Supporting Information

Pd/Au bimetallic nanoparticles anchored $BiVO_4/TiO_2$ nanotube arrays toward efficient photoelectrocatalytic Suzuki-Miyaura reactions

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(A) Characterizations of Pd/Au/$BiVO_4$/TiO_2 nanotube arrays

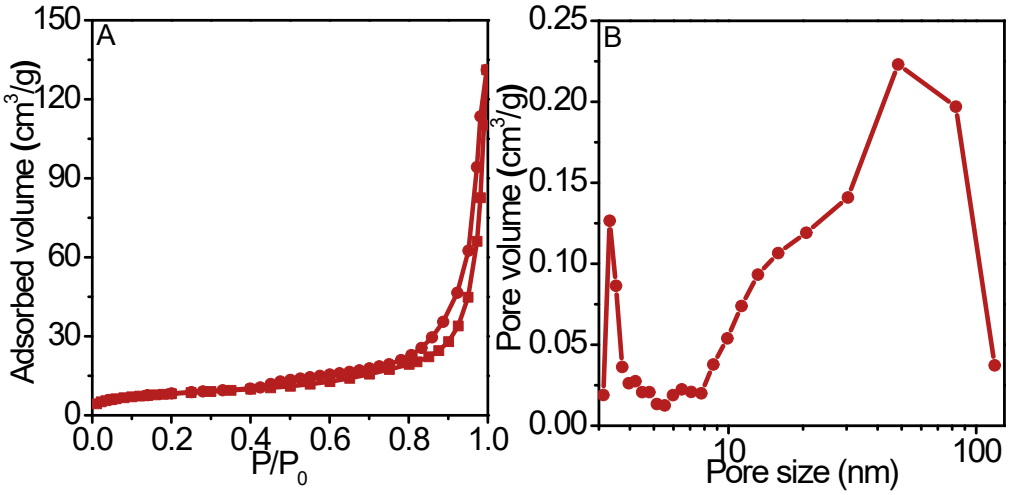


Fig. S1 (A) N_2 adsorption-desorption isotherm and (B) pore size distribution of Pd/Au/$BiVO_4$/TiO_2 nanotube arrays

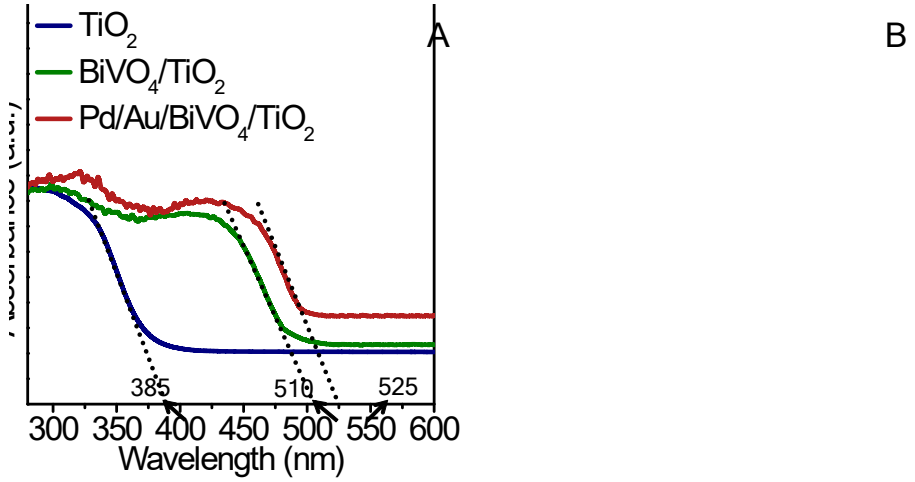


Fig. S2 (A) UV-visible absorption spectroscopy and (B) Fluorescence spectra of TiO_2, $BiVO_4$/TiO_2 and Pd/Au/$BiVO_4$/TiO_2 nanotube arrays.

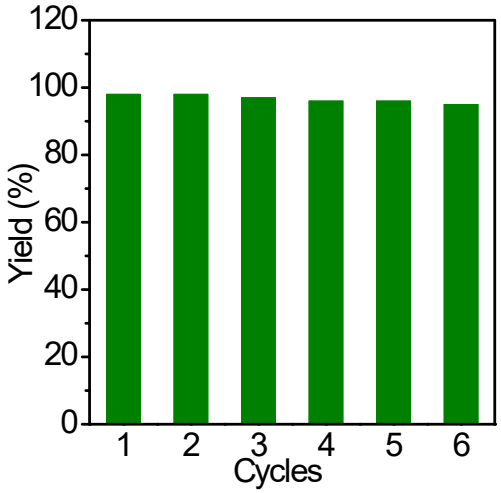


Fig. S3 Recyclability of Pd/Au/$BiVO_4$/TiO_2 nanotube arrays for photoelectrocatalytic Suzuki-Miyaura reactions.

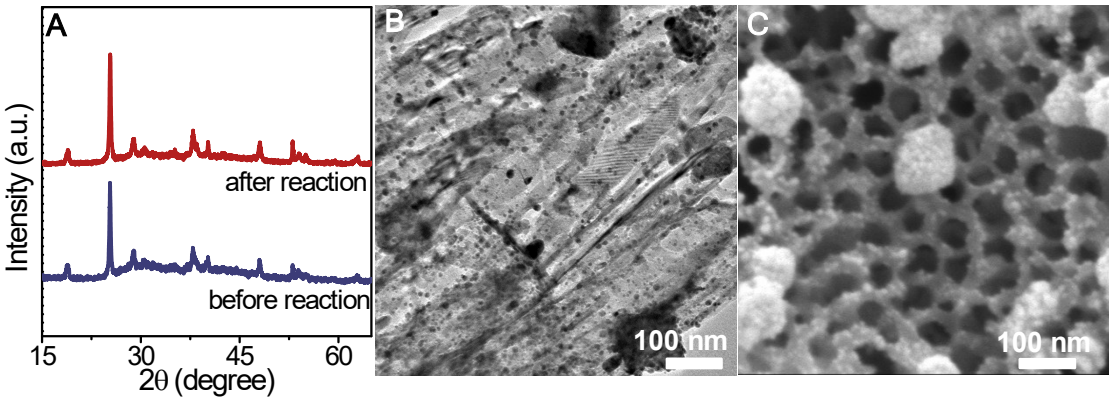
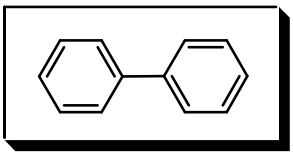


Fig. S4 (A) XRD pattern of Pd/Au/$BiVO_4$/TiO_2 nanotube arrays before and after cycling stability test, (B) TEM images and (C) SEM images of Pd/Au/$BiVO_4$/TiO_2 nanotube arrays after cycling stability test (**Fig. S3**).

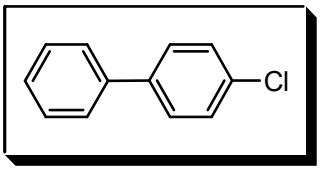
Table S1 Structure parameters of Pd/Au/$BiVO_4$/TiO_2 nanotube arrays

Samples	Specific surface area (m^2/g)			Pore volume (cm^3/g)		
	S_{BET}	S_{micro}	S_{meso}	V_{total}	V_{micro}	V_{meso}
Pd/Au/$BiVO_4$/TiO_2	31	4	27	0.205	0.001	0.204

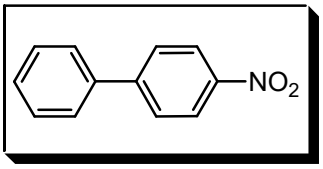
(B) Analytical Data



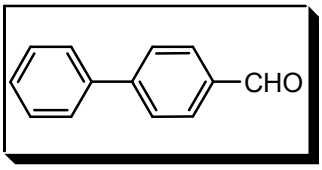
Biphenyl (3a)[3-5], white solid, mp: 66-69 °C (lit. mp 69-71 °C); IR (υ/cm^{-1}): 3053, 1953, 1596, 1546, 1482, 1344, 1168, 1085, 1005, 984, 907, 725, 696; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62-7.58 (m, 4H), 7.47-7.38 (m, 4H), 7.34 (t, J =7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.21, 128.74, 127.24, 127.15; MS *m*/*z* (%): 154 (M+, 100), 76 (52). Anal. Calcd. For $C_{12}H_{10}$: C, 93.46; H, 6.54; Found C, 93.06; H, 6.94.



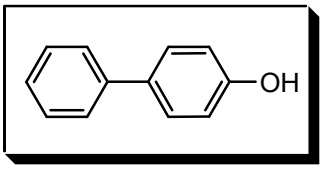
4-Chloridebiphenyl (3b)[3,4], white solid; colorless solid, mp: 77-78°C (lit. mp 78-79°C); IR *v*max(cm^{-1}): 3382, 3062, 1596, 1478, 1442, 1398, 1259, 1097, 1010, 907, 832, 758, 689. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.51 (m, 4H), 7.47-7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.97, 139.64, 133.35, 128.89, 128.87, 12838, 127.57, 126.97; MS *m*/*z* (%): 188 (M+, 100), 152 (74), 76 (37). Anal. Calcd. For $C_{12}H_9Cl$: C, 76.40; H, 4.81; Found C, 76.64; H, 4.38.



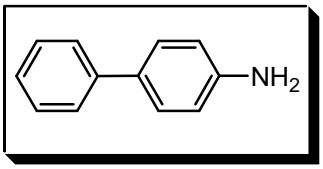
4-Nitrobiphenyl (3c)[3,5], yellow solid, mp: 111-113 °C (lit. mp 112-114 °C). IR (υ/cm^{-1}): 3068, 2925, 1602, 1573, 1522, 1476, 1442, 1353, 1176, 1078, 1010, 851, 742; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32-8.27 (m, 2H), 7.76-7.71 (m, 2H), 7.64-7.61 (d, J = 7.6 Hz, 2H), 7.52-7.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.60, 147.01, 138.73, 129.14, 128.90, 127.78, 127.36, 124.09; MS *m*/*z* (%): 199 (M+, 100), 152 (86), 151 (32), 76 (51). Anal. Calcd. For $C_{12}H_9NO_2$: Calcd. C, 72.35; H, 4.55; N, 7.03; Found C, 72.05; H, 4.32; N, 7.61.



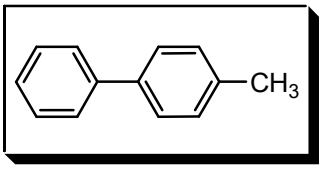
4-Carboxaldehydebiphenyl (3d)[3,5], white solid; mp: 57-58°C (lit. mp 57-59°C); IR (υ/cm^{-1}): 3360, 3032, 2838, 1694, 1603, 1223, 1167, 1008, 932, 832, 762; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.06 (s, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.51-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.92, 147.17, 139.69, 135.6, 130.25, 129.0, 128.45, 127.66, 127.34; MS *m*/*z* (%): 181 (M+, 100), 152 (69), 76 (46). Anal. Calcd. For $C_{13}H_{10}O$: C, 85.69; H, 5.53; Found C, 85.04; H, 5.83.



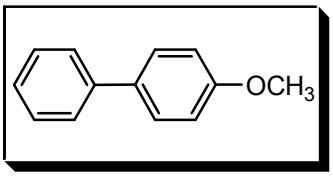
4-Phenylphenol (3e)[6]**,** white solid; mp: 145-146°C (lit. mp 146-147°C); IR (υ/cm^{-1}): 3350, 3043, 2950, 1658, 1450, 1268, 1163, 1052, 834, 757, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.33-7.29 (m, 1H), 6.91 (d, J = 8.4 Hz, 2H), 4.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.99, 140.72, 134.05, 128.71, 128.39, 126.70, 115.62; MS *m*/*z* (%): 170(M+, 100), 169(51), 154(20). Anal. Calcd. For $C_{12}H_{10}O$: C, 84.68; H, 5.92; Found C, 84.23; H, 5.68.



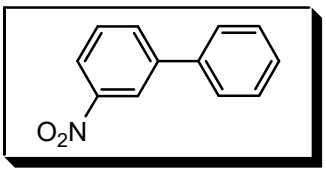
Biphenyl-4-amine (3f)[3,6], white solid; mp: 45-46°C (lit. mp 46-47°C); IR (υ/cm^{-1}): 3440, 3223, 3030, 2925, 1644, 1494, 1260, 1165, 1015, 836,760; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.52 (m, 2H), 7.43-7.36 (m, 4H), 7.26 (t, J = 8.4 Hz, 1H), 6.75 (d, J = 8.0 Hz, 2H), 3.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.81, 141.14, 131.57, 128.66, 128.01, 126.40, 126.25, 115.39. MS m/z (%): 169 (M+, 100), 141 (12). Anal. Calcd. For $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28; Found C, 85.55; H, 6.15; N, 8.30.



4-methylbiphenyl (3g)[3,4], white solid; mp: 46-47°C (lit. mp 44-47°C); IR (υ/cm^{-1}): 3045, 2938, 1605, 1568, 1464, 1380, 1253, 1130, 1008, 822,752, 692; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.33-7.30 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.45, 138.64, 137.44, 130.01, 129.31, 127.51, 127.23, 127.15, 20.71; MS m/z (%): 168 (M+, 100), 152 (26), 76 (15). Anal. Calcd. For $C_{13}H_{12}$: C, 92.81; H, 7.19; Found C, 92.33; H, 7.67.

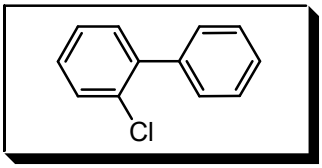


4-Methoxybiphenyl (3h)[3,4], white solid; mp: 87-88°C (lit. mp 85-87°C); IR (υ/cm^{-1}): 3053, 2970, 2918, 1604, 1592, 1531, 1486, 1230, 1080, 920, 830, 756, 673; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.51 (m, 4H), 7.41 (t, J = 7.6 Hz, 2H), 7.32-7.24 (m, 1H), 6.97(d, J = 7.2 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.10, 140.80, 133.74, 128.70, 128.14, 126.72, 126.64, 114.16, 55.32; MS *m*/*z* (%): 184 (M+, 100), 169 (M+-CH_3, 48). Anal. Calcd. For $C_{13}H_{12}O$: Calcd. C, 84.75; H, 6.57; Found C, 84.66; H, 6.61.

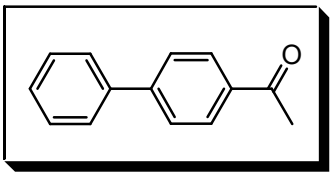


3-Nitrobiphenyl (3i)[3,7], yellow solid, mp: 60-61 °C (lit. mp 60-61 °C). IR (υ/cm^{-1}): 3085, 2944, 1625, 1575, 1531, 1350, 1286, 1067, 863, 810, 765, 728,692; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.65-7.59 (m, 3H), 7.52-7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.66, 142.81, 138.61, 133.01, 129.68, 129.13, 128.50, 127.12, 122.00, 121.91. MS m/z (%): 199 (M+, 81), 152 (100), 153 (54), 76 (46). Anal. Calcd. For $C_{12}H_9NO_2$: Calcd. C,

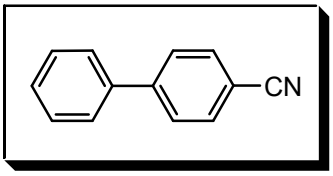
72.35; H, 4.55; N, 7.03; Found C, 71.68; H, 4.95; N, 7.42.



2-Chloridebiphenyl (3j)[3], colorless liquid, IR (υ/cm^{-1}): 3063, 3030, 2925, 2856, 1641, 1460, 1427, 1102, 1080,780, 752, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.35 (m, 6H), 7.34-7.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.50, 139.38, 132.47, 131.36, 129.91, 129.42, 128.51, 128.02, 127.58, 126.80; MS *m/z* (%): 188 (M+, 100), 152 (62), 76 (33). Anal. Calcd. For $C_{12}H_9Cl$: C, 76.40; H, 4.81; Found C, 76.88; H, 4.55.

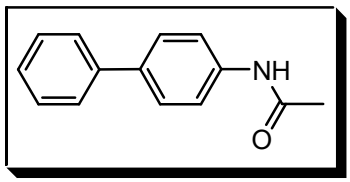


4-Acetylbiphenyl (3k)[3,8], white solid; mp: 120-121°C (lit. mp 121-122°C); IR (υ/cm^{-1}): 3053, 2988, 1680, 1602, 1406, 1359,1258,1183, 839, 760, 687, 590. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.74, 145.73, 139.80, 135.77, 128.91, 128.88, 128.20, 127.40, 127.22, 127.18, 26.64. MS m/z (%): 196 (M+, 44), 181 (100), 152 (60), 76 (33). Anal. Calcd. For $C_{14}H_{12}O$: Calcd. C, 85.68; H, 6.16; Found C, 85.45; H, 6.28.

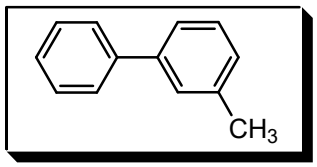


4-Cyanobiphenyl(3l)[3,5], white solid; mp: 85-86°C (lit. mp 86-87°C); IR (υ/cm^{-1}): 3066, 3025, 2934, 2227, 1608, 1520, 1485, 1374, 1185, 1068, 848, 768, 690. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.63 (m, 4H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.53-7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.54, 139.03, 132.50, 129.03, 128.58, 127.63, 127.13, 118.88, 110.78. MS m/z (%): 179 (M+, 100), 151 (16), 76 (24). Anal. Calcd. For $C_{13}H_9N$: Calcd. C, 87.12; H, 5.06; N, 7.82; Found C, 86.58; H, 5.76; N,

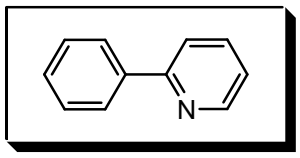
8.13.



N-Acetyl-4-aminobiphenyl (3m)[3,6], white solid; mp: 171-172°C (lit. mp 170--172°C); IR (υ/cm^{-1}): 3315, 3195, 2950, 1660, 1606, 1490, 1454, 1373, 1324, 1166, 1054, 842, 762, 693. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (s, 1H), 7.59-7.52 (m, 6H), 7.42 (t, *J* = 7.6Hz, 2H), 7.34-7.30 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 168.57, 140.40, 137.15, 137.10, 128.73, 127.53, 127.06, 126.77, 120.24, 24.55. MS m/z (%): 211 (M+, 46), 169 (100), 43 (39). Anal. Calcd. For $C_{14}H_{13}NO$: Calcd. C, 79.59; H, 6.20; N, 6.63; Found C, 78.33; H, 6.02; N, 7.23.

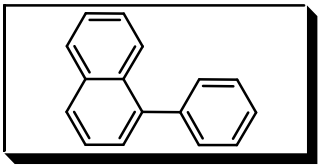


3-Methylbiphenyl (3n)[3,4], colorless liquid, IR (υ/cm^{-1}): 3032, 2921, 1696, 1601, 1482, 1072, 1033, 752, 697; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.58 (d, *J* = 7.6 Hz, 2H), 7.45-7.38 (m, 4H), 7.35-7.31 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 141.33, 141.21, 138.30, 128.67, 128.65, 127.97, 127.16, 124.25, 21.54. MS m/z (%): 168 (M+, 100), 153 (36), 76 (45). Anal. Calcd. For $C_{13}H_{12}$: Calcd. C, 92.81; H, 7.19; Found C, 93.65; H, 6.35.

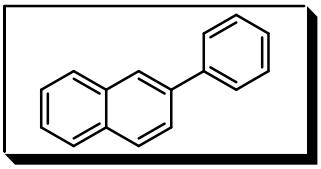


2-Phenylpyridine (3o)[3,9], colorless liquid, IR (υ/cm^{-1}): 3062, 3033, 2920, 1740, 1589, 1480, 1445, 1258, 1154, 1090, 1030, 801, 752, 695; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.86 (d, *J* = 4.2 Hz, 1H), 8.59 (d, *J* = 7.8 Hz,1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.60-7.58 (m, 2H), 7.51-7.47 (m, 2H), 7.43-7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 148.43, 148.30, 137.80, 136.63, 134.36, 129.06, 128.10, 127.13, 123.54. MS *m/z* (%): 155 (M+, 100). Anal. Calcd. For $C_{11}H_9N$: Calcd. C, 85.13; H, 5.85; N,

9.03; Found C, 84.25; H, 5.06; N, 9.89.



1-Phenylnaphthalene (3p)[3,4] , colorless liquid, IR (υ/cm^{-1}): 3057, 2927, 1592, 1494, 1395, 802, 778, 761, 704, 617; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.54-7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.73, 140.23, 133.76, 131.59, 130.06, 128.40, 128.24, 127.61, 127.21, 126.90, 126.00, 125.74, 125.36. MS m/z (%): 204 (M+, 100). Anal. Calcd. For $C_{16}H_{12}$: Calcd. C, 94.08; H, 5.92; Found C, 93.75; H, 6.25.



2-Phenylnaphthalene (3q)[3,5], white solid; mp: 96-97°C (lit. mp 95-96°C); IR (υ/cm^{-1}): 3053, 2925, 1947, 1597, 1495, 1453, 1130, 893, 862; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.92-7.85 (m, 3H), 7.73 (t, J = 8.2 Hz, 3H), 7.51-7.46 (m, 4H), 7.39-7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.10, 138.53, 133.65, 132.58, 128.84, 128.39, 128.18, 127.63, 127.41, 127.33, 126.27, 125.91, 125.78, 125.58. MS m/z (%): 204 (M+, 100). Anal. Calcd. For $C_{16}H_{12}$: Calcd. C, 94.08; H, 5.92; Found C, 93.45; H, 6.55.

(C) References

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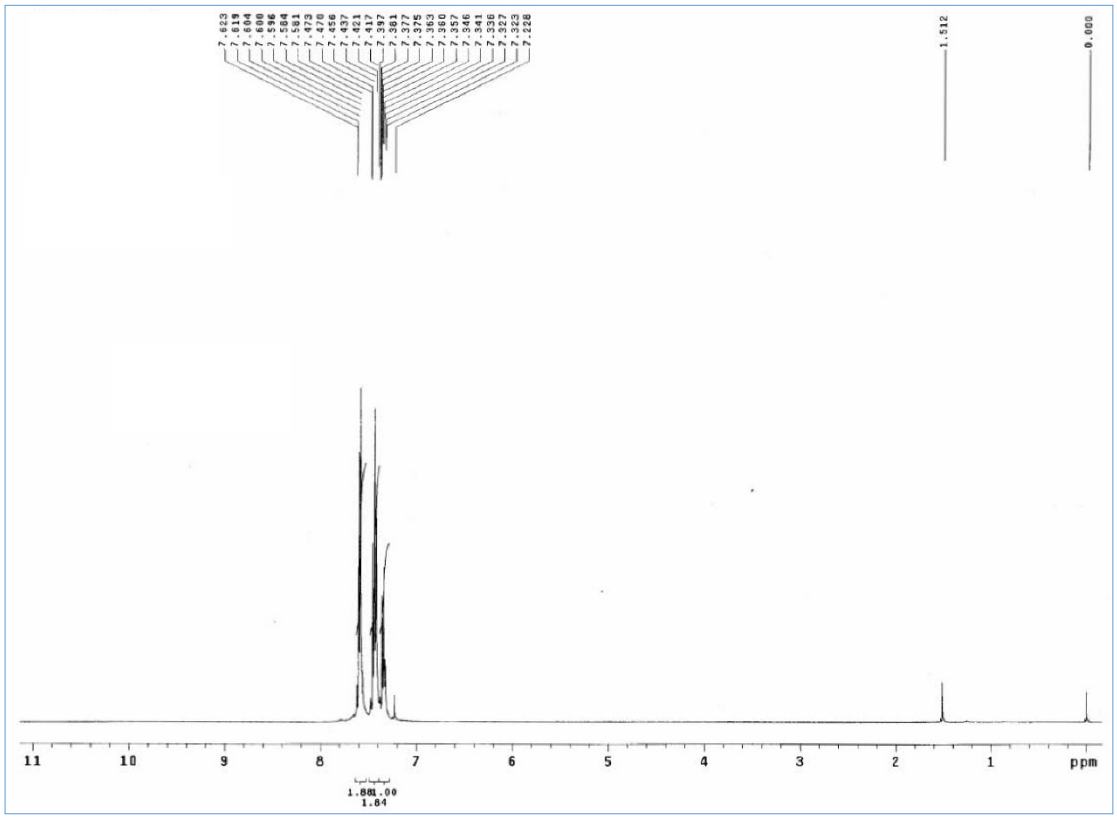
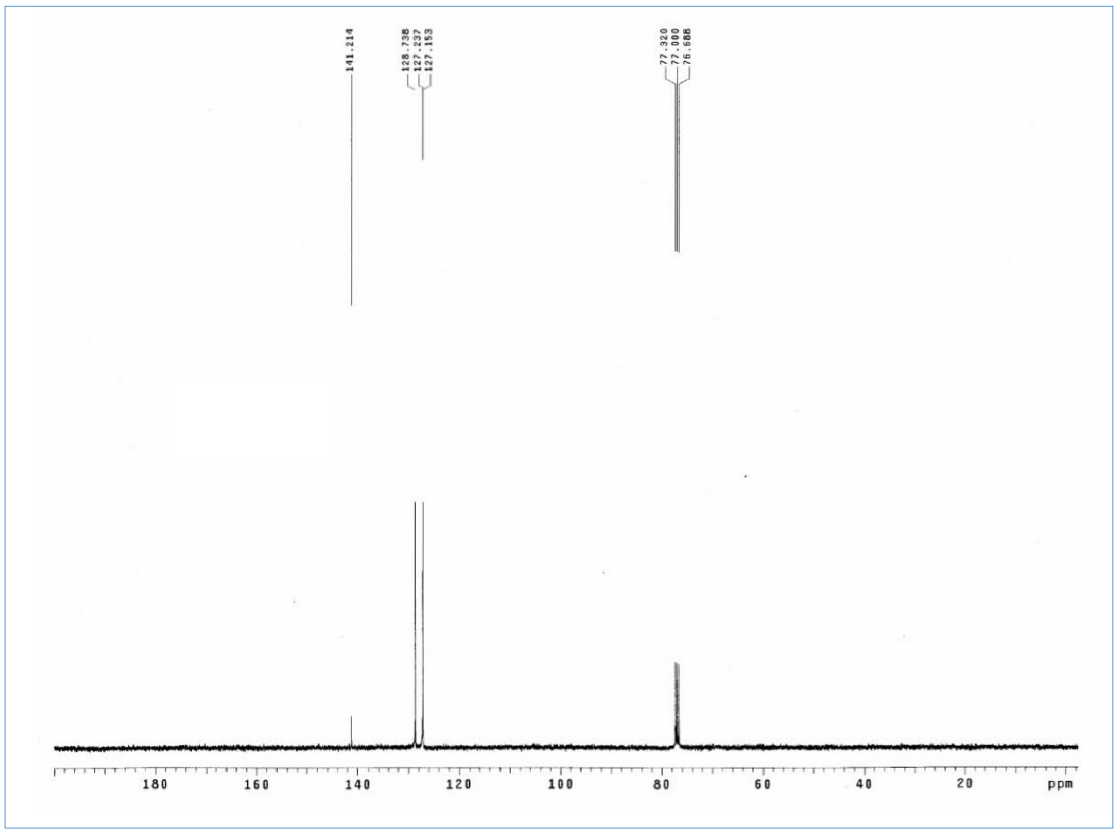
[9] V. Ramakrishna, N. D. Reddy, *Dalton Trans.*, 2017, **46**, 8598-8610.

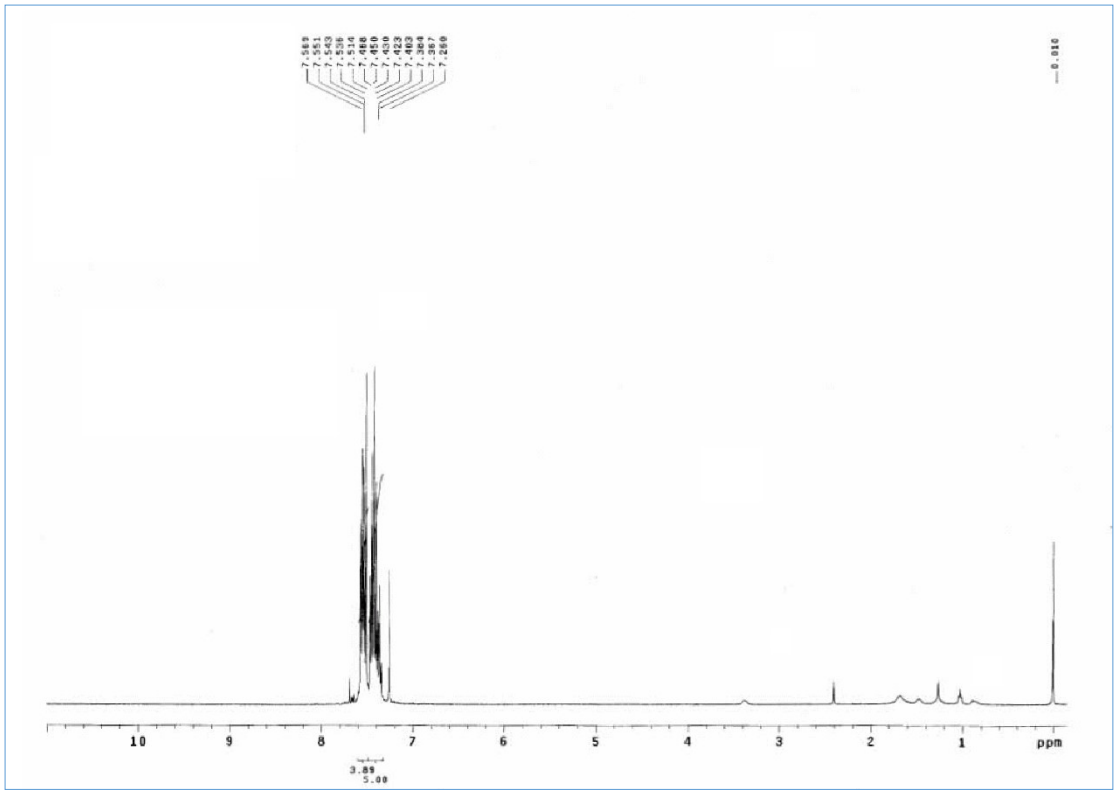
(D) ^{1}H NMR and ^{13}C NMR Spectra



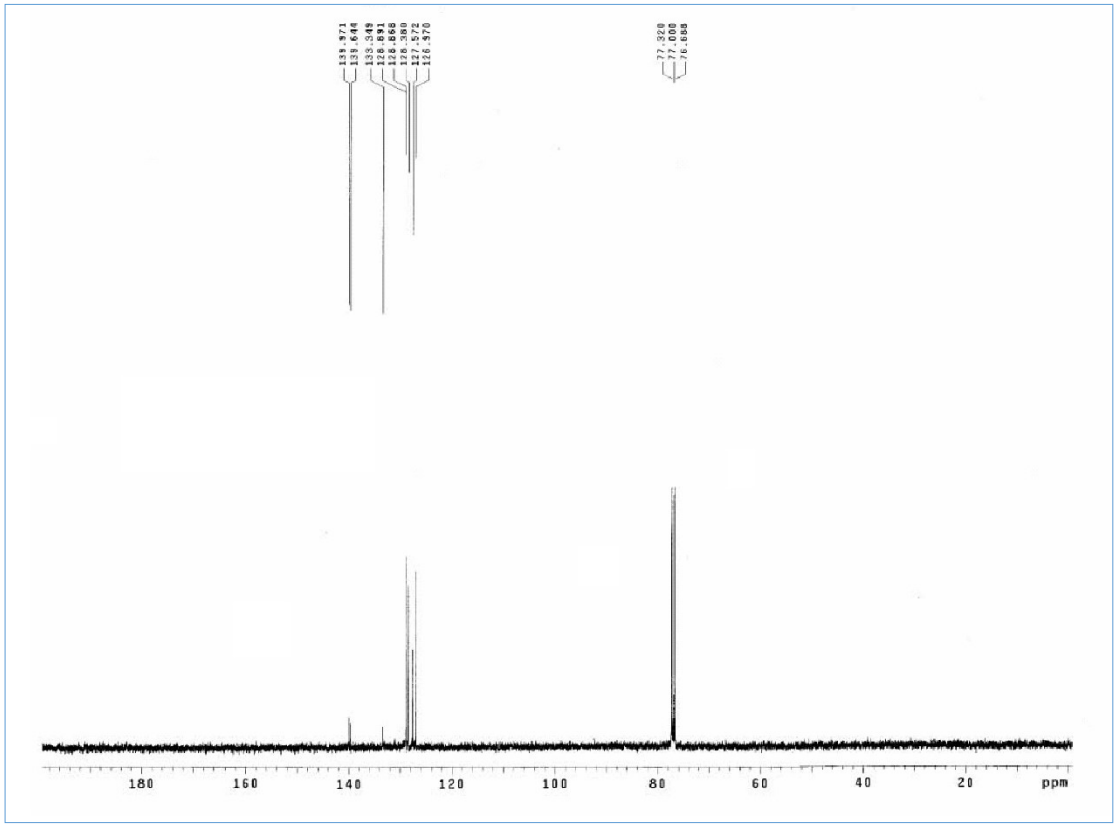
^{1}H NMR spectra for Biphenyl (3a)



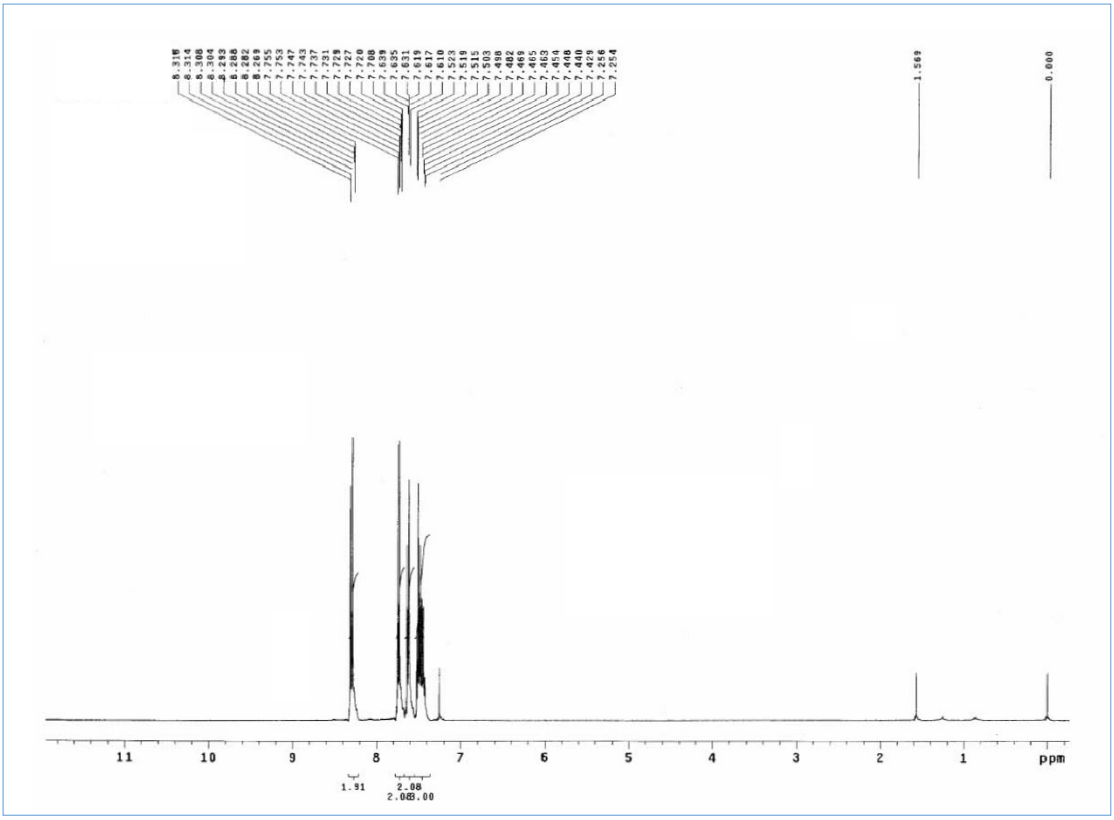
^{13}C NMR spectra for Biphenyl (3a)



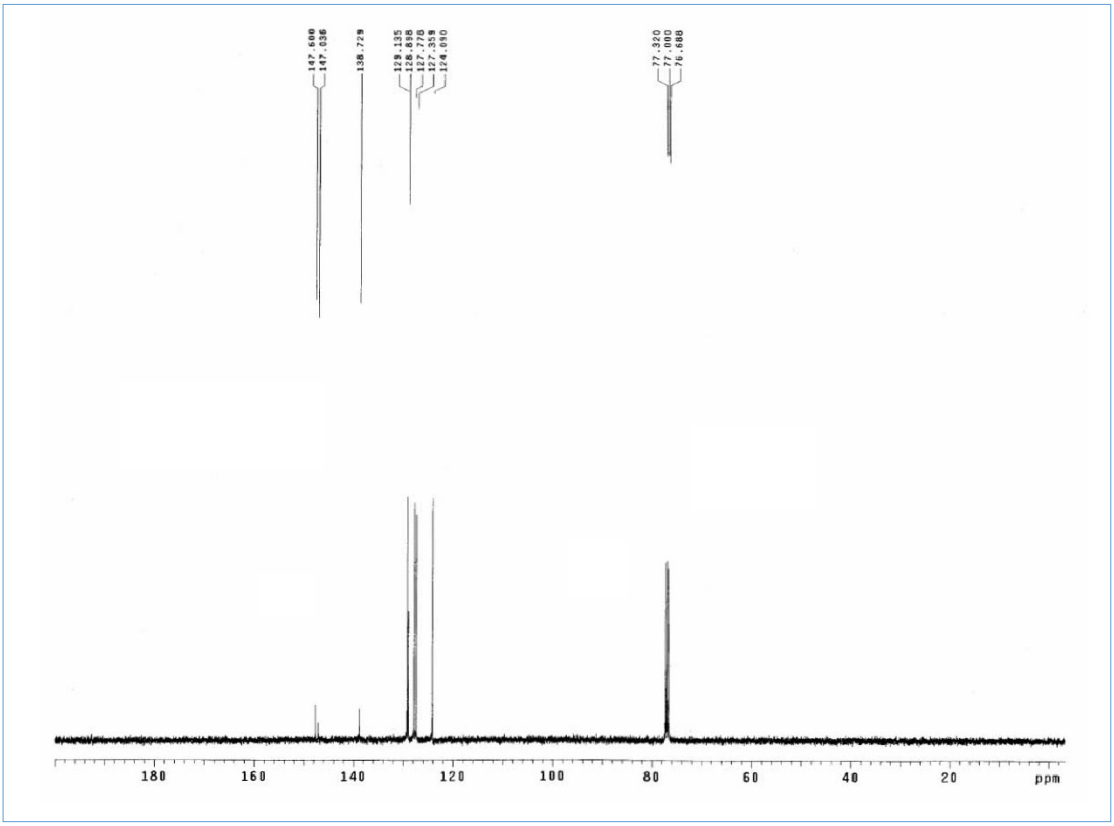
^{1}H NMR spectra for 4-Chloridebiphenyl (3b)



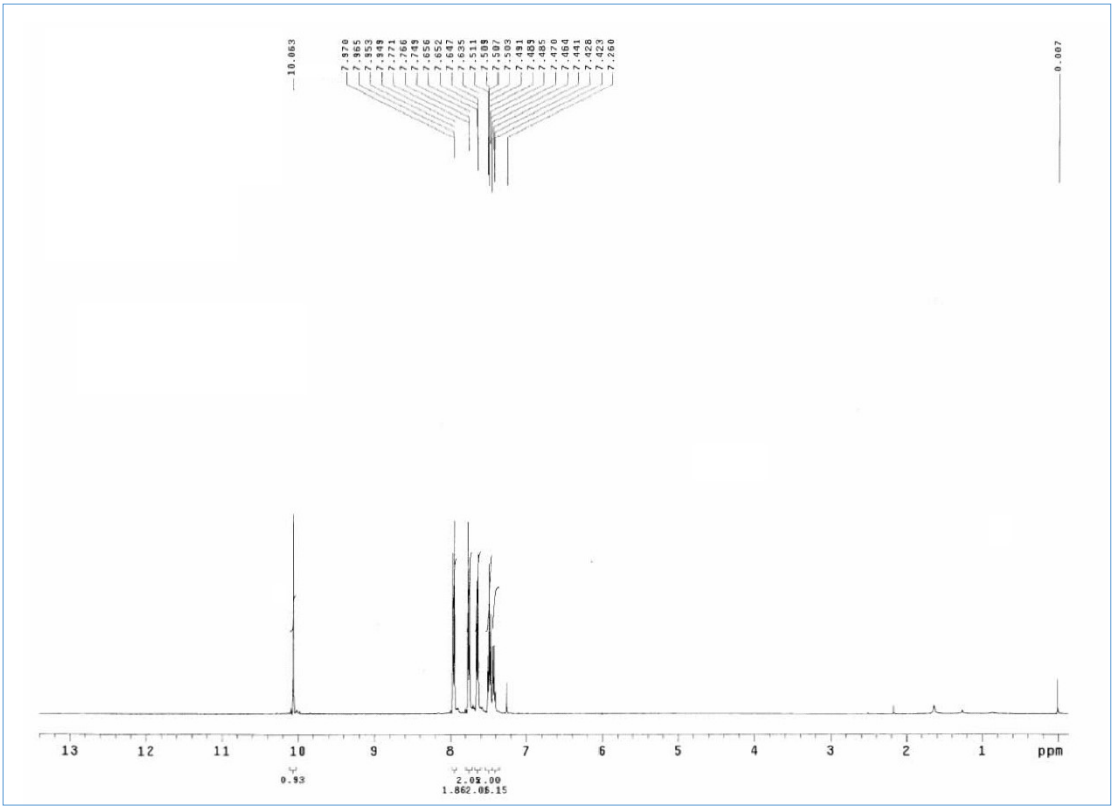
^{13}C NMR spectra for 4-Chloridebiphenyl (3b)



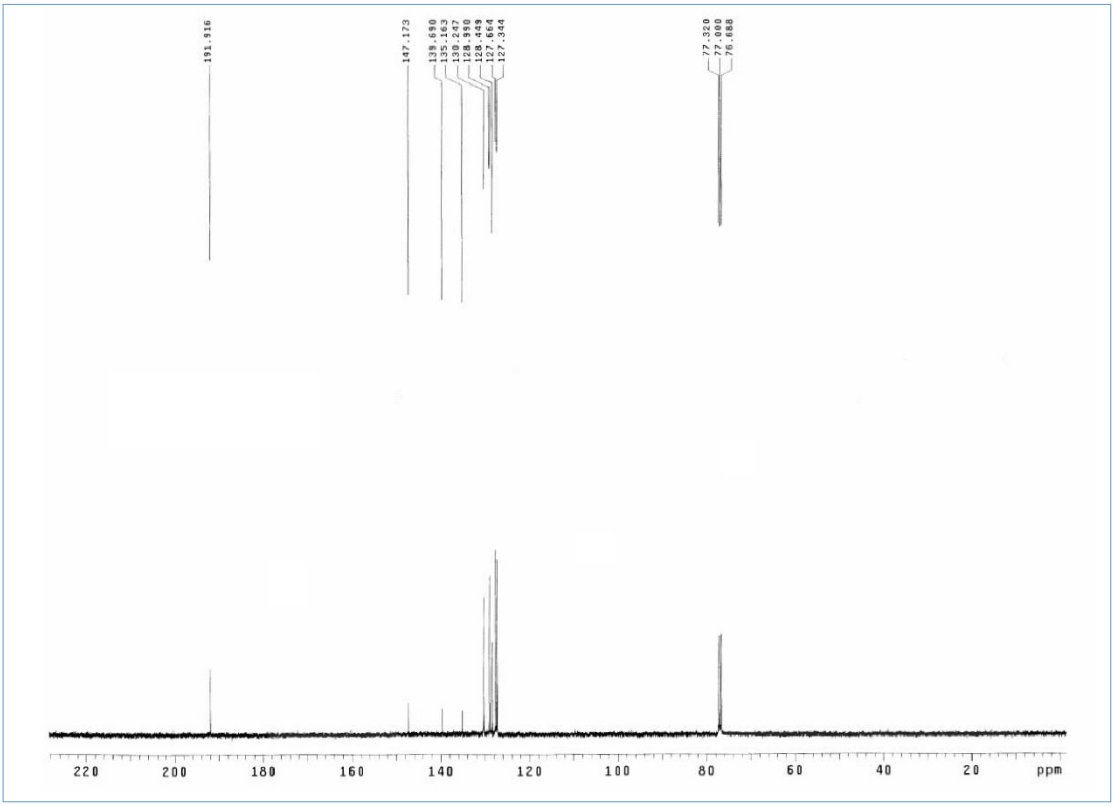
^{1}H NMR spectra for 4-Nitrobiphenyl (3c)



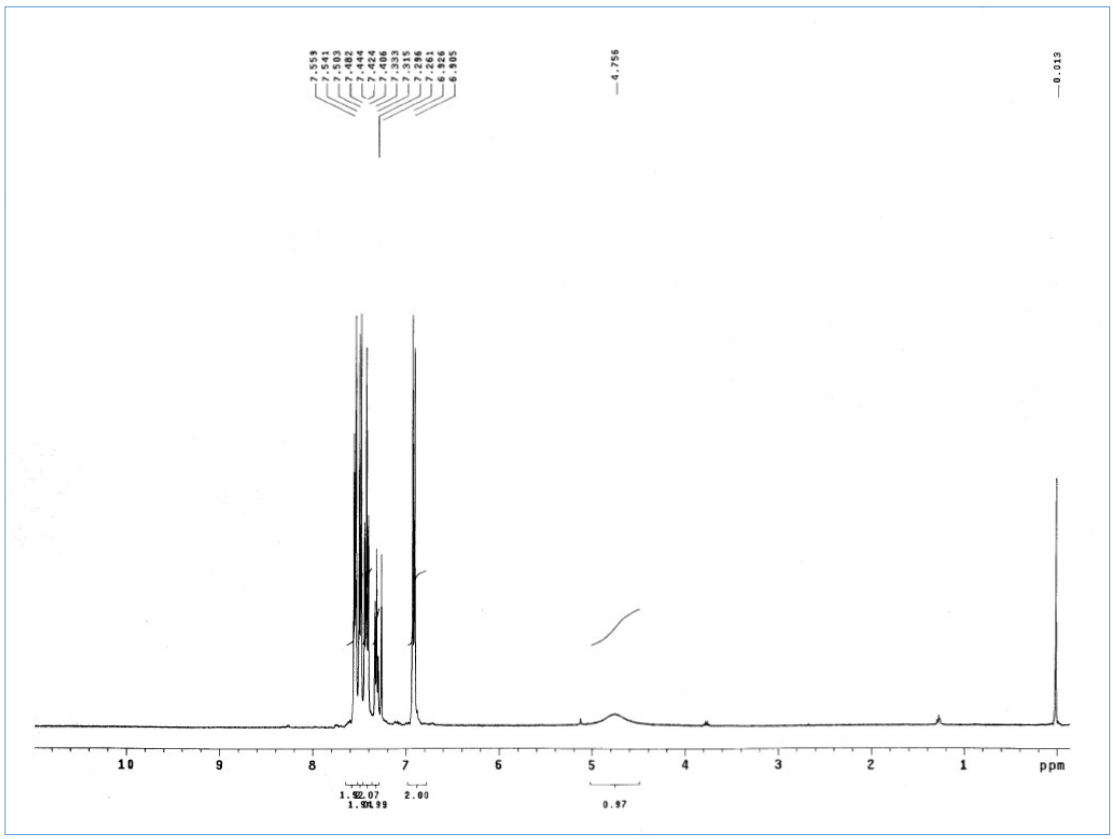
^{13}C NMR spectra for 4-Nitrobiphenyl (3c)



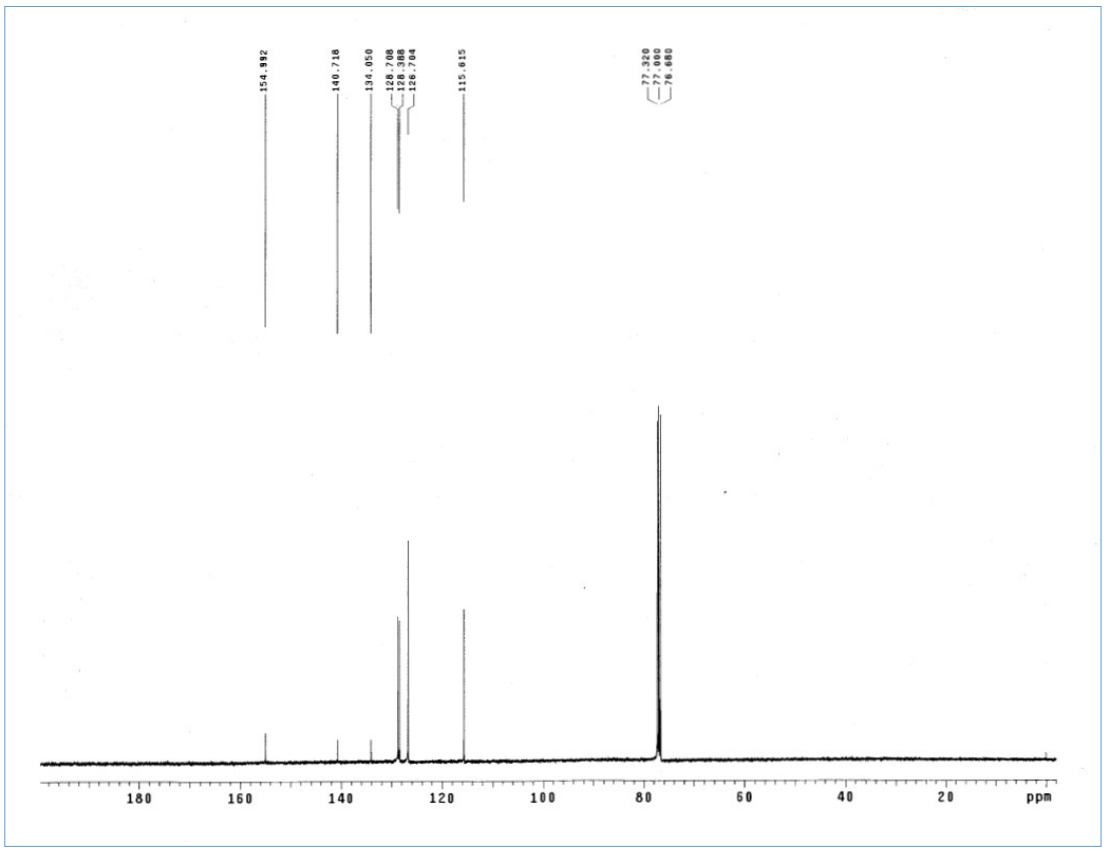
[1]H NMR spectra for 4-Carboxaldehydebiphenyl (3d)



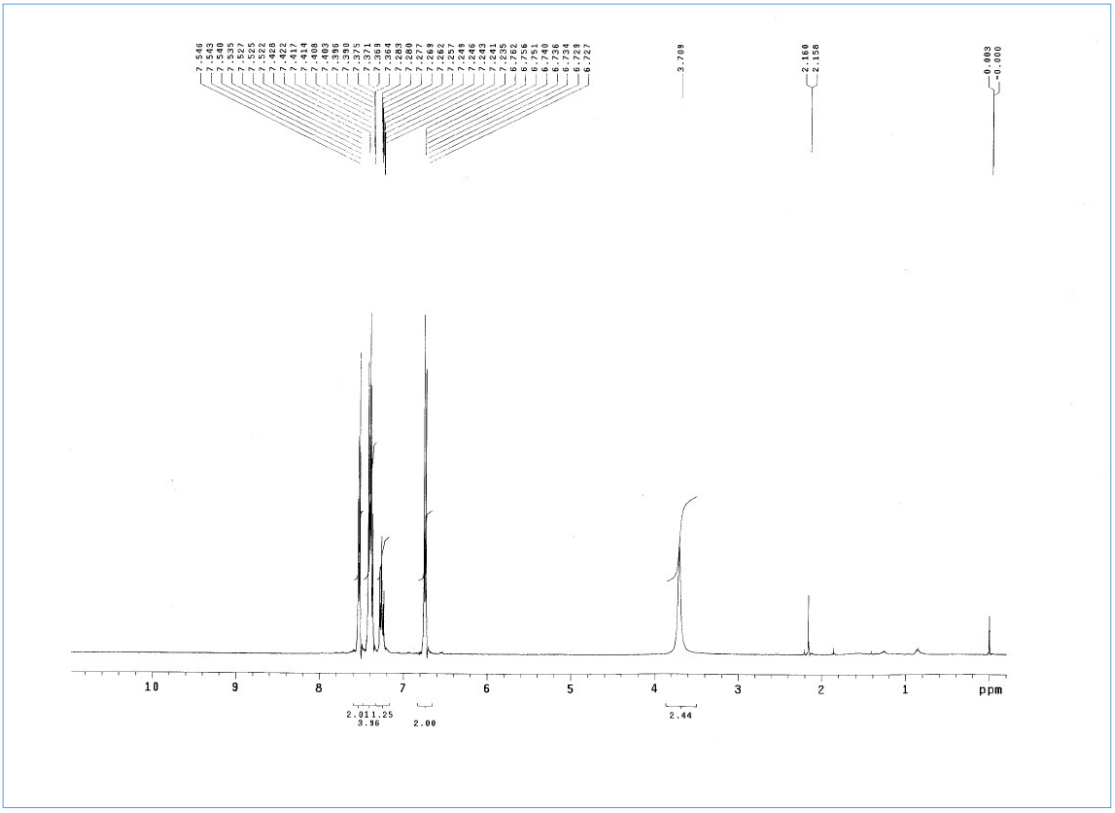
[13]C NMR spectra for 4-Carboxaldehydebiphenyl (3d)



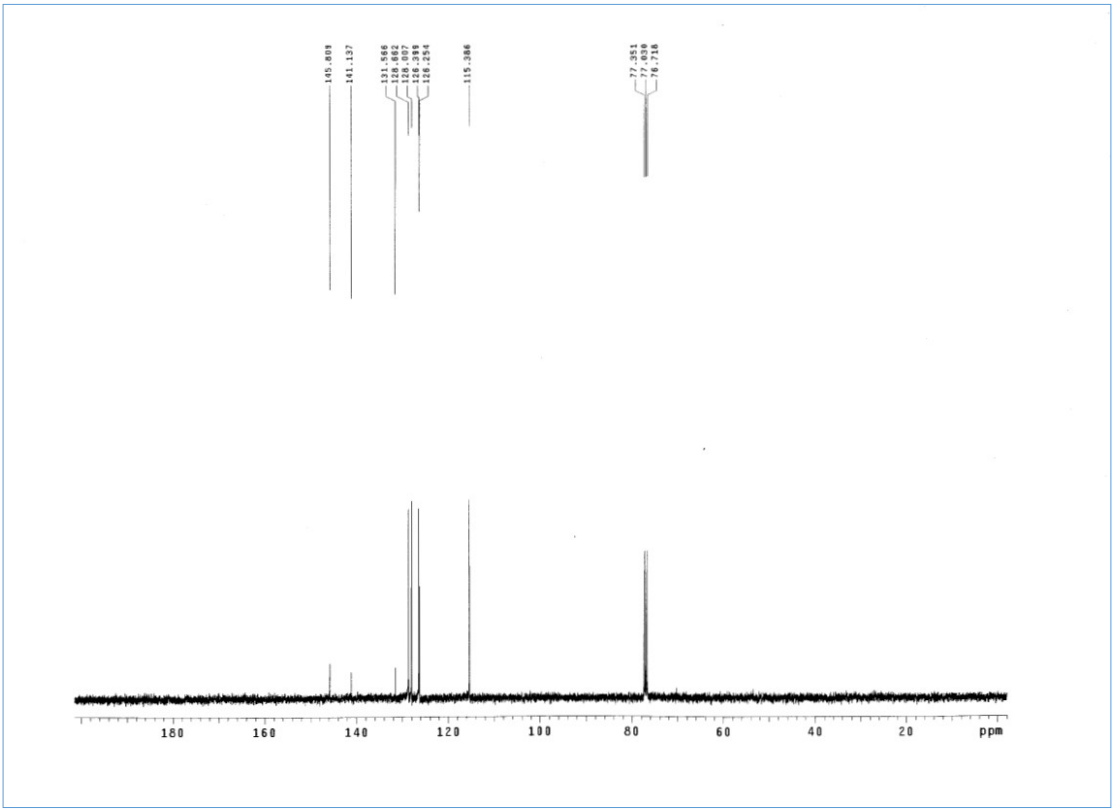
1H NMR spectra for 4-Phenylphenol (3e)



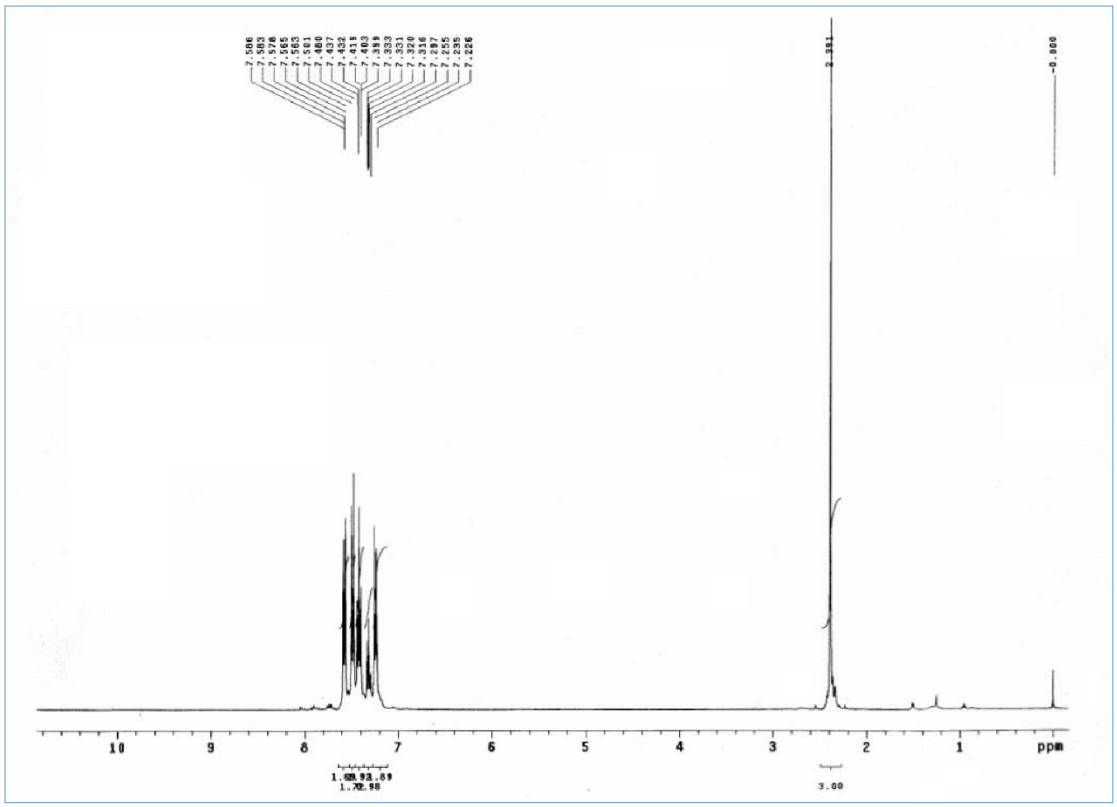
^{13}C NMR spectra for 4-Phenylphenol (3e)



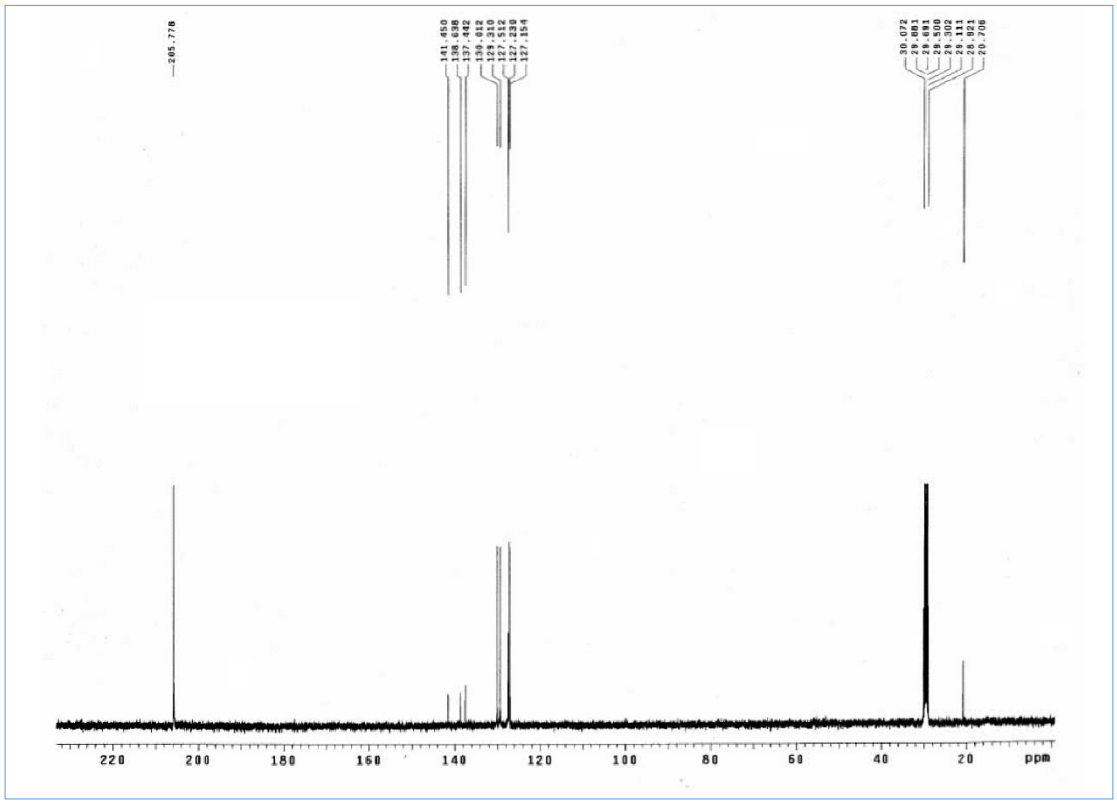
1H NMR spectra for Biphenyl-4-amine (3f)



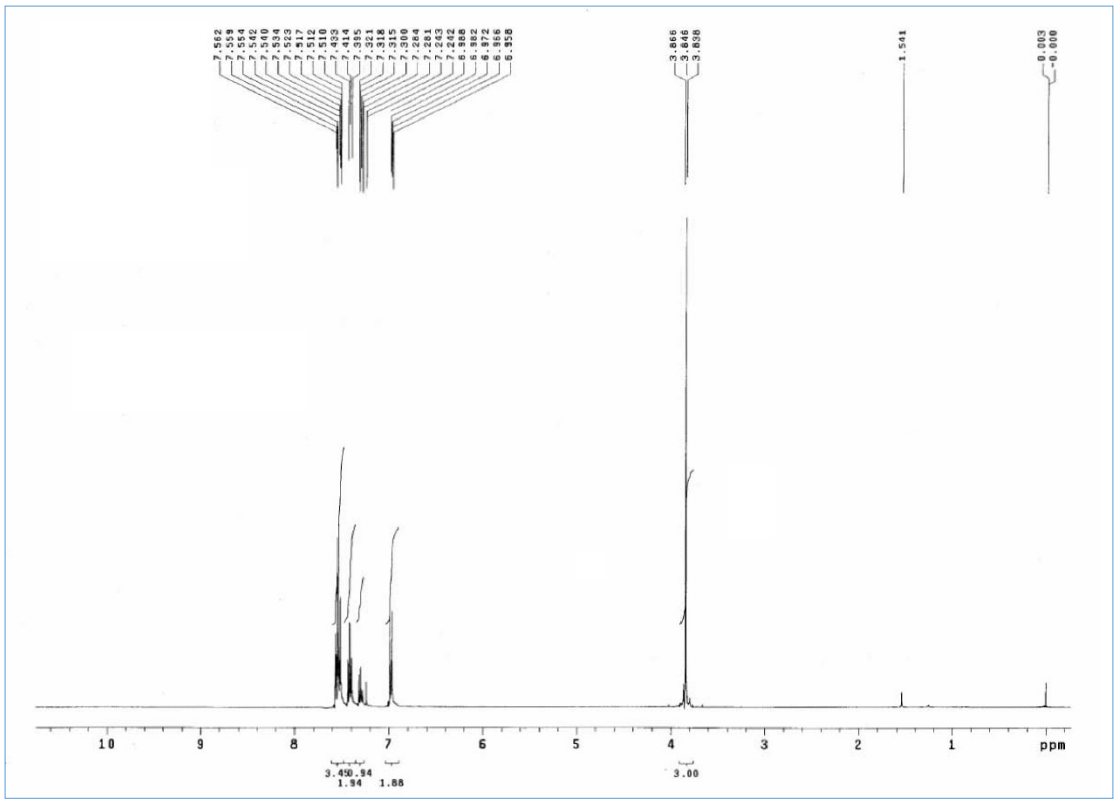
13C NMR spectra for Biphenyl-4-amine (3f)



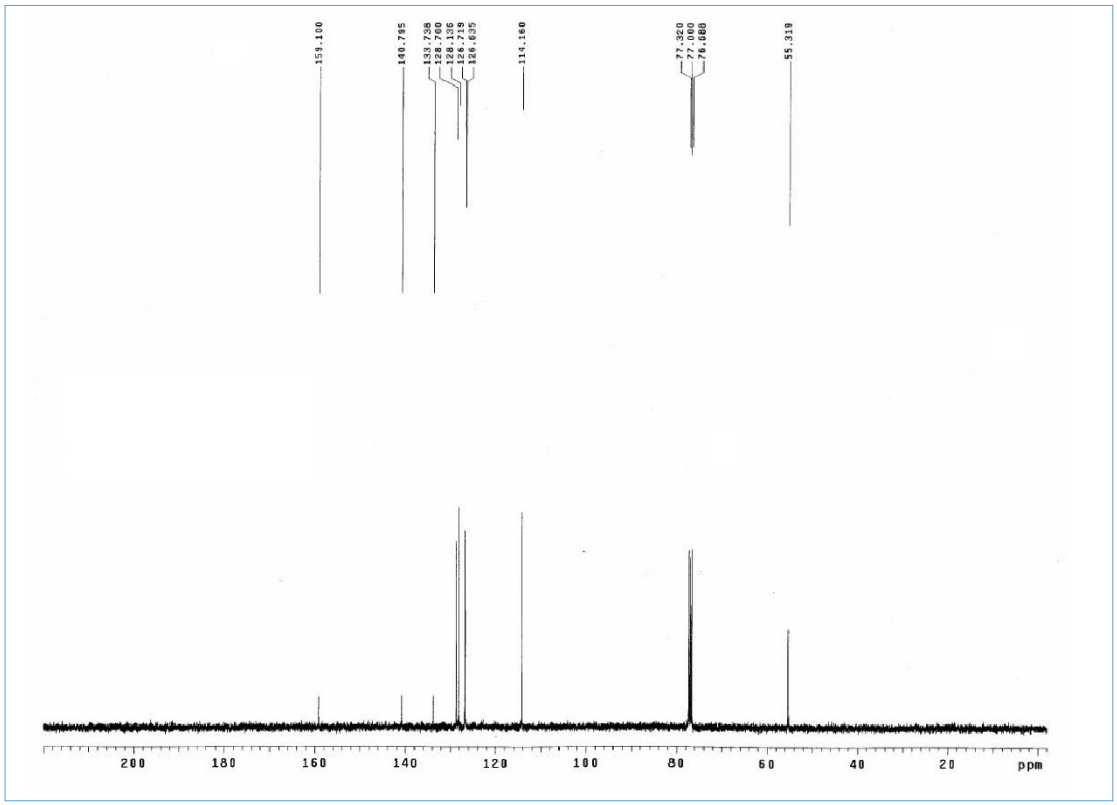
1H NMR spectra for 4-methylbiphenyl (3g)



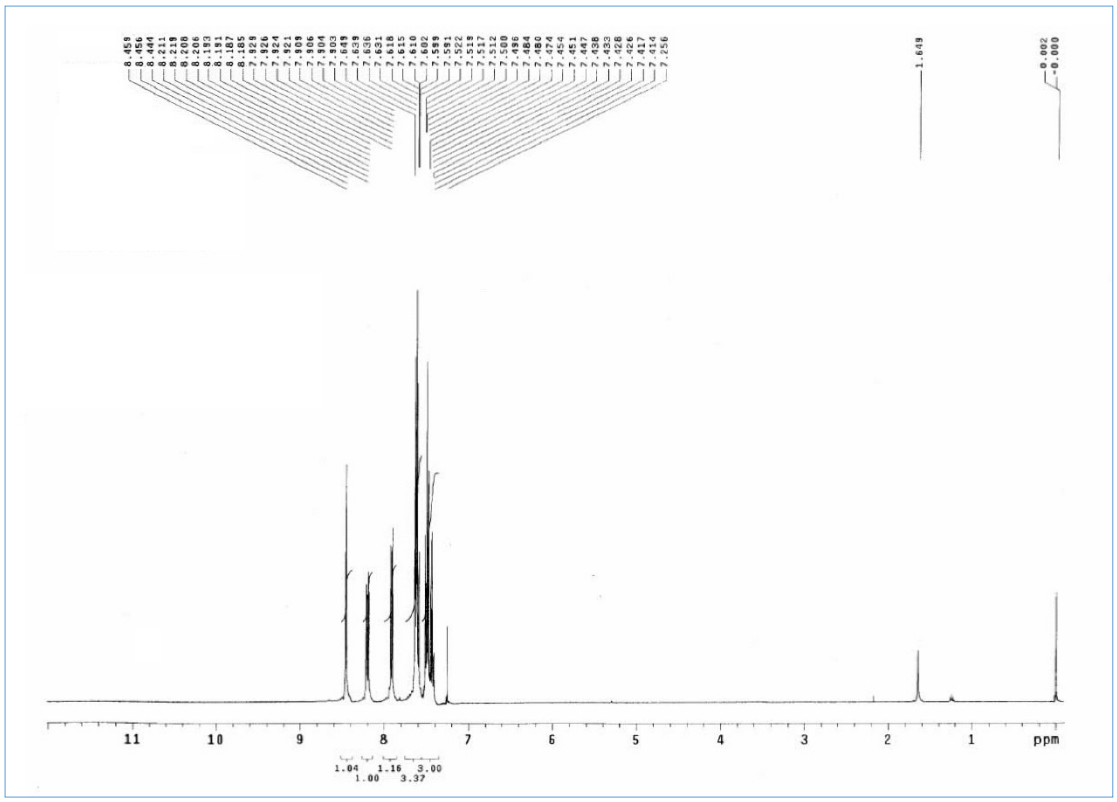
^{13}C NMR spectra for 4-methylbiphenyl (3g)



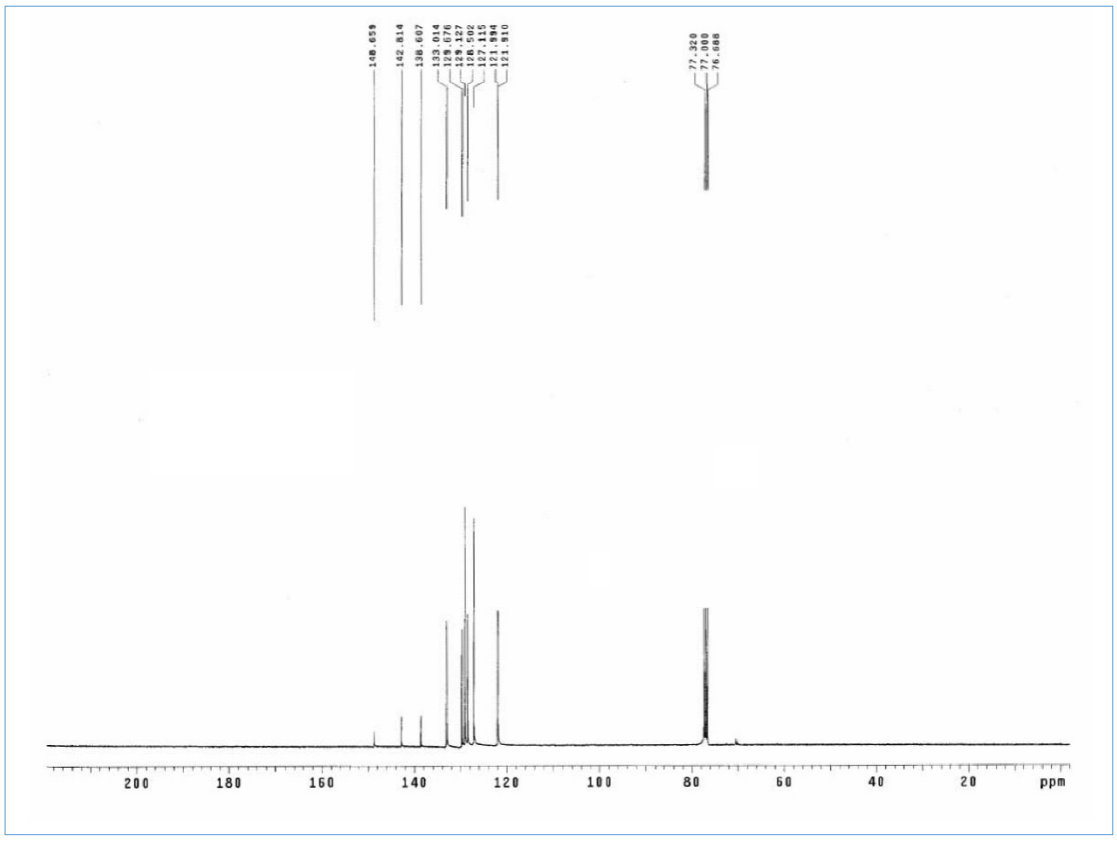
[1]H NMR spectra for 4-Methoxybipheny (3h)



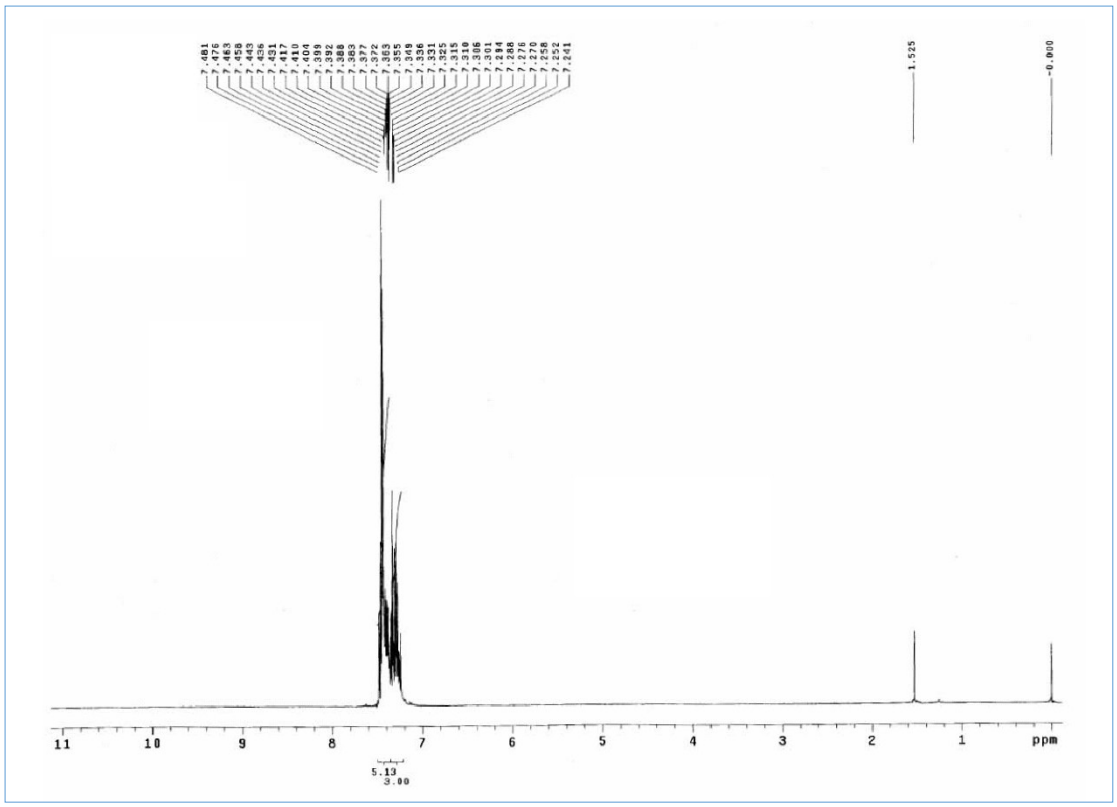
[13]C NMR spectra for 4-Methoxybipheny (3h)



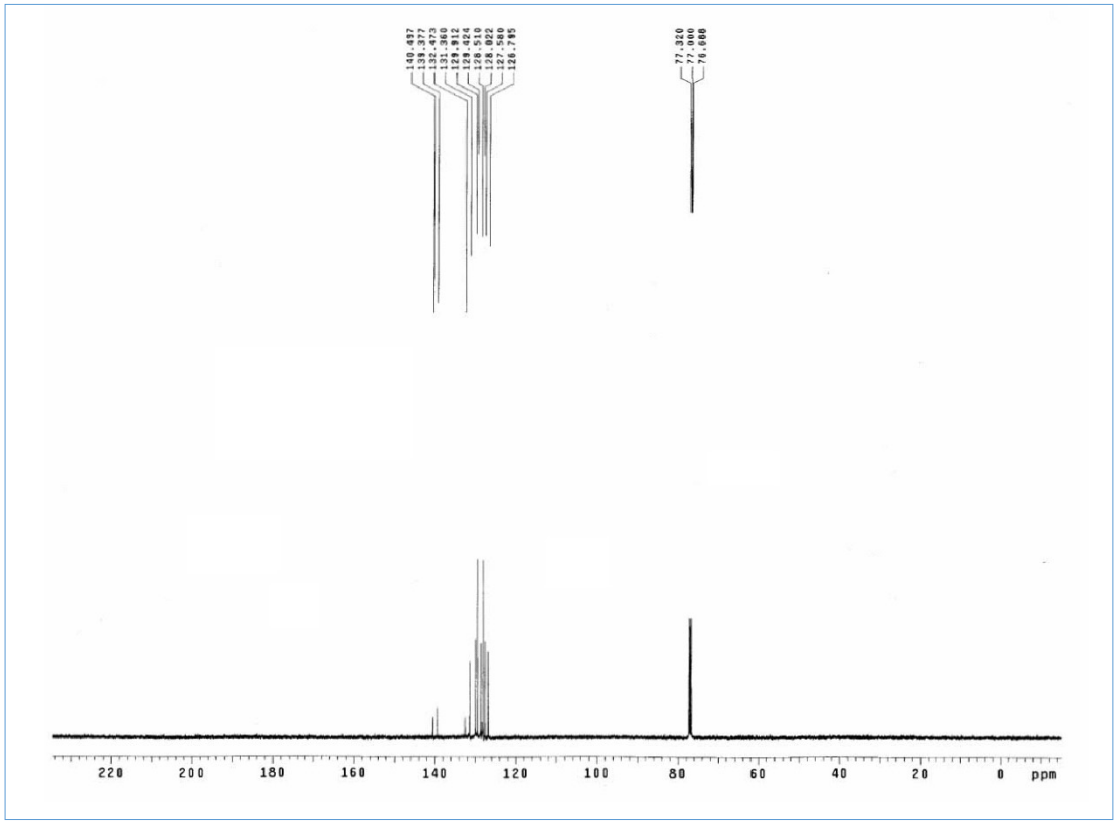
[1]H NMR spectra for 3-Nitrobiphenyl (3i)



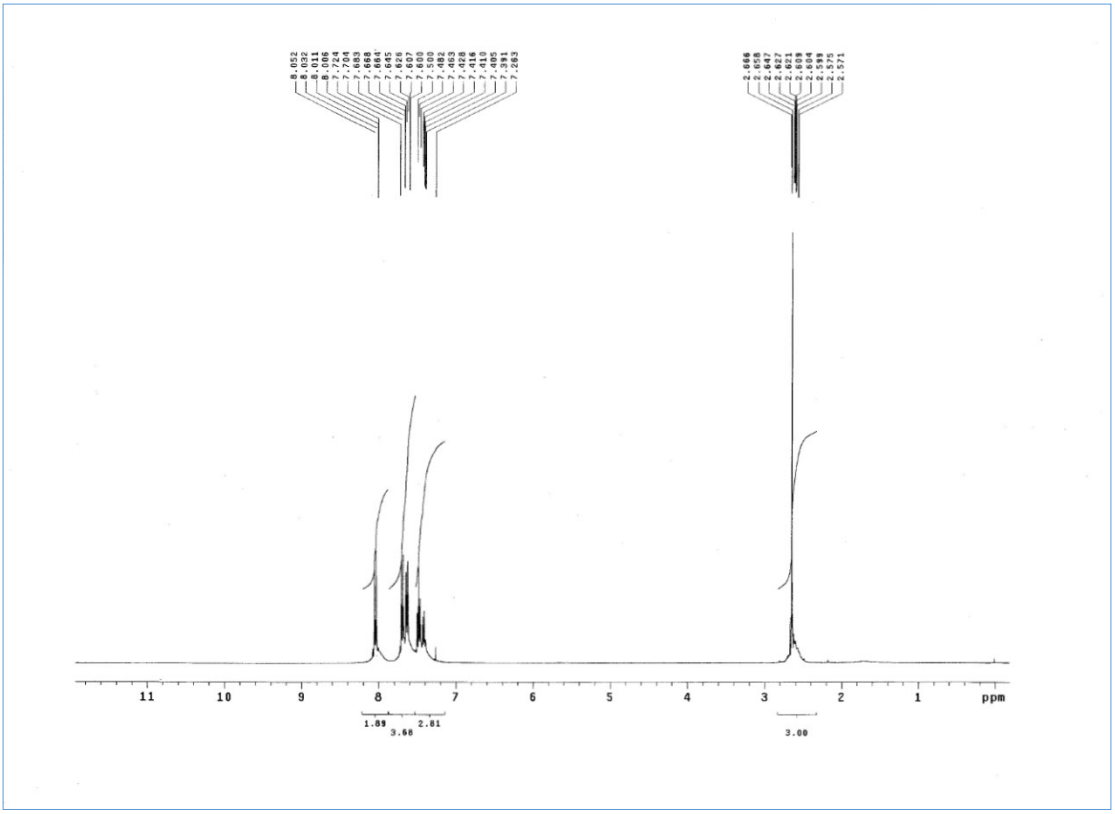
[13]C NMR spectra for 3-Nitrobiphenyl (3i)



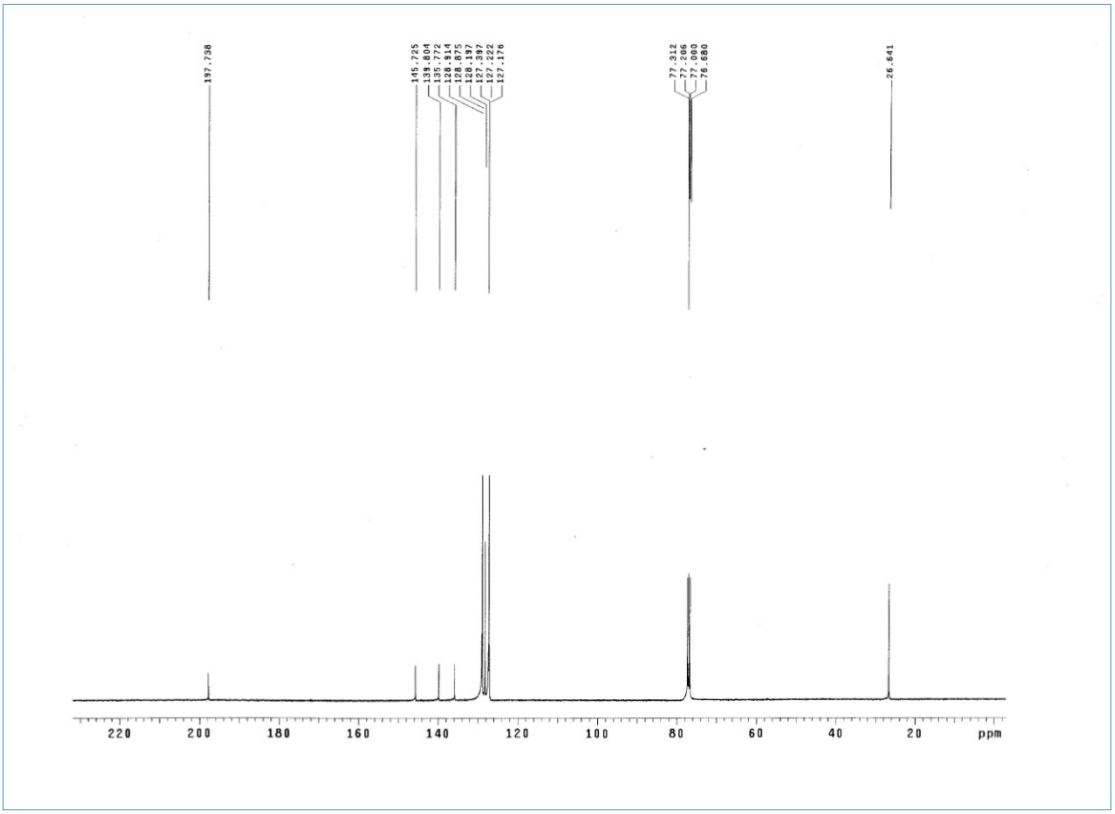
[1]H NMR spectra for 2-Chloridebiphenyl (3j)



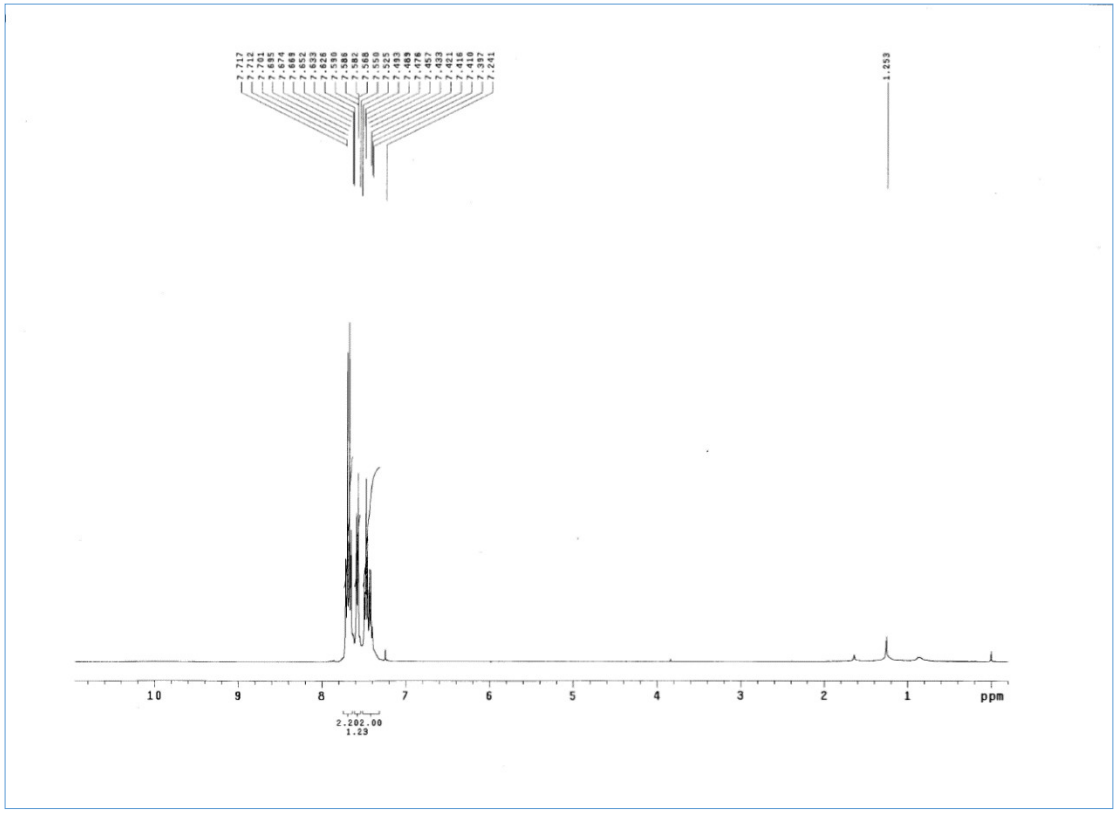
[13]C NMR spectra for 2-Chloridebiphenyl (3j)



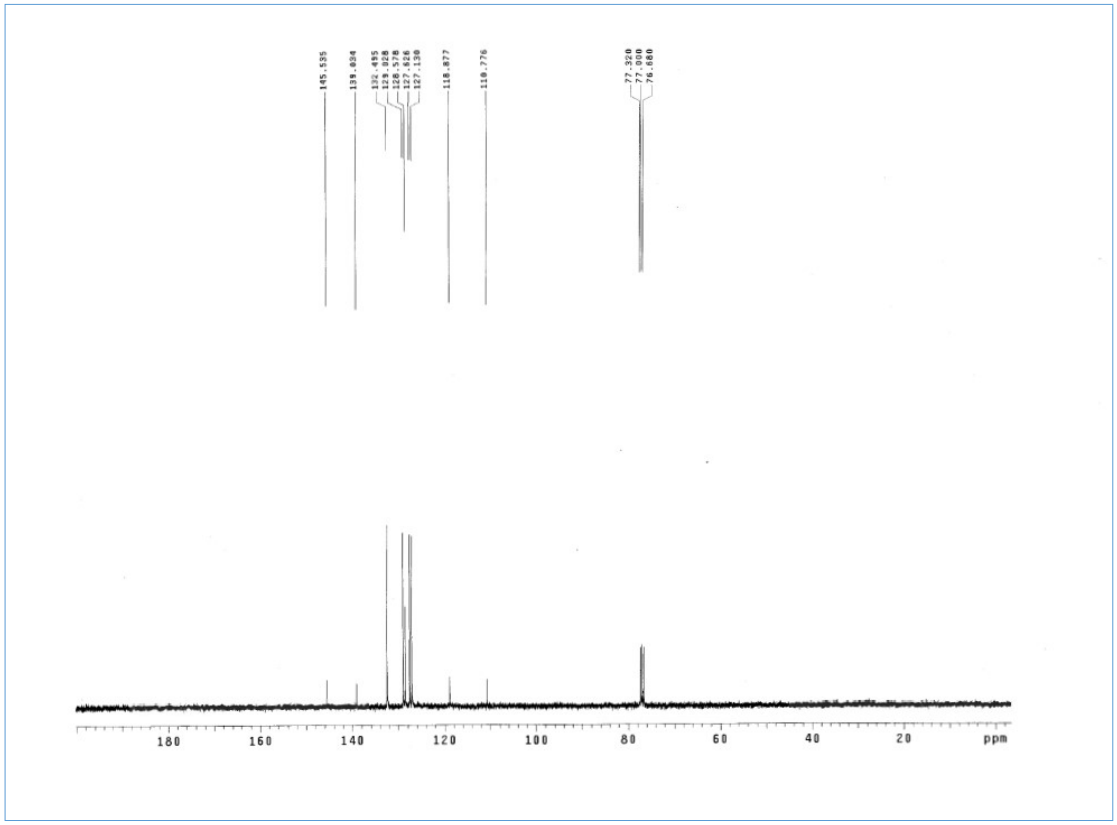
^{1}H NMR spectra for 4-Acetylbiphenyl (3k)



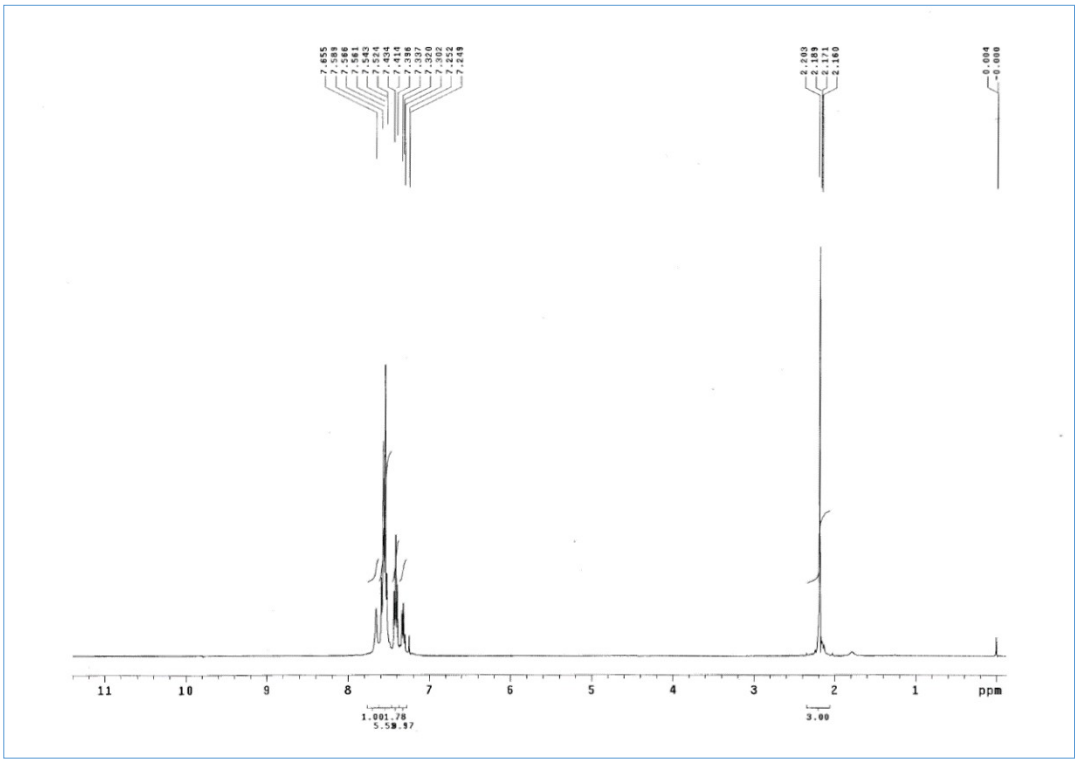
^{13}C NMR spectra for 4-Acetylbiphenyl (3k)



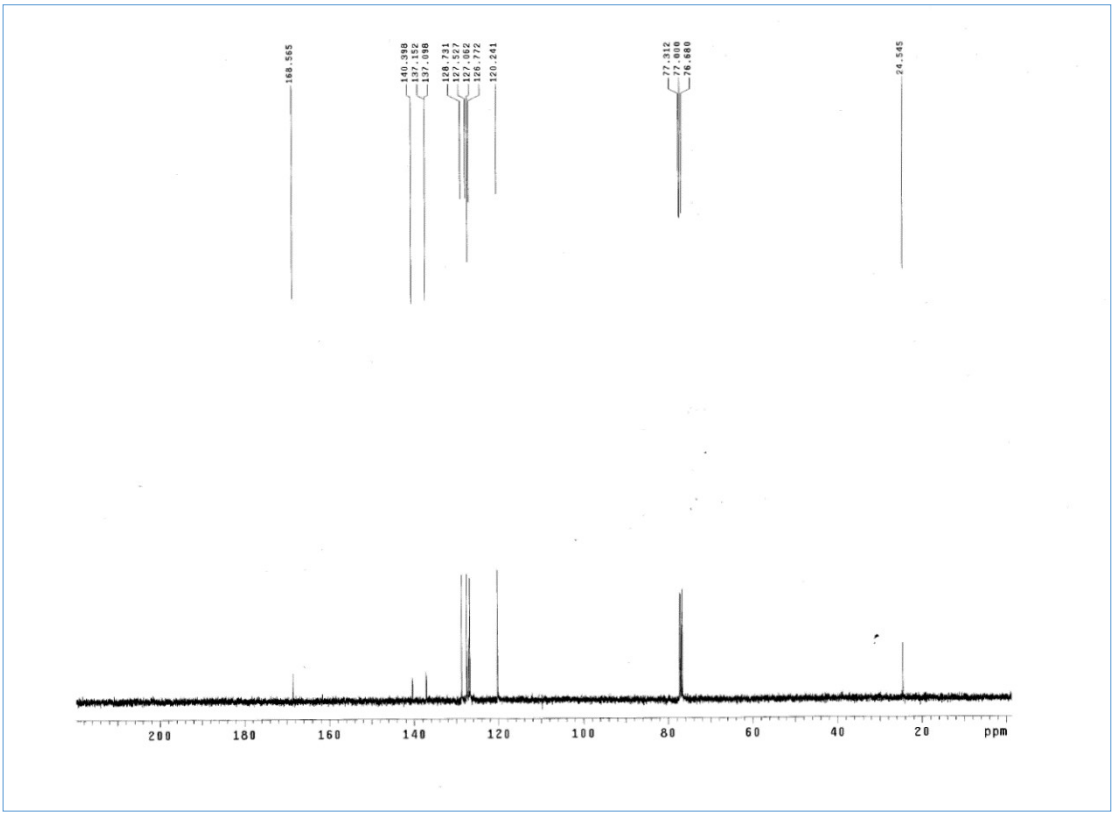
[1]H NMR spectra for 4-Cyanobiphenyl (3l)



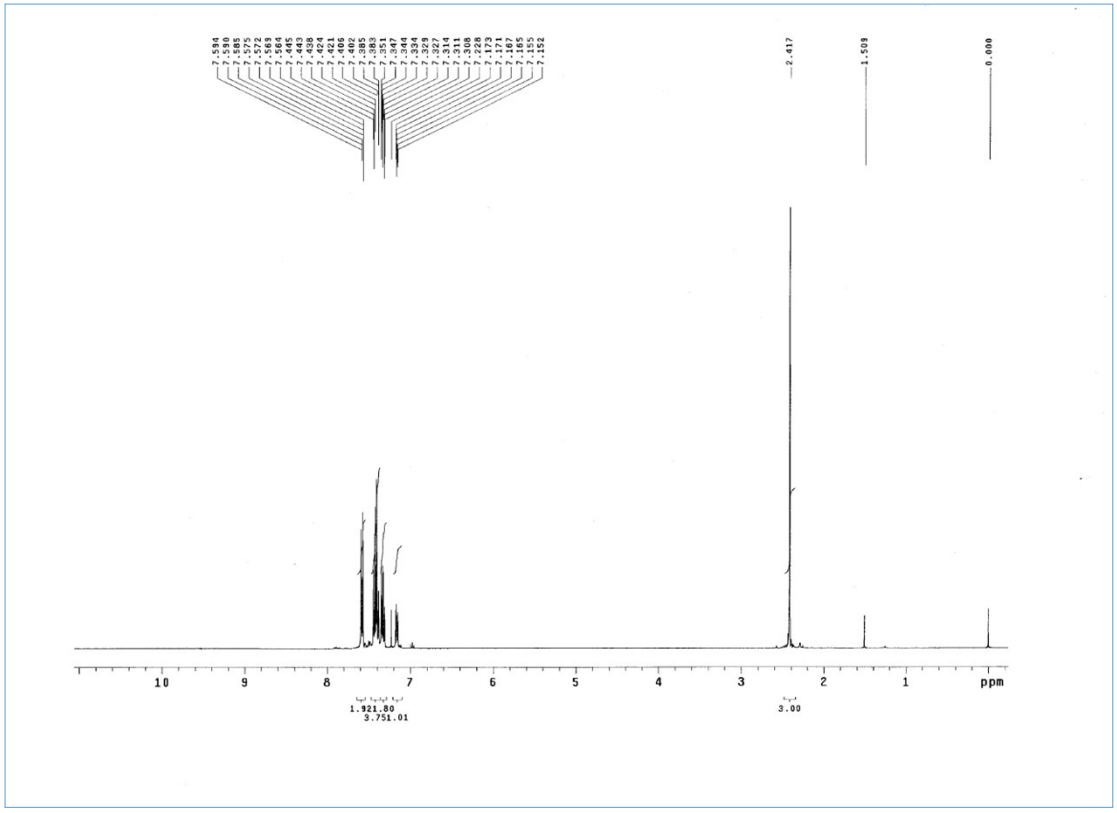
[13]C NMR spectra for 4-Cyanobiphenyl (3l)



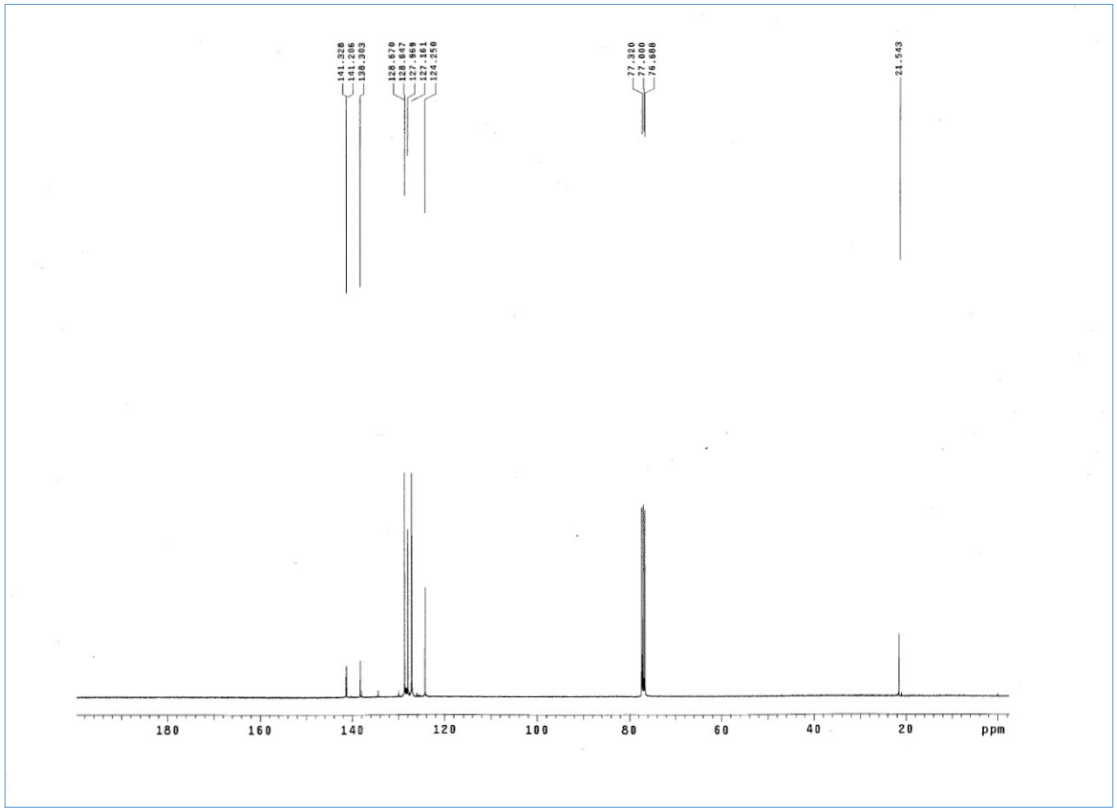
^{1}H NMR spectra for N-Acetyl-4-aminobiphenyl (3m)



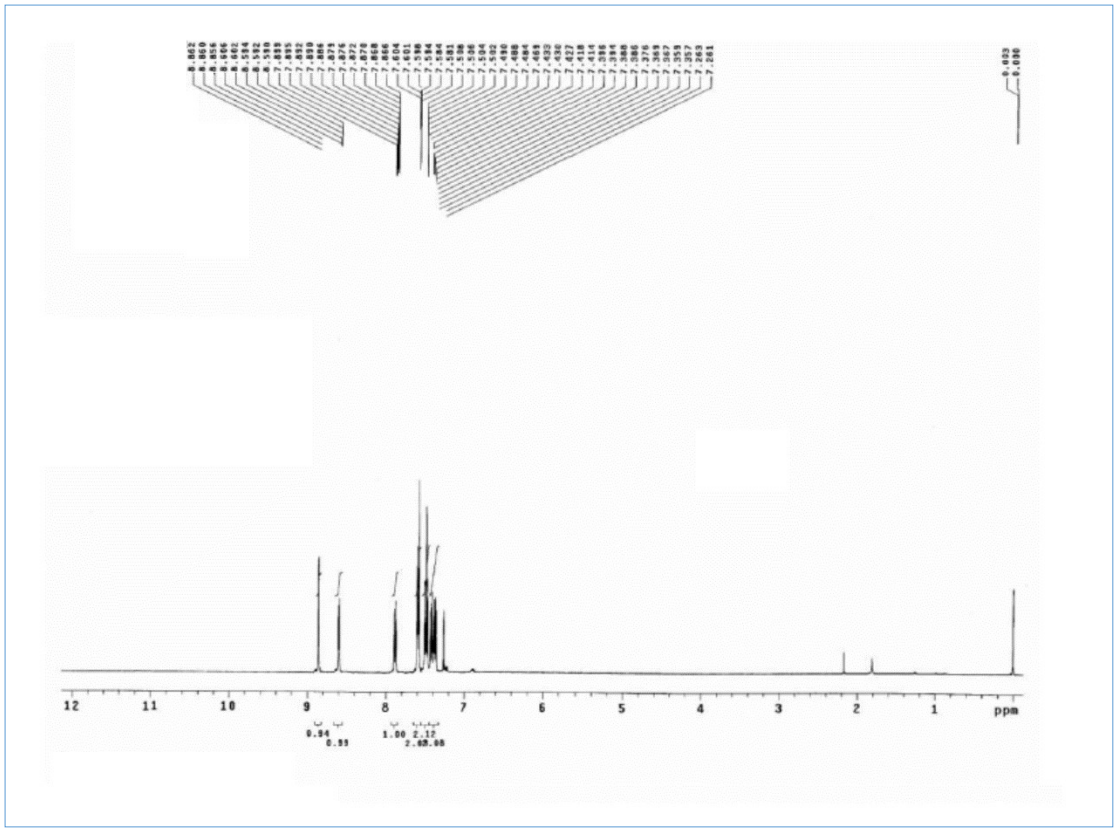
^{13}C NMR spectra for N-Acetyl-4-aminobiphenyl (3m)



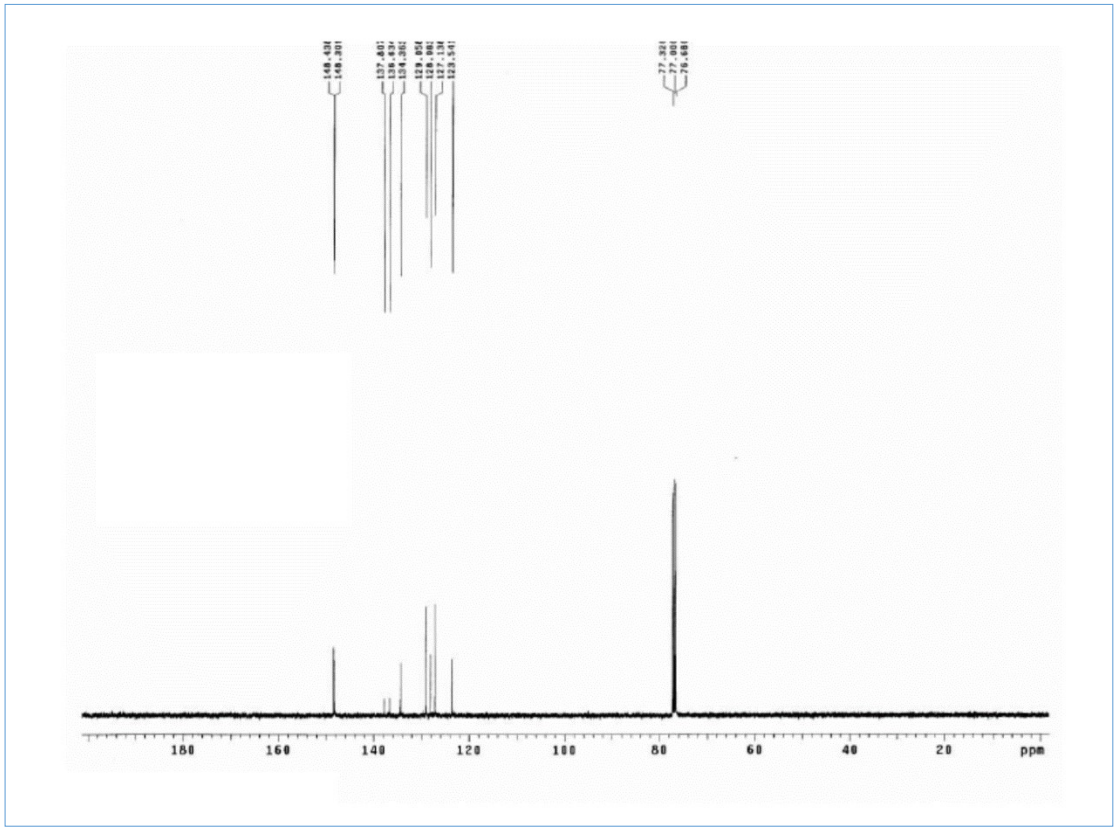
^{1}H NMR spectra for 3-Methylbiphenyl (3n)



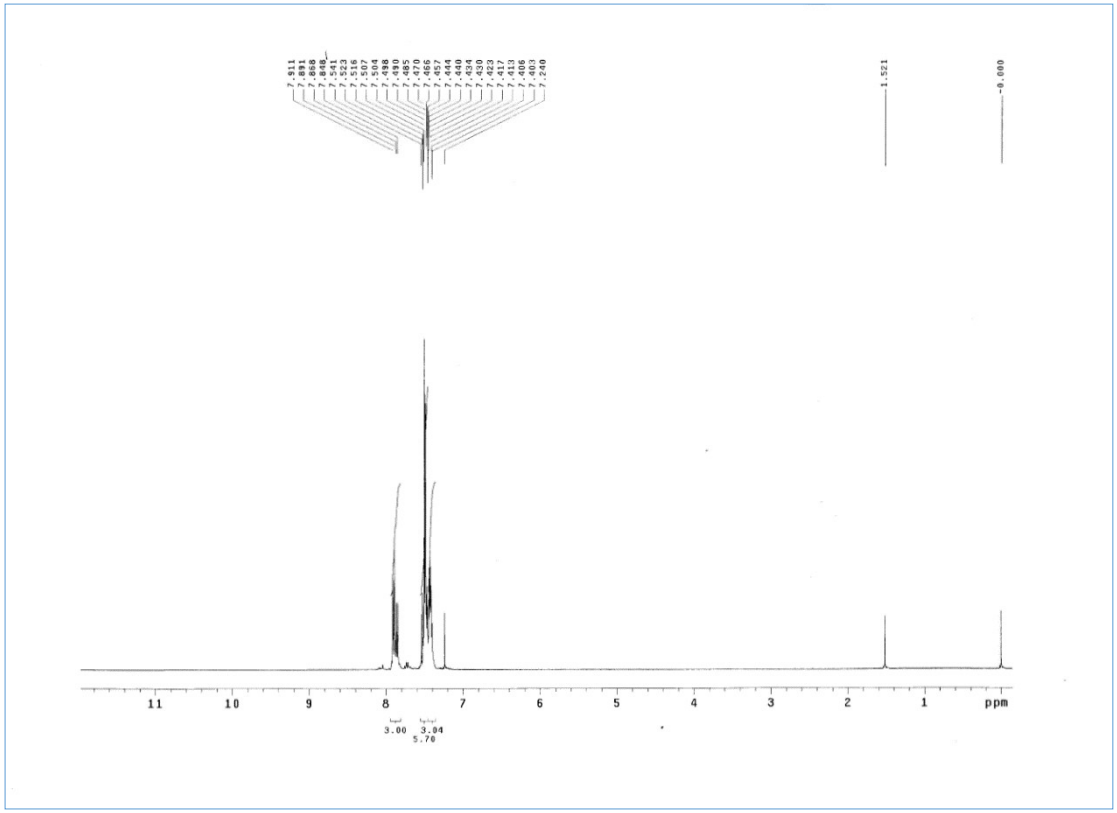
^{13}C NMR spectra for 3-Methylbiphenyl (3n)



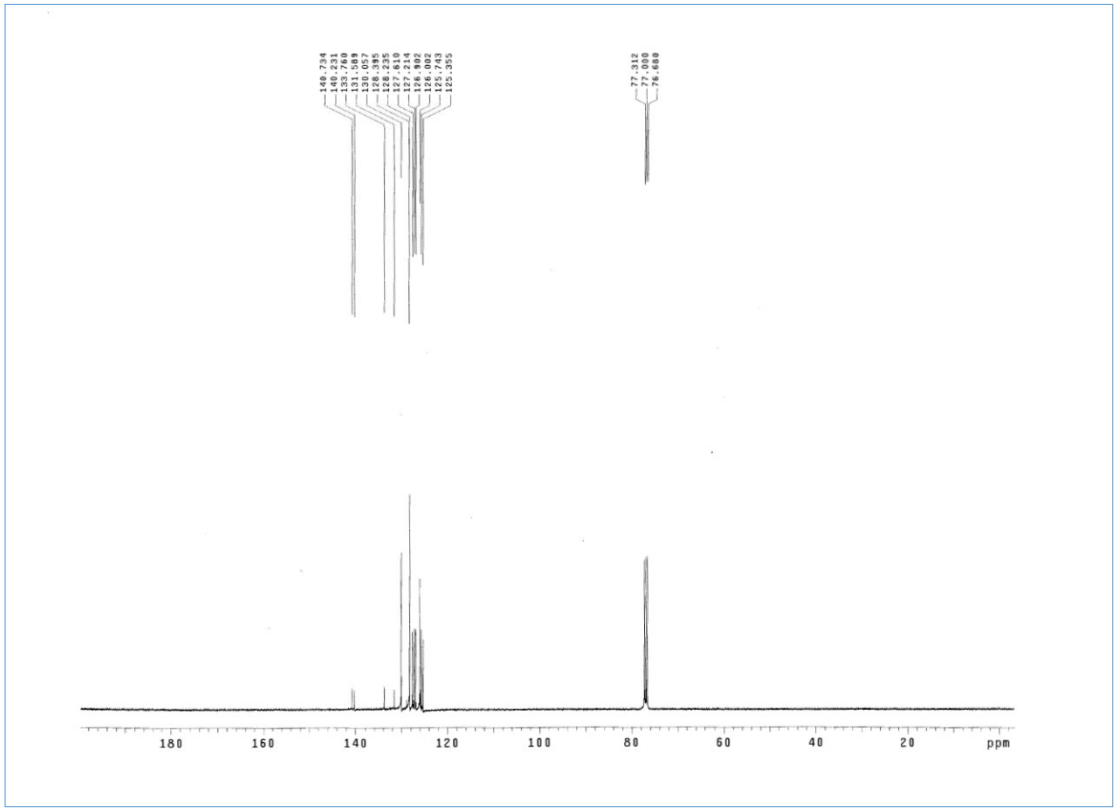
^{1}H NMR spectra for 3-Phenylpyridine (3o)



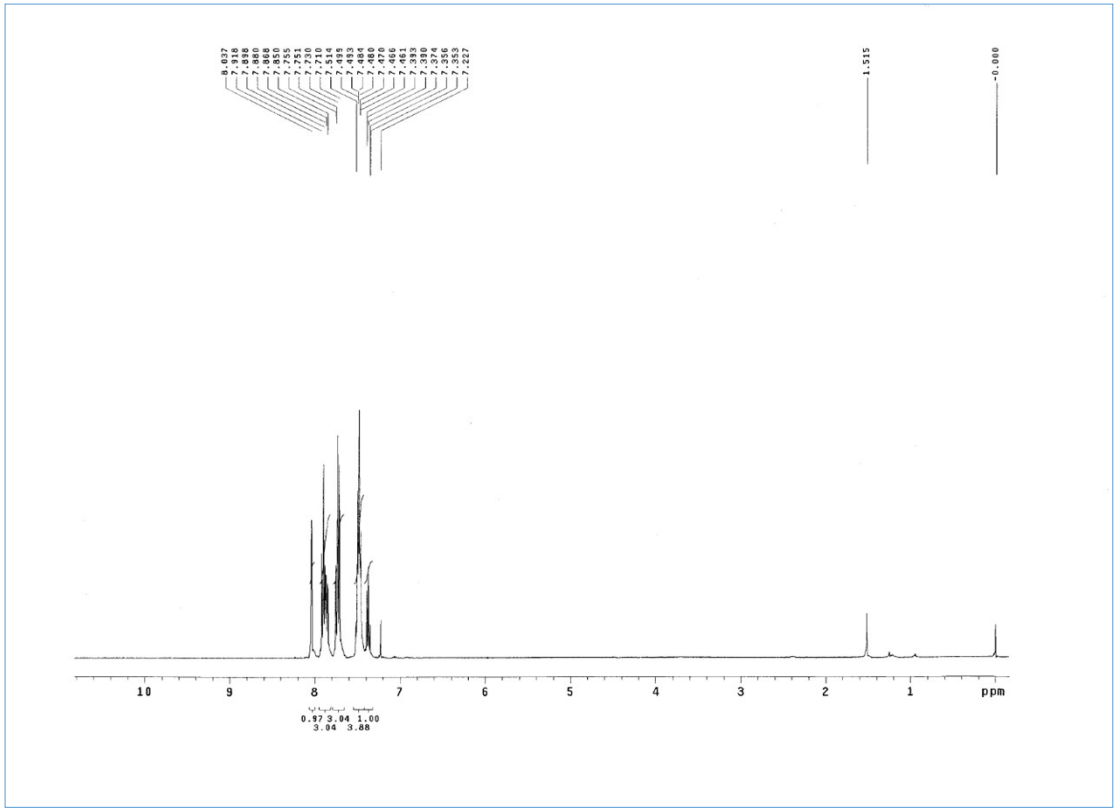
^{13}C NMR spectra for 3-Phenylpyridine (3o)



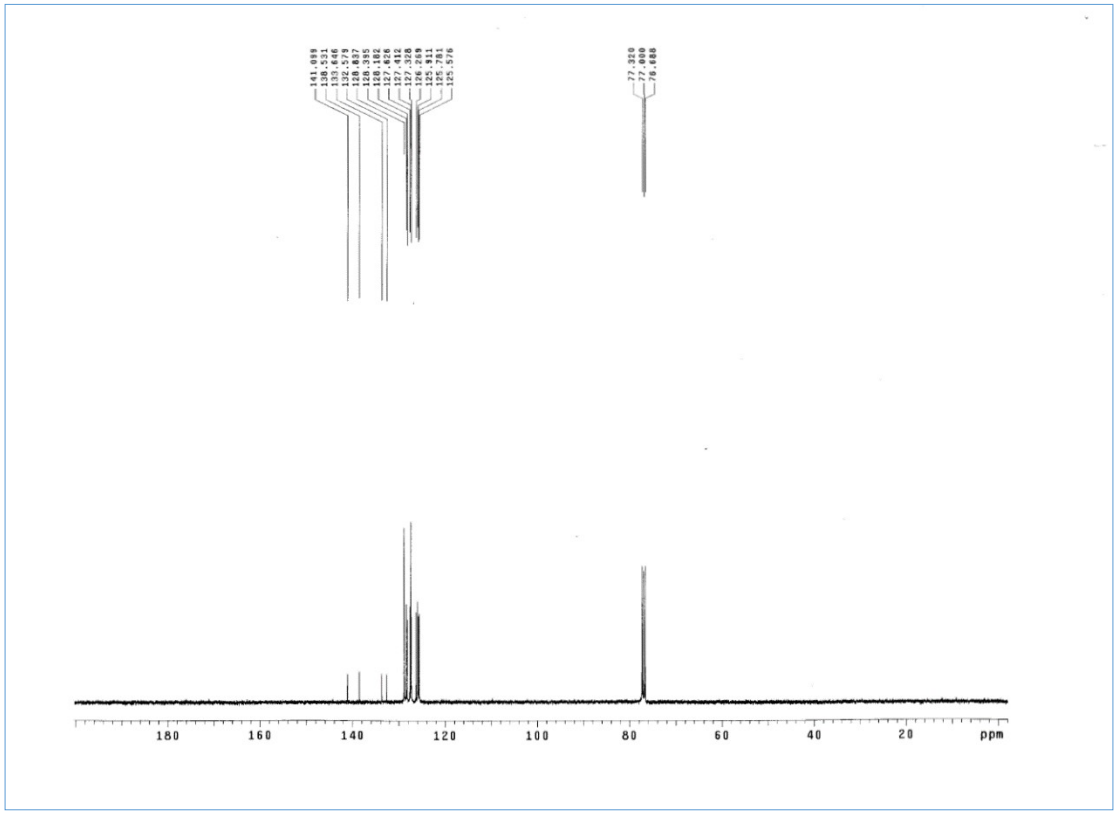
[1]H NMR spectra for 1-Phenylnaphthalene (3p)



13C NMR spectra for 1-Phenylnaphthalene (3p)



[1]H NMR spectra for 2-Phenylnaphthalene (3q)



[13]C NMR spectra for 2-Phenylnaphthalene (3q)