Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Retention of Palladium and Phosphine Ligands using Nanoporous Polydicyclopentadiene Membranes

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Experimental Section

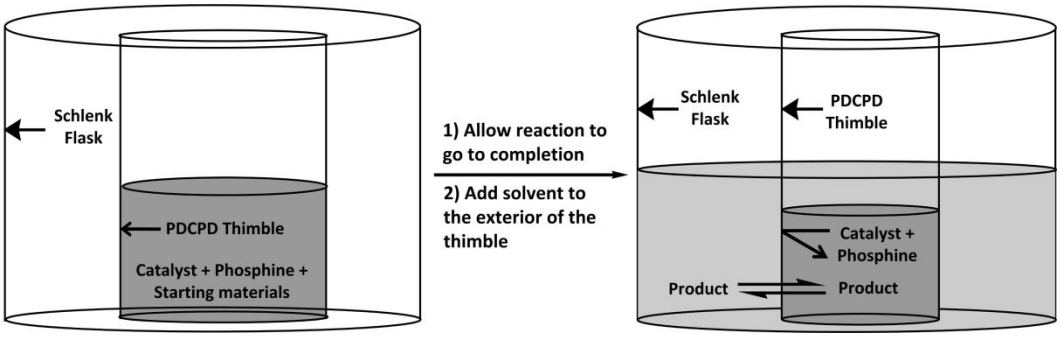
Materials. Dicyclopentadiene, palladium acetate, X-Phos, bromobenzene, bromotoluene, bromoanisole, iodotoluene, aniline, morpholine, phenylacetylene, diphenylamine, nitrobenzaldehyde, cholesterol, 1-octadecene, hexanoic acid, triphenylamine, tricyclohexylphosphine, triphenylamine, tributylamine, 1000 ppm palladium standard, and solvents were purchased at their highest purity from Aldrich and Acros and used as received.

Characterization. ^{1}H NMR and ^{13}C NMR spectra were acquired by Bruker DPX-300 at 300 MHz and 75 MHz respectively and referenced to TMS. Palladium concentrations were measured on a Varian 720-ES ICP optical emission spectrometer. IR spectra were acquired on a Bruker Tensor 27. The detector was the standard room temperature DTGS (deuterated tri-glycine sulfate) detector.

Fabrication of PDCPD thimbles. A mold was prepared by placing a cylindrical aluminum rod (18 mm x 86 mm) in a glass vial (20 mm x 78 mm) with paper spacers between the rod and glass. The rod was centered in the glass vial with the spacers and was ca 1 mm from the bottom of the glass vial. Commercially available dicyclopentadiene (24 mL, 0.177 mol) was heated at 35 °C for 10 min to melt it. The Grubbs second generation catalyst (15 mg, 0.017 mmol) was mixed with dichloromethane (0.5 mL) and added to the dicyclopentadiene and thoroughly mixed. This solution was then added to a mold via a pipette. The mold was heated in a water bath at 50 °C for 1.5 h. Next, the mold was immersed in liquid nitrogen to remove the glass vial from the PDCPD. The PDCPD on the rod was then swelled in dichloromethane mixed with ethyl vinyl ether to remove the PDCPD thimble from the aluminum rod. The thimbles were dried in air and then under vacuum.

A general description of how the experiments were completed using PDCPD thimbles. In the experiments described here, the PDCPD thimbles were initially added to glass reaction vessels. Next, the catalysts, solvent, and a stir bar were added to the interior of the thimbles. The reactions were completed at the indicated times and temperatures. Next, a stir

bar was added to the exterior of the thimbles with solvent to extract the product. The extraction was based on diffusion as no external pressure was applied. The solvent on the exterior of the thimble was easily removed from the glass vessel.



Buchwald-Hartwig reaction of bromobenzene with aniline. A PDCPD thimble containing $Pd(OAc)_2$ (10 mg, 0.045 mmol), X-Phos (42 mg, 0.089 mmol), and KO*t*-Bu (0.139 g, 1.25 mmol) was placed in a Schlenk flask with a stir bar. The whole set-up was evacuated and backfilled with N_2 three times. Under flowing N_2, bromobenzene (0.093 ml, 0.89 mmol), aniline (0.097 ml, 1.07 mmol), and toluene (5 mL) were added. The Schlenk flask was then heated in an oil bath at 80 °C for 7 h. The reaction was allowed to cool to room temperature. Hexane (15 mL) was added to the exterior of the thimble to extract the product. During the extraction, the solvents on the interior and exterior of the thimble were stirred. After 24 h, the solvent on the exterior was replaced with 15 mL of fresh hexane. After 48 h, the hexane extracts were combined, and the solvent was removed in vacuo. The amine was isolated as a white solid by column chromatography using hexanes/EtOAc (95/5). NMR spectra matched those reported in the literature.[1] ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.25-7.28 (m, 4H), 7.07 (d, 4H), 6.91 (t, 2H), 5.72 (s, 1H). ^{13}C NMR (75 MHz; $CDCl_3$, δ): 145.91, 132.18, 123.80, 120.61.

Buchwald-Hartwig reaction of bromotoluene with aniline. The same procedure as entry 1 was followed. The amine was isolated as a yellow solid by column chromatography using hexanes/EtOAc (95/5). NMR spectra matched those reported in the literature.[2] ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.20 (t, 2H), 7.04 (d, 2H), 6.93-6.99 (m, 4H), 6.81 (t, 1H), 5.54 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$, δ): 143.07, 139.37, 130.05, 128.98, 128.44, 119.40, 117.99, 115.96, 19.84.

Buchwald-Hartwig reaction of bromoanisole with aniline. The same procedure as entry 1 was followed. The amine was isolated as a brown solid by column chromatography using hexanes/EtOAc (95/5). NMR spectra matched those reported in the literature.[1,3] ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.21 (t, 2H), 7.09 (d, 2H), 6.83-6.92 (m, 5H), 5.50 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$, δ): 155.32, 143.04, 130.08, 128.96, 128.44, 119.40, 117.99, 115.95, 55.6.

Buchwald-Hartwig reaction of bromoanisole with morpholine. The same procedure as entry 1 was followed. The amine was isolated as a white solid by column chromatography using hexanes/EtOAc (95/5). NMR spectra matched those reported in the literature.[4] ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.83-6.91 (m, 4H), 3.84-3.87 (m, 4H), 3.77 (s, 3H), 3.03-3.07 (m, 4H). ^{13}C NMR (75 MHz; $CDCl_3$, δ): 156.63, 148.31, 120.51, 117.17, 69.74, 58.26, 53.50.

Buchwald-Hartwig reaction of iodotoluene with aniline. The same procedure as entry 1 was followed. The amine was isolated as a yellow solid by column chromatography using hexanes/EtOAc (95/5). NMR spectra matched those reported in the literature.[2] ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.23-7.27 (t, 2H), 7.09 (d, 2H), 7.01-7.05 (m, 4H), 6.87-6.93 (t, 1H), 5.63 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$, δ): 143.04, 139.37, 130.05, 128.96, 128.44, 119.40, 117.99, 115.96, 19.84.

Sonogashira coupling of 4-bromoanisole with phenylacetylene. A PDCPD thimble containing $Pd_2(dba)_3$ (16 mg, 0.0178 mmol), X-phos (16 mg, 0.035 mmol), and CuI (4.5 mg, 0.023 mmol) was placed in a Schlenk flask with a stir bar. The whole set-up was evacuated and backfilled with N_2 three times. Under flowing N_2, 4-bromoanisole (0.11 ml, 0.89 mmol), phenylacetylene (0.13 ml, 1.18 mmol), triethylamine (0.16 mL, 1.18 mmol), and toluene (5 mL) were added. The Schlenk flask was then heated in an oil bath at 80 °C for 7 h. The reaction was allowed to cool to room temperature. Hexane (15 mL) was added to the exterior of the thimble to extract the product. After 24 h, the solvent on the exterior was replaced with 15 mL of fresh hexane. After 48 h, the hexane extracts were combined and the solvent was removed in vacuo. The product was isolated by column chromatography using hexanes/EtOAc (95/5). NMR spectra matched those reported in the literature.[4] ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.45-7.52 (m, 4H), 7.31-7.33 (m, 3H), 6.85 (d, 2H), 3.82 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$, δ): 159.97, 133.39, 131.79, 128.66, 128.28, 123.95, 115.73, 114.35, 89.74, 88.43, 55.61.

Sonogashira coupling of 4-bromotoluene with phenylacetylene. The procedure from the previous paragraph was followed. The product was isolated by column chromatography using hexanes/EtOAc (95/5). NMR spectra matched those reported in the literature.[4] ^{1}H NMR

(300 MHz, $CDCl_3$, δ): 7.49-7.52 (m, 2H), 7.40 (d, 2H), 7.29-7.31 (m, 3H), 7.11 (d, 2H), 2.33 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$, δ): 138.73, 131.92, 131.87, 129.49, 128.68, 128.44, 123.87, 120.58, 89.96, 89.13, 21.85.

Procedure to measure the flux of diphenylamine and phosphine ligands or organic substrates (Table 2 in main text). Diphenylamine (0.059 mmol) and phosphine ligand or organic substrate (0.59 mmol) were dissolved in 4 mL of toluene and added to the interior of a PDCPD thimble. On the exterior 10 mL of fresh toluene was added. Aliquots (0.2 mL) were removed from the interior and exterior after 24 h and larger aliquots (1 mL) were removed from the interior and exterior after 48 h. A solution was prepared by adding 0.1 mL tetraethyleneglycol to 49.9 mL $CHCl_3$. 1 mL of this solution was diluted by adding 49 mL $CHCl_3$. Known amounts of the above solution were added to the aliquots to provide an internal standard to find the absolute concentration of the reagents. The solvent was removed in vacuo. ^1H NMR spectroscopy of the aliquots provided Se/Si after 24 h and 48 h.

Procedure to recycle Pd and X-Phos in a Buchwald-Hartwig reaction. A PDCPD thimble containing $Pd(OAc)_2$ (10 mg, 0.045 mmol), X-Phos (42 mg, 0.089 mmol), and KO*t*-Bu (0.14 g, 1.25 mmol) was placed in a Schlenk flask with a stir bar. The whole set-up was evacuated and backfilled with N_2 three times. Under flowing N_2, 4-bromotoluene (0.11 mL, 0.89 mmol), aniline (0.097 mL, 1.07 mmol), and toluene (5 mL) were added. The Schlenk flask was then heated in an oil bath at 80 °C for 7 h. Hexane (15 mL) was added to the exterior of the thimble to extract the product. During the extraction, the solvent on the interior and exterior of the thimble was stirred. After 24 h, the solvent on the exterior was replaced with 15 mL of fresh hexane. After 48 h, the hexane extracts were combined and the hexane was removed in vacuo. Toluene on the interior of the thimble was removed in vacuo. Fresh toluene (4 mL) was added to the interior of the thimble. The phosphine and palladium were allowed to diffuse to the toluene on the interior of the thimble for 24 h.

KO*t*-Bu (0.139 g, 1.25 mmol), 4-bromotoluene (0.11 mL, 0.89 mmol), and aniline (0.097 mL, 1.07 mmol) were added to the interior of the thimble for cycle 2. The Schlenk flask was heated at 80° C. After the reaction went to completion for 2nd cycle, the same procedure was followed as for cycle 1. Palladium and phosphine ligand could be recycled for 5 cycles by the same procedure. The thimble broke during the reaction of the 6th cycle.

The hexane extracts were analyzed to calculate the yield of product and the retention of palladium for each cycle. The yield of product was calculated based on ^1H NMR spectra of the extracts using internal standards of tetraethylene glycol. No evidence of the phosphine was

found in the products in the ^{1}H NMR spectra of extracts. The same extracts were used to prepare the sample for ICP-OES. The ICP-OES results determined the retention of palladium for each cycle.

Procedure to recycle Pd and X-Phos in a Buchwald-Hartwig reaction (3 h reaction cycles). A PDCPD thimble containing $Pd(OAc)_2$ (10 mg, 0.045 mmol), X-Phos (42 mg, 0.089 mmol), and KO*t*-Bu (0.14 g, 1.25 mmol) was placed in a Schlenk flask with a stir bar. The whole set-up was evacuated and backfilled with N_2 three times. Under flowing N_2, 4-bromotoluene (0.11 mL, 0.89 mmol), aniline (0.097 mL, 1.07 mmol), and toluene (5 mL) were added. The Schlenk flask was then heated in an oil bath at 80 °C for 3 h. Hexane (15 mL) was added to the exterior of the thimble to extract the product. During the extraction, the solvent on the interior and exterior of the thimble was stirred. After 24 h, the solvent on the exterior was replaced with 15 mL of fresh hexane. After 48 h, the hexane extracts were combined and the hexane was removed in vacuo. Toluene on the interior of the thimble was removed in vacuo. Fresh toluene (4 mL) was added to the interior of the thimble. The phosphine and palladium were allowed to diffuse to toluene on the interior of the thimble for 24 h.

KO*t*-Bu (0.139 g, 1.25 mmol), 4-bromotoluene (0.11 mL, 0.89 mmol), and aniline (0.097 mL, 1.07 mmol) were added to the interior of the thimble for cycle 2. The Schlenk flask was heated at 80° C. After 3 h of reaction for 2nd cycle, the same procedure was followed as for cycle 1. Four cycles were completed and each had only 3 h of heating at 80 ^{o}C to complete the reactions. The thimble broke during the extraction of the 5th cycle.

The hexane extracts were analyzed to calculate the yield of product and the retention of palladium for each cycle (Table 1). The yield of product was calculated based on ^{1}H NMR spectra of the extracts using internal standards of tetraethylene glycol. No evidence of the phosphine was found in the products in the ^{1}H NMR spectra of extracts. The same extracts were used to prepare the sample for ICP-OES. The ICP-OES results determined the retention of palladium for each cycle.

Table 1 Recycling experiments of 4-bromotoluene and aniline.

Cycle	Conversion	[a]NMR yield (%)	[b]Retention of Pd (%)	[c]Concentration of Pd in product (ppm)
1	84	77	99.97	10.1
2	76	70	99.97	10.1
3	74	67	99.77	82.1
4	73	65	99.97	10.1

[a]These values were found using tetraethylene glycol as an internal standard. [b]These values represent the amount of the Pd added to the interior of the thimble that did not extract to the exterior. [c]Measured by ICP-OES.

The results demonstrated that the catalyst activity was nearly constant over the course of 4 cycles. The product and unreacted starting materials were extracted to the exterior of PDCPD thimbles leaving behind palladium and X-Phos inside the thimble. The retention of palladium was excellent for 4 cycles.

ICP-OES sample preparation. After each reaction in Table 1 in the article went to completion on the interior of a thimble, hexane (15 mL) was added to the exterior of the thimble. After 24 h, the solvent on the exterior was replaced with 15 mL of fresh hexane. After 48 h, the hexane extracts were combined, and the solvent was removed in vacuo. HCl (0.85 mL), HNO_3 (0.85 mL), and H_2O (4.3 mL) were added to the crude product. A watch glass was placed on top of the jar and it was heated to 95 °C for 30 min. The solution was diluted to 10 mL with HCl to prepare the sample. The 1000 ppm palladium ICP standard was diluted with HCl to prepare standards to calibrate the instrument. The internal standard for the measurement was 1 ppm yttrium solution. After calibration with the standards, the sample gave a concentration in ppm.

Procedure to measure flux of diphenylamine. Diphenylamine (0.59 mmol) was dissolved in 4 mL of solvent and added to the interior of a PDCPD thimble. Solvent (10 mL) was added to the exterior. Aliquots of 0.1 mL were taken from the interior and the exterior of the thimble after 2, 4, 6, 8, 10, 12, 14, 16, 18, 22, 24, 26, 36, and 48 h. A solution was prepared by adding 0.1 mL tetraethyleneglycol to 49.9 mL $CHCl_3$. This solution was diluted by adding $CHCl_3$ (49 mL) to 1 mL of the original solution. Known amounts of the above solution was added to the aliquots to provide an internal standard to find absolute concentration of diphenylamine. The solvent was removed in vacuo. ^{1}H NMR spectroscopy of the aliquots provided Se/Si at different time intervals. The concentrations of diphenylamine as a function of time are shown in Figure 1 and Figure 2.

The permeability coefficient, P (cm s^{-1}), was measured by fitting the data to the equation (1) shown below.

$$C_1 = \frac{M_o}{V_1}\left(\frac{V_1}{V_1+V_2} + \frac{V_2}{V_1+V_2}\exp\left(-\left(1+\frac{V_1}{V_2}\right)\frac{PAt}{V_1}\right)\right)$$

Where C_1 is the concentration on the upstream side of the membrane, V_1 is the upstream volume, V_2 is the downstream volume, M_o is the total moles of $HNPh_2$ in the system, A is the membrane area, and t is the time. The permeability coefficient indicates how rapidly a solute

will pass through a membrane and is linearly proportional to diffusion coefficient, D, according to $P = D/\lambda$ where λ is the membrane thickness.

The data measured for the concentration of $HNPh_2$ through PDCPD in toluene, hexanes, and methanol all fit the equation well (Figures 1 and 2). The values for the permeation constant were 3.39 x 10^{-2} cm s^{-1} in toluene, 2.45 x 10^{-2} cm s^{-1} in hexanes, and 2.27 x 10^{-2} cm s^{-1} in methanol. The decrease in these values as the solvent was changed from one that swells PDCPD well to one that did not swell it well was expected because PDCPD is a hard, cross-linked polymer that becomes rubbery when swollen. The amount that each solvent swells PDCPD is found in the following reference.[5]

Flux is defined as the amount of a molecule that moves through a unit area per unit time. To find the flux of diphenylamine in toluene, hexanes, and methanol the initial concentrations of diphenylamine on the exterior were used (Figures 3, 4, and 5). At early times the flux of diphenylamine was almost entirely in one direction, so this approximation was used to calculate flux. The flux was found from the slope of a plot of the amount of diphenylamine on the exterior of the thimble versus time.

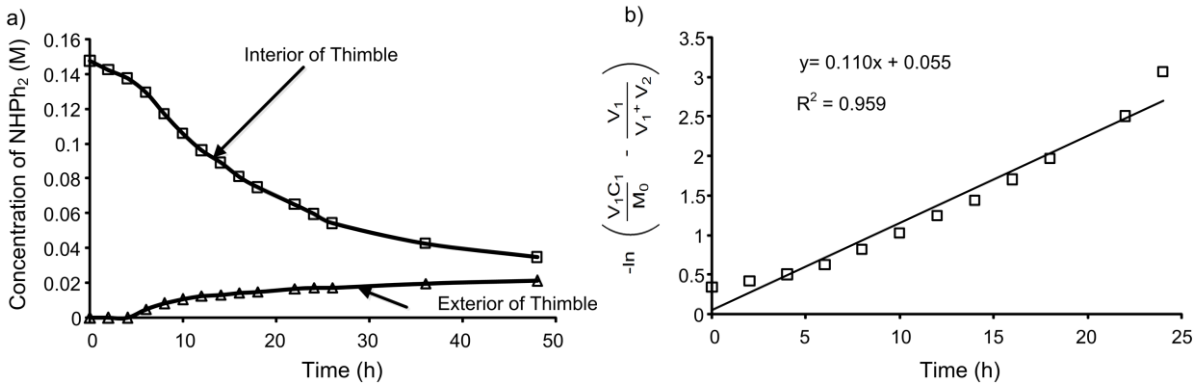


Figure 1: a) Diphenylamine was added to the interior of a thimble with methanol on the exterior and interior. The concentration of diphenylamine was monitored as a function of time and b) the data was fit to the equation in the text.

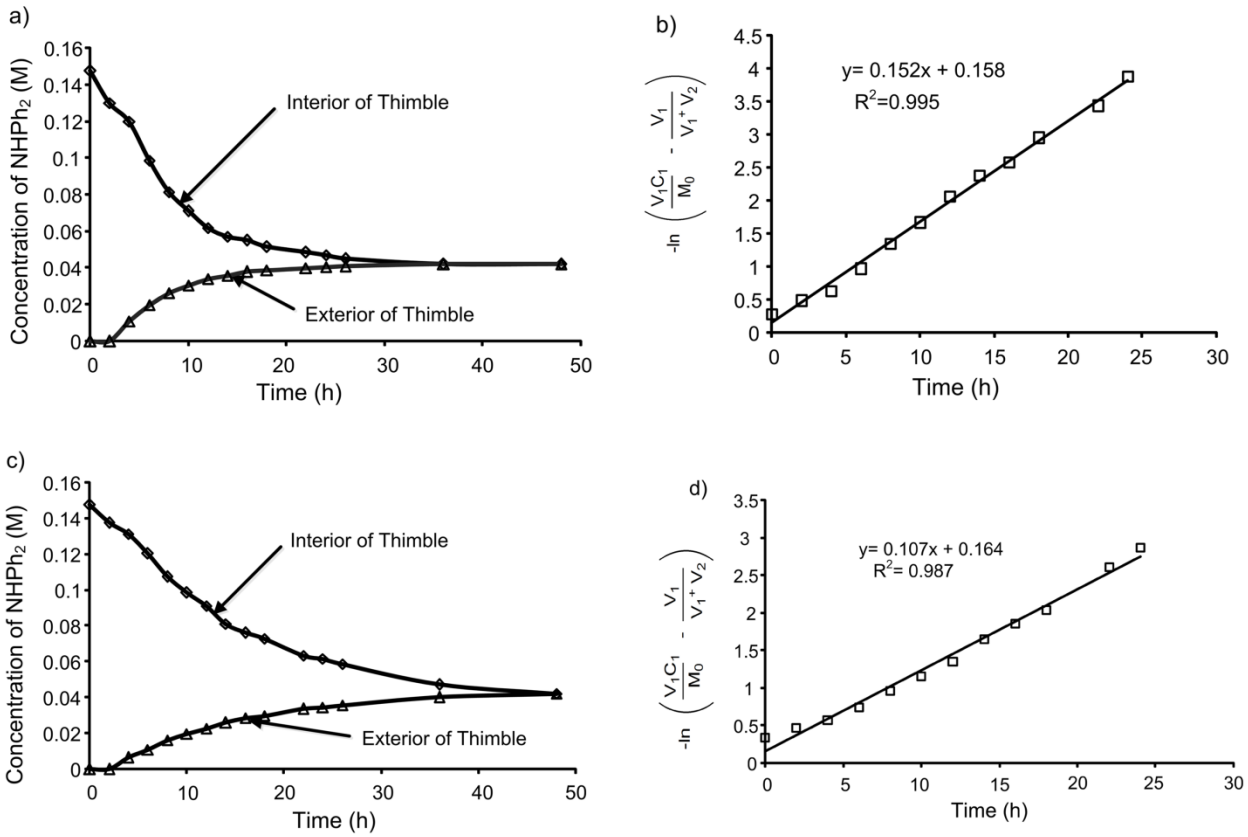


Figure 2. a) Diphenylamine was added to the interior of a thimble with toluene on the exterior and interior. The concentration of diphenylamine was monitored as a function of time and b) the data was fit to the equation in the text. c) and d) An identical experiment was completed using hexanes as the solvent.

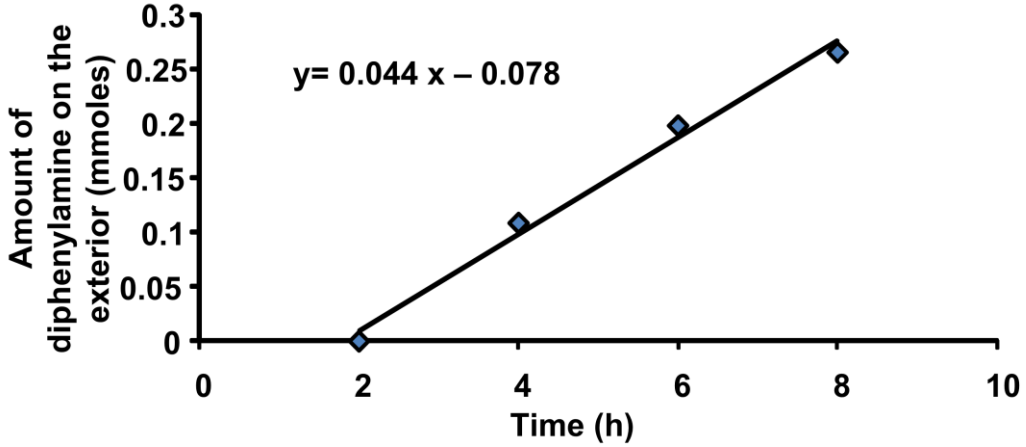


Figure 3. Flux of diphenylamine in toluene

Inner radius of the thimble = 0.9 cm

Height of solvent in the thimble = 2 cm

Area of the thimble = $\pi r^2 + 2\pi rh = 13.85\ cm^2$

Flux = Slope / Area

Flux of diphenylamine = 3.17×10^{-6} moles/cm^2 h for toluene

1.73×10^{-6} moles/cm^2 h for hexanes

1.22×10^{-6} moles/cm^2 h for methanol

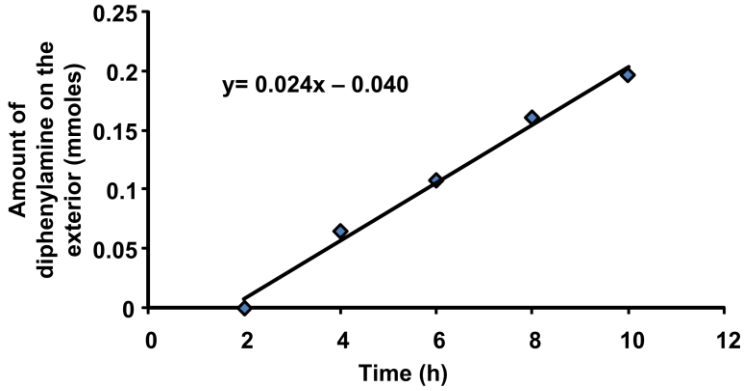


Figure 4. Flux of diphenylamine in hexanes

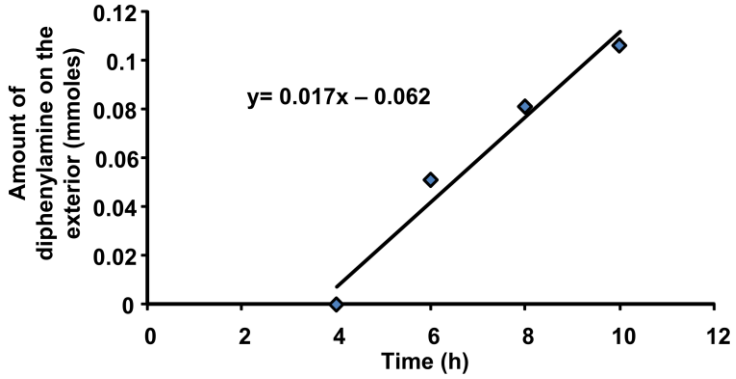


Figure 5. Flux of diphenylamine in methanol.

Procedure to measure the retention of $Pd(OAc)_2$ without X-Phos present. $Pd(OAc)_2$ (9.9 mg, 0.044 mmol) and octadecene (0.140 g, 0.565 mmol) were dissolved in 4 mL of toluene and added to the interior of a PDCPD thimble. Toluene (10 mL) was added to the exterior of the thimble. Aliquots (0.1 mL) were removed from the interior and exterior after 48 h. A solution was prepared by adding 0.1 mL tetraethyleneglycol to 49.9 mL $CHCl_3$. 1 mL of this solution was diluted by adding 49 mL $CHCl_3$. Known amounts of the above solution were added to the aliquots to provide an internal standard to find the absolute concentration of octadecene. The solvent was removed in vacuo. The concentrations of octadecene on the interior and exterior of the thimbles were measured from the ^1H NMR spectra of the aliquots. The remaining solvent

from the interior and exterior of the thimbles were removed separately and evaporated in vacuo. HCl (0.85 mL), HNO_3 (0.85 mL), and H_2O (4.3 mL) were added to the interior and exterior samples in a glass vial. A watch glass was placed on top of the vials and they were heated to 95 °C for 30 min. The solution was diluted to 10 mL with HCl to prepare the sample. The 1000 ppm palladium ICP standard was diluted with HCl to prepare standards to calibrate the instrument. The internal standard for the measurement was 1 ppm yttrium solution. After calibration with the standards, the concentration of Pd in the samples from the interior and exterior of the thimbles was measured.

Procedure to measure retention of $Pd(OAc)_2$ with X-Phos present. $Pd(OAc)_2$ (9.9 mg, 0.044 mmol), X-Phos (0.042 g, 0.088 mmol) and octadecene (0.140 g, 0.565 mmol) were dissolved in 4 mL of toluene and added to the interior of a PDCPD thimble. Toluene (10 mL) was added to the exterior of the thimble. Aliquots (0.1 mL) were removed from the interior and exterior after 48 h. A solution was prepared by adding 0.1 mL tetraethyleneglycol to 49.9 mL $CHCl_3$. 1 mL of this solution was diluted by adding 49 mL $CHCl_3$. Known amounts of the above solution were added to the aliquots to provide an internal standard to find the absolute concentration of octadecene. The solvent was removed in vacuo. The concentrations of octadecene on the interior and exterior of the thimbles were measured from the ^{1}H NMR spectra of the aliquots. The remaining solvent from the interior and exterior of the thimbles were removed separately and evaporated in vacuo. The samples removed from the interior and exterior of the thimbles were analyzed by ICP-OES as described above.

Procedure to measure retention of $Pd_2(dba)_3$ without X-Phos present. $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol) and octadecene (0.140 g, 0.565 mmol) were dissolved in 4 mL of toluene and added to the interior of a PDCPD thimble. Toluene (10 mL) was added to the exterior of the thimble. Aliquots (0.1 mL) were removed from the interior and exterior after 48 h. A solution was prepared by adding 0.1 mL tetraethyleneglycol to 49.9 mL $CHCl_3$. 1 mL of this solution was diluted by adding 49 mL $CHCl_3$. Known amounts of the above solution were added to the aliquots to provide an internal The concentrations of octadecene on the interior and exterior of the thimbles were measured from the ^{1}H NMR spectra of the aliquots. The remaining solvent from the interior and exterior of the thimbles were removed separately and evaporated in vacuo. HCl (0.85 mL), HNO_3 (0.85 mL), and H_2O (4.3 mL) were added to the interior and exterior samples in a glass vial. A watch glass was placed on top of the vials and they were heated to 95 °C for 30 min. The solution was diluted to 10 mL with HCl to prepare the sample. The 1000 ppm palladium ICP standard was diluted with HCl to prepare standards to calibrate the instrument.

The internal standard for the measurement was 1 ppm yttrium solution. After calibration with the standards, the concentration of Pd in the samples from the interior and exterior of the thimbles was measured.

Procedure to measure retention of $Pd_2(dba)_3$ with X-Phos present. $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), X-Phos (4.8 mg, 0.01 mmol) and octadecene (0.140 g, 0.565 mmol) were dissolved in 4 mL of toluene and added to the interior of a PDCPD thimble. Toluene (10 mL) was added to the exterior of the thimble. Aliquots (0.1 mL) were removed from the interior and exterior after 48 h. A solution was prepared by adding 0.1 mL tetraethyleneglycol to 49.9 mL $CHCl_3$. 1 mL of this solution was diluted by adding 49 mL $CHCl_3$. Known amounts of the above solution were added to the aliquots to provide an internal standard to find the absolute concentration of octadecene. The solvent was removed in vacuo. The concentrations of octadecene on the interior and exterior of the thimbles were measured from the ^{1}H NMR spectra of the aliquots. The remaining solvent from the interior and exterior of the thimbles were removed separately and evaporated in vacuo. The samples removed from the interior and exterior of the thimbles were analyzed by ICP-OES as described above.

Measurement of the critical area. Each molecule was drawn in Spartan `08 V1.2.0 and imaged using a ball and spoke representation. The energy was minimized by finding the equilibrium geometry at ground state with a semi-empirical method using AM1 parameters. The surface area and molecular volume were calculated based on a space filling model. The space filling model was a 3D molecular model with atoms represented by spheres whose radius was assumed to be the Van der Waals radius determined by the electron density cut-off at 0.002 electrons/Å^3. Each molecule was analyzed to find the conformation with the lowest rectangular, cross-sectional area (Table 1).

In Figure 6 two different images of the lowest energy conformer of diphenylamine are shown using ball and spoke models. Beneath these images are diphenylamine with an arrow to indicate how the molecule was viewed to find the cross-sectional area. To find the minimum cross-sectional area (Figure 6a), the molecule was viewed from many different angles. The image in Figure 6b is shown to demonstrate one of many ways to view diphenylamine that had a much larger cross-sectional area than in Figure 6a. The lowest cross-sectional area for triphenylphosphine (Figure 7) and cholesterol (Figure 8) were found using the same method.

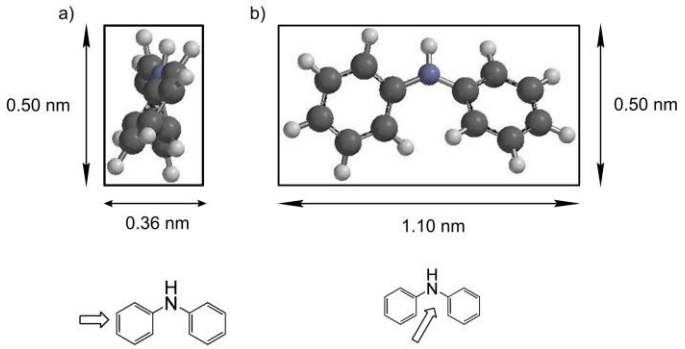


Figure 6. Two views of the lowest energy conformation of diphenylamine. The image in a) has the lowest cross-sectional area and the image in b) has a much larger cross-sectional area.

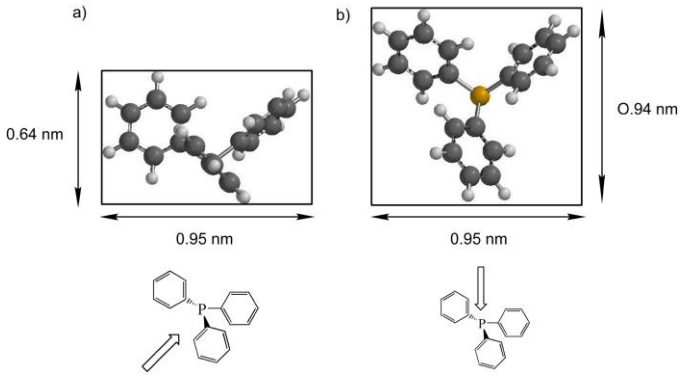


Figure 7. Two views of the lowest energy conformation of triphenylphosphine. The image in a) has the lowest cross-sectional area and the image in b) has a much larger cross-sectional area.

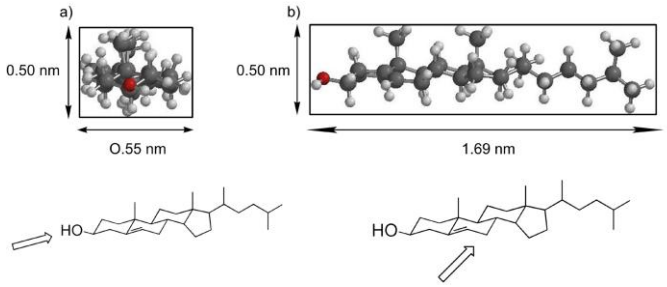


Figure 8. Two views of the lowest energy conformation of cholesterol. The image in a) has the lowest cross-sectional area and the image in b) has a much larger cross-sectional area.

Table 1. The physical parameters of molecules reported in this article.

Molecule	Permeates PDCPD	Molecular Weight (g mol^{-1})	Surface Area (nm^2)	Molecular Volume (nm^3)	Critical Area (nm^2)

hexanoic acid	Yes	116	1.65	0.135	0.067
p-nitrobenzaldehyde	Yes	151	1.64	0.142	0.060
diphenylamine	Yes	169	2.09	0.195	0.18
N-phenyl-*p*-toluidine	Yes	183	2.30	0.213	0.24
4-(4-methoxyphenyl)morpholine	Yes	191	2.34	0.217	0.20
4-(phenylethynyl)toluene	Yes	192	2.48	0.229	0.10
N-phenyl-*p*-anisidine	Yes	199	2.40	0.222	0.27
4-(phenylethynyl)anisole	Yes	208	2.58	0.238	0.24
octadecene	Yes	252	3.87	0.341	0.067
cholesterol	Yes	387	4.49	0.454	0.28
NBu_3	No	185	2.86	0.249	0.50
NPh_3	No	245	2.86	0.279	0.49
PPh_3	No	262	2.92	0.286	0.61
PCy_3	No	280	3.24	0.323	0.57
X-Phos	No	476	5.43	0.554	0.97

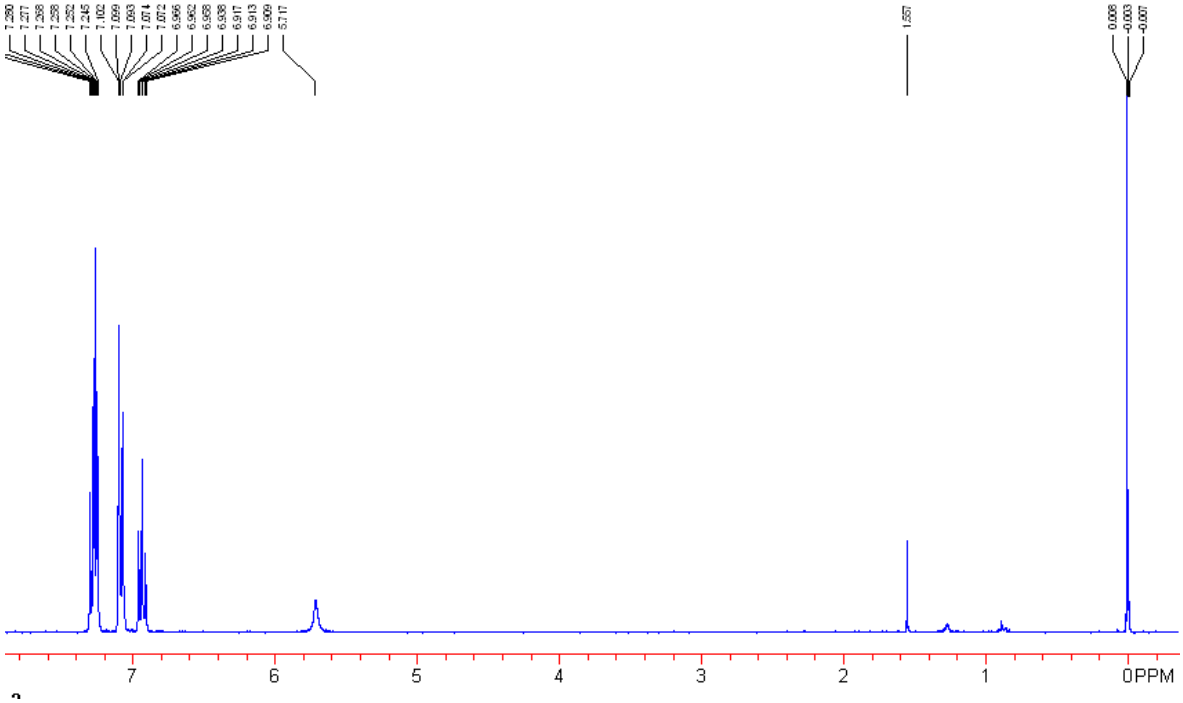


Figure 9. ^{1}H NMR spectrum of Entry 1, Table 1.

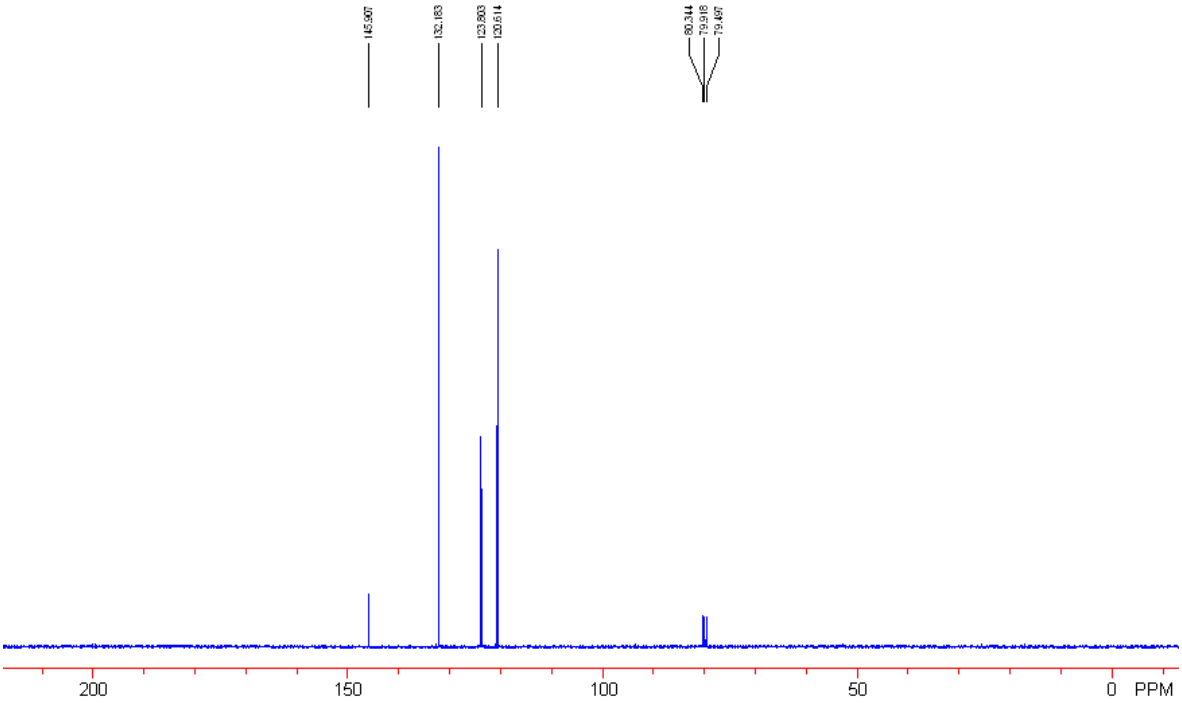


Figure 10. ^{13}C NMR spectrum of Entry 1, Table 1.

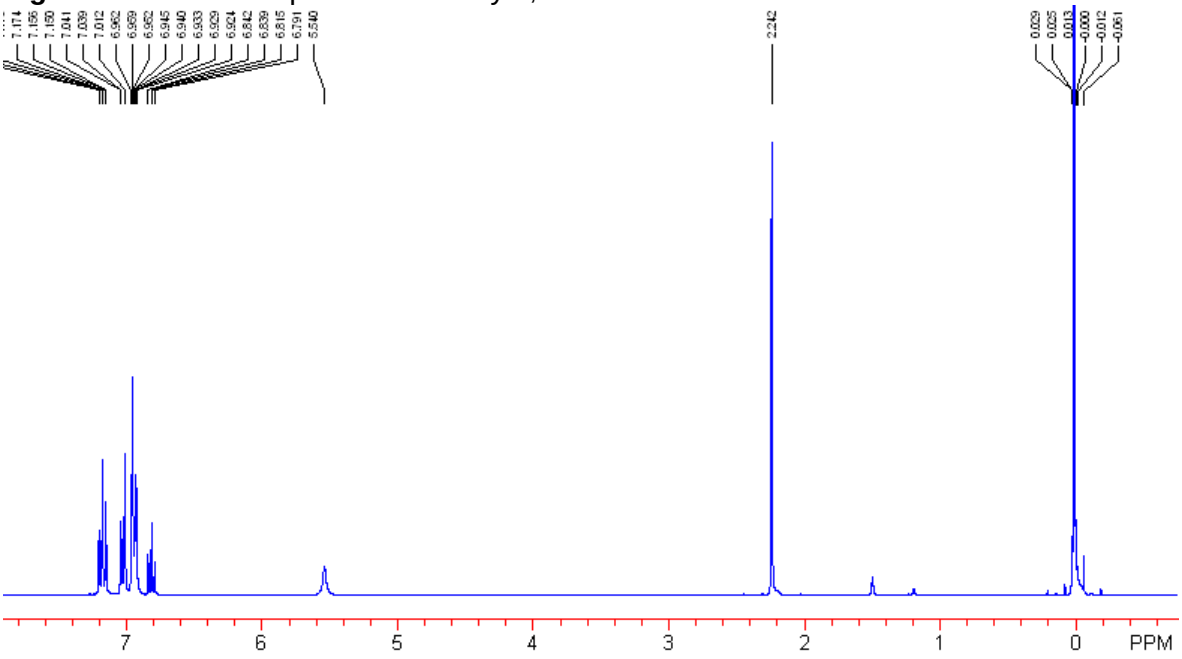


Figure 11. ^{1}H NMR spectrum of Entry 2, Table 1.

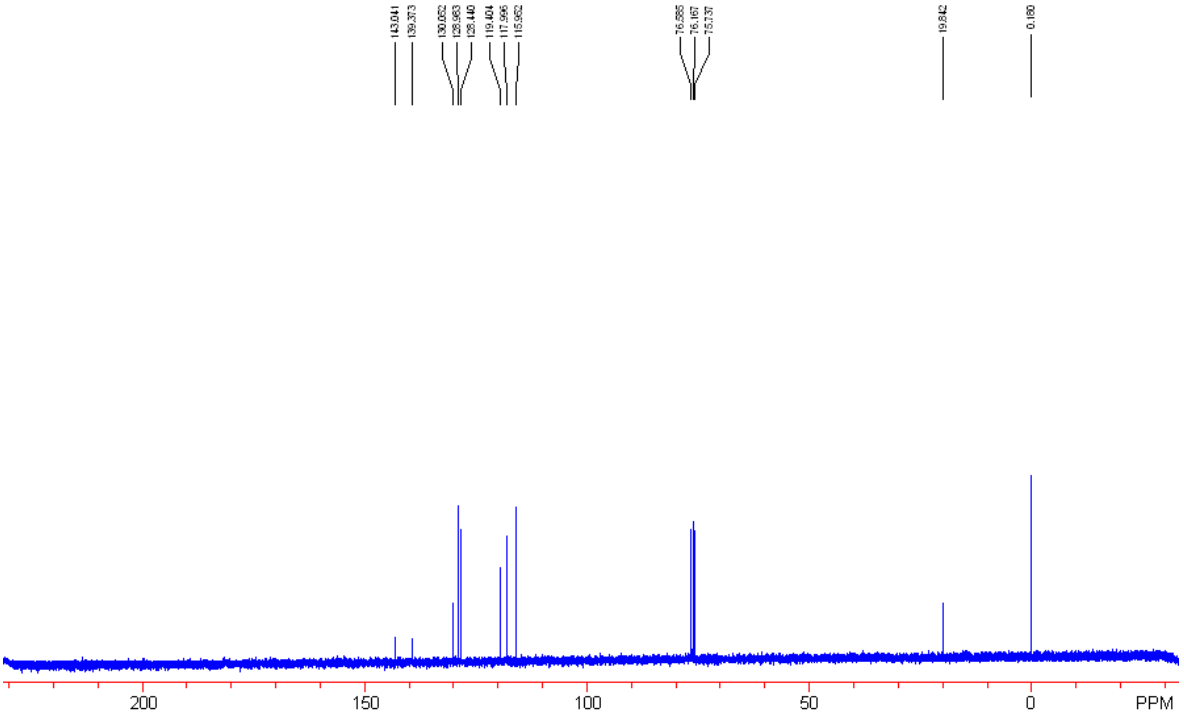


Figure 12. ^{13}C NMR spectrum of Entry 2, Table 1.

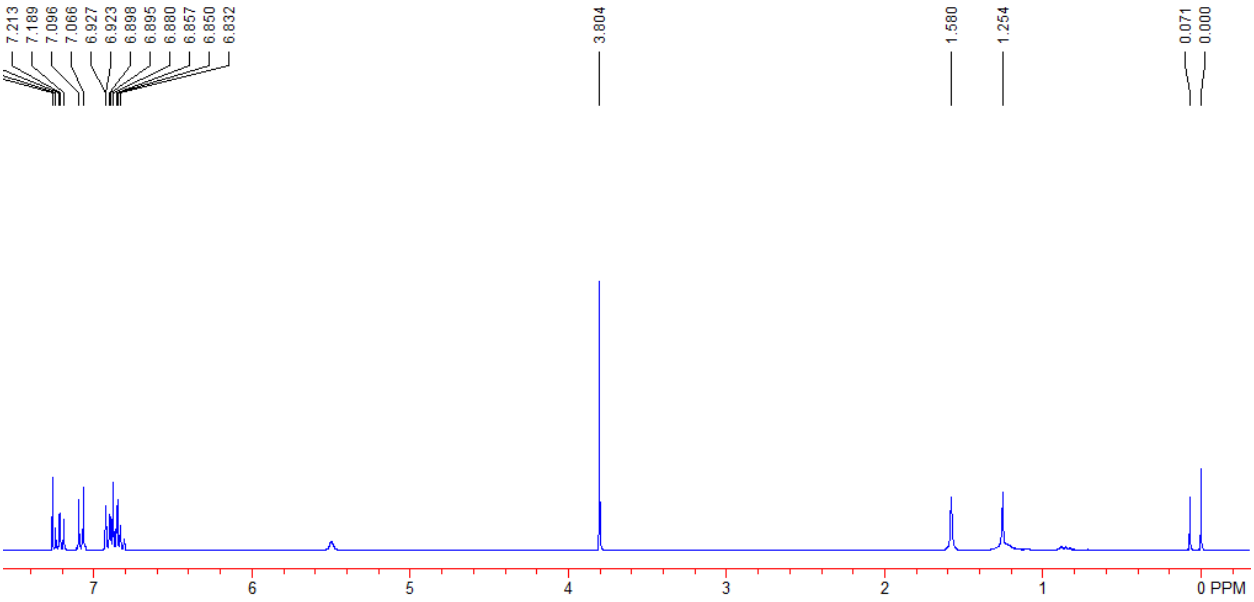


Figure 13. ^{1}H NMR spectrum of Entry 3, Table 1.

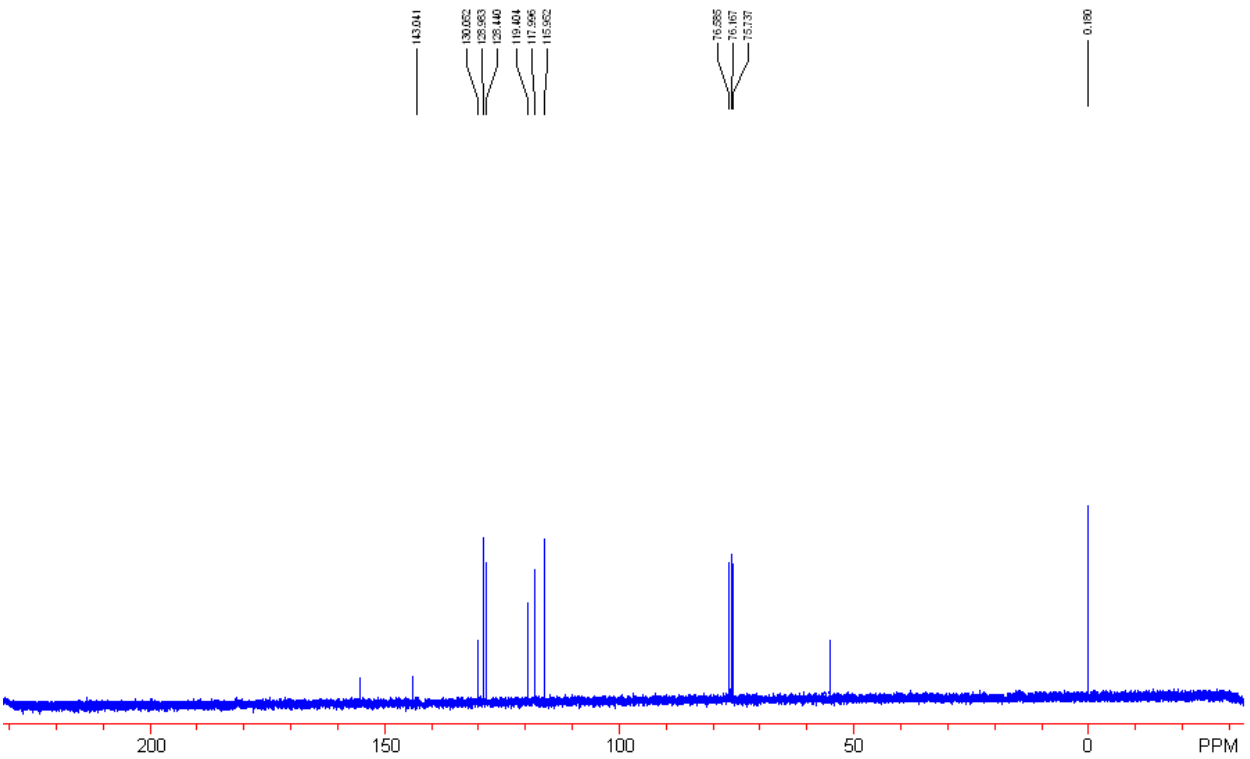


Figure 14. ^{13}C NMR spectrum of Entry 3, Table 1.

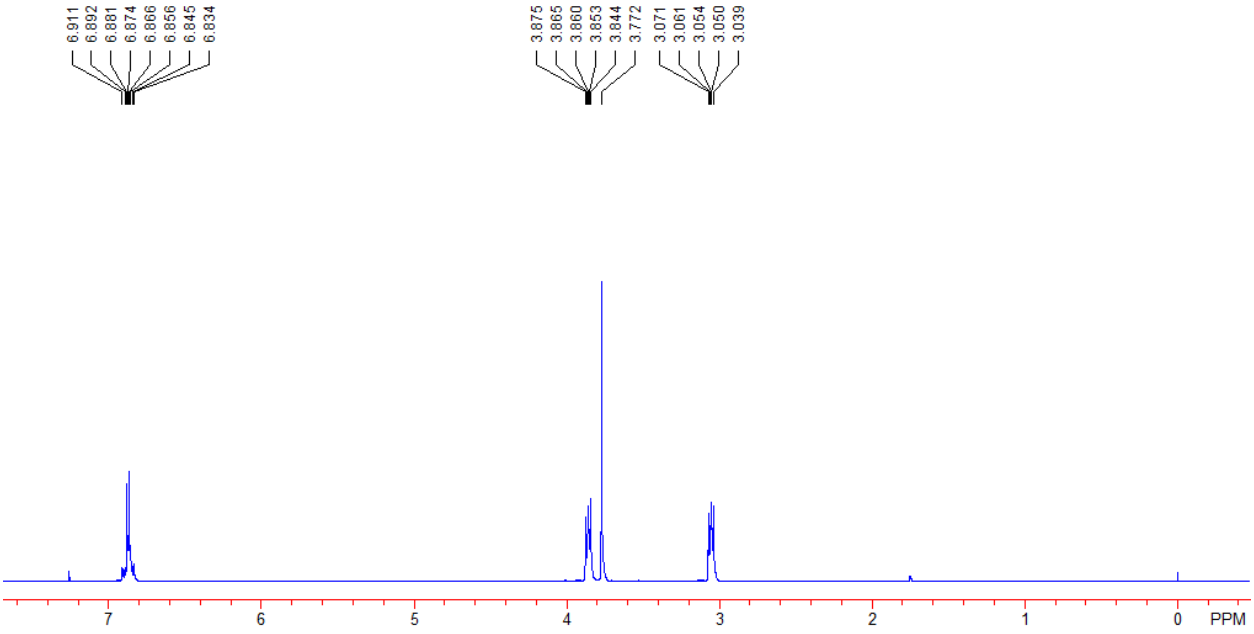


Figure 15. ^{1}H NMR spectrum of Entry 4, Table 1.

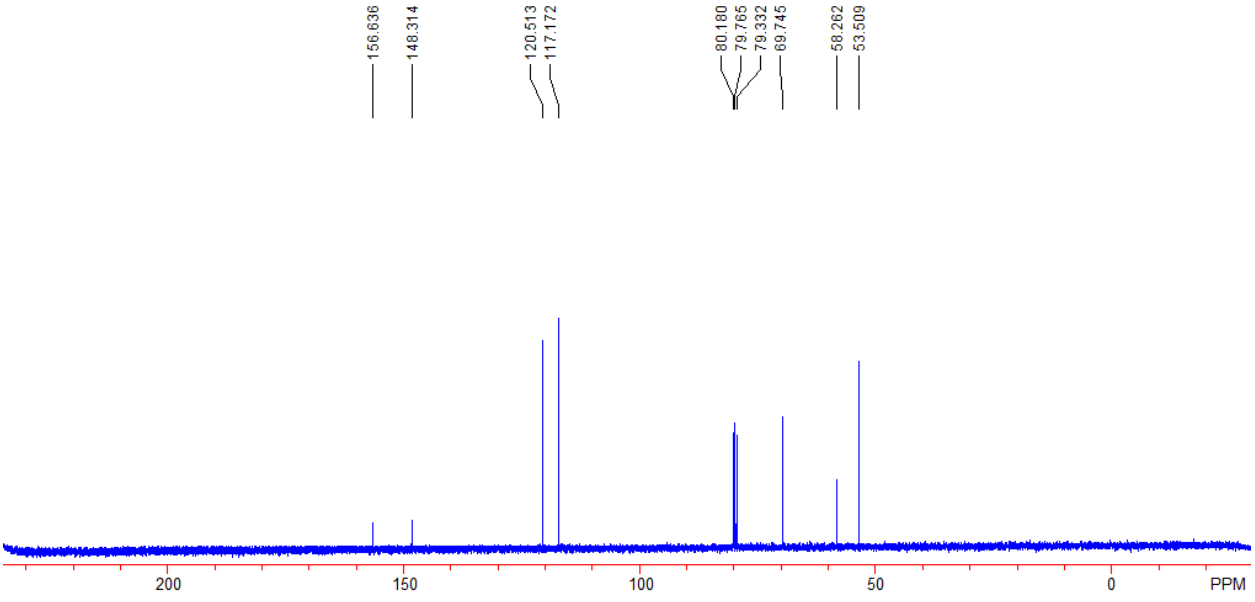


Figure 16. ^{13}C NMR spectrum of Entry 4, Table 1.

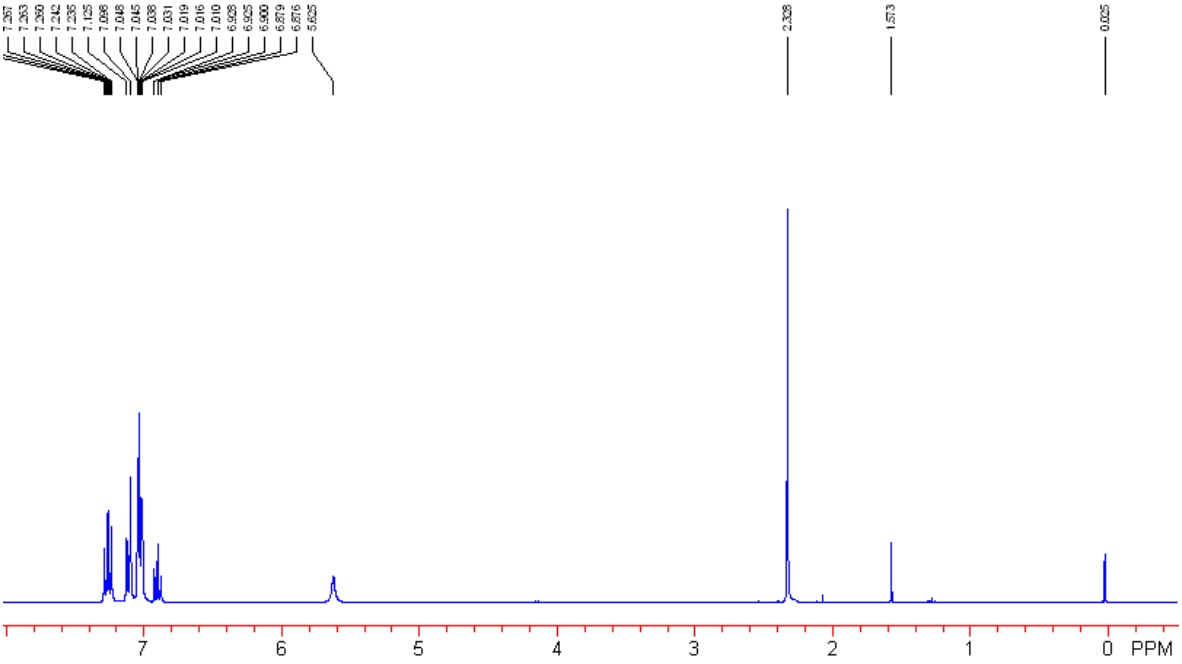


Figure 17. ^{1}H NMR spectrum of Entry 5, Table 1.

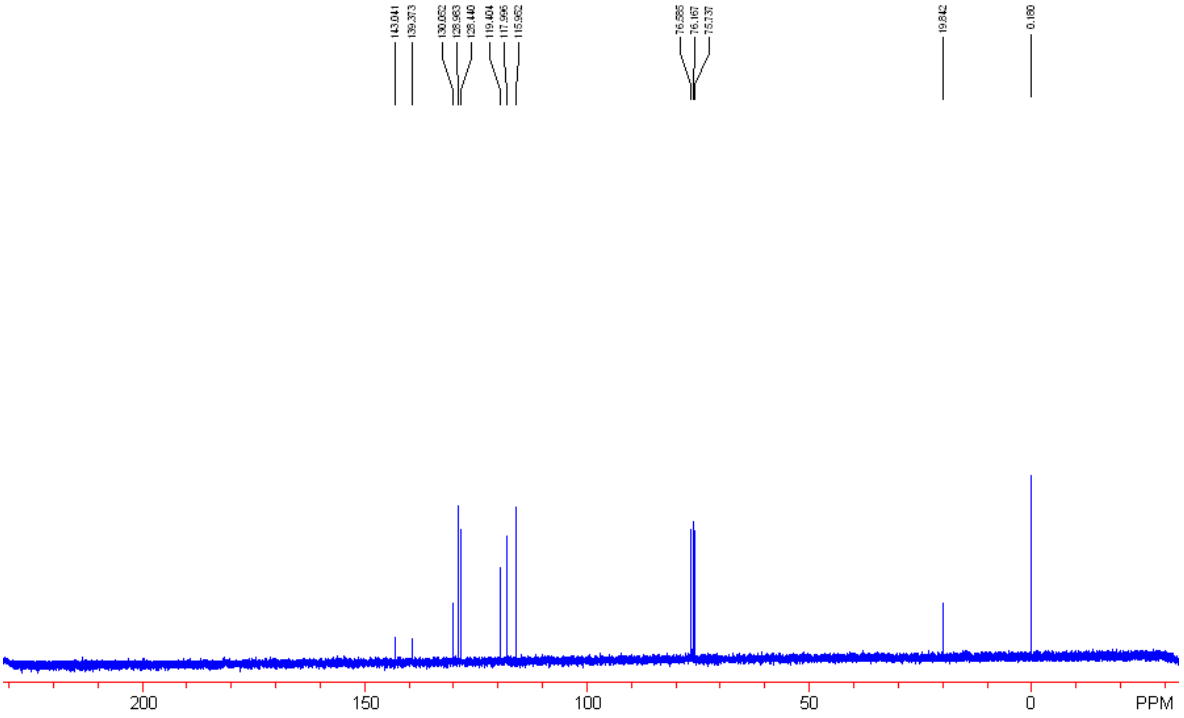


Figure 18. ^{13}C NMR spectrum of Entry 5, Table 1.

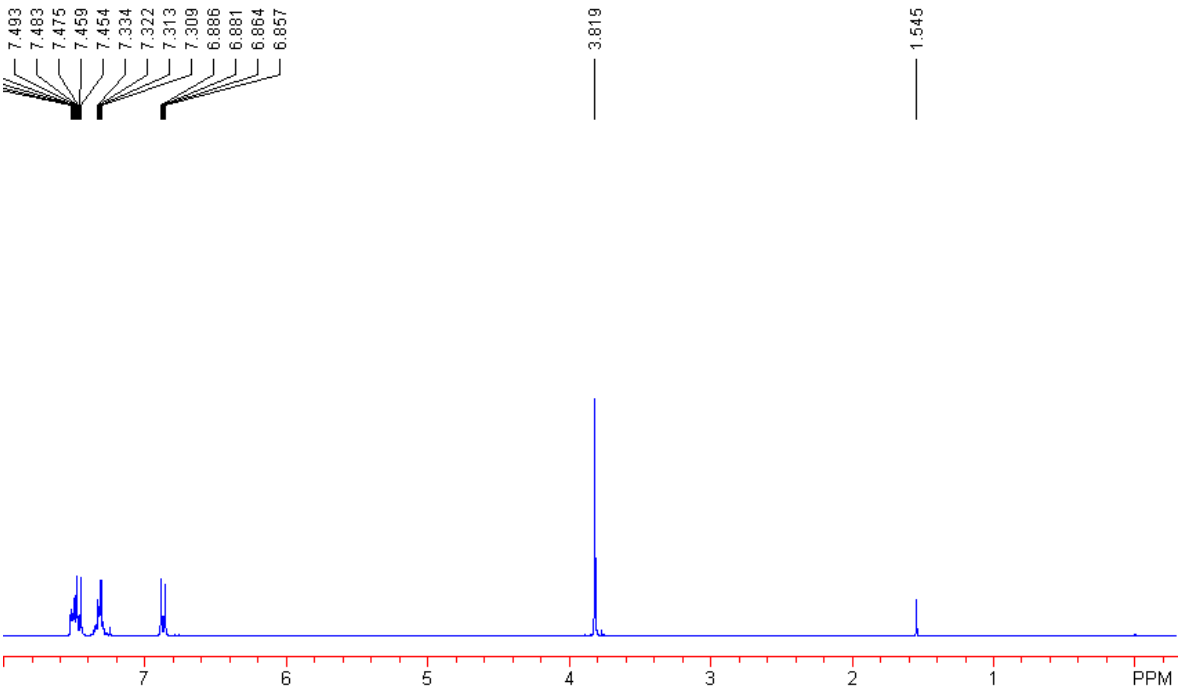


Figure 19. ^{1}H NMR spectrum of Entry 6, Table 1.

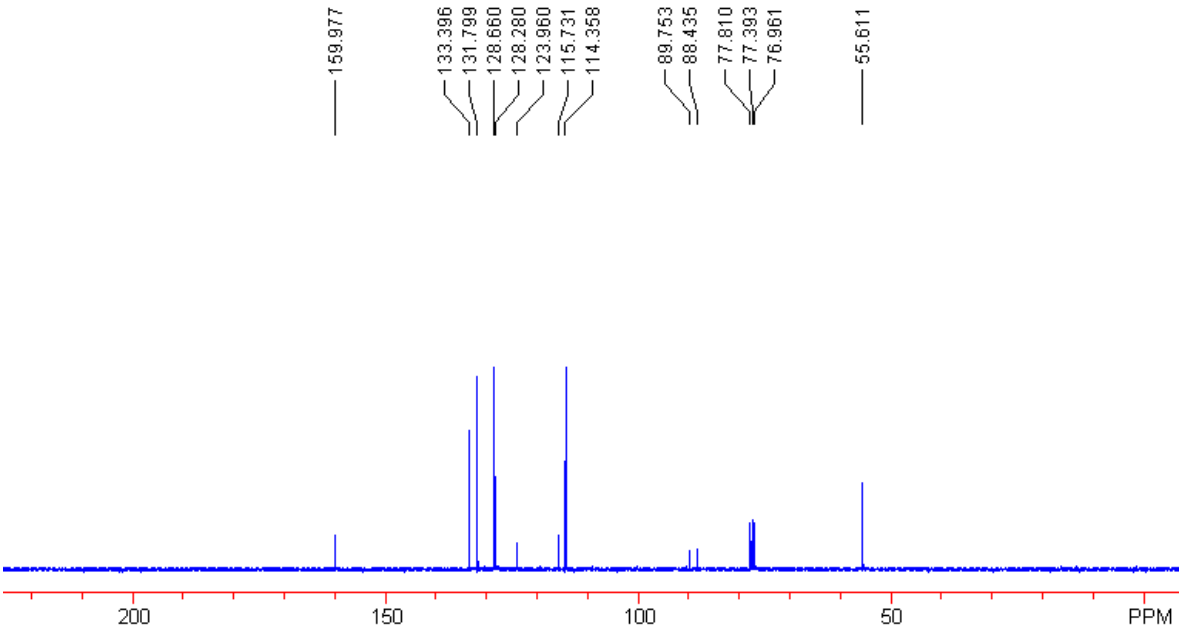


Figure 20. ^{13}C NMR spectrum of Entry 6, Table 1.

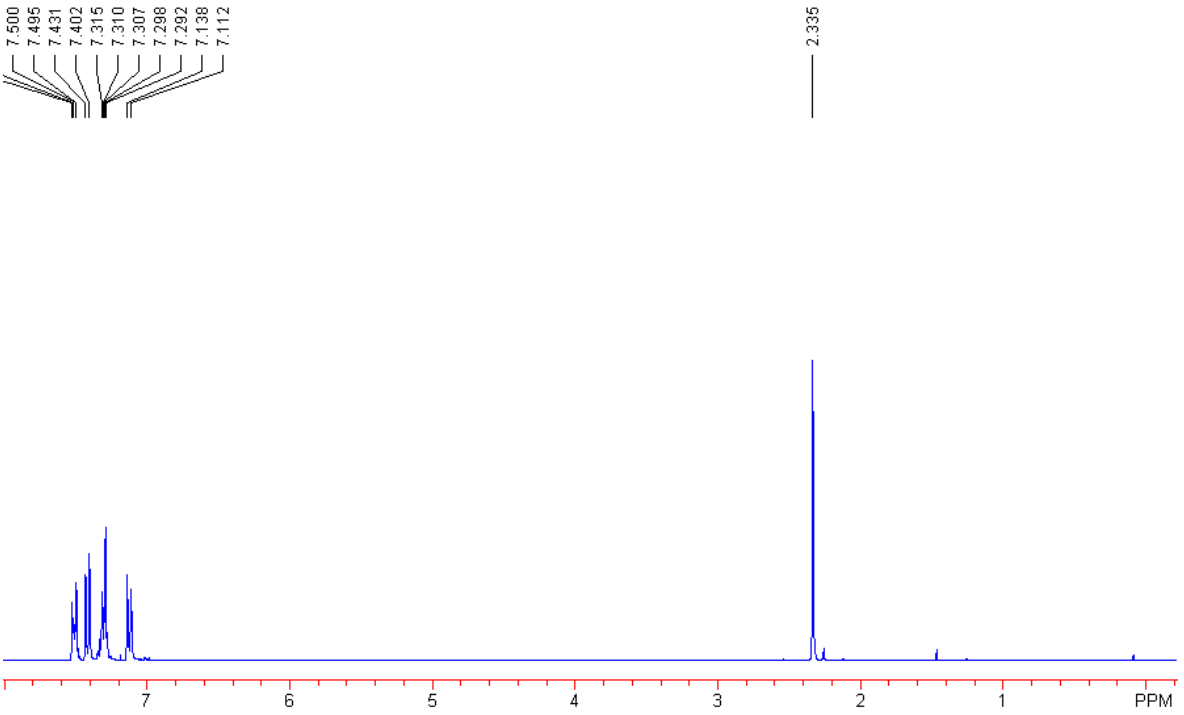


Figure 21. ^{1}H NMR spectrum of Entry 7, Table 1.

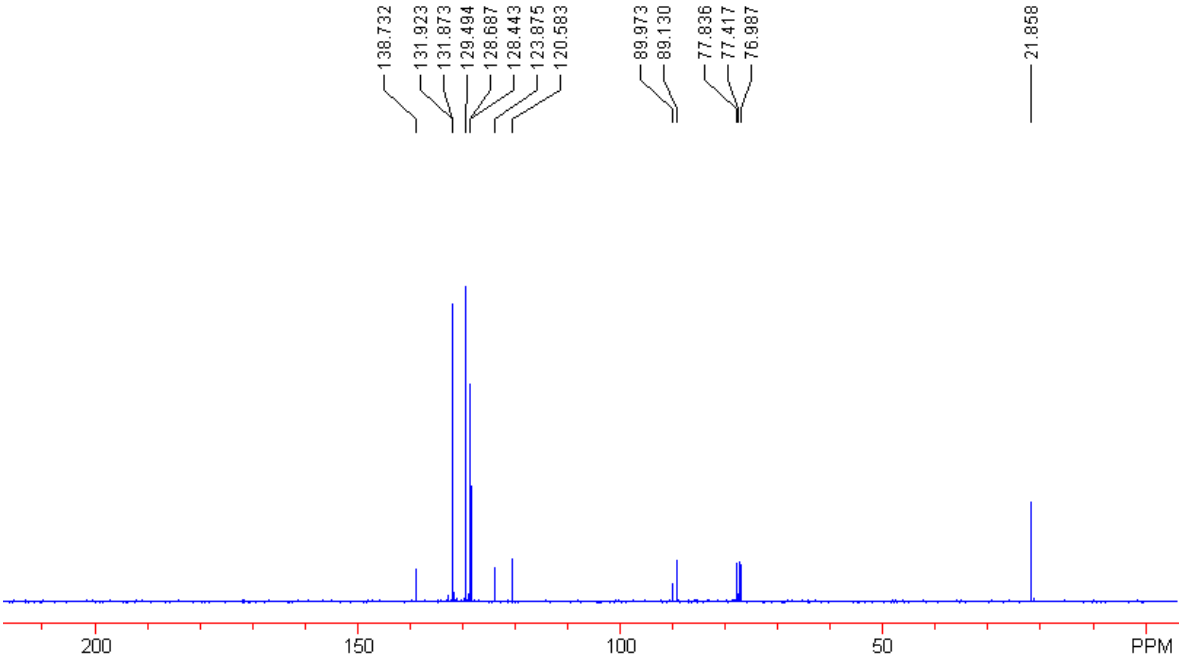


Figure 22. ^{13}C NMR spectrum of Entry 7, Table 1.

1 M. A. Carroll and R. A. Wood *Tetrahedron* **2007**, *63*, 11349.
2 S.-E. Park, S. B. Kang, K.-J. Jung, J.-E. Won, S.-G. Lee and Y.-J. Yoon *Synthesis* **2009**, *5*, 815.
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4 M. J. Calwey, F. G. N. Cloke, R. J. Fitzmaurice, S. E. Pearson, J. S. Scott and S. Caddick *Org. & Biomolecular Chem.* **2008**, *6*, 2820.
5 T. R. Long, A. Gupta, A. L. Miller II, D. G. Rethwisch and N. B. Bowden *J. Mater. Chem.* **2011**, DOI:10.1039/C1JM10970G.