

Supporting Information

Covalent Stabilization: A Sturdy Molecular Square from Reversible Metal–Ion Directed Self–Assembly

Alexandre G. L. Olive,[†] Kamil Parkan,[†] Cecile Givélet[†] and Josef Michl^{†,‡,*}

[†] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309–0215, U.S.A.

[‡] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

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Cis-Trans Isomerism on Pt:

Cis-(PR₃)₂PtX₂ complexes tend to isomerize to the thermodynamically favored *trans*-(PR₃)₂PtX₂ form (R = short alkyl, X = halogen) in non-polar solutions¹ and in the solid state.² The transformation can be induced photochemically³ or thermally.⁴ The coupling of this type of complex with an alkyne in the presence of CuI and Et₂NH generally leads to *trans*-(PR₃)₂PtX(C₂R') and *trans*-(PR₃)₂Pt(C₂R')₂ (R' = alkyl, aryl)⁵, but the alkynyl group may also prefer to bind *trans* to a phosphine.⁶

From the mode of synthesis, we would expect *cis*-**1** (X = I, NO₃) to form initially. Its ³¹P NMR spectrum is expected to display two doublets, each with two satellites due to coupling to Pt, with J_{Pt} ≈ 3200 Hz for the P atom *trans* and J_{Pt} ≈ 1600 Hz for the P atom *cis* to the alkynyl unit. We observe one singlet with two satellites (X = I: J_{Pt} = 2332.3 Hz; X = NO₃: J_{Pt} = 2324.7 Hz). This can be ascribed to a rapid intramolecular exchange of the phosphine ligands, which averages the two coupling constants. The ³¹P NMR spectrum of *trans*-**1** should show a single peak with two Pt satellites. Similar *trans*-(PEt₃)₂PtX(C₂R') compounds have a J_{Pt} constant of about 1800 Hz,⁷ distinct from what we observe, and it thus appears likely that the *cis* to *trans* isomerization has not taken place in the preparation of **1**.

In the case of **4y** (J_{Pt} = 2303.6 Hz), the situation is similar except that a polar solvent (CH₃NO₂) is used and the *cis* form should actually be favored.⁶ A singlet is observed, presumably again because of rapid exchange. For **5** a singlet is expected and the coupling constant, J_{Pt} = 2373.3 Hz, is consistent with those found for similar *cis*-bisalkynyl platinum compounds.^{8,9,10,11} For this type of structure, the Pt atom can also adopt a pseudo-tetrahedral conformation (J_{Pt} ≈ 2300 Hz).¹²

Methods and Materials:

Experimental Details

4,4'-Diethynylbiphenyl (**5**),^{13,14} *cis*-(PEt₃)₂PtI₂,¹⁵ and 1,2-di(pyridin-4-yl)ethyne (**2a**)¹⁶ were synthesized according to literature procedures. The starting materials were purchased from Aldrich and used as received. Diethylamine and dichloromethane were distilled over CaH₂. Deuterated solvents were used as received from Cambridge Isotope Laboratories. IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrophotometer. UV-vis spectra were recorded with a Varian Cary 6000i spectrophotometer. NMR spectra were recorded with an Inova 400 spectrometer or a Bruker AV-III 300 and all chemical shifts are given in ppm. For all "X" nuclei absolute indirect chemical shift referencing is applied.¹⁷ A Dbppste (DOSY Bipolar Pulse Pair Stimulated Echo) pulse sequence¹⁸ was used for the diffusion experiments. Mass spectra were obtained with a Hewlett Packard 5989B mass spectrometer.

Bis(pyridine)bis(triethylphosphine)platinum(II) Ditriflate. To a solution of *cis*-(PEt₃)₂Pt(OTf)₂ (0.421 g, 0.58 mmol) in CH₂Cl₂ (20 mL) was added dropwise 0.114 g (1.44 mmol) of anhydrous pyridine. The reaction mixture was stirred at room temperature over 1 h. Then 100 mL of diethylether were added, leading to the formation of a white precipitate. The pure product was collected by vacuum filtration (0.46 g, 87%). Mp 264 °C (dec). ¹H NMR (300 MHz, CD₂Cl₂) δ 9.29

(m, 4H, PyH_α), 7.90 (m, 2H, PyH_γ), 7.61 (t, *J* = 6.8 Hz, 4H, PyH_β), 1.80 (m, 12H, PCH₂CH₃), 1.31 (m, 18H, PCH₂CH₃). ³¹P NMR (162 MHz, CD₂Cl₂) δ -3.75 (s, *J*_{Pt-P} = 3110.0 Hz). ¹³C NMR (101 MHz, CD₂Cl₂) δ 151.33, 140.80, 127.94, 15.22 (PCH₂, ¹*J*_{C-P} = 38.5 Hz), 7.52 (PCH₂CH₃, ²*J*_{C-P} = 15.3 Hz). ¹⁹⁵Pt NMR (86 MHz, CD₂Cl₂) δ -4379.52 (*J*_{P-Pt} = 3006.8 Hz). IR (cm⁻¹): 424, 517, 572, 636, 698, 709, 732, 769, 1028, 1076, 1151, 1273, 1389, 1422, 1457, 1611, 2885, 2945, 2978, 3039, 3061, 3083, 3106. UV-Vis (CH₂Cl₂) λ_{max} (ε in L.mol⁻¹.cm⁻¹): 257 nm (5850), 267 nm (shoulder, 2412). HRMS (ESI⁺) calculated for (M - 2OTf): 294.6153, found 294.6141 (Δ = -4.1 ppm). For C₂₄H₄₀F₆N₂O₆P₂PtS₂ (887.73), calculated: 32.47 % C, 4.54 % H; found 32.47 % C, 4.70 % H.

Bis(trimethylsilylethynyl)bis(triethylphosphine)platinum(II). To a dichloromethane (10 mL) solution of bis(pyridine)bis(triethylphosphine)platinum ditriflate (0.222 g, 0.25 mmol), copper iodide (6 mg), and diethylamine (2 mL) was added dropwise 88 μL of trimethylsilylacetylene (61.3 mg, 0.63 mmol, 2.5 equiv.). The reaction mixture was stirred at room temperature for 12 h. The solvent was then removed by rotatory evaporation. The solids were suspended in water (25 mL) and extracted with CH₂Cl₂ (3 × 25 mL). The organic layers were recombined, dried over anhydrous MgSO₄, and evaporated. Chromatographic separation through silica gel using hexanes/THF (96/4) as eluent afforded the pure product (0.12 g, 78%). Mp 193 °C (dec). ¹H NMR (300 MHz, CD₂Cl₂) δ 1.95 (m, 6H, PCH₂CH₃), 1.06 (m, 9H, PCH₂CH₃), 0.14 – 0.03 (m, 9H, SiMe₃). ³¹P NMR (122 MHz, CD₂Cl₂) δ 4.26 (s, *J*_{Pt-P} = 2191.6 Hz). ¹³C NMR (75 MHz, CD₂Cl₂) δ 126.73 (m, ¹*J*_{Pt-C} = 131.2 Hz, ²*J*_{P-C} = 20.8 Hz, PtC), 109.08 (m, ²*J*_{Pt-C} = 26.09 Hz, PtCC), 16.88 (m, PCH₂), 8.17 (m, PCH₂CH₃), 0.52 (s, SiMe₃). ¹⁹⁵Pt NMR (64 MHz, CD₂Cl₂) δ -4776.46 (s, *J*_{P-Pt} = 2202.8 Hz). IR (cm⁻¹): 425, 463, 638, 688, 726, 754, 772, 834, 859, 1037, 1241, 1380, 1413, 1456, 2043, 2058, 2878, 2963. UV-Vis (CH₂Cl₂) λ_{max} (ε in L.mol⁻¹.cm⁻¹): 255 nm (12800), 291 nm (8750). HRMS (ESI⁺) calculated for M-Na⁺: 648.2310 found: 648.2294 (Δ = -2.5 ppm). For C₂₂H₄₈P₂PtSi₂•CHCl₃ (745.19): calculated: 37.08 % C, 6.63 % H; found: 37.48 % C, 6.94 % H.

Biphenyl-4,4'-diethynylbis[bis(triethylphosphine)iodoplatinum] (1, X = I). Diethylamine (5.85 mL, 0.056 mol) was added to a solution of **5** (0.190 g, 0.94 mmol), Pt(PEt₃)₂I₂ (1.42 g, 2.1 mmol), and CuI (0.044 g, 0.23 mmol) in CH₂Cl₂ (100 mL) under an atmosphere of Ar. The mixture was stirred in the dark at room temperature for 12 h, the solvent was removed under reduced pressure, and the remaining solids were partitioned between CH₂Cl₂ (200 mL) and water (200 mL). The aqueous layer was extracted twice more with CH₂Cl₂ (200 mL), the organic layers were recombined, dried with anhydrous MgSO₄, and the solvent was removed under reduced pressure. Flash chromatography of the resulting solids on silica gel with hexanes/THF (8/1) as eluent afforded white crystals of **1** (X = I, 0.71g, 57%). Further purification of this light-sensitive compound can be achieved by dissolution in a minimum amount of CH₂Cl₂ and addition of CH₃OH. Mp 183 °C (dec). ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.5 Hz, 4H, biphenyl), 7.33 (d, *J* = 8.4 Hz, 4H, biphenyl), 2.30 – 2.16 (m, 24H, PCH₂CH₃), 1.23 – 1.12 (m, 36H, PCH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 137.76, 131.27, 127.71, 126.40 (phe), 100.16 (PtC, ¹*J*_{C-Pt} = 399.6 Hz), 91.23 (Cphe, ²*J*_{C-Pt} = 31.6 Hz), 16.78 (PCH₂, ¹*J*_{C-P} = 36.6 Hz), 8.28 (PCH₂CH₃, ²*J*_{C-P} = 19.6 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 8.46 (s, *J*_{Pt-P} = 2324.7 Hz). ¹⁹⁵Pt NMR (86 MHz, CDCl₃) δ -4849.16 (*J*_{P-Pt} = 2332.3 Hz). IR (cm⁻¹) 2964, 2124, 1602, 1484, 1168, 1037, 985, 773, 627. UV-Vis (CH₂Cl₂) λ_{max} (ε in L.mol⁻¹.cm⁻¹): 310 (10 400), 268 (30 400). HRMS (ESI⁺) calculated for MCs⁺: 1449.0701 found 1449.0693 (Δ = -0.5 ppm). For C₄₀H₆₈I₂P₄Pt₂ (1316.8) Calculated : 36.48 % C, 5.20 % H; found 36.54 %C, 5.28 % H.

Biphenyl-4,4'-diethynylbis[bis(triethylphosphine)nitratoplatinum] (1, X = NO₃). To a stirred solution of **1** (1.33 g, 1.01 mmol) in CH₂Cl₂ (100 mL) at room temperature was added silver nitrate (0.343 g, 2.02 mmol), all at once. The reaction mixture was stirred in the absence of light at room temperature. After 10 h pentane (50 mL) was added, and the reaction mixture was stirred for 10 min. The resultant gray precipitate of AgI was removed by filtration under reduced pressure, and the filtrate was concentrated to 20 mL. The white solid was precipitated by addition of diethyl ether (50 mL) and collected by filtration under reduced pressure. Yield (0.93 g, 78%). Mp 201 °C (dec). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.48 (d, *J* = 8.2 Hz, 4H, biphenyl), 7.33 (d, *J* = 8.0 Hz, 4H, biphenyl), 2.07 – 1.91 (m, 24H, PCH₂CH₃), 1.31 – 1.17 (m, 36H, PCH₂CH₃). ³¹P NMR (162 MHz, CD₂Cl₂) δ 20.11 (s, *J*_{Pt-P} = 2324.7 Hz). ¹³C NMR (101 MHz, CD₂Cl₂) δ 137.99, 131.55, 127.22, 126.42 (phe), 103.38 (PtC, ¹*J*_{C-Pt} = 425.2 Hz), 68.51 (Cphe, ²*J*_{C-Pt} = 30.1 Hz), 14.62 (PCH₂, ¹*J*_{C-P} = 33.9 Hz), 7.82 (PCH₂CH₃, ²*J*_{C-P} = 19.0 Hz). ¹⁹⁵Pt NMR (86.02 MHz, CD₂Cl₂) –4235.23 (*J*_{P-Pt} = 2488.6 Hz). MS (ESI⁺) calculated 1189.36 (MH⁺), found 1189.1 (MH⁺). UV-Vis (CH₂Cl₂) λ_{max} (ε in L.mol⁻¹.cm⁻¹), 340 nm (40400). IR (cm⁻¹) 2964, 2124, 1484, 1380, 1257, 1168, 1037, 820, 773, 627. For C₄₀H₆₈N₂O₆P₄Pt₂•H₂O (1205.0) Calculated : 39.87 % C, 5.86 % H; Found 40.09 % C, 5.79% H.

Biphenyl-4,4'-diethynylbis[bis(triethylphosphine)hexynylplatinum] (7). To a stirred solution of **1** (0.107 g, 0.09 mmol) in CH₂Cl₂ (3 mL) at room temperature, under an inert atmosphere of Ar, was added pyridine (0.014 g, 0.18 mmol), all at once. After 10 min, diethylamine (1.0 mL, 0.01 mol) was added, along with hexyne (14 mg, 0.18 mmol), and CuI (0.010 g). The mixture was stirred in the dark at room temperature for 48 h, the solvent was removed under reduced pressure, and the remaining solids were partitioned between CH₂Cl₂ (20 mL) and water (20 mL). The aqueous layer was extracted with CH₂Cl₂ (2×20 mL) and the organic layers were recombined, dried with anhydrous MgSO₄, and the solvent was removed under reduced pressure. Flash chromatography of the resulting solids on silica gel with hexanes/THF (9/1) as eluent afforded white crystals of **7** (0.049 g, 45%). Mp 287 °C (dec). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.49 – 7.43 (d, 4H, *J* = 8.2 Hz, biphenyl), 7.33 – 7.27 (d, 4H, *J* = 8.2 Hz, biphenyl), 2.28 (m, 4H, C₂-CH₂-CH₂-CH₂-CH₃), 2.23 – 2.04 (m, 24H, PCH₂CH₃), 1.53 – 1.40 (m, 8H, C₂-CH₂-CH₂-CH₂-CH₃), 1.29 – 1.13 (m, 36H, PCH₂CH₃), 0.99 – 0.89 (m, 6H, C₂-CH₂-CH₂-CH₂-CH₃). ³¹P NMR (162 MHz, CD₂Cl₂) δ 11.15 (s, *J*_{Pt-P} = 2392.65 Hz). ¹³C NMR (75 MHz, CD₂Cl₂) δ 137.00, 131.01, 128.04, 126.02, 108.24, 107.87, 90.89, 32.73, 22.14, 21.19, 16.23 (¹*J*_{C-P} = 35.6 Hz), 13.53, 8.06 (²*J*_{C-P} = 23.3 Hz). ¹⁹⁵Pt NMR (86.02 MHz, CD₂Cl₂) –4770.49 (*J*_{P-Pt} = 2413.01 Hz). IR (cm⁻¹) 413, 525, 637, 733, 768, 823, 1007, 1037, 1105, 1174, 1212, 1252, 1320, 1375, 1409, 1454, 1488, 1599, 2094, 2827, 2874, 2930, 2961. UV-Vis (CH₂Cl₂) λ_{max} (ε in L.mol⁻¹.cm⁻¹): 357 nm (90000). HRMS (ESI⁺) calculated for M(Ag⁺)₂: 720.1538, found: 720.1509 (Δ = –4.0 ppm). For C₅₂H₈₆P₄Pt₂•3H₂O: 48.82 % C, 7.25 % H; found: 49.30 % C, 7.47 % H.

1,4-Bis(4-pyridyl)butadiyne (2c) was prepared via a modified literature procedure.¹⁹ Oxygen was bubbled through a deep green solution of CuCl (0.046 g, 0.4 mmol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 0.56 mL, 3.7 mmol) in CH₃CN (40 mL) and 4-ethynylpyridine hydrochloride (0.257 g, 1.8 mmol) were added. Immediately after the addition, the color of the solution turned brown. In the course of 3 h at room temperature, an abundant precipitate formed. This crude product was filtered off, washed with ether, and purified by flash chromatography column packed with silica gel and eluted with (hexane:ethyl acetate, 1:2). Pure **2c** was obtained as white crystalline powder (0.33 g, 90%). This compound is light sensitive. ¹H NMR (300 MHz, CDCl₃)

δ 8.66 (dd, $J = 4.4, 1.6$ Hz, 2H, α -Npyr), 7.40 (dd, $J = 4.4, 1.6$ Hz, 2H, β -Npyr).

General Procedure for the Formation of the Self-Assembled Rectangles 4a-4c. To a room temperature suspension of **1** ($X = \text{NO}_3$) in CH_2Cl_2 (10 mL/mmol) was added **2y** (1 eq.). Immediately after the addition the solution turned yellow. After 10 min diethyl ether was added ($5\times$ the volume of CH_2Cl_2) resulting in the formation of a yellow precipitate that was collected, washed with diethyl ether, and dried under reduced pressure to yield the desired compound quantitatively.

Molecular Rectangle 4a. **1** ($X = \text{NO}_3$) (38.0 mg, 0.032 mmol) and **2a** (5.0 mg, 0.032 mmol) afforded 40.0 mg of **4a** (93 %). Mp 145 °C (dec). ^1H NMR (300 MHz, CD_3NO_2) δ 8.92 (m, 8H, α -Npyr), 7.91 (m, 8H, β -Npyr), 7.62 (d, $J = 7.6$ Hz, 8H, biphenyl), 7.43 (d, $J = 7.6$ Hz, 8H, biphenyl), 1.96 (m, 48H, PCH_2CH_3), 1.28 (m, 72H, PCH_2CH_3). ^{31}P NMR (162 MHz, CD_3NO_2) δ 16.74 (s, $J_{\text{Pt-P}} = 2307.8$ Hz). ^{13}C NMR (75 MHz, CD_3NO_2) δ 154.34, 153.97, 147.20, 139.24, 132.38, 127.41, 126.67, 14.86 ($^1J_{\text{C-P}} = 35.5$ Hz), 7.88 ($^2J_{\text{C-P}} = 23.3$ Hz). ^{195}Pt NMR (86.02 MHz, CD_3NO_2) δ -4359.06 ($J_{\text{P-Pt}} = 2301.98$ Hz). IR (cm^{-1}): 3094, 3025, 2965, 2936, 2911, 2876, 2122, 1610, 1485, 1454, 1416, 1384, 1275, 1213, 1183, 1106, 1035, 821, 767, 732, 630, 508. UV-Vis (CH_2Cl_2) λ_{max} (ϵ in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 340 nm (91000). HRMS (ESI^+) calculated for $\text{M}^{4+} \text{NO}_3^-$: 833.2799, found: 833.2757 ($\Delta = -5.0$ ppm). For $\text{C}_{100}\text{H}_{152}\text{N}_8\text{O}_{12}\text{P}_8\text{Pt}_4$ (2686.43): 44.71 % C, 5.70 % H; found 45.11 % C, 5.92 % H.

Molecular Rectangle 4b. **1** ($X = \text{NO}_3$) (32.0 mg, 0.027 mmol) and **2b** (4.9 mg, 0.027 mmol) afforded 35.2 mg of **4b** (95 %). Mp 142 °C (dec). ^1H NMR (300 MHz, CD_3NO_2) δ 8.90 (m, 8H, α -Npyr), 7.89 (m, 8H, β -Npyr), 7.60 (d, $J = 7.5$ Hz, 8H, biphenyl), 7.42 (d, $J = 7.5$ Hz, 8H, biphenyl), 1.96 (m, 48H, PCH_2CH_3), 1.24 (m, 72H, PCH_2CH_3). ^{31}P NMR (162 MHz, CD_3NO_2) δ 18.66 (s, $J_{\text{Pt-P}} = 2294.4$ Hz). ^{13}C NMR (75 MHz, CD_3NO_2) δ 155.65, 134.32, 132.71, 129.34, 16.81 ($^1J_{\text{C-P}} = 34.2$ Hz), 9.78 ($^2J_{\text{C-P}} = 19.8$ Hz). ^{195}Pt NMR (86.02 MHz, CD_3NO_2) δ -4352.02 (d, $J_{\text{P-Pt}} = 2397.2$ Hz). IR (cm^{-1}): 3092, 3023, 2967, 2933, 2907, 2875, 2120, 1609, 1489, 1460, 1384, 1206, 1035, 824, 767, 734, 559. UV-Vis (CH_2Cl_2) λ_{max} (ϵ in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 340 nm (84000). HRMS (ESI^+) calculated for $\text{M}^{4+} \text{NO}_3^-$: 849.2700 found: 849.2655 ($\Delta = -5.3$ ppm). For $\text{C}_{104}\text{H}_{152}\text{N}_8\text{O}_{12}\text{P}_8\text{Pt}_4\cdot 5\text{H}_2\text{O}$ (2734.47): 44.22 % C, 5.78 % H; found 44.30 % C, 6.18 % H.

Molecular Rectangle 4c. **1** ($X = \text{NO}_3$) (143.2 mg, 0.120 mmol) and **2c** (24.6 mg, 0.120 mmol) afforded 155.1 mg of **4c** (92 %). Mp 138 °C (dec). ^1H NMR (400 MHz, CD_3NO_2) δ 8.86 (m, 8H, α -Npyr), 7.83 (m, 8H, β -Npyr), 7.60 (d, $J = 8.8$ Hz, 8H, biphenyl), 7.42 (d, $J = 8.2$ Hz, 8H, biphenyl), 2.06 (m, 48H, PCH_2), 1.39 – 1.03 (m, 72H, PCH_2CH_3). ^{31}P NMR (162 MHz, CD_3NO_2) δ 15.69 (s, $J_{\text{Pt-P}} = 2303.6$ Hz). ^{13}C NMR (101 MHz, CD_3NO_2) δ 152.81, 131.60, 130.43, 126.64, 14.05 ($^1J_{\text{C-P}} = 33.7$ Hz), 7.06 ($^2J_{\text{C-P}} = 19.1$ Hz). ^{195}Pt NMR (86 MHz, CD_3NO_2) δ -4354.59 (d, $J_{\text{P-Pt}} = 2346.1$ Hz). IR (cm^{-1}): 3091, 3024, 2962, 2934, 2912, 2872, 2119, 1605, 1488, 1454, 1413, 1385, 1336, 1271, 1034, 821, 766, 731. UV-Vis (CH_2Cl_2) λ_{max} (ϵ in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 340 nm (86000). HRMS (ESI^+) calculated for $\text{M}^{4+} \text{NO}_3^-$: 865.2794, found 865.2748 ($\Delta = -5.3$ ppm). For $\text{C}_{108}\text{H}_{152}\text{N}_8\text{O}_{12}\text{P}_8\text{Pt}_4\cdot \text{CH}_2\text{Cl}_2$ (2867.5): Calculated: 45.66 % C, 5.41 % H; Found 45.42 % C, 5.50 % H.

Molecular Square 5. Diethylamine (63 μL , 0.61 mmol) was added to a solution of **4c**, (0.088g, 0.032 mmol), 4,4'-diethynylbiphenyl (0.013 g, 0.064 mmol), and CuI (0.60 mg, 0.003 mmol, 5 mol%) in a $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$ mixture (1:1, 10 mL) at -25 °C, in absence of light. The reaction mixture was kept cold during 30 min, and then warmed up slowly to 25 °C, at which temperature the reaction was complete after additional 3 h. Over this time, the yellow suspension gradually turned red and a precipitate formed. The precipitate was filtered and washed with water (3×15 mL),

acetone (10 mL) and diethyl ether (3×15 mL). The product was chromatographed on silica gel with a $\text{CH}_2\text{Cl}_2/\text{THF}$ (3:2) mixture as eluent. It can be purified further by dissolution in CH_2Cl_2 and addition of diethyl ether to form a yellow precipitate which is collected (0.050 g, 62%). Mp 315 - 320 °C. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.48 (d, 16H, $J = 8.33$ Hz, pheH), 7.32 (d, 16H, $J = 8.33$ Hz, pheH), 2.21 (m, 48H, PCH_2CH_3), 1.26 (m, 72H, PCH_2CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 137.80, 131.67, 128.35, 126.68, 109.90, 68.53, 30.24 (Pain CH_2 , $^1J_{\text{C-P}} = 34.2$ Hz), 8.61 (PCH_2CH_3 , $^2J_{\text{C-P}} = 23.6$ Hz). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 11.39 (s, $J_{\text{Pt-P}} = 2362$ Hz). ^{195}Pt NMR (86 MHz, CD_2Cl_2) δ -4754.83 ($J_{\text{P-Pt}} = 2373.3$ Hz). IR (cm^{-1}): 3072, 3023, 2962, 2931, 2092, 1600, 1483, 1452, 1412, 1374, 1249, 1212, 1174, 1034, 821, 766, 731, 629, 540, 516. UV-Vis (CH_2Cl_2) λ_{max} (ϵ in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 378 nm (153500). MS (ESI^+) calculated for $(\text{M}-\text{CH}_3\text{CN})^+$: 2567.5, found 2567.8. For $\text{C}_{112}\text{H}_{152}\text{P}_8\text{Pt}_4 \cdot 2\text{CH}_2\text{Cl}_2$ (2694.7) Calculated: 50.78 % C, 5.83 % H; Found 50.92 % C, 5.62 % H.

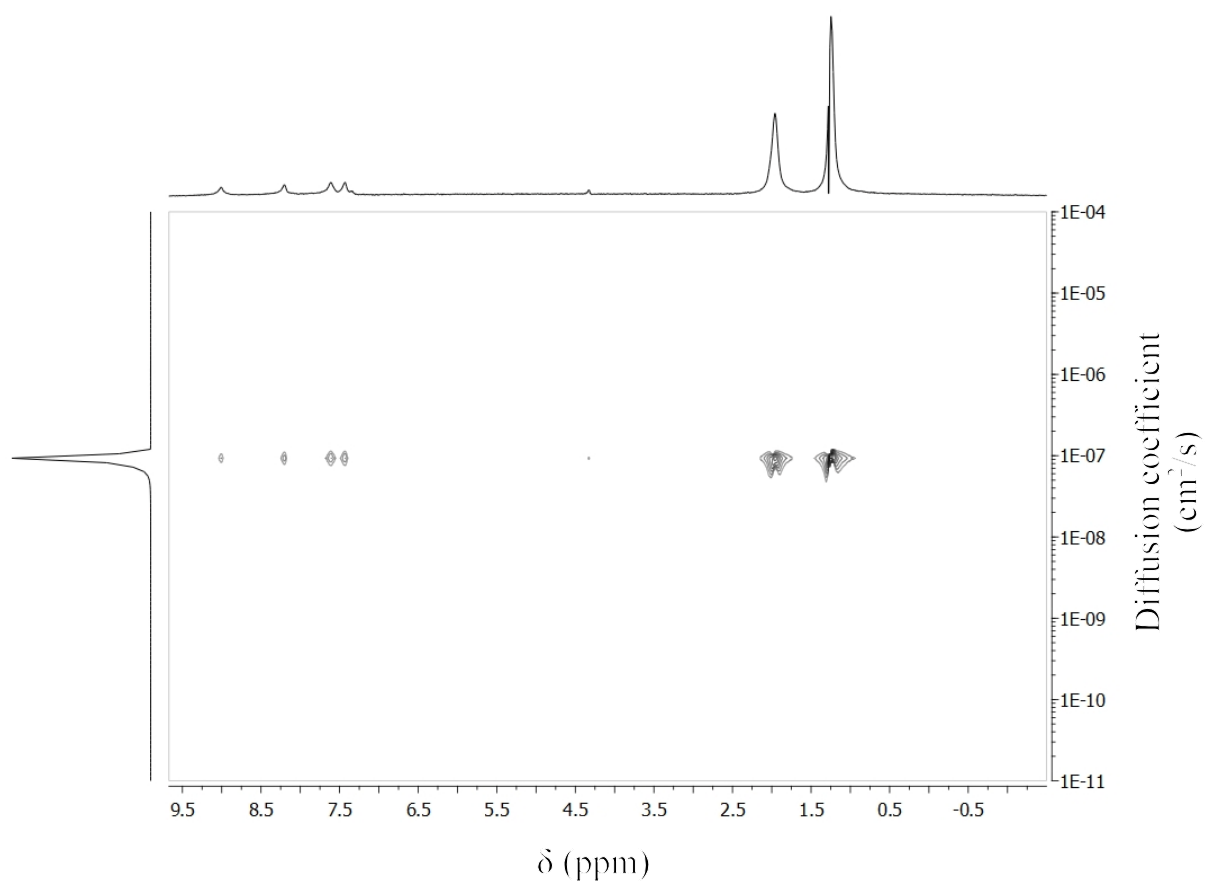


Figure S1a: DOSY-NMR of **4c** at 20°C in CD_3NO_2 (uncalibrated).

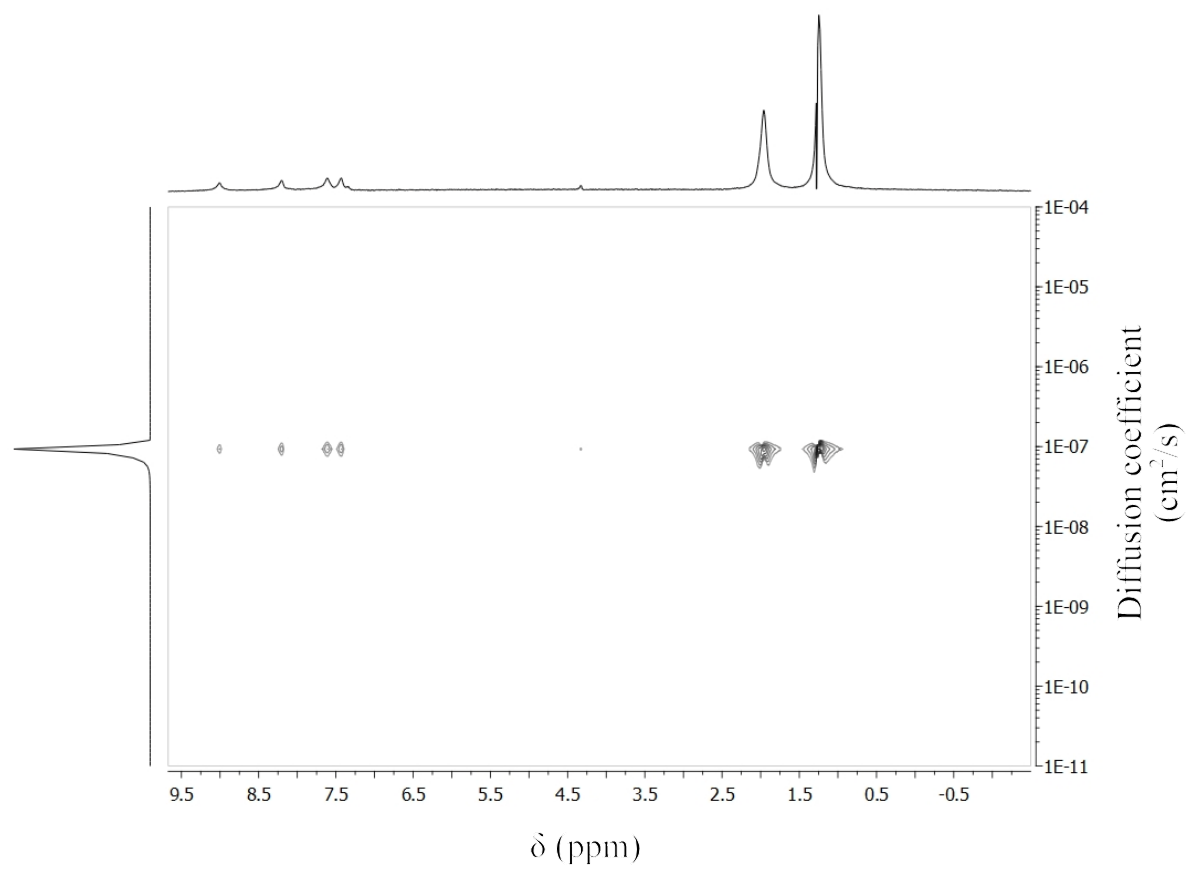


Figure S1b : DOSY-NMR of **4c** at 45°C in CD₃NO₂ (uncalibrated).

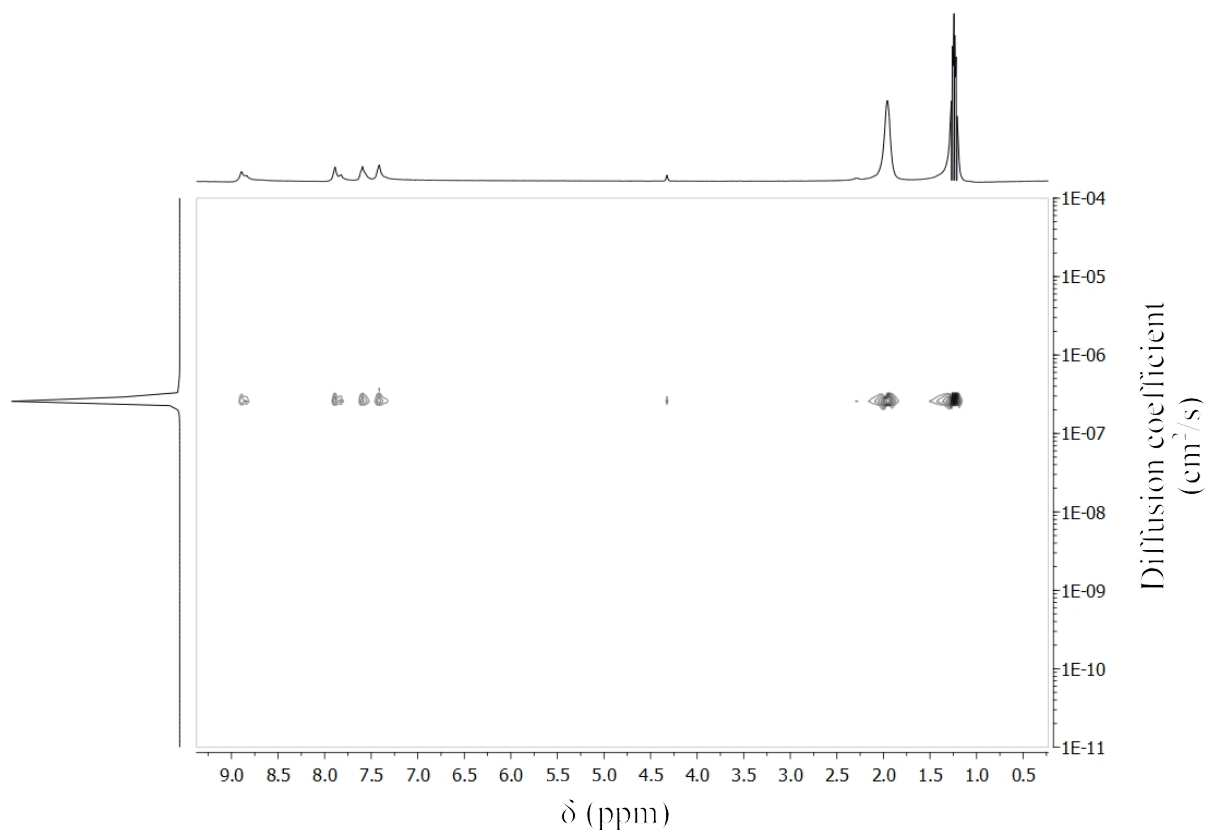


Figure S1c: DOSY-NMR of **4b** at 20°C in CD_3NO_2 (uncalibrated).

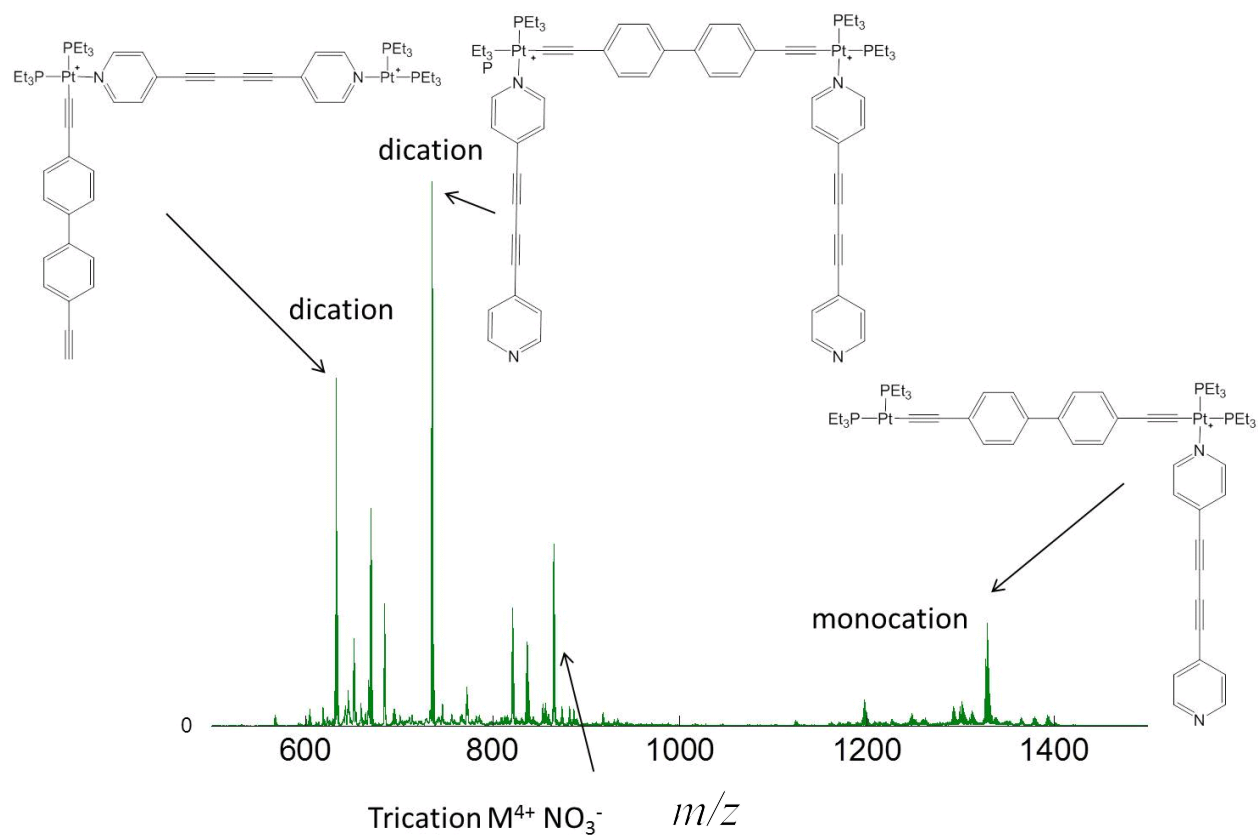


Figure S2 : ESI⁺-MS of **4c** with NO_3^- as counteranion.

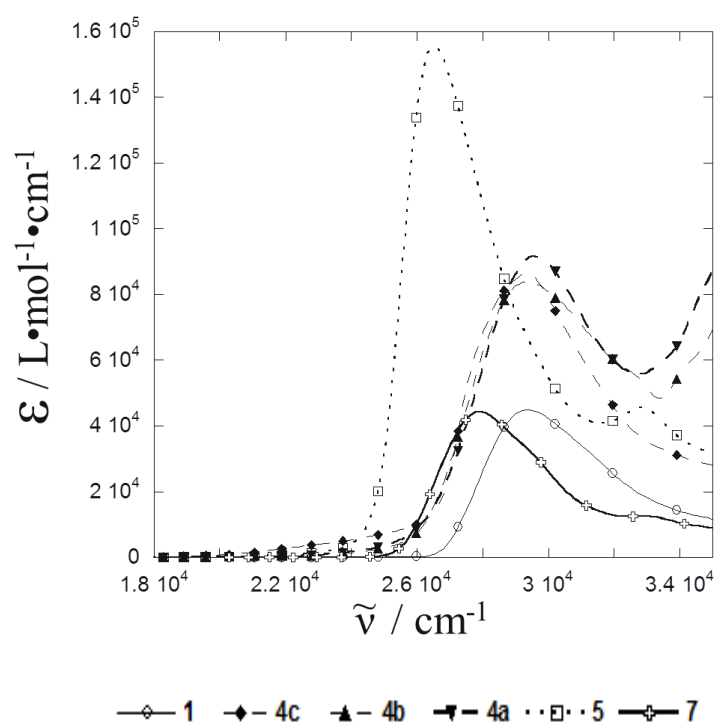


Figure S3: UV-vis absorption spectra in CH_2Cl_2 .

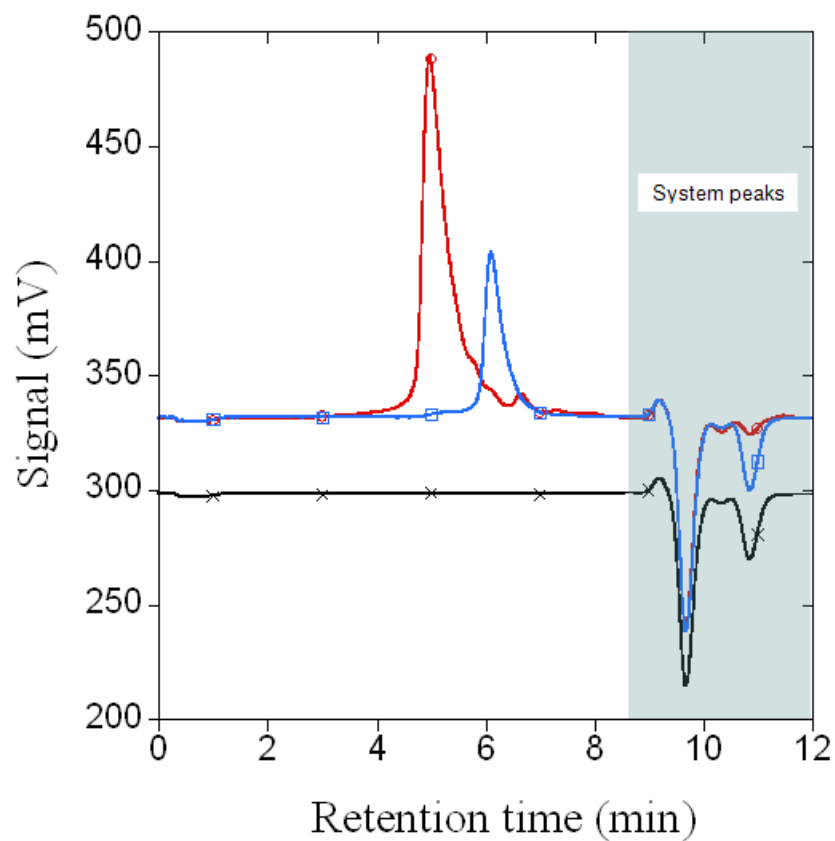


Figure S4: Gel permeation chromatograms in dichloromethane: blue: **5**, retention time 6.12 min (2500 ± 100 g/mol); red: products of an attempt to make **5** by the reaction of **1** ($X = \text{NO}_3$) with **3**, retention times 4.73 - 5.61 min ($6160 - 3845 \pm 100$ g/mol), 5.78 min (3400 ± 100 g/mol), 6.12 min (2500 ± 100 g/mol), 6.66 min (1082 ± 100 g/mol); black: dichloromethane. Calibrated against polystyrene standards.

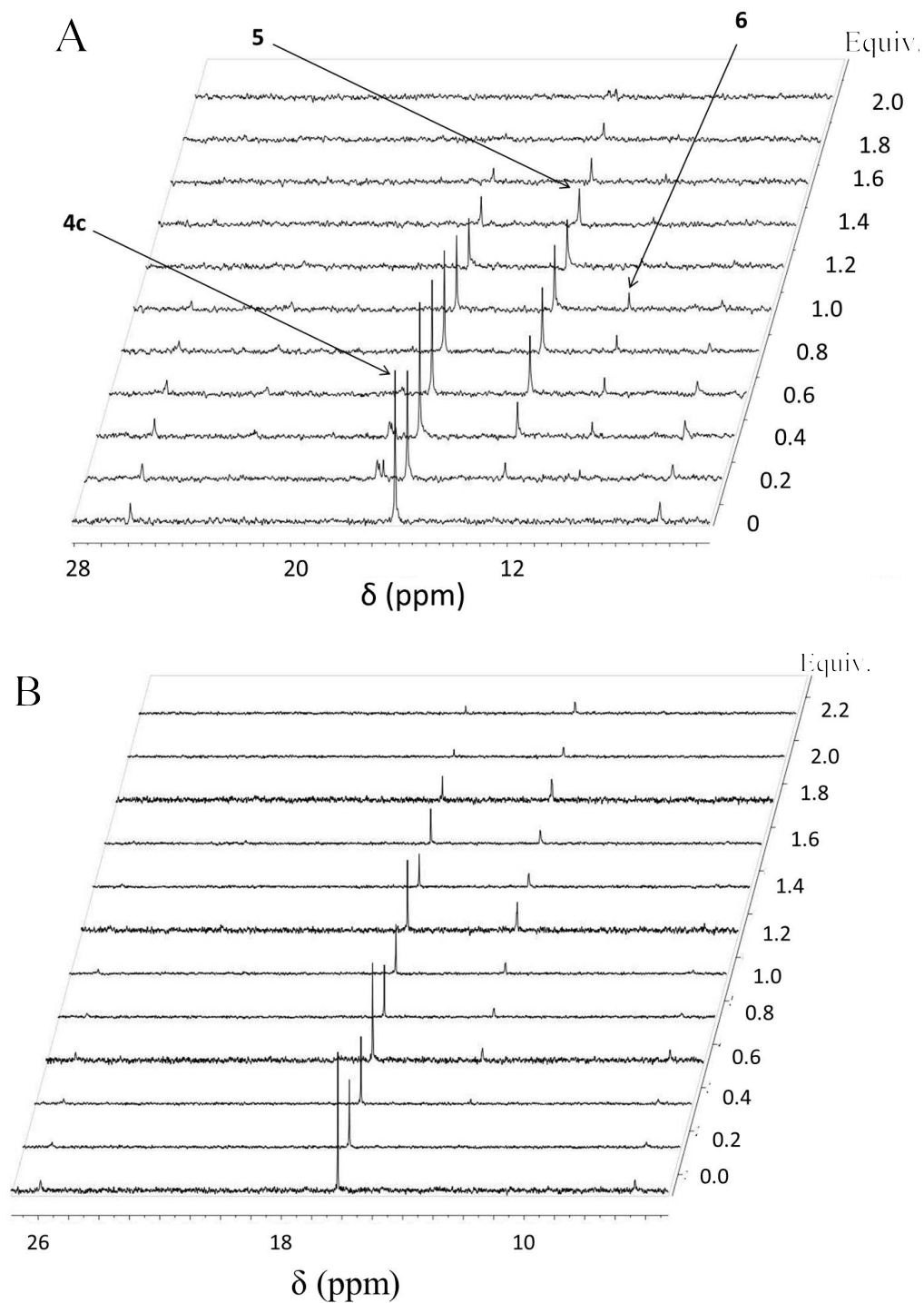


Figure S5: Covalent stabilization monitored by ^{31}P NMR, as a function of the number of equivalents of **3** added. Reaction time: A, 5 min; B, 1 h. The peak for **5** decreases with the number of equivalents because this product gradually precipitates.

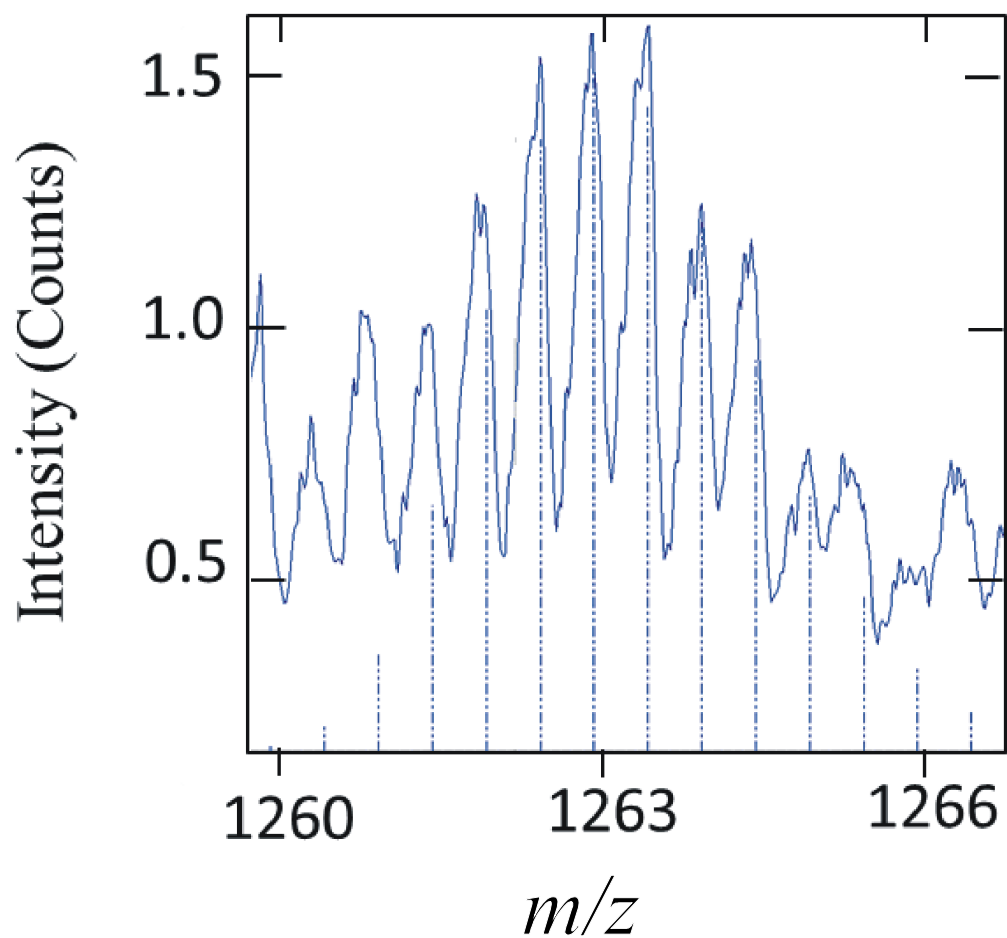
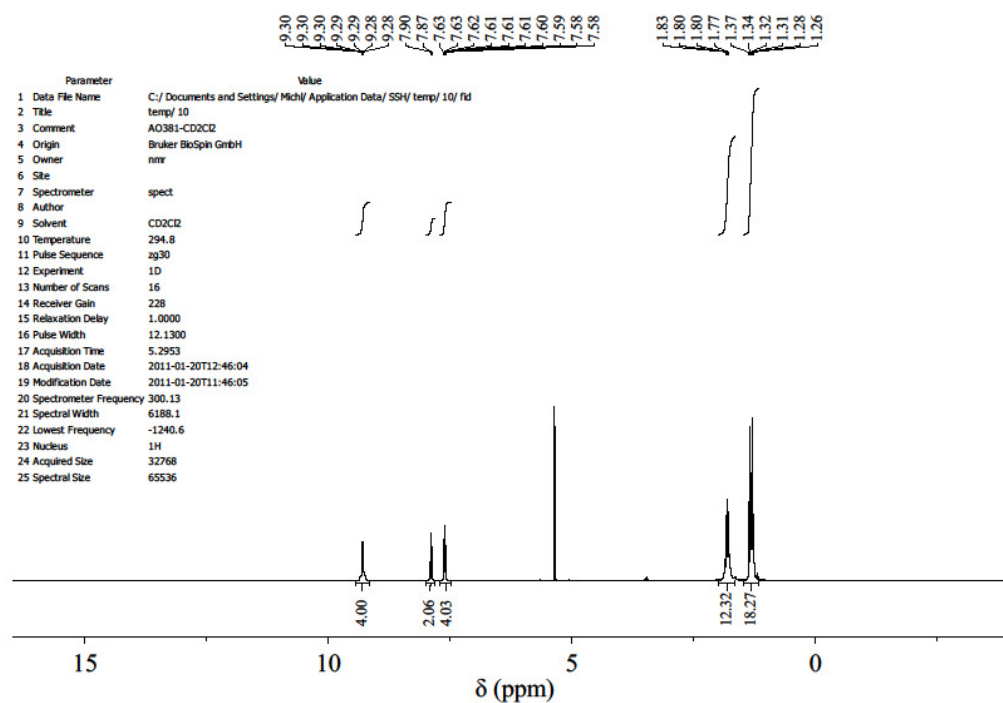
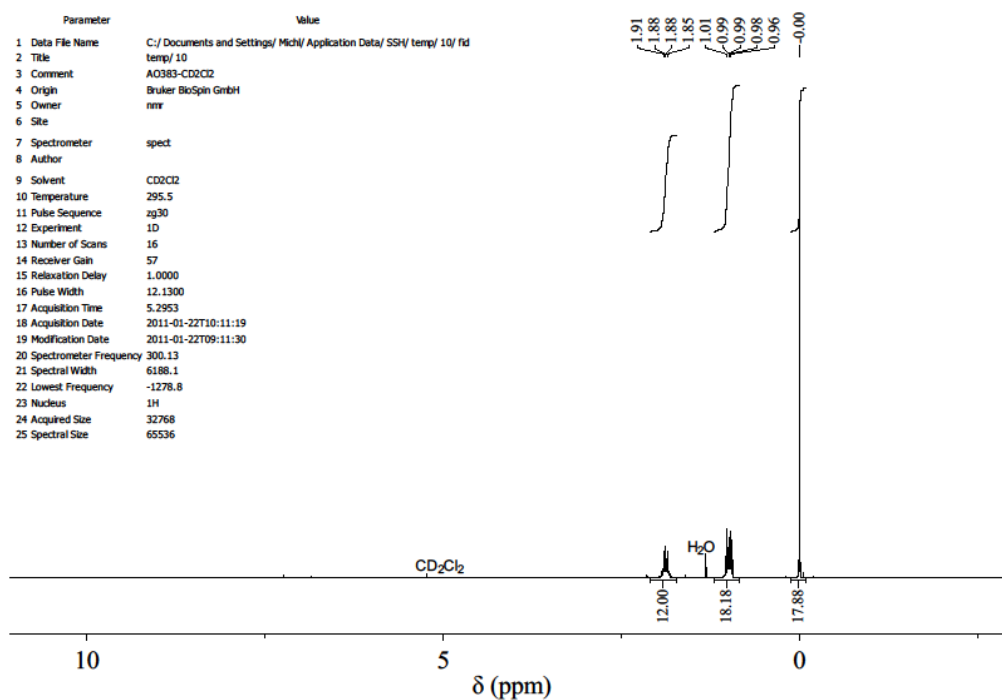


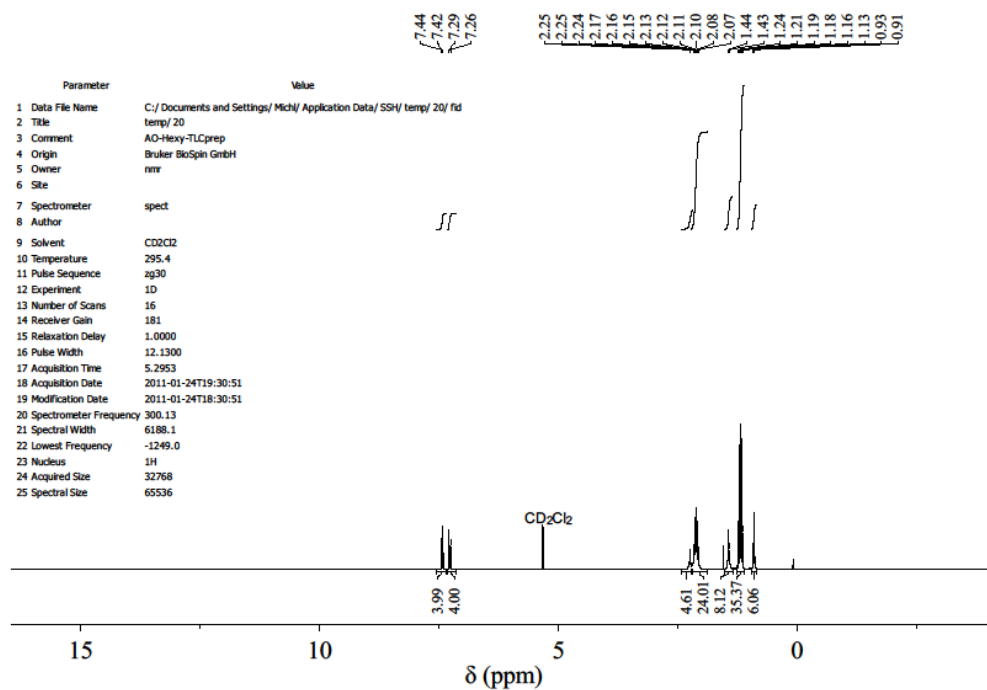
Figure S6: HRMS ESI⁺ mass spectrum of **6** present in a mixture of **4c** with 1 equivalent of **3** in the presence of CuI and Et₂NH in CH₂Cl₂. M^{2+} : calculated 1264.9225; found 1264.9512 ($\Delta = + 27.0$ ppm).



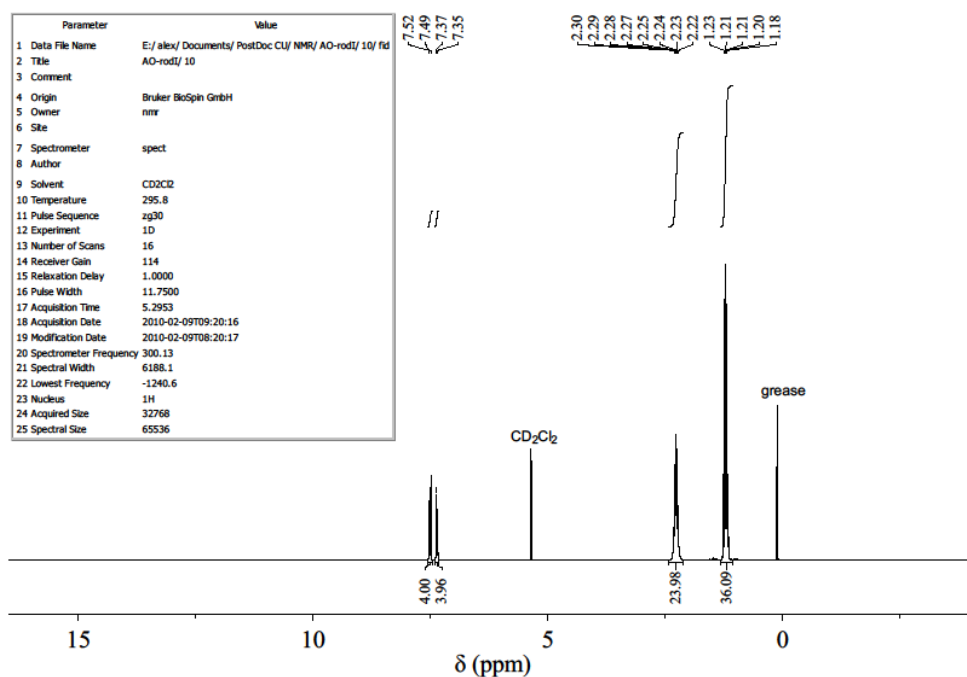
^1H NMR spectra of bis(pyridine)bis(triethylphosphine)platinum(II) ditriflate in CD_2Cl_2 .



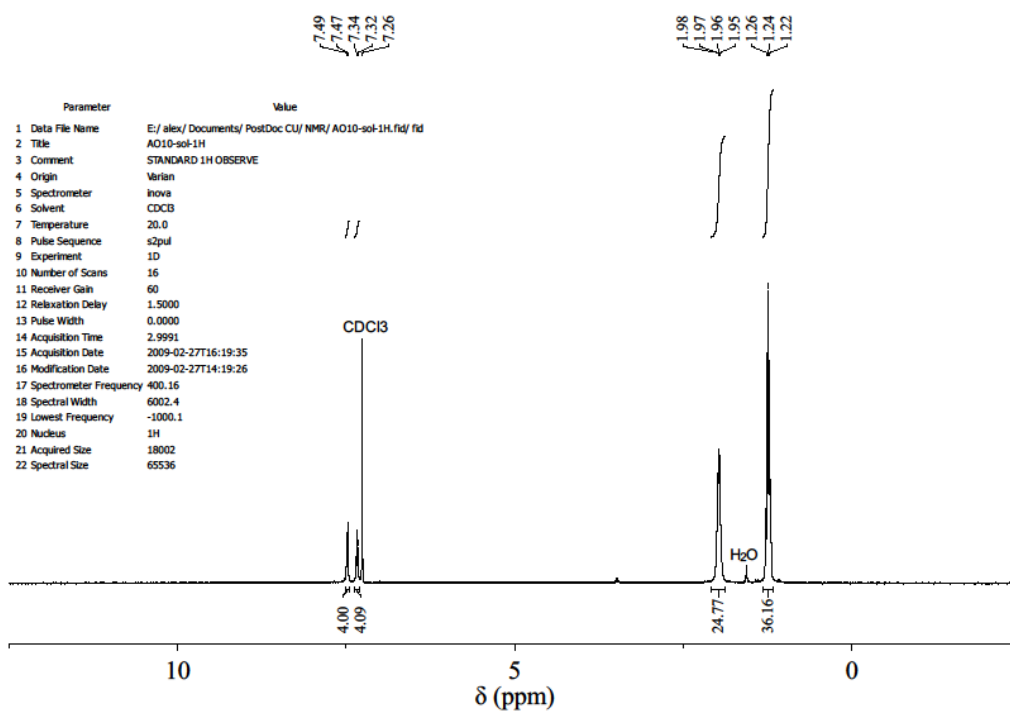
^1H NMR spectra of bis(trimethylsilyl)ethynylbis(triethylphosphine)platinum(II) in CD_2Cl_2 .



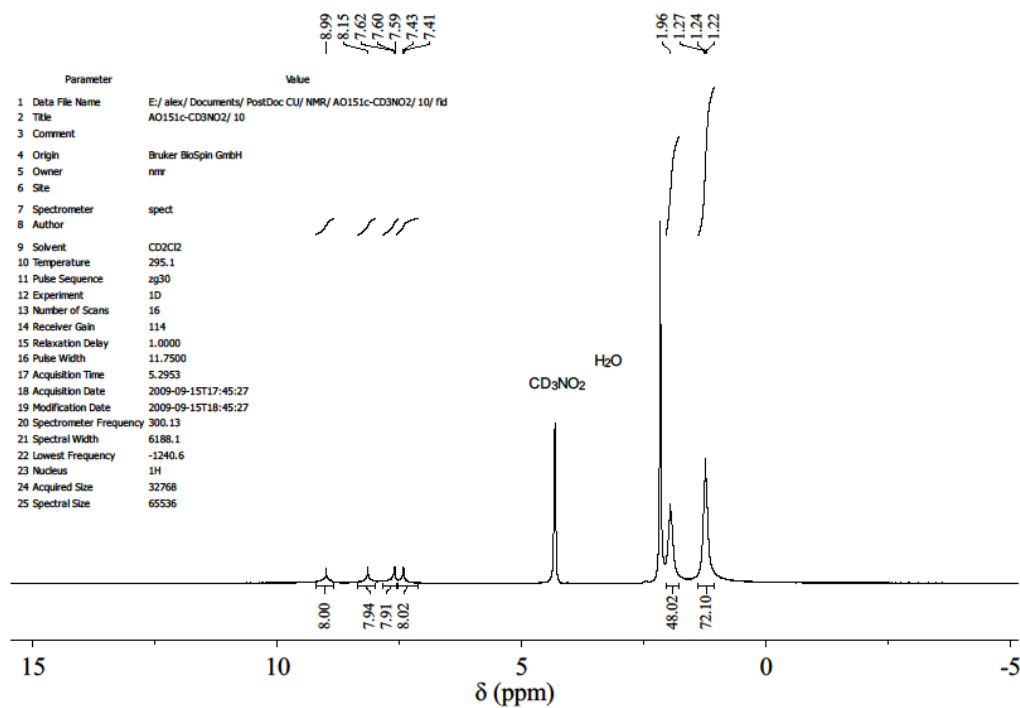
^1H NMR spectra of Biphényl-4,4'-diethynylbis[bis(triethylphosphine)hexynylplatinum] (**7**) in CD_2Cl_2 .



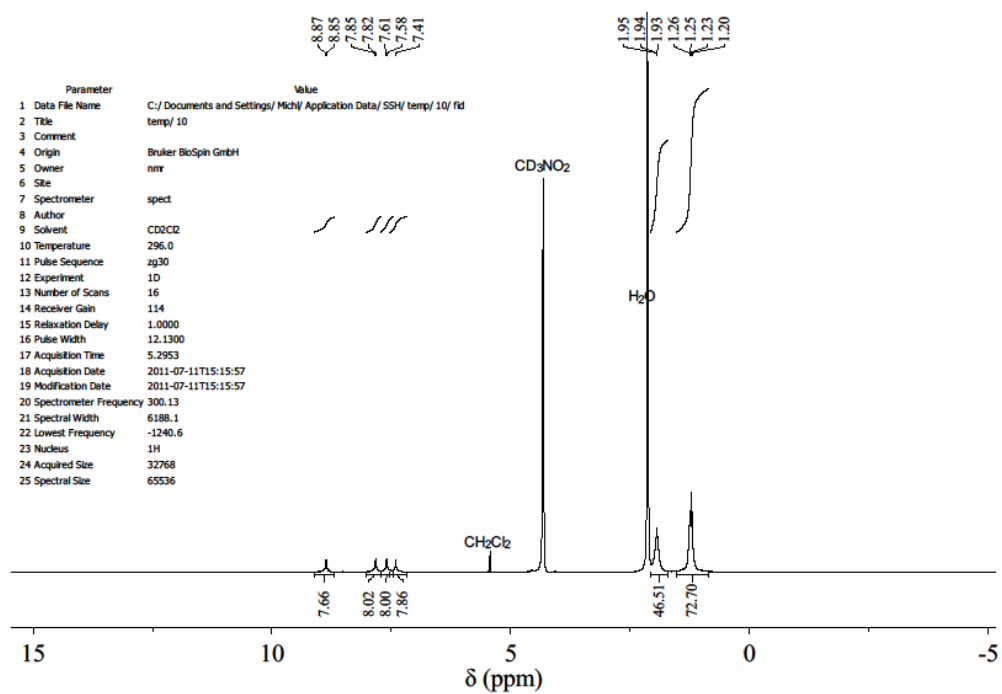
^1H NMR spectra of **1** ($\text{X} = \text{I}$) in CD_2Cl_2 .



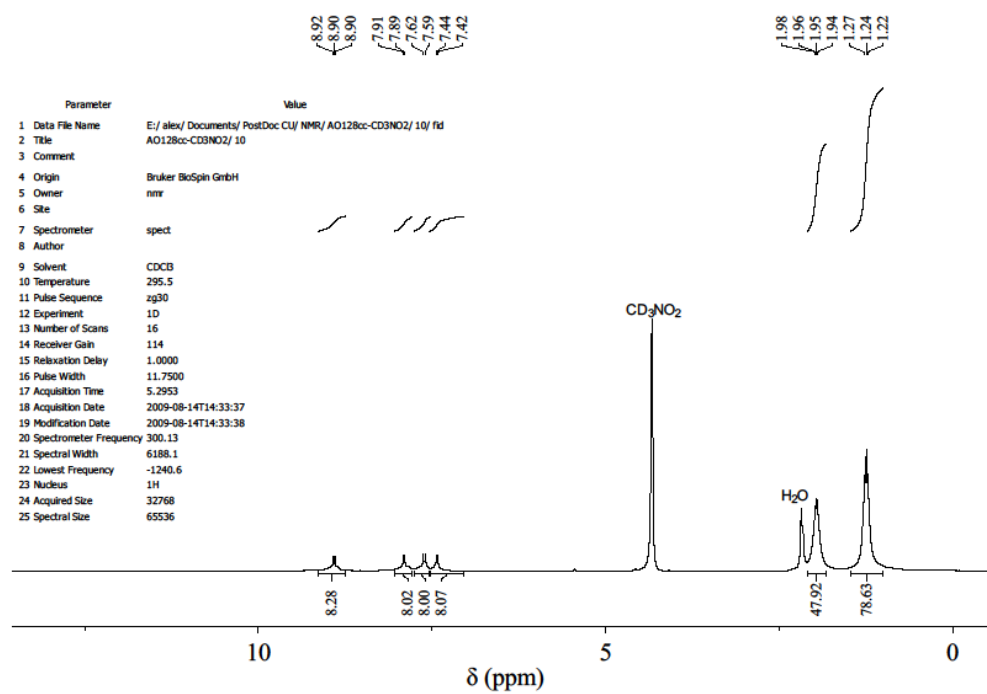
¹H NMR spectra of **1** (X = NO₃) in CDCl₃.



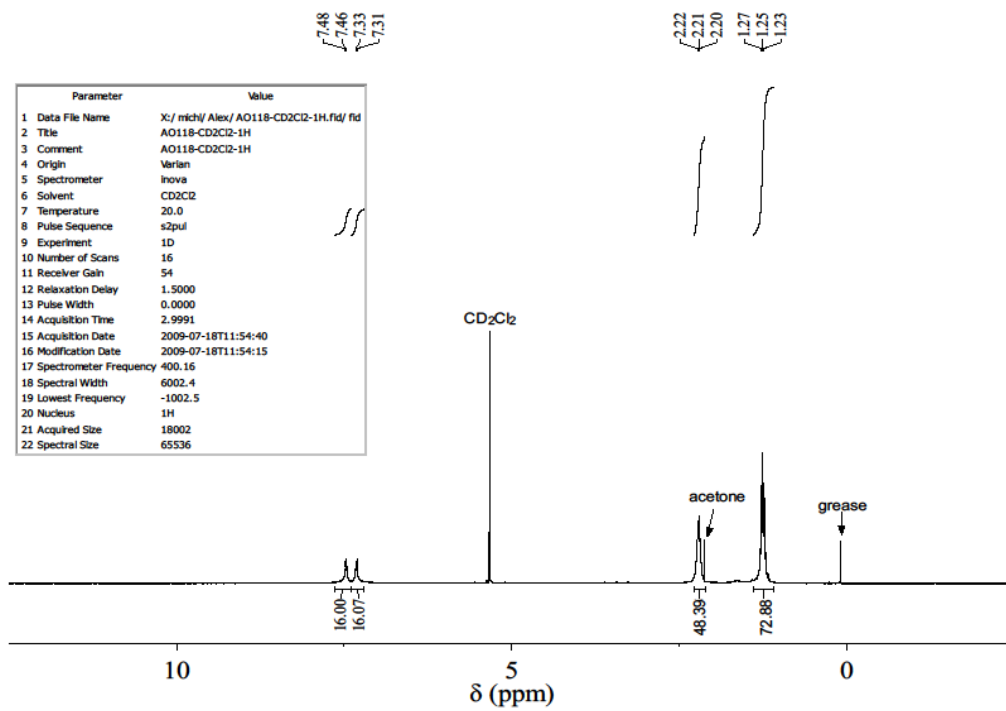
¹H NMR spectra of **4a** in CD₃NO₂.



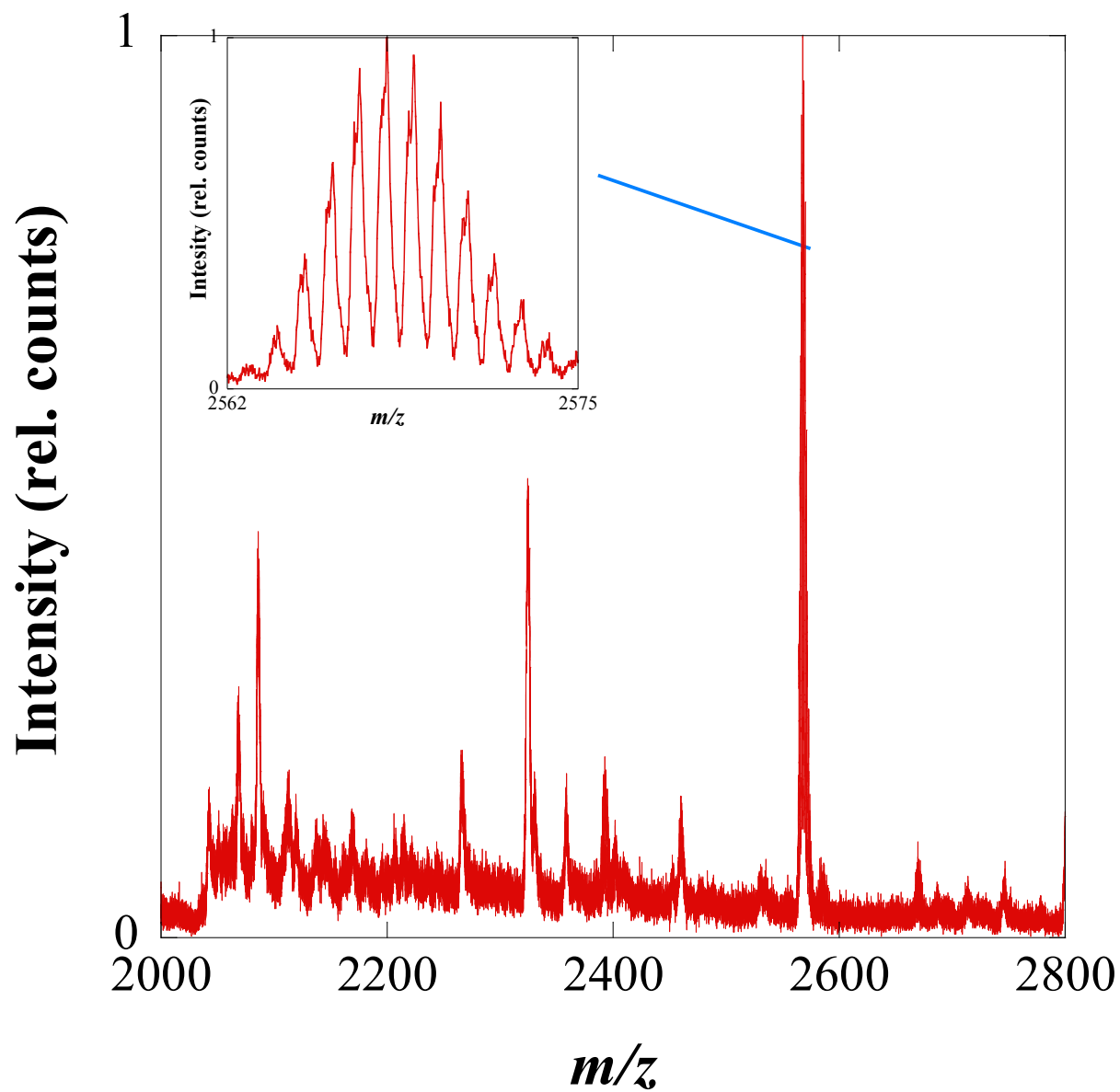
¹H NMR spectra of **4b** in CD₃NO₂.



¹H NMR spectra of **4c** in CD₃NO₂.



^1H NMR spectra of **5** in CD_2Cl_2 .



ESI⁺ MS for **5** in CH₂Cl₂ with 5-10% of CH₃CN

REFERENCES

1. Louw, W. J. *Inorg. Chem.* **1977**, *16*, 2147.
2. Rahn, J. A.; Baltusis, L.; Nelson, J. H. *Inorg. Chem.* **1990**, *29*, 750.
3. Goh, S. H.; Mok, C. Y. *J. Inorg. Chem.* **1977**, *39*, 531.
4. Fushimi, M.; Suzuki, M.; Uehara, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1809.
5. Cross, R. J.; Davidson, M. F. *J. Chem. Soc. Dalton Trans.* **1986**, 1987.
6. Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. *Chem. Comm.* **2003**, 278.
7. Shanmugaraju, S.; Bar, A. K.; Chi, K.-W.; Mukherjee, P. S. *Organometallics* **2010**, *29*, 2971.
8. Lee, S. J.; Luman, C. R.; Castellano, F. N.; Lin, W. *Chem. Comm.* **2003**, 2014.
9. Benito, J.; Berenguer, J. R.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. *Dalton Trans.* **2003**, 4331.
10. Janka, M.; Anderson, G. K.; Rath, N. P. *Organometallics* **2004**, *23*, 4382.
11. Hua, J.; Lin, W. *Org. Lett.* **2004**, *6*, 861.
12. Johnson, C. A.; Haley, M. M.; Rathner, E.; Han, F.; Weakley, T. J. R. *Organometallics* **2005**, *24*, 1161.
13. Park, J. S.; Wilson, J. N.; Hardcastle, K. I.; Bunz, U. H. F.; Srinivasarao, M. *J. Am. Chem. Soc.* **2006**, *128*, 7714.
14. Liu, L.; Liu, Z.; Xu, W.; Xu, H.; Zhang, D.; Zhu, D. *Tetrahedron* **2005**, *61*, 3813.
15. Cardolaccia, T.; Li, Y.; Schanze, K. S. *J. Am. Chem. Soc.* **2008**, *130*, 2535.
16. Anderson, H. L.; Walter, C.J.; Vidal-Ferran, A.; Hay, R. A.; Lowden, P. A.; Sanders, J. K. M. *J. Chem. Soc. Perkin Trans.* **1995**, *18*, 2275.
17. Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Granger, P.; Hoffman, R. E.;

- Zilm, K. W. *Pure Appl. Chem.* **2008**, *80*, 59.
18. Wu, D.; Chen, A.; Johnson, C. S. *J. Magn. Reson.* **1995**, *115 (Series A)*, 260.
19. Della Ciana, L.; Haim, A. *J. Heter. Chem.* **1984**, *21*, 607.