Supporting Information

for

Mixed *N*-Heterocyclic Carbene/Phosphite Ruthenium Complexes: Towards a New Generation of Olefin Metathesis Catalysts

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1 General Information

All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line and glovebox techniques. Solvents were dispensed from a solvent purification system. All other reagents were used without further purification. ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} 1D and 2D Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 400 Ultrashield spectrometer using the residual solvent peak as reference ($CHCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CH_2Cl_2, δ_H = 5.32 ppm, δ_C = 53.80 ppm.) at 298K. Variable temperature NMR spectra were carried out in CD_3NO_2. Gas chromatography (GC) analyses were performed on an Agilent 7890A apparatus equipped with a flame ionization detector and a (5%-Phenyl)-methylpolysiloxane column (30 m, 320 μm, film: 0.25 μm). Flash chromatography was conducted using 40-63 μm silica. Analytical TLCs were performed on Merck pre-coated silica 60-F_{254} plates. Elemental analyses were performed by the University of St Andrews Analytical Service.

2 Procedures for catalysis

Substrates **2**,[1] **4**,[2] **6**,[3] **8**[4] and **11**[2] were synthesised according to literature procedures. NMR spectra of the RCM products **3**,[1] **5**,[2] **7**,[5] **10**,[6] **12**,[7] **13**,[8] **14**,[8] **15**,[9] and **16**[2] were compared to previously reported analyses.

2.1 Procedure for Table 1 – Comparison *trans*/*cis*-Caz-1

A flame-dried schlenk was charged with a solution of the substrate (0.25 mmol) in 2.5 mL of solvent (0.1M, CH_2Cl_2 for room temperature experiments and toluene for 80°C) and **Caz-1** (1 to 2 mol%) was added. The reaction mixture was stirred at the appropriate temperature for the appropriate amount of time. The solvent was removed *in vacuo*. The conversion was determined by ^{1}H NMR ($CDCl_3$).

2.2 Procedure for Figure 4 – Comparison of catalysts

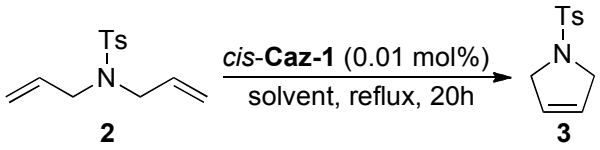
A reaction tube (Radleys carousel 12 reaction station) was charged with a solution of di(methallyl)tosylamine **11** (0.5 mmol) in toluene (0.5 mL) and the ruthenium pre-catalyst (0.5 mol%) was added. The reaction mixture was stirred at 80°C and aliquots were taken every 5 to 20 minutes. Each aliquot was then added to a solution of 40 μL of ethylvinyl ether and toluene. All samples were then subjected to GC analysis to determine the conversion of **11** to **12**.

2.3 Solvent optimisation

In order to test the reactivity limits of the phosphite system and to demonstrate its true potential, low catalyst loading experiments were conducted on RCM reactions using a less challenging substrate, namely **2**. As *cis*-**Caz-1** is efficient and stable at elevated temperature, several solvents with high boiling points were tested in the model RCM of **2**. All reactions were conducted at reflux in the presence of 0.01 mol% of *cis*-**Caz-1** (Table 1). Solvents with lower boiling point (*ca*. 80°C) and water gave poor conversions to **3** (entries 1-3). On the other hand, aromatic solvents proved highly beneficial to the system as they all lead to high conversion to the RCM product, independently of the reaction temperature (Table 1, entries 4-

6, 9). Finally, unusual solvents for RCM such as hexanol, dimethylacetamide (DMA) and ethylene glycol were evaluated and gave low conversions (Table 1, entries 7-10). Interestingly, DMA, which is known as a catalyst poison, surprisingly allowed for 20% of the cyclised product, which corresponds to a turnover number of 2 000.

Table S1 Solvent optimisation at low catalyst loading[a]



2 **3**

Entry	Solvent	T (°C)	Conv. (%)[b]
1	1,2-dichloroethane	80	20
2	dimethoxyethane	85	20
3	H2O	100	0
4	**toluene**	**110**	**77**
5	chlorobenzene	131	77
6	m-xylene	140	77
7	hexanol	156	44
8	dimethylacetamide	165	20
9	1,2-dichlorobenzene	180	72
10	ethylene glycol	197	2

[a] Reaction conditions: **2** (0.25 mmol), *cis*-**Caz-1** (0.01 mol%), solvent (0.5 mL), reflux, 20h. [b] Conversions were determined by ^{1}H NMR based on diene.

Procedure

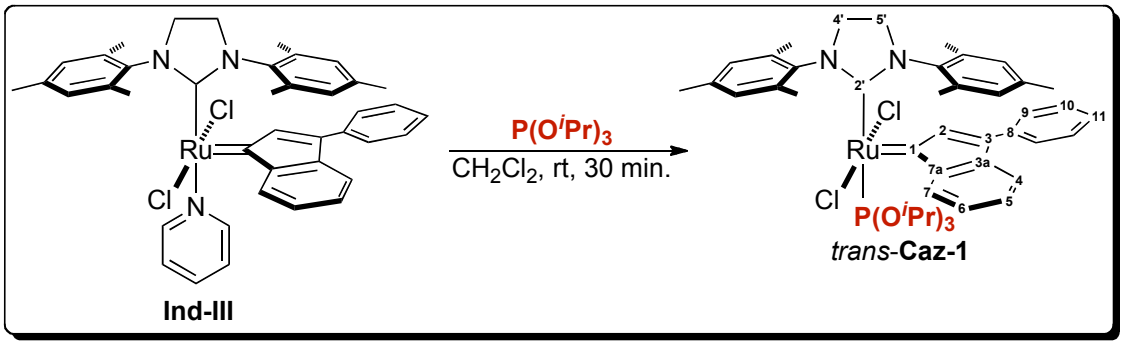
A reaction tube (Radleys carousel 12 reaction station) was charged with a solution of the substrate (0.25 mmol) in 2.5 mL of solvent and *cis*-**Caz-1** (0.01 mol% from stock solution). The reaction mixture was stirred at reflux temperature for 20 hours. The solvent was removed *in vacuo*. The conversion was determined by ^{1}H NMR ($CDCl_3$).

2.4 Procedure for Scheme 2 - Catalytic RCM at low catalyst loading

In the glovebox, a vial was charged with a stirring bar, substrate (0.25 mmol), pre-catalyst *cis*-**Caz-1** (from a stock solution of 2.2 mg in 2 mL of toluene), and 0.5 mL of toluene. The mixture was stirred outside the glovebox at the indicated temperature. After 20h, the reaction was stopped and solvent was evaporated. Flash chromatography (pentane/diethylether - 9:1 to 8:2 v:v) on silica gel afforded the title compounds.

3 Synthesis and characterisation of pre-catalysts Caz-1

3.1 *Trans*-Caz-1



Triisopropylphosphite (296 µL, 1.3 mmol) was added to a solution of **Ind-III** (1 g, 1.3 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for 30 min. The solvent was concentrated *in vacuo* to 1 mL and pentane (10 mL) was added. The solution was filtered and the solvent was removed *in vacuo*, leading to a microcrystalline red solid. *Trans*-**Caz-1** was obtained in 76% yield as a mixture of *trans* and *cis* isomers 9:1 (866 mg).

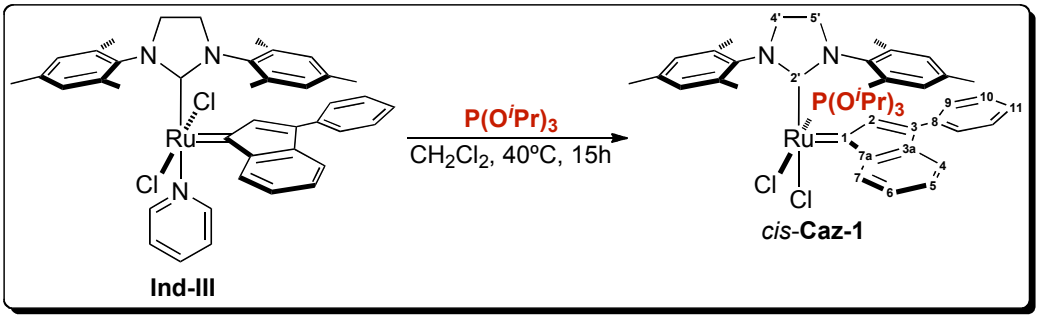
^{1}H NMR on mixture *trans*/*cis* 9:1 (CD_2Cl_2, 400 MHz): δ (ppm) = 0.88 (d, $^3J_{HH}$ = 6.1 Hz, 9H, CH-C*H*$_3$), 0.91 (d, $^3J_{HH}$ = 6.1 Hz, 9H, CH-C*H*$_3$), 1.80 (s, 3H, mesityl CH_3), 1.97 (s, 3H, mesityl CH_3), 2.25 (s, 3H, mesityl CH_3), 2.33 (s, 3H, mesityl CH_3), 2.69 (s, 3H, mesityl CH_3), 2.73 (s, 3H, mesityl CH_3), 3.75-3.91 (m, 2H, carbene H$^{4'}$), 4.00-4.08 (m, 5H, carbene H$^{5'}$ and C*H*-CH_3), 6.08 (s, 1H, mesityl CH), 6.44 (s, 1H, mesityl CH), 6.86 (s, 1H, indenylidene H^2), 6.99 (s, 1H, indenylidene H^4), 7.01 (s, 2H, mesityl CH), 7.15 (ddd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, indenylidene H^6), 7.24 (ddd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, indenylidene H^5), 7.39-7.42 (m, 2H, indenylidene H^{10}), 7.51-7.55 (m, 1H, indenylidene H^{11}), 7.70-7.73 (m, 2H, indenylidene H^9), 8.32 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, indenylidene H^7).

^{13}C-{^{1}H} NMR on mixture *trans*/*cis* 9:1 ($CDCl_3$ 100.6 MHz) δ (ppm) = 18.67 (s, mesityl CH_3), 18.73 (s, mesityl CH_3), 20.43 (s, mesityl CH_3), 20.45 (s, mesityl CH_3), 21.0 (s, mesityl CH_3), 21.2 (s, mesityl CH_3), 23.8 (s, CH-*C*H_3), 23.88 (s, CH-*C*H_3), 23.92 (s, CH-*C*H_3), 52.4 (d, $^4J_{CP}$ = 8.9 Hz, carbene *C*$^{4'}$), 52.45 (d, $^4J_{CP}$ = 11.2 Hz, carbene C$^{5'}$), 69.9 (d, $^2J_{CP}$ = 3.5 Hz, *C*H-CH_3), 116.5 (s, indenylidene *C*^{4}), 126.8 (s, indenylidene *C*^{9}), 128.3 (s, indenylidene *C*^{11}), 128.6 (s, indenylidene *C*^{5}), 128.7 (s, indenylidene *C*^{6}), 129.2 (s, indenylidene *C*^{10}), 129.37 (s, mesityl CH), 129.41 (s, mesityl CH), 129.79 (s, indenylidene *C*^{7}), 129.81 (s, mesityl CH), 135.7 (s, C^{IV}), 136.6 (s, C^{IV}), 136.7 (s, C^{IV}), 136.78 (s, C^{IV}), 136.81 (s, C^{IV}), 137.0 (s, C^{IV}), 137.4 (s, C^{IV}), 138.3 (s, indenylidene C^2), 138.6 (s, C^{IV}), 139.6 (s, 2C^{IV}), 141.0 (s, C^{IV}), 141.6 (s, C^{IV}), 143.5 (d, $^3J_{CP}$ = 1.9 Hz, indenylidene C^{7a}), 217.3 (d, $^2J_{CP}$ = 127.8 Hz, carbene C^2), 301.7 (d, $^2J_{CP}$ = 21.0 Hz, indenylidene C^1).

^{31}P-{^{1}H} NMR on mixture *trans*/*cis* 9:1 (CD_2Cl_2, 162 MHz) δ (ppm) = 113.8.

Elem. anal.: Calcd. for $C_{45}H_{57}Cl_2N_2O_3PRu$: C, 61.64; H, 6.55; N, 3.19. Found: C, 61.45; H, 6.34; N, 3.35.

3.2 *Cis*-Caz-1:



Under an inert atmosphere, triisopropylphosphite (60 µL, 0.26 mmol) was added to a solution of **Ind-III** (196 mg, 0.26 mmol) in dichloromethane (4 mL). The mixture was stirred for 15h at 40°C, allowed to cool to room temperature, and concentrated *in vacuo* to 1 mL. Pentane (10 mL) was added and the precipitate was collected by filtration and washed with pentane (3 x 5 mL). *Cis*-**Caz-1** was obtained as a brown solid in 85 % yield (193 mg, 0.22 mmol).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 0.58 (d, $^3J_{HH}$ = 5.9 Hz, 3H, CH-C*H*$_3$), 0.75 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH-C*H*$_3$), 0.92 (d, $^3J_{HH}$ = 5.8 Hz, 3H, CH-C*H*$_3$), 1.06 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH-C*H*$_3$), 1.43 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH-C*H*$_3$), 1.48 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH-C*H*$_3$), 1.58 (s, 3H, mesityl CH_3), 1.85 (s, 3H, mesityl CH_3), 2.33 (s, 3H, mesityl CH_3), 2.56 (s, 3H, mesityl CH_3), 2.64 (s, 3H, mesityl CH_3), 2.73 (s, 3H, mesityl CH_3), 3.23 (m, 1H, C*H*-CH_3), 3.58-3.67 (m, 1H, carbene H$^{4'}$), 3.76-3.91 (m, 3H, carbene H$^{4'}$H$^{5'}$), 4.30 (m, 1H, C*H*-CH_3), 4.82 (m, 1H, C*H*-CH_3), 6.13 (s, 1H, mesityl CH), 6.45 (s, 1H, indenylidene H^2), 6.48 (s, mesityl CH), 7.00 (s, 2H, mesityl CH), 7.14 (d, $^3J_{HH}$ = 7.2 Hz, 1H, indenylidene H^4), 7.30-7.36 (m, 2H, indenylidene H^5 and H^6), 7.38-7.42 (m, 2H, indenylidene H^{10}), 7.46-7.50 (m, 1H, indenylidene H^{11}), 7.69 (d, $^3J_{HH}$ = 7.2 Hz, 2H, indenylidene H^9), 8.87 (d, $^3J_{HH}$ = 7.1 Hz, 1H, indenylidene H^7).

^{13}C-{^{1}H} NMR ($CDCl_3$ 100.6 MHz) δ (ppm) = 19.1 (s, mesityl CH_3), 19.5 (s, mesityl CH_3), 20.6 (s, mesityl CH_3), 21.1 (s, mesityl CH_3), 21.4 (s, mesityl CH_3), 21.5 (s, mesityl CH_3), 24.0 (s, CH-*C*H_3), 24.05 (s, CH-*C*H_3), 24.3 (s, CH-*C*H_3), 24.4 (s, CH-*C*H_3), 24.72 (s, CH-*C*H_3), 24.74 (s, CH-*C*H_3), 52.0 (s, carbene C$^{4'}$H), 52.6 (s, carbene C$^{5'}$H), 69.55 (d, $^2J_{CP}$ = 11.7 Hz, *C*H-CH_3), 70.7 (d, $^2J_{CP}$ = 9.3 Hz, *C*H-CH_3), 72.9 (d, $^2J_{CP}$ = 3.6 Hz, *C*H-CH_3), 117.4 (s, indenylidene C^{4}H), 127.6 (s, indenylidene C^{9}H), 128.7 (s, indenylidene C^{11}H), 129.2 (s, indenylidene C^{10}H), 129.8 (s, indenylidene C^{6}H), 129.9 (s, indenylidene C^{5}H), 130.26 (s, mesityl CH), 130.31 (s, mesityl CH), 130.5 (s, mesityl CH and indenylidene C^{7}H), 135.0 (s, C^{IV}), 135.9 (s, C^{IV}), 136.8 (s, C^{IV}), 136.9 (s, C^{IV}), 137.0 (s, C^{IV}), 138.1 (s, C^{IV}), 138.25 (s, C^{IV}), 138.5 (s, C^{IV}), 138.6 (s, C^{IV}), 139.2 (s, C^{IV}), 140.4 (d, $^3J_{CP}$ = 15.9 Hz, indenylidene C^2), 141.2 (d, $^3J_{CP}$ = 2.6 Hz, indenylidene C^{7a}), 142.5 (s, C^{IV}), 208.95 (d, $^2J_{CP}$ = 13.4 Hz, carbene C$^{2'}$), 292.1 (d, $^2J_{CP}$ = 24.7 Hz, indenylidene C^1).

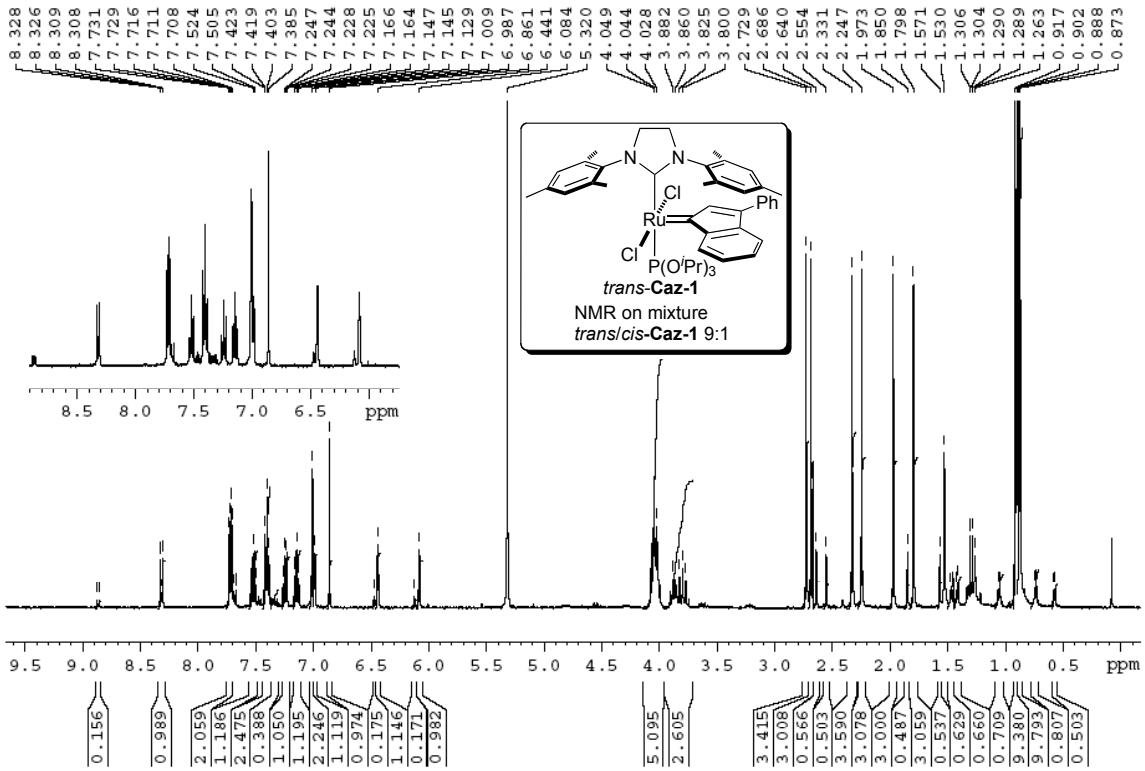
^{31}P-{^{1}H} NMR (CD_2Cl_2, 162 MHz) δ (ppm) = 122.0.

Elem. anal.: Calcd. for $C_{45}H_{57}Cl_2N_2O_3PRu$: C, 61.64; H, 6.55; N, 3.19. Found: C, 61.21; H, 6.24; N, 3.15.

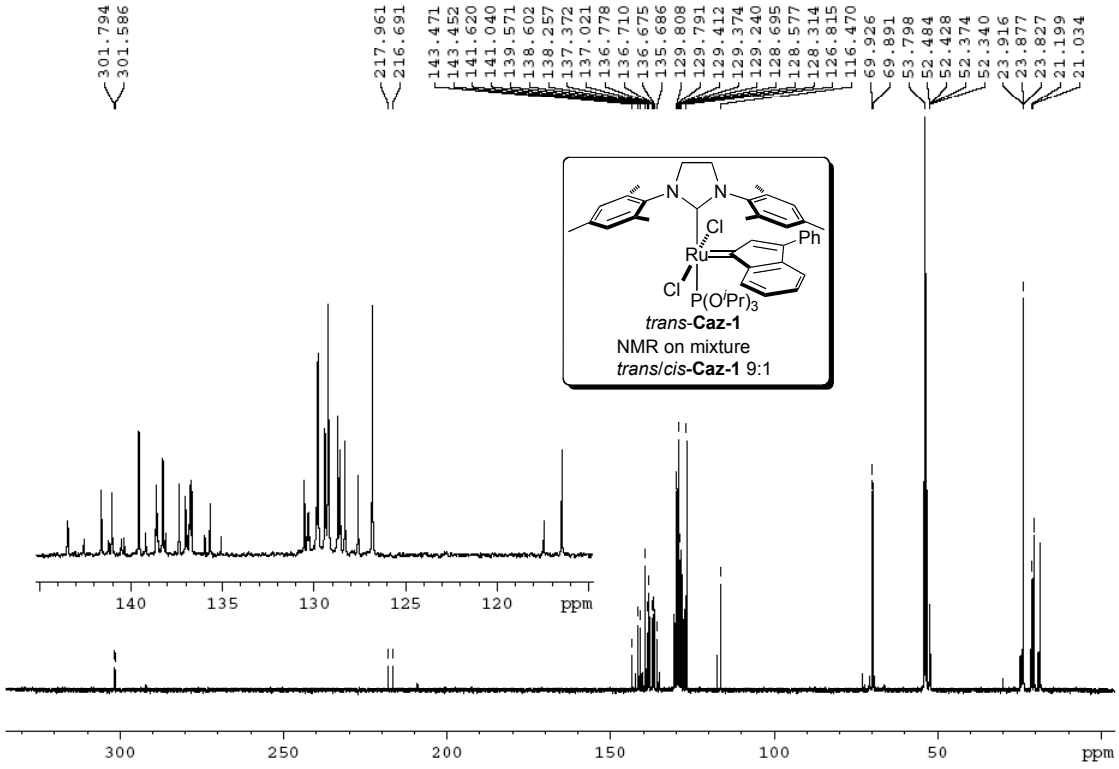
Crystal data for *cis*-**Caz-1**: Crystals were obtained by slow diffusion (CH_2Cl_2/n-dodecane). $C_{45}H_{57}Cl_2N_2O_3PRu$ M = 876.87, monoclinic, space group $P2_1/c$, a = 19.132 (2) Å, b = 9.5576 (11) Å, c = 24.397 (3) Å, β = 104.451 (3)°, V = 4320.0 (9) Å^3, Z = 4, ρ_{calcd} = 1.348 g.cm^{-3}, μ (Mo Kα) = 0.56 mm^{-1}, T = 125 (2) K, R_{int} = 0.132, 7916 unique reflections, R1 = 0.0897, wR2 = 0.1676 for 5696 reflections with $I > 2\sigma(I)$, R1 = 0.1341, wR2 = 0.1900 for all data, GOF = 1.197.

4 NMR spectra

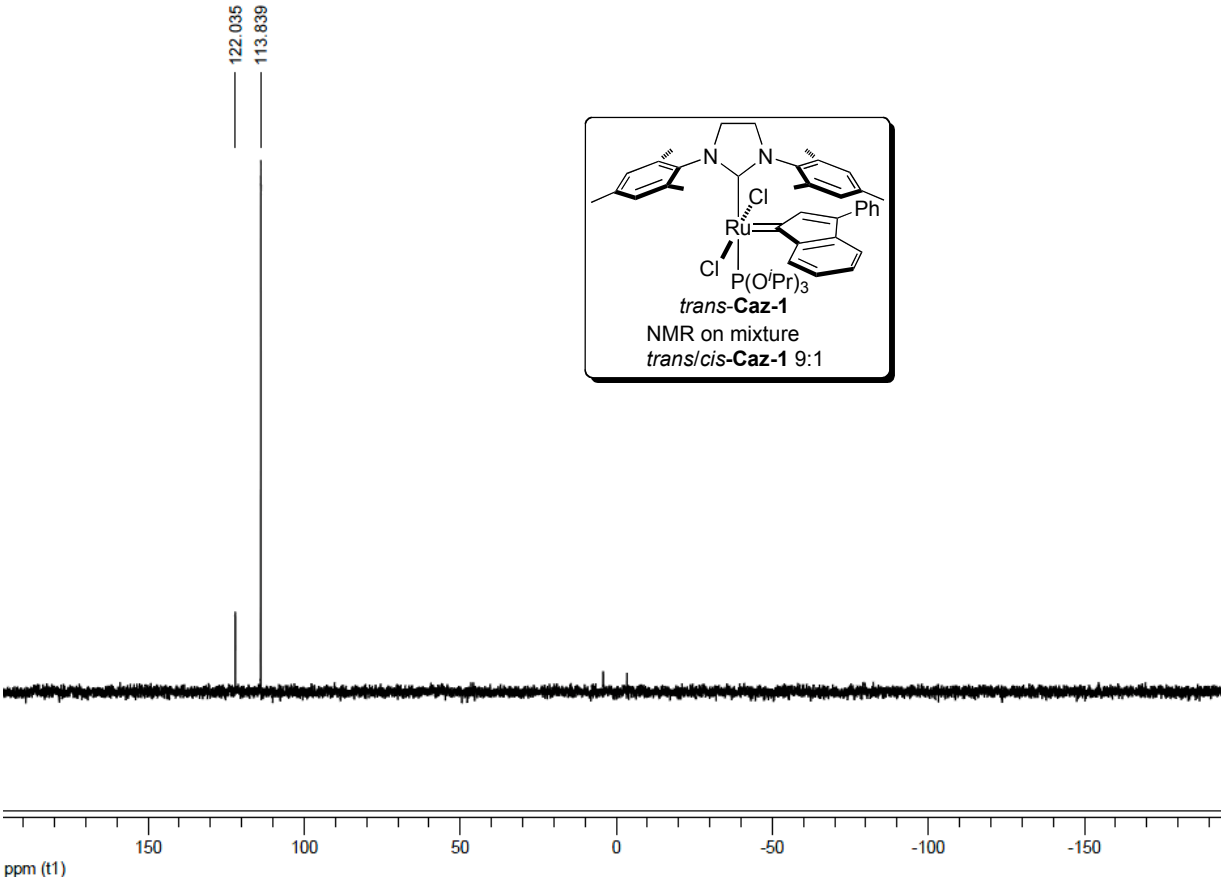
4.1 ^{1}H NMR (CD_2Cl_2) of *trans*-Caz-1 (contains 10% of cis-Caz-1)



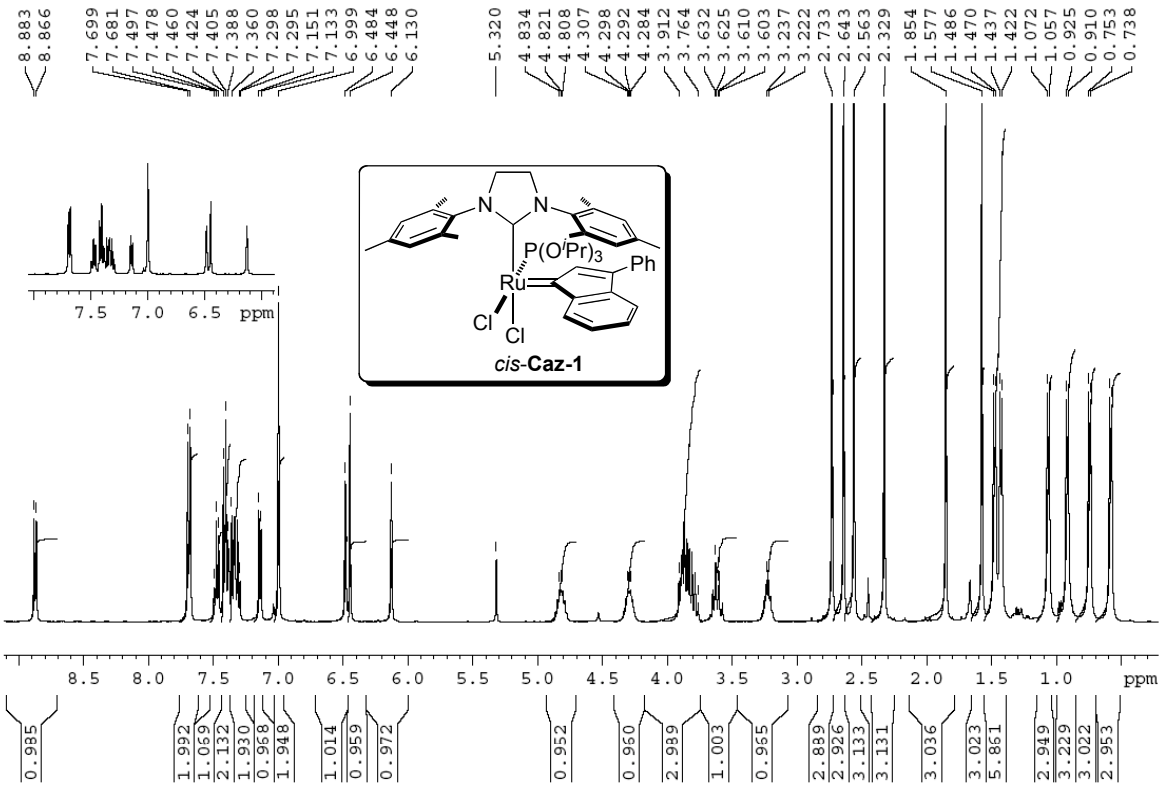
4.2 ^{13}C-{^{1}H} NMR (CD_2Cl_2) of *trans*-Caz-1 (contains 10% of cis-Caz-1)



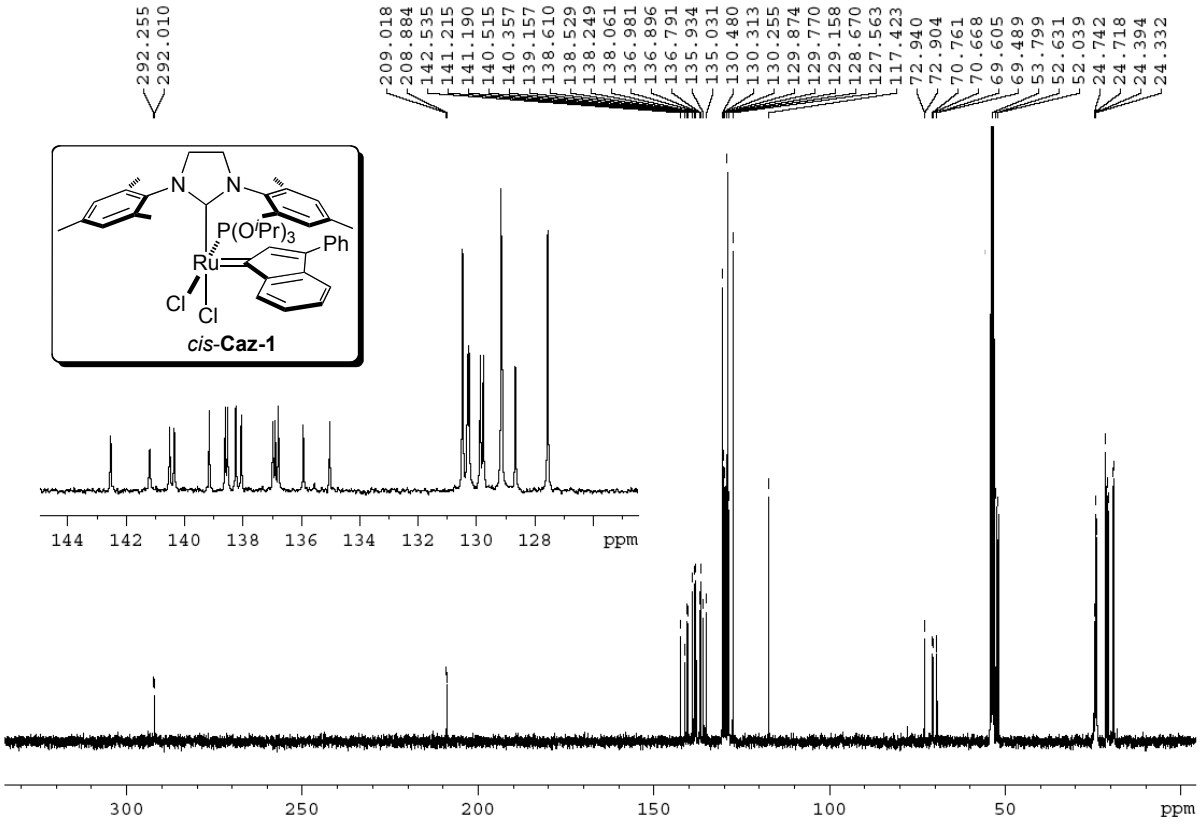
4.3 ^{31}P-{^{1}H} NMR (CD_2Cl_2) of *trans*-Caz-1 (contains 10% of cis-Caz-1)



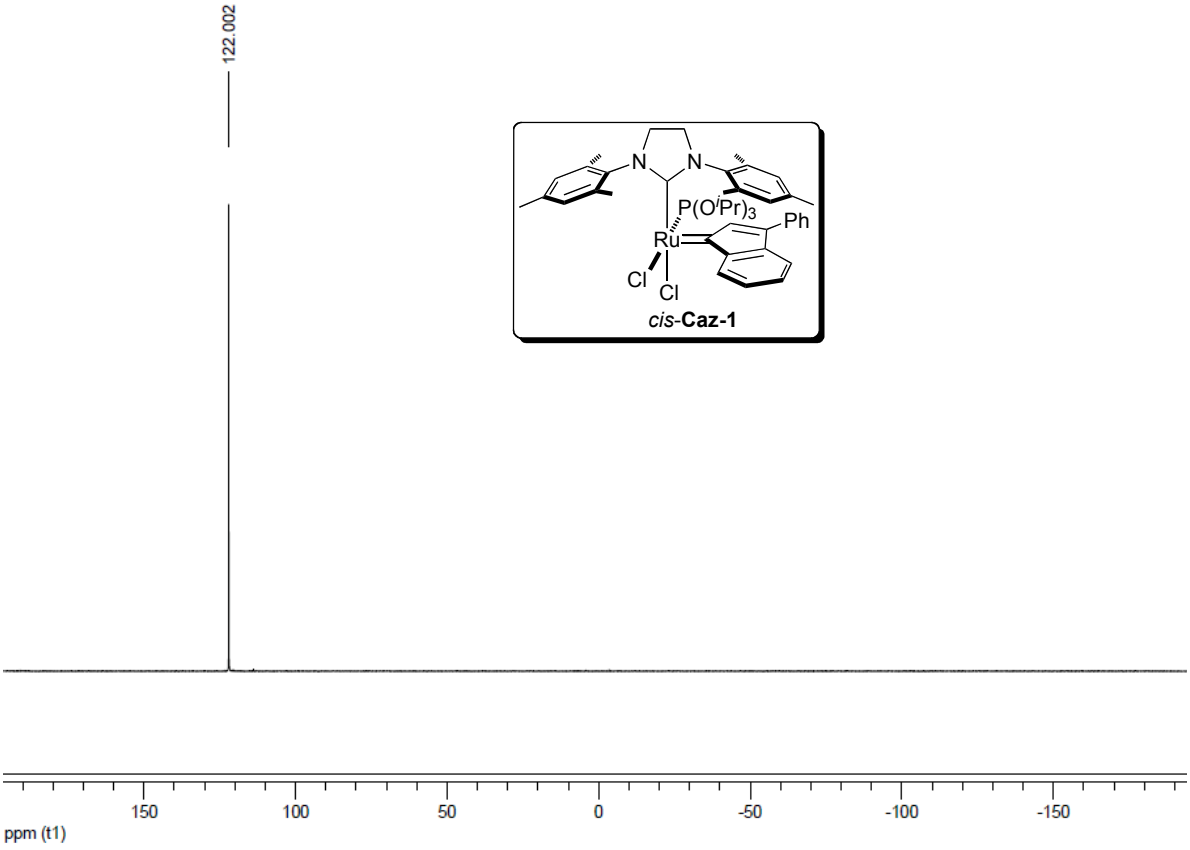
4.4 ^{1}H NMR (CD_2Cl_2) of *cis*-Caz-1

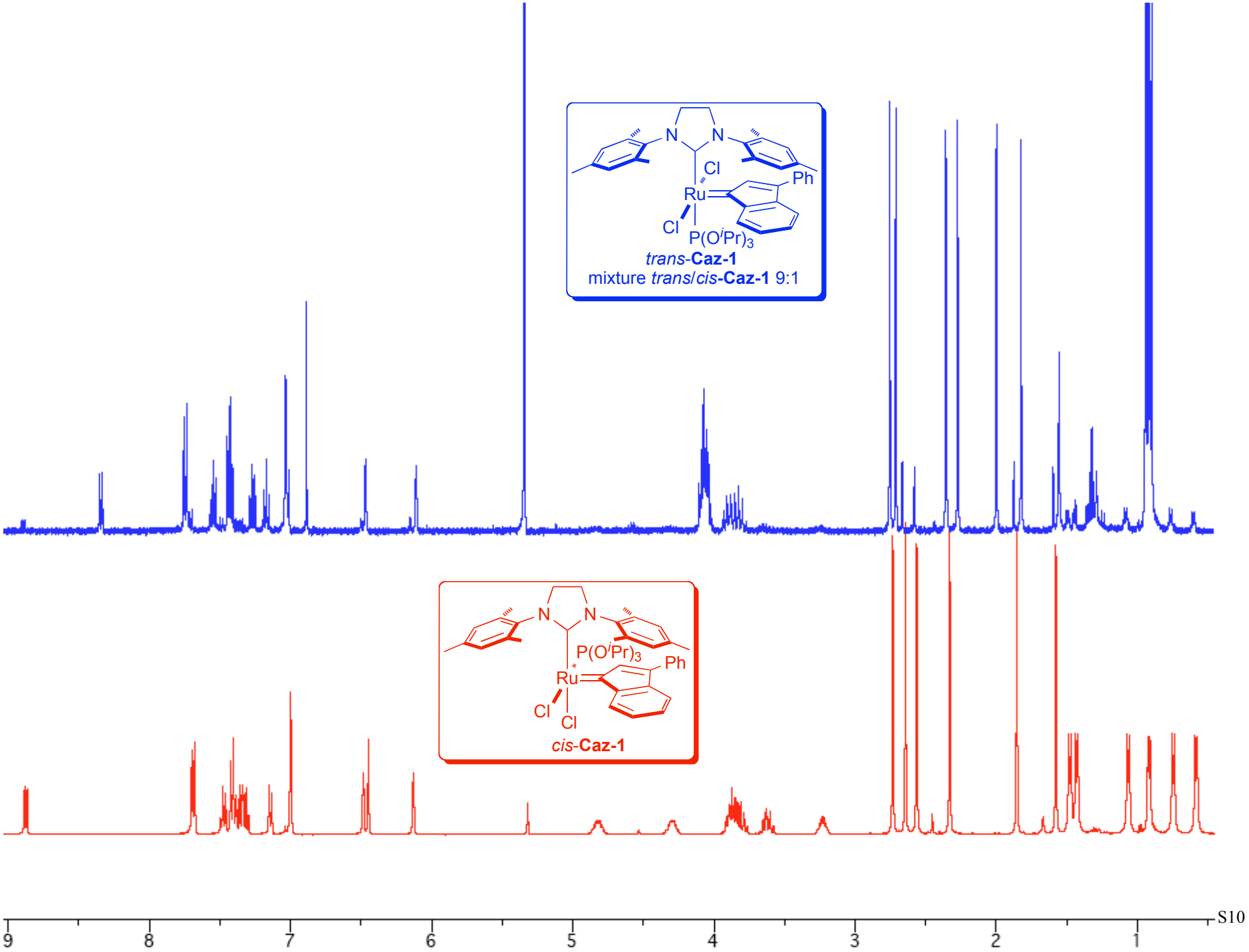


4.5 ^{13}C-{^{1}H} NMR (CD_2Cl_2) of *cis*-Caz-1



4.6 ^{31}P-{^{1}H} NMR (CD_2Cl_2) of *cis*-Caz-1




N
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P(O^{i}Pr)$_3$
trans-**Caz-1**
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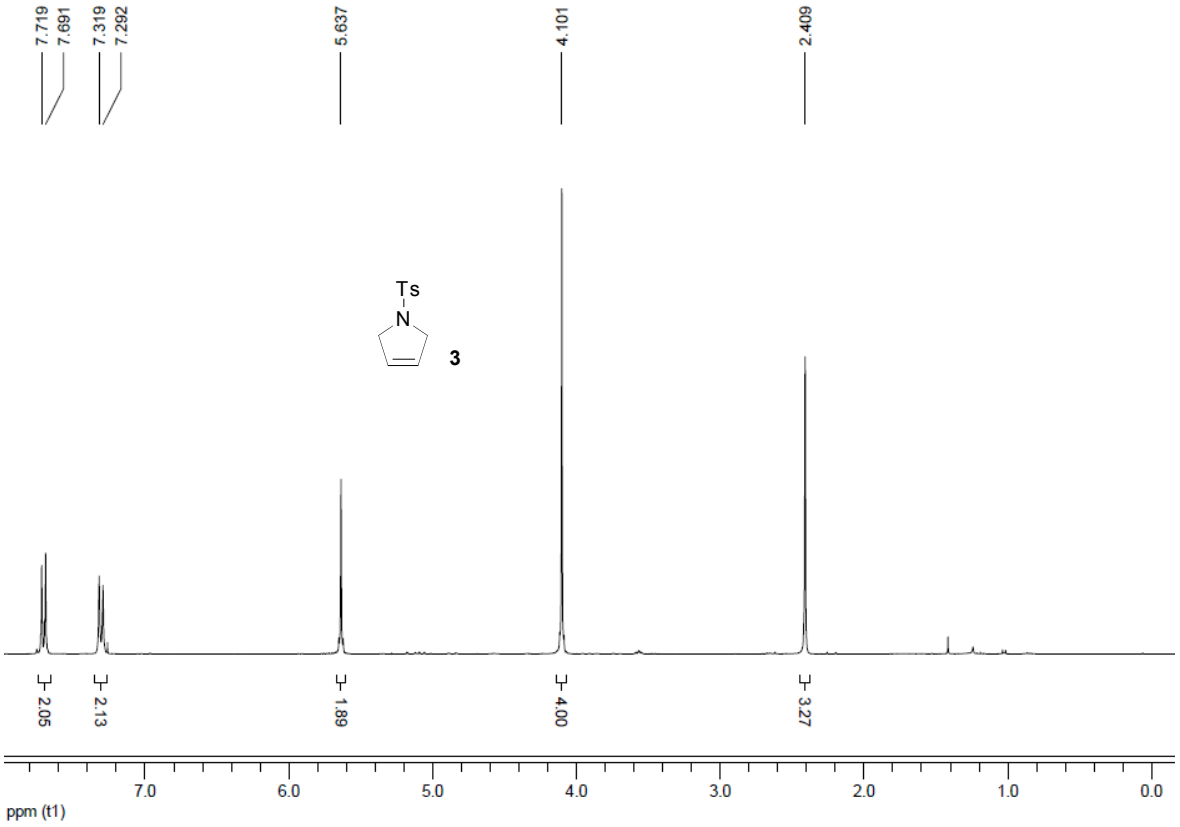
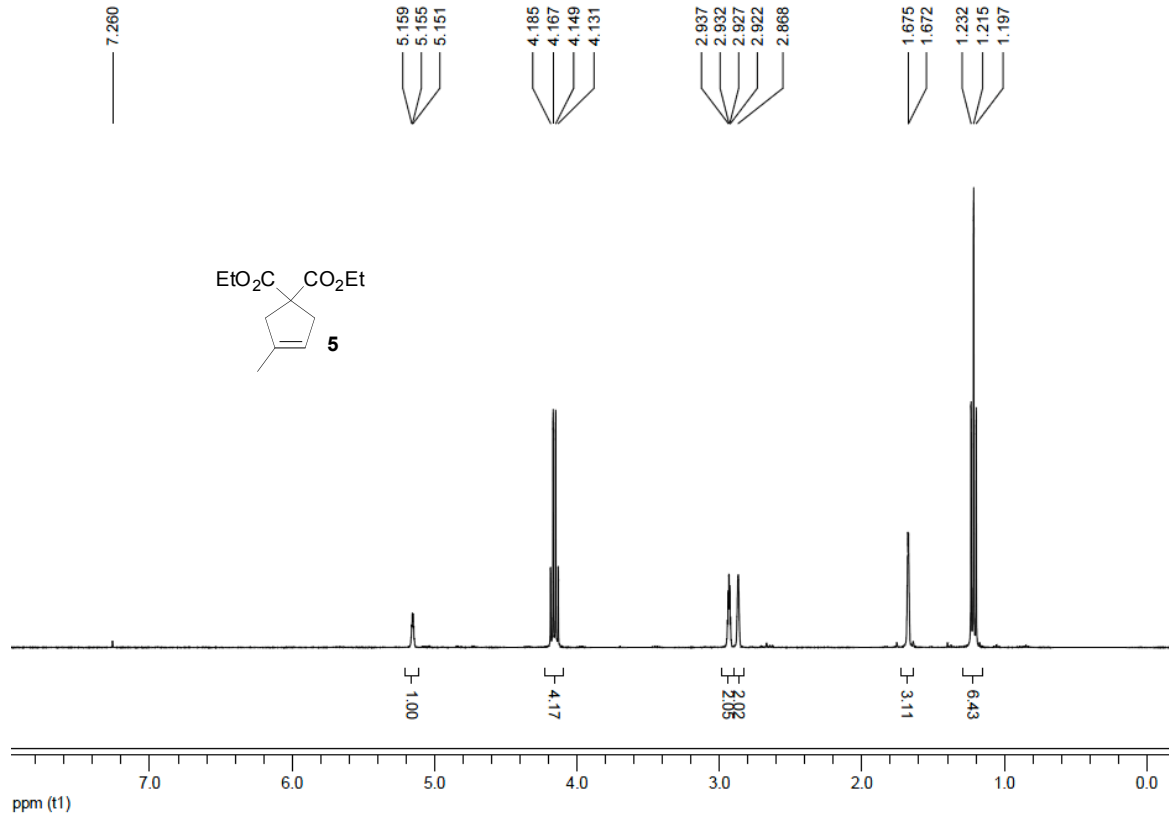
7
6
5
4
3
2
1

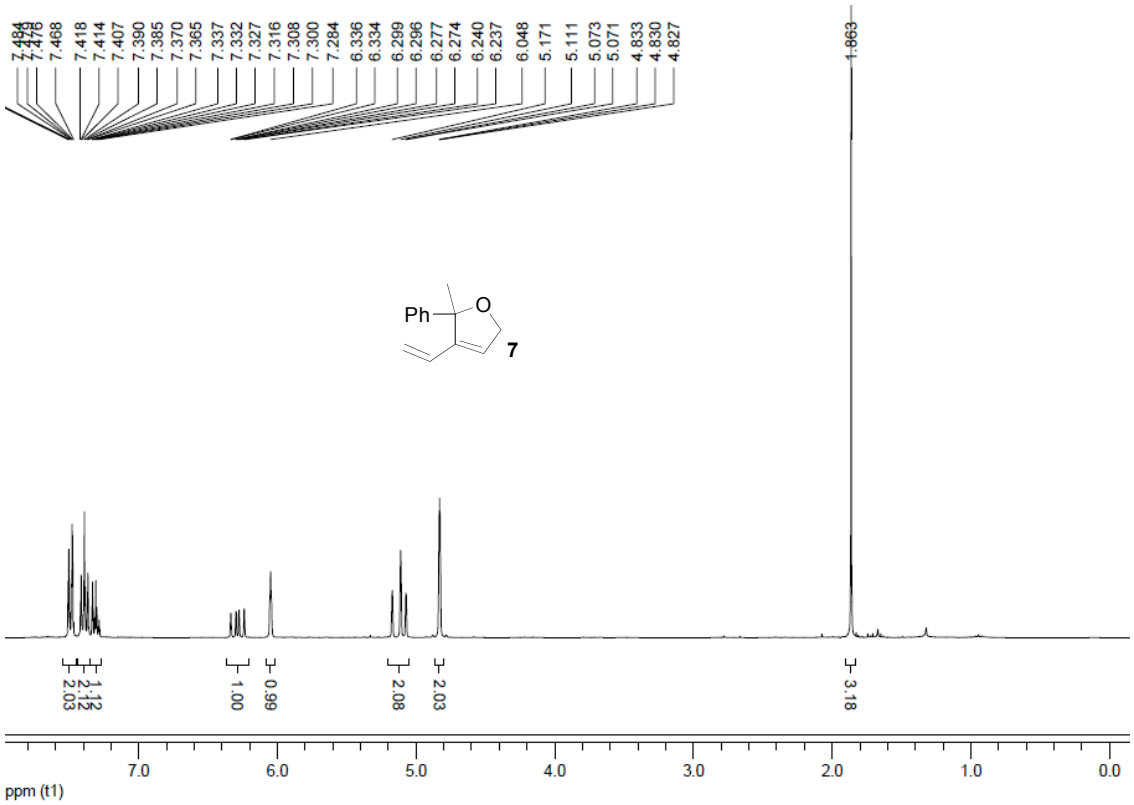
4.7 ^{1}H NMR ($CDCl_3$) of 3



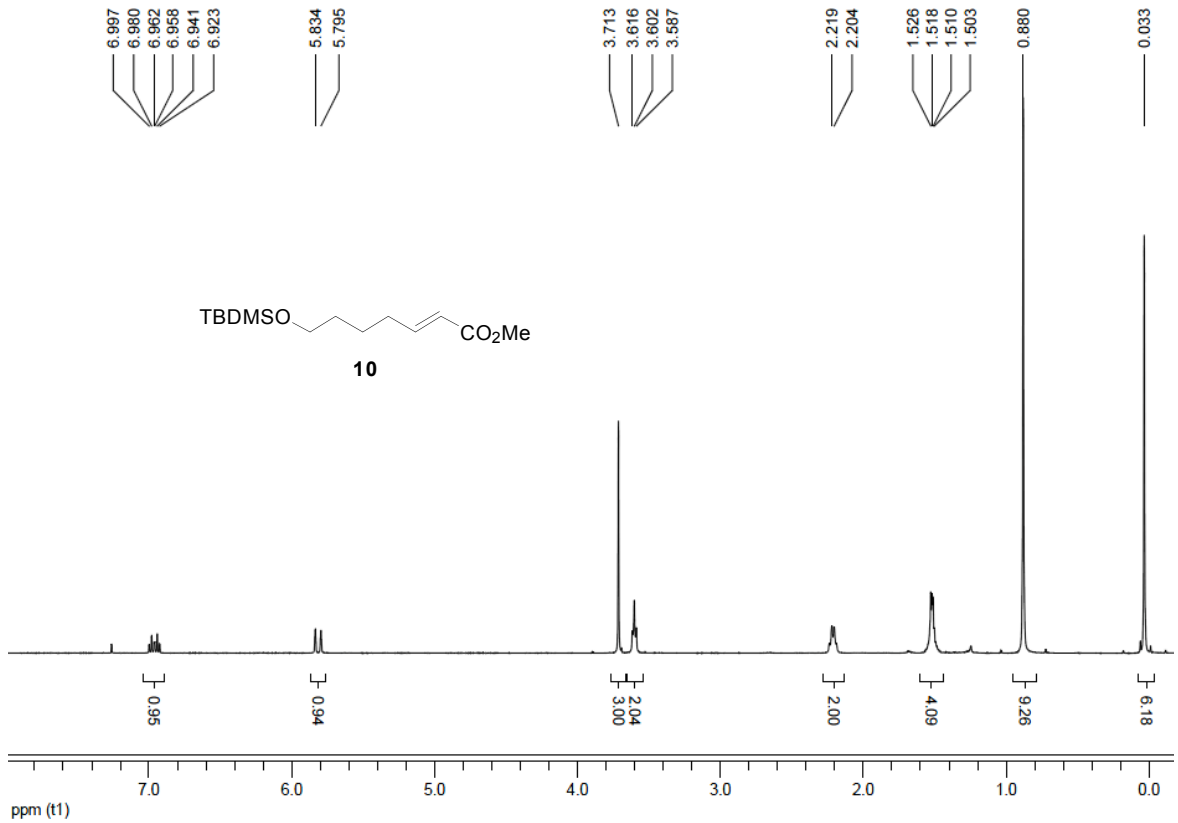
4.8 ^{1}H NMR ($CDCl_3$) of 5



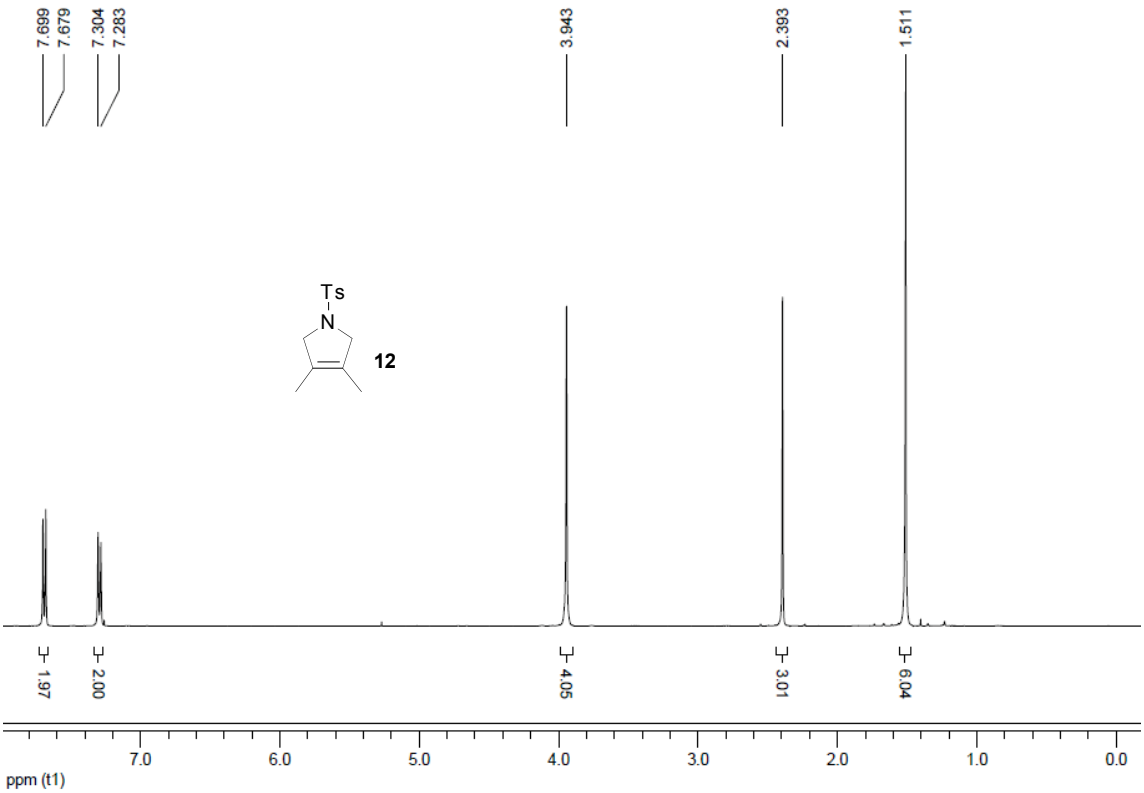
4.9 ^{1}H NMR ($CDCl_3$) of 7



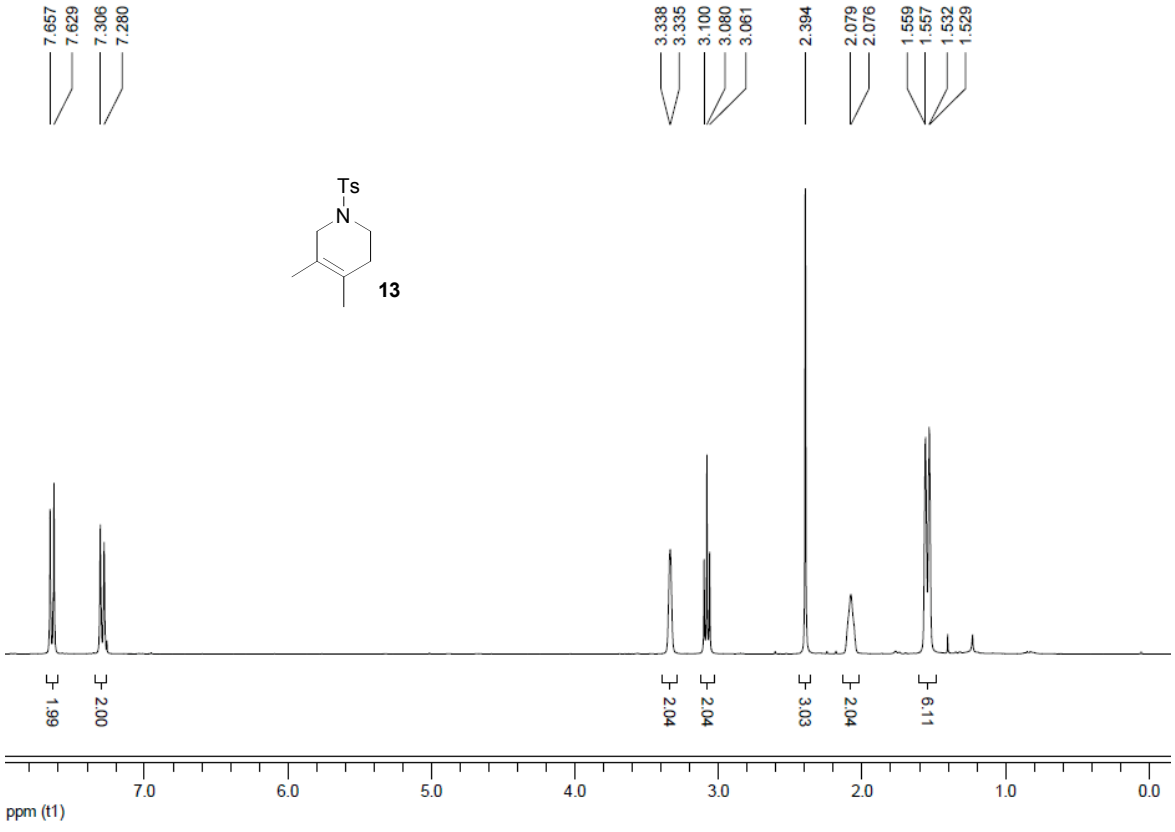
4.10 ^{1}H NMR ($CDCl_3$) of 10



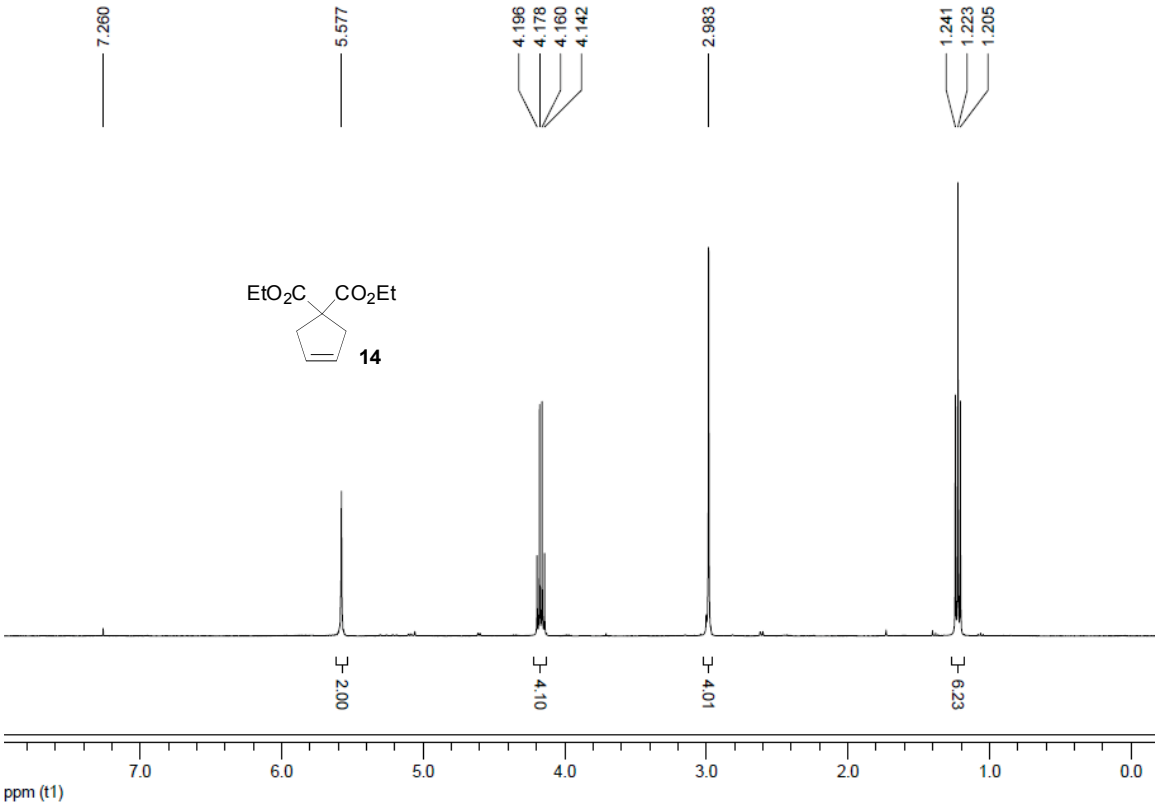
4.11 ^{1}H NMR ($CDCl_3$) of 12



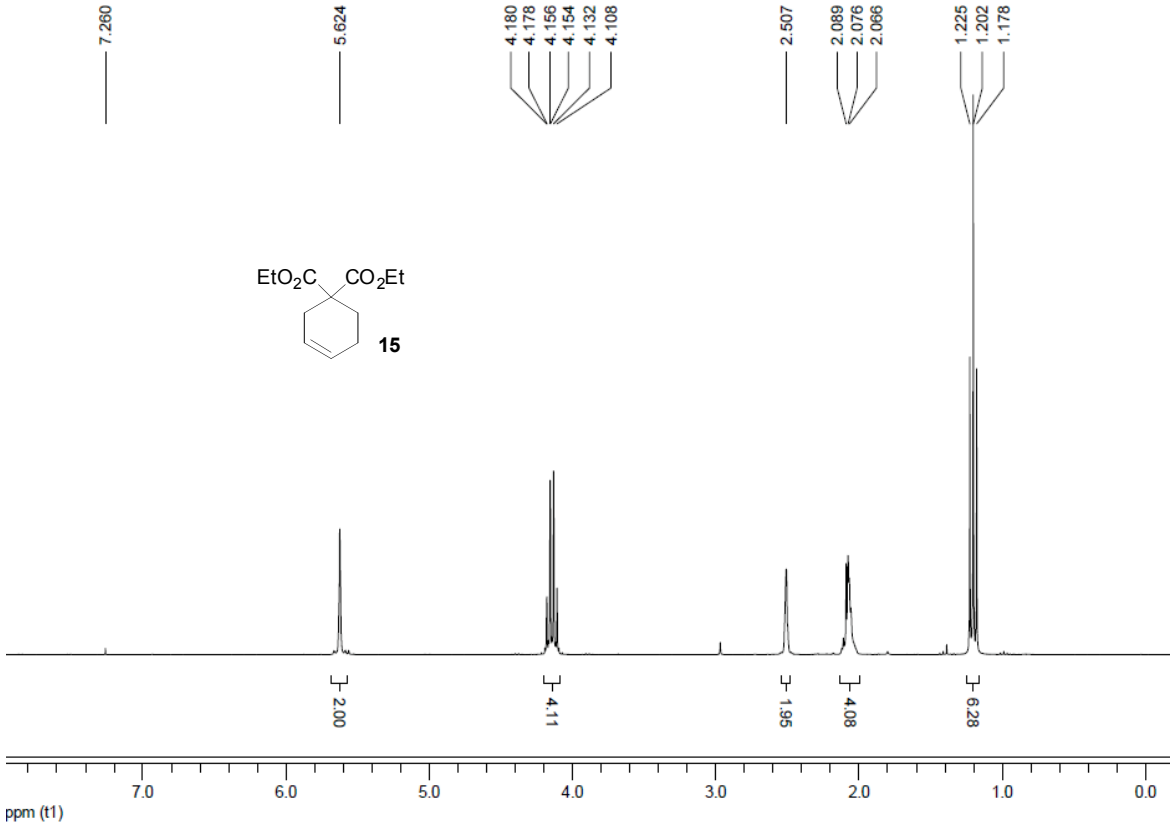
4.12 ^{1}H NMR ($CDCl_3$) of 13



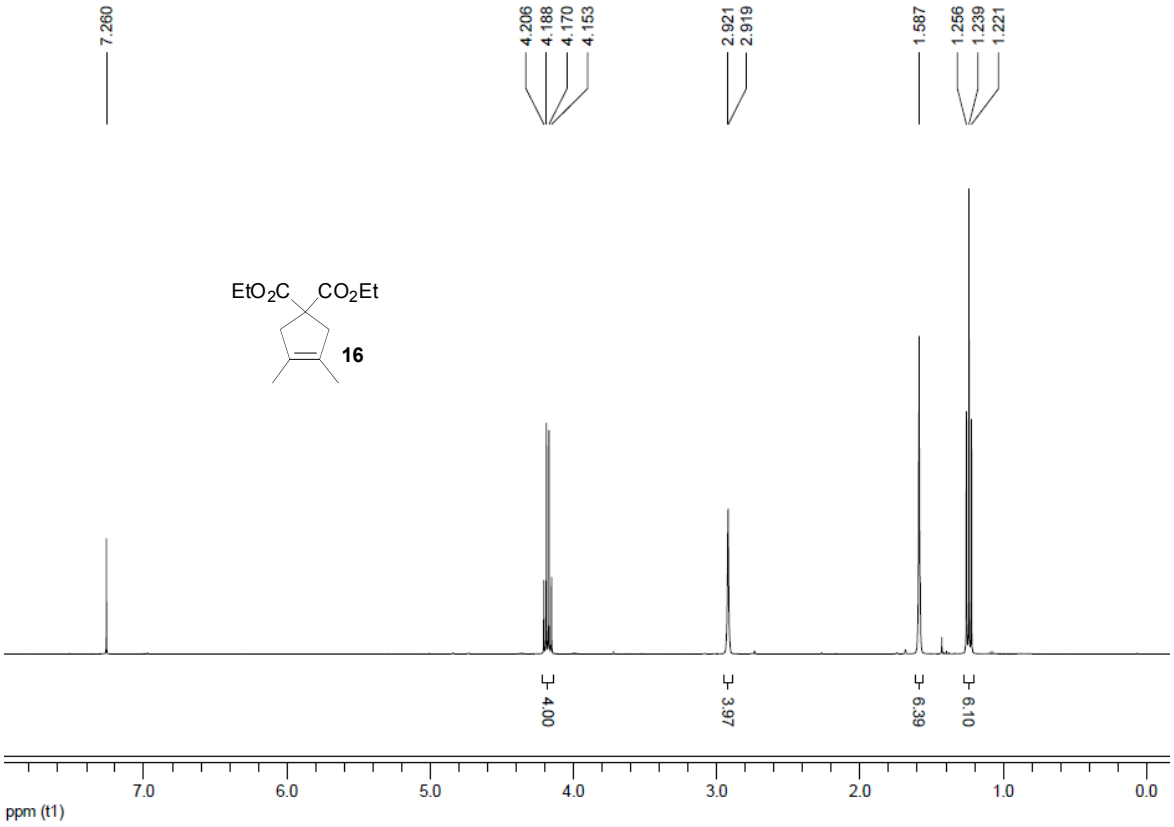
4.13 ^{1}H NMR ($CDCl_3$) of 14



4.14 ^{1}H NMR ($CDCl_3$) of 15



4.15 ^{1}H NMR ($CDCl_3$) of 16



5 NMR Kinetic studies, Eyring plot

Procedure for the kinetic plots:

In a glovebox, a J-Young tube was charged with *ca.* 4 mg of complex *trans*-**1** (*ca.* 90% pure) and 0.6 mL of CD_3NO_2. ^1H NMR spectra were recorded on a Varian Unity Plus-500 MHz spectrometer every 20 minutes at the appropriate temperature. 5 experiments were conducted at 30°C, 40°C, 50°C and 60°C and an additional at 40°C in the presence of 5 equiv of $P(O^iPr)_3$. Results are plotted in Fig. 1. Data for this plot are reported at the end of this section in Table 3.

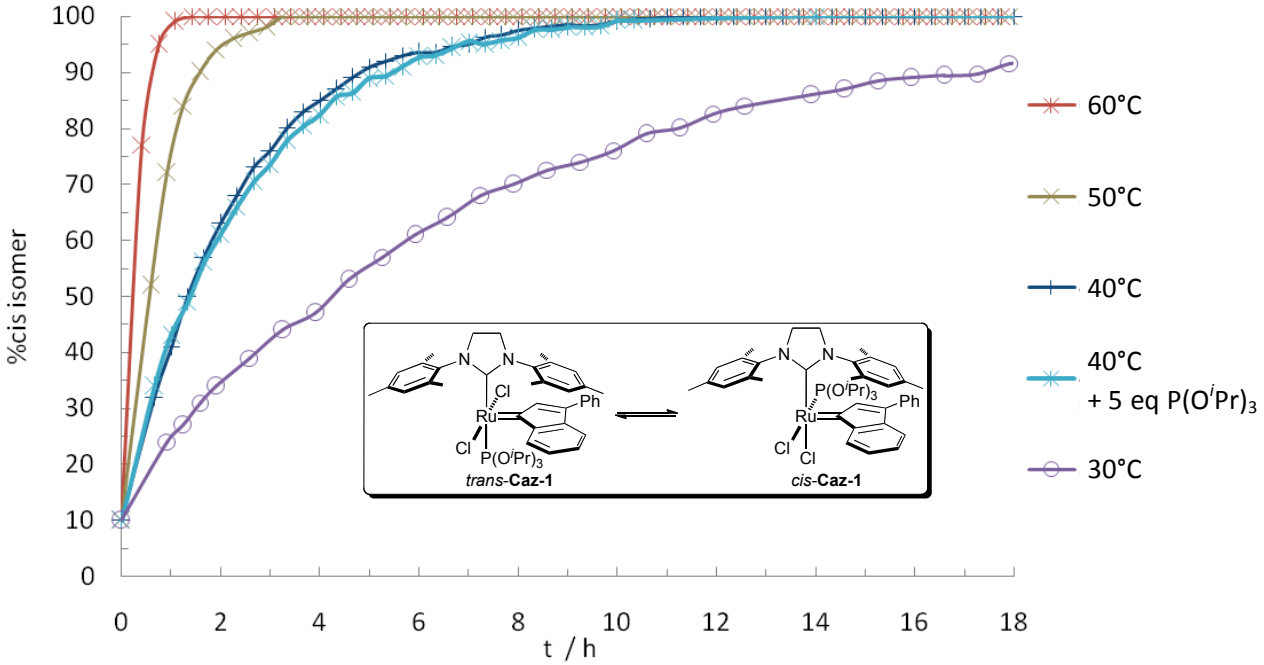


Fig. 1 Isomerisation of complex **1** in CD_3NO_2.

Equations leading to the Eyring plot:

As the observed kinetics in Fig. 1 seem to be first order, the following equations were used. The decrease in concentration of *trans*-**Caz-1** (indicated as *trans*-**1** in this section) over time can be written as equation (1):

$$V = -\frac{d[trans\text{-}\mathbf{1}]}{dt} = k.[trans\text{-}\mathbf{1}] \qquad (1)$$

$$-\frac{d[trans\text{-}\mathbf{1}]}{[trans\text{-}\mathbf{1}]} = k.dt \qquad (2)$$

Equation (2) represents the differential form of the rate low. Integration of (2) gives (3):

$$\ln[trans\text{-}\mathbf{1}] = -k.t + C \qquad (3)$$

C represents the constant of integration and is obtained when t = 0 and [*trans*-**1**] = [*trans*-**1**]$_0$.

$$C = \ln([trans\text{-}\mathbf{1}]_0) \qquad (4)$$

Finally, integrating equation (4) in equation (3) gives (5):

$$\ln\frac{[trans\text{-}\mathbf{1}]}{[trans\text{-}\mathbf{1}]_0} = -k.t \qquad (5)$$

Plots of equation (5) at the 4 different temperatures studied are represented in Fig. 2. As straight lines are obtained, the first assumption that reaction was first order is confirmed. The slopes of these straight lines gave kinetic constants k (see Table 2).

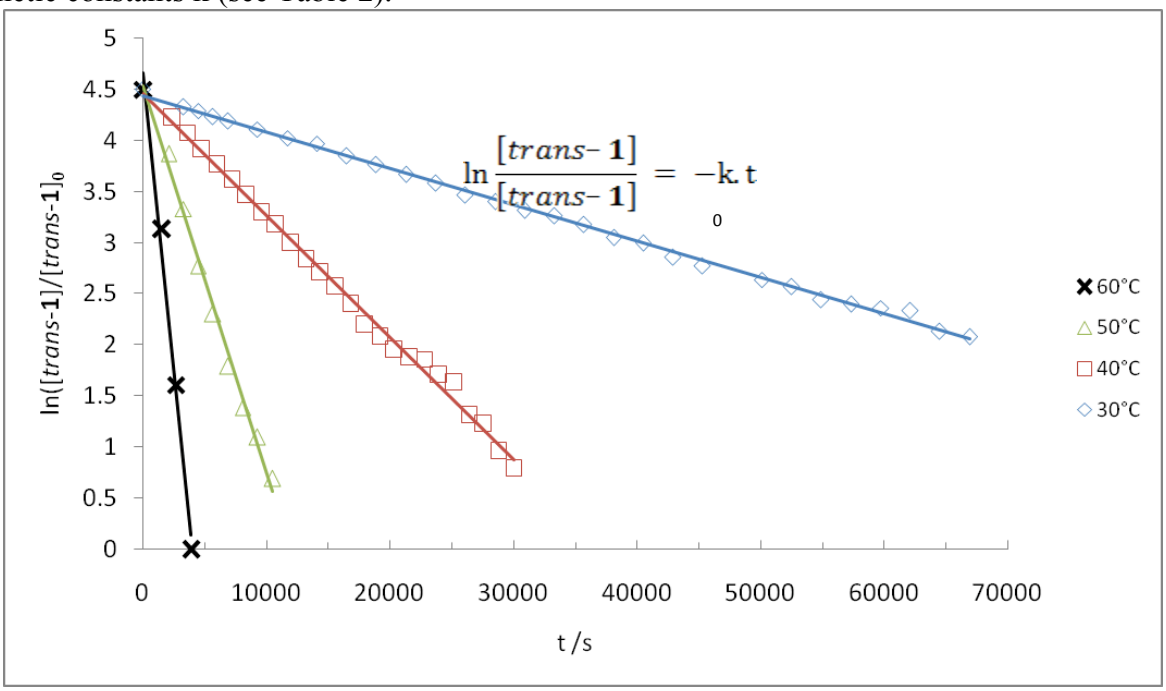


Fig. 2 Plots of ln([*trans*-**1**]/[*trans*-**1**]$_0$) against time (in seconds) at temperature from 30°C to 60°C.

Table 2 Kinetic constant values

Temperature (°C)	k (s^{-1})
30	0.0000355
40	0.0001197
50	0.0003778
60	0.0011587

The general form of the Eyring-Polanyi equation is the following:

$$k = k_B . \frac{T}{h} e^{-\frac{\Delta G^{\neq}}{RT}} \quad (6)$$

Where: - $\Delta G^{\neq}$ is the Gibbs energy of activation,
k_B is the Boltzmann's constant (1.38×10^{-23} J.K^{-1}),
h is Planck's constant (6.63×10^{-34} J.s),
R is the gas constant (8.32 J.K^{-1}.mol^{-1}) and
T is the absolute temperature (in K).

Knowing that $\Delta G^{\neq} = \Delta H^{\neq} - T.\Delta S^{\neq}$, linearising equation (6) gives (7):

$$\ln\frac{k}{T} = -\frac{\Delta H^{\neq}}{RT} + \ln\frac{k_B}{h} + \frac{\Delta S^{\neq}}{R} \quad (7)$$

Plot of ln(k/T) against 1/T, or in our case 1000/T, gives the Eyring plot (Fig. 3).
The slope of straight line gives:

$\frac{\Delta H^{\neq}}{R}$ = 11395 K

and the intercept:

$\ln\frac{k_B}{h} + \frac{\Delta S^{\neq}}{R}$ = 21.63

Finally, after conversions, the enthalpy of activation is $\Delta H^{\neq} = 22.6$ kcal.mol^{-1} and the entropy is $\Delta S^{\neq} = -4.2$ cal.mol^{-1}.K^{-1}.

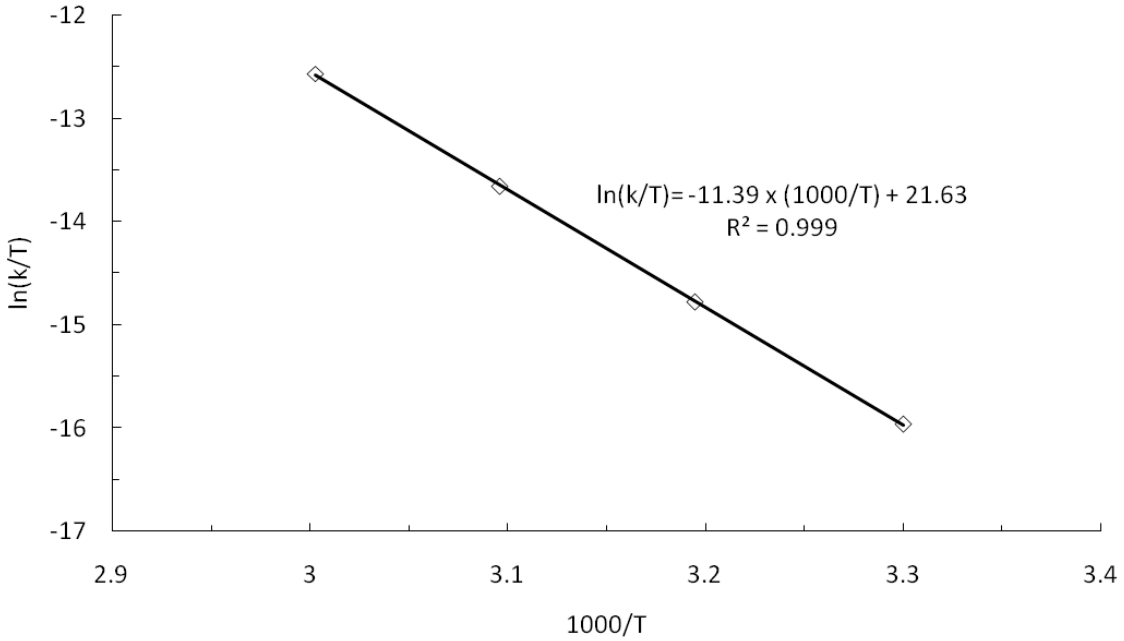


Fig. 3. Eyring plot of the *trans*/*cis* isomerisation of **1**.

Table 3 Kinetic data for Fig. 1

30°C		40°C		50°C		60°C	
Time (s)	[*trans*-**1**]/[*trans*-**1**]$_0$	Time (s)	[*trans*-**1**]/[*trans*-**1**]$_0$	Time (s)	[*trans*-**1**]/[*trans*-**1**]$_0$	Time (s)	[*trans*-**1**]/[*trans*-**1**]$_0$
0	90	0	90	0	90	0	90
3300	76	2400	68	2100	48	1500	23
4500	73	3600	59	3300	28	2700	5
5700	69	4800	50	4500	16	3900	1
6900	66	6000	43	5700	10	5100	0
9300	61	7200	37	6900	6		
11700	56	8400	32	8100	4		
14100	53	9600	27	9300	3		
16500	47	10800	24	10500	2		
18900	43	12000	20				
21300	39	13200	17				
23700	36	14400	15				
26100	32	15600	13				
28500	30	16800	11				
30900	27.5	18000	9				
33300	26	19200	8				
35700	24	20400	7				
38100	21	21600	6.5				
40500	20	22800	6.4				
42900	17.4	24000	5.5				
45300	16	25200	5.1				
50100	14	26400	3.7				
52500	13	27600	3.4				
54900	11.5	28800	2.6				
57300	11	30000	2.2				
59700	10.6						
62100	10.3						
64500	8.4						
66900	8						

6 References

1 Y. Terada, M. Mitsuhiro, A. Nishida, *Angew. Chem. Int. Ed.* **2004**, *116*, 4155-4157.
2 T. A. Kirkland, R. H. Grubbs, *J. Org. Chem.* **1997**, *62*, 7310-7318.
3 H. Clavier, S. P. Nolan *Chem. Eur. J.* **2007**, *13*, 8029-8036.
4 K. D. Schleicher, T. F. Jamison, *Org. Lett.* **2007**, *9*, 875-878.
5 A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236 –3253.
6 A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk,G. Dolgonos, K. Grela, *J. Am. Chem. Soc.* **2004**, *126*, 9318-9325.
7 A. Fürstner, O. Guth, A.Düffels, G. Seidel, M. Liebl, B. Gabor, R. Mynott, *Chem. Eur. J.* **2001**, *7*, 4811– 4820.
8 Q. Yao, Y. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 74-75.
9 a) G. B. Bachmann, H. A. Tanner, *J. Org. Chem.* **1939**, *4*, 493-501; b) B. A. Baylouny, *J. Am. Chem. Soc.* **1971**, *93*, 4621-4622.