Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

Palladacycle containing nitrogen and selenium: highly active pre-catalyst for the Suzuki–Miyaura coupling reaction and unprecedented conversion into nano-sized $Pd_{17}Se_{15}$

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S1. General Experimental Section.

^{1}H, $^{13}C\{^{1}H\}$ and $^{77}Se\{^{1}H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13, 75.47 and 57.24 MHz respectively with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. Elemental analyses were carried out with a Perkin–Elmer 2400 Series II C, H, N analyzer. Yields refer to isolated yields of compounds which have purity ≥ 95% [established by $^{1}H-NMR$]. All reactions were carried out in glassware dried in an oven, under ambient conditions, except the synthesis of $H_2N(CH_2)_3SePh$.

X-ray diffraction data for crystals of **1** was collected on a BRUKER AXS SMART−APEX diffractometer equipped with a CCD area detector (Kα = 0.71073 Å; monochromator, graphite). Frames were collected at $T = 298$ K by ω, φ, and 2θ-rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10s per frame with SMART. The measured intensities were reduced to F^2 and corrected for absorption with SADABS. Structure solution, refinement, and data output were carried out with the SHELXTL package by direct methods. Non-hydrogen atoms were refined anisotropically.

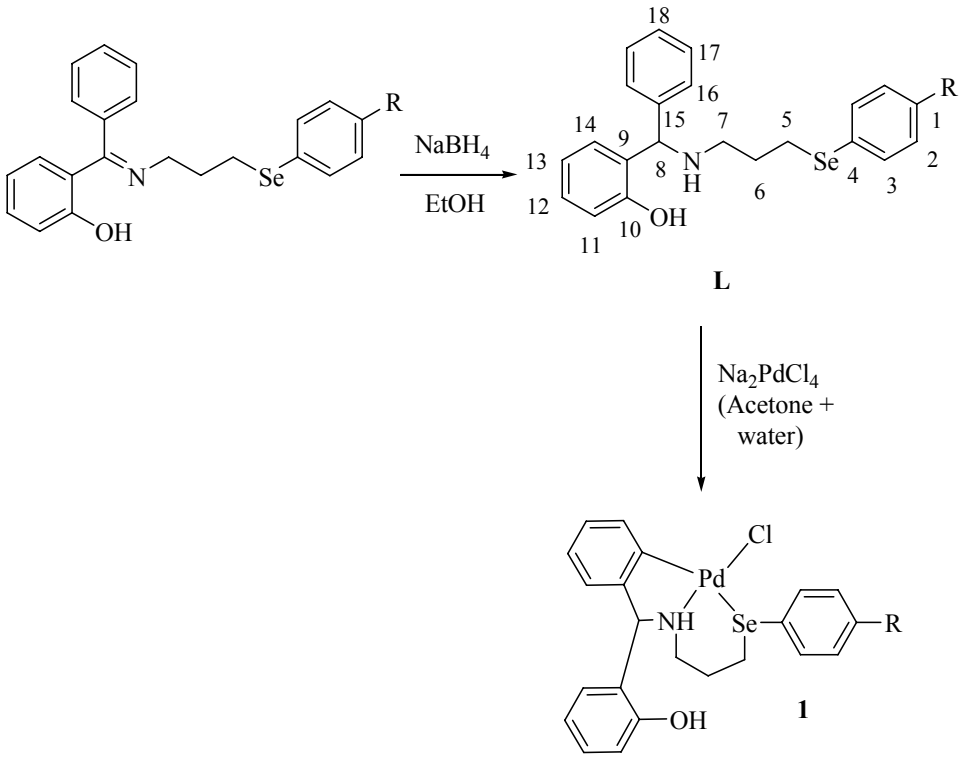
The nanostructural phase morphology of the sample was observed by using a Carl ZEISS EVO5O scanning electron microscope (SEM). Nanostructures at SEM for its elemental composition were analysed by EDX system Model QuanTax 200 which is based on the SDD technology and provides an energy resolution of 127 eV at Mn K alpha. Sample was mounted on a circular metallic sample holder with a sticky carbon tape.

Powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 Advance diffractometer with Ni-filtered Cu$K\alpha$ radiation using a scan speed of 1 s and scan step of 0.05 º. Thermogravimetric (TGA) was carried out using a Perkin–Elmer system in flowing nitrogen atmosphere, with a heating rate of 10 ºC/min. Transmission electron microscopic (TEM) studies were carried out using a JEOL JEM 200CX electron microscope operated at 200 kV. The TEM specimens were prepared as noted below. After dispersion of the powder in ethanol by ultrasonic treatment, a few drops were put onto a porous carbon film supported on a copper grid, and then dried in air. The magnetization studies were carried out at temperatures ranging from 5 to 300 K, in

applied fields of up to 10 kOe with a Quantum Design Physical Properties Measurement System.

S2. Starting Materials and Synthesis of 1.

Diphenyldiselenide, $NaBH_4$, 3-chloropropylamine hydrochloride, 2-hydroxybenzo-phenone, sodium tetrachloropalladate (Na_2PdCl_4), potassium carbonate and all starting aryl halides were procurred from Aldrich. Precursor amine $H_2N(CH_2)_3SePh$[1a] and selenated Schiff base $2{-}OH{-}C_6H_4{-}C(Ph){=}N{-}(CH_2)_3{-}Se{-}C_6H_5$[1b] were synthesized according the previously published procedure.

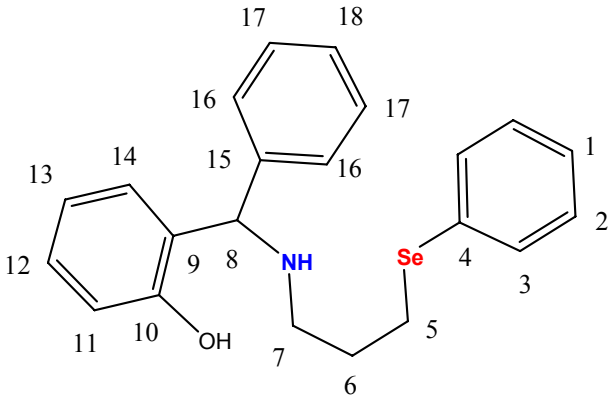


Scheme S2.1 Synthesis of Reduced Schiff Base Ligand (L) and Palladium Complex (1).

Synthesis of Reduced Schiff Base Ligand (L).

The $C_6H_5Se{-}(CH_2)_3{-}N{=}C(Ph)C_6H_4{-}2{-}OH$ (0.395 g, 1 mmol) prepared by reported method[1b] and $NaBH_4$ (0.0416 g, 1.1 mmol) were refluxed for 15 h in 100 mL dry ethanol. The solution was cooled and its solvent was removed on a rotary evaporator. The ligand

was leached into dry chloroform. The solvent was removed under vacuum. The **L** was obtained as light yellow liquid. Yield: 0.333 g (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.434 (s, 2H, NH + OH), 1.921−2.078 (m, 2H, H_6), 2.785−3.041 (m, 4H, H_5 + H_7), 4.952 (s, 1H, H_8), 6.843 (t, J = 7.5 Hz, 1H, H_{13}), 6.934 (d, J = 7.5 Hz, 1H, H_{14}), 6.986 (d, J = 8.1 Hz, 1H, H_{11}), 7.280 (t, J = 8.1 Hz, 1H, H_{12}), 7.322−7.428 (m, 8H, H_1 + H_2 + H_{16} + H_{17} + H_{18}), 7.554−7.585 (m, 2H, H_3); ^{13}C (75 MHz): δ 24.87 (C_6), 29.61 (C_5), 47.41 (C_7), 67.54 (C_8), 116.80 (C_{11}), 119.00 (C_{13}), 124.46 (C_9), 126.80 (C_1), 127.11 (C_{17}), 127.67 (C_{18}), 128.56 (C_{12}), 128.73 (C_{16}), 128.85 (C_{14}), 128.91 (C_2), 129.54 (C_4), 132.56 (C_3), 141.34 (C_{15}), 157.41 (C_{10}). ^{77}Se NMR (57 MHz): δ 293.63.



Synthesis of [PdCl(2−HO−C_6H_4−CH(Ph)−NH−$(CH_2)_3$−SeC_6H_5)] (1).

The $Na_2[PdCl_4]$ (0.294 g, 1 mmol) was dissolved in 5 mL of water. The solution of ligand **L** (0.397 g, 1 mmol) made in 10 mL of acetone was added to it with vigorous stirring. The mixture was further stirred for 2 h. The orange red solution was extracted with chloroform. The chloroform layer was washed with water, dried with anhydrous Na_2SO_4 and evaporated to dryness under vacuum to obtain **1** as an orange colored powder. Single crystal of **1** were grown from chloroform (containing few drops of hexane per 5 ml). Yield (0.381 g) 71%; m.p. 159 °C (d). Anal. Found: C, 44.16; H, 4.19; N, 2.29%. Calc. for $C_{22}H_{25}BClNO_4PdSe$: C, 44.11; H, 4.21; N, 2.34%. NMR: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.728 (m, 1H), 2.199−2.276 (m, 1H), 2.679–3.021 (m, 4H), 3.316 (s, 1H, CH), 5.365 (bs, 1H), 6.089 (d, J = 6.9 Hz, 1H), 6.783−6.922 (m, 5H), 7.189 (t, J = 6.9 Hz, 1H), 7.271 (d, J = 6.6 Hz, 1H), 7.436−7.437 (m, 3H), 7.605 (d, J = 7.5 Hz, 1H), 8.053−8.150

(m, 2H). ^{13}C (75 MHz): δ 17.69 (C_6), 31.85 (C_5), 53.24 (C_7), 66.56 (C_8), 113.80 (C_{11}), 118.83 (C_{13}), 124.26 (C_9), 127.29, 128.21, 128.37, 128.44, 128.56, 129.56, 129.68, 129.93, 129.99, 132.98, 133.53, 139.36, 161.39. ^{77}Se NMR (57 MHz, $CDCl_3$): δ 266.07.

S3. General Procedure for the Suzuki reaction of Aryl / Heteroaryl halides with Phenylboronic acid.

An oven-dried flask was charged with arylhalide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mol) and DMF/H_2O (2.0 ml / 1.0 ml). A solution of catalyst **1** in DMF (10^{-4} M, 100 μL, 10^{-5} mmol, 10^{-3} mol % / 10^{-3} M, 100 μL, 10^{-4} mmol, 10^{-2} mol % / 10^{-3} M, 1000 μL, 10^{-3} mmol, 10^{-1} mol %) was then added via syringe. The flask was placed on an oil bath at 110 °C under aerobic conditions and the reaction mixture stirred until maximum conversion of aryl halide to product occurred. The mixture was extracted with diethylether. The extract was washed with water and dried over anhydrous Na_2SO_4. The solvent of the extract was removed with rotary evaporator and the resulting residue purified by a column chromatography on silica gel.

Table S3.1 Suzuki Coupling Reactions Catalyzed by 1.[a]

Entry No.	Aryl / Heteroaryl Halide	T (h)	Yield[b] (%)	TON
1.[c]	1-Chloro-4-nitrobenzene	17	79	790
2.	1-Bromo-4-nitrobenzene	7	94	940
3.	4-Chlorobenzonitrile	16	94	940
4.	4-Bromobenzonitrile	4	95	950
5.	4-Chlorobenzaldehyde	17	87	870
6.	4-Bromobenzaldehyde	5	91	910
7.	4-Chlorobenzophenone	20	79	790
8.	4-Bromobenzophenone	5	87	870
9.	4-Chlorobenzoic acid	22	92	920
10.	4-Bromobenzoic acid	4	94	940
11.	3-Chlorobenzoic acid	20	90	900
12.	3-Bromobenzoic acid	5	92	920
13.	Chlorobenzene	17	93	930
14.	Bromobenzene	10	94	940
15.	4-Chlorotoluene	19	91	910
16.	4-Bromotoluene	5	95	950
17.	4-Chloroanisol	18	86	860
18.	4-Bromoanisol	19	93	930
23.	2-Chloropyridine	20	82	820
24.	2-Bromopyridine	13	91	910
25.	3-Chloropyridine	17	87	870
26.	3-Bromopyridine	9	96	960
27.	4-Chloropyridine	15	91	910
28.	4-Bromopyridine	5	95	950
29.	2-Bromothiophene[d]	12	94	940
30.	3-Bromoquinoline	15	95	950
31.	5-Bromopyrimidine	13	94	940

[a]Reaction conditions: 1.0 equiv of arylhalide / heteroarylhalide, 1.3 equiv of phenylboronic acid, and 2 equiv of base (K_2CO_3), 0.1 mol % of **1** was used, solvent aqueous DMF and bath temperature 110 °C. [b]In parentheses is shown the isolated yield after column chromatography. [c]The solvent used was MeOH. [d]The product was a mixture of cross-coupled product and biphenyl.

S4. Decomposition of Palladacycle 1 under Stoichiometric Conditions: Insitu generation of $Pd_{17}Se_{15}$ Nano-Particle.

A mixture of palladacycle **1** (0.50 mmol), phenylboronic acid (1 mmol), 4-chloronitrobenzene (1 mmol) and K_2CO_3 (2 mmol) in DMF (4 mL) and water (4mL) was heated at 100 ºC for 1.5 h, then cooled to room temperature. The solvent was decanted and black residue was washed with 4 mL of acetone.

The black residue thus formed was separated and subjected to appropriate studies. Powder X-ray diffraction results suggest the amorphous nature**.** The HR–TEM indicates black powder to be highly uniform and monodisperse spherical shaped nano-particles. The average size of these particles was found to be ~ 8 nm (Fig 1). The SEM–EDX studies have suggested that the composition of Pd-Se nano-particles (wt. %) Pd = 57.42%; and Se = 42.58% (Fig 2 and Fig 3) which is very close to the initial loaded stoichiometry. The amorphous powders were annealed in argon atmosphere at 450 ^{o}C for 5 h which led to the formation of crystalline $Pd_{17}Se_{15}$ nano-particles. The powder X-ray diffraction pattern of these nano-partiles (Fig. 5) was indexed on the basis of a primitive cubic unit cell[1c] (JCPDS # 73-1424) with the refined lattice parameter = 10.60Å and d values (*hkl*): 3.32 (310), 3.17 (311), 2.92 (320), 2.81 (321), 2.56 (410), 2.49 (411), 2.42 (311), 2.36 (420), 2.30 (430), 2.11 (431), 2.06 (511), 2.03 (440), 1.86 (433), 1.76 (600), 1.71 (532), 1.65 (540), 1.63 (541). On the basis of HR–TEM images of crystalline Pd-Se nano-particles, the agglomerated particles of an average size of ~ 20 nm appear to be assembled from spherical nano-particles of ~ 8 nm. TEM–EDX (Fig. 6) analysis supports the formation of Pd-Se nano-particles with the composition (wt %) Pd = 57.38% and Se = 42.62% which is similar to the mentioned earlier on the basis of SEM–EDX.

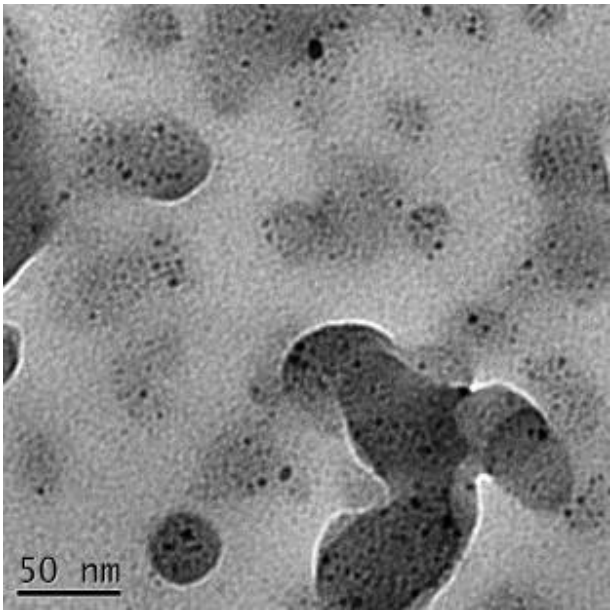


Fig. S4.1 HRTEM image of $Pd_{17}Se_{15}$ obtained from **1.**

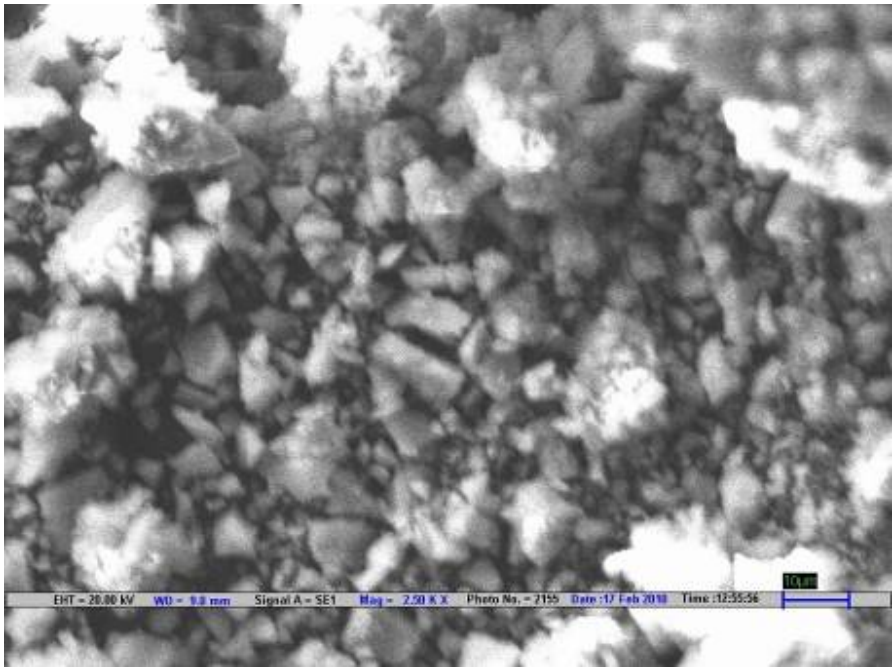


Fig. S4.2 SEM picture of $Pd_{17}Se_{15}$ obtained from **1.**

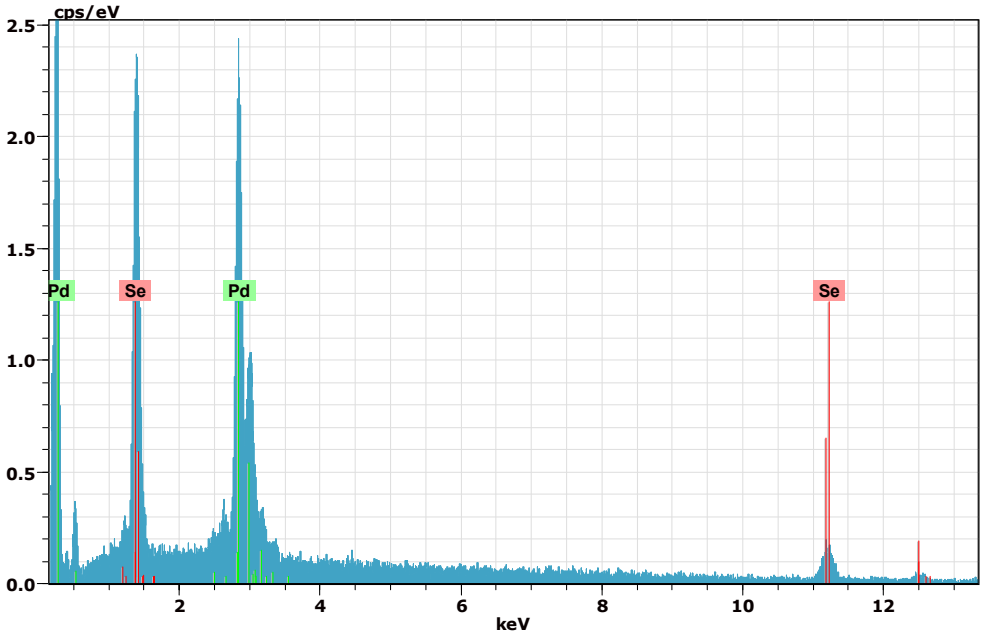


Fig. S4.3 SEM-EDX of $Pd_{17}Se_{15}$ nanocrystals obtained from **1.**

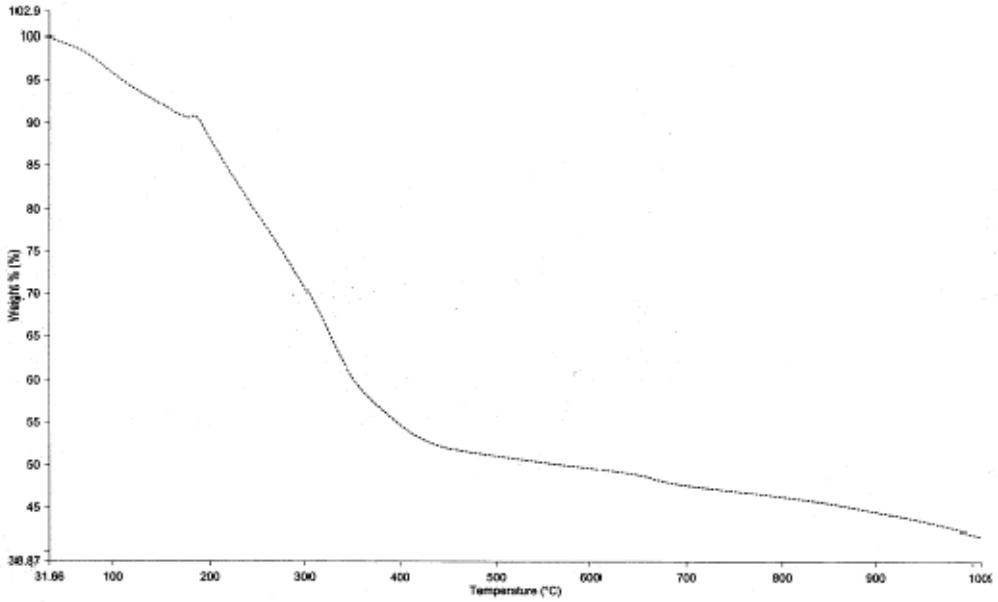


Fig. S4.4 TGA traces for amorphous black residue (initial weight: 7.773 mg).

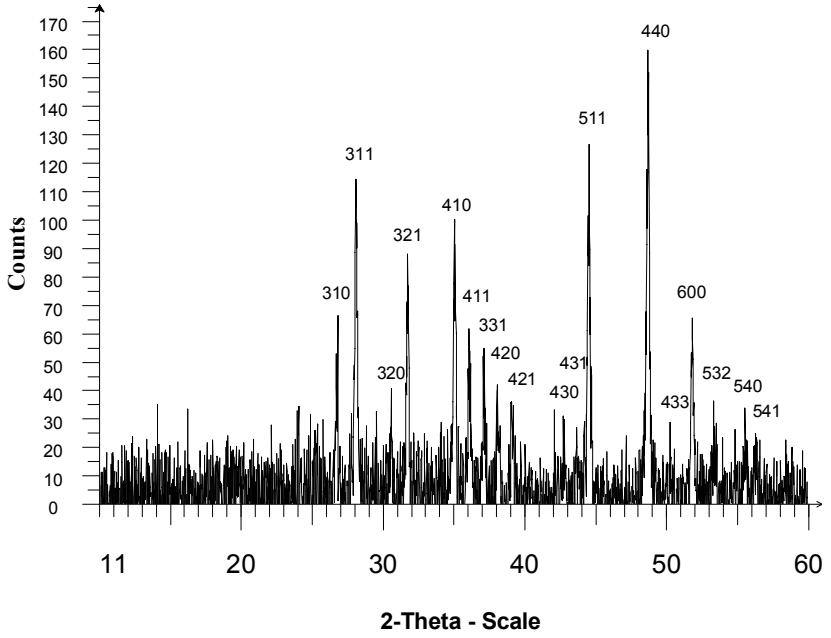


Fig. S4.5 XRD diffraction pattern for the product obtained from **1.** The pattern has been indexed and peaks with the following observed d (Å) values (hkl): 3.32 (310), 3.17 (311), 2.92 (320), 2.81 (321), 2.56 (410), 2.49 (411), 2.42 (311), 2.36 (420), 2.30 (430), 2.11 (431), 2.06 (511), 2.03 (440), 1.86 (433), 1.76 (600), 1.71 (532), 1.65 (540), 1.63 (541).

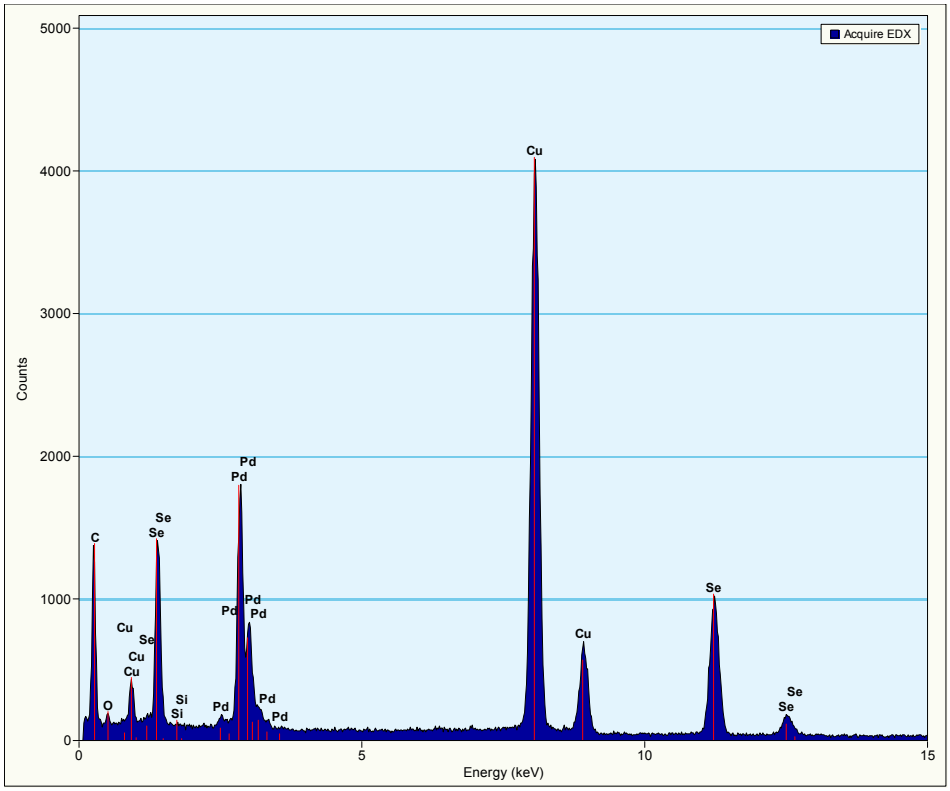


Fig. S4.6 Energy-dispersive X-ray spectrum (EDS) of $Pd_{17}Se_{15}$ nanocrystals after annealed at 450 ºC.

S4.1 Control Experiments

The comparable % conversions noticed when progress of reactions catalyzed with **1** / **$Pd_{17}Se_{15}$** with time was monitored by ^{1}H NMR (Fig S4.7 and Table S4.1)

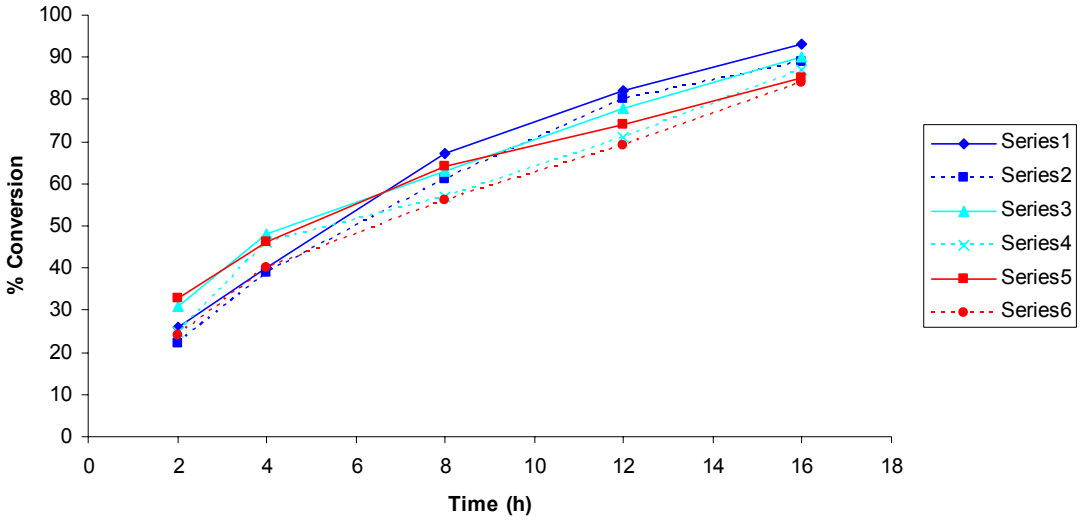


Fig. S4.7 Plot (Time versus % Conversion) in Time Controlled Experiments

Series 1: **1**, 4−Bromoanisole;

Series 2: **$Pd_{17}Se_{15}$**, 4−Bromoanisole;

Series 3: **1**, Bromobenzene;

Series 4: **$Pd_{17}Se_{15}$**, Bromobenzene;

Series 5: **1**, 4−Bromonitrobenzene;

Series 6: **$Pd_{17}Se_{15}$**, 4−Bromonitrobenzene;

Table S4.1 Conversions (%) at different times during the progress of Suzuki Coupling Reactions Catalyzed by 1 / $Pd_{17}Se_{15}$.[a]

Reactant	Time (h)	% Conversion[b]	
		Palladacycle **1**	$Pd_{17}Se_{15}$
4-Bromoanisole	2	26	22
	4	40	39
	8	67	61
	12	82	80
	16	93	89
Bromobenzene	2	31	25
	4	48	46
	8	63	57
	12	78	71
	16	90	87
4-Bromonitrobenzene	2	33	24
	4	46	40
	8	64	56
	12	74	69
	16	85	84

[a]Reaction conditions: 1.0 equiv of arylhalide, 1.3 equiv of phenylboronic acid, and 2 equiv of base (K_2CO_3), 0.01 mol % of **1** or **$Pd_{17}Se_{15}$** (freshly isolated)‡ was used, solvent aqueous DMF and bath temperature 110 °C. [b]NMR % Conversion.

‡ Generally isolated **$Pd_{17}Se_{15}$** nano particles show somewhat lower activity than those generated insitu, as expected because of aggregation of nano particles during separation and isolation work up.

S5. Crystal Structure and Crystal Data for Palladacycle 1.

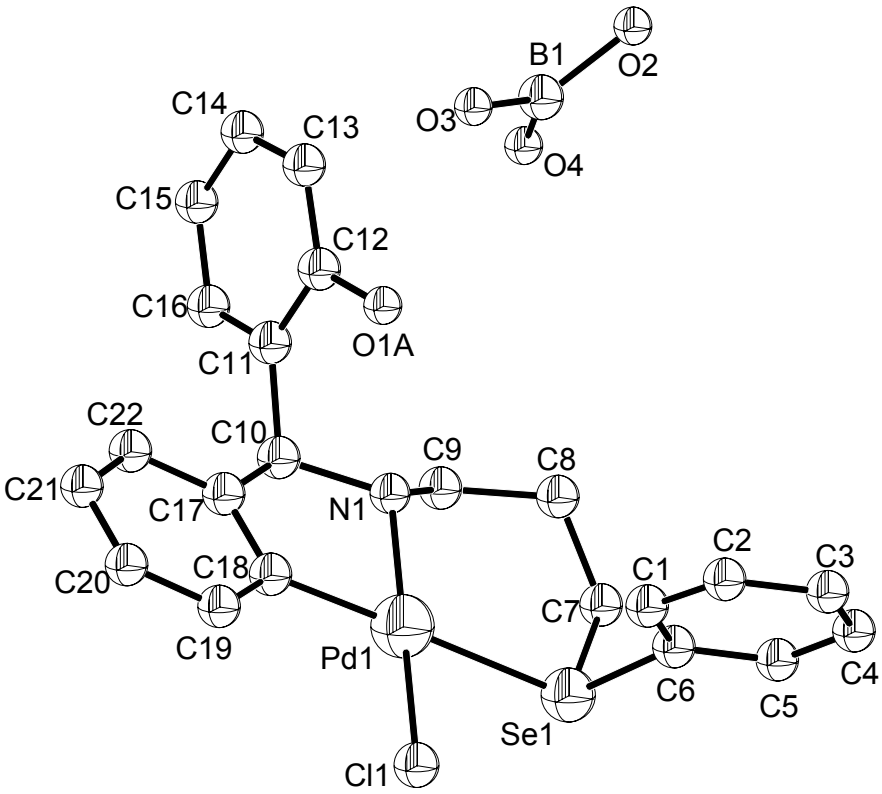


Fig. S5.1 ORTEP diagram of **1** with H_3BO_3 in crystal lattice.

Table S5.1 Crystal Data and Structure Refinement for Palladacycle 1.

Empirical formula	$C_{22}H_{22}ClNOPdSe.CHCl_3$	
Formula weight	656.58	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, *P−1*	
Unit cell dimensions	*a* = 8.713(5) Å	alpha (*α*) = 67.335(9)°
	b = 12.599(7) Å	beta (*β*) = 86.782(8)°
	c = 12.850(7) Å	gamma (*γ*) = 70.283(9)°.
V	1221.0(11) $Å^3$	
Z, Calculated density	2, 1.786 Mg/m^{-3}	
Absorption coefficient	2.705 mm^{-1}	
F(000)	648	
Crystal color and shape	Orange rod	
Crystal size	0.463 × 0.215 × 0.167 mm	
Theta range for data collection	1.86 to 25.00 deg.	
Limiting indices	$-10\le h\le 10$, $-14\le k\le 14$, $-15\le l\le 15$	
Reflections collected/unique	11512/3420 [*R(int)* = 0.0516]	
Completeness to $\theta = 25.00$	99.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.176 and 0.081	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4248 / 0 / 287	
Goodness-of-fit on F^2	1.123	
Final R indices [$I>2\sigma(I)$]	*R1* = 0.0600, *wR2* = 0.1677	
R indices (all data)	*R1* = 0.0758, *wR2* = 0.1760	
Largest diff. peak and hole	1.455 and −0.920 $e.Å^{-3}$	
CCDC#	773377	

Table S5.2 Selected Bond Lengths and Bond Angles of Palladacycle 1.

Bond Distance (Å)		Bond Angle (°)	
Pd(1)—C(15)	1.968(7)	C(15)—Pd(1)—Se(1)	178.2(2)
Pd(1)—N(1)	2.055(6)	C(15)—Pd(1)—N(1)	82.1(3)
Pd(1)—Cl(1)	2.325(2)	C(15)—Pd(1)—Cl(1)	94.9(2)
Pd(1)—Se(1)	2.5290(13)	N(1)—Pd(1)—Cl(1)	174.14(18)
Se(1)—C(4)	1.928(7)	N(1)—Pd(1)—Se(1)	97.59(18)
Se(1)—C(5)	1.953(9)	Cl(1)—Pd(1)—Se(1)	85.60(8)
N(1)—C(6)	1.484(9)	C(4)—Se(1)—C(5)	97.8(4)
N(1)—C(7)	1.512(9)	C(4)— Se(1)—Pd(1)	103.1(2)
O(1)—C9	1.362(10)	C(5)—Se(1)—Pd(1)	107.1(3)
C(7)—C(14)	1.513(11)	C(6)—N(1)—C(7)	110.4(6)
C(7)—C(8)	1.515(10)	C(6)—N(1)—Pd(1)	120.1(5)
C(6)—C(20)	1.510(11)	C(7)—N(1)—Pd(1)	111.3(4)
C(5)—C(20)	1.510(12)	N(1)—C(7)—C(14)	107.5(6)
C(15)—C(14)	1.406(11)	N(1)—C(7)—C(8)	112.8(6)
C(15)—C16	1.412(11)	C(14)—C(7)—C(8)	113.5(6)
		O(1)—C(9)—C(10)	121.7(7)
		O(1)—C(9)—C(8)	117.1(7)
		N(1)—C(6)—C(20)	113.8(7)
		C(20)—C(5)—Se(1)	113.7(6)
		C(5)—C(20)—C(6)	116.3(8)
		C(14)—C(15)—C(16)	115.7(7)
		C(14)—C(15)—Pd(1)	115.4(6)
		C(16)—C(15)— Pd(1)	128.9(6)

S6. NMR Data of Coupled Products of Suzuki reaction.

4-Nitrobiphenyl.[2] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.406−7.515 (m, 3H), 7.609 (d, J = 8.4 Hz, 2H), 7.709 (d, J = 9.0 Hz, 2H), 8.266 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz): δ 123.99, 127.03, 127.27, 127.67, 128.84, 129.06, 138.61, 146.95, 147.50.

4-Phenylbenzonitrile.[2] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.339−7.447 (m, 3H, aromatic), 7.490−7.521 (m, 2H, aromatic), 7.539−7.608 (m, 4H, aromatic). ^{13}C NMR (75 MHz): δ 110.37, 118.57, 126.78, 127.22, 128.32, 128.74, 132.15, 138.57, 145.05.

4−Phenylbenzaldehyde.[3] Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.391−7.508 (m, 3H), 7.628−7.655 (m, 2H), 7.755 (d, J = 8.4 Hz, 2H), 7.955 (d, J = 8.4 Hz, 2H), 10.058 (s, 1H); ^{13}C NMR (75 MHz): δ 127.35, 127.67, 128.45, 128.99, 130.25, 135.19, 139.70, 147.19, 191.90.

4−Acetylbiphenyl.[2] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.617 (s, 3H), 7.385−7.485 (m, 3H), 7.601−7.680 (m, 4H), 8.016 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz): δ 26.58, 127.13, 127.19, 128.16, 128.84, 128.88, 135.77, 139.77, 145.67, 197.66.

Biphenyl-4-carboxylic acid.[4] White solid. ^{1}H NMR (300 MHz, DMSO): δ 7.393−7.523 (m, 3H), 7.727 (d, J = 6.9 Hz, 2H), 7.793 (d, J = 8.4 Hz, 2H), 8.026 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz): δ 126.86, 127.00, 128.34, 129.13, 129.66, 130.02, 139.07, 144.36, 167.21.

Biphenyl-3-carboxylic acid.[3] White solid. ^{1}H NMR (300 MHz, DMSO): δ 7.407−7.456 (m, 1H), 7.525 (t, J = 7.8 Hz, 6.9 Hz, 2H), 7.630 (t, J = 7.8 Hz, 2H), 7.722 (d, J = 7.2 Hz, 2H), 7.961 (t, J = 8.7 Hz, 8.1 Hz, 2H), 8.209 (s, 1H). ^{13}C NMR (75 MHz): δ 126.81, 127.33, 127.92, 128.27, 129.12, 129.36, 131.13, 131.52, 139.29, 140.55, 167.26.

Biphenyl.[2] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.326 (t, J = 7.5 Hz, 2H), 7.423 (t, J = 7.5 Hz, 4H), 7.581 (d, J = 6.9 Hz, 4H); ^{13}C NMR (75 MHz): δ 127.14, 127.23, 128.73, 141.20, ppm.

4-Methylbiphenyl.[2] Colorless solid. ^{1}HNMR (300 MHz, $CDCl_3$): δ 2.375 (s, 3H), 7.228 (d, J = 7.8 Hz, 2H), 7.274−7.323 (m, 1H), 7.378−7.427 (m, 2H), 7.479 (d, J = 8.1 Hz, 2H), 7.552−7.580 (m, 2H). ^{13}C NMR (75 MHz) δ 21.07, 126.94, 126.96, 128.68, 129.45, 136.97, 138.33, 141.13.

4-Methoxybiphenyl.[2] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.818 (s, 3H), 6.959 (d, J = 8.4 Hz, 2H), 7.282−7.307 (m, 1H), 7.396 (t, J = 7.2 Hz, 2H), 7.500−7.550 (m, 4H). ^{13}C NMR (75 MHz): δ 55.28, 114.17, 126.62, 126.69, 128.11, 128.69, 133.73, 140.78, 159.11.

4−Phenylaniline.[2] Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.722 (br s, 2H), 6.752 (d, J = 8.4 Hz, 2H), 7.246−7.286 (m, 1H), 7.364−7.428 (m, 4H), 7.533 (d, J = 9.0 Hz, 2H). ^{13}C NMR (75 MHz): δ 114.93, 125.76, 125.81, 127.42, 128.28, 130.50, 140.70, 145.90.

4-Hydroxybiphenyl.[4] Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.915 (s, 1H, OH), 6.998 (d, J = 7.5 Hz, 2H), 7.300−7.548 (m, 7H). ^{13}C NMR (75 MHz): δ (ppm) = 115.64, 126.71, 128.38, 128.71, 134.05, 140.74, 155.02.

2−Phenylpyridine.[5] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.199–7.254 (m, 1H), 7.452–7.527 (m, 3H), 7.706–7.770 (m, 2H), 7.976 (d, J = 7.5 Hz, 2H), 8.686 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz): δ 120.54, 122.05, 126.88, 128.70, 128.91, 136.71, 139.36, 149.63, 157.44.

3−Phenylpyridine.[5] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.220− 7.431 (m, 4H), 7.491−7.556 (m, 2H), 7.772 (d, J = 7.8 Hz, 1H), 8.543 (d, J = 4.8 Hz, 1H), 8.822 (d,

J = 1.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.22, 126.71, 127.74, 128.70, 133.99, 136.22, 137.28, 147.77, 147.93.

4−Phenylpyridine.[5] Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.398−7.502 (m, 5H), 7.617 (d, *J* = 8.1 Hz, 2 H), 8.653 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (75 MHz): δ 121.60, 126.88, 129.03 (for three carbons), 137.88, 148.44, 149.85.

2−Phenylthiophene.[6] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.196−7.284 (m, 1H), 7.304−7.466 (m, 5H), 7.584−7.631 (m, 2H); ^{13}C NMR (75 MHz): δ 123.05, 124.78, 125.93, 127.44, 127.98, 128.86, 134.37, 144.40.

3−Phenylthiophene.[7] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.291–7.546 (m, 6H), 7.590−7.615 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 120.26, 126.18, 126.33, 126.44 (2C), 127.12, 128.79 (2C), 135.87, 142.41.

3−Phenylquinoline.[8] Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.496−7.596 (m, 4H), 7.695–7.726 (m, 3H), 7.878 (d, *J* = 8.1 Hz, 1H), 8.139 (d, *J* = 8.1 Hz, 1H), 8.300 (s, 1H), 9.177 (s, 1H); ^{13}C NMR (75 MHz): δ 126.29, 126.57, 127.25, 127.37, 127.38, 128.25, 128.44, 128.67, 132.44, 132.92, 136.86, 146.43, 148.94.

5−Phenylpyrimidine.[3] Light tan solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.441−7.602 (m, 5H), 8.959 (s, 2H), 9.211 (s, 1H). ^{13}C NMR (75 MHz): δ 127.00, 127.14, 128.74, 129.03, 129.44, 154.92, 157.48.

4−Nitro-*N*,*N*-dimethylaniline.[9] Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.117 (s, 6H), 6.609 (d, *J* = 9.3 Hz, 2H), 8.130 (d, *J* = 9.3 Hz, 2H). ^{13}C NMR (75 MHz): δ 40.27, 110.20, 126.12, 137.53, 155.12.

4−(*N*,*N*-Dimethylamino)benzaldehyde.[10] Dark wine red liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.044 (s, 6H), 6.668 (d, *J* = 9.0 Hz, 2H), 7.713 (d, *J* = 8.7 Hz, 2H), 9.712 (s, 1H, CHO). ^{13}C NMR (75 MHz): δ 39.83, 110.79, 126.20, 131.80, 154.16, 190.14.

S7. References

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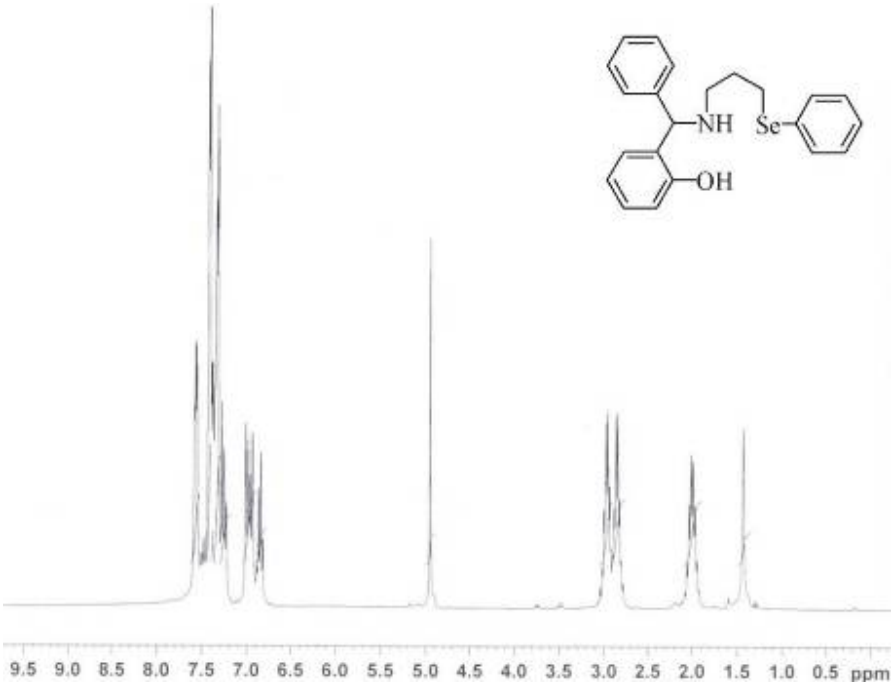
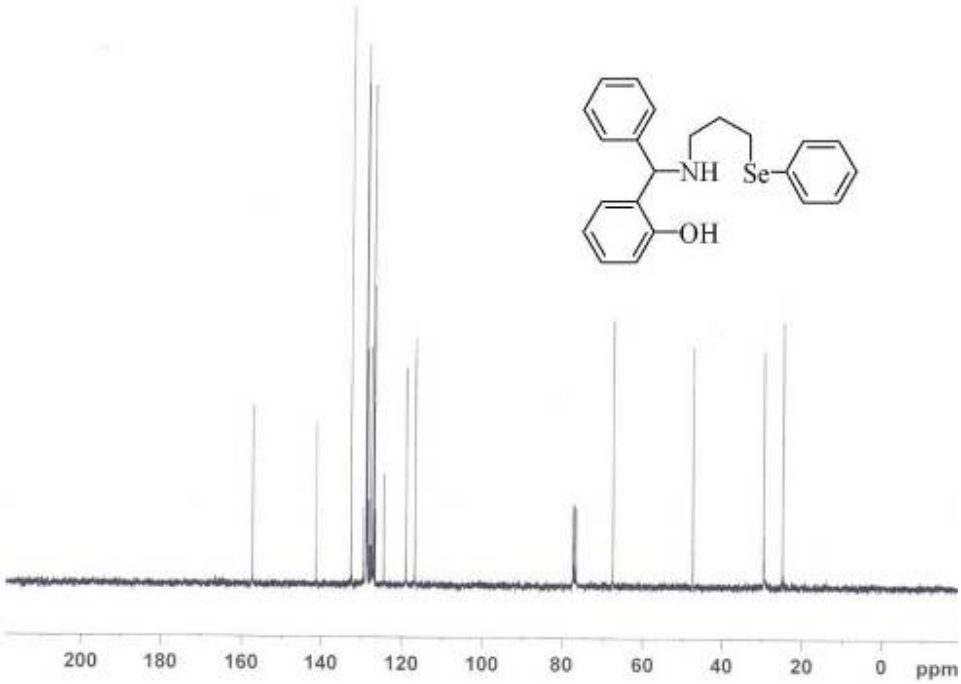
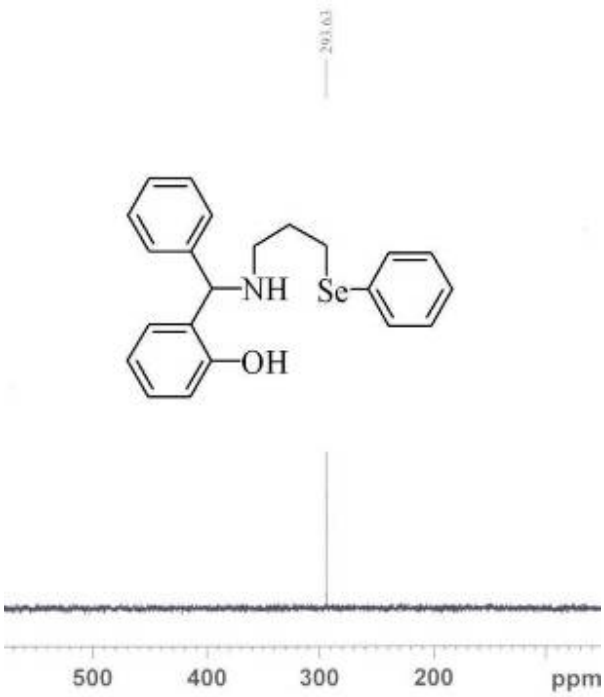
S8.1 ^{1}H, $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and DEPT 135 NMR Spectra of L and 1,



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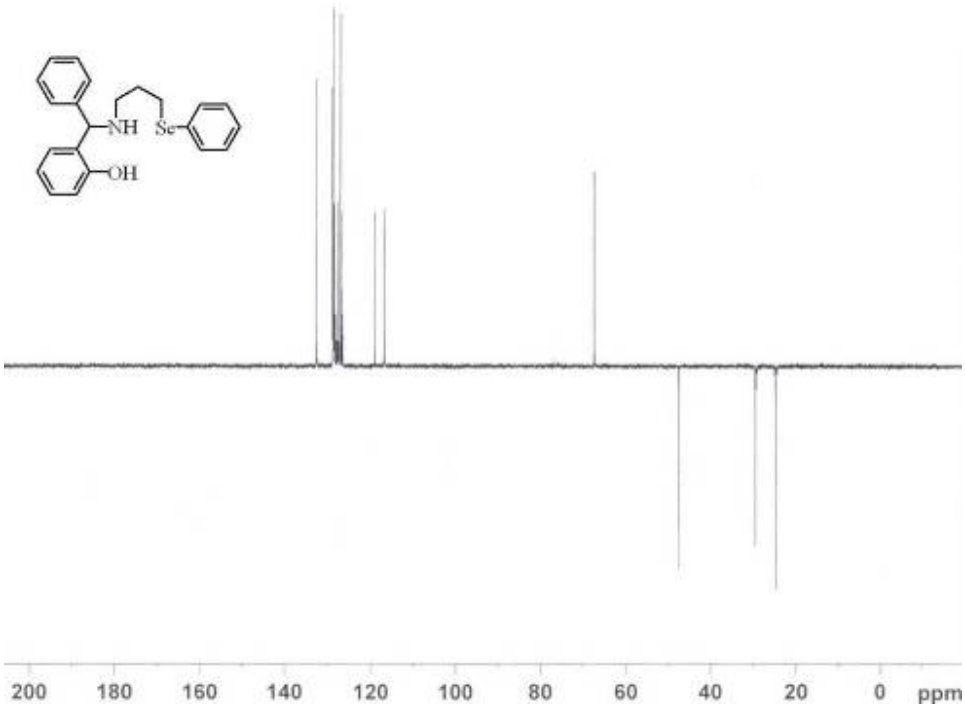
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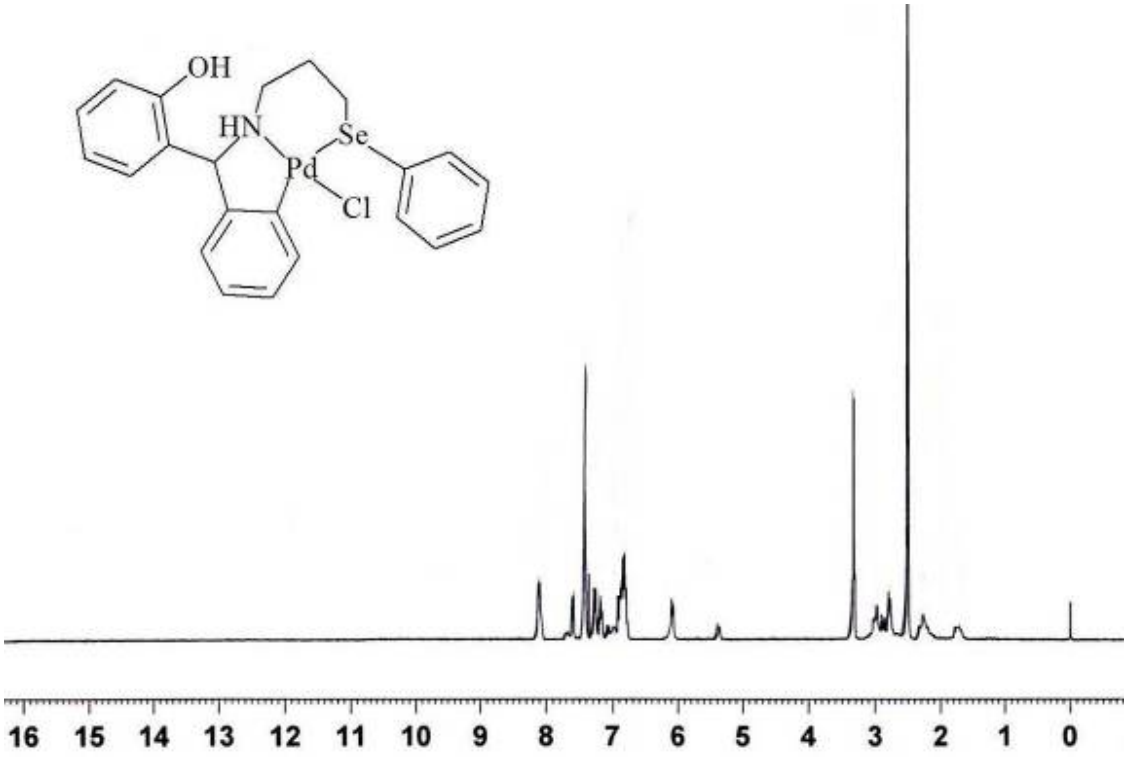
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Cl
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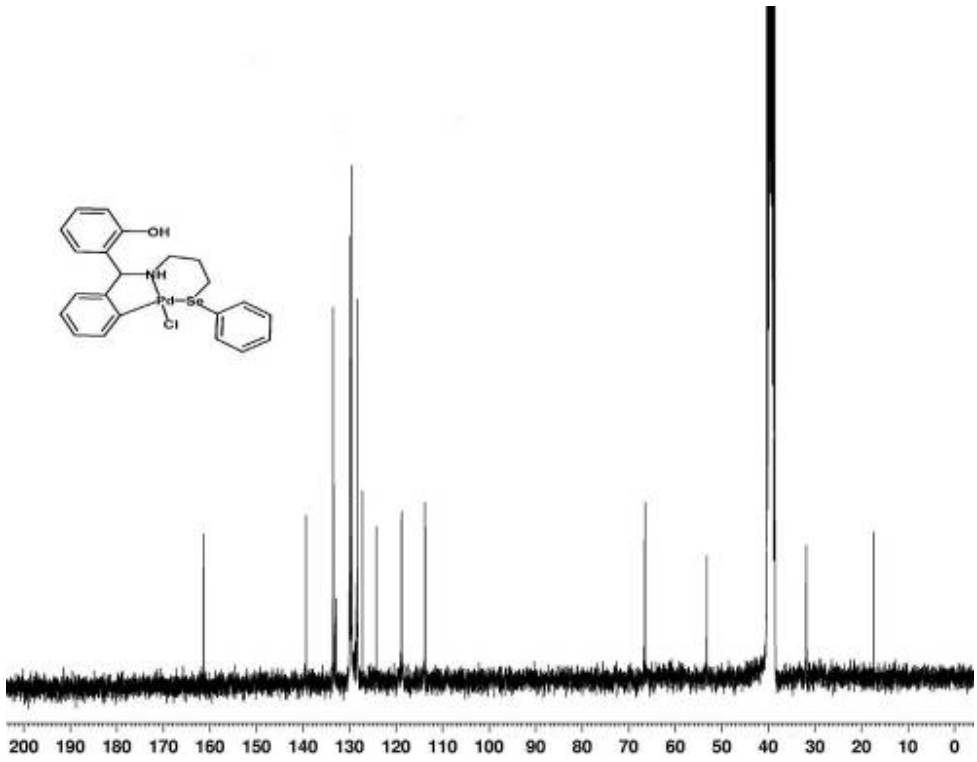
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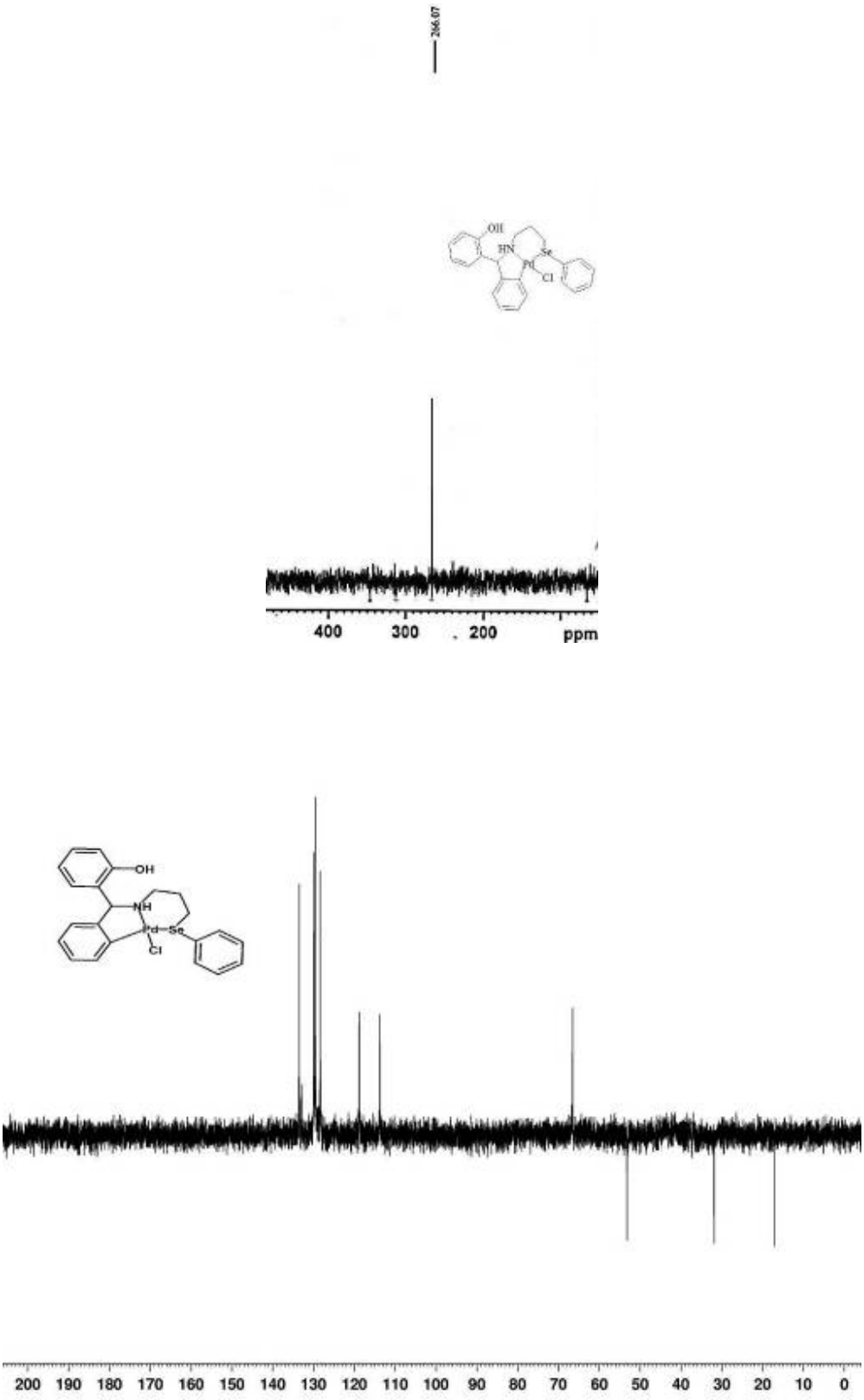
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NH
Pd
Se
Cl
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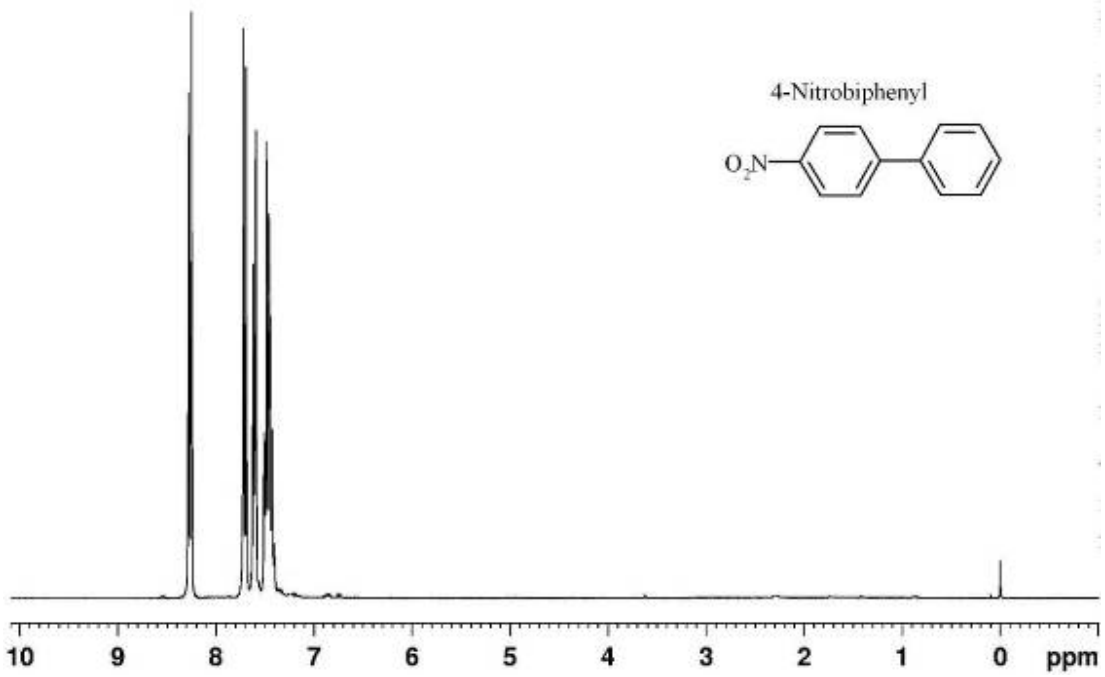
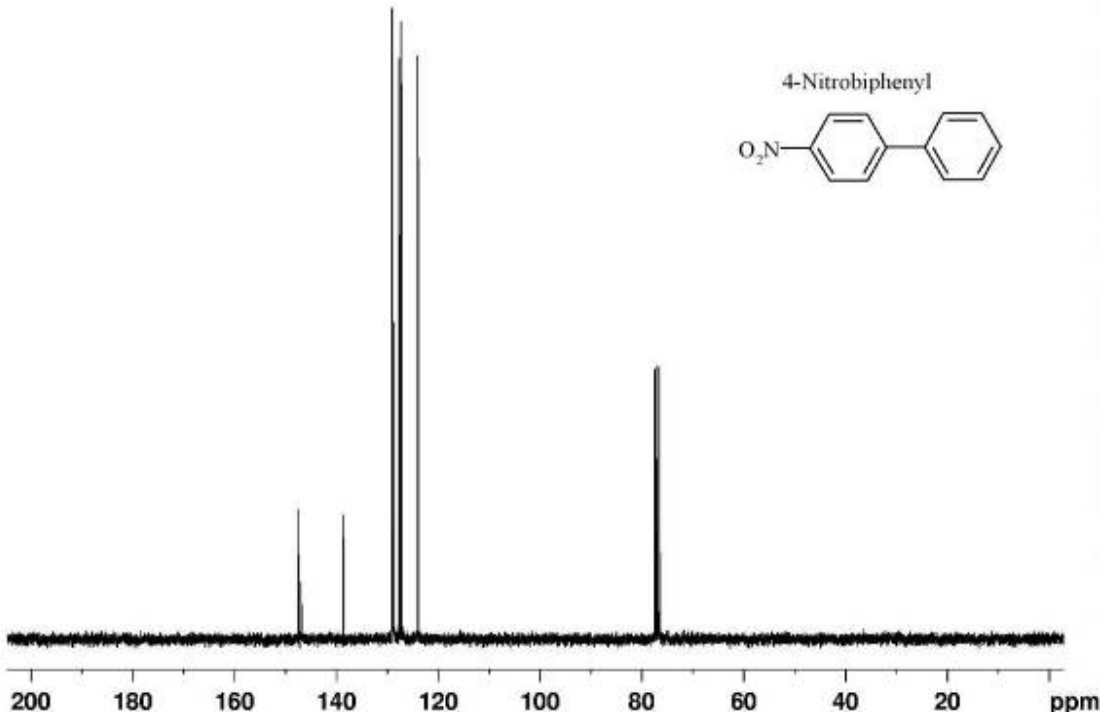
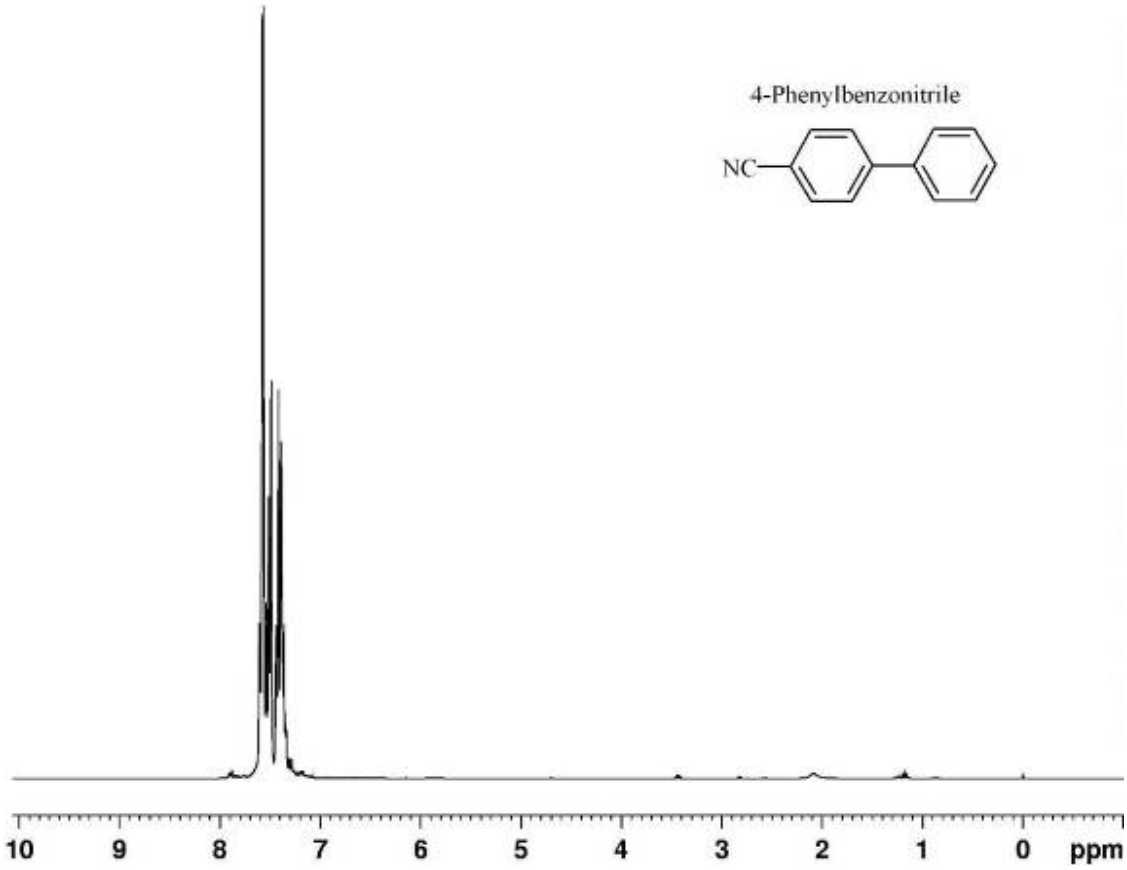
S8.2 ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of Coupled Products of Suzuki reaction.



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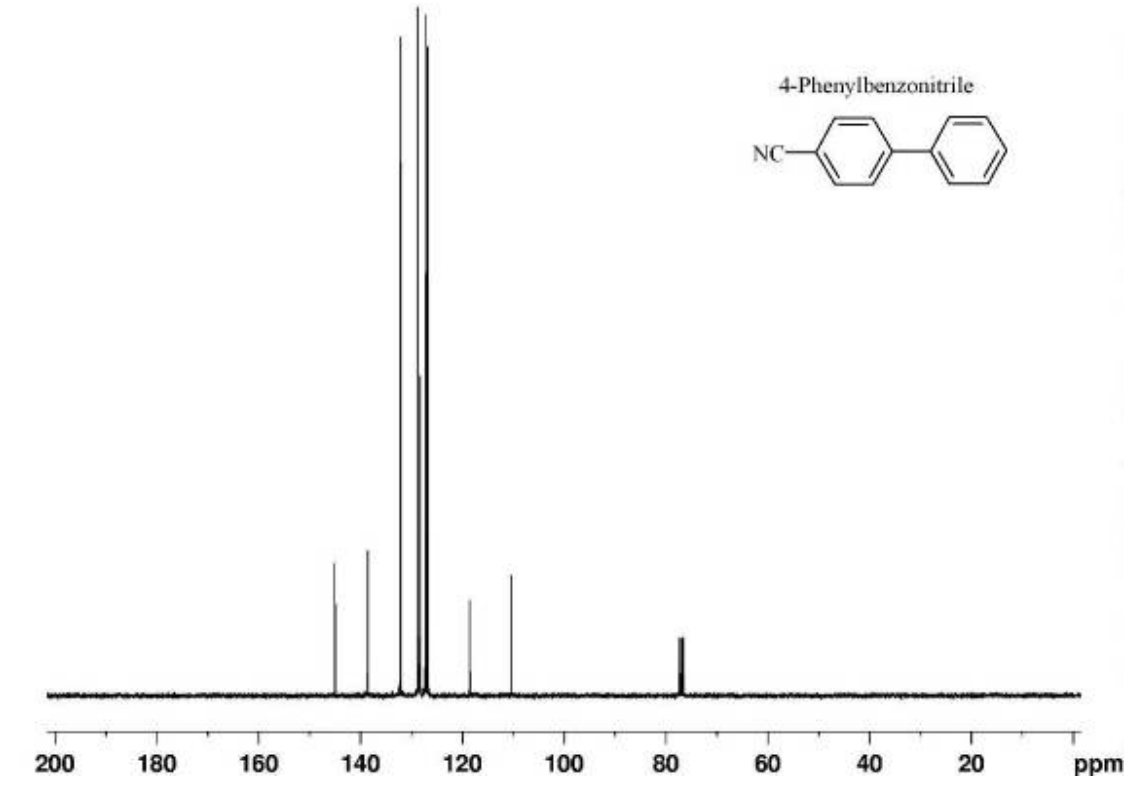
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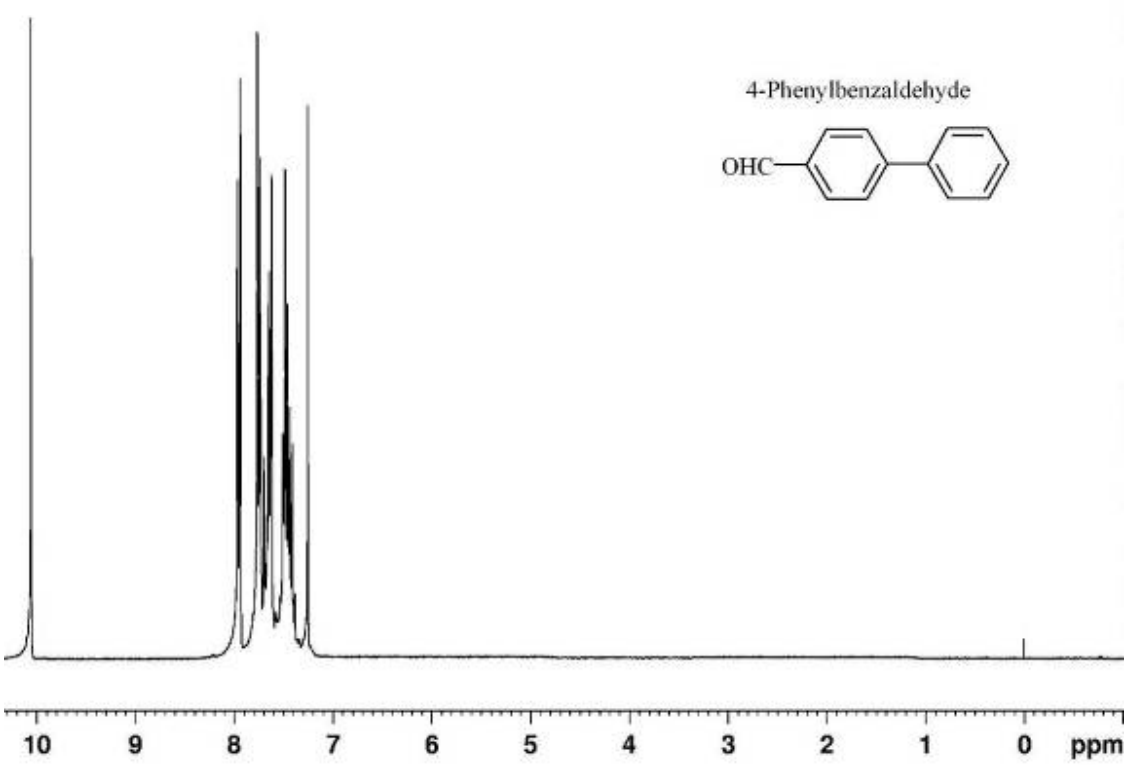
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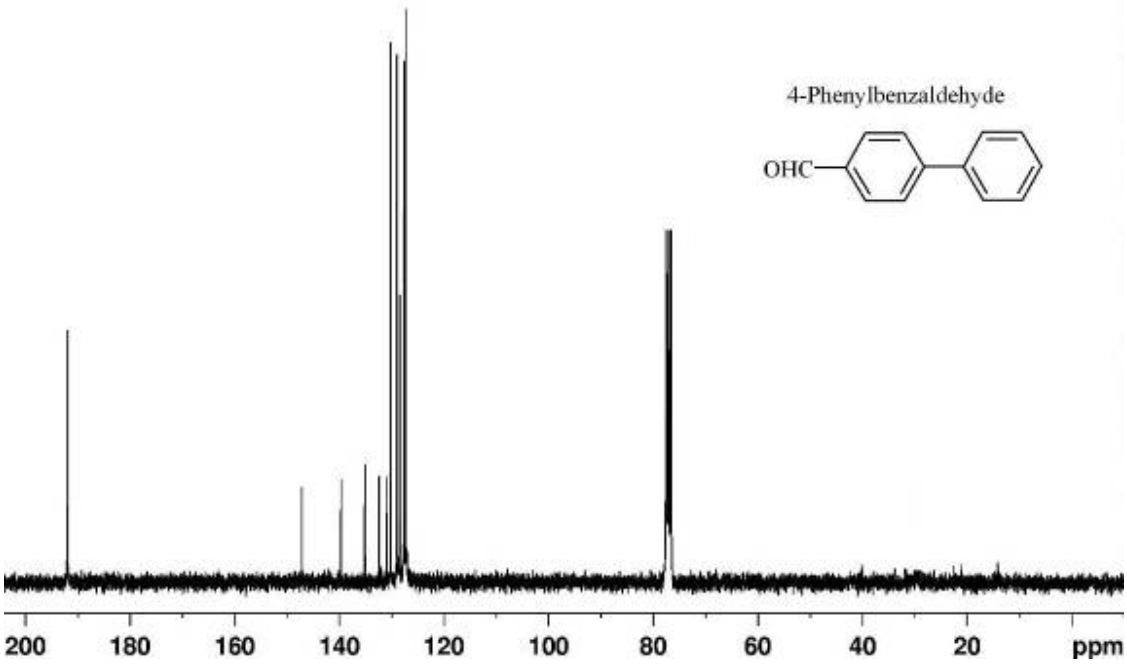
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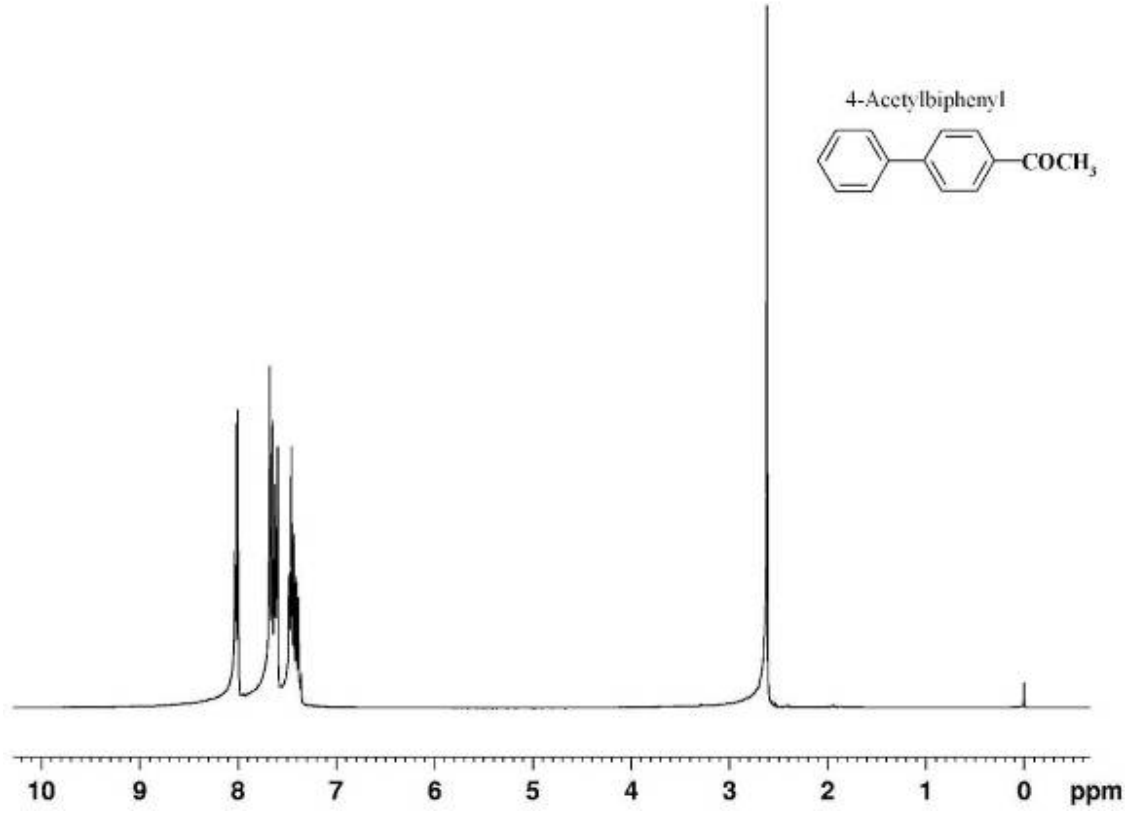
ppm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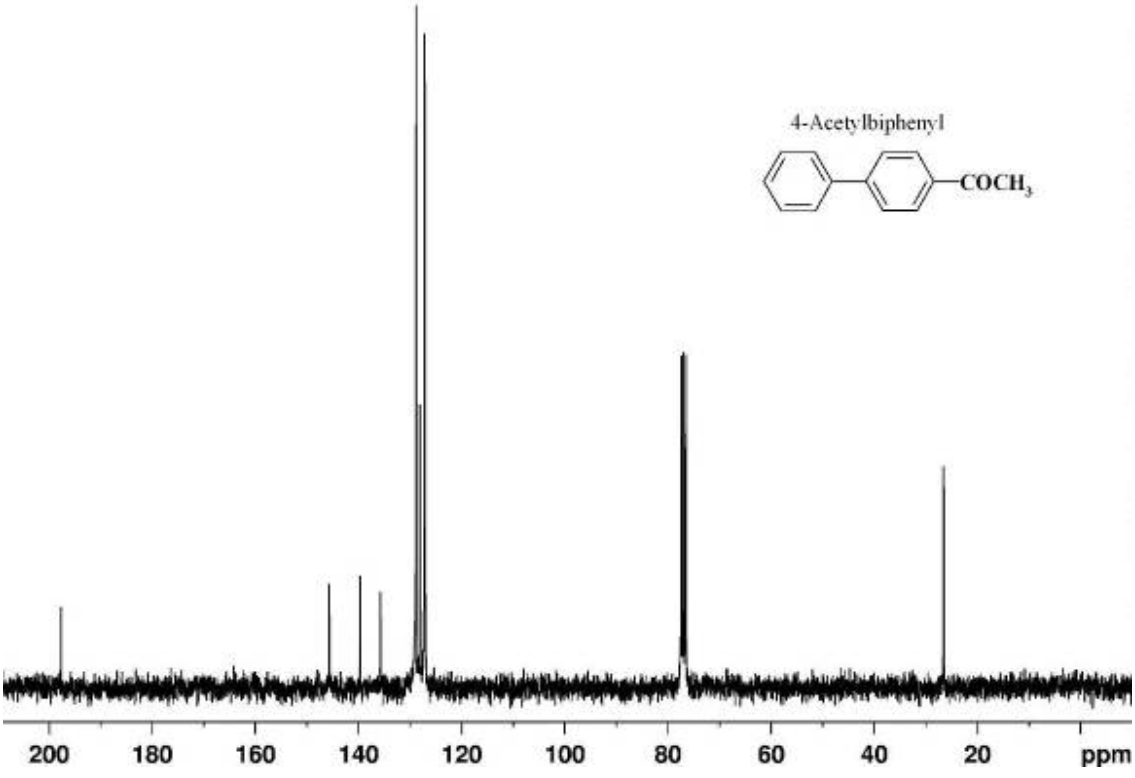
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COCH3
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140
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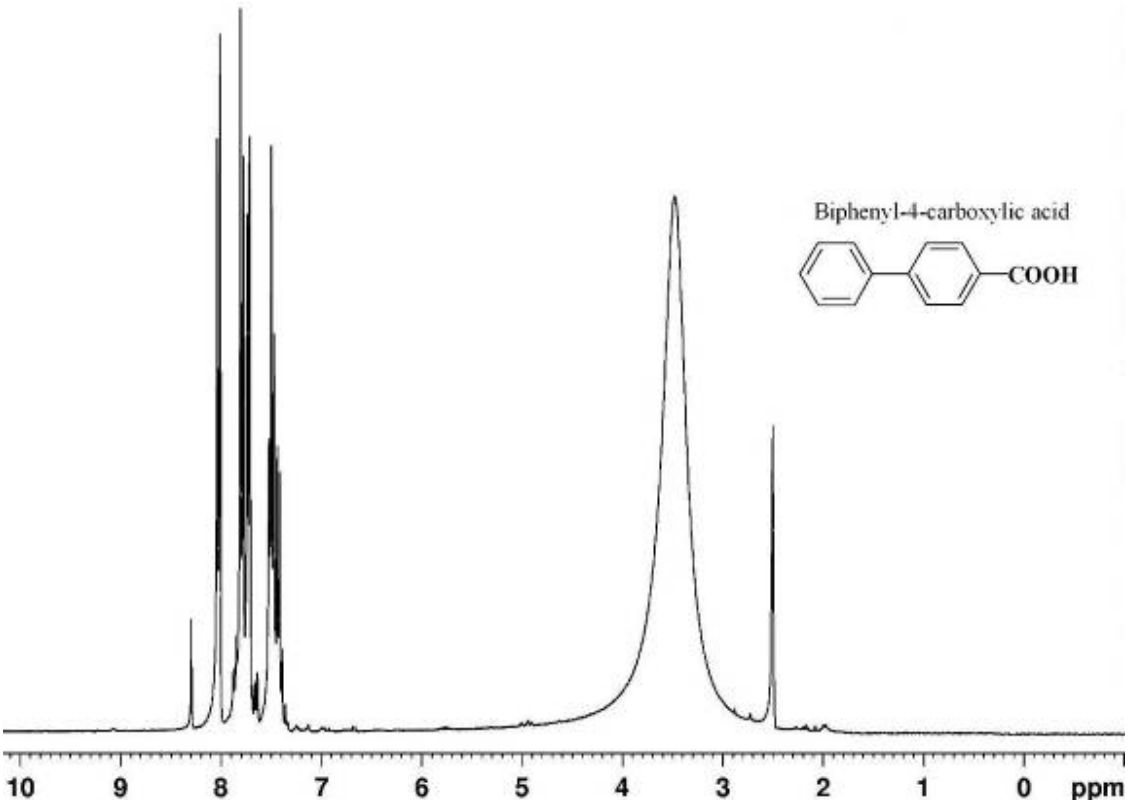
80
60
40
20
ppm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5
4
3
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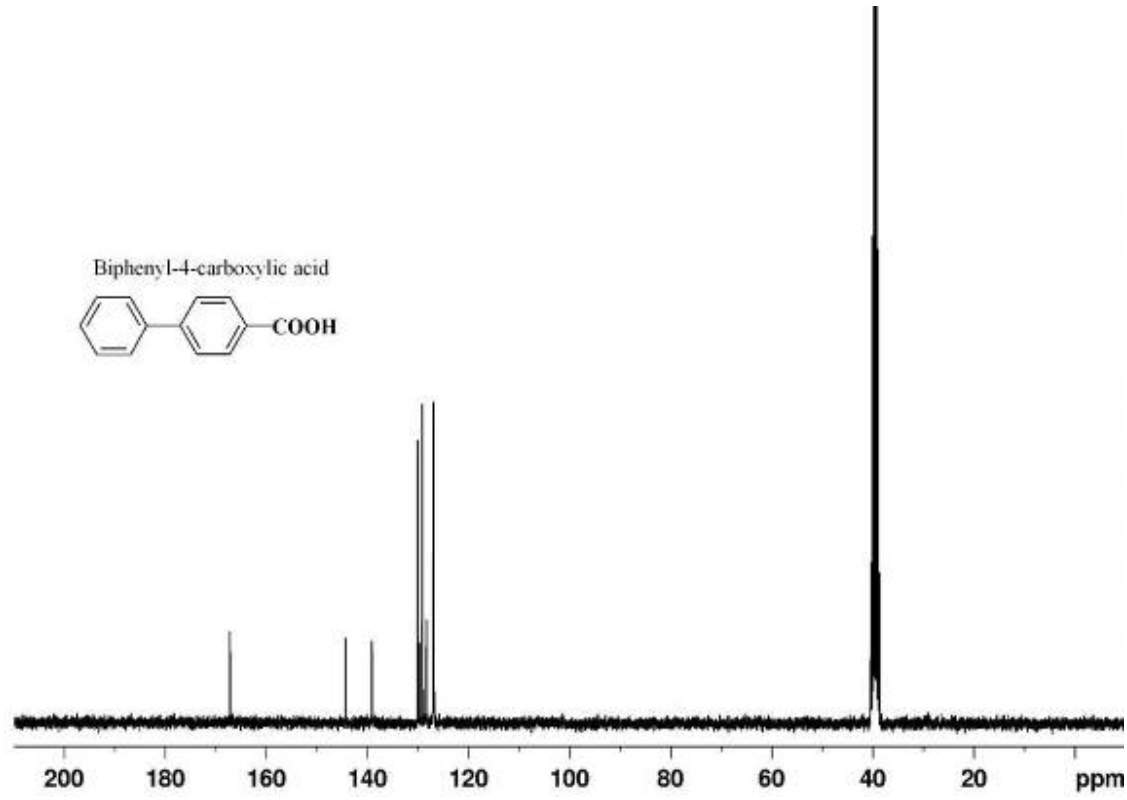
ppm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COOH
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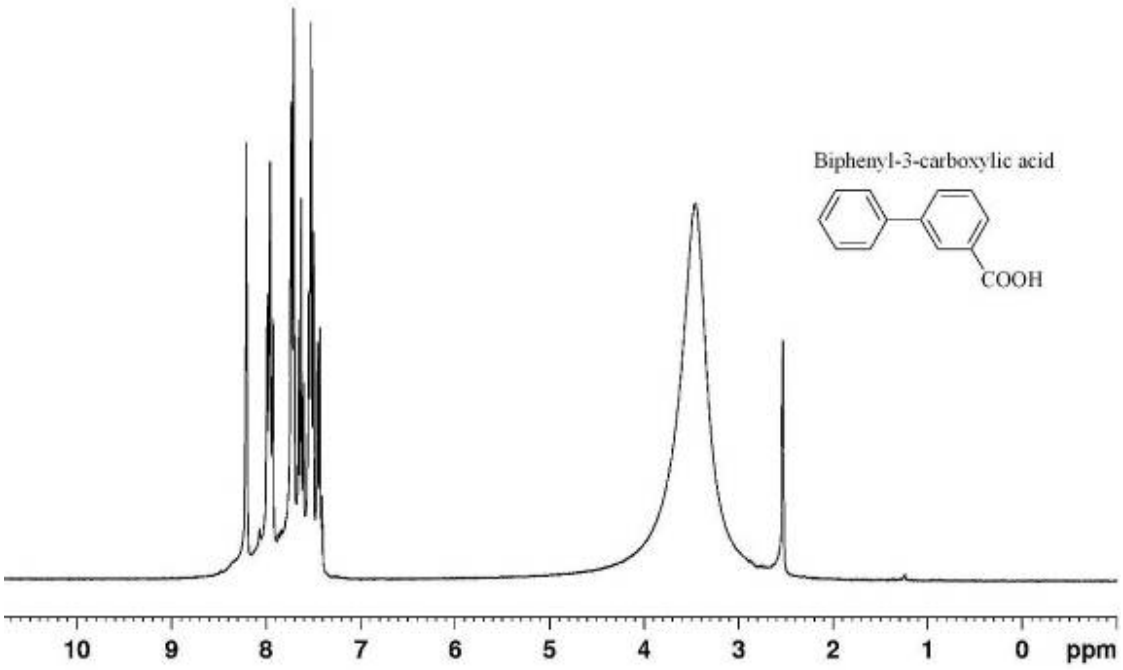
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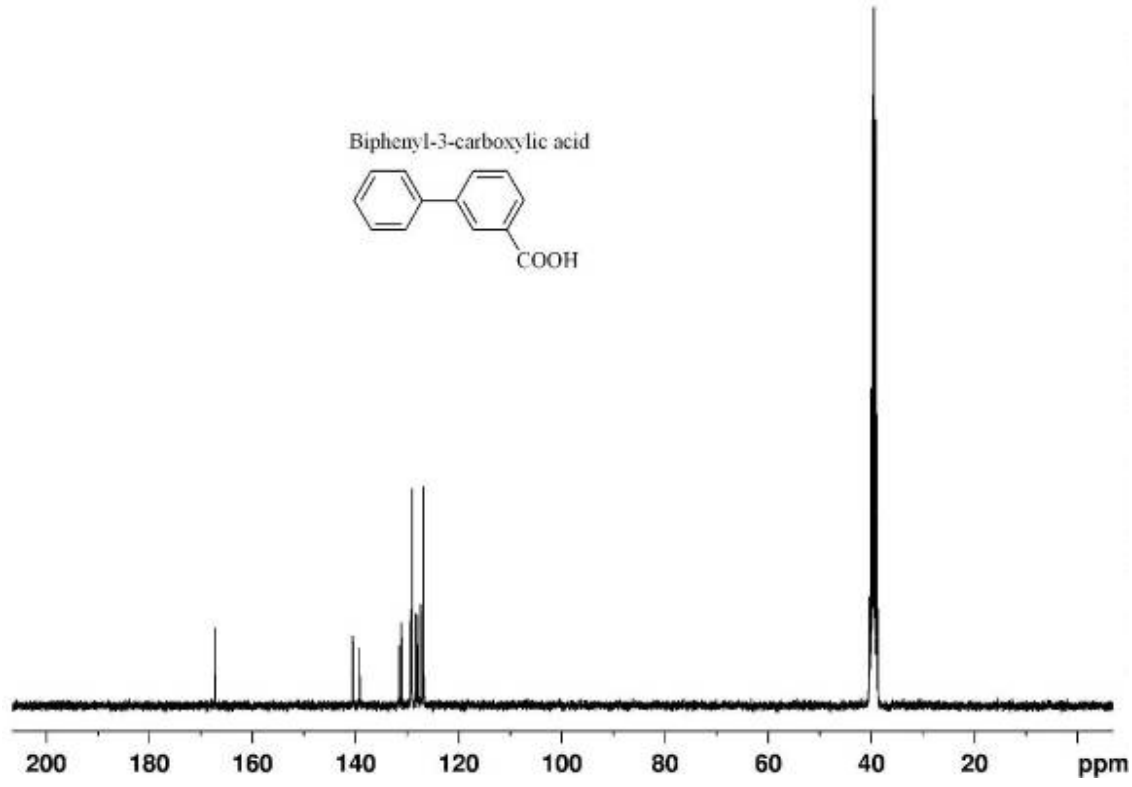
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COOH
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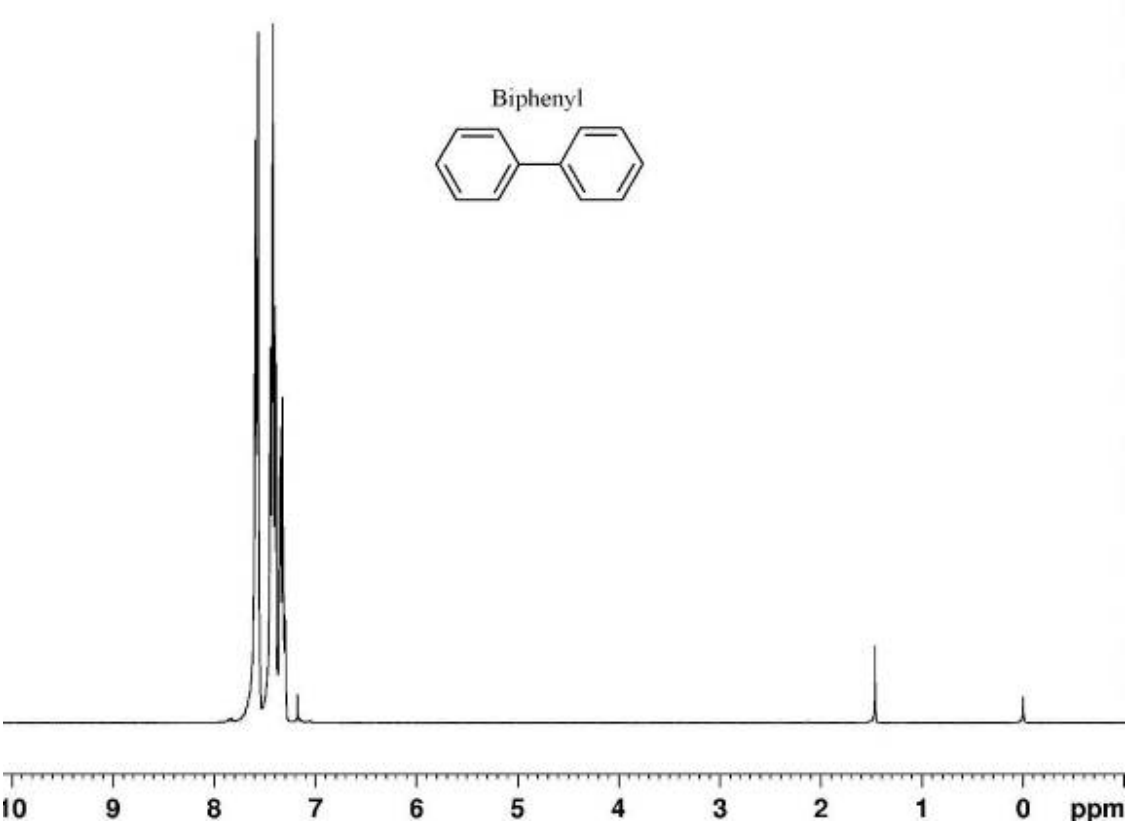
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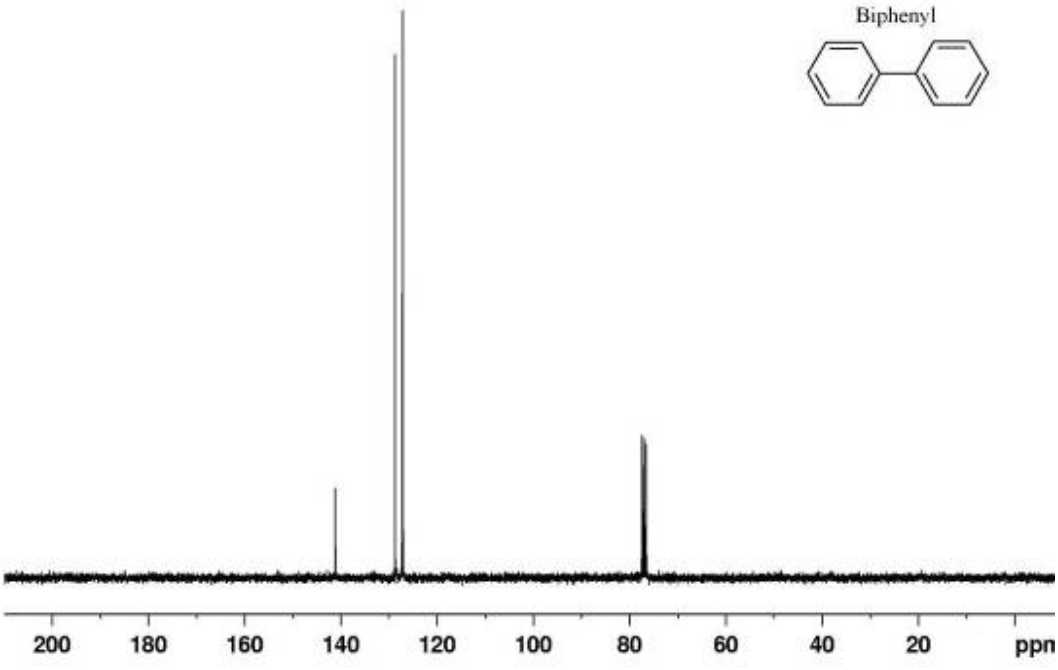
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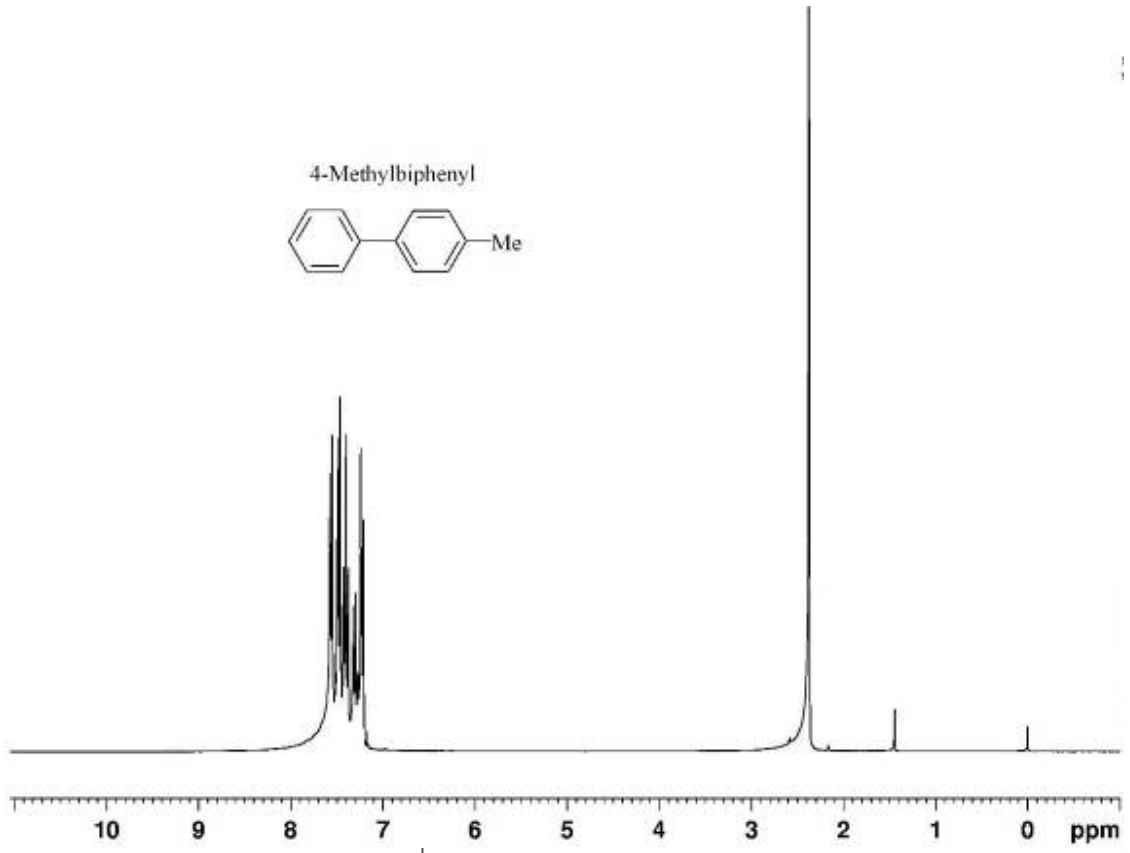
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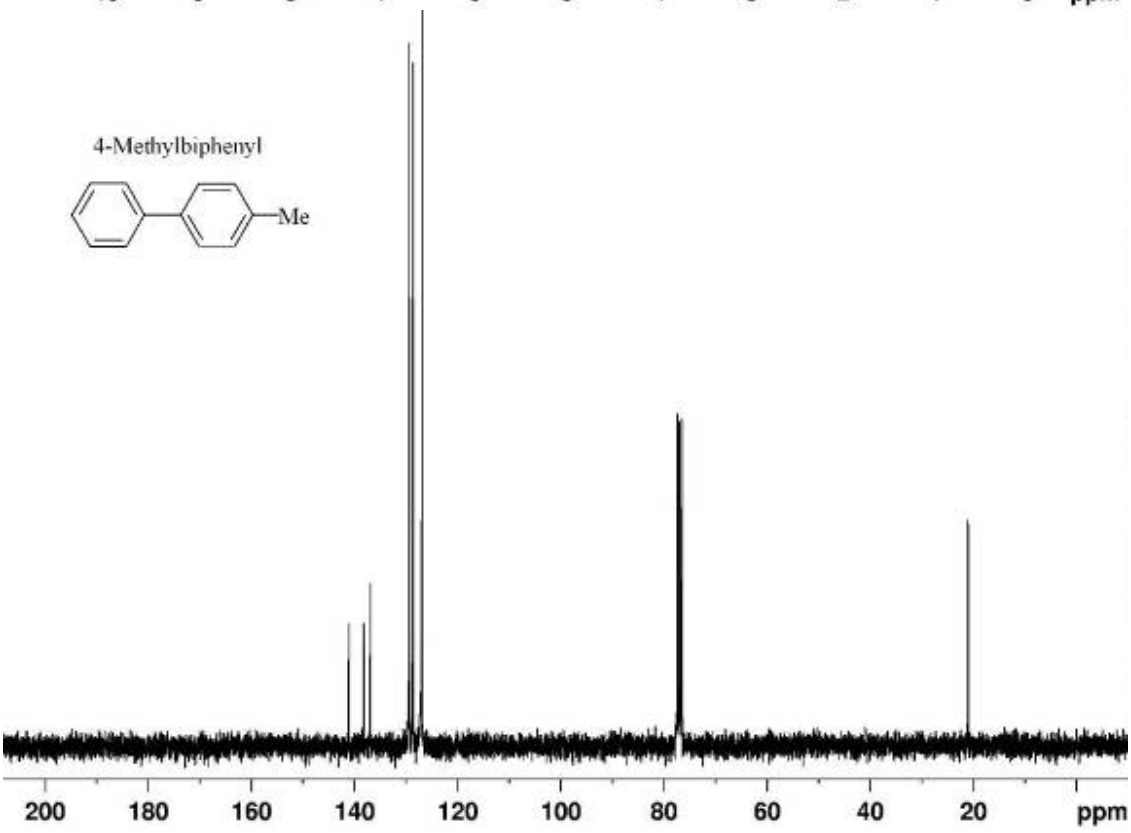
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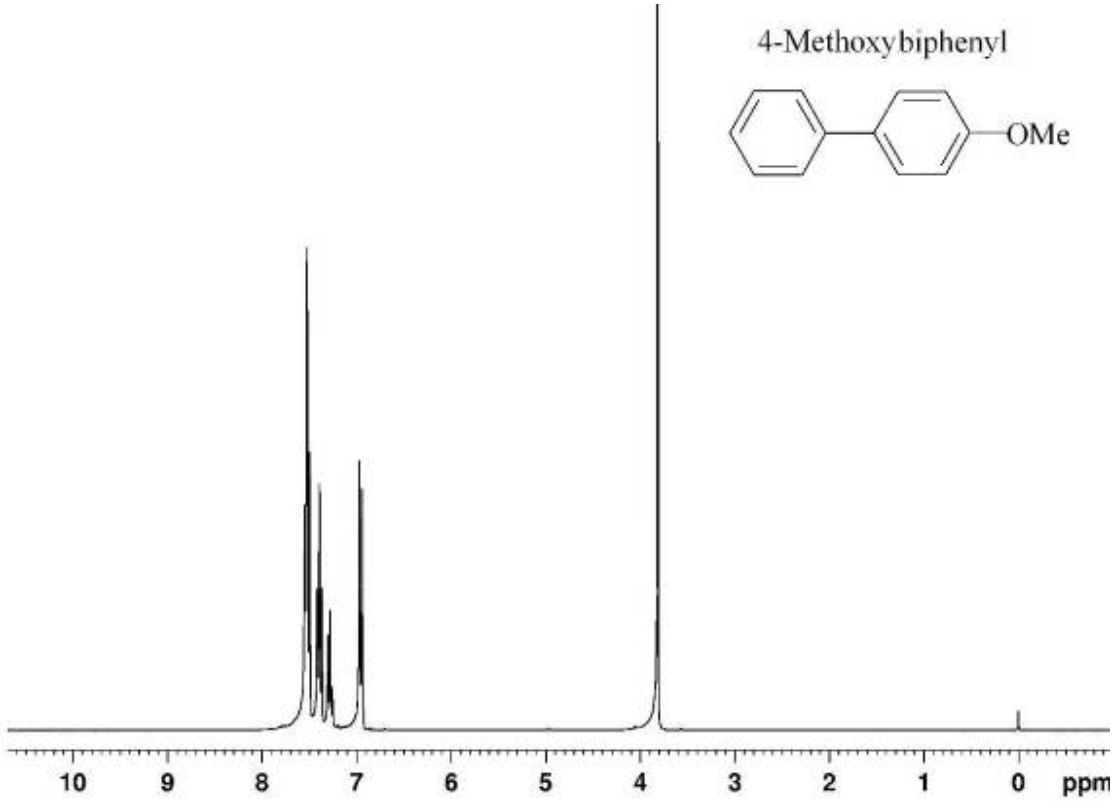
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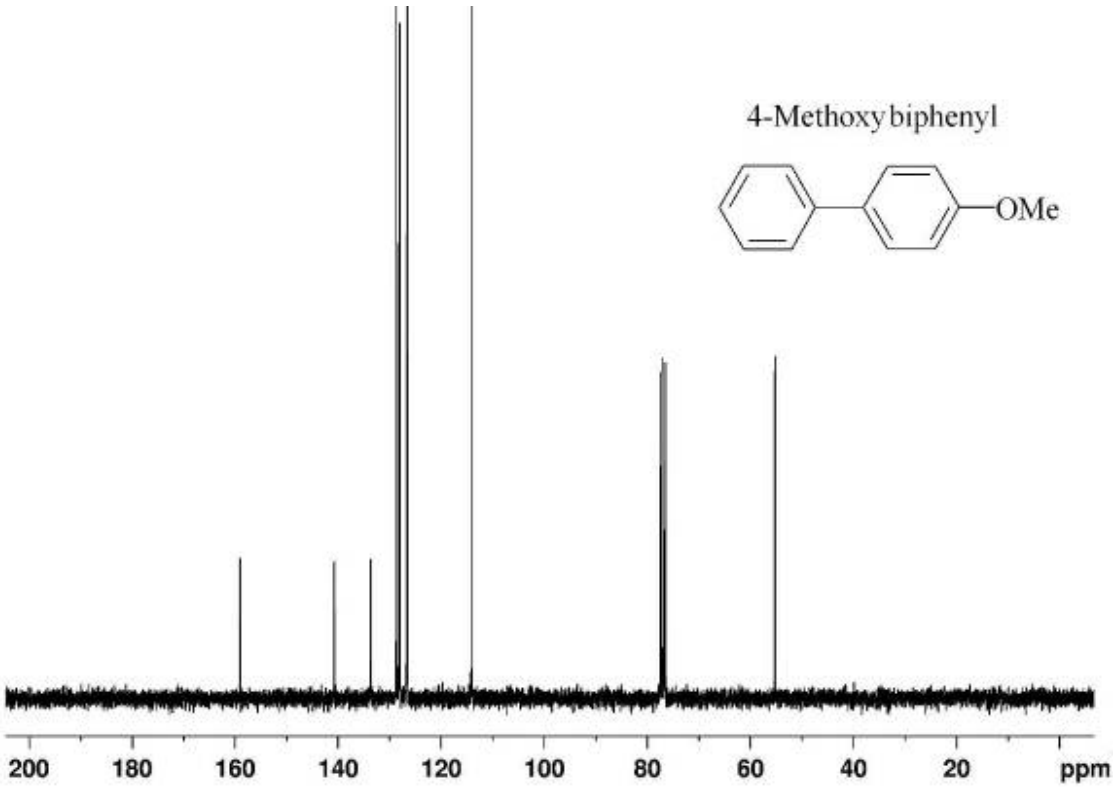
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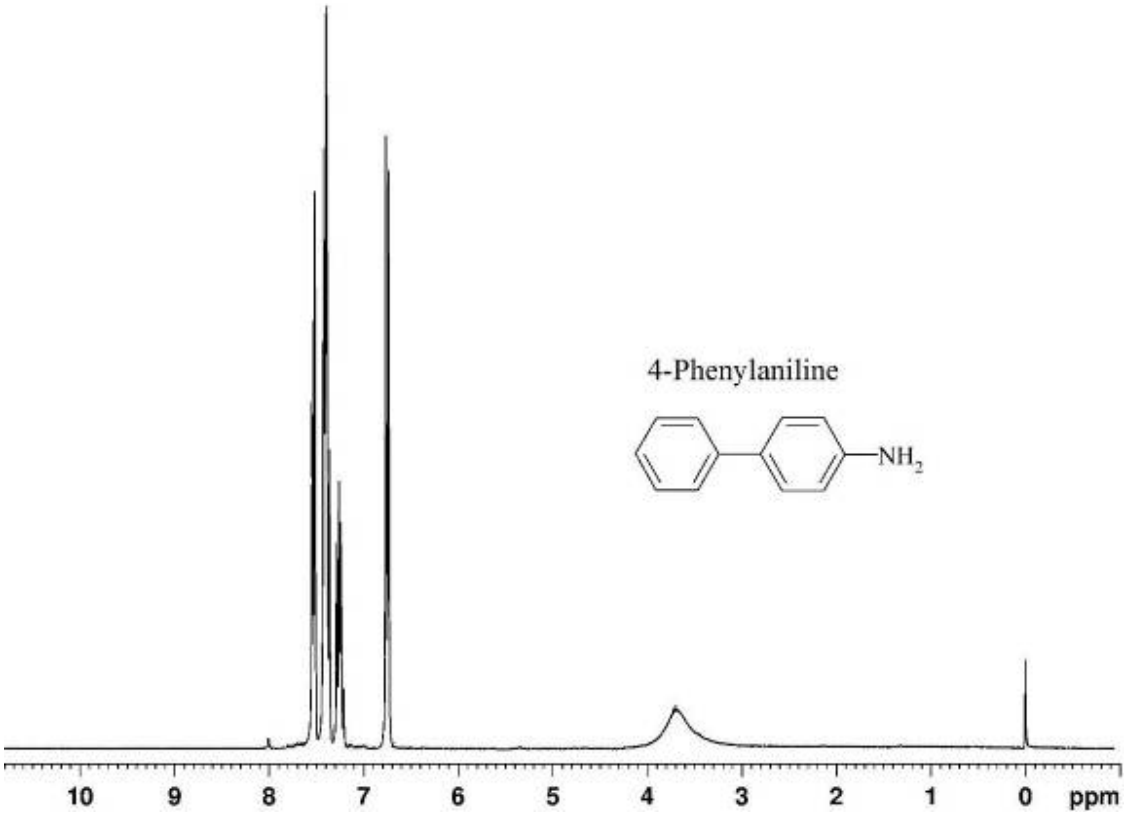
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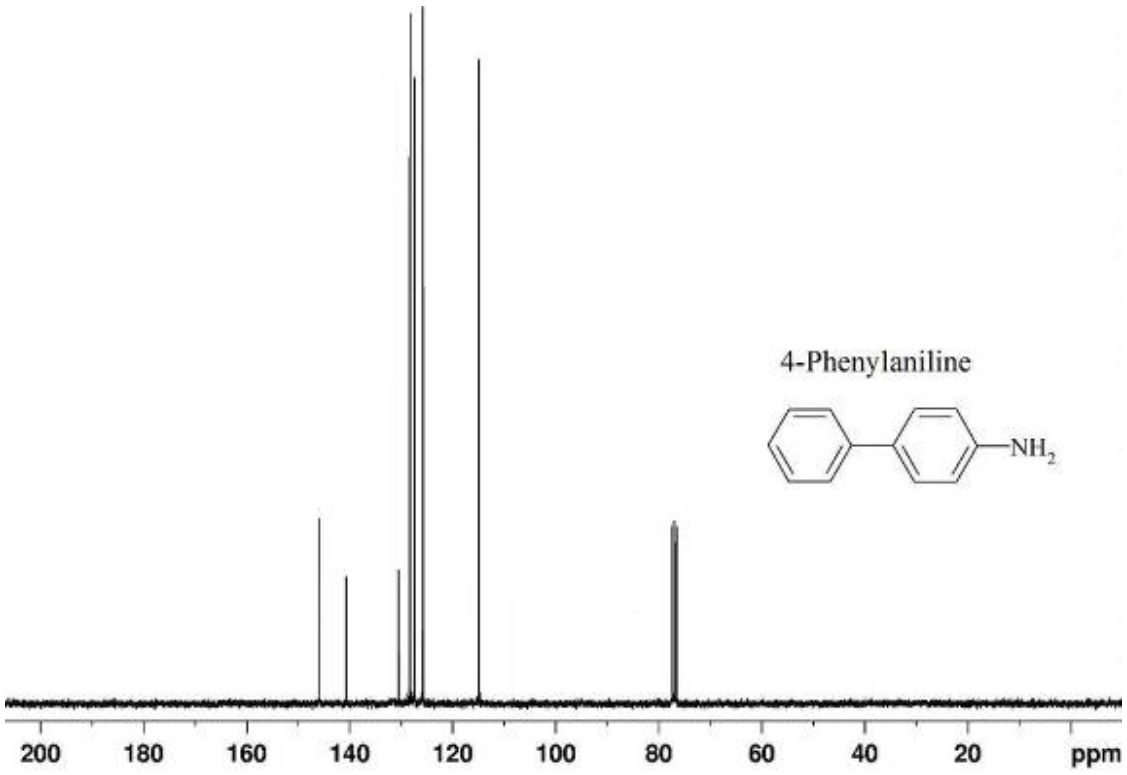
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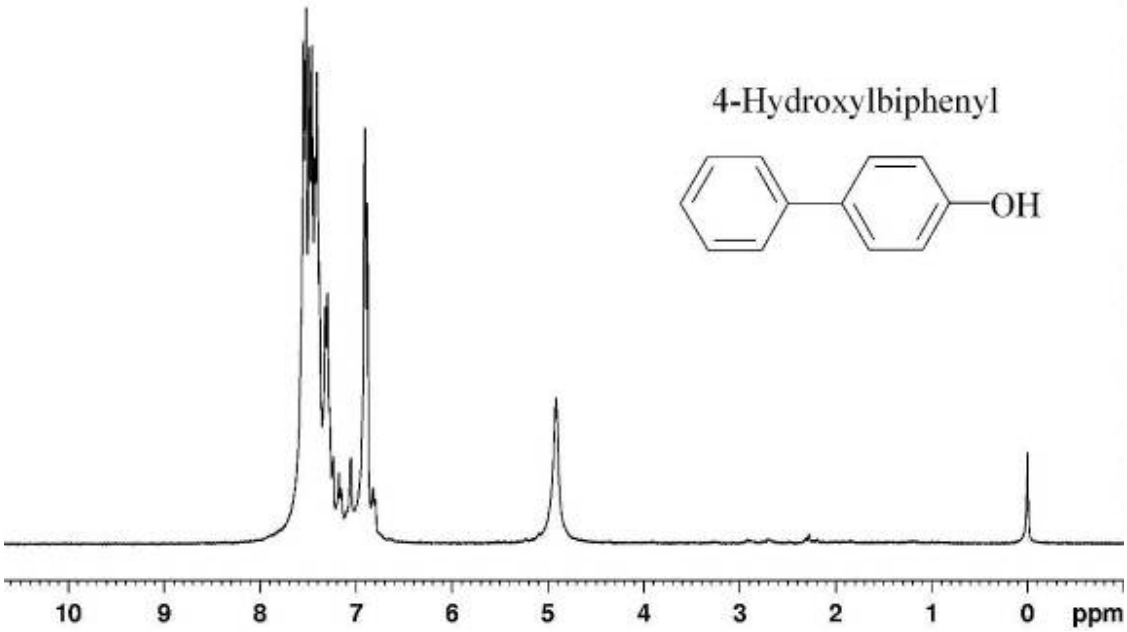
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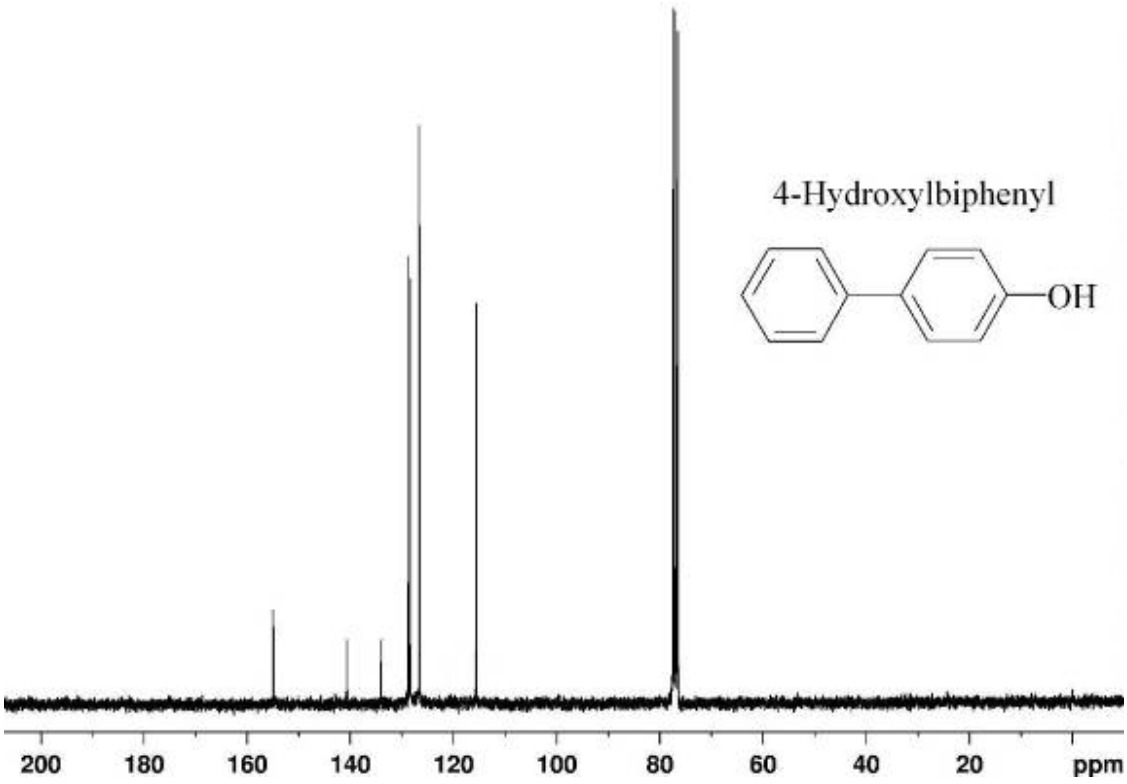
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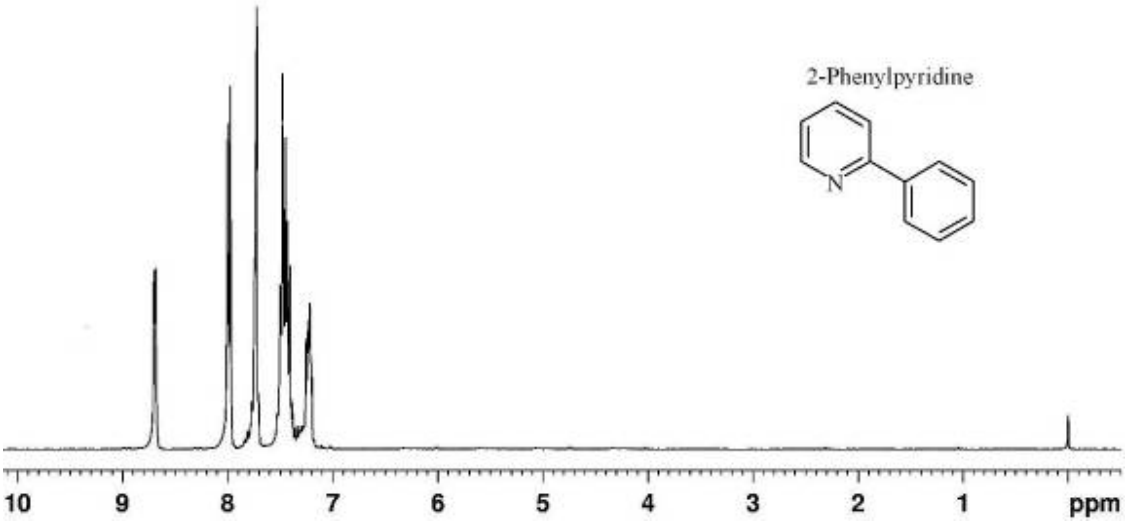
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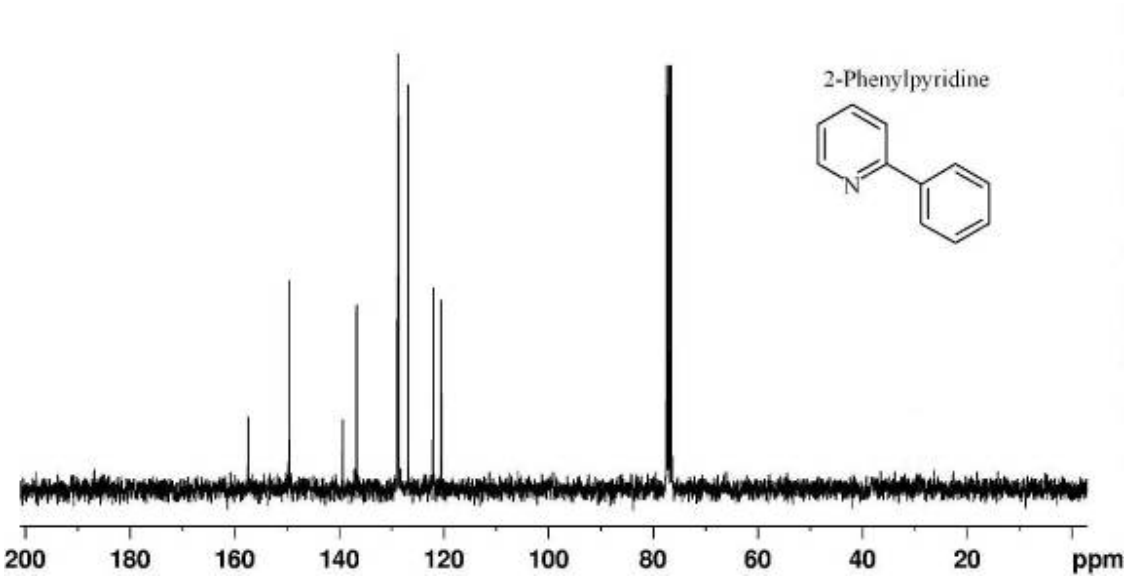
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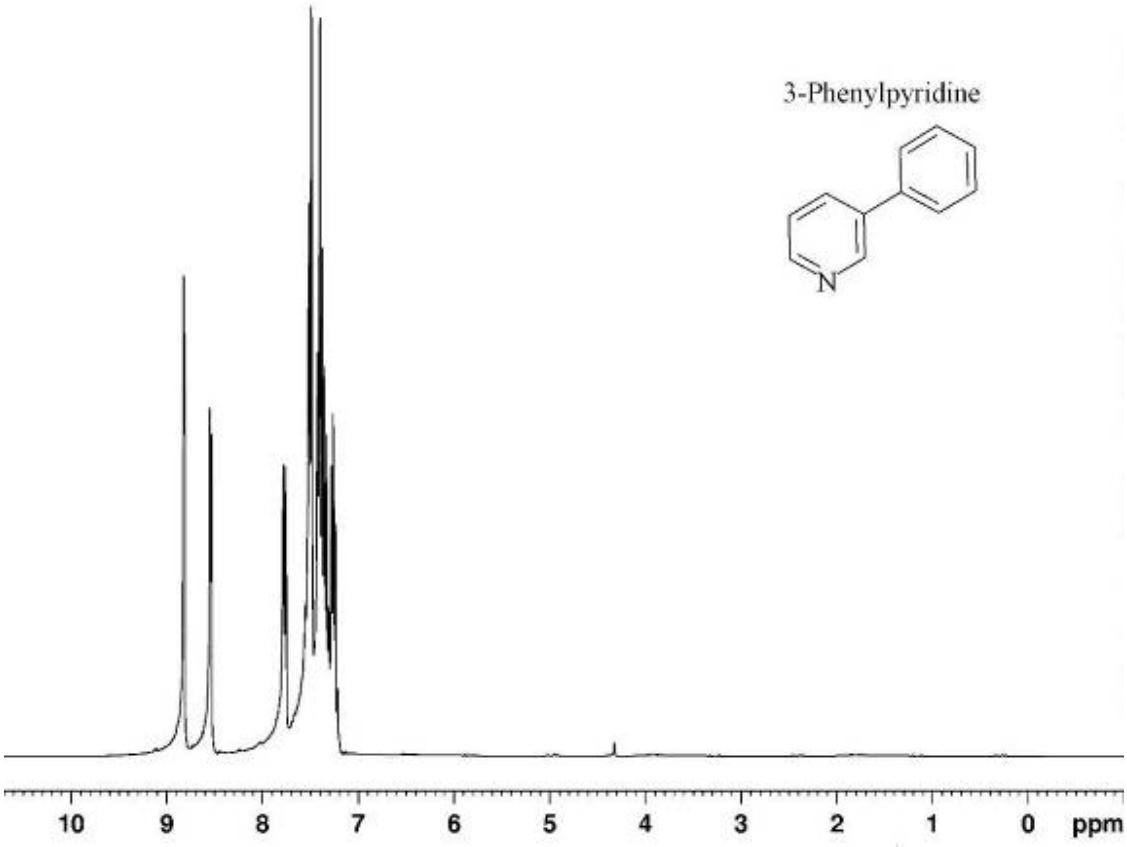
3-Phenylpyridine
N
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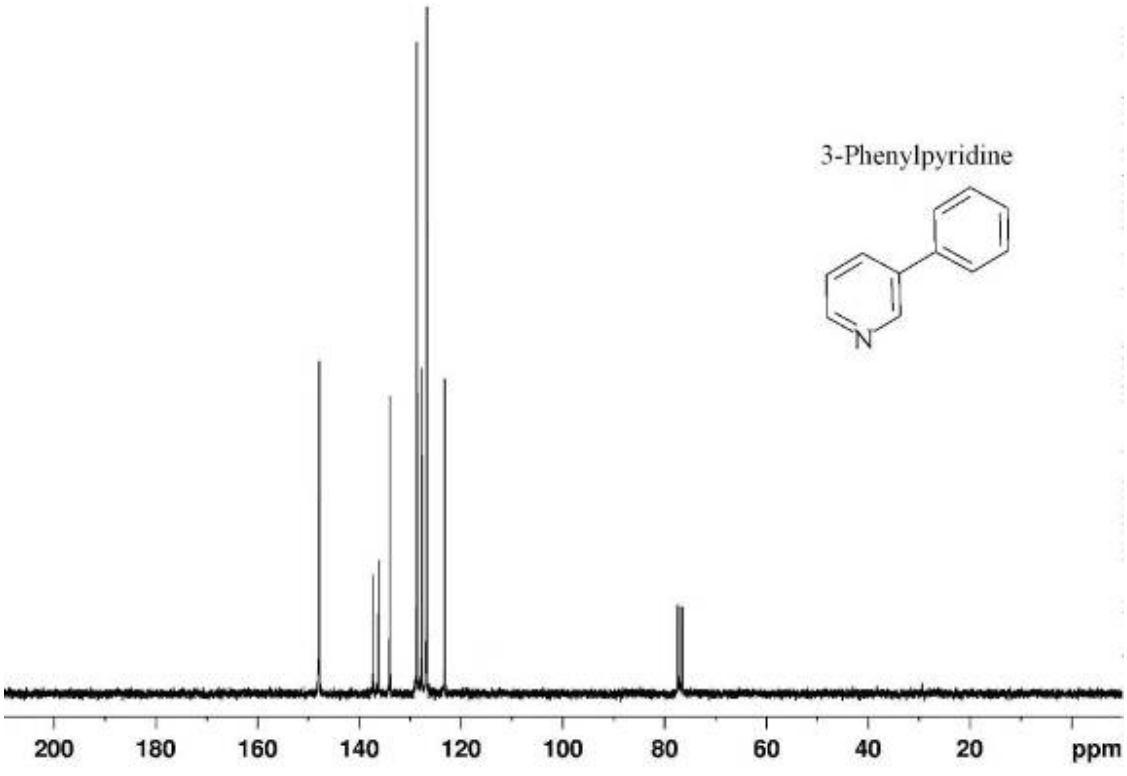
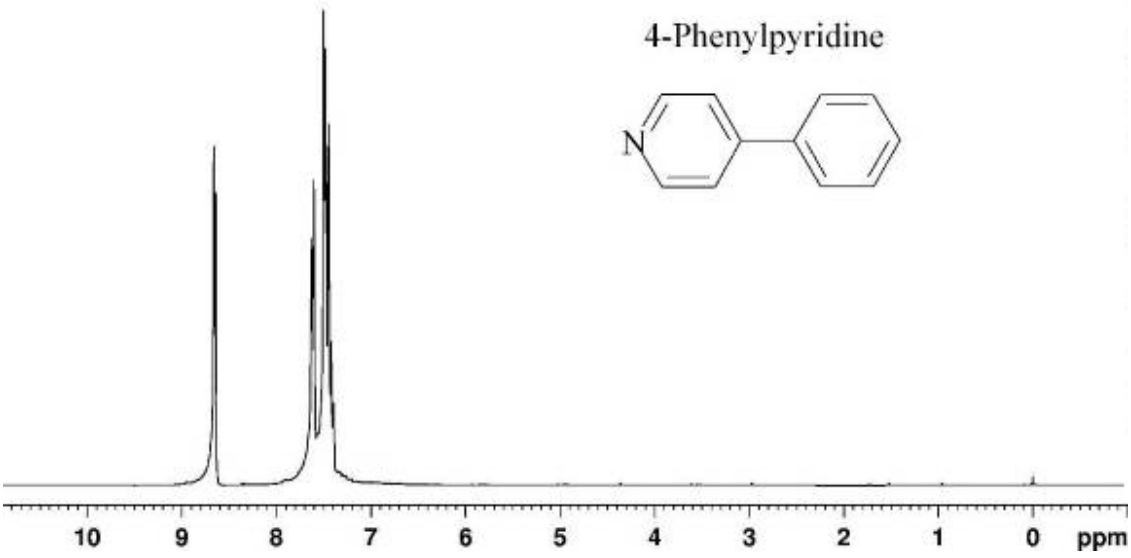
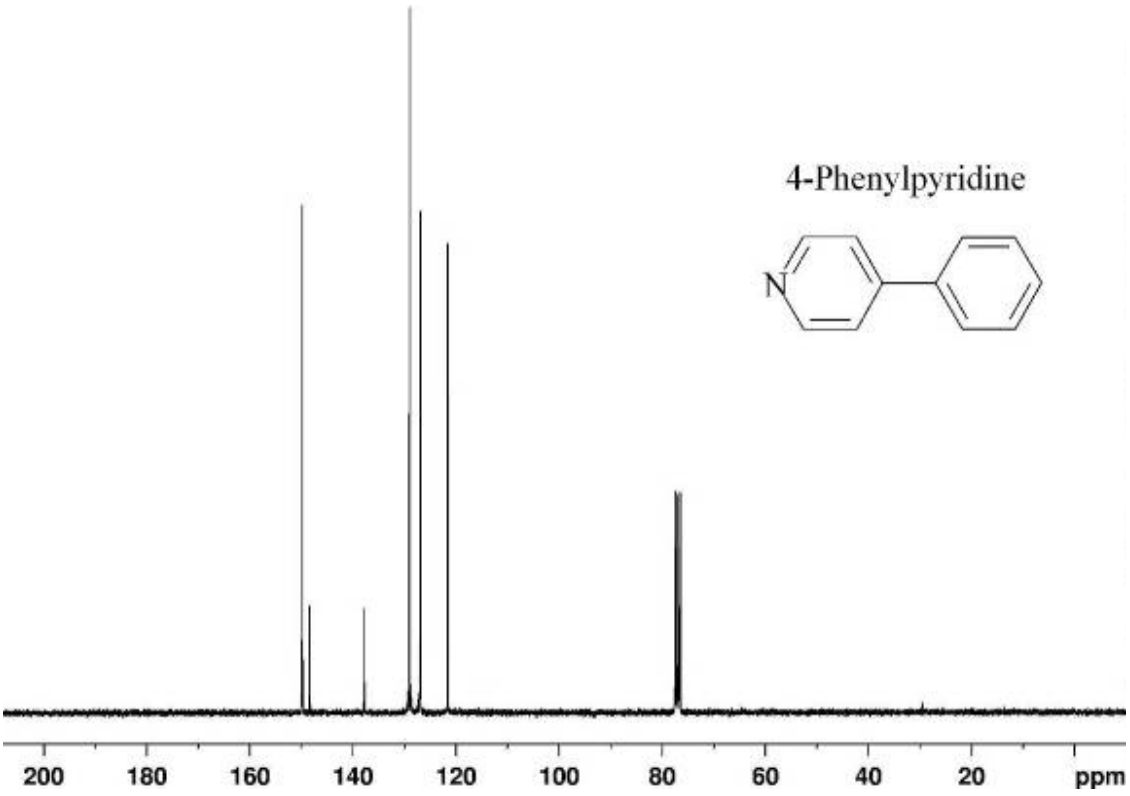
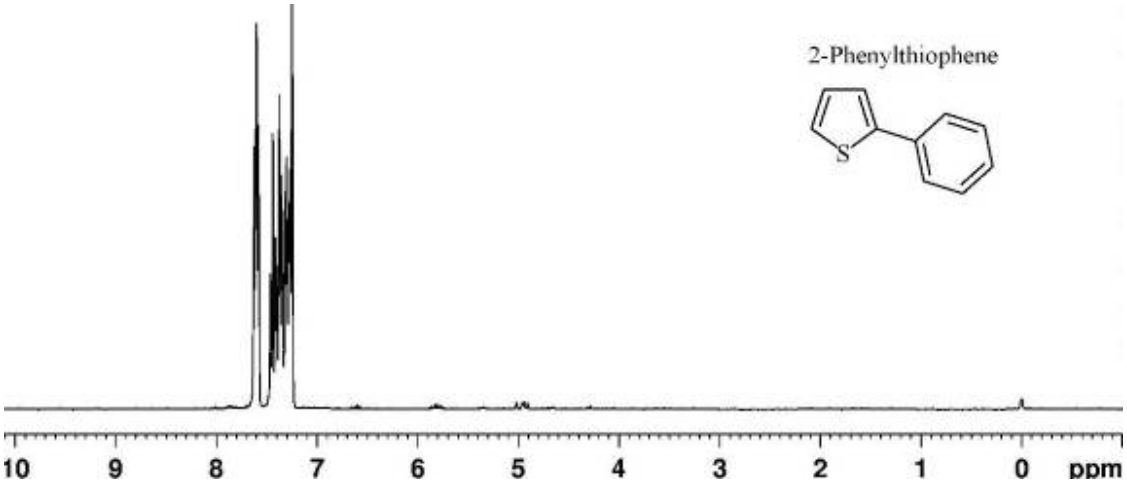
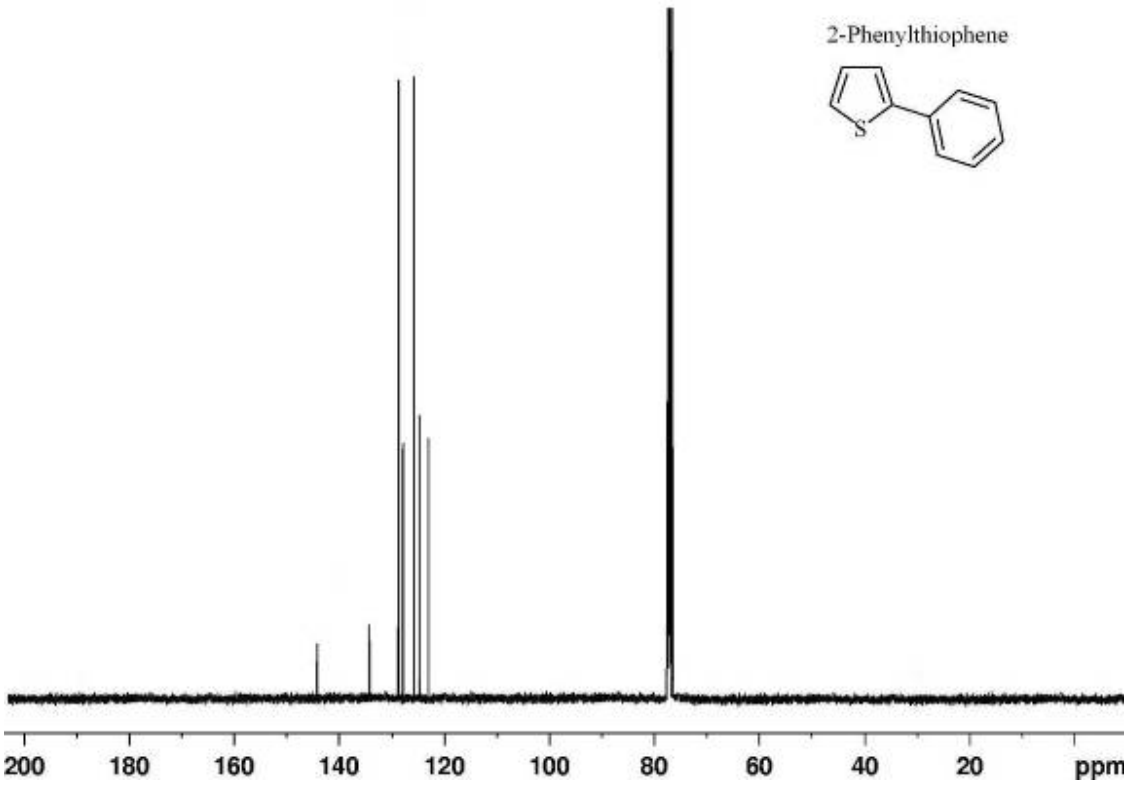
0
ppm

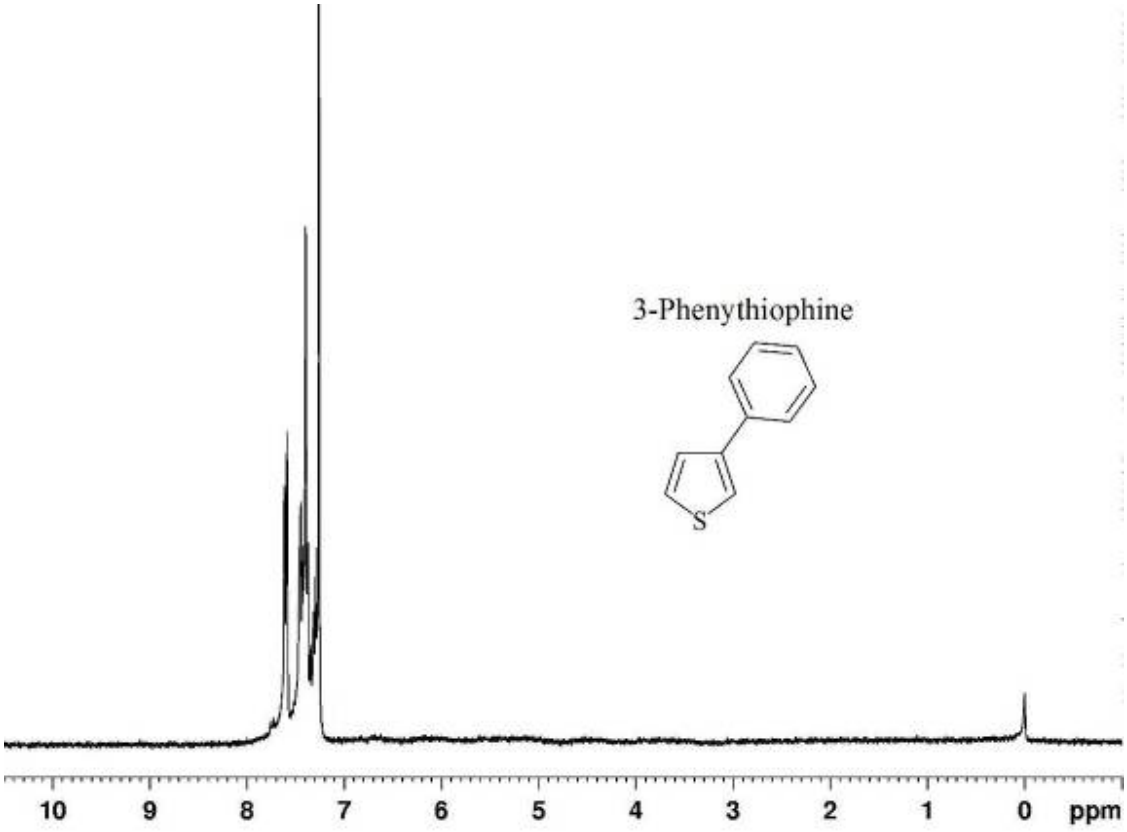

3-Phenylpyridine
N
200
180
160
140
120
100
80
60
40
20
ppm

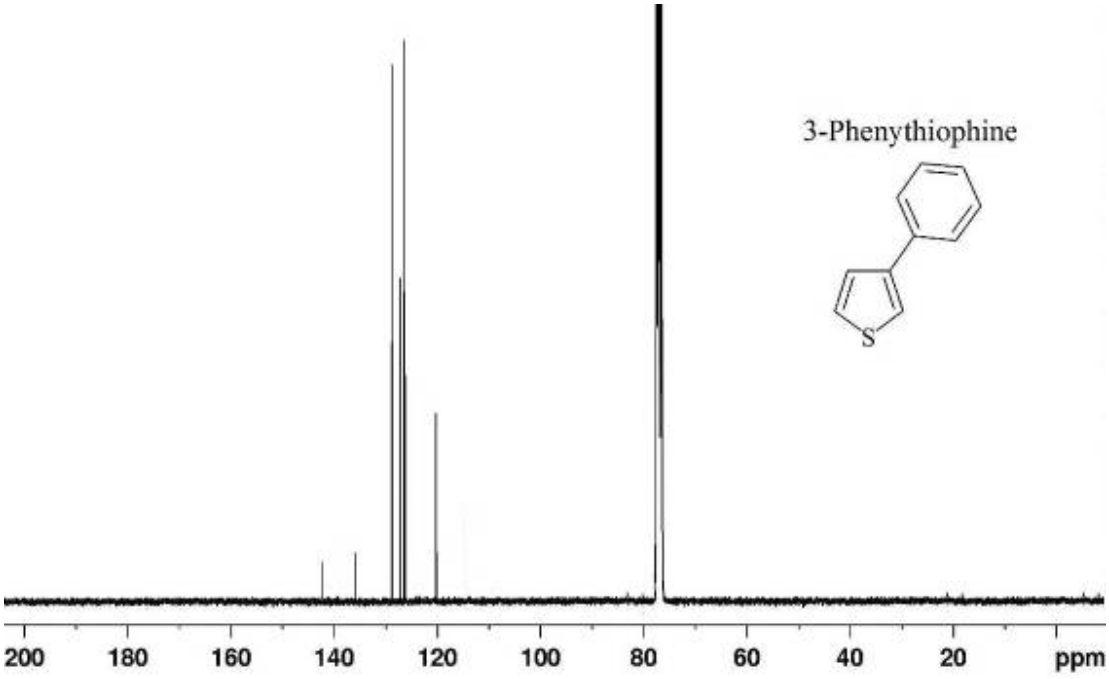

4-Phenylpyridine
N
10
9
8
7
6
5
4
3
2
1
0
ppm

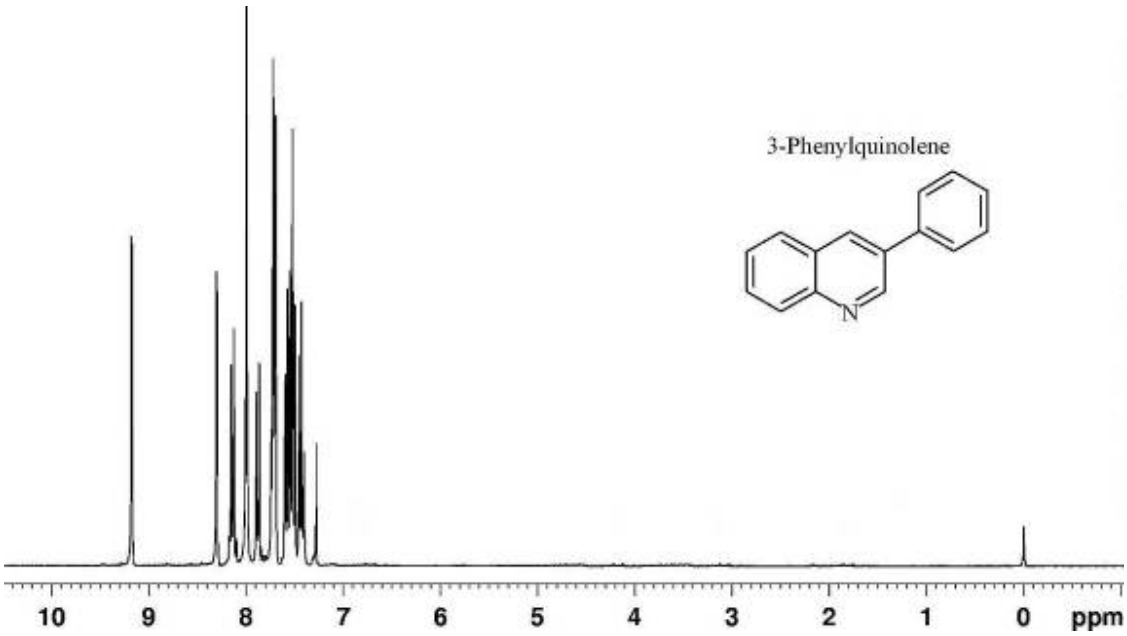

4-Phenylpyridine
N
200
180
160
140
120
100
80
60
40
20
ppm

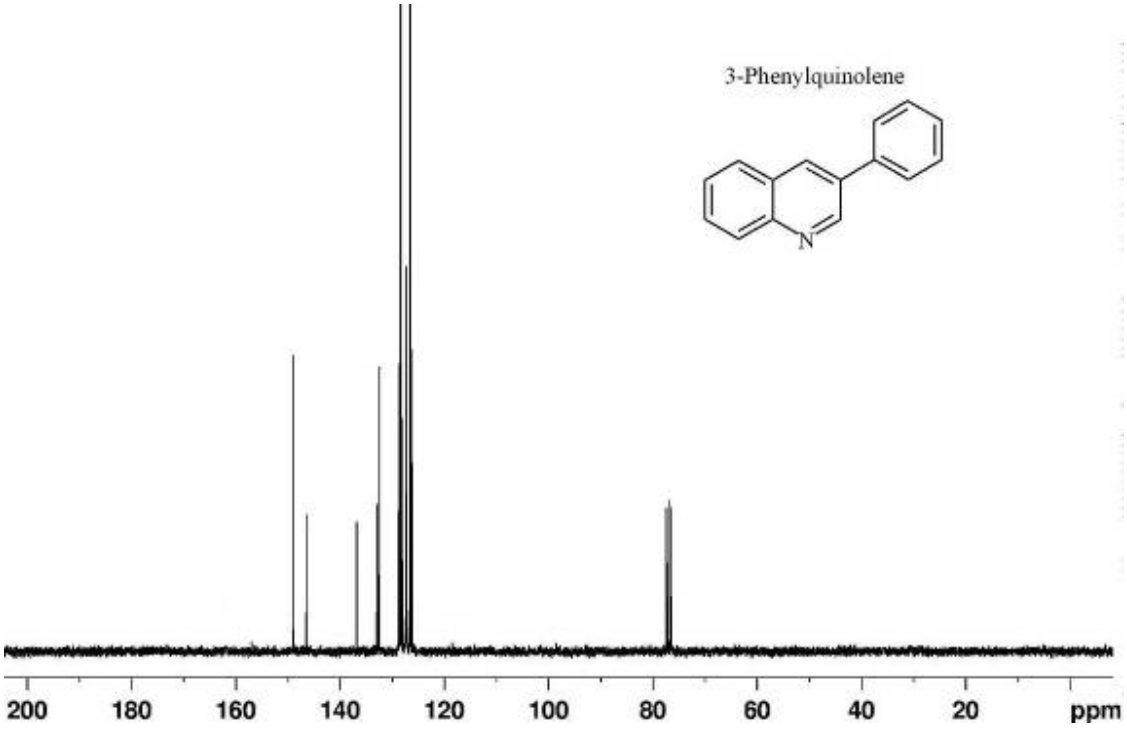

2-Phenylthiophene
S
10
9
8
7
6
5
4
3
2
1
0
ppm

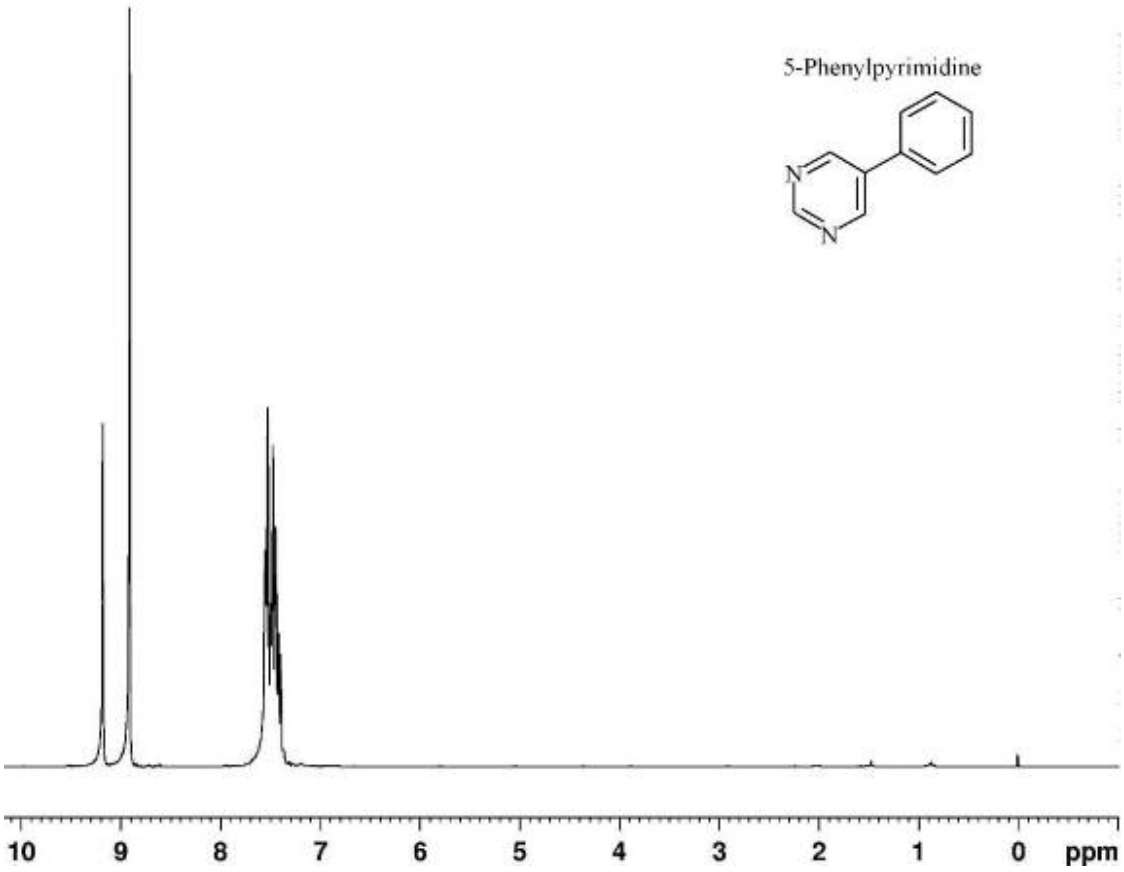

2-Phenylthiophene
S
200
180
160
140
120
100
80
60
40
20
ppm

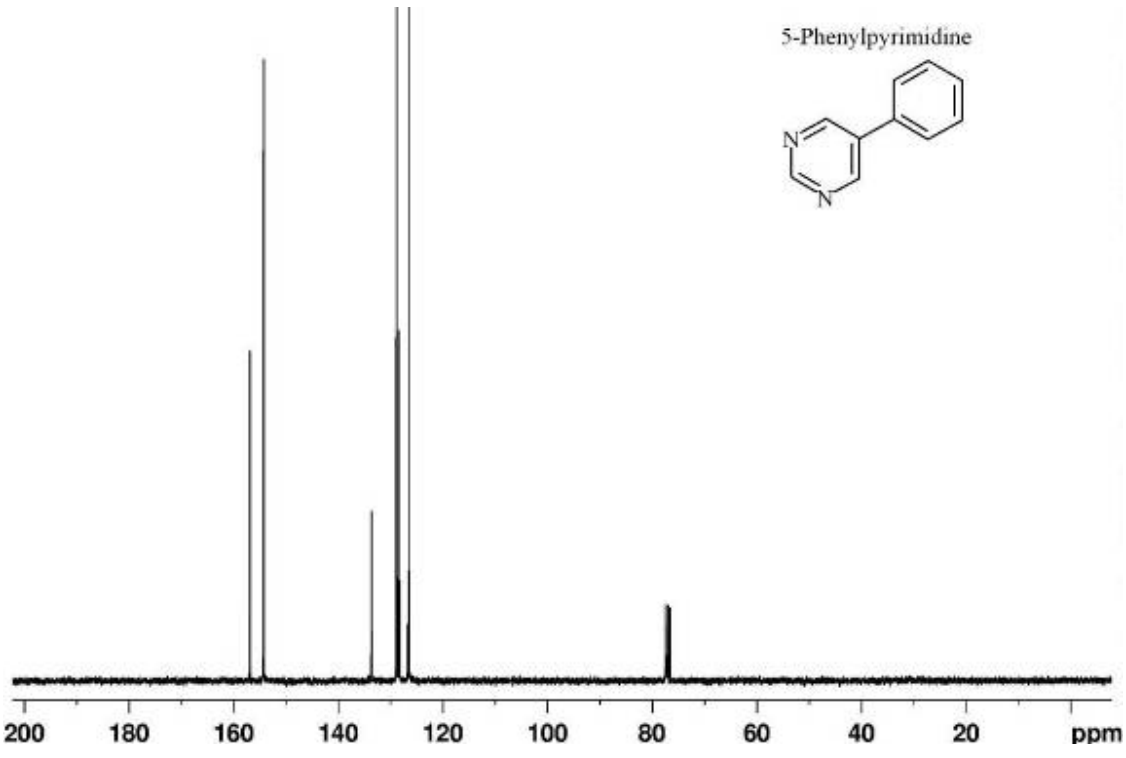

3-Phenythiophine
S
10
9
8
7
6
5
4
3
2
1
0
ppm

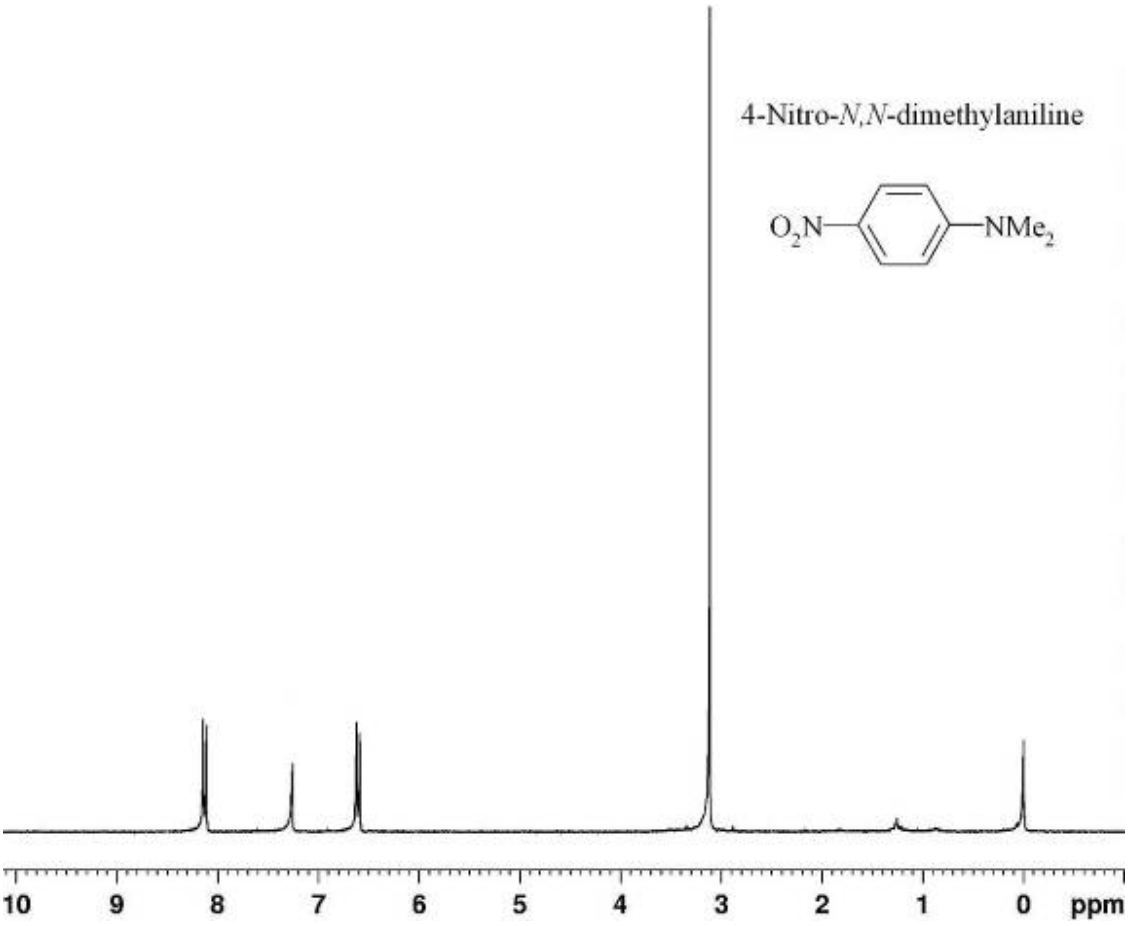

3-Phenythiophine
S
200
180
160
140
120
100
80
60
40
20
ppm

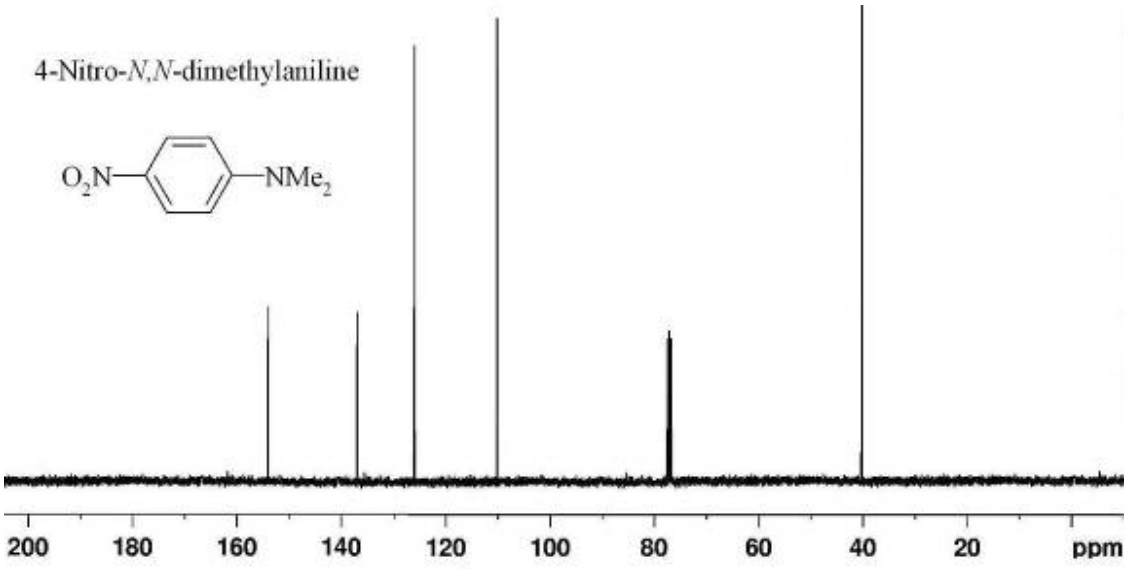

3-Phenylquinolene
N
10
9
8
7
6
5
4
3
2
1
0
ppm

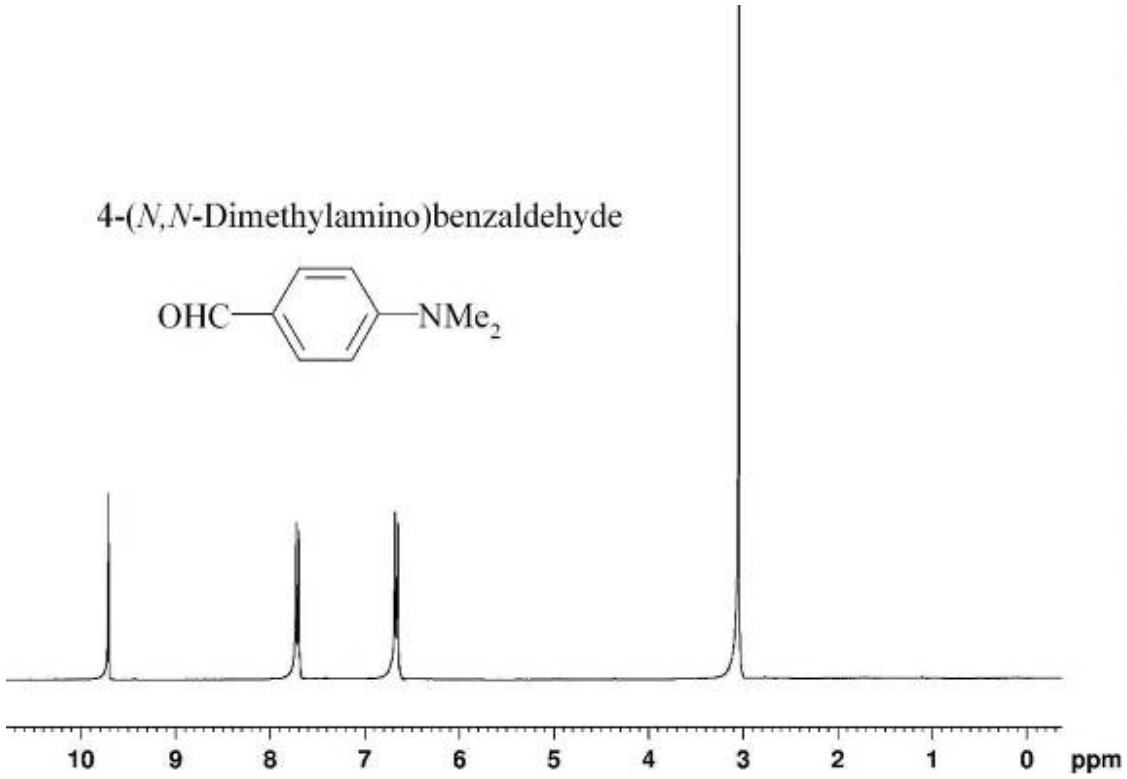

3-Phenylquinolene
N
200
180
160
140
120
100
80
60
40
20
ppm

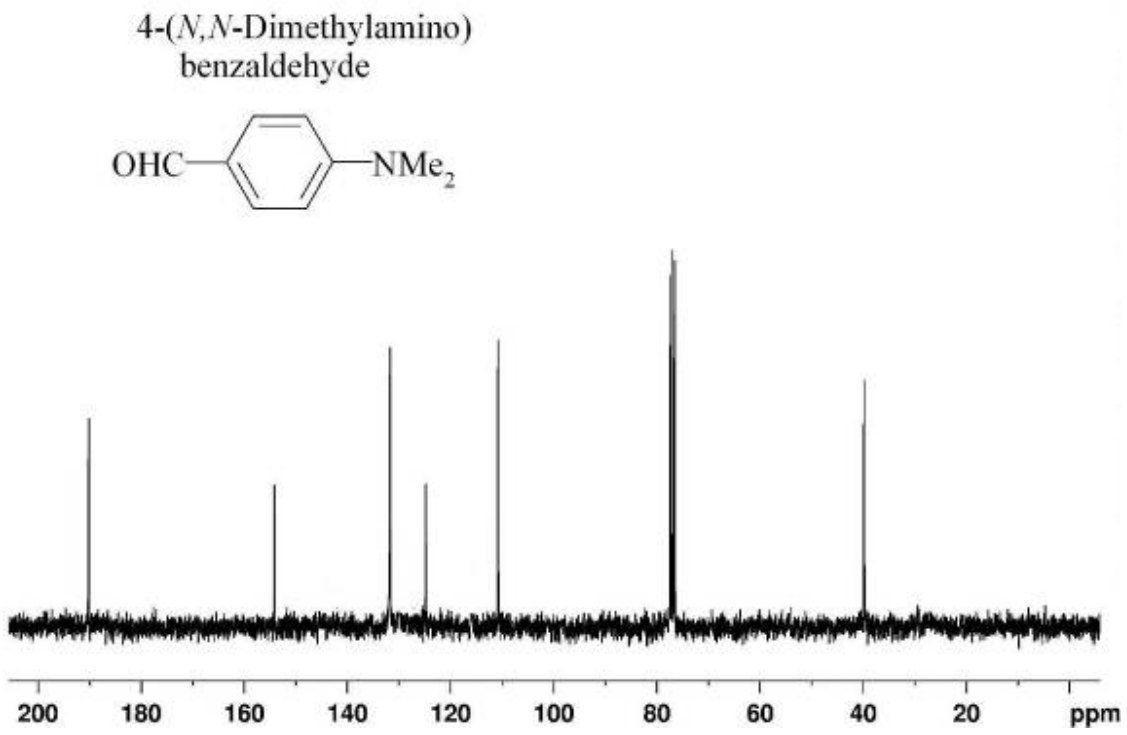

5-Phenylpyrimidine
N
N
10
9
8
7
6
5
4
3
2
1
0
ppm


5-Phenylpyrimidine
N
N
200
180
160
140
120
100
80
60
40
20
ppm


4-Nitro-N,N-dimethylaniline
O2N
NMe2
10
9
8
7
6
5
4
3
2
1
0
ppm


4-Nitro-N,N-dimethylaniline
O2N
NMe2
200
180
160
140
120
100
80
60
40
20
ppm


4-(N,N-Dimethylamino)benzaldehyde
OHC
NMe2
10
9
8
7
6
5
4
3
2
1
0
ppm


4-(N,N-Dimethylamino)
benzaldehyde
OHC
NMe2
200
180
160
140
120
100
80
60
40
20
ppm