Electronic Supplementary Material (ESI) for Dalton Transactions

Ruthenium-based complexes containing benzimidazolium tag covalently connected to *N*-heterocyclic carbene ligands: environmentally friendly catalysts for olefin metathesis transformations

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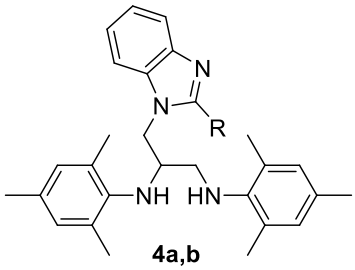
Contents

1. General

All manipulations were performed under a nitrogen atmosphere in a glove box (Unilab MBRAUN) or by standard Schlenk techniques unless specified otherwise. The solvents were dried by distillation over the following drying agents and were transferred under argon: toluene (Na), n-pentane, n-hexane, CH_2Cl_2 (CaH_2) and stored over MS 4A. Purchased starting materials and other chemicals or reagents (Aldrich, Fluka, and Merck) were used without further purification. Acrylic acid and its butyl ester were distilled prior to use.
Column chromatography: Merck silica gel 60 (230–400 mesh), Aluminum oxide, activated, neutral.
NMR spectra were recorded on a Varian 400 MHz spectrometer in the indicated solvent at 25 °C and are listed in parts per million downfield from TMS as an internal standard for proton and carbon, coupling constants (J) in Hz.
MS(ESI): Bruker: MicroTOF-Q II and Waters-Q-Tof 2

2. Synthesis procedures and analytical data

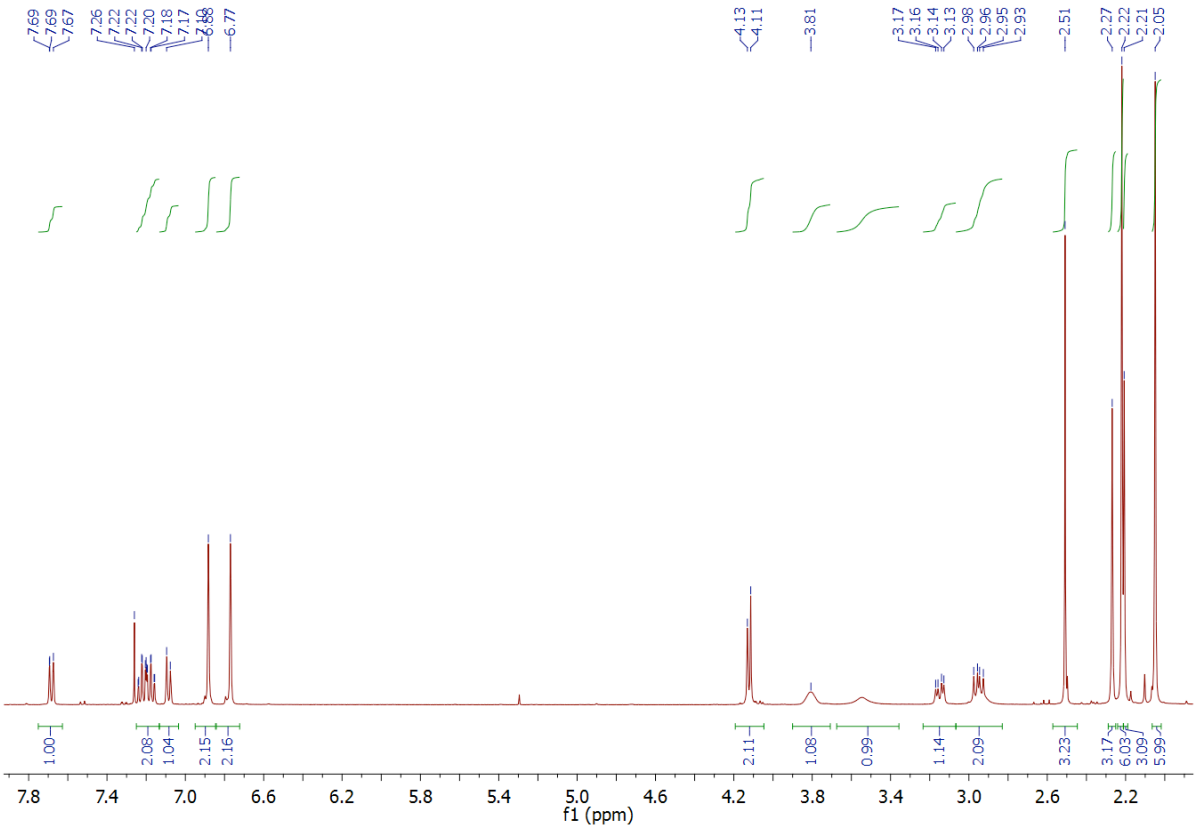
General procedure for synthesis of diamines 4a,b

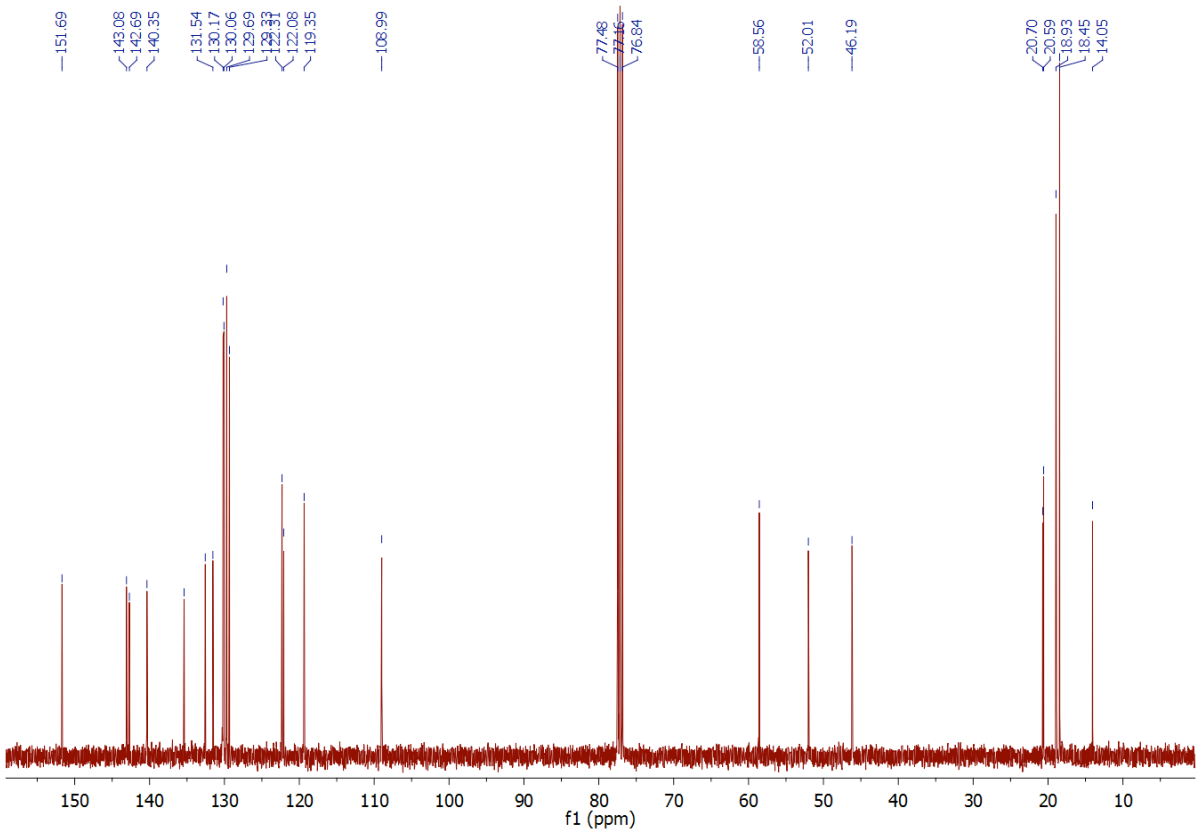


4a,b

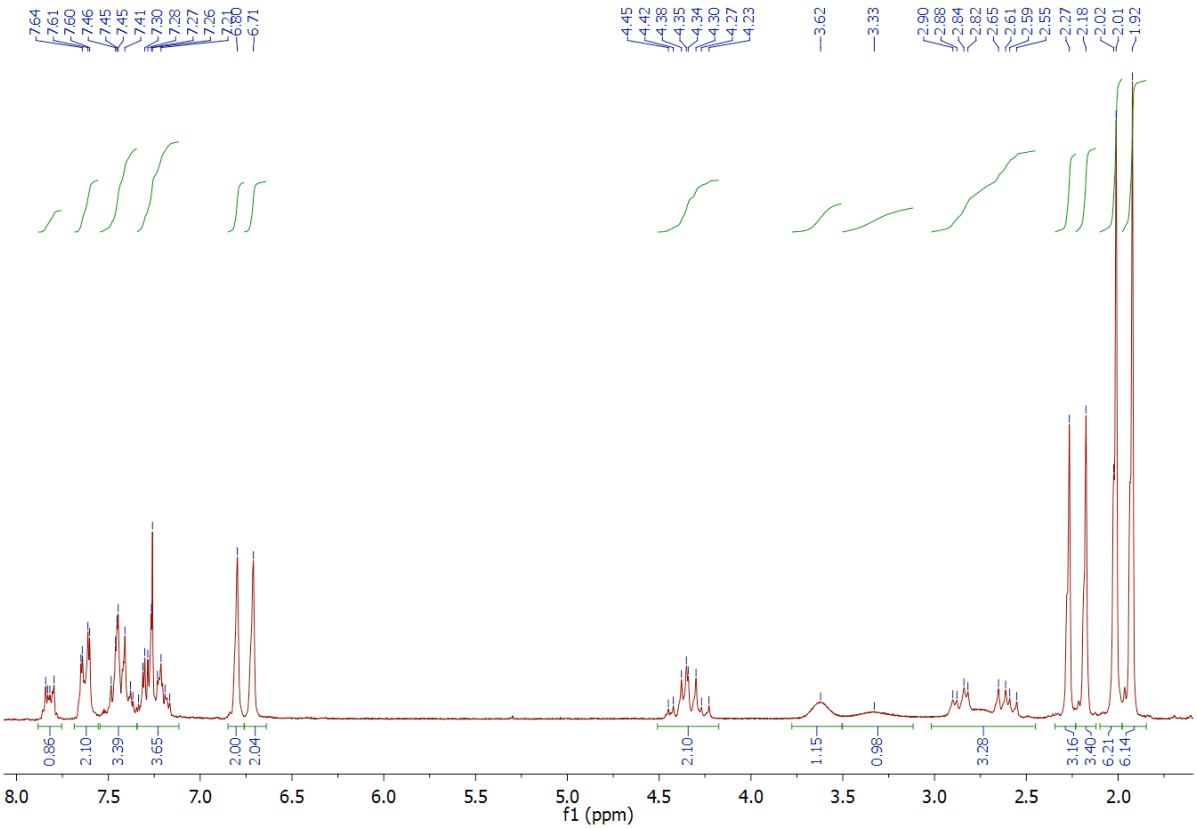
To a stirred solution of N-allyl-benzimiazole **3a,b** (2.96 g, 17.2 mmol) in 35 mL of dry dichloromethane under argon 4M solution of hydrogen chloride in dioxane (4.3 mL, 17.2 mmol) was added at 0°C and allowed to warm up to RT while stirring. To this, solution of bromine (0.9 mL, 17.2 mmol) in 5 mL of dry dichloromethane was added dropwise over 1 h and stirred at RT for another 3 h. After that time, solvent was evaporated to dryness, mesitylamine (24.5 mL, 172 mmol) was added and the mixture was heated under argon at 120°C overnight. After cooling down, 2 M solution of NaOH was added (70 mL), product was extracted (3x100 mL) to dichloromethane, organic phase was washed with water (150 mL), dried over anhydrous MgSO4 and solvent was evaporated. Excess of mesitylamine was distilled off under reduced pressure and residue was separated by column chromatography with gradient of ethyl acetate/cyclohexane (1/20 – 1/2) as eluent to obtain yellowish oil which was crystallized from n-hexane to obtain white powder.

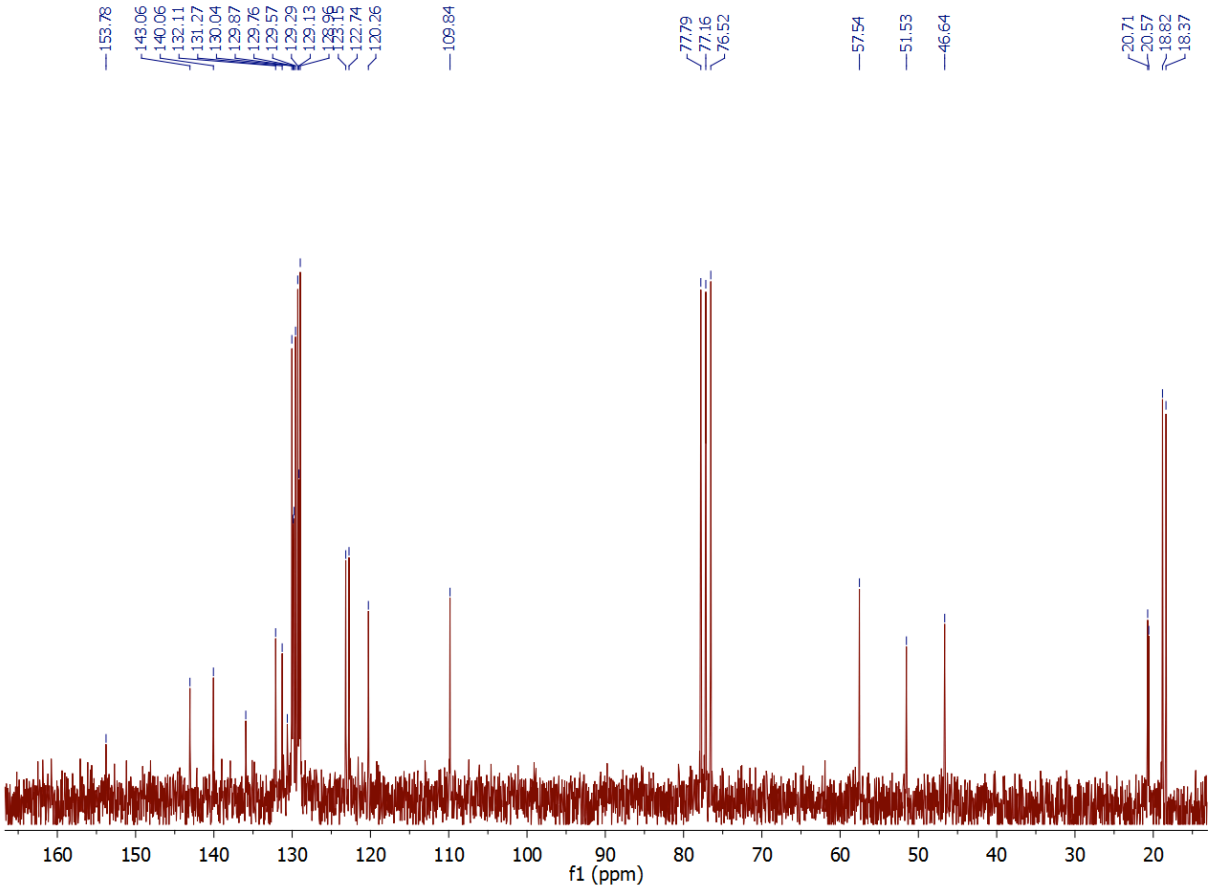
4a (4.2 g, 55 %) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.60 (m, 1H), 7.20 (dtd, J = 16.4, 7.3, 1.2 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 6.88 (s, 2H), 6.77 (s, 2H), 4.12 (d, J = 6.8 Hz, 2H), 3.81 (s, 1H), 3.54 (s, 1H), 3.15 (dd, J = 12.0, 4.8 Hz, 1H), 2.95 (dd, J = 12.0, 7.7 Hz, 2H), 2.51 (s, 3H), 2.27 (s, 3H), 2.22 (s, 6H), 2.21 (s, 3H), 2.05 (s, 6H); ^{13}C NMR (101 MHz, CDCl3) δ 151.7, 143.1, 142.7, 140.4, 135.4, 132.6, 131.5, 130.2, 130.1, 129.7, 129.3, 122.3, 122.1, 119.4, 109.0, 58.6, 52.0, 46.2, 20.7, 20.6, 18.9, 18.5, 14.1; HRMS calcd for $C_{29}H_{37}N_4^+$ [M+H$^+$] : m/z 441.301, found : m/z 441,301



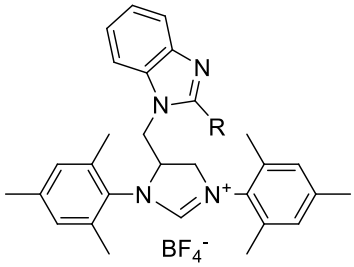


4b (4.6 g, 53 %) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 5.8, 3.4 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.53 – 7.36 (m, 3H), 7.36 – 7.08 (m, 3H), 6.80 (s, 2H), 6.71 (s, 2H), 4.34 (qd, J = 14.1, 6.7 Hz, 2H), 3.62 (s, 1H), 3.33 (s, 1H), 2.73 (m, 3H), 2.27 (s, 3H), 2.18 (s, 3H), 2.02 (s, 6H), 1.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 143.1, 140.1, 135.9, 132.1, 131.3, 130.6, 130.1, 129.9, 129.8, 129.6, 129.3, 129.1, 129.0, 123.2, 122.7, 120.3, 109.8, 57.5, 51.5, 46.6, 20.7, 20.6, 18.8, 18.4; HRMS calcd for $C_{34}H_{39}N_4^+$ [M+H$^+$] : m/z 503.317, found : m/z 503,317





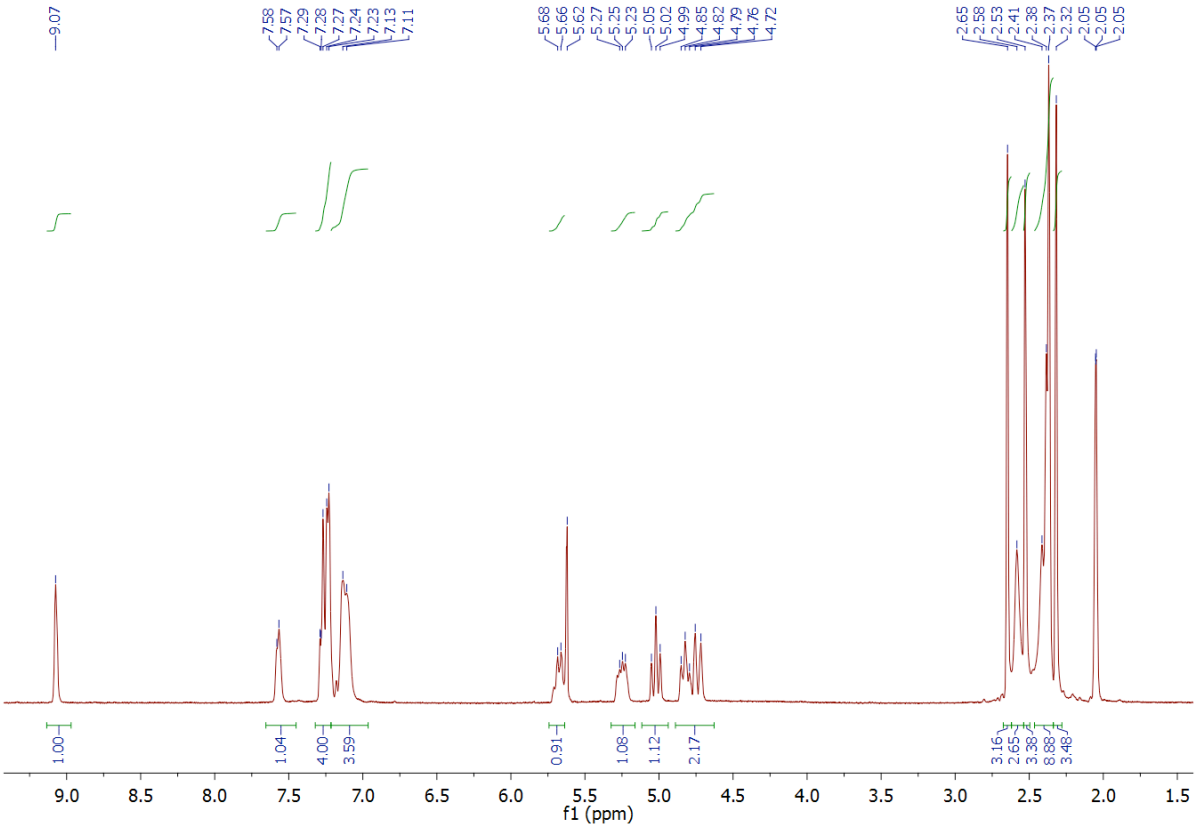
General procedure for synthesis of NHC salts 5:

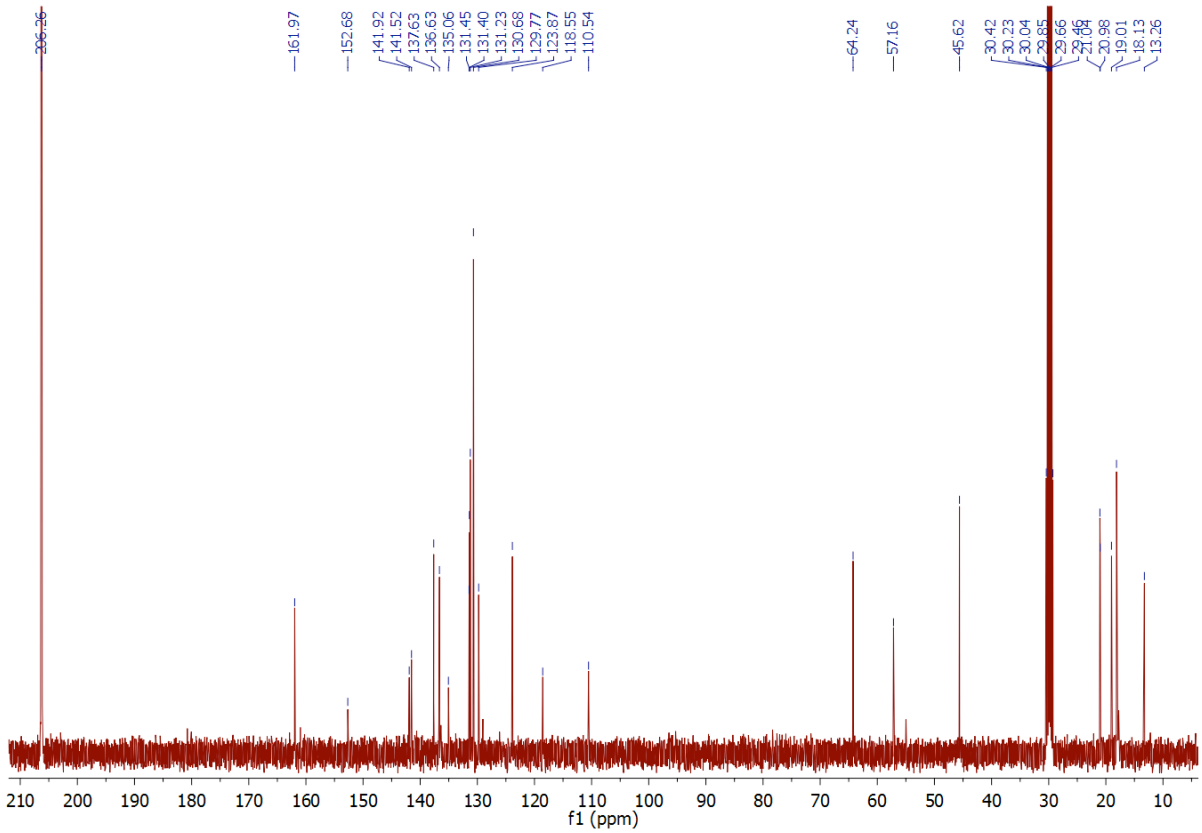


5a,b

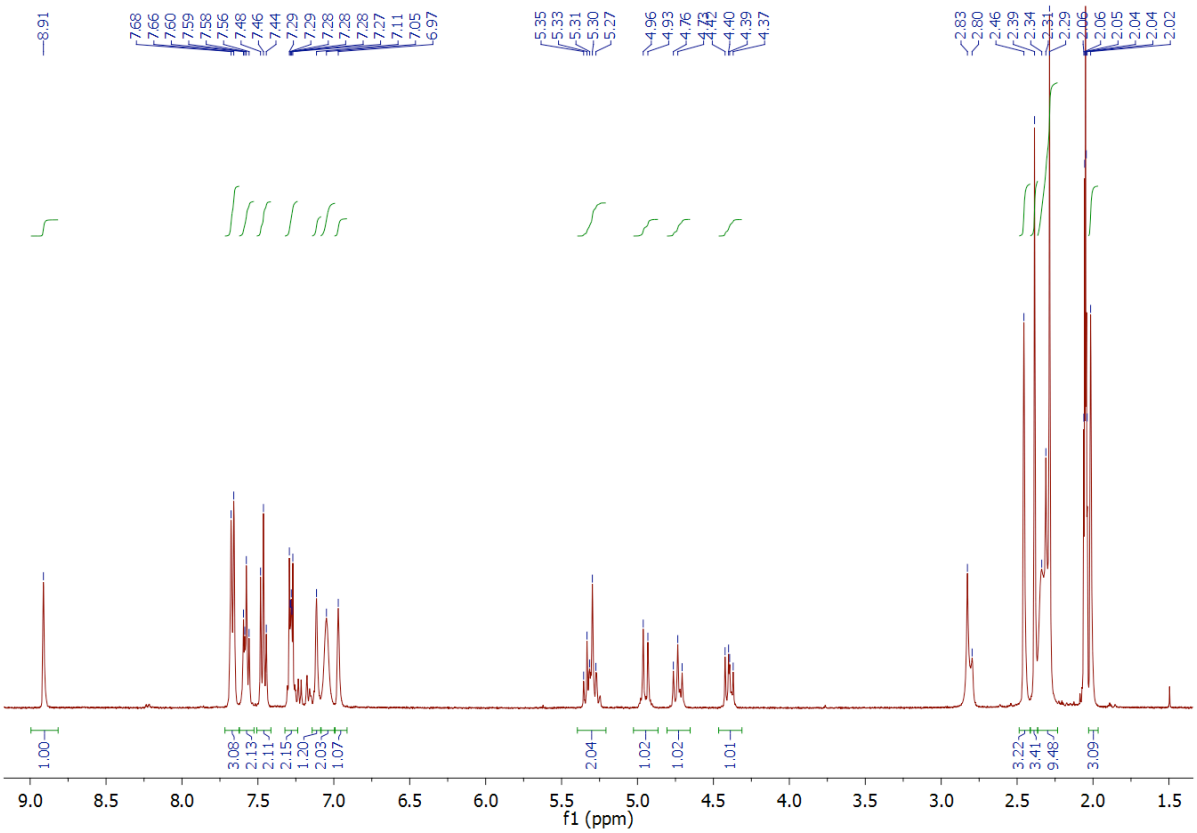
Amine **4** (2 g, 4.5 mmol), ammonium tetrafluoroborate (620 mg, 5.9 mmol) and triethyl orthoformate (7.6 mL, 45 mmol) were stirred at 85°C for 3h. After cooling down, diethyleter (20 mL) was added, precipitate was filtered and washed with diethyleter (50 mL). Product was purified by column chromatography with dichloromethane/acetone 8/1 as eluent followed by recrystallization from dichloromethane/toluene and dried in vacuum to obtain salts as white powder.

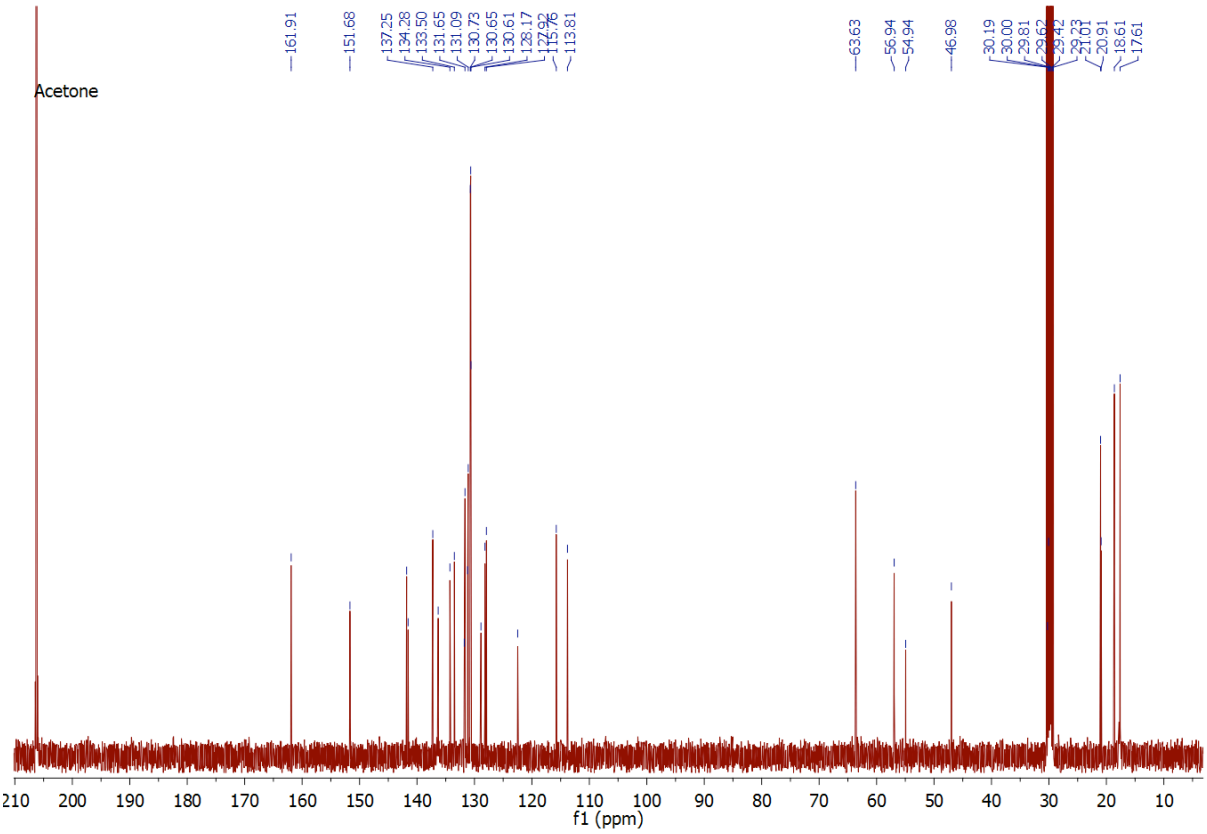
5a (1.8 g, 75 %) ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.09 (s, 1H), 7.69 – 7.63 (m, 1H), 7.43 – 7.30 (m, 3H), 7.23 (s, 1H), 7.14 (s, 1H), 7.12 (s, 1H), 7.10 (s, 1H), 5.74 (tdd, J = 11.4, 8.2, 3.5 Hz, 1H), 5.37 (dd, J = 15.6, 8.2 Hz, 1H), 5.05 (t, J = 11.9 Hz, 1H), 4.94 – 4.77 (m, 2H), 2.65 (s, 6H), 2.58 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 162.1, 153.0, 142.1, 141.6, 137.7, 137.0, 136.7, 134.1, 131.5, 131.4, 131.3, 130.7, 129.7, 125.3, 125.2, 117.3, 111.4, 64.0, 57.1, 46.0, 21.0, 20.9, 19.0, 18.1, 12.8. HRMS calcd for $C_{30}H_{35}N_4^+$ [M+] : m/z 451.286, found : m/z 451.286



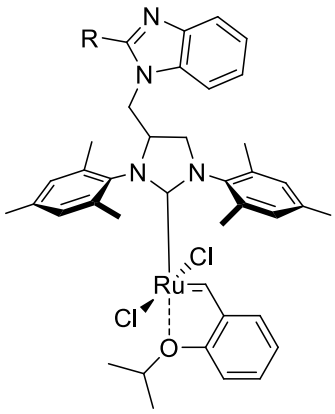


5b (2.1 g, 76 %) ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.93 (s, 1H), 8.04 – 7.89 (m, 1H), 7.81 (d, J = 7.3 Hz, 3H), 7.74 (t, J = 7.5 Hz, 1H), 7.55 (dd, J = 10.3, 6.3 Hz, 4H), 7.11 (s, 1H), 7.06 (s, 2H), 6.92 (s, 1H), 5.59 (dd, J = 15.2, 8.7 Hz, 1H), 5.42 (dd, J = 19.2, 8.1 Hz, 1H), 5.11 (dd, J = 15.3, 3.1 Hz, 1H), 4.82 (t, J = 11.8 Hz, 1H), 4.62 (d, J = 11.1 Hz, 1H), 4.59 (d, J = 11.6 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 6H), 2.30 (s, 6H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 161.7, 153.7, 144.3, 141.5, 136.9, 136.4, 131.5, 131.3, 131.1, 131.0, 130.8, 130.6, 130.1, 129.8, 129.3, 124.0, 123.4, 120.8, 111.0, 63.9, 56.8, 46.1, 21.0, 20.9, 18.8, 17.8. HRMS calcd for $C_{35}H_{37}N_4^+$ [M^+] : m/z 513.302, found : m/z 513.302





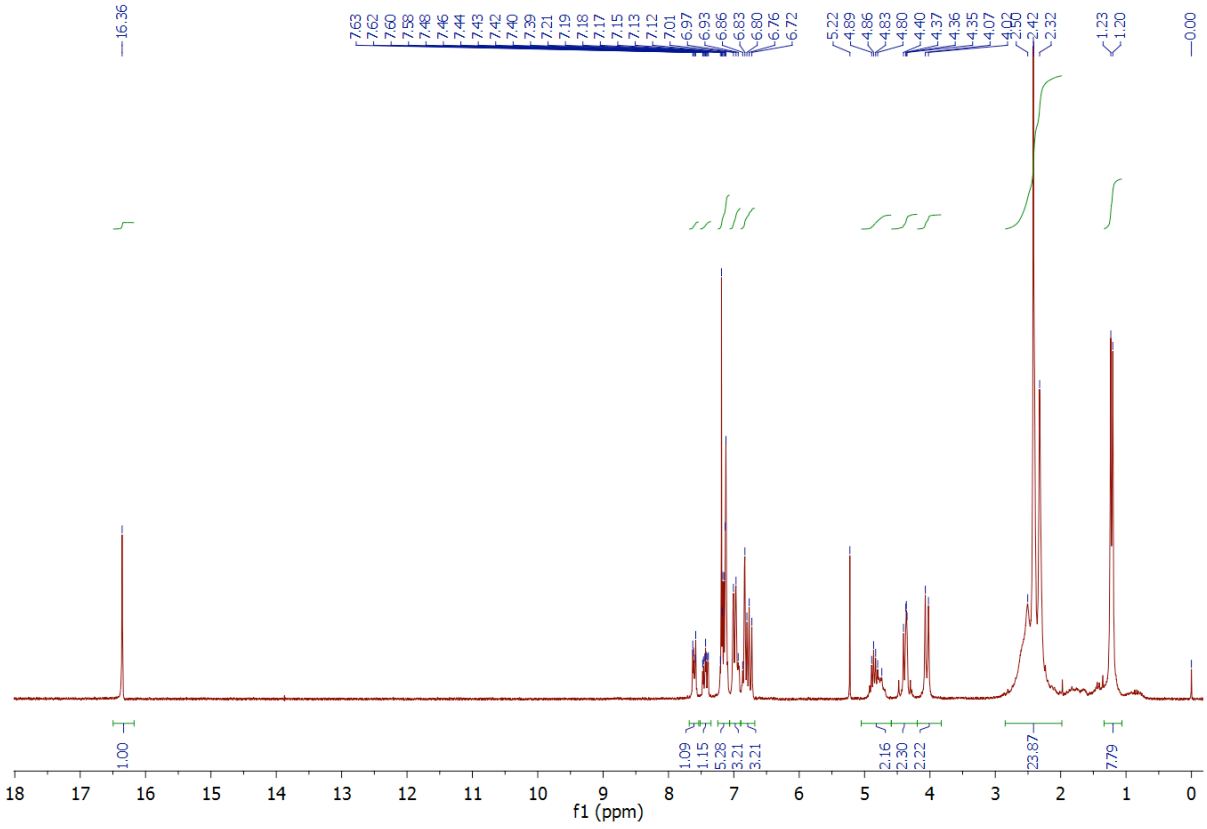
General procedure for synthesis of complexes 6

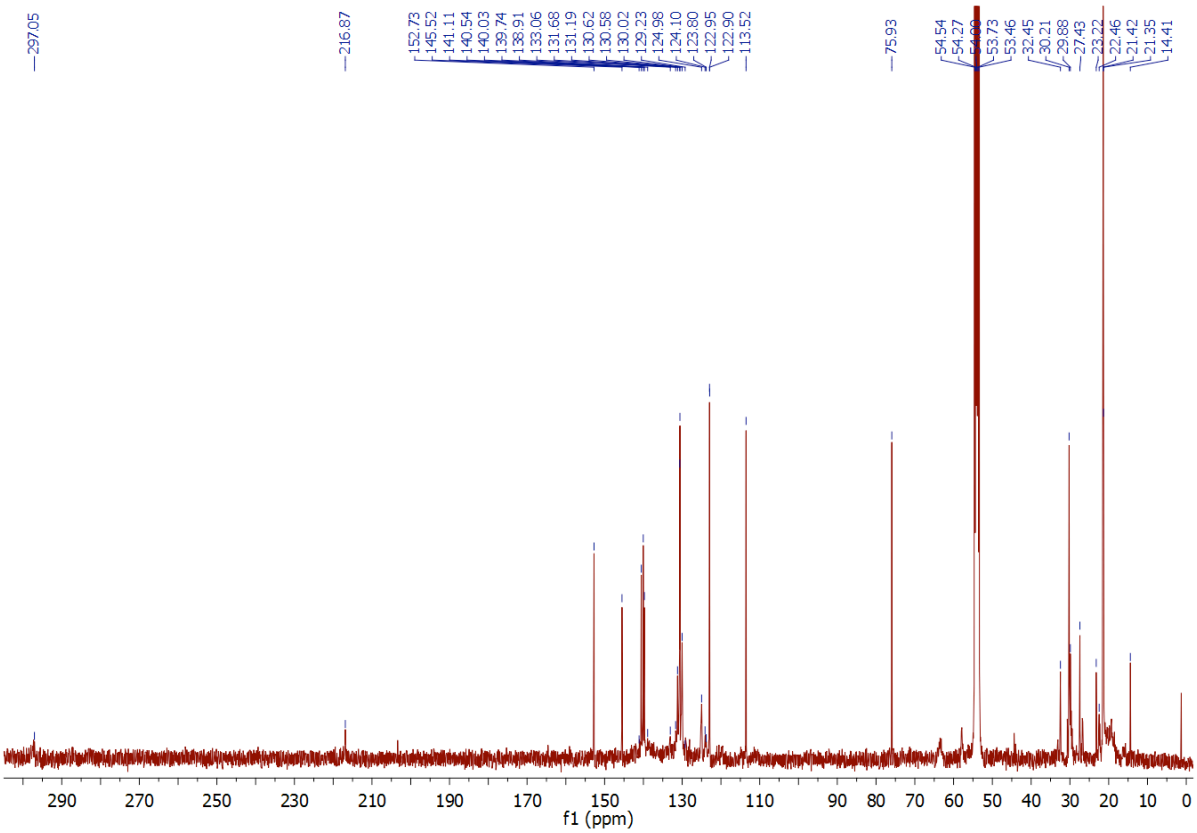


6a,b

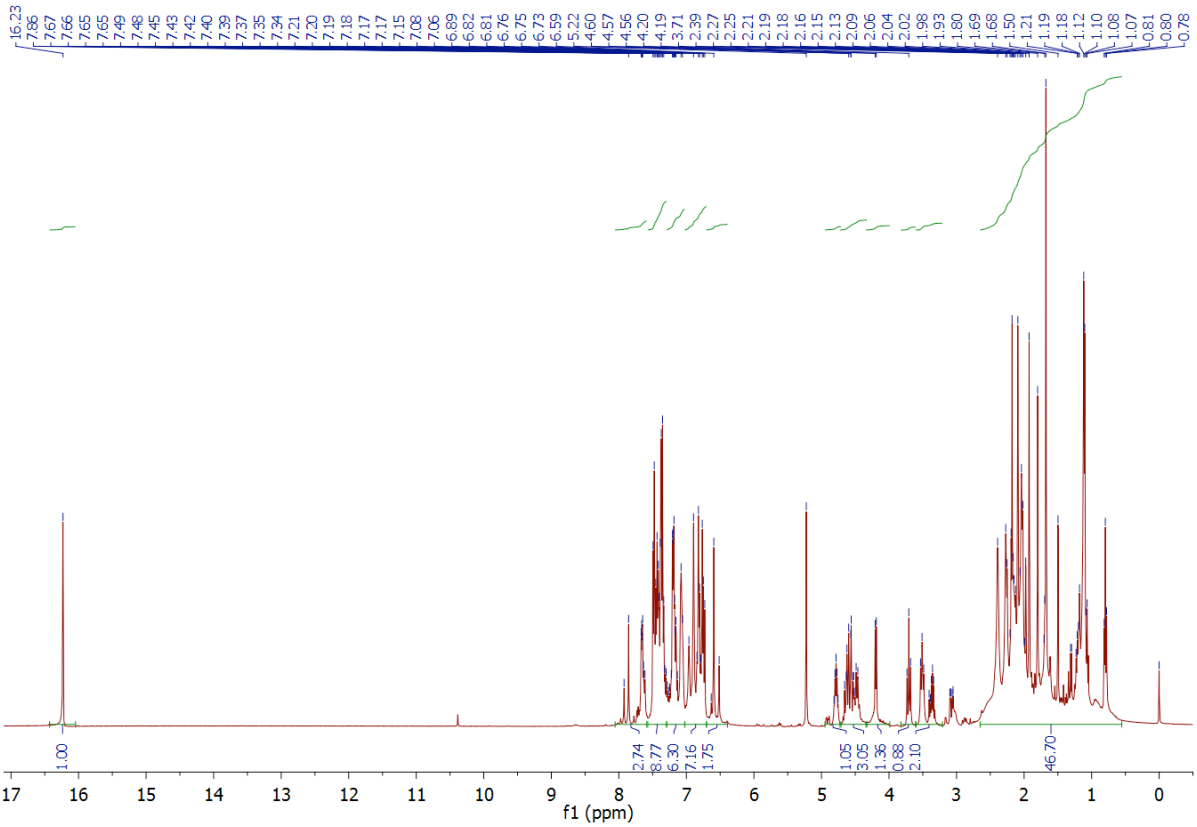
To the solution of **5** (101 mg, 0.186 mmol) in dry toluene (2mL) under argon solution of potassium t-amylate (103 µl, 0.17 mmol) was added and this mixture was allowed to stir for 30 min. After that time **2b** (93 mg, 0.155 mmol) was added and the solution was immersed to preheated bath to 85°C and stirred until complete consumption of **2b**. After cooling down, product was separated by column chromatography with ethyl acetate/cyclohexane (1/10 – 2/1) as eluent to obtain green crystals after crystallization from pentane.

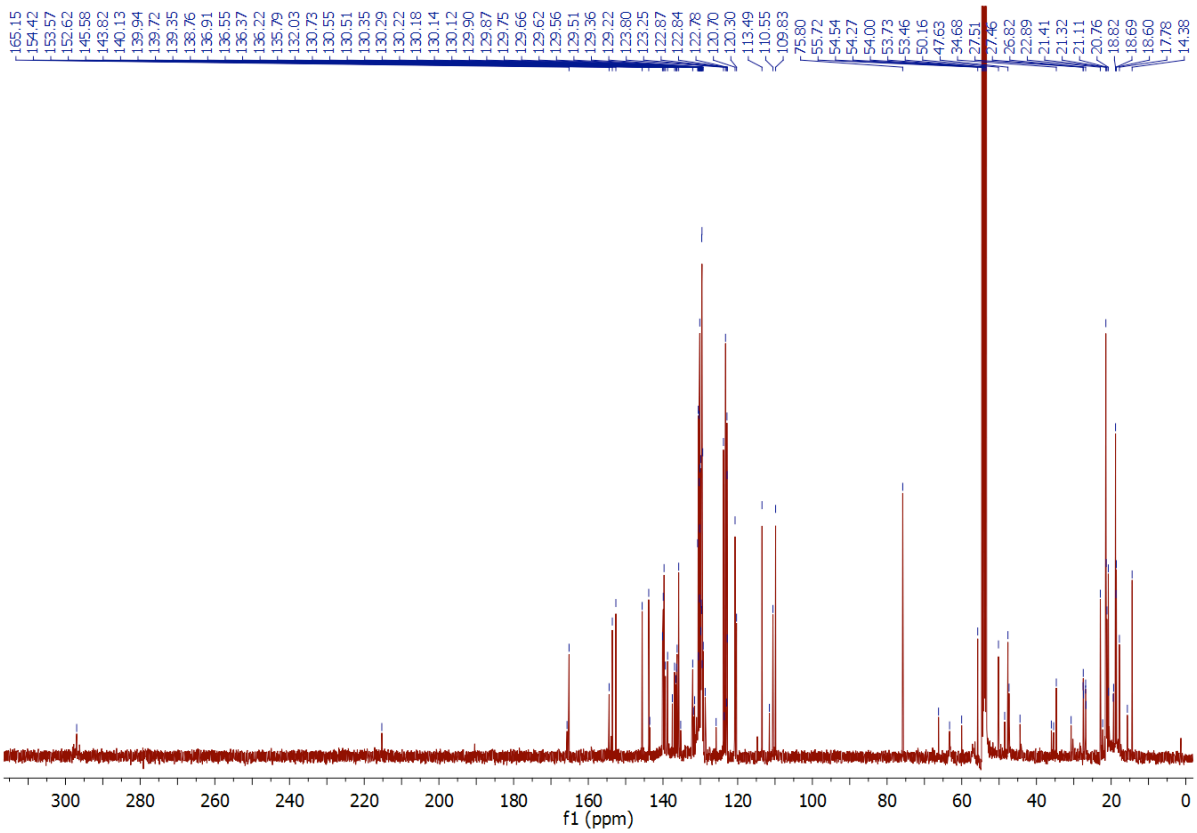
6a (111 mg, 93 %) ^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.36 (s, 1H), 7.61 – 7.53 (m, 2H), 7.38 – 7.18 (m, 4H), 7.10 (s, 1H), 7.06 (s, 1H), 6.99 – 6.90 (m, 2H), 6.87 (d, J = 8.3 Hz, 1H), 4.92 (dt, J = 12.2, 6.1 Hz, 1H), 4.79 (s, 2H), 4.53 (s, 1H), 4.14 (s, 2H), 2.55 (s, 6H), 2.49 (s, 3H), 2.44 (s, 3H), 2.40 (s, 3H), 2.35 (s, 6H), 1.26 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 297.3, 216.9, 152.7, 145.5, 140.5, 140.0, 139.7, 131.7, 131.2, 130.9, 130.8, 130.7, 130.6, 130.3, 130.2, 130.0, 125.1, 125.0, 123.0, 122.9, 113.5, 75.9, 32.5, 30.7, 30.2, 29.9, 27.4, 26.8, 26.7, 22.5, 21.4, 21.4. HRMS cald for $C_{40}H_{47}Cl_2N_4ORuNa$ [M+H$^+$] : m/z 773.214, found : m/z 773.212



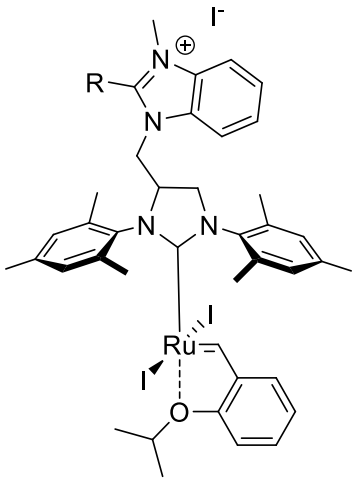


6b (122 mg, 95 %) ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.32 (s, 1H), 8.14 – 7.29 (m, 10H), 7.15 (s, 1H), 7.06 (s, 1H), 6.98 (s, 2H), 6.86 (d, J = 3.8 Hz, 2H), 6.78 (d, J = 8.2 Hz, 1H), 5.10 – 4.79 (m, 1H), 4.67 (s, 2H), 3.95 – 3.33 (m, 2H), 2.47 (s, 6H), 2.36 (s, 3H), 2.28 (s, 3H), 2.16 (s, 6H), 1.26 (dd, J = 7.9, 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 298.2, 219.3, 153.4, 153.1, 151.3, 145.3, 144.9, 140.1, 139.9, 139.7, 139.5, 139.3, 139.1, 138.7, 138.0, 136.8, 136.7, 136.1, 135.8, 135.4, 133.4, 132.0, 131.6, 131.4, 131.1, 131.0, 130.2, 130.2, 130.0, 129.9, 129.5, 127.2, 127.1, 123.4, 122.1, 113.5, 113.4, 111.5, 64.0, 63.0, 59.1, 57.8, 48.1, 34.2, 31.1, 27.0, 26.4, 26.3, 24.3, 24.0, 22.4, 22.2, 22.1, 22.0, 21.8, 21.4, 21.3, 21.2, 21.1, 21.1, 20.5. HRMS calcd for $C_{45}H_{489}Cl_2N_4ORuNa$ [$M+Na^+$] : m/z 855.214, found : m/z 855.215





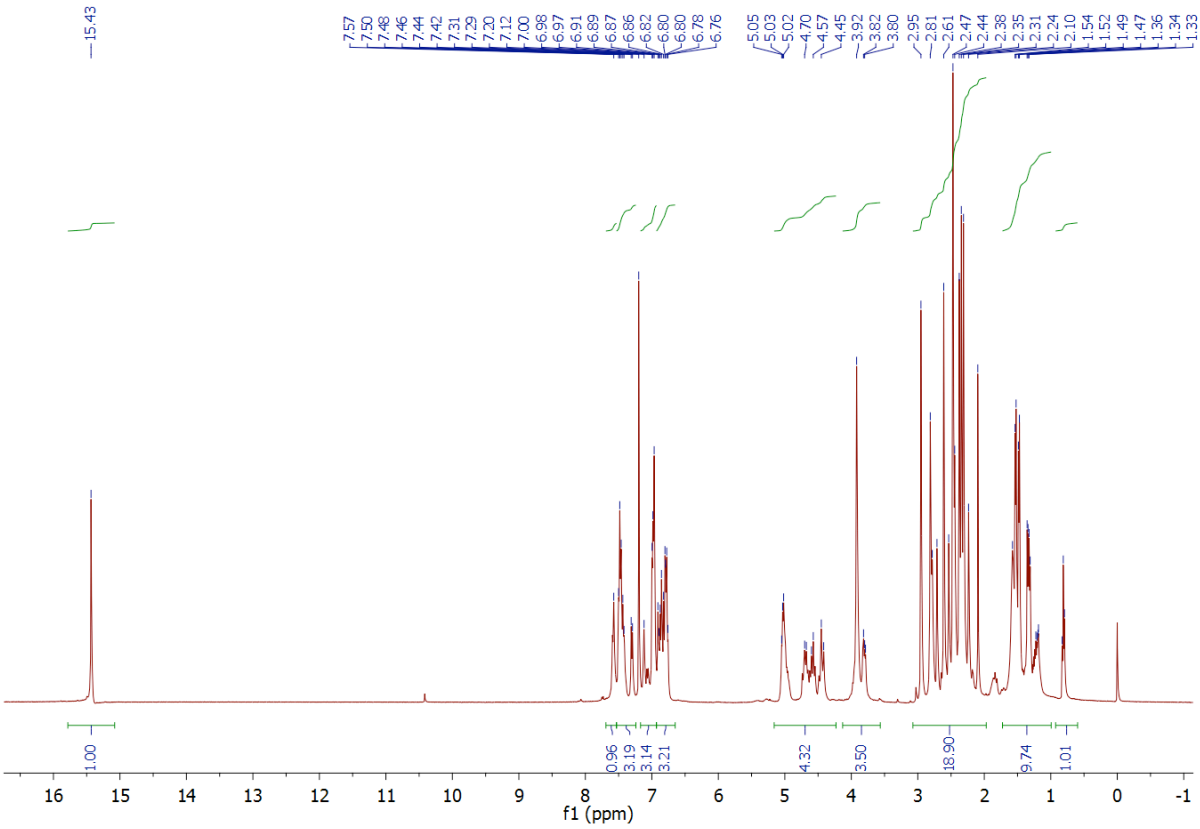
General procedure for synthesis of complexes 7

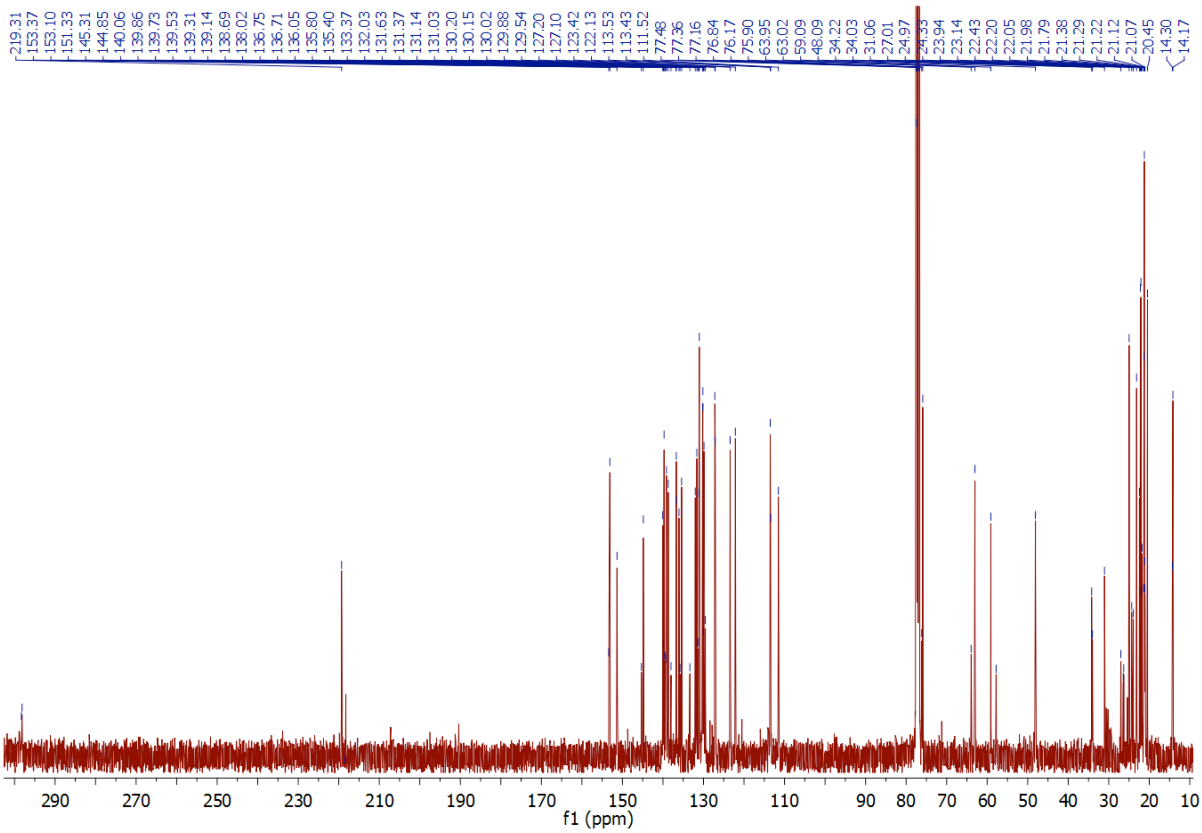


7a,b

Catalyst **6** (100 mg, 0.130 mmol) and methyl iodide (0.5 ml) were placed in microwave tube, purged with argon and irradiated (temperature 123°C, power - 250W, 10 minutes). After that time pentane (2 mL) was added, precipitate formed was extensively washed with pentane to remove excess of methyl iodide, dissolved in small quantity of acetone and filtrated over pad of silica, concentrated to small volume and precipitated by addition of pentane, filtered and dried in vacuum.

7a (117 mg, 90 %) ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.53 (d, 1H), 7.65 (d, 1H), 7.58 – 7.44 (m, 3H), 7.36 (d, 1H), 7.08 (dd, 3H), 6.98 – 6.66 (m, 4H), 5.17 – 4.98 (m, 2H), 4.70 (dd, J = 41.4, 10.6 Hz, 2H), 4.50 (d, J = 14.4 Hz, 1H), 3.98 (s, 3H), 3.02 (s, 3H), 2.88 (s, 3H), 2.67 (s, 3H), 2.53 (s, 6H), 2.41 (s, 6H), 1.64 (s, 1H), 1.59 (d, J = 5.9 Hz, 3H), 1.54 (d, J = 5.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 298.3, 298.2, 219.3, 218.3, 153.4, 153.1, 151.3, 145.3, 144.9, 140.0, 139.9, 139.7, 139.5, 139.3, 139.1, 138.7, 138.0, 136.8, 136.7, 136.1, 135.8, 135.4, 133.4, 132.0, 131.6, 131.4, 131.1, 131.0, 130.9, 130.2, 130.15, 130.0, 129.9, 129.6, 127.2, 127.1, 123.4, 122.1, 122.1, 113.5, 113.4, 111.5, 76.2, 75.9, 64.0, 63.0, 59.1, 57.8, 48.2, 48.1, 31.1, 30.6, 27.0, 26.4, 26.3, 25.4, 25.0, 24.3, 23.1, 22.4, 22.2, 22.1, 22.0, 21.8, 21.4, 21.3, 21.2, 21.1, 21.1, 20.5. HRMS calcd for $C_{41}H_{49}I_2N_4ORu^+$ [M^+] : m/z 969.104, found : m/z 969.104





7b (122 mg, 88 %) ^{1}H NMR (400 MHz, CD_2Cl_2) δ 15.46 (d, 1H), 8.10 – 7.42 (m, 9H), 7.39 – 6.81 (m, 8H), 5.03 (m, 1H), 4.82 – 4.42 (m, 4H), 3.88 (s, 3H), 3.58 (m, 1H), 3.02 (d, 3H), 2.63 – 2.14 (m, 15H), 1.51 (dd, J = 22.2, 6.1 Hz, 3H), 1.38 – 1.22 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 298.0, 297.8, 218.6, 217.6, 153.6, 153.4, 150.8, 145.6, 145.2, 140.3, 140.0, 139.9, 139.7, 139.7, 139.2, 138.9, 138.7, 138.6, 137.3, 137.1, 136.0, 135.9, 135.7, 133.9, 133.8, 133.1, 131.8, 131.8, 131.6, 131.3, 130.5, 130.4, 130.3, 130.2, 130.1, 129.8, 128.1, 127.9, 123.4, 122.5, 122.4, 120.8, 114.5, 114.0, 112.3, 76.7, 76.5, 64.3, 63.7, 59.8, 58.1, 49.0, 48.7, 34.3, 34.2, 24.1, 24.1, 22.9, 22.7, 22.4, 22.3, 22.0, 22.0, 22.0, 21.5, 21.4, 21.2, 21.0, 20.8, 20.5. HRMS calcd for $C_{46}H_{51}I_2N_4ORu^+$ [M^+] : m/z 1031.120, found : m/z 1031.120