SUPPORTING INFORMATION

Modifications of substituents on the chelating oxygen atom in stereoretentive Hoveyda-Grubbs-type complexes and their influence on catalytic properties

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1. General information

The synthesis of the benchmark Ru-catalysts **Ru10a**, **Ru12a-Ru16a** was carried out according to known protocols.[1-4] **Ru11a** was synthesised from Hoveyda-Grubbs 2nd generation catalyst **M201** (CAS: 1307233-23-3) (see Chapter 2). Zinc 3,6-dichlorobenzene-1,2-dithiolate salt was prepared according to literature.[5] The starting compounds for cross-metathesis reactions **2e-f** were prepared by known methods.[6-7] All other chemicals or reagents were purchased from Sigma-Aldrich, Apeiron Synthesis, and POCH and used without further purification unless stated otherwise. All reactions requiring exclusion of oxygen and moisture were carried out in dry glassware with dry solvents (SPS MBraun) under a dry and oxygen free argon atmosphere using standard Schlenk technique or glovebox. The addition of dry solvents or reagents was carried out using argon flushed stainless steel cannulas and plastic syringes.

For spectroscopic and analytic characterisations, the following devices were used:

Analytical thin layer chromatography (TLC) was performed on Merck Silica gel 60 F_{254} precoated aluminium sheets. Components were visualised by observation under UV light (254 nm or 365 nm) or dyed by aqueous $KMnO_4$ or anisaldehyde reagent.

Flash column chromatography was carried out using silica gel 60 (230 – 400 mesh), purchased from Merck.

GC chromatograms were recorded using a PerkinElmer Clarus 580 model. As capillary IntertCap 5MS-Sil column was employed with helium as carrier gas. GC conversions were determined based on the ratio of an internal standard (tetradecane) and the starting material.

^{1}H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at room temperature on Agilent Mercury spectrometers (400 MHz). The data were interpreted in first order spectra. Chemical shifts δ are reported in parts per million (ppm) downfield from trimethylsilane as reference to residual solvent signal: $CDCl_3$ [δ_H = 7.26 ppm] or CD_2Cl_2 [δ_H = 5.32 ppm]. The following abbreviations are used to indicate the signal multiplicity: s (singlet), d doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), etc., br. s (broad signal), m (multiplet). Coupling constants (*J*) are given in Hz and refer to H, H-couplings.

^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at room temperature on Agilent Mercury

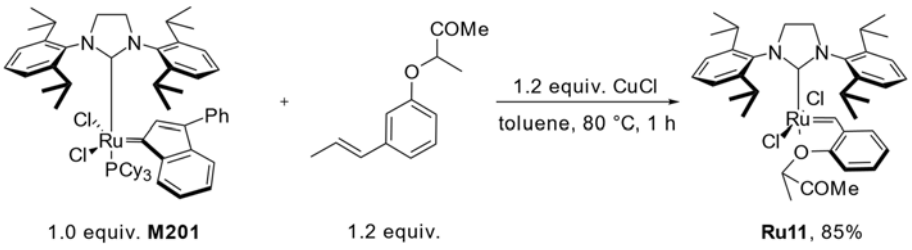
spectrometers (400 MHz). Chemical shifts are reported in δ units relative to the solvent signal: $CDCl_3$ [δ_H = 77.0 ppm (central line of the triplet)] or CD_2Cl_2 [δ_C = 53.8 ppm (central line of the quintet)]. If no coupling constants are given, the multiplicity refers to ^{1}H-decoupled spectra, otherwise the coupling constants belong to heteroatoms.

High resolution mass spectra (HR-MS) High resolution mass spectroscopy was obtained on AutoSpec Premier spectrometer.

Elemental Analyses were carried out at the Polish Academy of Science, Institute of Organic Chemistry.

IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer. Substances were applied as a film, solid or in solution. The obtained data was processed with the software Omni32. Wavenumbers are given in cm^{-1}.

2. Synthesis of Ru11a



1.0 equiv. **M201** 1.2 equiv. **Ru11**, 85%

Propenyl benzene derivative (49 mg, 0.24 mmol, 1.2 equiv.), CuCl (24 mg, 0.24 mmol, 1.2 equiv.), and dry toluene (10 mL) were placed in a Schlenk flask. Then, catalyst **M201** (207 mg, 0.20 mmol, 1.0 equiv.) was added and the resulting solution was stirred under argon at 80 ºC for 1 h. The reaction mixture was allowed to cool down to room temperature, concentrated under vacuum, dissolved in EtOAc (ca. 20 mL), white precipitate was filtered off, and the filtrate was concentrated under vacuum. The product was purified by column chromatography (SiO_2, eluent: from *n*-hexane to 30% EtOAc/*n*-hexane) giving **Ru11a** as a green band. The solvent was evaporated and product dissolved in a small amount of DCM, then *n*-pentane was added until green crystals precipitated. The precipitate was filtered off, washed with *n*-pentane and dried in vacuum to afford complex **Ru11** (125 mg, 0.17 mmol, 85% yield) as a green solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.43 (s, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 4H), 6.93 (d, *J* = 6.7 Hz, 2H), 6.56 (d, *J* = 8.3 Hz, 1H), 4.69 (q, *J* = 7.0 Hz, 1H), 4.21 (s,

4H), 3.57 (t, *J* = 6.7 Hz, 4H), 2.00 (s, 3H), 1.48 (d, *J* = 7.0 Hz, 3H), 1.25 (d, *J* = 6.7 Hz, 18H), 1.18 (d, *J* = 6.7 Hz, 6H).

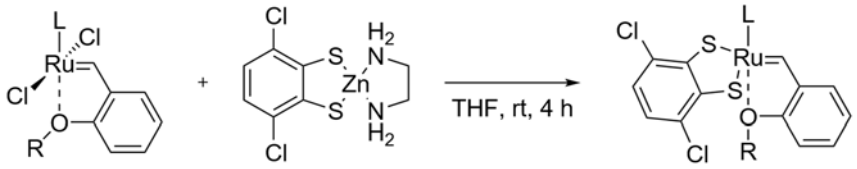
^{13}C NMR (101 MHz, CD_2Cl_2) δ 289.3, 212.2, 209.2, 152.7, 149.6, 144.0, 137.0, 130.1, 129.8, 124.7, 124.7, 124.0, 122.6, 112.7, 83.0, 55.0, 29.2, 29.2, 26.7, 25.6, 23.5, 23.4, 17.7.

HRMS: $[M]^+$. calcd for $C_{38}H_{50}Cl_2N_2O_2Ru$, 738.2287; found, 738.2285.

ATR-IR (cm^{-1}): 3070, 2965, 2926, 2867, 1717, 1592, 1577, 1475, 1456, 1441, 1411, 1387, 1363, 1325, 1294, 1263, 1232, 1209, 1180, 1161, 1129, 1107, 1083, 1047, 1038, 988, 927, 862, 802, 791, 768, 751, 698, 645, 554, 540, 460, 442.

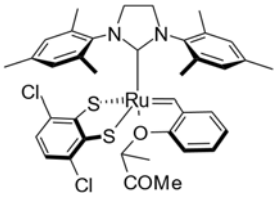
Elemental analysis calcd. for $C_{38}H_{50}Cl_2N_2O_2Ru$: C, 61.78; H, 6.82; N, 3.79. Found: C, 61.74; H, 6.81; N, 3.80.

3. General Procedure for the synthesis of catalysts Ru10b-Ru16b



In a glovebox a 20 mL vial was charged with corresponding ruthenium complex (1.0 equiv.) dissolved in anhydrous THF (10 mL) followed by zinc salt **1** (1.2 equiv.). The resulting mixture was stirred at room temperature for 4 hours. Next, THF was evaporated, the dark brown residue was dissolved in DCM (10 mL), and the obtained solution was filtered through a short pad of silica gel. DCM was evaporated to dryness, and residue was crystallised from DCM/*n*-hexane, the precipitate was filtered, and dried in vacuum.

a. Synthesis of ruthenium complex Ru10b



Following the general procedure, **Ru10a** (200 mg, 0.30 mmol, 1.0 equiv.), zinc salt **1** (119 mg, 0.36 mmol, 1.2 equiv.), and THF (10 mL) were used. The desired product **Ru10b** was obtained as a brown solid (176 mg, 0.22 mmol, 74% yield). Two diastereomers were observed; d.r. = 80:20. The major one is described.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 14.32 (s, 1H), 7.28 – 7.22 (m, 1H), 6.95 (br s, 3H), 6.90 (d, *J* = 8.1

Hz, 1H), 6.87 – 6.83 (m, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.64 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.38 (q, *J* = 7.5 Hz, 1H), 3.93 (s, 4H), 2.42 (br s, 6H), 2.26 (s, 3H), 2.24 (s, 7H), 2.18 (br s, 2H), 1.64 (d, *J* = 7.5 Hz, 3H), 1.51 (s, 3H).

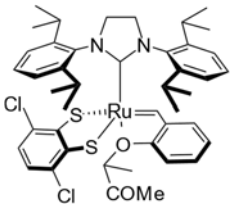
^{13}C NMR (101 MHz, CD_2Cl_2) δ 253.8, 217.3, 210.1, 208.4, 205.2, 204.5, 189.5, 160.1, 154.4, 154.0, 153.2, 141.5, 141.4, 139.6, 138.9, 136.9, 136.8, 136.3, 135.8, 131.6, 131.3, 130.0, 129.8, 129.6, 129.5, 129.0, 128.9, 128.3, 127.6, 125.8, 124.4, 124.2, 123.7, 123.4, 123.1, 121.9, 121.9, 118.3, 113.4, 113.0, 89.2, 86.3, 80.0, 52.6, 27.9, 26.5, 25.3, 21.2, 21.1, 19.0, 18.4, 18.2, 18.0, 17.5, 16.4.

HRMS: $[M]^+$. calcd for $C_{38}H_{40}Cl_2N_2O_2RuS_2$, 792.0946; found, 792.0938.

ATR-IR (cm^{-1}): 3065, 2950, 2916, 2855, 2732, 2551, 1734, 1719, 1608, 1591, 1573, 1524, 1475, 1450, 1423, 1395, 1376, 1332, 1262, 1174, 1156, 1108, 1084, 1062, 1032, 989, 952, 915, 848, 816, 783, 747, 575.

Elemental analysis calcd. for $C_{38}H_{40}Cl_2N_2O_2RuS_2$ × 0.6 DCM: C, 55.93; H, 5.23; N, 3.21. Found: C, 55.60; H, 4.91; N, 3.26.

b. Synthesis of ruthenium complex Ru11b



Following the general procedure, **Ru11a** (200 mg, 0.27 mmol, 1.0 equiv.), zinc salt **1** (108 mg, 0.32 mmol, 1.2 equiv.), and THF (10 mL) were used. The desired product **Ru11b** was obtained as a brown solid (232 mg, 0.26 mmol, 98% yield). Two diastereomers were observed; d.r. = 98:2. The major one is described.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 14.65 (s, 1H), 7.48 – 7.32 (m, 3H), 7.28 – 7.24 (m, 2H), 7.18 – 7.15 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.71 (br. s, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.55 (dd, *J* = 7.5, 1.6 Hz, 1H), 4.72 (q, *J* = 7.2 Hz, 1H), 4.38 (br. s, 1H), 4.20 (br. s, 1H), 4.11 – 3.67 (m, 4H), 3.09 (br. s, 1H), 2.46 (br. s, 1H), 2.01 (s, 3H), 1.93 (s, 3H), 1.43 – 1.19 (m, 11H), 1.12 (d, *J* = 7.2 Hz, 3H), 1.08 – 0.89 (m, 7H), 0.47 (s, 3H).

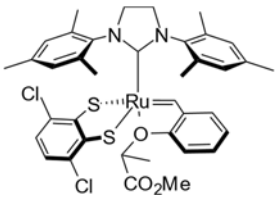
^{13}C NMR (101 MHz, CD_2Cl_2) δ 257.3, 219.6, 212.9, 208.4, 189.5, 160.1, 154.8, 147.6, 136.2, 136.1, 131.3, 130.2, 128.9, 124.7, 124.3, 121.8, 113.4, 79.9, 55.2, 29.4, 26.3, 23.6, 17.5.

HRMS: $[M]^+$. calcd for $C_{44}H_{52}Cl_2N_2O_2RuS_2$, 876.1885; found, 876.1874.

ATR-IR (cm^{-1}): 3068, 2963, 2925, 2867, 1712, 1589, 1575, 1525, 1475, 1453, 1441, 1409, 1396, 1362, 1334, 1263, 1237, 1198, 1182, 1157, 1123, 1108, 1078, 1065, 1047, 991, 922, 861, 803, 745, 620, 601, 552, 509, 458.

Elemental analysis calcd. for $C_{44}H_{52}Cl_2N_2O_2RuS_2$ × 0.2 DCM: C, 59.38; H, 5.91; N, 3.13. Found: C, 59.32; H, 5.92; N, 3.43.

c. Synthesis of ruthenium complex Ru12b



Following the general procedure, **Ru12a** (200 mg, 0.30 mmol, 1.0 equiv.), zinc salt **1** (119 mg, 0.36 mmol, 1.2 equiv.), and THF (10 mL) were used. The desired product **Ru12b** was obtained as a brown solid (138 mg, 0.17 mmol, 57% yield). Two diastereomers were observed; d.r. = 87:13. The major one is described.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 14.31 (s, 1H), 7.29 (ddd, *J* = 8.3, 7.3, 1.6 Hz, 1H), 7.07 – 6.97 (m, 1H), 6.94 – 6.81 (m, 5H), 6.66 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.57 (br. s, 1H), 6.20 (br. s, 1H), 5.52 (q, *J* = 7.3 Hz, 1H), 4.10 – 3.83 (m, 4H), 3.94 (s, 4H), 2.60 (br. s, 3H), 2.42 – 2.32 (m, 3H), 2.24 (s, 9H), 1.70 (d, *J* = 7.3 Hz, 5H).

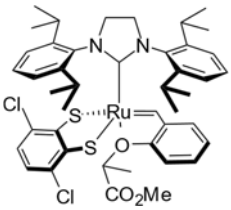
^{13}C NMR (101 MHz, CD_2Cl_2) δ 252.6, 217.3, 171.5, 154.0, 152.7, 141.4, 131.6, 130.0, 127.4, 124.4, 123.7, 123.4, 121.9, 117.4, 81.9, 52.9, 21.1, 18.8, 16.4.

HRMS: $[M]^+$. calcd for $C_{38}H_{40}Cl_2N_2O_3RuS_2$, 808.0895; found, 808.0882.

ATR-IR (cm^{-1}): 3002, 2948, 2918, 2854, 1741, 1607, 1595, 1591, 1574, 1546, 1524, 1479, 1434, 1397, 1379, 1334, 1317, 1287, 1277, 1262, 1246, 1180, 1157, 1108, 1092, 1063, 1030, 990, 974, 910, 846, 816, 783, 743, 602, 577, 568.

Elemental analysis calcd. for $C_{38}H_{40}Cl_2N_2O_3RuS_2$ × 0.8 DCM: C, 53.15; H, 4.78; N, 3.20. Found: C, 52.96; H, 4.77; N, 3.73.

d. Synthesis of ruthenium complex Ru13b



Following the general procedure, **Ru13a** (200 mg, 0.27 mmol, 1.0 equiv.), zinc salt **1** (108 mg, 0.32 mmol, 1.2 equiv.), and THF (10 mL) were used. The desired product **Ru13b** was obtained as a brown solid (169 mg, 0.19 mmol, 70% yield). Two diastereomers were observed; d.r. = 75:25. The major one is described.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 14.46 (s, 1H), 7.37 (s, 3H), 7.33 – 7.25 (m, 2H), 7.22 – 7.11 (m, 1H), 6.94 – 6.67 (m, 5H), 6.56 (d, *J* = 7.4 Hz, 1H), 4.98 (s, 1H), 4.30 (s, 1H), 4.04 (s, 3H), 3.95 – 3.81 (m, 2H), 3.82 – 3.70 (m, 2H), 3.61 (s, 3H), 1.90 (br.s, 3H), 1.35 – 1.17 (m, 16H), 0.99 (br.s, 5H), 0.47 (s, 3H).

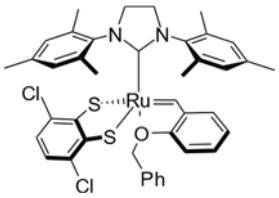
^{13}C NMR (101 MHz, CD_2Cl_2) δ 257.7, 212.9, 189.8, 172.1, 160.4, 154.8, 147.6, 136.1, 136.0, 132.4, 132.2, 131.3, 130.2, 128.9, 128.8, 128.5, 124.7, 124.3, 122.0, 113.7, 73.6, 55.3, 52.7, 29.4, 26.3, 23.6, 18.6.

HRMS: $[M]^+$. calcd for $C_{44}H_{52}Cl_2N_2O_3RuS_2$, 892.1834; found, 892.1836.

ATR-IR (cm^{-1}): 3067, 2960, 2926, 2866, 1737, 1690, 1597, 1577, 1524, 1477, 1453, 1440, 1408, 1395, 1362, 1335, 1308, 1264, 1237, 1200, 1158, 1127, 1110, 1080, 1065, 1049, 976, 932, 890, 838, 803, 755, 744, 620, 601, 550, 535, 458.

Elemental analysis calcd. for $C_{44}H_{52}Cl_2N_2O_3RuS_2$ × 0.1 DCM: C, 58.76; H, 5.84; N, 3.11. Found: C, 58.30; H, 5.72; N, 2.81.

e. Synthesis of ruthenium complex Ru14b



Following the general procedure, **Ru14a** (200 mg, 0.30 mmol, 1.0 equiv.), zinc salt **1** (119 mg, 0.36 mmol, 1.2 equiv.), and THF (10 mL) were used. The desired product **Ru14b** was obtained as a brown solid (180 mg, 0.22 mmol, 74% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 14.35 (s, 1H), 7.30 (s, 5H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.08 – 6.63 (m, 7H), 6.63 – 6.28 (m, 2H), 5.82 (d, *J* = 14.8 Hz, 1H), 5.58 (d, *J* = 14.6 Hz, 1H), 3.97 (s, 4H), 2.51 (s, 6H), 2.26 (s, 7H), 2.12 – 1.80 (m, 3H), 1.71 – 1.41 (m, 2H).

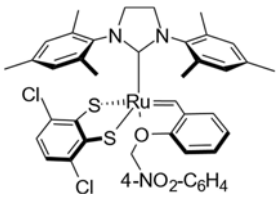
^{13}C NMR (101 MHz, CD_2Cl_2) δ 252.4, 216.9, 211.1, 156.0, 153.9, 141.4, 139.9, 135.5, 131.2, 129.7, 128.3, 127.9, 127.3, 126.8, 123.6, 122.9, 122.6, 121.4, 113.8, 77.8, 54.0, 53.7, 53.4, 53.1, 52.9, 51.3, 20.7, 18.7.

HRMS: $[M]^+$. calcd for $C_{41}H_{40}Cl_2N_2ORuS_2$, 812.0997; found, 812.0999.

ATR-IR (cm^{-1}): 2950, 2934, 2916, 2854, 1607, 1592, 1572, 1524, 1474, 1451, 1422, 1395, 1375, 1332, 1318, 1262, 1206, 1183, 1155, 1107, 1062, 1035, 989, 849, 815, 783, 743, 695, 600, 575, 418.

Elemental analysis calcd. for $C_{41}H_{40}Cl_2N_2ORuS_2$: C, 60.58; H, 4.96; N, 3.45. Found: C, 60.40; H, 5.17; N, 3.49.

f. Synthesis of ruthenium complex Ru15b



Following the general procedure, **Ru15a** (200 mg, 0.28 mmol, 1.0 equiv.), zinc salt **1** (112 mg, 0.33 mmol, 1.2 equiv.), and THF (10 mL) were used. The desired product **Ru15b** was obtained as a brown solid (194 mg, 0.23 mmol, 81% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 14.44 (s, 1H), 8.16 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.16 – 7.07 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.73 – 6.68 (m, 1H), 6.50 (d, *J* = 8.3 Hz, 2H), 5.89 (d, *J* = 15.6 Hz, 1H), 5.65 (d, *J* = 15.6 Hz, 1H), 3.98 (s, 4H), 2.76 – 2.12 (m, 18H).

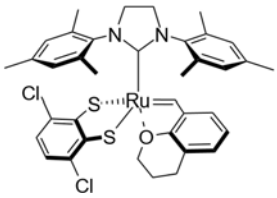
^{13}C NMR (101 MHz, $CDCl_3$) δ 251.5, 217.1, 155.1, 153.3, 147.6, 142.6, 140.5, 139.6, 131.4, 129.9, 127.6, 127.23, 124.0, 123.8, 123.3, 123.2, 121.8, 113.0, 76.1, 51.2, 21.0, 19.0.

HRMS: $[M]^+$. calcd for $C_{41}H_{39}Cl_2N_3O_3RuS_2$, 857.0848; found, 857.0845.

ATR-IR (cm^{-1}): 3648, 2950, 2916, 2855, 1606, 1574, 1520, 1479, 1454, 1423, 1396, 1376, 1343, 1262, 1206, 1182, 1156, 1108, 1062, 1011, 848, 816, 786, 738, 694, 621, 600, 575, 535, 418.

Elemental analysis calcd. for $C_{41}H_{39}Cl_2N_3O_3RuS_2$: C, 57.40; H, 4.58; N, 4.90. Found: C, 57.51; H, 4.69; N, 4.94.

g. Synthesis of ruthenium complex Ru16b



Following the general procedure, **Ru16a** (200 mg, 0.32 mmol, 1.0 equiv.), zinc salt **1** (129 mg, 0.38 mmol, 1.2 equiv.), and THF (10 mL) were used. The desired product **Ru16b** was obtained as a brown solid (200 mg, 0.26 mmol, 82% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 14.23 (s, 1H), 7.12 – 6.96 (m, 3H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.78 – 6.64 (m, 2H), 6.53 – 6.33 (m, 2H), 4.57 – 4.46 (m, 1H), 4.37 – 4.29 (m, 1H), 4.15 – 3.80 (m, 4H), 3.01 – 2.86 (m, 2H), 2.70 (s, 3H), 2.48 – 2.25 (m, 11H), 2.24 – 2.06 (m, 3H), 1.58 – 1.35 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 254.5, 218.3, 154.4, 153.6, 141.7, 140.0, 131.2, 130.2, 127.7, 123.0, 122.9, 122.8, 121.5, 120.8, 73.1, 23.3, 21.1, 18.9.

HRMS: $[M]^+$. calcd for $C_{37}H_{38}Cl_2N_2ORuS_2$, 762.0841; found, 762.0835.

ATR-IR (cm^{-1}): 2918, 2853, 1608, 1572, 1524, 1478, 1429, 1394, 1376, 1331, 1316, 1262, 1213, 1176, 1155, 1061, 1017, 979, 915, 876, 849, 814, 781, 762, 732, 600, 575, 560, 484, 418.
Elemental analysis calcd. for $C_{37}H_{38}Cl_2N_2ORuS_2$: C, 58.26; H, 5.02; N, 3.67. Found: C, 58.04; H, 5.02; N, 3.61.

4. Stability test

In a glovebox, an NMR tube was charged with **Ru** complex (0.005 mmol), anthracene (0.005 mmol) as the internal standard, and THF-d_8 (0.5 mL). The tube was sealed and shaken vigorously. An ^{1}H NMR spectrum was recorded for reference at time = 0. The tube was then left at room temperature or placed in an oil bath set at 60 °C. Degradation was monitored by observing the disappearance of the benzylidene signal by ^{1}H NMR for 48 hours (Figure S1).

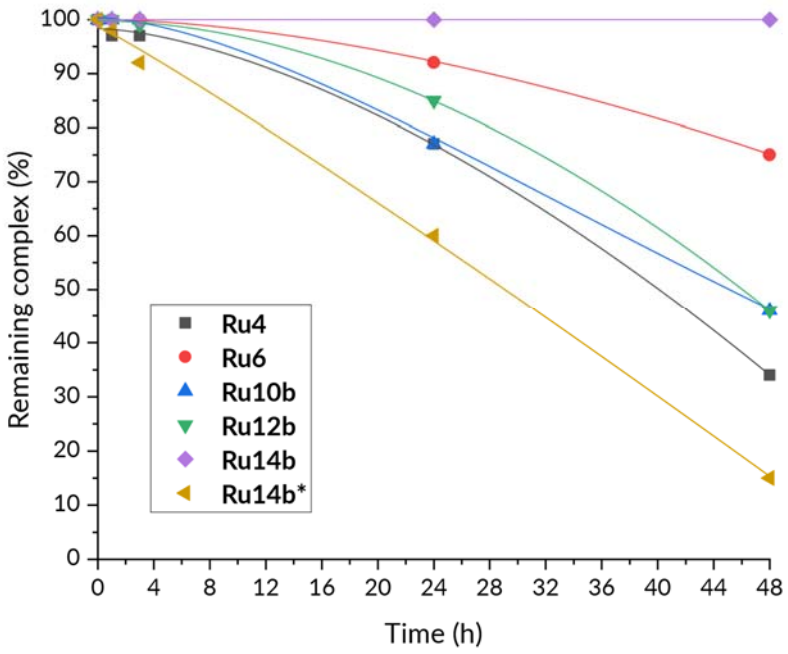


Figure S1. Relative decomposition rates of selected complexes measured in THF-d_8 at room temperature. Lines are a visual aid only. * Stability study was performed at 60 °C.

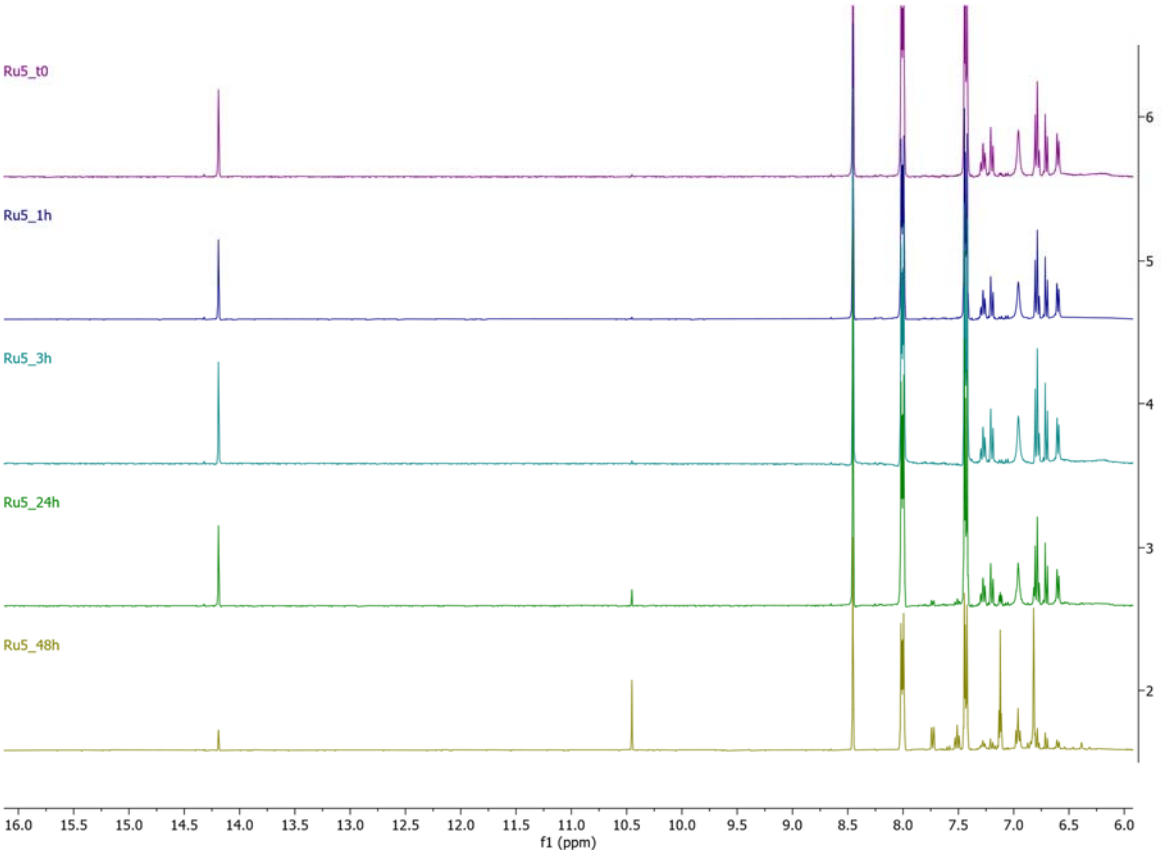


Figure S2. Stacked spectra for **Ru4**.

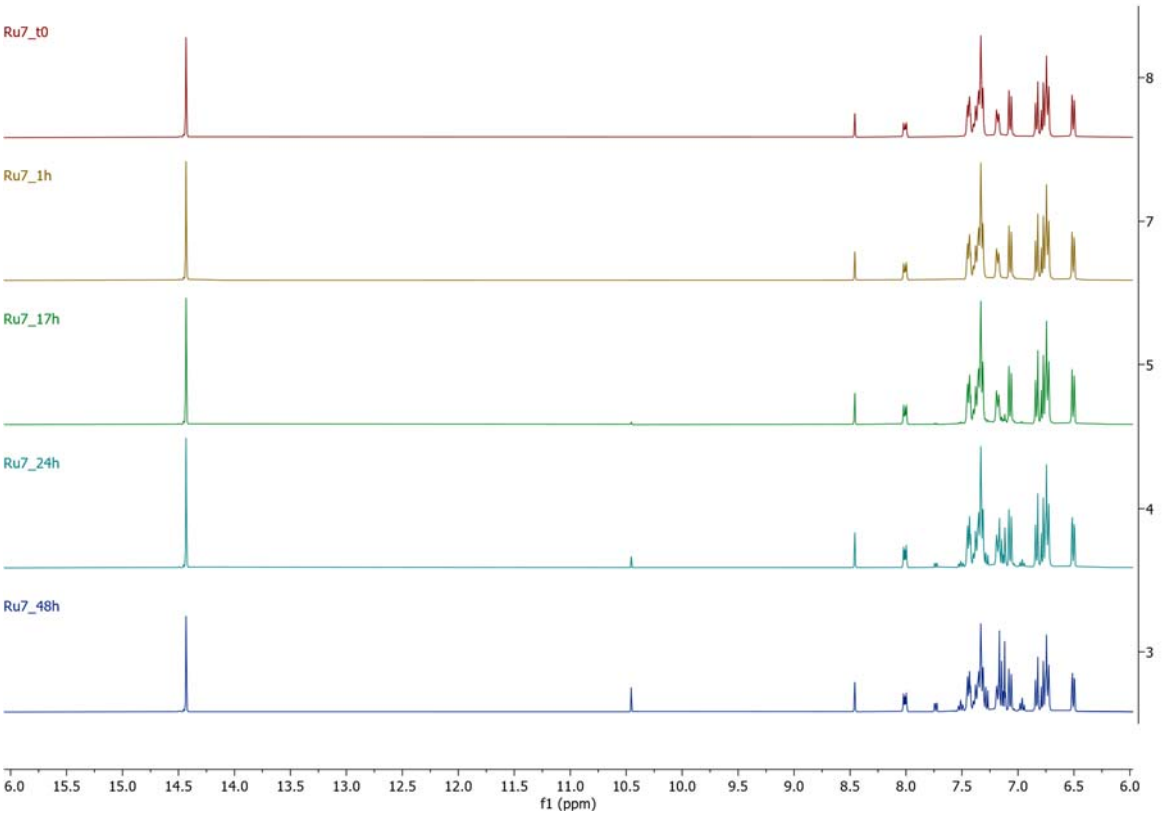


Figure S3. Stacked spectra for **Ru6**.

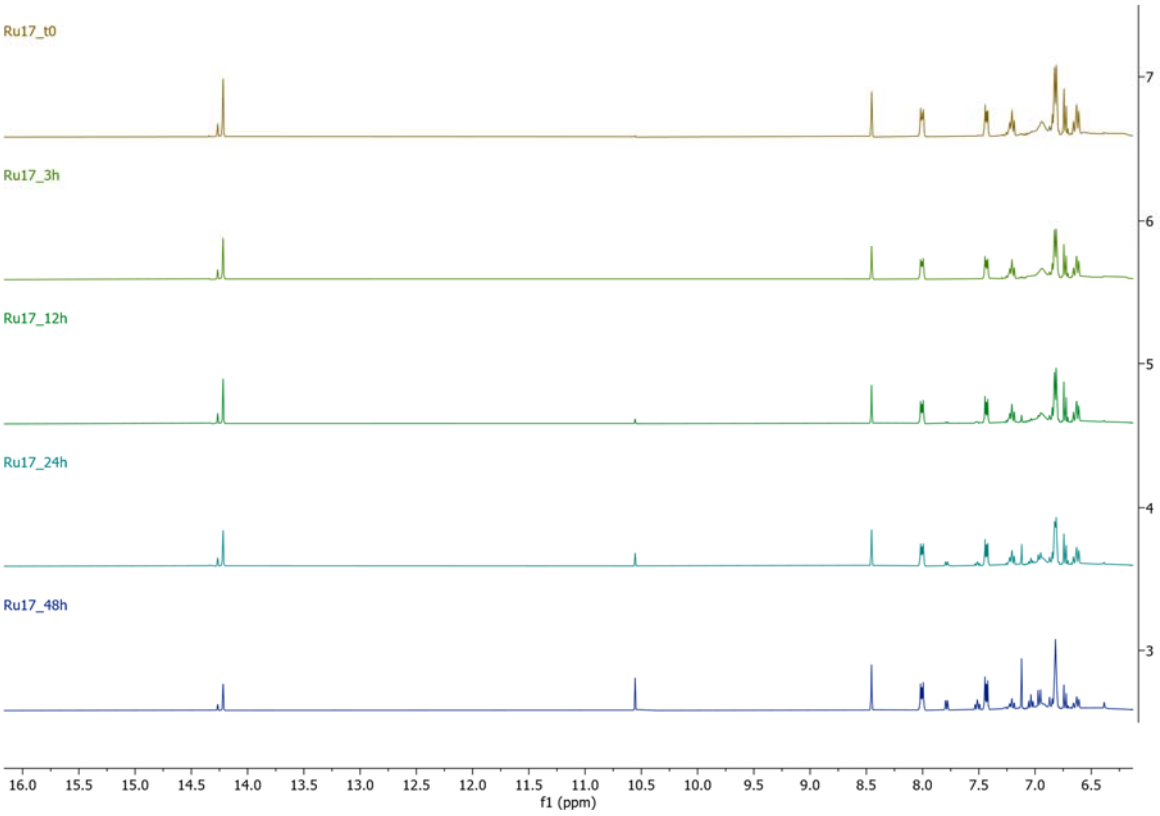


Figure S4. Stacked spectra for **Ru10b**.

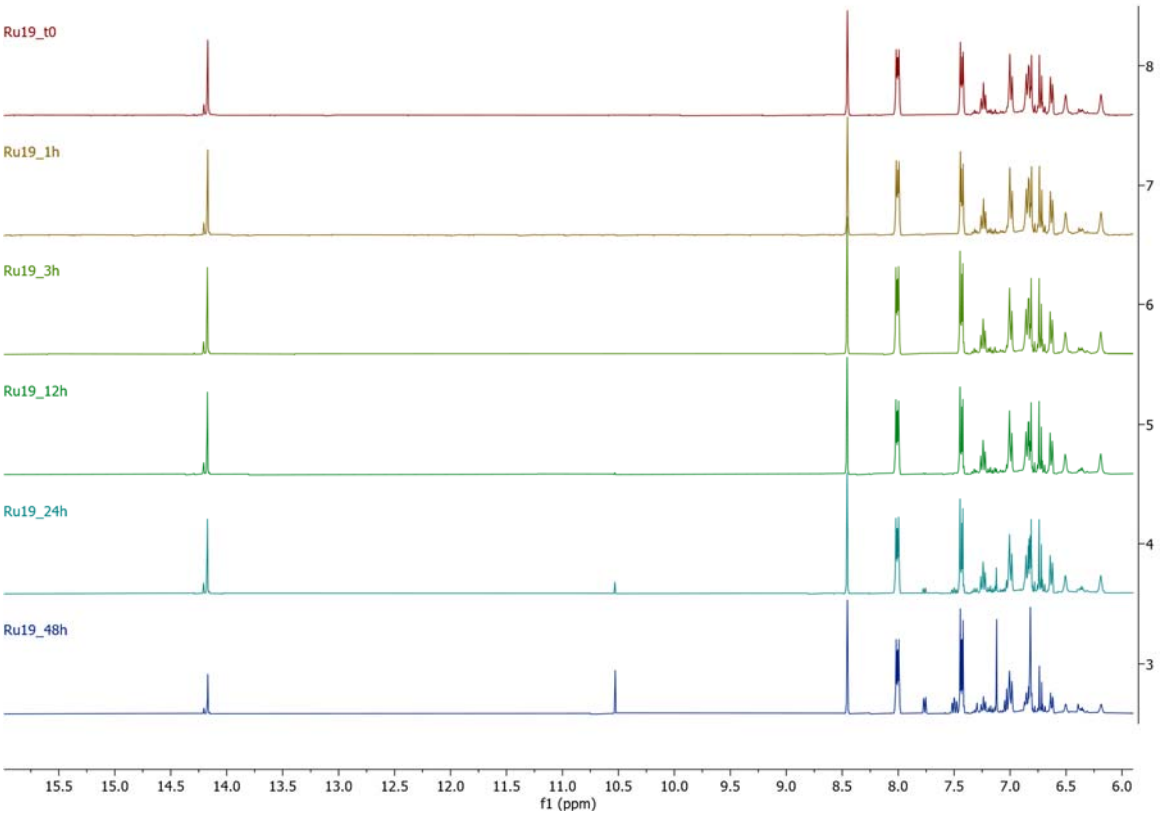


Figure S5. Stacked spectra for **Ru12b**.

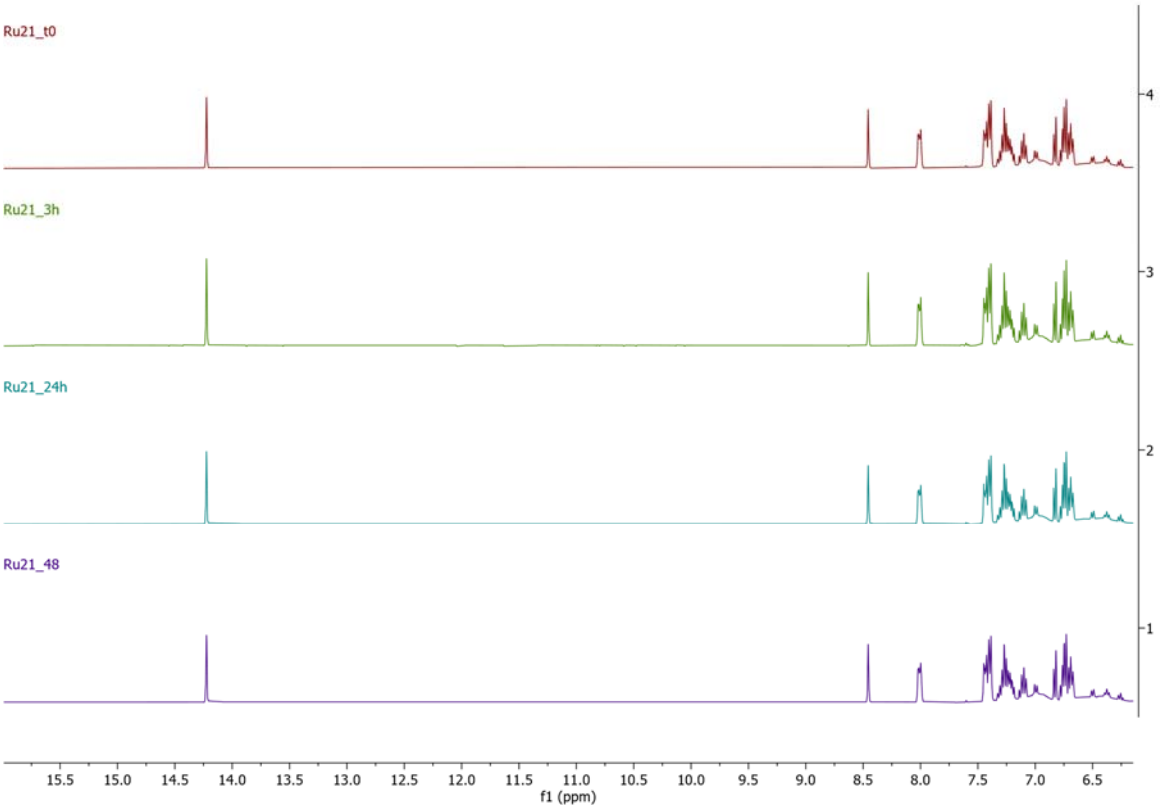


Figure S6. Stacked spectra for **Ru14b** at room temperature.

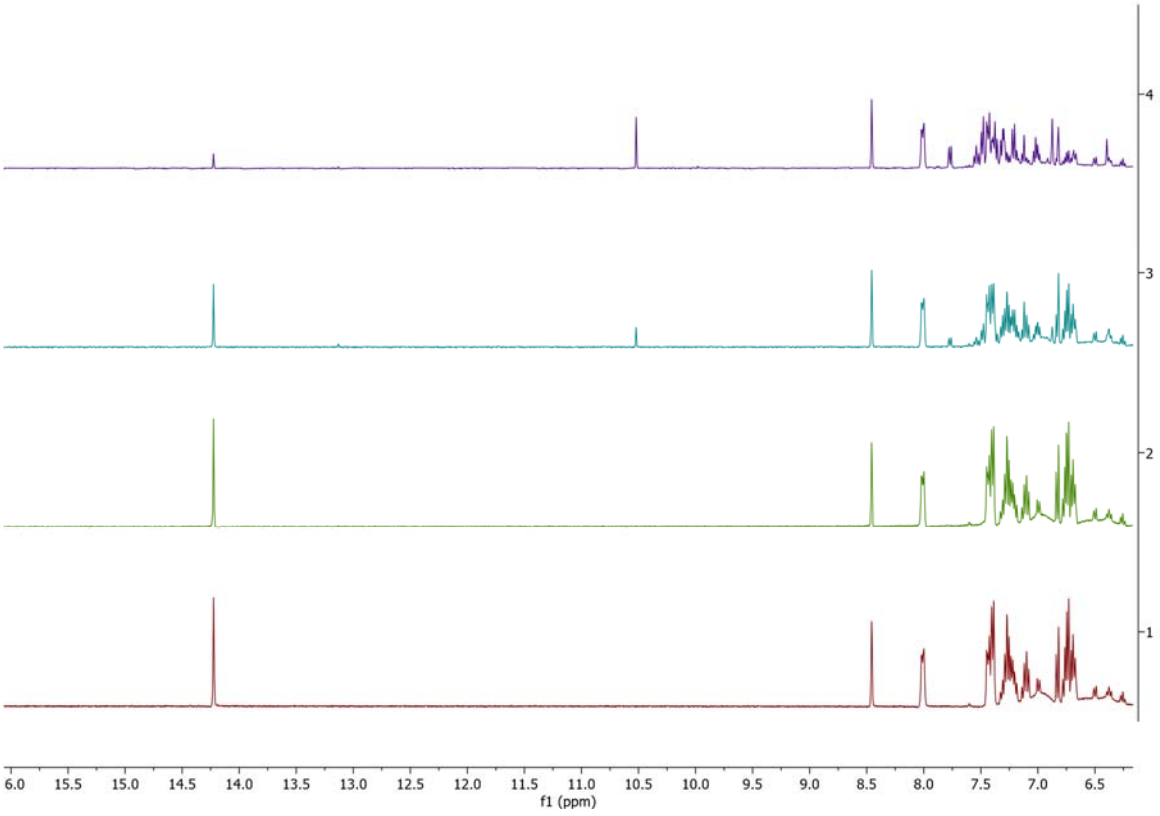


Figure S7. Stacked spectra for **Ru14b** at 60 ℃.

5. Activity tests

The activation of the catalysts **Ru4** and **Ru14b** were tested in the reaction with *n*-butyl vinyl ether **(a)** and cross-metathesis reaction of allylbenzene and *cis*-2-butene-1,4-diol **(b)**.

a) In a glovebox, to the NMR tube equipped with septum cap a solution of a corresponding Ru complex (~11 mg, 0.014 mmol, 1.0 equiv.) and anthracene (1.3 mg, 0.007 mmol, 0.5 equiv.) in THF-d_8 (0.7 mL) were placed. After that, through the septum *n*-butyl vinyl ether (56 µL, 0.42 mmol, 30.0 equiv.) was added using Hamilton syringe. Subsequently, the NMR measurements were conducted at the given times (see Table S1).

Table S1. Catalyst disappearance in the presence of *n*-butyl vinyl ether over time.

time, min	catalyst disappearance [%]	
	Ru4	**Ru14b**
1	59	6
2	85	17
3	95	26
4	100	36
5	-	42
10	-	65
15	-	83
20	-	90
25	-	96
30	-	100

Complex **Ru4** with standard benzylidene ligand reached the full conversion within first 4 minutes, whereas **Ru14b** at the same time gave 36% of the initiated product [Ru]=CH(OBu).[8] After prolonging the reaction to 30 minutes, the full conversion of catalyst Ru21 was achieved in the reaction with *n*-butyl-vinyl ether, forming a Fisher carbene.

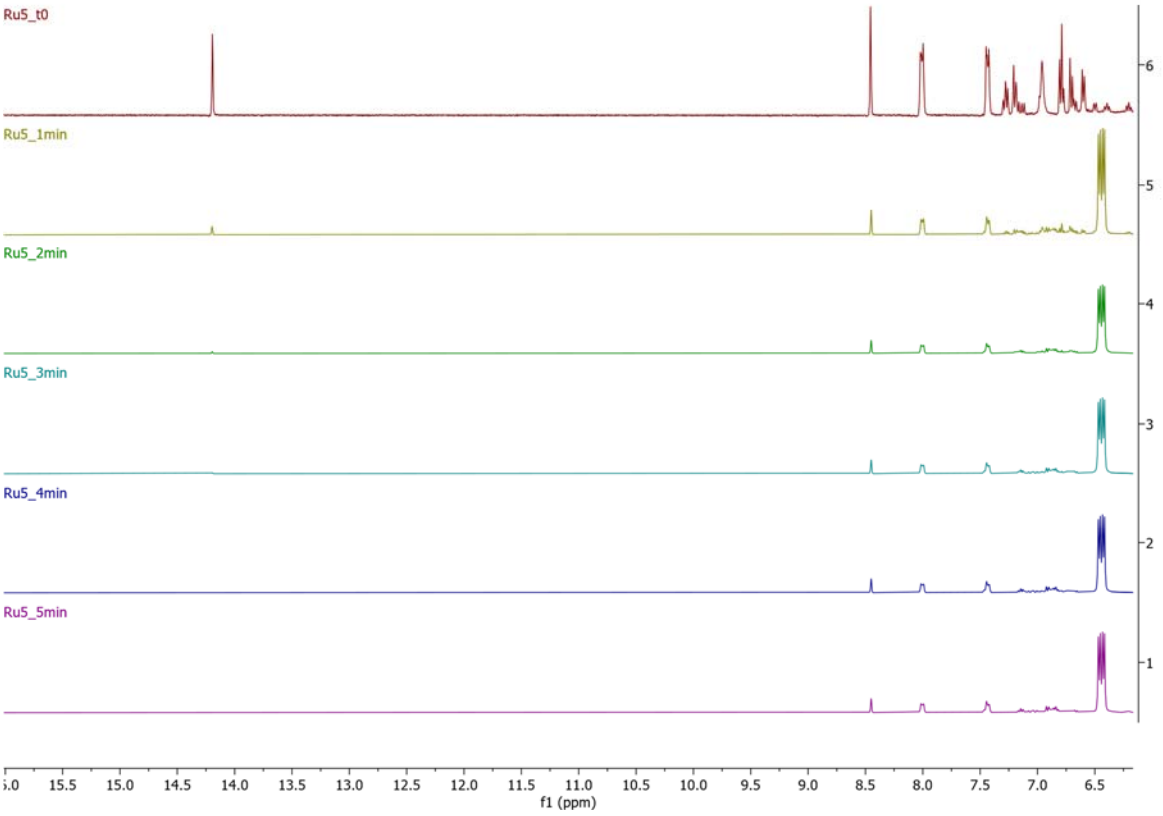


Figure S8. Stacked spectra for **Ru4** in the presence of *n*-butyl vinyl ether.

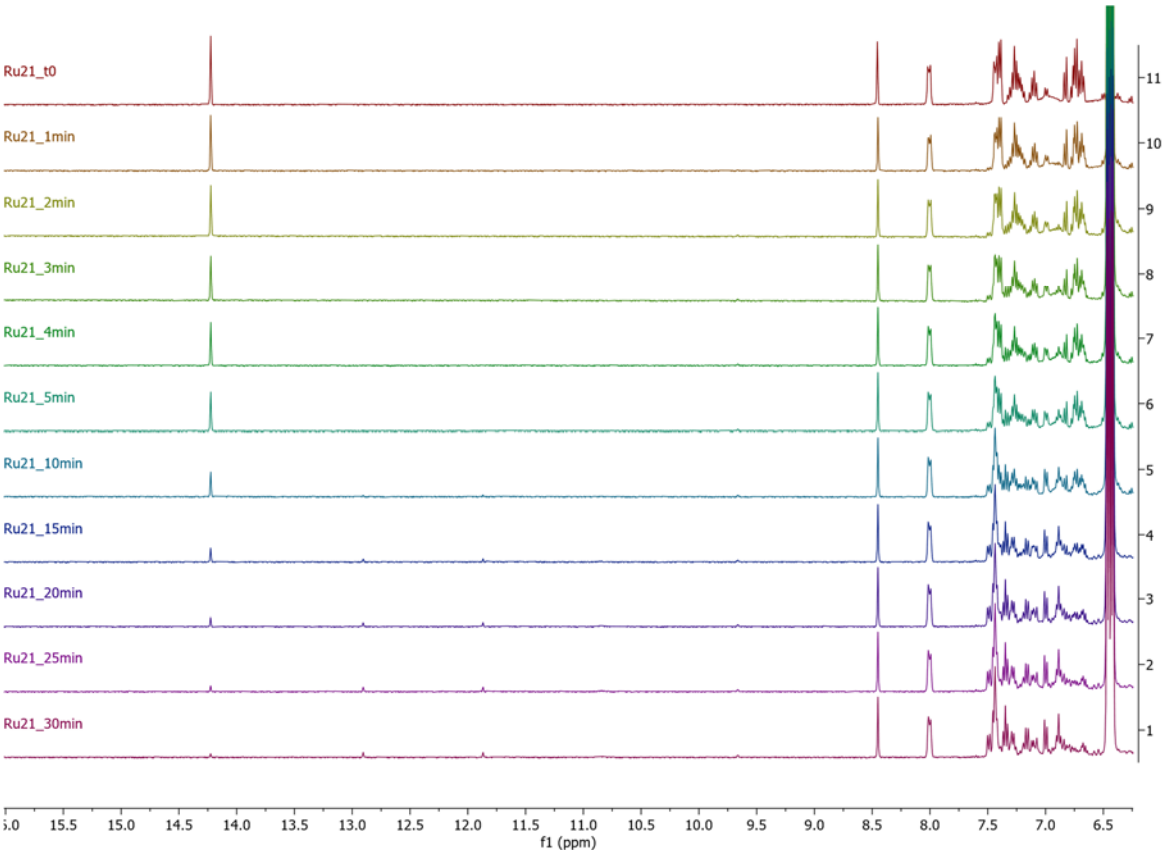


Figure S9. Stacked spectra for **Ru14a** in the presence of *n*-butyl vinyl ether.

b) In a glovebox, an NMR tube was charged with allylbenzene (14 mg, 0.12 mmol, 16 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (22 mg, 0.24 mmol, 21 µL, 2.4 equiv.), anthracene (18 mg, 0.10 mmol, 1.0 equiv.), as the internal standard, and THF-d_8 (0.5 mL). The tube was sealed and shaken vigorously. An ^{1}H NMR spectrum measured. After that, through the septum a solution of a corresponding Ru complex in THF-d_8 (0.2 mL) was added using Hamilton syringe. Subsequently, the NMR measurements were conducted each minute for 1 hour (see Table S2, Figure S2). Complex **Ru4** reached the maximum conversion within first ten minutes of the reaction, while the same cross-metathesis carried out in the presence of **Ru14b** proceeded much slower and a similar result (65% of conversion) was obtained only after one hour.

These two activation experiments support our hypothesis that in the presence of **Ru14b**, not all catalyst molecules immediately enter the catalytic cycle, but are slowly released over time due to higher stability, which allows achieving high yields.

Table S2. Conversion of the catalyst in the presence of allylbenzene and *cis*-2-butene-1,4-diol.

time, min	conv. [%]	
	Ru4	**Ru14b**
1	42	11
2	48	16
3	52	20
4	55	23
5	57	26
6	59	28
7	61	30
8	62	33
9	63	34
10	64	36
11	64	37
12	65	39
13	66	40
14	66	42
15	67	43
16	67	44
17	67	46
18	67	46
19	67	48
20	68	49
21	68	49
22	68	50

23	69	51
24	69	52
25	69	52
26	69	53
27	69	54
28	69	55
29	69	55
30	69	56
31	69	56
32	69	57
33	69	57
34	69	58
35	69	58
36	69	58
37	70	57
38	70	57
39	70	57
40	70	58
41	70	58
42	69	59
43	69	60
44	69	60
45	69	61
46	69	61
47	69	61
48	69	62
49	69	62
50	69	63
51	69	63
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59	69	65
60	69	65

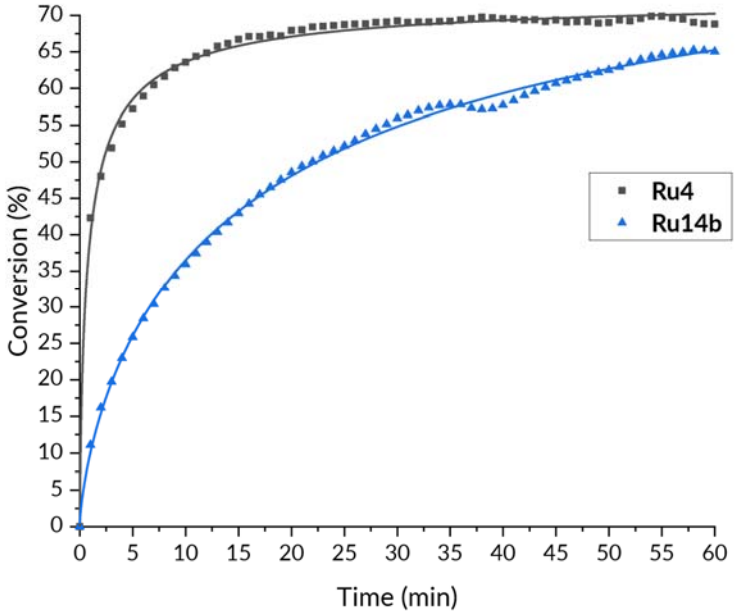
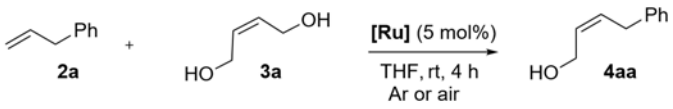


Figure S10. Activity profiles for **Ru4** and **Ru14b** in the presence of allylbenzene and *cis*-2-butene-1,4-diol. Lines are visual aid only.

6. Cross-metathesis reactions

Cross-metathesis reaction of allylbenzene and *cis*-2-butene-1,4-diol – catalyst comparison under an inert atmosphere and in air in THF



A. Cross-metathesis reaction under an inert atmosphere. In a 4 mL vial, allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (44 mg, 0.48 mmol, 42 µL, 2.4 equiv.), and tetradecane (used as an internal standard, 40 mg, 0.20 mmol, 53 µL, 1.0 equiv.) were mixed in a glovebox, followed by the addition of dry THF (1.2 mL). An aliquot (0.2 mL) of this solution was used for GC. Then, 5 mol% of a corresponding catalyst (**Ru4**, **Ru6**, **Ru10b-Ru16b**) was added in one portion. The resulting mixture was stirred under given conditions for 4 h (Table S2), an aliquot (0.2 mL) was taken, and the conversion of allylbenzene was determined by GC. All volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane). The product was obtained as a colourless oil.

B. Impact of air on cross-metathesis.

Method A. In a 4 mL vial, allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (44 mg, 0.48 mmol, 42 µL, 2.4 equiv.), and tetradecane (used as an internal standard, 40 mg, 0.20 mmol, 53 µL, 1.0 equiv.) were mixed in a glovebox, followed by the addition of dry THF (1.2 mL). An aliquot (0.2 mL) of this solution was used for GC. Then, 5 mol% of a corresponding catalyst (**Ru4**, **Ru6**, **Ru10b-Ru16b**) was added in one portion. The sealed reaction vessel was then transferred to a fume hood, the vial was opened to air, and the resulting mixture was stirred at room temperature for 4 h. When the reaction was completed, an aliquot (0.2 mL) was taken, the conversion of allylbenzene was determined by GC. All volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane). The product was obtained as a colourless oil. The data are summarised in Table S2.

Method B. In a 4 mL vial, allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (44 mg, 0.48 mmol, 42 µL, 2.4 equiv.), and tetradecane (used as an internal standard, 40 mg, 0.20 mmol, 53 µL, 1.0 equiv.) were mixed in a glovebox, followed by the addition of dry THF (1.2 mL). An aliquot (0.2 mL) of this solution was used for GC. Then, a sealed reaction vessel was transferred to a fume hood, a vial was opened to air, and the reaction mixture was stirred at room temperature for 30 min. After this time, **Ru14b** (8 mg, 0.01 mmol mmol, 5 mol%) was added in one portion and the resulting mixture was stirred for another 4 h. Next, an aliquot (0.2 mL) was taken and the conversion of allylbenzene was determined by GC. All volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane). The product was obtained as a colourless oil (Table S2, entry 16).

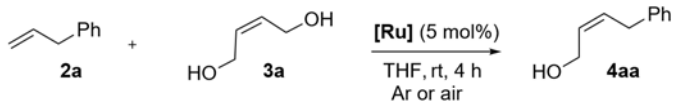
Table S3. Conditions of CM reaction of allylbenzene (**2a**) and *cis*-2-butene-1,4-diol (**3a**) in dry THF, conversion of allylbenzene (**2a**), isolated yield, and *Z*:*E* ratio of the CM product (**4aa**).

Entry	[Ru]	Ar or air	conv [%]	yield of **4aa** [%]	*Z*:*E* ratio
1	**Ru4**	Ar	74	68	96:4
2	**Ru4**	air	51	46	99:1
3	**Ru6**	Ar	59	59	99:1
4	**Ru6**	air	44	43	98:2
5	**Ru10b**	Ar	63	59	96:4
6	**Ru10b**	air	49	38	92:8
7	**Ru11b**	Ar	25	21	97:3

8[a]	**Ru11b**	Ar	33	30	86:14
9	**Ru11b**	air	17	-	-
10	**Ru12b**	Ar	78	72	98:2
11	**Ru12b**	air	50	42	99:1
12	**Ru13b**	Ar	nr	-	-
13	**Ru13b**	air	nr	-	-
14	**Ru14b**	Ar	82	80	98:2
15	**Ru14b**	air	50	46	>99:1
16 [b]	**Ru14b**	air	49	44	>99:1
17[c]	**Ru14b**	Ar	77	76	96:4
18	**Ru15b**	Ar	71	70	99:1
19	**Ru15b**	air	53	51	>99:1
20	**Ru16b**	Ar	28	25	>99:1
21	**Ru16b**	air	nr	-	-

[a] Reaction carried out at 60 °C. [b] Addition of cat. after 30 min to an open vial. [c] Reaction carried out at 45 °C.

Cross-metathesis reaction of allylbenzene and *cis*-2-butene-1,4-diol – antioxidants comparison under an inert atmosphere and in air in THF



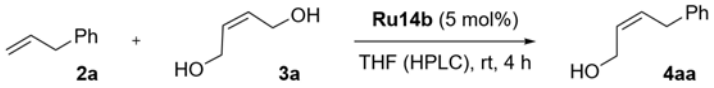
A. Cross-metathesis reaction under an inert atmosphere. In a 4 mL vial, allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (44 mg, 0.48 mmol, 42 µL, 2.4 equiv.), and tetradecane (used as an internal standard, 40 mg, 0.20 mmol, 53 µL, 1.0 equiv.) were mixed in a glovebox, followed by the addition of dry THF (1.2 mL). An aliquot (0.2 mL) of this solution was used for GC. Then, **Ru14b** (8 mg, 0.01 mmol, 5 mol%) and corresponding antioxidant (5% mol) were added in one portion. The resulting mixture was stirred at room temperature for 4 h. Next, an aliquot (0.2 mL) was taken and the conversion of allylbenzene was determined by GC. All volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane). The product was obtained as a colourless oil. The data are summarised in Table S3.

B. Impact of air on cross-metathesis. In a 4 mL vial, allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (44 mg, 0.48 mmol, 42 µL, 2.4 equiv.), and tetradecane (used as an internal standard, 40 mg,0.20 mmol, 53 µL, 1.0 equiv.) were mixed in a glovebox, followed by the addition of dry THF (1.2 mL). An aliquot (0.2 mL) of this solution was used for GC. Then, **Ru14b** (8 mg, 0.01 mmol, 5 mol%) and corresponding antioxidant (5% mol) were added in one portion. The sealed reaction vessel was then transferred to a fume hood, the vial was opened to air, and the resulting mixture was stirred at room temperature for 4 h. Next, an aliquot (0.2 mL) was taken and the conversion of allylbenzene was determined by GC. All volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane). The product was obtained as a colourless oil. The data are summarised in Table S3.

Table S4. Conditions of CM reaction of allylbenzene and *cis*-2-butene-1,4-diol in the presence of **Ru14b** in dry THF, conversion of allylbenzene (**2a**), isolated yield, and *Z*:*E* ratio of the CM product (**4aa**).

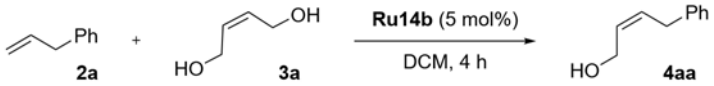
entry	Ar or air	additive	conv [%]	yield of **4aa** [%]	*Z*:*E* ratio
1	Ar	5 mol% BHT	80	79	96:4
2	air	5 mol% BHT	65	64	>98:2
3	Ar	5 mol% Vit.C	80	78	97:3
4	air	5 mol% Vit.C	45	34	>99
5	Ar	5 mol% HQ	80	78	97:3
6	air	5 mol% HQ	56	55	>99:1

Cross-Metathesis reaction of allylbenzene and *cis*-2-butene-1,4-diol in THF (HPLC)



In a 4 mL vial, allylbenzene (53 mg, 0.44 mmol, 60 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (82 mg, 0.88 mmol, 76 µL, 2.4 equiv.) and tetradecane (used as an internal standard, 80 mg, 0.40 mmol, 105 µL, 1.0 equiv.) were mixed under a fume hood. Then, the vial was filled with THF (2.2 mL, HPLC). An aliquot (0.2 mL) of this solution was used for GC. Then, the reaction mixture was divided into two vials by 1.0 mL in each. Next, **Ru14b** (8 mg, 0.01 mmol, 5 mol%) was added to each vial in one portion, followed by the addition of 5% mol of butylhydroxytoluene (BHT) to one of the vials. The resulting mixtures were stirred at room temperature for 4 h. When the reaction was completed, aliquots (0.2 mL) were taken, the conversion of allylbenzene was determined by GC (0% in both cases).

Cross-metathesis reaction of allylbenzene and *cis*-2-butene-1,4-diol in DMC

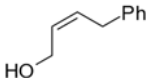


A. Cross-metathesis reaction in inert atmosphere. In a 4 mL vial, allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (44 mg, 0.48 mmol, 42 µL, 2.4 equiv.), and tetradecane (used as an internal standard, 40 mg, 0.20 mmol, 53 µL, 1.0 equiv.) were mixed in a glovebox, followed by the addition of dry DMC (1.2 mL). An aliquot (0.2 mL) of this solution was used for GC. Then, **Ru14b** (8 mg, 0.01 mmol, 5 mol%) was added in one portion. The resulting mixture was stirred for 4 h under given conditions. Next, an aliquot (0.2 mL) was taken and the conversion of allylbenzene was determined by GC. All volatiles were removed under reduced pressure and the crude product was purified using column chromatography

(SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane). The product was obtained as a colourless oil.

B. Impact of air on cross-metathesis reaction in DMC.

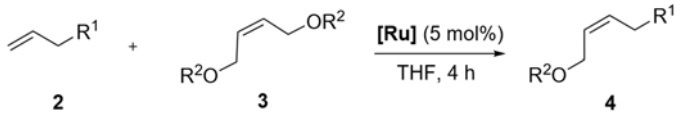
In a 4 mL vial, allylbenzene (53 mg, 0.44 mmol, 60 µL, 1.2 equiv.), *cis*-2-butene-1,4-diol (82 mg, 0.88 mmol, 76 µL, 2.4 equiv.) and tetradecane (used as an internal standard, 80 mg, 0.40 mmol, 105 µL, 1.0 equiv.) were mixed under a fume hood. Then, the vial was filled with DMC (2.2 mL). An aliquot (0.2 mL) of this solution was used for GC. Then, **Ru14b** (8mg, 0.01 mmol, 5 mol%) was added to each vial in one portion, followed by the addition butylhydroxytoluene (2 mg, 0.01 mmol, 5% mol) to one of the vials. The sealed reaction was then transferred to a fume hood, the vial was opened to air. The resulting mixture was stirred at room temperature for 4 h. Next, aliquots (0.2 mL) were taken and the conversion of allylbenzene was determined by GC (47% in both cases). All volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane). The product was obtained as a colourless oil in 46% yield for both reactions (11 mg, 0.07 mmol, *Z*:*E* ratio >99).



^{1}H NMR (400 MHz, $CDCl_3$), (ppm) for *Z*-isomer (major): δ 7.33 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 5.79 – 5.70 (m, 2H), 4.32 (d, *J* = 5.1 Hz, 2H), 3.45 (d, *J* = 5.8 Hz, 2H). OH not seen due to D-H exchange. **^{13}C NMR (101 MHz, $CDCl_3$)**, (ppm) δ 140.2, 131.2, 129.3, 128.6, 128.3, 126.1, 58.6, 33.6.

Analytical data for this compound are consistent with previously reported data.[9]

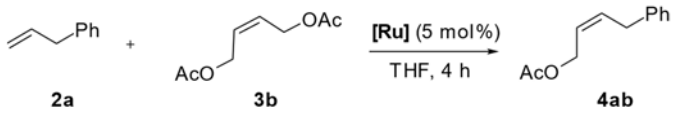
General procedure for cross-metathesis reaction of terminal and internal olefin



In a 4 mL vial, terminal olefin **2** (1.2 equiv.), internal olefin **3** (2.4 equiv.), and tetradecane (used as an internal standard, 1.0 equiv., 53 µL) were mixed in a glovebox. Then, the vial was filled with dry THF (1.2 mL). An aliquot (0.2 mL) of this solution was used for GC. Then, 5 mol% of a corresponding catalyst (**Ru4**, **Ru6** or **Ru14b**) was added in one portion. The resulting mixture was stirred at given temperature for 4 h. When the reaction was completed, an aliquot (0.2 mL) was taken, the conversion of terminal olefin **2** was determined by GC. All volatiles were

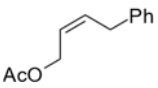
removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane).

Cross-metathesis reaction of allylbenzene and *(Z)*-1,4-diacetoxy-2-butene



2a **3b** **4ab**

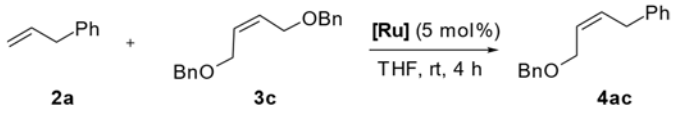
The reaction was carried out following the general procedure using allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.) and *cis*-1,4-diacetoxy-2-butene (87 mg, 0.48 mmol, 81 µL, 2.4 equiv.). The product was obtained as a colourless oil.



^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.15 (m, 3H), 5.90 – 5.75 (m, 1H), 5.74 – 5.58 (m, 1H), 4.77 – 4.70 (m, 2H), 3.48 (d, *J* = 8.2 Hz, 2H), 2.08 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**, (ppm) δ 171.0, 139.8, 133.4, 128.5, 128.4, 126.2, 124.2, 77.3, 77.0, 76.7, 60.2, 33.8, 21.0.

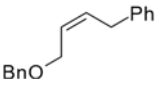
Analytical data for this compound are consistent with previously reported data.[10]

Cross-metathesis reaction of allylbenzene and (*Z*)-1,4-bis(benzyloxy)but-2-ene



2a **3c** **4ac**

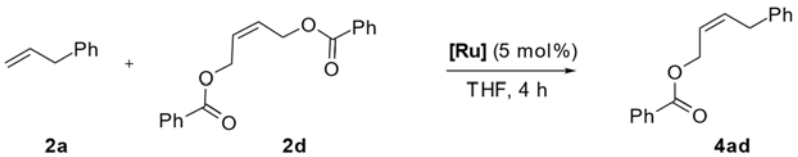
The reaction was carried out following the general procedure using allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.) and *cis*-1,4-bis(benzyloxy)but-2-ene (129 mg, 0.48 mmol, 2.4 equiv.). The product was obtained as a colourless oil.



^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 7.40 – 7.34 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 3H), 7.24 – 7.16 (m, 3H), 5.85 – 5.72 (m, 2H), 4.57 (s, 2H), 4.20 (d, *J* = 5.9 Hz, 2H), 3.43 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)**, (ppm) δ 140.2, 138.3, 131.9, 128.5, 128.4, 128.4, 127.8, 127.6, 127.1, 126.1, 72.3, 65.7, 33.8.

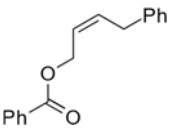
Analytical data for this compound are consistent with previously reported data (*E* isomer).[11]

Cross-metathesis reaction of allylbenzene and (*Z*)-but-2-ene-1,4-diyl dibenzoate



2a **2d** **4ad**

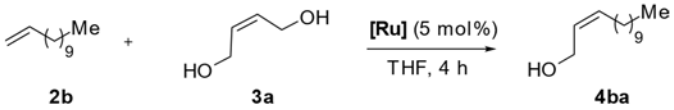
The reaction was carried out following the general procedure using allylbenzene (29 mg, 0.24 mmol, 33 µL, 1.2 equiv.) and *cis*-but-2-ene-1,4-diyl dibenzoate (142 mg, 0.48 mmol, 2.4 equiv.). The product was obtained as a colourless oil.



^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 8.08 – 8.03 (m, 2H), 7.58 – 7.52 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.17 (m, 3H), 5.94 – 5.73 (m, 2H), 4.98 (d, *J* = 6.7 Hz, 2H), 3.54 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)**, (ppm) δ 166.5, 139.8, 133.7, 132.9, 130.2, 129.6, 128.6, 128.4, 128.3, 126.2, 124.3, 60.7, 33.9.

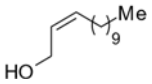
Analytical data for this compound are consistent with previously reported data.[12]

Cross-metathesis reaction of 1-dodecene and (*Z*)-2-butene-1,4-diol



2b **3a** **4ba**

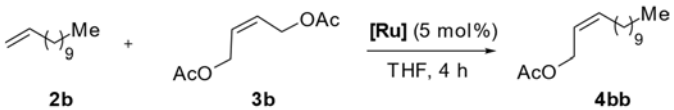
The reaction was carried out following the general procedure using 1-dodecene (40.4 mg, 0.24 mmol, 53 µL, 1.2 equiv.) and *cis*-2-butene-1,4-diol (44 mg, 0.48 mmol, 42 µL, 2.4 equiv.). The product was obtained as a colourless oil.



^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 5.65 – 5.48 (m, 2H), 4.19 (d, *J* = 6.0 Hz, 2H), 2.12 – 2.01 (m, 2H), 1.27 (d, *J* = 4.0 Hz, 16H), 0.92 – 0.84 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**, (ppm) δ 133.5, 128.4, 58.8, 32.0, 29.8 (3C), 29.6, 29.5, 29.4, 27.6, 22.8, 14.3.

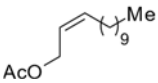
Analytical data for this compound are consistent with previously reported data.[13]

Cross-metathesis reaction of 1-dodecene and *(Z)*-1,4-diacetoxy-2-butene



2b **3b** **4bb**

The reaction was carried out following the general procedure using 1-dodecene (40.4 mg, 0.24 mmol, 53 µL, 1.2 equiv.) and *cis*-1,4-diacetoxy-2-butene (87 mg, 0.48 mmol, 81 µL, 2.4 equiv.). The product was obtained as a colourless oil.

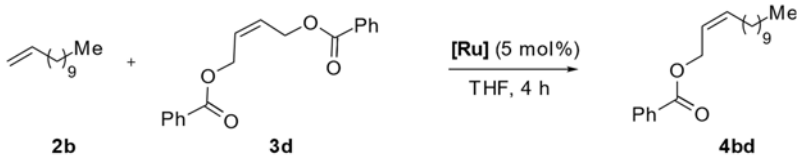


^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 5.69 – 5.60 (m, 1H), 5.56 – 5.48 (m, 1H), 4.62 (d, *J* = 8.2 Hz, 2H), 2.06 (s, 3H), 1.26 (s, 18H), 0.91 – 0.84 (m,

3H). **^{13}C NMR (101 MHz, $CDCl_3$)**, (ppm) δ 171.2, 135.7, 123.3, 60.6, 32.0, 29.8 (2C), 29.6, 29.6, 29.5, 29.3, 27.7, 22.8, 21.12, 14.2.

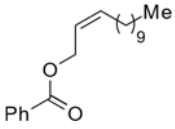
Analytical data for this compound are consistent with previously reported data.[14]

Cross-metathesis reaction of 1-dodecene and (*Z*)-but-2-ene-1,4-diyl dibenzoate



2b **3d** **4bd**

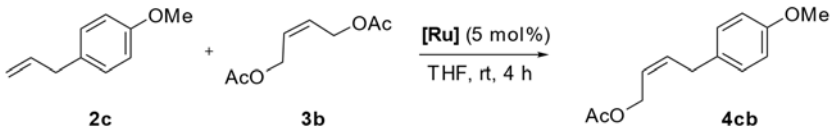
The reaction was carried out following the general procedure using 1-dodecene (40.4 mg, 0.24 mmol, 53 µL, 1.2 equiv.) and *cis*-but-2-ene-1,4-diyl dibenzoate (142 mg, 0.48 mmol, 2.4 equiv.). The product was obtained as a colourless oil.



^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 8.09 – 8.02 (m, 2H), 7.59 – 7.51 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.75 – 5.62 (m, 2H), 4.87 (d, *J* = 5.7 Hz, 2H), 2.17 (q, *J* = 6.4 Hz, 2H), 1.43 – 1.19 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**, (ppm) δ 166.6, 135.8, 132.9, 130.3, 129.6, 128.3, 123.2, 60.9, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 27.6, 22.7, 14.1.

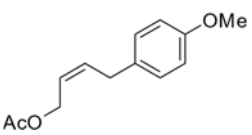
Analytical data for this compound are consistent with previously reported data.[15]

Cross-metathesis reaction of allylanisole and *(Z)*-1,4-diacetoxy-2-butene



2c **3b** **4cb**

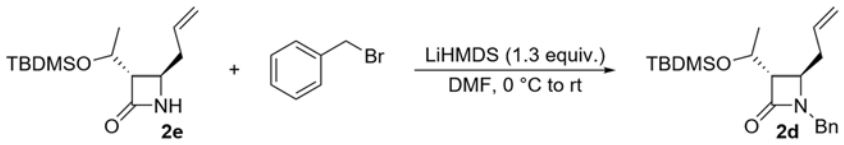
The reaction was carried out following the general procedure using 1-dodecene allylanisole (36.3 mg, 0.24 mmol, 37 µL, 1.2 equiv.) and *cis*-1,4-diacetoxy-2-butene (87 mg, 0.48 mmol, 81 µL, 2.4 equiv.). The product was obtained as a colourless oil.



^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.84 – 5.74 (m, 1H), 5.68 – 5.58 (m, 1H), 4.72 (d, *J* = 6.9 Hz, 2H), 3.77 (s, 3H), 3.40 (d, *J* = 7.5 Hz, 2H), 2.07 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**, (ppm) δ 171.0, 158.0, 133.9, 131.8, 129.3, 123.9, 114.0, 60.2, 55.3, 32.9, 21.0.

Analytical data for this compound are consistent with previously reported data.[16]

Synthesis of (3*S*,4*R*)-4-allyl-1-benzyl-3-((*S*)-1-((tert-butyldimethylsilyl)oxy)ethyl)azetidine-2-one



2e (0.6 g, 2.23 mmol. 1.0 equiv.) was dissolved in DMF (10 ml) in a round-bottom flask, then, LiHMDS (0.5 g, 2.89 mmol, 1.3 equiv.) was added at 0 °C and a clear solution was formed after stirring for 30 minutes. Benzyl bromide (0.571 g, 3.34 mmol, 1.5 equiv.) was added dropwise, then stirred at room temperature for 2 h, quenched with water (15 mL), extracted with methyl *tert*-butyl ether (3×10 mL) and the organic phase was collected. The organic phase was dried over anhydrous sodium sulphate, filtered and the filtrate was concentrated under vacuum to obtain crude product. The crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 20% EtOAc/*n*-hexane) to give **2d** as a colourless oil in 61% (0.489 g, 1.36 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ 7.36 – 7.25 (m, 5H), 5.69 – 5.59 (m, 1H), 5.08 – 5.03 (m, 2H), 4.55 (d, *J* = 16 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.63 – 3.59 (m, 1H), 2.82 (ddd, *J* = 8 Hz, 4 Hz, 2 Hz, 1H), 2.39 – 2.16 (m, 2H), 1.17 (d, *J* = 8 Hz, 3H), 0.84 (s, 9H), 0.04 (d, *J* = 12 Hz, 6H).

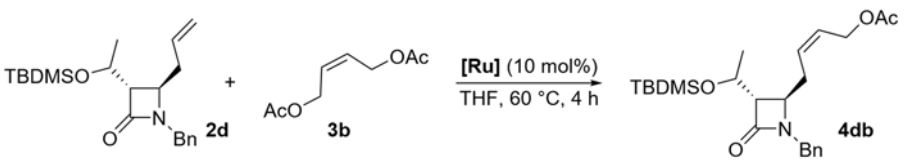
^{13}C NMR (101 MHz, $CDCl_3$) (ppm) δ 167.8, 136.1, 133.4, 128.7, 128.2, 127.5, 118.3, 65.5, 62.5, 53.5, 44.5, 37.1, 25.8, 22.9, 18.0, -4.6, -4.7.

HRMS (ESI) *m/z* Calcd. for $C_{21}H_{33}NO_2Si$: 382.2178; Found: 382.2180.

ATR-IR (cm^{-1}): 3066, 3031, 2954, 2928, 2896, 2856, 1748, 1642, 1496, 1472, 1456, 1434, 1402, 1372, 1366, 1360, 1252, 1144, 1111, 1095, 1067, 1053, 988, 955, 917, 834, 817, 809, 776, 756, 722, 698, 685, 664, 459.

Elemental analysis calcd. for $C_{21}H_{33}NO_2Si$: C, 70.15; H, 9.25; N, 3.90. Found: C, 70.29; H, 9.28; N, 3.79.

Cross-metathesis reaction of (*3S*,4*R*)-4-allyl-1-benzyl-3-((*S*)-1-((*tert*-butyldimethylsilyl)-oxy)ethyl)azetidin-2-one with *(Z)*-1,4-diacetoxy-2-butene



In a 4 mL vial, **2d** (0.20 mmol, 72 mg, 1.0 equiv.), *cis*-1,4-diacetoxy-2-butene (109 mg, 0.60 mmol, 100 µL, 3.0 equiv.) were mixed in dry THF (1.0 mL) in a glovebox. Then, 10 mol% of a corresponding catalyst (**Ru4** or **Ru14b**) was added in one portion. The resulting mixture was stirred at 60 °C for 4 h. When the reaction was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from DCM to 2% MeOH/DCM). The product was obtained as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major) δ 7.38 – 7.26 (m, 5H), 5.67 – 5.46 (m, 2H), 4.59 – 4.47 (m, 3H), 4.23 – 4.11 (m, 2H), 3.63 – 3.56 (m, 1H), 2.81 (dd, *J* = 5.0, 2.2 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.28 – 2.14 (m, 1H), 2.03 (s, 3H), 1.18 (d, *J* = 6.3 Hz, 3H), 0.88 – 0.81 (s, 9H), 0.04 (d, *J* = 15.0 Hz, 6H).

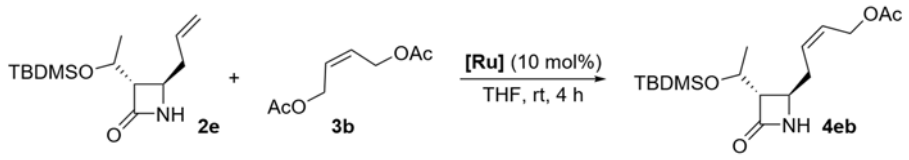
^{13}C NMR (101 MHz, $CDCl_3$), (ppm) δ 170.7, 167.6, 135.9, 129.4, 128.7, 128.3, 127.6, 126.4, 65.4, 62.7, 59.8, 53.4, 30.5, 25.8, 22.9, 20.9, 17.9, -4.6, -4.7.

HRMS (ESI) *m/z* Calcd. for $C_{24}H_{37}NO_4Si$: 454.2390; Found: 454.2388.

ATR-IR (cm^{-1}): 3447, 2939, 1716, 1603, 1531, 1508, 1486, 1465, 1418, 1398, 1381, 1265, 1227, 1198, 1148, 1121, 1065, 1032, 973, 850, 797, 748, 605, 428.

Elemental analysis calcd. for $C_{24}H_{37}NO_4Si$: C, 66.78; H, 8.64; N, 3.24. Found: C, 66.76; H, 8.61; N, 3.42.

Cross-metathesis reaction of (3*S*,4*R*)-3-[(1*R*)-1-(*tert*-butyldimethylsilyloxy)ethyl]-4-(prop-2-enyl)-2-azetidinone and *(Z)*-1,4-diacetoxy-2-butene



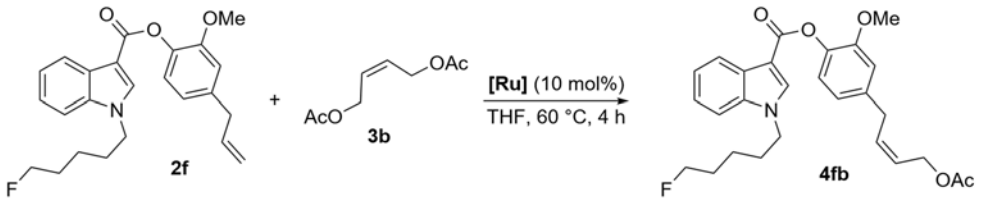
In a 4 mL vial, **2e** (0.20 mmol, 53.9 mg, 1.0 equiv.), *cis*-1,4-diacetoxy-2-butene (109 mg, 0.60 mmol, 101 µL, 3.0 equiv.) were mixed in dry THF (1.0 mL) in a glovebox. Then, 10 mol% of a corresponding catalyst (**Ru4**, **Ru6** or **Ru14b**) was added in one portion. The resulting mixture was stirred at room temperature or at 60 °C for 4 h. When the reaction was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from DCM to 5% MeOH/DCM). The product was obtained as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 6.03 (s, 1H), 5.66 (q, *J* = 6.7 Hz, 2H), 4.61 (d, *J* = 5.7 Hz, 2H), 4.16 (p, *J* = 6.2 Hz, 1H), 3.72 – 3.65 (m, 1H), 2.80 (dd, *J* = 5.0, 2.3 Hz, 1H), 2.46 (qt, *J* = 13.7, 6.5 Hz, 2H), 2.05 (s, 3H), 1.20 (d, *J* = 6.3 Hz, 3H), 0.86 (s, 9H), 0.06 (d, *J* = 2.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$), (ppm) δ 170.9, 168.3, 129.6, 126.7, 65.4, 63.8, 60.0, 50.1, 32.9, 25.7, 22.7, 21.0, 17.9, -4.2, -5.0.

Analytical data for this compound are consistent with previously reported data.[25]

Cross-metathesis reaction of 4-allyl-2-methoxyphenyl-1-(fluoromethyl)-1*H*-indole-3-carboxylate and *(Z)*-1,4-diacetoxy-2-butene



In a 4 mL vial, **2f** (0.20 mmol, 75 mg 1.0 equiv.), *cis*-1,4-diacetoxy-2-butene (109 mg, 0.60 mmol, 100 µL, 3.0 equiv.) were mixed in dry THF (1.0 mL) in a glovebox. Then, 10 mol% of a corresponding catalyst (**Ru4** or **Ru14b**) was added in one portion. The resulting mixture was stirred at 60 ℃ for 4 h. When the reaction was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from *n*-hexane to 30% EtOAc/*n*-hexane). The product was obtained as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major) δ 8.30 – 8.21 (m, 1H), 8.00 (s, 1H), 7.43 – 7.36 (m, 1H), 7.36 – 7.22 (m, 2H), 7.11 (d, J = 8.0 Hz, 1H), 6.87 – 6.78 (m, 2H), 5.92 – 5.80 (m, 1H), 5.76 – 5.63 (m, 1H), 4.75 (dd, J = 6.8, 1.4 Hz, 2H), 4.50 (t, J = 5.9 Hz, 1H), 4.38 (t, J = 5.9 Hz, 1H), 4.20 (t, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.49 (d, J = 7.5 Hz, 2H), 2.09 (s, 3H), 1.96 (p, J = 7.5 Hz, 2H), 1.82 – 1.65 (m, 2H), 1.56 – 1.43 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), (ppm) δ 171.0, 162.8, 151.6, 138.3, 138.3, 136.6, 135.1, 133.3, 127.1, 124.4, 123.3, 122.9, 122.1, 122.0, 120.5, 112.7, 110.0, 106.1, 84.5, 82.8, 60.2, 56.0, 56.0, 47.0, 33.7, 30.0, 29.9, 29.6, 22.9, 22.8, 21.0.

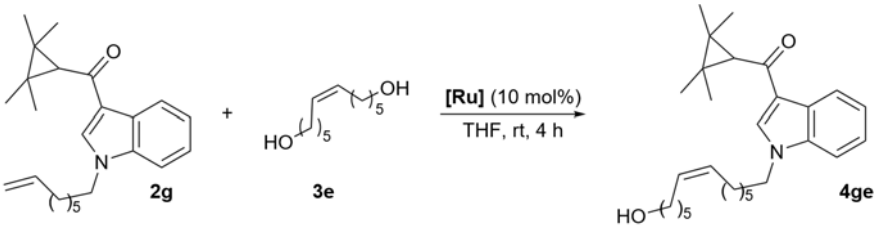
^{19}F NMR (376 MHz, $CDCl_3$), δ -218.57 (tt, *J* = 47.2, 25.8 Hz).

HRMS (ESI) *m/z* Calcd. for $C_{27}H_{30}FNO_5$: 490.2006; Found: 490.2007.

ATR-IR (cm^{-1}): 2939, 1716, 1604, 1532, 1508, 1486, 1465, 1418, 1399, 1381, 1266, 1256, 1227, 1213, 1198, 1180, 1165, 1158, 1148, 1121, 1095, 1065, 1033, 975, 910, 849, 796, 748, 741,

730, 647, 605, 429.

Cross-metathesis reaction of (1-(oct-7-en-1-yl)-1*H*-indol-3-yl)(2,2,3,3-tetramethyl-cyclopropyl)methanone with *(Z)*-dodec-6-ene-1,12-diol



2g 3e 4ge

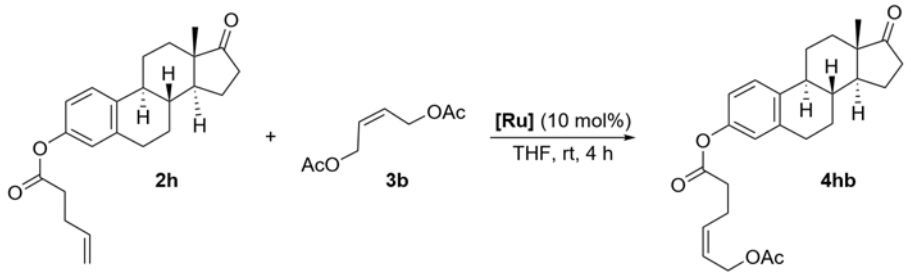
In a 4 mL vial, **2g** (0.20 mmol, 70.3 mg, 1.0 equiv.) with *cis*-dodec-6-ene-1,12-diol (120 mg, 0.60 mmol, 101 µL, 3.0 equiv.) were mixed in dry THF (1.0 mL) in a glovebox. Then, 10 mol% of a corresponding catalyst (**Ru6 or Ru14b**) was added in one portion. The resulting mixture was stirred for 4 h at room temperature. When the reaction was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from hexane to 50% EtOAc/*n*-hexane). The product was obtained as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major) δ 8.43 – 8.36 (m, 1H), 7.66 (s, 1H), 7.37 – 7.31 (m, 1H), 7.31 – 7.22 (m, 2H), 5.40 – 5.27 (m, 2H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.08 – 1.93 (m, 5H), 1.92 – 1.83 (m, 2H), 1.61 – 1.51 (m, 2H), 1.33 (d, *J* = 16.7 Hz, 23H).

^{13}C NMR (101 MHz, $CDCl_3$), (ppm) δ 194.7, 136.6, 133.5, 130.4, 130.2, 129.9, 129.6, 126.4, 122.8, 122.7, 122.1, 119.6, 109.6, 77.4, 77.0, 76.7, 63.0, 47.0, 41.6, 32.7, 32.6, 32.5, 32.4, 31.6, 29.9, 29.5, 29.4, 29.3, 28.8, 28.6, 27.1, 27.0, 26.8, 25.4, 25.2, 24.1, 17.0.

Analytical data for this compound are consistent with previously reported data.[25]

Cross-metathesis reaction of *O*-(4-pentenoyl)estrone with *(Z)*-1,4-diacetoxy-2-butene



2h 3b 4hb

In a 4 mL vial, **2h** (0.20 mmol, 70.5 mg, 1.0 equiv.), *cis*-1,4-diacetoxy-2-butene (109 mg, 0.60 mmol, 101 µL, 3.0 equiv.) were mixed in dry THF (1.0 mL) in a glovebox. Then, 10 mol% of a corresponding catalyst (**Ru4**, **Ru6** or **Ru14b**) was added in one portion. The resulting mixture

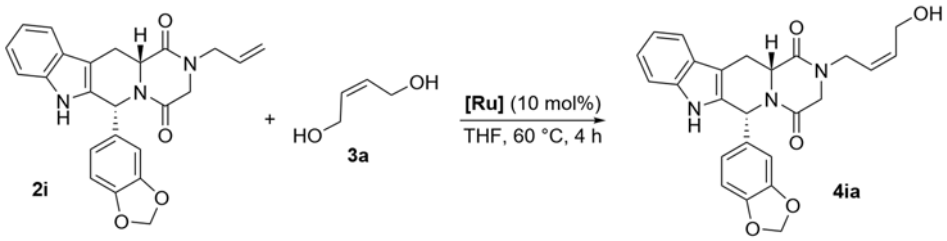
was stirred at room temperature or 60 ℃ for 4 h. When the reaction was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from hexane to 40% EtOAc/*n*-hexane). The product was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major) δ 7.28 (d, J = 8.6 Hz, 1H), 6.84 (dd, J = 8.4, 2.7 Hz, 1H), 6.81 – 6.78 (m, 1H), 5.74 – 5.59 (m, 2H), 4.67 (d, J = 6.3 Hz, 2H), 2.94 – 2.85 (m, 2H), 2.68 – 2.59 (m, 2H), 2.59 – 2.53 (m, 2H), 2.52 – 2.45 (m, 1H), 2.44 – 2.37 (m, 1H), 2.33 – 2.24 (m, 1H), 2.21 – 1.92 (m, 7H), 1.69 – 1.37 (m, 6H), 0.91 (s, 3H).

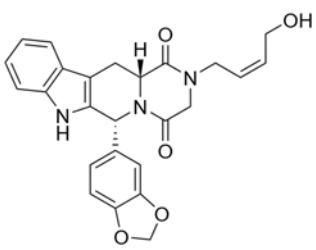
^{13}C NMR (101 MHz, $CDCl_3$), (ppm) δ 220.8, 171.5, 148.5, 138.0, 137.4, 132.4, 126.4, 125.3, 121.5, 118.7, 60.2, 50.4, 47.9, 44.1, 38.0, 35.9, 33.9, 31.5, 29.4, 26.3, 25.7, 23.0, 21.6, 21.0, 13.8.

Analytical data for this compound are consistent with previously reported data.[17]

Cross-metathesis reaction of Cialis derivative 2f and *(Z)*-2-butene-1,4-diol



In a 4 mL vial, Cialis derivative **2i** (0.20 mmol, 83 mg, 1.0 equiv.), *cis*-2-butene-1,4-diol (56 mg, 0.60 mmol, 53 µL, 3.0 equiv.) were mixed in dry THF (1.0 mL) in a glovebox. Then, 10 mol% of a corresponding catalyst (**Ru4** or **Ru14b**) was added in one portion. The resulting mixture was stirred at 60 ℃ for 4 h. When the reaction was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from DCM to 2% MeOH/DCM). The product was obtained as a colourless oil.



^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): 7.85 (s, 1H), 7.60 (d, *J* = 7.0 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.22 – 7.12 (m, 2H), 6.89 – 6.81 (m, 1H), 6.76 – 6.65 (m, 2H), 6.15 (s, 1H), 6.01 – 5.92 (m, 1H), 5.91 – 5.83 (m, 2H), 5.60 – 5.49 (m, 1H), 4.43 – 4.20 (m, 4H), 4.18 – 4.08 (m, 1H), 4.04 – 3.93 (m, 2H), 3.80 – 3.71 (m, 1H), 3.29 – 3.13 (m, 1H).

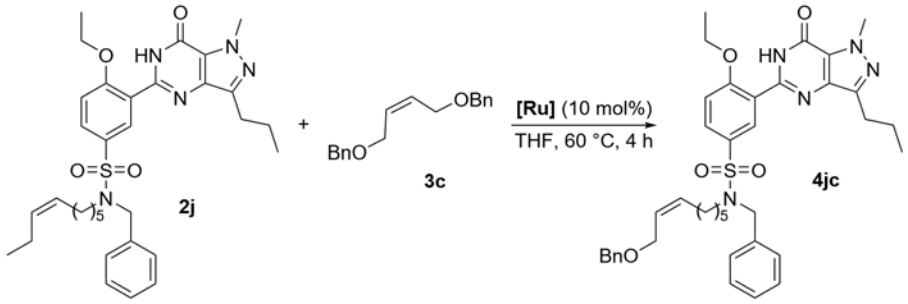
^{13}C NMR (101 MHz, $CDCl_3$), (ppm) δ 166.8, 166.5, 147.9, 147.2, 136.5, 135.2, 134.1, 132.7,

126.2, 124.2, 122.6, 120.8, 120.2, 118.6, 111.2, 108.3, 107.4, 106.5, 101.2, 58.1, 56.7, 56.3, 50.3, 43.4, 23.7.

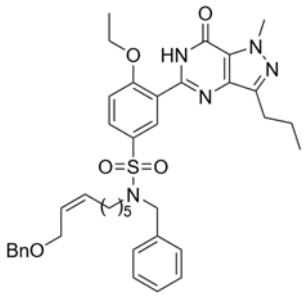
ATR-IR (cm^{-1}): 3466, 3322, 2894, 1651, 1625, 1500, 1487, 1438, 1428, 1326, 1310, 1280, 1238, 1196, 1148, 1121, 1093, 1025, 916, 832, 789, 745, 692, 595, 545, 475.

HRMS (ESI) *m/z* Calcd. For $C_{25}H_{23}N_3O_5$: 468.1535; Found: 468.1532.

Cross-metathesis reaction of (6*R*,12a*R*)-2-allyl-6-(benzo[*d*][1,3]dioxol-5-yl)-2,3,6,7,12,12a-hexahydropyrazino[1',2':1,6]pyrido[3,4-*b*]indole-1,4-dione and *(Z)*-1,4-bis(benzyloxy)but-2-ene



In a 4 mL vial, **2j** (0.20 mmol, 121 mg, 1.0 equiv.), *cis*-1,4-bis(benzyloxy)but-2-ene (0.60 mmol, 161 mg, 3.0 equiv.) were mixed in dry THF (1.0 mL) in a glovebox. Then, 10 mol% of a corresponding catalyst (**Ru4** or **Ru14b**) was added in one portion. The resulting mixture was stirred for at 60 ℃ for 4 h. When the reaction was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from hexane to 40% EtOAc/*n*-hexane). The product was obtained as a colourless oil.



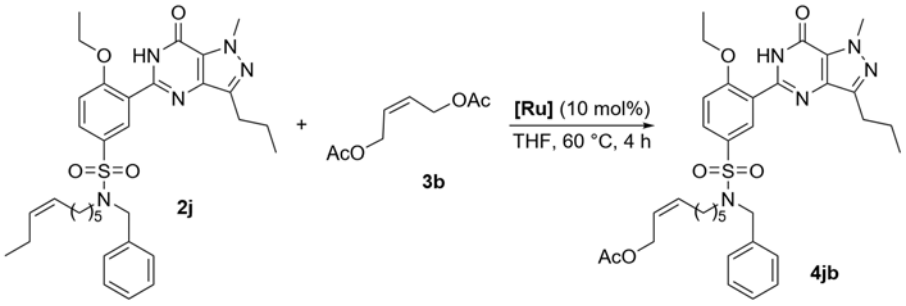
^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major): δ 10.87 (s, 1H), 8.90 (d, *J* = 2.4 Hz, 1H), 7.90 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.36 – 7.21 (m, 10H), 7.12 (d, *J* = 8.9 Hz, 1H), 5.59 – 5.41 (m, 2H), 4.47 (s, 2H), 4.40 – 4.33 (m, 4H), 4.27 (s, 3H), 3.99 (d, *J* = 6.5 Hz, 2H), 3.18 – 3.09 (m, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.93 – 1.80 (m, 4H), 1.63 (t, *J* = 7.0 Hz, 3H), 1.43 – 1.32 (m, 2H), 1.23 – 1.06 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), (ppm) δ 158.9, 153.6, 146.9, 146.6, 138.4, 138.3, 136.3, 133.5, 133.3, 131.1, 130.4, 128.4, 128.3, 127.8, 127.6, 126.2, 124.5, 121.0, 113.0, 72.1, 66.0, 65.6, 52.1, 48.3, 38.2, 28.9, 28.0, 27.8, 27.3, 26.2, 22.3, 14.6, 14.1.

ATR-IR (cm^{-1}): 3317, 2931, 2858, 1695, 1625, 1599, 1592, 1583, 1570, 1560, 1546, 1535, 1514, 1490, 1477, 1455, 1423, 1393, 1373, 1338, 1288, 1276, 1261, 1246, 1193, 1152, 1134, 1100, 1053, 1024, 957, 929, 853, 814, 801, 734, 709, 697, 661, 652, 634, 607, 598, 586, 442.

HRMS (ESI) *m/z* Calcd. For $C_{39}H_{47}N_5O_5S$: 698.3376; Found: 698.3367.

Cross-metathesis reaction of (6*R*,12a*R*)-2-allyl-6-(benzo[*d*][1,3]dioxol-5-yl)-2,3,6,7,12,12a-hexahydropyrazino[1',2':1,6]pyrido[3,4-*b*]indole-1,4-dione with *(Z)*-1,4-diacetoxy-2-butene



In a 4 mL vial, **2j** (0.20 mmol, 121 mg, 1.0 equiv.), *cis*-1,4-diacetoxy-2-butene (109 mg, 0.60 mmol, 101 µL, 3.0 equiv.) were mixed in dry THF (1.0 mL) in a glovebox. Then, 10 mol% of a corresponding catalyst (**Ru6** or **Ru14b**) was added in one portion. The resulting mixture was stirred at room temperature for **Ru6** and at 60 ℃ for **Ru14b** for 4 h. When the reaction was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO_2, eluent: from hexane to 40% EtOAc/*n*-hexane). The product was obtained as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$), (ppm) *Z*-isomer (major) δ 10.86 (s, 1H), 8.93 – 8.84 (m, 1H), 7.93 – 7.85 (m, 1H), 7.30 (d, *J* = 4.2 Hz, 4H), 7.13 (d, *J* = 8.7 Hz, 1H), 5.55 – 5.40 (m, 2H), 4.52 (d, *J* = 6.1 Hz, 2H), 4.40 – 4.32 (m, 4H), 4.26 (s, 3H), 3.14 (t, *J* = 7.7 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.03 (s, 3H), 1.94 (q, *J* = 6.8 Hz, 2H), 1.85 (h, *J* = 7.7 Hz, 2H), 1.66 – 1.60 (m, 3H), 1.38 (h, *J* = 6.7 Hz, 2H), 1.27 – 1.09 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), (ppm) δ 170.9, 159.0, 153.6, 146.9, 146.6, 138.4, 136.3, 134.7, 133.5, 131.11, 130.4, 128.6, 128.3, 127.8, 124.5, 123.6, 121.0, 113.0, 66.0, 60.4, 60.2, 52.1, 48.2, 38.2, 28.8, 27.9, 27.7, 27.2, 26.2, 22.3, 21.0, 14.5, 14.0.

Analytical data for this compound are consistent with previously reported data.[25]

8. Crystallographic information

X-ray data collection and refinement of data

Good quality single-crystal of investigated compound was selected for the X-ray diffraction experiments at T = 100(2) K. Diffraction data were collected on the Agilent Technologies SuperNova Dual Source diffractometer with CuKα radiation (λ = 1.54184 Å) using CrysAlis RED software.[26] The analytical numerical absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid[27] implemented in SCALE3 ABSPACK scaling algorithm, was applied.[26] The structural determination procedure was carried out using the SHELX package.[28] The structures were solved with direct methods and then successive least-square refinement was carried out based on the full-matrix least-squares method on F2 using the SHELXL program.[28] The figures for this publication were prepared using Olex2 program.[29]

Table S5. Summary of XRD analysis of **Ru14b.**

Crystal data	
CCDC deposition number	**2362612**
Identification code	**Ru14b**
Chemical formula	$C_{41}H_{40}Cl_2N_2ORuS_2$
Formula weight	812.84
Crystal system,	Orthorhombic
Space group	*Pbca*
Temperature /K	100(2)
a, *b*, *c* /Å	8.31031 (8), 20.0084 (2), 44.3627 (5)
α/°	90
β/°	90
γ/°	90
*V*olume/Å^3	7376.46 (13)
Z	8
Z′	1
Wavelength/Å	1.54184
Radiation type	Cu K_α
μ (mm^{-1})	6.10
Crystal size (mm)	0.12 × 0.11 × 0.06

Data collection	
Diffractometer	SuperNova, Dual, Cu at home/near, HyPix
Absorption correction	Analytical *CrysAlis PRO* 1.171.42.70a (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.634, 0.790
No. of measured, independent and observed [$I > 2s(I)$] reflections	24189, 6513, 5583
R_{int}	0.043
$(\sin q/l)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.034, 0.090, 1.02
No. of reflections	6513
No. of parameters	448
H-atom treatment	H-atom parameters constrained
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	1.16, -0.55

Table S6: Bond Lengths for **Ru14b.**

Ru1—S1	2.2819 (7)	C19—H19C	0.9800
Ru1—S2	2.2754 (7)	C20—H20A	0.9800
O1—Ru1	2.253 (2)	C20—H20B	0.9800
C1—Ru1	2.052 (3)	C20—H20C	0.9800
C1—N1	1.354 (4)	C21—H21A	0.9800
C1—N2	1.343 (4)	C21—H21B	0.9800
C2—N2	1.477 (4)	C21—H21C	0.9800
C2—H2A	0.9900	C22—Ru1	1.838 (3)
C2—H2B	0.9900	C22—H22	0.9500
C2—C3	1.518 (4)	C22—C23	1.459 (4)
C3—N1	1.482 (4)	C23—C24	1.399 (4)
C3—H3A	0.9900	C23—C28	1.403 (4)
C3—H3B	0.9900	C24—H24	0.9500
C4—N1	1.431 (4)	C24—C25	1.385 (5)
C4—C5	1.401 (4)	C25—H25	0.9500
C4—C9	1.398 (4)	C25—C26	1.398 (5)
C5—C6	1.397 (4)	C26—H26	0.9500
C5—C10	1.502 (4)	C26—C27	1.398 (5)
C6—H6	0.9500	C27—H27	0.9500
C6—C7	1.390 (5)	C27—C28	1.383 (4)
C7—C8	1.394 (5)	C28—O1	1.388 (4)
C7—C11	1.508 (4)	C29—O1	1.452 (3)
C8—H8	0.9500	C29—H29A	0.9900
C8—C9	1.387 (4)	C29—H29B	0.9900
C9—C12	1.508 (5)	C29—C30	1.512 (4)
C10—H10A	0.9800	C30—C31	1.385 (4)
C10—H10B	0.9800	C30—C35	1.392 (4)
C10—H10C	0.9800	C31—H31	0.9500
C11—H11A	0.9800	C31—C32	1.391 (5)
C11—H11B	0.9800	C32—H32	0.9500
C11—H11C	0.9800	C32—C33	1.390 (5)
C12—H12A	0.9800	C33—H33	0.9500

C12—H12B	0.9800	C33—C34	1.372 (5)
C12—H12C	0.9800	C34—H34	0.9500
C13—N2	1.435 (4)	C34—C35	1.392 (5)
C13—C14	1.398 (4)	C35—H35	0.9500
C13—C18	1.397 (5)	C36—S1	1.762 (3)
C14—C15	1.397 (4)	C36—C37	1.404 (4)
C14—C19	1.498 (4)	C36—C41	1.399 (4)
C15—H15	0.9500	C37—Cl1	1.743 (3)
C15—C16	1.400 (5)	C37—C38	1.377 (5)
C16—C17	1.387 (5)	C38—H38	0.9500
C16—C20	1.509 (4)	C38—C39	1.383 (5)
C17—H17	0.9500	C39—H39	0.9500
C17—C18	1.382 (5)	C39—C40	1.385 (5)
C18—C21	1.515 (4)	C40—Cl2	1.747 (3)
C19—H19A	0.9800	C40—C41	1.404 (4)
C19—H19B	0.9800	C41—S2	1.759 (3)

Table S7: Values of valence angles for **Ru14b**.

S2—Ru1—S1	88.17 (3)	C18—C17—H17	119.0
O1—Ru1—S1	88.06 (5)	C13—C18—C21	121.2 (3)
O1—Ru1—S2	167.67 (6)	C17—C18—C13	118.5 (3)
C1—Ru1—S1	139.23 (8)	C17—C18—C21	120.3 (3)
C1—Ru1—S2	88.00 (8)	C14—C19—H19A	109.5
C1—Ru1—O1	102.46 (9)	C14—C19—H19B	109.5
C22—Ru1—S1	119.56 (9)	C14—C19—H19C	109.5
C22—Ru1—S2	92.94 (9)	H19A—C19—H19B	109.5
C22—Ru1—O1	78.76 (10)	H19A—C19—H19C	109.5
C22—Ru1—C1	101.17 (12)	H19B—C19—H19C	109.5
C36—S1—Ru1	105.69 (11)	C16—C20—H20A	109.5
C41—S2—Ru1	105.50 (11)	C16—C20—H20B	109.5
C28—O1—Ru1	111.33 (17)	C16—C20—H20C	109.5
C28—O1—C29	119.1 (2)	H20A—C20—H20B	109.5
C29—O1—Ru1	128.74 (17)	H20A—C20—H20C	109.5
C1—N1—C3	111.5 (2)	H20B—C20—H20C	109.5
C1—N1—C4	126.1 (2)	C18—C21—H21A	109.5
C4—N1—C3	119.6 (2)	C18—C21—H21B	109.5
C1—N2—C2	112.7 (2)	C18—C21—H21C	109.5
C1—N2—C13	125.2 (2)	H21A—C21—H21B	109.5
C13—N2—C2	121.9 (2)	H21A—C21—H21C	109.5
N1—C1—Ru1	131.4 (2)	H21B—C21—H21C	109.5
N2—C1—Ru1	119.7 (2)	Ru1—C22—H22	120.2
N2—C1—N1	107.8 (3)	C23—C22—Ru1	119.5 (2)
N2—C2—H2A	111.5	C23—C22—H22	120.2
N2—C2—H2B	111.5	C24—C23—C22	124.1 (3)
N2—C2—C3	101.4 (2)	C24—C23—C28	117.9 (3)
H2A—C2—H2B	109.3	C28—C23—C22	118.0 (3)
C3—C2—H2A	111.5	C23—C24—H24	119.6
C3—C2—H2B	111.5	C25—C24—C23	120.8 (3)
N1—C3—C2	102.0 (2)	C25—C24—H24	119.6
N1—C3—H3A	111.4	C24—C25—H25	120.1
N1—C3—H3B	111.4	C24—C25—C26	119.8 (3)
C2—C3—H3A	111.4	C26—C25—H25	120.1
C2—C3—H3B	111.4	C25—C26—H26	119.6
H3A—C3—H3B	109.2	C25—C26—C27	120.9 (3)
C5—C4—N1	119.3 (3)	C27—C26—H26	119.6
C9—C4—N1	119.2 (3)	C26—C27—H27	121.0
C9—C4—C5	121.4 (3)	C28—C27—C26	118.0 (3)
C4—C5—C10	122.0 (3)	C28—C27—H27	121.0

C6—C5—C4	118.0 (3)	O1—C28—C23	112.3 (3)
C6—C5—C10	120.0 (3)	C27—C28—O1	125.0 (3)
C5—C6—H6	119.1	C27—C28—C23	122.6 (3)
C7—C6—C5	121.7 (3)	O1—C29—H29A	108.4
C7—C6—H6	119.1	O1—C29—H29B	108.4
C6—C7—C8	118.6 (3)	O1—C29—C30	115.3 (2)
C6—C7—C11	120.6 (3)	H29A—C29—H29B	107.5
C8—C7—C11	120.8 (3)	C30—C29—H29A	108.4
C7—C8—H8	119.2	C30—C29—H29B	108.4
C9—C8—C7	121.6 (3)	C31—C30—C29	122.5 (3)
C9—C8—H8	119.2	C31—C30—C35	119.3 (3)
C4—C9—C12	121.2 (3)	C35—C30—C29	118.0 (3)
C8—C9—C4	118.5 (3)	C30—C31—H31	120.0
C8—C9—C12	120.3 (3)	C30—C31—C32	119.9 (3)
C5—C10—H10A	109.5	C32—C31—H31	120.0
C5—C10—H10B	109.5	C31—C32—H32	119.8
C5—C10—H10C	109.5	C33—C32—C31	120.3 (3)
H10A—C10—H10B	109.5	C33—C32—H32	119.8
H10A—C10—H10C	109.5	C32—C33—H33	120.1
H10B—C10—H10C	109.5	C34—C33—C32	119.9 (3)
C7—C11—H11A	109.5	C34—C33—H33	120.1
C7—C11—H11B	109.5	C33—C34—H34	120.0
C7—C11—H11C	109.5	C33—C34—C35	120.0 (3)
H11A—C11—H11B	109.5	C35—C34—H34	120.0
H11A—C11—H11C	109.5	C30—C35—H35	119.8
H11B—C11—H11C	109.5	C34—C35—C30	120.5 (3)
C9—C12—H12A	109.5	C34—C35—H35	119.8
C9—C12—H12B	109.5	C37—C36—S1	121.9 (2)
C9—C12—H12C	109.5	C41—C36—S1	119.8 (2)
H12A—C12—H12B	109.5	C41—C36—C37	118.3 (3)
H12A—C12—H12C	109.5	C36—C37—Cl1	119.3 (3)
H12B—C12—H12C	109.5	C38—C37—Cl1	117.7 (3)
C14—C13—N2	120.6 (3)	C38—C37—C36	123.0 (3)
C18—C13—N2	117.5 (3)	C37—C38—H38	120.6
C18—C13—C14	121.8 (3)	C37—C38—C39	118.8 (3)
C13—C14—C19	122.1 (3)	C39—C38—H38	120.6
C15—C14—C13	117.3 (3)	C38—C39—H39	120.6
C15—C14—C19	120.6 (3)	C38—C39—C40	118.9 (3)
C14—C15—H15	119.0	C40—C39—H39	120.6
C14—C15—C16	122.1 (3)	C39—C40—Cl2	117.8 (2)
C16—C15—H15	119.0	C39—C40—C41	123.1 (3)
C15—C16—C20	121.0 (3)	C41—C40—Cl2	119.1 (2)

C17—C16—C15	118.1 (3)	C36—C41—S2	120.5 (2)
C17—C16—C20	120.9 (3)	C36—C41—C40	117.5 (3)
C16—C17—H17	119.0	C40—C41—S2	121.9 (2)
C18—C17—C16	122.0 (3)		

Table S8: Values of torsion angles for **Ru14b**.

Ru1—C1—N1—C3	−175.6 (2)	C14—C15—C16—C20	−178.6 (3)
Ru1—C1—N1—C4	23.8 (5)	C15—C16—C17—C18	2.3 (5)
Ru1—C1—N2—C2	162.4 (2)	C16—C17—C18—C13	0.3 (5)
Ru1—C1—N2—C13	−23.3 (4)	C16—C17—C18—C21	179.5 (3)
Ru1—C22—C23—C24	179.6 (2)	C18—C13—N2—C1	−93.9 (4)
Ru1—C22—C23—C28	2.1 (4)	C18—C13—N2—C2	79.8 (4)
Cl1—C37—C38—C39	−175.5 (2)	C18—C13—C14—C15	5.3 (4)
Cl2—C40—C41—S2	−0.3 (4)	C18—C13—C14—C19	−173.4 (3)
Cl2—C40—C41—C36	179.4 (2)	C19—C14—C15—C16	176.2 (3)
S1—C36—C37—Cl1	−9.0 (4)	C20—C16—C17—C18	179.7 (3)
S1—C36—C37—C38	173.1 (3)	C22—C23—C24—C25	−176.2 (3)
S1—C36—C41—S2	5.2 (3)	C22—C23—C28—O1	−2.6 (4)
S1—C36—C41—C40	−174.5 (2)	C22—C23—C28—C27	176.1 (3)
O1—C29—C30—C31	36.3 (4)	C23—C22—Ru1—S1	80.6 (2)
O1—C29—C30—C35	−147.4 (3)	C23—C22—Ru1—S2	170.2 (2)
N1—C1—N2—C2	−6.7 (3)	C23—C22—Ru1—O1	−0.6 (2)
N1—C1—N2—C13	167.5 (3)	C23—C22—Ru1—C1	−101.3 (2)
N1—C4—C5—C6	−179.2 (3)	C23—C24—C25—C26	−0.7 (5)
N1—C4—C5—C10	1.7 (4)	C23—C28—O1—Ru1	2.0 (3)
N1—C4—C9—C8	178.3 (3)	C23—C28—O1—C29	172.5 (2)
N1—C4—C9—C12	−3.4 (4)	C24—C23—C28—O1	179.7 (2)
N2—C1—N1—C3	−8.2 (4)	C24—C23—C28—C27	−1.6 (4)
N2—C1—N1—C4	−168.8 (3)	C24—C25—C26—C27	0.3 (5)
N2—C2—C3—N1	−20.3 (3)	C25—C26—C27—C28	−0.5 (5)
N2—C13—C14—C15	−177.5 (3)	C26—C27—C28—O1	179.8 (3)
N2—C13—C14—C19	3.8 (4)	C26—C27—C28—C23	1.2 (4)
N2—C13—C18—C17	178.4 (3)	C27—C28—O1—Ru1	−176.7 (2)
N2—C13—C18—C21	−0.7 (4)	C27—C28—O1—C29	−6.2 (4)
C2—C3—N1—C1	18.7 (4)	C28—C23—C24—C25	1.3 (4)
C2—C3—N1—C4	−179.3 (3)	C29—C30—C31—C32	175.3 (3)
C3—C2—N2—C1	17.8 (3)	C29—C30—C35—C34	−174.8 (3)
C3—C2—N2—C13	−156.6 (3)	C30—C29—O1—Ru1	−121.4 (2)
C4—C5—C6—C7	−0.2 (4)	C30—C29—O1—C28	70.0 (3)
C5—C4—N1—C1	68.7 (4)	C30—C31—C32—C33	−0.5 (5)
C5—C4—N1—C3	−90.5 (4)	C31—C30—C35—C34	1.7 (5)

C5—C4—C9—C8	−4.1 (4)	C31—C32—C33—C34	1.5 (5)
C5—C4—C9—C12	174.1 (3)	C32—C33—C34—C35	−0.9 (5)
C5—C6—C7—C8	−1.8 (5)	C33—C34—C35—C30	−0.7 (5)
C5—C6—C7—C11	−179.9 (3)	C35—C30—C31—C32	−1.1 (5)
C6—C7—C8—C9	1.0 (4)	C36—C37—C38—C39	2.4 (5)
C7—C8—C9—C4	1.9 (4)	C36—C41—S2—Ru1	−6.6 (3)
C7—C8—C9—C12	−176.3 (3)	C37—C36—S1—Ru1	179.5 (2)
C9—C4—N1—C1	−113.7 (3)	C37—C36—C41—S2	−175.1 (2)
C9—C4—N1—C3	87.1 (4)	C37—C36—C41—C40	5.2 (4)
C9—C4—C5—C6	3.3 (4)	C37—C38—C39—C40	2.9 (5)
C9—C4—C5—C10	−175.8 (3)	C38—C39—C40—Cl2	176.4 (2)
C10—C5—C6—C7	178.9 (3)	C38—C39—C40—C41	−4.1 (5)
C11—C7—C8—C9	179.1 (3)	C39—C40—C41—S2	−179.7 (2)
C13—C14—C15—C16	−2.5 (5)	C39—C40—C41—C36	0.0 (4)
C14—C13—N2—C1	88.8 (4)	C40—C41—S2—Ru1	173.1 (2)
C14—C13—N2—C2	−97.5 (3)	C41—C36—S1—Ru1	−0.9 (3)
C14—C13—C18—C17	−4.3 (4)	C41—C36—C37—Cl1	171.3 (2)
C14—C13—C18—C21	176.6 (3)	C41—C36—C37—C38	−6.6 (5)
C14—C15—C16—C17	−1.2 (5)		

9. Computational methods and results

Density functional theory (DFT) calculations were performed using the quantum-chemistry code Jaguar version 11.2[18] and similar two-step protocol used in our previous studies.[19] In the first step, calculations were performed using B3LYP-D3 functional[20] with the Gaussian 6-31G** basis set for all atoms apart from ruthenium, for which the small-core, quasi-relativistic effective core potential developed at Los Alamos National Laboratory together with an associated double ζ plus polarization basis set, was used (standard LACVP** keyword in the Jaguar code).[21] In the second step electronic energies were obtained from the single-point M06 calculations that included a triple ζ basis set plus polarization and diffuse functions, 6-311G++(d,p) (for Ru: standard LACV3P++** keyword in Jaguar).[22] The polarizable continuum model (PCM) was employed to account for solvent effects, with THF as the solvent.[23] Gibbs free energies were defined as the sum of electronic energy (from the single-point M06 calculations), solvation energy, thermal correction to enthalpy, zero-point energy correction, and the negative product of temperature and entropy at 298.15 K. In all cases, standard convergence criteria and an ultrafine grid for DFT calculations were used.

Table S9: Single-point PCM energy (E), zero-point energy (ZPE), entropy (S), correction to enthalpy (H) and Gibbs free energy (G) values for systems investigated in this study.

system	E (Ha)	ZPE (kcal/mol)	S (cal/mol)	H (kcal/mol)	G (Ha)
Ru4 active	-3428.6473	430.5	25.05	29.2	-3428.0339
Ru4 O_2 attack	-3578.9564	435.0	261.6	30.6	-3578.3387
Ru4 ts	-3578.9222	434.1	256.5	30.1	-3578.3043
Ru4 oxo	-3579.0852	435.6	262.8	30.9	-3578.4666
Ru6 active	-3664.3937	540.2	273.2	33.1	-3663.6099
Ru6 O_2 attack	-3814.6993	544.8	284.6	34.5	-3813.9113
Ru6 ts	-3814.6589	543.6	281.3	34.2	-3813.8718
Ru6 oxo	-3814.8363	545.9	284.1	34.7	-3814.0461
Ru10b active	-3543.1372	451.5	260.6	30.6	-3542.4926
Ru10b O_2 attack	-3693.4453	456.0	270.7	32.0	-3692.7963
Ru10b ts	-3693.4115	455.4	264.5	31.4	-3692.7615
Ru10b oxo	-3693.5765	456.4	269.4	31.9	-3692.9263
Ru12b active	-3617.1755	439.7	264.7	31.1	-3616.5509
Ru12b O_2 attack	-3767.4806	444.3	273.6	32.4	-3766.8508
Ru12b ts	-3767.4506	443.5	269.0	31.9	-3766.8209
Ru12b oxo	-3767.6129	445.1	274.3	32.6	-3766.9819
Ru14b active	-3580.9829	446.4	257.6	30.1	-3580.3458
Ru14b O_2 attack	-3731.2941	451.1	266.1	31.4	-3730.6516
Ru14b ts	-3731.2587	450.1	262.9	31.0	-3730.6168
Ru14b oxo	-3731.4228	452.0	268.1	31.7	-3730.7793
Hov-II active	-2402.5806	392.3	223.3	25.1	-2402.0216
Hov-II O_2 attack	-2552.8713	396.6	231.3	26.4	-2552.3071
Hov-II oxo	-2552.9927	397.1	236.9	26.9	-2552.4295
O_2	-150.2917	2.4	49.0	2.1	-150.3079
Ru4 et attack	-3507.2077	465.5	255.8	30.3	-3506.5390
Hov-II et attack	-2481.1462	426.3	234.4	26.8	-2480.5355
et	-78.5404	32.1	55.1	2.5	-78.5115

10. Copies of NMR spectra

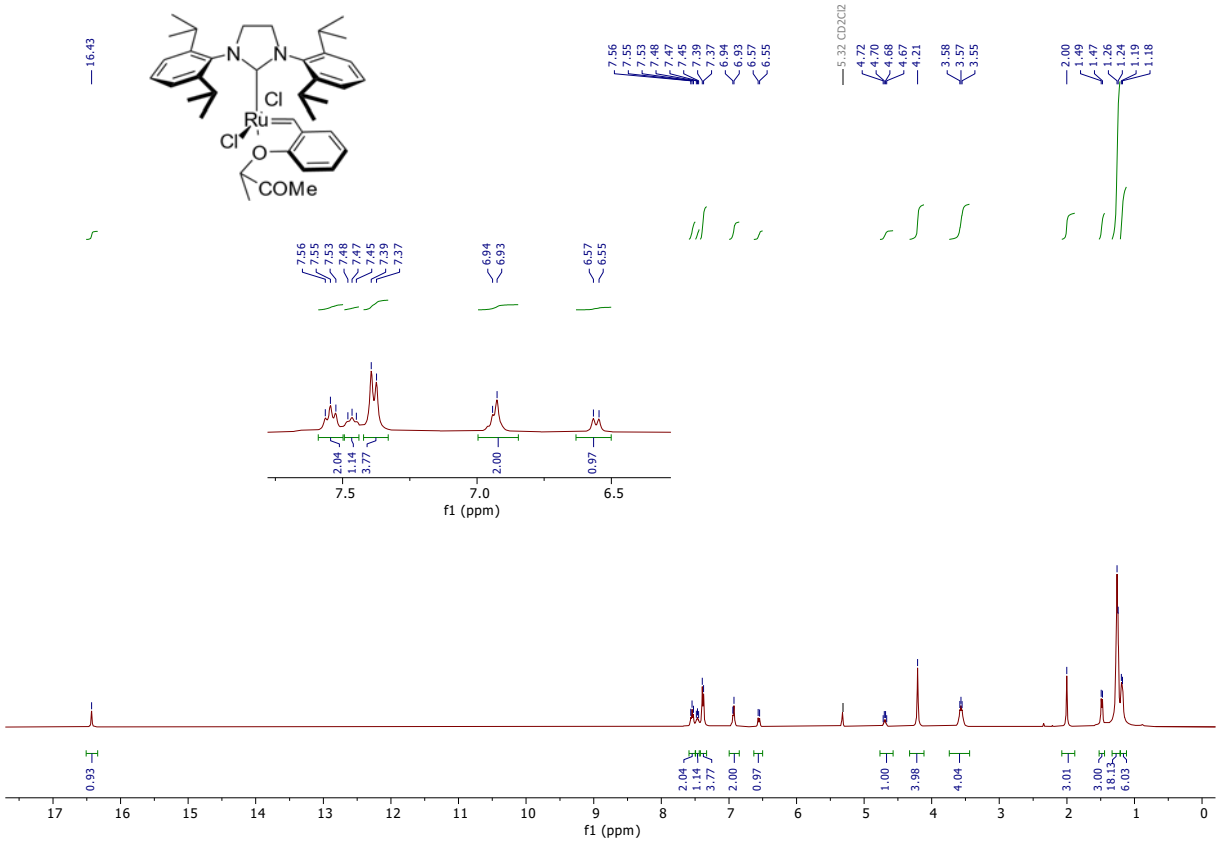


Figure S11. ^{1}H NMR spectrum for **Ru11a.**

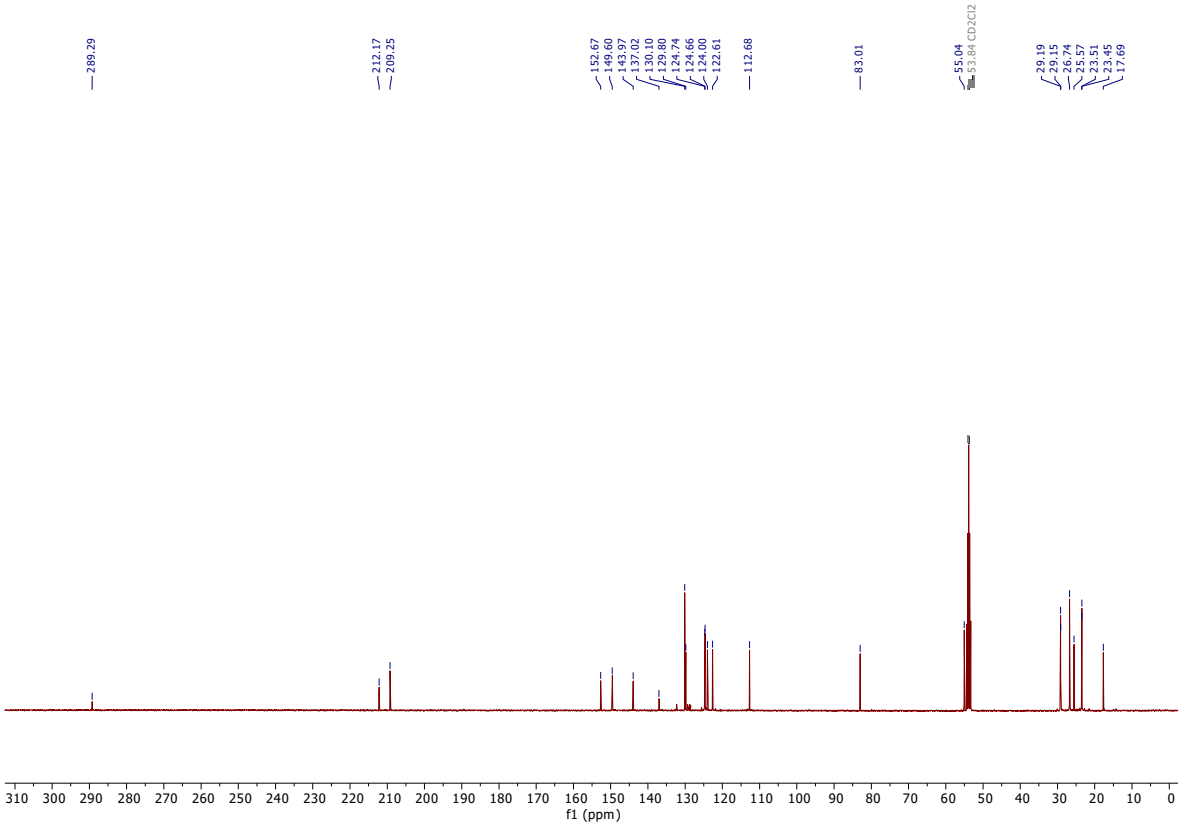


Figure S12. ^{13}C NMR spectrum for **Ru11a.**

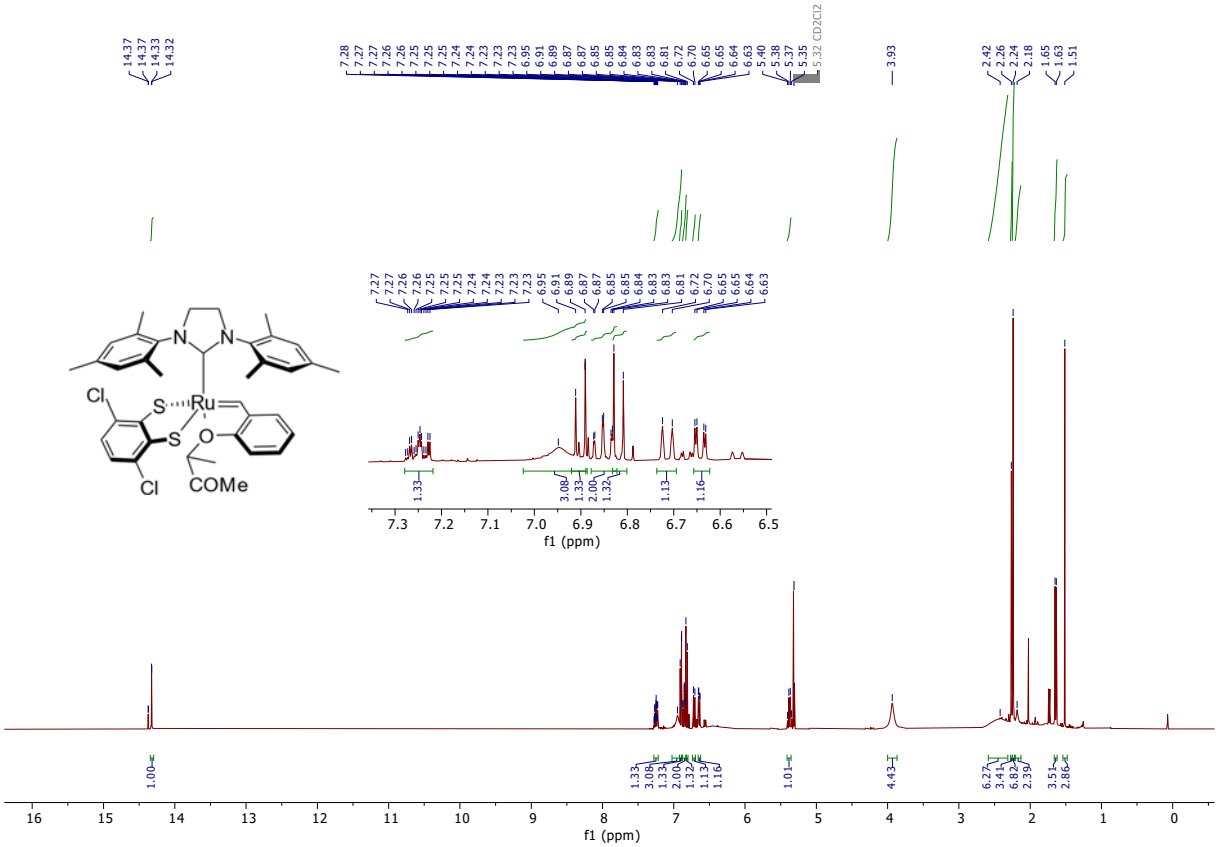


Figure S13. ^{1}H NMR spectrum for **Ru10b.**

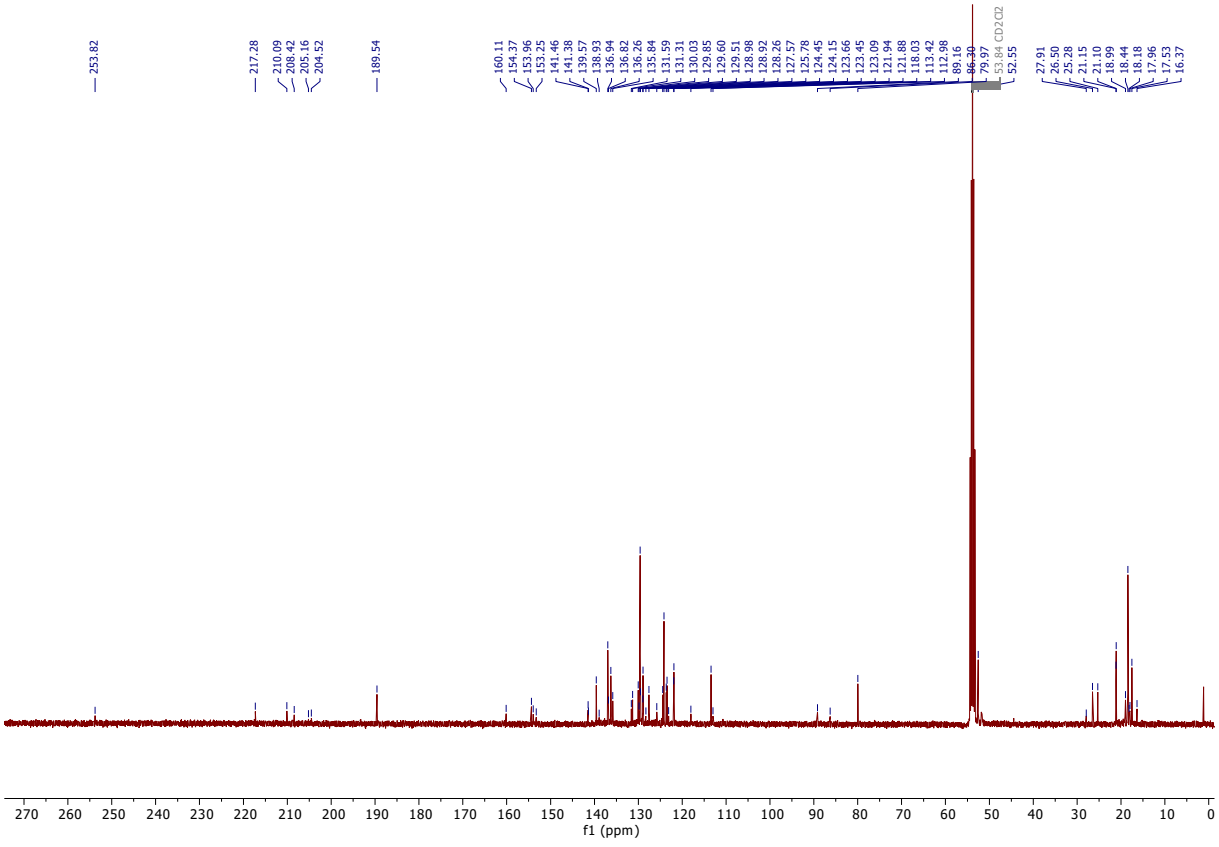


Figure S14. ^{13}C NMR spectrum for **Ru10b.**

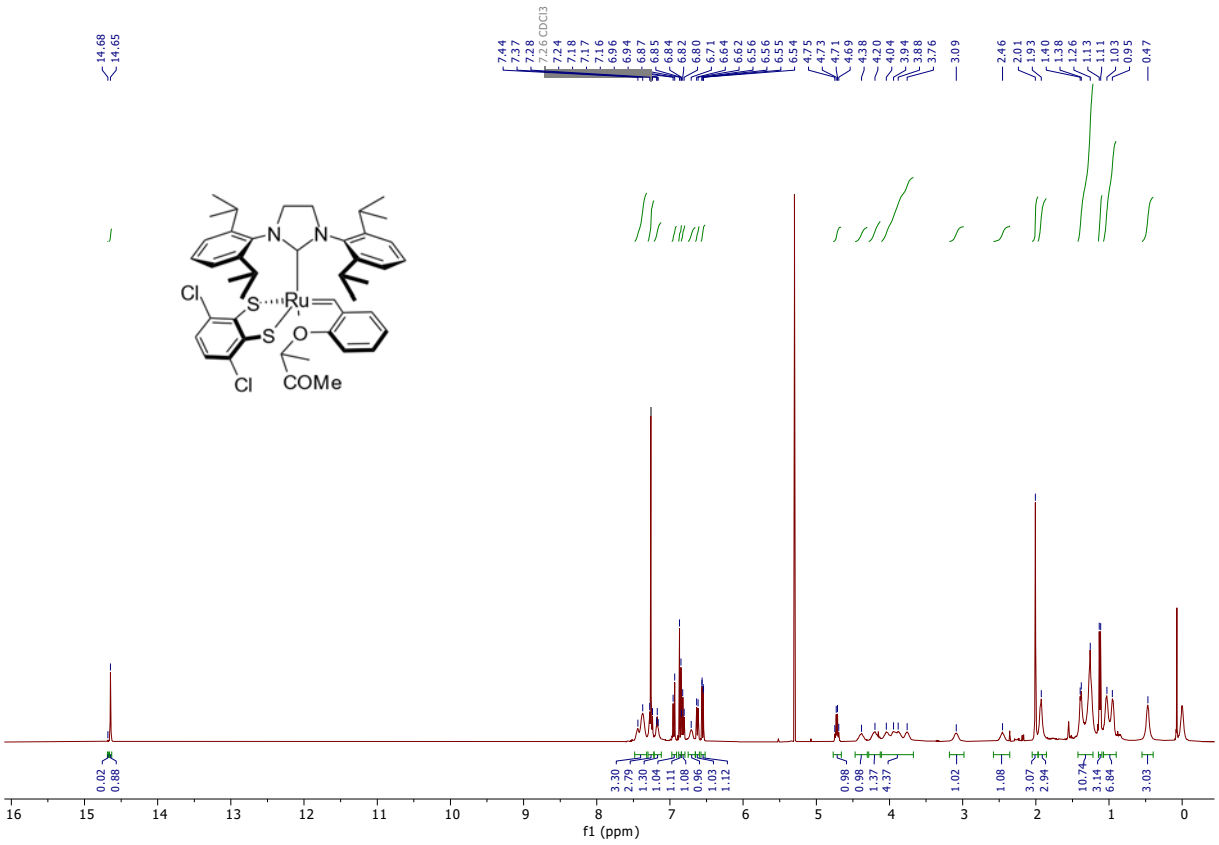


Figure S15. [1]H NMR spectrum for **Ru11b.**

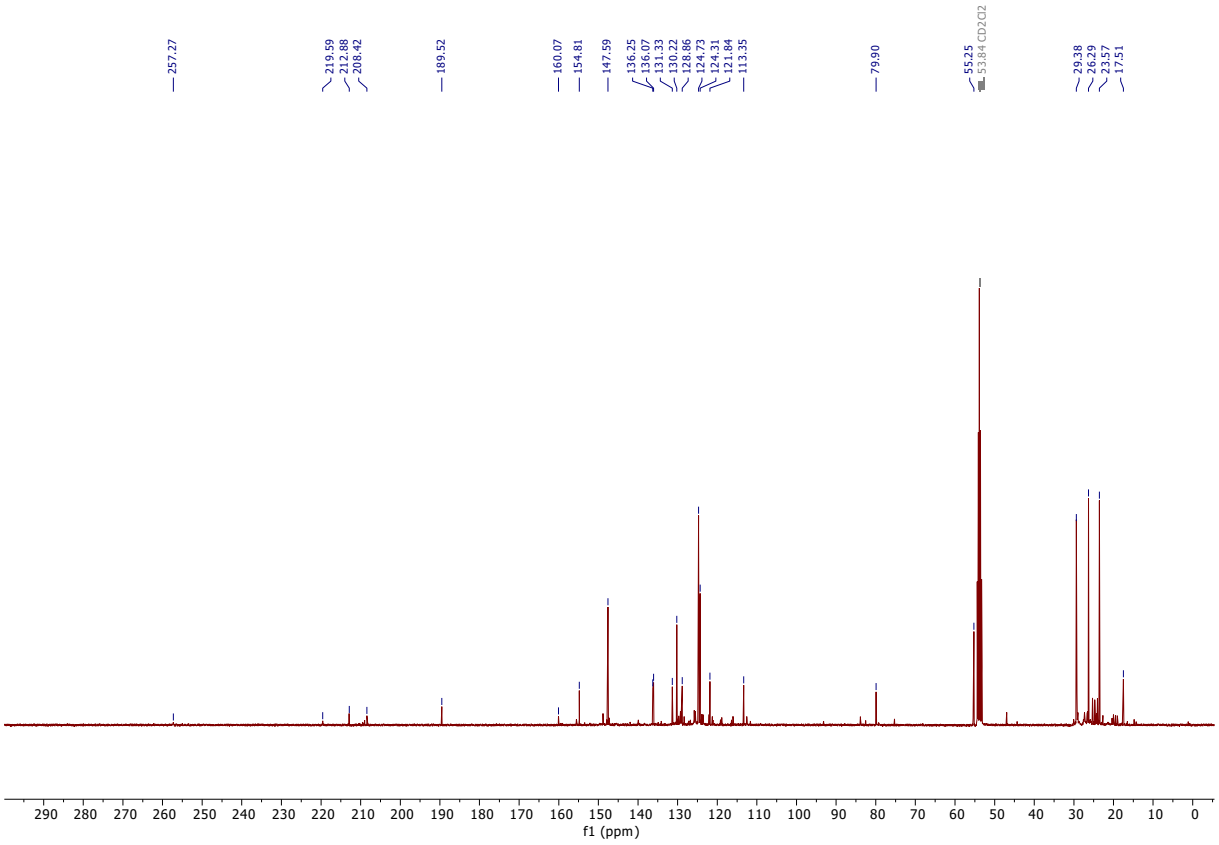


Figure S16. [13]C NMR spectrum for **Ru11b.**

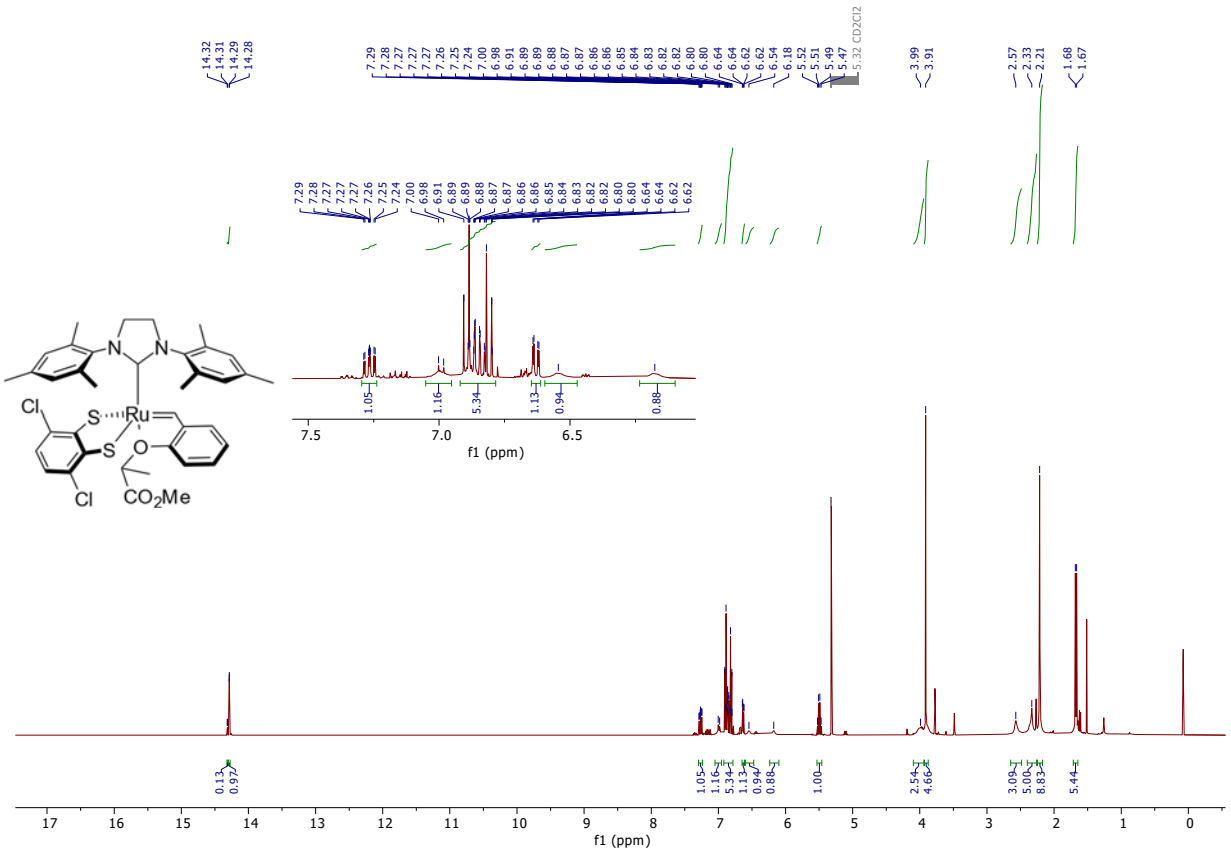


Figure S17. ^{1}H NMR spectrum for **Ru12b**.

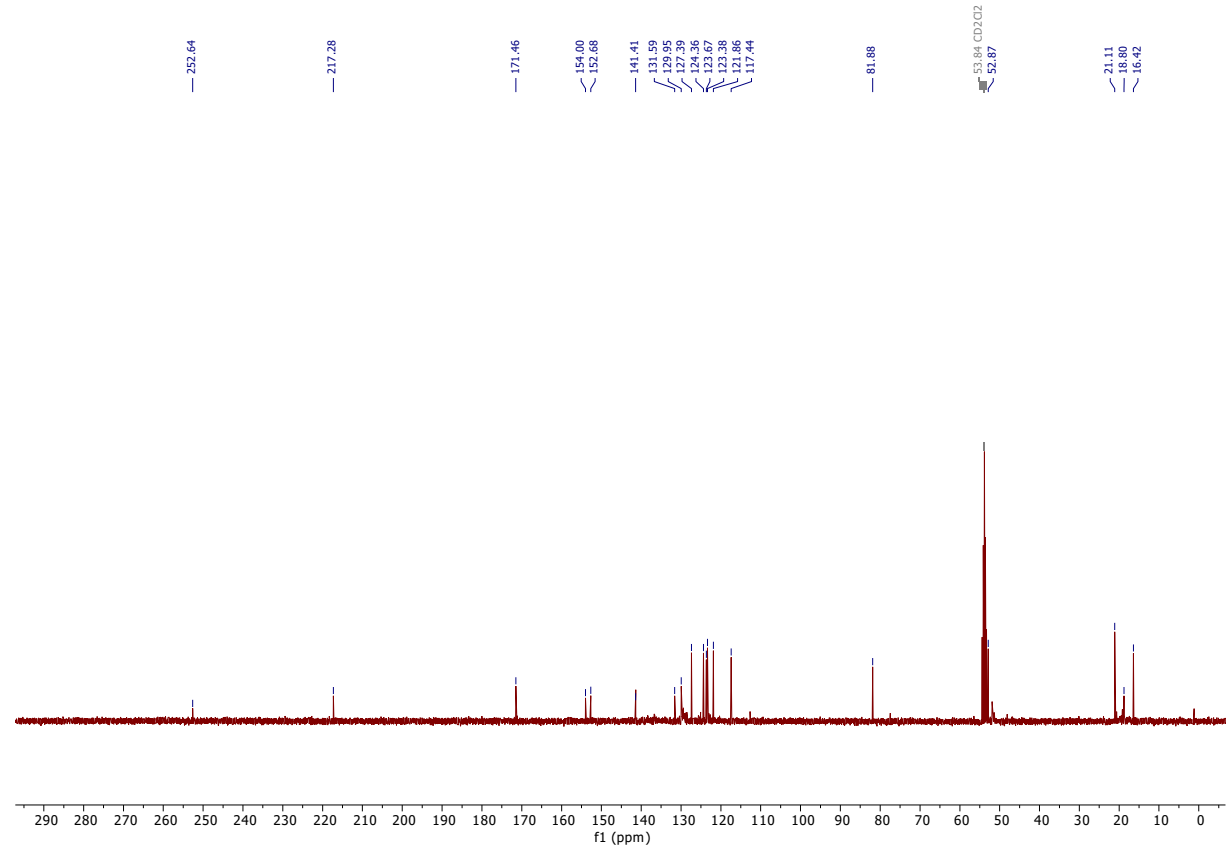


Figure S18. ^{13}C NMR spectrum for **Ru12b.**

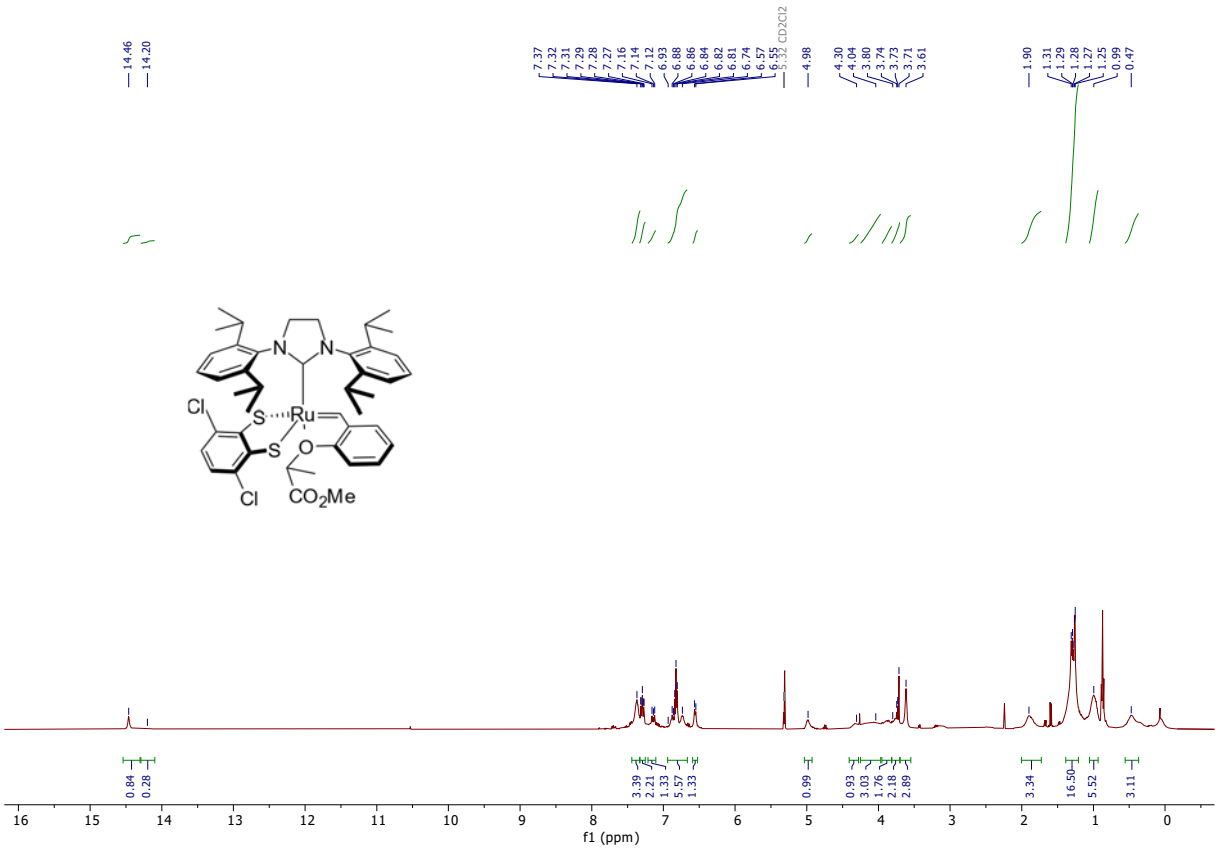


Figure S19. ^{1}H NMR spectrum for **Ru13b.**

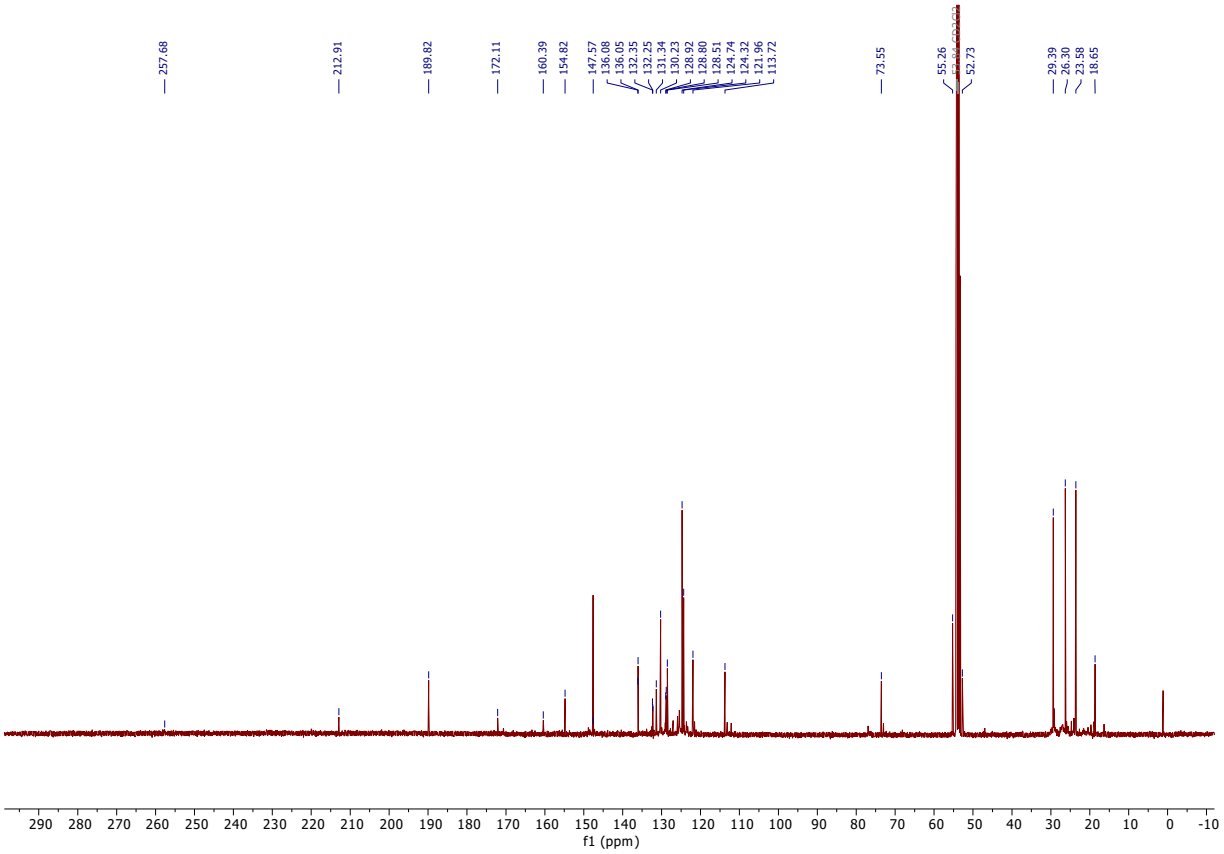


Figure S20. ^{13}C NMR spectrum for **Ru13b.**

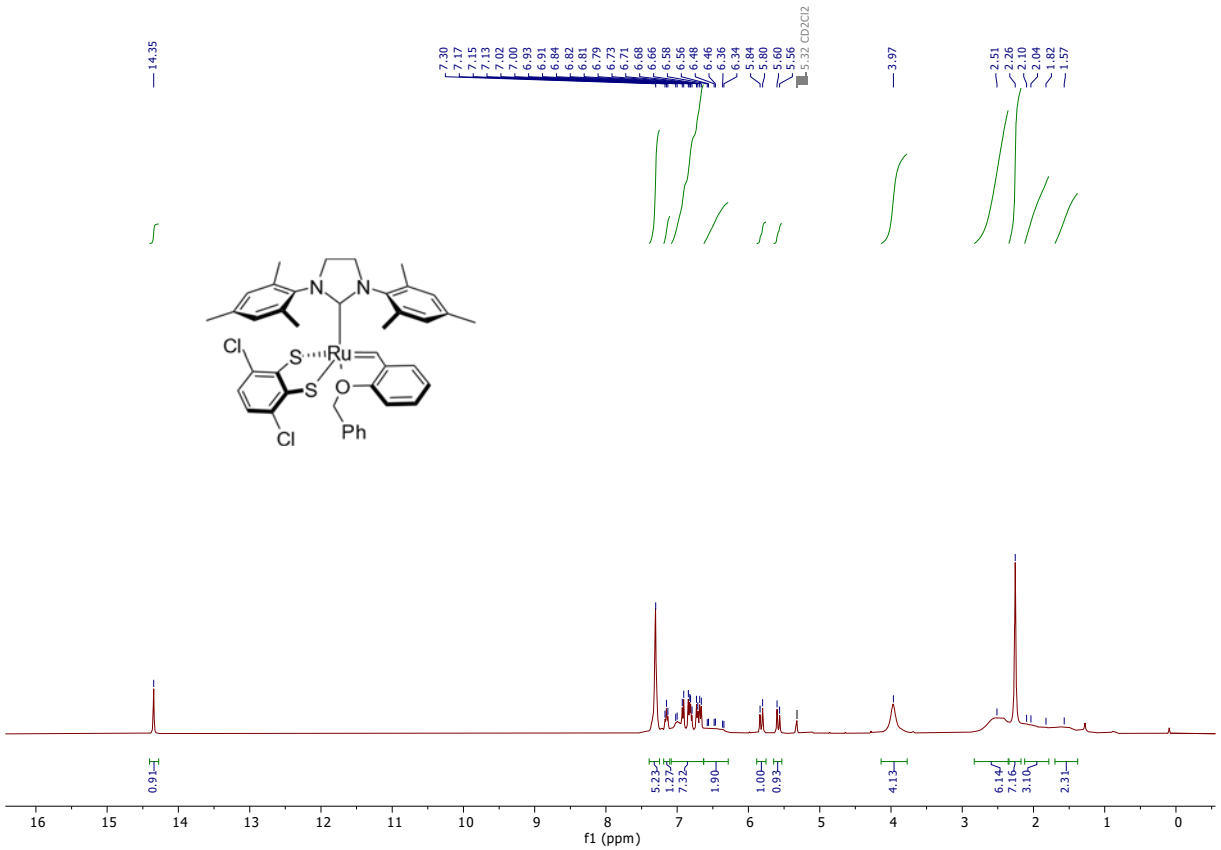


Figure S21. ^{1}H NMR spectrum for **Ru14b.**

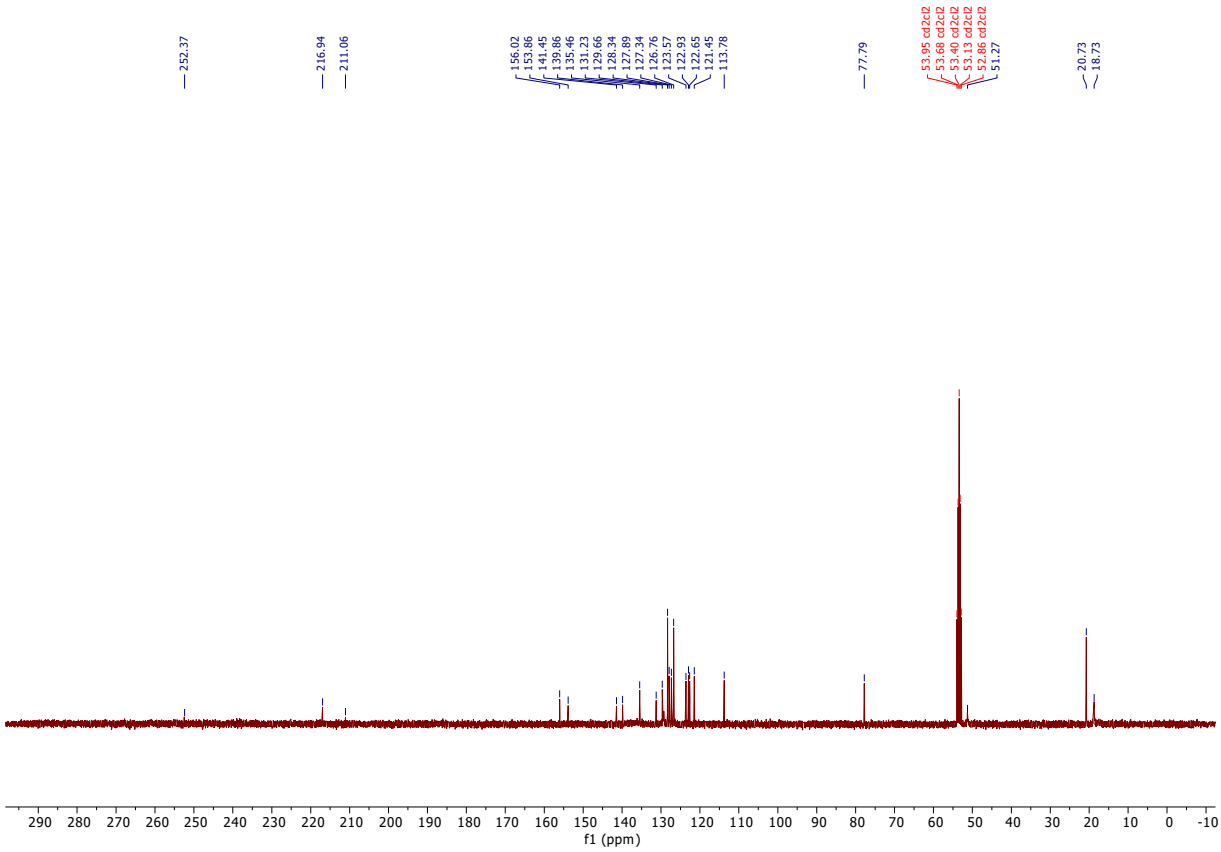


Figure S22. ^{13}C NMR spectrum for **Ru14b.**

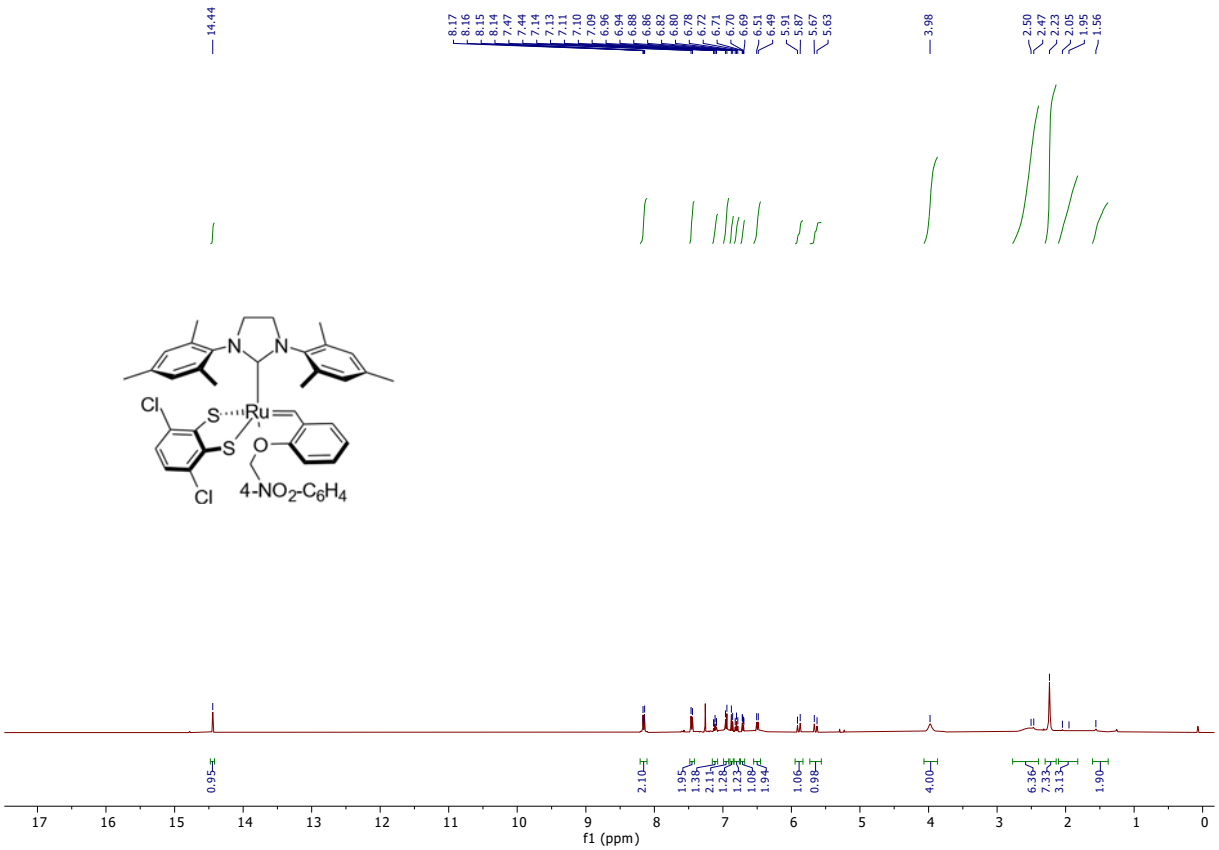


Figure S23. ^{1}H NMR spectrum for **Ru15b.**

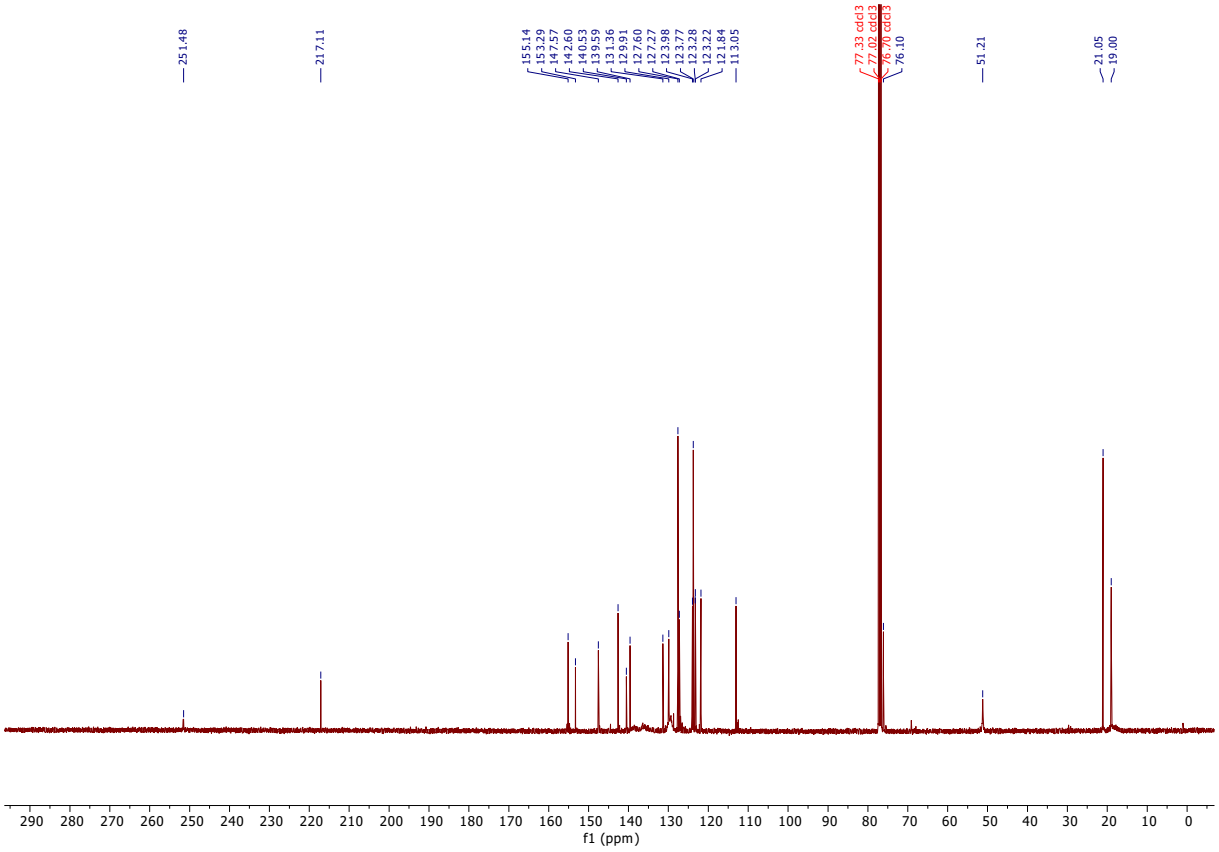


Figure S24. ^{13}C NMR spectrum for **Ru15b.**

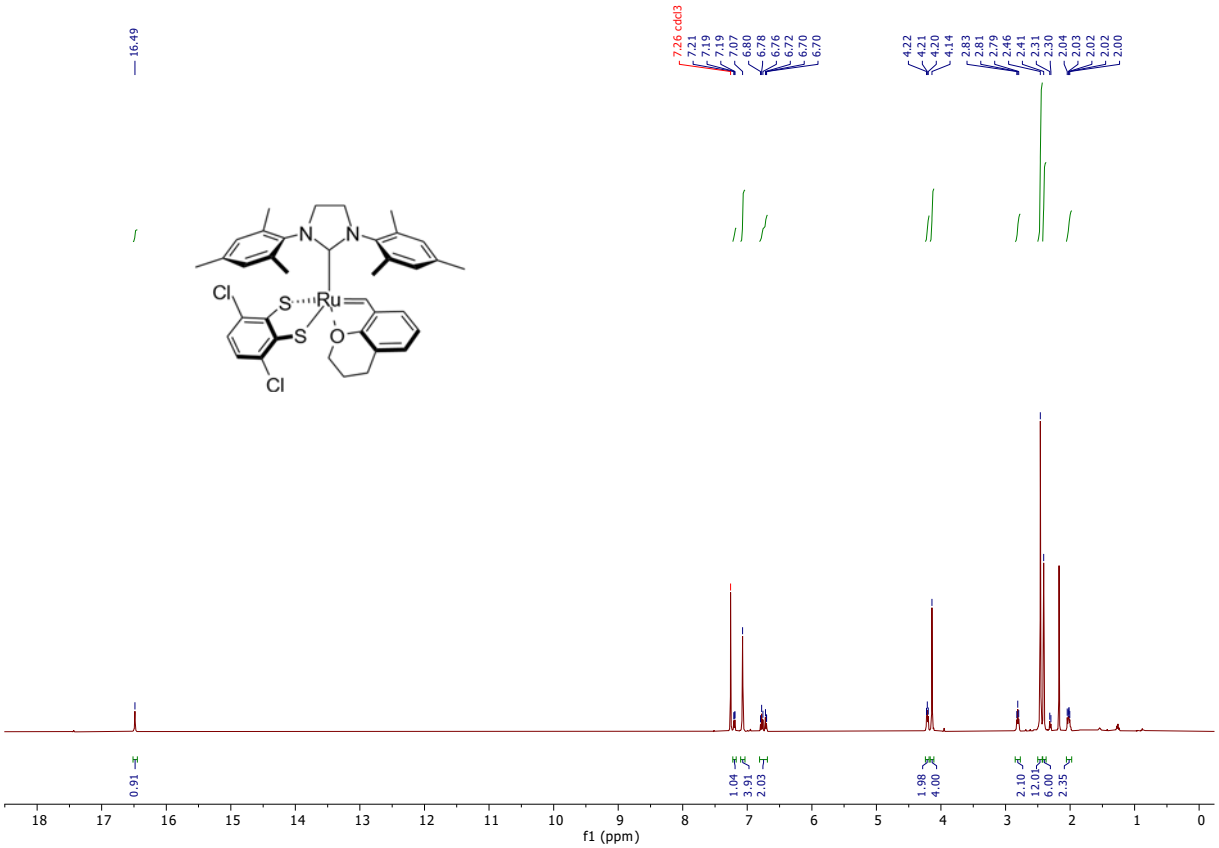


Figure S25. ^{1}H NMR spectrum for **Ru16b.**

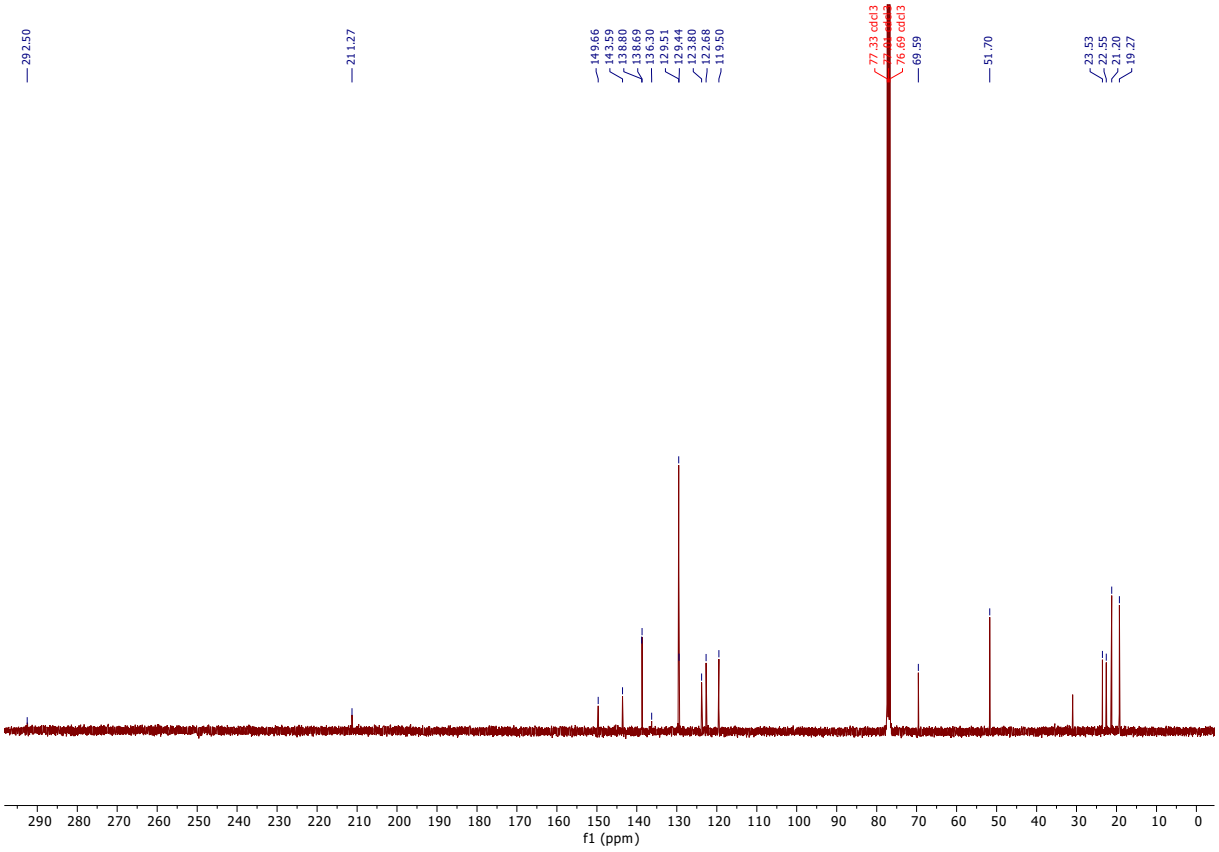


Figure S26. ^{13}C NMR spectrum for **Ru16b.**

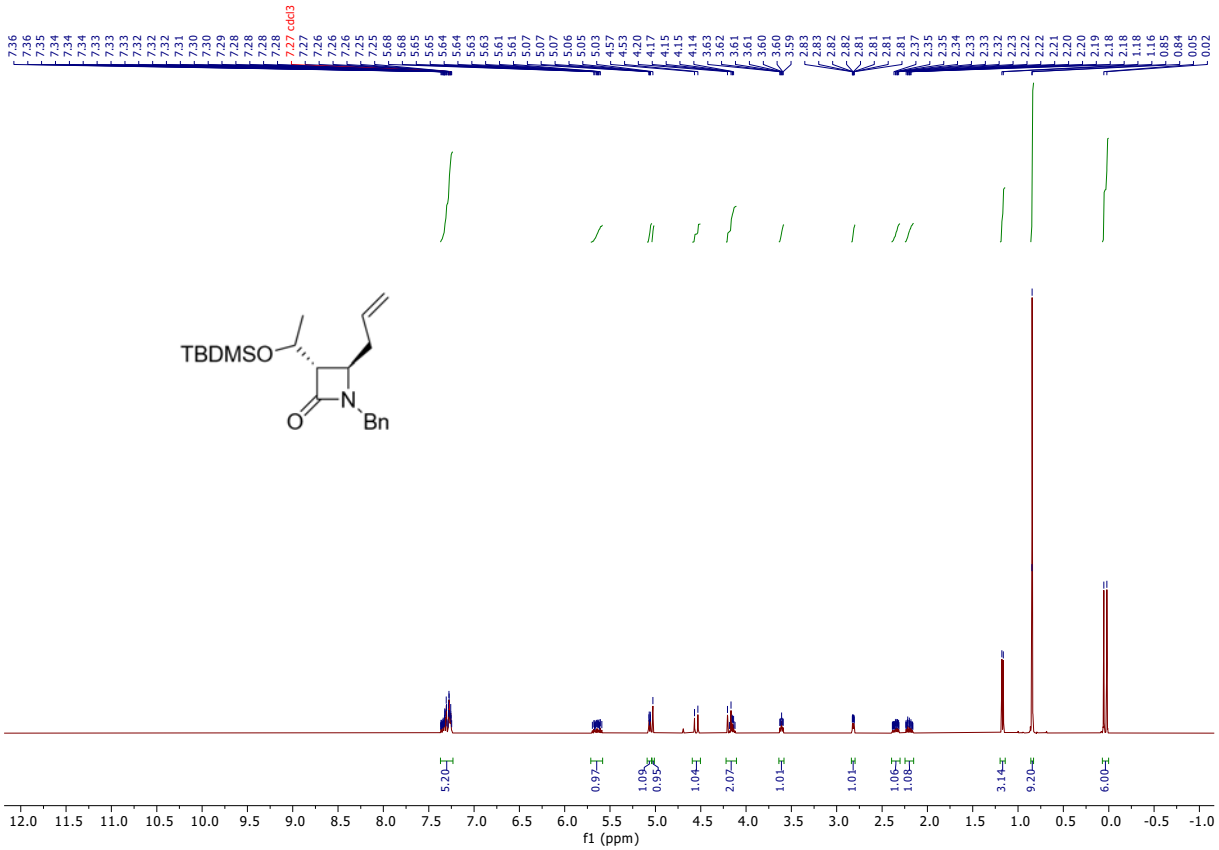


Figure S27. ^{1}H NMR spectrum for **2d.**

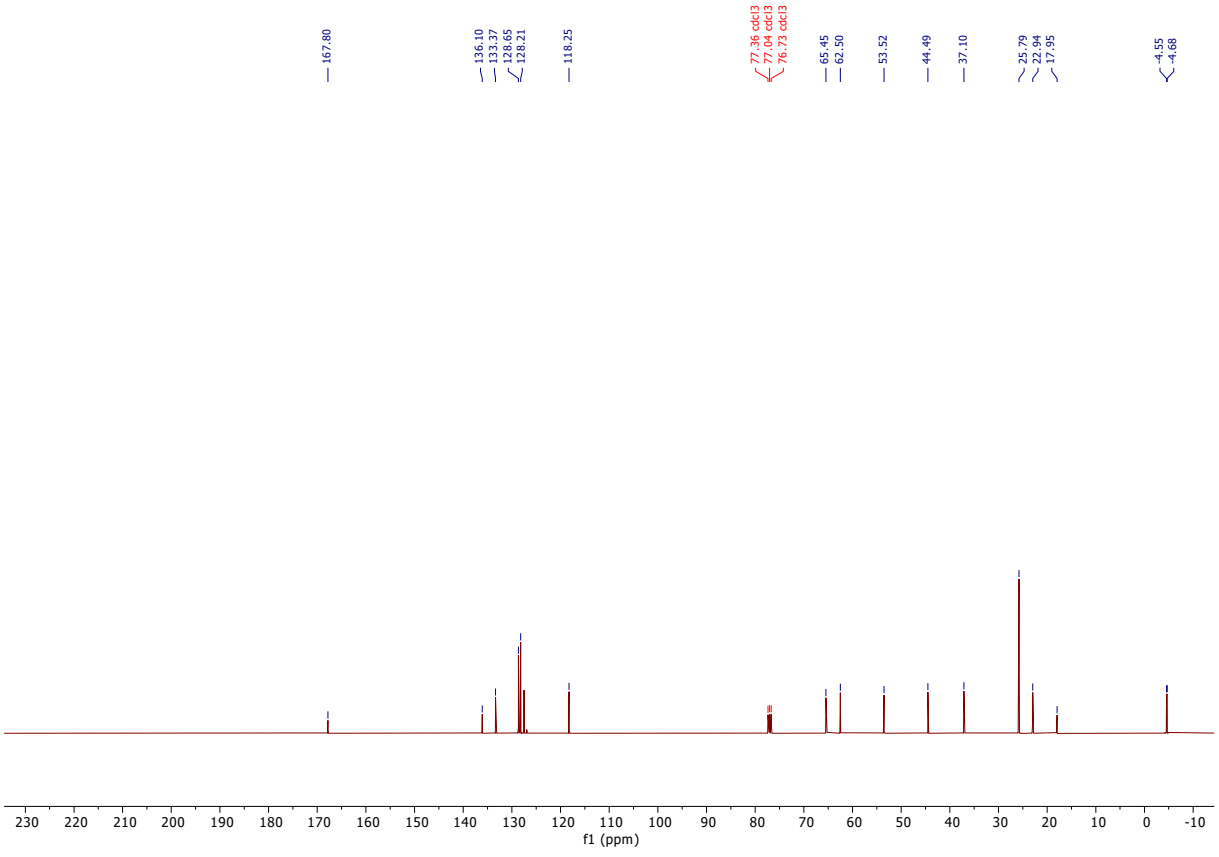


Figure S28. ^{13}C NMR spectrum for **2d.**

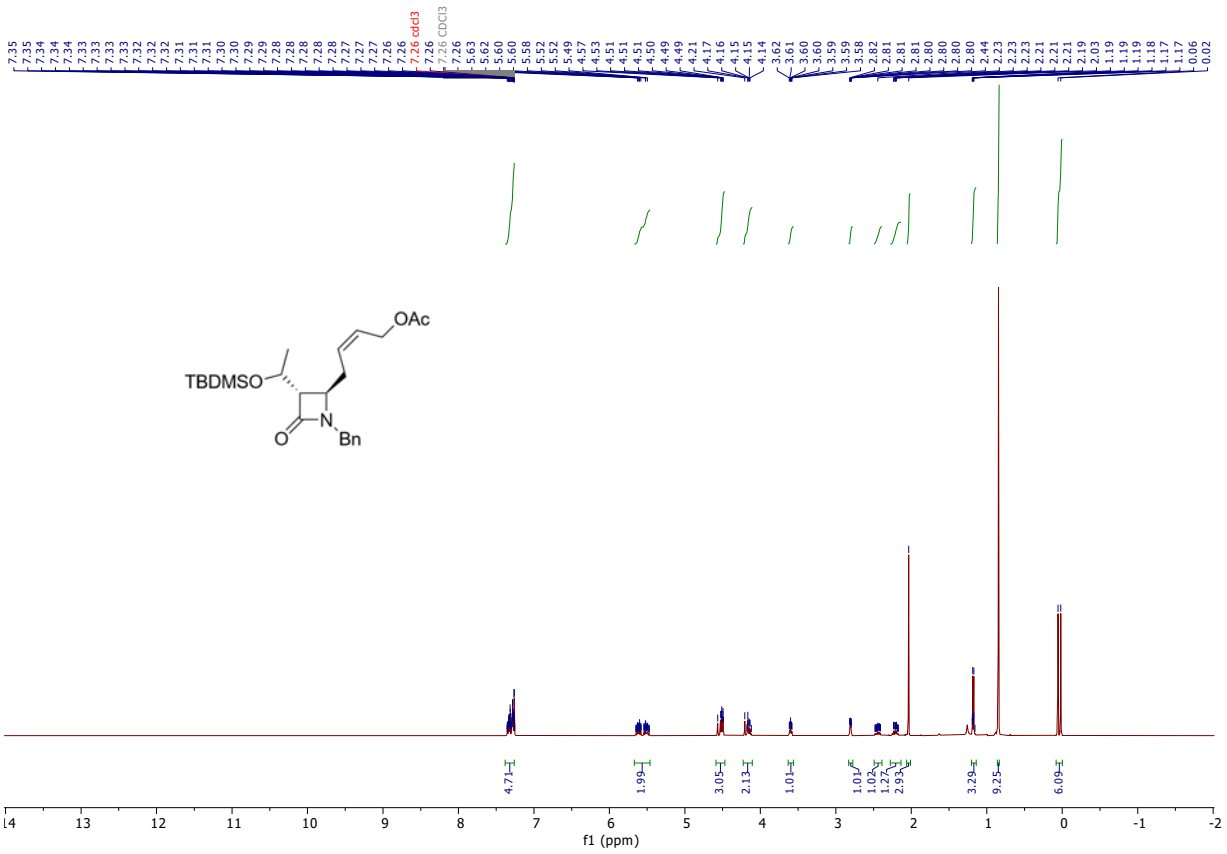


Figure S29. ^{1}H NMR spectrum for **4db.**

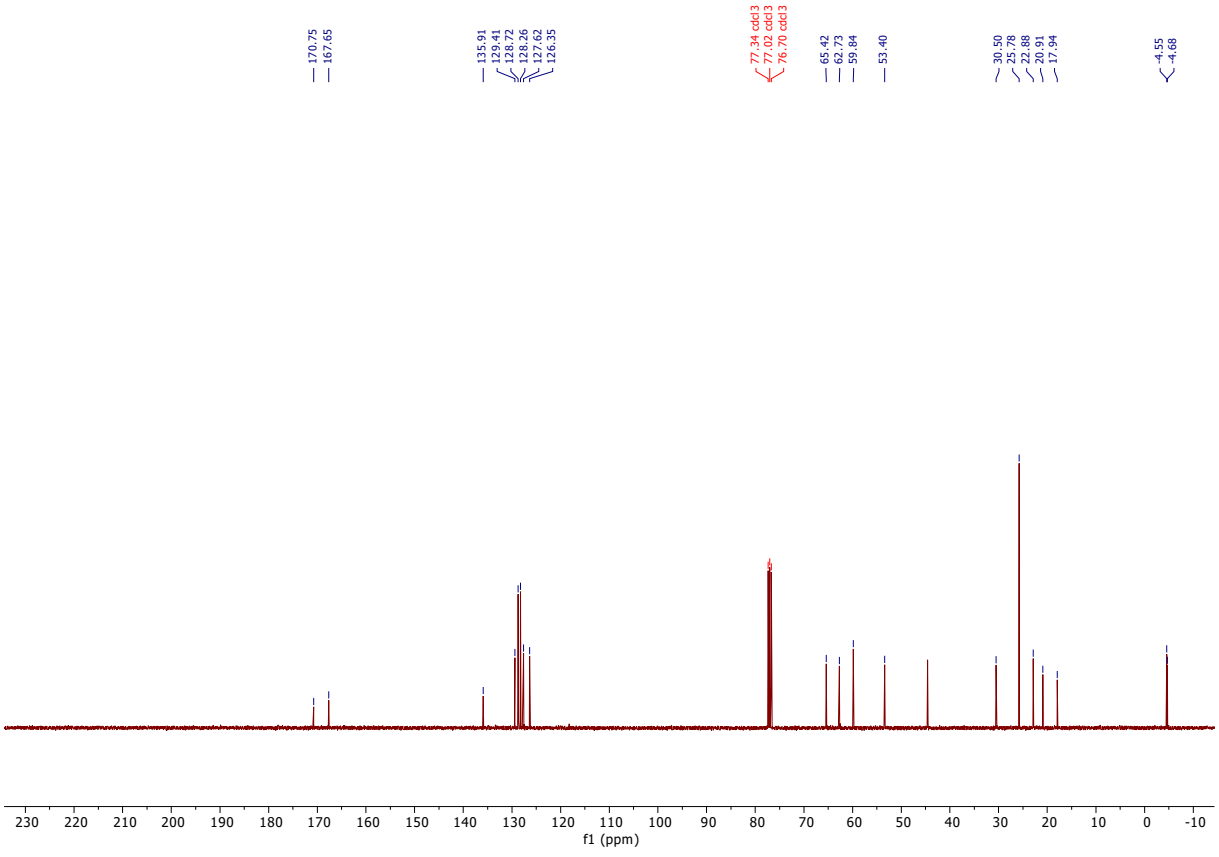


Figure S30. ^{13}C NMR spectrum for **4db.**

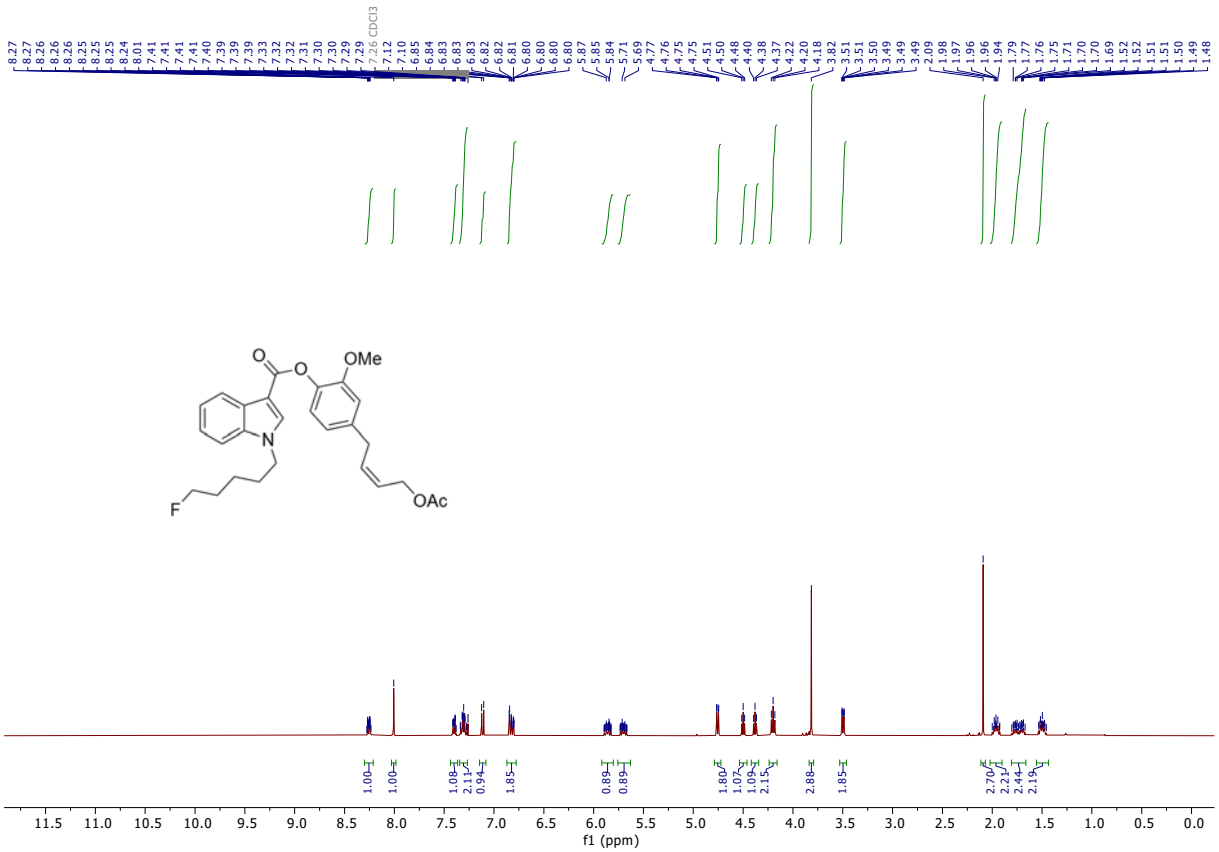


Figure S31. ^{1}H NMR spectrum for **4fb.**

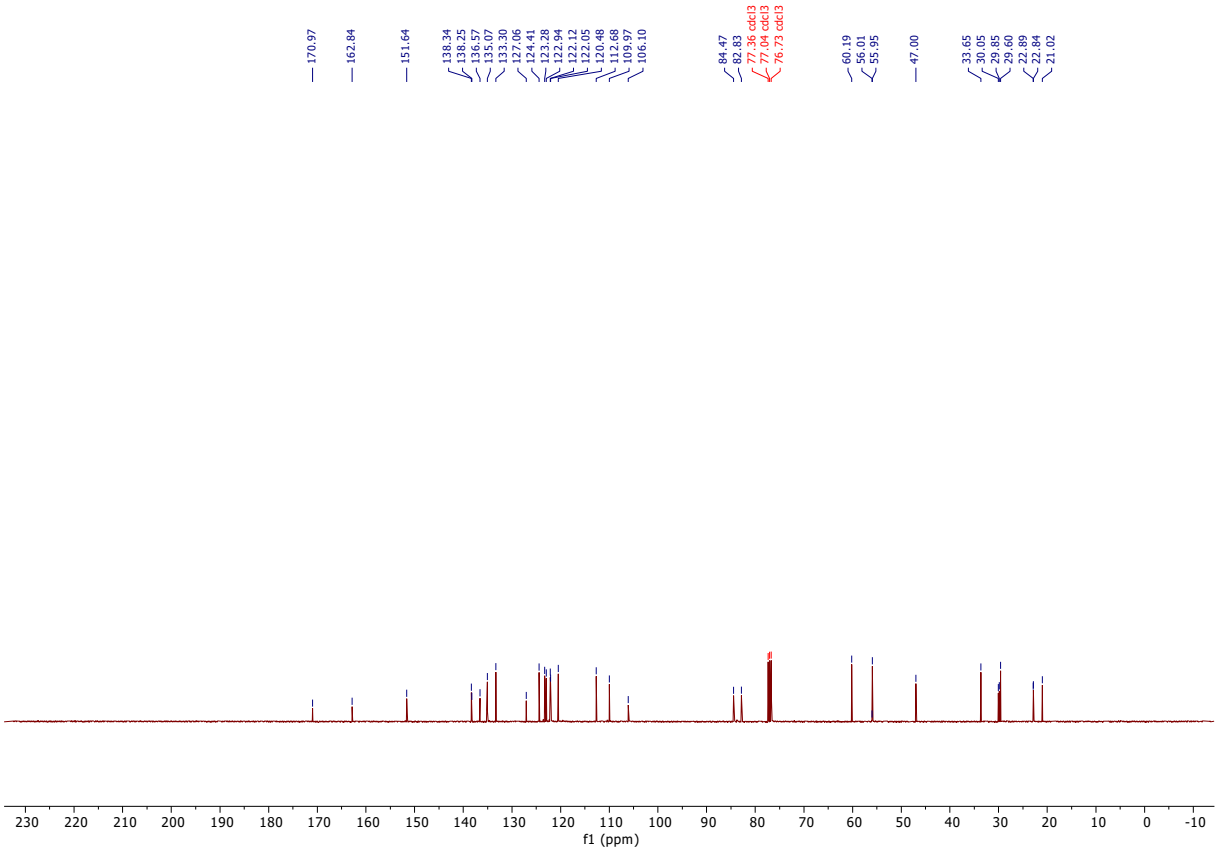


Figure S32. ^{13}C NMR spectrum for **4fb.**

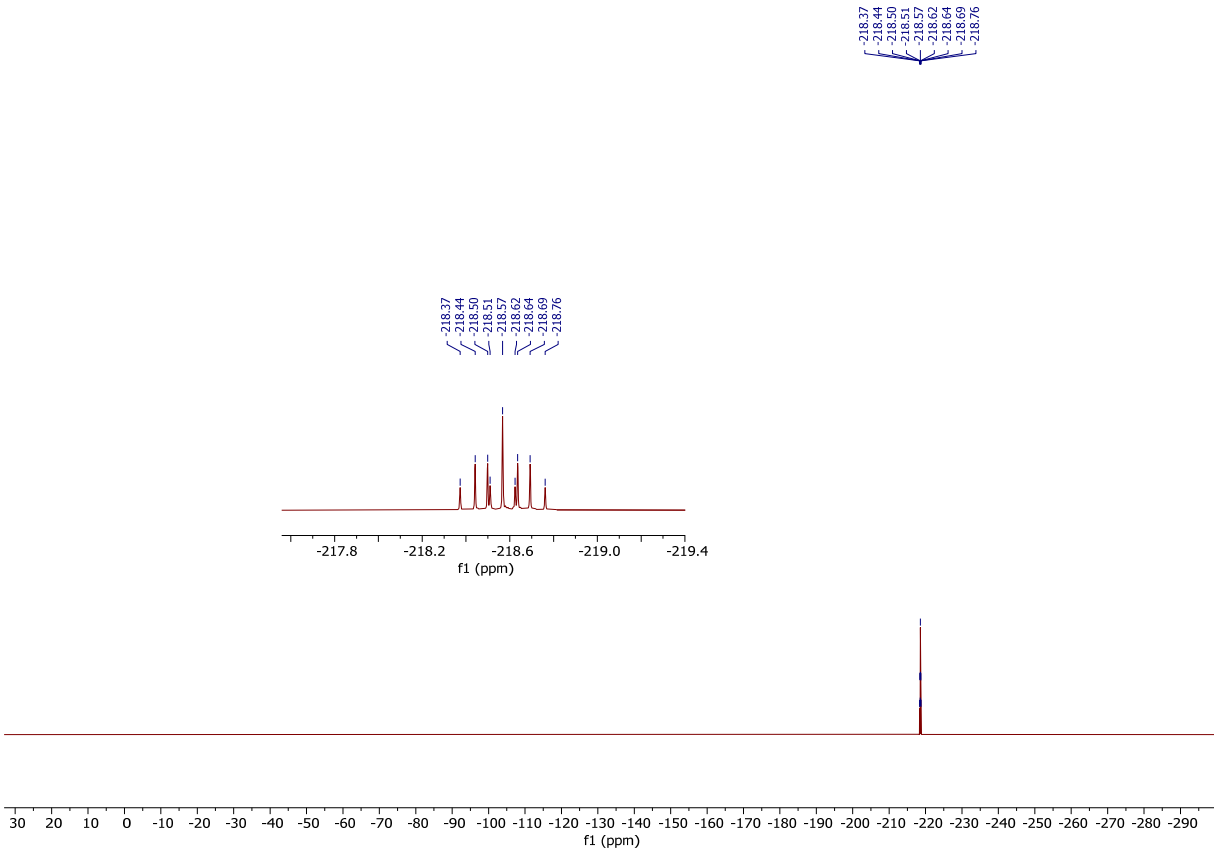


Figure S33. ^{19}F NMR spectrum for **4fb.**

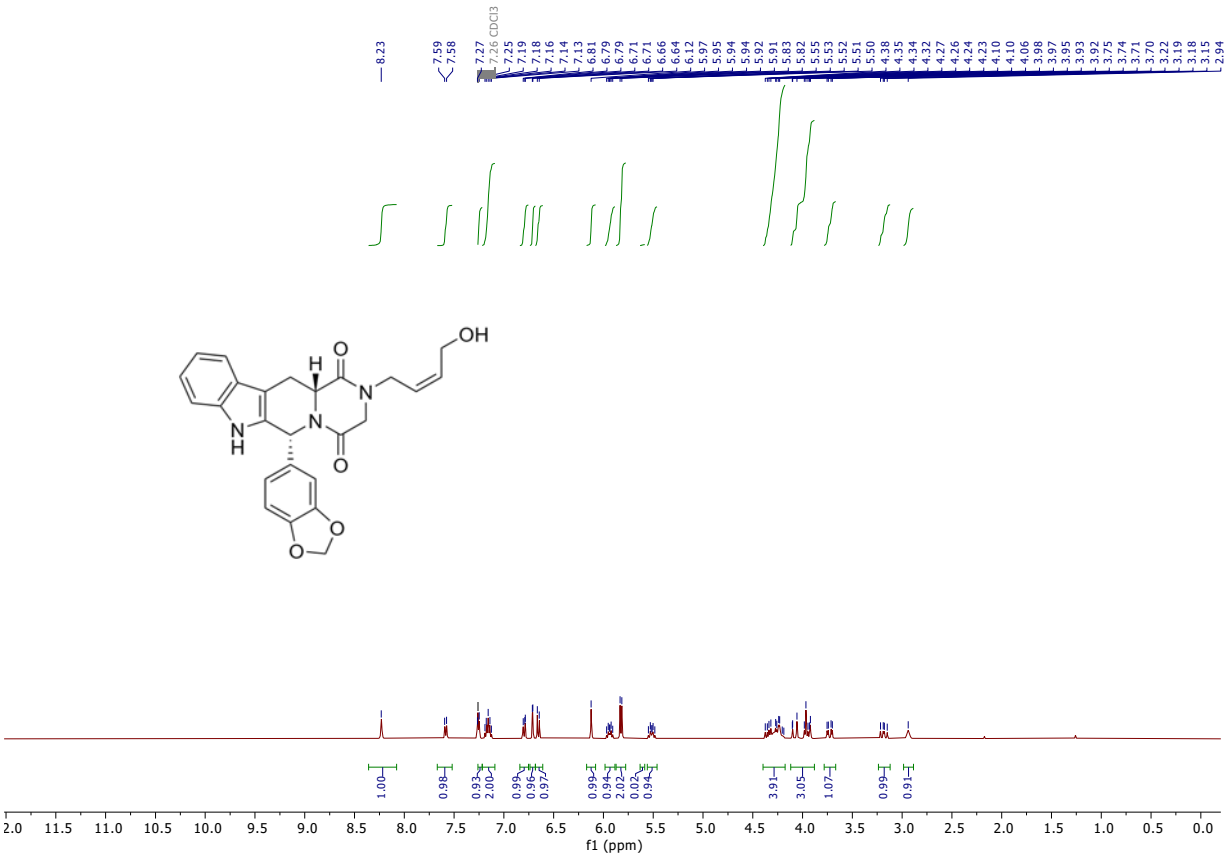


Figure S34. ^{1}H NMR spectrum for **4ia.**

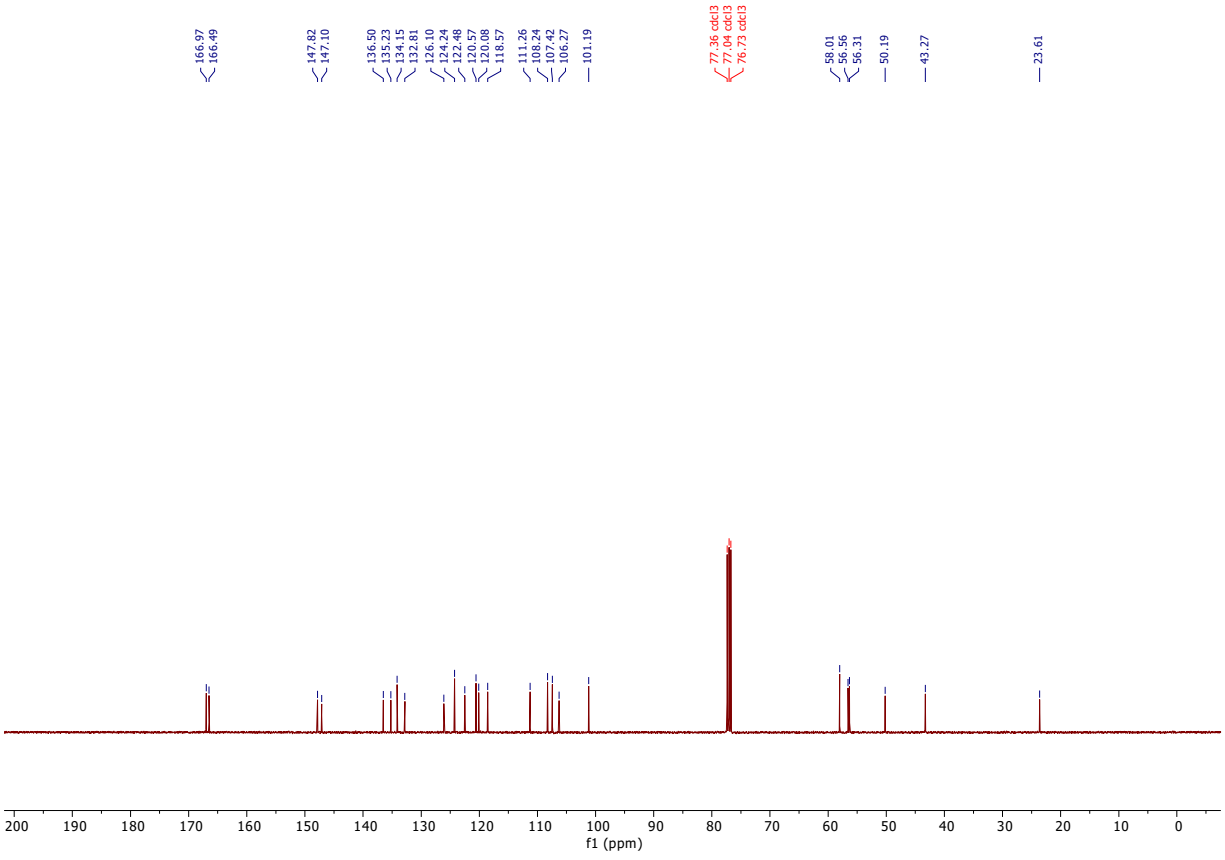


Figure S35. ^{13}C NMR spectrum for **4ia.**

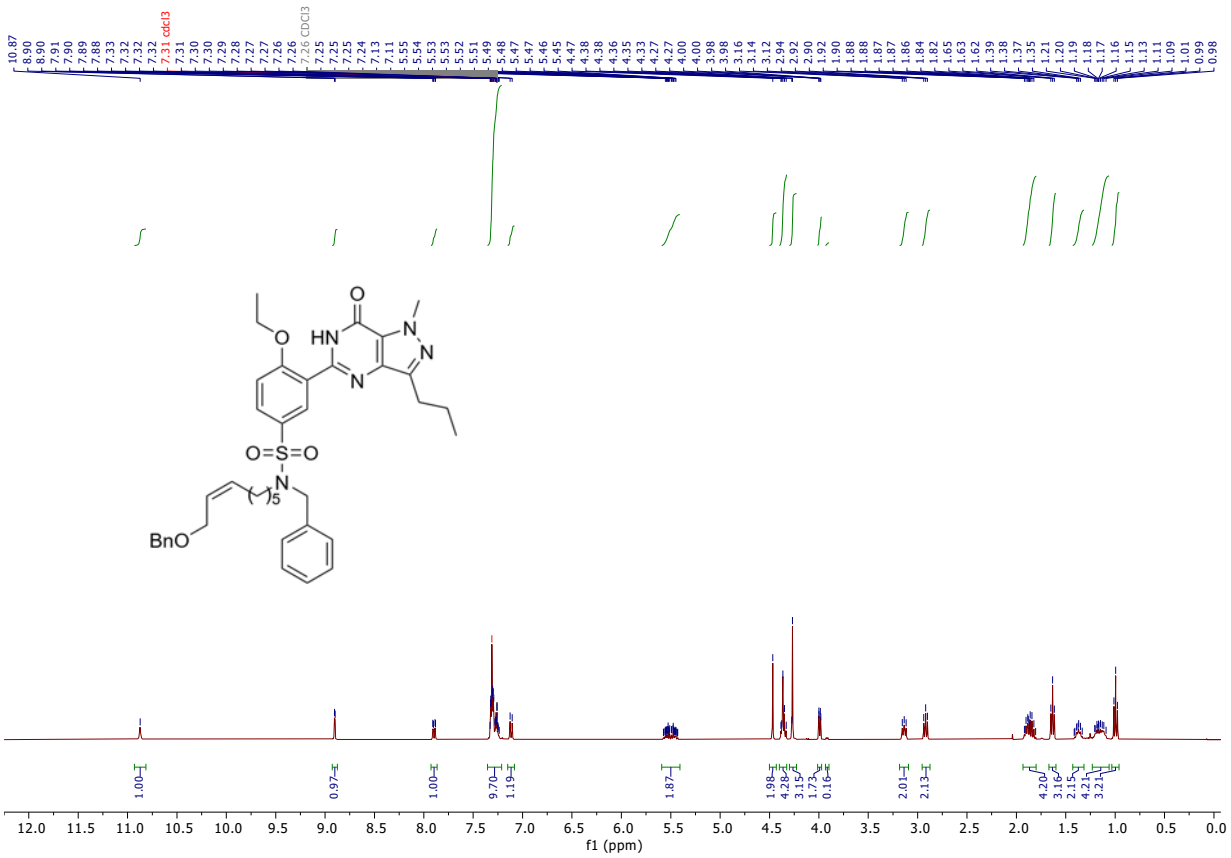


Figure S36. ^{1}H NMR spectrum for **4jc.**

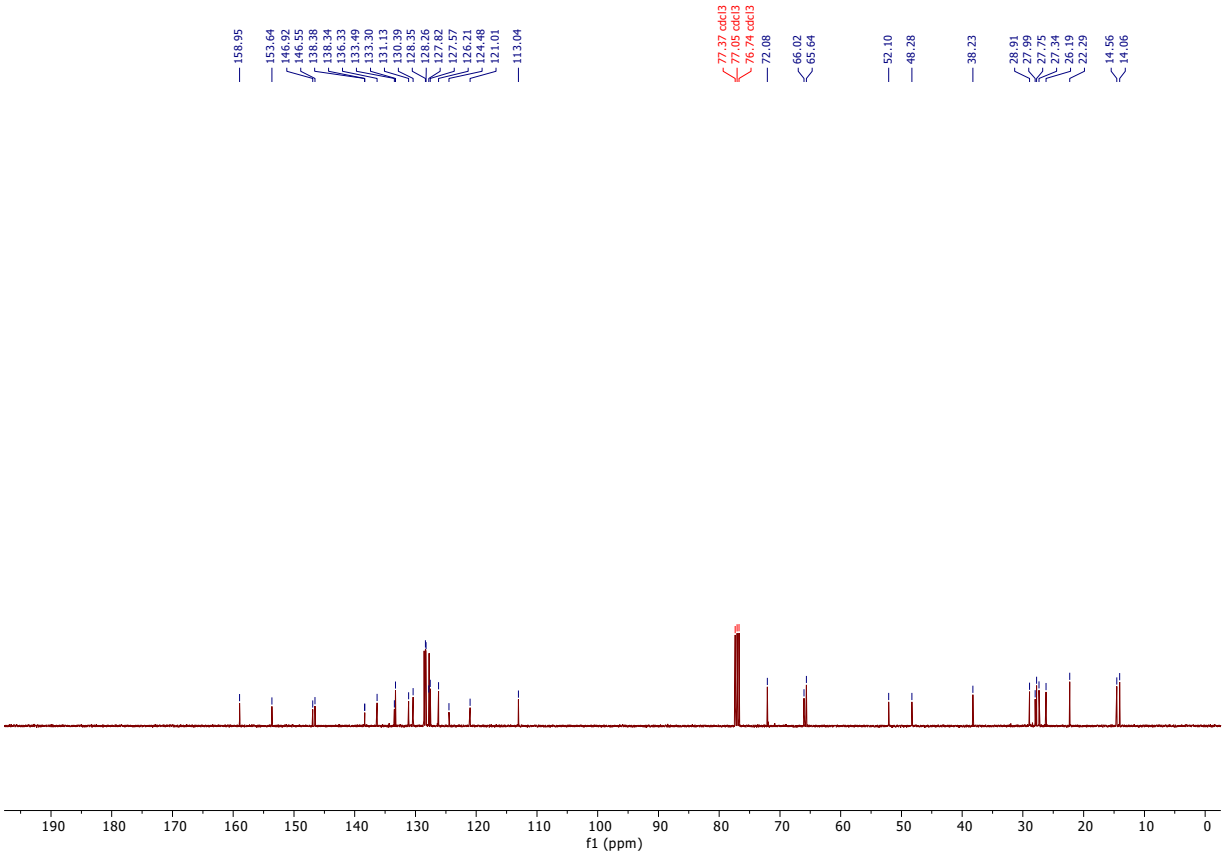


Figure S37. ^{13}C NMR spectrum for **4jc.**

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