Recycling Pd Colloidal Catalysts Using Polymeric Phosphine Ligands and Polyethylene as a Solid Solvent

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Supporting Information

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General Procedures. Vinyl terminated PIB (Glissopal 1000, 1300 and 2300) with M_n values of 1000, 1300 or 2300 Da, was provided by BASF. Polyethylene (Polywax TM 400) was provided by Baker-Hughes. Other reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. ^1H NMR spectra were recorded on an Inova 500 spectrometer operating at 499.95 MHz or on an Inova 300 spectrometer operating at 299.91 MHz. ^{13}C NMR spectra were recorded on an Inova 500 or Inova 300 spectrometers operating at 125.72 MHz or 75.41 MHz respectively. ^{31}P NMR were recorded on an Inova 300 spectrometer operating at 121.42 MHz. Chemical shifts are reported in ppm with reference to the residual protons resonances in $CDCl_3$. Coupling constants (*J* values) are reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), dd (doublet of doublet) and m (multiplet). A NexION 300D Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine Pd metal content in polar solvent phase. UV-Vis spectra were recorded on a Cary 100 UV-Vis spectrometer and Scanning Electron Microscopic imagers (SEM) were obtained on a JEOL-JSM-7500F microscope. All reactions were carried out under nitrogen atmosphere unless otherwise noted.

ICP-MS analysis procedure. Samples were taken from the DMF phase. These samples were dissolved in 2 mL of concentrated nitric acid by heating at 120 °C for 24 h. The solution that formed was cooled to room temperature and 2 mL of concentrated sulfuric acid was added. This solution was heated to 120 °C for 48 h. At this point, the concentrated acid solution was diluted with 1% nitric acid solution and this diluted sample was analyzed by ICP-MS.

2,6-Dimethyl-4-(polyisobutyl)aniline (1).[1] A mixture of 9.32 g (76.9 mmol) of 2,6-dimethylaniline, 10.10 g (7.77 mmol) of PIB, and 1.52 g (10.2 mmol) of anhydrous aluminum chloride were stirred for 3 d at 200 °C in a pressure vessel. Then the reaction mixture was cooled and added to 100 mL of water. After extraction with 200 mL of hexane, the organic layer was washed with three 100-mL portions of 10% aqueous ethanol. Then organic phase was dried with Na_2SO_4 and solvent was removed under reduced pressure to afford light yellow colored viscous oil. This crude compound was purified with silica column chromatography using hexane and dichloromethane as eluents to obtain **1** in 60% yield. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.95 (s, 2 H), 3.50 (broad, 1H), 2.19 (s, 6 H), 0.8–2.0 (m).

1-[(2,6-Dimethyl-4-polyisobutyl)phenyl]azo-4-phenol (3).[1] A solution of **1** (0.99 g, 0.83 mmol) in 3.5 mL of dichloromethane was cooled to 0 °C and mixed with cold $BF_3.Et_2O$ (0.15 mL, 0.83 mL). After stirring for few minutes, isopentyl nitrite (0.14 mL, 0.98 mmol) was added and the reaction mixture was stirred for 1 h at 0 °C. At this point, the reaction solution was added to a test tube containing 3 mL of water. Then the bottom dichloromethane layer which contained the PIB-diazonium salt **2** was added drop wise to a solution of 2 eq. of phenol and K_2CO_3 in dichloromethane at 0 °C. After 12 h stirring at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in hexane and washed with 10% aqueous ethanol (50 mL), aqueous $NaHCO_3$ (50 mL) and water (50 mL). The organic phase was dried with Na_2SO_4 and the solvent was removed under reduced pressure to afford the product azo-dye as a highly colored viscous material in 90% yield. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.84 (d, 2 H, *J*= 8.9), 7.09 (s, 2 H), 6.95(d, 2H, *J* = 8.9), 2.40 (s, 6 H), 0.8–2.0 (m).

4-Butoxyphenyl-4-(2,6-dimethyl-4-polyisobutylphenyl)diazene (4). To a 25-mL round-bottomed flask was added **3** (1.96 g, 0.78 mmol) in 5 mL of heptane, *n*-butyl bromide (0.13 mL, 1.17 mmol), K_2CO_3 (1.57 mmol, 0.21 g) in 5 mL of dimethyl formamamide. The reaction mixture was heated at reflux overnight. The reaction solution was cooled to room temperature and added to a separatory funnel. The bottom DMF phase was removed and 100 mL of hexane was added to the funnel. The hexane phase was washed with 3 10-mL portions of 10% aq. Ethanol, with 3 10-mL portions of brine, dried over anhydrous Na_2SO_4, and filtered. Then the filtrate was concentrated under reduced pressure to obtain bright orange color viscous oil as a pure product in quantitative yield (1.5 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.82 (d, 2H, *J* = 8.8), 7.10 (s, 2H), 6.95 (d, 2H, *J* = 8.8), 2.39 (s, 6H), 0.76 – 1.82 (m); ^{13}C NMR (125 MHz, CDCl3) δ (ppm):162.0, 150.7, 149.1, 147.6, 130.6, 127.6, 124.5, 115.1, 60.6–14.4 multiple peaks.

Palladation of 4-butoxyphenyl-4-(2, 6-dimethyl-4-polyisobutylphenyl)diazene (5). To a 50-mL round-bottomed flask equipped with a magnetic stir bar was added **4** (0.72 g, 0.30 mmol), $Pd(PhCN)_2Cl_2$ (0.132 g, 0.344 mmol) in 30 mL of chloroform. The resulting homogeneous solution was stirred for 24 h at room temperature. Then the solvent was evaporated under reduced pressure and 100 mL of hexane was added to the oily residue. The solution was transferred to a separatory funnel and the hexane solution was washed with first with 3 50-mL portions of acetonitrile and finally with 50 ml of brine. The organic phase was dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuum to obtain red viscous oil in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.74 (d, 1H, *J* = 8.5), 7.08 (s, 2H), 6.68 (d, 1H, *J* = 8.5), 6.61 (s, 1H), 3.98 (t, 2H), 2.33 (s, 6H), 1.75 – 0.89 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) : 161.7, 160.0, 157.7, 150.5, 147.2, 130.8, 130.0, 125.9, 118.9, 111.6, 59.3 – 13.9 multiple peaks.

General procedure for the Heck and Suzuki reactions in heptane/DMF under thermomorphic conditions. A 10-mL Schlenk tube equipped with a stir bar was charged with catalyst **5** (0.01 mmol) dissolved in 2 mL of heptane and 2 mL of DMF containing 1 mmol of aryl halide, 1.2 mmol of *n*-butyl acrylate or 1.4 mmol of phenyl boronic acid and 2 mmol of K_2CO_3. The mixture was stirred at 100 °C for 6 - 12 h. After the reaction was complete, the solution was led to cool to room temperature at which point the heptane and DMF separated into two phases. Then the bottom DMF phase was isolated by a gravity separation and the solvent was removed under reduced pressure to obtain a crude product which was purified by silica gel column chromatography (hexane/ethyl acetate: 4:1) to afford the pure product. Recycling the catalyst was achieved by adding 2 mL of heptane saturated DMF containing fresh substrates in the appropriate amounts followed by heating as described above.

General procedure for the Heck and Suzuki reactions in THF/DMF/Polyethylene system. A 10-mL screw-capped vial equipped with a stir bar was charged with catalyst **5** (0.01 mmol) dissolved in 2 mL of THF, aryl halide (1 mmol), *n*-butyl acrylate (1.2 mmol) or phenyl boronic acid (1.4 mmol) and K_2CO_3 (2 mmol) in 2 mL of DMF. Polyethylene (Polywax 400) (1.5 g) was also added to this reaction mixture. The mixture was stirred with heating at 90 ºC for 12 h. At this point, the solution was perturbed to form two phases by adding a small amount of hot water (~ 2 mL). The upper liquid Polywax phase solidified on cooling. That solid wax was separated from the solution by vacuum filtration and the waxy phase was rinsed with methanol (5 mL). Then the filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to afford pure coupling product.

The catalyst was recycled by adding fresh THF/DMF containing substrates in appropriate amounts to the waxy solid followed by heating as described above. Reactions carried out in the presence of **21** using Polywax were carried out in a similar manner.

Butyl (*E*)-3-(4-acetylphenyl)-2-propenoate (9).[2, 3] The reaction was carried out on a 1 mmol scale and the product was isolated as colorless oil in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 7.97 (d, 2H, *J* = 7.5), 7.69 (d, 1H, *J* = 16.7), 7.61 (d, 2H, *J* = 7.5), 6.53 (d, 1H, *J* = 16.7), 4.22 (t, 2H, J = 7.4), 2.62 (s, 3H), 1.67 (m, 2H), 1.43 (m, 2H), 0.94 (t, 3H, J= 7.3); ^{13}C NMR (125 MHz, CDCl3) δ (ppm) :197.9, 167.2, 143.6, 139.4, 138.6, 129.5, 128.8, 121.5, 65.3, 31.4, 27.3, 19.83, 14.39.

Butyl (*E*)-3-phenyl-2-propenoate (10).[4] The reaction was carried out on a 1 mmol scale and the product was isolated as colorless oil in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.69 (d, 1H, *J* = 16.7), 7.54 (m, 4H), 7.40 (m, 2H), 6.45 (d, 1H, *J* = 16.6), 4.22 (t, 2 H, *J* = 6.9), 1.70 (m, 2 H), 1.45 (m, 2 H), 0.97 (t, 3 H, *J* = 8.2); ^{13}C NMR (75 MHz, CDCl3) δ (ppm): 166.9, 144.3, 134.2, 130.0, 127.9, 118.5, 64.3, 31.0, 19.2, 13.9.

Phenylacetophenone (15).[5] The reaction was carried out on a 1 mmol scale and the product was isolated in 94% yield as a white solid; **mp =** 122 - 124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.57 (d, 2H, *J* = 6.4), 7.67 (m, 4H), 7.48 (m, 3H), 2.60 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) : 197.6, 146.1, 139.1, 135.6, 129.0, 127.4 (m), 27.0.

1-Chloro-4-phenylbenzene (16).[6] The reaction was carried out on a 1 mmol scale and the product was isolated in 90% yield as a white solid; **mp** = 75 - 78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.54 (m, 4H), 7.43 (m, 4H), 7.37 (t, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 140.5, 140.3, 134.1, 129.6, 129.5,128.9, 128.1, 127.4.

4-(4-Methoxyphenyl)benzene (17).[7] The reaction was carried out on a 1 mmol scale and the pure product was isolated in 89% yield as a white solid; **mp** = 86 - 89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.56 (m, 4H), 7.43 (t, 2H), 7.33 (t, 1H), 7.00 (d, 2H, *J* = 8.39), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 156.6, 138.1, 130.9, 126.0, 125.6, 124.4, 124.1, 112.0, 53.0.

PIB-bound azo-Pd(II) complex with triphenylphosphine (18). To a Schlenk tube equipped with a stir bar was added PIB-azo-Pd complex (**5**) (0.015 mmol), triphenylphosphine (0.029 mmol) in 2 mL of dichloromethane. Then the tube was sealed with a rubber septum and degassed the reaction solution using three freeze thaw pump cycles. Then the reaction solution was stirred 12 h at room temperature. After 12 h time period the solvent was evaporated under reduced pressure and the residue was purified by a flash column with hexane:ethyl acetate (vol:vol, 4:1) to obtain **18** as a bright yellow color oil in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.90 (d, 1H. *J* = 8.9), 7.70 (m, 5H), 7.39 (m, 10H), 7.03 (s, 2H), 6.60 (dd, 1H, *J* = 8.65, *J* = 2.59), 5.95 (m, 1H), 3.14 (t, 2H), 2.36 (s, 6H), 1.80-0.8 multiple peaks); ^{31}P NMR (122 MHz, ^{1}H-decoupled, H_3PO_4 as an external standard, $CDCl_3$) δ (ppm): 28.9.

4-(3-Phenyl-2-propenyl) morpholine (19).[3] To a Schlenk tube equipped with a magnetic stir bar was added cinnamylacetate (1 mmol), morpholine (4 mmol), catalyst **5** (0.01 mmol) and polyisobutylene-bound phosphine (**21**) (0.02 mmol) in 5 mL of heptane. The tube was sealed with a rubber septum and the reaction solution was degassed using three freeze thaw pump cycles. Then the reaction mixture was heated with an oil bath regulated at 80 ºC for 12 h. After the reaction was complete the reaction mixture was cooled to room temperature and the products were extracted with 2 5-mL portions of acetonitrile. The acetonitrile phases were combined and evaporated under vacuum to obtain the crude product which was purified by silica gel column chromatography to afford the pure product in 86% yield as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.38 (d, 2H, *J* = 8.62), 7.30 (t, 2H), 7.22 (t, 1H), 6.53 (d, 1H, *J* = 15.4), 6.25 (m, 1H), 3.73 (m, 4H), 3.15 (m, 2H), 2.49 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) : 137.2, 134.2, 129.0, 128.2, 127.0, 126.9, 126.5, 67.6, 62.1, 54.2.

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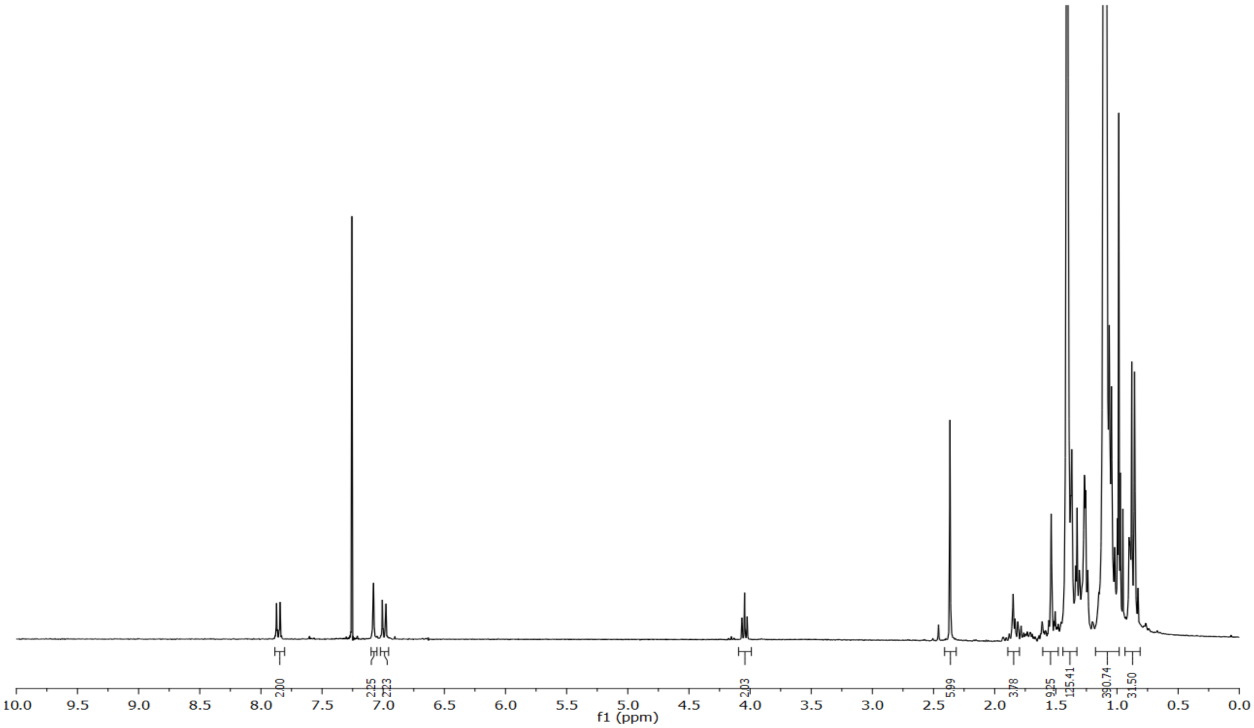
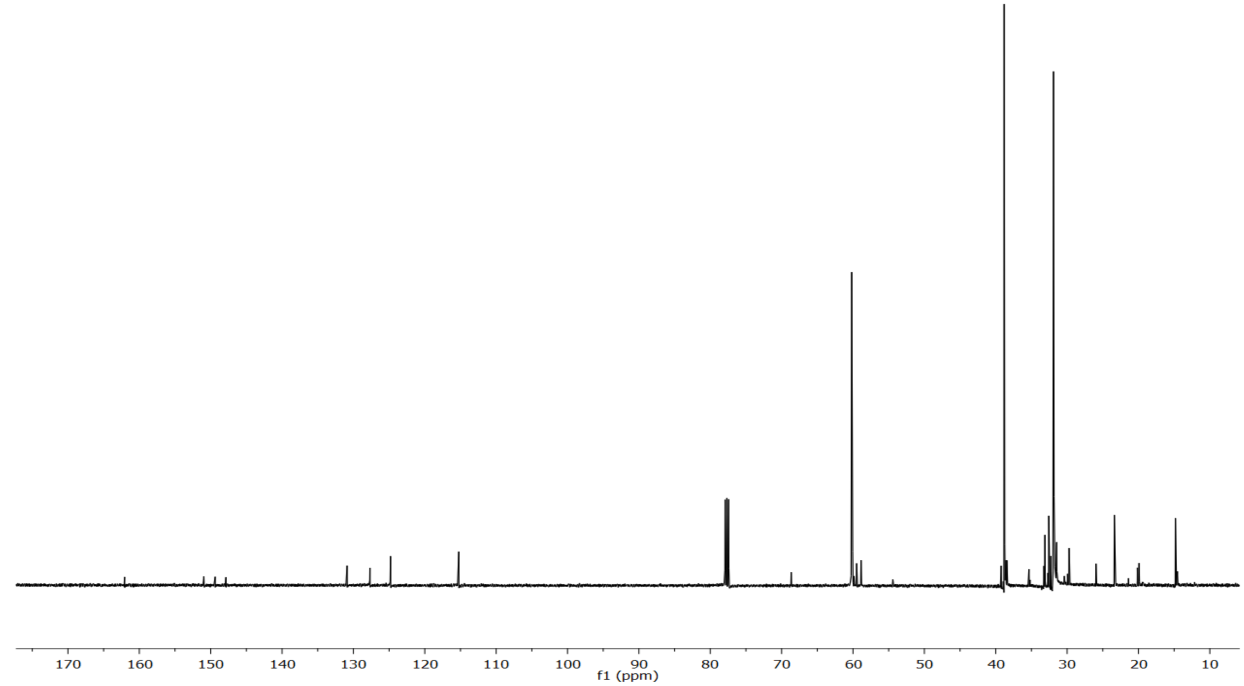
^{1}H NMR and ^{13}C NMR

4-Butoxyphenyl-4-(2, 6-dimethyl-4-polyisobutylphenyl) diazene **(4)**





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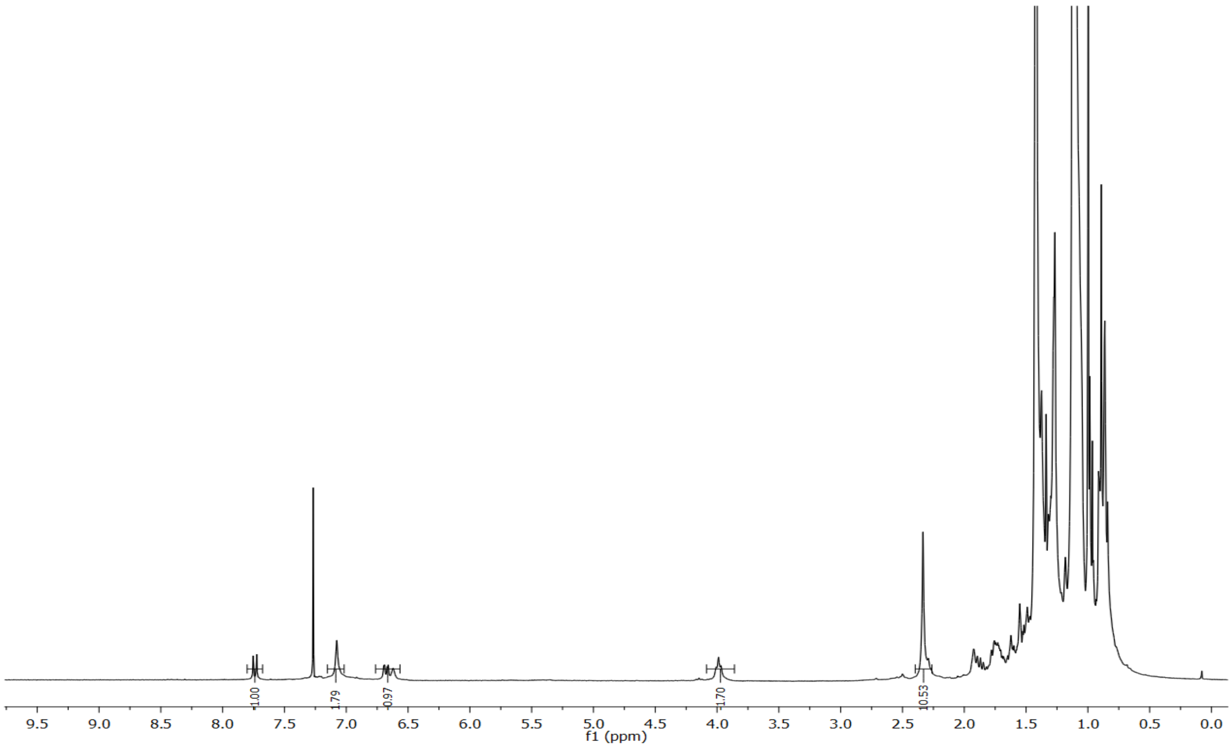

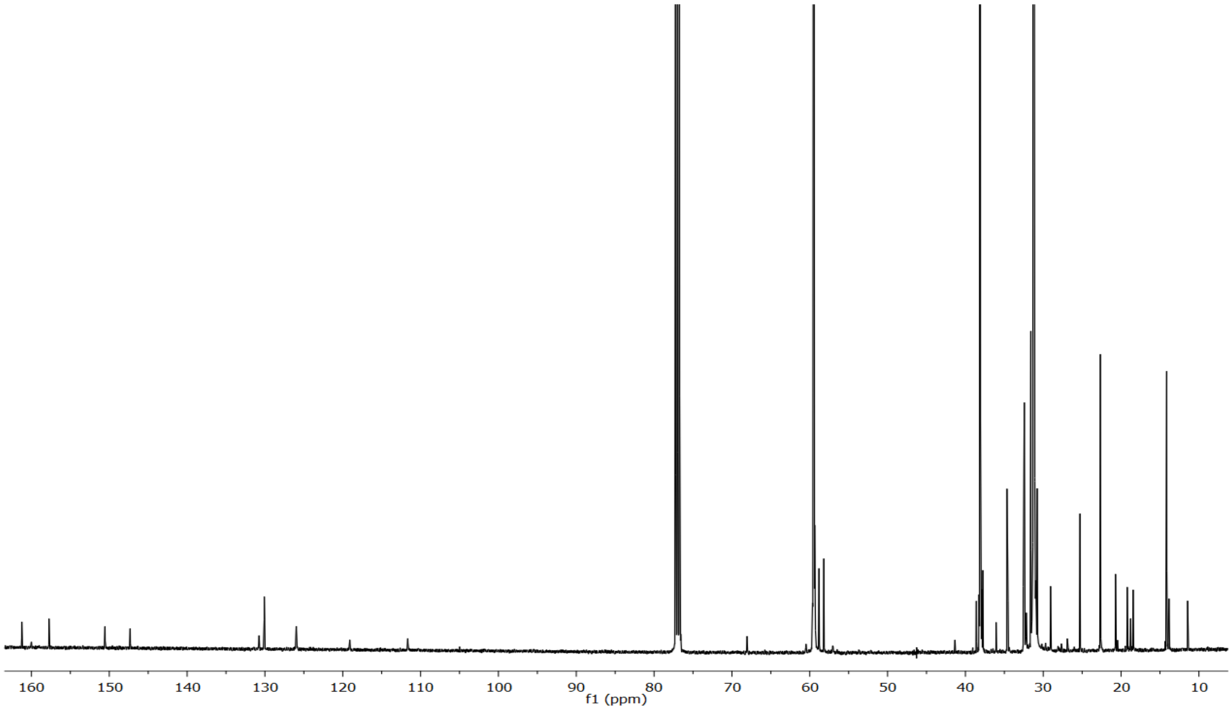

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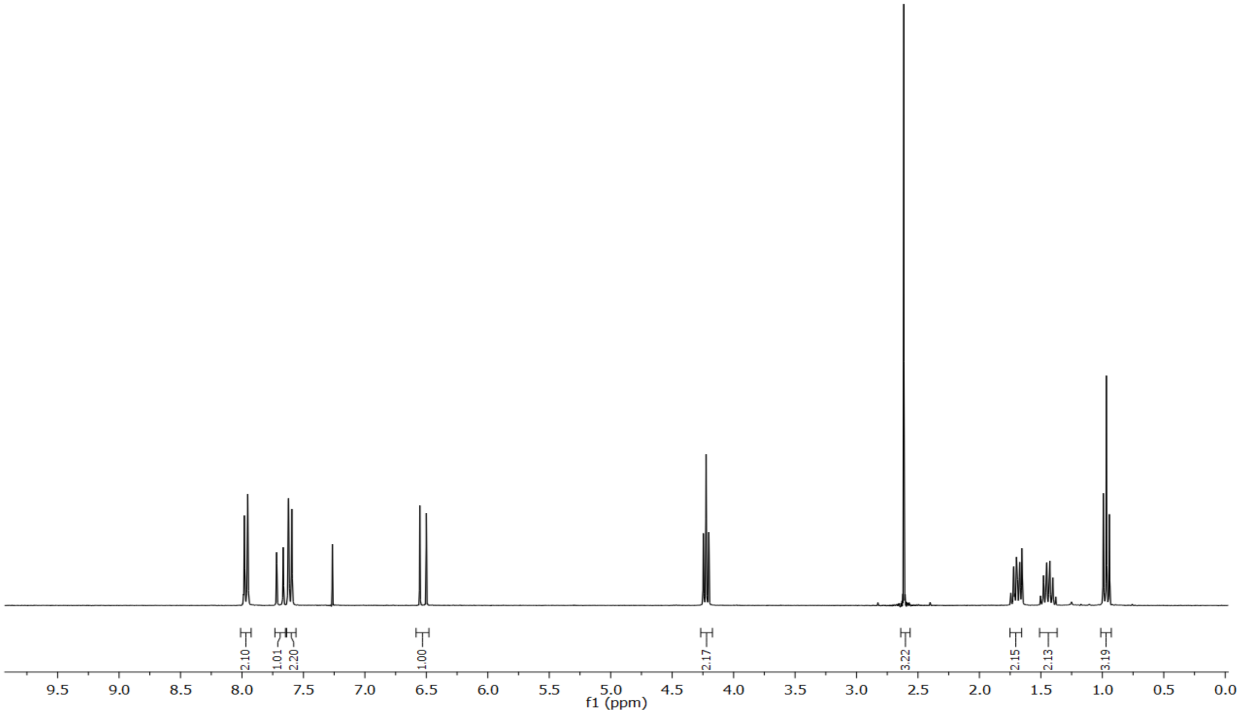

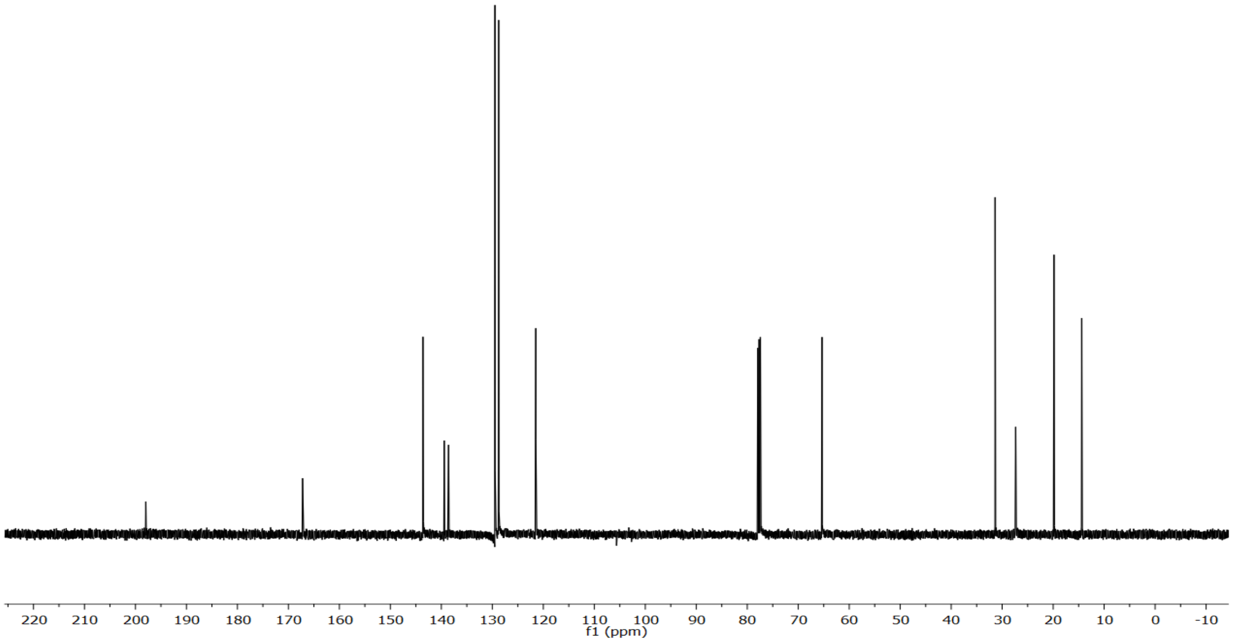

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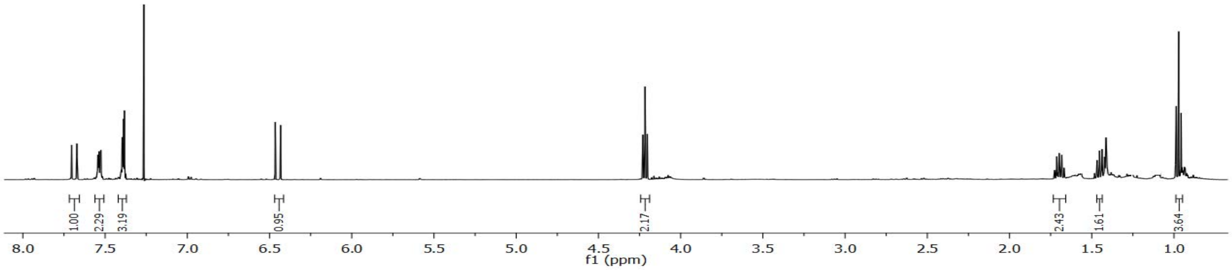
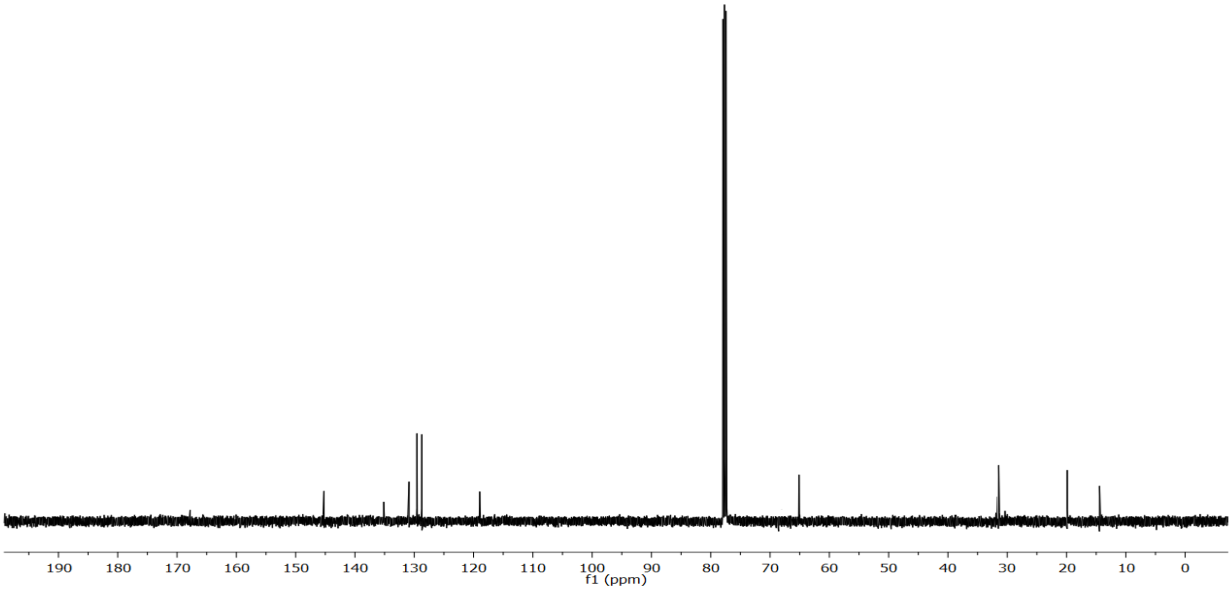
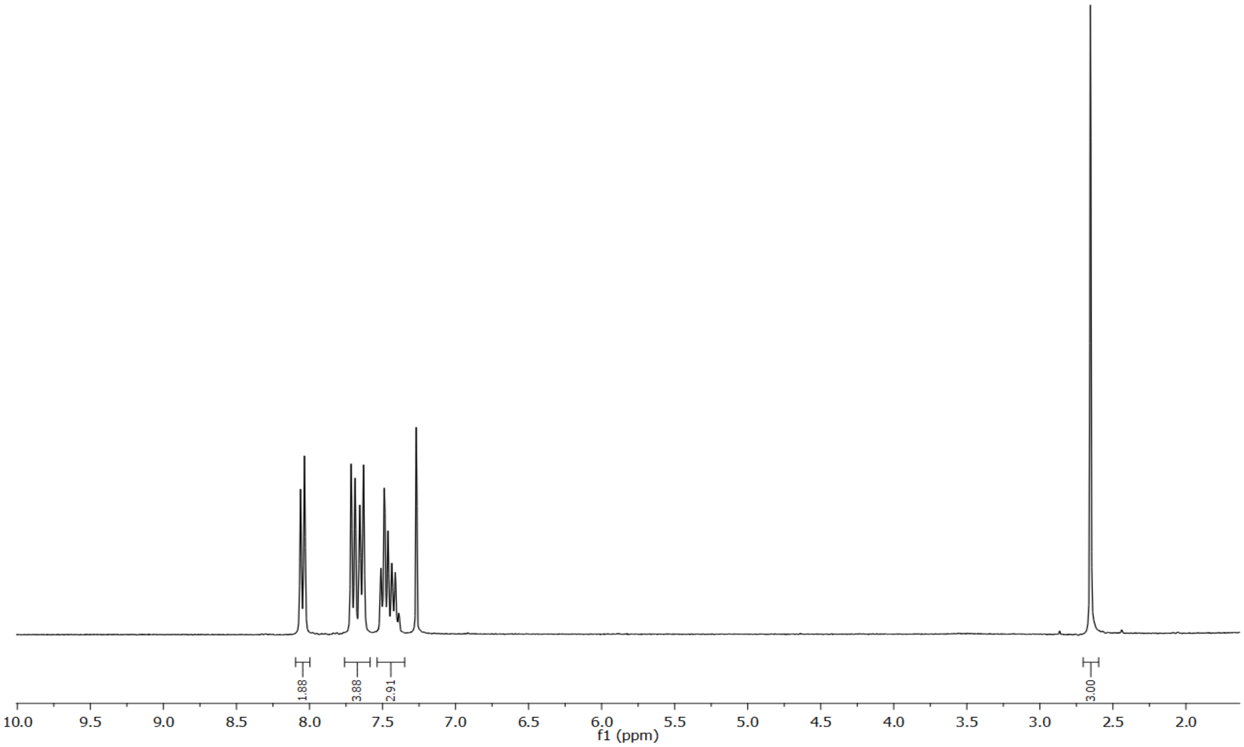
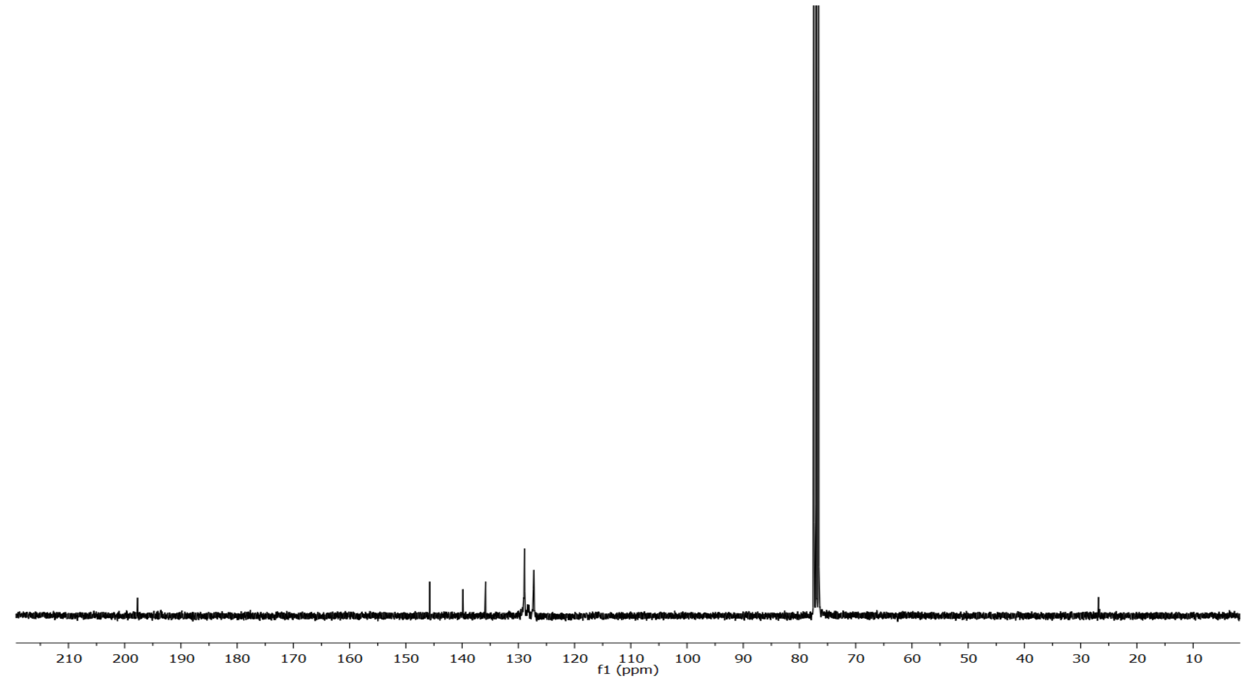


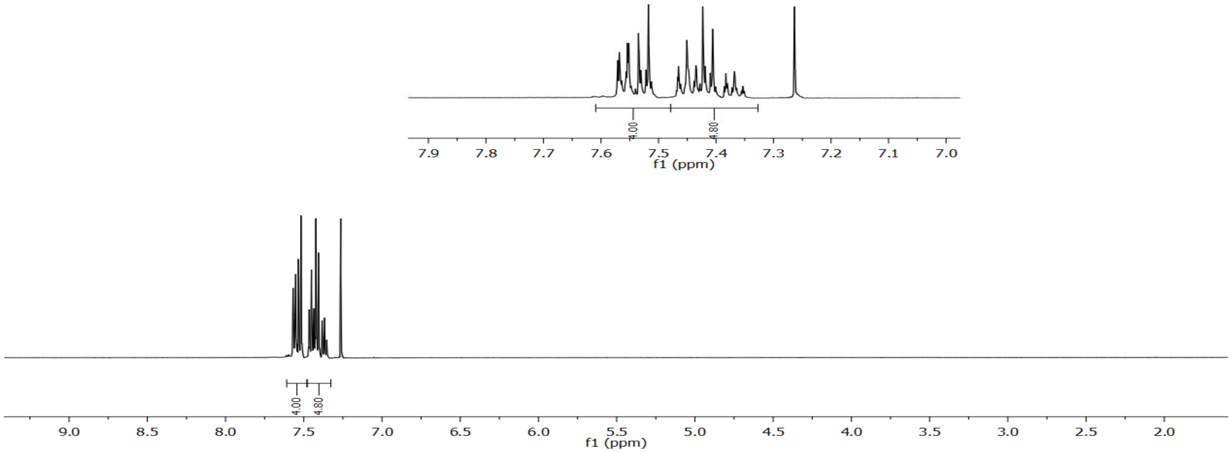


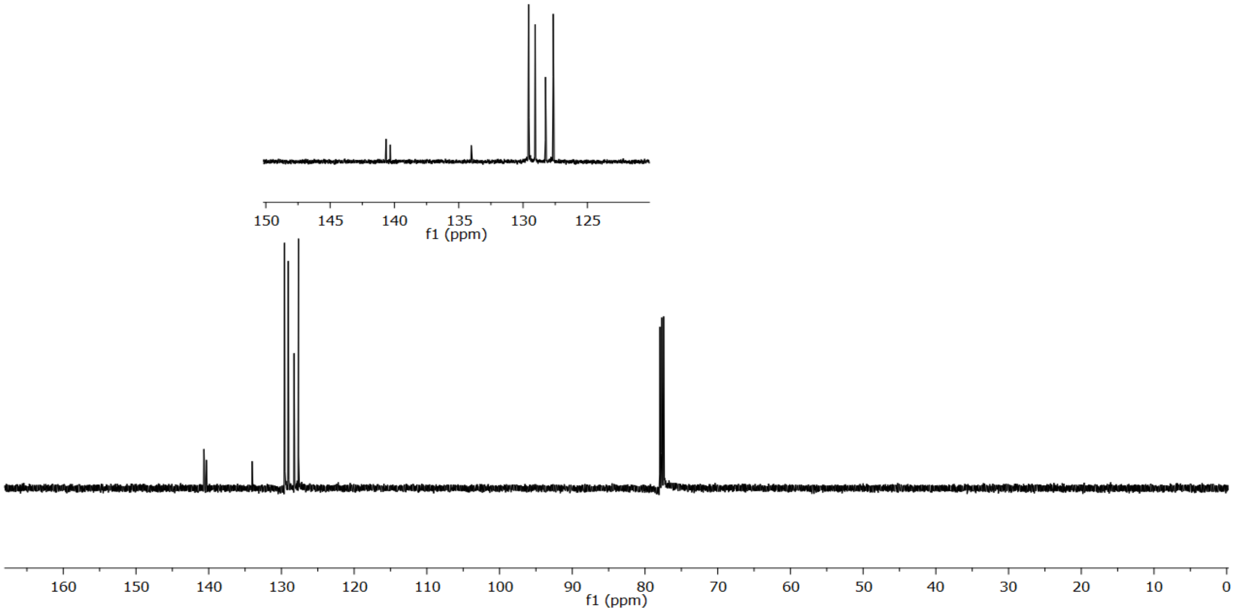
Phenylacetophenone (**15**)





1-Chloro-4-phenylbenzene (**16**)





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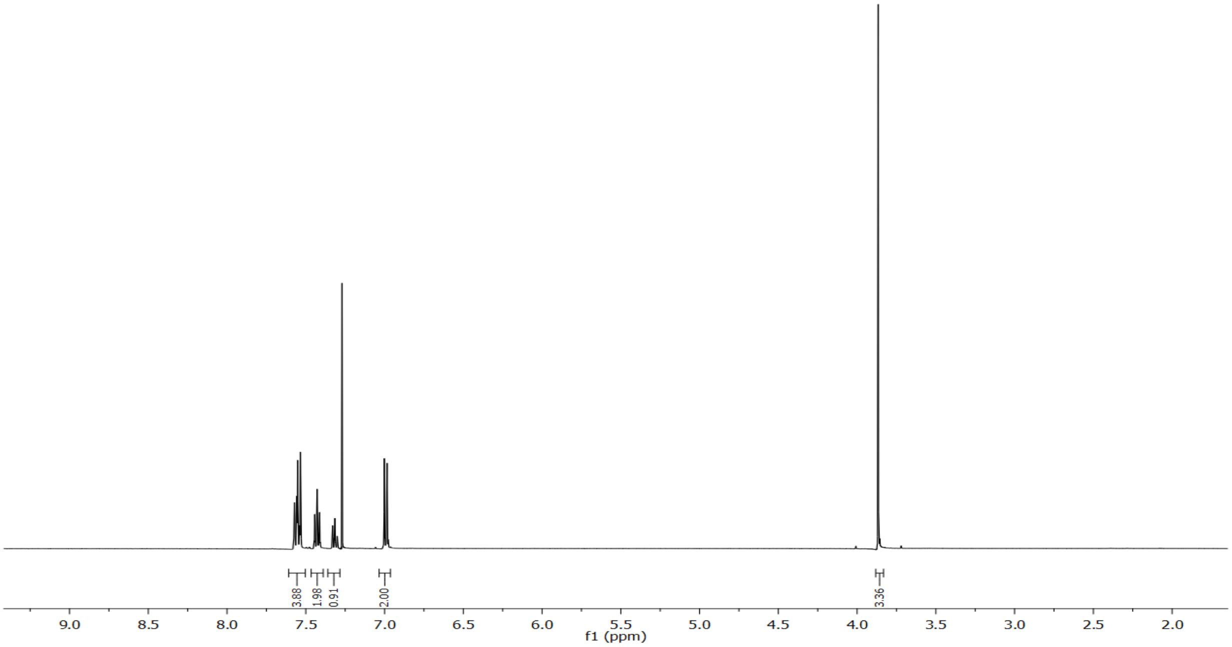
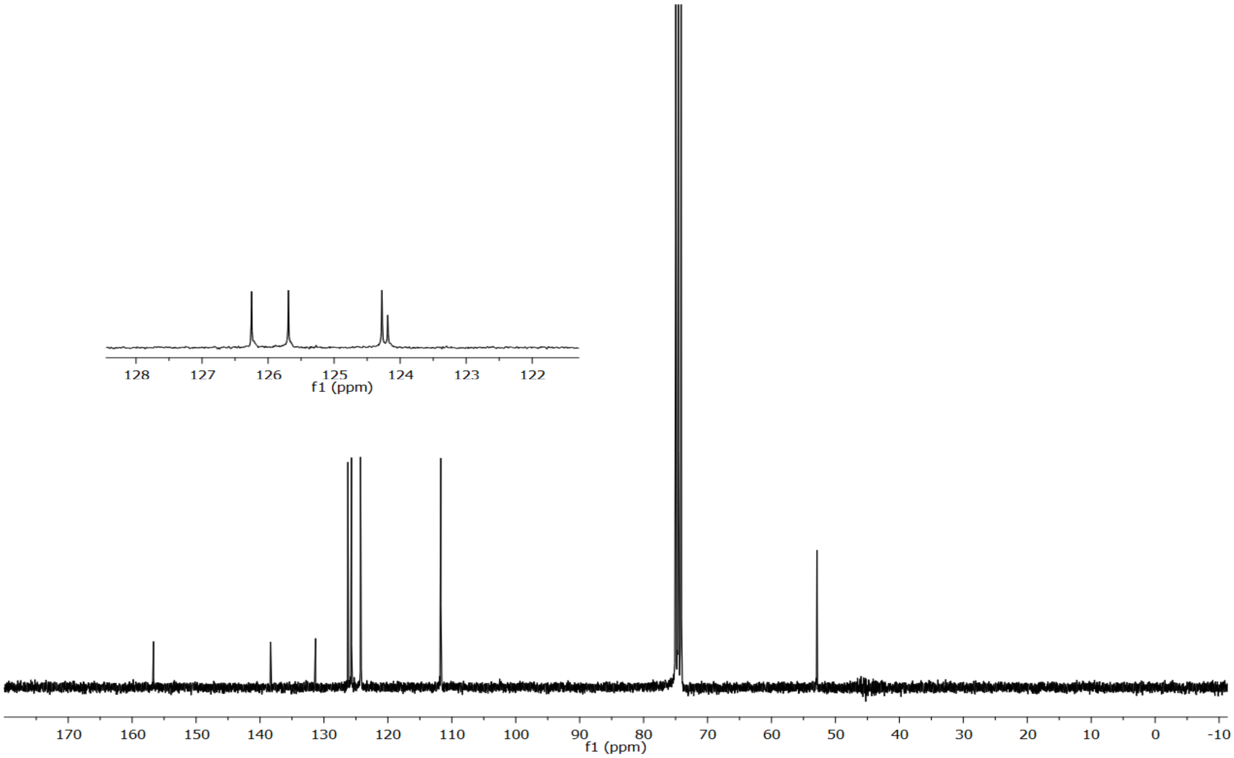
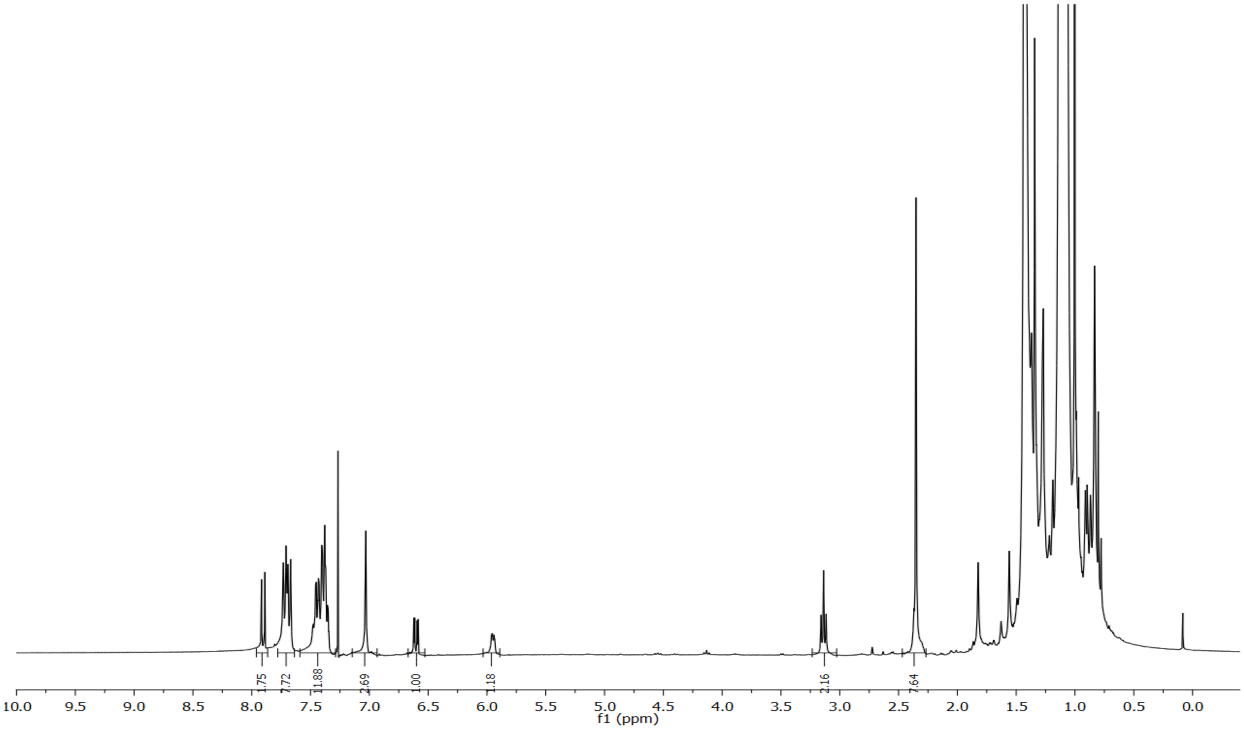
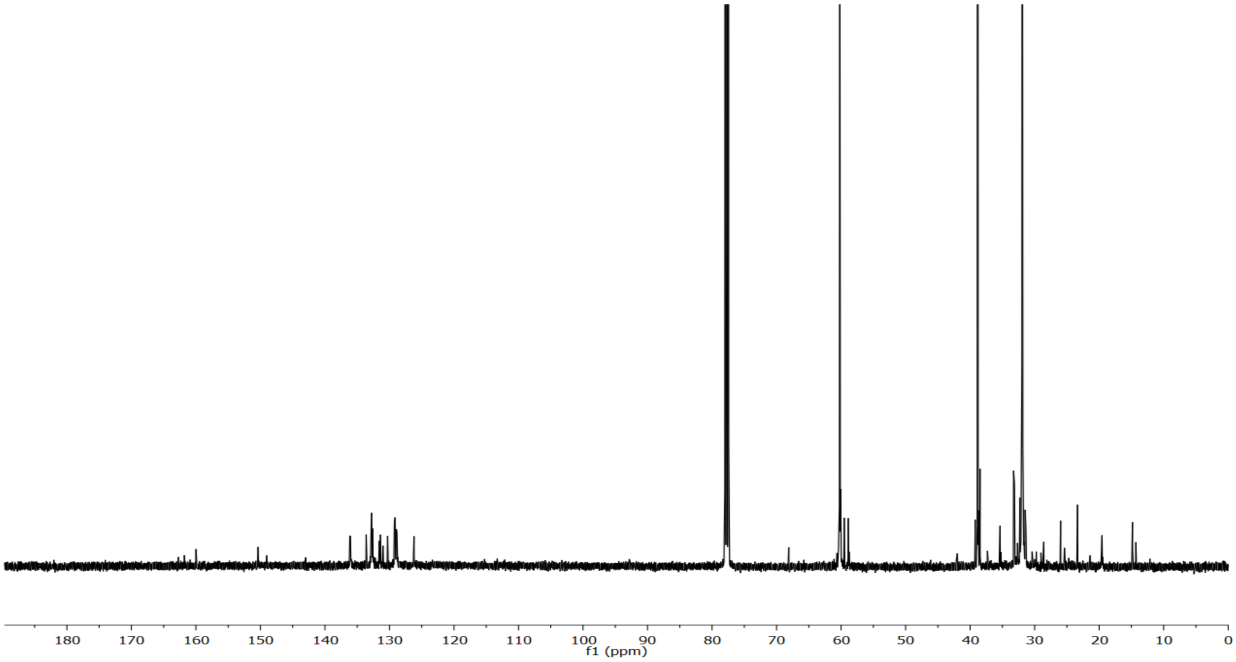




PIB-azo-Pd(II) complex with triphenylphosphine (**18**)





4-(3-Phenyl-2-propenyl) morpholine (**19**)