Electronic Supplementary Material (ESI) for ChemComm.

Catenane-based Mechanically-Linked Block Copolymers

Supporting information

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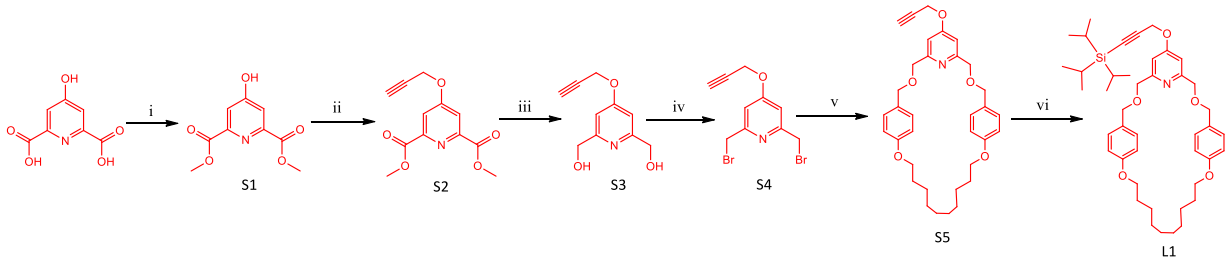
1. General remarks

1.1. Materials and Methods. Chelidamic acid hydrate, Propargyl bromide, Potassium carbonate (K_2CO_3), Sodium borohydride ($NaBH_4$), Phosphorus tribromide (PBr_3), Sodium hydride (NaH), Triisopropylsilyl chloride (Tips-Cl), Sulphuric acid (H_2SO_4), Imidazole, Diphenylphosphate (DPP), Copper Bromide, Tris(benzyltriazolylmethyl)amine (TBTA) and Sodium sulphite (Na_2SO_3) were purchased from Sigma Aldrich or Acros Organics and were used directly without any further purification. Compounds **S1**,[1] **S2**,[2] 1,10-bis[p-(Hydroxymethyl)phenoxy]decane (**I-1**),[3] Dimethyl-2,6-Pyridylcarboxylate (**I-2**),[4] 4-Hydroxymethyl-2,6-Dimethyl-Pyridylcarboxylate (**I-3**),[5] 4-(hex-5-enyloxy)benzylamine (**I-4**)[6] and azide functionalized Poly(ethylene oxide) (PEO_{44}-N_3, Mn: 2000 g/mol)[7] have been synthesized following literature procedures. Solvents were dried by conventional methods and distilled under Argon atmosphere before being used. Degassed solvents were prepared either by freeze-pump-thaw cycles or by purging of Argon gas with stirring. Thin layer chromatography's (TLC) were performed on TLC aluminium sheets coated with Silica gel (0.25 mm thick, 60 F254, Merck, Germany). The plates were visualized using ultraviolet light (256 nm) and developed using $KMnO_4$ and/or phosphomolybdic acid solution in ethanol. Column and Flash chromatographies were carried out using Merck Silica Gel 60 (230-400 mesh). Size exclusion chromatography was performed on Bio Beads SX1 (Bio-Rad) swelling with CH_2Cl_2.

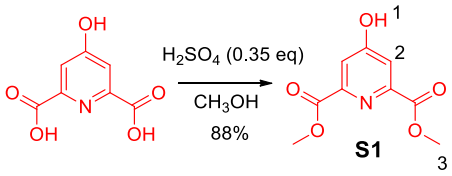
1.2. Instrumentation. ^{1}H NMR measurements were recorded on Bruker AVANCE 300 and 500 MHz FT-NMR spectrometers, and ^{13}C NMR spectra were recorded on Bruker 75 and 125 MHz FT-NMR spectrometers. All spectra were internally referenced to solvent residual signals ($CDCl_3$: 7.26 ppm, CD_2Cl_2: 5.32 ppm, $(CD_3)_2SO$: 2.50 ppm, CD_3OD: 3.31 ppm). The high accuracy mass spectrometry analyses were performed on a ThermoScientific Q-Exactive mass spectrometer. The analyte solutions (1 mg/mL) were delivered to the ESI source by a Harvard Apparatus syringe pump at a flow rate of 5 μL/min. Typical ESI conditions were: capillary voltage, 3.5 kV; cone voltage, 30 V; source temperature, 80°C; desolvation temperature, 120°C, capillary temperature 320°C. Molar masses (Mn) and dispersity (Đ) of the polymers were measured on an Agilent size exclusion chromatography (SEC) system equipped with an Agilent 1100/1200 pump (35°C; eluent: DMF; flow rate of 1 mL/min), an Agilent differential refractometer and two PSS GRAM columns (Beads 10 μm; porosity of column 1: 1000 Å; porosity of column 2: 100 Å). The calibration was performed using polystyrene standards.

2. Synthesis of monodendate macrocycle L1



Scheme 1. Reagents and conditions: i) H_2SO_4, CH_3OH, Δ, 5h, 88%; ii) 3-bromo-1-propyne, K_2CO_3, CH_3CN, Δ, 24h, 80.8%; iii) $NaBH_4$, CH_3CH_2OH, Δ, 4h, 58%; iv) PBr_3, CH_2Cl_2, Δ, 24h, 85%; v) 1,10-bis[p-(Hydroxymethyl)phenoxy]decane (**I-1**), NaH, THF, Δ, 48h, 18% ; vi) Triisopropylsilyl chloride, NaH, Δ, 24h, 78% .

2.1. Synthesis of Dimethyl 4-hydroxypyridine-2,6-dicarboxylate (S1)



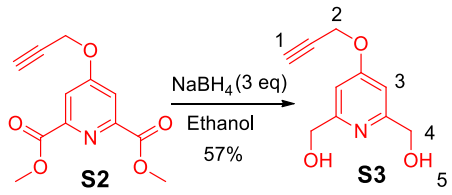
This compound was prepared following a slight modification of a literature procedure.[1] Chelidamic acid hydrate (6.5 g, 35.5 mmol) was suspended in methanol (200 mL) and sulphuric acid (97%) (1.22g, 12 mmol) was carefully added at room temperature with vigorous stirring. The yellow solution was refluxed at 90° C for 4 h and the solvents evaporated. Water (300 mL) was then added and the solution was extracted with ethylacetate (4×150 mL). The organic phase was dried with anhydrous Na_2SO_4 and evaporated to give product as a white solid (6.6 g, 88%).

^{1}H NMR (500 MHz, [D_6] DMSO): δ 11.59 (s, 1H,(1)), 7.57 (s, 2 H, (2)), 3.86 (s, 6H, (3));

^{13}C NMR (125 MHz, [D_6] DMSO): δ 166.48, 165.38, 149.88, 115.83, 53.18

IR (ATR-FTIR): ν 669, 700, 736, 771, 879, 887, 914, 937, 975, 991, 1022, 1041, 1108, 1155, 1186, 1218, 1247, 1269, 1353, 1386, 1425, 1438, 1598, 1718, 3228, 3244, cm^{-1}

2.2. Synthesis of 4-(Prop-2-yn-1-yloxy))-2,6-dihydroxymethyl pyridine (S3)



To a solution of **S2** (5 g, 20 mmol) in 100 mL ethanol was added carefully $NaBH_4$ (2.28g, 60 mmol). The solution was refluxed for 1 hour. Upon cooling, the solvent was removed. The obtained powder was dissolved in 150 mL of 2.5

mol/L aqueous K_2CO_3 and refluxed for one hour. After cooling, the precipitated pure product was filtered and washed with water to obtain the product as a white powder (2.25 g, 57%).

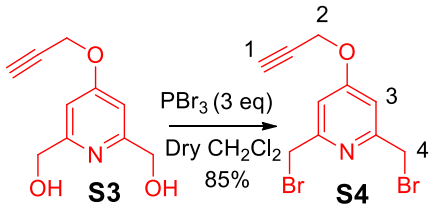
^{1}H NMR (500 MHz, [D$_6$] DMSO): δ 6.91 (s, 2H, (3)), 5.38 (t, 2 H,(4)), 4.88 (d, 2H, (2)), 4.47 (d, 4H, (4)), 3.64 (t, 1H, (1))

^{13}C NMR (125 MHz, [D$_6$]DMSO): δ 165.35 (C), 163.68 (C), 105.22 (C), 79.0-79.5 (-C≡CH), 64.53 (-C-OH), 55.89 (-OCH2)

HRMS (m/z) (ESI+): m/z=194.0814 $[M+H]^+$ (calcd. 194.0817 for C10H12NO3)

IR (ATR-FTIR): ν 669, 684, 771, 856, 937, 987, 1022, 1053, 1087, 1164, 1218, 1313, 1332, 1363, 1367, 1417, 1444, 1456, 1488, 1508, 1521, 1541, 1558, 1606, 1683, 2314, 2329, 2840, 3085, 3261, 3305, 3674, 3749 cm^{-1}

2.3. Synthesis of 4-(Prop-2-yn-1-yloxy))-2,6-dibromomethyl pyridine (S4)



To a suspension of **S3** (1.85 g, 9.5 mmol) in dry CH_2Cl_2 (100 mL) is added drop wise a solution of PBr_3 (7.77 g, 29 mmol) in CH_2Cl_2. The mixture is refluxed for 24 hours under Ar. The mixture is then cooled down and washed with 2.5 mol/L aqueous K_2CO_3. The aqueous phases are extracted twice with CH_2Cl_2. The combined organic phases are dried over anhydrous Na_2SO_4, filtered and the solvent removed under vacuum. The crude product was purified by column chromatography (silicagel, EP/EtOAc (70:30)) to yield the desired pure product (2.6 g, 85%) as a pinkish white crystalline solid.

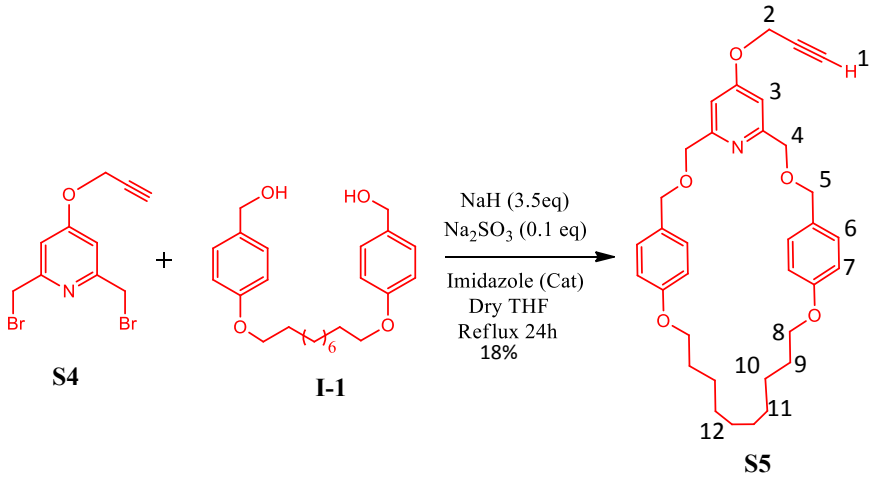
^{1}H NMR (500 MHz, CDCl$_3$): δ 6.99 (s, 2H, (3)), 4.80 (d, 2H, (2)), 4.51 (s, 4H, (4)), 2.63 (t, 1H, (1));

^{13}C NMR (125 MHz, CDCl$_3$): δ 165.56 (C), 158.70 (C), 110.02 (C), 77.69 (-C≡CH), 56.26 (-OCH2-), 33.85 (-CH2-Br)

HRMS (m/z) (ESI+): m/z= 317.9126 $[M+H]^+$ (calcd. 317.9124 for C10H10Br2NO).

IR (ATR-FTIR): ν 684, 754, 771, 860, 887, 910, 954,70 989, 1020, 1041, 1155, 1209, 1222, 1321, 1382, 1423, 1446, 1564, 1593, 3284, 3294 cm-1.

2.4. Synthesis of monodentate macrocycle (S5)



A flame dried 1 litre three-neck round bottom flask was fitted with a condenser and with a 150 mL addition funnel and was filled with argon. NaH (0.426 g (60% mineral oil), 10.6 mmol) was carefully added and the flask was flushed again with argon. The NaH was washed with freshly dried hexane for 10 min. The hexane was carefully removed using gas tight syringe. The alcohol **I-1** (1.028 g, 2.7 mmol) and a small amount of powdered and dried Na_2SO_3 (oxygen scavenger) and Imidazole (0.1 mmol) were carefully transferred to the round bottom flask. Dry THF (800 mL) was carefully transferred to the round bottom flask using double tipped needle. The mixture was stirred under Ar at 65°C for 1 hour. The dibromo derivative **S4** (0.85 g, 2.7 mmol) was placed in the addition funnel with THF (100mL) and was added dropwise overnight. The reaction mixture was allowed to stir for 2 days at 65°C. After cooling, the solution was filtered and the solvent removed under vacuum. The residue was dissolved in CH_2Cl_2 and washed twice with water. The organic phases were dried over Na_2SO_4 filtered and the solvent removed under vacuum. The crude product was purified on column chromatography (silicagel, DCM/EtOAC 85:15) to yield the pure macrocycle **S5** as white crystalline solid (0.27g, 18%).

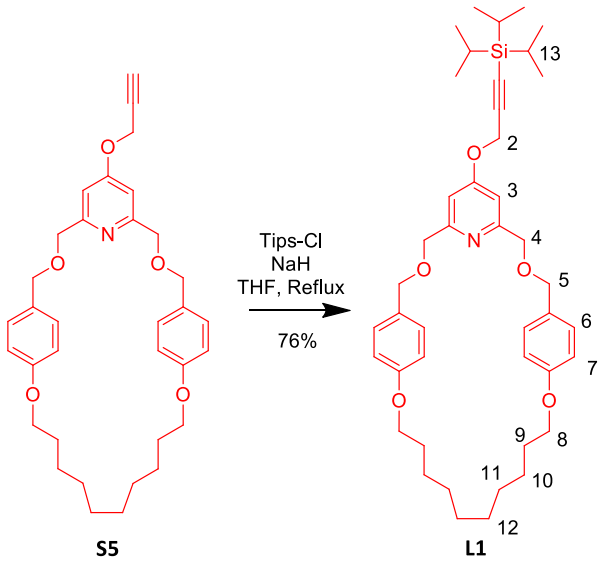
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23-7.20 (d, 4H (7)), 6.96 (s, 2H (3)), 6.81-6.79 (d, 4H (6)), 4.77 (d, 2H (2)), 4.59 (s, 4H (4)), 4.36 (s, 4H (5)), 3.96 (t, 4H (8)), 2.58 (t, 1H (1)), 1.74-1.69 (m, 4H (9)), 1.43-1.39 (m, 4H (10)), 1.27 (b, 8H (11, 12)).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.20, 159.96, 158.89, 130.21, 129.36, 114.74, 106.47, 76.88, 76.40, 72.38, 70.94, 67.50, 55.65, 29.56, 28.82, 28.70, 25.77

HRMS (m/z) (ESI+): m/z= 544.3067 $[M+H]^+$ (calcd. 544.3063 for $C_{34}H_{42}NO_5$,)

IR (ATR-FTIR): ν 825, 1010, 1022, 1053, 1097, 1151, 1172, 1244, 1313, 1361, 1452, 1510, 1583, 1596, 2852, 2921 cm^{-1}.

2.5. Synthesis of silylated monodentate macrocycle (**L1**)



S5 **L1**

A flame dried 50 mL two neck round bottom flask was fitted with a condenser, sealed with septa, and filled with argon. NaH (0.088 g (60% mineral oil), 2.2 mmol) was carefully added and the flask was flushed with argon. The NaH was washed with freshly dried hexane for 10 min. The hexane was carefully removed using gas tight syringe. The macrocycle **S5** (0.24 g, 0.4 mmol) and Triisopropylsilylchloride (Tips-Cl) (0.944 ml, 4.4 mmol) dissolved in 25mL of dry THF were carefully transferred dropwise in to the round bottom flask containing NaH under argon. The mixture is stirred for 1 day at 60°C. After being cooled down the reaction mixture is filtered and the solvent removed in vaccuo. The obtained slurry is purified on column chromatography to yield **L1** as a colourless semi solid (0.236g, 78%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23-7.21 (d, 4H (7)), 7.20 (s, 2H (3)), 6.82-6.79 (d, 4H (6)), 4.80 (s, 2H (2)), 4.58 (s, 4H (4)), 4.33 (s, 4H (5)), 3.97 (t, 4H (8)), 1.75-1.70 (m, 4H (9)), 1.43-1.40 (m, 4H (10)), 1.28 (b, 8H (11, 12)).

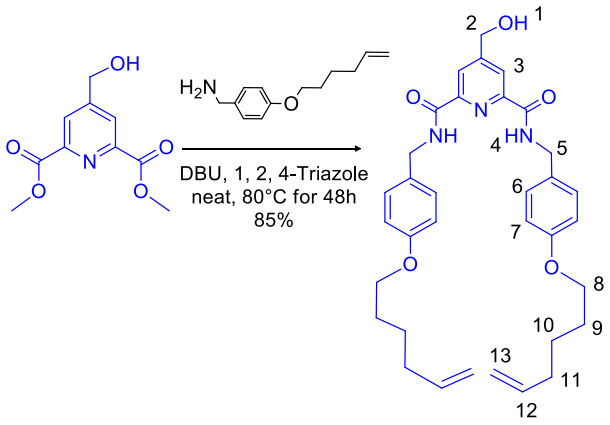
^{13}C NMR (125 MHz, $CDCl_3$): δ 165.68, 159.96, 159.16, 130.51, 129.70, 115.04, 107.13, 101.15, 90.71, 72.69, 71.33, 67.80, 56.89, 29.90, 29.15, 29.00, 26.09, 18.92, 11.46.

HRMS (m/z) (ESI+): m/z=700.4392 $[M+H]^+$, (calcd. 700.4397 for $C_{43}H_{62}NO_5Si$).

IR (ATR-FTIR): ν 667, 771, 825, 848, 883, 995, 1022, 1053, 1101, 1151, 1172, 1218, 1245, 1311, 1361, 1458, 1510, 1581, 1596, 2862, 2912, 2921, 2937 cm^{-1}.

3. Synthesis of L2.Pd.CH_3CN

3.1. Synthesis of tridentate ligand (**L2**)



A reaction mixture consisting of 4-Hydroxymethyl-2,6-Dimethyl-Pyridylcarboxylate (**I-3**)[5] (1 g, 4.2 mmol), and 4-(hex-5-enyloxy)benzylamine (**I-4**)[6] (2.07 g, 10.1 mmol), 1,2,4-triazole (87 mg, 1.26 mmol) and DBU (192 mg, 1.26 mmol) was stirred at a 85°C for 24 h and then purified on silica gel column chromatography (CH_2Cl_2- EtOAC, 70:30) to yield **L2** as yellowish solid (yield 2.18 g, 85 %).

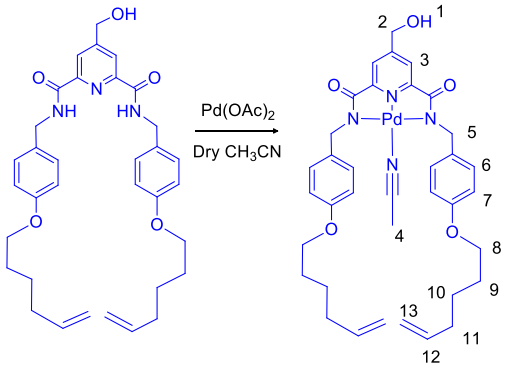
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (s, 2H (3)), 7.98 (t, 2H (4)), 7.22 (d, 4H (7)), 6.85-6.82 (d, 4H (6)), 5.90-5.76 (m, 2H (12)), 5.31-4.99 (m, 4H (13)), 4.96 (d, 2H (2)), 4.60 (d, 4H (5)), 3.94 (t, 4H (8)), 2.72 (t, 1H (1)), 2.16-2.09 (q, 4H (9)), 1.84-1.75 (m, 4H (11)), 1.57-1.51 (m, 4H (10)).

^{13}C NMR (125 MHz, $CDCl_3$): δ 164.19, 158.86, 155.15, 149.14, 138.86, 130.39, 130.27, 129.37, 122.97, 115.19, 114.94, 68.21, 63.42, 43.33, 33.83, 29.08, 25.70.

HRMS (m/z) (ESI+): m/z= 572.3117 $[M+H]^+$, (calcd. 572.3119 for $C_{34}H_{42}N_3O_5$)

IR (ATR-FTIR): ν 823, 887, 910, 954, 997, 1033, 1056, 1112, 1174, 1244, 1299, 1336, 1359, 1392, 1421, 1431, 1456, 1473, 1512, 1533, 1583, 1610, 1650, 2910, 3265, 3288, 3315 cm^{-1}.

3.2. Synthesis of **L2.Pd.CH_3CN**



To a solution of **L2** (0.5 g, 0.87 mmol) in anhydrous acetonitrile (25 mL), was added palladium (II) acetate (0.235 g, 1 mmol) and the reaction mixture was stirred at room temperature for 5 h under an Argon atmosphere and the solution was concentrated under reduced pressure. The resulting precipitate was filtered, washed with diethylether (50 mL) and dried under suction to yield the product **L2.Pd.CH_3CN** as dark greenish solid (0.45 g, 71%).

^1H NMR (500 MHz, $CDCl_3$): δ 7.74 (s, 2H (3)), 7.20 (d, 4H (7)), 6.80 (d, 4H (6)), 5.84-5.78 (m, 1H (12)), 5.45-5.44 (m, 1H (12)), 5.03-4.96 (m, 4H (13)), 4.74 (d, 2H (2)), 4.44 (s, 4H (5)), 4.38(s, 1H (1)), 3.93-3.89 (t, 4H (8)), 2.13-2.09 (m, 4H (9)), 1.97 (s, 1H (4)), 1.80-1.51 (m, 12H (11, 10)).

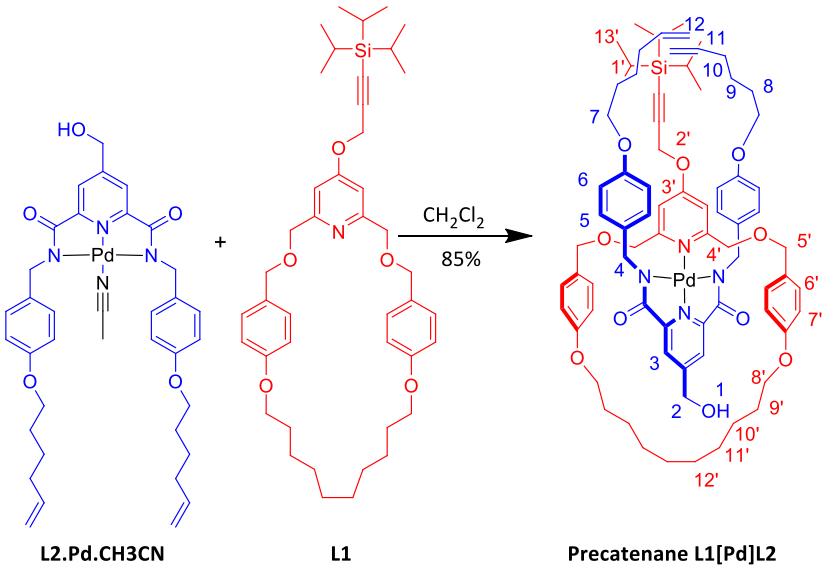
^{13}C NMR (125 MHz, $CDCl_3$): δ 170.88, 158.57, 158.06, 152.98, 138.89, 133.63, 128.73, 122.69, 117.27, 116.90, 115.09, 114.59, 68.20, 63.58, 49.91, 33.81, 29.13, 25.70.

HRMS (m/z) (ESI+): m/z= 717.2274 $[M+H]^+$, (calcd. 717.2263 for $C_{36}H_{43}N_4O_5Pd$).

IR (ATR-FTIR): ν 819, 881, 914, 972, 997, 1014, 1068, 1107, 1134, 1172, 1220, 1244, 1290, 1338, 1375, 1404, 1429, 1450, 1508, 1554, 1583, 1606, 1629, 2910, 2935 cm^{-1}.

4. Synthesis of the precatenane, and catenanes CatTIPS, Cat1 and Cat2

4.1. Synthesis of precatenane **L1[Pd]L2**



L2.Pd.CH3CN **L1** **Precatenane L1[Pd]L2**

To a solution of **L1** (0.150 g, 2.1 mmol, 1.0 equiv.) in dry CH_2Cl_2: CH_3CN (25 mL, 95:5, v/v) was added **L2.Pd.CH_3CN** (0.170 g, 2.3 mmol, 1.1 equiv.) and the solution was stirred at room temperature for 5 h. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography (CH_2Cl_2: EtOAc, 50:50) to give the precatenane **L1[Pd]L2** as yellowish solid (0.222 g, 85%).

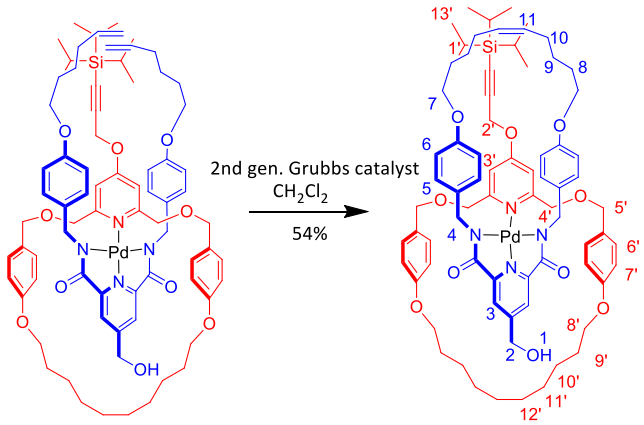
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H (3)), 7.93 (s, 1H (3)), 7.15 (d, 4H (7')), 6.81 (s, 2H (3')), 6.71 (d, 4H (6')), 6.64 (d, 2H (6)), 6.53 (d, 2H (5)), 5.86-5.76 (m, 5H (5,6,11)), 5.09-5.00 (m, 6H (2,12)), 4.81 (s, 2H (2')), 4.68-4.65 (d, 2H (4')), 4.32 (d, 2H (4)), 4.17-4.15 (d, 2H (4')), 3.98-3.94(m, 10H (4, 7,8')), 3.75 (t, 2H (8')), 3.20 (b, 1H (1)), 2.16-2.13 (m, 4H (9)), 1.81-1.75 (m, 7H (10,9')), 1.64-1.57 (m, 8H (10',11')), 1.31-1.27 (m, 4H (12')), 1.10 (m, 30H (1',13')).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.33, 166.22, 159.21, 158.10, 152.62, 138.66, 131.22, 128.61, 128.01, 122.27, 122.05, 114.96, 114.89, 114.27, 108.29, 91.62, 68.04, 67.80, 67.62, 63.53, 57.27, 48.29, 33.58, 29.91, 28.96, 28.87, 28.72, 25.81, 25.54, 25.49, 18.69, 11.17.

HRMS (m/z) (ESI+): m/z= 1375.6336 $[M+H]^+$, (calcd. 1375.6322 for $C_{77}H_{101}N_4O_{10}PdSi$).

IR (ATR-FTIR): ν 651, 673, 771, 827, 883, 912, 993, 1027, 1064, 1099, 1159, 1172, 1218, 1242, 1307, 1340, 1357, 1388, 1436, 1458, 1508, 1560, 1593, 1610, 2860, 2921, 2931 cm^{-1}.

4.2. Synthesis of catenane **CatTIPS**



To a solution of precatenane **L1[Pd]L2** (0.2 g, 1.5 mmol) in CH_2Cl_2 (500 mL) was added Grubbs' second generation olefin metathesis catalyst (12 mg, 0.15 mmol, 10 mol%). The solution was stirred for 2 days in the dark at 35° C, after which the solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (CH_2Cl_2: EtOAc, 60:40 as eluent) to yield catenane **CatTIPS** as a yellowish solid (0.154 g, 54%).

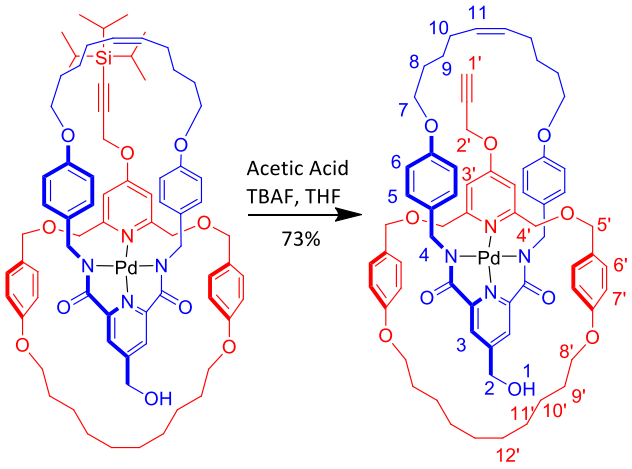
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H (3)), 8.05 (s, 1H (3)), 7.45 (d, 2H (7')), 7.28 (s, 1H, (3')) 7.07-7.03 (m, 2H (6')), 6.88-6.81 (m, 4H (7', 6')), 6.55-6.48 (m, 4H (6,5)), 6.06-6.02 (m, 1H (3')), 5.77 (m, 1H (1)), 5.6 (s, 2H (11)), 5.54-5.51 (d, 4H (6, 5)), 5.4-4.7 (m, 8H (2, 2',4, 4', 5')), 5.00-4.8 (d, 6H (4)), 4.58-4.47 (d, 2H (4')), 4.15-3.86 (m, 8H, (8', 7)), 3.81-3.49 (m,4H, (5' or 4')), 2.94-2.64 (m, 1H, (5' or 4' or 4)), 2.32- 2.12 (m, 4H, (8)) 1.91-1.47(m, 12H, (9, 9', 10), 1.38-0.73 (m 36H, (10', 11', 12', 1', 13')).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.79, 171.69, 171.17, 166.15, 166.11, 162.34, 159.96, 159.63, 159.11, 159.01, 158.35, 157.75, 157.53, 156.76, 156.37, 154.40, 152.62, 152.33, 137.67, 134.58, 132.68, 132.50, 131.73, 131.37, 131.09, 130.86, 130.35, 130.22, 130.10, 128.75, 128.57, 128.54, 128.40, 128.29, 127.72, 124.65, 122.31, 122.27, 118.76, 115.29, 115.24, 115.00, 114.91, 114.75, 114.75, 114.48, 114.20, 113.92, 113.34, 108.52, 106.17, 99.75, 91.43, 72.48, 68.80, 68.25, 68.19, 67.64, 67.49, 67.36, 66.82, 66.67, 66.62, 63.40, 57.32, 49.79, 49.29, 34.45, 32.13, 32.04, 31.78, 30.43, 30.09, 30.04, 29.81, 29.63, 29.48, 29.37, 29.16, 29.11, 28.97, 28.92, 28.71, 28.49, 28.29, 28.18, 27.97, 27.69, 26.53, 26.21, 25.95, 25.81, 25.66, 25.35, 22.81, 19.92, 18.97, 18.62, 14.24, 11.45, 11.23, 11.00.

HRMS (m/z) (ESI+): m/z= 1347.6021 $[M+H]^+$, (calcd. 1347.6009 for $C_{75}H_{97}N_4O_{10}PdSi$).

IR (ATR-FTIR): ν 667, 771, 823, 881, 933, 952, 993, 1014, 1027, 1062, 1099, 1157, 1172, 1218, 1244, 1309, 1338, 1359, 1386, 1436, 1458, 1508, 1558, 1587, 1608, 2860, 2906, 2931 cm^{-1}.

4.3. Synthesis of desilylated catenane **Cat1**



CatTIPS **Cat1**

A solution of tetrabutylammonium fluoride (0.070 mL, 2.4 mmol, 2.2 eq) and glacial acetic acid (0.016 mL, 2.7 mmol, and 2.5 eq) in THF (5 mL) was stirred for 20 min under argon. This mixture was then added to the **CatTIPS** (150 mg, 1.1 mmol, 1 eq). After stirring for overnight at room temperature, the solution was concentrated under reduced pressure. The reaction mixture was extracted with EtOAc. The combined organic phases were dried over sodium sulphate, filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography (Silica gel, CH_2Cl_2/AcOEt: 5/5 to 4/6) to yield catenane **Cat1** as a yellowish solid (0.11 mg, 73%).

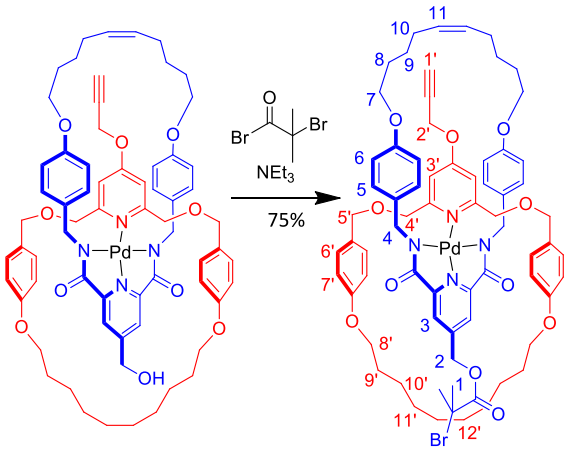
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H (3)), 8.00 (s, 1H (3)), 7.46-7.44 (dd, 2H (7')), 7.19-7.17 (s, 1H (3')), 7.07-7.02 (d, 2H (6')), 6.86-6.75 (m, 4H (7', 6')), 6.52-6.47 (m, 4H (6,5)), 6.04-5.78 (m, 1H (3')), 5.7-5.55 (m, 3H (1, 11)), 5.52-5.42 (m, 4H (6, 5)), 5.37-4.7 (m, 10H (4, 4',2, 5',2')), 4.65-4.35 (dd, 2H (4 or 4' or 5')), 4.15-3.4 (m, 12H (8', 7 and 4 or 4')), 3.0-3.65 (m, 2H (1')), 2.36- 2.08 (m, 4H, (8)) 1.91-1.42(m, 15H, (9, 9', 10), 1.38-0.54 (m 18H, (10', 11', 12')).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.33, 166.22, 159.21, 158.10, 152.62, 138.66, 131.22, 128.61, 128.01, 122.27, 122.05, 114.96, 114.89, 114.27, 108.29, 91.62, 68.04, 67.80, 67.62, 63.53, 57.27, 48.29, 33.58, 29.91, 28.96, 28.87, 28.72, 25.81, 25.54, 25.49, 18.69, 11.17.

HRMS (m/z) (ESI+): m/z= 1191.4690 $[M+H]^+$, (calcd. 1191.4675 for $C_{66}H_{77}N_4O_{10}Pd$)

IR (ATR-FTIR): ν 848, 995, 1016, 1062, 1099, 1157, 1172, 1218, 1242, 1307, 1340, 1359, 1394, 1434, 1458, 1508, 1589, 1608, 2852, 2900, 2945 cm^{-1}.

4.4. Synthesis of catenane **Cat2**



Cat1 **Cat2**

To a solution of **Cat1** (1 eq, 0.029 mmol, 0.035 g) in 1mL of dry DCM, trimethylamine (3 eq, 0.009mmol, 0.009g, 12 µL) is added. Then, α-Bromoisobutyryl bromide (1.2 eq, 0.035mmol, 0.008g, 4µL) is added dropwise to the mixture. The mixture is stirred for 18 hours at room temperature under argon atmosphere. Then, 3mL of water are added to the mixture and is slowly stirred for 5 minutes. The organic phase is washed twice with water. The combined organic phases are then dried over sodium sulphate, filtered and then concentrated under reduced pressure. The crude residue was purified by column chromatography (Silica gel, CH_2Cl_2) to yield catenane **Cat2** as a yellow solid (0.033 g, 75%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H (3)), 7.90 (s, 1H (3)), 7.47-7.44 (dd, 2H (7')), 7.21 (s, 1H (3')), 7.09-7.02 (d, 2H (6')), 6.88-6.75 (m, 4H (7', 6')), 6.51-6.47 (m, 4H (6,5)), 6.15-5.98 (m, 1H (3')), 5.67-5.35 (m, 8H (11, 5,6)), 5.34-5.09 (m, 4H (2,2')), 5.00-4.75 (m, 4H (4, 4', 5')), 4.12-3.77 (dd, 8H (8', 7)), 3.77-3.48 (m, 4H (4 or 4' or 5')), 2.74 (t, 1H (1')), 2.36- 2.1 (m, 4H, (8)) 2.08(s, 6H, (1)), 1.9-1.45 (m, 12H, (9, 9', 10)), 1.44-0.54(m, 16H, (10', 11', 12')).

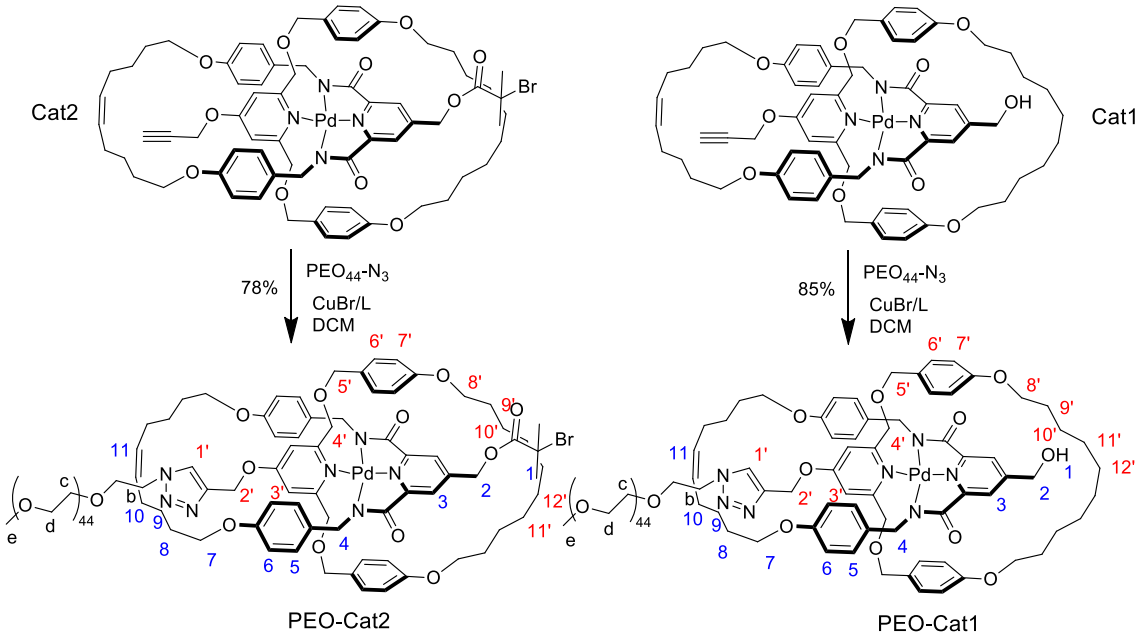
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.17, 170.52, 168.19, 165.70, 162.70, 159.55, 159.49, 158.89, 157.63, 156.58, 153.08, 152.79, 150.26, 132.55, 131.62, 130.95, 130.81, 130.66, 130.15, 130.01, 128.26, 127.53, 122.45, 122.33, 115.17, 114.88, 114.06, 113.22, 107.46, 107.04, 72.52, 68.80, 67.69, 67.52, 67.32, 66.60, 66.46, 65.33, 55.92, 54.75, 49.74, 49.14, 31.97, 31.72, 30.70, 29.91, 28.98, 28.77, 28.50, 28.32, 28.23, 28.05, 25.85, 25.65.

HRMS (m/z) (ESI+): m/z= 1339.4189 $[M+H]^+$, (calcd. 1339.4193 for $C_{70}H_{82}BrN_4O_{11}Pd$)

IR (ATR-FTIR): ν 810, 819, 848, 948, 993, 1043, 1091, 1103, 1218, 1244, 1299, 1323, 1348, 1452, 1458, 1508, 1608, 1741, 2867,2900 cm^{-1}.

5. Synthesis of A-cat-B block copolymers

5.1. Synthesis of **PEO-Cat**



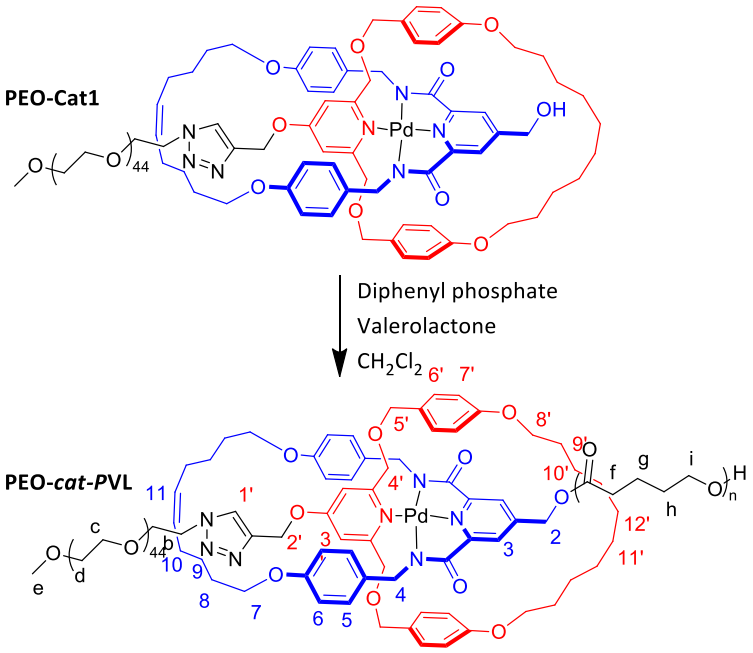
Cat1 or **Cat2** (1 eq., 0.051 mmol), azide end-functionalized poly(ethylene oxide) (PEO_{44}-(N_3)) (1.1 eq., 0.051 mmol, 0.104 g) and Tris(benzyltriazolylmethyl)amine (TBTA) (1.2 eq., 0.056 mmol, 0.029 g) were introduced in a Schlenk tube and 4 mL of DCM were added and the solution was degassed by bubbling argon for 15 minutes. CuBr (1.1 eq., 0.051 mmol, 0.007 g) was added to the mixture contained in the Schlenk tube and the mixture was degassed once more by bubbling argon for 10 minutes. The Schlenk tube was filled with Ar and transferred in a preheated oil bath at 35°C and stirred for 20h. Then, the solution was allowed to cool to RT and diluted with DCM (50 mL), washed with an EDTA aqueous solution (200 mg/L, 3x15 mL), brine (15 mL), dried over anhydrous sodium sulphate, filtered and concentrated under vacuum. The resulting crude mixture was purified by size exclusion chromatography using Bio-Beads S-X1 (Bio-Rad) with CH_2Cl_2 as eluent. The resulting polymer was a yellow solid (yield: 78 or 85%, quantitative conversion with respect to the catenane).

^{1}H NMR (500 MHz, $CDCl_3$) ***PEO-Cat1****:* δ 8.08 (s, 1H (3)), 7.91 (s, 2H (3, 1')), 7.46-7.43 (dd, 2H (7')), 7.22 (m, 1H (3')), 7.05-7.04 (d, 2H (6')), 6.80-6.65 (m, 4H (7', 6')), 6.47-6.41 (m, 4H (5, 6)), 6.11 4-5.8 (m, 1H (3')), 5.7-4.25 (m, 16H (5, 6, 2, 2', 4, 4', 5')), 4.96 (s, 2H (2')), 4.64 (s, 2H (b)), 4.1-3.78 (m, 10H (1, 7, 8')), 3.65 (m, 197H (c,d)), 3.37 (s, 3H (e)), 2.25- 0.5 (34H, (9', 10', 11', 12', 8, 9, 10)).

^{1}H NMR (500 MHz, $CDCl_3$) ***PEO-Cat2****:* δ 7.91 (s, 1H (1')), 7.90 (s, 2H (3)), 7.84 (s, 1H (3)), 7.42 (d, 2H (7')), 7.24 (m, 1H (3')), 7.07-7.04 (d, 2H (6')), 6.84-6.70 (m, 4H (7', 6')), 6.47-6.41 (m, 4H (5, 6)), 6.11 4-6.01 (m, 1H (3')), 5.7-4.25 (m,

16H (5, 6, 2, 2', 4, 4', 5')), 4.96 (s, 2H (2')), 4.64 (s, 2H (b)), 4.1-3.78 (m, 8H (1, 7, 8')), 3.65 (m, 229H (c,d)), 3.37 (s, 3H (e)),2.05 (6H, 1) 2.25- 0.5 (34H, (9', 10', 11', 12', 8, 9, 10)).

5.2. Synthesis of **PEO-*cat*-PVL**

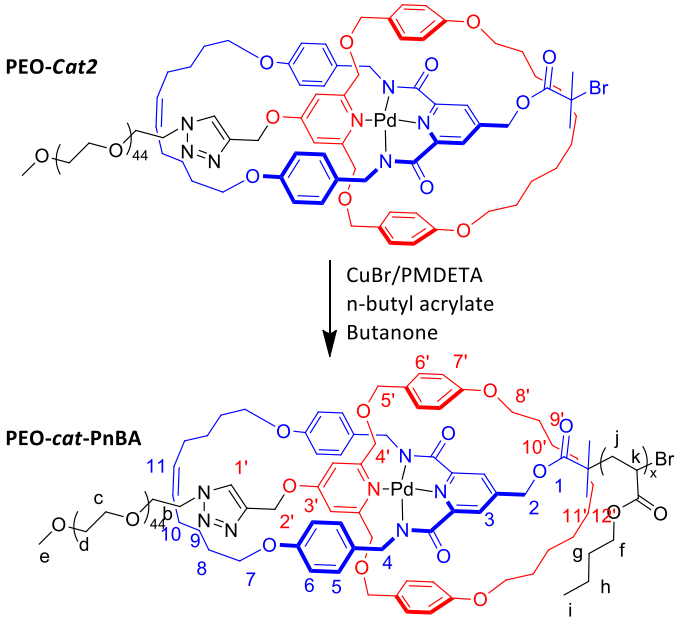


Diphenylphosphate (DPP) (0.0045g, 0.018 mmol) was added to a 1M solution of **PEO-Cat1** (0.027 g, 0.0086 mmol) in dry CH_2Cl_2. δ-valerolactone (VL) (0.078 mL, 0.86 mmol), previously distilled over CaH_2, was then added to the solution to initiate the polymerization under an Argon atmosphere. After 3 h stirring at room temperature, 5µL of triethylamine was added to the solution and stirred for additional 30 minutes. The polymer was isolated by precipitation from CH_2Cl_2 in methanol to give the pure copolymer **PEO-*cat*-PVL**.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (s, 1H (1')), 7.91 (s, 1H (3, 1')), 7.46-7.43 (dd, 2H (7')), 7.22 (m, 1H (3')), 7.05-7.04 (d, 2H (6')), 6.80-6.65 (m, 4H (7', 6')), 6.47-6.41 (m, 4H (5, 6)), 6.11 4-5.8 (m, 1H (3')), 5.7-4.25 (m, 16H (5, 6, 2, 2', 4, 4', 5')), 4.96 (s, 2H (2')), 4.64 (s, 2H (b)), 4.1-4.0 (459H (i)), 3.65 (m, 197H (CH2 from PEO)), 3.37 (s, 3H (c,d)), 3.5-2.25 (465H, f), 2-1.5 (989H, g,h). Mn PnBA block (^{1}H NMR): 21000 g/mol.

SEC analysis (Solvent: DMF, calibration: Polystyrene standards): M_n = 9600 g/mol, Đ = 1.11

5.3. Synthesis of **PEO-*cat*-PnBA**

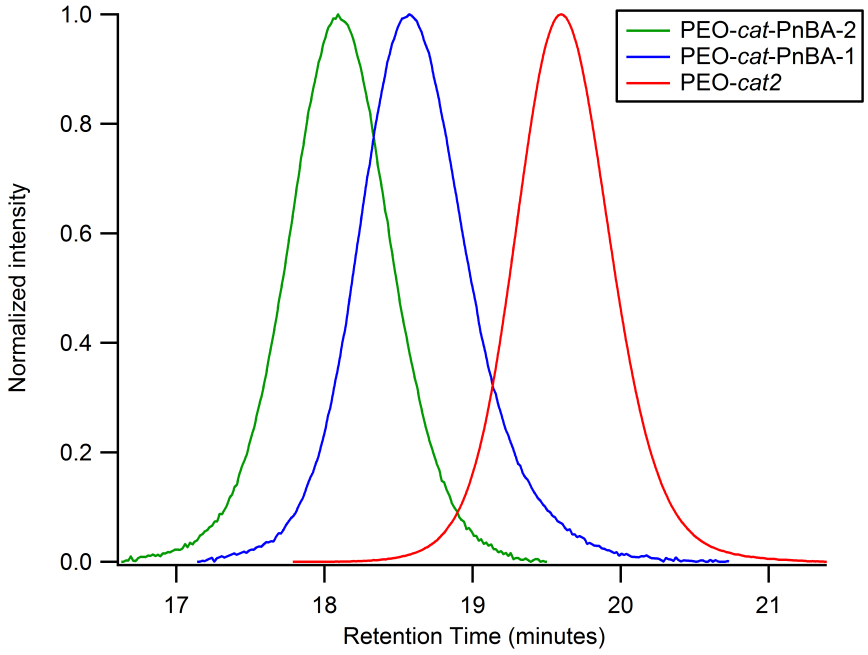


To a solution of **PEO-Cat2** (0.028 g, 0.0083 mmol) and PMDETA (0.002 ml, 0.0092 mmol) in 0.4 mL of methylethyl ketone. n-butyl acrylate (nBA) (0.120 mL, 0.83 mmol), previously filtered through a basic alumina column, was added to the solution. After that, Argon was bubbled for 15 minutes in order to degas the solution. CuBr (0.001 g, 0.0083 mmol) was then added and the solution was degassed by bubbling Ar for 10 minutes. The mixture was then heated at 60°C for 5 hours under argon atmosphere in an oil bath. The polymerisation was stopped by freezing the mixture in liquid nitrogen and the reaction vessel was opened to air. Then, the solution was diluted with DCM (50 mL), washed with an EDTA aqueous solution (200 mg/L, 3x15 mL). The resulting crude mixture was purified by size exclusion chromatography using Bio-Beads S-X1 (Bio-Rad) with CH_2Cl_2 as eluent in order to give the pure copolymer **PEO-*cat*-PnBA**.

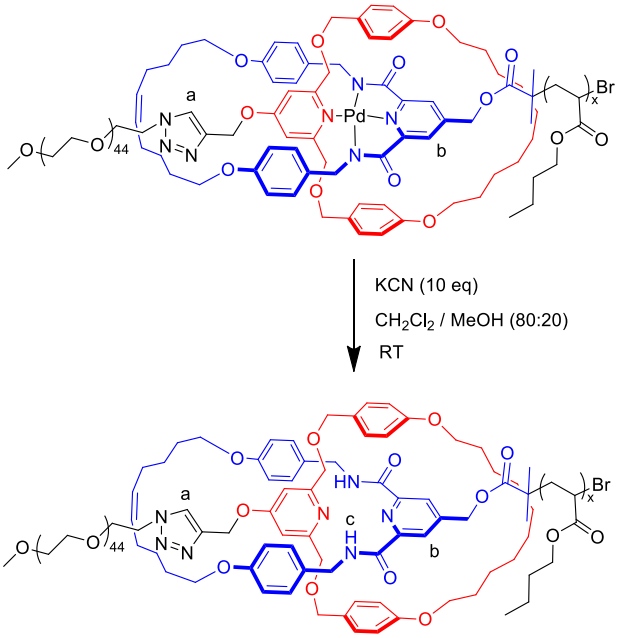
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (s, 1H (3)), 7.91 (s, 2H (3, 1')), 7.46-7.43 (dd, 2H (7')), 7.22 (m, 1H (3')), 7.05-7.04 (d, 2H (6')), 6.80-6.65 (m, 4H (7', 6')), 6.47-6.41 (m, 4H (5, 6)), 6.11 4-5.8 (m, 1H (3')), 5.7-4.25 (m, 16H (5,6, 2, 2', 4, 4', 5')), 4.96 (s, 2H (2')), 4.64 (s, 2H (b)), 4.3-4.75 (76H (f)), 3.65 (m, 188H (c,d)), 3.37 (s, 3H (e)), 2.5- 1.2 (263H j, k, g, g + 9', 10', 11', 12', 8, 9, 10)), 0.94 (109H (i)).

SEC analysis (DMF, calibration: Polystyrene standards):

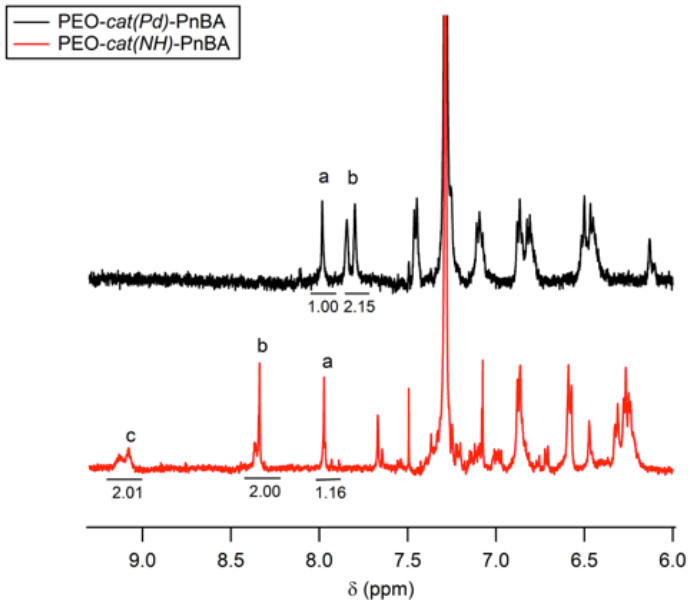
Entry	Time (h)	M_n GPC (g/mol)	M_n ^{1}H-NMR (g/mol)	M_n ^{1}H-NMR PnBA block (g/mol)	Đ
PEO-*cat*-PnBA-1	3	7800	7690	4350	1.08
PEO-*cat*-PnBA-2	5	10500	12300	8960	1.11



5.4. Demetallation of **PEO-c*at*-PnBA**



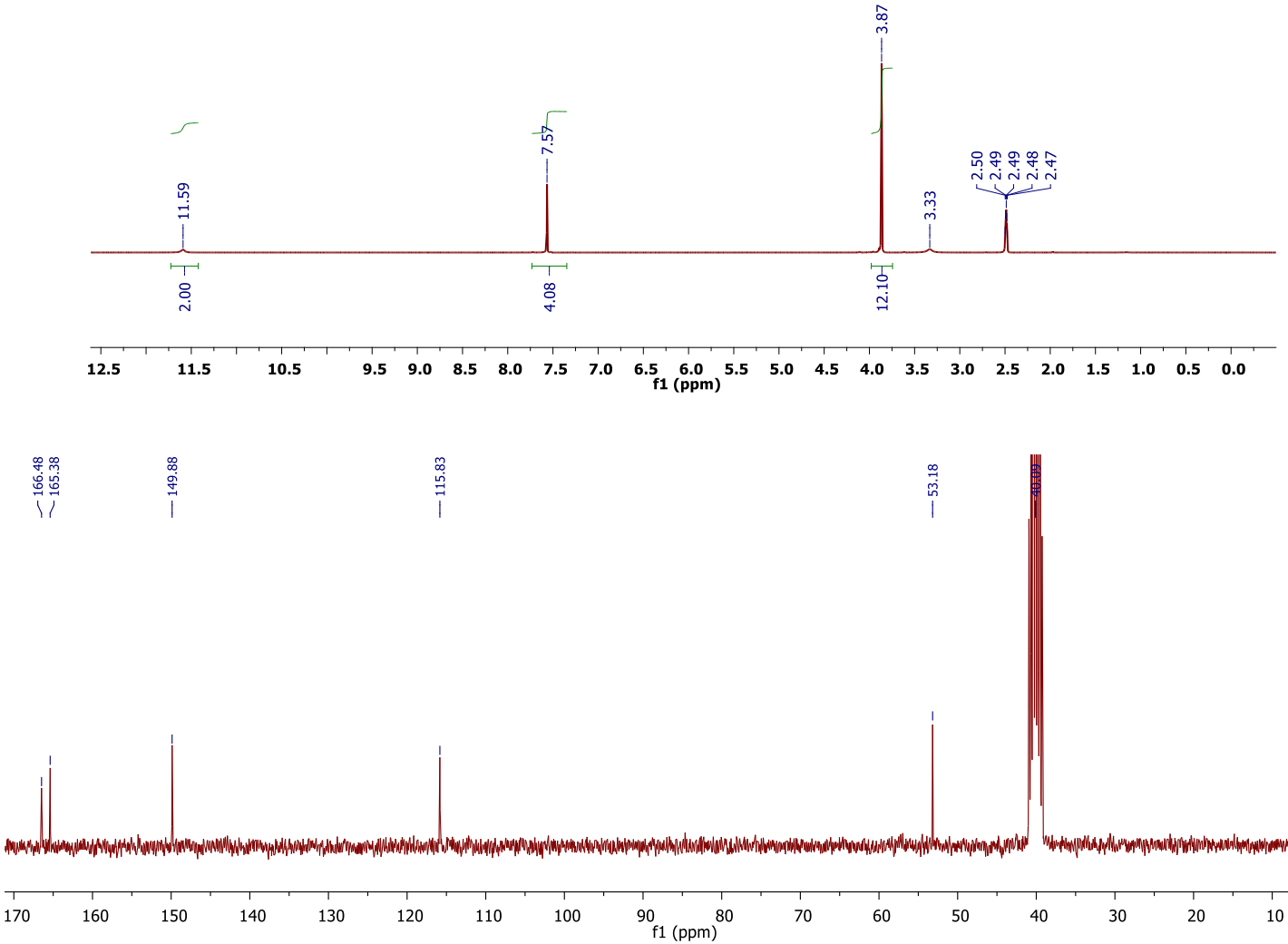
To a solution of a PEO-*cat*-PnBA in dichloromethane was added a KCN (10 eq.) solution in methanol, for a final DCM/MeOH ratio of 80/20. The solution was stirred for one hour. The solution was then washed three times with water. The organic layers were dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to yield the demetallated copolymer as a very slightly yellowish powder (yield =90%).



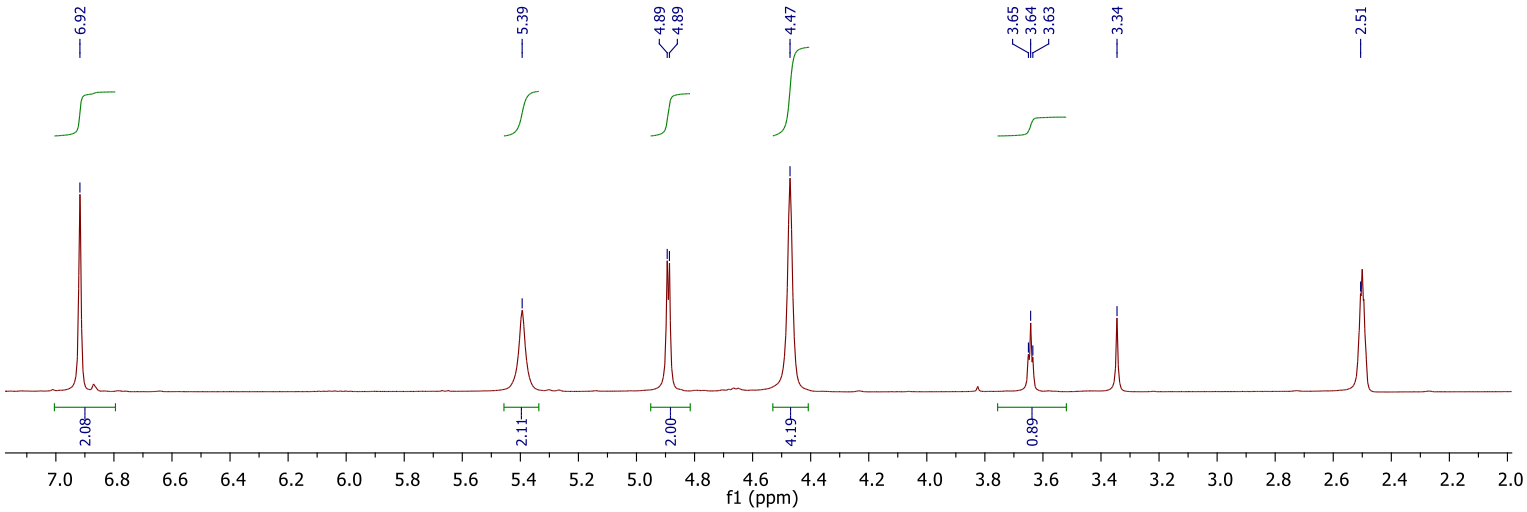
[1]H-NMR shows the quantitative palladium removal indicated by the re-appearance of the amide protons, and the shift of the aromatic protons. PEO-*cat(Pd)*-PnBA refers to the sample containing palladium. PEO-*cat(NH)*-PnBA refers to the palladium free sample.

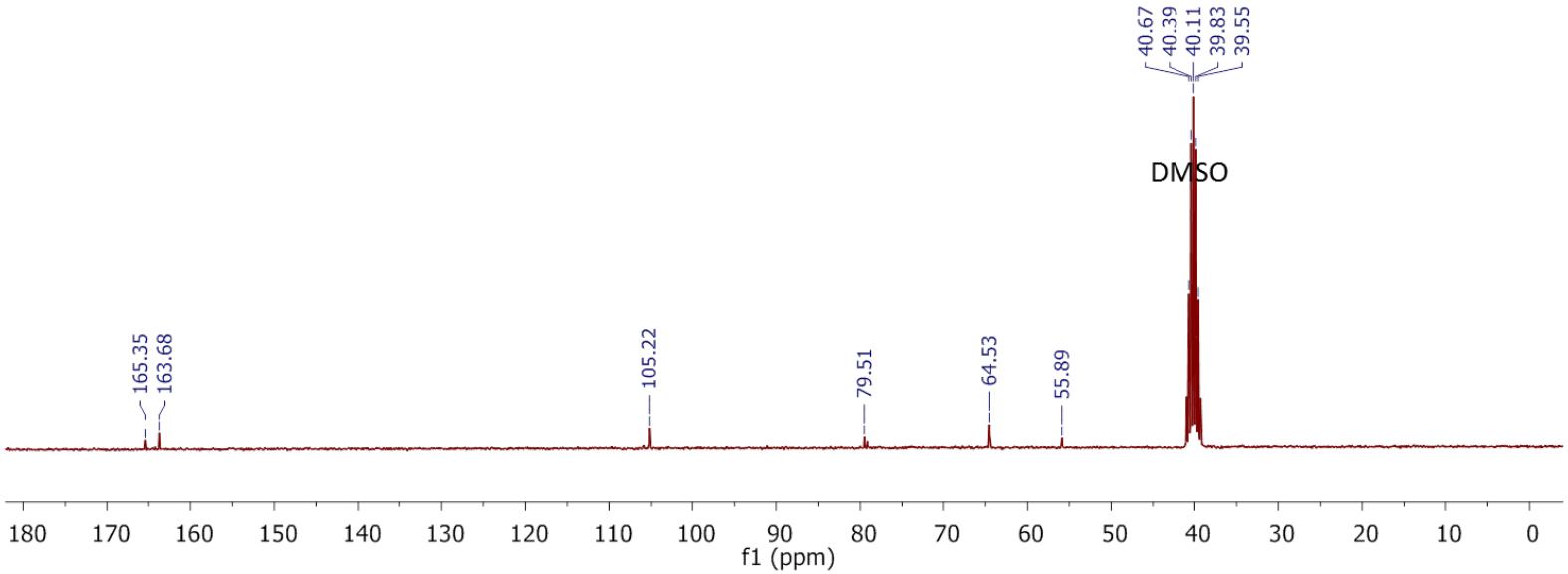
6. Chromatograms and spectra

6.1. ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectra of compound S1.

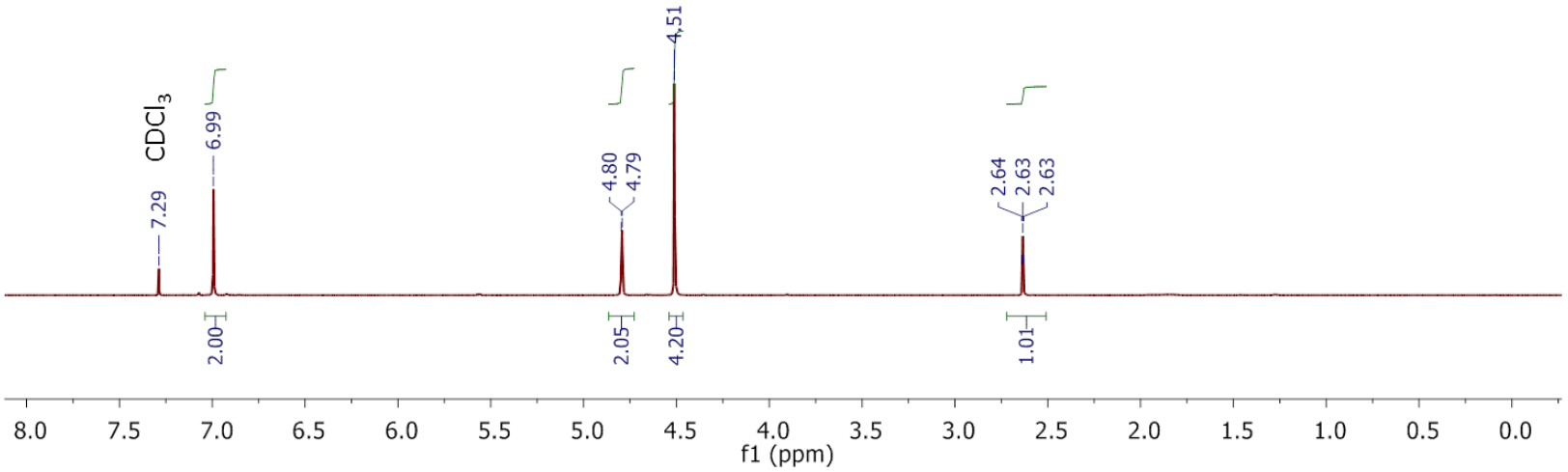


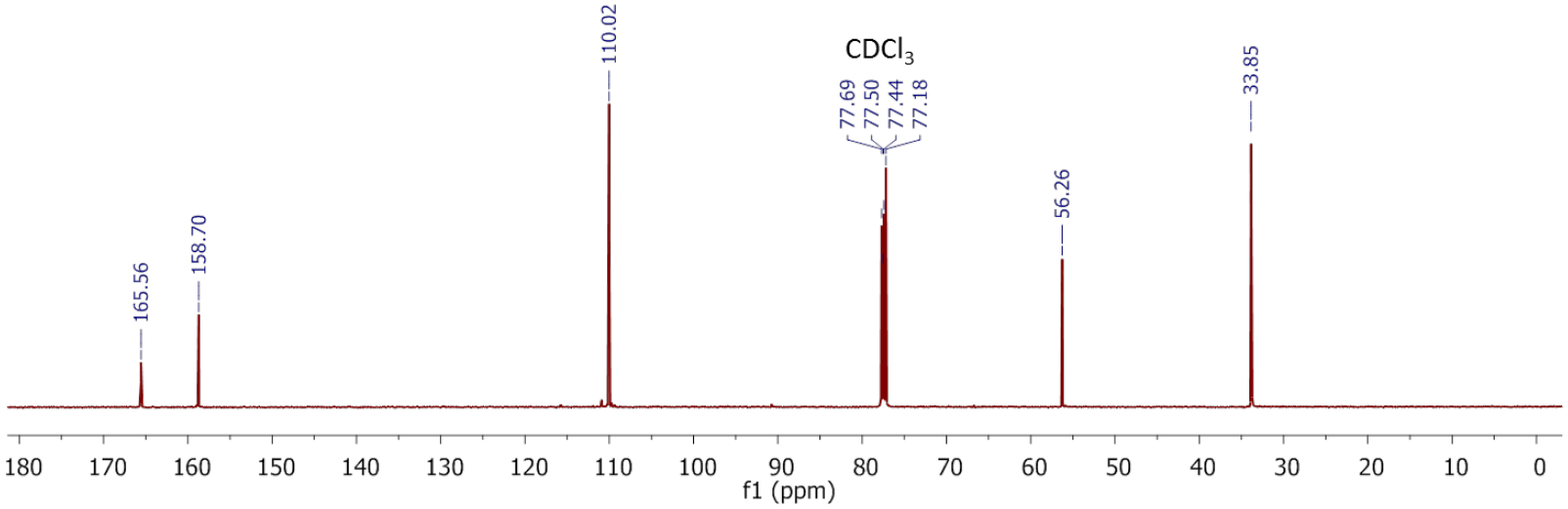
6.2. ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectra of compound S3.



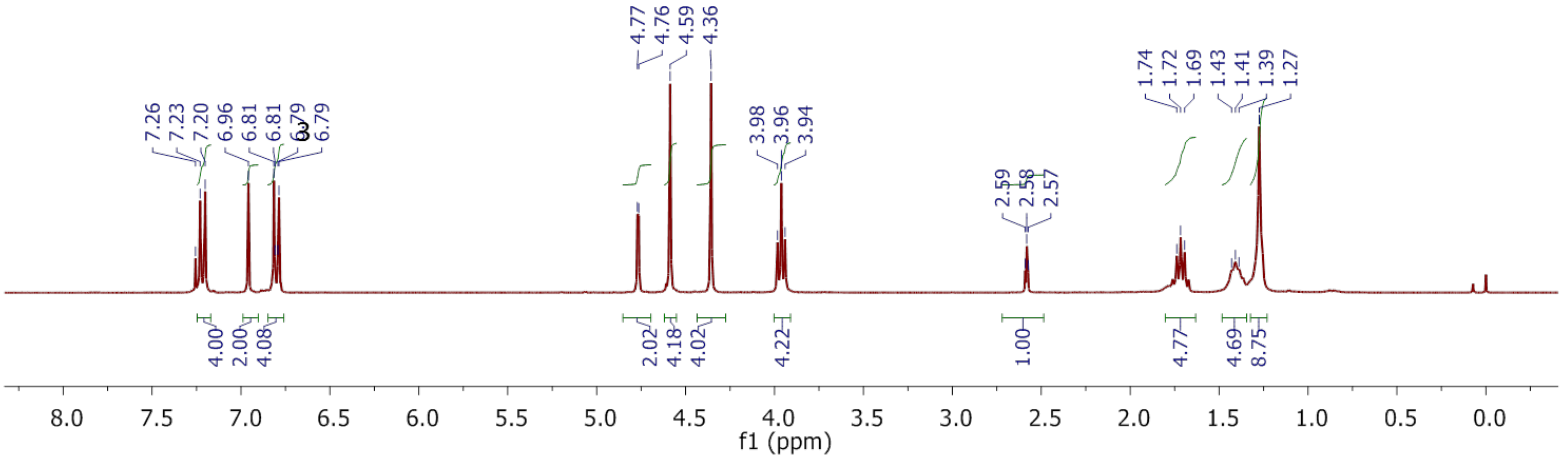


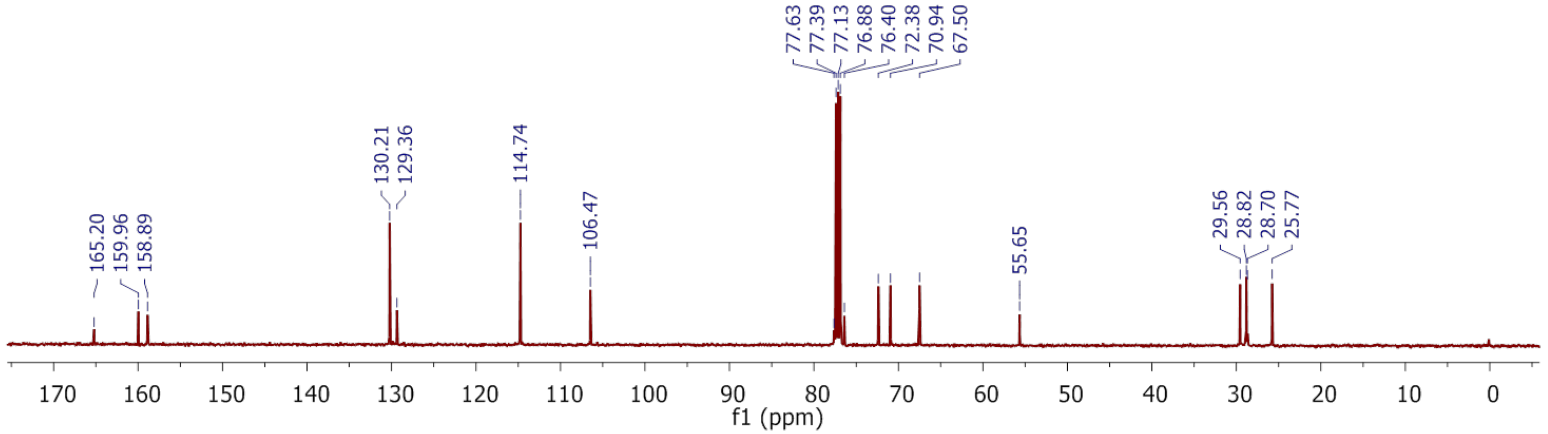
6.3. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of compound S4.



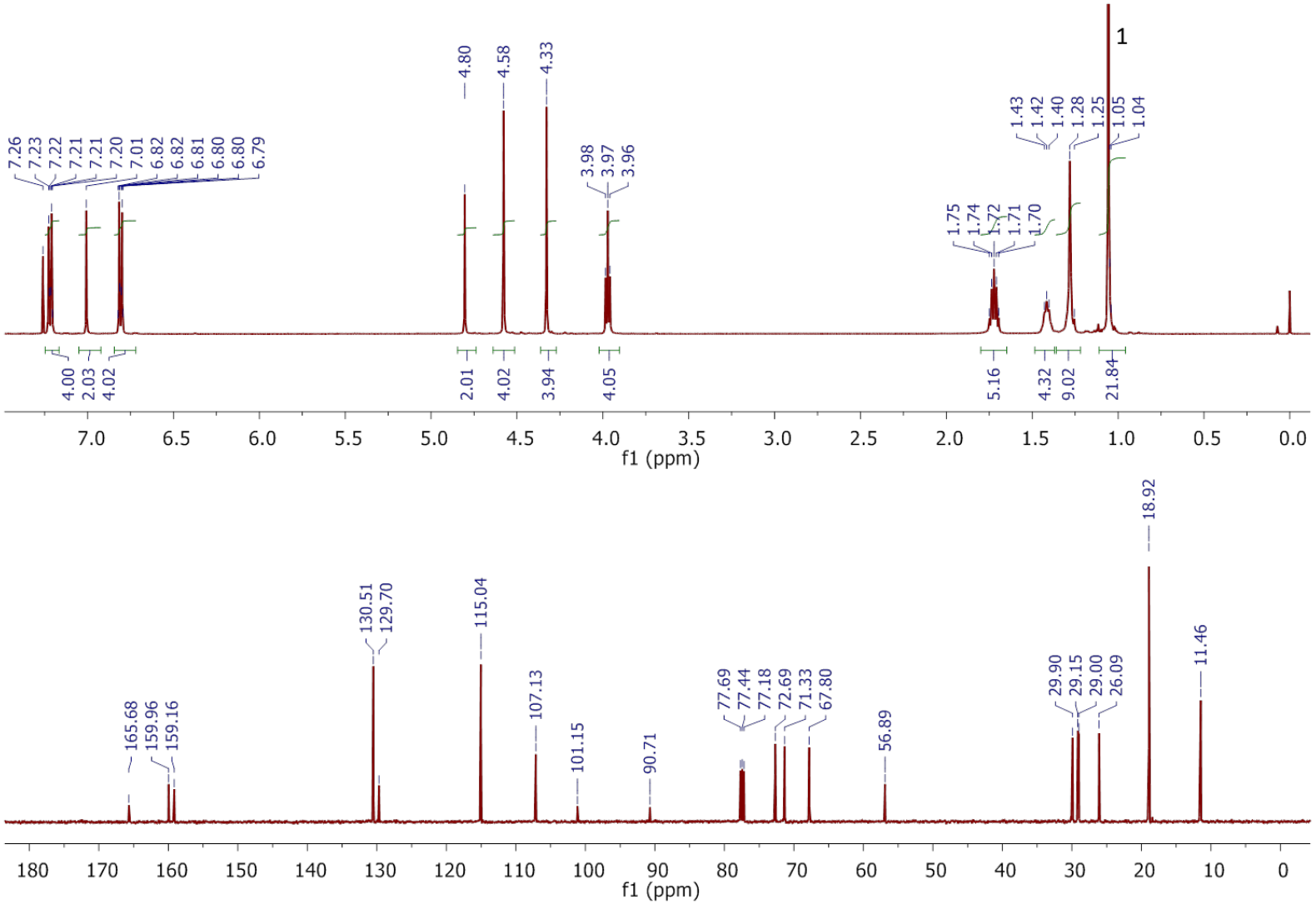


6.4. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of compound S5.

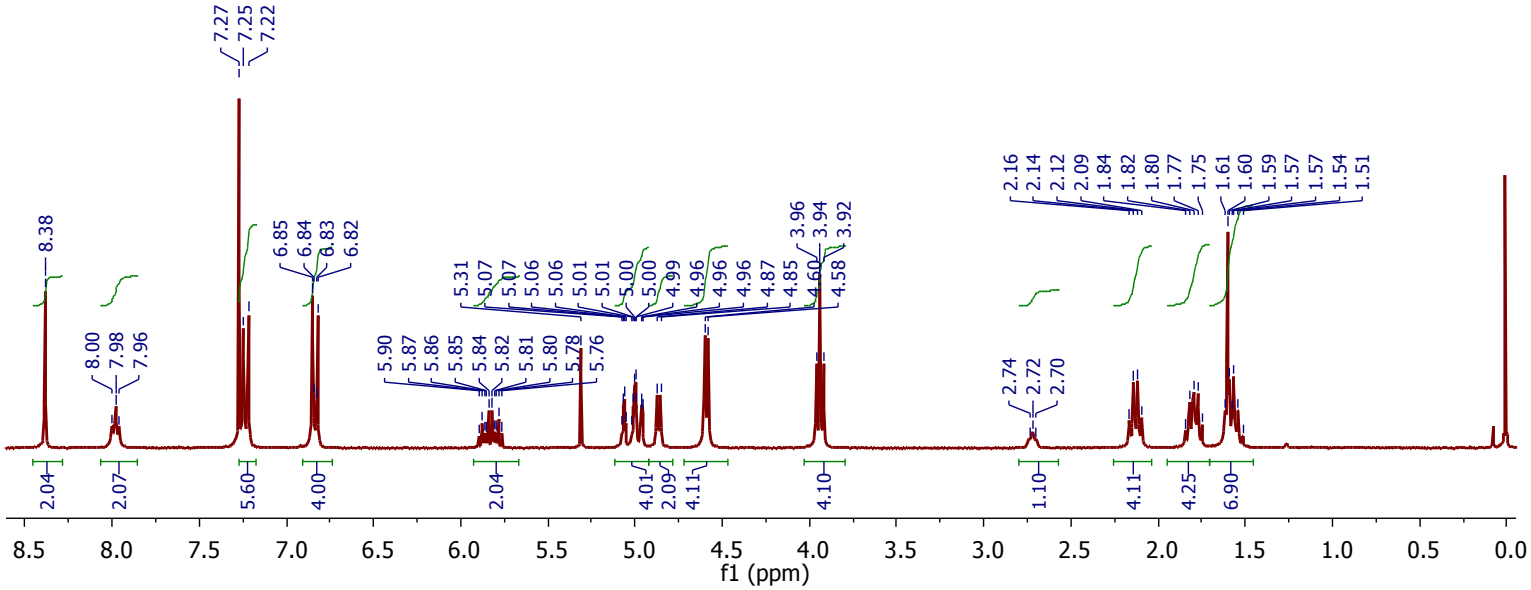


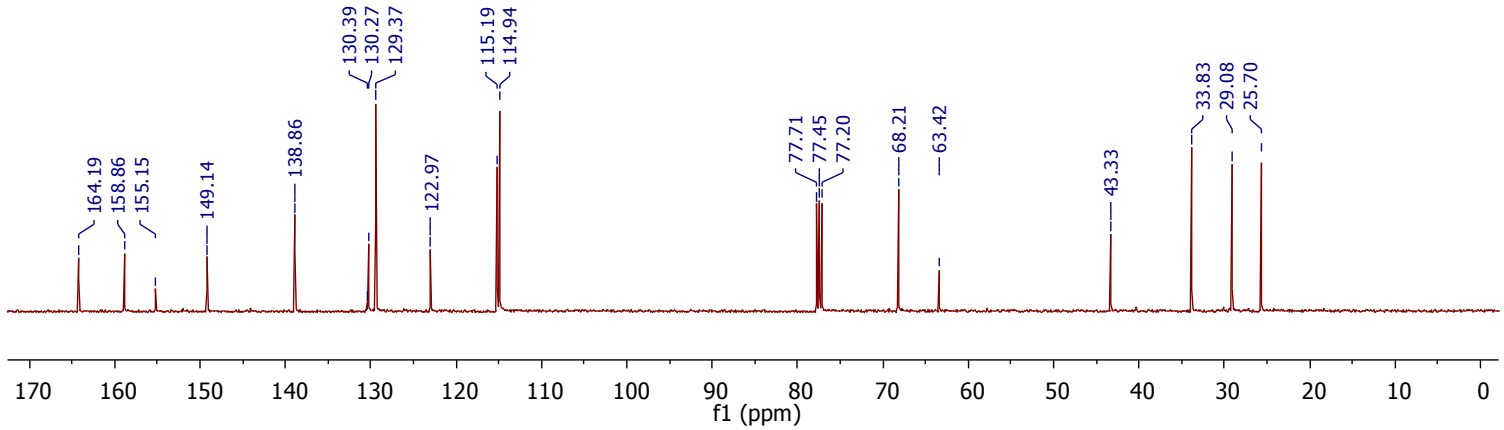


6.5. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of compound L1.

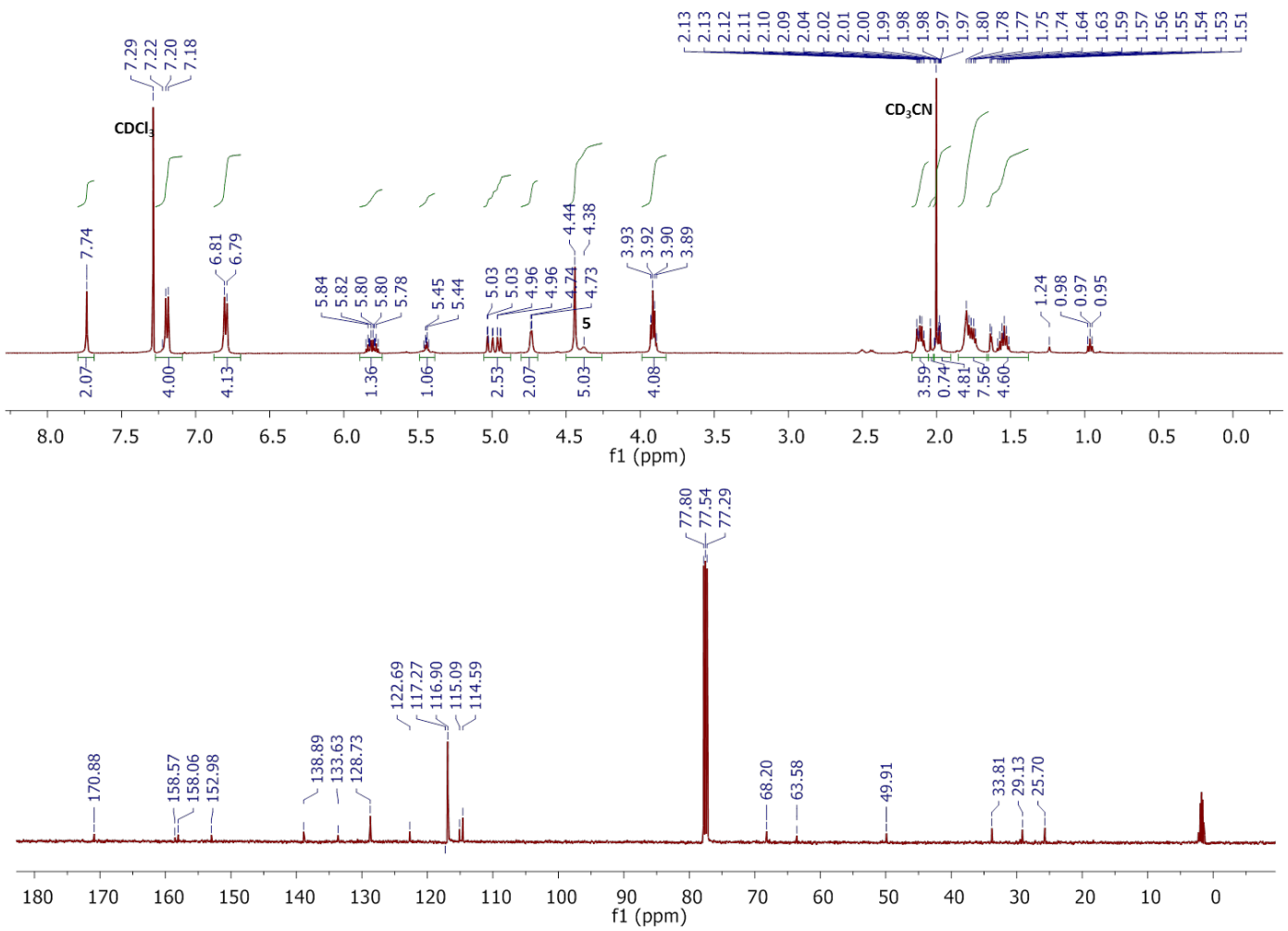


6.6. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of compound L2.

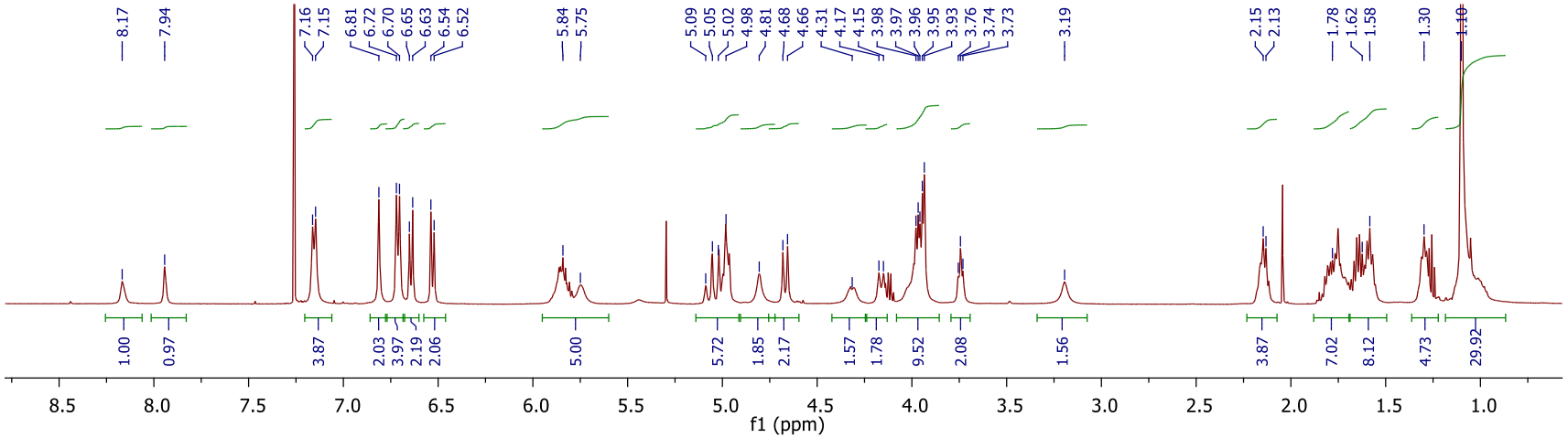


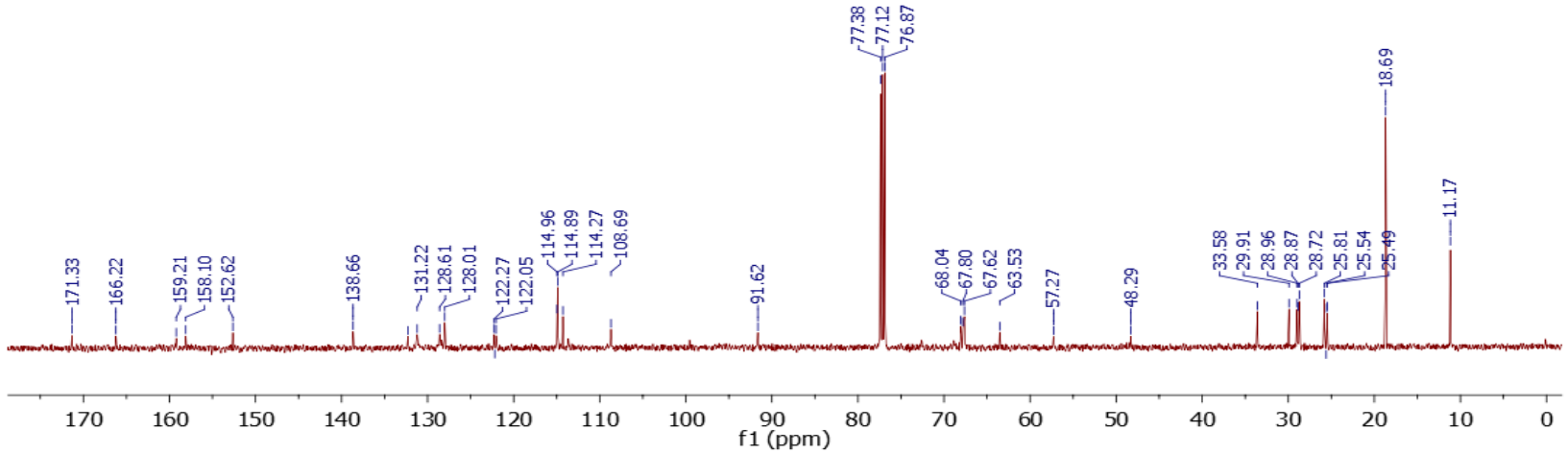


6.7. ^{1}H-NMR (500 MHz, $CDCl_3/CD_3CN$, 95/5, v/v) and ^{13}C-NMR (125 MHz, $CDCl_3/CD_3CN$, 95/5, v/v) spectra of compound L2.Pd.CH_3CN.

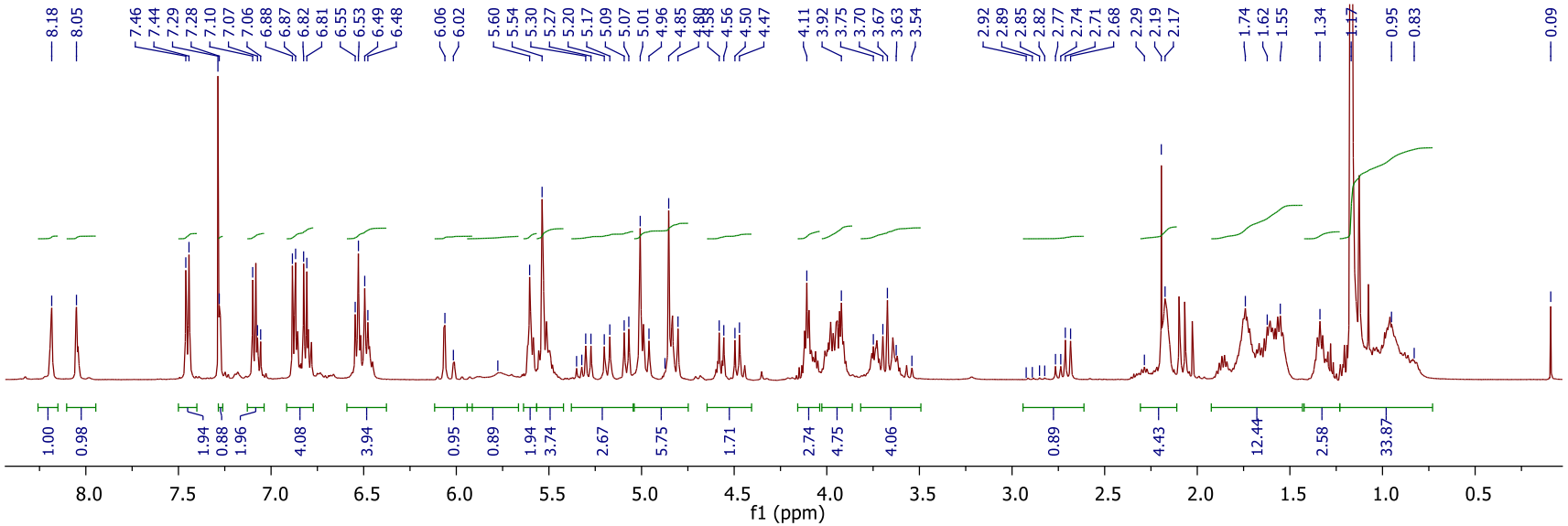


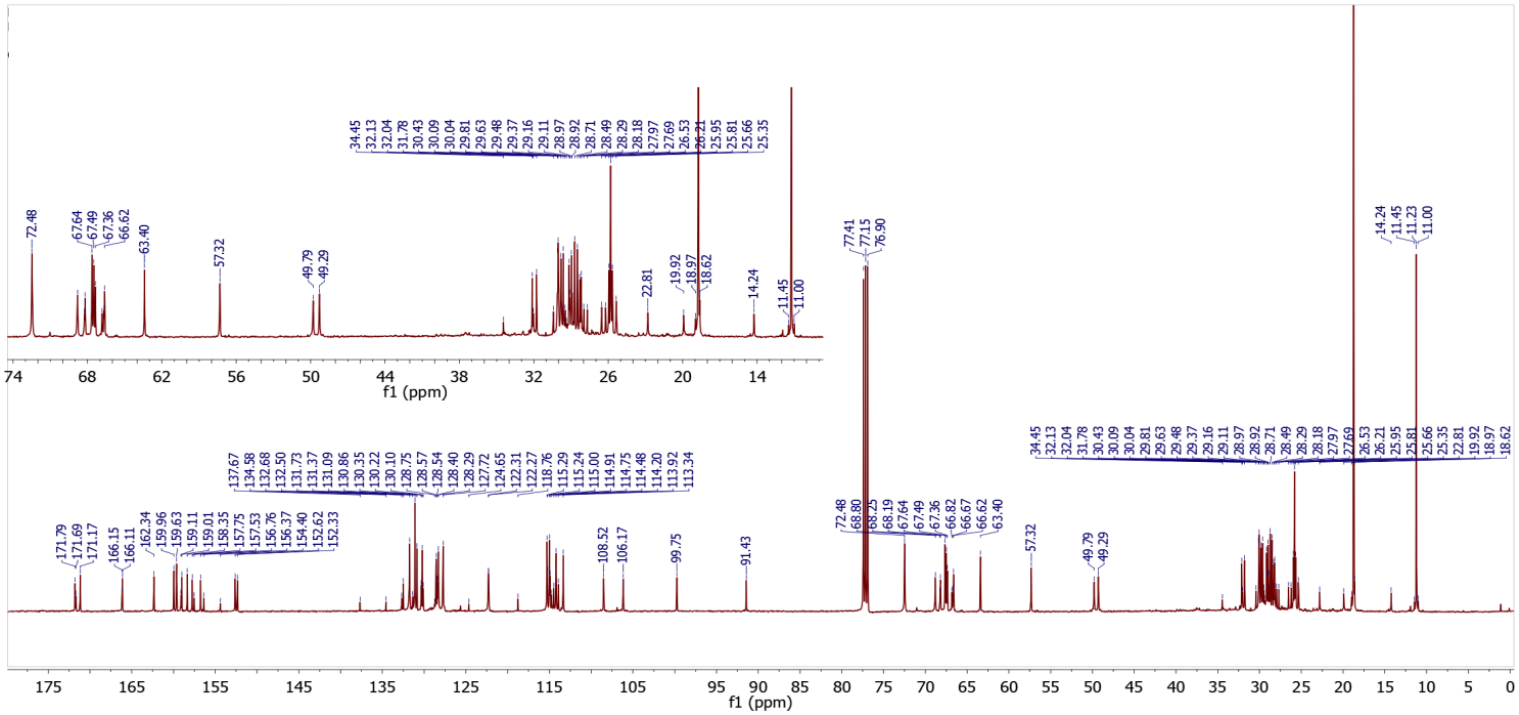
6.8. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of precatenane L1[Pd]L2.



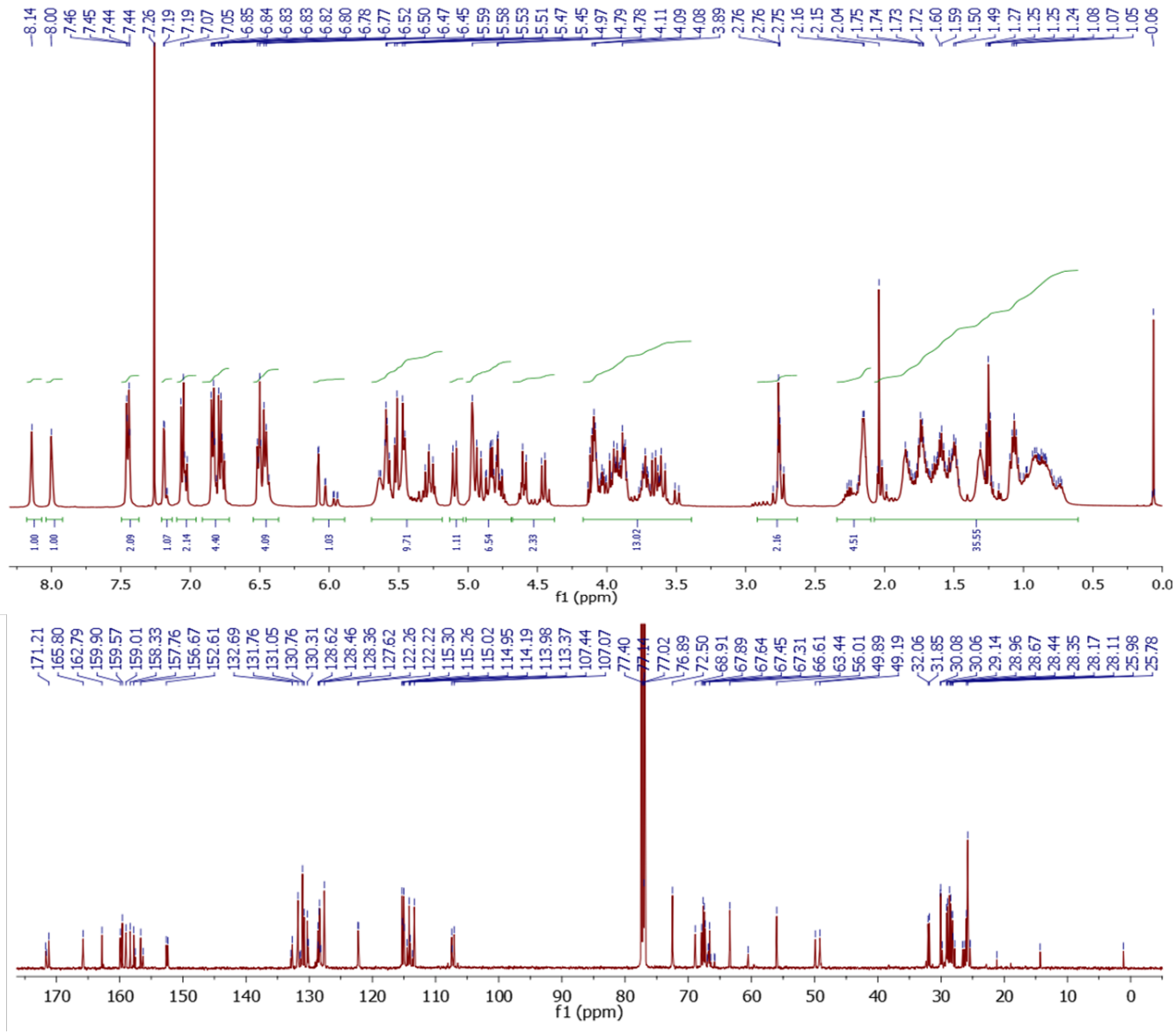


6.9. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR spectra of silylated catenane CatTIPS

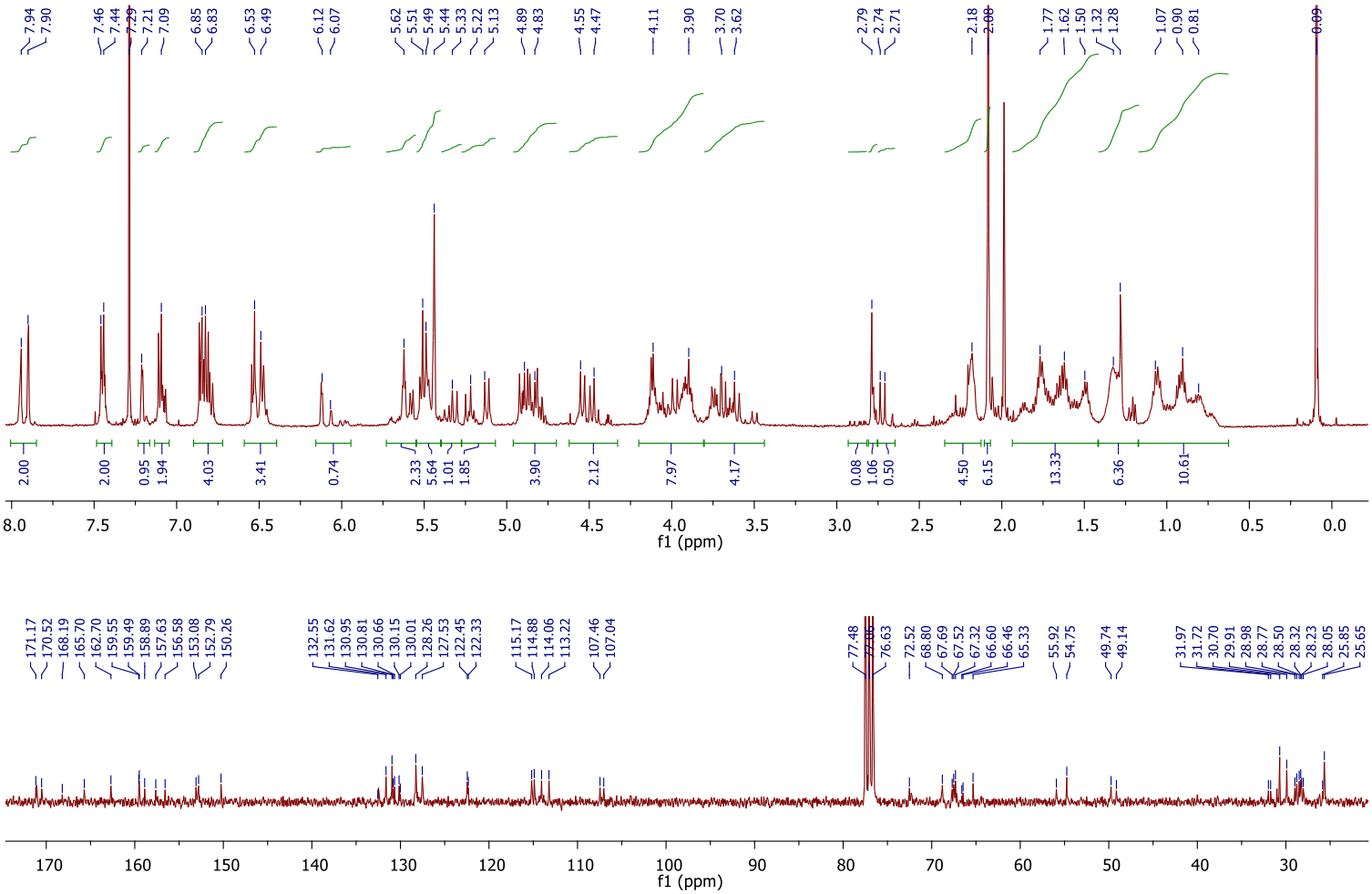



f1 (ppm)
f1 (ppm)

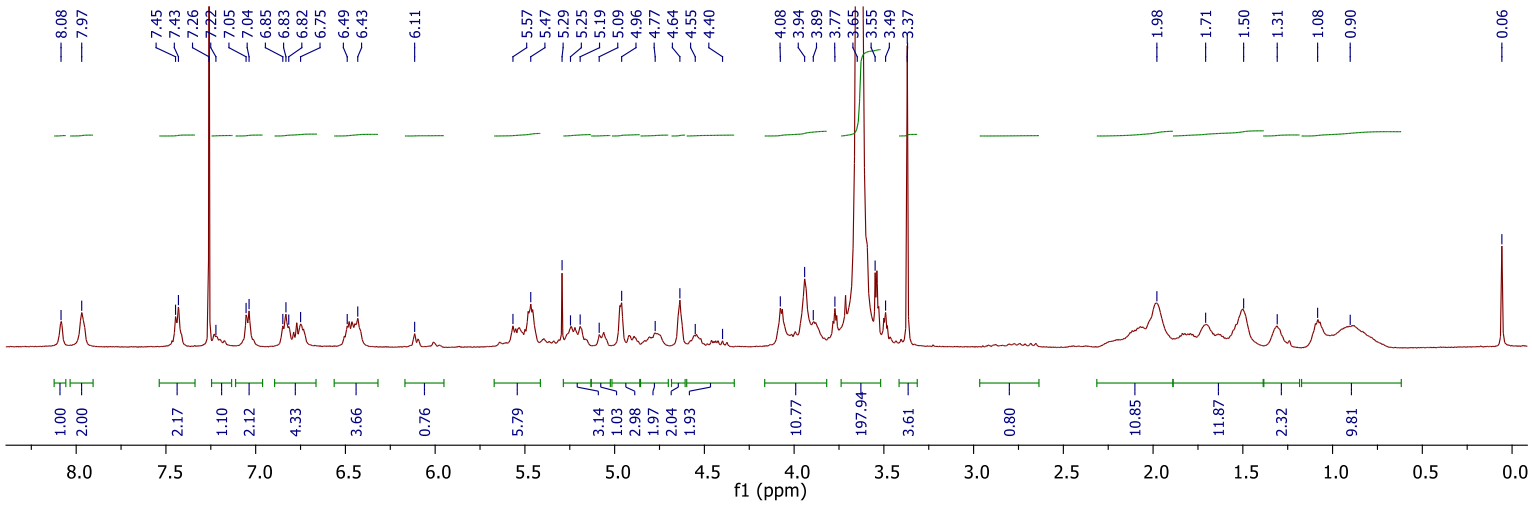
6.10. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of desilylated catenane Cat1.



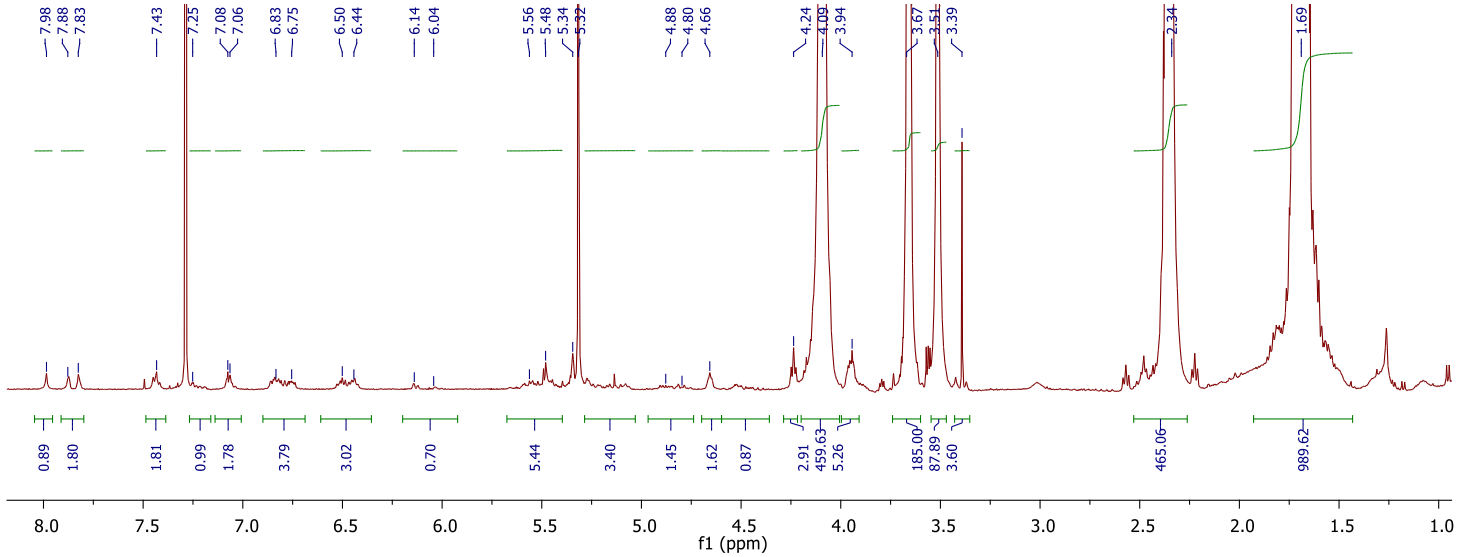
6.11. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of catenane Cat2.



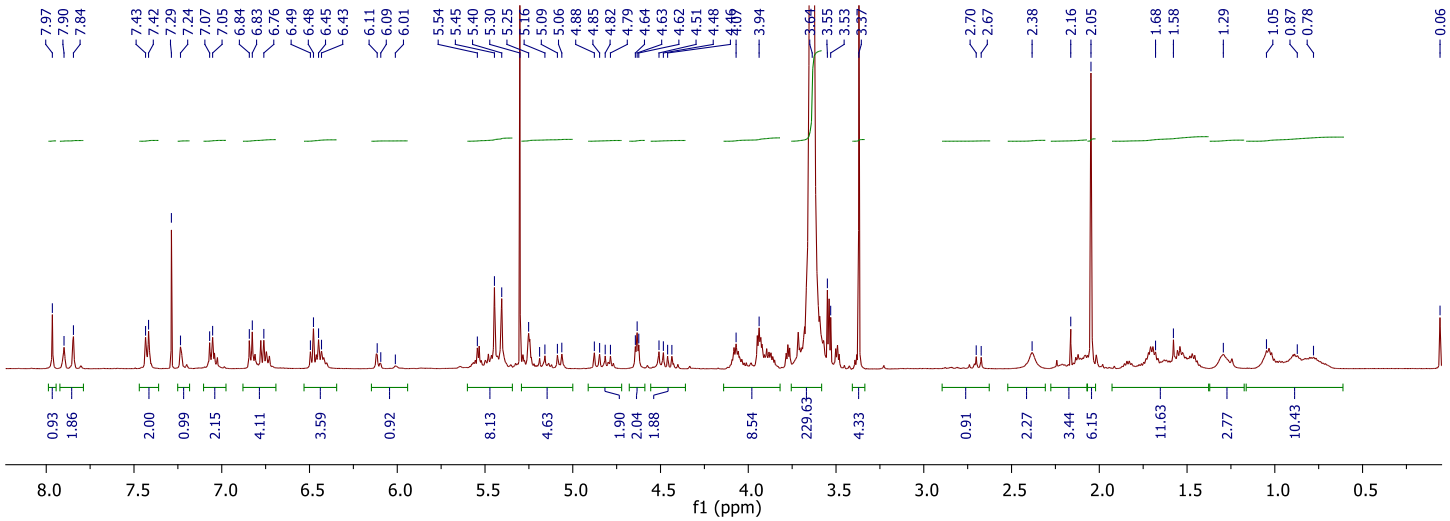
6.12. ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of PEO-Cat1.



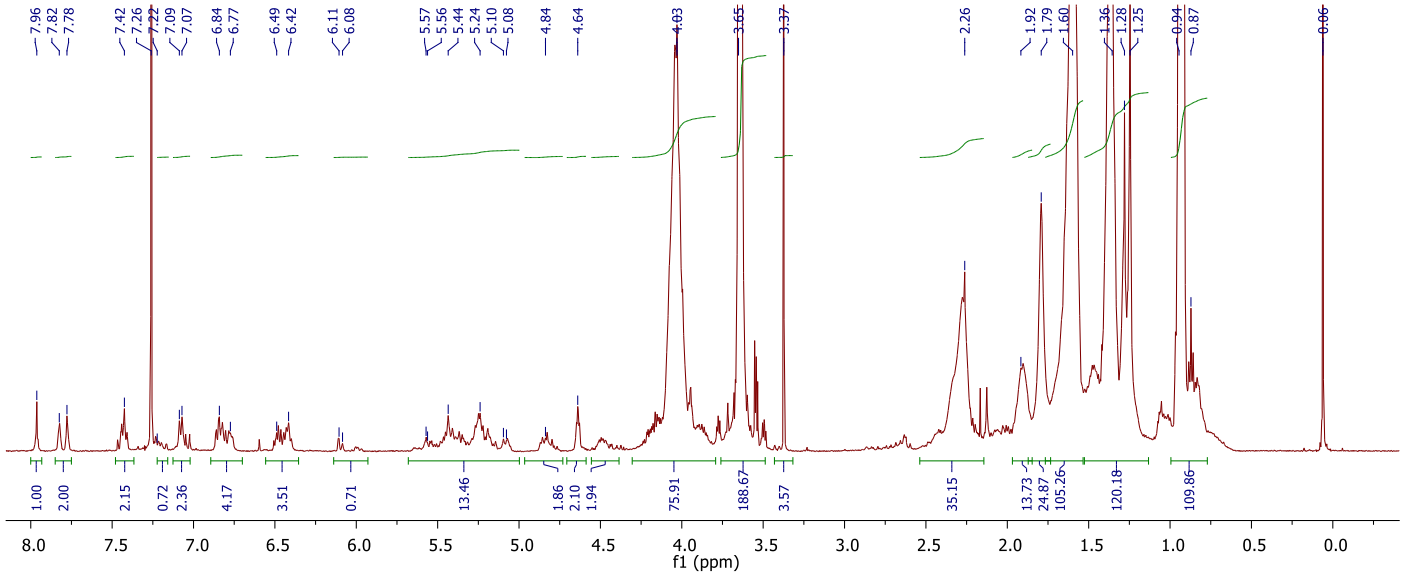
6.13. ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of PEO-*cat*-PVL.



6.14. ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of PEO-Cat2.

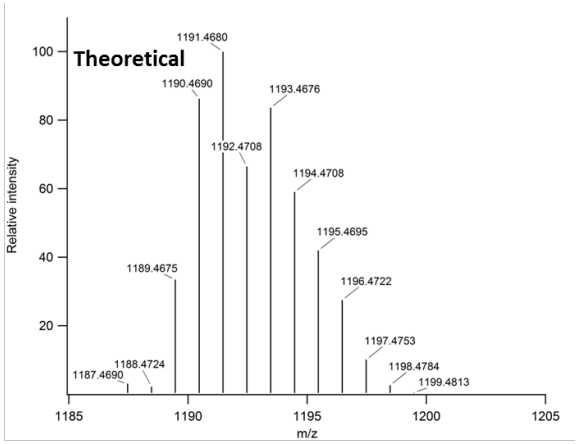


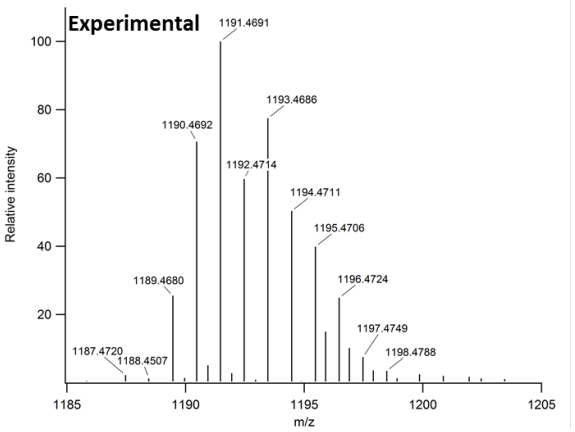
6.15. ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of PEO-*cat*-PnBA.



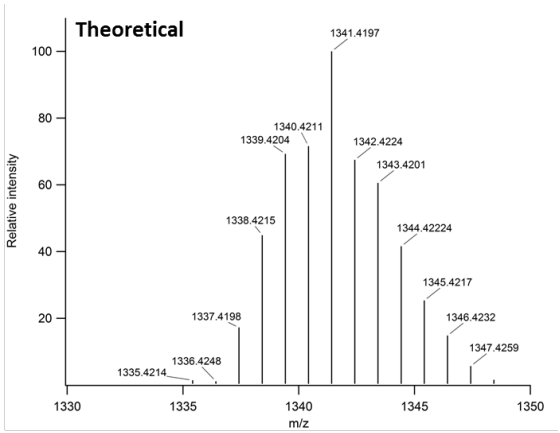
7. High resolution mass spectra of **Cat1** and **Cat2.**

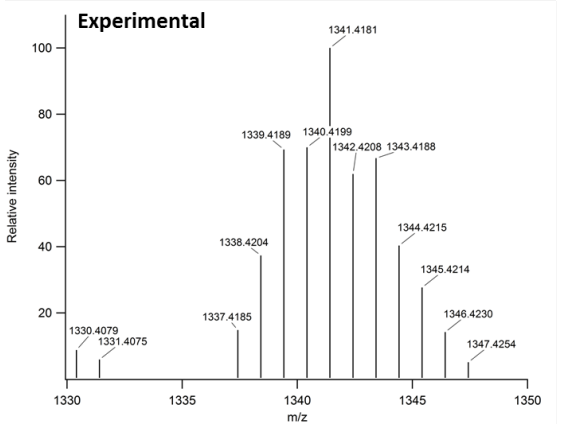
Cat1





Cat2





8. Crystallographic and refinement details of precatenane L1[Pd]L2, CatTIPS and Cat1.

Table 1. Crystal data and structure refinement details

Identification code		**Precatenane L1[Pd]L2**	**CatTIPS**	**Cat1**
Empirical formula		C_{77} H_{100} N_4 O_{10} Pd Si	C_{75} H_{96} N_4 O_{10} Pd Si	C_{75} H_{93} N_4 O_{13} Pd
Formula weight		1376.09	1348.04	1364.93
Temperature		150(2) K	150(2) K	100(2) K
Wavelength		0.71073 Å	0.71073 Å	0.82103 Å
Crystal system		Monoclinic		
Space group		*P*2_1/c	*C*2/c	*I*2/a
Unit cell dimensions	a	24.3213(16) Å	39.473(13) Å	37.2375(9) Å
	b	10.0020(5) Å	12.0530(16) Å	11.7434(2) Å
	c	32.0407(18) Å	35.420(12) Å	32.5955(9) Å
	b	111.912(7)°	114.26(4)°	101.666(3)°
Volume		7231.2(8) $Å^3$	15363(9) $Å^3$	13959.4(6) $Å^3$
Z		4	8	8
Density (calculated)		1.264 g/cm^3	1.166 g/cm^3	1.299 g/cm^3
Absorption coefficient		0.333 mm^{-1}	0.312 mm^{-1}	0.476 mm^{-1}
F(000)		2920	5712	5768
Crystal size		0.50 x 0.25 x 0.02 mm^3	0.30 x 0.06 x 0.05 mm^3	0.25 x 0.1 x 0.08 mm^3
q range for data collection		2.786 to 21.637°.	2.764 to 14.411°.	1.751 to 29.525°.
Reflections collected		29172	7909	93341
Independent reflections		8264 [$R_{(int)}$ = 0.1065]	2470 [$R_{(int)}$ = 0.1195]	12338 [$R_{(int)}$ = 0.0648]
Completeness		97.6 % (to q= 21.637°)	96.8 %	97.6 %
Absorption correction		Semi-empirical from equivalents		

Max. and min. transm.	1.00000 and 0.80355	1.00000 and 0.77881	1.00000 and 0.82434
Refinement method	Full-matrix least-squares on F^2		
Data /restraints /parameters	8264 / 20 / 845	2470 / 851 / 748	12338 / 118 / 930
Goodness-of-fit on F^2	1.039	1.066	1.007
Final R indices [I>2s(I)]	R_1 = 0.0960, wR_2 = 0.2177	R_1 = 0.1127, wR_2 = 0.2238	R_1 = 0.0710, wR_2 = 0.1949
R indices (all data)	R_1 = 0.1373, wR_2 = 0.2456	R_1 = 0.1694, wR_2 = 0.2565	R_1 = 0.0771, wR_2 = 0.2022
Largest diff. peak and hole	2.442 and -1.111 e.Å^{-3}	0.406 and -0.294 e.Å^{-3}	1.062 and -0.876 e.Å^{-3}

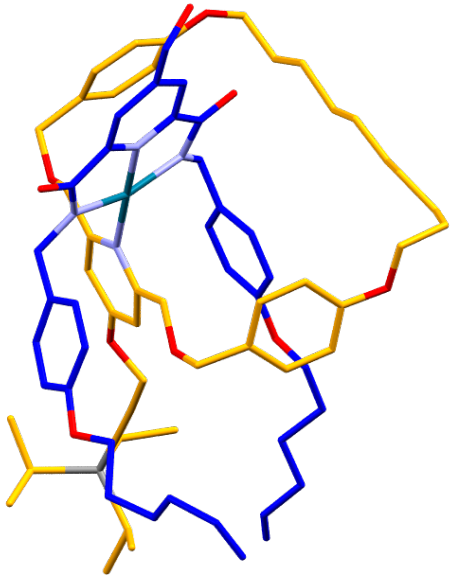


Figure S1: Precatenane L1[Pd]L2

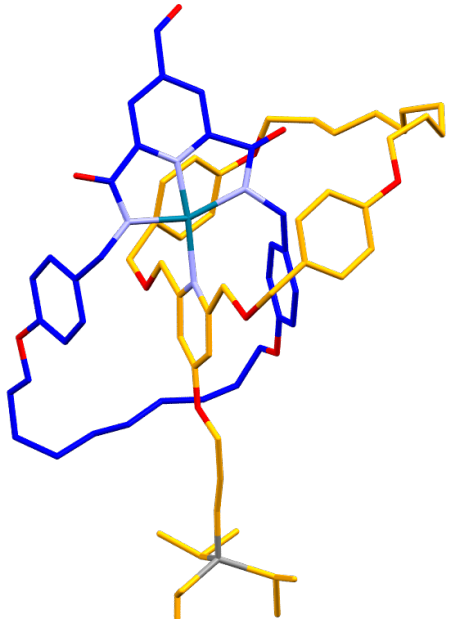


Figure S2: CatTIPS

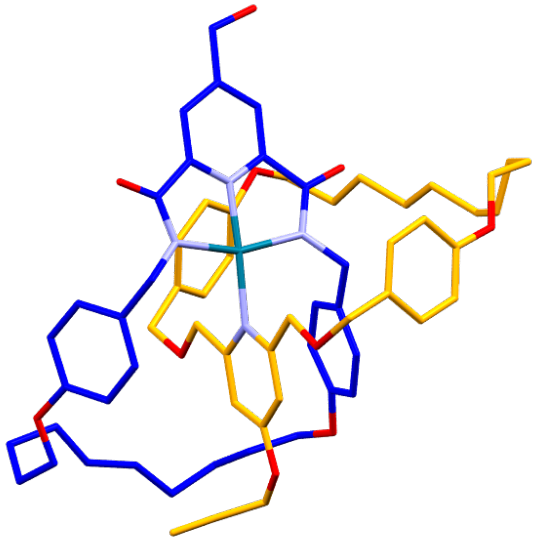


Figure S3: Cat1

Single crystal analysis

Crystals were obtained by slow evaporation of a CH_2Cl_2 solution (**L1[Pd]L2**, colorless plate-like and **CatTIPS**, yellow needles) or CH_2Cl_2 /acetone solution (**Cat1**, red rods).

L1[Pd]L2 and **CatTIPS** were measured on a laboratory instrument (Rigaku UltraX18 generator, MoKa radiation, Xenocs mirrors) using a MAR345 image plate detector. The crystals were flash-cooled to 150K into a N2 gas-flow (oxford cryostream).

Data for Cat1 were measure at the SNBL beamline (ESRF synchrotron, France) onto a Pilatus 2M detector, l=0.82103Å, Si(111) monochromator. The crystals were flash cooled to 100K prior to the data collection. To overcome the geometrical restraints imposed by the instrument setup – resulting in low data completeness, a total of 3 data-sets on two different crystals were collected and, after integration, scaled in xprep.

All reflections were integrated in CrysalisPRO [8] and the implemented absorption correction was applied. Structure solution was performed by SHELXS and Full-matrix least-squares refinement on F^2 by SHELXL2014/7 [9]. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions in riding mode with temperature factors fixed at 1.2 times U_{eq} of the parent atoms. Table S1 regroups the crystallographic and refinement details for the reported structures.

For **L1[Pd]L2** diffraction data were truncated beyond 0.96Å during data integration, to maintain a significant I/s ratio for the outer resolution shell. Some rigid bond restrains were imposed to prevent atoms from going non-positive defined.

For **CatTIPS** all tested crystals diffracted poorly, the crystal quality is deteriorated by the partial evaporation of solvent molecules. The total cavity size of 1625.9Å^3 (distributed over 8 sites) was treated by the squeeze algorithm (PLATON)[10], locating 249 electrons. The here reported structure diffracted up to 1.42Å, the low data/parameter ratio was increased by distance and angle restraints, mostly on the rather flexible alkyl chains. Given the poor diffraction data and the extensive use of restraints, care must be taken when reviewing individual bonds and angles and only global features such as connectivity, crystal packing or orientation of the functional groups should be considered.

For Cat1 disorder was observed for the alkyl chain containing the double bond as well as for one of the 3 located acetone molecules. Proper distance restraints were set up to correctly model the disorder and allow the refinement to converge. Platon Squeeze, was used to treat 4 small cavities (109Å^3, 31 electrons), possibly containing more severely disordered/partially occupied acetone molecules.

CCDC 1431727-1431729 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures

9. References:

1. T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores and C.-J. Li, *Org. Lett*., 2011, **13**, 442–445.
2. F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson and F. Huang, *Angew. Chem. Int. Ed*., 2010, **49**, 1090 –1094.
3. a) A.-M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin and D. B. Walker, *J. Am. Chem. Soc.*, 2005, **127**, 12612-12619; b) U. Lüning, E. Mak, M. Zindler, B. Hartkopf and R. Herges, *Eur. J. Org. Chem.,* 2010, 4932–4940, c) C. A. Schalley, G. Silva, C. F. Nising and P. Linnart, *Helvetica Chimica Acta*, 2002, **85**, 1578-1596.
4. W. Q. Ong, H. Zhao, Z. Du, J. Z. Y. Yeh, C. Ren, L. Z. W. Tan, K. Zhang, H. Zeng, *Chem. Commun*., 2011,**47**, 6416-6418,
5. R. Shelkov and A. Melman, *Eur. J. Org. Chem*., 2005, 1397–1401.
6. D. A. Leigh, P. J. Lusby, S. J. Teat, A. J. Wilson and J. K.Y. Wong, Angew. Chem., 2001, 113, 1586-1591; Angew. Chem. Int. Ed., 2001, 40, 1538-1543.
7. A. V. Quaethem, P. Lussis, D. A. Leigh, A.-S. Duwez and C.-A. Fustin, Chem. Sci., 2014, 5, 1449-1452.
8. Rigaku Oxford Diffraction, (2014), CrysAlisPro Software system, version 1.171. 37.31, Rigaku Corporation, Oxford, UK
9. Sheldrick, G. M. (2008). Acta Cryst. A64, 112--122.
10. Spek, A. L. (2009). Acta Cryst. D65, 148--155.