Bis(Cyclic Alkyl Amino Carbene) Ruthenium Complexes: A Versatile, Highly Efficient Tool for Olefin Metathesis

Rafał Gawin, Anna Kozakiewicz, Piotr A. Guńka, Paweł Dąbrowski, and Krzysztof Skowerski*

anie_201609009_sm_misellaneous_information.pdf
SUPPORTING INFORMATION

Table of contents
1. Materials and methods ........................................................................................................... 3
2. Synthesis of salt 10h ............................................................................................................... 5
3. Synthesis of ruthenium complexes 15a-h ............................................................................. 6
   3.1. Complex 15a ....................................................................................................................... 6
   3.2. Complex 15b ....................................................................................................................... 8
   3.3. Complex 15c ....................................................................................................................... 10
   3.4. Complex 15d ....................................................................................................................... 12
   3.5. Complex 15e ....................................................................................................................... 13
   3.6. Complex 15f ....................................................................................................................... 14
   3.7. Complex 15g ....................................................................................................................... 16
   3.8. Complex 15h ....................................................................................................................... 17
4. Synthesis of 12f from 15f and 13 ....................................................................................... 19
5. Synthesis of 12a from 15a and 13 in the presence of CuCl .............................................. 19
6. Representative procedure and kinetic plots for reaction of 15f with 13 ....................... 20
7. Procedure for stability of 15f in solution ............................................................................ 20
8. X-Ray Crystallography ....................................................................................................... 22
9. Metathesis reactions ............................................................................................................ 26
   9.1. RCM of diethyl diallylmalonate 17 .................................................................................. 26
   9.2. Ethenolysis of methyl oleate 7 ....................................................................................... 27
   9.3. RCM of 19 ....................................................................................................................... 29
   9.4. RCM of 21 ....................................................................................................................... 30
   9.5. RCM of 23 ....................................................................................................................... 30
   9.6. RCM of 25 ....................................................................................................................... 30
   9.7. SM of 1-decene 8 ............................................................................................................ 31
   9.8. SM of 9 ............................................................................................................................ 31
   9.9. SM of 7 ............................................................................................................................ 32
   9.10. CM of 9 with methyl acrylate 29 .................................................................................. 32
9.11.  En-yne metathesis of 31 ........................................................................................................ 33
9.12.  ROMP of norbornene 33 .................................................................................................... 33
10.   NMR spectra of salts 10 .............................................................................................................. 35
11.   NMR spectra of complexes 15a-h......................................................................................... 44
12.   NMR Spectra of metathesis reactions products .................................................................... 91
13.   HRMS analysis of complexes 15a-h.................................................................................. 112
14.   Elemental analysis scans ..................................................................................................... 121
1. Materials and methods

NMR spectra were acquired on Bruker spectrometers (NMR Avance III HD 500 MHz and NMR Avance 600 MHz). High-resolution mass spectrometry was performed at the Mass Spectrometry Facility, Institute of Organic Chemistry, Polish Academy of Sciences. Elemental analysis was performed by analytical laboratory at the Institute of Organic Chemistry, Polish Academy of Sciences. Gas Chromatographic analyses were conducted using an PerkinElmer Clarus 680 GC equipped with GL Sciences InertCap® 5MS/NP column. 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 KMnO₄ water solution. The column chromatography was performed using silica gel 60 (230–400 mesh). Ethenolysis reactions were performed in Büchi AG miniclane steel type 3/100 mL reactor.

Brown crystals of 15a and 15e were obtained from the dichloromethane/n-pentane solution, orange crystals of 15f and brown crystals of 15b were obtained from the dichloromethane/methanol solution, and orange crystals of 15c were obtained from dichloromethane/nitromethane solution. The X-ray data for all reported structures were collected at 293(2) K with an Oxford Sapphire CCD diffractometer using MoKα radiation λ = 0.71073 Å and ω-2θ method. Structures were solved by direct methods and refined with the full-matrix least-squares method on F² with the use of SHELX-2014 invoked from Olex2 (15a) and SHELX-97 program package (15b, 15c, 15e and 15f). The analytical absorption corrections were applied (CrysAlisPro Software System for 15a and RED171 package of programs Oxford Diffraction, 2000 for compounds 15b, 15c, 15e and 15f). Positions of hydrogen atoms have been found from the electron density maps and hydrogen atoms were constrained during refinement. In 15a and 15e the disordered solvent (n-pentane) molecules were found. The molecules were so badly disordered that they could not be modeled even with restrains and were, therefore, treated with the SQUEEZE procedure implemented in PLATON. The data collection and refinement processes are summarized in Table 1SI.

Oleic acid was purchased from Sigma-Aldrich (90% purity) and was subjected to several crystallizations to remove other fatty acids. Methyl oleate (obtained by esterification of oleic acid with methanol using H₂SO₄ as catalyst) was purified by filtration through pad of activated neutral alumina, degassed, purged with argon and stored over activated neutral alumina (2 wt%). Ethylene gas was

---

[1] a) G. M. Sheldrick, Acta Crystallogr. 2015, C71, 3-8; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341; c) G. M. Sheldrick, Acta Crystallogr. 2008, A64, 112-122.
[2] a) CrysAlisPro Software System Ver. 171.38.41, Rigaku OD, Oxford, UK, 2015; b) CrysAlis CCD171 and RED171 package of programs, Oxford Diffraction, 2000.
[3] A. L. Spek, Acta Crystallogr. 2015, C71, 9-19.
purchased and used as received from Air Liquide (99.99% purity). Ruthenium complexes 14b, 14a, 12g and salts 10a – 10h were prepared according to the methods reported in the literature.

Preparation of catalysts was carried out under Ar in pre-dried glassware using Schlenk techniques. All work-up and purification procedures were carried out with reagent grade solvents in air. Toluene was washed with citric acid (2.5 wt% in water) and water, filtered through activated neutral alumina, degassed by purging with argon and stored over activated 4Å molecular sieves. Dichloromethane was degassed by purging with argon and stored over activated 4Å molecular sieves. All other reagents were purchased from Sigma-Aldrich and used without further purification.

Before GC analysis or distillation metathesis reactions were quenched with 1,4-Bis(3-isocyanopropyl)piperazine [SnatchCat, CAS: 51641-96-4] (4.4 equivalents relative to catalyst) or ethyl vinyl ether.

SEC-MALLS was composed of an 1100 Agilent isocratic pump, autosampler, degasser, thermostatic box for columns, a photometer MALLS DAWN EOS (Wyatt Technology Corporation, Santa Barbara, CA), and differential refractometer Optilab Rex. ASTRA 4.90.07 software (Wyatt Technology Corporation) was used for data collecting and processing. Two PLGel 5microns MIXD-C columns were used for separation. The samples were injected as a solution in methylene chloride. The volume of the injection loop was 100 mL. Methylene chloride was used as a mobile phase at flow rate of 0.8 mL·min⁻¹. The calibration of the DAWN EOS was carried out by p. a. grade toluene and normalization with a polystyrene standard of 30,000 g/mol. molar mass. The measurements were carried out at room temperature.

[4] E. A. Shaffer, C.-L. Chen, A. M. Beatty, E. J. Valente, H.-J. Schanz, J. Organomet. Chem. 2007, 692, 5221–5233.
[5] a) K. J. Harlow, A. F. Hill, J. D. E. T. Wilton-Ely, J. Chem. Soc., Dalton Trans. 1999, 285-292; b) A. Fürstner, J. Grabowski, C. W. Lehmann, J. Org. Chem. 1999, 64, 8275-8280; c) H.-J. Schanz, L. Jafarpour, E. D. Stevens, S. P. Nolan, Organometallics, 1999, 18, 5187-5190.
[6] V. M. Marx, A. H. Sullivan, M. Melaimi, S. C. Virgil, B. K. Keitz, D. S. Weinberger, G. Bertrand, R. H. Grubbs, Angew. Chem. Int. Ed. 2015, 54, 1919-1923.
[7] R. Jazzar, R. D. Dewhurst, J.-B. Bourg, B. Donnadieu, Y. Canac, G. Bertrand, Angew. Chem. Int. Ed. 2007, 46, 2899–2902; Angew. Chem. 2007, 119, 2957–2960.
2. Synthesis of salt 10h

Isobutyraldehyde (4.69 g, 65.0 mmol, 1.3 equiv) and formic acid (0.1 mL) were added to the solution of 1-amino-2,7-diisopropynaphthalene (11.37 g, 50.0 mmol) in toluene (60 mL). Molecular sieves (4Å, 10g) were added and mixture was placed in oil bath at 55 °C (without stirring, occasionally shaken) for 48h. Mixture was cooled to rt and filtered. Toluene and excess of isobutyraldehyde were evaporated under reduced pressure. Residue was dried in vacuum to give imine A as red-brown oil (13.93g, 99%) which was used in the next step without further purification.

Imine A (13.90 g, 49.4 mmol) in dry THF (25 mL) was added dropwise within 1h under argon to a solution of lithium diisopropylamide (25.9 mL, 2M in THF, 51.9 mmol, 1.05 equiv) in dry THF (150 mL) at -40 °C. Mixture was stirred for 15 min at -40 °C and then allowed to warm to rt and stirred for additional 2h. Mixture was cooled to -20 °C and 3-chloro-2-methylprop-1-en (5.02 g, 54.3 mmol, 1.1 equiv) was added dropwise within 5 min. Mixture was allowed to warm to rt and stirring was continued overnight. Solvent and volatiles were evaporated under reduced pressure and dried in vacuum. Residue was redissolved in cyclohexane and passed through pad of alumina which was washed with cyclohexane. Cyclohexane was evaporated under reduced pressure and residue was dried in vacuum to give imine B as red-brown oil (13.63 g, 82%) which was used in next step without further purification.

HCl (25.3 mL, 4M in dioxane, 101.0 mmol, 2.5 equiv) was added dropwise under argon to the stirred solution of imine B (13.6 g, 40.5 mmol) in dry acetonitrile (60 mL). Mixture was stirred overnight at 80 °C. Solvents were evaporated under reduced pressure. Water (300 mL) was added and turbid emulsion was washed with DCM (3x25 mL). Nest solution of NH$_4$BF$_4$ (8.50 g, 81.0 mmol, 2 equiv) in water (200 mL) was added to the aqueous layer. Precipitate was filtered and washed with water and diethyl ether. Product was dried in air overnight and then in vacuum, white solid, 10h, 4.39 g (26%).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 9.08 (s, 1H), 7.97 (d, $J = 8.7$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.52-7.40 (m, 2H), 7.14 (s, 1H), 3.04 (hept, $J = 6.7$ Hz, 1H), 2.83 (hept, $J = 6.7$ Hz, 1H), 2.56-2.46 (m, 2H), 1.75 (s, 3H), 1.67 (s, 3H), 1.53 (s, 3H), 1.44 (s, 3H), 1.40 (d, $J = 6.7$ Hz, 3H), 1.28 (dd, $J = 8.5, 6.8$ Hz, 6H), 1.19 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 193.4, 148.9, 142.7, 131.9, 131.2, 128.5, 127.9, 127.1, 126.1, 122.8, 117.9, 84.5, 49.1, 48.3, 34.3, 29.8, 29.7, 28.1, 26.5, 26.0, 25.3, 23.7, 23.4, 21.9.

HRMS-ESI (m/z): Calcd for C$_{24}$H$_{34}$N$^+$ [M-BF$_4$]$^+$: 336.2691; found 336.2695.
3. Synthesis of ruthenium complexes 15a-h

3.1. Complex 15a

Method A:

Dry deoxygenated toluene (14 mL) was added under argon atmosphere to salt 10a (1.20 g, 3.48 mmol, 2 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 3.48 mL, 3.48 mmol, 2 equiv). After 1 minute solid 14a was added (1.60 g, 1.74 mmol, 1 equiv). The mixture was stirred at 80°C for 20 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of silica gel which was then washed with toluene. Solvents were evaporated under reduced pressure. Crude product was isolated by silica gel column chromatography (eluent: ethyl acetate / cyclohexane 5:95→10:90 v/v). Red-brown fraction was collected and evaporated to dryness. Residue was dissolved in 50 mL of n-pentane. Solvent was evaporated to 25% of initial volume – precipitate formed during evaporation was filtered, washed with a minimal amount of cold n-pentane and dried in vacuum to give red crystalline solid 15a (1.07 g, 70%).

Method B:

Dry deoxygenated toluene (10 mL) was added under argon atmosphere to salt 10a (1.40 g, 4.05 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 4.05 mL, 4.05 mmol, 3 equiv). After 1 minute solid 14a was added (1.25 g, 1.35 mmol, 1 equiv). The mixture was stirred at 80°C for 20 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of silica gel which was then washed with toluene. Solvents were evaporated under reduced pressure. Crude product was isolated by silica gel column chromatography (eluent: ethyl acetate / cyclohexane 5:95→10:90 v/v). Red-brown fraction was collected and evaporated to dryness. Residue was dissolved in 50 mL of n-pentane. Solvent was evaporated to 25% of initial volume – precipitate formed during evaporation was filtered, washed with a minimal amount of cold n-pentane and dried in vacuum to give red crystalline solid 15a (1.02 g, 86%).
Method C:

Dry deoxygenated toluene (50 mL) was added under argon atmosphere to salt 10a (10.00 g, 29.0 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 29.0 mL, 29.0 mmol, 3 equiv). After 1 minute solid 14b was added (8.56 g, 9.66 mmol, 1 equiv). The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of silica gel which was then washed with toluene. Solvents were evaporated under reduced pressure. Crude product was isolated by silica gel column chromatography (eluent: ethyl acetate / cyclohexane 5:95→10:90 v/v). Red-brown fraction was collected and evaporated to dryness. Residue was dissolved in 200 mL of n-pentane. Solvent was evaporated to 25% of initial volume – precipitate formed during evaporation was filtered, washed with a minimal amount of cold n-pentane and dried in vacuum to give red crystalline solid 15a (5.02 g, 59%).

1H NMR (C6D6, 500 MHz): δ = 9.80-9.00 (m, 1H), 8.20-7.20 (m, 8H), 7.12-6.15 (m, 7H), 3.86-3.66 (m, 1H), 3.30-2.50 (m, 6H), 2.37 (d, J = 13.0 Hz, 9H), 1.75-1.22 (m, 12H), 1.10-0.85 (m, 20H).

13C NMR (CD2Cl2, 125 MHz): δ = 279.9, 278.5, 277.8, 276.2, 145.5, 144.1, 143.6, 143.5, 141.3, 141.1, 140.8, 140.7, 140.2, 139.0, 138.6, 138.4, 137.9, 137.6, 134.3, 134.1, 130.6, 129.8, 129.4, 129.2, 128.2, 127.9, 127.6, 127.4, 127.0, 126.9, 126.7, 125.7, 125.5, 124.9, 124.7, 116.5, 116.1, 81.3, 79.7, 61.5, 56.9, 56.4, 55.0, 34.7, 32.5, 32.0, 31.5, 31.0, 30.5, 30.3, 30.0, 29.9, 29.6, 29.2, 27.5, 27.4, 25.3, 25.2, 24.7, 22.9, 14.8, 14.7, 14.4, 13.5, 13.2, 12.9.

HRMS-ESI (m/z): Calcd for C51H68N2Cl3Ru [M]⁺: 876.3490; found 876.3471.
Anal. Calcd for C51H68N2Cl3Ru: C 69.84; H 7.36; N 3.19; Cl 8.08; found C 69.88; H 7.22; N 3.21; Cl 8.05.
3.2. Complex 15b

Dry deoxygenated toluene (35 mL) was added under argon atmosphere to salt 10b (4.97 g, 15.0 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 15.0 mL, 15.0 mmol, 3 equiv). After 1 minute solid 14b was added (4.43 g, 5.0 mmol, 1 equiv).

The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of Celite which was washed with toluene. Toluene was evaporated under reduced pressure. Crude product was isolated by silica gel chromatography (eluent: cyclohexane -> ethyl acetate / cyclohexane 10:90 v/v). Red band was collected and solvent was evaporated to dryness. Residue was dissolved in DCM and excess of nitromethane was added. DCM was slowly removed under reduced pressure. Precipitate was filtered and washed with cold nitromethane. After drying in vacuum, orange-red crystalline 15b was obtained 1.58 g (37%).

\(^1\)H NMR (C\(_6\)D\(_6\), 500 MHz): \(\delta = 9.07\) (dd, \(J = 7.2, 1.2\) Hz, 1H), 7.88 (d, \(J = 7.2\) Hz, 2H), 7.73 (s, 1H), 7.36-7.26 (m, 3H), 7.03-6.96 (m, 2H), 6.89 (d, \(J = 6.6\) Hz, 1H), 6.34 (br. s, 2H), 5.89 (br. s, 2H), 2.41 (s, 6H), 2.34 (s, 6H), 2.31 (s, 6H), 2.11 (s, 6H), 1.74 (s, 6H), 1.71-1.64 (m, 4H), 0.89 (s, 6H), 0.83 (s, 6H).

\(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 125 MHz): \(\delta = 280.2, 277.9, 144.0, 140.7, 138.2, 137.9, 137.4, 136.4, 135.8, 135.4, 134.1, 129.7, 129.6, 129.3, 129.2, 127.3, 127.0, 126.6 (2xC), 115.5, 80.9, 56.9, 54.5, 32.3, 32.1, 30.2, 29.5, 21.6, 21.4, 21.0, 14.4.

\(^{13}\)C NMR (C\(_6\)D\(_6\), 151 MHz): \(\delta = 279.8, 278.1, 143.8, 140.4, 137.9, 137.8, 136.9, 135.7, 135.4, 135.1, 133.2, 129.7, 129.2, 128.9, 128.8, 126.8, 126.4, 126.2, 125.8, 114.9, 79.8, 56.2, 53.7, 32.0, 31.8, 29.3, 28.6, 21.4, 21.2, 20.6.

HRMS-ESI (m/z): Calcd for C\(_{49}\)H\(_{60}\)N\(_2\)Cl\(_2\)Ru [M\(^+\)]: 848.3177; found 848.3161.

Anal. Calcd for C\(_{49}\)H\(_{60}\)N\(_2\)Cl\(_2\)Ru: C 69.32; H 7.12; N 3.30; Cl 8.35; found: C 69.40; H 7.03; N 3.22; Cl 8.56.
| Signal number | $^1$C [ppm] | $^1$H [ppm] |
|---------------|-------------|-------------|
| 1             | 279.75      | x           |
| 2             | 278.09      | x           |
| 3             | 143.84      | x           |
| 4             | 140.43      | x           |
| 5             | 137.91      | x           |
| 6             | 137.84      | x           |
| 7             | 136.94      | 1H, s, 7.73 |
| 8             | 135.73      | x           |
| 9             | 135.44      | x           |
| 10            | 135.13      | x           |
| 11            | 133.22      | x           |
| 12            | 129.66      | 1H, dd, 9.07, $\delta$=7.2, $\gamma$=1.2 Hz |
| 13            | 129.24      | 2H, s, 6.34 (2 x 1H arom) |
| 14            | 128.87      | 2H, s, 5.89 (2 x 1H arom) |
| 15            | 128.84      | x           |
| 16            | 127.89      | Solvent    |
| 17            | 127.73      | Solvent    |
| 18            | 127.57      | Solvent    |
| 19            | 126.78      | 2H, m, 7.03 - 6.96 (1H arom, C 19 in solvent) |
| 20            | 126.39      | 2H, d, 7.88, $\delta$=7.2 (2 x 1H arom) |
| 21            | 126.19      | x           |
| 22            | 125.85      | 2H, m, 7.03 - 6.96 (1H arom) |
| 23            | 114.89      | 1H, d, 6.89, $\delta$=6.6 Hz |
| 24            | 79.77       | x           |
| 25            | 56.22       | x           |
| 26            | 53.67       | 4H, m, 1.71-1.64 |
| 27            | 32.01       | 6H, s, 2.34 (2 x CH$_3$) |
| 28            | 31.85       | 6H, s, 2.41 (2 x CH$_3$) |
| 29            | 29.32       | 6H, s, 0.89 (2 x CH$_3$) |
| 30            | 28.64       | 6H, s, 0.83 (2 x CH$_3$) |
| 31            | 21.38       | 6H, s, 2.31 (2 x CH$_3$) |
| 32            | 21.21       | 6H, s, 2.11 (2 x CH$_3$) |
| 33            | 20.58       | 6H, s, 1.74 (2 x CH$_3$) |

x-quaternary carbon
3.3. Complex 15c

Dry deoxygenated toluene (21 mL) was added under argon atmosphere to salt 10c (3.54 g, 9.0 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 9.0 mL, 9.0 mmol, 3 equiv). After 1 minute solid 14b was added (2.66 g, 3.0 mmol, 1 equiv). The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of Celite which was washed with toluene. Toluene was evaporated under reduced pressure. Residue was dissolved in diethyl ether and the mixture was passed through a short pad of Celite which was washed with diethyl ether. Solvent was concentrated in vacuum to minimal amount and crude product was precipitated by addition of n-pentane. Product was filtered and washed with cold n-pentane. Crude product was dissolved in DCM and excess of nitromethane was added. DCM was slowly removed under reduced pressure. Precipitate was filtered and washed with cold nitromethane. After drying in vacuum, dark red crystalline 15c was obtained 1.078 g (37%).

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ = 9.57 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 7.2 Hz, 2H), 7.61 (s, 1H), 7.52 (d, J = 7.3 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.37-7.16 (m, 5H), 7.15-7.11 (m, 1H), 7.08-6.80 (m, 5H), 6.64 (s, 1H), 6.42 (s, 1H), 5.90 (s, 1H), 2.85 (s, 3H), 2.32 (s, 6H), 2.22 (s, 3H), 2.19 (s, 3H), 2.10 (d, J = 12.5 Hz, 1H), 1.95-1.84 (m, 2H), 1.77 (s, 3H), 1.70 (s, 3H), 1.64 (d, J = 12.7 Hz, 1H), 1.50 (s, 3H), 0.80 (s, 3H), 0.72 (s, 3H), 0.67 (s, 3H), 0.61 (s, 3H).

$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): $\delta$ = 286.8, 278.5, 272.1, 148.7, 147.8, 144.8, 141.2, 139.1, 138.8, 138.5, 138.2, 137.7, 137.6, 136.6, 136.1, 136.0, 135.2, 134.3, 131.7, 131.0, 130.3, 130.2, 129.8, 129.6, 128.8, 128.6, 128.1, 127.5, 127.3 (2xC), 127.0, 126.7, 126.4, 116.0, 116.9, 82.0, 81.9, 68.8, 65.0, 57.0, 55.6, 30.4, 40.2, 29.6, 28.5, 27.9, 27.4, 24.6, 24.3, 21.9, 21.1, 21.0.

$^{13}$C NMR (C$_6$D$_6$, 151 MHz): $\delta$ = 287.9, 279.5, 273.0, 148.6, 148.2, 144.4, 140.9, 138.8, 138.0, 137.8, 137.6 (2xC), 137.4, 136.0, 135.9, 135.7, 134.9, 134.7, 130.9, 130.7, 130.1, 129.8, 129.3, 129.1, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.4, 127.3, 126.9 (2xC), 126.6, 126.1, 115.7, 80.9, 80.7, 68.2, 64.6, 56.0, 53.9, 30.4, 29.0, 28.7, 28.4, 26.8, 26.1, 24.4, 24.1, 22.8, 21.5, 20.6, 20.5.

HRMS-ESI (m/z): Calcd for C$_{59}$H$_{64}$N$_2$Cl$_2$Ru [M]$: 972.3490; found 972.3483.

Anal. Calcd for C$_{59}$H$_{64}$N$_2$Cl$_2$Ru: C 72.82; H 6.63; N 2.88; Cl 7.29; found: C 72.88; H 6.78; N 2.71; Cl 7.16.
| Signal number | $^1$C [ppm] | $^1$H [ppm] |
|--------------|------------|------------|
| 1            | 287.86     | x          |
| 2            | 279.47     | x          |
| 3            | 273.00     | x          |
| 4            | 148.64     | NI         |
| 5            | 148.22     | x          |
| 6            | 144.44     | x          |
| 7            | 140.92     | x          |
| 8            | 138.85     | $1H$, s, 7.61 |
| 9            | 138.05     | NI         |
| 10           | 137.84     | NI         |
| 11           | 137.64     | x          |
| 12           | 137.57     | NI         |
| 13           | 137.37     | x          |
| 14           | 135.97     | NI         |
| 15           | 135.94     | x          |
| 16           | 135.74     | NI         |
| 17           | 134.90     | x          |
| 18           | 130.70     | $1H$, s, 6.90 |
| 19           | 130.88     | $1H$, s, 6.64 |
| 20           | 130.09     | $1H$, d, 9.57, $J=7.6$ Hz |
| 21           | 129.81     | $1H$, s, 6.42 |
| 22           | 129.34     | $1H$, s, 5.90 |
| 23           | 129.13     | 2H, d, 8.14, $J=7.6$ Hz |
| 24           | 128.43     | 2H, d, 7.73, $J=7.2$ Hz |
| 25           | 128.33     | NI         |
| 26           | 128.01     | NI         |
| 27           | 127.88     | Solvent   |
| 28           | 127.83     | NI         |
| 29           | 127.72     | Solvent   |
| 30           | 127.65     | NI         |
| 31           | 127.56     | Solvent   |
| 32           | 127.37     | 2H, t, 7.44, $J=7.6$ Hz |
| 33           | 127.26     | NI         |
| 34           | 126.91     | 2H, d, 7.52, $J=7.3$ Hz |
| 35           | 126.88     | NI         |
| 36           | 126.63     | $1H$, m, 7.08-7.00 |
| 37           | 126.09     | $1H$, t, 6.85, $J=7.6$ Hz and $1H$, m, 7.24-7.18 |
| 38           | 115.74     | $1H$, d, 6.96, $J=7.2$ Hz |
| 39           | 80.89      | x          |
| 40           | 80.65      | x          |
| 41           | 68.17      | x          |
| 42           | 64.55      | x          |
| 43           | 56.00      | 2H (1H 1.87 + 1H 1.64) |
| 44           | 53.95      | 2H (1H 2.10 + 1H 1.91) |
| 45           | 30.43      | 3H, s, 1.70 |
| 46           | 28.96      | 3H, s, 0.72 |
| 47           | 28.65      | 3H, s, 1.50 |
| 48           | 28.42      | 3H, s, 0.80 |
| 49           | 26.76      | 3H, s, 0.67 |
| 50           | 26.09      | 3H, s, 0.61 |
| 51           | 24.45      | 3H, s, 2.32 |
| 52           | 24.15      | 3H, s, 2.85 |
| 53           | 22.82      | 3H, s, 2.32 |
| 54           | 21.49      | 3H, s, 2.22 |
| 55           | 20.55      | 3H, s, 2.19 |
| 56           | 20.48      | 3H, s, 1.77 |
| 57           | 134.69     | NI         |

x-quaternary carbon; NI-not identified
3.4. Complex 15d

Dry deoxygenated toluene (14 mL) was added under argon atmosphere to salt 10d (1.99 g, 6.0 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 6.0 mL, 6.0 mmol, 3 equiv). After 1 minute solid 14b was added (1.77 g, 2.0 mmol, 1 equiv). The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of Celite which was washed with toluene. Toluene was evaporated under reduced pressure. Crude product was isolated by silica gel chromatography (eluent: cyclohexane -> ethyl acetate / cyclohexane 10:90 v/v). Red band was collected and solvent was evaporated to dryness. Residue was dissolved in DCM and excess of methanol was added. DCM was slowly removed under reduced pressure. Precipitate was filtered and washed with cold methanol. After drying in vacuum, orange crystalline 15d was obtained 0.59 g (35%)

$^1$H NMR (C$_6$D$_6$, 500 MHz): δ = 9.88-8.80 (m, 1H), 8.38-7.53 (m, 3H), 7.48-7.20 (m, 4H), 7.12-6.85 (m, 3H), 6.75-6.10 (m, 5H), 3.90-2.90 (m, 2H), 2.87-2.67 (m, 1H), 2.66-2.50 (m, 1H), 2.46-2.22 (m, 12H), 2.21-2.01 (m, 3H), 1.80-1.20 (m, 7H), 1.14-0.65 (m, 18H).

$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): δ = 280.4, 280.3, 277.9, 277.8, 277.6, 144.2, 144.1, 141.1, 141.0, 140.9, 139.5, 139.4, 139.1 (2xC), 138.8, 137.9, 137.8 (2xC), 137.4, 135.5, 135.0, 134.6, 134.5, 131.0, 130.5, 129.7, 129.3, 129.2, 129.1, 129.0, 128.7, 128.4, 127.8, 127.7, 127.4, 127.3, 127.0, 126.8, 126.7, 126.6, 126.5, 125.2, 124.3, 116.3, 116.2, 116.1, 81.9, 80.6, 80.5, 61.5, 57.0, 56.9, 56.5, 54.9, 54.8, 54.7, 54.6, 32.7, 32.4 (2xC), 32.0, 31.8, 31.0, 30.2, 29.6, 29.5, 29.1, 28.8, 27.4, 25.2, 25.1, 24.6, 22.1, 21.8, 14.7, 13.1, 12.7.

HRMS-ESI (m/z): Calcd for C$_{49}$H$_{60}$N$_2$Cl$_2$Ru [M$^+$]: 848.3177; found 848.3159.

Anal. Calcd for C$_{49}$H$_{60}$N$_2$Cl$_2$Ru: C 69.32; H 7.12; N 3.30; Cl 8.35; found: C 69.15; H 7.30; N 3.48; Cl 8.40.
3.5. Complex 15e

Dry deoxygenated toluene (21 mL) was added under argon atmosphere to salt 10e (3.54 g, 9.0 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 9.0 mL, 9.0 mmol, 3 equiv). After 1 minute solid 14b was added (2.66 g, 3.0 mmol, 1 equiv). The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of Celite which was washed with toluene. Toluene was evaporated under reduced pressure. Residue was dissolved in diethyl ether and the mixture was washed through a short pad of Celite which was washed with diethyl ether. Solvent was concentrated under reduced pressure to minimal amount and crude product was precipitated by addition of n-pentane. Product was filtered and washed with cold n-pentane and with cold nitromethane. After drying in vacuum, orange-red crystalline 15e was obtained 0.815 g (28%).

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ = 9.69-9.49 (m, 1H), 8.17-7.96 (m, 2H), 7.82-7.65 (m, 2H), 7.60-7.19 (m, 10H), 7.14-6.45 (m, 10H), 6.37-6.10 (m, 1H), 3.14-2.76 (m, 4H), 2.74–2.46 (m, 2H), 2.42-2.24 (m, 4H), 2.10-1.35 (m, 10H), 1.08-0.92 (m, 5H), 0.85-0.30 (m, 13H).

$^{13}$C NMR (C$_6$D$_6$, 125 MHz): $\delta$ = 290.2, 289.9, 289.0, 288.6, 280.9, 279.2, 279.1, 274.5, 274.2, 274.0, 149.4, 149.3 (2xC), 149.2, 149.0, 148.3, 145.3 (2xC), 145.2, 144.4, 144.2, 144.1 (2xC), 142.4, 142.1, 141.9, 141.8 (2xC), 141.1, 140.9, 139.6, 139.4, 139.2, 139.1, 139.0, 138.8, 138.6, 138.2, 138.1 (2xC), 136.9, 136.6, 136.0 (2xC), 135.7, 135.6, 135.5, 135.2, 131.1, 131.0, 130.9, 130.8, 130.7, 130.6, 130.4, 130.3, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.1 (2xC), 129.0, 128.7, 128.3, 128.0, 127.9, 127.8 (2xC), 127.7 (3xC), 127.6 (2xC), 127.3, 127.2, 126.8 (2xC), 126.7, 126.5, 126.3, 124.8, 124.6, 116.9 (2xC), 81.7, 81.5, 81.1, 80.9, 80.7, 69.1, 69.0, 65.4, 65.3, 65.2, 56.8, 56.7, 56.6, 55.5, 55.1, 53.9, 53.6, 31.0, 30.7, 30.2, 29.9 (2xC), 29.6 (2xC), 29.5, 29.3, 29.2, 29.0, 28.0, 27.9, 27.6, 27.4 (2xC), 27.3, 27.1, 25.8, 25.5, 25.4, 25.2, 25.1 (2xC), 25.0, 24.2, 24.0, 22.7, 22.6, 14.9, 14.8, 14.0, 13.8, 12.6 (2xC).

HRMS-ESI (m/z): Calcd for C$_{59}$H$_{69}$N$_2$Cl$_2$Ru [M$^+$]: 972.3490; found 972.3475.

Anal. Calcd for C$_{59}$H$_{69}$N$_2$Cl$_2$Ru: C 72.82; H 6.63; N 2.88; Cl 7.29; found: C 72.69; H 6.68; N 2.71; Cl 7.07.
3.6. Complex 15f

Dry deoxygenated toluene (70 mL) was added under argon atmosphere to salt 10f (12.22 g, 30.0 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 30.0 mL, 30.0 mmol, 3 equiv). After 1 minute solid 14b was added (8.87 g, 10.0 mmol, 1 equiv). The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of Celite which was washed with toluene. Toluene was evaporated under reduced pressure. Residue was dissolved in diethyl ether and the mixture was passed through a short pad of Celite which was washed with diethyl ether. Solvent was concentrated under reduced pressure to minimal amount and residue was dissolved in DCM and excess of nitromethane was added. DCM was slowly removed under reduced pressure. Precipitate was filtered and washed with cold nitromethane. After drying in vacuum, dark red crystalline 15f was obtained 6.07 g (60%).

$^1$H NMR (CD$_2$Cl$_2$, 500 MHz): $\delta = 9.59$ (d, $J = 7.5$ Hz, 1H), 8.06 (d, $J = 7.7$ Hz, 2H), 7.76 (d, $J = 7.4$ Hz, 2H), 7.49-7.43 (m, 3H), 7.42-7.37 (m, 2H), 7.37-7.31 (m, 2H), 7.31-7.18 (m, 5H), 7.14-7.06 (m, 4H), 7.01-6.97 (m, 1H), 6.68 (t, $J = 7.3$ Hz, 1H), 6.81 (d, $J = 7.6$ Hz, 1H), 6.64 (t, $J = 7.6$ Hz, 1H), 6.34 (d, $J = 7.5$ Hz, 1H), 4.14 (dq, $J = 14.9$; 7.2 Hz, 1H), 3.10-2.98 (m, 2H), 2.98-2.84 (m, 2H), 2.83-2.73 (m, 1H), 2.73-2.63 (m, 1H), 2.57-2.48 (m, 1H), 2.05 (d, $J = 12.3$ Hz, 1H), 1.91 (d, $J = 12.4$ Hz, 1H), 1.84 (d, $J = 12.7$ Hz, 1H), 1.78 (s, 3H), 1.62 (d, $J = 12.7$ Hz, 1H), 1.48-1.40 (m, 6H), 1.03 (dt, $J = 14.5$; 7.3 Hz, 6H), 0.95 (dt, $J = 14.5$; 7.3 Hz, 3H), 0.77 (s, 3H), 0.71 (s, 3H), 0.63 (s, 3H), 0.50 (s, 3H).

$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): $\delta = 288.1, 279.5, 273.4, 148.9, 147.8, 144.9, 143.8 (2xC), 143.3, 141.6, 141.4, 140.2, 139.0, 138.1, 137.9, 137.5, 135.0, 130.0, 129.9, 129.7, 129.2, 128.8, 128.7, 128.2, 128.1, 127.8, 127.7, 127.6, 127.4, 127.3 (2xC), 127.2 (3xC), 126.6, 126.5, 126.4, 126.3 (2xC), 126.1, 124.7, 116.5, 81.5, 80.5, 68.9, 65.1, 57.1, 55.4, 32.2, 31.5, 30.2, 29.7, 29.4, 29.1, 28.6, 28.0, 27.7, 27.6, 27.3, 27.2, 26.6, 25.7, 25.5, 24.8 (2xC), 24.4, 16.3, 16.1, 14.5, 14.4, 14.0, 13.6, 13.4, 12.4.

$^{13}$C NMR (CD$_2$Cl$_2$, 151 MHz): 289.4, 280.0, 274.2, 148.8, 148.1, 144.5, 143.2 (2xC), 141.5, 141.2, 140.0, 138.6, 137.8, 137.4 (2xC), 135.6, 129.4, 129.1, 128.5, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 127.2 (2xC), 126.7, 126.1 (2xC), 126.0, 124.3, 116.3, 80.7, 79.3, 68.2, 64.5, 55.9, 53.6, 29.2 (2xC), 28.9, 28.7, 27.5, 27.1, 26.7, 25.5, 25.3, 24.5, 14.3 (2xC), 13.6, 12.2.

HRMS-ESI (m/z): Calcld for C$_{61}$H$_{68}$N$_2$Cl$_2$Ru [M$^+$]: 1000.3803; found 1000.3798.

Anal. Calcld for C$_{61}$H$_{68}$N$_2$Cl$_2$Ru: C 73.18; H 6.85; N 2.80; Cl 7.08; found: C 73.14; H 7.00; N 2.95; Cl 7.10.
| Signal number | $^1$C [ppm] | $^1$H [ppm] |
|--------------|-------------|-------------|
| 1            | 289.43      | x           |
| 2            | 279.98      | x           |
| 3            | 274.20      | x           |
| 4            | 148.85      | x, NI       |
| 5            | 148.08      | x, NI       |
| 6            | 144.46      | x           |
| 7            | 143.21      | x           |
| 8            | 143.18      | x           |
| 9            | 141.46      | x, NI       |
| 10           | 141.18      | x, NI       |
| 11           | 140.00      | x           |
| 12           | 138.65      | 1H, s, 7.48 |
| 13           | 137.84      | x           |
| 14           | 137.43      | x           |
| 15           | 137.41      | x           |
| 16           | 135.59      | x           |
| 17           | 129.40      | 2H, s, 8.07 |
| 18           | 129.07      | x, NI       |
| 19           | 128.46      | x, NI       |
| 20           | 128.05      | x, NI       |
| 21           | 127.92      | 1H, m, 7.70 + Solvent |
| 22           | 127.75      | 1H, d, 6.64 J=7.6 Hz + Solvent |
| 23           | 127.67      | 1H, m, 7.19 + Solvent |
| 24           | 127.55      | NI          |
| 25           | 127.30      | NI          |
| 26           | 127.17      | NI          |
| 27           | 127.12      | 1H, m, 7.12 |
| 28           | 127.06      | NI          |
| 29           | 126.72      | 1H, d, 9.60, J=7.6 Hz |
| 30           | 126.13      | NI          |
| 31           | 126.07      | 1H, t, 6.89, J=7.2 Hz |
| 32           | 126.01      | 1H, d, 6.82, J=7.2 Hz |
| 33           | 124.35      | 1H, d, 6.33, J=7.2 Hz |
| 34           | 116.27      | 1H, d, 6.98, J=7.2 Hz |
| 35           | 80.73       | x           |
| 36           | 79.33       | x           |
| 37           | 68.21       | x           |
| 38           | 64.50       | x           |
| 39           | 55.89       | 2H, m,1.82-1.56 |
| 40           | 53.58       | 2H, m, 2.04 - 1.89 |
| 41           | 29.19       | 3H, s, 0.68 |
| 42           | 29.16       | 3H, s, 1.78 |
| 43           | 28.95       | 3H, s, 1.45 |
| 44           | 28.66       | 3H, s, 0.74 |
| 45           | 27.52       | 2H, m (1H, m, 3.07-2.99) + (1H, m, 2.72-2.65) |
| 46           | 27.09       | 2H, m (1H, m, 2.95-2.85) + (1H, m, 2.82-2.76) |
| 47           | 26.74       | 2H, m (1H, m, 4.18-4.11) + (1H, m, 2.95-2.85) |
| 48           | 26.55       | 3H, s, 0.61 |
| 49           | 25.32       | 3H, s, 0.48 |
| 50           | 24.49       | 2H, m (1H, m, 3.07-2.99) + (1H, m, 2.53-2.47) |
| 51           | 14.32       | 3H, t, 1.01, J=7.2 Hz |
| 52           | 14.26       | 3H, t, 0.93, J=7.2 Hz |
| 53           | 13.64       | 3H, t, 1.44, J=7.2 Hz |
| 54           | 12.24       | 3H, t, 1.04, J=7.2 Hz |

x-quaternary carbon; NI-not identified
3.7. Complex 15g

Dry deoxygenated toluene (56 mL) was added under argon atmosphere to salt 10g (8.29 g, 24.0 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 24.0 mL, 24.0 mmol, 3 equiv). The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Triethylamine (5 mL) was added and the mixture was passed through a pad of silica gel (deactivated with triethylamine), which was washed with 75 mL of toluene/triethylamine (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent cyclohexane/triethylamine (95:5 v/v) -> cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The residue was dissolved in 150 mL of n-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtered, washed with minimal amount of cold n-pentane. After drying in vacuum, orange-brown crystalline 15g was obtained 2.89 g (41%).

$^1$H NMR (CD$_2$Cl$_2$, 500 MHz): $\delta = 10.05-8.65$ (m, 1H), 8.50-7.45 (m, 3H), 7.40-7.15 (m, 7H), 7.05-6.05 (m, 5H), 3.86-3.62 (m, 1H), 3.12-2.89 (m, 1H), 2.86-2.02 (m, 8H), 1.92-1.11 (m, 22H), 1.10-0.65 (m, 14H), 0.44 (s, 2H).

$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): $\delta = 281.7, 281.0, 280.1, 279.1, 278.5, 147.6, 146.3, 142.0, 141.8, 141.1, 140.9, 139.9, 139.8, 139.5, 137.7, 136.7, 136.4, 136.1, 134.0, 131.8, 130.7, 130.0, 129.8, 129.5, 129.4, 129.2, 129.0, 128.7, 127.5, 127.3, 127.2, 127.0, 126.6, 125.8, 125.4, 116.6, 116.5, 80.3, 80.3, 62.7, 61.9, 61.4, 57.3, 56.8, 56.0, 32.0, 31.4, 30.8, 30.0, 28.9, 28.8, 28.6, 28.4, 27.8, 27.5, 27.3, 26.9, 26.5, 26.4, 25.7, 25.4, 24.0, 23.8, 23.2, 22.7.

HRMS-ESI (m/z): Calcd for C$_{51}$H$_{64}$N$_2$Cl$_2$Ru $[M]^+$: 876.3490; found 876.3477.

Anal. Calcd for C$_{51}$H$_{64}$N$_2$Cl$_2$Ru: C 69.84; H 7.36; N 3.19; Cl 8.08; found: C 69.94; H 7.43; N 3.14; Cl 8.17.
3.8. Complex 15h

Method A:

Dry deoxygenated toluene (8 mL) was added under argon atmosphere to salt 10h (0.847 g, 2.0 mmol, 2 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 2.0 mL, 2.0 mmol, 2 equiv). After 1 minute solid 14b was added (0.887 g, 1.0 mmol, 1 equiv). The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Triethylamine (1 mL) was added and the mixture was passed through a pad of silica gel (deactivated with triethylamine), which was washed with 25 mL of toluene/triethylamine (95:5 v/v). Solvents were evaporated under reduced pressure. The crude product was isolated by column chromatography on silica gel (deactivated with triethylamine; eluent cyclohexane/triethylamine (95:5 v/v) -> cyclohexane/ethyl acetate/triethylamine (90:5:5 v/v/v)). Red brown fraction was collected and concentrated to dryness. The residue was dissolved in 40 mL of n-pentane. Solvent was evaporated to 25% of its original amount – precipitate formed during evaporation was filtered, washed with minimal amount of cold n-pentane. After drying in vacuum, orange-brown crystalline 15h (Fraction A) was obtained 0.147 g (14%). The filtrate was evaporated to dryness. Residue was dissolved in a small amount of DCM and excess of methanol was added. DCM was evaporated under reduced pressure – precipitate formed during evaporation was filtered, washed with minimal amount of cold methanol. After drying in vacuum, red crystalline 15h (Fraction B) was obtained 0.184 g (18%).

\[^1\text{H} \text{NMR (C}_2\text{D}_6, 500 \text{MHz)}: \delta = 9.86-8.38 \text{ (m, 1H), 8.35-7.65 \text{ (m, 6H), 7.62-7.53 \text{ (m, 1H), 7.51-7.45 \text{ (m, 1H), 7.44-7.37 \text{ (m, 1H), 7.35-7.25 \text{ (m, 5H), 7.10-6.55 \text{ (m, 5H), 4.04-3.72 \text{ (m, 1H), 3.45-2.75 \text{ (m, 3H), 2.08-1.94 \text{ (m, 3H), 1.65-1.05 \text{ (m, 35H), 0.98-0.71 \text{ (m, 14H) (mixture of isomers).}}}}}}\]

\[^{13}\text{C} \text{NMR (CD}_2\text{Cl}_2, 125 \text{ MHz)}: \delta = 282.3, 281.1, 280.2, 279.0, 278.9, 277.5, 145.9, 145.3, 144.5 (2\text{xC}), 144.4, 142.8, 142.4, 141.2, 140.6, 140.2, 138.0, 137.5, 135.0, 134.7, 134.4 (2\text{xC}), 134.2, 133.2, 132.8, 132.6 (2\text{xC}), 132.5, 132.4 (2\text{xC}), 132.2, 131.8 (2\text{xC}), 131.4, 131.2, 130.6, 130.5, 129.5, 129.4, 129.2, 129.1, 129.0, 128.9, 128.7, 128.4, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 127.2 (2\text{xC}), 127.1, 126.9, 126.2, 126.0, 125.7 (2\text{xC}), 125.6, 125.4, 125.2, 125.1, 124.7, 123.7, 123.6, 116.1, 115.6, 115.3, 81.5, 81.3, 80.8, 80.1, 62.0, 61.5, 56.5, 56.2, 55.8, 55.3, 54.8, 35.5, 35.4, 35.0, 34.3, 33.2 (3\text{xC}), 31.6, 31.5, 31.3 (2\text{xC}), 30.8, 30.7, 30.6 (2\text{xC}), 30.5 (2\text{xC}), 30.4, 30.2, 30.1, 30.0, 29.9, 29.7, 29.5 (2\text{xC}), 28.9 (2\text{xC}),
28.8, 28.7, 28.3, 27.6, 27.5, 27.3, 26.8, 26.2, 26.0, 25.7 (2xC), 25.4, 24.9, 24.8, 24.7, 24.6, 24.5, 24.4, 24.3, 24.2, 23.8, 23.3, 23.2, 23.1 (2xC), 23.0, 22.9, 22.5.

Analytical data of Fraction A (mainly isomer A):
HRMS-ESI (m/z): Calcd for $C_{63}H_{76}N_2Cl_2Ru [M]$: 1032.4429; found 1032.4402.
Anal. Calcd for $C_{63}H_{76}N_2Cl_2Ru$: C 73.23; H 7.41; N 2.71; Cl 6.86; found: C 73.19; H 7.46; N 2.60; Cl 6.84.

Analytical data of Fraction B (mainly isomer B):
HRMS-ESI (m/z): Calcd for $C_{63}H_{76}N_2Cl_2Ru [M]$: 1032.4429; found 1032.4426.
Anal. Calcd for $C_{63}H_{76}N_2Cl_2Ru$: C 73.23; H 7.41; N 2.71; Cl 6.86; found: C 73.16; H 7.31; N 2.74; Cl 6.97.

Method B:

Dry deoxygenated toluene (0.7 mL) was added under argon atmosphere to salt 10h (0.127 g, 0.3 mmol, 3 equiv). Resulted suspension was heated up to 80 °C and solution of LiHMDS in toluene was added (1M, 0.3 mL, 3.0 mmol, 3 equiv). After 1 minute solid 14b was added (0.089 g, 0.1 mmol, 1 equiv). The mixture was stirred at 80°C for 2 minutes and then cooled to room temperature. Reaction mixture was passed through a short pad of Celite which was washed with toluene. Toluene was evaporated under reduced pressure. Residue was dissolved in diethyl ether and the mixture was passed through a short pad of Celite which was washed with diethyl ether. Nitromethane was added and diethyl ether was slowly removed under reduced pressure - precipitate formed during evaporation was filtered, washed with minimal amount of cold nitromethane. After drying in vacuum, orange-brown crystalline 15h (Fraction A) was obtained 0.025 g (24%). The filtrate was concentrated to ca. 2 mL and was stored overnight at -20 °C. Precipitate was filtered and washed with minimal amount of cold nitromethane. After drying in vacuum, red crystalline 15h (Fraction B) was obtained 0.015 g (15%).
4. Synthesis of 12f from 15f and 13

13 (0.033g, 0.187 mmol, 1.2 eq) was added under argon to the solution of 15f (0.156 g, 0.156 mmol) in toluene (3.1 mL) and flask was placed in oil bath heated to 60°C. Reaction mixture was stirred at this temperature for 60 minutes. After cooling down to room temperature mixture was poured onto silica gel and product was eluted with ethyl acetate/cyclohexane (1:9 v/v) mixture. Green band was collected and solvents were removed. After drying on high vacuum the green solid 12f was obtained, 86mg (86%).

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = [17.89$ (s, 0.25H), 16.52 (s, 0.75H), 1H], 8.55-7.70 (m, 2H), 7.60-7.18 (m, 6H), 7.12-7.07 (m, 1H), 6.98-6.84 (m, 1H), 6.68-6.43 (m, 1H), 6.38 (d, $J = 8.3$ Hz, 1H), 4.60-4.45 (m, 1H), 3.10-2.00 (m, 8H), 2.00-1.14 (m, 9H), 1.07 (s, 5H), 0.99 (s, 3H), 0.85 (br. s, 2H).

$^{13}$C NMR (C$_6$D$_6$, 125 MHz): $\delta = 296.9$, 296.6, 265.0, 153.4, 150.9, 146.3, 144.9, 144.5, 144.3, 143.7, 139.7, 130.9, 130.1, 129.7, 129.5, 128.0, 127.7, 127.3, 124.0, 122.2, 113.8, 78.0, 75.8, 75.1, 64.2, 63.8, 58.3, 49.3, 31.2, 30.3, 29.8, 28.1, 27.5, 26.4, 25.9, 25.0, 22.7, 22.6, 16.3, 15.7, 15.0.

HRMS-ESI (m/z): Calcd for C$_{33}$H$_{41}$NOClRu [M-Cl]$^+$: 604.1920; found 604.1917.

Anal. Calcd for C$_{33}$H$_{41}$NOCl$_2$Ru: C 61.96; H 6.46; N 2.19; Cl 11.08; found: C 61.93; H 6.59; N 2.14; Cl 11.23.

5. Synthesis of 12a from 15a and 13 in the presence of CuCl

13 (0.228g, 0.129 mmol, 1.2 eq) was added under argon to the solution of 15a (0.948 g, 1.08 mmol) in toluene (10 mL) and flask was placed in oil bath heated to 60°C. CuCl was added (0.214 g, 2.16 mmol, 2 eq). Reaction mixture was stirred at 60°C for 30 minutes. After cooling down to room temperature mixture was poured onto silica gel and product was eluted with ethyl acetate/cyclohexane (1:9 v/v) mixture. Green band was collected and solvents were removed. The residue was dissolved in ethyl acetate and filtered.
The solvent was evaporated, the residue was washed with isopropanol. After drying on high vacuum the green solid 12a was obtained, 390 mg (62%).

$^1$H NMR in agreement with literature data.$^8$

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = 16.41$ (s, 1H), 7.33-7.28 (m, 1H), 7.22-7.18 (m, 2H), 7.16-7.11 (m, 1H), 7.01 (dd, $J = 7.6$; 1.6 Hz, 1H), 6.64 (td, $J = 7.4$; 0.8 Hz, 1H), 6.46-6.42 (m, 1H), 4.67 (septet, $J = 6.1$ Hz, 1H), 2.87-2.78 (m, 2H), 2.45-2.35 (m, 2H), 2.23 (s, 6H), 1.77 (s, 2H), 1.70 (d, $J = 6.1$ Hz, 6H), 0.97-0.92 (m, 12H).

6. Representative procedure and kinetic plots for reaction of 15f with 13.

Solution of 13 (7.04 mg, 0.04 mmol, 2 equiv) in toluene-d$_8$ (0.1 mL) and solution of diethylmalonate (internal standard, 7 mg) in toluene-d$_8$ (0.1 mL) were added under nitrogen to the solution of complex 15f (20.0 mg, 0.02 mmol) in toluene-d$_8$ (0.6 mL). Mixture was transferred to the NMR tube which was placed in the spectrometer at 60°C. The data were collected over a time period of about 3500s. Completion of the reaction was accompanied with the change of the colour from dark red to olive-green. Formation of complex 12f was confirmed by comparison of characteristic benzylidene proton chemical shift with authentic sample.

Integration of characteristic proton of 15f (dublet 9.43 ppm) and diethyl malonate CH$_2$(CO$_2$CH$_2$CH$_3$)$_2$ (quartet 3.90 ppm) were recorded. First order plots of ln($C_{15f}$) vs time are shown on Figure 1SI. Same procedure was used for experiments with 4, 6 and 8 equiv of 13.

7. Procedure for stability of 15f in solution.

Solution of diethylmalonate (internal standard, 7 mg) in toluene-d$_8$ (0.1 mL) was added under nitrogen to the solution of complex 15f (20.0 mg, 0.02 mmol) in toluene-d$_8$ (0.7 mL). Mixture was transferred to the NMR tube which was placed in the spectrometer at 60°C. The data were collected over a time period of about 3500s. Due to the formation of several new peaks originated from decomposition of 15f the disappearance of characteristic proton from indenyldiene ligand could be reliably measured only within 2000s. Integration of characteristic proton of 15f (dublet 9.43 ppm) and diethyl malonate CH$_2$(CO$_2$CH$_2$CH$_3$)$_2$ (quartet 3.90 ppm) were recorded. Stability of 15f is shown on Figure 2SI.

[8] D. R. Anderson, V. Lavallo, D. J. O’Leary, G. Bertrand, R. H. Grubbs, Angew. Chem. Int. Ed. 2007, 46, 7262-7265.
Figure 1SI. First order plots of ln(C_{15f}) vs time for reactions between 15f and 13 for various C_{13}: 0.05, 0.1, 0.15 and 0.2 M.

Figure 2SI. Stability of 15f in toluene-d₈ at 60°C
8. X-Ray Crystallography

Crystal structure of 15a-c, 15e, and 15f.

The asymmetric part of 15a and 15f structures contain a single molecules of the bis-CAAC-Ru complex. In asymmetric unit of 15b and 15c structures are the bis-CAAC-Ru complex molecule and one solvent molecule, CH$_3$OH and CH$_2$Cl$_2$, respectively. While the asymmetric part of 15e structure consists of two bis-CAAC-Ru complex molecules. Ru ions in these complexes are five-coordinated in the distorted square pyramidal geometry with two chloride ions, two carbon atoms of CAAC ligands and carbon atom of indenylidene ligand in the apical position (Figure 2 and Figure1SI). For all structures, the Ru-Cl and Ru-C$_{\text{carbene}}$ distances are very similar, while the Ru-C$_{\text{indenylidene}}$ distance is significantly different. For 15b catalyst, the Ru-C$_{\text{indenylidene}}$ distance of 1.850(6) Å is the shortest, while in 15f is the longest, with distance being Ru-C$_{25\text{indenylidene}}$ 1.877(10) Å. For 15b, the Ru-C$_{2\text{carbene}}$ distance (2.085(6) Å) is the shortest among the structures described here. Contrary, the Ru-C$_{\text{carbene}}$ distances are the longest for 15e catalyst (Table 2SI). These geometry parameters are very similar to those reported for (NHC)(NHC')indenylidene complexes (e.g. 5).

Contrary, in the structure of the CAAC-benzylidenes complex (e.g. 12a) the analogous Ru-C$_{\text{carbene}}$ and Ru-Cl distances are significantly shorter than these found in 15a-c, 15e, and 15f. The N-DEP (DEP: 2,6 - diethylphenyl) moieties of 15a and N-TMP (TMP: 2,4,6 – trimethylphenyl) groups of 15b are positioned on the same side with respect to the coordination pyramid base. In 15a, the distance between the Ru ion and the Cl$_2$(C$_{\text{carbene}}$)$_2$ best plane (0.404 Å) is similar to that found in the 15b (0.393 Å) complex. While, the architecture of 15c and 15e catalysts are quite similar to that in 15f. The N-TMP moiety of CAAC ligands of 15c and the N-EMP (EMP: 2-ethyl-6-methylphenyl) moieties of 15e are on the opposite side with respect to the RuCl$_2$(C$_{\text{carbene}}$)$_2$ best plane, as N-DEP groups in 15f. Consequently, only one N-TMP (15c), N-EMP (15e), and N-DEP (15f) moiety is on the same side as indenylidene ligand. The Ru atom of 15c is positioned 0.315 Å above the coordination pyramid base towards the carbon atom of indenylidene ligand, while in 15e the distance between the Ru ion and the Cl$_2$(C$_{\text{carbene}}$)$_2$ best plane is 0.315 and 0.328 Å in molecule 1 and 2, respectively. While, this distance in 15f (0.320 Å) is similar to that found in 15c and 15e. In both molecules of 15e catalyst the rotational disorder of EMP ring was detected, reflecting rotation around N1-C15 and N71-C85 bond, respectively in molecule 1 and 2. In molecule 1 the occupancy in two populations refined to 55 and 45 %, while in molecule 2 refined to 63 and 37%. 
Figure 1SI. X-ray crystal structure of 15b, 15c, and 15e. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. The solvent molecule (CH$_3$OH) of 15b, (CH$_2$Cl$_2$) of 15c, and second complex molecule of 15e are omitted for clarity.
Table 1SI. Crystal data and structure refinement for 15a, 15b, 15c, 15e, and 15f.

| Empirical formula | 15a | 15b | 15c | 15e | 15f |
|------------------|-----|-----|-----|-----|-----|
| CCDC             | 1498937 | 1498938 | 1510232 | 1498939 | 1498940 |
| Chemical formula | C_{31}H_{68}N_{5}Cl_{2}Ru | C_{30}H_{68}N_{6}OC_{2}Ru | C_{32}H_{54}N_{5}Cl_{2}Ru | C_{31}H_{66}N_{4}Cl_{2}Ru | C_{31}H_{66}N_{4}Cl_{2}Ru |
| Formula weight   | 877.01 | 881.00 | 994.32 | 973.09 | 1001.14 |
| Crystal system, space group | Triclinic, P-1 | Triclinic, P-1 | Triclinic, P-1 | Triclinic, P-1 | Triclinic, P-1 |
| a [Å]            | 12.6088(6) | 12.2208(8) | 11.7646(8) | 12.602(3) | 12.708(3) |
| b [Å]            | 14.7178(7) | 12.5079(8) | 12.9023(7) | 18.481(4) | 13.970(3) |
| c [Å]            | 15.2580(7) | 14.8638(8) | 18.3942(10) | 24.942(5) | 15.459(4) |
| α [°]            | 100.789(4) | 80.719(5) | 88.354(5) | 77.37(3) | 111.13(2) |
| β [°]            | 92.805(4) | 87.683(5) | 88.309(4) | 79.47(3) | 93.77(2) |
| γ [°]            | 99.383(4) | 84.663(5) | 65.430(5) | 75.04(3) | 92.25(2) |
| V [Å³]           | 2735.0(2) | 2231.8(2) | 2537.7(3) | 5427(2) | 2548.5(11) |
| Z, ρcalc [g cm⁻³] | 2.1065 | 2.1311 | 2.1301 | 4.1.191 | 2.1305 |
| Absorption coefficient; mm⁻¹ | 0.414 | 0.509 | 0.480 | 0.424 | 0.454 |
| F(000)           | 924 | 928 | 1041 | 2040 | 1052 |
| Crystal size [mm] | 0.49 x 0.30 x 0.15 | 0.51 x 0.36 x 0.31 | 0.20 x 0.18 x 0.05 | 0.22 x 0.07 x 0.02 | 0.15 x 0.07 x 0.04 |
| Theta range for data collection [°] | 2.16 to 28.38 | 2.15 to 25.00 | 1.97 to 28.46 | 2.16 to 23.25 | 2.17 to 23.25 |
| hkl range        | -16 shs 14, -19s ks 19, -19s i ≤18 | -14 shs 14, -14s ks 14, -16s i ≤17 | -14 shs 14, -17s ks 16, -24s i ≤23 | -13 shs 13, -19s ks 20, -27s i ≤27 | -17s i ≤17 |
| Reflections collected/unique | 19429 / 11919 [R(int) = 0.0390] | 13164 / 7861 [R(int) = 0.0489] | 17796 / 11285 [R(int) = 0.0525] | 28379 / 15553 [R(int) = 0.1579] | 12837 / 7284 [R(int) = 0.2078] |
| Completeness to theta | 25.00, 99.7% | 25.00, 99.9% | 25.00, 100.0% | 23.25, 99.9% | 23.25, 99.5% |
| Max. and min. transmission | 1.0000 and 0.7747 | 0.8573 and 0.7817 | 0.9769 and 0.9118 | 0.9928 and 0.9117 | 0.9819 and 0.9369 |
| Data/restraints/parameters | 11919 / 0 / 517 | 7861 / 0 / 508 | 11285 / 9 / 606 | 15553 / 188 / 1174 | 7284 / 12 / 595 |
| Goodness-of-fit on F² | 1.034 | 1.072 | 1.081 | 0.755 | 0.825 |
| Final R indices [I > 2o(I)] | R1 = 0.0527, wR2 = 0.1343 | R1 = 0.0796, wR2 = 0.2128 | R1 = 0.0635, wR2 = 0.1681 | R1 = 0.0844, wR2 = 0.1766 | R1 = 0.0833, wR2 = 0.0744 |
| R indices (all data) | R1 = 0.0734, wR2 = 0.1510 | R1 = 0.1099, wR2 = 0.2275 | R1 = 0.1127, wR2 = 0.2137 | R1 = 0.2567, wR2 = 0.2160 | R1 = 0.2760, wR2 = 0.1099 |
| Residual peaks [eÅ⁻³] | 0.814 and -1.012 | 2.790 and -0.689 | 1.489 and -1.002 | 0.538 and -0.642 | 0.474 and -0.590 |
Table 2SI. Bond lengths [Å] and angles [°] within the coordination sphere for 15a, 15b, 15c, 15e, and 15f.

|        | 15a     | 15b     | 15c     |
|--------|---------|---------|---------|
| **Bond length [Å]** |         |         |         |
| Ru1-Cl1 | 2.429(8) | Ru1-Cl1 | 2.416(2) | Ru1-Cl1 | 2.4093(14) |
| Ru1-Cl2 | 2.4014(9) | Ru1-Cl2 | 2.410(2) | Ru1-Cl2 | 2.3843(15) |
| Ru1-C9\textsubscript{carbene} | 2.100(3) | Ru1-C9\textsubscript{carbene} | 2.101(6) | Ru1-C7\textsubscript{carbene} | 2.143(5) |
| Ru1-C20\textsubscript{indenylidene} | 1.853(3) | Ru1-C19\textsubscript{indenylidene} | 1.850(6) | Ru1-C24\textsubscript{indenylidene} | 1.862(5) |
| Ru1-C35\textsubscript{carbene} | 2.108(3) | Ru1-C42\textsubscript{carbene} | 2.085(6) | Ru1-C45\textsubscript{carbene} | 2.088(5) |
| **Angles [°]** |         |         |         |
| C20-Ru1-C35 | 104.94(13) | C19-Ru1-C42 | 102.6(3) | C24-Ru1-C45 | 100.3(2) |
| C20-Ru1-C9 | 103.95(13) | C19-Ru1-C9 | 103.8(3) | C24-Ru1-C7 | 98.8(2) |
| C35-Ru1-C9 | 151.09(13) | C42-Ru1-C9 | 153.6(3) | C45-Ru1-C7 | 160.45(19) |
| C20-Ru1-Cl2 | 99.33(11) | C19-Ru1-Cl2 | 99.4(2) | C24-Ru1-Cl2 | 98.25(16) |
| C35-Ru1-Cl2 | 86.59(9) | C42-Ru1-Cl2 | 87.7(2) | C45-Ru1-Cl2 | 97.48(15) |
| C9-Ru1-Cl2 | 89.85(9) | C9-Ru1-Cl2 | 90.62(18) | C7-Ru1-Cl2 | 83.87(13) |
| C20-Ru1-Cl1 | 94.11(10) | C19-Ru1-Cl1 | 95.3(2) | C24-Ru1-Cl1 | 94.97(16) |
| C35-Ru1-Cl1 | 89.87(9) | C42-Ru1-Cl1 | 88.61(16) | C45-Ru1-Cl1 | 82.31(15) |
| C9-Ru1-Cl1 | 86.99(9) | C9-Ru1-Cl1 | 86.37(18) | C7-Ru1-Cl1 | 91.90(13) |
| Cl2-Ru1-Cl1 | 166.56(3) | Cl2-Ru1-Cl1 | 165.35(6) | Cl2-Ru1-Cl1 | 166.59(5) |

|        | 15e (MOL1) | 15e (MOL2) | 15f     |
|--------|------------|------------|---------|
| **Bond length [Å]** |         |         |         |
| Ru1-Cl1 | 2.427(4) | Ru2-Cl3 | 2.392(4) | Ru1-Cl1 | 2.387(3) |
| Ru1-Cl2 | 2.397(4) | Ru2-Cl4 | 2.413(4) | Ru1-Cl2 | 2.418(3) |
| Ru1-C7\textsubscript{carbene} | 2.116(13) | Ru1-C7\textsubscript{carbene} | 2.134(15) | Ru1-C7\textsubscript{carbene} | 2.093(11) |
| Ru1-C24\textsubscript{indenylidene} | 1.852(14) | Ru1-C94\textsubscript{indenylidene} | 1.873(14) | Ru1-C24\textsubscript{indenylidene} | 1.877(10) |
| Ru1-C45\textsubscript{carbene} | 2.174(16) | Ru1-C115\textsubscript{carbene} | 2.178(15) | Ru1-C46\textsubscript{carbene} | 2.103(11) |
| **Angles [°]** |         |         |         |
| C24-Ru1-C45 | 102.0(6) | C94-Ru2-C115 | 99.0(6) | C25-Ru1-C46 | 102.6(4) |
| C24-Ru1-C7 | 99.3(6) | C94-Ru2-C77 | 103.6(6) | C25-Ru1-C7 | 101.2(4) |
| C45-Ru1-C7 | 158.5(6) | C115-Ru2-C77 | 157.2(6) | C46-Ru1-C7 | 156.2(4) |
| C24-Ru1-Cl2 | 96.9(4) | C94-Ru2-Cl4 | 95.4(4) | C25-Ru1-Cl2 | 94.4(4) |
| C45-Ru1-Cl2 | 97.7(4) | C115-Ru2-Cl4 | 93.9(4) | C46-Ru1-Cl2 | 84.0(3) |
| C7-Ru1-Cl2 | 82.9(3) | C77-Ru2-Cl4 | 81.2(3) | C7-Ru1-Cl2 | 94.3(3) |
| C24-Ru1-Cl1 | 94.0(4) | C94-Ru2-Cl3 | 95.7(4) | C25-Ru1-Cl1 | 95.5(4) |
| C45-Ru1-Cl1 | 82.0(3) | C115-Ru2-Cl3 | 82.3(4) | C46-Ru1-Cl1 | 96.6(3) |
| C7-Ru1-Cl1 | 93.3(3) | C77-Ru2-Cl3 | 98.3(3) | C7-Ru1-Cl1 | 81.0(3) |
| Cl2-Ru1-Cl1 | 168.87(15) | Cl4-Ru2-Cl3 | 168.77(14) | Cl2-Ru1-Cl1 | 169.67(12) |
9. Metathesis reactions

9.1. RCM of diethyl diallylmalonate 17

General procedure of catalyst 12g and 15a-15h comparison in RCM of 17 at 40 °C

A solution of catalyst (0.001 mmol, 0.1 mol%) in 100 µL of toluene was added at 40 °C under argon to a solution of diethyl diallylmalonate 17 (240.3 mg, 1.0 mmol) in toluene (9.7 mL). Mixture was stirred under argon for 1h. Samples of the reaction mixture were taken at defined time intervals and were immediately quenched by addition of excess of ethyl vinyl ether.

| Time (min) | 12g GC Conversion (%) | 15a GC Conversion (%) | 15b GC Conversion (%) | 15c GC Conversion (%) | 15d GC Conversion (%) | 15e GC Conversion (%) | 15f GC Conversion (%) | 15g GC Conversion (%) | 15h (fr. A) GC Conversion (%) | 15h (fr. B) GC Conversion (%) |
|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|-----------------------------|-----------------------------|
| 2          | 6                      | -                      | -                      | 0.5                    | 3                      | 14                     | 2                      | 1                      | 1                           |                             |
| 4          | 23                     | -                      | -                      | 1                      | 6                      | 25                     | 7                      | 2                      | 5                           |                             |
| 6          | 43                     | -                      | -                      | 1.5                    | 9                      | 37                     | 14                     | 3                      | 8                           |                             |
| 8          | 60                     | -                      | -                      | 2                      | 12                     | 49                     | 21                     | 4                      | 10                          |                             |
| 10         | 73                     | -                      | -                      | 2.8                    | 15                     | 60                     | 30                     | 5                      | 13                          |                             |
| 15         | 90                     | -                      | -                      | 4.5                    | 24                     | 81                     | 48                     | 9                      | 20                          |                             |
| 20         | 95                     | -                      | -                      | 6                      | 32                     | 92                     | 63                     | 13                     | 27                          |                             |
| 30         | 98                     | -                      | -                      | 9                      | 49                     | 99                     | 86                     | 22                     | 41                          |                             |
| 60         | 99                     | 1                      | 8                      | 19                     | 1                      | 86                     | 99                     | 99                     | 49                          | 67                          |

RCM of 17 with 15a at different temperatures and with CuCl

Catalyst 15a (1.75 mg, 0.002 mmol, 0.1 mol%) in 50 µL of toluene was added under argon at defined temperature to a solution of diethyl diallylmalonate 17 (480.6 mg, 2.0 mmol) in toluene (19.5 mL). Optionally CuCl (1.98 mg, 0.02 mmol) was added before the catalyst. Mixture was stirred under argon for 6h. Samples of the reaction mixture were taken at defined time intervals and were immediately quenched by addition of excess of ethyl vinyl ether.

| Time (min) | 60 °C | 70 °C | 80 °C | 90 °C | 60°C + CuCl |
|------------|-------|-------|-------|-------|-------------|
| 10         | -     | -     | 10    | 16    | -           |
| 15         | 1.6   | 3     | 15    | 23    | >99         |
| 30         | 3     | 7     | 37    | 42    | -           |
| 60         | 10    | 20    | 70    | 62    | -           |
| 120        | 22    | 43    | 91    | 84    | -           |
| 180        | 38    | 57    | -     | -     | -           |
| 240        | 55    | 68    | 97    | 95    | -           |
| 360        | 79    | 82    | 99    | 99    | -           |
9.2. Ethenolysis of methyl oleate 7

General Procedure of ethenolysis of methyl oleate (7)

\[
\begin{align*}
\text{COO}^{-} & \quad \text{Me} \quad \text{Ru} \\
\text{COO}^{-} + \text{ethylene} & \rightarrow \text{COO}^{-} + \text{Me} + \text{MeOOC-} + \text{MeCOO}^{-}
\end{align*}
\]

Solution of catalyst (0.675 µmol, 10 ppm or 0.337 µmol, 5 ppm or 0.202 µmol, 3 ppm) in toluene (100 µL) was added to a degassed methyl oleate (20.0g, 67.5 mmol). The mixture was immediately transferred (vacuum conveying) to pressure reactor (equipped with magnetic stir bar) which was then pressurized with ethylene (150 psi). The reactor was placed in oil bath at appropriate temperature. The mixture was stirred for 2h or 4h. After that time sample of the reaction mixture was collected via the dip-tube and was immediately quenched with SnatchCat (4.4 eq in relation to catalyst) and diluted with toluene. Sample was analyzed by GC. Conversion was calculated using residual methyl stearate as internal standard. Selectivity and yield was calculated using response factors presented below.

Response factors calculation

To a vial were precisely weighed following substances:

| Substance        | m [mg] | purity by GC [%] | Corr. mass [mg] |
|------------------|--------|------------------|-----------------|
| 1-decene (8)     | 23.91  | 99.9             | 23.89           |
| 9-DAME (9)       | 28.74  | 98.0             | 28.16           |
| octadec-9-en (27)| 20.65  | 98.0             | 20.24           |
| MO (7)           | 18.74  | 96.3             | 18.05           |
| Diester (28)     | 19.75  | 97.4             | 19.24           |

The mixture was dissolved in 10 mL of toluene and analyzed by GC (7 injections). The average area for each substance was divided by mass of the substance. These numbers were transformed to Response factors (relative to methyl oleate 7) with assumption that for methyl oleate Response factor = 1.0.

| Inj. | Area 8 | Area 9 | Area 27 | Area 7 | Area 28 |
|------|--------|--------|---------|--------|---------|
| 1    | 100746.4 | 11351.2 | 145336.9 | 123993.1 | 106112.0 |
| 2    | 105781.9 | 118828.4 | 151855.7 | 122763.5 | 102162.5 |
| 3    | 99763.2  | 109879.7 | 143326.5 | 122116.5 | 103948.4 |
| 4    | 98953.4  | 108863.8 | 141006.5 | 120267.5 | 103377.9 |
| 5    | 107025.8 | 121535.6 | 150425.0 | 119504.5 | 98853.3  |
| 6    | 98814.6  | 109361.8 | 142179.0 | 119320.3 | 102305.1 |
| 7    | 99514.2  | 110000.3 | 141657.5 | 119578.7 | 102780.5 |
| Av. area | 101514.2 | 112831.5 | 145112.4 | 121077.7 | 102791.4 |
| Av. area / mass | 4249.9 | 4006.1 | 7170.6 | 6709.2 | 5343.6 |

Response factor 0.63 0.60 1.07 1.00 0.80
In further calculations GC areas of each component were transformed using Response factors. Conversion, selectivity, yield and TON were calculated from following equations:

\[
\text{Conversion} = 100 \times \left( 1 - \frac{A_7 \times A_{IS}^0}{A_7^0 \times A_{IS}} \right)
\]

\[
\text{Selectivity} = 100 \times \frac{n_8 + n_9}{(n_8 + n_9) + 2 \times (n_{27} + n_{28})}
\]

\[
\text{Yield} = \frac{\text{Conversion} \times \text{Selectivity}}{100}
\]

\[
\text{TON} = \frac{\text{Yield} \times n_7^0 / n_{\text{cat}}^0}{100}
\]

\(A_7, A_{IS}\): GC area of methyl oleate (7) and internal standard (methyl stearate) at the end of the reaction

\(A_7^0, A_{IS}^0\): GC area of methyl oleate (7) and internal standard (methyl stearate) before the reaction

\(n_8, n_9, n_{27}, n_{28}\): moles of 1-decene (8), 9-DAME (9), octadec-9-en (27) and diester (28)

\(n_7^0, n_{\text{cat}}^0\): initial moles of methyl oleate (7) and moles of catalyst used

**Representative example of calculations (5 ppm of 15g, Entry 11, Table 2 in main text)**

| Area          | 8   | 9   | 27  | 7   | 28  | Int. std. |
|---------------|-----|-----|-----|-----|-----|-----------|
| Before rxn    |     |     |     |     |     |           |
| Inj. 1        | 0   | 0   | 0   | 1466912.5 | 0   | 27235.4   |
| Inj. 2        | 0   | 0   | 0   | 1458288.1 | 0   | 27053.5   |
| Inj. 3        | 0   | 0   | 0   | 1495153.8 | 0   | 27738.4   |
| Average area  | 0   | 0   | 0   | 1473451.5 | 0   | 27342.4   |
| After 4h      |     |     |     |     |     |           |
| Inj. 1        | 164650.0 | 213650.2 | 27451.8 | 667594.4 | 28765.4 | 23722.5   |
| Inj. 2        | 164182.7 | 213994.4 | 27540.1 | 670082.7 | 28976.0 | 23790.9   |
| Inj. 3        | 164326.1 | 213495.8 | 27558.4 | 674666.2 | 29188.5 | 23957.4   |
| Average area  | 164386.3 | 213713.5 | 27516.8 | 670781.1 | 28976.6 | 23823.6   |
| Resp. factor  | 0.63 | 0.60 | 1.07 | 1.00   | 0.80   |           |
| M [g/mol]     | 140.27 | 184.28 | 252.48 | 296.49 | 340.50  |           |
| Average area/Resp. factor/M | 1860.20 | 1932.87 | 101.86 | 2262.41 | 106.38  |           |

\[
\text{Conversion} = 100 \times \left( 1 - \frac{670781.1 \times 27342.4}{1473451.5 \times 23823.6} \right) = 47.8\%
\]

\[
\text{Selectivity} = 100 \times \frac{1860.20 + 1932.87}{(1860.20 + 1932.87) + 2 \times (101.86 + 106.38)} = 90.1\%
\]

\[
\text{Yield} = \frac{47.8 \times 90.1}{100} = 43.0\%
\]

\[
\text{TON} = \frac{43.0 \times 22.73 \text{ mmol}}{0.00011365 \text{ mmol}} = 86000
\]

28
GC chromatogram of crude reaction mixture (5 ppm of 15g, Entry 11, Table 2 in main text):

9.3. RCM of 19

Solution of 15f (0.044 mg, 0.044 µmol, 30 ppm) in toluene (50 µL) was added at 60 °C under argon to a solution of 19 (509.0 mg, 1.461 mmol) in toluene (5.3 mL). Mixture was stirred for 30 min and second portion of 15f (30 ppm) in toluene (50 µL) was added. After additional 1.5h the reaction mixture was cooled to rt and quenched with SnatchCat (4.4 eq in relation to catalyst). Sample of the mixture was analyzed by GC (96% of conversion). Toluene was evaporated and residue was dissolved in minimal amount of DCM. TBME was added and DCM was slowly evaporated under reduced pressure. The product was filtered, washed with TBME and dried in vacuum. White crystalline solid, 429 mg (92%).

Same procedure was applied for the reaction catalyzed by 1.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 7.73$ (d, $J = 8.3$ Hz, 2H), $7.26$ (d, $J = 8.1$ Hz, 2H), 5.86-5.76 (m, 2H), 4.61-4.51 (m, 2H), 4.32-4.24 (m, 1H), 4.24-4.10 (m, 2H), 3.47-3.36 (m, 2H), 2.38 (s, 3H), 2.15-1.87 (m, 3H), 1.80-1.71 (m, 1H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 169.5$, 143.3, 135.7, 129.4, 127.4, 125.8, 124.9, 59.0, 53.3, 53.0, 48.3, 30.3, 24.8, 21.4.
9.4. RCM of 21

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{N} & \quad \text{C} & \quad \text{Ph} \\
\text{O} & \quad \text{C} & \quad \text{C} & \quad \text{N} & \quad \text{Ph} \\
\text{21} & \quad \xrightarrow{\text{15f (50 ppm)}} & \quad \text{O} & \quad \text{N} & \quad \text{C} & \quad \text{Ph} \\
& & & \quad \text{22}
\end{align*}
\]

Solution of 15f (0.039 mg, 0.039 µmol, 50 ppm) in toluene (50 µL) was added at 55 °C under argon to a solution of 21 (212.0 mg, 0.776 mmol) in toluene (3 mL). Reaction mixture was stirred for 1h. After that time it was quenched with SnatchCat (4.4 eq in relation to catalyst) and sample was analyzed by GC (conversion >99%). Product was isolated by silica gel chromatography (ethyl acetate/cyclohexane 10/90), colorless oil, 173.0 mg, 91%.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 7.39-7.27\) (m, 5H), 5.74-5.62 (m, 2H), 5.19-5.10 (m, 2H), 4.46-4.06 (m, 2H), 3.64-3.56 (m, 1H), 2.26-2.08 (m, 2H), 1.93-1.67 (m, 2H), 1.15 (dd, \(J = 6.4; 4.5\) Hz, 3H).

\(^1^3\)C NMR (CDCl\(_3\), 125 MHz): \(\delta = 156.0\) (2xC), 137.2, 137.1, 131.7, 131.4, 128.4, 128.3, 127.8, 127.7, 127.6, 127.4, 66.9, 66.7, 52.5, 52.3, 39.4, 39.1, 34.0, 33.9, 27.1, 26.9, 19.6, 19.1.

9.5. RCM of 23

\[
\begin{align*}
\text{CH}_2 & \quad \text{O} & \quad \text{C} & \quad \text{C} & \quad \text{N} & \quad \text{O} \\
\text{CH}_2 & \quad \text{O} & \quad \text{C} & \quad \text{C} & \quad \text{N} & \quad \text{O} \\
\text{23} & \quad \xrightarrow{\text{15f (250 ppm)}} & \quad \text{O} & \quad \text{C} & \quad \text{C} & \quad \text{N} & \quad \text{O} \\
& & & \quad \text{24}
\end{align*}
\]

Solution of 15f (0.040 mg, 0.040 µmol, 250 ppm) in toluene (500 µL) was added in five equal portions (15 minutes intervals) at 70 °C under argon to a solution of 23 (213.0 mg, 0.799 mmol) in toluene (160 mL, \(C_{54} = 5\) mM). After additional 1h sample of the reaction mixture (1 mL) was withdrawn and quenched with SnatchCat (4.4 eq in relation to catalyst). The sample was analyzed by GC (external standard was used for calculations). Conversion 95%, yield 91%. Mixture of isomers \(E/Z\) (65:35). The identity of product was confirmed by comparison of retention time with sample previously authenticated by NMR.\(^9\)

9.6. RCM of 25

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{S} & \quad \text{N} & \quad \text{C} & \quad \text{Ph} \\
\text{O} & \quad \text{S} & \quad \text{N} & \quad \text{C} & \quad \text{Ph} \\
\text{25} & \quad \xrightarrow{\text{15f (1000 ppm)}} & \quad \text{O} & \quad \text{S} & \quad \text{N} & \quad \text{C} & \quad \text{Ph} \\
& & & \quad \text{26}
\end{align*}
\]

\[\text{[9]}\quad \text{K. Skowerski, P. Kasprzycki, M. Bieniek, T. K. Olszewski, Tetrahedron, 2013, 69, 7408-7415.}\]
Solution of 15f (0.182 mg, 0.182 µmol, 1000 ppm) in toluene (500 µL) was added in 10 equal portions (10 minutes intervals) at 60 °C under argon to a solution of 25 (509.0 mg, 1.82 mmol) in toluene (6.8 mL). After additional 1h sample of the reaction mixture was withdrawn and quenched with SnatchCat (4.4 eq in relation to catalyst). The sample was analyzed by GC (conversion 90%). Product was isolated by silica gel chromatography to give white crystalline solid 26, 361.0 mg (79%).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 7.70$ (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 3.96 (s, 4H), 2.41 (s, 3H), 1.53 (s, 6H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 143.2, 134.2, 129.6, 127.4, 126.1, 58.7, 21.4, 11.0$.

9.7. SM of 1-decene 8

Solution of 15f (0.037 mg, 0.037 µmol, 1 ppm) in toluene (50 µL) was added at 60 °C under argon to neat 8 (5.22 g, 37.2 mmol). Mixture was stirred for 2h (argon was bubbled through the reaction mixture). After that time reaction mixture was cooled to rt and quenched with SnatchCat (4.4 eq in relation to catalyst). Sample of the reaction mixture was analyzed by GC. Conversion calculated with external standard was 64%, yield 63%, selectivity 98%. TON = 315000. Mixture of isomers E/Z (4:1). Product was isolated by distillation (107 °C, 4.2x10^{-2} mbar), colorless liquid, 2.58g, 55%.

Same procedure was applied for the reaction catalyzed by 1 and 2.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 5.39$ (ddd, $J = 5.3; 3.7; 1.6$ Hz, 2H, E), 5.35 (ddd, $J = 5.7; 4.4; 1.1$ Hz, 2H, Z), 2.06-1.91 (m, 4H), 1.38-1.18 (m, 24H), 0.88 (t, $J = 6.9$ Hz, 6H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 130.4$ (E), 129.9 (Z), 32.6, 31.9, 29.8 (Z), 29.7 (E), 29.5 (Z, E, 2xC), 29.3, 29.2 (E), 27.2 (Z), 22.7, 14.1.

9.8. SM of 9

Solution of 15f (0.060 mg, 0.060 µmol, 2 ppm) in toluene (50 µL) was added at 60 °C under argon to neat 9 (5.53 g, 30.0 mmol). Mixture was stirred for 2h (argon was bubbled through the reaction mixture). After that time reaction mixture was cooled to rt and quenched with SnatchCat (4.4 eq in relation to catalyst). Sample of the reaction mixture was analyzed by GC. Conversion calculated with external standard was 69%, yield 68%, selectivity 98%. TON = 170000. Mixture of isomers E/Z (1.5:1). Product was isolated using column chromatography (ethyl acetate/cyclohexene 5/95), colorless solid (melting slightly above rt), 3.17g, 62%.
\[^1\]H NMR (CDCl\textsubscript{3}, 500 MHz): \(\delta = 5.36\) (ddd, \(J = 5.3; 3.7; 1.6\) Hz, 2H, \(E\)), 5.32 (ddd, \(J = 5.7; 4.3; 1.1\) Hz, 2H, \(Z\)), 3.65 (s, 6H), 2.29 (t, \(J = 7.5\) Hz, 4H), 2.03-1.90 (m, 4H), 1.68-1.56 (m, 4H), 1.35-1.23 (m, 16H).

\[^13\]C NMR (CDCl\textsubscript{3}, 125 MHz): \(\delta = 174.2\) (\(E\), \(Z\), 2xC), 130.3 (\(E\)), 129.8 (\(Z\)), 51.4, 34.1, 32.5, 29.6 (\(Z\)), 29.5 (\(E\)), 29.1 (4xC), 28.9, 27.1(\(Z\)), 24.9 (\(E\)).

9.9. SM of 7

![Chemical Reaction Diagram]

Solution of 15f (0.066 mg, 0.066 \(\mu\)mol, 5 ppm) in toluene (500 \(\mu\)L) was added in 5 equal portions (30 min intervals) at 55 °C under argon to neat 7 (19.25 g, 65.9 mmol). Reaction mixture was stirred for 1h. After that time reaction mixture was cooled to rt and quenched with SnatchCat (4.4 eq in relation to catalyst). Sample of the reaction mixture was analyzed by GC. Conversion calculated using residual methyl stearate as an internal standard was 45%.

9.10. CM of 9 with methyl acrylate 29

![Chemical Reaction Diagram]

Solution of 15f (0.109 mg, 0.109 \(\mu\)mol, 50 ppm) in toluene (50 \(\mu\)L) was added at 60 °C under argon to a solution of 9 (400.0 mg, 2.17 mmol), 29 (0.98 mL, 10.9 mmol, 5 equiv) and methyl stearate (20 mg, internal standard) in toluene (4 mL). After 1h, 2h and 3h, another portions (50 ppm each) of 15f were added (200 ppm of 15f total). After additional 1h sample of the reaction mixture was withdrawn, quenched with SnatchCat (4.4 eq in relation to catalyst) and analyzed with GC, conversion 99%, yield 97%, selectivity 98%. \(E/Z = 87:13\). Product was isolated using column chromatography (ethyl acetate/cyclohexene 5/95), colorless oil, 498.0 mg, 95%.

Isomer \(E\):

\[^1\]H NMR (CDCl\textsubscript{3}, 500 MHz): \(\delta = 6.94\) (dt, \(J = 15.7; 7.0\) Hz, 1H), 5.80 (dt, \(J = 15.6; 1.6\) Hz, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 2.28 (t, \(J = 7.5\) Hz, 2H), 2.17 (dq, \(J = 7.1; 1.6\) Hz, 2H), 1.64-1.56 (m, 2H), 1.47-1.39 (m, 2H), 1.33-1.26 (m, 6H).

\[^13\]C NMR (CDCl\textsubscript{3}, 125 MHz): \(\delta = 174.2, 167.1, 149.6, 133.4, 120.8, 51.4, 51.3, 34.0, 32.1, 29.0, 28.9, 27.9, 24.8.\)
Isomer Z:

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 6.22$ (dt, $J = 11.6$; 7.5 Hz, 1H), 5.76 (dt, $J = 11.5$; 1.7 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 2.64 (dq, $J = 7.5$; 1.7 Hz, 2H), 2.30 (t, $J = 7.5$ Hz, 2H), 1.65-1.56 (m, 2H), 1.47-1.39 (m, 2H), 1.34-1.28 (m, 6H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 174.3, 166.8, 150.8, 119.2, 51.4, 51.0, 34.1, 29.1, 29.0, 28.9, 24.9, 24.8.

9.11. En-yne metathesis of 31

![Diagram]

Solution of 15f (0.552 mg, 0.552 µmol, 250 ppm) in toluene (50 µL) was added at 60 °C under argon to a solution of 31 (548.0 mg, 2.21 mmol) in toluene (8.2 mL). Reaction mixture was stirred for 2h, then cooled to rt, quenched with SnatchCat (4.4 eq in relation to catalyst) and analyzed with GC (conversion 94%). Product was isolated by silica gel chromatography (ethyl acetate/cyclohexane 5/95) to give colorless oil 32, 433.0 mg, 79%.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 7.40$-7.28 (m, 10H), 6.30-6.22 (m, 1H), 6.22-6.20 (m, 1H), 5.37-5.32 (m, 1H), 5.13 (dq, $J = 11.0$; 1.2 Hz, 1H), 4.82-4.80 (m, 2H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 143.6, 143.3, 129.7, 127.9, 127.8, 127.4, 124.9, 117.5, 94.5, 73.2.

9.12. ROMP of norbornene 33

![Diagram]

CuCl (12.0 mg, 0.118 mmol) and solution of 15f (7.87 mg, 7.86 µmol, 1000 ppm) in DCM (50 µL) were added at 27 °C under argon to a solution of 33 (740.0 mg, 7.86 mmol) in DCM (79 mL). After 10 min reaction mixture was filtered through a Schott funnel in order to remove CuCl and excess of ethyl vinyl ether was added. Reaction mixture was concentrated to 50% of initial volume and excess of methanol was added. Precipitated product was filtered, washed with methanol and dried in vacuum to give polymer 34 as bright pink solid, 647.0 mg, 87%. $\text{cis}/\text{trans} = 1:0.9$; $M_n = 61060$; $M_w = 110600$; PDI = 1.812.

$^1$H NMR (CD$_2$Cl$_2$, 500 MHz): $\delta = 5.41$-5.34 (br, 1H, $\text{trans}$), 5.25-5.16 (br, 1H, $\text{cis}$), 2.90-2.70 (br, 1H, $\text{cis}$), 2.52-2.36 (1H, $\text{trans}$), 1.94-1.68 (m, 3H), 1.44-1.22 (m, 2H), 1.12-0.92 (m, 1H).

$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): $\delta = 134.4, 133.7, 133.6, 133.5, 44.1, 43.8, 43.3, 42.7, 41.9, 39.2, 39.0, 33.6, 33.5, 32.9, 32.8.
### ASTRA 6 Report AS-C06 087 R68

**File Name:** WyatInstall1.0029 AS-C06 087 R68.afex

**Collection Operator:** GPC/Eclipse (GPC/Eclipse (Eclipse))

**Processing Operator:** GPC/Eclipse (Eclipse)

**Sample:** AS-C06 087 48

---

### Configuration

- **Concentration Source:** 
- **Flow Rate:** 0.600 ml/min

**Light Scattering Instrument:** GPC/Eclipse

**Cell Type:** Fixed Window

- **Wavelength:** 664.1 nm
- **Calibration Constant:** 3.108 x 10^-3 1/°F cm

**RI Instrument:**

**Solvent:** methylene chloride

**Temperature Correction Enabled:**

**Refractive Index:** 1.624

---

### Processing

**Collection Time:** Friday, September 02, 2016 01:22:06 AM Central European Daylight Time

**Processing time:** Friday, September 02, 2016 02:11:53.624 AM Central European Daylight Time

**Peak settings:**
- **Peak Name:** Peak 1
- **Peak Limits (mL):** 9.946 - 11.512
- **Light Scattering Model:** 2dim
- **Fit Degree:** 1
- **drift (mL/g):** 0.0790

---

### Results/Fitting Procedure

**Results/Fitting Procedure**

| Data       | Fit Model | Degree | R² | Extrapolation |
|------------|-----------|--------|----|---------------|
| peak area  | none      | n/a    | n/a| none          |
| root radius| none      | n/a    | n/a| none          |

**Results**

### Peak Results

**Peak 1**

- **Mass**
  - **Injected Mass (g):** 0.000
  - **Calculated Mass (g):** 0.000
  - **Mass Recovery (%):** 88.0%
  - **Mass Fraction (%):** 100.0%

- **Mean and Standard Deviation (g/mol):**
  - **Mn:** 6.16 x 10^6 (±3.03%)
  - **Mw:** 8.64 x 10^6 (±3.27%)
  - **Mn:** n/a
  - **Mw:** 2.54 x 10^6 (±3.96%)

- **Polydispersity:**
  - **Mw/Mn:** 1.022 (±3.20%)
  - **Mw/Mn:** 4.135 (±4.82%)

- **rms radius moments (mm):**
  - **Mr:** 0.0 (±0.0%)
  - **Mr:** 22.0 (±5.0%)
  - **Mz:** 22.4 (±4.8%)
10. NMR spectra of salts

500AP230
user ap
1H NMR, P1-103-R7, 15-0014
PROTON1m CDCl3 (C: \ap) nmrssu 17

NMR spectrum of an unknown compound, showing peaks at various chemical shifts.
1H NMR, AS-COSMOS-063-R2, 16-0059B
PROTON1m CDC3 (C:\\\-\\ap) nmrsu 12
1H NMR, AS-COSMOS-059-R2, 16-500AP11

PROTON1m CDCl3 (C:\\ap) nmsu 11

Ph
N
BF4

10f

fi (ppm)
1H NMR, AS-COSMOS-016-R3, 15-1029B
PROTON1m CDC3 (C:\\ap) nmrsu 10
500AP438
user ap
1H NMR, AS-COSMOS-027-R3, 15-1272B
PROTON1m CDCl3 (C:\\ap) nmrsvu 57

10h
11. NMR spectra of complexes 15a-h
$^{1}$H-$^{1}$H ROESY spectrum (500 MHz) of 15a (region corresponding to proton marked in red).\textsuperscript{10}

\textsuperscript{10} B. Yu, Y. Xie, F. B. Hamad, K. Leus, A. A. Lyapkov, K. Van Hecke, F. Verpoort, \textit{New J. Chem.} \textbf{2015}, 39, 1858-1867.
$^1$H NMR (500 MHz) spectra of 15a recorded at different temperatures showing coalescence of proton marked in red at 70 °C.
ROESY spectrum (500 MHz) of 15b (region corresponding to proton marked in red).
$^1$H-$^1$H COSY spectrum (600 MHz) of 15b.
$^1$H-$^{13}$C HSQC spectrum (600 MHz) of 15b.
$^1$H-$^{13}$C HMBC spectrum (600 MHz) of 15b.
$^1$H-$^1$H ROESY spectrum (500 MHz) of 15c (region corresponding to proton marked in red).
$^1$H-$^1$H COSY spectrum (600 MHz) of 15c.
$^1$H-$^{13}$C HSQC spectrum (600 MHz) of $^{15}$c.
$^1$H-$^{13}$C HMBC spectrum (600 MHz) of 15c.
$^1$H-$^1$H ROESY spectrum (500 MHz) of 15d (region corresponding to proton marked in red).
$^1$H-$^1$H ROESY spectrum (500 MHz) of 15e (region corresponding to proton marked in red).
$^1$H-$^1$H ROESY spectrum (500 MHz) of 15f (region corresponding to proton marked in red).
\(^1\)H-\(^1\)H COSY spectrum (600 MHz) of 15f.
$^{1}H-^{13}C$ HSQC spectrum (600 MHz) of 15f.
$^{1}$H-$^{13}$C HMBC spectrum (600 MHz) of 15f.
1H NMR, AS-COSMOS-067-R1-FR2, 16-0867B
PROTON1m C606 {C:\\\ap} nmsu 16
$^1$H-$^1$H ROESY spectrum (500 MHz) of 15g (region corresponding to proton marked in red).
Fraction A
\(^{1}\text{H}-^{1}\text{H}\) ROESY spectrum (500 MHz) of 15h, Fraction A (region corresponding to proton marked in red).
Fraction A

13C NMR, AS-COSMOS-027-R8-PEN, 15-3031B, 4h C13CPD3h CD2Cl2 (C:\\ap) nrmsu 11
Fraction B
$^1$H-$^1$H ROESY spectrum (500 MHz) of 15h, Fraction B (region corresponding to proton marked in red).
Fraction B
Superimposition of $^1$H NMR spectra of 15h Fraction A (red) and 15h Fraction B (blue).
Comparison of $^1$H NMR spectra of complexes 15a-h (region corresponding to proton marked in red).
12. NMR Spectra of metathesis reactions products
16-500AP156
user ap
1H NMR, AS-COSMOS-065-9-DAME, 16-1235B
PROTON1m CDC3 (C:\\ap) nmrsu 14

\begin{figure}
\centering
\includegraphics[width=\textwidth]{nmr_spectrum}
\caption{NMR spectrum of compound 9 showing proton chemical shifts and coupling constants.}
\end{figure}
1H NMR, AS-COSMOS-087-R53, 16-1765B
PROTONIm CDCl3 (C:\\\~ap) nmrsu 22
1H NMR, AS-COSMOS-087-R11, 16-1010B
PROTON1m CDCl3 (C:\\\ap) nmrsu 42

26
16-S00AP121
user ap
13C NMR, AS-COSMOS-087-R11, 16-1010B
C13CPD1h CDC3 {C:\\ap} nmr42

26

143.21
134.22
129.63
127.41
126.13
77.25 CDC3
77.00 CDC3
76.75 CDC3
58.75
21.44
11.04
13C NMR, AS-COSMOS-087-R22-FR2, 16-1232B
C13CP01h CDCl3 (C:\\\ap) nmrsvu 11

27

\[ \text{Chemical shifts: } 130.36, 129.90, 77.28, 77.06, 76.73, 72.62, 32.62, 31.92, 29.79, 29.67, 29.53, 29.51, 29.33, 29.18, 29.02, 22.69, 14.11 \]
13C NMR, AS-COSMOS-087-R34, z81233B
C13CPD1h CDCl3 \{C:\ap\} ppm

MeOC{y}CH({z})COOMe

28

174.2

130.27

129.80

77.25 CDCl3

77.00 CDCl3

76.75 CDCl3

51.38

24.91

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

fl (ppm)
(E)-30

$\text{MeOOC} \begin{array}{c} \text{COOMe} \\ \end{array}$

13C NMR, AS-COSMOS-087-R15-E, 16-1092B
C13CPD1h CDCl3 (C:\\ap) nmrusu

| Peak | 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90  | 80  | 70  | 60  | 50  | 40  | 30  | 20  | 10  | 0   |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

- 17.63
- 167.12
- 149.58
- 133.36
- 120.85

- 77.25 CDCl3
- 77.00 CDCl3
- 76.75 CDCl3

- 52.26
- 51.40
- 51.32
- 24.00
- 24.11
- 28.95
- 28.89
- 24.84
1H NMR, AS-COSMOS-087-R68, 16-1857B
PROTON1m CD2Cl2 (C:\\ap) nrmsu 2
13. HRMS analysis of complexes 15a-h
**Single Mass Analysis**

Tolerance = 3.0 mDa  /  DBE: min = -1.5, max = 300.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 5

Monoisotopic Mass, Odd and Even Electron Ions

102 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

| Mass   | Calc Mass | mDa  | PPM  | DBE | Formula    | i-FIT | i-FIT Norm | Fit Conf % | C  | H  | N  | Cl | Ru |
|--------|-----------|------|------|-----|------------|-------|------------|------------|----|----|----|----|----|
| 848.3161 | 848.3159  | 0.2  | 0.2  | 250 | C50 H55 N4 Cl Ru | 788.4 | 0.702  | 49.55 | 50 | 55 | 4  | 1  | 1  |
| 848.3177 | -1.6      | -1.9 | 20.0 | C49 H50 N2 Cl2 Ru | 788.4 | 0.684  | 50.43 | 49 | 60 | 2  | 2  | 1  |
**Single Mass Analysis**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 150.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

9 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

| C  | O  | H  | N  | Cl | Ru |
|----|----|----|----|----|----|
| 0  | 0  | 100| 2  | 2  | 1  |

| Mass  | Calc. Mass | mDa  | PPM  | DBE  | Formula | i-FIT | i-FIT Norm | Fit Conf % | C | H | N | Cl | Ru |
|-------|------------|------|------|------|---------|-------|------------|------------|---|---|---|----|----|
| 972.3483 | 972.3490 | -0.7 | -0.7 | 28.0 | C39 H64 N2 Cl2 Ru | 456.4 | n/a | 59 | 64 | 2 | 2 | 1 |
Single Mass Analysis
Tolerance = 3.0 mDa / \( \Delta m = 0.000 \text{ mass} = 150 \text{ mDa} \)
Element prediction: Off
Number of isotopic peaks used for iFIT = 3
Monoisotopic Mass, Oxid and Even Electron ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

| Elements Used | C 0-160 | H 0-160 | N 2-2 | O 2-2 | P 0-1 | S 0-1 |
|---------------|---------|---------|-------|-------|------|-------|
| Mass          | Calc. Mass | mDa | ppm | DBE | Formula | \( \Delta m \) | \( \Delta m \text{ mDa} \) | Confidence % | C | H | N | O | S |
| 848.3159      | 848.3177 | -2.8 | -2.1 | 20.0 | C49 H90 N2 Cl2 Ru | 208.4 n/a | n/a | 49 | 60 | 2 | 2 | 1 |

15d
Single Mass Analysis

Tolerance = 3.0 mDa / DDE: min = -1.5, max = 150.0
Element prediction: OFF
Number of isotope peaks used for iPIT = 3
Monoisotopic Mass, Odd and Even Electron Ion
9 formula(s) evaluated with 1 result within limits (up to 50 closest results for each mass)

Elements Used:
C 6-100 H 6-100 N 2-2 Cl 2-2 Ru 1-1

| Mass   | Calc. Mass | mDa | PPM | DDE | Formula | iPIT | iPIT Norm | Fit Cont % | C   | H   | N   | Cl   | Ru   |
|--------|------------|-----|-----|-----|---------|------|-----------|------------|-----|-----|-----|-----|------|
| 972.3473 | 972.3490   | 1.5 | -1.5 | 28.6 | C59 H94 N2 Cl2 Ru1 | 142.1 | n/a       | n/a        | 59  | 64  | 2   | 2   | 1    |
**Single Mass Analysis**

- **Tolerance = 3.0 mDa**
- **DBE: min = -1.5, max = 150.0**
- **Element prediction: Off**
- **Number of isotope peaks used for i-FIT = 3**
- **Monoisotopic Mass, Odd and Even Electron Ions**
- **With formula(s) evaluated within limits (up to 5 closest results for each mass)**

**Elements Used:**
- C: 0-100
- H: 0-100
- N: 2-2
- Cl: 2-2
- Ru: 1-1

| Mass     | Calc. Mass | mDa  | PPM  | DBE | Formula | i-FIT | i-FIT Norm | Fit Cont % | C | H | N | Cl | Ru |
|----------|------------|------|------|-----|---------|-------|------------|------------|---|---|---|----|----|
| 1000.3798 | 1000.3623  | -0.5 | -0.5 | 28.0| C61 H68 N2 Cl2 Ru | 427 | 427 | 427 | 61 | 68 | 2  | 2  | 1  |
### Single Mass Analysis

**Tolerance = 3.0 mDa**  
**DBE: min = -1.5, max = 300.0**  
**Element prediction: Off**  
**Number of isotope peaks used for i-FIT = 5**  

**Monoisotopic Mass, Odd and Even Electron Ions**  
102 formula(e) evaluated with 2 results within limits (all results up to 1000 for each mass)

**Elements Used:**

| Mass | Calc. Mass | mDa | PPM | DBE | Formula | i-FIT | i-FIT Norm | Fit Conf % | C | H | N | Cl | Ru |
|------|------------|-----|-----|-----|---------|-------|------------|------------|---|---|---|----|----|
| 876.3477 | 876.3472 | 0.5 | 0.6 | 25.0 | C52 H59 N Cl Ru | 831.9 | 0.702 | 49.54 | 52 | 59 | 4 | 1 | 1 |
| 876.3490 | -1.3 | -1.5 | 20.0 | C51 H64 N2 Cl Ru | 831.9 | 0.684 | 50.46 | 51 | 64 | 2 | 2 | 1 |

### Single Mass Analysis

**Tolerance = 3.0 mDa**  
**DBE: min = -1.5, max = 300.0**  
**Element prediction: Off**  
**Number of isotope peaks used for i-FIT = 6**  

**Monoisotopic Mass, Even Electron Ions**  
103 formula(e) evaluated with 2 results within limits (all results up to 1000 for each mass)

**Elements Used:**

| Mass | Calc. Mass | mDa | PPM | DBE | Formula | i-FIT | i-FIT Norm | Fit Conf % | C | H | N | Cl | Ru |
|------|------------|-----|-----|-----|---------|-------|------------|------------|---|---|---|----|----|
| 841.3815 | 841.3820 | -0.5 | -0.6 | 15.5 | C50 H69 Cl2 Ru | 992.7 | 0.694 | 50.86 | 50 | 69 | 2 | 1 |
| 841.3802 | 1.3 | 1.5 | 20.5 | C51 H64 N2 Cl Ru | 992.7 | 0.702 | 49.54 | 51 | 64 | 2 | 1 | 1 |
Single Mass Analysis
Tolerance = 3.0 mDa  
DBE: min = -1.5, max = 300.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 5  
Monoisotopic Mass, Odd and Even Electron Ions  
103 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)  
Elements Used: C: 0-100  
H: 0-100  
N: 0-5  
Cl: 1-2  
Ru: 1-1

| Mass | Calcd Mass | mDa | PPM | DBE | Formula | i-FIT | i-FIT Norm | Fit Conf % | C | H | N | Cl | Ru |
|------|------------|-----|-----|-----|---------|-------|------------|------------|---|---|---|----|----|
| 1032.4402 | 1032.4411 | -0.9 | -0.9 | 31.0 | C64 H71 N4 Cl Ru | 867.8 | 0.702 | 49.54 | 64 | 71 | 1 | 1 |
| 1032.4429 | 1032.4411 | -2.7 | -2.6 | 20.0 | C63 H76 N2 Cl2 Ru | 867.7 | 0.684 | 50.46 | 63 | 76 | 2 | 2 | 1 |

Single Mass Analysis
Tolerance = 3.0 mDa  
DBE: min = -1.5, max = 300.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 5  
Monoisotopic Mass, Even Electron Ions  
103 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)  
Elements Used: C: 0-100  
H: 0-100  
N: 0-5  
Cl: 1-2  
Ru: 1-1

| Mass | Calcd Mass | mDa | PPM | DBE | Formula | i-FIT | i-FIT Norm | Fit Conf % | C | H | N | Cl | Ru |
|------|------------|-----|-----|-----|---------|-------|------------|------------|---|---|---|----|----|
| 597.4716 | 597.4741 | -2.5 | -2.5 | 26.5 | C63 H76 N2 Cl Ru | 0.0 | n/a | n/a | 63 | 76 | 2 | 1 | 1 |
Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 300.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5
Monoisotopic Mass. Odd and Even Electron Ions
103 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100  H: 0-100  N: 0-5  Cl: 1-2  Ru: 1-1

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 300.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5
Monoisotopic Mass. Even Electron Ions
103 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100  H: 0-100  N: 0-5  Cl: 1-2  Ru: 1-1
14. Elemental analysis scans
ANALIZA Nr 13/2016

RAFAŁ GAWIN

imię i nazwisko

nr zespołu (telefon)

symbol substancji

skład pierwiastkowy

temp. topnienia lub wrzenia

właściwości (hygroskop, wybuch itp.)

C 72,82 H 6,63 N 2,88 Cl 7,28

przybliżony skład %

pierwiastki do oznaczenia

WYNIK

\[ \%C = 72,88; \%H = 6,66; \%N = 2,88; \%Cl = 7,28 \]

UWAGI

KIEROWNIK

Pracowni Analizy Elementarnych

mgr inż. Krystyna Markiewicz

15c

15d

ANALIZA Nr 15/2016

RAFAŁ GAWIN

imię i nazwisko

nr zespołu (telefon)

symbol substancji

skład pierwiastkowy

temp. topnienia lub wrzenia

właściwości (hygroskop, wybuch itp.)

C 69,32 H 7,42 N 3,30 Cl 8,35

przybliżony skład %

pierwiastki do oznaczenia

WYNIK

\[ \%C = 69,32; \%H = 7,42; \%N = 3,30; \%Cl = 8,35 \]

UWAGI

KIEROWNIK

Pracowni Analizy Elementarnych

mgr inż. Krystyna Markiewicz

15c

15d
| ANALIZA Nr | 14/2016 |
|------------|---------|
| RAFAŁ GALIN |
| [Address] |
| [Telephone] |
| As-Cosmos-062 - R4 | >25 mg |
| symbol substancji |
| temp. topnienia lub wrzenia |
| właściwości (hygroskop. wybuch itp.) |
| przybliżony skład % |

| WYNIK |
|-------|
| % C - 72.87 | 72.68 |
| % H - 6.61 | 6.68 |
| % N - 2.81 | 2.81 |
| % Cl - 7.60 | 7.07 |

| UWAGI |
|-------|
| KIEROWNIK |
| Pracowni Analizy Elementarnej |
| mgr inż. Krystyna Markuliska |

| ANALIZA Nr |
|------------|
| 18/2016 |
| RAFAŁ GALIN |
| [Address] |
| [Telephone] |
| As-Cosmos-059 - R3-PEN |
| symbol substancji |
| temp. topnienia lub wrzenia |
| właściwości (hygroskop. wybuch itp.) |
| przybliżony skład % |

| WYNIK |
|-------|
| % C - 73.14 | 73.07 |
| % H - 7.00 | 6.85 |
| % N - 2.85 | 2.80 |
| % Cl - 7.10 | 6.84 |

| UWAGI |
|-------|
| KIEROWNIK |
| Pracowni Analizy Elementarnej |
| mgr inż. Krystyna Markuliska |

[Chemical structures 15e and 15f]
ICHO PAN ZESPÓŁ XVII
PRACOWNIA ANALITYCZNA
ul. Kasprowa 44/52
01-224 Warszawa
tel. (022) 345-20-04
tel. (022) 345-20-01

ANALIZA Nr 9/2016

RAFAŁ CALINSKI

APELION SYNTHESIS S.A.

C54H64Cl2N2Ru
skład pierwiastkowy

analyzy (hygroskop, wybuch itp.)
pierwiastki do oznaczenia

WYNIK

\%
C - 62,84 ; 62,83
H - 7,43 ; 7,45
N - 5,14 ; 5,15
Cl - 8,17 ; 8,31

KIEROWNIK

Pracowni Analizy Elementaryjnej

mgr inż. Krzysztof Markiewicz

12.01.16

15g
**ANALIZA Nr 235/2016**

**APEIRON SYNTHES S.A.**

**Rafał Gajun**

**nr zespołu (telefon)**

**AS-COSMOS-027-08-PEN**

**symbol substancji**

**C₆H₄NO₂C₆H₄Ru**

**skład pierwiastkowy**

**CHNCI**

**pierwiastki do oznaczenia**

**WYNIK**

**UWAGI**

**KIEROWNIK**

**Pracowni Analizy Elendmentycznej**

**mgr inż. Krystyna Markolikowa**

**14.03.16**

---

**Fraction A**

**Fraction B**