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Cyclic(alkyl)(amino)carbene Ruthenium Complexes for *Z*-Stereoselective (Asymmetric) Olefin Metathesis

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Contents

1. General information

All manipulations were carried out in an Ar filled glovebox or using standard Schlenk techniques. Glassware was dried in an oven overnight at 150 °C or flame dried prior to use. Toluene, dichloromethane (DCM) and tetrahydrofuran (THF), used for complex synthesis and catalysis reactions, were purified using MBraun Solvent Purification Systems and freeze-pump-thaw degassed prior to use. Reactions were monitored by thin-layer chromatography (TLC) carried out on aluminium backed silica gel 60 (F254) plates from MERCK (grain-size distribution 60/20 μm); visualised using 254 nm UV light and $KMnO_4/K_2CO_3$/NaOH in water for staining. Columns chromatography were performed with silica gel (spherical, particle size 40 μm, neutral) purchased from Sigma-Aldrich. The eluents employed are reported as volume percentages.

NMR: For Ru chloride complexes and catalysis products, multinuclear NMR spectra were recorded on a Bruker ARX400 400 MHz spectrometer. For Ru catechothiolate complexes multinuclear NMR spectra were recorded on a Bruker NEO 500 MHz spectrometer fitted with a TCI cryoprobe, belonging to the PRISM core Facility (Biogenouest, UMS Biosit, Université de Rennes 1) at 280 K. For nucleus other than ^{1}H spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard. Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities in ^{1}H NMR are reported using following abbrevations: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, ddd = double double doublet, dt = double triplet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. When not specified, spectra were recorded at 298 K.

High Resolution Mass Spectrometry (HRMS): For Ru complexes HRMS were recorded on a Thermo Fisher Q-Exactive spectrometer using ESI, and HRMS for catalysis products were recorded on a Bruker MaXis 4G spectrometer using ESI or ASAP at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1.

Preparative chiral HPLC: ^{Prep}HPLC Chiral separations of Ru chloride complexes were performed on an Agilent 1260 Infinity unit (pump G1311C, autosampler G1329B, DAD G1365D and fraction collector G1364C), monitored by Agilent OpenLAB CDS Chemstation LC at Aix-Marseille University.

Trade name	Chiral Stationary Phase	Seller*
Chiralpak IE	Amylose tris(3,5-dichloro-phenylcarbamate) immobilized on silica	CTE

* CTE: Chiral Technologies Europe (Illkirch, France)

Optical rotations: Optical rotations for the complexes were measured at Aix Marseille University on a Jasco P-2000 polarimeter with a sodium lamp (589 nm), a halogen lamp (578, 546, 436, 405, 365 and 325 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

Electronic Circular Dichroism (ECD) and UV: ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical path length was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample. The spectra are presented without smoothing and further data processing.

X-Ray crystallography: Intensity data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector using MoKα radiation (0.71073 Å) at T = 150 K. Data reduction was performed using the SHELXT program. The structures were resolved using the software SHELXS-97 by the direct methods and refined using SHELXL-2013-4. Ellipsoids are drawn at 50% probability. Some hydrogens are omitted for clarity. For absolute configuration determination Flack parameter was refined to zero value.

%Vbur were determined using SambVCa free online server[1] and the crystalline structure obtained from X-Ray diffraction of the dichloride Ru-complexes **Ru-3** with bondi radii scale by 1.17, sphere radius of 3.5 Å, Ru atom at the center of the sphere, 0.10 mesh spacing, and H atoms included.

Steric Exclusion Chromatography (SEC): Weight average molar mass (M_w) and dispersity ($Đ = M_w/M_n$) values were measured by SEC in THF at 40 °C (flow rate = 1.0 mL/min) on a GPC2502 Viscotek apparatus equipped with a refractive index detector Viscotek VE 3580 RI, a guard column Viscotek TGuard, Org 10 x 4.6 mm, a LT5000L gel column 300 x 7.8 mm and a GPC/SEC OmniSEC Software. All elution curves were calibrated with polystyrene standards.

***E/Z* ratio determination:** Some *E/Z* ratio were determined with:

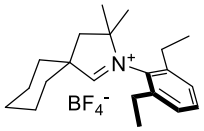
- a GC/MS-QP2010-SE Shimadzu (Injector: 280°C – Detector: EI/SQ (Ion Source temperature: 200°C; Interface temperature: 250°C); injection volume of 1 µL; Carrier gas: Helium.
- A GC-2014 Shimadzu; Injector: 250°C – Detector: 250°C – FID; injection volume of 1 µL; Carrier gas: Helium.

Enantiomeric excess (ee) determination: by HPLC analysis (High Performance Liquid Chromatography) using an Alliance e2695 Waters® HPLC with a UV/visible detector 2489 Waters®.

2. Synthesis of HG-2 type CAAC-Ru-complexes

2.1. Reagents

KHMDS (0.5M in Toluene) and CuCl were purchased from Sigma-Aldrich, entered in the glove box and used as received. **Ind-1** (86% purity) and **HG1** Ru-complexes were generously offered by Umicore AG&Co, stored in a glove box and used as received. 2-isopropoxystyrene[2] and 1-isopropoxy-4-nitro-2-vinylbenzene[3] were synthesized from salicylaldehyde by alkylation and Wittig olefination following a previously reported procedure.[2,3] CAAC salt precursors were synthesized according to literature procedure.[4] **CAAC-a,**[5]**c-f,**[6]**d-e,**[7] are known compounds. Prior to use, they were dried under high vacuum at 60°C overnight and stored in a glove box.



Chemical Formula: $C_{21}H_{32}BF_4N$
Molecular Weight: 385,30

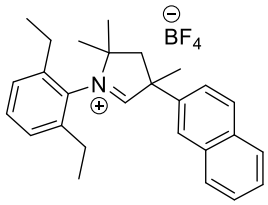
CAAC-b was synthesized according to the same procedure and obtained as a white powder with an overall yield of 56 %.

^{1}H NMR (400 MHz, *CD_3CN*): 9.22 – 9.16 (m, 1H), 8.04 – 7.95 (m, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 3.13 – 2.99 (m, 2H), 2.95 – 2.81 (m, 4H), 2.49 – 2.38 (m, 2H), 2.36 – 2.26 (m, 2H), 2.25 – 2.15 (m, 2H), 2.13 – 2.09 (m, 1H), 2.07 – 1.96 (m, 2H), 1.97 – 1.82 (m, 7H), 1.64 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, *CD_3CN*): 191.1, 140.7, 132.3 (2C), 131.9, 128.7 (2C), 85.2, 53.7, 46.0, 34.8, 28.7 (2C), 25.6 (2C), 25.2 (2C), 22.1 (2C), 15.5 (2C).

^{11}B NMR (128 MHz, *CD_3CN*): δ -1.2.

^{19}F NMR (376 MHz, *CD_3CN*): δ -151.6 (small), -151.7.



Chemical Formula: $C_{27}H_{32}BF_4N$
Molecular Weight: 457,36

CAAC-h was synthesized according to the same procedure and obtained as a white powder with an overall yield of 71 %.

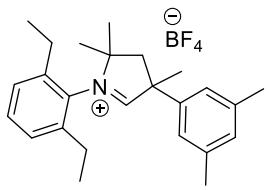
^{1}H NMR (400 MHz, *$CD_3CN/CDCl_3$ 1/1*): δ (ppm) 9.33 (s, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.93 – 7.81 (m, 3H), 7.61 – 7.54 (m, 3H), 7.54 – 7.49 (m, 1H), 7.43 – 7.33 (m, 2H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.82 (d, *J* = 14.0 Hz, 1H), 2.69 (dq, *J* = 15.1, 7.6 Hz, 1H), 2.52 (dq, *J* = 15.2, 7.5 Hz, 2H), 2.32 (dq, *J* = 14.7, 7.4 Hz, 1H), 2.01 (s, 3H), 1.58 (s, 3H), 1.38 (s, 3H), 1.28 (t, *J* = 7.5 Hz, 3H), 1.17 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, *CD_3CN*): δ (ppm) 189.7, 141.0, 140.8, 139.7, 134.3, 133.7, 132.6, 131.9, 130.9, 129.1, 129.0, 129.0, 128.7, 128.3, 128.1, 125.7, 124.5, 85.9, 56.4, 49.3, 28.3, 27.5, 27.5, 25.8, 25.8, 15.9, 15.7.

^{11}B NMR (128 MHz, *$CDCl_3$*): δ (ppm) 4.2.

^{19}F NMR (376 MHz, *$CDCl_3$*): δ (ppm) -147.0 (small), -147.1.

HRMS for $C_{27}H_{32}N$ (M^+) 370.2529, found 370.2522.



Chemical Formula: $C_{25}H_{34}BF_4N$
Molecular Weight: 435,36

CAAC-i was synthesized according to the same procedure and obtained as a white powder with an overall yield of 44 %.

^{1}H NMR (500 MHz, *CDCl$_3$*): δ (ppm) 9.57 (s, 1H), 7.46 (t, *J*= 7.5 Hz, 1H), 7.32 (d, *J*= 7.5 Hz, 1H), 7.25 (d, *J*= 7.5 Hz, 1H), 7.05 (s, 2H), 6.98 (s, 1H), 3.11 (d, *J*= 14.0 Hz, 1H), 2.63 (d, *J*= 14.0 Hz, 1H), 2.58 (dt, *J*= 7.5 Hz, 1H), 2.57 (dt, *J*= 7.5 Hz, 1H), 2.39 (dt, *J*= 7.5 Hz, 1H), 2.22 (dt, *J*= 7.5 Hz, 1H), 2.32 (s, 6H), 1.92 (s, 3H), 1.52 (s, 3H), 1.31 (s, 3H), 1.29 (t, *J*= 7.5 Hz, 3H), 1.15 (t, *J*= 7.5 Hz, 3H).

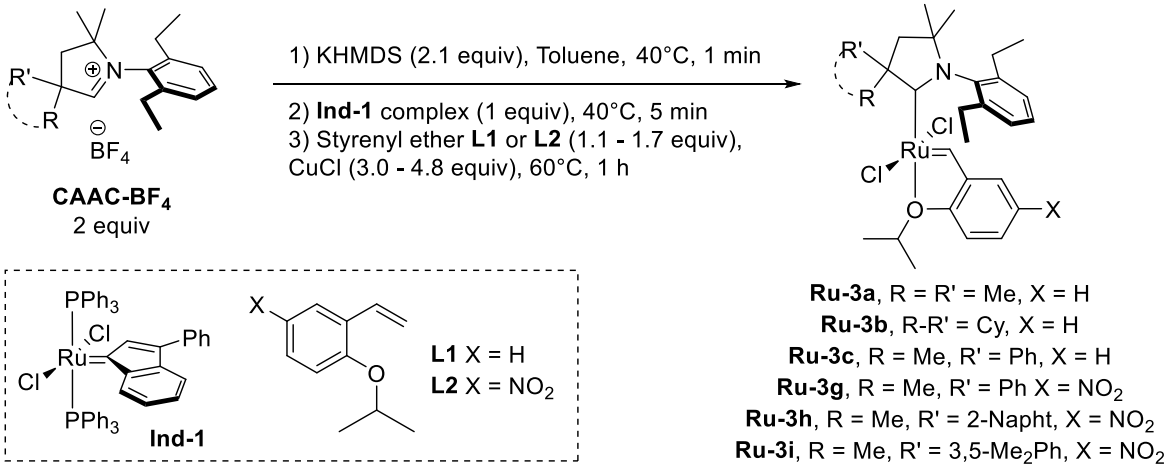
^{13}C NMR (125 MHz, *CDCl$_3$*): δ (ppm) 190.9, 141.2, 140.4, 140.2 (2C), 139.8, 131.8, 131.0, 130.5, 128.3, 128.1, 123.6, 83.6, 55.3, 48.7, 28.8, 27.0, 26.7, 24.8, 24.7, 21.2 (2C), 15.5, 14.5.

^{11}B NMR (128 MHz, *CDCl$_3$*): δ (ppm) -0.98.

^{19}F NMR (376 MHz, *CDCl$_3$*): δ (ppm) -151.0 (small), -151.1

HRMS for $C_{25}H_{34}N$ (M^+): calc.: 348.2686, found: 348.2682.

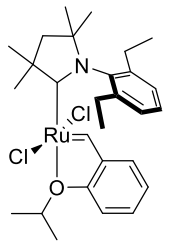
2.2. General procedure for $^{N\text{-}DEP}$CAAC-Ru-3[8]



In a glove box, CAAC.BF_4 (2 equiv) was dissolved in dry and degassed toluene (10 mL/mmol Ru). KHMDS (0.5 M in toluene, 2.1 equiv) was added. The mixture was allowed to stirred 1 minute at 40°C. Then, **Ind-1** complex (1 equiv) was added. The mixture was stirred 5 minutes at 40°C. Styrenyl ether **L1** or **L2** (1.1 – 1.7 equiv) and CuCl (3.0 – 4.8 equiv) were added and the mixture was stirred 1 hour at 60°C out of the glove box under Ar atmosphere.

The solvent was removed under vacuum and the product was purified by silica gel column chromatography. The solid was then dissolved in the minimum amount of DCM and precipitated in pentane.

2.3.Analytical data of $^{N\text{-}DEP}$CAAC-Ru-3



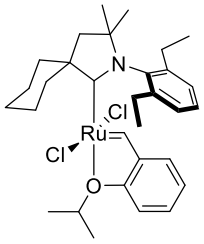
Chemical Formula: $C_{28}H_{39}Cl_2NORu$
Molecular Weight: 577,60

Ru-3a was prepared according to general procedure for the complex synthesis using the corresponding **CAAC-a** (248 mg, 0.72 mmol, 2.0 equiv), toluene (5.0 mL), KHMDS solution (1.5 mL, 0.75 mmol, 2.1 equiv), **Ind-1** complex (390 mg, 0.36 mmol, 1.0 equiv), styrenyl ether **L1** (100 mg, 0.62 mmol, 1.7 equiv) and CuCl (143 mg, 1.4 mmol, 4.0 equiv). The desired product was obtained after purification (eluent: pentane/acetone 10/0 to 9/1) as a green solid (245 mg, 83 % yield).

^{1}H NMR (400 MHz, *CDCl$_3$*): δ (ppm) 16.33 (s, 1H, C*H*$_{alkylidene}$), 7.58 (dd, *J* = 8.2, 7.2 Hz, 1H, C*H*$_{ar}$), 7.52 (ddd, *J* = 8.3, 6.2, 2.9 Hz, 1H, C*H*$_{ar}$), 7.44 (d, *J* = 7.7 Hz, 2H, C*H*$_{ar}$), 6.93 (d, *J* = 8.4 Hz, 1H, C*H*$_{ar}$), 6.89 – 6.80 (m, 2H, C*H*$_{ar}$), 5.16 (sept, *J* = 6.1 Hz, 1H, C*H*O), 2.70 – 2.45 (m, 4H, C*H*$_2$), 2.19 (s, 2H, C*H*$_{2\ backbone}$), 2.11 (s, 6H, C*H*$_3$), 1.77 (d, *J* = 6.1 Hz, 6H, C*H*$_3$), 1.32 (s, 6H, C*H*$_3$), 0.93 (t, *J* = 7.4 Hz, 6H, C*H*$_{3\ ethyl}$).

^{13}C NMR (101 MHz, *CDCl$_3$*): δ (ppm) 297.2 (C$_{carbene}$), 266.3 (*C*H$_{alkylidene}$), 152.4 (*C*$_{q\ ar}$), 143.9 (*C*$_{q\ ar}$), 143.4 (2C, *C*$_{q\ ar}$), 138.6 (*C*$_{q\ ar}$), 130.7 (*C*H$_{ar}$), 128.9 (*C*H$_{ar}$), 126.8 (2C, *C*H$_{ar}$), 123.5 (*C*H$_{ar}$), 122.0 (*C*H$_{ar}$), 113.1 (*C*H$_{ar}$), 78.3 (*C*$_q$), 75.0 (*C*HO), 56.0 (*C*$_q$), 52.0 (*C*H$_2$), 29.7 (2C, *C*H$_3$), 28.6 (2C, *C*H$_2$), 24.8 (2C, *C*H$_3$), 22.1 (2C, *C*H$_3$), 14.5 (2C, *C*H$_3$).

Analytical data for this compound were consistent with the previously reported data.[9]



Chemical Formula: $C_{31}H_{43}Cl_2NORu$
Molecular Weight: 617,66

Ru-3b was prepared according to general procedure for the complex synthesis with the corresponding **CAAC-b** (181 mg, 0.47 mmol, 2.0 equiv), toluene (3.0 mL), KHMDS solution (0.85 mL, 0.43 mmol, 1.8 equiv), **Ind-1** complex (251 mg, 0.24 mmol, 1.0 equiv), styrenyl ether **L1** (43 mg, 0.27 mmol, 1.1 equiv) and CuCl (69 mg, 0.7 mmol, 3.0 equiv). The desired product was obtained after purification (eluent: toluene) as a green solid (111 mg, 76 % yield)

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 16.46 (s, 1H, C*H*$_{alkylidene}$), 7.64 – 7.49 (m, 2H, C*H*$_{ar}$), 7.46 (d, *J* = 7.7 Hz, 2H, C*H*$_{ar}$), 6.95 (d, *J* = 8.4 Hz, 1H, C*H*$_{ar}$), 6.91 – 6.83 (m, 2H, C*H*$_{ar}$), 5.17 (sept, *J* = 6.1 Hz, 1H, C*H*O), 3.35 – 3.23 (m, 2H, C*H*$_2$), 2.65 (dq, *J* = 14.9, 7.4 Hz, 2H, C*H*$_{2\ ethyl}$), 2.53 (dq, *J* = 14.9, 7.4 Hz, 2H, C*H*$_{2\ ethyl}$), 2.34 – 2.24 (m, 4H, C*H*$_{2\ backbone}$ + C*H*$_2$), 2.00 – 1.92 (m, 2H, C*H*$_2$), 1.87 – 1.82 (m, 2H, C*H*$_2$), 1.80 (d, *J* = 6.1 Hz, 6H, C*H*$_3$), 1.65 – 1.47 (m, 2H, C*H*$_2$), 1.33 (s, 6H, C*H*$_3$), 0.95 (t, *J* = 7.4 Hz, 6H, C*H*$_{3\ ethyl}$).

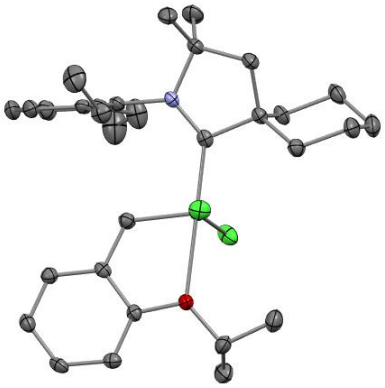
^{13}C NMR (101 MHz, *CDCl$_3$*): δ (ppm) 298.3 (*C*$_{carbene}$), 266.1 (*C*H$_{alkylidene}$), 152.4 (*C*$_{q\ ar}$), 144.1 (*C*$_{q\ ar}$), 143.4 (2C, *C*$_{q\ ar}$), 138.6 (*C*$_{q\ ar}$), 130.8 (*C*H$_{ar}$), 128.8 (*C*H$_{ar}$), 126.8 (2C, *C*H$_{ar}$), 123.7 (*C*H$_{ar}$), 122.0

(CH_{ar}), 113.2 (CH_{ar}), 78.2 (*C*HO), 74.9 (CH_2), 62.0 (CH_2), 44.8 (C_q), 35.7 (2C, CH_2), 29.1 (2C, CH_2), 25.6 (C_q), 24.8 (2C, CH_3), 23.1 (2C, CH_2), 22.1 (2C, CH_3), 14.5 (2C, CH_3)

Analytical data for this compound were consistent with the previously reported data.[9]

X-Ray diffraction :

CCDC number : 2172112

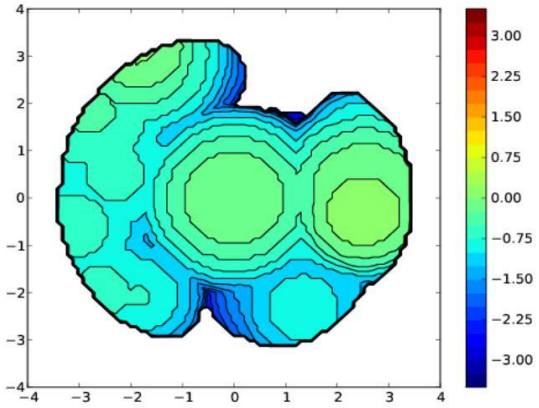


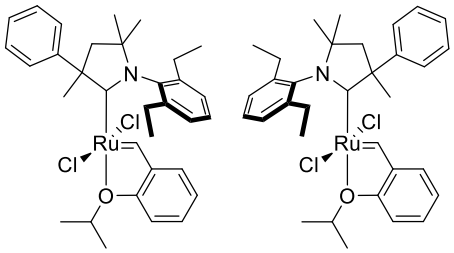
Vbur :

%V Free	%V Buried	% V Tot/V Ex
65.0	**35.0**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	30.4	14.5	44.9	**67.8**	32.2
NW	27.7	17.1	44.9	**61.8**	38.2
NE	30.7	14.2	44.9	**68.4**	31.6
SE	27.8	17.0	44.9	**62.0**	38.0

Steric Map



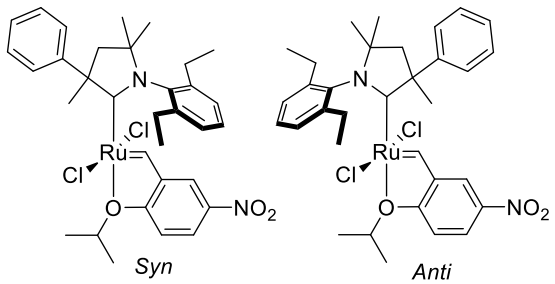


Chemical Formula: $C_{33}H_{41}Cl_2NORu$
Molecular Weight: 639,67

Ru-3c was prepared according to general procedure for the complex synthesis using the corresponding **CAAC-c** (395 mg, 0.97 mmol, 2.1 equiv), toluene (4.0 mL), KHMDS solution (1.94 mL, 0.97 mmol, 2.1 equiv), **Ind-1** complex (430 mg, 0.46 mmol, 1.0 equiv), styrenyl ether **L1** (157 mg, 0.97 mmol, 2.1 equiv) and CuCl (168 mg, 1.7 mmol, 3.7 equiv). The mixture was stirred 30 min at 60°C. The desired product was obtained after purification (eluent: toluene) as a green solid (245 mg, 83 % yield) as a mixture of conformers (*Syn/Anti* ratio in toluene-D_8: 72:28).

^{1}H NMR (400 MHz, Toluene-D_8) as conformer mixture (72/28): δ (ppm) 17.76 (s, 0.28H), 16.40 (s, 0.72H), 8.27 (br s, 1.5H), 7.81 (br s, 0.7H), 7.46 (br s, 1.6H), 7.35 – 7.17 (m, 5H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.58 (br s, 1.2H), 6.38 (d, *J* = 8.3 Hz, 1H), 4.52 (sept, *J* = 6.2 Hz, 1H), 3.76 – 3.36 (m, 0.7H), 3.01 – 2.70 (m, 2.3H), 2.40 (m, 3H), 1.98 – 1.87 (m, 1H), 1.57 – 1.42 (m, 2.8H), 1.42 – 1.24 (m, 5.2H), 1.11 (br s, 3.5H), 1.03 (br s, *J* = 9.9 Hz, 6H), 0.81 (m, *J* = 6.4 Hz, 2.5H)

^{13}C NMR (101 MHz, Toluene-*D_8*) as conformer mixture (72/28): δ (ppm) 301.7 – 300.0 (1C) 263.6, 152.5, 144.3, 143.7, 143.5, 143.2, 138.8, 131.1, 129.4, 129.1, 128.8, 127.6, 127.2, 126.9, 123.9, 121.9, 113.4, 78.0, 74.7, 63.5, 48.5, 31.3, 28.0, 27.6, 25.8, 24.3, 22.5, 22.3, 14.9, 14.4.
Analytical data for this compound were consistent with the previously reported data.[5]

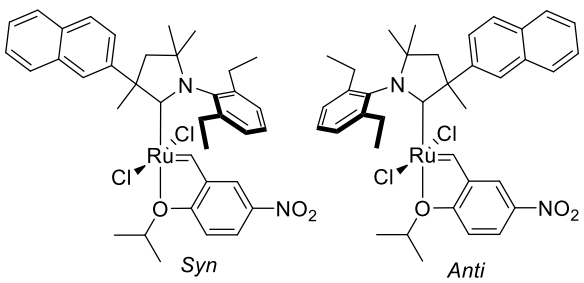


Chemical Formula: $C_{33}H_{40}Cl_2N_2O_3Ru$
Molecular Weight: 684,65

Ru-3g was prepared according to general procedure for the complex synthesis using the corresponding **CAAC-g** (514 mg, 1.26 mmol, 1.9 equiv), toluene (7.0 mL), KHMDS solution (2.5 mL, 1.25 mmol, 1.9 equiv), **Ind-1** complex (625 mg, 0.66 mmol, 1.0 equiv), styrenyl ether **L2** (165 mg, 0.8 mmol, 1.2 equiv) and CuCl (290 mg, 2.93 mmol, 4.4 equiv). The mixture was stirred 1.5 hour at 60°C. The desired product was obtained after purification (eluent: toluene) as a green solid (327 mg, 72 % yield) as a mixture of conformers (*Syn/Anti* ratio in $CDCl_3$: 78:22).

^{1}H NMR (400 MHz, *$CDCl_3$*) as conformer mixture (78/22): δ (ppm) 17.77 (s, 0.22H), 16.44 (s, 0.78H), 8.50 – 8.33 (m, 1H), 8.21 (br s, 1.5H), 7.76 – 7.28 (m, 7.3H), 6.96 (d, *J* = 9.1 Hz, 1.2H), 5.06 – 5.00 (m, 1H), 3.15 (br s, 1H), 2.70 (br s, 1H), 2.52 – 2.18 (m, 6H), 2.01 (br s, 1H), 1.53 – 1.25 (m, 12H), 1.09 (br s, 3H), 0.84 (br s, 3H).

^{13}C NMR (101 MHz, *$CDCl_3$*) as conformer mixture (78/22): δ (ppm) 295.0, 260.6, 156.5, 143.5, 143.1, 142.7, 138.2, 132.1, 129.5, 129.4, 128.7, 128.5, 127.7, 127.4, 127.1, 125.4, 118.2, 113.2, 63.2, 48.4, 31.1, 29.7, 27.6, 25.6, 24.2, 22.2, 14.8, 14.3.
Analytical data for this compound were consistent with the previously reported data.[8]



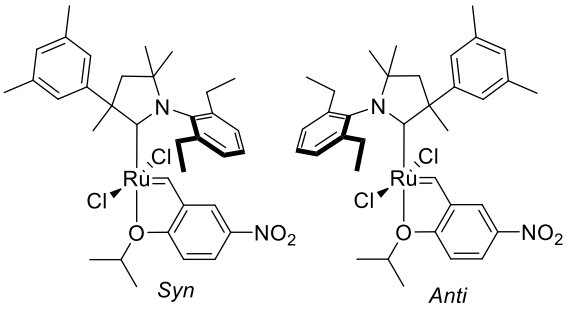
Chemical Formula: $C_{37}H_{42}Cl_2N_2O_3Ru$
Molecular Weight: 734,72

Ru-3h was prepared according to general procedure for the complex synthesis using the corresponding **CAAC-h** (366 mg, 0.80 mmol, 2.1 equiv), Toluene (3.5 mL), KHMDS solution (1.6 mL, 0.80 mmol, 2.1 equiv), **Ind-1** complex (355 mg, 0.38 mmol, 1.0 equiv), styrenyl ether **L2** (88 mg, 0.42 mmol, 1.1 equiv) and CuCl (139 mg, 1.40 mmol, 3.7 equiv). The mixture was stirred 30 minutes at 60°C. The desired product was obtained after purification (eluent: toluene) as a green solid (157 mg, 56% yield) as a mixture of conformers (*syn/anti* ratio in $CDCl_3$: 72:28).

^{1}H NMR (400 MHz, *$CDCl_3$*) as conformer mixture (72/28): δ (ppm) 17.98 (s, 0.28H), 16.44 (s, 0.72H), 8.71 – 8.12 (m, 3H), 8.02 – 7.81 (m, 3H), 7.75 – 7.02 (m, 6H), 6.98 – 6.89 (m, 1H), 4.95 – 4.85 (m, 1H), 3.44 – 3.14 (m, 1H), 2.75 (br s, 2.5H), 2.65 – 2.48 (m, 4.5H), 2.25 – 1.97 (m, 1H), 1.44 (m, 12H), 1.09 (m, 3.5H), 0.89 (br s, 2.5H).

^{13}C NMR (101 MHz, *$CDCl_3$*) as conformer mixture (72/28): δ (ppm) 294.9 – 294.3 (1C), 260.9, 156.6, 143.6, 143.4, 142.7, 139.3, 138.2, 133.6, 132.8, 129.6, 128.8, 128.6, 128.3, 128.0, 127.6, 127.5, 127.3, 127.2, 126.3, 126.1, 125.4, 118.2, 113.3, 78.9, 63.2, 49.1, 32.8, 31.7, 31.3, 29.8, 27.8, 27.4, 26.6, 26.3, 25.8, 24.4, 22.8, 21.9, 21.7, 15.0, 14.4, 14.2.

HRMS: for C_{37} H_{42} N_2 O_3 $^{35}Cl_2$ ^{102}Ru ($M^{+\cdot}$): calc.: 734.16105, found: 734.1613.



Chemical Formula: $C_{35}H_{44}Cl_2N_2O_3Ru$
Molecular Weight: 712,72

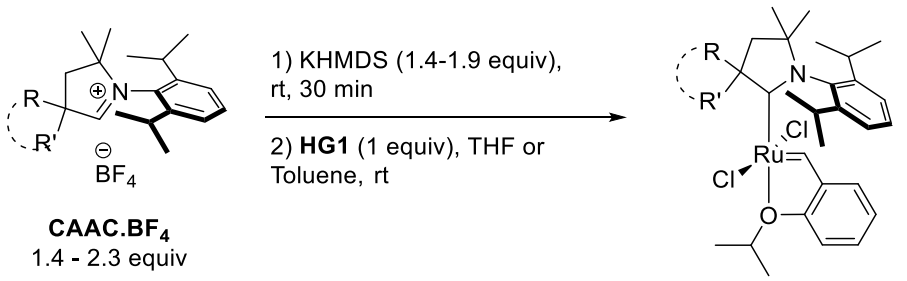
Ru-3i was prepared according to general procedure for the complex synthesis using the corresponding **CAAC-i** (744 mg, 1.71 mmol, 2.0 equiv), toluene (6.8 mL), KHMDS solution (3.4 mL, 1.70 mmol, 2.0 equiv), **Ind-1** complex (800 mg, 0.86 mmol, 1.0 equiv), styrenyl ether **L2** (219 mg, 1.06 mmol, 1.2 equiv) and CuCl (308 mg, 3.10 mmol, 3.6 equiv). The mixture was stirred 30 minutes at 60°C. The desired product was obtained after purification (eluent: toluene) as a green solid (436 mg, 71 % yield) as a mixture of conformers (*syn/anti* ratio in $CDCl_3$: 68:32).

^{1}H NMR (400 MHz, *$CDCl_3$*) as conformer mixture (68/32): δ (ppm) 17.94 (s, 0.32H), 16.44 (s, 0.68H), 8.58 – 8.38 (m, 1.3H), 8.25 – 8.08 (m, 0.5H), 7.63 (br s, 2.3H), 7.49 (br s, 2.6H), 7.05 – 6.88 (m, 2.3H), 5.04 (br s, 1H), 3.45 – 3.03 (m, 1.2H), 2.65 (m, 2.5H), 2.46 – 2.30 (m, 8.8H), 1.94 (m, 0.8H), 1.55 – 1.30 (m, 15H), 1.10 (s, 1.3H), 0.91 (m, 3.4H).

^{13}C NMR (101 MHz, *$CDCl_3$*) as conformer mixture (68/32): δ (ppm) 293.9 – 293.2 (1C), 261.1, 156.6, 143.7, 143.4, 142.8, 140.5, 138.2, 129.5, 128.0, 127.4, 127.1, 125.3, 124.8, 118.2, 113.2, 78.7, 63.7, 62.6, 57.7, 50.0, 31.3, 30.3, 28.3, 27.8, 26.7, 25.8, 24.4, 21.9, 16.1, 15.0, 14.4.

HRMS for C_{35} H_{44} N_2 O_3 $^{35}Cl_2$ ^{102}Ru ($M^{+\cdot}$): calc.: 712.1767, found: 712.1766.

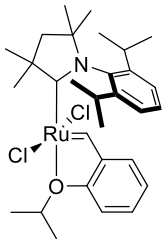
2.4.General procedure for $^{N\text{-}DIPP}$CAAC-Ru-3[4]



In a glove box, CAAC.BF_4 (1.4-2.3 equiv) was dissolved in dry and degassed THF or Toluene. KHMDS (0.5 M in toluene, 1.4-2.9 equiv) was added. The mixture was allowed to stirred 30 minutes at room temperature. Then, **HG1** complex (1 equiv) was then added. The mixture was stirred the indicated time at rt.

The solvent was removed under vacuum and the product was purified by column chromatography (eluent: Toluene). The solid was then diluted in the minimum amount of DCM and precipitated in pentane.

2.5.Analytical data of $^{N\text{-}DIPP}$CAAC-Ru-3



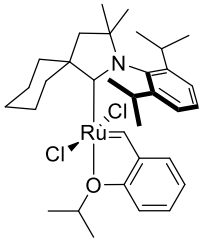
Chemical Formula: $C_{30}H_{43}Cl_2NORu$
Molecular Weight: 605,66

Ru-3d was prepared according to general procedure for the synthesis of complexes with the corresponding **CAAC-d** (202 mg, 0.54 mmol, 1.4 equiv), Toluene (5.0 mL), KHMDS solution (1.1 mL, 0.55 mmol, 1.4 equiv) and **HG1** complex (230 mg, 0.38 mmol, 1 equiv). The mixture was stirred 1 h at room temperature. The desired product was obtained as a green solid (162 mg, 70 % yield).

^{1}H NMR (400 MHz, *$CDCl_3$*): δ (ppm) 16.39 (d, *J* = 0.9 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.53 – 7.42 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.88 – 6.76 (m, 2H), 5.16 (sept, *J* = 6.1 Hz, 1H), 3.00 (sept, *J* = 6.5 Hz, 2H), 2.18 (s, 2H), 2.13 (s, 6H), 1.80 (d, *J* = 6.1 Hz, 6H), 1.35 (s, 6H), 1.27 (d, *J* = 6.7 Hz, 6H), 0.69 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (101 MHz, *$CDCl_3$*): δ (ppm) 294.5-294.4 (1 C), 267.3, 152.9, 148.4 (2 C), 142.8, 136.5, 130.6, 129.4, 125.7 (2 C), 123.6, 121.9, 113.2, 77.9, 75.0, 56.2, 51.7, 29.8 (2 C), 29.3 (2 C), 28.4 (2 C), 26.5 (2 C), 24.3 (2 C), 22.2 (2 C).

Analytical data for this compound were consistent with the previously reported data.[5]



Chemical Formula: $C_{30}H_{47}Cl_2NORu$
Molecular Weight: 645,71

Ru-3e was prepared according to general procedure for the synthesis of complexes with the corresponding **CAAC-e** (145 mg, 0.35 mmol, 2.3 equiv), THF (5 mL), KHMDS (86 mg, 0.43 mmol, 2.9 equiv) and **HG1** complex (86 mg, 0.15 mmol, 1 equiv). The mixture was stirred 16 h at room temperature. The desired product was obtained as a green solid (75 mg, 77% yield).

^{1}H NMR (400 MHz, *$CDCl_3$*): δ (ppm) 16.49 (d, *J* = 0.8 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.54 – 7.41 (m, 3H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.87 – 6.76 (m, 2H), 5.15 (hept, *J* = 6.1 Hz, 1H), 3.33 (td, *J* = 12.4, 3.8 Hz, 2H), 3.00 (hept, *J* = 6.5 Hz, 2H), 2.29 (s, 4H), 1.98 – 1.90 (m, 2H), 1.79 (d, *J* = 6.1 Hz, 7H), 1.60 – 1.48 (m, 3H), 1.34 (s, 6H), 1.25 (d, *J* = 6.6 Hz, 6H), 0.69 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (101 MHz, *$CDCl_3$*): δ (ppm) 295.6, 267.2, 152.8, 148.4, 143.0, 136.5, 130.6, 129.4, 125.7, 123.7, 121.9, 113.3, 77.8, 74.9, 62.3, 44.5, 34.9, 30.4, 28.4, 26.6, 25.5, 24.4, 23.1, 22.2, 22.2.

Analytical data for this compound were consistent with the previously reported data.[5]

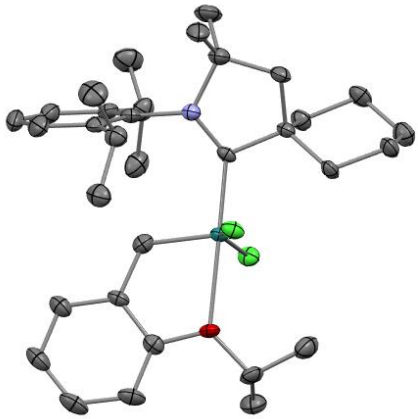
%V Free	%V Buried	% V Tot/V Ex
61.7	**38.3**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	28.5	16.3	44.9	**63.6**	36.4
NW	24.7	20.2	44.9	**55.0**	45.0
NE	31.8	13.1	44.9	**70.8**	29.2
SE	25.7	19.2	44.9	**57.3**	42.7

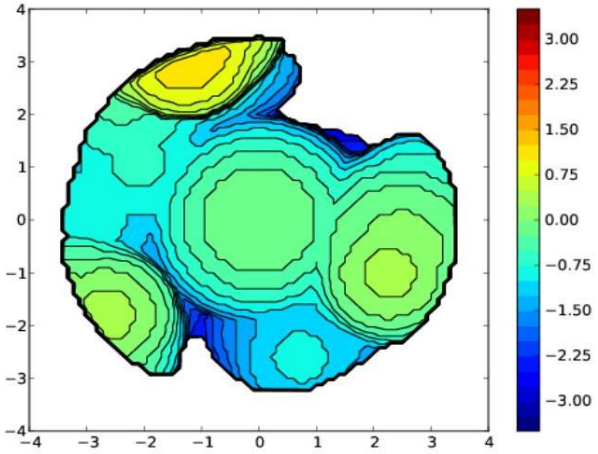
X-Ray diffraction :

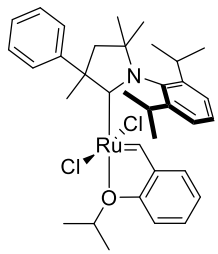
Vbur :

CCDC number : 2172111



Steric Map





Chemical Formula: $C_{35}H_{45}Cl_2NORu$
Molecular Weight: 667,72

Ru-3f was prepared according to general procedure for the synthesis of complexes with the corresponding **CAAC-f** (205 mg, 0.47 mmol, 1.7 equiv), THF (7.0 mL), KHMDS (1.0 mL, 0.50 mmol, 1.8 equiv) and HG1 complex (166 mg, 0.28 mmol, 1 equiv). The mixture was stirred 2 h at room temperature. The desired product was obtained as a green solid (117 mg, 63 % yield).

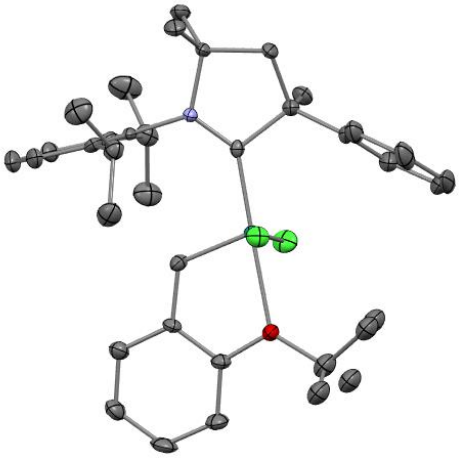
^{1}H NMR (400 MHz, *CDCl$_3$*): δ (ppm) 16.55 (s, 1H), 8.28 (d, *J*= 7.8 Hz, 2H), 7.64 (t, *J*= 7.7 Hz, 1H), 7.56 (t, *J*= 7.6 Hz, 2H), 7.53 – 7.42 (m, 3H), 7.38 (t, *J*= 7.3 Hz, 1H), 6.86 (d, *J*= 8.4 Hz, 1H), 6.79 (t, *J*= 7.4 Hz, 1H), 6.71 (dd, J_1 = 7.5, J_2 = 1.7 Hz, 1H), 4.96 (sept, *J*= 6.1 Hz, 1H), 3.16 (d, *J*= 12.9 Hz, 1H), 3.13 – 3.06 (m, 1H), 3.06 – 2.94 (m, 1H), 2.31 – 2.41 (m, 4H), 1.58 (d, *J*= 6.1 Hz, 3H), 1.52 (s, 3H), 1.46 – 1.39 (m, 6H), 1.36 (d, *J*= 6.6 Hz, 3H), 1.27 (d, *J*= 6.7 Hz, 3H), 0.85 (d, *J*= 6.5 Hz, 3H), 0.54 (d, *J*= 6.3 Hz, 3H).

^{13}C NMR (101 MHz, *CDCl$_3$*): δ (ppm) 297.9 - 297.7 (1C), 264.7, 152.9, 148.6, 148.3, 143.0, 142.7, 136.8, 130.9, 129.6, 129.3, 129.2, 129.2, 129.2, 127.5, 126.0, 125.8, 124.0, 121.7, 113.4, 77.5, 74.7, 63.2, 48.3, 32.8, 28.9, 28.7, 28.3, 27.7, 27.4, 26.4, 24.5, 24.4, 22.6, 22.3.

Analytical data for this compound were consistent with the previously reported data.[5]

X-Ray diffraction :

CCDC number : 1941524

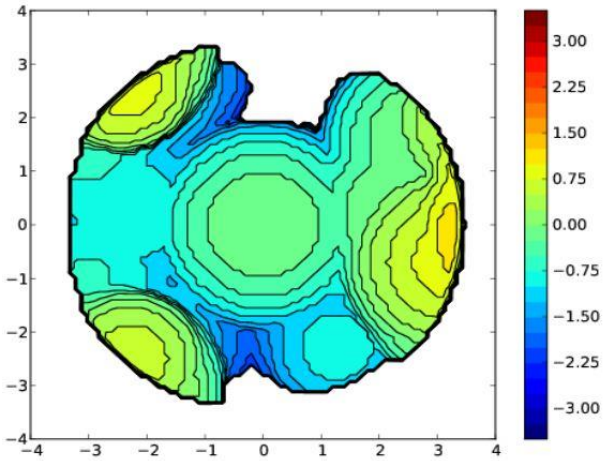


Vbur :

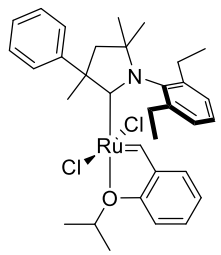
%V Free	%V Buried	% V Tot/V Ex
59.6	40.4	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	27.0	17.9	44.9	60.2	39.8
NW	27.6	17.3	44.9	61.5	38.5
NE	27.3	17.5	44.9	60.9	39.1
SE	25.0	19.8	44.9	55.8	44.2

Steric Map



3. Resolution of chiral chloride Ru complexes on preparative HPLC

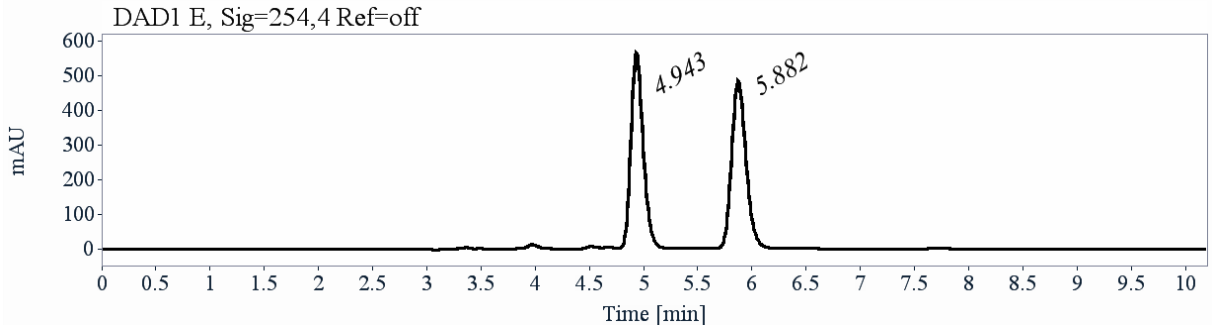


Chemical Formula: $C_{33}H_{41}Cl_2NORu$
Molecular Weight: 639,67

Ru-3c

Analytical chiral HPLC separation: Chiralpak IE column with a UV and CD detector at l = 254 nm; flow rate 1 mL/min; eluent: heptane / EtOH / DCM 60/20/20; 1st enantiomer **(+)-(*R*)-Ru-3c**: Rt = 4.94 min and 2nd enantiomer **(-)-(*S*)-Ru-3c**: Rt = 5.88 min.

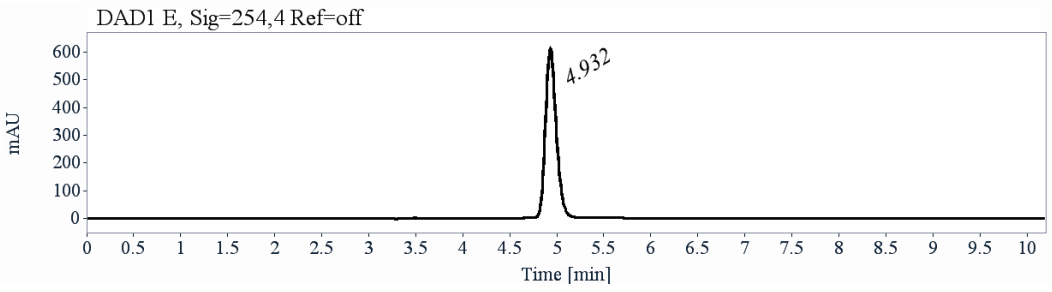
Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IE	Heptane / EtOH/ DCM (60/20/20)	4.94	0.68	5.88	0.99	1.47	4.21



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.94	4414	49.64	0.68		
5.88	4478	50.36	0.99	1.47	4.21
Sum	8893	100.00			

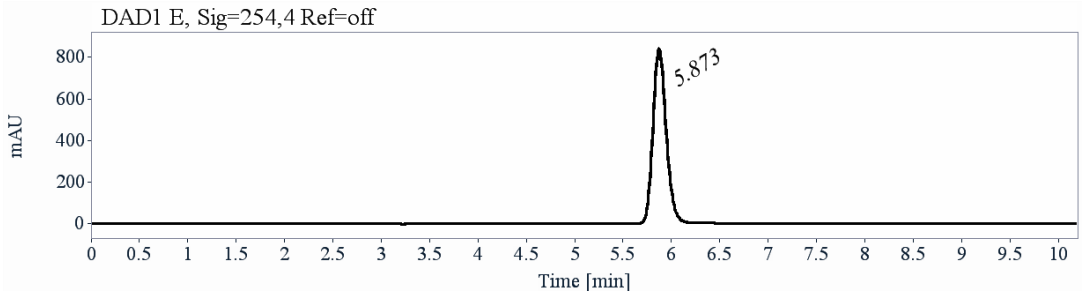
Preparative separation: The preparative chiral HPLC separation was done on a Chiralpak IE column (250 x 10 mm, 5 µm) with heptane / EtOH / DCM (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm with multiple injections (60 times 100 µL, every 6.6 min). From 225 mg of racemic mixture dissolved in 6 mL of DCM, 97 mg of the first eluted enantiomer with ee > 99.5% (**(+)-(*R*)-Ru-3c**: 43% yield) and 100 mg of the second eluted enantiomer with ee > 99.5% (**(-)-(*S*)-Ru-3c**: 44% yield) were obtained.

- 1st fraction eluted:



RT [min]	Area	Area%
4.93	5026	100.00
Sum	5026	100.00

- 2nd fraction eluted:



RT [min]	Area	Area%
5.87	8065	100.00
Sum	8065	100.00

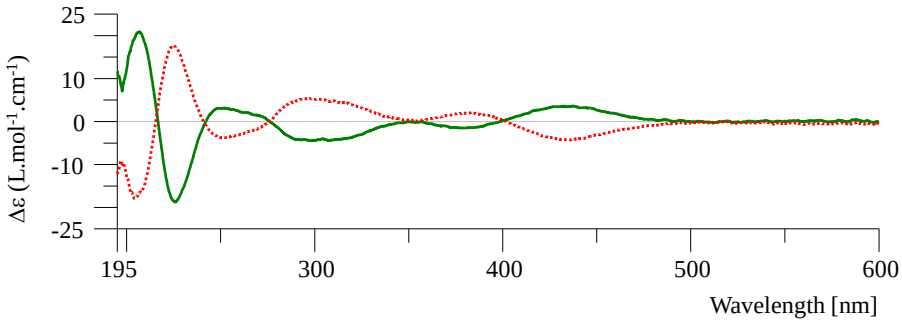
Optical rotations

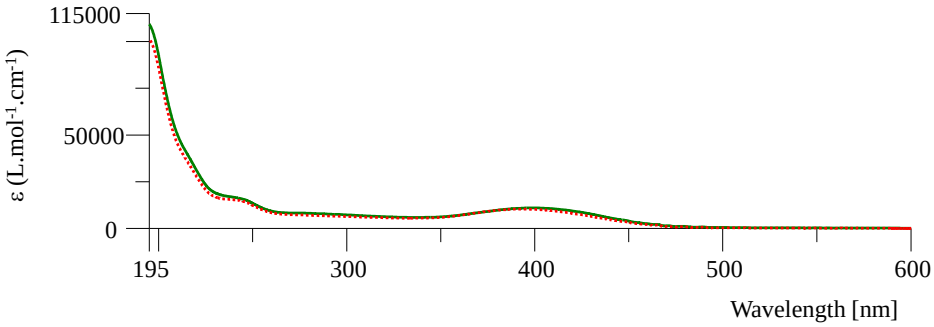
λ (nm)	**(+)-(*R*)-Ru-3c** First eluted enantiomer on Chiralpak IE $[a]_l^{25}$ (CH_2Cl_2, c =0.02)	**(-)-(*S*)-Ru-3c** Second eluted enantiomer on Chiralpak IE $[a]_l^{25}$ (CH_2Cl_2, c =0.02)
589	+ 565	- 565
578	+ 425	- 425
546	+ 55	- 55

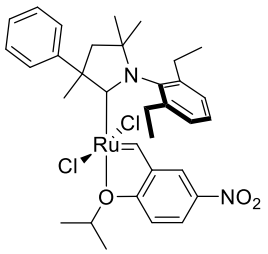
Electronic Circular Dichroism:

(+)-(*R*)-Ru-3c (first eluted enantiomer on Chiralpak IE): green solid line, concentration = 0.168 mmol.L^{-1} in acetonitrile.

(-)-(*S*)-Ru-3c (second eluted enantiomer on Chiralpak IE): red dotted line, concentration = 0.168 mmol.L^{-1} in acetonitrile.



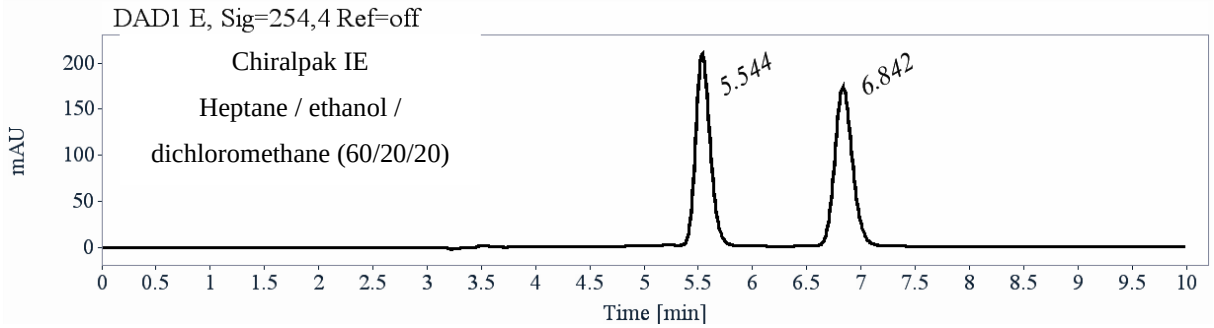




Chemical Formula: $C_{33}H_{40}Cl_2N_2O_3Ru$
Molecular Weight: 684,65

Ru-3g

Analytical chiral HPLC separation: Chiralpak IE column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: heptane / EtOH / DCM 60/20/20; 1st enantiomer **(+)-(*R*)-Ru-3g**: Rt = 5.54 min and 2nd enantiomer **(-)-(*S*)-Ru-3g**: Rt = 6.84 min.

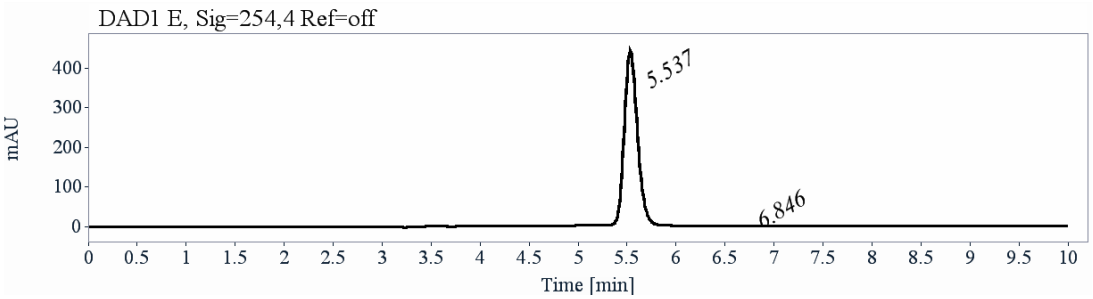


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.54	1973	50.00	0.88		
6.84	1973	50.00	1.32	1.50	4.77
Sum	3946	100.00			

Preparative separation: The preparative chiral HPLC separation was done on a Chiralpak IE column (250 x 10 mm, 5 µm) with heptane / EtOH / DCM (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm with multiple injections (23 times 350 µL, every 7.7 min). From 103 mg of racemic mixture dissolved in 8 mL of DCM / Hexanes (60/40), 50 mg of the first eluted

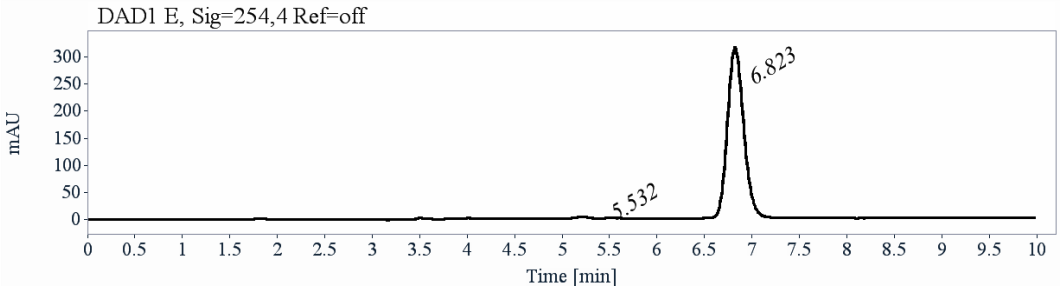
enantiomer with ee 99.5% (**(+)-(*R*)-Ru-3g**: 49% yield) and 50 mg of the second eluted enantiomer with ee 99% (**(-)-(*S*)-Ru-3g**: 49% yield) were obtained.

- 1st fraction eluted:



RT [min]	Area	Area%
5.54	4160	99.79
6.85	9	0.21
Sum	4168	100.00

- 2nd fraction eluted:



RT [min]	Area	Area%
5.53	19	0.50
6.82	3761	99.50
Sum	3780	100.00

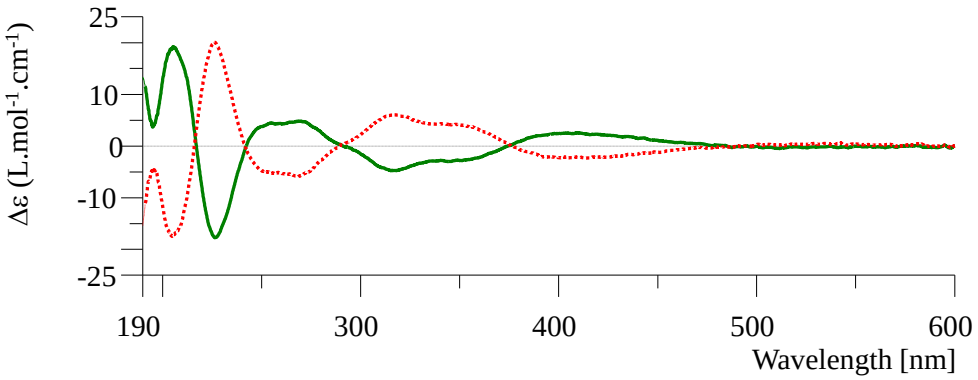
Optical rotations

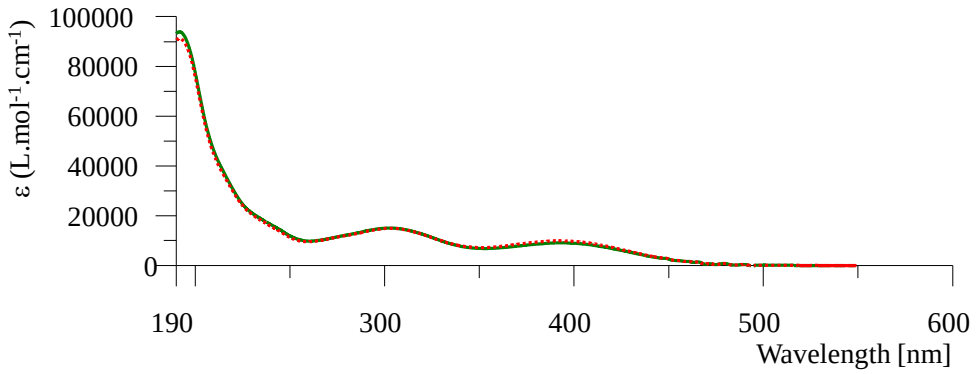
λ (nm)	**(+)-(*R*)-Ru-3g** First eluted enantiomer on Chiralpak IE $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c =0.018)	**(-)-(*S*)-Ru-3g** Second eluted enantiomer on Chiralpak IE $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c =0.02)
589	+ 179	- 179
578	+ 92	- 92
546	- 33	+ 34

Electronic Circular Dichroism:

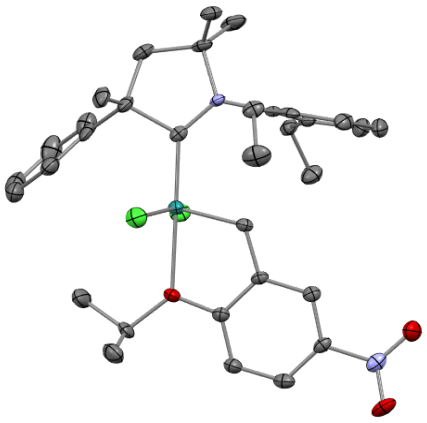
(+)-(*R*)-Ru-3g (first eluted enantiomer on Chiralpak IE): green solid line, concentration = 0.183 mmol.L^{-1} in acetonitrile.

(-)-(*S*)-Ru-3g (second eluted enantiomer on Chiralpak IE): red dotted line, concentration = 0.187 mmol.L^{-1} in acetonitrile.





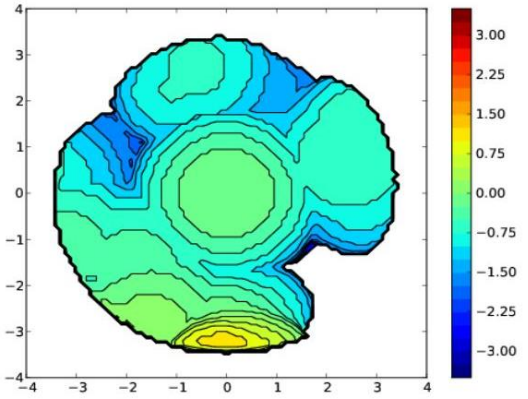
X-ray diffraction: Crystals of the second enantiomer of (-)-**Ru-3g** suitable for XRD were grown by slow diffusion of cyclohexane into chloroform, providing confirmation of the absolute configuration as the ***(S)***-enantiomer. CCDC number: 1941529

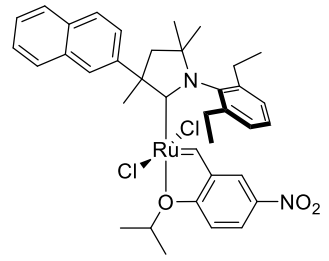


%V Free	%V Buried	% V Tot/V Ex
63.4	36.6	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	24.3	20.6	44.9	54.1	45.9
NW	30.4	14.5	44.9	67.7	32.3
NE	29.1	15.7	44.9	65.0	35.0
SE	30.0	14.9	44.9	66.8	33.2

Steric Map

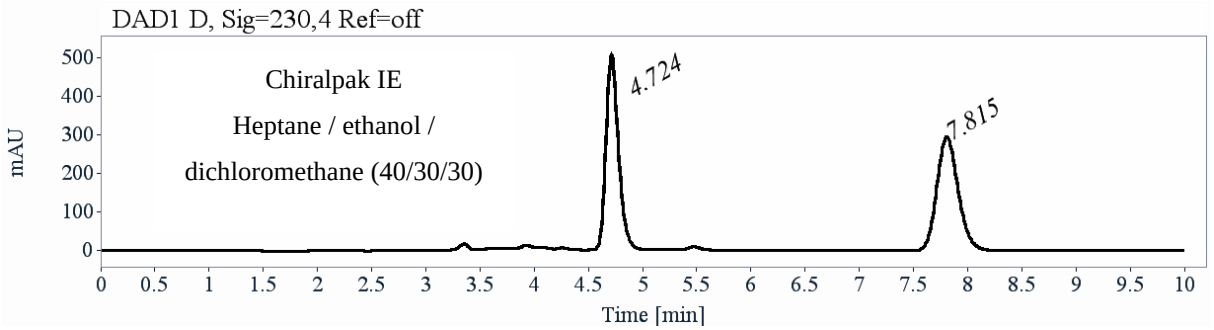




Chemical Formula: $C_{37}H_{42}Cl_2N_2O_3Ru$
Molecular Weight: 734,72

Ru-3h

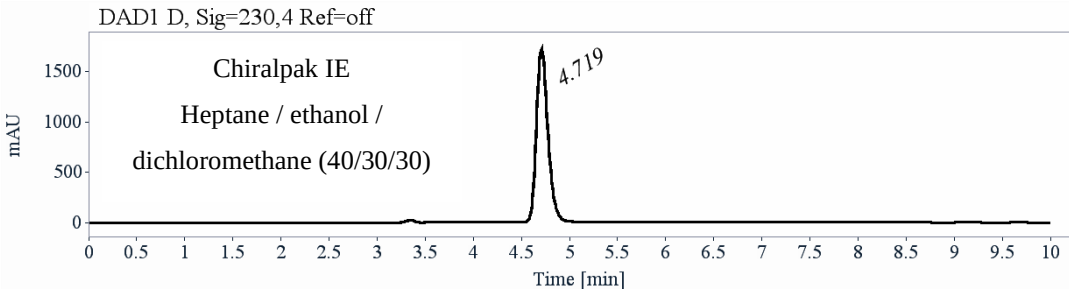
Analytical chiral HPLC separation: Chiralpak IE column with a UV and CD detector at λ = 230 nm; flow rate 1 mL/min; eluent: heptane / EtOH / DCM 40/30/30; 1st enantiomer **(+)-(*R*)-Ru-3h**: Rt = 4.72 min and 2nd enantiomer **(-)-(*S*)-Ru-3h**: Rt = 7.81 min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.72	4080	50.00	0.60		
7.81	4081	50.00	1.65	2.74	10.88
Sum	8161	100.00			

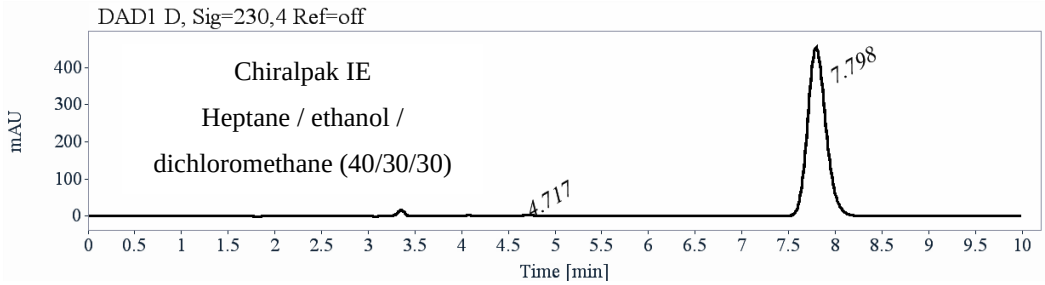
Preparative separation: The preparative chiral HPLC separation was done on a Chiralpak IE column (250 x 10 mm, 5 µm) with heptane / EtOH / DCM (40/30/30) as mobile phase, flow-rate = 5 mL/min, UV detection at 230 nm with multiple injections (25 times 200 µL, every 9.0 min). From 151 mg of racemic mixture dissolved in 5 mL of DCM, 68 mg of the first eluted enantiomer with ee > 99.5% (**(+)-(*R*)-Ru-3h**: 45% yield) and 66 mg of the second eluted enantiomer with ee >99.5% (**(-)-(*S*)-Ru-3h**: 44% yield) were obtained.

- 1st fraction eluted:



RT [min]	Area	Area%
4.72	14390	100.00
Sum	14390	100.00

- 2nd fraction eluted:



RT [min]	Area	Area%
4.78	6	0.21
7.59	2953	99.79

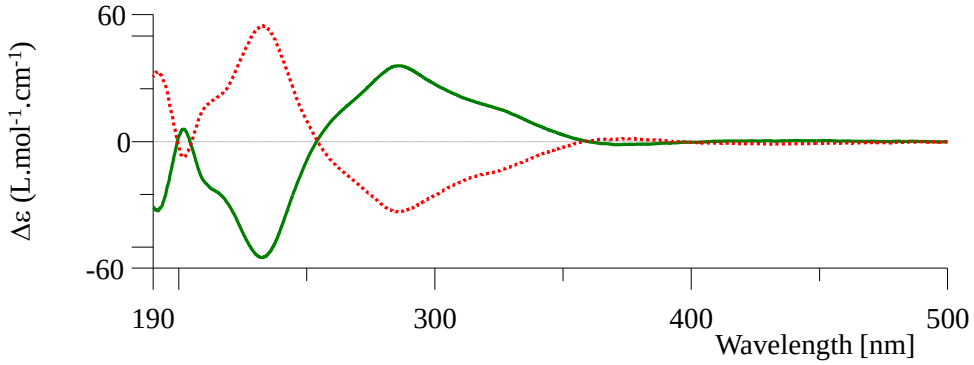
Optical rotations

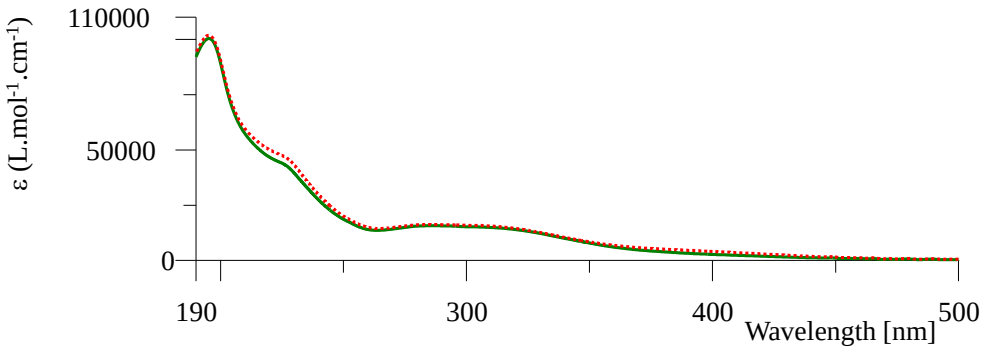
λ (nm)	**(+)-(*R*)-Ru-3h** First eluted enantiomer on Chiralpak IE $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.022)	**(-)-(*S*)-Ru-3h** Second eluted enantiomer on Chiralpak IE $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.018)
589	+ 281	- 278
578	+ 253	- 250
546	+ 249	- 246

Electronic Circular Dichroism:

(+)-(*R*)-Ru-3h (first eluted enantiomer on Chiralpak IE): green solid line, concentration = 0.181 mmol.L^{-1} in acetonitrile.

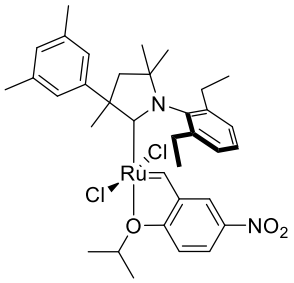
(-)-(*S*)-Ru-3h (second eluted enantiomer on Chiralpak IE): red dotted line, concentration = 0.177 mmol.L^{-1} in acetonitrile.





X-ray diffraction: As attempts to obtain suitable crystals for XDR failed, absolute configurations of **(+)-Ru-3h** and **(-)-Ru-3h** were assigned by comparison of the configuration of catalysis products of the other complexes:

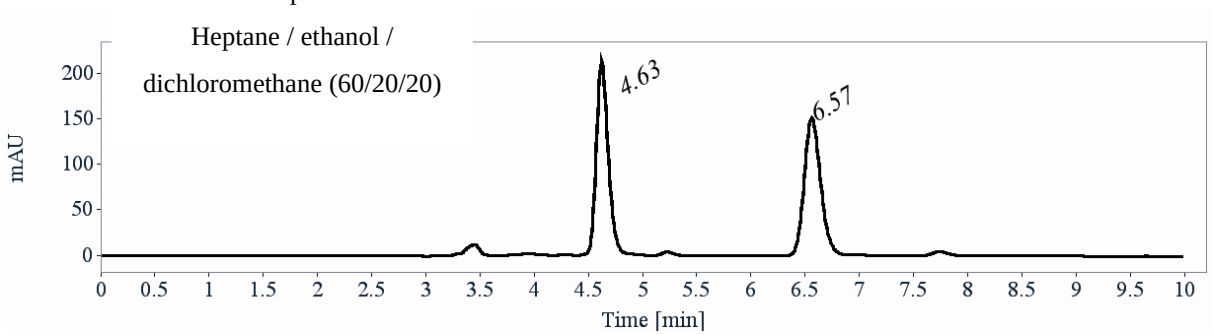
- 1st eluted enantiomer: **(+)-(*R*)-Ru-3h**
- 2nd eluted enantiomer: **(-)-(*S*)- Ru-3h**



Chemical Formula: $C_{35}H_{44}Cl_2N_2O_3Ru$
Molecular Weight: 712.72

Ru-3i

Analytical chiral HPLC separation: Chiralpak IE column with a UV and CD detector at λ = 230 nm; flow rate 1 mL/min; eluent: heptane / EtOH / DCM 60/20/20; 1st enantiomer **(+)-(*R*)-Ru-3i**: Rt = 4.63 min and 2nd enantiomer **(-)-(*S*)-Ru-3i**: Rt = 6.57 min.

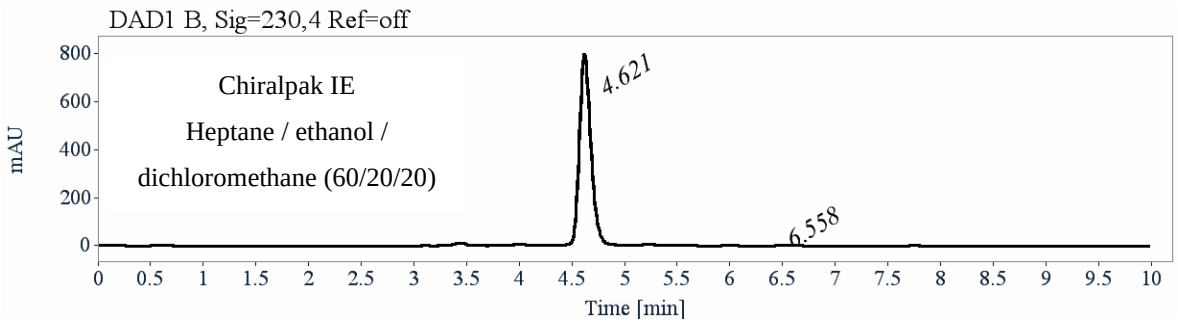


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.63	1646	50.31	0.57		
6.57	1626	49.69	1.23	2.15	8.17
Sum	3272	100.00			

Preparative separation: The preparative chiral HPLC separation was done on a Chiralpak IE column (250 x 10 mm, 5 µm) with heptane / EtOH / DCM (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 230 nm with multiple injections (16 times 250 µL, every 8.0 min). From 152 mg of racemic mixture dissolved in 4 mL of DCM, 72 mg of the first eluted enantiomer with

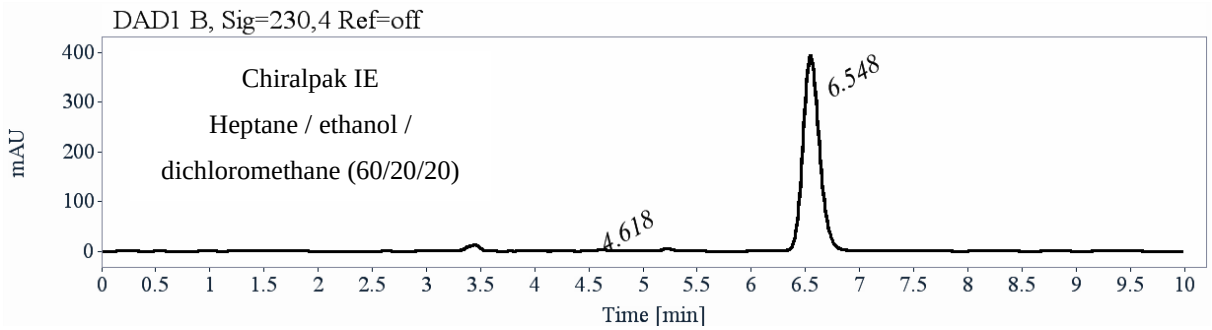
ee > 99.5% (**(+)-(*R*)-Ru-3i**: 47% yield) and 72 mg of the second eluted enantiomer with ee 99% (**(-)-(*S*)-Ru-3i**: 47% yield) were obtained.

- 1st fraction eluted:



RT [min]	Area	Area%
4.62	6039	99.84
6.56	10	0.16
Sum	6049	100.00

- 2nd fraction eluted:



RT [min]	Area	Area%
4.62	22	0.51
6.55	4188	99.49
Sum	4209	100.00

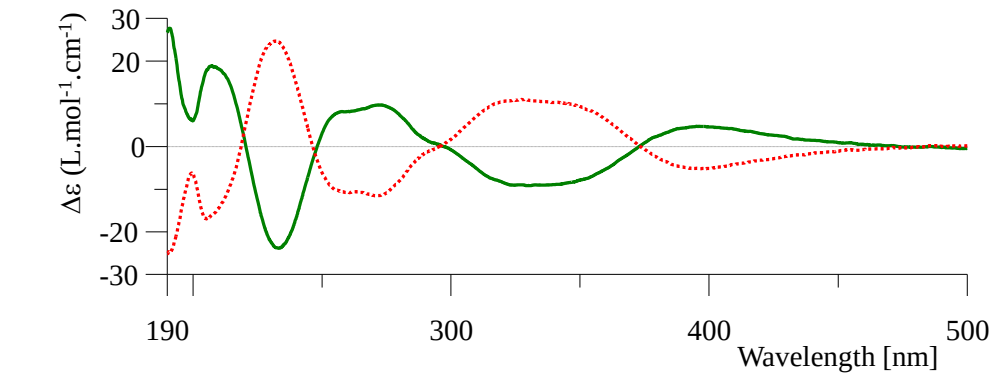
Optical rotations

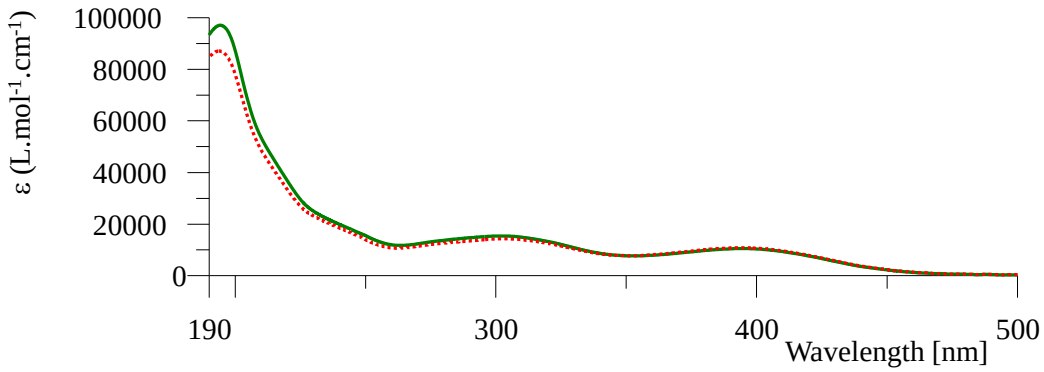
λ (nm)	**(+)-(*R*)-Ru-3i** First eluted enantiomer on Chiralpak IE $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.022)	**(-)-(*S*)-Ru-3i** Second eluted enantiomer on Chiralpak IE $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.018)
589	+ 277	- 275
578	+ 212	- 209
546	+ 161	- 159

Electronic Circular Dichroism:

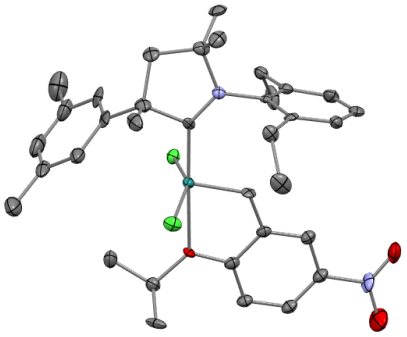
(+)-(*R*)-Ru-3i (first eluted enantiomer on Chiralpak IE): green solid line, concentration = 0.184 mmol.L^{-1} in acetonitrile.

(-)-(*S*)-Ru-3i (second eluted enantiomer on Chiralpak IE): red dotted line, concentration = 0.183 mmol.L^{-1} in acetonitrile.

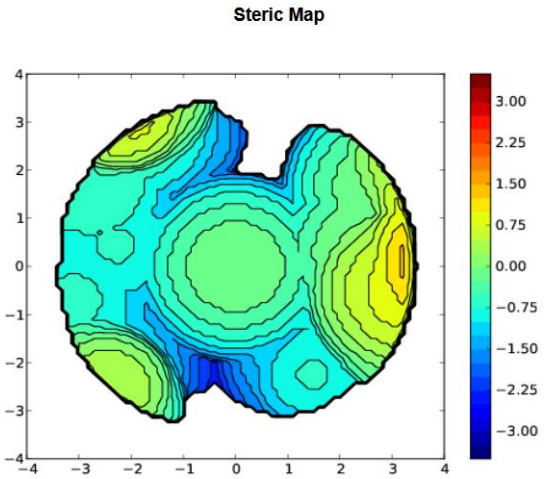




X-ray diffraction: Crystals of the second enantiomer of (-)-**Ru-3i** suitable for XRD were grown by slow diffusion of cyclohexane into chloroform, providing confirmation of the absolute configuration as the ***(S)***-enantiomer. CCDC number: 2164941.



Vbur:



%V Free	%V Buried	% V Tot/V Ex
60.2	39.8	99.9

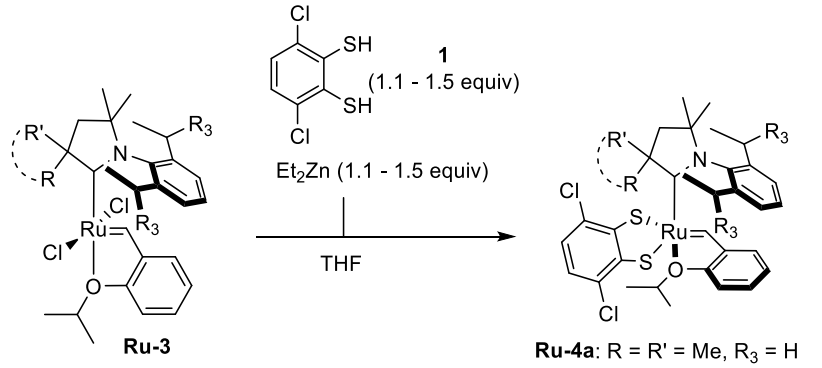
Quadrant	V f	V b	V t	%V f	%V b
SW	28.7	16.2	44.9	64.0	36.0
NW	27.4	17.5	44.9	61.0	39.0
NE	26.8	18.1	44.9	59.7	40.3
SE	25.2	19.7	44.9	56.2	43.8

4. Synthesis of CAAC-*bis* thiolate complexes

4.1. Reagents

Et_2Zn (1 M in hexanes) and 3,6-dichloro-1,2-benzenedithiol **1** were purchased from Sigma Aldrich and used as received.

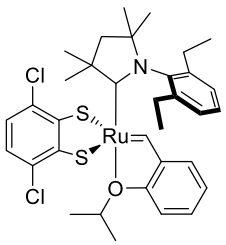
4.2. General procedure



Ru-4a: R = R' = Me, R_3 = H
Ru-4b: R-R' = Cy, R_3 = H
Ru-4c: R = Me, R' = Ph, R_3 = H
Ru-4d: R = R' = Me, R_3 = Me

In a flame dried vial, 3,6-dichlorobenzene-1,2-dithiol **1** (1.1 - 1.5 equiv) and diethyl zinc solution (1 M in hexanes, 1.1 - 1.5 equiv) were dissolved in dry and degassed THF. After 5 minutes of stirring at room temperature, the mixture was entered in the glove box. The desired **Ru-3** complex (1.0 equiv) was dissolved in THF and was added to the previous mixture. After 20 minutes of stirring at room temperature for $^{N\text{-DEP}}$CAAC-Ru and 6 hours of stirring at 40 °C for **Ru-4d**, crude mixture was filtered through a Celite® pad in the glove box (eluent: THF). Still in the glove box, volatiles were removed under vacuum. The solid was diluted in DCM and filtered through a second Celite pad (eluent: DCM). The compound was then washed with pentane and filtered through cotton. Volatiles were removed under vacuum. Final products being highly sensitive to air and moisture, they were stored in Ar filled freezer, used in dry and deoxygenated solvents in glove box.

4.3. Analytical data of dithiolate complexes



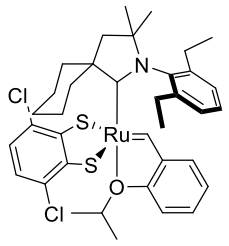
Chemical Formula: $C_{34}H_{41}Cl_2NORuS_2$
Molecular Weight: 715,80

Ru-4a was prepared according to general procedure for the dithiolate complexes synthesis with **Ru-3a** (47 mg, 0.08 mmol, 1.0 equiv), 1,6-dichloro-1,2-benzene dithiol **1** (23 mg, 0.11 mmol, 1.4 equiv), Et_2Zn (0.12 mL, 0.12 mmol, 1.5 equiv) and THF (1.1 mL). The desired product was obtained after purification as a brown solid (56.1 mg, 97 % yield).

^{1}H NMR (500 MHz, *THF-D$_8$*): δ (ppm) 13.78 (s, 1H, C$H_{alkylidene}$), 7.48 (d, J = 7.7 Hz, 1H, CH_{ar}), 7.36 – 7.28 (m, 1H, CH_{ar}), 7.26 (d, J = 8.4 Hz, 1H, CH_{ar}), 7.19 (t, J = 7.7 Hz, 1H, CH_{ar}), 6.90 (d, J = 8.1 Hz, 1H, CH_{ar}), 6.84 (d, J = 8.2 Hz, 1H, CH_{ar}), 6.77 (t, J = 7.3 Hz, 1H, CH_{ar}), 6.62 (dd, J = 7.6, 1.6 Hz, 1H, CH_{ar}), 6.55 (d, J = 7.7 Hz, 1H, CH_{ar}), 5.79 (sept, J = 7.0 Hz, 1H, CHO), 3.25 (dq, J = 14.9, 7.4 Hz, 1H, CH_2), 2.74 (dq, J = 15.0, 7.4 Hz, 1H, CH_2), 2.26 – 2.06 (m, 3H, CH_2 + C$H_{2\ backbone}$), 1.94 – 1.88 (m, 6H, 2 x CH_3), 1.82 (s, 3H, CH_3), 1.64 (t, J = 7.4 Hz, 3H, CH_3), 1.60 – 1.48 (m, 4H, CH_2 + CH_3), 1.39 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 0.76 (t, J = 7.4 Hz, 3H, CH_3).

^{13}C NMR (125 MHz, THF-*D$_8$*): δ (ppm) 272.7 ($C_{carbene}$), 246.5 (CH$_{alkylidene}$), 154.5 ($C_{q\ ar}$), 154.1 ($C_{q\ ar}$), 142.0 ($C_{q\ ar}$), 141.3 ($C_{q\ ar}$), 140.5 ($C_{q\ ar}$), 139.5 ($C_{q\ ar}$), 139.0 ($C_{q\ ar}$), 131.5 ($C_{q\ ar}$), 129.6 ($C_{q\ ar}$), 127.9 (CH$_{ar}$), 127.4 (CH$_{ar}$), 126.1 (CH$_{ar}$), 125.2 (CH$_{ar}$), 124.8 (CH$_{ar}$), 122.8 (CH$_{ar}$), 121.9 (CH$_{ar}$), 120.9 (CH$_{ar}$), 114.2 (CH$_{ar}$), 78.6 (CHO), 54.2 (CH$_2$), 51.5 (CH$_3$), 31.8 (CH$_3$), 31.6 (CH$_3$), 29.7 (C_q), 29.6 (C_q), 27.7 (CH$_2$), 25.4 (CH$_3$), 22.6 (CH$_3$), 21.5 (CH$_3$), 21.2 (CH$_2$), 14.5 (CH$_3$), 11.4 (CH$_3$).

Attempts to obtain HRMS and crystals of **Ru-4a** failed due to its high sensibility towards air and moisture.



Chemical Formula: $C_{37}H_{45}Cl_2NORuS_2$
Molecular Weight: 755,86

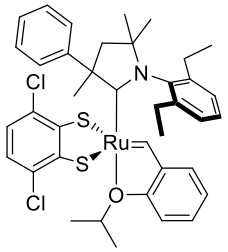
Ru-4b was prepared according to general procedure for the dithiolate complexes synthesis with **Ru-3b** (70 mg, 0.11 mmol, 1.0 equiv), 1,6-dichloro-1,2-benzene dithiol **1** (26 mg, 0.12 mmol, 1.1 equiv), Et_2Zn (0.12 mL, 0.12 mmol, 1.1 equiv) and THF (2 mL). The desired product was obtained after purification as a brown solid (84 mg, 99 % yield).

^{1}H NMR (500 MHz, *THF-D$_8$*): δ (ppm) 13.81 (s, 1H, C$H_{alkylidene}$), 7.49 (dd, J = 7.9, 1.5 Hz, 1H, CH_{ar}), 7.33 (ddd, J = 8.7, 7.2, 1.7 Hz, 1H, CH_{ar}), 7.28 – 7.17 (m, 2H, CH_{ar}), 6.88 (d, J = 8.1 Hz, 1H, CH_{ar}), 6.82 (d, J = 8.1 Hz, 1H, CH_{ar}), 6.78 (td, J = 7.4, 0.9 Hz, 1H, CH_{ar}), 6.63 – 6.52 (m, 2H, CH_{ar}), 5.80 (sept, J = 6.7 Hz, 1H, CHO), 3.31 (dq, J = 15.0, 7.4 Hz, 1H, CH_2), 2.75 (dq, J = 15.0, 7.4 Hz, 1H, CH_2), 2.64 (td, J = 12.9, 3.9 Hz, 1H, CH_2), 2.27 (d, J = 13.1 Hz, 1H, C$H_{2\ backbone}$), 2.23 – 2.08 (m, 3H, CH_2 + C$H_{2\ backbone}$), 2.09 – 2.02 (m, 1H, CH_2), 1.98 (d, J = 6.7 Hz, 3H, CH_3), 1.86 (d, J = 6.6 Hz, 3H, CH_3), 1.81 – 1.76 (m, 1H, CH_2), 1.74 – 1.68 (m, 2H, CH_2), 1.65 (t, J = 7.4 Hz, 3H, CH_3), 1.62 – 1.54 (m, 2H, CH_2), 1.47 (dt, J = 16.2, 7.7 Hz, 1H, CH_2), 1.42 – 1.29 (m, 5H, CH_2 + CH_3), 1.22 (s, 3H, CH_3), 0.69 (t, J = 7.4 Hz, 3H, CH_3).

^{13}C NMR (125 MHz, THF-*D$_8$*): δ (ppm) 273.4 ($C_{carbene}$), 248.3 (CH$_{alkylidene}$), 154.4 ($C_{q\ ar}$), 154.1 ($C_{q\ ar}$), 142.3 ($C_{q\ ar}$), 141.3 ($C_{q\ ar}$), 140.7 ($C_{q\ ar}$), 139.5 ($C_{q\ ar}$), 139.1 ($C_{q\ ar}$), 131.5 ($C_{q\ ar}$), 129.6 ($C_{q\ ar}$), 127.8 (CH$_{ar}$), 127.5 (CH$_{ar}$), 126.2 (CH$_{ar}$), 125.1 (CH$_{ar}$), 124.9 (CH$_{ar}$), 122.7 (CH$_{ar}$), 121.9 (CH$_{ar}$), 120.9 (CH$_{ar}$), 114.4 (CH$_{ar}$), 78.6 (CHO), 60.4 (CH$_2$), 45.0 (CH$_2$), 40.8 (C_q), 39.7 (CH$_2$), 30.6 (C_q),

27.7 (*C*H$_3$), 25.8 (*C*H$_3$), 25.4 (*C*H$_2$), 24.8 (*C*H$_3$), 22.8 (*C*H$_2$), 22.6 (*C*H$_2$), 22.5 (*C*H$_2$), 22.0 (*C*H$_2$), 20.6 (*C*H$_3$), 14.8 (*C*H$_3$), 11.2 (*C*H$_3$).

Attempts to obtain HRMS and crystals of **Ru-4b** failed due to its high sensibility towards air and moisture.



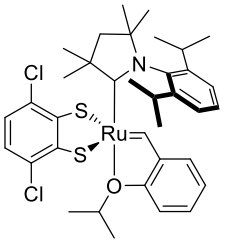
Chemical Formula: $C_{39}H_{43}Cl_2NORuS_2$
Molecular Weight: 777,87

Ru-4c was prepared according to general procedure for the dithiolate complexes synthesis with **Ru-3c** (63 mg, 0.10 mmol, 1.0 equiv), 1,6-dichloro-1,2-benzene dithiol **1** (31 mg, 0.15 mmol, 1.5 equiv), Et_2Zn (0.14 mL, 0.14 mmol, 1.4 equiv) and THF (1.4 mL). The desired product was obtained after purification as a brown solid (75 mg, 97 % yield).

^{1}H NMR (500 MHz, *THF-D$_8$*): δ (ppm) 13.80 (s, 1H, C*H*$_{alkyllidene}$), 7.81 (d, *J* = 7.7 Hz, 2H, C*H*$_{ar}$), 7.43 (t, *J* = 7.6 Hz, 3H, C*H*$_{ar}$), 7.32 (t, *J* = 7.4 Hz, 1H, C*H*$_{ar}$), 7.24 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H, C*H*$_{ar}$), 7.14 (t, *J* = 7.7 Hz, 1H, C*H*$_{ar}$), 7.09 (d, *J* = 8.4 Hz, 1H, C*H*$_{ar}$), 6.84 (d, *J* = 8.0 Hz, 1H, C*H*$_{ar}$), 6.77 (d, *J* = 8.1 Hz, 1H, C*H*$_{ar}$), 6.68 (t, *J* = 7.3 Hz, 1H, C*H*$_{ar}$), 6.54 (dd, *J* = 7.6, 1.7 Hz, 1H, C*H*$_{ar}$), 6.50 (d, *J* = 7.6 Hz, 1H, C*H*$_{ar}$), 4.09 - 4.02 (m, 1H, C*H*O), 3.27 (dq, *J* = 15.1, 7.4 Hz, 1H, C*H*$_2$), 2.99 (d, *J* = 13.1 Hz, 1H, C*H*$_{2\ backbone}$), 2.72 (dq, *J* = 15.0, 7.4 Hz, 1H, C*H*$_2$), 2.30 (d, *J* = 13.1 Hz, 1H, C*H*$_{2\ backbone}$), 2.16 - 2.04 (m, 4H, C*H*$_3$ + C*H*$_2$), 1.80 – 1.76 (m, 1H, C*H*$_2$), 1.62 (t, *J* = 7.4 Hz, 3H, C*H*$_3$), 1.52 (s, 3H, C*H*$_3$), 1.38 (d, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.26 (d, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.23 (s, 3H, C*H*$_3$), 0.77 (t, *J* = 7.4 Hz, 3H, C*H*$_3$).

^{13}C NMR (125 MHz, THF-*D$_8$*): δ (ppm) 270.5 (*C*$_{carbene}$), 253.8 (*C*H$_{alkylidene}$), 154.6 (*C*$_{q\ ar}$), 153.7 (*C*$_{q\ ar}$), 145.5 (*C*$_{q\ ar}$), 143.0 (*C*$_{q\ ar}$), 140.9 (*C*$_{q\ ar}$), 140.9 (*C*$_{q\ ar}$), 139.6 (*C*$_{q\ ar}$), 139.1 (*C*$_{q\ ar}$), 131.2 (*C*H$_{ar}$), 129.7 (*C*$_{q\ ar}$), 129.2 (2C, *C*H$_{ar}$), 128.1 (*C*H$_{ar}$), 127.8 (2C, *C*H$_{ar}$), 127.7 (*C*$_{q\ ar}$), 127.1 (*C*H$_{ar}$), 126.1 (*C*H$_{ar}$), 125.4 (*C*H$_{ar}$), 124.6 (*C*H$_{ar}$), 122.4 (*C*H$_{ar}$), 121.5 (*C*H$_{ar}$), 120.9 (*C*H$_{ar}$), 114.0 (*C*H$_{ar}$), 81.0 (*C*H$_2$), 78.4 (C*H*O), 62.3 (*C*H$_2$), 49.0 (*C*$_q$), 30.6 (*C*H$_2$), 29.7 (*C*H$_3$), 28.9 (*C*H$_3$), 28.9 (*C*H$_3$), 23.1 (*C*$_q$), 21.3 (*C*H$_3$), 20.3 (*C*H$_3$), 14.4 (*C*H$_3$), 11.6 (*C*H$_3$).

Attempts to obtain HRMS and crystals of **Ru-4c** failed due to its high sensibility towards air and moisture.



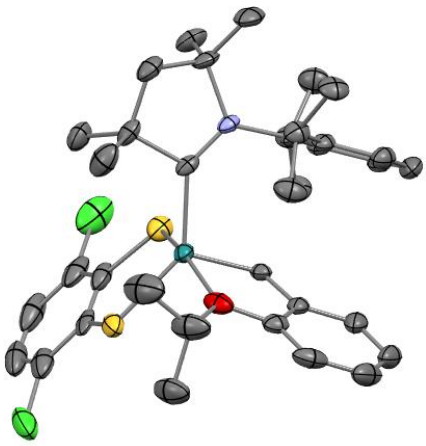
Chemical Formula: $C_{36}H_{45}Cl_2NORuS_2$
Molecular Weight: 743,85

Ru-4d was prepared according to general procedure for the dithiolate complexes synthesis with **Ru-3d** (82.4 mg, 0.14 mmol, 1 equiv), 1,6-dichloro-1,2-benzene dithiol **1** (43.8 mg, 0.21 mmol, 1.5 equiv), Et_2Zn (0.2 mL, 0.20 mmol, 1.5 equiv) and THF (2 mL). The desired product was obtained after purification as a brown solid (100.5 mg, 99 % yield).

^{1}H NMR (400 MHz, *THF-D$_8$*): δ (ppm) 14.15 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.22 (q, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.75 – 6.63 (m, 2H), 6.63 – 6.57 (m, 1H), 5.90 – 5.76 (m, 1H), 3.79 – 3.71 (m, 1H), 2.49 (sept, *J* = 6.8 Hz, 1H), 2.11 – 1.98 (m, 5H), 1.87 (d, *J* = 6.7 Hz, 3H), 1.79 (d, *J* = 6.7 Hz, 3H), 1.78 – 1.74 (m, 6H), 1.46 (s, 3H), 1.33 (d, *J* = 6.5 Hz, 3H), 1.19 (s, 3H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.40 (d, *J* = 6.8 Hz, 3H).

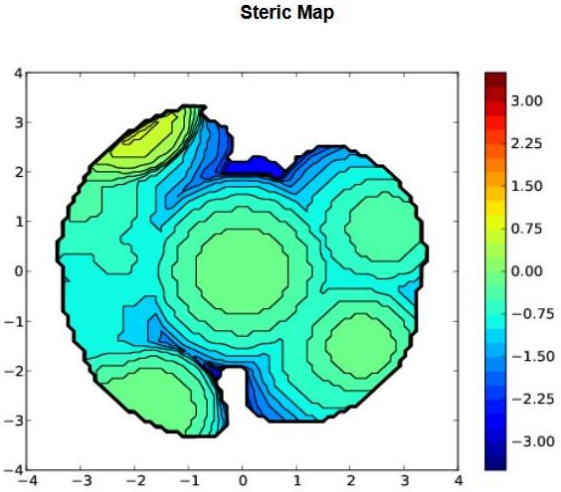
^{13}C NMR (101 MHz, THF-*D$_8$*): δ (ppm) 276.5, 250.9, 154.7, 154.6, 147.9, 147.2, 143.2, 142.4, 140.0, 132.8, 130.8, 129.9, 128.5, 125.9, 125.9, 125.8, 124.0, 122.9, 122.2, 116.3, 83.2, 78.7, 56.6, 54.0, 36.4, 33.8, 32.6, 29.9, 29.5, 29.1, 27.2, 26.7, 24.9, 24.4, 22.7, 22.4.

HRMS for $C_{36}H_{45}NO^{35}Cl_2S_2{}^{102}Ru$: calc.: 743.13576; found: 743.1359. Source: ESI.



X-ray diffraction: Crystals of **Ru-4d** suitable for XRD were grown by slow diffusion of benzene in hexanes in a glovebox. CCDC number: 2190002.

Vbur:



%V Free	%V Buried	% V Tot/V Ex
64.6	35.4	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	28.9	16.0	44.9	64.4	35.6
NW	28.1	16.8	44.9	62.7	37.3
NE	31.0	13.9	44.9	69.0	31.0
SE	28.0	16.8	44.9	62.5	37.5

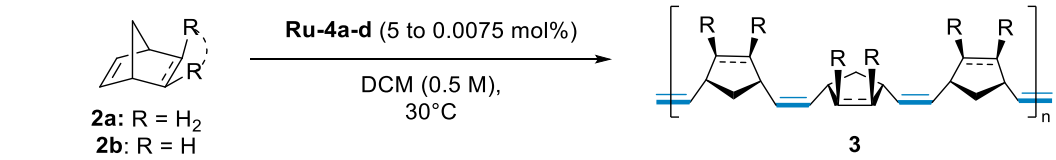
5. Ring-Opening Metathesis Polymerization

5.1. Reagents

Norbornene **2a** was purcharsed from Sigma Aldrich, sublimed under Ar prior to use and stored in a glove box. Norbornadiene **2b** was purchased from Sigma Aldrich, distilled over molecular sieves 4 Å and stored in a freezer in a glove box. *Cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (**2f**) was purchased from TCI and recrystallized in cyclohexane prior to use. ((1*R*,2*R*,3*S*,4*S*)-bicyclo[2.2.1]hept-5-ene-2,3-diyl)dimethanol (**2c**),[7] ((1*R*,2*S*,3*R*,4*S*)-bicyclo[2.2.1]hept-5-ene-2,3-diyl)bis (methylene) diacetate (**2d**),[6] (3a*R*,4*R*,7*S*,7a*S*) 2-phenyl-3a,4,7,7a-tetrahydro-1H-4,7-methano*iso*indole-1,3(2H)-dione (**2e**)[10], (3a*R*,4*S*,7*R*,7a*S*)-3a,4,7,7a-tetrahydro-4,7-epoxyiso-

benzofuran-1,3-dione (**2g**),[8] were prepared according to literature procedures and dried under high vacuum prior to use.

5.2. General procedure for Z-ROMP



2a: R = H_2
2b: R = H
2c: R = CH_2OH
2d: R = CH_2OAc
2e: R = C(=O)N(-Ph)C(=O)
2f: R = C(=O)OC(=O)

3

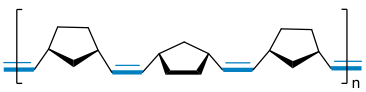
In a flame-dried vial in an Ar filled glove box, the norbornene derivative **2** (0.5 mmol, 1.0 equiv) was dissolved in DCM (1 mL). A fresh solution of the desired complex was added (5 – 0.0075 mol%). The mixture was vigorously stirred the indicated time at 30 °C. Aliquots were taken and analysed by ^{1}H NMR to monitor the reaction. When full conversion was reached, reaction was quenched with ethyl vinyl ether. The desired polymer was obtained after precipitation in methanol. *Z/E* ratio was determined by ^{1}H NMR and tacticity by quantitative ^{13}C NMR (with total nOe decoupling and relaxation delay of 15 sec) by comparison with published spectra.

5.3. Additional results of the article in ROMP

Entry	Substrate	Conditions	Yield (%)	*Z/E*	Syndiotacticity
1	**2a**	**Ru-4c** (5 mol%)	85	99/1	>95%
2	**2a**	**Ru-4c** (1 mol%)	90	98/2	>95%
3	**2a**	**Ru-4c** (0.0075 mol%)	nd	75/25	Nd
4	**2b**	**Ru-4b** (0.1 mol%) c = 2 M in DCM	89	99/1	70%

Table S 1: Additional results in ROMP

5.4. Analytical data of ROMP products



3a

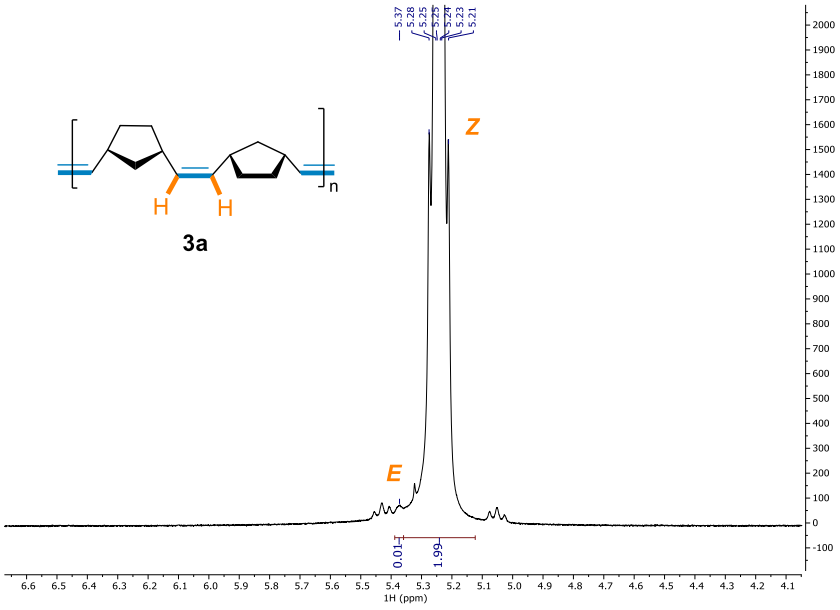
The general procedure for *Z*-ROMP reactions was followed using norbornene **2a** (48.0 mg, 0.51 mmol, 1.0 equiv) and 55 µL of a fresh solution of the complex **Ru-4d** (8.0 mg in 1.0 mL of DCM, 0.0006 mmol, 0.1 mol%). The mixture was stirred 30 minutes. **3a** was obtained after precipitation in methanol (39.8 mg, 89% yield, >98/2 *Z/E*).

^{1}H NMR (400 MHz, *CDCl$_3$*, *cis*): δ (ppm) 5.25 – 5.18 (m, 2H, C*H*$_{alkene}$), 2.88 – 2.72 (m, 2H, 2 x C*H*), 1.93 (dt, *J* = 12.9, 6.7 Hz, 1H, C*H*$_2$), 1.88 – 1.77 (m, 2H, C*H*$_2$), 1.48 – 1.32 (m, 2H, C*H*$_2$), 1.05 (dt, *J* = 12.5, 10.3 Hz, 1H, C*H*$_2$).

^{13}C NMR (101 MHz, *CDCl$_3$*, *cis*): δ (ppm) 133.9 (2C, *C*H$_{alkene}$), 42.7 (*C*H$_2$), 38.6 (2C, *C*H), 33.2 (2C, *C*H$_2$).

Analytical data for this compound were consistent with the previously reported data for syndiotactic *Z*-3a.[11]

***Z*-selectivity determination by ^{1}H NMR** (with **Ru-4d**, 0.1 mol%) : >98/2[12,13]



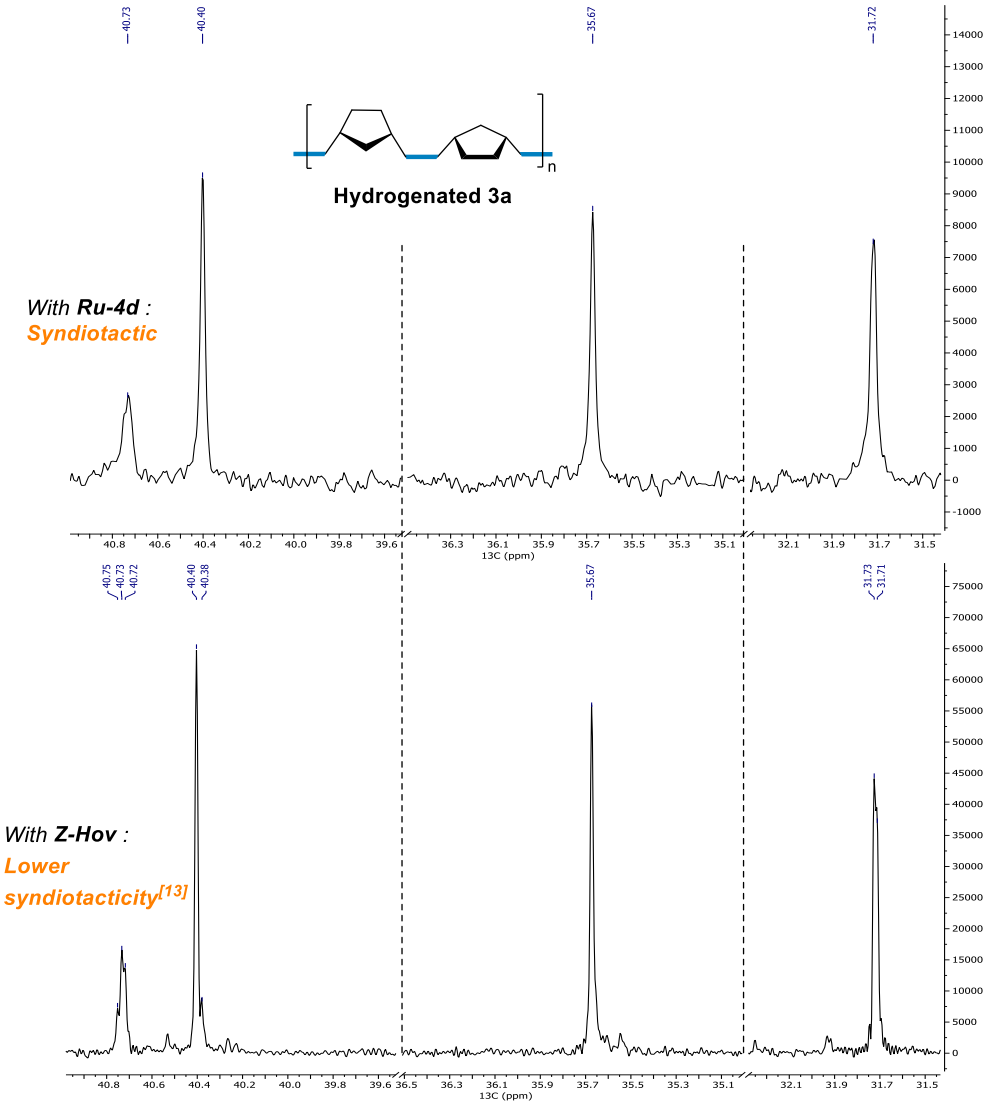
Syndiotacticity was determined by quantitative ^{13}C NMR on the hydrogenated polymer.[11] 39.8 mg of polynorbornene was dissolved in 2 mL of *p*-xylene. *p*-toluenesulfone hydrazide (414.0 mg, 2.223 mmol) was added. The mixture was heated at 120°C for 5 h. The mixture was cooled down to room temperature and MeOH was added. The desired polymer precipitated, the supernatant was removed and the polymer was dried under high vacuum. Tacticity was determined by ^{13}C NMR at 60°C in $CDCl_3$.

^{1}H NMR (400 MHz, *CDCl$_3$*, *cis*): δ (ppm) 1.99 – 1.85 (m, 1H), 1.85 – 1.58 (m, 4H), 1.41 – 1.23 (m, 4H), 1.23 – 1.05 (m, 2H), 0.75 – 0.57 (m, 1H).

^{13}C NMR (101 MHz, *CDCl$_3$*, *cis*): δ (ppm) 40.7, 40.4, 35.7, 31.7.

Analytical data for this compound were consistent with the previously reported data for syndiotactic *Z*-3a.[11]

Syndiotacticity determination by ^{13}C NMR:[14]

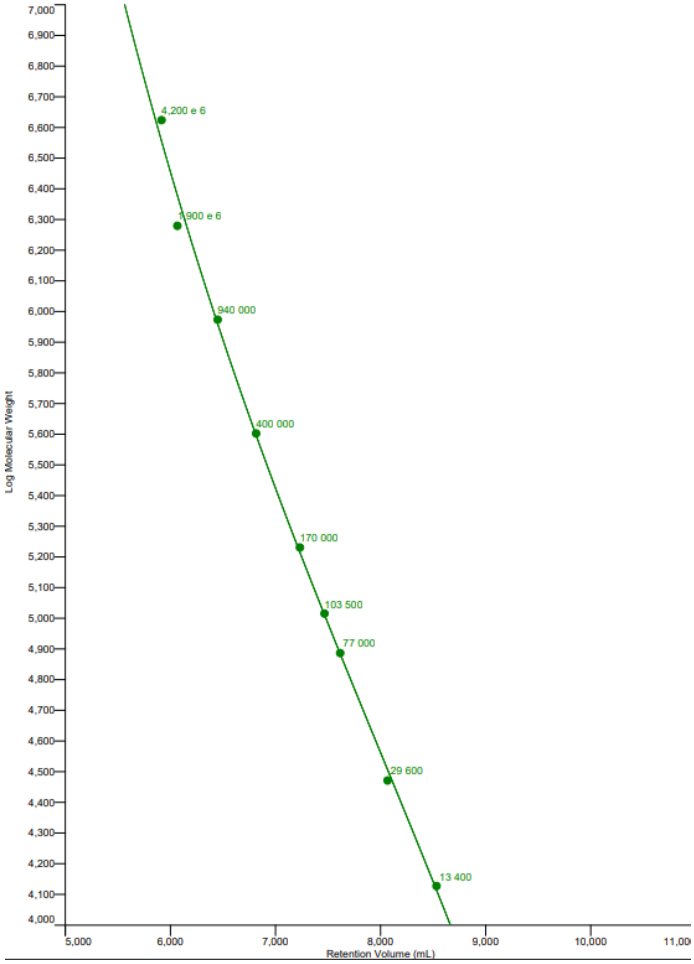


M_w, M_n, and Đ of polynorbornenes were determined by SEC analysis. The polymer was dissolved in THF (2 mg/mL) 24 hours before the analysis. The sample was filter through syringe filter (0.2 µm pores) before injection.

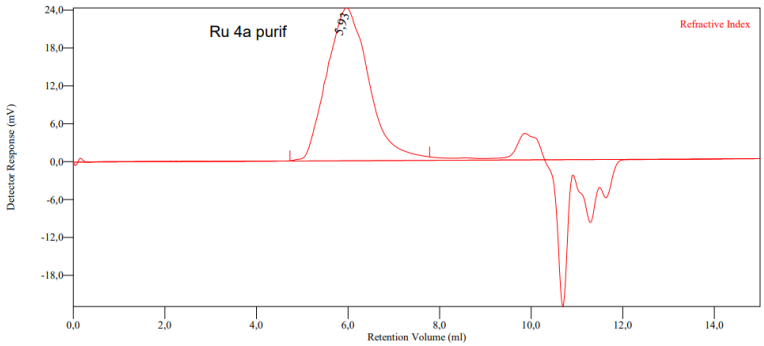
Entry	Catalyst	Yield (%)	*Z/E*	Syndiotacticity	M_w (kg/mol)	M_n (kg/mol)	Đ
1	Ru-4a	93	97:3	>95	5 478	1 264	4.3
2	Ru-4b	91	96:4	>95	5 351	1 362	3.9
3	Ru-4c	98	92:8	>95	2 452	489	5.0
4	Ru-4d	89	>98:2	>95	**563**	290	**1.9**
5	Z-Hov	92	>98:2	-	731	260	2.8

Table S 2: M_w, M_n, and Đ of polynorbornenes

SEC calibration curve

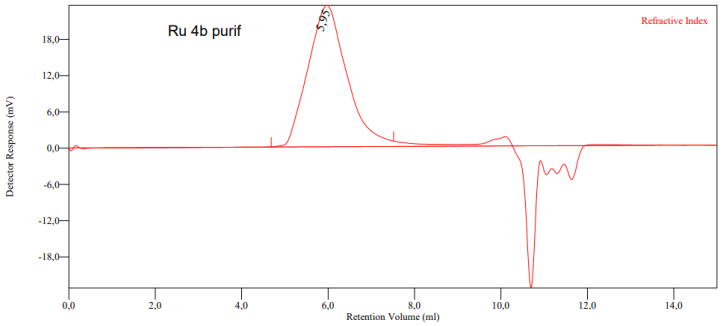


*SEC chromatogram with **Ru-4a** (0.1 mol%)*



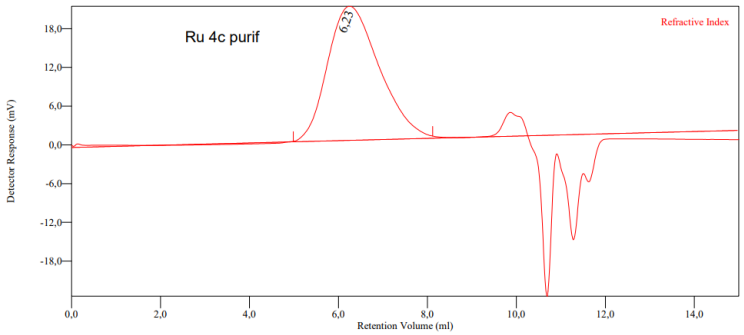
Peak RV - (ml)	5,933
Mn - (Daltons)	1,264 e 6
Mw - (Daltons)	5,478 e 6
Mz - (Daltons)	1,712 e 7
Mp - (Daltons)	3,319 e 6
Mw / Mn	4,333
Percent Above Mw: 0	0,000
Percent Below Mw: 0	0,000
Mw 10.0% Low	342 353
Mw 10.0% High	2,376 e 7
RI Area - (mvml)	25,70
UV Area - (mvml)	0,00

*SEC chromatogram with **Ru-4b** (0.1 mol%)*



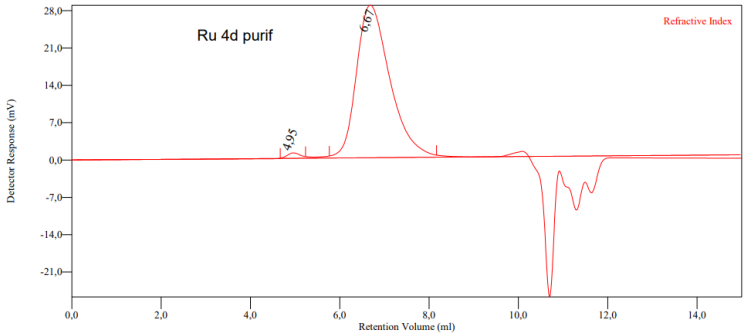
Peak RV - (ml)	5,950
Mn - (Daltons)	1,362 e 6
Mw - (Daltons)	5,351 e 6
Mz - (Daltons)	1,578 e 7
Mp - (Daltons)	3,179 e 6
Mw / Mn	3,928
Percent Above Mw: 0	0,000
Percent Below Mw: 0	0,000
Mw 10.0% Low	349 274
Mw 10.0% High	2,356 e 7
RI Area - (mvml)	24,30
UV Area - (mvml)	0,00

*SEC chromatogram with **Ru-4c** (0.1 mol%)*



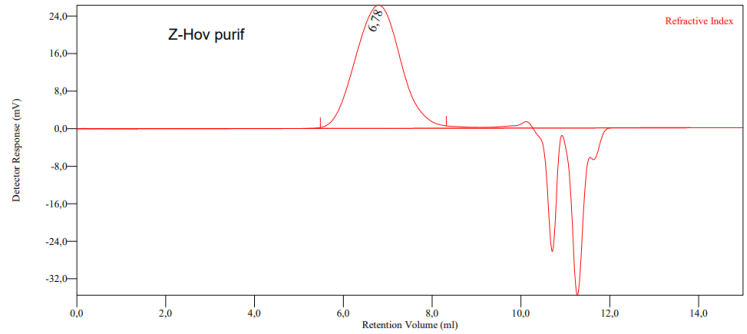
Peak RV - (ml)	6,233
Mn - (Daltons)	488 770
Mw - (Daltons)	2,452 e 6
Mz - (Daltons)	9,382 e 6
Mp - (Daltons)	1,509 e 6
Mw / Mn	5,018
Percent Above Mw: 0	0,000
Percent Below Mw: 0	0,000
Mw 10.0% Low	120 655
Mw 10.0% High	1,145 e 7
RI Area - (mvml)	27,95
UV Area - (mvml)	0,00

*SEC chromatogram with **Ru-4d** (0.1 mol%)*



Peak RV - (ml)	4,950	6,667
Mn - (Daltons)	7,009 e 7	289 670
Mw - (Daltons)	8,626 e 7	563 250
Mz - (Daltons)	1,066 e 8	983 318
Mp - (Daltons)	8,012 e 7	536 506
Mw / Mn	1,231	1,944
Percent Above Mw: 0	0,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	3,506 e 7	92 376
Mw 10.0% High	1,598 e 8	1,600 e 6
RI Area - (mvml)	0,33	24,79
UV Area - (mvml)	0,00	0,00

*SEC chromatogram with **Ru-4d** (0.1 mol%)*



Peak RV - (ml)	6,783
Mn - (Daltons)	259 899
Mw - (Daltons)	731 300
Mz - (Daltons)	1,967 e 6
Mp - (Daltons)	421 830
Mw / Mn	2,814
Percent Above Mw: 0	0,000
Percent Below Mw: 0	0,000
Mw 10.0% Low	76 918
Mw 10.0% High	2,912 e 6
RI Area - (mvml)	30,87
UV Area - (mvml)	0,00

3b

The general procedure for *Z*-ROMP reactions was followed using norbornadiene **2b** (55 µL, 0.54 mmol, 1.0 equiv) and 76 µL of a fresh solution of the complex **Ru-4b** (8.1 mg in 1.5 mL of DCM,

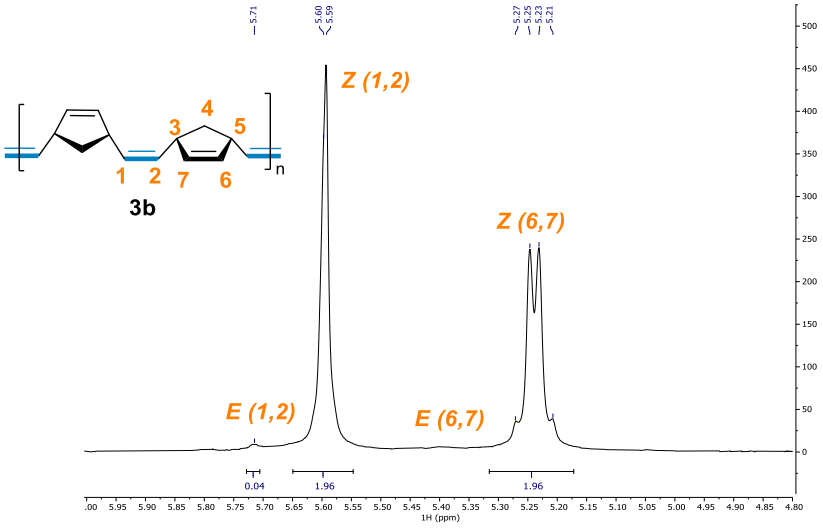
0.00054 mmol, 0.1 mol%). The mixture was stirred 15 minutes. **3b** was obtained after precipitation in methanol (48.9 mg, 98% yield, >98/2 *Z*/*E*).

^{1}H NMR (400 MHz, *CDCl$_3$*, *cis*, ~75% syndiotactic polymer): δ (ppm) 5.65 – 5.55 (m, 2H, C*H*$_{alkene}$), 5.26 – 5.19 (m, 2H, C*H*$_{alkene}$), 3.71 – 3.58 (m, 2H, 2 x C*H*), 2.46 – 2.39 (m, 1H, C*H*$_2$), 1.32 – 1.19 (m, 1H, C*H*$_2$).

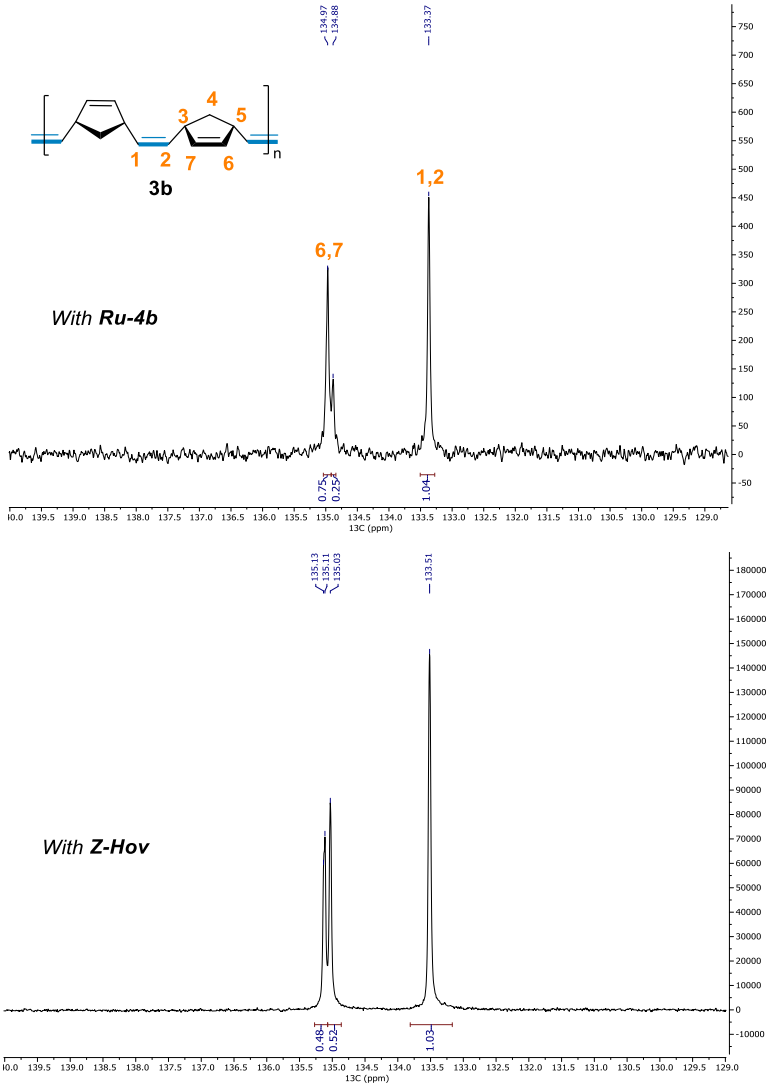
^{13}C NMR (101 MHz, *CDCl$_3$*, *cis*, ~75% syndiotactic polymer): δ (ppm) 135.1 (2C, *C*H$_{alkene}$), 133.5 (2C, *C*H$_{alkene}$), 44.1 (*C*H$_2$), 39.9 (2C, *C*H).

Analytical data for this compound were consistent with the previously reported data.[14]

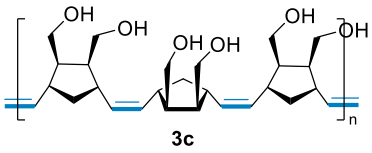
***Z*-selectivity determination by ^{1}H NMR** (with **Ru-4b**, 0.1 mol%) : 98/2[13]



Syndiotacticity determination by quantitative ^{13}C NMR (with **Ru-4b**, 0.1 mol%): ~75%



M_w, M_n, and Đ of polynorbornenes could not be determined because the obtained polymer is not soluble in THF.

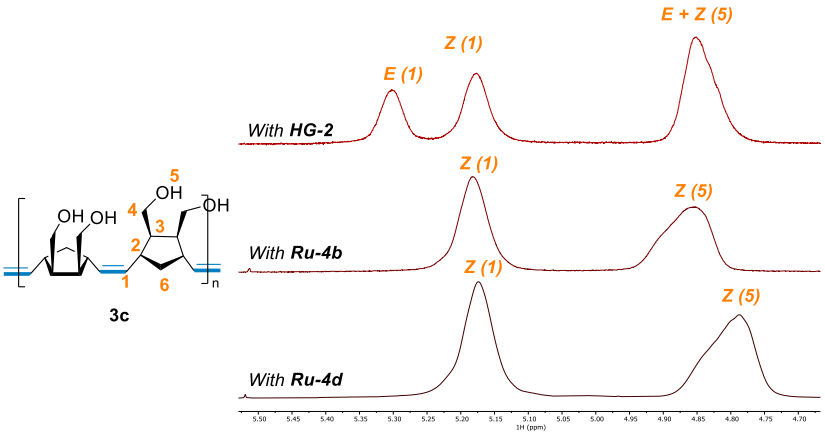


The general procedure for *Z*-ROMP reactions was followed using **2c** (50.0 mg, 0.32 mmol, 1.0 equiv) and 45 µL of a fresh solution of the complex **Ru-4d** (8.0 mg in 1.5 mL of DCM, 0.00032 mmol, 0.1 mol%). The mixture was stirred 1 hour. Conversion of 89% was determined according to the recovered starting material in the filtrate (5.4 mg). **3c** was obtained after precipitation in methanol (44.3 mg, 88% yield, >98/2 *Z*/*E*).

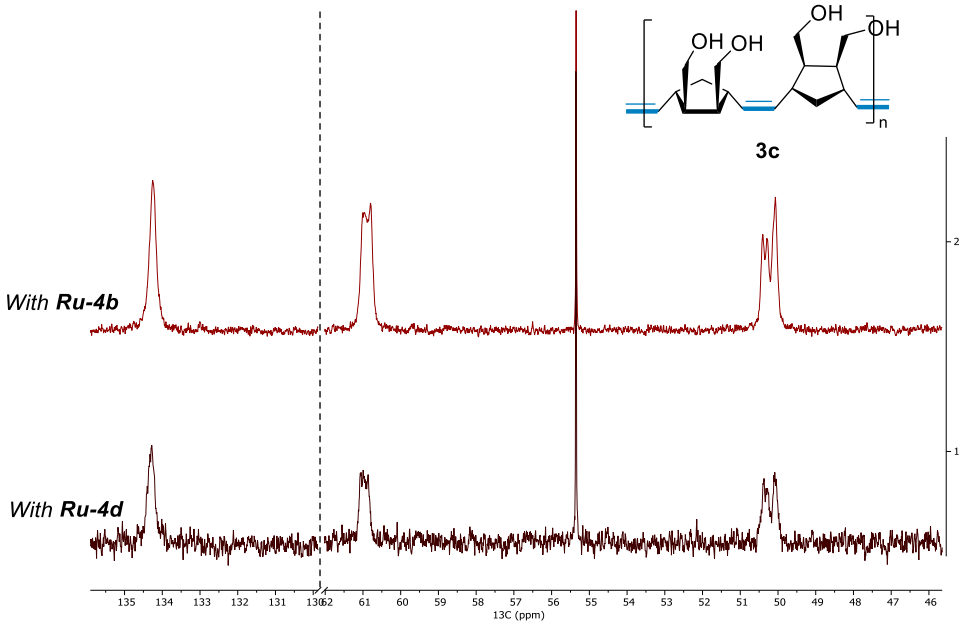
^{1}H NMR (400 MHz, *DMSO-d$_6$*, *cis*): δ (ppm) 5.27 – 5.06 (m, 2H), 4.92 – 4.78 (m, 2H), 3.46 – 3.26 (m, 4H), 2.65 – 2.44 (m, 2H), 1.95 – 1.69 (m, 3H), 1.12 – 0.91 (m, 1H).

^{13}C NMR (101 MHz, *DMSO-d$_6$*, *cis*): δ (ppm) 134.1, 60.8, 50.1, 49.9, 40.8.

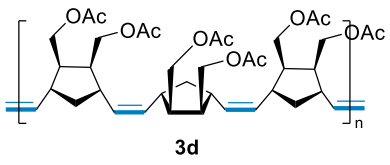
***Z*-selectivity determination by ^{1}H NMR**: >98/2.



Atactic according to the broad ^{13}C NMR spectra:



M_w, M_n, and Đ of polynorbornenes could not be determined because the obtained polymer is not soluble in THF.

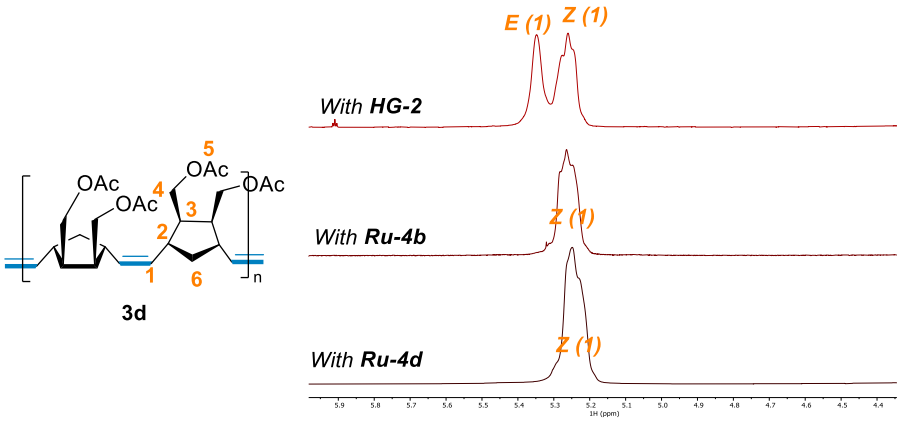


The general procedure for *Z*-ROMP reactions was followed using **2d** (48.2 mg, 0.20 mmol, 1.0 equiv) and 28 µL of a fresh solution of the complex **Ru-4d** (8.0 mg in 1.5 mL of DCM, 0.0002 mmol, 0.1 mol%). The mixture was stirred 30 minutes. **3d** was obtained after precipitation in methanol (45.2 mg, 94% yield, >98/2 *Z*/*E*).

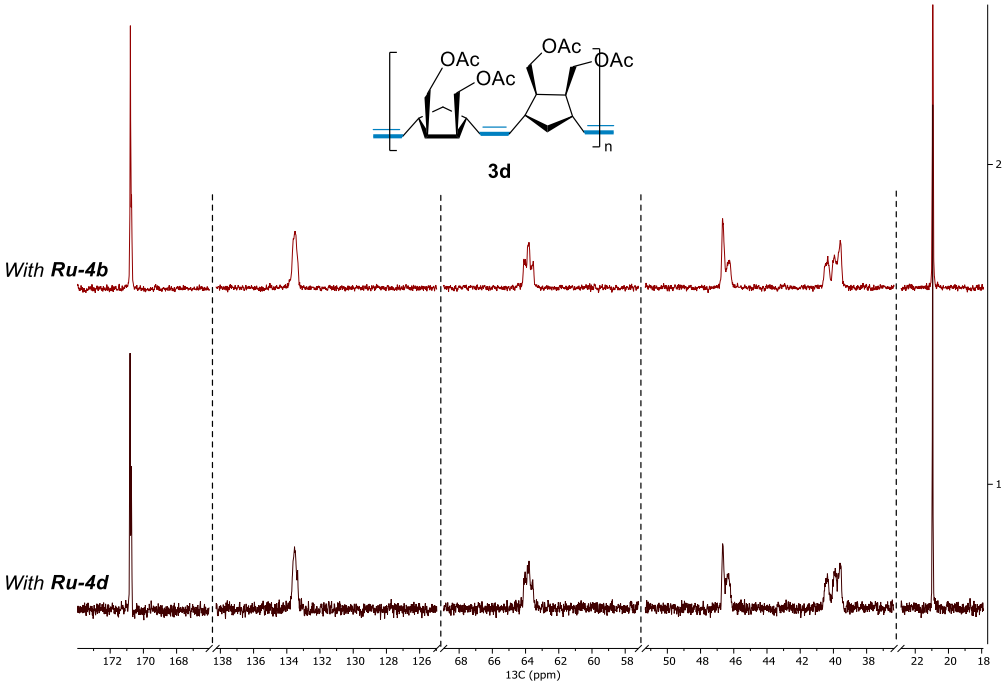
^{1}H NMR (400 MHz, *CDCl*$_3$, *cis*): δ (ppm) 5.33 – 5.19 (m, 2H, C*H*$_{alkene}$), 4.19 – 3.99 (m, 4H, 2 x C*H*$_2$), 2.77 – 2.56 (m, 2H, 2 x C*H*), 2.25 – 1.96 (m, 9H, 2 x C*H*$_3$ + 2 x C*H* + C*H*$_2$), 1.26 – 1.09 (m, 1H, C*H*$_2$).

^{13}C NMR (101 MHz, *CDCl*$_3$, *cis*): δ (ppm) 170.8 (2C, *C*=O), 133.5 (2C, *C*H$_{alkene}$), 63.9 (2C, *C*H$_2$), 46.7 (4C, *C*H), 39.6 (*C*H$_2$), 20.9 (2C, *C*H$_3$).

***Z*-selectivity determination by ^{1}H NMR**: >98/2.



Atactic according to the broad ^{13}C NMR spectra:



M_w, M_n, and Đ of polynorbornenes could not be determined because the obtained polymer is not soluble in THF.

6. Cross-metathesis

6.1. Reagents

Cis-1,4-diol-2-butene **14a**, *Cis*-1,4-diacetoxy-2-butene **14b**, 1-decene **13**, styrene, 5-hexenoic acid, 4-bromopentene, 10-undecenal, 1-phenyl-3-buten-1-ol, 3-methyl-1,4-pentadiene, were purchased from Sigma Aldrich, filtered through basic alumina, freeze/pump/thaw (3 cycles) and stored in a freezer under Ar prior to use.

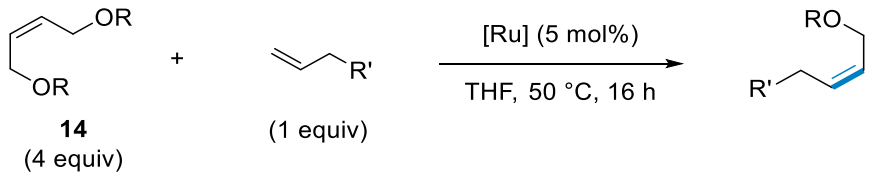
6.2. Additional results in CM between 14a (4 equiv) and 13

Entry	Solvent	Temperature	Complex (loading)	Conversion (NMR Yield)[a]
1	THF	rt	**Ru-4c** (5 mol%)	0
2	Toluene	80°C	**Ru-4c** (5 mol%)	20 (<5%)
3	THF	50°C	**Ru-4c** (4x1.25 mol%)	17 (6)
4	$CHCl_3$	rt	**Ru-4d** (5 mol%)	30 (25)
5	$CHCl_3$	50°C	**Ru-4d** (5 mol%)	36 (33)

[a] Determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

*Table S 3: Additional results in CM between **13** and **14a***

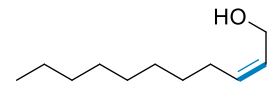
6.3. General procedure for CM with isolated complex



In a flame dried microwave tube in a glove box, the desired cross-partner (0.20 mmol, 1.0 equiv), *cis*-2-butene-1,4-diol **14a** (65 µL, 0.80 mmol, 4.0 equiv) or *cis*-2-butene-1,4-diacetoxy **14b** (130 µL, 0.80 mmol, 4.0 equiv) and trimethoxybenzene (IS, 11.1 mg, 0.066 mmol, 0.33 equiv) were placed. The freshly prepared solution of the desired ruthenium complex (0.01 mmol, 5 mol%) in THF (0.5 mL) was added. The mixture was stirred out of the glove box under Ar steam at 50°C for 16 hours. The reaction was quenched with EVE. Conversion was determined by ^{1}H NMR. Product was purified by silica gel column chromatography. *Z/E* ratio was determined by ^{1}H NMR on the purified product (*E* and *Z* products are not separable by silica gel with this eluent system). A purple fraction composed of complex degradation products was coeluted with the product. The product was filtered over activated charcoal pipette (eluent: DCM).

6.4. Analytical data of CM products

(Z)-undec-2-en-1-ol (15)



Chemical Formula: $C_{11}H_{22}O$
Molecular Weight: 170,30

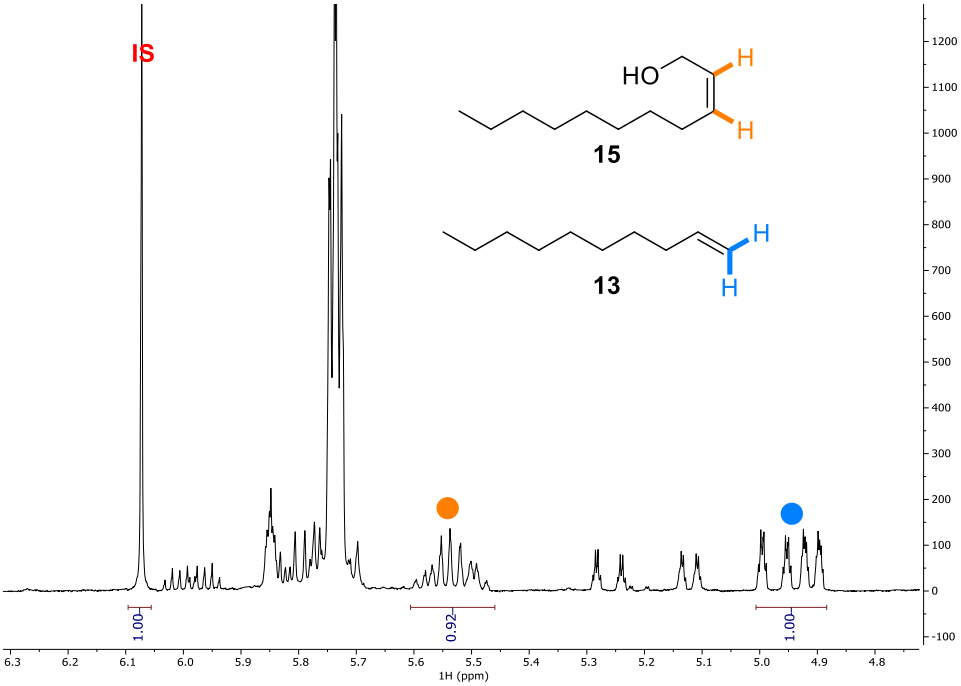
The general procedure for *Z*-CM reactions was followed using 1-decene **13** (38 µL, 0.20 mmol, 1.0 equiv) and **Ru-4d** (7.4 mg, 0.01 mmol, 5 mol%). **15** was isolated after purification (eluent: Pentane:Et_2O 9:1) as a colourless oil (16.4 mg, 48% yield, 98/2 *Z/E*).

^{1}H NMR of *Z*-isomer (400 MHz, $CDCl_3$) δ (ppm) 5.73 – 5.47 (m, 2 H, CH_{alkene}), 4.21 (d, *J* = 6.1 Hz, 2 H, CH_2OH), 2.20 – 2.01 (m, 2 H, CH_2), 1.48 – 1.18 (m, 13 H, 6 x CH_2 + O*H*), 0.98 – 0.81 (m, 3 H, CH_3).

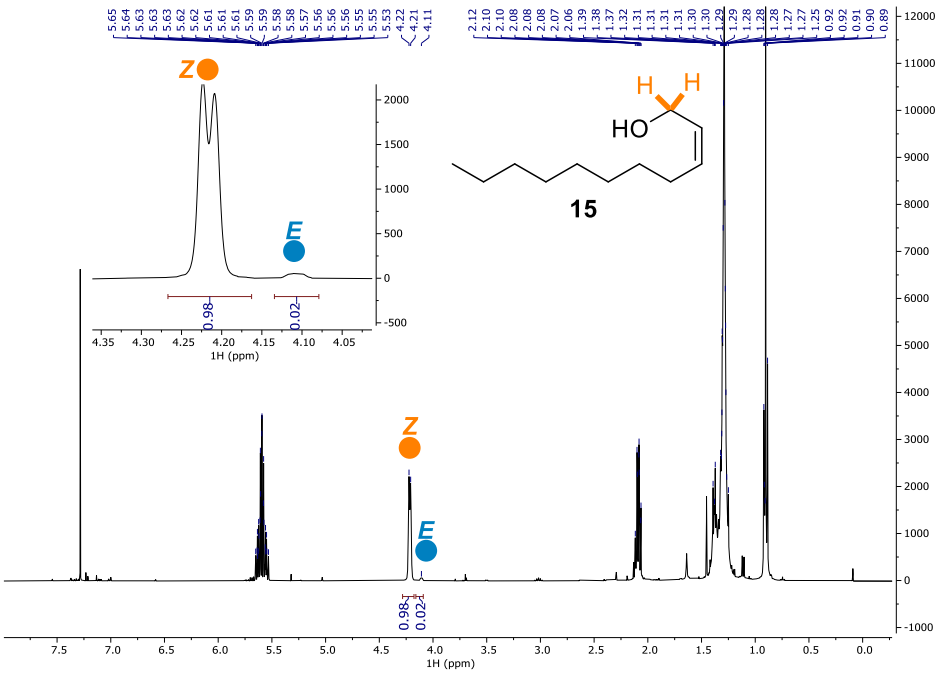
^{13}C NMR of *Z*-isomer (101 MHz, $CDCl_3$) δ (ppm) 133.3 (CH_{alkene}), 128.3 (CH_{alkene}), 58.6 (CH_2OH), 31.9 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 27.4 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

Analytical data for this compound were consistent with the previously reported data.[15]

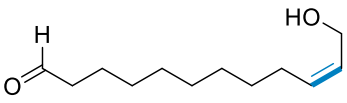
Conversion determination by ^{1}H NMR: with **Ru-4d** (Table 2, entry 5) 50% conv., 46% NMR yield.



***Z*-selectivity determination by ^{1}H NMR: Ru-4d** (Table 2, entry 5) 98/2



(Z)-12-hydroxydodec-10-enal (16)



Chemical Formula: $C_{12}H_{22}O_2$
Molecular Weight: 198,31

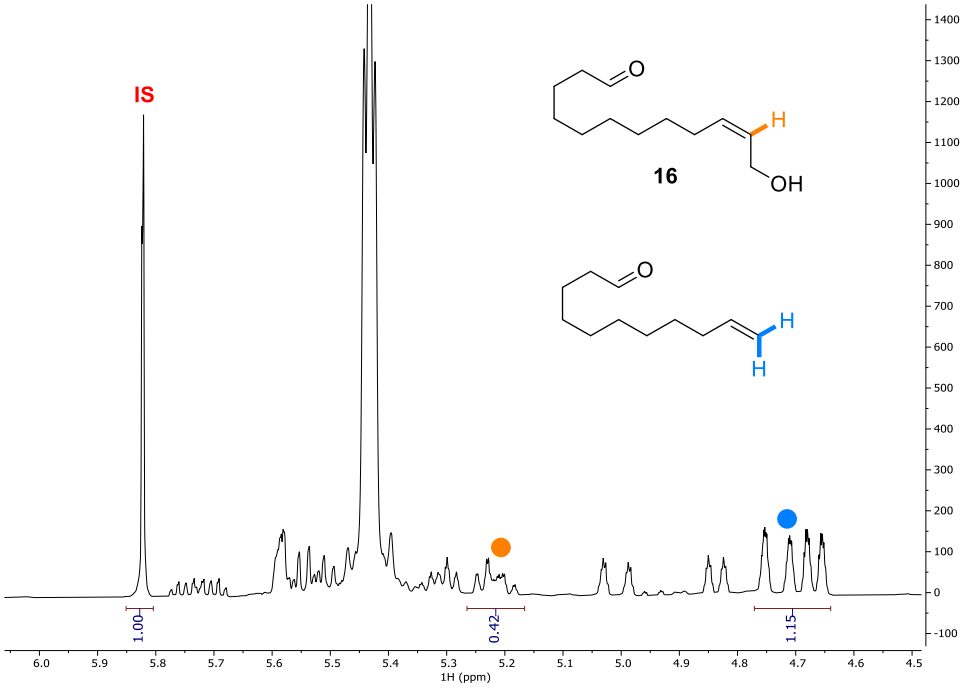
The general procedure for *Z*-CM reactions was followed using undecylenic aldehyde (40 µL, 0.20 mmol, 1.0 equiv) and **Ru-4d** (7.4 mg, 0.01 mmol, 5 mol%). **16** was isolated after purification (eluent: pentane:Et_2O 9:1) as a yellow oil (15.4 mg, 39% yield, 98/2 *Z*/*E*).

^{1}H NMR of *Z*-isomer (400 MHz, $CDCl_3$) δ (ppm) 9.75 (t, *J* = 1.9 Hz, 1H, C*H*O), 5.64 – 5.46 (m, 2H, CH_{alkene}), 4.19 (d, *J* = 6.2 Hz, 2H, CH_2OH), 2.41 (td, *J* = 7.3, 1.9 Hz, 2H, CH_2), 2.06 (dt, *J* = 7.1, 7.1 Hz, 2H, CH_2), 1.65 – 1.60 (m, 2H, CH_2), 1.39 – 1.23 (m, 11H, 5 x CH_2 + O*H*).

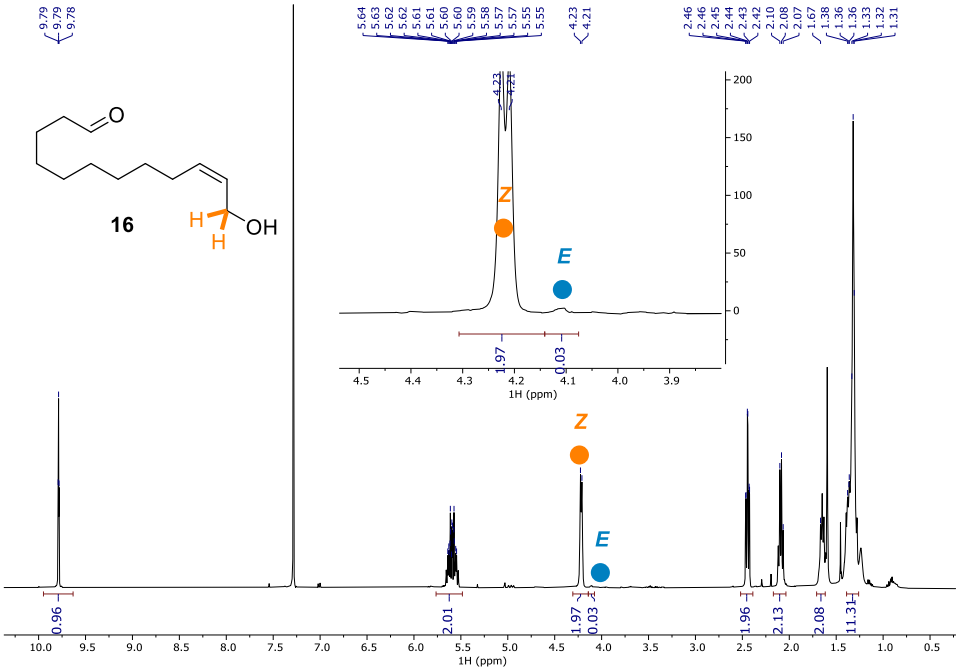
^{13}C NMR of *Z*-isomer (101 MHz, $CDCl_3$) δ (ppm) 203.0 (*C*=O), 133.2 (*C*H$_{alkene}$), 128.4 (*C*H$_{alkene}$), 58.6 (*C*H$_2$OH), 43.9 (*C*H$_2$), 29.5 (*C*H$_2$), 29.3 (*C*H$_2$), 29.2 (*C*H$_2$), 29.1 (*C*H$_2$), 29.1 (*C*H$_2$), 27.4 (*C*H$_2$), 22.0 (*C*H$_2$).

Analytical data for this compound were consistent with the previously reported data.[16]

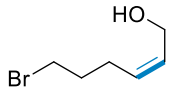
Conversion determination by ^{1}H NMR: (with **Ru-4d**, 5 mol%): 43% conv., 41% NMR yield.



***Z*-selectivity determination by ^{1}H NMR** (with **Ru-4d**, 5 mol%): 98/2



(Z)-6-bromohex-2-en-1-ol (17)



Chemical Formula: $C_6H_{11}BrO$
Molecular Weight: 179,06

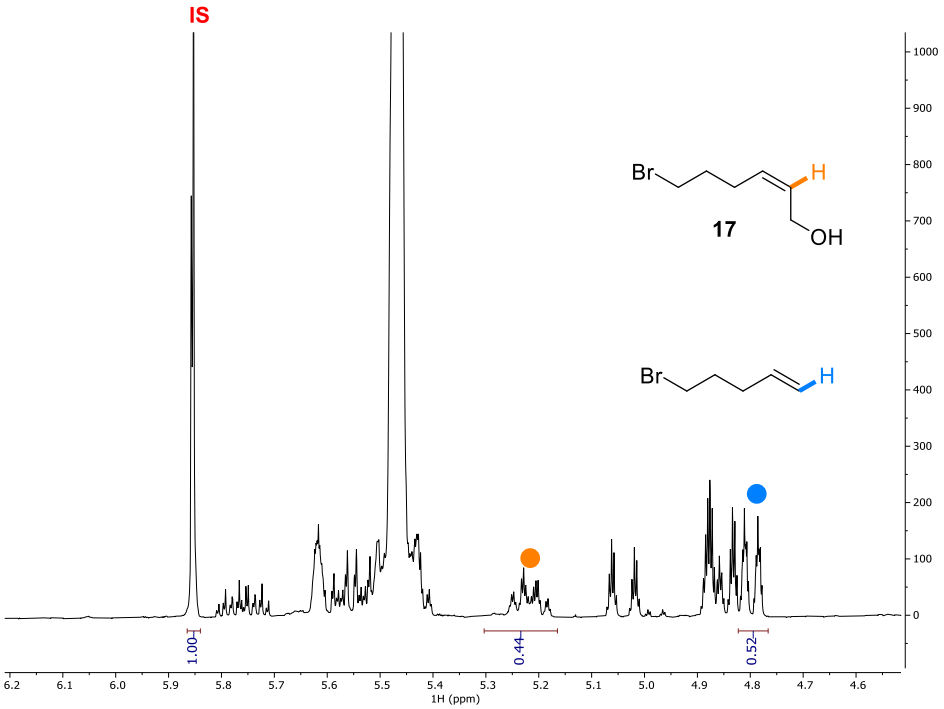
The general procedure for *Z*-CM reactions followed using 5-bromopent-1-ene (24 µL, 0.20 mmol, 1.0 equiv) and **Ru-4d** (7.4 mg, 0.01 mmol, 5 mol%). **17** was isolated after purification (eluent: pentane:Et_2O 9:1) as a yellow oil (15.3 mg, 43% yield, >98/2 *Z*/*E*).

^{1}H NMR of *Z*-isomer (400 MHz, $CDCl_3$) δ (ppm) 5.73 – 5.65 (m, 1H, C*H*$_{alkene}$), 5.52 – 5.43 (m, 1H, C*H*$_{alkene}$), 4.25 – 4.20 (m, 2H, C*H*$_2$OH), 3.42 (t, *J* = 6.5 Hz, 2H, C*H*$_2$Br), 2.31 – 2.23 (m, 2H, C*H*$_2$), 1.98 – 1.89 (m, 2H, C*H*$_2$). O*H* not seen due to D-H exchange

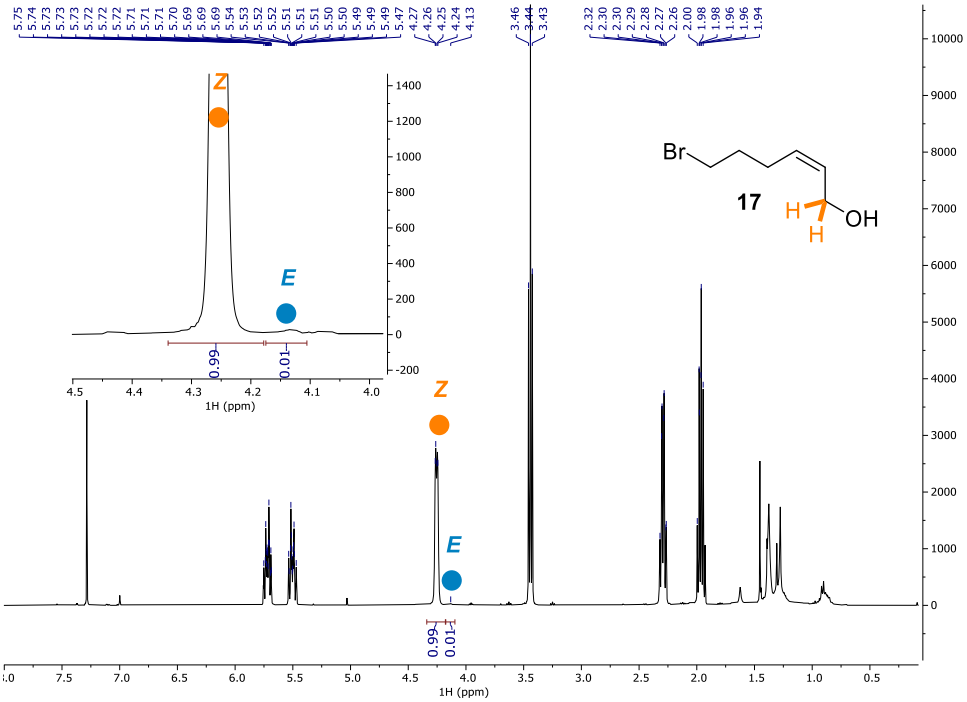
^{13}C NMR of *Z*-isomer (101 MHz, $CDCl_3$) δ (ppm) 130.7 (*C*H$_{alkene}$), 130.4 (*C*H$_{alkene}$), 58.6 (*C*H$_2$OH), 33.3 (*C*H$_2$Br), 32.2 (*C*H$_2$), 25.8 (*C*H$_2$).

Analytical data for this compound were consistent with the previously reported data.[16]

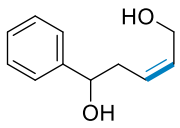
Conversion determination by ^{1}H NMR (with **Ru-4d**, 5 mol%): 48% conv., 43% NMR yield



***Z*-selectivity determination by ^{1}H NMR** (with **Ru-4d**, 5 mol%): >98/2



(Z)-5-phenylpent-2-ene-1,5-diol (18)



Chemical Formula: $C_{11}H_{14}O_2$
Molecular Weight: 178,23

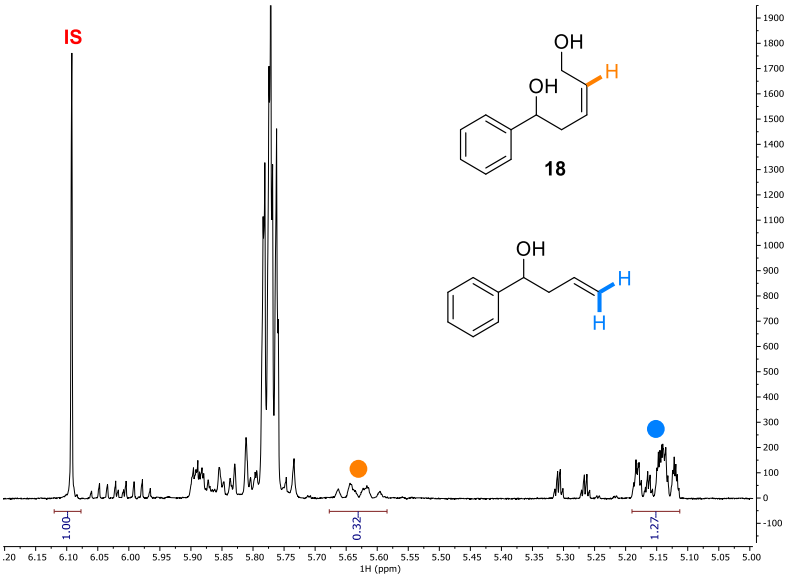
The general procedure for *Z*-CM reactions was followed using 4-phenyl-1-buten-4-ol (30 µL, 0.20 mmol, 1.0 equiv), and **Ru-4d** (7.4 mg, 0.01 mmol, 5 mol%). **18** was isolated after purification (eluent: pentane:Et_2O 7:3 to 0:10 Et_2O) as a colorless oil (10.9 mg, 31% yield, >98/2 *Z*/*E*).

^{1}H NMR (400 MHz, $CDCl_3$), *Z*-isomer (major): δ (ppm) 7.37 – 7.30 (m, 4H CH_{ar}), 7.30 – 7.22 (m, 1H, CH_{ar}), 5.87 – 5.75 (m, 1H, CH_{alkene}), 5.64 – 5.54 (m, 1H, CH_{alkene}), 4.70 (dd, J = 7.9, 4.5 Hz, 1H, CHOH), 4.10 (dd, J = 12.4, 7.9 Hz, 1H, CH_2OH), 3.97 (dd, J = 12.4, 6.9 Hz, 1H, CH_2OH), 3.24 (br s, 1H, OH), 2.82 (br s, 1H, OH), 2.64 – 2.52 (m, 1H, CH_2), 2.51 – 2.40 (m, 1H, CH_2).

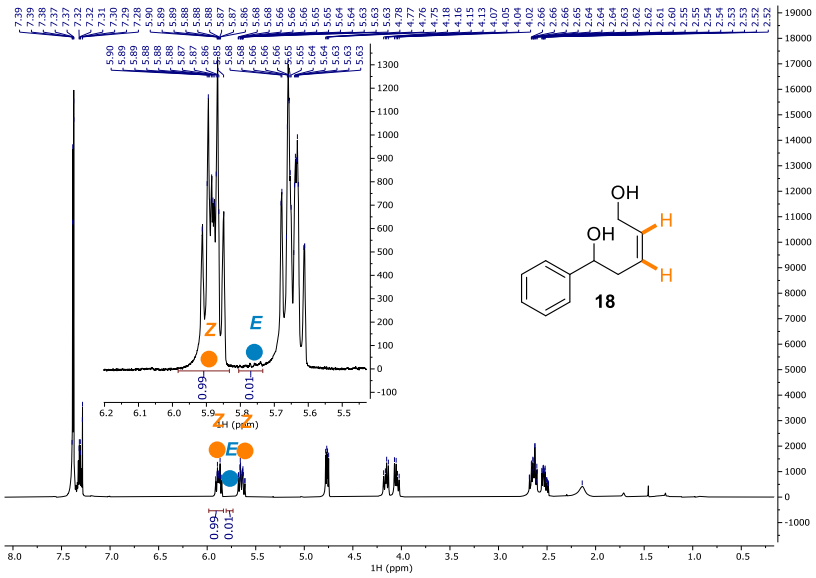
^{13}C NMR (101 MHz, $CDCl_3$), *Z*-isomer (major): δ (ppm) 144.1 ($C_{q\ ar}$), 131.6 (CH$_{alkene}$), 129.0 (CH$_{alkene}$), 128.5 (2C, CH$_{ar}$), 127.7 (CH$_{ar}$), 125.9 (2C, CH$_{ar}$), 73.0 (CH_2OH), 57.6 (CHOH), 37.2 (CH_2).

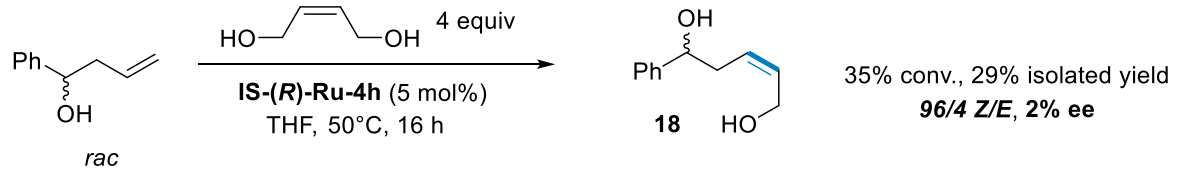
Analytical data for this compound were consistent with the previously reported data.[17]

Conversion determination by ^{1}H NMR: with **Ru-4d** (37% conv., 32% NMR yield)



***Z*-selectivity determination by ^{1}H NMR** (with **Ru-4d**, 5 mol%) : >98/2.[16]





Scheme S 1: CM with optically pure ***IS-(R)-Ru-4h***

***ee* determination by chiral HPLC** (with *IS-(R)*-**Ru-4h**, 5 mol%, 35% conv., 29% yield, 96/4 *Z/E*) :

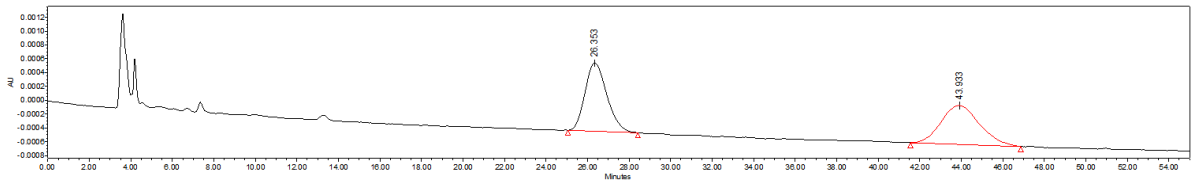
Column OB (250 x 4.6 mm, 10 µm)

Mobile phase: Hexanes:*i*PrOH 97:3

Flow rate: 1 mL/min

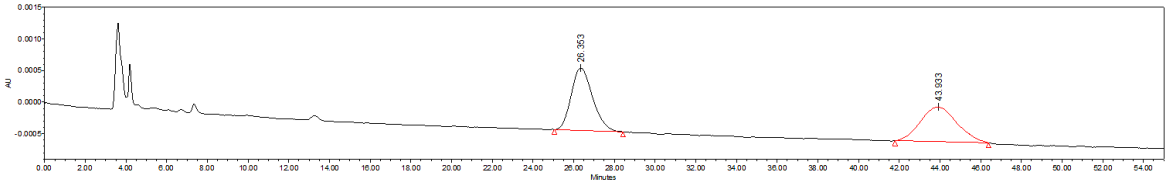
Detection at 254 nm.

Racemic mixture



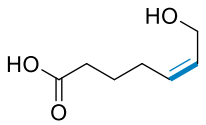
Peak	Ret. Time (min)	Area	Area%	Height
1	26.353	72234	49.80	986
2	43.933	72811	50.20	565

With ***(R)-Ru-4h*** *(2% ee)*



Peak	Ret. Time (min)	Area	Area%	Height
1	26.353	72081	51.45	984
2	43.933	68016	48.55	550

(*Z*)-7-hydroxyhept-5-enoic acid (19)



Chemical Formula: $C_7H_{12}O_3$
Molecular Weight: 144,17

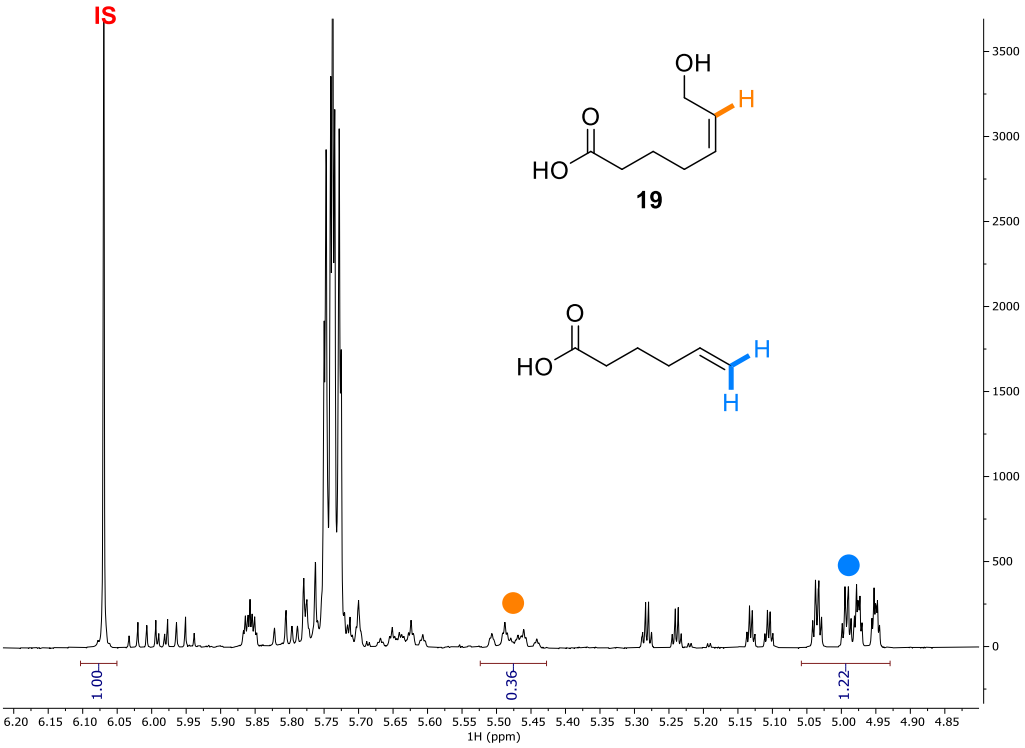
The general procedure for *Z*-CM reactions was followed using 5-hexenoic acid (24 µL, 0.20 mmol, 1.0 equiv), and **Ru-4d** (7.4 mg, 0.01 mmol, 5 mol%). **19** was isolated after purification (eluent: Et_2O:AcOH 95:5) as a colourless oil (10.4 mg, 36% yield, 95/5 *Z/E*).

^{1}H NMR (400 MHz, $CDCl_3$), *Z*-isomer (major): δ (ppm) 5.85 (br s, 2H), 5.75 – 5.62 (m, 1H), 5.59 – 5.47 (m, 1H), 4.20 (dd, *J* = 6.9, 1.3 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.20 – 2.11 (m, 2H), 1.76 (quint, *J* = 7.2 Hz, 2H).

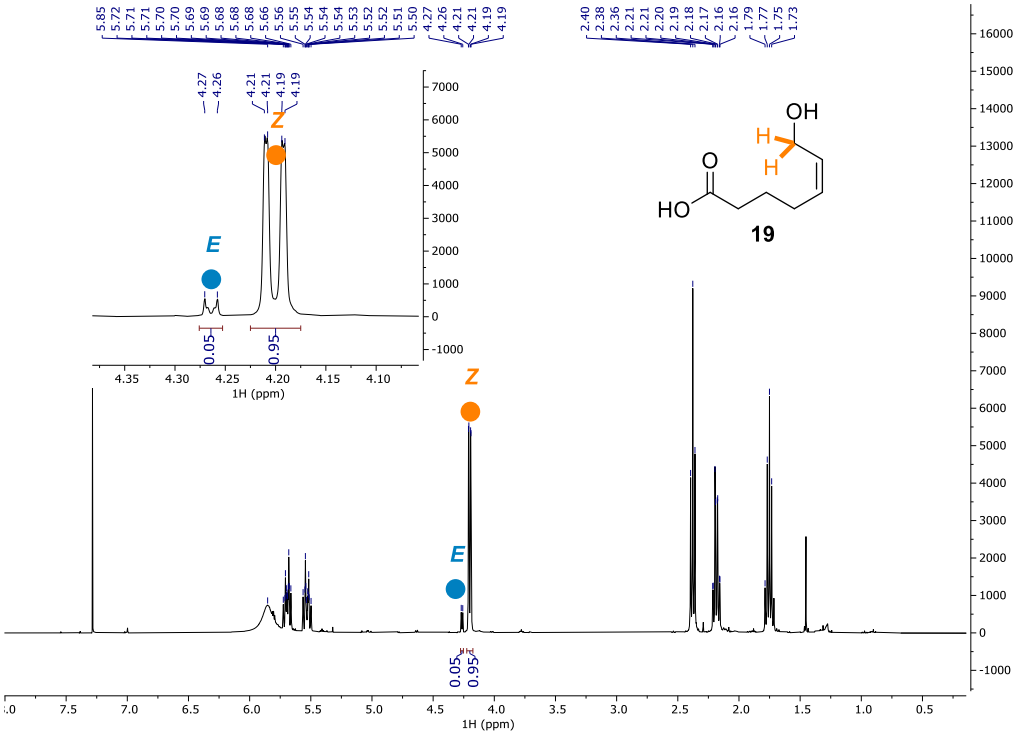
^{13}C NMR (101 MHz, $CDCl_3$), *Z*-isomer (major): δ (ppm) 178.8, 131.7, 129.5, 58.2, 33.2, 26.4, 24.3.

Analytical data for this compound were consistent with the previously reported data.[18]

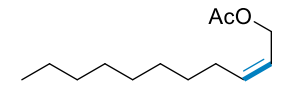
Conversion determination by ^{1}H NMR: with **Ru-4d** (39% conv., 36% NMR yield)



***Z*-selectivity determination by ^{1}H NMR** (with **Ru-4d**, 5 mol%) : 95/5.[16]



(*Z*)-undec-2-en-1-yl acetate (20)



Chemical Formula: $C_{13}H_{24}O_2$
Molecular Weight: 212,33

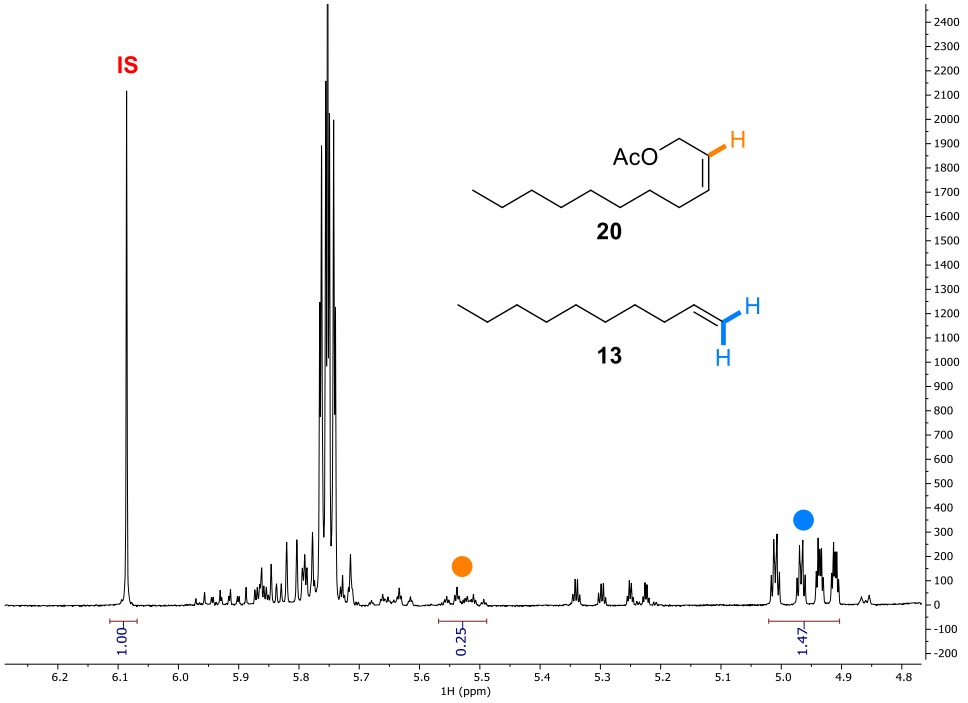
The general procedure for *Z*-CM reactions was followed using 1-decene **13** (38 µL, 0.20 mmol, 1.0 equiv) and **Ru-4d** (7.4 mg, 0.01 mmol, 5 mol%). **20** was isolated after purification (eluent: Pentane:Et_2O 9:1) as a colourless oil (10.8 mg, 25% yield, >98/2 *Z/E*).

^{1}H NMR of *Z*-isomer (400 MHz, $CDCl_3$) δ (ppm) 5.75 – 5.61 (m, 1 H), 5.61 – 5.47 (m, 1 H), 4.64 (d, *J* = 6.9 Hz, 2 H), 2.16 – 2.05 (m, 5 H), 1.40 – 1.21 (m, 12 H), 0.96 – 0.85 (m, 3 H)

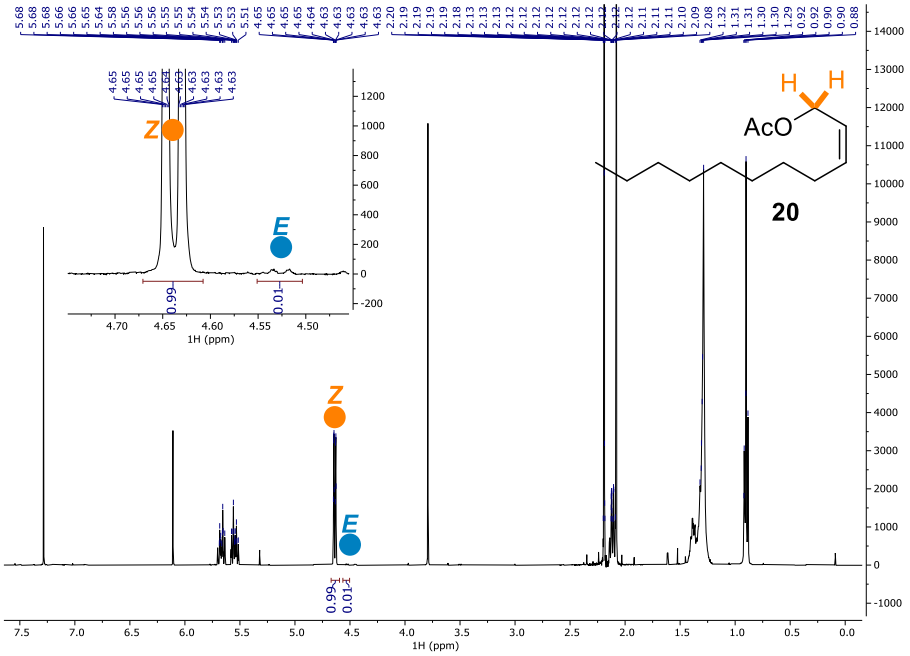
^{13}C NMR of *Z*-isomer (101 MHz, $CDCl_3$) δ (ppm) 171.0, 135.6, 123.2, 60.4, 31.9, 29.4, 29.4, 29.3, 29.2, 27.5, 22.7, 21.0, 14.1.

Analytical data for this compound were consistent with the previously reported data.[15]

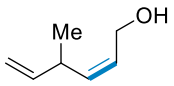
Conversion determination by ^{1}H NMR: with **Ru-4d**: 27% conv., 25% NMR yield.



***Z*-selectivity determination by ^{1}H NMR: Ru-4d**: >98/2



(Z)-4-methylhexa-2,5-dien-1-ol (21)



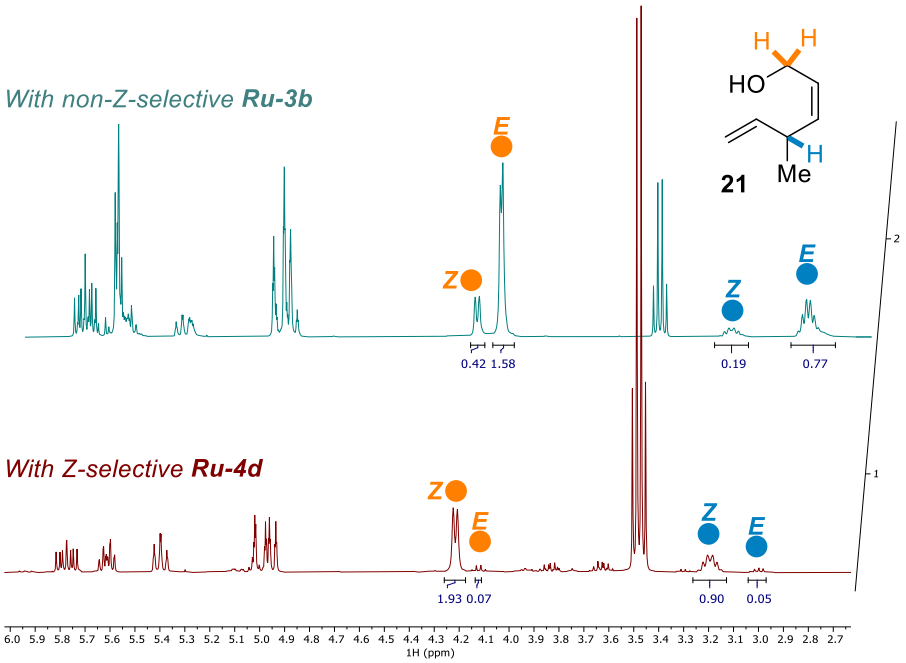
Chemical Formula: $C_7H_{12}O$
Molecular Weight: 112,17

The general procedure for *Z*-CM reactions was followed using 3-methyl-1,4-pentadiene (18 µL, 0.20 mmol, 1.0 equiv) and **Ru-4d** (7.4 mg, 0.01 mmol, 5 mol%). **21** was isolated after purification (eluent: Pentane:Et_2O 9:1) and careful evaporation of the solvent as a colourless volatile liquid (4.1 mg, 18% yield, 97/3 *Z/E*).

^{1}H NMR of *Z*-isomer (400 MHz, $CDCl_3$) δ (ppm) 5.77 (ddd, *J* = 17.3, 10.3, 6.1 Hz, 1H), 5.61 (dtd, *J* = 10.9, 4.2, 1.3 Hz, 1H), 5.40 (dd, *J* = 10.8, 1.4 Hz, 1H), 5.00 (dt, *J* = 17.2, 1.6 Hz, 1H), 4.95 (dt, *J* = 10.3, 1.5 Hz, 1H), 4.22 (d, *J* = 6.7 Hz, 2H), 3.24 – 3.14 (m, 1H), 1.55 (br s, 1H), 1.09 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR of *Z*-isomer (101 MHz, $CDCl_3$) δ (ppm) 142.3, 136.4, 127.8, 113.1, 63.6, 39.9, 19.5.

***Z*-selectivity determination by ^{1}H NMR: Ru-4d**: 97/3 (Note that the *E*-**21** is known in the litterature)[19]

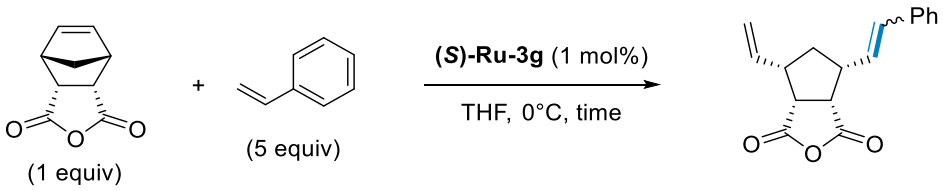


7. Z-(A)ROCM

7.1. Reagents

Styrene, *para*-methoxystyrene and *para*-trifluoromethylstyrene, allyl acetate, allyl benzene, 1-undecenal, but-3-en-1-yl acetate and 1-decene were distilled over molecular sieve (4Å), filtered through basic alumina, degassed *via* 3 cycles of freeze/pump/thaw and stored in a freezer under Ar, prior to use. *Cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (**2f**) was purchased from TCI and recrystallized in cyclohexane prior to use. ((1*R*,2*R*,3S,4S)-bicyclo[2.2.1]hept-5-ene-2,3-diyl)dimethanol (**2c**),[20] ((1*R*,2*R*,3*S*,4*S*)-bicyclo[2.2.1]hept-5-ene-2,3-diyl)bis(methylene) diacetate (**2d**),[21] (3a*R*,4*S*,7*R*,7a*S*)-3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione (**2e**),[22] (3a*R*,4*R*,7*S*,7a*S*) 2-phenyl-3a,4,7,7a-tetrahydro-1H-4,7-methano*iso*indole-1,3(2H)-dione (**2g**)[10] were prepared according to literature procedures and dried under high vacuum prior to use. (1*R*,4*S*,5*S*,6*R*)-5,6-bis((benzyloxy)methyl)bicyclo[2.2.1] hept-2-ene (**2h**)[23] and (1*R*,4*R*,5*S*, 6*S*)-5,6-bis(((*tert*-butyldimethylsilyl)oxy)methyl)bicyclo[2.2.1]hept-2-ene (**2i**)[24] were prepared according to literature procedures, filtered through basic alumina, degassed *via* 3 cycles of freeze/pump/thaw and stored in a freezer under Ar, prior to use.

7.2. Preliminary results in AROCM with dichloride (S)-Ru-3g complex (not in the main text)



In a flame-dried 10-mL Schlenk under Ar, *Cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (32.8 mg, 0.2 mmol, 1.0 equiv) and styrene (0.12 mL, 1.0 mmol, 5.0 equiv) were diluted in THF (1 mL). The mixture was cooled down to 0 °C. 0.33 mL of a freshly prepared solution of the precatalyst **(*S*)-Ru-3g** was added (8.0 mg in 2.0 mL, 0.002 mmol, 1 mol%). The mixture was stirred 2 hours at 0 °C. Aliquots were taken, quenched with ethyl vinyl ether and analysed by SFC with chiral stationary phase for *ee* and *E/Z* determination. The desired product was obtained after column chromatography (eluent: Pentane:EtOAc, 10:0 to 9:1) as a colourless oil (32.2 mg, 61% yield).

Entry	Time (min)	*E/Z*	ee (of *E* product)
1	10	83/17	71 %
2	20	83/17	72 %
3	30	83/17	65 %
4	45 (complete conversion reached)	82/18	65 %
5	60	82/18	65 %
6	90	82/18	67 %
7	120	82/18	65 %

*Table S 4: Evolution of ee through time during AROCM between endo norbornene anhydride and styrene with **Ru-3g***

^{1}H NMR (400 MHz, *$CDCl_3$*) of *E* isomer (major product): δ (ppm) 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 6.52 (d, *J*= 15.8 Hz, 1H), 6.30 (dd, *J*= 15.8, 8.0 Hz, 1H), 6.03 – 5.92 (m, 1H), 5.24 (d, *J*= 1.1 Hz, 1H), 5.20 (dt, *J*= 6.7, 1.3 Hz, 1H), 3.62 – 3.49 (m, 2H), 3.21 – 3.11 (m, 1H), 3.11 – 3.00 (m, 1H), 2.14 (dt, *J*= 13.0, 5.4 Hz, 1H), 1.57 (dt, *J*= 12.9, 12.9 Hz, 1H).

^{13}C NMR (101 MHz, *$CDCl_3$*) of *E* isomer (major product): δ (ppm) 170.7 (2C), 136.8, 134.9, 132.4, 128.7, 127.9 (2C), 126.6, 126.5 (2C), 117.6, 50.0, 49.6, 46.9, 46.4, 36.7.

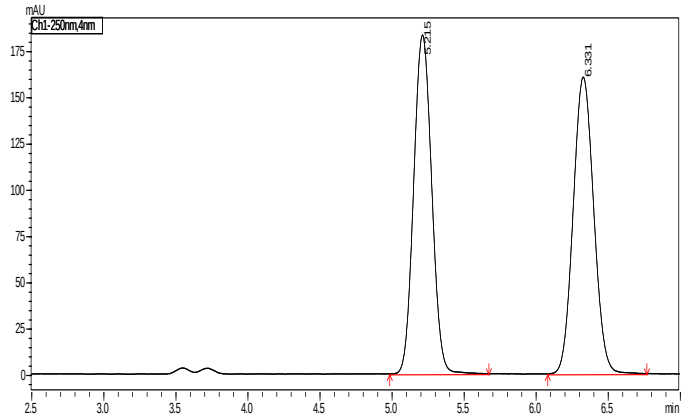
Analytical data for this compound were consistent with the previously reported data.[25]

ee determination by SFC on chiral stationary phase:

Flow: 2.0 mL/min
Pump A: sCO_2 – Pump B: EtOH – Back Pressure Regulator: 150 bar
Column: IC: 150 x 3 mm x 3 µm at 40°C
Injection: 5 µL - Run time: 16 min
Detection PDA between 200 and 450 nm (6.25 Hz) – constant: 0.640 s

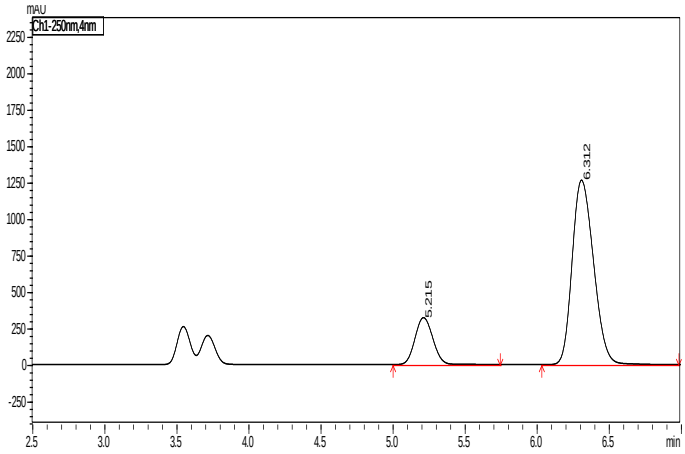
Time (min)	% Pump A	% Pump B
0.01	96.5	3.5
10.00	96.5	3.5
10.50	70	30
13.50	70	30
14.00	96.5	3.5
16.00	96.5	3.5

Racemic mixture:



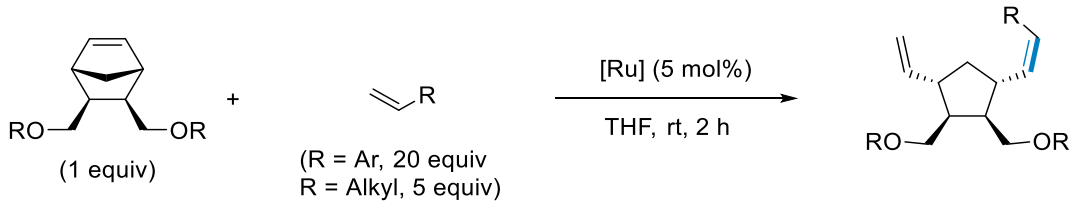
Peak	Ret. Time (min)	Area	Height	Area%
1	5.215	1593519	182958	50.024
2	6.331	1591962	160201	49.976

Aliquot at 45 min (65% ee):



Peak	Ret. Time (min)	Area	Height	Area%
1	5.215	2780936	321370	17.554
2	6.312	13061415	1262508	82.446

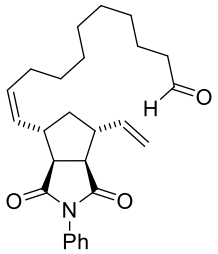
7.3. General procedure for Z-ROCM with isolated complex



In a glove box, in a flame-dried 10-mL Schlenk, the desired substrate (0.2 mmol, 1.0 equiv) and the desired cross partner were diluted in THF (1 mL). A freshly prepared solution of the desired catalyst was added (0.5 mL, 0.01 mmol, 5 mol%). The mixture was stirred the indicated time at room temperature. Out of the glove box, the reaction was quenched with ethyl vinyl ether. Volatiles were removed under vacuum. 1,3,5-trimethoxybenzene (11.1 mg, 0.066 mmol, 0.33 equiv) was added and conversion was determined by ^{1}H NMR. The crude mixture was analysed to determine *E/Z* ratio (by GC or ^{1}H NMR). Product was purified by silica gel column chromatography.

7.4. Analytical data of ROCM products

(*Z*)-11-((3a*S*,4*S*,6*R*,6a*R*)-1,3-dioxo-2-phenyl-6-vinyloctahydrocyclopenta[c]pyrrol-4-yl)undec-10-enal (11):



Chemical Formula: $C_{26}H_{33}NO_3$
Molecular Weight: 407,55

The general procedure for *Z*-ROCM reactions was followed using **2e** (48 mg, 0.20 mmol, 1.0 equiv), 1-undecenal (0.2 mL, 1.00 mmol, 5.0 equiv) and 0.5 mL of **Ru-4d** solution (29.8 mg in 2.0 mL, 0.01 mmol, 5 mol%). The reaction was stirred 4 h. The desired product **11** was obtained after column chromatography (eluent: Pentane:EtOAc 10:0 to 8:2) as a colourless oil (44.6 mg, 55% yield).

^{1}H NMR (400 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 9.74 (t, *J* = 1.9 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.40 – 7.34 (m, 1H), 7.31 – 7.27 (m, 2H), 5.99 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.52 (dt, *J* = 10.8, 7.3 Hz, 1H), 5.40 (ddt, *J* = 10.7, 9.1, 1.5 Hz, 1H), 5.24 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.14 (dt, *J* = 10.3, 1.2 Hz, 1H), 3.24 – 3.05 (m, 3H), 2.94 – 2.81 (m, 1H), 2.39 (td, *J* = 7.4, 1.9 Hz, 2H), 2.19 – 1.98 (m, 3H), 1.66 – 1.54 (m, 3H), 1.34 – 1.26 (m, 10H).

^{13}C NMR (101 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 203.1, 177.3 (2C), 138.8, 132.5, 132.1, 130.6, 129.2 (2C), 128.5, 126.5 (2C), 116.0, 52.3, 51.1, 47.9, 44.0, 42.8, 42.0, 29.7, 29.4 (2C), 29.3, 29.2, 27.8, 22.2.

HRMS for $C_{26}H_{33}O_3NNa$ $[M+Na]^+$ calc.: 430.23526; found: 430.2359. Source: ESI.

***Z*-selectivity determination** by GC on the crude mixture:

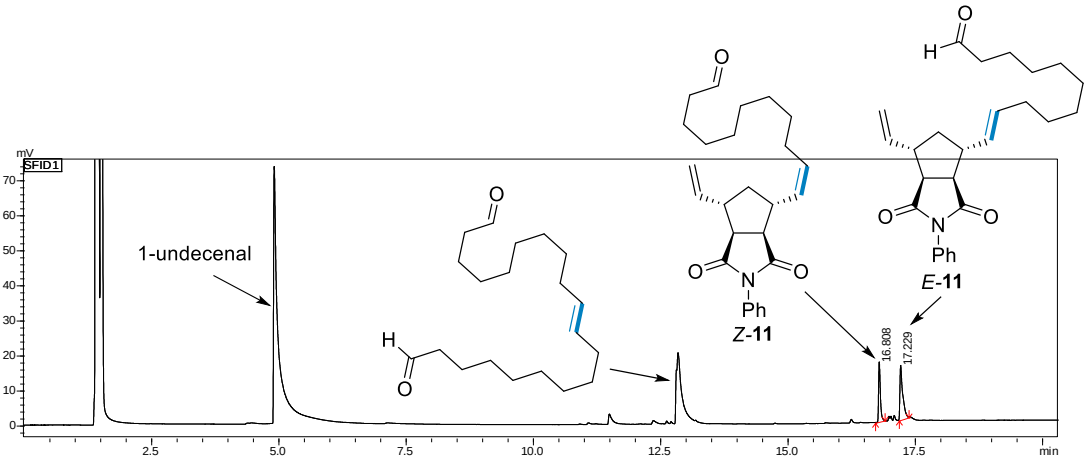
Tr-5 column (30.0 m x 0.25 mm ID ; 0.25 µm thickness) (Thermo Scientific)

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

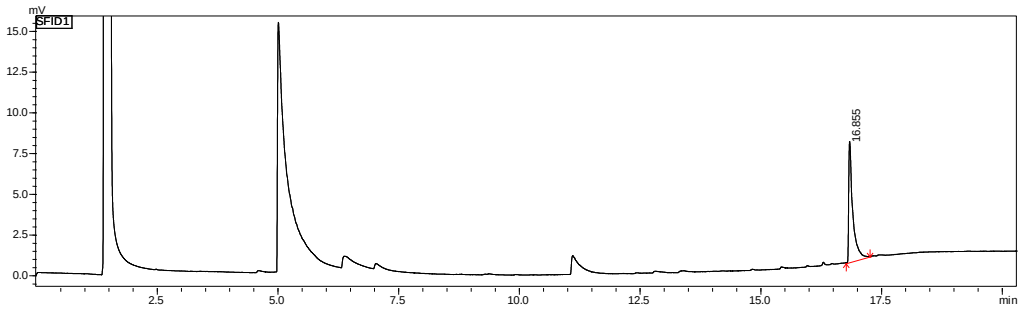
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	0
15	300	10

*With non-selective complex **Ru-3b***



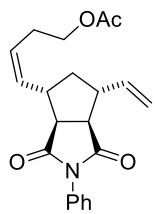
Peak	Ret. Time (min)	Area	Area%
1	16.808	40306	40.726
2	17.229	58663	59.274

*With **Ru-4d:** >99/1 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	16.855	42308	100.0

(*Z*)-4-((3a*S*,4*S*,6*R*,6a*R*)-1,3-dioxo-2-phenyl-6-vinyloctahydrocyclopenta[c]pyrrol-4-yl)but-3-en-1-yl acetate (12):



Chemical Formula: $C_{21}H_{23}NO_4$
Molecular Weight: 353,42

The general procedure for *Z*-ROCM reactions was followed using **2e** (48 mg, 0.20 mmol, 1.0 equiv), but-3-en-1-yl acetate (114 mg, 1.00 mmol, 5.0 equiv) and 0.5 mL of **Ru-4d** solution (29.8 mg in 2.0 mL, 0.01 mmol, 5 mol%). The reaction was stirred 4 h. The desired product **12** was obtained after column chromatography (eluent: Pentane:EtOAc 10:0 to 8:2) as a colourless oil (32.7 mg, 46% yield).

^{1}H NMR (400 MHz, *$CDCl_3$*) of *Z* isomer: δ (ppm) 7.53 – 7.45 (m, 2H), 7.45 – 7.35 (m, 1H), 7.35 – 7.26 (m, 2H), 6.01 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.63 – 5.49 (m, 2H), 5.27 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.18 (dt, *J* = 10.3, 1.2 Hz, 1H), 4.12 (t, *J* = 6.9 Hz, 2H), 3.27 – 3.09 (m, 3H), 2.96 – 2.83 (m, 1H), 2.55 – 2.45 (m, 2H), 2.23 – 2.13 (m, 1H), 2.05 (s, 3H), 1.73 – 1.58 (m, 1H).

^{13}C NMR (101 MHz, *$CDCl_3$*) of *Z* isomer: δ (ppm) 177.3, 177.1, 171.2, 138.5, 133.5, 132.0, 129.2 (2C), 128.6, 127.2, 126.5 (2C), 116.2, 63.8, 52.1, 51.0, 47.9, 42.7, 41.8, 27.4, 21.1.

HRMS for $C_{21}H_{23}O_4NNa$ $[M+Na]^+$ calc.: 376.15193; found: 376.1520. Source: ESI.

***Z*-selectivity determination** by GC on the crude mixture:

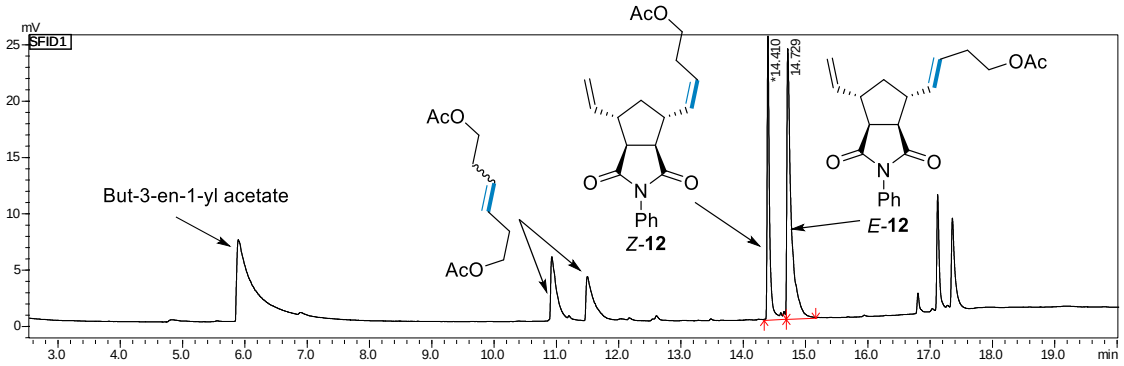
Tr-5 column (30.0 m x 0.25 mm ID ; 0.25 µm thickness) (Thermo Scientific)

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

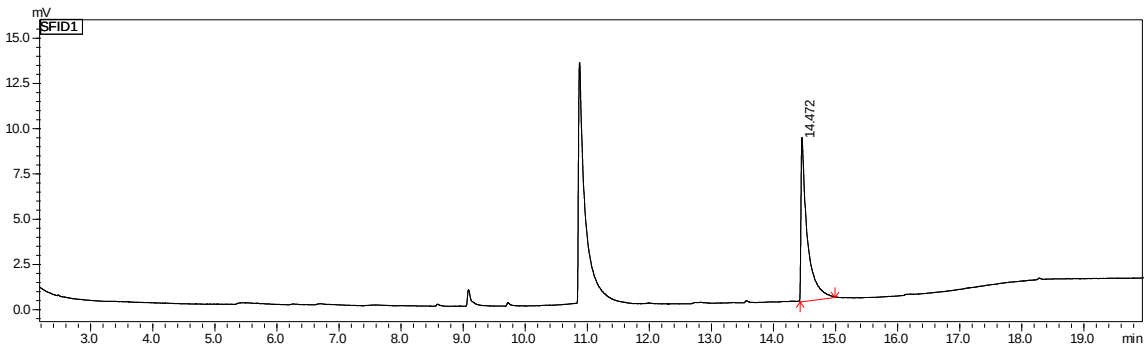
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	0
15	300	10

*With non-selective complex **Ru-3b***



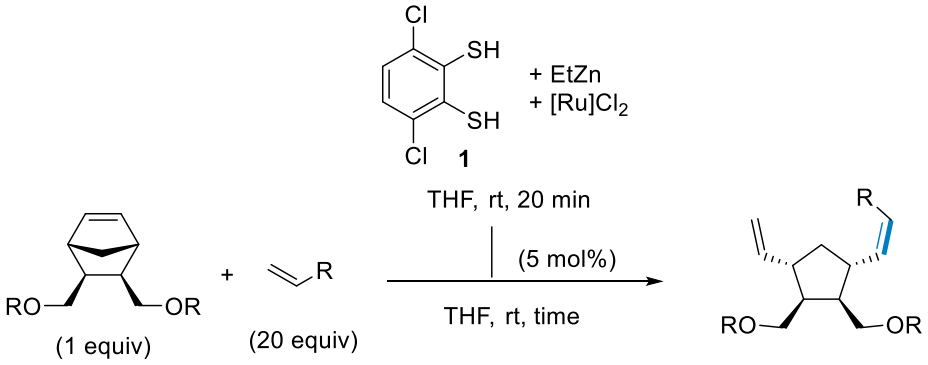
Peak	Ret. Time (min)	Area	Area%
1	14.410	66449	36.822
2	14.729	114010	63.178

*With **Ru-4d:** >99/1 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	14.472	62353	100.0

7.5. General procedure for Z-AROCM with complex generated in-situ

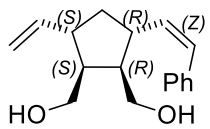


Out of the glove box, **IS-Ru** were formed according to a literature procedure:[16] In a flame-dried 4-mL vial under Ar, 1,4-dichlorocatechol dithiolate **1** (8 mg, 0.038 mmol, 1.5 equiv) and diethyl zinc solution (1 M in hexanes, 38 µL, 0.038 mmol, 1.5 equiv) were dissolved in THF (2.5 mL). The desired complex (0.025 mmol, 1.0 equiv) was added. The green mixture was stirred 20 minutes at room temperature and turned to brown. This freshly prepared solution of catalyst was used without further purification.

In a flame-dried 10-mL Schlenk under Ar, the desired substrate (0.2 mmol, 1.0 equiv) and the desired cross partner (4.0 mmol, 20.0 equiv) were diluted in THF (0.33 mL). The previously prepared solution of the desired complex (1.0 mL, 0.01 mmol, 5 mol%) was added. The mixture was stirred until completion at room temperature. The reaction was quenched with ethyl vinyl ether. Volatiles were removed under vacuum. The crude mixture was analysed to determine *E/Z* ratio (by GC or ^{1}H NMR). Product was purified by silica gel column chromatography. Enantiomeric excesses (ee) were determined on chiral stationary phase by HPLC.

7.6. Analytical data of AROCM products

(3-styryl-5-vinylcyclopentane-1,2-diyl)dimethanol (23):



Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2c** (31 mg, 0.20 mmol, 1.0 equiv), styrene (0.46 mL, 4.01 mmol, 20.0 equiv) and 1 mL of (*S*)-**Ru-4h** solution obtained from 2nd eluted (+)-(*S*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 30 minutes. The desired product **23** was obtained after column chromatography (eluent: Pentane:EtOAc, 10:0 to 8:2) as a colourless oil (23 mg, 44% yield, Table 3, entry 5). Insoluble polymer **3c** was also visible in

the schlenk at the end of the reaction (not quantified). Absolute configuration of the major product as shown, determined by comparison with chromatograms of the literature.[26]

^{1}H NMR (400 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 7.39 – 7.30 (m, 2H, C*H*$_{ar}$), 7.30 – 7.21 (m, 3H, C*H*$_{ar}$), 6.51 (d, *J* = 11.5 Hz, 1H, C*H*$_{alkene}$), 5.84 – 5.71 (m, 1H, C*H*$_{alkene}$), 5.55 (dd, *J* = 11.6, 10.1 Hz, 1H, C*H*$_{alkene}$), 5.09 – 4.96 (m, 2H, C*H*$_{2\ alkene}$), 3.69 – 3.55 (m, 4H, C*H*$_2$), 3.14 (br s, 2H, O*H*), 2.84 – 2.71 (m, 1H, C*H*), 2.30 –2.14 (m, 3H, C*H*$_2$ + C*H*), 2.03 (dt, *J* = 12.4, 6.2 Hz, 1H, C*H*), 1.39 (dt, *J* = 12.4, 11.2 Hz, 1H, C*H*).

^{13}C NMR (101 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 141.4 (*C*H$_{ar}$), 137.4 (*C*$_{q\ ar}$), 135.8 (*C*H$_{alkene}$), 129.8 (*C*H$_{alkene}$), 128.5 (2C, *C*H$_{ar}$), 128.3 (2C, *C*H$_{ar}$), 126.7 (*C*H$_{alkene}$), 114.5 (*C*H$_{2\ alkene}$), 62.0 (2C, *C*H$_2$OH), 50.5 (*C*H), 48.5 (*C*H), 46.3 (*C*H), 40.1 (*C*H), 39.8 (*C*H$_2$).

Analytical data for this compound were consistent with the previously reported data.[27]

***Z*-selectivity determination** by GC/MS on the crude mixture.

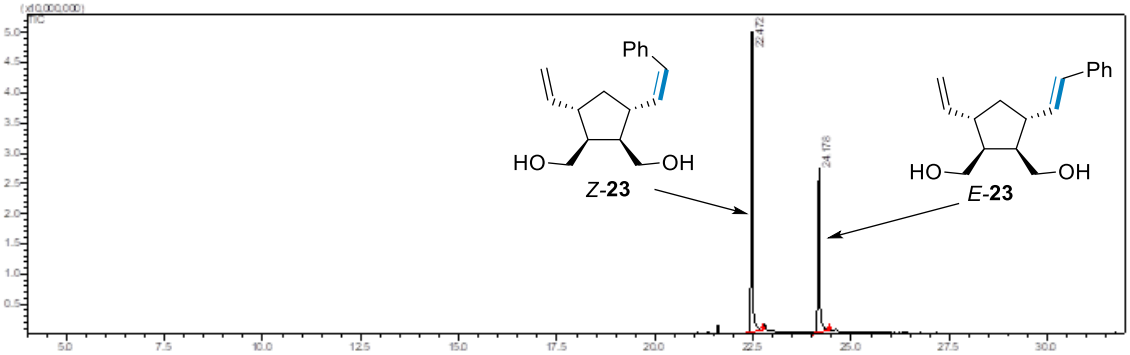
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 30.0 cm/s

Temperature protocol:

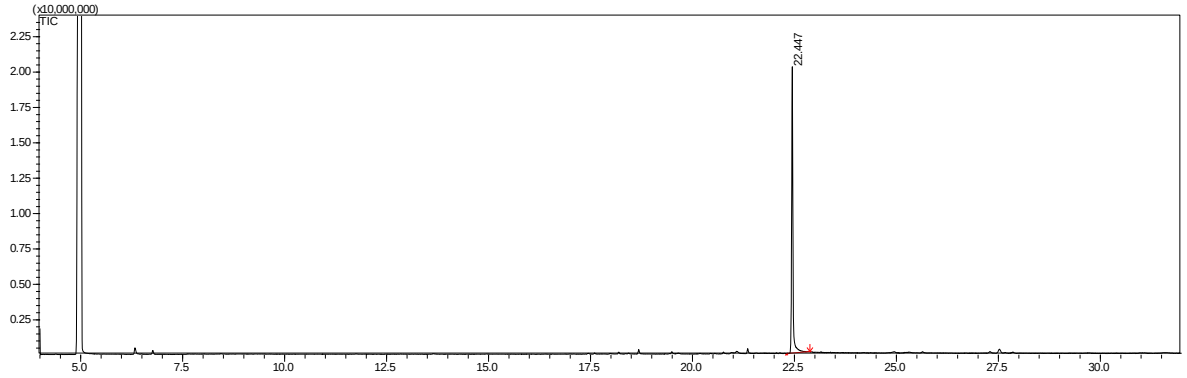
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	70	4
10	250	10

*With non-selective complex rac-**Ru-3c***



Peak	Ret. Time (min)	Area	Area%
1	22.472	127410836	60.14
2	24.178	84436473	39.86

*With (S)-**Ru-4h**: >99/1 Z/E (Table 3, entry 5)*



Peak	Ret. Time (min)	Area	Area%
1	22.447	44319004	100

ee determination by HPLC on Chiral stationary phase on the purified product:

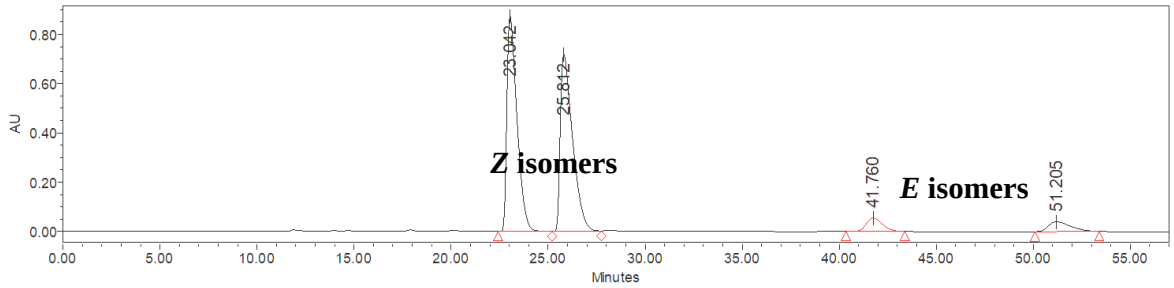
Column OD-3 (250 x 4.6 mm, 3 µm)

Mobile phase: Hexanes:*i*PrOH 98:2

Flow rate: 1 mL/min

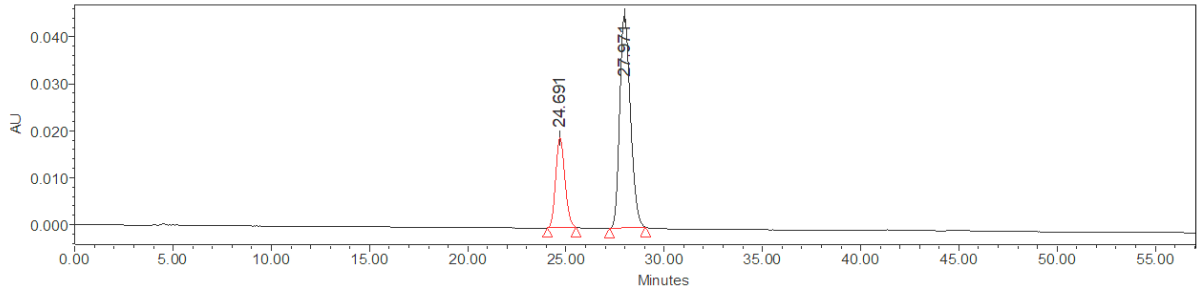
Detection at 254 nm.

Racemic mixtures (Z and E isomers):



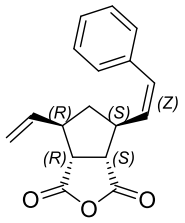
Peak	Ret. Time (min)	Area	Area%	Height
1	23.042	31617319	45.40	872976
2	25.812	31669989	45.47	717566
3	41.760	3193241	4.59	54558
4	51.205	3164596	4.54	39814

*With **(S)-Ru-4h** (78.5/21.5 er; 57% ee) (Table 3, entry 5)*



Peak	Ret. Time (min)	Area	Area%	Height
1	24.691	384857	21.59	19084
2	27.971	1398042	78.41	45210

4-((Z)-styryl)-6-vinyltetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (4):



Chemical Formula: $C_{17}H_{16}O_3$
Molecular Weight: 268,31

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2f** (33 mg, 0.20 mmol, 1.0 equiv), styrene (0.46 mL, 4.01 mmol, 20.0 equiv) and 1 mL of (*R*)-**Ru-4h** solution obtained from 1st eluted (+)-(*R*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 30 minutes. The desired product **4** was obtained after column chromatography (eluent: Pentane:EtOAc, 10:0 to 8:2) as a colourless oil (30 mg, 56% yield). Note that when the same reaction was performed at 0°C, and no conversion was observed after 3 hours.

^{1}H NMR (400 MHz, *$CDCl_3$*) of *Z* isomer: δ (ppm) 7.42 – 7.34 (m, 2H, C*H*$_{ar}$), 7.32 – 7.26 (m, 3H, C*H*$_{ar}$), 6.66 (d, *J* = 11.4 Hz, 1H, C*H*$_{alkene}$), 5.97 – 5.84 (m, 1H, C*H*$_{alkene}$), 5.60 (dd, *J* = 11.3, 9.8 Hz, 1H, C*H*$_{alkene}$), 5.29 – 5.15 (m, 2H, C*H*$_{2\ alkene}$), 3.54 – 3.41 (m, 1H, C*H*), 3.40 – 3.28 (m, 2H, C*H*$_2$), 2.90 (d, *J* = 14.3 Hz, 1H, C*H*), 2.21 (dt, *J* = 12.4, 6.0 Hz, 1H, C*H*), 1.68 (dt, *J* = 12.9, 11.2 Hz, 1H, C*H*).

^{13}C NMR (101 MHz, *$CDCl_3$*) of *Z* isomer: 170.7 (2C), 136.8, 134.9, 132.4, 128.7, 127.9 (2C), 126.6, 126.5 (2C), 117.6, 50.0, 49.6, 46.9, 46.4, 36.7.

HRMS for $C_{17}H_{16}O_3Na$ $[M+Na]^+$ calc.: 291.09971 ; found: 291.0996. Source: ESI.

$[\alpha]_D^{25}$ of *Z* isomer = +94 (c = 0.1 g/mL, CH_2Cl_2, 67% ee).

***Z*-selectivity determination** by GC/MS

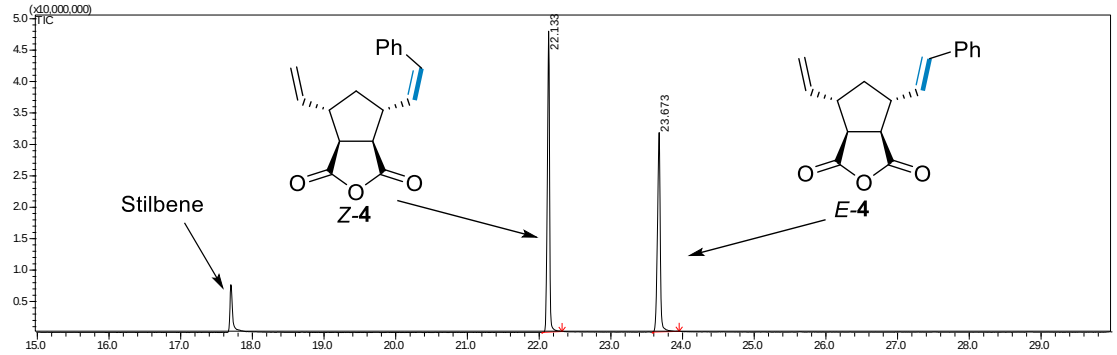
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 30.0 cm/s

Temperature protocol:

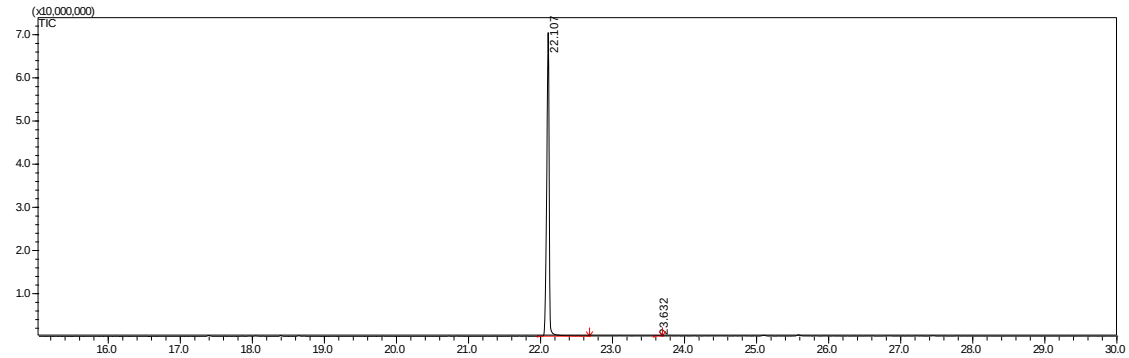
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	70	4
10	250	10

*With non-selective complex rac-**Ru-3h***



Peak	Ret. Time (min)	Area	Area%
1	22.133	104849598	54.80
2	23.673	86468781	45.20

*With IS-(R)-**Ru-4h:** 99/1 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	22.107	165194994	99.89
2	23.632	175808	0.11

ee determination by HPLC on Chiral stationary phase:

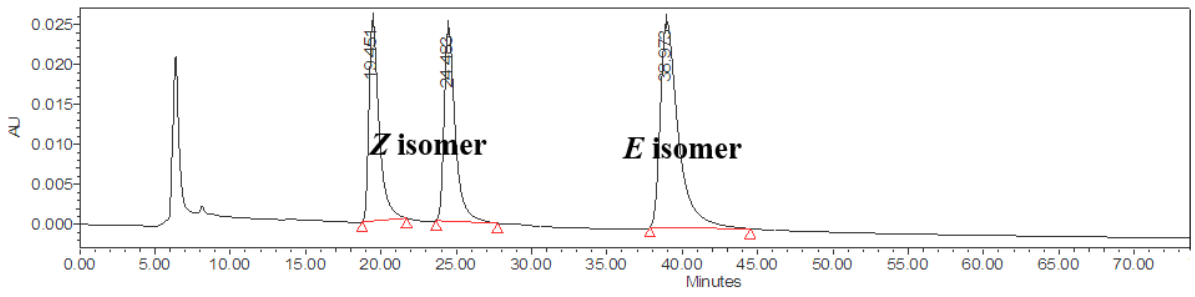
Column OJ-H (250 x 4.6 mm, 5 µm)

Mobile phase: Hexanes:^{i}PrOH 70:30

Flow rate: 0.75 mL/min

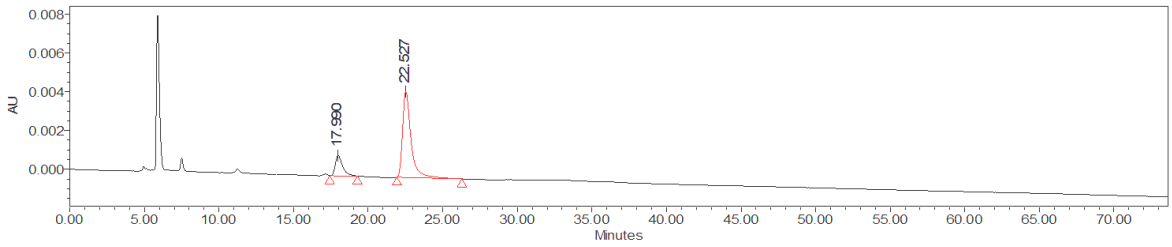
Detection at 254 nm.

Racemic mixture:



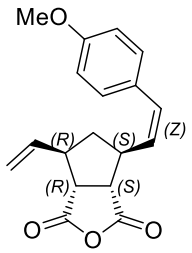
Peak	Ret. Time (min)	Area	Area%	Height
1	19.451	1177918	17.71	25129
2	24.483	1251970	18.82	24177
3	38.973	2151138	32.34	25791
4	76.137	2071137	31.13	15346

*With **(R)-Ru-4h** (83/17 er; 67% ee)*



Peak	Ret. Time (min)	Area	Area%	Height
1	17.990	35211	16.74	1046
2	22.527	175136	83.26	4448

4-((Z)-4-methoxystyryl)-6-vinyltetrahydro-1H-cyclopenta[c]furan-1,3 (3aH)-dione (5):



Chemical Formula: $C_{18}H_{18}O_4$
Molecular Weight: 298,34

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2f** (33 mg, 0.20 mmol, 1.0 equiv), *p*-methoxystyrene (0.53 mL, 4.00 mmol, 20.0 equiv) and 1 mL of (*R*)-**Ru-4h** solution obtained from 1st eluted (+)-(*R*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 5 hours (90% conversion determined by ^{1}H NMR). The desired product **5** was obtained after column chromatography (eluent: Pentane:EtOAc, 10:0 to 7:3) as a colourless oil (37.7 mg, 63% yield).

^{1}H NMR (400 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 7.27 – 7.21 (m, 2H, C*H*$_{ar}$), 6.91 – 6.85 (m, 2H, C*H*$_{ar}$), 6.43 (d, *J* = 11.5 Hz, 1H, C*H*$_{alkene}$), 5.92 – 5.77 (m, 1H, C*H*$_{alkene}$), 5.43 (dd, *J* = 11.4, 9.8 Hz, 1H, C*H*$_{alkene}$), 5.18 – 5.10 (m, 1H, C*H*$_{2\ alkene}$), 5.06 (d, *J* = 10.3 Hz, 1H, C*H*$_{2\ alkene}$), 3.90 – 3.72 (m, 4H, C*H*$_3$ + C*H*), 3.70 – 3.54 (m, 1H, C*H*), 3.12 – 3.02 (m, 2H, C*H*$_2$), 2.30 – 2.19 (m, 1H, C*H*), 1.53 – 1.40 (m, 1H, C*H*).

^{13}C NMR (101 MHz, *CDCl$_3$*) of *Z* isomer: 172.0, 171.9, 158.9, 137.3, 131.6, 130.3, 129.7 (2C), 128.6, 116.9, 113.9 (2C), 52.4, 51.3, 47.9, 43.0, 42.7, 29.7.

HRMS for $C_{18}H_{18}O_4Na$ $[M+Na]^+$ calc.: 321.11028 ; found: 321.1102. Source: ESI.

$[\alpha]_D^{25}$ of *Z* isomer = +155 (c = 0.1 g/mL, CH_2Cl_2, 67% ee).

***Z*-selectivity determination** by GC/MS on the crude mixture:

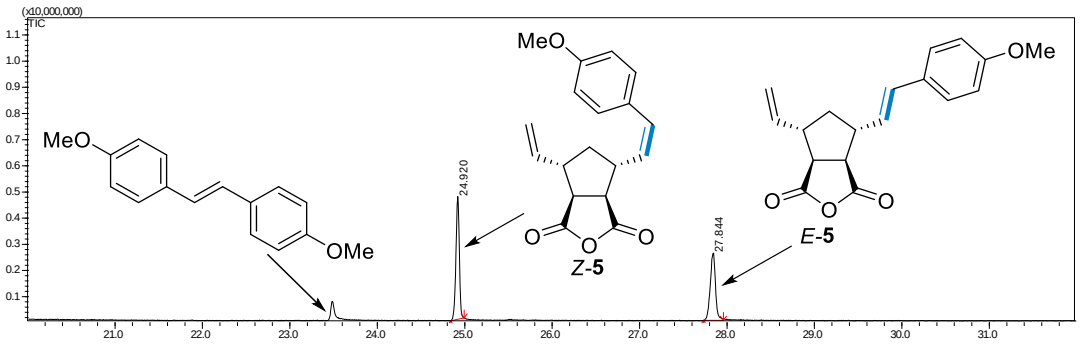
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 30.0 cm/s

Temperature protocol:

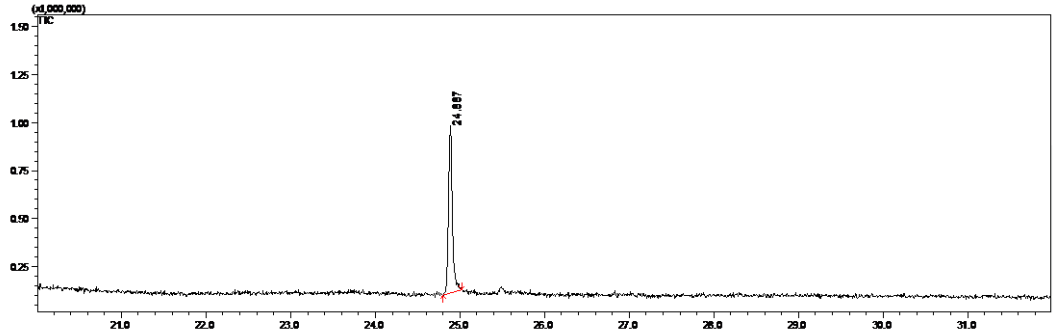
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	70	4
10	250	10

*With non-selective complex rac-**Ru-3h***



Peak	Ret. Time (min)	Area	Area%
1	24.920	12739479	54.20
2	27.844	10765060	45.80

*With **(R)-Ru-4h**: 99/1 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	24.887	2795067	100

ee determination by HPLC on chiral stationary phase on the purified product:

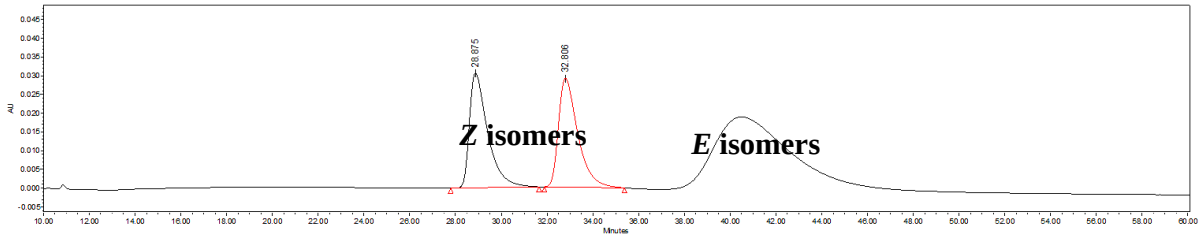
Column OJ-H (250 x 4.6 mm, 5 µm)

Mobile phase: Hexanes:^{i}PrOH 80:20

Flow rate: 1 mL/min

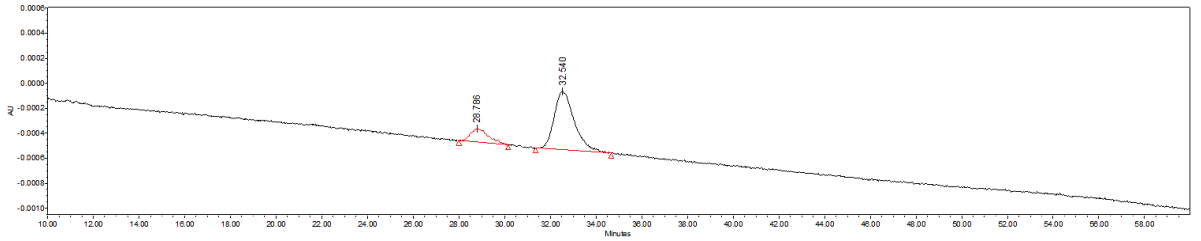
Detection at 254 nm.

Racemic mixture:



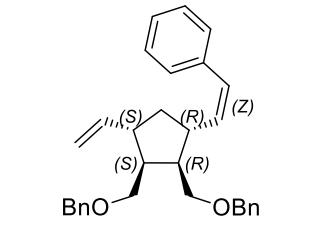
Peak	Ret. Time (min)	Area	Area%	Height
1	28.875	1698284	50.00	30600
2	32.806	1698210	50.00	29074

*With **(R)-Ru-4h** (83.5/16.5 er; 67% ee):*



Peak	Ret. Time (min)	Area	Area%	Height
1	28.786	5660	16.66	104
2	32.540	28311	83.34	467

((((3-((Z)-styryl)-5-vinylcyclopentane-1,2-diyl)bis(methylene))bis(oxy))bis(me-thylene)) dibenzene (24):



Chemical Formula: $C_{31}H_{34}O_2$
Molecular Weight: 438,61

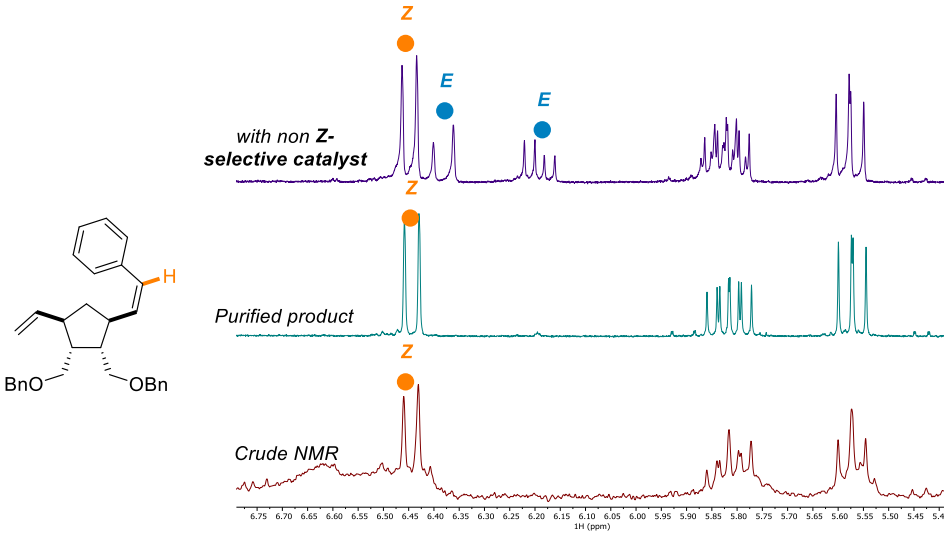
The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2h** (67 mg, 0.20 mmol, 1.0 equiv), styrene (0.46 mL, 4.01 mmol, 20.0 equiv) and 1 mL of (*S*)-**Ru-4h** solution obtained from 2nd eluted (-)-(*S*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 30 minutes. The desired product **24** was obtained after column chromatography (eluent: Pentane:Et_2O, 10:0 to 98:2) as a colourless oil (29 mg, 33% yield). Insoluble polymer **3h** was also visible in the schlenk at the end of the reaction (neither quantified nor characterized).

^{1}H NMR (400 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 7.40 – 7.16 (m, 15H, CH_{ar}), 6.44 (d, *J* = 11.6 Hz, 1H, CH_{alkene}), 5.81 (ddd, *J* = 17.1, 10.1, 8.0 Hz, 1H, CH_{alkene}), 5.57 (dd, *J* = 11.6, 10.2 Hz, 1H, CH_{alkene}), 5.08 – 4.92 (m, 2H, C$H_{2\ alkene}$), 4.47 – 4.26 (m, 4H, 2 x OCH_2), 3.61 – 3.44 (m, 4H, 2 x OCH_2), 3.26 – 3.17 (m, 1H, C*H*), 2.60 – 2.50 (m, 1H, C*H*), 2.25 – 2.07 (m, 3H, CH_2 + C*H*), 1.48 – 1.32 (m, 1H, C*H*).

^{13}C NMR (101 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 142.5 (CH_{alkene}), 138.7 ($C_{q\ ar}$), 138.6 ($C_{q\ ar}$), 137.7 ($C_{q\ ar}$), 137.0 (CH_{alkene}), 128.8 (CH_{ar}), 128.6 (2C, CH_{ar}), 128.3 (2C, CH_{ar}), 128.2 (2C, CH_{ar}), 128.2 (2C, CH_{ar}), 127.6 (2C, CH_{ar}), 127.6 (2C, CH_{ar}), 127.4 (CH_{ar}), 127.3 (CH_{ar}), 126.5 (CH_{alkene}), 113.7 ($CH_{2\ alkene}$), 73.0 (OCH_2Ph), 73.0 (OCH_2Ph), 70.2 (OCH_2), 70.0 (OCH_2), 48.3 (*C*H), 46.5 (*C*H), 46.5 (CH_2), 40.5 (*C*H), 40.3 (*C*H).

HRMS for $C_{31}H_{34}O_2Na$ $[M+Na]^+$ calc.: 461.24510 ; found: 461.2455. Source: ESI

***Z*-selectivity determination by ^{1}H NMR** on the crude mixture: >98/2



ee determination by HPLC on Chiral stationary phase on the purified product:

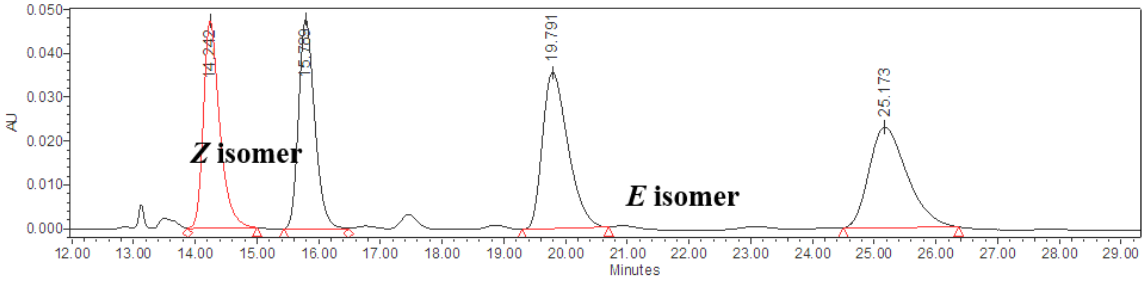
Column OD-3 (250 x 4.6 mm, 3 µm)

Mobile phase: Hexanes:*i*PrOH 99.5:0.5

Flow rate: 0.75 mL/min

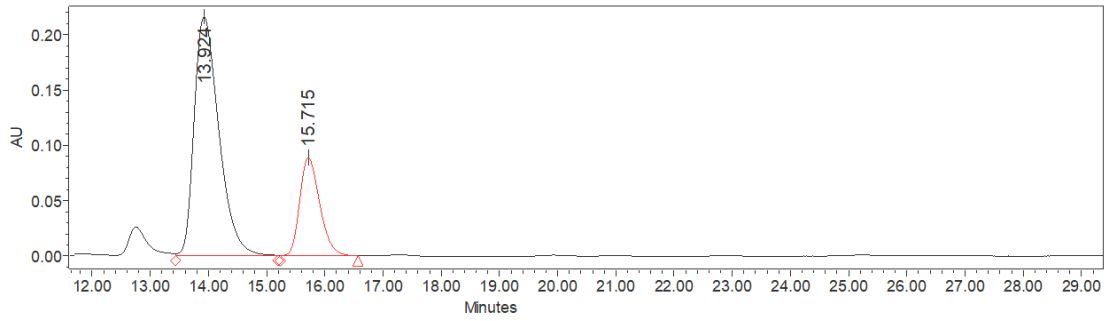
Detection at 254 nm

Racemic mixture (Z and E isomers):



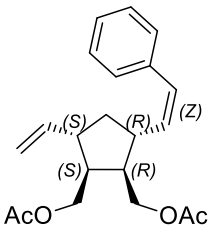
Peak	Ret. Time (min)	Area	Area%	Height
1	14.242	868460	23.17	47281
2	15.789	871006	23.24	47796
3	19.791	1026160	27.38	35686
4	25.173	981930	26.20	22906

*With **(S)-Ru-4h** (75/25 er; 50% ee):*



Peak	Ret. Time (min)	Area	Area%	Height
1	13.924	6358931	75.15	215574
2	15.715	2102432	24.85	88576

(3-((Z)-styryl)-5-vinylcyclopentane-1,2-diyl)bis(methylene) diacetate (25):



Chemical Formula: $C_{21}H_{26}O_4$
Molecular Weight: 342,44

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2d** (48 mg, 0.20 mmol, 1.0 equiv), styrene (0.46 mL, 4.01 mmol, 20.0 equiv) and 1 mL of (*S*)-**Ru-4h** solution obtained from 2nd eluted (-)-(*S*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 16 hours (50% conversion determined by ^{1}H NMR). The desired product **25** was obtained after column chromatography (eluent: Pentane:Et_2O, 10:0 to 9:1) as a colourless oil (21 mg, 31% yield).

^{1}H NMR (400 MHz, *$CDCl_3$*) of *Z* isomer: δ (ppm) 7.40 – 7.30 (m, 2H, C*H*$_{ar}$), 7.28 – 7.17 (m, 3H, C*H*$_{ar}$), 6.50 (d, *J* = 11.5 Hz, 1H, C*H*$_{alkene}$), 5.78 (ddd, *J* = 17.1, 10.1, 8.0 Hz, 1H, C*H*$_{alkene}$), 5.52 (dd, *J* = 11.5, 10.2 Hz, 1H, C*H*$_{alkene}$), 5.12 – 4.97 (m, 2H, C*H*$_{2\ alkene}$), 4.25 – 4.19 (m, 4H, OC*H*$_2$), 3.10 – 2.96 (m, 1H¸ C*H*), 2.49 – 2.36 (m, 1H, C*H*), 2.34 – 2.18 (m, 2H, C*H*$_2$), 2.19 – 2.10 (m, 1H, C*H*), 2.01 (s, 3H, *CH*$_3$), 1.89 (s, 3H, *CH*$_3$), 1.55 – 1.32 (m, 1H, C*H*).

^{13}C NMR (101 MHz, *$CDCl_3$* of *Z* isomer: δ (ppm) 171.2, 171.0, 141.3, 137.5, 135.4, 129.9, 128.6 (2C), 128.4 (2C), 126.9, 114.7, 64.3, 63.8, 46.8, 46.6, 45.0, 40.5, 40.0, 21.0, 20.9.

HRMS for $C_{21}H_{26}O_4Na$ $[M+Na]^+$ calc.: 365.17233; found: 365.1727. Source: ESI

***Z*-selectivity determination** by GC/MS on the crude mixture:

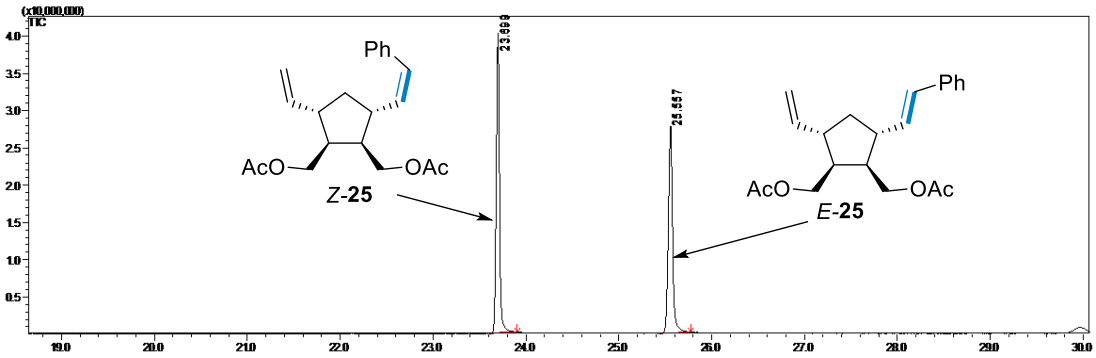
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 30.0 cm/s

Temperature protocol:

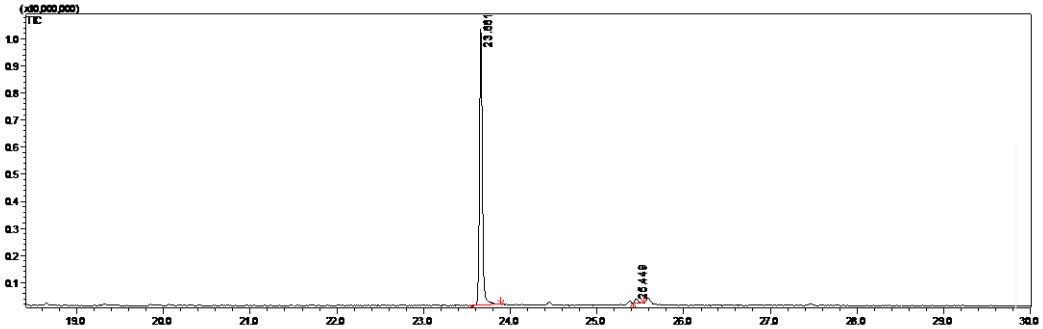
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	70	4
10	250	10

*With non-selective complex rac-**Ru-3h***



Peak	Ret. Time (min)	Area	Area%
1	23.699	96480488	52.37
2	25.557	87754214	47.63

*With **(S)-Ru-4h:** 98/2 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	23.661	23081581	97.83
2	25.449	512504	2.17

ee determination by HPLC on chiral stationary phase on the purified product:

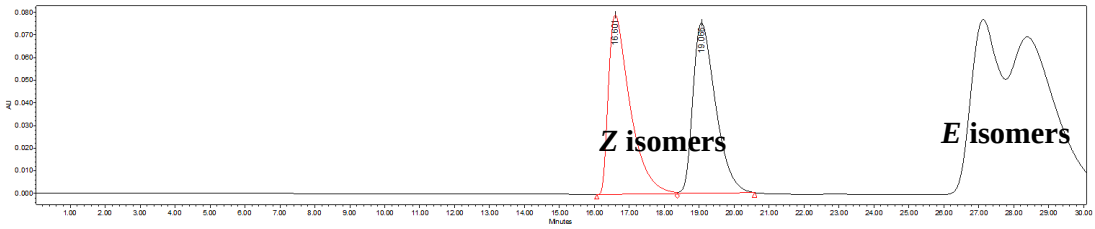
Column OD-3 (250 x 4.6 mm, 3 µm)

Mobile phase: Cyclohexane:*i*PrOH 99.7:0.3

Flow rate: 1 mL/min

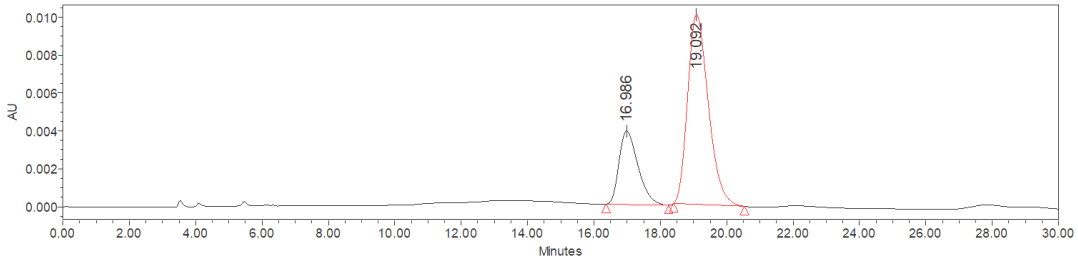
Detection at 254 nm

Racemic mixtures (E & Z isomers):



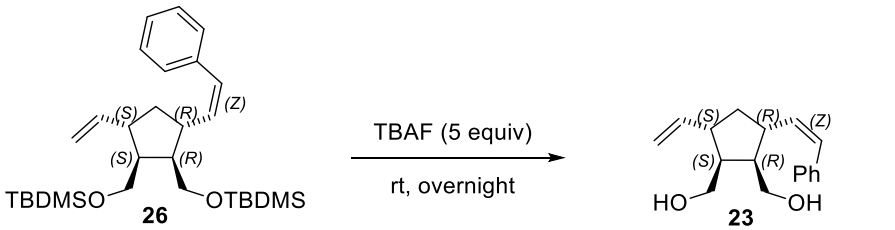
Peak	Ret. Time (min)	Area	Area%	Height
1	16.601	3422643	50.31	79218
2	19.066	3381130	49.69	75241

*With **(S)-Ru-4h** (74/26 er; 47% ee):*



Peak	Ret. Time (min)	Area	Area%	Height
1	16.986	154508	26.26	3884
2	19.092	433828	73.74	10021

3-((Z)-styryl)-5-vinylcyclopentane-1,2-diyl)bis(methylene))bis(oxy))bis (*tert*-butyldimethylsilane) (26) followed by TBDMS deprotection:



Chemical Formula: $C_{29}H_{50}O_2Si_2$
Molecular Weight: 486,89

Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2i** (79 mg, 0.20 mmol, 1.0 equiv), styrene (0.46 mL, 4.01 mmol, 20.0 equiv) and 1 mL of (*S*)-**Ru-4h** solution obtained from 2nd eluted (-)-(*S*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 30 minutes. Insoluble polymer was also visible in the schlenk at the end of the reaction (neither quantified nor characterized). Product **26** was neither isolated nor analyzed due to its highly non-polar character, but deprotected into product **23**. Cleavage of the TBDMS groups was performed with TBAF (1 M in THF, 1 mL, 1.0 mmol, 5.0 equiv) at room temperature overnight. The product was extracted with Et_2O (3 x 5 mL), dried over $MgSO_4$, and concentrated under vacuum. The corresponding diol **23** was isolated by column chromatography (eluent: Pentane:EtOAc 10:0 to 7:3) as a colourless oil (20 mg, 36% yield over two steps).

Analytical methods and data for this compound matched with the above description for compound **23**.

***Z*-selectivity determination** by GC/MS on the crude mixture.

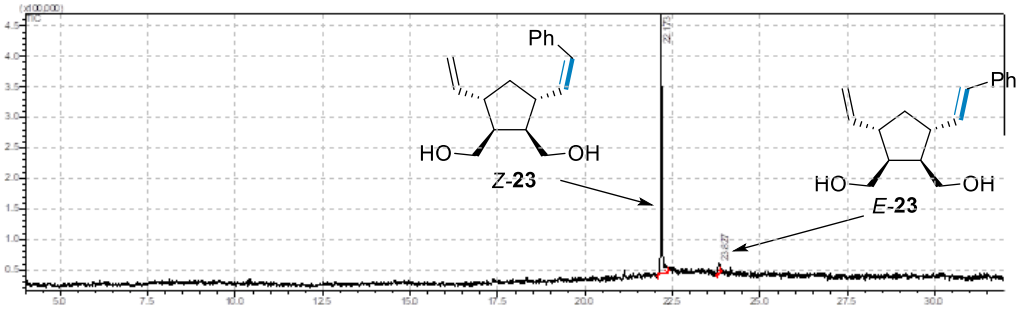
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 30.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	70	4
10	250	10

*With **(S)-Ru-4h**: 95/5 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	22.173	1013892	94.93
2	23.827	54147	5.07

ee determination by HPLC on Chiral stationary phase on the purified product:

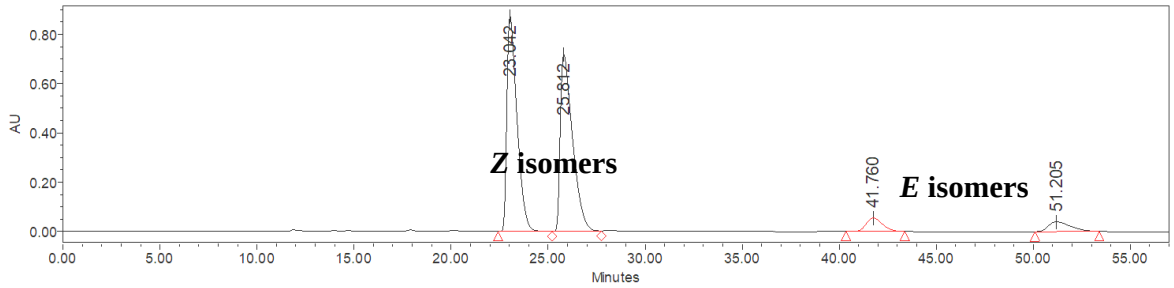
Column OD-3 (250 x 4.6 mm, 3 µm)

Mobile phase: Hexanes:*i*PrOH 98:2

Flow rate: 1 mL/min

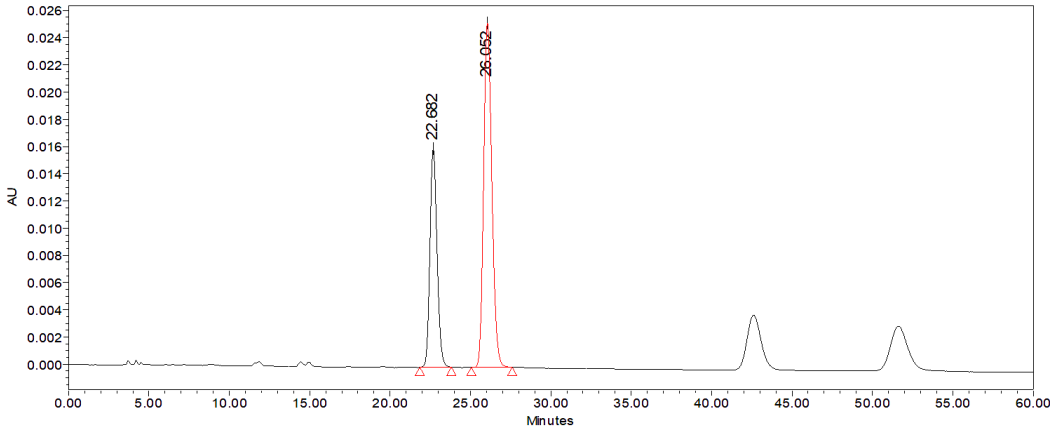
Detection at 254 nm.

Racemic mixtures (Z and E isomers):



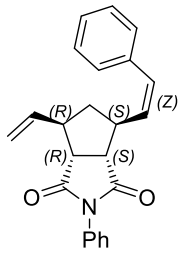
Peak	Ret. Time (min)	Area	Area%	Height
1	23.042	31617319	45.40	872976
2	25.812	31669989	45.47	717566
3	41.760	3193241	4.59	54558
4	51.205	3164596	4.54	39814

*With **(S)-Ru-4h** (64.5/35.5 er; 29% ee)*



Peak	Ret. Time (min)	Area	Area%	Height
1	22.682	494804	35.48	16064
2	26.052	899715	64.52	25307

2-phenyl-4-((Z)-styryl)-6-vinyltetrahydrocyclopenta[c]pyrrole-1,3(2H, 3aH)-dione (6):



Chemical Formula: $C_{23}H_{21}NO_2$
Molecular Weight: 343,43

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2e** (48 mg, 0.20 mmol, 1.0 equiv), styrene (0.46 mL, 4.01 mmol, 20.0 equiv) and 1 mL of (*R*)-**Ru-4h** solution obtained from 1st eluted (+)-(*R*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 30 minutes. The desired product **6** was obtained after column chromatography (eluent: Pentane:EtOAc 10:0 to 8:2) as a colourless oil (57 mg, 83% yield).

^{1}H NMR (400 MHz, *$CDCl_3$*) of *Z* isomer: δ (ppm) 7.52 – 7.44 (m, 2H, C*H*$_{ar}$), 7.43 – 7.34 (m, 5H, C*H*$_{ar}$), 7.32 – 7.21 (m, 3H, C*H*$_{ar}$), 6.66 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*$_{alkene}$), 6.01 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H, C*H*$_{alkene}$), 5.71 (dd, *J* = 11.4, 9.9 Hz, 1H, C*H*$_{alkene}$), 5.26 (dt, *J* = 17.2, 1.3 Hz, 1H, C*H*$_2$ $_{alkene}$), 5.17 (dt, *J* = 10.3, 1.2 Hz, 1H, C*H*$_2$ $_{alkene}$), 3.49 – 3.36 (m, 1H, C*H*), 3.35 – 3.19 (m, 2H, C*H*$_2$), 2.95 – 2.83 (m, 1H, C*H*), 2.20 (dt, *J* = 12.3, 6.0 Hz, 1H, C*H*), 1.74 (dt, *J* = 12.6, 11.1 Hz, 1H, C*H*).

^{13}C NMR (101 MHz, *$CDCl_3$*) of *Z* isomer: δ (ppm) 177.1 (*C*=O), 176.8 (*C*=O), 138.7 (*C*H$_{ar}$)), 136.8 (*C*$_{q\ ar}$), 132.9 (*C*H$_{ar}$), 131.2 (*C*$_{q\ ar}$), 129.1 (2C, *C*H$_{ar}$), 128.7 (2C, *C*H$_a$), 128.5 (*C*H$_{alkene}$), 128.4 (2C, *C*H$_a$), 128.4 (*C*H$_{alkene}$), 127.0 (*C*H$_{alkene}$), 126.4 (2C, *C*H$_a$), 116.0 (*C*H$_2$ $_{alkene}$), 52.1 (*C*H), 51.1 (*C*H), 47.4 (*C*H), 42.8 (*C*H), 42.4 (*C*H$_2$).

HRMS for $C_{23}H_{22}O_2N$ $[M+H]^+$ calc.: 344.16450; found: 344.1641. Source: ESI

***Z*-selectivity determination** by GC/MS on the crude mixture:

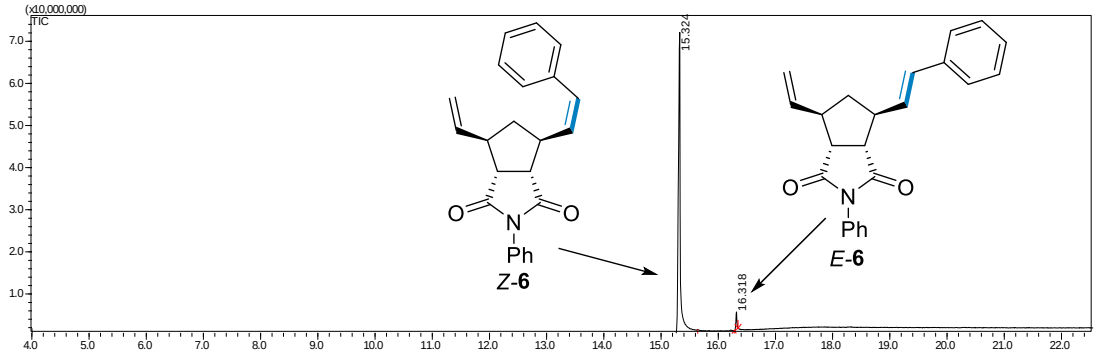
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	0
15	300	20

*With **(R)-Ru-4h:** 97/3 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	15.324	175571865	97.02
2	16.318	5396386	2.98

ee determination by HPLC on Chiral stationary phase on the purified product:

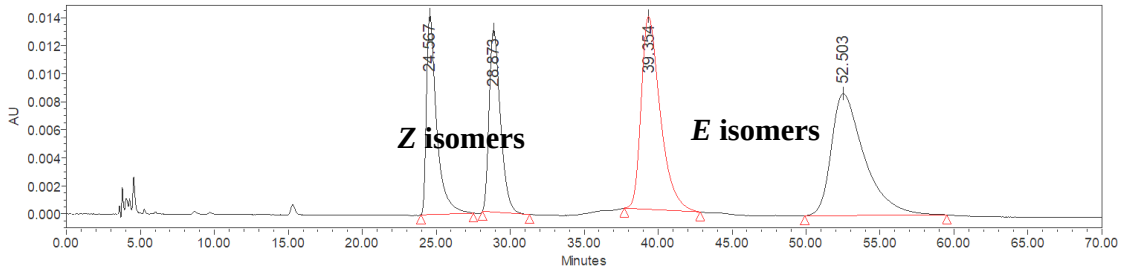
Column OD-3 (250 x 4.6 mm, 3 µm)

Mobile phase: Hexanes:*i*PrOH 90:10

Flow rate: 1 mL/min

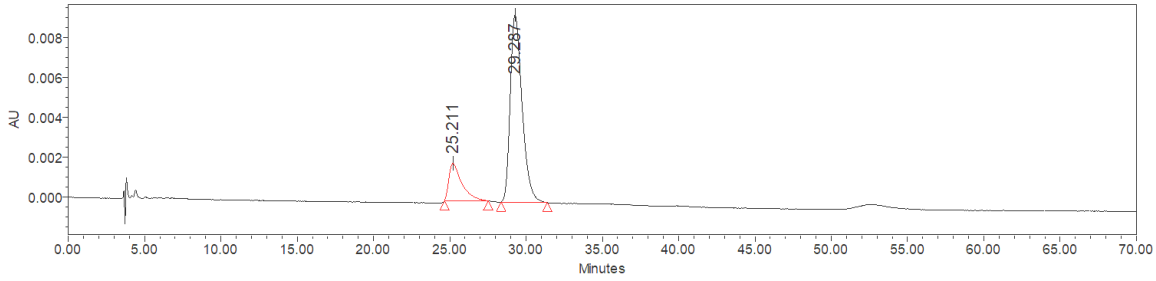
Detection at 254 nm.

Racemic mixtures



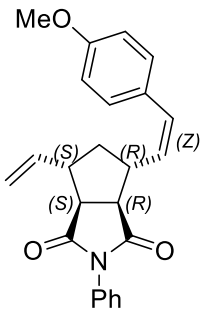
Peak	Ret. Time (min)	Area	Area%	Height
1	24.567	683353	17.29	14223
2	28.873	688562	17.42	12994
3	39.354	1232100	31.18	13751
4	52.503	1347894	34.11	8708

*With **(R)-Ru-4h** (82/18 er; 64% ee):*



Peak	Ret. Time (min)	Area	Area%	Height
1	25.211	109802	17.83	1891
2	29.287	505986	82.17	9392

4-((Z)-4-methoxystyryl)-2-phenyl-6-vinyltetrahydrocyclopenta[c]pyrrole-1,3(2H,3aH)-dione (7):



Chemical Formula: $C_{24}H_{23}NO_3$
Molecular Weight: 373,45

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2e** (48 mg, 0.20 mmol, 1.0 equiv), *p*-methoxystyrene (0.53 mL, 4.00 mmol, 20.0 equiv) and 1 mL of (*R*)-**Ru-4h** solution obtained from 1st eluted (+)-(*R*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 30 min. The desired product **7** was obtained after column chromatography (eluent: Pentane:EtOAc 10:0 to 85:15) as a colourless oil (57.2 mg, 77% yield).

^{1}H NMR (400 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 7.50 – 7.41 (m, 2H), 7.41 – 7.33 (m, 1H), 7.31 – 7.19 (m, 4H), 6.91 – 6.83 (m, 2H), 6.55 (d, *J* = 11.1 Hz, 1H), 5.99 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.60 (dd, *J* = 11.4, 9.8 Hz, 1H), 5.23 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.14 (dt, *J* = 10.3, 1.2 Hz, 1H), 3.80 (s, 3H), 3.47 – 3.36 (m, 1H), 3.27 – 3.17 (m, 2H), 2.92 – 2.82 (m, 1H), 2.18 (dt, *J* = 12.3, 6.0 Hz, 1H), 1.70 (dt, *J* = 12.8, 10.9 Hz, 1H).

^{13}C NMR (101 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 177.1, 176.9, 158.6, 138.7, 131.9, 131.8, 130.6, 129.9 (2 C), 129.3, 129.1 (2 C), 128.5, 126.4 (2 C), 115.9, 113.8 (2 C), 55.3, 52.2, 51.1, 47.5, 42.8, 42.3.

HRMS for $C_{24}H_{23}NO_3Na$ $[M+Na]^+$, calc.: 396.15701; found: 396.1570. Source: ESI.

$[\alpha]_D^{25}$ of *Z* isomer = +132 (c = 0.1 g/mL, CH_2Cl_2, 64% ee).

***Z*-selectivity determination** by GC/MS on the crude mixture:

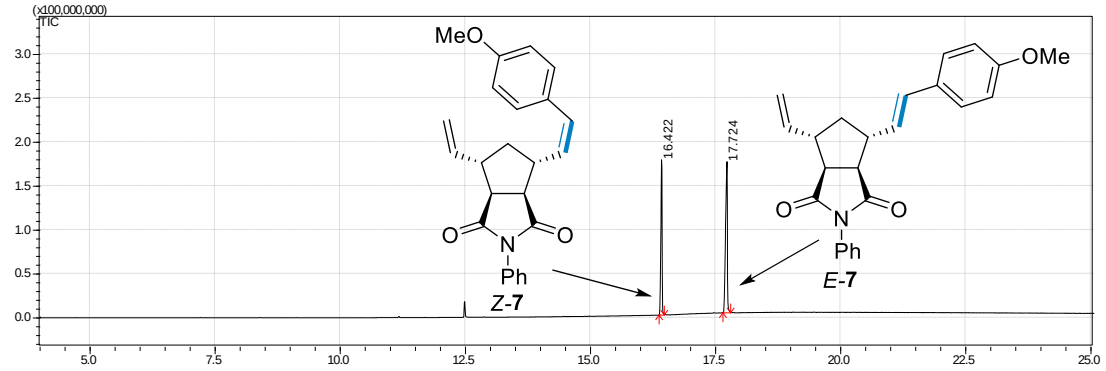
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

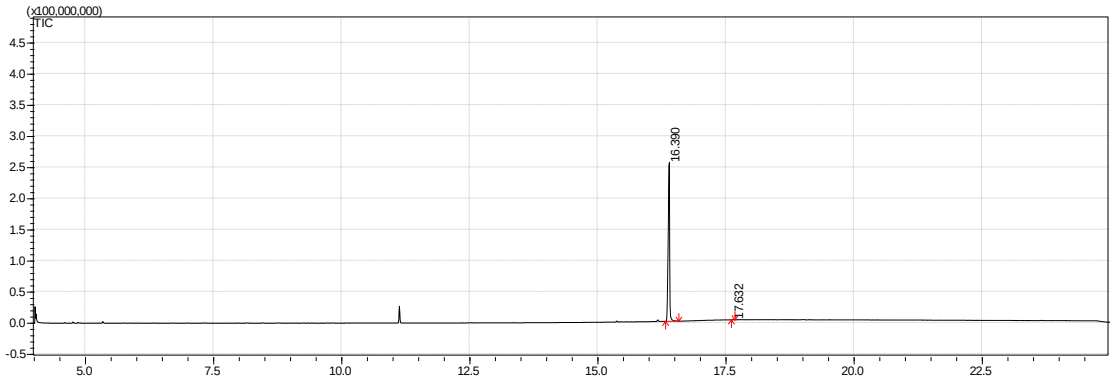
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	0
15	300	20

*With **HG2:***



Peak	Ret. Time (min)	Area	Area%
1	16.422	306810776	41.53
2	17.724	431994146	58.47

*With **(R)-Ru-4h:** 99/1 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	16.390	516082768	99.65
2	17.632	1805663	0.35

ee determination by HPLC on Chiral stationary phase on the purified product:

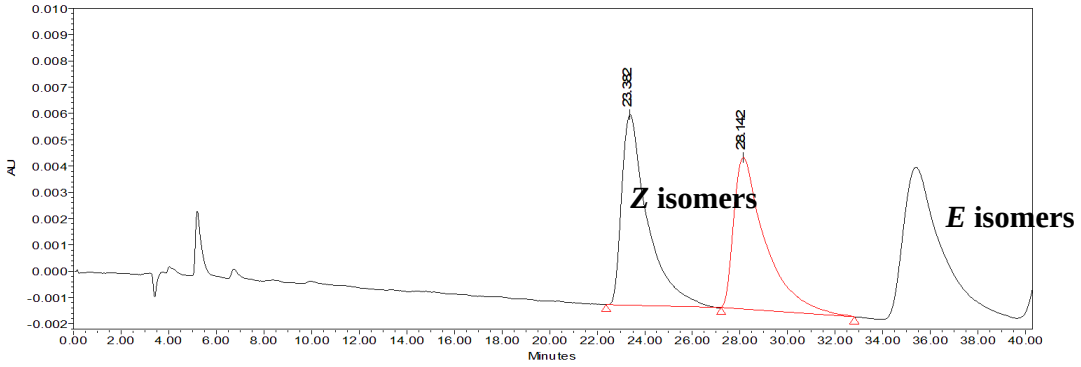
Column IA (250 x 4.6 mm, 3 µm)

Mobile phase: Hexanes:*i*PrOH 90:10

Flow rate: 1 mL/min

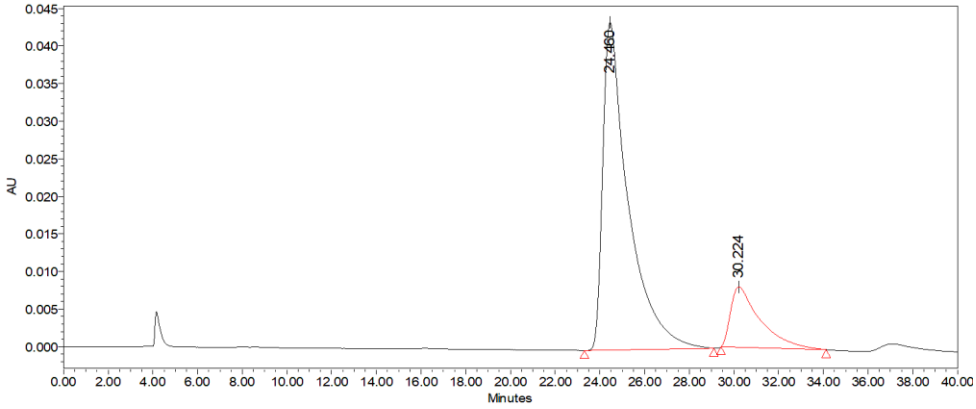
Detection at 254 nm.

Racemic mixture



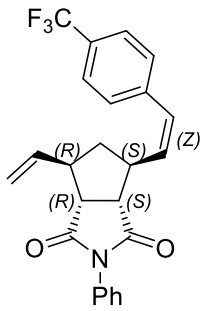
Peak	Ret. Time (min)	Area	Area%	Height
1	23.382	546211	50.67	7242
2	28.142	531672	49.33	5762

*With **(R)-Ru-4h** (82.5/17.5 er; 64% ee):*



Peak	Ret. Time (min)	Area	Area%	Height
1	24.460	3458707	82.51	43604
2	30.224	733099	17.49	8046

2-phenyl-4-((Z)-4-(trifluoromethyl)styryl)-6-vinyltetrahydrocyclopenta[c]pyrrole-1,3(2H, 3aH)-dione (8):



Chemical Formula: $C_{24}H_{20}F_3NO_2$
Molecular Weight: 411,42

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2e** (48 mg, 0.20 mmol, 1.0 equiv), *p*-trifluoromethylstyrene (0.59 mL, 4.00 mmol, 20.0 equiv) and 1 mL of (*R*)-**Ru-4h** solution obtained from 1st eluted (+)-(*R*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 30 min. The desired product **8** was obtained after column chromatography (eluent: Pentane:EtOAc 10:0 to 9:1) as a colourless oil (53.9 mg, 66% yield).

^{1}H NMR (400 MHz, *$CDCl_3$*) of *Z* isomer: δ (ppm) 7.59 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.42 (m, 4H), 7.42 – 7.34 (m, 1H), 7.24 – 7.17 (m, 2H), 6.63 (d, *J* = 11.4 Hz, 1H), 5.98 (ddd, *J* = 17.0, 10.3, 6.6

Hz, 1H), 5.78 (dd, *J* = 11.4, 9.9 Hz, 1H), 5.24 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.16 (dt, *J* = 10.3, 1.2 Hz, 1H), 3.38 – 3.17 (m, 3H), 2.85 (dt, *J* = 12.7, 6.4 Hz, 1H), 2.16 (dt, *J* = 12.3, 5.9 Hz, 1H), 1.72 (dt, *J* = 12.8, 11.0 Hz, 1H).

^{13}C NMR (101 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 176.8 (2C), 140.4, 138.3, 134.8, 131.7, 129.8, 129.2, 129.2 (q, J^2 (C-F) = 16.2 Hz, 2C), 129.0 (2C), 128.6, 126.4 (2C), 125.3 (q, J^3 (C-F) = 3.8 Hz, 2 C), 124.32 (q, J^4 (C-F) = 272.0 Hz), 116.2, 51.9, 50.9, 47.5, 42.7, 42.1.

^{19}F NMR (376 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) -62.5.

HRMS for $C_{24}H_{20}NO_2F_3Na$ $[M+Na]^+$, calc.: 434.13383; found: 434.1334. Source: ESI.

$[\alpha]_D^{25}$ of *Z* isomer = +24 (c = 0.1 g/mL, CH_2Cl_2, 50% ee).

***Z*-selectivity determination** by GC/MS on the crude mixture:

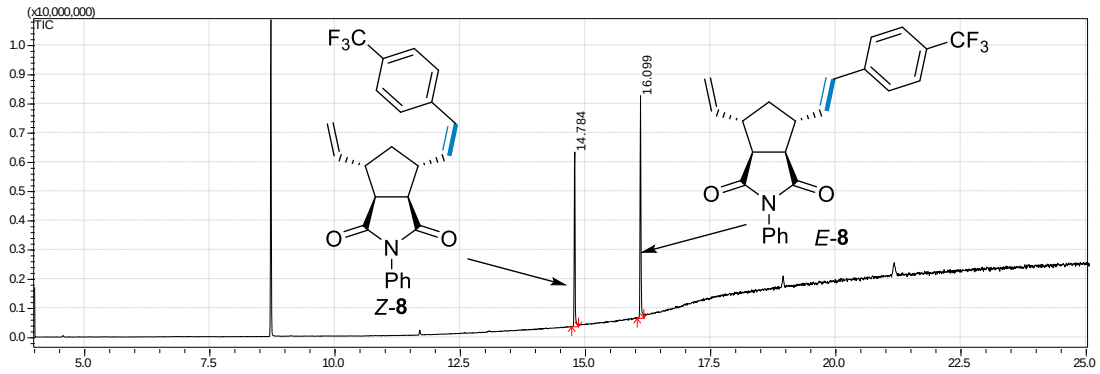
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

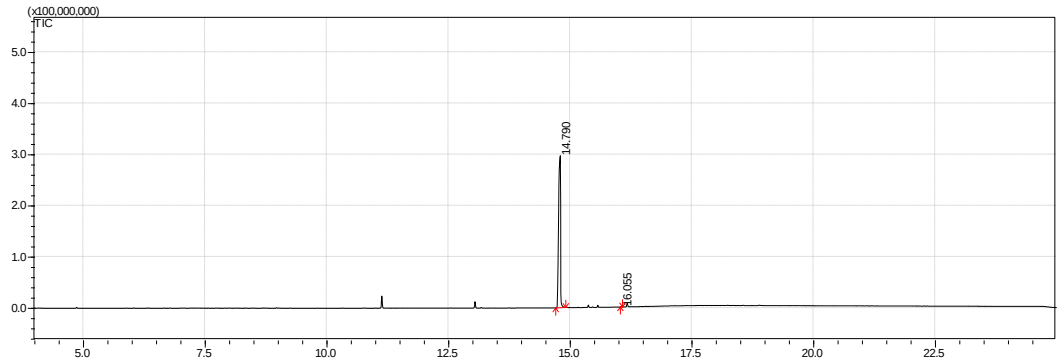
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	0
15	300	20

*With **HG2:***



Peak	Ret. Time (min)	Area	Area%
1	14.784	7461917	45.13
2	16.099	9073888	54.87

*With **(R)-Ru-4h:** 99/1 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	14.790	848024409	99.89
2	16.055	966827	0.11

ee determination by HPLC on Chiral stationary phase on the purified product:

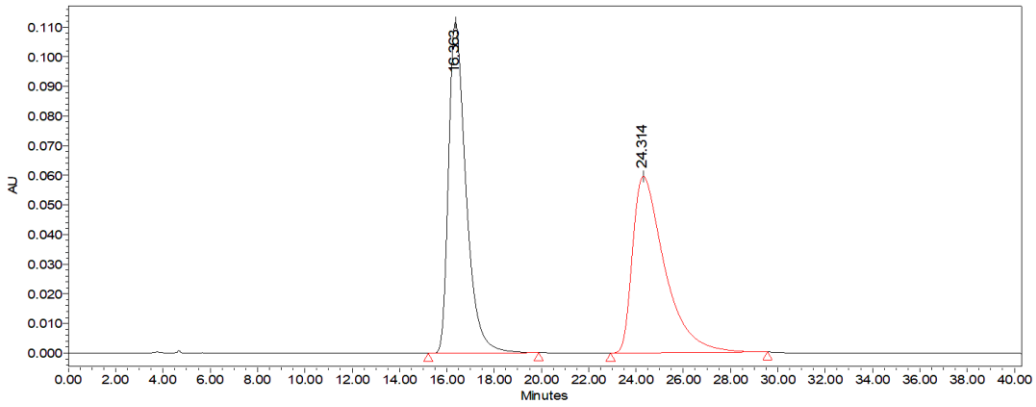
Column OJ-H (250 x 4.6 mm, 3 µm)

Mobile phase: Hexanes:*i*PrOH 80:20

Flow rate: 1 mL/min

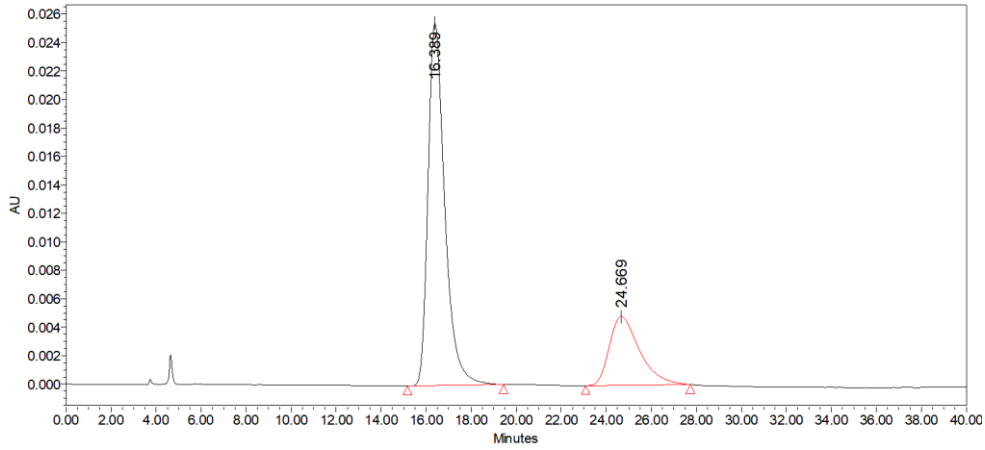
Detection at 254 nm.

Racemic mixture



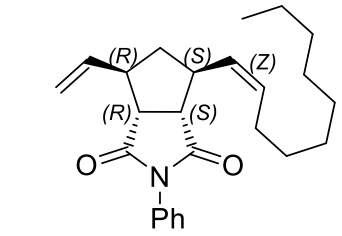
Peak	Ret. Time (min)	Area	Area%	Height
1	16.363	5730580	50.51	111583
2	24.314	5614510	49.49	59572

*With **(R)-Ru-4h** (75/25 er; 50% ee):*



Peak	Ret. Time (min)	Area	Area%	Height
1	16.389	1316633	74.52	25468
2	24.669	450273	25.48	4835

4-(dec-1-en-1-yl)-2-phenyl-6-vinyltetrahydrocyclopenta[c]pyrrole-1,3(2H,3aH) -dione (10):



Chemical Formula: $C_{25}H_{33}NO_2$
Molecular Weight: 379,54

The general procedure for *Z*-AROCM reactions with *in situ* generated complex was followed using **2i** (48 mg, 0.20 mmol, 1.0 equiv), 1-decene **13** (0.19 mL, 1.00 mmol, 5.0 equiv) and 1 mL of (*R*)-**Ru-4h** solution obtained from 1st eluted (+)-(*R*)-**Ru-3h** (18.4 mg in 2.5 mL, 0.01 mmol, 5 mol%). The reaction was stirred 4 hours (88% conversion determined by ^{1}H NMR). The desired product **10** was obtained after column chromatography (eluent: Pentane:EtOAc 10:0 to 85:15) as a colourless oil (61 mg, 80% yield).

^{1}H NMR (400 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 7.53 – 7.44 (m, 2H, C*H*$_{ar}$), 7.44 – 7.36 (m, 1H, C*H*$_{ar}$), 7.36 – 7.29 (m, 2H, C*H*$_{ar}$), 6.01 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H, C*H*$_{alkene}$), 5.61 – 5.50 (m, 1H, C*H*$_{alkene}$), 5.47 – 5.38 (m, 1H, C*H*$_{alkene}$), 5.27 (dt, *J* = 17.1, 1.3 Hz, 1H, C*H*$_{2\ alkene}$), 5.17 (dt, *J* = 10.3, 1.3 Hz, 1H, C*H*$_{2\ alkene}$), 3.27 – 3.08 (m, 3H, C*H*$_2$ + C*H*), 2.97 – 2.84 (m, 1H, C*H*), 2.22 – 2.08 (m, 3H, C*H*$_2$ + C*H*), 1.71 – 1.58 (m, 1H, C*H*), 1.36 – 1.23 (m, 12H, C*H*$_{2\ alkyl}$), 0.93 – 0.86 (m, 3H, C*H*$_3$).

^{13}C NMR (101 MHz, *CDCl$_3$*) of *Z* isomer: δ (ppm) 177.3 (*C*=O), 177.2 (*C*=O), 138.7 (*C*H$_{alkene}$), 132.6 (*C*H$_{alkene}$), 131.9 (*C*$_{q\ ar}$), 130.3 (*C*H$_{alkene}$), 129.1 (2C, *C*H$_{ar}$), 128.4 (*C*H$_{ar}$), 126.4 (2C, *C*H$_{ar}$), 115.9 (*C*H$_{alkene}$), 52.1 (*C*H), 51.0 (*C*H), 47.7 (*C*H), 42.7 (*C*H), 41.9 (*C*H$_{2\ cycle}$), 31.9 (*C*H$_{2\ alkyl}$), 29.6 (*C*H$_{2\ alkyl}$), 29.5 (*C*H$_{2\ alkyl}$), 29.3 (*C*H$_{2\ alkyl}$), 29.3 (*C*H$_{2\ alkyl}$), 27.7 (*C*H$_{2\ alkyl}$), 22.7 (*C*H$_{2\ alkyl}$), 14.1 (*C*H$_3$).

HRMS for $C_{25}H_{34}O_2N$ $[M+H]^+$ calc.: 380.25840; found: 380.2580. Source: ESI

***Z*-selectivity determination** by GC/MS on the crude mixture

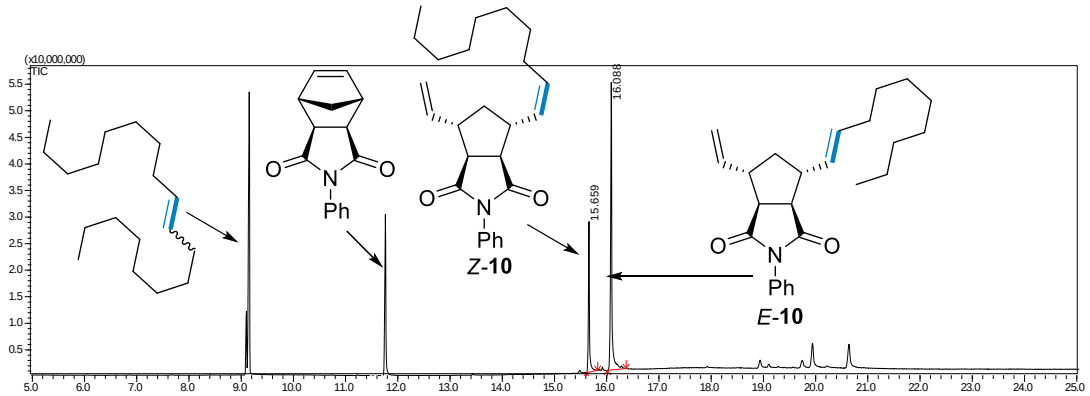
SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

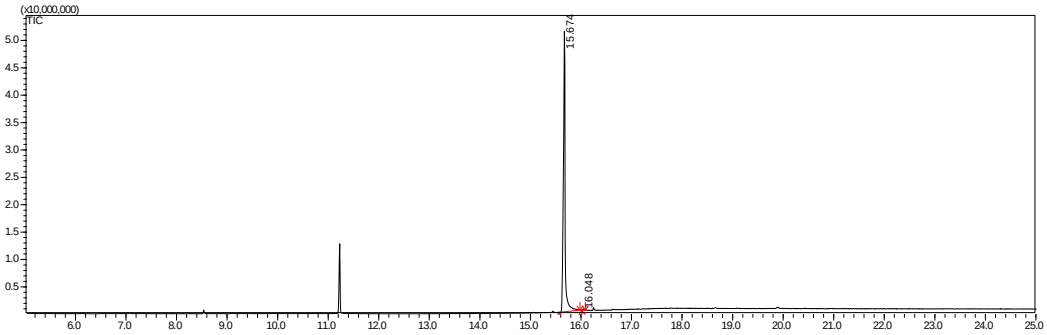
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	0
15	300	20

*With non-selective rac-**Ru-3h:***



Peak	Ret. Time (min)	Area	Area%
1	15.659	42334484	29.61
2	16.088	100617683	70.39

*With **(R)-Ru-4h**: 99/1 Z/E*



Peak	Ret. Time (min)	Area	Area%
1	15.672	122277483	99.67
2	16.048	407559	0.33

ee determination by HPLC on Chiral stationary phase on the purified product:

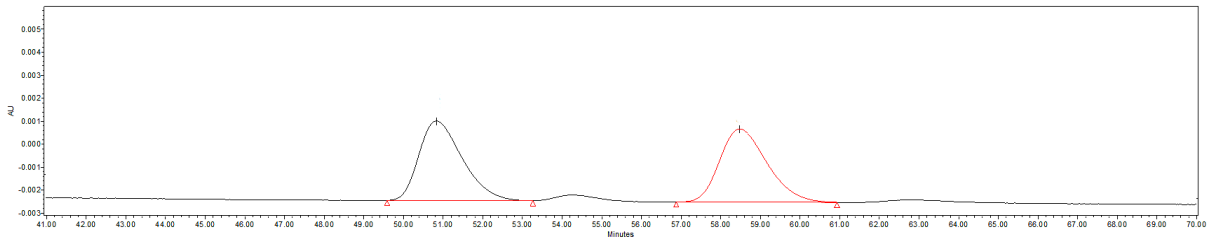
Column OD-3 (250 x 4.6 mm, 3 µm)

Mobile phase: Hexanes:*i*PrOH 98:2

Flow rate: 1 mL/min

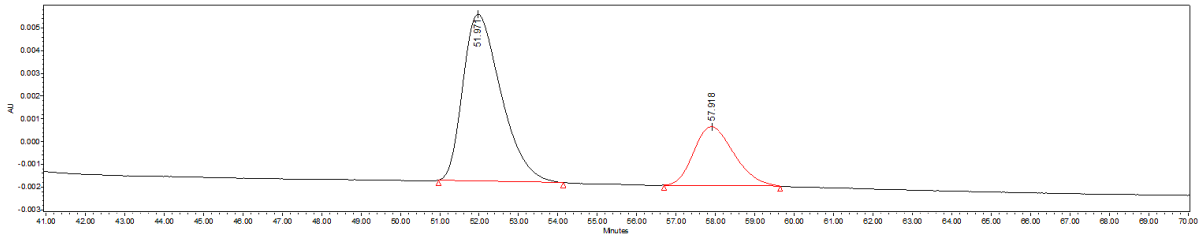
Detection at 254 nm.

Racemic mixture :



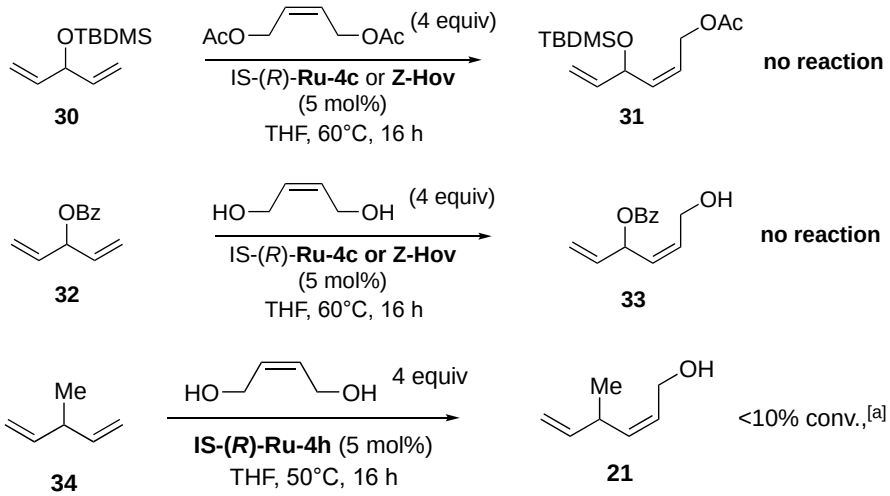
Peak	Ret. Time (min)	Area	Area%	Height
1	50.891	333781	49.89	4400
2	58.538	335195	50.11	4044

*With **(R)-Ru-4h** (72.5/27.5 er; 45% ee):*



Peak	Ret. Time (min)	Area	Area%	Height
1	51.971	492978	72.81	7339
2	57.918	184093	27.19	2592

8. Preliminary study in ACM



9. References - Experimental section

[1] L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano, L. Cavallo, *Nat. Chem.* **2019**, *11*, 872–879.

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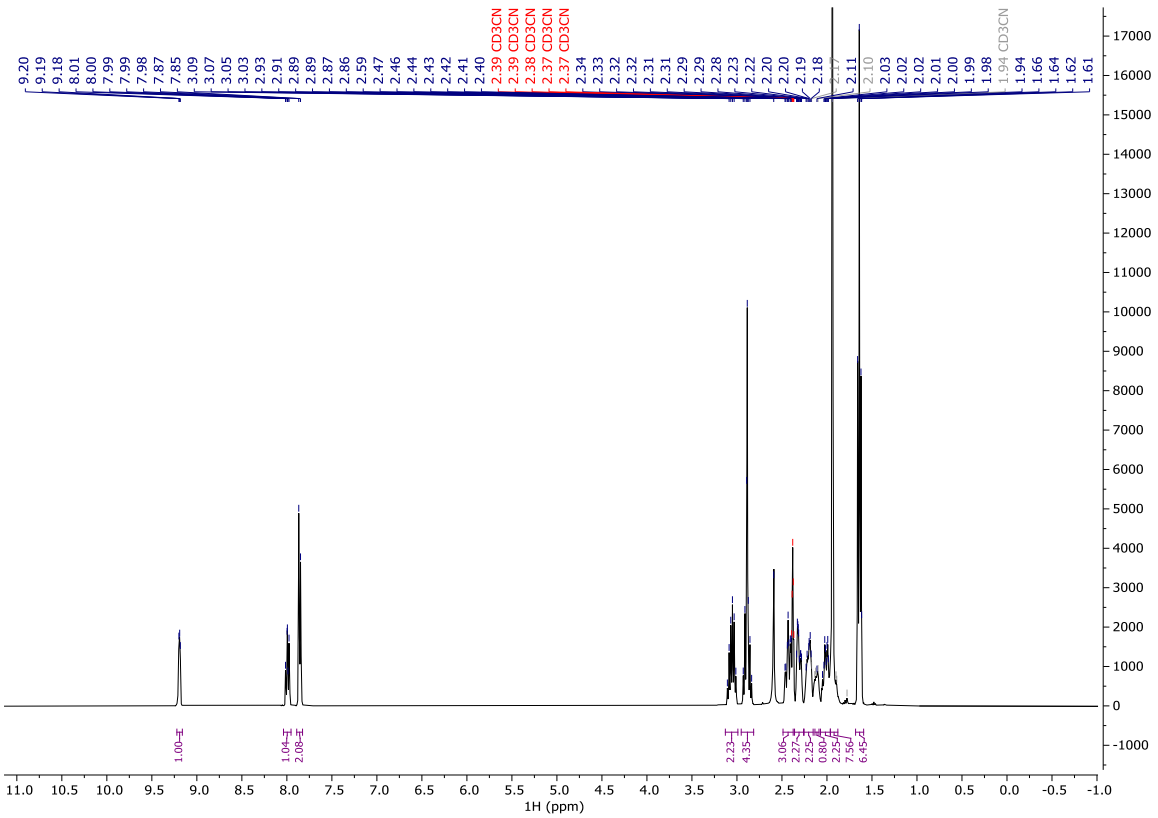
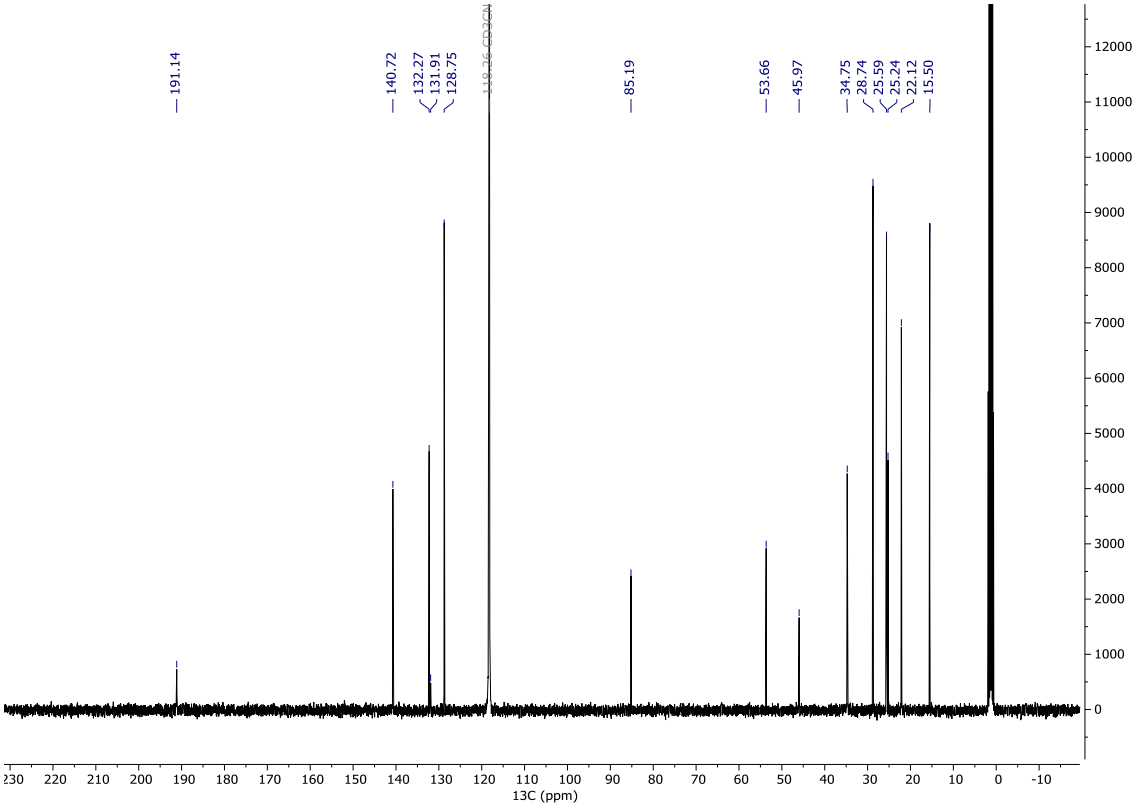
10. NMR data

10.1. NMR of CAAC salts

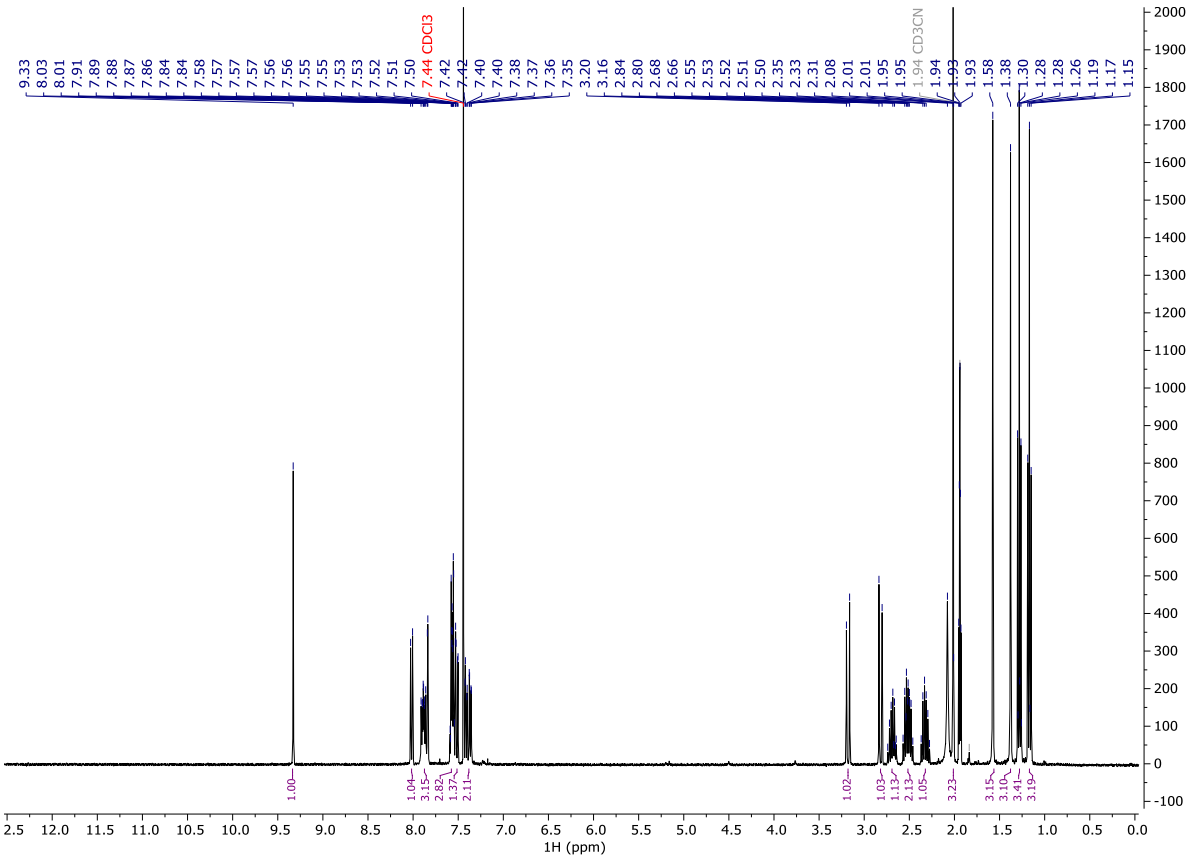
^{1}H NMR of **CAAC-b** (400 MHz, CD_3CN):



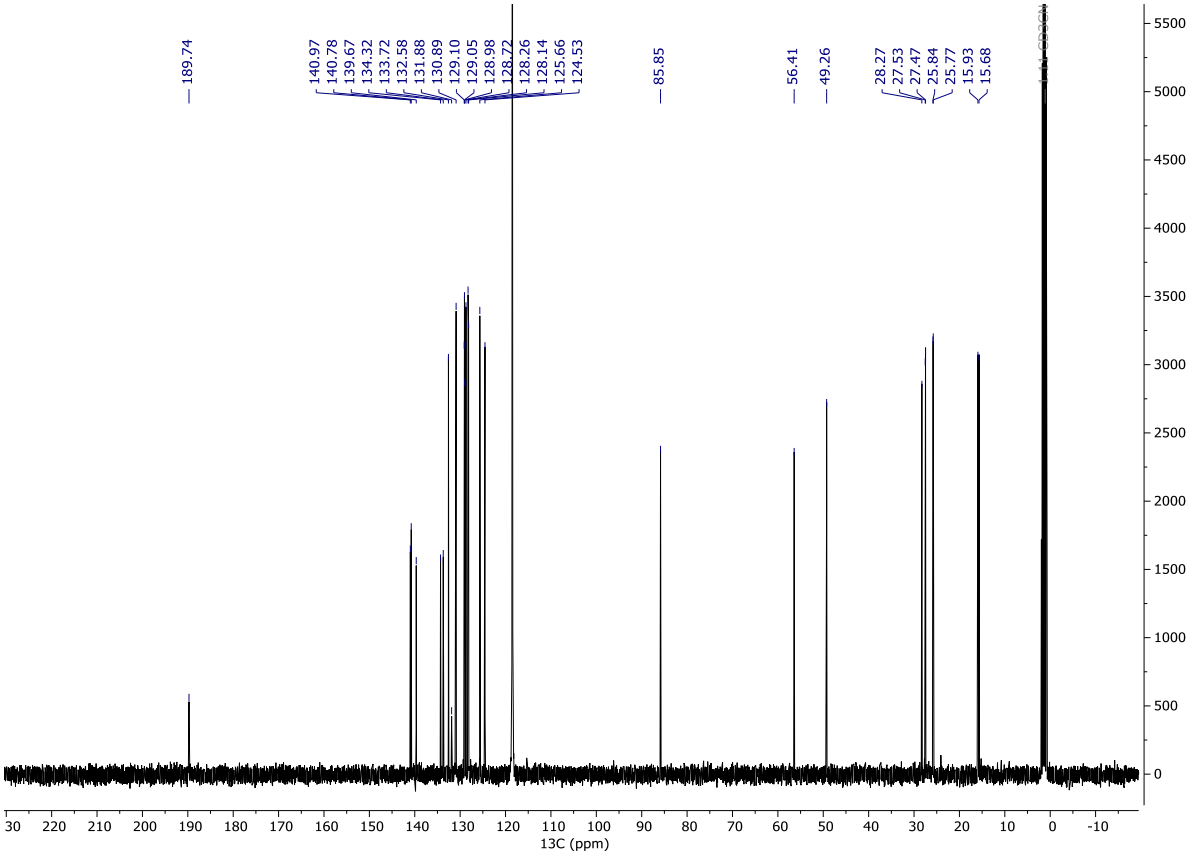
^{13}C NMR of **CAAC-b** (400 MHz, CD_3CN):



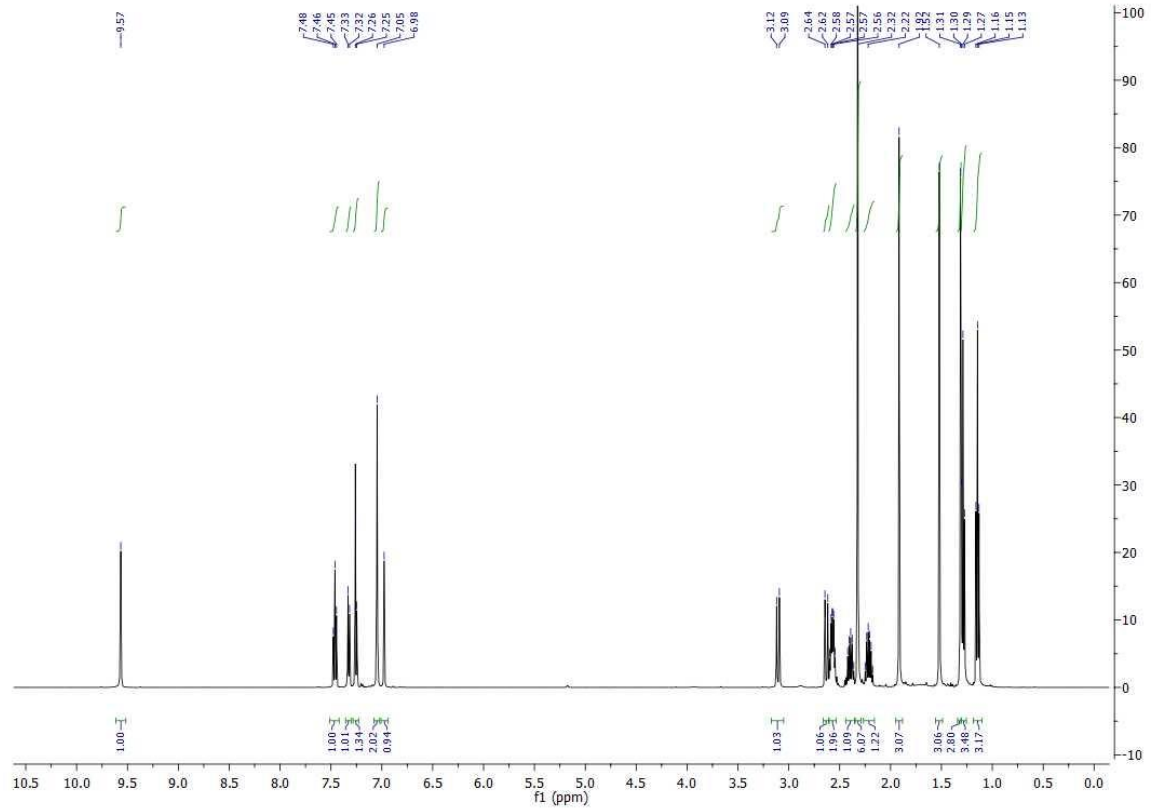
^{1}H NMR of **CAAC-h** (400 MHz, $CD_3CN/CDCl_3$):



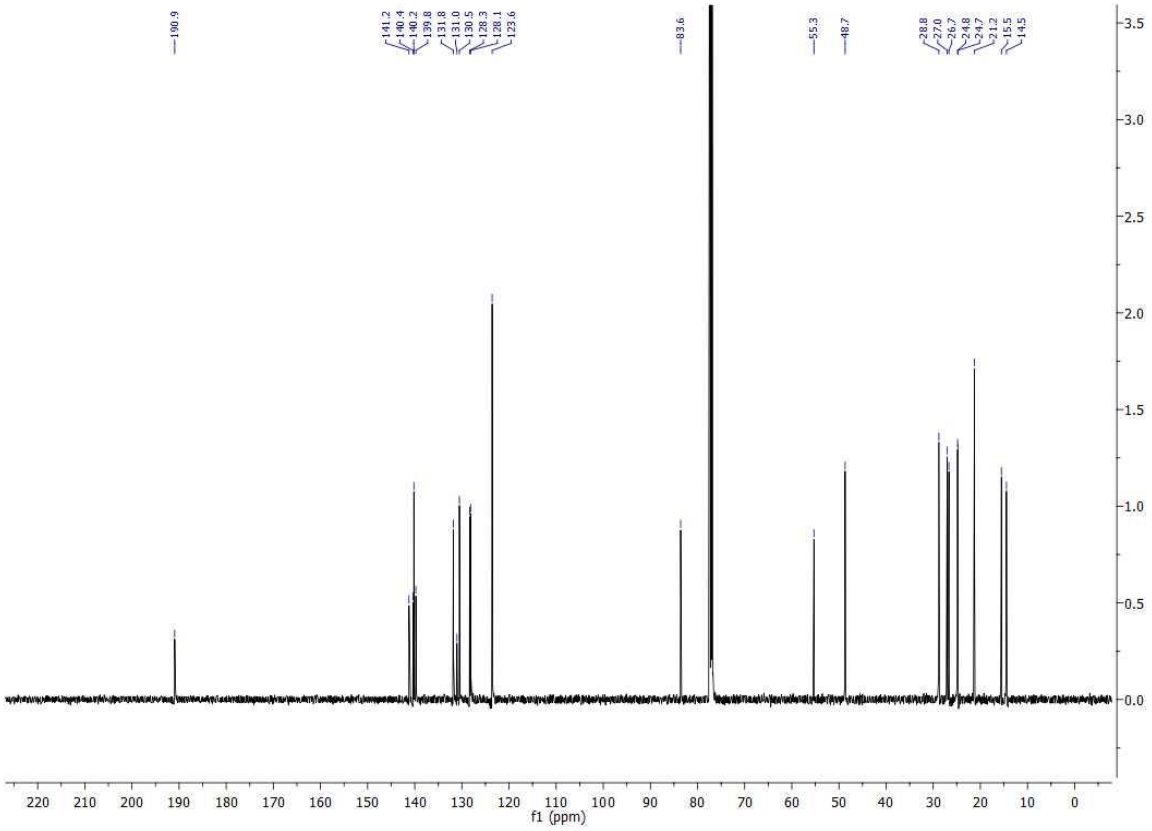
^{13}C NMR of **CAAC-h** (101 MHz, CD_3CN):



^{1}H NMR of **CAAC-i** (400 MHz, $CDCl_3$):

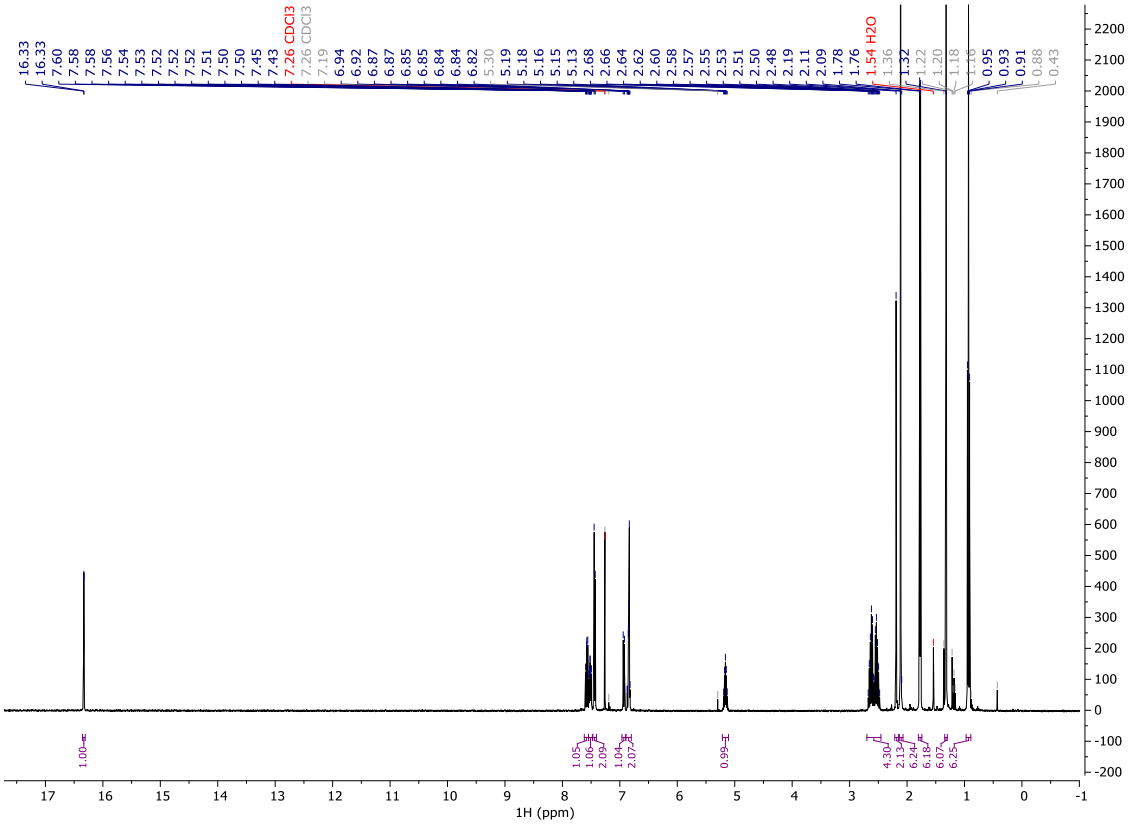


^{13}C NMR of **CAAC-i** (101 MHz, $CDCl_3$):

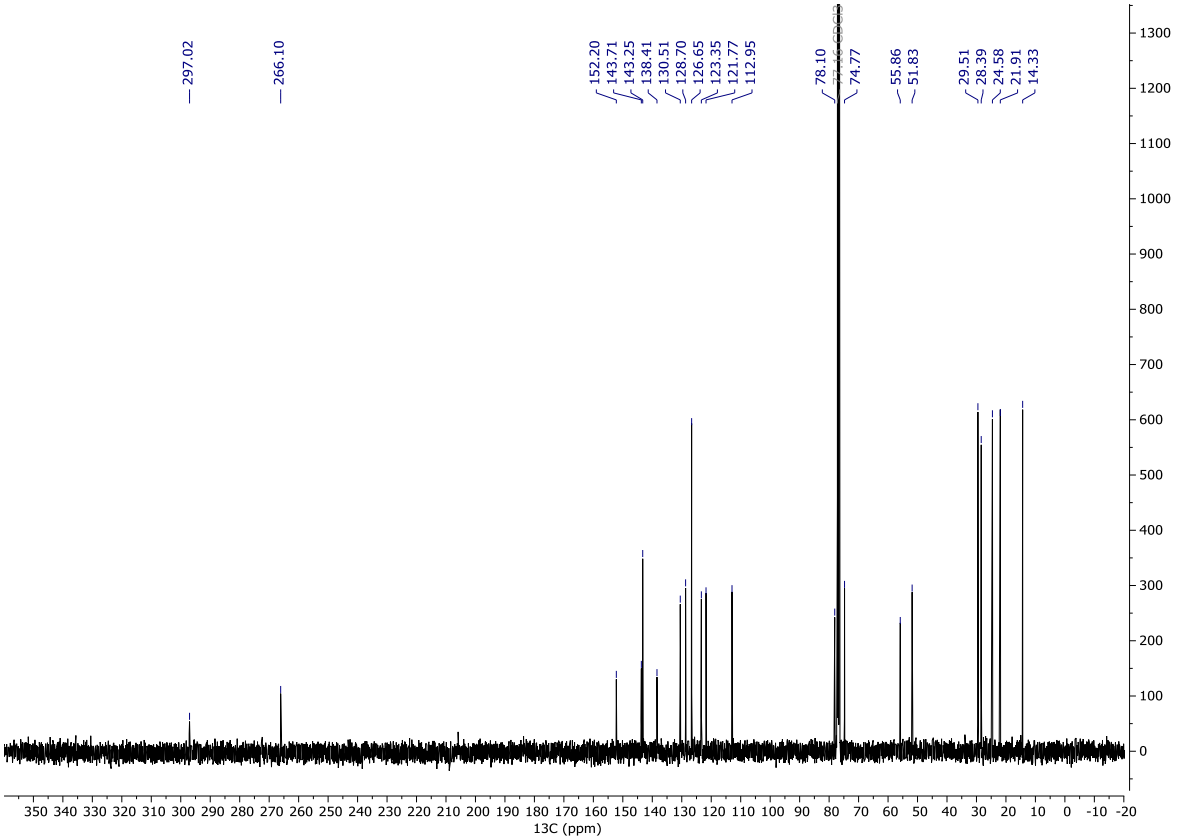


10.2. NMR of Ru-3 complexes

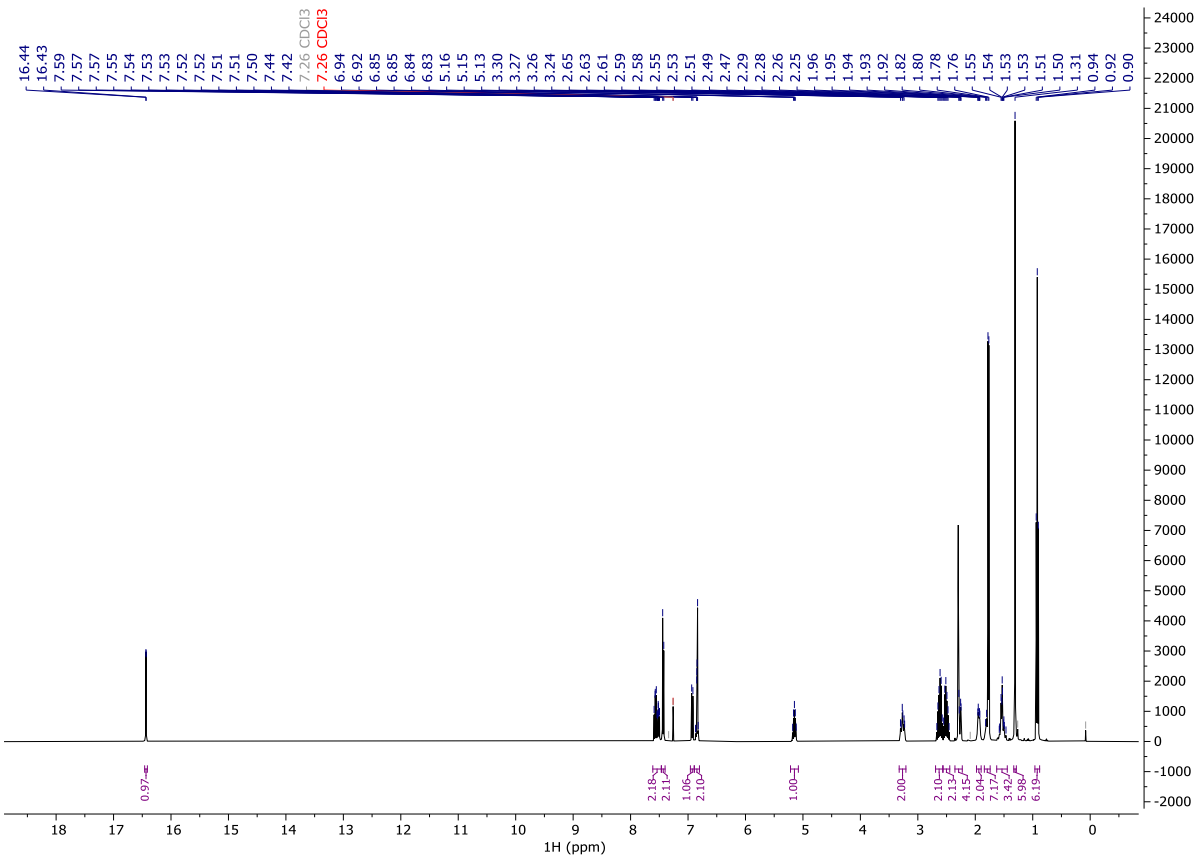
^{1}H NMR of **Ru-3a** (400 MHz, $CDCl_3$):



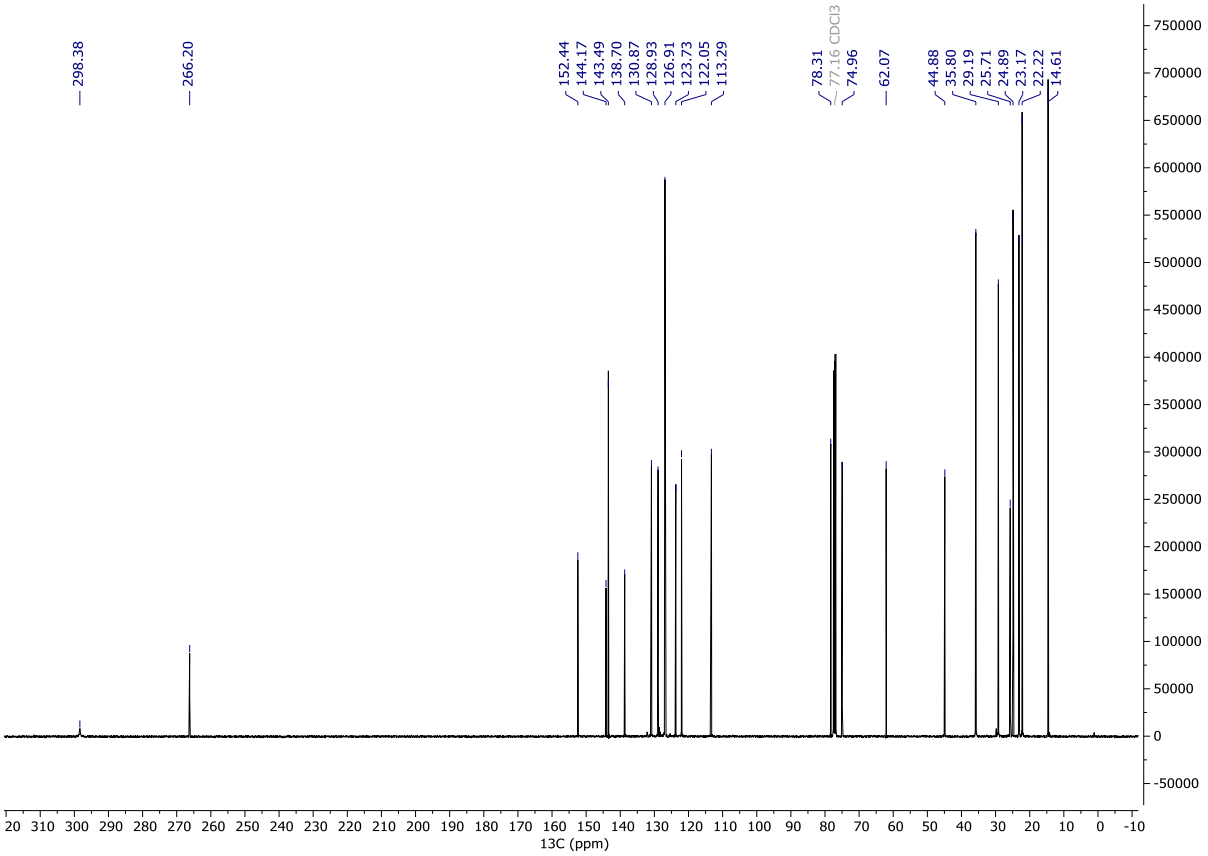
^{13}C NMR of **Ru-3a** (101 MHz, $CDCl_3$):



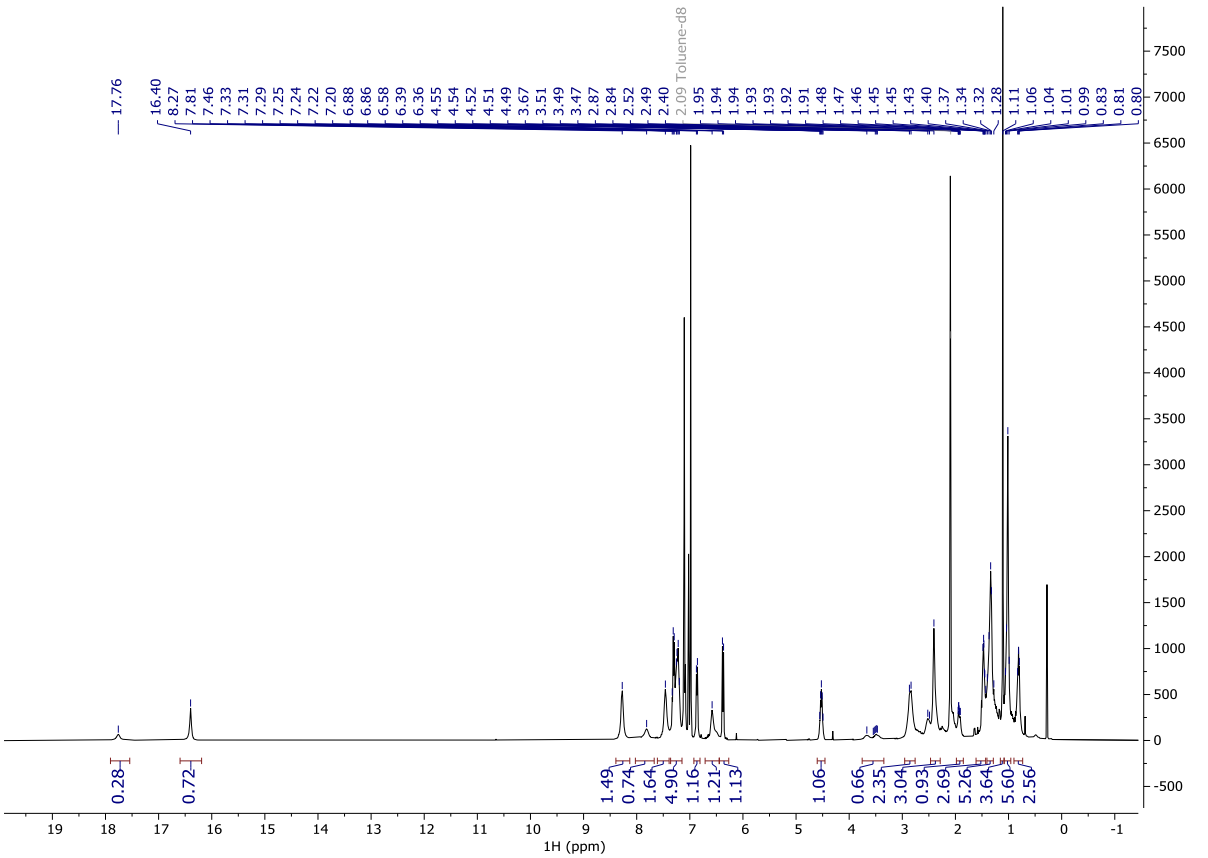
^{1}H NMR of **Ru-3b** (400 MHz, $CDCl_3$):



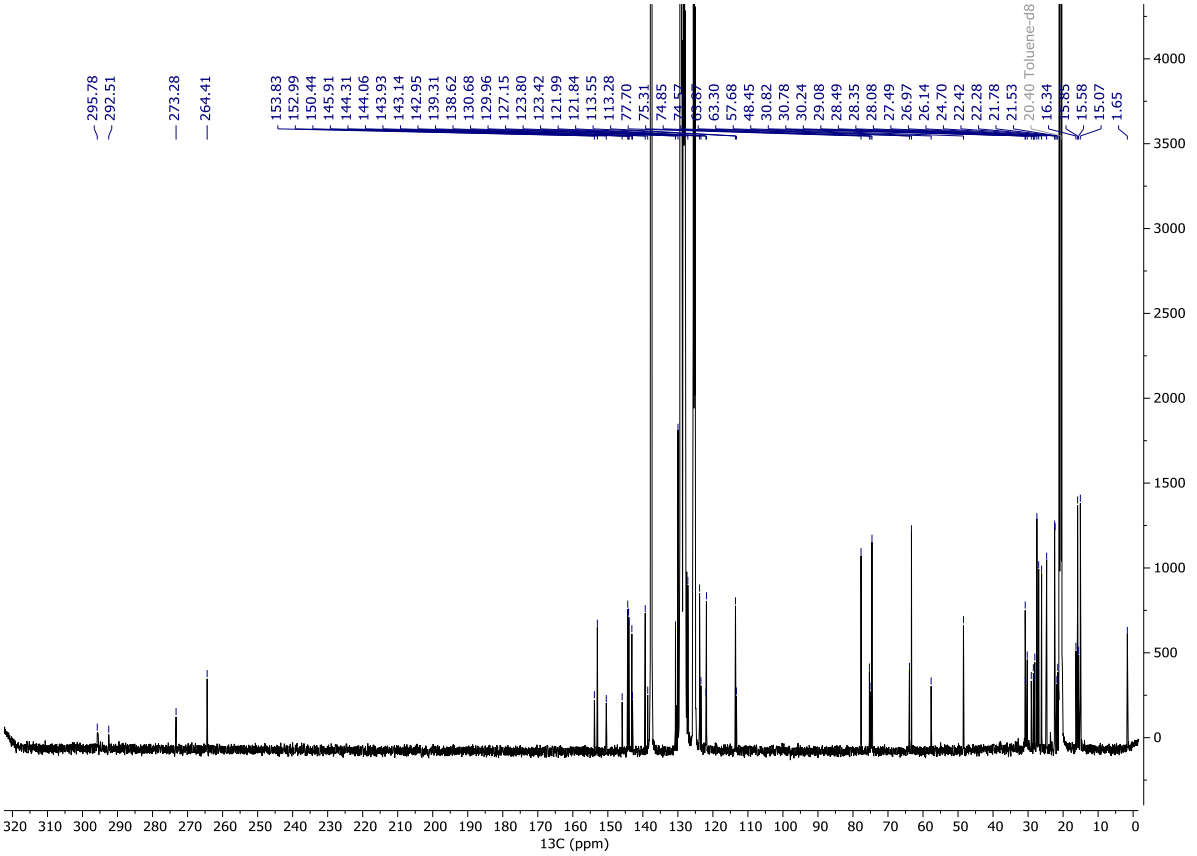
^{13}C NMR of **Ru-3b** (101 MHz, $CDCl_3$):



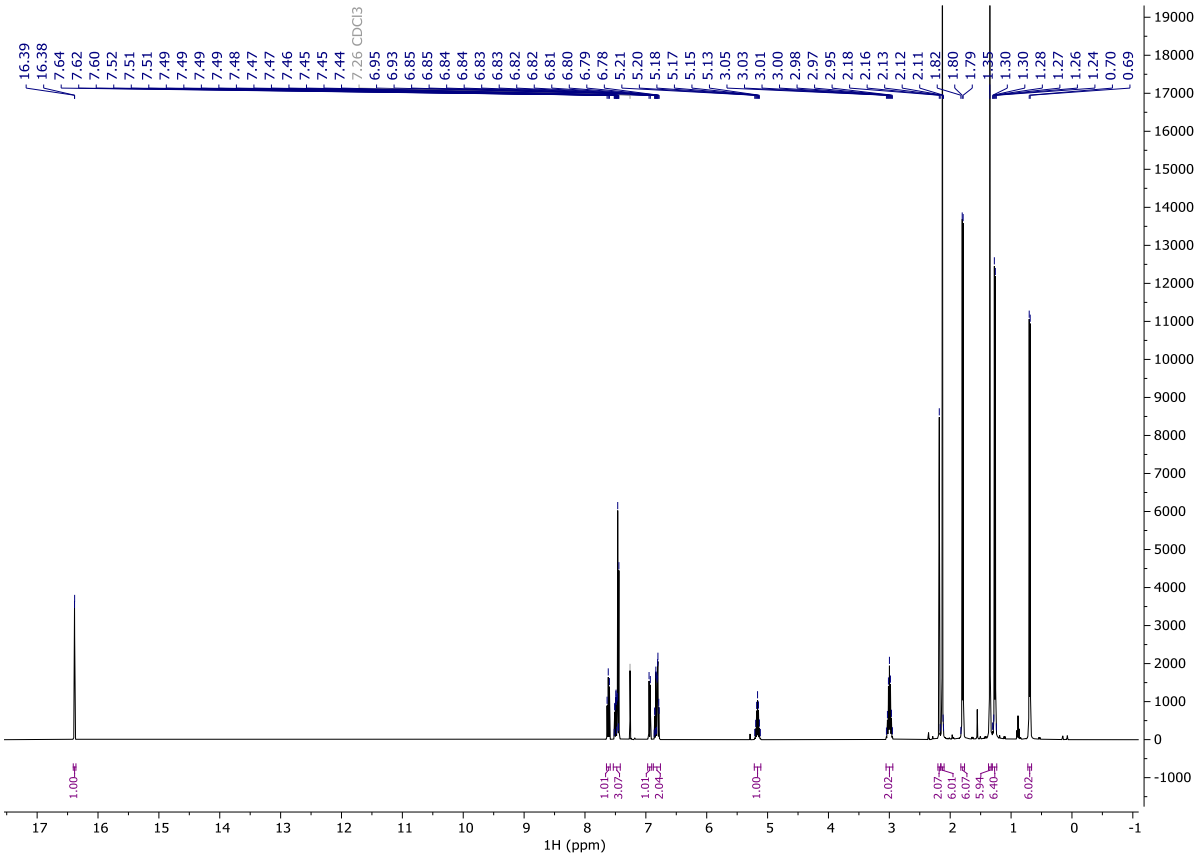
^{1}H NMR (400 MHz, *Tol-D_8*) of **Ru-3c**:



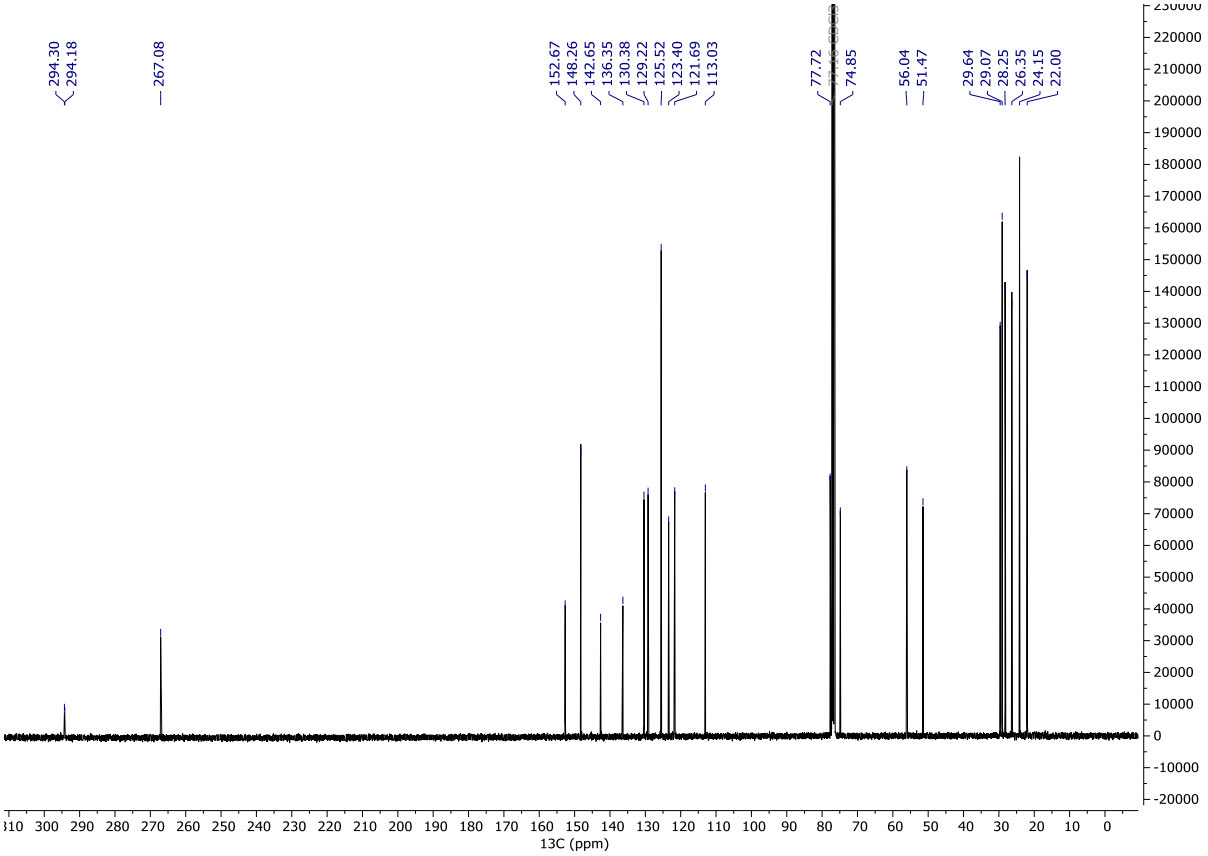
^{13}C NMR (125 MHz, *Tol-D_8*) of **Ru-3c** at -20°C:



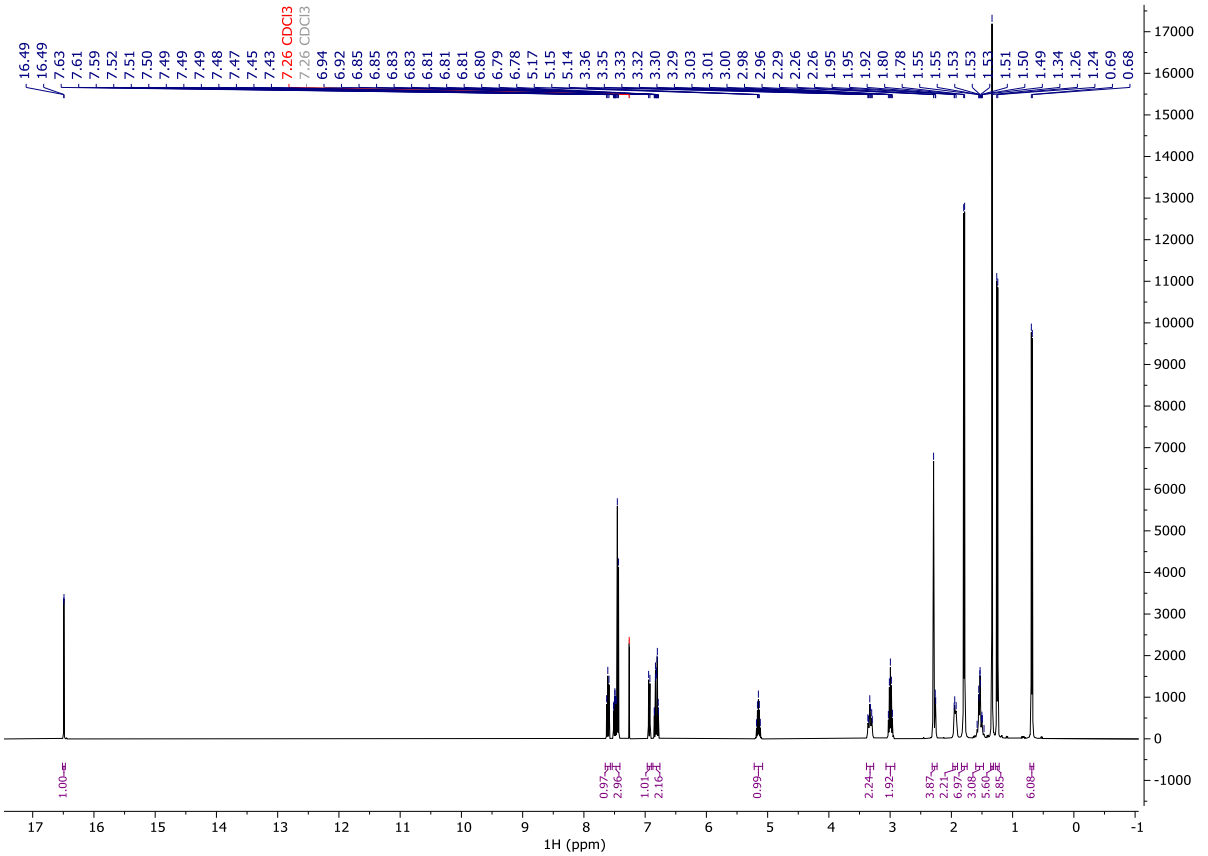
^{1}H NMR of **Ru-3d** (400 MHz, $CDCl_3$):



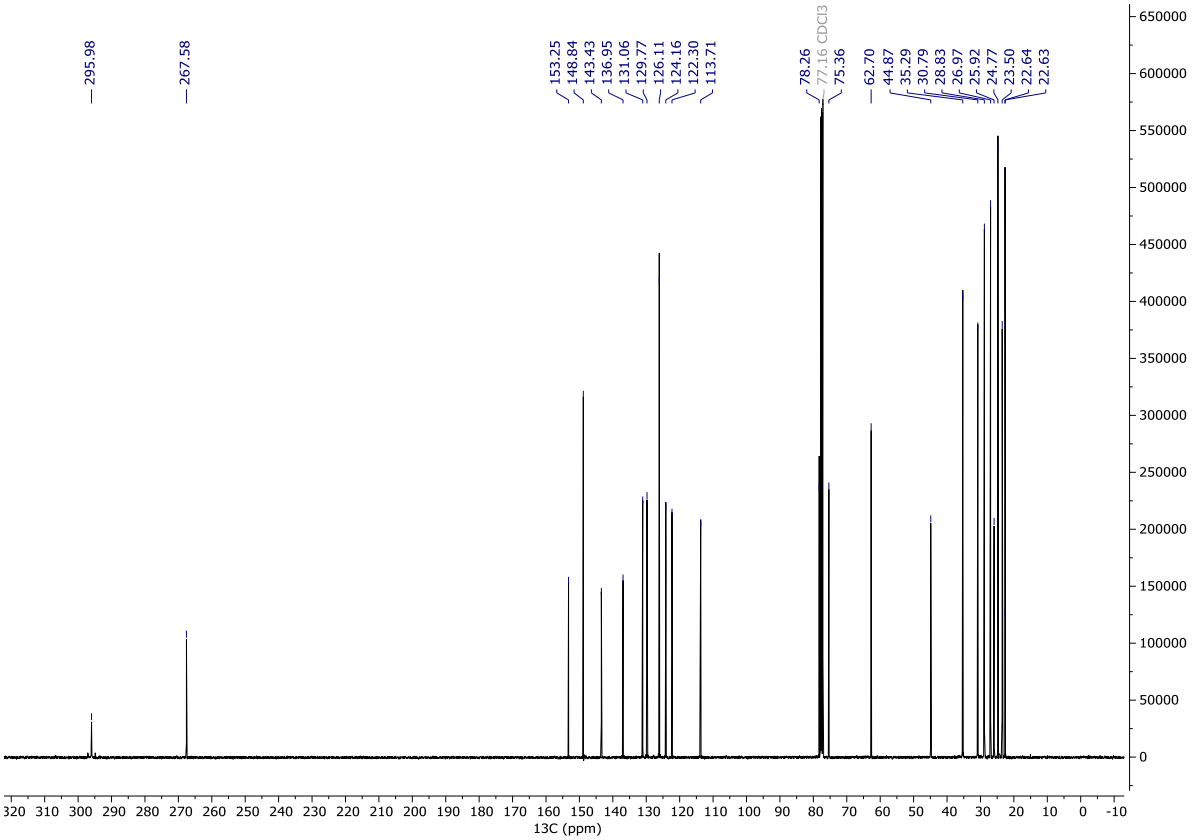
^{13}C NMR of **Ru-3d** (101 MHz, $CDCl_3$):



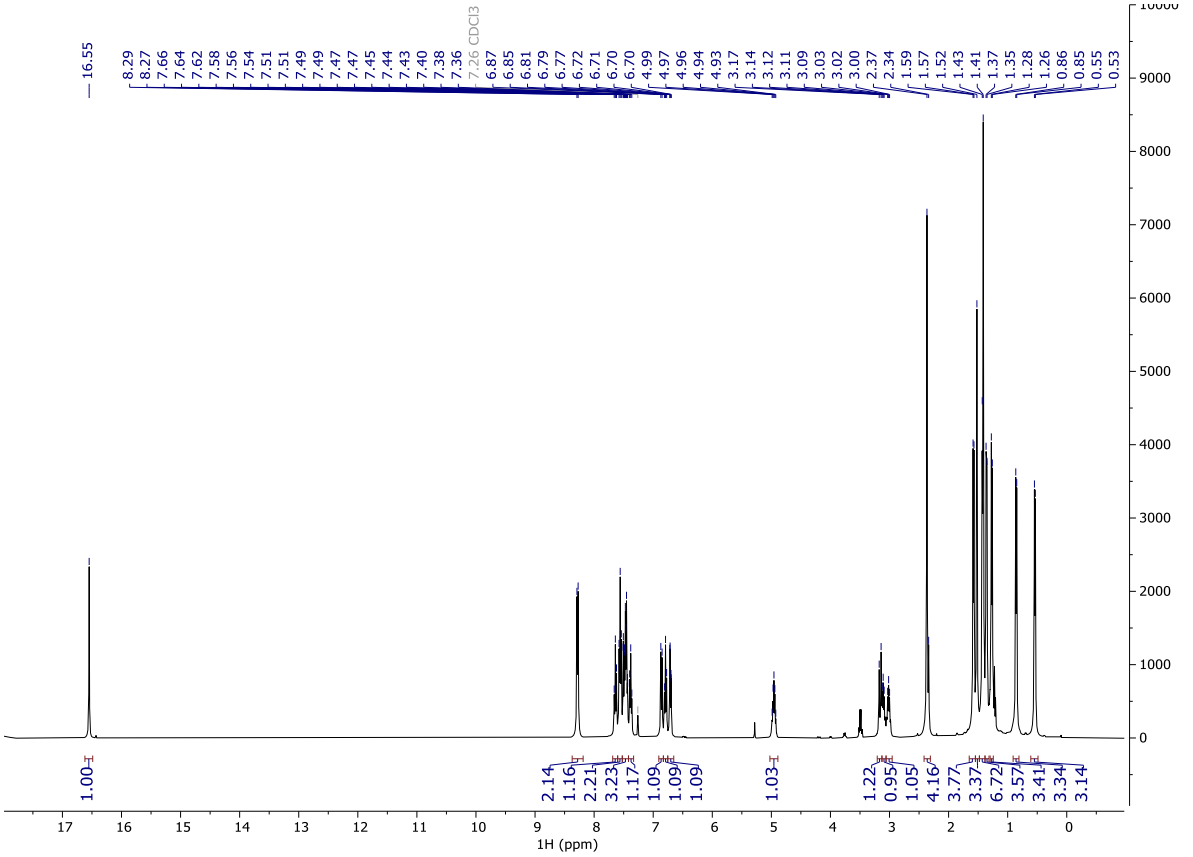
^{1}H NMR of **Ru-3e** (400 MHz, $CDCl_3$):



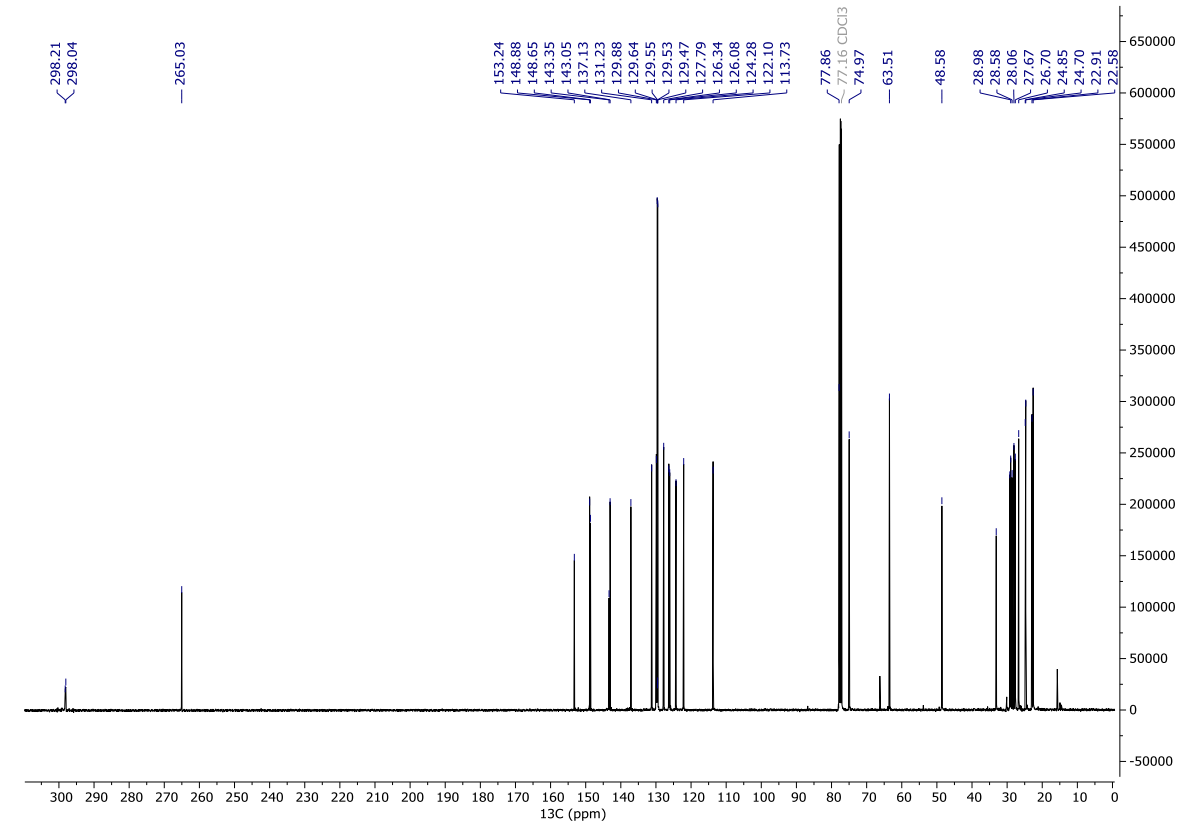
^{13}C NMR of **Ru-3e** (101 MHz, $CDCl_3$):



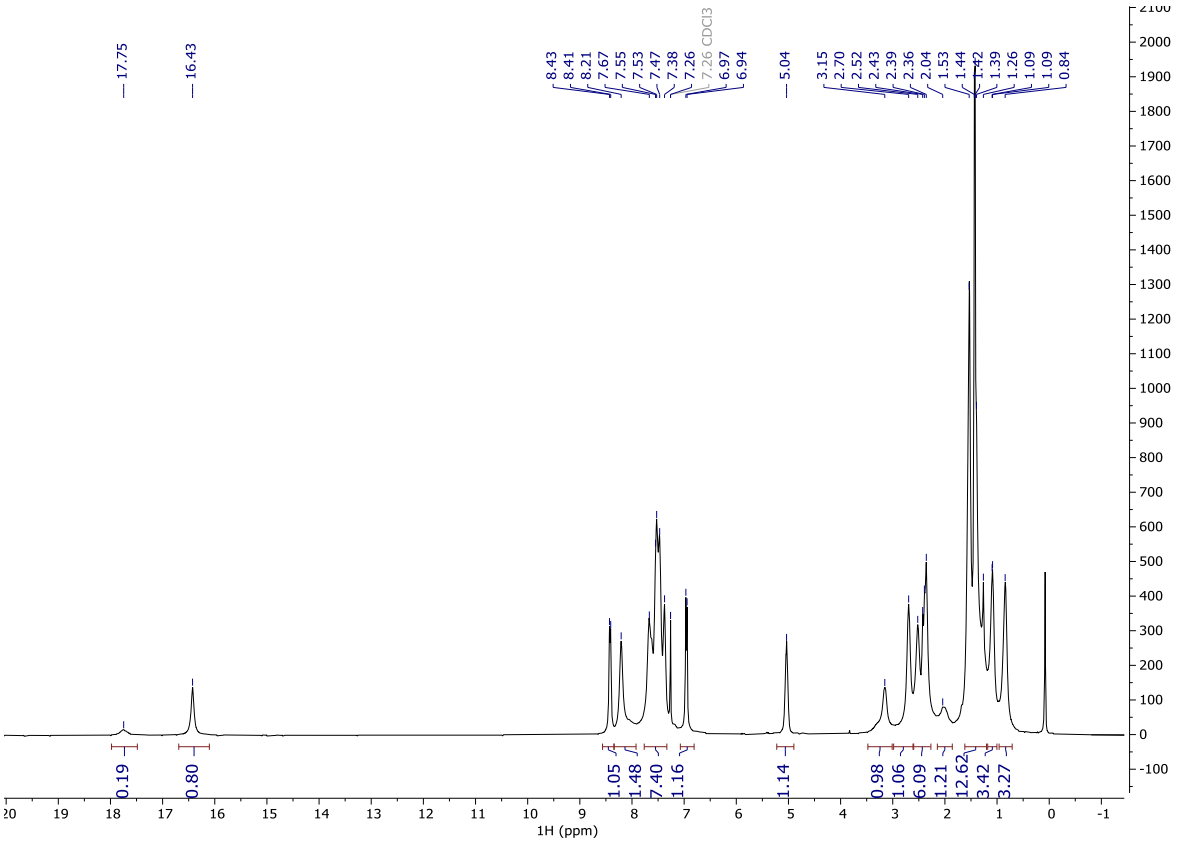
^{1}H NMR of **Ru-3f** (400 MHz, $CDCl_3$):



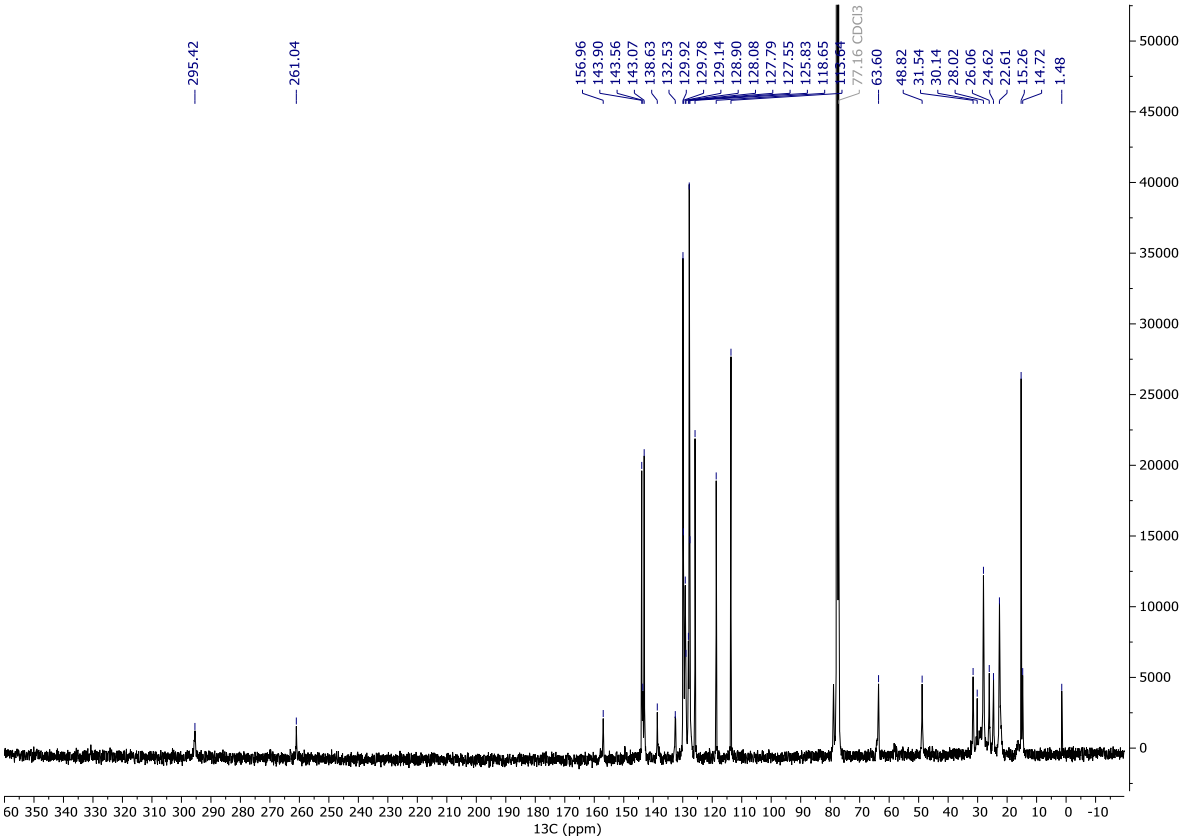
^{13}C NMR of **Ru-3f** (101 MHz, $CDCl_3$):



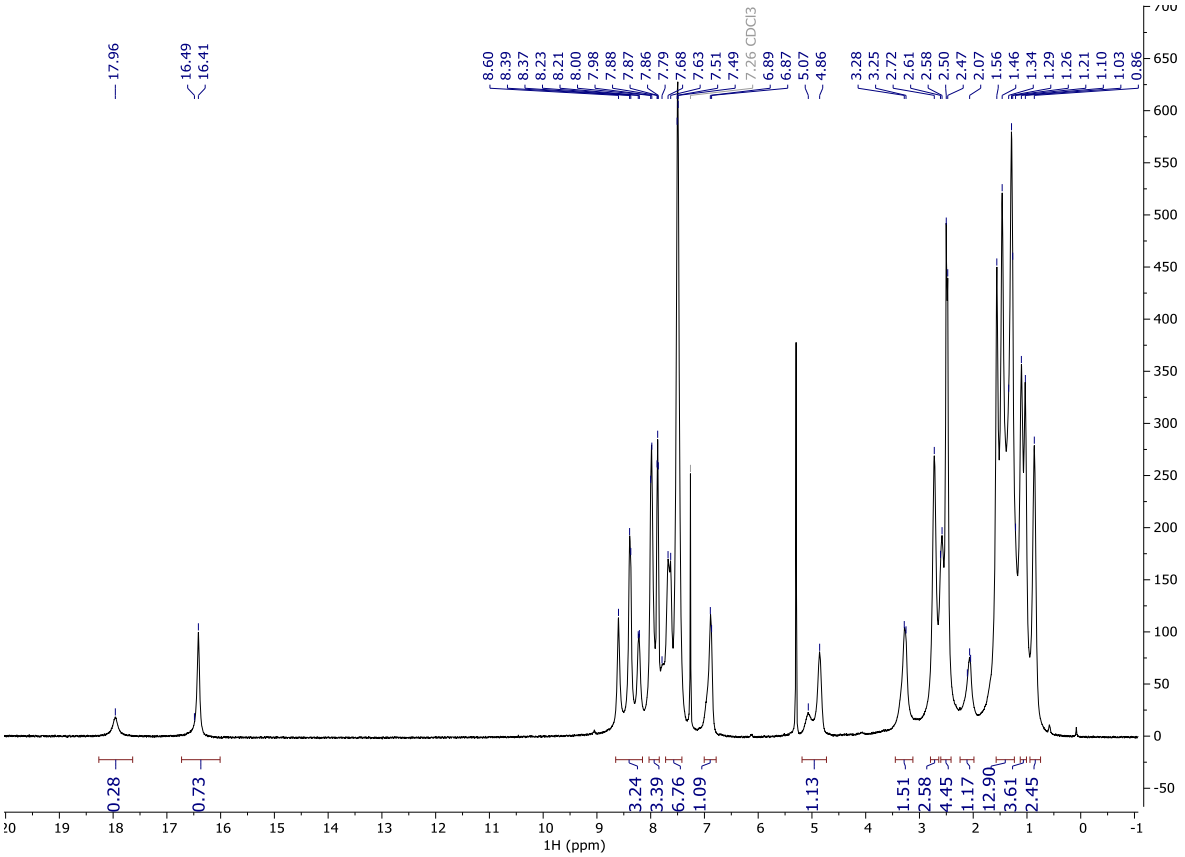
^{1}H NMR of **Ru-3g** (400 MHz, $CDCl_3$), 2 rotamers at 20°C:



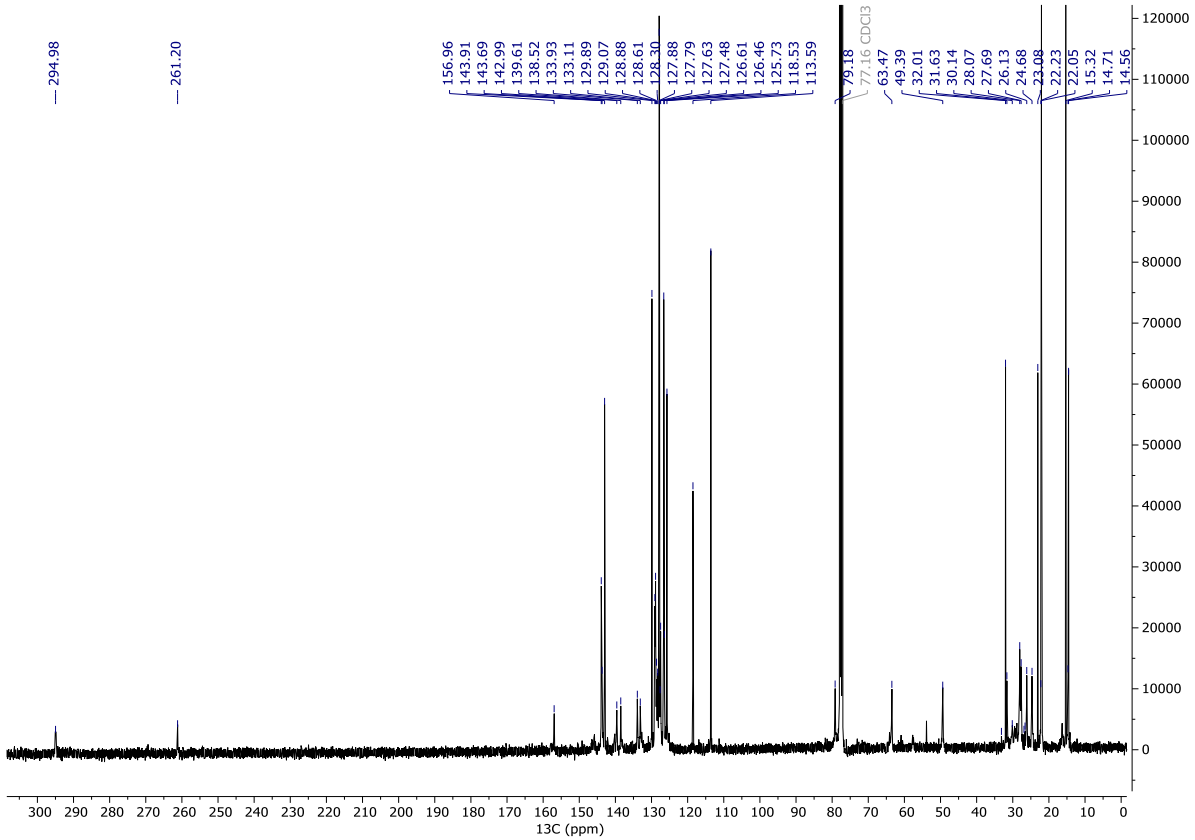
^{13}C NMR (101 MHz, *CDCl$_3$*) of **Ru-3g** 2 rotamers at 20°C:



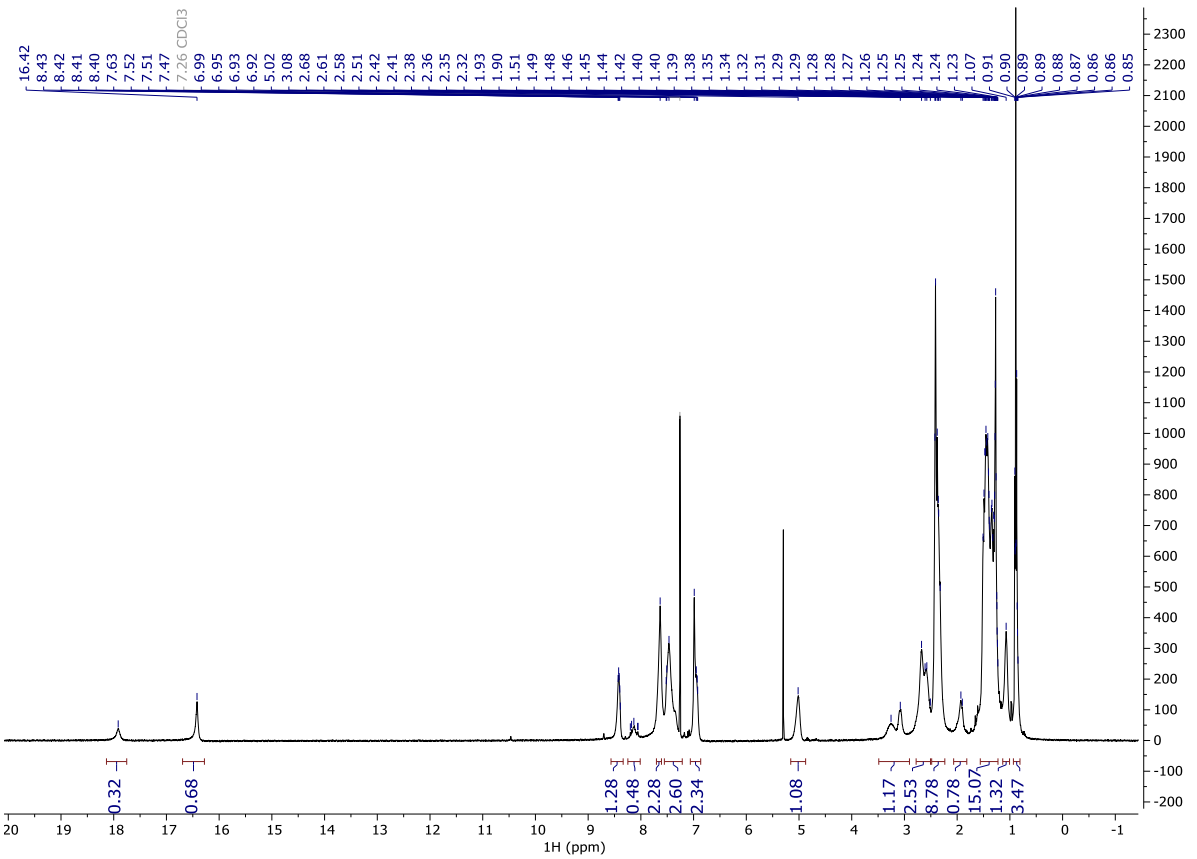
^{1}H NMR (400 MHz, *CDCl$_3$*) of **Ru-3h** 2 rotamers at 20°C:



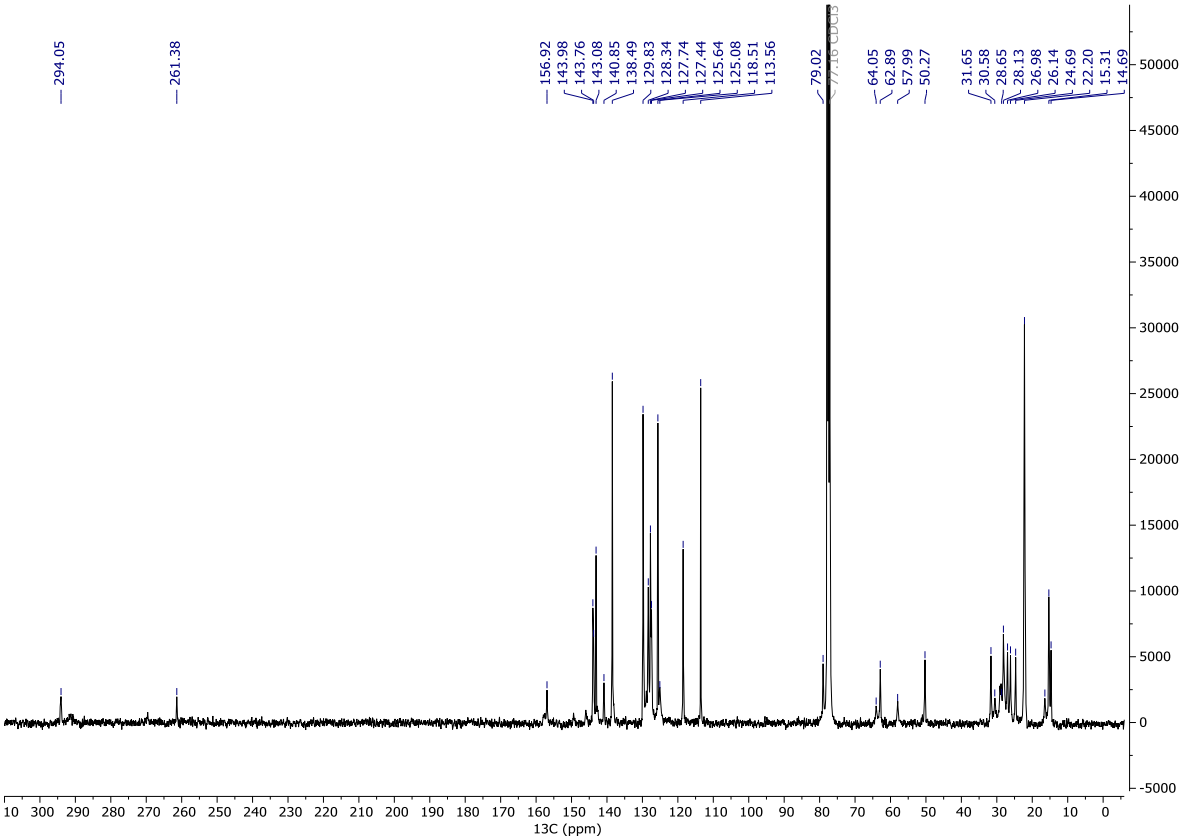
^{13}C NMR (101 MHz, *CDCl$_3$*) of **Ru-3h**, 2 rotamers at 20°C:



^{1}H NMR (400 MHz, *CDCl$_3$*) of **Ru-3i,** 2 rotamers at 20°C:

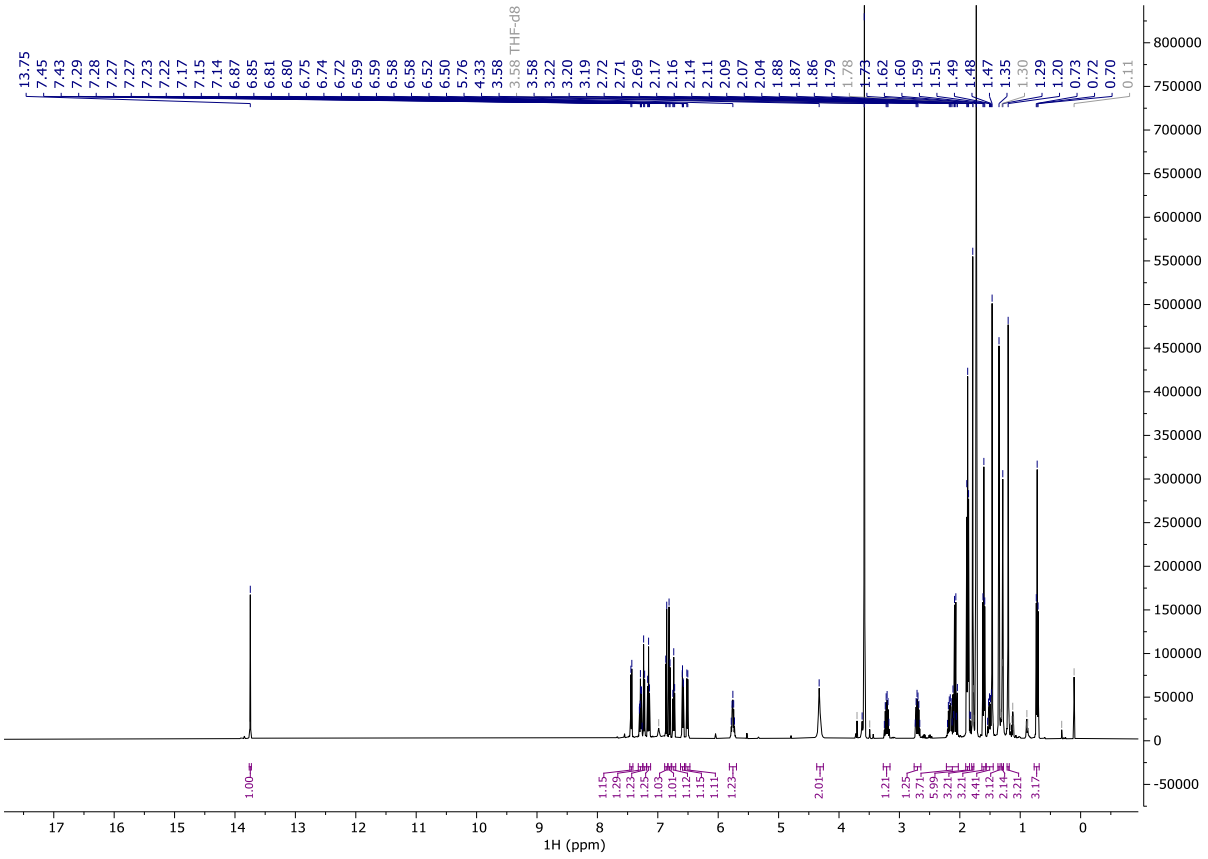


^{13}C NMR (101 MHz, *CDCl$_3$*) of **Ru-3i,** 2 rotamers at 20°C:

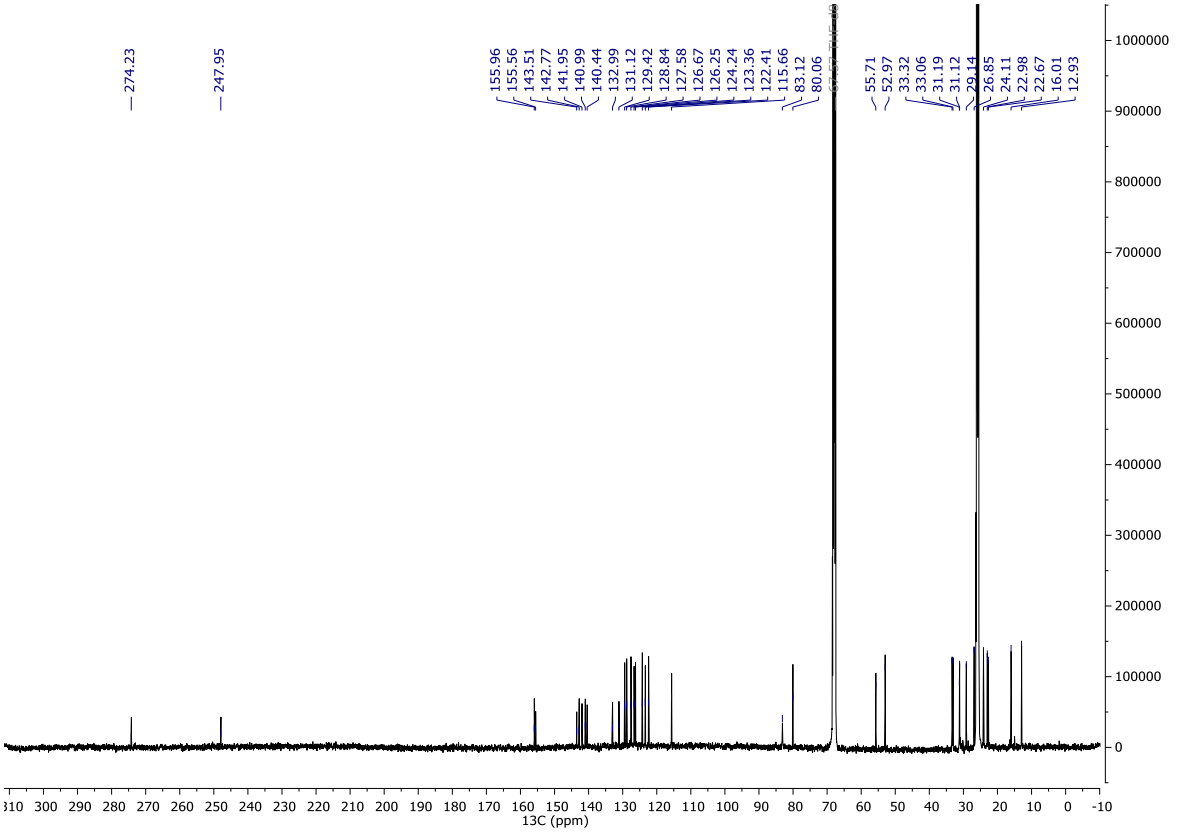


10.3. NMR of Ru-4 complexes

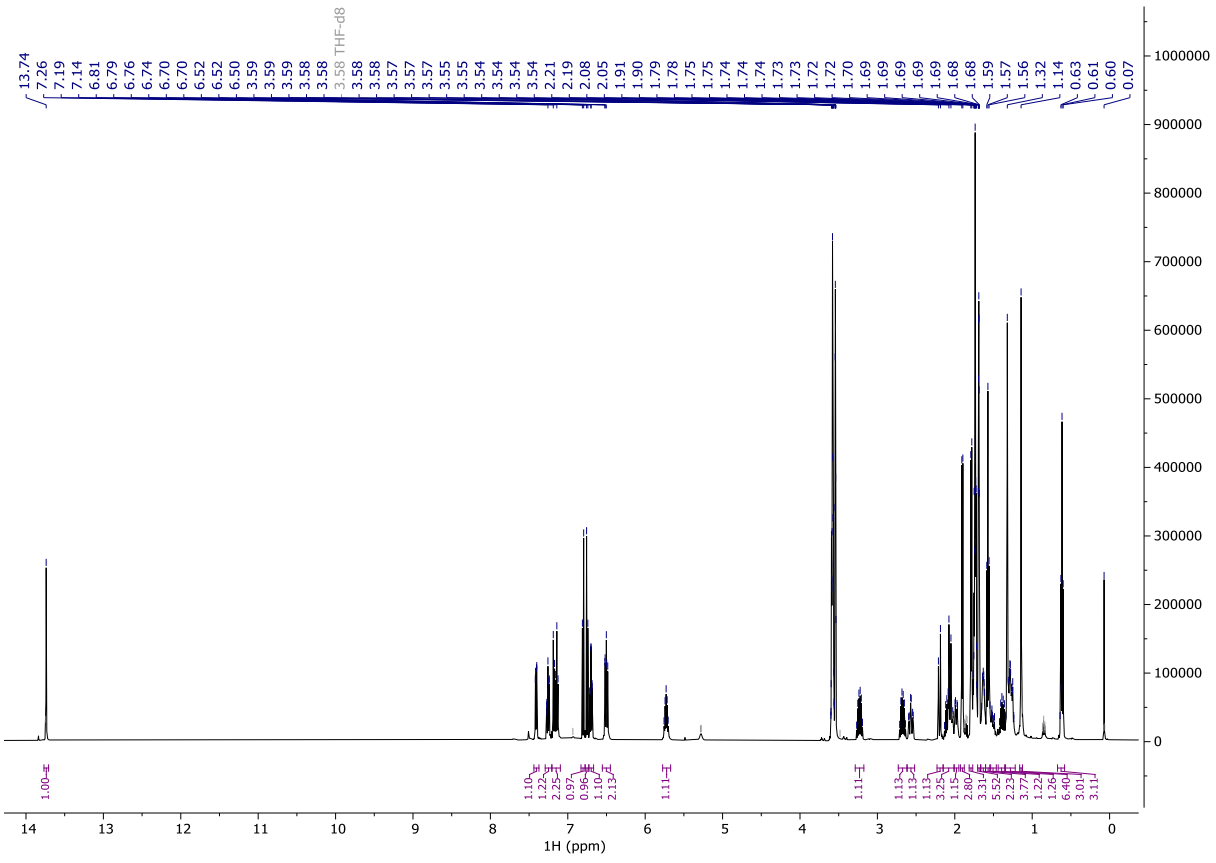
^{1}H NMR (500 MHz, *THF-D$_8$*) of **Ru-4a** at 15 °C**:**



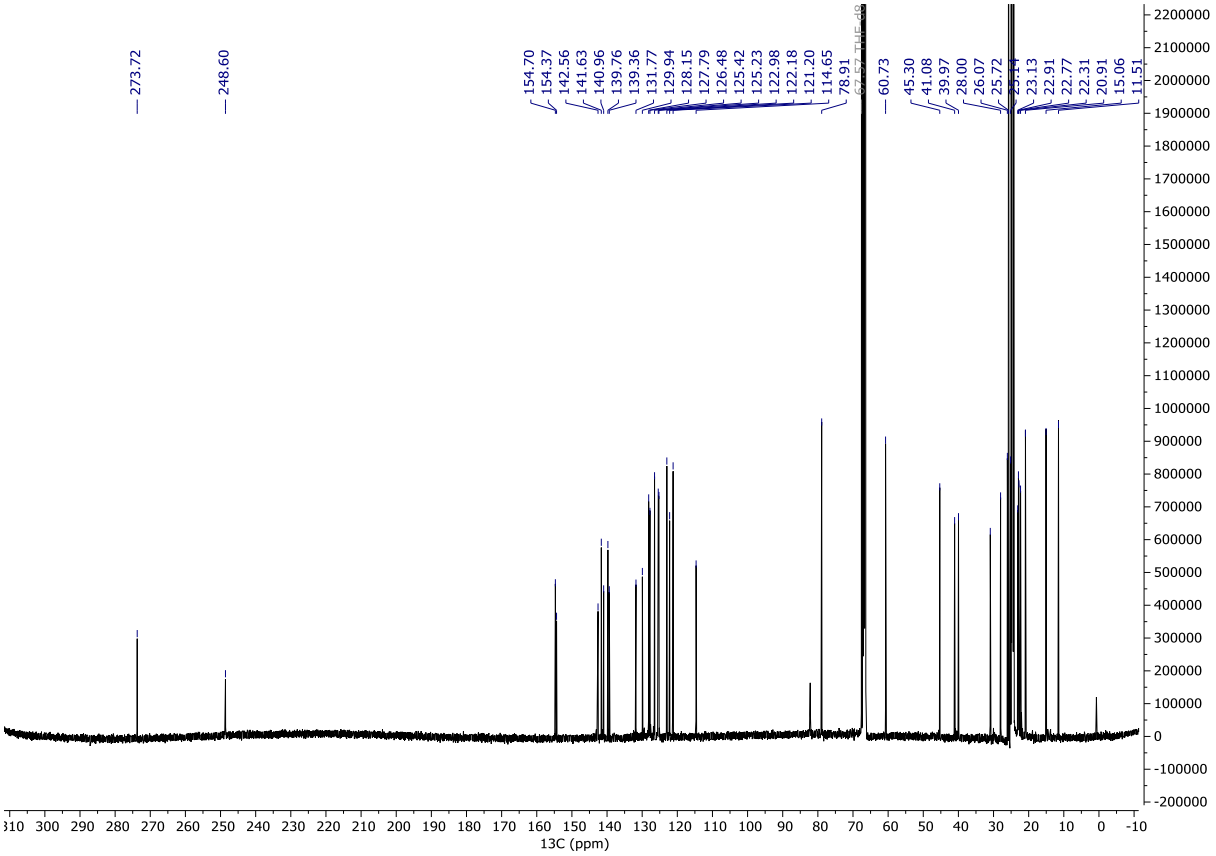
^{13}C NMR (125 MHz, *THF-D$_8$*) of **Ru-4a** at 15 °C**:**



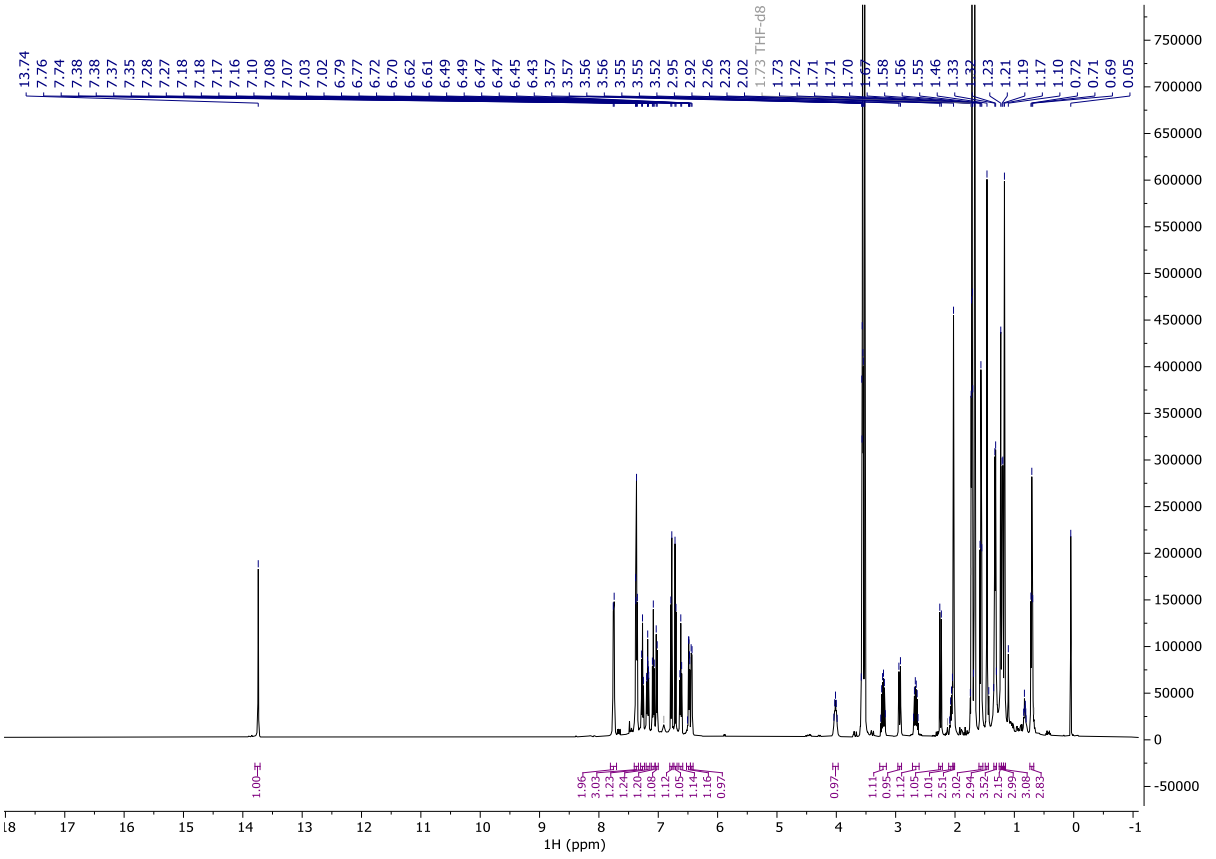
^{1}H NMR (500 MHz, *THF-D$_8$*) of **Ru-4b** at 15 °C**:**



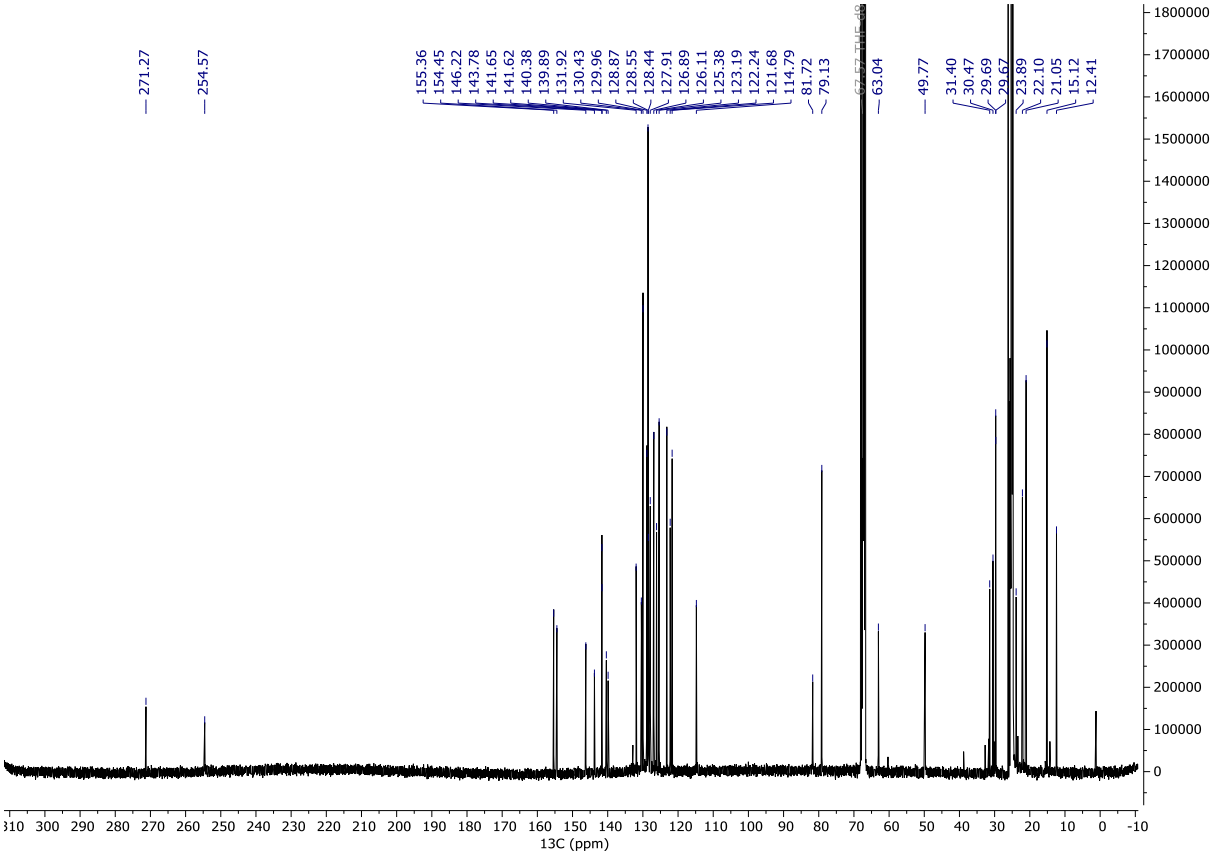
^{13}C NMR (125 MHz, *THF-D$_8$*) of **Ru-4b** at 15 °C**:**



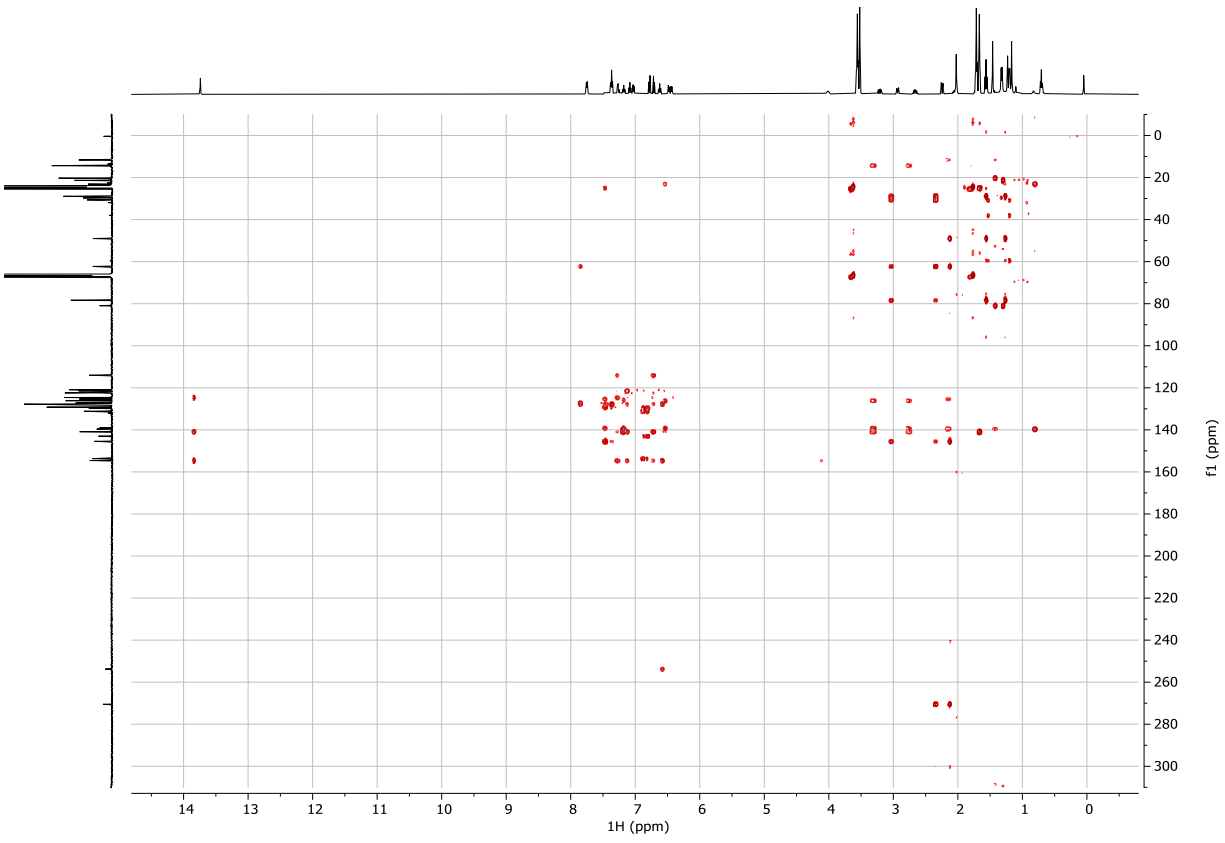
^{1}H NMR (500 MHz, *THF-D$_8$*) of **Ru-4c** at 15 °C**:**



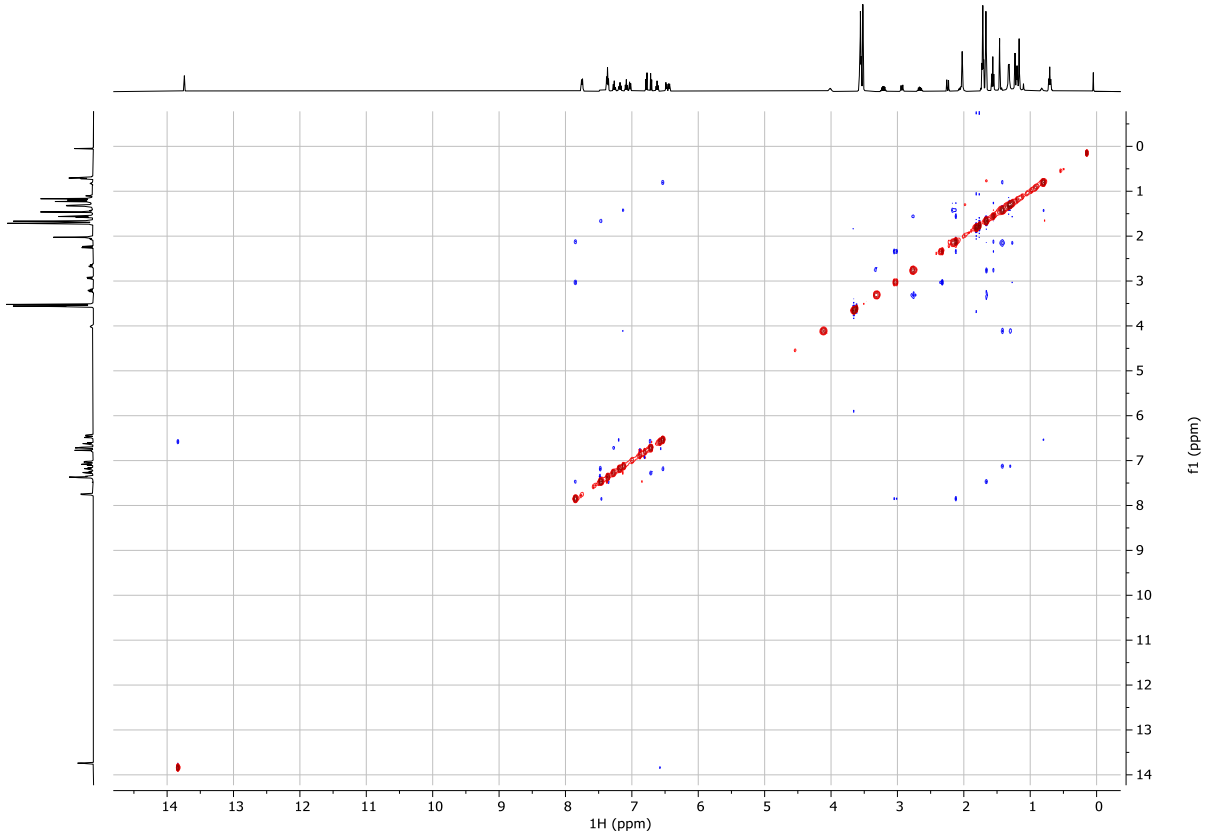
^{13}C NMR (125 MHz, *THF-D*$_8$) of **Ru-4c** at 15 °C**:**



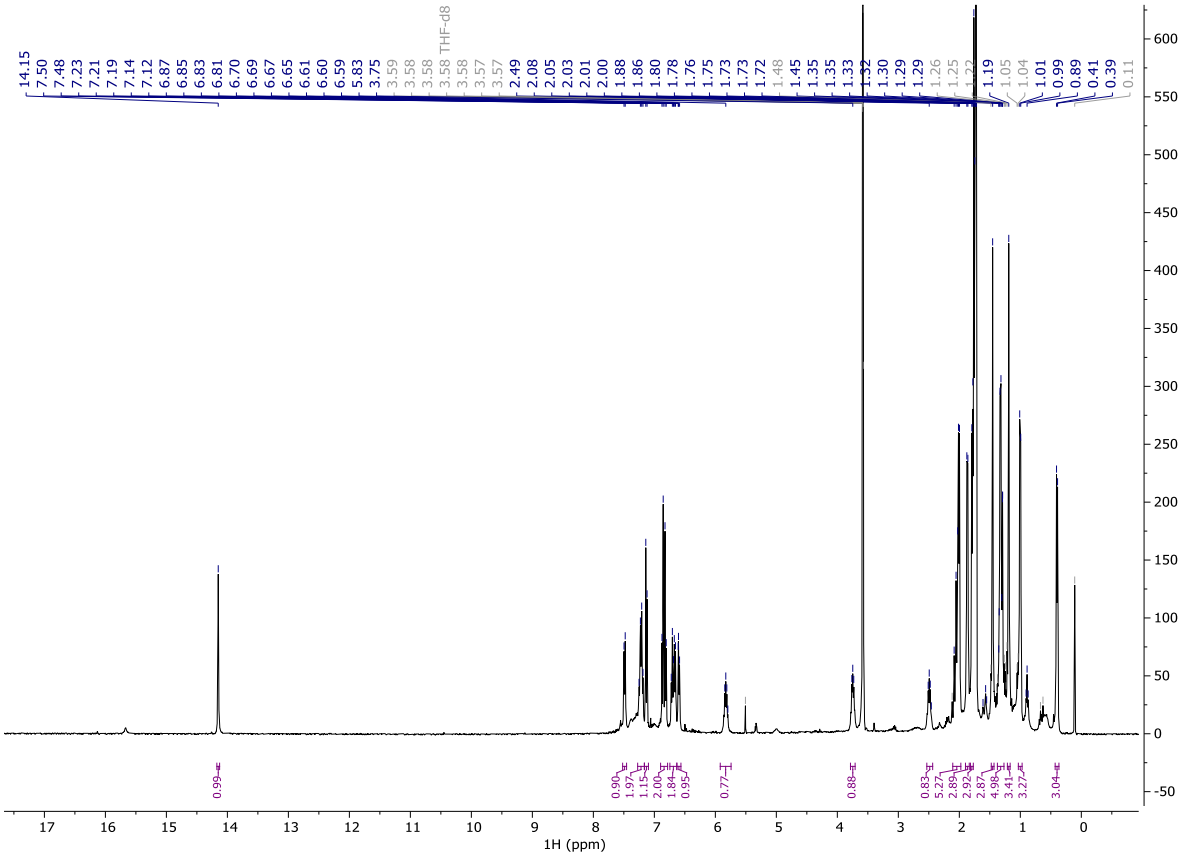
HSQC NMR (*THF-D*$_8$) of **Ru-4c** at 15 °C**:**



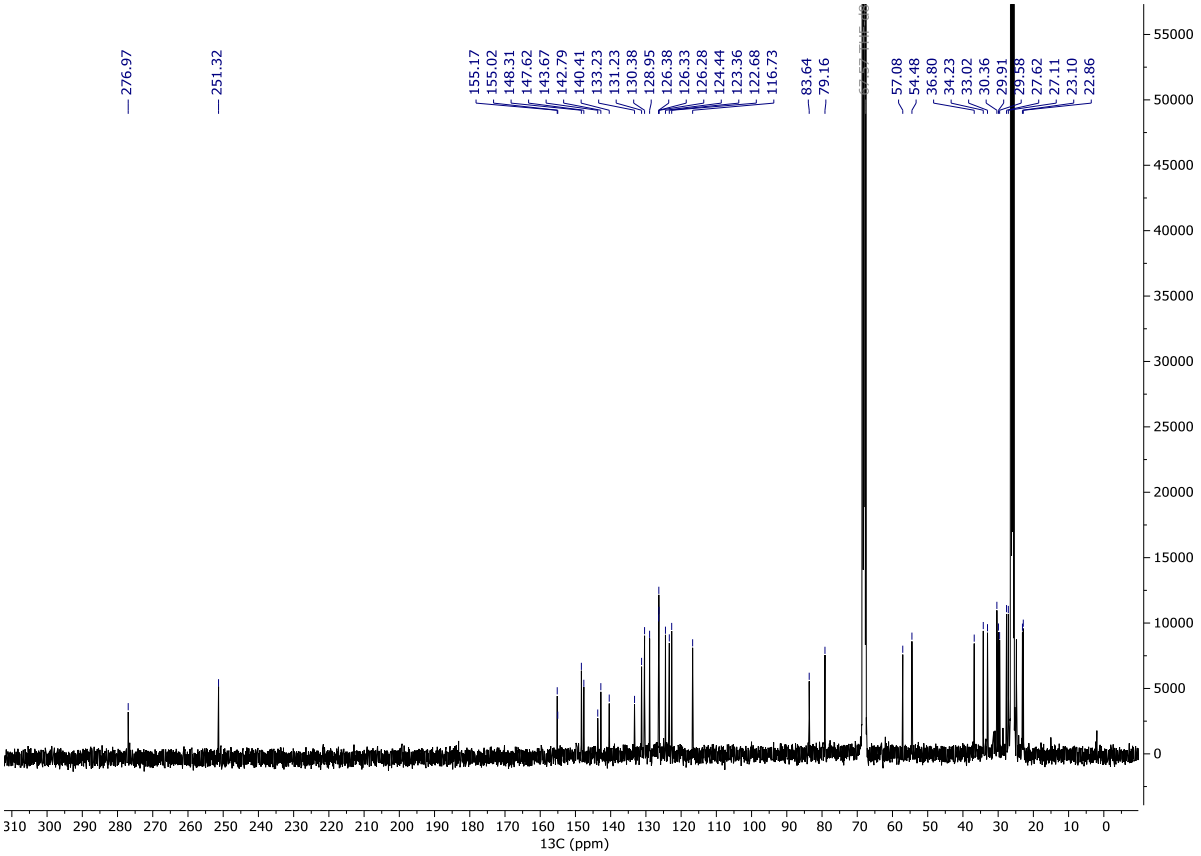
NOESY NMR (*THF-D*$_8$) of **Ru-4c** at 15 °C**:**



^{1}H NMR (400 MHz, *THF-D*$_8$) of **Ru-4d:**

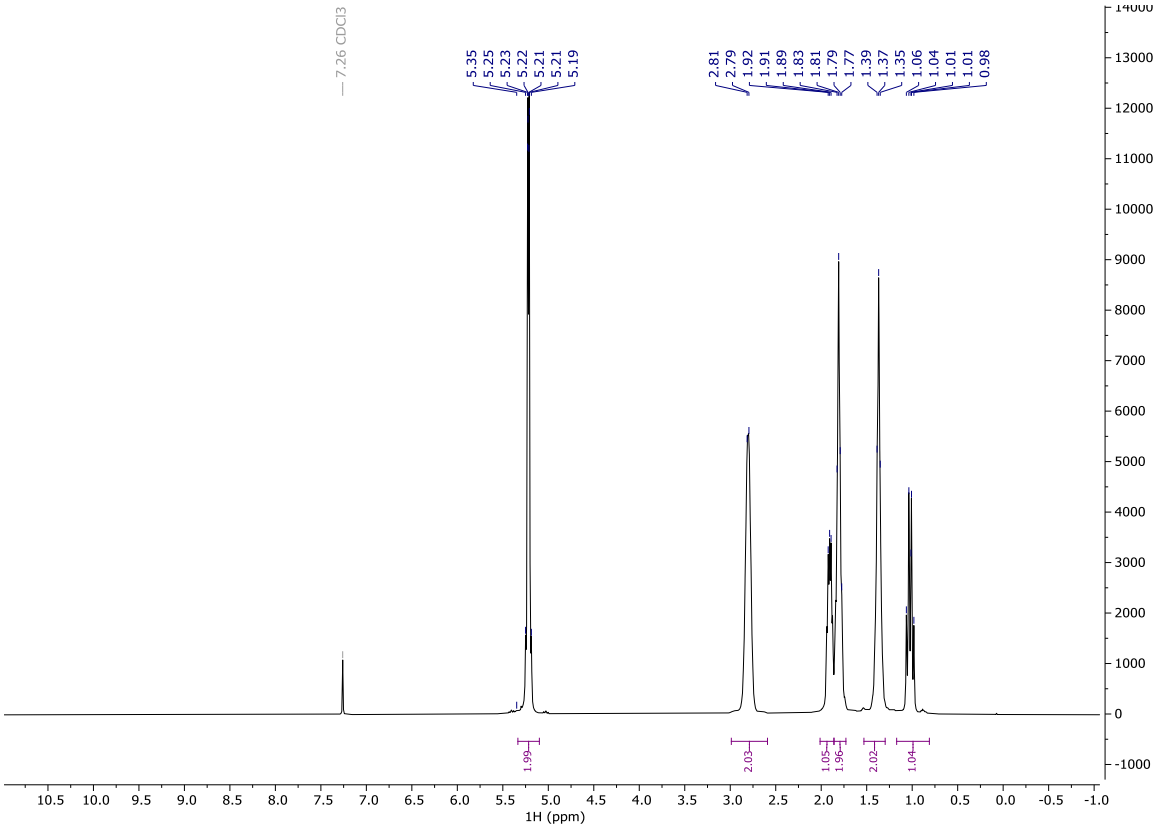


^{13}C NMR (101 MHz, *THF-D_8*) of **Ru-4d:**

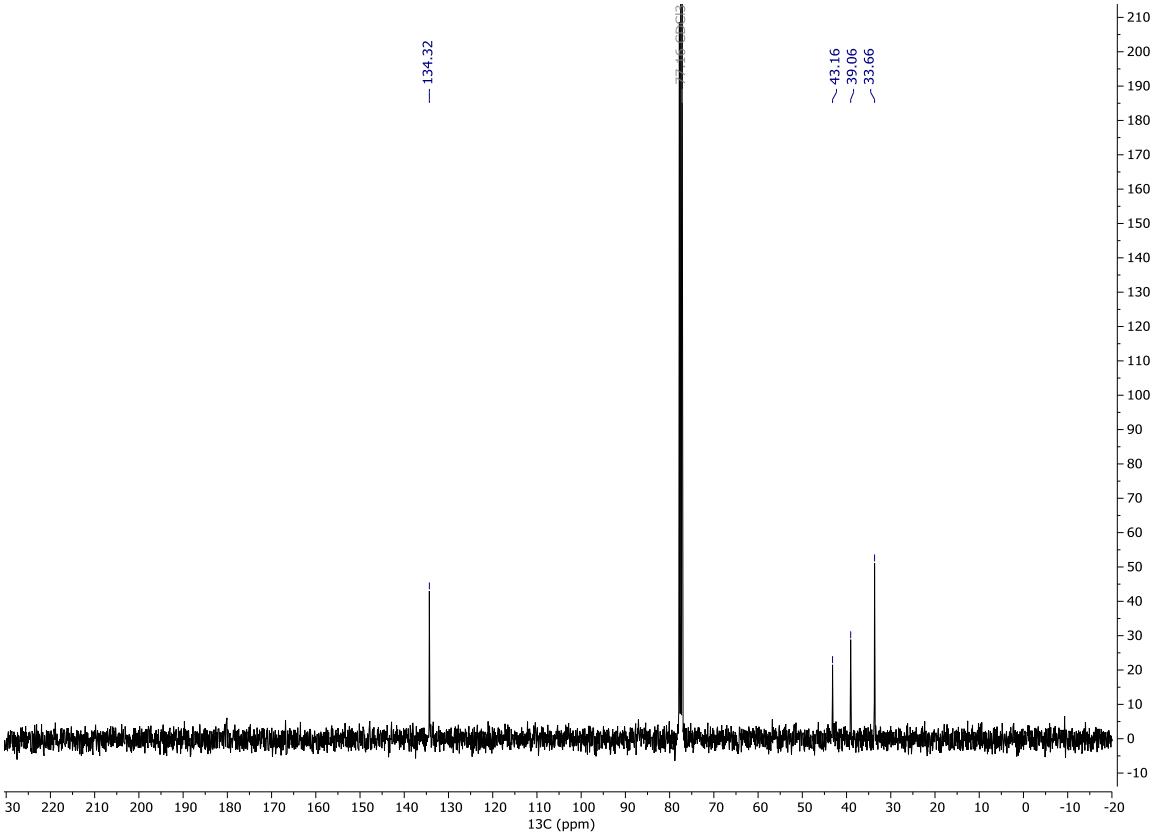


10.4. NMR of polymers

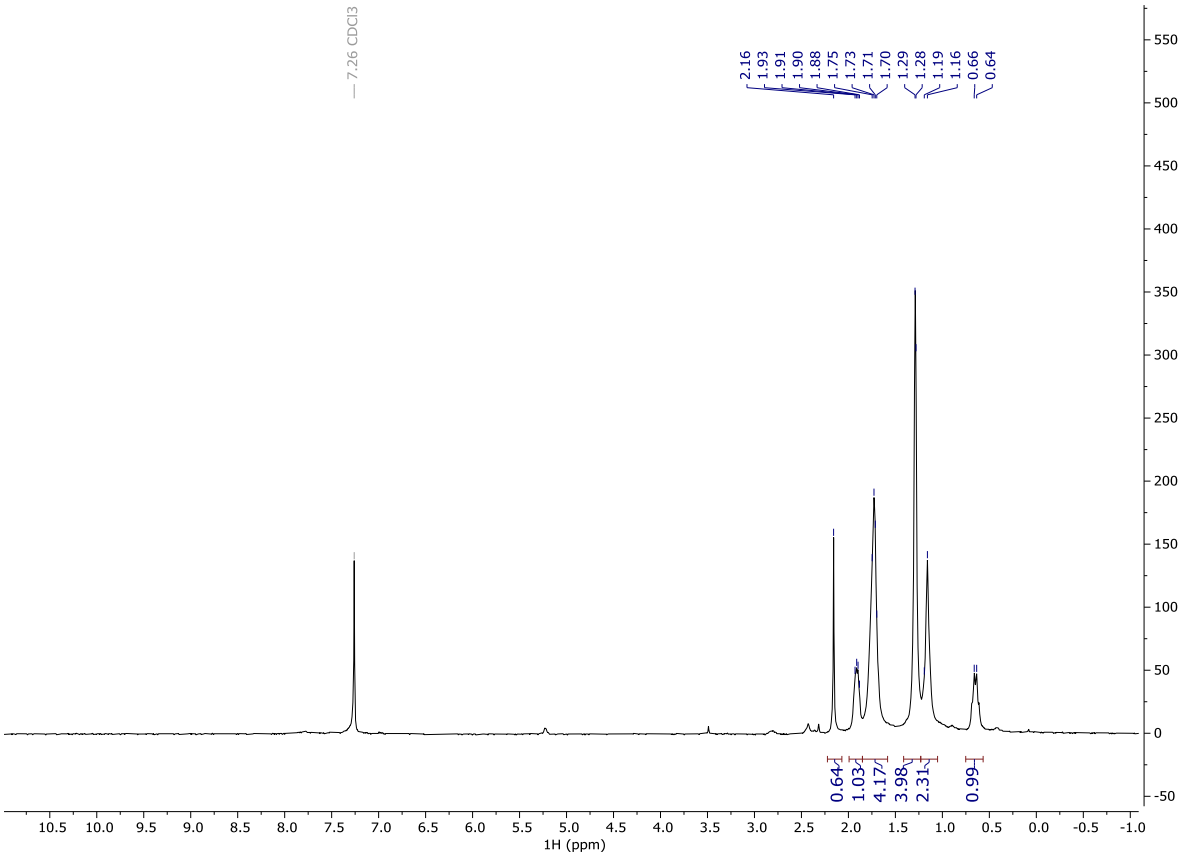
^{1}H NMR (400 MHz, *$CDCl_3$*) of **3a** obtained with **Ru-4d** (0.1 mol%):



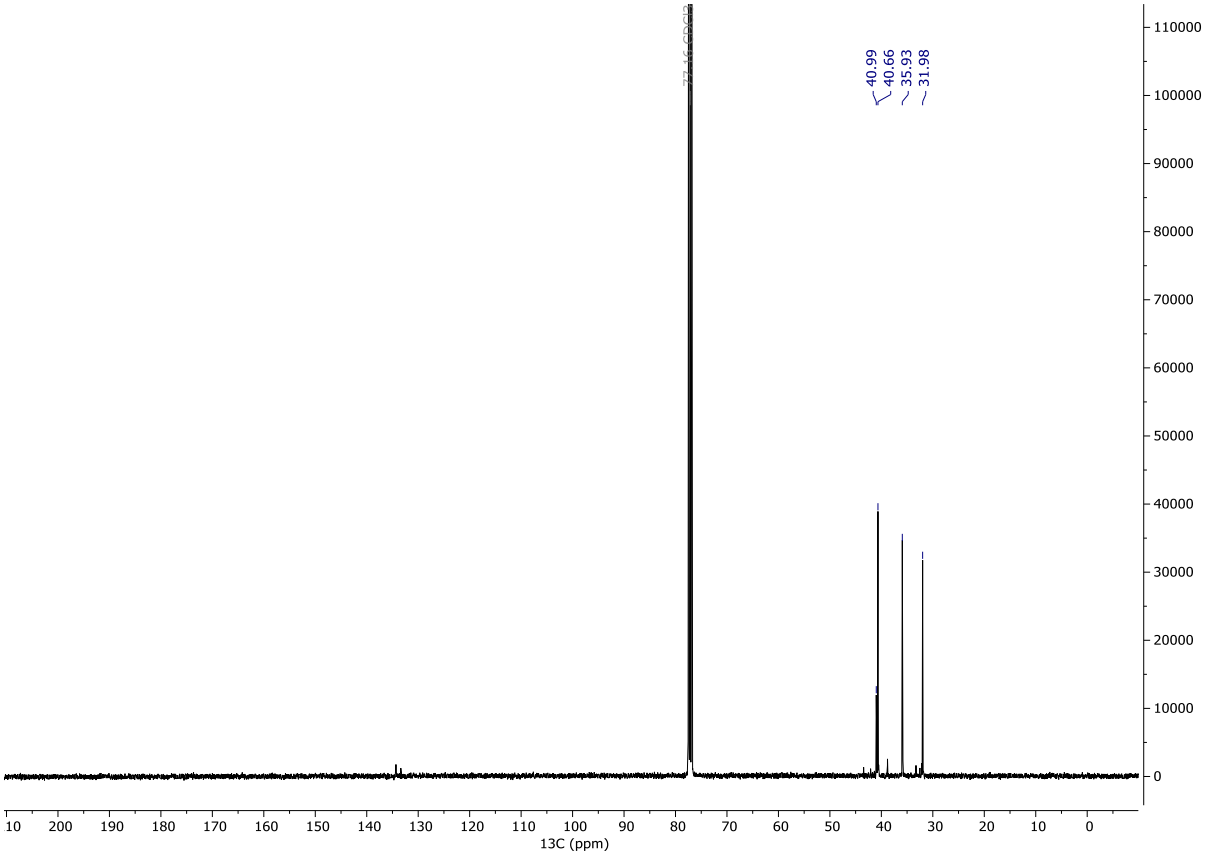
^{13}C NMR (101 MHz, *$CDCl_3$*) of **3a** obtained with **Ru-4d** (0.1 mol%):



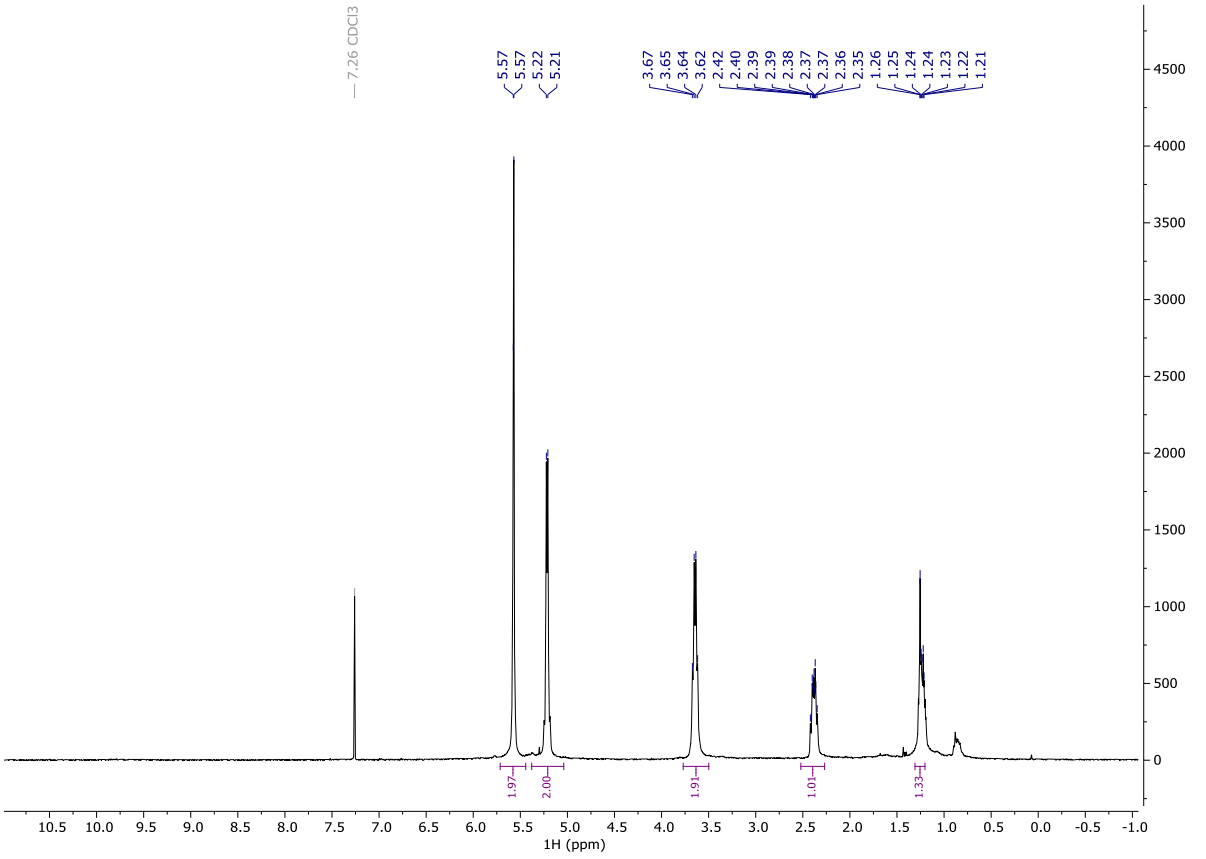
^{1}H NMR (400 MHz, *$CDCl_3$*) of H_2-**3a** at 55 °C:



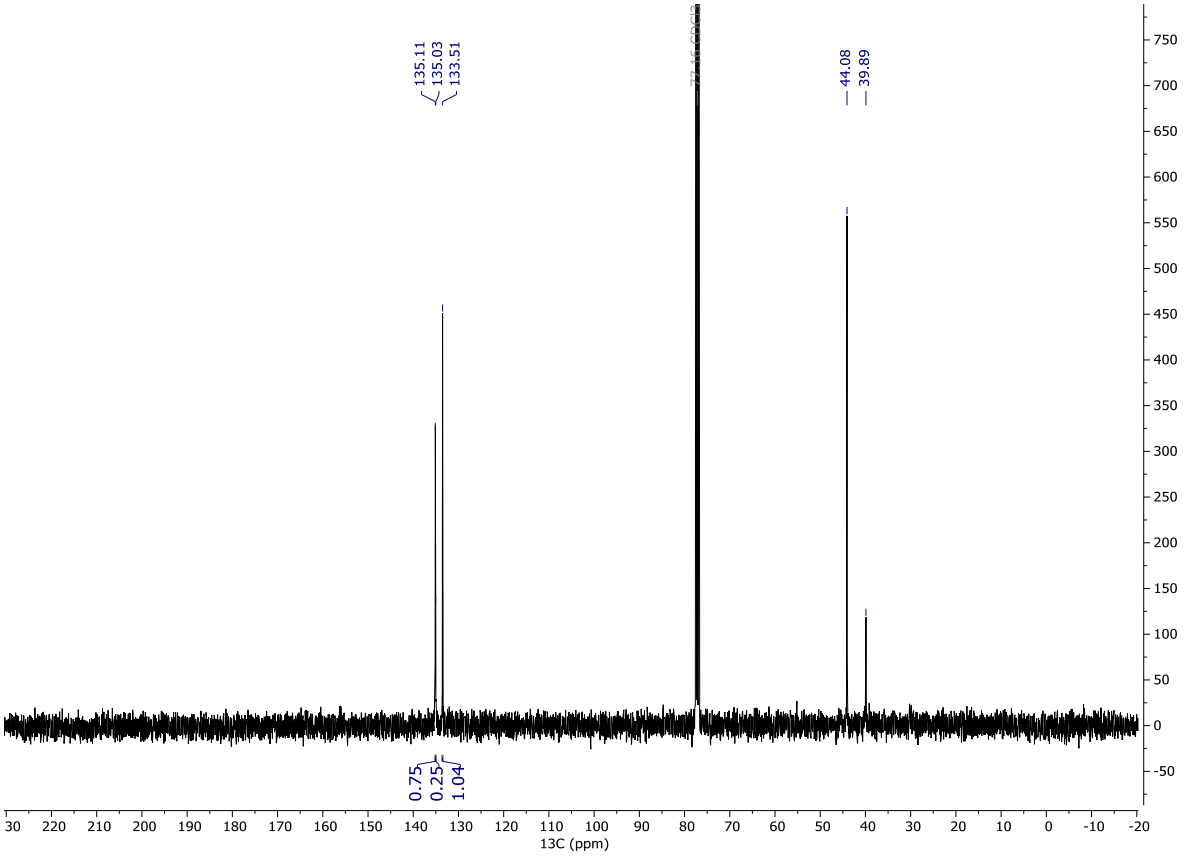
^{13}C NMR (101 MHz, *CDCl$_3$*) of H$_2$-**3a** at 55 °C:



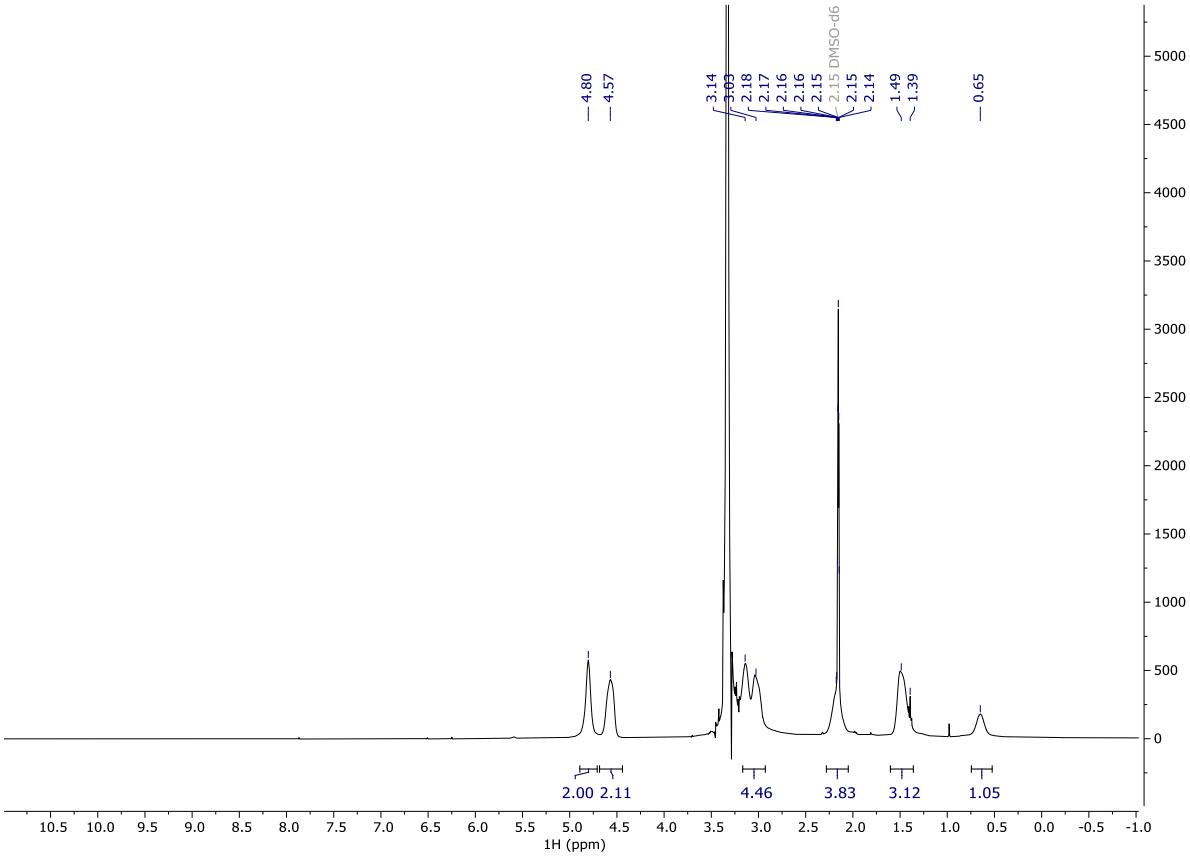
^{1}H NMR (400 MHz, *CDCl$_3$*) of **3b** obtained with **Ru-4d** (0.1 mol%):



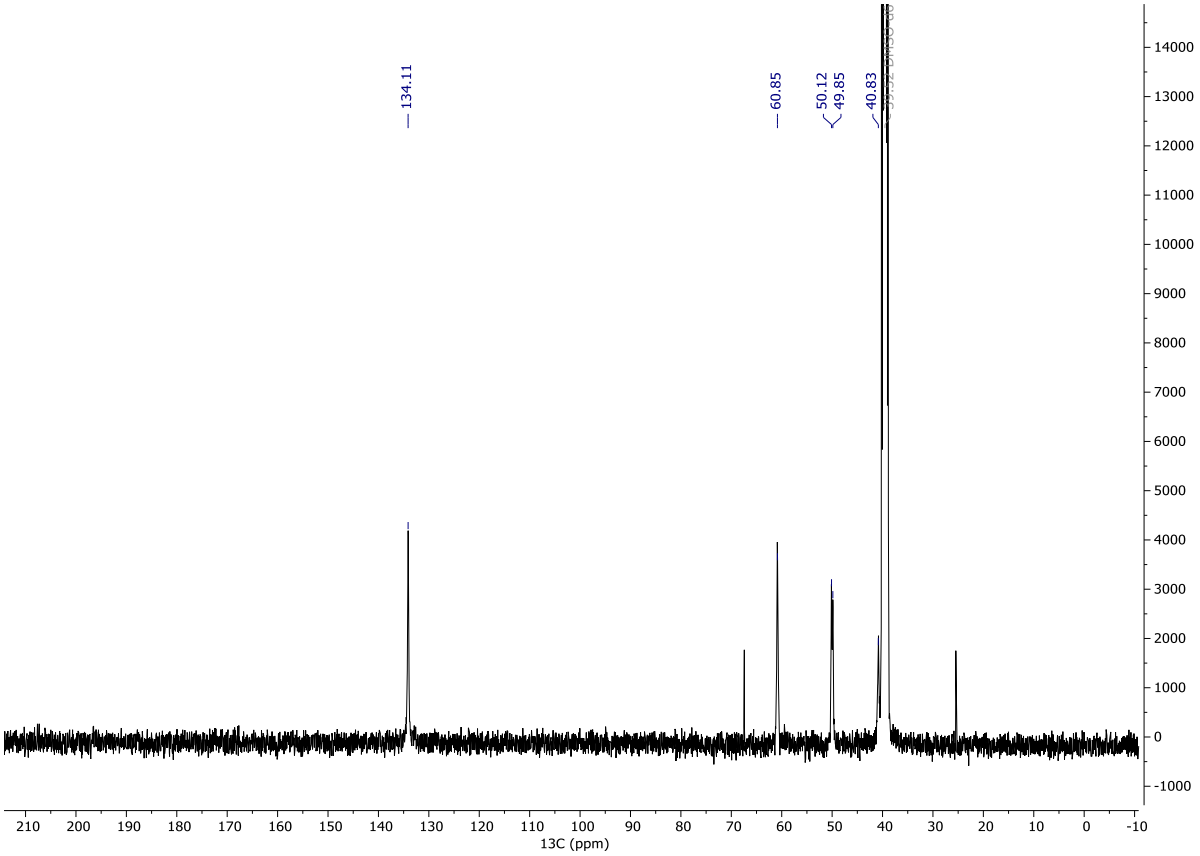
^{13}C NMR (101 MHz, *CDCl$_3$*) of **3b** obtained with **Ru-4d** (0.1 mol%):



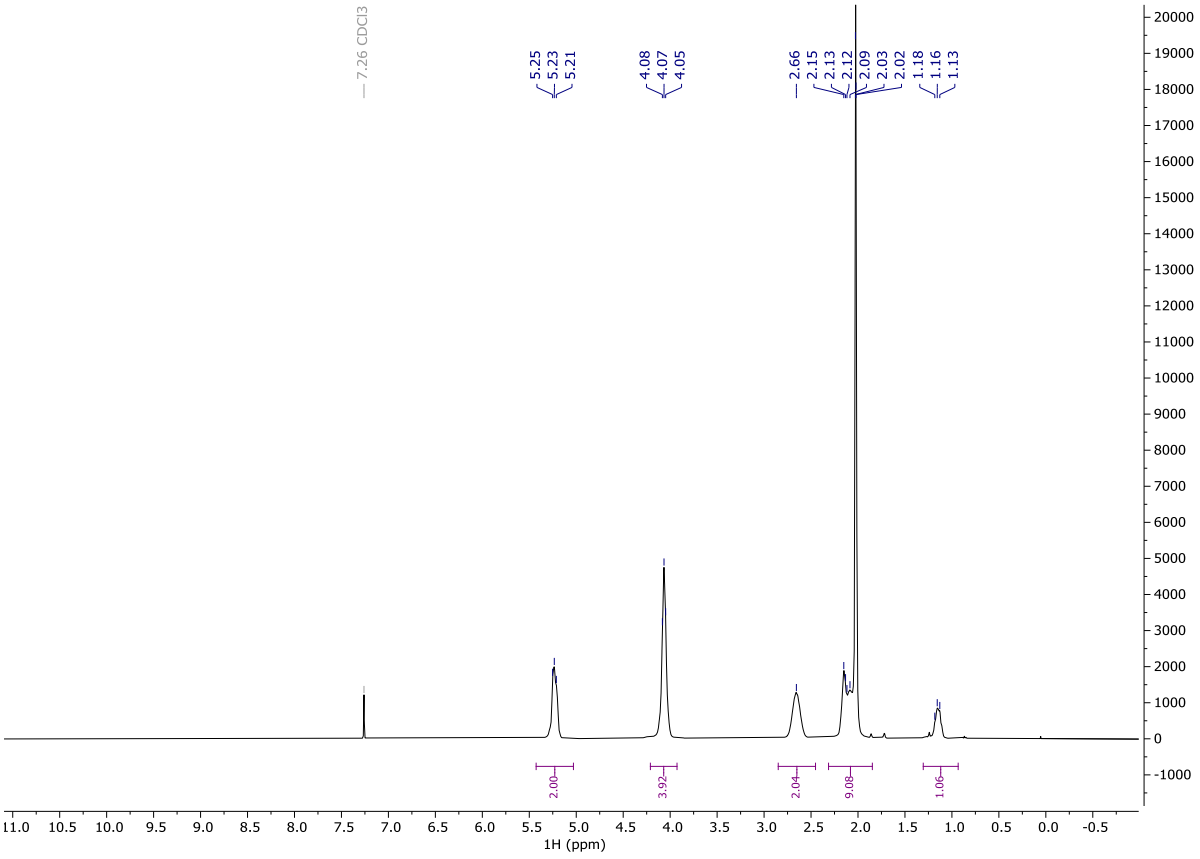
^{1}H NMR (400 MHz, *DMSO-D$_6$*) of **3c** obtained with **Ru-4d** (0.1 mol%):



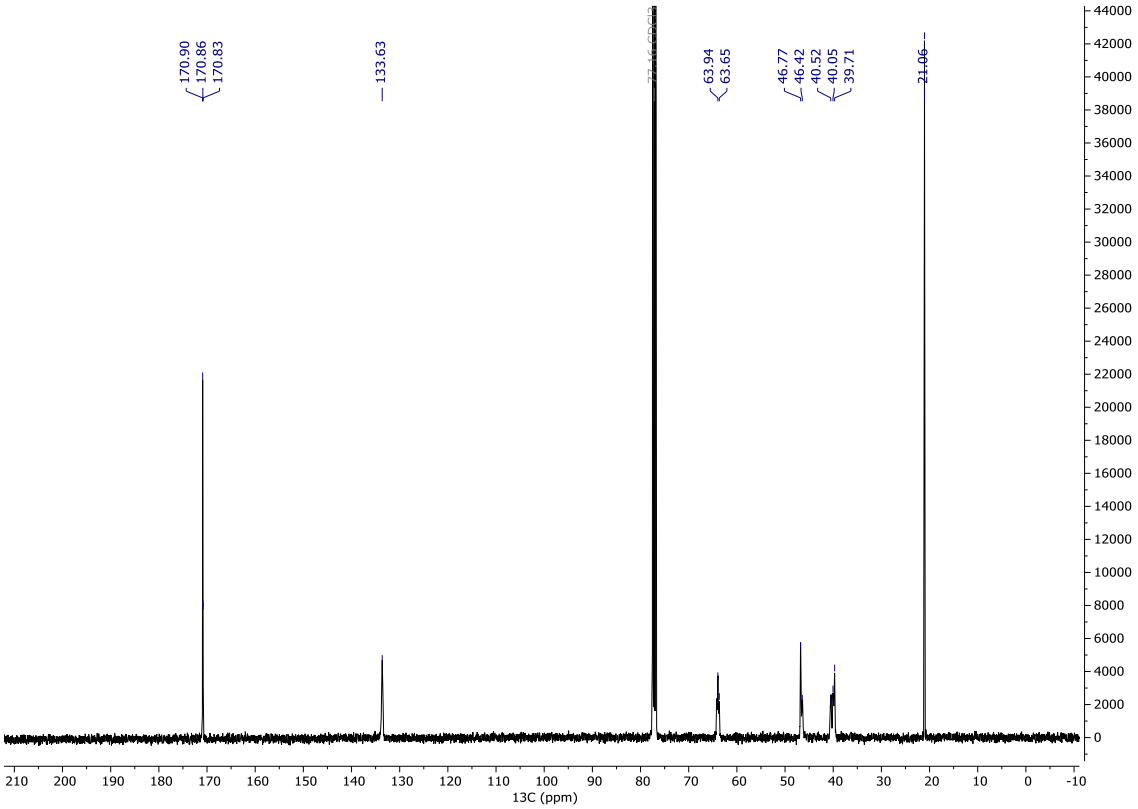
^{13}C NMR (101 MHz, *DMSO-D$_6$*) of **3c** obtained with **Ru-4d** (0.1 mol%):



^{1}H NMR (400 MHz, *CDCl$_3$*) of **3d** obtained with **Ru-4d** (0.1 mol%):

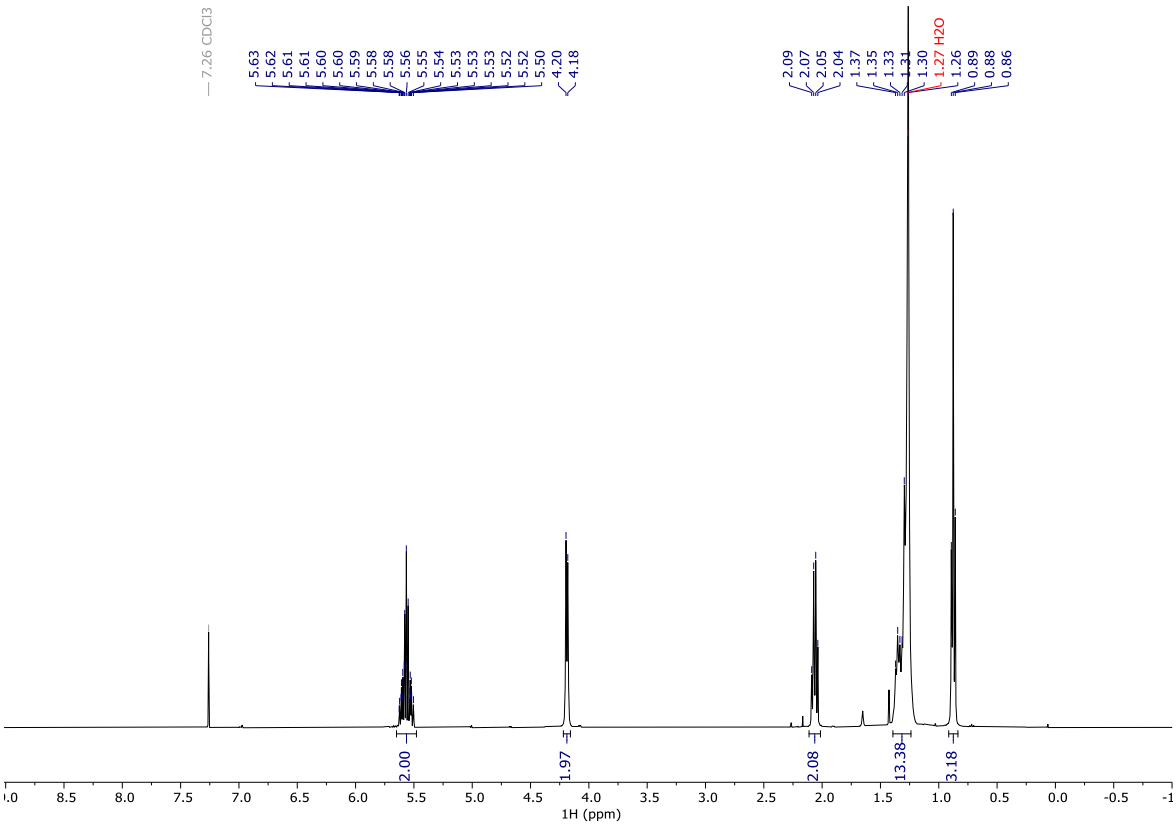


^{13}C NMR (101 MHz, *CDCl$_3$*) of **3d** obtained with **Ru-4d** (0.1 mol%):

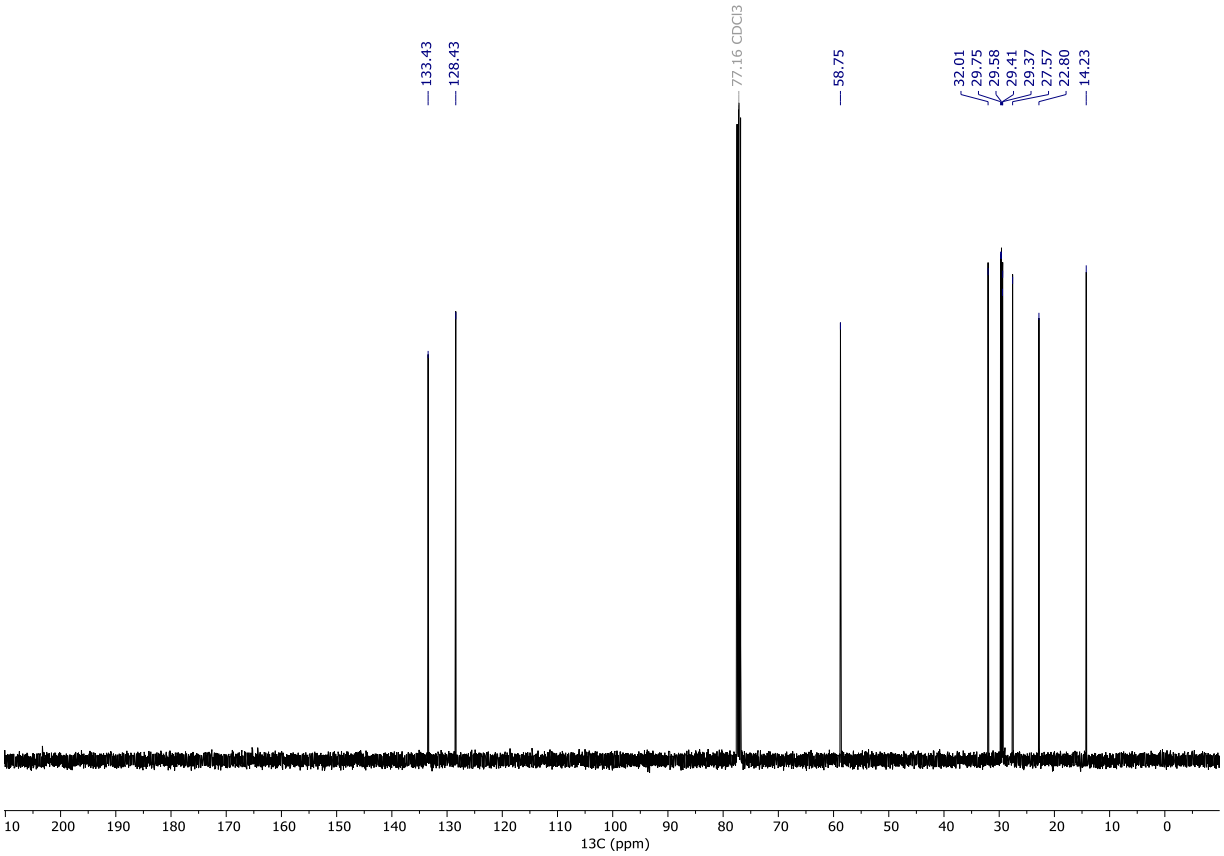


10.5. NMR of CM-products

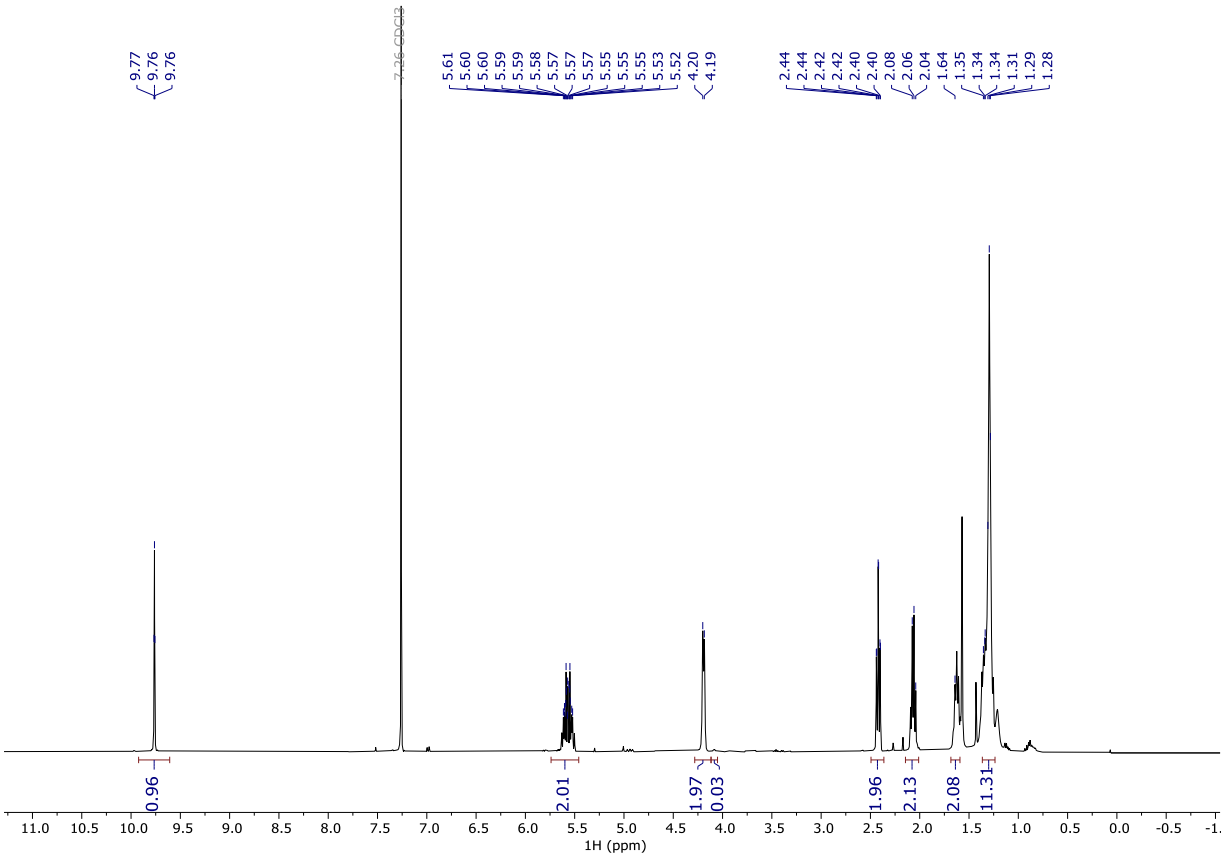
^{1}H NMR (400 MHz, *CDCl$_3$*) of **15:**



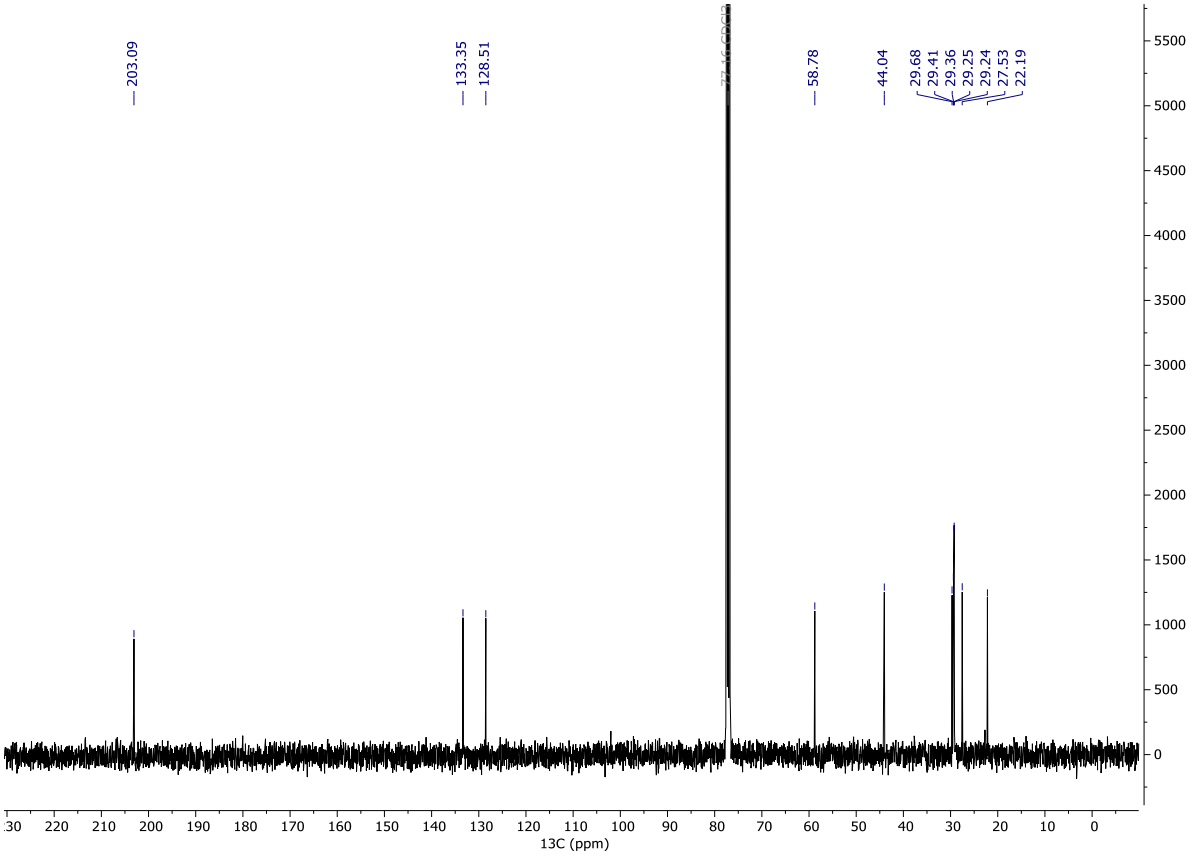
^{13}C NMR (101 MHz, *CDCl$_3$*) of **15:**



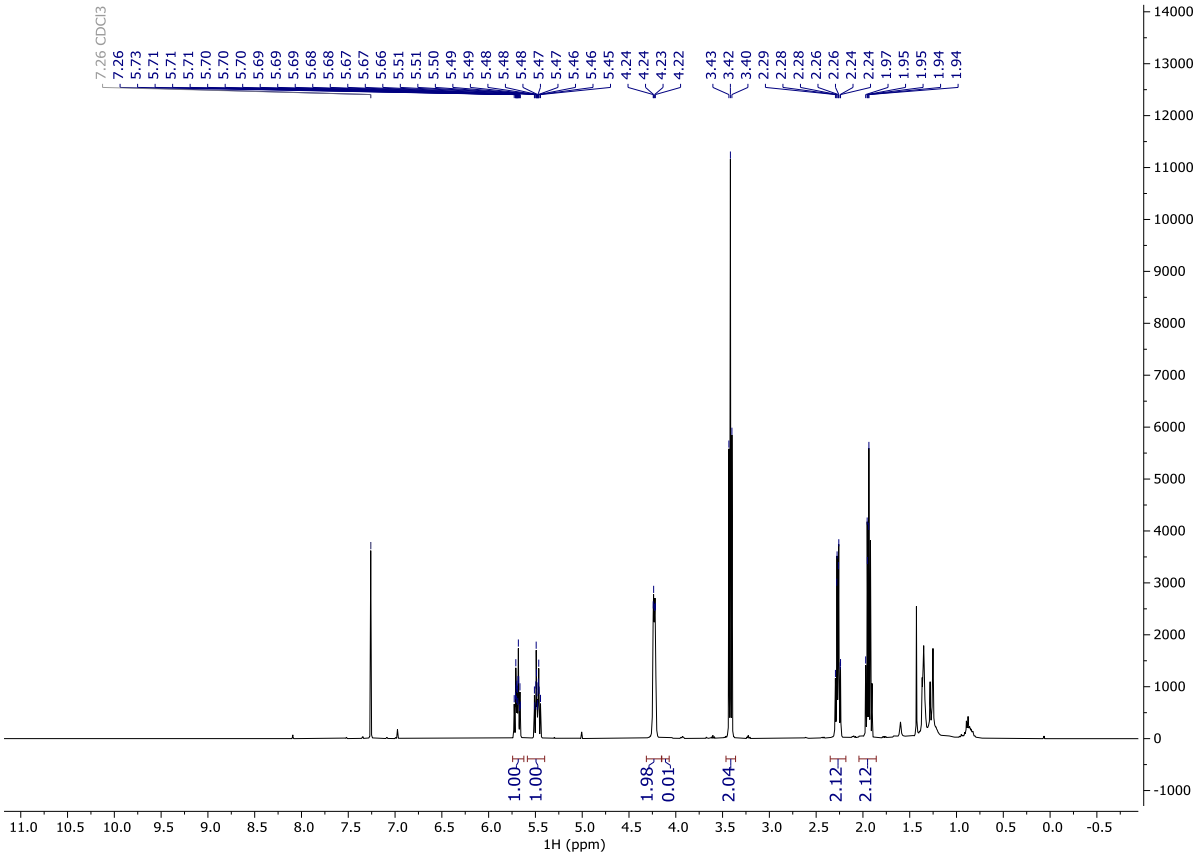
^{1}H NMR (400 MHz, *CDCl$_3$*) of **16:**



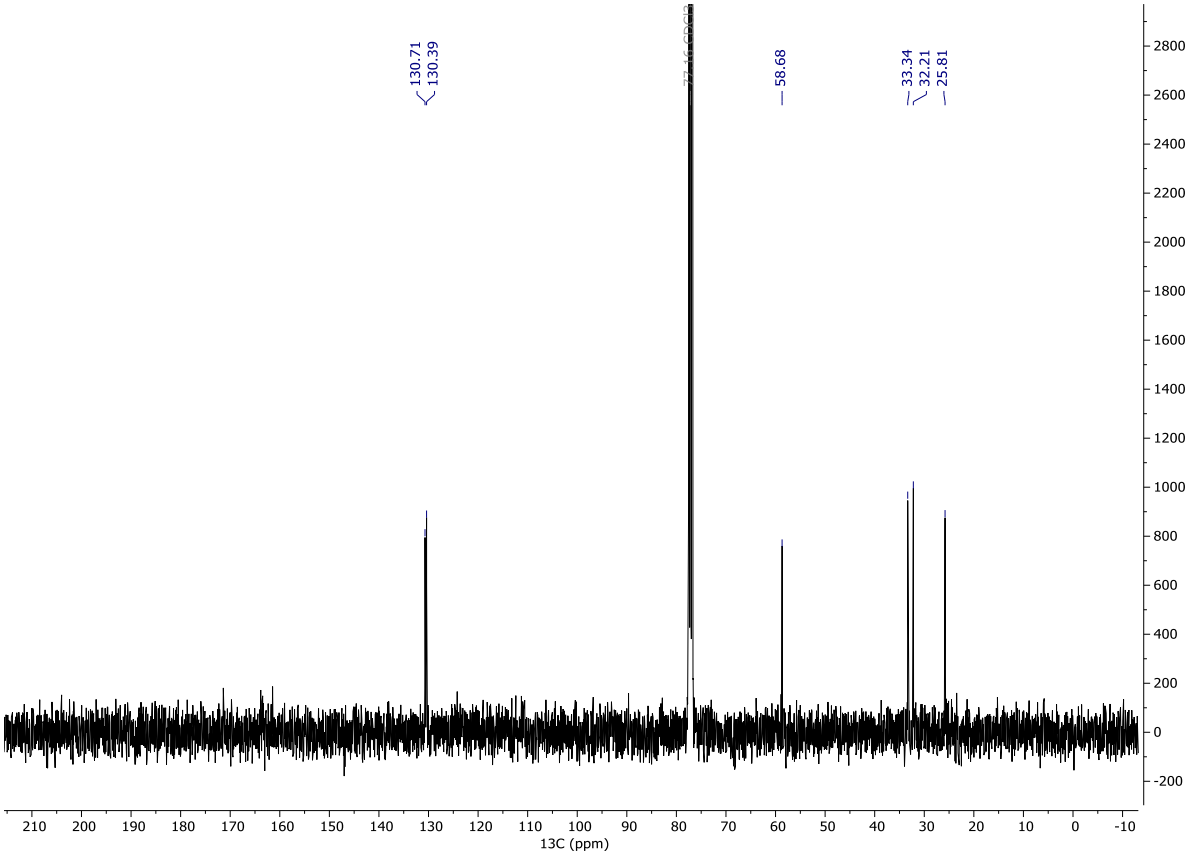
^{13}C NMR (101 MHz, *CDCl$_3$*) of **16:**



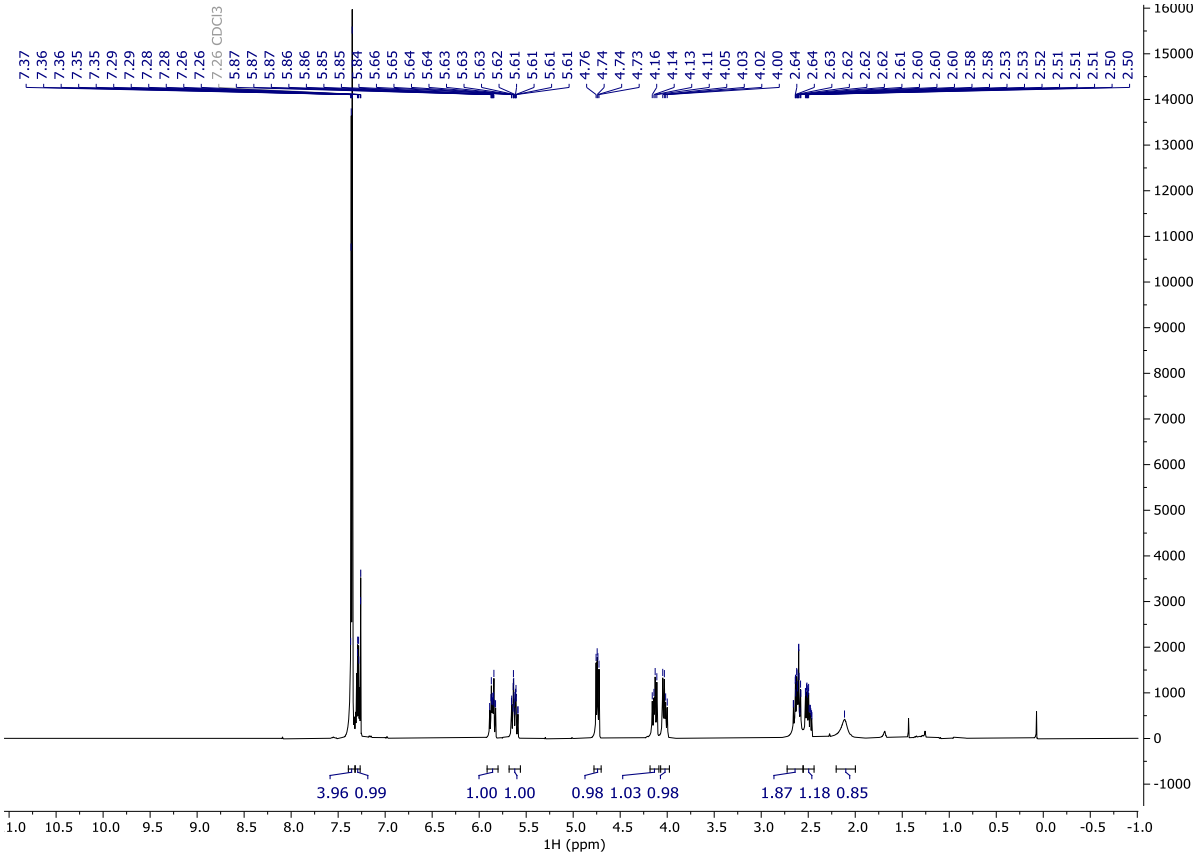
^{1}H NMR (400 MHz, *CDCl$_3$*) of **17:**



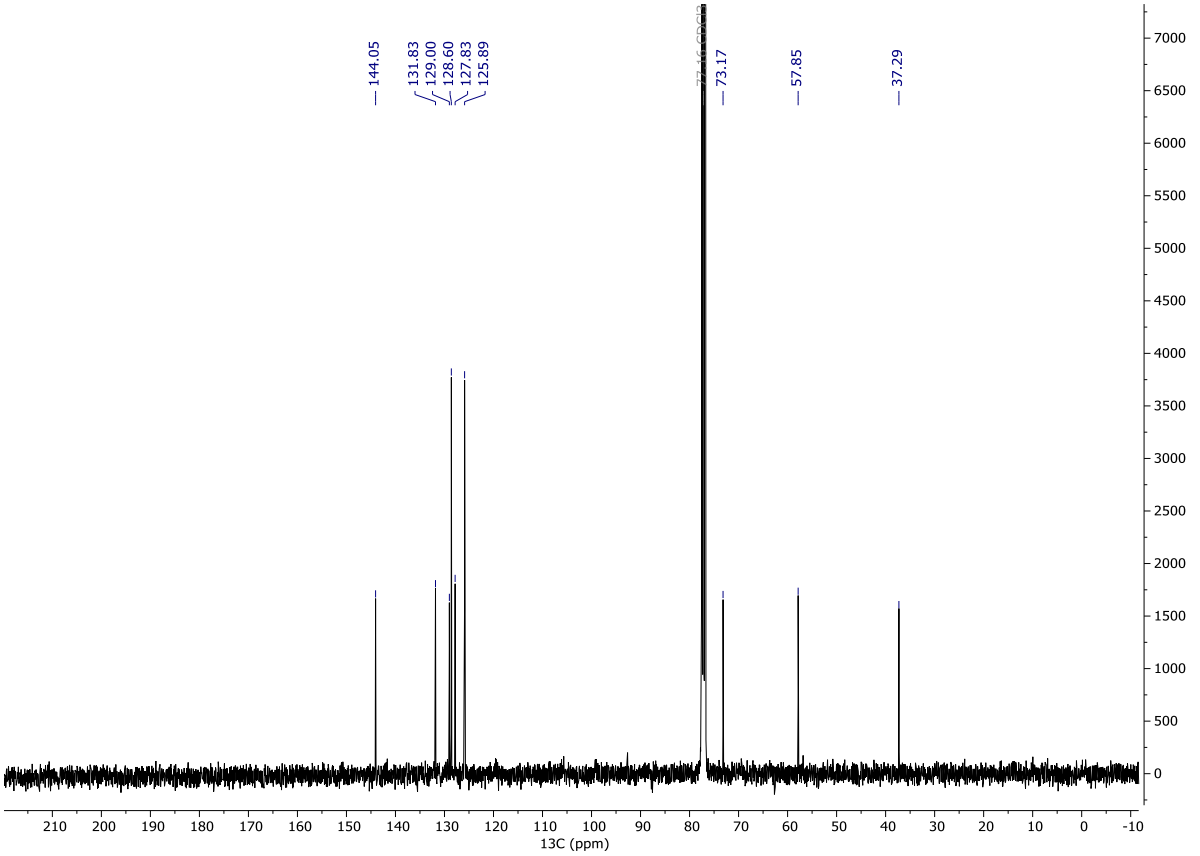
^{13}C NMR (101 MHz, *CDCl$_3$*) of **17:**



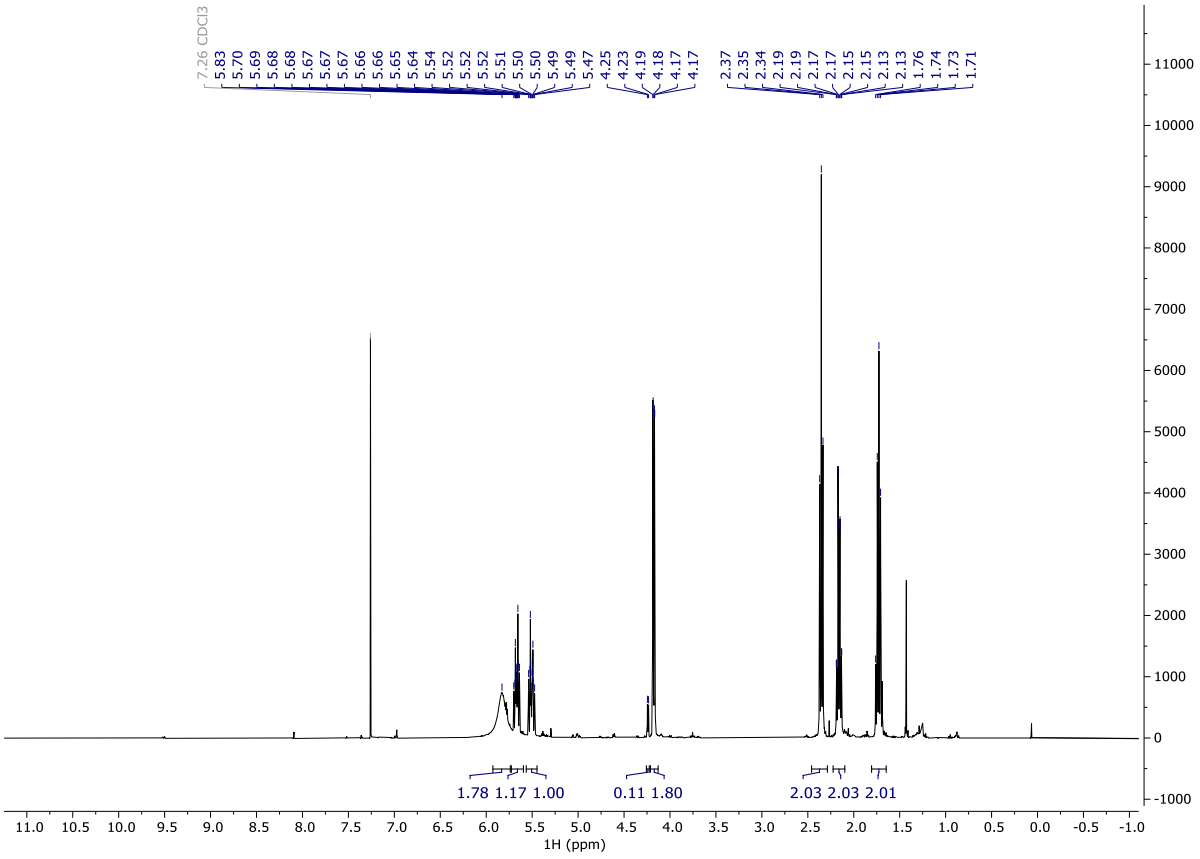
^{1}H NMR (400 MHz, *CDCl$_3$*) of **18:**



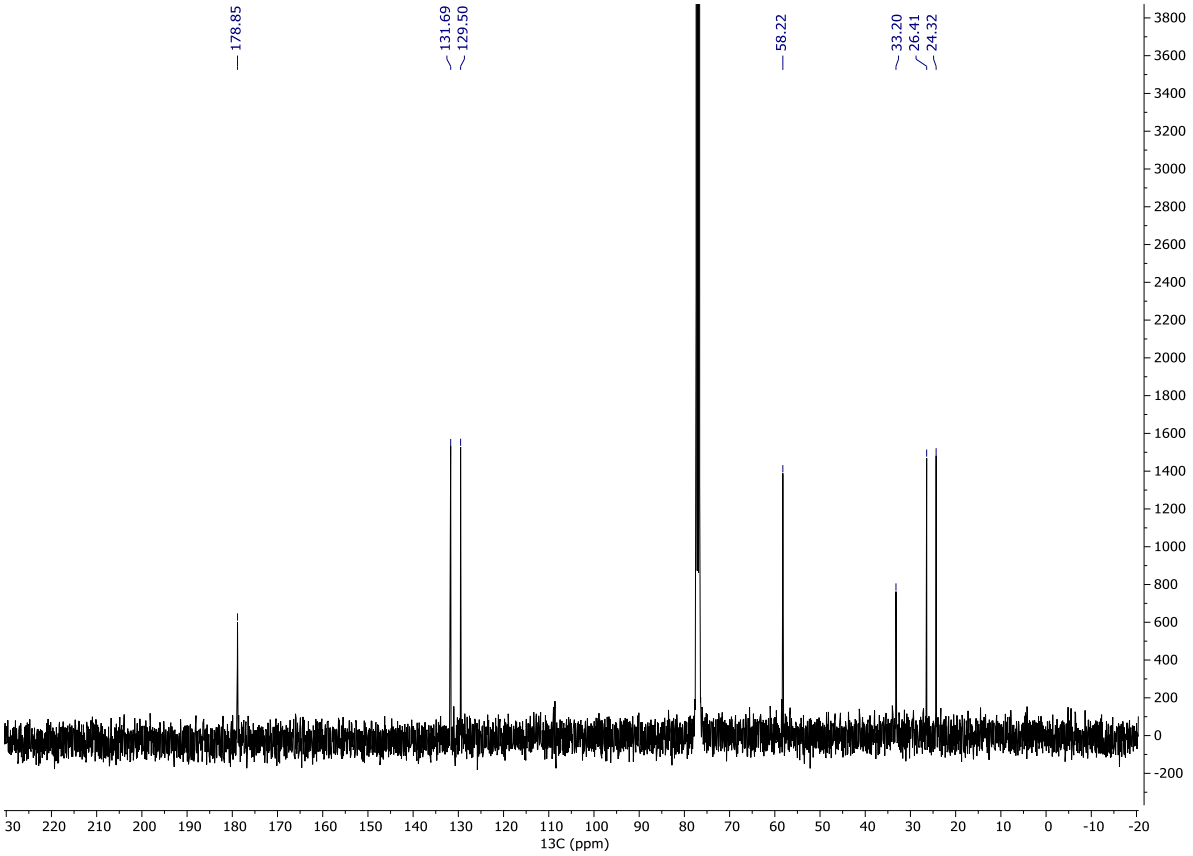
^{13}C NMR (101 MHz, *CDCl$_3$*) of **18:**



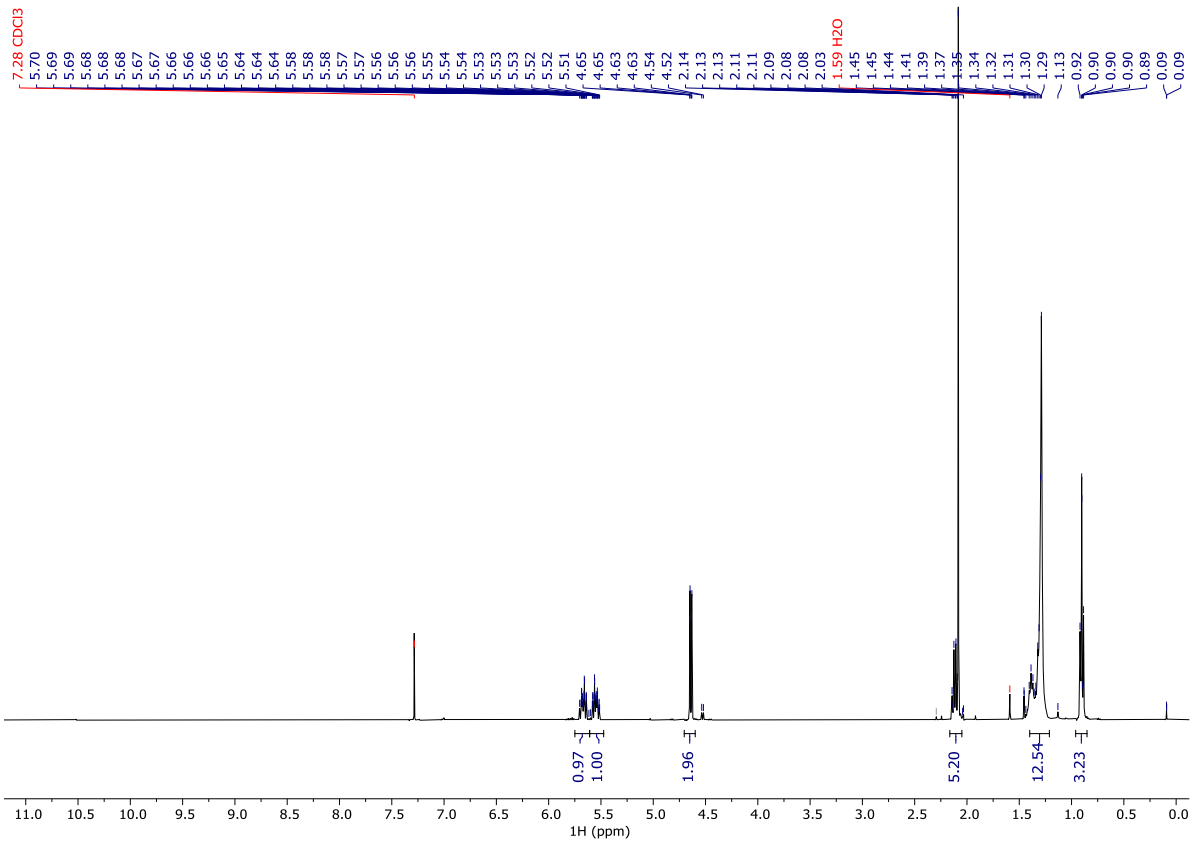
^{1}H NMR (400 MHz, *CDCl$_3$*) of **19:**



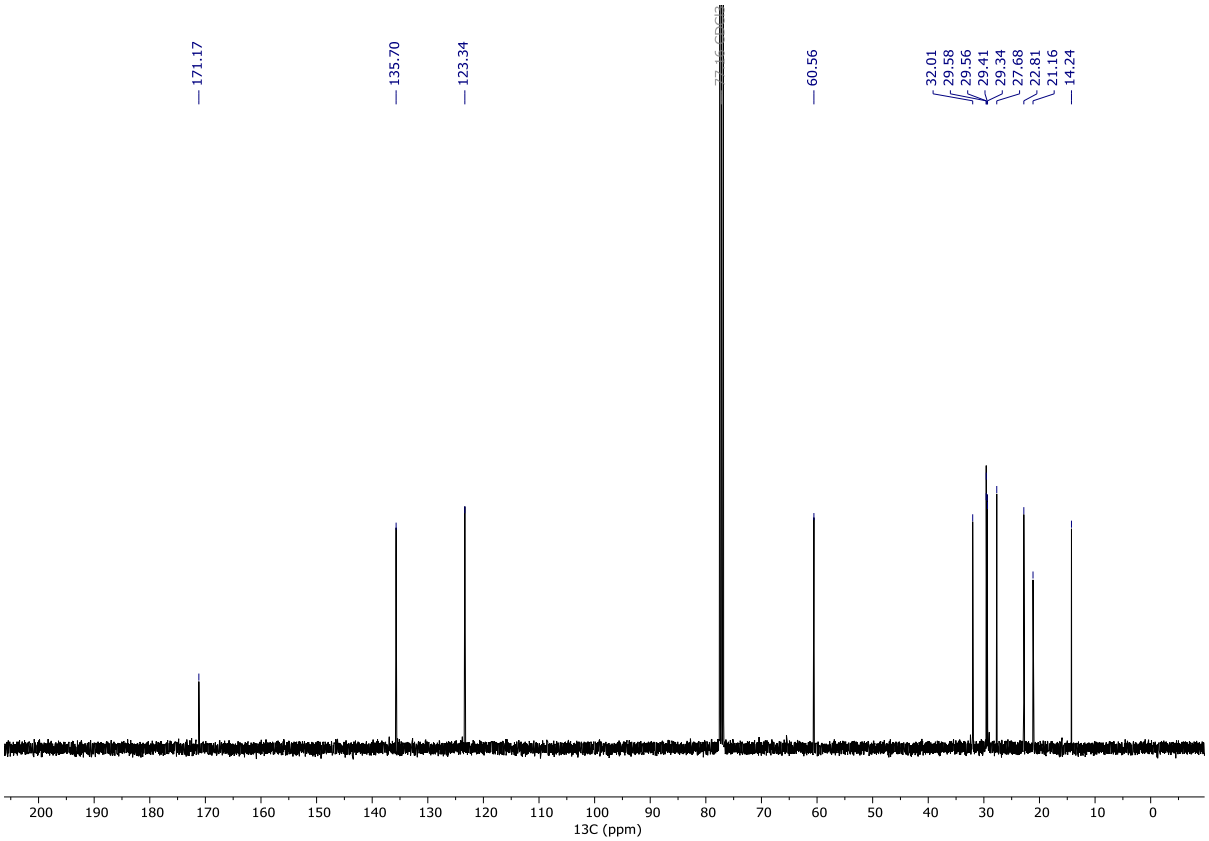
^{13}C NMR (101 MHz, *CDCl$_3$*) of **19:**



^{1}H NMR (400 MHz, *CDCl$_3$*) of **20:**

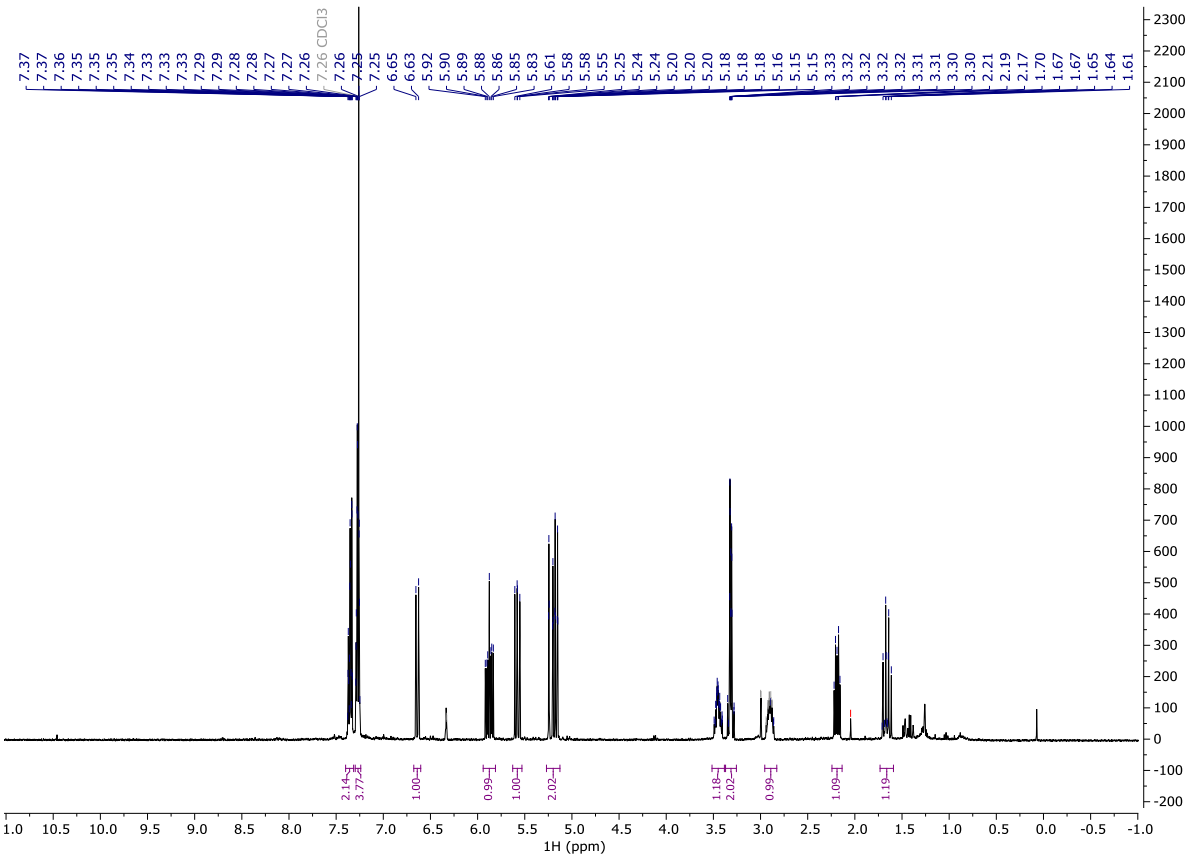


^{13}C NMR (101 MHz, *CDCl$_3$*) of **20:**

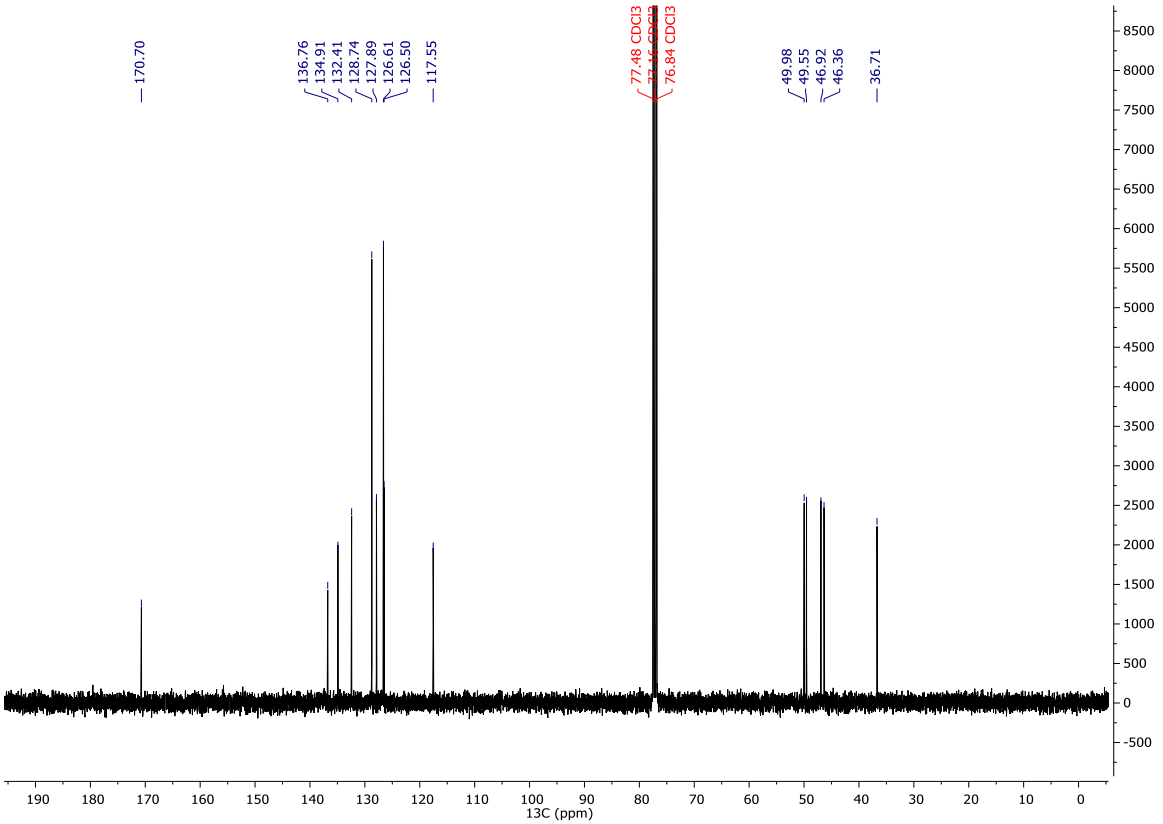


10.6. NMR of AROCM-products

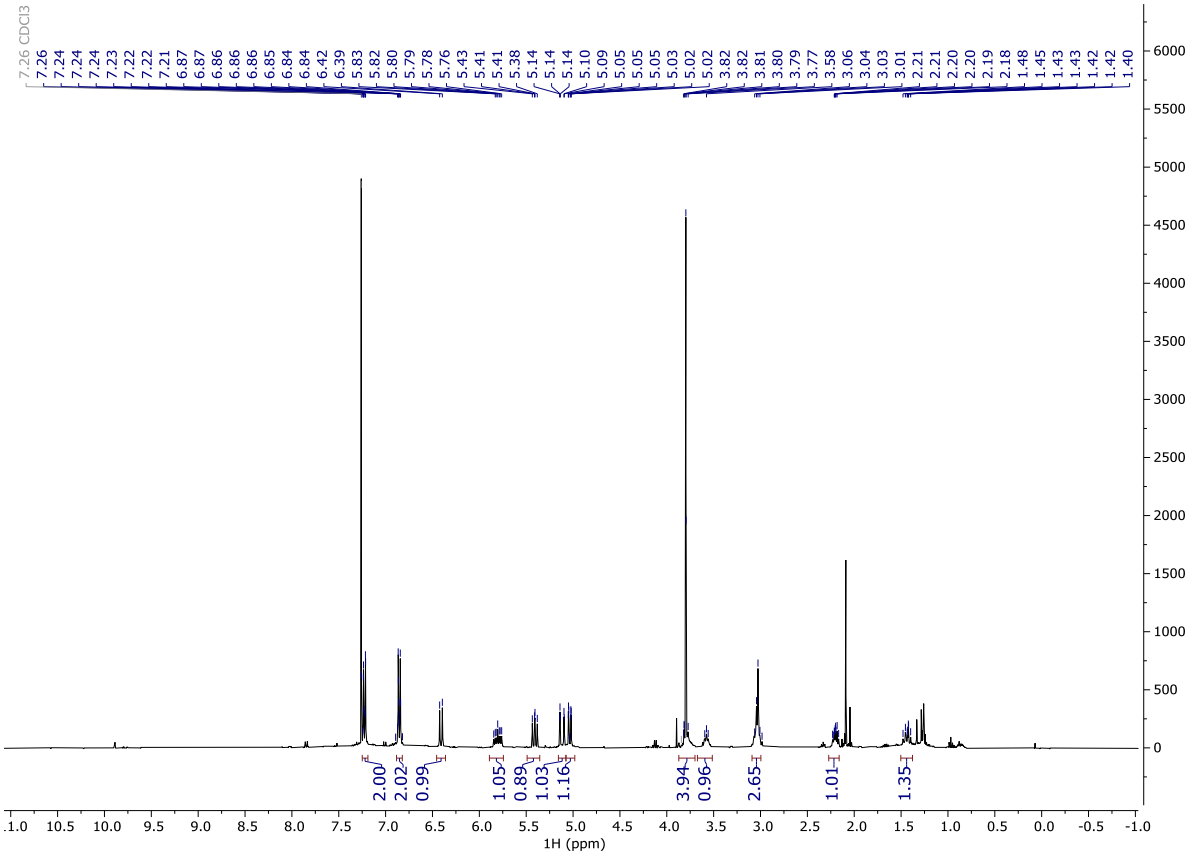
^{1}H NMR of **4** (400 MHz, $CDCl_3$):



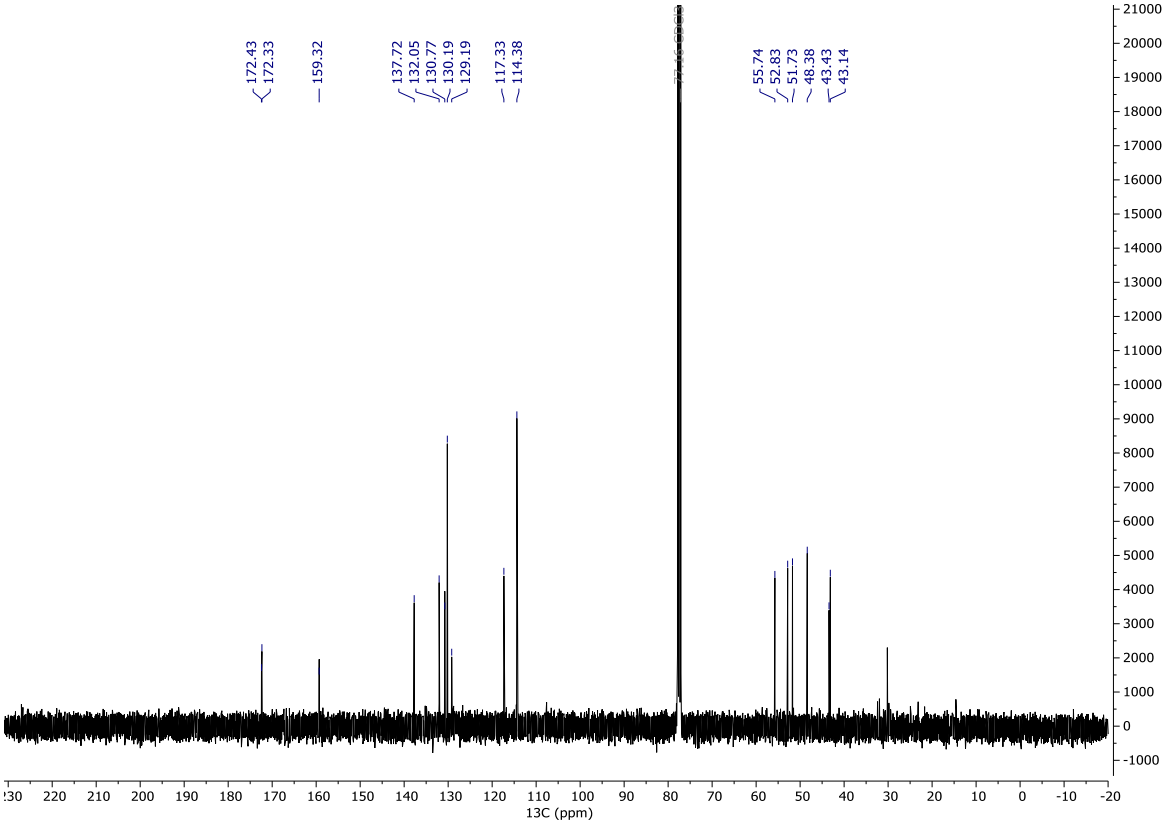
^{13}C NMR of **4** (101 MHz, $CDCl_3$):



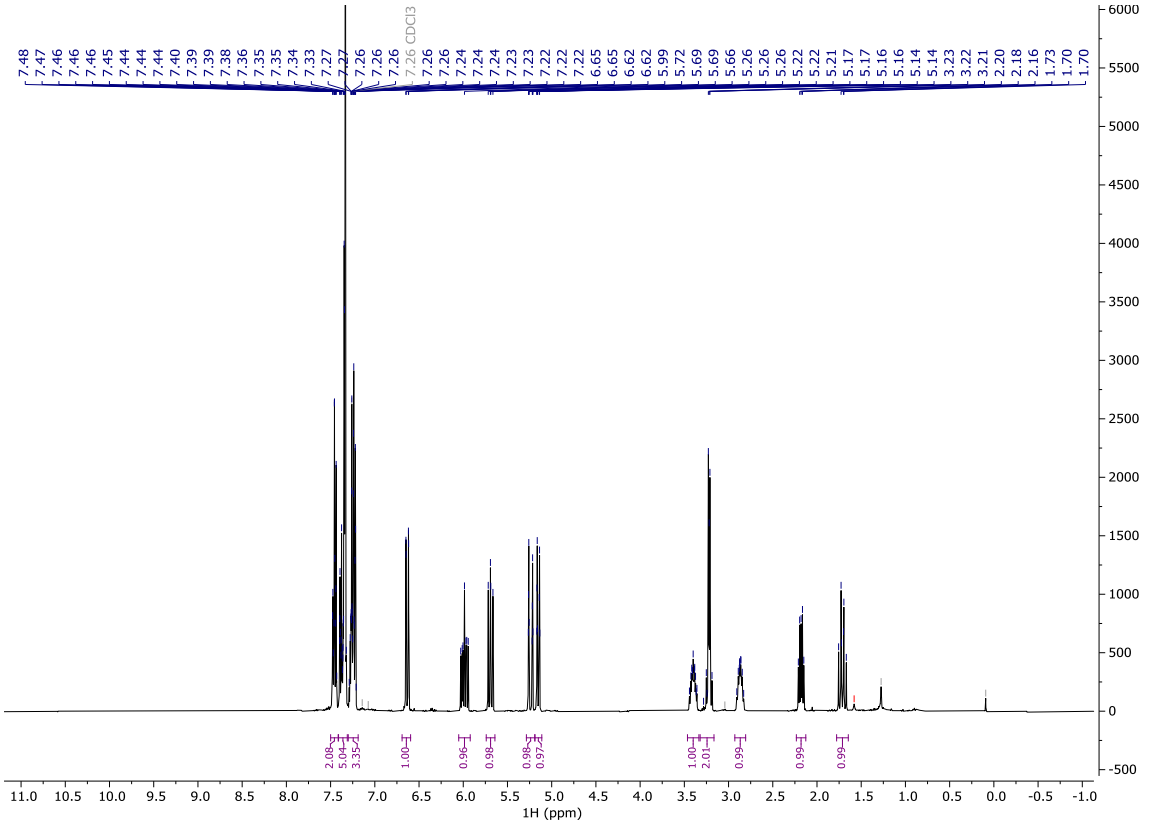
[1]H NMR of **5** (400 MHz, $CDCl_3$):



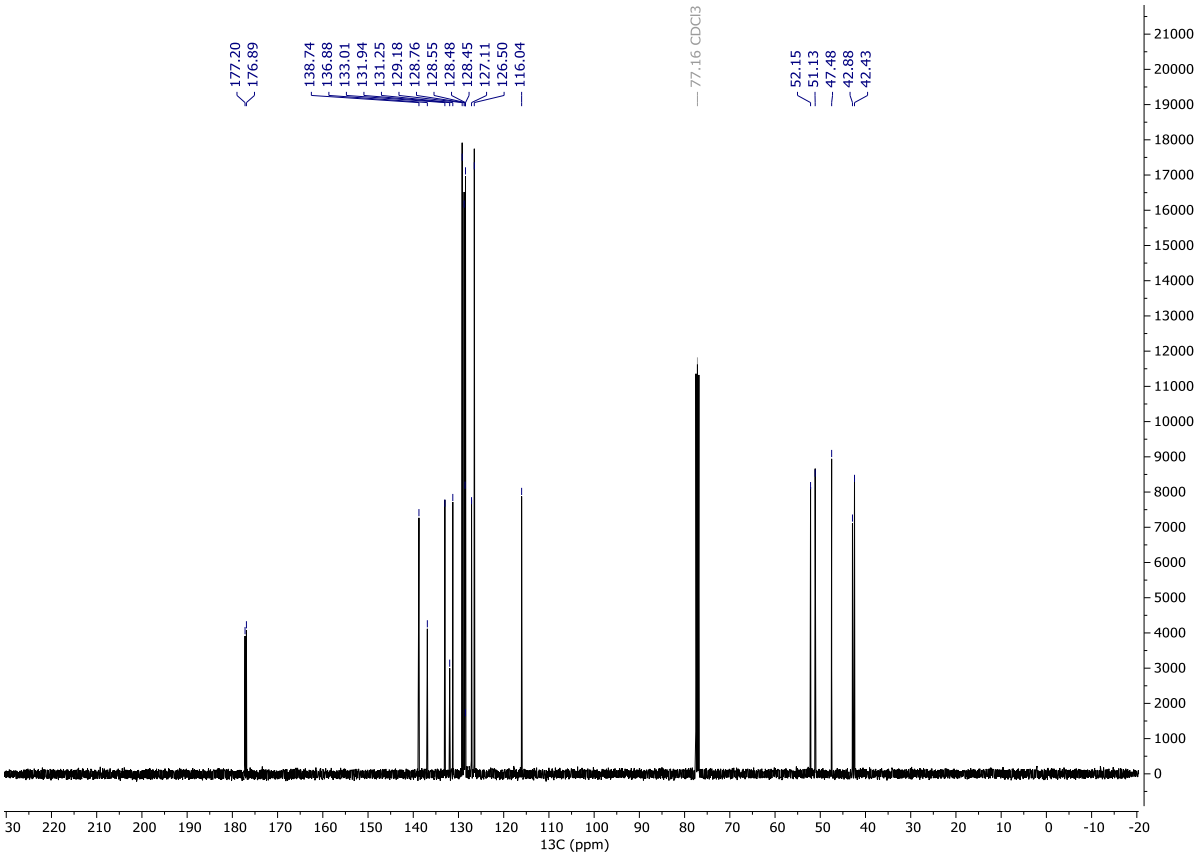
[13]C NMR of **5** (101 MHz, $CDCl_3$):



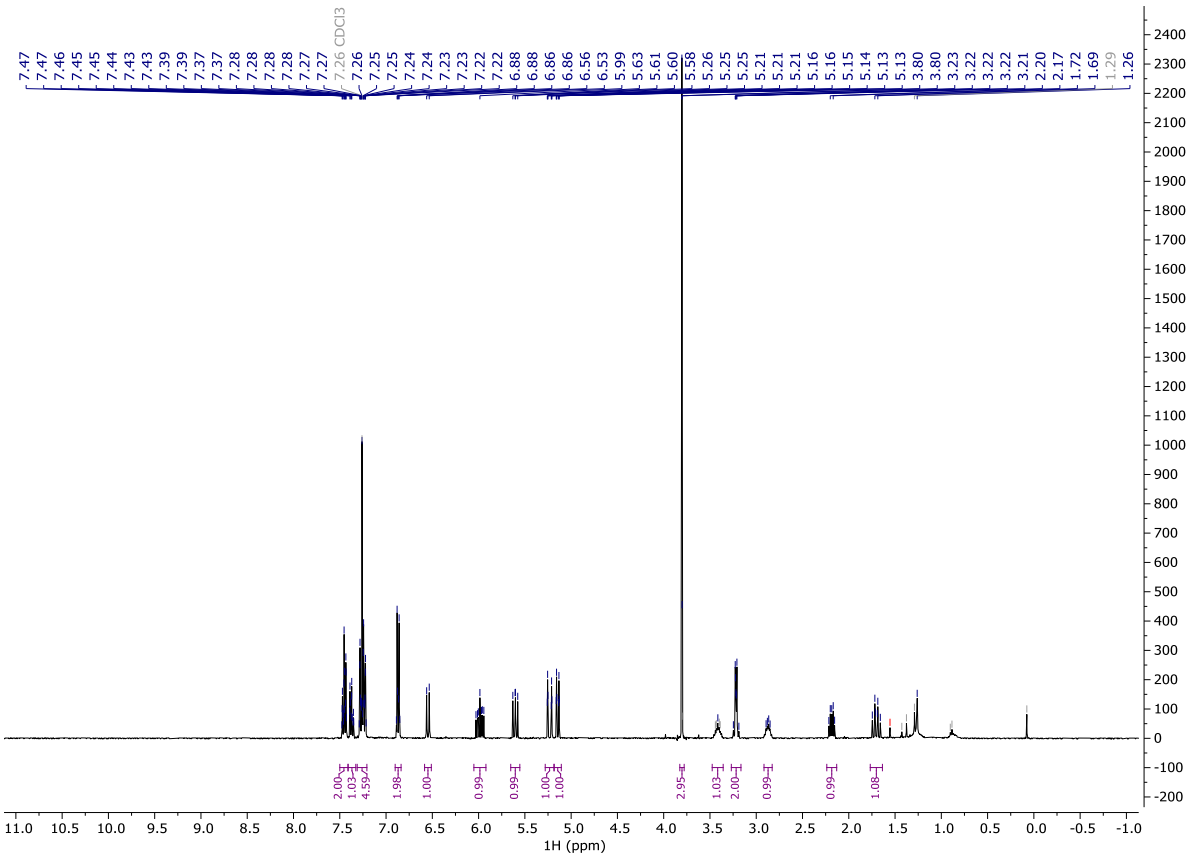
^{1}H NMR of **6** (400 MHz, $CDCl_3$):



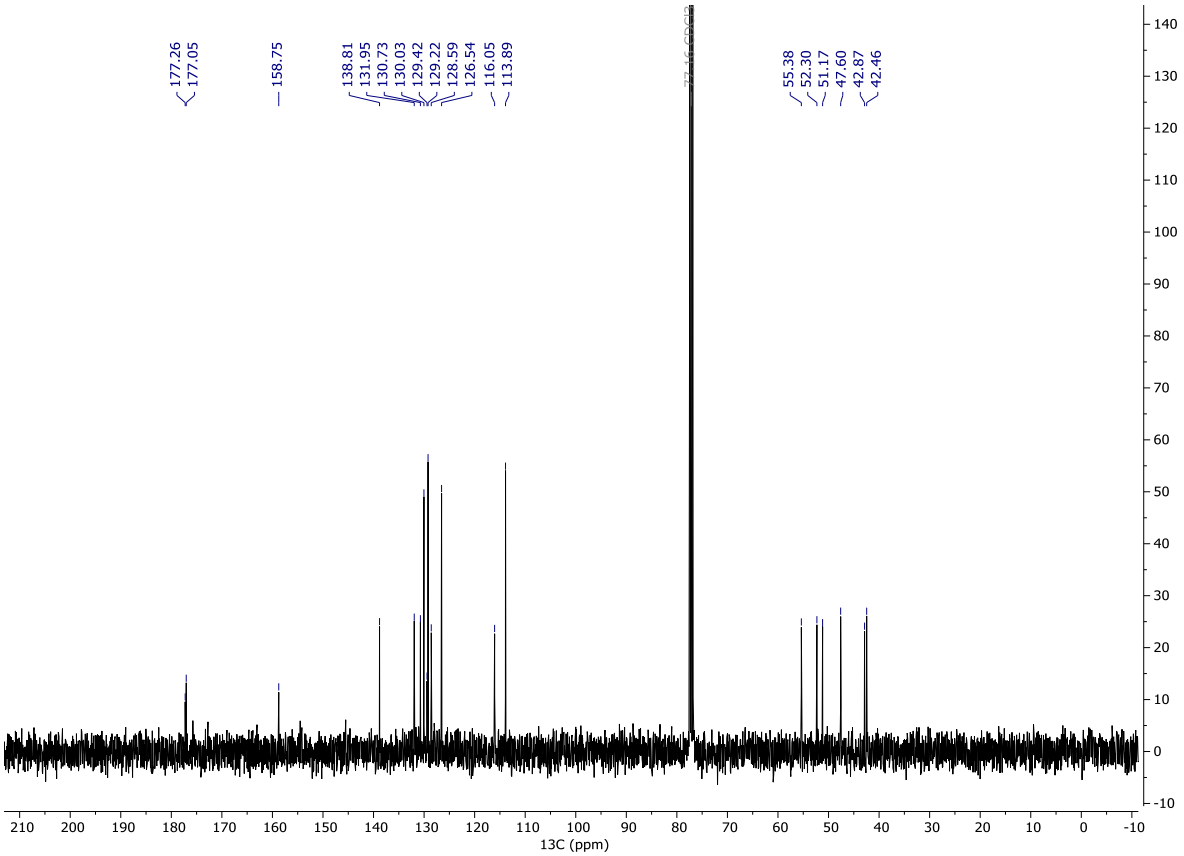
^{13}C NMR of **6** (101 MHz, $CDCl_3$):



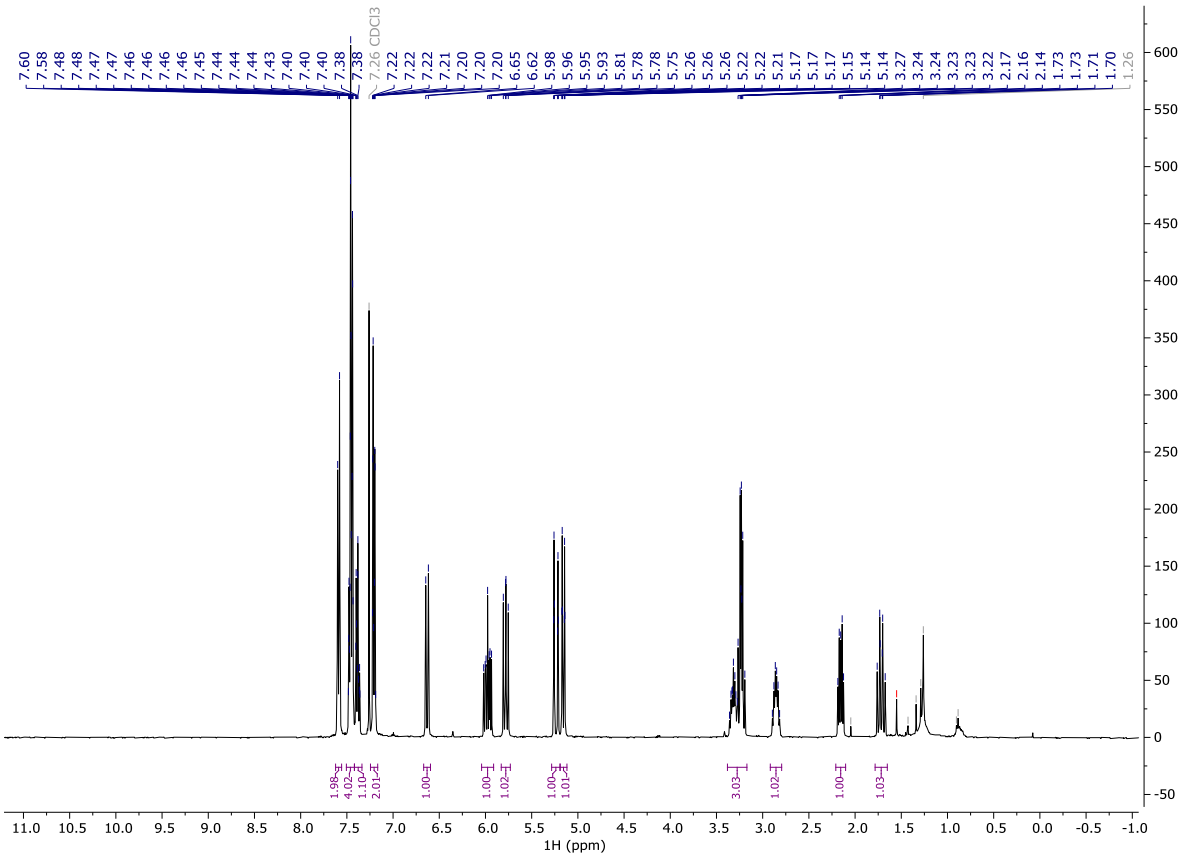
^{1}H NMR of **7** (400 MHz, $CDCl_3$):



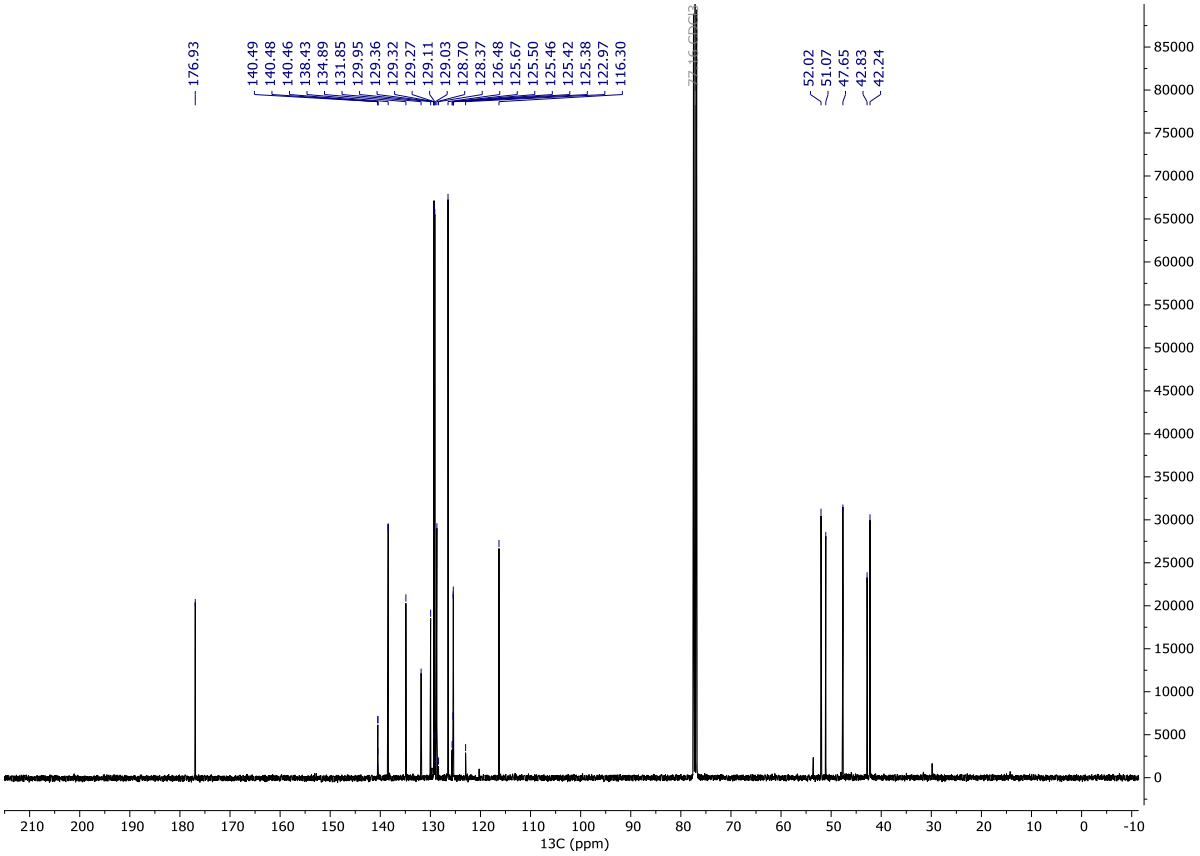
^{13}C NMR of **7** (101 MHz, $CDCl_3$):



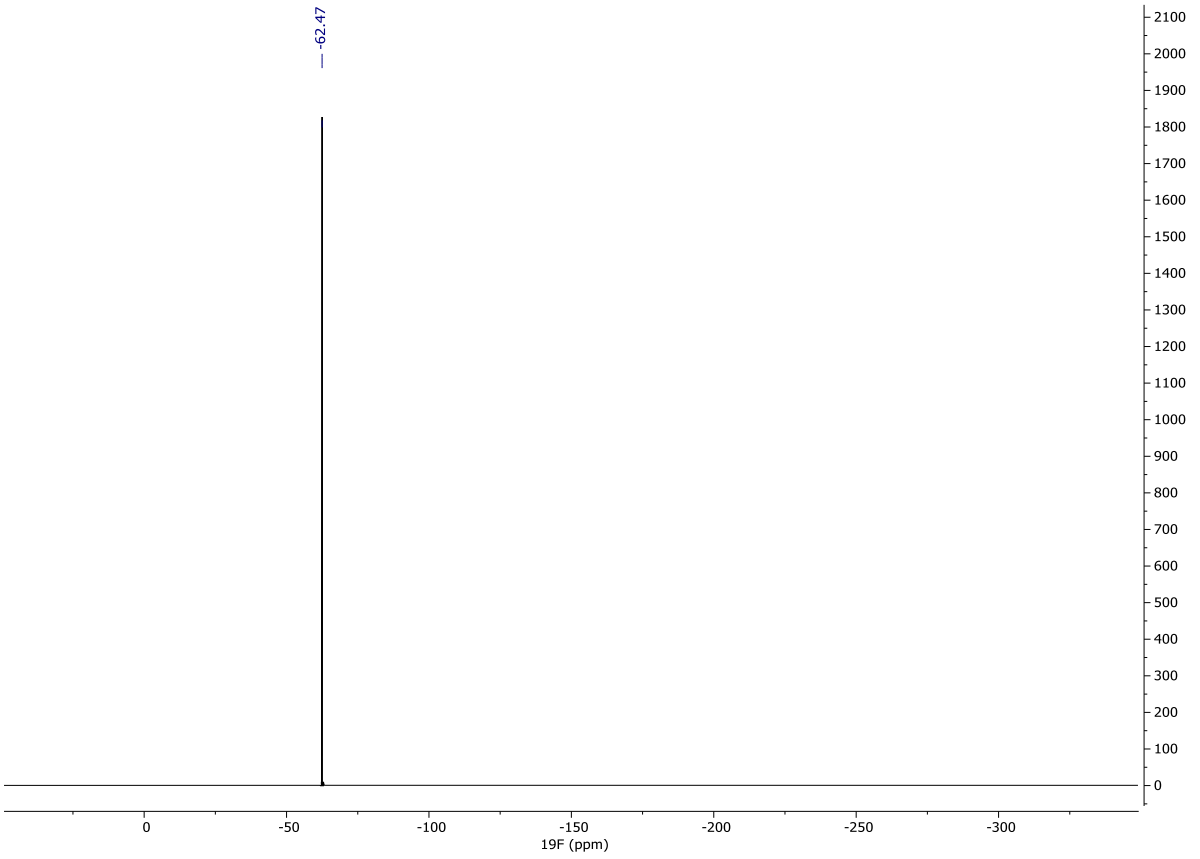
^{1}H NMR of **8** (400 MHz, $CDCl_3$):



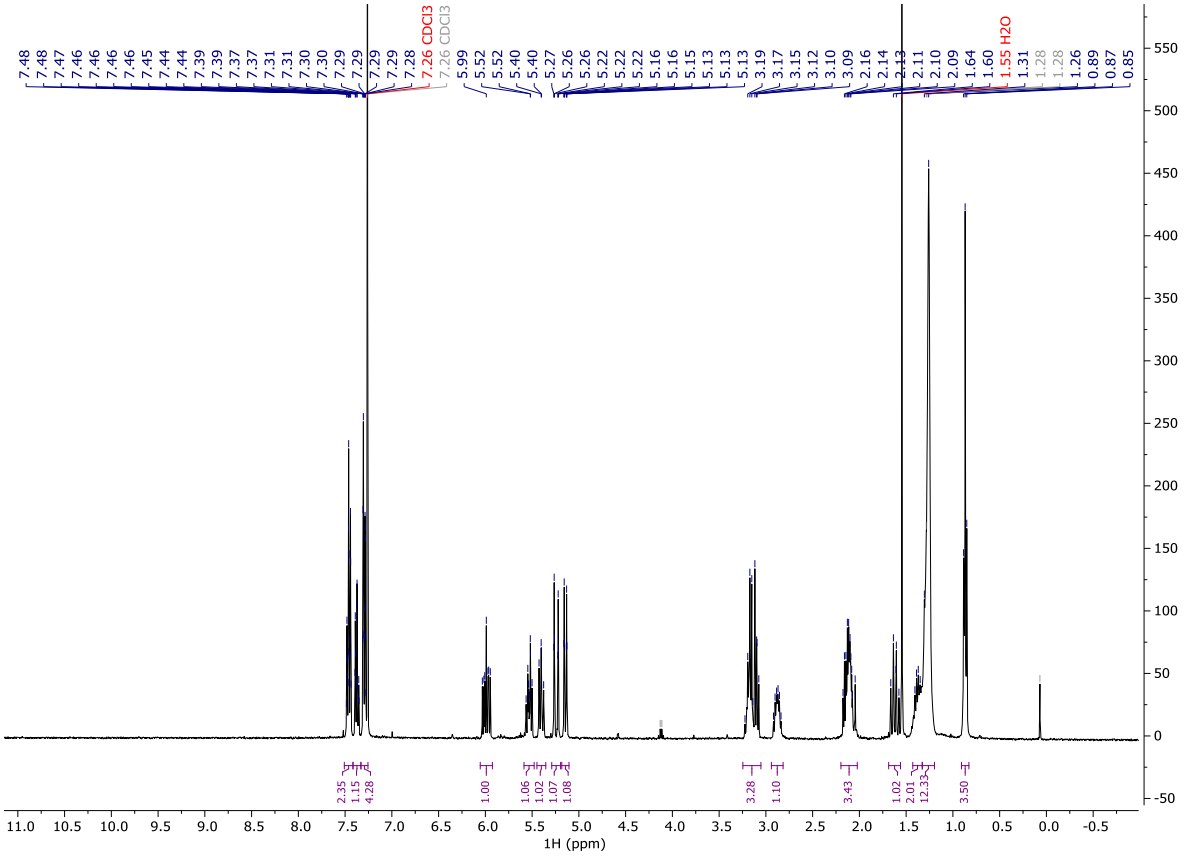
^{13}C NMR of **8** (101 MHz, $CDCl_3$):



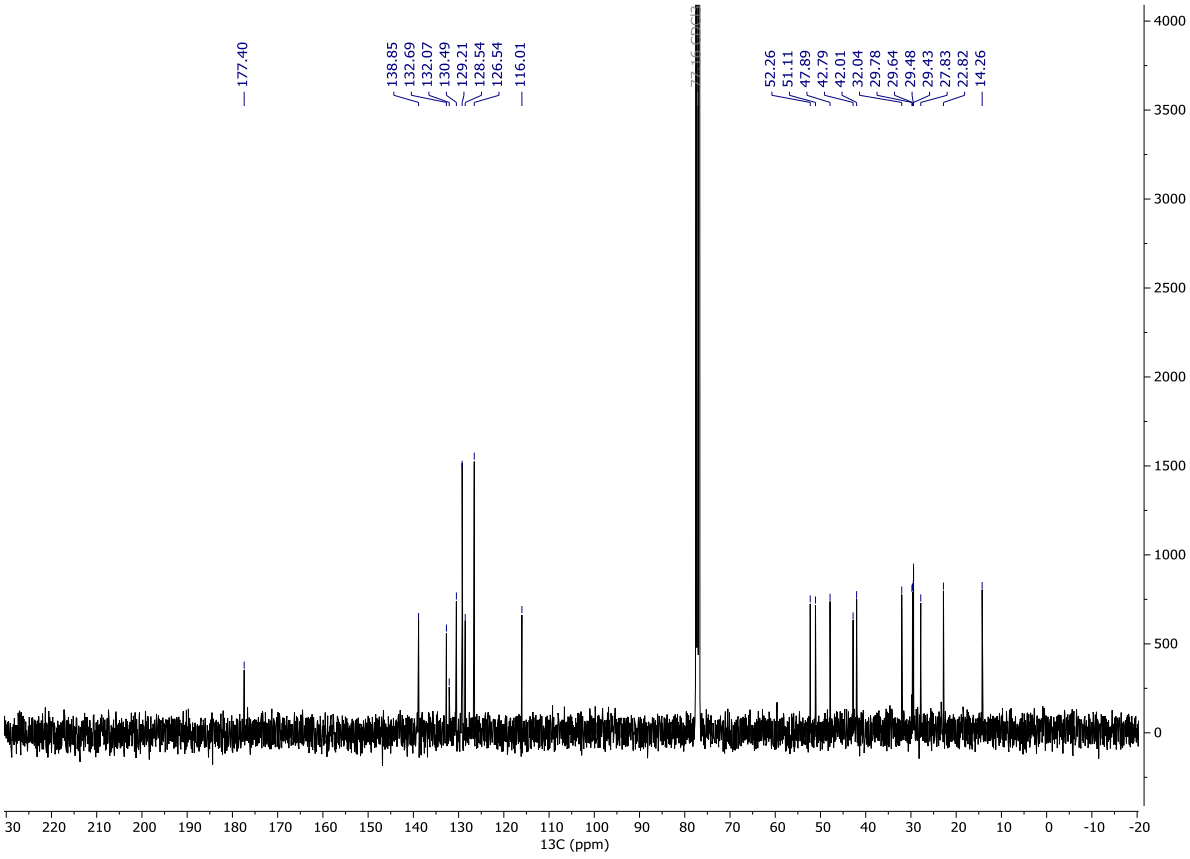
^{19}F NMR of **8** (376 MHz, $CDCl_3$):



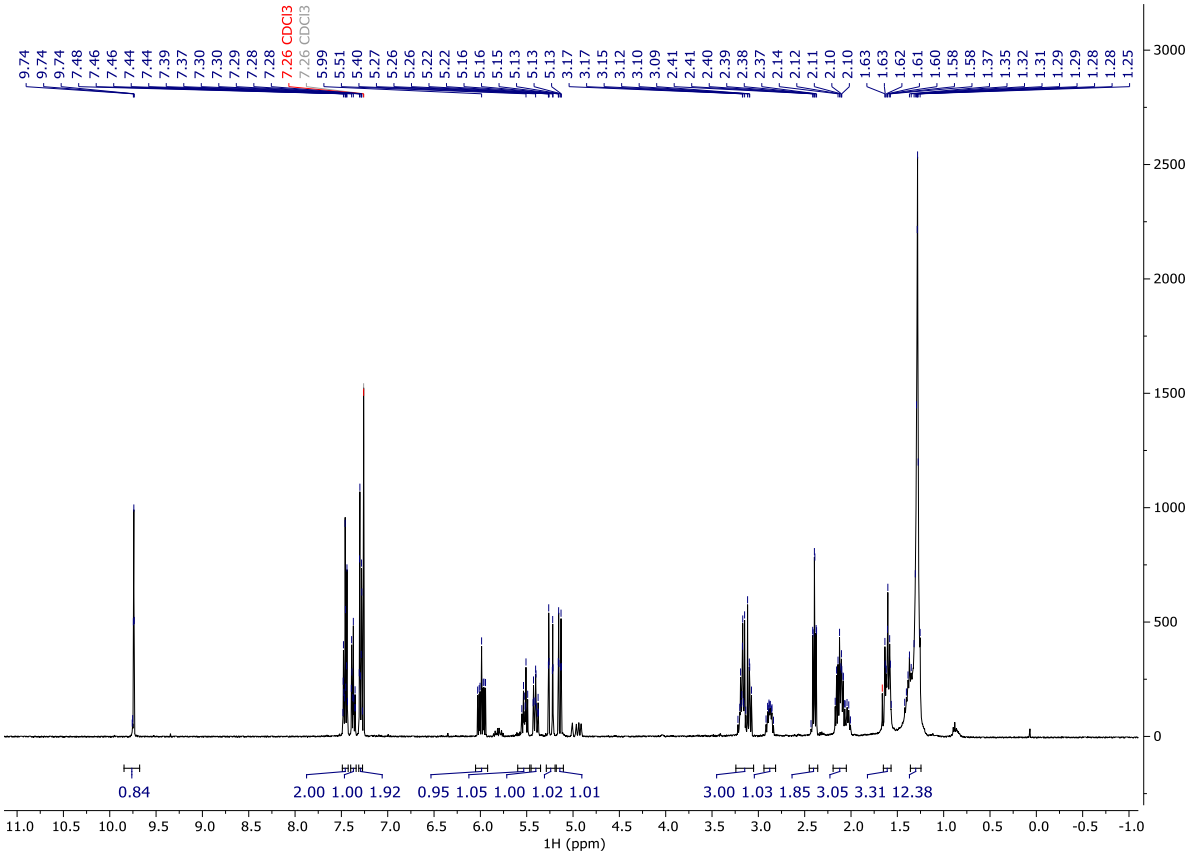
^{1}H NMR of **10** (400 MHz, $CDCl_3$):



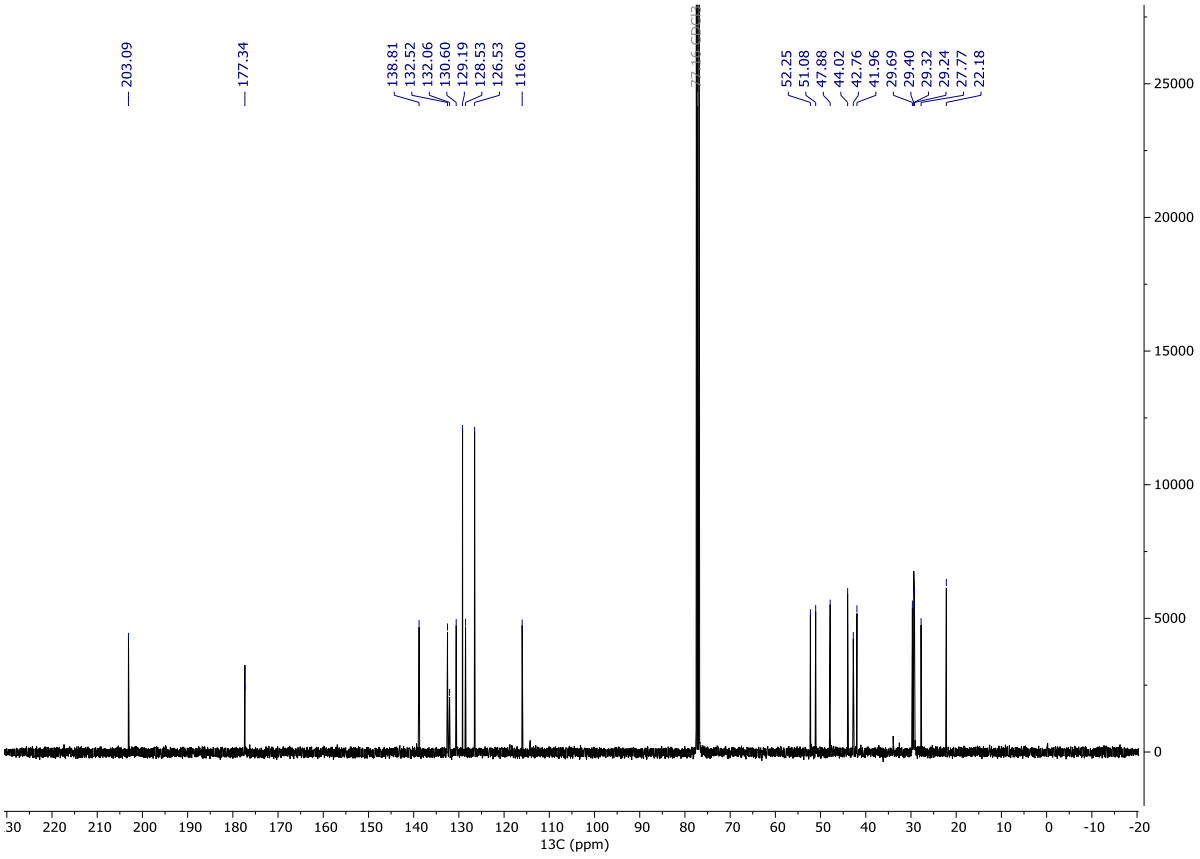
^{13}C NMR of **10** (101 MHz, $CDCl_3$):



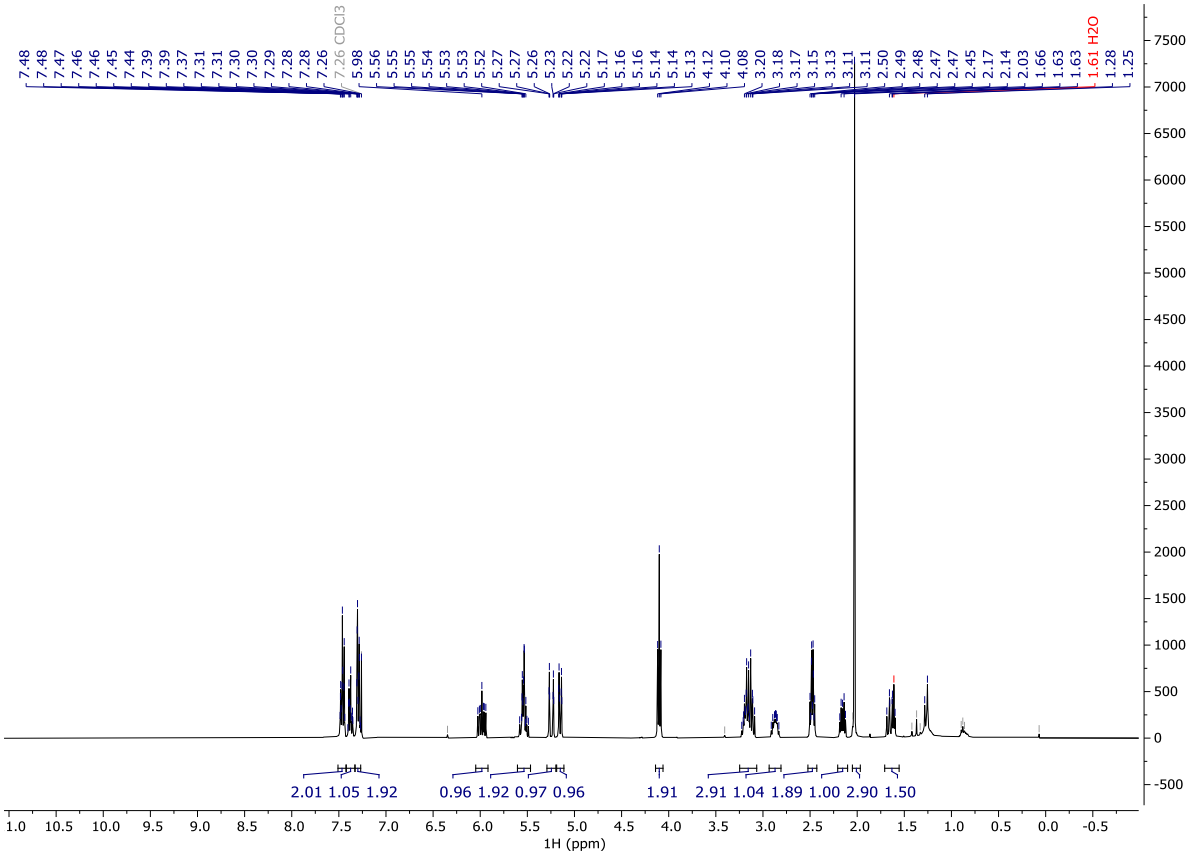
^{1}H NMR of **11** (400 MHz, $CDCl_3$):



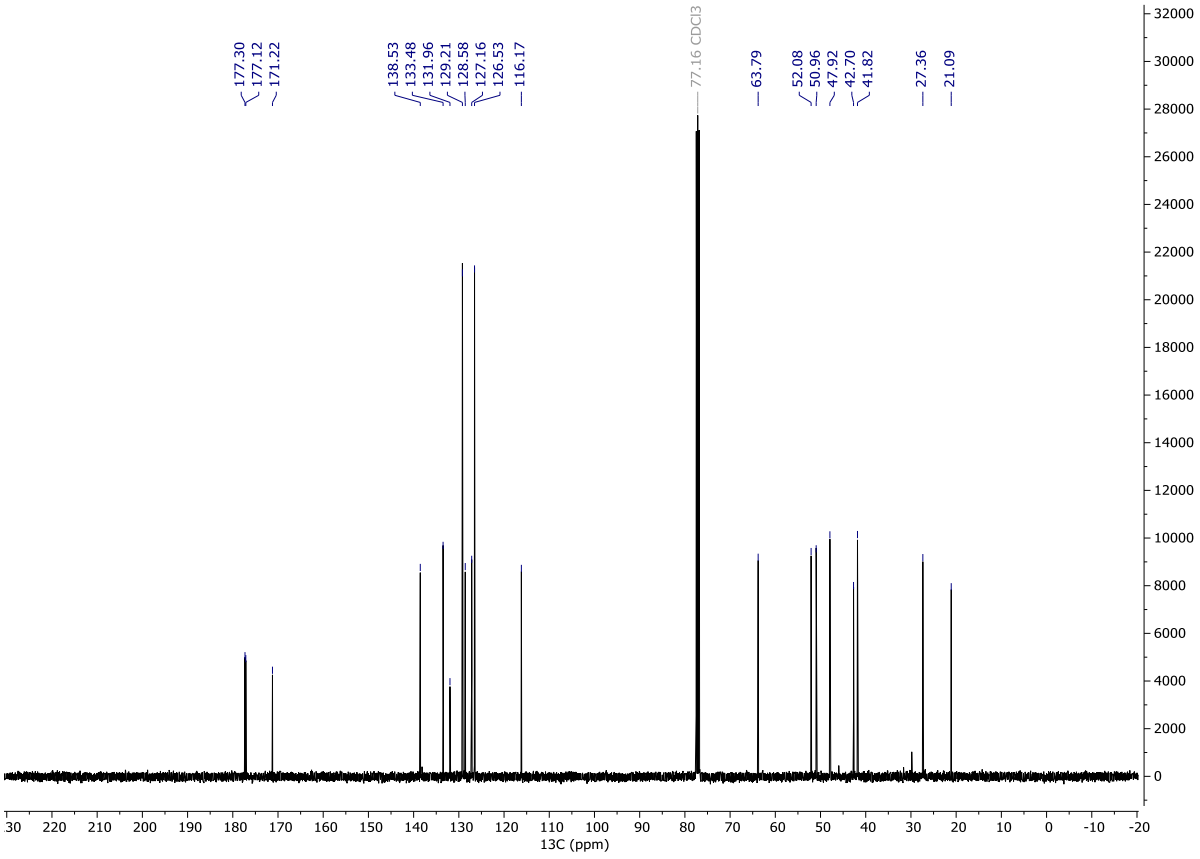
^{13}C NMR of **11** (101 MHz, $CDCl_3$):



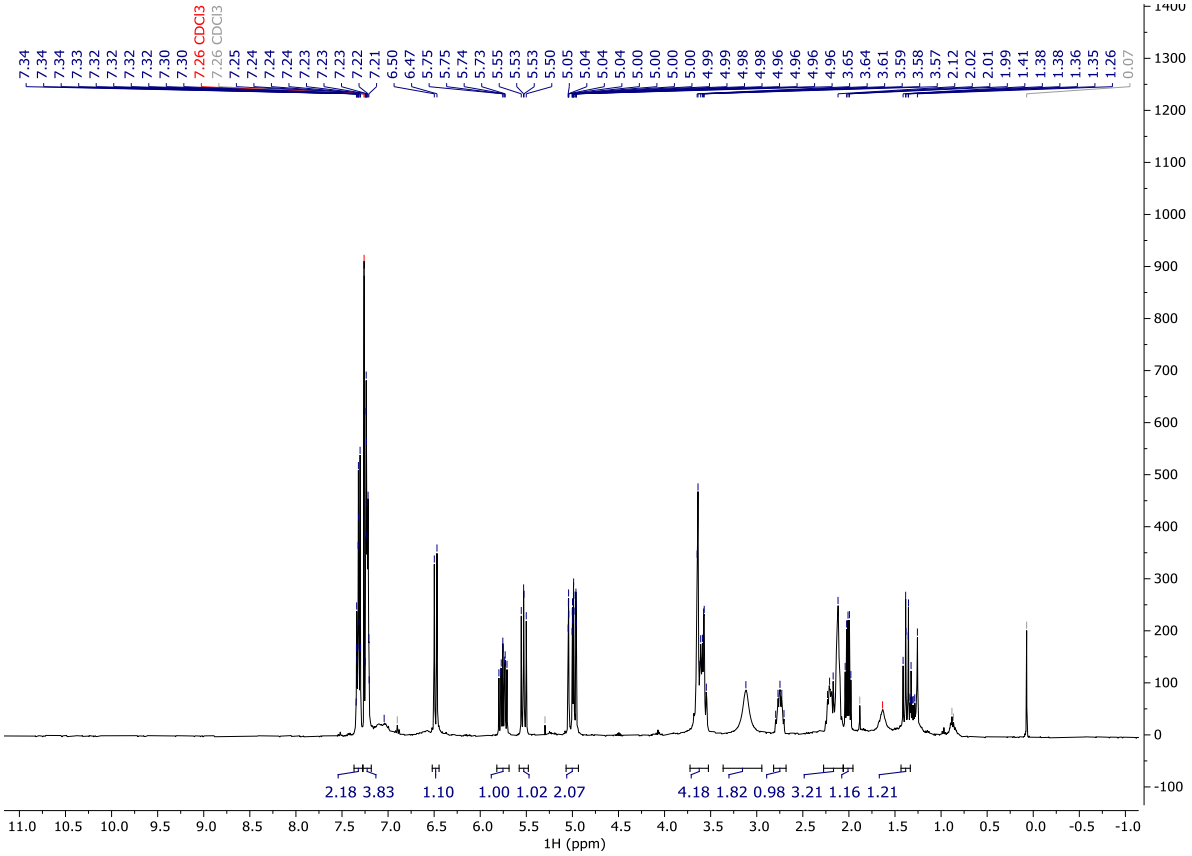
^{1}H NMR of **12** (400 MHz, $CDCl_3$):



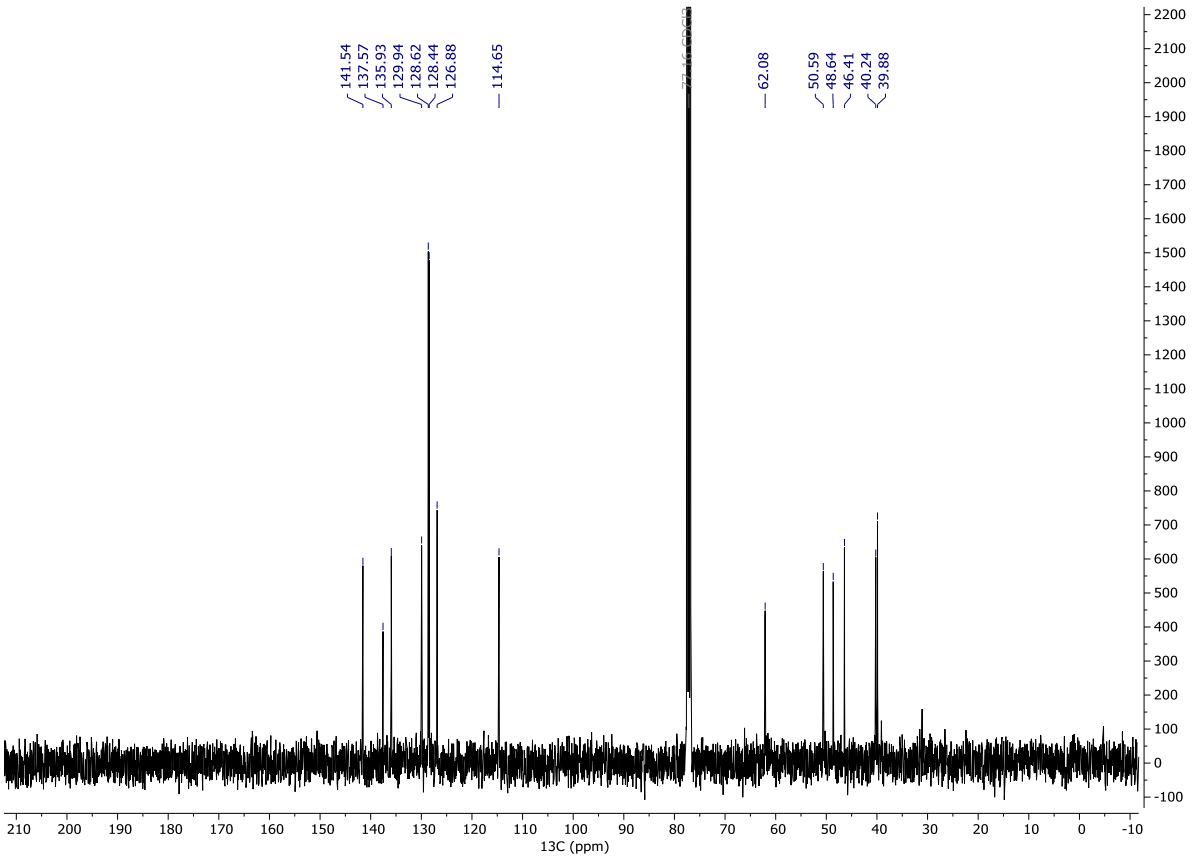
^{13}C NMR of **12** (101 MHz, $CDCl_3$):



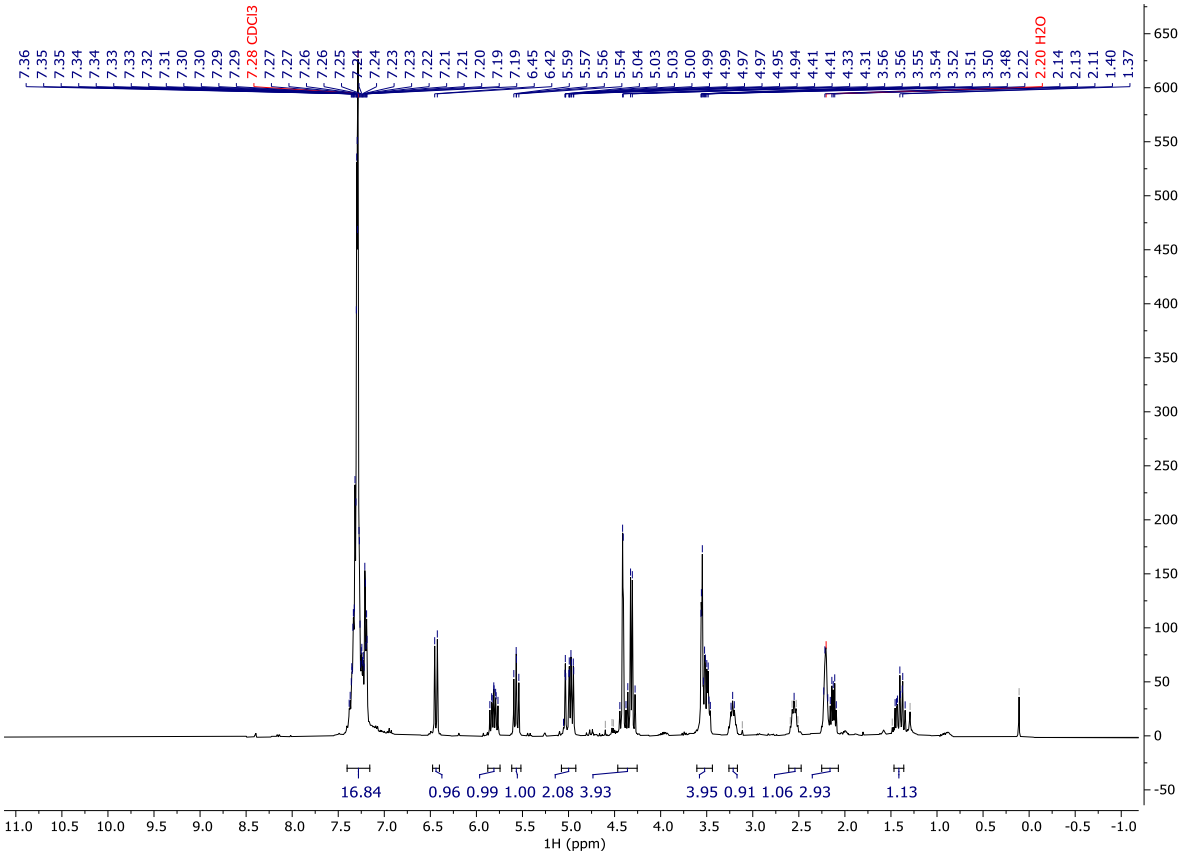
^{1}H NMR of **23** (400 MHz, $CDCl_3$):



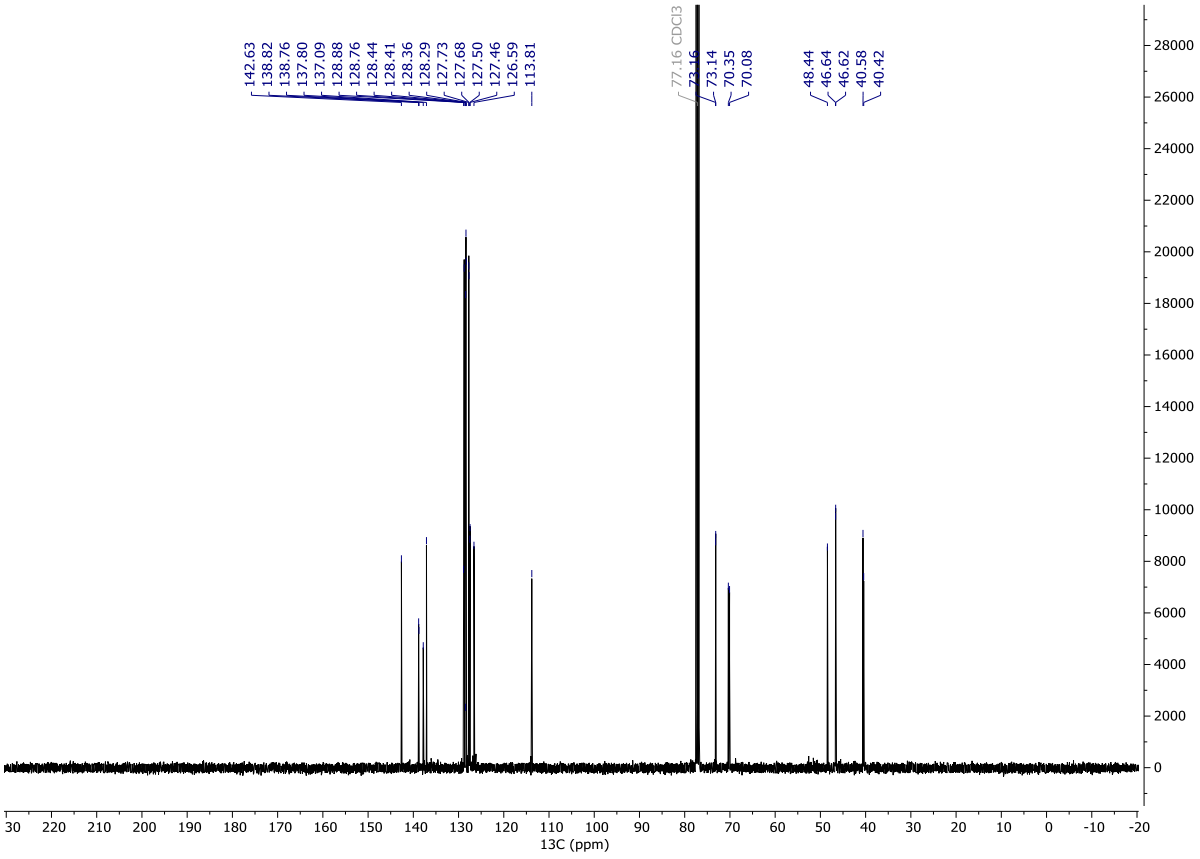
^{13}C NMR of **23** (101 MHz, $CDCl_3$):



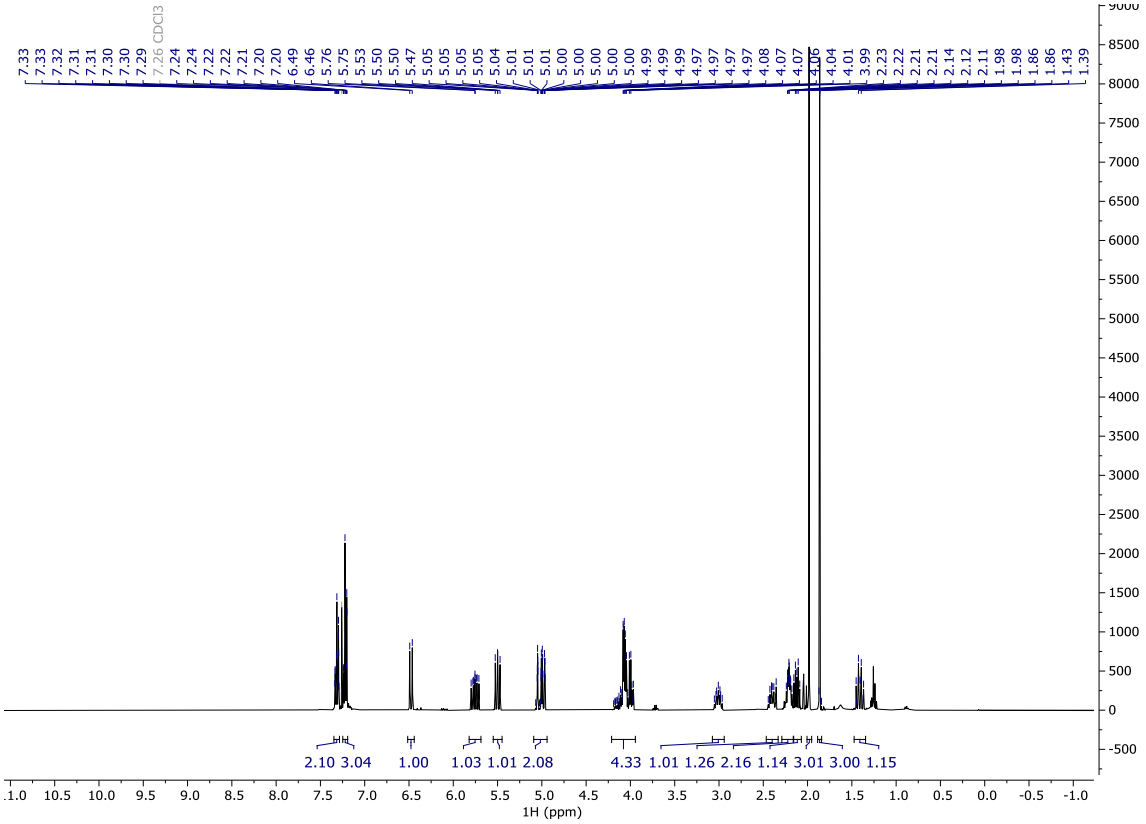
^{1}H NMR of **24** (400 MHz, $CDCl_3$):



^{13}C NMR of **24** (101 MHz, $CDCl_3$):



^{1}H NMR of **25** (400 MHz, $CDCl_3$):



^{13}C NMR of **25** (101 MHz, $CDCl_3$):