Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information belonging to the manuscript

Generation of a metallomacrocycle by rearrangement of a six-coordinate precursor complex

by

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Experimental Procedures

General Remarks. Chemicals were obtained from commercial suppliers and used without further purification. Air- or moisture sensitive reactions were performed in dry glassware under an inert gas atmosphere (nitrogen). Light sensitive reactions were performed under excluding of light by using foiled glassware. Methanol was dried over magnesium and distilled under nitrogen prior to use. Tetrahydrofuran was dried over sodium with benzophenone for indication and distilled under an inert atmosphere. Other solvents used were dried and purified by a MBraun MB-SPS-800 drying system. ATR-IR spectra were recorded with a Perkin-Elmer Spectrum 100 FT-IR spectrometer. NMR spectra were obtained with a Bruker Puls-FT-NMR spectrometer AMX400 at 400.1 MHz (^{1}H) and 100.6 MHz (^{13}C) and a Bruker FT-NMR spectrometer AMX600 at 600 MHz (^{1}H) and 151 MHz (^{13}C) at room temperature. Chemical shifts δ [parts per million] are reported with respect to residual solvent signals as internal standards. The assignment of the resonances is according to the numbering schemes given below. Elemental analyses were measured by the microanalytical laboratory at the Fachbereich Chemie of the Technische Universität Kaiserslautern.

Common electrospray ionization mass spectrometry (ESI-MS) was performed with an ion trap instrument (Bruker amaZon ETD). The investigated cations were produced in the positive and negative electrospray ionization mode. The scan speed was 8100 $m/z \cdot s^{-1}$ in enhanced-resolution scan mode (0.25 fwhm/m/z). The scan range was at least 70 to 1500 m/z. Sample solutions of complexes in dichloromethane at concentrations of approximately 10 - 5 M were continuously infused into the ESI chamber at a flow rate of 2 $\mu L \cdot min^{-1}$ by using a syringe pump. N_2 gas was used as drying gas at a flow rate of 3.0 to 4.0 $L \cdot min^{-1}$ heated to 220 °C. The solutions were sprayed at a nebulizer gas pressure of 0.2 to 0.28 bar with the electrospray needle held at 4.5 kV. Helium was used as a buffer gas with a partial pressure of ca. $3 \cdot 10^{-3}$ mbar inside the ion trap. Bruker trapControl 7.2 software controlled the instrument and data analysis was performed with Data Analysis 4.2 software.

Chlorido(tetrahydrothiophene)gold(I) (**0**) [1] (2-(chloromethyl)phenyl)diphenylphosphine (**3**),[2] and 2,6-bis(5-butyl-1H-pyrazol-3-yl)pyridine (**4**) [3] were prepared according to procedures published in the literature.

2,6-Bis(*N*-benzyl-*o*-diphenylphosphine-5-butylpyrazol-3-yl)pyridine (1): 546 mg (13.6 mmol, 60% suspension in oil) of sodium hydride were suspended in 65 mL of tetrahydrofuran. 2.01 g (6.20 mmol) of 2,6-bis(5-butyl-1H-pyrazol-3-yl)pyridine were added in small portions. The reaction mixture was stirred for 3 h at room temperature. Then the solvent was removed under reduced pressure and the pale yellow residue was dissolved in 55 mL of dimethoxyethane. 3.85 g (12.4 mmol) of (2-(chloromethyl-)phenyl)diphenyl phosphine were added in one portion and the reaction mixture was stirred and heated to reflux for 24 h. After cooling to room temperature the solvent was removed under reduced pressure. The yellow residue was dissolved in 50 mL of chloroform, washed three times with 25 mL of deionized water. The organic layer was dried over magnesium sulfate. Removing of the solvent

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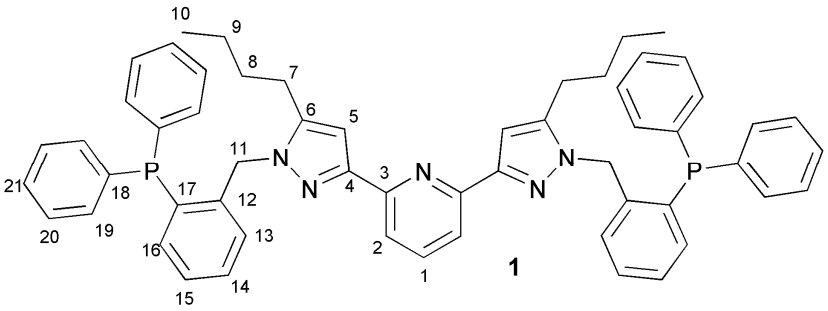
1 R. Usón, A. Laguna, D. A. Briggs, H. H. Murray and J. P. Fackler, *Inorg. Synth.*, 1989, **26**, 85-91.

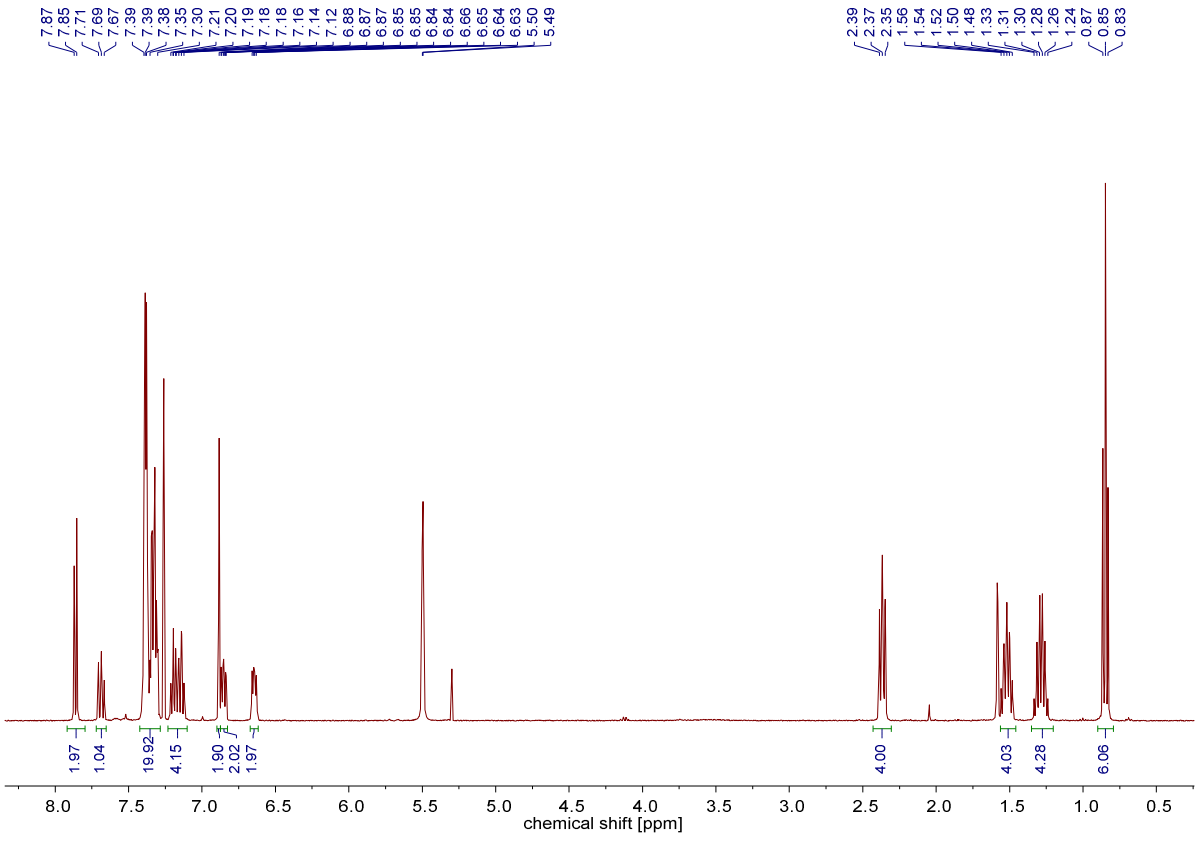
2 A.-E. Wang, J.-H. Xie, L.-X. Wang and Q.-L. Zhou, *Tetrahedron*, 2005, **61**, 259-266; A.-E. Wang, J. Zhong, J.-H. Xie, K. Li and Q.-L. Zhou, *Adv. Synth. Catal.*, 2004, **346**, 595-598; J. Zhong, J.-H. Xie, A.-E. Wang, W. Zhang and Q.-L. Zhou, *Synlett*, 2006, 1193-1196; J. Trampert, M. Nagel, T. Grimm, Y. Sun and W. R. Thiel, *Z. Allg. Anorg. Chem.*, 2018, **644**, 963-972.

3 D. Zabel, A. Schubert, G. Wolmershäuser, R. L. Jones Jr. and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2008, 3648-3654; A.-K. Pleier, H. Glas, M. Grosche, P. Sirsch and W. R. Thiel, *Synthesis*, 2001, 55-62.

resulted in a pale yellow solid. Recrystallization from *n*-pentane gave colorless crystals. Yield: 5.16 g (5.92 mmol, 95%). Anal. calcd. for $C_{57}H_{55}N_5P_2$: C 78.51, H 6.36, N 8.03, found: C 78.37, H 6.43, N 8.00. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.87 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-2), 7.69 (t, $^3J_{HH}$ = 8.0 Hz, 1H, H-1), 7.39-7.30 (m, 20H, H19, H20, H21), 7.20 (dt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, H14), 7.14 (t, $^3J_{HH}$ = 7.1 Hz, 2H, H15), 6.88 (s, 2H, H5), 6.85 (ddd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, $^3J_{PH}$ = 4.7 Hz, 2H, H16), 6.64 (dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.2 Hz, $^4J_{PH}$ = 4.6 Hz, 2H, H13), 5.50 (d, $^4J_{HH}$ = 4.0 Hz, 4H, H11), 2.37 (t, $^3J_{HH}$ = 8.0 Hz, 4H, H7), 1.52 (quint., ^3JHH = 8.0 Hz, 4H, H8), 1.30 (sext., ^3JHH = 8.0 Hz, 4H, H9), 0.85 (t, $^3J_{HH}$ = 8.0 Hz, 6H, H10). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 152.1 (s, C3), 151.2 (s, C1), 145.3 (s, C6), 141.4 (d, $^1J_{PC}$ = 21.9 Hz, C17), 136.9 (s, C4), 135.4 (d, $^1J_{PC}$ = 9.1 Hz, C18), 134.2 (d, $^2J_{PC}$ = 19.9 Hz, C19), 132.7 (s, C16), 129.4 (s, d, $^2J_{PC}$ = 17.0 Hz, C12), 129.3 (2×s, C14, C21), 128.8 (d, $^3J_{PC}$ = 7.2 Hz, C20), 127.4 (s, C15), 126.2 (d, J_{PC} = 4.8 Hz, C13), 118.3 (s, C2), 103.9 (s, C5), 51.3 (d, J_{PC} = 29.2 Hz, C11), 30.5 (s, C7), 25.2 (s, C8), 22.3 (s, C9), 13.8 (s, C10). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ -15.63 (s). IR-ATR: $\tilde{\nu}$ (cm^{-1}) 3051w, 2911w, 1592w, 1571m, 1482m, 1433s, 1372m, 1222m, 1192m, 1090m, 1026m, 818w, 753s, 741s.



^{1}H NMR spectrum, compound **1**, 400.1 MHz, $CDCl_3$, room temperature



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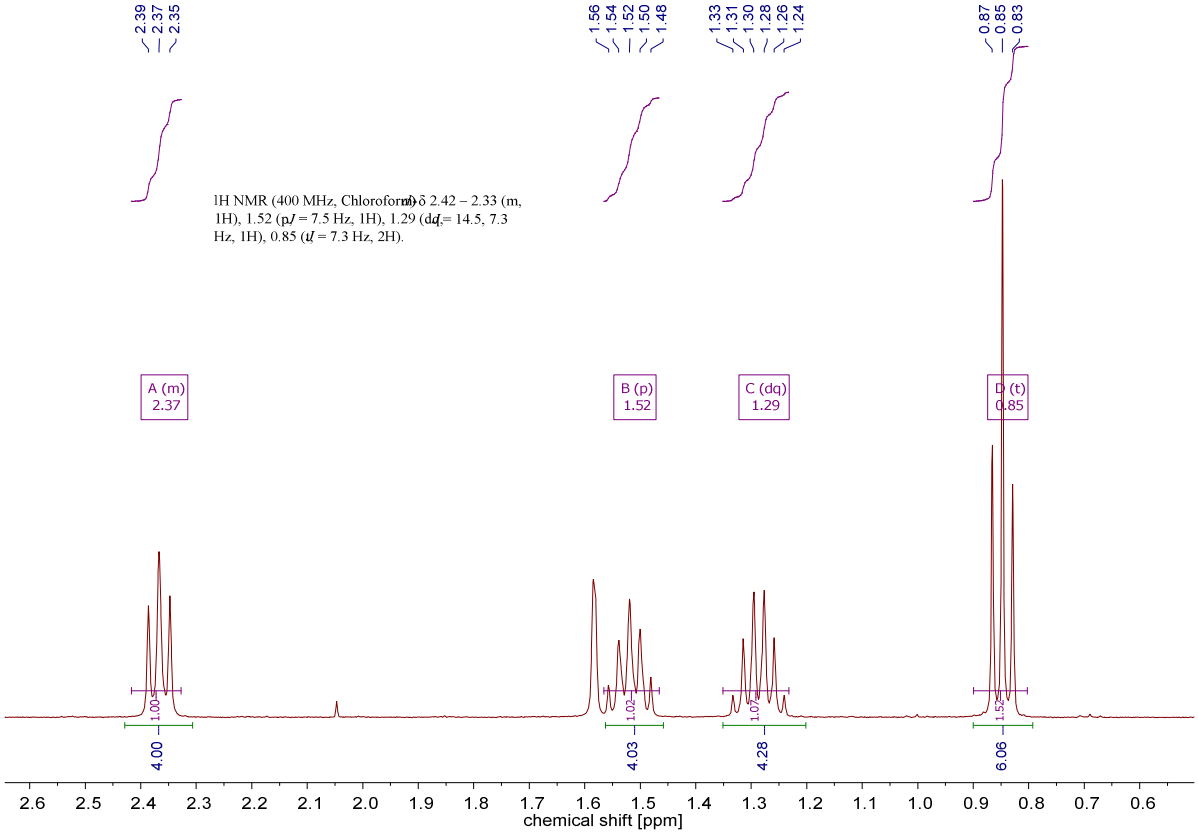

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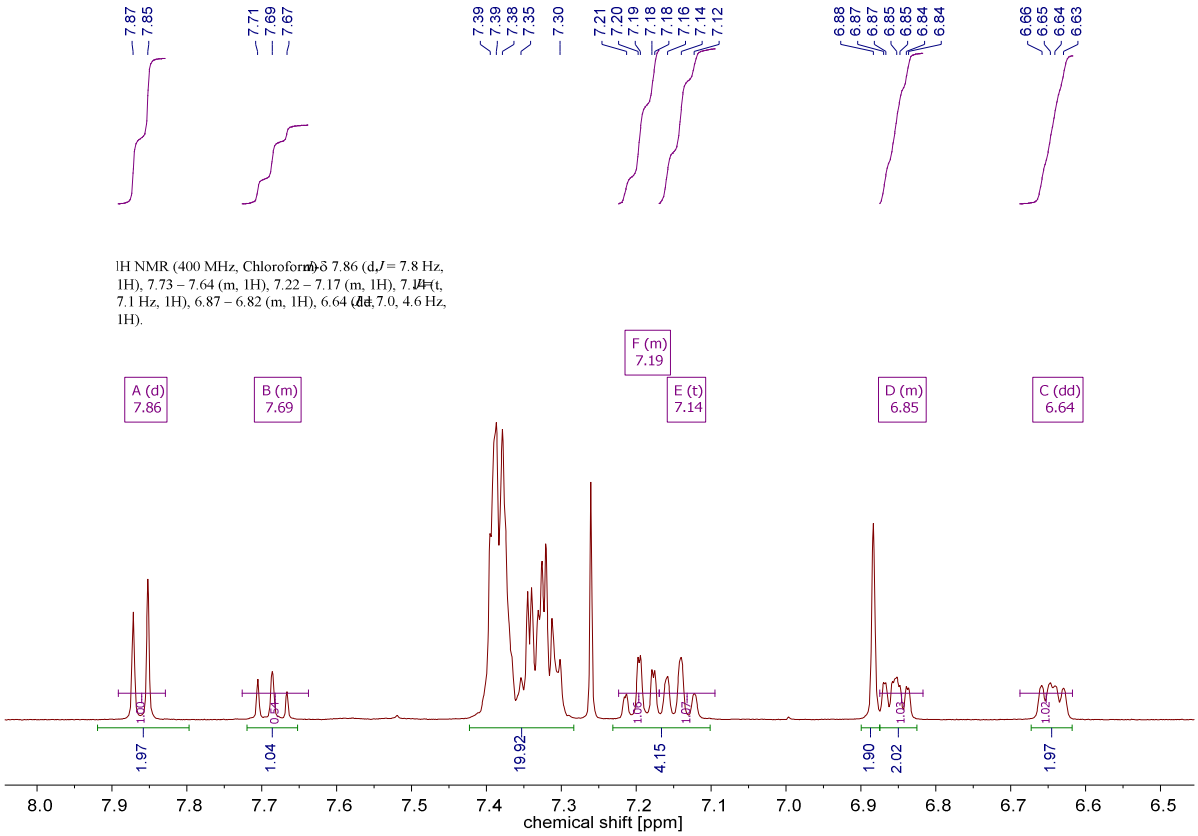
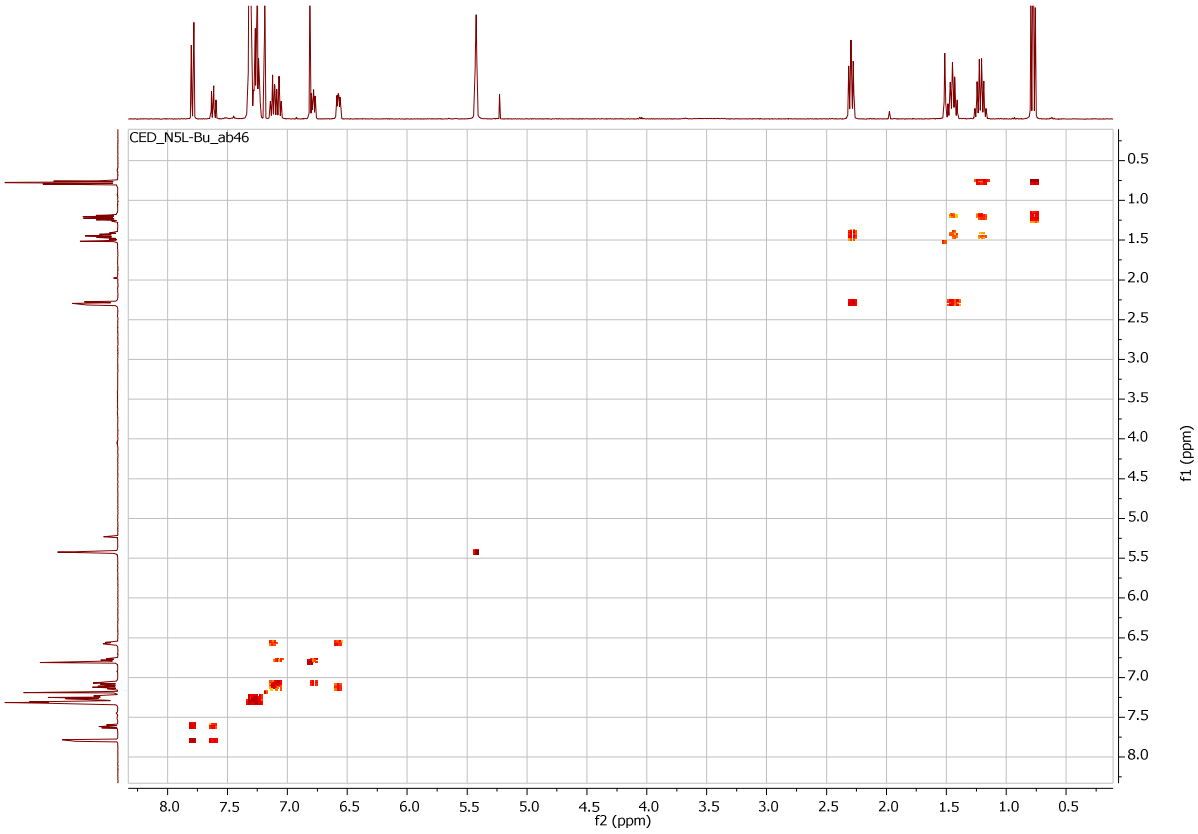
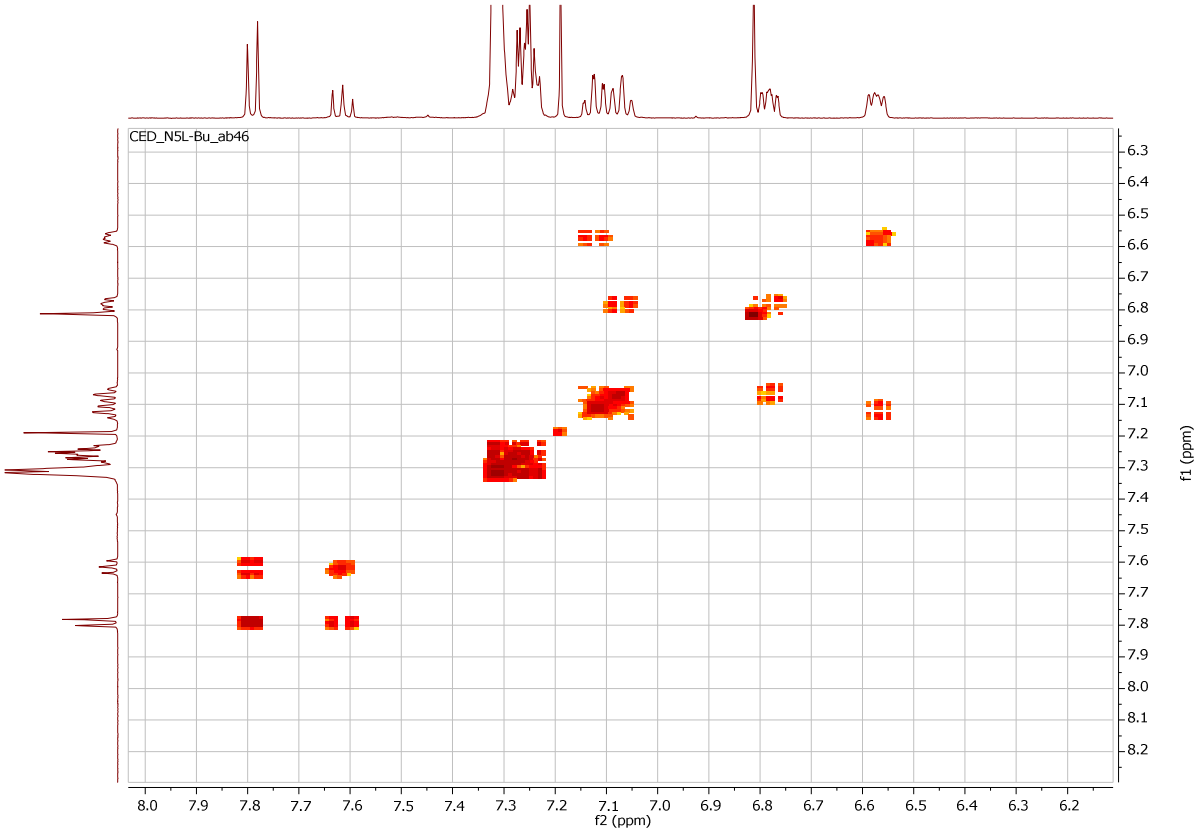


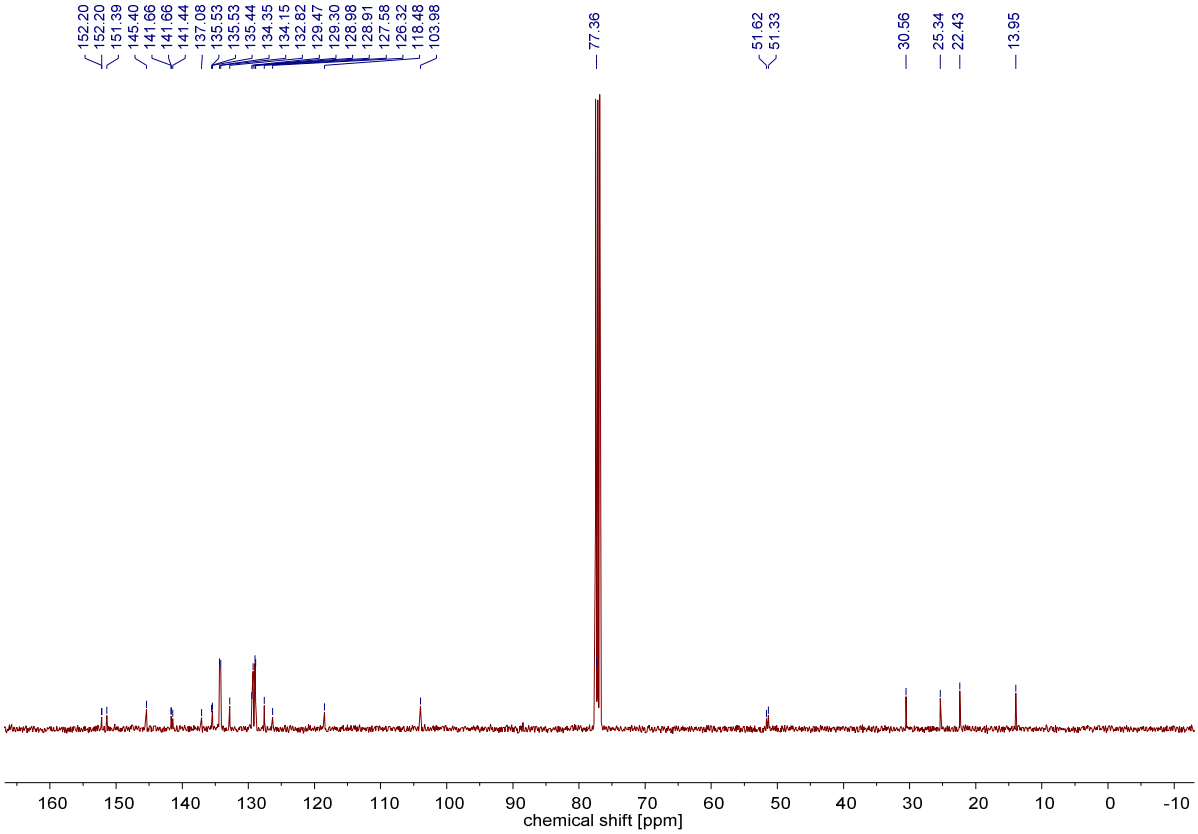
H,H-COSY NMR spectrum, compound **1**, 400.1 MHz, $CDCl_3$, room temperature



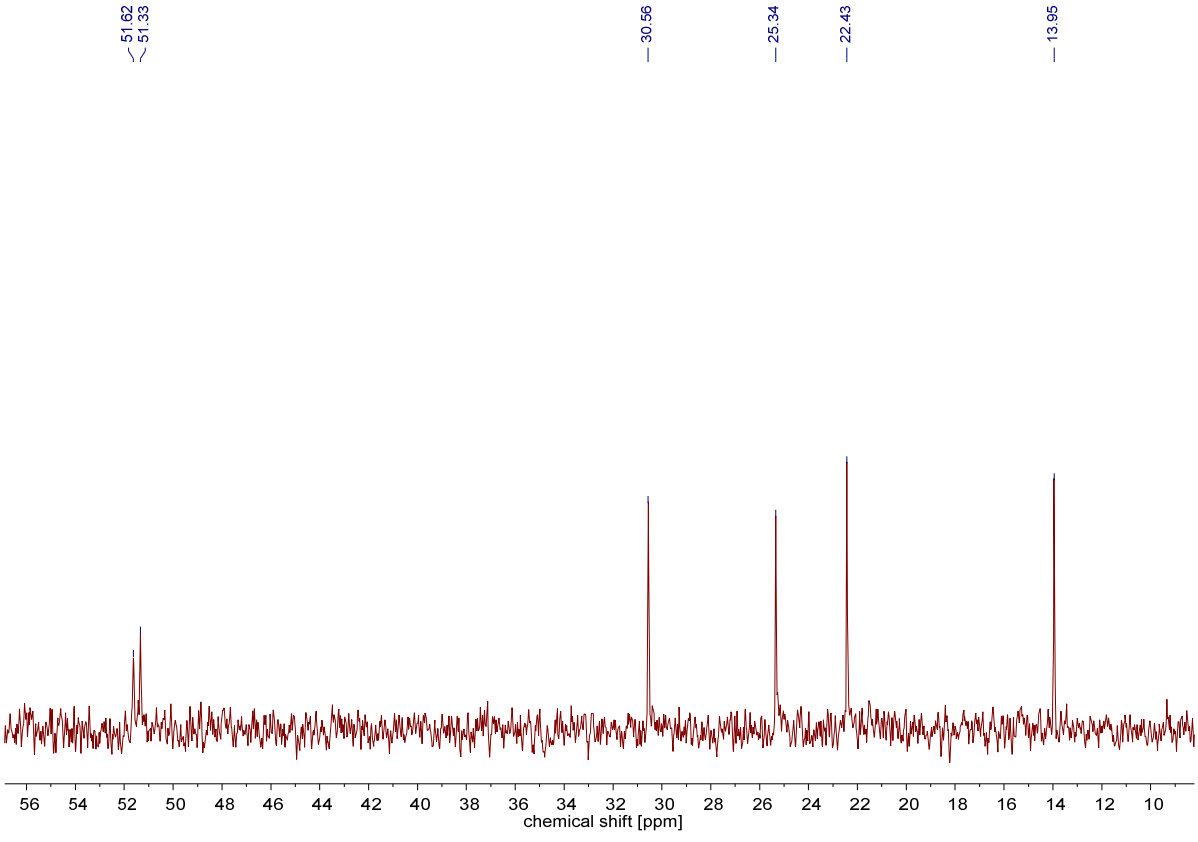
H,H-COSY NMR spectrum (enlarged) , compound **1**, 400.1 MHz, $CDCl_3$, room temperature



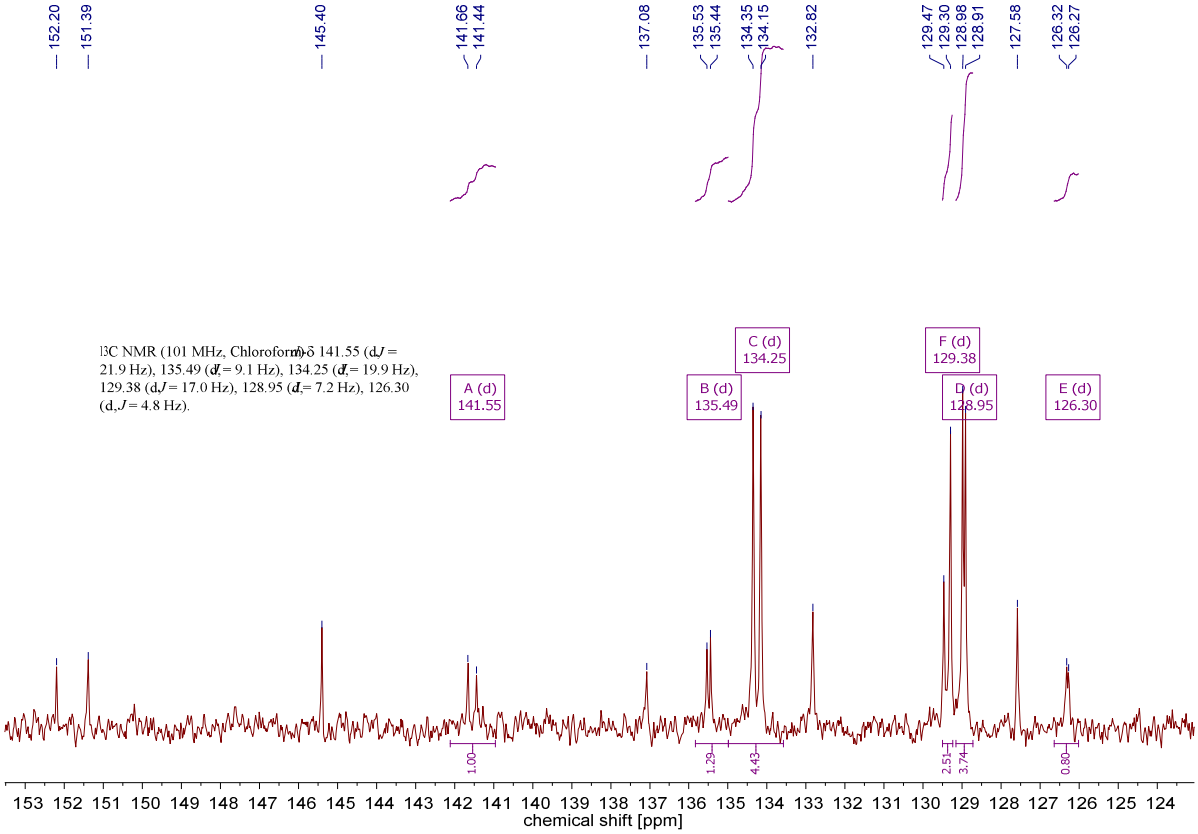
^{13}C NMR spectrum, compound **1**, 100.6 MHz, $CDCl_3$, room temperature



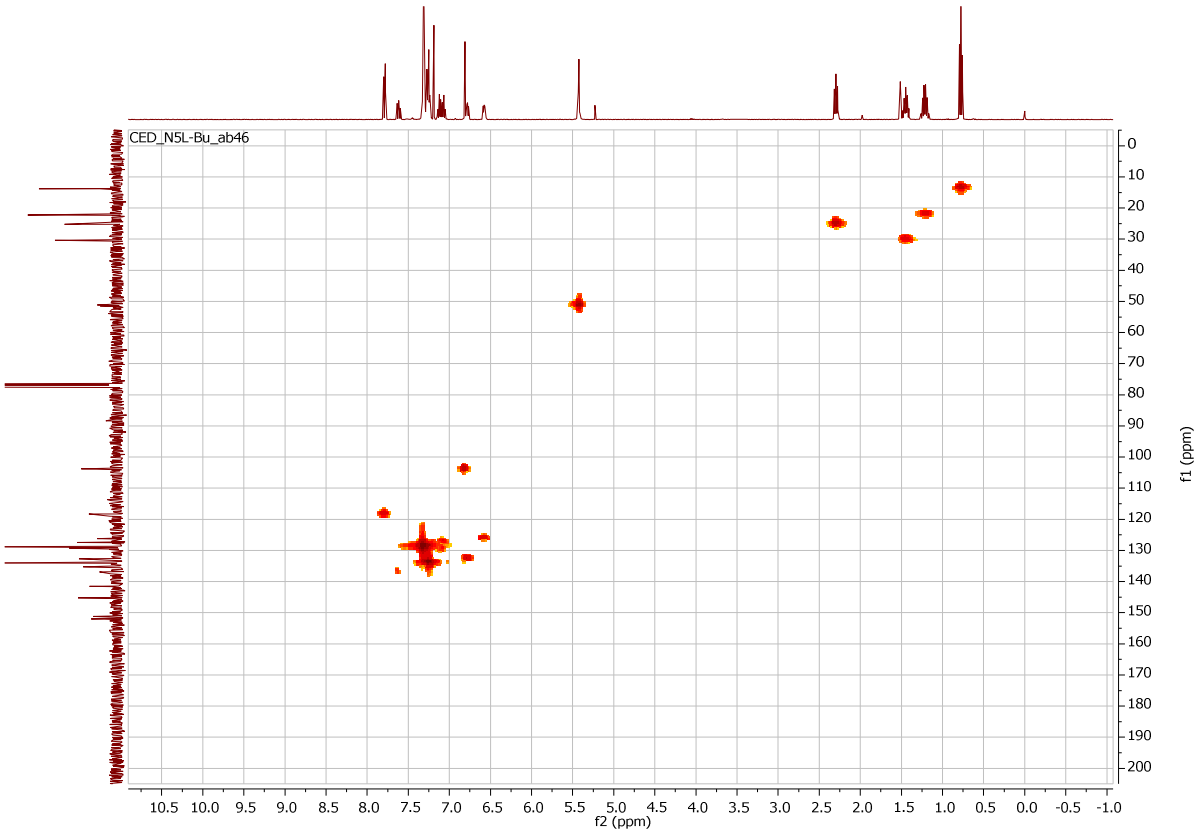
^{13}C NMR spectrum (enlarged), compound **1**, 100.6 MHz, $CDCl_3$, room temperature



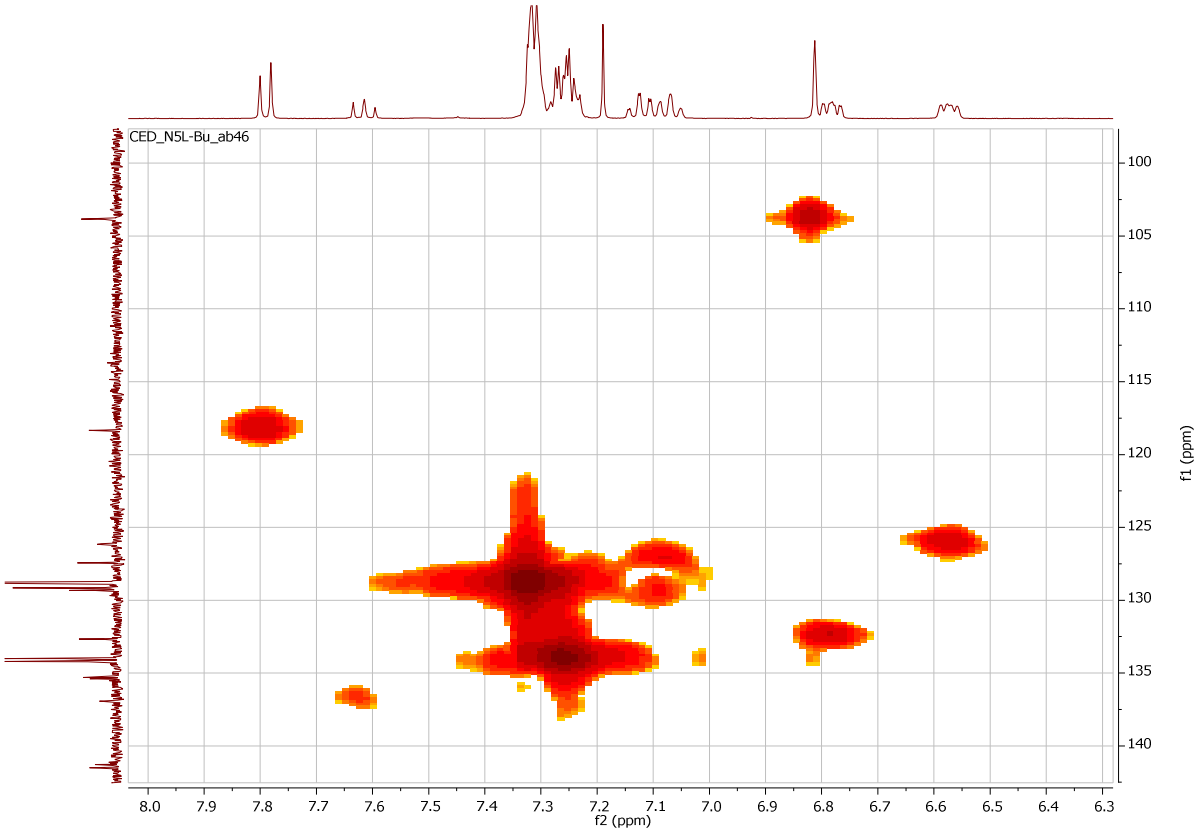
^{13}C NMR spectrum (enlarged), compound **1**, 100.6 MHz, $CDCl_3$, room temperature



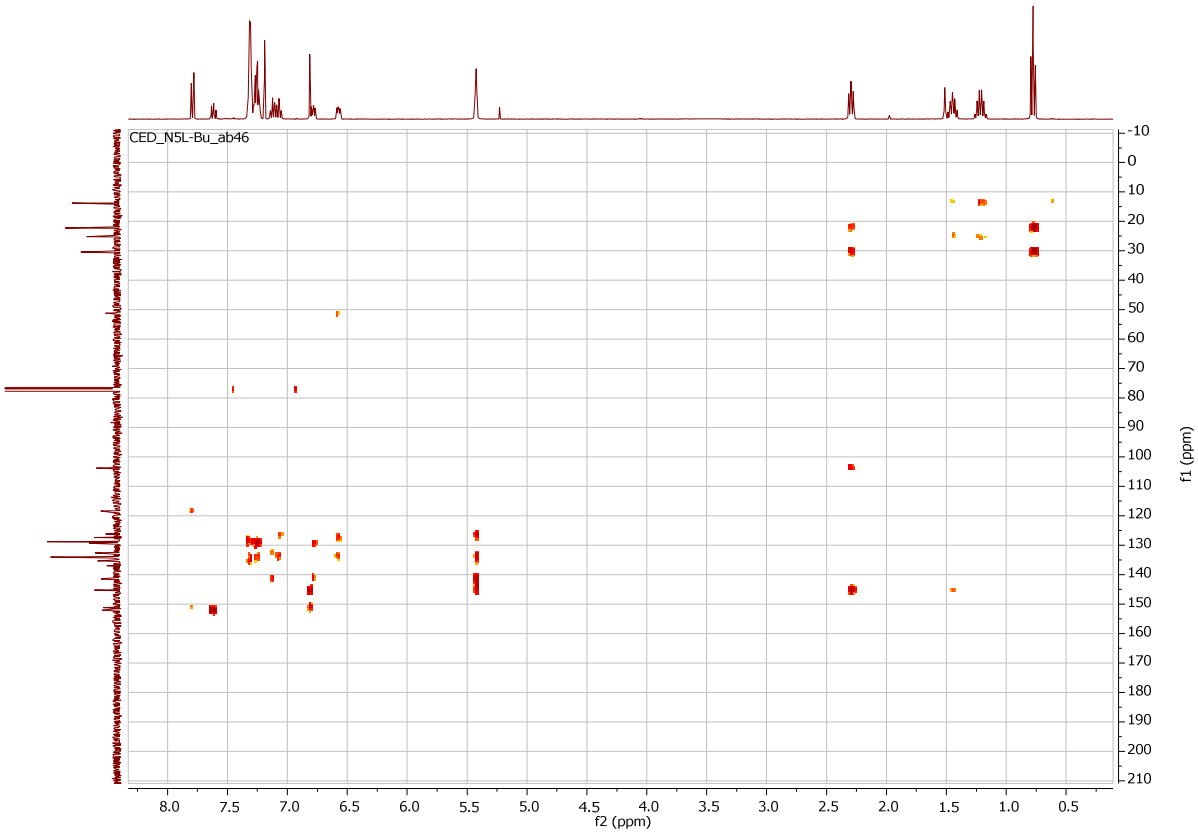
HSQC NMR spectrum, compound **1**, $CDCl_3$, room temperature



HSQC NMR spectrum (enlarged), compound **1**, $CDCl_3$, room temperature

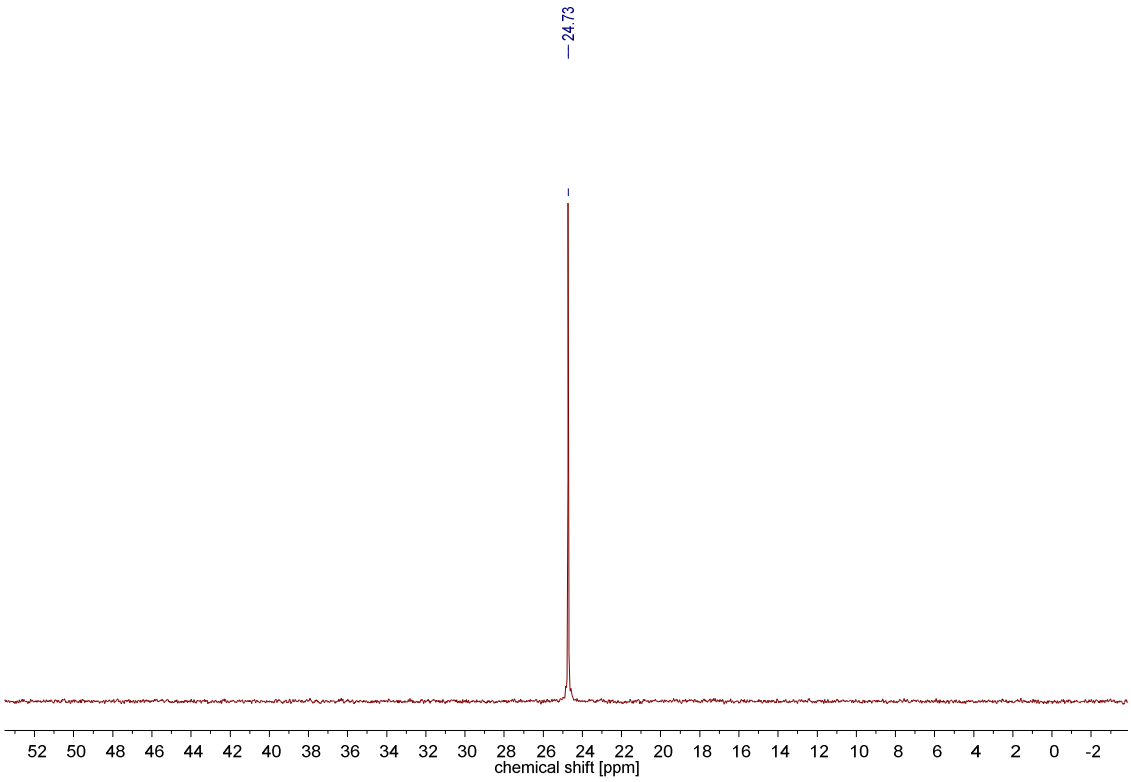


HMBC NMR spectrum, compound **1**, $CDCl_3$, room temperature

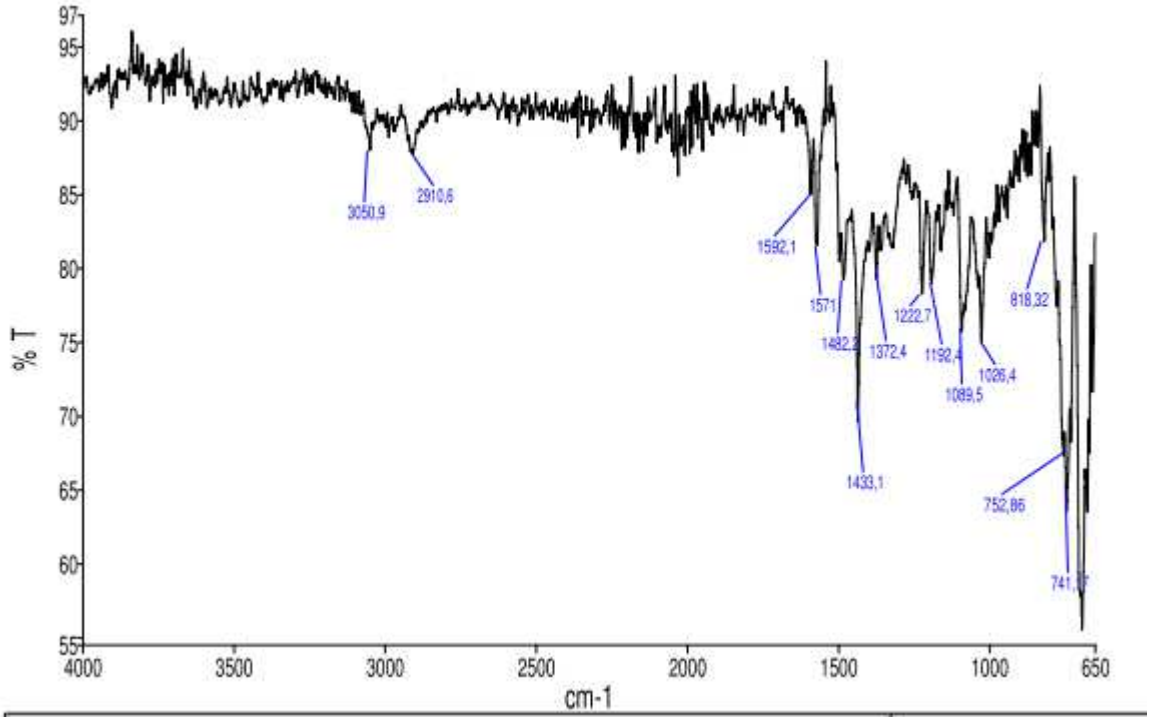


HMBC NMR spectrum (enlarged), compound **1**, $CDCl_3$, room temperature

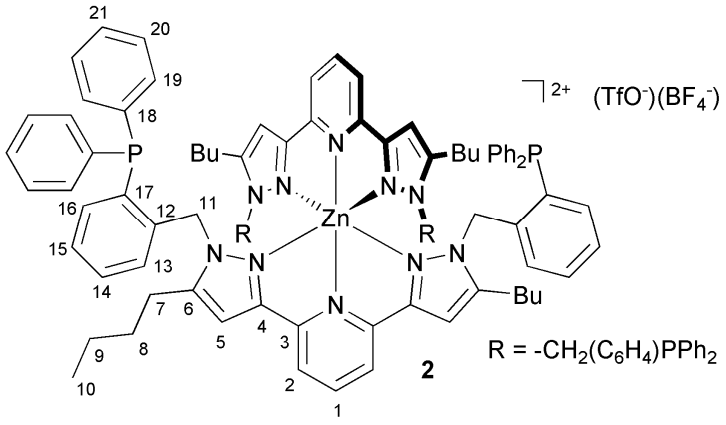
^{31}P NMR spectrum, compound **1**, 162.0 MHz, $CDCl_3$, room temperature



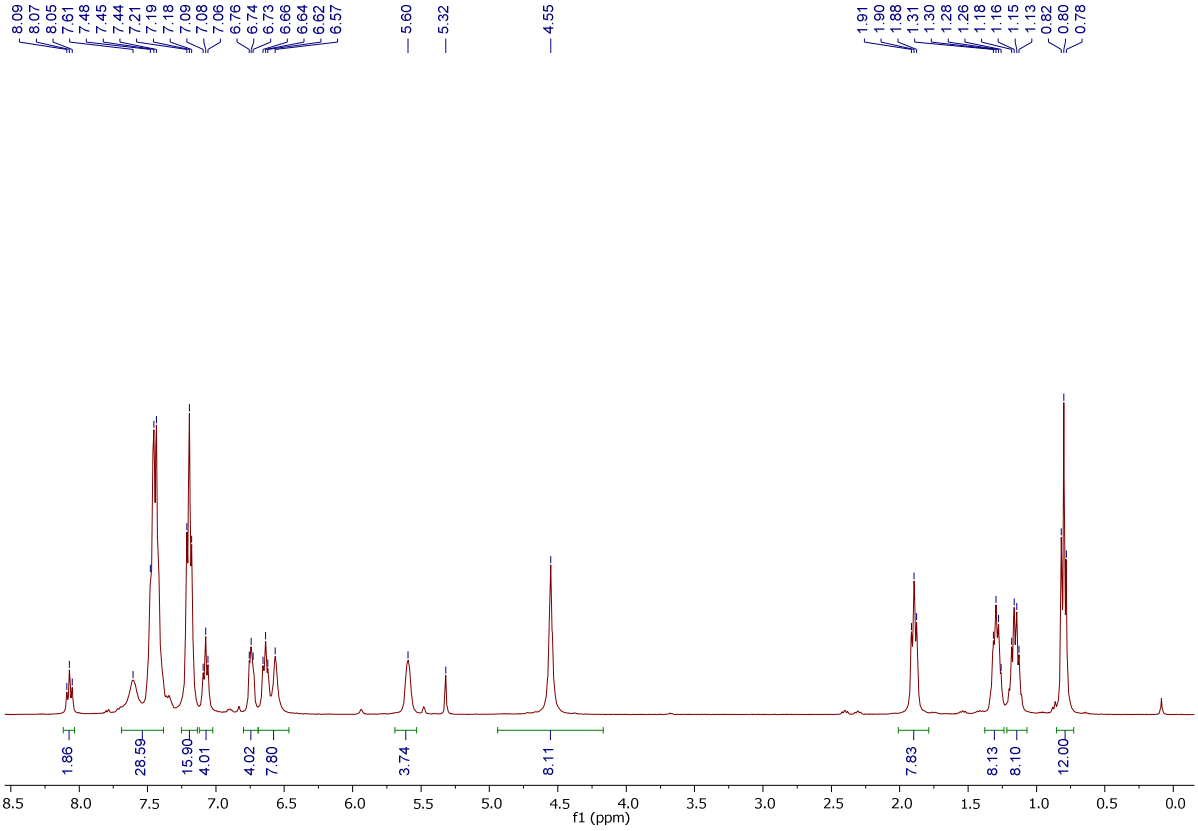
IR spectrum, compound **1**, ATR



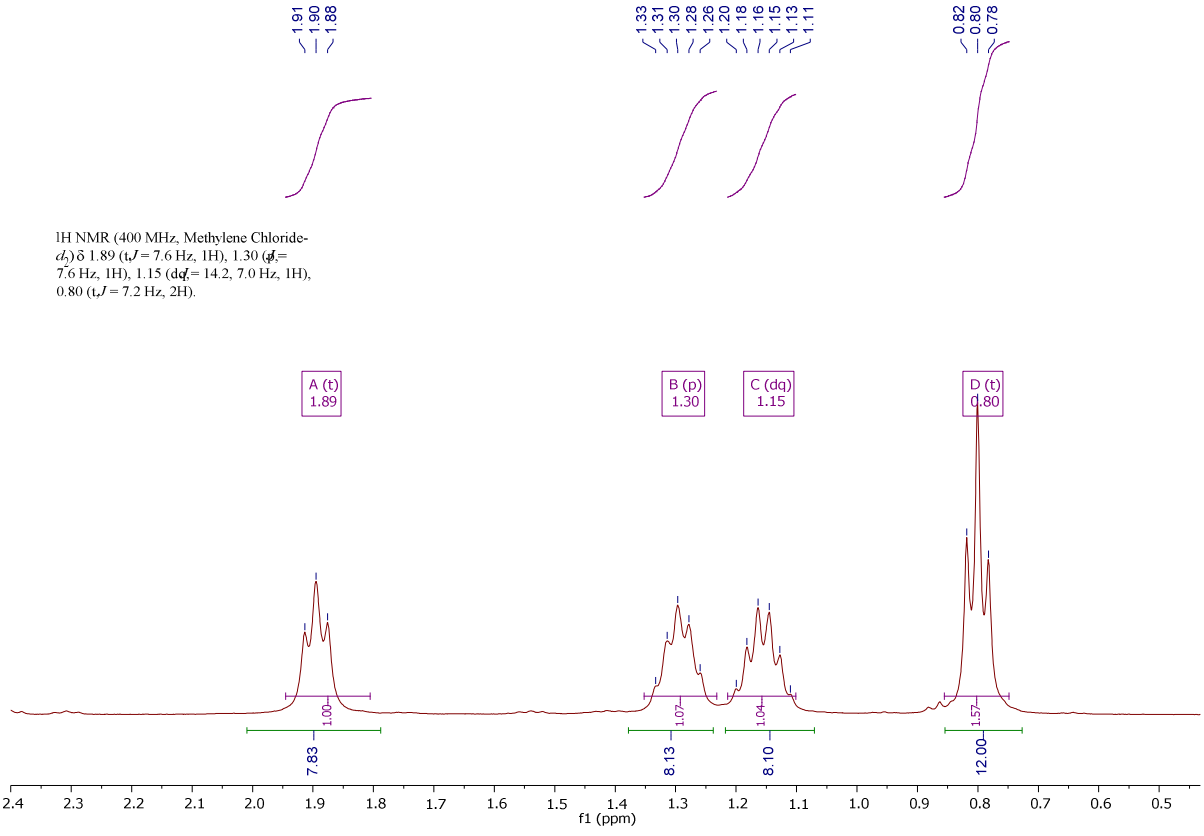
[Bis(2,6-bis(*N*-benzyl-*o*-diphenylphosphine-5-butylpyrazol-3-yl)pyridine)zinc(II)] tetrafluoroborate triflate (2): 120 mg (0.33 mmol) of dried zinc triflate and 576 mg (0.66mmol) of ligand **1** were suspended in 50 mL of methanol and stirred for 1 h under reflux. Then 73.9 mg (0.66 mmol) of sodium tetrafluoroborate were added and the hot reaction mixture was allowed to slowly cool down to room temperature. The colorless suspension was concentrated to 10 mL under reduced pressure and cooled down to 0 °C. The precipitated colorless solid was isolated, washed with cold methanol (10 mL) and dried under reduced pressure. Yield: 480 mg (234 µmol, 71%). Anal. calcd. for $C_{115}H_{110}BF_7N_{10}O_3P_4SZn$: C 67.53, H 5.42, N 6.85, S 1.57; found: C 67.37, H 5.42, N 6.95, S 1.27. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.07 (t, $^3J_{HH}$ = 7.8 Hz, 2H, H1), 7.61 (br, 4H, H2), 7.55-7.36 (m, 24H, H20, H21), 7.19 (t, $^3J_{HH}$ = 7.3 Hz, 16H, H19), 7.08 (t, $^3J_{HH}$ = 7.2 Hz, 4H, H15), 6.76-6.74 (m, 4H, H16), 6.64 (t, $^3J_{HH}$ = 7.0 Hz, 8H, H14), 6.56 (br, 4H, H5), 5.60 (br, 4H, H13), 4.55 (br, s, 8H, H11), 1.90 (t, $^3J_{HH}$ = 8.6 Hz, 8H, H7), 1.30 (q, $^3J_{HH}$ = 7.6 Hz 8H, H8), 1.15 (sext, $^3J_{HH}$ = 7.0 Hz, 8H, H9), 0.80 (t, $^3J_{HH}$ = 7.2 Hz, 12H, H10). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 151.3 (s, C6), 146.4, 146.1 (2×s, C3, C4), 144.4 (s, C1), 137.4 (d, $^1J_{PC}$ = 21.0 Hz, C17), 135.3 (d, $^1J_{PC}$ = 17.4 Hz, C18), 134.7 (s, C12), 134.2 (d, $^2J_{PC}$ = 20.2 Hz, C19), 133.4 (s, C16), 130.5 (s, C21), 129.7 (d, $^2J_{PC}$ = 7.5 Hz, C20), 129.1 (s, C14), 128.6 (s, C15), 123.5 (d, $^3J_{PC}$ = 4.2 Hz, C13), 121.8 (s, C2), 104.7 (s, C5), 51.4 (d, $^3J_{PC}$ = 27.5 Hz, C11), 29.9 (s, C7), 25.4 (s, C8), 22.7 (s, C9), 13.9 (s, C10). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ -16.24 (s). ^{19}F NMR (376.0 MHz, $CDCl_3$): δ -78.7 (s, TfO^-), -152.7 (s, BF_4^-). IR-ATR: $\tilde{\nu}$ (cm^{-1}): 3136w, 3060w, 2958w, 2935w, 2873w, 1616w, 1591w, 1578w, 1500m, 1469m, 1456m, 1437s, 1382w, 1277s, 1264s, 1235m, 1183s, 1164s, 1132s, 1117s, 1096s, 1054vs, 1030vs, 997s, 916m, 821m, 752s, 723vs, 695vs. ESI-MS: m/z calcd. for $[C_{114}H_{110}N_{10}P_4Zn]^{2+}$ 904.36, found 904.34; m/z calcd. for $[BF_4]^-$ 87.00, found 86.77; m/z calcd. for $[CF_3O_3S]^-$ 148.95, found 148.67.



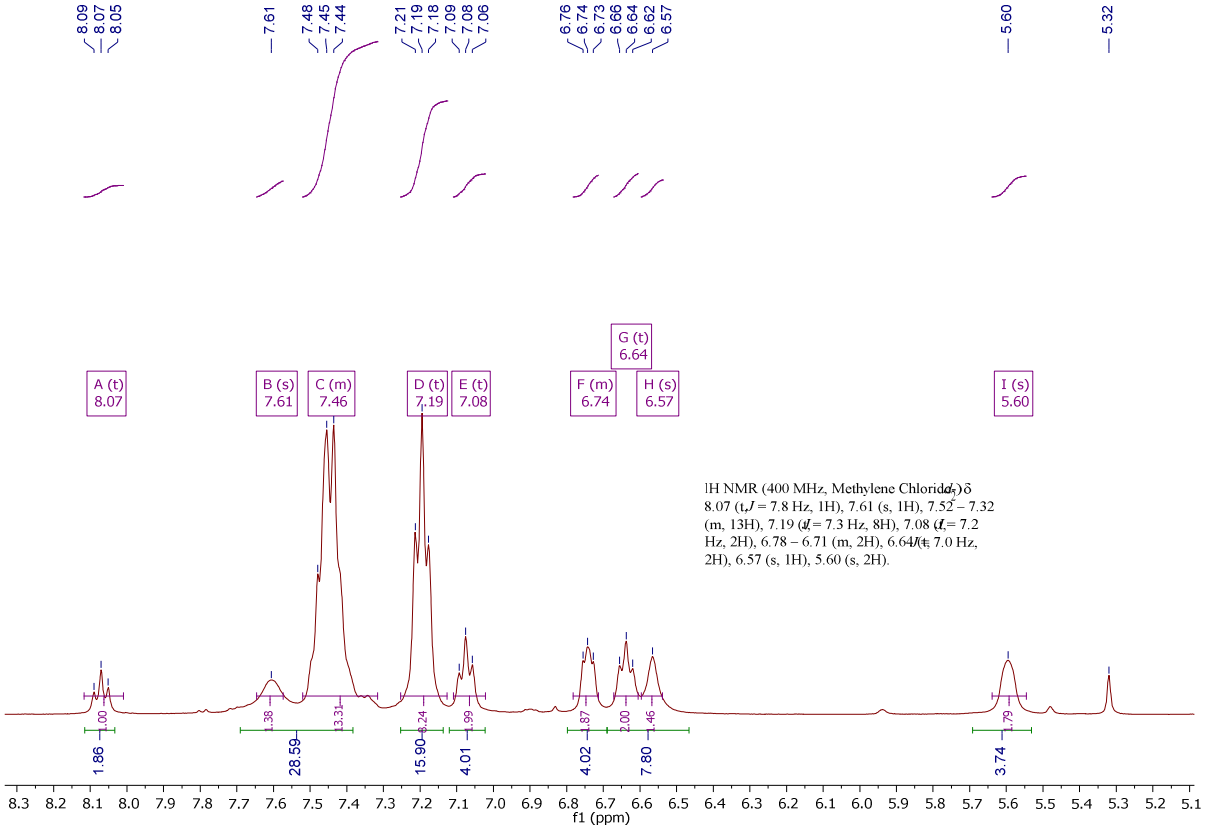
^{1}H NMR spectrum, compound **2**, 400.1 MHz, $CDCl_3$, room temperature



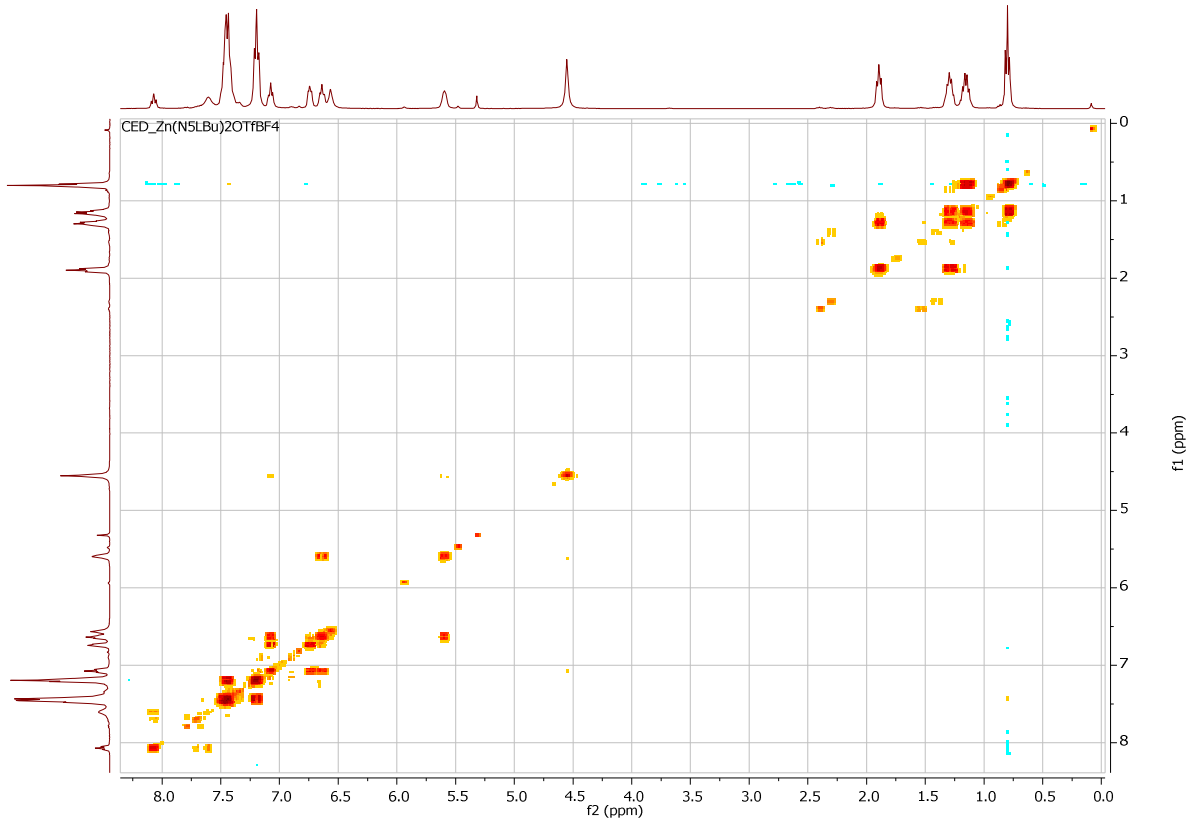
^{1}H NMR spectrum (enlarged), compound **2**, 400.1 MHz, $CDCl_3$, room temperature



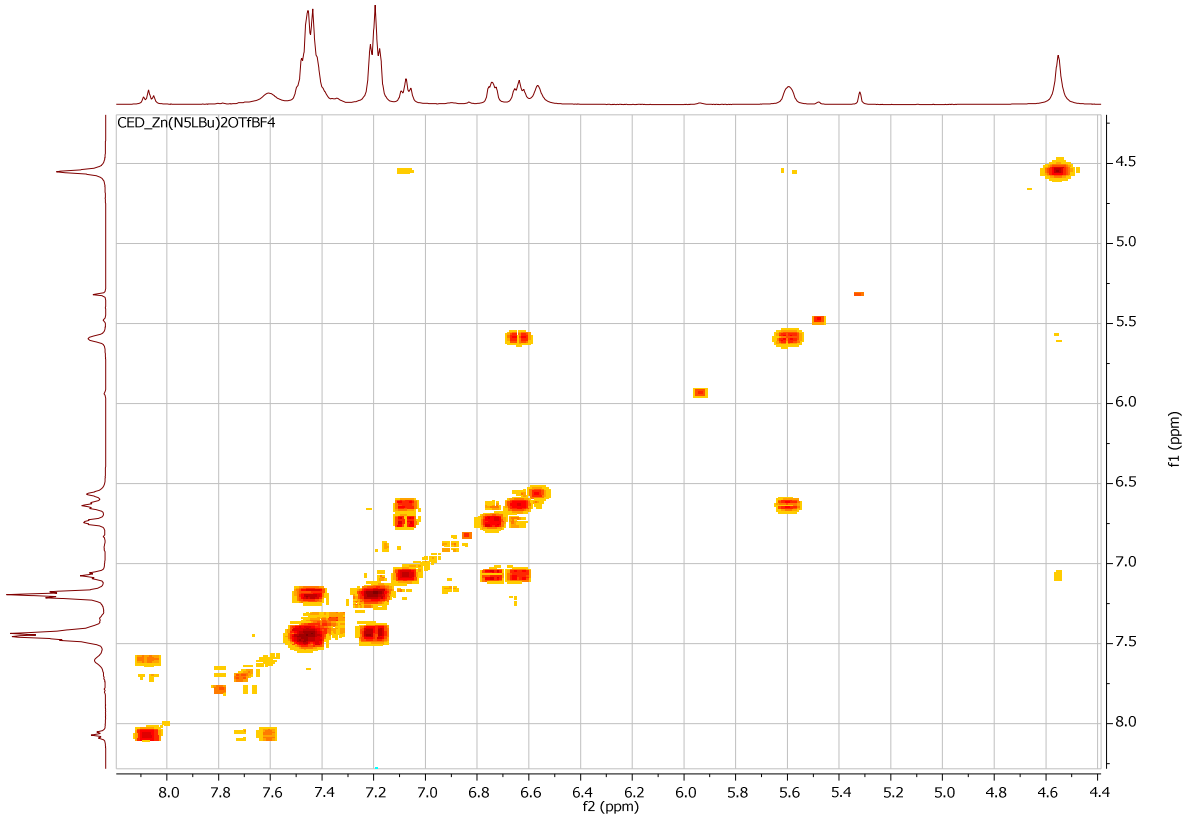
^{1}H NMR spectrum (enlarged), compound **2**, 400.1 MHz, $CDCl_3$, room temperature



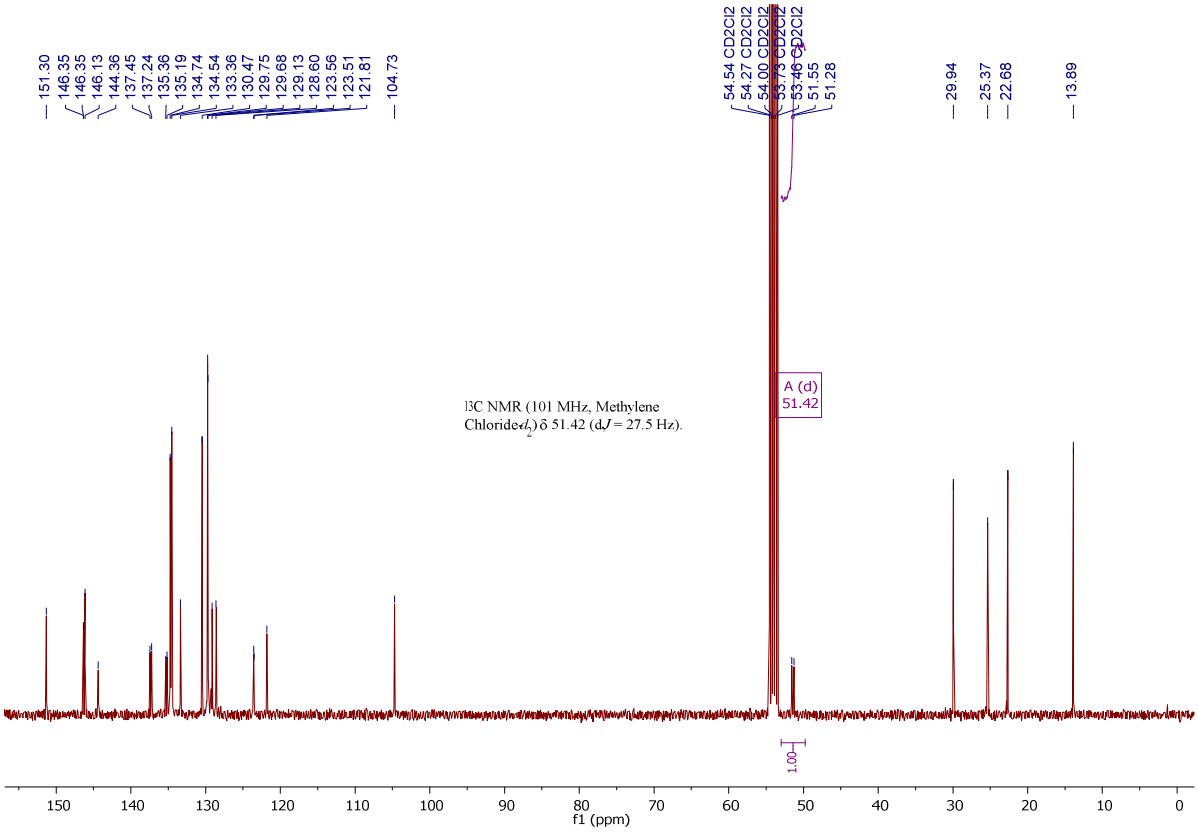
H,H-COSY NMR spectrum, compound **2**, 400.1 MHz, $CDCl_3$, room temperature



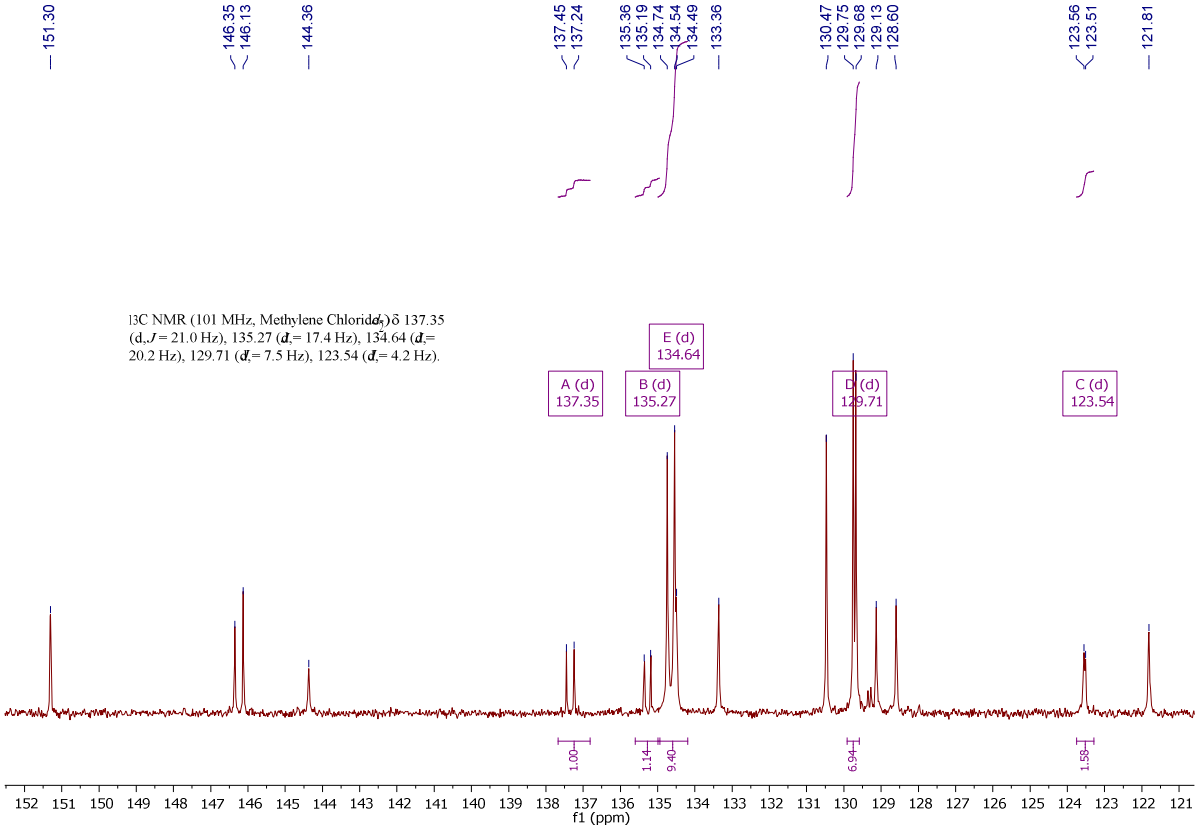
H,H-COSY NMR spectrum (enlarged), compound **2**, 400.1 MHz, $CDCl_3$, room temperature



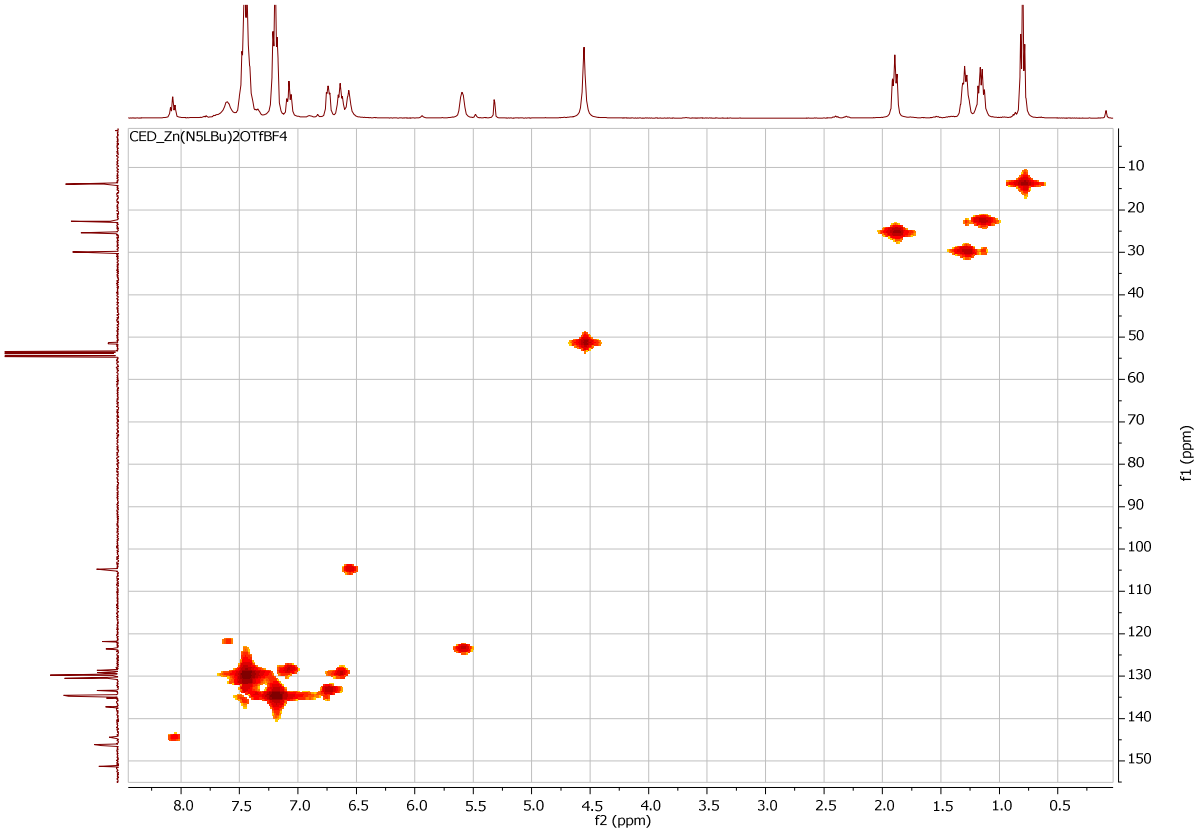
^{13}C NMR spectrum, compound **2**, 100.6 MHz, $CDCl_3$, room temperature



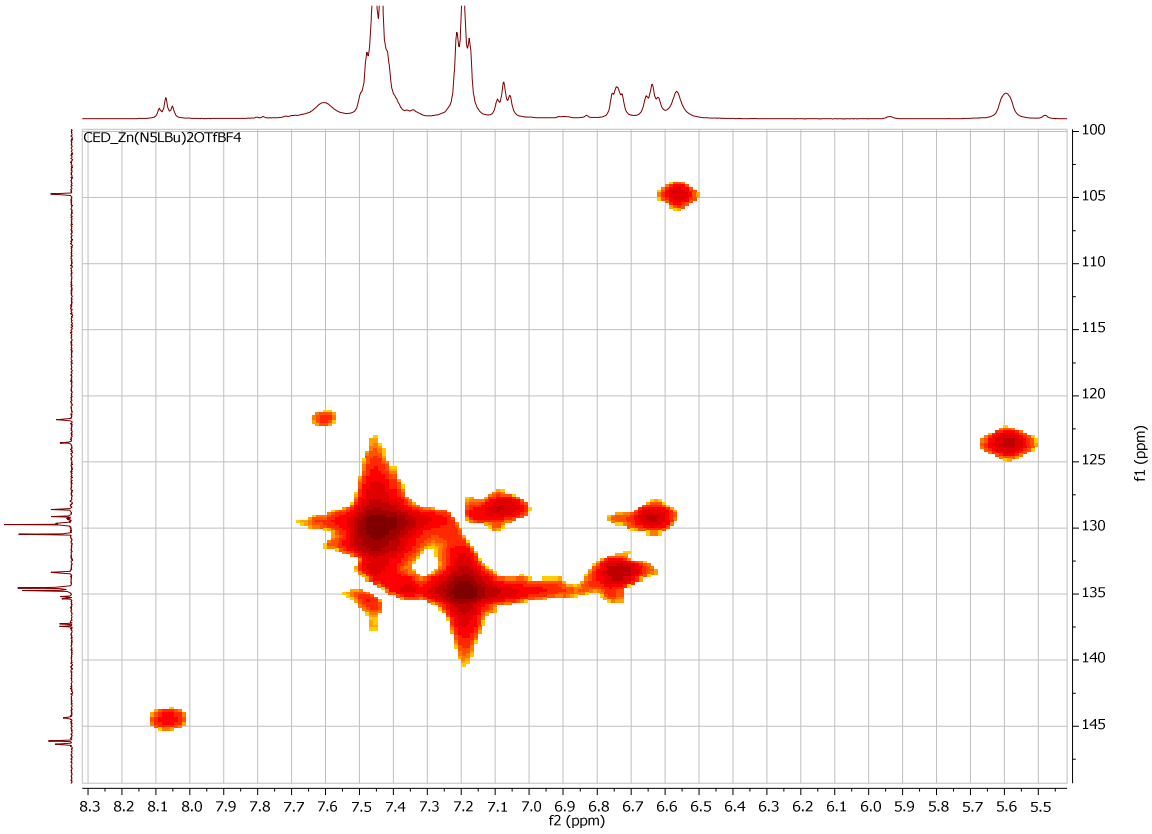
^{13}C NMR spectrum (enlarged), compound **2**, 100.6 MHz, $CDCl_3$, room temperature



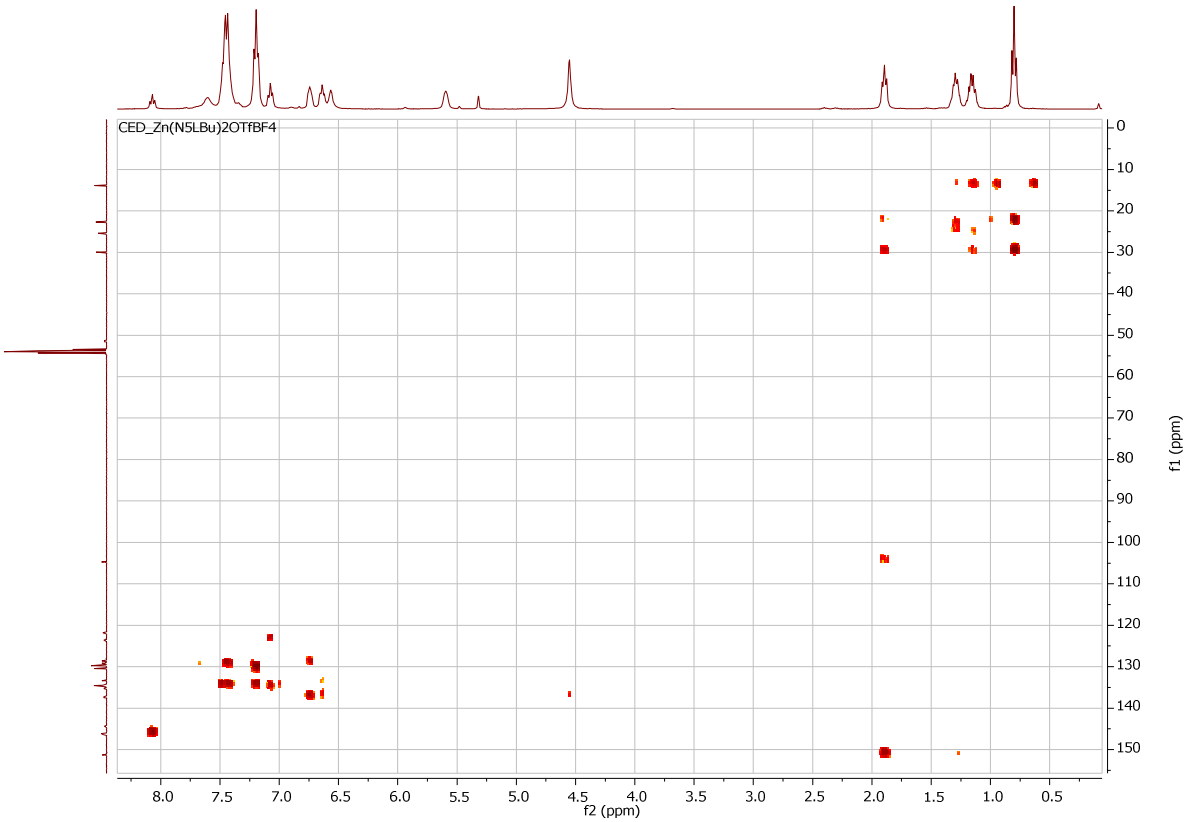
HSQC NMR spectrum, compound **2**, $CDCl_3$, room temperature



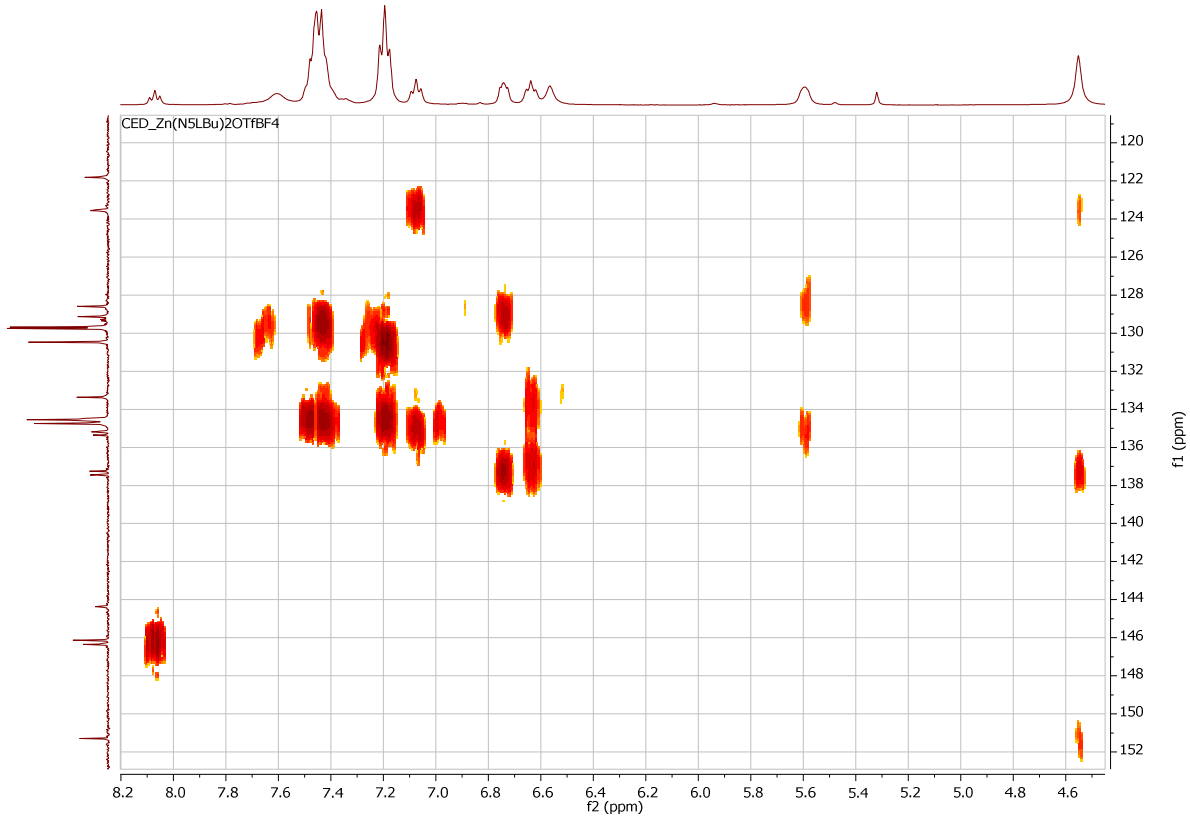
HSQC NMR spectrum (enlarged), compound **2**, $CDCl_3$, room temperature



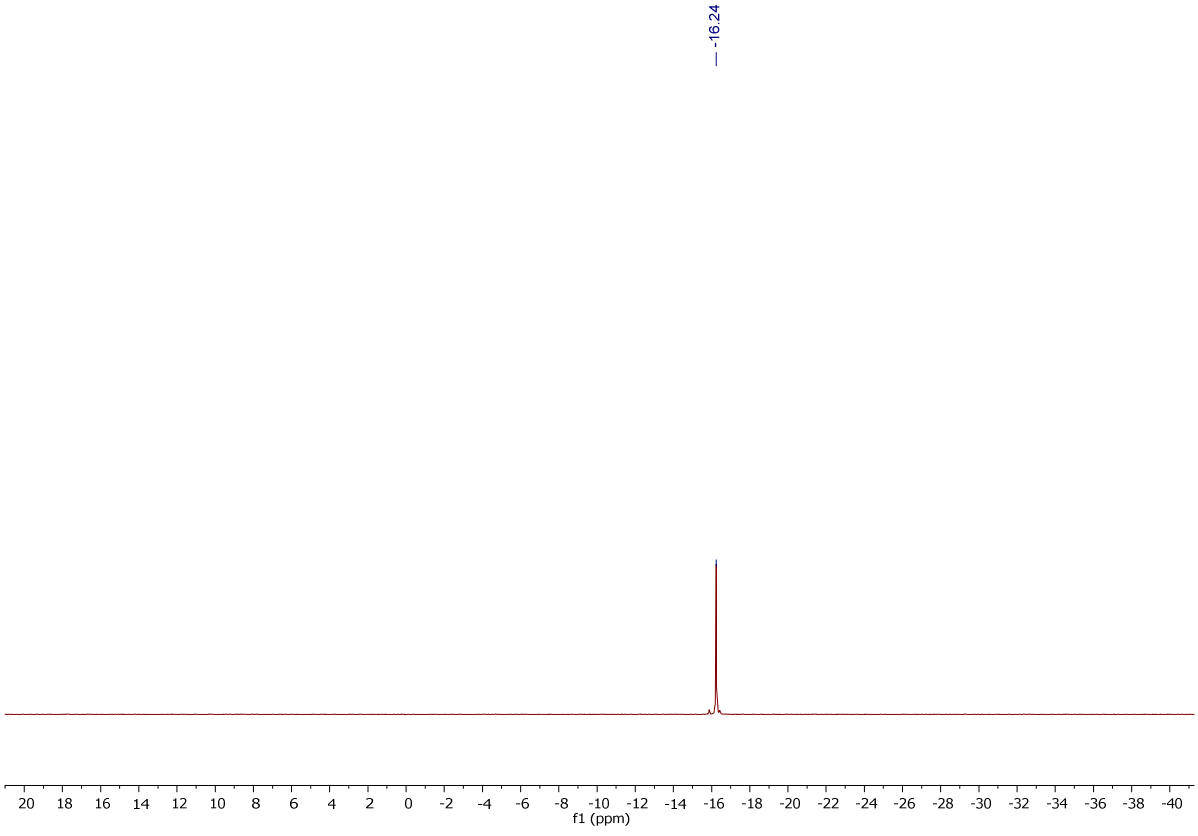
HMBC NMR spectrum, compound **2**, $CDCl_3$, room temperature



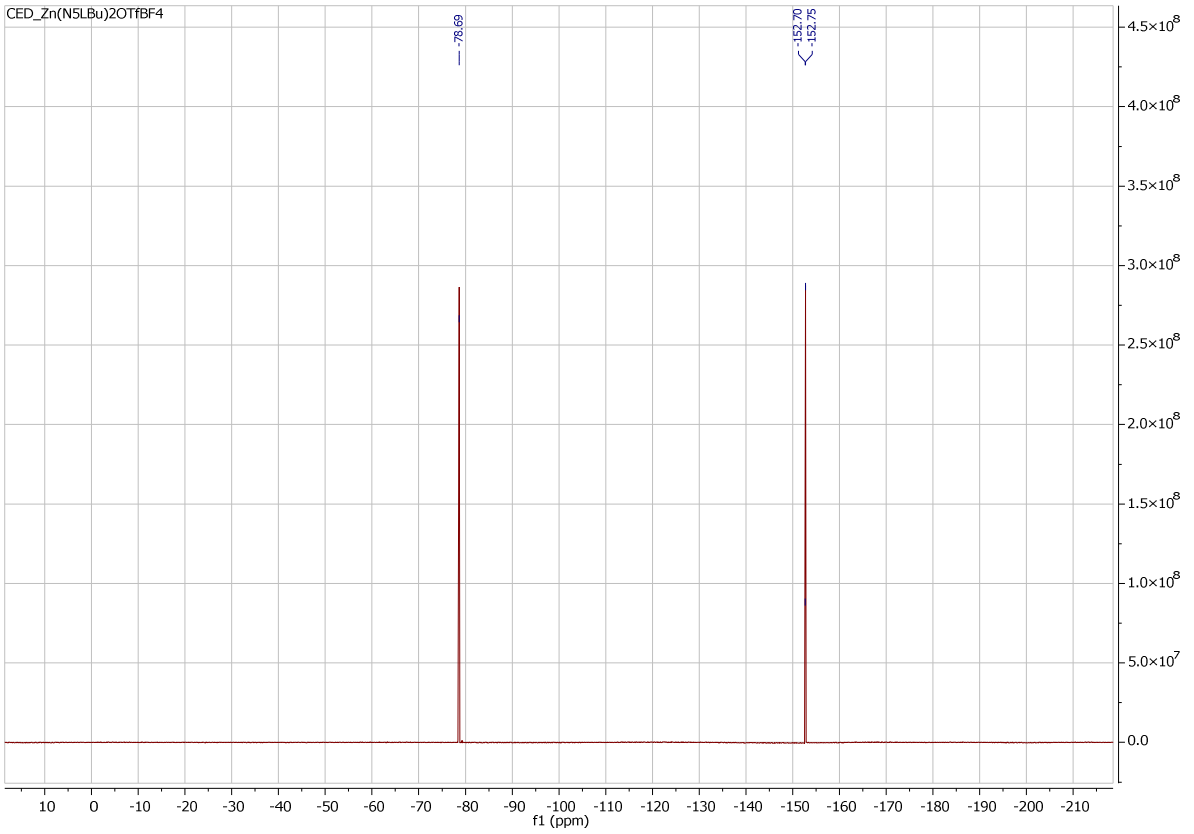
HMBC NMR spectrum (enlarged), compound **2**, $CDCl_3$, room temperature



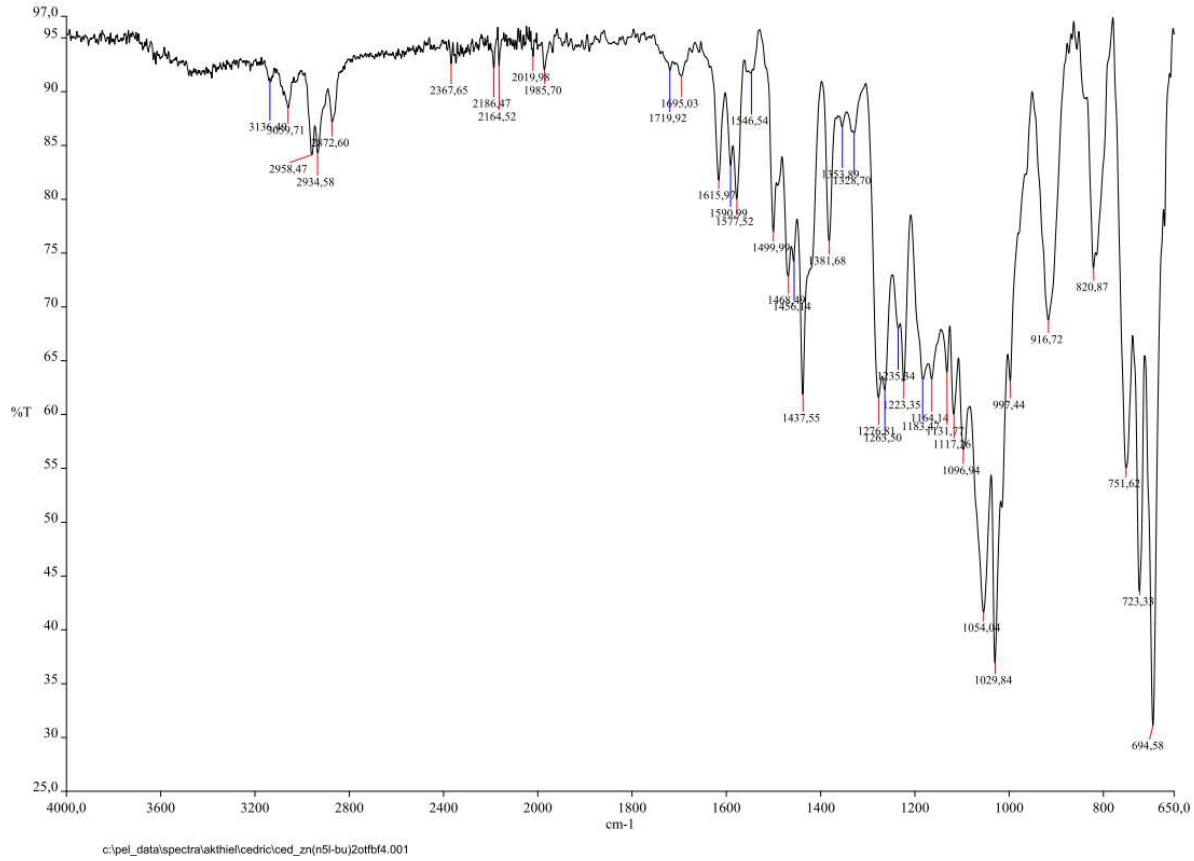
^{31}P NMR spectrum, compound **2**, 162.0 MHz, $CDCl_3$, room temperature



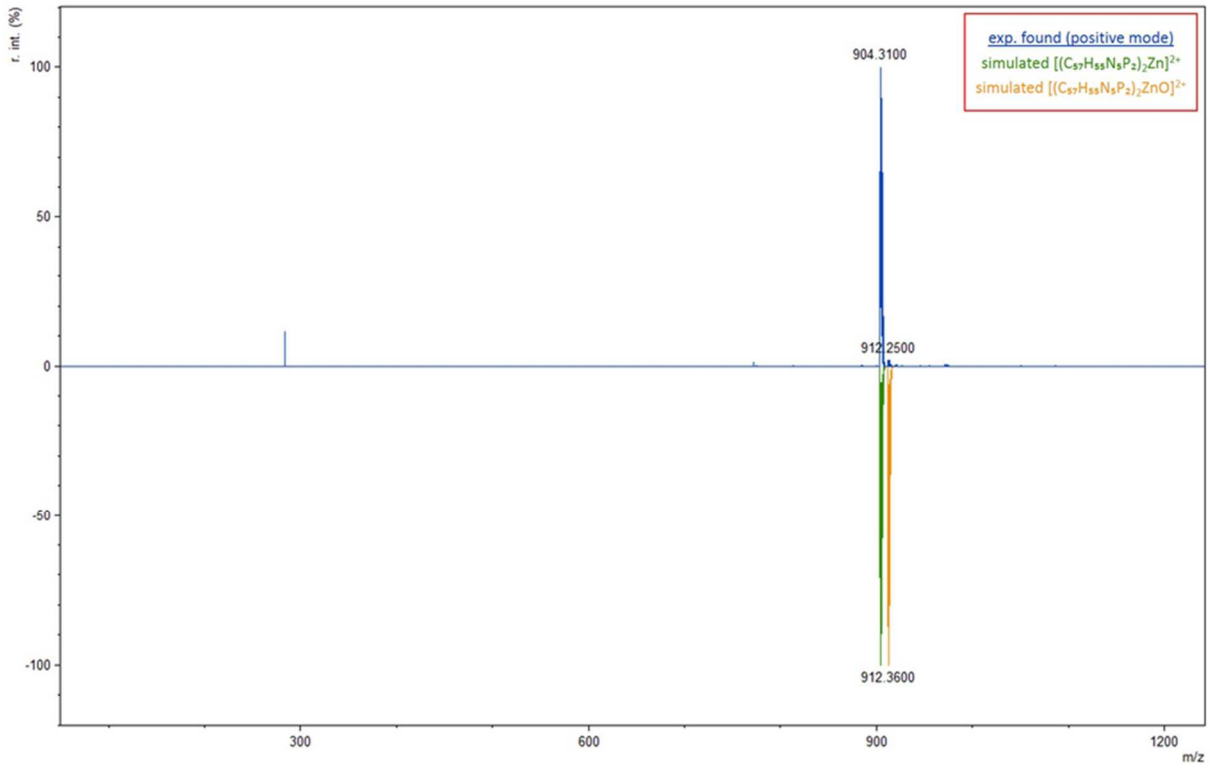
^{19}F NMR spectrum, compound **2**, 362.0 MHz, $CDCl_3$, room temperature



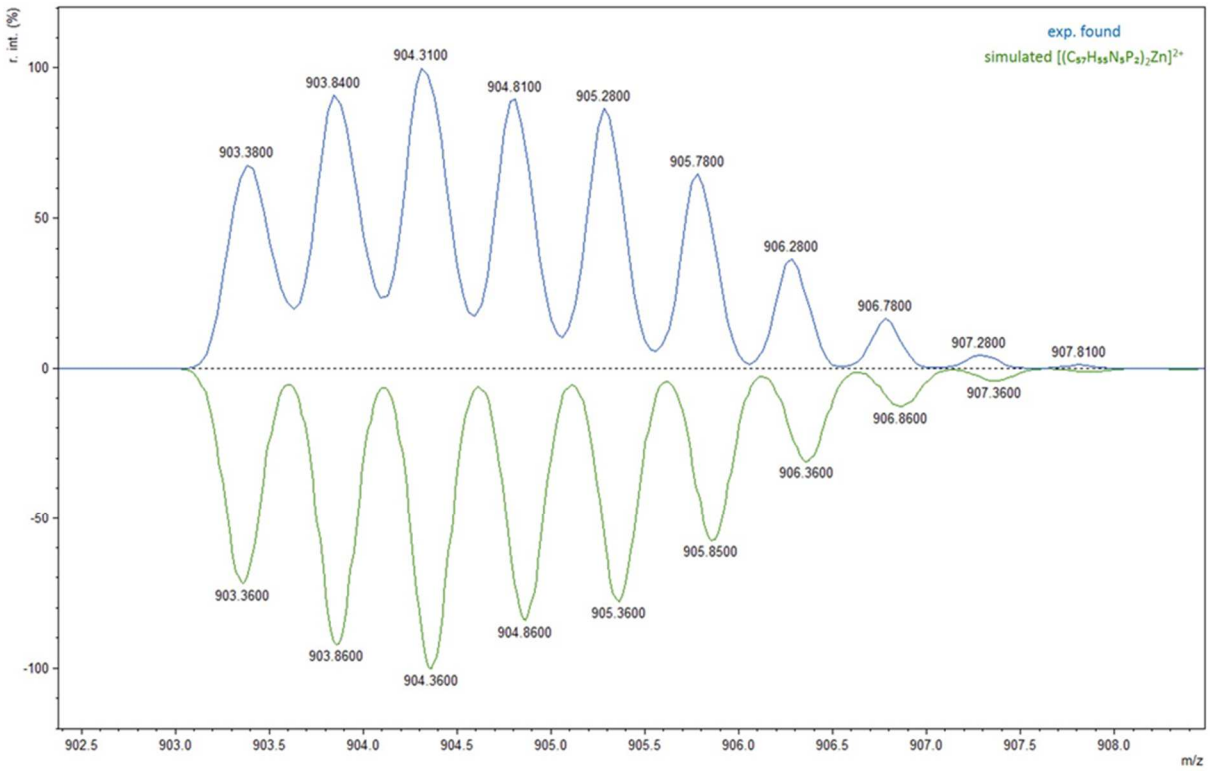
IR spectrum, compound **2**, ATR



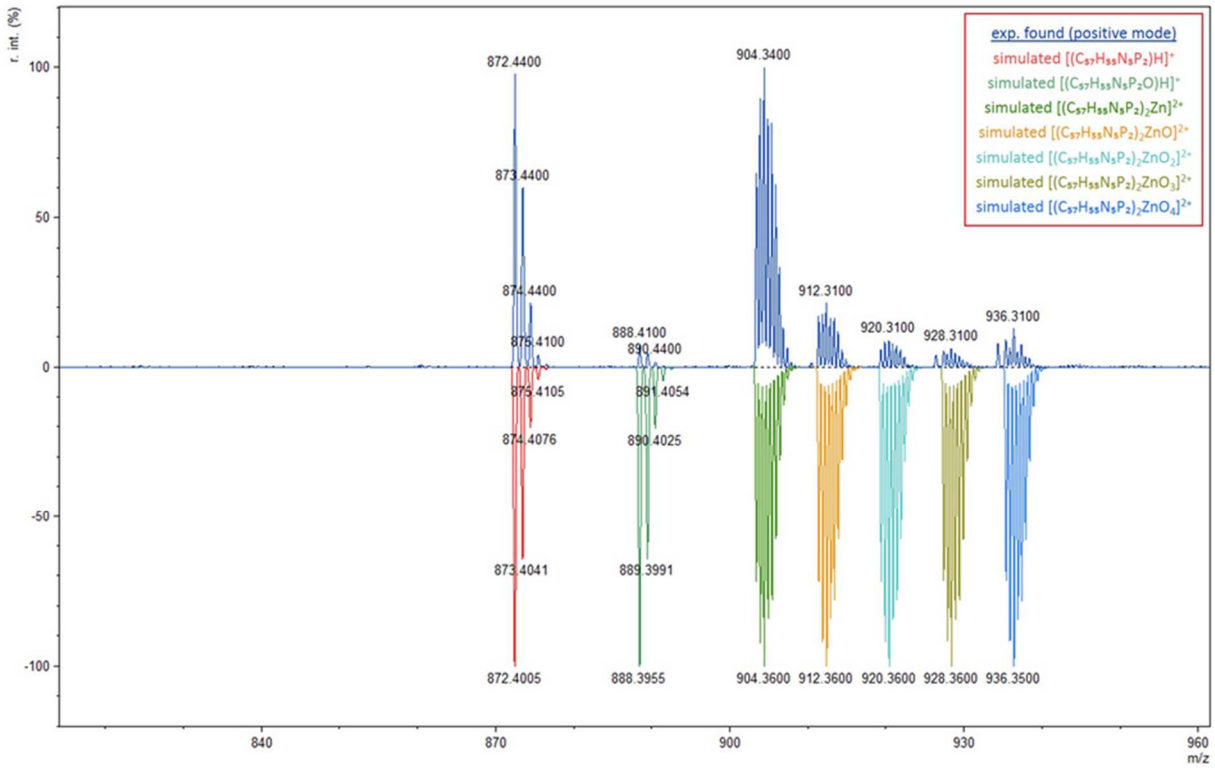
ESI-MS spectrum, compound **2**, positive mode



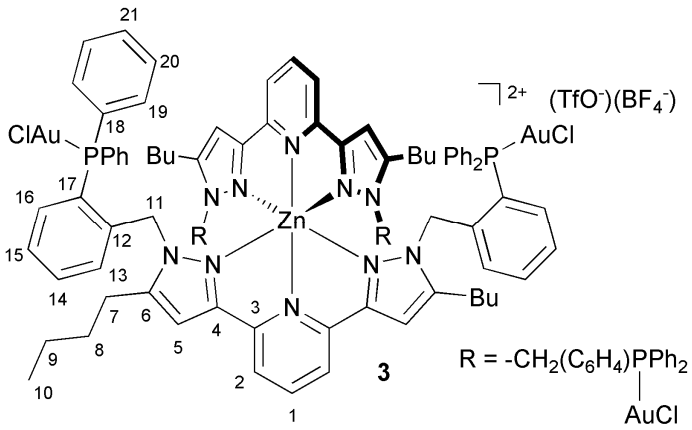
ESI-MS spectrum (enlarged), compound **2**, positive mode



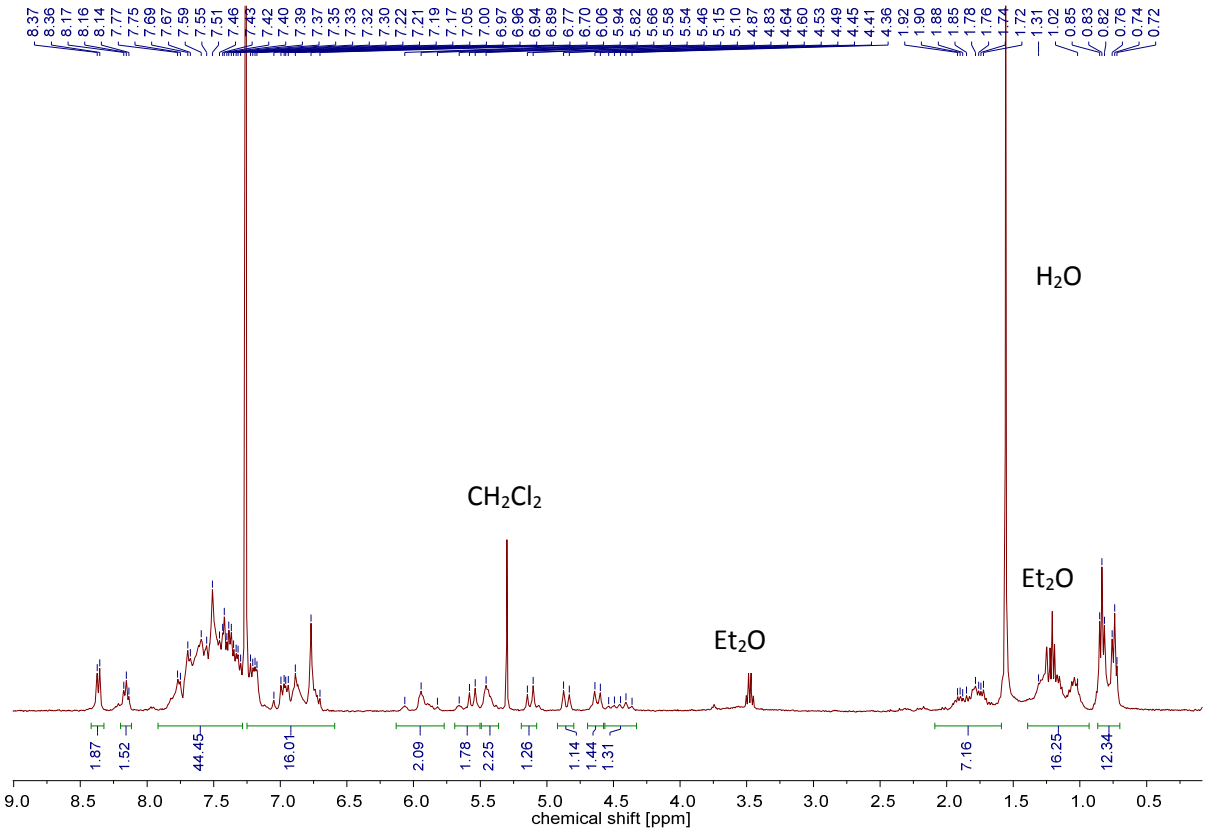
ESI-MS spectrum (enlarged), compound **2**, positive mode, cascade of oxidations



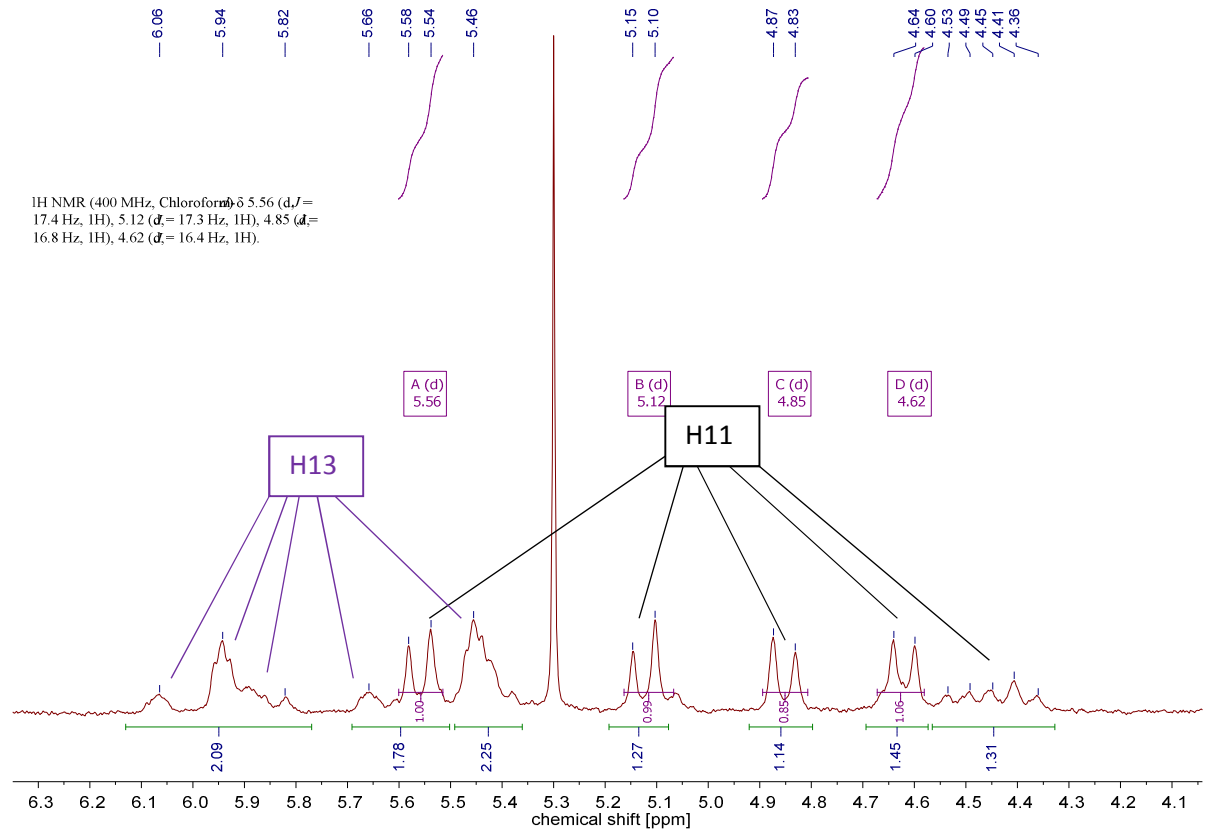
[Bis(2,6-bis(*N*-benzyl-*o*-diphenylphosphine-5-butylpyrazol-3-yl)pyridine)di(chloridogold(I))zinc(II)] tetrafluoroborate triflate (3): 39.9 mg (19.5 µmol) of the homoleptic zinc(II) complex **2** was dissolved in 12 mL dichloromethane and added slowly to a solution of 25 mg (78.0 µmol) of chlorido(tetrahydrothiophene)gold(I) in 10 mL of dichloromethane. The colorless solution was stirred for 16 h at room temperature before the solvent was removed under reduced pressure and the colorless residue was suspended in 20 mL of diethylether. It was isolated by filtration and was washed twice with 15 mL of *n*-pentane. Drying under reduced pressure resulted in a colorless solid. Yield: 42 mg (14.1 µmol, 72%). Anal. calcd. for $C_{115}H_{110}Au_4BCl_4F_7N_{10}O_3P_4SZn$: C 46.43, H 3.73, N 4.71, S 1.08; found: C 46.36, H 3.74, N 4.75, S 0.94. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.36 (t, $^3J_{HH}$ = 8.0 Hz, H2), 8.16 (d, $^3J_{HH}$ = 8.0 Hz, H1), 7.77-6.65 (m, H_{Ar}), 6.06, 5.94, 5.90, 5.82, 5.66, 5.46 (6×m, H13), 5.56, 5.12, 4.85, 4.62, 4.51, 4.47, 4.43, 4.39 (7×d, $^2J_{HH}$ ca. 17 Hz,H11), 1.98-1.65 (m, H7), 1.32-1.10 (m, H8), 1.10-0.95 (m, H9), 0.74 (t, $^3J_{HH}$ = 8.0 Hz, H10). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 21.91, 21.68, 21.44, 20.90, 20.35, 20.28 (6×s). ^{19}F NMR (376.0 MHz, $CDCl_3$): δ -78.7 (s, TfO^-), -152.7 (s, BF_4^-). ESI-MS: m/z calcd. for $[C_{114}H_{110}Au_4Cl_4N_{10}P_4Zn]^{2+}$ = 1367.23, found 1367.16, calcd. for $[C_{57}H_{55}Au_2ClN_5P_2]^+$ = 1300.29, found 1300.27.



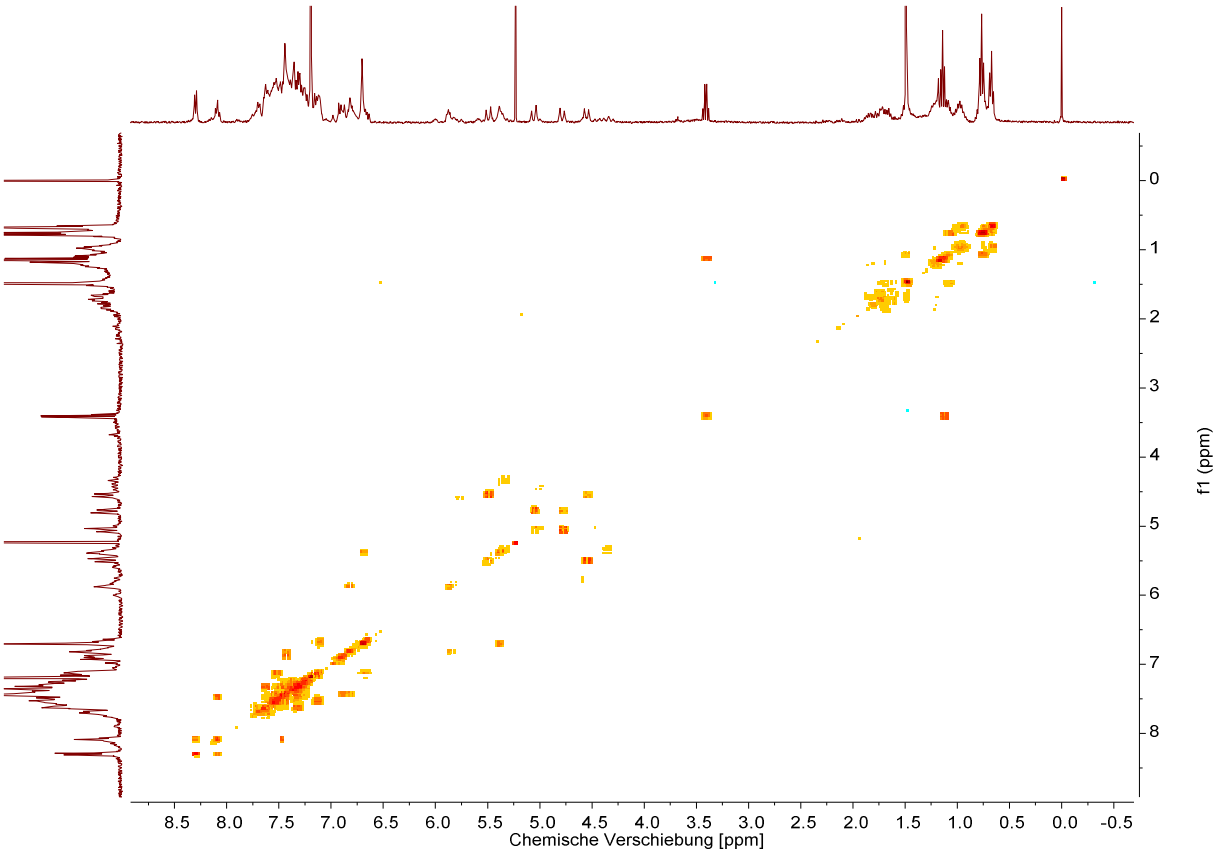
^{1}H NMR spectrum, compound **3**, 400.1 MHz, $CDCl_3$, room temperature



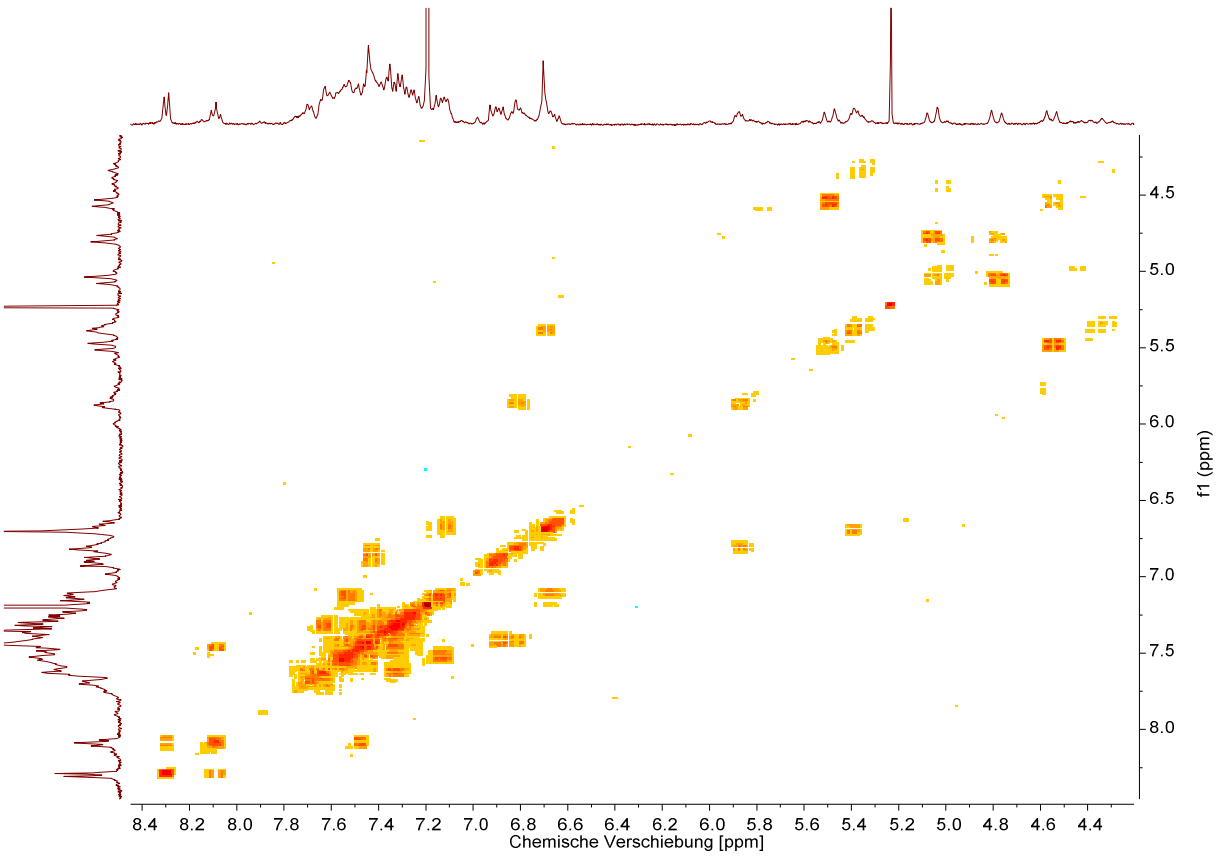
^{1}H NMR spectrum (enlarged), compound **3**, 400.1 MHz, $CDCl_3$, room temperature



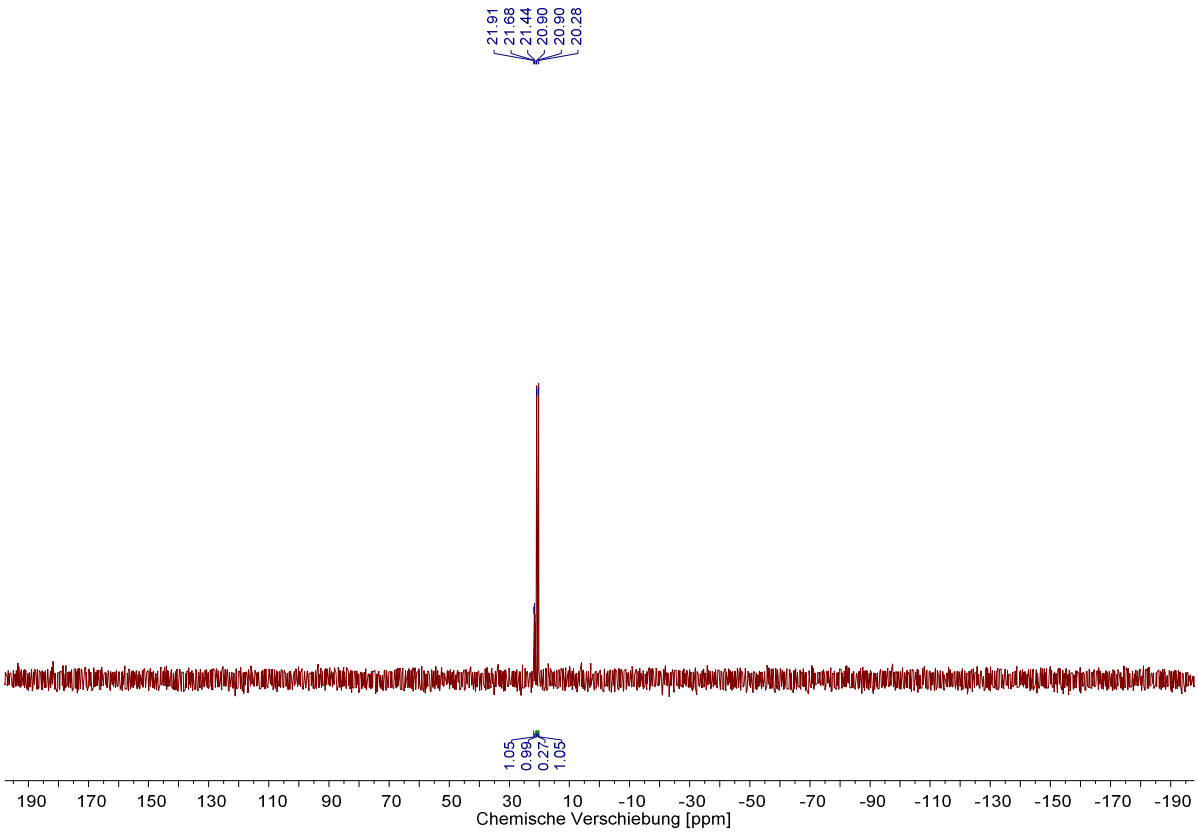
H,H-COSY NMR spectrum, compound **3**, 400.1 MHz, $CDCl_3$, room temperature



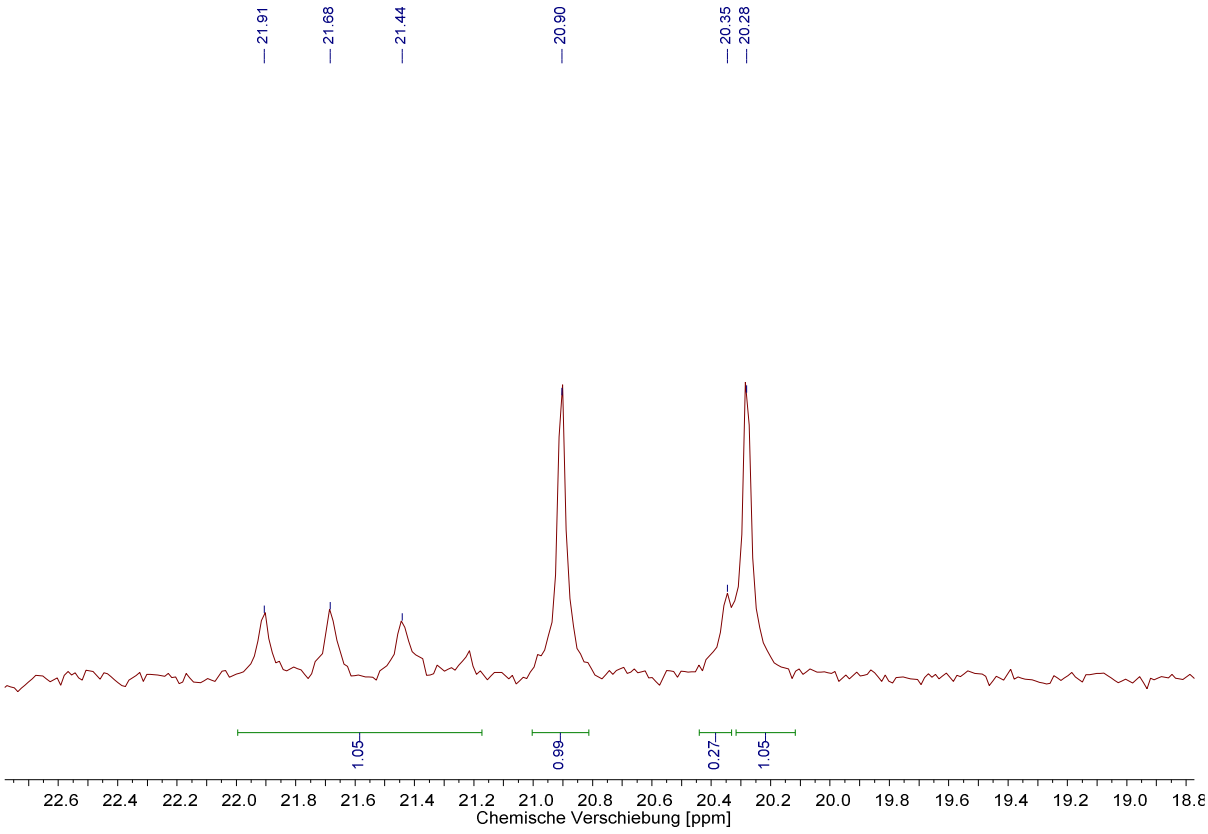
H,H-COSY NMR spectrum (enlarged), compound **3**, 400.1 MHz, $CDCl_3$, room temperature



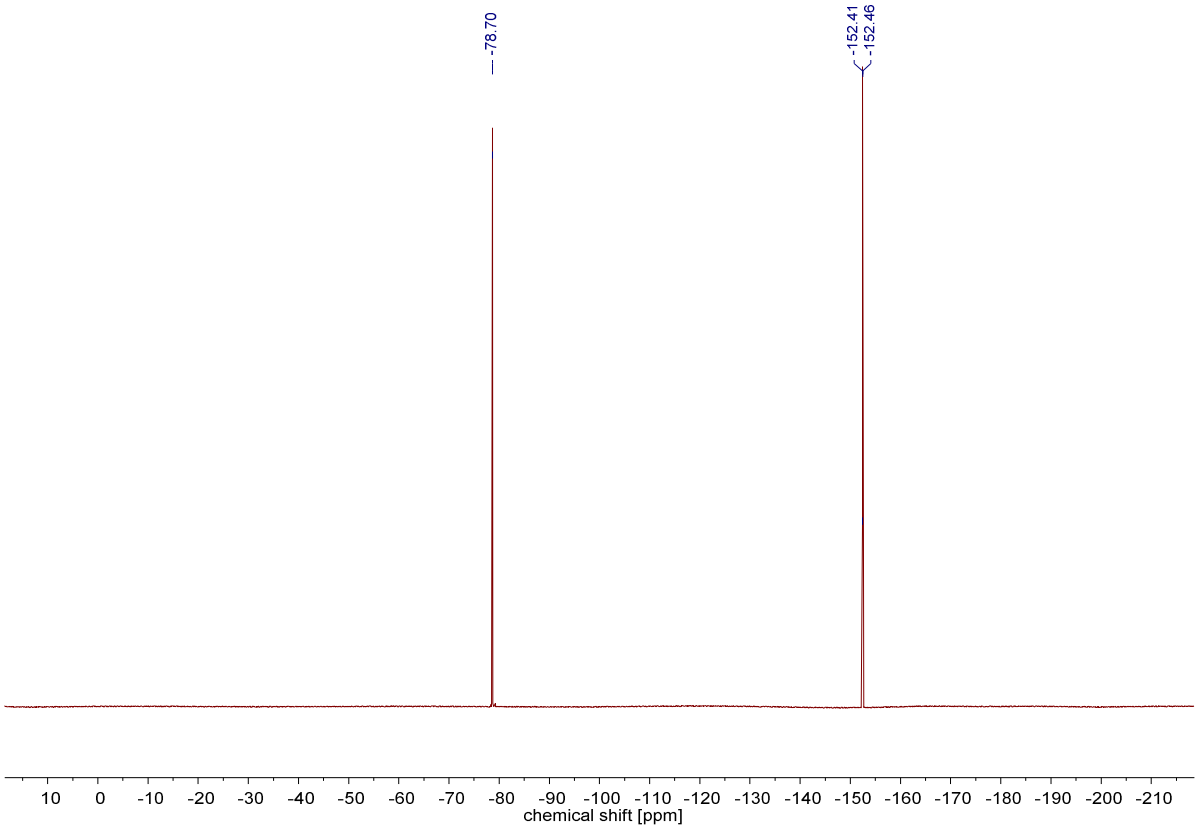
^{31}P NMR spectrum, compound **3**, 162.0 MHz, $CDCl_3$, room temperature



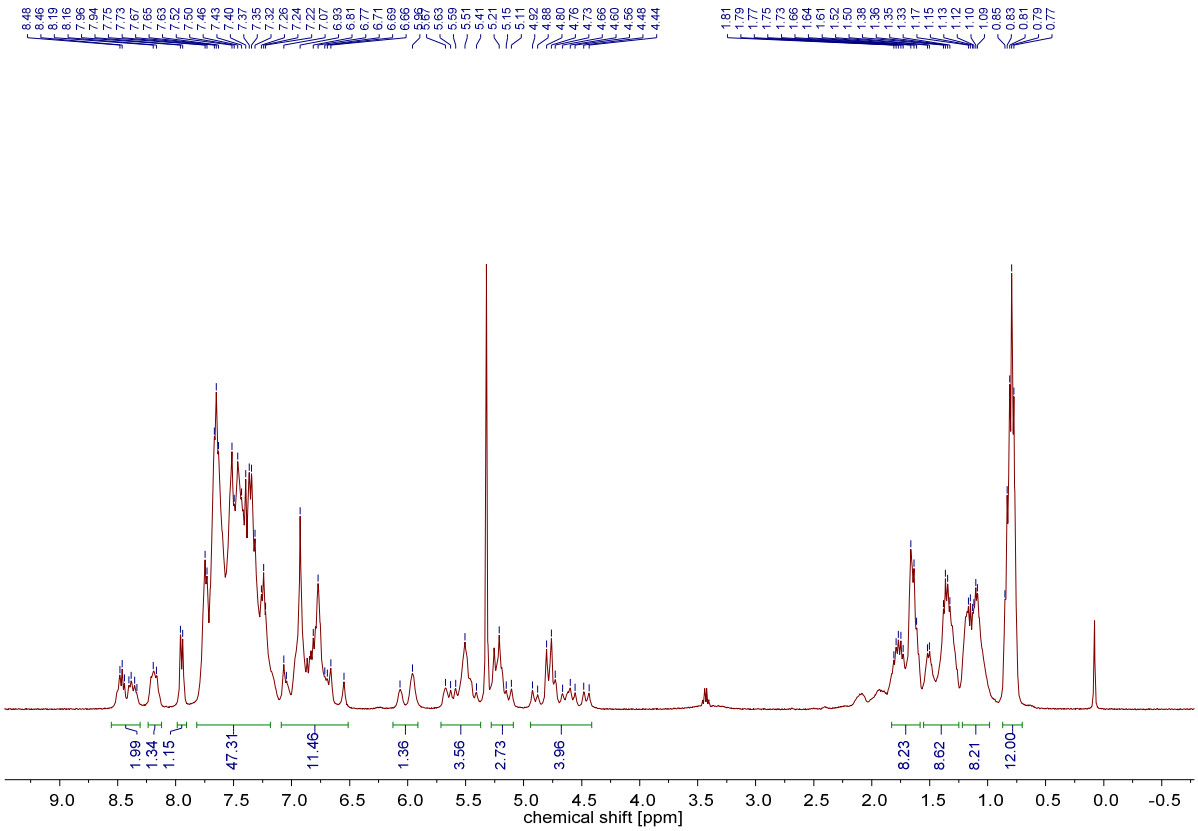
^{31}P NMR spectrum (enlarged), compound **3**, 162.0 MHz, MHz, $CDCl_3$, room temperature



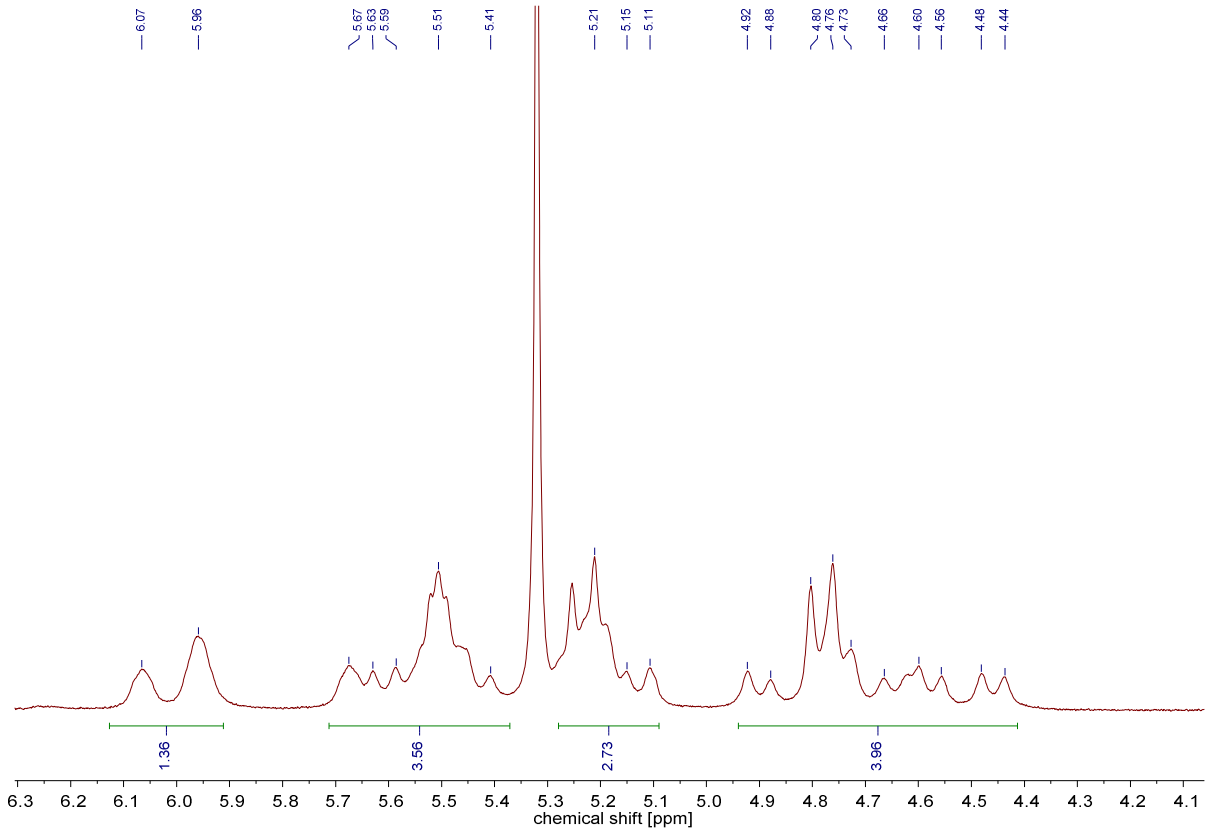
^{19}F NMR spectrum, compound **3**, 362 MHz, $CDCl_3$, room temperature



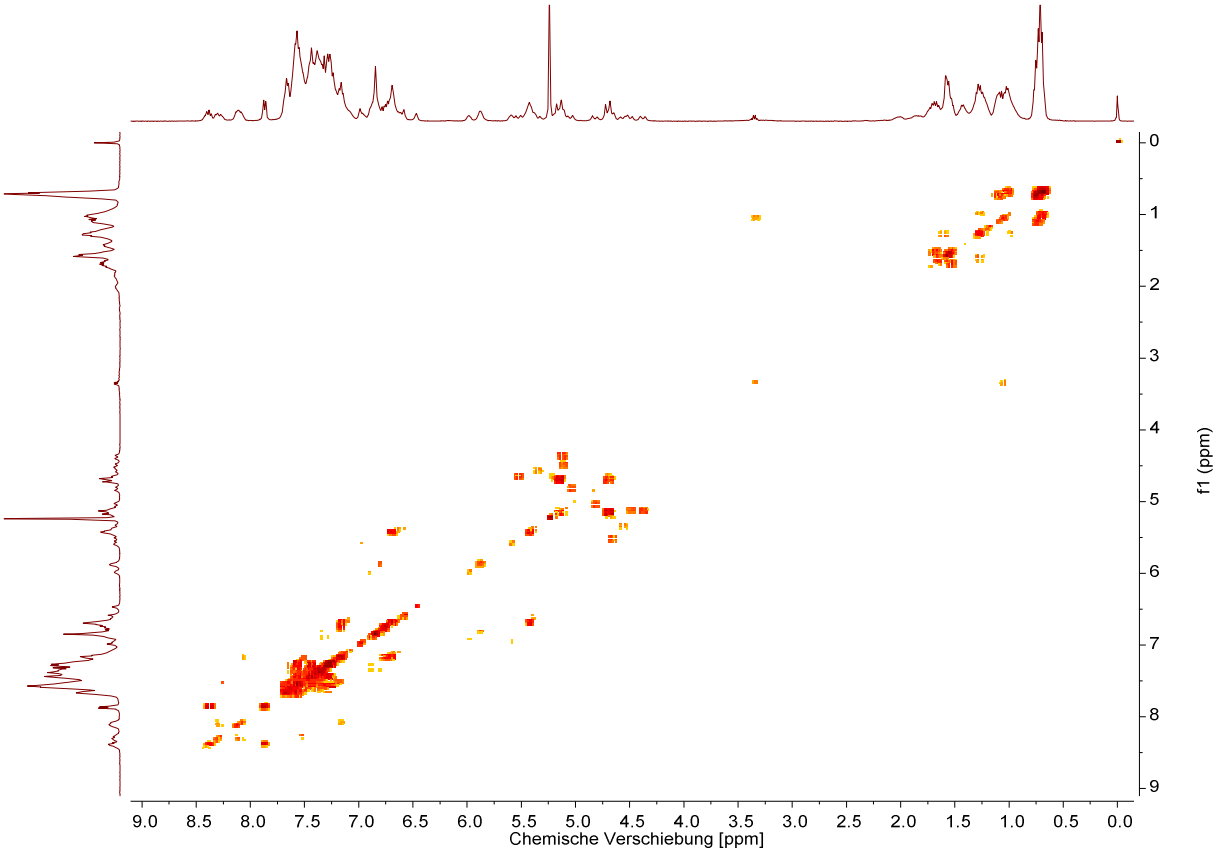
^{1}H NMR spectrum, compound **3**, 400.1 MHz, CD_2Cl_2, room temperature



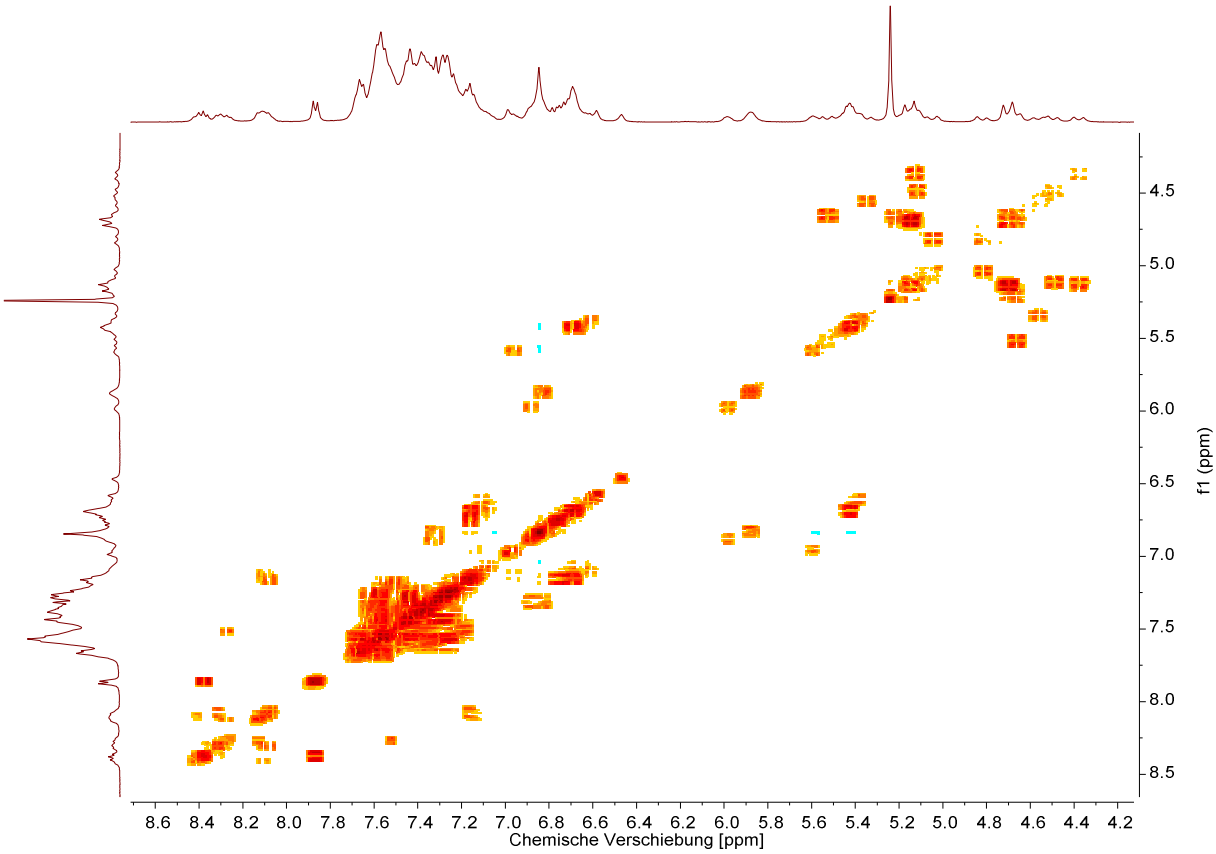
^{1}H NMR spectrum (enlarged), compound **3**, 400.1 MHz, CD_2Cl_2, room temperature



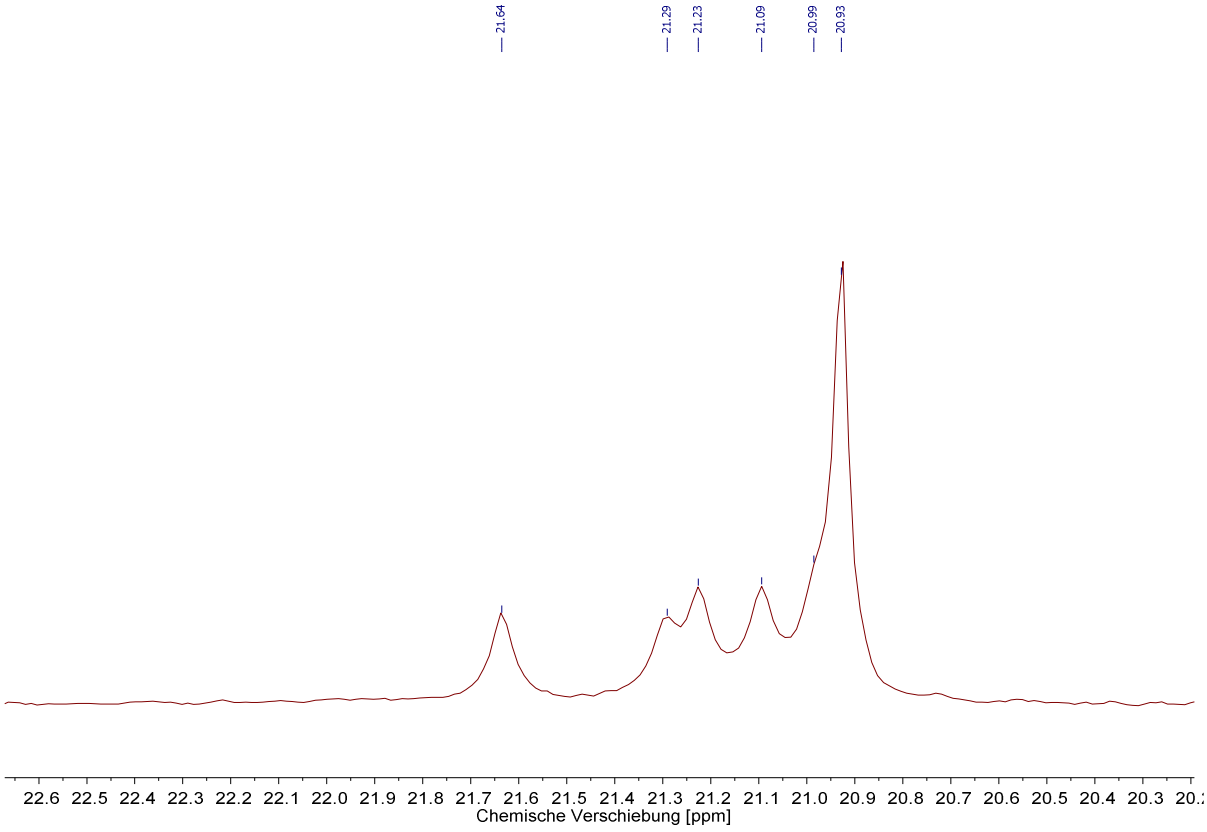
H,H-COSY NMR spectrum, compound **3**, 400.1 MHz, CD_2Cl_2, room temperature



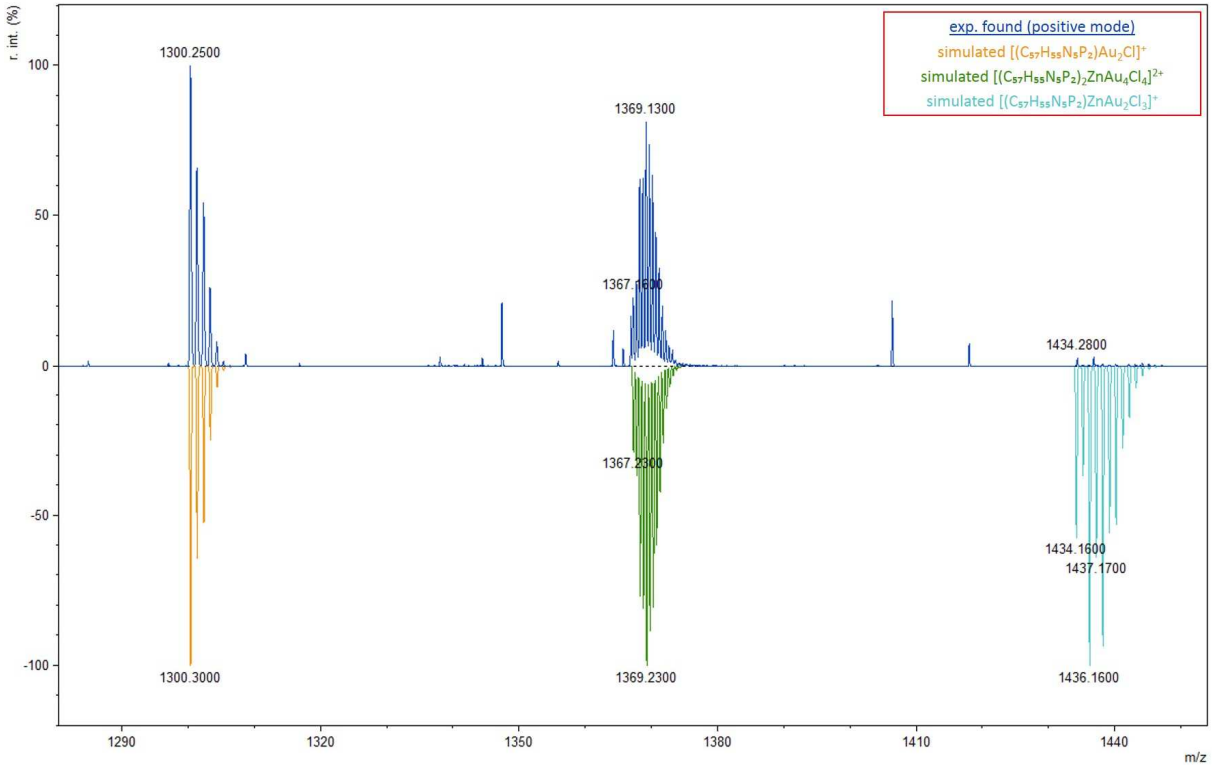
H,H-COSY NMR spectrum (enlarged), compound **3**, 400.1 MHz, CD_2Cl_2, room temperature



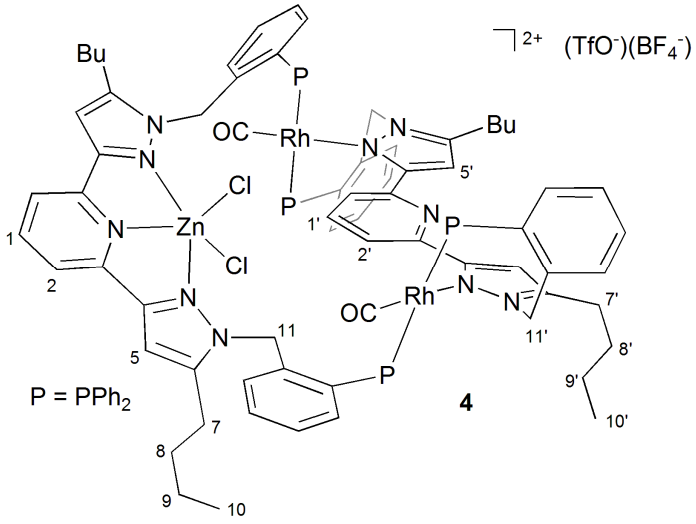
^{31}P NMR spectrum (enlarged), compound **3**, 162.0 MHz, CD_2Cl_2, room temperature



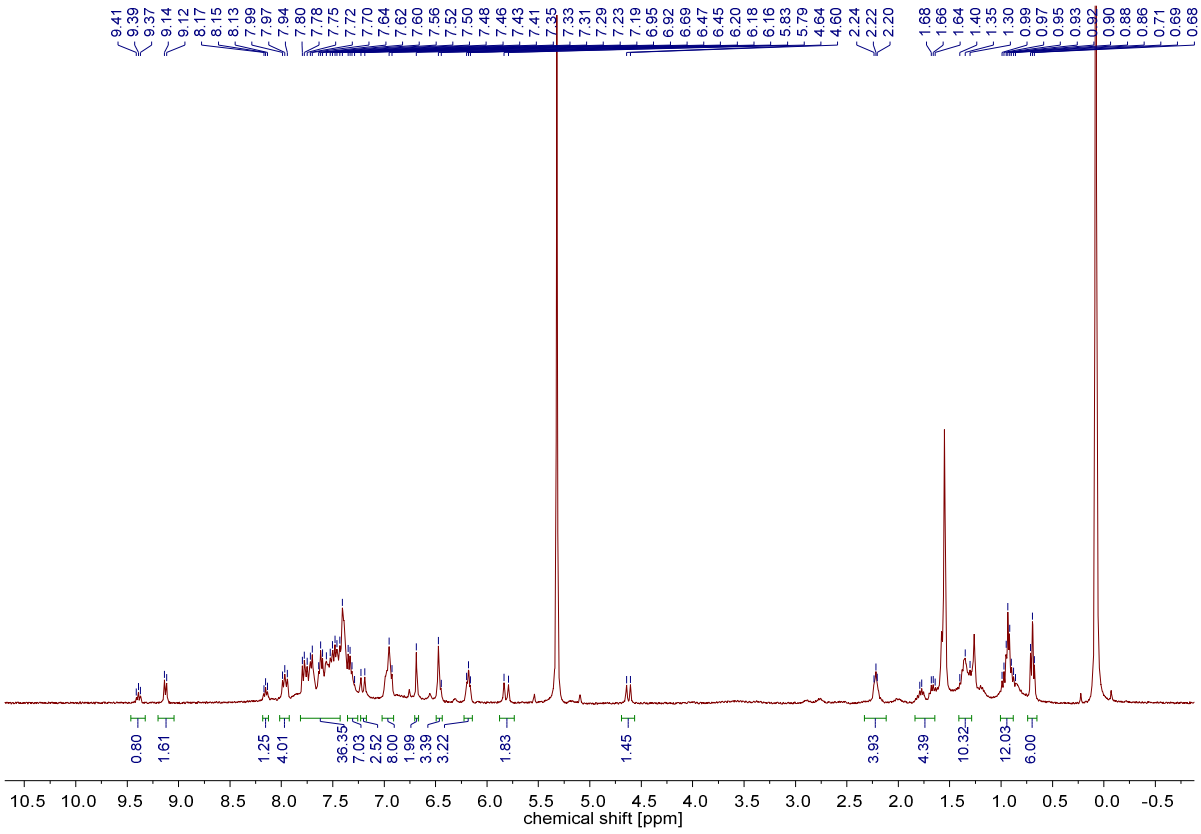
ESI-MS spectrum, compound **3**, positive mode



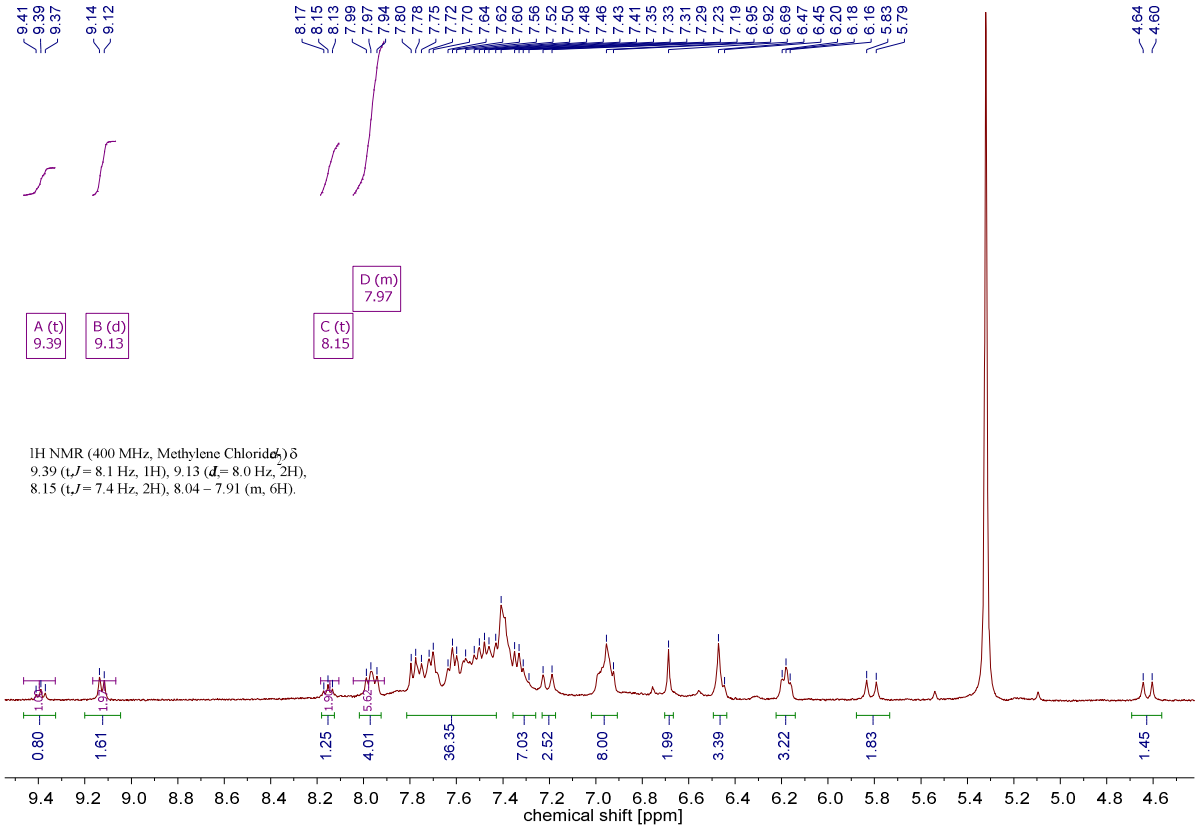
[(Bis((2,6-bis(*N*-benzyl-*o*-diphenylphosphine-5-butylpyrazol-3-yl)pyridine)carbonylrhodium(I))(di-chloridozinc(II))] tetrafluoroborate triflate (4): A solution of 127 mg (62.0 µmol) of the zinc(II) complex **2** in 12 mL of chloroform and a solution of 97.0 mg (62.0 µmol) of [(di-μ-chloridotetracarbonyldirhodium(I)] in 12 mL of chloroform were added parallel and drop-wise to a flask containing 5 mL of chloroform over a period 30 min under constant stirring. Hereby a yellow precipitate forms. The reaction mixture was stirred for additional 60 min at room temperature. The yellow precipitate was isolated by filtration, redissolved in 5 mL of dichloromethane and crystallized by slow diffusion of diethylether into this solution. Yield: 131 mg (55.0 µmol, 88%). Anal. calcd. for $C_{117}H_{110}BCl_2F_7N_{10}O_5P_4Rh_2SZn{\cdot}CH_2Cl_2$: C 57.54, H 4.58, N 5.69, S 1.30; found: C 57.88, H 4.79, N 5.75, S 1.32. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 9.39 (t, $^3J_{HH}$ = 8.1 Hz, 1H, H1'), 9.13 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H2'), 8.15 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H1), 7.99-7.95 (m, 4H), 7.77 (t, $^3J_{HH}$ = 7.4 Hz, 2H, H2), 7.83-7.24 (m, 50H), 7.21 (d, $^2J_{HH}$ = 15.1 Hz, 2H, H11a), 6.95 (d, ^2J = 17.0 Hz, 2H, H11'b), 6.95 (m, 6H), 6.69 (s, 2H, H5 or H5'), 6.47-6.45 (m, 3H, H5 or H5' andH_{Ar}), 6.20-6.16 (m, 3H), 5.81 (d, ^2J = 17.0 Hz, 2H, H11'a), 4.62 d, $^2J_{HH}$ = 15.2 Hz, 2H, H11b), 2.24 (t, $^3J_{HH}$ = 8.0 Hz, 4H, H7 or H7'), 1.78, 1.66 (2×m, 4H, H7 or H7'), 1.41-1.29 (m, 8H, H8, H8'), 1.01-0.85 (m, 8H, H9, H9'), 0.93 (t, 6H, $^3J_{HH}$ = 8.0 Hz, H10 or H10'), 0.69 (t, $^3J_{HH}$ = 8.0 Hz, 6H, H10 or H10'). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 21.03 (dd, $^1J_{RhP}$ = 294.5, $^2J_{PP}$ = 122.1 Hz), 14.96 (dd, $^1J_{RhP}$ = 294.0, $^2J_{PP}$ = 122.8 Hz). ^{19}F NMR (376.0 MHz, CD_2Cl_2): δ -78.87 (s, TfO^-), -152.93 (s, BF_4^-). IR (ATR, cm^{-1}): $\tilde{\nu}$ 3057w, 2961m, 2932w, 2872w, 2000s ν_{CO}(antisym.), 1978s ν_{CO}(sym.), 1615w, 1575w, 1549w, 1500w, 1468m, 1436s, 1416m, 1382w, 1260vs, 1223w, 1187w, 1142m, 1090vs, 1052vs, 1029vs, 869w, 797vs, 745vs, 693vs.



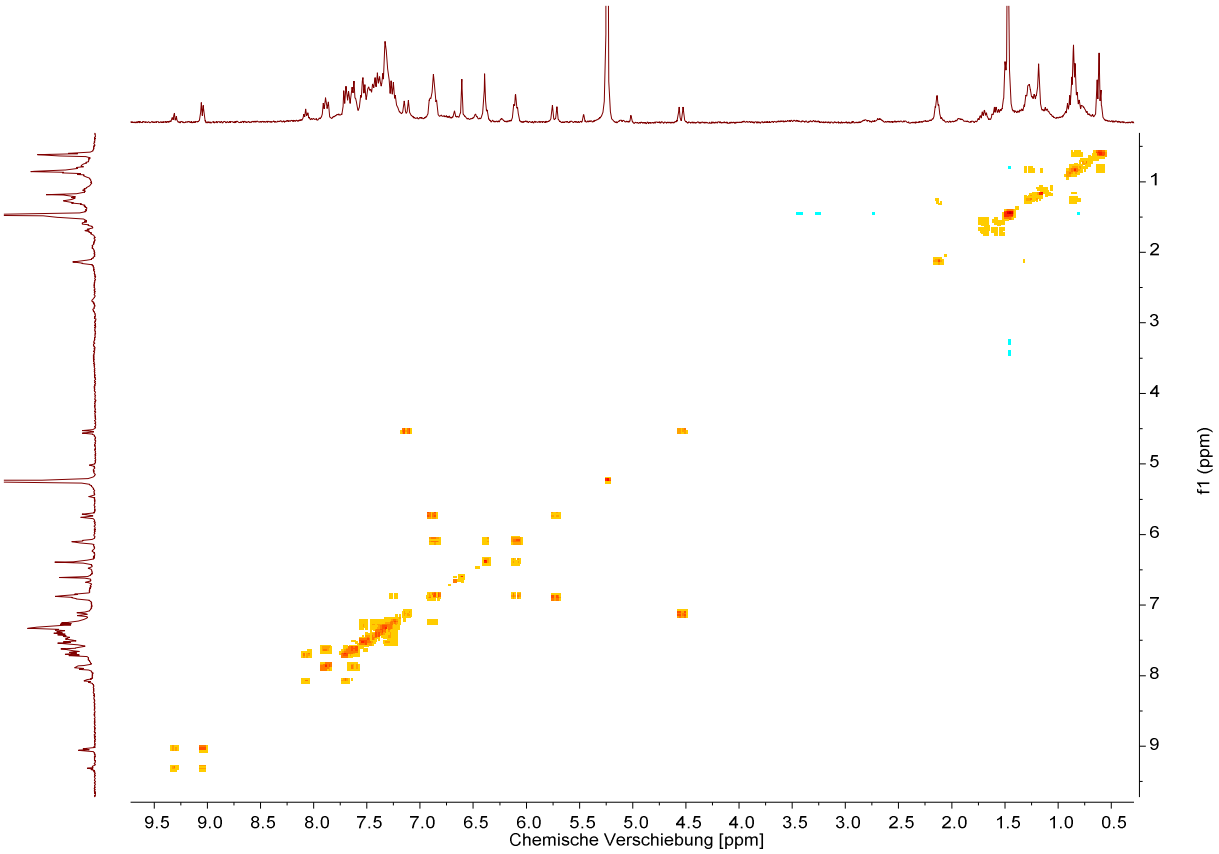
^{1}H NMR spectrum, compound **4**, 400.1 MHz, CD_2Cl_2, room temperature



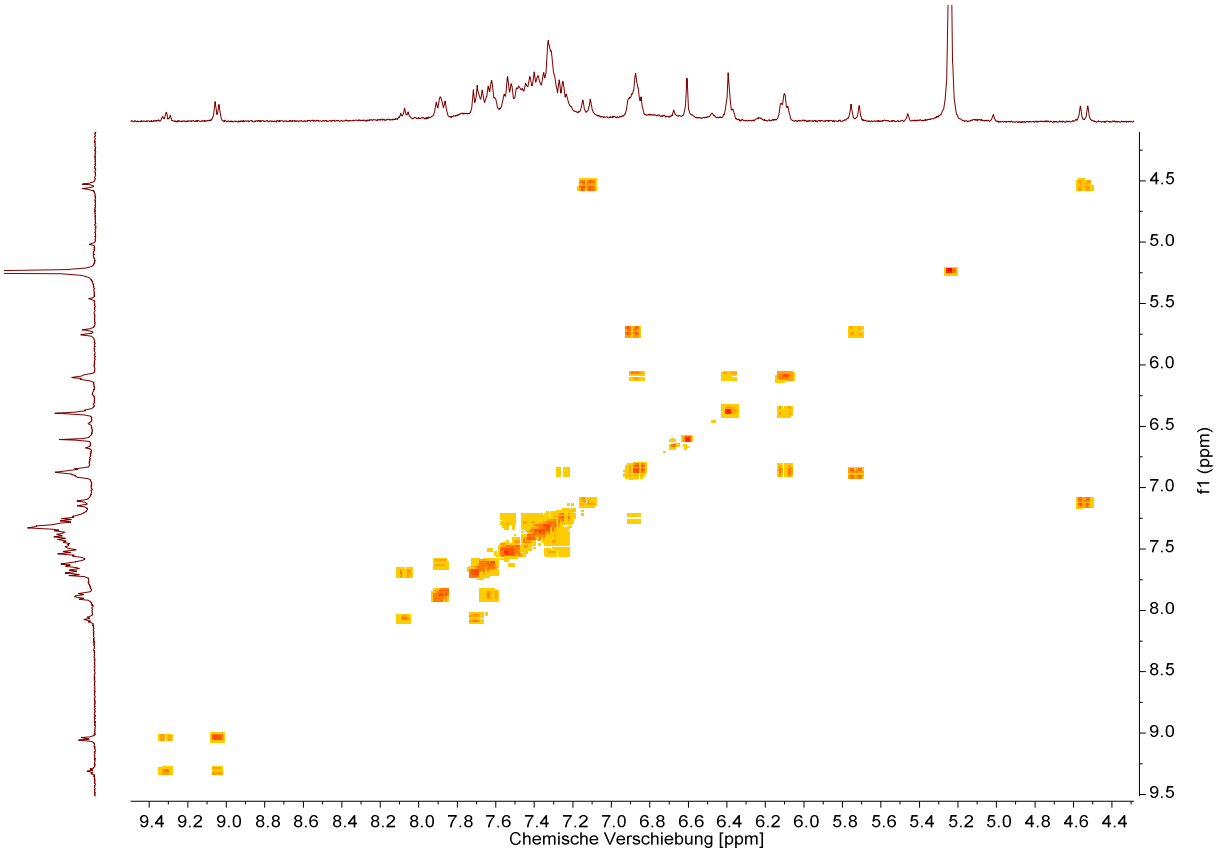
^{1}H NMR spectrum (enlarged), compound **4**, 400.1 MHz, CD_2Cl_2, room temperature



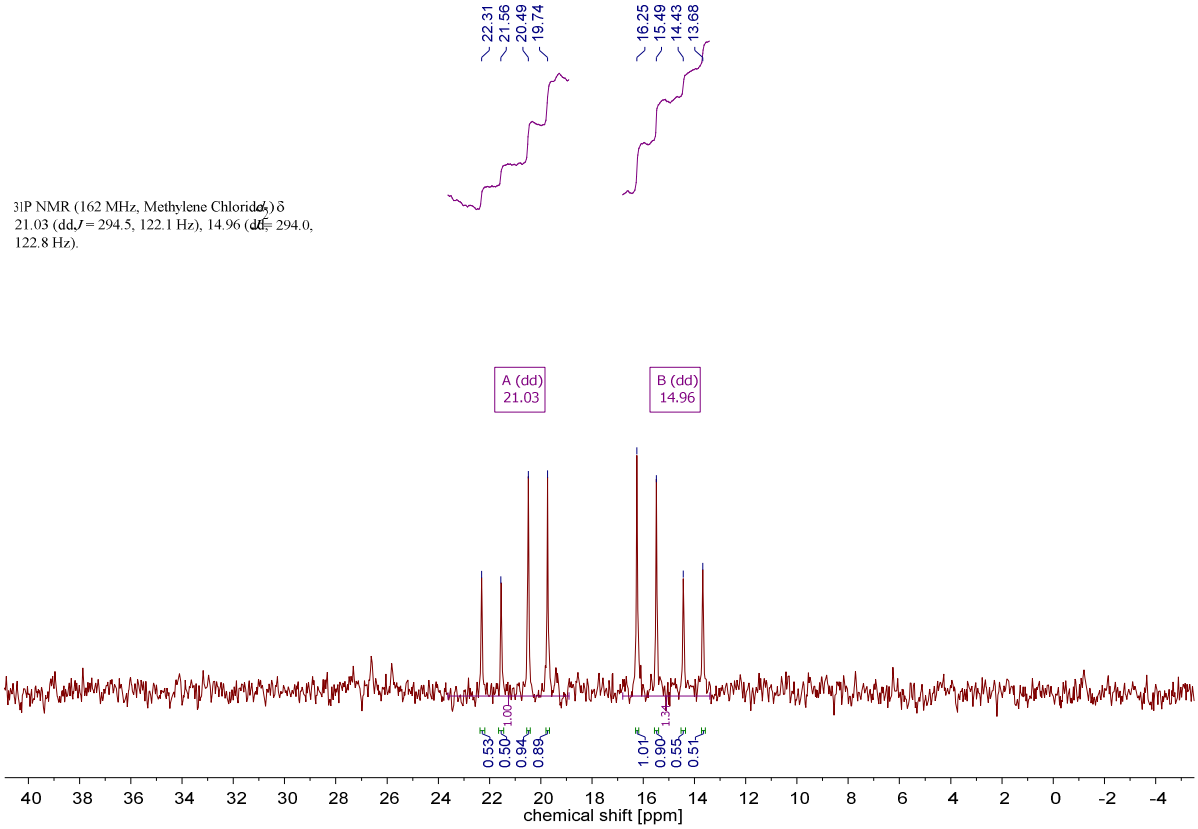
H,H-COSY NMR spectrum, compound **4**, 400.1 MHz, CD_2Cl_2, room temperature



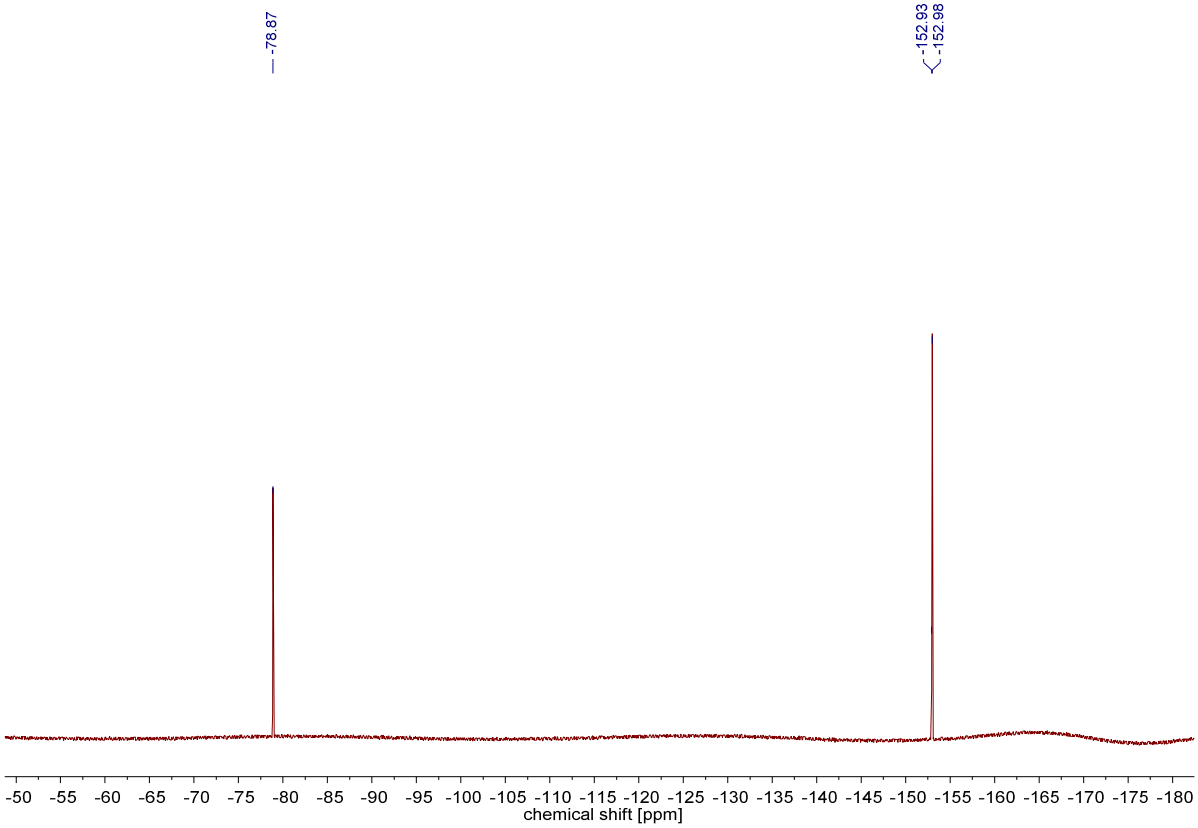
H,H-COSY NMR spectrum (enlarged), compound **4**, 400.1 MHz, CD_2Cl_2, room temperature



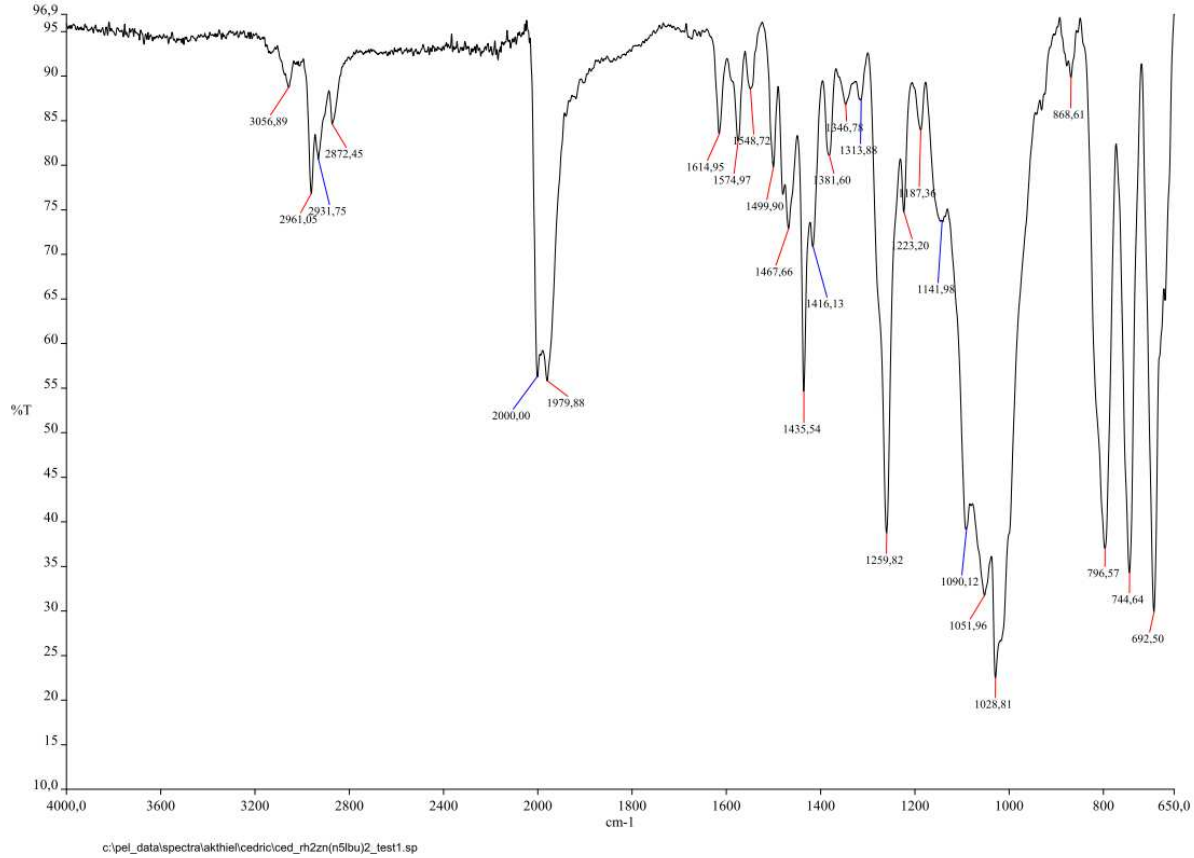
^{31}P NMR spectrum (enlarged), compound **4**, 162.0 MHz, CD_2Cl_2, room temperature



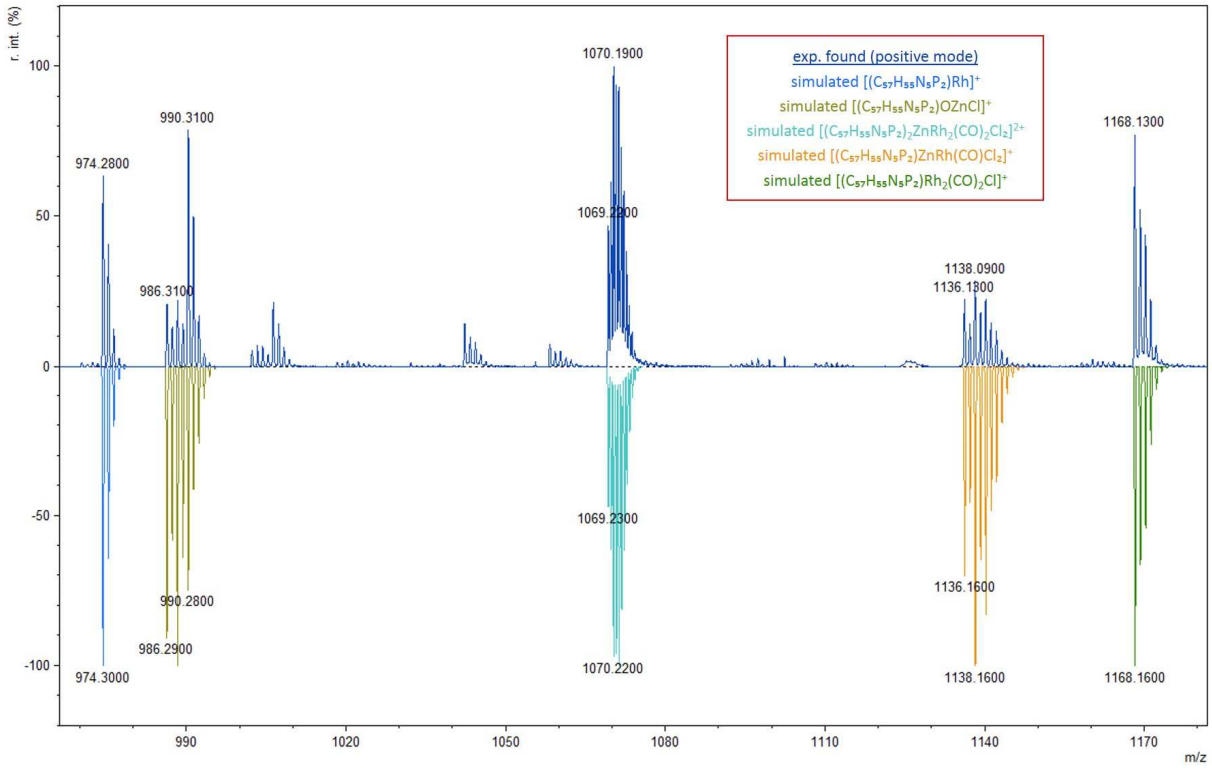
^{19}F NMR spectrum, compound **3**, 362 MHz, $CDCl_3$, room temperature



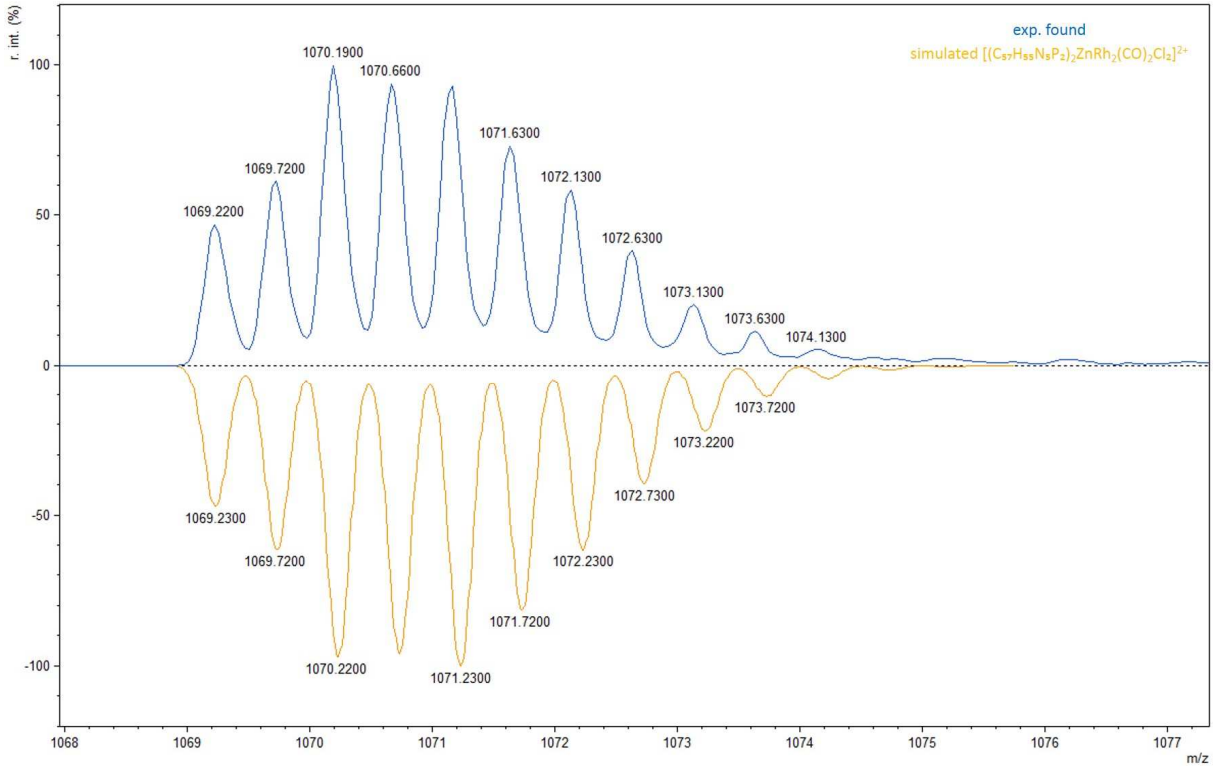
IR spectrum, compound **4**, ATR



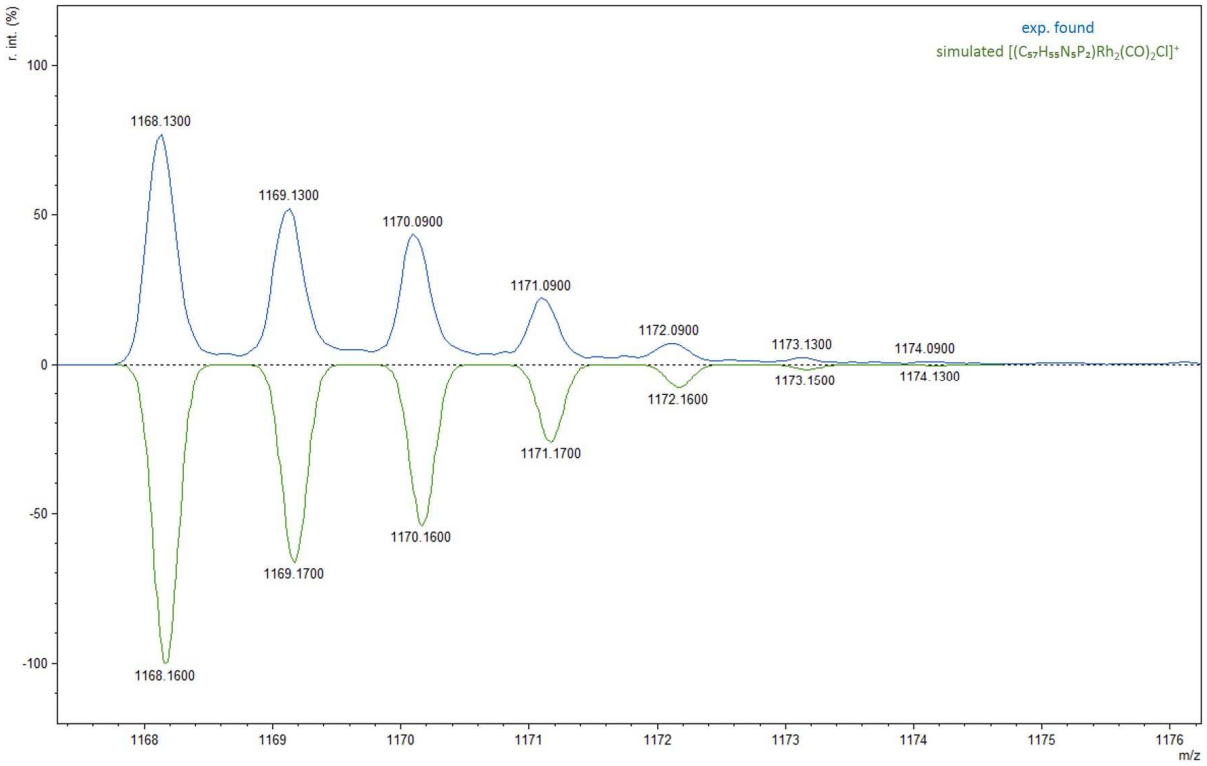
ESI-MS spectrum, positive mode



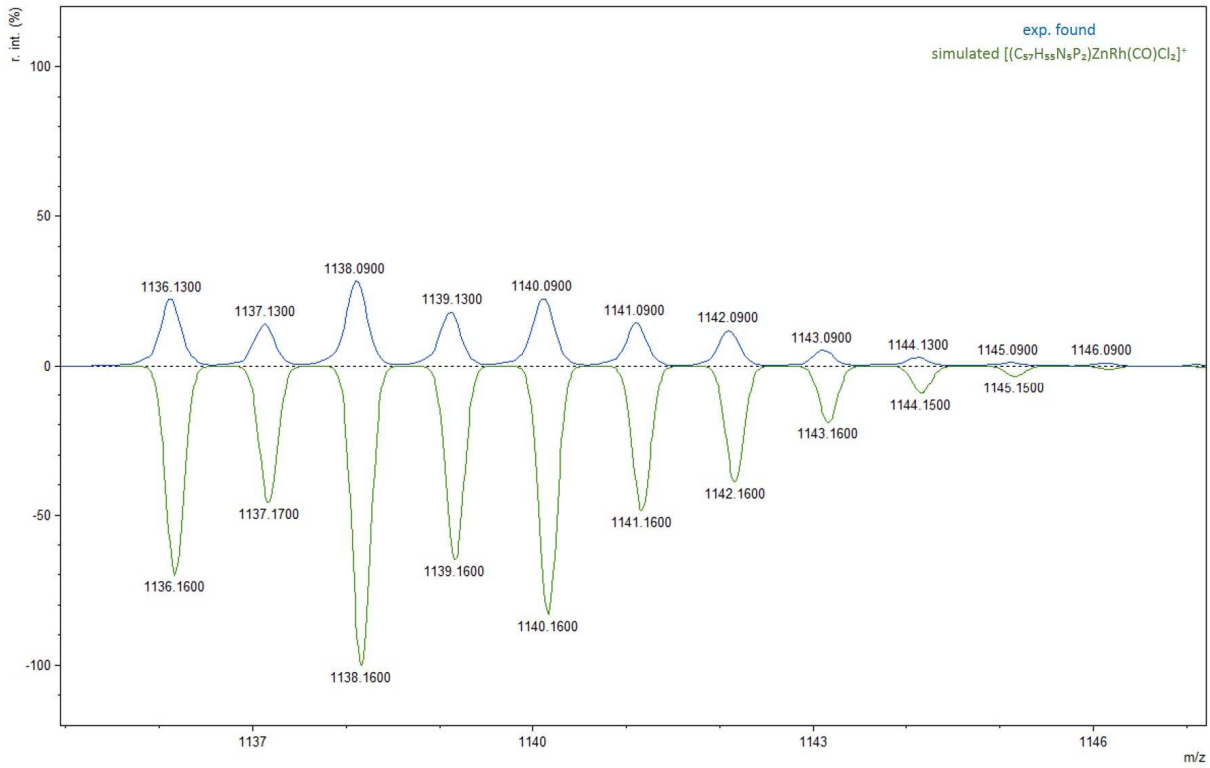
ESI-MS spectrum (enlarged), positive mode



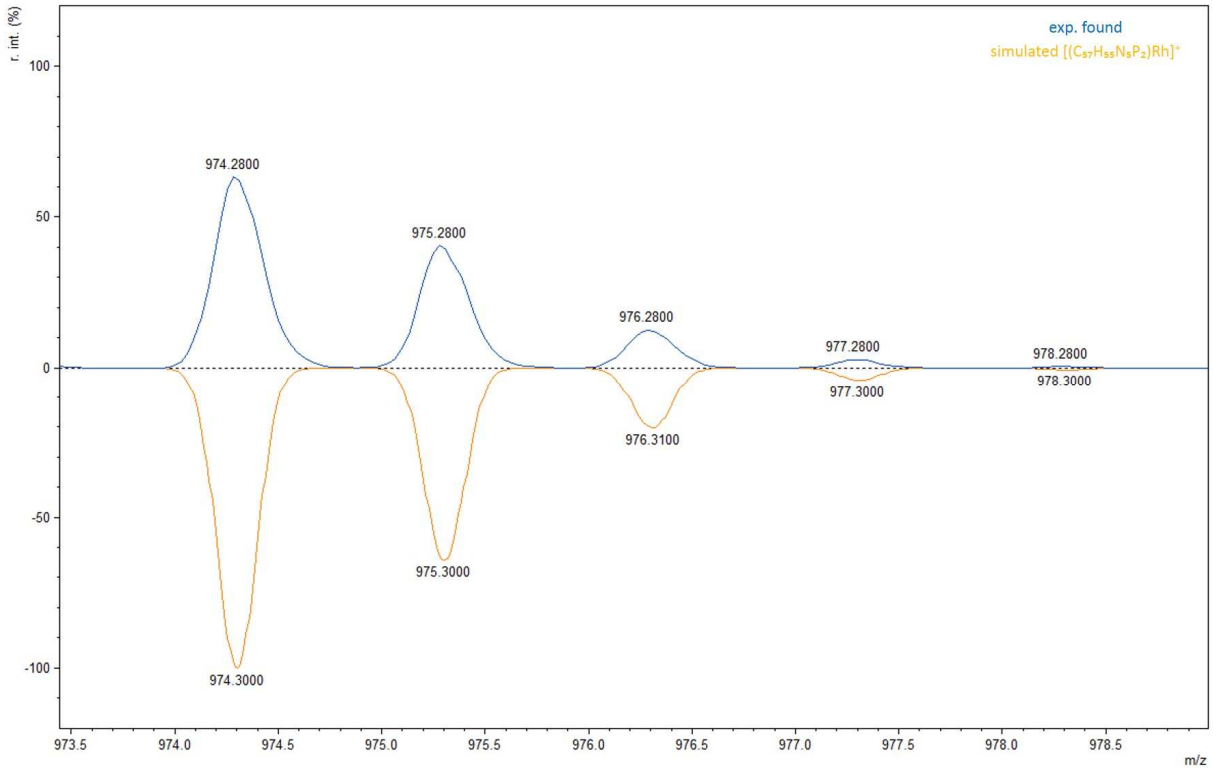
ESI-MS spectrum (enlarged), positive mode



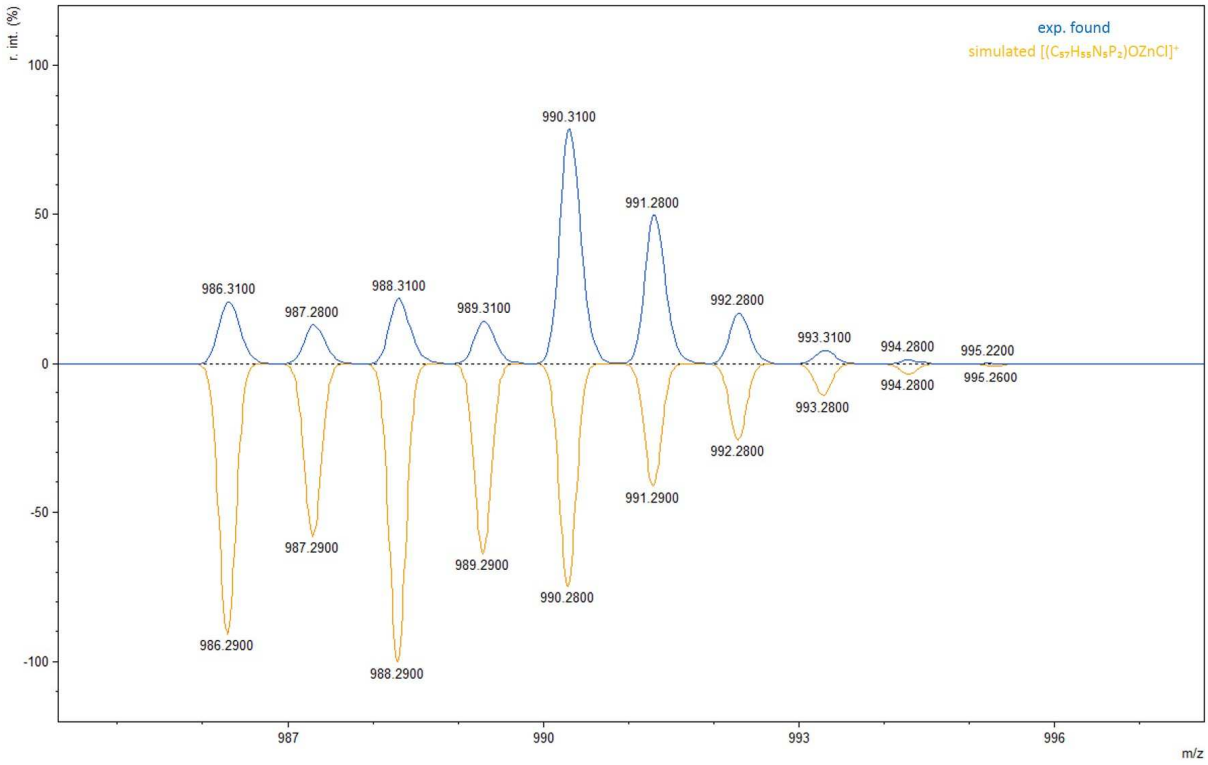
ESI-MS spectrum (enlarged), positive mode



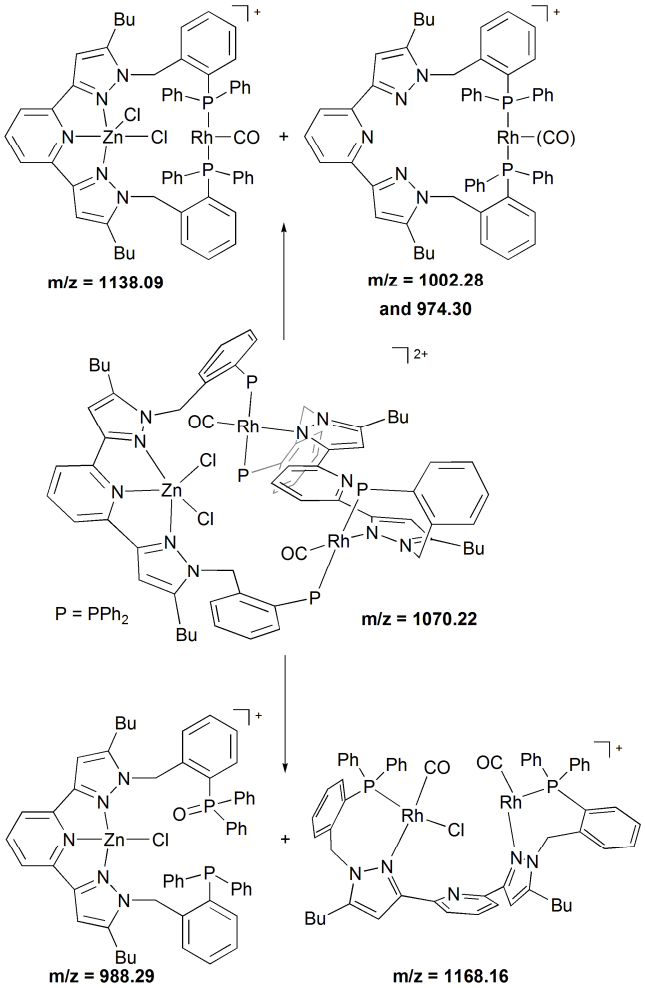
ESI-MS spectrum (enlarged), positive mode



ESI-MS spectrum (enlarged), positive mode



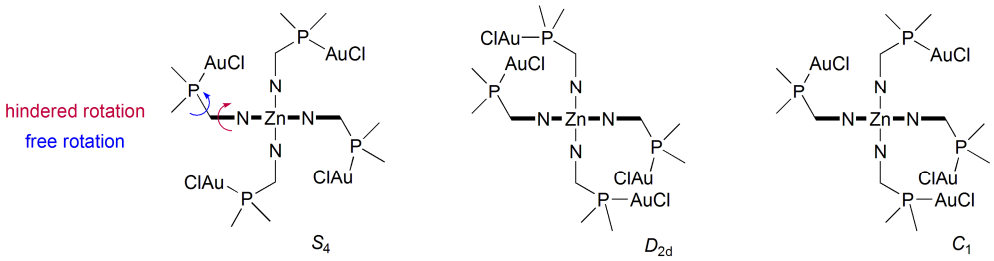
Fragmentation channels



Fragmentation channels of the $ZnRh_2$ complex **4** under ESI-MS conditions (m/z values for the calculated ion are given).

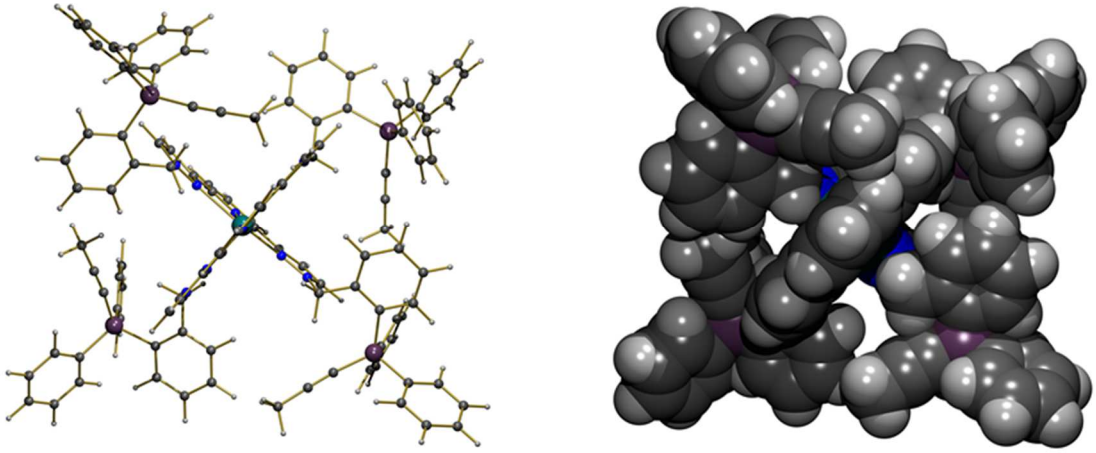
Semi-empirical calculations on the molecular structures of the conformers of the Au_4Zn complex 3.

The ^{31}P NMR spectrum of **3** shows two intense resonances that can in our opinion be interpreted by the presence of two highly symmetric conformers as mentioned in the manuscript. In the 1H NMR spectrum there are two intense pairs of doublets of doublets, with H-H couplings typical for magnetically inequivalent protons at methylene groups. This proves that a co-planar orientation of the 1,2-difunctionalized phenylene unit to the pyrazole ring is not possible. There is even no rapid movement of these units from one to the other side by rotation around the N-CH_2 bond according to the NMR time-scale. Under these restrictions, it is plausible, that conformers with a S_4 and a D_{2d} symmetric are formed, both having a highly symmetric arrangement of the P-Au-Cl moieties thus resulting in only one ^{31}P NMR resonance for each of these two conformers. However, rotation around the P-(C_6H_4) bond, although largely hindered, should still be possible, leading to an unsymmetrical (C_1) conformer that gives four ^{31}P NMR resonances.

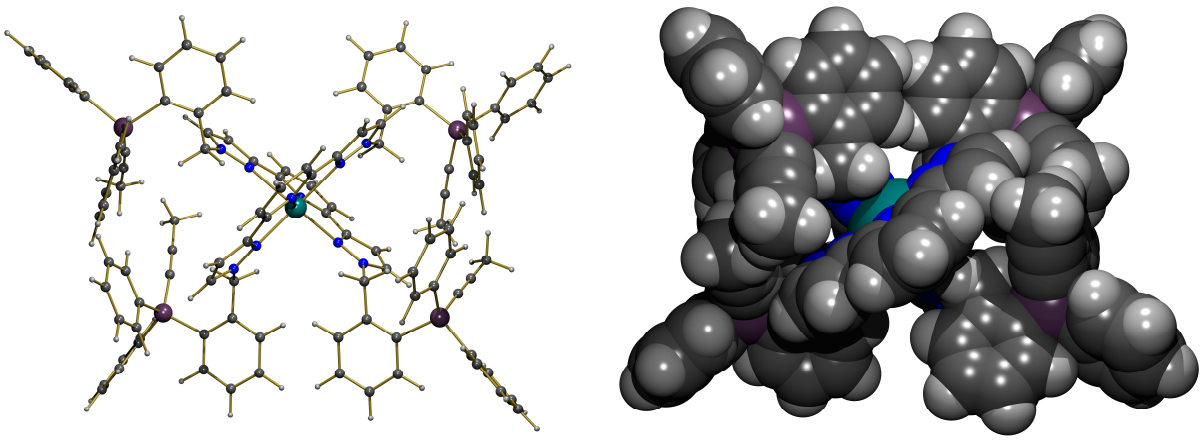


View along the N-Zn-N axis, the upper ligand is represented by thick, the lower ligand is represented by thin lines. "N" stands for the pyrazole rings.

For visualization of the molecular structures of the conformers, we performed semi-empirical calculations. The calculations were carried out with the Gaussian16 program package using the PM3 method. Since PM3 is not suitable for the calculation of gold, the four P-Au-Cl moieties were substituted by four Ge (for P) and a prop-1-in-1-yl group (-C≡C-Me). The linear Ge-C≡C-Me moieties have approximately the same size as the P-Au-Cl moieties of compound **3** and their terminal methyl groups have a radius similar to the Cl ligands. These variations allowed to apply PM3 for optimizing the geometries of the conformers.



PM3-calculated molecular structure of the S_4 symmetric conformer of the compound modelling **3**; view along the N-Zn-N axis, Zn^{2+} (cyan), Ge (violet), ball-stick model (left), space filling model (right)



PM3-calculated molecular structure of the D_{2d} symmetric conformer of the compound modelling **3**; view along the N-Zn-N axis, Zn^{2+} (cyan), Ge (violet), ball-stick model (left), space filling model (right)

X-ray structure analyses

Crystal data and refinement parameters are collected in the Table below. CCDC 1954209 and 1954210 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/data_request/cif.

The structure of compound **1** was solved using direct method of SIR92,[4] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[5] Semi-empirical absorption correction from equivalents (Multiscan) was carried out for ligand **1**. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model.

The structure of **4** was solved with *SHELXT*.[6] The structure was refined by full-matrix least-squares based on F^2 using *SHELXL* (Re. 859) [7] and *SHELXle* [8] as a graphical interface. The structure was checked for a higher symmetry using *PLATON*.[9] **4** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit containes one molecule of the dication, two anions (BF_4^- and $CF_3SO_3^-$), and three free solvent molecules (two molecules of dichloromethane and one molecule of diethylether). All non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms were assigned to idealized positions and given thermal parameters equal to either 1.5 (methyl hydrogen atoms) or 1.2 (non-methyl hydrogen atoms) times the thermal displacement parameters of the atoms to which they were attached. Advanced Hirshfeld restraints were applied to all atoms in the structure. Similarity restraints on 1,2- and 1,3-distances were used to model disorder components. U_{ij} components of disordered atoms were restrained with similar ADP restraints. Both *n*-butyl groups of of **4** are disordered and were modeled across two positions. The main occupied disorder components refined to an occupancy of 63.3% and 81.9%, respectively. Two half-occupied triflate ($CF_3SO_3^-$) anions were found in the

4 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435-435.
5 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.
6 G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.
7 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.
8 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Cryst.*, 2011, **44**, 1281–1284.
9 A. L. Spek, PLATON: A Multipurpose Crystallographic Tool. University of Utrecht, The Netherlands, 2008.

asymmetric unit adding up to one fully occupied triflate anion. Both half-occupied anions are disordered and located on inversion centers. Each disorder was modeled across two positions. The occupancies of the main disorder components refined to 80.3% and 69.7%, respectively. The disorder of the triflate anions is not resolved well and led to either non-positively defined or pathological displacement ellipsoids of the atoms. Thus, the ellipsoids were constrained to be identical between the disorder components. Two of the three free solvent molecules in the lattice are disordered too. One molecule of dichloromethane and the diethylether molecule were modeled across two positions. The occupancy of the main disorder components refined to 52.4% and 81.5%, respectively. The disorder of the dichloromethane molecule is poorly resolved, so, the most pathological ellipsoids were constrained to be identical between the components.

Table 1. Crystallographic data, data collection and refinement.

	1	**4**
empirical formula	$C_{57}H_{55}N_5P_2$	$C_{123}H_{124}BCl_6F_7N_{10}O_6P_4Rh_2SZn$
formula weight	872.00	2621.95
crystal size [mm]	0.304x0.289x0.199	0.358x0.238x0.123
T [K]	150(2)	150(2)
λ [Å]	1.54184	1.54184
crystal system	monoclinic	triclinic
space group	$P2_1/c$	P-1
a [Å]	15.7507(3)	15.3537(3)
b [Å]	17.1271(3)	19.4633(4)
c [Å]	18.3836(3)	22.6951(5)
α [°]	90	90.780(2)
β [°]	104.119(2)	106.494(2)
γ [°]	90	109.253(2)
V [Å^3]	4809.42(15)	6096.0(2)
Z	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.204	1.428
μ [mm^{-1}]	1.147	4.824
θ-range [°]	3.579-62.681	3.202-62.743
refl. coll.	20342	51266
indep. refl.	7649 [R_{int} = 0.0224]	19392 [R_{int} = 0.0332]
data/restr./param.	7649/21/590	19392/3547/1702
final R indices [$I>2\sigma(I)$] [a]	0.0362, 0.0933	0.0525, 0.1525
R indices (all data)	0.0407, 0.0978	0.0622, 0.1599
GooF [b]	1.038	1.047
$\Delta\rho_{max}/_{min}$ (e·Å^{-3})	0.663/-0.227	4.146/-1.314

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $\omega R2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^2]^{1/2}$. [b] $GooF = [\Sigma\omega(F_o^2 - F_c^2)^2/(n\text{-}p)]^{1/2}$.