



Supporting Information

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# Dormant Ruthenium Catalyst Bearing Chelating Carboxylate Ligand: In Situ Activation and Application in Metathesis Reactions

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# 1. General

## 1.1. Equipment and chemicals used

The catalyst preparation was carried out under argon in pre-dried glassware using Schlenk techniques. The anhydrous solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), *n*-pentane, *n*-hexane, *n*-pentane, CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>). Flash column chromatography was performed using E. Merck silica gel 60 (230–400 mesh). NMR spectra were recorded in CDCl<sub>3</sub>; chemical shifts ( $\delta$ ) are given in ppm relative to TMS, coupling constants are (*J*) in Hz. IR spectra: wavenumbers are in cm<sup>-1</sup>. MS (FD/FAB) were recorded on GCT Premier spectrometer from Waters. MS (EI, LSIMS) spectra were recorded on AMD 604 Intetra GmbH spectrometer. MS (ESI) spectra were recorded on Mariner Perseptive Biosystems, Inc. GC/MS measurements were done on HP 5890 with HP 5 column. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw. Catalyst **3a** and ligands precursors **2** were prepared according to the published method.<sup>1</sup> Model substrates (**4a–4f**) and products (**5a–5f**) were previously obtained and characterised.<sup>1,2,3</sup> All other commercially available chemicals were used as received.

## 1.2. Analytical methods

Comparative RCM experiments with dienes **4a** and **4b** (CH<sub>2</sub>Cl<sub>2</sub>, [diene] = 0.02 M, 40 °C, 24 h; refer to Table 1 and Figure 2) were performed as follows. To a stirred solution of catalyst (5 mol%) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) placed under argon in a Schlenk tube a solution of diene **4a,b** (0.50 mmol, 120.2 mg) and *n*-nonane (used as an internal standard, 0.25–0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added in a single portion at 40 °C and the reaction mixture was stirred for 24 h at the same temperature. Aliquots (0.25 mL), taken in regular intervals, were quenched immediately with ice-cold solution of ethyl-vinyl ether (0.25 mL, 2 M in CH<sub>2</sub>Cl<sub>2</sub>) and analysed by GC, using HP 6890 chromatograph with HP 5 column.

# 2. Preparation and characterization of catalysts

## 2.1. Dormant catalyst **3c**

Ligand **2b** (49.5 mg; 0.24 mmol), CuCl (23.8 mg; 0.24 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were placed in a

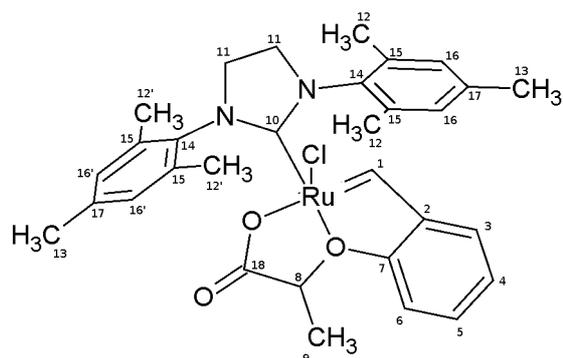
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[1] Bieniek, M.; Bujok, R.; Cabaj, M.; Lugań, N.; Lavigne, G.; Arlt, D.; Grela, K. *J. Am. Chem. Soc.* **2006**, *128*, 13652–13653

[2] A. Michrowska, K. Mennecke, U. Kunz, A. Kirschning, K. Grela, *J. Am. Chem. Soc.* **2006**, *128*, 13261–13267.

[3] K. Grela, A. Michrowska, M. Bieniek, M. Kim, R. Klajn, *Tetrahedron* **2003**, *59*, 4525–4531.

Schlenk flask. Afterwards carbene complex **1a** (169.8 mg; 0.20 mmol) was added and the resulting solution was stirred under argon at 40 °C for 40 min. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was dissolved in EtOAc (ca. 10 mL), white solid was filtered off and the filtrate was concentrated under vacuum. The product was purified by column chromatography on silica gel (Merck, grade 9385, 230-400 mesh, no pre-treatment). Elution with *c*-hexane-EtOAc (2:1) (ca. 200 mL) then *c*-hexane-EtOAc (1:1) removes **3c** as a green band. The solvent was evaporated and product dissolved in small amount CH<sub>2</sub>Cl<sub>2</sub>, then *n*-pentane was added until green crystals precipitated. The precipitate was filtered off, washed with *n*-pentane and dried in vacuo to afford complex **3c** (104.8



**Scheme 1:** Arbitrary numbering scheme in **3c**

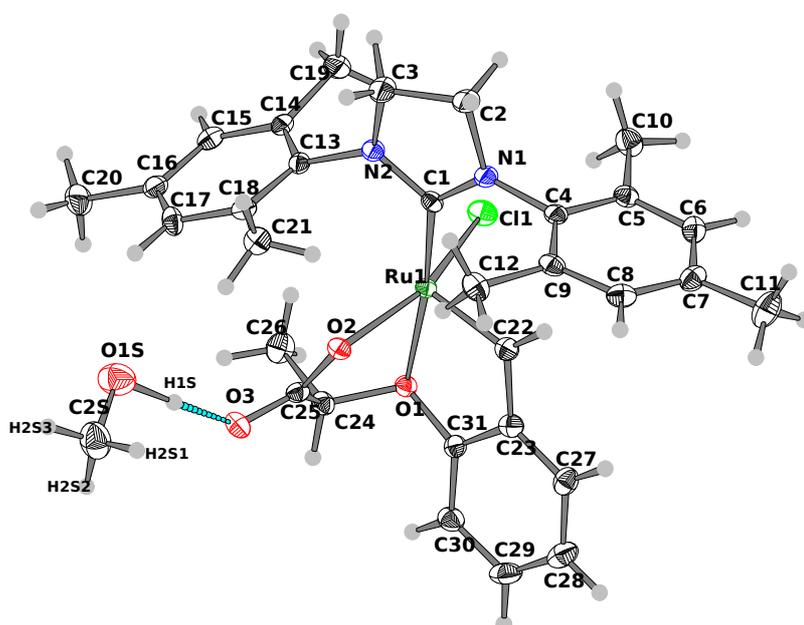
mg, 84%) as a green solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 16.52 (s, 1H; 1-H), 7.49–7.52 (m, 1H; 5-H), 7.11 (s, 2H; 16-H), 7.06 (s, 2H; 16'-H), 7.02–7.05 (m, 1H; 4-H), 6.97 (d, *J* = 8.23 Hz, 1H; 6-H), 6.95 (d, *J* = 7.57 Hz, 1H; 3-H), 4.65 (q, *J* = 7.02 Hz, 1H; 8-H), 4.21 (s, 4H; 11-H), 2.47 (bs, 6H; 12-H), 2.39 (s, 6H; 13-H), 2.37 (s, 6H; 12'-H), 1.19 (d, *J* = 7.02 Hz, 3H; 9-H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 293.3 (C1), 210.3 (C10), 181.5 (C18), 154.6 (C7), 146.7 (C2), 139.3, 138.8, 130.0 (C5), 129.6 (C16'), 129.4 (C16), 126.6 (C4), 122.2 (C3), 119.1 (C6), 84.1 (C8), 51.4 (C11), 21.0 (C13), 19.00 (C9), 18.8 (C12), 18.5 (C12') (where assignments of the NMR signals are given (based on 2D <sup>1</sup>H, <sup>13</sup>C-chemical shift correlated spectra: GHSQC, GHMBC), they are unambiguous and refer to the arbitrary numbering shown in Scheme 1); IR (film from CH<sub>2</sub>Cl<sub>2</sub>): ν = 3483, 3044, 2977, 2919, 2861, 2736, 1662, 1607, 1594, 1571, 1483, 1451, 1401, 1376, 1318, 1297, 1269, 1185, 1151, 1100, 1069, 1017, 944, 918, 879, 846, 795, 752, 734, 700, 645, 617, 577, 501, 471, 438, 421 cm<sup>-1</sup>; HRMS (FD/FI): *m/z* calcd for C<sub>31</sub>H<sub>35</sub>N<sub>2</sub>O<sub>3</sub><sup>35</sup>Cl<sup>102</sup>Ru: [M<sup>+</sup>] 620.1380 found, 620.1357; elemental analysis (%) calcd for C<sub>31</sub>H<sub>35</sub>N<sub>2</sub>O<sub>3</sub>ClRu (620.16): C 60.04, H 5.69, N 4.52, Cl 5.72; found: C 59.92, H 5.69, N 4.55, Cl 5.48.

## 2.2. Solid state structure of catalyst **3c**

The structure of **3c** compound (see Figure 1) has been determined by single crystal X-ray diffraction technique. The main aim was to reveal the details of the coordination of the ruthenium atom by the carboxylate group moiety substituted in place of the isopropyl function of the original Hoveyda catalyst. It was particularly interesting to compare this structure with the previously determined

structure of the ester-substituted Hoveyda-type catalyst **3a**<sup>1</sup> which presented unusual ruthenium coordination as well as uncommon chemical properties.

The compound **3c** crystallizes, in common  $P2_1/c$  space group of the monoclinic system, similarly to the previously studied **3a**. However, the unit cell dimensions for the current compound are different from those of **3a** and the cell volume is smaller, suggesting closer packing and different intermolecular interactions. This may be due to the smaller size of the carboxylic substituents as well as the different kind of solvent molecule co-crystallized with the main compound. There is one independent ruthenium complex in the crystallographic asymmetric part of the unit cell, connected with one solvent molecule – methanol – by a strong, linear hydrogen bond. The geometry of the hydrogen bond is summarized in Table 1. It is worth to mention, that the solvent molecule is well stabilized in the structure.



**Figure 1.** ORTEP representation of the **3c** structure – full contents of the asymmetric part of the unit cell including solvent molecule. Thermal displacement ellipsoids are shown at the 50% probability level.

Table 1. Summary of the geometry of solvent – **3c** complex hydrogen bond.

Distance	[Å]
O(1S)-H(1S)	1.22(5)
O(3)-H(1S)	1.58(5)
O(3)-O(1S)	2.778(2)
Angle	[°]
O(1S)-H(1S)-O(3)	167(4)

Analogically to most Hoveyda-type catalysts, the ruthenium center in **3c** is pentacoordinate, and the geometry of the ligands is very close to the square pyramid. The benzylidene carbene carbon atom

resides always in the apical position. The two opposite corners of the basal square are occupied by oxygen atom from the ether moiety and carbene carbon from the imidazole ring accordingly. Another corner of the basal plane is occupied by a single chlorine atom, whereas the oxygen from the carboxyl group takes place in the remaining corner. This is a feature that distinguishes the **3c** structure from both **3a**<sup>1</sup> and the simple Hoveyda catalyst, where two chlorine atoms located in trans in the basal plane took part in the ruthenium coordination.

The fact that the carboxylate moiety coordinates ruthenium replacing one of the chlorine atoms influences the geometry around the ether-oxygen. The O1 atom in **3c** compound presents the geometry suggesting the sp<sup>3</sup> hybridization type, with valence angles values closer to 110 degrees. The O(1) – C(31) bond length is 1.409 Å, and it is significantly longer than the analogical O(1) – C(26) connection in the Hoveyda catalyst **1h** or O(1) – C(36) connection in the **3a** compound.<sup>1</sup> The coordination of the ruthenium by O1 oxygen in the **3c** compound seems to take place by a single lone electron pair, which suggests a different strength and character of the interaction than there was the case in **3a** or the Hoveyda structure.<sup>4</sup> The O1 – Ru1 distance in **3c** is significantly shorter than the same distance in the Hoveyda model catalyst, but similar to the distance found for the ester-substituted **3a** compound. This may be due to the comparable electron-withdrawing properties of the carboxylate and ester substituents.

In contrast to the **3a** structure, where the O2 oxygen formed the additional coordination site of the ruthenium on one of the tops of the square bi-pyramid, in the carboxyl – substituted compound the O2 oxygen atom replaces one of the chlorines in the coordination of the central metal ion in the cis position with respect to the O1 oxygen. The interactions are stronger in the case of **3c** from the geometrical point of view. The distance O2 – Ru1 is quite short (2.055 Å, compared with 2.536 Å in **3a** structure) while the O2 – C25 distance is significantly elongated (1.291 Å, compared with 1.194 Å in **3a** structure).

Table 2a and Table 2b present selected geometrical details concerning the ruthenium coordination and the neighbourhood of the coordinating oxygen atom. Table 2a presents the comparison of the geometry of the **3c** and **3a** compounds, whereas the Table 2b contains the comparison of the **3c** with the Hoveyda catalyst **1h**.<sup>5</sup> It is easily visible that the O2 atom is bound more closely to the ruthenium when replacing the second chlorine atom in the carboxyl-substituted compound. The geometry of the square pyramid ruthenium coordination typical for the Hoveyda-type catalysts is not disturbed by the replacement of the chlorine by oxygen, according to the table 2b. The valence angles values in the case of both structures are very similar.

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[4] Theoretical and structural studies on such O–Ru  $\pi$ -type conjugation are undergoing and will be published by us in the due course; b) M. Barbasiewicz, M. Bieniek, A. Michrowska, A. Szadkowska, A. Makal, K. Woźniak, K. Grela, *Adv. Synth. Catal.* **2007**, *349*, 193–203.

[5] S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168.

Table 2a.

<b>BONDS</b>	<b>3a</b>	<b>3c</b>
<i>Ru(1)-C(4) C(22)</i>	1.820(3)	1.832(2)
<i>Ru(1)-C(1)</i>	1.984(3)	1.9812(19)
<i>Ru(1)-O(1)</i>	2.207(2)	2.2286(14)
<i>Ru(1)-Cl(1)</i>	2.3583(10)	2.3222(5)
<i>Ru(1)-Cl(2)</i>	2.3560(11)	-
<i>Ru(1)-O(2)</i>	2.536(2)	2.0553(14)
<i>O(2)-C(6) C(25)</i>	1.194(4)	1.291(2)
<i>O(1)-C(36) C(31)</i>	1.371(4)	1.409(2)
<i>O(1)-C(5) C(24)</i>	1.442(4)	1.466(2)
<b>ANGLES</b>		
<i>C(4) C(22)-Ru(1)-C(1)</i>	100.47(14)	102.12(9)
<i>C(4) C(22)-Ru(1)-O(1)</i>	81.19(12)	81.89(7)
<i>C(1)-Ru(1)-O(1)</i>	176.56(12)	173.81(7)
<i>C(4) C(22)-Ru(1)-Cl(1)</i>	94.67(12)	102.50(6)
<i>C(1)-Ru(1)-Cl(1)</i>	91.61(10)	90.74(6)
<i>O(1)-Ru(1)-Cl(1)</i>	85.24(7)	93.01(4)
<i>C(4) C(22)-Ru(1)-Cl(2)</i>	97.75(12)	-
<i>C(1)-Ru(1)-Cl(2)</i>	94.97(10)	-
<i>O(1)-Ru(1)-Cl(2)</i>	87.76(7)	-
<i>Cl(1)-Ru(1)-Cl(2)</i>	164.63(3)	-
<i>C(4) C(22)-Ru(1)-O(2)</i>	147.16(10)	97.23(7)
<i>C(1)-Ru(1)-O(2)</i>	112.35(5)	97.79(7)
<i>O(1)-Ru(1)-O(2)</i>	66.01(11)	76.89(5)
<i>Cl(1)-Ru(1)-O(2)</i>	84.51(6)	156.35(4)
<i>C(36)-O(1)-C(5) C(31)-O(1)-C(24)</i>	121.8(3)	114.95(15)
<i>C(36)-O(1)-Ru(1) C(31)-O(1)-Ru(1)</i>	110.39(19)	107.43(11)
<i>C(5)-O(1)-Ru(1) C(24)-O(1)-Ru(1)</i>	126.0(2)	105.37(11)
<i>O(2)-C(6)-C(5) O(2)-C(25)-C(24)</i>	125.6(3)	117.77(18)
<i>C(6)-O(2)-Ru(1) C(25)-O(2)-Ru(1)</i>	112.48(19)	116.24(13)

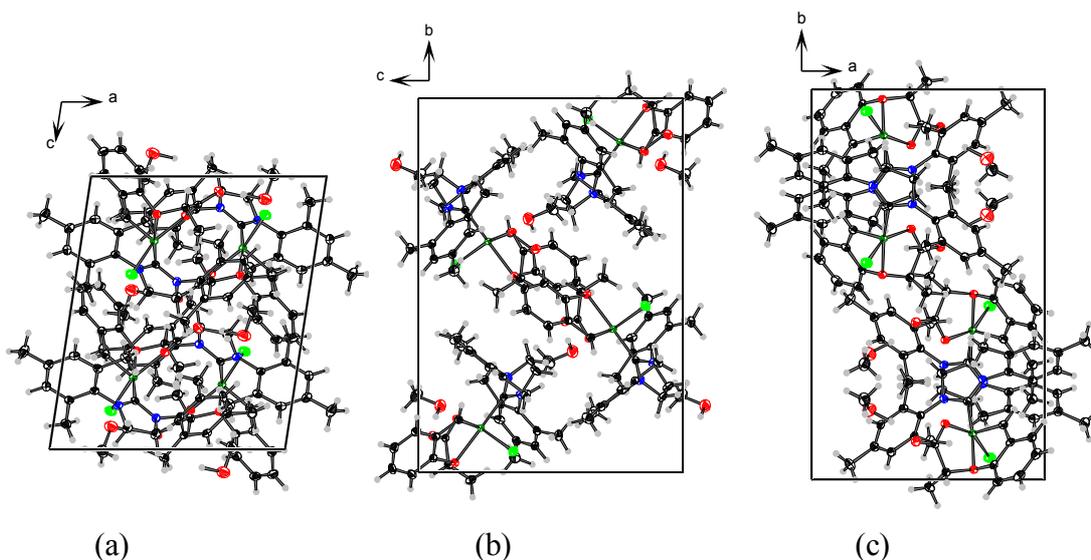
Table 2b.

<b>BONDS</b>	<b>1h</b>	<b>3c</b>
<i>Ru(1)-C(22)</i>	1.8286(15)	1.832(2)
<i>Ru(1)-C(1)</i>	1.9791(15)	1.9812(19)
<i>Ru(1)-O(1)</i>	2.2562(10)	2.2286(14)
<i>Ru(1)-Cl(1)</i>	2.3279(4)	2.3222(5)
<i>Ru(1)-Cl(2) O(2)</i>	2.3380(4)	2.0553(14)
<i>O(2)-C(25)</i>	-	1.291(2)
<i>O(1)-C(26) C(31)</i>	1.3701(18)	1.409(2)
<i>O(1)-C(23) C(24)</i>	1.4694(18)	1.466(2)

**ANGLES**

<b>C(22)-Ru(1)-C(1)</b>	101.33(6)	102.12(9)
<b>C(22)-Ru(1)-O(1)</b>	79.43(5)	81.89(7)
<b>C(1)-Ru(1)-O(1)</b>	176.06(5)	173.81(7)
<b>C(22)-Ru(1)-Cl(1)</b>	100.19(5)	102.50(6)
<b>C(1)-Ru(1)-Cl(1)</b>	96.76(4)	90.74(6)
<b>O(1)-Ru(1)-Cl(1)</b>	86.88(3)	93.01(4)
<b>C(22)-Ru(1)-Cl(2) O(2)</b>	100.39(5)	97.23(7)
<b>C(1)-Ru(1)-Cl(2) O(2)</b>	90.69(4)	97.79(7)
<b>O(1)-Ru(1)-Cl(2) O(2)</b>	85.37(3)	76.89(5)
<b>Cl(1)-Ru(1)-Cl(2) O(2)</b>	156.251(15)	156.35(4)
<b>C(26)-O(1)-C(23) C(31)-O(1)-C(24)</b>	119.93(12)	114.95(15)
<b>C(26)-O(1)-Ru(1) C(31)-O(1)-Ru(1)</b>	110.10(9)	107.43(11)
<b>C(23)-O(1)-Ru(1) C(24)-O(1)-Ru(1)</b>	129.79(9)	105.37(11)
<b>O(2)-C(25)-C(24)</b>	-	117.77(18)
<b>C(25)-O(2)-Ru(1)</b>	-	116.24(13)

The crystal structure of the **3c** (see Figure 2) seems to be stabilized mainly by weak C – H interactions among the carbon atoms from aromatic rings and the hydrogens from the methyl groups, including the methyl group of the solvent. There are some short contacts between the O1S solvent oxygen and the H17 and H21C hydrogens from the methyl group (2.473(3) and 2.552(3) Å accordingly as well as one short contact between the Cl1 chlorine and H15 (2.814(3) Å). The overall packing is rather close, with the solvent molecule located neatly under the NHC substituent on the opposite site with respect to the styrenyl ligand. The packing in the min crystallographic directions was presented on the Figure 2.



**Figure 2.** The R013501 packing visualized along: the X direction (a), the Y direction (b) and along the Z direction (c)

### 2.3. X-ray data collection and structure refinement

The structure of **3c** complex was determined in single-crystal X-ray diffraction experiment. The measurement was performed on a Kuma KM4CCD  $\kappa$ -axis diffractometer with graphite-monochromated Mo K $\alpha$  radiation (50.0 kV, 40.0 mÅ) at liquid nitrogen temperature (100K). The crystal (0.32x0.22x0.02mm) was positioned at 62 mm from the KM4CCD camera. The frames were measured at 1.0° intervals with 12 seconds exposition time pre frame. The analytical absorption correction was applied to all the collected datasets, and the transmittance maximal and minimal values are reported in Table 3. Data reduction and analysis were carried out with CrysAlisCCD and CrysAlisRED Kuma Diffraction programs.

The structure was solved by direct methods approach using the SHELXS-97 program<sup>6,7</sup> Then refinement was carried out with the SHELXL-97. The refinement was based on  $F^2$  for all reflections except those with negative intensities. Weighted R factors wR and all goodness-of-fit S values were based on  $F^2$ , whereas conventional R factors were based on the amplitudes, with  $F$  set to zero for negative  $F^2$ . The  $F_0^2 > 2\sigma(F_0^2)$  criterion was applied only for R factors calculation was not relevant to the choice of reflections for the refinement. The R factors based on  $F^2$  are for both structures about twice as large as those based on  $F$ . Most of the hydrogen atoms were located in idealized geometrical positions and their thermal displacement parameters were constrained on the basis of thermal displacement parameters of the neighbouring atoms. One exception was a hydrogen atom from the hydroxyl group of the solvent molecule, engaged in strong hydrogen bond, where both position and thermal displacement parameter was left free to vary. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol. C.<sup>8</sup>

Table 3. Crystal data and structure refinement for **3c**.

Identification code	r003501
Empirical formula	C <sub>32</sub> H <sub>39</sub> C <sub>1</sub> N <sub>2</sub> O <sub>4</sub> Ru
Formula weight	652.17
Temperature	100 (2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.6477 (6) Å alpha = 90deg b = 19.2179 (10) Å beta = 98.575 (4) deg. c = 13.7667 (7) Å gamma = 90 deg.
Volume	3047.2 (3) Å <sup>3</sup>
Z, Calculated density	4, 1.422 Mg/m <sup>3</sup>

[6] G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467–473.

[7] G. M. Sheldrick, SHELXL93. *Program for the Refinement of Crystal Structures.*, Univ. of Göttingen, Germany.

[8] *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer:Dordrecht, **1992**, Vol. C.

Absorption coefficient	0.641 mm <sup>-1</sup>
F(000)	1352
Crystal size	0.32x0.22x0.02mm
Theta range for data collection	3.18 to 27.50 deg.
Limiting indices	-15<=h<=14, -22<=k<=24, -17<=l<=16
Reflections collected / unique	27587/6946 [R(int) = 0.0185]
Completeness to theta = 27.50	99.4%
Absorption correction	Analytical
Max. and min. transmission	0.9668 and 0.7495
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6946 / 0 / 373
Goodness-of-fit on F <sup>2</sup>	1.159
Final R indices [I>2sigma(I)]	R1=0.0309, wR2 = 0.0715
R indices (all data)	R1=0.0368, wR2 = 0.0758
Largest diff. peak and hole	0.945 and -0.434 e. Å <sup>-3</sup>

The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 648129

## 2.4. Formation and isolation of **3b**

To a **3c** (62.0 mg, 0.1 mmol) in 2 mL CH<sub>2</sub>Cl<sub>2</sub>, a solution of HCl in THF was added (0.1 M, 1.0 mL, 0.1 mmol). Resulting solution was stirred under argon at room temperature for 30 min. The reaction mixture was concentrated under vacuum and crystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane to afford **3b** as green microcrystalline solid (59.4 mg, 90%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 16.74 (s, 1H; 1-H), 10.55 (bs, 1H; 19-H), 7.56–7.58 (m, 1H; 5-H), 7.09 (s, 4H; 16-H), 7.00–7.03 (m, 2H; 4-H, 6-H), 6.80 (d, *J* = 8.15 Hz, 1H; 3-H), 4.96 (q, *J* = 6.84 Hz, 1H; 8-H), 4.22 (s, 4H; 11-H), 2.46 (bs, 6H; 12-H), 2.43 (s, 6H; 13-H), 2.42 (s, 6H; 12'-H), 1.40 (d, *J* = 6.84 Hz, 3H; 9-H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 299.1 (C1), 208.8 (C10), 170.1 (C18), 151.2 (C7), 143.7 (C2), 139.2, 130.7, 129.6, 129.5, 124.5 (C4), 123.1 (C3), 111.9 (C6), 51.5 (C11), 22.3 (C13), 18.5 (C12), 16.6, 14.0; IR (film from CH<sub>2</sub>Cl<sub>2</sub>): ν = 3510, 3053, 2977, 2919, 2736, 2552, 1761, 1662, 1606, 1595, 1575, 1481, 1453, 1443, 1400, 1378, 1327, 1297, 1264, 1203, 1158, 1130, 1109, 1076, 1024, 989, 936, 920, 854, 825, 799, 748, 703, 645, 610, 579, 550, 498, 472, 436, 421 cm<sup>-1</sup>

## 2.5. In situ formation of **3b** and **3d**, **3e**

To a stirred solution of **3c** (62.0 mg, 0.1 mmol) in 2 mL CH<sub>2</sub>Cl<sub>2</sub> a solution of HCl in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M, 1.0 mL, 0.1 mmol), a solution of TfOH in CH<sub>2</sub>Cl<sub>2</sub> (0.05 M, 2.0 mL, 0.1 mmol) or a solution of perfluorononanoic acid (46.4 mg, 0.1 mmol) in AcOEt (0.5 mL) was added. The resulting solution was stirred under argon at room temperature for 30 min. After this time the resulted *in situ* formed complexes **3b**, **3d**, and **3e** are ready to be used for metathesis reactions. In a separate experiment the

reaction mixture was concentrated under vacuum and dissolved in CDCl<sub>3</sub>. The <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) analysis shows complete conversion of **3c** into a new complex. The diagnostic benzyldiene proton shifts: **3b** δ = 16.74; **3d** δ = 17.24 and **3e** δ = 16.67 ppm.

### 3. Representative procedure of metathesis and catalyst recovery

A reaction flask equipped with a magnetic stirring bar was charged under argon with a solution of catalyst **3b**, **3c** (or prepared *in situ* catalysts **3b**, **3d**, **3e**) (5 mol%) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). A solution of dienophile **4a** (50.3 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added and the reaction mixture was stirred for 1–24 h at 40 °C. The reaction mixture was passed through a cartridge/pipette containing silica gel (0.6–1.0 g). The cartridge was washed with an additional portion of CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and then with EtOAc (5 mL). The CH<sub>2</sub>Cl<sub>2</sub> fraction was concentrated under reduced pressure to yield N-*p*-tosyl-2,5-dihydro-1*H*-pyrrole (**5a**) as a colourless solid (40.2 mg, 90% of yield, >95% purity (GC)). After evaporation of the EtOAc fraction catalyst **3c** was obtained as a green microcrystalline solid (5.9 mg, 95% of yield, 96% purity (NMR)).



a)



b)

**Figure 3.** Efficiency of silica gel removal of **3b** (left), **1h** (center) and **1a** (right) after RCM of **4b** (5 mol % of Ru-catalyst, 2 h, 40 °C, DCM). a) - b) Different stages of DCM elution.

## 4. Copies of MS and NMR spectra

### 4.1. MS (FD/TOF) Isotopic pattern of 3c

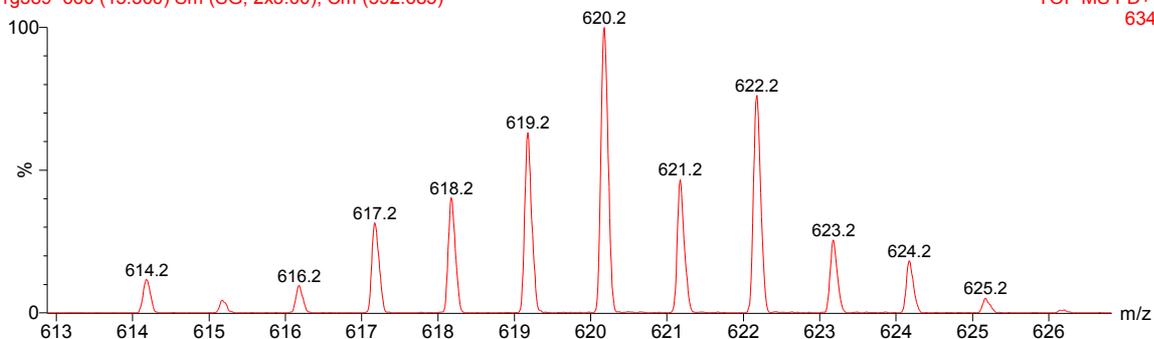
R003301; R. Gawin  
operator: Grzegorz Spólnik

CAB013

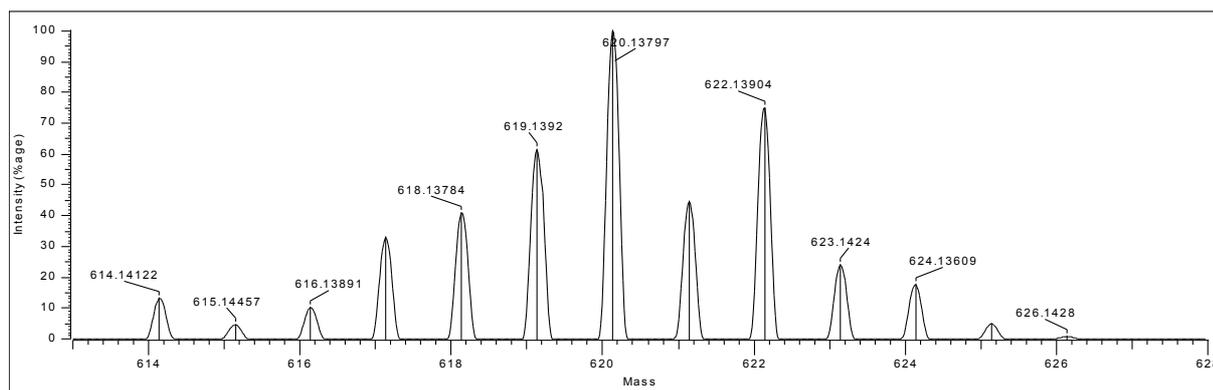
15:05:59 29-Jan-2007

rg389 660 (15.300) Sm (SG, 2x3.00); Cm (592:685)

TOF MS FD+  
634

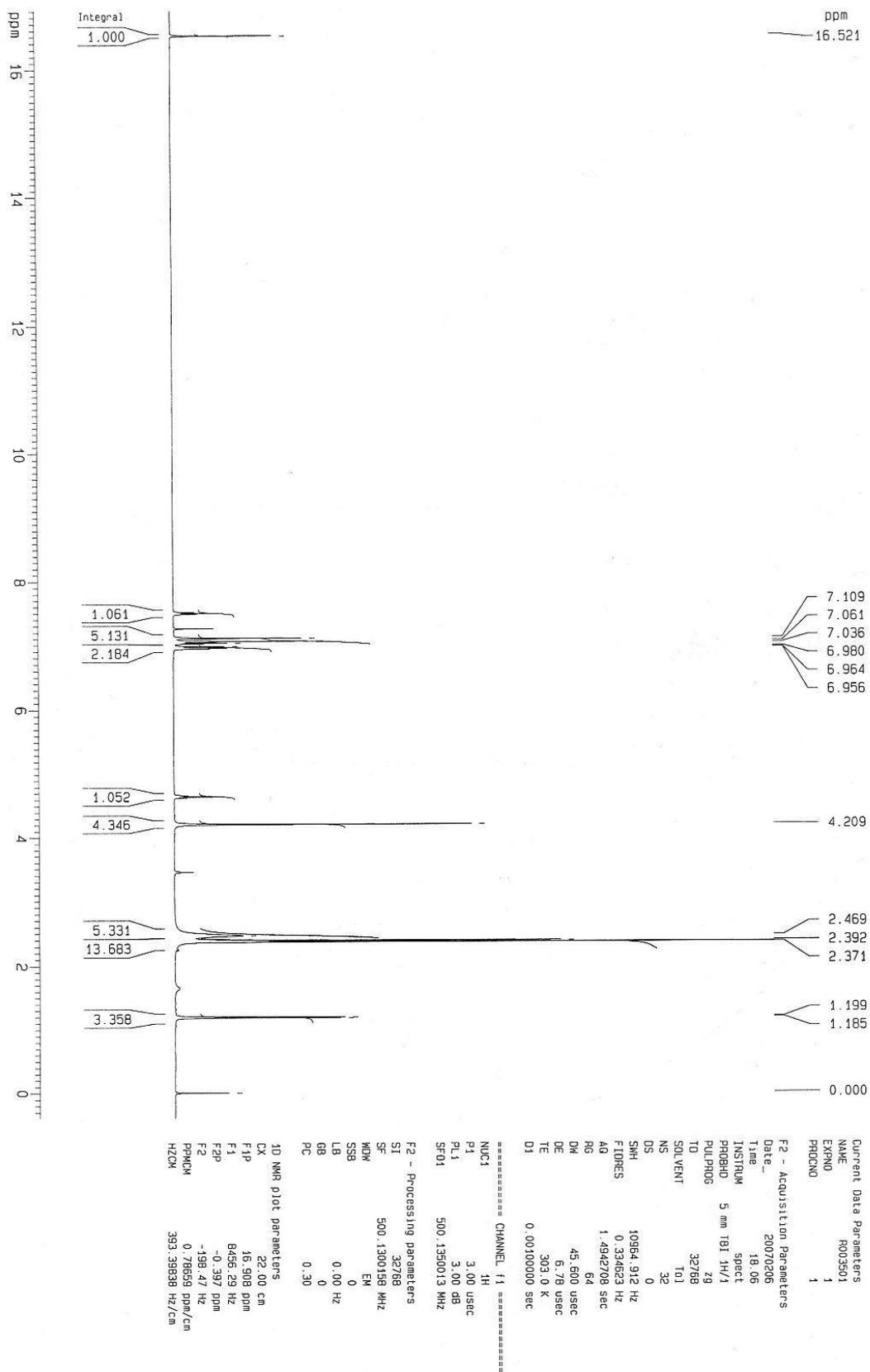


a) experimental isotopic pattern for 3c

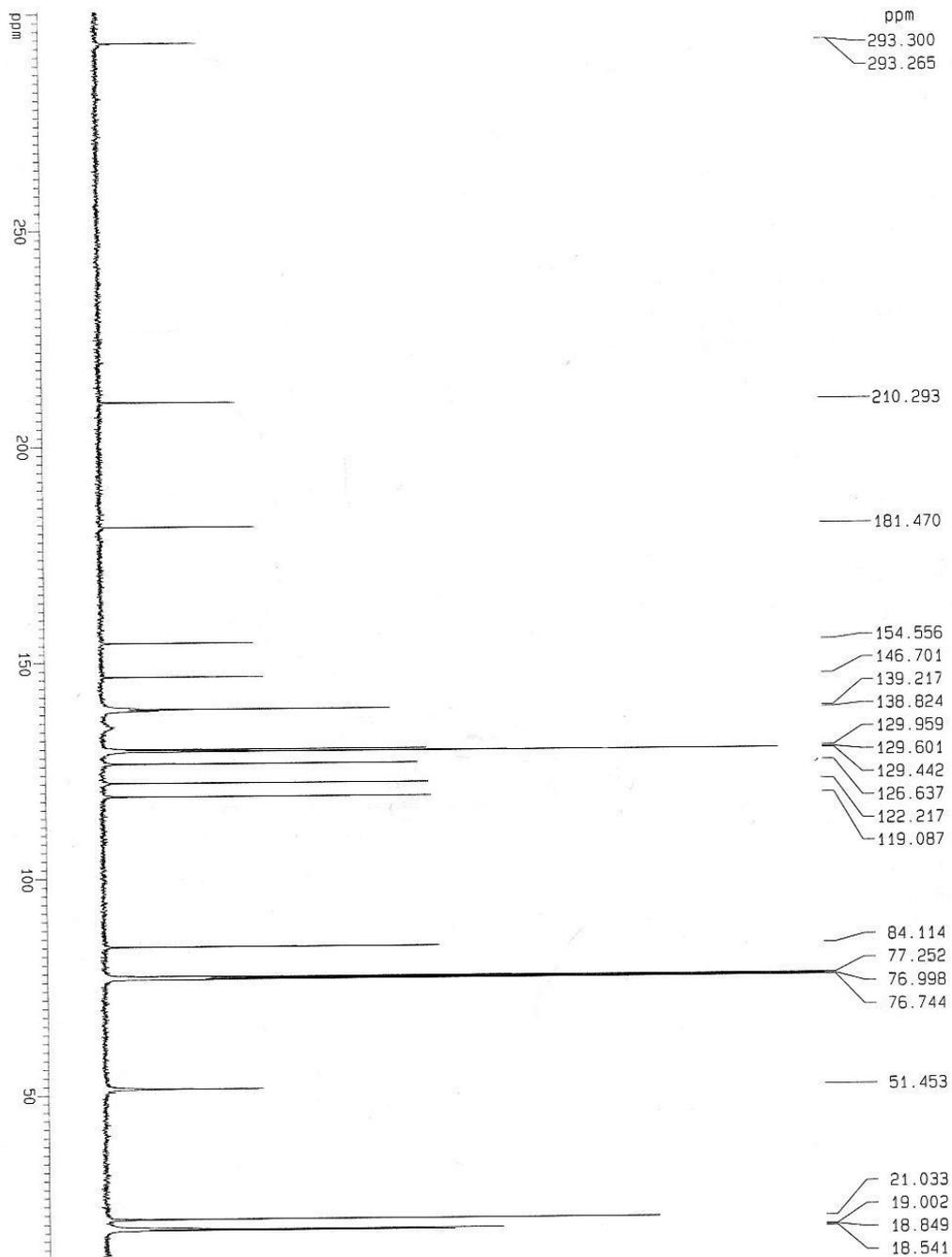


b) theoretical isotopic pattern for 3c

## 4.2. <sup>1</sup>H NMR spectrum of 3c



### 4.3. <sup>13</sup>C NMR spectrum of 3c



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 EXPNO 4  
 PROCNO 1

F2 - Acquisition Parameters  
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 Time 23.38

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 SOLVENT DMSO  
 NS 29355  
 DS 0

SMH 45454.547 Hz  
 FIDRES 0.693581 Hz  
 AQ 0.7209460 sec  
 RG 2500

DW 11.000 usec  
 DE 7.10 usec  
 TE 303.0 K

D1 0.50000000 sec  
 D11 0.03000000 sec  
 D12 0.0002000 sec

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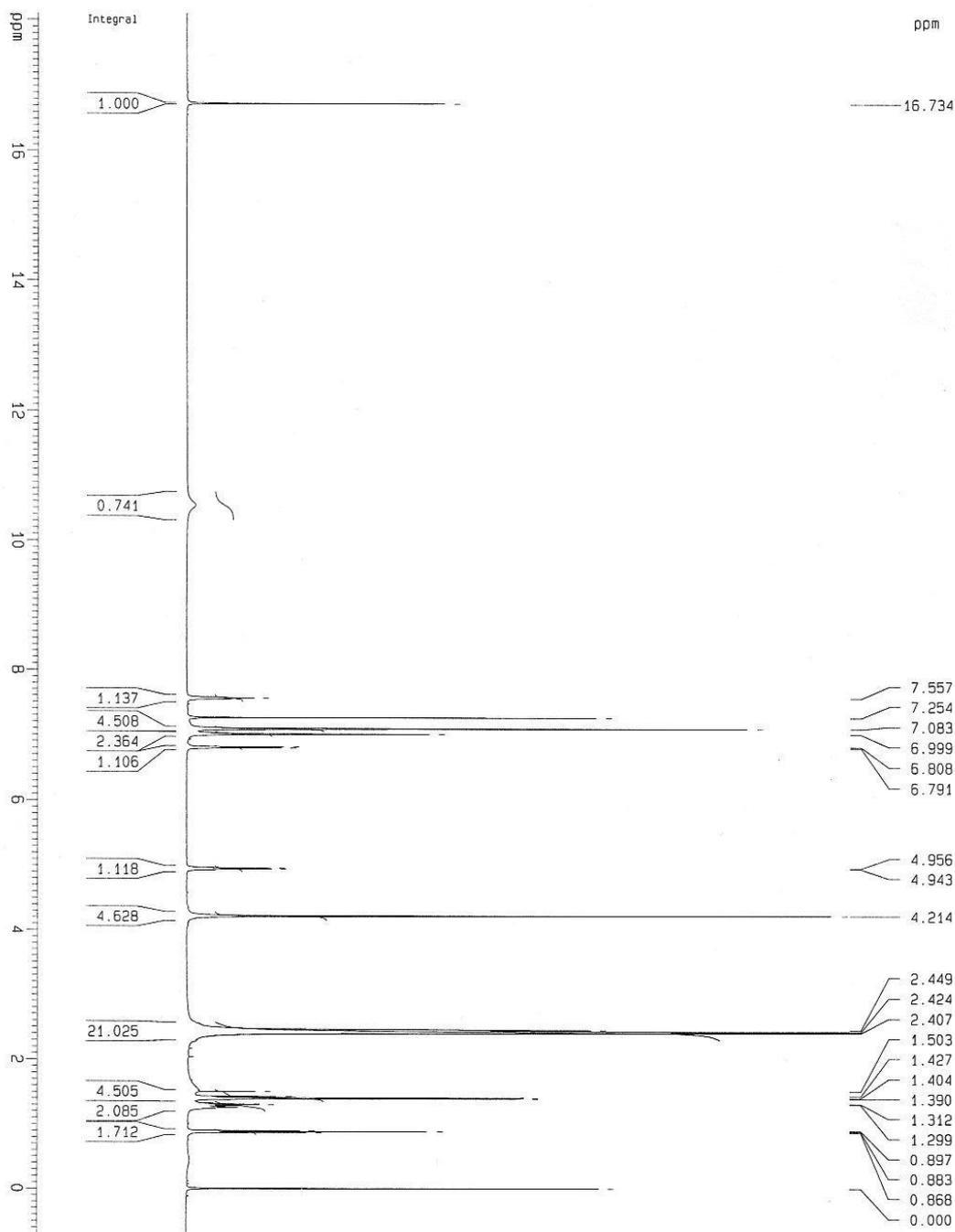
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 PL13 32.00 dB  
 SF02 500.1335009 MHz

F2 - Processing parameters  
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 LB 4.00 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
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 F2P 10.159 ppm  
 F2 1277.52 Hz

PPMCK 13.19977 ppm/cm  
 HZCM 1659.97412 Hz/cm

# 4.4. <sup>1</sup>H NMR spectrum of 3b



```

Current Data Parameters
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PROCNO   1

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RG        128
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DE        6.78 usec
TE        303.0 K
D1        0.00100000 sec

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PL1       3.00 dB
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GB        0
PC        7.00

1D NMR plot parameters
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F1        9051.44 Hz
F2P       -0.726 ppm
F2        -363.10 Hz
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HZCM     427.93387 Hz/cm
    
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