Supporting Information

Improving Grubbs II Type Ruthenium Catalysts by Appropriately Modifying the N-Heterocyclic Carbene Ligand

Ludovic Vieille-Petit, Xinjun Luan, Michele Gatti, Sascha Blumentritt, Anthony Linden, Hervé Clavier, Steven P. Nolan, and Reto Dorta.*

1. Synthesis and characterization of complexes of general formula $[RuCl_2(NHC)(=CHPh)(PCy_3)]$ (2a-e) and of decomposition product 2c'.

1.1. General information

All manipulations were carried out under an inert atmosphere of nitrogen using Schlenk or glovebox (Mecaplex or Innovative Technology) techniques. Solvents were either distilled from appropriate drying agents or purged with argon and collected after passage through alumina columns in a solvent purification system (Innovative Technology). Deuterated NMR solvents were purchased from Armar Chemicals, degassed and dried over activated molecular sieves of appropriate size. NMR spectra were recorded using Bruker ARX-300, AV2-400 and AV-600 spectrometers and treated with MestReC. Mass spectra and elemental analyses were recorded by the analytical services of the Institute of Organic Chemistry (UZH). $[RuCl_2(=CHPh)(PCy_3)_2]$ was purchased from Aldrich. $[RuCl_2(SIMes)(=CH\text{-}Ph)(PCy_3)]$ (**GII**),[1] {$RuCl_2$[1,3-bis(*o*-tolyl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} (**GII'**),[2] and $[RuCl_2\{(2,7)\text{-}SIMeNap\}(=CH\text{-}Ph)(PCy_3)]$ (**11**)[3] were prepared according to literature procedures. Details on the synthesis and characterization of the imidazolinium salts and the free carbenes are available elsewhere.[4] Crystals were mounted on a glass fibre and used for a low-temperature X-ray structure determination. All measurements were made on a *Nonius KappaCCD* area-detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler.

---

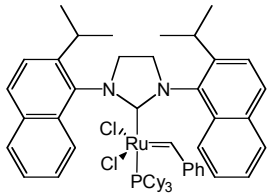
1 (a) M. Scholl, S. Ding, C. W. Lee, and R. H. Grubbs, *Org. Lett.,* 1999, **1**, 953. (b) T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Sholl, T.-L. Choi, S. Ding, M. W. Day, and R. H. Grubbs, *J. Am. Chem. Soc.,* 2003, **125**, 2546.

2 I. C. Stewart, T. Ung, A. A. Pletnev, J. M. Berlin, R. H. Grubbs, and Y. Schrodi, *Org. Lett.,* 2007, **9**, 1589.

3 X. Luan, R. Mariz, M. Gatti, C. Costabile, A. Poater, L. Cavallo, A. Linden, and R. Dorta, *J. Am. Chem. Soc.,* 2008, **130**, 6848.

4 L. Vieille-Petit, X. Luan, R. Mariz, S. Blumentritt, A. Linden, R. Dorta, *Eur. J. Inorg. Chem.,* 2009, Early View.

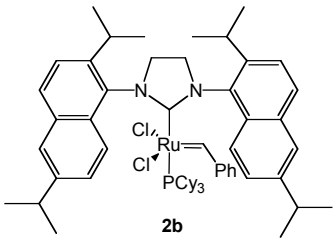
1.2. {$RuCl_2$[1,3-bis(2-isopropyl-naphthalen-1-yl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} [$RuCl_2${(2)-SIPrNap}(=CHPh)(PCy_3)] (2a)



2a

In 80 mL of toluene, a mixture of free carbene (2)-SIPrNap (**1a**) (414 mg, 1.018 mmol) and [$RuCl_2$(=CHPh)(PCy_3)$_2$] (821 mg, 0.998 mmol) was stirred at room temperature. After 24 hours, the ^{31}P NMR spectrum of the dark violet solution showed the presence of a small amount of starting complex, and an additional portion of the free carbene was added (121 mg, 0.298 mmol). The solution was stirred for another hour. After control of complete consumption of [$RuCl_2$(=CH-Ph)(PCy_3)$_2$], the solution was evaporated to dryness and dried overnight under vacuum. The dark-red residue was washed with 20 mL of methanol and dissolved in a minimum of CH_2Cl_2. Slow diffusion of MeOH into this concentrated solution gave **2a** as dark red crystals suitable for X-ray structure analysis. Yield: 663 mg (70%). Spectroscopic data for **2a**: ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 19.18 and 19.12 (2s, 1H, Ru=C*H*-Ph), 8.73-6.65 (m, 17H, H_{arom}), 4.38-3.42 (m, 6H, N(CH_2)$_2$N and ArC*H*(CH_3)$_2$), 1.96-0.49 (m, 45H, ArCH(CH_3)$_2$ and P(C_6H_{11})$_3$). ^{31}P{^{1}H} (162 MHz, CD_2Cl_2, 27 °C): δ 29.84 and 29.53 (2s). MS (ESI, MeOH-CH_2Cl_2): *m/z* = 913.7 [M-Cl]$^+$. Elemental analysis: calcd. for $C_{54}H_{69}Cl_2N_2PRu \cdot 2MeOH$: C 66.39 %, H 7.66 %, N 2.76 %; found : C 66.13 %, H 7.72 %, N 3.02 %.

1.3. {$RuCl_2$[1,3-bis(2,6-diisopropyl-naphthalen-1-yl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} [$RuCl_2${(2,6)-SIPrNap}(=CHPh)(PCy_3)] (2b)

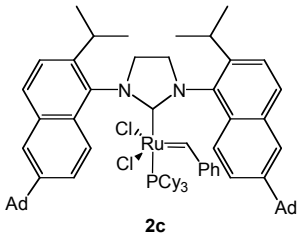


2b

In 80 mL of toluene, a mixture of free carbene (2,6)-SIPrNap (**1b**) (329 mg, 0.670 mmol) and [$RuCl_2$(=CHPh)(PCy_3)$_2$] (540 mg, 0.656 mmol) was stirred at room temperature. After 24 hours, the ^{31}P NMR spectrum of the dark violet solution

showed the presence of a small amount of starting complex, and an additional portion of the free carbene was added (32 mg, 0.065 mmol). The solution was stirred for another hour. After control of complete consumption of [$RuCl_2$(=CH-Ph)(PCy_3)$_2$], the solution was evaporated to dryness and dried overnight under vacuum. The dark-red residue was washed with 20 mL of methanol and dissolved in a minimum of CH_2Cl_2. Slow diffusion of MeOH into this concentrated solution gave **2b** as dark red crystals suitable for X-ray structure analysis. Yield: 495 mg (73%). Spectroscopic data for **2b**: ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 19.20 and 19.10 (2s, 1H, Ru=C*H*-Ph), 8.67-6.64 (m, 15H, H_{arom}), 4.39-2.96 (m, 8H, N(CH_2)$_2$N and ArC*H*(CH_3)$_2$), 1.96-0.54 (m, 57H, ArCH(CH_3)$_2$ and P(C_6H_{11})$_3$). ^{31}P{^{1}H} (162 MHz, CD_2Cl_2, 27 °C): δ 30.09 and 29.80 (2s). MS (ESI, MeOH-CH_2Cl_2): *m/z* = 997.8 [M-Cl]$^+$. Elemental analysis: calcd. for $C_{60}H_{81}Cl_2N_2PRu \cdot MeOH \cdot ½CH_2Cl_2$: C 66.68 %, H 7.83 %, N 2.53 %; found : C 66.72 %, H 7.67 %, N 2.74 %.

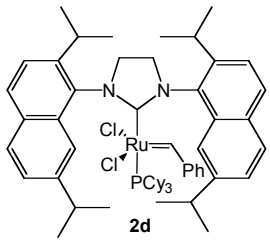
1.4. {$RuCl_2$[1,3-bis(2-isopropyl-6-adamantyl-naphthalen-1-yl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} [$RuCl_2${(2,6)-SIPrAdNap)(=CHPh)(PCy_3)] (2c)



2c

In 80 mL of toluene, a mixture of free carbene (2,6)-SIPrAdNap (**1c**) (602 mg, 0.892 mmol) and [$RuCl_2$(=CHPh)(PCy_3)$_2$] (699 mg, 0.850 mmol) was stirred at room temperature. After 24 hours, the solution was evaporated to dryness and dried overnight under vacuum. The dark-red residue was suspended in ether (60 mL) and MeOH (100 mL) was added. After centrifugation, the pink precipitate was collected and dried under vacuum. Another crop of clean compound was obtained by taking the mother liquor to dryness, redissolving it in ether/pentane and precipitating it at -35°C. Overall yield: 405 mg, (39%). Spectroscopic data for **2c** (one isomer only was isolated): ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 19.12 (s, 1H, Ru=C*H*-Ph), 8.74-6.63 (m, 15H, H_{arom}), 4.36-3.95 (m, 4H, N(CH_2)$_2$N), 2.16-0.52 (m, 77H, ArC*H*(CH_3)$_2$, ArCH(CH_3)$_2$, P(C_6H_{11})$_3$ and Ar-Ad.). ^{31}P{^{1}H} (121 MHz, CD_2Cl_2, 27 °C): δ 30.06 (s). MS (ESI, MeOH-CH_2Cl_2): *m/z* = 1181.9 [M-Cl]$^+$. Elemental analysis: calcd. for $C_{74}H_{97}Cl_2N_2PRu \cdot MeOH \cdot Et_2O$: C 71.68 %, H 8.45 %, N 2.12 %; found : C 71.66 %, H 8.35 %, N 2.54 %.

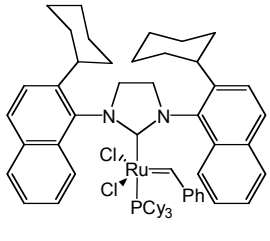
1.5. {$RuCl_2$[1,3-bis(2,7-diisopropyl-naphthalen-1-yl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} [$RuCl_2${(2,7)-SIPrNap}(=CHPh)(PCy_3)] (2d)



2d

In 140 mL of toluene, a mixture of free carbene (2,7)-SIPrNap (**1d**) (800 mg, 1.630 mmol) and [$RuCl_2$(=CHPh)(PCy_3)$_2$] (1.315 g, 1.600 mmol) was stirred at room temperature. After 24 hours, the ^{31}P NMR spectrum of the dark violet solution showing the presence of a small amount of starting complex, and an additional portion of the free carbene was added (146 mg, 0.298 mmol). The solution was stirred for another hour. After control of complete consumption of [$RuCl_2$(=CHPh)(PCy_3)$_2$], the solution was evaporated to dryness and dried overnight under vacuum. The dark-red residue was washed with 20 mL of methanol and dissolved in a minimum of CH_2Cl_2. Slow diffusion of MeOH into this concentrated solution gave **2d** as dark red crystals suitable for X-ray structure analysis. Yield: 1.223 g (74%). Spectroscopic data for **2d**: ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 19.23 and 19.20 (2s, 1H, Ru=C*H*-Ph), 8.56-6.66 (m, 15H, H_{arom}), 4.42-3.14 (m, 8H, N(CH_2)$_2$N and ArC*H*(CH_3)$_2$), 1.98-0.56 (m, 57H, ArCH(CH_3)$_2$ and P(C_6H_{11})$_3$). ^{31}P{^{1}H} (162 MHz, CD_2Cl_2, 27 °C): δ 29.49 and 29.22 (2s). MS (ESI, MeOH-CH_2Cl_2): *m/z* = 997.8 [M-Cl]$^+$. Elemental analysis: calcd. for $C_{60}H_{81}Cl_2N_2PRu \cdot 3/2MeOH$: C 68.31 %, H 8.11 %, N 2.59 %; found : C 68.19 %, H 8.22 %, N 2.98 %.

1.6. {$RuCl_2$[1,3-bis(2-cyclohexyl-naphthalen-1-yl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} [$RuCl_2${(2)-SICyNap}(=CHPh)(PCy_3)] (2e)

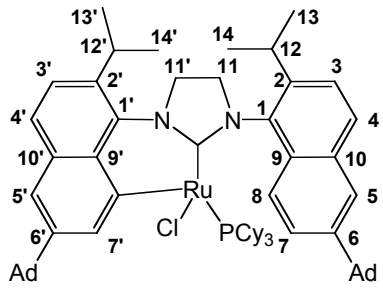


2e

In 60 mL of toluene, a mixture of free carbene (2)-SICyNap (**1e**) (414 mg, 0.851 mmol) and [$RuCl_2$(=CH-Ph)(PCy_3)$_2$] (700 mg, 0.850 mmol) was stirred at room temperature. After 28 hours, the ^{31}P NMR spectrum of the dark violet solution showed complete consumption of [$RuCl_2$(=CHPh)(PCy_3)$_2$] and the solution was

evaporated to dryness and dried overnight under vacuum. Ether (ca. 20 mL) was added to the resulting dark red residue and the insoluble fraction was separated by centrifugation and collected. To the resulting clear solution was added MeOH (ca. 50 mL) and the resulting precipitate was filtered. Solid materials were combined and washed with MeOH (2 x 5 mL). After drying overnight under vacuum, **2e** was obtained as a fine pink powder. Yield: 612 mg (70%). Crystals suitable for X-ray structure analysis were obtained by slow diffusion of MeOH into a concentrated solution of **2e** in CH_2Cl_2. Spectroscopic data for **2e**: ^{1}H NMR (400 MHz, CD_2Cl_2, 0 °C): δ 19.23 and 19.11 (2s, 1H, Ru=C*H*-Ph), 8.77-6.31 (m, 17H, H_{arom}), 4.30-3.50 (m, 4H, N(CH_2)$_2$N), 2.54-0.38 (m, 55H, P(C_6H_{11})$_3$ and Ar(C_6H_{11})). ^{31}P{^{1}H} (162 MHz, CD_2Cl_2, 0 °C): δ 30.29 and 29.73 (2s). MS (ESI, MeOH-CH_2Cl_2): *m/z* = 993.7 [M-Cl]$^+$. Elemental analysis: calcd. for $C_{60}H_{77}Cl_2N_2PRu \cdot MeOH$: C 69.04 %, H 7.69 %, N 2.64 %; found : C 69.14 %, H 7.58 %, N 3.00 %.

1.7. 14-electron decomposition product 2c'



2c'

To a saturated solution of [$RuCl_2${(2,6)-SIPrAdNap)(=CHPh)(PCy_3)] (**2c**) in CH_2Cl_2 was slowly added MeOH. The initially formed microcrystalline material (1 day) dissolved over time and after 5 days, dark crystals of **2c'** were obtained (50-65% yield depending on the sample). Spectroscopic data for **2c'**: ^{1}H NMR (600 MHz, CD_2Cl_2, 27 °C): δ 8.88 (d, J = 1.7 Hz, 1H, H-7'), 8.00 (d, J = 1.4 Hz, 1H, H-5), 7.82 (d, J = 8.6 Hz, 1H, H-4), 7.68 (dd, J_1 = 8.5 Hz, J_2 = 1.4 Hz, 1H, H-7), 7.46 (d, J = 8.6 Hz, 1H, H-3), 7.44 (m, 1H, H-8), 7.40 (d, J = 8.5 Hz, 1H, H-4'), 7.20 (d, J = 8.5 Hz, 1H, H-3'), 6.92 (d, J = 1.7 Hz, 1H, H-5'), 5.05 (m, 1H, H-11'), 4.50 (m, 1H, H-11), 4.07 (m, 1H, H-11), 3.96 (m, 1H, H-11'), 3.68 (sept, ^3J = 6.9 Hz, 1H, H-12), 3.41 (sept, ^3J = 6.8 Hz, 1H, H-12'), 2.10-0.94 (series of m and br, 63H, H_{ad} and P(C_6H_{11})$_3$, 1.53 (d, ^3J = 6.8 Hz, 3H, H-13'), 1.48 (d, ^3J = 6.9 Hz, 3H, H-14), 1.43 (d, ^3J = 6.9 Hz, 3H, H-13), 1.32 (d, ^3J = 6.8 Hz, 3H, H-14'). ^{13}C{^{1}H} (150 MHz, CD_2Cl_2, 27 °C) *: δ 142.5 (C-2), 138.2 (C-7'), 135.6 (C-9'), 135.3 (C-7), 130.7 (C-2'), 129.9 (C-9), 128.5 (C-4), 126.6

(C-5), 126.3 (C-4'), 123.5 (C-3), 122.8 (C-3'), 114.6 (C-5'), 106.4 (C-8), 55.0 (C-11'), 52.3 (C-11), 51.0, 44.0, 43.8, 37.7, 37.5, 37.2, 36.6, 30.2, 30.0, 29.8, 29.6 (C-12'), 29.3, 28.7 (C-12), 27.9, 27.8, 27.6, 26.9, 26.9, 26.5, 25.9 (C-14'), 25.2 (C-13), 24.1 (C-13'), 22.2 (C14). $^{31}P\{^{1}H\}$ (162 MHz, CD_2Cl_2, 27 °C): δ 77.63 (s).

* Due to the low solubility of the complex, quaternary carbons C-1', C-6', C-8', C-1, C-6, C-10', C-10 and N*C*-Ru do not appear on the spectrum, even after a prolonged time (2 days).

1.8. Analytical data of the Mother Liquor of 2c'

The supernatant solution containing crystalline **2c'** is collected and dried under vacuum.

-) The ^{1}H NMR spectrum (CD_2Cl_2) can be found as Figure S16 below and does not show any signals belonging to metal-bound benzylidene or Ruthenium-H species.

-) The ^{31}P NMR spectrum (CD_2Cl_2) is shown in Figure S17. A main signal at ca. 28 ppm is attributed to a phosphine-containing Ru-species. Previously identified PCy_3HCl,[5] is not detected (ca. 33.8 ppm). It is though of note that a solution of the mother liquor prepared in C_6D_6 decomposes over the course of 1 day and gives significant amounts of the phosphine salt.

-) GC-MS spectra of the mother liquor can be found in Figure S18. Comparison with an authentic sample (Figure S19) shows that the major organic fragment recovered from the mother liquor is stilbene.

1.9. X-ray data

Table S1: Selected bond lengths in complexes **2a**, **2b**, **2d**, **2e** and **GII**

	Ru-C(NHC)	Ru-alkylidene	Ru-P
GII	2.085(2)	1.835(2)	2.4245(5)
2a	2.074(2)	1.847(2)	2.4180(5)
2b	2.069(4)	1.830(4)	2.434(1)
2d	2.080(5)	1.846(5)	2.432(1)
2e	2.067(3)	1.834(4)	2.4191(9)

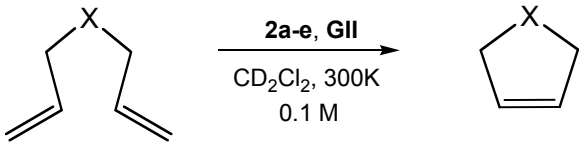
[5] S. H. Hong, A. Chlenov, M. W. Day, R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2007, **46**, 5148.

2. Catalytic experiments (Ring-Closing Metathesis (RCM))

2.1. General remarks

All catalytic samples were prepared under an inert atmosphere of nitrogen using gloveboxes. C_6F_6 was distilled from P_2O_5. Unless indicated otherwise, all reactions were run in NMR tubes equipped with a screw-cap septum top at 300K (27 °C) at a 0.1 M substrate/solvent ratio and the conversions were followed by ^{1}H NMR spectroscopy. The following substrates were synthesized according to literature procedures: **3**,[6] **4**,[7] **7**, **8**.[8]

2.2. RCM of diallyltosylamide (3) and diethyldiallyl malonate (4)



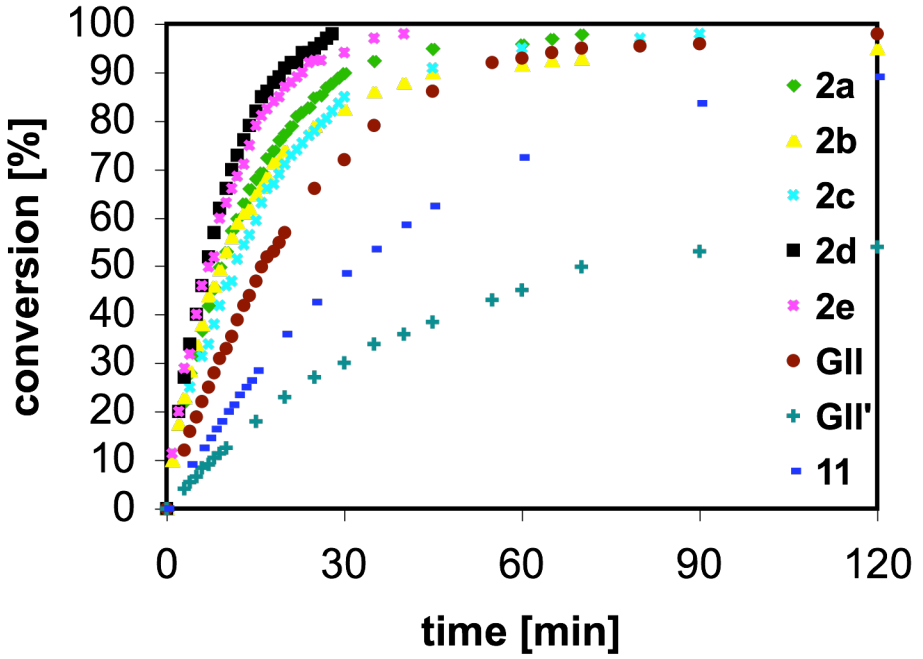
3: X = NTs
4: X = $C(CO_2Et)_2$

2.2.1 Catalyst loading of 1 mol %: To get precisely the required quantity of catalyst, a solution of the appropriate ruthenium complex (4.10^{-3} mmol) in 2 mL of CH_2Cl_2 was prepared. 400 µL of this solution was transferred to a NMR tube, evaporated to dryness and the residue was dried for one hour under vacuum. The tube was then closed with a screw-cap septum top. Separately, in a small vial, substrates **3** and **4** (0.08 mmol, 18.9 mg and 19.2 mg, respectively) were dissolved in 0.8 mL (0.1 M) of CD_2Cl_2 and then transferred via syringe to the respective NMR tubes containing the catalyst. The tube was vigorously stirred for a few seconds (the reaction time was started at this point) and introduced to the spectrometer and conversions were followed by registration of the ^{1}H NMR spectra.

2.2.2 Catalyst loading of 0.1 mol%: To get the required quantity of catalyst, a solution of the appropriate ruthenium complex (8.10^{-3} mmol) in 10 mL of CH_2Cl_2 was prepared. 100 µL of this solution was transferred to a NMR tube, evaporated to dryness and the residue was dried for one hour under vacuum. The tube was then closed with a screw-cap septum top. Separately, in a small vial, substrates **3** and **4** (0.08 mmol, 18.9 mg and 19.2 mg, respectively) were dissolved in 0.8 mL (0.1 M) of

6 Y. Terada, M. Mitsuhiro, and A. Nishida, *Angew. Chem. Int. Ed.*, 2004, **43**, 4063.
7 T. Ritter, A. Hejl, A. G. Wenzel, T. W. Funk, and R. H. Grubbs, *Organometallics* 2006, **25**, 5740.
8 J. M. Berlin, K. Campbell, T. Ritter, T. W. Funk, A. Chlenov, and R. H. Grubbs, *Org. Lett.*, 2007, **9**, 1339.

CD_2Cl_2 and then transferred via syringe to the respective NMR tube containing the catalyst. The tube was vigorously stirred for a few seconds (the reaction time was started at this point) and introduced to the spectrometer and conversions were followed by registration of the ^1H NMR spectra.



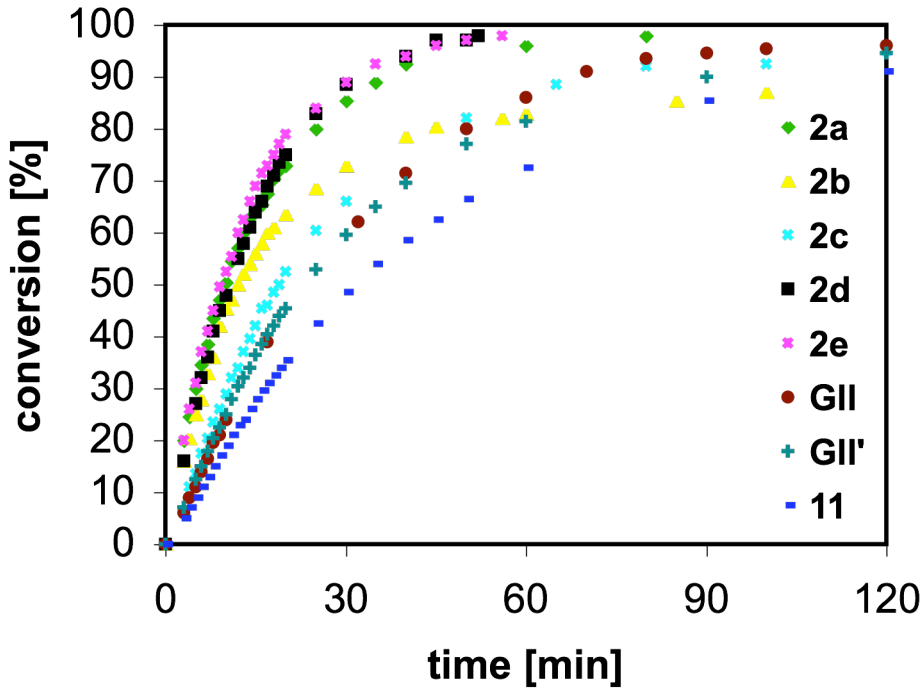
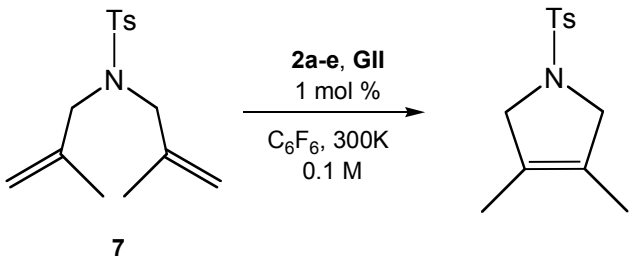


Figure S1: Kinetic data for the RCM of **3** (0.1 mol %)

Figure S2: Kinetic data for the RCM of **4** (0.1 mol %)

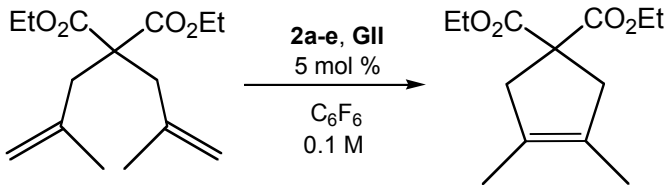
2.3. **RCM of dimethallyltosylamide (7) (1 mol%)**



7

To get the required quantity of catalyst, a solution of the appropriate ruthenium complex (4.10^{-3} mmol) in 2 mL of CH_2Cl_2 was prepared. 400 µL of this solution was transferred to a NMR tube, evaporated to dryness and the residue was dried for one hour under vacuum. The tube was then closed with a screw-cap septum top. Separately, in a small vial, substrate **7** (0.08 mmol, 21.2 mg) was dissolved in 0.8 mL (0.1 M) of C_6F_6 and then transferred via syringe to the NMR tube containing the catalyst. The tube was vigorously stirred for a few seconds (the reaction time was started at this point) and introduced to the spectrometer and conversions were followed by registration of the ^{1}H NMR spectra.

2.4. **RCM of diethyldimethallyl malonate (8) with 5 mol % of catalyst**



8

For practical reasons, the appropriate complex (4.10^{-3} mmol) was dissolved in the minimum amount of CH_2Cl_2. This solution was transferred to a NMR tube, evaporated to dryness and the residue was dried for one hour under vacuum. The tube was then closed with a screw-cap septum top. Separately, in a small vial, substrate **8** (0.08 mmol, 19.2 mg) was dissolved in 0.8 mL (0.1 M) of C_6F_6 and then transferred via syringe to the NMR tube containing the catalyst. The tube was vigorously stirred for a few seconds (the reaction time was started at this point) and introduced to an ultrasonic bath at room temperature. After 4 hours, the conversion was determined by ^{1}H NMR spectroscopy (temperature of the bath after 4 hours: 70 °C).

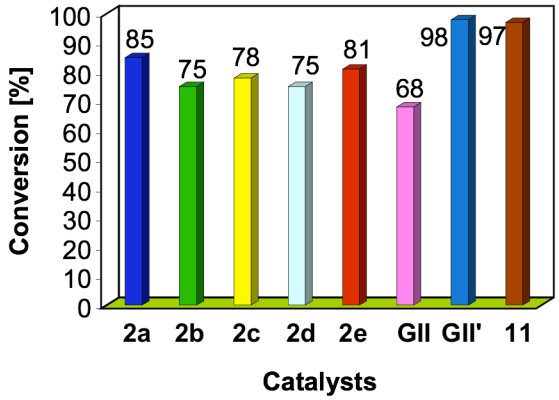


Figure S3: Data for the RCM of **8**

3. ^{1}H and $^{31}P\{^{1}H\}$ spectra of complexes of general formula $[RuCl_2(NHC)(=CHPh)(PCy_3)]$ (2a-e) and 2c'

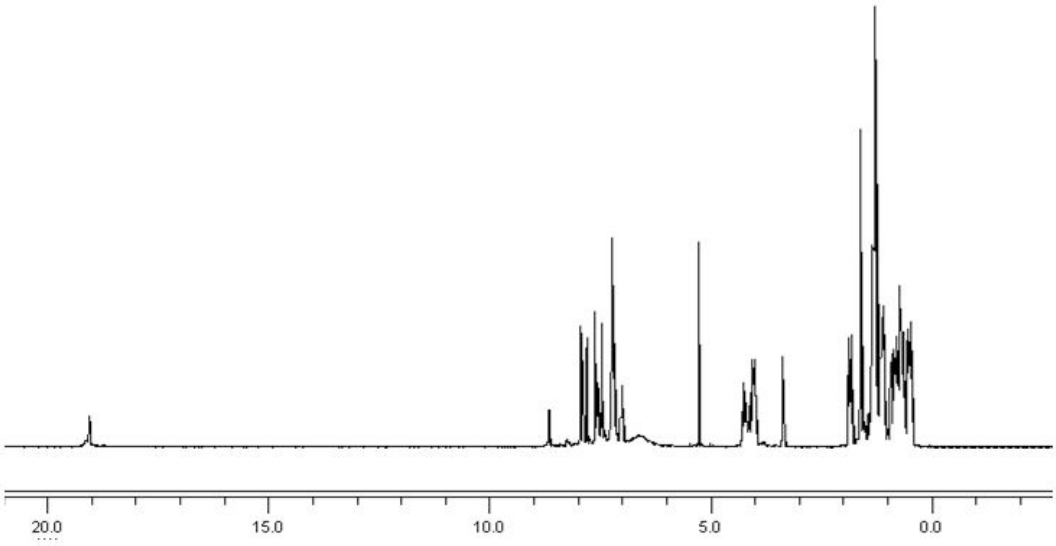


Figure S4: ^{1}H NMR spectrum of **2a** (400 MHz, CD_2Cl_2, 27 °C)

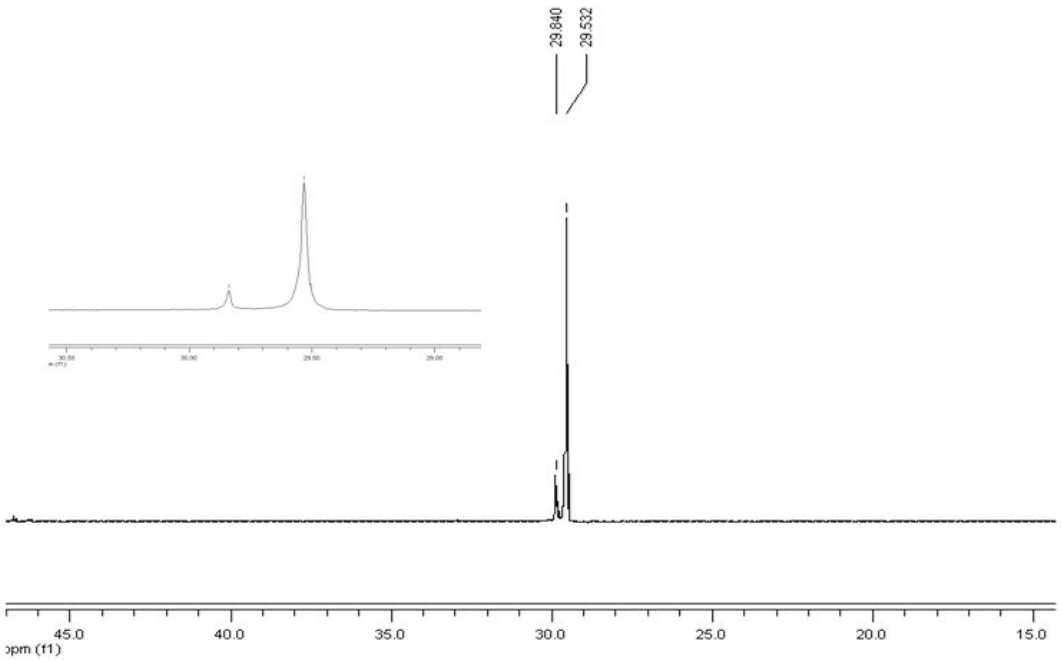


Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum of **2a** (162 MHz, CD_2Cl_2, 27 °C)

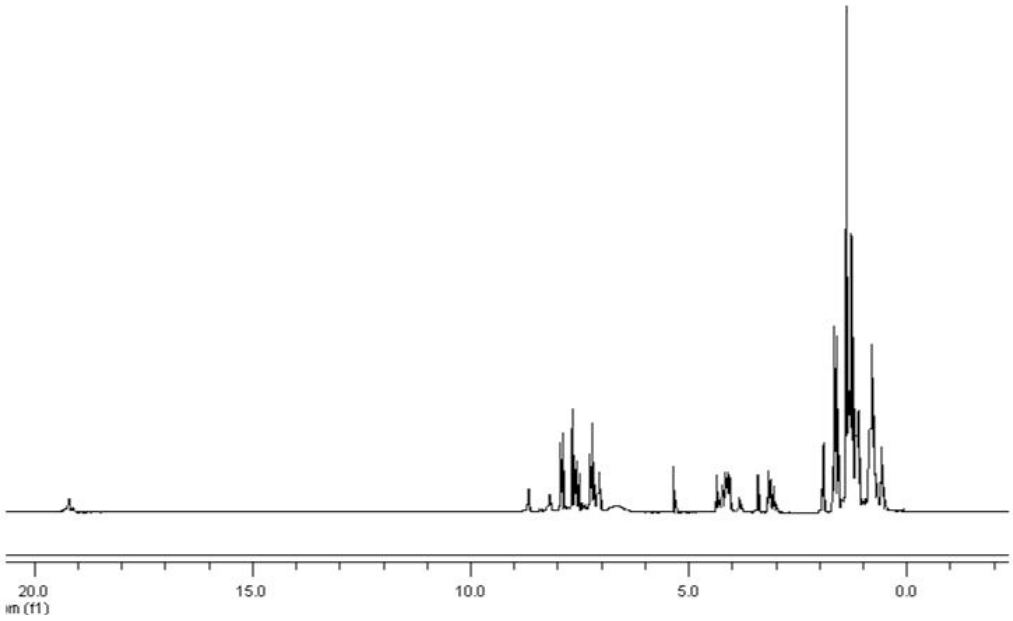


Figure S6: ^{1}H NMR spectrum of **2b** (400 MHz, CD_2Cl_2, 27 °C)

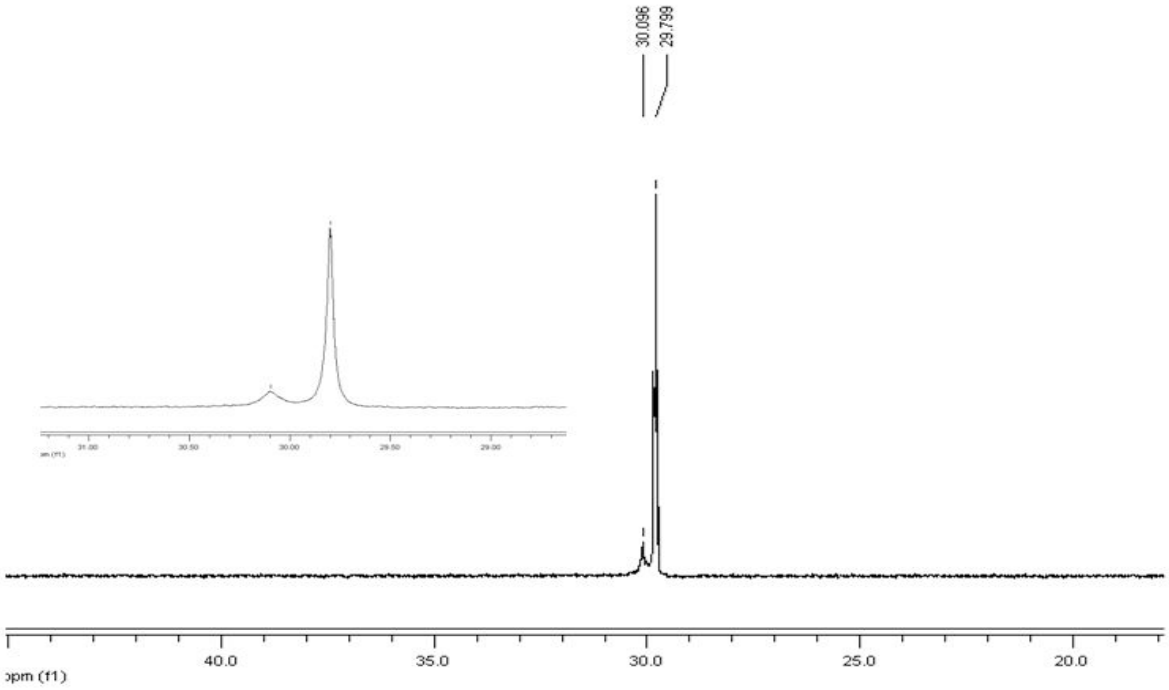


Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum of **2b** (162 MHz, CD_2Cl_2, 27 °C)

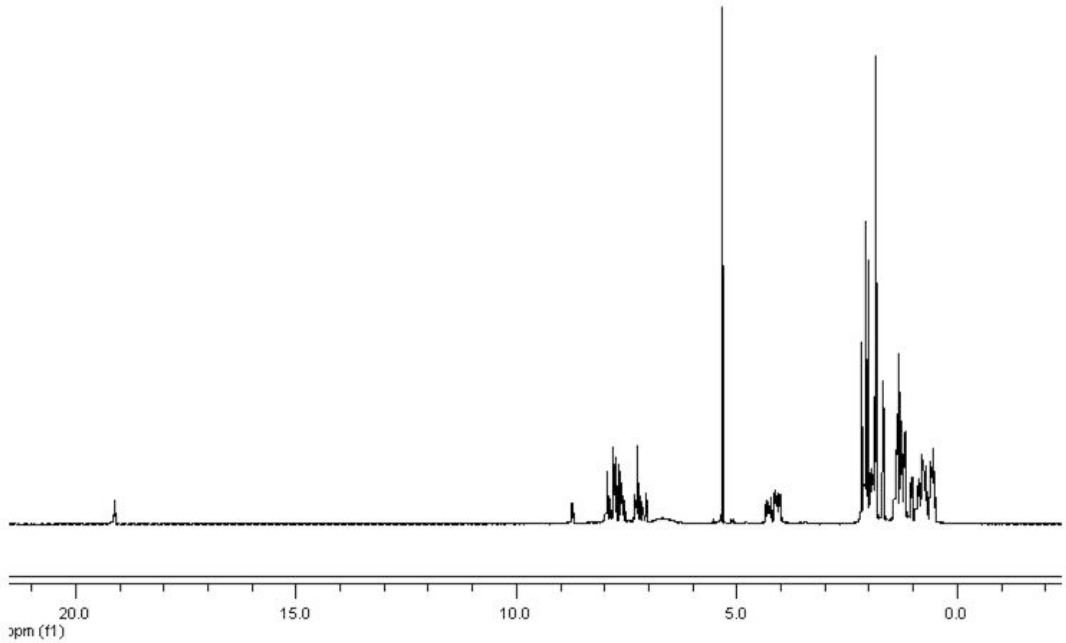


Figure S8: ^{1}H NMR spectrum of **2c** (400 MHz, CD_2Cl_2, 27 °C)

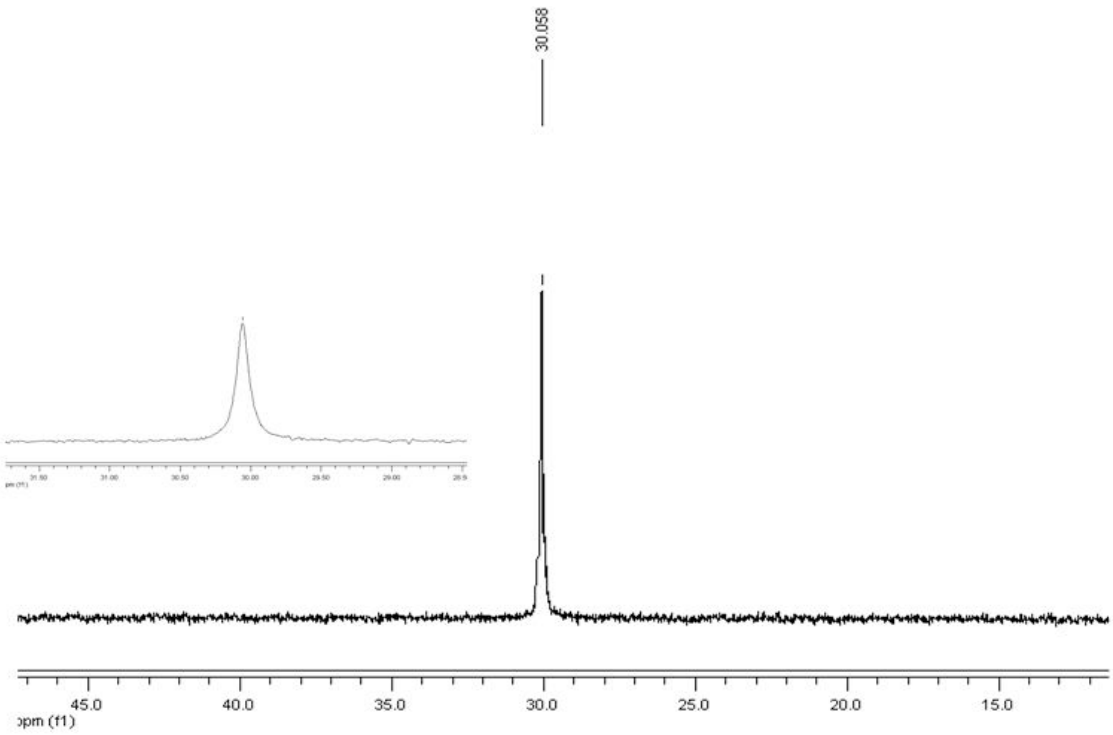


Figure S9: ^{31}P{^{1}H} NMR spectrum of **2c** (121 MHz, CD_2Cl_2, 27 °C)

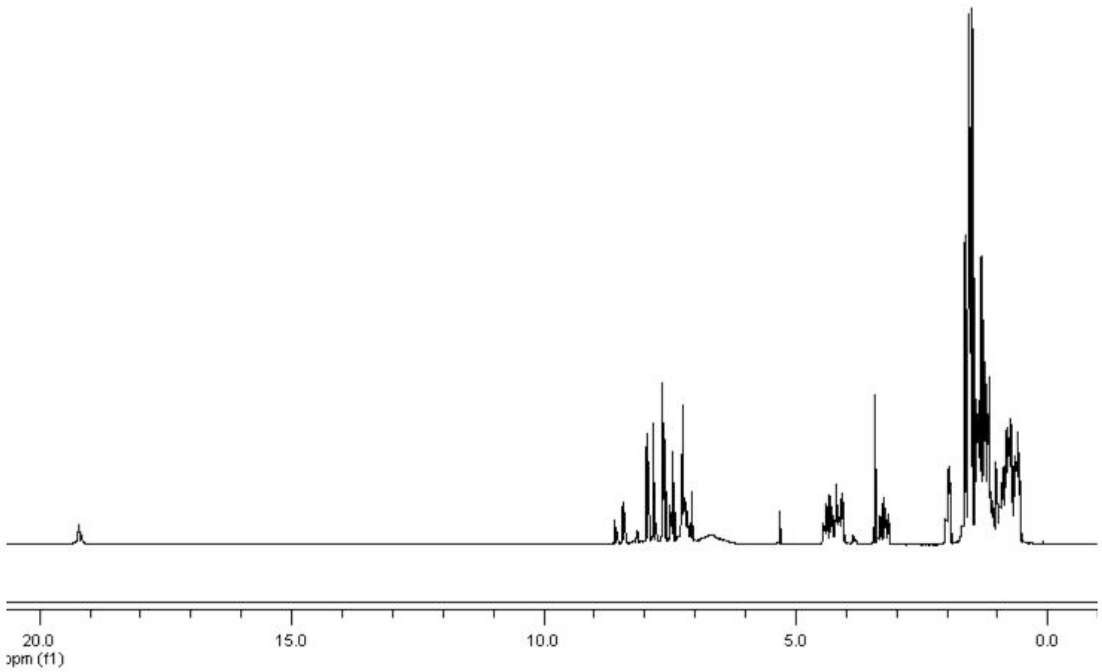


Figure S10: ^{1}H NMR spectrum of **2d** (400 MHz, CD_2Cl_2, 27 °C)

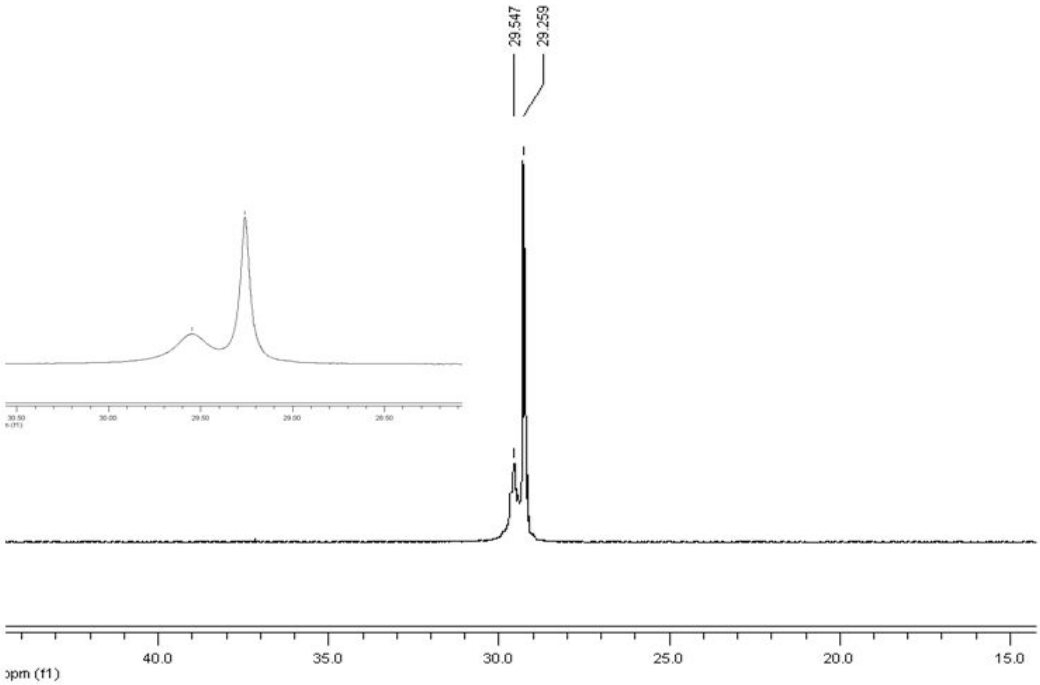


Figure S11: ^{31}P{^{1}H} NMR spectrum of **2d** (162 MHz, CD_2Cl_2, 27 °C)

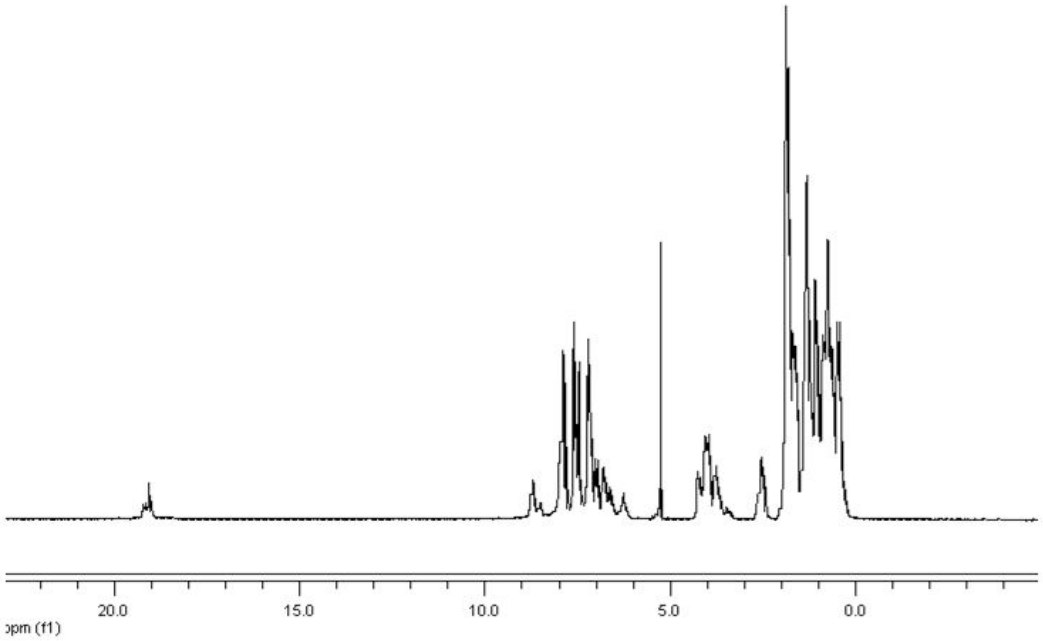


Figure S12: ^{1}H NMR spectrum of **2e** (400 MHz, CD_2Cl_2, 0 °C)

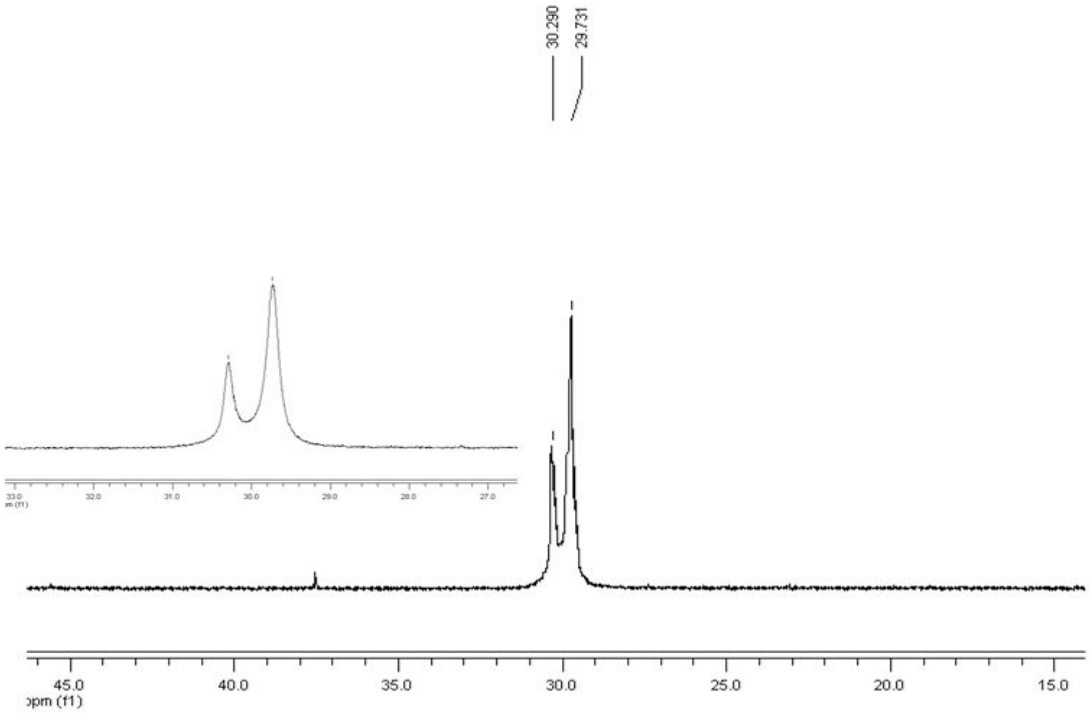


Figure S13: ^{31}P{^{1}H} NMR spectrum of **2e** (162 MHz, CD_2Cl_2, 0 °C)

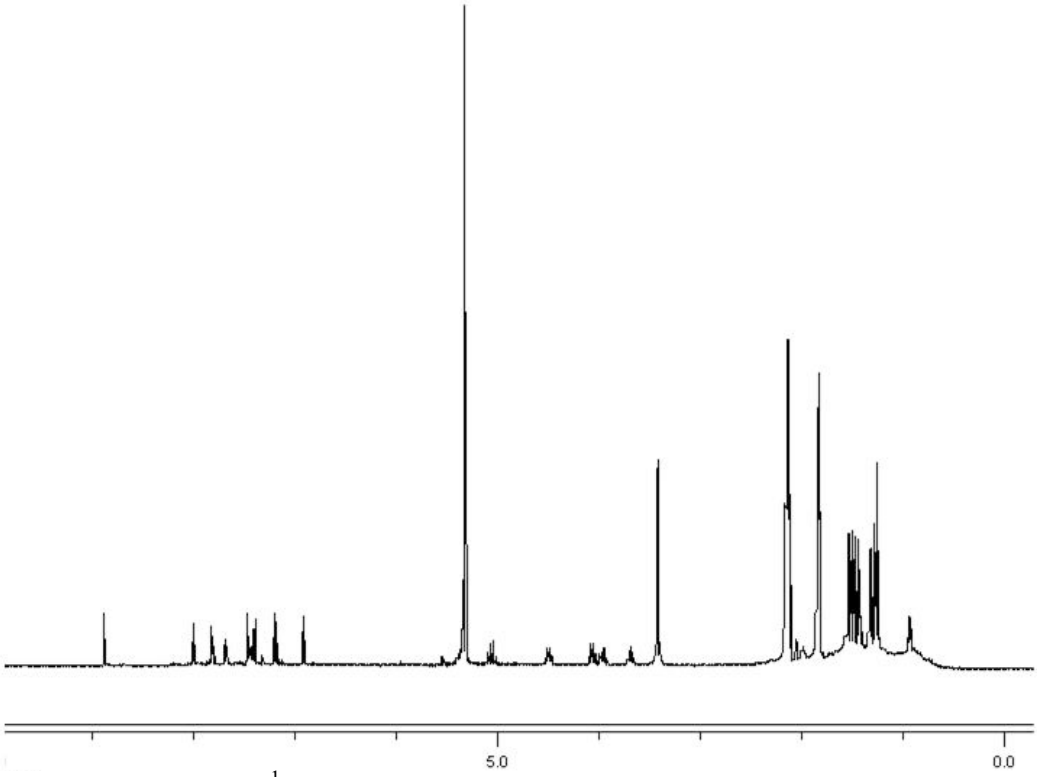


Figure S14: ^{1}H NMR spectrum of **2c'** (400 MHz, CD_2Cl_2, 27 °C)

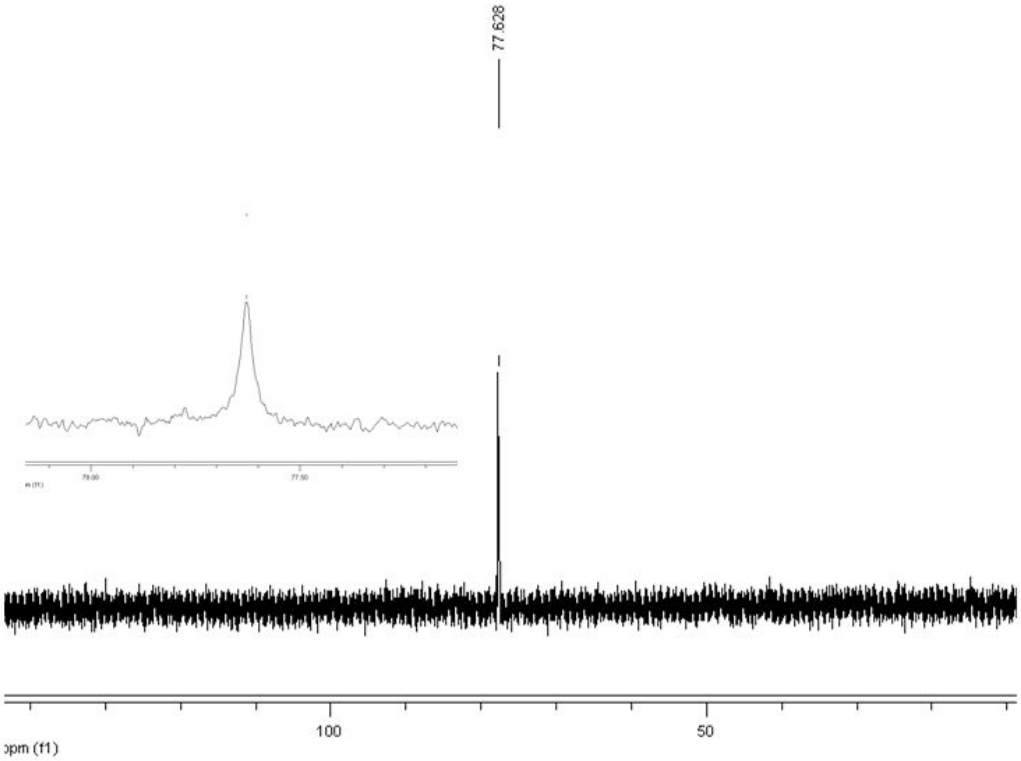


Figure S15: $^{31}P\{^{1}H\}$ NMR spectrum of **2c'** (162 MHz, CD_2Cl_2, 27 °C)

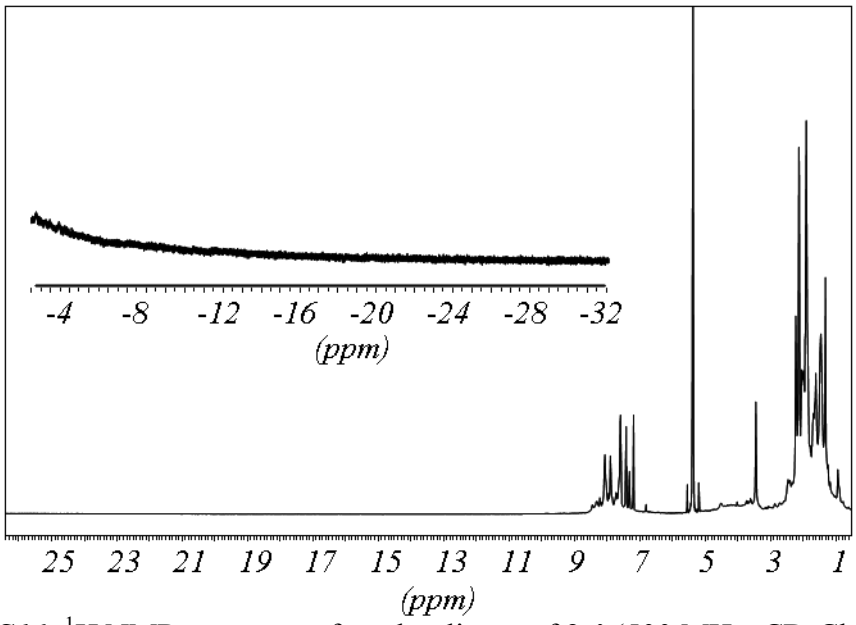


Figure S16: ^{1}H NMR spectrum of mother liquor of **2c'** (500 MHz, CD_2Cl_2, 27 °C)

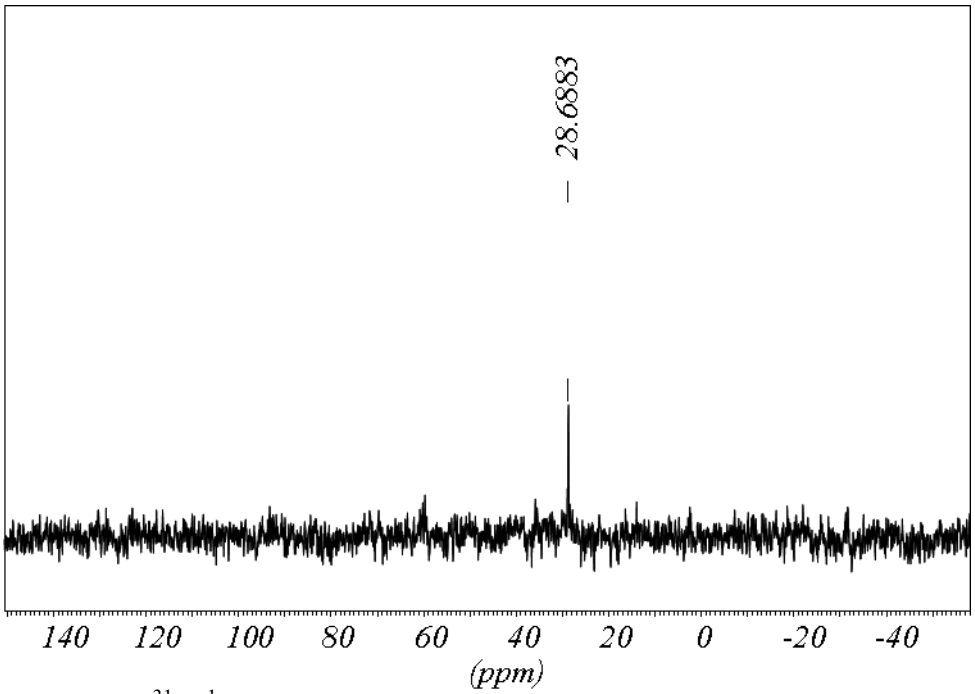


Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of ML of **2c'** (203 MHz, CD_2Cl_2, 27 °C)

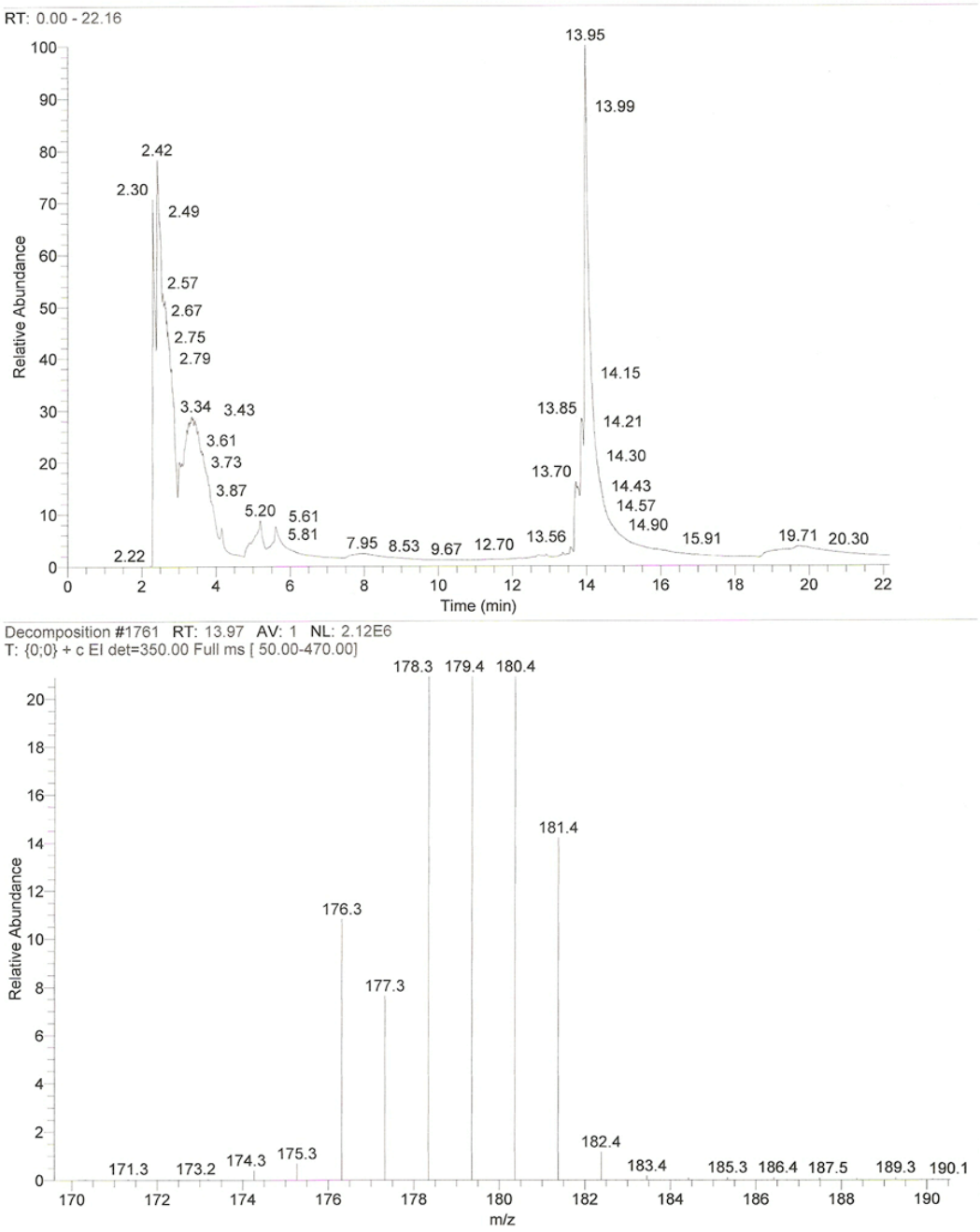


Figure S18: GC-MS analysis of the mother liquor of **2c'**.

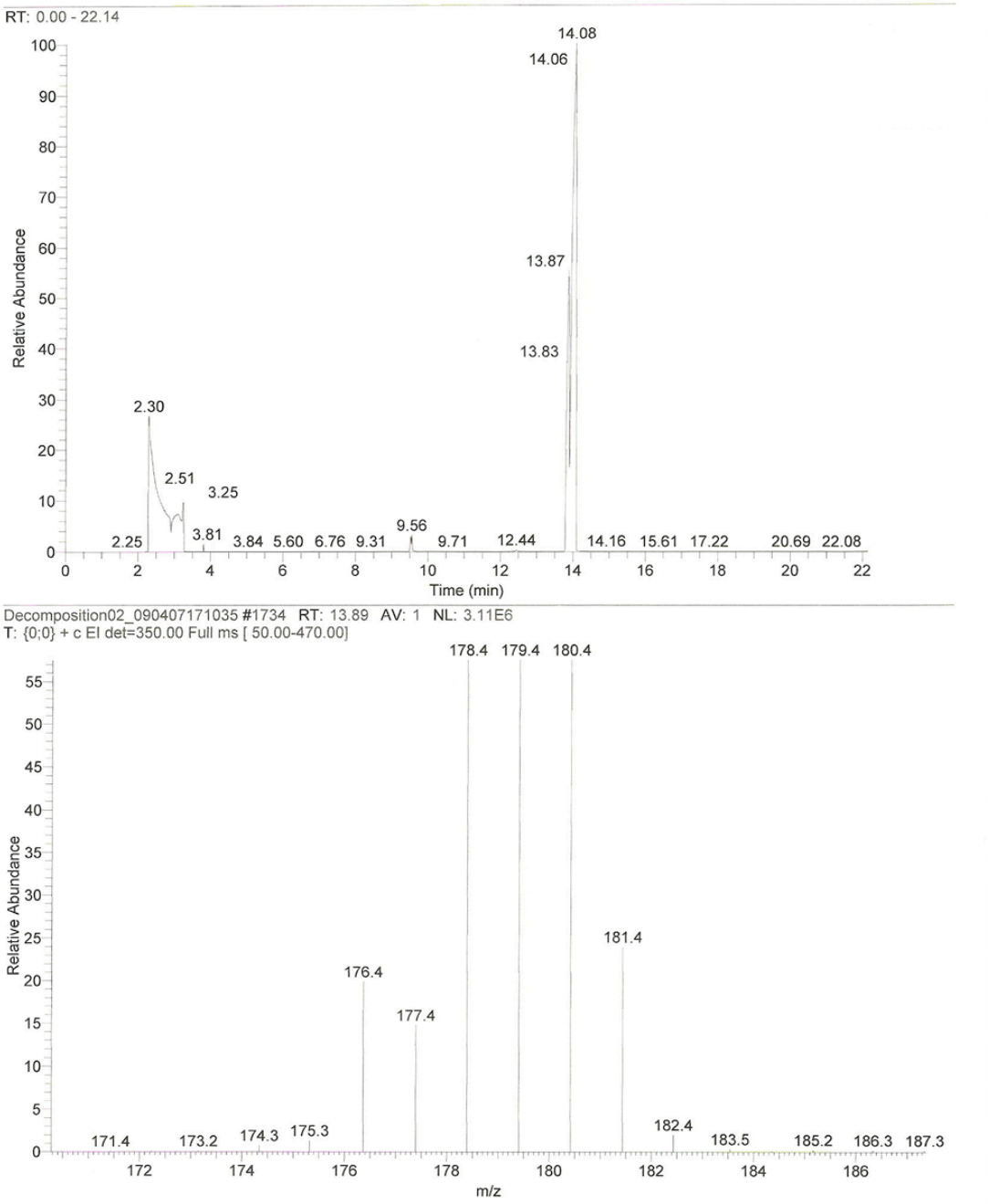


Figure S19: GC-MS analysis of stilbene