Supporting Information

Synthesis and Catalytic Properties of Sulfur-Chelated Ruthenium Benzylidenes Bearing a Cyclic (Alkyl)(amino)carbene Ligand

*Illya Rozenberg,[†] Or Eivgi,[†] Alex Frenklah,[†] Danielle Butilkov,[†] Sebastian Kozuch,[†] Israel Goldberg[‡] and N. Gabriel Lemcoff[†§]**

[†] Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel

[§] Ilse Katz Institute for Nanoscale Science and Technology, Beer-Sheva 8410501, Israel

[‡] School of Chemistry, Tel-Aviv University, Tel-Aviv 69978, Israel

** e-mail: lemcoff@bgu.ac.il*

Table of Contents

1. General

All commercially available solvents and reagents were of reagent grade and used without further purification unless otherwise stated. When stated, solvents were dried by passage through an MBraun solvent purification system.

NMR spectra were recorded on Bruker DPX 400 or DPX 500 instruments; chemical shifts, given in ppm, are relative to the residual solvent peaks.[1] ^{19}F-NMR analyses were done without prior calibration, and the reported spectra are used to show number of fluorine-containing species in the sample.

Gas chromatography data was obtained using an Agilent 6850 GC equipped with an Agilent 5973 MSD working under standard conditions and an Agilent HP5-MS column.

High resolution mass spectroscopy (HRMS) was performed using a Thermoscientific LTQU XL Orbitrap instrument equipped with APCI.

Purification by column chromatography was performed on Fluka silica gel (35-75 µm). TLC analyses were performed using Merck pre-coated silica gel (0.2 mm) aluminium sheets.

UV-Vis spectra were recorded using Shimadzu UV-3600 UV-Vis-NIR spectrophotometer.
Irradiation experiments were carried out using either a Rayonet RPR-200 instrument or an LZC-ORG (Luzchem) instrument. The experiments were carried out in normal glass vessels unless otherwise stated (for UV-C experiments quartz vessels were used).

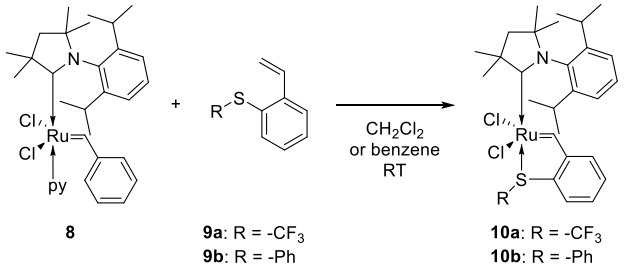
Molecular weights and polydispersity indices (PDIs) of the polymers were determined by size exclusion chromatography (SEC) analyses in tetrahydrofuran (THF) at 35°C using an Agilent 1200 HPLC equipped with two Shodex GPC LF-804 columns and a Shodex KF-803 column. The flow rate was set to 1 mL·min^{-1}. Wyatt's miniDAWN TriStar laser light-scattering system, ViscoStarTM viscometer, and OptilabVR rEX refractometer were used as detectors set up in series in a triple detector format. Prior to measurements, polymer solutions were filtered through Millipore 0.20 µm PTFE filters.

The X-ray measurements (ApexDuo, Bruker-AXS, MoKα radiation) were carried out at ca. 110(2) K on crystals coated with a thin layer of amorphous oil to minimize crystal deterioration, possible structural disorder and related thermal motion effects, and to optimize the precision of the structural results. The crystal structure was solved by direct methods and refined by full matrix least-squares (SHELXTL-2014 and SHELXL-2014).[2-3]

Cyclic (alkyl)(amino)carbene precursors **7a** and **7b** were synthesized as triflate salts according to method described in paper by Bertrand and coworkers.[4] Compounds **6**[5], **8**[6], **10a**[7], **10b**[8], **12**[9], **14a**,[7] **14b**[8] and **15**[10] were synthesized according published procedures.

2. Synthesis of CAAC bearing complexes

2.1. General procedure for the synthesis of complexes containing DiPP-CAAC



Scheme S1. Synthesis of the complexes **10a** and **10b**

Complex **8** (1eq) was dissolved in benzene or CH_2Cl_2 inside 4 mL vial equipped with magnetic bar. Styrene (**9a** or **9b**) (1.5 eq.) was added as a solution in matching solvent. Total concentration of **8** in solvent was 0.05M. The vial was filled with argon before sealing and the solution was left for overnight stirring at RT. The reaction mixture was purified on silica packed and eluted with CH_2Cl_2/hexane (1:1) as green bands. The complexes can be easily recrystallized by slow diffusion of hexane into concentrated solutions of **10a** or **10b** in CH_2Cl_2.

2.1.1. Complex 10a (*trans*)

Dark green solid 10 mg (0.0154 mmol, 46%) from 21 mg (0.0335 mmol) of **8**.

^{1}H NMR (400 MHz, CH_2Cl_2) δ **16.81** (d, 1H, J=0.8Hz), **7.75** (d, 1H, J=8Hz), **7.66** (two t, 2H, both J=7.6Hz), **7.47** (d, 2H, J=7.6Hz), **7.37** (dt, 1H, J=7.6; 1.2Hz), **6.81** (dd, 1H, J=7.6; 1.2Hz), **3.03** (m, 2H), **2.23** (s, 2H), **2.07** (s, 6H), **1.40** (s, 6H), **1.27** (d, 6H, J=6.8Hz), **0.60** (d, 6H, J=6.4Hz).

^{13}C NMR (101 MHz, CH_2Cl_2) δ 296.41, 263.11, 195.26, 159.31, 148.48, 136.00, 134.86, 133.13, 130.71, 130.35, 126.47, 124.27, 80.37, 57.94, 54.00, 51.95, 30.00, 29.54, 29.05, 26.68, 24.63

^{19}F NMR (376 MHz, CD_2Cl_2) δ -42.24.

HRMS: *m/z* calcd. for [$C_{28}H_{36}Cl_2F_3NRuS$ + Na]: 670.08333, found: 670.08234

2.1.2. Complex 10b (*trans*)

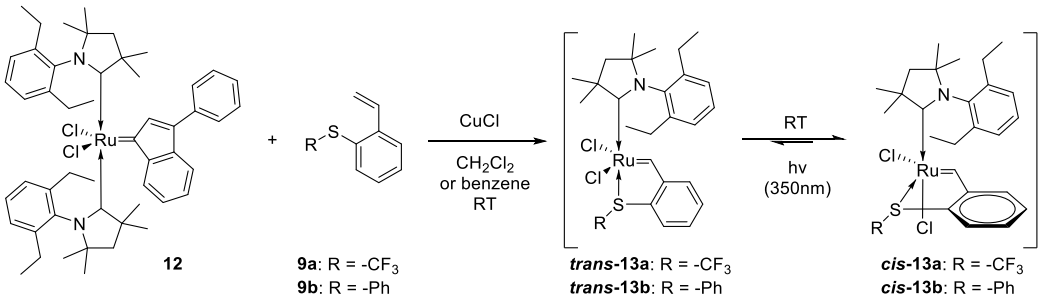
Green solid 8.5 mg (0.013 mmol, 41%) from 20 mg (0.032 mmol) of **8**.

^{1}H NMR (400 MHz, CD_2Cl_2) δ **16.86** (s,1H), **7.66** (t, 1H, J=7.6Hz), **7.52** (td, 1H, J=7.6; 1.2Hz), **7.48** (d, 2H, J=7.6Hz), **7.38** (d, 1H, J=7.6Hz), **7.30-7.20** (m, 4H), **7.12-7.10** (m, 2H), **6.77** (dd, 1H, J=7.6; 0.8Hz), **3.08** (septet, 2H, J=6.4Hz), **2.17** (s, 2H), **2.01** (s, 6H), **1.39** (s, 6H), **1.27** (d, 6H, J=6.4Hz), **0.65** (d, 6H, J=6.4Hz).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 295.80, 265.66, 158.37, 148.68, 136.40, 133.68, 132.53, 131.85, 130.88, 130.53, 130.39, 130.15, 128.91, 126.34, 123.68, 79.96, 58.06, 54.00, 52.05, 30.05, 29.53, 29.04, 26.78, 24.60

HRMS: *m/z* calcd. for [$C_{33}H_{41}Cl_2NRuS$]: 655.13748, found: 655.13733

2.2. Procedures for synthesis of complexes containing DEtP-CAAC



Scheme S2. Synthesis of the complexes **13a** and **13b**

2.2.1. *trans*-13a and *cis*-13a

The catalyst **12** (52.5 mg, 0.06 mmol, 1 eq.) was dissolved in 3 mL dry CH_2Cl_2 in pressure vessel equipped with magnetic stirring bar, followed by styrene **9a** (14.7 mg, 0.072 mmol, 1.2 eq.) in 1 mL and CuCl (11.8mg, 0.12mmol, 2eq). The air was replaced by argon before sealing the vessel. The reaction was stirred overnight at 40°C. The color changed from brown-red to green (indication for formation of ***trans*-13a**) after two hours and green-brown for the final solution. The crude solution was filtered of CuCl through 0.22µm PTFE filter and the solvent was evaporated. The residue was redissolved in toluene and was purified "as is" by column chromatography on silica, ***trans*-13a** elutes first as a dark green band with a gradient of cyclohexane → 10% ethyl acetate in cyclohexane followed by ***cis*-13a** that elutes as a purple band with 80% ethyl acetate in cyclohexane. The solvent was evaporated and trituration with pentane afforded the complexes as solids (33% of ***trans*-13a** and 17% ***cis*-13a**). Isomerization to ***cis*-13a** can be avoided by stopping the reaction earlier (see above comment).

Purified ***trans*-13a** can also be fully converted to ***cis*-13a** by redissolving it in CH_2Cl_2 and heating in a pressure vessel to 50°C until starting material is not detected by TLC (up to 43% of ***cis*-13a** after column chromatography).

trans-13a

^{1}H NMR (400 MHz, CD_2Cl_2) δ **16.89** (d, 1H, J=0.8Hz), **7.75** (d, 1H, J=7.6Hz), **7.69** (dt, 1H, J=7.2; 1.2Hz), **7.62** (t, 1H, J=7.6Hz), **7.46** (d, 2H, J=7.6Hz), **7.39** (dt, 1H, J=7.6; 1.2Hz), **6.84** (dd, 1H, J=8.0; 1.6Hz), **2.56** (broad m, 4H), **2.21** (s,2H), **2.10** (s, 6H), **1.36** (s, 6H), **0.88** (broad m, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 300.29, 261.89, 143.35, 140.32, 137.82, 134.95, 133.15, 130.86, 129.77, 127.56, 123.95, 120.31, 80.74, 57.67, 54.00, 52.41, 30.11, 28.83, 25.29, 14.73.

^{19}F NMR (376 MHz, CD_2Cl_2) δ 20.02.

HRMS: *m/z* calcd. for [$C_{26}H_{32}Cl_2F_3NRuS$ - Cl]: 584.09341, found: 584.09393

cis-13a

^{1}H NMR (400 MHz, CD_2Cl_2) δ **16.24** (d, 1H, J=1.2Hz), **7.71** (dd, 1H, J=7.6; 0.8Hz), **7.60** (td, 1H, J=7.2; 1.2Hz), **7.31** (overlapping dd, 1H, J=7.6; 0.8Hz), **7.28** (overlapping td, 1H, J=7.6; 0.8Hz), **7.04** (t, 1H, J=7.6Hz), **6.92** (dd, 1H, J=8.0; 1.2Hz), **6.32** (broad d, 1H, J=8Hz), **3.15** (broad m, 1H), **2.56** (broad m, 1H), **2.23** (s, 3H), **2.18** (s, 1H), **2.17** (s, 1H), **2.02** (overlapping m, 4H), **1.51** (broad m, 1H), **1.37** (t, 3H, J=7.6Hz), **1.31** (s, 3H), **1.20** (s, 3H), **0.93** (t, 3H, J=7.6Hz)

^{13}C NMR (101 MHz, CD_2Cl_2) δ 277.76, 266.82, 154.94, 142.69, 140.24, 137.02, 135.09, 132.72, 132.02, 131.38, 130.51, 129.72, 128.88, 127.46, 126.84, 125.60, 123.92, 80.43, 55.40, 54.00, 52.65, 34.16, 31.35, 31.15, 28.33, 26.04, 24.09, 15.30, 14.02[11]

^{19}F NMR (376 MHz, CD_2Cl_2) δ 23.01

HRMS: *m/z* calcd. for [$C_{26}H_{32}Cl_2F_3NRuS$ - Cl]: 584.09341, found: 584.09204

2.2.2. *trans*-13b

12 (0.034 mmol; 30 mg) was dissolved in 1 mL benzene inside a pressure vessel equipped with a stirring bar. Then, styrene **9b** (0.041 mmol; 9 mg; 1.2 eq.) dissolved in 0.5 mL of benzene and CuCl (0.068 mmol; 7 mg; 2 eq.) were added. The air inside the vessel was replaced by argon and then the vessel was sealed. The reaction was stirred at 30°C overnight. The solution was purified "as is" by column chromatography on silica, with gradient of hexane to 5% ethyl acetate in hexane. The solvent was evaporated to afford 10 mg (0.016 mmol, 47%) of ***trans*-13b** as a green solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ **16.95** (d, 1H, J=0.4Hz), **7.63** (t, 1H, J=8Hz), **7.56** (dt, 1H, J=7.6; 1.2Hz), **7.47** (d, 2H, J=7.6Hz) , **7.40** (d, 1H, J=7.6Hz), **7.29-7.20** (m, 4H), **7.09** (m, 2H), **6.82** (dd, 1H, J=7.6; 0.8Hz), **2.66** (sextet, 2H, J=7.6Hz), **2.56** (sextet, 2H, J=7.6Hz), **2.17** (s, 2H), **2.03** (s, 6H), **1.35** (s, 6H), **0.91** (t, 6H, J=7.6Hz).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 299.31, 264.46, 159.65, 143.58, 138.23, 133.82, 133.48, 132.24, 130.98, 130.53, 129.57, 129.18, 128.90, 128.81, 127.44, 123.47, 80.37, 57.78, 52.42, 30.07, 28.83, 25.31, 14.85.

HRMS: *m/z* calcd. for [$C_{31}H_{37}Cl_2NRuS$ - Cl]: 592.13733, found: 592.13910

2.2.3. *cis*-13b

12 (0.114 mmol; 100 mg) was dissolved in 4 mL CH_2Cl_2 inside a pressure vessel equipped with a stirring bar. Then, styrene **9b** (0.137 mmol; 29 mg; 1.2eq) dissolved in 1 mL of CH_2Cl_2 was added, followed by CuCl (0.228 mmol; 22.5 mg; 2 eq.). The air inside the vessel was replaced by argon and then the vessel was sealed. The reaction was stirred at 30°C overnight. The solution was

filtered through a 0.22µm PTFE filter and the solvent was evaporated. The residue was redissolved in toluene and was purified "as is" by column chromatography on silica, by elution with a gradient of hexane → 50% ethyl acetate in hexane → 80% ethyl acetate in hexane. The solvent was evaporated and after several cycles of trituration with pentane, 25 mg (0.040 mmol, 35%) of ***cis*-13b** as a blue-grey solid was obtained.

^{1}H NMR (400 MHz, CD_2Cl_2) δ **16.40** (s, 1H), **7.45-7.29** (m, 5H), **7.21-7.08** (m, 5H), **6.89** (d, 1H, J=7.2Hz), **6.41** (d, 1H, J=7.6Hz), **3.25** (m, 1H), **2.59** (m, 1H), **2.18** (m, 6H), **2.09** (s, 3H), **1.64** (m, 1H), **1.40** (m, 3H), **1.29** (s, 1H), **1.24** (s, 1H), **0.90** (m, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 277.49, 269.60, 155.34, 143.05, 140.96, 138.29, 137.32, 133.49, 130.72, 130.46, 130.39, 130.26, 129.38, 129.18, 127.21, 126.78, 124.94, 79.56, 55.17, 54.00, 52.87, 34.28, 31.15, 31.08, 30.25, 28.62, 26.07, 24.13, 15.28, 13.89.

HRMS: *m/z* calcd. for [$C_{31}H_{37}Cl_2NRuS$ + Na]: 650.09595, found: 650.09851

3. Spectroscopic data of reported complexes

3.1. NMR spectra of 10a

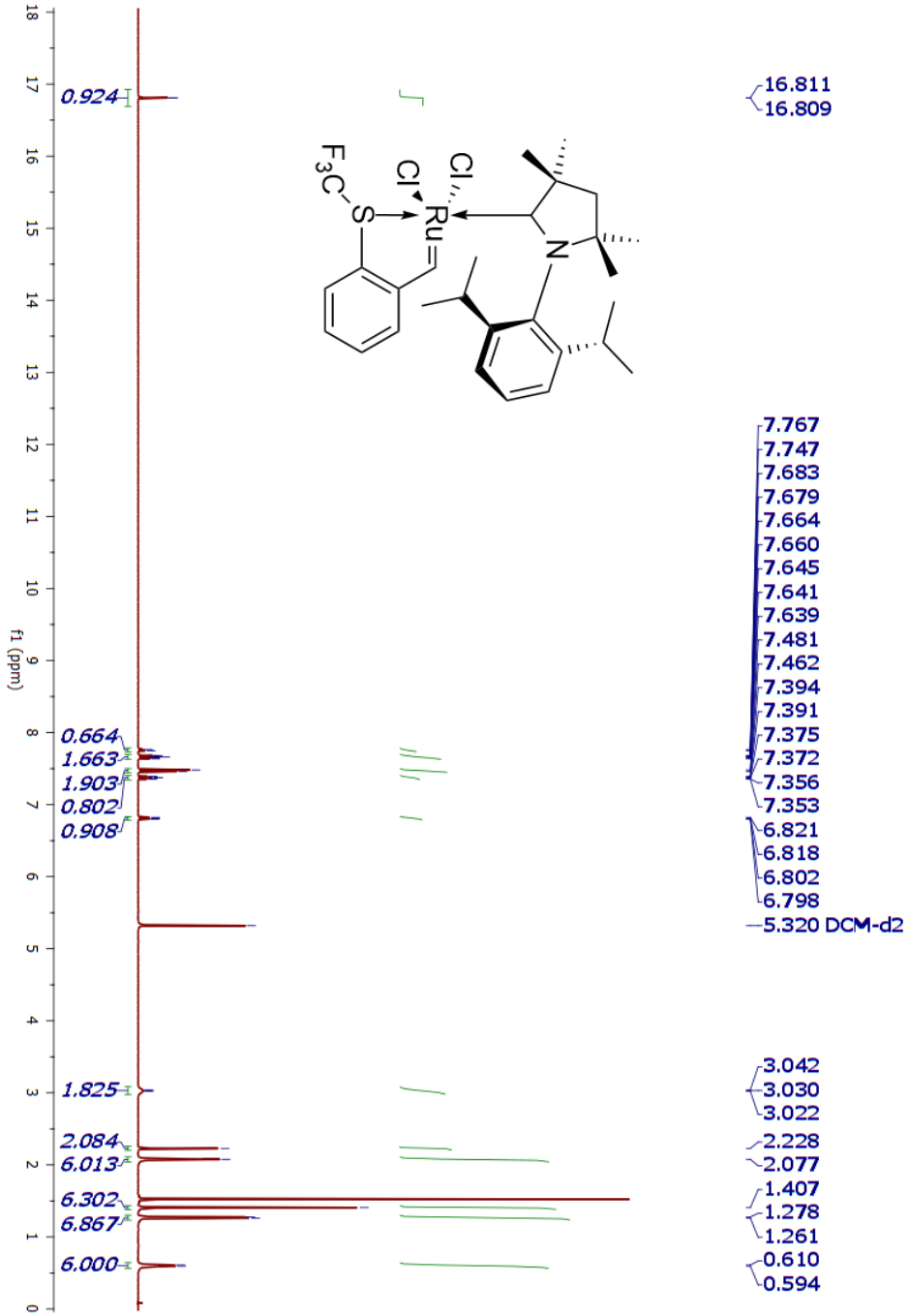


Figure S1. Full ^{1}H-NMR spectrum of **10a**

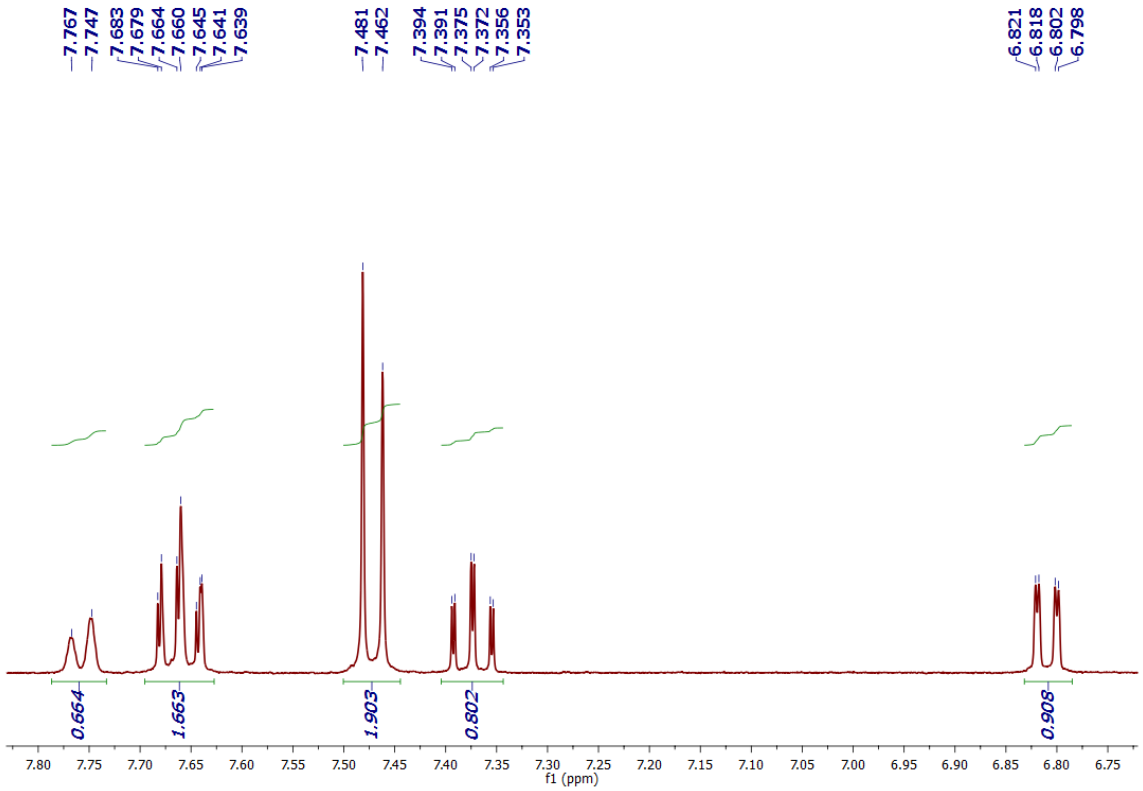


Figure S2. Aromatic protons region of ^{1}H-NMR spectrum of **10a**

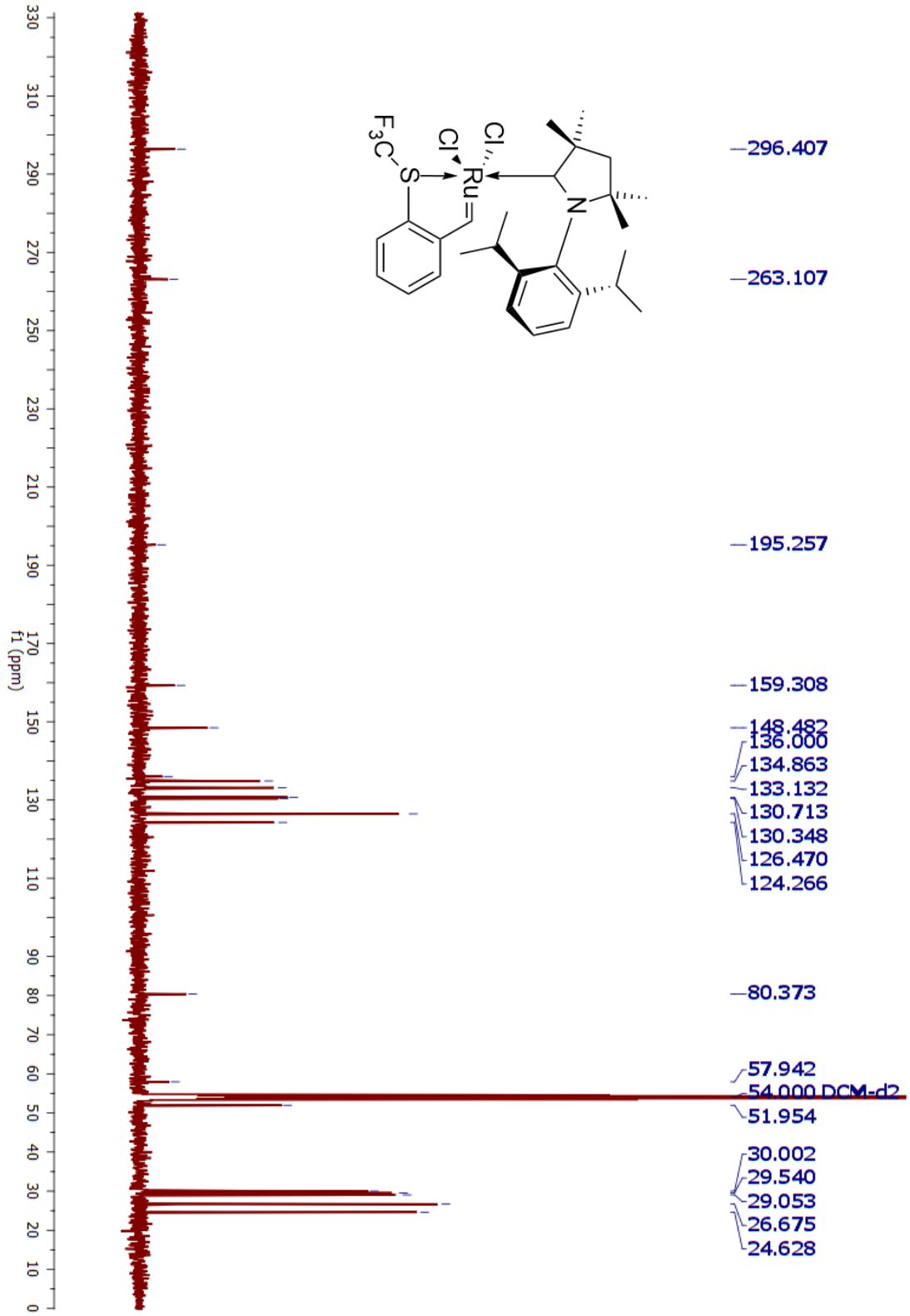


Figure S3. Full ^{13}C-NMR spectrum of **10a**

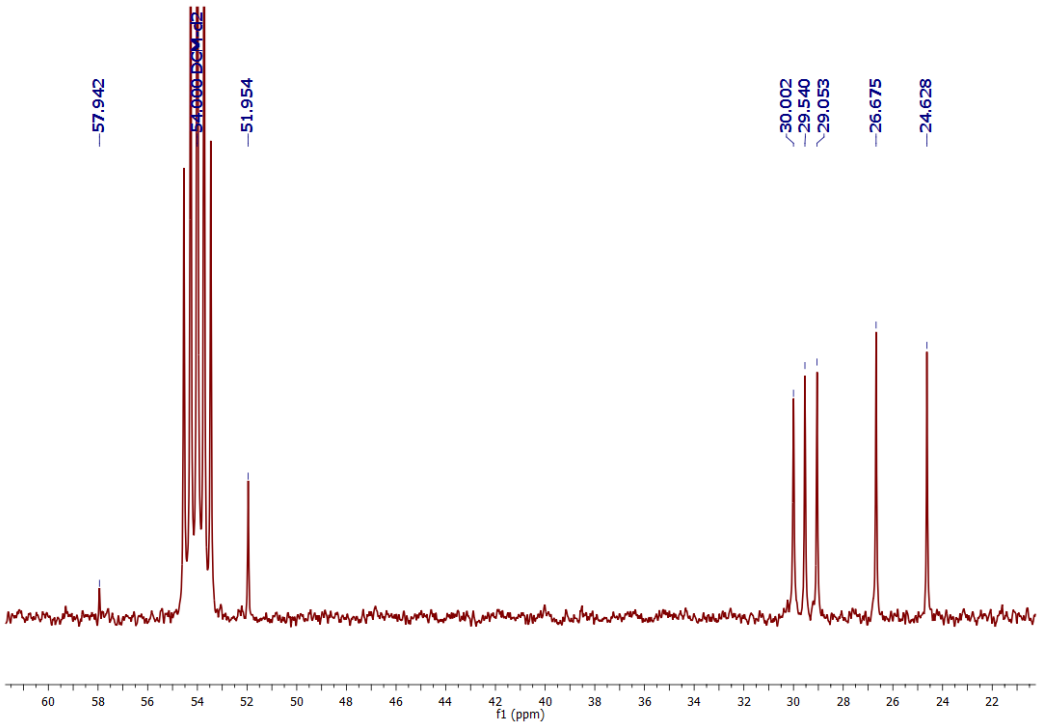


Figure S4. Expansion of aliphatic region in ^{13}C-NMR spectrum of **10a**

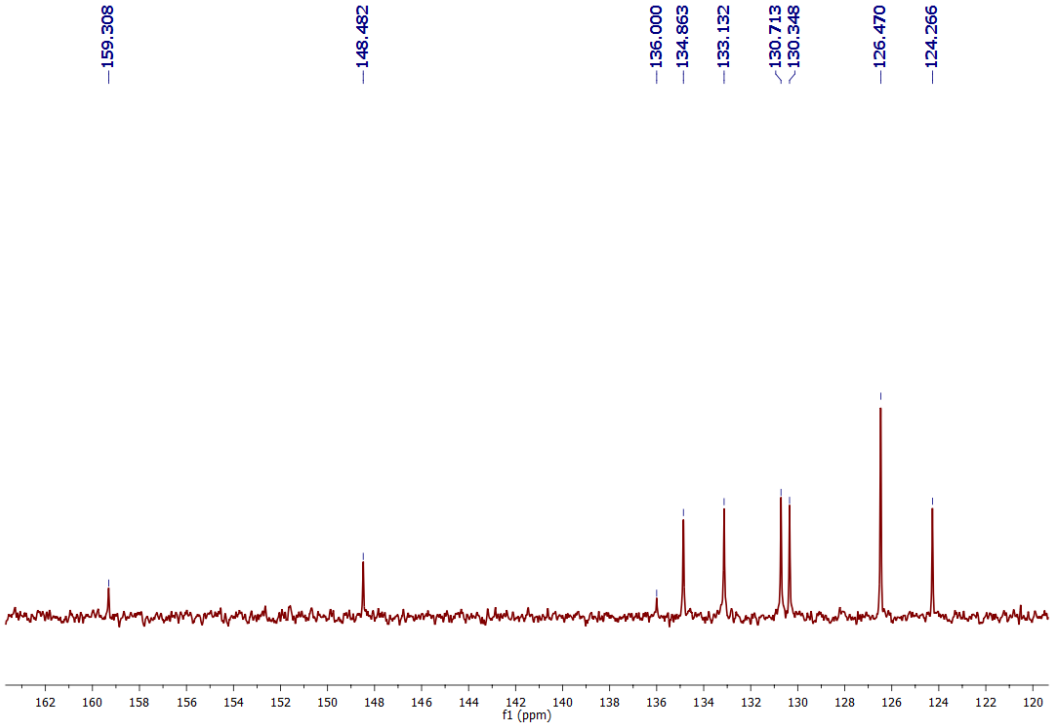


Figure S5. Expansion of aromatic region in ^{13}C-NMR spectrum of **10a**

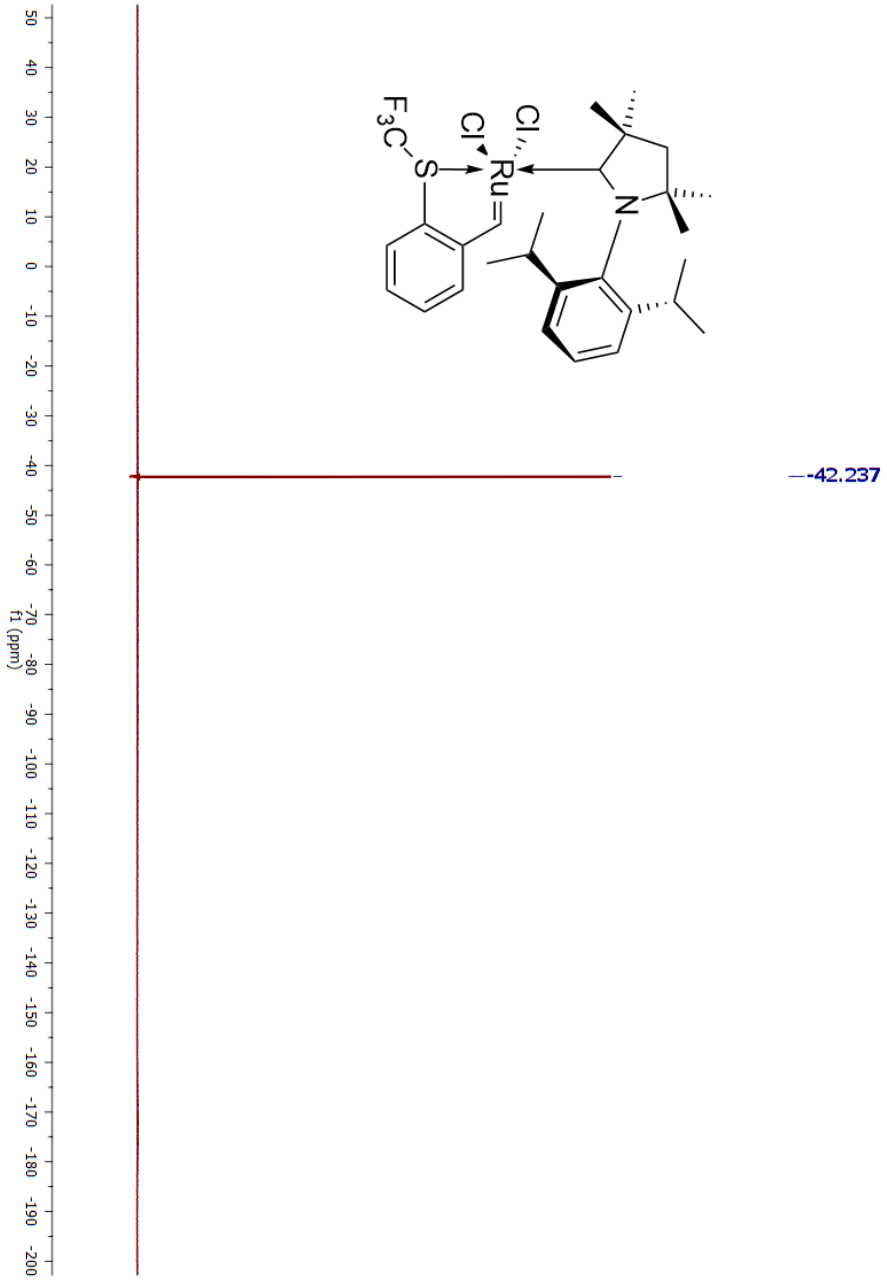


Figure S6. ^{19}F-NMR spectrum of **10a**

3.2. HRMS of 10a

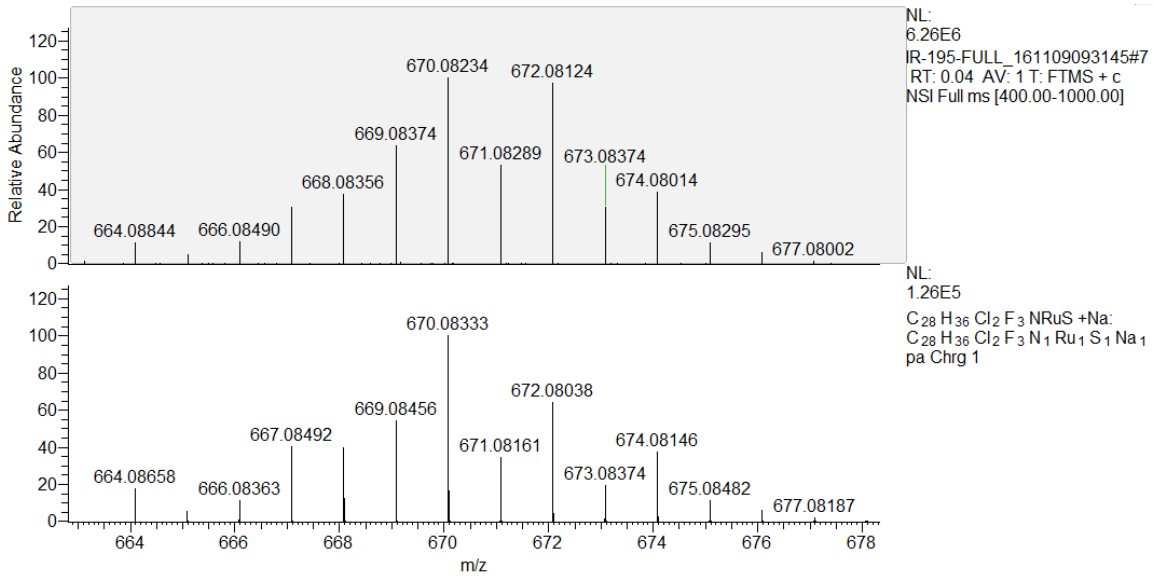


Figure S7. Experimental (grey) and simulated (white) HRMS spectra of **10a**.

3.3. UV-Vis of 10a in CH_2Cl_2

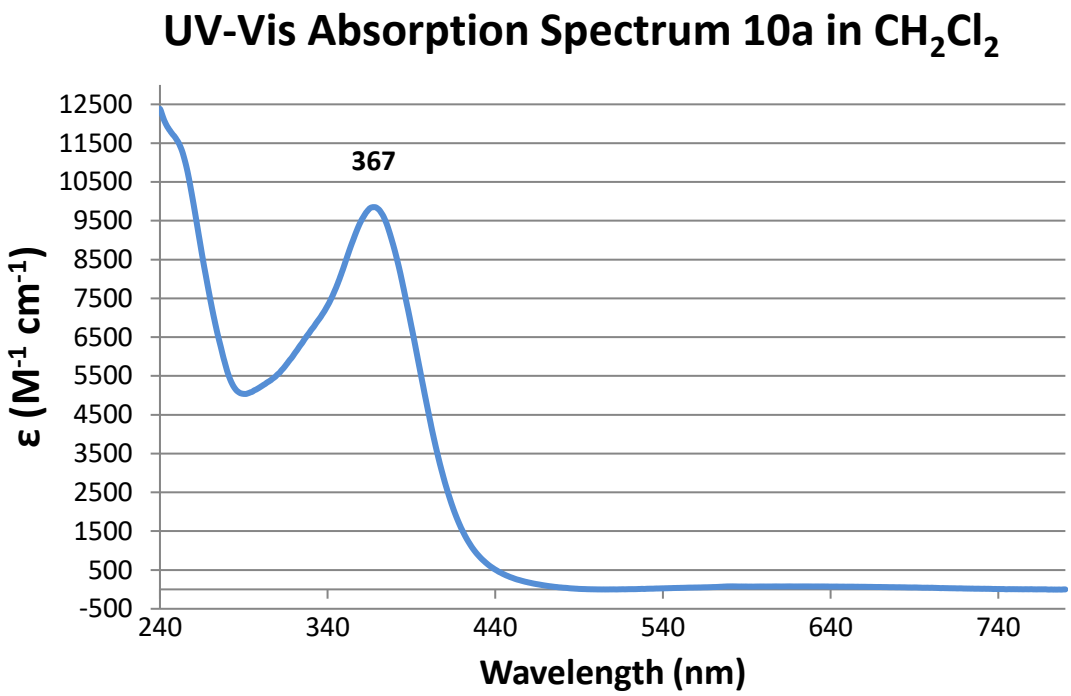


Figure S8. UV-Vis spectrum of **10a**. Concentration of **10a**: 10^{-4}M in CH_2Cl_2

3.4. NMR spectra of 10b

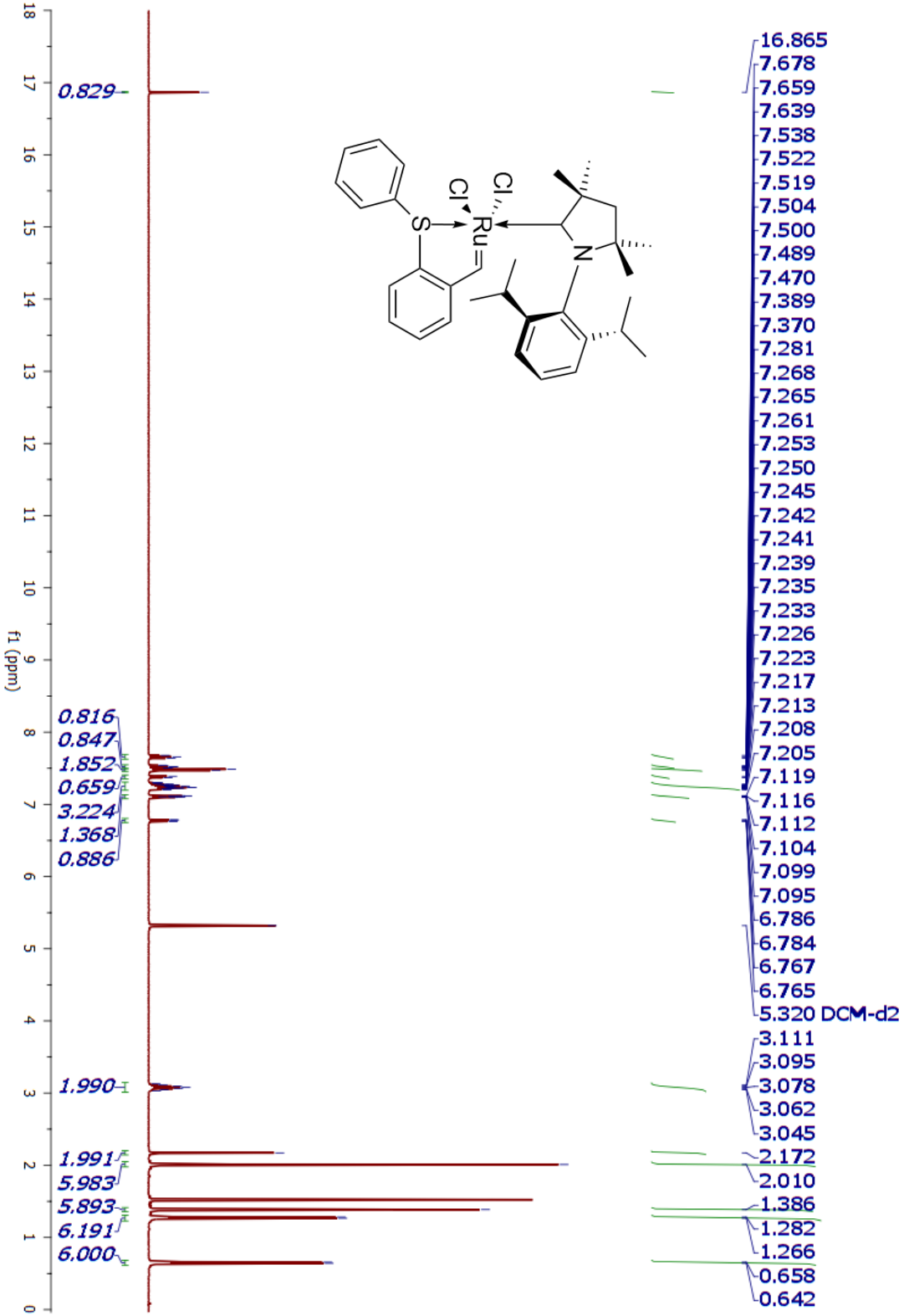


Figure S9. Full ^{1}H-NMR spectrum of **10b**

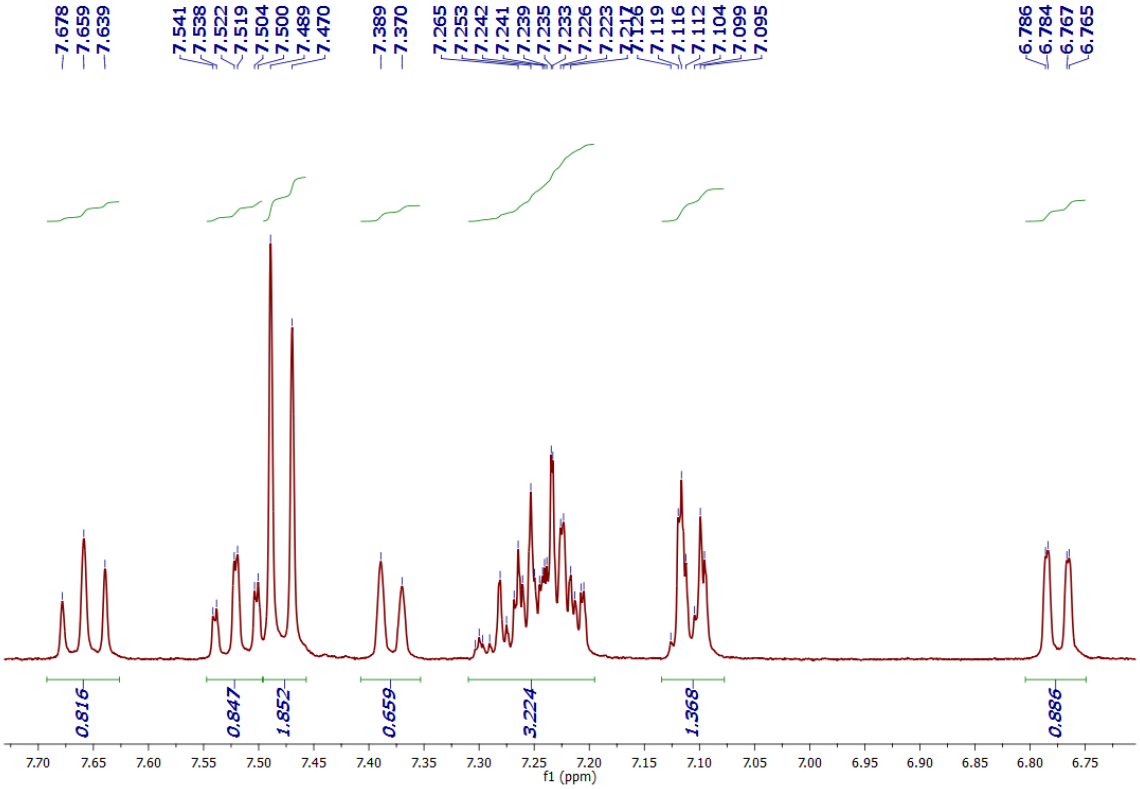


Figure S10. Aromatic protons region of ^{1}H-NMR spectrum of **10b**

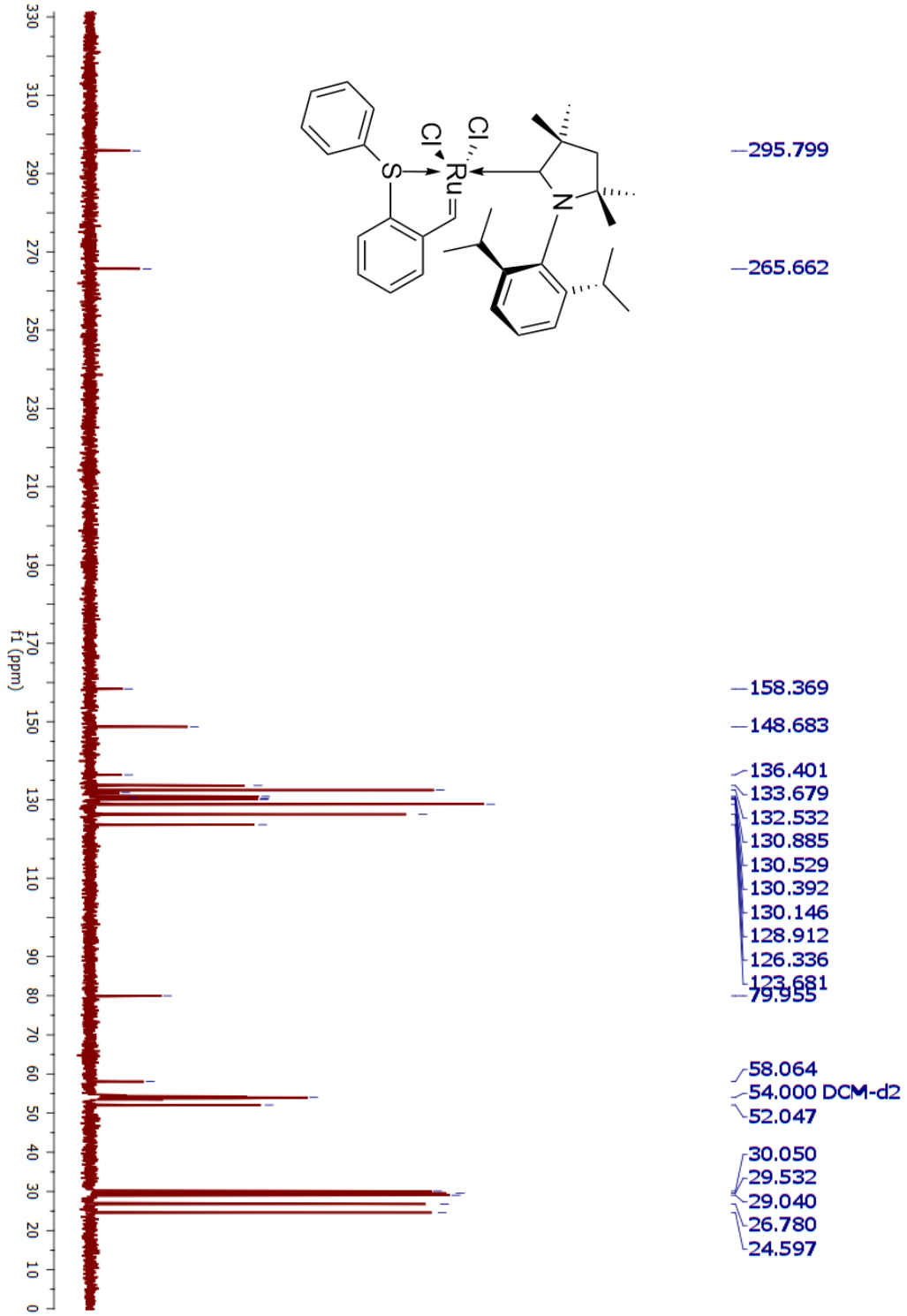


Figure S11. Full ^{13}C-NMR spectrum of **10b**

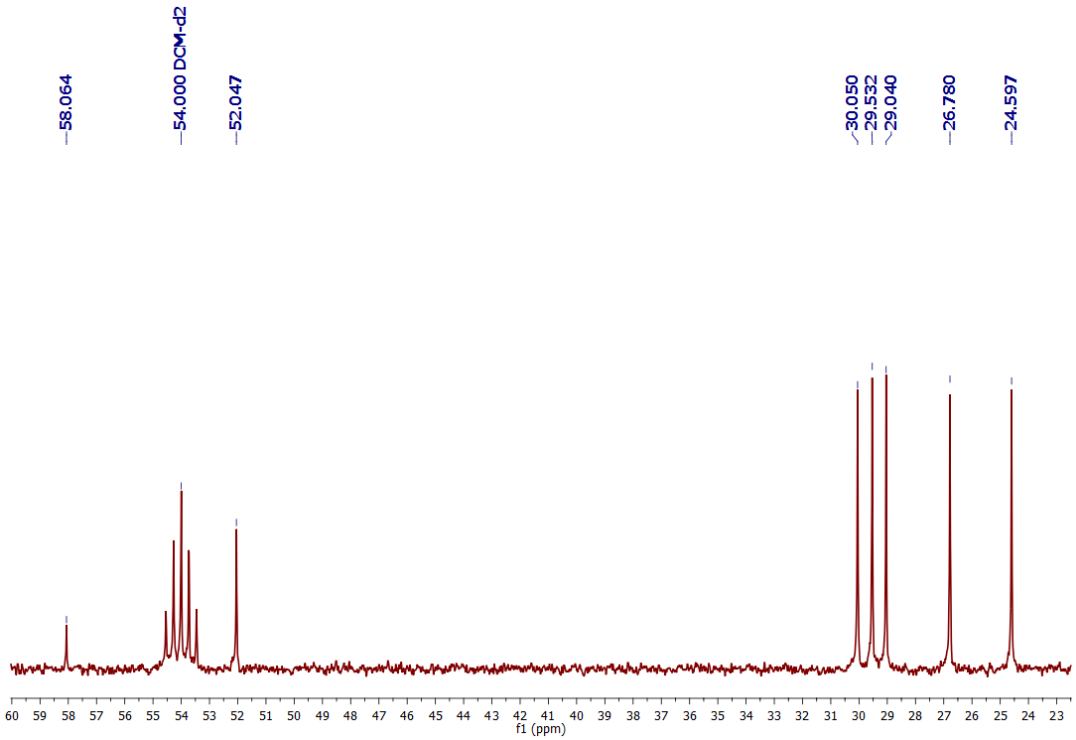


Figure S12. Expansion of aliphatic region in ^{13}C-NMR spectrum of **10b**

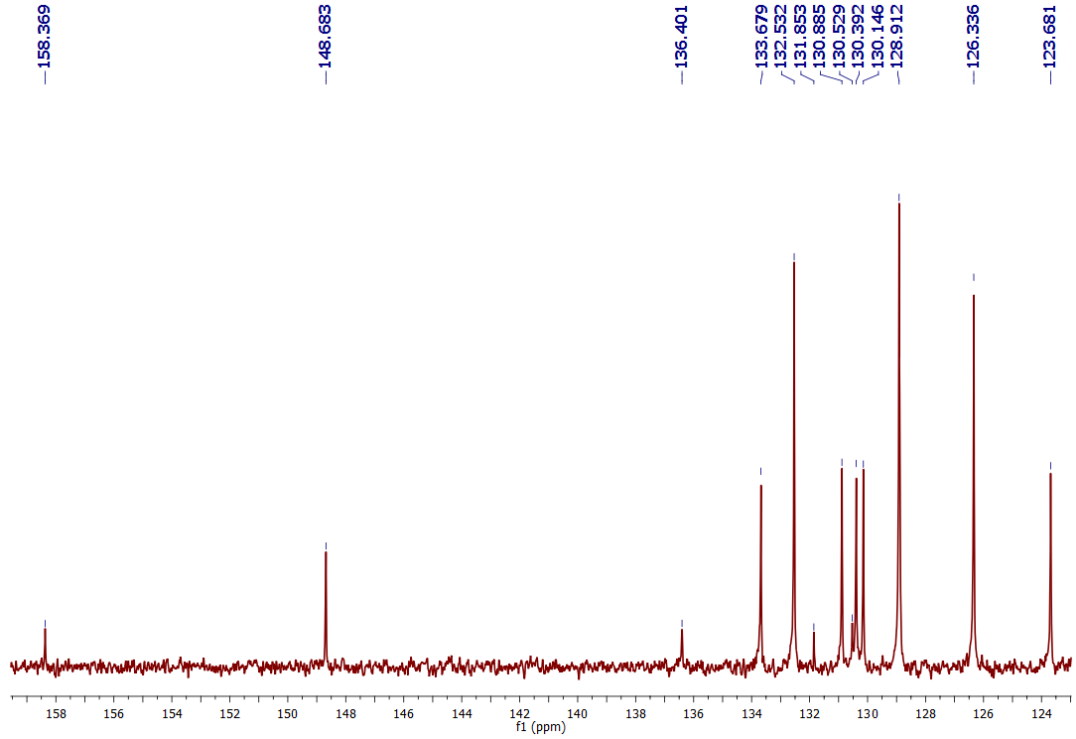


Figure S13. Expansion of aromatic region in ^{13}C-NMR spectrum of **10b**

3.5. HRMS of 10b

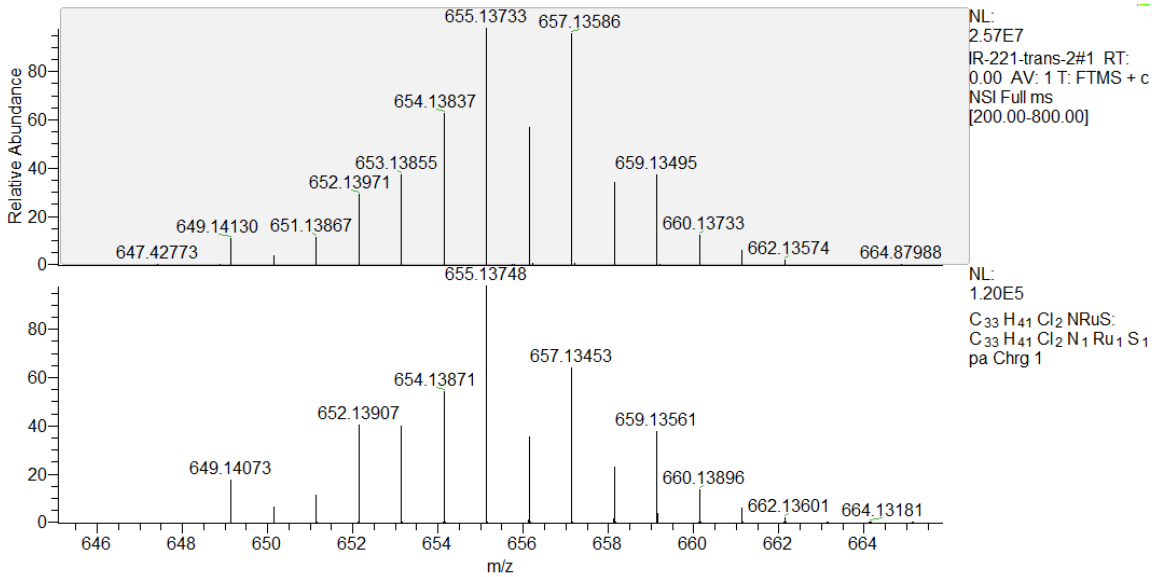


Figure S14. Experimental (grey) and simulated (white) HRMS spectra of **10b**

3.6. UV-Vis of 10b in CH_2Cl_2

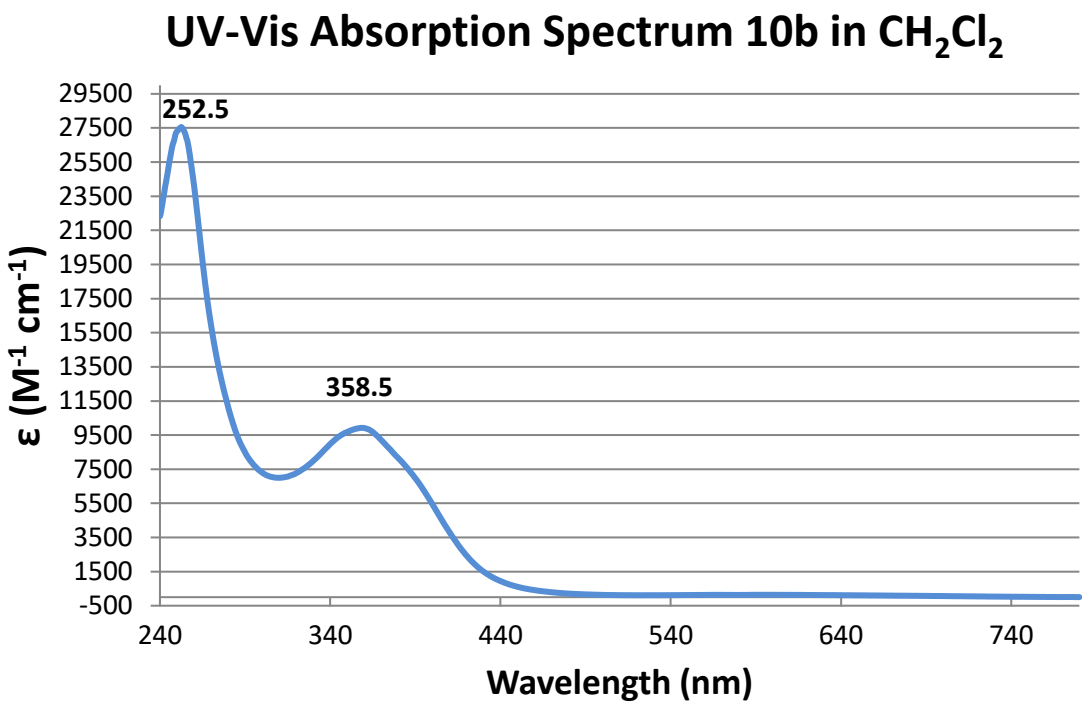


Figure S15. UV-Vis spectrum of **10b**. Concentration of **10b**: 10^{-4}M in CH_2Cl_2

3.7. NMR spectra of *trans*-13a

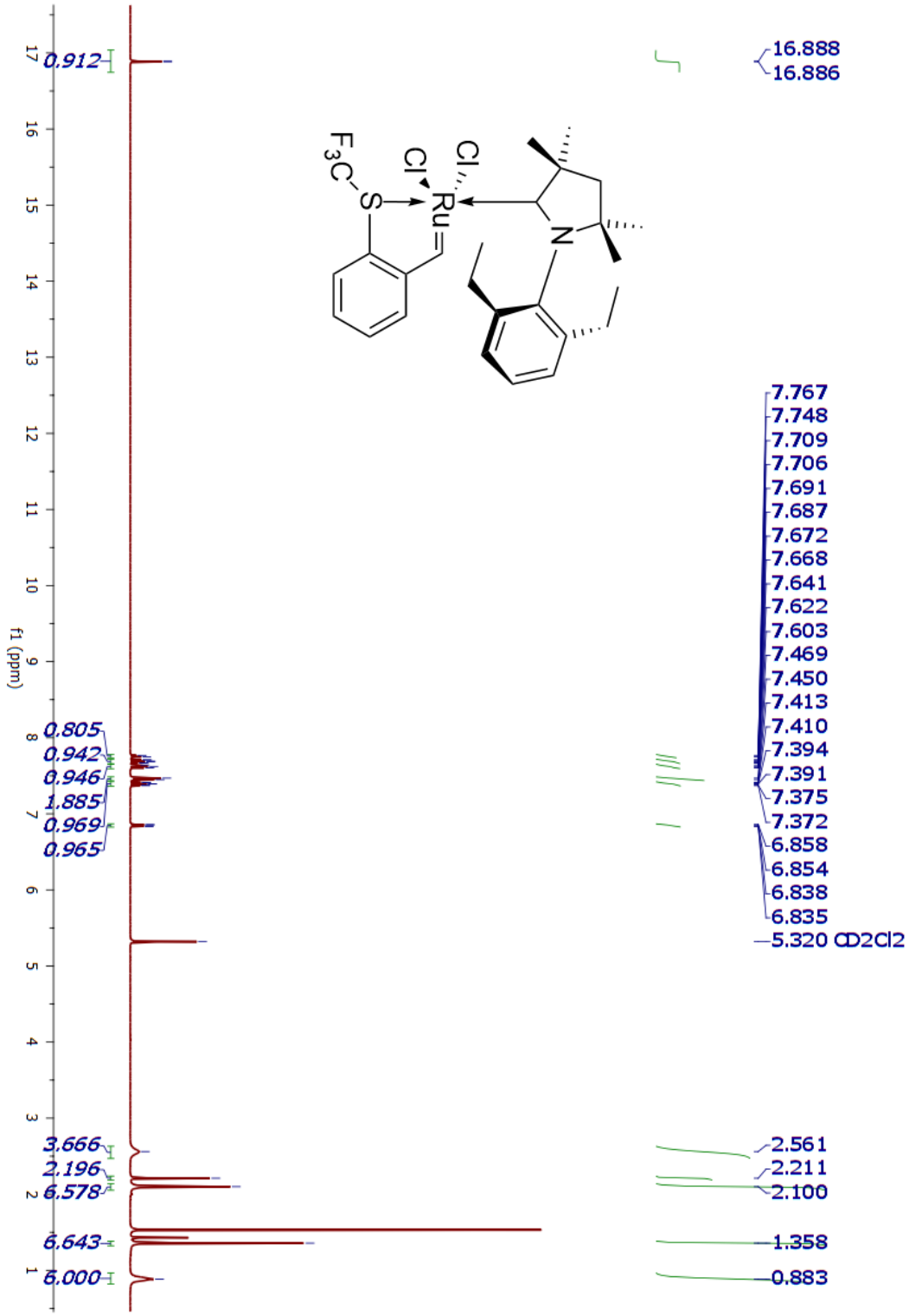


Figure S16. Full ^{1}H-NMR spectrum of ***trans*-13a**

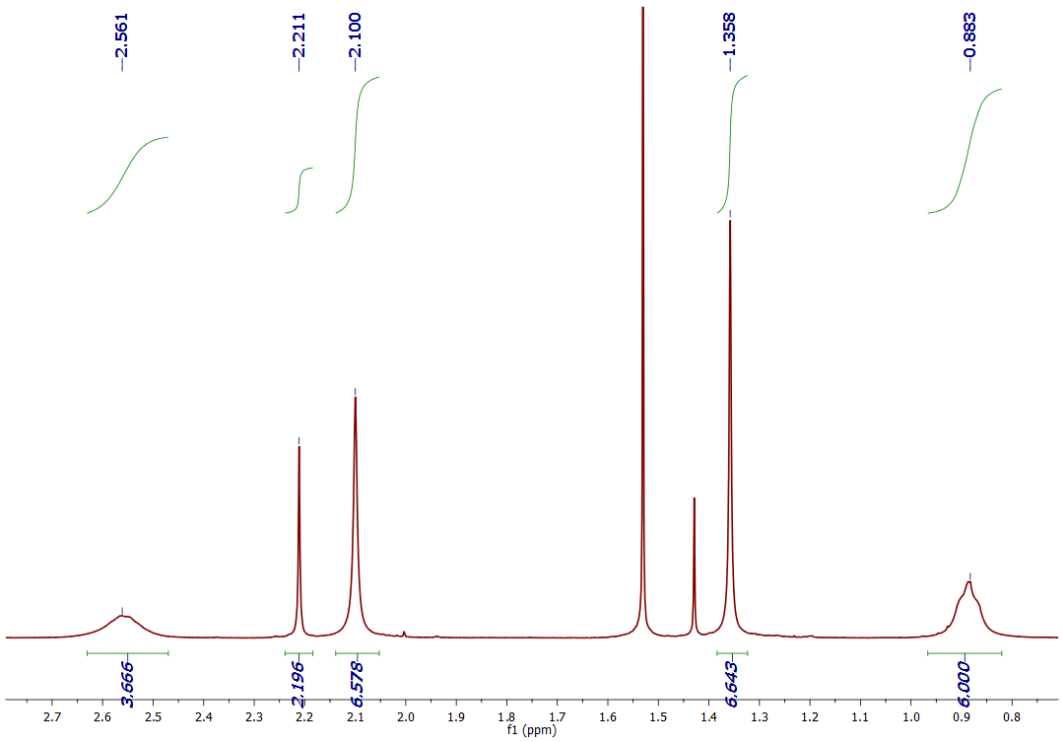


Figure S17. Aliphatic protons region of ^{1}H-NMR spectrum of ***trans*-13a**

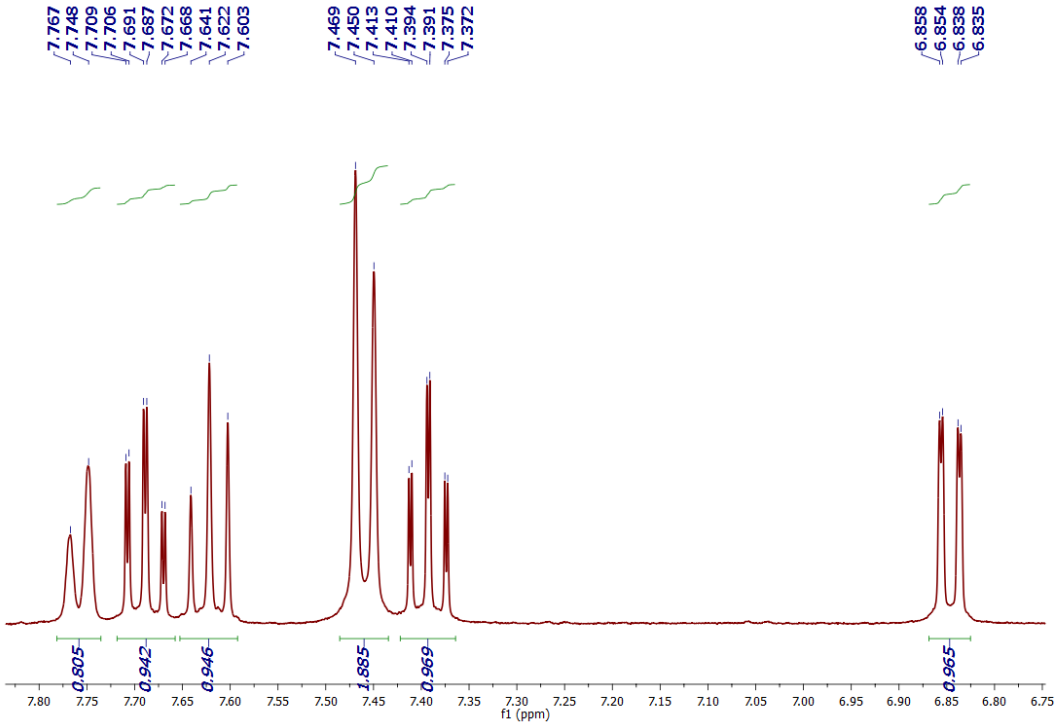


Figure S18. Aromatic protons region of ^{1}H-NMR spectrum of ***trans*-13a**

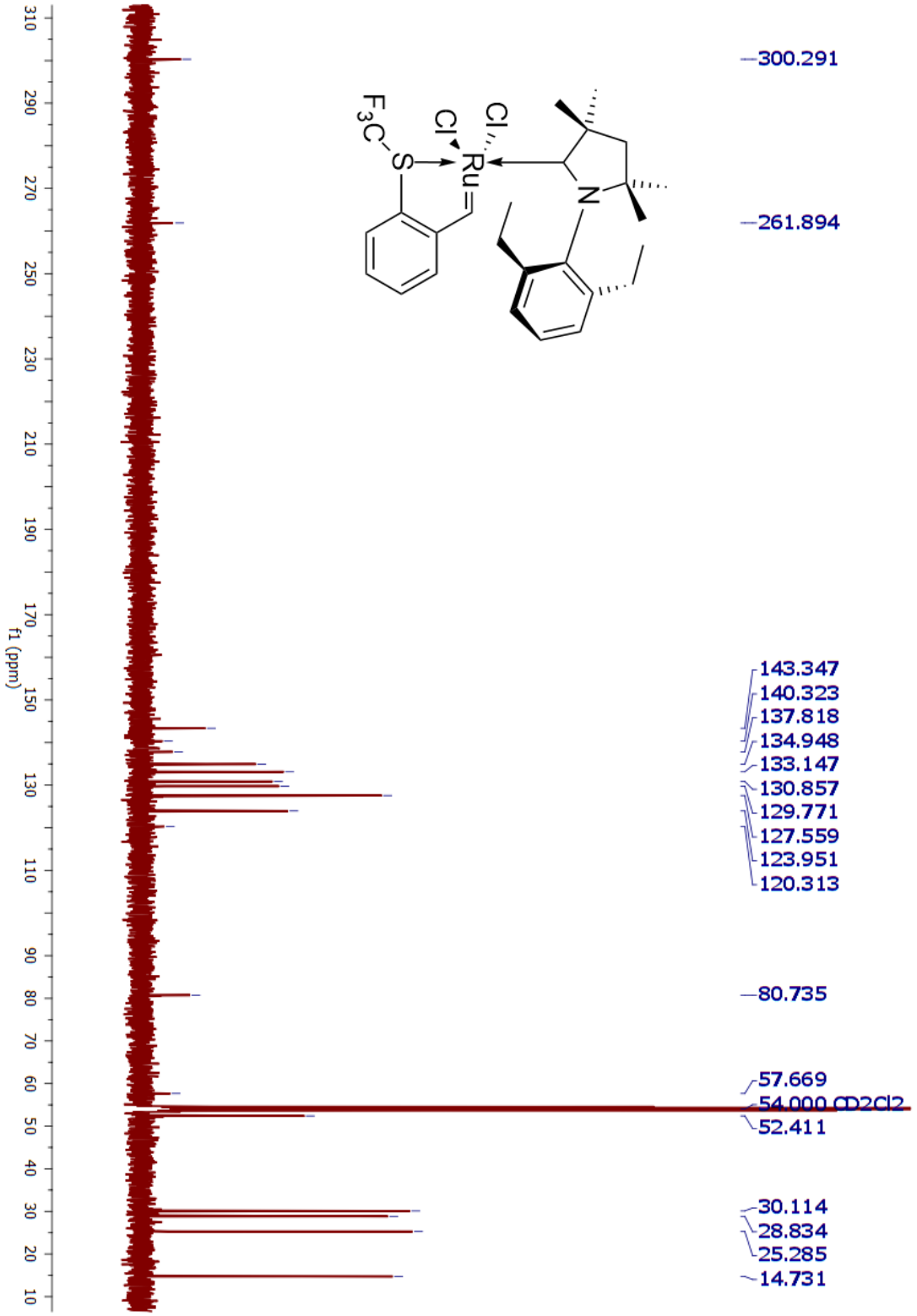


Figure S19. Full ^{13}C-NMR spectrum of ***trans*-13a**

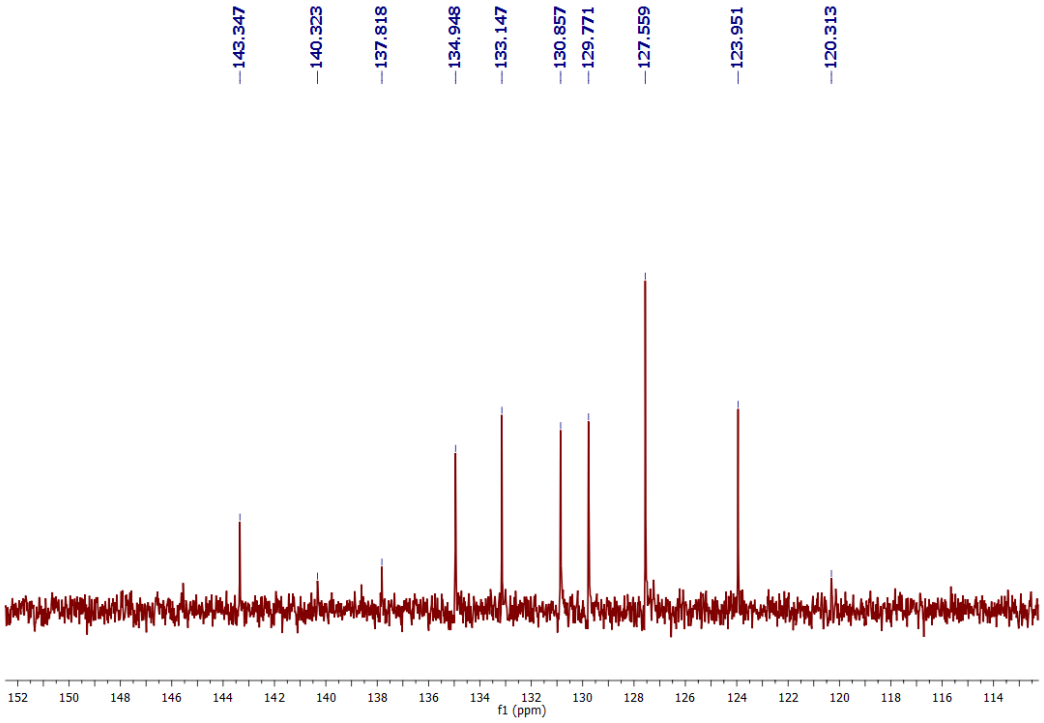


Figure S20. Expansion of aromatic carbons region in ^{13}C-NMR spectrum of ***trans*-13a**

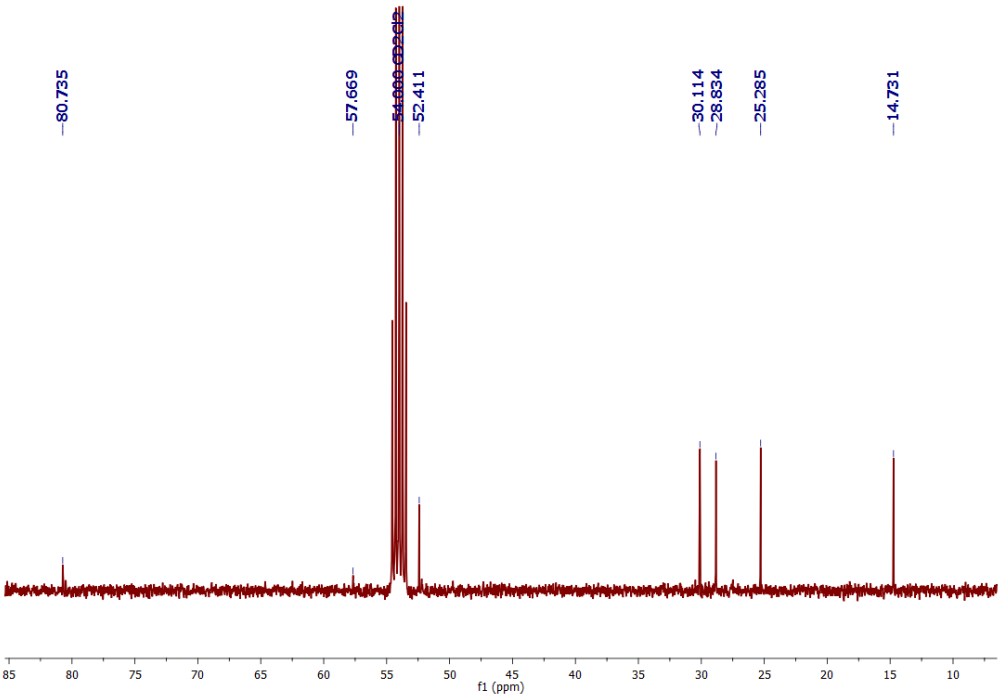


Figure S21. Expansion of aliphatic carbons region in ^{13}C-NMR spectrum of ***trans*-13a**

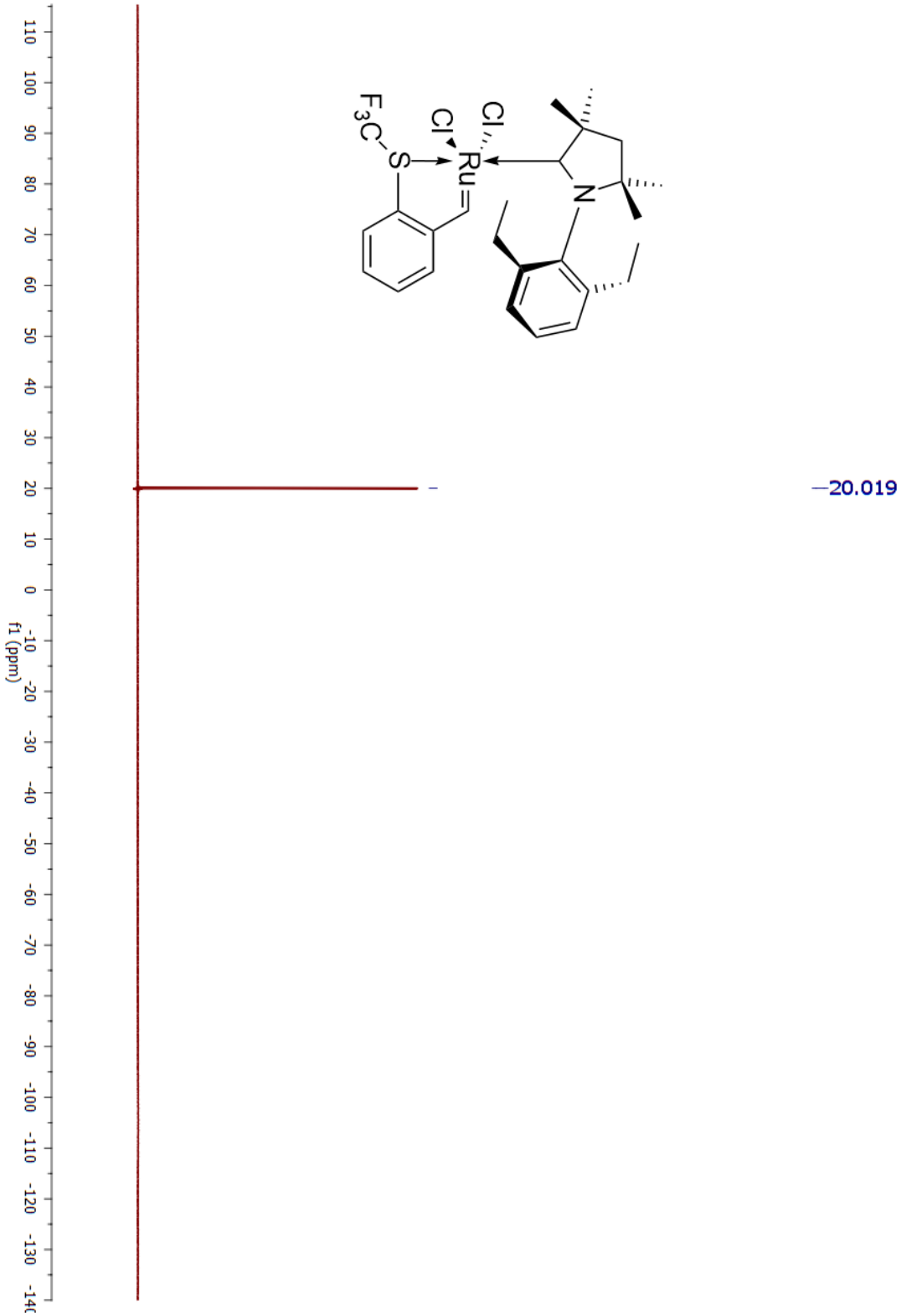


Figure S22. ^{19}F-NMR spectrum of ***trans*-13a**

3.8. HRMS of *trans*-13a

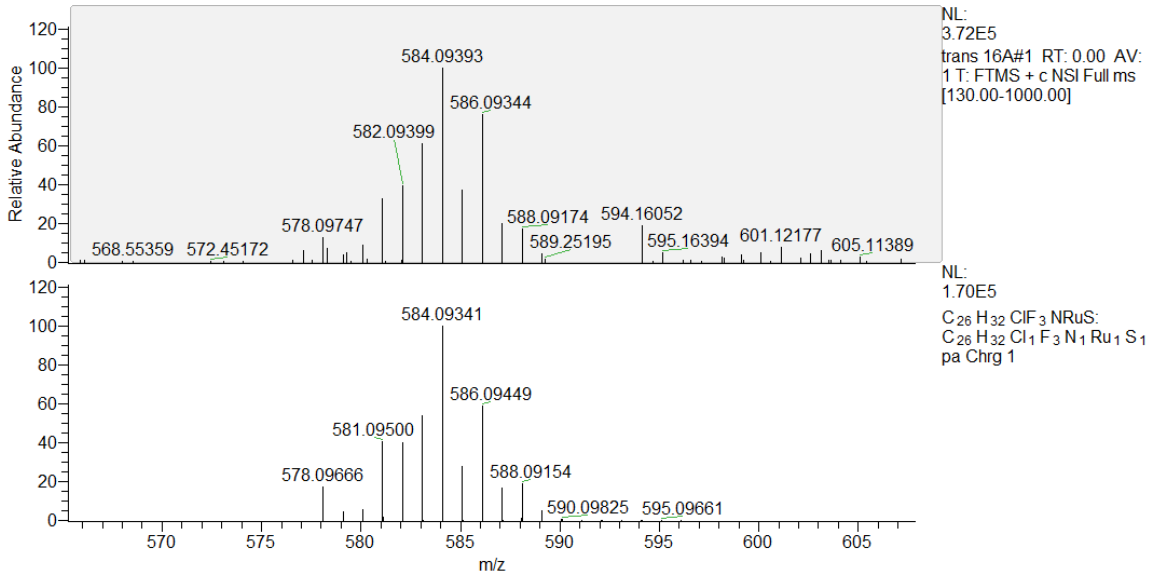


Figure S23. Experimental (grey) and simulated (white) HRMS spectra of ***trans*-13a** ([M –Cl] $^{+}$)

3.9. UV-Vis spectrum of *trans*-13a

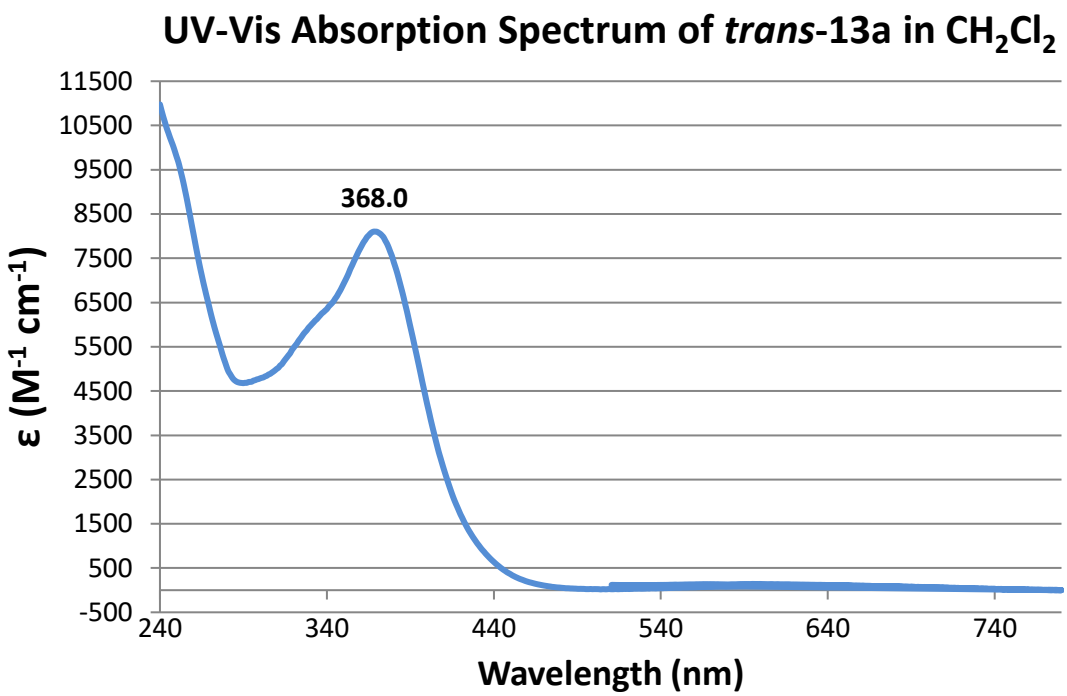


Figure S24. UV-Vis spectrum of ***trans*-13a**. Concentration of ***trans*-13a**: 10^{-4}M in CH_2Cl_2

3.10. NMR spectra of *cis*-13a

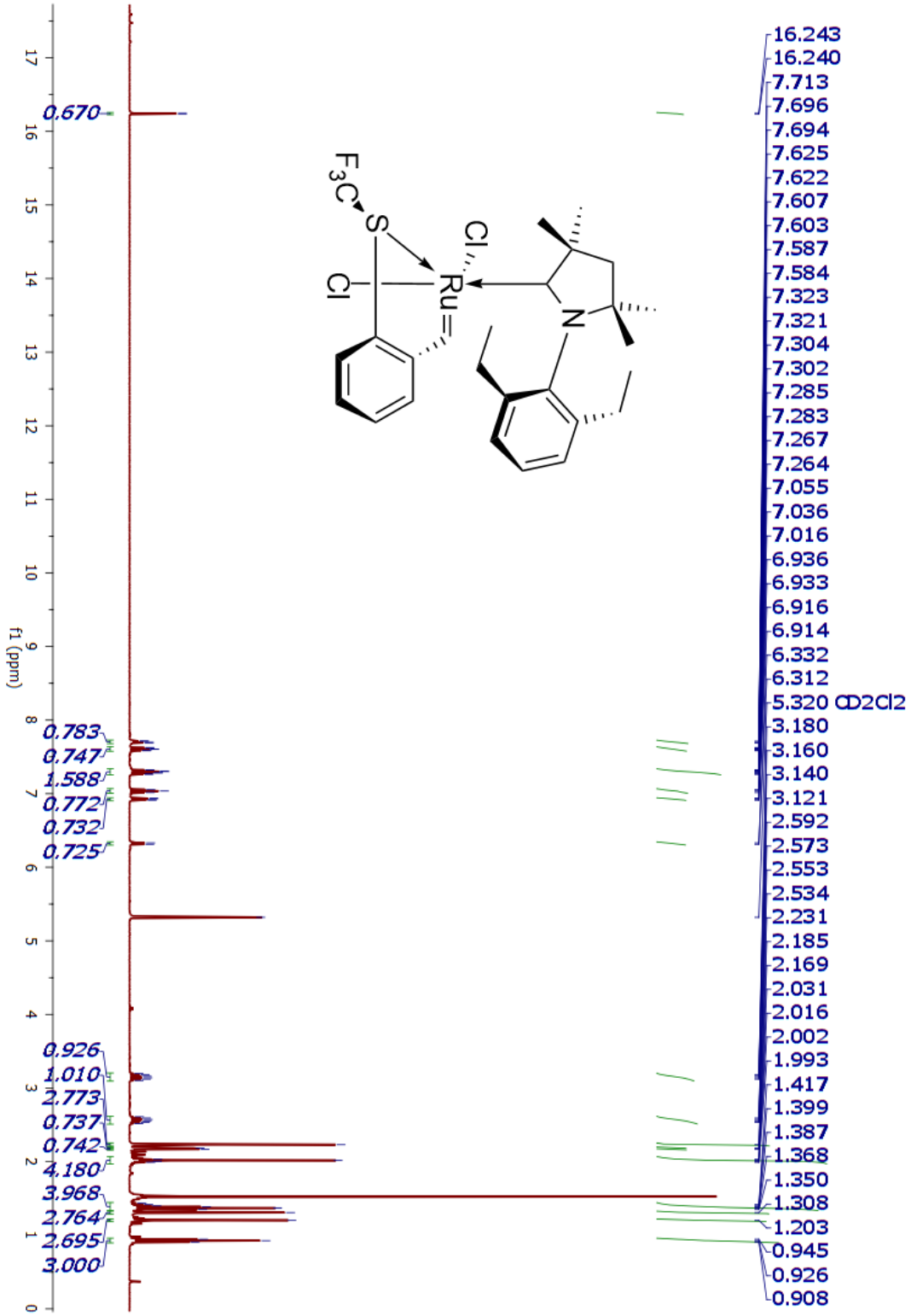


Figure S25. Full ^{1}H-NMR spectrum of ***cis*-13a**

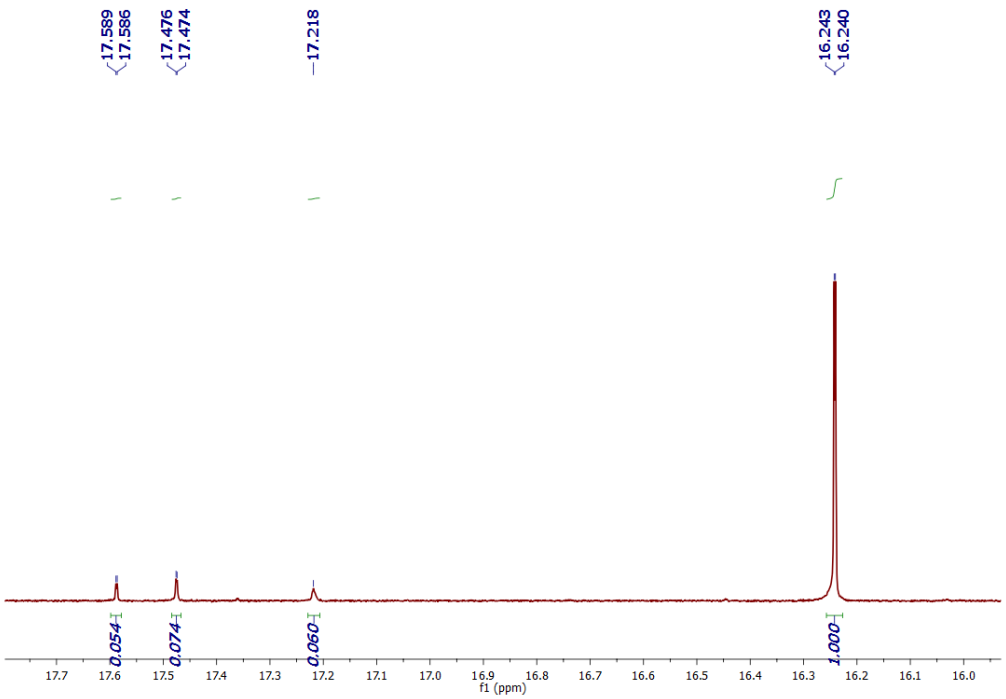


Figure S26. Carbene protons region of ^{1}H-NMR spectrum of ***cis*-13a**.

None of the downfield proton peaks belong to ***trans*-13a**, so most likely they belong to rotamers of ***cis*-13a**, as well as small peaks in other regions of the spectrum.

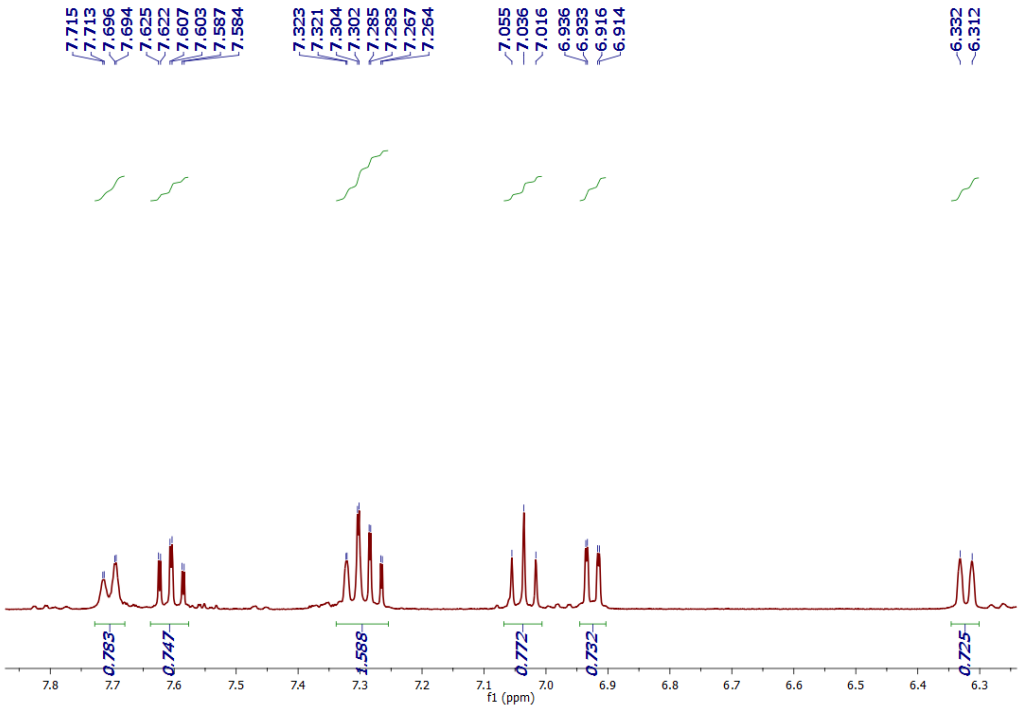


Figure S27. Aromatic protons region of ^{1}H-NMR spectrum of ***cis*-13a**

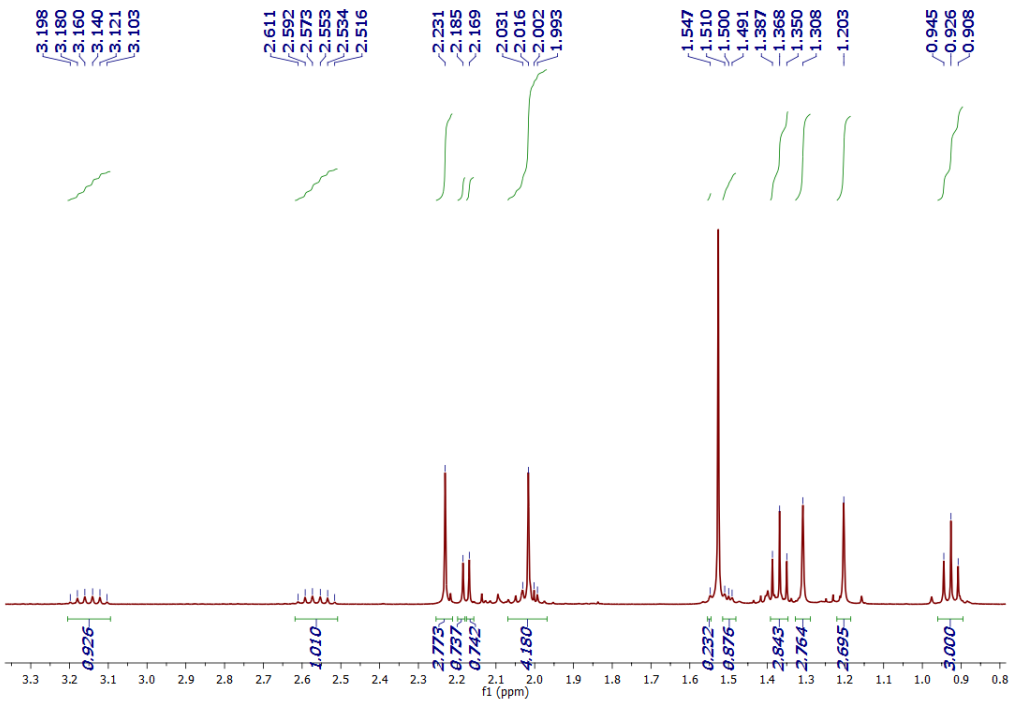


Figure S28. Aliphatic protons region of ^{1}H-NMR spectrum of ***cis*-13a**

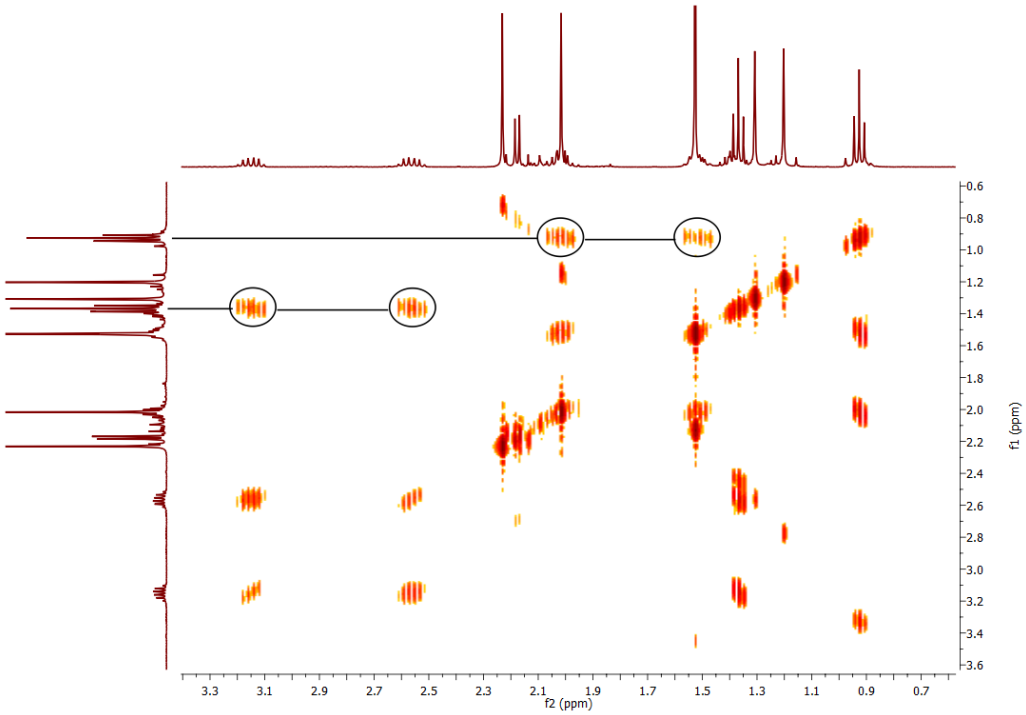


Figure S29. Partial COSY spectrum of ***cis*-13a** with expansion of aliphatic protons region.

The marked correlations belong to diastereotopic methylene protons of two different ethyl groups on CAAC ligand.

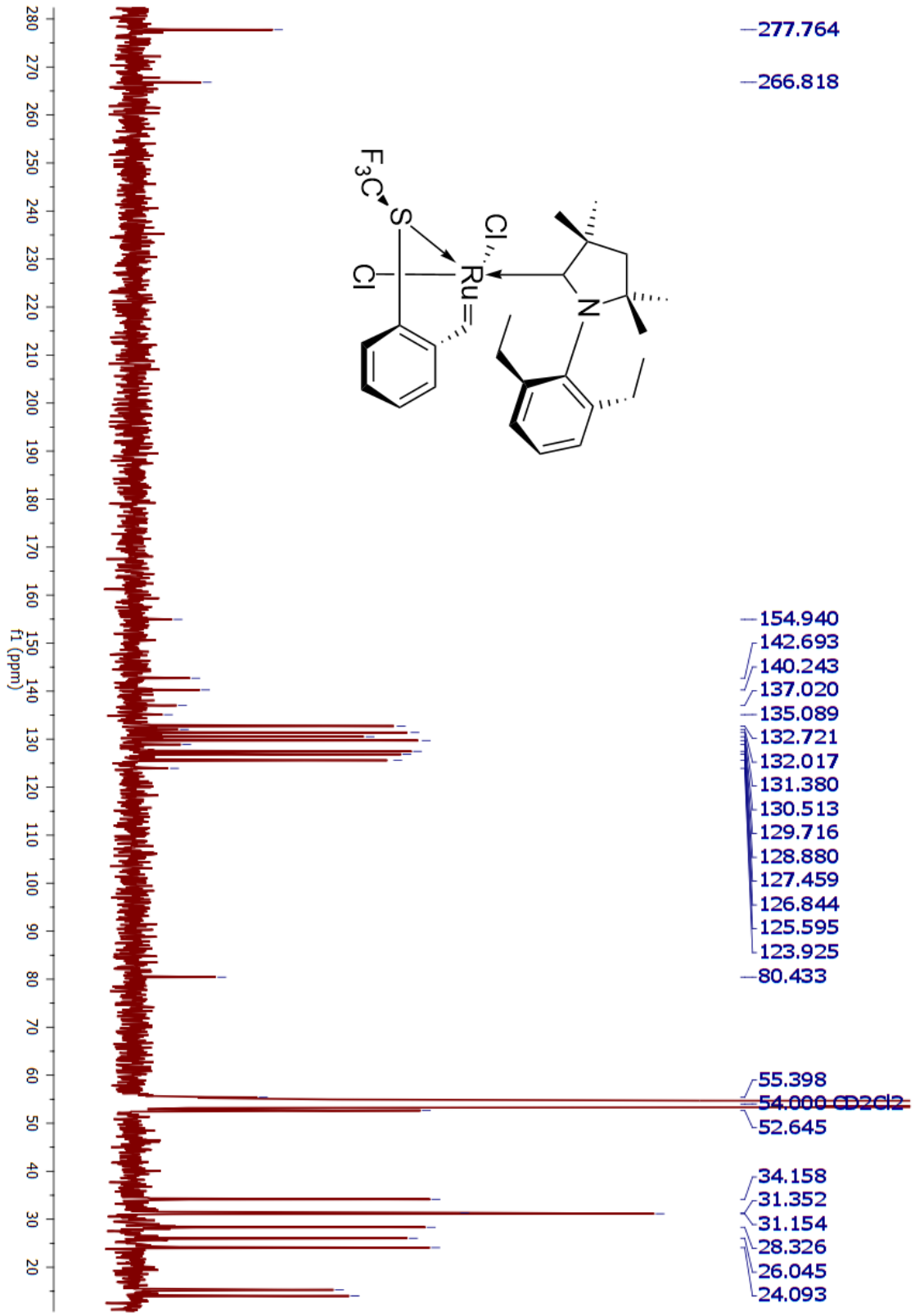


Figure S30. Full ^{13}C-NMR spectrum of ***cis*-13a**

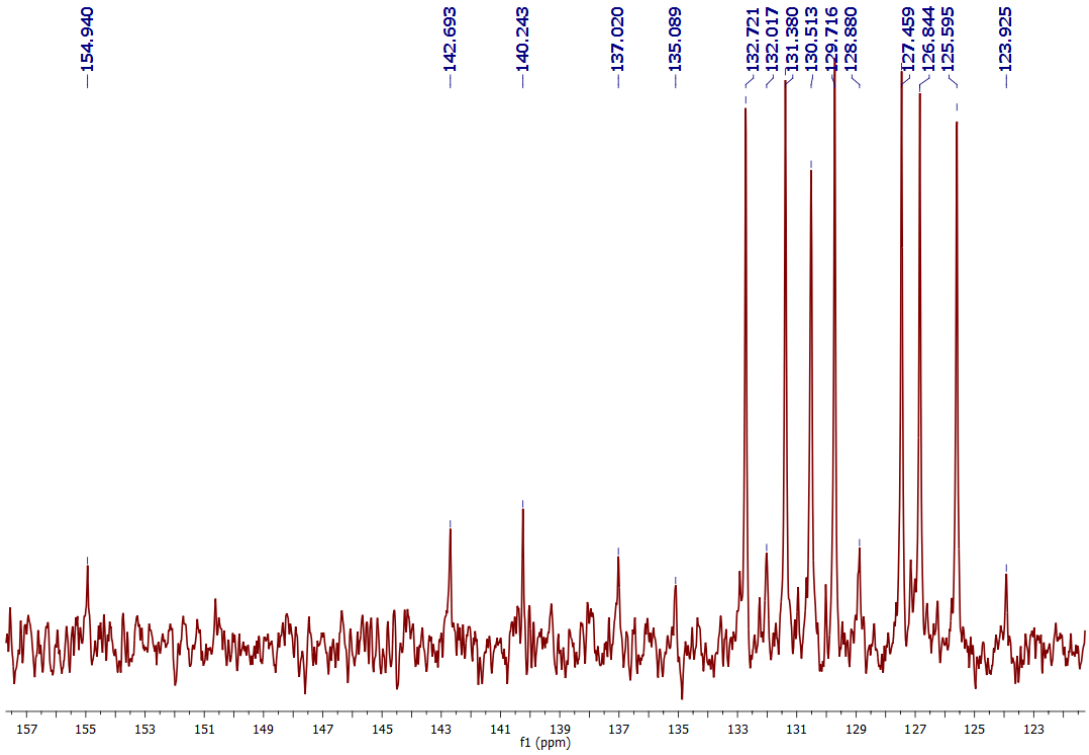


Figure S31. Expansion of aromatic region in ^{13}C-NMR spectrum of ***cis*-13a**

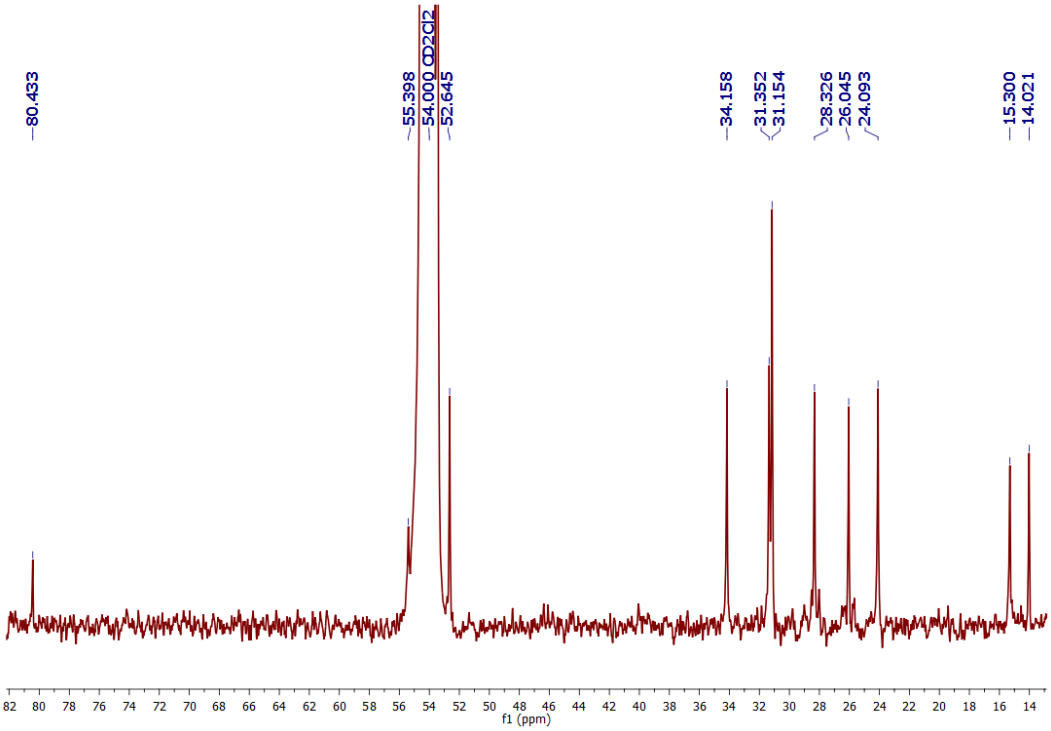


Figure S32. Expansion of aliphatic region in ^{13}C-NMR spectrum of ***cis*-13a**

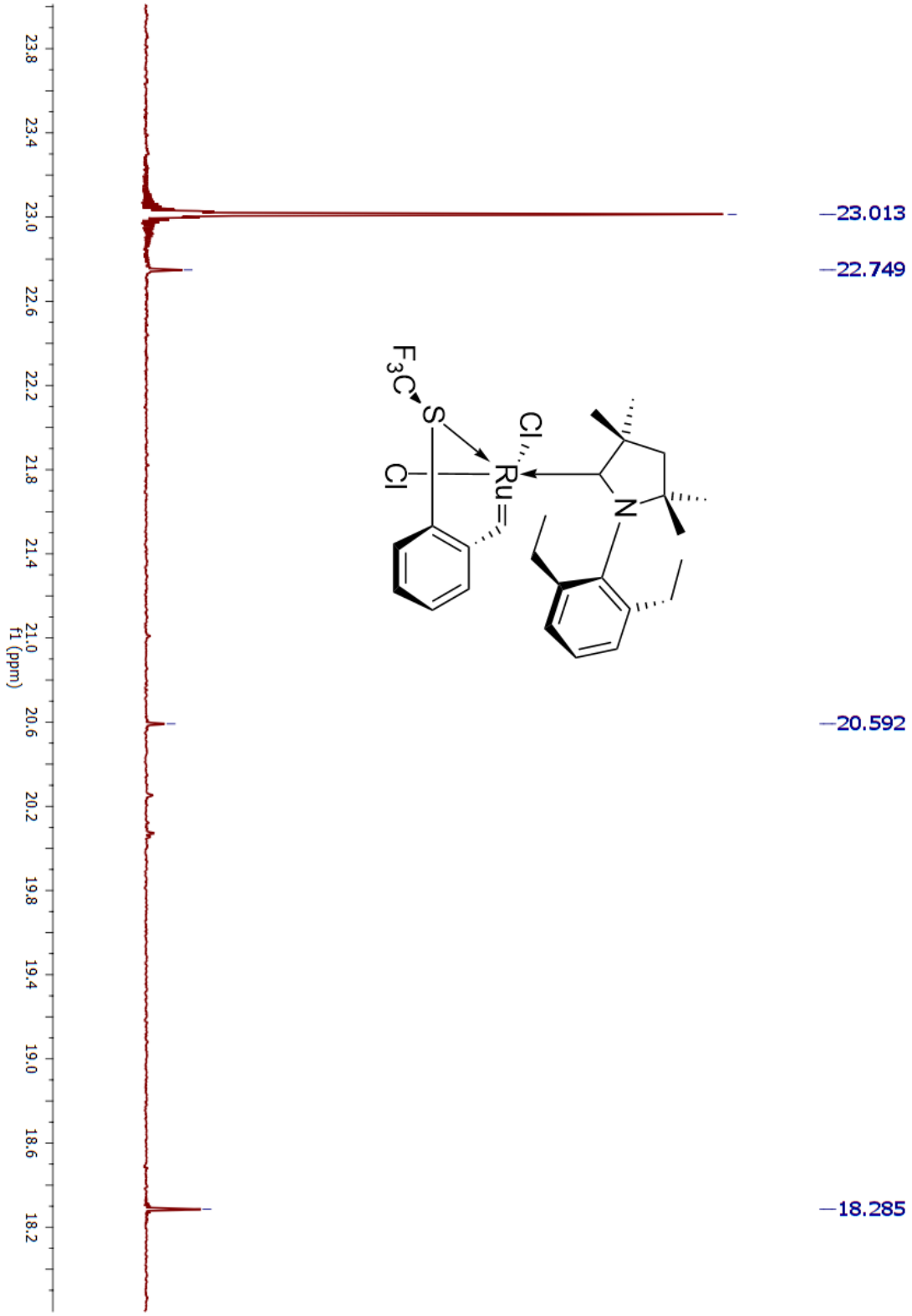


Figure S33. ^{19}F-NMR spectrum of ***cis*-13a**

3.11. HRMS of *cis*-13a

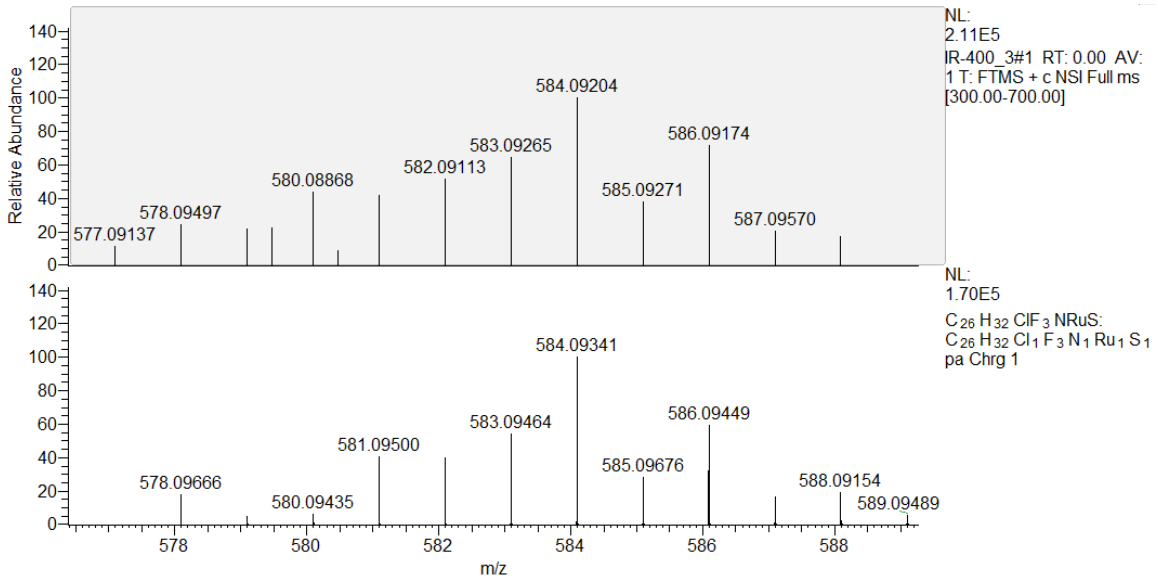


Figure S34. Experimental (grey) and simulated (white) HRMS spectra of ***cis*-13a** ([M –Cl] $^{+}$)

3.12. UV-Vis of *cis*-13a

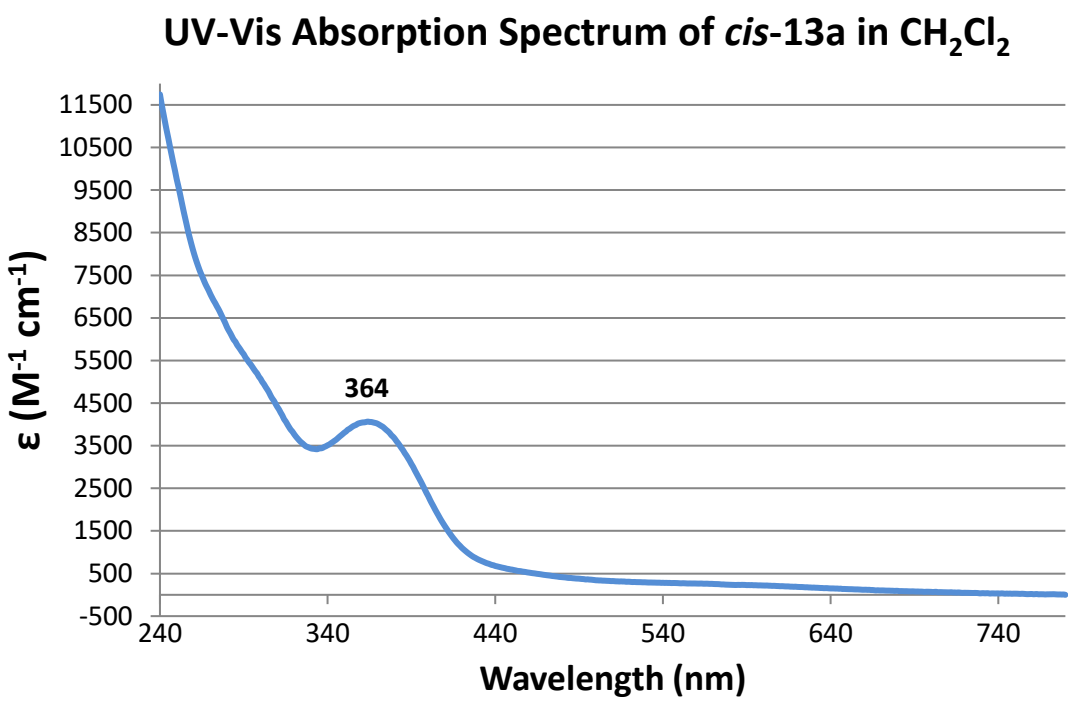


Figure S35. UV-Vis spectrum of ***cis*-13a**. Concentration of ***cis*-13a**: 1×10^{-4}M CH_2Cl_2

3.13. NMR spectra of *trans*-13b

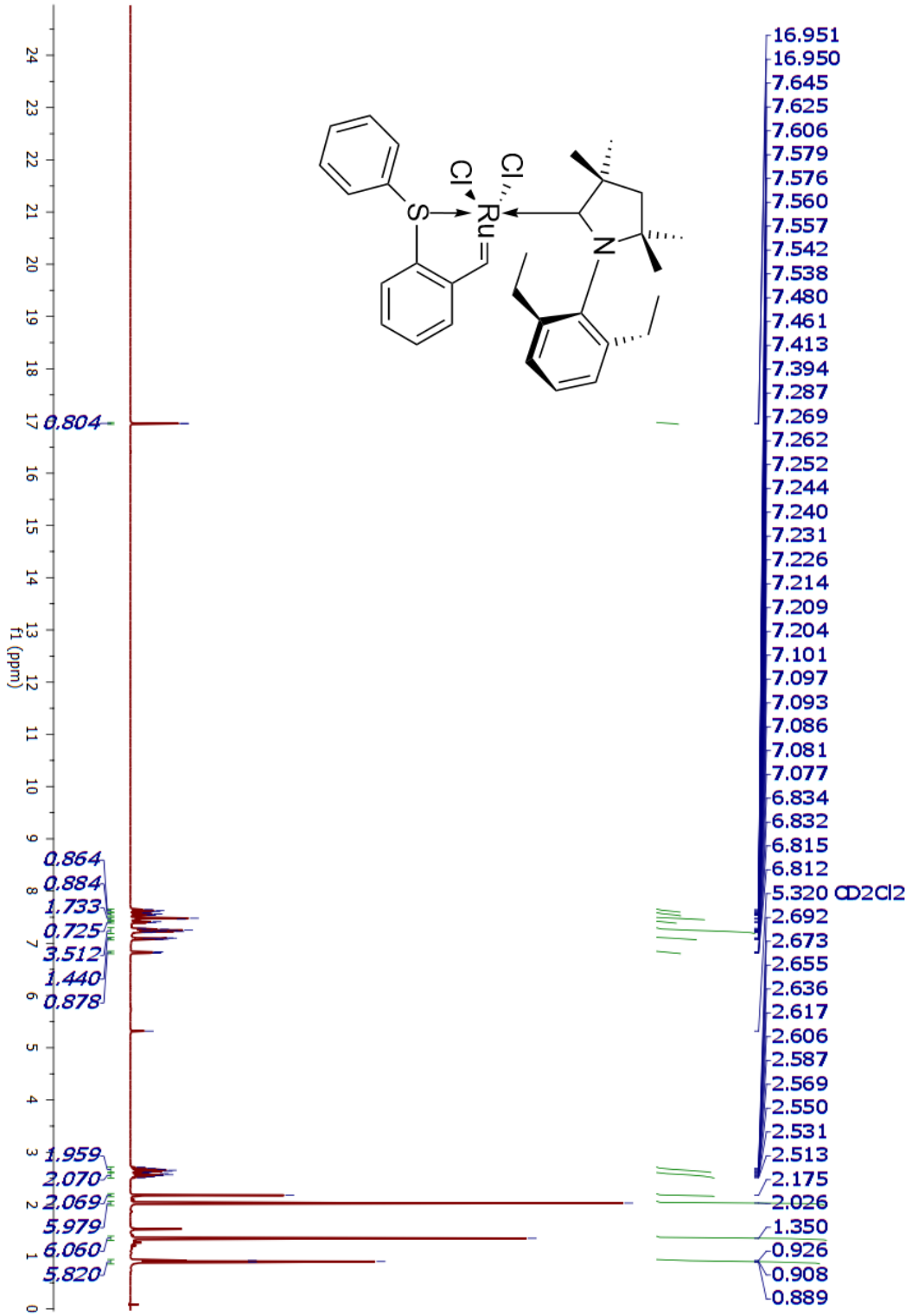


Figure S36. Full ^{1}H-NMR spectrum of ***trans*-13b**

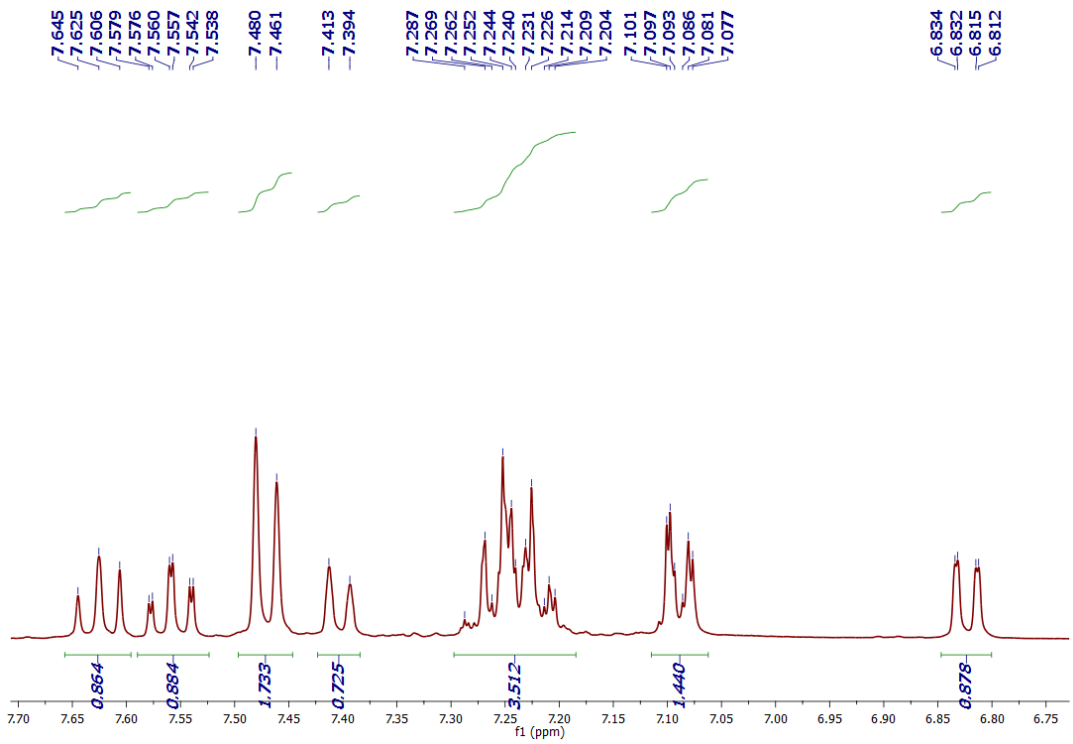


Figure S37. Aromatic protons region of ^{1}H-NMR spectrum of ***trans*-13b**

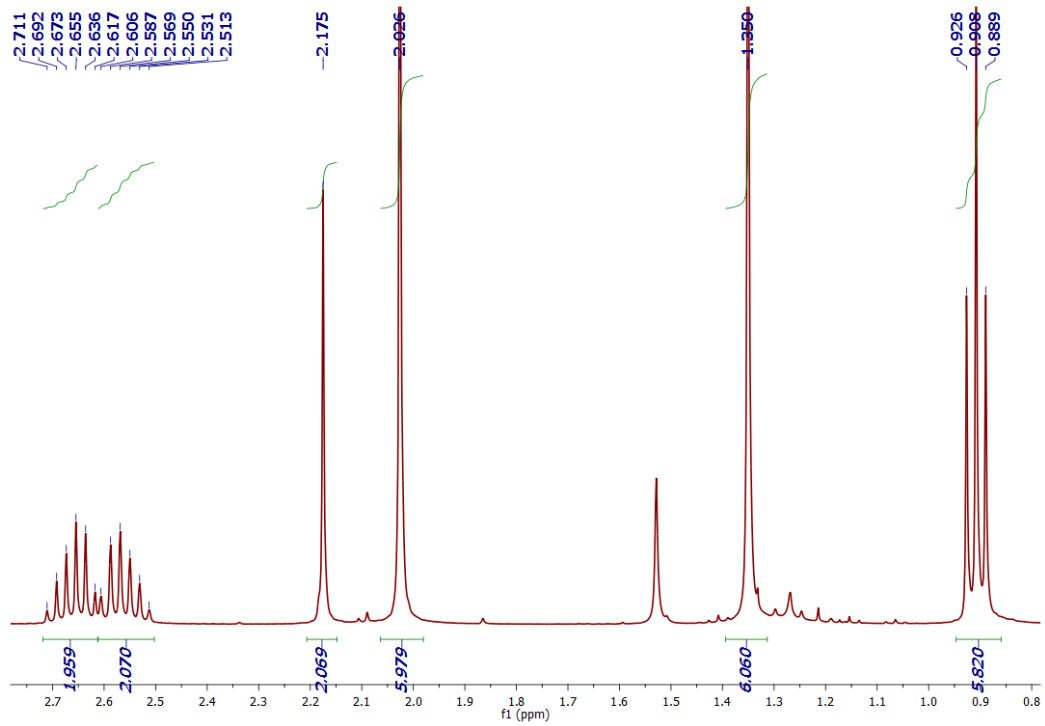


Figure S38. Aliphatic protons region of ^{1}H-NMR spectrum of ***trans*-13b**

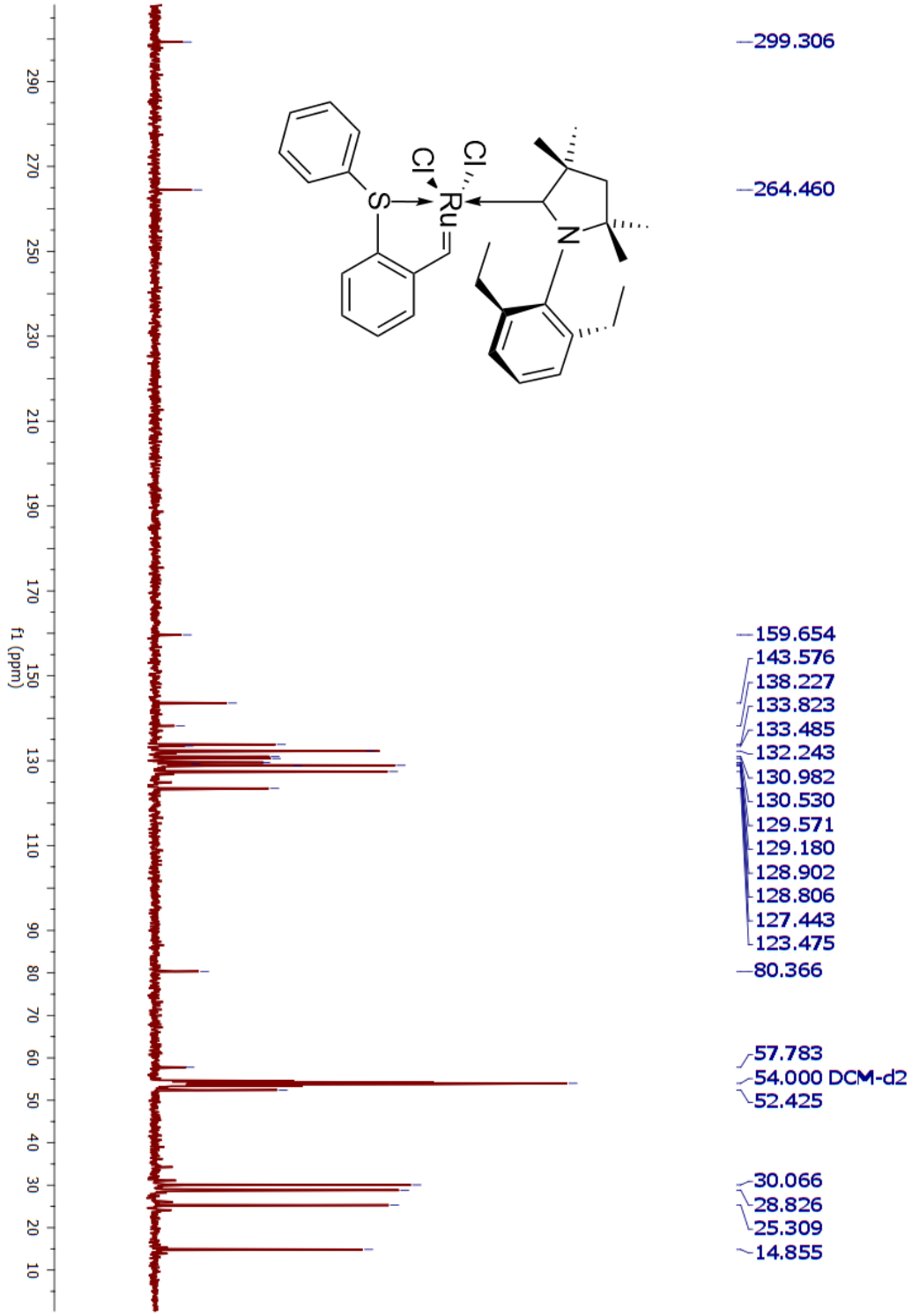


Figure S39. Full ^{13}C-NMR spectrum of ***trans*-13b.**[12]

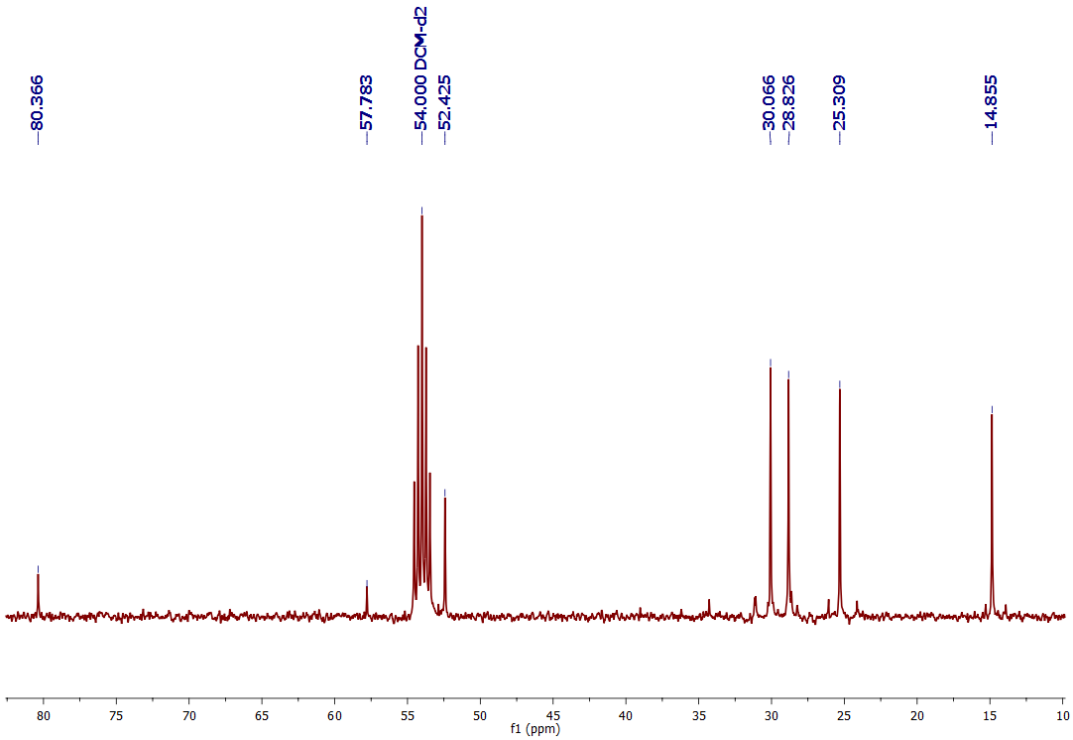


Figure S40. Expansion of aliphatic region in ^{13}C-NMR spectrum of ***trans*-13b**.[12]

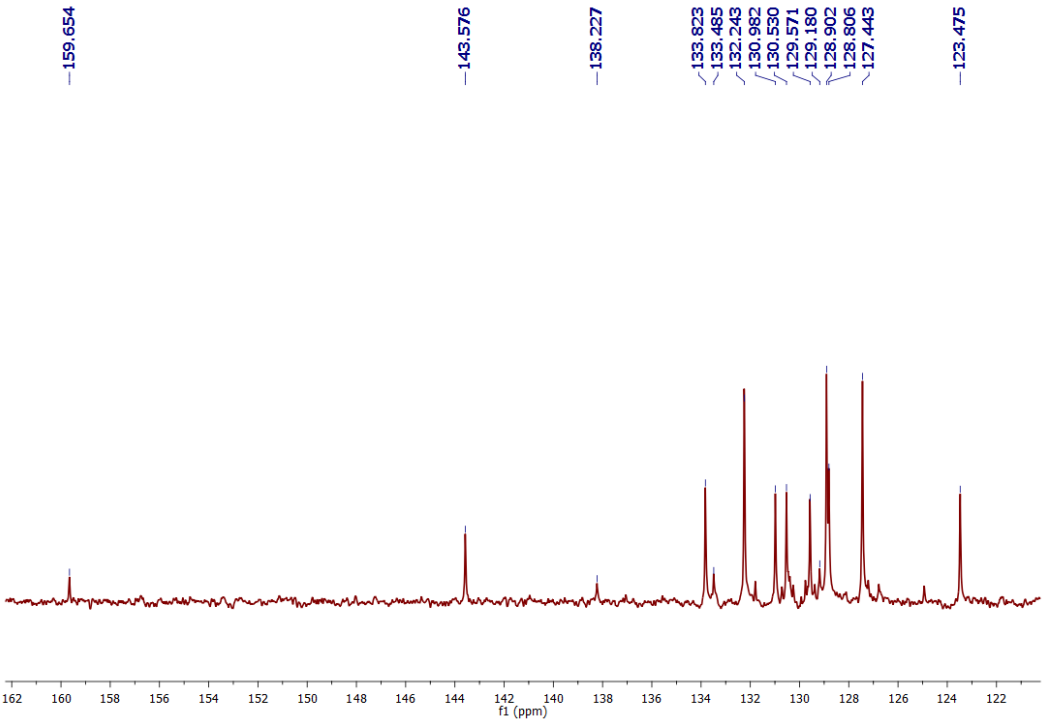


Figure S41. Expansion of aromatic region in ^{13}C-NMR spectrum of ***trans*-13b**.[12]

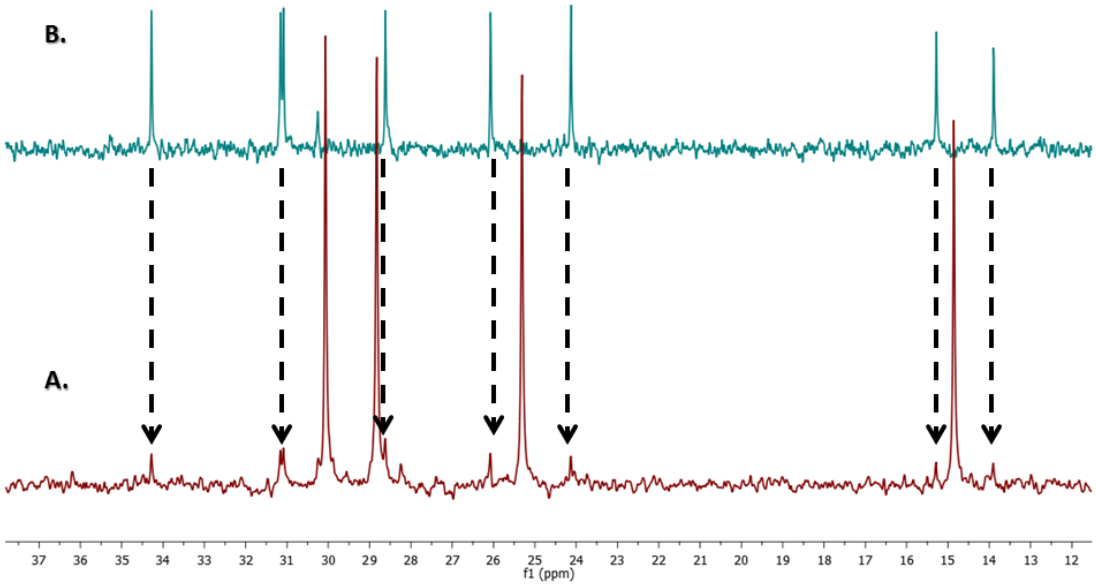


Figure S42. Expansion of aliphatic region in ^{13}C-NMR spectrum of ***trans*-13b** (**A.**) with the spectrum of ***cis*-13b** (**B.**). The NMRs detail the spontaneous isomerization of ***trans*-13b** to ***cis*-13b** during data acquisition**.**

3.14. HRMS of *trans*-13b

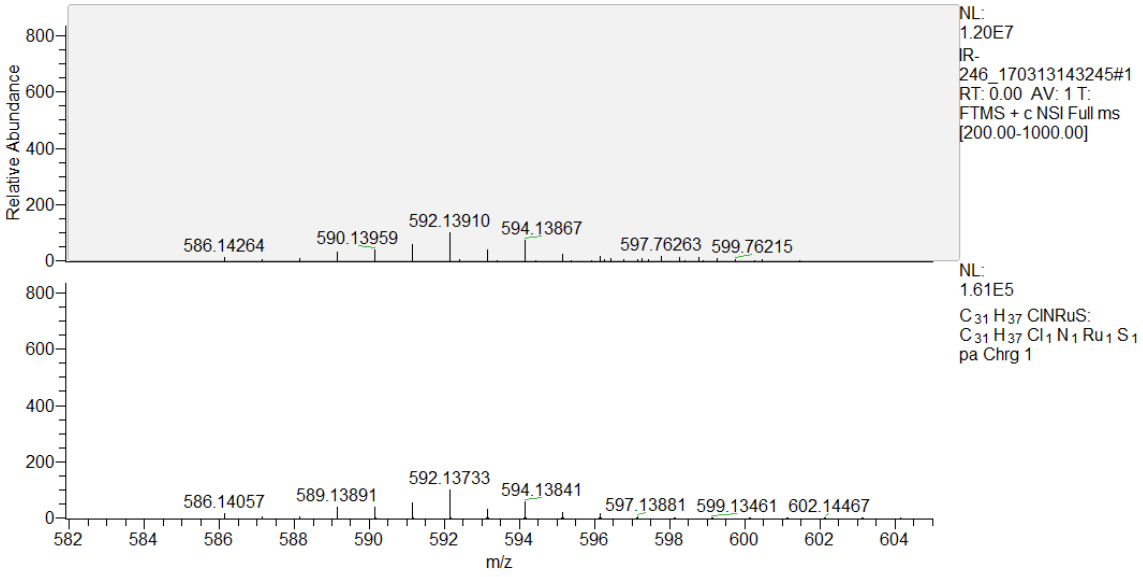


Figure S43. Experimental (grey) and simulated (white) HRMS spectra of ***trans*-13b** ([M –Cl] $^{+}$)

3.15. UV-Vis of *trans*-13b

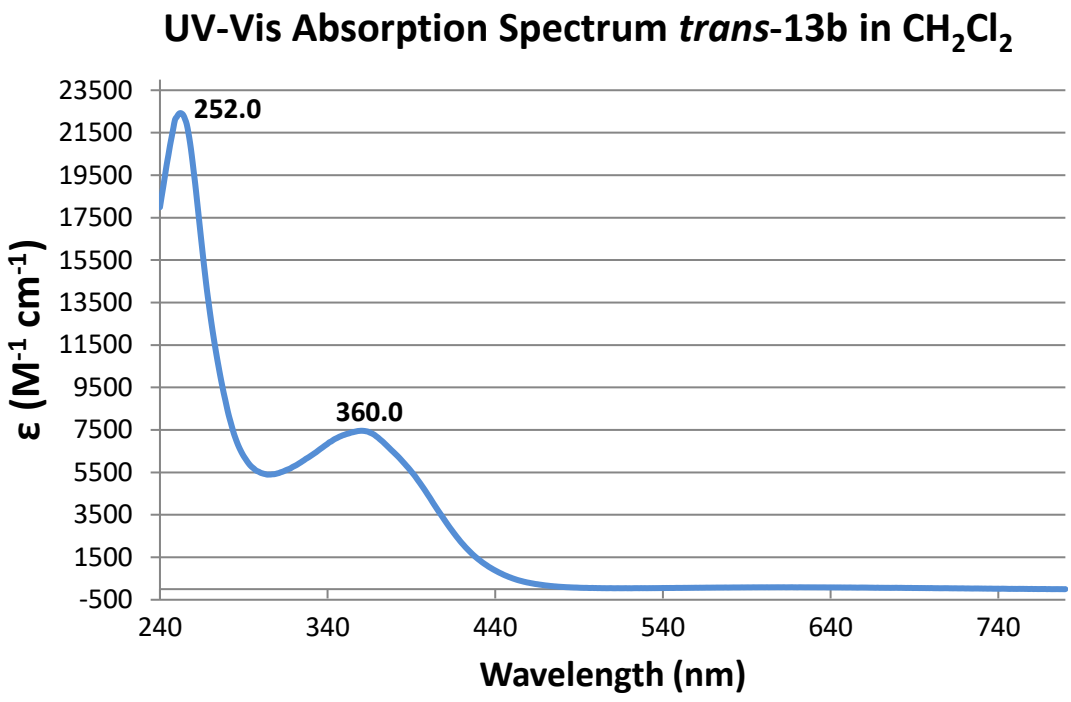


Figure S44. UV-Vis spectrum of ***trans*-13b**. Concentration of ***trans*-13b**: 10^{-4}M in CH_2Cl_2

3.16. NMR spectra of *cis*-13b

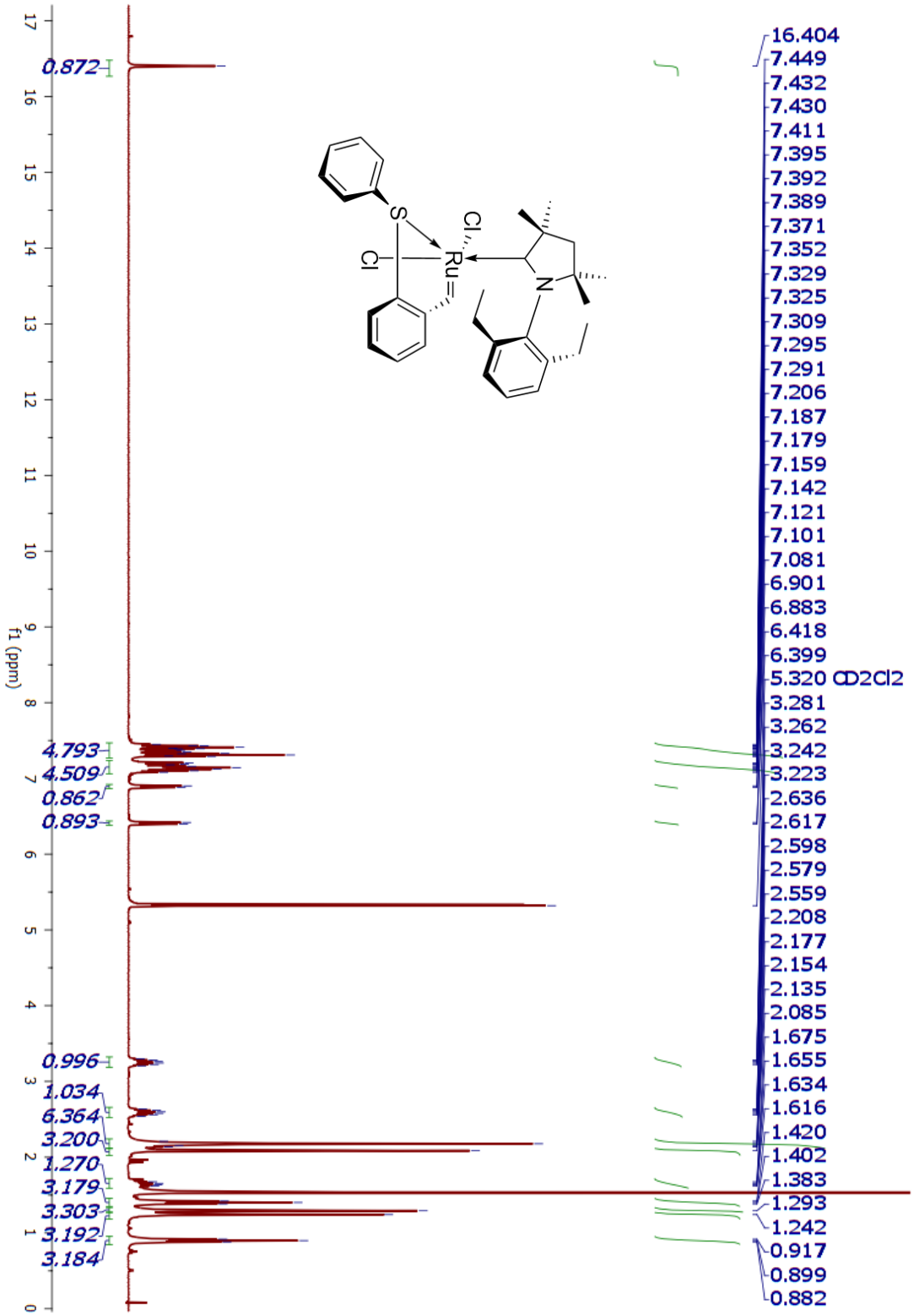


Figure S45. Full ^{1}H-NMR spectrum of ***cis*-13b**

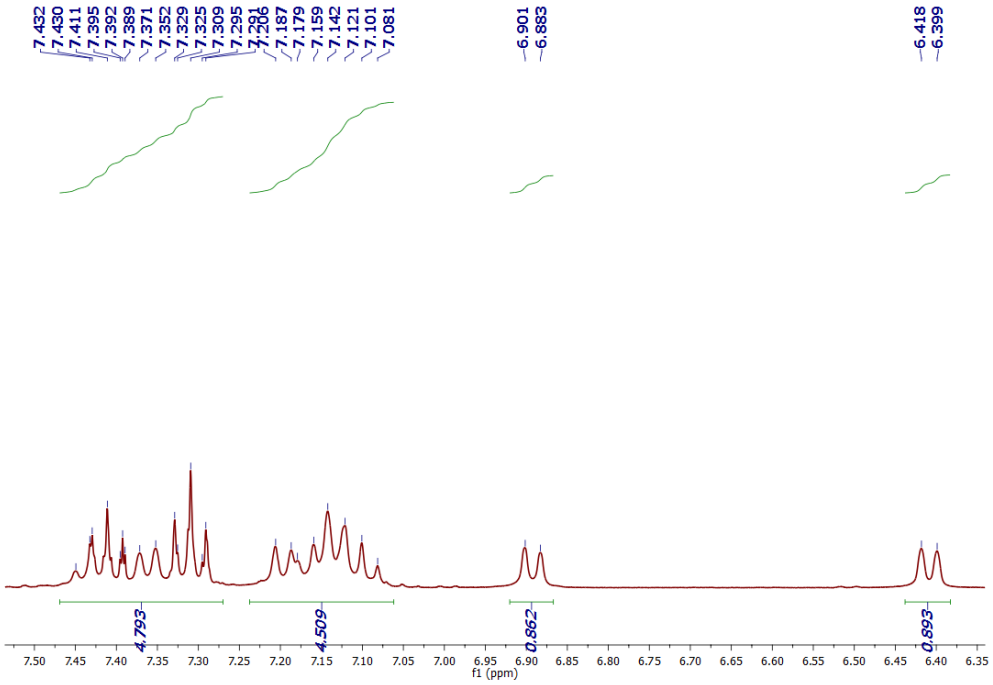


Figure S46. Aromatic protons region of ^{1}H-NMR spectrum of ***cis*-13b**

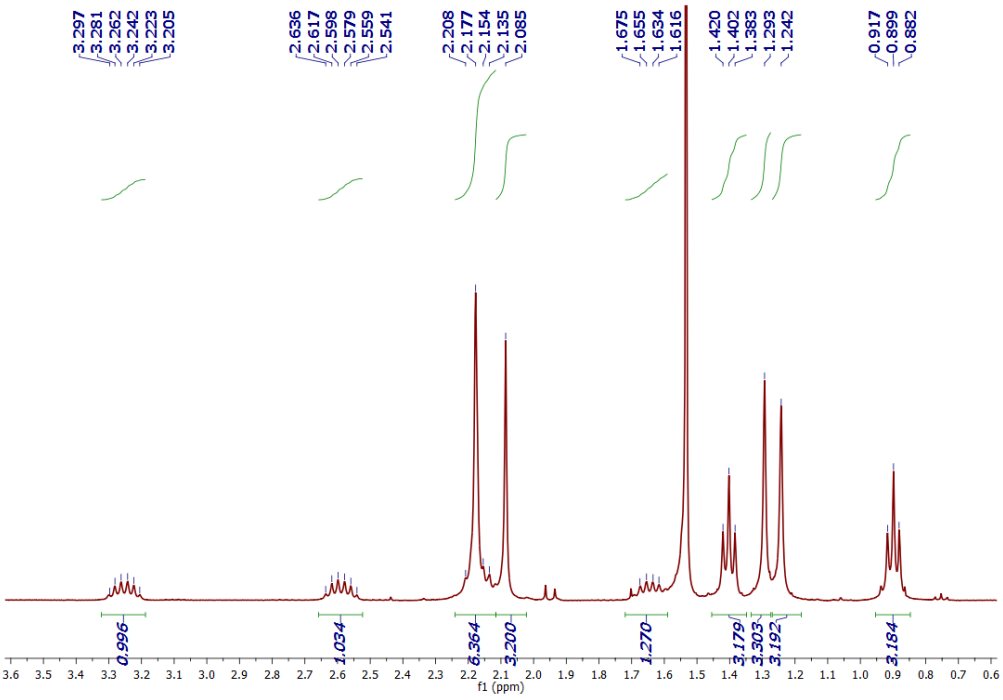


Figure S47. Aliphatic protons region of ^{1}H-NMR spectrum of ***cis*-13b.**

The signal at 2.15 ppm is an overlap of three different peaks: one of the methyl groups on the CAAC backbone, the methylene (CH_2) of the CAAC backbone and one of the diastereotopic protons belonging to one of the N-aryl ethyl groups.

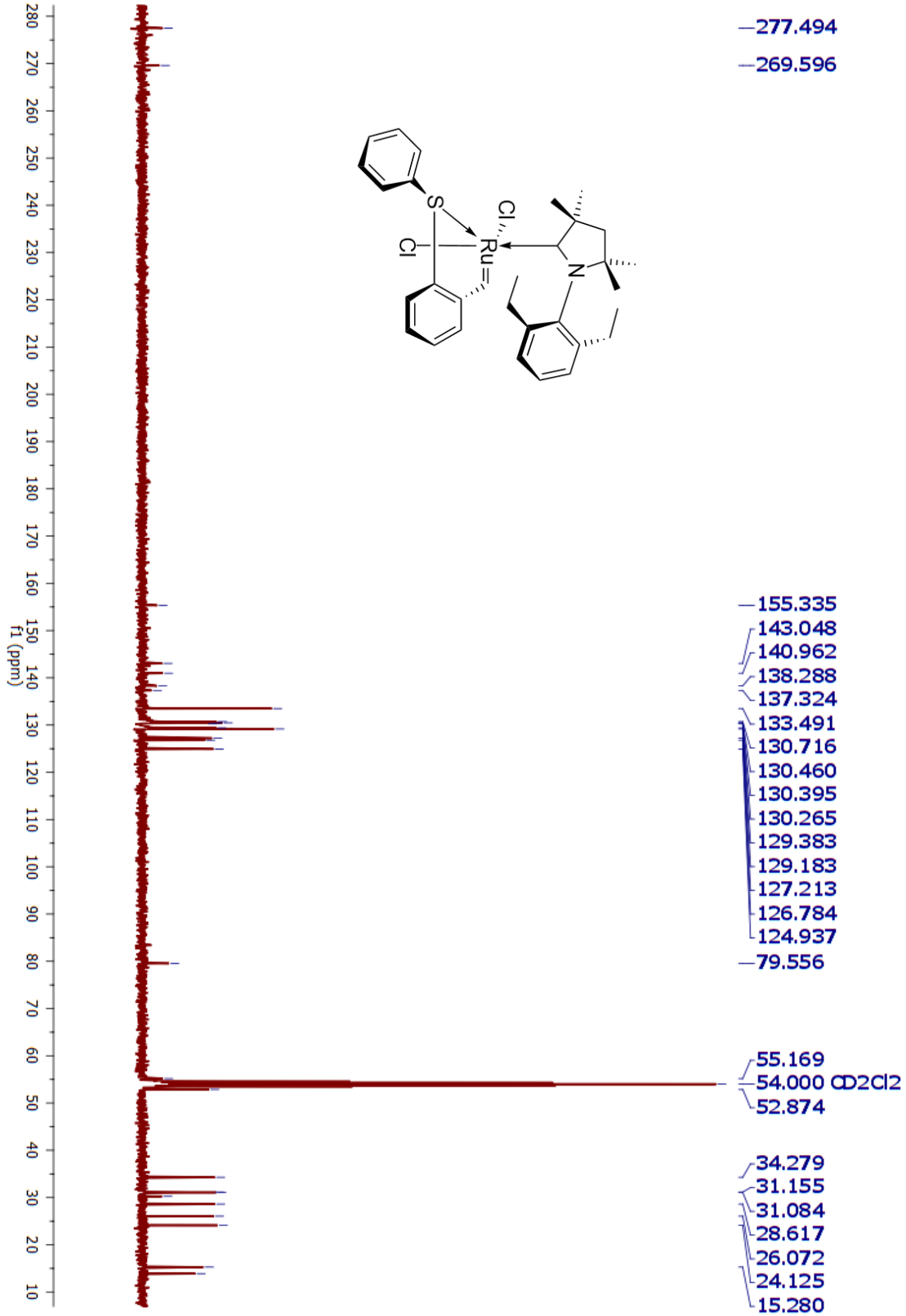


Figure S48. Full ^{13}C-NMR spectrum of ***cis*-13b**

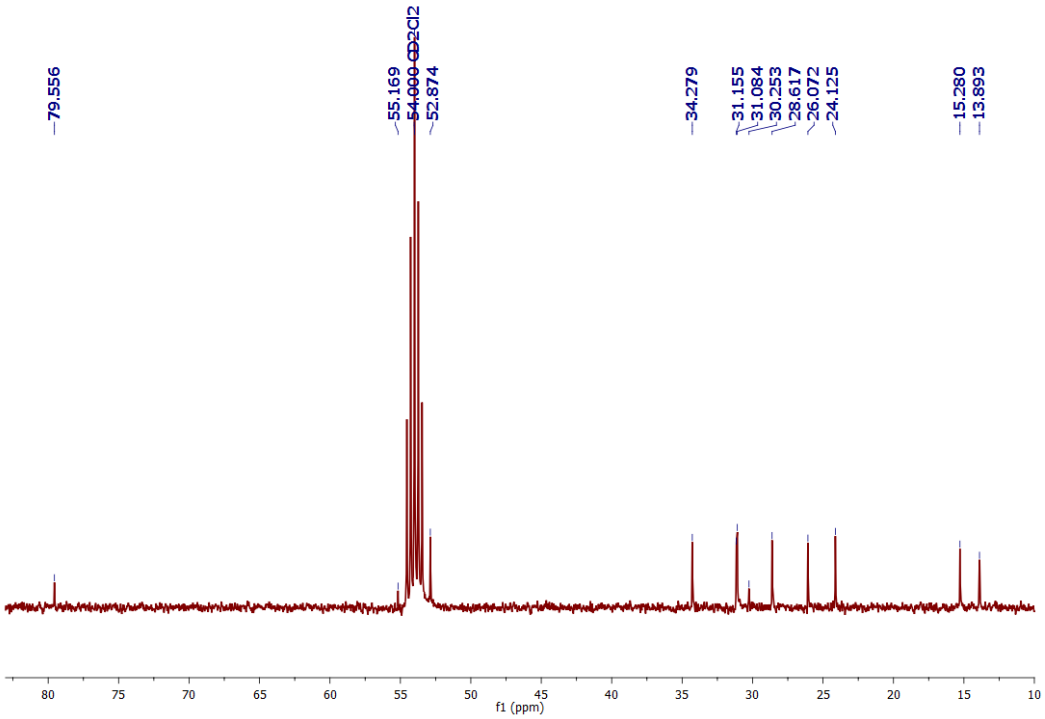


Figure S49. Expansion of aliphatic region in ^{13}C-NMR spectrum of ***cis*-13b**

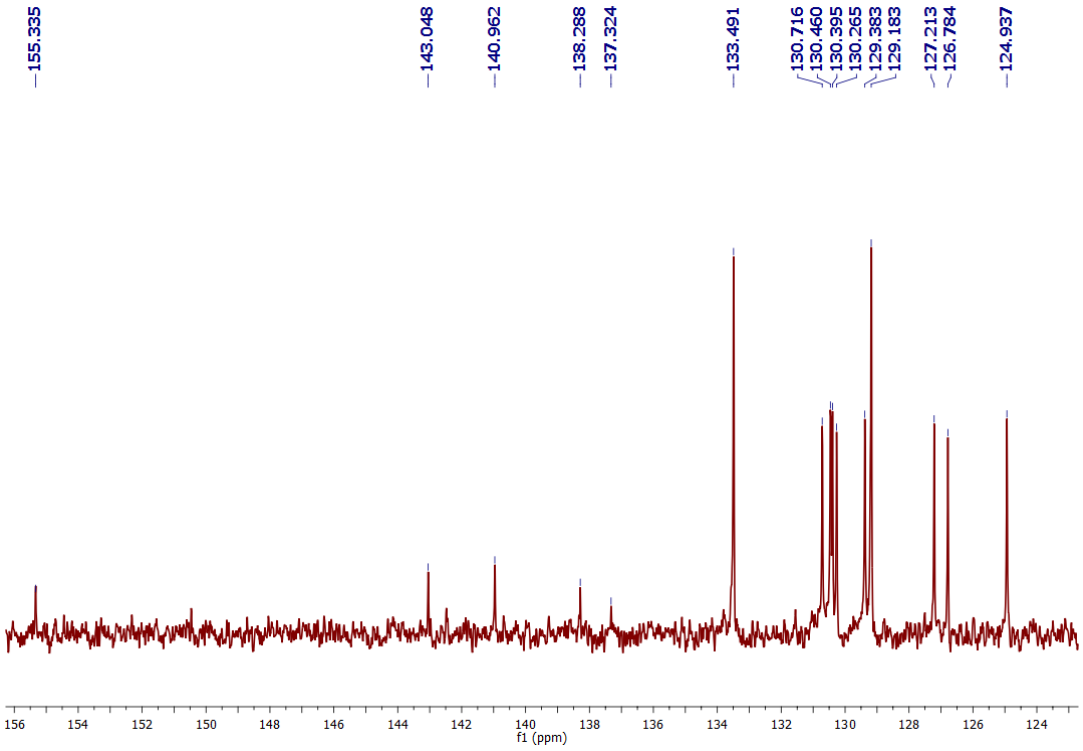


Figure S50. Expansion of aromatic region in ^{13}C-NMR spectrum of ***cis*-13b**

3.17. HRMS of *cis*-13b

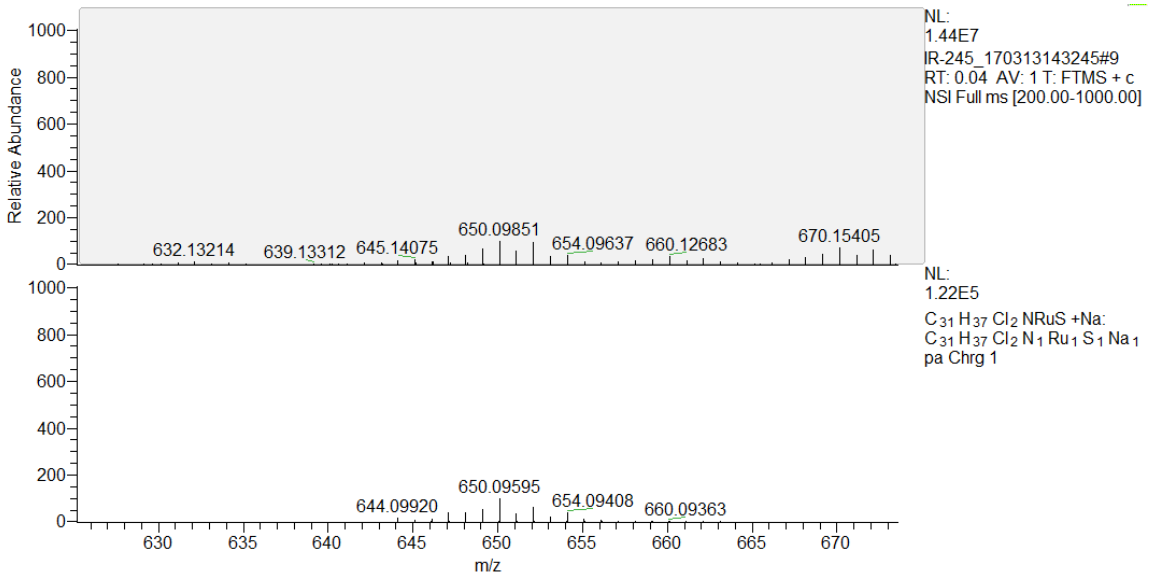


Figure S51. Experimental (grey) and simulated (white) HRMS spectra of ***cis*-13b** ([M +Na] $^{+}$)

3.18. UV-Vis of *cis*-13b

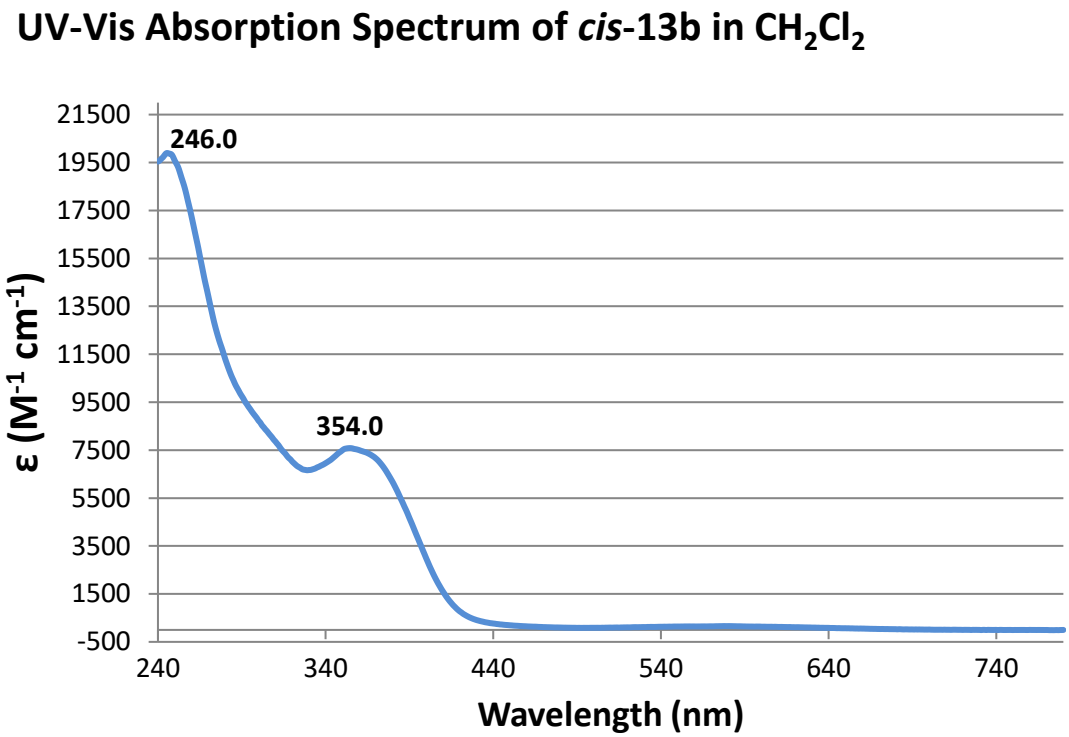


Figure S52. UV-Vis spectrum of ***cis*-13b**. Concentration of ***cis*-13b**: 10^{-4}M in CH_2Cl_2

4. X-Ray data of complexes

4.1. Crystallographic data and structure refinement

Table S1. Crystal data and structure refinement for complexes **10a**, **10b**, ***cis*-13a** and ***cis*-13b**

	10a	**10b**	***cis*-13a**	***cis*-13b**
Formula	$C_{28}H_{36}Cl_2F_3NRuS$	$C_{33}H_{41}Cl_2NRuS$	$C_{26}H_{32}Cl_2F_3NRuS$	$C_{31}H_{37}Cl_2NRuS$
Formula weight	647.61	655.70	619.55	712.57
Temperature /K	110	110	110	110
Wavelength / Å	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	tetragonal	triclinic	orthorhombic
Space group	$Pna2_1$	$P4_3$	$P\text{-}1$	$Pca2_1$
a /Å	16.3382(7)	10.0186(3)	11.0669(3)	19.8680(7)
b /Å	16.5805(7)	10.0186(3)	14.1689(4)	9.2131(3)
c /Å	10.4655(5)	30.9734(11)	17.6536(5)	17.5258(7)
α /°	90	90	103.228(1)	90
β /°	90	90	94.276(1)	90
γ /°	90	90	100.447(1)	90
V /Å^3	2835.1(2)	3108.9(2)	2630.52(13)	3208.0(2)
Z	4	4	4	4
μ /mm^{-1}	0.853	0.766	0.916	0.910
Dc /g·cm^{-3}	1.517	1.401	1.564	1.475
Index ranges	$-20 \le h \le 21$, $-21 \le k \le 20$, $-13 \le l \le 10$	$-12 \le h \le 11$, $-13 \le k \le 10$, $-37 \le l \le 41$	$-14 \le h \le 14$, $-18 \le k \le 18$, $-23 \le l \le 20$	$-26 \le h \le 26$, $-10 \le k \le 12$, $-23 \le l \le 20$
F(000)	1328.0	1360.0	1264.0	1464.0
θ range /	2.30 - 27.693	2.03 - 28.517	1.99 - 28.443	2.05 - 28.287
Appearance	brown needle	brown needle	brown needle	green prism
Crystal size /mm^3	0.36 x 0.10 x 0.07	0.30 x 0.18 x 0.13	0.34 x 0.18 x 0.15	0.26 x 0.24 x 0.17
GOF on F^2	1.004	1.003	1.025	1.005
Reflections collected / unique	5509 / 5184 [R(int) = 0.0248]	7096 / 6728 [R(int) = 0.0323]	13050 / 10699 [R(int) = 0.0292]	7307 / 6938 [R(int) = 0.0326]
Data / restraints / parameters	5509 / 1 / 333	7096 / 1 / 351	13050 / 0 / 625	7307 / 1 / 358
R indices (all data)	R_1 = 0.0235, wR_2 = 0.0438	R_1 = 0.0314, wR_2 = 0.0583	R_1 = 0.0502, wR_2 = 0.0955	R_1 = 0.0296, wR_2 = 0.0607
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0201, wR_2 = 0.0423	R_1 = 0.0283, wR_2 = 0.0571	R_1 = 0.0377, wR_2 = 0.0869	R_1 = 0.0273, wR_2 = 0.0596
Max. and min. transmission	0.766, 0.403	0.907, 0.803	0.875, 0.746	0.861, 0.798
Largest diff. peak and hole /e·A^{-3}	0.278, -0.339	0.275, -0.336	1.628, -1.384	0.722, -1.050

4.2. Bond lengths and angles for 10a

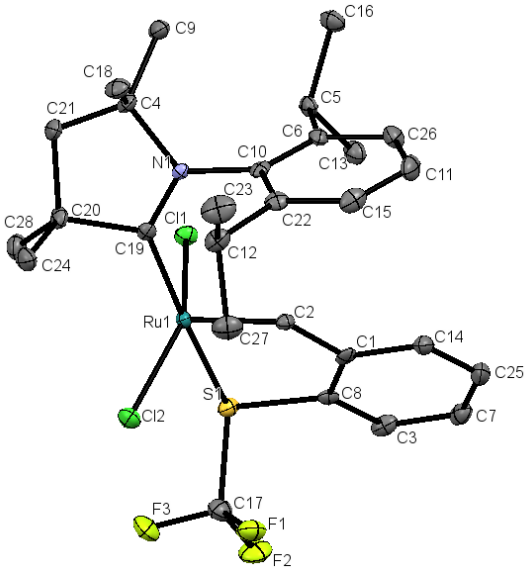


Figure S53. ORTEP representation (50% probability ellipsoids) of complex **10a**

Table S2. Bond lengths [Å] of **10a**.

Number	Atom1	Atom2	Length	Number	Atom1	Atom2	Length
1	Ru1	Cl1	2.3398(8)	**21**	C4	C21	1.525(4)
2	Ru1	Cl2	2.3251(7)	**22**	C5	C6	1.515(4)
3	Ru1	S1	2.4910(8)	**23**	C5	C13	1.527(4)
4	Ru1	C2	1.832(2)	**24**	C5	C16	1.543(4)
5	Ru1	C19	1.992(3)	**25**	C6	C10	1.412(4)
6	S1	C8	1.783(3)	**26**	C6	C26	1.402(4)
7	S1	C17	1.824(3)	**27**	C7	C25	1.387(4)
8	F1	C17	1.328(3)	**28**	C10	C22	1.410(4)
9	F2	C17	1.341(4)	**29**	C11	C15	1.377(4)
10	F3	C17	1.324(3)	**30**	C11	C26	1.381(4)
11	N1	C4	1.534(3)	**31**	C12	C22	1.519(4)
12	N1	C10	1.456(3)	**32**	C12	C23	1.533(5)
13	N1	C19	1.325(3)	**33**	C12	C27	1.526(4)
14	C1	C2	1.460(4)	**34**	C14	C25	1.389(4)
15	C1	C8	1.395(4)	**35**	C15	C22	1.396(4)
16	C1	C14	1.401(4)	**36**	C19	C20	1.540(4)
17	C3	C7	1.381(4)	**37**	C20	C21	1.541(4)
18	C3	C8	1.388(4)	**38**	C20	C24	1.543(4)
19	C4	C9	1.531(4)	**39**	C20	C28	1.529(4)
20	C4	C18	1.523(4)				

Table S3. Bond angles [°] of **10a**.

Number	Atom1	Atom2	Atom3	Angle	Number	Atom1	Atom2	Atom3	Angle
1	Cl1	Ru1	Cl2	152.57(3)	**35**	S1	C8	C1	115.4(2)
2	Cl1	Ru1	S1	79.04(2)	**36**	S1	C8	C3	122.1(2)
3	Cl1	Ru1	C2	102.36(8)	**37**	C1	C8	C3	122.4(3)
4	Cl1	Ru1	C19	87.60(8)	**38**	N1	C10	C6	121.4(2)
5	Cl2	Ru1	S1	93.69(3)	**39**	N1	C10	C22	117.4(2)
6	Cl2	Ru1	C2	103.05(8)	**40**	C6	C10	C22	121.2(3)
7	Cl2	Ru1	C19	97.88(8)	**41**	C15	C11	C26	119.8(3)
8	S1	Ru1	C2	83.62(8)	**42**	C22	C12	C23	112.4(3)
9	S1	Ru1	C19	166.62(8)	**43**	C22	C12	C27	111.4(2)
10	C2	Ru1	C19	100.2(1)	**44**	C23	C12	C27	110.3(3)
11	Ru1	S1	C8	95.69(9)	**45**	C1	C14	C25	120.1(3)
12	Ru1	S1	C17	115.7(1)	**46**	C11	C15	C22	121.3(3)
13	C8	S1	C17	97.8(1)	**47**	S1	C17	F1	113.9(2)
14	C4	N1	C10	119.7(2)	**48**	S1	C17	F2	110.7(2)
15	C4	N1	C19	115.0(2)	**49**	S1	C17	F3	108.2(2)
16	C10	N1	C19	125.1(2)	**50**	F1	C17	F2	106.7(2)
17	C2	C1	C8	120.6(2)	**51**	F1	C17	F3	109.0(2)
18	C2	C1	C14	121.6(2)	**52**	F2	C17	F3	108.1(2)
19	C8	C1	C14	117.7(3)	**53**	Ru1	C19	N1	134.1(2)
20	Ru1	C2	C1	123.6(2)	**54**	Ru1	C19	C20	116.7(2)
21	C7	C3	C8	118.8(3)	**55**	N1	C19	C20	108.0(2)
22	N1	C4	C9	110.0(2)	**56**	C19	C20	C21	102.6(2)
23	N1	C4	C18	112.8(2)	**57**	C19	C20	C24	108.0(2)
24	N1	C4	C21	100.8(2)	**58**	C19	C20	C28	114.3(2)
25	C9	C4	C18	107.6(2)	**59**	C21	C20	C24	111.5(2)
26	C9	C4	C21	111.7(2)	**60**	C21	C20	C28	112.0(2)
27	C18	C4	C21	113.8(2)	**61**	C24	C20	C28	108.4(2)
28	C6	C5	C13	111.8(2)	**62**	C4	C21	C20	106.8(2)
29	C6	C5	C16	111.9(2)	**63**	C10	C22	C12	124.0(3)
30	C13	C5	C16	108.3(2)	**64**	C10	C22	C15	118.4(3)
31	C5	C6	C10	125.7(3)	**65**	C12	C22	C15	117.6(3)
32	C5	C6	C26	116.8(3)	**66**	C7	C25	C14	120.7(3)
33	C10	C6	C26	117.5(3)	**67**	C6	C26	C11	121.9(3)
34	C3	C7	C25	120.2(3)					

4.3. Bond lengths and angles for 10b

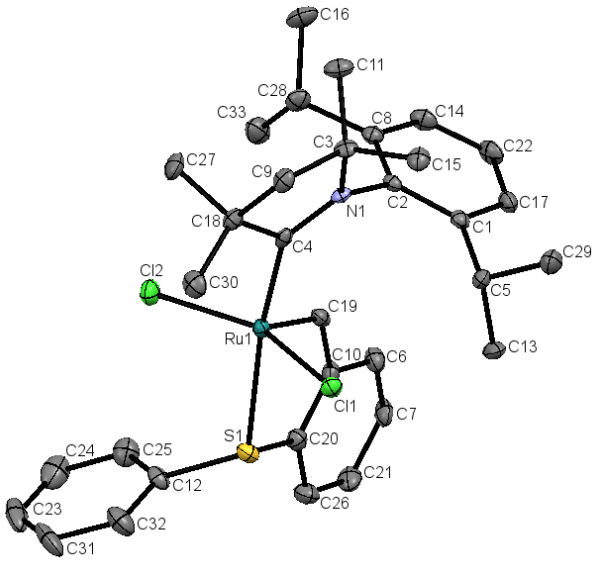


Figure S54. ORTEP representation (50% probability ellipsoids) of complex **10b**

Table S4. Bond lengths [Å] of **10b**.

Number	Atom1	Atom2	Length	Number	Atom1	Atom2	Length
1	Ru1	Cl1	2.3340(9)	**22**	C6	C10	1.407(5)
2	Ru1	Cl2	2.333(1)	**23**	C7	C21	1.386(6)
3	Ru1	S1	2.475(1)	**24**	C8	C14	1.396(5)
4	Ru1	C4	1.994(3)	**25**	C8	C28	1.523(4)
5	Ru1	C19	1.836(3)	**26**	C9	C18	1.534(6)
6	S1	C12	1.784(4)	**27**	C10	C19	1.456(4)
7	S1	C20	1.770(4)	**28**	C10	C20	1.394(5)
8	N1	C2	1.459(4)	**29**	C12	C25	1.382(6)
9	N1	C3	1.528(4)	**30**	C12	C32	1.379(6)
10	N1	C4	1.320(4)	**31**	C14	C22	1.385(5)
11	C1	C2	1.410(4)	**32**	C16	C28	1.537(5)
12	C1	C5	1.521(5)	**33**	C17	C22	1.380(6)
13	C1	C17	1.393(5)	**34**	C18	C27	1.551(5)
14	C2	C8	1.409(4)	**35**	C18	C30	1.513(6)
15	C3	C9	1.531(5)	**36**	C20	C26	1.397(5)
16	C3	C11	1.520(5)	**37**	C21	C26	1.381(5)
17	C3	C15	1.520(5)	**38**	C23	C24	1.382(7)
18	C4	C18	1.542(4)	**39**	C23	C31	1.375(7)
19	C5	C13	1.539(4)	**40**	C24	C25	1.383(6)
20	C5	C29	1.530(5)	**41**	C28	C33	1.533(6)
21	C6	C7	1.386(5)	**42**	C31	C32	1.383(6)

Table S5. Bond angles [°] of **10b**.

Number	Atom1	Atom2	Atom3	Angle	Number	Atom1	Atom2	Atom3	Angle
1	Cl1	Ru1	Cl2	152.04(4)	**36**	C6	C7	C21	120.0(3)
2	Cl1	Ru1	S1	82.35(3)	**37**	C2	C8	C14	118.3(3)
3	Cl1	Ru1	C4	85.48(9)	**38**	C2	C8	C28	124.3(3)
4	Cl1	Ru1	C19	105.7(1)	**39**	C14	C8	C28	117.3(3)
5	Cl2	Ru1	S1	92.13(3)	**40**	C3	C9	C18	107.0(3)
6	Cl2	Ru1	C4	98.26(9)	**41**	C6	C10	C19	121.5(3)
7	Cl2	Ru1	C19	100.8(1)	**42**	C6	C10	C20	118.3(3)
8	S1	Ru1	C4	167.80(9)	**43**	C19	C10	C20	120.2(3)
9	S1	Ru1	C19	82.9(1)	**44**	S1	C12	C25	123.9(3)
10	C4	Ru1	C19	101.3(1)	**45**	S1	C12	C32	115.5(3)
11	Ru1	S1	C12	115.9(1)	**46**	C25	C12	C32	120.5(4)
12	Ru1	S1	C20	97.0(1)	**47**	C8	C14	C22	121.2(3)
13	C12	S1	C20	105.0(2)	**48**	C1	C17	C22	122.5(3)
14	C2	N1	C3	119.1(2)	**49**	C4	C18	C9	102.9(3)
15	C2	N1	C4	124.6(3)	**50**	C4	C18	C27	107.7(3)
16	C3	N1	C4	115.8(3)	**51**	C4	C18	C30	114.1(3)
17	C2	C1	C5	124.7(3)	**52**	C9	C18	C27	110.3(3)
18	C2	C1	C17	117.3(3)	**53**	C9	C18	C30	113.9(3)
19	C5	C1	C17	117.9(3)	**54**	C27	C18	C30	107.8(3)
20	N1	C2	C1	120.6(3)	**55**	Ru1	C19	C10	124.5(2)
21	N1	C2	C8	118.0(3)	**56**	S1	C20	C10	114.9(3)
22	C1	C2	C8	121.4(3)	**57**	S1	C20	C26	123.7(3)
23	N1	C3	C9	100.3(3)	**58**	C10	C20	C26	121.3(3)
24	N1	C3	C11	111.3(3)	**59**	C7	C21	C26	120.8(3)
25	N1	C3	C15	110.8(3)	**60**	C14	C22	C17	119.3(3)
26	C9	C3	C11	115.4(3)	**61**	C24	C23	C31	120.1(4)
27	C9	C3	C15	111.2(3)	**62**	C23	C24	C25	120.6(4)
28	C11	C3	C15	107.7(3)	**63**	C12	C25	C24	119.0(4)
29	Ru1	C4	N1	134.1(2)	**64**	C20	C26	C21	119.1(3)
30	Ru1	C4	C18	116.8(2)	**65**	C8	C28	C16	112.2(3)
31	N1	C4	C18	107.8(3)	**66**	C8	C28	C33	110.9(3)
32	C1	C5	C13	109.8(3)	**67**	C16	C28	C33	110.0(3)
33	C1	C5	C29	113.1(3)	**68**	C23	C31	C32	119.7(4)
34	C13	C5	C29	107.7(3)	**69**	C12	C32	C31	120.1(4)
35	C7	C6	C10	120.5(3)					

4.4. Bond lengths and angles for *cis*-13a

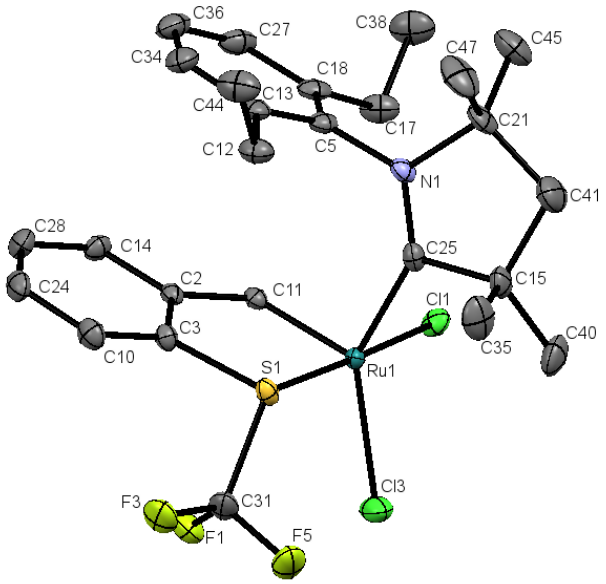


Figure S55. ORTEP representation (50% probability ellipsoids) of complex ***cis*-13a**

Table S6. Bond lengths [Å] of ***cis*-13a**.

Number	Atom1	Atom2	Length	Number	Atom1	Atom2	Length
1	Ru1	S1	2.3165(7)	**20**	C10	C24	1.394(5)
2	Ru1	Cl1	2.3689(7)	**21**	C12	C13	1.514(4)
3	Ru1	Cl3	2.3859(9)	**22**	C12	C44	1.530(4)
4	Ru1	C11	1.840(3)	**23**	C13	C34	1.391(5)
5	Ru1	C25	1.975(2)	**24**	C14	C28	1.387(4)
6	S1	C3	1.787(3)	**25**	C15	C25	1.542(4)
7	S1	C31	1.838(3)	**26**	C15	C35	1.528(3)
8	F1	C31	1.326(3)	**27**	C15	C40	1.554(5)
9	F3	C31	1.343(3)	**28**	C15	C41	1.528(5)
10	F5	C31	1.323(4)	**29**	C17	C18	1.509(4)
11	N1	C5	1.457(4)	**30**	C17	C38	1.526(4)
12	N1	C21	1.532(4)	**31**	C18	C27	1.397(5)
13	N1	C25	1.314(3)	**32**	C21	C41	1.539(5)
14	C2	C3	1.395(3)	**33**	C21	C45	1.510(4)
15	C2	C11	1.458(3)	**34**	C21	C47	1.520(4)
16	C2	C14	1.398(4)	**35**	C24	C28	1.383(4)
17	C3	C10	1.389(4)	**36**	C27	C36	1.379(4)
18	C5	C13	1.408(3)	**37**	C34	C36	1.372(4)
19	C5	C18	1.411(4)				

Table S7. Bond angles [°] of ***cis*-13a**

Number	Atom1	Atom2	Atom3	Angle	Number	Atom1	Atom2	Atom3	Angle
1	S1	Ru1	Cl1	176.11(3)	**33**	C25	C15	C35	108.7(2)
2	S1	Ru1	Cl3	94.69(3)	**34**	C25	C15	C40	113.2(2)
3	S1	Ru1	C11	84.17(8)	**35**	C25	C15	C41	102.4(2)
4	S1	Ru1	C25	93.72(7)	**36**	C35	C15	C40	107.5(3)
5	Cl1	Ru1	Cl3	85.63(3)	**37**	C35	C15	C41	114.2(3)
6	Cl1	Ru1	C11	92.28(8)	**38**	C40	C15	C41	110.9(3)
7	Cl1	Ru1	C25	88.32(7)	**39**	C18	C17	C38	115.8(3)
8	Cl3	Ru1	C11	119.30(8)	**40**	C5	C18	C17	124.2(2)
9	Cl3	Ru1	C25	142.92(8)	**41**	C5	C18	C27	117.6(3)
10	C11	Ru1	C25	97.5(1)	**42**	C17	C18	C27	118.0(3)
11	Ru1	S1	C3	100.27(9)	**43**	N1	C21	C41	100.5(2)
12	Ru1	S1	C31	112.2(1)	**44**	N1	C21	C45	111.0(2)
13	C3	S1	C31	96.5(1)	**45**	N1	C21	C47	111.5(2)
14	C5	N1	C21	120.0(2)	**46**	C41	C21	C45	111.0(3)
15	C5	N1	C25	125.3(2)	**47**	C41	C21	C47	114.0(3)
16	C21	N1	C25	114.7(2)	**48**	C45	C21	C47	108.7(3)
17	C3	C2	C11	118.2(2)	**49**	C10	C24	C28	120.3(3)
18	C3	C2	C14	118.0(2)	**50**	Ru1	C25	N1	137.0(2)
19	C11	C2	C14	123.7(2)	**51**	Ru1	C25	C15	113.6(2)
20	S1	C3	C2	113.0(2)	**52**	N1	C25	C15	109.1(2)
21	S1	C3	C10	124.2(2)	**53**	C18	C27	C36	121.2(3)
22	C2	C3	C10	122.7(2)	**54**	C14	C28	C24	121.1(3)
23	N1	C5	C13	118.6(2)	**55**	S1	C31	F1	114.2(2)
24	N1	C5	C18	119.8(2)	**56**	S1	C31	F3	109.6(2)
25	C13	C5	C18	121.6(2)	**57**	S1	C31	F5	109.3(2)
26	C3	C10	C24	118.0(3)	**58**	F1	C31	F3	107.0(2)
27	Ru1	C11	C2	124.3(2)	**59**	F1	C31	F5	108.8(2)
28	C13	C12	C44	115.1(2)	**60**	F3	C31	F5	107.8(2)
29	C5	C13	C12	124.4(2)	**61**	C13	C34	C36	121.6(3)
30	C5	C13	C34	117.7(2)	**62**	C27	C36	C34	120.3(3)
31	C12	C13	C34	117.7(2)	**63**	C15	C41	C21	107.2(3)
32	C2	C14	C28	119.8(2)					

4.5. Bond lengths and angles for *cis*-13b

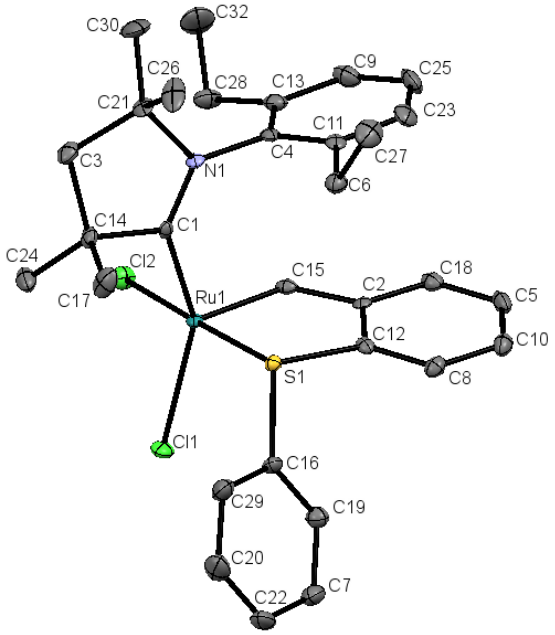


Figure S56. ORTEP representation (50% probability ellipsoids) of complex ***cis*-13b**

Table S8. Bond lengths [Å] of ***cis*-13b.**

Number	Atom1	Atom2	Length	Number	Atom1	Atom2	Length
1	Ru1	S1	2.3306(8)	**21**	C6	C11	1.518(4)
2	Ru1	Cl1	2.3779(9)	**22**	C6	C27	1.537(6)
3	Ru1	Cl2	2.3948(8)	**23**	C7	C19	1.393(5)
4	Ru1	C1	1.965(3)	**24**	C7	C22	1.387(5)
5	Ru1	C15	1.838(3)	**25**	C8	C10	1.387(5)
6	S1	C12	1.775(3)	**26**	C8	C12	1.390(5)
7	S1	C16	1.789(3)	**27**	C9	C13	1.390(5)
8	N1	C1	1.322(4)	**28**	C9	C25	1.379(5)
9	N1	C4	1.446(4)	**29**	C11	C23	1.387(5)
10	N1	C21	1.528(5)	**30**	C13	C28	1.512(5)
11	C1	C14	1.540(5)	**31**	C14	C17	1.549(4)
12	C2	C12	1.401(4)	**32**	C14	C24	1.522(5)
13	C2	C15	1.461(4)	**33**	C16	C19	1.388(5)
14	C2	C18	1.398(5)	**34**	C16	C29	1.388(5)
15	C3	C14	1.537(5)	**35**	C20	C22	1.385(5)
16	C3	C21	1.522(5)	**36**	C20	C29	1.387(5)
17	C4	C11	1.413(5)	**37**	C21	C26	1.530(5)
18	C4	C13	1.408(4)	**38**	C21	C30	1.530(5)
19	C5	C10	1.389(5)	**39**	C23	C25	1.386(5)
20	C5	C18	1.385(5)	**40**	C28	C32	1.528(5)

Table S9. Bond angles [°] of ***cis*-13b.**

Number	Atom1	Atom2	Atom3	Angle	Number	Atom1	Atom2	Atom3	Angle
1	S1	Ru1	Cl1	91.14(3)	**34**	C4	C11	C23	118.1(3)
2	S1	Ru1	Cl2	175.66(3)	**35**	C6	C11	C23	117.5(3)
3	S1	Ru1	C1	90.08(8)	**36**	S1	C12	C2	113.7(2)
4	S1	Ru1	C15	83.8(1)	**37**	S1	C12	C8	124.8(2)
5	Cl1	Ru1	Cl2	88.63(3)	**38**	C2	C12	C8	121.4(3)
6	Cl1	Ru1	C1	145.67(8)	**39**	C4	C13	C9	117.7(3)
7	Cl1	Ru1	C15	114.3(1)	**40**	C4	C13	C28	123.1(3)
8	Cl2	Ru1	C1	92.55(8)	**41**	C9	C13	C28	119.1(3)
9	Cl2	Ru1	C15	92.3(1)	**42**	C1	C14	C3	101.7(3)
10	C1	Ru1	C15	99.9(1)	**43**	C1	C14	C17	108.2(3)
11	Ru1	S1	C12	99.6(1)	**44**	C1	C14	C24	114.2(3)
12	Ru1	S1	C16	115.7(1)	**45**	C3	C14	C17	112.8(3)
13	C12	S1	C16	104.2(1)	**46**	C3	C14	C24	111.6(3)
14	C1	N1	C4	124.6(3)	**47**	C17	C14	C24	108.2(3)
15	C1	N1	C21	114.4(3)	**48**	Ru1	C15	C2	124.5(2)
16	C4	N1	C21	120.9(3)	**49**	S1	C16	C19	123.7(2)
17	Ru1	C1	N1	136.4(2)	**50**	S1	C16	C29	115.4(2)
18	Ru1	C1	C14	114.7(2)	**51**	C19	C16	C29	120.9(3)
19	N1	C1	C14	108.9(2)	**52**	C2	C18	C5	120.6(3)
20	C12	C2	C15	117.3(3)	**53**	C7	C19	C16	118.8(3)
21	C12	C2	C18	118.5(3)	**54**	C22	C20	C29	120.0(3)
22	C15	C2	C18	124.2(3)	**55**	N1	C21	C3	100.6(3)
23	C14	C3	C21	107.0(3)	**56**	N1	C21	C26	111.8(3)
24	N1	C4	C11	120.1(3)	**57**	N1	C21	C30	111.2(3)
25	N1	C4	C13	118.8(3)	**58**	C3	C21	C26	112.8(3)
26	C11	C4	C13	121.2(3)	**59**	C3	C21	C30	112.2(3)
27	C10	C5	C18	119.8(3)	**60**	C26	C21	C30	108.2(3)
28	C11	C6	C27	114.0(3)	**61**	C7	C22	C20	120.0(3)
29	C19	C7	C22	120.6(3)	**62**	C11	C23	C25	121.7(3)
30	C10	C8	C12	118.7(3)	**63**	C9	C25	C23	119.1(3)
31	C13	C9	C25	122.2(3)	**64**	C13	C28	C32	114.0(3)
32	C5	C10	C8	121.1(3)	**65**	C16	C29	C20	119.7(3)
33	C4	C11	C6	124.2(3)					

5. Computational data

5.1. Rotation of DiPP-CAAC around C_{CAAC}-Ru axis

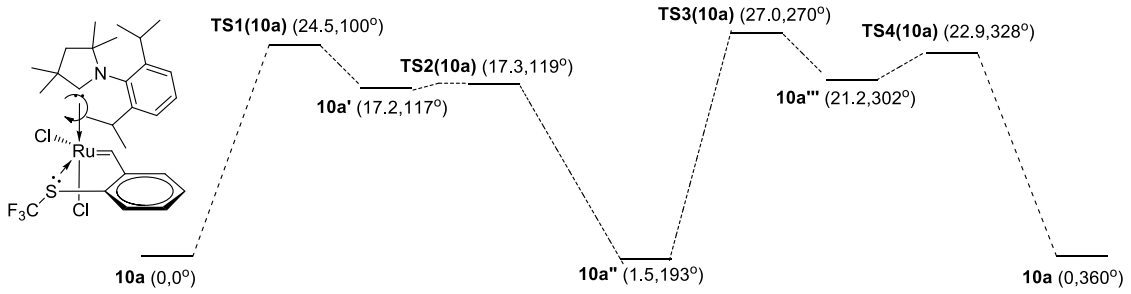


Figure S57. Full rotation diagram of DiPP-CAAC ligand around C_{CAAC}-Ru bond in complex ***cis*-10a**. Values in parentheses are relative Gibbs free energies of transition states and intermediates in kcal/mol and dihedral angles N-C_{CAAC}-Ru-$C_{benzylidene}$ in °.

5.2. Relative energies of *cis*-Cl_2 isomers of the complexes 10 and 13

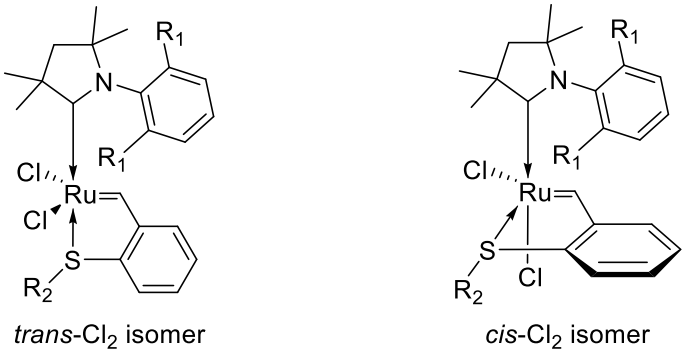


Figure S58. Structures of *trans* and *cis* isomers of S-chelated complexes bearing CAAC ligands.

Table S10. Computed relative energies of *trans*-Cl_2 isomers of of S-chelated complexes bearing CAAC ligands.

Complex	R_1	R_2	Relative energy of *trans*-Cl_2 isomer (kcal/mol)
10a	*i*Pr	CF_3	-0.2
10b	*i*Pr	Ph	1.5
13a	Et	CF_3	3.5
13b	Et	Ph	5.6

5.3. Computational details

DFT optimizations and relaxed PES scan were performed using B97D3/Def2-SVP//MN15/Def2-TZVP under Gaussian 16.[13] Intermediates and rate determining transition state were identified using frequency calculations. Solvent effects have been estimated in single point calculations based on PCM model for DCM.

5.4. XYZ parameters and SP energies

10a (***cis*-Cl$_2$**)

E(RMN15) = -2855.02700977 A.U.

Ru	0.788134	-1.202656	-0.618376
Cl	-0.669574	-2.422783	-2.088265
C	0.533209	0.340665	-1.586690
C	1.154991	1.622022	-1.274765
C	2.003723	1.704494	-0.147284
C	0.938444	2.797306	-2.027698
C	2.585994	2.904299	0.263959
C	1.529091	4.005352	-1.638158
H	0.292855	2.747852	-2.911006
C	2.344650	4.063211	-0.495145
H	3.220879	2.940967	1.153751
H	1.348894	4.913699	-2.224819
H	2.798645	5.013125	-0.190210
S	2.159830	0.140278	0.739166
C	4.020506	-0.124746	0.521723
H	-0.014201	0.275014	-2.539386
C	-0.715562	-1.175509	0.607665
N	-1.854750	-0.476584	0.686063
C	-0.740174	-2.332045	1.644519
C	-0.621233	-3.740407	1.022795
C	-2.097704	-2.101383	2.364016
C	0.428808	-2.139843	2.640739
C	-2.957245	-1.257851	1.408248
H	-1.932714	-1.537790	3.299178
H	-2.591105	-3.049693	2.629951
C	-3.700191	-2.161294	0.403469
C	-3.953314	-0.349837	2.123476
H	-1.410782	-3.940329	0.285347
H	-0.681490	-4.489861	1.832277
H	0.344688	-3.867152	0.505846
H	1.400328	-2.355129	2.165131
H	0.298750	-2.839689	3.486156
H	0.458403	-1.113028	3.043819
H	-2.999469	-2.666651	-0.278554
H	-4.417990	-1.590511	-0.200301
H	-4.268878	-2.923802	0.963575
H	-3.496185	0.190520	2.963669
H	-4.773007	-0.969042	2.526438
H	-4.394115	0.385758	1.429819
C	-2.448751	2.495905	-1.556408
C	-1.960151	3.525312	-0.750226
C	-1.529075	3.239538	0.546035
C	-1.552946	1.927638	1.050599
C	-1.985679	0.878477	0.188876
C	-2.471328	1.158540	-1.117607
C	-3.116171	0.110871	-2.015736
H	-2.816939	2.728240	-2.561023
H	-1.174133	4.052733	1.188065
C	-1.225070	1.728223	2.530830
H	-2.825966	-0.878470	-1.636399
H	-1.325304	0.655135	2.756087
Cl	2.535037	-2.684700	-1.201140
C	-2.663727	0.154225	-3.484198
H	-3.180432	-0.641797	-4.048412
H	-2.905257	1.115610	-3.973087
H	-1.585430	-0.041269	-3.581795
C	-4.651338	0.269299	-1.944491
H	-4.968869	1.210072	-2.430909
H	-5.154052	-0.567014	-2.463279
H	-5.019835	0.303058	-0.904726
C	-2.240253	2.499250	3.404789
H	-2.136217	2.207174	4.465723
H	-2.065663	3.588183	3.341225
H	-3.281471	2.315322	3.093143
C	0.202818	2.141974	2.920221
H	0.343560	2.036721	4.011344
H	0.956192	1.515349	2.423556
H	0.408111	3.193947	2.654562
F	4.418721	-0.071646	-0.743518
F	4.672848	0.844495	1.204478
F	4.334565	-1.299228	1.064724
H	-1.925732	4.553758	-1.127927

TS1(10a)

E(RMN15) = -2854.98789415 A.U.

Ru	-0.376413	-1.741243	0.144456
Cl	0.386712	-3.612530	1.474686
C	-0.951645	-1.108661	1.797223
C	-1.657310	0.151786	1.958343
C	-2.037332	0.865292	0.794501
C	-1.995119	0.702381	3.216823
C	-2.713520	2.082951	0.859843
C	-2.672909	1.924122	3.294441
H	-1.713420	0.158745	4.125987
C	-3.035464	2.610145	2.122534
H	-2.987194	2.617990	-0.052358
H	-2.926250	2.346664	4.273714
H	-3.567993	3.565890	2.187897
S	-1.501003	0.080316	-0.738748
C	-3.227523	-0.337644	-1.414917
H	-0.886374	-1.770876	2.674734
C	1.396283	-0.848780	-0.191995
N	1.734952	0.347410	-0.747798
C	2.484437	-1.888283	-0.633579
C	3.321030	-2.296651	0.604135
C	3.344901	-1.125351	-1.659072
C	1.951251	-3.160950	-1.339637
C	3.071238	0.372255	-1.498234
H	3.052337	-1.433808	-2.676061
H	4.418015	-1.353742	-1.548167
C	4.141217	1.110614	-0.683175
C	2.992267	1.001093	-2.893384
H	3.919065	-1.455139	0.991823
H	4.023463	-3.095342	0.305504
H	2.671658	-2.689408	1.401519
H	1.477283	-3.864352	-0.644020
H	2.812133	-3.664631	-1.816902
H	1.225052	-2.905613	-2.131154
H	4.371184	0.600192	0.262019
H	3.825084	2.143000	-0.458799
H	5.071338	1.159017	-1.274654
H	2.165431	0.576128	-3.484533
H	3.934381	0.756941	-3.415222
H	2.907093	2.092782	-2.868750
C	0.768651	2.763530	1.970963
C	0.052150	3.738642	1.281511
C	-0.054969	3.645924	-0.105182
C	0.487929	2.568831	-0.829925
C	1.197136	1.557057	-0.110986
C	1.380692	1.687561	1.304428
C	2.326479	0.826734	2.145280
H	0.882808	2.845165	3.056731
H	-0.601870	4.421997	-0.649831
C	0.305455	2.627852	-2.346746
H	2.769818	0.065984	1.492629
H	0.642861	1.669430	-2.763542
Cl	-1.663265	-3.271456	-1.091775
C	1.659012	0.061792	3.297778
H	2.432609	-0.418468	3.922822
H	1.066716	0.729617	3.948041
H	1.005670	-0.733191	2.914106
C	3.479716	1.697952	2.693718
H	3.125724	2.361864	3.502563
H	4.273345	1.055158	3.116289
H	3.928698	2.335011	1.914193
C	1.158807	3.780977	-2.927590
H	1.241868	3.695046	-4.026110
H	0.687441	4.754606	-2.703091
H	2.175063	3.815795	-2.500856
C	-1.150062	2.828395	-2.811821
H	-1.187986	2.831491	-3.916005
H	-1.811221	2.029623	-2.452691
H	-1.561838	3.794956	-2.471211
F	-3.951749	-1.093071	-0.598349
F	-3.901836	0.824872	-1.605355
F	-3.085176	-0.922999	-2.600698
H	-0.414982	4.570396	1.820315

10a'

E(RMN15) = -2854.99955554 A.U.

Ru	0.434700	-1.502880	-0.311820
Cl	0.464988	-3.585037	-1.497694
C	1.461855	-0.801401	-1.738956
C	2.463122	0.243531	-1.547103
C	2.525560	0.880100	-0.283686
C	3.312582	0.728772	-2.570087
C	3.347309	1.977330	-0.036997
C	4.156962	1.820415	-2.333828
H	3.282267	0.248089	-3.555252
C	4.168244	2.451713	-1.077159
H	3.349483	2.456406	0.947076
H	4.804944	2.193520	-3.135456
H	4.818009	3.317370	-0.903584
S	1.440704	0.163323	0.976838
C	2.810421	-0.852260	1.827839
H	1.398680	-1.188212	-2.774122
C	-1.321526	-0.707767	-0.752477
N	-1.937575	0.329864	-0.167221
C	-2.309426	-1.379133	-1.744182
C	-1.678660	-1.436958	-3.151937
C	-3.511180	-0.397318	-1.734242
C	-2.756823	-2.799122	-1.328079
C	-3.456811	0.324188	-0.382234
H	-4.471830	-0.913328	-1.889807
H	-3.397937	0.344330	-2.545240
C	-4.055362	1.729206	-0.420695
C	-4.140215	-0.491202	0.734965
H	-1.271223	-0.455602	-3.452333
H	-2.461437	-1.721430	-3.878754
H	-0.873777	-2.186742	-3.184450
H	-1.901154	-3.487455	-1.311144
H	-3.493191	-3.157806	-2.069748
H	-3.226320	-2.815850	-0.335227
H	-3.687756	2.320355	-1.270524
H	-3.849160	2.284565	0.509040
H	-5.150280	1.635354	-0.524079
H	-3.570082	-1.395770	0.989943
H	-5.144743	-0.792698	0.391459
H	-4.266127	0.105383	1.648059
C	-0.001343	3.500739	0.141014
C	0.144051	3.627416	1.524996
C	-0.464586	2.698023	2.370312
C	-1.167177	1.588457	1.863490
C	-1.270882	1.455715	0.454517
C	-0.745997	2.449259	-0.422275
C	-1.049655	2.500676	-1.920606
H	0.447705	4.248917	-0.521074
H	-0.366439	2.810223	3.454855
C	-1.774018	0.601551	2.851491
H	-1.783759	1.711865	-2.138841
H	-2.107571	-0.277915	2.282588
Cl	-0.594525	-2.580969	1.615305
C	0.165910	2.226260	-2.816255
H	-0.091691	2.403185	-3.876096
H	1.021923	2.874382	-2.558443
H	0.490922	1.183629	-2.716911
C	-1.695663	3.852070	-2.295840
H	-0.955857	4.671868	-2.272039
H	-2.104315	3.806470	-3.321559
H	-2.513832	4.125002	-1.607537
C	-2.979272	1.244184	3.569495
H	-3.510664	0.492927	4.181130
H	-2.646326	2.053345	4.245074
H	-3.701956	1.688766	2.863561
C	-0.762689	0.083497	3.888206
H	-1.245165	-0.678082	4.525253
H	0.092858	-0.402090	3.401456
H	-0.394667	0.890896	4.547305
F	3.276143	-1.820456	1.025199
F	3.838673	-0.057075	2.169596
F	2.314100	-1.404314	2.933508
H	0.718941	4.461676	1.944403

TS2(10a)

E(RMN15) = -2854.99936882 A.U.

Ru	0.434475	-1.499887	-0.294672
Cl	0.470565	-3.593872	-1.462537
C	1.479113	-0.825461	-1.722674
C	2.483715	0.217100	-1.536912
C	2.534604	0.875789	-0.284261
C	3.344605	0.682292	-2.559640
C	3.355899	1.975889	-0.049087
C	4.188341	1.776794	-2.334526
H	3.323509	0.183853	-3.536177
C	4.188006	2.430411	-1.089307
H	3.349325	2.472438	0.926282
H	4.844973	2.134539	-3.136113
H	4.837432	3.298061	-0.924656
S	1.435125	0.184987	0.978178
C	2.793183	-0.819539	1.859823
H	1.427749	-1.231763	-2.750821
C	-1.313275	-0.707585	-0.768342
N	-1.939975	0.327352	-0.188097
C	-2.288171	-1.382939	-1.769083
C	-1.645862	-1.456235	-3.170078
C	-3.487462	-0.397852	-1.780636
C	-2.738713	-2.799314	-1.338808
C	-3.455100	0.325554	-0.429337
H	-4.447176	-0.909857	-1.953473
H	-3.356206	0.342438	-2.590178
C	-4.048983	1.732427	-0.480068
C	-4.163109	-0.485234	0.675294
H	-1.252957	-0.473544	-3.485581
H	-2.417620	-1.767772	-3.897670
H	-0.828929	-2.193341	-3.182596
H	-1.906632	-3.511090	-1.423969
H	-3.561232	-3.118999	-2.003414
H	-3.091736	-2.830180	-0.299140
H	-3.663020	2.322654	-1.322292
H	-3.860080	2.287349	0.453606
H	-5.141821	1.641360	-0.605430
H	-3.610495	-1.399557	0.932447
H	-5.167218	-0.770858	0.317252
H	-4.292102	0.108548	1.589646
C	-0.004028	3.495295	0.148346
C	0.118702	3.623511	1.534380
C	-0.505259	2.696101	2.370626
C	-1.200916	1.586877	1.853582
C	-1.282412	1.453067	0.443402
C	-0.741722	2.444740	-0.425935
C	-1.021102	2.495526	-1.929115
H	0.457120	4.241851	-0.507223
H	-0.424463	2.809338	3.456478
C	-1.822009	0.600432	2.832958
H	-1.756895	1.711288	-2.157669
H	-2.145477	-0.280428	2.259977
Cl	-0.583087	-2.572686	1.636520
C	0.206162	2.210399	-2.805179
H	-0.032722	2.389792	-3.868979
H	1.063988	2.850413	-2.533516
H	0.519243	1.164653	-2.700776
C	-1.652305	3.850289	-2.317024
H	-0.907736	4.665409	-2.283339
H	-2.045079	3.805146	-3.348943
H	-2.479450	4.129821	-1.642172
C	-3.038964	1.241677	3.532194
H	-3.576744	0.490754	4.138650
H	-2.717453	2.053610	4.209957
H	-3.753058	1.682529	2.815252
C	-0.824399	0.087141	3.885416
H	-1.308955	-0.685189	4.507703
H	0.046671	-0.383514	3.411649
H	-0.480001	0.894678	4.557042
F	3.260877	-1.805089	1.079878
F	3.822394	-0.021988	2.193500
F	2.286696	-1.347291	2.972575
H	0.688100	4.457245	1.962231

10a''

E(RMN15) = -2855.02459080 A.U.

Ru	-0.409108	-0.511039	-1.014626
Cl	0.821421	-2.043722	-2.402984
C	-1.859694	-1.638161	-1.018441
C	-3.098957	-1.376529	-0.296226
C	-3.200378	-0.180790	0.455784
C	-4.197480	-2.266460	-0.279510
C	-4.330731	0.128854	1.214028
C	-5.341697	-1.963232	0.469132
H	-4.137784	-3.194734	-0.860229
C	-5.411652	-0.771001	1.210994
H	-4.377465	1.055460	1.793831
H	-6.188127	-2.659720	0.476933
H	-6.308907	-0.539582	1.796380
S	-1.690653	0.803851	0.416555
C	-2.421721	2.407880	-0.277821
H	-1.840081	-2.511219	-1.695096
C	0.678020	-1.258887	0.454709
N	1.842245	-0.672330	0.760503
C	0.514937	-2.533126	1.295363
C	-0.709248	-2.331953	2.218835
C	1.826914	-2.558147	2.139437
C	0.317711	-3.817653	0.474084
C	2.825349	-1.634509	1.416110
H	2.225596	-3.578192	2.256646
H	1.629494	-2.161265	3.150514
C	3.807320	-0.932254	2.348747
C	3.596948	-2.409123	0.328723
H	-0.659297	-1.368905	2.755750
H	-0.735913	-3.143046	2.969031
H	-1.648576	-2.359840	1.646716
H	-0.584645	-3.743354	-0.151360
H	0.195707	-4.671282	1.164983
H	1.165381	-4.015288	-0.197112
H	3.317116	-0.527924	3.245016
H	4.327037	-0.109281	1.829400
H	4.570352	-1.657650	2.678744
H	2.922873	-2.763134	-0.466806
H	4.093822	-3.278208	0.794344
H	4.375858	-1.787435	-0.133864
C	1.447043	3.023275	1.084731
C	1.853168	3.465379	-0.178170
C	2.413255	2.562789	-1.081189
C	2.529379	1.191760	-0.779757
C	2.019764	0.744857	0.469887
C	1.530612	1.669044	1.444104
C	1.230342	1.282859	2.893763
H	1.055335	3.745567	1.809267
H	2.761022	2.918280	-2.055106
C	3.287564	0.286146	-1.739797
H	1.280460	0.184780	2.964819
H	2.966042	-0.746792	-1.545865
Cl	-0.602910	0.987382	-2.831284
C	-0.152754	1.708505	3.415587
H	-0.255812	1.423561	4.478370
H	-0.292164	2.802820	3.353303
H	-0.968212	1.238411	2.847413
C	2.323516	1.879212	3.810958
H	2.214746	2.976620	3.876961
H	2.238547	1.471111	4.834983
H	3.338890	1.672662	3.436084
C	4.798764	0.415178	-1.446999
H	5.374029	-0.309509	-2.051803
H	5.156024	1.430034	-1.701629
H	5.037077	0.244267	-0.382548
C	3.012740	0.558002	-3.226808
H	3.485057	-0.233782	-3.834185
H	1.933568	0.553708	-3.439397
H	3.440718	1.523454	-3.555057
F	-3.220435	2.221726	-1.322561
F	-3.150504	2.992449	0.704560
F	-1.423310	3.227425	-0.595604
H	1.747071	4.521711	-0.450832

TS3

E(RMN15) = -2854.98402040 A.U.

Ru	-0.670576	0.524551	-0.533122
Cl	0.950745	0.654633	-2.238170
C	-1.297270	-1.036105	-1.325592
C	-2.531908	-1.714244	-0.963940
C	-3.368859	-1.122360	0.013749
C	-2.925337	-2.958072	-1.510789
C	-4.534120	-1.743982	0.467896
C	-4.094950	-3.587717	-1.068445
H	-2.293948	-3.424103	-2.276791
C	-4.897913	-2.985149	-0.083615
H	-5.151026	-1.272408	1.238131
H	-4.386153	-4.556688	-1.490393
H	-5.811155	-3.483374	0.261527
S	-2.716860	0.417662	0.688030
C	-4.072916	1.562487	0.009240
H	-0.765443	-1.425202	-2.213278
C	0.517909	-0.511279	0.814569
N	1.850564	-0.647594	0.738036
C	0.047713	-1.196055	2.136698
C	-0.735276	-0.240390	3.067056
C	1.375963	-1.510714	2.866959
C	-0.795900	-2.460936	1.878170
C	2.446389	-1.613173	1.790177
H	1.310011	-2.421841	3.482989
H	1.625047	-0.674767	3.541822
C	3.823471	-1.167155	2.283527
C	2.523579	-3.055941	1.249984
H	-0.273368	0.760000	3.103551
H	-0.709999	-0.663634	4.087864
H	-1.789728	-0.123200	2.789947
H	-1.784155	-2.208666	1.473348
H	-0.952037	-2.997322	2.830831
H	-0.317311	-3.151989	1.167545
H	3.808371	-0.136176	2.666451
H	4.584389	-1.221220	1.490813
H	4.129033	-1.839684	3.104557
H	1.622584	-3.331422	0.682495
H	2.608209	-3.742653	2.109813
H	3.399142	-3.219023	0.613726
C	3.949336	2.318188	-0.081670
C	4.886633	1.780044	-0.964642
C	4.738659	0.462006	-1.401997
C	3.696879	-0.357019	-0.936326
C	2.793431	0.190159	0.012044
C	2.879392	1.552694	0.414250
C	1.852792	2.246205	1.308850
H	4.037108	3.365688	0.222495
H	5.438887	0.059790	-2.142023
C	3.563383	-1.748211	-1.551264
H	0.915444	1.657013	1.269975
H	2.681868	-2.227969	-1.100069
Cl	-1.244616	2.717988	-1.200786
C	1.484599	3.647444	0.792194
H	0.595347	4.021110	1.329102
H	2.303248	4.370549	0.959338
H	1.238956	3.619764	-0.280574
C	2.294614	2.309772	2.781561
H	3.251941	2.854586	2.875785
H	1.540265	2.839749	3.391084
H	2.436399	1.307732	3.217879
C	4.813327	-2.614145	-1.285648
H	4.634261	-3.661902	-1.588906
H	5.673800	-2.246101	-1.872423
H	5.122857	-2.609566	-0.226425
C	3.299040	-1.694586	-3.070704
H	3.196479	-2.722326	-3.466686
H	2.378478	-1.132752	-3.286940
H	4.136717	-1.213556	-3.606948
F	-4.177141	1.539012	-1.314787
F	-5.255847	1.150040	0.522085
F	-3.847661	2.797525	0.444767
H	5.712331	2.397523	-1.337076

10a'''

E(RMN15) = -2854.99323673 A.U.

Ru	0.645519	-0.825180	-0.530098
Cl	-0.844557	-1.168082	-2.316132
C	1.075169	0.877747	-1.213712
C	2.053544	1.756630	-0.593577
C	2.963300	1.182492	0.332186
C	2.166958	3.145993	-0.847682
C	3.934483	1.934823	0.995312
C	3.117458	3.915132	-0.166225
H	1.488304	3.611026	-1.571846
C	4.003855	3.316154	0.749056
H	4.627848	1.450548	1.691140
H	3.180250	4.993322	-0.355139
H	4.756090	3.923961	1.264500
S	2.729842	-0.582207	0.618566
C	4.007846	-1.220909	-0.637001
H	0.741271	1.165549	-2.224581
C	-0.390013	-0.091802	0.977473
N	-1.587516	0.506004	0.858359
C	-0.046883	-0.195551	2.501946
C	0.255310	-1.657219	2.893779
C	-1.369611	0.274578	3.164931
C	1.136917	0.692407	2.961975
C	-2.038199	1.198936	2.144083
H	-1.206313	0.769043	4.136055
H	-2.024735	-0.595622	3.336513
C	-3.557290	1.268682	2.292725
C	-1.462569	2.628530	2.180162
H	-0.582271	-2.326008	2.639187
H	0.420113	-1.706371	3.985870
H	1.147151	-2.045143	2.379612
H	2.102128	0.184672	2.822613
H	1.039567	0.888183	4.043667
H	1.188155	1.660213	2.444007
H	-4.027058	0.277213	2.243739
H	-4.012343	1.896678	1.510555
H	-3.788435	1.716510	3.275342
H	-0.403883	2.656201	1.885781
H	-1.550207	3.032470	3.203857
H	-2.016763	3.296008	1.506581
C	-4.401811	-1.033802	-1.021039
C	-4.791824	0.013780	-1.859849
C	-4.028645	1.182143	-1.905849
C	-2.901228	1.348093	-1.081425
C	-2.569560	0.307191	-0.186225
C	-3.281987	-0.926254	-0.179861
C	-2.866748	-2.150583	0.633929
H	-4.968546	-1.971031	-1.029209
H	-4.300122	1.977885	-2.608159
C	-2.031717	2.584065	-1.269455
H	-1.879267	-1.942305	1.071403
H	-1.168350	2.485369	-0.588533
Cl	1.019987	-3.189681	-0.359232
C	-2.680525	-3.391746	-0.260660
H	-2.220978	-4.206045	0.326509
H	-3.649340	-3.758517	-0.646601
H	-2.019528	-3.166089	-1.110366
C	-3.839973	-2.472034	1.783741
H	-4.854916	-2.677110	1.396953
H	-3.501286	-3.372129	2.328209
H	-3.923604	-1.651348	2.515967
C	-2.776797	3.893009	-0.947563
H	-2.087882	4.756661	-0.989459
H	-3.583799	4.076091	-1.679591
H	-3.245169	3.875031	0.051446
C	-1.486738	2.625822	-2.713349
H	-0.693719	3.390055	-2.811356
H	-1.086304	1.642556	-3.008323
H	-2.286280	2.888626	-3.429143
F	3.618990	-1.029339	-1.901824
F	5.165715	-0.563235	-0.449451
F	4.210414	-2.515794	-0.423174
H	-5.672184	-0.095539	-2.504153

TS4

E(RMN15) = -2854.99044971 A.U.

Ru	0.706255	-0.893358	-0.585215
Cl	-0.768334	-1.184173	-2.390208
C	0.954758	0.870371	-1.146886
C	1.947445	1.774633	-0.576332
C	2.771358	1.304962	0.478842
C	2.150977	3.112903	-0.994698
C	3.660493	2.127665	1.172636
C	3.041128	3.950747	-0.311938
H	1.603169	3.487423	-1.862252
C	3.778160	3.473619	0.786162
H	4.273999	1.717788	1.981671
H	3.168597	4.988249	-0.642932
H	4.467753	4.136982	1.320359
S	2.663492	-0.461620	0.769392
C	4.193246	-0.941898	-0.251913
H	0.451186	1.200401	-2.072392
C	-0.557512	-0.558717	0.885774
N	-1.653434	0.227516	0.932889
C	-0.471402	-1.370415	2.227032
C	-0.533234	-2.883126	1.910254
C	-1.744598	-0.902864	2.985610
C	0.781909	-1.128917	3.097744
C	-2.137878	0.442821	2.362029
H	-1.573606	-0.814034	4.069919
H	-2.563599	-1.627054	2.842283
C	-3.634841	0.724805	2.456437
C	-1.334910	1.600595	2.988302
H	-1.422213	-3.143107	1.317262
H	-0.571564	-3.445785	2.861135
H	0.354155	-3.207105	1.342138
H	1.647390	-1.694906	2.729088
H	0.573398	-1.485885	4.121288
H	1.067767	-0.066596	3.164503
H	-4.234436	-0.120182	2.093906
H	-3.922979	1.618650	1.882110
H	-3.893189	0.898035	3.515580
H	-0.255152	1.480900	2.810303
H	-1.508026	1.623295	4.078418
H	-1.637889	2.572835	2.577861
C	-4.151140	-0.163000	-1.821337
C	-4.112135	1.084066	-2.442517
C	-3.293805	2.085643	-1.918676
C	-2.472452	1.857313	-0.798672
C	-2.486486	0.568127	-0.209299
C	-3.363399	-0.447743	-0.693438
C	-3.574102	-1.803016	-0.018421
H	-4.804931	-0.945267	-2.220857
H	-3.289005	3.071765	-2.392673
C	-1.661195	3.028581	-0.256887
H	-2.995929	-1.801478	0.914119
H	-0.845684	2.614195	0.362140
Cl	1.643472	-3.019799	-1.114687
C	-3.090737	-3.008858	-0.844935
H	-3.332247	-3.945774	-0.309366
H	-3.593423	-3.043113	-1.827774
H	-2.009308	-2.967493	-1.035321
C	-5.057486	-2.003141	0.365803
H	-5.679247	-2.195296	-0.526488
H	-5.163026	-2.877793	1.033345
H	-5.484806	-1.123434	0.877723
C	-2.543470	3.950792	0.613173
H	-1.938704	4.755325	1.070776
H	-3.324477	4.424156	-0.008934
H	-3.059341	3.408744	1.420479
C	-1.033125	3.881953	-1.373017
H	-0.300833	4.588359	-0.946557
H	-0.529373	3.258097	-2.127153
H	-1.796723	4.484447	-1.895625
F	4.042156	-0.705993	-1.554515
F	5.240616	-0.213440	0.183194
F	4.461883	-2.225610	-0.042305
H	-4.727373	1.281236	-3.328252

10a (***trans*-Cl$_2$**)

E(RMN15) = -2855.02779846 A.U

Ru	-0.596610	-0.925105	-0.477075
Cl	-0.784304	-1.980304	1.625700
C	-0.736963	0.880233	-0.186000
C	-1.950650	1.659414	-0.391319
C	-3.193509	1.040252	-0.681156
C	-1.908451	3.074941	-0.356865
C	-4.342845	1.789315	-0.950312
C	-3.057929	3.830602	-0.611339
H	-0.953088	3.564981	-0.133078
C	-4.274290	3.192041	-0.908325
H	-5.284474	1.282336	-1.183032
H	-3.008269	4.925436	-0.584295
H	-5.172725	3.785118	-1.114175
S	-3.207807	-0.753318	-0.706805
C	-4.110279	-1.019532	0.903567
H	0.141238	1.483039	0.078669
Cl	-0.825400	-0.939032	-2.821827
C	1.316884	-1.159558	-0.368488
N	2.302620	-0.460876	0.218573
C	1.912501	-2.499110	-0.868873
C	0.951777	-3.695063	-0.750542
C	3.151898	-2.661191	0.035808
C	2.308975	-2.346207	-2.358873
C	3.599755	-1.238438	0.429603
H	3.962121	-3.225017	-0.456183
H	2.860097	-3.211932	0.946289
C	4.037357	-1.183777	1.895880
C	4.741022	-0.681310	-0.434012
H	0.611795	-3.842293	0.285273
H	1.462745	-4.610772	-1.098788
H	0.062175	-3.554555	-1.391853
H	1.425344	-2.119849	-2.974870
H	2.758295	-3.293851	-2.706539
H	3.045934	-1.545393	-2.519652
H	3.253715	-1.568495	2.564951
H	4.299179	-0.157579	2.200462
H	4.935170	-1.814284	2.019637
H	4.532284	-0.745276	-1.510342
H	5.658771	-1.259604	-0.232013
H	4.941974	0.371951	-0.178188
C	2.048322	2.783041	2.104393
C	2.388109	3.698182	1.105651
C	2.612626	3.244163	-0.196851
C	2.551875	1.875550	-0.515684
C	2.271006	0.950599	0.531233
C	1.960119	1.401639	1.844263
C	1.399788	0.506413	2.945442
H	1.818653	3.147260	3.111412
H	2.827852	3.966503	-0.991578
C	2.677137	1.474764	-1.982613
H	1.386271	-0.528931	2.572069
H	2.686251	0.378339	-2.034378
C	1.442622	1.942116	-2.780398
H	1.524898	1.614847	-3.832027
H	0.515373	1.508526	-2.377517
H	1.355304	3.044065	-2.769800
C	3.969995	1.994626	-2.637926
H	4.073741	1.576213	-3.655324
H	3.958893	3.095037	-2.738064
H	4.868832	1.720669	-2.060673
C	-0.066886	0.886146	3.243656
H	-0.487994	0.196546	3.995083
H	-0.140455	1.915493	3.639911
H	-0.694953	0.808888	2.343677
C	2.220736	0.566087	4.247930
H	3.290935	0.359635	4.085415
H	2.142714	1.559569	4.726079
H	1.834975	-0.175063	4.970723
H	2.451751	4.768443	1.336138
F	-5.403425	-0.645815	0.778440
F	-4.077113	-2.324411	1.184121
F	-3.591368	-0.323452	1.917863

10b (***trans*-Cl$_2$**)

E(RMN15) = -2788.23669904 A.U.

Ru	-0.636623	-0.199966	-0.021426
Cl	-1.334595	-0.373280	2.235556
C	0.172054	1.444035	0.089107
C	-0.545818	2.708087	0.157711
C	-1.953221	2.753725	-0.038615
C	0.133465	3.915590	0.454912
C	-2.656911	3.958454	0.079661
C	-0.571850	5.115154	0.590919
H	1.221010	3.884578	0.594854
C	-1.966746	5.135997	0.410502
H	-3.738141	3.985848	-0.096181
H	-0.038116	6.040458	0.837095
H	-2.519601	6.077388	0.511508
S	-2.709150	1.218770	-0.551485
C	-4.065419	0.980042	0.702889
H	1.262942	1.534367	0.181591
Cl	-0.749027	-0.710124	-2.334289
C	0.905800	-1.370638	0.097844
N	2.215518	-1.214681	-0.159555
C	0.645375	-2.879309	0.336883
C	0.678726	-3.163722	1.859383
C	1.835948	-3.537275	-0.391463
C	-0.707190	-3.371226	-0.207972
C	2.990111	-2.514480	-0.360805
H	1.551856	-3.728747	-1.440322
H	2.128824	-4.499680	0.060944
C	4.000524	-2.750619	0.771302
C	3.751555	-2.501968	-1.689068
H	1.633750	-2.875704	2.323702
H	0.536416	-4.247325	2.022889
H	-0.123538	-2.612633	2.373124
H	-1.549027	-2.869558	0.303491
H	-0.809326	-4.454681	-0.015417
H	-0.803802	-3.184786	-1.287788
H	3.522789	-2.835716	1.756556
H	4.738140	-1.932257	0.809170
H	4.546459	-3.689662	0.576783
H	3.075132	-2.331677	-2.539528
H	4.237207	-3.483903	-1.827109
H	4.538857	-1.730879	-1.695100
C	4.154087	1.691951	1.182985
C	4.518205	2.359437	0.010631
C	4.042220	1.898373	-1.218565
C	3.233147	0.749643	-1.315775
C	2.941404	0.035751	-0.120189
C	3.357489	0.533017	1.149063
C	2.893350	-0.054066	2.478784
H	4.482083	2.083747	2.151884
H	4.281430	2.455623	-2.130622
C	2.610645	0.433797	-2.672279
H	2.332810	-0.973718	2.265177
H	2.008162	-0.481482	-2.568871
C	1.635360	1.559111	-3.079262
H	1.136247	1.299765	-4.028548
H	0.848928	1.699128	-2.322471
H	2.167286	2.518200	-3.218228
C	3.655283	0.230777	-3.786453
H	3.155966	-0.099007	-4.715223
H	4.184705	1.173126	-4.017732
H	4.416731	-0.520952	-3.522910
C	1.912873	0.907528	3.180992
H	1.533545	0.449504	4.111480
H	2.409841	1.859223	3.444587
H	1.040597	1.127283	2.547750
C	4.059874	-0.407546	3.420054
H	4.808783	-1.053856	2.933288
H	4.581396	0.500031	3.774381
H	3.679490	-0.934598	4.313744
H	5.149612	3.254864	0.057839
H	-4.704559	1.876729	0.664519
H	-3.574162	0.891533	1.684184
C	-4.818241	-0.263740	0.314168
C	-5.893266	-0.195441	-0.593952
C	-4.411716	-1.523300	0.798517
C	-6.558886	-1.359593	-1.000465
H	-6.205199	0.779944	-0.988322
C	-5.076584	-2.687705	0.389552
H	-3.566288	-1.575089	1.492972
C	-6.150483	-2.610041	-0.510218
H	-7.396229	-1.291841	-1.705289
H	-4.751112	-3.661638	0.774669
H	-6.668103	-3.521935	-0.831364

10b (***cis*-Cl$_2$**)

E(RMN15) = -2788.23903903 A.U.

Ru	-0.366719	-1.458197	0.059701
Cl	0.477259	-2.367757	2.111267
C	-0.847189	0.105135	0.921410
C	-1.503326	1.237253	0.274871
C	-1.803003	1.136191	-1.101639
C	-1.854954	2.429945	0.943211
C	-2.362786	2.191185	-1.820574
C	-2.426271	3.494771	0.235539
H	-1.663762	2.510856	2.018321
C	-2.662952	3.387354	-1.144995
H	-2.581023	2.079091	-2.888634
H	-2.685691	4.420928	0.761620
H	-3.103033	4.227445	-1.694964
S	-1.530824	-0.502391	-1.790317
C	-3.338965	-1.121998	-1.680801
H	-0.780954	0.153456	2.019859
C	1.432658	-1.034902	-0.438004
N	2.313005	-0.078835	-0.098169
C	2.160791	-2.133931	-1.275042
C	2.187996	-3.533755	-0.622954
C	3.586614	-1.533265	-1.418365
C	1.482250	-2.251423	-2.659635
C	3.759209	-0.546217	-0.253945
H	3.666560	-0.985476	-2.374107
H	4.364154	-2.313682	-1.416119
C	4.214817	-1.274081	1.028032
C	4.724326	0.597014	-0.560790
H	2.639402	-3.520735	0.378442
H	2.777185	-4.206967	-1.271501
H	1.172424	-3.946408	-0.522802
H	0.496043	-2.735939	-2.572757
H	2.116974	-2.869676	-3.320682
H	1.347872	-1.263705	-3.132999
H	3.433497	-1.947300	1.410744
H	4.475506	-0.562904	1.823096
H	5.118026	-1.867247	0.802070
H	4.540200	1.049809	-1.544505
H	5.753974	0.199948	-0.559529
H	4.665420	1.387913	0.205596
C	1.311624	2.943043	1.911315
C	1.011570	3.840407	0.884692
C	1.209952	3.463173	-0.445059
C	1.692492	2.185263	-0.773836
C	1.928708	1.260029	0.282749
C	1.766427	1.638299	1.642694
C	2.169782	0.747407	2.811354
H	1.181108	3.254545	2.953025
H	0.994345	4.177308	-1.246978
C	2.039706	1.895150	-2.234768
H	2.278924	-0.277390	2.428593
H	2.513912	0.903585	-2.272197
Cl	-1.490993	-3.565873	-0.394156
C	1.140866	0.672146	3.951223
H	1.534953	0.027696	4.756549
H	0.928178	1.662469	4.393698
H	0.198025	0.215341	3.616034
C	3.521555	1.241906	3.373370
H	3.399370	2.218194	3.877827
H	3.921903	0.525787	4.113749
H	4.277669	1.380189	2.581592
C	3.060425	2.926786	-2.762400
H	3.460814	2.604891	-3.741022
H	2.589202	3.915367	-2.907181
H	3.906665	3.063549	-2.068227
C	0.824732	1.837819	-3.171737
H	1.158077	1.697015	-4.216184
H	0.158407	1.001629	-2.917159
H	0.231799	2.767849	-3.124816
H	0.629125	4.840175	1.120943
H	-3.800016	-0.765042	-2.615665
H	-3.201965	-2.214769	-1.699279
C	-4.049331	-0.623194	-0.462265
C	-4.829604	0.548994	-0.530633
C	-3.878370	-1.250732	0.789881
C	-5.397992	1.102387	0.623362
H	-4.978924	1.040516	-1.498563
C	-4.448353	-0.697842	1.944131
H	-3.286552	-2.168932	0.852965
C	-5.198806	0.485499	1.868002
H	-5.991408	2.021525	0.551178
H	-4.297881	-1.195357	2.909427
H	-5.634838	0.922036	2.774696

13a (***trans*-Cl$_2$**)

E(RMN15) = -2776.47821128 A.U.

Ru	-0.408597	-0.914187	-0.263370
Cl	-0.844370	-2.284758	1.583317
C	-0.628518	0.782659	0.398758
C	-1.809976	1.606259	0.177501
C	-2.972882	1.081226	-0.442375
C	-1.801745	2.982724	0.512521
C	-4.074676	1.887903	-0.741481
C	-2.905011	3.793361	0.225651
H	-0.904036	3.401691	0.982630
C	-4.040519	3.250619	-0.400505
H	-4.954140	1.454797	-1.228234
H	-2.881070	4.858413	0.484414
H	-4.901733	3.888622	-0.629788
S	-2.944339	-0.667835	-0.837950
C	-4.090643	-1.254002	0.512472
H	0.158938	1.273891	0.985147
Cl	-0.347916	-0.499934	-2.601512
C	1.521045	-1.070136	-0.236452
N	2.509145	-0.164219	-0.172900
C	2.158942	-2.446424	-0.547588
C	2.357330	-3.228852	0.774259
C	3.513633	-2.046527	-1.176429
C	1.314303	-3.312361	-1.498446
C	3.884958	-0.668269	-0.589769
H	3.387829	-1.949933	-2.268460
H	4.299921	-2.797542	-0.992201
C	4.842788	-0.734023	0.612174
C	4.509876	0.242643	-1.654607
H	2.980456	-2.682476	1.498136
H	2.861000	-4.186039	0.548215
H	1.388724	-3.434319	1.253927
H	0.344578	-3.575009	-1.036579
H	1.845326	-4.259208	-1.704262
H	1.114891	-2.795995	-2.449834
H	4.499576	-1.428187	1.391199
H	4.968279	0.263673	1.065510
H	5.832817	-1.076163	0.265185
H	3.879018	0.306755	-2.552829
H	5.485123	-0.181928	-1.950522
H	4.686024	1.260083	-1.267197
C	2.425592	2.642859	2.286247
C	2.301952	3.751101	1.442621
C	2.163578	3.560102	0.064439
C	2.185335	2.272671	-0.505925
C	2.383863	1.167270	0.361331
C	2.454397	1.333898	1.770109
C	2.462076	0.174793	2.748879
H	2.493226	2.786151	3.371177
H	2.026188	4.427191	-0.591096
C	1.924159	2.124332	-1.992331
H	2.561195	-0.775912	2.211852
H	1.846375	1.058739	-2.249382
C	0.639419	2.819572	-2.466521
H	0.500952	2.655939	-3.549078
H	-0.238842	2.395853	-1.955434
H	0.656679	3.909460	-2.287499
C	1.193267	0.105318	3.615814
H	1.272728	-0.724162	4.340550
H	1.031285	1.038976	4.183322
H	0.304550	-0.090224	2.994518
H	2.295155	4.764541	1.861562
F	-5.357535	-0.861682	0.250343
F	-4.059125	-2.589499	0.524340
F	-3.768387	-0.782294	1.718463
H	3.353017	0.266137	3.400113
H	2.788698	2.534008	-2.550357

13a (***cis*-Cl$_2$**)

E(RMN15) = -2776.48377206 A.U.

Ru	0.570932	-1.190313	-0.662717
Cl	-0.870252	-2.227167	-2.271265
C	0.367923	0.427650	-1.521461
C	1.011459	1.667503	-1.100752
C	1.851882	1.645022	0.037034
C	0.810516	2.906141	-1.748951
C	2.445104	2.799109	0.550645
C	1.407223	4.070912	-1.251215
H	0.167145	2.941510	-2.634576
C	2.218749	4.022471	-0.105487
H	3.078366	2.750872	1.441212
H	1.234090	5.028737	-1.755398
H	2.679531	4.937912	0.283028
S	2.000134	0.013508	0.797488
C	3.843024	-0.274584	0.469572
H	-0.167074	0.444494	-2.485694
C	-0.939085	-1.145438	0.542764
N	-1.982556	-0.325237	0.687592
C	-1.104989	-2.371312	1.479074
C	-1.270624	-3.705645	0.718510
C	-2.370649	-1.986822	2.296522
C	0.126378	-2.491364	2.406742
C	-3.141036	-0.952012	1.458102
H	-2.066042	-1.522254	3.250810
H	-2.990294	-2.866043	2.535304
C	-4.113055	-1.623070	0.468776
C	-3.909233	0.068891	2.299263
H	-2.105189	-3.681049	0.003947
H	-1.448774	-4.510218	1.454363
H	-0.361098	-3.947753	0.145746
H	1.022437	-2.793899	1.838633
H	-0.072121	-3.263089	3.172403
H	0.342482	-1.540482	2.923229
H	-3.577891	-2.222165	-0.282649
H	-4.721561	-0.873393	-0.058764
H	-4.800125	-2.281830	1.027835
H	-3.279537	0.546186	3.065732
H	-4.734490	-0.450456	2.816448
H	-4.347465	0.858633	1.666538
C	-2.678979	2.803133	-1.268417
C	-2.143383	3.758220	-0.402960
C	-1.511012	3.359110	0.780430
C	-1.432310	2.002765	1.130008
C	-2.019227	1.048938	0.253231
C	-2.624165	1.426275	-0.968525
C	-3.172999	0.408524	-1.947444
H	-3.143660	3.125109	-2.205735
H	-1.061548	4.115009	1.429507
C	-0.706429	1.551480	2.383434
H	-2.693934	-0.563878	-1.756706
H	0.083980	0.842277	2.082444
Cl	2.215116	-2.825935	-1.146671
C	-2.979421	0.753329	-3.428684
H	-3.265037	-0.111257	-4.051770
H	-3.588062	1.616480	-3.753102
H	-1.921918	0.980630	-3.650510
C	-0.085742	2.646194	3.248330
H	0.435013	2.196677	4.111768
H	0.654285	3.238780	2.683379
H	-0.848700	3.341747	3.642208
F	4.159933	-0.202267	-0.818176
F	4.549879	0.672313	1.126828
F	4.173320	-1.462382	0.968511
H	-2.195926	4.822568	-0.660855
H	-4.255456	0.274391	-1.755293
H	-1.387078	0.941339	3.002326

13b (***trans*-Cl$_2$**)

E(RMN15) = -2709.68781425 A.U.

Ru	0.135138	-1.019873	-0.251885
Cl	-0.320444	-2.271616	1.693770
C	-0.216243	0.700353	0.279859
C	-1.438597	1.422893	-0.044427
C	-2.529808	0.759802	-0.663524
C	-1.540213	2.817855	0.181266
C	-3.669091	1.461125	-1.070959
C	-2.684286	3.519743	-0.214769
H	-0.695521	3.337796	0.649334
C	-3.745786	2.845862	-0.842874
H	-4.496383	0.928047	-1.549412
H	-2.748711	4.600637	-0.042148
H	-4.640497	3.396705	-1.155290
S	-2.380890	-1.010815	-0.873981
C	-3.378868	-1.584404	0.604497
H	0.516770	1.282599	0.854407
Cl	0.312157	-0.772527	-2.603524
C	2.074159	-1.059081	-0.111804
N	3.007726	-0.094263	-0.065836
C	2.808991	-2.411422	-0.285060
C	2.975319	-3.081130	1.101538
C	4.172703	-1.978781	-0.870626
C	2.070921	-3.394966	-1.209397
C	4.430437	-0.540679	-0.373833
H	4.104581	-1.971875	-1.972027
H	4.989084	-2.664315	-0.587543
C	5.324627	-0.459173	0.875476
C	5.058369	0.326490	-1.473032
H	3.532077	-2.449818	1.810415
H	3.536267	-4.025124	0.976881
H	1.993769	-3.299859	1.548150
H	1.093765	-3.682699	-0.779104
H	2.666393	-4.319828	-1.315935
H	1.894435	-2.961679	-2.205703
H	4.979676	-1.113868	1.687355
H	5.367960	0.574917	1.257007
H	6.350142	-0.764679	0.605658
H	4.471672	0.287758	-2.402162
H	6.070226	-0.058642	-1.689713
H	5.156202	1.378118	-1.155321
C	2.635786	2.872211	2.170120
C	2.497323	3.908211	1.241307
C	2.443623	3.610833	-0.123799
C	2.566393	2.289268	-0.594766
C	2.778785	1.261876	0.360615
C	2.763936	1.533803	1.754666
C	2.782925	0.450142	2.816280
H	2.637236	3.096451	3.243465
H	2.293650	4.418963	-0.848301
C	2.391189	2.019848	-2.076611
H	2.959063	-0.529359	2.356276
H	2.386097	0.935742	-2.256975
C	1.095086	2.601993	-2.660073
H	1.018707	2.349822	-3.731746
H	0.216926	2.167886	-2.157433
H	1.044696	3.701520	-2.565513
C	1.476883	0.372158	3.625070
H	1.560121	-0.401097	4.409283
H	1.240317	1.332376	4.117272
H	0.632227	0.088611	2.976702
H	2.412374	4.946966	1.582621
H	3.633188	0.637479	3.500640
H	3.258981	2.439596	-2.622208
H	-3.348876	-2.682044	0.503325
H	-2.805579	-1.308967	1.502007
C	-4.771379	-1.034230	0.594652
C	-5.751166	-1.550725	-0.277715
C	-5.101670	0.064945	1.410484
C	-7.030202	-0.982850	-0.330319
H	-5.497533	-2.395997	-0.929269
C	-6.382734	0.633254	1.362047
H	-4.338897	0.483974	2.077195
C	-7.349534	0.112937	0.489669
H	-7.782930	-1.395150	-1.013013
H	-6.623068	1.490033	2.002747
H	-8.350927	0.557769	0.447602

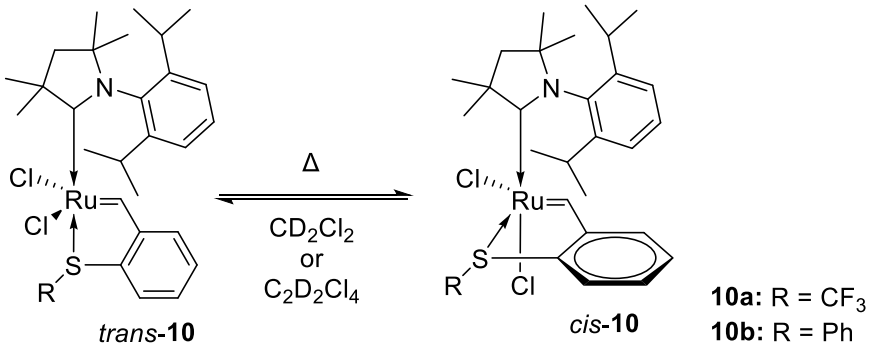
13b (***cis*-Cl$_2$**)

E(RMN15) = -2709.69675624 A.U.

Ru	0.298265	-0.597840	-1.220380
Cl	-1.008913	-2.185810	-2.467964
C	-0.914045	0.734172	-1.570170
C	-0.744448	2.126714	-1.172583
C	0.422190	2.482353	-0.453125
C	-1.684548	3.139479	-1.466762
C	0.651993	3.793279	-0.027315
C	-1.460844	4.456139	-1.047815
H	-2.591528	2.874377	-2.020777
C	-0.295586	4.785740	-0.333335
H	1.553268	4.044132	0.544041
H	-2.197541	5.234735	-1.277263
H	-0.124193	5.818131	-0.006852
S	1.481197	1.094322	-0.034322
C	3.134041	1.570087	-0.782379
H	-1.759286	0.503301	-2.239985
C	-0.453558	-1.370559	0.387066
N	-1.600655	-1.177105	1.048172
C	0.328212	-2.537676	1.042026
C	0.499575	-3.753393	0.105463
C	-0.539697	-2.858267	2.291549
C	1.732433	-2.050146	1.467859
C	-1.949868	-2.315556	1.998797
H	-0.127510	-2.331571	3.170024
H	-0.552949	-3.935775	2.522329
C	-2.820845	-3.353756	1.264846
C	-2.692841	-1.834853	3.246511
H	-0.460612	-4.132813	-0.271445
H	1.016077	-4.558863	0.658006
H	1.105487	-3.489602	-0.776819
H	2.370698	-1.841456	0.593046
H	2.226031	-2.836707	2.067137
H	1.681870	-1.131919	2.076859
H	-2.418735	-3.589210	0.268313
H	-3.851792	-2.989491	1.141538
H	-2.860355	-4.281079	1.862622
H	-2.093364	-1.138551	3.852680
H	-2.932133	-2.709725	3.875547
H	-3.640602	-1.338166	2.979230
C	-4.292708	1.263209	0.096184
C	-3.944932	2.344719	0.907039
C	-2.808348	2.275708	1.721025
C	-2.019022	1.116006	1.757584
C	-2.409696	0.012534	0.948730
C	-3.532128	0.075771	0.088837
C	-3.905185	-1.064621	-0.836257
H	-5.167131	1.339138	-0.557785
H	-2.526430	3.143772	2.322700
C	-0.759257	1.048373	2.600550
H	-3.009712	-1.676285	-1.025573
H	0.066880	0.711169	1.953292
Cl	2.034026	-0.816308	-2.849357
C	-4.492966	-0.650142	-2.189818
H	-4.583693	-1.535753	-2.841649
H	-5.495284	-0.193190	-2.102980
H	-3.834499	0.069162	-2.707892
C	-0.334927	2.337002	3.302593
H	0.621797	2.179962	3.831020
H	-0.187879	3.158906	2.580699
H	-1.078121	2.669032	4.049994
H	-4.549169	3.259528	0.890134
H	-4.634975	-1.718828	-0.320483
H	-0.863560	0.244346	3.351194
H	3.204937	2.662806	-0.663195
H	3.084235	1.286074	-1.844837
C	4.204197	0.838150	-0.023541
C	4.663570	-0.418195	-0.466483
C	4.708571	1.364586	1.183186
C	5.616434	-1.125808	0.280870
H	4.250648	-0.836460	-1.391303
C	5.660400	0.657217	1.928533
H	4.345661	2.336963	1.540850
C	6.115967	-0.592986	1.478771
H	5.967513	-2.101843	-0.075017
H	6.048445	1.080704	2.862792
H	6.859565	-1.149077	2.062305

6. Thermally and photoinduced isomerization of precatalysts

6.1. Thermal isomerization of DiPP-CAAC bearing complexes



Scheme S3. Thermal isomerization of complexes **10**

All the NMR spectra were calibrated on residual solvent peaks of dichloromethane-d_2 (5.32 ppm) and 1,1,2,2-tetrachloroethane-d_2 (6.00 ppm). Thermal isomerization and decomposition of the complexes was followed by changes in NMR signals of benzylidene protons of **10a** (at 16.81 ppm) and **10b** (at 16.86 ppm) and appearance of the new peaks.

The NMR samples of complexes **10** in CD_2Cl_2 were heated to 35°C in oil-bath under argon atmosphere.

For solvent replacement CD_2Cl_2 was evaporated directly from test-tube by blowing argon on it, and the residue was redissolved in $C_2D_2Cl_4$. The NMR samples of complexes in $C_2D_2Cl_4$ were heated to 75°C and 100°C in oil-bath under argon atmosphere.

6.1.1. Thermal isomerization of 10a

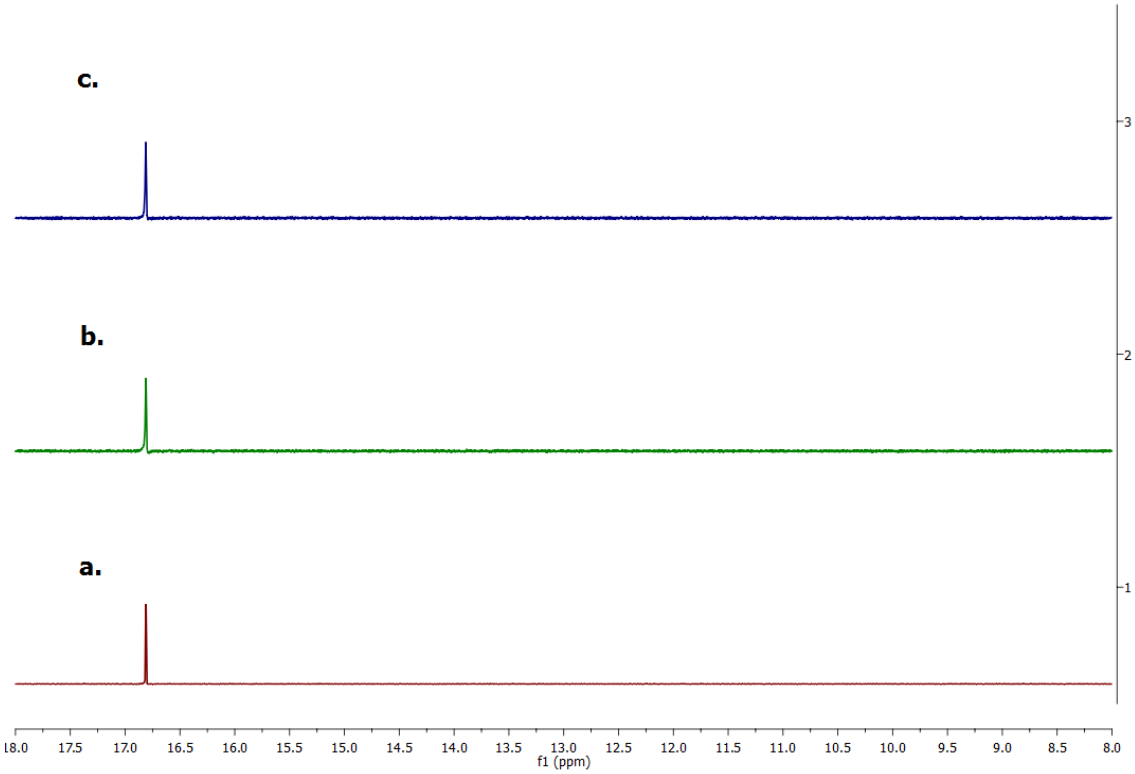


Figure S59. ^{1}H-NMR spectra of **10a** in CD_2Cl_2 at following condition: **a.** @ RT; **b.** 1h @ 35°C; **c.** 15h 20m @ 35°C (overnight).

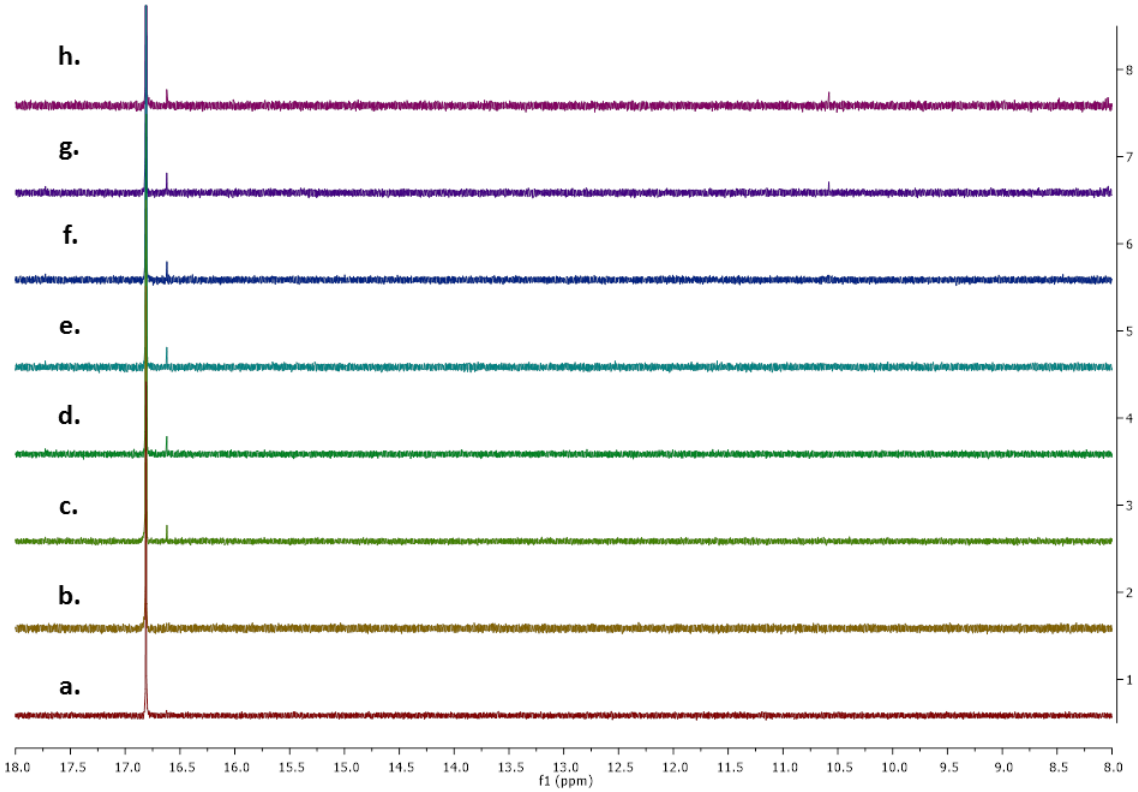


Figure S60. ^{1}H-NMR spectra of **10a** in $C_2D_2Cl_4$ after solvent exchange at following conditions: **a.** @ RT; **b.** 1.5h @ 35°C; **c.** 1h @ 75°C; **d.** 2h @ 75°C; **e.** 4h @ 75°C; **f.** 6h @ 75°C; **g.** 71 @ 75°C (weekend); **h.** 1h @ 100°C.

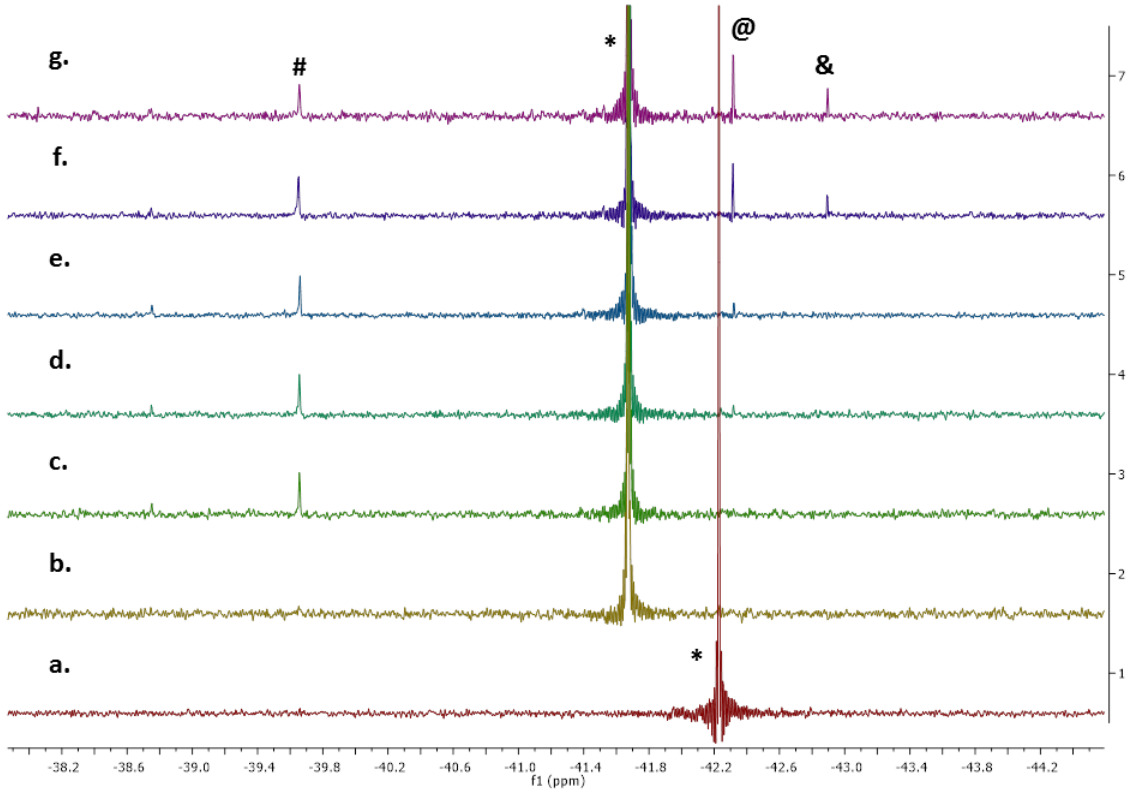


Figure S61. ^{19}F-NMR spectra of **10a**: **a.** @ RT in CD_2Cl_2; **b.** @ RT in $C_2D_2Cl_4$ (after 15h20m at 35°C in CD_2Cl_2); **c.** 2h @ 75°C (after 1.5h at 35°C in $C_2D_2Cl_4$); **d.** 4h @ 75°C; **e.** 6h @ 75°C; **f.** 71h @ 75°C (weekend); **g.** 1h @ 100°C.

(*****) – **10a**-*trans*; (**#**) – minor isomer of **10a**; (**@**) and (**&**) – fluorine-containing decomposition products of **10a**

6.1.2. Thermal isomerization 10b

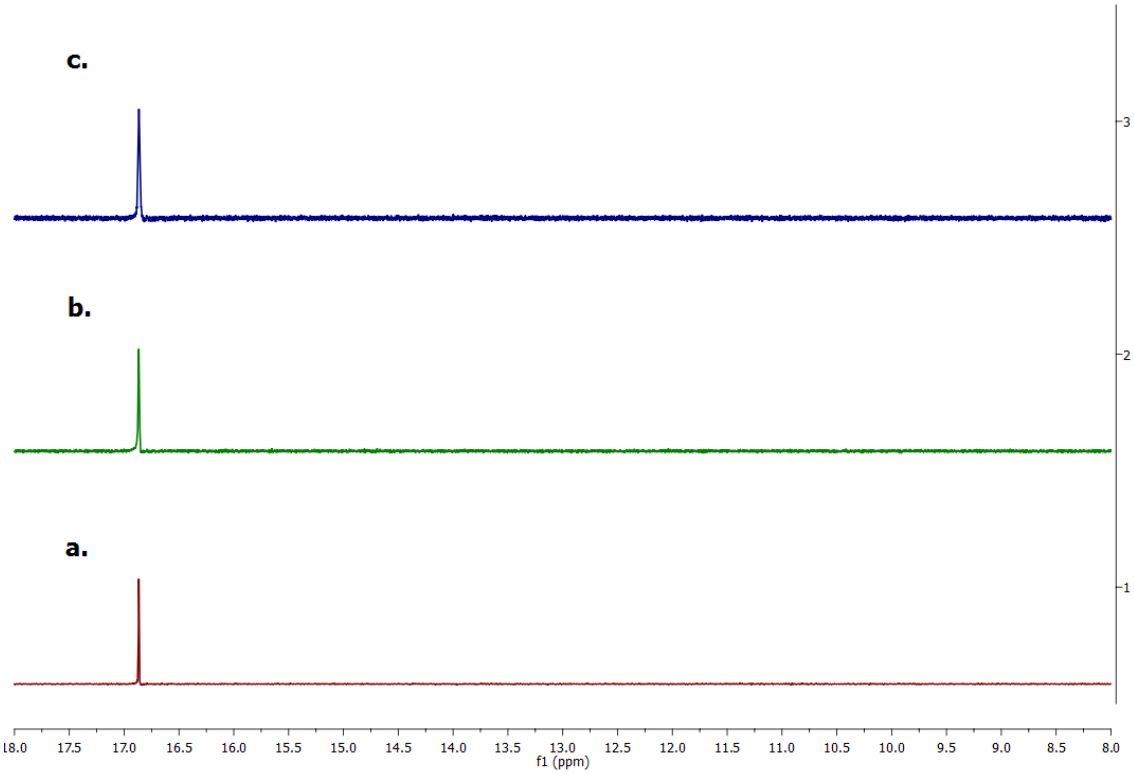


Figure S62. ^{1}H-NMR spectra of **10b** in CD_2Cl_2: **a.** @ RT; **b.** 1h @ 35°C; **c.** 15h 20m @ 35°C (overnight).

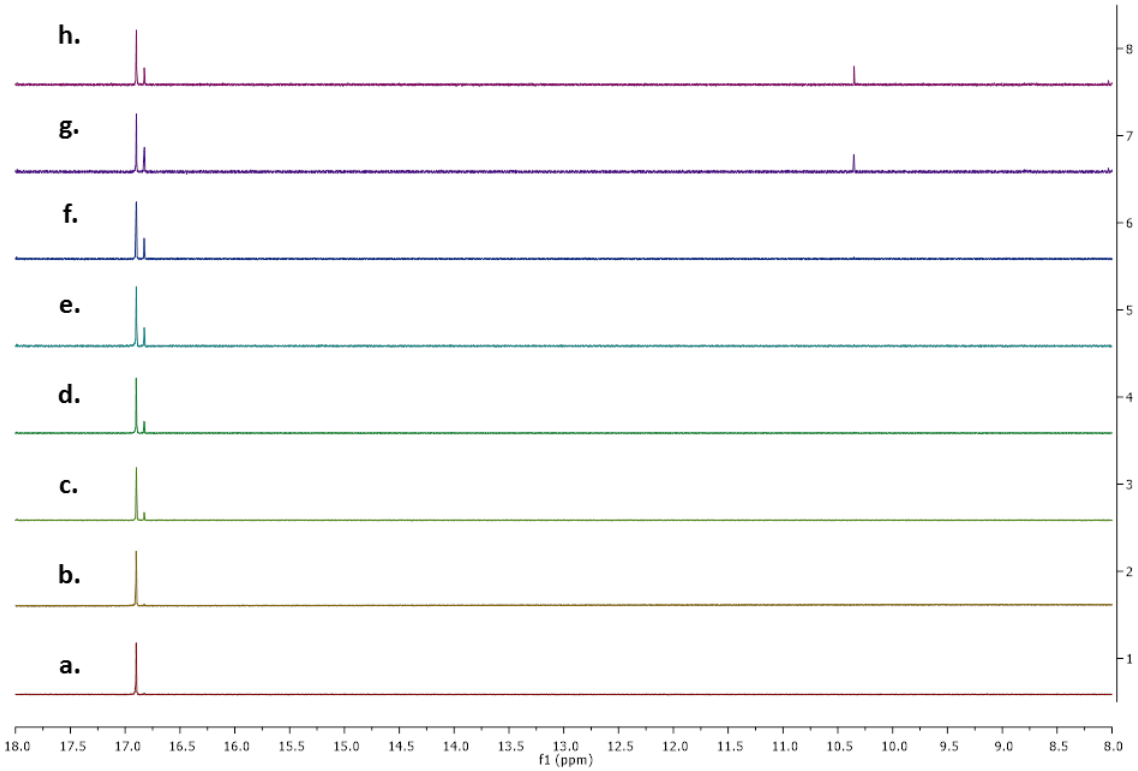
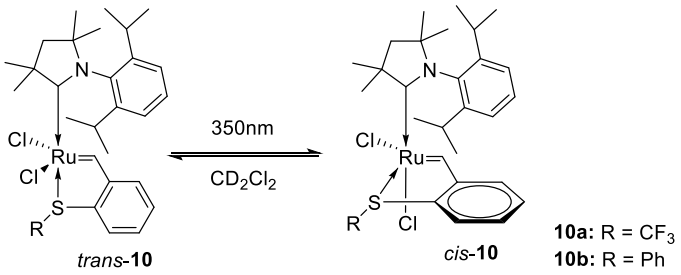


Figure S63. ^{1}H-NMR of **10b** in $C_2D_2Cl_4$ after solvent exchange: **a.** @ RT; **b.** 1.5h @ 35°C; **c.** 1h @ 75°C; **d.** 2h @ 75°C; **e.** 4h @ 75°C; **f.** 6h @ 75°C; **g.** 71h @ 75°C (weekend); **h.** 1h @ 100°C.

6.2. Photoisomerization of DiPP-CAAC bearing complexes



Scheme S4. Photo-induced isomerization of complexes **10** under 350nm irradiation.

The NMR experiments were carried in Pyrex 5 mm NMR test-tubes under an argon atmosphere in a Rayonet RPR-200 equipped with 16 lamps (350 nm). Cooling of samples in the reactor was effected by blowing compressed air through the apparatus. Photoisomerization and decomposition of the complexes was followed by changes in NMR signals of benzylidene protons of **10a** at 16.81 ppm and **10b** at 16.86 ppm and appearance of the new peaks. All the NMR spectra were calibrated on residual solvent peaks of dichloromethane-d_2 (5.32 ppm).

For NOESY NMR experiment of **10b**, the CD_2Cl_2 solution of the complex was bubbled with argon.

6.2.1. Photoisomerization of 10a

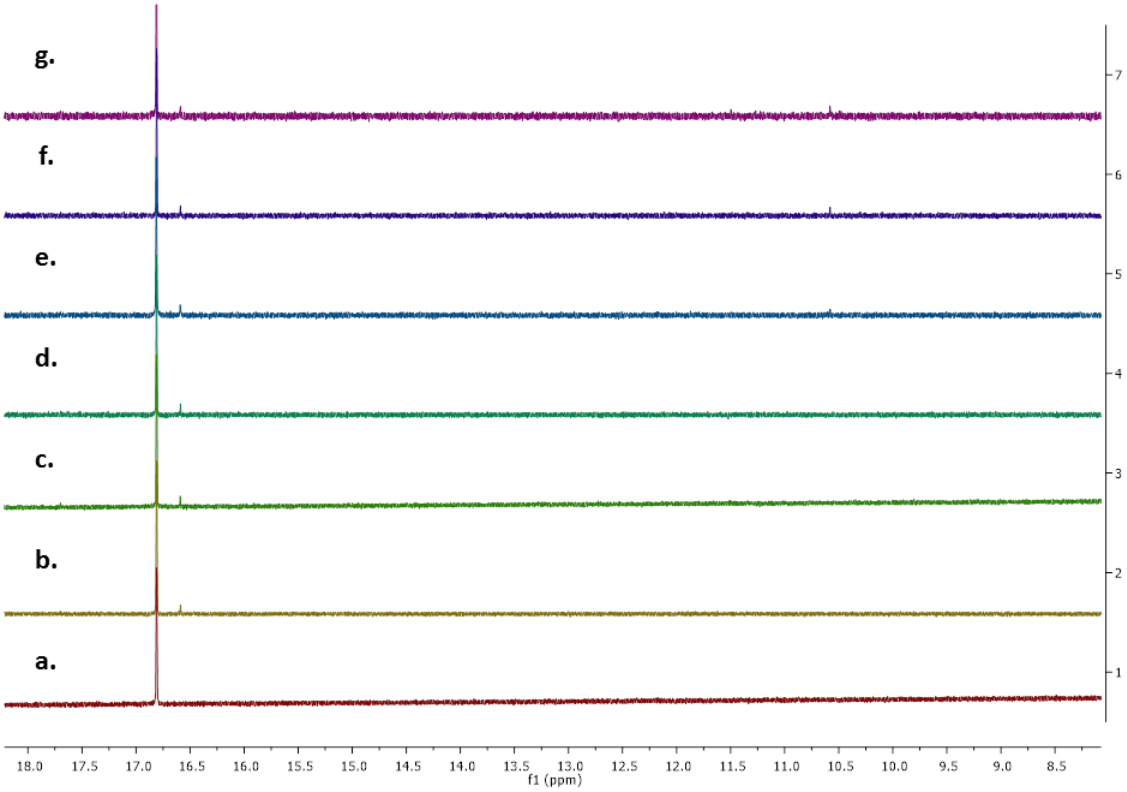


Figure S64. ^{1}H-NMR of spectra **10a** in CD_2Cl_2: **a.** before irradiation; **b.** 1h @ 350nm; **c.** 2h @ 350nm; **d.** 4h @ 350nm; **e.** 20h @ 350nm; **f.** 25.5h @ 350nm; **g.** 14h @ RT.

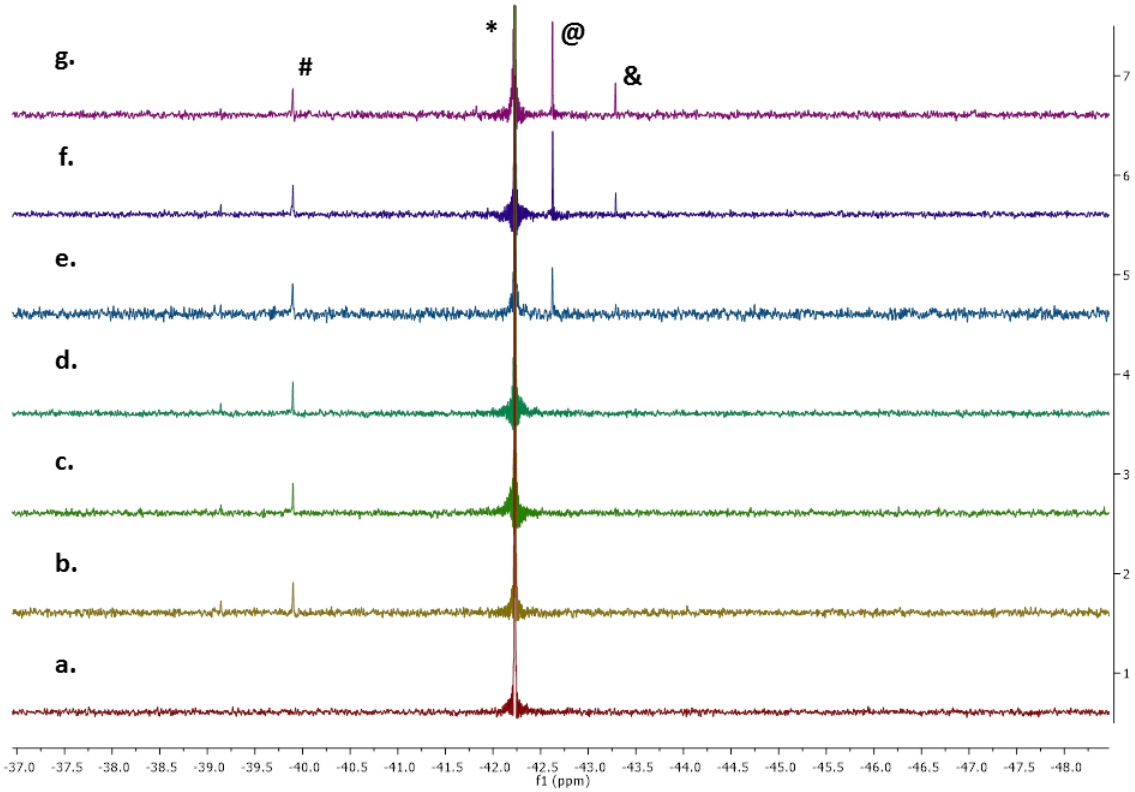


Figure S65. ^{19}F-NMR spectra of **10a** in CD_2Cl_2: **a.** before irradiation; **b.** 1h @ 350nm; **c.** 2h @ 350nm; **d.** 4h @ 350nm; **e.** 20h @ 350nm; **f.** 25.5h @ 350nm; **g.** 14h @ RT.

(*****) – **10a**-*trans*; (**#**) – minor isomer of **10a**; (**@**) and (**&**) – fluorine-containing decomposition products of **10a**

6.2.2. Photoisomerization of 10b

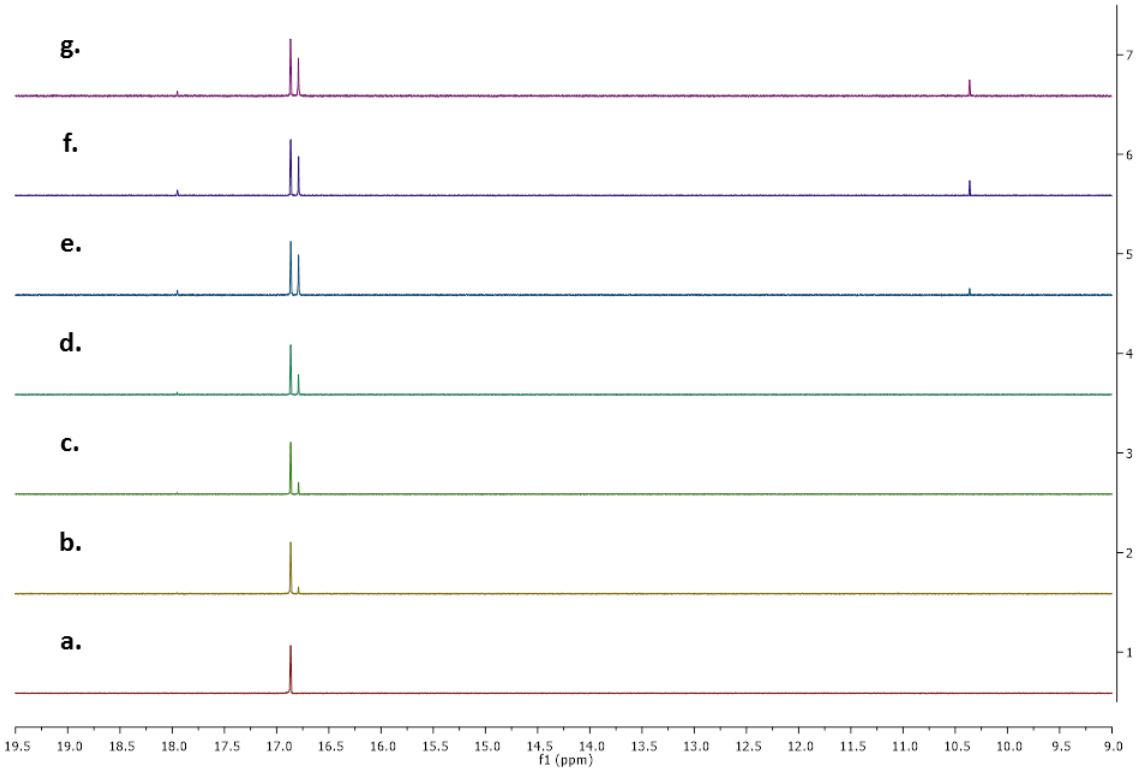


Figure S66. ^{1}H-NMR spectra of **10b** in CD_2Cl_2: **a.** before irradiation; **b.** 1h @ 350nm; **c.** 2h @ 350nm; **d.** 4h @ 350nm; **e.** 20h @ 350nm; **f.** 25.5h @ 350nm; **g.** 14h @ RT.

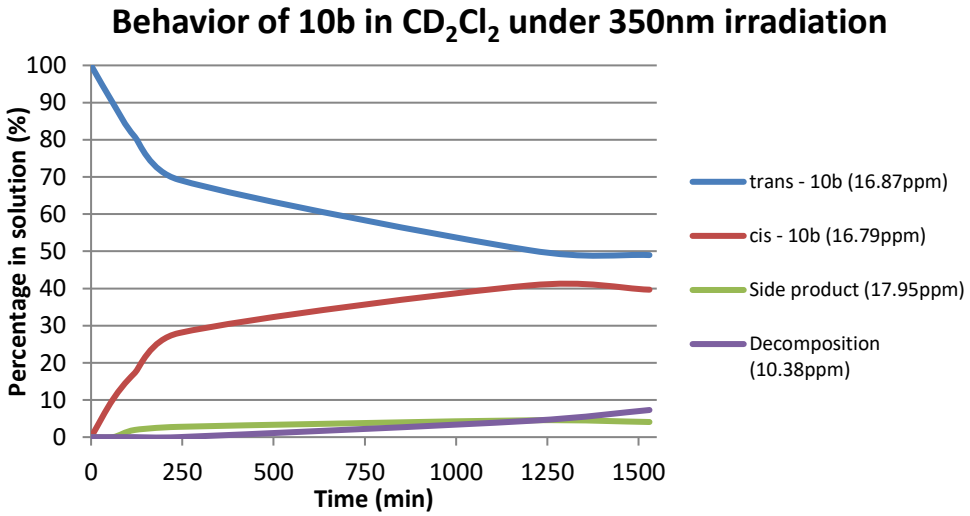


Figure S67. Summary of behavior of **10b** in CD_2Cl_2 under irradiation at 350nm. The percentage of compounds was calculated from the integration of the relevant peaks in the ^{1}H-NMR spectra above.

6.2.3. Photoisomerization of 10b – assignment of configuration by ^{1}H-NMR

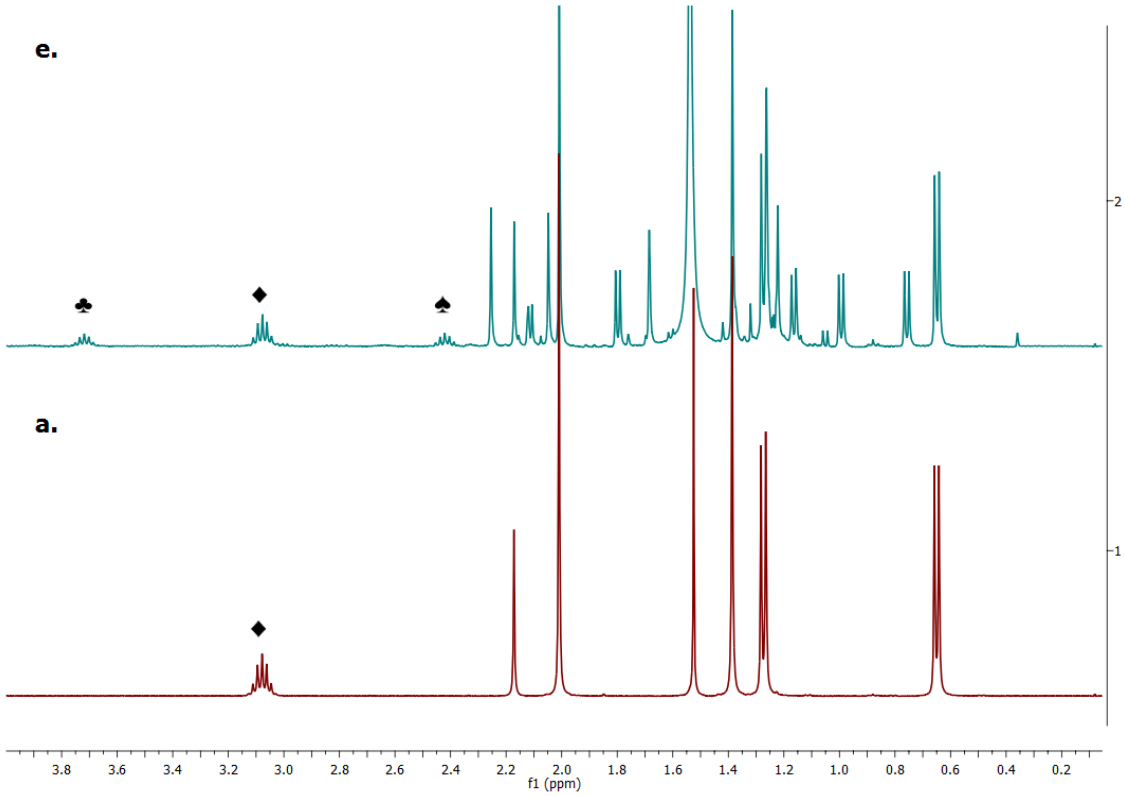
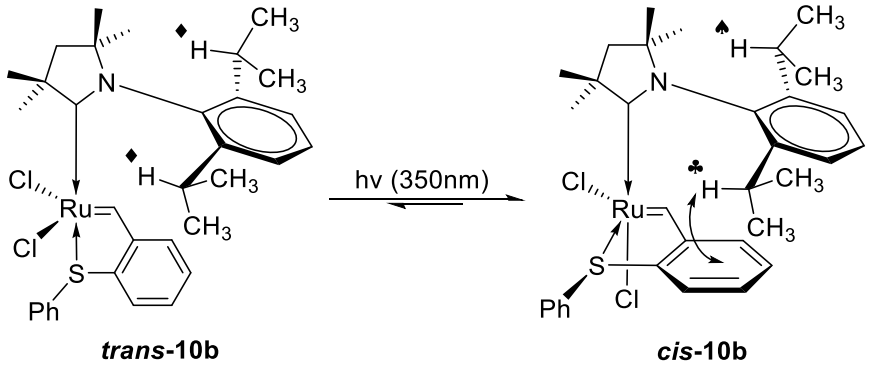


Figure S68. ^{1}H-NMR of spectra of **10b** in CD_2Cl_2 at following conditions: **a.** before irradiation; **e.** after 20h (in total) @ 350nm. The marked signals belong to following protons:



Scheme S5. Followed protons for the configuration assignment by ^{1}H-NMR of photoisomerization product of ***trans*-10b**

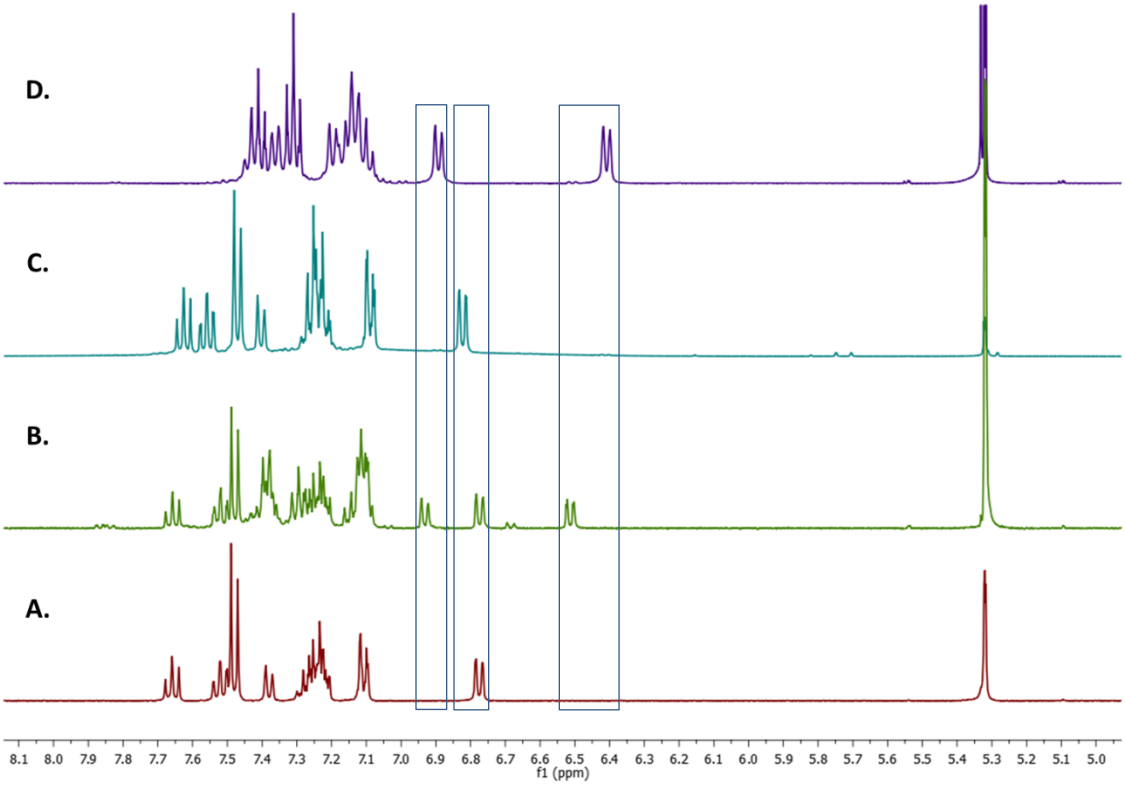
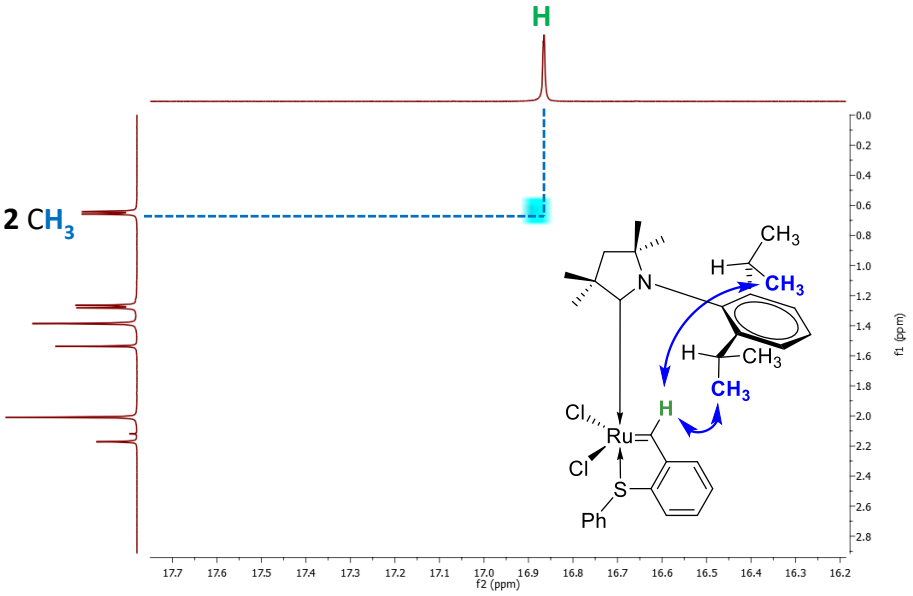


Figure S69. Expansion of the aromatic region in ^{1}H-NMR of spectra for clear assignment of relative configuration in mixture of complexes **10b** after irradiation at 350nm in CD_2Cl_2: **A.** ***trans*-10b** before irradiation ("a." from previous figure); **B.** mixture of ***trans*-10b** and ***cis*-10b** after 20h (in total) @ 350nm ("e." from previous figure); **C.** pure ***trans*-13b**; **D.** pure ***cis*-13b**.

6.2.4. Photoisomerization of 10b – Following photoisomerization by NOESY NMR



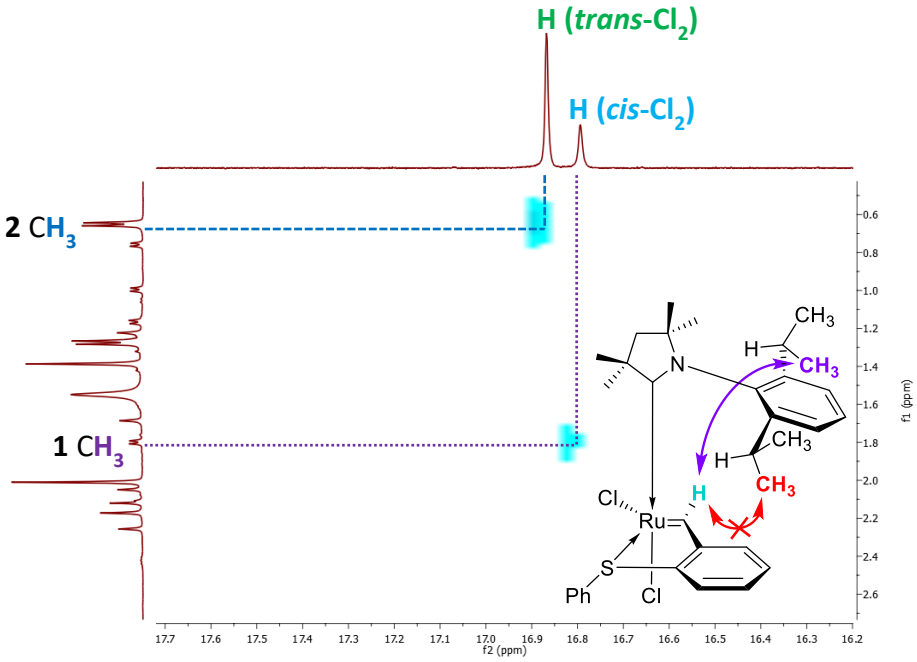
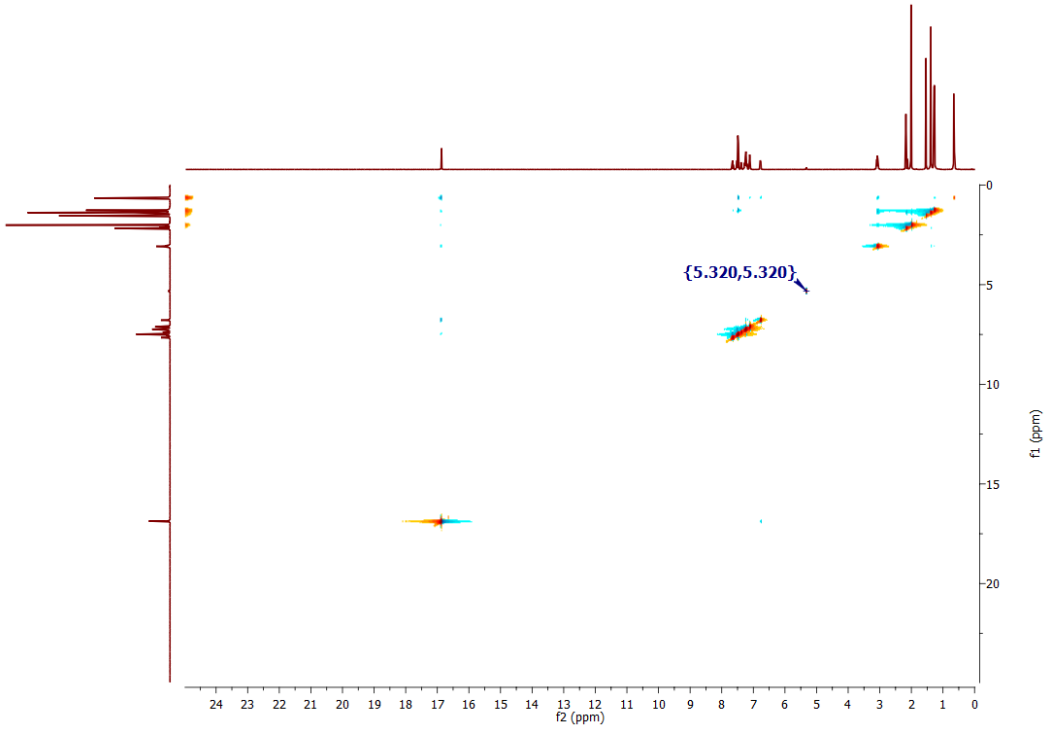


Figure S70. Following photoisomerization of **10b** at 350nm light in CD_2Cl_2. ***Top:*** before irradiation; ***Bottom:*** after 24h of irradiation (***trans-10b***/***cis-10b*** = 2.46).

A correlation of the benzylidene proton of *cis*-**10b** is observed only to one out of four methyl groups of the two isopropyl groups after irradiation as expected for the *cis* isomer.



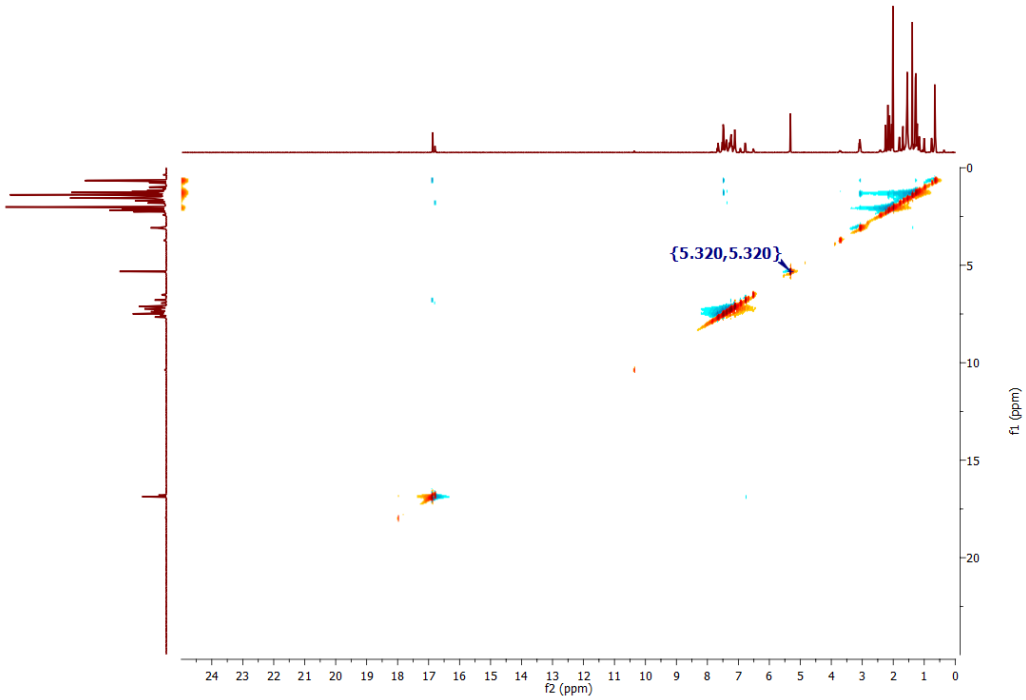
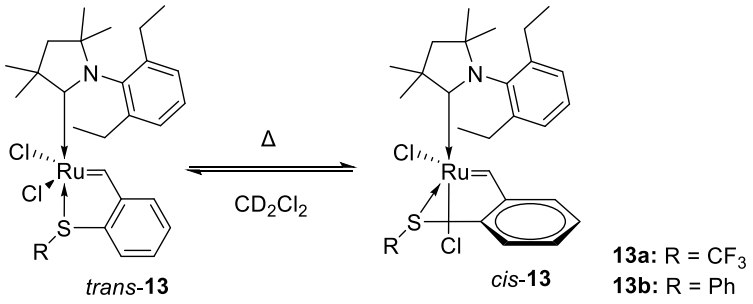


Figure S71. Expanded NOESY NMR spectra for following photoisomerization of **10b** at 350nm light in CH_2Cl_2. ***Top:*** before irradiation; ***Bottom:*** after 24h of irradiation (***trans*-10b**/***cis*-10b**= 2.46).

6.3. Thermal isomerization of DEtP-CAAC bearing complexes

Thermal isomerization of the complexes was followed the same way as described above.



Scheme S6. Thermal isomerization of complexes **13.**

6.3.1. Thermal isomerization of *trans*-13a

Peak at 16.88 ppm is assigned to ***trans*-13a** and a growing peak at 16.24 ppm is assigned to ***cis*-13a**.

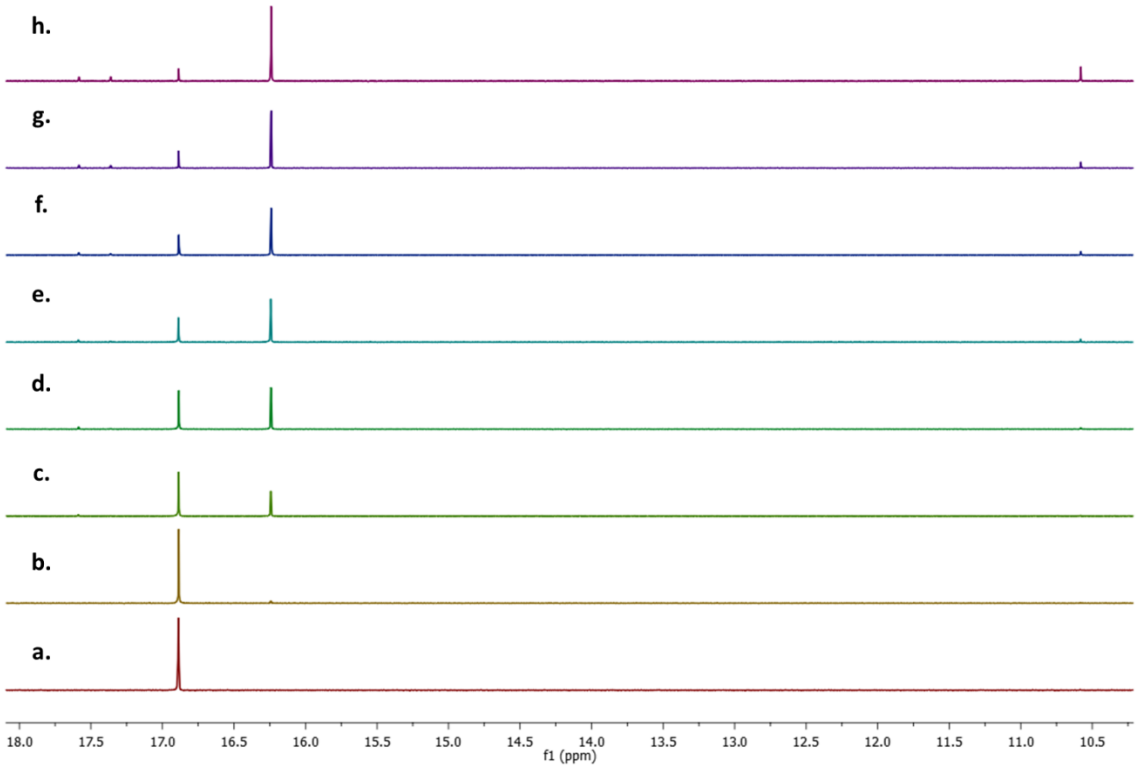


Figure S72. Thermal isomerization of ***trans*-13a** at 40°C in CD_2Cl_2: ***a. trans*-13a** only (0% *cis*); ***b.*** 1h (3% *cis*); ***c***. 17.5h (34% *cis*); ***d.*** 23.5h (49% *cis*); ***e.*** 40.5h (64% *cis*); ***f.*** 47h (69% *cis*); **g.** 53h (76% *cis*); **h.** 71h (86% *cis*)

6.3.2. Thermal isomerization of *trans*-13b

Peak at 16.95 ppm is assigned to ***trans*-13b** and a growing peak at 16.41 ppm is assigned to ***cis*-13b**.

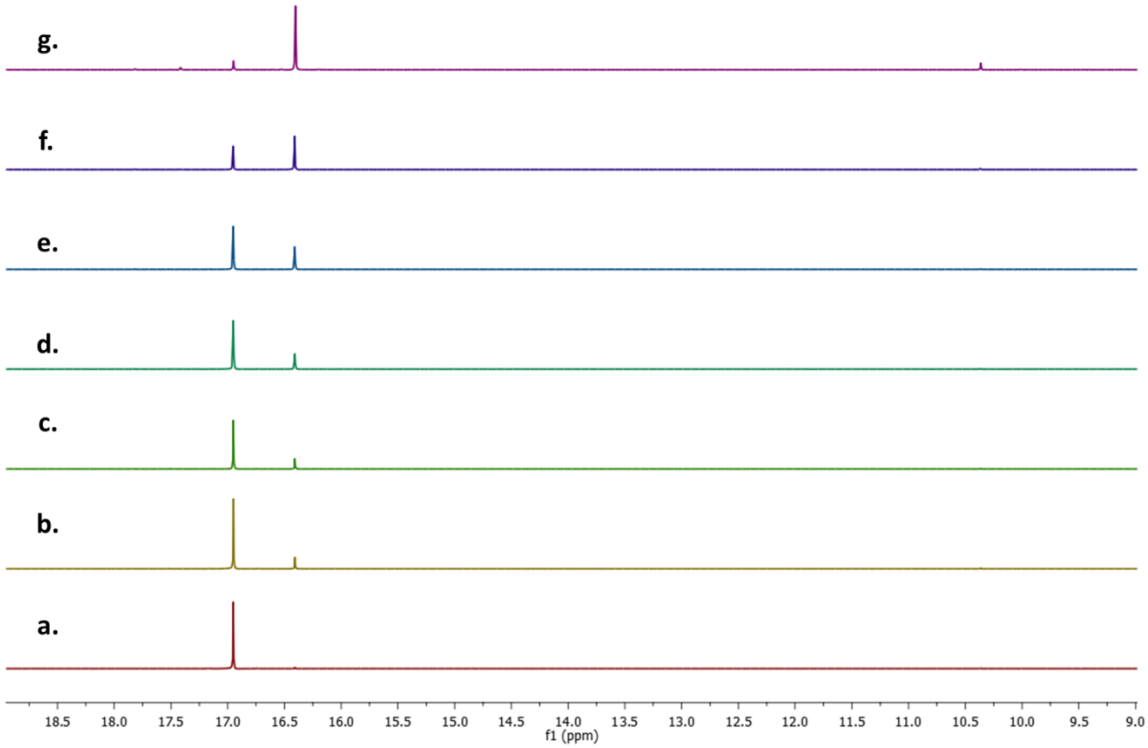


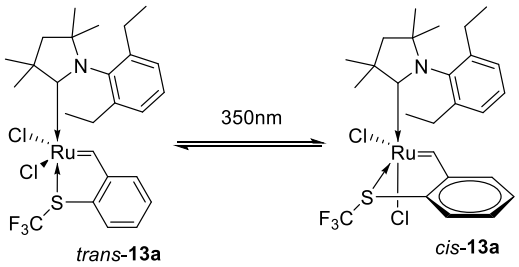
Figure S73. Thermal isomerization of ***trans*-13b** at RT in CD_2Cl_2: ***a. trans*-13b** only (0% *cis*); ***b.*** 3h 50min (14% *cis*); ***c***. 20h 50min (17% *cis*); ***d.*** 23h 20min (24% *cis*); ***e.*** 27h (34% *cis*); ***f.*** 45h (59% *cis*); ***g.*** 94h (89% *cis*)

6.4. Photoisomerization of DEtP-CAAC bearing complexes

Photo-induced isomerization of the complexes was followed the same way as described above. Complexes ***trans*-13a, *cis*-13a** and ***cis*-13b** were irradiated in a Rayonet photoreactor at 350nm. The time in captions denotes the total irradiation time.

6.4.1. Photoisomerization of *trans*-13a ("*trans*-to-*cis*")

Peak at 16.88 ppm is assigned to ***trans*-13a** and a growing peak at 16.24 ppm is assigned to ***cis*-13a**.



Scheme S7. Photo-induced isomerization of ***trans*-13a** under 350nm irradiation.

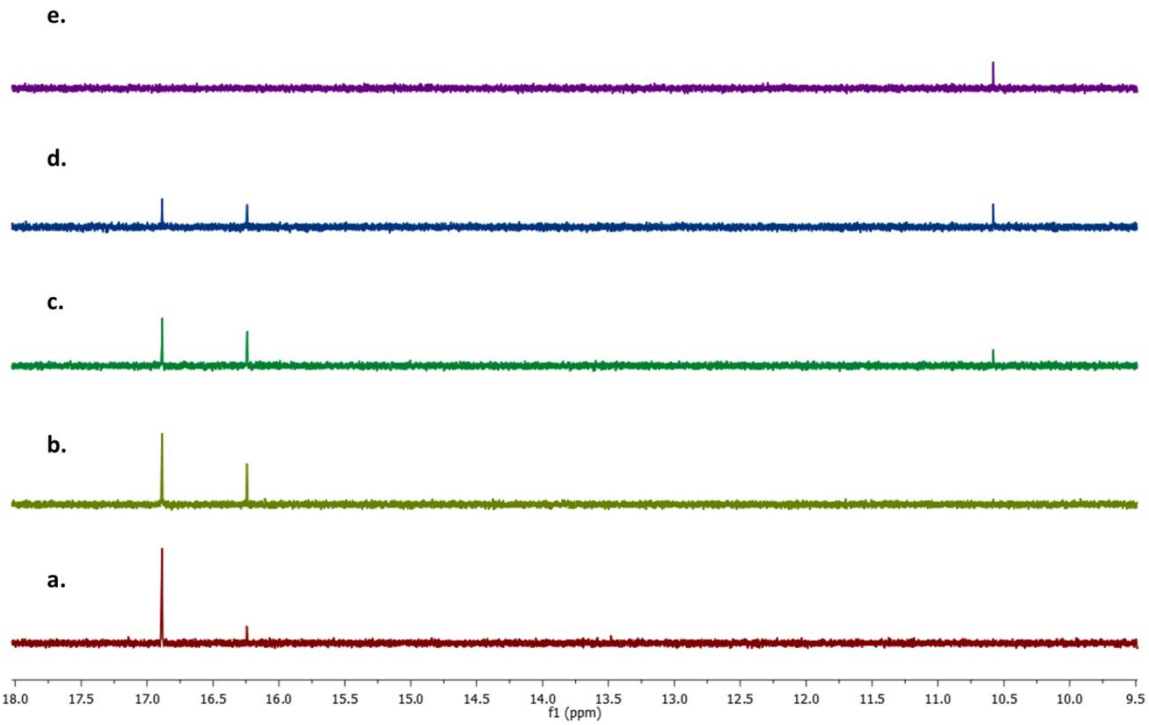
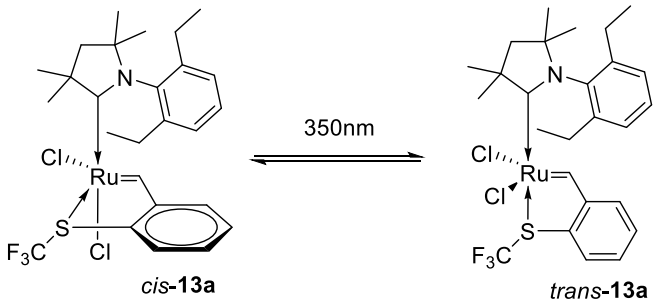


Figure S74. Photoisomerization of ***trans*-13a** at 350nm in CD_2Cl_2: ***a. starting mixture*** (*cis*/*trans* = 0.14); ***b.*** 1h @ 350nm (*cis*/*trans* = 0.60); ***c***. 2h @ 350nm (*cis*/*trans* = 0.54); ***d.*** 3h @ 350nm (*cis*/*trans* = 0.70); ***e.*** 5h @ 350nm (full decomposition)

6.4.2. Photoisomerization of *cis*-13a ("*cis*-to-*trans*")

Peak at 16.88 ppm is assigned to ***trans*-13a** and a growing peak at 16.24 ppm is assigned to ***cis*-13a**.



Scheme S8. Photo-induced isomerization of ***cis*-13a** under 350nm irradiation.

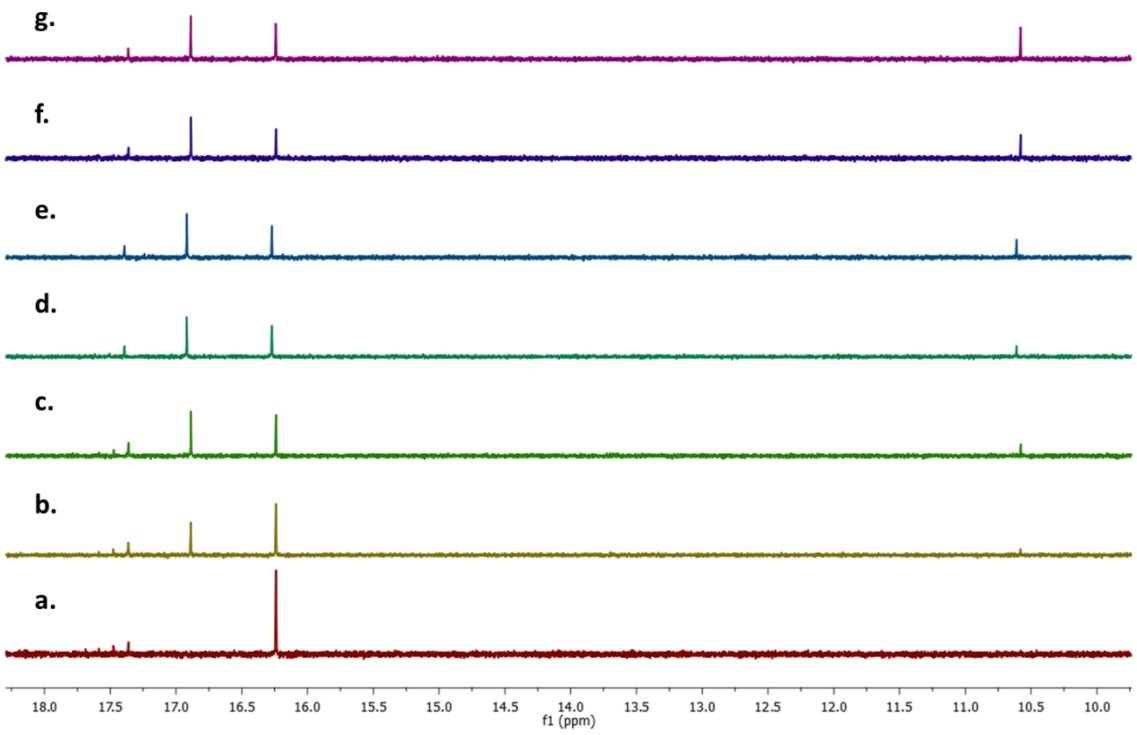
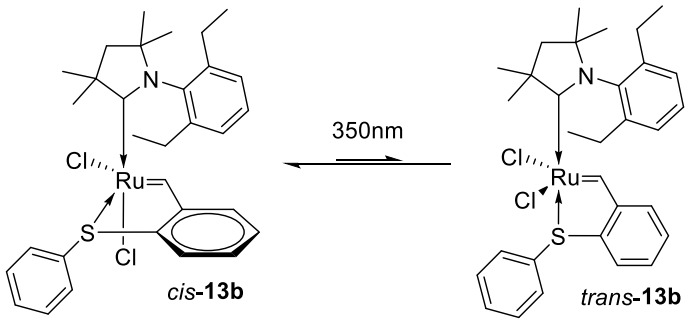


Figure S75. Photoisomerization of ***cis*-13a** at 350nm in CD_2Cl_2: ***a. cis*-13a** only (*cis*/*trans* = 100% *cis*); ***b.*** 1h @ 350nm (*cis*/*trans* = 1.59); ***c***. 2h @ 350nm (*cis*/*trans* = 0.95); ***d.*** 3h @ 350nm (*cis*/*trans* = 0.73); ***e.*** 5h @ 350nm (*cis*/*trans* = 0.67); ***f.*** 7h @ 350nm (*cis*/*trans* = 0.75); ***g.*** overnight at RT in darkness (*cis*/*trans* = 0.84).

6.4.3. Photoisomerization of *cis*-13b ("*cis*-to-*trans*")

Peak at 16.94 ppm belongs to ***trans*-13b** and a growing peak at 16.40 ppm belongs to ***cis*-13b**.



Scheme S9. Photo-induced isomerization of ***cis*-13b** under 350nm irradiation.

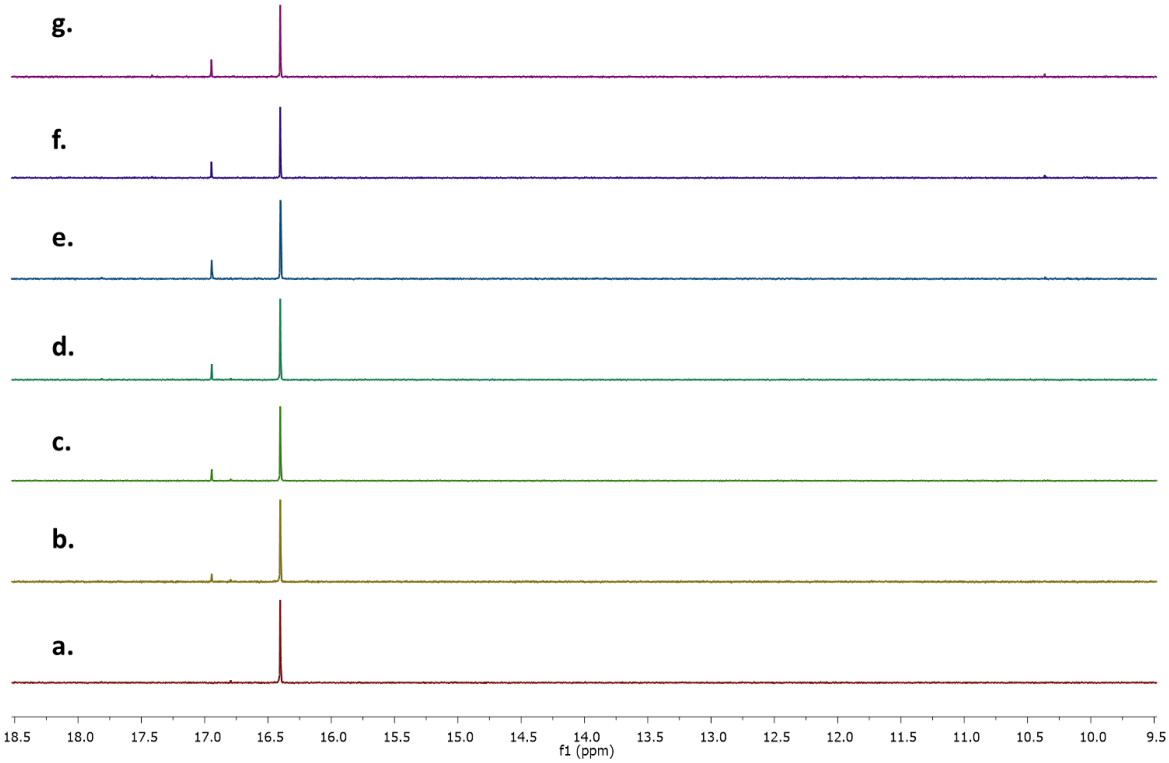


Figure S76. Photoisomerization of ***cis*-13b** at 350nm in CD_2Cl_2: ***a. cis*-13b** only; ***b.*** 1h @ 350nm (*cis/trans* = 10.53); ***c.*** 2h @ 350nm (*cis/trans* = 6.94); ***d.*** 3h @ 350nm (*cis/trans* = 5.08); ***e.*** 5h @ 350nm (*cis/trans* = 4.27); ***f.*** 7h @ 350nm (*cis/trans* = 4.08); ***g.*** 10.5h @ 350nm (*cis/trans* = 4.15).

7. Activity testing of the precatalysts in olefin metathesis reactions

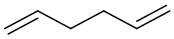
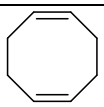
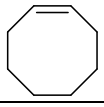
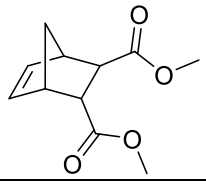
7.1. Polymerizations (ADMET and ROMP)

Thermal activation of precatalysts **10** and ***cis*-13** in polymerization reactions was followed by ^{1}H-NMR spectroscopy in $C_2D_2Cl_4$ (calibrated as residual solvent peak at 6.00ppm). Mesitylene (0.2 equivalents, 20%mol) was added to stock solutions of monomers (0.5M) and a singlet at 6.83ppm (aromatic protons of mesitylene) was used as internal standard for following of reaction progress comparing to the signals in **Table S10**. Samples were measured at t_0 (no catalyst added), after 1h, 3h and 24h of heating (unless otherwise specified). Catalyst was dissolved as stock solution in $C_2D_2Cl_4$ and was added as 20µL containing 0.1 mol% of precatalyst (in total reaction mixture). The polymerization reactions were carried at 35°C and 75°C.

In case of photoactivation at 350nm, argon gas was blown into the test-tube prior to irradiation.

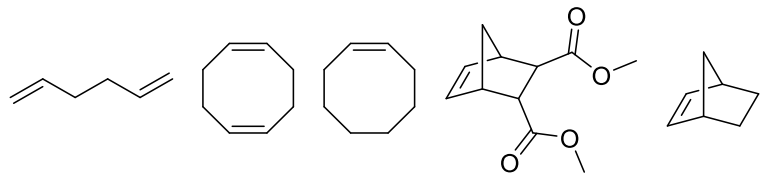
The size of the **pM4** was determined by a GPC system equipped with a triple detector (light-scattering detector, viscometer and refractometer). The polymers were dissolved in THF (2 mg/mL) and filtered through 0.22 µm filter.

Table S11. Monomers and monitored signals in ^{1}H-NMR

Entry	Monomer	Signal monitored
M1		multiplet at 5.86ppm
M2		broad multiplet at 5.62ppm
M3		multiplet at 5.66ppm
M4		multiplet at 6.23ppm
M5		multiplet at 6.02ppm

7.1.1. Results of reactivity testing

Table S12. Monomer conversions of thermal and photoactivated polymerization reactions with various catalysts



M1 **M2** **M3** **M4** **M5**

Notes: *a*. [Cat]/[M_x]/[mesitylene]=1/1000/200, [M_x]=0.5M in $C_2D_2Cl_4$;

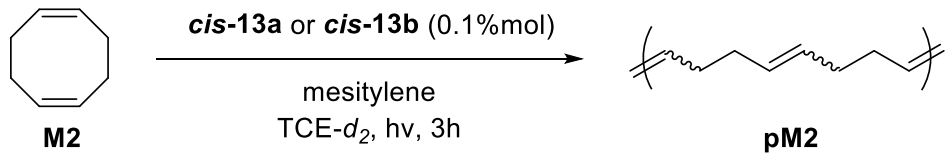
b. Conversion was determined by integration of ^{1}H-NMR signals.

c. After 4 hours of heating.

d. In parentheses: conversion after heating to 100°C of the same sample for 1h.

		trans-10a[a]			*trans*-10b[a]			*cis*-13a[a]			*cis*-13b[a]		
Activation method	**Monomer**	**1h[b]**	**3h[b]**	**24h[b]**	**1h[b]**	**3h[b]**	**24h[b]**	**1h[b]**	**3h[b]**	**24h[b]**	**1h[b]**	**3h[b]**	**24h[b]**
35°C	**M1**	0	0	5	0	0	0	0	0	0	0	0	0
	M2	0	0	0	0	0	0	0	0	2	0	0	0
	M3	0	0	17	0	0	0	0	0	10	0	0	0
	M4	0	0	0	0	0	0	0	0	0	0	0	0
	M5	64	83	100	24	52	83	17	40	99	10	19	78
75°C	**M1**	20	48[c]	54	0	4[c]	22	7	22	39	9	16	35
	M2	0	0	0	0	0	0	19	37	60	4	4	10
	M3	48	60	77	0	8	22	91	97	100	18	26	34
	M4	0	0	32	0	0	0	5	9	27	0	0	4
	M5	100	100	100	100	100	100	99	100	100	96	100	100
350nm	**M1**	0	0	0 (50)[d]	0	0	0	15	30	33	0	0	9
	M2	0	0	0	0	0	0	28	34	34	0	0	0
	M3	0	0	0 (50)[d]	0	0	0	83	94	97	0	3	10
	M4	0	0	0	0	0	0	0	0	0	0	0	0
	M5	63	93	98 (100)[d]	11	55	71	100	100	100	100	100	100
419nm	**M1**							5	14	24			
	M2							36	90	100			
	M3							90	100	100			
	M4							0	0	5			
	M5							100	100	100			

7.1.2. Screening wavelengths for effective photo-activation of *cis*-13a and *cis*-13b

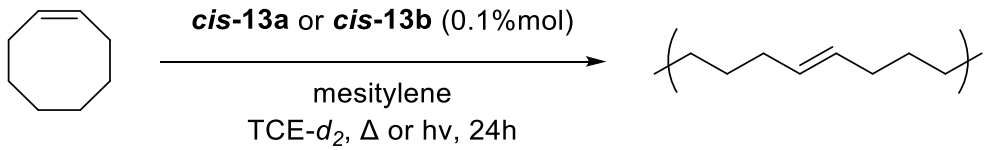


Scheme S10. Screening of wavelengths for effective photo-activation of *cis*-**13** pre-catalysts by ROMP of **M2.**

Table S13. Conversions of **M2** with *cis*-**13a** and *cis*-**13b** under irradiation with various wavelengths .

complex	time (h)	conversion (%)			
		dark control	254nm	350nm	419nm
cis-13a	0	0	0	0	0
	1	0	25	28	54
	3	5	36	34	90
cis-13b	0		0	0	0
	1		0	0	0
	3		12	0	0

7.1.3. Polymerization of M3 (*cis*-cyclooctene) by *cis*-13 initiators



Scheme S11. Polymerization of **M3** with ***cis*-13**.

Table S14. Data regarding **pM3** obtained by *cis*-**13** initiators

Entry	Catalyst	Activation	Conversion (%)[a]	Z/E ratio[a]	Mw (kDa)[b]	Mn (kDa)[b]	PDI[b]
1	***cis*-13a**	75°C	98	1/1.9	29	16	1.8
2		350nm	100	1/2.1	102	68	1.5
3	***cis*-13b**	75°C	45	1/0.8	150	120	1.2
4		350nm	16	1/1.0	----	----	----

a) Determined by integration of ^{1}H-NMR spectrum of the same polymer that was analysed by SEC.

b) Determined by GPC equipped with triple detector

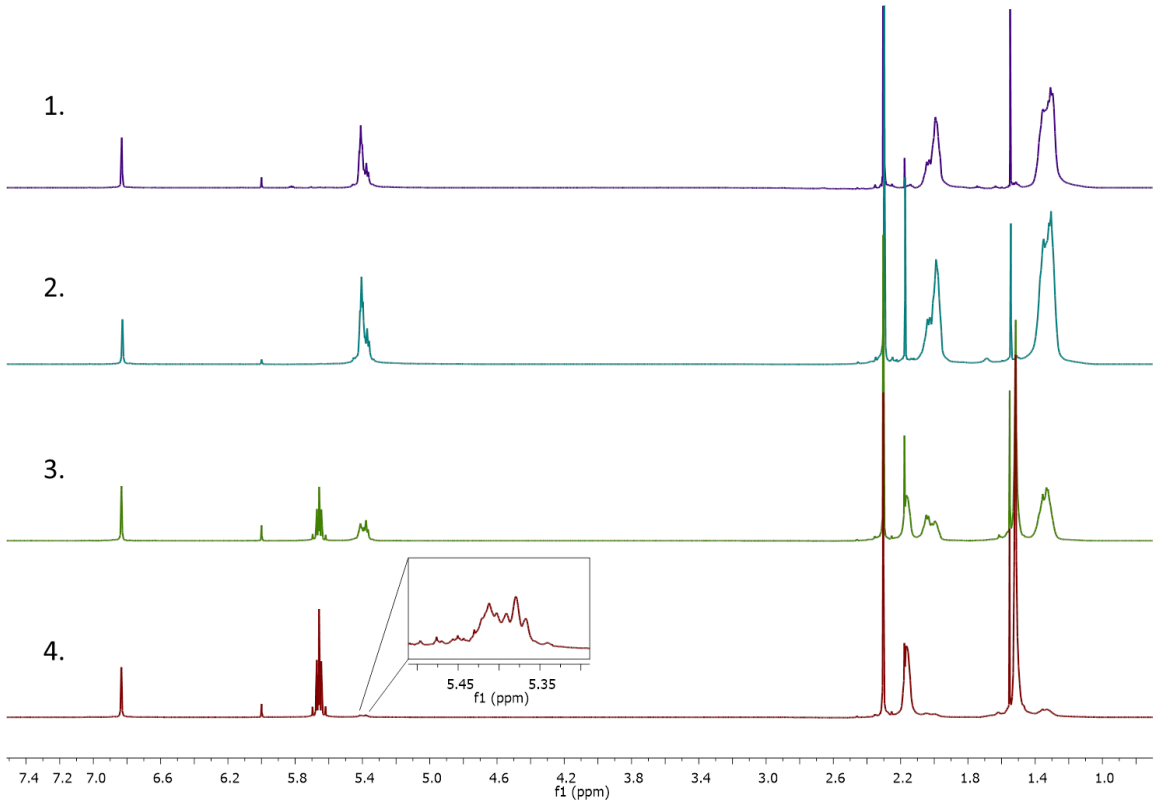


Figure S77. ^{1}H-NMR spectra of **pM3** polymerized by ***cis*-13** (in TCE-d_2). The numbers match the entries numbering in the table above.

GPC chromatograms of pM3 made by *cis*-13 initiators

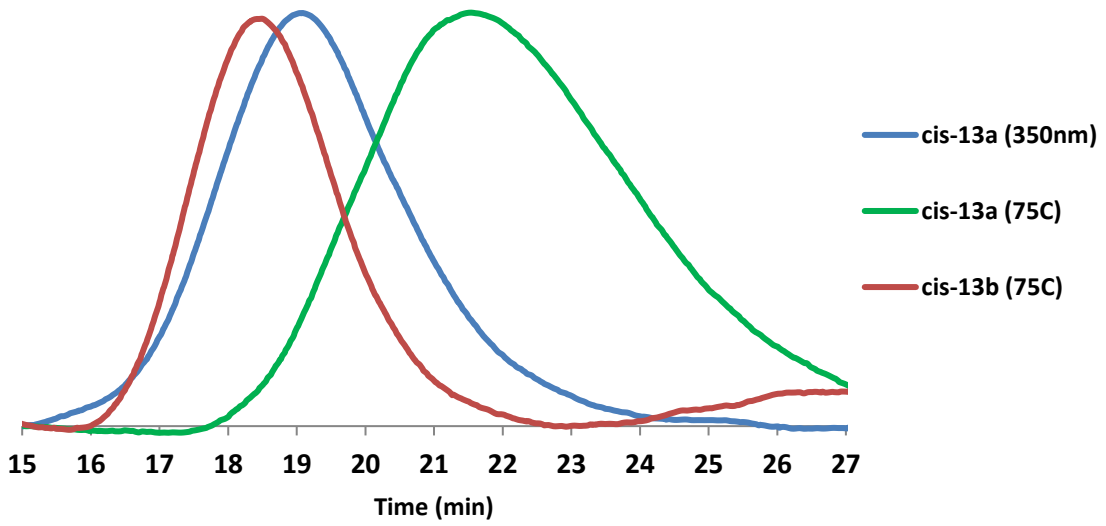


Figure S78. GPC chromatograms (refractive index detector) of polymers **pM3** obtained by ***cis*-13**.

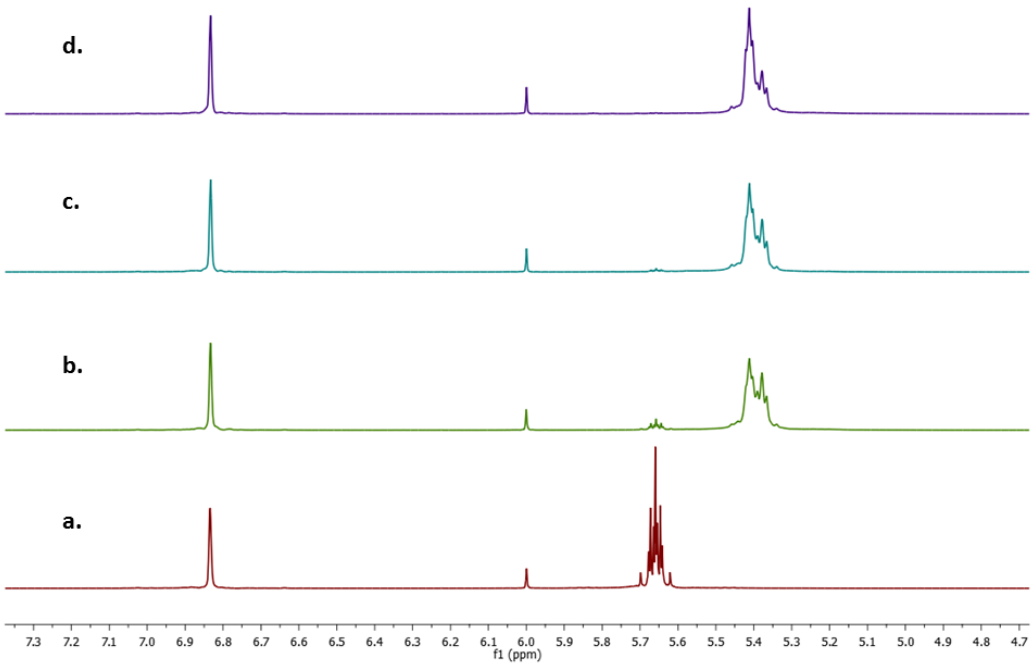


Figure S79. Change in Z/E ratio over time in ROMP of **M3** by ***cis*-13a** at 75°C. a. before addition of catalyst; b. after 1h; c. after 3h; d. after 24h

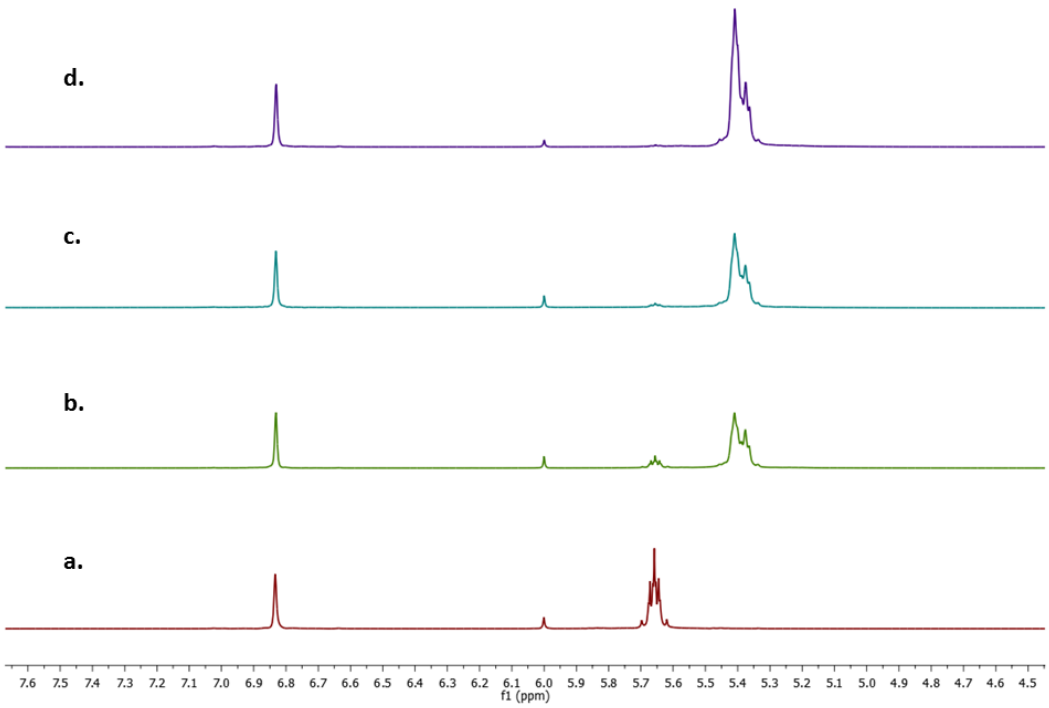


Figure S80. Change in Z/E ratio over time in ROMP of **M3** by ***cis*-13a** at 350nm. a. before addition of catalyst; b. after 1h; c. after 3h; d. after 24h

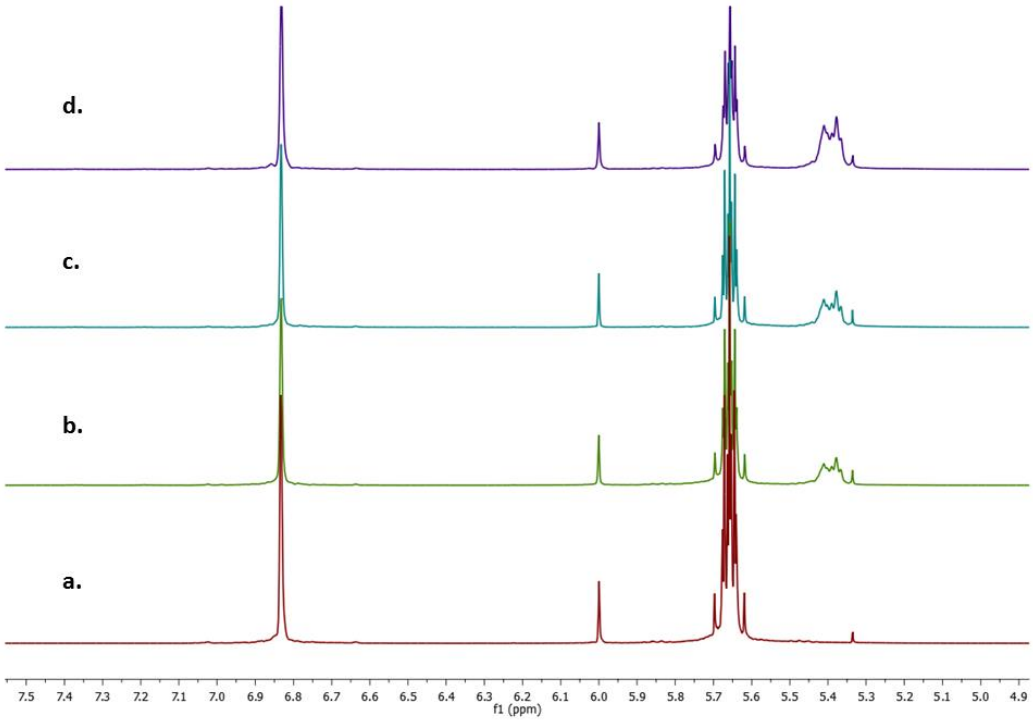
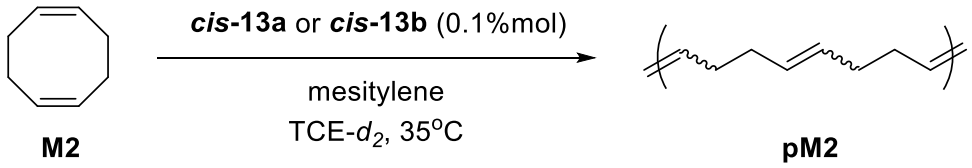


Figure S81. Change in Z/E ratio over time in ROMP of **M3** by ***cis*-13b** at 75°C. a. before addition of catalyst; b. after 1h; c. after 3h; d. after 24h

7.1.4. Latency of cis-13 precatalysts in presence of M2 (COD)



Scheme S12. Polymerization of **M2** with ***cis*-13** precatalysts.

7.1.4.1. cis-13a

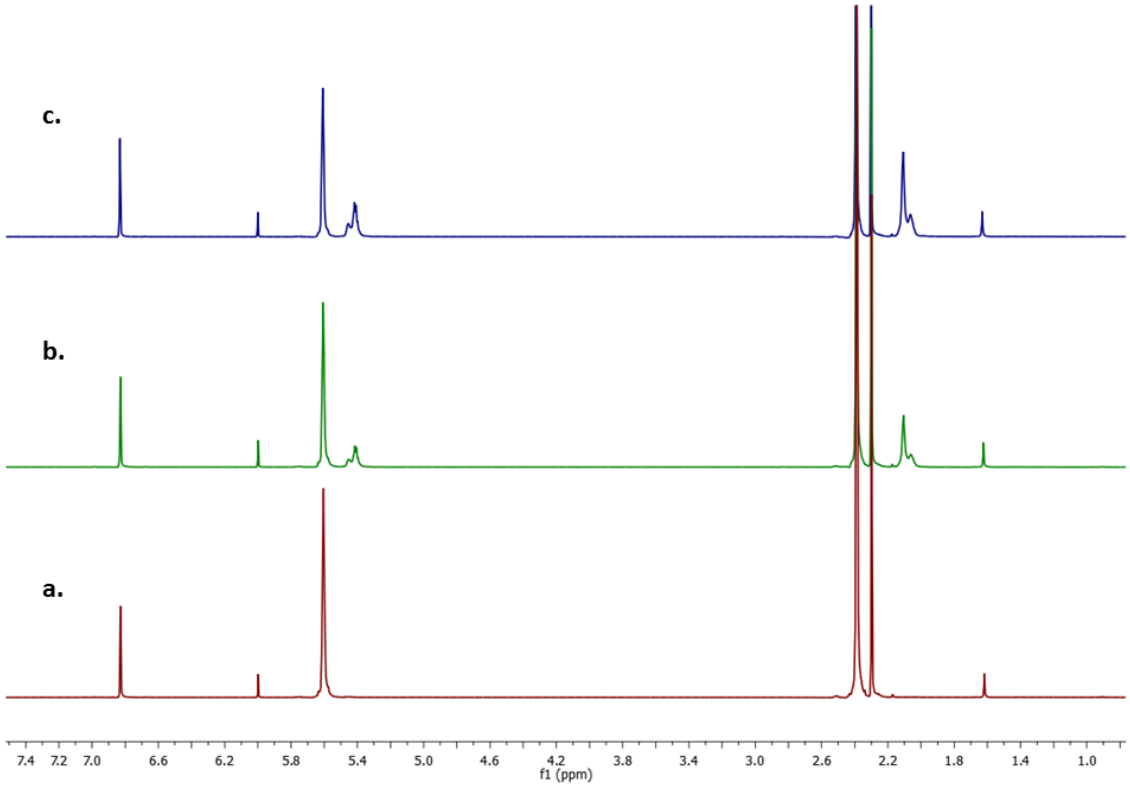


Figure S82. ^{1}H-NMR spectra of **M2** in presence of *cis*-**13a** after **a.** 0h (0% conversion), **b.** 3 days (19% conversion), and **c.** 10 days (29% conversion).

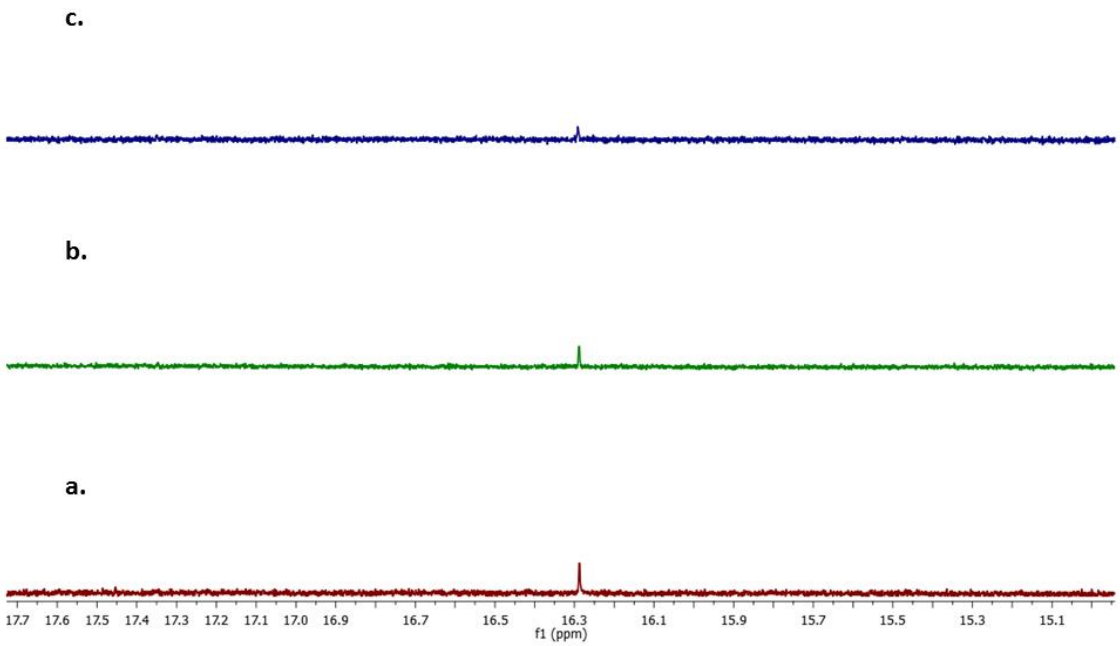


Figure S83. Carbenes region in ^{1}H-NMR spectra of **M2** in presence of *cis*-**13a** after **a.** 0h, **b.** 3 days, and **c.** 10 days.

7.1.4.2. cis-13b

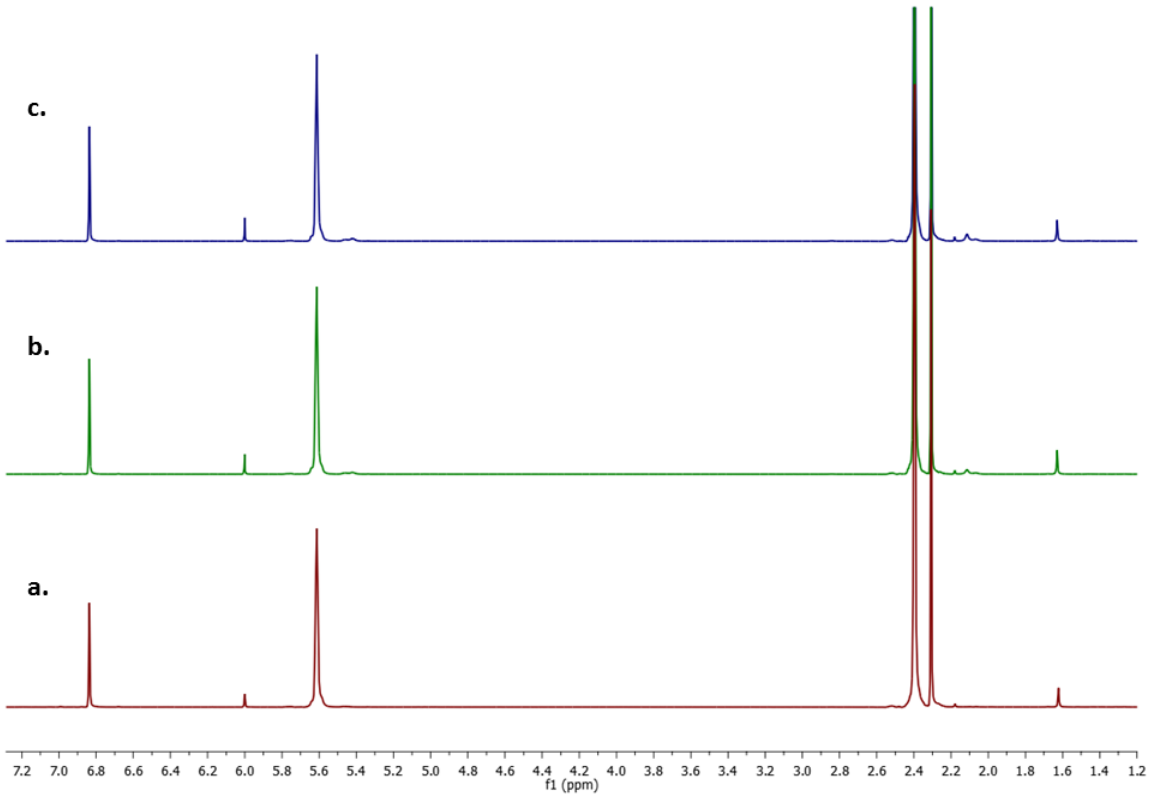


Figure S84. ^{1}H-NMR spectra of **M2** in presence of *cis*-**13b** after **a.** 0h (0% conversion), **b.** 3 days (0% conversion), and **c.** 10 days (4% conversion).

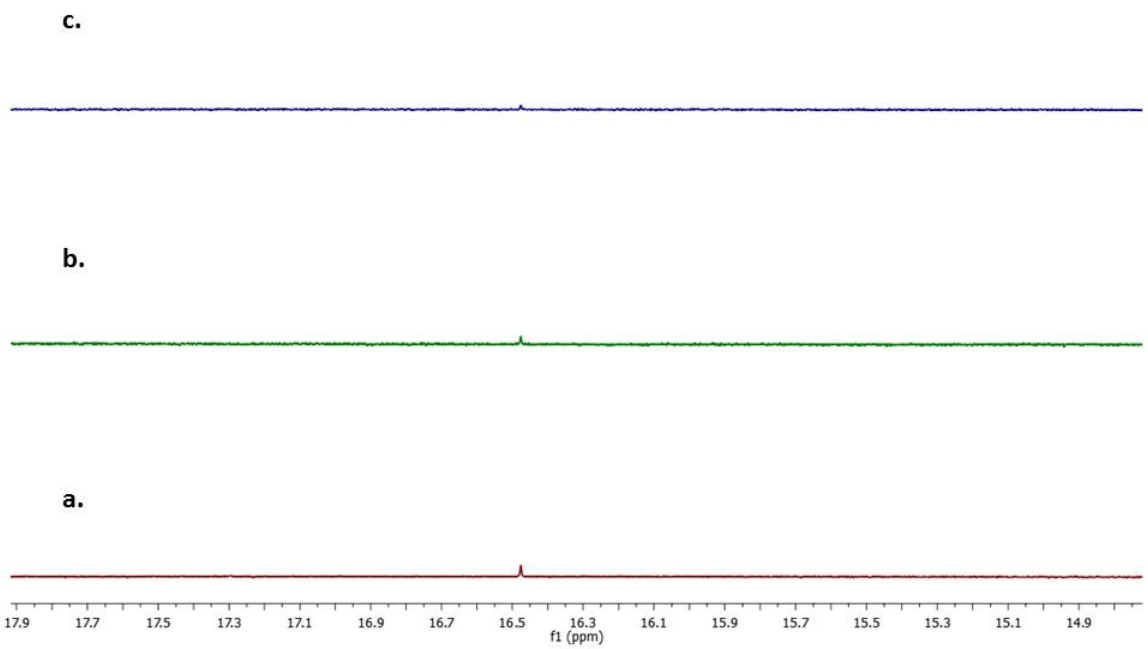
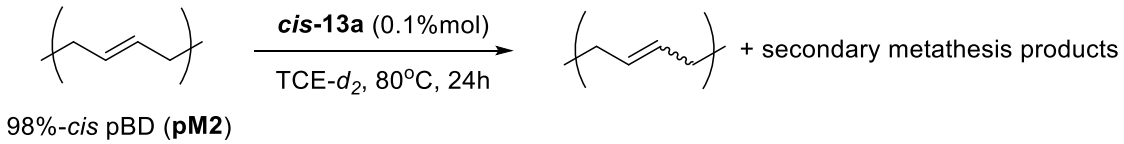


Figure S85. Carbenes region in ^{1}H-NMR spectra of **M2** in presence of *cis*-**13b** after **a.** 0h, **b.** 3 days, and **c.** 10 days.

7.1.5. Secondary metathesis reactions of pM2 (pBD) with *cis*-13a



Scheme S13. Secondary metathesis reactions of pBD in presence of ***cis*-13a**

Procedure: 25 mg pBD (**pM2**) (98% *cis*, M_w = 2.459×10^5Da , M_w/M_n=2.29) dissolved in 900 µL of $C_2D_2Cl_4$. The catalyst ***cis*-13a** (0.1mol%) was added in 100 µL of $C_2D_2Cl_4$. The reaction mixture was left for heating at 80°C for the specified periods of time and the reaction progress was monitored by ^{1}H-NMR.

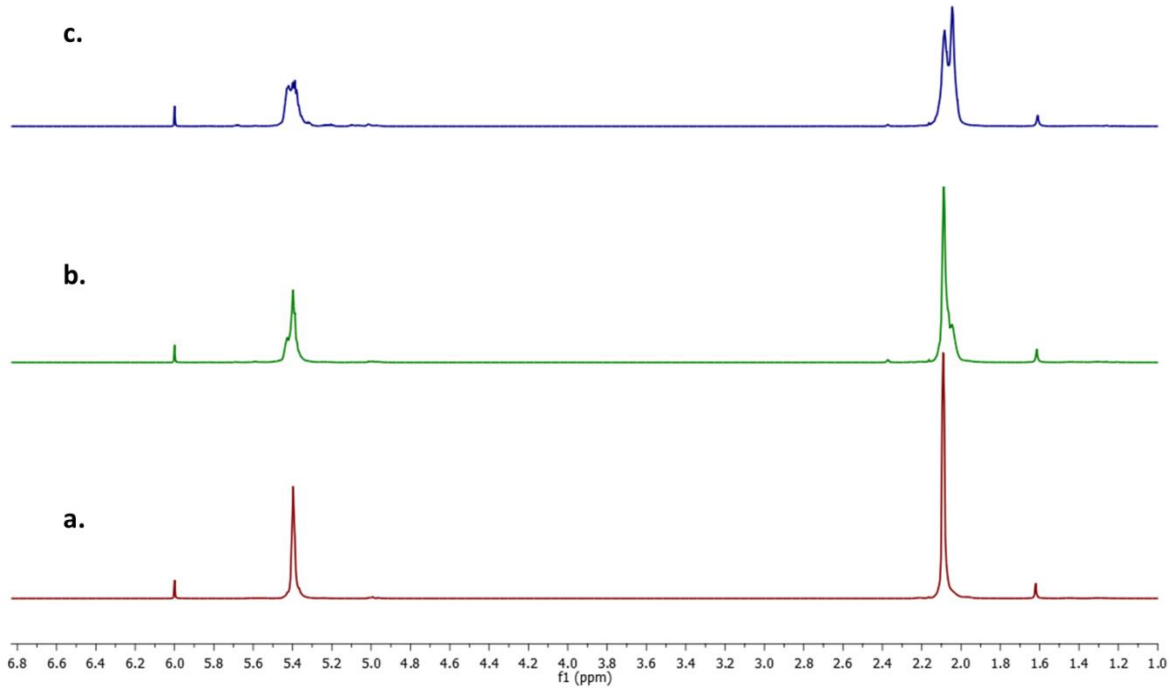


Figure S86. Following the progress of secondary metathesis reactions of pBD in the presence of ***cis*-13a** in $C_2D_2Cl_4$: a. before addition of the catalyst, b. after 2.5h at 80°C and c. after 24h at 80°C (*E/Z* = 1/0.96).

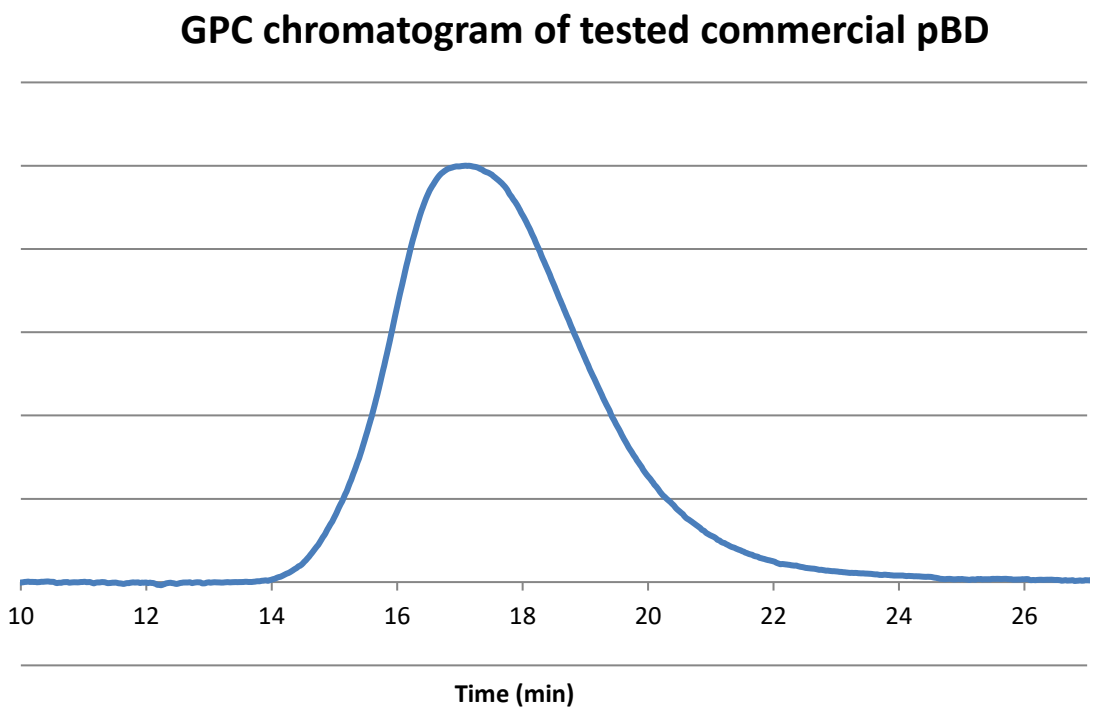
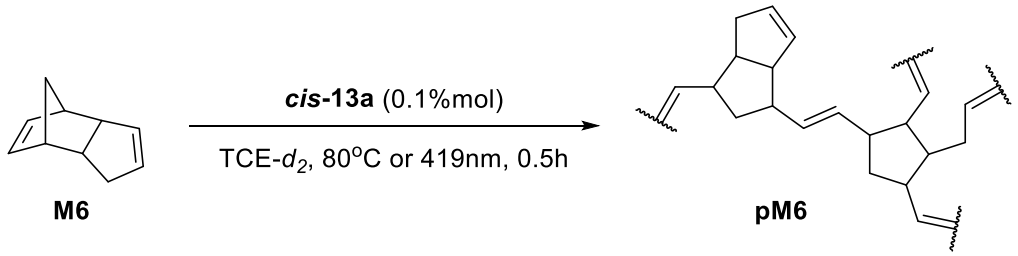


Figure S87. GPC chromatogram of commercial pBD (**pM2**) (Sigma-Aldrich, 98% *cis*, Mw = 246kDa, PDI=2.26).

7.1.6. Latency of cis-13a towards M6 (DCPD)



Scheme S14. Polymerization of **M6** (DCPD) with ***cis*-13a** pre-catalyst.

The procedure is same as for the reactions in the section 7.1.1. In control experiment the NMR test tube was covered with aluminium foil and kept at 35°C for 0.5 hours.

7.1.6.1. Polymerization at 80°C

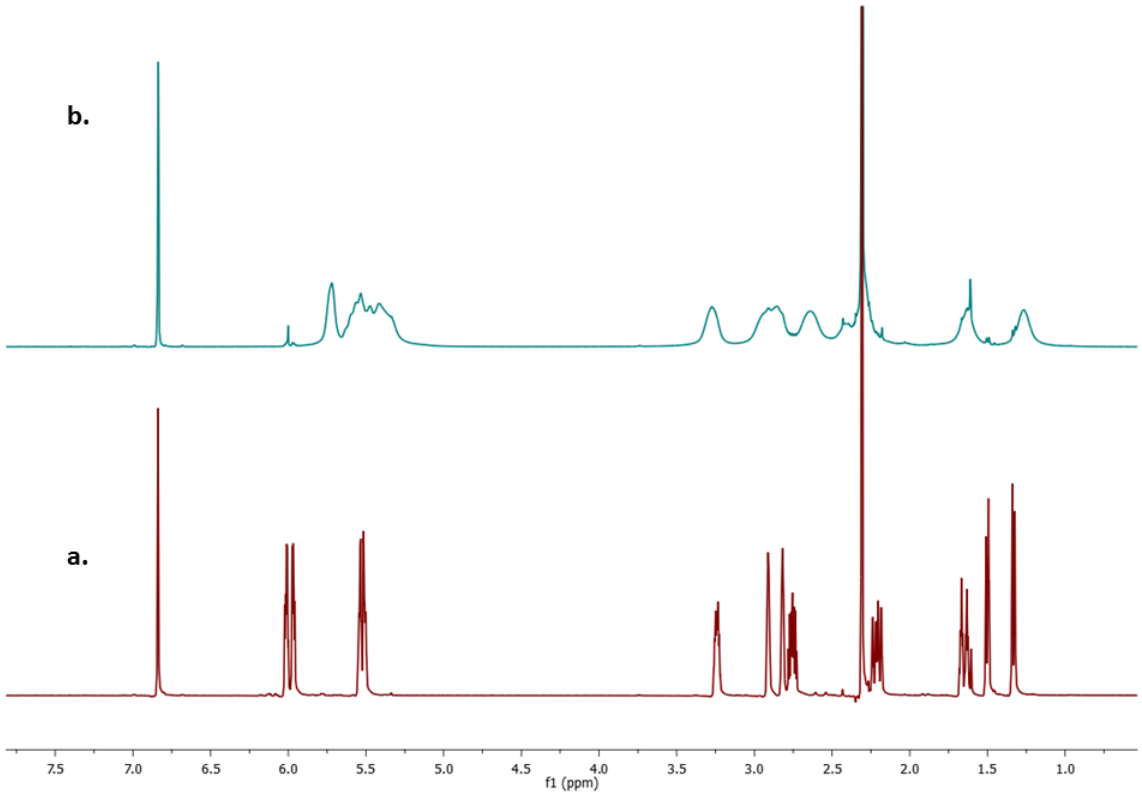


Figure S88. Polymerization of **M6** by ***cis*-13a** in TCE-d_2 at 80°C: a. before reaction; b. after 0.5h (100% conversion).

7.1.6.2. Polymerization at 419nm

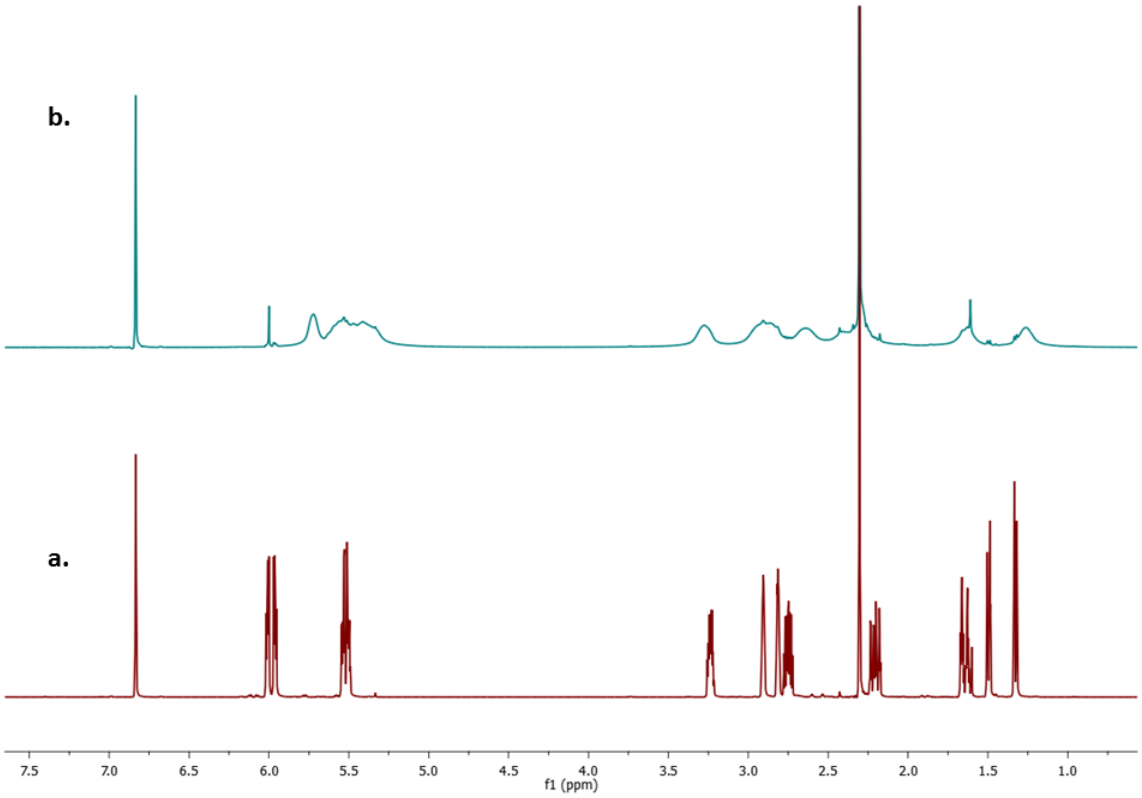


Figure S89. Polymerization of **M6** by ***cis*-13a** in TCE-d_2 at 419nm: a. before reaction; b. after 0.5h (100% conversion).

7.1.6.3. Dark control experiment at 35°C

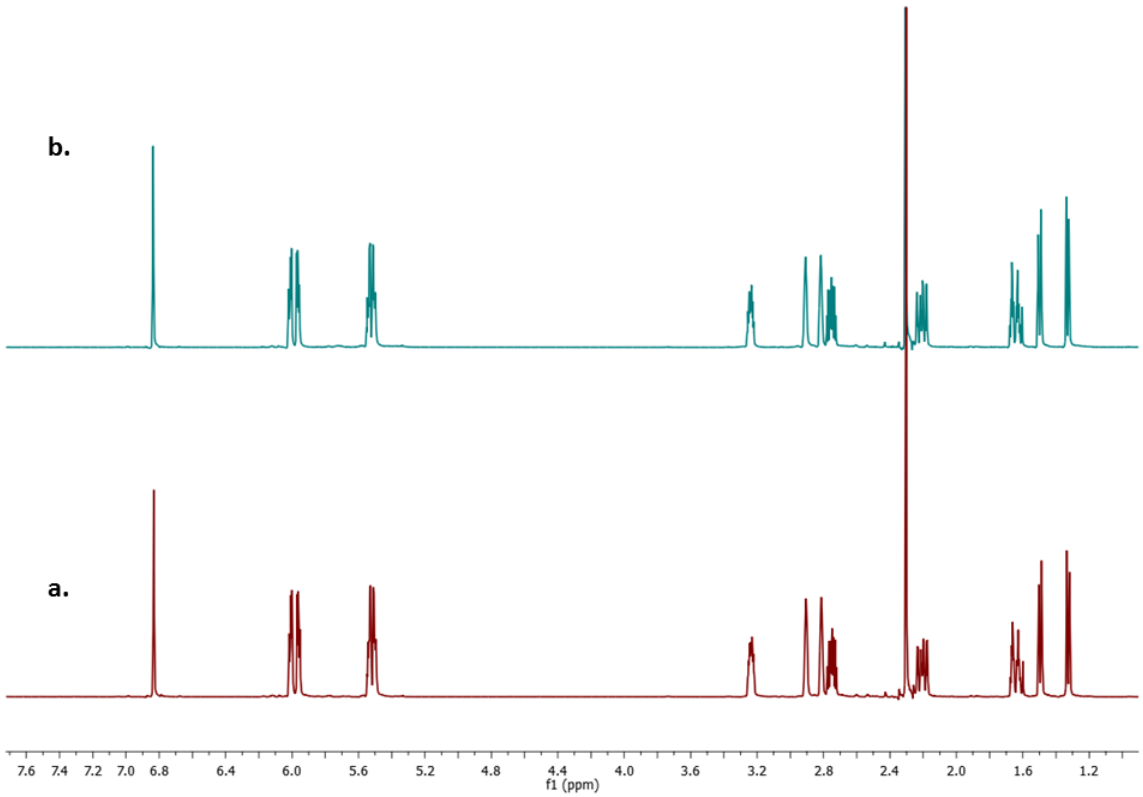
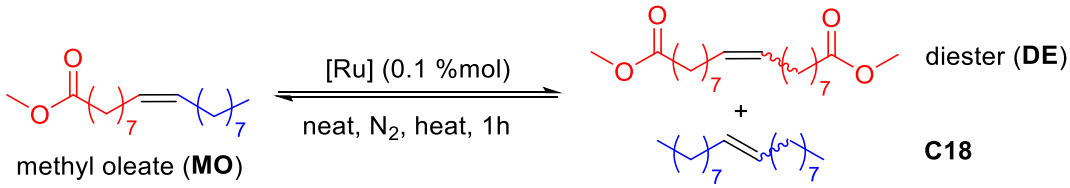


Figure S90. Dark control polymerization of **M6** by ***cis*-13a** in TCE-d_2 at 35°C: a. before reaction; b. after 0.5h (7% conversion).

7.2. Methyl oleate self-metathesis



Scheme S15. Self-metathesis of methyl oleate

Procedure: methyl oleate (**MO**) (210 µL, 0.62 mmol) was introduced into a pear-shaped flask equipped with a small magnet and a condenser. The air in the flask was replaced by N_2. The catalyst (0.001eq, 0.62 µmol) was added as CH_2Cl_2 solution. Then, the reaction was heated to 100°C or 120°C for 1h. After cooling of the reaction mixture to room temperature, 50µL of crude mixture were mixed with 25µL of mesitylene, and the sample, diluted in CH_2Cl_2, was injected to the GC-MS.

All the peaks in GC chromatogram were identified according to their mass. "X+n" and "X-n" (n is an integer) are homologues of X that differ by $(-CH_2-)_n$ units. The analysis of %isomerization was carried out by following the previously published method.[14]

CH_2Cl_2 was evaporated from the vessel by high vacuum followed by refilling the vessel with N_2 before beginning of the heating at 120°C.

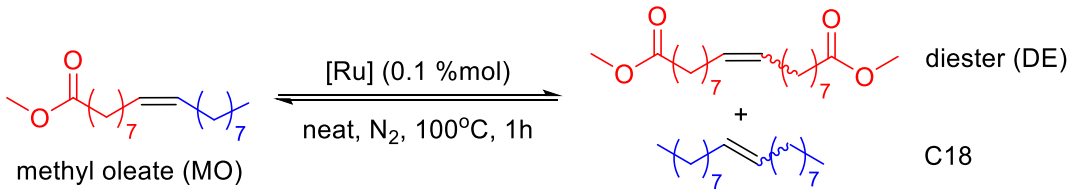
$$\%\boldsymbol{isomerization}(\boldsymbol{C18}) = \frac{\ldots+\%(C18-1)+\%(C18+1)+\ldots}{\ldots+\%(C18-1)+\%(C18)+\%(C18+1)+\ldots} \times 100\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{MO}) = \frac{\ldots+\%(MO-1)+\%(MO+1)+\ldots}{\ldots+\%(MO-1)+\%(MO)+\%(MO+1)+\ldots} \times 100\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{DE}) = \frac{\ldots+\%(DE-1)+\%(DE+1)+\ldots}{\ldots+\%(DE-1)+\%(DE)+\%(DE+1)+\ldots} \times 100\%$$

$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{\%\boldsymbol{isomerization}(\boldsymbol{C18})+\%\boldsymbol{isomerization}(\boldsymbol{MO})+\%\boldsymbol{isomerization}(\boldsymbol{DE})}{3}$$

7.2.1. Self-metathesis at 100°C



Scheme S16. Self-metathesis of methyl oleate at 100°C

7.2.1.1. trans-10a

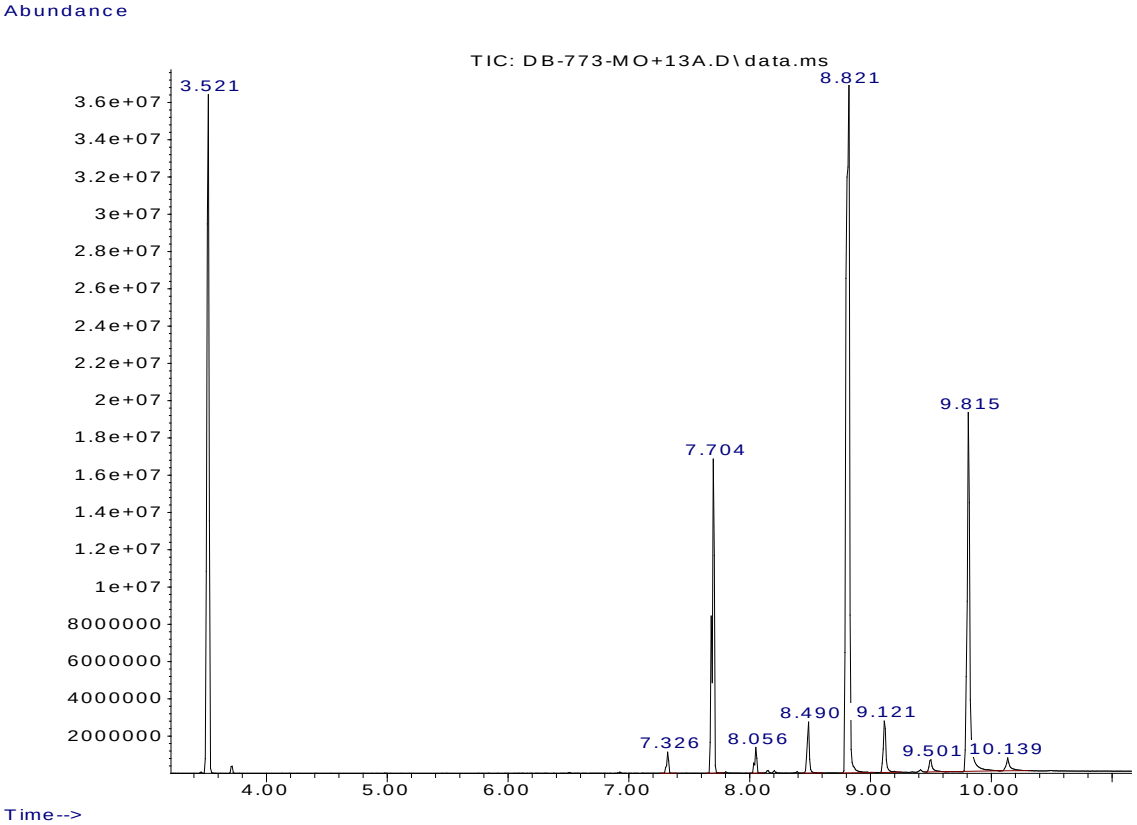


Figure S91. Self-metathesis of **MO** by ***trans*-10a** at 100°C.

Table S15. GC-MS chromatogram analysis of self-metathesis of **MO** with *trans*-**10a** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.521	Mesitylene	35789347	479537358	63.16%	25.15%
2	7.326	C18-1 (C17)	995880	13272747	1.75%	0.70%
3	7.704	C18	14917031	226326550	29.81%	11.87%
4	8.056	C18+1 (C19)	1213156	16869726	2.22%	0.89%
5	8.490	MO-1	2475473	35009882	4.61%	1.84%
6	8.821	MO	36172286	759194007	100.00%	39.81%
7	9.121	MO+1	2617870	43126632	5.68%	2.26%
8	9.501	DE-1	649962	12899481	1.70%	0.68%
9	9.815	DE	17934847	305595922	40.25%	16.02%
10	10.139	DE+1	641411	15241699	2.01%	0.80%

$$\%\boldsymbol{isomerization}(\boldsymbol{C18}) = \frac{0.70+0.89}{0.70+11.87+0.89} \times 100\% = \mathbf{11.81}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{MO}) = \frac{1.84+2.26}{1.84+39.81+2.26} \times 100\% = \mathbf{9.34}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{DE}) = \frac{0.68+0.80}{0.68+16.02+0.80} \times 100\% = \mathbf{8.46}\%$$

$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{11.81\%+9.34\%+8.46\%}{3} = \mathbf{9.87}\%$$

7.2.1.2. trans-10b

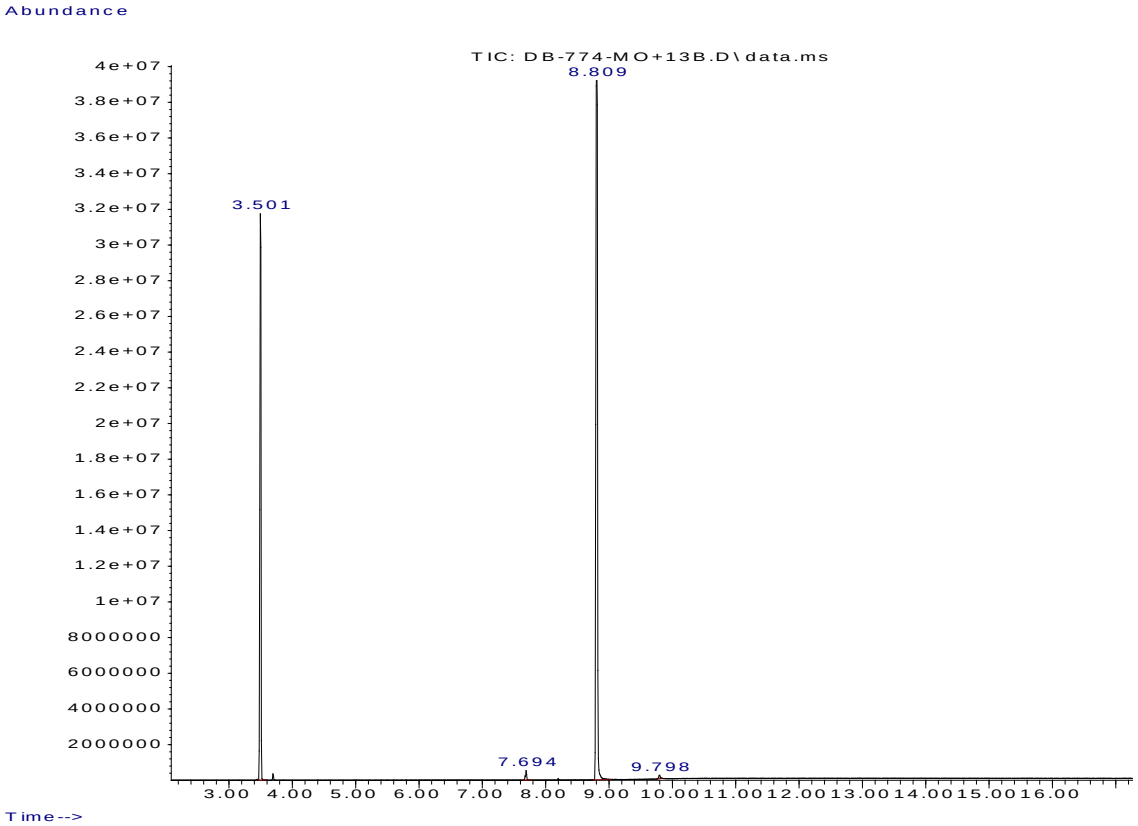


Figure S92. Self-metathesis of **MO** by ***trans*-10b** at 100°C.

Table S16. GC-MS chromatogram analysis of self-metathesis of **MO** with *trans*-**10b** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.501	Mesitylene	31894136	415996830	54.71%	35.07%
2	7.694	C18	485649	6859240	0.90%	0.58%
3	8.809	MO	239916773	760352579	100.00%	64.09%
4	9.798	DE	201175	3122187	0.41%	0.26%

Also after 24h under the reactions conditions (100°C, ***trans*-10b**), self-metathesis of **MO** was not observed in this case.

7.2.1.3. trans-13a

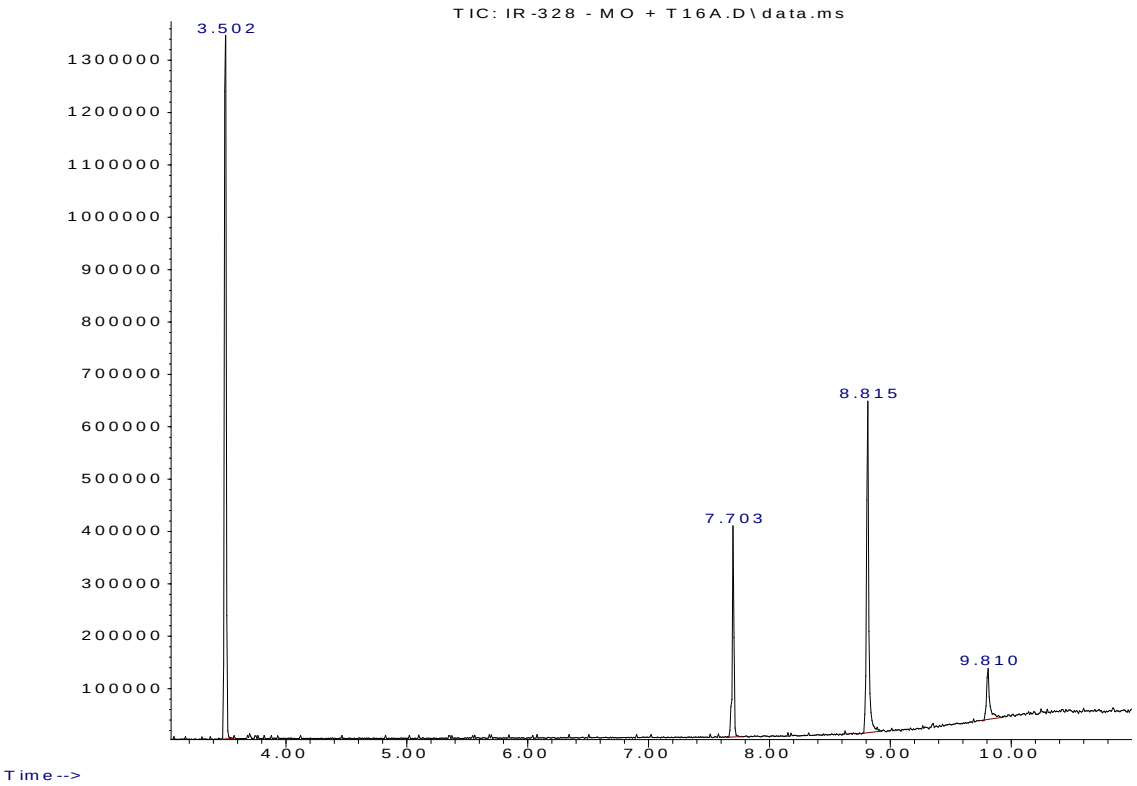


Figure S93. Self-metathesis of **MO** by ***trans*-13a** at 100°C.

Table S17. GC-MS chromatogram analysis of self-metathesis of **MO** with *trans*-**13a** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.502	Mesitylene	1344918	15479303	100.00%	52.659%
2	7.703	C18	331911	3916095	25.30%	13.322%
3	8.815	MO	584951	8244292	53.26%	28.046%
4	9.810	DE	91122	1755614	11.34%	5.972%

7.2.1.4. trans-13b

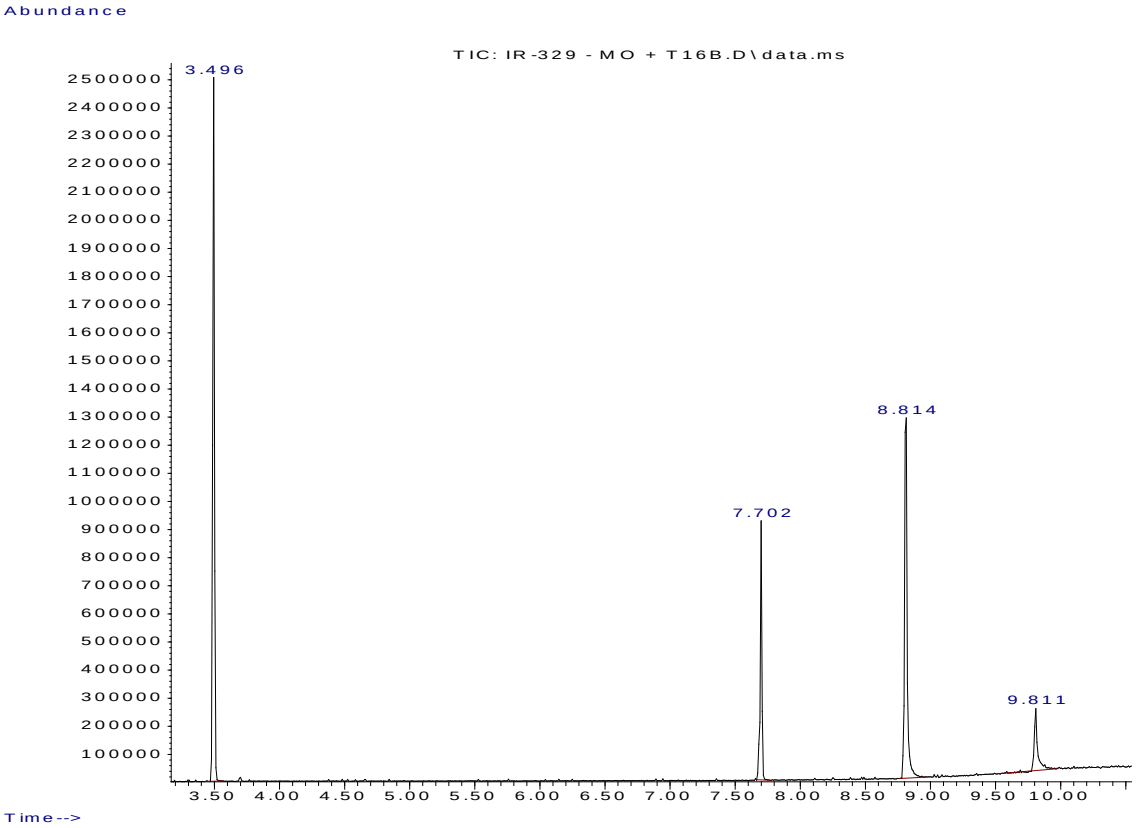


Figure S94. Self-metathesis of **MO** by ***trans*-13b** at 100°C.

Table S18. GC-MS chromatogram analysis of self-metathesis of **MO** with *trans*-**13b** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.496	Mesitylene	2241382	23887508	100.00%	44.172%
2	7.702	C18	744317	7973415	33.38%	14.744%
3	8.814	MO	1299934	18352463	76.83%	33.937%
4	9.811	DE	196966	3865406	16.18%	7.148%

7.2.1.5. cis-13a

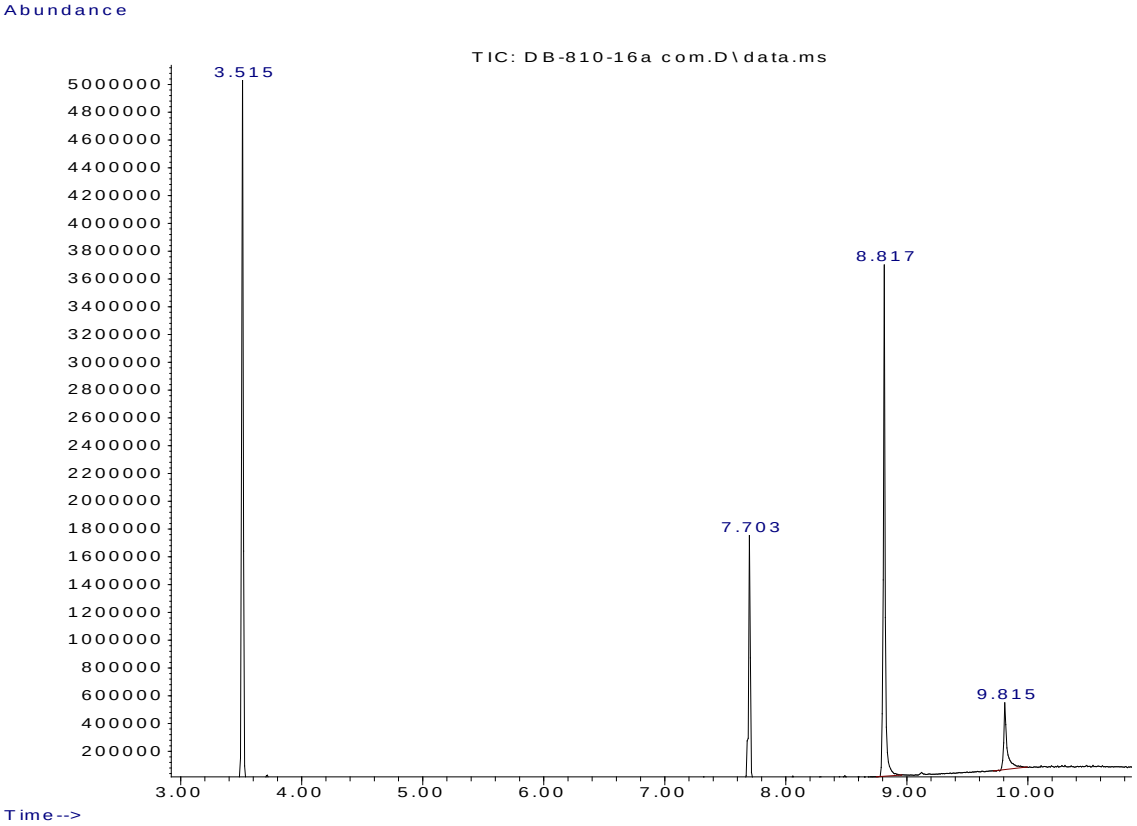


Figure S95. Self-metathesis of **MO** by ***cis*-13a** at 100°C.

Table S19. GC-MS chromatogram analysis of self-metathesis of **MO** with *cis*-**13a** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.515	Mesitylene	4441566	48158711	100.00%	42.691%
2	7.703	C18	1441518	16630076	34.53%	14.742%
3	8.817	MO	3097774	39181864	81.36%	34.734%
4	9.815	DE	434264	8836030	18.35%	7.833%

7.2.1.6. cis-13b

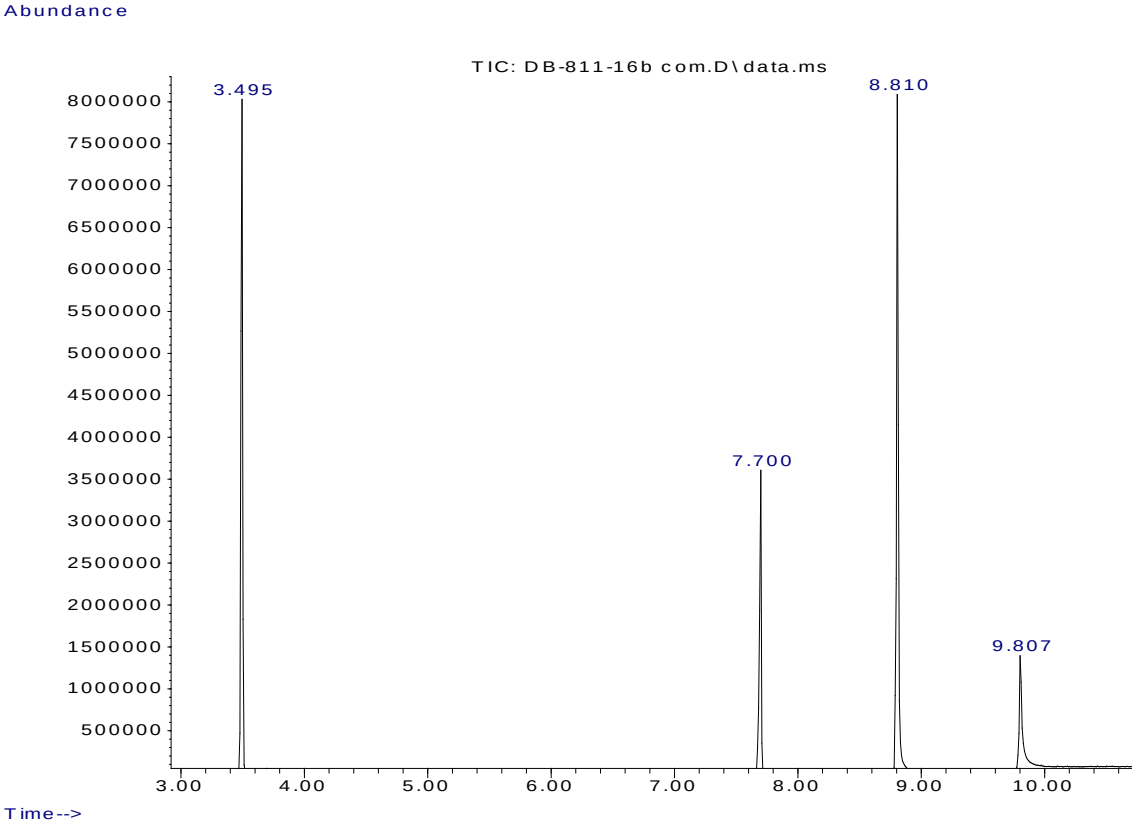


Figure S96. Self-metathesis of **MO** by ***cis*-13b** at 100°C.

Table S20. GC-MS chromatogram analysis of self-metathesis of **MO** with *cis*-**13b** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.495	Mesitylene	7391645	80835632	89.59%	34.812%
2	7.700	C18	3158122	35822544	39.70%	15.427%
3	8.810	MO	7357932	90225111	100.00%	38.856%
4	9.807	DE	1210556	25321770	28.07%	10.905%

7.2.1.7. cis-14a

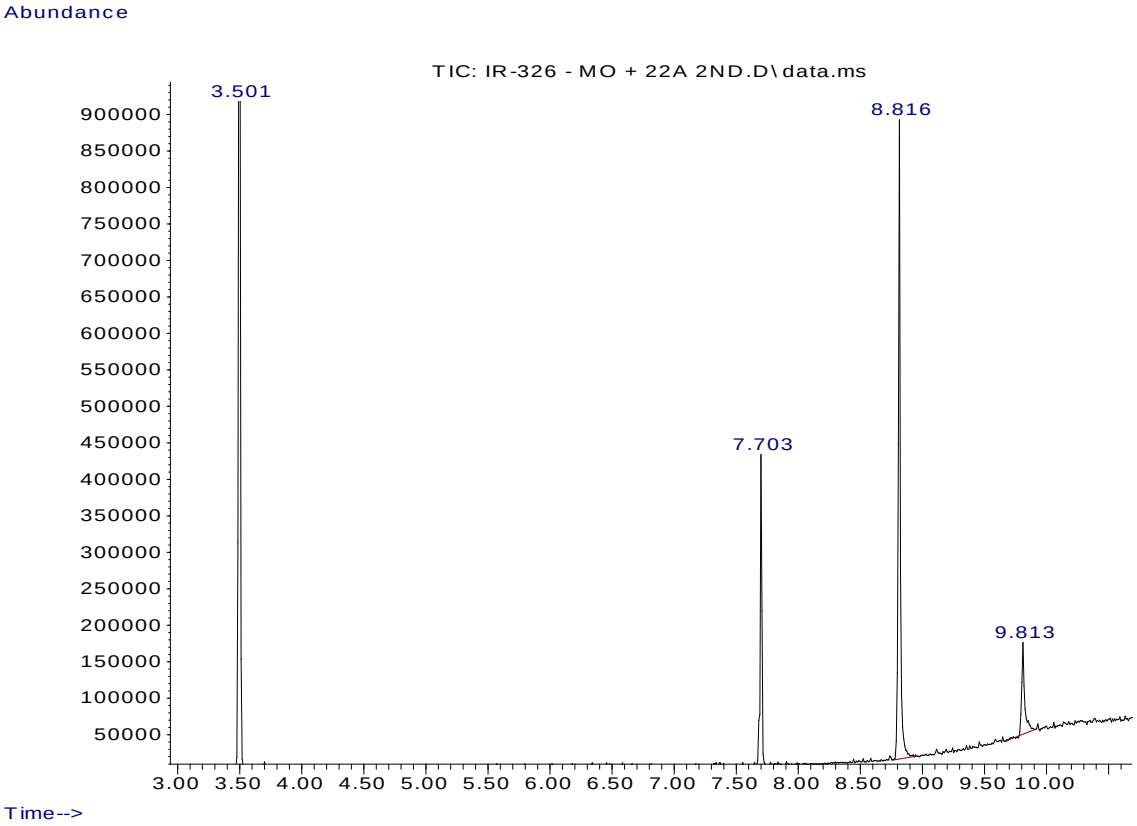


Figure S97. Self-metathesis of **MO** by ***cis*-14a** at 100°C.

Table S21. GC-MS chromatogram analysis of self-metathesis of **MO** with *cis*-**14a** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.501	Mesitylene	1154120	14147825	100.00%	46.836%
2	7.703	C18	351883	4109537	29.05%	13.604%
3	8.816	MO	758784	9885642	69.87%	32.726%
4	9.813	DE	110224	2064187	14.59%	6.833%

7.2.1.8. cis-14b

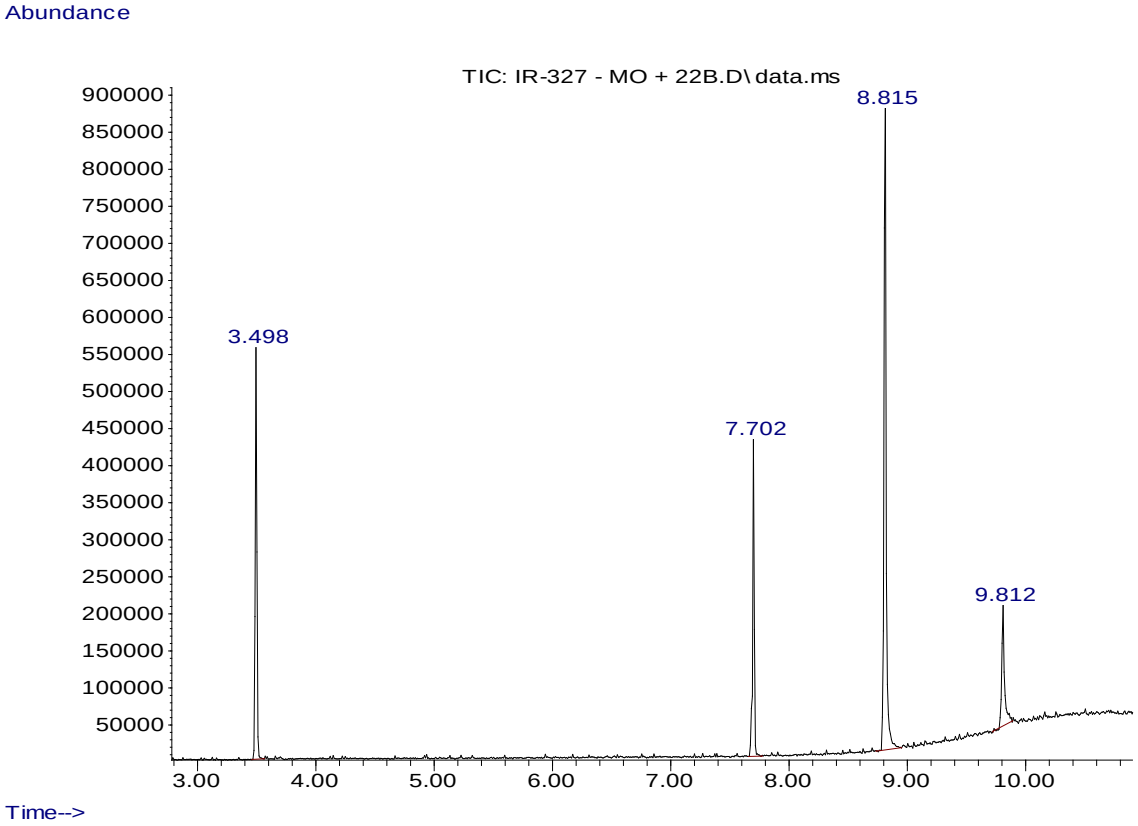


Figure S98. Self-metathesis of **MO** by ***cis*-14b** at 100°C.

Table S22. GC-MS chromatogram analysis of self-metathesis of **MO** with *cis*-**14b** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.498	Mesitylene	482004	5547382	47.38%	23.274%
2	7.702	C18	348585	4034902	34.46%	16.928%
3	8.815	MO	854918	11708389	100.00%	49.121%
4	9.812	DE	144207	2544921	21.74%	10.677%

7.2.1.9. Hoveyda-Grubbs 2nd generation (HG2) catalyst

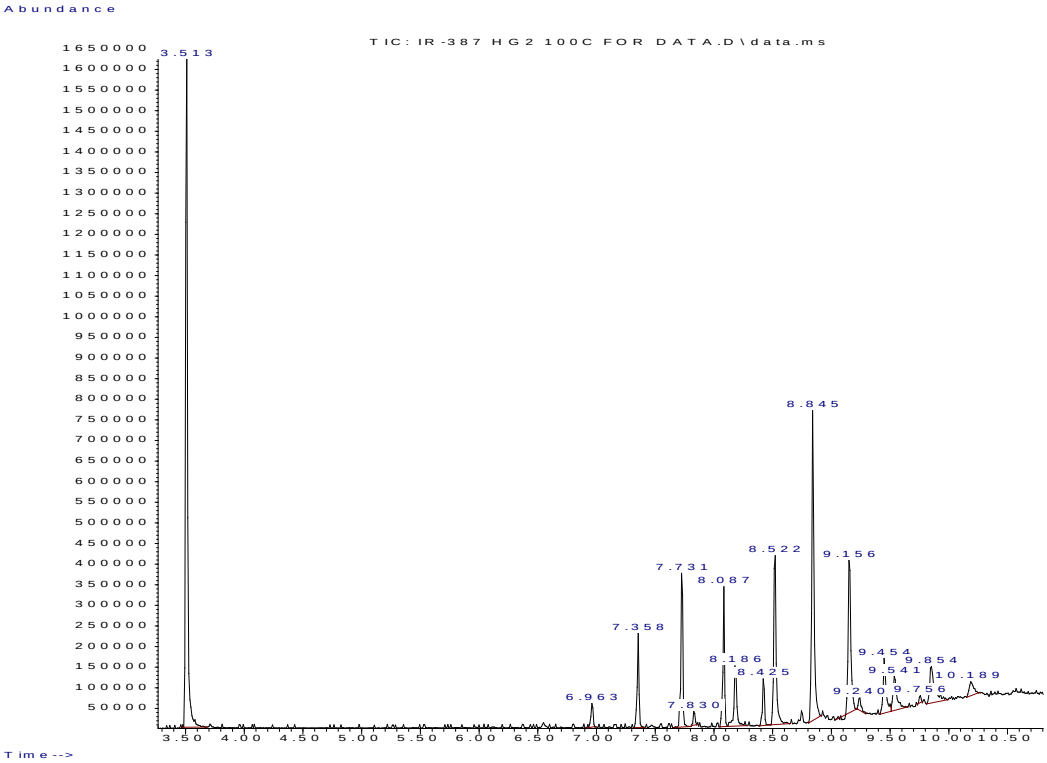


Figure S99. Self-metathesis of **MO** by ***HG2*** at 100°C.

Table S23. GC-MS chromatogram analysis of self-metathesis of **MO** with **HG2** at 100°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.513	Mesitylene	1486844	20014844	100.00%	30.323%
2	6.963	C18-2 (C16)	58554	788724	3.94%	1.195%
3	7.358	C18-1 (C17)	195696	2457683	12.28%	3.723%
4	7.731	C18	365635	4651221	23.24%	7.047%
5	7.830	MO-3	35654	391237	1.95%	0.593%
6	8.079	C18+1 (C19)	284810	3278241	16.38%	4.967%
7	8.186	MO-2	142000	2455760	12.27%	3.721%
8	8.425	C18+2 (C20)	105578	1394365	6.97%	2.113%
9	8.522	MO-1	403183	6281187	31.38%	9.516%
10	8.845	MO	702833	10079482	50.36%	15.271%
11	9.156	MO+1	362850	5812906	29.04%	8.807%
12	9.454	MO+2	123836	2351252	11.75%	3.562%
13	9.541	DE-1	78897	1895227	9.47%	2.871%
14	9.756	MO+3	17640	190209	0.95%	0.288%
15	9.854	DE	88334	2578318	12.88%	3.906%
16	10.189	DE+1	34078	903466	4.51%	1.369%

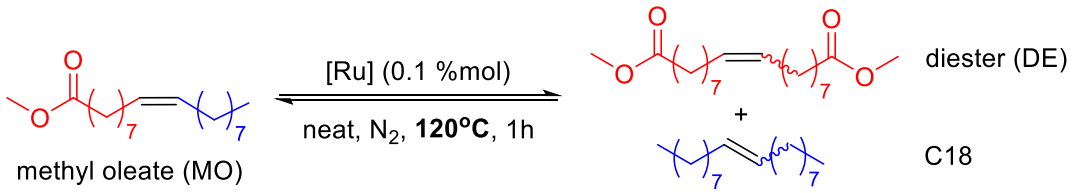
$$\%\boldsymbol{isomerization}(\boldsymbol{C18}) = \frac{1.19 + 3.72 + 4.97 + 0.21}{1.19 + 3.72 + 7.05 + 4.97 + 0.21} \times 100\% = \mathbf{58.87}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{MO}) = \frac{0.59 + 3.72 + 9.52 + 8.81 + 3.56 + 0.29}{0.59 + 3.72 + 9.52 + 15.27 + 8.81 + 3.56 + 0.29} \times 100\% = \mathbf{63.43}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{DE}) = \frac{2.87 + 1.37}{2.87 + 3.91 + 1.37} \times 100\% = \mathbf{51.67}\%$$

$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{58.87 + 63.43 + 51.67}{3} = \mathbf{57.99}\%$$

7.2.2. Self-metathesis at 120°C



Scheme S17. Self-metathesis of methyl oleate at 120°C

7.2.2.1. trans-10a

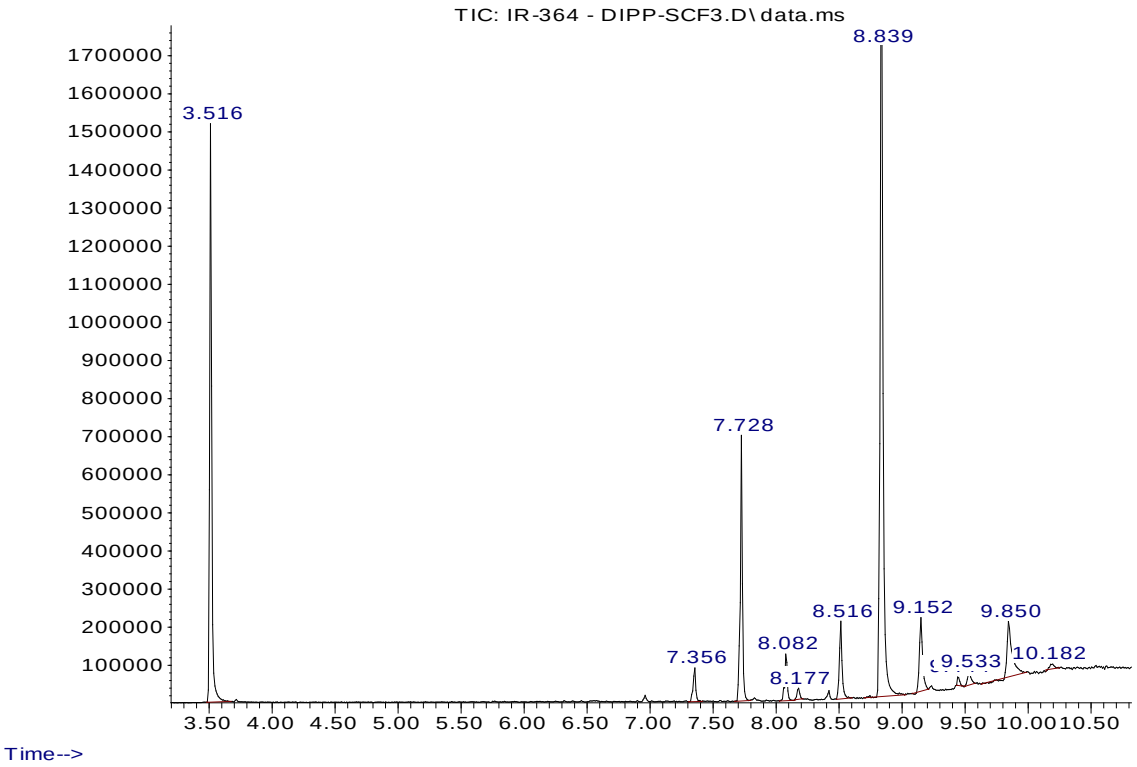


Figure S100. Self-metathesis of **MO** by ***trans*-10a** at 120°C.

Table S24. GC-MS chromatogram analysis of self-metathesis of **MO** with *trans*-**10a** at 120°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.516	Mesitylene	1364033	17321891	55.52%	24.308%
2	7.356	C18-1 (C17)	83066	1280333	4.10%	1.797%
3	7.728	C18	631725	8049604	25.80%	11.296%
4	8.082	C18+1 (C19)	113673	1721290	5.52%	2.416%
5	8.177	MO-2	29651	416479	1.33%	0.584%
6	8.516	MO-1	186037	3002079	9.62%	4.213%
7	8.839	MO	1814763	31197354	100.00%	43.780%
8	9.152	MO+1	181444	3213150	10.30%	4.509%
9	9.444	MO+2	24223	295347	0.95%	0.414%
10	9.533	DE-1	34878	654150	2.10%	0.918%
11	9.850	DE	137776	3776671	12.11%	5.300%
12	10.182	DE+1	13478	330996	1.06%	0.464%

$$\%\boldsymbol{isomerization}(\boldsymbol{C18}) = \frac{1.80 + 2.42}{1.80 + 11.30 + 2.42} \times 100\% = \mathbf{27.19}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{MO}) = \frac{0.58 + 4.21 + 4.51 + 0.41}{0.58 + 4.21 + 43.78 + 4.51 + 0.41} \times 100\% = \mathbf{18.15}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{DE}) = \frac{0.92 + 0.46}{0.92 + 5.3 + 0.46} \times 100\% = \mathbf{20.68}\%$$

$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{27.19 + 18.15 + 20.68}{3} = \mathbf{22.01}\%$$

7.2.2.2. trans-10b

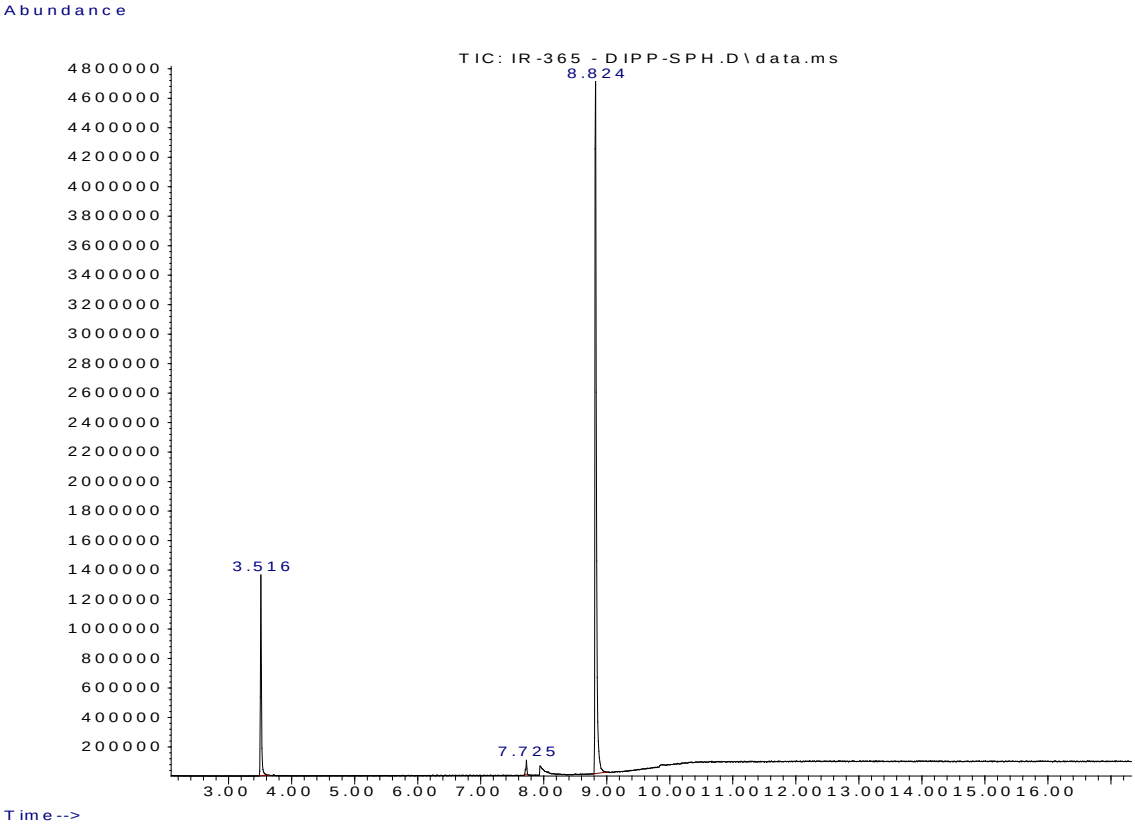


Figure S101. Self-metathesis of **MO** by ***trans*-10b** at 120°C.

No reaction was observed in this case (in accordance with the experiment at 100°C).

7.2.2.3. cis-13a

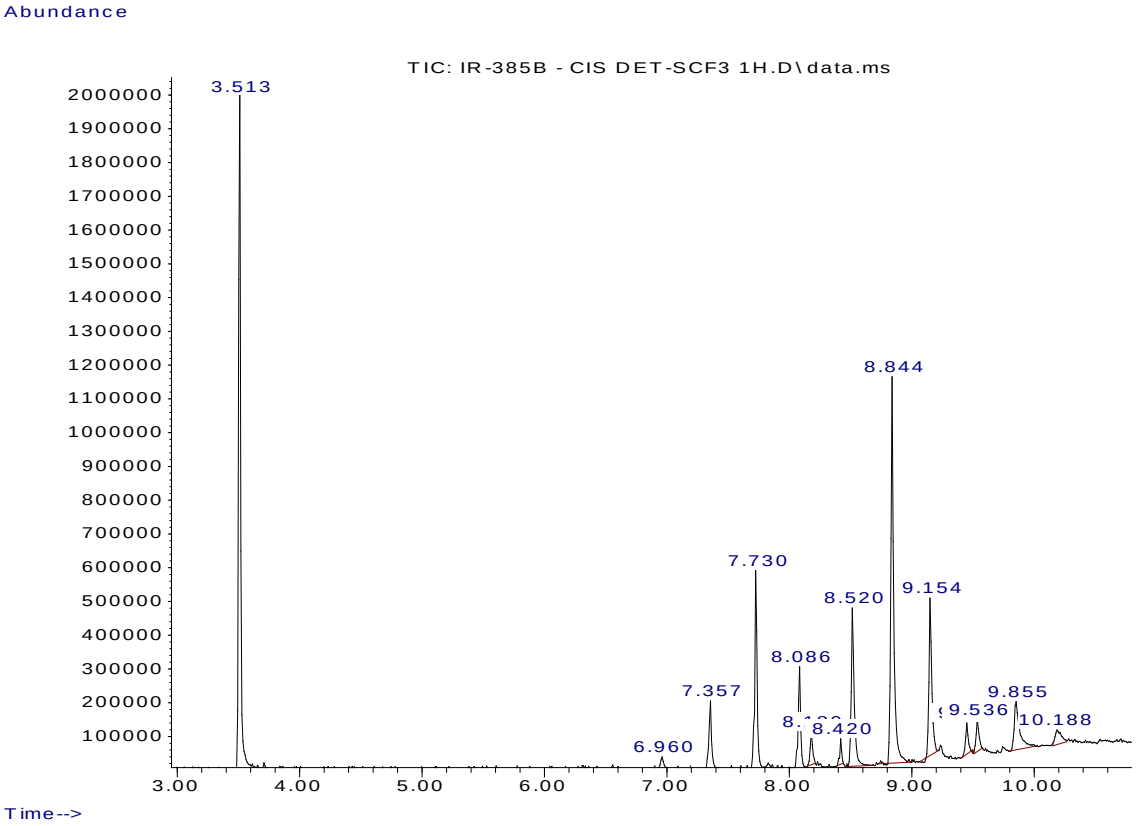


Figure S102. Self-metathesis of **MO** by ***cis*-13a** at 120°C.

Table S25. GC-MS chromatogram analysis of self-metathesis of **MO** with *cis*-**13a** at 120°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.513	Mesitylene	1818843	24617605	100.00%	29.157%
2	6.960	C18-2 (C16)	32615	490284	1.99%	0.581%
3	7.357	C18-1 (C17)	182952	2976023	12.09%	3.525%
4	7.730	C18	546310	7739071	31.44%	9.166%
5	8.086	C18+1 (C19)	272955	3981302	16.17%	4.715%
6	8.180	MO-2	96525	1343414	5.46%	1.591%
7	8.420	C18+2 (C20)	75729	798633	3.24%	0.946%
8	8.520	MO-1	410483	7968578	32.37%	9.438%
9	8.837	MO	1065054	18456777	74.97%	21.860%
10	9.154	MO+1	430859	7265634	29.51%	8.605%
11	9.449	MO+2	91985	1362470	5.53%	1.614%
12	9.536	DE-1	94545	1554878	6.32%	1.842%
13	9.855	DE	139574	4394970	17.85%	5.205%
14	10.188	DE+1	43331	1480877	6.02%	1.754%

$$\%\boldsymbol{isomerization}(\boldsymbol{C18}) = \frac{0.58 + 3.52 + 4.71 + 0.95}{0.58 + 3.52 + 9.17 + 4.71 + 0.95} \times 100\% = \mathbf{51.56}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{MO}) = \frac{1.59 + 9.44 + 8.60 + 1.61}{1.59 + 9.44 + 21.86 + 8.60 + 1.61} \times 100\% = \mathbf{49.28}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{DE}) = \frac{1.84 + 1.75}{1.84 + 5.20 + 1.75} \times 100\% = \mathbf{40.84}\%$$

$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{51.56\% + 49.28\% + 40.84\%}{3} = \mathbf{47.23}\%$$

7.2.2.4. cis-13b

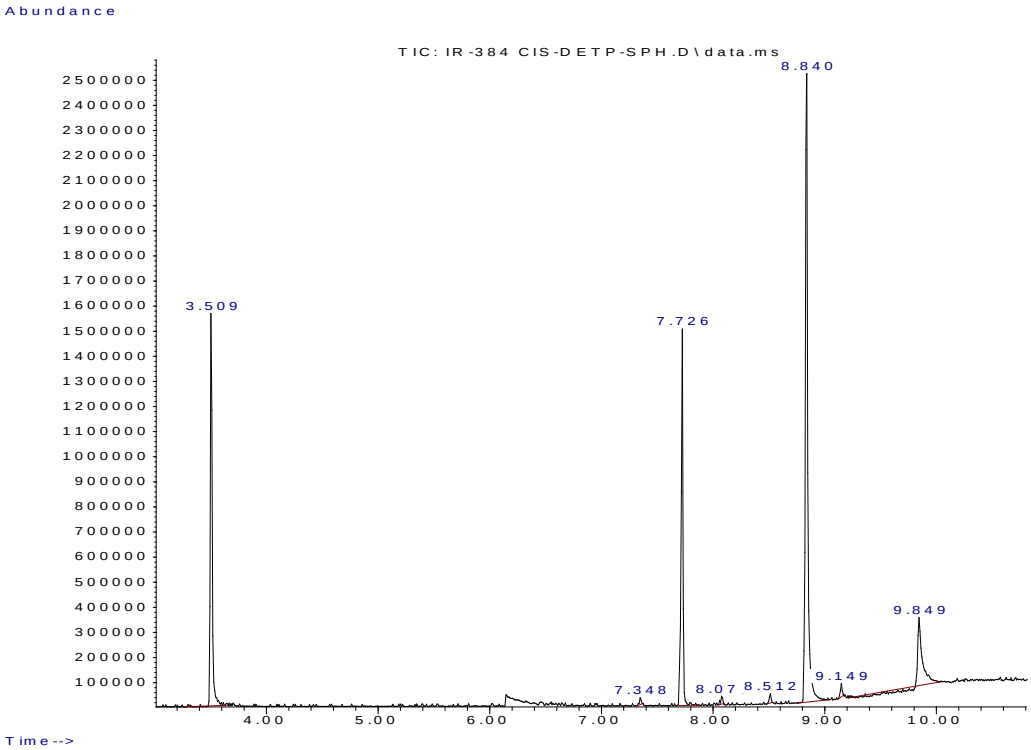


Figure S103. Self-metathesis of **MO** by ***cis*-13b** at 120°C.

Table S26. GC-MS chromatogram analysis of self-metathesis of **MO** with *cis*-**13b** at 120°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.509	Mesitylene	1437779	19195732	49.70%	23.427%
2	7.348	C18-1 (C17)	27804	307426	0.80%	0.375%
3	7.726	C18	1410930	17186516	44.50%	20.975%
4	8.079	C18+1 (C19)	32693	402195	1.04%	0.491%
5	8.512	MO-1	37429	423396	1.10%	0.517%
6	8.840	MO	2515493	38619661	100.00%	47.132%
7	9.149	MO+1	53093	582980	1.51%	0.711%
8	9.849	DE	247969	5221078	13.52%	6.372%

$$\%\boldsymbol{isomerization(C18)} = \frac{0.37 + 0.49}{0.37 + 20.97 + 0.49} \times 100\% = \mathbf{3.94}\%$$

$$\%\boldsymbol{isomerization(MO)} = \frac{0.52 + 0.71}{0.52 + 47.13 + 0.71} \times 100\% = \mathbf{2.54}\%$$

$$\%\boldsymbol{isomerization(DE)} = \frac{0}{6.37} \times 100\% = \mathbf{0}\%$$

$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{3.94+2.54+0}{3} = \mathbf{2.16}\%$$

7.2.2.5. *cis*-14a

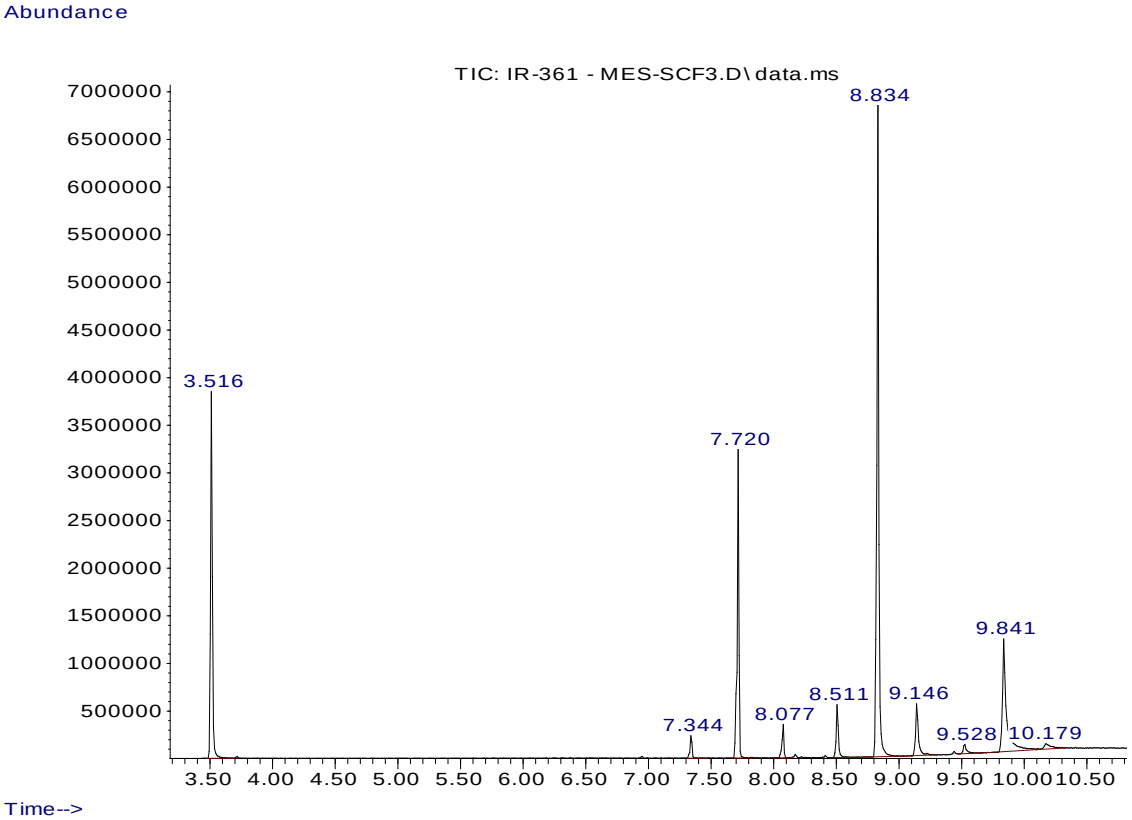


Figure S104. Self-metathesis of **MO** by ***cis*-14a** at 120°C.

Table S27. GC-MS chromatogram analysis of self-metathesis of **MO** with *cis*-**14a** at 120°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.516	Mesitylene	3426121	39873985	51.79%	19.853%
2	7.344	C18-1 (C17)	221742	2745985	3.57%	1.367%
3	7.720	C18	2861231	31806721	41.31%	15.836%
4	8.077	C18+1 (C19)	327104	3713238	4.82%	1.849%
5	8.511	MO-1	496738	6680731	8.68%	3.326%
6	8.834	MO	6326625	76987840	100.00%	38.332%
7	9.146	MO+1	507097	8249333	10.72%	4.107%
8	9.528	DE-1	92992	1899486	2.47%	0.946%
9	9.841	DE	1092891	26524527	34.45%	13.206%
10	10.179	DE+1	52402	2363855	3.07%	1.177%

$$\%\boldsymbol{isomerization}(\boldsymbol{C18}) = \frac{1.37 + 1.85}{1.37 + 15.84 + 1.85} \times 100\% = \mathbf{16.89}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{MO}) = \frac{3.33 + 4.11}{3.33 + 38.33 + 4.11} \times 100\% = \mathbf{16.26}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{DE}) = \frac{0.95 + 1.18}{0.95 + 13.21 + 1.18} \times 100\% = \mathbf{13.88}\%$$

$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{16.89 + 16.26 + 13.88}{3} = \mathbf{15.68}\%$$

7.2.2.6. *cis*-14b

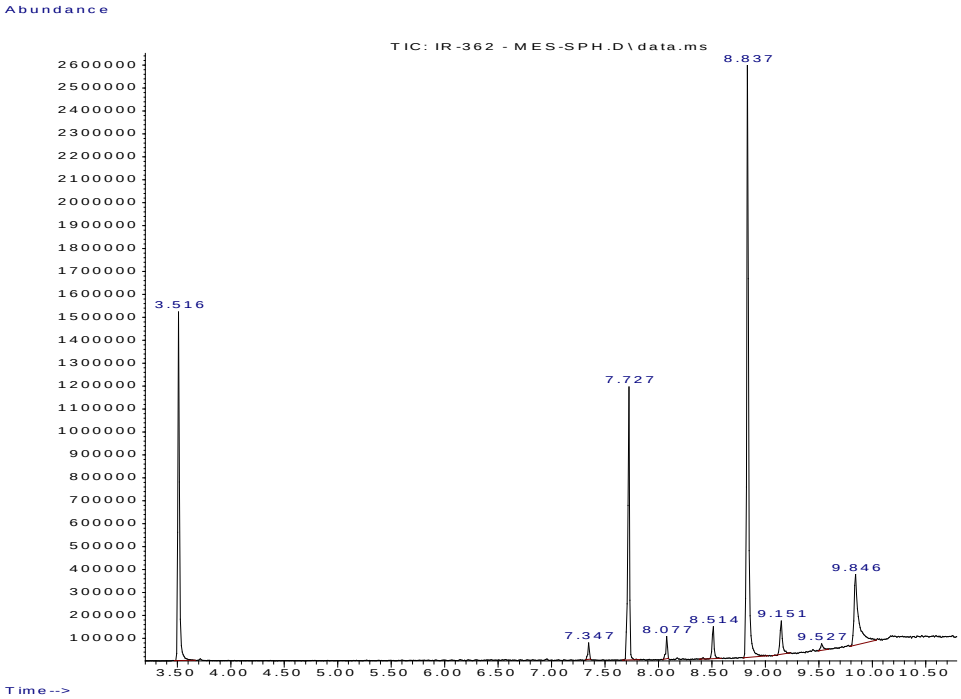


Figure S105. Self-metathesis of **MO** by ***cis*-14b** at 120°C.

Table S28. GC-MS chromatogram analysis of self-metathesis of **MO** with *cis*-**14b** at 120°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.516	Mesitylene	1355160	16765590	52.05%	21.663%
2	7.347	C18-1 (C17)	71899	690012	2.14%	0.892%
3	7.727	C18	1086791	13090813	40.64%	16.915%
4	8.077	C18+1 (C19)	98781	996735	3.09%	1.288%
5	8.514	MO-1	131531	1867171	5.80%	2.413%
6	8.837	MO	2431623	32211664	100.00%	41.622%
7	9.151	MO+1	136972	2199925	6.83%	2.843%
8	9.527	DE-1	28708	492545	1.53%	0.636%
9	9.846	DE	297621	9076727	28.18%	11.728%

$$\%\boldsymbol{isomerization(C18)} = \frac{0.89 + 1.29}{0.89 + 16.92 + 1.29} \times 100\% = \mathbf{11.41}\%$$

$$\%\boldsymbol{isomerization(MO)} = \frac{2.41 + 2.84}{2.41 + 41.61 + 2.84} \times 100\% = \mathbf{11.20}\%$$

$$\%\boldsymbol{isomerization(DE)} = \frac{0.64}{0.64 + 11.73} \times 100\% = \mathbf{5.17}\%$$

$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{11.41 + 11.20 + 5.17}{3} = \mathbf{9.26}\%$$

7.2.2.7. Hoveyda-Grubbs 2nd generation (HG2) catalyst

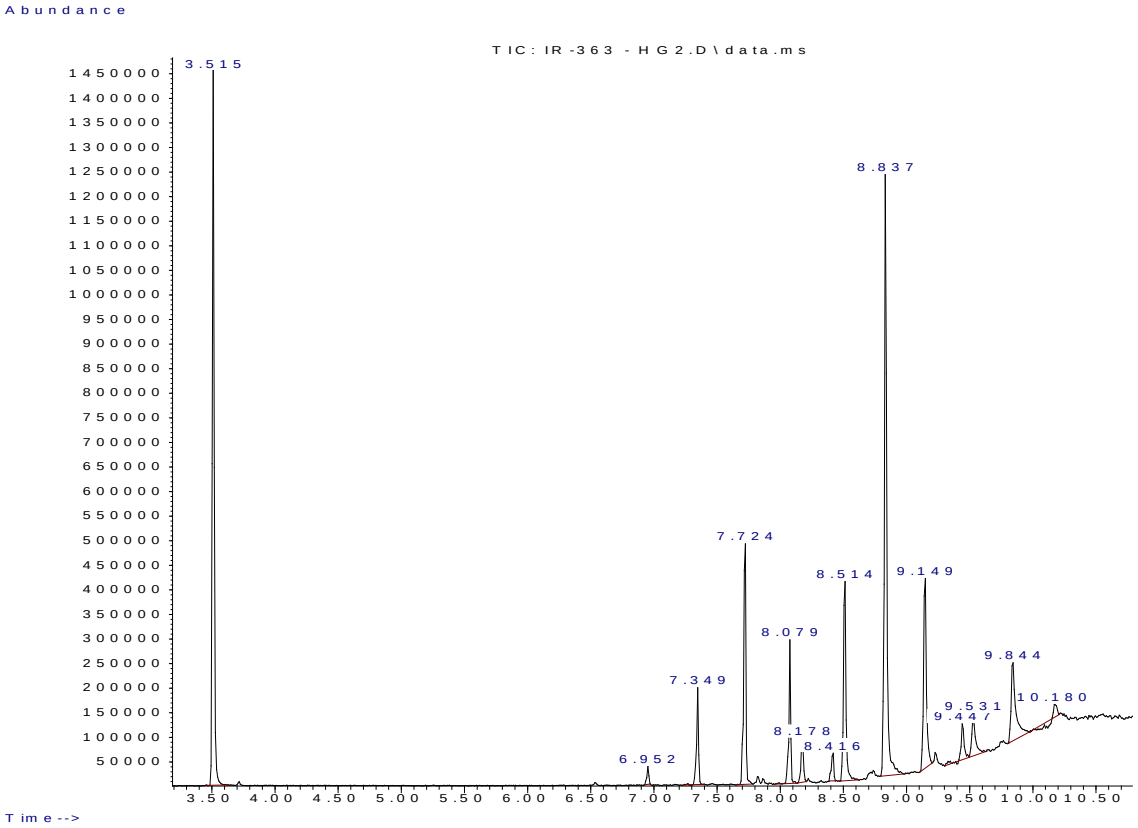


Figure S106. Self-metathesis of **MO** by ***HG2*** at 120°C.

Table S29. GC-MS chromatogram analysis of self-metathesis of **MO** with **HG2** at 120°C.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.515	Mesitylene	1304894	15442315	95.27%	23.915%
2	6.952	C18-2 (C16)	36392	384248	2.37%	0.595%
3	7.349	C18-1 (C17)	175729	2059642	12.71%	3.190%
4	7.724	C18	470402	6341680	39.12%	9.821%
5	8.079	C18+1 (C19)	255119	2892449	17.84%	4.480%
6	8.178	MO-2	84886	1186736	7.32%	1.838%
7	8.416	C18+2 (C20)	60190	738995	4.56%	1.144%
8	8.514	MO-1	398548	5749066	35.47%	8.904%
9	8.837	MO	1140473	16209049	100.00%	25.103%
10	9.149	MO+1	383719	5971245	36.84%	9.248%
11	9.447	MO+2	70819	1234760	7.62%	1.912%
12	9.531	DE-1	81747	1674198	10.33%	2.593%
13	9.844	DE	158263	4039718	24.92%	6.256%
14	10.174	DE+1	32431	646574	3.99%	1.001%

$$\%\boldsymbol{isomerization}(\boldsymbol{C18}) = \frac{0.59 + 3.19 + 4.48 + 1.14}{0.59 + 3.19 + 9.82 + 4.48 + 1.14} \times 100\% = \mathbf{48.91}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{MO}) = \frac{1.84 + 8.90 + 9.25 + 1.91}{1.84 + 8.90 + 25.10 + 9.25 + 1.91} \times 100\% = \mathbf{46.60}\%$$

$$\%\boldsymbol{isomerization}(\boldsymbol{DE}) = \frac{2.59 + 1.00}{2.59 + 6.26 + 1.00} \times 100\% = \mathbf{36.45}\%$$

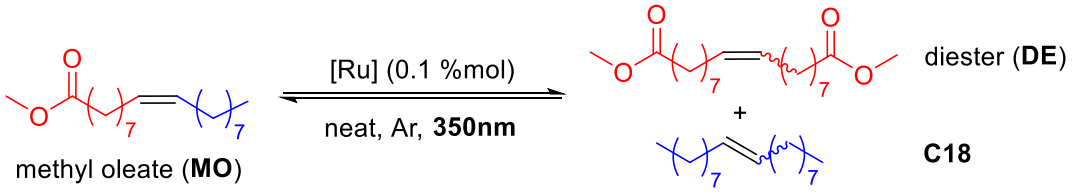
$$\boldsymbol{average}\ \%\boldsymbol{isomerization} = \frac{48.91\% + 46.60\% + 36.45\%}{3} = \mathbf{43.99}\%$$

7.2.2.8. Summary of the results for thermal isomerization in self-metathesis of methyl oleate

Table S30. Summary of average isomerization percentage in thermally activated self-metathesis of MO.

Catalyst	Average isomerization at 100°C	Average isomerization at 120°C	Remarks
10a (*trans*)	10%	22%	
10b *(trans)*	no reaction	no reaction	no reaction even at 160°C
***trans*-13a**	0%	NA	
***cis*-13a**	0%	47%	
***trans*-13b**	0%	NA	
***cis*-13b**	0%	2%	
***cis*-14a**	0%	16%	
***cis*-14b**	0%	9%	
HG2	58%	44%	

7.2.3. Photo-activated self-metathesis of methyl oleate with *cis*-13a and *cis*-14a



Scheme S18. Self-metathesis of methyl oleate at 350nm irradiation

General procedure: precatalyst (***cis*-13a** or ***cis*-14a**) (0.001 eq., 0.3 µmol, 0.2 mg) was dissolved in 20 µL of CH_2Cl_2 inside a 1.5 mL vial equipped with small magnet. Methyl oleate (**MO**) (110 µL, 0.32 mmol) was added by syringe. The air in the vial was replaced by argon gas. Then, the reaction mixture was irradiated in a Luzchem LZC-ORG photoreactor overnight (14h) with 350nm lamps. At the end of the reaction, 50 µL of the crude mixture were mixed with 10 µL of mesitylene, and the mixture was injected to GC-MS for analysis.

The dark control experiments were done with the same amounts and conditions, but the vial was wrapped completely with aluminium foil.

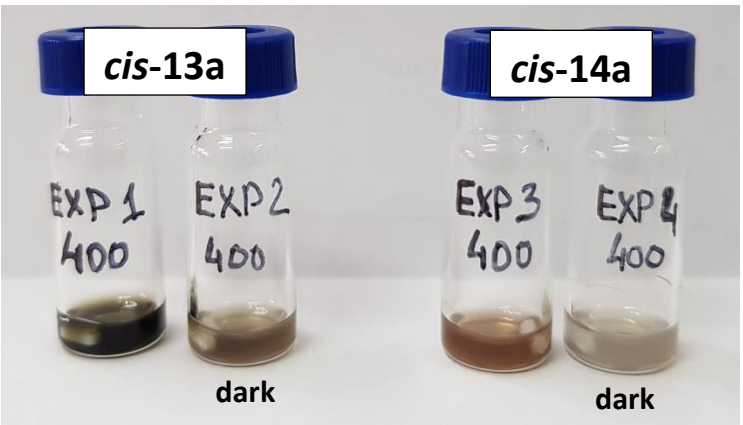


Figure S107. The vials after reaction.

7.2.3.1. Methyl oleate and cis-13a irradiated by 350nm

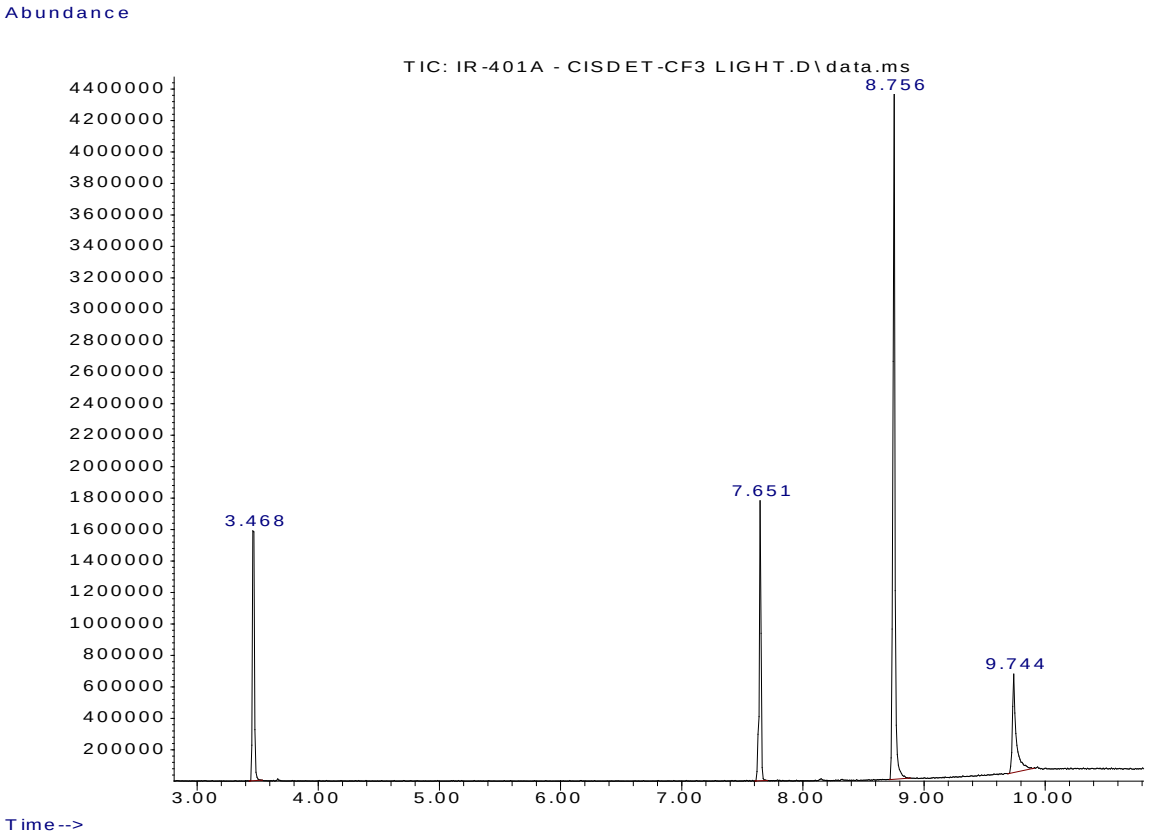


Figure S108. Self-metathesis of **MO** by ***cis*-13a** at 350nm irradiation.

Table S31. GC-MS chromatogram analysis of photoinduced (350 nm) self-metathesis of **MO** with *cis*-**13a**.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.468	Mesitylene	1631447	19599426	37.33%	18.866%
2	7.651	C18	1581907	18451002	35.15%	17.761%
3	8.756	MO	4104013	52498956	100.00%	50.535%
4	9.744	DE	589336	13337532	25.41%	12.839%

7.2.3.2. Methyl oleate and cis-13a irradiated by 350nm - dark control experiment

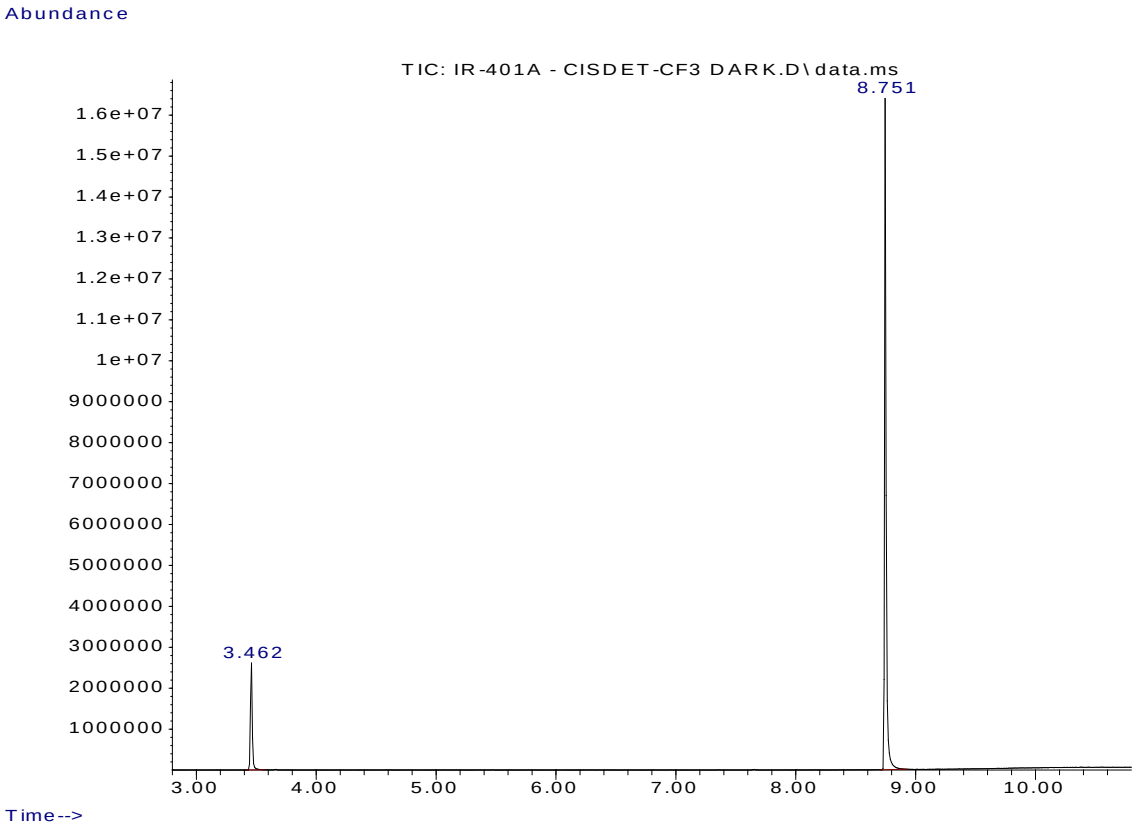


Figure S109. Self-metathesis of **MO** by ***cis*-13a** at 350nm irradiation (dark control).

7.2.3.3. Methyl oleate and cis-14a irradiated by 350nm

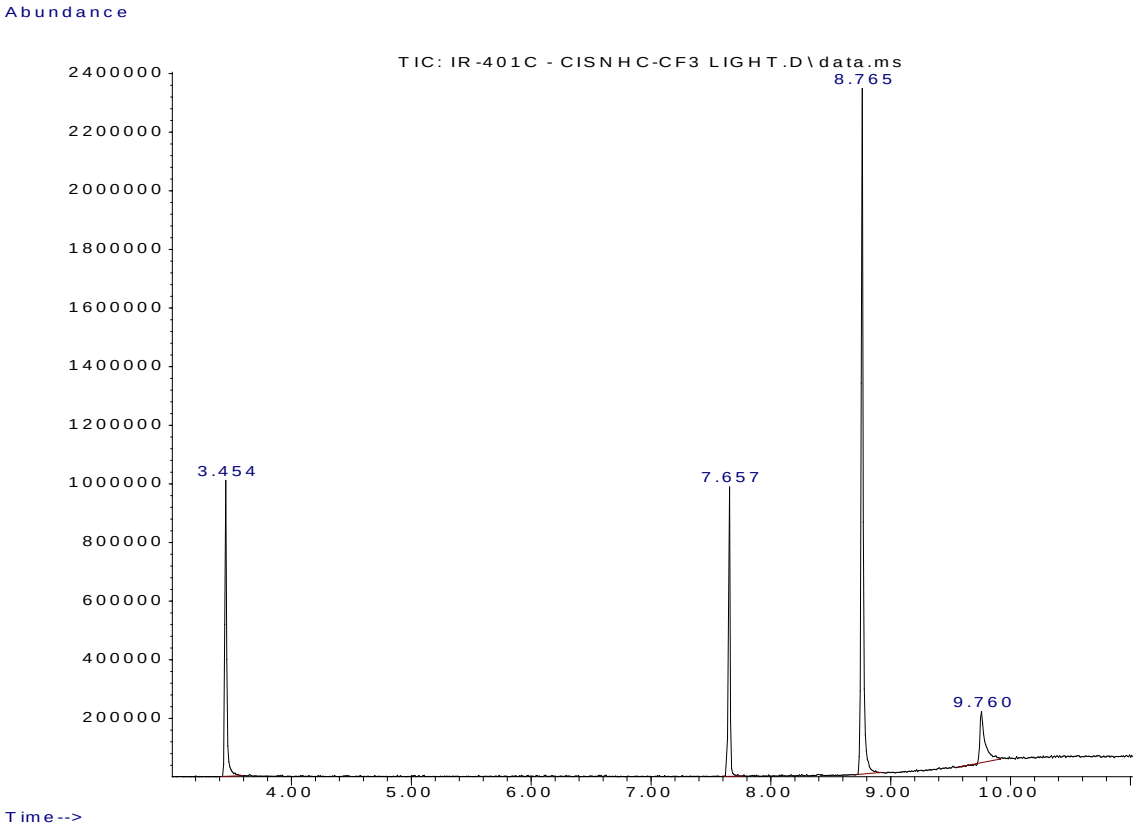


Figure S110. Self-metathesis of **MO** by ***cis*-14a** at 350nm irradiation.

Table S32. GC-MS chromatogram analysis of photoinduced (350 nm) self-metathesis of **MO** with *cis*-**14a**.

peak	R.T. (min)	identification	peak height	corr. area	corr. % max.	% of total
1	3.454	Mesitylene	897048	11539013	39.99%	20.670%
2	7.657	C18	883411	10384564	35.99%	18.602%
3	8.765	MO	2191445	28851797	100.00%	51.683%
4	9.760	DE	169923	5049309	17.50%	9.045%

7.2.3.3. Methyl oleate and cis-14a irradiated by 350nm - dark control experiment

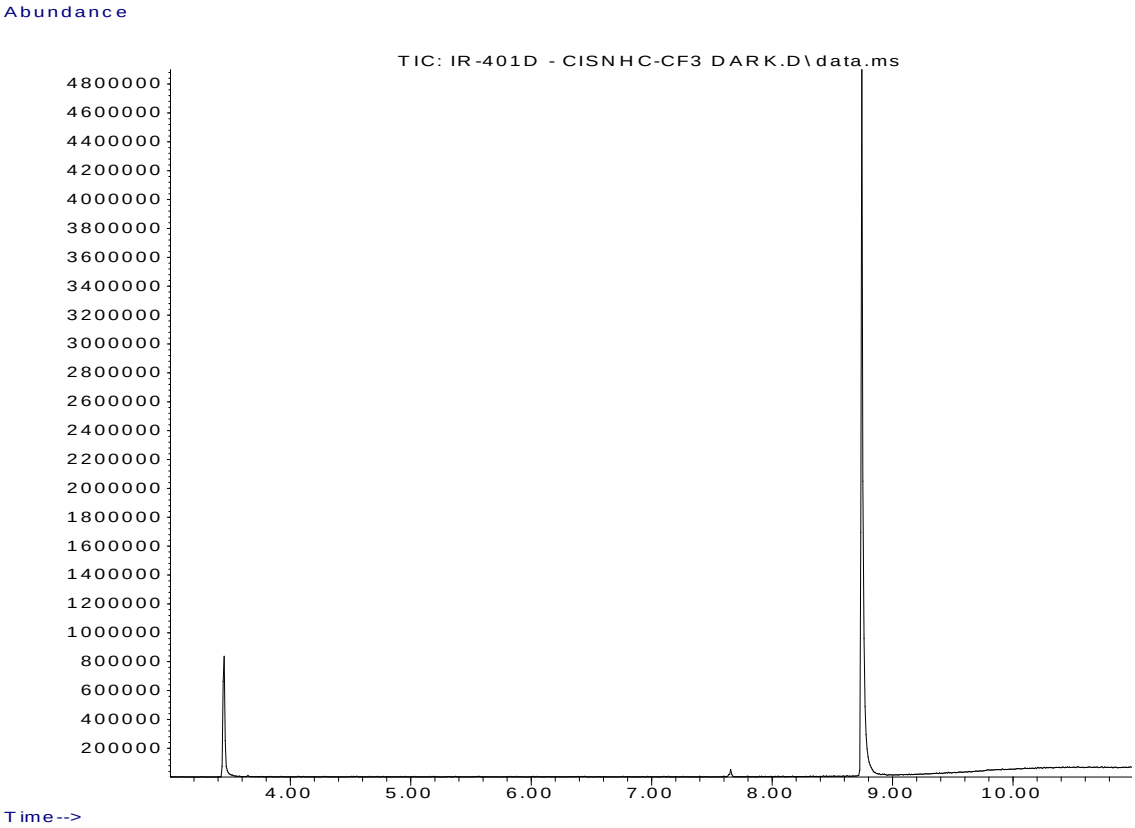
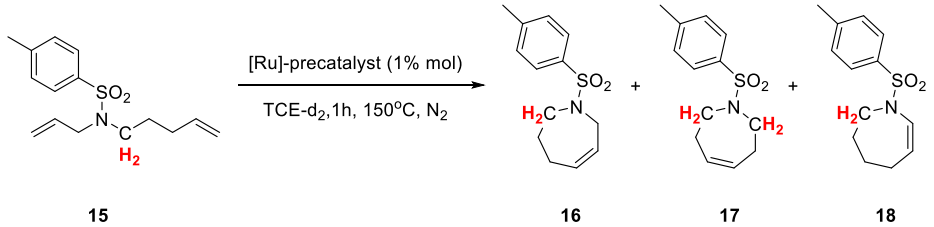


Figure S111. Self-metathesis of **MO** by ***cis*-14a** at 350nm irradiation (dark control).

7.3. RCM of N-allyl-N-(pent-4-en-1-yl)tosylsulfonamide (15)



Scheme S19. RCM of **15**. The protons marked by red color were used for following the conversion.

15 (0.05 mmol) was dissolved in 480µL of $C_2D_2Cl_4$ inside a pear-shaped flask equipped with a small magnet and a condenser. The air in the flask was replaced by N_2. The precatalyst (0.01eq, 0.5 µmol) was dissolved in 20µL $C_2D_2Cl_4$ and added to the reaction. Then, the reaction was heated to 150°C for 1h. After cooling the reaction mixture to room temperature, the solution was analysed by ^{1}H-NMR.

The analysis of compound distribution in the final reaction mixture was done following the previously published method.[11] The analysis is based on the relative integration values of the protons shown on the scheme above.

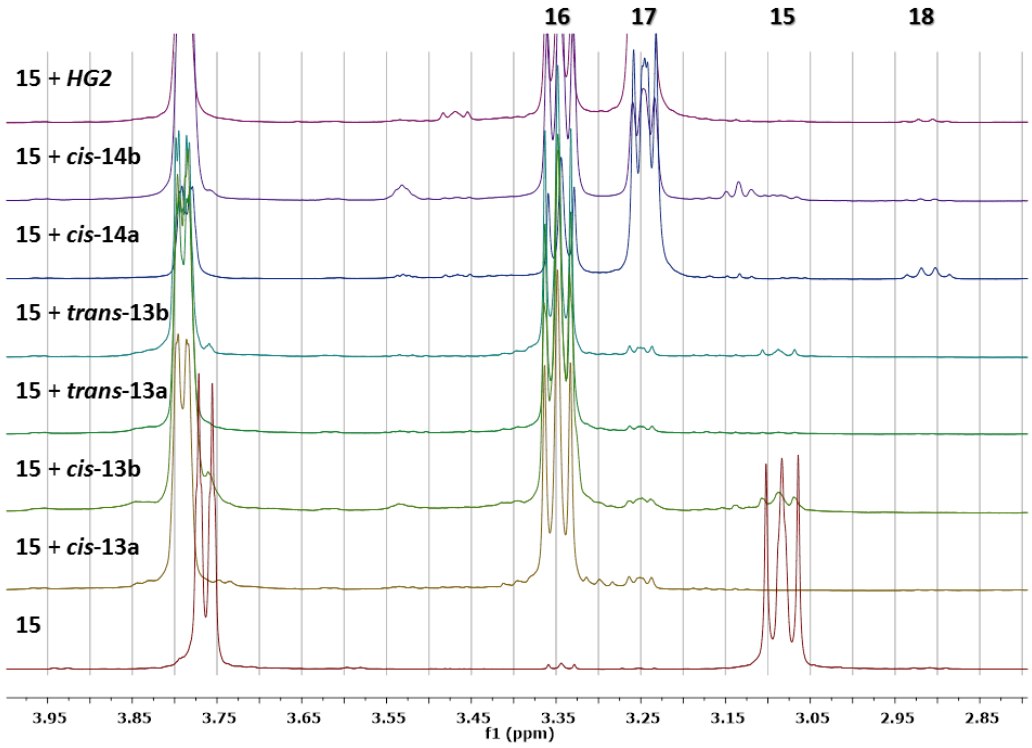


Figure S112. ^{1}H-NMR spectra of reaction mixture of RCM of **15** after 1h at 150°C.

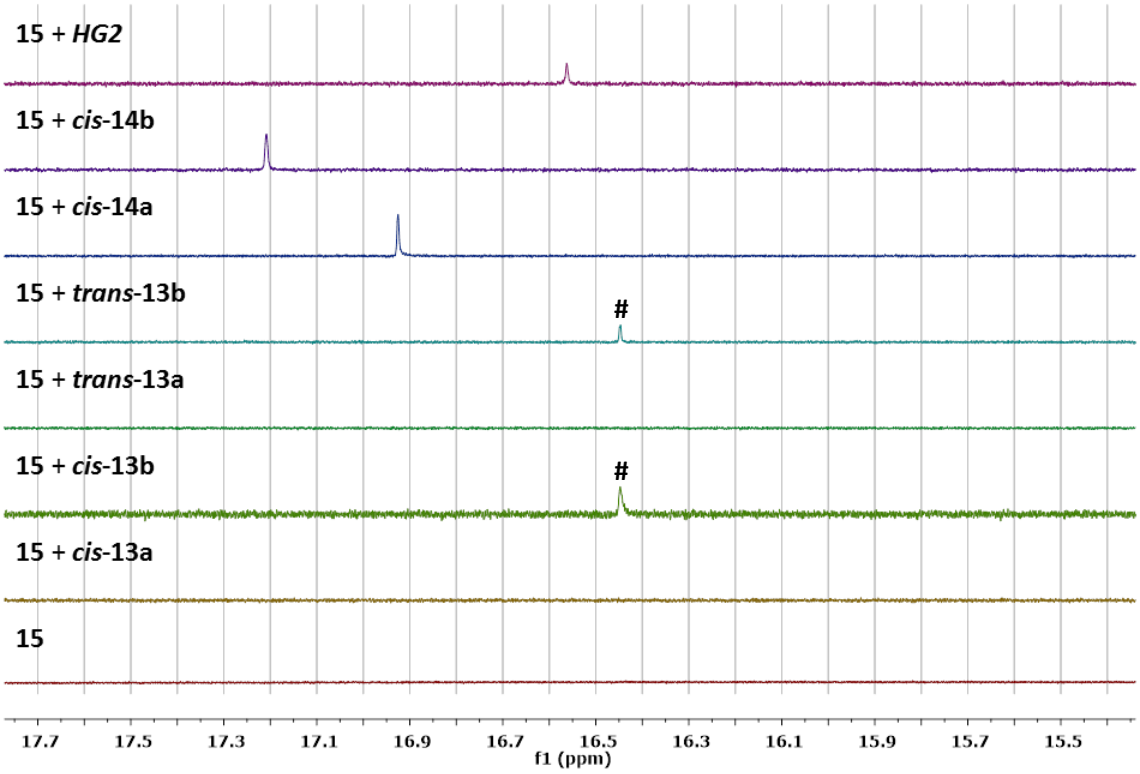


Figure S113. Expansion of carbene region in ^{1}H-NMR spectra of reaction mixture of RCM of **15** after 1h at 150°C. The spectra show that, with the exception of ***trans*-13a**, all benzylidenes are still present in the solution after the reaction is over.

- carbene of ***cis*-13b**.

8. References

(1) Fulmer, G.R.; Miller, A.J.M.; Sherden, N.H.; Gottlieb, H.E.; Nudelman, A.; Stoltz, B.M.; Bercaw, J.E.; Goldberg, K.I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* 2010, 29, 2176-2179.

(2) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, 71, 3-8.

(3) Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* 2015, 71, 3-8.

(4) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. Stable Cyclic (Alkyl)(Amino)Carbenes as Rigid or Flexible, Bulky, Electron-Rich Ligands for Transition-Metal Catalysts: A Quaternary Carbon Atom Makes the Difference. *Angew. Chem., Int. Ed.* 2005, 44, 5705-5709.

(5) Getty, K.; Delgado-Jaime, M. U.; Kennepohl, P. Assignment of pre-edge features in the Ru K-edge X-ray absorption spectra of organometallic ruthenium complexes. *Inorg. Chim. Acta* 2008, 361, 1059-1065.

(6) Anderson, D. R.; Lavallo, V.; O'Leary, D. J.; Bertrand, G.; Grubbs, R. H. Synthesis and Reactivity of Olefin Metathesis Catalysts Bearing Cyclic (Alkyl)(Amino)Carbenes. *Angew. Chem., Int. Ed.* 2007, 46, 7262-7265.

(7) Ginzburg, Y.; Anaby, A.; Vidavsky, Y.; Diesendruck, C. E.; Ben-Asuly, A.; Goldberg, I.; Lemcoff, N. G. Widening the Latency Gap in Chelated Ruthenium Olefin Metathesis Catalysts. *Organometallics* 2011, 30, 3430-3437.

(8) Kost, T.; Sigalov, M.; Goldberg, I.; Ben-Asuly, A.; Lemcoff, N. G. Latent sulfur chelated ruthenium catalysts: Steric acceleration effects on olefin metathesis. *J. Organomet. Chem.* 2008, 693, 2200-2203.

(9) Gawin, R.; Kozakiewicz, A.; Guńka, P. A.; Dąbrowski, P.; Skowerski, K. Bis(Cyclic Alkyl Amino Carbene) Ruthenium Complexes: A Versatile, Highly Efficient Tool for Olefin Metathesis. *Angew. Chem., Int. Ed.* 2017, 56, 981-986.

(10) Che, C.; Li, W.; Lin, S.; Chen, J.; Zheng, J.; Wu, J.-c.; Zheng, Q.; Zhang, G.; Yang, Z.; Jiang, B. Magnetic nanoparticle-supported Hoveyda-Grubbs catalysts for ring-closing metathesis reactions. *Chem. Commun.* 2009, 5990-5992.

(11) One peak that belongs to split CF_3 carbon signal is not visible on spectrum (probably overlaps with one of the aromatic carbons' peaks.

(12) Some of the low intensity peaks belong to ***cis*-13b** that appears due to spontaneous isomerization during data collection.

(13) Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

(14) Butilkov, D.; Frenklah, A.; Rozenberg, I.; Kozuch, S.; Lemcoff, N. G. Highly Selective Olefin Metathesis with CAAC-Containing Ruthenium Benzylidenes. *ACS Catal.* 2017, 7, 7634-7637.