# Latent ruthenium based olefin metathesis catalyst with a sterically demanding NHC ligand

**Anita Leitgeb,[a] Mudassar Abbas,[a] Roland C. Fischer,[b] Albert Poater,[c,d] Luigi Cavallo[e] and Christian Slugovc[a,]***

***ESI***

All reactions were carried out under nitrogen in pre-dried glassware using Schlenk techniques if not noted otherwise. Materials were obtained from commercial sources (Aldrich, Fluka or Alfa Aesar) and were used without further purification. NMR ($^{1}H$, $^{13}C$) spectra were recorded on a Bruker Avanze 300MHz and INOVA 500 MHz spectrometer, respectively in $CDCl_3$. Chemical shifts are given in ppm relative to a $SiMe_4$ standard. The solvent peak of $CDCl_3$ was used for referencing the NMR spectra to 7.26 ($^{1}H$) and 77.16 ppm ($^{13}C$), respectively.

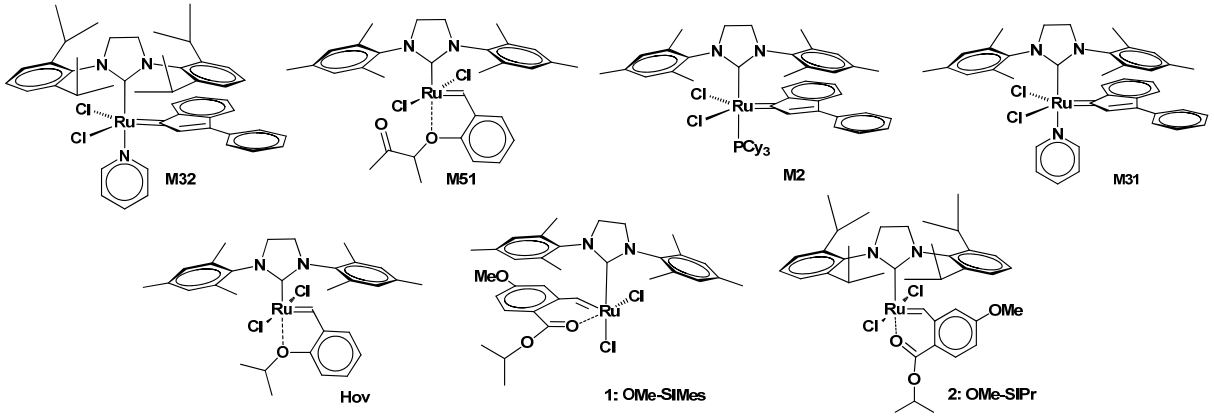



Figure 1: Ruthenium catalysts employed in the study

**(SPY-5-31)-dichloro-(κ²(C,O)-(2-iso-propyl ester-5-methoxy benzylidene)-(1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene)-ruthenium (2)**

SIPr-py complex **M31** (400mg, 0.48 mmol, 1 eq) was dissolved in 15 mL of freshly degassed DCM. Vinyl ligand **L-1** (1.3 eq, 137 mg, 0.63 mmol) was added. The mixture was stirred for 48 h at room temperature, whilst the colour turned from red to green. The solvent was reduced to 3 mL, precipitation with n-pentane yielded a light green powder. Several washings using ultrasonic wave completely removed residual ligand and other impurities. The final clean complex was isolated 72% yield (267 mg). Crystals were obtained by dissolving a small amount of the complex in DCM and

overlaying it with n-pentane in a loosely closed glass vial. XRD revealed 1 eq of DCM in the crystal structure, which is also confirmed by elemental analysis.

$^{1}$H-NMR ($CDCl_3$): 18.49 (s, 1H, Ru=C*H*); 8.00-7.97(d, 1H, $^{3}J_{HH}$ = 8.7 Hz, lig$^{5}$); 7.53 (t, 2H, $^{3}J_{HH}$ = 7.3 Hz, SIPr$^{4}$); 7.39-7.37 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz, SIPr$^{3}$); 7.26-7.01 (dd, 1H, $^{3}J_{HH}$ = 6.1 Hz, $^{4}J_{HH}$ = 2.6 Hz, lig$^{4}$); 6.13-6.12 (d, 1H, $^{4}J_{HH}$ = 2.6 Hz, lig$^{2}$); 5.30 (s, $CH_2Cl_2$); 5.15 (hep, 1H, lig$^{Pri}$); 4.12 (s, 4H, $NCH_2$); 3.83 (s, 3H, OMe); 3.69 (bhep, 4H, SIPr$^{Pri}$); 1.35-1.18 (30H, lig$^{Me}$, SIPr$^{Me}$).

$^{13}$C-NMR ($CDCl_3$) 299.3(1C, Ru=*C*); 214.2 (1C, NCN); 172.8 (1C, C=O); 165.0, 160.1, 149.7, 149.1, 137.3, 134.2, 129.5, 124.8, 115.0, 113.9, 109.0 (18C, 2mes$^{1-6}$, bz$^{1-6}$); 71.7 (1C, OPr$^{i}$); 55.9 (1C, OMe); 54.6 (2C, NCCN), 53.6 ($CH_2Cl_2$); 28.7 (2C, mesPr$^{i}$); 26.6 (2C, mesPr$^{i}$), 24.2 (8C, $CH_3^{mes}$); 21.7 (2C, $OC(CH_3)_2$).

Elemental analysis of **6** calculated for $C_{40}H_{54}Cl_4N_2O_3Ru$ (853.75 g/mol): C, 56.27; H, 6.38; N, 3.28; found (Ø): C, 56.34; H, 6.37; N, 3.59.

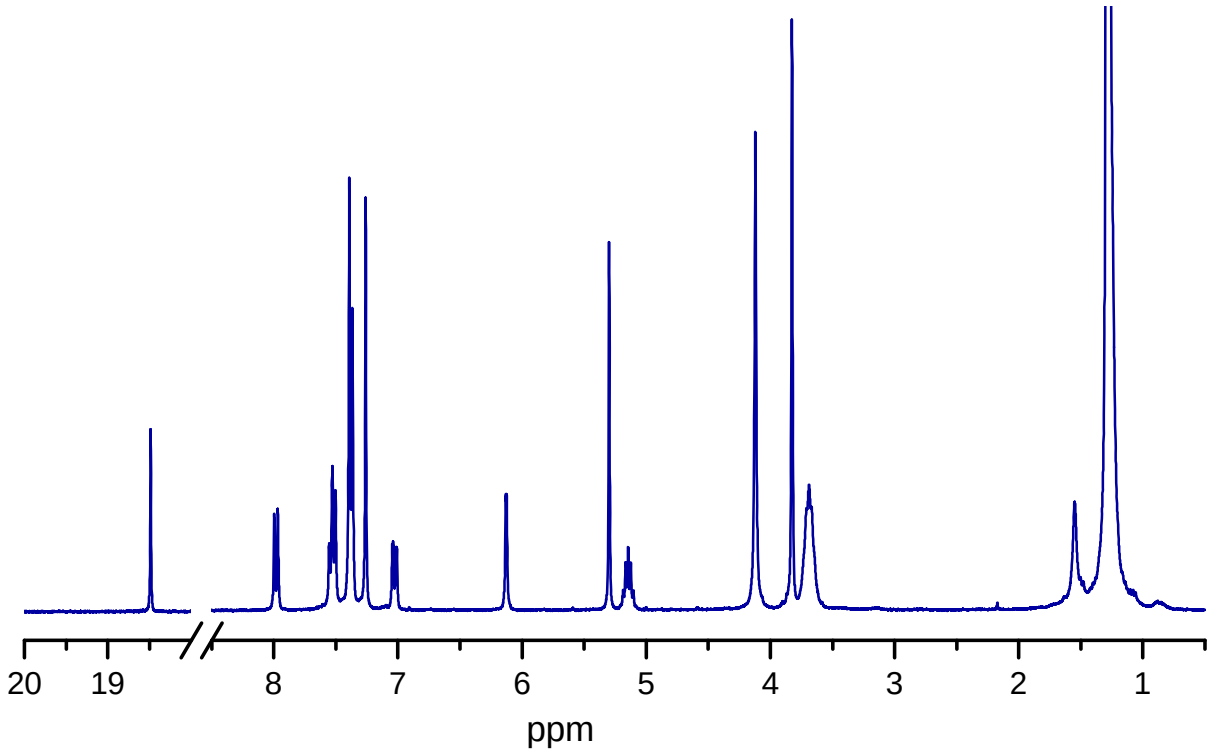



Figure 2: *trans* Dichloro complex **2** ($^{1}$H-NMR, $CDCl_3$, 300 MHz)

**(SPY-5-34)-dichloro-(κ$^2$(C,O)-(2-iso-propyl ester-5-methoxy benzylidene)-(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)-ruthenium (1)**

Preparation of complex 6a has already been published in Zirngast, M.; Pump, E.; Leitgeb, A.; Albering, J. H.; Slugovc, C. *Chem. Commun.* **2011**, *47*, 2261-2263.

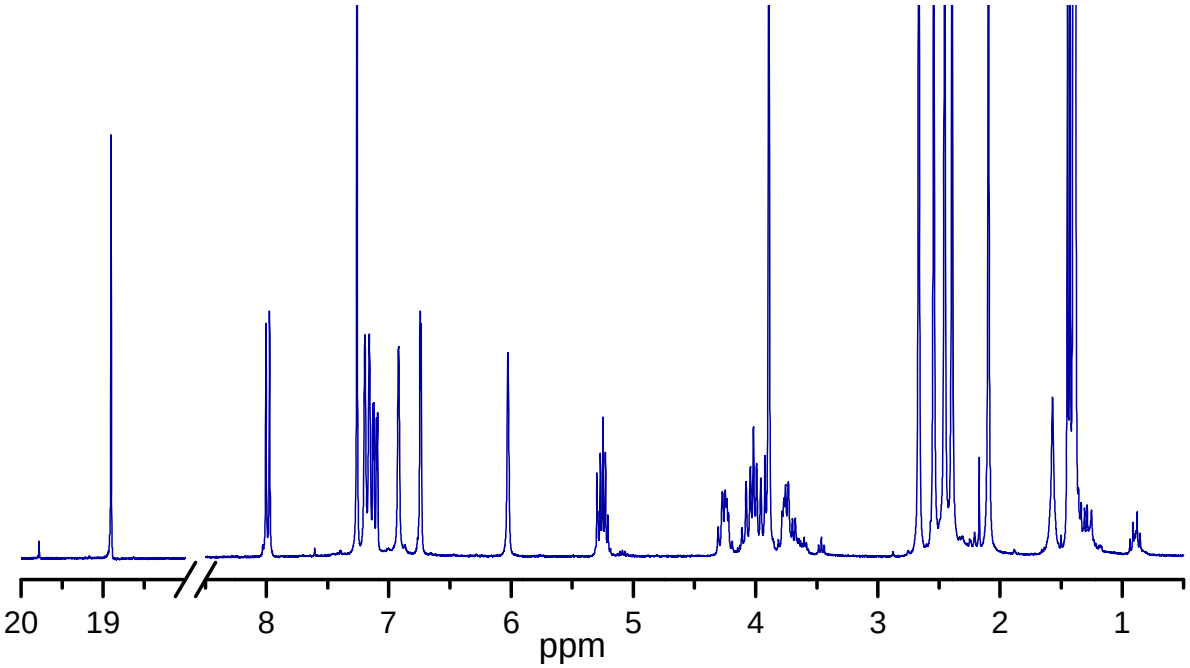



Figure 3: *cis* Dichloro complex **1** ($^1$H-NMR, $CDCl_3$, 300 MHz)

## STRUCTURAL COMPARISON OF 1 (SIMES) AND 2 (SIPR)

It was possible to obtain crystal structures from the complexes featuring a methoxy substituted ligand. The opposite chloride configuration of the two structures that had been suggested due two $^1$H-NMR spectra was confirmed. In the following tables, structure determining bond features are summarized.

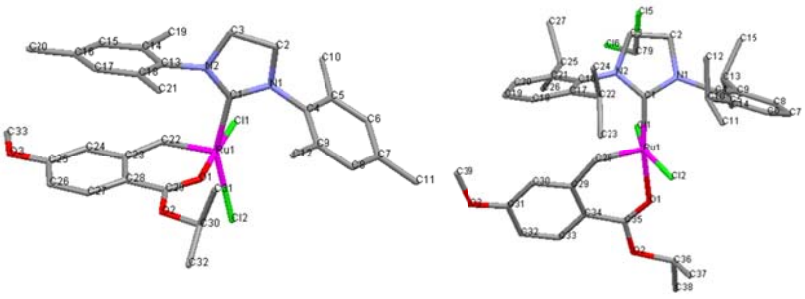


Figure 4: Crystal structures of 1: *cis*-dichloro config. (left) and 2: *trans*-dichloro config. (right)

Table 1: Selected bond lengths

| 1: SIMes | | | 2 -SIPr | | |
|---|---|---|---|---|---|
| **Atom1** | **Atom2** | **Length (Å)** | **Atom1** | **Atom2** | **Length (Å)** |
| Ru1 | Cl1 | 2.3708(5) | Ru1 | Cl1 | 2.3401(5) |
| Ru1 | Cl2 | 2.3643(5) | Ru1 | Cl2 | 2.3461(5) |
| Ru1 | C1 | 2.020(2) | Ru1 | C1 | 1.998(2) |
| Ru1 | C22 | 1.811(2) | Ru1 | C28 | 1.820(2) |
| Ru1 | O1 | 2.092(1) | Ru1 | O1 | 2.132(1) |
| N2 | C1 | 1.345(2) | N2 | C1 | 1.359(2) |
| N2 | C3 | 1.481(2) | N2 | C3 | 1.481(3) |
| N1 | C1 | 1.346(2) | N1 | C1 | 1.361(2) |
| N1 | C2 | 1.481(2) | N1 | C2 | 1.477(3) |
| C3 | C2 | 1.524(3) | C3 | C2 | 1.517(3) |

Table 2: Selected bond angles

| 1: SIMes | | | | 2: SIPr | | | |
|---|---|---|---|---|---|---|---|
| **Atom1** | **Atom2** | **Atom3** | **Angle (°)** | **Atom1** | **Atom2** | **Atom3** | **Angle (°)** |
| Cl1 | Ru1 | Cl2 | 91.48(2) | Cl1 | Ru1 | Cl2 | 159.05(2) |
| Cl1 | Ru1 | C1 | 90.30(5) | Cl1 | Ru1 | C1 | 88.53(5) |
| Cl1 | Ru1 | C22 | 90.16(6) | Cl1 | Ru1 | C28 | 98.47(6) |
| Cl1 | Ru1 | O1 | 177.64(4) | Cl1 | Ru1 | O1 | 84.73(4) |
| Cl2 | Ru1 | O1 | 86.23(4) | Cl2 | Ru1 | O1 | 85.51(4) |
| C1 | Ru1 | C22 | 98.14(8) | C1 | Ru1 | C28 | 99.56(8) |
| C22 | Ru1 | O1 | 90.04(7) | C28 | Ru1 | O1 | 88.76(7) |
| C1 | N1 | C2 | 113.1(2) | C1 | N1 | C2 | 111.8(2) |

Table 3: Distortion of NHC ligand

| | **Atom1** | **Atom2** | **Atom3** | **Atom4** | **Torsion (°)** |
|---|---|---|---|---|---|
| **1: SIMes** | N1 | C2 | C3 | N2 | 6.8 (2) |
| **2: SIPr** | N1 | C2 | C3 | N2 | 23.2 (2) |

Table 4: Burried volume of NHC

| | $V_{bur}$ [a] |
|---|---|
| **1: SIMes** | 32.8% |
| **2: SIPr** | 33.6% |

[a] (sambVca web application https://www.molnac.unisa.it/OMtools/sambvca.php)

## COMPUTATIONAL DETAILS

All the DFT static calculations were performed at the GGA level with the Gaussian09 set of programs,[1] using the BP86 functional of Becke and Perdew.[2] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, O, and Cl (SVP keyword in Gaussian).[3] For Ru we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set contracted (standard SDD keywords in gaussian09).[4] The geometry optimizations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations. The BP86 and M06 reported energies have been optimized via single point calculations on the BP86/SVP geometries with a triple zeta valence plus 1 polarization function on main group atoms (TZVP keyword in Gaussian). Solvent effects were estimated with the polarizable continuum solvation model PCM using dichloromethane as solvent.[5] The D3 dispersion term of the reported BP86-D3 energies were obtained with the dftd3 code of Grimme"

Table 5: Coordinate data sets for DFT optimized complexes

| **1-cis** | | | | **1-trans** | | | |
|---|---|---|---|---|---|---|---|
| Ru | 0.510311 | -0.103916 | -0.920904 | Ru | -0.477347 | 0.226170 | 0.295203 |
| Cl | 0.366998 | -1.856153 | -2.545452 | Cl | -0.684006 | 0.018664 | 2.646047 |
| Cl | 1.562907 | 1.268394 | -2.535435 | Cl | -1.164964 | 0.832654 | -1.878977 |
| O | 0.702352 | 1.567756 | 0.343520 | O | -0.581408 | 2.365484 | 0.644325 |
| O | 0.301327 | 3.696173 | 0.952780 | O | -0.037161 | 4.532896 | 0.393270 |
| O | -5.566435 | 2.564862 | -1.034634 | O | 5.712665 | 2.333575 | -0.927637 |
| N | 1.865809 | -2.017914 | 0.823041 | N | -1.968083 | -2.307008 | 0.055717 |
| N | -0.303846 | -2.383612 | 1.022978 | N | 0.173306 | -2.796312 | 0.237249 |
| C | 0.628784 | -1.569830 | 0.441658 | C | -0.707130 | -1.743107 | 0.118481 |
| C | 1.804896 | -3.291428 | 1.565741 | C | -1.969310 | -3.758854 | 0.311435 |
| H | 2.130499 | -4.136345 | 0.918450 | H | -2.355882 | -3.971113 | 1.333898 |
| H | 2.469403 | -3.263653 | 2.453801 | H | -2.621100 | -4.287174 | -0.414705 |
| C | 0.312680 | -3.381057 | 1.927887 | C | -0.486417 | -4.117986 | 0.166297 |
| H | 0.112052 | -3.109721 | 2.990131 | H | -0.256188 | -4.611083 | -0.806869 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.114936 | -4.388794 | 1.752063 | H | -0.118307 | -4.784647 | 0.973127 |
| C | 3.109291 | -1.361426 | 0.512816 | C | -3.221178 | -1.644410 | -0.206071 |
| C | 3.915746 | -1.812865 | -0.566869 | C | -4.075180 | -1.260002 | 0.861728 |
| C | 5.123730 | -1.129726 | -0.815039 | C | -5.297499 | -0.631110 | 0.539921 |
| H | 5.745062 | -1.461132 | -1.663767 | H | -5.954042 | -0.309115 | 1.366012 |
| C | 5.557062 | -0.048482 | -0.024856 | C | -5.710117 | -0.422196 | -0.788218 |
| C | 4.760062 | 0.331535 | 1.073902 | C | -4.878235 | -0.899589 | -1.821495 |
| H | 5.099691 | 1.149410 | 1.731888 | H | -5.200512 | -0.788588 | -2.870619 |
| C | 3.543553 | -0.311428 | 1.367288 | C | -3.644023 | -1.520403 | -1.559601 |
| C | 3.521304 | -2.994047 | -1.418739 | C | -3.755358 | -1.574907 | 2.303926 |
| H | 3.579280 | -3.945843 | -0.845232 | H | -4.031657 | -2.626428 | 2.544442 |
| H | 2.483614 | -2.888986 | -1.805682 | H | -2.681261 | -1.434256 | 2.537935 |
| H | 4.201959 | -3.093815 | -2.286600 | H | -4.337923 | -0.925916 | 2.987529 |
| C | 6.831071 | 0.694442 | -0.357184 | C | -7.004421 | 0.293392 | -1.104550 |
| H | 7.280579 | 1.163957 | 0.541386 | H | -7.527194 | -0.168030 | -1.967881 |
| H | 7.588466 | 0.026482 | -0.815415 | H | -7.697774 | 0.291875 | -0.239406 |
| H | 6.630737 | 1.508176 | -1.088682 | H | -6.814528 | 1.355958 | -1.373586 |
| C | 2.732323 | 0.093804 | 2.576439 | C | -2.804229 | -2.052595 | -2.696080 |
| H | 1.769745 | 0.556709 | 2.276608 | H | -1.889863 | -1.434917 | -2.819118 |
| H | 2.486274 | -0.777769 | 3.219598 | H | -2.482916 | -3.101068 | -2.519347 |
| H | 3.287859 | 0.823908 | 3.197715 | H | -3.369010 | -2.025385 | -3.648759 |
| C | -1.734242 | -2.261813 | 1.002199 | C | 1.607321 | -2.796888 | 0.176305 |
| C | -2.491119 | -3.144614 | 0.188231 | C | 2.347744 | -2.941261 | 1.378539 |
| C | -3.897456 | -3.064121 | 0.254696 | C | 3.750529 | -3.043485 | 1.286473 |
| H | -4.493047 | -3.743279 | -0.378605 | H | 4.333747 | -3.149558 | 2.216863 |
| C | -4.559319 | -2.154048 | 1.102410 | C | 4.423628 | -3.020055 | 0.047896 |
| C | -3.773932 | -1.292852 | 1.895544 | C | 3.655346 | -2.865661 | -1.124638 |
| H | -4.269276 | -0.568538 | 2.564127 | H | 4.162530 | -2.837565 | -2.104179 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.366595 | -1.332914 | 1.868903 | C | 2.250448 | -2.756134 | -1.088722 |
| C | -1.814591 | -4.130084 | -0.732916 | C | 1.652873 | -2.958167 | 2.718847 |
| H | -2.558868 | -4.674825 | -1.346327 | H | 2.388318 | -2.985745 | 3.546628 |
| H | -1.100486 | -3.609881 | -1.410683 | H | 1.002243 | -2.065694 | 2.848312 |
| H | -1.232079 | -4.890377 | -0.167327 | H | 0.995393 | -3.848279 | 2.828738 |
| C | -6.069782 | -2.127819 | 1.190755 | C | 5.924848 | -3.198236 | -0.021124 |
| H | -6.451979 | -1.107441 | 1.399473 | H | 6.348926 | -2.769189 | -0.951589 |
| H | -6.542677 | -2.492481 | 0.256304 | H | 6.435412 | -2.727409 | 0.843971 |
| H | -6.432955 | -2.781619 | 2.014567 | H | 6.198332 | -4.276657 | -0.007517 |
| C | -1.553429 | -0.399116 | 2.734375 | C | 1.458745 | -2.545103 | -2.357858 |
| H | -0.865154 | -0.951229 | 3.409672 | H | 0.633449 | -3.280327 | -2.463479 |
| H | -0.920129 | 0.267177 | 2.112195 | H | 0.983398 | -1.540235 | -2.368580 |
| H | -2.209267 | 0.232894 | 3.364009 | H | 2.106987 | -2.631890 | -3.251650 |
| C | -1.307516 | 0.137359 | -1.017396 | C | 1.347977 | 0.370474 | 0.087202 |
| H | -1.910541 | -0.619464 | -1.568542 | H | 1.974028 | -0.543050 | 0.052441 |
| C | -2.059273 | 1.336106 | -0.638766 | C | 2.144522 | 1.588138 | -0.084005 |
| C | -3.438126 | 1.355898 | -0.981447 | C | 3.520979 | 1.384402 | -0.385846 |
| H | -3.847839 | 0.466181 | -1.479478 | H | 3.880088 | 0.346087 | -0.436790 |
| C | -4.249176 | 2.475514 | -0.718891 | C | 4.393902 | 2.461921 | -0.626177 |
| C | -3.683841 | 3.616396 | -0.092878 | C | 3.900700 | 3.788963 | -0.559132 |
| H | -4.328032 | 4.487399 | 0.098373 | H | 4.593946 | 4.621543 | -0.749876 |
| C | -2.335664 | 3.616734 | 0.251054 | C | 2.560376 | 4.009156 | -0.252013 |
| H | -1.894116 | 4.501125 | 0.731203 | H | 2.175876 | 5.036678 | -0.189129 |
| C | -1.502176 | 2.496536 | -0.002539 | C | 1.665998 | 2.937909 | -0.010047 |
| C | -0.096215 | 2.532658 | 0.415752 | C | 0.268871 | 3.225373 | 0.357315 |
| C | 1.731628 | 3.889386 | 1.244236 | C | -1.429062 | 4.908290 | 0.682799 |
| H | 2.121840 | 2.921613 | 1.620330 | H | -1.817511 | 4.172230 | 1.416899 |
| C | 1.790588 | 4.950793 | 2.336902 | C | -2.246208 | 4.829044 | -0.606087 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 1.235769 | 4.628651 | 3.241229 | H | -2.221677 | 3.804363 | -1.028394 |
| H | 2.845508 | 5.135485 | 2.624507 | H | -3.304024 | 5.090629 | -0.396604 |
| H | 1.357876 | 5.909496 | 1.982922 | H | -1.855782 | 5.539926 | -1.363957 |
| C | 2.458545 | 4.269158 | -0.044077 | C | -1.366183 | 6.300836 | 1.299982 |
| H | 2.062367 | 5.222395 | -0.452072 | H | -0.939473 | 7.034767 | 0.584919 |
| H | 3.539979 | 4.404021 | 0.164778 | H | -2.386800 | 6.638150 | 1.572719 |
| H | 2.353611 | 3.474452 | -0.811885 | H | -0.744798 | 6.302589 | 2.217997 |
| C | -6.187719 | 1.474537 | -1.707247 | C | 6.273245 | 1.028848 | -1.006247 |
| H | -6.157815 | 0.544142 | -1.097919 | H | 5.788615 | 0.420265 | -1.802063 |
| H | -7.241510 | 1.770682 | -1.866240 | H | 7.342361 | 1.166171 | -1.254918 |
| H | -5.711770 | 1.276288 | -2.693163 | H | 6.189977 | 0.486207 | -0.038398 |

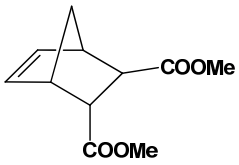
| **2-cis** | | | | **2-trans** | | | |
|---|---|---|---|---|---|---|---|
| Ru | 0.265086 | 0.117834 | -1.075801 | Ru | 0.086836 | 0.722976 | 0.117776 |
| Cl | 0.124388 | -1.800461 | -2.499907 | Cl | 0.773707 | 1.330579 | -2.039731 |
| Cl | 0.931547 | 1.412626 | -2.955325 | Cl | 0.185255 | 0.969611 | 2.461126 |
| O | 0.488061 | 1.921795 | -0.030860 | O | -0.780344 | 2.717113 | 0.137407 |
| O | 0.048838 | 4.118722 | 0.199594 | O | -2.284643 | 4.370204 | -0.105896 |
| N | -0.144306 | -2.199250 | 0.950562 | N | 0.748978 | -2.245631 | 0.619371 |
| N | 1.945569 | -1.534613 | 0.644306 | N | 2.515102 | -0.954067 | 0.301822 |
| C | 0.636278 | -1.252946 | 0.339087 | C | 1.128862 | -0.960545 | 0.277093 |
| C | 2.098209 | -2.841084 | 1.311244 | C | 3.076520 | -2.186573 | 0.888530 |
| H | 2.479111 | -3.599315 | 0.591107 | H | 3.967647 | -2.524127 | 0.323759 |
| H | 2.817101 | -2.774071 | 2.152799 | H | 3.386156 | -2.002648 | 1.942227 |
| C | 0.661329 | -3.141022 | 1.764669 | C | 1.899042 | -3.157659 | 0.795916 |
| H | 0.503170 | -2.941105 | 2.848542 | H | 1.771760 | -3.775584 | 1.707390 |
| H | 0.360290 | -4.188133 | 1.566469 | H | 1.979140 | -3.849857 | -0.074431 |
| C | -1.580424 | -2.235201 | 1.062532 | C | -0.547504 | -2.868741 | 0.554051 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.312211 | -3.213304 | 0.326380 | C | -0.994125 | -3.414512 | -0.687035 |
| C | -3.710559 | -3.271521 | 0.508872 | C | -2.226328 | -4.101314 | -0.706677 |
| H | -4.292321 | -4.019127 | -0.052985 | H | -2.589432 | -4.528688 | -1.655392 |
| C | -4.369803 | -2.403888 | 1.388227 | C | -2.990443 | -4.256960 | 0.458710 |
| C | -3.633541 | -1.460200 | 2.117681 | C | -2.529758 | -3.725720 | 1.671082 |
| H | -4.155622 | -0.792466 | 2.820456 | H | -3.132600 | -3.856939 | 2.583594 |
| C | -2.233580 | -1.359710 | 1.983321 | C | -1.304749 | -3.029922 | 1.750577 |
| C | -1.640398 | -4.224285 | -0.604158 | C | -0.199401 | -3.276306 | -1.987519 |
| H | -0.602568 | -3.871002 | -0.777093 | H | 0.717358 | -2.694331 | -1.761288 |
| C | -1.465925 | -0.381608 | 2.875867 | C | -0.825333 | -2.498131 | 3.100066 |
| H | -0.474508 | -0.213596 | 2.406545 | H | 0.031641 | -1.822369 | 2.902104 |
| C | 3.064554 | -0.653378 | 0.411901 | C | 3.422088 | 0.063306 | -0.183602 |
| C | 3.842383 | -0.770211 | -0.776892 | C | 3.856242 | -0.008880 | -1.543239 |
| C | 4.912912 | 0.133969 | -0.951295 | C | 4.756953 | 0.969030 | -2.007162 |
| H | 5.514634 | 0.076348 | -1.871232 | H | 5.088511 | 0.940059 | -3.056807 |
| C | 5.226602 | 1.092946 | 0.019084 | C | 5.239872 | 1.974991 | -1.159768 |
| C | 4.486939 | 1.153256 | 1.209119 | C | 4.853435 | 1.995063 | 0.184756 |
| H | 4.763767 | 1.885963 | 1.984443 | H | 5.264797 | 2.766153 | 0.854831 |
| C | 3.404333 | 0.281605 | 1.436896 | C | 3.956615 | 1.038038 | 0.708179 |
| C | 3.611532 | -1.877584 | -1.803898 | C | 3.458450 | -1.153891 | -2.478186 |
| H | 2.590406 | -2.281865 | -1.641916 | H | 2.577616 | -1.655930 | -2.026866 |
| C | 2.692176 | 0.308349 | 2.791503 | C | 3.678345 | 1.029595 | 2.211862 |
| H | 1.827089 | -0.383151 | 2.725056 | H | 2.784213 | 0.396642 | 2.387655 |
| C | -1.562700 | 0.230725 | -0.993488 | C | -1.593569 | 0.025464 | -0.186476 |
| H | -2.175826 | -0.639445 | -1.319040 | H | -1.718622 | -1.071406 | -0.266398 |
| C | -2.332134 | 1.451629 | -0.749522 | C | -2.865394 | 0.730388 | -0.369246 |
| C | -3.737520 | 1.365874 | -0.938864 | C | -3.997577 | -0.101268 | -0.604506 |
| H | -4.150979 | 0.388049 | -1.222932 | H | -3.833653 | -1.188643 | -0.619170 |

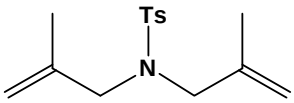
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.571866 | 2.489912 | -0.791470 | C | -5.282010 | 0.435240 | -0.810135 |
| C | -4.000511 | 3.740769 | -0.443224 | C | -5.465304 | 1.840766 | -0.784156 |
| H | -4.662893 | 4.612968 | -0.339527 | H | -6.474624 | 2.246479 | -0.947686 |
| C | -2.625904 | 3.842758 | -0.247918 | C | -4.371610 | 2.670787 | -0.553785 |
| H | -2.183539 | 4.810574 | 0.026014 | H | -4.507725 | 3.761029 | -0.531089 |
| C | -1.768233 | 2.720986 | -0.384832 | C | -3.071265 | 2.149077 | -0.342756 |
| C | -0.336121 | 2.867391 | -0.088183 | C | -1.950367 | 3.068664 | -0.088385 |
| C | 1.489044 | 4.424026 | 0.279653 | C | -1.218851 | 5.360404 | 0.106227 |
| H | -5.462423 | -2.470840 | 1.516482 | H | -3.945478 | -4.806057 | 0.423757 |
| H | 6.066018 | 1.787844 | -0.144491 | H | 5.936102 | 2.736556 | -1.546589 |
| C | -2.310796 | -4.292984 | -1.990678 | C | -0.974516 | -2.477797 | -3.057355 |
| H | -1.749023 | -4.989791 | -2.647234 | H | -1.240146 | -1.466106 | -2.691619 |
| H | -3.356186 | -4.666015 | -1.933687 | H | -0.353171 | -2.350476 | -3.968085 |
| H | -2.303026 | -3.299899 | -2.481307 | H | -1.907942 | -2.999052 | -3.359965 |
| C | -1.601409 | -5.627902 | 0.045040 | C | 0.237704 | -4.654222 | -2.531810 |
| H | -2.625747 | -6.036067 | 0.183864 | H | -0.637701 | -5.272605 | -2.823906 |
| H | -1.041966 | -6.339435 | -0.598440 | H | 0.873752 | -4.533154 | -3.433766 |
| H | -1.118262 | -5.621102 | 1.045004 | H | 0.814798 | -5.232663 | -1.780341 |
| C | -2.144344 | 0.996347 | 3.002230 | C | -1.897968 | -1.650016 | 3.812026 |
| H | -1.484320 | 1.696564 | 3.555534 | H | -2.788755 | -2.251440 | 4.095225 |
| H | -2.360360 | 1.439664 | 2.010705 | H | -1.481162 | -1.216058 | 4.744282 |
| H | -3.099353 | 0.940585 | 3.566640 | H | -2.228161 | -0.806762 | 3.173584 |
| C | -1.242699 | -0.987937 | 4.281883 | C | -0.342058 | -3.650849 | 4.009379 |
| H | -0.636483 | -0.305041 | 4.914210 | H | 0.070341 | -3.250892 | 4.959670 |
| H | -2.213013 | -1.153567 | 4.797175 | H | -1.174471 | -4.340487 | 4.268264 |
| H | -0.722954 | -1.967161 | 4.241923 | H | 0.450314 | -4.260050 | 3.525895 |
| C | 3.654712 | -1.375711 | -3.259761 | C | 3.046064 | -0.689986 | -3.888573 |
| H | 4.668632 | -1.024825 | -3.551021 | H | 2.702432 | -1.558180 | -4.490058 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 3.381181 | -2.201399 | -3.948206 | H | 2.222189 | 0.047863 | -3.832603 |
| H | 2.930909 | -0.551423 | -3.419598 | H | 3.895678 | -0.232592 | -4.439147 |
| C | 4.630274 | -3.021732 | -1.584943 | C | 4.604942 | -2.189899 | -2.572576 |
| H | 4.422413 | -3.862673 | -2.279923 | H | 4.300247 | -3.061578 | -3.190434 |
| H | 5.669420 | -2.676033 | -1.775315 | H | 5.504220 | -1.740364 | -3.045513 |
| H | 4.601772 | -3.419411 | -0.548356 | H | 4.916828 | -2.569826 | -1.577231 |
| C | 2.129561 | 1.696910 | 3.152918 | C | 3.349832 | 2.426256 | 2.774968 |
| H | 1.413629 | 2.046024 | 2.383060 | H | 2.503118 | 2.890360 | 2.232088 |
| H | 1.601508 | 1.659991 | 4.129228 | H | 3.056850 | 2.346144 | 3.842266 |
| H | 2.935421 | 2.455688 | 3.245710 | H | 4.222245 | 3.112527 | 2.723597 |
| C | 3.626202 | -0.213962 | 3.907618 | C | 4.873613 | 0.409928 | 2.974522 |
| H | 4.500634 | 0.456965 | 4.044919 | H | 5.788549 | 1.029555 | 2.856210 |
| H | 3.089348 | -0.269175 | 4.878459 | H | 4.650605 | 0.340293 | 4.060559 |
| H | 4.021994 | -1.224892 | 3.676382 | H | 5.119702 | -0.609479 | 2.610619 |
| O | -5.916976 | 2.479776 | -0.969829 | O | -6.398211 | -0.304083 | -1.039935 |
| C | -6.549963 | 1.260764 | -1.345309 | C | -6.284157 | -1.721256 | -1.089393 |
| H | -6.175054 | 0.888835 | -2.324683 | H | -5.606727 | -2.050851 | -1.908482 |
| H | -6.404232 | 0.468509 | -0.577742 | H | -5.913270 | -2.139341 | -0.127181 |
| H | -7.628917 | 1.487857 | -1.432898 | H | -7.302747 | -2.106325 | -1.284360 |
| C | 2.009099 | 4.696403 | -1.129818 | C | -0.500019 | 5.618671 | -1.217180 |
| H | 1.841779 | 3.818750 | -1.788582 | H | -0.042229 | 4.687641 | -1.606661 |
| H | 1.506793 | 5.582014 | -1.571976 | H | -1.203093 | 6.022049 | -1.975514 |
| H | 3.099827 | 4.896790 | -1.092207 | H | 0.310678 | 6.361061 | -1.065615 |
| C | 1.612019 | 5.603635 | 1.236932 | C | -1.901595 | 6.588488 | 0.697760 |
| H | 2.679053 | 5.881872 | 1.354112 | H | -2.424778 | 6.336935 | 1.642096 |
| H | 1.066382 | 6.488761 | 0.848810 | H | -1.145663 | 7.369334 | 0.918526 |
| H | 1.206792 | 5.353360 | 2.238151 | H | -2.641352 | 7.014722 | -0.011570 |
| H | 1.992517 | 3.528736 | 0.697003 | H | -0.508164 | 4.919031 | 0.835658 |

## SYNTHESIS OF SUBSTRATES




The norbornene based monomer *exo,endo*-Dimethylbicyclo[2.2.1] hept-5-ene-2,3-dicarboxylate were synthesized according to literature procedures with Diels-Alder reactions of cyclopentadiene and the corresponding fumaric acid derivative.[6]

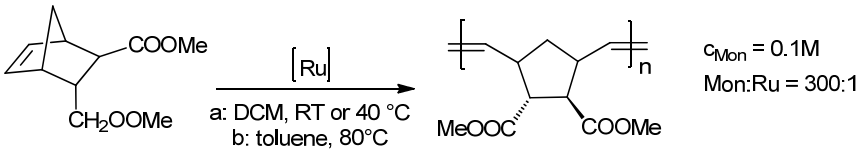


RCM substrate

The RCM substrate 4-methyl-N,N-bis(2-methylallyl)benzenesulfonamide was synthesized according to literature.[7] 4-methylbenzenesulfonamide (1-58 g, 9.04 mmol, 1 eq), 3-bromo-2-methylprop-1-ene (2.6 mL, 25.8 mmol, 2.85 eq) and potassium carbonate (4.75 g, 27.12 mmol, 3 q) were put into a reactor together with 50 mL of acetonitrile and a stirring bar. The reactor was closed and the reaction was allowed to stir for 48 h at 110°C. After that time it was cooled to room temperature, $K_2CO_3$ was filtered off, and the solvent was rota-evaporated. The crude product was purified with column chromatography (silica, cyclohexane/ acetylacetate: 3+1) to yield a yellow oil (2.35 g, 93%). (TLC: $r_f$ = 0.61)

## REACTIVITY IN VARIOUS METATHESIS REACTIONS

### Ring opening metathesis polymerization (ROMP)



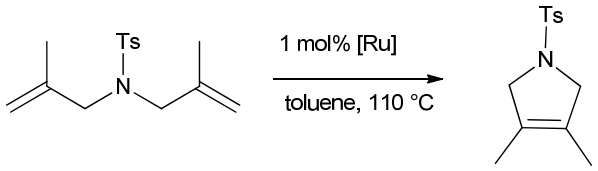

Scheme 1: Benchmark reactions for ROMP

As reference initiators both 3rd generation starting complexes **M31** and **M32** as well 2nd generation complex **M2** and **Hov** were included in the study, each in their respective reasonable temperature scope. **Fehler! Verweisquelle konnte nicht gefunden werden.** summarizes the number molecular weight (Mn), corresponding polydispersity indices (PDIs) obtained by GPC analysis and reaction times for full conversion for polymers synthesized using the abovementioned initiators.

Table 6: ROMP benchmark

| initiator | DCM, rt or 40°C | | | toluene, 80°C | | |
|---|---|---|---|---|---|---|
| | $M_n$ (g/mol) | PDI | time | $M_n$ (g/mol) | PDI | time |
| **M31**[a] | 45000 | 1.07 | 10 min | n.d. | n.d. | n.d.[a] |
| **M32**[a] | 48800 | 1.2 | 2 h | n.d. | n.d. | n.d.[a] |
| **Hov**[a] | 89000 | 1.3 | < 1 h | n.d. | n.d. | n.d.[a] |
| **M2**[a] | 292000 | 2.3 | 4 h | 72420 | 2.7 | 1h |
| **1: SIMes**[b] | 442740 | 2.2 | 5 h | 114260 | 2.4 | 10 min |
| **2: SIPr**[b] | 264150 | 1.7 | 5 h | 214390 | 1.5 | 10 min |

**Ring closing metathesis (RCM)**




Scheme 2: RCM reaction with challenging substrate [substrate] = 0.1M

The RCM reaction was carried out in degassed puresolv toluene under nitrogen conditions in small glass vials with sealed screw caps, heated in an alumina mold. 10 experiments under the same conditions were performed with complexes **1** and **2** each. Conversion was determined by NMR spectroscopy after 1h, 4h and in case of increased conversion after that time, 24h. All reactions were stopped after 24 hours. The finally reached conversions are shown in Figure 5.

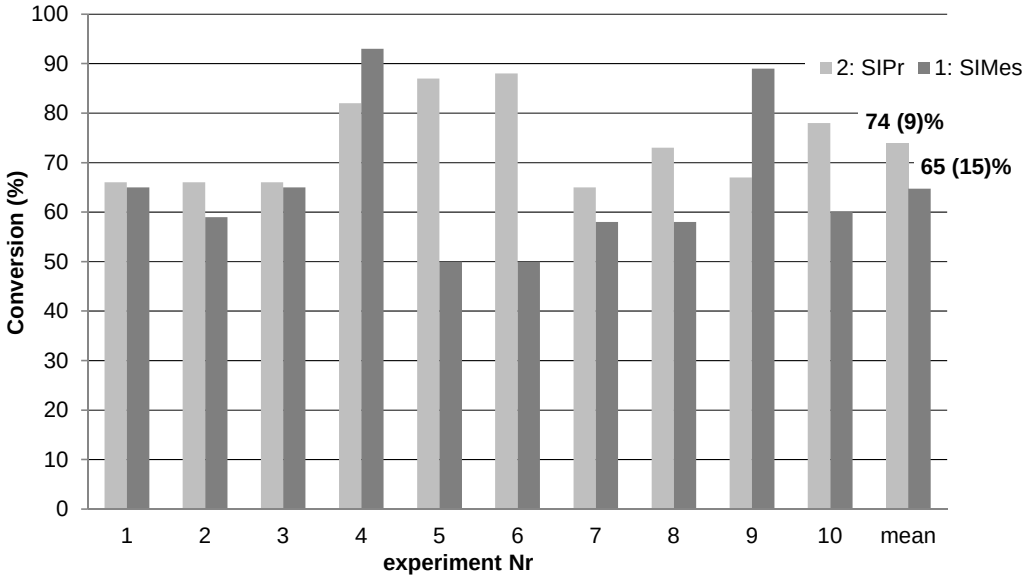



Figure 5: Conversion of 4-methyl-N,N-bis(2-methylallyl)benzenesulfonamide) to 3,4-dimethyl-1-tosyl-2,5-dihydro-1H-pyrrole by RCM, performed with complexes 1 and 2.

**Cross metathesis (CM)**

**Typical Procedure (catalyst loading 0.1 mol%).** A Schlenk tube equipped with a magnetic stirring bar was charged with methyl vinyl ketone (2.10 g, 0.0299 mol). 1-hexene (0.84 g, 9.98 mmol) was added diluted in 5mL of dried diethyl ether under inert atmosphere of nitrogen. The reaction mixture was heated to 35°C (oil bath temperature), the catalyst **2** (7.50 mg, 00998 mmol) was added and the reaction was run for 16h. Afterwards, the reaction mixture was concentrated under reduced pressure in order to remove excess of methyl vinyl ketone and 1-hexene and a sample for NMR measurement was taken. In case of full conversion yield was determined by adding the ethyl vinyl ether into the reaction mixture and passing the reaction mixture over a short silica gel column using cyclohexane as a solvent. Drying of the appropriate fractions yielded product **A** ((*E*)-oct-3-en-2-one) as colorless oil with bitter almond smell. More than 90% isolated yield of the cross metathesis products were obtained in all cases where full conversion was observed by NMR. **$^1$H-NMR of A** (300 MHz, $CDCl_3$): 6.73–6.66 (m, 1H, –CH=CH–$COCH_3$), 6.02–5.97 (d, 1H, –CH=CH–$COCH_3$), 2.12-2.06 (t, 3H, –CO*C*$H_3$), 2.12–2.06 (m, 2H, $CH_2$–CH=CH), 1.39-1.04 (m, 4H, $CH_2$), 0.82-0.64 (7, 3H, $CH_3$).

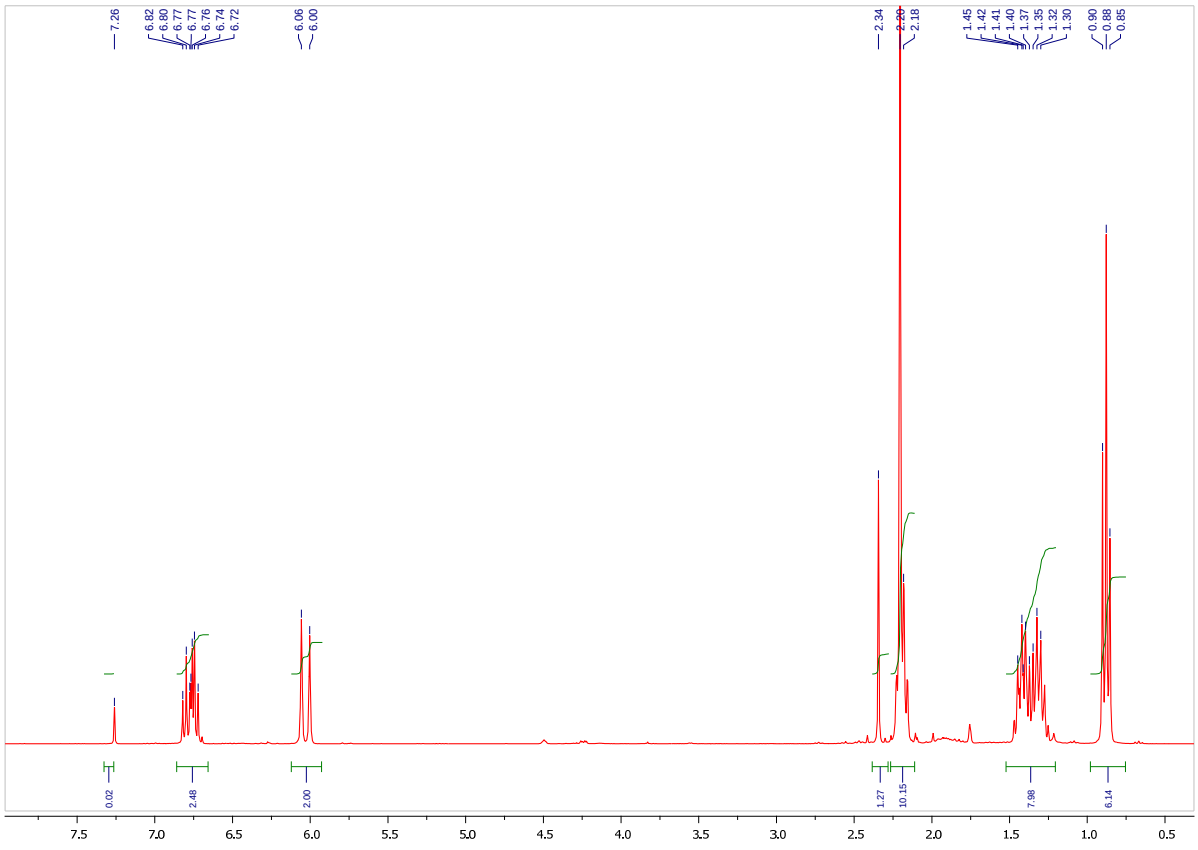



Figure 7: $^1$H-NMR of the raw product of above described procedure

## REFERENCES


1. Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
2. (a) A. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100. (b) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824. c) J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406-7406.
3. A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys*., 1992, **97**, 2571-2577.
4. (a) U. Haeusermann, M. Dolg, H. Stoll, H. Preuss, *Mol. Phys*., 1993, **78**, 1211-1224. (b) W. Kuechle, M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys*., 1994, **100**, 7535-7542. (c) T. Leininger, A. Nicklass, H. Stoll, M. Dolg, P. Schwerdtfeger, *J. Chem. Phys*., 1996, **105**, 1052-1059.
5. (a) V. Barone, M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001. (b) J. Tomasi, M. Persico, *Chem. Rev*., 1994, **94**, 2027-2094.
6. Kirmse, W.; Mrotzeck, U.; Siegfried, R. *Chem. Ber*. **1991**, *124*, 241-245.
7. Elias, X.; Moreau, J. *Adv. Synth. Catal*. **2006**, *348*, 751-762.