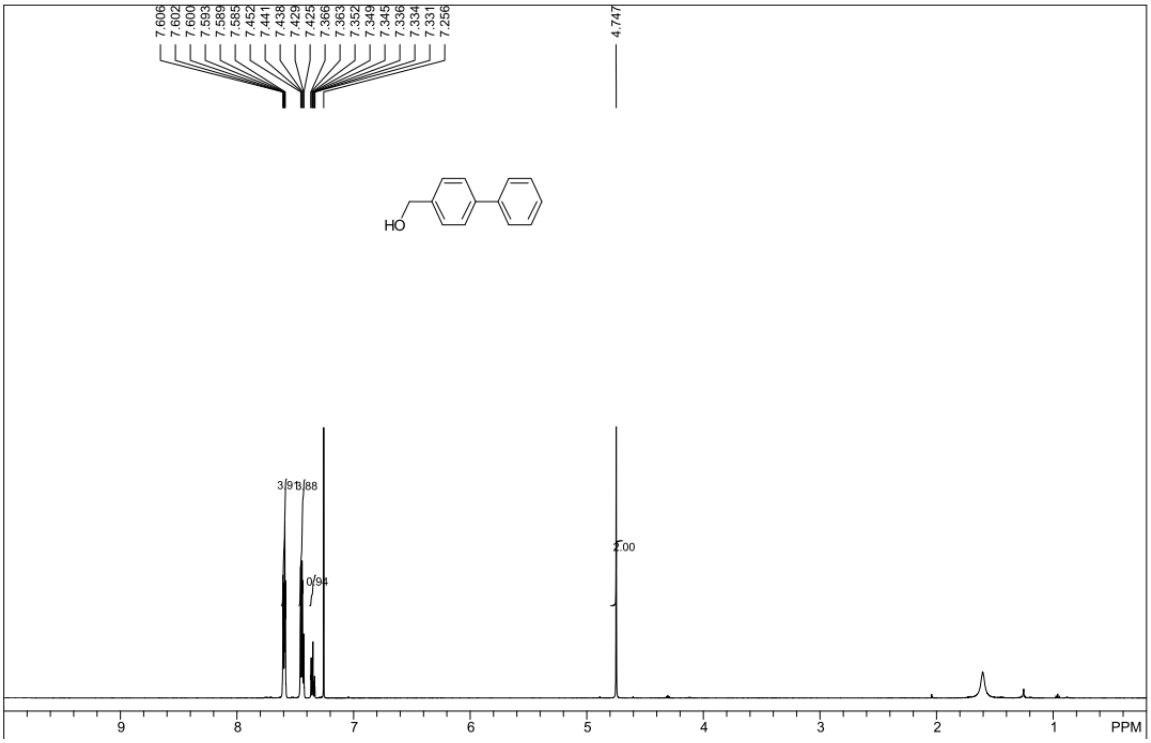


Figure 8. ^{1}H NMR and ^{13}C NMR spectrum of 4-biphenylmethanol.



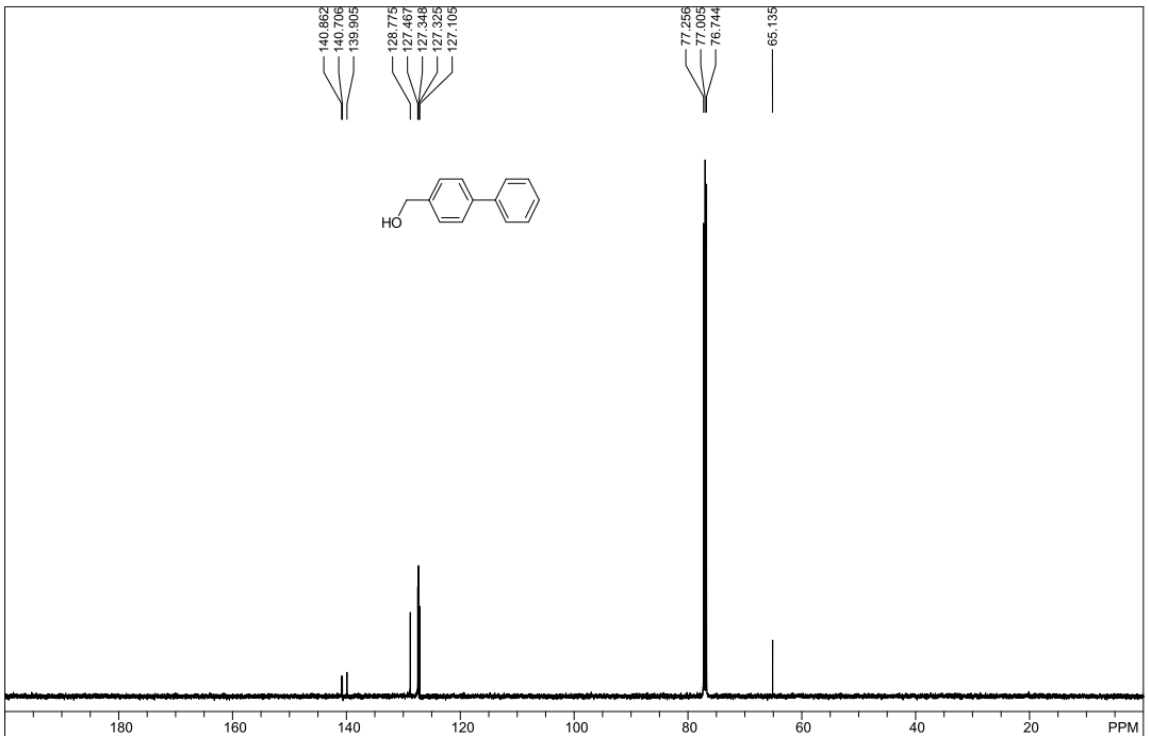
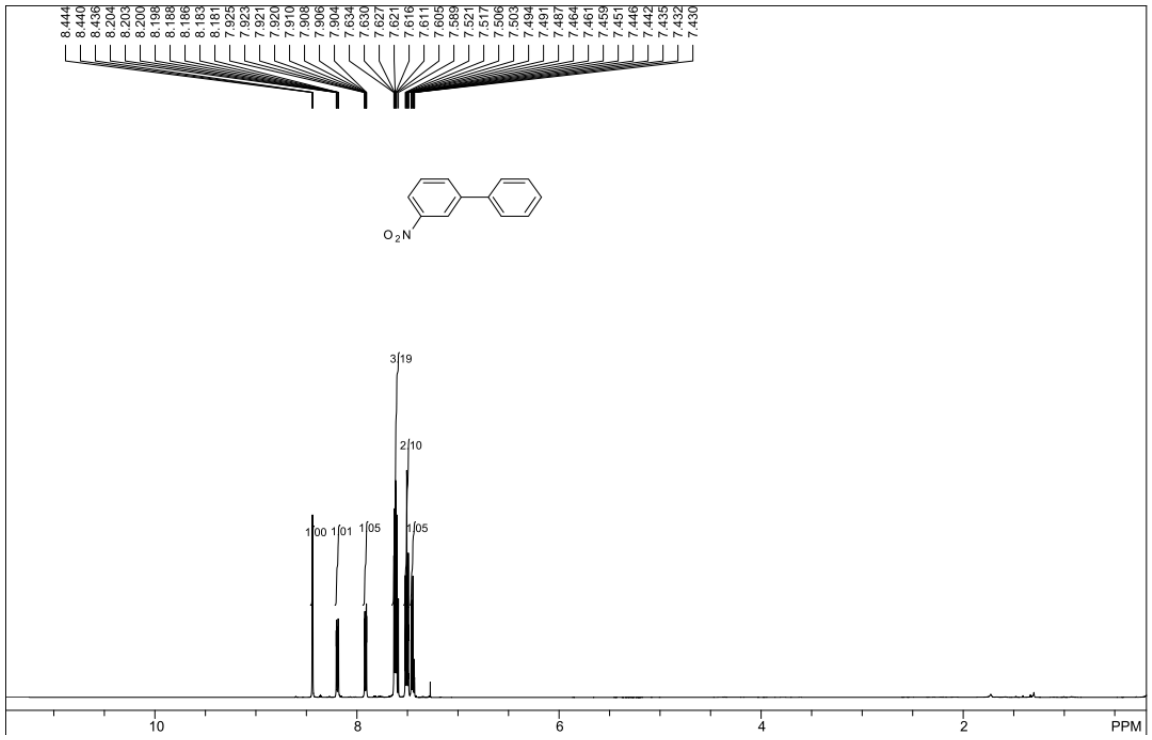


Figure 9. ^{1}H NMR and ^{13}C NMR spectrum of 3-nitrobiphenyl.



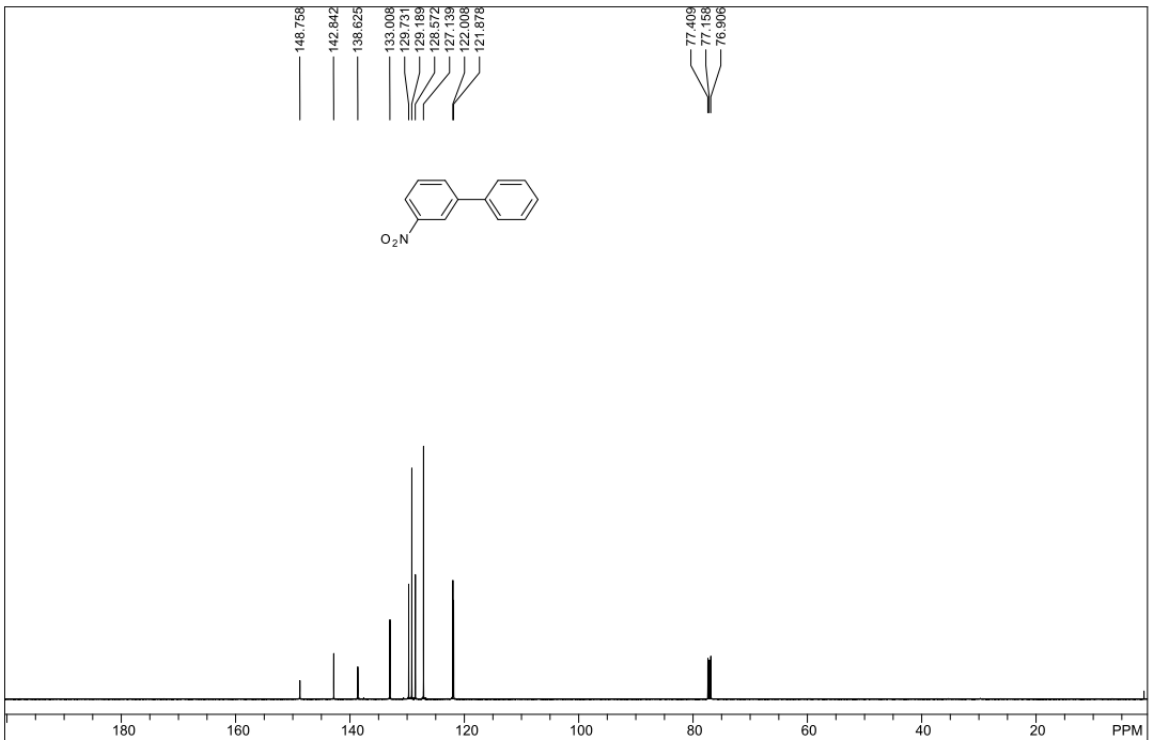
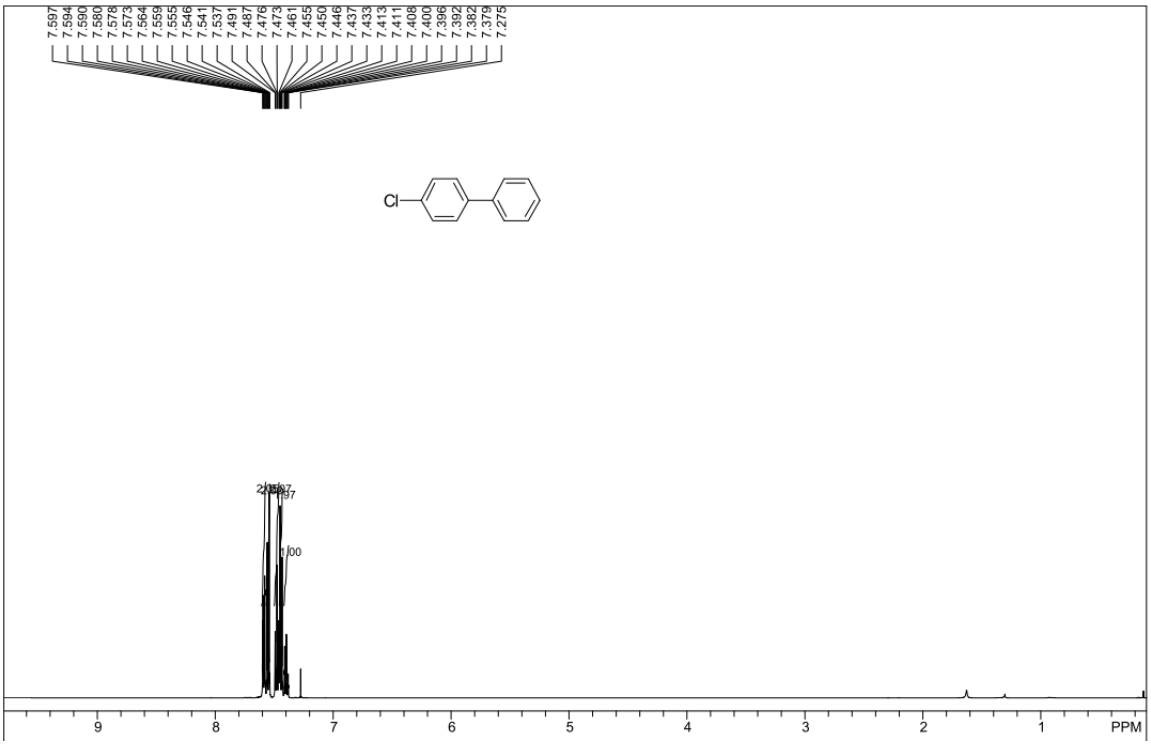


Figure 10. ^{1}H NMR and ^{13}C NMR spectrum of 4-chlorobiphenyl.



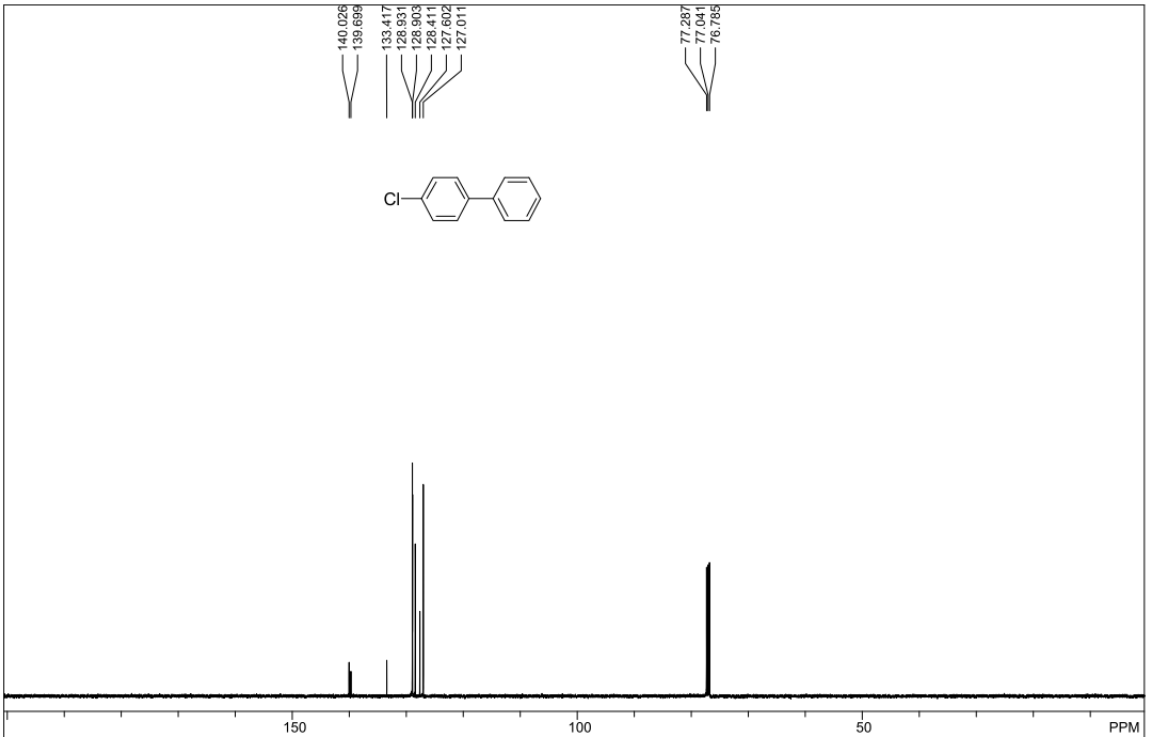
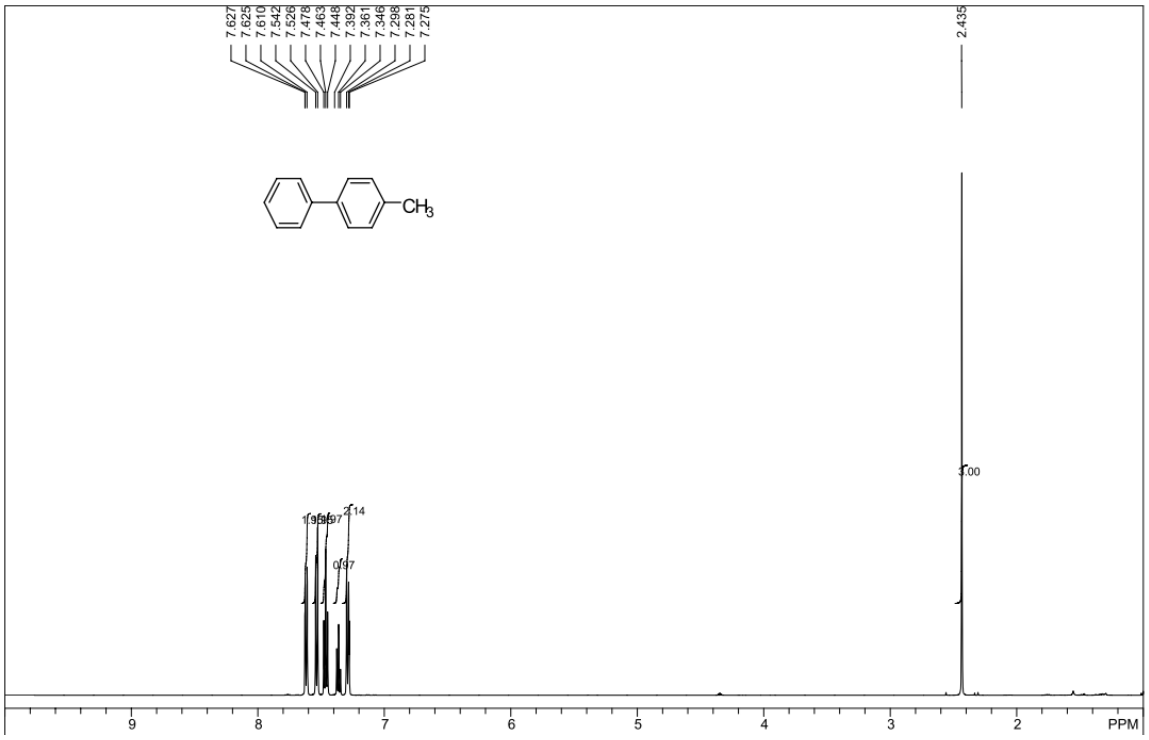


Figure 11. ^{1}HNMR and ^{13}CNMR spectrum of 4-methylbiphenyl.



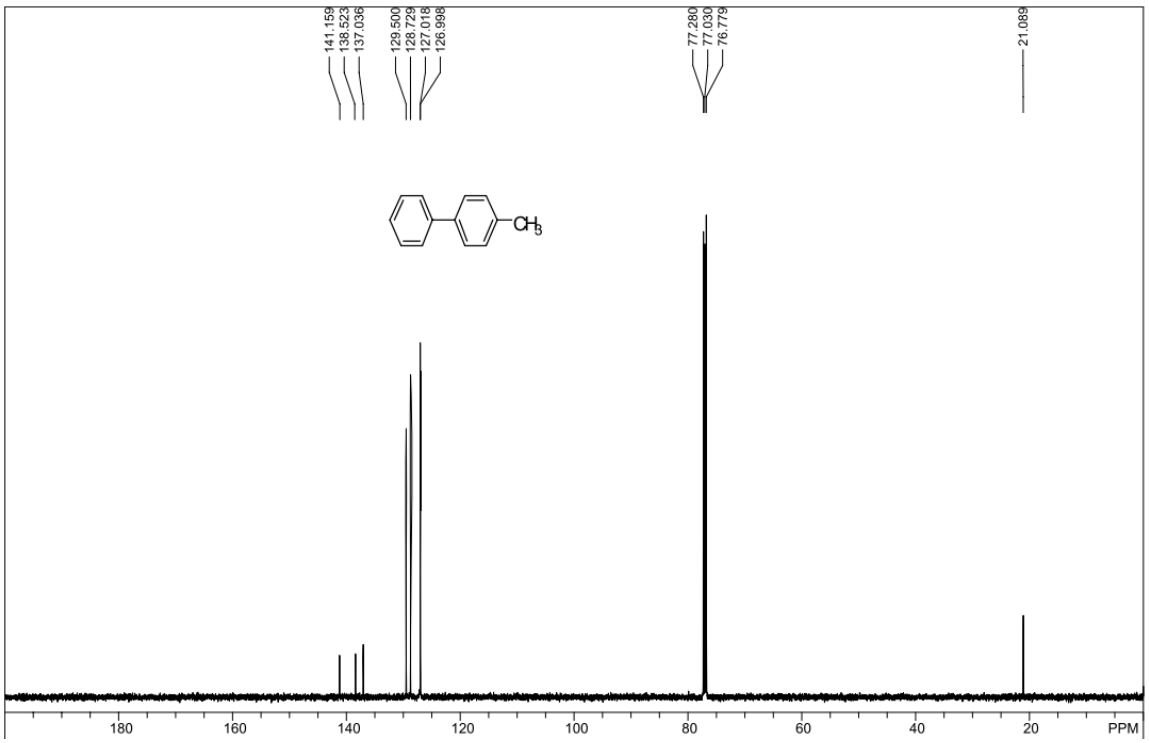


Figure 12. ^{1}HNMR and ^{13}CNMR spectrum of 3-phenylanisol.

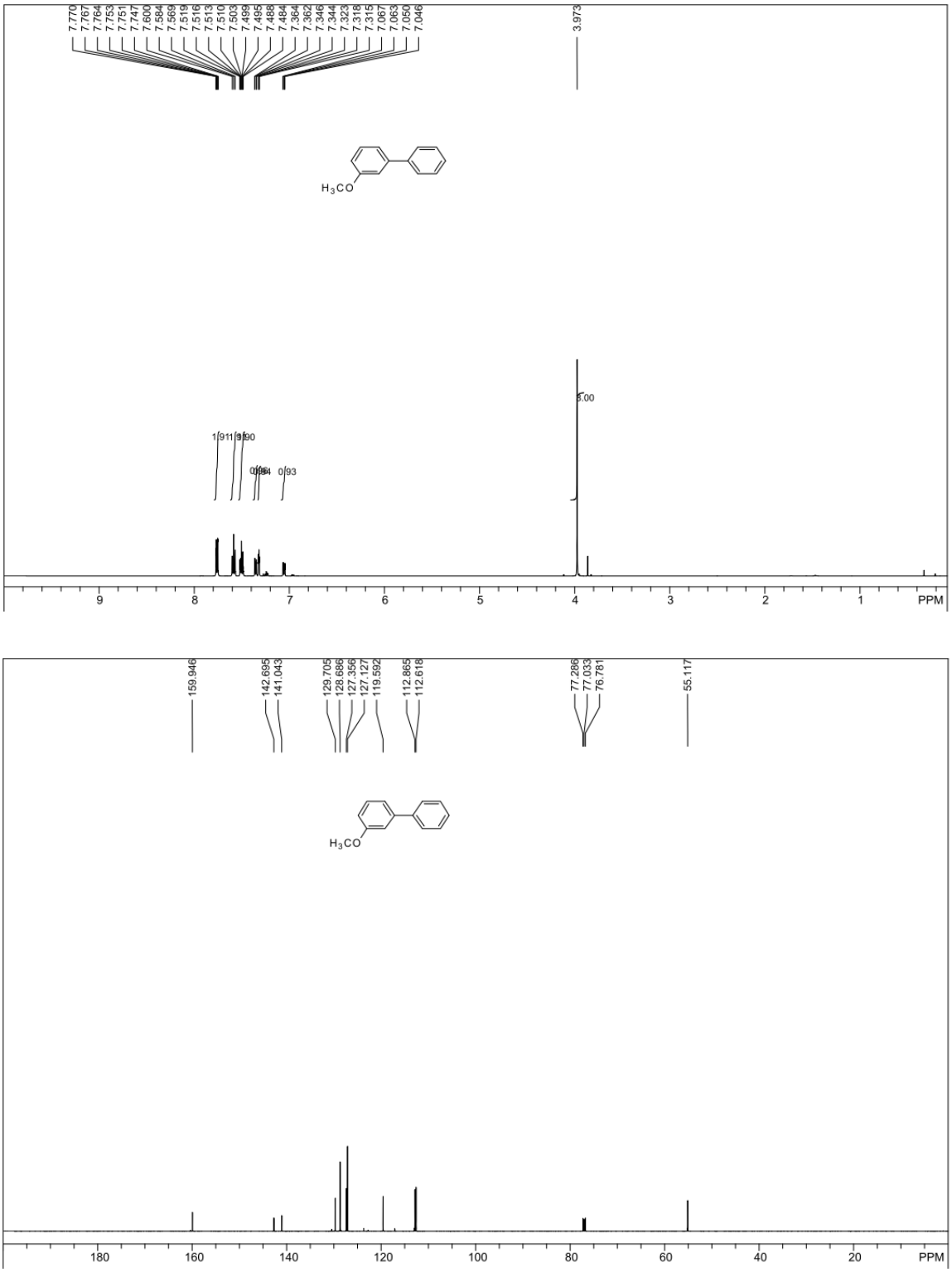
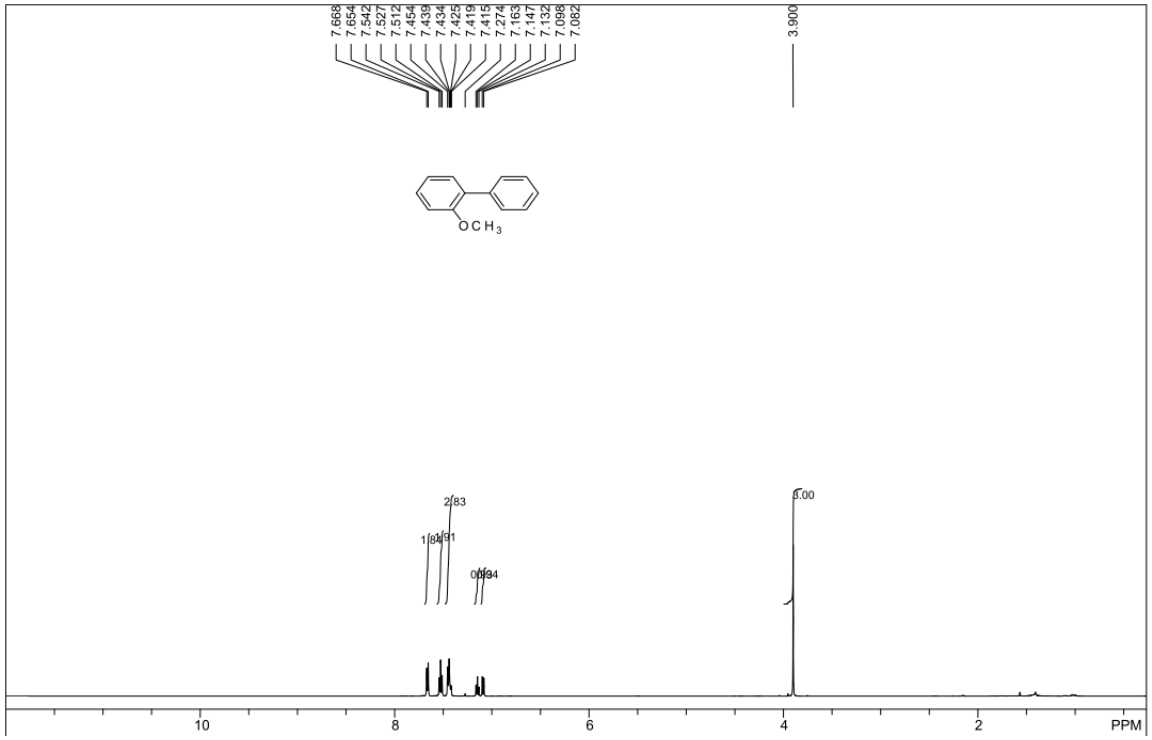


Figure 13. ^{1}H NMR and ^{13}C NMR spectra of 2-phenylanisol.



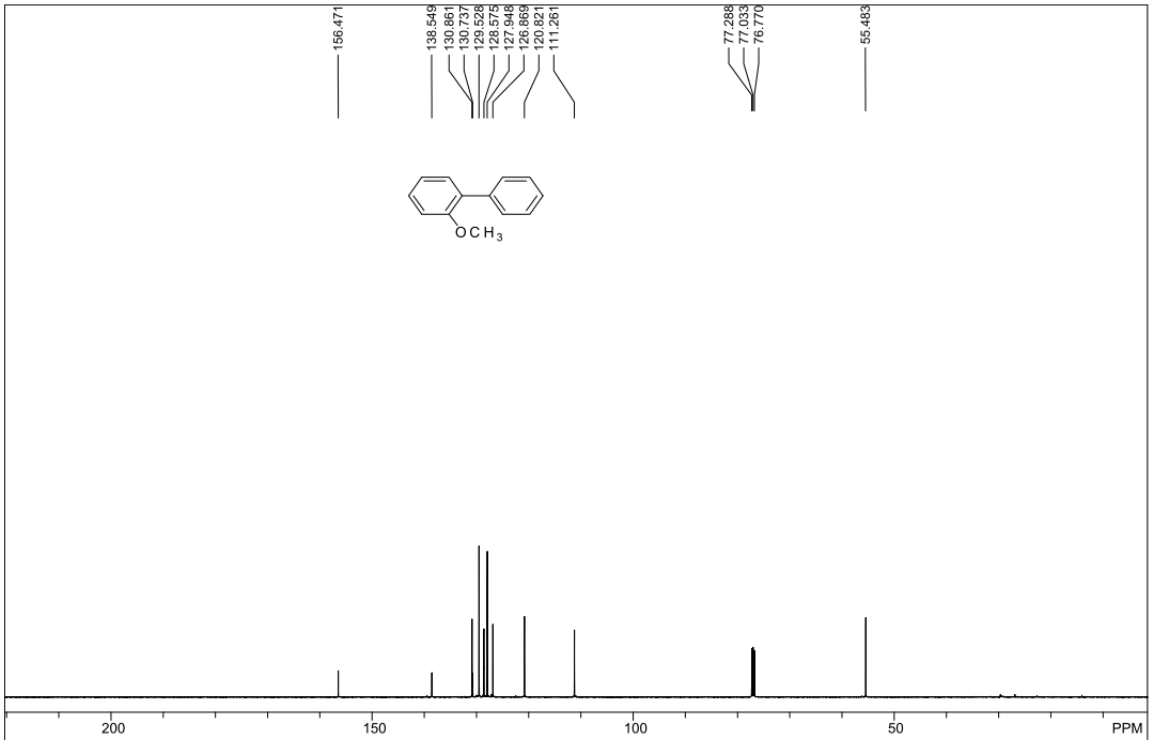
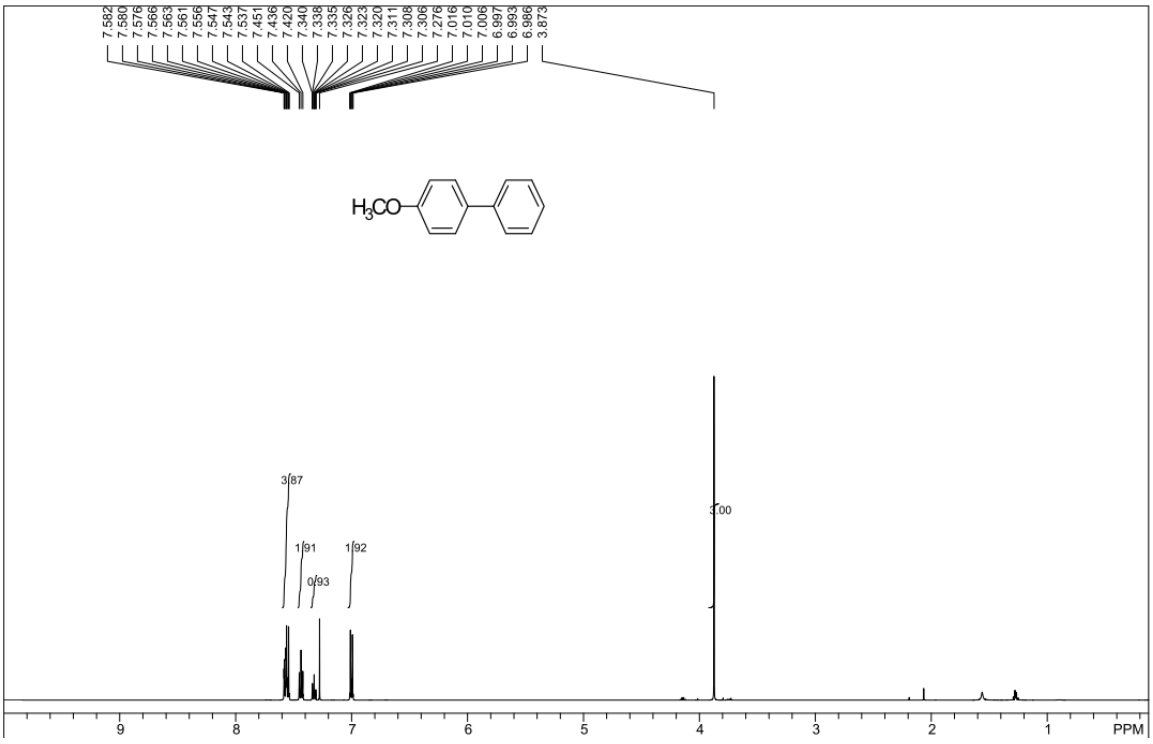


Figure 14. ^{1}H NMR and ^{13}C NMR spectra of 4-methoxybiphenyl.



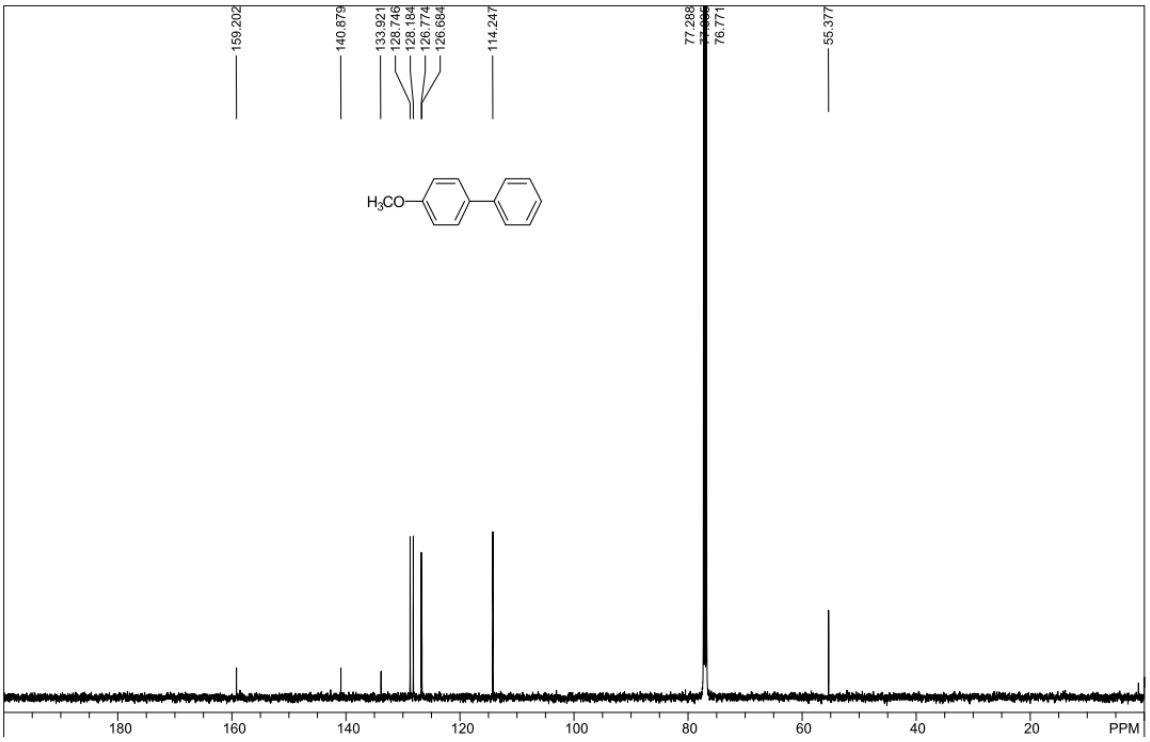


Figure 15. ^{1}H NMR and ^{13}C NMR spectra of 4-acetyl-4'-methoxy-biphenyl.

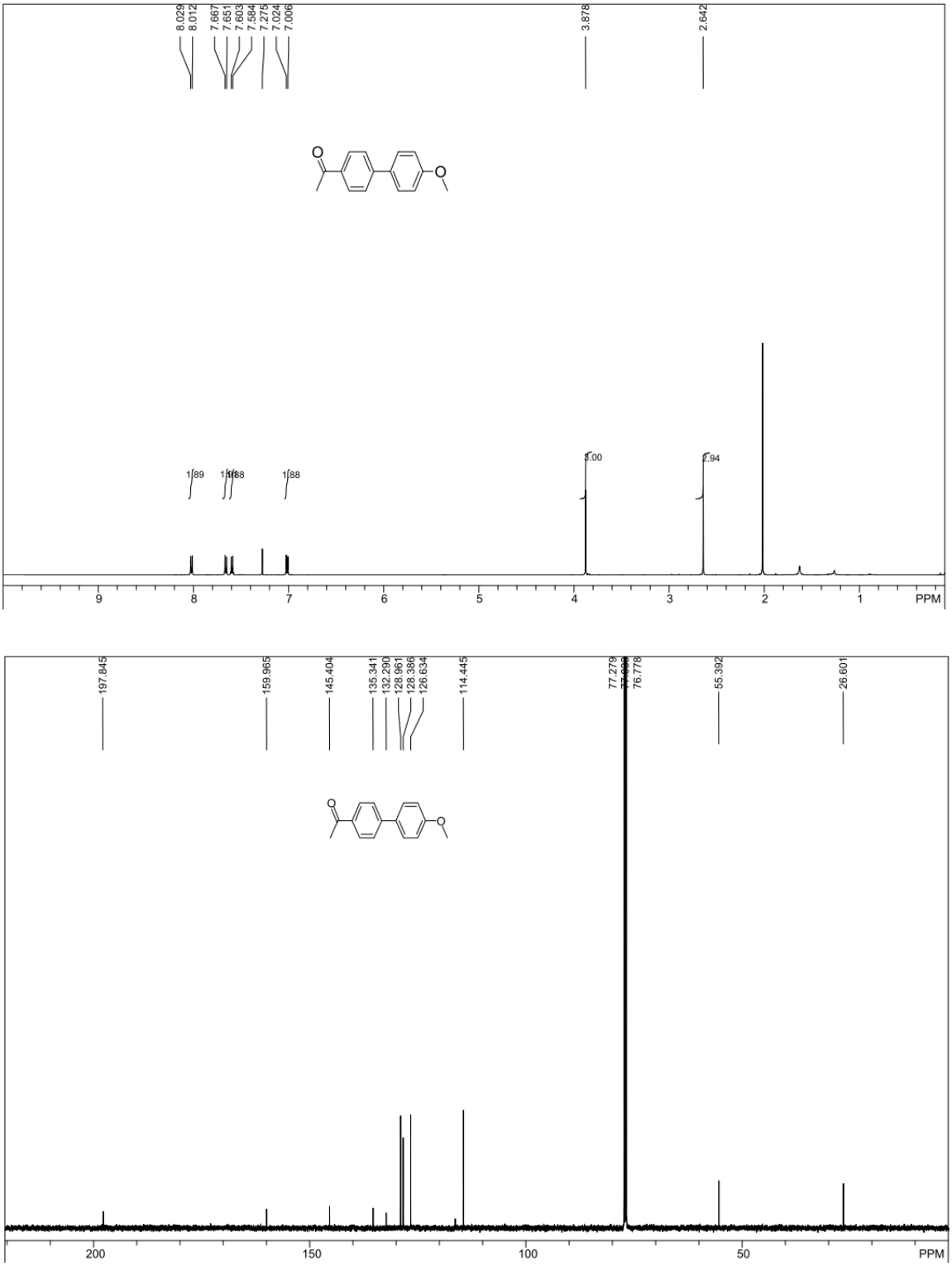


Figure 16. ^{1}H NMR and ^{13}C NMR spectra of 4-fluoro-4'-methoxy-biphenyl.

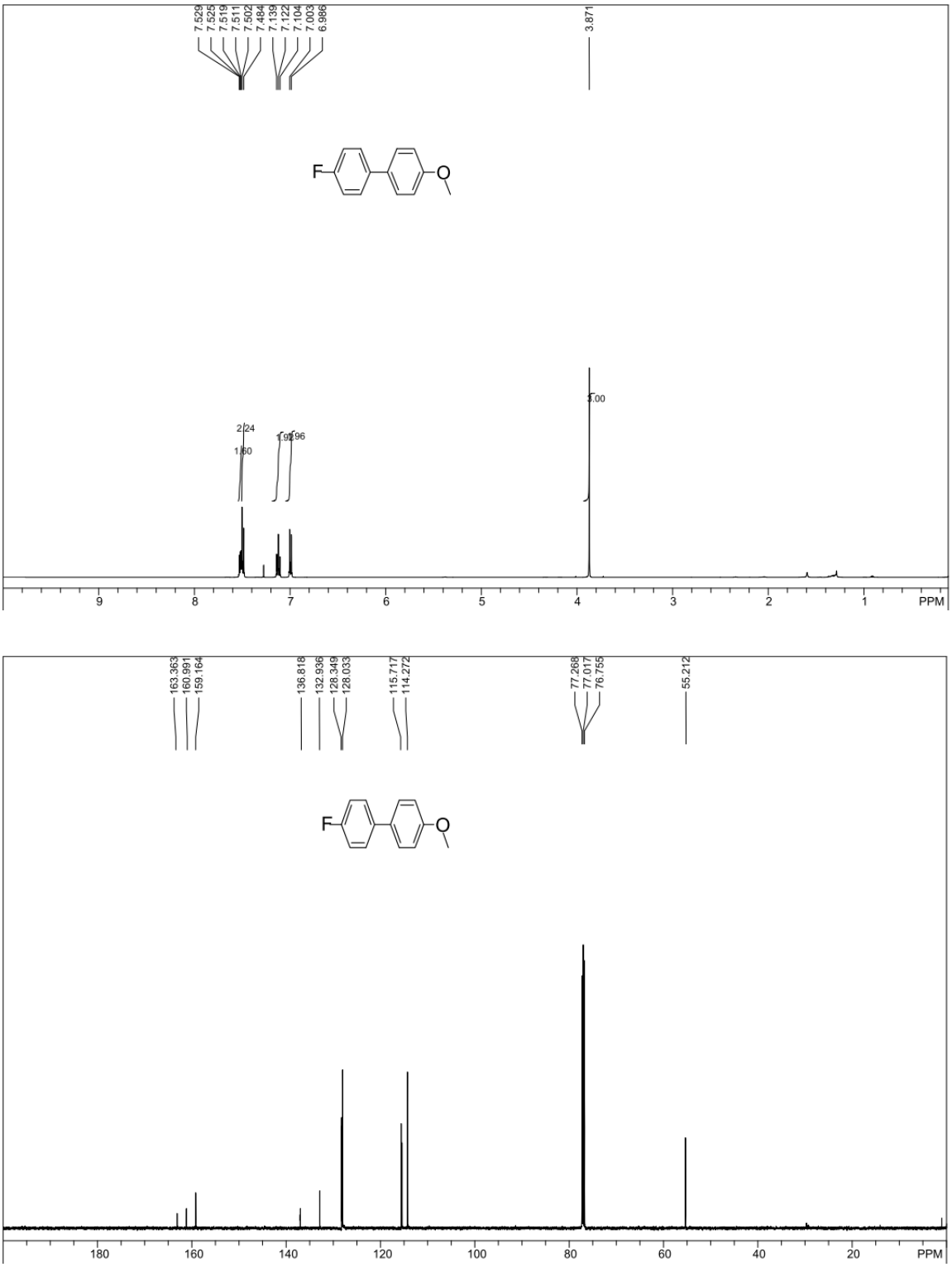
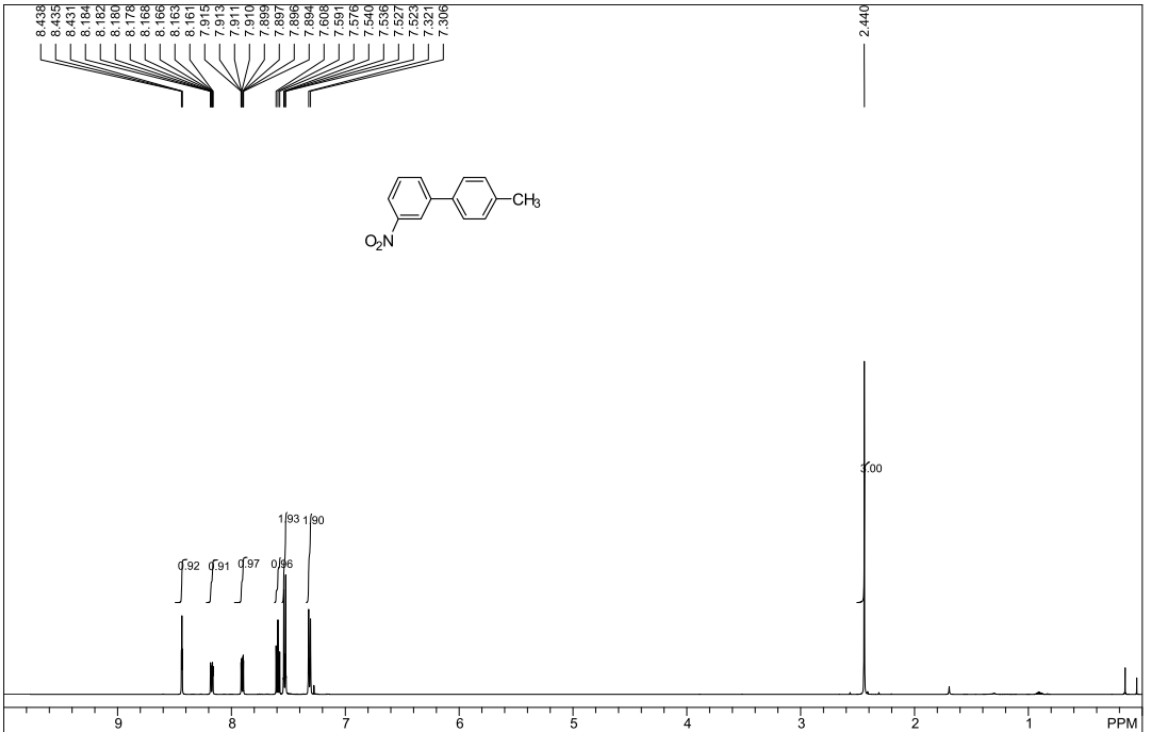


Figure 17. ^{1}H NMR and ^{13}C NMR spectra of 3-nitro-4'-methyl-biphenyl.



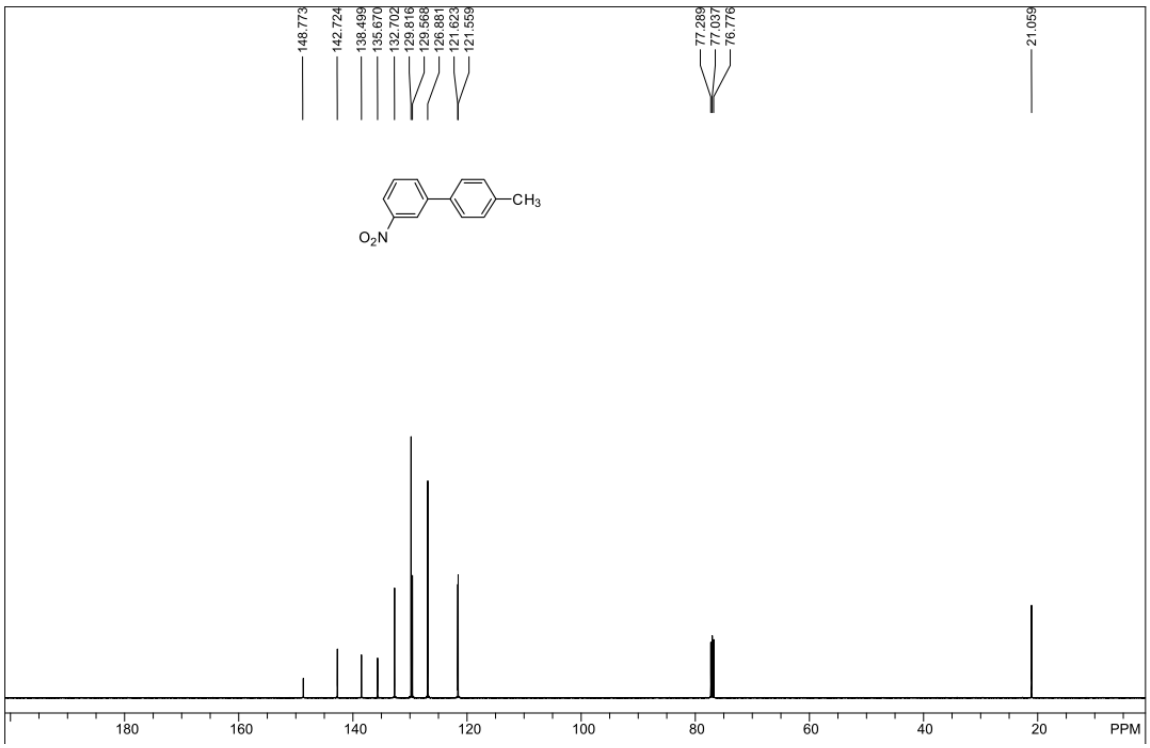
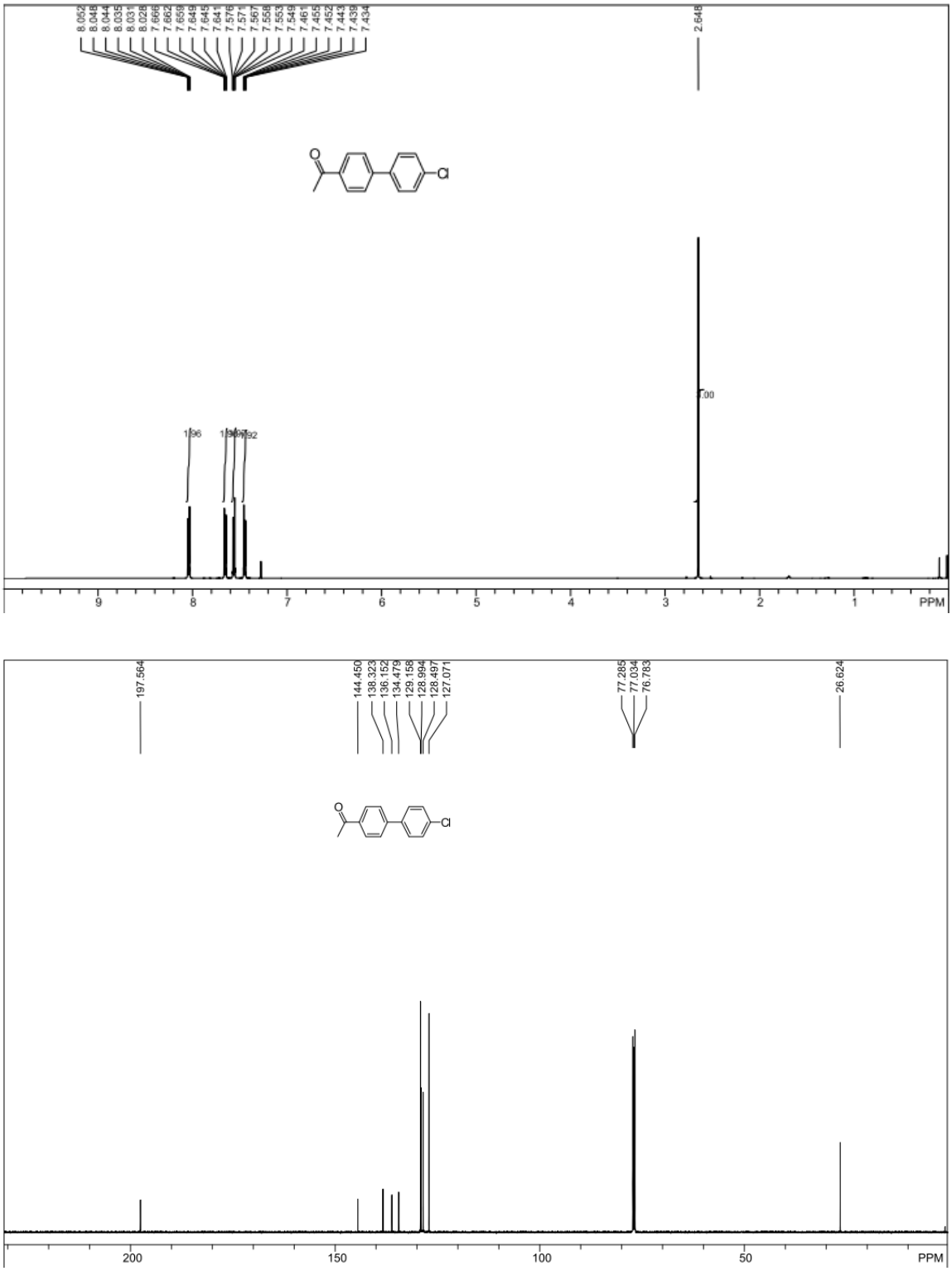


Figure 18. ^{1}H NMR and ^{13}C NMR spectra of 3-nitro-4’-methyl-biphenyl.



Reference

1 G. Zhang, Y. Wang, X. Wen, C. Ding and Y. Li, *Chem. Commun.*, 2012, **48**, 2979.