Synthesis and catalytic activity of ruthenium indenylidene complexes bearing unsymmetrical NHC containing a heteroaromatic moiety

Michał Smoleń[a], Wioletta Kośnik[a], Rafał Loska[b], Roman Gajda[a], Maura Malińska[a],

Krzysztof Woźniak[a] and Karol Grela*[a]

[a] Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury Street 101, 02-089 Warsaw

[b] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

-SUPPORTING INFORMATION-

Table of Contents:

Experimental Details S3-S18

NMR Spectra of Diamines **2a**, **2b**, **2c**, **2d** S19-S26

NMR Spectra of Imidazolinium Salts **3a**, **3b**, **3c**, **3d** S27-S34

NMR Spectra of Chloroform-NHC Adducts **4a**, **4b**, **4c**, **4d** S35-S42

NMR Spectra of Pre-Catalysts **5a**, **5b**, **5c**, **5d**, **7** S43-S56

High Resolution Mass Spectra **5a**, **5b**, **5c**, **5d** S57-S64

X-ray Data S65-S98

References S99

1. General Considerations

Preparation of catalysts was carried out under Ar in pre-dried glassware using Schlenk techniques. All reagents were purchased from Sigma-Aldrich Chemical Company and used without further purification. The HPLC grade toluene 99.9% containing the following impurities (≤ 0.0005% non-volatile matter, ≤ 0.0005% thiophene, ≤0.001% free acid, ≤0.02% water) was purchased from Sigma-Aldrich Chemical company. Dry toluene was obtained by distillation over K under atmosphere of argon. Ethyl oleate was purified by filtration through thin pad of aluminum oxide (neutral, activity I).

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F_{254} precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization of TLC plates was performed by UV light (254 nm) and $KMnO_4$ water solution. The flash column chromatography was performed using silica gel 60 (230–400 mesh). The ^1H and ^{13}C chemical shifts are referenced to $CDCl_3$ (δ = 7.26 and δ = 77.16 ppm respectively) or CD_2Cl_2 (δ = 5.32 and 53.84 ppm respectively), coupling constants (*J*) are in Hz.[1] The ^{31}P chemical shifts are referenced to 85% H_3PO_4 (δ = 0.00 ppm).

^1H, ^{13}C, ^{31}P NMR spectra were recorded on Agilent 400-MR DD2 400 MHz spectrometer, on a Varian VNMRS 500 MHz and 600 MHz. Spectra were reported as follows: chemical shift (δ ppm), multiplicity, integration, coupling constant (Hz). IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory, wave numbers are in cm^{-1}. Elemental-analyses were provided by analytical laboratory at the Institute of Organic Chemistry, PAS. Melting points were recorded on OptiMelt SRS apparatus with heating rate 2 °C/min. Mass spectra were collected on LCT Micromass TOF HiRes apparatus at the Faculty of Chemistry University of Warsaw. The ethenolysis reactions were performed in autoclave reactors: Roth Model I and Amar Equipments Pvt. Ltd. BS-250ml.

Compounds:

***N*¹-mesitylethane-1,2-diamine** was prepared according to Marshall's [2] procedure.

1-benzothiophene-2-carbaldehyde (1c) and **1-benzofuran-2-carbaldehyde (1d)** were prepared according to Gillaizeau's [3] procedure.

1.1 General procedure for RCM and Ene-Yne reactions (Table 2, entry 1-3)

Comparative experiments with model substrates (refer to Table 2, entry 1-3) were performed in HPLC grade toluene on air at 50 ºC with initial concentration of substrates c = 0.1 M and catalysts loadings 1 mol% (entry 1 and 2) or 2 mol% (entry 3). To a stirred solution of substrate (1 eq) and durene (1 eq used as internal standard) in HPLC grade toluene, solution of one catalyst (**5a**, **5b**, **5c**, **5d**, **6**, **7** or **Hoveyda II**) in HPLC grade toluene was added in a single portion **at 50 ºC**. The reaction mixture was left at 50 ºC. After 5, 10, 30, 60, 120, 180, 240, minutes aliquots (50 µL) were taken and immediately ethyl vinyl ether (100 µL) was added. Then HPLC grade toluene (500 µL) was added, and solution was analyzed by GC chromatography, using EP Clarus 580 chromatograph with InterCap MS5/Sil column.

1.2 General procedure for CM (Table 2, entry 4)

Comparative experiment with model substrate (refer to Table 2, entry 4) was performed in HPLC grade toluene on air at 50 ºC with initial concentration of allylbenzene (c = 0.1 M) and catalysts loading 2 mol%. To a stirred solution of allylbenzene (1 eq) and (*Z*)-1,4-diacetoxy-2-butene (2 eq) in HPLC grade toluene, solution of one catalyst (**5a**, **5b**, **5c**, **5d** **6**, **7** or **Hoveyda II**) in HPLC grade toluene was added in a single portion at 50 ºC. The reaction mixture was left at 50 ºC for 3 hours (**5a**, **5b**, **5c**, **5d**, **6**) or 5 hours (**7**, **Hoveyda II**). After this time the mixture was immediately cooled down to room temperature, ethyl vinyl ether was added and the mixture was stirred for 15 minutes. After this time the solvent was evaporated, and the residue was purified by column chromatography (10% EtOAc/*c*-hexane). After evaporation of the solvents the residue was dried under vacuum. *E*/*Z* ratio was determined by gas chromatography.

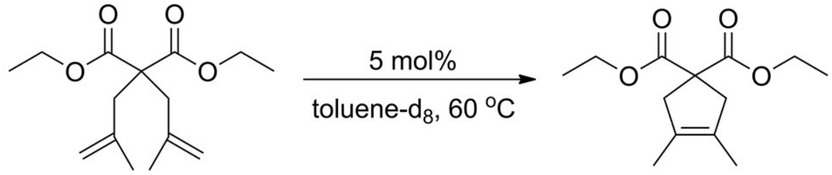
1.3 General procedure for DRRM (Table 1, entry 4-13)

Comparative experiment with model substrate (refer to Table 1, entry 4-13) was performed in $CDCl_3$ saturated with ethylene on air at r.t. or 50 ºC with initial concentration of **10** (c = 0.02 M, 1 eq) durene (0.5 eq) and catalysts loading 5 mol%. To a stirred solution of **10** in $CDCl_3$ saturated with ethylene, solution of one catalyst (**5a**, **5b**, **5c**, **5d** or **6**) in $CDCl_3$ was added in a single portion at r.t. or 50 ºC. The reaction mixture was left at rt for 17 hours or at 50 °C for 1 hour. The starting solution of **10** with durene was analyzed by GC. Then a reaction mixture was transferred to a vial and ethyl vinyl ether (100 μL) was added. The solution was analyzed by GC chromatography, using EP Clarus 580 chromatograph with InterCap MS5/Sil column.

1.4 General procedure for ethenolysis of ethyl oleate (22)

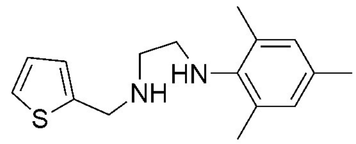
Ethyl oleate (**22**) (4.66 g, 15 mmol) and tetradecane as a internal standard (0.8 ml) were placed in the autoclave equipped with a stir bar. Then, a solution of the catalyst (0.1 ml, 0.0075 mmol, 500 ppm) in dry DCM was added to the ethyl oleate. The autoclave was sealed and purged with ethylene, pressurized to 10 bar. The ethenolysis reaction was performed for 3 hours at 50 °C, at constant pressure 10 bar. Then, ethylene was released from the autoclave. Prior to GC analysis, the reaction mixture (1.0 mL) was taken, placed in GC vial and quenched by adding a 2.0 M solution of ethyl vinyl ether (4.0 mL) in DCM. An aliquots obtained solution (0.2 mL) was placed in vial, and DCM was added to an overall volume of 1 mL. The solution was analyzed by GC chromatography, using EP Clarus 580 chromatograph with InterCap MS5/Sil column.

1.5 Procedure for RCM of diethyl 2,2-bis(2-methylallyl)malonate



In NMR tube was placed diethyl 2,2-bis(2-methylallyl)malonate (18.8 mg, 0.07 mmol, c = 0.1 M) and toluene-d_8 (0.6 mL). The stock solution of the precatalyst was prepared by dissolving **5a** (16.2 mg, 0.0175 mmol) in toluene-d_8 (0.5 mL). The obtained solution of the catalyst (0.1 mL) was added to NMR tube and the reaction progress was monitored by NMR spectroscopy. The conversion of 15% was achieved after 3 h of measurement.

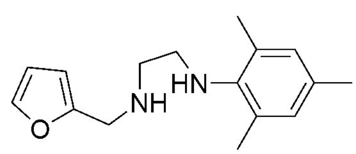
Compound 2a



To a solution of N^1-mesitylethane-1,2-diamine (12.5 g, 70 mmol) in 150 mL of methanol, thiophene-2-carbaldehyde (**1a)** (8.01 g, 70 mmol) was added in one portion. After 5 minutes 3 drops of 85% formic acid and (1 g) of anhydrous sodium sulfate were added. The reaction mixture was stirred at RT. After 24 h, sodium borohydride (22.3 g, 560 mmol) was added in ten portions, and then mixture was stirred for 24 h. (If all amount of the sodium borohydride will not dissolve, more methanol must be added). Then 200 mL of 5% NaOH was added and all amount of methanol was evaporated. (If not all methanol is removed, more water must be added, to obtain two layers during extraction). The crude product was extracted with methylene chloride (4x100 mL). Organic extracts were combined and dried over Na_2SO_4, filtered, and the solvent was evaporated. The residue was purified by column chromatography on silica (10% then 75% AcOEt/*c*-hex). The solvents were evaporated to afford the product as a clear colorless oil, which was dried under vacuum. Yield: 15.4 g (80%)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25 (dd, 1H, *J* = 5.0 and *J* = 1.3 Hz), 7.00 – 6.97 (m, 2H), 6.86 (s, 2H), 4.07 (br s, 2H), 3.10 – 3.07 (m, 2H), 2.93 – 2.91 (m, 2H), 2.67 (br s, 2H), 2.33 (s, 6H), 2.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.1, 143.7, 131.1, 129.7, 129.5, 126.7, 124.9, 124.5, 49.2, 48.3, 48.2, 20.6, 18.5 ppm; IR (thin film from CH_2Cl_2): ν = 3351, 3069, 2938, 2915, 2852, 2730, 1593, 1485, 1443, 1371, 1304, 1232, 1112, 1036, 852, 823, 697 cm $^{-1}$; Anal. Calcd. for $C_{16}H_{22}N_2S$: C, 70.03; H, 8.08; N, 10.21; S, 11.68; found: C, 70.15; H, 8.09; N, 10.26; S, 11.84; LRMS ESI (m/z) calcd. for $C_{16}H_{22}N_2NaS$ $[M+Na]^+$ 297.1, found 297.1

Compound 2b

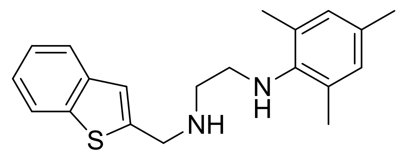


The same procedure as described for compound **2a** was employed using: N^1-mesitylethane-1,2-diamine (12.5 g, 70 mmol), methanol (150 mL), furan-2-carbaldehyde **(1b)** (6.73 g, 70 mmol) and sodium borohydride (22.3 g, 560 mmol).

Yield: 14.1 g (78%) of the slight-yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (dd, 1H, *J* = 1.9 and *J* = 0.9 Hz), 6.83 (br s, 2H), 6.33 (dd, 1H, *J* = 3.2 and *J* = 1.9 Hz), 6.20 (dd, 1H, *J* = 3.2 and *J* = 0.8 Hz) 3.84 (s, 2H), 3.06 – 3.04 (m, 2H), 2.85 – 2.83 (m, 2H), 2.63 (br s, 2H), 2.28 (s, 6H), 2.24 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.0, 143.7, 141.9, 131.2, 129.8, 129.5, 110.2, 107.0, 49.1, 48.2, 46.0, 20.7, 18.5 ppm; IR (thin film from CH_2Cl_2): ν = 3352, 3115, 2939, 2916, 2853, 2731, 1597, 1485, 1447, 1373, 1304, 1232, 1148, 1010, 854, 803, 734 cm $^{-1}$; Anal. Calcd. for $C_{16}H_{22}N_2O$: C, 74.38; H, 8.58; N, 10.84; Found: C, 74.36; H, 8.51; N, 10.81; LRMS ESI (m/z) calcd. for $C_{16}H_{22}N_2NaO$ $[M+Na]^+$ 281.1, found 281.1

Compound 2c

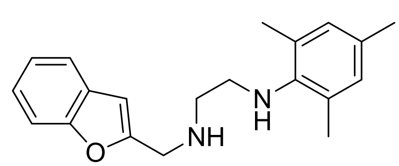


The same procedure as described for compound **2a** was employed using: N^1-mesitylethane-1,2-diamine (6.24 g, 35 mmol), methanol (150 mL), 1-benzothiophene-2-carbaldehyde **(1c)** (5.68 g, 35 mmol) and sodium borohydride (13.2 g, 350 mmol).

Yield: 9.58 g (84%) of the yellowish oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82-7.80 (m, 1H), 7.72-7.70 (m, 1H), 7.36-7.28 (m, 2H), 7.18 (br s, 1H), 6.83 (br s, 2H), 4.15 (br, 2H), 3.10 – 3.07 (m, 2H), 2.94 – 2.92 (m, 2H), 2.87 (br s, 2H), 2.30 (s, 6H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 143.7, 139.9, 139.8, 131.3, 129.8, 129.5, 124.3, 124.1, 123.3, 122.5, 121.6, 49.1, 49.0, 48.1, 20.7, 18.6 ppm; IR (thin film from CH_2Cl_2): ν = 3352, 3055, 2995, 2938, 2913, 2851, 2730, 1592, 1485, 1457, 1437, 1372, 1341, 1305, 1234, 1186, 1155, 1141, 1129, 1111, 1065, 1031, 1014, 977, 935, 855, 823, 746, 727, 709 cm $^{-1}$; Anal. Calcd. for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88; Found: C, 73.98; H, 7.58; N, 8.71; S, 10.14; LRMS ESI (m/z) calcd. for $C_{20}H_{24}N_2NaS$ $[M+Na]^+$ 347.2, found 347.2

Compound 2d

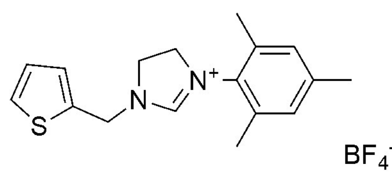


The same procedure as described for compound **2a** was employed using: N^1-mesitylethane-1,2-diamine (6.42 g, 36 mmol), methanol (150 mL), 1-benzofuran-2-carbaldehyde **(1d)** (5.68 g, 35 mmol) and sodium borohydride (13.6 g, 360 mmol).

Yield: 9.34 g (84%) of the yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.53 (m, 1H), 7.47-7.45 (m, 1H), 7.29-7.20 (m, 2H), 6.83 (br s, 2H) 6.59 (br s, 1H), 4.00 (br s, 2H), 3.09 – 3.06 (m, 2H), 2.91 – 2.88 (m, 2H), 2.81 (br s, 2H), 2.28 (s, 6H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 155.1, 143.6, 131.4, 129.9, 129.5, 128.5, 124.0, 122.8, 120.9, 111.2, 104.1, 49.2, 48.1, 46.4, 20.7, 18.5 ppm; IR (thin film from CH_2Cl_2): ν = 3352, 3033, 2995, 2940, 2914, 2852, 2730, 1892, 1775, 1602, 1586, 1485, 1454, 1373, 1303, 1253, 1234, 1172, 1151, 1138, 1104, 1031, 1010, 941, 877, 854, 827, 801, 751, 702 cm^{-1}; Anal. Calcd. for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.08; Found: C, 77.78; H, 7.79; N, 9.14; LRMS ESI (m/z) calcd. for $C_{20}H_{24}N_2NaO$ $[M+Na]^+$ 331.2, found 331.1

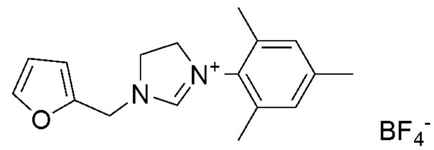
Compound 3a



In a flask were placed **2a** (15.4 g, 56.1 mmol), triethyl orthoformate (84.8 g, 561 mmol) and reaction was stirred at RT in an open flask. After 10 minutes 3 M hydrogen chloride in dioxane (37.4 mL, 112 mmol) was added dropwise. The mixture was stirred further for another 10 minutes at RT and then 12 h at 80 ºC. After this time the temperature was increased to 120 ºC and stirred for 1 h. After cooling the mixture, the solvent was evaporated. The product (slight-yellowish oil) was dissolved in mixture of solvents (water:methanol 2:1), and ammonium tetrafluoroborate (6.67 g, 61.7 mmol) was added in a few portions, and then the mixture was stirred for 1 h. Methanol was evaporated, and mixture was extracted with CH_2Cl_2 (3x75 mL). Organic extracts were combined and dried over $MgSO_4$, filtered and solvent was evaporated. The product was crystallized from mixture of methylene chloride and toluene. The obtained product was filtered, washed with toluene and *n*-hexane and dried under vacuum to give white powder. Yield: 15.9 g (76%)

mp: 142.1−143.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (s, 1H), 7.33 (dd, 1H, J = 5.1 and J = 1.2 Hz), 7.21 (dd, 1H, J = 3.5 Hz and J = 1.2 Hz), 6.99 (dd, 1H, J = 5.1 and J = 3.5 Hz), 6.88 (br s, 2H), 5.01 (s, 2H), 4.17 – 4.08 (m, 4H), 2.25 (s, 3H), 2.21 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.0, 140.4, 135.5, 134.5, 130.6, 130.0, 129.9, 127.9, 127.6, 51.2, 48.3, 46.5, 21.1, 17.5 ppm; IR (KBr): ν = 3089, 2921, 2743, 1643, 1450, 1488, 1376, 1250, 1217, 1185, 1134, 1053, 860, 712, 470 cm^{-1}; Anal. Calcd. for $C_{17}H_{21}BF_4N_2S$: C, 54.85; H, 5.69; N, 7.53; S, 8.61; Found: C, 54.78, H, 5.79, N, 7.37, S, 8.72; LRMS ESI (m/z) calcd. for $C_{17}H_{21}N_2S$ [M-BF_4^-]$^+$ 285.1, found 285.1

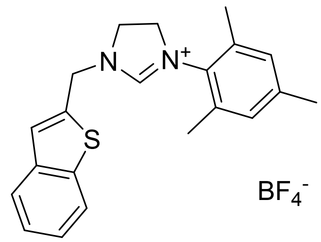
Compound 3b



In a flask were placed **2b** (14.2 g, 55.0 mmol), triethyl orthoformate (83.2 g, 550 mmol) and reaction was stirred at RT in an open flask. After 10 minutes 3 M hydrogen chloride in dioxane (36.7 mL, 110 mmol) was added dropwise. The mixture was stirred further for 10 minutes at RT and then 12 h at 80 ºC. After this time the temperature was increased to 120 ºC and stirred for 1 h. After cooling the mixture, solvent was evaporated. The product (black oil) was dissolved in mixture of solvents (water:methanol 2:1), and ammonium tetrafluoroborate (6.54 g, 60.5 mmol) was added in a few portions, and then the mixture was stirred for 1 h. Methanol was evaporated, and mixture was extracted with CH_2Cl_2 (3x75 mL). Organic extracts were combined and dried over $MgSO_4$, filtered and solvent was evaporated. The residue was dissolved in small amount of DCM and filtered through silica (eluent AcOEt). The ethyl acetate was removed and product was crystallized from mixture of methylene chloride and toluene. The obtained product was filtered, washed with toluene and *n*-hexane and dried under vacuum to give white powder. Yield: 13.4 g (68%)

mp: 131.4-132.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (s, 1H), 7.41 (dd, 1H, *J* = 1.9 and *J* = 0.8 Hz), 6.88 (br s, 2H), 6.55 (dd, 1H, *J* = 3.2 Hz and *J* = 0.5 Hz), 6.35 (dd, 1H, *J* = 3.2 and *J* = 1.9 Hz), 4.84 (s, 2H), 4.17 – 4.09 (m, 4H), 2.25 (s, 3H), 2.21 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 146.4, 143.9, 140.4, 135.5, 130.5, 130.0, 111.6, 111.1, 51.2, 48.7, 44.6, 21.1, 17.5 ppm; IR (KBr): ν = 3126, 2974, 2929, 1650, 1489, 1367, 1300, 1256, 1188, 1138, 1055, 964, 857, 845, 752, 470 cm^{-1}; Anal. Calcd. for $C_{17}H_{21}BF_4N_2O$: C, 57.33, H, 5.94, N, 7.87; Found: C, 57.05, H, 6.14, N, 7.70. LRMS ESI (m/z) calcd. for $C_{17}H_{21}N_2O$ [M-BF_4^-]$^+$ 269.1, found 269.1

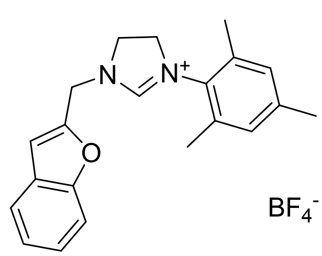
Compound 3c



In a flask were placed **2c** (8.83 g 27.2 mmol), triethyl orthoformate (41.1 g, 272 mmol) and reaction was stirred at RT in an open flask. After 10 minutes 2 M hydrogen chloride in dioxane (27.2 mL, 54.4 mmol) was added dropwise. The mixture was stirred further for 10 minutes at RT and then 12 h at 90 ºC. After this time the temperature was increased to 130 ºC and stirred for 1 h. After cooling the mixture, the crude product was filtered, washed with *n*-hexane, and dried. The crude product was dissolved in hot water and ammonium tetrafluoroborate (3.23 g, 29.9 mmol) was added in a few portions, and then the mixture was stirred for 1 h. To the mixture was added 100 mL of CH_2Cl_2, and product was extracted with CH_2Cl_2 (3x50 mL). Organic extracts were combined and dried over $MgSO_4$, filtered and solvent was evaporated. The product was crystallized from mixture of methylene chloride and toluene. The obtained product was filtered, washed with toluene and *n*-hexane and dried under vacuum to give white powder. Yield: 8.58 g (75%)

mp: 178 - 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 7.78-7.72 (m, 2H), 7.43 (s, 1H), 7.37-7.31 (m, 2H), 6.86 (s, 2H), 5.12 (s, 2H), 4.22 – 4.07 (m, 4H), 2.23 (br s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 140.5, 140.4, 139.5, 135.5, 135.3, 130.5, 130.0, 126.8, 125.3, 124.9, 124.4, 122.6, 51.2, 48.4, 47.4, 21.1, 17.5 ppm; IR (KBr): ν = 3086, 3056, 3032, 2977, 2924, 2895, 1975, 1934, 1816, 1644, 1568, 1538, 1513, 1488, 1478, 1463, 1440, 1391, 1375, 1306, 1298, 1274, 1259, 1240, 1195, 1163, 1148, 1135, 1058, 1030, 980, 962, 900, 868, 856, 839, 763, 730, 672, 645, 574, 520, 479, 471 cm^{-1}; Anal. Calcd. for $C_{21}H_{23}BF_4N_2S$: C, 59.73; H, 5.49; N, 6.63; S, 7.59; Found: C, 59.63, H, 5.58, N, 6.58; S, 7.78; LRMS ESI (m/z) calcd. for $C_{21}H_{23}N_2S$ $[M-BF_4^-]^+$ 335.2, found 335.1

Compound 3d

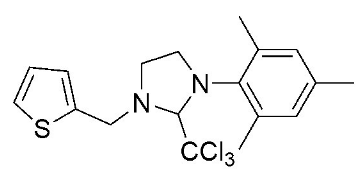


The same procedure as described for compound **3c** was employed using: **2d** (8.5 g, 27.6 mmol), triethyl orthoformate (46.8 mL, 276 mmol) and 2 M hydrogen chloride in dioxane (27.6 mL, 55.1 mmol)

Yield: 8.45 g (76%) of the white powder.

mp = 192 – 194 °C ; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.23 (s, 1H), 7.65 – 7.62 (m, 1H), 7.52 - 7.50 (m, 1H), 7.39 – 7.34 (m, 1H), 7.31 – 7.27 (m, 1H), 7.01 (br. s, 1H), 6,99 (br. s, 2H), 5.04 (s, 2H), 4.28 - 4.14 (m, 4H), 2.30 (s, 3H), 2.28 (s, 6H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 159.2, 155.9, 148.9, 141.2, 135.7, 130.6, 130.4, 128.2, 125.8, 123.8, 122.2, 111.7, 108.8, 51.6, 49.3, 45.8, 21.2, 17.7 ppm; IR (KBr): ν = 3116, 3102, 3033, 2982, 2929, 2906, 2866, 1955, 1911, 1826, 1789, 1646, 1589, 1519, 1487, 1478, 1453, 1441, 1385, 1339, 1313, 1304, 1275, 1243, 1221, 1206, 1189, 1171, 1144, 1109, 1099, 1065, 1046, 1029, 978, 957, 876, 859, 829, 817, 758, 713, 673, 603, 522, 503, 471 cm^{-1}; Anal. Calcd. for $C_{21}H_{23}BF_4N_2O$: C, 62.09; H, 5.71; N, 6.90; Found: C, 62.25, H, 5.67, N, 6.92. LRMS ESI (m/z) calcd. for $C_{21}H_{23}N_2O$ $[M-BF_4^-]^+$ 319.2, found 319.1

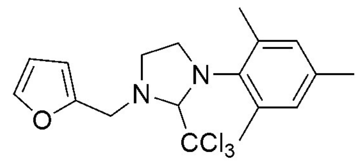
Compound 4a



In a three-necked flask (100 mL) were placed the solid powdered 85% KOH (6.60 g, 100.0 mmol) and dry toluene (40 mL) under argon. The reaction mixture was stirred rapidly at RT. The flask was equipped with a reflux condenser. Then dry $CHCl_3$ (0.82 mL, 10.0 mmol) was added to the suspension. After 10 minutes at room temperature **3a** (1.12 g, 3.0 mmol) was added, and the reaction mixture was heated at 60 ºC for 75 minutes. The mixture was allowed to cool to room temperature and filtered. The solid residue was washed with toluene (2x15 mL). The supernatant was concentrated under vacuum to a yellow oil. The crude product was purified first through a silica gel pad (5% AcOEt/*c*-hex), and then by recrystallization from boiling *n*-hexane to yield white product (794 mg, 66%).

mp: 115.2-117.4 °C decomp.; NMR ^{1}H (500 MHz, $CDCl_3$): δ = 7.27-7.26 (m, 1H), 7.04-7.03 (m, 1H), 6.98 (dd, 1H, J = 5.1 and J = 3.4 Hz), 6.88 (br s, 1H), 6.87 (br s, 1H), 4.92 (s, 1H), 4.76 (d, 1H, J = 13.6 Hz), 4.48 (d, 1H, J = 14.1 Hz), 3.86-3.81 (m, 1H), 3.57 (ddd, 1H, J = 9.7 Hz, J = 7.1 Hz and J = 5.5 Hz), 3.23 (ddd, 1H, J = 8.9 Hz, J = 8.1 Hz, and J = 5.5 Hz), 3.03 (ddd, 1H, J = 9.7 Hz, J = 8.0 Hz, and J = 6.5 Hz), 2.38 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.7, 142.8, 138.9, 135.3, 132.8, 130.1, 129.7, 126.6, 125.1, 124.9, 108.1, 93.0, 56.6, 53.0, 52.7, 20.9, 19.8, 19.5 ppm; IR (KBr): ν = 3115, 3068, 2943, 2911, 2854, 2825, 2725, 1792, 1766, 1735, 1608, 1539, 1479, 1431, 1372, 1355, 1327, 1312, 1248, 1224, 1194, 1091, 1036, 1001, 993, 969, 946, 912, 888, 855, 839, 809, 775, 709, 637, 578, 558, 485 cm^{-1}; Anal. Calcd. for $C_{18}H_{21}Cl_3N_2S$: C, 53.54, H, 5.24, N, 6.94, S, 7.94, Cl, 26.34; Found: C, 53.52, H, 5.21, N, 6.77, S, 8.22, Cl, 26.09. LRMS ESI (m/z) calcd. for $C_{17}H_{21}N_2S$ $[M\text{-}CCl_3]^+$ 285.1, found 285.2

Compound 4b

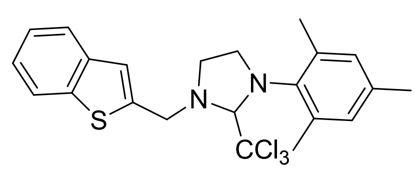


The same procedure as described for compound **4a** was employed using: the solid powdered 85% KOH (6.60 g, 100.0 mmol), dry toluene (40 mL), dry $CHCl_3$ (0,82 mL, 10.0 mmol) and **3b** (1.12 g, 3.0 mmol)

Yield: 384 mg (33%) of the slightly-yellowish powder.

mp: 60.6-61.6 °C decomp.; NMR ^{1}H (500 MHz, $CDCl_3$): δ = 7.41 (dd, 1H, *J* = 1.8 and *J* = 0.9 Hz), 6.86 (br. s, 1H), 6.82 (br. s, 1H), 6.38-6.37 (m, 1H), 6.35-6.34 (m, 1H), 4.90 (s, 1H), 4.48 (d, 1H, *J* = 14.8 Hz), 4.34 (d, 1H, *J* = 14.8 Hz), 3.83 - 3.78 (m, 1H), 3.62-3.57 (m, 1H), 3.23-3.16 (m, 2H), 2.36 (s, 3H), 2.25 (s, 3H), 2.15 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.8, 142.6, 142.2, 138.7, 135.1, 133.0, 130.0, 129.7, 110.5, 108.6, 108.1, 91.9, 53.2, 53.1, 52.6, 20.9, 19.6, 19.5 ppm; IR (KBr): ν = 3145, 3108, 2987, 2953, 2941, 2916, 2876, 2848, 2733, 1774, 1744, 1717, 1672, 1596, 1573, 1551, 1484, 1462, 1429, 1361, 1344, 1312, 1293, 1261, 1234, 1208, 1185, 1163, 1149, 1113, 1074, 1013, 968, 921, 902, 860, 800, 770, 756, 733, 632, 607, 588, 579, 557, 471 cm^{-1}; Anal. Calcd. for $C_{18}H_{21}Cl_3N_2O$: C, 55.76, H, 5.46, N, 7.22, Cl, 27.43; Found: C, 55.71, H, 5.47, N, 7.13, Cl, 27.36. LRMS ESI (m/z) calcd. for $C_{17}H_{21}N_2O$ $[M\text{-}CCl_3]^+$ 269.2, found 269.2

Compound 4c

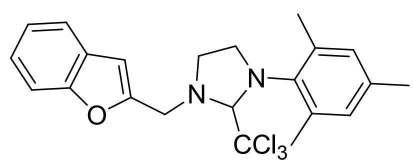


The same procedure as described for compound **4a** was employed using: the solid powdered 85% KOH (2.97 g, 45 mmol), dry toluene (20 mL), dry $CHCl_3$ (0,37 mL, 4.5 mmol) and **3c** (570 mg, 1.35 mmol).

Yield: 495 mg (81%) of the yellowish powder.

mp: 138 – 142 °C decomp..; NMR ^{1}H (400 MHz, $CDCl_3$): δ = 7.83-7.81 (m, 1H), 7.74-7.72 (m, 1H), 7.36-7.28 (m, 2H), 7.25 (s, 1H), 6.89 (br. s, 1H), 6.88 (br. s, 1H), 4.95 (s, 1H), 4.87 (d, 1H, *J* = 14.2 Hz), 4.53 (d, 1H, *J* = 14.3 Hz), 3.88-3.82 (m, 1H), 3.61 (ddd, 1H, *J* = 9.7 Hz, *J* = 7.1 Hz, and *J* = 5.6 Hz), 3.25 (ddd, 1H, *J* = 8.8 Hz, *J* = 8.1 Hz, and *J* = 5.6 Hz), 3.04 (ddd, 1H, *J* = 9.7 Hz, *J* = 8.0 Hz and *J* = 6.4 Hz), 2.38 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 142.7, 140.2, 139.7, 138.9, 135.4, 132.7, 130.2, 129.7, 124.2, 124.1, 123.3, 122.5, 121.2, 108.0, 93.3, 57.5, 53.1, 52.8, 20.9, 19.9, 19.5 ppm; IR (KBr): ν = 3061, 2972, 2950, 2894, 2866, 2825, 1924, 1892, 1783, 1739, 1669, 1606, 1574, 1480, 1456, 1437, 1371, 1352, 1336, 1326, 1308, 1269, 1248, 1224, 1204, 1186, 1159, 1137, 1127, 1059, 1003, 971, 948, 930, 911, 879, 856, 815, 782, 763, 742, 723, 692, 672, 631, 584, 559, 540, 481, 461, 427 cm^{-1}; Anal. Calcd. for $C_{22}H_{23}Cl_3N_2S$: C, 58.22, H, 5.11, N, 6.17, S, 7.07, Cl, 23.43; Found: C, 58.24, H, 4.99, N, 5.98, S, 7.25, Cl, 23.38. LRMS ESI (m/z) calcd. for $C_{21}H_{23}N_2S$ $[M\text{-}CCl_3]^+$ 335.2, found 335.2

Compound 4d



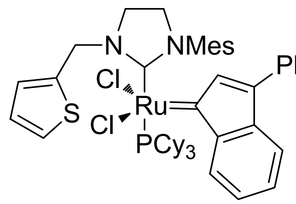
The same procedure as described for compound **4a** was employed using: the solid powdered 85% KOH (2.97 g, 45 mmol), dry toluene (20 mL), dry $CHCl_3$ (0,37 mL, 4.5 mmol) and **3d** (548 mg, 1.35 mmol).

Yield: 465 mg (78%) of the yellowish powder.

mp: 123 – 125 °C decomp.; NMR ^{1}H (400 MHz, $CDCl_3$): δ = 7.58-7.56 (m, 1H), 7.48-7.46 (m, 1H), 7.30-7.21 (m, 2H), 6.86 (br. s, 1H), 6.82 (br. s, 1H), 6.76 (s, 1H), 4.95 (s, 1H), 4.67 (d, 1H, *J* = 15.3 Hz), 4.46 (d, 1H, *J* = 15.3 Hz), 3.88-3.80 (m, 1H), 3.75-3.66 (m, 1H), 3.27-3.20 (m, 2H), 2.37 (s, 3H), 2.25 (s, 3H), 2.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 155.1, 142.6, 138.8, 135.3, 132.9, 130.1, 129.7, 128.6, 124.0, 122.8, 120.9, 111.2, 108.1, 105.0, 92.6, 54.3, 53.5, 52.7, 20.9, 19.6, 19.5 ppm; IR (KBr): ν = 3116, 3070, 3052, 3016, 2981, 2916, 2865, 2819, 2757, 2726, 1920, 1886, 1807, 1772, 1734, 1667, 1604, 1587, 1473, 1454, 1433, 1389, 1358, 1302, 1276, 1255, 1202, 1172, 1146, 1125, 1106, 1083, 1032, 1001, 957, 926, 906, 886, 856, 793, 742, 709, 638, 604, 583, 539, 511, 501, 470, 447, 429 cm^{-1}; Anal. Calcd. for $C_{22}H_{23}Cl_3N_2O$: C, 60.36, H, 5.30, N, 6.40, Cl, 24.29;

Found: C, 60.59, H, 5.24, N, 6.35, Cl, 24.09. LRMS ESI (m/z) calcd. for $C_{21}H_{23}N_2O$ $[M-CCl_3]^+$ 319.2, found 319.2

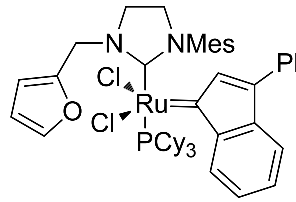
Compound 5a



In a Schlenk flask were placed 365 mg (0.904 mmol) of **4a** and 417 mg (0.452 mmol) of Umicore™ **M1**. Then 30 mL of dry toluene was added, and solution was heated at 65 ºC for 15 h. The mixture was allowed to cool to room temperature. Solvent was evaporated, and the crude product was purified by column chromatography on silica (10% EtOAc:*c*-hex then 30% EtOAc:*c*-hex) and then by slow evaporation from the mixture of solvents CH_2Cl_2:CH_3OH. The product was dried under vacuum to give red powder. Yield 232 mg (55%)

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.37 (d, 1H, J = 7.4 Hz), 7.71 (dd, 2H, J = 8.1 Hz, and J = 1.0 Hz), 7.54 – 7.50 (m, 1H), 7.46 (dd, 1H, J = 3.4 Hz, and J = 0.6 Hz), 7.44-7.40 (m, 3H), 7.23 (dt, 1H, J = 7.4, J = 1.0 Hz), 7.16 (dt, 1H, J = 7.5 Hz J = 0.9 Hz), 7.13 (s, 1H), 7.10 (dd, 1H, J = 5.1 Hz and J = 3.5 Hz), 7.04 (d, 1H, J = 7.2 Hz), 6.38 (s, 1H), 6.00 (s, 1H), 5.91 (d, 1H, J = 14.6 Hz), 5.83 (d, 1H, J = 14.6 Hz), 3.78-3.65 (m, 4H), 2.41-2.34 (m, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.87 (s, 3H), 1.83-1.80 (m, 3H), 1.72-1.69 (m, 3H), 1.62-1.59 (m, 3H), 1.56 – 1.51 (m, 6H), 1.44-1.30 (m, 6H), 1.16-1.04 (m, 6H), 1.01-0.93 (m, 3H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 291.5 (d, $J_{P,C}$ = 5.0 Hz), 216.7 (d, $J_{P,C}$ = 69.3 Hz), 144.2, 140,9. 138.3, 138.1, 137.5, 137.4, 137.1, 137.1, 136.9, 136.3, 129.3, 129.0, 128.9, 128.8, 128.8, 128.3, 128.0, 127.6, 127.3, 127.0, 126.7, 116.5, 52.4 (d, $J_{P,C}$ = 2.0 Hz), 51.0, 48.5 (d, $J_{P,C}$ = 3.1 Hz), 32.8, 32.7, 29.9, 29.9, 28.3, 28.2, 28.1, 28.0, 26.9, 21.1, 18.5, 18.4 ppm. ^{31}P{1H} NMR (162 MHz, CD_2Cl_2): δ = 35.21 ppm; IR (KBr): ν = 3109, 3053, 2921, 2849, 1743, 1608, 1588, 1537, 1487, 1445, 1355, 1318, 1302, 1268, 1250, 1222, 1173, 1130, 1108, 1072, 1043, 1027, 1004, 976, 914, 886, 847, 774, 752, 732, 697, 647, 619, 578, 523, 508, 489 cm^{-1}; Anal. Calcd. for $C_{50}H_{63}ClN_2PRuS$: C, 64.78, H, 6.85, N, 3.02, S, 3.46, Cl, 7.65; Found: C, 64.59, H, 6.94, N, 3.08, S, 3.32, Cl, 7.44. HRMS ESI (m/z) calcd. for $C_{50}H_{63}Cl_2N_2PRuS$ $[M-Cl]^+$ 891.3182, found 891.3191.

Compound 5b

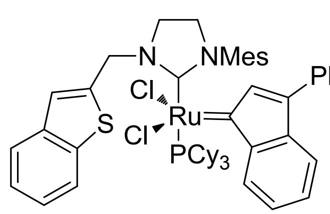


The same procedure as described for compound **5a** was employed using: **4b** (93.1 mg, 0.24 mmol), Umicore™ **M1** (111 mg, 0.12 mmol) and dry toluene (8 mL).

Yield: 35.7 mg (32 %) of the red powder.

^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.35 (d, 1H, *J* = 7.4 Hz), 7.71 (dd, 2H, *J* = 8.1 Hz, and *J* = 1.2 Hz), 7.55 (dd, 1H, *J* = 1.7 Hz, and *J* = 0.7 Hz), 7.53-7.50 (m, 1H), 7.43-7.41 (m, 2H), 7.23 (dt, 1H, *J* = 7.4 Hz, and *J* = 1.0 Hz), 7.16 (dt, 1H, *J* = 7.5 Hz, and *J* = 0.9 Hz), 7.12 (s, 1H), 7.04 (d, 1H, *J* = 7.2 Hz), 6.76 (d, 1H, *J* = 3.2 Hz), 6.49 (dd, 1H, *J* = 3.2 Hz and *J* = 1.8 Hz), 6.38 (s, 1H), 5.99 (s, 1H), 5.76 (d, 1H, *J* = 14.8 Hz), 5.69 (d, 1H, *J* = 14.8 Hz), 3.81-3.66 (m, 4H), 2.41-2.35 (m, 3H), 2.09 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H), 1.84-1.82 (m, 3H), 1.72-1.70 (m, 3H), 1.64-1.62 (m, 3H), 1.57 – 1.53 (m, 6H), 1.44-1.31 (m, 6H), 1.16-1.06 (m, 6H), 1.04-0.96 (m, 3H) ppm; ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 291.5 (d, $J_{P,C}$ = 5.0 Hz), 217.1 (d, $J_{P,C}$ = 69.6 Hz), 149.9, 144.2, 143.3, 140.9, 138.1, 137.5, 137.4, 137.1, 137.1, 136.9, 136.3, 129.3, 129.0, 128.8, 128.8, 128.3, 128.1, 127.6, 126.7, 116.5, 111.2, 110.7, 52.5 (br. s), 49.1 (d, $J_{P,C}$ = 2.4 Hz), 48.9, 32.8, 32.7, 29.9, 29.9, 28.3, 28.2, 28.1, 28.0, 26.9, 21.1, 18.5, 18.4 ppm; ^{31}P{1H} NMR (162 Hz, CD_2Cl_2): δ = 34.96 ppm; IR (KBr): ν = 3111, 3052, 2923, 2849, 1746, 1608, 1589, 1537, 1488, 1445, 1378, 1352, 1320, 1302, 1268, 1254, 1227, 1196, 1173, 1144, 1073, 1047, 1027, 1009, 976, 936, 915, 884, 846, 817, 775, 751, 733, 698, 671, 647, 618, 599, 580, 524, 508, 491, 464, 448 cm^{-1}; Anal. Calcd. for $C_{50}H_{63}Cl_2N_2OPRu$: C, 65.92, H, 6.97, N, 3.08, Cl, 7.78; Found: C, 66.11, H, 7.09, N, 2.82, Cl, 7.56; HRMS ESI (m/z) calcd. for $C_{50}H_{63}ClN_2OPRu$ $[M-Cl]^+$ 875.3410, found 875.3430

Compound 5c

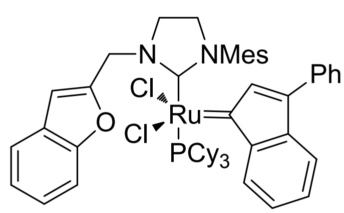


The same procedure as described for compound **5a** was employed using: **4c** (454 mg, 1.00 mmol), Umicore™ **M1** (462 mg, 0.50 mmol) and dry toluene (30 mL).

Yield: 147 mg (30 %) of the red powder.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.37 (dd, 1H, J = 7.5 Hz, and J = 0.9 Hz), 7.91-7.89 (m, 1H), 7.86-7.83 (m, 1H), 7.73-7.71 (m, 2H), 7.65 (br. s, 1H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.40-7.34 (m, 2H), 7.25 (dt, 1H, J = 7.4 Hz, J = 1.2 Hz), 7.17 (dt, 1H, J = 7.5 Hz J = 1.2 Hz), 7.14 (s, 1H), 7.05 (dd, 1H, J = 7.2 Hz and J = 1.0 Hz), 6.39 (br. s, 1H), 6.00 (br. s, 1H), 6.00 (d, 1H, J = 14.3 Hz) 5.92 (d, 1H, J = 14.3 Hz), 3.84-3.64 (m, 4H), 2.43-2.34 (m, 3H), 2.12 (s, 3H), 2.01 (s, 3H), 1.88 (s, 3H), 1.84-1.81 (m, 3H), 1.73-1.70 (m, 3H), 1.62 - 1.59 (m,3H), 1.56 – 1.52 (m, 6H), 1.43 – 1.27 (m, 6H), 1.17-0.97 (m, 9H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 291.6 (d, $J_{P,C}$ = 5.2 Hz), 217.1 (d, $J_{P,C}$ = 69.3 Hz), 144.1, 141.4, 140.9, 139.8, 139.8, 138.2, 138.2, 137.5, 137.5, 137.4, 137.1, 137.0, 136.9, 136.2, 129.3, 129.0, 128.8, 128.8, 128.3, 128.1, 127.6, 126.7, 125.4, 124.9, 124.7, 124.0, 122.9, 116.5, 52.5 (d, $J_{P,C}$ = 2.1 Hz), 51.9, 48.6 (d, $J_{P,C}$ = 3.2 Hz), 32.8, 32.6, 29.9, 28.3, 28.2, 28.1, 28.0, 26.9, 26.9, 21.1, 18.5, 18.4 ppm. ^{31}P{1H} NMR (162 Hz, CD_2Cl_2): δ = 35.30 ppm; IR (KBr): ν = 3110, 3052, 2920, 2847, 1608, 1588, 1537, 1486, 1444, 1377, 1353, 1319, 1297, 1268, 1253, 1229, 1200, 1173, 1155, 1115, 1070, 1027, 1005, 976, 915, 885, 847, 774, 751, 728, 697, 647, 619, 581, 562, 508, 483, 450, 405 cm^{-1}; Anal. Calcd. for $C_{54}H_{65}Cl_2N_2PRuS$: C, 66.38, H, 6.71, N, 2.87, S, 3.28, Cl, 7.26; Found: C, 66.18, H, 6.79, N, 2.77, S, 3.34, Cl, 7.37. HRMS ESI (m/z) calcd. for $C_{54}H_{65}ClN_2PRuS$ [M-Cl]$^+$ 941.3338, found 941.3332.

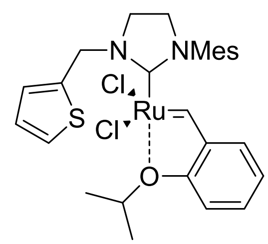
Compound 5d



In a Schlenk flask were placed **4d** (438.0 mg, 1.00 mmol) and Umicore™ **M1** (462 mg, 0.50 mmol). Then dry THF (30 mL) was added, and the solution was heated at 75 ºC for 40 minutes. The mixture was allowed to cool to room temperature. Solvent was evaporated, and crude product was purified by column chromatography on silica (10% EtOAc:*c*-hex, then 30% EtOAc:*c*-hex) and then by slow evaporation from the mixture of solvents CH_2Cl_2:CH_3OH. The product was dried under vacuum to give red powder. Yield 49.0 mg (10 %)

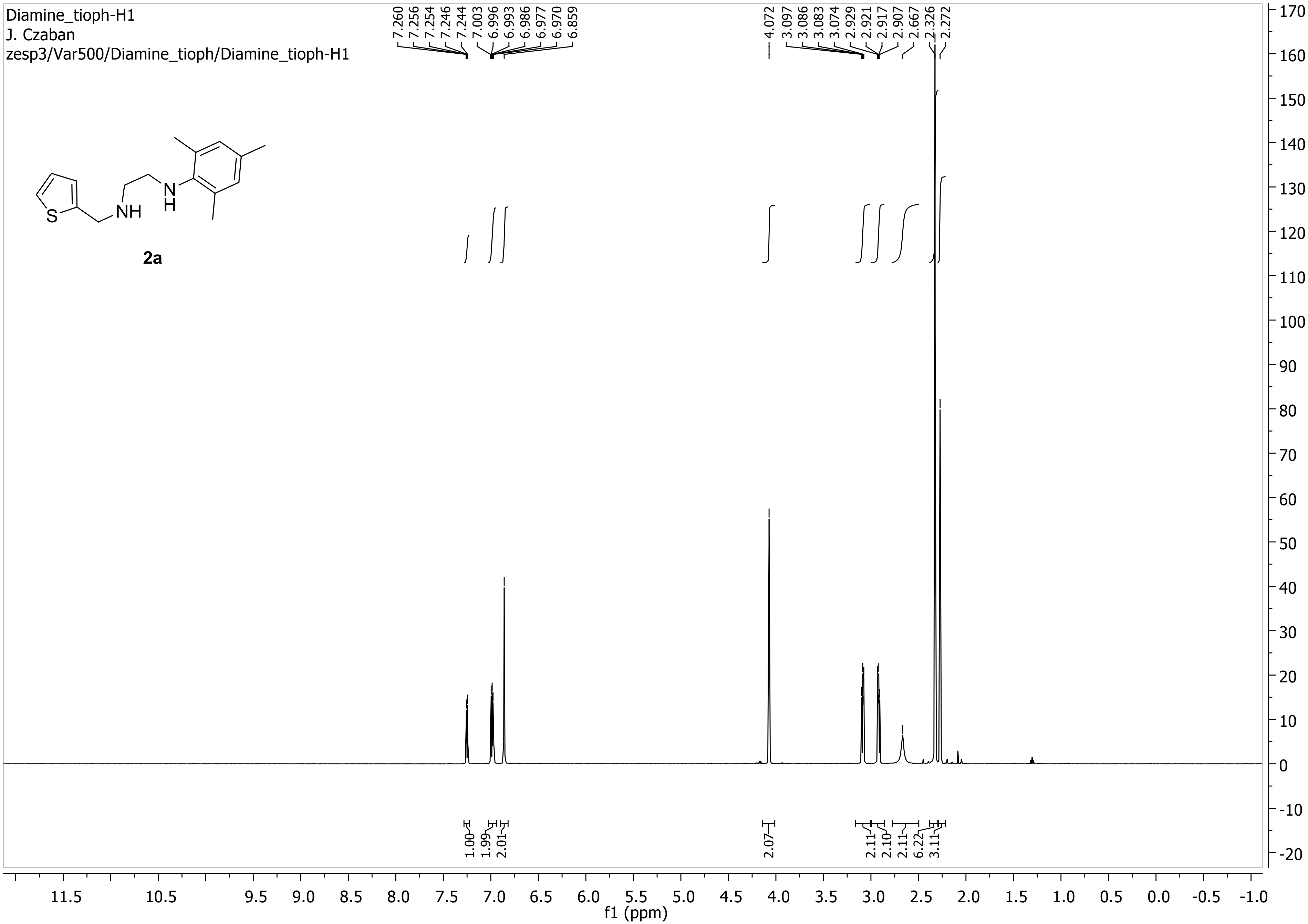
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.35 (d, 1H, J = 7.5 Hz), 7.73 – 7.69 (m, 2H), 7.67 – 7.65 (m, 1H), 7.58 – 7.51 (m, 2H), 7.45 – 7.40 (m, 2H), 7.34 (dt, 1H, J = 8.1 Hz, J = 1.4 Hz), 7.29 – 7.22 (m, 2H), 7.19 (br. s, 1H), 7.17 – 7.15 (m, 1H), 7.13 (s, 1H), 7.05 (dd, 1H, J = 7.2 Hz and J = 0.7 Hz), 6.39 (br. s, 1H), 6,00 (br. s, 1H), 5.92 (d, 1H, J = 15.3 Hz), 5.83 (d, 1H, J = 15.3 Hz), 3.93 – 3.69 (m, 4H), 2.42 – 2.33 (m, 3H), 2.11 (s, 3H), 2.00 (s, 3H), 1.87 (s, 3H), 1.84 – 1.80 (m, 3H), 1.71 – 1.69 (m, 3H), 1.61 – 1.53 (m, 9H), 1.45 – 1.30 (m, 6H), 1.16 – 0.95 (m, 9H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 291.8 (d, $J_{P,C}$ = 5.2 Hz), 217.6 (d, $J_{P,C}$ = 69.8 Hz), 155.5, 152.8, 144.1 (br. s), 140.8, 137.5 (br. s), 137.4, 137.1, 137.0, 136.9, 136.2, 129.3, 129.0, 129.0, 128.8, 128.8, 128.3, 128.1, 128.0, 127.6, 126.7, 124.8, 123.3, 121.7, 116.5, 111.6, 107.3, 52.6 (d, $J_{P,C}$ = 2.1 Hz), 49.4 (d, $J_{P,C}$ = 3.2 Hz), 49.3, 32.9, 32.7, 29.9, 29.9, 28.3, 28.2, 28.1, 28.0, 26.9, 21.1, 18.5, 18.4 ppm. ^{31}P{1H} NMR (162 MHz, CD_2Cl_2): 34.62 ppm. IR (KBr): ν = 3437, 3108, 3051, 2924, 2848, 1609, 1587, 1536, 1487, 1444, 1377, 1355, 1322, 1299, 1266, 1251, 1216, 1168, 1129, 1106, 1072, 1027, 1005, 976, 957, 915, 886, 847, 817, 775, 752, 738, 698, 649, 619, 581, 526, 509, 492, 430, 405 cm $^{-1}$; Anal. Calcd. for $C_{54}H_{65}Cl_2N_2OPRu$: C, 67.49, H, 6.82, N, 2.91, Cl, 7.38; Found: C, 67.32, H, 6.79, N, 2.82, Cl, 7.11. HRMS ESI (m/z) calcd. for $C_{54}H_{65}ClN_2PRuO$ $[M-Cl]^+$ 925.3567, found 925.3582.

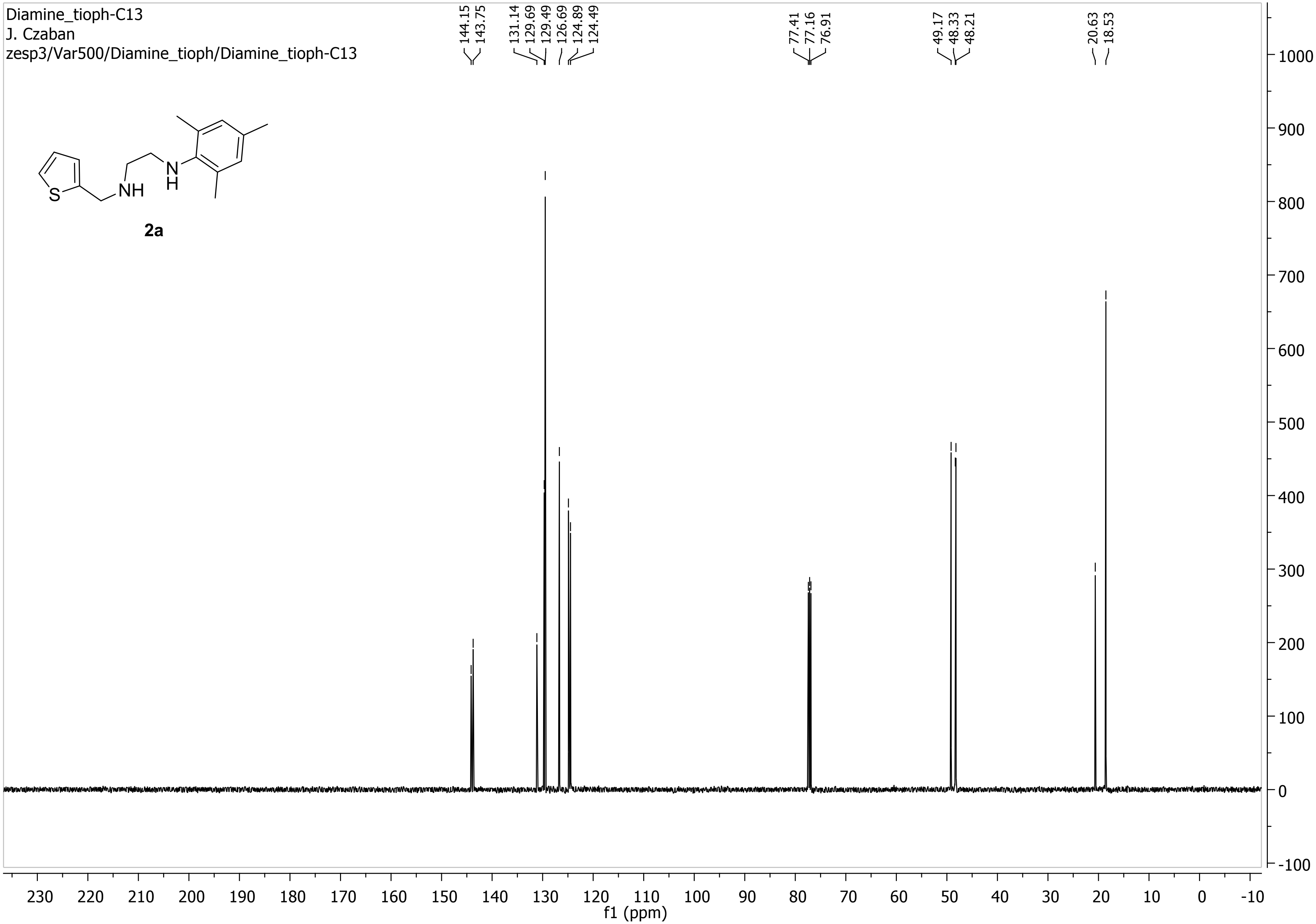
Compound 7



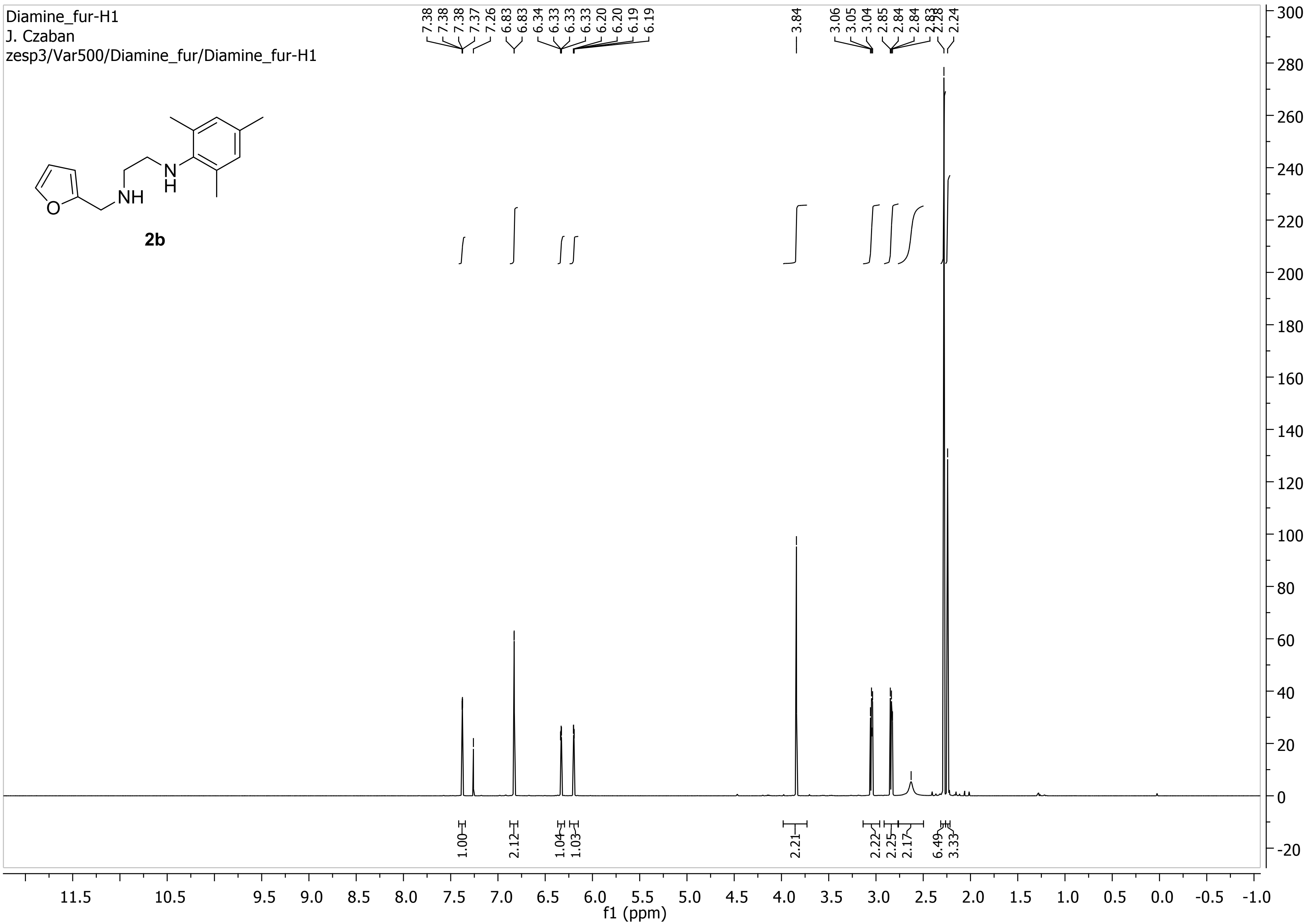
In a Schlenk flask were placed **3a** (265 mg, 0.713 mmol) and dry toluene (20 mL). The 25% solution of potassium *tert*-amylate in toluene (0.4 mL) was added at 75 ºC. The reaction mixture was stirred for 1 minute. After this time the solid **Hoveyda I** catalyst (389 mg, 0.648 mmol) was added in one portion and the reaction mixture was stirred for additional 5 minutes at 75 ºC. Then the solid CuCl (64.8 mg, 0.648 mmol) was added and the resulting mixture was stirred 5 minutes. The reaction mixture was cooled down, filtered through silica and flushed with the warm (50 ºC) mixture of solvents (75% *v*/*v* EtOAc:*c*-hex). The solvents were evaporated. The residue was recrystallized twice from the mixture CH_2Cl_2:CH_3OH. The crude product was dried on rotary evaporator, and then dissolved in warm (50 ºC) EtOAc. The solution was filtered fast through a cotton wool, and solvent was evaporated. The residue was recrystallized three times from the mixture CH_2Cl_2:CH_3OH. The product was dried under vacuum to give green powder. Yield 252 mg (64 %)

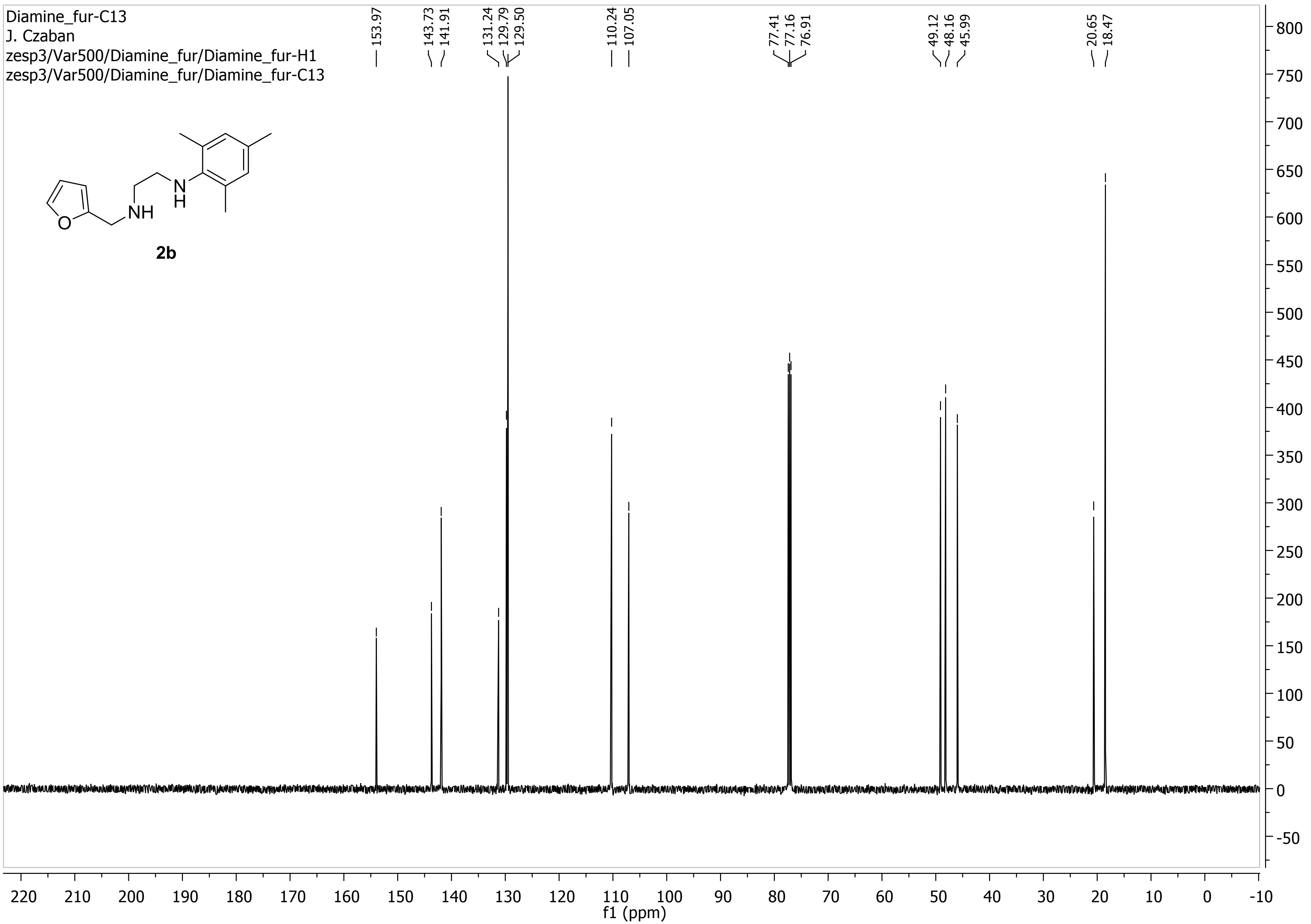
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 16.13 (s, 1H), 7.57 (ddd, 1H, J = 8.8 Hz, J = 6.7 Hz, J = 2.4 Hz), 7.40 (dd, 1H, J = 5.1 Hz, J = 1.2 Hz), 7.35 (d, 1H, J = 3.4 Hz), 7.11 (s, 2H), 7.08 (dd, 1H, J = 5.1 Hz, J = 3.5 Hz), 7.02 – 6.95 (m, 3H), 5.78 (s, 2H), 5.19 (septet, 1H, J = 6.1 Hz), 3.96 – 3.91 (m, 2H), 3.78 – 3.73 (m, 2H), 2.47 (s, 3H), 2.22 (s, 6H), 1.72 (d, 6H, J = 6.1 Hz) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 290.5, 209.8, 152.7, 144.0, 139.4, 139.2, 138.3, 138.0, 129.9, 128.5, 127.1, 126.9, 122.9, 122.5, 113.3, 75.6, 52.3, 51.0, 48.1, 22.2, 21.3, 18.1 ppm; IR (KBr): *ν* = 3077, 3061, 3026, 2979, 2917, 2882, 1953, 1913, 1834, 1731, 1606, 1589, 1574, 1483, 1451, 1415, 1382, 1335, 1303, 1293, 1271, 1246, 1219, 1192, 1162, 1154, 1144, 1109, 1094, 1036, 964, 934, 903, 878, 853, 840, 796, 787, 772, 752, 732, 704, 665, 644, 616, 582, 570, 480, 438 cm^{-1}; Anal. Calcd. for $C_{27}H_{32}Cl_2N_2ORuS$: C, 53.64, H, 5.33, N, 4.63, S, 5.30, Cl, 11.73; Found: C, 53.39, H, 5.44, N, 4.38, S, 5.39, Cl, 11.87.


Diamine_tioph-H1
J. Czaban
zesp3/Var500/Diamine_tioph/Diamine_tioph-H1
2a
f1 (ppm)

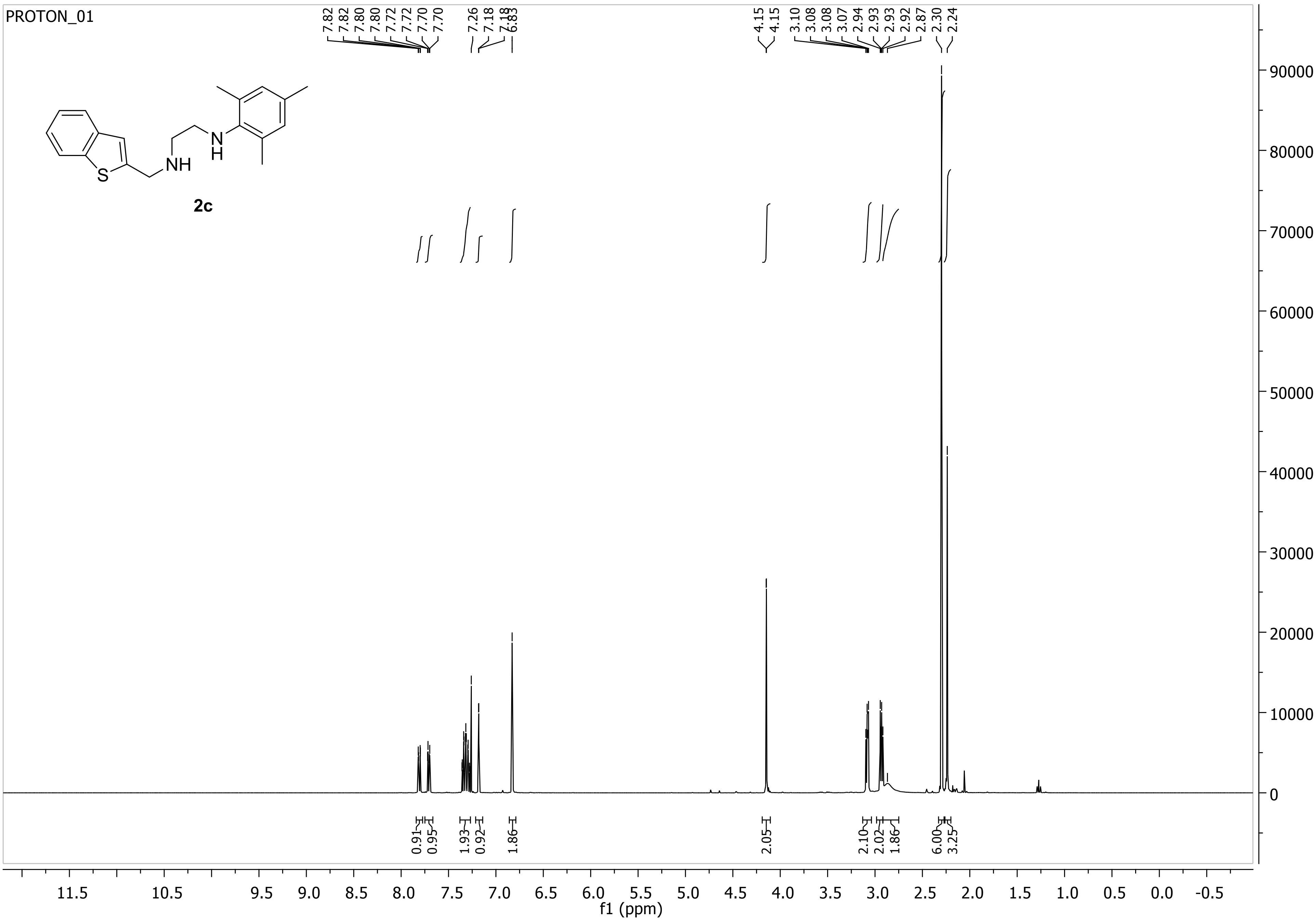


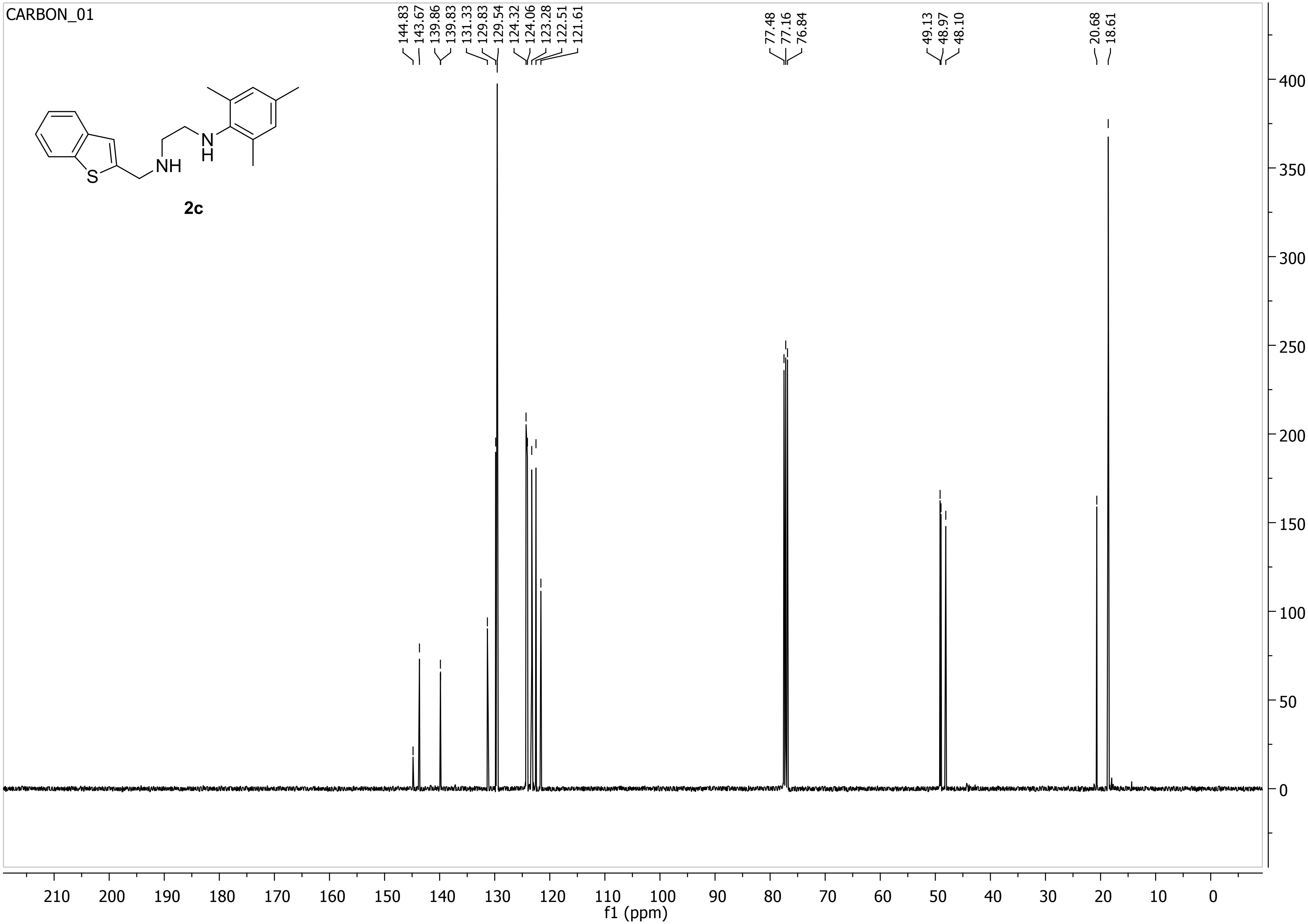
Diamine_tioph-C13
J. Czaban
zesp3/Var500/Diamine_tioph/Diamine_tioph-C13
144.15
143.75
131.14
129.69
129.49
126.69
124.89
124.49
77.41
77.16
76.91
49.17
48.33
48.21
20.63
18.53
S
NH
N
H
2a
1000
900
800
700
600
500
400
300
200
100
0
-100
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

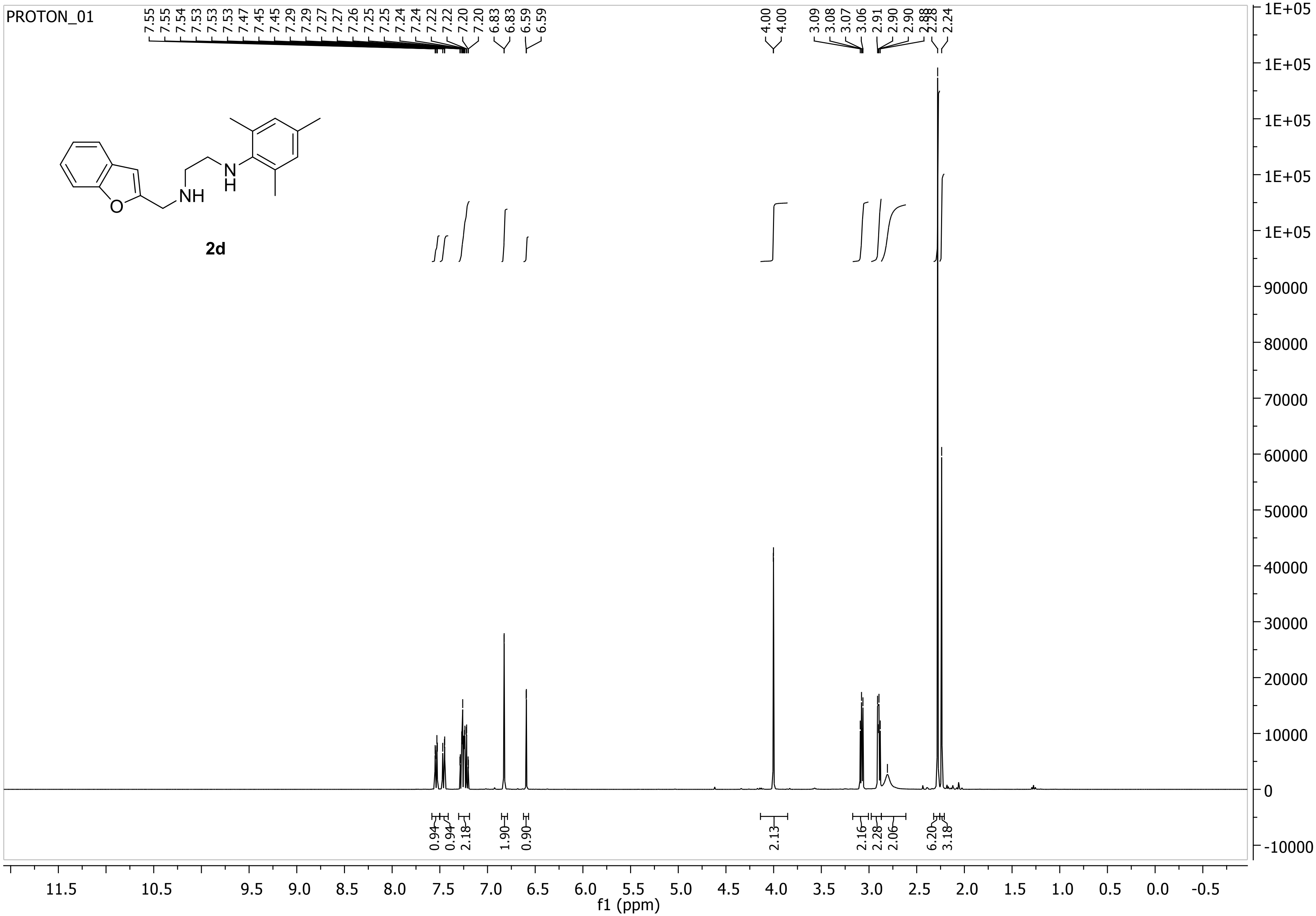

Diamine_fur-H1
J. Czaban
zesp3/Var500/Diamine_fur/Diamine_fur-H1
2b
7.38 7.38 7.38 7.37 7.26 6.83 6.83 6.34 6.33 6.33 6.33 6.20 6.20 6.19 6.19
3.84
3.06 3.05 3.04 2.85 2.84 2.84 2.83 2.28 2.24
1.00 2.12 1.04 1.03 2.21 2.22 2.25 2.17 6.49 3.33
f1 (ppm)



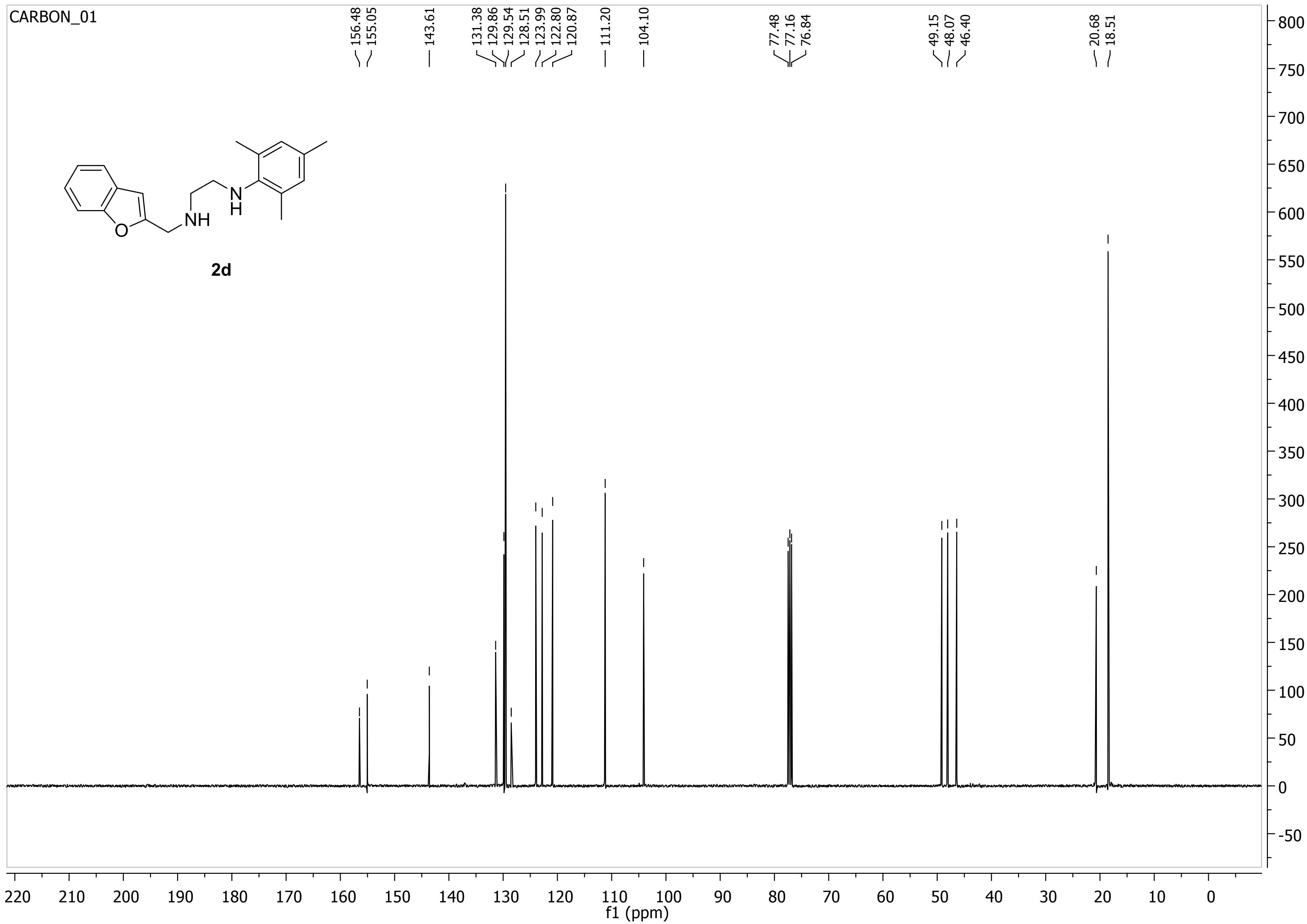
Diamine_fur-C13
J. Czaban
zesp3/Var500/Diamine_fur/Diamine_fur-H1
zesp3/Var500/Diamine_fur/Diamine_fur-C13
153.97
143.73
141.91
131.24
129.79
129.50
110.24
107.05
77.41
77.16
76.91
49.12
48.16
45.99
20.65
18.47
NH
N
H
O
2b
f1 (ppm)

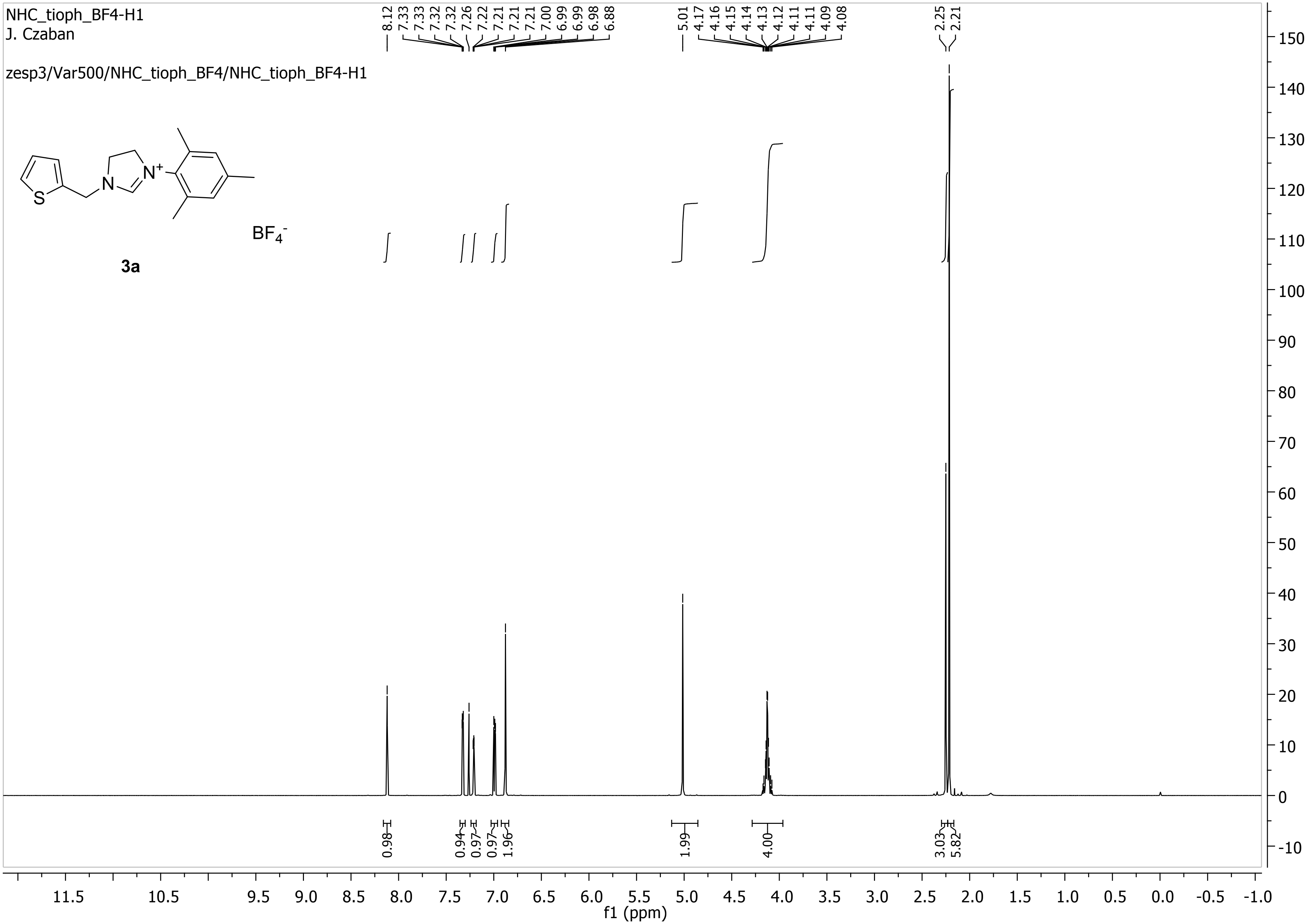

PROTON_01
7.82
7.82
7.80
7.80
7.72
7.72
7.70
7.70
7.26
7.18
7.18
6.83
4.15
4.15
3.10
3.08
3.08
3.07
2.94
2.93
2.93
2.92
2.87
2.30
2.24
NH
N
H
S
2c
0.91
0.95
1.93
0.92
1.86
2.05
2.10
2.02
1.86
6.00
3.25
f1 (ppm)

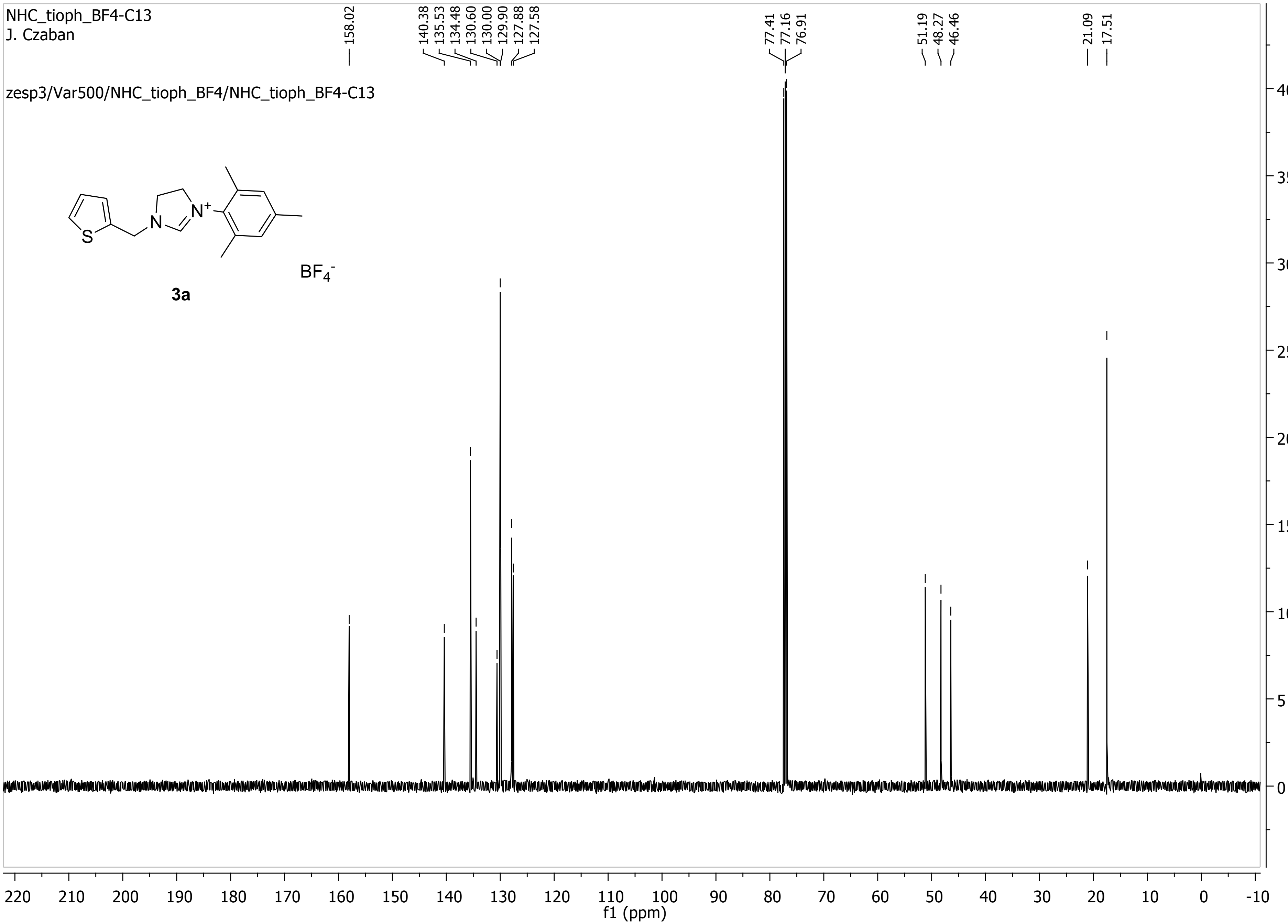

CARBON_01
144.83
143.67
139.86
139.83
131.33
129.83
129.54
124.32
124.06
123.28
122.51
121.61
77.48
77.16
76.84
49.13
48.97
48.10
20.68
18.61
2c
f1 (ppm)

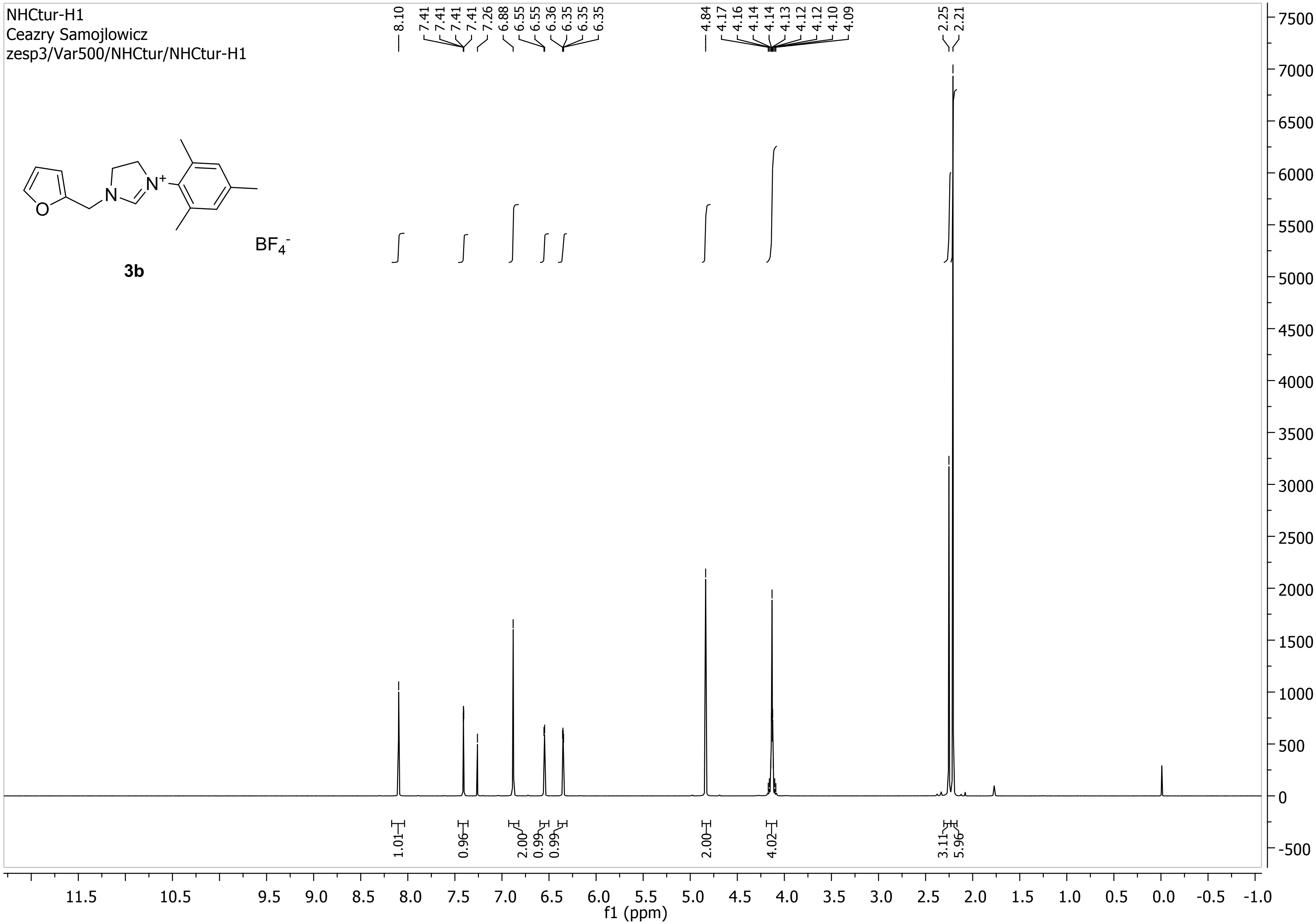


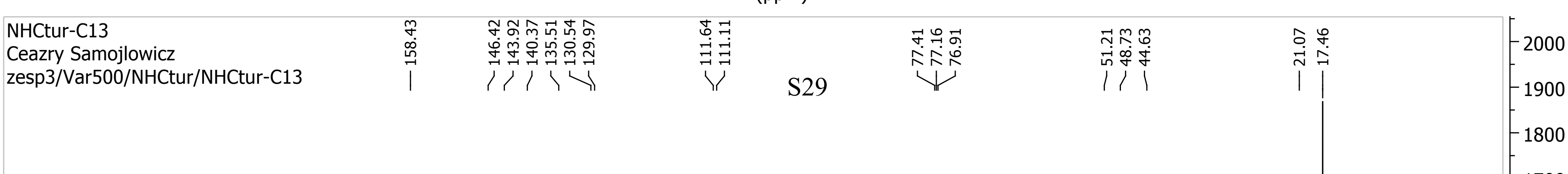
2d
PROTON_01
7.55
7.55
7.54
7.53
7.53
7.53
7.47
7.45
7.45
7.29
7.29
7.27
7.27
7.26
7.25
7.25
7.24
7.24
7.22
7.22
7.20
7.20
6.83
6.83
6.59
6.59
4.00
4.00
3.09
3.08
3.07
3.06
2.91
2.90
2.90
2.88
2.28
2.24
0.94
0.94
2.18
1.90
0.90
2.13
2.16
2.28
2.06
6.20
3.18
f1 (ppm)

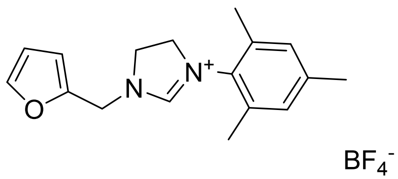

CARBON_01
156.48
155.05
143.61
131.38
129.86
129.54
128.51
123.99
122.80
120.87
111.20
104.10
77.48
77.16
76.84
49.15
48.07
46.40
20.68
18.51
NH
N
H
O
2d
f1 (ppm)


NHC_tioph_BF4-H1
J. Czaban
zesp3/Var500/NHC_tioph_BF4/NHC_tioph_BF4-H1
8.12 7.33 7.33 7.32 7.32 7.26 7.22 7.21 7.21 7.21 7.00 6.99 6.99 6.98 6.88
5.01 4.17 4.16 4.15 4.14 4.13 4.12 4.11 4.11 4.09 4.08
2.25 2.21
BF4-
3a
0.98 0.94 0.97 0.97 1.96 1.99 4.00 3.03 5.82
f1 (ppm)

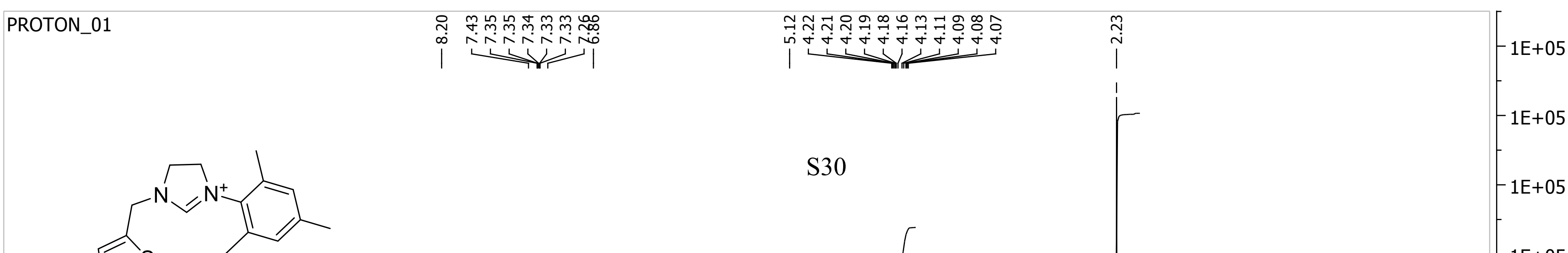

NHC_tioph_BF4-C13
J. Czaban
zesp3/Var500/NHC_tioph_BF4/NHC_tioph_BF4-C13
158.02
140.38
135.53
134.48
130.60
130.00
129.90
127.88
127.58
77.41
77.16
76.91
51.19
48.27
46.46
21.09
17.51
BF4-
3a
f1 (ppm)


NHCtur-H1
Ceazry Samojlowicz
zesp3/Var500/NHCtur/NHCtur-H1
8.10 7.41 7.41 7.41 7.41 7.26 6.88 6.55 6.55 6.36 6.35 6.35 6.35
4.84 4.17 4.16 4.14 4.14 4.13 4.12 4.12 4.10 4.09
2.25 2.21
BF4-
3b
1.01 0.96 2.00 0.99 0.99 2.00 4.02 3.11 5.96
f1 (ppm)

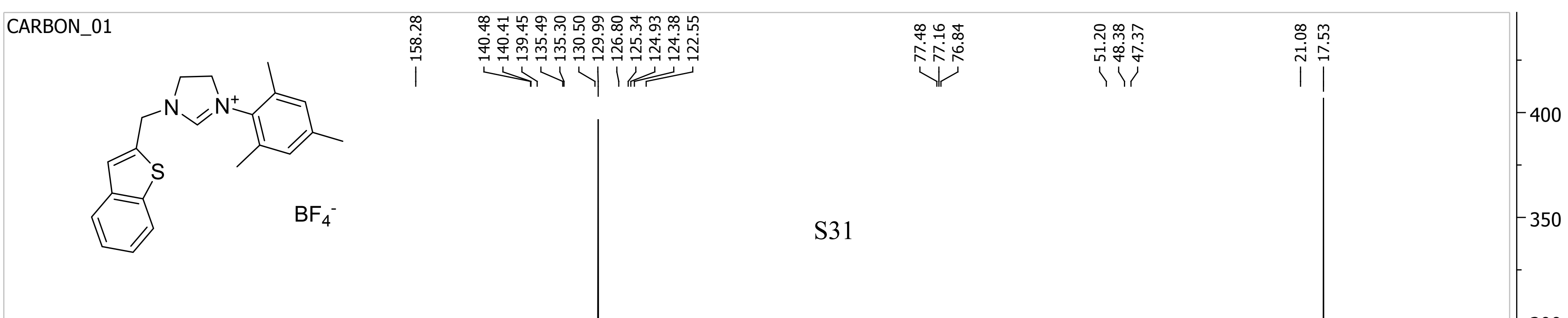

NHCtur-C13
Ceazry Samojlowicz
zesp3/Var500/NHCtur/NHCtur-C13
158.43
146.42 143.92 140.37 135.51 130.54 129.97
111.64 111.11
77.41 77.16 76.91
51.21 48.73 44.63
21.07 17.46


N
N+
O
BF4-

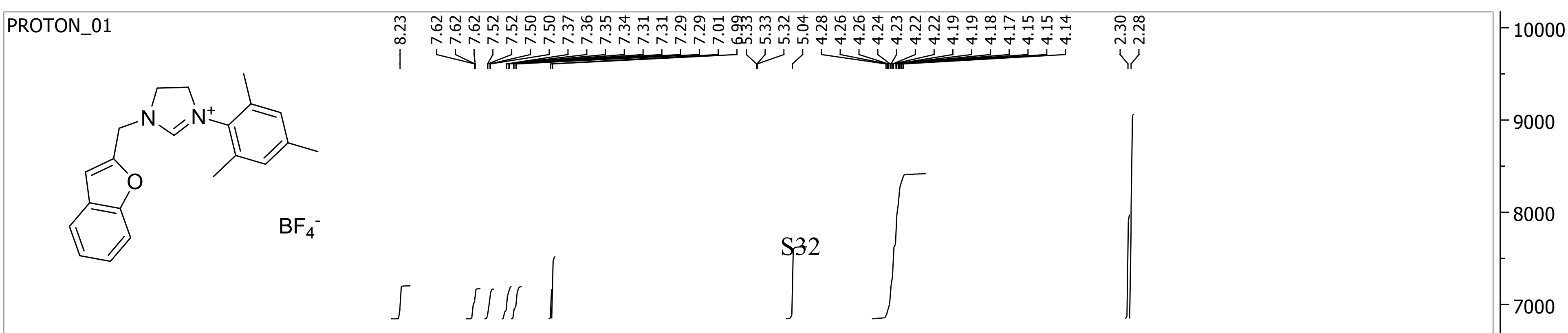
3b


PROTON_01
8.20
7.43
7.35
7.35
7.34
7.33
7.33
7.26
6.86
5.12
4.22
4.21
4.20
4.19
4.18
4.16
4.13
4.11
4.09
4.08
4.07
2.23
1E+05
1E+05
1E+05

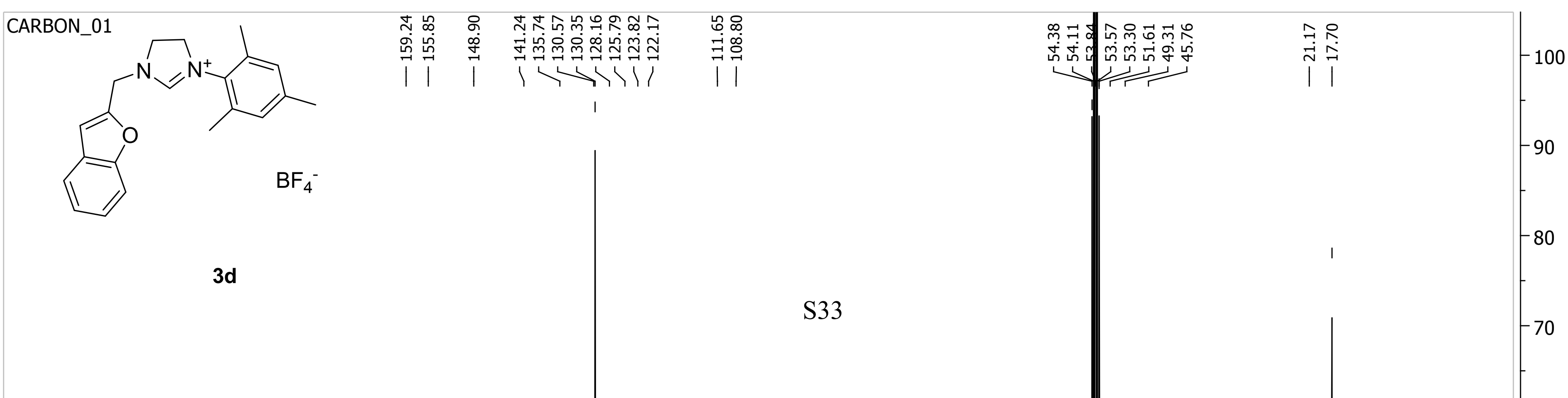
3c


CARBON_01
158.28
140.48
140.41
139.45
135.49
135.30
130.50
129.99
126.80
125.34
124.93
124.38
122.55
77.48
77.16
76.84
51.20
48.38
47.37
21.08
17.53
N
N+
S
BF_4^-
400
350

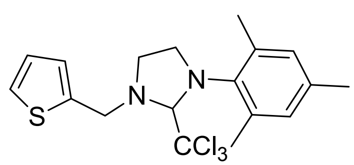
3c


PROTON_01
8.23
7.62
7.62
7.62
7.52
7.52
7.50
7.50
7.37
7.36
7.35
7.34
7.31
7.31
7.29
7.29
7.01
6.99
5.33
5.33
5.32
5.04
4.28
4.26
4.26
4.24
4.23
4.22
4.22
4.19
4.19
4.18
4.17
4.15
4.15
4.14
2.30
2.28
N
N+
O
BF4-
10000
9000
8000
7000

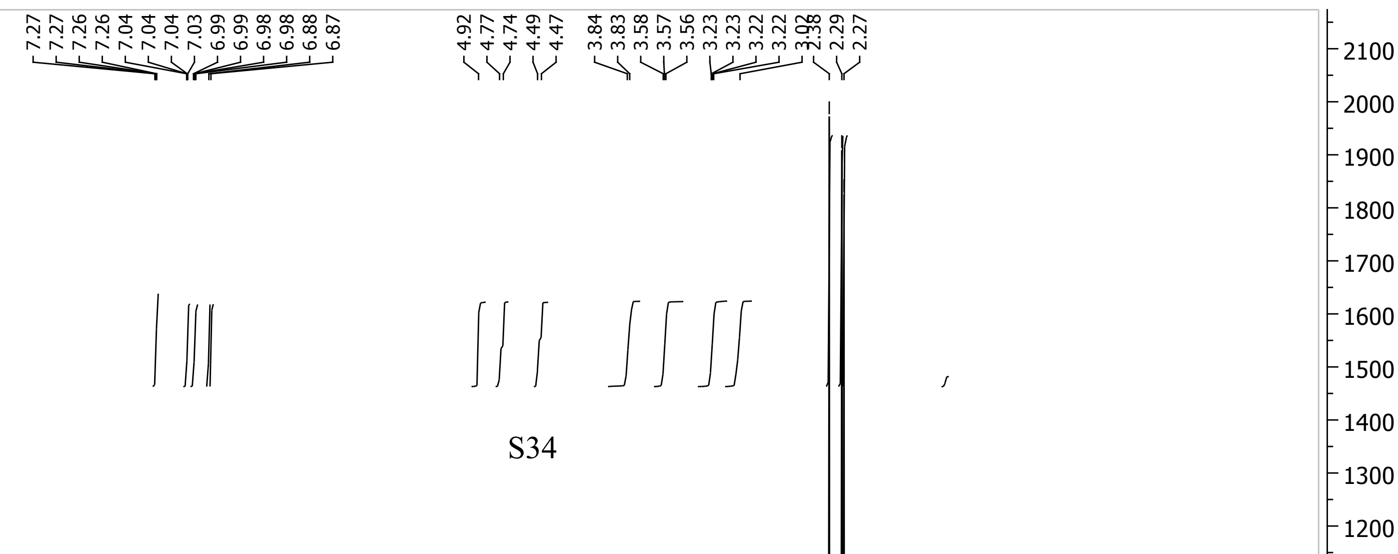
3d

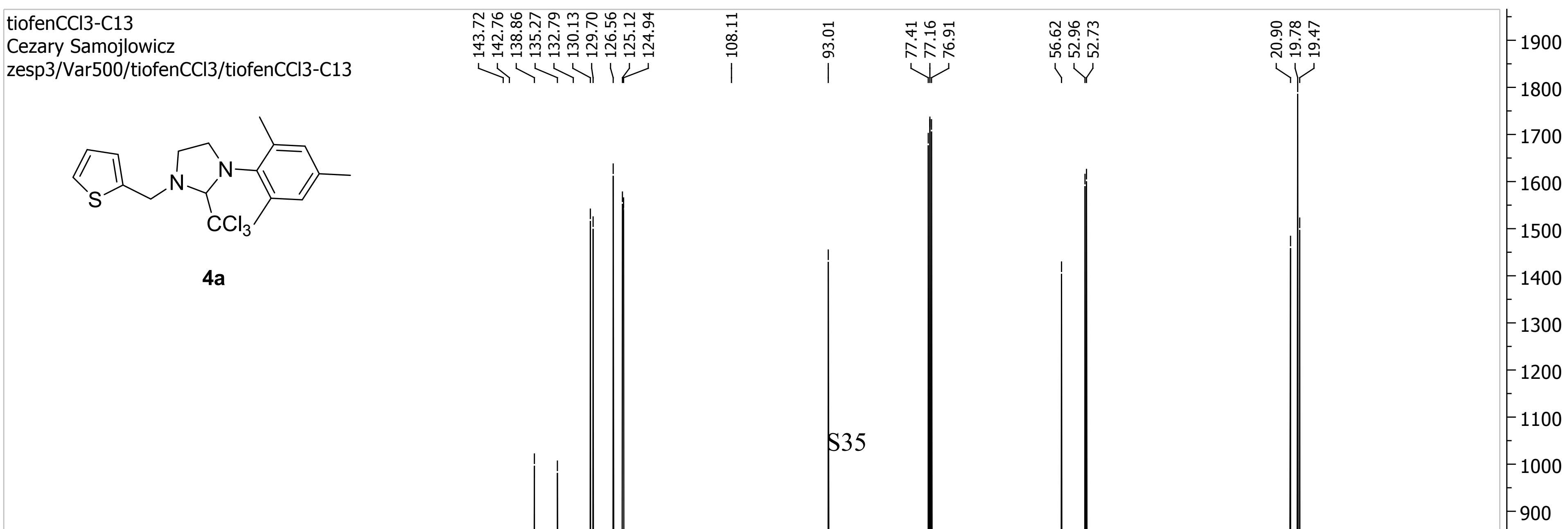

CARBON_01
BF4-
3d
159.24
155.85
148.90
141.24
135.74
130.57
130.35
128.16
125.79
123.82
122.17
111.65
108.80
54.38
54.11
53.84
53.57
53.30
51.61
49.31
45.76
21.17
17.70
100
90
80
70

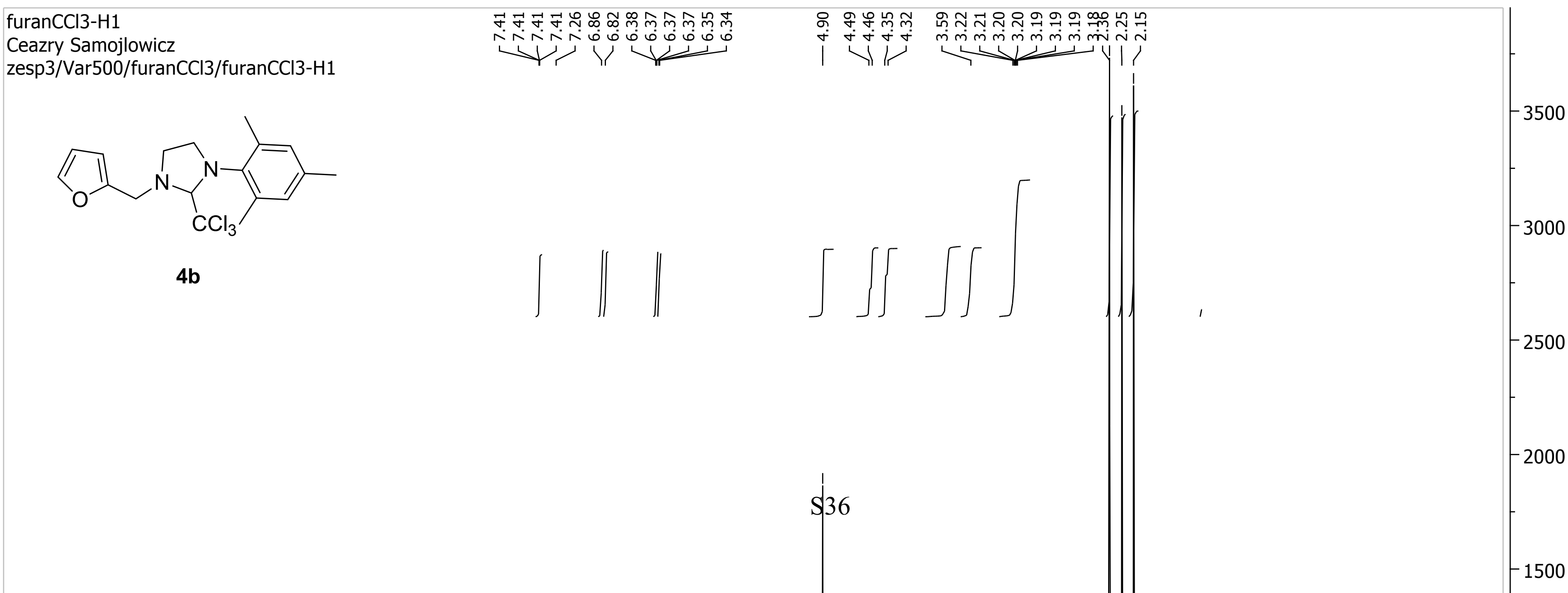
tiofenCCl3-H1
Cezary Samojlowicz
zesp3/Var500/tiofenCCl3/tiofenCCl3-H1



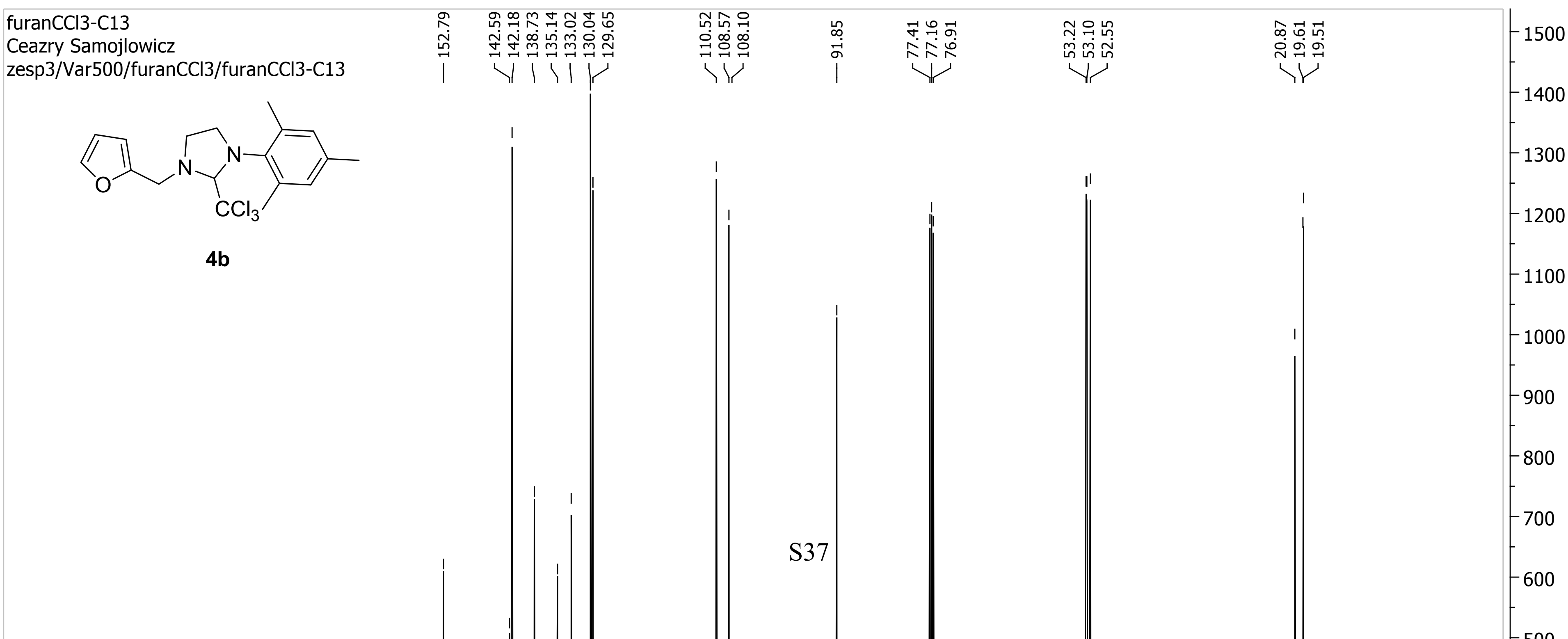
4a

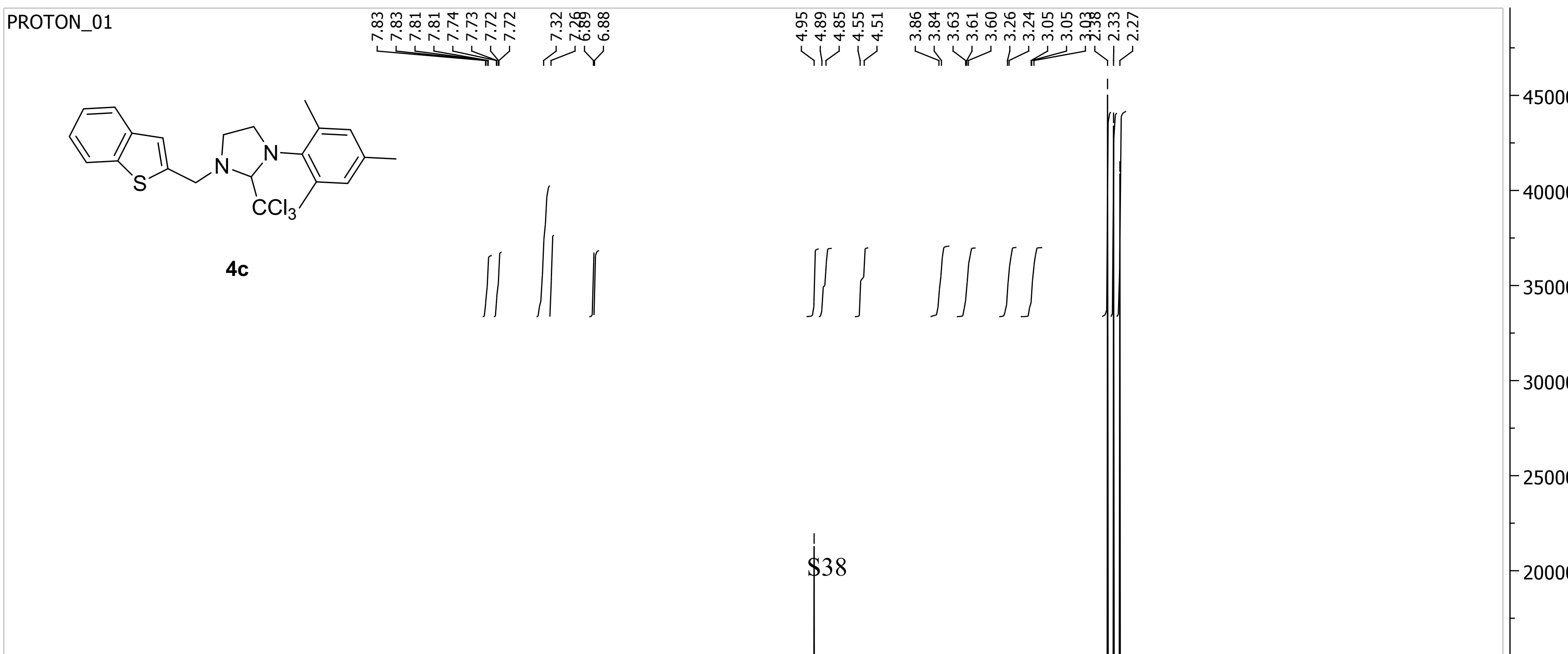



tiofenCCl3-C13
Cezary Samojlowicz
zesp3/Var500/tiofenCCl3/tiofenCCl3-C13
4a
143.72
142.76
138.86
135.27
132.79
130.13
129.70
126.56
125.12
124.94
108.11
93.01
77.41
77.16
76.91
56.62
52.96
52.73
20.90
19.78
19.47
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900

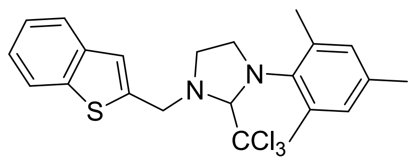


furanCCl3-H1
Ceazry Samojlowicz
zesp3/Var500/furanCCl3/furanCCl3-H1
4b
7.41
7.41
7.41
7.41
7.26
6.86
6.82
6.38
6.37
6.37
6.37
6.35
6.34
4.90
4.49
4.46
4.35
4.32
3.59
3.22
3.21
3.20
3.20
3.19
3.19
3.19
3.18
2.36
2.25
2.15
3500
3000
2500
2000
1500

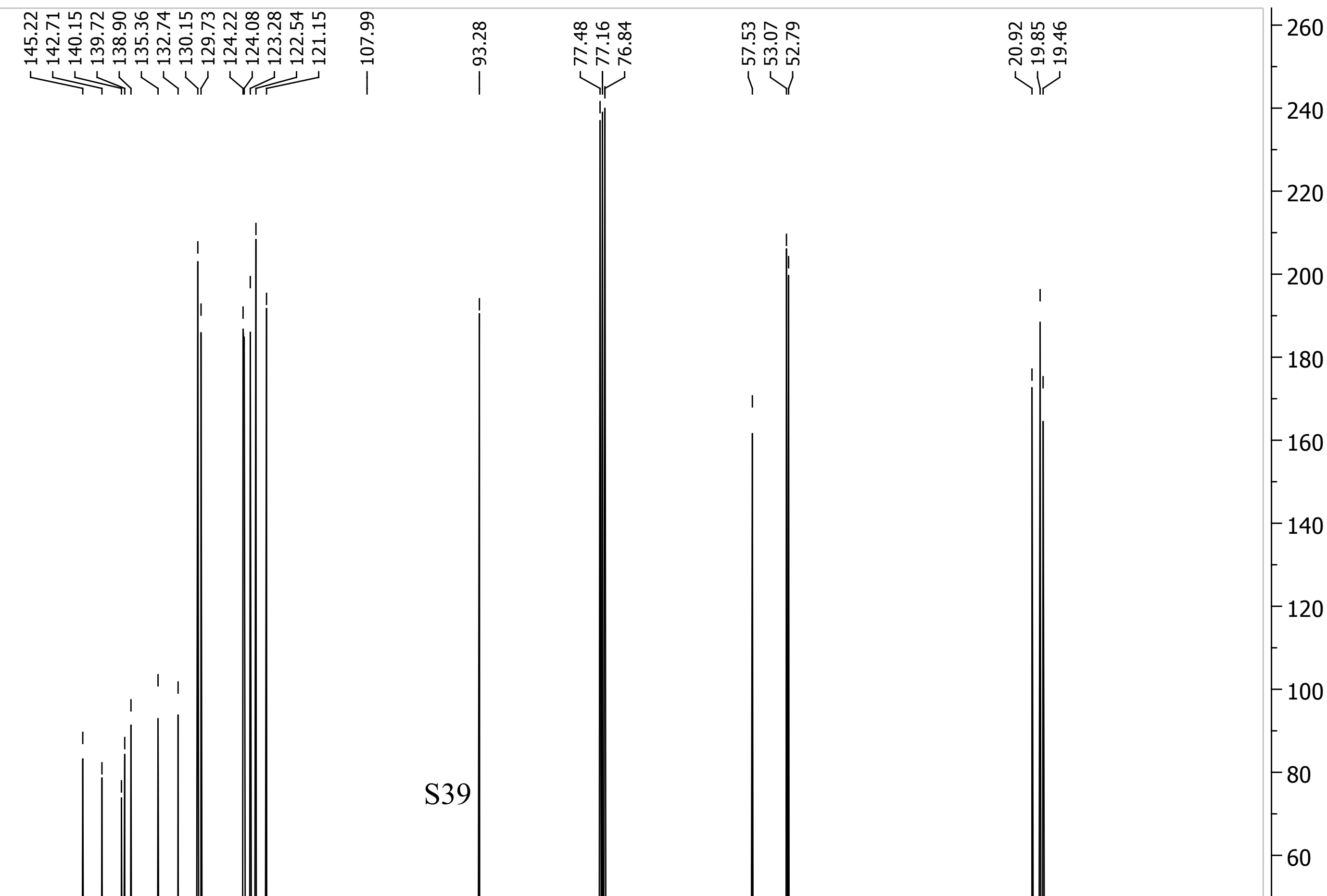

furanCCl3-C13
Ceazry Samojlowicz
zesp3/Var500/furanCCl3/furanCCl3-C13
4b
152.79
142.59
142.18
138.73
135.14
133.02
130.04
129.65
110.52
108.57
108.10
91.85
77.41
77.16
76.91
53.22
53.10
52.55
20.87
19.61
19.51
1500
1400
1300
1200
1100
1000
900
800
700
600
500



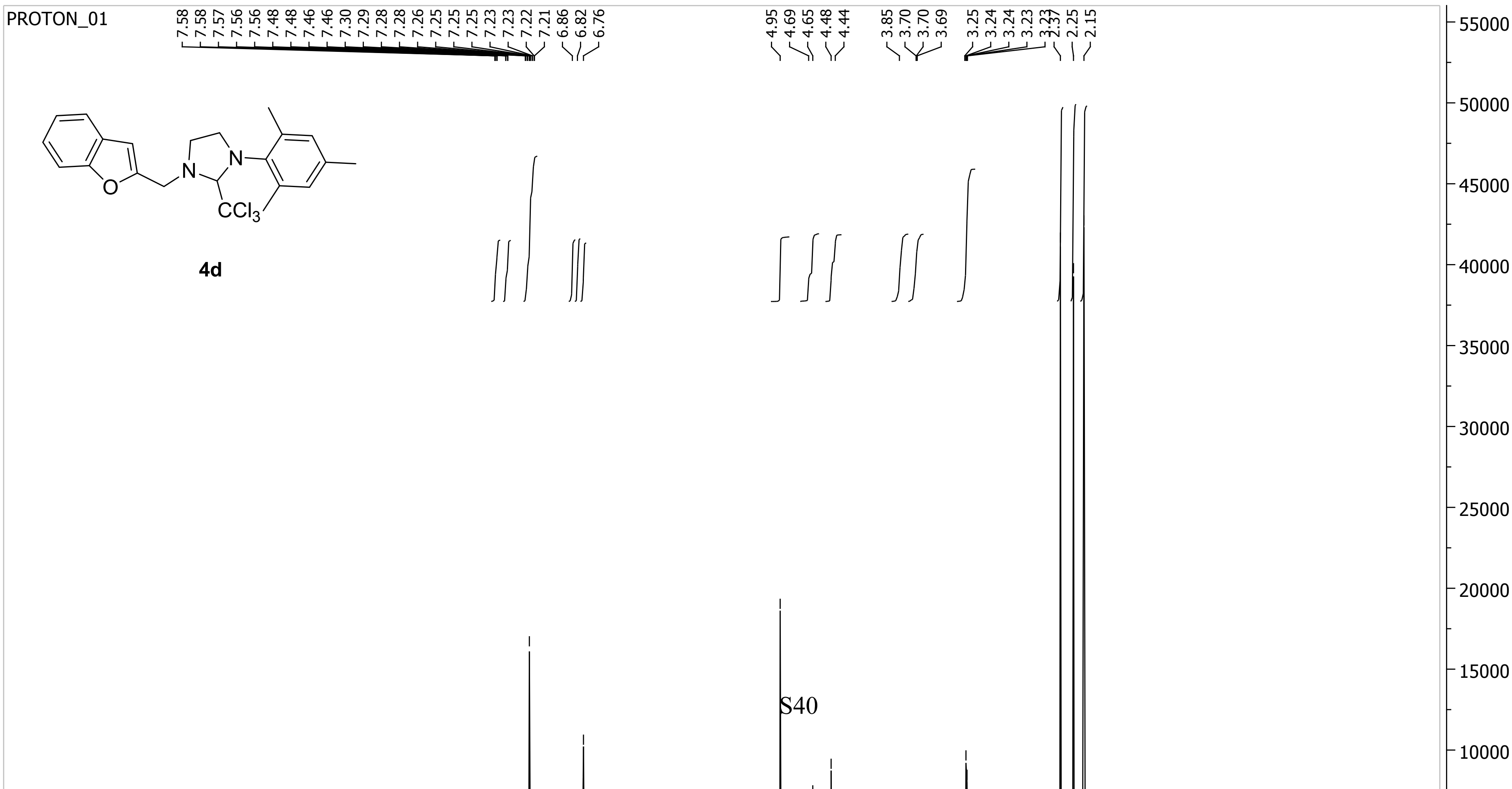
PROTON_01
7.83
7.83
7.81
7.81
7.74
7.73
7.72
7.72
7.32
7.26
6.89
6.88
4.95
4.89
4.85
4.55
4.51
3.86
3.84
3.63
3.61
3.60
3.26
3.24
3.05
3.05
3.03
2.38
2.33
2.27
N
N
S
CCl3
4c
45000
40000
35000
30000
25000
20000

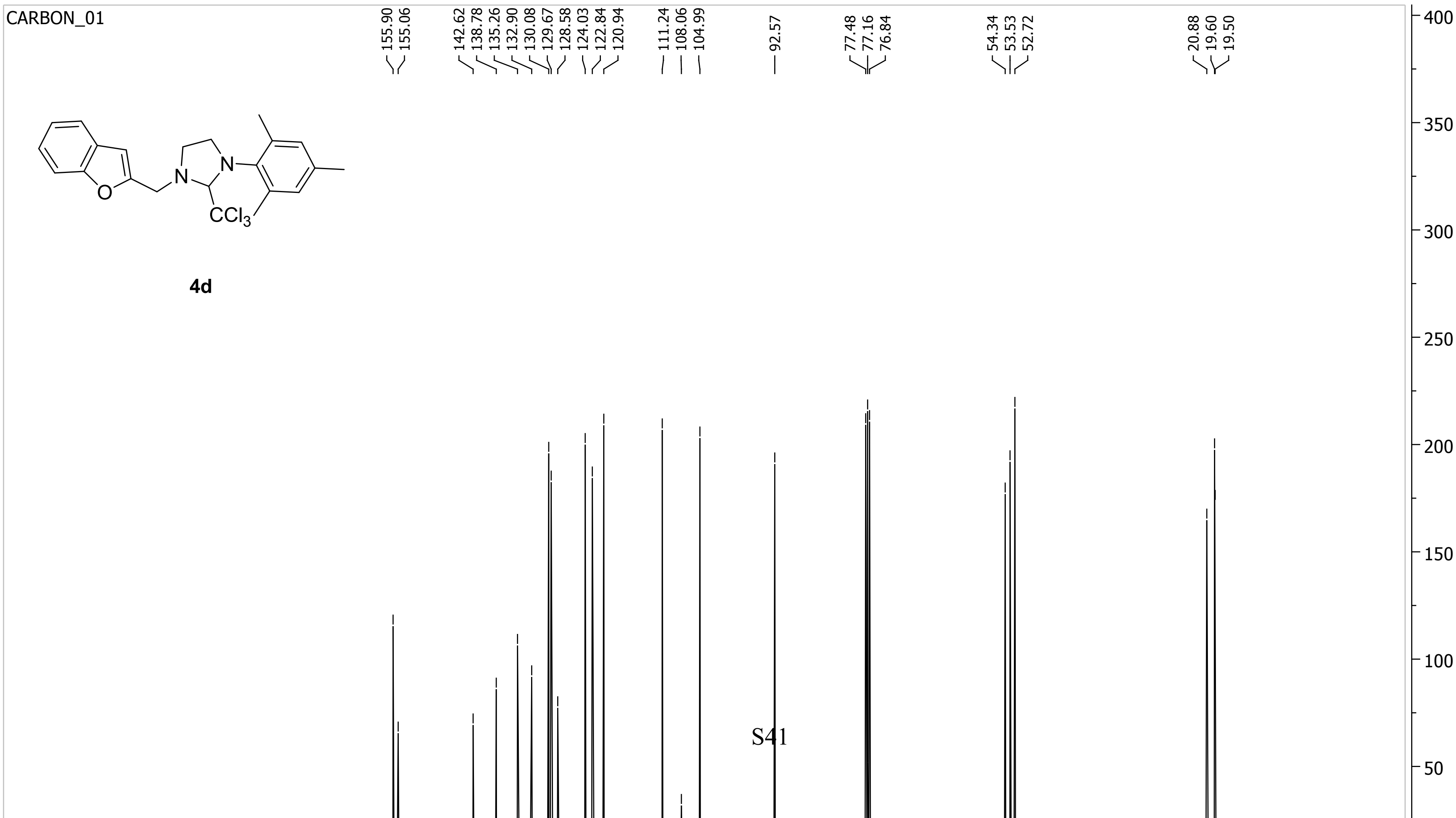


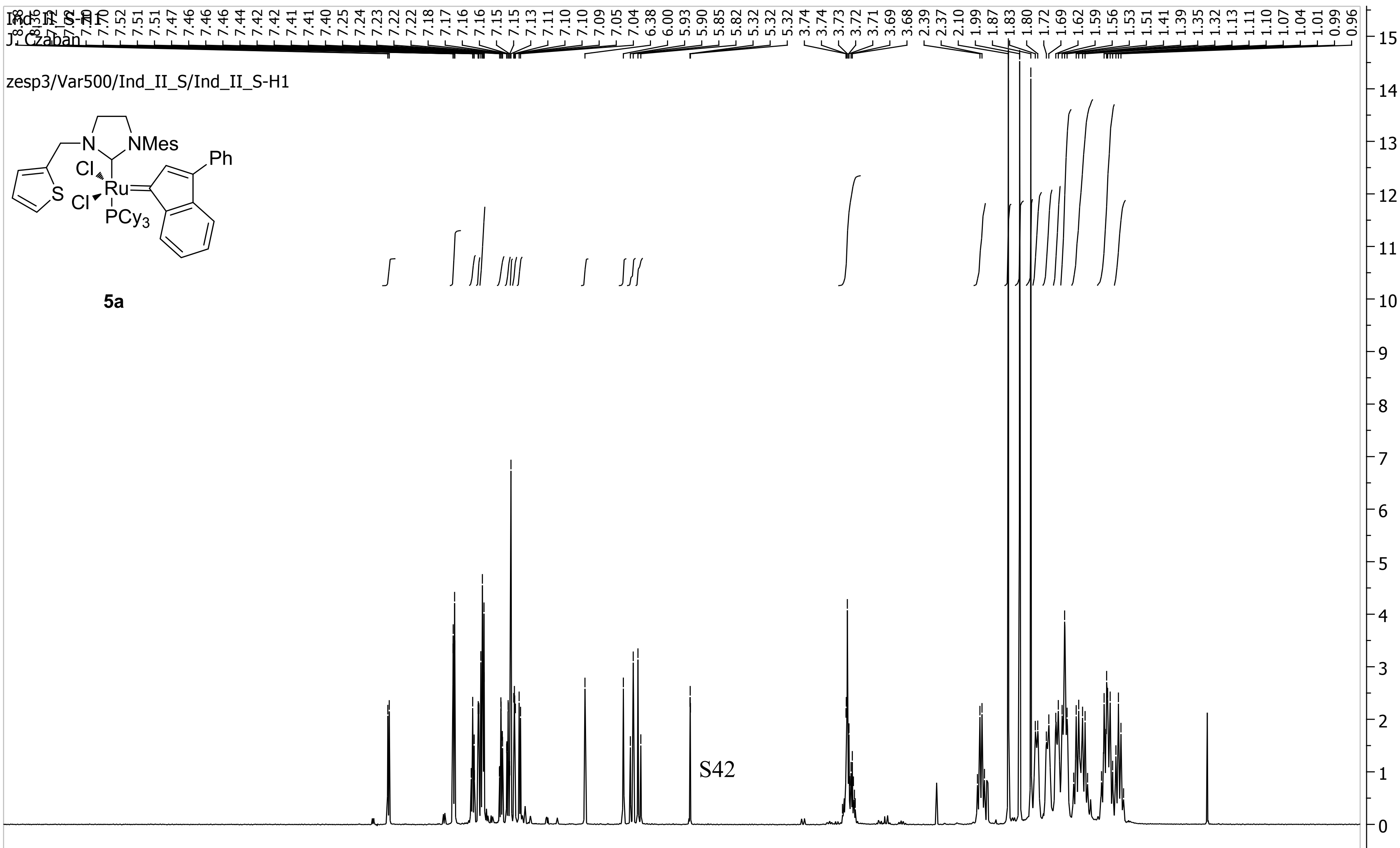
4c

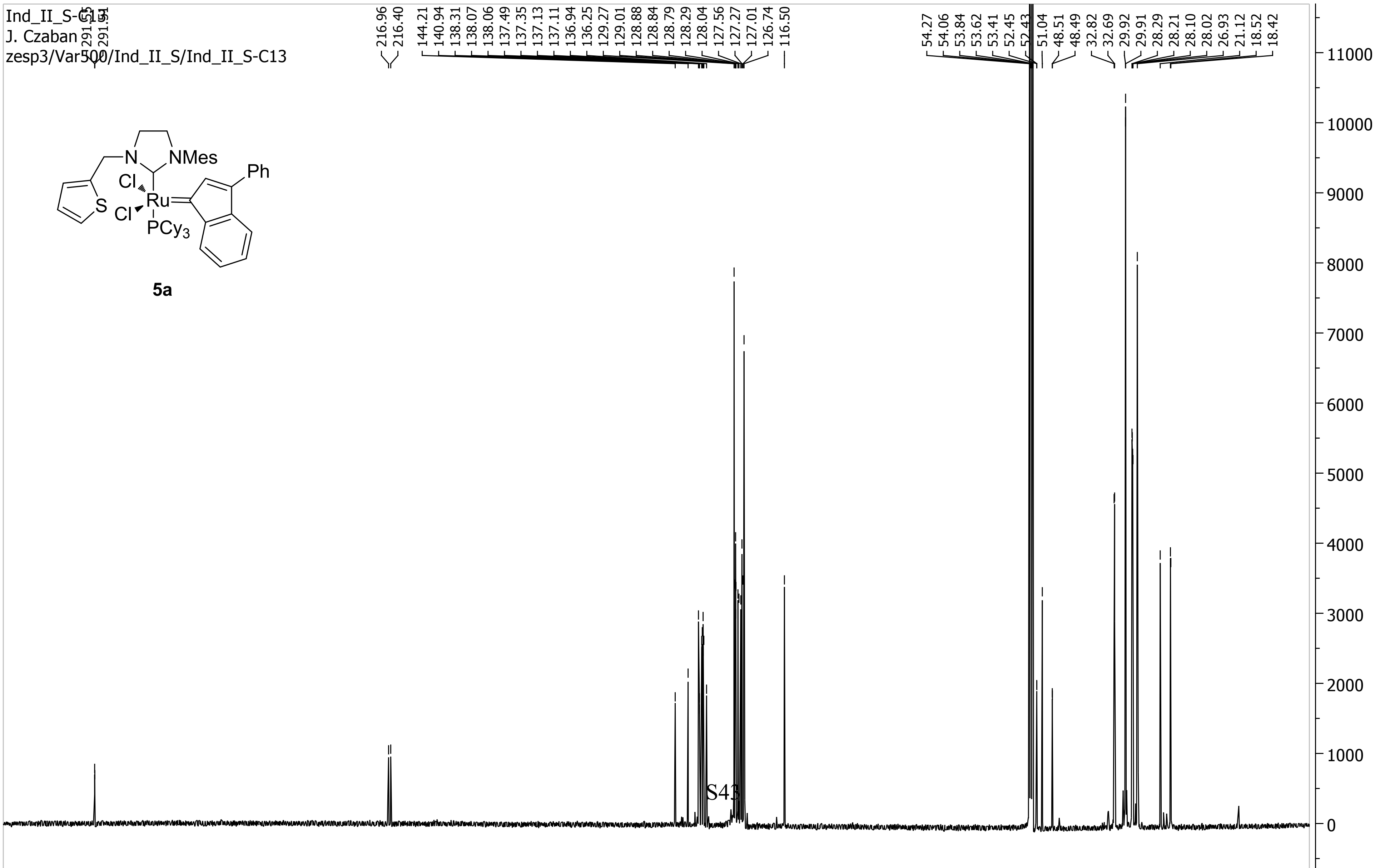


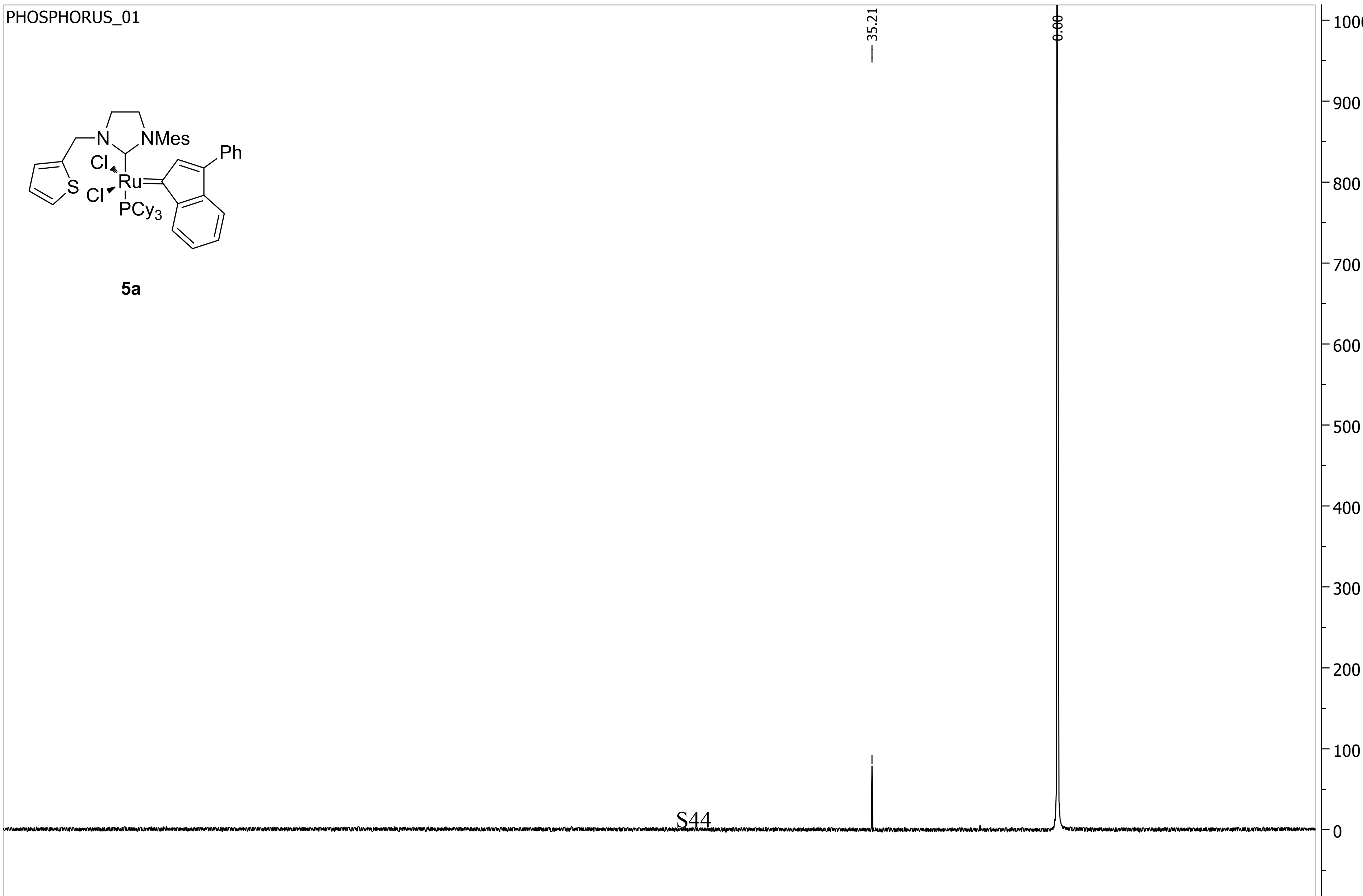
CARBON_01
145.22
142.71
140.15
139.72
138.90
135.36
132.74
130.15
129.73
124.22
124.08
123.28
122.54
121.15
107.99
93.28
77.48
77.16
76.84
57.53
53.07
52.79
20.92
19.85
19.46
260
240
220
200
180
160
140
120
100
80
60

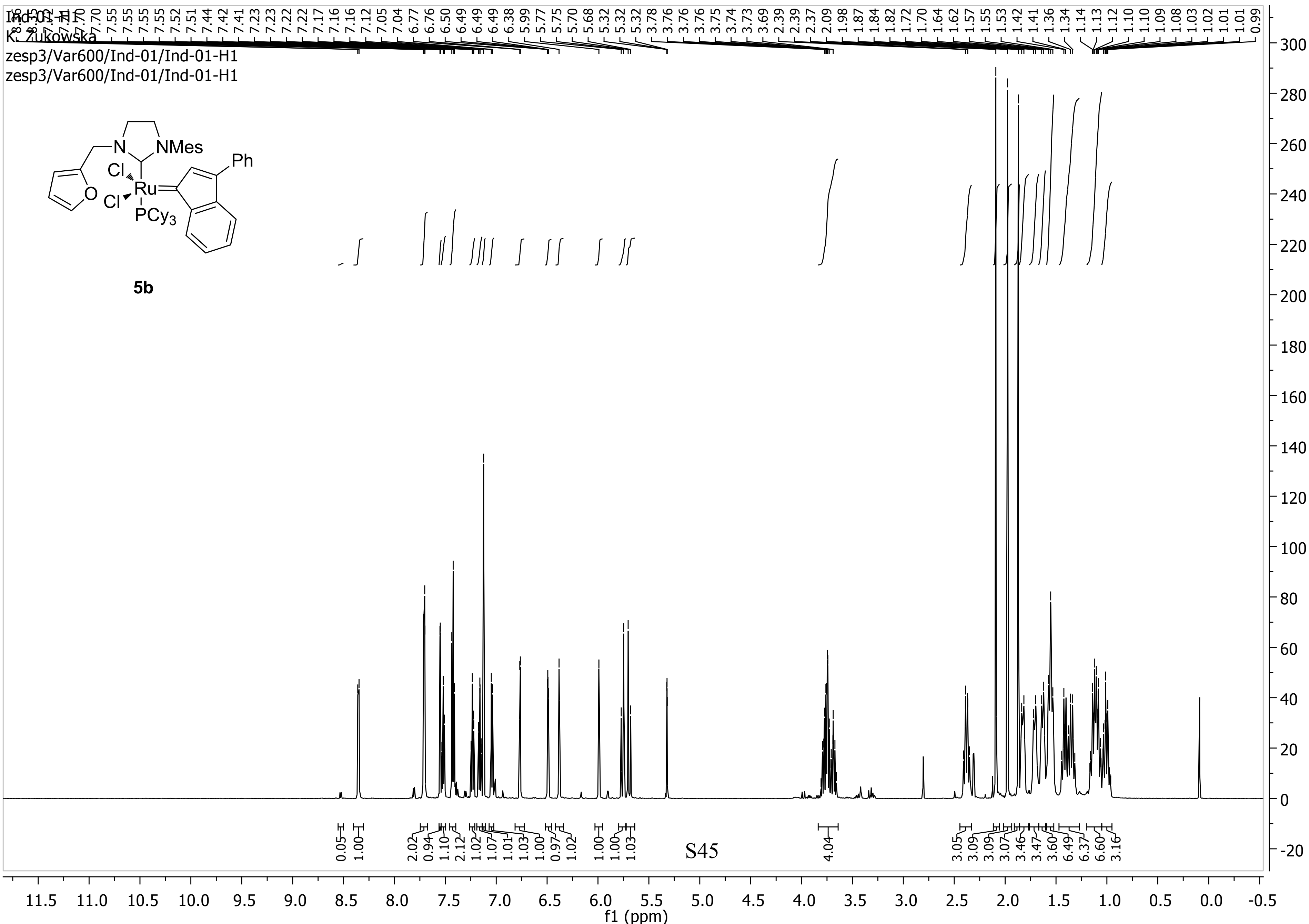

PROTON_01
7.58
7.58
7.57
7.56
7.48
7.48
7.46
7.46
7.30
7.29
7.28
7.28
7.26
7.25
7.25
7.25
7.23
7.23
7.22
7.21
6.86
6.82
6.76
4.95
4.69
4.65
4.48
4.44
3.85
3.70
3.70
3.69
3.25
3.24
3.24
3.23
3.23
2.37
2.25
2.15
N
N
O
CCl3
4d
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000

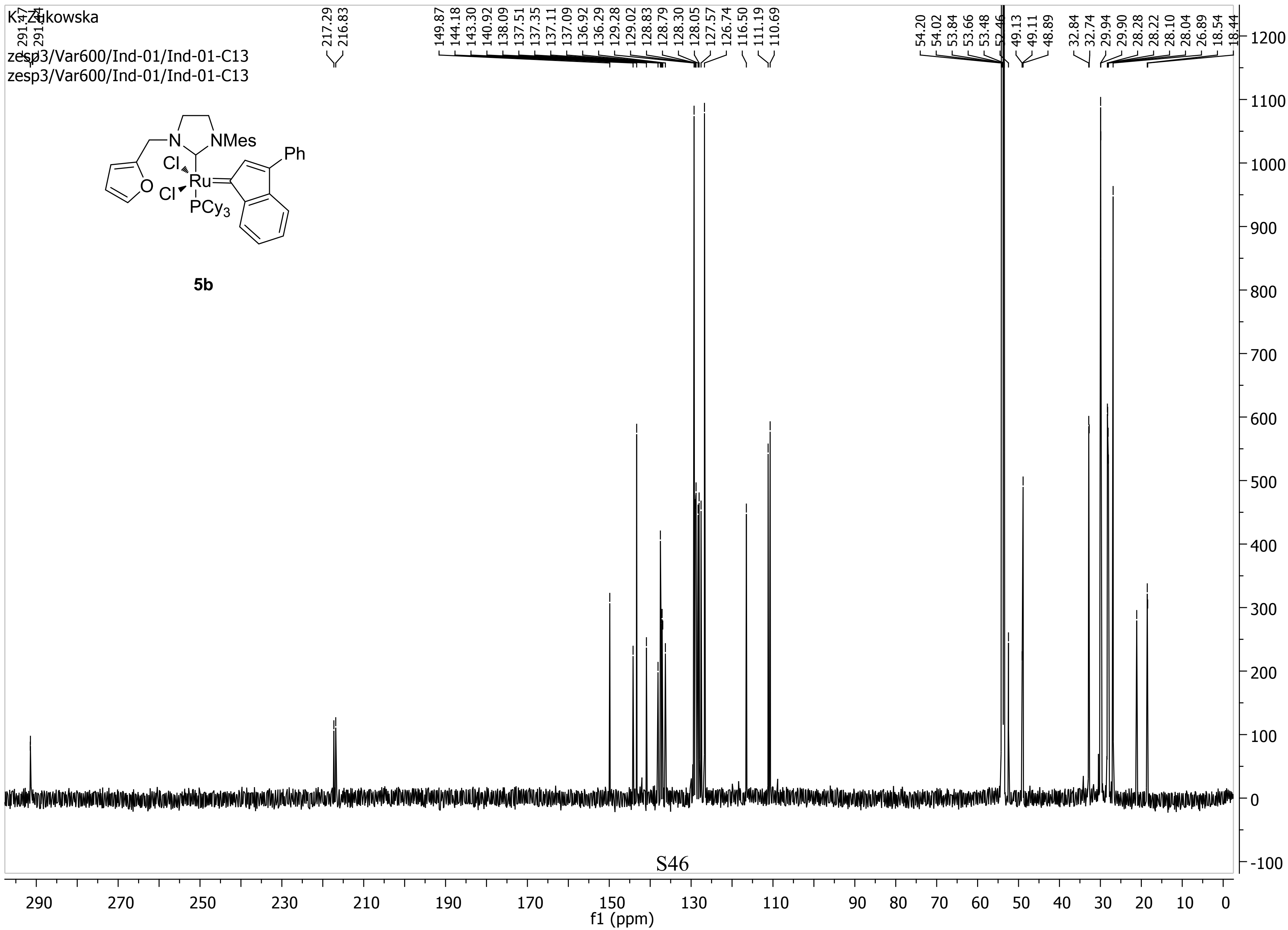

CARBON_01
155.90
155.06
142.62
138.78
135.26
132.90
130.08
129.67
128.58
124.03
122.84
120.94
111.24
108.06
104.99
92.57
77.48
77.16
76.84
54.34
53.53
52.72
20.88
19.60
19.50
N
N
O
CCl3
4d
400
350
300
250
200
150
100
50


Ind_II_S-H1
J. Czaban
zesp3/Var500/Ind_II_S/Ind_II_S-H1
NMes
Ph
Cl
Ru
S
Cl
PCy3
5a
7.70 7.52 7.51 7.51 7.47 7.46 7.46 7.44 7.42 7.42 7.41 7.41 7.40 7.25 7.24 7.23 7.22 7.22 7.18 7.17 7.16 7.15 7.15 7.13 7.11 7.10 7.10 7.09 7.05 7.04 6.38 6.00 5.93 5.90 5.85 5.82 5.32 5.32 5.32 3.74 3.74 3.73 3.72 3.71 3.69 3.68 2.39 2.37 2.10 1.99 1.87 1.83 1.80 1.72 1.69 1.62 1.59 1.56 1.53 1.51 1.41 1.39 1.35 1.32 1.13 1.11 1.10 1.07 1.04 1.01 0.99 0.96
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

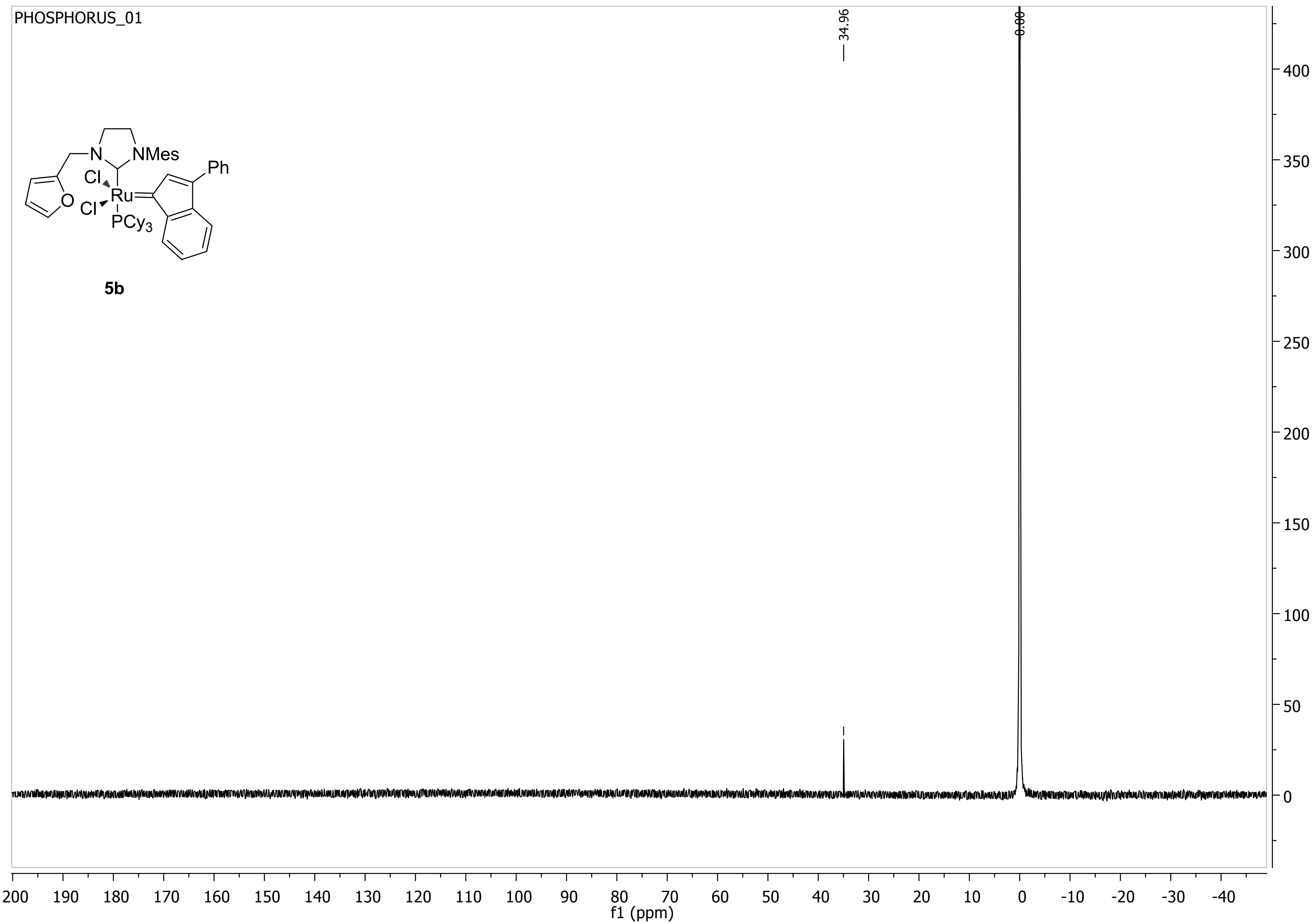

Ind_II_S-C13
J. Czaban
zesp3/Var500/Ind_II_S/Ind_II_S-C13
216.96
216.40
144.21
140.94
138.31
138.07
138.06
137.49
137.35
137.13
137.11
136.94
136.25
129.27
129.01
128.88
128.84
128.79
128.29
128.04
127.56
127.27
127.01
126.74
116.50
54.27
54.06
53.84
53.62
53.41
52.45
52.43
51.04
48.51
48.49
32.82
32.69
29.92
29.91
28.29
28.21
28.10
28.02
26.93
21.12
18.52
18.42
N
NMes
Ph
Cl
Ru
S
Cl
PCy3
5a
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

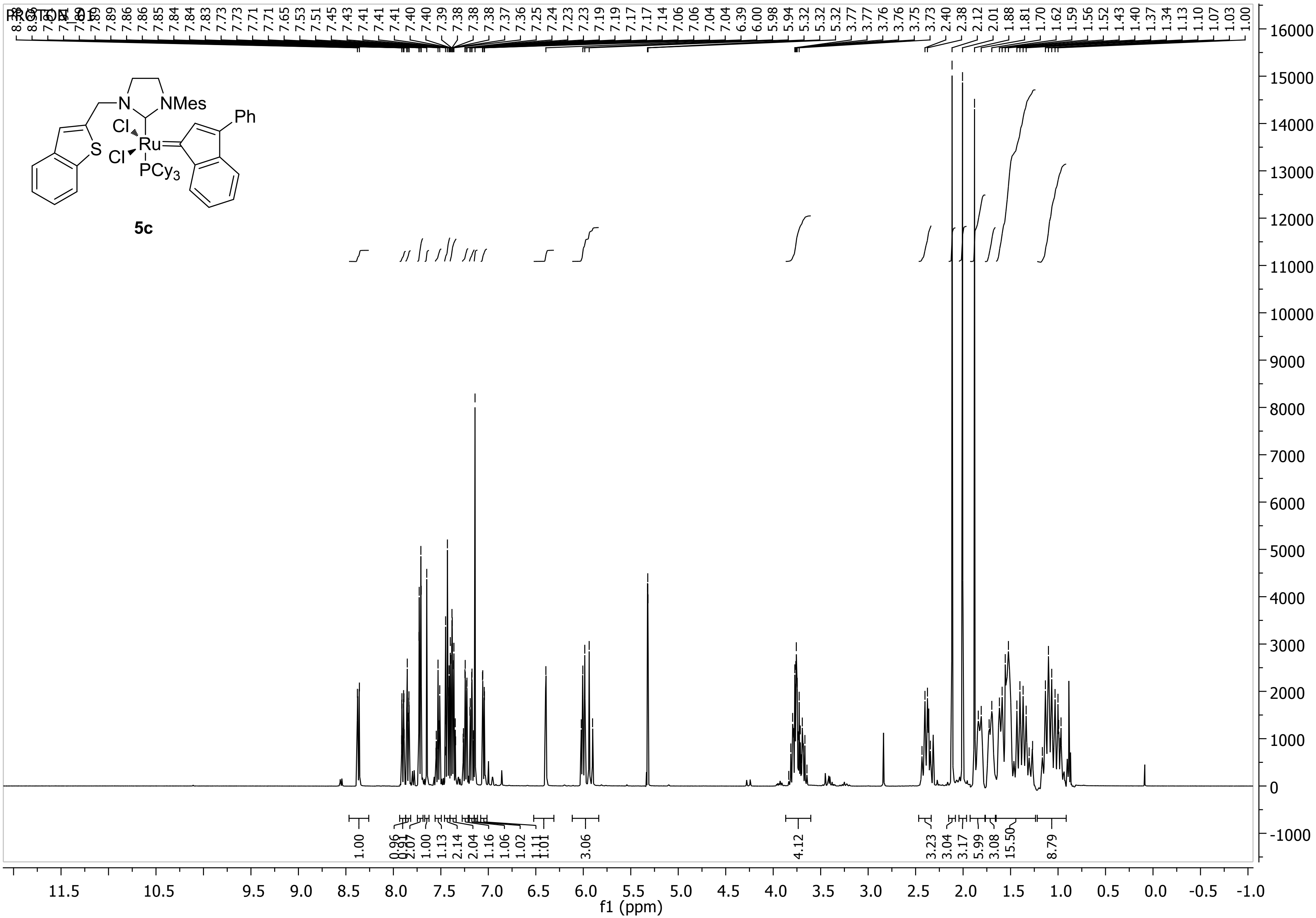

PHOSPHORUS_01
35.21
0.00
1000
900
800
700
600
500
400
300
200
100
0
N
NMes
Ph
Cl
Ru
S
Cl
PCy3
5a

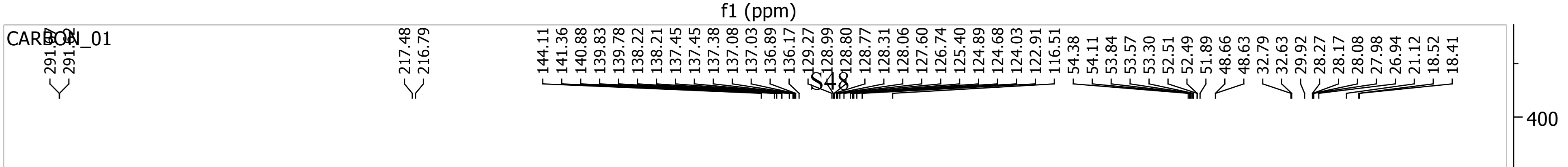

Ind-01-H1
K. Żukowska
zesp3/Var600/Ind-01/Ind-01-H1
zesp3/Var600/Ind-01/Ind-01-H1
NMes
Ph
Cl
Ru
Cl
O
PCy3
5b
f1 (ppm)

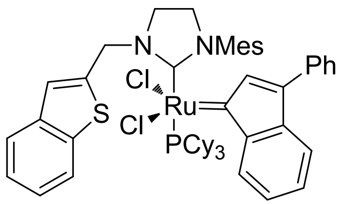


K. Żukowska
zesp3/Var600/Ind-01/Ind-01-C13
zesp3/Var600/Ind-01/Ind-01-C13
291.47
291.24
217.29
216.83
149.87
144.18
143.30
140.92
138.09
137.51
137.35
137.11
137.09
136.92
136.29
129.28
129.02
128.83
128.79
128.30
128.05
127.57
126.74
116.50
111.19
110.69
54.20
54.02
53.84
53.66
53.48
52.46
49.13
49.11
48.89
32.84
32.74
29.94
29.90
28.28
28.22
28.10
28.04
26.89
18.54
18.44
NMes
Ph
Cl
Ru
O
PCy3
5b
f1 (ppm)

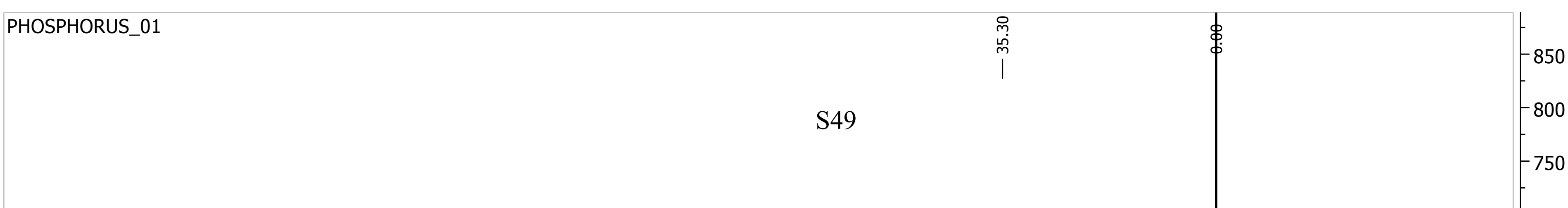

PHOSPHORUS_01
34.96
0.00
NMes
Ph
N
Cl
Ru
O
Cl
PCy3
5b
f1 (ppm)

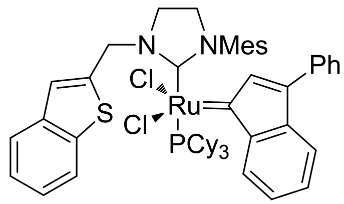

PROTON_01
7.89 7.86 7.86 7.85 7.84 7.84 7.83 7.73 7.73 7.71 7.71 7.65 7.53 7.51 7.45 7.43 7.41 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.36 7.25 7.24 7.23 7.23 7.19 7.19 7.17 7.17 7.14 7.06 7.06 7.04 7.04 6.39 6.00 5.98 5.94 5.32 5.32 5.32 3.77 3.77 3.76 3.76 3.75 3.73 2.40 2.38 2.12 2.01 1.88 1.81 1.70 1.62 1.59 1.56 1.52 1.43 1.40 1.37 1.34 1.13 1.10 1.07 1.03 1.00
NMes
Ph
Cl
Ru
N
S
Cl
PCy3
5c
1.00 2.07 1.00 1.13 2.14 2.04 1.16 1.06 1.02 1.11 1.01 3.06 4.12 3.23 3.04 3.17 5.99 3.08 15.50 8.79
16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


CARBON_01
217.48 216.79
144.11 141.36 140.88 139.83 139.78 138.22 138.21 137.45 137.45 137.38 137.08 137.03 136.89 136.17 129.27 128.99 128.80 128.77 128.31 128.06 127.60 126.74 125.40 124.89 124.68 124.03 122.91 116.51
54.38 54.11 53.84 53.57 53.30 52.51 52.49 51.89 48.66 48.63 32.79 32.63 29.92 28.27 28.17 28.08 27.98 26.94 21.12 18.52 18.41
400

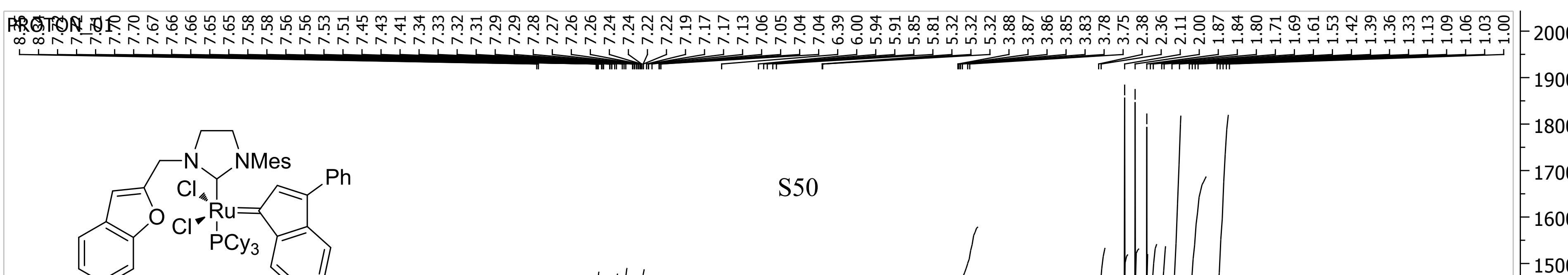


5c

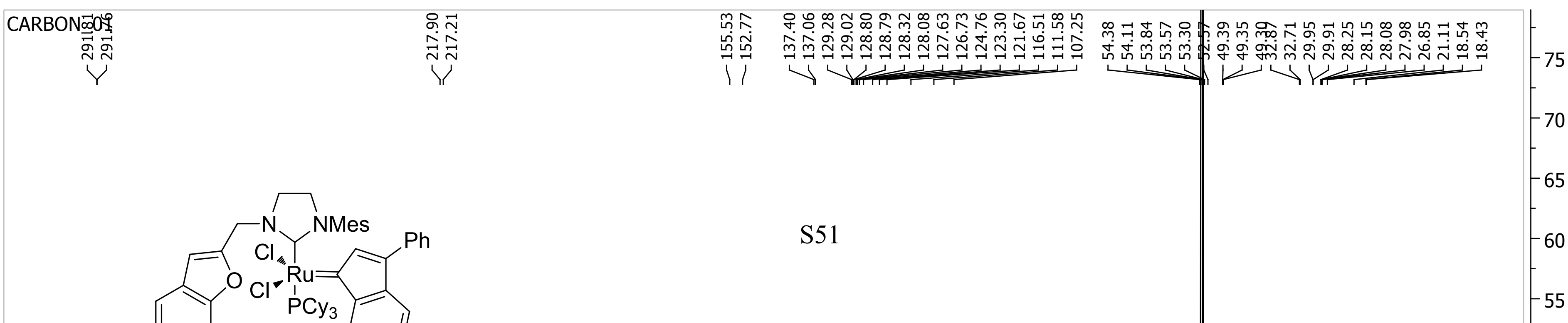



NMes
Ph
Cl
Ru
S
Cl
PCy3

5c

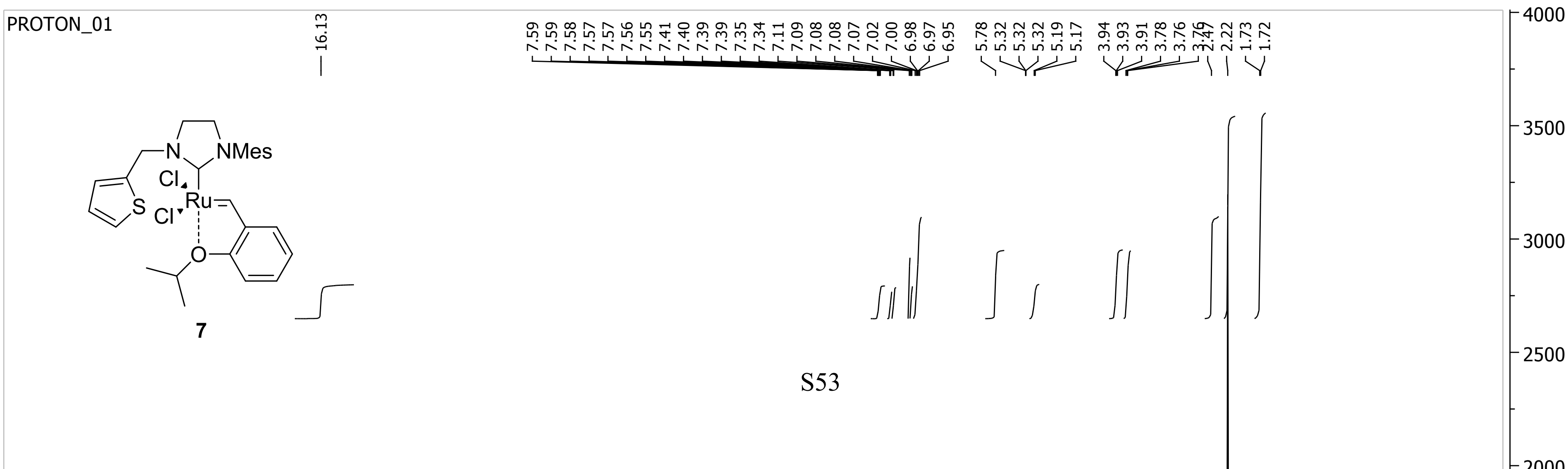

PROTON_01
7.70
7.67
7.66
7.66
7.65
7.65
7.58
7.58
7.56
7.56
7.53
7.51
7.45
7.43
7.41
7.34
7.33
7.32
7.31
7.29
7.29
7.28
7.27
7.26
7.26
7.24
7.24
7.22
7.22
7.19
7.17
7.17
7.13
7.06
7.05
7.04
7.04
6.39
6.00
5.94
5.91
5.85
5.81
5.32
5.32
5.32
3.88
3.87
3.86
3.85
3.83
3.78
3.75
2.38
2.36
2.11
2.00
1.87
1.84
1.80
1.71
1.69
1.61
1.53
1.42
1.39
1.36
1.33
1.13
1.09
1.06
1.03
1.00
2000
1900
1800
1700
1600
1500
NMes
Ph
Cl
Ru
O
Cl
PCy3

5d

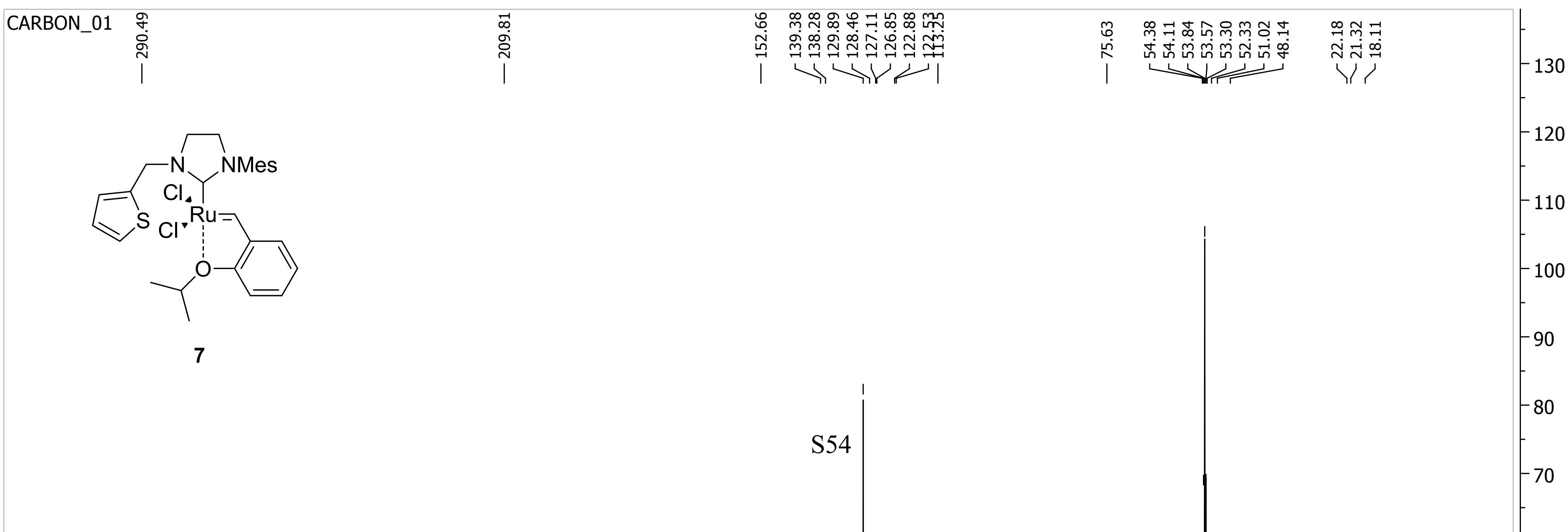

CARBON-01
291.81
291.76
217.90
217.21
155.53
152.77
137.40
137.06
129.28
129.02
128.80
128.79
128.32
128.08
127.63
126.73
124.76
123.30
121.67
116.51
111.58
107.25
54.38
54.11
53.84
53.57
53.30
49.39
49.35
32.71
29.95
29.91
28.25
28.15
28.08
27.98
26.85
21.11
18.54
18.43
75
70
65
60
55
N
NMes
Ph
Cl
Ru
Cl
O
PCy3

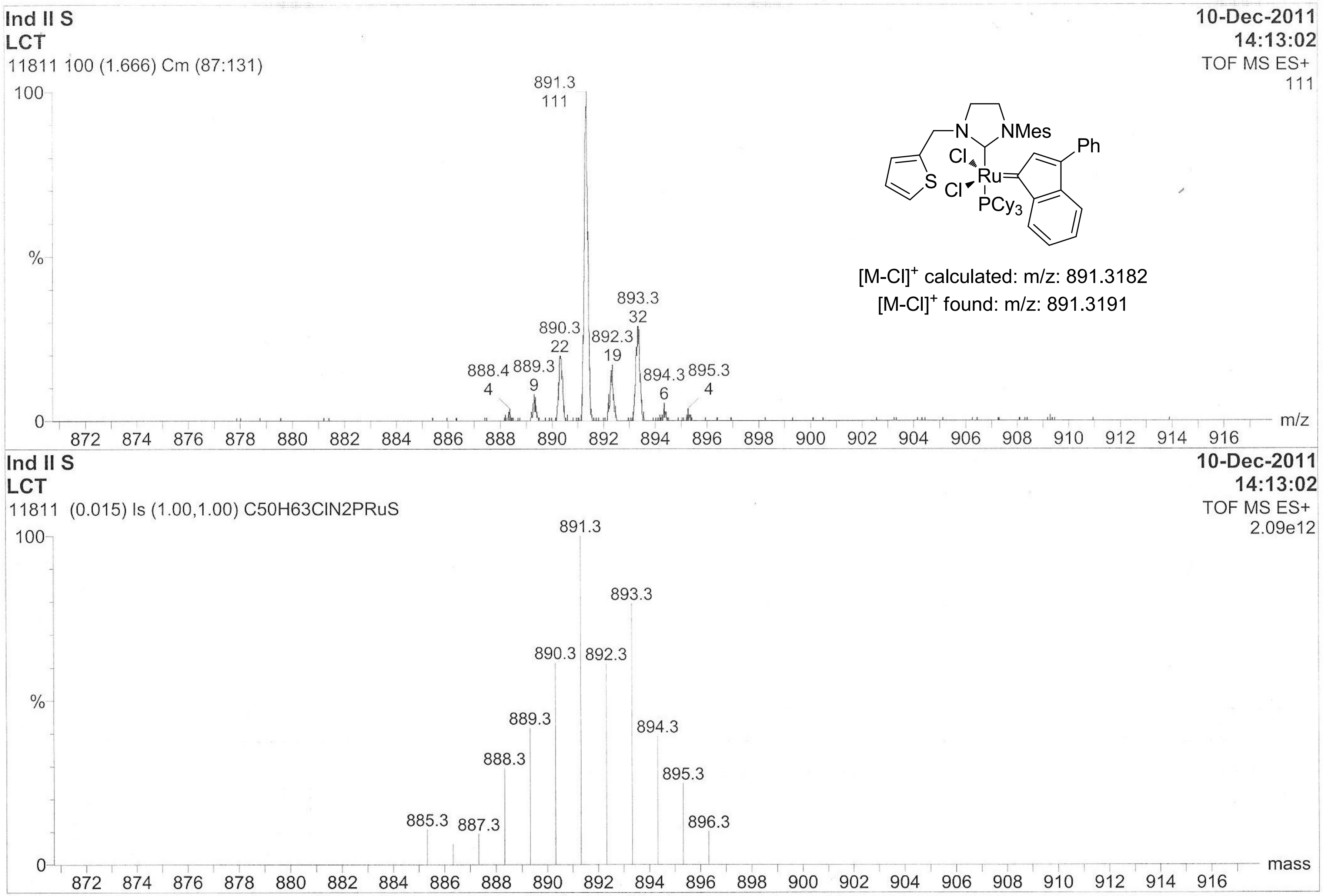

PHOSPHORUS_01
34.62
0.00
NMes
N
Ph
Cl
Ru
Cl
O
PCy3
260
240
220
200
180
160

5d



PROTON_01
16.13
7.59 7.59 7.58 7.57 7.57 7.56 7.55 7.41 7.40 7.39 7.39 7.35 7.34 7.11 7.09 7.08 7.08 7.07 7.02 7.00 6.98 6.97 6.95
5.78 5.32 5.32 5.32 5.19 5.17
3.94 3.93 3.91 3.78 3.76 2.47 2.22 1.73 1.72
N
NMes
Cl
Cl
Ru
S
O
7
4000
3500
3000
2500
2000


CARBON_01
290.49
209.81
152.66
139.38
138.28
129.89
128.46
127.11
126.85
122.88
122.53
113.25
75.63
54.38
54.11
53.84
53.57
53.30
52.33
51.02
48.14
22.18
21.32
18.11
NMes
N
Cl
Cl
Ru
S
O
7
130
120
110
100
90
80
70

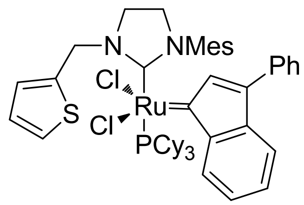

Ind II S
LCT
11811 100 (1.666) Cm (87:131)
10-Dec-2011
14:13:02
TOF MS ES+
111
891.3
111
890.3
22
892.3
19
893.3
32
888.4
4
889.3
9
894.3
6
895.3
4
100
%
0
m/z
872 874 876 878 880 882 884 886 888 890 892 894 896 898 900 902 904 906 908 910 912 914 916
N
NMes
Ph
S
Cl
Ru
Cl
PCy3
[M-Cl]+ calculated: m/z: 891.3182
[M-Cl]+ found: m/z: 891.3191
Ind II S
LCT
11811 (0.015) Is (1.00,1.00) C50H63ClN2PRuS
10-Dec-2011
14:13:02
TOF MS ES+
2.09e12
891.3
893.3
890.3
892.3
889.3
894.3
888.3
895.3
885.3
887.3
896.3
100
%
0
mass
872 874 876 878 880 882 884 886 888 890 892 894 896 898 900 902 904 906 908 910 912 914 916

Elemental Composition Report

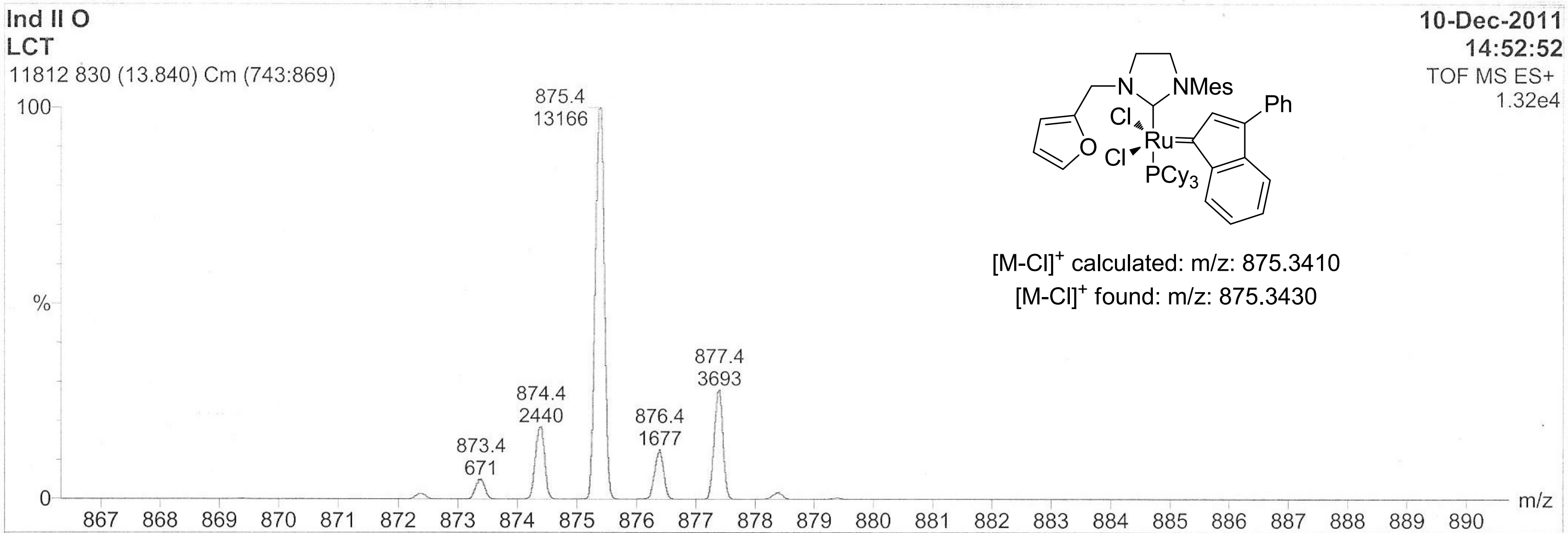
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -0.5, max = 50.0

Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 30 closest results for each mass)

Minimum:				-0.5	
Maximum:		5.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
891.3191	891.3182	0.9	1.0	20.5	C50 H63 N2 P S Cl Ru

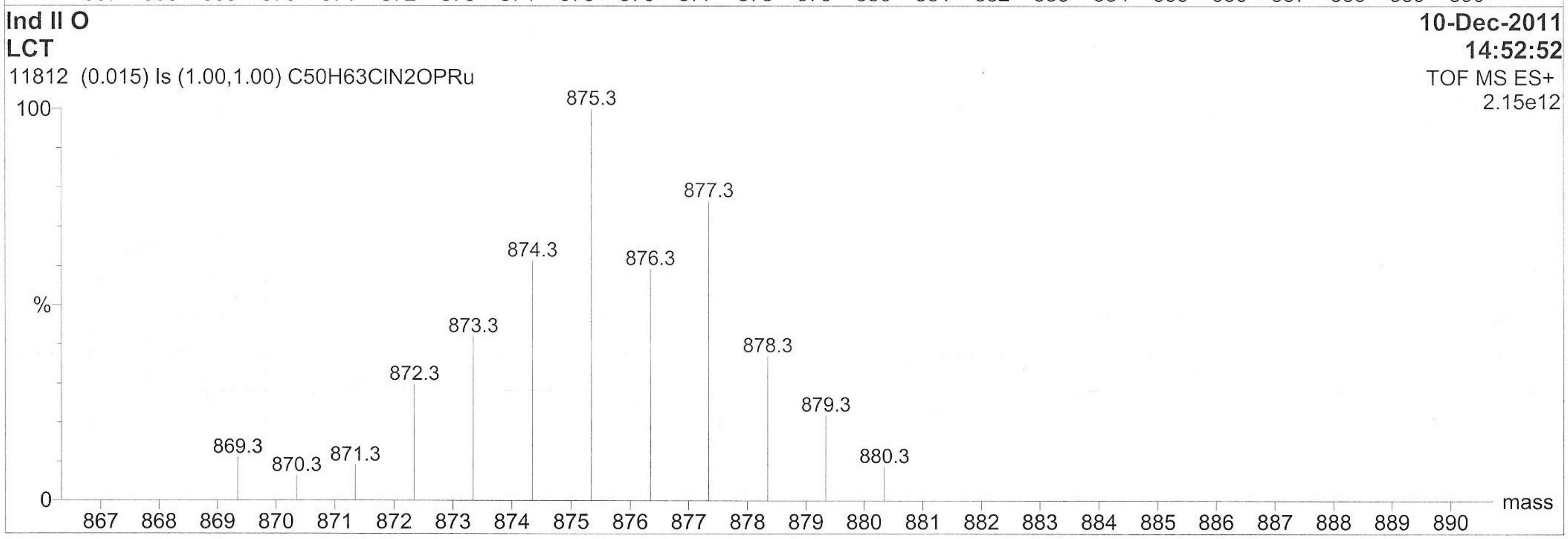


$[M-Cl]^+$ calculated: m/z: 891.3182
$[M-Cl]^+$ found: m/z: 891.3191



[M-Cl]$^+$ calculated: m/z: 875.3410

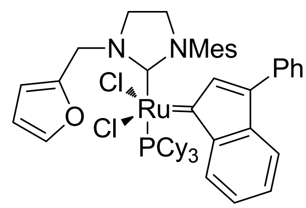
[M-Cl]$^+$ found: m/z: 875.3430



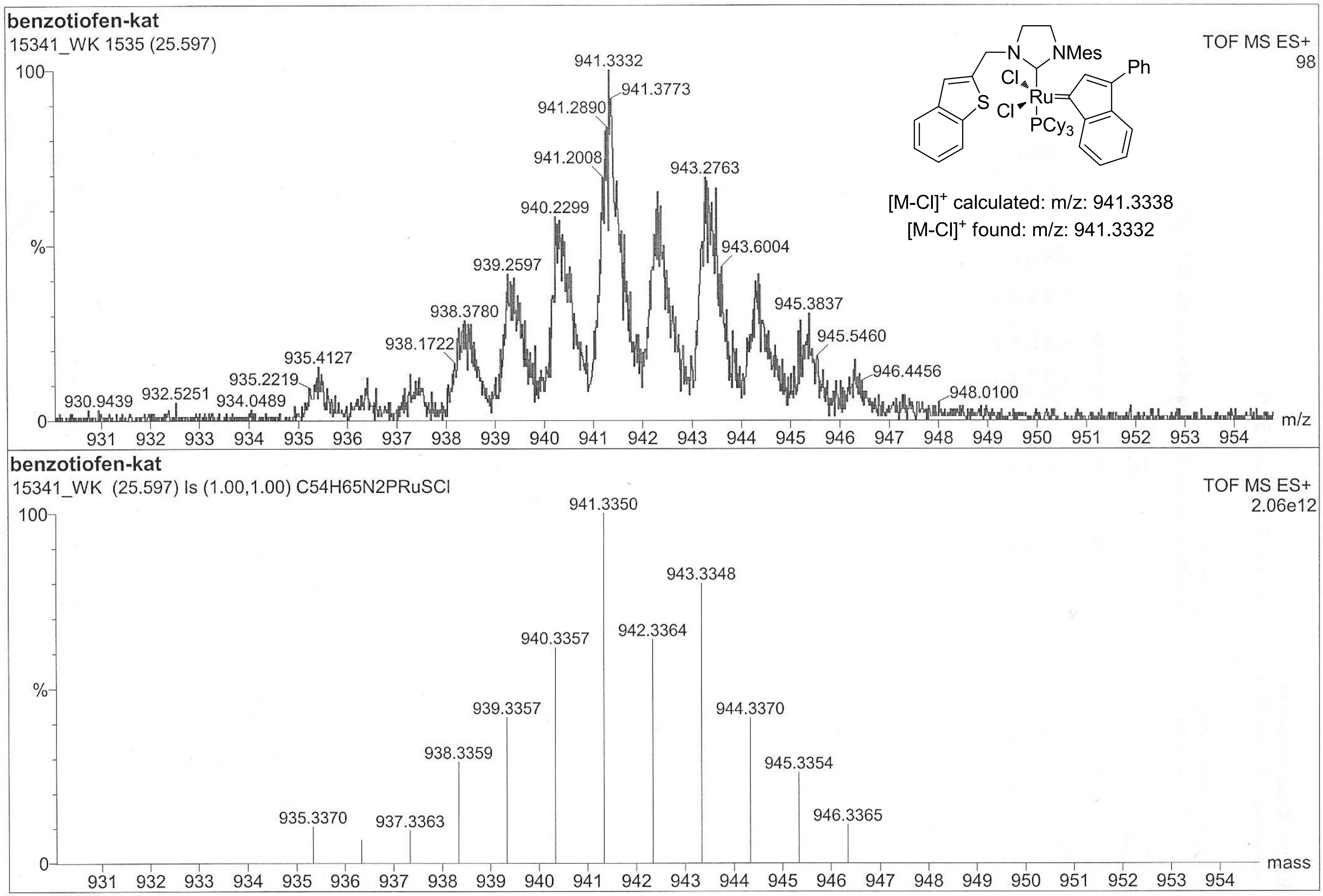
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -0.5, max = 50.0

Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 30 closest results for each mass)

Mass	Calc. Mass	mDa	PPM	DBE	Formula
Minimum:				-0.5	
Maximum:		5.0	5.0	50.0	
875.3430	875.3410	2.0	2.2	20.5	C50 H63 N2 O P Cl Ru



$[M\text{-}Cl]^+$ calculated: m/z: 875.3410
$[M\text{-}Cl]^+$ found: m/z: 875.3430


benzotiofen-kat
15341_WK 1535 (25.597)
TOF MS ES+
98
941.3332
941.3773
941.2890
941.2008
943.2763
940.2299
943.6004
939.2597
945.3837
938.3780
945.5460
938.1722
935.4127
946.4456
935.2219
948.0100
930.9439
932.5251
934.0489
N
NMes
Ph
Cl
S
Ru
Cl
PCy3
[M-Cl]+ calculated: m/z: 941.3338
[M-Cl]+ found: m/z: 941.3332
m/z
benzotiofen-kat
15341_WK (25.597) Is (1.00,1.00) C54H65N2PRuSCl
TOF MS ES+
2.06e12
941.3350
943.3348
942.3364
940.3357
939.3357
944.3370
938.3359
945.3354
935.3370
937.3363
946.3365
mass

Elemental Composition Report

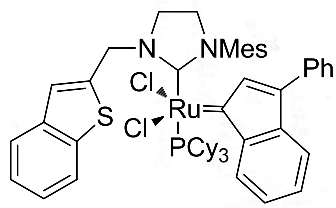
Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -0.5, max = 50.0

Monoisotopic Mass, Odd and Even Electron Ions

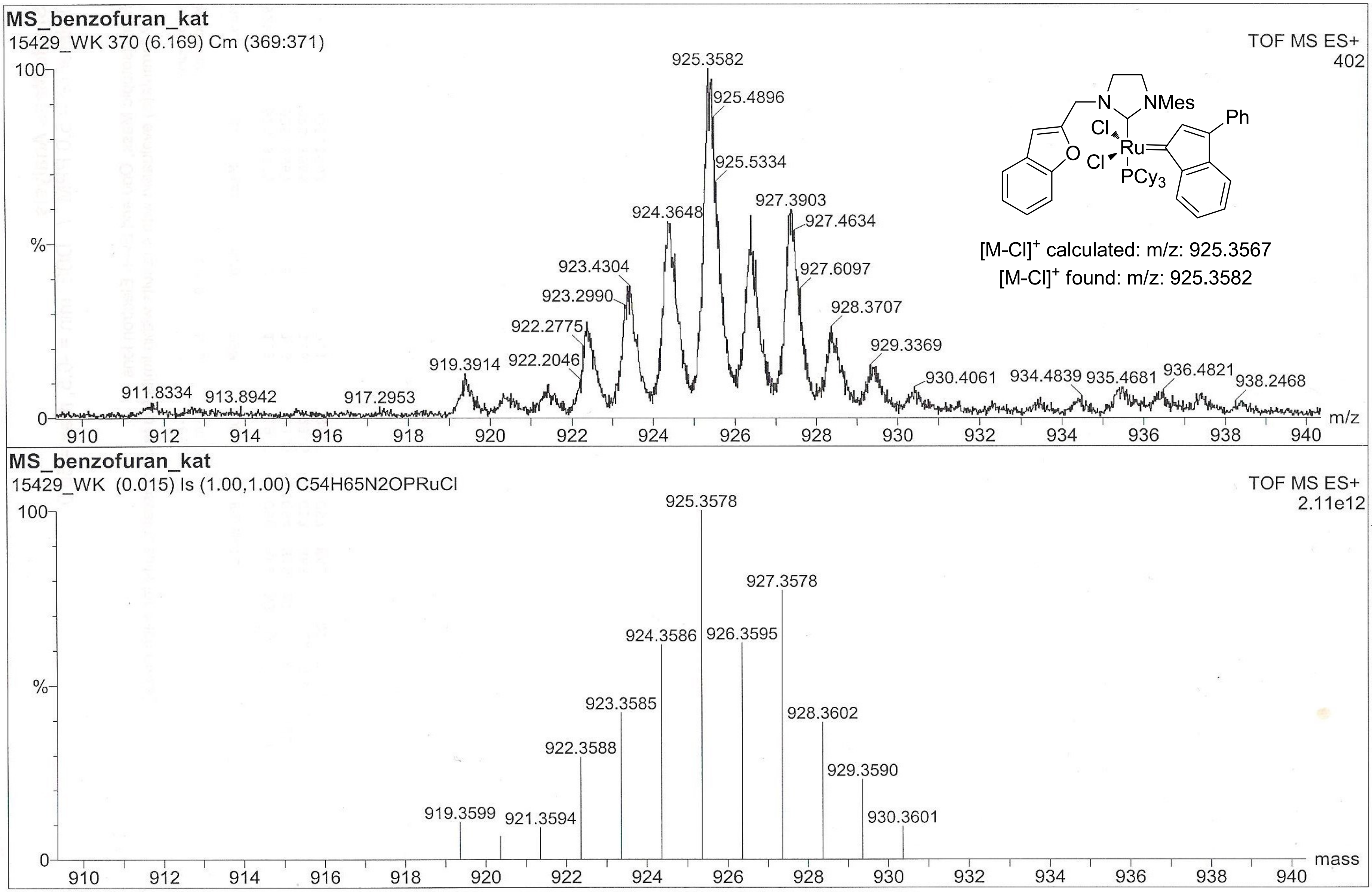
149 formula(e) evaluated with 5 results within limits (up to 30 closest results for each mass)

Minimum:				-0.5	
Maximum:		200.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
941.3332	941.3338	-0.6	-0.7	23.5	C54 H65 N2 P S Cl Ru
	941.3341	-0.9	-1.0	19.0	C50 H68 N3 P2 S Cl Ru
	941.3360	-2.8	-2.9	14.0	C49 H73 N P2 S Cl2 Ru
	941.3372	-4.0	-4.2	18.5	C51 H69 N2 P S2 Cl Ru
	941.3375	-4.3	-4.6	14.0	C47 H72 N3 P2 S2 Cl Ru



$[M-Cl]^+$ calculated: m/z: 941.3338

$[M-Cl]^+$ found: m/z: 941.3332


MS_benzofuran_kat
15429_WK 370 (6.169) Cm (369:371)
TOF MS ES+
402
925.3582
925.4896
925.5334
924.3648
927.3903
927.4634
927.6097
923.4304
923.2990
922.2775
928.3707
929.3369
919.3914
922.2046
930.4061
934.4839
935.4681
936.4821
938.2468
911.8334
913.8942
917.2953
m/z
NMes
Ph
Cl
Ru
Cl
PCy3
O
N
[M-Cl]+ calculated: m/z: 925.3567
[M-Cl]+ found: m/z: 925.3582
MS_benzofuran_kat
15429_WK (0.015) Is (1.00,1.00) C54H65N2OPRuCl
TOF MS ES+
2.11e12
925.3578
927.3578
924.3586
926.3595
923.3585
928.3602
922.3588
929.3590
919.3599
921.3594
930.3601
mass

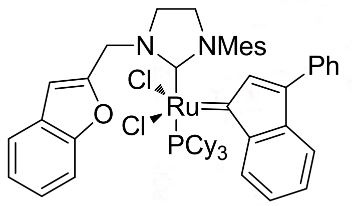
Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -0.5, max = 50.0

Monoisotopic Mass, Odd and Even Electron Ions
132 formula(e) evaluated with 4 results within limits (up to 30 closest results for each mass)

Minimum:				-0.5	
Maximum:		200.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
925.3582	925.3570	1.2	1.3	19.0	C50 H68 N3 O P2 Cl Ru
	925.3567	1.5	1.6	23.5	C54 H65 N2 O P Cl Ru
	925.3565	1.7	1.8	23.5	C53 H65 N2 O2 P2 Ru
	925.3562	2.0	2.1	28.0	C57 H62 N O2 P Ru



$[M-Cl]^+$ calculated: m/z: 925.3567
$[M-Cl]^+$ found: m/z: 925.3582

X-RAY Analysis

The single crystal X-ray diffraction data collection for **5a** and **5b** was performed on a Kuma KM4CCD 4-axis X-ray diffractometer with graphite-monochromated MoKα radiation. The data collection for **5c** and **7** was performed on an Agilent SuperNova 4-axis X-ray diffractometer with mirror-monochromated MoKα radiation and for **5d** on an Agilent SuperNova 4-axis X-ray diffractometer with mirror-monochromated CuKα radiation.

The diffractometers were equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. Small single crystals were positioned at 50 mm from the KM4CCD camera. 403, 967 and 448 frames were measured at 1^{o} intervals with a counting time of 15, 30 and 60 sec for **5a**, **5b** and **5c**, respectively. The data were corrected for the Lorentz and polarization effects. The multi-scan absorption correction was applied for **5a**, **5b** and **5c**. In the case of **5d** and **7** an analytical absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction Ltd. suit of programs [4].

The structures were solved by direct methods and refined using SHELXL [5]. The refinements were based on F^2 for all reflections except those with some very negative F^2. The weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $Fo^2>2(Fo^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in ref. 4.[6].

Some geometric and ADP restrains were required during refinement. The side occupancy factors (SOFs) for the disorder rings were refined as constrained in such a way as to sum up to 1. The disordered dichloromethane moieties (solvent molecules) were also found and refined for the **5a** and **5b** structures.

After structure solution for **5c**, it was found that 10% of the total cell volume was filled in with disordered solvent molecules, which could not be modeled in terms of atomic sites. From this point on, residual peaks were removed and the solvent region was refined as a diffuse contribution without specific atom positions by using the PLATON [7] module SQUEEZE [8] which subtracts electron density from the void regions by appropriately modifying the diffraction intensities of the overall structure. An electron count over the solvent region provided an estimate for the number of solvent molecules removed from the cell (1 molecule of dichloromethane). Applying this procedure led to an improvement of all refinement parameters and a minimization of residuals.

In the case of **5d**, some large voids, potentially accessible for solvent molecules, have been found. However, no solvent molecules could be modeled in terms of atomic sites. Moreover, structure was refined as an inversion twin.

The lattice parameters and the final *R*-indices obtained for the refinement of the structures are presented in **Table 3a** and **3b**. Selected geometrical parameters for **5a**, **5b, 5c**, **5d** and **7** structures are shown in Table 4, Table 5, Table 6, Table7 and Table 8, respectively.

Table S3a. X-ray experimental details for 5a and 5b.

	5a	**5b**
Crystal data		
Chemical formula	$C_{50}H_{63}Cl_2N_2PRuS \cdot 0.5(CH_2Cl_2)$	$C_{50}H_{63}Cl_2N_2OPRu \cdot 0.5(CH_2Cl_2)$
M_r	969.48	953.42
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*
Temperature (K)	100	100
a **(Å)**	31.4399 (9)	31.4469 (8)
b **(Å)**	14.5840 (5)	14.5027 (4)
c **(Å)**	24.2430 (7)	24.1761 (5)
β (°)	112.519 (3)	112.309 (3)
V **(Å^3)**	10268.3 (6)	10200.6 (5)
Z	8	8
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.57	0.53
Crystal size (mm)	0.40 × 0.10 × 0.10	0.20 × 0.10 × 0.10
Data collection		
Diffractometer	KUMA4 CCD diffractometer	KUMA4 CCD diffractometer
Absorption correction	Multi-scan	Multi-scan
T_{min}, T_{max}	0.805, 0.946	0.894, 0.945
No. of measured, independent and observed [$I > 2\square(I)$] reflections	51125, 9735, 7283	45508, 9687, 7870
R_{int}	0.052	0.035
θ values (°)	$\theta_{max} = 25.7$, $\theta_{min} = 1.9$	$\theta_{max} = 25.7$, $\theta_{min} = 1.9$
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.156, 1.07	0.048, 0.138, 1.08
No. of reflections	9735	9687
No. of parameters	631	667
No. of restraints	82	218
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ **(e Å^{-3})**	1.18, -0.59	1.46, -0.66

Table S3b. X-ray experimental details for 5c, 5d and 7.

	5c	**5d**	**7**
Crystal data			
Chemical formula	$C_{54}H_{65}Cl_2N_2PRuS$	$C_{54}H_{65}Cl_2N_2OPRu$	$C_{27}H_{32}Cl_2N_2ORuS$
***M*r**	977.08	961.02	604.57
Crystal system, space group	Monoclinic, C2/c	Monoclinic, *C*2	Triclinic, *P*-1
Temperature (K)	100	90	100
***a* (Å)**	29.2136(7)	32.4848(12)	10.5766(2)
***b* (Å)**	14.4024(3)	13.6107(3)	15.0612(3)
***c* (Å)**	24.4525(10)	24.3944(7)	34.1951(6)
α (°)	90	90	85.6667 (14)
β (°)	97.527(3)	109.926(4)	88.7614 (16)
γ (°)	90	90	89.6770 (17)
V (Å^3)	10199.6(5)	10140.1(6)	5430.27 (18)
Z	8	8	8
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.52	4.06	0.87
Crystal size (mm)	0.15 x 0.15 x 0.10	0.15 × 0.08 × 0.03	0.11 × 0.09 × 0.07
Data collection			
Diffractometer	Agilent, SuperNova, diffractometer	Agilent, SuperNova, Atlas diffractometer	Agilent, SuperNova, Eos diffractometer
Absorption correction	Multi-scan	Analytical	Analytical
T_{min}, T_{max}	0.926, 0.950	0.432, 0.812	0.934, 0.954
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	41767, 9687, 6721	45437, 19297, 15821	146961, 38148, 26876
R_{int}	0.065	0.049	0.073
θ values (°)	$\theta_{max} = 25.7$, $\theta_{min} = 1.7$	$\theta_{max} = 77.2$, $\theta_{min} = 1.9$	$\theta_{max} = 32.7$, $\theta_{min} = 1.7$
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.180, 1.04	0.057, 0.179, 1.10	0.058, 0.133, 1.08
No. of reflections	9687	19297	38148
No. of parameters	600	1232	1277
No. of restraints	290	473	132
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.93, -0.54	1.88, -1.21	1.34, -1.10

Table S4. Selected geometric parameters 5a (Å, º)

C1—Ru1	2.064 (4)	C29A—C30A	1.386 (9)
C1—N1	1.352 (5)	C30A—C31A	1.386 (8)
C1—N2	1.322 (6)	C23B—C22B	1.49 (5)
C2—C3	1.520 (7)	C22B—C21B	1.43 (7)
C2—N1	1.486 (6)	C21B—C20B	1.28 (6)
C3—N2	1.476 (5)	C26B—C27B	1.44 (5)
C4—C5	1.399 (6)	C26B—C31B	1.40 (2)
C4—C11	1.409 (7)	C27B—C28B	1.38 (5)
C4—N1	1.431 (6)	C28B—C29B	1.48 (5)
C5—C6	1.392 (7)	C29B—C30B	1.38 (5)
C5—C9	1.499 (7)	C30B—C31B	1.32 (6)
C6—C7	1.390 (7)	C32—C33	1.535 (6)
C7—C8	1.392 (7)	C32—C37	1.526 (7)
C7—C50	1.502 (7)	C32—P1	1.864 (4)
C8—C11	1.383 (7)	C33—C34	1.529 (7)
C10—C11	1.513 (7)	C34—C35	1.501 (9)
C12—N2	1.449 (6)	C35—C36	1.517 (7)

C12—C13A	1.581 (11)	C36—C37	1.527 (6)
C12—C13B	1.25 (2)	C38—C39	1.541 (6)
Ru1—C17A	1.858 (5)	C38—C43	1.518 (6)
Ru1—C17B	1.829 (16)	C38—P1	1.857 (4)
Ru1—Cl1	2.4053 (12)	C39—C40	1.525 (7)
Ru1—Cl2	2.4052 (11)	C40—C41	1.516 (7)
Ru1—P1	2.4596 (10)	C41—C42	1.523 (6)
C17A—C18A	1.474 (9)	C42—C43	1.523 (6)
C17A—C24A	1.524 (8)	C44—C45	1.538 (6)
C18A—C19A	1.360 (9)	C44—C49	1.532 (7)
C19A—C25A	1.480 (7)	C44—P1	1.849 (5)
C19A—C26A	1.485 (8)	C45—C46	1.521 (8)
C25A—C24A	1.401 (8)	C46—C47	1.524 (8)
C25A—C20A	1.372 (8)	C47—C48	1.528 (7)
C24A—C23A	1.391 (8)	C48—C49	1.509 (7)
C17B—C18B	1.47 (2)	S1—C16A	1.735 (13)
C17B—C24B	1.51 (2)	S1—C13A	1.750 (10)
C18B—C19B	1.348 (19)	C16A—C15A	1.285 (16)
C19B—C25B	1.470 (19)	C15A—C14A	1.25 (2)
C19B—C26B	1.46 (5)	C14A—C13A	1.45 (2)
C25B—C24B	1.40 (2)	S1B—C16B	1.684 (19)
C25B—C20B	1.32 (4)	S1B—C13B	1.705 (18)
C24B—C23B	1.36 (4)	C16B—C15B	1.28 (2)
C20A—C21A	1.393 (8)	C15B—C14B	1.19 (2)
C21A—C22A	1.389 (10)	C14B—C13B	1.54 (2)
C22A—C23A	1.400 (8)	C100—Cl4	1.50 (4)
C26A—C27A	1.386 (8)	C100—Cl3	1.763 (10)
C26A—C31A	1.396 (9)	Cl3A—C101	1.780 (10)
C27A—C28A	1.388 (8)	Cl4A—C101	1.787 (10)
C28A—C29A	1.396 (9)		
N1—C1—Ru1	131.6 (3)	C27A—C28A—C29A	119.8 (6)
N2—C1—Ru1	119.6 (3)	C30A—C29A—C28A	119.8 (5)
N2—C1—N1	108.7 (4)	C31A—C30A—C29A	119.9 (5)
N1—C2—C3	103.4 (4)	C30A—C31A—C26A	120.8 (5)
N2—C3—C2	101.3 (4)	C24B—C23B—C22B	112 (3)
C5—C4—C11	121.3 (5)	C21B—C22B—C23B	119 (4)
C5—C4—N1	120.1 (5)	C20B—C21B—C22B	122 (5)
C11—C4—N1	118.5 (4)	C21B—C20B—C25B	121 (4)
C4—C5—C9	120.6 (5)	C27B—C26B—C19B	120 (3)
C6—C5—C4	118.1 (5)	C31B—C26B—C19B	122 (4)
C6—C5—C9	121.4 (4)	C31B—C26B—C27B	118 (4)
C7—C6—C5	122.2 (4)	C28B—C27B—C26B	122 (4)
C6—C7—C8	118.0 (5)	C27B—C28B—C29B	116 (4)
C6—C7—C50	121.0 (5)	C30B—C29B—C28B	120 (4)
C8—C7—C50	120.9 (5)	C31B—C30B—C29B	123 (4)

C11—C8—C7	122.3 (5)	C30B—C31B—C26B	121 (4)
C4—C11—C10	120.8 (5)	C33—C32—P1	113.6 (3)
C8—C11—C4	118.1 (4)	C37—C32—C33	110.2 (4)
C8—C11—C10	121.1 (5)	C37—C32—P1	113.0 (3)
N2—C12—C13A	110.9 (6)	C34—C33—C32	109.1 (4)
C13B—C12—N2	121.3 (14)	C35—C34—C33	112.2 (4)
C1—Ru1—Cl1	87.49 (13)	C34—C35—C36	111.2 (5)
C1—Ru1—Cl2	87.25 (12)	C35—C36—C37	111.5 (4)
C1—Ru1—P1	160.71 (13)	C32—C37—C36	111.0 (4)
C17A—Ru1—C1	100.0 (4)	C39—C38—P1	116.2 (3)
C17A—Ru1—Cl1	97.5 (3)	C43—C38—C39	109.8 (4)
C17A—Ru1—Cl2	102.3 (3)	C43—C38—P1	114.6 (3)
C17A—Ru1—P1	99.2 (4)	C40—C39—C38	110.7 (4)
C17B—Ru1—C1	95 (3)	C41—C40—C39	112.0 (5)
C17B—Ru1—Cl1	99.6 (12)	C40—C41—C42	111.3 (4)
C17B—Ru1—Cl2	100.0 (12)	C43—C42—C41	111.2 (4)
C17B—Ru1—P1	104 (3)	C38—C43—C42	111.4 (4)
Cl1—Ru1—P1	88.85 (4)	C45—C44—P1	119.6 (4)
Cl2—Ru1—Cl1	160.10 (4)	C49—C44—C45	108.7 (4)
Cl2—Ru1—P1	89.81 (4)	C49—C44—P1	113.5 (3)
C18A—C17A—Ru1	123.7 (6)	C46—C45—C44	109.4 (4)
C18A—C17A—C24A	102.2 (5)	C45—C46—C47	112.9 (5)
C24A—C17A—Ru1	134.0 (6)	C46—C47—C48	111.4 (4)
C19A—C18A—C17A	112.7 (7)	C49—C48—C47	110.1 (4)
C18A—C19A—C25A	107.8 (5)	C48—C49—C44	110.3 (4)
C18A—C19A—C26A	125.1 (6)	C1—N1—C2	111.2 (4)
C25A—C19A—C26A	127.1 (5)	C1—N1—C4	130.2 (4)
C24A—C25A—C19A	108.2 (5)	C4—N1—C2	118.6 (3)
C20A—C25A—C19A	131.3 (5)	C1—N2—C3	114.0 (4)
C20A—C25A—C24A	120.4 (6)	C1—N2—C12	123.5 (4)
C25A—C24A—C17A	109.0 (5)	C12—N2—C3	120.2 (4)
C23A—C24A—C17A	130.8 (6)	C32—P1—Ru1	112.31 (14)
C23A—C24A—C25A	120.1 (6)	C38—P1—Ru1	116.29 (13)
C18B—C17B—Ru1	118 (2)	C38—P1—C32	101.0 (2)
C18B—C17B—C24B	104.7 (16)	C44—P1—Ru1	111.24 (14)
C24B—C17B—Ru1	136 (3)	C44—P1—C32	103.8 (2)
C19B—C18B—C17B	110.4 (17)	C44—P1—C38	111.0 (2)
C18B—C19B—C25B	108.8 (17)	C16A—S1—C13A	88.0 (5)
C18B—C19B—C26B	120 (3)	C15A—C16A—S1	114.8 (10)
C26B—C19B—C25B	131 (3)	C14A—C15A—C16A	114.9 (16)
C24B—C25B—C19B	109.0 (17)	C15A—C14A—C13A	116 (2)
C20B—C25B—C19B	130 (3)	C12—C13A—S1	118.5 (5)
C20B—C25B—C24B	121 (3)	C14A—C13A—C12	134.7 (12)
C25B—C24B—C17B	106.9 (16)	C14A—C13A—S1	106.7 (11)
C23B—C24B—C17B	128 (3)	C16B—S1B—C13B	90.3 (11)
C23B—C24B—C25B	124 (3)	C15B—C16B—S1B	112.4 (16)

C25A—C20A—C21A	120.5 (6)	C14B—C15B—C16B	121 (2)
C22A—C21A—C20A	119.0 (7)	C15B—C14B—C13B	110 (2)
C21A—C22A—C23A	121.4 (6)	C12—C13B—S1B	112.5 (14)
C24A—C23A—C22A	118.5 (5)	C12—C13B—C14B	138.9 (17)
C27A—C26A—C19A	119.3 (6)	C14B—C13B—S1B	105.7 (13)
C27A—C26A—C31A	118.9 (5)	Cl4—C100—Cl3	115 (3)
C31A—C26A—C19A	121.7 (5)	Cl3A—C101—Cl4A	110.1 (10)
C26A—C27A—C28A	120.7 (6)		

C1—Ru1—C17A—C18A	92.3 (10)	C27B—C26B—C31B—C30B	1 (6)
C1—Ru1—C17A—C24A	-89.9 (12)	C27B—C28B—C29B—C30B	-8 (5)
C1—Ru1—C17B—C18B	-91 (7)	C28B—C29B—C30B—C31B	4 (6)
C1—Ru1—C17B—C24B	104 (10)	C29B—C30B—C31B—C26B	-1 (7)
C2—C3—N2—C1	-10.2 (5)	C31B—C26B—C27B—C28B	-6 (6)
C2—C3—N2—C12	-173.8 (4)	C32—C33—C34—C35	57.8 (6)
C3—C2—N1—C1	-9.6 (6)	C33—C32—C37—C36	57.5 (5)
C3—C2—N1—C4	169.8 (4)	C33—C32—P1—Ru1	61.3 (4)
C4—C5—C6—C7	1.4 (6)	C33—C32—P1—C38	-174.1 (3)
C5—C4—C11—C8	1.3 (6)	C33—C32—P1—C44	-58.9 (4)
C5—C4—C11—C10	179.6 (4)	C33—C34—C35—C36	-56.0 (6)
C5—C4—N1—C1	-92.4 (6)	C34—C35—C36—C37	54.0 (6)
C5—C4—N1—C2	88.3 (5)	C35—C36—C37—C32	-55.2 (6)
C5—C6—C7—C8	0.3 (7)	C37—C32—C33—C34	-57.9 (5)
C5—C6—C7—C50	-177.3 (4)	C37—C32—P1—Ru1	-65.2 (3)
C6—C7—C8—C11	-1.3 (7)	C37—C32—P1—C38	59.4 (3)
C7—C8—C11—C4	0.5 (7)	C37—C32—P1—C44	174.5 (3)
C7—C8—C11—C10	-177.8 (5)	C38—C39—C40—C41	-55.6 (7)
C9—C5—C6—C7	179.8 (4)	C39—C38—C43—C42	-57.5 (6)
C11—C4—C5—C6	-2.3 (6)	C39—C38—P1—Ru1	172.4 (3)
C11—C4—C5—C9	179.4 (4)	C39—C38—P1—C32	50.5 (4)
C11—C4—N1—C1	91.6 (6)	C39—C38—P1—C44	-59.1 (4)
C11—C4—N1—C2	-87.6 (5)	C39—C40—C41—C42	54.4 (7)
Ru1—C1—N1—C2	-174.5 (4)	C40—C41—C42—C43	-54.4 (6)
Ru1—C1—N1—C4	6.2 (7)	C41—C42—C43—C38	56.7 (6)
Ru1—C1—N2—C3	-177.1 (3)	C43—C38—C39—C40	56.6 (6)
Ru1—C1—N2—C12	-14.1 (6)	C43—C38—P1—Ru1	-57.8 (4)
Ru1—C17A—C18A—C19A	176.5 (7)	C43—C38—P1—C32	-179.7 (3)
Ru1—C17A—C24A—C25A	-175.4 (10)	C43—C38—P1—C44	70.7 (4)
Ru1—C17A—C24A—C23A	0.9 (17)	C44—C45—C46—C47	55.1 (6)
Ru1—C17B—C18B—C19B	-174 (5)	C45—C44—C49—C48	62.6 (5)
Ru1—C17B—C24B—C25B	170 (8)	C45—C44—P1—Ru1	-160.7 (3)
Ru1—C17B—C24B—C23B	-18 (15)	C45—C44—P1—C32	-39.8 (4)
C17A—Ru1—C17B—C18B	114 (30)	C45—C44—P1—C38	68.1 (4)
C17A—Ru1—C17B—C24B	-51 (18)	C45—C46—C47—C48	-52.7 (6)
C17A—C18A—C19A—C25A	0.5 (8)	C46—C47—C48—C49	54.1 (6)
C17A—C18A—C19A—C26A	-179.6 (7)	C47—C48—C49—C44	-59.9 (5)

C17A—C24A—C23A—C22A	-176.1 (8)	C49—C44—C45—C46	-59.0 (5)
C18A—C17A—C24A—C25A	2.8 (9)	C49—C44—P1—Ru1	68.8 (3)
C18A—C17A—C24A—C23A	179.0 (6)	C49—C44—P1—C32	-170.2 (3)
C18A—C19A—C25A—C24A	1.4 (6)	C49—C44—P1—C38	-62.4 (4)
C18A—C19A—C25A—C20A	-175.3 (6)	C50—C7—C8—C11	176.3 (4)
C18A—C19A—C26A—C27A	32.1 (8)	N1—C1—N2—C3	4.6 (5)
C18A—C19A—C26A—C31A	-148.7 (6)	N1—C1—N2—C12	167.5 (4)
C19A—C25A—C24A—C17A	-2.6 (7)	N1—C2—C3—N2	11.0 (5)
C19A—C25A—C24A—C23A	-179.3 (4)	N1—C4—C5—C6	-178.1 (4)
C19A—C25A—C20A—C21A	179.1 (5)	N1—C4—C5—C9	3.6 (6)
C19A—C26A—C27A—C28A	178.6 (6)	N1—C4—C11—C8	177.2 (4)
C19A—C26A—C31A—C30A	-178.3 (6)	N1—C4—C11—C10	-4.5 (6)
C25A—C19A—C26A—C27A	-148.0 (5)	N2—C1—N1—C2	3.6 (5)
C25A—C19A—C26A—C31A	31.1 (8)	N2—C1—N1—C4	-175.8 (4)
C25A—C24A—C23A—C22A	-0.2 (8)	N2—C12—C13A—S1	92.4 (7)
C25A—C20A—C21A—C22A	-0.9 (9)	N2—C12—C13A—C14A	-83 (2)
C24A—C17A—C18A—C19A	-2.0 (10)	N2—C12—C13B—S1B	-84 (2)
C24A—C25A—C20A—C21A	2.8 (8)	N2—C12—C13B—C14B	119 (3)
C17B—Ru1—C17A—C18A	118 (26)	Cl1—Ru1—C17A—C18A	3.5 (10)
C17B—Ru1—C17A—C24A	-64 (24)	Cl1—Ru1—C17A—C24A	-178.6 (11)
C17B—C18B—C19B—C25B	4 (6)	Cl1—Ru1—C17B—C18B	-179 (6)
C17B—C18B—C19B—C26B	179 (5)	Cl1—Ru1—C17B—C24B	15 (10)
C17B—C24B—C23B—C22B	-172 (7)	Cl2—Ru1—C17A—C18A	-178.4 (9)
C18B—C17B—C24B—C25B	4 (8)	Cl2—Ru1—C17A—C24A	-0.5 (13)
C18B—C17B—C24B—C23B	176 (6)	Cl2—Ru1—C17B—C18B	-3 (7)
C18B—C19B—C25B—C24B	-1 (4)	Cl2—Ru1—C17B—C24B	-168 (9)
C18B—C19B—C25B—C20B	-171 (3)	P1—Ru1—C17A—C18A	-86.5 (10)
C18B—C19B—C26B—C27B	35 (5)	P1—Ru1—C17A—C24A	91.3 (12)
C18B—C19B—C26B—C31B	-144 (4)	P1—Ru1—C17B—C18B	89 (7)
C19B—C25B—C24B—C17B	-2 (7)	P1—Ru1—C17B—C24B	-76 (10)
C19B—C25B—C24B—C23B	-174 (5)	P1—C32—C33—C34	174.1 (4)
C19B—C25B—C20B—C21B	170 (4)	P1—C32—C37—C36	-174.2 (3)
C19B—C26B—C27B—C28B	175 (3)	P1—C38—C39—C40	-171.3 (4)
C19B—C26B—C31B—C30B	-179 (3)	P1—C38—C43—C42	169.5 (3)
C25B—C19B—C26B—C27B	-150 (3)	P1—C44—C45—C46	168.4 (4)
C25B—C19B—C26B—C31B	30 (6)	P1—C44—C49—C48	-161.7 (3)
C25B—C24B—C23B—C22B	-1 (7)	S1—C16A—C15A—C14A	3 (2)
C24B—C17B—C18B—C19B	-5 (8)	C16A—S1—C13A—C12	-175.5 (9)
C24B—C25B—C20B—C21B	1 (6)	C16A—S1—C13A—C14A	0.7 (15)
C24B—C23B—C22B—C21B	7 (6)	C16A—C15A—C14A—C13A	-2 (3)
C20A—C25A—C24A—C17A	174.5 (7)	C15A—C14A—C13A—C12	176.0 (15)
C20A—C25A—C24A—C23A	-2.3 (7)	C15A—C14A—C13A—S1	1 (3)
C20A—C21A—C22A—C23A	-1.5 (10)	C13A—C12—N2—C1	130.3 (5)
C21A—C22A—C23A—C24A	2.1 (9)	C13A—C12—N2—C3	-67.8 (6)
C26A—C19A—C25A—C24A	-178.5 (5)	C13A—C12—C13B—S1B	-21 (3)
C26A—C19A—C25A—C20A	4.9 (9)	C13A—C12—C13B—C14B	-178 (8)

C26A—C27A—C28A—C29A	0.1 (10)	C13A—S1—C16A—C15A	-2.0 (11)
C27A—C26A—C31A—C30A	0.8 (9)	S1B—C16B—C15B—C14B	3 (2)
C27A—C28A—C29A—C30A	0.1 (11)	C16B—S1B—C13B—C12	-169 (2)
C28A—C29A—C30A—C31A	0.1 (11)	C16B—S1B—C13B—C14B	-4.7 (18)
C29A—C30A—C31A—C26A	-0.5 (10)	C16B—C15B—C14B—C13B	-6 (3)
C31A—C26A—C27A—C28A	-0.6 (9)	C15B—C14B—C13B—C12	165 (3)
C23B—C22B—C21B—C20B	-9 (7)	C15B—C14B—C13B—S1B	7 (3)
C22B—C21B—C20B—C25B	5 (7)	C13B—C12—N2—C1	149.2 (11)
C20B—C25B—C24B—C17B	169 (5)	C13B—C12—N2—C3	-48.8 (12)
C20B—C25B—C24B—C23B	-3 (8)	C13B—C12—C13A—S1	-33 (5)
C26B—C19B—C25B—C24B	-176 (4)	C13B—C12—C13A—C14A	152 (6)
C26B—C19B—C25B—C20B	14 (6)	C13B—S1B—C16B—C15B	2.0 (13)
C26B—C27B—C28B—C29B	9 (5)		

Table S5. Selected geometric parameters 5b (Å, º)

C1—Ru1	2.063 (4)	C27A—C32A	1.403 (7)
C1—N1	1.341 (5)	C28A—C29A	1.379 (7)
C1—N2	1.330 (5)	C29A—C30A	1.383 (8)
C2—C3	1.520 (6)	C30A—C31A	1.379 (8)
C2—N1	1.481 (5)	C31A—C32A	1.385 (7)
C3—N2	1.469 (5)	C21B—C22B	1.37 (5)
C4—C5	1.397 (5)	C22B—C23B	1.46 (5)
C4—C9	1.403 (6)	C23B—C24B	1.38 (4)
C4—N1	1.434 (5)	C27B—C28B	1.39 (4)
C5—C6	1.391 (6)	C27B—C32B	1.39 (5)
C5—C10	1.503 (6)	C28B—C29B	1.33 (4)
C6—C7	1.395 (6)	C29B—C30B	1.43 (4)
C7—C8	1.394 (6)	C30B—C31B	1.36 (5)
C7—C11	1.500 (6)	C31B—C32B	1.42 (6)
C8—C9	1.383 (6)	C33—C34	1.534 (5)
C9—C12	1.505 (5)	C33—C38	1.528 (5)
C13—C14	1.462 (7)	C33—P1	1.845 (4)
C13—N2	1.453 (5)	C34—C35	1.529 (6)
C14—C15B	1.487 (19)	C35—C36	1.506 (7)
C14—O1B	1.27 (6)	C36—C37	1.522 (6)
C14—C15A	1.39 (5)	C37—C38	1.516 (6)
C14—O1A	1.323 (10)	C39—C40	1.537 (5)
Ru1—C18A	1.862 (5)	C39—C45	1.523 (5)
Ru1—C18B	1.813 (16)	C39—P1	1.856 (4)
Ru1—Cl1	2.4006 (9)	C40—C41	1.536 (6)
Ru1—Cl2	2.4058 (9)	C41—C42	1.520 (6)
Ru1—P1	2.4577 (9)	C42—C44	1.523 (5)
C18A—C19A	1.487 (9)	C44—C45	1.528 (5)
C18A—C25A	1.519 (7)	C46—C47	1.538 (5)
C19A—C20A	1.359 (6)	C46—C51	1.532 (5)

C20A—C26A	1.496 (7)	C46—P1	1.857 (4)
C20A—C27A	1.471 (9)	C47—C48	1.529 (6)
C26A—C25A	1.396 (6)	C48—C49	1.515 (7)
C26A—C21A	1.376 (7)	C49—C50	1.521 (6)
C25A—C24A	1.383 (6)	C50—C51	1.526 (5)
C18B—C19B	1.48 (2)	C16B—C17B	1.57 (5)
C18B—C25B	1.49 (2)	C16B—O1B	1.32 (6)
C19B—C20B	1.338 (18)	C15B—C17B	1.43 (3)
C20B—C26B	1.501 (18)	C16A—C15A	1.44 (5)
C20B—C27B	1.45 (4)	C16A—C17A	1.24 (2)
C26B—C25B	1.389 (18)	C17A—O1A	1.407 (15)
C26B—C21B	1.345 (18)	Cl6—C1R	1.599 (2)
C25B—C24B	1.36 (3)	C1R—Cl5	1.598 (14)
C21A—C22A	1.392 (8)	Cl3—Cl4	2.38 (2)
C22A—C23A	1.381 (9)	Cl3—C2R	1.485 (16)
C23A—C24A	1.394 (7)	Cl4—C2R	1.525 (16)
C27A—C28A	1.398 (9)		
N1—C1—Ru1	132.7 (3)	C25A—C24A—C23A	119.3 (5)
N2—C1—Ru1	118.7 (3)	C28A—C27A—C20A	120.3 (5)
N2—C1—N1	108.5 (3)	C28A—C27A—C32A	117.6 (6)
N1—C2—C3	102.8 (3)	C32A—C27A—C20A	122.1 (6)
N2—C3—C2	101.8 (3)	C29A—C28A—C27A	121.7 (5)
C5—C4—C9	121.5 (4)	C28A—C29A—C30A	119.5 (5)
C5—C4—N1	119.9 (3)	C31A—C30A—C29A	120.4 (5)
C9—C4—N1	118.5 (3)	C30A—C31A—C32A	120.1 (5)
C4—C5—C10	121.0 (4)	C31A—C32A—C27A	120.7 (6)
C6—C5—C4	118.1 (4)	C26B—C21B—C22B	121 (3)
C6—C5—C10	120.9 (3)	C21B—C22B—C23B	116 (4)
C5—C6—C7	122.0 (4)	C24B—C23B—C22B	124 (3)
C6—C7—C11	121.1 (4)	C25B—C24B—C23B	114 (3)
C8—C7—C6	117.9 (4)	C28B—C27B—C20B	122 (3)
C8—C7—C11	121.0 (4)	C32B—C27B—C20B	120 (4)
C9—C8—C7	122.3 (4)	C32B—C27B—C28B	118 (4)
C4—C9—C12	120.4 (4)	C29B—C28B—C27B	122 (3)
C8—C9—C4	118.1 (4)	C28B—C29B—C30B	122 (3)
C8—C9—C12	121.5 (4)	C31B—C30B—C29B	117 (3)
N2—C13—C14	114.5 (4)	C30B—C31B—C32B	121 (3)
C13—C14—C15B	117.6 (10)	C27B—C32B—C31B	120 (4)
O1B—C14—C13	129 (2)	C34—C33—P1	119.8 (3)
O1B—C14—C15B	113 (2)	C38—C33—C34	108.5 (3)
C15A—C14—C13	128 (2)	C38—C33—P1	113.6 (3)
O1A—C14—C13	121.2 (6)	C35—C34—C33	109.4 (4)
O1A—C14—C15A	110 (2)	C36—C35—C34	113.0 (4)
C1—Ru1—Cl1	87.21 (11)	C35—C36—C37	111.6 (4)
C1—Ru1—Cl2	87.49 (10)	C38—C37—C36	110.4 (4)

C1—Ru1—P1	160.30 (11)	C37—C38—C33	110.1 (3)
C18A—Ru1—C1	100.3 (3)	C40—C39—P1	116.4 (3)
C18A—Ru1—Cl1	97.2 (3)	C45—C39—C40	109.1 (3)
C18A—Ru1—Cl2	102.3 (3)	C45—C39—P1	114.1 (3)
C18A—Ru1—P1	99.3 (3)	C41—C40—C39	111.0 (4)
C18B—Ru1—C1	95 (2)	C42—C41—C40	111.1 (4)
C18B—Ru1—Cl1	102.4 (10)	C41—C42—C44	110.8 (3)
C18B—Ru1—Cl2	96.8 (10)	C42—C44—C45	111.1 (3)
C18B—Ru1—P1	105 (2)	C39—C45—C44	111.2 (3)
Cl1—Ru1—Cl2	160.39 (4)	C47—C46—P1	113.8 (3)
Cl1—Ru1—P1	88.87 (3)	C51—C46—C47	110.4 (3)
Cl2—Ru1—P1	89.79 (3)	C51—C46—P1	112.9 (2)
C19A—C18A—Ru1	123.6 (5)	C48—C47—C46	109.7 (3)
C19A—C18A—C25A	102.8 (4)	C49—C48—C47	111.5 (4)
C25A—C18A—Ru1	133.6 (6)	C48—C49—C50	110.8 (4)
C20A—C19A—C18A	111.9 (5)	C49—C50—C51	111.4 (4)
C19A—C20A—C26A	108.0 (4)	C50—C51—C46	111.1 (3)
C19A—C20A—C27A	124.8 (5)	O1B—C16B—C17B	103 (4)
C27A—C20A—C26A	127.2 (4)	C17B—C15B—C14	101.4 (16)
C25A—C26A—C20A	108.1 (4)	C15B—C17B—C16B	107.4 (19)
C21A—C26A—C20A	129.7 (4)	C14—O1B—C16B	115 (4)
C21A—C26A—C25A	122.1 (5)	C17A—C16A—C15A	110 (3)
C26A—C25A—C18A	109.1 (5)	C14—C15A—C16A	103 (3)
C24A—C25A—C18A	131.7 (5)	C16A—C17A—O1A	110.0 (14)
C24A—C25A—C26A	119.0 (5)	C14—O1A—C17A	107.0 (9)
C19B—C18B—Ru1	116.2 (18)	C1—N1—C2	111.9 (3)
C19B—C18B—C25B	106.5 (15)	C1—N1—C4	129.4 (3)
C25B—C18B—Ru1	135 (2)	C4—N1—C2	118.7 (3)
C20B—C19B—C18B	109.5 (16)	C1—N2—C3	113.5 (3)
C19B—C20B—C26B	107.9 (16)	C1—N2—C13	123.3 (3)
C19B—C20B—C27B	121 (2)	C13—N2—C3	119.8 (3)
C27B—C20B—C26B	131 (2)	C33—P1—Ru1	111.33 (12)
C25B—C26B—C20B	109.9 (15)	C33—P1—C39	111.35 (17)
C21B—C26B—C20B	130 (2)	C33—P1—C46	103.65 (17)
C21B—C26B—C25B	120 (2)	C39—P1—Ru1	116.36 (11)
C26B—C25B—C18B	105.6 (15)	C39—P1—C46	101.34 (16)
C24B—C25B—C18B	129 (2)	C46—P1—Ru1	111.67 (12)
C24B—C25B—C26B	125 (2)	Cl5—C1R—Cl6	110.3 (12)
C26A—C21A—C22A	118.4 (5)	C2R—Cl3—Cl4	38.2 (8)
C23A—C22A—C21A	120.3 (6)	C2R—Cl4—Cl3	37.0 (8)
C22A—C23A—C24A	120.8 (6)	Cl3—C2R—Cl4	104.8 (14)

C1—Ru1—C18A—C19A	-91.7 (7)	C21B—C26B—C25B—C18B	-170 (4)
C1—Ru1—C18A—C25A	87.5 (8)	C21B—C26B—C25B—C24B	-1 (5)
C1—Ru1—C18B—C19B	92 (4)	C21B—C22B—C23B—C24B	3 (5)
C1—Ru1—C18B—C25B	-105 (6)	C22B—C23B—C24B—C25B	-4 (5)

C2—C3—N2—C1	10.7 (5)	C27B—C20B—C26B—C25B	178 (3)
C2—C3—N2—C13	170.7 (4)	C27B—C20B—C26B—C21B	-7 (6)
C3—C2—N1—C1	10.1 (5)	C27B—C28B—C29B—C30B	-8 (6)
C3—C2—N1—C4	-169.7 (3)	C28B—C27B—C32B—C31B	-3 (6)
C4—C5—C6—C7	-1.0 (5)	C28B—C29B—C30B—C31B	9 (5)
C5—C4—C9—C8	-1.4 (5)	C29B—C30B—C31B—C32B	-7 (5)
C5—C4—C9—C12	-179.2 (3)	C30B—C31B—C32B—C27B	4 (6)
C5—C4—N1—C1	91.8 (5)	C32B—C27B—C28B—C29B	5 (6)
C5—C4—N1—C2	-88.5 (4)	C33—C34—C35—C36	-55.4 (5)
C5—C6—C7—C8	-0.4 (5)	C34—C33—C38—C37	-62.4 (4)
C5—C6—C7—C11	178.0 (3)	C34—C33—P1—Ru1	162.4 (3)
C6—C7—C8—C9	0.9 (6)	C34—C33—P1—C39	-66.0 (3)
C7—C8—C9—C4	0.0 (6)	C34—C33—P1—C46	42.2 (3)
C7—C8—C9—C12	177.8 (4)	C34—C35—C36—C37	52.7 (5)
C9—C4—C5—C6	1.9 (5)	C35—C36—C37—C38	-54.1 (5)
C9—C4—C5—C10	-179.3 (3)	C36—C37—C38—C33	59.6 (5)
C9—C4—N1—C1	-92.3 (5)	C38—C33—C34—C35	59.1 (5)
C9—C4—N1—C2	87.4 (4)	C38—C33—P1—Ru1	-67.1 (3)
C10—C5—C6—C7	-179.8 (3)	C38—C33—P1—C39	64.6 (3)
C11—C7—C8—C9	-177.5 (4)	C38—C33—P1—C46	172.7 (3)
C13—C14—C15B—C17B	174.6 (10)	C39—C40—C41—C42	56.7 (6)
C13—C14—O1B—C16B	-173.2 (15)	C40—C39—C45—C44	58.0 (5)
C13—C14—C15A—C16A	171.2 (11)	C40—C39—P1—Ru1	-170.4 (3)
C13—C14—O1A—C17A	-171.7 (9)	C40—C39—P1—C33	60.6 (4)
C14—C13—N2—C1	-137.4 (4)	C40—C39—P1—C46	-49.1 (4)
C14—C13—N2—C3	64.7 (5)	C40—C41—C42—C44	-55.3 (6)
C14—C15B—C17B—C16B	-3.1 (15)	C41—C42—C44—C45	55.7 (5)
Ru1—C1—N1—C2	173.6 (3)	C42—C44—C45—C39	-57.8 (5)
Ru1—C1—N1—C4	-6.6 (6)	C45—C39—C40—C41	-57.4 (5)
Ru1—C1—N2—C3	177.4 (3)	C45—C39—P1—Ru1	61.1 (3)
Ru1—C1—N2—C13	18.2 (5)	C45—C39—P1—C33	-67.9 (3)
Ru1—C18A—C19A—C20A	-178.3 (5)	C45—C39—P1—C46	-177.5 (3)
Ru1—C18A—C25A—C26A	177.6 (7)	C46—C47—C48—C49	-57.8 (5)
Ru1—C18A—C25A—C24A	1.9 (12)	C47—C46—C51—C50	-56.3 (4)
Ru1—C18B—C19B—C20B	175 (3)	C47—C46—P1—Ru1	-62.2 (3)
Ru1—C18B—C25B—C26B	-171 (5)	C47—C46—P1—C33	57.8 (3)
Ru1—C18B—C25B—C24B	20 (9)	C47—C46—P1—C39	173.3 (3)
C18A—Ru1—C18B—C19B	-131 (19)	C47—C48—C49—C50	57.0 (5)
C18A—Ru1—C18B—C25B	31 (10)	C48—C49—C50—C51	-55.5 (5)
C18A—C19A—C20A—C26A	-0.7 (6)	C49—C50—C51—C46	55.5 (5)
C18A—C19A—C20A—C27A	-179.7 (6)	C51—C46—C47—C48	57.1 (4)
C18A—C25A—C24A—C23A	175.7 (6)	C51—C46—P1—Ru1	64.7 (3)
C19A—C18A—C25A—C26A	-3.1 (7)	C51—C46—P1—C33	-175.3 (3)
C19A—C18A—C25A—C24A	-178.8 (5)	C51—C46—P1—C39	-59.8 (3)
C19A—C20A—C26A—C25A	-1.4 (5)	C15B—C14—O1B—C16B	-5 (2)
C19A—C20A—C26A—C21A	175.4 (5)	C15B—C14—C15A—C16A	-34.1 (15)

C19A—C20A—C27A—C28A	-32.4 (9)	C15B—C14—O1A—C17A	94 (2)
C19A—C20A—C27A—C32A	146.8 (6)	C17B—C16B—O1B—C14	2 (2)
C20A—C26A—C25A—C18A	2.8 (6)	O1B—C14—C15B—C17B	4.8 (15)
C20A—C26A—C25A—C24A	179.1 (4)	O1B—C14—C15A—C16A	74 (20)
C20A—C26A—C21A—C22A	-179.0 (5)	O1B—C14—O1A—C17A	-13.0 (18)
C20A—C27A—C28A—C29A	178.9 (6)	O1B—C16B—C17B—C15B	0.9 (19)
C20A—C27A—C32A—C31A	-179.2 (6)	C16A—C17A—O1A—C14	0 (2)
C26A—C20A—C27A—C28A	148.8 (6)	C15A—C14—C15B—C17B	17 (2)
C26A—C20A—C27A—C32A	-32.0 (9)	C15A—C14—O1B—C16B	-81 (20)
C26A—C25A—C24A—C23A	0.4 (7)	C15A—C14—O1A—C17A	-1.3 (17)
C26A—C21A—C22A—C23A	0.8 (10)	C15A—C16A—C17A—O1A	1 (2)
C25A—C18A—C19A—C20A	2.3 (7)	C17A—C16A—C15A—C14	-1.6 (18)
C25A—C26A—C21A—C22A	-2.7 (8)	O1A—C14—C15B—C17B	-80 (2)
C18B—Ru1—C18A—C19A	-136 (16)	O1A—C14—O1B—C16B	30.3 (19)
C18B—Ru1—C18A—C25A	43 (15)	O1A—C14—C15A—C16A	1.8 (15)
C18B—C19B—C20B—C26B	-4 (4)	N1—C1—N2—C3	-4.8 (5)
C18B—C19B—C20B—C27B	177 (4)	N1—C1—N2—C13	-164.0 (4)
C18B—C25B—C24B—C23B	170 (4)	N1—C2—C3—N2	-11.5 (4)
C19B—C18B—C25B—C26B	-8 (5)	N1—C4—C5—C6	177.6 (3)
C19B—C18B—C25B—C24B	-177 (3)	N1—C4—C5—C10	-3.5 (5)
C19B—C20B—C26B—C25B	-1 (4)	N1—C4—C9—C8	-177.2 (3)
C19B—C20B—C26B—C21B	174 (3)	N1—C4—C9—C12	5.0 (5)
C19B—C20B—C27B—C28B	-32 (5)	N2—C1—N1—C2	-3.7 (4)
C19B—C20B—C27B—C32B	145 (4)	N2—C1—N1—C4	176.0 (4)
C20B—C26B—C25B—C18B	5 (4)	N2—C13—C14—C15B	-88.5 (10)
C20B—C26B—C25B—C24B	175 (3)	N2—C13—C14—O1B	79.4 (17)
C20B—C26B—C21B—C22B	-175 (3)	N2—C13—C14—C15A	64.4 (16)
C20B—C27B—C28B—C29B	-178 (3)	N2—C13—C14—O1A	-127.2 (9)
C20B—C27B—C32B—C31B	180 (3)	Cl1—Ru1—C18A—C19A	-3.3 (7)
C26B—C20B—C27B—C28B	149 (3)	Cl1—Ru1—C18A—C25A	175.9 (8)
C26B—C20B—C27B—C32B	-33 (6)	Cl1—Ru1—C18B—C19B	-179 (4)
C26B—C25B—C24B—C23B	3 (5)	Cl1—Ru1—C18B—C25B	-17 (7)
C26B—C21B—C22B—C23B	0 (5)	Cl2—Ru1—C18A—C19A	178.6 (6)
C25B—C18B—C19B—C20B	7 (5)	Cl2—Ru1—C18A—C25A	-2.2 (9)
C25B—C26B—C21B—C22B	0 (5)	Cl2—Ru1—C18B—C19B	4 (5)
C21A—C26A—C25A—C18A	-174.2 (5)	Cl2—Ru1—C18B—C25B	167 (6)
C21A—C26A—C25A—C24A	2.1 (7)	P1—Ru1—C18A—C19A	86.8 (6)
C21A—C22A—C23A—C24A	1.6 (10)	P1—Ru1—C18A—C25A	-94.0 (8)
C22A—C23A—C24A—C25A	-2.1 (9)	P1—Ru1—C18B—C19B	-87 (4)
C27A—C20A—C26A—C25A	177.6 (5)	P1—Ru1—C18B—C25B	75 (7)
C27A—C20A—C26A—C21A	-5.6 (8)	P1—C33—C34—C35	-168.2 (3)
C27A—C28A—C29A—C30A	0.3 (10)	P1—C33—C38—C37	161.7 (3)
C28A—C27A—C32A—C31A	0.0 (10)	P1—C39—C40—C41	171.8 (3)
C28A—C29A—C30A—C31A	0.0 (11)	P1—C39—C45—C44	-170.0 (3)
C29A—C30A—C31A—C32A	-0.3 (11)	P1—C46—C47—C48	-174.8 (3)
C30A—C31A—C32A—C27A	0.3 (10)	P1—C46—C51—C50	175.0 (3)

C32A—C27A—C28A—C29A	-0.3 (10)		

Table S6. Selected geometric parameters for 5c (Å, º)

Ru1—P1	2.4622 (13)	C18B—C19B	1.352 (17)
Ru1—Cl2	2.4151 (13)	C19B—C20B	1.413 (17)
Ru1—Cl1	2.4105 (13)	C22—C23	1.521 (8)
Ru1—C1	2.054 (5)	C22—C30	1.514 (8)
Ru1—C22	1.850 (5)	C23—C24	1.330 (9)
P1—C37	1.850 (5)	C23—C28	1.432 (9)
P1—C48	1.855 (5)	C24—C25	1.455 (9)
P1—C49	1.849 (5)	C25—C26	1.339 (11)
N1—C1	1.340 (7)	C26—C27	1.435 (11)
N1—C2	1.477 (7)	C27—C28	1.394 (9)
N1—C4	1.447 (7)	C28—C29	1.448 (9)
N2—C1	1.342 (6)	C29—C30	1.328 (8)
N2—C3	1.474 (7)	C29—C31A	1.500 (11)
N2—C13	1.458 (7)	C29—C31B	1.50 (3)
C2—C3	1.524 (9)	C31A—C32A	1.369 (11)
C4—C5	1.405 (7)	C31A—C36A	1.392 (11)
C4—C9	1.379 (7)	C32A—C33A	1.408 (11)
C5—C6	1.398 (7)	C33A—C34A	1.392 (12)
C5—C11	1.496 (7)	C34A—C35A	1.385 (12)
C6—C7	1.388 (7)	C35A—C36A	1.420 (11)
C7—C8	1.389 (8)	C31B—C32B	1.359 (19)
C7—C12	1.503 (8)	C31B—C36B	1.399 (19)
C8—C9	1.408 (8)	C32B—C33B	1.415 (19)
C9—C10	1.515 (8)	C33B—C34B	1.40 (2)
C13—C14A	1.478 (13)	C34B—C35B	1.38 (2)
C13—C14B	1.512 (14)	C35B—C36B	1.427 (19)
S1A—C14A	1.740 (11)	C37—C38	1.528 (7)
S1A—C21A	1.714 (12)	C37—C42	1.547 (7)
C14A—C15A	1.395 (12)	C38—C39	1.553 (7)
C15A—C16A	1.435 (13)	C39—C40	1.525 (9)
C16A—C21A	1.366 (13)	C40—C41	1.521 (8)
C16A—C17A	1.388 (19)	C41—C42	1.513 (8)
C21A—C20A	1.35 (2)	C43—C44	1.544 (8)
S1B—C14B	1.742 (11)	C43—C48	1.524 (7)
S1B—C21B	1.757 (11)	C44—C45	1.527 (8)
C14B—C15B	1.404 (12)	C45—C46	1.503 (8)
C15B—C16B	1.425 (12)	C46—C47	1.537 (8)
C16B—C21B	1.389 (13)	C47—C48	1.531 (7)
C16B—C17B	1.414 (19)	C49—C50	1.547 (7)
C21B—C20B	1.49 (2)	C49—C54	1.530 (7)
C17A—C18A	1.366 (15)	C50—C51	1.535 (7)
C18A—C19A	1.355 (17)	C51—C52	1.513 (7)

C19A—C20A	1.398 (18)	C52—C53	1.517 (8)
C17B—C18B	1.358 (15)	C53—C54	1.543 (7)
Cl2—Ru1—P1	90.92 (5)	C19A—C18A—C17A	120.8 (15)
Cl1—Ru1—P1	88.63 (4)	C18A—C19A—C20A	121.5 (16)
Cl1—Ru1—Cl2	159.50 (5)	C21A—C20A—C19A	117.1 (16)
C1—Ru1—P1	160.24 (15)	C18B—C17B—C16B	118.2 (14)
C1—Ru1—Cl2	85.41 (15)	C19B—C18B—C17B	119.6 (14)
C1—Ru1—Cl1	88.12 (14)	C18B—C19B—C20B	128.1 (15)
C22—Ru1—P1	100.19 (16)	C19B—C20B—C21B	110.7 (15)
C22—Ru1—Cl2	101.68 (17)	C23—C22—Ru1	134.5 (4)
C22—Ru1—Cl1	98.57 (17)	C30—C22—Ru1	123.4 (4)
C22—Ru1—C1	99.6 (2)	C30—C22—C23	102.1 (5)
C37—P1—Ru1	110.97 (17)	C24—C23—C22	132.3 (7)
C37—P1—C48	111.4 (2)	C24—C23—C28	121.5 (6)
C48—P1—Ru1	116.52 (16)	C28—C23—C22	106.1 (5)
C49—P1—Ru1	111.33 (17)	C23—C24—C25	119.1 (7)
C49—P1—C37	103.1 (2)	C26—C25—C24	121.3 (8)
C49—P1—C48	102.3 (2)	C25—C26—C27	119.3 (7)
C1—N1—C2	112.3 (4)	C28—C27—C26	119.9 (7)
C1—N1—C4	129.6 (4)	C23—C28—C29	111.0 (5)
C4—N1—C2	117.7 (4)	C27—C28—C23	118.8 (6)
C1—N2—C3	112.9 (4)	C27—C28—C29	130.1 (6)
C1—N2—C13	122.8 (4)	C28—C29—C31A	129.9 (6)
C13—N2—C3	121.2 (4)	C28—C29—C31B	112.5 (12)
N1—C1—Ru1	133.4 (4)	C30—C29—C28	107.4 (6)
N1—C1—N2	108.3 (4)	C30—C29—C31A	122.7 (7)
N2—C1—Ru1	118.3 (4)	C30—C29—C31B	138.7 (13)
N1—C2—C3	102.6 (5)	C29—C30—C22	113.4 (6)
N2—C3—C2	101.7 (4)	C32A—C31A—C29	120.9 (8)
C5—C4—N1	117.9 (5)	C32A—C31A—C36A	119.6 (8)
C9—C4—N1	119.9 (5)	C36A—C31A—C29	119.4 (8)
C9—C4—C5	122.0 (5)	C31A—C32A—C33A	121.0 (8)
C4—C5—C11	121.3 (5)	C34A—C33A—C32A	119.3 (8)
C6—C5—C4	117.8 (5)	C35A—C34A—C33A	120.8 (8)
C6—C5—C11	120.9 (5)	C34A—C35A—C36A	118.7 (8)
C7—C6—C5	121.9 (5)	C31A—C36A—C35A	120.5 (8)
C6—C7—C8	118.6 (5)	C32B—C31B—C29	130 (2)
C6—C7—C12	119.8 (5)	C32B—C31B—C36B	116 (2)
C8—C7—C12	121.7 (5)	C36B—C31B—C29	114 (2)
C7—C8—C9	121.5 (5)	C31B—C32B—C33B	122 (2)
C4—C9—C8	118.2 (5)	C34B—C33B—C32B	121 (2)
C4—C9—C10	120.7 (5)	C35B—C34B—C33B	120 (2)
C8—C9—C10	121.1 (5)	C34B—C35B—C36B	116 (2)
N2—C13—C14A	117.4 (7)	C31B—C36B—C35B	125 (2)
N2—C13—C14B	108.8 (7)	C38—C37—P1	120.2 (3)

C21A—S1A—C14A	92.5 (6)	C38—C37—C42	108.7 (4)
C13—C14A—S1A	118.9 (8)	C42—C37—P1	113.2 (4)
C15A—C14A—C13	131.4 (10)	C37—C38—C39	110.0 (4)
C15A—C14A—S1A	109.7 (8)	C40—C39—C38	111.4 (5)
C14A—C15A—C16A	113.1 (10)	C41—C40—C39	111.7 (5)
C21A—C16A—C15A	112.1 (11)	C42—C41—C40	111.9 (5)
C21A—C16A—C17A	120.3 (12)	C41—C42—C37	108.6 (5)
C17A—C16A—C15A	127.6 (13)	C48—C43—C44	110.5 (5)
C16A—C21A—S1A	112.3 (9)	C45—C44—C43	111.0 (5)
C20A—C21A—S1A	125.5 (12)	C46—C45—C44	110.3 (5)
C20A—C21A—C16A	122.0 (13)	C45—C46—C47	111.4 (5)
C14B—S1B—C21B	89.1 (6)	C48—C47—C46	111.2 (4)
C13—C14B—S1B	122.7 (8)	C43—C48—P1	115.9 (4)
C15B—C14B—C13	123.4 (9)	C43—C48—C47	109.5 (4)
C15B—C14B—S1B	113.9 (9)	C47—C48—P1	114.8 (4)
C14B—C15B—C16B	111.0 (10)	C50—C49—P1	113.1 (3)
C21B—C16B—C15B	112.3 (10)	C54—C49—P1	113.0 (3)
C21B—C16B—C17B	122.4 (11)	C54—C49—C50	110.0 (4)
C17B—C16B—C15B	125.2 (12)	C51—C50—C49	110.9 (4)
C16B—C21B—S1B	113.3 (8)	C52—C51—C50	111.1 (4)
C16B—C21B—C20B	120.2 (12)	C51—C52—C53	110.9 (4)
C20B—C21B—S1B	126.2 (11)	C52—C53—C54	110.8 (5)
C18A—C17A—C16A	118.2 (14)	C49—C54—C53	110.9 (4)

Ru1—P1—C37—C38	159.6 (4)	C21B—S1B—C14B—C15B	-6.0 (11)
Ru1—P1—C37—C42	-69.5 (4)	C21B—C16B—C17B—C18B	6 (2)
Ru1—P1—C48—C43	-174.9 (4)	C17A—C16A—C21A—S1A	-175.1 (11)
Ru1—P1—C48—C47	55.9 (4)	C17A—C16A—C21A—C20A	1 (3)
Ru1—P1—C49—C50	66.6 (4)	C17A—C18A—C19A—C20A	0 (3)
Ru1—P1—C49—C54	-59.3 (4)	C18A—C19A—C20A—C21A	0 (3)
Ru1—C22—C23—C24	1.1 (10)	C17B—C16B—C21B—S1B	172.9 (11)
Ru1—C22—C23—C28	177.3 (4)	C17B—C16B—C21B—C20B	-1 (2)
Ru1—C22—C30—C29	-178.0 (4)	C17B—C18B—C19B—C20B	-5 (3)
P1—Ru1—C22—C23	-90.9 (5)	C18B—C19B—C20B—C21B	10 (3)
P1—Ru1—C22—C30	88.2 (4)	C22—C23—C24—C25	176.3 (6)
P1—C37—C38—C39	-166.7 (4)	C22—C23—C28—C27	-175.9 (5)
P1—C37—C42—C41	160.9 (4)	C22—C23—C28—C29	2.0 (6)
P1—C49—C50—C51	176.7 (4)	C23—C22—C30—C29	1.3 (6)
P1—C49—C54—C53	-176.5 (4)	C23—C24—C25—C26	-0.1 (11)
Cl2—Ru1—C22—C23	2.2 (5)	C23—C28—C29—C30	-1.2 (7)
Cl2—Ru1—C22—C30	-178.7 (4)	C23—C28—C29—C31A	174.6 (7)
Cl1—Ru1—C22—C23	178.9 (5)	C23—C28—C29—C31B	-170.4 (12)
Cl1—Ru1—C22—C30	-1.9 (4)	C24—C23—C28—C27	0.8 (9)
N1—C2—C3—N2	-14.1 (7)	C24—C23—C28—C29	178.7 (6)
N1—C4—C5—C6	-177.6 (5)	C24—C25—C26—C27	-1.8 (12)
N1—C4—C5—C11	3.5 (8)	C25—C26—C27—C28	3.2 (12)

N1—C4—C9—C8	177.3 (5)	C26—C27—C28—C23	-2.7 (10)
N1—C4—C9—C10	-3.6 (8)	C26—C27—C28—C29	179.9 (7)
N2—C13—C14A—S1A	65.6 (12)	C27—C28—C29—C30	176.4 (7)
N2—C13—C14A—C15A	-116.1 (13)	C27—C28—C29—C31A	-7.8 (12)
N2—C13—C14B—S1B	59.5 (12)	C27—C28—C29—C31B	7.2 (14)
N2—C13—C14B—C15B	-117.9 (11)	C28—C23—C24—C25	0.6 (10)
C1—Ru1—C22—C23	89.4 (5)	C28—C29—C30—C22	-0.2 (7)
C1—Ru1—C22—C30	-91.5 (4)	C28—C29—C31A—C32A	-28.1 (11)
C1—N1—C2—C3	11.9 (8)	C28—C29—C31A—C36A	151.3 (8)
C1—N1—C4—C5	-98.1 (7)	C28—C29—C31B—C32B	-38 (2)
C1—N1—C4—C9	85.9 (7)	C28—C29—C31B—C36B	147.6 (18)
C1—N2—C3—C2	13.5 (7)	C29—C31A—C32A—C33A	179.2 (8)
C1—N2—C13—C14A	-145.3 (7)	C29—C31A—C36A—C35A	-176.5 (8)
C1—N2—C13—C14B	-146.3 (7)	C29—C31B—C32B—C33B	-175 (2)
C2—N1—C1—Ru1	176.3 (5)	C29—C31B—C36B—C35B	-180 (3)
C2—N1—C1—N2	-3.8 (7)	C30—C22—C23—C24	-178.1 (7)
C2—N1—C4—C5	89.5 (7)	C30—C22—C23—C28	-1.9 (6)
C2—N1—C4—C9	-86.5 (7)	C30—C29—C31A—C32A	147.2 (7)
C3—N2—C1—Ru1	173.3 (4)	C30—C29—C31A—C36A	-33.4 (11)
C3—N2—C1—N1	-6.6 (7)	C30—C29—C31B—C32B	157.6 (16)
C3—N2—C13—C14A	56.0 (9)	C30—C29—C31B—C36B	-17 (3)
C3—N2—C13—C14B	55.0 (8)	C31A—C29—C30—C22	-176.3 (6)
C4—N1—C1—Ru1	3.5 (9)	C31A—C29—C31B—C32B	109 (4)
C4—N1—C1—N2	-176.6 (5)	C31A—C29—C31B—C36B	-65 (3)
C4—N1—C2—C3	-174.4 (5)	C31A—C32A—C33A—C34A	-0.9 (11)
C4—C5—C6—C7	1.1 (8)	C32A—C31A—C36A—C35A	2.9 (13)
C5—C4—C9—C8	1.5 (8)	C32A—C33A—C34A—C35A	-0.8 (14)
C5—C4—C9—C10	-179.4 (5)	C33A—C34A—C35A—C36A	3.5 (15)
C5—C6—C7—C8	-0.2 (8)	C34A—C35A—C36A—C31A	-4.5 (14)
C5—C6—C7—C12	-178.6 (5)	C36A—C31A—C32A—C33A	-0.2 (11)
C6—C7—C8—C9	-0.1 (8)	C31B—C29—C30—C22	164.6 (17)
C7—C8—C9—C4	-0.5 (8)	C31B—C29—C31A—C32A	-69 (3)
C7—C8—C9—C10	-179.7 (5)	C31B—C29—C31A—C36A	111 (3)
C9—C4—C5—C6	-1.8 (8)	C31B—C32B—C33B—C34B	1 (2)
C9—C4—C5—C11	179.3 (5)	C32B—C31B—C36B—C35B	5 (4)
C11—C5—C6—C7	180.0 (5)	C32B—C33B—C34B—C35B	-4 (4)
C12—C7—C8—C9	178.2 (5)	C33B—C34B—C35B—C36B	8 (4)
C13—N2—C1—Ru1	13.0 (7)	C34B—C35B—C36B—C31B	-8 (5)
C13—N2—C1—N1	-166.9 (5)	C36B—C31B—C32B—C33B	-1 (2)
C13—N2—C3—C2	174.1 (5)	C37—P1—C48—C43	56.4 (5)
C13—C14A—C15A—C16A	178.1 (13)	C37—P1—C48—C47	-72.8 (4)
C13—C14B—C15B—C16B	-177.5 (12)	C37—P1—C49—C50	-174.4 (4)
S1A—C14A—C15A—C16A	-3.6 (11)	C37—P1—C49—C54	59.8 (4)
S1A—C21A—C20A—C19A	175.2 (15)	C37—C38—C39—C40	-55.2 (7)
C14A—C13—C14B—S1B	-115 (6)	C38—C37—C42—C41	-62.7 (6)
C14A—C13—C14B—C15B	68 (5)	C38—C39—C40—C41	51.6 (7)

C14A—S1A—C21A—C16A	-4.9 (13)	C39—C40—C41—C42	-54.8 (7)
C14A—S1A—C21A—C20A	179.1 (19)	C40—C41—C42—C37	59.9 (6)
C14A—C15A—C16A—C21A	0.0 (12)	C42—C37—C38—C39	60.5 (6)
C14A—C15A—C16A—C17A	178.7 (13)	C43—C44—C45—C46	-56.7 (8)
C15A—C16A—C21A—S1A	3.7 (15)	C44—C43—C48—P1	171.0 (4)
C15A—C16A—C21A—C20A	179.8 (16)	C44—C43—C48—C47	-57.3 (6)
C15A—C16A—C17A—C18A	-179.8 (12)	C44—C45—C46—C47	56.1 (7)
C16A—C21A—C20A—C19A	0 (3)	C45—C46—C47—C48	-57.0 (6)
C16A—C17A—C18A—C19A	1 (3)	C46—C47—C48—P1	-170.8 (4)
C21A—S1A—C14A—C13	-176.7 (11)	C46—C47—C48—C43	56.9 (6)
C21A—S1A—C14A—C15A	4.7 (11)	C48—P1—C37—C38	-68.7 (5)
C21A—C16A—C17A—C18A	-1 (2)	C48—P1—C37—C42	62.1 (4)
S1B—C14B—C15B—C16B	4.9 (11)	C48—P1—C49—C50	-58.6 (4)
S1B—C21B—C20B—C19B	-179.4 (14)	C48—P1—C49—C54	175.5 (4)
C14B—C13—C14A—S1A	72 (5)	C48—C43—C44—C45	57.9 (8)
C14B—C13—C14A—C15A	-110 (6)	C49—P1—C37—C38	40.3 (5)
C14B—S1B—C21B—C16B	5.8 (13)	C49—P1—C37—C42	171.2 (4)
C14B—S1B—C21B—C20B	178.7 (18)	C49—P1—C48—C43	-53.2 (4)
C14B—C15B—C16B—C21B	-0.4 (11)	C49—P1—C48—C47	177.6 (4)
C14B—C15B—C16B—C17B	-177.4 (13)	C49—C50—C51—C52	56.5 (6)
C15B—C16B—C21B—S1B	-4.2 (14)	C50—C49—C54—C53	56.0 (6)
C15B—C16B—C21B—C20B	-177.6 (14)	C50—C51—C52—C53	-57.2 (6)
C15B—C16B—C17B—C18B	-177.1 (12)	C51—C52—C53—C54	57.2 (7)
C16B—C21B—C20B—C19B	-7 (3)	C52—C53—C54—C49	-57.1 (6)
C16B—C17B—C18B—C19B	-4 (3)	C54—C49—C50—C51	-55.8 (6)
C21B—S1B—C14B—C13	176.3 (12)		

Table S7. Selected geometric parameters for 5d (Å, º)

P1—Ru1	2.449 (2)	C45—C46	1.51 (2)
P1—C37	1.826 (12)	C46—C47	1.530 (19)
P1—C43	1.855 (12)	C47—C48	1.53 (2)
P1—C49	1.852 (9)	C49—C50	1.547 (13)
Ru1—Cl1	2.416 (3)	C49—C54	1.515 (14)
Ru1—Cl2	2.392 (3)	C50—C51	1.523 (14)
Ru1—C1	2.063 (10)	C51—C52	1.516 (15)
Ru1—C22A	1.726 (19)	C52—C53	1.516 (16)
Ru1—C22B	2.01 (2)	C53—C54	1.507 (17)
N1—C1	1.329 (15)	P2—Ru2	2.454 (2)
N1—C2	1.485 (15)	P2—C91	1.848 (12)
N1—C4	1.426 (17)	P2—C97	1.887 (11)
N2—C1	1.362 (17)	P2—C103	1.873 (10)
N2—C3	1.473 (13)	Ru2—C76	1.867 (11)
N2—C13	1.415 (15)	Ru2—Cl3	2.408 (2)
O1—C14	1.385 (13)	Ru2—Cl4	2.399 (2)
O1—C21	1.378 (16)	Ru2—C55	2.088 (10)

C3—C2	1.51 (2)	C76—C77	1.480 (15)
C4—C5	1.406 (17)	C76—C84	1.494 (12)
C4—C9	1.391 (15)	C77—C78	1.396 (15)
C5—C6	1.387 (19)	C77—C82	1.409 (14)
C5—C11	1.500 (15)	C78—C79	1.413 (17)
C6—C7	1.409 (16)	C79—C80	1.365 (16)
C7—C8	1.40 (2)	C80—C81	1.417 (17)
C7—C12	1.50 (2)	C81—C82	1.366 (17)
C8—C9	1.39 (2)	C82—C83	1.481 (14)
C9—C10	1.52 (2)	C83—C84	1.367 (13)
C13—C14	1.516 (18)	C83—C85	1.470 (12)
C14—C15	1.373 (17)	O2—C68	1.366 (12)
C15—C16	1.433 (19)	O2—C75	1.388 (17)
C16—C17	1.41 (2)	N3—C55	1.310 (13)
C16—C21	1.399 (16)	N3—C56	1.479 (14)
C17—C18	1.41 (2)	N3—C58	1.421 (14)
C18—C19	1.371 (19)	N4—C55	1.341 (14)
C19—C20	1.43 (2)	N4—C57	1.466 (13)
C20—C21	1.376 (18)	N4—C67	1.432 (13)
C22A—C23A	1.53 (2)	C56—C57	1.492 (16)
C22A—C30A	1.51 (2)	C58—C59	1.403 (17)
C23A—C28A	1.43 (3)	C58—C63	1.402 (13)
C23A—C24A	1.41 (3)	C59—C60	1.379 (17)
C28A—C29A	1.45 (4)	C59—C65	1.491 (14)
C28A—C27A	1.43 (3)	C60—C61	1.397 (15)
C29A—C30A	1.35 (2)	C61—C62	1.389 (16)
C29A—C31A	1.46 (3)	C61—C66	1.508 (16)
C22B—C23B	1.50 (3)	C62—C63	1.402 (15)
C22B—C30B	1.53 (3)	C63—C64	1.491 (17)
C23B—C28B	1.44 (3)	C67—C68	1.481 (17)
C23B—C24B	1.33 (4)	C68—C69	1.327 (17)
C28B—C29B	1.47 (5)	C69—C70	1.453 (18)
C28B—C27B	1.41 (4)	C70—C71	1.40 (2)
C29B—C30B	1.35 (3)	C70—C75	1.365 (18)
C29B—C31B	1.48 (4)	C71—C72	1.34 (2)
C24A—C25A	1.36 (3)	C72—C73	1.40 (2)
C25A—C26A	1.39 (4)	C73—C74	1.39 (2)
C26A—C27A	1.38 (3)	C74—C75	1.39 (2)
C24B—C25B	1.44 (5)	C85—C86	1.402 (13)
C25B—C26B	1.38 (3)	C85—C90	1.417 (13)
C26B—C27B	1.36 (4)	C86—C87	1.407 (14)
C31A—C32A	1.42 (3)	C87—C88	1.377 (17)
C31A—C36A	1.39 (3)	C88—C89	1.410 (16)
C32A—C33A	1.42 (2)	C89—C90	1.366 (12)
C33A—C34A	1.38 (3)	C91—C92	1.542 (16)
C34A—C35A	1.37 (2)	C91—C96	1.534 (16)

C35A—C36A	1.37 (3)	C92—C93	1.533 (19)
C31B—C32B	1.43 (3)	C93—C94	1.484 (18)
C31B—C36B	1.38 (3)	C94—C95	1.57 (2)
C32B—C33B	1.45 (3)	C95—C96	1.50 (2)
C33B—C34B	1.38 (3)	C97—C98	1.505 (14)
C34B—C35B	1.38 (3)	C97—C102	1.513 (17)
C35B—C36B	1.38 (3)	C98—C99	1.533 (15)
C37—C38	1.559 (13)	C99—C100	1.54 (2)
C37—C42	1.536 (18)	C100—C101	1.509 (17)
C38—C39	1.523 (19)	C101—C102	1.498 (15)
C39—C40	1.52 (2)	C103—C104	1.492 (15)
C40—C41	1.546 (16)	C103—C108	1.524 (16)
C41—C42	1.544 (16)	C104—C105	1.520 (18)
C43—C44	1.521 (16)	C105—C106	1.531 (18)
C43—C48	1.520 (19)	C106—C107	1.501 (16)
C44—C45	1.540 (19)	C107—C108	1.540 (16)
C37—P1—Ru1	111.1 (3)	C48—C43—C44	107.8 (11)
C37—P1—C43	103.9 (6)	C43—C44—C45	108.7 (12)
C37—P1—C49	101.5 (5)	C46—C45—C44	111.5 (13)
C43—P1—Ru1	111.6 (4)	C45—C46—C47	112.1 (13)
C49—P1—Ru1	116.2 (3)	C48—C47—C46	109.0 (12)
C49—P1—C43	111.4 (5)	C43—C48—C47	110.3 (12)
Cl1—Ru1—P1	89.92 (9)	C50—C49—P1	115.2 (7)
Cl2—Ru1—P1	89.23 (9)	C54—C49—P1	115.0 (8)
Cl2—Ru1—Cl1	160.61 (12)	C54—C49—C50	109.6 (9)
C1—Ru1—P1	159.5 (4)	C51—C50—C49	110.7 (9)
C1—Ru1—Cl1	88.4 (3)	C52—C51—C50	112.7 (10)
C1—Ru1—Cl2	85.7 (3)	C51—C52—C53	110.8 (9)
C22A—Ru1—P1	99.3 (6)	C54—C53—C52	113.2 (10)
C22A—Ru1—Cl1	89.5 (6)	C53—C54—C49	110.8 (11)
C22A—Ru1—Cl2	109.7 (5)	C91—P2—Ru2	113.0 (3)
C22A—Ru1—C1	101.1 (7)	C91—P2—C97	103.6 (5)
C22B—Ru1—P1	99.3 (9)	C91—P2—C103	111.0 (5)
C22B—Ru1—Cl1	106.1 (8)	C97—P2—Ru2	110.3 (3)
C22B—Ru1—Cl2	93.2 (8)	C103—P2—Ru2	115.4 (4)
C22B—Ru1—C1	100.8 (9)	C103—P2—C97	102.2 (5)
C1—N1—C2	113.2 (11)	C76—Ru2—P2	99.7 (3)
C1—N1—C4	127.1 (10)	C76—Ru2—Cl3	96.1 (3)
C4—N1—C2	119.7 (10)	C76—Ru2—Cl4	102.4 (3)
C1—N2—C3	112.8 (10)	C76—Ru2—C55	100.5 (4)
C1—N2—C13	124.2 (9)	Cl3—Ru2—P2	89.19 (9)
C13—N2—C3	121.6 (10)	Cl4—Ru2—P2	89.13 (8)
C21—O1—C14	106.3 (9)	Cl4—Ru2—Cl3	161.41 (9)
N1—C1—Ru1	133.4 (10)	C55—Ru2—P2	159.5 (3)
N1—C1—N2	108.0 (10)	C55—Ru2—Cl3	85.9 (3)

N2—C1—Ru1	118.6 (8)	C55—Ru2—Cl4	89.2 (3)
N2—C3—C2	103.0 (10)	C77—C76—Ru2	132.7 (7)
N1—C2—C3	103.0 (10)	C77—C76—C84	104.2 (9)
C5—C4—N1	119.6 (10)	C84—C76—Ru2	123.1 (8)
C9—C4—N1	119.5 (12)	C78—C77—C76	133.3 (10)
C9—C4—C5	120.5 (13)	C78—C77—C82	118.1 (10)
C4—C5—C11	120.4 (12)	C82—C77—C76	108.5 (9)
C6—C5—C4	119.4 (11)	C77—C78—C79	119.8 (10)
C6—C5—C11	120.0 (12)	C80—C79—C78	121.6 (11)
C5—C6—C7	121.3 (13)	C79—C80—C81	118.2 (12)
C6—C7—C12	120.4 (14)	C82—C81—C80	120.9 (10)
C8—C7—C6	117.5 (14)	C77—C82—C83	108.8 (9)
C8—C7—C12	122.0 (12)	C81—C82—C77	121.2 (10)
C9—C8—C7	122.3 (12)	C81—C82—C83	130.1 (9)
C4—C9—C8	118.7 (13)	C84—C83—C82	107.5 (8)
C4—C9—C10	121.1 (14)	C84—C83—C85	125.3 (9)
C8—C9—C10	120.2 (11)	C85—C83—C82	127.2 (9)
N2—C13—C14	115.0 (10)	C83—C84—C76	110.9 (9)
O1—C14—C13	115.5 (9)	C68—O2—C75	105.1 (9)
C15—C14—O1	111.0 (11)	C55—N3—C56	110.8 (9)
C15—C14—C13	133.2 (10)	C55—N3—C58	130.2 (9)
C14—C15—C16	106.4 (10)	C58—N3—C56	119.0 (8)
C17—C16—C15	135.8 (11)	C55—N4—C57	111.5 (9)
C21—C16—C15	106.2 (11)	C55—N4—C67	125.4 (9)
C21—C16—C17	118.0 (12)	C67—N4—C57	120.6 (8)
C18—C17—C16	118.3 (11)	N3—C55—Ru2	131.5 (8)
C19—C18—C17	121.4 (14)	N3—C55—N4	110.5 (9)
C18—C19—C20	121.8 (13)	N4—C55—Ru2	117.9 (7)
C21—C20—C19	115.2 (12)	N3—C56—C57	104.0 (8)
O1—C21—C16	110.1 (11)	N4—C57—C56	102.5 (8)
C20—C21—O1	124.6 (11)	C59—C58—N3	119.0 (9)
C20—C21—C16	125.3 (13)	C63—C58—N3	120.5 (10)
C23A—C22A—Ru1	129.3 (12)	C63—C58—C59	120.5 (10)
C30A—C22A—Ru1	129.2 (13)	C58—C59—C65	120.7 (10)
C30A—C22A—C23A	101.6 (14)	C60—C59—C58	118.3 (9)
C28A—C23A—C22A	107.9 (19)	C60—C59—C65	121.0 (11)
C24A—C23A—C22A	131.5 (17)	C59—C60—C61	123.0 (11)
C24A—C23A—C28A	120 (2)	C60—C61—C66	121.3 (11)
C23A—C28A—C29A	108.8 (18)	C62—C61—C60	117.5 (10)
C27A—C28A—C23A	119 (3)	C62—C61—C66	121.1 (10)
C27A—C28A—C29A	132 (2)	C61—C62—C63	121.6 (10)
C28A—C29A—C31A	123.6 (18)	C58—C63—C62	118.9 (11)
C30A—C29A—C28A	109.0 (16)	C58—C63—C64	120.7 (10)
C30A—C29A—C31A	127.3 (19)	C62—C63—C64	120.3 (9)
C29A—C30A—C22A	112.4 (15)	N4—C67—C68	116.0 (10)
C23B—C22B—Ru1	131.2 (18)	O2—C68—C67	113.7 (9)

C23B—C22B—C30B	103.7 (18)	C69—C68—O2	112.4 (11)
C30B—C22B—Ru1	125.0 (16)	C69—C68—C67	133.7 (10)
C28B—C23B—C22B	107 (2)	C68—C69—C70	106.7 (10)
C24B—C23B—C22B	131 (2)	C71—C70—C69	137.3 (11)
C24B—C23B—C28B	122 (3)	C75—C70—C69	104.9 (11)
C23B—C28B—C29B	110 (2)	C75—C70—C71	117.8 (13)
C27B—C28B—C23B	120 (4)	C72—C71—C70	120.0 (13)
C27B—C28B—C29B	131 (3)	C71—C72—C73	120.8 (16)
C28B—C29B—C31B	123 (2)	C74—C73—C72	121.9 (16)
C30B—C29B—C28B	108.2 (18)	C75—C74—C73	114.1 (15)
C30B—C29B—C31B	128 (3)	C70—C75—O2	110.9 (11)
C29B—C30B—C22B	111 (2)	C70—C75—C74	125.5 (14)
C25A—C24A—C23A	119 (2)	C74—C75—O2	123.5 (13)
C24A—C25A—C26A	122 (2)	C86—C85—C83	121.0 (9)
C27A—C26A—C25A	122 (2)	C86—C85—C90	118.8 (8)
C26A—C27A—C28A	118 (2)	C90—C85—C83	120.3 (9)
C23B—C24B—C25B	117 (2)	C85—C86—C87	120.4 (10)
C26B—C25B—C24B	120 (3)	C88—C87—C86	120.0 (11)
C27B—C26B—C25B	123 (3)	C87—C88—C89	119.7 (9)
C26B—C27B—C28B	117 (3)	C90—C89—C88	121.1 (10)
C32A—C31A—C29A	119 (2)	C89—C90—C85	120.1 (9)
C36A—C31A—C29A	125 (2)	C92—C91—P2	112.5 (8)
C36A—C31A—C32A	116 (2)	C96—C91—P2	118.8 (9)
C33A—C32A—C31A	120.4 (19)	C96—C91—C92	110.3 (10)
C34A—C33A—C32A	119.9 (16)	C93—C92—C91	109.5 (10)
C35A—C34A—C33A	120.0 (17)	C94—C93—C92	112.8 (12)
C34A—C35A—C36A	120.2 (17)	C93—C94—C95	111.4 (14)
C35A—C36A—C31A	123.1 (18)	C96—C95—C94	111.7 (15)
C32B—C31B—C29B	117 (3)	C95—C96—C91	110.8 (13)
C36B—C31B—C29B	128 (3)	C98—C97—P2	113.4 (8)
C36B—C31B—C32B	114 (3)	C98—C97—C102	112.1 (10)
C31B—C32B—C33B	121 (3)	C102—C97—P2	111.8 (7)
C34B—C33B—C32B	119 (3)	C97—C98—C99	110.1 (10)
C33B—C34B—C35B	120 (3)	C98—C99—C100	110.9 (10)
C36B—C35B—C34B	120 (2)	C101—C100—C99	110.8 (10)
C35B—C36B—C31B	125 (2)	C102—C101—C100	111.5 (11)
C38—C37—P1	113.8 (9)	C101—C102—C97	112.2 (9)
C42—C37—P1	112.4 (7)	C104—C103—P2	117.2 (8)
C42—C37—C38	109.3 (10)	C104—C103—C108	109.9 (9)
C39—C38—C37	111.3 (11)	C108—C103—P2	113.7 (8)
C40—C39—C38	111.2 (10)	C103—C104—C105	110.7 (12)
C39—C40—C41	112.3 (11)	C104—C105—C106	112.1 (11)
C42—C41—C40	109.9 (11)	C107—C106—C105	109.3 (11)
C37—C42—C41	113.7 (10)	C106—C107—C108	110.5 (10)
C44—C43—P1	119.8 (10)	C103—C108—C107	109.9 (13)
C48—C43—P1	113.2 (8)		

P1—Ru1—C22A—C23A	91.2 (15)	C43—P1—C49—C50	56.8 (10)
P1—Ru1—C22A—C30A	-89.6 (16)	C43—P1—C49—C54	-72.0 (10)
P1—C37—C38—C39	-177.7 (9)	C43—C44—C45—C46	-57.8 (15)
P1—C37—C42—C41	178.1 (7)	C44—C43—C48—C47	-64.5 (12)
P1—C43—C44—C45	-166.6 (10)	C44—C45—C46—C47	54.1 (17)
P1—C43—C48—C47	160.7 (8)	C45—C46—C47—C48	-54.1 (18)
P1—C49—C50—C51	171.7 (9)	C46—C47—C48—C43	59.5 (15)
P1—C49—C54—C53	-170.9 (9)	C48—C43—C44—C45	62.0 (14)
Ru1—P1—C37—C38	-62.1 (9)	C49—P1—C37—C38	173.7 (8)
Ru1—P1—C37—C42	62.8 (8)	C49—P1—C37—C42	-61.4 (8)
Ru1—P1—C43—C44	161.4 (9)	C49—P1—C43—C44	-66.9 (11)
Ru1—P1—C43—C48	-69.6 (8)	C49—P1—C43—C48	62.1 (9)
Ru1—P1—C49—C50	-173.9 (8)	C49—C50—C51—C52	54.9 (15)
Ru1—P1—C49—C54	57.3 (10)	C50—C49—C54—C53	57.6 (15)
Ru1—C22A—C23A—C28A	177 (2)	C50—C51—C52—C53	-52.1 (15)
Ru1—C22A—C23A—C24A	2 (3)	C51—C52—C53—C54	52.9 (16)
Ru1—C22A—C30A—C29A	-179.3 (13)	C52—C53—C54—C49	-56.7 (16)
Ru1—C22B—C23B—C28B	174 (3)	C54—C49—C50—C51	-56.9 (15)
Ru1—C22B—C23B—C24B	-9 (5)	P2—Ru2—C76—C77	95.1 (9)
Ru1—C22B—C30B—C29B	-173 (2)	P2—Ru2—C76—C84	-82.6 (7)
Cl1—Ru1—C22A—C23A	-179.0 (16)	P2—C91—C92—C93	-166.6 (8)
Cl1—Ru1—C22A—C30A	0.2 (15)	P2—C91—C96—C95	169.5 (14)
Cl2—Ru1—C22A—C23A	-1.4 (17)	P2—C97—C98—C99	177.2 (8)
Cl2—Ru1—C22A—C30A	177.8 (14)	P2—C97—C102—C101	-176.3 (7)
N1—C4—C5—C6	-178.1 (10)	P2—C103—C104—C105	-170.7 (10)
N1—C4—C5—C11	6.4 (15)	P2—C103—C108—C107	167.3 (9)
N1—C4—C9—C8	177.5 (10)	Ru2—P2—C91—C92	62.8 (8)
N1—C4—C9—C10	-3.5 (16)	Ru2—P2—C91—C96	-166.3 (10)
N2—C3—C2—N1	-1.7 (14)	Ru2—P2—C97—C98	66.1 (9)
N2—C13—C14—O1	-129.5 (10)	Ru2—P2—C97—C102	-61.7 (8)
N2—C13—C14—C15	57.7 (16)	Ru2—P2—C103—C104	163.8 (10)
O1—C14—C15—C16	-1.2 (14)	Ru2—P2—C103—C108	-66.2 (10)
C1—Ru1—C22A—C23A	-90.8 (16)	Ru2—C76—C77—C78	1.9 (18)
C1—Ru1—C22A—C30A	88.4 (16)	Ru2—C76—C77—C82	-174.7 (8)
C1—N1—C2—C3	2.6 (15)	Ru2—C76—C84—C83	177.7 (7)
C1—N1—C4—C5	-91.8 (14)	C76—C77—C78—C79	-177.5 (11)
C1—N1—C4—C9	95.6 (14)	C76—C77—C82—C81	175.0 (10)
C1—N2—C3—C2	0.5 (14)	C76—C77—C82—C83	-4.8 (11)
C1—N2—C13—C14	-126.4 (12)	C77—C76—C84—C83	-0.6 (10)
C3—N2—C1—Ru1	-177.6 (8)	C77—C78—C79—C80	3.8 (19)
C3—N2—C1—N1	1.2 (13)	C77—C82—C83—C84	4.4 (11)
C3—N2—C13—C14	68.1 (14)	C77—C82—C83—C85	-174.7 (9)
C2—N1—C1—Ru1	176.1 (10)	C78—C77—C82—C81	-2.2 (16)
C2—N1—C1—N2	-2.4 (14)	C78—C77—C82—C83	178.0 (9)
C2—N1—C4—C5	86.6 (14)	C78—C79—C80—C81	-3.0 (19)

C2—N1—C4—C9	-86.0 (14)	C79—C80—C81—C82	-0.4 (18)
C4—N1—C1—Ru1	-5.4 (18)	C80—C81—C82—C77	3.1 (18)
C4—N1—C1—N2	176.1 (10)	C80—C81—C82—C83	-177.3 (11)
C4—N1—C2—C3	-176.0 (10)	C81—C82—C83—C84	-175.3 (11)
C4—C5—C6—C7	2.5 (16)	C81—C82—C83—C85	5.6 (18)
C5—C4—C9—C8	5.0 (16)	C82—C77—C78—C79	-1.1 (16)
C5—C4—C9—C10	-176.1 (11)	C82—C83—C84—C76	-2.2 (10)
C5—C6—C7—C8	1.0 (16)	C82—C83—C85—C86	33.7 (15)
C5—C6—C7—C12	-176.2 (10)	C82—C83—C85—C90	-147.0 (10)
C6—C7—C8—C9	-1.6 (17)	C83—C85—C86—C87	179.7 (10)
C7—C8—C9—C4	-1.4 (17)	C83—C85—C90—C89	-179.9 (10)
C7—C8—C9—C10	179.7 (12)	C84—C76—C77—C78	179.9 (11)
C9—C4—C5—C6	-5.6 (16)	C84—C76—C77—C82	3.3 (10)
C9—C4—C5—C11	179.0 (10)	C84—C83—C85—C86	-145.2 (10)
C11—C5—C6—C7	178.0 (10)	C84—C83—C85—C90	34.1 (15)
C12—C7—C8—C9	175.5 (11)	Cl3—Ru2—C76—C77	-174.7 (9)
C13—N2—C1—Ru1	15.8 (15)	Cl3—Ru2—C76—C84	7.6 (7)
C13—N2—C1—N1	-165.4 (10)	Cl4—Ru2—C76—C77	3.8 (10)
C13—N2—C3—C2	167.5 (12)	Cl4—Ru2—C76—C84	-173.9 (7)
C13—C14—C15—C16	171.8 (11)	O2—C68—C69—C70	0.1 (13)
C14—O1—C21—C16	1.5 (13)	N3—C56—C57—N4	8.1 (13)
C14—O1—C21—C20	-179.9 (12)	N3—C58—C59—C60	177.9 (9)
C14—C15—C16—C17	179.5 (14)	N3—C58—C59—C65	-3.1 (14)
C14—C15—C16—C21	2.0 (14)	N3—C58—C63—C62	-178.9 (9)
C15—C16—C17—C18	-178.8 (15)	N3—C58—C63—C64	3.1 (14)
C15—C16—C21—O1	-2.2 (14)	N4—C67—C68—O2	136.8 (9)
C15—C16—C21—C20	179.2 (13)	N4—C67—C68—C69	-49.6 (17)
C16—C17—C18—C19	1 (2)	C55—Ru2—C76—C77	-87.7 (10)
C17—C16—C21—O1	179.8 (11)	C55—Ru2—C76—C84	94.6 (8)
C17—C16—C21—C20	1 (2)	C55—N3—C56—C57	-7.5 (13)
C17—C18—C19—C20	-1 (3)	C55—N3—C58—C59	91.6 (13)
C18—C19—C20—C21	0 (2)	C55—N3—C58—C63	-90.6 (14)
C19—C20—C21—O1	-178.9 (12)	C55—N4—C57—C56	-6.8 (13)
C19—C20—C21—C16	-1 (2)	C55—N4—C67—C68	127.5 (11)
C21—O1—C14—C13	-174.5 (9)	C56—N3—C55—Ru2	-171.6 (9)
C21—O1—C14—C15	-0.1 (13)	C56—N3—C55—N4	3.3 (13)
C21—C16—C17—C18	-1.6 (19)	C56—N3—C58—C59	-90.2 (12)
C22A—C23A—C28A—C29A	4 (3)	C56—N3—C58—C63	87.6 (12)
C22A—C23A—C28A—C27A	-179 (2)	C57—N4—C55—Ru2	178.1 (8)
C22A—C23A—C24A—C25A	175.9 (18)	C57—N4—C55—N3	2.4 (13)
C23A—C22A—C30A—C29A	0.1 (18)	C57—N4—C67—C68	-72.2 (13)
C23A—C28A—C29A—C30A	-4 (3)	C58—N3—C55—Ru2	6.7 (18)
C23A—C28A—C29A—C31A	179 (2)	C58—N3—C55—N4	-178.4 (10)
C23A—C28A—C27A—C26A	3 (4)	C58—N3—C56—C57	174.0 (10)
C23A—C24A—C25A—C26A	2 (3)	C58—C59—C60—C61	1.6 (16)
C28A—C23A—C24A—C25A	1 (4)	C59—C58—C63—C62	-1.2 (14)

C28A—C29A—C30A—C22A	3 (2)	C59—C58—C63—C64	-179.1 (9)
C28A—C29A—C31A—C32A	147 (3)	C59—C60—C61—C62	-2.0 (16)
C28A—C29A—C31A—C36A	-40 (4)	C59—C60—C61—C66	176.5 (10)
C29A—C28A—C27A—C26A	178 (3)	C60—C61—C62—C63	0.8 (15)
C29A—C31A—C32A—C33A	178 (2)	C61—C62—C63—C58	0.7 (14)
C29A—C31A—C36A—C35A	-175.3 (19)	C61—C62—C63—C64	178.6 (10)
C30A—C22A—C23A—C28A	-3 (2)	C63—C58—C59—C60	0.1 (14)
C30A—C22A—C23A—C24A	-178 (2)	C63—C58—C59—C65	179.0 (9)
C30A—C29A—C31A—C32A	-30 (3)	C65—C59—C60—C61	-177.4 (10)
C30A—C29A—C31A—C36A	144 (2)	C66—C61—C62—C63	-177.7 (10)
C22B—Ru1—C22A—C23A	0 (3)	C67—N4—C55—Ru2	-20.1 (14)
C22B—Ru1—C22A—C30A	179 (100)	C67—N4—C55—N3	164.2 (10)
C22B—C23B—C28B—C29B	1 (4)	C67—N4—C57—C56	-169.6 (10)
C22B—C23B—C28B—C27B	-179 (4)	C67—C68—C69—C70	-173.6 (12)
C22B—C23B—C24B—C25B	176 (3)	C68—O2—C75—C70	0.9 (13)
C23B—C22B—C30B—C29B	4 (4)	C68—O2—C75—C74	178.7 (14)
C23B—C28B—C29B—C30B	2 (5)	C68—C69—C70—C71	-179.8 (14)
C23B—C28B—C29B—C31B	175 (3)	C68—C69—C70—C75	0.4 (13)
C23B—C28B—C27B—C26B	1 (6)	C69—C70—C71—C72	178.5 (15)
C23B—C24B—C25B—C26B	6 (5)	C69—C70—C75—O2	-0.8 (14)
C28B—C23B—C24B—C25B	-6 (4)	C69—C70—C75—C74	-178.5 (15)
C28B—C29B—C30B—C22B	-4 (4)	C70—C71—C72—C73	1 (2)
C28B—C29B—C31B—C32B	150 (4)	C71—C70—C75—O2	179.4 (10)
C28B—C29B—C31B—C36B	-32 (6)	C71—C70—C75—C74	2 (2)
C29B—C28B—C27B—C26B	-179 (4)	C71—C72—C73—C74	1 (3)
C29B—C31B—C32B—C33B	-177 (3)	C72—C73—C74—C75	-1 (3)
C29B—C31B—C36B—C35B	-176 (4)	C73—C74—C75—O2	-177.7 (15)
C30B—C22B—C23B—C28B	-3 (4)	C73—C74—C75—C70	0 (3)
C30B—C22B—C23B—C24B	174 (3)	C75—O2—C68—C67	174.4 (10)
C30B—C29B—C31B—C32B	-38 (5)	C75—O2—C68—C69	-0.6 (13)
C30B—C29B—C31B—C36B	140 (4)	C75—C70—C71—C72	-1.8 (19)
C24A—C23A—C28A—C29A	-180 (2)	C85—C83—C84—C76	176.9 (9)
C24A—C23A—C28A—C27A	-4 (4)	C85—C86—C87—C88	-0.3 (17)
C24A—C25A—C26A—C27A	-2 (4)	C86—C85—C90—C89	-0.6 (15)
C25A—C26A—C27A—C28A	0 (4)	C86—C87—C88—C89	0.4 (18)
C27A—C28A—C29A—C30A	180 (3)	C87—C88—C89—C90	-0.6 (18)
C27A—C28A—C29A—C31A	3 (5)	C88—C89—C90—C85	0.7 (16)
C24B—C23B—C28B—C29B	-177 (3)	C90—C85—C86—C87	0.4 (16)
C24B—C23B—C28B—C27B	3 (6)	C91—P2—C97—C98	-55.2 (9)
C24B—C25B—C26B—C27B	-2 (6)	C91—P2—C97—C102	177.0 (7)
C25B—C26B—C27B—C28B	-1 (5)	C91—P2—C103—C104	-65.9 (12)
C27B—C28B—C29B—C30B	-178 (5)	C91—P2—C103—C108	64.2 (10)
C27B—C28B—C29B—C31B	-4 (7)	C91—C92—C93—C94	-57.1 (15)
C31A—C29A—C30A—C22A	179.4 (19)	C92—C91—C96—C95	-59 (2)
C31A—C32A—C33A—C34A	-4 (4)	C92—C93—C94—C95	54 (2)
C32A—C31A—C36A—C35A	-1 (3)	C93—C94—C95—C96	-53 (2)

C32A—C33A—C34A—C35A	2 (3)	C94—C95—C96—C91	55 (2)
C33A—C34A—C35A—C36A	1 (3)	C96—C91—C92—C93	58.2 (13)
C34A—C35A—C36A—C31A	-1 (3)	C97—P2—C91—C92	-177.8 (8)
C36A—C31A—C32A—C33A	4 (4)	C97—P2—C91—C96	-46.9 (12)
C31B—C29B—C30B—C22B	-177 (3)	C97—P2—C103—C104	44.0 (12)
C31B—C32B—C33B—C34B	-8 (6)	C97—P2—C103—C108	174.1 (9)
C32B—C31B—C36B—C35B	2 (6)	C97—C98—C99—C100	55.8 (13)
C32B—C33B—C34B—C35B	5 (7)	C98—C97—C102—C101	55.1 (12)
C33B—C34B—C35B—C36B	1 (6)	C98—C99—C100—C101	-56.0 (14)
C34B—C35B—C36B—C31B	-5 (6)	C99—C100—C101—C102	55.2 (13)
C36B—C31B—C32B—C33B	5 (6)	C100—C101—C102—C97	-54.7 (12)
C37—P1—C43—C44	41.7 (10)	C102—C97—C98—C99	-55.1 (12)
C37—P1—C43—C48	170.7 (8)	C103—P2—C91—C92	-68.8 (9)
C37—P1—C49—C50	-53.3 (10)	C103—P2—C91—C96	62.2 (12)
C37—P1—C49—C54	177.9 (9)	C103—P2—C97—C98	-170.6 (8)
C37—C38—C39—C40	-57.6 (13)	C103—P2—C97—C102	61.5 (8)
C38—C37—C42—C41	-54.5 (12)	C103—C104—C105—C106	-56.6 (19)
C38—C39—C40—C41	56.7 (13)	C104—C103—C108—C107	-59.1 (15)
C39—C40—C41—C42	-53.4 (14)	C104—C105—C106—C107	56.0 (19)
C40—C41—C42—C37	53.4 (13)	C105—C106—C107—C108	-57.0 (18)
C42—C37—C38—C39	55.8 (12)	C106—C107—C108—C103	59.5 (16)
C43—P1—C37—C38	58.0 (9)	C108—C103—C104—C105	57.5 (17)
C43—P1—C37—C42	-177.1 (7)		

Table S8. Selected geometric parameters for 7 (Å, º)

Ru1—O1	2.244 (3)	C52—C53	1.440 (6)
Ru1—Cl1	2.3363 (10)	C53—C54	1.354 (6)
Ru1—Cl2	2.3341 (10)	Ru3—O3	2.278 (3)
Ru1—C10	1.826 (4)	Ru3—Cl5	2.3334 (9)
Ru1—C1	1.958 (4)	Ru3—Cl6	2.3412 (9)
C20—C21	1.501 (5)	Ru3—C70	1.825 (4)
C20—N2	1.466 (5)	Ru3—C61	1.973 (4)
C21—S1A	1.633 (12)	S3—C81	1.715 (4)
C21—C22A	1.39 (2)	S3—C84	1.710 (4)
C21—S1B	1.688 (5)	O3—C76	1.372 (4)
C21—C22B	1.390 (13)	O3—C77	1.479 (4)
S1A—C24A	1.72 (2)	N6—C61	1.355 (5)
C22A—C23A	1.45 (2)	N6—C62	1.474 (5)
C24A—C23A	1.335 (17)	N6—C80	1.463 (5)
S1B—C24B	1.733 (9)	N5—C61	1.344 (5)
C22B—C23B	1.453 (14)	N5—C63	1.481 (5)
C24B—C23B	1.332 (10)	N5—C64	1.431 (5)
O1—C16	1.382 (4)	C70—C71	1.463 (5)
O1—C17	1.468 (5)	C71—C72	1.403 (5)
N1—C1	1.348 (5)	C71—C76	1.411 (5)

N1—C3	1.482 (5)	C72—C73	1.387 (5)
N1—C4	1.440 (5)	C73—C74	1.395 (5)
N2—C1	1.357 (5)	C74—C75	1.393 (5)
N2—C2	1.466 (5)	C75—C76	1.385 (5)
C10—C11	1.453 (5)	C77—C79	1.503 (5)
C11—C12	1.395 (5)	C77—C78	1.518 (6)
C11—C16	1.403 (5)	C63—C62	1.520 (5)
C12—C13	1.395 (5)	C64—C65	1.409 (5)
C13—C14	1.386 (6)	C64—C69	1.397 (5)
C14—C15	1.394 (6)	C65—C66	1.387 (5)
C15—C16	1.383 (5)	C65—C65A	1.512 (5)
C17—C18	1.514 (6)	C66—C67	1.399 (5)
C17—C19	1.520 (6)	C67—C68	1.397 (5)
C2—C3	1.528 (6)	C67—C67A	1.505 (5)
C4—C5	1.393 (6)	C68—C69	1.391 (5)
C4—C9	1.400 (6)	C69—C69A	1.509 (5)
C5—C6	1.398 (5)	C80—C81	1.509 (5)
C5—C5A	1.512 (6)	C81—C82	1.418 (5)
C6—C7	1.396 (6)	C82—C83	1.439 (5)
C7—C8	1.401 (6)	C83—C84	1.360 (6)
C7—C7A	1.511 (5)	Ru4—O4	2.263 (3)
C8—C9	1.399 (6)	Ru4—Cl7	2.3364 (10)
C9—C9A	1.507 (6)	Ru4—Cl8	2.3406 (10)
Ru2—O2	2.281 (3)	Ru4—C100	1.831 (4)
Ru2—Cl4	2.3375 (9)	Ru4—C91	1.954 (4)
Ru2—Cl3	2.3442 (9)	S4—C111	1.716 (4)
Ru2—C40	1.830 (4)	S4—C114	1.691 (4)
Ru2—C31	1.969 (4)	O4—C106	1.370 (5)
S2—C51	1.716 (4)	O4—C107	1.473 (5)
S2—C54	1.715 (4)	N301—C91	1.347 (5)
O2—C46	1.373 (4)	N301—C93	1.483 (5)
O2—C47	1.473 (4)	N301—C94	1.439 (5)
N3—C31	1.350 (5)	N302—C91	1.366 (5)
N3—C33	1.476 (5)	N302—C92	1.462 (5)
N3—C34	1.436 (5)	N302—C110	1.473 (5)
N4—C31	1.350 (5)	C100—C101	1.440 (5)
N4—C32	1.466 (5)	C101—C102	1.406 (5)
N4—C50	1.463 (5)	C101—C106	1.402 (5)
C40—C41	1.459 (5)	C102—C103	1.383 (6)
C41—C42	1.395 (5)	C103—C104	1.398 (6)
C41—C46	1.409 (5)	C104—C105	1.394 (6)
C42—C43	1.390 (5)	C105—C106	1.390 (5)
C43—C44	1.392 (5)	C107—C108	1.521 (6)
C44—C45	1.392 (5)	C107—C109	1.523 (6)
C45—C46	1.391 (5)	C92—C93	1.521 (6)
C47—C48	1.505 (6)	C94—C95	1.394 (5)

C47—C49	1.510 (5)	C94—C99	1.393 (5)
C32—C33	1.520 (5)	C95—C96	1.402 (5)
C34—C35	1.401 (5)	C95—C95A	1.517 (6)
C34—C39	1.403 (5)	C96—C97	1.386 (6)
C35—C36	1.393 (5)	C97—C98	1.397 (6)
C35—C35A	1.510 (5)	C97—C97A	1.512 (5)
C36—C37	1.393 (5)	C98—C99	1.396 (5)
C37—C38	1.400 (5)	C99—C99A	1.508 (6)
C37—C37A	1.509 (5)	C110—C111	1.499 (5)
C38—C39	1.402 (5)	C111—C112	1.408 (5)
C39—C39A	1.500 (5)	C112—C113	1.453 (6)
C50—C51	1.510 (5)	C113—C114	1.349 (7)
C51—C52	1.395 (5)		
O1—Ru1—Cl1	87.59 (8)	C51—C52—C53	110.1 (4)
O1—Ru1—Cl2	89.31 (8)	C54—C53—C52	113.9 (4)
Cl2—Ru1—Cl1	154.00 (4)	C53—C54—S2	111.8 (3)
C10—Ru1—O1	79.82 (14)	O3—Ru3—Cl5	88.65 (7)
C10—Ru1—Cl1	101.58 (12)	O3—Ru3—Cl6	91.11 (7)
C10—Ru1—Cl2	103.26 (12)	Cl5—Ru3—Cl6	153.31 (3)
C10—Ru1—C1	102.95 (16)	C70—Ru3—O3	79.03 (13)
C1—Ru1—O1	176.79 (13)	C70—Ru3—Cl5	104.64 (11)
C1—Ru1—Cl1	90.24 (11)	C70—Ru3—Cl6	101.49 (11)
C1—Ru1—Cl2	91.61 (11)	C70—Ru3—C61	102.36 (16)
N2—C20—C21	115.8 (3)	C61—Ru3—O3	178.60 (12)
C20—C21—S1A	120.7 (6)	C61—Ru3—Cl5	90.82 (10)
C20—C21—S1B	121.4 (3)	C61—Ru3—Cl6	88.78 (11)
C22A—C21—C20	126.0 (12)	C84—S3—C81	92.2 (2)
C22A—C21—S1A	113.3 (12)	C76—O3—Ru3	110.5 (2)
C22B—C21—C20	126.2 (6)	C76—O3—C77	119.0 (3)
C22B—C21—S1B	112.0 (6)	C77—O3—Ru3	128.8 (2)
C21—S1A—C24A	91.7 (11)	C61—N6—C62	112.4 (3)
C21—C22A—C23A	111.6 (19)	C61—N6—C80	123.9 (3)
C23A—C24A—S1A	114.2 (19)	C80—N6—C62	119.2 (3)
C24A—C23A—C22A	109 (2)	C61—N5—C63	112.1 (3)
C21—S1B—C24B	91.7 (4)	C61—N5—C64	127.1 (3)
C21—C22B—C23B	111.7 (9)	C64—N5—C63	120.5 (3)
C23B—C24B—S1B	113.2 (7)	C71—C70—Ru3	119.4 (3)
C24B—C23B—C22B	111.5 (8)	C72—C71—C70	123.3 (3)
C16—O1—Ru1	110.0 (2)	C72—C71—C76	118.6 (3)
C16—O1—C17	119.9 (3)	C76—C71—C70	118.1 (3)
C17—O1—Ru1	129.6 (2)	C73—C72—C71	120.4 (3)
C1—N1—C3	112.7 (3)	C72—C73—C74	119.8 (4)
C1—N1—C4	125.8 (3)	C75—C74—C73	121.0 (4)
C4—N1—C3	120.9 (3)	C76—C75—C74	118.9 (4)
C1—N2—C20	120.5 (3)	O3—C76—C71	112.9 (3)

C1—N2—C2	112.9 (3)	O3—C76—C75	125.8 (3)
C2—N2—C20	118.7 (3)	C75—C76—C71	121.2 (3)
C11—C10—Ru1	118.2 (3)	O3—C77—C79	105.8 (3)
C12—C11—C10	123.1 (3)	O3—C77—C78	109.5 (3)
C12—C11—C16	118.5 (3)	C79—C77—C78	113.3 (3)
C16—C11—C10	118.4 (3)	N6—C61—Ru3	119.6 (3)
C13—C12—C11	120.1 (4)	N5—C61—Ru3	133.1 (3)
C14—C13—C12	119.9 (4)	N5—C61—N6	107.3 (3)
C13—C14—C15	121.4 (4)	N5—C63—C62	102.2 (3)
C16—C15—C14	117.9 (4)	N6—C62—C63	100.8 (3)
O1—C16—C11	112.9 (3)	C65—C64—N5	119.8 (3)
O1—C16—C15	124.9 (3)	C69—C64—N5	118.3 (3)
C15—C16—C11	122.2 (3)	C69—C64—C65	121.9 (3)
O1—C17—C18	109.4 (3)	C64—C65—C65A	121.4 (3)
O1—C17—C19	105.9 (3)	C66—C65—C64	117.8 (3)
C18—C17—C19	113.5 (4)	C66—C65—C65A	120.7 (3)
N1—C1—Ru1	134.2 (3)	C65—C66—C67	121.9 (3)
N1—C1—N2	107.6 (3)	C66—C67—C67A	121.2 (4)
N2—C1—Ru1	118.1 (3)	C68—C67—C66	118.5 (3)
N2—C2—C3	102.3 (3)	C68—C67—C67A	120.3 (3)
N1—C3—C2	102.4 (3)	C69—C68—C67	121.6 (3)
C5—C4—N1	119.2 (3)	C64—C69—C69A	120.9 (3)
C5—C4—C9	122.0 (4)	C68—C69—C64	118.2 (3)
C9—C4—N1	118.7 (3)	C68—C69—C69A	120.8 (3)
C4—C5—C6	118.6 (4)	N6—C80—C81	111.0 (3)
C4—C5—C5A	121.1 (4)	C80—C81—S3	120.8 (3)
C6—C5—C5A	120.3 (4)	C82—C81—S3	112.6 (3)
C7—C6—C5	121.1 (4)	C82—C81—C80	126.6 (3)
C6—C7—C8	118.9 (4)	C81—C82—C83	108.6 (4)
C6—C7—C7A	120.8 (4)	C84—C83—C82	114.9 (4)
C8—C7—C7A	120.2 (4)	C83—C84—S3	111.6 (3)
C9—C8—C7	121.4 (4)	O4—Ru4—Cl7	88.75 (8)
C4—C9—C9A	121.5 (4)	O4—Ru4—Cl8	88.69 (8)
C8—C9—C4	118.0 (4)	Cl7—Ru4—Cl8	153.55 (4)
C8—C9—C9A	120.5 (4)	C100—Ru4—O4	79.41 (14)
O2—Ru2—Cl4	88.99 (7)	C100—Ru4—Cl7	102.81 (12)
O2—Ru2—Cl3	90.85 (7)	C100—Ru4—Cl8	102.57 (12)
Cl4—Ru2—Cl3	153.72 (3)	C100—Ru4—C91	101.45 (16)
C40—Ru2—O2	78.95 (12)	C91—Ru4—O4	178.58 (13)
C40—Ru2—Cl4	103.85 (11)	C91—Ru4—Cl7	89.95 (11)
C40—Ru2—Cl3	101.89 (11)	C91—Ru4—Cl8	92.22 (12)
C40—Ru2—C31	102.44 (15)	C114—S4—C111	92.9 (2)
C31—Ru2—O2	178.59 (12)	C106—O4—Ru4	109.4 (2)
C31—Ru2—Cl4	90.47 (10)	C106—O4—C107	120.7 (3)
C31—Ru2—Cl3	89.06 (11)	C107—O4—Ru4	129.7 (2)
C54—S2—C51	92.0 (2)	C91—N301—C93	112.6 (3)

C46—O2—Ru2	110.3 (2)	C91—N301—C94	127.1 (3)
C46—O2—C47	119.5 (3)	C94—N301—C93	120.2 (3)
C47—O2—Ru2	128.6 (2)	C91—N302—C92	112.4 (3)
C31—N3—C33	112.4 (3)	C91—N302—C110	120.0 (3)
C31—N3—C34	126.6 (3)	C92—N302—C110	120.6 (3)
C34—N3—C33	120.6 (3)	C101—C100—Ru4	118.7 (3)
C31—N4—C32	112.5 (3)	C102—C101—C100	122.9 (4)
C31—N4—C50	123.6 (3)	C106—C101—C100	118.3 (3)
C50—N4—C32	119.4 (3)	C106—C101—C102	118.7 (3)
C41—C40—Ru2	119.5 (3)	C103—C102—C101	120.5 (4)
C42—C41—C40	123.1 (3)	C102—C103—C104	119.4 (4)
C42—C41—C46	118.7 (3)	C105—C104—C103	121.6 (4)
C46—C41—C40	118.1 (3)	C106—C105—C104	118.2 (4)
C43—C42—C41	120.6 (3)	O4—C106—C101	113.7 (3)
C42—C43—C44	119.6 (4)	O4—C106—C105	124.7 (4)
C43—C44—C45	121.2 (4)	C105—C106—C101	121.6 (4)
C46—C45—C44	118.6 (3)	O4—C107—C108	110.4 (3)
O2—C46—C41	113.2 (3)	O4—C107—C109	105.5 (3)
O2—C46—C45	125.7 (3)	C108—C107—C109	112.6 (4)
C45—C46—C41	121.2 (3)	N301—C91—Ru4	134.9 (3)
O2—C47—C48	109.7 (3)	N301—C91—N302	106.7 (3)
O2—C47—C49	105.6 (3)	N302—C91—Ru4	118.5 (3)
C48—C47—C49	113.9 (3)	N302—C92—C93	101.6 (3)
N3—C31—Ru2	133.4 (3)	N301—C93—C92	101.4 (3)
N3—C31—N4	106.9 (3)	C95—C94—N301	120.1 (3)
N4—C31—Ru2	119.7 (3)	C99—C94—N301	117.8 (3)
N4—C32—C33	101.2 (3)	C99—C94—C95	122.1 (3)
N3—C33—C32	101.6 (3)	C94—C95—C96	117.8 (4)
C35—C34—N3	118.2 (3)	C94—C95—C95A	121.3 (4)
C35—C34—C39	122.1 (3)	C96—C95—C95A	120.8 (4)
C39—C34—N3	119.7 (3)	C97—C96—C95	121.7 (4)
C34—C35—C35A	120.8 (3)	C96—C97—C98	118.9 (4)
C36—C35—C34	118.3 (3)	C96—C97—C97A	121.0 (4)
C36—C35—C35A	120.8 (3)	C98—C97—C97A	120.0 (4)
C35—C36—C37	121.6 (4)	C99—C98—C97	121.0 (4)
C36—C37—C38	118.7 (3)	C94—C99—C98	118.5 (4)
C36—C37—C37A	120.7 (4)	C94—C99—C99A	121.1 (4)
C38—C37—C37A	120.6 (4)	C98—C99—C99A	120.4 (4)
C37—C38—C39	121.9 (3)	N302—C110—C111	111.5 (3)
C34—C39—C39A	121.7 (3)	C110—C111—S4	121.4 (3)
C38—C39—C34	117.4 (3)	C112—C111—S4	111.5 (3)
C38—C39—C39A	120.8 (3)	C112—C111—C110	127.1 (4)
N4—C50—C51	111.1 (3)	C111—C112—C113	109.5 (4)
C50—C51—S2	120.8 (3)	C114—C113—C112	113.8 (4)
C52—C51—S2	112.2 (3)	C113—C114—S4	112.3 (3)
C52—C51—C50	127.0 (3)		

Ru1—O1—C16—C11	5.1 (4)	C50—N4—C31—N3	168.7 (3)
Ru1—O1—C16—C15	-175.1 (3)	C50—N4—C32—C33	-179.2 (3)
Ru1—O1—C17—C18	-100.6 (3)	C50—C51—C52—C53	179.6 (4)
Ru1—O1—C17—C19	22.1 (5)	C51—S2—C54—C53	0.9 (3)
Ru1—C10—C11—C12	173.7 (3)	C51—C52—C53—C54	-0.6 (5)
Ru1—C10—C11—C16	-7.3 (5)	C52—C53—C54—S2	-0.3 (5)
C20—C21—S1A—C24A	-179.5 (10)	C54—S2—C51—C50	-179.7 (3)
C20—C21—C22A—C23A	-179.8 (19)	C54—S2—C51—C52	-1.2 (3)
C20—C21—S1B—C24B	-173.9 (6)	Ru3—O3—C76—C71	0.1 (3)
C20—C21—C22B—C23B	173.4 (6)	Ru3—O3—C76—C75	-177.8 (3)
C20—N2—C1—Ru1	-20.0 (5)	Ru3—O3—C77—C79	31.1 (4)
C20—N2—C1—N1	158.3 (3)	Ru3—O3—C77—C78	-91.4 (3)
C20—N2—C2—C3	-163.8 (3)	Ru3—C70—C71—C72	-179.6 (3)
C21—C20—N2—C1	146.2 (4)	Ru3—C70—C71—C76	-0.3 (4)
C21—C20—N2—C2	-67.0 (5)	S3—C81—C82—C83	-1.1 (4)
C21—S1A—C24A—C23A	-1 (3)	O3—Ru3—C70—C71	0.3 (3)
C21—C22A—C23A—C24A	-1 (3)	Cl5—Ru3—C70—C71	-85.4 (3)
C21—S1B—C24B—C23B	0.8 (10)	Cl6—Ru3—C70—C71	89.2 (3)
C21—C22B—C23B—C24B	-0.3 (13)	N6—C80—C81—S3	45.7 (4)
S1A—C21—C22A—C23A	0.2 (18)	N6—C80—C81—C82	-135.2 (4)
S1A—C21—S1B—C24B	9.4 (10)	N5—C63—C62—N6	-21.1 (4)
S1A—C21—C22B—C23B	-123 (6)	N5—C64—C65—C66	-179.3 (3)
S1A—C24A—C23A—C22A	1 (4)	N5—C64—C65—C65A	-1.4 (5)
C22A—C21—S1A—C24A	0.5 (13)	N5—C64—C69—C68	177.7 (3)
C22A—C21—S1B—C24B	-24 (15)	N5—C64—C69—C69A	-0.6 (5)
C22A—C21—C22B—C23B	3.1 (18)	C70—C71—C72—C73	-179.7 (3)
S1B—C21—S1A—C24A	-2.7 (14)	C70—C71—C76—O3	0.1 (5)
S1B—C21—C22A—C23A	148 (15)	C70—C71—C76—C75	178.1 (3)
S1B—C21—C22B—C23B	0.9 (10)	C71—C72—C73—C74	0.8 (5)
S1B—C24B—C23B—C22B	-0.4 (14)	C72—C71—C76—O3	179.4 (3)
C22B—C21—S1A—C24A	58 (5)	C72—C71—C76—C75	-2.6 (5)
C22B—C21—C22A—C23A	-9 (2)	C72—C73—C74—C75	-1.3 (6)
C22B—C21—S1B—C24B	-0.9 (7)	C73—C74—C75—C76	-0.1 (6)
O1—Ru1—C10—C11	7.5 (3)	C74—C75—C76—O3	179.8 (3)
Cl1—Ru1—C10—C11	-77.9 (3)	C74—C75—C76—C71	2.1 (5)
Cl2—Ru1—C10—C11	94.3 (3)	C76—O3—C77—C79	-164.8 (3)
N1—C4—C5—C6	-179.0 (3)	C76—O3—C77—C78	72.7 (4)
N1—C4—C5—C5A	-1.1 (6)	C76—C71—C72—C73	1.1 (5)
N1—C4—C9—C8	178.8 (3)	C77—O3—C76—C71	-166.8 (3)
N1—C4—C9—C9A	1.0 (6)	C77—O3—C76—C75	15.3 (5)
N2—C20—C21—S1A	80.4 (9)	C61—Ru3—C70—C71	-179.6 (3)
N2—C20—C21—C22A	-99.5 (16)	C61—N6—C62—C63	21.7 (4)
N2—C20—C21—S1B	-96.2 (4)	C61—N6—C80—C81	-143.9 (3)
N2—C20—C21—C22B	91.9 (8)	C61—N5—C63—C62	16.3 (4)
N2—C2—C3—N1	12.9 (4)	C61—N5—C64—C65	82.4 (5)

C10—C11—C12—C13	179.5 (4)	C61—N5—C64—C69	-96.1 (4)
C10—C11—C16—O1	0.4 (5)	C63—N5—C61—Ru3	178.3 (3)
C10—C11—C16—C15	-179.5 (4)	C63—N5—C61—N6	-3.3 (4)
C11—C12—C13—C14	-0.1 (6)	C63—N5—C64—C65	-91.0 (4)
C12—C11—C16—O1	179.4 (3)	C63—N5—C64—C69	90.5 (4)
C12—C11—C16—C15	-0.4 (6)	C62—N6—C61—Ru3	166.3 (3)
C12—C13—C14—C15	-0.3 (6)	C62—N6—C61—N5	-12.4 (4)
C13—C14—C15—C16	0.3 (6)	C62—N6—C80—C81	61.7 (4)
C14—C15—C16—O1	-179.8 (4)	C64—N5—C61—Ru3	4.5 (6)
C14—C15—C16—C11	0.0 (6)	C64—N5—C61—N6	-177.1 (3)
C16—O1—C17—C18	70.7 (4)	C64—N5—C63—C62	-169.3 (3)
C16—O1—C17—C19	-166.6 (3)	C64—C65—C66—C67	2.0 (6)
C16—C11—C12—C13	0.5 (6)	C65—C64—C69—C68	-0.9 (6)
C17—O1—C16—C11	-167.8 (3)	C65—C64—C69—C69A	-179.1 (4)
C17—O1—C16—C15	12.0 (6)	C65—C66—C67—C68	-1.6 (6)
C1—Ru1—C10—C11	-170.9 (3)	C65—C66—C67—C67A	178.3 (4)
C1—N1—C3—C2	-8.6 (4)	C66—C67—C68—C69	-0.1 (6)
C1—N1—C4—C5	92.0 (5)	C67—C68—C69—C64	1.3 (6)
C1—N1—C4—C9	-86.9 (5)	C67—C68—C69—C69A	179.5 (4)
C1—N2—C2—C3	-14.5 (4)	C69—C64—C65—C66	-0.8 (5)
C2—N2—C1—Ru1	-168.7 (3)	C69—C64—C65—C65A	177.1 (3)
C2—N2—C1—N1	9.7 (4)	C65A—C65—C66—C67	-175.9 (4)
C3—N1—C1—Ru1	177.8 (3)	C67A—C67—C68—C69	179.9 (4)
C3—N1—C1—N2	-0.1 (4)	C80—N6—C61—Ru3	10.4 (5)
C3—N1—C4—C5	-97.8 (5)	C80—N6—C61—N5	-168.2 (3)
C3—N1—C4—C9	83.4 (5)	C80—N6—C62—C63	178.8 (3)
C4—N1—C1—Ru1	-11.3 (6)	C80—C81—C82—C83	179.8 (4)
C4—N1—C1—N2	170.8 (3)	C81—S3—C84—C83	-0.5 (3)
C4—N1—C3—C2	-180.0 (3)	C81—C82—C83—C84	0.7 (5)
C4—C5—C6—C7	0.4 (6)	C82—C83—C84—S3	0.0 (5)
C5—C4—C9—C8	0.0 (6)	C84—S3—C81—C80	-179.9 (3)
C5—C4—C9—C9A	-177.8 (4)	C84—S3—C81—C82	1.0 (3)
C5—C6—C7—C8	-0.4 (6)	Ru4—O4—C106—C101	4.2 (4)
C5—C6—C7—C7A	-179.4 (4)	Ru4—O4—C106—C105	-175.6 (3)
C6—C7—C8—C9	0.2 (6)	Ru4—O4—C107—C108	-104.7 (3)
C7—C8—C9—C4	0.0 (6)	Ru4—O4—C107—C109	17.2 (4)
C7—C8—C9—C9A	177.9 (4)	Ru4—C100—C101—C102	175.1 (3)
C9—C4—C5—C6	-0.2 (6)	Ru4—C100—C101—C106	-4.8 (5)
C9—C4—C5—C5A	177.7 (4)	S4—C111—C112—C113	-0.5 (4)
C5A—C5—C6—C7	-177.5 (4)	O4—Ru4—C100—C101	5.2 (3)
C7A—C7—C8—C9	179.1 (4)	Cl7—Ru4—C100—C101	-81.0 (3)
Ru2—O2—C46—C41	-0.2 (4)	Cl8—Ru4—C100—C101	91.5 (3)
Ru2—O2—C46—C45	179.2 (3)	N301—C94—C95—C96	-179.7 (3)
Ru2—O2—C47—C48	91.2 (3)	N301—C94—C95—C95A	-2.0 (6)
Ru2—O2—C47—C49	-31.9 (4)	N301—C94—C99—C98	179.2 (3)
Ru2—C40—C41—C42	179.0 (3)	N301—C94—C99—C99A	0.6 (5)

Ru2—C40—C41—C46	-0.6 (4)	N302—C92—C93—N301	-21.5 (4)
S2—C51—C52—C53	1.2 (4)	N302—C110—C111—S4	-93.4 (4)
O2—Ru2—C40—C41	0.3 (3)	N302—C110—C111—C112	85.5 (5)
Cl4—Ru2—C40—C41	86.5 (3)	C100—C101—C102—C103	-179.4 (4)
Cl3—Ru2—C40—C41	-88.2 (3)	C100—C101—C106—O4	-0.4 (5)
N3—C34—C35—C36	-176.3 (3)	C100—C101—C106—C105	179.4 (4)
N3—C34—C35—C35A	1.9 (5)	C101—C102—C103—C104	0.4 (6)
N3—C34—C39—C38	178.4 (3)	C102—C101—C106—O4	179.7 (3)
N3—C34—C39—C39A	1.8 (5)	C102—C101—C106—C105	-0.5 (6)
N4—C32—C33—N3	21.2 (4)	C102—C103—C104—C105	-1.2 (6)
N4—C50—C51—S2	-46.5 (4)	C103—C104—C105—C106	1.1 (6)
N4—C50—C51—C52	135.3 (4)	C104—C105—C106—O4	179.5 (4)
C40—C41—C42—C43	-179.7 (3)	C104—C105—C106—C101	-0.3 (6)
C40—C41—C46—O2	0.5 (5)	C106—O4—C107—C108	71.2 (4)
C40—C41—C46—C45	-179.0 (3)	C106—O4—C107—C109	-166.9 (3)
C41—C42—C43—C44	-1.2 (6)	C106—C101—C102—C103	0.5 (6)
C42—C41—C46—O2	-179.1 (3)	C107—O4—C106—C101	-172.5 (3)
C42—C41—C46—C45	1.4 (5)	C107—O4—C106—C105	7.7 (6)
C42—C43—C44—C45	1.3 (6)	C91—Ru4—C100—C101	-173.6 (3)
C43—C44—C45—C46	0.1 (6)	C91—N301—C93—C92	17.1 (4)
C44—C45—C46—O2	179.2 (3)	C91—N301—C94—C95	88.4 (5)
C44—C45—C46—C41	-1.4 (6)	C91—N301—C94—C99	-92.3 (5)
C46—O2—C47—C48	-73.0 (4)	C91—N302—C92—C93	21.6 (4)
C46—O2—C47—C49	163.8 (3)	C91—N302—C110—C111	-167.5 (3)
C46—C41—C42—C43	-0.1 (5)	C92—N302—C91—Ru4	169.2 (3)
C47—O2—C46—C41	166.7 (3)	C92—N302—C91—N301	-11.6 (5)
C47—O2—C46—C45	-13.8 (5)	C92—N302—C110—C111	43.9 (5)
C31—Ru2—C40—C41	-179.9 (3)	C93—N301—C91—Ru4	174.7 (3)
C31—N3—C33—C32	-16.3 (4)	C93—N301—C91—N302	-4.3 (5)
C31—N3—C34—C35	93.9 (4)	C93—N301—C94—C95	-90.6 (5)
C31—N3—C34—C39	-84.2 (5)	C93—N301—C94—C99	88.7 (5)
C31—N4—C32—C33	-22.0 (4)	C94—N301—C91—Ru4	-4.3 (6)
C31—N4—C50—C51	143.4 (3)	C94—N301—C91—N302	176.6 (4)
C32—N4—C31—Ru2	-166.1 (3)	C94—N301—C93—C92	-163.8 (3)
C32—N4—C31—N3	12.6 (4)	C94—C95—C96—C97	0.1 (6)
C32—N4—C50—C51	-62.0 (4)	C95—C94—C99—C98	-1.5 (6)
C33—N3—C31—Ru2	-178.4 (3)	C95—C94—C99—C99A	180.0 (4)
C33—N3—C31—N4	3.2 (4)	C95—C96—C97—C98	-0.7 (6)
C33—N3—C34—C35	-92.7 (4)	C95—C96—C97—C97A	-178.4 (4)
C33—N3—C34—C39	89.2 (4)	C96—C97—C98—C99	0.1 (6)
C34—N3—C31—Ru2	-4.5 (6)	C97—C98—C99—C94	0.9 (6)
C34—N3—C31—N4	177.1 (3)	C97—C98—C99—C99A	179.4 (4)
C34—N3—C33—C32	169.4 (3)	C99—C94—C95—C96	1.0 (6)
C34—C35—C36—C37	-2.5 (5)	C99—C94—C95—C95A	178.7 (4)
C35—C34—C39—C38	0.4 (5)	C95A—C95—C96—C97	-177.6 (4)
C35—C34—C39—C39A	-176.3 (3)	C97A—C97—C98—C99	177.9 (4)

C35—C36—C37—C38	1.1 (6)	C110—N302—C91—Ru4	18.2 (5)
C35—C36—C37—C37A	-179.1 (4)	C110—N302—C91—N301	-162.5 (3)
C36—C37—C38—C39	1.1 (5)	C110—N302—C92—C93	172.3 (4)
C37—C38—C39—C34	-1.8 (5)	C110—C111—C112—C113	-179.5 (4)
C37—C38—C39—C39A	174.9 (3)	C111—S4—C114—C113	-1.1 (4)
C39—C34—C35—C36	1.7 (5)	C111—C112—C113—C114	-0.3 (6)
C39—C34—C35—C35A	179.9 (3)	C112—C113—C114—S4	1.0 (6)
C35A—C35—C36—C37	179.4 (4)	C114—S4—C111—C110	180.0 (3)
C37A—C37—C38—C39	-178.7 (3)	C114—S4—C111—C112	0.9 (3)
C50—N4—C31—Ru2	-10.0 (5)		

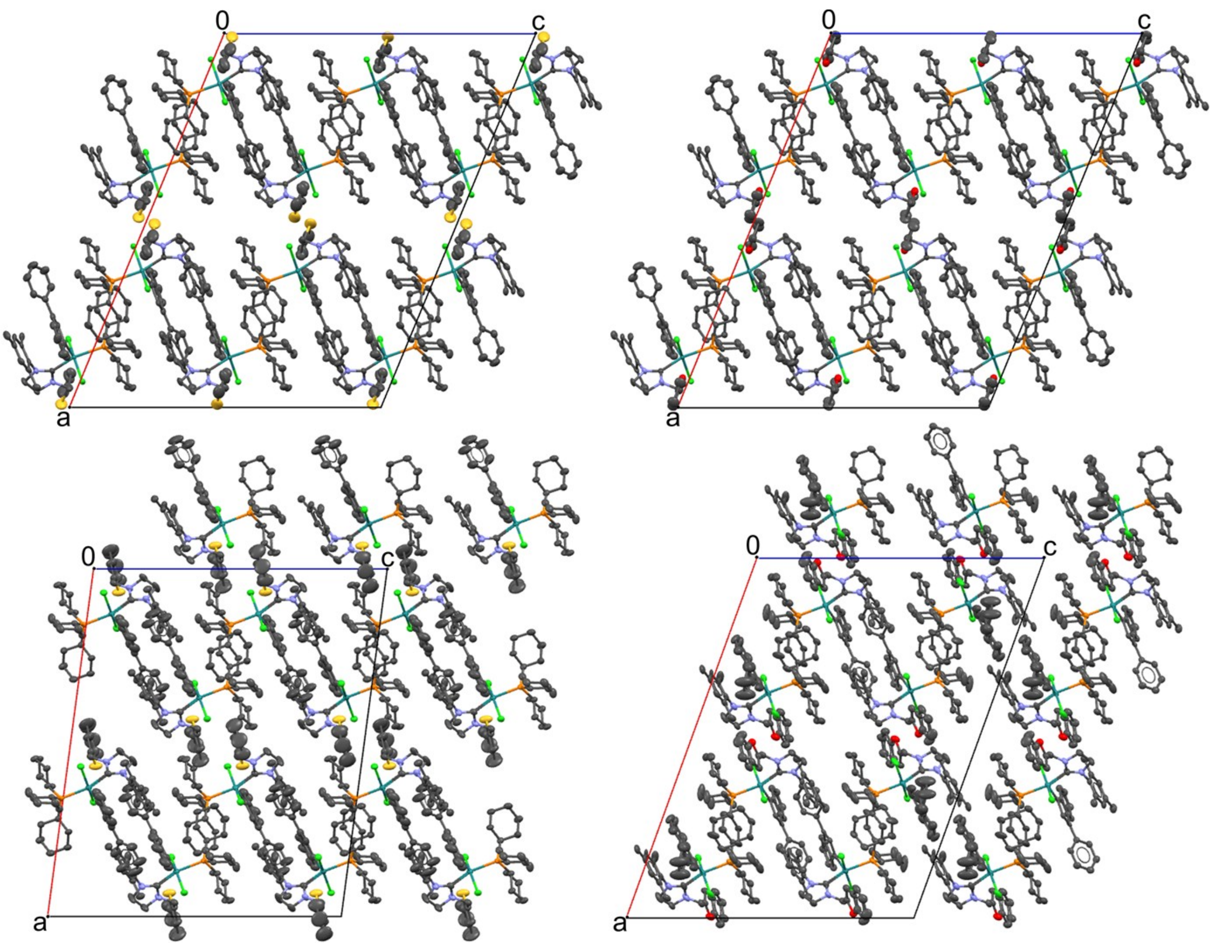


Fig S1. Molecular arrangement of the investigated compounds. From left to right: in the upper row **5a** and **5b**, in the lower row **5c** and **5d**. Solvent molecules (dichloromethane) and hydrogen atoms as well as disordered parts have been removed for clarity.

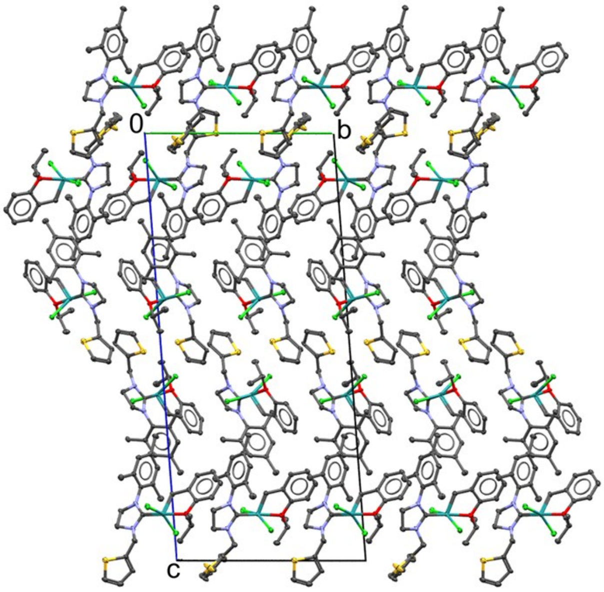


Fig S2. Molecular arrangement of the catalyst **7**. View along ***a*** axis, hydrogen atoms have been removed for clarity.

References

1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics* 2010, **29**, 2176–2179.
2. C. Marshall, M. F. Ward and J. M. S. Skakle, *Synthesis* 2006, **6**, 1040–1044.
3. N. Gigant, E. Claveau, P. Bouyssou and I. Gillaizeau, *Org. Lett.* 2012, **14**, 844–847.
4. Agilent Technologies *Agilent Technologies UK Ltd.* 2012**,** Oxford, UK, Xcalibur/SuperNova CCD system, CrysAlisPro Software system, Version 1.171.36.32.
5. G. M. Sheldrick, *Acta. Cryst. A* 2008, **64**, 112–122.
6. *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer, Dordrecht 1992, Vol. C.
7. A. Spek, *Acta Cryst. D* 2009, **65**, 145–155.
8. P. Van der Sluis and A.Spek, *Acta Cryst. A* 1990, **46**, 194–201.