Supplementary Information

Hoveyda-Grubbs catalyst analogues bearing derivatives of *N*-phenylpyrrol in carbene ligand - structure, stability, activity and unique ruthenium-phenyl interactions.

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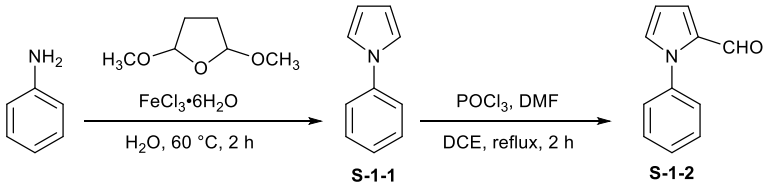
1. General considerations

Preparation of catalysts was carried out under Ar in pre-dried glassware using Schlenk techniques. All standard reagents were purchased from Sigma-Aldrich Chemical Company and were used without further purification. Catalyst **Hov-tioph** was prepared according published procedure: K. Grela, M. Smoleń, Polish Pat. Appl. P.410329 (2014); PCT Pat. Appl. PCT/IB2015/059287 (2017). Anhydrous solvents (THF, DCM, toluene, hexane) were obtained using mBraun's SPS. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 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 and 70-230 mesh). The ^1H and ^{13}C chemical shifts are referenced to $CDCl_3$ (δ = 7.26 and δ = 77.00 ppm respectively) or CD_2Cl_2 (δ = 5.32 and 54.00 ppm respectively), or toluene-d_8 (δ = 2.09 and 20.40 ppm respectively). ^1H and ^{13}C NMR spectra were recorded on Agilent 400-MR DD2 400 MHz spectrometer. 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 or provided by analytical laboratory at the Institute of Organic Chemistry, PAS. Reactions under argon atmosphere were set up using following technique: 1) solid reagents were weighed in reaction vessel under air 2) air was evacuated from vessel and replaced with argon (3-5 times) 3) anhydrous, degassed solvent and liquid reagents were introduced into reaction vessel.

2. Synthetic procedures

Synthesis of **S-1-2**



Iron(III) chloride hexahydrate (1.62 g, 6 mmol, 0.02 equiv.) was added to a mixture of aniline (27.4 mL, 300 mmol, 1.0 equiv.) and 2,5-dimethoxytetrahydrofurane (46.6 mL, 360 mmol, 1.2 equiv.) in water (240 mL) at 60 °C. The mixture was stirred at this temperature for 2 h, then diluted with AcOEt. The residue was filtered through Celite. The organic solution was separated, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified using column chromatography (silica, *c*-hex, then *c*-hex/AcOEt 95:5), to give 31.0 g (217 mmol, 72%) of **S-1-1** as a white solid.

m.p. 58-59 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 7.46 – 7.34 (m, 4H), 7.29 – 7.19 (m, 1H), 7.09 (t, *J* = 2.2 Hz, 2H), 6.35 (t, *J* = 2.2 Hz, 2H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ178.9, 138.6, 132.4, 130.9, 129.0, 128.1, 125.9, 121.8, 110.7.

Both m.p. and NMR spectra are consistent with previously reported ones.

DMF (13.0 mL, 168 mmol, 1.2 equiv.) was placed in 500 mL round-bottom flask, and cooled with salt/ice bath below 0 °C. $POCl_3$ (15.7 mL, 168 mmol, 1.2 equiv.) was added dropwise and let to stir for 30 min. Next, solution of **S-1-1** (20.0 g, 140 mmol, 1.0 equiv.) in DCE (300 mL) was added. Cooling bath was removed and the reaction mixture was stirred at reflux for 3 h. After cooling to r.t. the mixture was washed with concentrated aqueous Na_2CO_3 solution and distilled water (x 2). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified using column chromatography (silica, *c*-hex/AcOEt 90:10), to give 20.1 g (118 mmol, 84%) of **S-1-2** as a white solid.

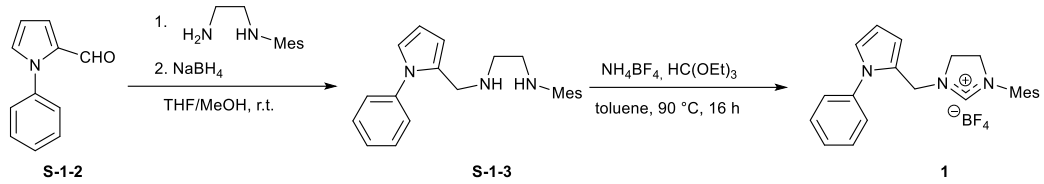
m.p. 32-33 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 9.56 (d, *J* = 1.5 Hz, 1H), 7.50 – 7.37 (m, 3H), 7.37 – 7.30 (m, 2H), 7.15 (dd, *J* = 4.0, 1.7 Hz, 1H), 7.06 (ddd, *J* = 2.4, 1.7, 0.6 Hz, 1H), 6.39 (dd, *J* = 4.0, 2.6 Hz, 1H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 140.7, 129.5, 125.6, 120.5, 119.3, 110.3.

Both m.p. and NMR spectra are consistent with previously reported ones.

Synthesis of **1**



S-1-2 **S-1-3** **1**

A 250 mL round-bottom flask was charged with *N*-(1,3,5-trimethylphenyl)etylenediamine (3.57 g, 20 mmol, 1.0 equiv.) and THF (80 mL), then **S-1-2** (3.42 g, 20 mmol, 1.0 equiv.) was added. After 5 minutes formic acid (2 drops) and anhydrous Na_2SO_4 (ca 0.8 g) were added. The mixture was stirred at r.t. for 18 h. Second portion of anhydrous Na_2SO_4 (ca 1.0 g), methanol (20 mL) and catalytic amount of *p*TSA (ca 100 mg) were added, due to incomplete conversion of substrate (monitored by TLC). After next 6 h of stirring at r.t. the mixture was cooled with water/ice bath and $NaBH_4$ (1.89 g, 50 mmol, 2.5 equiv.) was added in portions. The mixture was stirred for further 48 h at r.t., then aqueous solution of NaOH (50 ml, 5%) was added in portions. The mixture was concentrated in vacuo and extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (50 mL) and dried over anhydrous Na_2SO_4. Drying agent was filtered off, the mixture was concentrated in vacuo and the residue was purified by column chromatography (*c*-hex/AcOEt 90:10 + 2% TEA), to give 4.55 g (13.6 mmol, 68%) of **S-1-3** as a light yellow oil.

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 7.46 (d, *J* = 4.3 Hz, 4H), 7.42 – 7.33 (m, 1H), 6.88 – 6.80 (m, 3H), 6.31 – 6.24 (m, 2H), 3.80 (d, *J* = 0.5 Hz, 2H), 3.00 – 2.94 (m, 2H), 2.79 – 2.73 (m, 2H), 2.24 (dt, *J* = 6.8, 0.6 Hz, 9H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 143.7, 140.1, 131.6, 131.0, 129.5, 129.3, 129.2, 129.1, 127.1, 122.4, 109.4, 108.1, 49.0, 48.1, 45.1, 20.5, 18.3.

EA calcd. for $C_{22}H_{27}N_3$: C, 79.24; H, 8.16; N 12.60 found: C, 79.36; H, 8.23; N 12.74.

LRMS (ESI): calcd. for $[M+H]^+$: 334.2 found 334.2.

IR (neat) ν (cm^{-1}) = 3355, 3102, 2938, 2915, 2852, 2831, 1599, 1500, 1485, 1454, 1372, 1325, 1304, 1233, 1167, 1157, 1100, 1074, 1033, 979, 963, 913, 885, 854, 766, 712, 697, 622, 607, 584, 566, 537, 502.

S-1-3 (667 mg, 2 mmol, 1.0 equiv.) was placed in a 50 mL round-bottom flask under argon atmosphere. Anhydrous toluene (5 mL) was added, then solution was charged with triethyl orthoformate (1.0 mL, 6 mmol, 3.0 equiv.) and NH_4BF_4 (315 mg, 3 mmol, 1.5 equiv.). The mixture was heated to 90 °C and stirred for 16 h. After cooling to r.t. the colorless supernatant was discarded and resulting orange oil was dissolved in water/methanol mixture (1:2, about 30 mL). Pentane (10 mL) and additional portion of ammonium tetrafluoroborate (315 mg, 3 mmol, 1.5 equiv.) were added and mixture was kept in fridge for 2 days. The mixture was transferred into a separation funnel, diethyl ether (20 mL) was added. After intense shaking layers were separated (upper and colorless was discarded, lower and yellow was extracted with DCM (2x20 mL)). Organic phases were combined and *n*-heptane (10 mL) was added. Evaporation of solvents in vacuo resulted in forming of almost white (little pink) foam, which was easily scratched from glass to obtain 0.72 g of pinkish powder. The crude product was dissolved in minimal amount of EtOH (about 8 mL), then 8 mL of Et_2O was added and solution was left in fridge overnight. Resulting precipitate was filtered, washed with Et_2O (5 mL) and dried to obtain 0.42 g (0.97 mmol, 49%) of **1** as a white powder.

m.p. 151-153 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 7.44 – 7.51 (m, 3H), 7.32 – 7.37 (m, 3H), 6.87 (dd, *J* = 2.9, 1.8 Hz, 1H), 6.83 – 6.79 (m, 2H), 6.44 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.23 (dd, *J* = 3.6, 2.9 Hz, 1H), 4.95 (s, 2H), 3.96 – 3.88 (m, 2H), 3.85 – 3.76 (m, 2H), 2.21 (s, 3H), 1.99 (s, 6H).

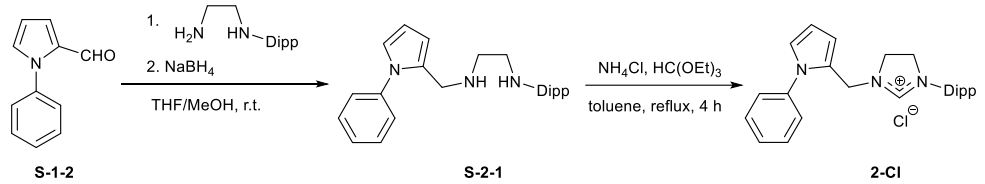
^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 157.2, 140.2, 138.9, 135.2, 130.2, 130.1, 129.7, 128.1, 125.2, 124.9, 122.9, 114.0, 109.0, 50.7, 47.8, 44.3, 20.9, 17.3.

EA calcd. for $C_{23}H_{26}BF_4N_3$: C, 64.05; H, 6.08; B, 2.51; F 17.62; N, 9.74 found: C, 63.92; H, 5.92; N 9.59.

LRMS (ESI): calcd. for $[M\text{-}BF_4]^+$: 344.5 found 344.1.

IR (KBr) ν (cm^{-1}) = 3144, 3077, 2975, 2951, 2890, 1894, 1816, 1764, 1742, 1644, 1597, 1552, 1499, 1455, 1422, 1371, 1329, 1315, 1293, 1286, 1270, 1240, 1201, 1183, 1170, 1139, 1058, 1032, 920, 885, 873, 855, 807, 772, 733, 700, 659, 631, 614, 603, 573, 540, 520, 505, 476, 444, 428.

Synthesis of **2**



A 250 mL round-bottom flask was charged with *N*-(2,6-diisopropylphenyl)etylenediamine (4.41 g, 20 mmol, 1.0 eq) and THF (80 mL). Then **S-1-2** (3.42 g, 20 mmol, 1.0 equiv.) was added and after 5 minutes formic acid (2 drops) followed by anhydrous Na_2SO_4. (ca 0.8g). The mixture was stirred at r.t. for 18 h. Second portion of anhydrous Na_2SO_4 (ca 1.0 g), methanol (20 mL) and catalytic amount of pTSA (ca 100 mg) were added, due to incomplete conversion of substrate (monitored by TLC). After next 6 h of stirring at r.t. the mixture was cooled with water/ice bath. $NaBH_4$ (1.89 g, 50 mmol, 2.5 equiv.) was added in portions. The mixture was stirred for 48 h at r.t., then aqueous solution of NaOH (50 ml, 5%) was added in portions. The mixture was concentrated in vacuo and extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (50 ml) and dried over anhydrous Na_2SO_4. Drying agent was filtered off, mixture was concentrated in vacuo and residue was purified by column chromatography (*c*-hex/AcOEt 90:10 + 2% TEA), to give 3.74 g (10.0 mmol, 50%) of **S-2-1** as a light yellow oil, which was used directly in next reaction.

A 100 mL round-bottom flask was charged with **S-2-1** (1.20 g, 3.2 mmol, 1.0 equiv.) and ammonium chloride (188 mg, 3.52 mmol 1.1 equiv.), and under argon atmosphere. Anhydrous toluene (10 mL) was added, followed by triethyl orthoformate (8.0 mL, 47.1 mmol, 14.7 equiv.). Obtained mixture was stirred at reflux for 3 h, then condenser was removed, and stirring continued for 45 min. Mixture was concentrated in vacuo to 1/3 volume, Et_2O (70mL) was added. Resulting precipitate was filtered, washed with Et_2O (2x25 mL) and dried to obtain 0.75 g (2.25 mmol, 70%) of **2-Cl** as a grey powder.

Reaction was repeated in bigger (7 mmol) scale with similar (67%) yield.

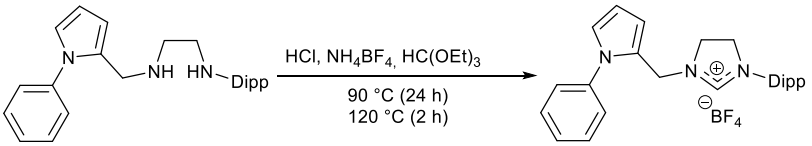
m.p. 163-165 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 9.37 (s, 1H), 7.53 – 7.44 (m, 2H), 7.42 – 7.30 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.86 (dd, *J* = 2.9, 1.8 Hz, 1H), 6.44 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.25 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.34 (s, 2H), 3.95 (ddd, *J* = 11.4, 8.6, 2.4 Hz, 2H), 3.84 (ddd, *J* = 12.0, 8.6, 2.4 Hz, 2H), 2.65 (p, *J* = 6.8 Hz, 2H), 1.18 (dd, *J* = 10.9, 6.8 Hz, 12H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 158.7, 146.3, 130.9, 129.9, 128.0, 125.4, 124.8, 124.6, 123.7, 113.0, 109.1, 53.1, 48.0, 44.7, 28.6, 24.9, 24.3.

IR (neat) ν (cm^{-1}): 2962, 1634, 1496, 1456, 1379, 1364, 1333, 1268, 1217, 1206, 1163, 797, 751, 696, 562, 555, 479, 459.

HRMS (ESI): calcd. for $[M]^+$: 386.2596 found 386.2592.



S-2-1 **2**

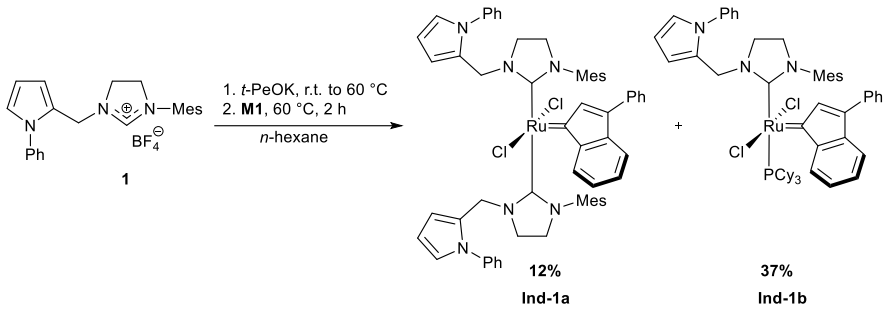
S-2-1 (10.0 g, 26.7 mmol, 1.0 equiv.) was dissolved in triethyl orthoformate (45.4 mL, 267 mmol, 10 equiv.) and stirred 10 minutes. Next, 4M solution of HCl in dioxane (13.3 mL, 53.4 mmoL, 1.0 equiv.) was added dropwise. Mixture was stirred for additional 10 minutes at r.t. and then 24 h at 90 °C (opened flask). After this time the temperature was increased to 120 °C and stirring continued for 2 h. After cooling to r.t., the solvent was removed in vacuo. The product was dissolved in 1:1 mixture of methanol and water. Then ammonium tetrafluoroborate was added in a few portions, and mixture was stirred for 1 h. The methanol was removed in vacuo. The mixture was extracted with CH_2Cl_2 (3x75 ml), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The residue was crystallized (CH_2Cl_2 : toluene) to give 6.50 g (13.7 mmol, 51%) of **2** as colorless crystals.

m.p. 163-165 °C

^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 7.61 (t, *J* = 0.7 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.49 – 7.40 (m, 2H), 7.39 – 7.33 (m, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.96 (dd, *J* = 2.9, 1.8 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.31 (dd, *J* = 3.6, 2.8 Hz, 1H), 4.93 (s, 2H), 4.07 – 3.96 (m, 2H), 3.93 – 3.83 (m, 2H), 2.66 (p, *J* = 6.8 Hz, 2H), 1.19 (dd, *J* = 24.3, 6.8 Hz, 1H).

^{13}C NMR (100 MHz, 25 °C, CD_2Cl_2): δ 157.5, 147.0, 139.3, 131.7, 130.5, 128.8, 126.0, 125.7, 125.5, 114.1, 109.7, 54.0, 48.9, 44.8, 29.0, 25.0, 24.5.

Synthesis of **Ind-1a & Ind-1b**



An oven-dried Schlenk tube was charged with **1** (151 mg, 0.35 mmol, 1.0 equiv.) under argon atmosphere. Anhydrous *n*-hexane (10 mL) was added, followed by dropwise addition of 25% solution of potassium tert-pentoxide in toluene (0.22 mL, 0.35 mmol, 1.0 equiv). Resulting mixture was stirred for 20 min at r.t. then 5 min at 60 °C. Umicore **M1** catalyst (323 mg, 0.35 mmol, 1.0 equiv.) was added in one portion, mixture was stirred at 60 °C for 2 h. After cooliung to r.t. reaction mixture was directly separated using column chromatography (*n*-hex/AcOEt 95:5 to 80:20). A) 123 mg of brick-red/orange solid was obtained (**M1** recovery, 0.133 mmol, 38%) B) 126 mg of deep red crystalline solid (monoNHC complex **Ind-1b**), 0.128 mmol, 37%) C) 22 mg of brick-red/orange crystalline solid (bisNHC complex **Ind-1a**, 0.021 mmol, 12% based on NHC).

Ind-1b (monoNHC)

m.p. >130 °C (decomposition)

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 8.41 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.75 – 7.63 (m, 2H), 7.57 – 7.28 (m, 9H), 7.31 – 7.09 (m, 3H), 7.16 (s, 2H), 7.11 – 6.98 (m, 1H), 6.92 (ddd, *J* = 17.0, 3.2, 1.8 Hz, 2H), 6.45 – 6.30 (m, 2H), 6.06 – 5.94 (m, 1H), 5.88 (d, *J* = 14.5 Hz, 1H), 5.69 (d, *J* = 14.4 Hz, 1H), 3.60 – 3.41 (m, 4H), 2.45 – 2.34 (m, 2H), 2.39 – 2.27 (m, 1H), 2.04 (d, *J* = 1.0 Hz, 3H), 1.92 (s, 3H), 1.93 – 1.76 (m, 7H), 1.76 – 1.61 (m, 4H), 1.53 (s, 1H), 1.49 – 1.19 (m, 7H), 1.23 – 0.89 (m, 7H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 216.6, 215.9, 143.9, 140.5, 139.5, 137.5, 137.2, 136.9, 136.8, 136.7, 136.1, 132.9, 129.7, 128.8, 128.6, 128.5, 128.3, 128.0, 127.5, 126.7, 126.4, 126.2, 123.3, 123.0, 116.0, 112.9, 109.1, 51.5, 48.3, 46.7, 35.7, 35.1, 32.5, 32.3, 29.6, 29.5, 27.8, 27.7, 27.7, 27.6, 27.0, 26.9, 26.5, 26.4, 26.3, 26.2, 25.4, 22.3, 21.0.

HRMS (ESI): calcd. for $[M]^+$: 985.3571 found 985.3549.

IR (neat) ν (cm^{-1}): 2919, 2848, 1598, 1499, 1487, 1444, 1355, 1325, 1297, 1264, 1173, 1028, 1004, 847, 774, 766, 752, 734, 715, 696, 618, 581, 509, 405.

Ind-1a (bisNHC)

m.p. >130 °C (decomposition)

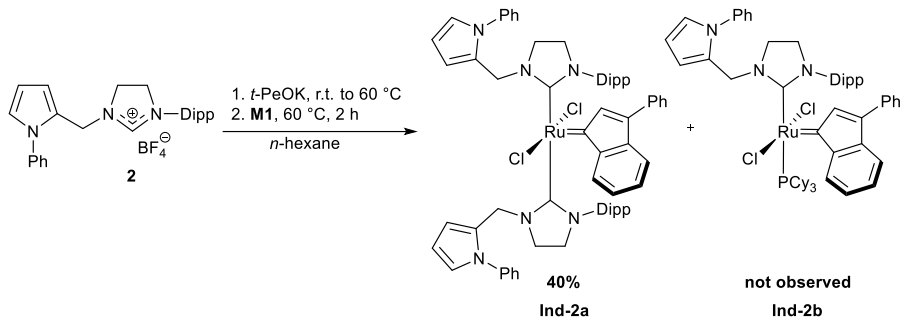
^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 8.20 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.60 – 7.32 (m, 6H), 7.36 – 7.29 (m, 3H), 7.34 – 7.24 (m, 1H), 7.19 (dt, *J* = 3.6, 2.2 Hz, 2H), 7.12 – 6.99 (m, 2H), 7.04 – 6.88 (m, 5H), 6.89 – 6.76 (m, 3H), 6.39 (dd, *J* = 3.6, 2.8 Hz, 2H), 6.25 – 6.19 (m, 2H), 5.79 (d, *J* = 2.0 Hz, 2H), 5.70 (s, 3H), 3.56 – 3.35 (m, 8H), 1.98 (s, 6H), 1.78 (s, 6H), 1.71 (s, 6H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 218.6, 143.0, 139.8, 139.2, 137.0, 136.6, 136.5, 136.5, 136.36, 135.6, 135.4, 129.4, 128.9, 128.6, 128.5, 128.2, 127.8, 127.5, 127.4, 127.2, 127.0, 126.8, 126.6, 126.1, 125.9, 122.5, 114.8, 112.1, 109.2, 51.8, 48.3, 46.9, 26.9, 20.8, 18.4, 18.3.

HRMS (ESI): calcd. for $[M+Na]^+$: 1071.3198 found 1071.3177; calcd. for $[M+K]^+$: 1087.2937 found 1087.2916.

IR (neat) ν (cm^{-1}): 1598, 1498, 1487, 1446, 1436, 1424, 1355, 1323, 1260, 1157, 1028, 847, 766, 751, 736, 715, 696, 665, 638, 580, 541.

Synthesis of **Ind-2a**



2 (142 mg, 0.3 mmol, 1.0 equiv.) was placed in a Schlenk flask under argon atmosphere, afterwhich anhydrous *n*-hexane (10 mL) was added. To resulting suspension 25% solution of potassium tert-pentoxide in toluene (0.19 mL, 0.3 mmol, 1.0 equiv.) was added and the mixture was let to stir for 30 min. Then resulting light-yellow solution was added (via syringe) to the solution of Umicore **M1** catalyst (277 mg, 0.3 mmol, 1.0 equiv.) in toluene (10 mL). The mixture was heated to 60 °C and stirred for 45 min. After cooling to r.t. solvents were evaporated and the residue purified on silica gel (*c*-hex/AcOEt 19:1 to 4:1), yielding: 1) 120 mg of deep orange solid (**M1** recovery, 0.130 mmol, 43%) 2) 75 mg of **Ind-2a** as a red crystalline powder (0.066 mmol, 40% based on NHC).

m.p. 212-213 °C

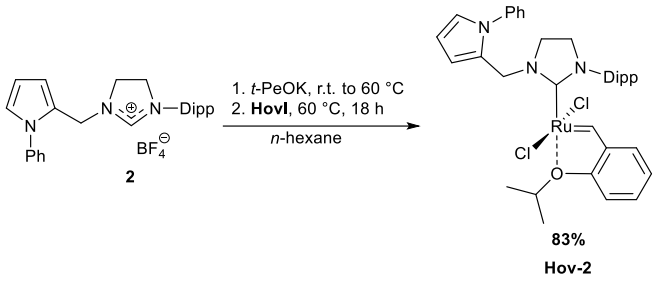
^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 8.50 – 8.43 (m, 1H), 7.74 (s, 1H), 7.63 – 7.51 (m, 3H), 7.42 (s, 2H), 7.35 (dd, *J* = 8.2, 7.3 Hz, 2H), 7.25 – 7.12 (m, 2H), 7.11 – 6.93 (m, 4H), 6.88 – 6.67 (m, 4H), 6.67 – 6.53 (m, 3H), 6.30 (t, *J* = 7.7 Hz, 2H), 6.07 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.90 (s, 1H), 5.85 (dd, *J* = 3.2, 1.3 Hz, 1H), 5.77 (s, 1H), 4.48 (s, 1H), 4.19 – 4.06 (m, 2H), 3.90 (hept, *J* = 7.0 Hz, 1H), 3.53 (ddd, *J* = 11.3, 10.2, 8.8 Hz, 1H), 3.32 (ddd, *J* = 11.3, 10.2, 8.0 Hz, 1H), 3.21 – 3.12 (m, 1H), 3.13 (s, 3H), 2.93 (q, *J* = 11.2, 10.6 Hz, 1H), 2.82 (d, *J* = 15.0 Hz, 1H), 2.60 (ddd, *J* = 12.3, 10.2, 8.8 Hz, 1H), 2.36 (s, 1H), 1.72 (s, 4H), 1.60 (d, *J* = 6.5 Hz, 3H), 1.54 (s, 2H), 1.36 – 1.21 (m, 7H), 1.04 (s, 4H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.61 – 0.47 (m, 4H), 0.26 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, 25 °C, CD_2Cl_2): δ 150.2, 135.9, 130.1, 129.7, 129.4, 129.1, 129.1, 128.6, 128.3, 127.6, 127.3, 127.2, 127.0, 126.0, 125.8, 124.4, 124.2, 123.9, 123.6, 121.8, 118.0, 109.3, 109.1, 54.4, 48.6, 48.1, 44.0, 30.4, 29.0, 27.6, 26.8, 26.6, 24.4, 23.4, 22.9, 22.1.

HRMS (ESI): calcd. for $[M]^+$: 1132.4239 found 1132.4237.

IR (neat) ν (cm^{-1}): 2960, 2865, 1599, 1588, 1499, 1475, 1440, 1423, 1409, 1353, 1250, 1222, 799, 780, 774, 758, 753, 717, 712, 700, 692, 638, 615, 538.

Synthesis of **Hov-2**



2 (156 mg, 0.33 mmol, 1.1 equiv.) was placed in a Schlenk tube under argon atmosphere. Anhydrous *n*-hexane (10 mL) was added. Resulting suspension was charged with 1.7M solution of potassium *tert*-amylate in toluene (0.21 mL, 0.33 mmol, 1.1 equiv.), the mixture was stirred for 15 min, then **Hov1** catalyst (180 mg, 0.3 mmol, 1.0 equiv.) was added in one portion. Resulting dark brown mixture was stirred for 18 h at 50 °C. Light brown solid precipitated. After cooling to r.t. solid was collected by filtration and washed with *n*-pentane (10 mL) to give 202 mg of light brown powder, which was re-dissolved in DCM and filtered through pad of Celite. Mixture was concentrated in vacuo, residue crystallized (DCM/heptane) to obtain 175 mg (0.248 mmol, 83%) of **Hov-2** as a light brown powder.

m.p. 211-212 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 16.15 (s, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.52 – 7.36 (m, 3H), 7.33 (d, *J* = 7.7 Hz, 2H), 6.95 – 6.89 (m, 2H), 6.88 – 6.74 (m, 3H), 6.35 (dd, *J* = 3.5, 2.8 Hz, 1H), 5.75 (s, 2H), 5.15 (q, *J* = 6.2 Hz, 1H), 3.80 – 3.64 (m, 2H), 3.58 – 3.40 (m, 2H), 2.98 (q, *J* = 6.7 Hz, 2H), 1.78 (d, *J* = 6.1 Hz, 6H), 1.13 (d, *J* = 6.9 Hz, 6H), 0.83 (d, *J* = 6.7 Hz, 5H).

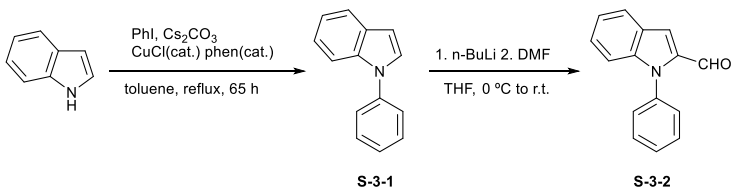
^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 210.0, 152.7, 148.4, 143.4, 139.5, 137.4, 129.5, 129.5, 129.3, 127.5, 126.2, 124.8, 123.4, 122.3, 122.1, 122.9, 122.2, 108.9, 75.2, 54.8, 47.8, 47.2, 27.7, 25.6, 23.8, 22.2.

EA calcd. for $C_{36}H_{43}Cl_2N_3ORu$: C, 61.27; H, 6.14; Cl, 10.05; N, 5.95 found: C, 61.49; H, 5.99; Cl, 10.21; N, 6.00.

HRMS (ESI): calcd. for $[M]^+$: 670.2137 found 670.2138.

IR (neat) ν (cm^{-1}): 2965, 2886, 1599, 1589, 1578, 1500, 1474, 1451, 1421, 1382, 1325, 1309, 1294, 1269, 1247, 1226, 1218, 1146, 1111, 1097, 1054, 1034, 938, 842, 808, 788, 765, 743, 714, 697, 672, 643, 584, 543.

Synthesis of ***N*-phenylindole-2-carboxyaldehyde**



Indole (14.2 g, 120 mmol, 1.0 equiv.), cesium carbonate (59.2 g, 180 mmol, 1.5 equiv.), copper(I) chloride (1.2 g, 12 mmol, 0.1 equiv.) and 1,10-phenantroline (3.24 g, 18 mmol, 0.15 equiv.) were placed in 250 mL round bottom flask under argon atmosphere and dissolved in anhydrous toluene (30 mL). Iodobenzene (29.4 g, 144 mmol, 1.2 equiv.) was then added and the reaction mixture was stirred at reflux for 65 h. After cooling to r.t, the residue was diluted with Et_2O (100 mL) and filtered through pad of Celite. Filtrate was concentrated in vacuo and distilled under reduced pressure (144-147 °C at 4 - 5 mbar) to give 22.9 g (119 mmol, 99%) of **S-3-1** as a colorless oil.

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 8.07 – 7.96 (m, 1H), 7.87 (ddd, *J* = 7.1, 2.3, 0.9 Hz, 1H), 7.77 – 7.64 (m, 4H), 7.59 – 7.43 (m, 4H), 6.97 (dd, *J* = 3.3, 0.9 Hz, 1H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 139.6, 135.7, 129.4, 129.3, 127.8, 126.2, 124.1, 122.3, 121.1, 120.3, 110.4, 103.5.

^{1}H and ^{13}C NMR spectra are consistent with previously reported.

S-3-1 (4.83 g, 25 mmol, 1.0 equiv.) was placed in 250 mL three necked round-bottom flask under argon atmosphere. Anhydrous THF (80 mL) was added, flask was equipped with bubbler and septum, resulting solution was cooled with water/ice bath. 2.5M solution of *n*-BuLi in hexanes (11.0 mL, 27.5mmol, 1.1 equiv.) was added dropwise (10 min), resulting mixture was stirred for 10 min at bath temperature, then additional 60 min at r.t. Mixture was cooled in water/ice bath once again, after which anhydrous DMF (2.5 mL, 32 mmol, 1.3 equiv.) was added dropwise. Stirring was continued for 30 min at r.t., then 10% aqueous solution of NH_4Cl (100 mL) was added. Mixture was extracted with AcOEt (3x100 mL), combined organic phases were washed with brine (100 mL) and dried over anhydrous Na_2SO_4. Drying agent was filtered off, the residue (dark yellow oil) was purified by column chromatography (*c*-hex/AcOEt 90:10), to obtain 4.99 g (22.6 mmol, 90%) of **S-3-2** as a viscous orange oil, which crystallized overnight to form yellow, crystalline solid.

m.p. 70-71 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 9.86 (s, 1H), 7.82 – 7.75 (m, 1H), 7.57 – 7.45 (m, 4H), 7.45 (d, *J* = 0.9 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.35 – 7.31 (m, 1H), 7.24 – 7.18 (m, 2H).

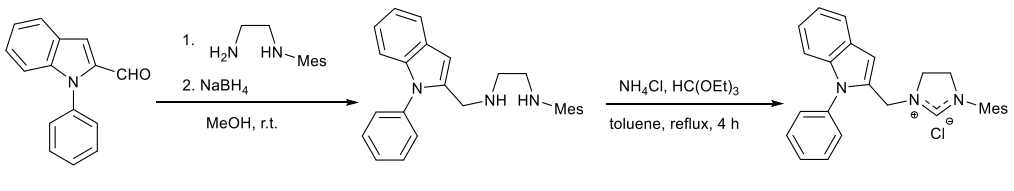
^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 181.7, 141.0, 137.0, 136.3, 129.4, 128.4, 127.8, 127.1, 126.4, 123.3, 121.7, 115.5, 111.6.

EA calcd. for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33 found: C, 81.68; H, 5.13; N 6.24.

LRMS (ESI): calcd. for $[M+H]^+$: 222.3 found 222.1.

IR (neat) ν (cm^{-1}): 1664, 1612, 1593, 1519, 1495, 1477, 1451, 1399, 1376, 1357, 1313, 1216, 1129, 1116, 1071, 1031, 1019, 1007, 995, 940, 910, 861, 822, 759, 745, 693, 629, 603, 586, 547, 465, 439, 412.

Synthesis of **3**



S-3-2 **S-3-3** **3**

S-3-2 (5.53 g, 25.0 mmol, 1.0 equiv.), *N*-(2,6-diisopropylphenyl)-ethylenediamine (4.46 g, 25.0 mmol. 1.0 equiv.) and pTsOH·H_2O (95 mg, 0.5 mmol, 0.02 equiv.) were placed in 250 mL round-bottom flask under argon atmosphere. MeOH (50 mL) and molecular sieves (3 Å, activated) were added. Resulting mixture was stirred at r.t. for 6 h, then $NaBH_4$ (1.89 g, 50 mmol, 2.0 equiv.) was added and the mixture was stirred at r.t. for additional 18 h. Water (15 mL) was added carefully, MeOH was removed in vacuo. 10% solution K_2CO_3 in water (50 mL) was added, mixture was transferred into separation funnel and extracted with AcOEt (3 x 75 m). The combined organic phases were washed with brine (100 mL) and dried over anhydrous Na_2SO_4. Solvent was removed in vacuo, residue was purified by column chromatography (aluminum oxide, *c*-hex/AcOEt 90:10 to 60:40). 8.89 g (20.6 mmol, 82%) of **S-3-3** as a light yellow oil was obtained. Product was used directly in next transformation.

S-3-3 (7.67 g, 20.0 mmol, 1.0 equiv.) and NH_4Cl (1.12g, 21.0 mmol, 1.05 equiv.) were placed in 100 Ml round-bottom flask under argon atmosphere. Triethylorthoformate and anhydrous toluene (5 mL) were added. Mixture was stirred at 120 °C for 3.5 h, then cooled to r.t. Et_2O (30 mL) was added, mixture stirred for 30 min at r.t. then concentrated in vacuo, dissolved in DCM, filtered through pad of celite and concentrated again. Residue was crystallized (MeOH/MTBE, fridge) to obtain 5.77 g (13.4 mmol, 67%) of **3** as pale yellow crystals.

m.p. 98-101 °C

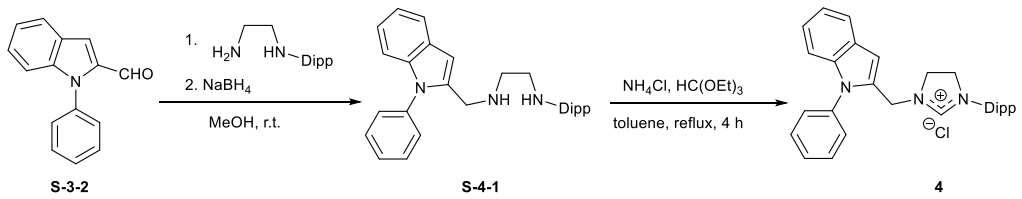
^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 9.10 (s, 1H), 7.64 – 7.48 (m, 3H), 7.45 – 7.34 (m, 3H), 7.21 – 7.08 (m, 3H), 6.80 (d, *J* = 6.7 Hz, 3H), 5.41 (s, 2H), 3.90 (dqd, *J* = 16.6, 8.5, 2.4 Hz, 4H), 3.33 (d, *J* = 4.0 Hz, 2H), 2.19 (s, 3H), 2.09 (s, 6H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 158.9, 140.0, 138.6, 134.9, 130.6, 130.2, 129.7, 128.4, 127.2, 127.0, 123.2, 120.9, 120.8, 110.4, 106.3, 50.6, 50.0, 47.9, 45.0, 20.8, 17.8.

HRMS (ESI): calcd. for $[M]^+$: 394.2283 found 394.2279.

IR (neat) ν (cm^{-1}): 3316, 2916, 1634, 1596, 1498, 1485, 1455, 1369, 1339, 1265, 1214, 1208, 1140, 1033, 1018, 1006, 856, 761, 749, 734, 722, 701, 601, 574, 556, 473

Synthesis of **4**



S-3-2 **S-4-1** **4**

S-3-2 (3.10 g, 14.0 mmol, 1.0 equiv.), *N*-(2,6-diisopropylphenyl)-ethylenediamine (3.09 g, 14.0 mmol. 1.0 equiv.) and pTsOH·H_2O (53 mg, 0.28 mmol, 0.02 equiv.) were placed in 250 mL round-bottom flask under argon atmosphere. MeOH (50 mL) and molecular sieves (3 Å, activated) were added. Resulting mixture was stirred at r.t. for 6 h, then $NaBH_4$ (1.85 g, 49 mmol, 3.5 equiv.) was added and the mixture was stirred at r.t. for additional 18 h. After this period water (15 mL) was added carefully and MeOH was removed in vacuo. 10% Aqueous solution of K_2CO_3 (50 mL) was added, the mixture was transferred into separation funnel and extracted with AcOEt (3 x 75 m). The combined organic phases were washed with brine (100 mL) and dried over anhydrous Na_2SO_4. Drying agent was filtered off and solvent was

removed in vacuo. The residue was purified by column chromatography (neutral Al_2O_3, *c*-hex/AcOEt 90:10 to 60:40) to give 4.54 g (10.7 mmol, 76%) of **S-4-1** as a light yellow oil.

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 7.68 – 7.59 (m, 1H), 7.58 – 7.49 (m, 2H), 7.48 – 7.39 (m, 3H), 7.20 – 7.10 (m, 3H), 7.10 – 6.99 (m, 3H), 6.60 (s, 1H), 3.91 (d, *J* = 0.8 Hz, 2H), 3.23 (p, *J* = 6.9 Hz, 2H), 2.88 (dd, *J* = 6.7, 4.3 Hz, 2H), 2.79 (dd, *J* = 6.5, 4.0 Hz, 2H), 1.19 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 143.3, 142.4, 139.2, 138.5, 137.7, 129.6, 128.0, 127.8, 127.7, 123.6, 123.5, 121.7, 120.2, 120.2, 110.2, 102.0, 51.1, 48.8, 45.6, 26.9, 24.3.

HRMS (ESI): calcd. for $[M+H]^+$: 426.2904 found 426.2917.

IR (neat) ν (cm^{-1}): 2959, 1595, 1498, 1455, 1383, 1362, 1329, 1254, 1208, 1108, 1016, 783, 747, 737, 698, 640, 615, 610, 575, 562, 433, 414.

S-4-1 (4.26 g, 10.0 mmol, 1.0 equiv.) and NH_4Cl (642 mg, 12.0 mmol, 1.2 equiv.) were placed in 100 mL round-bottom flask under argon atmosphere. Triethylorthoformate (8.5 mL, 50 mmol, 5.0 equiv.) and anhydrous toluene (5 mL) were added. Mixture was stirred at 120 °C for 4 h, then cooled to r.t. Et_2O (30 mL) was added, mixture stirred for 30 min at r.t. afterwhich precipitated solid was collected on Schott funnel and washed with additional Et_2O (2×25 mL) to obtain 4.00 g (8.5 mmol, 85%) of **4** as a beige solid.

m.p. 228-230 °C

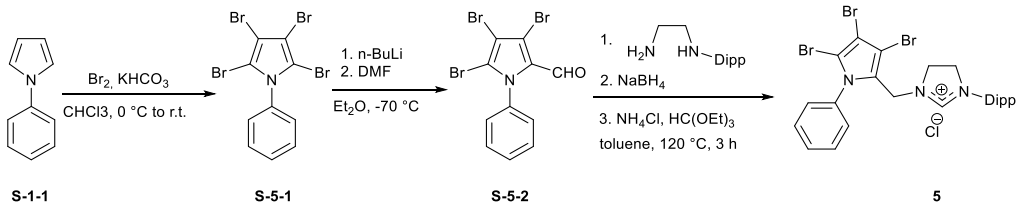
^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 9.42 (s, 1H), 7.62 – 7.57 (m, 1H), 7.56 – 7.50 (m, 2H), 7.46 – 7.35 (m, 3H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.20 – 7.08 (m, 5H), 6.83 (s, 1H), 5.46 (s, 2H), 4.05 – 3.75 (m, 4H), 2.67 (q, *J* = 6.8 Hz, 2H), 1.18 (d, *J* = 6.7 Hz, 6H), 1.15 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 159.0, 146.2, 138.7, 136.4, 131.1, 131.0, 130.1, 129.6, 128.5, 127.4, 127.2, 124.8, 123.2, 121.0, 120.9, 110.5, 105.9, 53.1, 48.2, 44.9, 28.5, 24.8, 24.3.

HRMS (ESI): calcd. for $[M-Cl]^+$: 436.2747 found 436.2765.

IR (neat) ν (cm^{-1}): 2965, 1597, 1497, 1493, 1483, 1456, 1429, 1363, 1355, 1344, 1333, 1271, 1253, 1237, 1221, 1208, 1054, 1015, 811, 792, 764, 751, 738, 717, 700, 618, 567, 557, 464.

Synthesis of **5**



S-1-1 (5.01 g, 35.0 mmol, 1.0 equiv.) and potassium hydrogencarbonate (14.37 g, 144.0 mmol, 4.1 equiv.) and chloroform (100 mL) were placed in 250 mL round-bottom flask. The mixture was cooled (water/ice bath), and then solution of Br_2 (23.16 g, 144.0 mmol, 4.1 equiv.) in chloroform (20 ml) was added dropwise (for 10 min). The resulting dark mixture was stirred for 60 min, then bath was removed and the mixture was stirred additionally at r.t. for 19 h. 1% solution of $KHCO_3$ in water (100 mL) was

added, layers were separated and organic phase was washed with 5% solution of $Na_2S_2O_3$ in water (2 x 100 mL), brine (150 mL), then dried over anhydrous Na_2SO_4. Solvent was evaporated, the residue purified by filtration on silica (*c*-hex/AcOEt 9:1) followed by column chromatography (*c*-hex/DCM 7:1 then 2:1). Two fractions were collected: 1) 10.14 g of dark red oil - mixture of brominated pyrroles (mostly 2,3,4,5-tetrabrominated) 2) 2.05 g of dark yellow solid, possibly polymeric by-product, which was discarded. Mixture 1) was purified by another chromatography (*n*-hex/DCM 9:1), obtaining 6.40 g (14.0 mmol, 40%) of **S-5-1** as light orange crystalline solid.

m.p. 83-86 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$ δ 7.53 – 7.44 (m, 2H), 7.46 – 7.37 (m, 1H), 7.38 – 7.30 (m, 2H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 138.1, 133.8, 129.8, 129.4, 128.6, 104.5, 102.6.

EA calcd. for $C_{10}H_5Br_4N$: C, 26.18; H, 1.10; Br, 69.67; N, 3.05 found: C, 26.17; H, 0.96; Br, 69,60; N 3.14.

^{1}H NMR spectrum is consistent with previously reported[1].

S-5-1 (4.59 g, 10.0 mmol, 1.0 equiv.) was placed in 250 mL round bottom flask under argon atmosphere. Anhydrous Et_2O (50 mL) was added and resulting solution was cooled to -70 °C. Solution of *n*-BuLi (4.2 mL, 10.5 mmol, 2.5M in hexanes, 1.05 equiv.) was added dropwise (5 min), at the end of addition the mixture became so dense (white precipitation) that it was not possible to stir it anymore, so second portion of Et_2O (20 mL) was added, which solved the problem. Suspension was stirred for 30 min at -70 °C, then anhydrous DMF (1.0 mL, 13.0 mmol, 1.3 equiv.) was added dropwise. The mixture slowly became intense pink-colored. Stirring was continued for 20 min at -70 °C, then cooling bath was removed and the mixture stirred for additional 30 min at r.t. - mixture became clear (no precipitate), raspberry-red colored. 10% solution of NH_4Cl in water (50 mL) was added, organic phase turned orange. Layers were separated, aqueous was extracted with Et_2O (2x50 mL), combined organic phases were washed with brine (50 mL) and dried over anhydrous Na_2SO_4. Drying agent was filtered off, solvent removed in vacuo and the residue (light yellow solid) was purified via column chromatography (320 mL of SiO_2, *c*-hex/AcOEt 95/5), to give 2.60 g (6.4 mmol, 64%) of **S-5-2** as light yellow crystals.

m.p. 115-117 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 9.43 (s, 1H), 7.66 – 7.37 (m, 3H), 7.29 – 7.17 (m, 2H).

^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 177.1, 136.9, 130.2, 129.9, 129.3, 127.9, 117.2, 112.4, 105.8.

EA calcd. for $C_{11}H_6Br_3NO$: C, 32.39; H, 1.48; Br, 58.77; N, 3.43 found: C, 32.22; H, 1.34; Br, 3,49; N 58.85.

HRMS (ESI): calcd. for $[M]^+$: 454.7155 found 454.7158.

IR (neat) ν (cm^{-1}): 1672, 1595, 1495, 1439, 1388, 1366, 1348, 1328, 1293, 1217, 1173, 1066, 1044, 1024, 991, 915, 827, 778, 754, 730, 686, 667, 630, 559, 518, 438, 424.

[1] F. Faigl, S. Deák, Z. Mucsi, T. Hergert, L. Balázs, B. Sándor, B. Balázs, T. Holczbauer, M. Nyerges and B. Mátravölgyi, *Tetrahedron*, 2016, **72**, 5444–5455.

S-5-3 (2.04 g, 5.0 mmol, 1.0 equiv.), pTSA·$2H_2O$ (19 mg, 0.1 mmol, 0.02 equiv.) and *N*-(2,6-diisopropylphenyl)etylenediamine (1.10 g, 5.0 mmol, 1.0 equiv.) were placed in 100 mL round-bottom flask under argon atmosphere, MeOH (25 mL) and molecular sieves (3 Å, activated) were added, and resulting mixture was stirred at r.t. for 6 h, then $NaBH_4$ (567 mg, 15.0 mmol, 3.0 equiv.), and THF (HPLC grade, 25mL) were added and the mixture was stirred at r.t. for additional 18 h. Water (15 mL) was added carefully, MeOH was removed in vacuo. 10% solution of K_2CO_3 in water (50 mL) was added, the mixture was transferred into separation funnel and extracted with AcOEt (3 x 75 m). The combined organic phases were washed with brine (100 mL) and dried over anhydrous Na_2SO_4. Solvent was removed in vacuo, the crude amine was placed in 100 mL round-bottom flask along with NH_4Cl (267 mg, 5.0 mmol) under argon atmosphere. Triethyl orthoformate (10 mL) and anhydrous toluene (10 mL) were added, resulting mixture was stirred vigorously under reflux for 3 h, then condenser was removed and stirring at 120 °C was continued for 30 min. Mixture was cooled to r.t., Et_2O (50 mL) was added, precipitated solid was collected by filtration and washed with Et_2O (3 x 15 mL). The crude product was dissolved in DCM and filtered through pad of Celite, the solution was concentrated to 10 mL and treated with Et_2O (80 mL). Filtration and washing was repeated, 2.10 g (3.2 mmol, 64%) of **5** as a white powder was obtained (after vacuum drying).

m.p. 160-162 °C

^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 9.65 (s, 1H), 7.60 – 7.48 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.11 (m, 4H), 5.27 (s, 2H), 4.11 – 3.98 (m, 2H), 3.92 – 3.82 (m, 2H), 3.59 (q, *J* = 7.1 Hz, 1H), 2.80 (hept, *J* = 6.8 Hz, 2H), 1.30 – 1.13 (m, 12H).

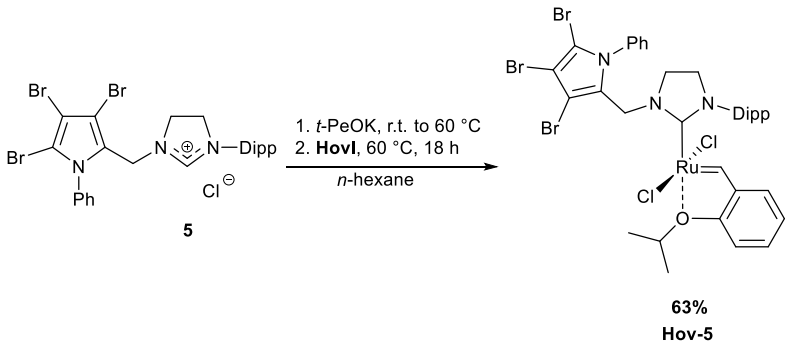
^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 159.5, 146.3, 136.0, 131.1, 130.3, 130.1, 129.4, 128.3, 124.9, 124.3, 107.3, 103.0, 102.9, 53.2, 47.7, 44.3, 28.6, 26.0, 25.0, 24.5.

EA calcd. for $C_{26}H_{29}Br_3ClN_3$: C, 47.41; H, 4.44; N, 6.38 found: C, 47.48; H, 4.66; N, 6,39.

HRMS (ESI): calcd. for $[M+Na]^+$: 427.7897 found 427.7887.

IR (neat) ν (cm^{-1}): 2965, 1627, 1598, 1496, 1456, 1445, 1397, 1373, 1328, 1297, 1267, 1232, 1200, 1158, 1096, 1082, 1055, 1051, 1005, 803, 755, 699, 556, 508, 477, 459.

Synthesis of **Hov-5**



5 (198 mg, 0.30 mmol, 1.0 equiv.) was placed in a Schlenk tube under argon atmosphere. Anhydrous *n*-hexane (10 mL) was added. Resulting suspension was charged with 1.7M solution of potassium *tert*-amylate (0.19 mL, 0.30 mmol, 1.0 equiv.), the mixture was stirred for 15 min at r.t. and 5 min at 60 °C. Next, **Hov1** catalyst (180 mg, 0.3 mmol, 1.0 equiv.) was added in one portion. Resulting dark brown mixture was stirred for 18 h at 60 °C. Light brown solid precipitated. After cooling to r.t. solid was

collected by filtration and washed with *n*-pentane (10 mL), to give 202 mg of light brown powder, which was re-dissolved in DCM and filtered through pad of Celite. The mixture was concentrated in vacuo, residue was purified by column chromatography (*n*-hexane:AcOEt 9:1 to 7:3), followed by crystallization (DCM/MeOH) to obtain 178 mg (0.19 mmol, 63%) of **Hov-5** as a light brown powder. Product is a mixture of unseparable isomers **A** (~85% by the benzylidene ^{1}H integrity) and **B** (~15% by the benzylidene ^{1}H integrity). There is neither any interconversion between **A** and **B** nor coalescence of signals measurable by ^{1}H NMR in temperature range from 30 ºC to 80 ºC (toluene-d_8).

m.p. >170 °C (with decomposition)

^{1}H NMR (400 MHz, 25 °C, toluene-d_8): δ 15.99 (s, 1H, isomer **A**), 15.87 (s, 1H, isomer **B**), 7.37 (t, *J* = 7.7 Hz, 1H, isomer **A**), 7.23 – 7.14 (m, 5H, isomer **A**), 7.14 – 7.04 (m, 3H, isomer **A**), 7.00 (dt, *J* = 15.5, 1.2 Hz, 2H, isomer **A**), 6.90 (ddt, *J* = 9.4, 6.2, 1.4 Hz, 3H, isomer **A**), 6.61 (t, *J* = 7.4 Hz, 1H, isomer **A**), 6.37 (d, *J* = 8.3 Hz, 1H, isomer **A**), 6.00 (s, 2H, isomer **A**), 5.98 (s, 2H, isomer **B**), 4.60 (p, *J* = 6.1 Hz, 1H, isomer **A**), 3.26 (t, *J* = 9.2 Hz, 2H, isomer **A**), 2.99 (dt, *J* = 13.6, 8.4 Hz, 4H, isomer **A**), 2.09 (p, *J* = 2.2 Hz, 2H, isomer **A**), 1.67 (d, *J* = 6.1 Hz, 1H, isomer **B**), 1.63 (d, *J* = 6.1 Hz, 3H, isomer **A**), 1.11 (d, *J* = 7.0 Hz, 6H, isomer **A**), 0.94 (d, *J* = 6.5 Hz, 3H, isomer **B**), 0.87 (d, *J* = 6.6 Hz, 6H, isomer **A**).

^{13}C NMR (100 MHz, 25 °C, toluene-d_8,): δ (mixture of isomers **A** and partially **B)** 284.0, 215.0, 153.1, 148.6, 143.5, 138.1, 137.4, 129.7, 129.6, 128.8, 128.6, 128.6, 127.9, 127.9, 127.7, 127.7, 125.1, 125.0, 124.8, 122.3, 122.0, 112.9, 106.8, 103.7, 103.0, 54.8, 48.0, 45.8, 27.9, 25.7, 24.1, 22.0, 21.0, 19.8.

EA calcd. for $C_{11}H_6Br_3NO$: C, 45.88; H, 4.28; N, 4.46 found: C, 45.90; H, 4.24; N 4.59.

HRMS (ESI): calcd. for $[M\text{-}Cl]^+$: 903.9545 found 903.9433.

IR ($CHCl_3$) ν (cm^{-1}): 3068, 2965, 2925, 2867, 1589, 1576, 1496, 1476, 1455, 1424, 1404, 1385, 1353, 1329, 1297, 1279, 1265, 1217, 1200, 1181, 1157, 1141, 1114, 1098, 1074, 1055, 1037, 1005, 970, 937, 879, 843, 808, 795, 754, 694, 665, 644, 617, 606, 580, 519, 491, 450.

3. X-ray analysis

The single crystal diffraction data collection for **Hov-5** was performed on two SuperNova diffractometers with mirror-monochromated MoKα radiation. The diffractometers were equipped with an Oxford Cryosystems nitrogen gas-flow apparatus and measurements were conducted at 100K. The analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid was used [1].The CrysAlis PRO program was applied for the data collection and its further reduction. [2]. The structure of **Hov-5** was solved by direct methods and refined using SHELXL [3] program in cooperation with the Olex2 program [4]. The refinements were based on F^2. Some geometric and ADP restrains were required during refinement. The lattice parameters and the final *R*-indices obtained for the refinement of the structures of **Hov-5** are presented in Table S1. Selected geometrical parameters are shown in Table S2.

CCDC 1543827 entry contains the supplementary crystallographic data (CIF files) for this paper.

Table S1. X-ray experimental details for **Hov-5**.

	Hov-5
Crystal data	
Chemical formula	$C_{36}H_{40}Br_3Cl_2N_3ORu \cdot 0.5(C_6H_6)$
M_r	981.46

Crystal system, space group	Triclinic, *P*-1
Temperature (K)	100
a (Å)	11.32563 (18)
b (Å)	15.0796 (2)
c (Å)	23.9878 (4)
α (Å)	82.4683 (13)
β (Å)	79.5062 (13)
γ (Å)	87.5942 (13)
V (Å^3)	3992.82 (11)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	3.56
Crystal size (mm)	0.53 × 0.39 × 0.07
Data collection	
Diffractometer	SuperNova, Eos
Absorption correction	Analytical + empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.279, 0.803
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	141711, 24382, 19335
R_{int}	0.064
θ values (°)	θ_{max} = 30.5, θ_{min} = 1.5
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.085, 1.04
No. of reflections	24382
No. of parameters	903

No. of restraints	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.60, -1.12

Table S2. Selected geometric parameters **Hov-5** (Å, °)

Ru1—Cl1	2.3640 (6)	C19—C20	1.359 (4)
Ru1—Cl2	2.3485 (7)	C21—C22	1.374 (4)
Ru1—O1	2.2778 (19)	C21—C26	1.388 (4)
Ru1—C1	1.965 (3)	C22—C23	1.392 (4)
Ru1—C27	1.832 (3)	C23—C24	1.379 (5)
Ru2—Cl3	2.3485 (6)	C24—C25	1.393 (5)
Ru2—Cl4	2.3450 (6)	C25—C26	1.379 (4)
Ru2—O2	2.2613 (18)	C27—C28	1.452 (4)
Ru2—C37	1.970 (3)	C28—C29	1.401 (4)
Ru2—C63	1.837 (3)	C28—C33	1.403 (4)
Br1—C18	1.871 (3)	C29—C30	1.388 (4)
Br2—C19	1.867 (3)	C30—C31	1.383 (5)
Br3—C20	1.858 (3)	C31—C32	1.390 (4)
Br4—C54	1.874 (3)	C32—C33	1.392 (4)
Br5—C55	1.860 (3)	C34—C35	1.517 (4)
Br6—C56	1.855 (3)	C34—C36	1.515 (4)
O1—C33	1.373 (3)	C38—C39	1.519 (4)
O1—C34	1.469 (3)	C40—C41	1.410 (4)
O2—C69	1.372 (3)	C40—C45	1.402 (4)
O2—C70	1.476 (3)	C41—C42	1.393 (4)
N1—C1	1.356 (3)	C41—C49	1.517 (4)
N1—C2	1.473 (3)	C42—C43	1.384 (4)
N1—C4	1.437 (3)	C43—C44	1.382 (4)

N2—C1	1.360 (3)	C44—C45	1.399 (4)
N2—C3	1.466 (3)	C45—C46	1.519 (4)
N2—C16	1.463 (3)	C46—C47	1.518 (4)
N3—C17	1.387 (3)	C46—C48	1.521 (4)
N3—C20	1.381 (3)	C49—C50	1.534 (4)
N3—C21	1.440 (4)	C49—C51	1.526 (4)
N4—C37	1.358 (3)	C52—C53	1.492 (4)
N4—C38	1.482 (3)	C53—C54	1.371 (4)
N4—C40	1.434 (3)	C54—C55	1.409 (4)
N5—C37	1.358 (3)	C55—C56	1.368 (4)
N5—C39	1.471 (3)	C57—C58	1.381 (4)
N5—C52	1.469 (3)	C57—C62	1.391 (4)
N6—C53	1.389 (3)	C58—C59	1.392 (4)
N6—C56	1.379 (3)	C59—C60	1.378 (4)
N6—C57	1.442 (3)	C60—C61	1.392 (5)
C2—C3	1.527 (4)	C61—C62	1.382 (4)
C4—C5	1.406 (4)	C63—C64	1.447 (4)
C4—C9	1.398 (4)	C64—C65	1.400 (4)
C5—C6	1.395 (4)	C64—C69	1.403 (4)
C5—C10	1.514 (4)	C65—C66	1.393 (4)
C6—C7	1.381 (4)	C66—C67	1.384 (4)
C7—C8	1.383 (4)	C67—C68	1.393 (4)
C8—C9	1.394 (4)	C68—C69	1.391 (4)
C9—C13	1.525 (4)	C70—C71	1.509 (4)
C10—C11	1.535 (4)	C70—C72	1.517 (4)
C10—C12	1.532 (4)	C73—C74	1.363 (5)
C13—C14	1.520 (4)	C73—C78	1.378 (5)
C13—C15	1.522 (4)	C74—C75	1.374 (5)
C16—C17	1.499 (4)	C75—C76	1.389 (5)

C17—C18	1.374 (4)	C76—C77	1.387 (5)
C18—C19	1.413 (4)	C77—C78	1.376 (5)
Cl2—Ru1—Cl1	150.31 (2)	C23—C24—C25	120.0 (3)
O1—Ru1—Cl1	88.98 (5)	C26—C25—C24	120.2 (3)
O1—Ru1—Cl2	88.42 (5)	C25—C26—C21	119.0 (3)
C1—Ru1—Cl1	86.88 (8)	Ru1—C27—H27	124.8 (19)
C1—Ru1—Cl2	95.80 (8)	C28—C27—Ru1	119.3 (2)
C1—Ru1—O1	175.67 (9)	C28—C27—H27	115.8 (19)
C27—Ru1—Cl1	106.79 (9)	C29—C28—C27	122.9 (3)
C27—Ru1—Cl2	101.71 (9)	C29—C28—C33	118.8 (3)
C27—Ru1—O1	78.94 (10)	C33—C28—C27	118.3 (2)
C27—Ru1—C1	101.05 (11)	C30—C29—C28	120.4 (3)
Cl4—Ru2—Cl3	150.37 (2)	C31—C30—C29	119.5 (3)
O2—Ru2—Cl3	87.44 (5)	C30—C31—C32	121.9 (3)
O2—Ru2—Cl4	89.07 (5)	C31—C32—C33	118.2 (3)
C37—Ru2—Cl3	87.24 (7)	O1—C33—C28	113.3 (2)
C37—Ru2—Cl4	95.93 (7)	O1—C33—C32	125.4 (3)
C37—Ru2—O2	174.63 (9)	C32—C33—C28	121.2 (3)
C63—Ru2—Cl3	105.77 (8)	O1—C34—C35	110.2 (2)
C63—Ru2—Cl4	102.45 (8)	O1—C34—C36	106.1 (2)
C63—Ru2—O2	79.29 (9)	C36—C34—C35	112.0 (3)
C63—Ru2—C37	101.46 (11)	N4—C37—Ru2	132.66 (19)
C33—O1—Ru1	110.02 (16)	N4—C37—N5	107.0 (2)
C33—O1—C34	119.5 (2)	N5—C37—Ru2	119.17 (19)
C34—O1—Ru1	129.01 (16)	N4—C38—C39	101.6 (2)
C69—O2—Ru2	110.38 (15)	N5—C39—C38	101.1 (2)
C69—O2—C70	119.6 (2)	C41—C40—N4	118.9 (2)
C70—O2—Ru2	128.94 (16)	C45—C40—N4	119.0 (2)

C1—N1—C2	112.6 (2)	C45—C40—C41	122.0 (2)
C1—N1—C4	127.3 (2)	C40—C41—C49	122.6 (2)
C4—N1—C2	119.0 (2)	C42—C41—C40	117.7 (3)
C1—N2—C3	112.2 (2)	C42—C41—C49	119.7 (2)
C1—N2—C16	122.8 (2)	C43—C42—C41	121.2 (3)
C16—N2—C3	119.6 (2)	C44—C43—C42	120.1 (3)
C17—N3—C21	126.1 (2)	C43—C44—C45	121.2 (3)
C20—N3—C17	108.8 (2)	C40—C45—C46	122.7 (2)
C20—N3—C21	125.1 (2)	C44—C45—C40	117.7 (3)
C37—N4—C38	111.9 (2)	C44—C45—C46	119.6 (3)
C37—N4—C40	129.1 (2)	C45—C46—C48	111.9 (2)
C40—N4—C38	118.0 (2)	C47—C46—C45	111.1 (2)
C37—N5—C39	111.5 (2)	C47—C46—C48	110.5 (3)
C37—N5—C52	122.2 (2)	C41—C49—C50	110.5 (2)
C52—N5—C39	120.3 (2)	C41—C49—C51	111.4 (2)
C53—N6—C57	125.4 (2)	C51—C49—C50	109.8 (3)
C56—N6—C53	108.8 (2)	N5—C52—C53	112.0 (2)
C56—N6—C57	125.5 (2)	N6—C53—C52	124.1 (2)
N1—C1—Ru1	132.55 (19)	C54—C53—N6	106.6 (2)
N1—C1—N2	106.4 (2)	C54—C53—C52	129.3 (2)
N2—C1—Ru1	120.26 (18)	C53—C54—Br4	126.4 (2)
N1—C2—C3	101.5 (2)	C53—C54—C55	109.4 (2)
N2—C3—C2	100.9 (2)	C55—C54—Br4	124.2 (2)
C5—C4—N1	118.8 (2)	C54—C55—Br5	126.7 (2)
C9—C4—N1	119.4 (2)	C56—C55—Br5	126.8 (2)
C9—C4—C5	121.9 (2)	C56—C55—C54	106.4 (2)
C4—C5—C10	122.7 (2)	N6—C56—Br6	122.5 (2)
C6—C5—C4	117.8 (3)	C55—C56—Br6	128.6 (2)
C6—C5—C10	119.5 (3)	C55—C56—N6	108.8 (2)

C7—C6—C5	121.1 (3)	C58—C57—N6	118.7 (3)
C6—C7—C8	120.2 (3)	C58—C57—C62	121.6 (3)
C7—C8—C9	121.0 (3)	C62—C57—N6	119.6 (3)
C4—C9—C13	122.3 (2)	C57—C58—C59	118.9 (3)
C8—C9—C4	118.1 (3)	C60—C59—C58	120.3 (3)
C8—C9—C13	119.6 (3)	C59—C60—C61	120.0 (3)
C5—C10—C11	109.7 (2)	C62—C61—C60	120.5 (3)
C5—C10—C12	112.2 (2)	C61—C62—C57	118.6 (3)
C12—C10—C11	111.0 (2)	Ru2—C63—H63	124.4 (17)
C14—C13—C9	111.1 (2)	C64—C63—Ru2	118.6 (2)
C14—C13—C15	110.8 (3)	C64—C63—H63	117.0 (17)
C15—C13—C9	111.7 (2)	C65—C64—C63	122.9 (2)
N2—C16—C17	111.5 (2)	C65—C64—C69	118.3 (2)
N3—C17—C16	123.3 (2)	C69—C64—C63	118.8 (2)
C18—C17—N3	106.5 (2)	C66—C65—C64	120.6 (3)
C18—C17—C16	130.1 (2)	C67—C66—C65	119.4 (3)
C17—C18—Br1	126.1 (2)	C66—C67—C68	121.8 (3)
C17—C18—C19	109.1 (2)	C69—C68—C67	117.9 (3)
C19—C18—Br1	124.8 (2)	O2—C69—C64	113.0 (2)
C18—C19—Br2	126.9 (2)	O2—C69—C68	125.1 (2)
C20—C19—Br2	126.5 (2)	C68—C69—C64	121.9 (3)
C20—C19—C18	106.6 (2)	O2—C70—C71	105.7 (2)
N3—C20—Br3	122.4 (2)	O2—C70—C72	109.8 (2)
C19—C20—Br3	128.6 (2)	C71—C70—C72	112.6 (2)
C19—C20—N3	109.0 (2)	C74—C73—C78	119.8 (3)
C22—C21—N3	119.2 (2)	C73—C74—C75	120.9 (3)
C22—C21—C26	121.5 (3)	C74—C75—C76	119.5 (3)
C26—C21—N3	119.3 (3)	C77—C76—C75	119.9 (3)
C21—C22—C23	119.1 (3)	C78—C77—C76	119.3 (3)

C24—C23—C22	120.2 (3)	C77—C78—C73	120.6 (3)
Ru1—O1—C33—C28	-2.4 (3)	C21—C22—C23—C24	0.2 (4)
Ru1—O1—C33—C32	178.5 (2)	C22—C21—C26—C25	0.0 (4)
Ru1—O1—C34—C35	-93.7 (3)	C22—C23—C24—C25	-0.7 (5)
Ru1—O1—C34—C36	27.8 (3)	C23—C24—C25—C26	0.9 (5)
Ru1—C27—C28—C29	-177.3 (2)	C24—C25—C26—C21	-0.5 (4)
Ru1—C27—C28—C33	2.4 (4)	C26—C21—C22—C23	0.2 (4)
Ru2—O2—C69—C64	-1.2 (3)	C27—C28—C29—C30	179.2 (3)
Ru2—O2—C69—C68	178.8 (2)	C27—C28—C33—O1	0.5 (4)
Ru2—O2—C70—C71	-23.9 (3)	C27—C28—C33—C32	179.6 (3)
Ru2—O2—C70—C72	97.8 (3)	C28—C29—C30—C31	1.2 (5)
Ru2—C63—C64—C65	179.8 (2)	C29—C28—C33—O1	-179.8 (2)
Ru2—C63—C64—C69	-0.1 (3)	C29—C28—C33—C32	-0.7 (4)
Br1—C18—C19—Br2	-0.1 (4)	C29—C30—C31—C32	-1.0 (5)
Br1—C18—C19—C20	-179.3 (2)	C30—C31—C32—C33	-0.1 (5)
Br2—C19—C20—Br3	2.3 (4)	C31—C32—C33—O1	-180.0 (3)
Br2—C19—C20—N3	179.66 (19)	C31—C32—C33—C28	1.0 (4)
Br4—C54—C55—Br5	1.8 (4)	C33—O1—C34—C35	71.0 (3)
Br4—C54—C55—C56	-179.6 (2)	C33—O1—C34—C36	-167.5 (2)

Br5—C55—C56—Br6	-2.3 (4)	C33—C28—C29—C30	-0.4 (4)
Br5—C55—C56—N6	179.1 (2)	C34—O1—C33—C28	-169.8 (2)
Cl1—Ru1—C27—C28	-88.2 (2)	C34—O1—C33—C32	11.1 (4)
Cl2—Ru1—C27—C28	83.3 (2)	C37—Ru2—C63—C64	174.2 (2)
Cl3—Ru2—C63—C64	83.8 (2)	C37—N4—C38—C39	17.1 (3)
Cl4—Ru2—C63—C64	-87.1 (2)	C37—N4—C40—C41	-97.6 (3)
O1—Ru1—C27—C28	-2.7 (2)	C37—N4—C40—C45	86.6 (3)
O2—Ru2—C63—C64	-0.4 (2)	C37—N5—C39—C38	25.6 (3)
N1—C2—C3—N2	23.1 (3)	C37—N5—C52—C53	-166.3 (2)
N1—C4—C5—C6	-179.0 (2)	C38—N4—C37—Ru2	-168.9 (2)
N1—C4—C5—C10	2.4 (4)	C38—N4—C37—N5	-1.7 (3)
N1—C4—C9—C8	178.7 (2)	C38—N4—C40—C41	94.9 (3)
N1—C4—C9—C13	-0.9 (4)	C38—N4—C40—C45	-80.9 (3)
N2—C16—C17—N3	-54.5 (3)	C39—N5—C37—Ru2	153.46 (18)
N2—C16—C17—C18	121.0 (3)	C39—N5—C37—N4	-15.8 (3)
N3—C17—C18—Br1	179.91 (19)	C39—N5—C52—C53	43.1 (3)
N3—C17—C18—C19	-0.2 (3)	C40—N4—C37—Ru2	23.0 (4)
N3—C21—C22—C23	-179.5 (2)	C40—N4—C37—N5	-169.9 (2)
N3—C21—C26—C25	179.7 (3)	C40—N4—C38—C39	-173.3 (2)
N4—C38—C39—N5	-23.9 (3)	C40—C41—C42—C43	1.8 (4)
N4—C40—C41—C42	-177.2 (2)	C40—C41—C49—C50	-115.1 (3)
N4—C40—C41—C49	2.6 (4)	C40—C41—C49—C51	122.6 (3)
N4—C40—C45—C44	176.1 (2)	C40—C45—C46—C47	-105.7 (3)
N4—C40—C45—C46	-4.6 (4)	C40—C45—C46—C48	130.3 (3)

N5—C52—C53—N6	50.1 (3)	C41—C40—C45—C44	0.4 (4)
N5—C52—C53—C54	-126.7 (3)	C41—C40—C45—C46	179.7 (2)
N6—C53—C54—Br4	179.31 (19)	C41—C42—C43—C44	-0.9 (4)
N6—C53—C54—C55	0.0 (3)	C42—C41—C49—C50	64.8 (3)
N6—C57—C58—C59	-179.2 (2)	C42—C41—C49—C51	-57.6 (3)
N6—C57—C62—C61	179.6 (3)	C42—C43—C44—C45	-0.3 (4)
C1—Ru1—C27—C28	-178.3 (2)	C43—C44—C45—C40	0.6 (4)
C1—N1—C2—C3	-16.7 (3)	C43—C44—C45—C46	-178.8 (3)
C1—N1—C4—C5	98.1 (3)	C44—C45—C46—C47	73.6 (3)
C1—N1—C4—C9	-83.2 (3)	C44—C45—C46—C48	-50.4 (4)
C1—N2—C3—C2	-24.8 (3)	C45—C40—C41—C42	-1.5 (4)
C1—N2—C16—C17	166.4 (2)	C45—C40—C41—C49	178.3 (2)
C2—N1—C1—Ru1	171.3 (2)	C49—C41—C42—C43	-178.1 (3)
C2—N1—C1—N2	1.9 (3)	C52—N5—C37—Ru2	0.6 (3)
C2—N1—C4—C5	-94.6 (3)	C52—N5—C37—N4	-168.6 (2)
C2—N1—C4—C9	84.1 (3)	C52—N5—C39—C38	179.1 (2)
C3—N2—C1—Ru1	-155.74 (18)	C52—C53—C54—Br4	-3.4 (4)
C3—N2—C1—N1	15.2 (3)	C52—C53—C54—C55	177.3 (3)
C3—N2—C16—C17	-41.6 (3)	C53—N6—C56—Br6	-179.2 (2)
C4—N1—C1—Ru1	-20.7 (4)	C53—N6—C56—C55	-0.4 (3)

C4—N1—C1—N2	169.9 (2)	C53—N6—C57—C58	63.8 (4)
C4—N1—C2—C3	174.2 (2)	C53—N6—C57—C62	-115.4 (3)
C4—C5—C6—C7	-0.3 (4)	C53—C54—C55—Br5	-178.9 (2)
C4—C5—C10—C11	108.2 (3)	C53—C54—C55—C56	-0.3 (3)
C4—C5—C10—C12	-128.1 (3)	C54—C55—C56—Br6	179.1 (2)
C4—C9—C13—C14	-121.4 (3)	C54—C55—C56—N6	0.4 (3)
C4—C9—C13—C15	114.2 (3)	C56—N6—C53—C52	-177.2 (2)
C5—C4—C9—C8	-2.7 (4)	C56—N6—C53—C54	0.2 (3)
C5—C4—C9—C13	177.7 (2)	C56—N6—C57—C58	-109.8 (3)
C5—C6—C7—C8	-1.3 (5)	C56—N6—C57—C62	71.0 (4)
C6—C5—C10—C11	-70.4 (3)	C57—N6—C53—C52	8.3 (4)
C6—C5—C10—C12	53.4 (4)	C57—N6—C53—C54	-174.2 (2)
C6—C7—C8—C9	1.0 (5)	C57—N6—C56—Br6	-4.7 (4)
C7—C8—C9—C4	1.0 (4)	C57—N6—C56—C55	174.0 (3)
C7—C8—C9—C13	-179.4 (3)	C57—C58—C59—C60	-0.2 (4)
C8—C9—C13—C14	59.1 (4)	C58—C57—C62—C61	0.4 (4)
C8—C9—C13—C15	-65.3 (3)	C58—C59—C60—C61	0.0 (4)
C9—C4—C5—C6	2.4 (4)	C59—C60—C61—C62	0.3 (5)
C9—C4—C5—C10	-176.2 (2)	C60—C61—C62—C57	-0.5 (4)
C10—C5—C6—C7	178.3 (3)	C62—C57—C58—C59	0.0 (4)
C16—N2—C1—Ru1	-1.9 (3)	C63—C64—C65—C66	-179.5 (3)
C16—N2—C1—N1	169.1 (2)	C63—C64—C69—O2	1.0 (3)
C16—N2—C3—C2	-179.6 (2)	C63—C64—C69—C68	-179.0 (3)

C16—C17—C18—Br1	3.8 (4)	C64—C65—C66—C67	-1.7 (4)
C16—C17—C18—C19	-176.3 (3)	C65—C64—C69—O2	-179.0 (2)
C17—N3—C20—Br3	178.64 (19)	C65—C64—C69—C68	1.1 (4)
C17—N3—C20—C19	1.1 (3)	C65—C66—C67—C68	1.4 (5)
C17—N3—C21—C22	-68.7 (4)	C66—C67—C68—C69	0.0 (4)
C17—N3—C21—C26	111.6 (3)	C67—C68—C69—O2	178.7 (3)
C17—C18—C19—Br2	-179.95 (19)	C67—C68—C69—C64	-1.3 (4)
C17—C18—C19—C20	0.9 (3)	C69—O2—C70—C71	169.4 (2)
C18—C19—C20—Br3	-178.6 (2)	C69—O2—C70—C72	-68.9 (3)
C18—C19—C20—N3	-1.2 (3)	C69—C64—C65—C66	0.4 (4)
C20—N3—C17—C16	175.9 (2)	C70—O2—C69—C64	167.8 (2)
C20—N3—C17—C18	-0.5 (3)	C70—O2—C69—C68	-12.2 (4)
C20—N3—C21—C22	108.3 (3)	C73—C74—C75—C76	0.2 (5)
C20—N3—C21—C26	-71.4 (4)	C74—C73—C78—C77	0.3 (6)
C21—N3—C17—C16	-6.6 (4)	C74—C75—C76—C77	0.3 (5)
C21—N3—C17—C18	176.9 (2)	C75—C76—C77—C78	-0.5 (5)
C21—N3—C20—Br3	1.2 (4)	C76—C77—C78—C73	0.1 (6)
C21—N3—C20—C19	-176.4 (2)	C78—C73—C74—C75	-0.5 (6)

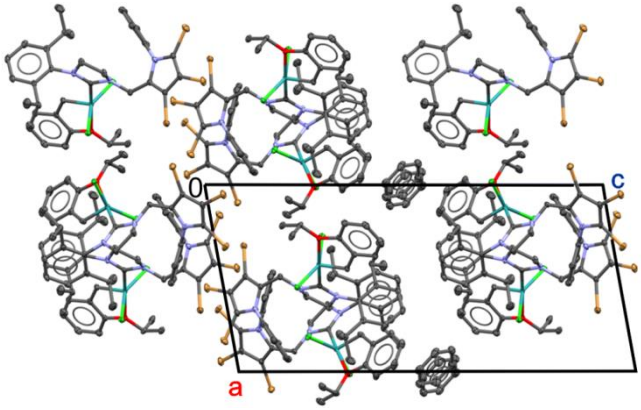


Figure S1. Molecular arrangement of Hov-5. View along the ***b*** axis. Hydrogen atoms were omitted for clarity.

4. Results of computational studies

The results of the DFT/M06-D3 studies are presented in Table S3 and are not in agreement with experimental data, probably due to the poor description of the Ru^{2+}-phenyl interactions. In view of this fact we performed domain based local pair-natural orbital coupled-cluster (DLPNO-CCSD(T)) single-point calculations on the DFT-optimized geometries and these results are presented in the manuscript.

Table S3. Total energy values (E) and free energy values (G; as defined in the manuscript) for the of the activation mechanism of precatalysts **Hov-2** and **Hov-5**. "pre" stands for pre-catalyst, "ts" for the transition state, "act" for activated catalyst, “ts2” for the transition state to the non-active conformation and “non-act” for the non-active conformation.

complex	structure	M06-D3 gas-phase, lacv3p**++ E (Hartrees)	DLPNO-CCSD(T) gas-phase E (Hartrees)	solvation E in toluene (Hartrees)	zero-point E correction (kcal/mol)	entropy (cal/mol)	thermal correction to enthalpy (kcal/mol)	G (Hartrees)
Hov-2	pre	-2650.777924	-2644.911658	-0.000369	448.047	249.789	25.133	-2650.142856
	ts	-2650.746172	-2644.876741	-0.000901	447.421	254.768	25.436	-2650.114515
	act	-2650.750034	-2644.879550	-0.000994	447.720	260.389	25.875	-2650.119964
	ts2	-2650.743761	-2644.876872	0.000154	447.714	248.096	24.801	--2650.108426
	non-act	2650.748093	-2644.881210	-0.000009	447.769	258.167	25.787	-2650.116045
Hov-5	pre	-2688.377096	-10360.136427	0.001036	428.802	280.328	28.273	-2687.780791
	ts	-2688.344761	-10360.101641	0.000349	428.104	286.552	28.622	-2687.752655
	act	-2688.353531	-10360.104627	0.000073	428.417	284.841	28.503	-2687.760580
	ts2	-2688.338972	-10360.097491	0.002118	428.771	274.862	27.797	-2687.739797
	non-act	-2688.349987	-10360.102603	0.001563	428.707	286.994	28.872	-2687.755518

Table S4. SAPT0 decomposition of the interaction energies (kcal/mol) between the phenylpyrrole and the core of the ruthenium catalyst.

complex	structure	E_{SAPT0}	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{elst} (%)	E_{ind} (%)	E_{disp} (%)
Hov-2	pre	-1.75	-1.60	13.82	-2.45	-11.52	10	16	74
	nonact	-5.83	-8.47	20.28	-4.19	-13.45	32	16	52
Hov-5	pre	-1.17	-0.72	13.54	-2.38	-11.60	5	16	79
	nonact	-7.09	-13.08	26.95	-5.27	-15.70	38	15	47

Cartesian coordinates of selected, studied systems.

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86
Hov-2
Ru1 5.5767 -0.5407 17.3426
Cl2 3.4164 -1.4838 17.7743
Cl3 7.3368 0.1624 15.8935
O4 4.5546 1.5237 16.9301
N5 6.1515 -3.3140 16.8426
N6 6.6640 -2.9113 18.9217
C7 8.8859 -1.1866 21.3238
C8 7.1307 -2.2686 20.1037
C9 5.9835 0.3860 18.8655
C10 6.2495 -2.1311 21.1888
C11 5.5453 -3.1087 15.5335
C12 6.0973 -4.6273 17.4847
C13 8.4577 -1.8131 20.1525
C14 4.7510 2.3331 17.9980
C15 5.3343 3.7849 20.3076
C16 5.7881 2.4812 20.1813
C17 8.0313 -1.0321 22.4063
C18 9.4227 -1.9662 18.9952
C19 6.8802 -4.3529 18.7536
C20 6.2719 -2.3264 17.7673
C21 5.5101 1.7380 19.0275
C22 6.7277 -1.5047 22.3396
C23 4.2968 3.6406 18.1146
C24 4.8103 -2.5958 21.1314
C25 3.8874 0.9279 14.7389
H26 8.3852 -0.5405 23.3106
C27 3.6134 1.8730 15.8849
C28 4.5975 4.3551 19.2721
H29 3.8511 2.9022 15.5734
H30 9.9069 -0.8122 21.3869
H31 6.5991 -0.0112 19.6794
H32 5.0457 -4.8910 17.6941
H33 6.5378 -5.4063 16.8529
H34 5.5510 4.3589 21.2046
H35 6.3663 2.0037 20.9729
H37 8.9051 -2.4563 18.1560
H39 7.9566 -4.5606 18.6256
H40 6.5150 -4.8983 19.6314
H41 6.0631 -1.3755 23.1931
H42 3.7188 4.1081 17.3230
H44 4.6186 -2.9974 20.1261
H46 3.2695 1.2055 13.8778
H47 4.9431 0.9594 14.4492
H48 3.6274 -0.0990 15.0293
H49 4.2428 5.3796 19.3620
C50 2.1967 1.7616 16.4080
H51 1.4865 2.0048 15.6095
H52 2.0168 0.7336 16.7450
H53 2.0093 2.4364 17.2498
H54 4.4467 -3.0721 15.6198
H55 5.8834 -2.1217 15.1761
C56 5.8979 -4.2124 14.6026
C57 5.0516 -5.1071 13.9919
C58 5.8418 -6.0806 13.3316
C59 7.1525 -5.7631 13.5734
N60 7.1974 -4.6179 14.3388
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C65 10.5183 -4.3982 15.9491
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H71 11.2294 -5.0571 16.4439
H72 9.0659 -5.9627 15.6046
H73 7.9713 -2.0524 14.2090
H74 10.0808 -1.1380 15.0894
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C74 10.5998 -2.8516 19.4018
H75 10.2617 -3.8336 19.7566
H76 11.2719 -3.0118 18.5504
H77 11.1858 -2.3921 20.2086
C77 9.8991 -0.6078 18.4869
H78 10.4313 -0.0477 19.2673
H79 10.5877 -0.7419 17.6429
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H82 4.6881 -3.3358 23.1806
H83 3.5238 -4.0721 22.0691
C83 3.8483 -1.4264 21.3353
H84 3.9616 -0.9818 22.3334
H85 4.0114 -0.6435 20.5840
H86 2.8108 -1.7652 21.2322
86
Hov-2 second conformation
Ru1 5.3848 -0.6264 17.4891
Cl2 3.1727 -0.8564 18.4260
Cl3 7.3318 -0.3612 16.0738
O4 4.7303 1.5225 16.8278
N5 5.8569 -3.4930 17.2236
N6 6.2481 -2.9080 19.2938
C7 8.6361 -1.1717 21.5118
C8 6.7618 -2.1853 20.4114
C9 6.0238 0.4044 18.8674
C10 5.9244 -1.8944 21.4974
C11 5.8832 -3.3993 15.7693
C12 6.4001 -4.7035 17.8380
C13 8.1229 -1.8253 20.3923
C14 4.9683 2.3786 17.8460
C15 5.6659 3.9380 20.0555
C16 6.0304 2.6018 20.0138
C17 7.8285 -0.8850 22.6047
C18 9.0257 -2.1032 19.2063
C19 6.2857 -4.3746 19.3136
C20 5.9117 -2.4225 18.0730
C21 5.6869 1.8015 18.9164
C22 6.4874 -1.2404 22.5947
C23 4.5961 3.7170 17.8827
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C25 4.2572 0.9540 14.5784
H26 8.2487 -0.3758 23.4699
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H30 9.6845 -0.8771 21.5249
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H33 7.4482 -4.8524 17.5233
H34 5.9292 4.5552 20.9103
H35 6.5805 2.1395 20.8337
H37 8.4032 -2.4262 18.3610
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H42 4.0353 4.1694 17.0704
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H55 6.0600 -4.4202 15.3959
C56 4.6006 -2.8716 15.2198
C57 3.3586 -2.7940 15.8086
C58 2.4281 -2.3991 14.8144
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C65 7.5401 -1.9714 11.9147
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C68 5.1693 -3.4103 11.7325
C69 6.0968 -3.4680 10.7005
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H75 4.7975 -4.3127 22.1553
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H77 3.1364 -3.7287 22.3931
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H78 3.7229 -0.7618 22.9188
H79 3.8009 -0.1968 21.2267
H80 2.5253 -1.3080 21.7320
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H81 9.4887 -4.1493 19.8301
H82 10.6311 -3.4618 18.6570
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86
Hov-2-ts

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N5 6.5086 -3.4088 16.5142
N6 6.5454 -2.9385 18.6470
C7 8.2391 -1.1763 21.4206
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C9 6.0933 0.3736 18.3597
C10 5.6598 -2.0314 20.7264
C11 6.2249 -3.2554 15.0904
C12 6.3015 -4.7001 17.1727
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H41 5.0622 -1.1716 22.6038
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H47 1.6862 0.5543 16.4268
H48 1.3818 0.1068 18.1075
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C58 6.9686 -6.3688 13.2176
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N60 8.0866 -4.8214 14.3781
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H62 6.7473 -7.2491 12.6285
H63 9.1686 -6.4940 13.6139
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C67 9.1567 -4.2256 15.0961
C68 9.4632 -2.8789 14.9350
C69 10.5235 -2.3279 15.6440
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H71 11.5727 -5.0910 17.3191
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H75 9.9050 -3.8668 20.3187
H76 11.1437 -3.1067 19.2989
H77 10.7236 -2.3943 20.8654
C77 9.8235 -0.7188 18.8215
H78 10.1257 -0.0889 19.6688
H79 10.7091 -0.8875 18.1963
H80 9.0963 -0.1683 18.2106
C80 3.7348 -3.5057 21.3414
H81 4.3994 -4.3778 21.3886
H82 3.6535 -3.1004 22.3590
H83 2.7383 -3.8526 21.0432
C83 3.3093 -1.2489 20.3078
H84 3.2113 -0.7679 21.2910
H85 3.6554 -0.4982 19.5850
H86 2.3085 -1.5716 19.9927

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Hov-2-act

Ru1 5.6471 -0.5898 17.4989
Cl2 3.4159 -1.3916 17.5835
Cl3 7.5016 0.0812 16.1786
O4 3.5281 1.1785 20.2947
N5 6.1948 -3.3382 16.7920
N6 6.7667 -3.0250 18.8739
C7 8.7962 -1.1805 21.3571
C8 7.1838 -2.4130 20.0892
C9 5.8034 0.2370 19.0995
C10 6.3194 -2.4803 21.1933
C11 5.6222 -3.0872 15.4723
C12 6.2813 -4.6894 17.3505
C13 8.4413 -1.7918 20.1542
C14 4.2371 2.1109 19.6279
C15 5.8152 3.8826 18.1294
C16 6.1815 2.5474 18.2411
C17 7.9427 -1.2013 22.4517
C18 9.4251 -1.8134 19.0024

C19 7.1077 -4.4246 18.5933
C20 6.2888 -2.4083 17.7707
C21 5.4172 1.6477 18.9946
C22 6.7208 -1.8552 22.3739
C23 3.8769 3.4530 19.5145
C24 4.9725 -3.1683 21.1242
C25 1.4094 0.1867 20.6795
H26 8.2367 -0.7096 23.3769
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C28 4.6654 4.3250 18.7680
H29 1.7507 2.1801 19.9925
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H74 10.1891 -1.0602 15.0378
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C77 9.9660 -0.4255 18.6725
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H83 3.9082 -4.8068 22.0672
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C13 8.0189 -2.7444 21.2862
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C15 7.7872 2.7722 17.5771
C16 7.6968 1.4728 18.0664
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C18 9.3289 -3.0113 20.5786
C19 6.7095 -5.2099 19.4233
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C22 5.6152 -2.2451 22.6428
C23 5.5946 3.2555 18.4826
C24 4.2178 -3.2100 20.7908
C25 2.0889 1.1174 19.6309
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H33 8.5074 0.7609 17.9137
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C12 5.9044 -4.5762 17.4132
C13 7.8629 -2.0877 20.6064
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C16 4.1902 2.0441 19.0812
C17 7.1933 -1.4715 22.8517
C18 8.9594 -2.1850 19.5644
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C20 6.0907 -2.3243 17.9090
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C24 4.0918 -2.7463 21.0597
C25 10.0757 2.6949 18.5180
H26 7.4535 -1.0812 23.8336
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C28 4.6363 4.3970 18.9272
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H85 3.3745 -0.7012 20.8905
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Cl3 7.5087 0.0581 15.9533
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C10 6.3683 -2.1781 21.2561
C11 5.7318 -3.1476 15.5944
C12 6.2447 -4.6772 17.5450
C13 8.5766 -1.8517 20.2225
C14 4.8941 2.2748 18.0445
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C16 5.9167 2.4320 20.2342
C17 8.1419 -1.0643 22.4726
C18 9.5396 -1.9896 19.0612
C19 7.0057 -4.4075 18.8286
C20 6.4272 -2.3788 17.8317
C21 5.6506 1.6858 19.0792
C22 6.8411 -1.5438 22.4049
C23 4.4300 3.5792 18.1572
C24 4.9301 -2.6443 21.1955
C25 4.0528 0.8572 14.7843
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C27 3.7696 1.8042 15.9264
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H31 6.7405 -0.0581 19.7428
H32 5.1845 -4.9252 17.7307
H33 6.6895 -5.4660 16.9280
H34 5.6595 4.3085 21.2545
H35 6.4928 1.9594 21.0302
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H55 6.1177 -2.1873 15.2155
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C58 5.9074 -6.0952 13.3318
C59 7.2271 -5.7462 13.4798
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Br58 5.2240 -7.5377 12.2969
Br59 8.7450 -6.5408 12.6494
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C65 10.5088 -4.3163 16.1191
C66 9.3341 -4.8508 15.6109
C67 8.5217 -4.0651 14.7941
C68 8.8597 -2.7530 14.4978
C69 10.0299 -2.2183 15.0278
H70 11.7809 -2.5802 16.2215
H71 11.1511 -4.9255 16.7519
H72 9.0408 -5.8761 15.8320
H73 8.2082 -2.1503 13.8694
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H75 10.3999 -3.8688 19.7756

H76 11.4101 -2.9933 18.6059
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H80 9.1595 -0.0012 18.2536
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H82 4.7960 -3.3615 23.2518
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Cl3 7.6857 -0.4479 15.8709
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C10 5.7637 -1.7791 21.1850
C11 5.9358 -3.4381 15.6065
C12 6.7099 -4.6457 17.6693
C13 8.1334 -1.7123 20.5197
C14 5.2330 2.4687 17.6390
C15 5.7878 3.9485 19.9440
C16 6.1761 2.6206 19.8673
C17 7.4168 -0.7201 22.6078
C18 9.2417 -1.9890 19.5234
C19 6.6704 -4.2689 19.1401
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C21 5.9015 1.8610 18.7226
C22 6.1048 -1.0954 22.3529
C23 4.8344 3.7989 17.7127
C24 4.3271 -2.1670 20.9156
C25 4.7073 1.2240 14.2774
H26 7.6591 -0.1833 23.5231
C27 4.2982 2.1060 15.4263
C28 5.1191 4.5247 18.8668
H29 4.6221 3.1378 15.2215
H30 9.4454 -0.7147 21.9017
H31 6.8307 0.0852 19.4970
H32 6.0489 -5.4888 17.4316
H33 7.7258 -4.8851 17.3180
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H35 6.6897 2.1328 20.6962
H37 8.8145 -2.5392 18.6722
H39 7.5871 -4.5311 19.6817
H40 5.8167 -4.7184 19.6691
H41 5.3247 -0.8455 23.0701
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H46 4.1956 1.5360 13.3599
H47 5.7900 1.2648 14.1198
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C58 2.2609 -2.8076 15.3053
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Br57 3.1660 -4.4589 17.5788
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Br59 1.8850 -1.1024 12.9238
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C65 6.8101 -1.5185 11.7167
C66 6.0667 -1.5063 12.8925
C67 4.9430 -2.3176 12.9897
C68 4.5603 -3.1388 11.9309
C69 5.3008 -3.1322 10.7573
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H75 4.6173 -4.2580 21.5035
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C77 3.3585 -1.0248 21.2059
H78 3.2855 -0.8087 22.2808
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H80 2.3561 -1.2897 20.8505
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C12 6.1810 -4.6428 17.2082
C13 7.9321 -1.7664 20.2346
C14 4.4890 2.4611 18.0220
C15 6.7691 4.0786 18.3112
C16 6.8669 2.7017 18.4241
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H39 7.7175 -4.5546 18.7576
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C69 10.4537 -2.2791 15.4242
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H74 10.7487 -1.2553 15.2085
C74 10.2053 -2.7967 20.0119
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H76 11.0470 -2.9740 19.3310
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C77 9.6785 -0.6293 18.8372
H78 10.0040 -0.0029 19.6784
H79 10.5440 -0.7895 18.1819
H80 8.9313 -0.0794 18.2516
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H81 4.2598 -4.3056 21.4176
H82 3.5034 -3.0175 22.3651
H83 2.6041 -3.7823 21.0461
C83 3.1872 -1.1855 20.2946
H84 3.0835 -0.6944 21.2722
H85 3.5398 -0.4426 19.5667
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86
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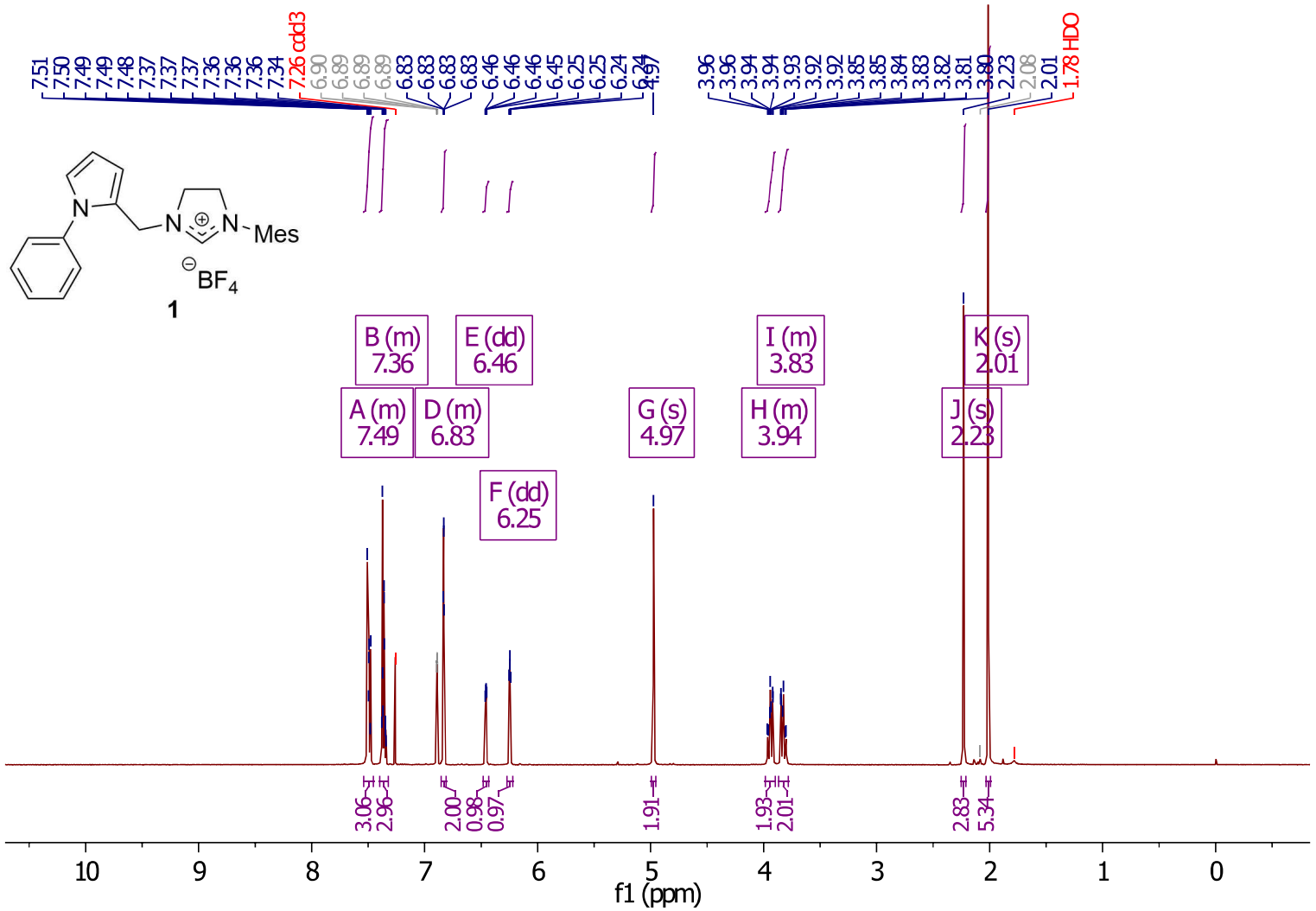
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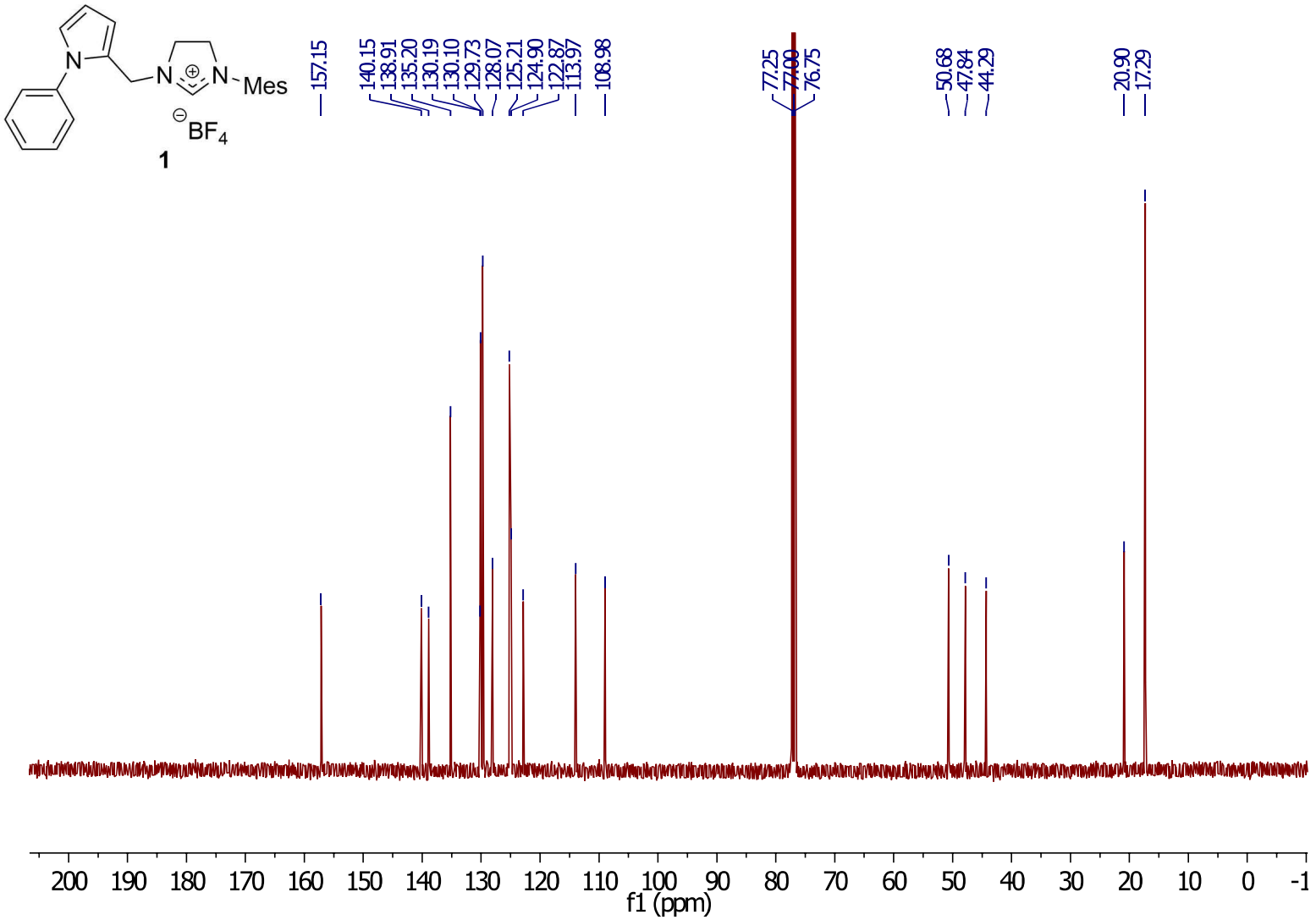
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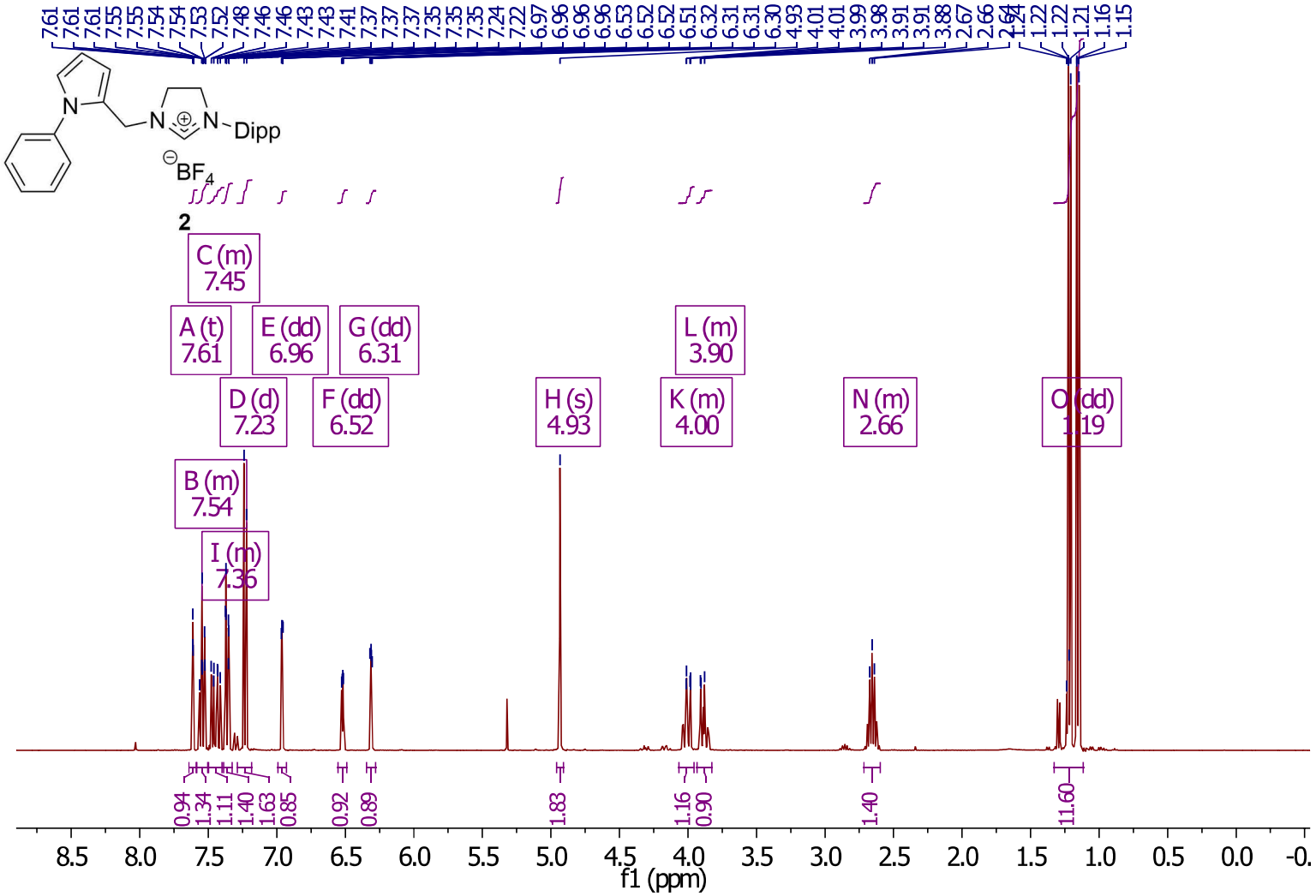
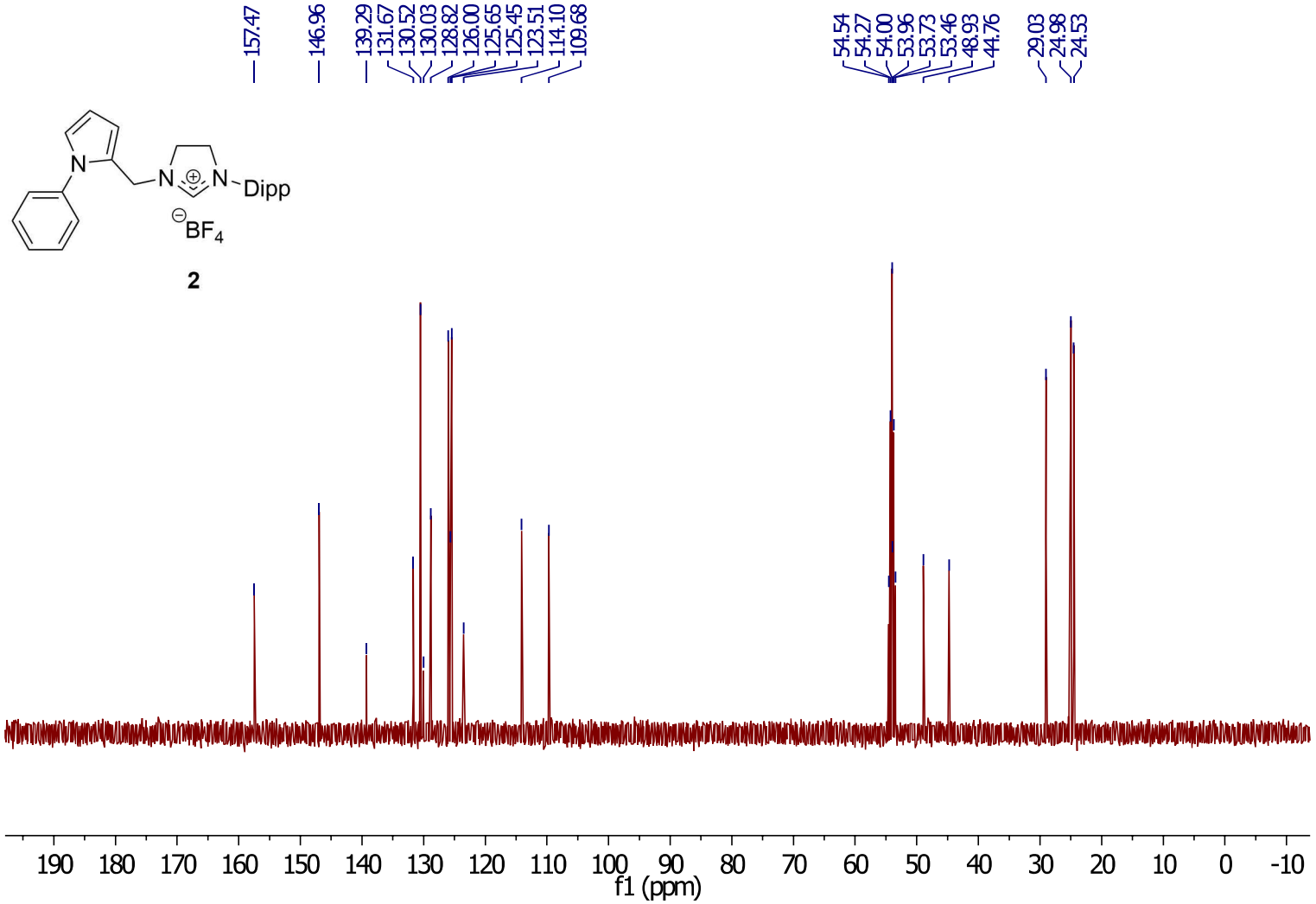
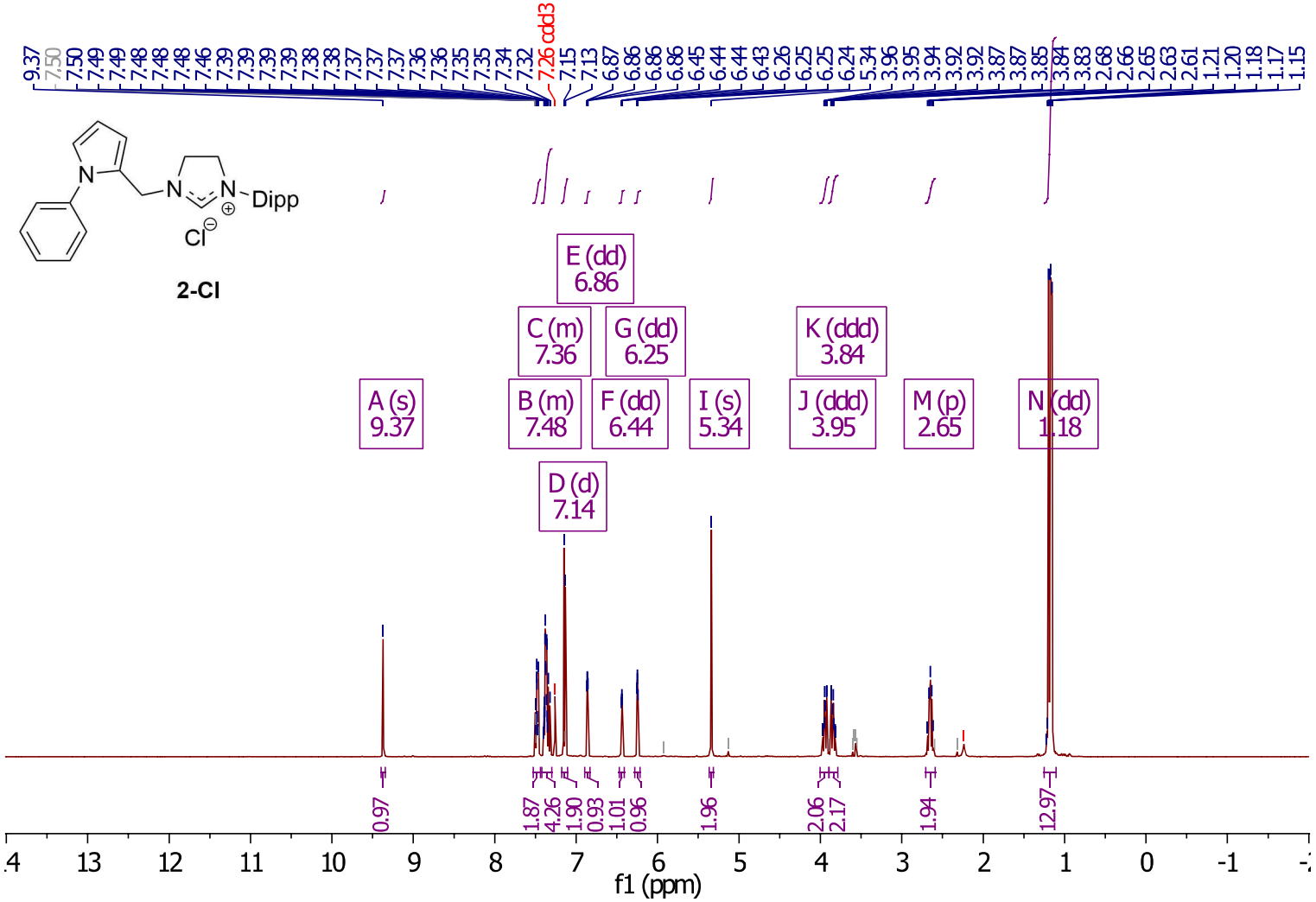
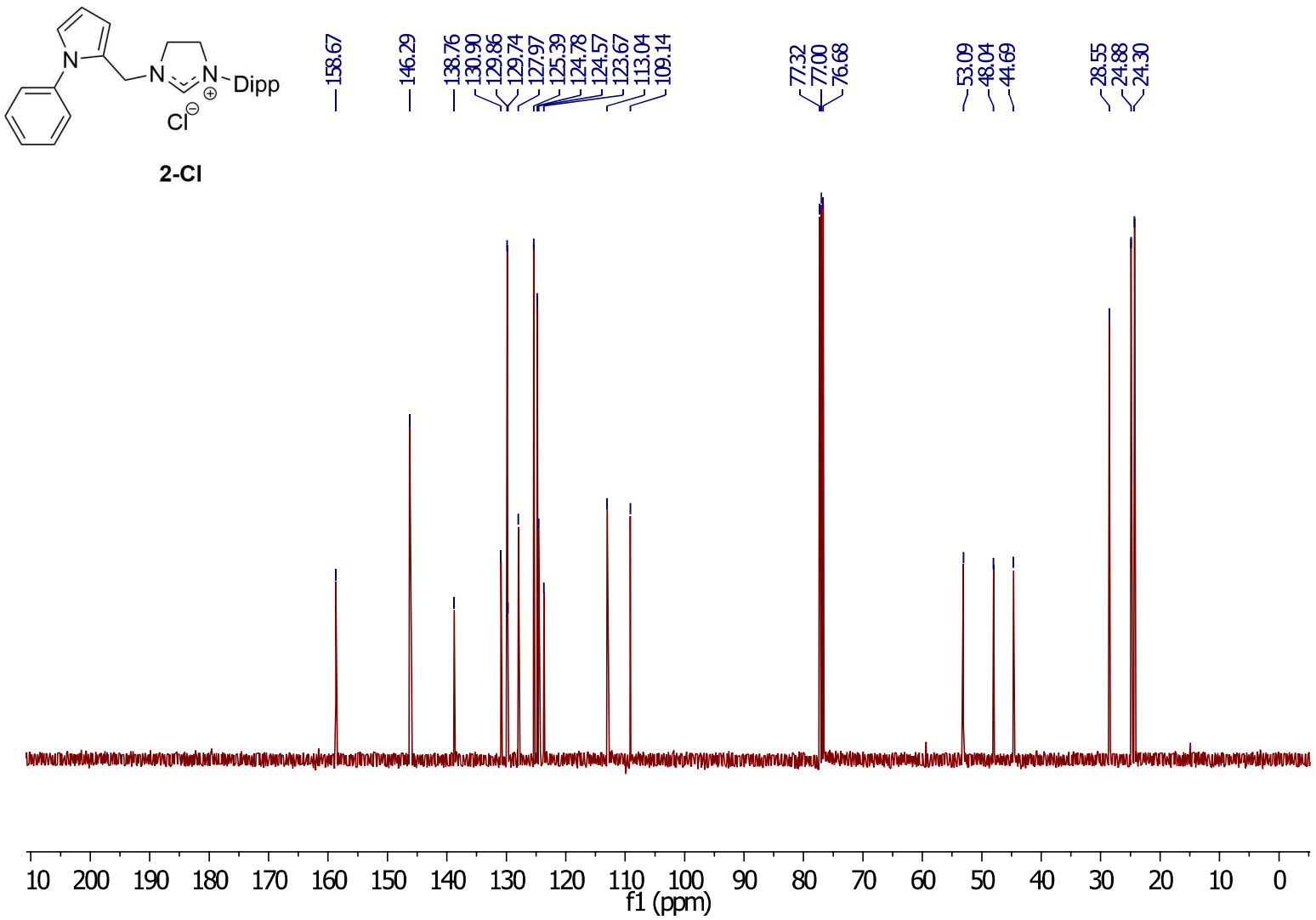
Mes
BF4
1
157.15
140.15
138.91
135.20
130.19
130.10
129.73
128.07
125.21
124.90
122.87
113.97
108.98
77.25
77.00
76.75
50.68
47.84
44.29
20.90
17.29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

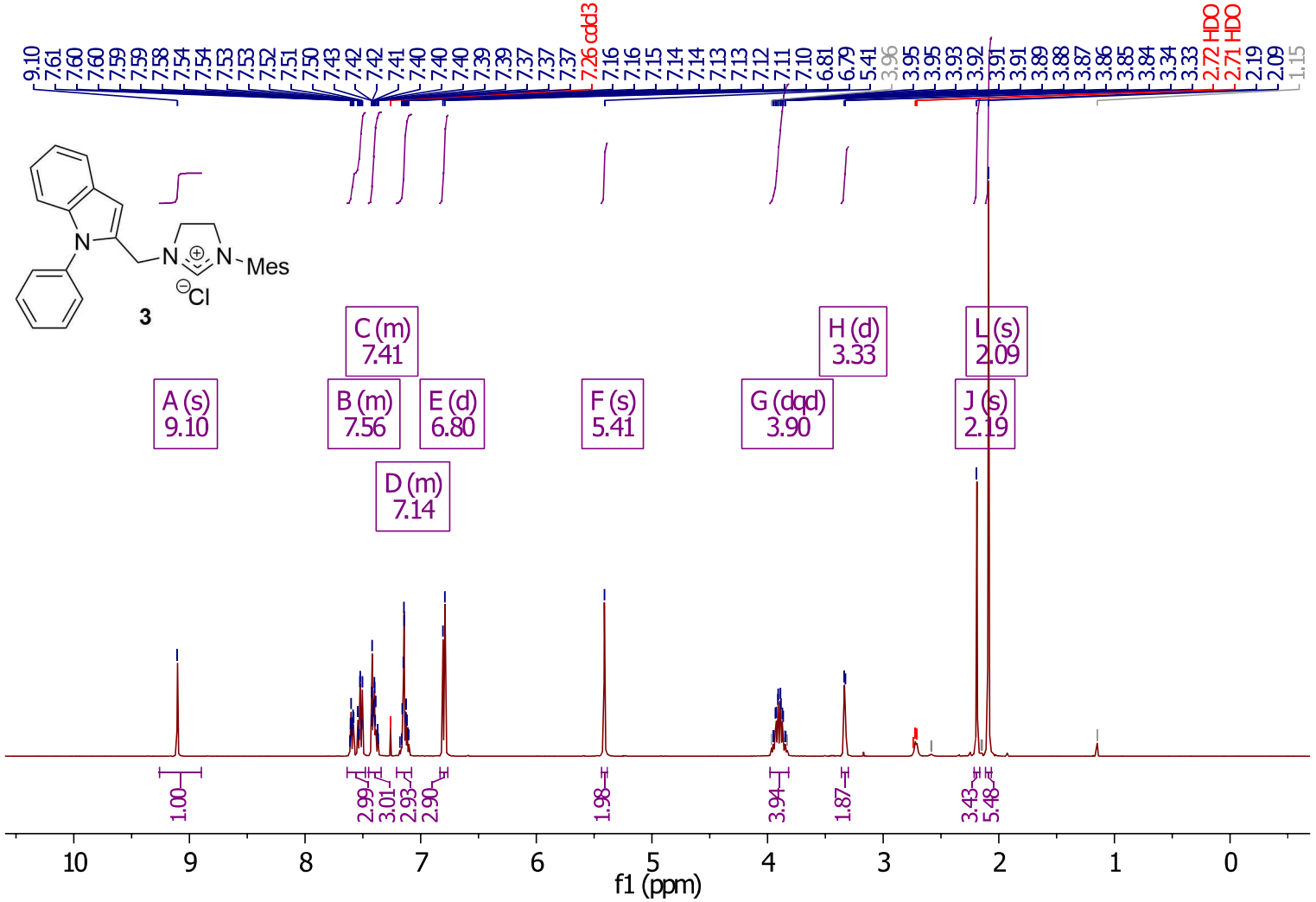

7.61 7.61 7.61 7.55 7.55 7.54 7.54 7.53 7.52 7.48 7.46 7.46 7.43 7.43 7.41 7.37 7.37 7.37 7.35 7.35 7.35 7.24 7.22 6.97 6.96 6.96 6.96 6.53 6.52 6.52 6.51 6.32 6.31 6.31 6.30 4.93 4.01 4.01 3.99 3.98 3.91 3.91 3.88 2.67 2.66 2.64 1.24 1.22 1.22 1.21 1.16 1.15
N
N
N
Dipp
BF4
2
C (m) 7.45
A (t) 7.61
E (dd) 6.96
G (dd) 6.31
L (m) 3.90
D (d) 7.23
F (dd) 6.52
H (s) 4.93
K (m) 4.00
N (m) 2.66
O (dd) 1.19
B (m) 7.54
I (m) 7.36
0.94 1.34 1.11 1.40 1.63 0.85 0.92 0.89 1.83 1.16 0.90 1.40 11.60
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.
f1 (ppm)

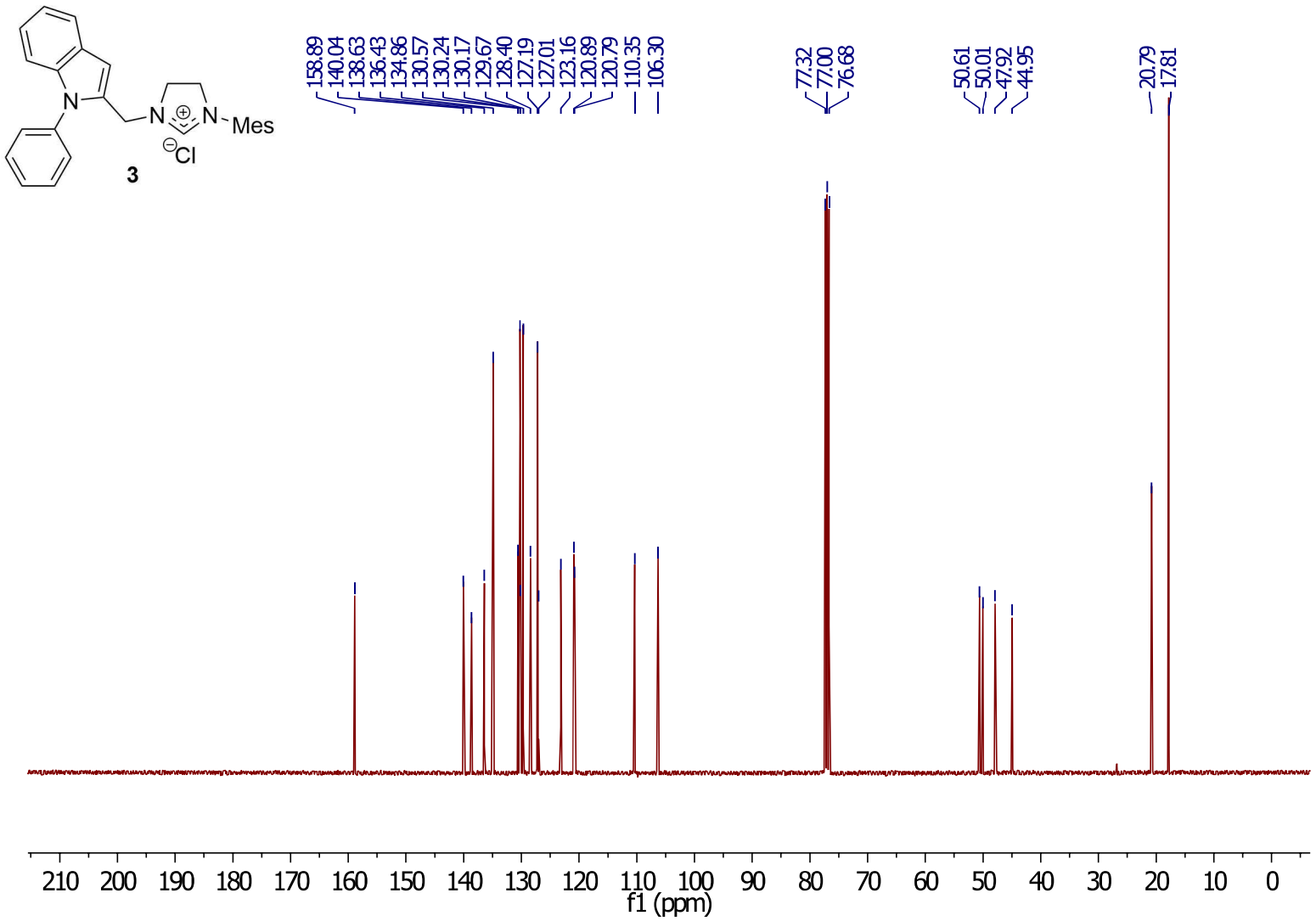

157.47
146.96
139.29
131.67
130.52
130.03
128.82
126.00
125.65
125.45
123.51
114.10
109.68
54.54
54.27
54.00
53.96
53.73
53.46
48.93
44.76
29.03
24.98
24.53
N
N
N
Dipp
BF4
2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

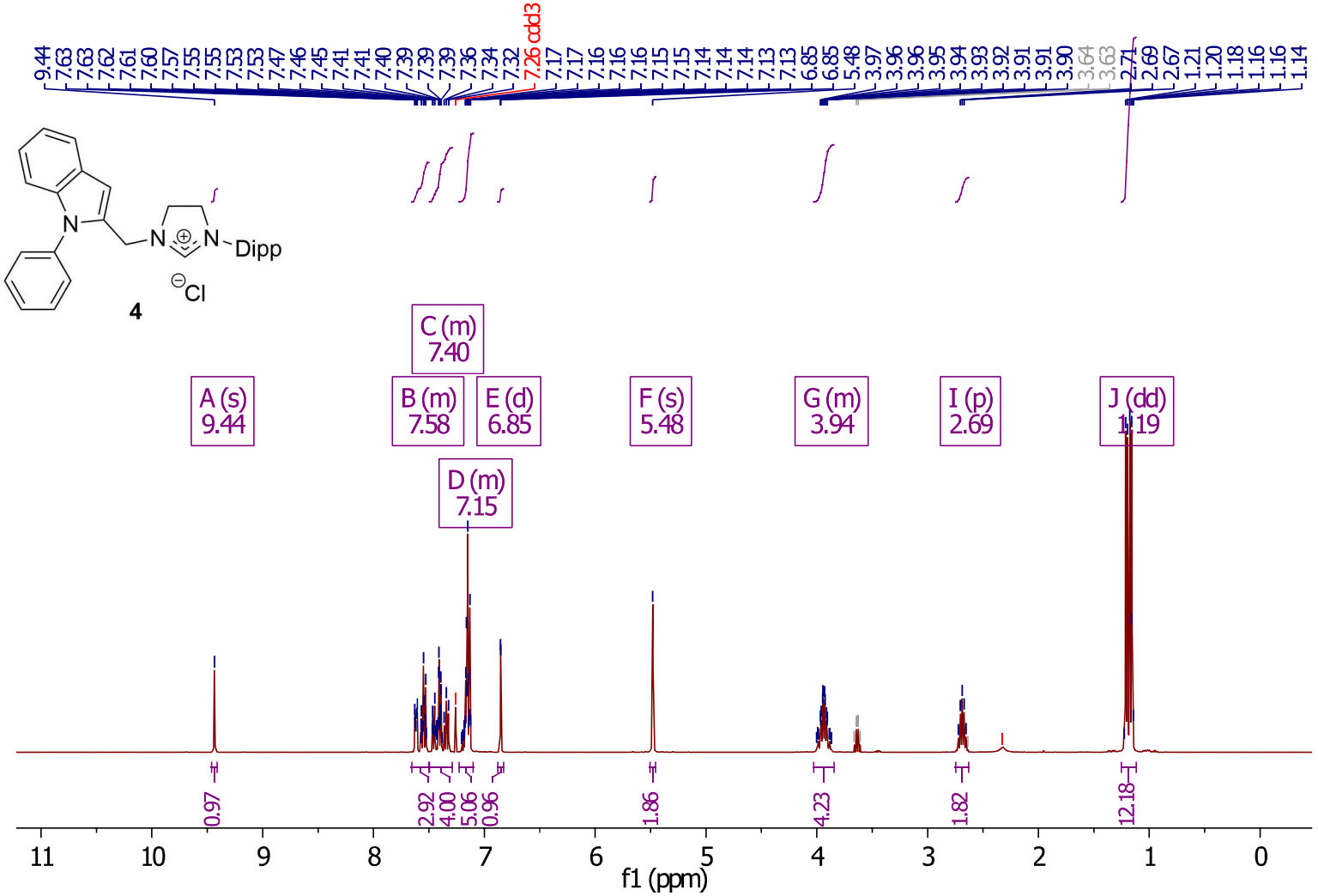

9.37
7.50
7.49
7.48
7.46
7.39
7.38
7.37
7.36
7.35
7.34
7.32
7.26 cdcl3
7.15
7.13
6.87
6.86
6.45
6.44
6.43
6.26
6.25
6.24
5.34
3.96
3.95
3.94
3.92
3.87
3.85
3.84
3.83
2.68
2.66
2.65
2.63
2.61
1.21
1.20
1.18
1.17
1.15
N
N
Dipp
Cl
2-Cl
A (s) 9.37
B (m) 7.48
C (m) 7.36
D (d) 7.14
E (dd) 6.86
F (dd) 6.44
G (dd) 6.25
I (s) 5.34
J (ddd) 3.95
K (ddd) 3.84
M (p) 2.65
N (dd) 1.18
0.97
1.87
4.26
1.90
0.93
1.01
0.96
1.96
2.06
2.17
1.94
12.97
f1 (ppm)

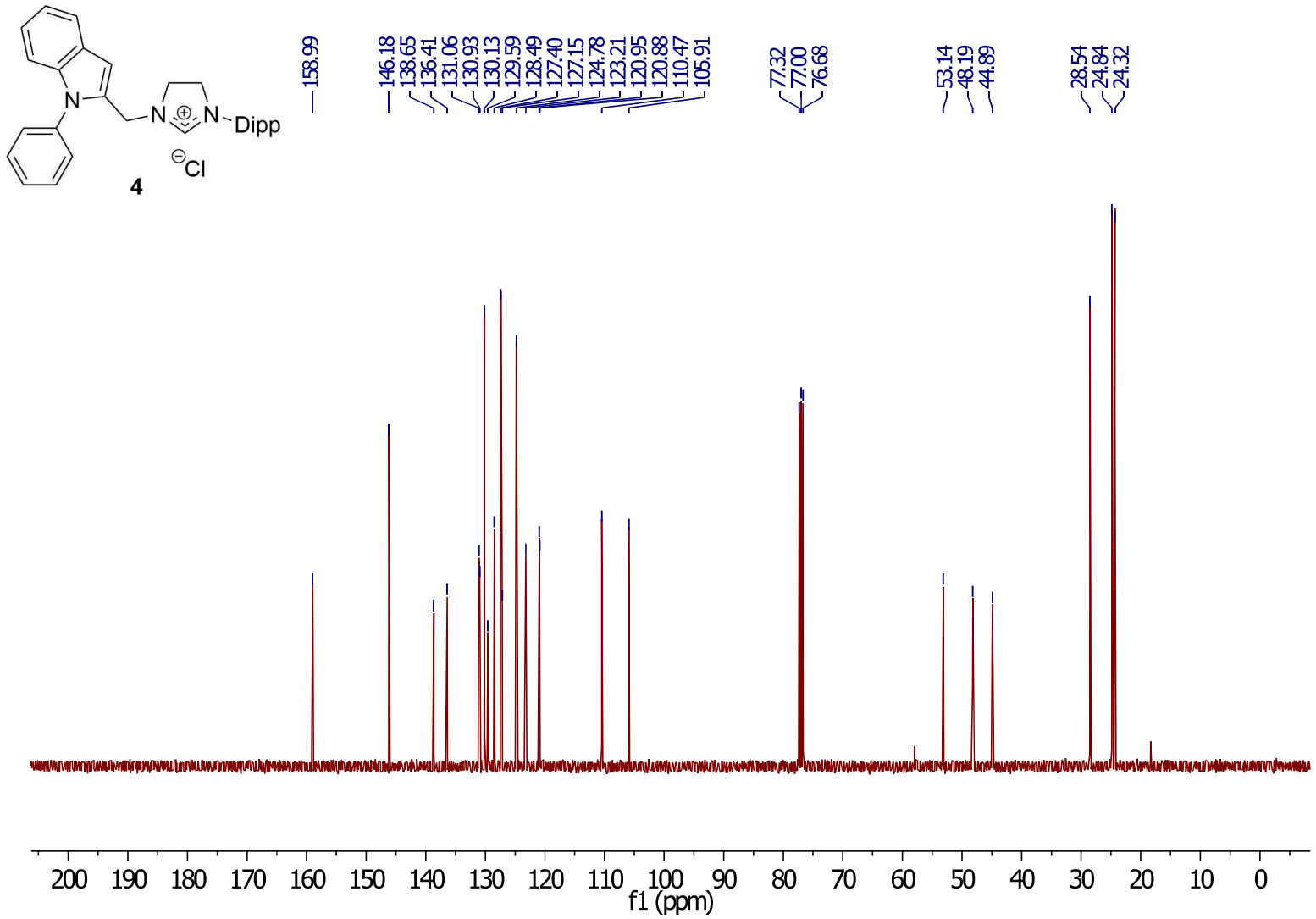

N
N
N
Dipp
Cl
158.67
146.29
138.76
130.90
129.86
129.74
127.97
125.39
124.78
124.57
123.67
113.04
109.14
77.32
77.00
76.68
53.09
48.04
44.69
28.55
24.88
24.30
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

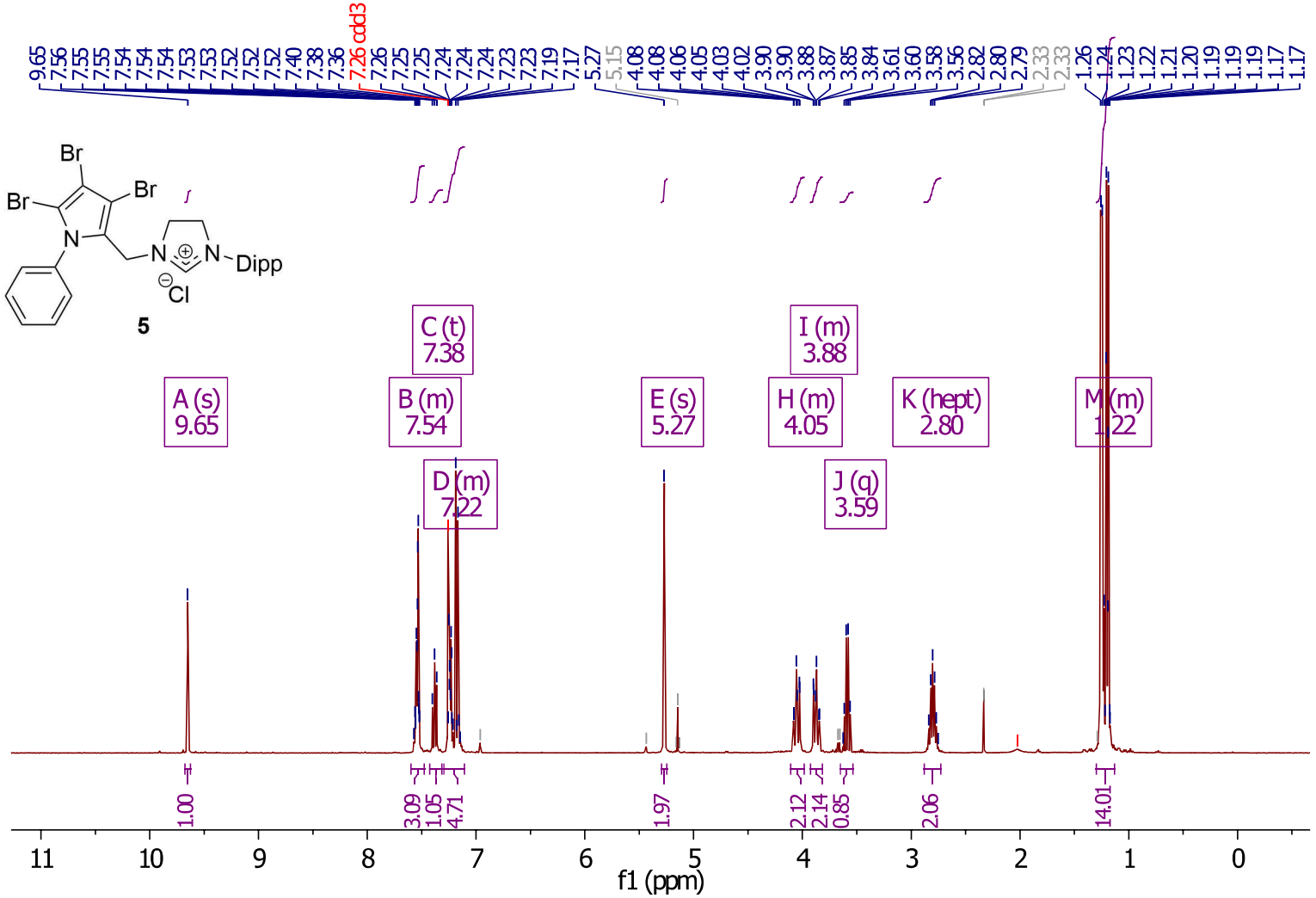
2-Cl

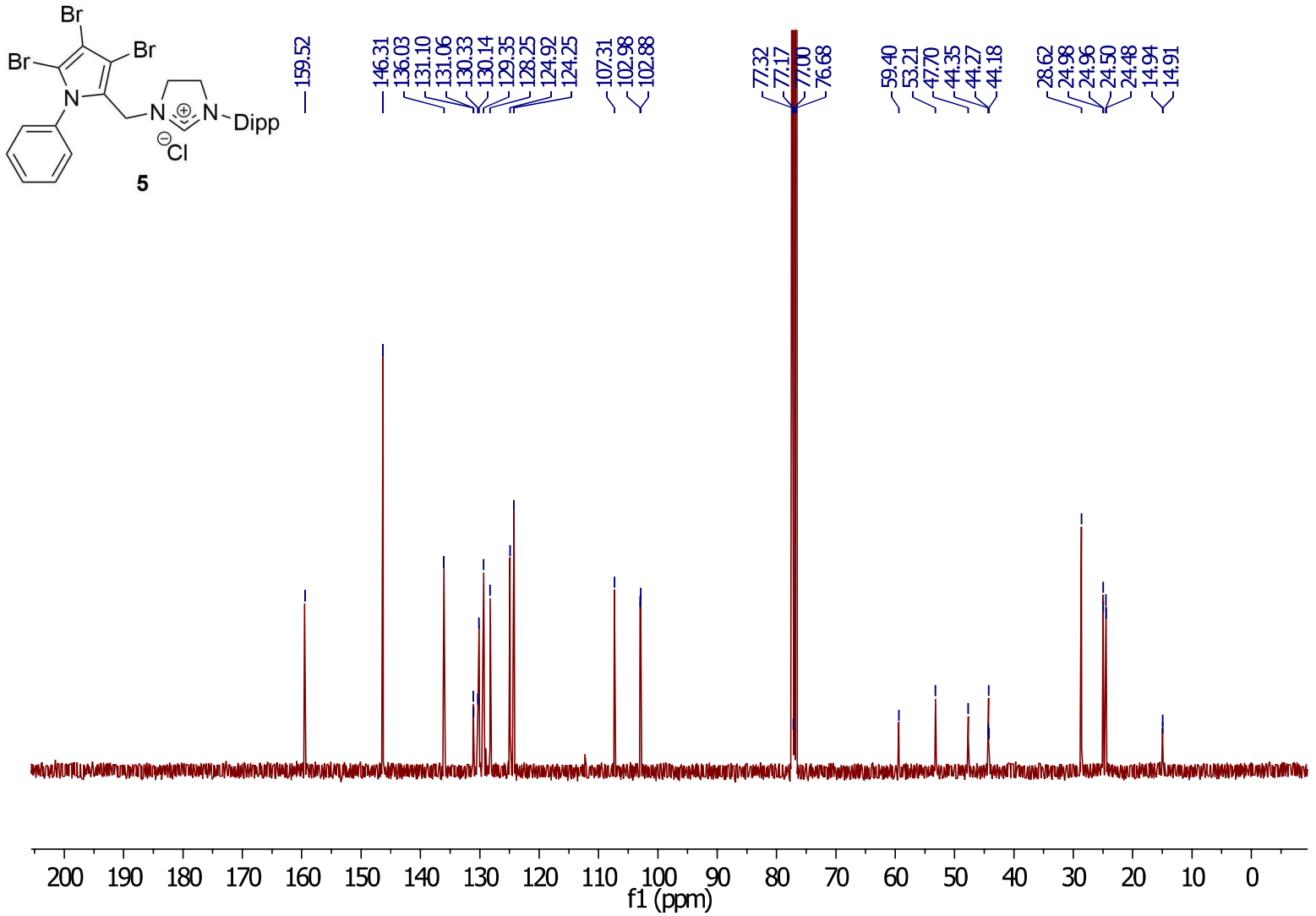

9.10
7.61
7.60
7.60
7.59
7.59
7.58
7.54
7.54
7.53
7.53
7.52
7.51
7.50
7.43
7.42
7.42
7.41
7.40
7.40
7.40
7.39
7.39
7.37
7.37
7.37
7.26 cdcl3
7.16
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.11
7.10
6.81
6.79
5.41
3.96
3.95
3.95
3.93
3.92
3.91
3.91
3.89
3.88
3.87
3.86
3.85
3.84
3.34
3.33
2.72 HDO
2.71 HDO
2.19
2.09
1.15
Mes
Cl
3
A (s)
9.10
B (m)
7.56
C (m)
7.41
D (m)
7.14
E (d)
6.80
F (s)
5.41
G (dqd)
3.90
H (d)
3.33
J (s)
2.19
L (s)
2.09
1.00
2.99
3.01
2.93
2.90
1.98
3.94
1.87
3.43
5.48
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

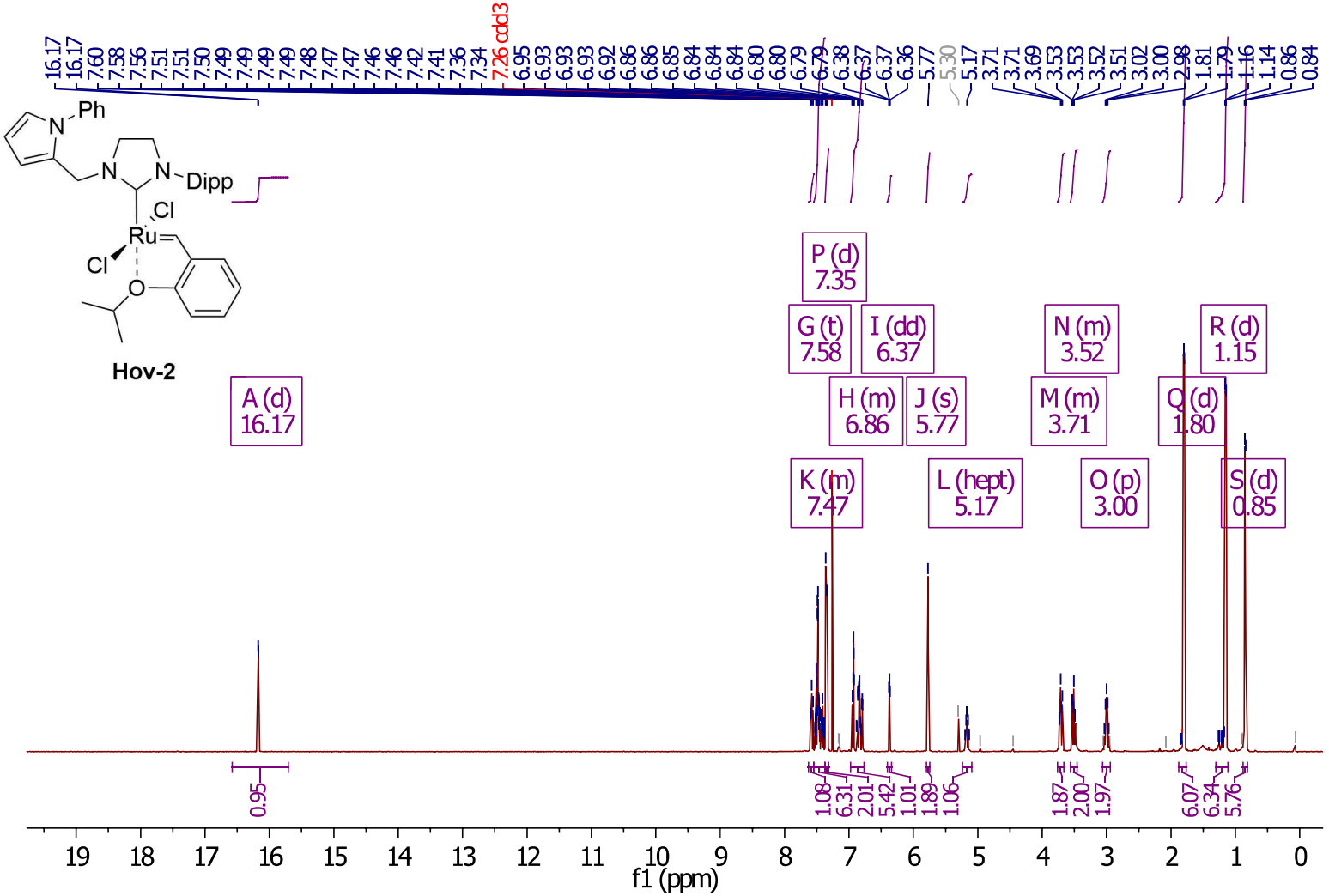

158.89
140.04
138.63
136.43
134.86
130.57
130.24
130.17
129.67
128.40
127.19
127.01
123.16
120.89
120.79
110.35
106.30
77.32
77.00
76.68
50.61
50.01
47.92
44.95
20.79
17.81
N
N
Mes
Cl
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

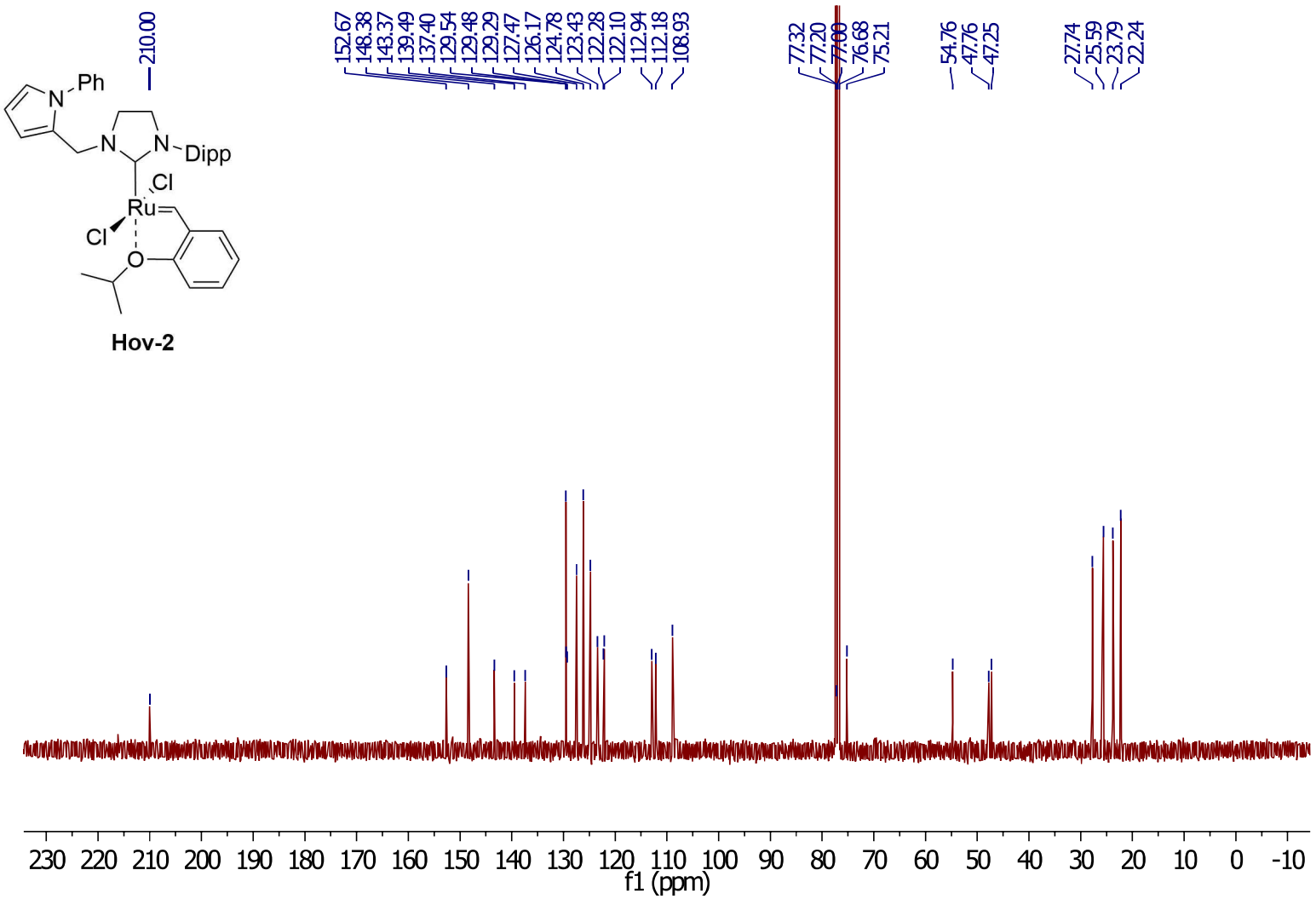

9.44
7.63
7.63
7.62
7.61
7.60
7.57
7.55
7.55
7.53
7.53
7.47
7.46
7.45
7.41
7.41
7.40
7.39
7.39
7.39
7.36
7.34
7.32
7.26 cdd3
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.14
7.14
7.14
7.13
7.13
6.85
6.85
5.48
3.97
3.96
3.96
3.95
3.94
3.93
3.92
3.91
3.91
3.90
3.64
3.63
2.71
2.69
2.67
1.21
1.20
1.18
1.16
1.16
1.14
N
N
N
Dipp
Cl
4
A (s)
9.44
C (m)
7.40
B (m)
7.58
E (d)
6.85
F (s)
5.48
G (m)
3.94
I (p)
2.69
J (dd)
1.19
D (m)
7.15
0.97
2.92
4.00
5.06
0.96
1.86
4.23
1.82
12.18
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

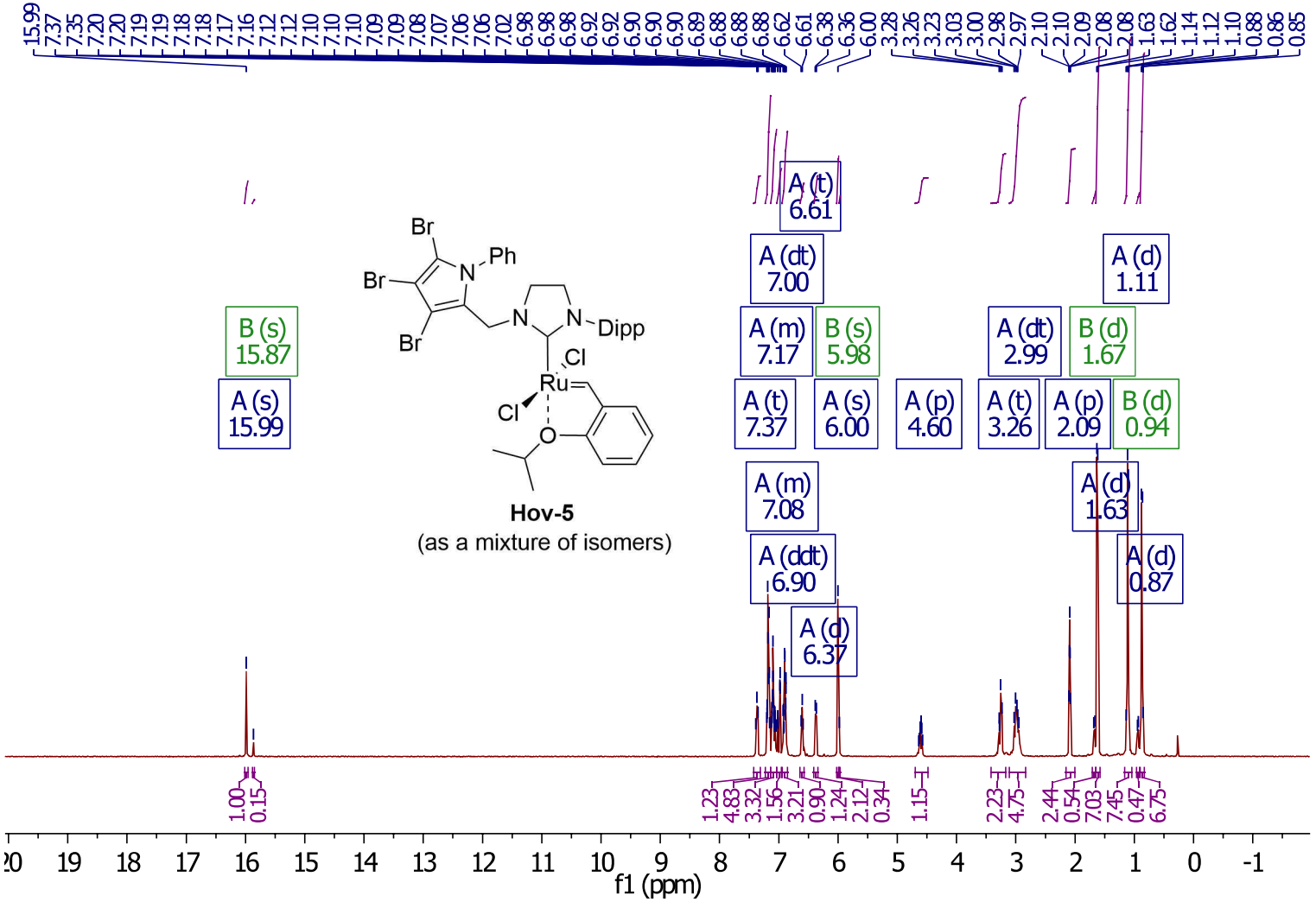

158.99
146.18
138.65
136.41
131.06
130.93
130.13
129.59
128.49
127.40
127.15
124.78
123.21
120.95
120.88
110.47
105.91
77.32
77.00
76.68
53.14
48.19
44.89
28.54
24.84
24.32
N
N
N
Dipp
Cl
4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

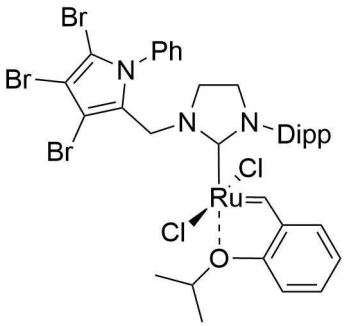

Br
Br
Br
N
N
N
Dipp
Cl
5
A (s)
9.65
B (m)
7.54
C (t)
7.38
D (m)
7.22
E (s)
5.27
H (m)
4.05
I (m)
3.88
J (q)
3.59
K (hept)
2.80
M (m)
1.22
1.00
3.09
1.05
4.71
1.97
2.12
2.14
0.85
2.06
14.01
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


Br
Br
Br
N
N
N
Dipp
Cl
5
159.52
146.31
136.03
131.10
131.06
130.33
130.14
129.35
128.25
124.92
124.25
107.31
102.98
102.88
77.32
77.17
77.00
76.68
59.40
53.21
47.70
44.35
44.27
44.18
28.62
24.98
24.96
24.50
24.48
14.94
14.91
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

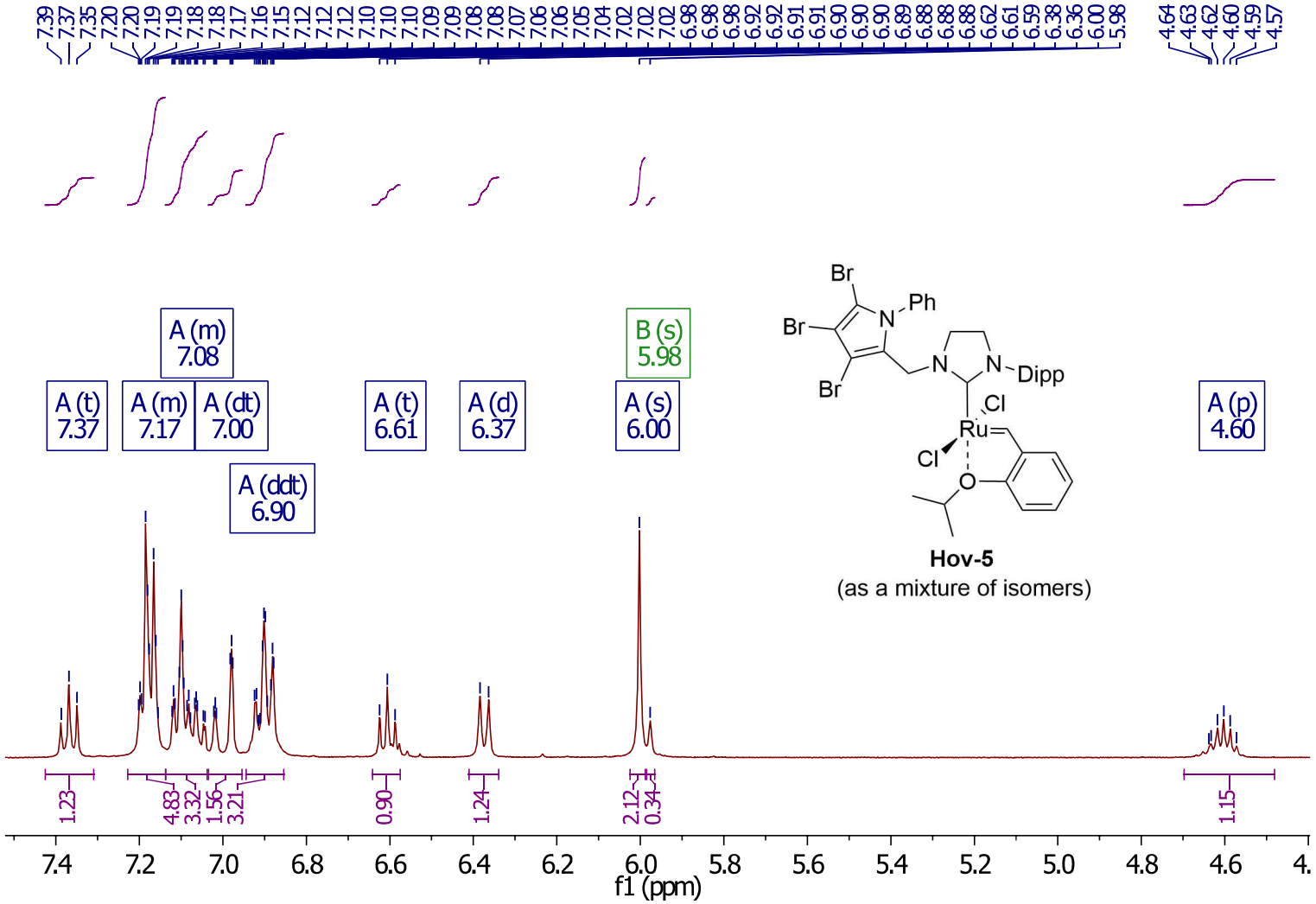

Ph
N
N
N
Dipp
Cl
Ru
Cl
O
Hov-2
A (d) 16.17
P (d) 7.35
G (t) 7.58
I (dd) 6.37
H (m) 6.86
J (s) 5.77
K (m) 7.47
L (hept) 5.17
N (m) 3.52
M (m) 3.71
O (p) 3.00
Q (d) 1.80
R (d) 1.15
S (d) 0.85
0.95
1.08
6.31
2.01
5.42
1.01
1.89
1.06
1.87
2.00
1.97
6.07
6.34
5.76
19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

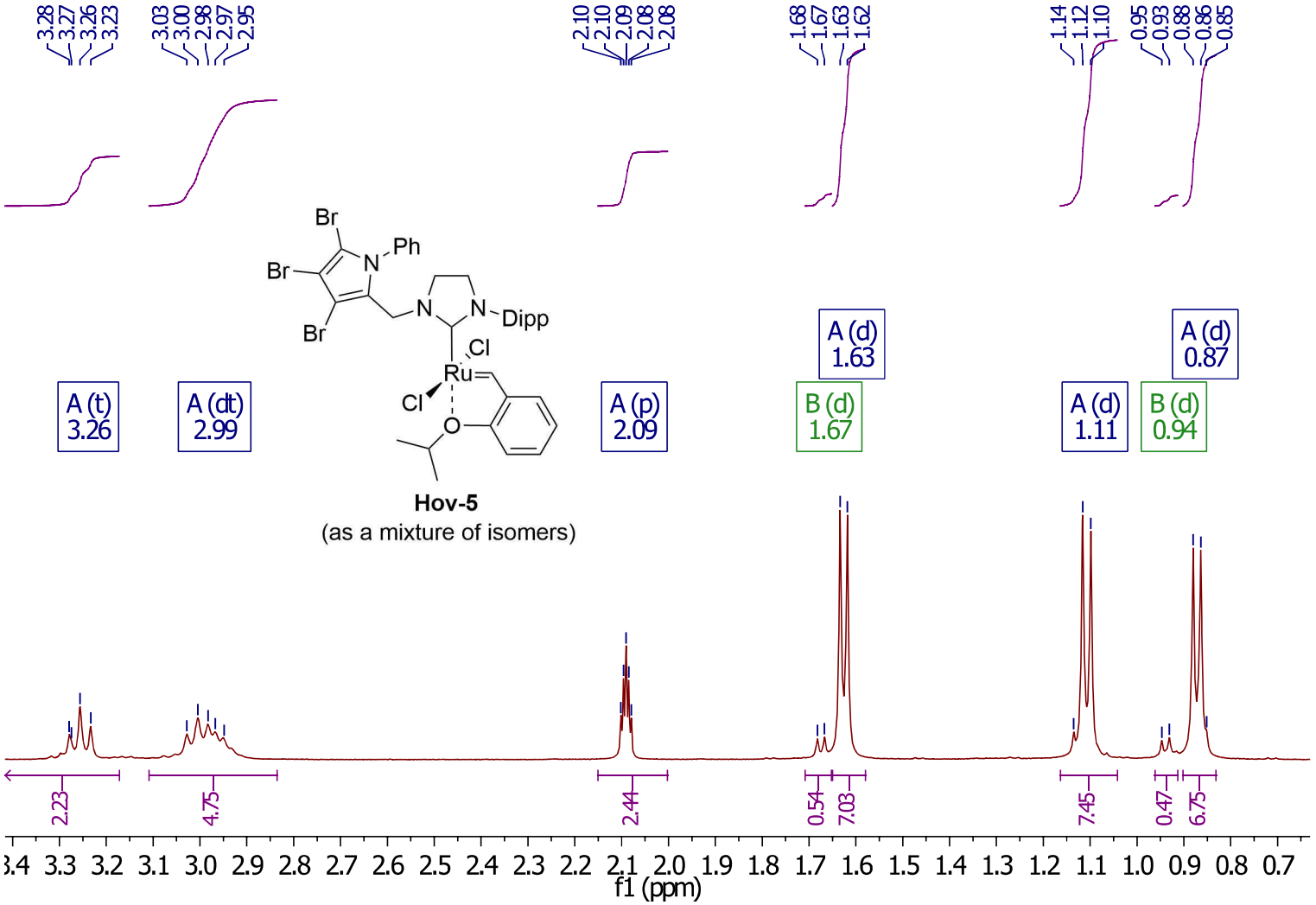

210.00
152.67
148.38
143.37
139.49
137.40
129.54
129.48
129.29
127.47
126.17
124.78
123.43
122.28
122.10
112.94
112.18
108.93
77.32
77.20
77.00
76.68
75.21
54.76
47.76
47.25
27.74
25.59
23.79
22.24
Ph
N
N
N
Dipp
Cl
Ru
Cl
O
Hov-2
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

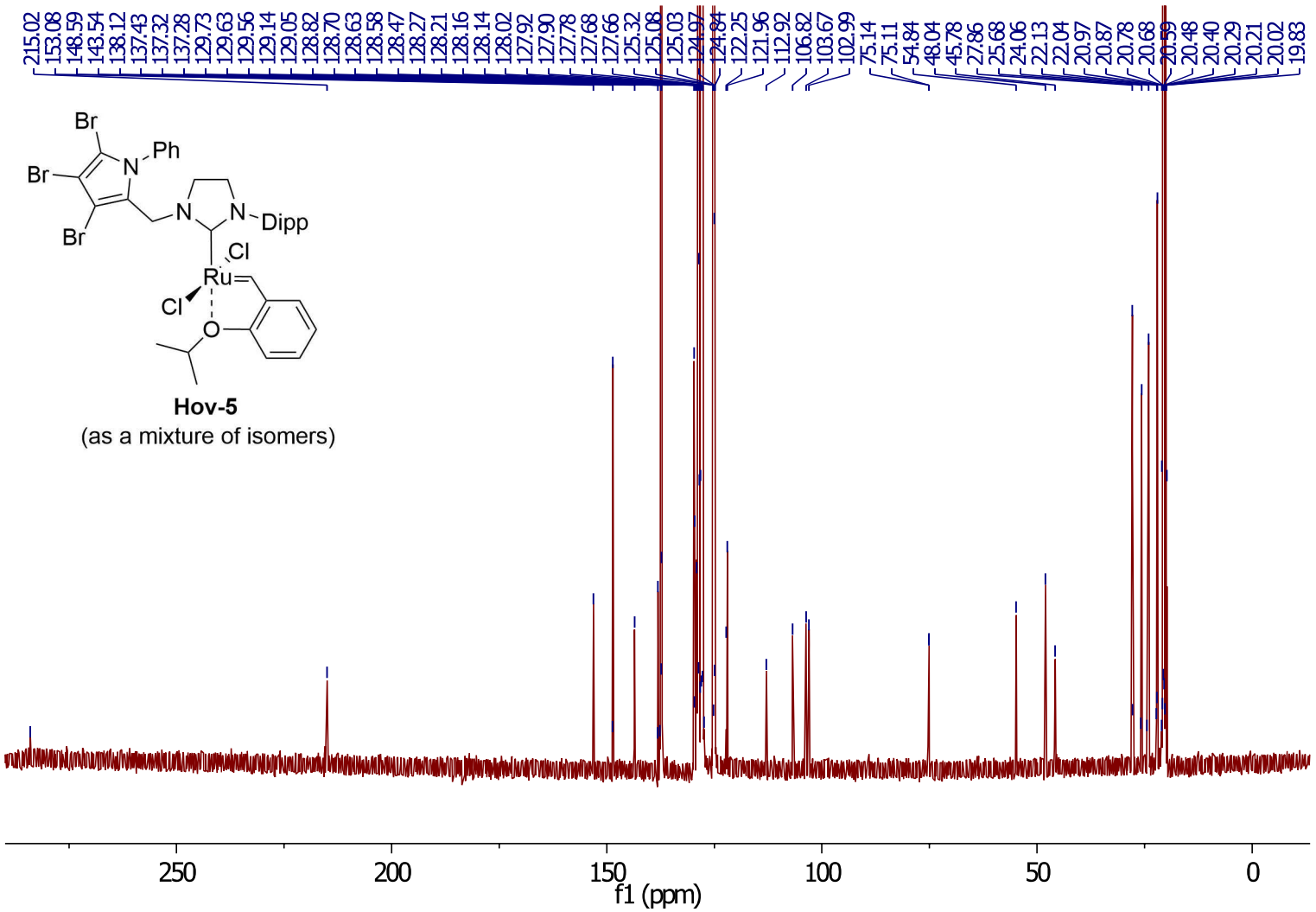

Br
Br
Br
N
Ph
N
N
Dipp
Cl
Ru
Cl
O
Hov-5
(as a mixture of isomers)
B (s) 15.87
A (s) 15.99
A (t) 6.61
A (dt) 7.00
A (m) 7.17
B (s) 5.98
A (t) 7.37
A (s) 6.00
A (p) 4.60
A (dt) 2.99
B (d) 1.67
A (t) 3.26
A (p) 2.09
B (d) 0.94
A (d) 1.11
A (m) 7.08
A (d) 1.63
A (ddt) 6.90
A (d) 0.87
A (d) 6.37
f1 (ppm)

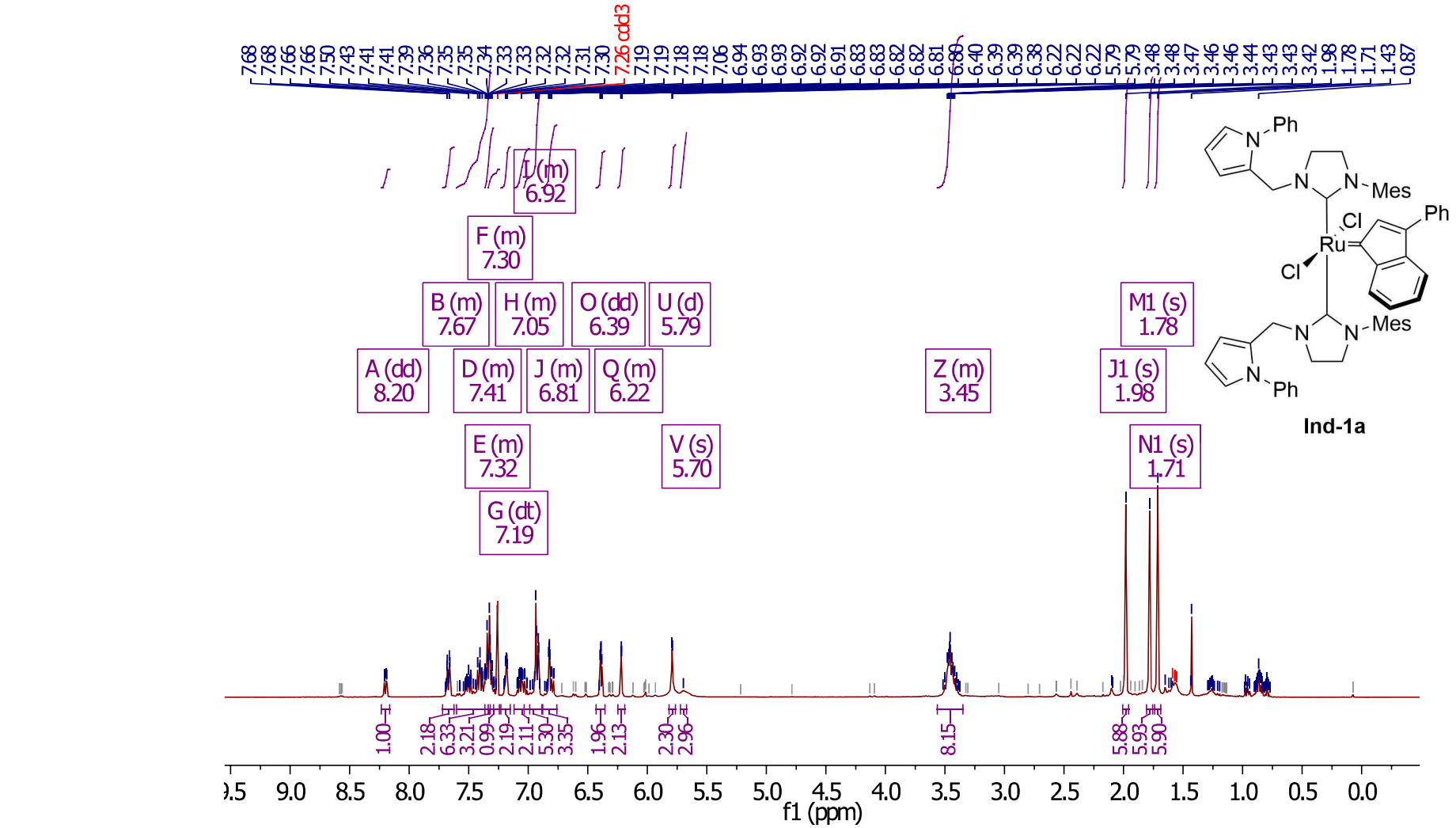


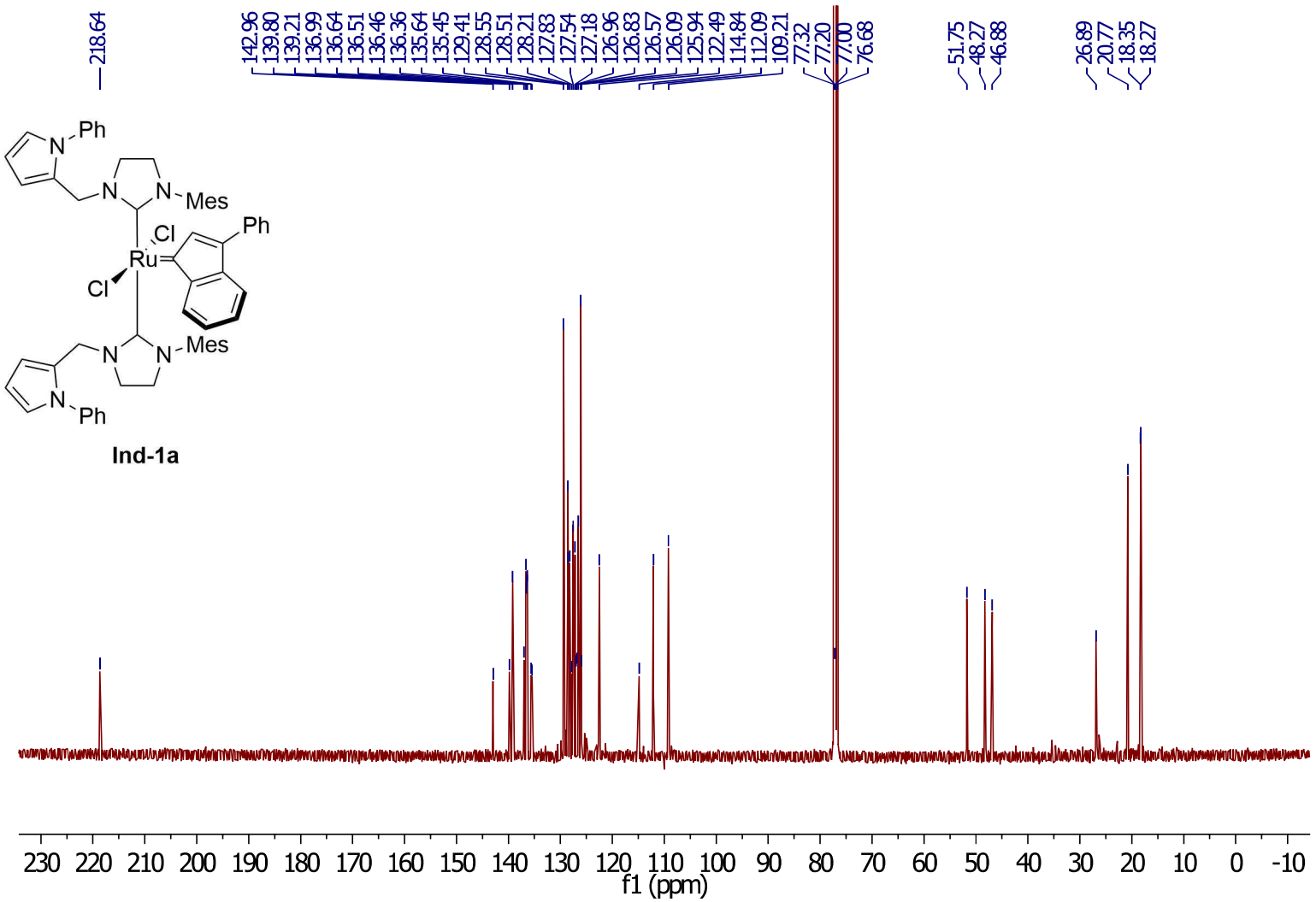
Hov-5
(as a mixture of isomers)

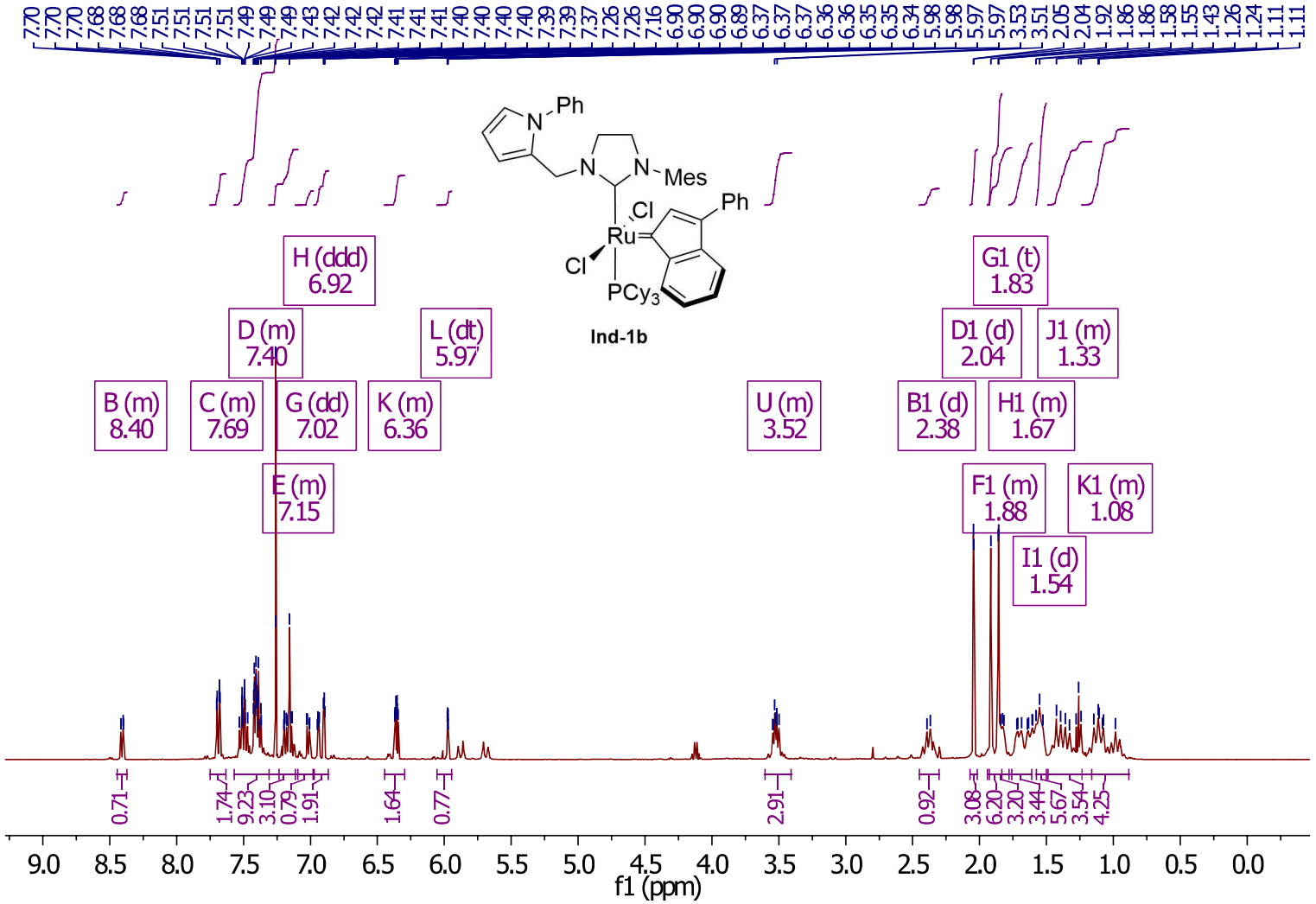

A (t) 7.37
A (m) 7.17
A (dt) 7.00
A (m) 7.08
A (ddt) 6.90
A (t) 6.61
A (d) 6.37
B (s) 5.98
A (s) 6.00
A (p) 4.60
1.23
4.83
3.32
1.56
3.21
0.90
1.24
2.12
0.34
1.15
f1 (ppm)
Br
Ph
N
Br
Br
N
N
Dipp
Cl
Ru
Cl
O
Hov-5
(as a mixture of isomers)

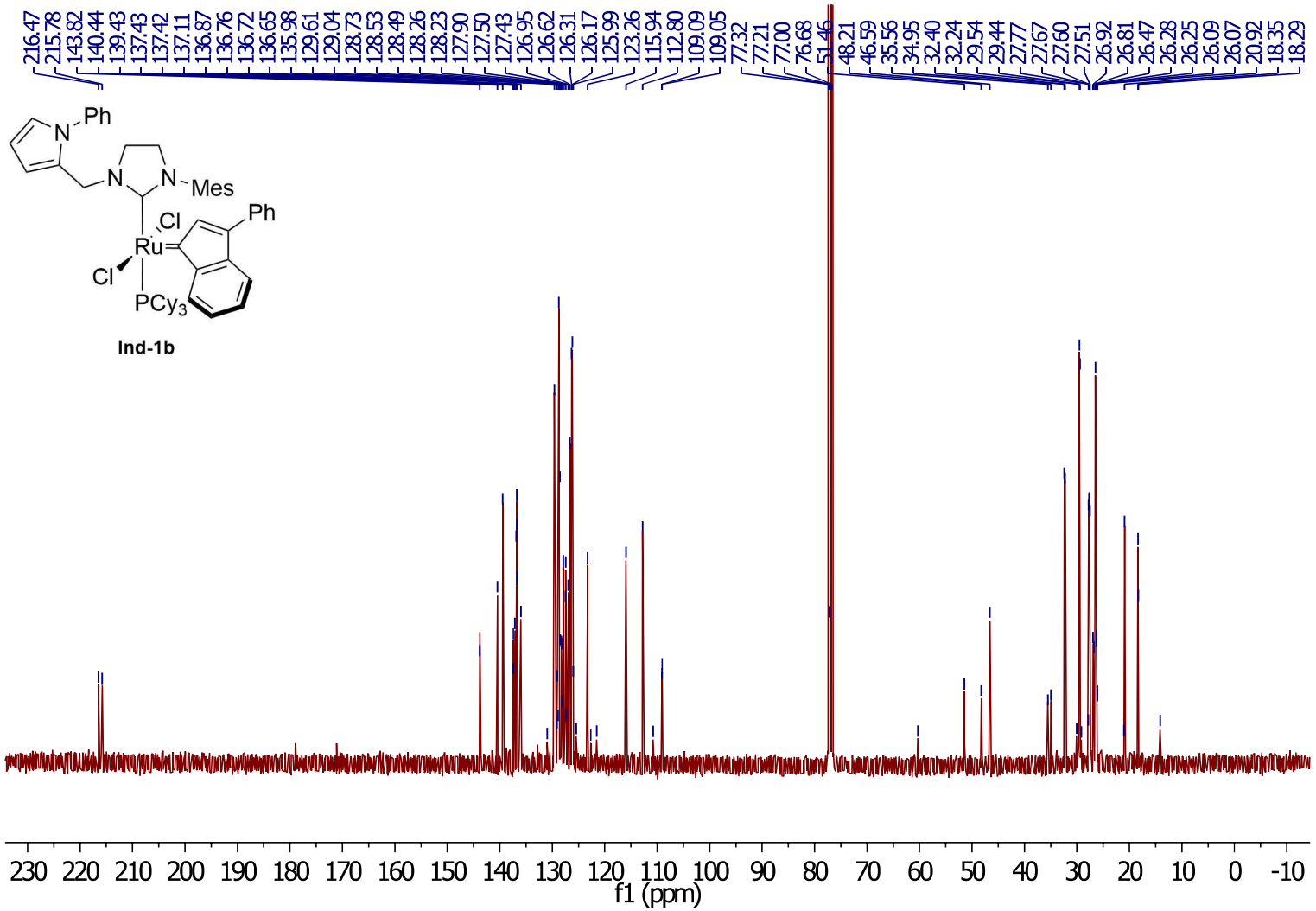

3.28
3.27
3.26
3.23
3.03
3.00
2.98
2.97
2.95
2.10
2.10
2.09
2.08
2.08
1.68
1.67
1.63
1.62
1.14
1.12
1.10
0.95
0.93
0.88
0.86
0.85
Br
Br
Br
N
Ph
N
N
Dipp
Cl
Ru
Cl
O
A (t)
3.26
A (dt)
2.99
A (p)
2.09
A (d)
1.63
B (d)
1.67
A (d)
1.11
A (d)
0.87
B (d)
0.94
Hov-5
(as a mixture of isomers)
2.23
4.75
2.44
0.54
7.03
7.45
0.47
6.75
3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7
f1 (ppm)

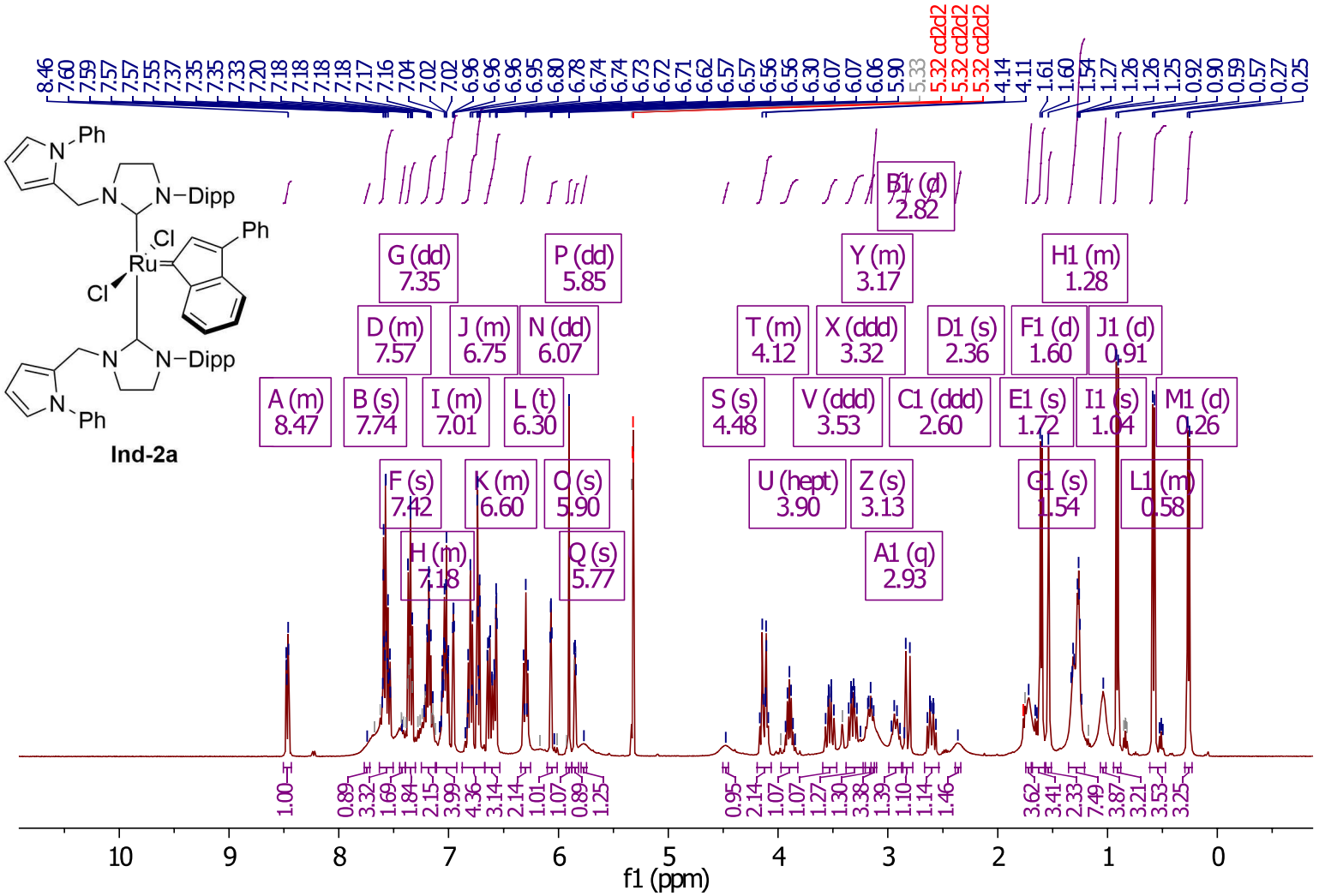

215.02
153.08
148.59
143.54
138.12
137.43
137.32
137.28
129.73
129.63
129.56
129.14
129.05
128.82
128.70
128.63
128.58
128.47
128.27
128.21
128.16
128.14
128.02
127.92
127.90
127.78
127.68
127.66
125.32
125.08
125.03
124.97
124.84
122.25
121.96
112.92
106.82
103.67
102.99
75.14
75.11
54.84
48.04
45.78
27.86
25.68
24.06
22.13
22.04
20.97
20.87
20.78
20.68
20.59
20.48
20.40
20.29
20.21
20.02
19.83
Br
Ph
N
Br
Br
N
N
Dipp
Cl
Ru
Cl
O
Hov-5
(as a mixture of isomers)
250
200
150
100
50
0
f1 (ppm)

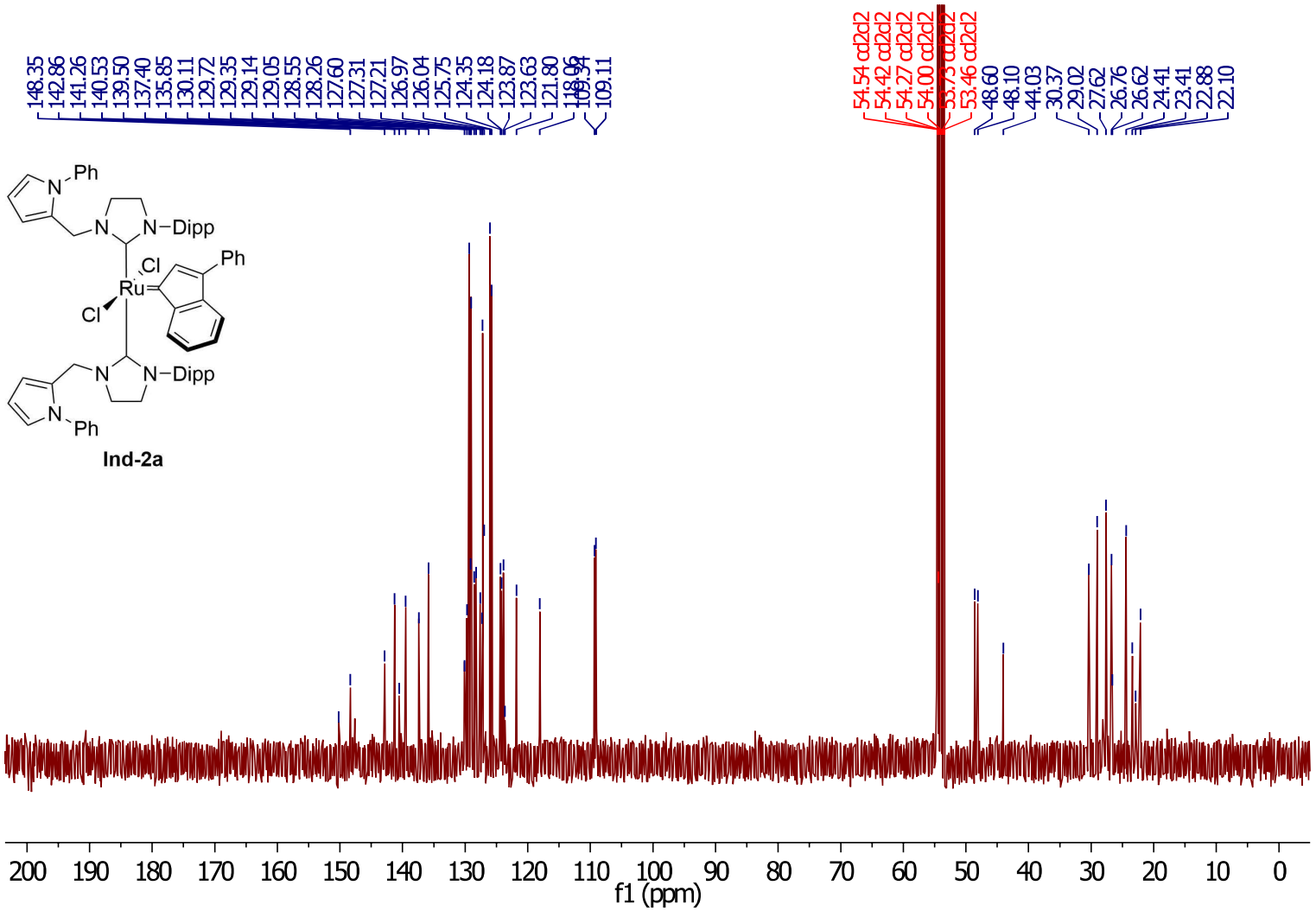

7.68 7.68 7.66 7.66 7.50 7.43 7.41 7.41 7.39 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.26 cdd3 7.19 7.19 7.18 7.18 7.06 6.94 6.93 6.93 6.92 6.92 6.91 6.83 6.83 6.82 6.82 6.81 6.80 6.40 6.39 6.39 6.38 6.22 6.22 6.22 5.79 5.79 3.48 3.48 3.47 3.46 3.46 3.44 3.43 3.43 3.42 1.98 1.78 1.71 1.43 0.87
C (m) 6.92
F (m) 7.30
B (m) 7.67
H (m) 7.05
O (dd) 6.39
U (d) 5.79
A (dd) 8.20
D (m) 7.41
J (m) 6.81
Q (m) 6.22
Z (m) 3.45
M1 (s) 1.78
J1 (s) 1.98
E (m) 7.32
V (s) 5.70
N1 (s) 1.71
G (dt) 7.19
1.00 2.18 6.33 3.21 0.99 2.19 2.11 5.30 3.35 1.96 2.13 2.30 2.96 8.15 5.88 5.93 5.90
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
f1 (ppm)
Ph
N
N
Mes
Cl
Ru
Cl
Ph
N
N
Mes
N
Ph
Ind-1a


218.64
142.96
139.80
139.21
136.99
136.64
136.51
136.46
136.36
135.64
135.45
129.41
128.55
128.51
128.21
127.83
127.54
127.18
126.96
126.83
126.57
126.09
125.94
122.49
114.84
112.09
109.21
77.32
77.20
77.00
76.68
51.75
48.27
46.88
26.89
20.77
18.35
18.27
Ph
N
N
Mes
Cl
Ru
Ph
Cl
N
N
Mes
N
Ph
Ind-1a
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)


Ph
N
N
N
Mes
Cl
Ph
Ru
Cl
PCy3
Ind-1b
H (ddd) 6.92
D (m) 7.40
L (dt) 5.97
B (m) 8.40
C (m) 7.69
G (dd) 7.02
K (m) 6.36
E (m) 7.15
U (m) 3.52
G1 (t) 1.83
D1 (d) 2.04
J1 (m) 1.33
B1 (d) 2.38
H1 (m) 1.67
F1 (m) 1.88
K1 (m) 1.08
I1 (d) 1.54
0.71
1.74
9.23
3.10
0.79
1.91
1.64
0.77
2.91
0.92
3.08
6.20
3.20
3.44
5.67
3.54
4.25
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
f1 (ppm)


216.47
215.78
143.82
140.44
139.43
137.43
137.42
137.11
136.87
136.76
136.72
136.65
135.98
129.61
129.04
128.73
128.53
128.49
128.26
128.23
127.90
127.50
127.43
126.95
126.62
126.31
126.17
125.99
123.26
115.94
112.80
109.09
109.05
77.32
77.21
77.00
76.68
51.46
48.21
46.59
35.56
34.95
32.40
32.24
29.54
29.44
27.77
27.67
27.60
27.51
26.92
26.81
26.47
26.28
26.25
26.09
26.07
20.92
18.35
18.29
N
Ph
N
N
Mes
Cl
Ru
Ph
Cl
PCy3
Ind-1b
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)


Ph
N
N–Dipp
Cl
Ru
Ph
Cl
N
N–Dipp
N
Ph
Ind-2a
A (m) 8.47
B (s) 7.74
I (m) 7.01
L (t) 6.30
D (m) 7.57
J (m) 6.75
N (dd) 6.07
G (dd) 7.35
P (dd) 5.85
F (s) 7.42
K (m) 6.60
O (s) 5.90
H (m) 7.18
Q (s) 5.77
S (s) 4.48
V (ddd) 3.53
C1 (ddd) 2.60
T (m) 4.12
X (ddd) 3.32
Y (m) 3.17
U (hept) 3.90
Z (s) 3.13
A1 (q) 2.93
B1 (d) 2.82
D1 (s) 2.36
F1 (d) 1.60
J1 (d) 0.91
E1 (s) 1.72
I1 (s) 1.04
M1 (d) 0.26
H1 (m) 1.28
G1 (s) 1.54
L1 (m) 0.58
f1 (ppm)


148.35
142.86
141.26
140.53
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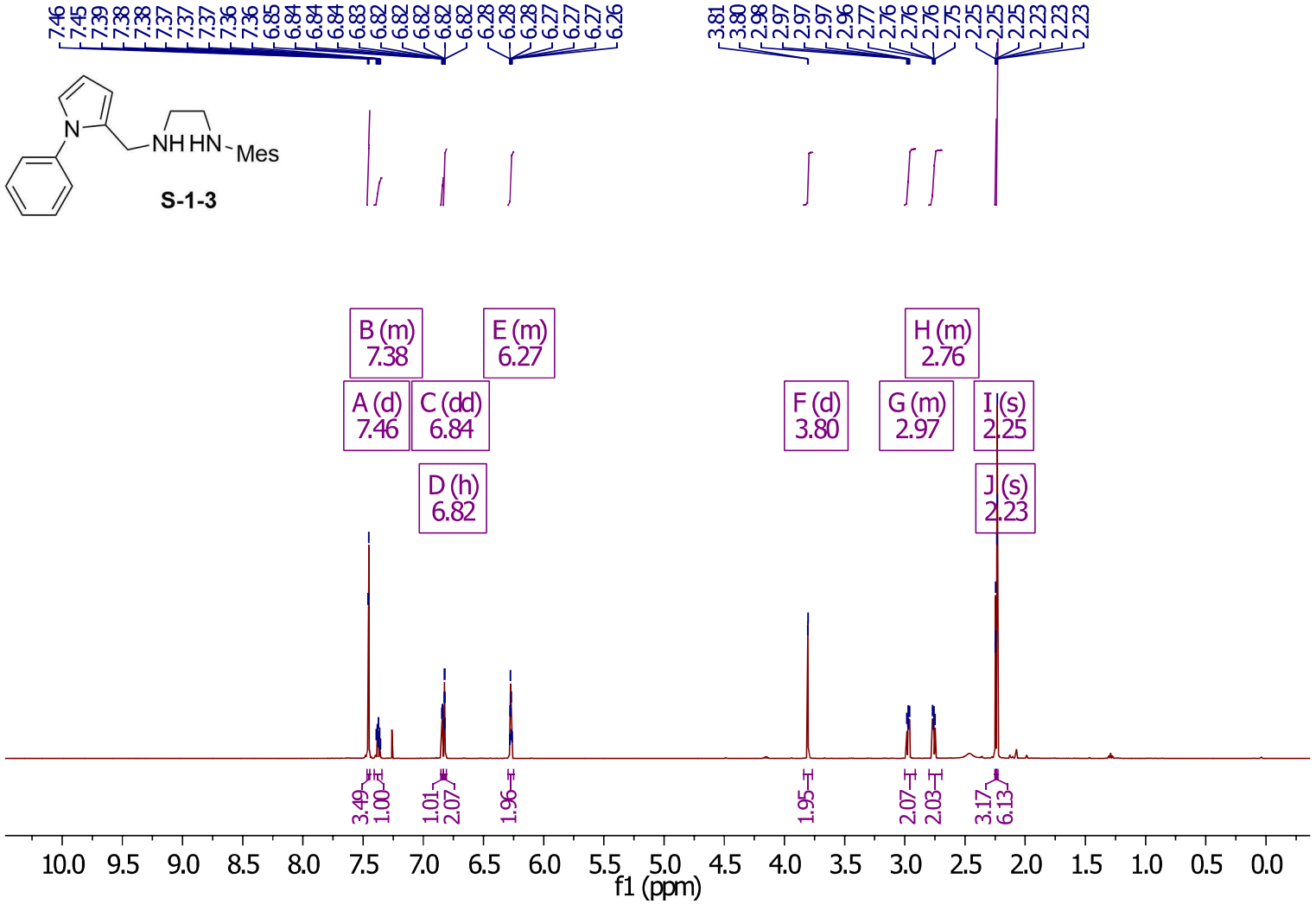
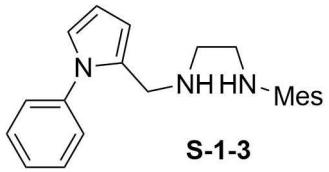
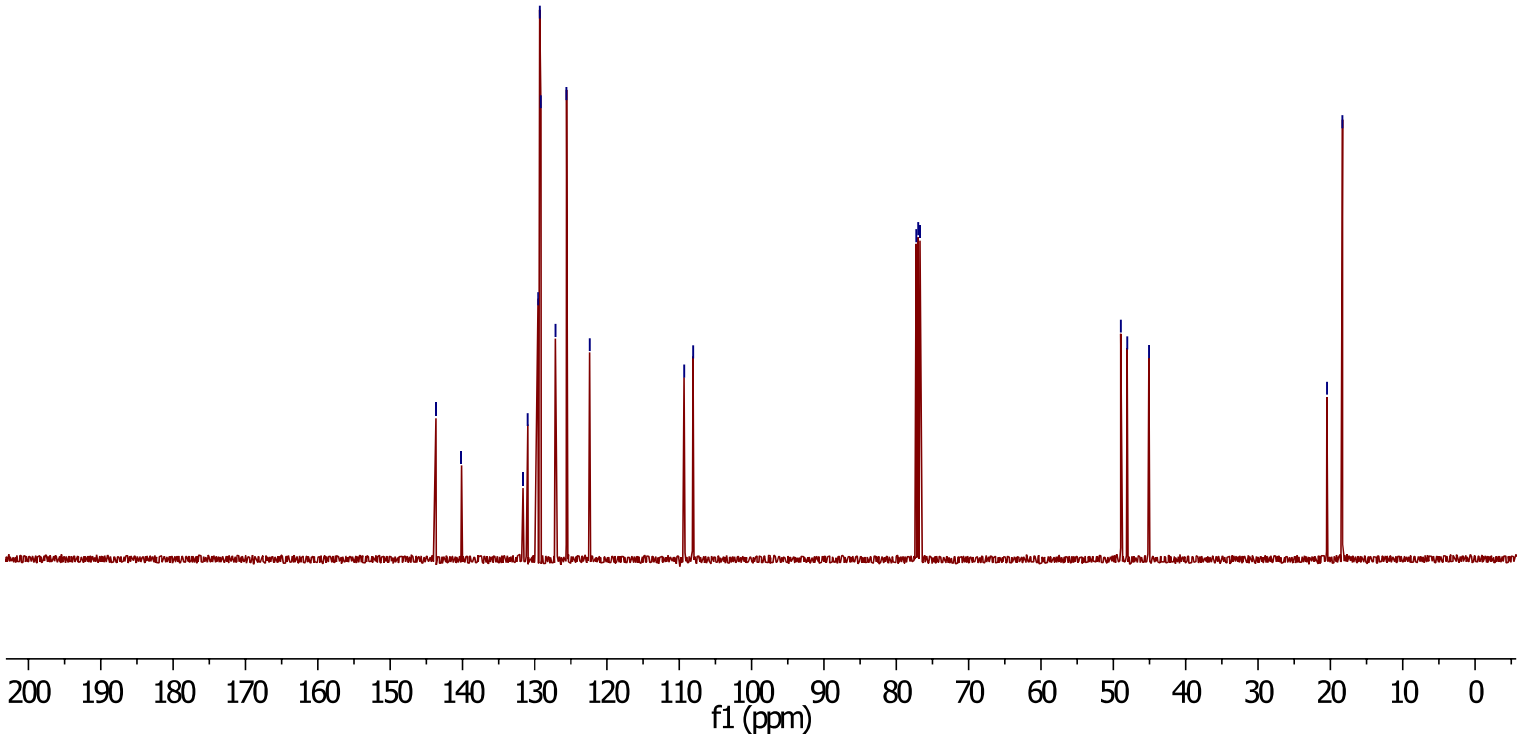
137.40
135.85
130.11
129.72
129.35
129.14
129.05
128.55
128.26
127.60
127.31
127.21
126.97
126.04
125.75
124.35
124.18
123.87
123.63
121.80
109.11
54.54 cd2cl2
54.42 cd2cl2
54.27 cd2cl2
54.00 cd2cl2
53.73 cd2cl2
53.46 cd2cl2
48.60
48.10
44.03
30.37
29.02
27.62
26.76
26.62
24.41
23.41
22.88
22.10
N
Ph
N
N–Dipp
Cl
Ru
Ph
Cl
N
N–Dipp
N
Ph
Ind-2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

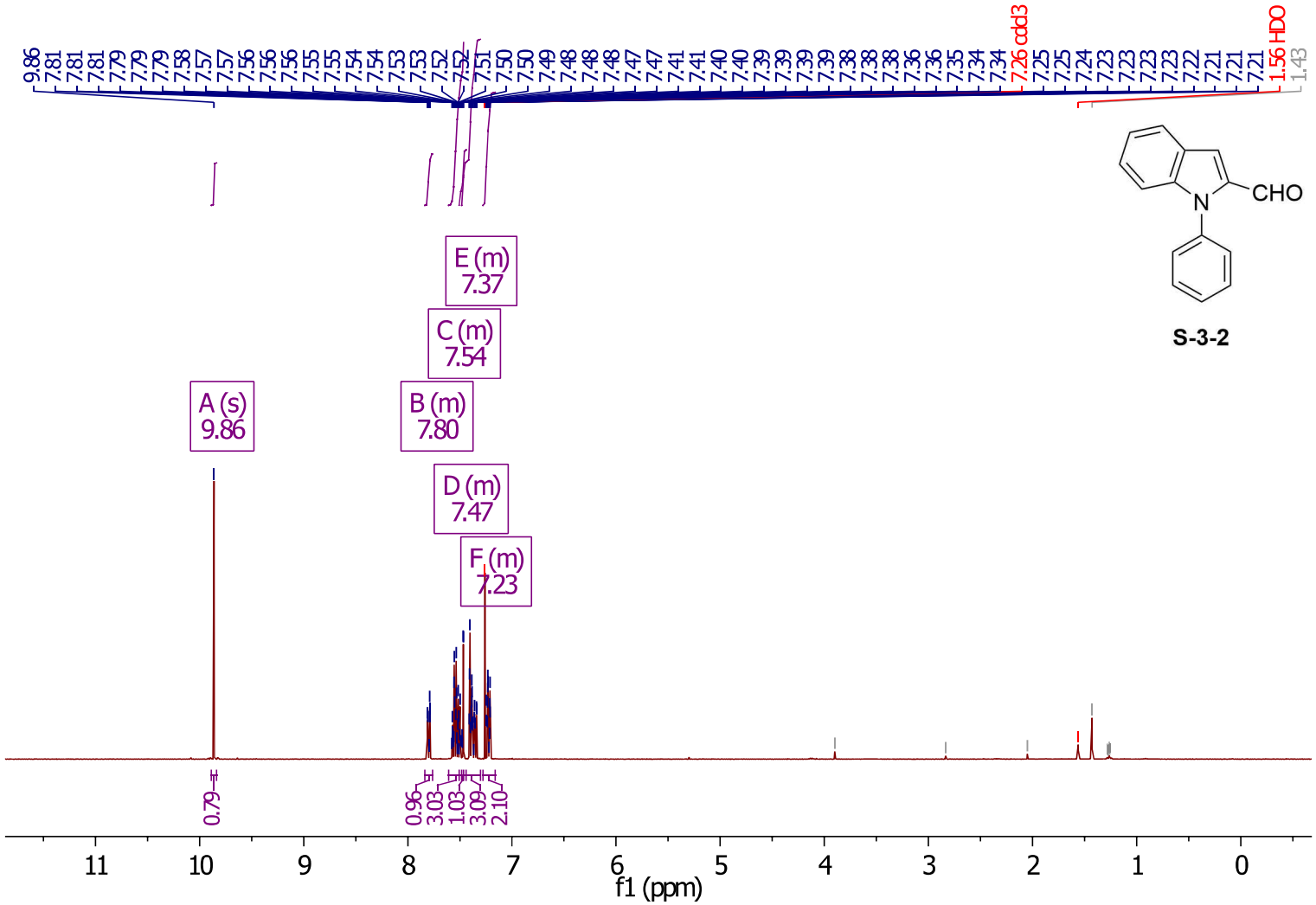

7.46
7.45
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
6.85
6.84
6.84
6.84
6.83
6.82
6.82
6.82
6.82
6.28
6.28
6.28
6.27
6.27
6.26
3.81
3.80
2.98
2.97
2.97
2.97
2.96
2.77
2.76
2.76
2.76
2.75
2.25
2.25
2.25
2.23
2.23
2.23
N
NH HN
Mes
S-1-3
B (m)
7.38
E (m)
6.27
H (m)
2.76
A (d)
7.46
C (dd)
6.84
F (d)
3.80
G (m)
2.97
I (s)
2.25
D (h)
6.82
J (s)
2.23
3.49
1.00
1.01
2.07
1.96
1.95
2.07
2.03
3.17
6.13
10.0
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
f1 (ppm)

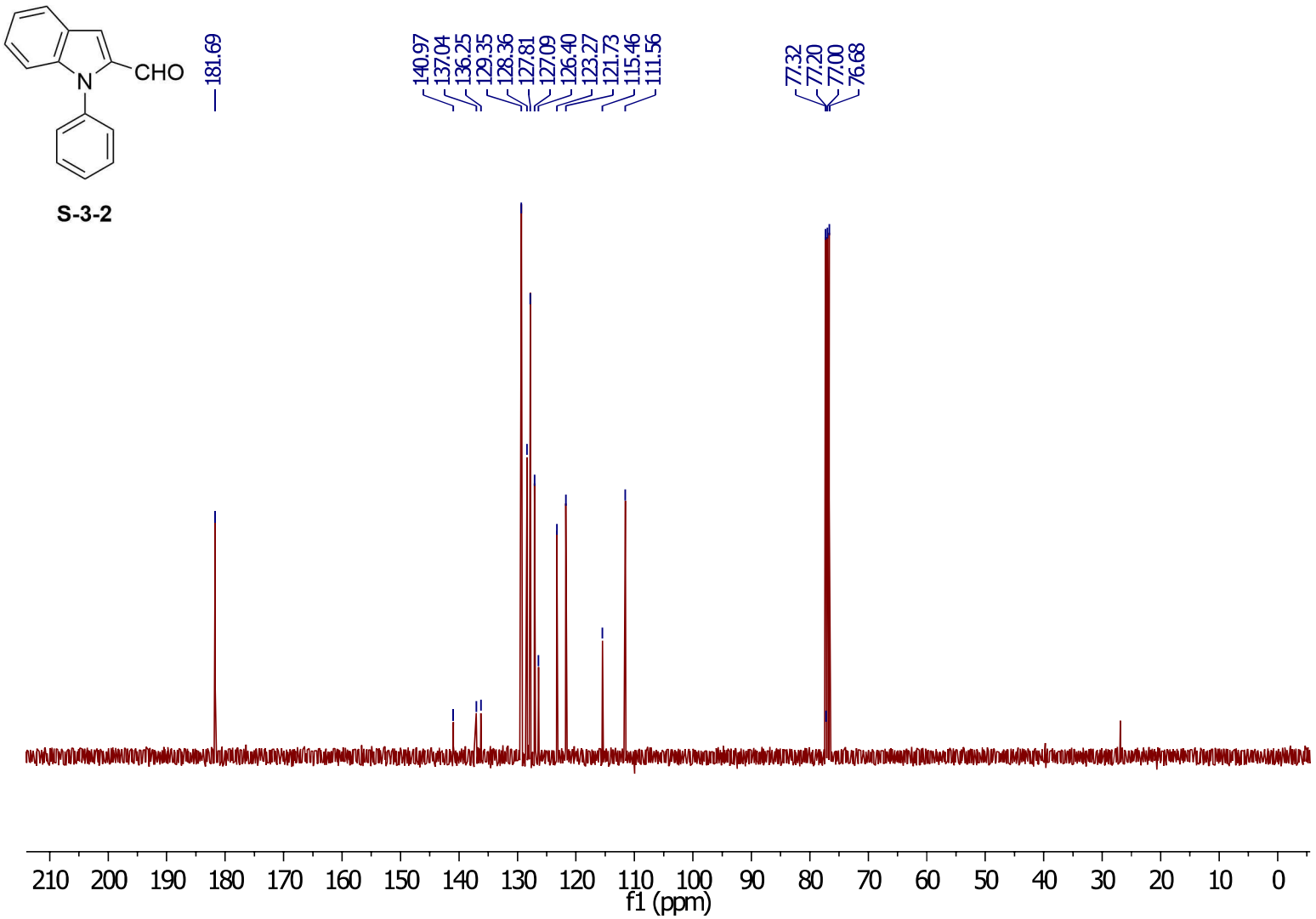


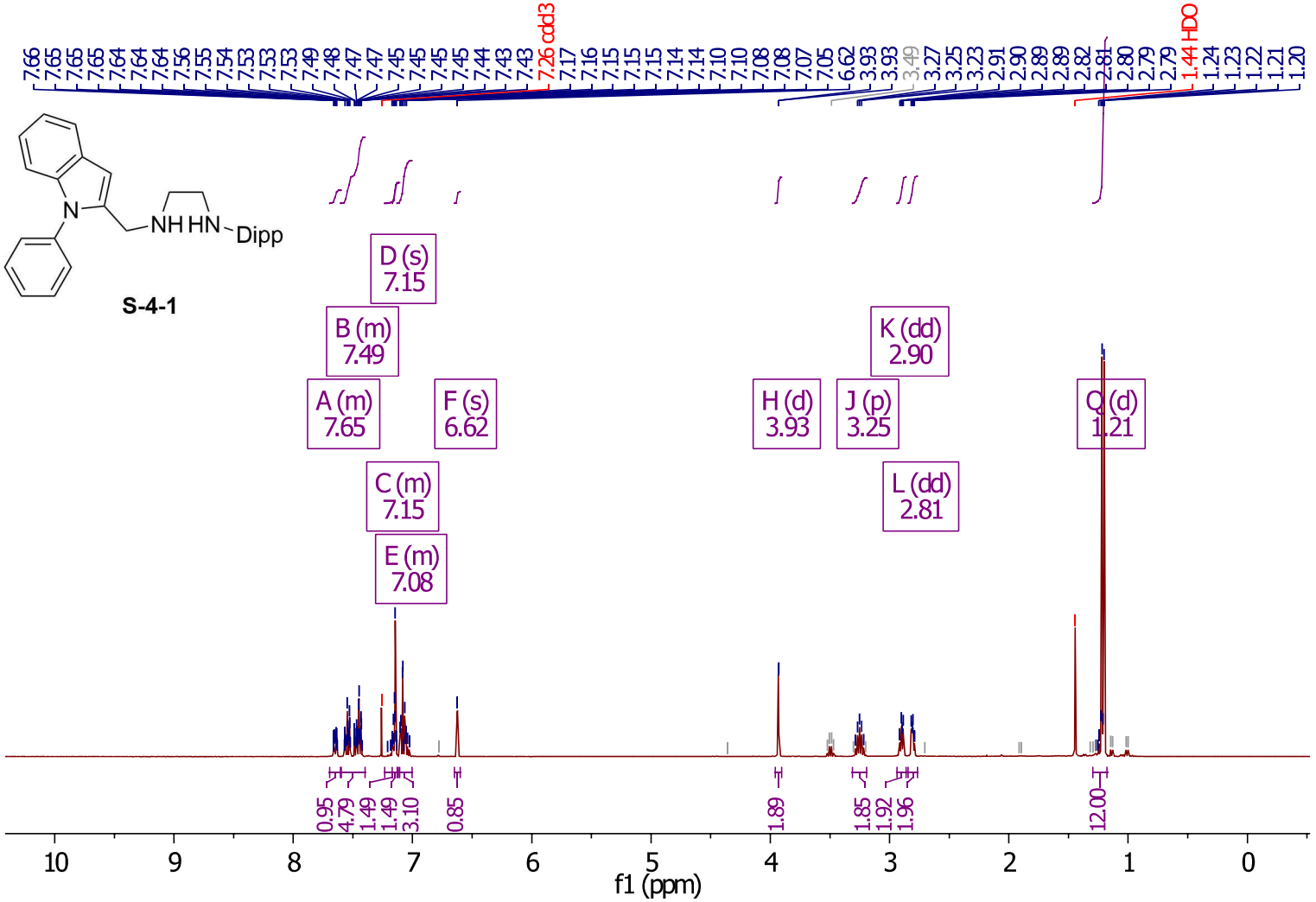
S-1-3

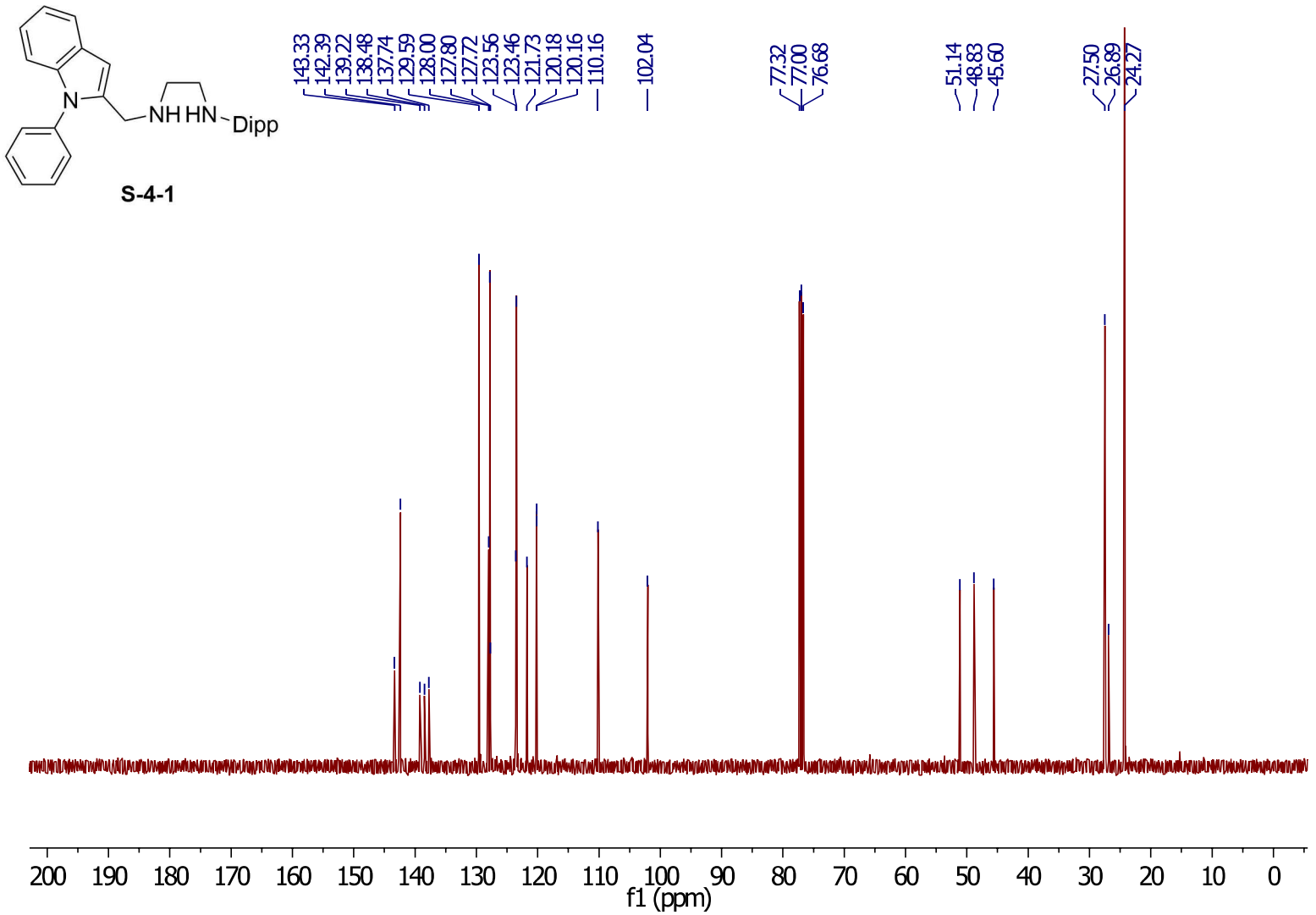
143.65
140.12
131.61
130.96
129.54
129.30
129.15
127.13
125.61
122.39
109.35
108.10
77.25
77.00
76.75
48.99
48.09
45.08
20.49
18.34

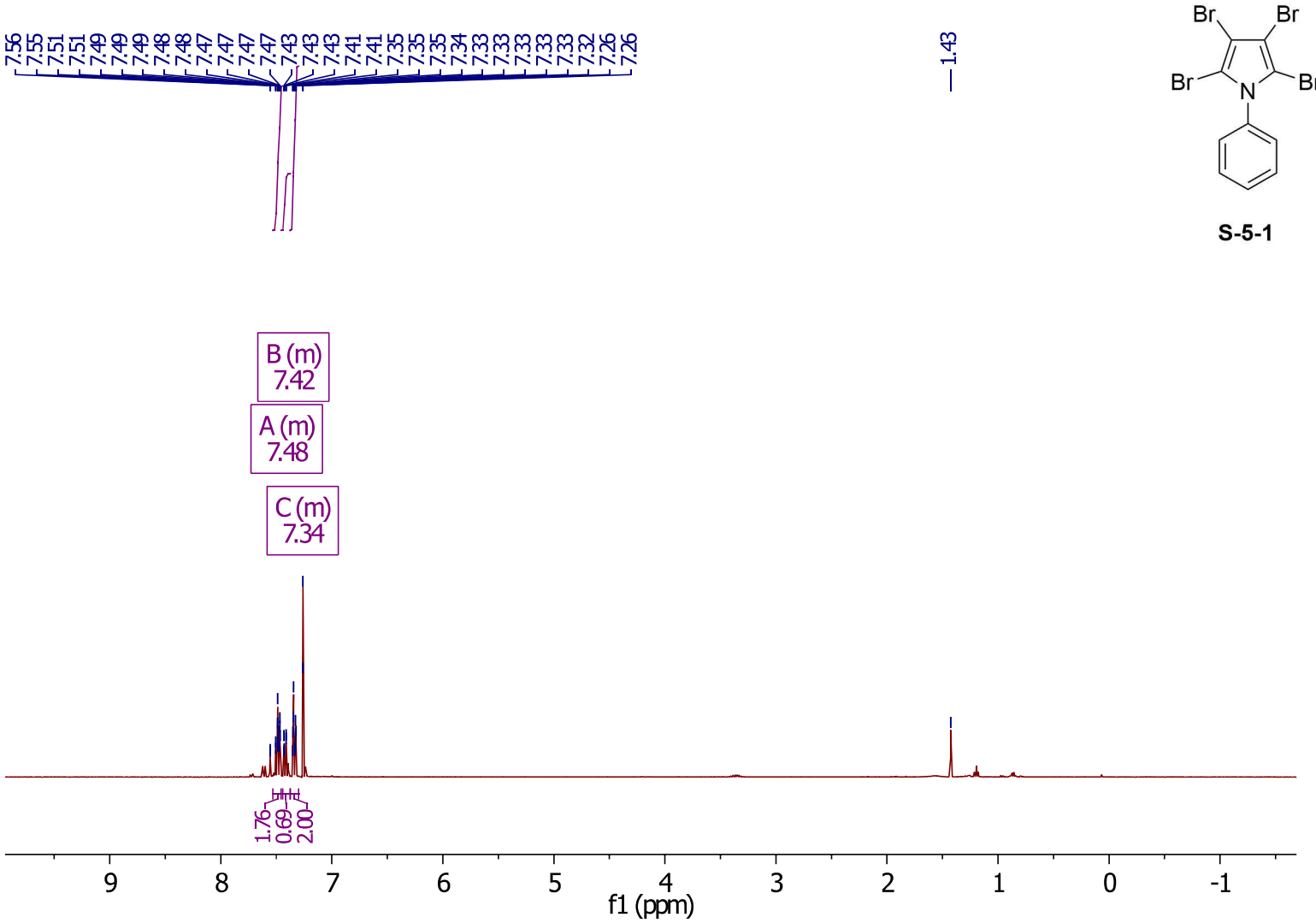


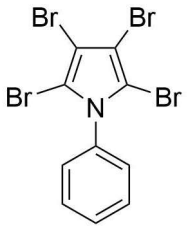

9.86
7.81
7.81
7.81
7.79
7.79
7.79
7.58
7.57
7.57
7.56
7.56
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.39
7.38
7.38
7.38
7.36
7.36
7.35
7.34
7.34
7.26 cdcl3
7.25
7.25
7.24
7.23
7.23
7.23
7.23
7.22
7.21
7.21
7.21
1.56 HDO
1.43
E (m)
7.37
C (m)
7.54
A (s)
9.86
B (m)
7.80
D (m)
7.47
F (m)
7.23
0.79
0.96
3.03
1.03
3.09
2.10
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
N
CHO
S-3-2


CHO
N
S-3-2
181.69
140.97
137.04
136.25
129.35
128.36
127.81
127.09
126.40
123.27
121.73
115.46
111.56
77.32
77.20
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.66 7.65 7.65 7.65 7.64 7.64 7.64 7.56 7.55 7.54 7.53 7.53 7.53 7.49 7.48 7.47 7.47 7.45 7.45 7.45 7.44 7.43 7.43 7.26 cdcl3 7.17 7.16 7.15 7.15 7.15 7.14 7.14 7.10 7.10 7.08 7.08 7.07 7.05 6.62 3.93 3.93 3.49 3.27 3.25 3.23 2.91 2.90 2.89 2.89 2.82 2.81 2.80 2.79 2.79 1.44 HDO 1.24 1.23 1.22 1.21 1.20
N
NH HN
Dipp
S-4-1
D (s) 7.15
B (m) 7.49
A (m) 7.65
F (s) 6.62
C (m) 7.15
E (m) 7.08
H (d) 3.93
K (dd) 2.90
J (p) 3.25
L (dd) 2.81
Q (d) 1.21
0.95 4.79 1.49 1.49 3.10 0.85 1.89 1.85 1.92 1.96 12.00
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

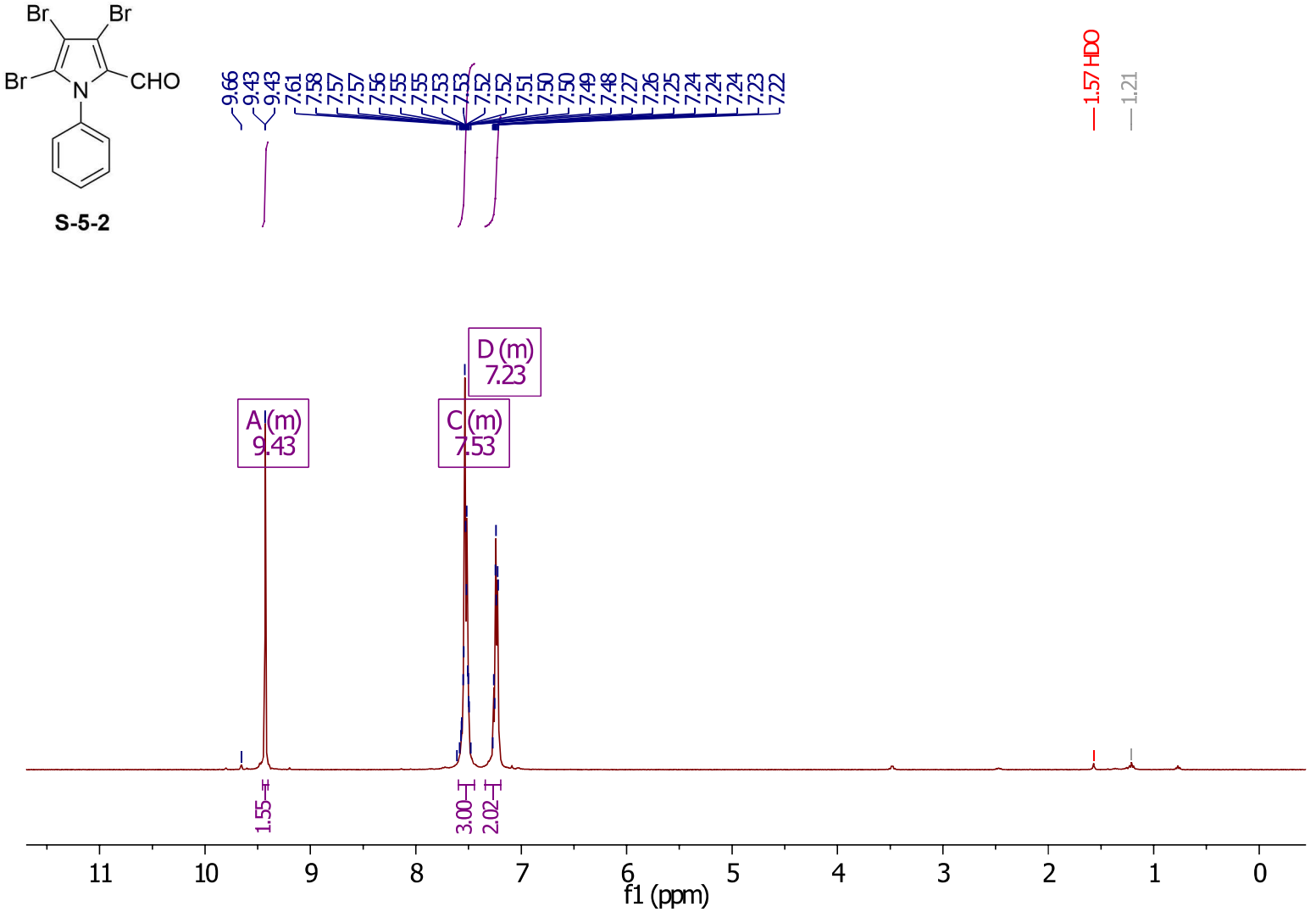

N
NH HN
Dipp
S-4-1
143.33
142.39
139.22
138.48
137.74
129.59
128.00
127.80
127.72
123.56
123.46
121.73
120.18
120.16
110.16
102.04
77.32
77.00
76.68
51.14
48.83
45.60
27.50
26.89
24.27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

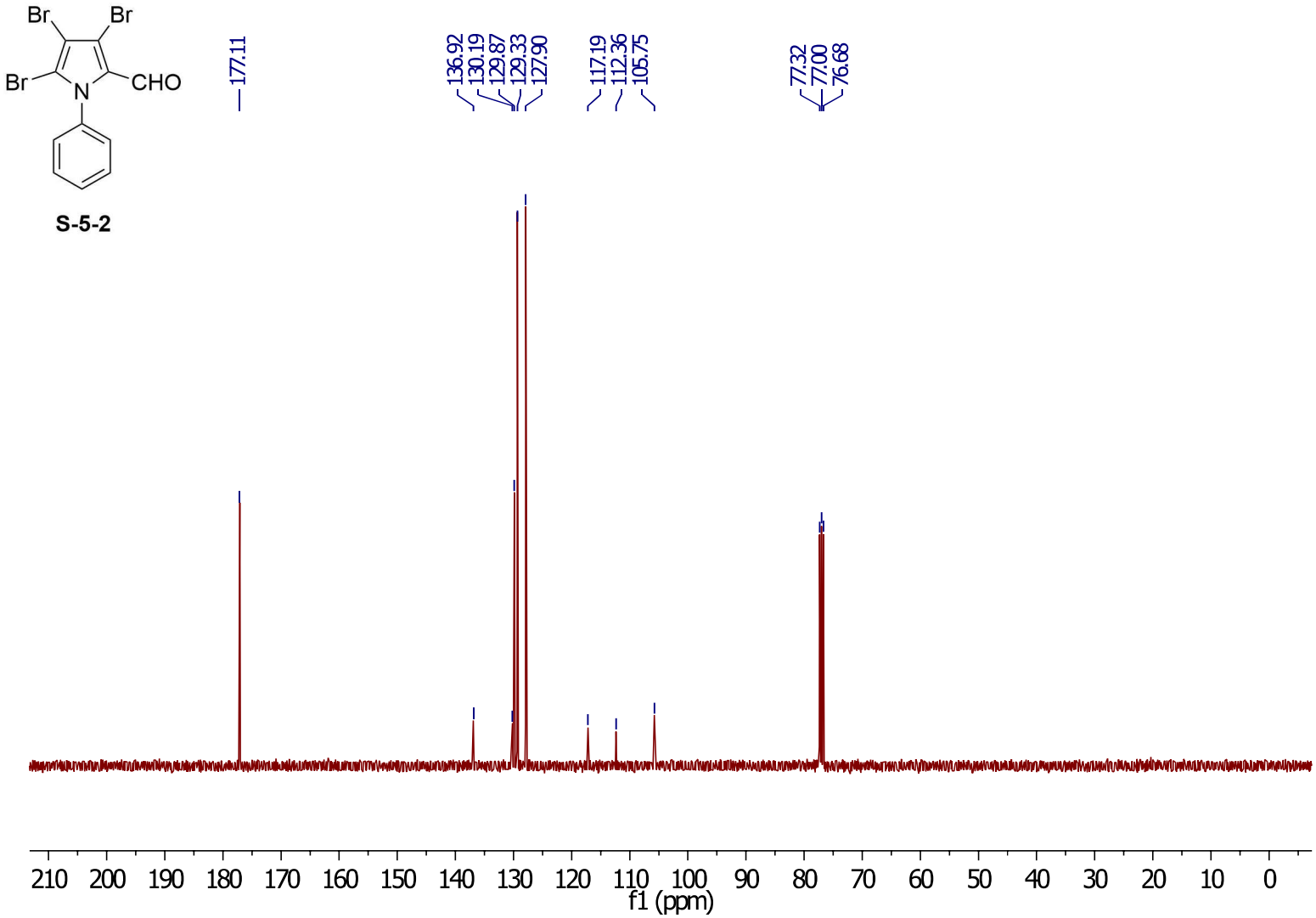

7.56
7.55
7.51
7.51
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.47
7.43
7.43
7.43
7.41
7.41
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.33
7.33
7.32
7.26
7.26
1.43
Br
Br
Br
Br
N
S-5-1
B (m)
7.42
A (m)
7.48
C (m)
7.34
1.76
0.69
2.00
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


Br
Br
Br
N
Br

S-5-1

138.07
133.76
129.76
129.24
128.60
104.46
102.60
77.32
77.00
76.68
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)


Br
Br
Br
N
CHO
S-5-2
9.66
9.43
9.43
7.61
7.58
7.57
7.57
7.56
7.55
7.55
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.27
7.26
7.25
7.24
7.24
7.24
7.23
7.22
1.57 HDO
1.21
A (m)
9.43
C (m)
7.53
D (m)
7.23
1.55
3.00
2.02
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


Br
Br
Br
N
CHO
S-5-2
177.11
136.92
130.19
129.87
129.33
127.90
117.19
112.36
105.75
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)