Catalytic asymmetric hydrogenation using [2.2]paracyclophane based chiral 1,2,3-triazol-5-ylidene-Pd complex under ambient conditions and 1 atmosphere of H_2

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Electronic Supporting Information:

Contents:

General Experimental Procedures

All reactions were performed in an oven dried Schlenk round bottom flask under nitrogen atmosphere. Air and moisture sensitive chemicals were handled under schlenk technique. All the crude compounds were purified by column chromatography by using 100-200 silica gel. TLC plates were purchased from Merck (TLC silica gel 60 F_{254} 0.25 mm) and plates were visualized under UV light (254 nm) or aqueous $KMnO_4$ solution as the developing agent. Commercial solvents were purified by distillation prior to use. HPLC grade methanol was used as solvent for hydrogenation reactions. Infrared (IR) spectra were recorded on a JASCO 4100 FT-IR spectrometer. Proton nuclear magnetic resonance spectra (NMR spectra) were measured on Bruker AVANCE 400 MHz and 500 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) (δ scale) from tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded on Bruker Avance 100 MHz and 125 MHz spectrometers with complete proton decoupling. Notation abbreviations are s = singlet, d = doublet, t = triplet, m = multiplet, coupling constants were reported in Hz. High-resolution mass spectra (HRMS) were recorded on a Micromass ESI Q-TOF micro mass spectrometer equipped with a Harvard Apparatus syringe pump. Single crystal X-ray crystallographic data were collected on a Bruker-AXS Kappa CCD-Diffractometer fitted with graphite-monochromator and Mo K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares techniques against F2 (SHELXL-97). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program. Waters HPLC (Model 2996) instrument fitted with Chiral IA (15cm x 0.46 cm), Chiral OD and OJ (25 x 0.46 cm) columns were used for analysis of products from catalytic asymmetric hydrogenation reaction to determine the enantiomeric ratios and *n*-hexane/2-propanol mixture was used as eluent, 254 nm was used as detector wavelength. Optical rotations were measured on a JASCO polarimeter (P-2000).

Synthesis and resolution of 4-formyl[2.2]paracyclophane (8):

Synthesis of racemic 4-formyl[2.2]paracyclophane and its resolution to optically pure S_p (+) isomer was carried out as described in the literature[1,2]. Optical purity was ascertained to be 98.5 % ee by chiral HPLC analysis of the pure enantiomer in comparison with the racemic mixture.

HPLC condition: CHIRALPAK OD, (25 x 0.46 cm), n-hexane/2-propanol (90:10, v/v), flow rate = 1 mL/min, 254 nm UV Detector, retention time = 12.08 min (*S* isomer), retention time = 17.41 min (*R* isomer)

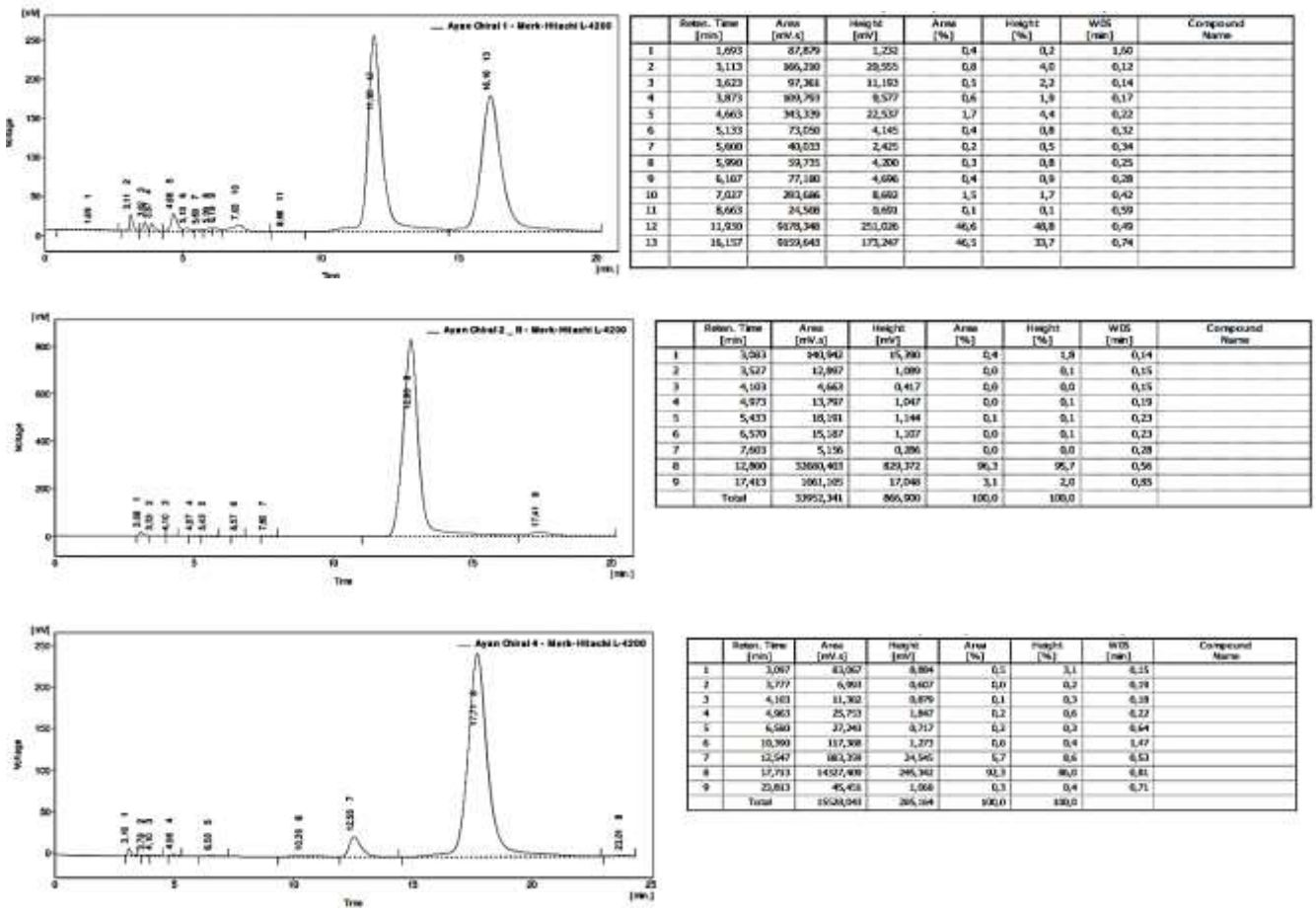
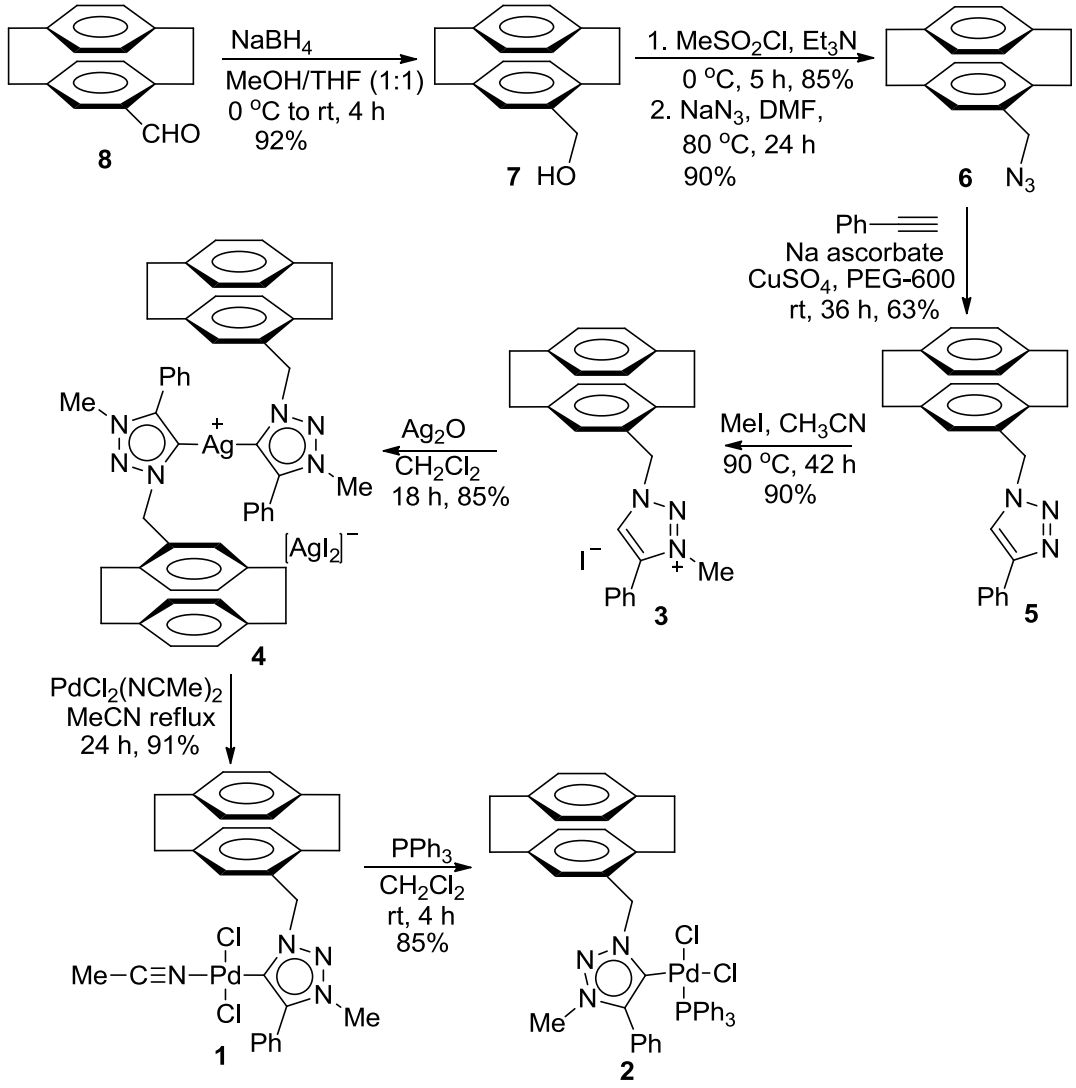


Figure S1: HPLC traces of racemic mixture (top), S_p(+) isomer (middle) and R_p(-) isomer (bottom) of 4-formyl-[2.2]paracyclophane (**8**). Optical purity of S_p(+) isomer of **8** = 98.5 % ee, optical purity of R_p(-) isomer of **8** = 97 % ee.

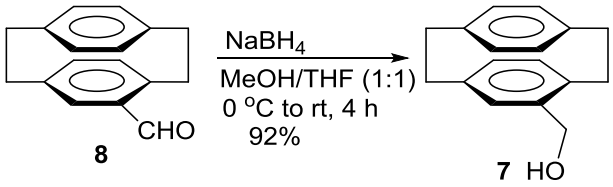
Synthetic scheme for the synthesis of complexes 1 and 2:

The following synthetic sequence (Scheme S1) was carried out independently starting from either the racemic mixture or the optically pure S_p (+) form of 4-formyl-[2.2]paracyclophane (**8**) .



Scheme S1. Synthesis of racemic and optically pure isomers of complexes **1** and **2.**

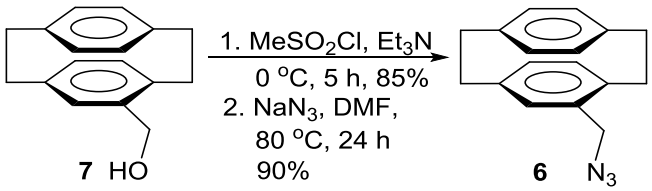
Synthesis of alcohol **7**:



To a stirred solution of S_p(+) **8** (2 g, 8.5 mmol) in dry THF and methanol (1:1, 30 mL), sodium borohydride (961 mg, 25.4 mmol) was added in small portions under nitrogen atmosphere at ice cold conditions and reaction mixture was allowed to stir at room temperature for four hour. After removal of the solvents the crude product was extracted using CH_2Cl_2 (3 x 50 mL). After removal of CH_2Cl_2 the product was purified by column chromatography on silica gel using ethyl acetate and hexane mixture as eluent (40:60 v/v). Alcohol **7** was obtained as a colorless crystalline solid (1.85 g, 7.76 mmol, 92%) was obtained as pure product.

S_p(+) **7:** Mp: 110 °C (lit 111-112 °C)[3]; $[\alpha_D]^{25}$ +65.37 (c = 0.535, $CHCl_3$) (lit $[\alpha_D]^{28}$ + 67.6)[3]; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.60 (dd, *J* = 8 Hz, 2 Hz, 1H), 6.55-6.46 (m, 4H), 6.39-6.38 (m, 2H), 4.69 and 4.37 (doublet of AB quartet, *J* = 13 Hz, 3 Hz, 1H), 3.42-3.37 (m, 1H), 3.17-2.98 (m, 6H), 2.89-2.83 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 140.41, 139.85, 139.66, 139.37, 137.60, 135.12, 133.45, 133.36, 132.50, 132.29, 132.23, 129.16, 64.61, 35.41, 35.16, 34.51, 32.92; IR (KBr) : 3245, 3004, 2924, 2850, 1596, 1498, 1435, 1207, 1151, 1022 cm^{-1}; HRMS (ESI; m/z) Calcd for $C_{17}H_{18}ONa$ 261.1255 (M + Na), found 261.1266.

Synthesis of azide **6**:



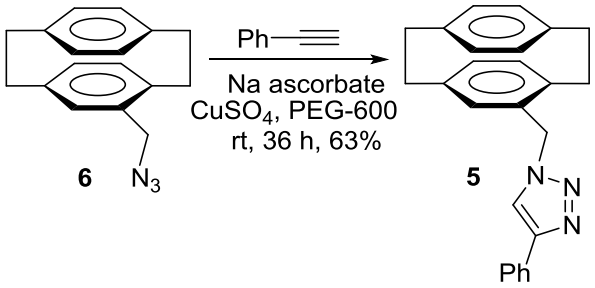
Compound **7** (1 g, 4.19 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and allowed to stir under nitrogen atmosphere. Triethylamine (0.88 mL, 6.2 mmol) was added drop wise into the reaction mixture under ice cold conditions. Mesyl chloride (0.42 mL, 5.03 mmol) was added in a drop wise manner into the same reaction mixture. Reaction mixture was allowed to stir for the next 5 h under N_2 atmosphere.

After ascertaining the completion of the reaction by TLC the reaction was quenched with brine solution and the organic part was extracted with CH_2Cl_2 (3 x 50 mL). The organic extract was dried over anhydrous sodium sulphate and then the solvent was removed. The mesylate was obtained as a colorless solid **(**1.12 g, 3.56 mmol, 85%). The crude was used for the next step without any further purification.

The mesylate of **7** (1 g, 3.16 mmol) was dissolved in dry DMF. Solid sodium azide (0.82 g, 12.6 mmol) was added to reaction mixture portion wise. Then reaction mixture was heated to 90 ^{o} C for the next 24 h. The reaction was quenched with ice water and extracted with ethyl acetate. Removal of the solvent gave pure azide **6** as a colorless solid (0.748 g, 90 %).

Azide **6**: Mp: 78 ^{o}C; $[\alpha_D]^{25}$ +28.01 (c = 0.86, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.59-6.49 (m, 5H), 6.40 (dd, *J* = 8 Hz, 2 Hz, 1H), 6.34 (s, 1H), 4.32 and 4.07 (AB quartet, *J* = 14 Hz, 1H), 3.38-3.31 (m, 1H), 3.17-2.93 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.49, 139.74, 139.24, 138.00, 135.37, 134.29, 133.97, 133.56, 133.38, 132.95, 132.36, 129.24, 53.83, 35.39, 35.12, 34.48, 33.09; IR (KBr): 2927, 2857, 2089, 1721, 1596, 1498, 1463, 1403, 1253, 1082 cm^{-1}; HRMS (ESI; m/z) Calcd for $C_{17}H_{17}N_3Na$ 286.1319 (M + Na), found 286.1315.

Synthesis of triazole **5**:



Azide **6** (1 g, 3.80 mmol) was dissolved in polyethylene glycol (PEG-600, 20 mL) and then phenylacetylene (0.41 mL, 3.80 mole) and sodium ascorbate (752 mg, 3.80 mole) were added. The reaction mixture was degassed for 30 min by purging with N_2. An aqueous solution of $CuSO_4$ (90 mg, 0.38 mmol) was added to the reaction mixture dropwise and again the reaction mixture was degassed for 15 min. It was allowed to stir for 24 h under the nitrogen atmosphere. A colorless solid precipitated during the course of the reaction. It was filtered through glass crucible and washed with water and hexane. Crude product was purified by column chromatography on silica gel using ethyl acetate and

hexane solvent mixture (50:50 v/v). Pure triazole **5** (0.874 g, 2.39 mmol, 63%) was obtained as a colorless solid.

Triazole **5**: Mp: 188 ^{o}C; $[\alpha_D]^{25}$ + 53.26 (c = 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, *J* = *7* Hz, 2H), 7.40 (s, 1H), 7.38-7.34 (m, 2H), 7.30-7.27 (m, 1H), 6.77 (dd, *J* = 8 Hz, 1 Hz, 1H), 6.59 (dd, *J* = 8 Hz, 2 Hz 1H), 6.55 (dd, *J* = 8 Hz, 2 Hz, 1H), 6.53-6.50 (m, 2H), 6.46 (dd, *J* = 8 Hz, 2Hz, 1H), 6.18 (s, 1H), 5.57 and 5.22 (AB quartet, *J* = 15 Hz, 1H), 3.33-2.83 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 148.05, 141.07, 139.72, 139.24, 138.35, 135.70, 134.05, 133.80, 133.66, 133.49, 133.41, 132.42, 130.67, 128.95, 128.87, 128.19, 125.73, 119.76, 53.32, 35.32, 34.99, 34.44, 33.04; IR (KBr): 3133, 3067, 3029, 2927, 2857, 1903, 1605, 1494, 1466, 1347, 1225, 1102, 1078, 1046 cm^{-1}. HRMS **(**ESI; m/z**)** Calcd for $C_{25}H_{23}N_3$ 366.1970 (M+H), found 366.1988. The optical purity of triazole **5** was ascertained by HPLC analysis: CHIRALPAK IA,(25 x 0.46 cm), t-butyl methyl ether-ethanol (98:2, v/v), flow rate = 1.5 mL/min, 254 nm UV Detector, retention time of S_p(+) **5** = 9.0 min, retention time of R_p(+) **5** = 10.8 min. The optical purity of the S_p(+) **5** was >97% ee.

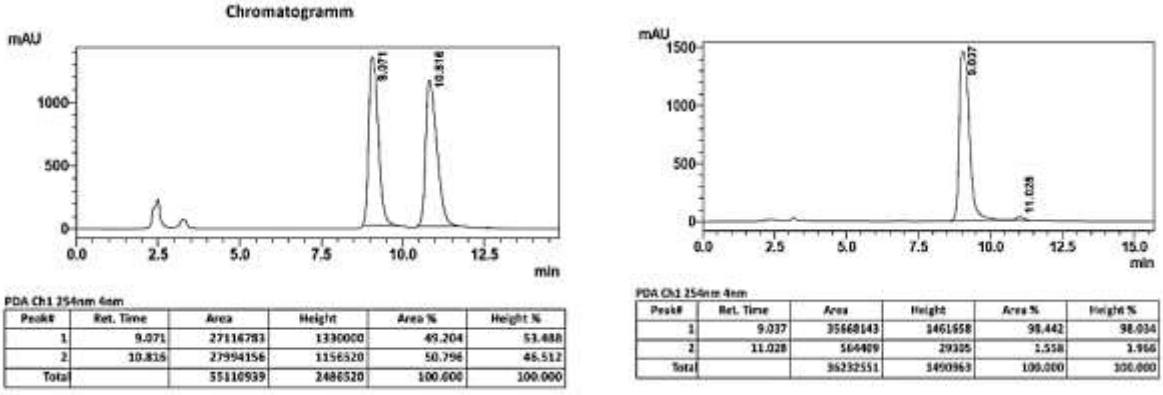
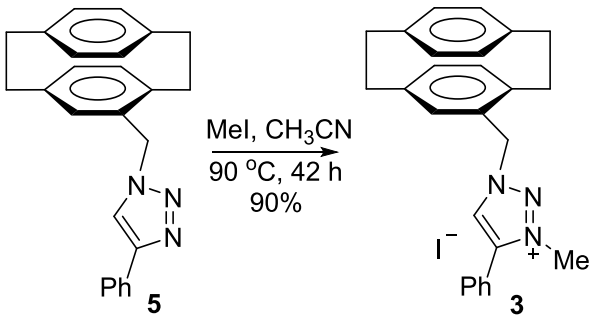


Figure S2: HPLC traces of racemic mixture (left) and S_p(+) isomer (right) of triazole **5**.

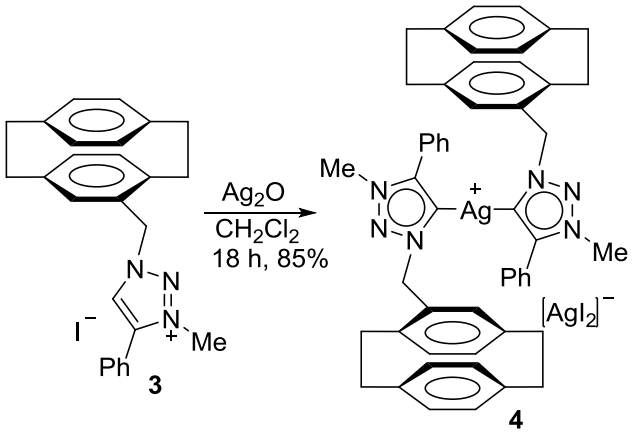
Synthesis of triazolium iodide **3**:



Triazole **5** (800 mg, 2.19 mmol) was dissolved in acetonitrile (3 mL) and then methyl iodide (1.09 mL, 17.52 mmol) was added. The reaction mixture was heated to 90 ^{o}C for 42 h in a teflon lined sealed steel reactor. The solid crude reaction mixture was washed with hexane and ethyl acetate and purified by re-crystallization from acetonitrile. Triazolium salt 3 was obtained as an off-white solid (0.99 g, 2.95 mmol, 90%).

Triazolium salt **3**: Mp: 210 ^{o}C; ^{1}H NMR **(**500 MHz, $CDCl_3$): δ(ppm) 8.91 (s, 1H), 7.62-7.61 (m, 2H), 7.58-7.50 (m, 3H), 6.75 (s, 1H), 6.67 (d, *J* = 7 Hz, 1H), 6.63-6.49 (m, 5H), 5.97 and 5.82 (AB quartet, *J* = 14 Hz, 1H), 4.21 (s, 3H), 3.65-3.60 (m, 1H), 3.24-3.21 (m, 2H), 3.17-3.05 (m, 4H), 2.98-2.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 143.01, 141.81, 139.77, 139.34, 139.30, 136.40, 136.02, 134.87, 133.71, 133.39, 132.76, 132.14, 130.72, 130.12, 129.83, 129.69, 129.40, 121.81, 56.83, 39.04, 35.31, 34.92, 34.85, 33.59; IR (KBr): 3053, 2948, 2924, 2850, 1910, 1616, 1592, 1491, 1435, 1323, 1278, 1151, 1074, 1018 cm^{-1}; HRMS (ESI; m/z) calculated for $C_{26}H_{26}N_3$ 381.2205 (M+H), found 381.2204.

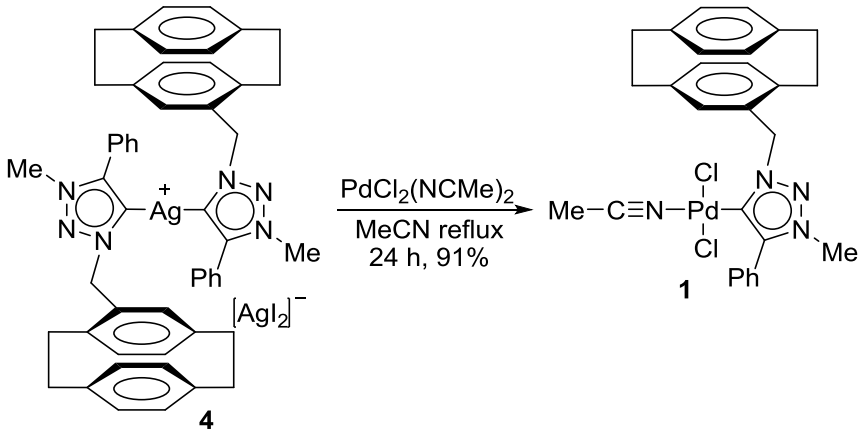
Synthesis of silver complex **4**:



Triazolium iodide **3** (800 mg, 1.57 mmol) was dissolved in dry CH_2Cl_2 (25 mL) and freshly prepared silver oxide (219 mg, 0.95 mmol) was added to reaction mixture in small portions. Then reaction mixture was allowed to stir for 24 h under nitrogen atmosphere in dark (covered with black cloth). The crude reaction mixture was filtered through celite. Evaporation of solvent gave the crude product as an off white solid (0.82 mg, 0.67 mmol, 85%). Mp: 255 ^{o}C; $[\alpha_D]^{25}$ + 21.35 (c = 0.32, $CHCl_3$) ^{1}H NMR(400 MHz, $CDCl_3$): δ (ppm) 7.46 (s, 10H), 6.63-6.47 (m, 14H), 5.59 and 5.24 (AB quartet, *J* = 14 Hz, 2H), 4.02 (s, 6H), 3.67-3.61 (m, 1H), 3.19-2.80 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.51, 148.74, 140.91, 139.69, 139.22, 138.47, 135.83, 135.22, 133.73, 133.67, 133.57, 133.35, 132.40, 130.18, 129.43, 129.22,

127.31, 65.93, 58.36, 37.52, 35.25, 34.96, 34.63, 33.69, 15.35; IR (KBr): 3032, 3007, 2920, 2850, 1633, 1592, 1498, 1431, 1312, 1158, 1071, 1018 cm^{-1}; HRMS (ESI; m/z) calcd for $C_{52}H_{50}N_6Ag$ 867.3140, found 867.3147. The ^1H NMR spectra of complex **4** obtained from racemic **3** as well as optically pure **3** were identical, only one AB quartet was observed for the CH_2 signals (see spectrum on page 33). This suggests that diastereomers of **4** were not formed in this reaction. Only a racemic mixture (*SS* and *RR*) was formed from racemic **3** and meso isomer (*RS*) was not formed.

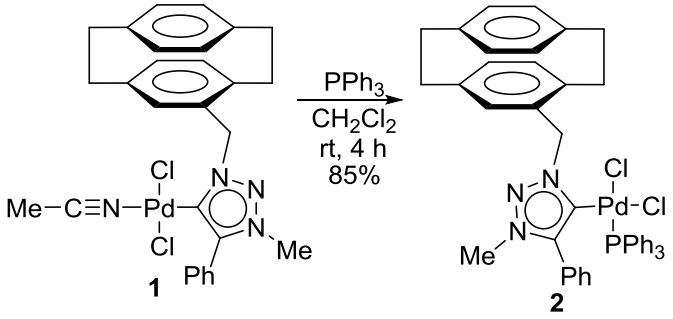
Synthesis of complex **1**:



Silver complex **4** (250 mg, 0.20 mmol) was dissolved in minimum volume of acetonitrile (10 mL) and then bis(acetonitrile)dichloropalladium(II) (110 mg, 0.43 mmol) was added. Reaction mixture was refluxed overnight. Removal of solvent and recrystallization in CH_2Cl_2-acetonitrile solvent mixture (80:20 v/v) gave complex **1** as a yellow crystalline solid (164 mg, 0.27 mmol, 81%).

Complex **1**: Mp: 235-237 ^oC; $[\alpha_D]^{25}$ + 30.91 (c = 0.123, CH_2Cl_2) ^1H NMR (400 MHz, CD_3CN): δ (ppm) 7.94-7.92 (m, 2H), 7.63-7.58 (m, 3H), 7.17 (d, *J* = 8Hz, 1H), 6.89 (d, *J* = 8Hz, 1H), 6.66 (s, 1H), 6.62-6.56 (m, 4H), 6.01-5.93 (AB quartet, *J* = 15 Hz, 2H), 3.88 (s, 3H), 3.69-3.63 (m, 1H), 3.27-2.93 (m, 7H), 1.96-1.92 (m, methyl peak of acetonitrile merged with solvent residual peak); ^{13}C NMR (125 MHz, CD_3CN): δ (ppm) 143.83, 141.73, 140.89, 140.52, 139.40, 136.12, 134.93, 134.66, 134.53, 134.20, 133.77, 131.49, 130.92, 130.04, 129.64, 57.42, 38.78, 35.80, 35.40, 34.98, 34.03; IR (KBr): 2930, 2846, 2322, 2294, 1745, 1624, 1592, 1480, 1442, 1407, 1326, 1253,1162, 1071, 1022. HRMS (ESI; m/z) calcd for $C_{28}H_{29}N_4Cl_2Pd$ 597.0804, found 597.0798.

Synthesis of complex 2:



To a stirred solution of complex **1** (250 mg, 0.418 mmol) in CH_2Cl_2 (5 mL), solid triphenylphosphine (132 mg, 0.5 mmol) was added. The reaction mixture was allowed to stir at room temperature under nitrogen atmosphere for 6 h. Crude product was purified by re crystallization DCM-Methanol (90:10 v/v). White crystalline solid (290 mg, 0.354mmol, 85%) was obtained as pure product.

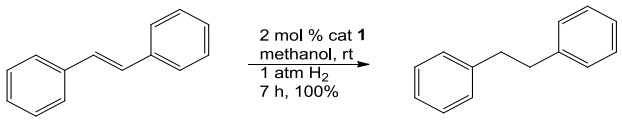
Complex **2**: Mp: 250-252 ^{o}C; ^{1}H NMR (400 MHz, DMSO): δ (ppm) 7.60-7.43 (m, 9H), 7.23-7.21 (m, 6H), 6.90-6.70 (m, 8H), 6.53 (s, 3H), 6.39 (d, *J* = 7 Hz, 1H), 5.92 (d, *J* = 8 Hz, 1H), 5.91-5.83 (AB quartet, *J* = 12 Hz, 1H), 5.63-5.59 (AB quartet, *J* = 9 Hz, 1H), 3.96-3.85 (m, 1H), 3.79 (s, 3H), 3.25-2.88 (m, 7H); ^{13}C NMR (100 MHz, DMSO): δ (ppm) 150.25, 149.88 , 141.99 , 141.94 , 140.08, 139.99, 139.19, 139.10, 138.98 , 138.33, 136.46, 135.35, 134.88, 134.79, 133.81, 133.70, 133.48, 133.21, 133.03, 132.82, 132.25, 132.12, 131.35, 130.60, 130.51, 130.04, 129.84, 129.77, 129.67, 129.33, 129.24, 128.35, 127.87, 127.76, 125.44, 57.54, 54.64, 37.74 , 34.66 , 34.55, 34.38, 34.23, 33.97, 33.70, 32.89; IR: 3057, 2924, 2850, 2364, 2330, 1592, 1473, 1435, 1312, 1089. HRMS (ESI; m/z) Calcd for $C_{44}H_{41}Cl_2N_3PPd$ (M+H) 818.1450, found 818.1442.

General procedure for catalytic hydrogenation:

Substrate (100 mg) was dissolved in methanol (5 mL) and then complex rac-**1** (2 mol %) was added to the reaction mixture. The reaction flask was flushed with hydrogen and a balloon filled with hydrogen gas was attached to the flask. The pressure of hydrogen gas in the balloon was 1.05 atmosphere (795 mm Hg). The reaction mixture was allowed to stir under H_2 atmosphere at room temperature until starting substrate disappeared (TLC monitoring) (7-20 h). Solvent was evaporated under vacuum to give the crude hydrogenated product. The crude product was passed through short column of 100-200 mesh silica gel and eluted with hexane to obtain pure hydrogenated product. For asymmetric hydrogenation of prochiral substrates S_p-**1** (2 mol %) was used as the catalyst. The enantiomeric ratios of the products

obtained from the hydrogenation of prochiral substrates were determined by HPLC analysis on a chiral stationary phase column and by measurement of optical rotation values.

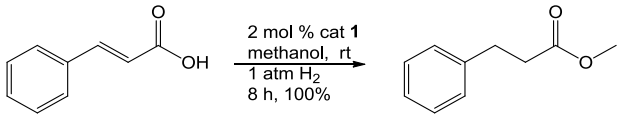
***E*-Stilbene to 1, 2-diphenylethane (Table 1, entry 1):**



Hydrogenation of 100 mg (0.55 mmol) of *E*-stilbene with catalyst **1** (6.57 mg, 0.011 mmol, 2 mol %) in 5 ml of methanol for 7 h gave 99.8 mg (0.55 mmol, 100 %) of 1,2-diphenylethane. In another batch after completion of reaction 100 mg (0.55 mmol) *E*-stilbene was added to the same reaction mixture and reaction was continued until completion. In a similar manner the reaction was continued up to 13 cycles by adding 100 mg of *E*-stilbene successively to the same reaction mixture after ascertaining the completion of the reaction prior to each further addition. The overall yield was 1.29 g (0.70 mmol, 98 %). Turnover number after 13 cycles was 640.

1,2-Diphenylethane[3]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.29-7.25 (m, 4H), 7.20-7.16 (m, 6H), 2.91 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 128.62, 128.58, 128.50, 128.46, 126.04, 38.07.

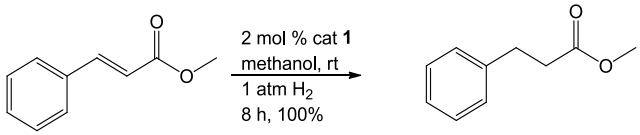
***E*-Cinnamic acid to methyl 3-phenylpropanoate (Table 1, entry 2):**



Hydrogenation of 100 mg (0.67 mmol) of *E*-cinnamic acid using catalyst **1** (7.77 mg, 0.013 mmol, 2 mol %) in 5 ml of methanol for 8 h gave 108 mg (0.65 mmol, 100 %) of methyl 3-phenylpropanoate.

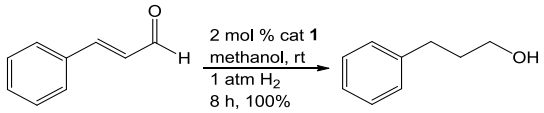
Methyl 3-phenylpropanoate[4]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30-7.26 (m, 2H), 7.21-7.18 (m, 3H), 3.66 (s, 3H), 2.95 (t, *J* = 8 Hz, 3H), 2.63 (t, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 173.33, 140.51, 128.50, 128.25, 126.26, 51.57, 35.69, 30.95.

Methyl E-cinnamate to methyl 3-phenylpropionate (Table 1, entry 3):



Hydrogenation of 100 mg (0.61 mmol) methyl E-cinnamate using catalyst **1** (7.17 mg, 0.012 mmol, 2 mol %) in 5 ml of methanol for 8 h gave 101 mg (0.60 mmol, 100 %) of Methyl 3-phenylpropanoate.

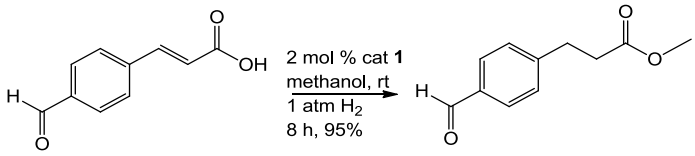
***E*-Cinnamaldehyde to 3-phenylpropanol (Table 1, entry 4):**



Hydrogenation of 100 mg (0.75 mmol) *E*-Cinnamladehyde using catalyst **1** (8.96 mg, 0.015 mmol, 2 mol %) in 5 ml of methanol for 8 h gave 102 mg (0.75 mmol, 100 %) of 3-Phenylpropanol.

3-Phenylpropanol[5]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.29-7.24 (m, 2H), 7.20-7.16 (m, 3H), 3.66 (t, *J* = 8 Hz, 2H), 2.70 (t, *J* = 8 Hz, 2H), 1.92-1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 141.82, 128.42, 128.40, 125.86, 62.27, 34.21, 32.08.

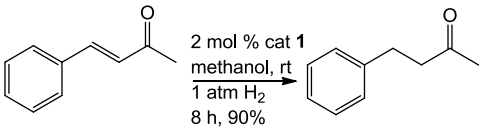
4-Formyl-*E*-cinnamic acid to methyl 3-(4-formylphenyl)propanoate (Table 1, entry 5):



Hydrogenation of 100 mg (0.56 mmol) substrate using catalyst **1** (6.57 mg, 0.011 mmol, 2 mol %) in 5 ml of methanol for 8 h yielded 109 mg (0.539 mmol, 95%) of the product.

Methyl 3-(4-formylphenyl)propanoate[6] **:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 9.98 (s, 1H), 7.81 (d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 8 Hz, 2H), 3.67 (s, 3H), 3.03 (t, *J* = 8 Hz, 2H), 2.67 (t, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 192.04, 172.97, 147.93, 130.220, 129.17, 51.96, 35.16, 31.17, 29.85.

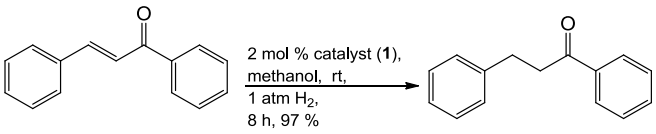
***E*-Benzalacetone to 4-phenyl-2-butanone (Table 1, entry 6):**



Hydrogenation of 100 mg (0.68 mmol) of *E*-Benzalacetone in 5 ml of methanol using catalyst **1** (7.77 mg, 0.013mmol, 2 mol %) for 8h gave crude product that was purified by column chromatography using silica gel and ethyl acetate–hexane (10:90 v/v) as eluant. 91 mg (0.61 mmol, 90%) of 4-phenyl-2-butanone was obtained as pure product.

4-Phenyl-2-butanone[7]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 2.91-2.74 (AA'BB' pattern, *J* = 8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 208.14, 141.10, 128.62, 128.41, 126.24, 45.30, 30.20, 29.85.

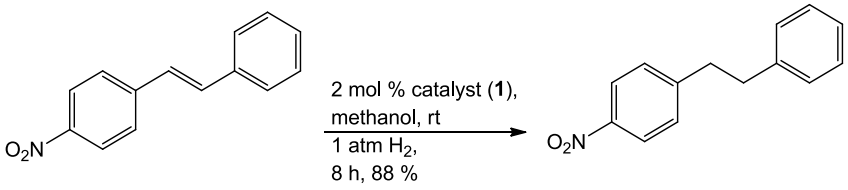
***E*-Benzalacetophenone to 1,3-diphenyl-1-propanone (Table 1, entry 7):**



Hydrogenation of 100 mg (0.48 mmol) benzalacetophenone using catalyst **1** (5.73 mg, 0.0096 mmol, 2 mol %) in 5 ml of methanol for 8 h gave the crude product which was filtered through small celite bed and methanol was concentrated under vacuum. 98 mg (0.46 mmol, 97%) of 1,3-Diphenyl-1-propanone was obtained as pure product.

1,3-Diphenyl-1-propanone[8,9] **:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.94-7.97 (m, 2H), 7.55-7.52 (m, 1H), 7.47-7.43 (m, 2H), 7.32-7.24 (m, 4H), 7.22-7.18 (m, 1H), 3.32-3.28 (m, 2H), 3.07 (t, *J* = 8 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 199.37 141.43, 137.00, 133.19, 128.74, 128.66, 128.56, 128.17, 126.27, 40.59, 30.27.

***E*-4-Nitrostilbene to 1-(4-nitrophenyl)-2-phenylethane (Table 1, entry 8):**



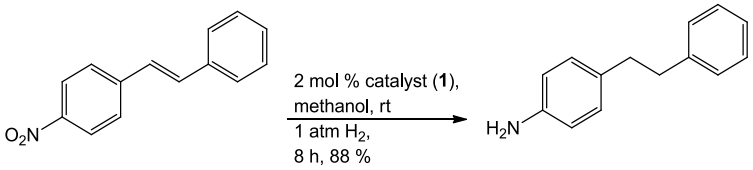
Hydrogenation of 100 mg (0.44 mmol) substrate using catalyst **1** (5.30 mg, 0.009 mmol, 2 mol %) in 5 ml of methanol for 8 h gave crude product. Reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. Finally the crude product was purified by column

chromatography using silica gel and ethyl acetate–hexane (10:90 v/v) as eluant. 76 mg (0.33 mmol, 76%) was obtained as pure product.

1-(4-Nitrophenyl)-2-phenylethane[10]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.14-8.10 (m,2H), 7.30-7.26 (m, 4H), 7.22-7.18 (m, 1H), 7.14-7.12 (m, 2H), 3.05-3.01 (m, 2H), 2.97-2.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 149.55, 146.57, 140.59, 129.48, 128.64, 128.60, 128.57, 126.46, 123.74, 37.81, 37.36; IR (KBr): 2915, 2847, 1598, 1512, 1338, 1260, 1103.

E-4-Nitrostilbene was synthesized according to literature procedure[11].

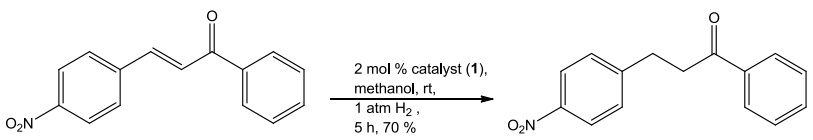
_E_-4-Nitrostilbene to 1-(4-aminophenyl)-2-phenylethane (Table 1, entry 9):



Hydrogenation of 100 mg (0.44 mmol) substrate using catalyst **1** (5.30 mg, 0.009 mmol, 2 mol %) in 5 ml of methanol for 8 h yielded crude product. Reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. Finally the crude product was purified by column chromatography using silica gel and ethyl acetate–hexane (30:70 v/v) as eluant. 77 mg (0.39 mmol, 88%) was obtained as pure product.

1-(4-Aminophenyl)-2-phenylethane **[10] :** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.29-7.24 (m,2H), 7.19-7.16 (m, 3H), 6.98-6.95 (m, 2H), 6.63-6.60 (m, 2H), 3.55(br, s, 2H), 2.88-2.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 144.41, 142.19, 132.08, 129.35, 128.61, 128.40, 125.91, 115.37, 38.43, 37.24.

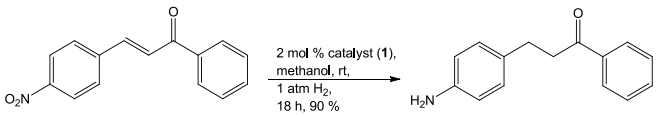
(E)-3-(4-Nitrophenyl)-1-phenylprop-2-en-1-one to 3-(4-nitrophenyl)-1-phenylpropan-1-one (Table 1, entry 10):



100 mg (0.39 mmol) unsaturated substrate was hydrogenated (5 h) using catalyst **1** (4.71 mg, 0.008 mmol, 2 mol %). 5 ml of methanol was used as solvent. Reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. Finally the crude product was purified by column chromatography using silica gel and ethyl acetate–hexane (10:90 v/v) as eluant. 71 mg (0.27 mmol, 70%) was obtained as pure product.

3-(4-Nitrophenyl)-1-phenylpropan-1-one**[12]:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.14-8.13 (m, 2H), 7.96-7.93 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.41 (m, 4H), 3.37-3.34 (m, 2H), 3.18 (t, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 198.28, 149.33, 146.66, 136.63, 133.54, 129.50, 128.86, 128.13, 123.91, 39.54, 29.86; IR (KBr): 3061, 2926, 2851, 1680, 1655, 1606, 1516, 14441, 1338, 1216, 1103, 1017.

(E)-3-(4-Nitrophenyl)-1-phenylprop-2-en-1-one to 3-(4-aminophenyl)-1-phenylpropan-1-one (Table 1, entry 11):

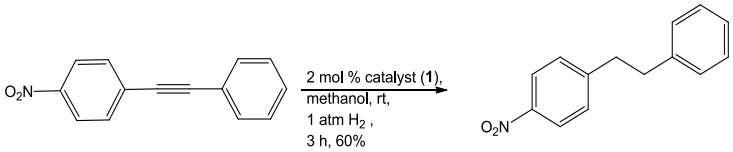


100 mg (0.39 mmol) unsaturated substrate was hydrogenated (18 h) using catalyst **1** (4.71 mg, 0.008 mmol, 2 mol %). 5 ml of methanol was used as solvent. Reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. Finally the crude product was purified by column chromatography using silica gel and ethyl acetate–hexane (30:70 v/v) as eluant. 81 mg (0.35 mmol, 90%) was obtained as pure product.

3-(4-Aminophenyl)-1-phenylpropan-1-one**[13]** : ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.96-7.93 (m, 2H), 7.54-7.52 (m, 1H), 7.46-7.42 (m, 2H), 7.05-7.02 (m, 2H), 6.64-6.62 (m, 2H), 3.57 (br, s, 2H), 3.26-3.22 (m, 2H), 2.97-2.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 199.78, 144.67, 137.10, 133.11, 131.39, 129.36, 128.71, 128.19, 115.49, 41.02, 29.54.

Compound *E*-4-Nitrobenzalacetophenone was prepared according to literature procedure[14].

1-(4-Nitrophenyl)-2-phenylethyne to 1-(4-nitrophenyl)-2-phenylethane

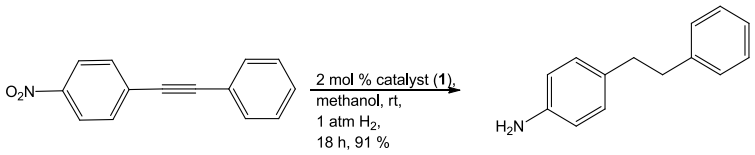


100 mg (0.45 mmol) unsaturated substrate was hydrogenated (3 h) using catalyst **1** (5.35 mg, 0.009 mmol, 2 mol %). 5 ml of methanol was used as solvent. Reaction mixture was filtered through small

celite bed and then methanol was evaporated under vacuum. Finally the crude product was purified by column chromatography using silica gel and ethyl acetate–hexane (10:90, v/v) as eluant. 62 mg (0.27 mmol, 60%) was obtained as pure product.

1-(4-Nitrophenyl)-2-phenylethane **[10] :** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.14-8.10 (m,2H), 7.30-7.26 (m, 4H), 7.22-7.18 (m, 1H), 7.14-7.12 (m, 2H), 3.05-3.01 (m, 2H), 2.97-2.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 149.55, 146.57, 140.59, 129.48, 128.64, 128.60, 128.57, 126.46, 123.74, 37.81, 37.36; IR (KBr): 2915, 2847, 1598, 1512, 1338, 1260, 1103.

1-Nitro-4-(phenylethynyl)benzene to 1-(4-aminophenyl)-2-phenylethane:

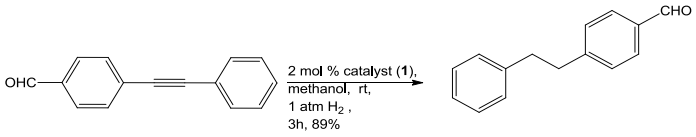


100 mg (0.44 mmol) unsaturated substrate was hydrogenated (18 h) using catalyst **1** (5.35 mg, 0.009 mmol, 2 mol %). 5 ml of methanol was used as solvent. Reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. Finally the crude product was purified by column chromatography using silica gel and ethyl acetate–hexane (30:70 v/v) as eluant. 81 mg (0.41 mmol, 91%) was obtained as pure product.

1-(4-Aminophenyl)-2-phenylethane[10] **:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.29-7.24 (m,2H), 7.19-7.16 (m, 3H), 6.98-6.95 (m, 2H), 6.63-6.60 (m, 2H), 3.55(br, s, 2H), 2.88-2.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 144.41, 142.19, 132.08, 129.35, 128.61, 128.40, 125.91, 115.37, 38.43, 37.24.

Compound 1-(4-Nitrophenyl)-2-phenylethyne was prepared according to literature procedure [15].

1-(4-Formylphenyl)-2-phenylethyne to **1-(4-formylphenyl)-2-phenylethane:**



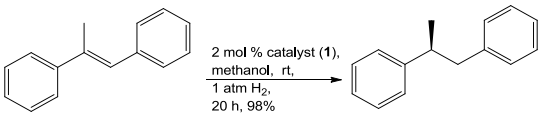
100 mg (0.48 mmol) unsaturated substrate was hydrogenated (3 h) using catalyst **1** (5.71 mg, 0.009 mmol, 2 mol %). 5 ml of methanol was used as solvent. Reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. Finally the crude product was purified by

column chromatography using silica gel hexane as eluant. 91 mg (0.43 mmol, 89%) was obtained as pure product.

1-(4-Formylphenyl)-2-phenylethane [16] **:** ^{1}H NMR (400 MHz, CDCl3): δ (ppm): 9.97 (s, 1H), 7.80-7.77 (m, 2H), 7.32-7.27 (m, 4H), 7.22-7.18 (m, 1H), 7.16-7.14 (m, 2H), 3.03-2.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 192.20, 149.23, 141.05, 134.73, 130.07, 129.35, 128.61, 128.58, 128.54, 126.31, 38.20, 37.50.

Compound 1-(4-formylphenyl)-2-phenylethyne was prepared according to literature procedure [17].

1, 2-Diphenylpropene to (*S*)-1,2-diphenylpropane :

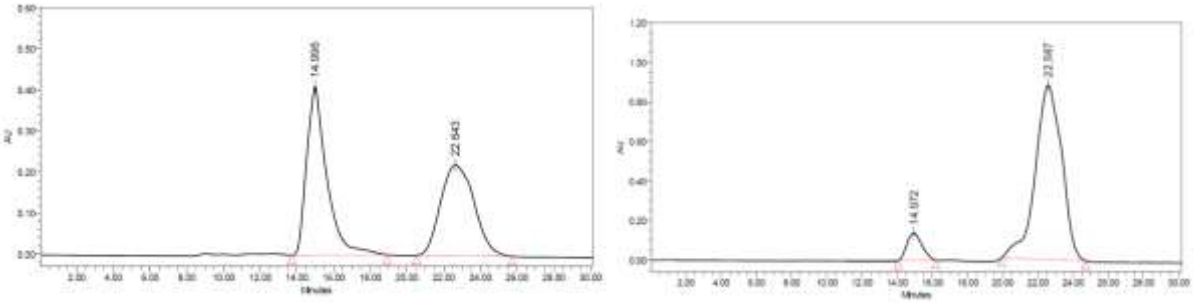


100 mg (0.51 mmol) of 1,2-diphenylpropene was hydrogenated using catalyst S_p-**1** (5.98 mg, 0.010 mmol, 2 mol %). 5 ml of methanol was used as solvent. After completion (20 h) of reaction (monitored by TLC) reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. 99 mg (0.50 mmol, 98%) was obtained as pure product.

84% ee; $[\alpha_D]^{25}$ +42.74 (c = 1.0, $CHCl_3$)[lit. value $[\alpha_D]^{25}$ + 53.0° (c = 2.3, $CHCl_3$, 78% ee)] [18]

HPLC condition: Chiracel OJ-H (25cm x 0.46 cm), *n*-hexane/2-propanol (99:1 v/v), flow rate = 0.5 mL/min, 254 nm UV Detector, t_r = 14.99 min (minor), t_r = 22.58 min (major),

1,2-Diphenylpropane[4]**:** ^{1}H NMR **(**400 MHz, $CDCl_3$): δ(ppm) 7.29-7.13 (8H, m), 7.08-7.06 (m, 2H), 3.04-2.91 (m, 2H), 2.78-2.73 (m, 1H), 1.23 (d, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.13, 140.95, 129.29, 128.43, 128.22, 127.18, 126.14, 125.96, 45.18, 41.99, 21.28; HRMS **(**ESI; m/z**)** Calcd. for $C_{15}H_{16}$ Na (M+Na): 219.1150, found 219.1147.



	RT	Area	% Area	% Height

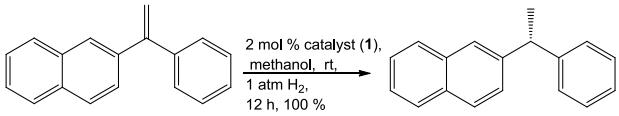
1	14.996	30978934	52.48	65.04
2	22.643	28046621	47.52	34.96

	RT	Area	% Area	% Height
1	14.972	8114213	8.10	13.49
2	22.587	92111422	91.90	86.51

Figure S3: HPLC traces of racemic mixture (left) and S (+) isomer (right).

Optical purity of 1,2-diphenylpropane is 84 % ee.

2-(1-Phenylvinyl)naphthalene to (*R*)-2-(1-phenylethyl)naphthalene:

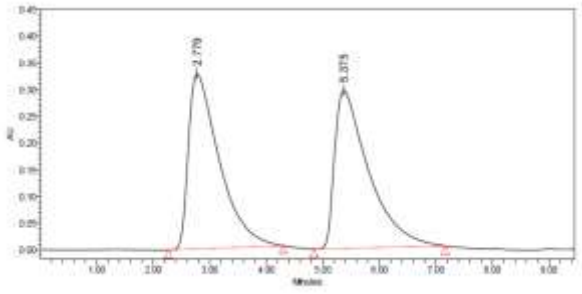


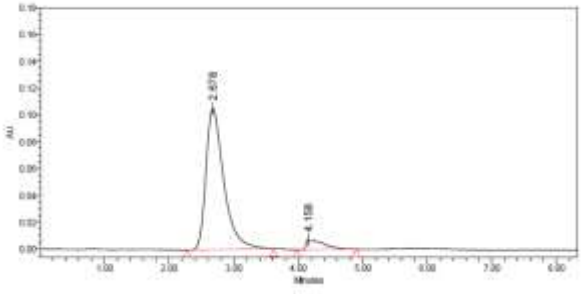
100 mg (0.43mmol) of 2-(1-Phenylvinyl)naphthalene was hydrogenated using catalyst S_p-**1** (5.19 mg, 0.009 mmol, 2 mol %). 5 ml of methanol was used as solvent. After completion (12 h) of reaction (monitored by TLC) reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. 100 mg (0.43 mmol, 98%) was obtained as pure product.

87% ee; $[\alpha_D]^{25}$ -42.08 (c = 1.0, $CHCl_3$); [lit Value $[\alpha_D]^{25}$ –46.3 (c = 1.0, $CHCl_3$, 98% ee)] [19]

HPLC condition: Chiracel OJ-H (25cm x 0.46 cm), *n*-hexane/2-propanol (99:1), flow rate = 1 mL/min, 254 nm UV Detector, t_r = 2.67 min (major), t_r = 4.15 min (minor),

(*R*)-2-(1-Phenylethyl)naphthalene **[16] :** ^{1}H NMR **(** 400 MHz, $CDCl_3$): δ(ppm) 7.77-7.66 (m, 4H), 7.44-7.36 (m, 2H), 7.29-7.21 (m, 5H), 7.18-7.15 (m, 1H), 4.31-4.25 (quartet, 1H), 1.70 (d, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 146.23, 143.78, 133.54, 132.11, 128.40, 127.95, 127.76, 127.73, 127.57, 126.84, 126.10, 125.94, 125.37, 44.87, 21.77; HRMS **(**ESI; m/z**)** Calcd. for $C_{18}H_{16}Na$ (M+Na): 255.1150, found 255.1153.





	RT	Area	% Area	% Height
1	2.779	12431842	50.07	52.53
2	5.375	12397862	49.93	47.47

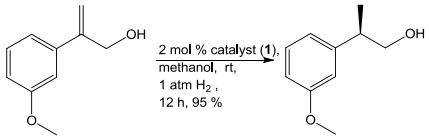
	RT	Area	% Area	% Height
1	2.678	2016748	93.50	93.29
2	4.158	140151	6.50	6.71

Figure S4: HPLC traces of racemic mixture (left) and R (-) isomer (right).

Optical purity of (*R*)-2-(1-phenylethyl)naphthalene is 87 % ee.

Compound 2-(1-phenylvinyl)naphthalene was prepared according to literature procedure [20].

2-(3-Methoxyphenyl)prop-2-en-1-ol to (R)-2-(3-methoxyphenyl)propane-1-ol :

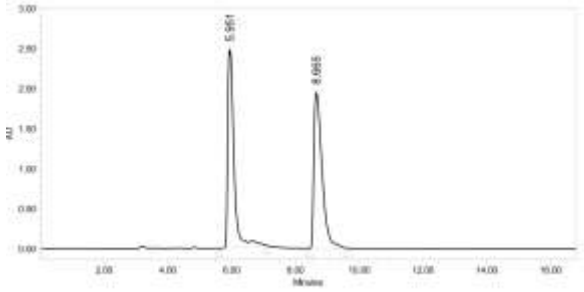


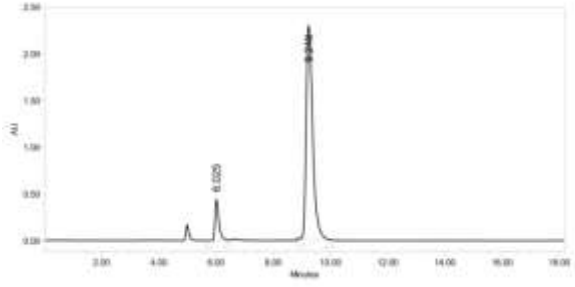
100 mg (0.61mmol) of 2-(3-Methoxyphenyl)prop-2-en-1-ol was hydrogenated using catalyst S_p-**1** (7.17 mg, 0.012 mmol, 2 mol %). 5 ml of methanol was used as solvent. After completion (12 h) of reaction (monitored by TLC) reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. 96 mg (0.58 mmol, 95%) was obtained as pure product.

80.12 % ee; $[\alpha_D]^{25}$ +41.91(c = 1.0, $CHCl_3$,); [lit. value $[\alpha_D]^{20}$ +2.8 (c = 1.0, $CHCl_3$, 37% ee)] [21]

HPLC condition: Chiracel IA (15cm x 0.46 cm), *n*-hexane/2-propanol (95:5), flow rate = 0.5 mL/min, 254 nm UV Detector, t_r = 6.02 min (major), t_r = 9.24 min (minor),

2-(3-Methoxyphenyl)propane-1-ol[21]**:** ^{1}H NMR **(**400 MHz, $CDCl_3$): δ(ppm) 7.27-7.23 (m, 1H), 6.84-6.76 (m, 3H), 3.80 (s, 3H), 3.70 (d, *J* = 8 Hz, 2H), 2.97-2.88 (m, 1H), 1.27 (d, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.02, 145.53, 129.79, 119.95, 113.64, 111.90, 68.78, 55.32, 42.67, 17.69; HRMS **(**ESI; m/z**)** Calcd. for $C_{10}H_{14}O_2$ Na (M+Na): 189.0891, found 189.0900.





	RT	Area	% Area	% Height
1	5.951	33710389	49.24	56.1
2	8.665	34749191	50.76	43.90

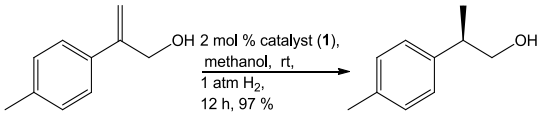
	RT	Area	% Area	% Height
1.	6.025	3948618	9.94	16.15
2.	9.248	35778219	90.06	83.85

Figure S5: HPLC traces of racemic mixture (left) and R (+) isomer (right).

Optical purity of 2-(3-methoxyphenyl)propane is > 80 % ee.

Compound 2-(3-methoxyphenyl)prop-2-en-1-ol was synthesized according to literature procedure [22].

2-(*p*-Tolyl)prop-2-en-1-ol to (R)-2-*p*-tolylpropane-1-ol :

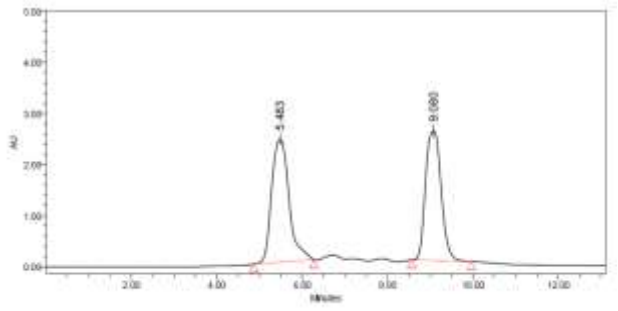


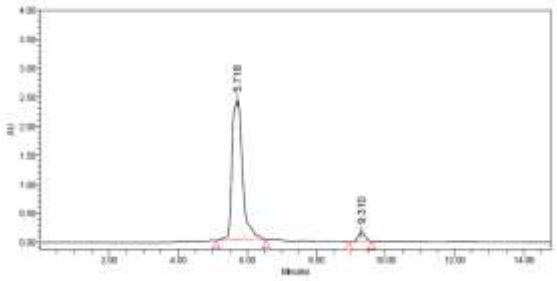
100 mg (0.67 mmol) of 2-(*p*-Tolyl)prop-2-en-1-ol was hydrogenated using catalyst S_p-**1** (7.77 mg, 0.013 mmol, 2 mol %). 5 ml of methanol was used as solvent. After completion (12 h) of reaction (monitored by TLC) reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. 98mg (0.65 mmol, 97%) was obtained as pure product.

91.18 % ee; $[\alpha_D]^{25}$ +13.20 (c = 1.0, $CHCl_3$); [lit value $[\alpha_D]^{20}$ +8.7 (c = 2.75, $CHCl_3$, 74% ee)][21]

HPLC condition: Chiracel IA (15cm x 0.46 cm), *n*-hexane/2-propanol (98:2 v/v), flow rate = 1 mL/min, 254 nm UV Detector, t_r = 5.71 min (major), t_r = 9.31 min (minor),

(R)-2-p-Tolylpropane-1-ol[21] **:** ^{1}H NMR **(** 400 MHz, $CDCl_3$): δ (ppm) 7.16-7.11 (4H, m), 3.68 (d, *J* = 8 Hz, 2H), 2.96-2.87 (m, 1H), 2.33 (s, 3H), 1.26 (d, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.67, 136.37, 129.48, 127.49, 68.90, 42.16, 21.13, 17.79; HRMS **(**ESI; m/z**)** Calcd. for $C_{10}H_{14}ONa$ (M+Na): 173.0942, found 173.0935.





	RT	Area	% Area	% Height
1	5.483	67953111	51.43	48.73
2	9.080	64180659	48.57	51.27

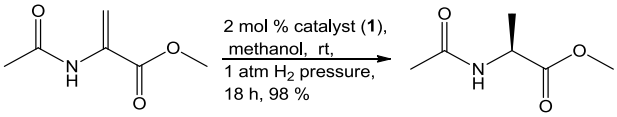
	RT	Area	% Area	% Height
1	5.718	50861987	95.59	93.55
2	9.310	2346140	4.541	6.45

Figure S6: HPLC traces of racemic mixture (left) and R(+) isomer (right)

Optical purity of R(+)-2-*p*-Tolylpropane-1-ol isomer is > 91 % ee.

Compound 2-(p-Tolyl)prop-2-en-1-ol was synthesized according to literature procedure [22].

Methyl 2-acetamidoacrylate to (S)-methyl 2-acetamidopropanoate :



100 mg (0.70 mmol) of methyl 2-acetamidoacrylate was hydrogenated using catalyst S_p-**1** (7.77 mg, 0.013 mmol, 2 mol %). 5 ml of methanol was used as solvent. After completion (18 h) of reaction (monitored by TLC) reaction mixture was filtered through small celite bed and then methanol was evaporated under vacuum. 99 mg (0.68 mmol, 98%) was obtained as pure product.

$[\alpha_D]^{25}$ -74.22 (c = 1.0, H_2O, 81 % ee) [lit. value $[\alpha_D]^{25}$ −91.4 (c = 1.0, H_2O), ee >99%][23]. The enantiomeric excess reported here is based on optical rotation values.

(S)-Methyl 2-acetamidopropanoate [24]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 6.08 (s, 1H). 4.64-4.56 (m, 1H), 3.75 (s, 3H), 2.02 (s, 3H), 1.40 (d, *J* = 8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 173.74, 169.80, 52.50, 48.12, 23.13, 18.49; HRMS **(**ESI; m/z**)** Calcd. for $C_6H_{12}N0_3$ (M+H): 146.0817, found 146.0815.

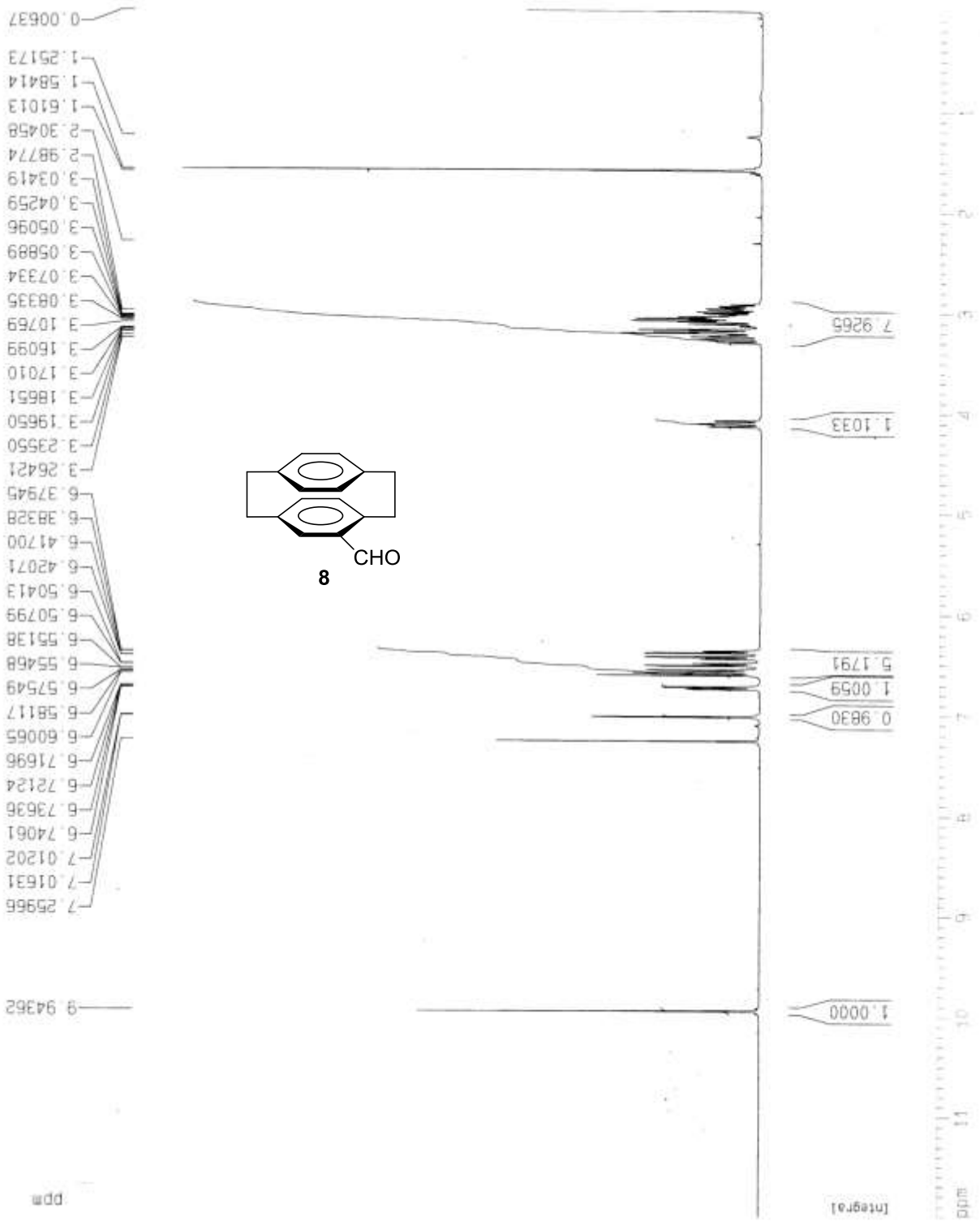


Figure S7. 400 MHz ^{1}H NMR spectrum of compound **8** in $CDCl_3$.

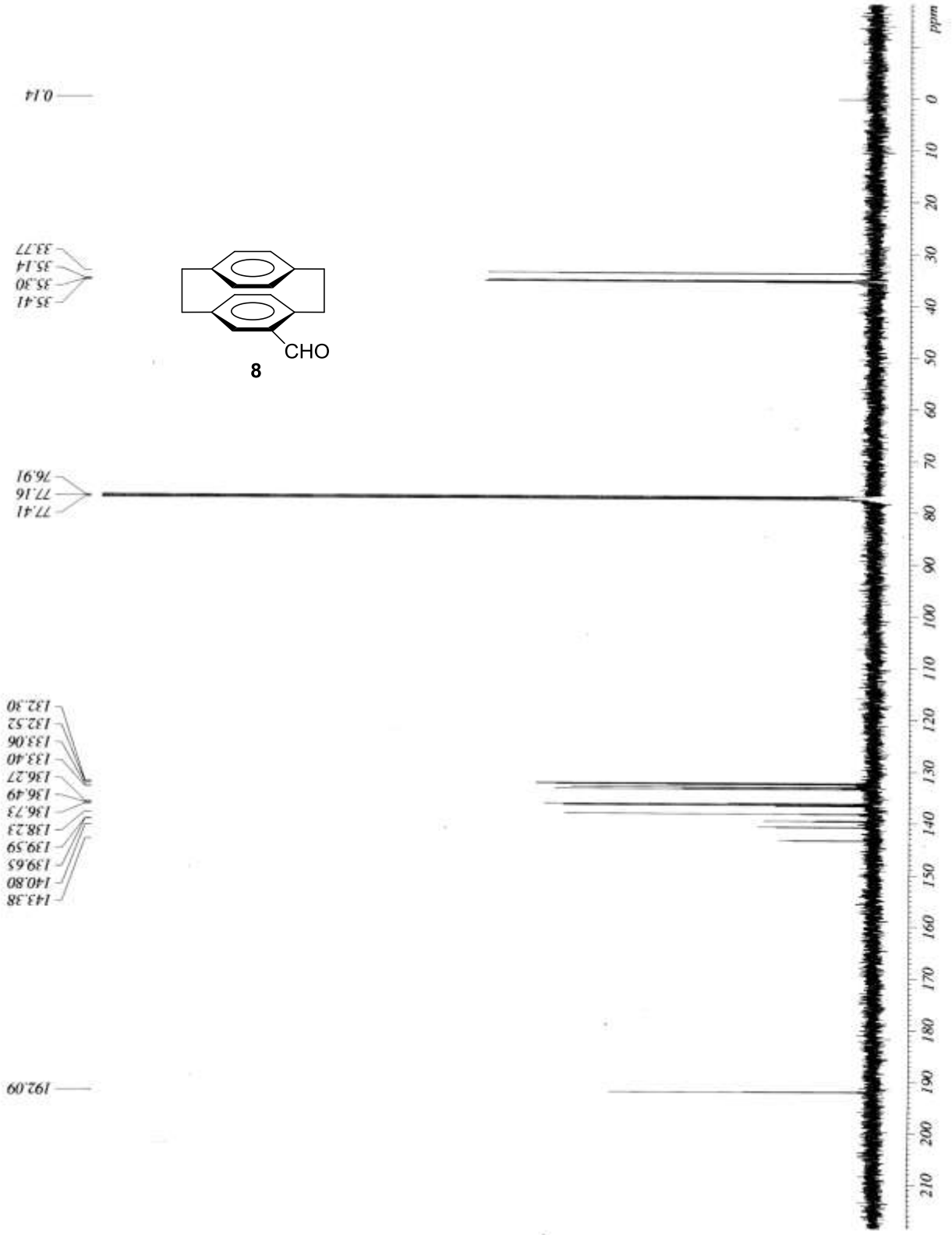


Figure S8. 100 MHz ^{13}C NMR spectrum of compound **8** in $CDCl_3$.

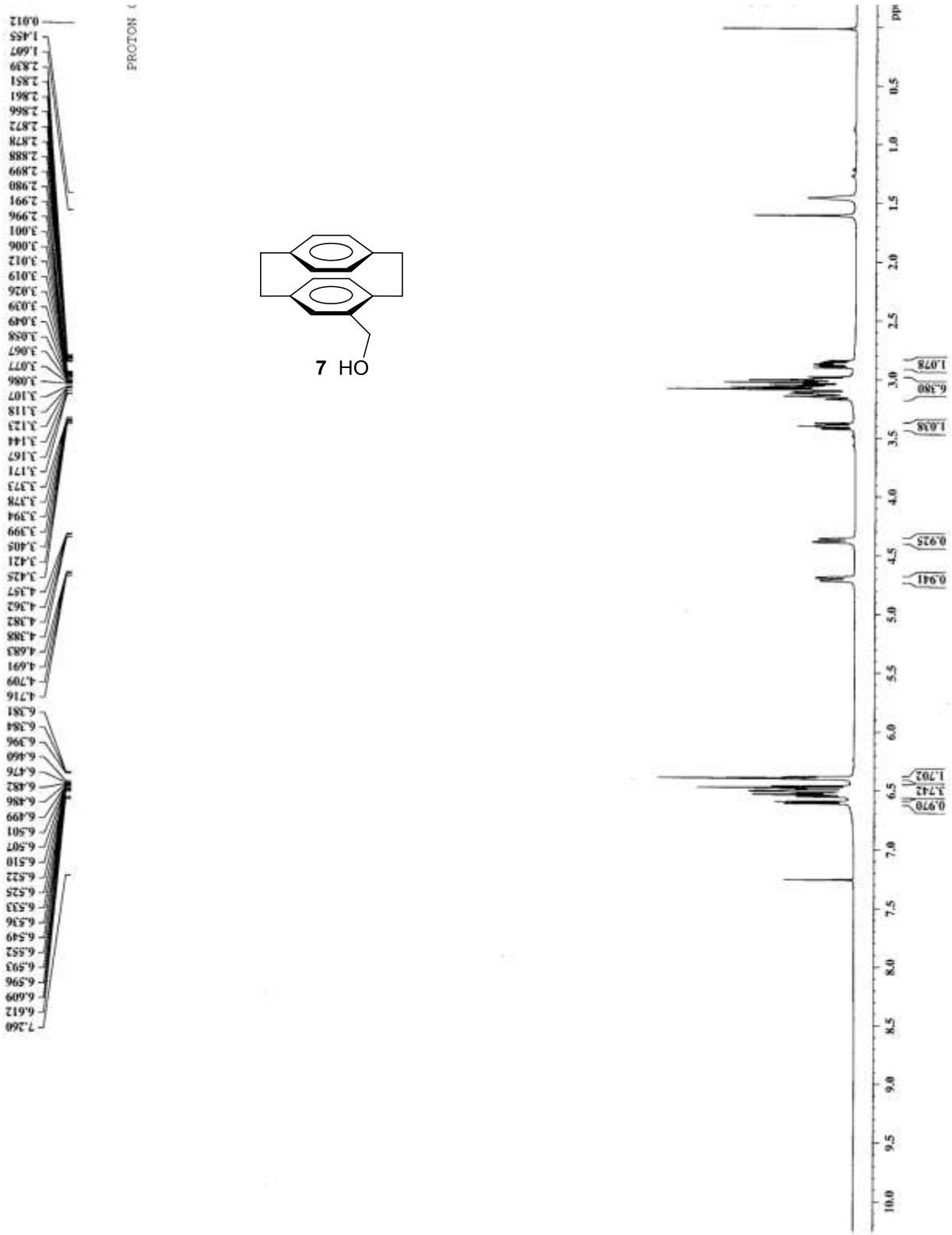


Figure S9. 500 MHz ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

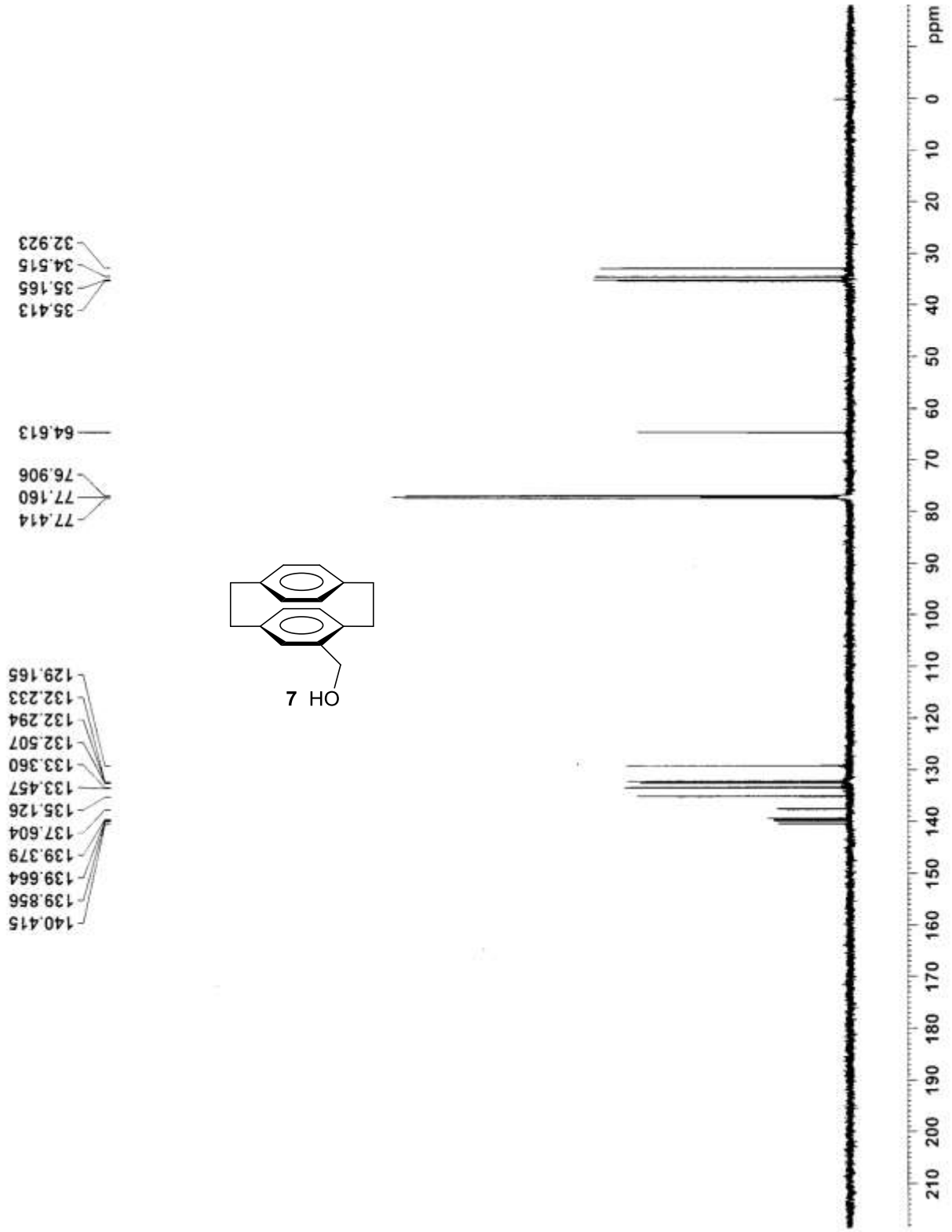


Figure S10. 125MHz ^{13}C NMR spectrum of compound **7** in $CDCl_3$.

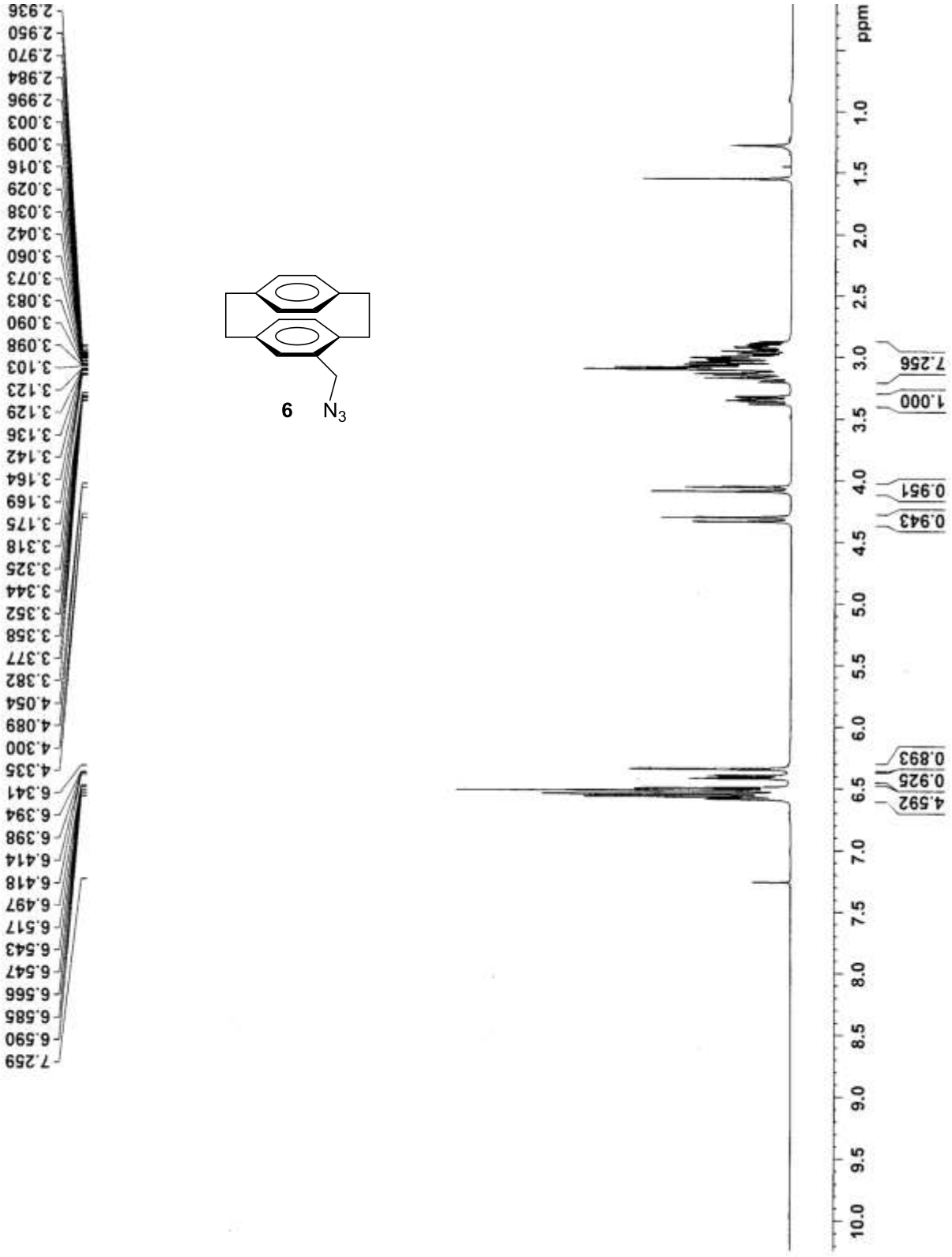


Figure S11. 400 MHz ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

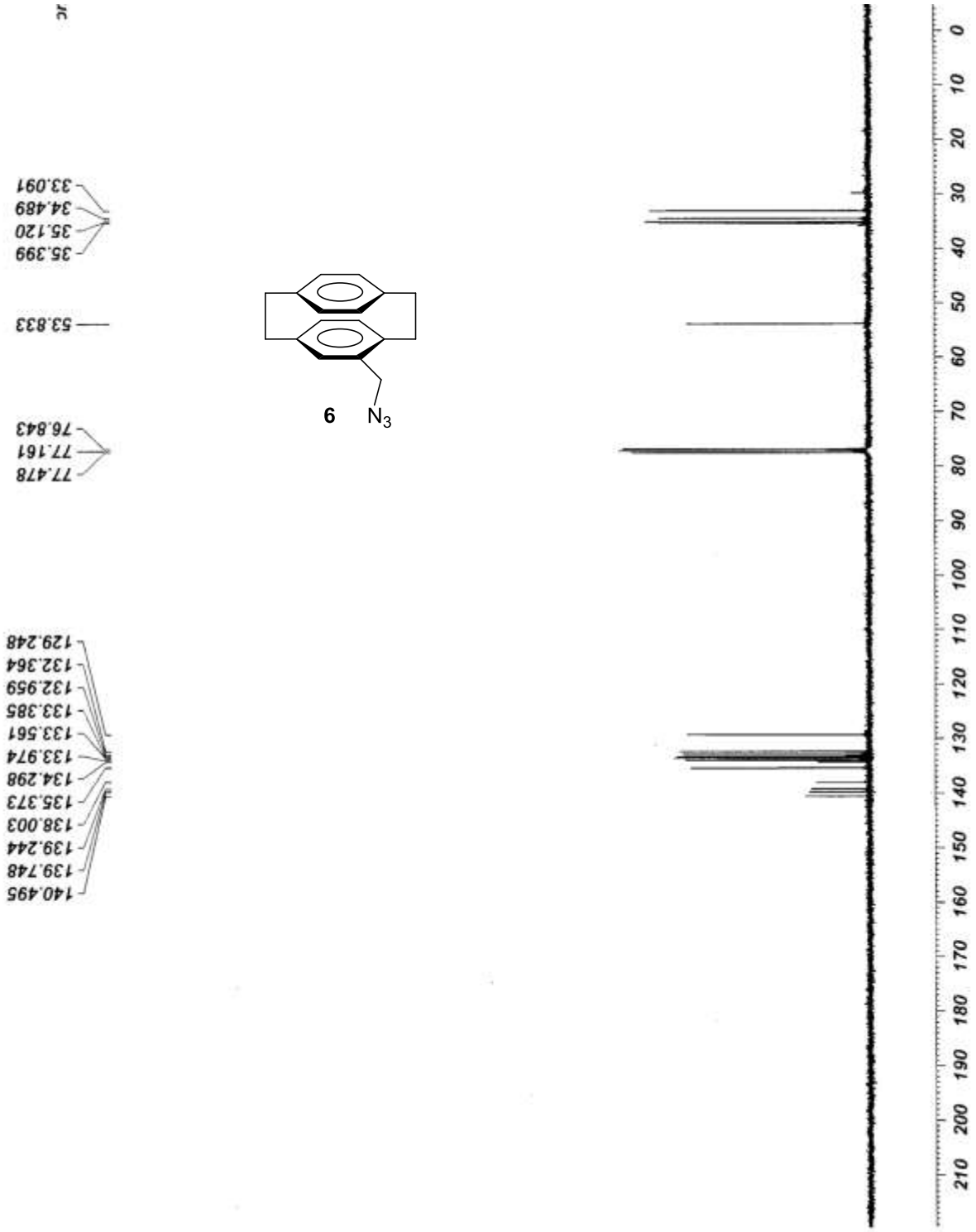


Figure S12. 100 MHz ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

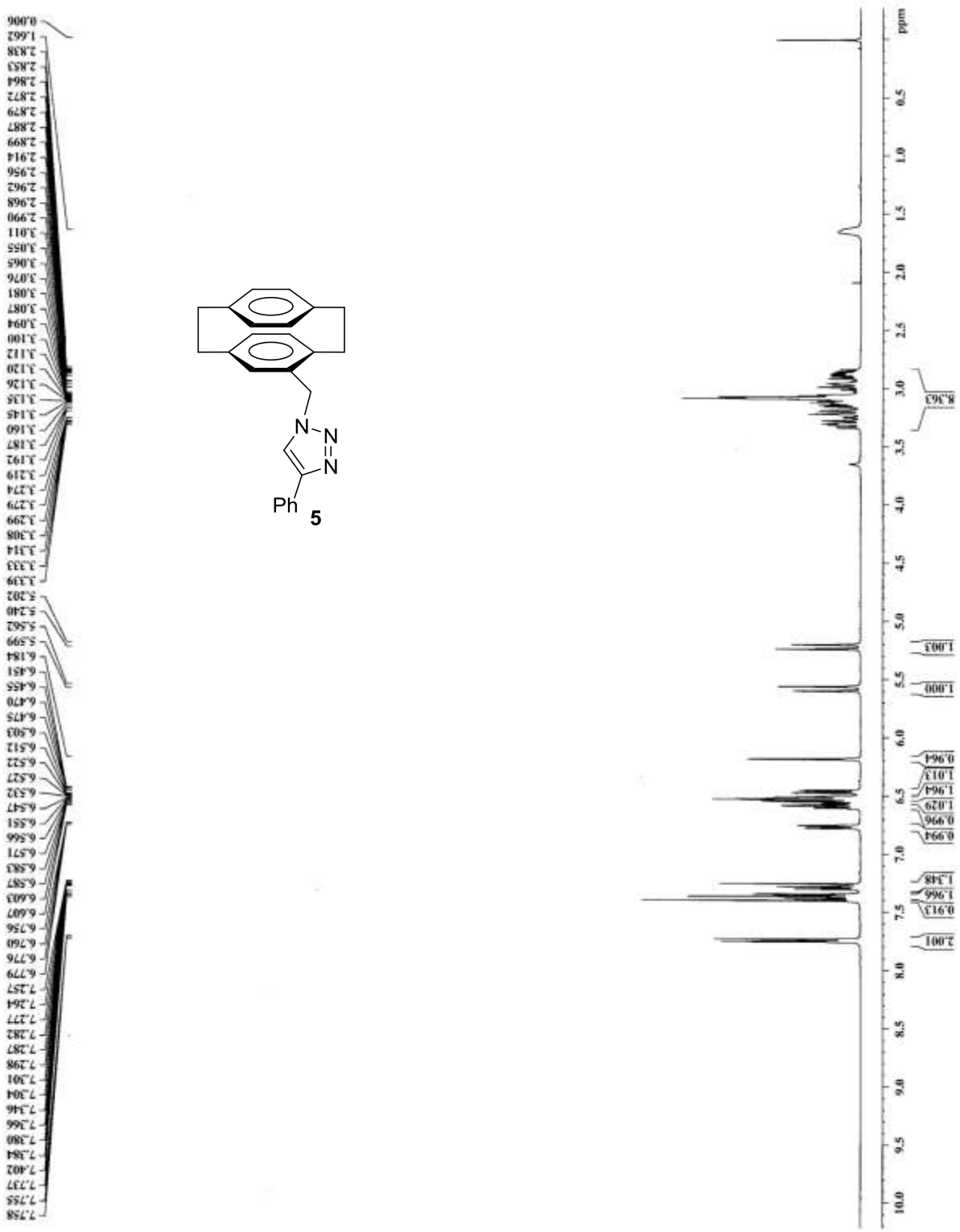


Figure S13. 400 MHz ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

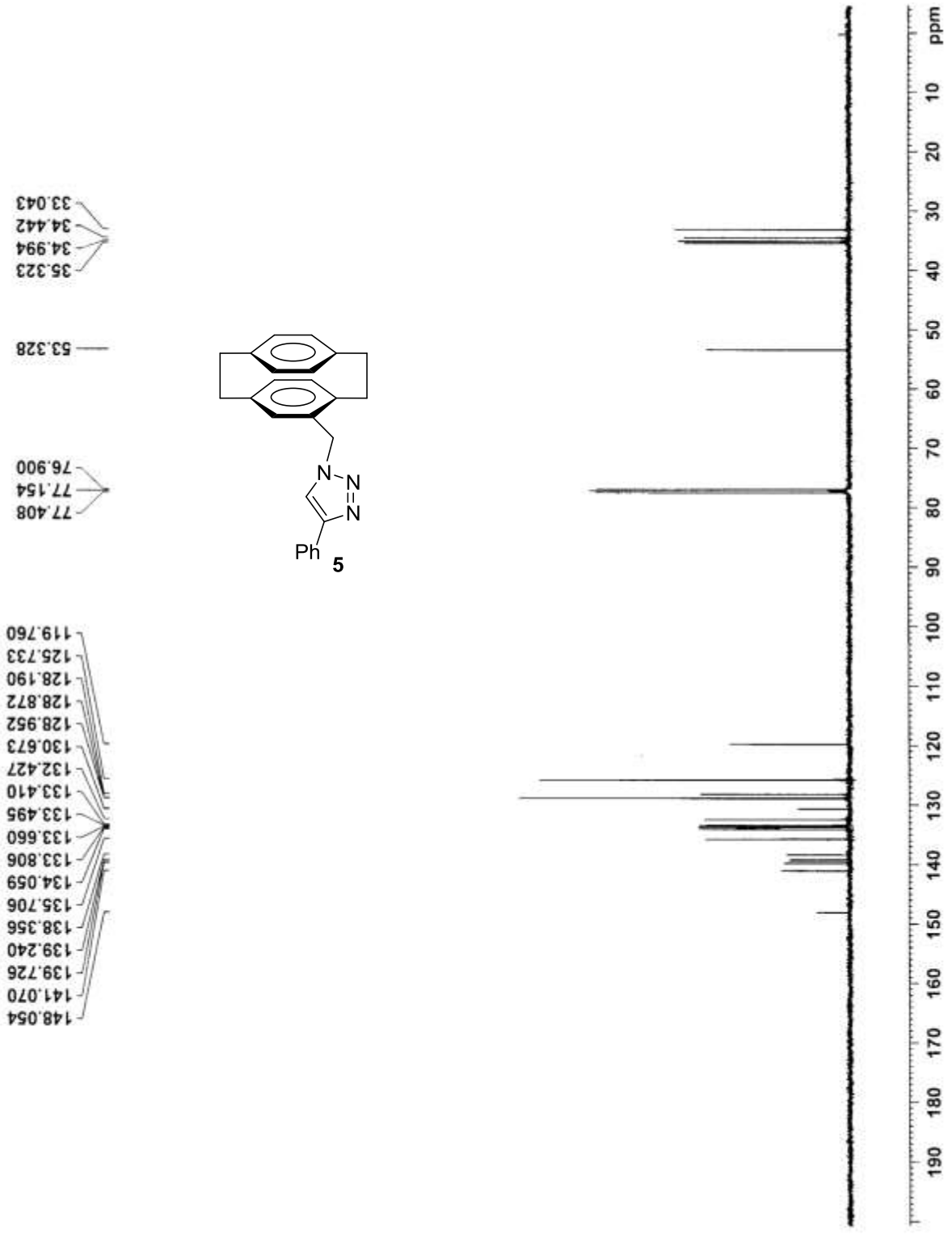


Figure S14. 100 MHz ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

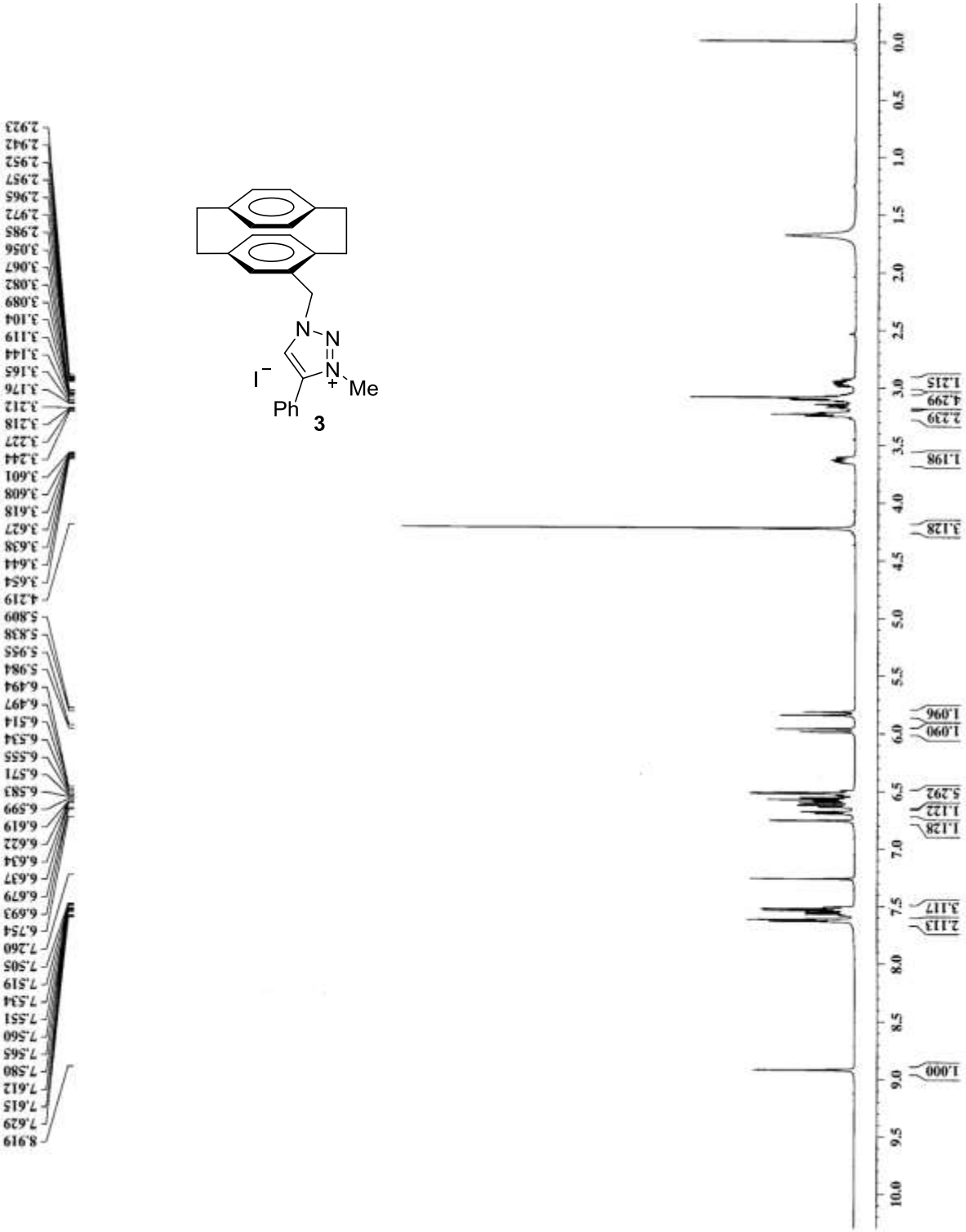


Figure S15. 500 MHz ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

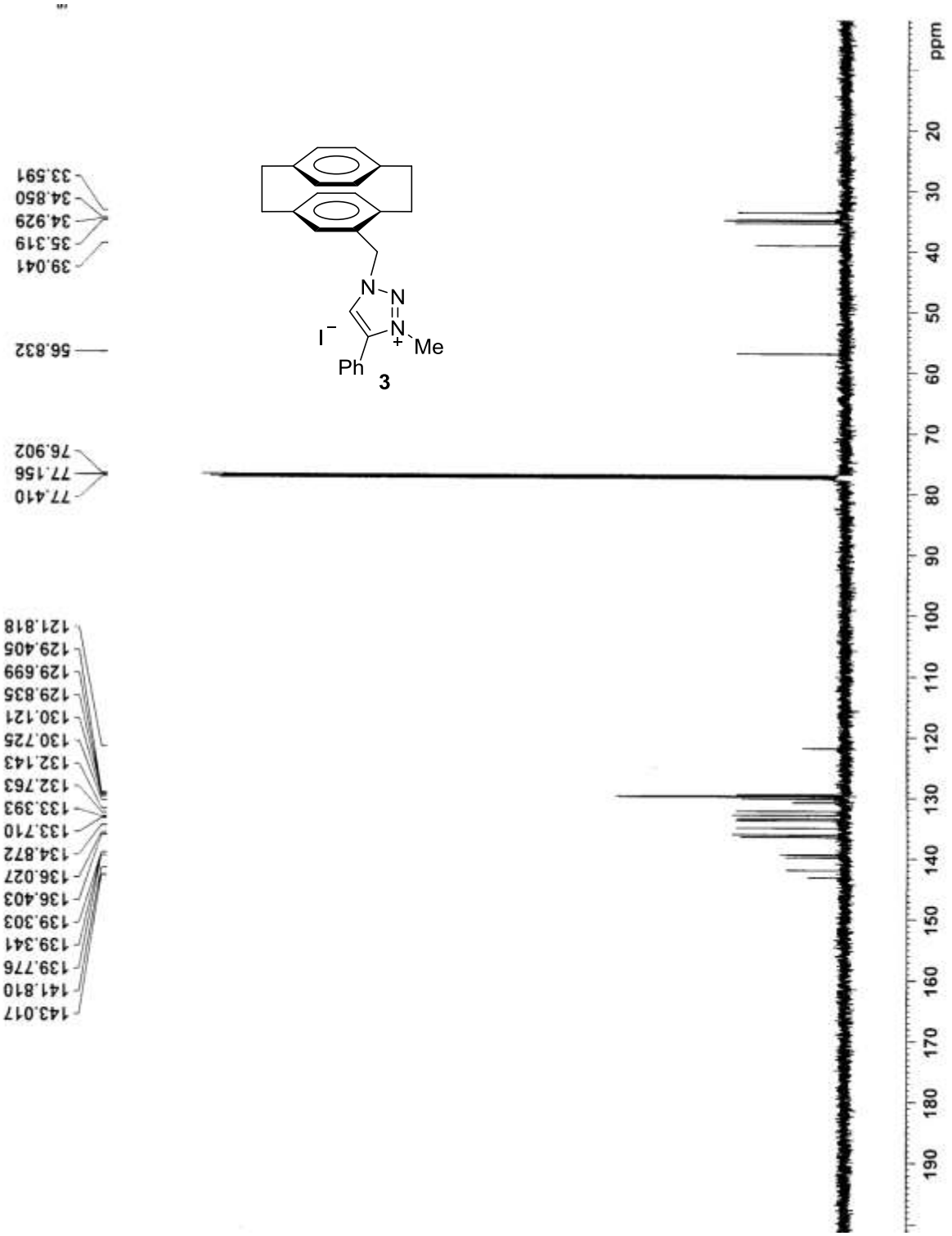


Figure S16. 125 MHz ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

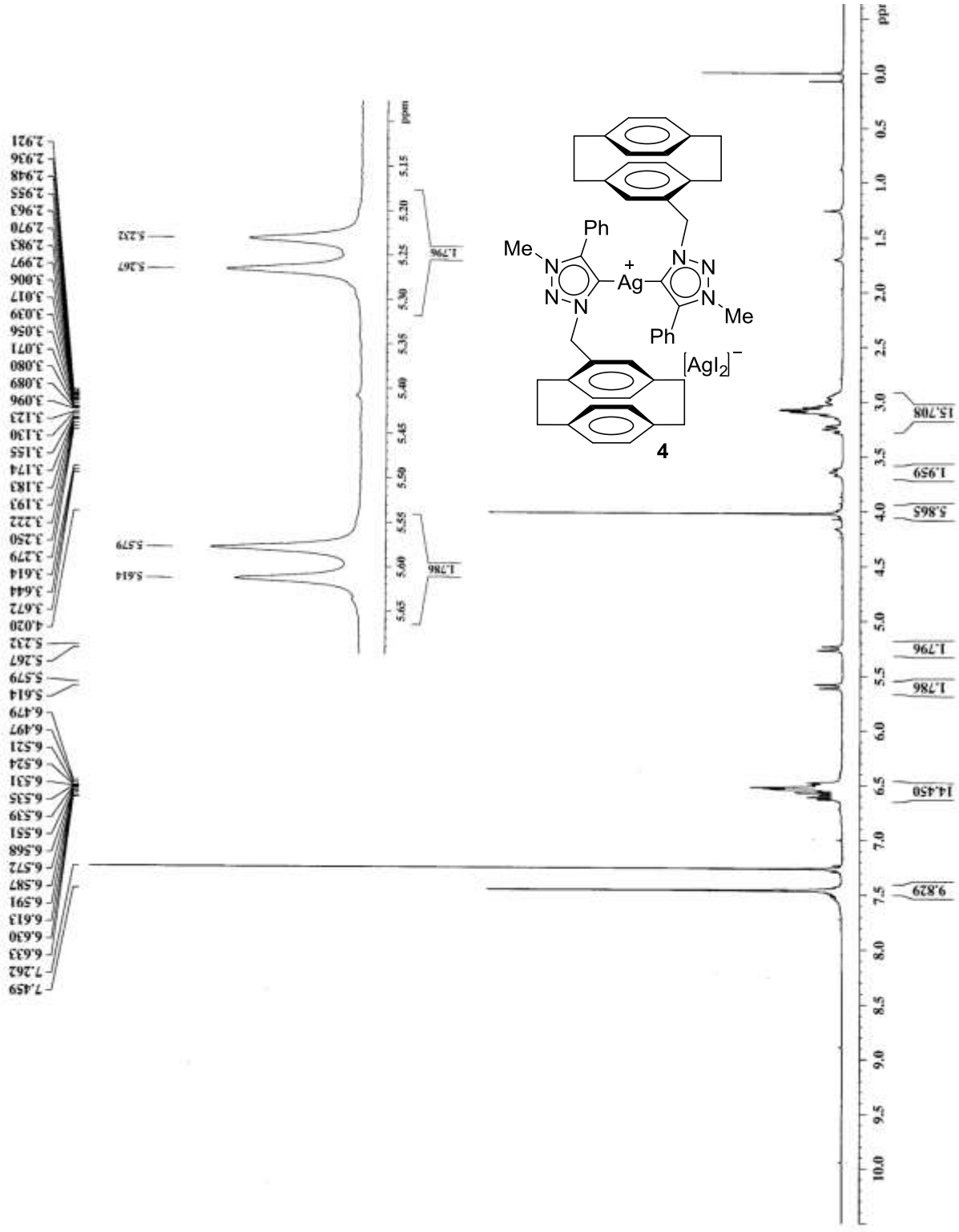


Figure S17. 400 MHz ^{1}H NMR spectrum of compound **4** in $CDCl_3$. Inset shows the region between 5.15 to 5.65 ppm.

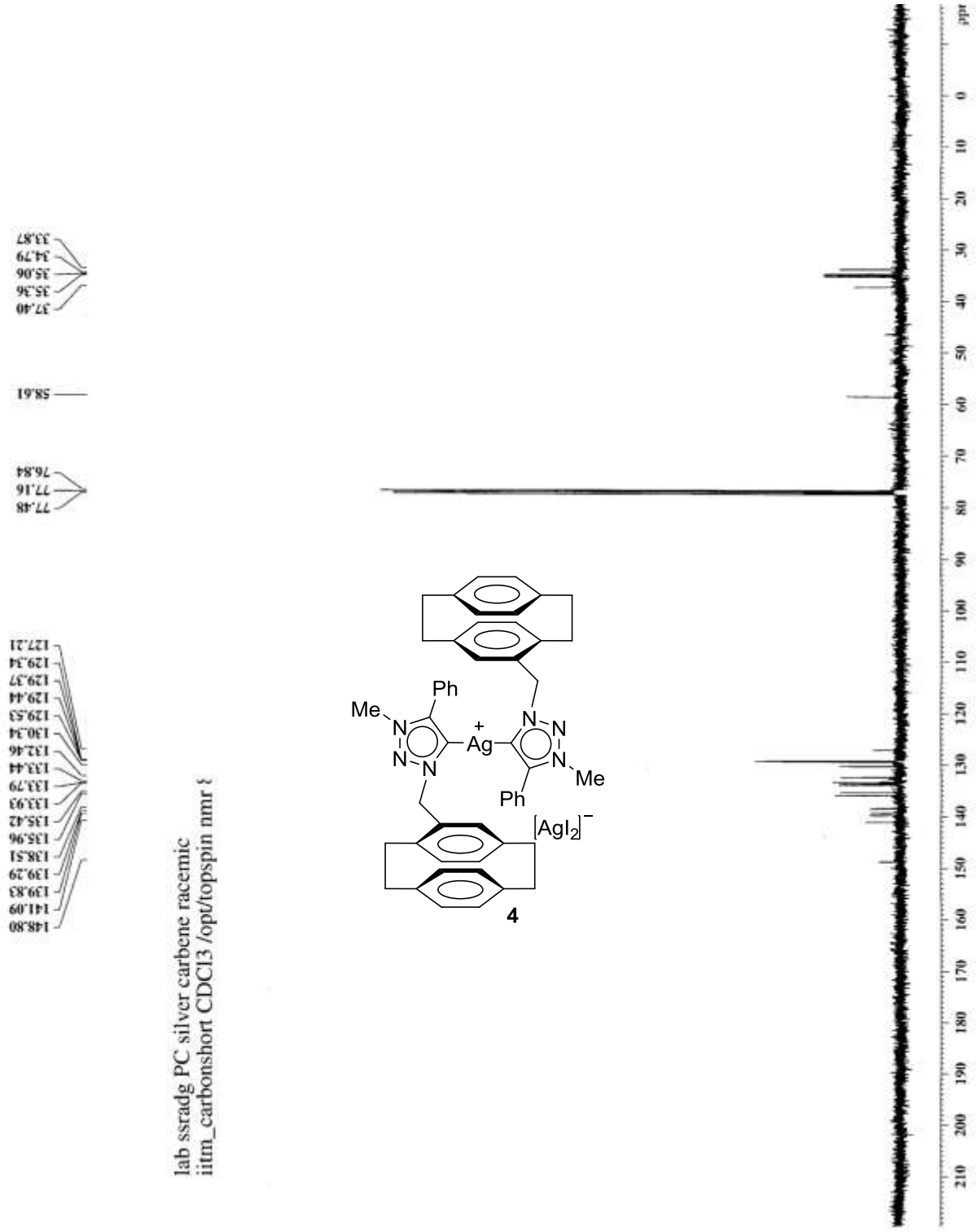


Figure S18. 100 MHz ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

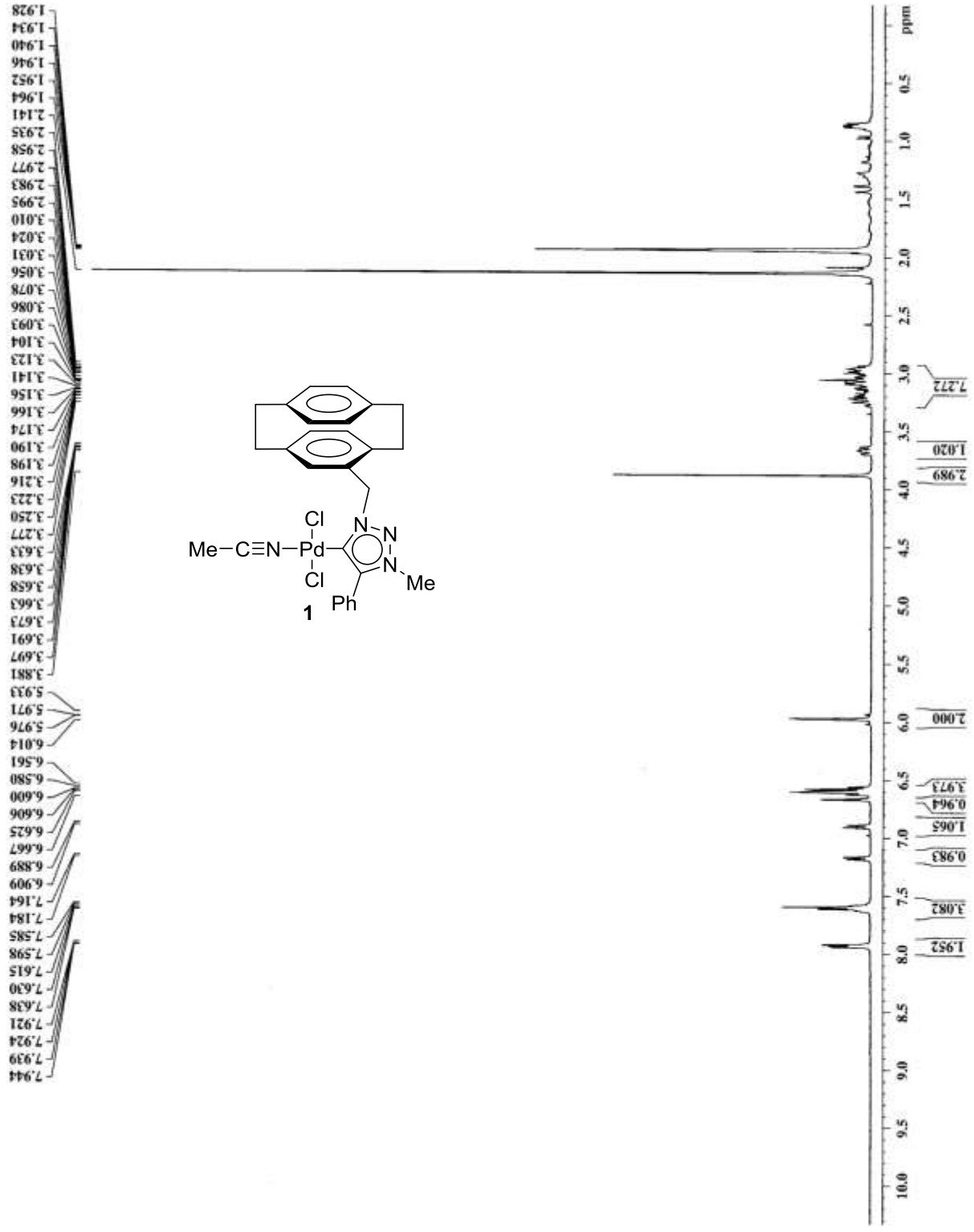


Figure S19. 500 MHz ^{1}H NMR spectrum of compound **1** in CD_3CN.

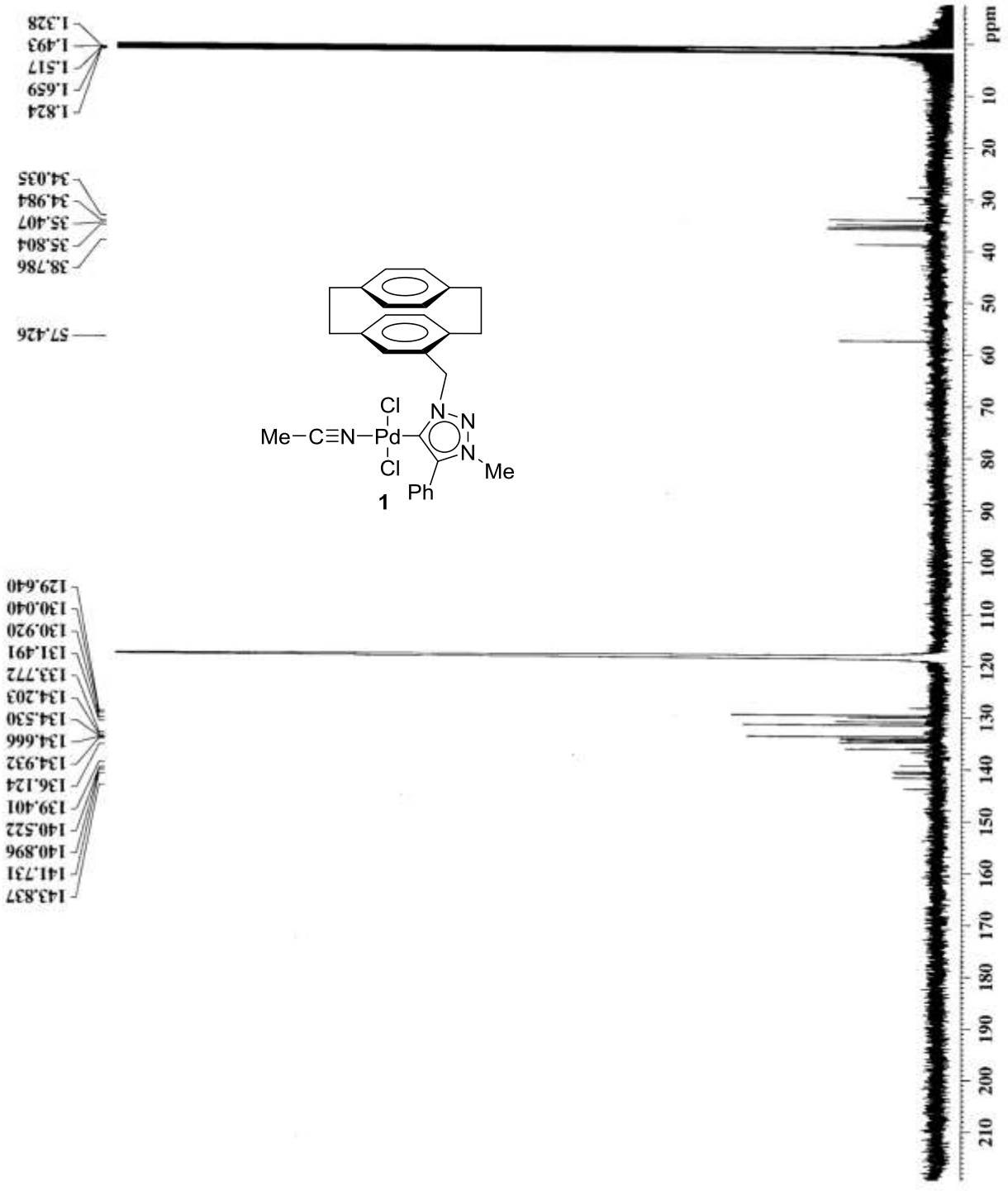


Figure S20. 125 MHz ^{13}C NMR spectrum of compound **1** in CD_3CN.

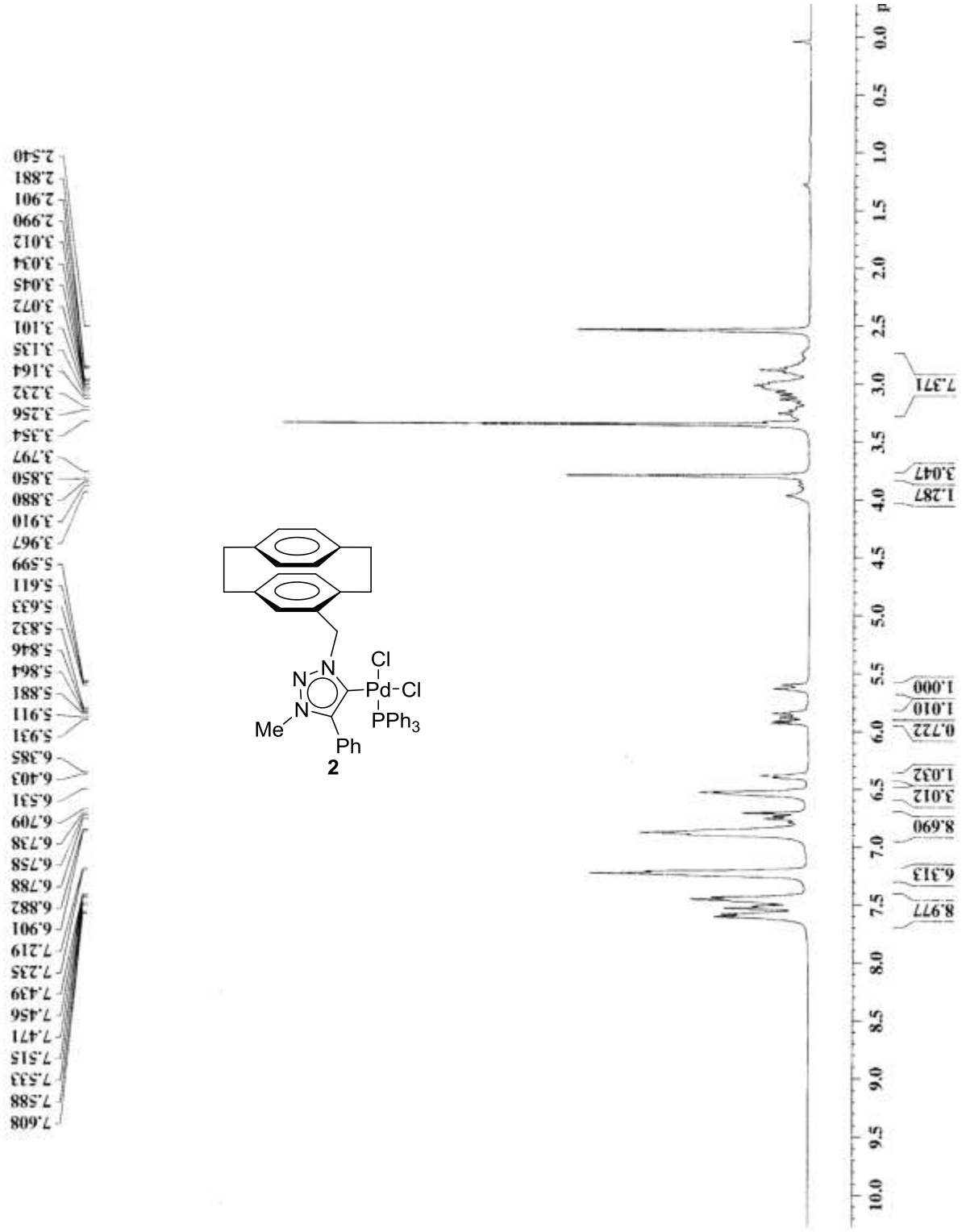


Figure S21. 400 MHz ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

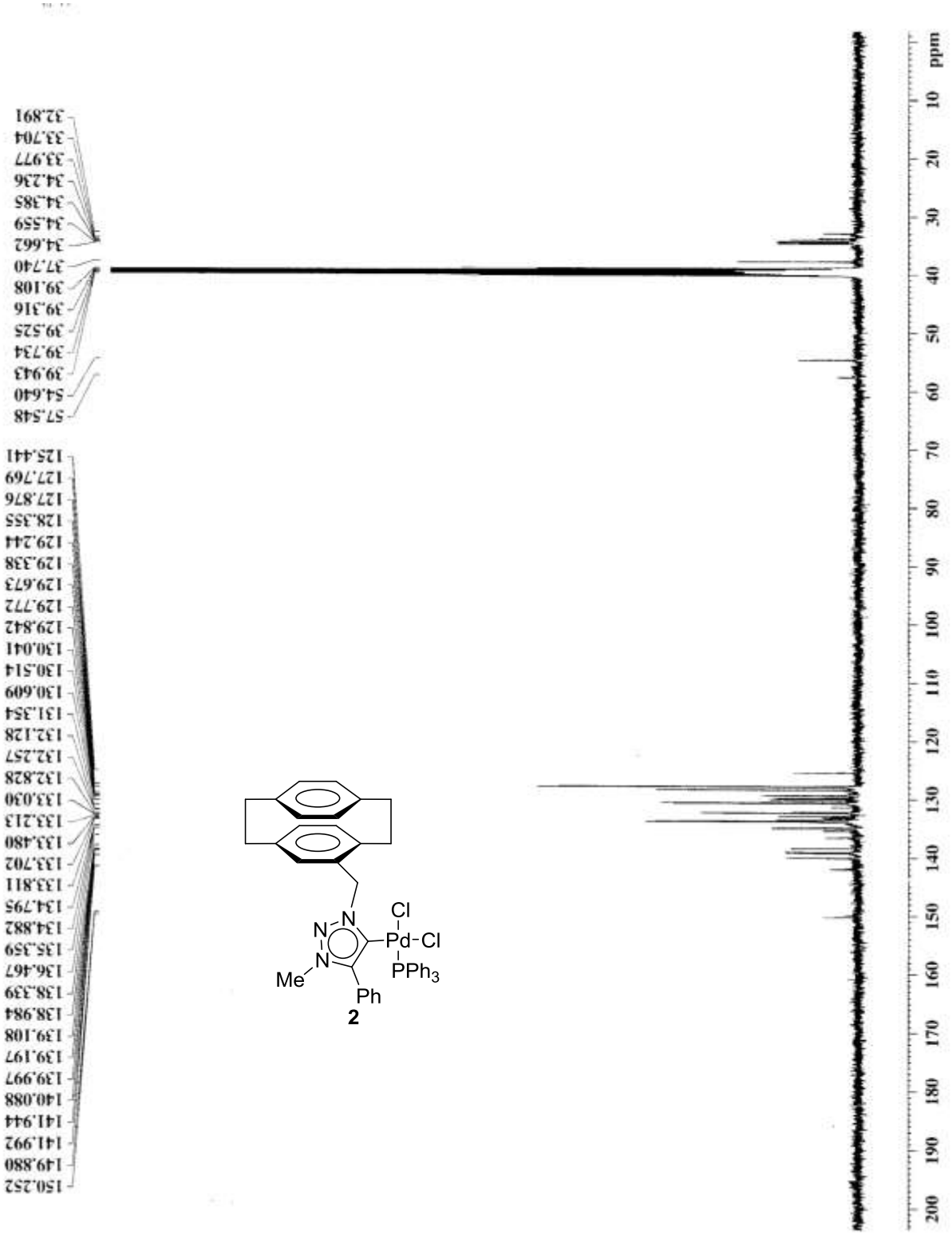


Figure S22. 100 MHz ^{13}C NMR spectrum of compound **2** in DMSO-d_6.

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