Supporting Information
© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2019

Bimolecular Cross-Metathesis of a Tetrasubstituted Alkene with Allylic Sulfones

Rishi R. Sapkota, Jacqueline M. Jarvis, Tanner M. Schaub, Marat R. Talipov, and Jeffrey B. Arterburn*©201x The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.
**Table of Contents**

Supplementary Experimental Procedures ........................................................................1
General Considerations ....................................................................................................1

Synthesis of (1a) ............................................................................................................1
Synthesis of (1b) ............................................................................................................1
Synthesis of allylic sulfide (1c) ....................................................................................2
Synthesis of allylic sulfone (1d) ..................................................................................2

General procedure(I) for homodimerization of 1b,1c and 1d ........................................8

General procedure(II) for cross-metathesis reactions of (1b,1c and 1d) with trisubstituted alkene ....9

Vinyl (1b) and 2-methyl-2-butene (1S) cross-metathesis: ............................................9
Sulfide (1c) and 2-methyl-2-butene (1S) cross-metathesis: ..........................................11
Sulfone (1d) and 2-methyl-2-butene (1S) cross-metathesis: .........................................12
Sulfone (1d) and citral (2S) cross-metathesis: .............................................................14

Sulfone (1d) and squalene (3S) cross-metathesis: .......................................................15

General procedure(III) for cross-metathesis reactions of (1c and 1d) with tetrasubstituted alkene ...........16

Sulfide (1c) and 2,3-dimethyl-2-butene (4S) cross-metathesis ....................................16
Sulfone (1d) and 2,3-dimethyl-2-butene (4S) cross-metathesis ....................................17
Methyl allyl sulfone (12) and 2,3-dimethyl-2-butene (4S) cross-metathesis .....................18

Phenyl allyl sulfone (15) and 2,3-dimethyl-2-butene (4S) cross-metathesis .....................18

1-(allyloxy)-4-methoxybenzene (18) and 2,3-dimethyl-2-butene (4S) cross-metathesis ..........18

Computational details ..................................................................................................19

Validation of the computational model ........................................................................20

Hg(II) –2,3-dimethyl-2-butene (4S) initiation reaction evaluation ....................................22

Reaction of allylsulfone carbene and 2,3-dimethyl-2-butene (4S) ...................................31

Reaction of allylsulfide carbene and 2,3-dimethyl-2-butene (4S) ...................................40

NMR Spectra of synthetic compounds .........................................................................49-69

1H NMR of 1a ................................................................................................................49
19F NMR of 1a ................................................................................................................49
13C NMR of 1a ................................................................................................................50
1H NMR of 1b ................................................................................................................50
19F NMR of 1b ................................................................................................................51
13C NMR of 1b ................................................................................................................51
1H NMR of 1c ................................................................................................................52
19F NMR of 1c ................................................................................................................52
13C NMR of 1c ................................................................................................................53
1H NMR of 1d ................................................................................................................53
19F NMR of 1d ................................................................................................................54
13C NMR of 1d ................................................................................................................54
1H NMR of 2d ................................................................................................................55
19F NMR of 2d ................................................................................................................55
13C NMR of 2d ................................................................................................................56
SUPPORTING INFORMATION

\[ ^1H\text{ NMR of } 4b \] ................................................................. 56
\[ ^13C\text{ NMR of } 4c \] ................................................................. 59
\[ ^19F\text{ NMR of } 4b \] ................................................................. 57
\[ ^1H\text{ NMR of } 4c \] ................................................................. 58
\[ ^19F\text{ NMR of } 4c \] ................................................................. 60
\[ ^13C\text{ NMR of } 4c \] ................................................................. 59
\[ ^1H\text{ NMR of } 4d \] ................................................................. 60-61
\[ ^13C\text{ NMR of } 4d \] ................................................................. 61
\[ ^1H\text{ NMR of } 5d \] ................................................................. 62
\[ ^13C\text{ NMR of } 5d \] ................................................................. 62
\[ ^19F\text{ NMR of } 5d \] ................................................................. 63
\[ ^1H\text{ NMR of } 6d \] ................................................................. 64
\[ ^13C\text{ NMR of } 6d \] ................................................................. 64
\[ ^19F\text{ NMR of } 6d \] ................................................................. 65
\[ ^1H\text{ NMR of } 13 \] ................................................................. 66
\[ ^13C\text{ NMR of } 13 \] ................................................................. 66
\[ ^1H\text{ NMR of } 14 \] ................................................................. 67
\[ ^13C\text{ NMR of } 14 \] ................................................................. 67
\[ ^1H\text{ NMR of } 16 \] ................................................................. 68
\[ ^13C\text{ NMR of } 16 \] ................................................................. 68
\[ ^1H\text{ NMR of } 17 \] ................................................................. 69
\[ ^1H\text{ NMR of } 18 \] ................................................................. 69
\[ ^1H\text{ NMR of mixture of } 18 \text{ and } 19 \] ................................. 70

References .................................................................................. 71

List of Schemes

Scheme 1 Synthesis of metathesis probes ........................................ 1
Scheme 2 Homodimerization reaction of the metathesis probes ........ 9
Scheme 3 Reaction of HG(II) and 2,3-dimethyl-2-butene (4S) ......... 22
Scheme 4 Reaction of allylsulfone carbene and 2,3-dimethyl-2-butene(4S) ................................................................. 31
Scheme 5 Reaction of allylsulfide carbene and 2,3-dimethyl-2-butene (4S) .............................................................................. 40

List of Figures

Figure S1. Normalized fluorescence and absorption spectra of 1a in 1-octanol ................................................................. 4
Figure S2. Normalized fluorescence/absorption spectra of 1b in 1-octanol ................................................................. 5
Figure S3. Normalized absorption/fluorescence spectra of 1c 1-octanol ................................................................. 6
Figure S4. Normalized absorption/fluorescence spectra of 1d in 1-octanol ................................................................. 7
Figure S5 LC-UV-MS chromatogram of (1b) and 2-methyl-2-butene (1S) cross-metathesis ................................................................. 10
Figure S6 Relative abundance of total peak area for (1b) and 2-methyl-2-butene (1S) cross-metathesis .................. 10
Figure S7 LC-UV-MS chromatogram of (1c) and 2-methyl-2-butene (1S) cross-metathesis ................................................................. 11
Figure S8 Relative abundance of total peak area for (1c) and 2-methyl-2-butene (1S) cross-metathesis .................. 12
Figure S9. LC-UV-MS chromatogram of allylic sulfone (1d) and 2-methyl-2-butene (1S) cross-metathesis reaction ................................................................. 13
Figure S10. Relative abundance of total peak area for allylic sulfone (1d) and 2-methyl-2-butene (1S) cross-metathesis ................................................................. 13
Figure S11. Cross-metathesis of 2d with 2-methyl-2-butene (1S) .............................................................................. 14
List of tables

Table S1. Photophysical properties of the compounds ................................................................. 3
Table S2. RP-LC gradients for separation of metathesis probes reaction products .......................... 8
Table S3. Comparison of the structural parameters of HG(II) pre-catalyst, obtained by X-ray crystallography and DFT calculations ............................................................. 20
**Experimental Procedures**

**General Considerations**

Unless otherwise noted, all operations were performed in a fume hood using oven-dried (135 °C) glassware with distilled and degassed solvents under an atmosphere of purified dry nitrogen gas. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories. ²H, ¹³C, and ¹⁹F NMR spectra were recorded on a 300 MHz Oxford NMR spectrometer. ¹H NMR chemical shifts are reported in ppm from tetramethylsilane referenced to the internal standard (CDCl₃: δ = 7.27 ppm, DMSO-d₆: δ = 2.50 ppm). Data reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ¹³C NMR chemical shifts are reported referenced in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃: δ = 77 ppm, DMSO-d₆: δ = 39.5). ¹⁹F NMR chemical shifts are reported with respect to added internal standard C₆F₆ (δ = -164.9 ppm). Preparative column chromatography was carried out using pre-packed silica cartridges (4g) in a Combiflash chromatograph. High performance liquid chromatography was conducted using an Agilent 1100 LC system (Agilent Technologies, Santa Clara, CA) equipped with a diode array detector (DAD). High resolution mass spectrometry was performed on a hybrid linear ion trap 7 Tesla Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Thermo Fisher, San Jose, CA), or an Orbitrap Fusion Mass Spectrometer (Thermo Fisher, San Jose, CA) at the New Mexico State University Chemical Analysis and Instrumentation Laboratory.

**Synthesis of 2-(9H-fluoren-9-ylidene)-3,3-difluoro-6-ido-2,3-dihydro-[1,2,4,3]triazaborolo[4,5-a]pyridin-2-ium-3-uide (1a)**

2-Hydrazinyl-5-iodopyridine[¹] (1.17 g, 5 mmol) was combined with 9-fluorenone (0.9 g, 5 mmol) in ethanol and refluxed for 4h to yield the hydrazone as yellow colored solid (1.78 g, 4.56 mmol, 90%). The hydrazone ([Z]-2-(9H-fluoren-9-ylidene) hydrazono)-5-ido-1,2-dihydropyridine (1a) was used directly without further purification. To a mixture of hydrazone: (Z)-2-(9H-fluoren-9-ylidene) hydrazono)-5-ido-1,2-dihydropyridine (0.397 g, 1 mmol) and BF₃·EtO (0.705 g, 5 mmol) in dry toluene (5 mL) was added DBU (0.33 g, 2.2 mmol) and heated at about 90 °C for 8h. Volatiles were removed in vacuo. The residue was dissolved in dichloromethane (25 mL), washed with water, the organic layer was separated, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with hexanes/EtOAc (70:30) eluent to isolate the product 1a (0.426 g, 96 %) as a red solid. RF = 0.39 (20:80, EtOAc: Hexane); ¹H NMR (300 MHz, CDCl₃): δ 8.98 (d, J =7.78 Hz, 1H), 8.37 (d, J =7.78 Hz, 1H), 7.79 (s, 1H), 7.60 (dd, J = 9.24, 1.91 Hz, 1H), 7.61-7.56 (m, 2H), 7.44 (dt, J = 7.48, 1.17 Hz, 1H), 7.38 (dt, J = 7.48, 1.03 Hz, 1H), 7.32 (dt, J = 7.63, 1.32 Hz, 1H), 7.28 (dt, J = 5.72, 1.17 Hz, 1H), 6.73 (d, J = 9.39 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) 159.2, 156.3, 150.7, 148.4, 141.84, 141.71, 141.09, 132.6, 132.1, 131.6, 131.1, 128.6, 128.5, 126.6 (t, J = 8.98 Hz, 1C), 120.1, 119.7, 115.2, 70.2; ¹⁹F NMR (300 MHz, CDCl₃): δ = -149.09 (q, J = 28 Hz, 2F). FT-IR (solid): 3058.6, 2923.68, 1630.59, 1608.41, 1520.63, 1471.48, 1443.52, 1407.84, 1358.66, 1299.84, 1100.24, 1074.20, 1034.67, 1016.35; UV-Vis (octanol) λmax: 537 nm, ε = 40,100 M⁻¹cm⁻¹; λmin: 572nm; Φ = 0.80. Log Pow = 0.79. HRMS (m/z): calcd for [M+H]+ C₁₈H₁₂BF₂N₃: 446.0167; found: 446.0162.

**Synthesis of 2-(9H-fluoren-9-ylidene)-3,3-difluoro-6-vinyl-2,3-dihydro-[1,2,4,3]triazaborolo[4,5-a]pyridin-2-ium-3-uide (1b)**

To bis(dicyclohexylamino)palladium acetate (7 mg, 0.04 mmol), 0.5 mL of dioxane was added, followed by vinyl pinacolboronate (135 µL, 0.8 mmol), 1a (178 mg, 0.4 mmol) and cesium carbonate (260 mg, 0.8 mmol)[²]. The reaction mixture was heated at 80 °C for 7h. The reaction mixture was diluted with 20 mL of diethyl ether and washed with 20 mL of 20% HCl and 20 mL of water. The organic layer was separated, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography eluting with EtOAc/hexane (5:95) to obtain the product 1b as a red solid (106 mg, 75%). RF = 0.48 (10:90, EtOAc: hexane); ¹H NMR (300 MHz,
Synthesis of 6-(allylthio)-2-(9H-fluoren-9-ylidene)-3,3-difluoro-2,3-dihydro-[1,2,4,3]triazaborolo[4,5-a]pyridin-2-ium-3-uide (1c)

Following the literature procedure the C-S coupling was carried out as follows: [10] The iodide 1a (178 mg, 0.4 mmol), Pd2dba3 (36 mg, 10 mol%), DPPP (44 mg, 20 mol%), allyl mercaptan (96 μL, 1.2 mmol) and N,N-diisopropyl amine (76 μL, 0.44 mmol) were combined in a sealed tube under an atmosphere of nitrogen. The reaction mixture was heated at 110 °C in toluene (0.1 M) for 7h. The reaction was cooled to room temperature and diluted with 20 mL of ether, washed with 20 mL of water and 20 mL of 1 M HCl solution. The organic layer was separated, dried over Na2SO4, and concentrated in vacuo. The residue was purified by column chromatography eluting with EtOAc/hexane (1:99) to obtain the product 1c as a red solid (106 mg, 72%). Rf = 0.48 (30:70, EtOAc/hexane); 1H NMR (300 MHz, CDCl3): δ 8.97 (d, J = 7.78 Hz, 1H), 8.39 (d, J = 10.56 Hz, 1H), 4.96 (d, J = 17.02 Hz, 1H); 13C NMR (75 MHz, CDCl3) 159.9, 150.2, 147.2, 141.7, 141.6, 140.5, 133.2, 132.4, 132.2, 132.0, 131.5, 131.1, 128.6, 128.4, 128.5 (t, J = 9.21 Hz, 1C), 120.0, 119.7, 118.5, 116.2, 113.4, 40.0; 19F NMR (282 MHz, CDCl3): δ -149.45 (q, J = 30.34 Hz, 2F). FT-IR (solid): 3068.32, 2918.86, 1761.41, 1608.41, 1544.30, 1528.38, 1500.41, 1157.13, 1117.59, 1099.27, 1080.95; UV-Vis (octanol) λmax: 537 nm, Φ = 34,200 M–cm–1; λem: 618 nm; Φf = 0.06. Log Pow = 1.43. HRMS/(m/z): calcd for [M+H]+ C26H21BF2N3S: 392.12043; found: 392.11995.

Synthesis of 6-(allylsulfonyl)-2-(9H-fluoren-9-ylidene)-3,3-difluoro-2,3-dihydro-[1,2,4,3]triazaborolo[4,5-a]pyridin-2-ium-3-uide (1d)

Oxone (230 mg, 0.75 mmol) in water (1.5 mL) was added to a cooled (0 °C) solution of the allylic sulfide 1c (98 mg, 0.25 mmol) in acetone (3.0 mL). The reaction mixture was stirred at room temperature for 3h. [11] The reaction mixture was diluted with dichloromethane (15 mL), washed with water, the organic layer was separated, dried over Na2SO4, and concentrated under reduced pressure. The residue was purified by column chromatography eluting with dichloromethane to isolate the product 1d as a red solid (75 mg, 0.177 mmol, 71%). Rf = 0.18 (30:70, EtOAc/hexane); 1H NMR (300 MHz, CDCl3): δ 8.88 (d, J = 7.78 Hz, 1H), 8.34 (d, J = 7.61 Hz, 1H), 8.34 (d, J = 8.36 Hz, 1H), 8.09 (bs, 1H), 7.63–7.27 (m, 7H), 6.82 (dd, J = 9.39, 3.37 Hz, 1H), 5.96–5.81 (m, 1H), 5.47 (dd, J = 10.12, 2.93 Hz, 1H), 5.30–5.29 (m, 1H), 3.84 (dd, J = 7.68, 2.64 Hz, 2H); 13C NMR (75 MHz, CDCl3) 159.9, 154.0, 142.4, 142.4, 140.3, 137.8, 133.7, 132.9, 132.8, 131.9, 130.5, 128.8, 127.7, 127.3 (t, J = 9.21 Hz, 1C), 125.4, 124.4, 120.7, 120.2, 119.9, 113.3, 61.0; 19F NMR (282 MHz, CDCl3): δ -148.45 (q, J = 28.61 Hz, 2F). FT-IR (solid): 3078.93, 2926.57, 1636.37, 1609.37, 1528.38, 1500.41, 1422.30, 1454.13, 1161.95, 1139.77, 1016.35; UV-Vis (octanol) λmax: 507 nm, Φ = 24,615 M–cm–1; λem: 531 nm; Φf = 0.13. Log Pow = 2.00. HRMS/(m/z): calcd for [M+H]+ C26H17BF2N3S: 424.11026; found: 424.10981.
## Table S1 Photophysical properties of the compounds

| SN | $\lambda_{max}$ | $\lambda_{emis}$ | Stoke's shift | Absorptivity $\epsilon$ | Quantum Yield | Brightness |
|----|-----------------|-----------------|---------------|------------------------|--------------|------------|
| 1a | 537             | 560             | 23            | 38,250                 | 0.87         | 33,277     |
| 1b | 537             | 601             | 64            | 33,500                 | 0.18         | 6,030      |
| 1c | 531             | 618             | 87            | 34,200                 | 0.06         | 2,200      |
| 1d | 507             | 531             | 24            | 24,600                 | 0.13         | 3,200      |
Figure S1. Normalized fluorescence and absorption spectra of 1a in 1-octanol solution. 1a has a Stoke's shift of 35 nm and a $\Phi_f = 0.80$ when excited at 520 nm. A calculated $\varepsilon = 40,100 \text{ M}^{-1} \text{cm}^{-1}$, with a $\lambda_{\text{max}} = 537 \text{ nm}$, $\lambda_{\text{em}} = 570 \text{ nm}$ with brightness = 32,100.
Figure S2. Normalized fluorescence/absorption spectra of 1b in 1-octanol reveal a Stokes shift of 58nm, $\lambda_{\text{max}} = 539\text{nm}$ and $\lambda_{\text{em}} = 601\text{nm}$. $F_0 = 0.18$ when excited at 530nm.
Figure S3. Normalized absorption/fluorescence spectra of 1c 1-octanol. Stoke’s shift is 86nm with Φf of 0.06, when excited at 520nm. A calculated ε = 34,200 M⁻¹ cm⁻¹, with a λmax = 531nm and λem = 617nm.
Figure S4. Normalized absorption/fluorescence spectra of 1d in 1-octanol. The Stoke's shift is 24 nm with $\Phi_f = 0.13$, when excited at 490 nm. A calculated $\varepsilon = 24,600$ M$^{-1}$cm$^{-1}$, with a $\lambda_{\text{max}} = 507$ nm and $\lambda_{\text{em}} = 531$ nm.
## Table S2. RP-LC gradients for separation of metathesis probes reaction products.

|                  | Time | A       | B       |
|------------------|------|---------|---------|
|                  |      | H$_2$O 0.1% formic acid | CH$_3$CN 0.1% formic acid |
| Citral           |      |         |         |
|                  | 0    | 50      | 50      |
|                  | 5    | 30      | 70      |
|                  | 25   | 25      | 75      |
|                  | 30   | 1       | 99      |
| Geranyl Acetone  | 0    | 50      | 50      |
|                  | 5    | 20      | 80      |
|                  | 25   | 1       | 99      |
|                  | 35   | 1       | 99      |
| Q10              | 0    | 50      | 50      |
|                  | 5    | 20      | 80      |
|                  | 15   | 10      | 90      |
|                  | 50   | 1       | 99      |
|                  | 200  | 1       | 99      |
| RS-VII-133       | 0    | 50      | 50      |
| RS-VII-144       | 10   | 30      | 70      |
| RS-VII-145       | 55   | 10      | 90      |
|                  | 55.1 | 1       | 99      |
|                  | 60   | 1       | 99      |
| RS-VII-118       | 0    | 50      | 50      |
|                  | 5    | 20      | 80      |
|                  | 30   | 10      | 90      |
| RS-VII-58        | 0    | 50      | 50      |
|                  | 5    | 20      | 80      |
|                  | 35   | 10      | 90      |
|                  | 40   | 1       | 99      |
General procedure (I) for homodimerization of 1b, 1c and 1d:

The metathesis probe (0.05 mmol), HG(II) catalyst (1.5 mg, 0.0025 mmol) and dichloromethane (1 mL, 0.5M) were combined in a flask under an atmosphere of nitrogen and heated to reflux for the specified time. The reaction progress was monitored by TLC. The product distributions were analyzed by HPLC-MS and NMR.

Homodimerization of 1b:

Following the general procedure (I), homodimerization of the vinyl probe (1b) was attempted but only trace amounts of the homodimer 2b, were observed. Extending the reaction time to 12 h resulted in decomposition of 1b that produced uncharacterized oligomeric products.

Homodimerization of 1c:

Following the general procedure (I), allylic sulfide probe (1c) was heated for 2h, resulting in a dark solution and fine precipitate. The solids were filtered to afford the homodimer 2c (17 mg, 0.022 mmol, 90%). Due to very poor solubility of 1c we were unable to obtain a high resolution 13C NMR spectrum. 1H NMR (300 MHz, CDCl3) δ 3.35 (d, J = 1.17 Hz, 4H), 5.42 (d, J = 6.46 Hz, 2H), 6.88 (s, 1H), 6.83 (s, 1H), 7.31 – 7.53 (m, 7H), 7.53 – 7.67 (m, 5H), 8.41 (s, 1H), 8.37 (s, 1H), 8.98 (d, J = 8.22 Hz, 2H); HRMS (m/z): calcd for [M+H]+ C84H88N2O2S2B2F2; 755.2017; found: 755.2009.

Homodimerization of 1d:

Following the general procedure (I), 1d was heated for 2h, resulting in a dark solution with orange precipitate. The solids were filtered to afford the homodimer 2d (18 mg, 0.022 mmol, 91%). Due to very poor solubility of 1d we were unable to obtain a high resolution 13C NMR spectrum. 1H NMR (300 MHz, DMSO-d6) δ 8.88 (d, J = 7.7 Hz, 2H), 8.31 – 8.18 (m, 3H), 7.85 (dd, J = 10.6, 8.5 Hz, 5H), 7.53 (q, J = 7.8 Hz, 4H), 7.35 (td, J = 8.0, 3.5 Hz, 4H), 7.14 (d, J = 9.5 Hz, 2H), 5.88 – 5.76 (m, 2H), 4.45 – 4.27 (m, 4H); 13C NMR (50 MHz, DMSO-d6) δ 160.03, 152.59, 141.79, 141.66, 139.78, 139.34, 134.20, 133.22, 132.33, 131.01, 129.76, 129.15, 128.74, 126.82, 126.36, 122.55, 121.32, 120.91, 113.54, 57.86; 19F NMR (282 MHz, DMSO-d6) δ -147.18, -147.37. HRMS (m/z): calcd for [M+Na]+ C86H98N2O2S2B2F2Na: 841.16257; found: 841.16334.

General procedure (II) for cross metathesis reactions of 1b, 1c, 1d with 2-methyl-2-butene (1S):

The compound (1b, 1c, 1d: 0.05 mmol), HG(II) catalyst (1.5 mg, 0.0025 mmol) and dichloromethane and heated at 40 °C. The product distributions were analyzed at 30 minutes and 8h, respectively. An aliquot (50 µL) of the reaction mixture was passed through a short column of silica gel (800 mg) eluted with dichloromethane and the colored fractions were collected and analyzed as a mixture by LC-MS. The respective quantification histogram and the LC chromatogram are shown for each product mixture. The trisubstituted products (4b) were isolated and characterized by HPLC-MS, NMR spectroscopy and mass spectrometry.

Vinyl probe (1b) and 2-methyl-2-butene (1S) cross metathesis:

Following the general procedure II, after 8h reaction time compound 4b was isolated by column chromatography eluting with EtOAc/hexane (1:99) to yield a red colored solid (15 mg, 0.04mmol, 40%). Rf = 0.25 (5.95, EtOAc/hexane). 1H NMR (300 MHz, CDCl3) δ 8.05 (d, J = 7.63 Hz, 1H), 8.43 (d, J = 7.63 Hz, 1H), 7.69-7.60 (m, 2H), 7.52-7.29 (m, 6H), 6.92 (d, J = 9.10 Hz, 1H), 6.01 (s, 1H), 1.92 (d, J = 1.17 Hz, 3H), 1.88(d, J = 1.17 Hz, 3H); 13C NMR (50 MHz, CDCl3) δ 19.5, 26.76, 112.84, 119.58, 119.78, 119.95,
Based on the LC-MS UV detection, at 30 min 3b was formed as major product (66%) and 4b as minor (27%). The products at 8h are 3b 52% and 4b 40 % respectively and traces of homodimer 2b were detected.

Figure S5 HPLC-UV-MS chromatogram of (1b) and 2-methyl-2-butene (1S) cross reaction products after 30 min and 8h reaction times. UV detection at 525 nm was used for relative quantitation of reaction products and HRMS detection was used to identify the reaction products.

Figure S6 Relative abundance of total peak area for (1b) and 2-methyl-2-butene (1S) cross- metathesis reaction products after 30 min and 8h reaction times. UV detection at 525 nm was used for relative quantitation of reaction products and HRMS detection was used to identify the reaction products.
Sulfide probe (1c) and 2-methyl-2-butene(1S) cross-metathesis:

Following the general procedure II, after 8h reaction time compound 4c was isolated by column chromatography eluting with EtOAc/hexane (10:90) to yield a dark red solid (25 mg, 0.059 mmol, 61%). Rf = 0.59 (30:70, EtOAc/ hexane); \(^1\)H NMR (300 MHz, CDCl$_3$); δ 9.03 (d, \(J = 6.75\) Hz, 1H), 8.41 (d, \(J = 7.78\) Hz, 1H), 8.0 (s, 1H), 7.69 - 7.28 (m, 8H), 6.85 (d, \(J = 8.80\) Hz, 1H), 5.25 (tt, \(J = 7.48, 1.32\) Hz, 1H), 3.35 (d, \(J = 7.34\) Hz, 2H), 1.75 (s, 3H), 1.42(s, 3H); \(^1^3\)C NMR (75 MHz, CDCl$_3$) 159.8,150.0, 147.6, 141.7, 141.5, 140.9, 137.3, 134.6, 131.4, 131.9, 131.4, 128.5, 128.4, 126.4 (t, \(J = 9.02\) Hz, 1C), 124.3, 120.0, 119.7, 119.0, 116.5, 113.1, 34.7, 25.5, 17.4; \(^1^9\)F NMR (282 MHz, CDCl$_3$); δ -149.45 (q, \(J = 30.34\) Hz, 2F). HRMS/(m/z): calcd for [M+H]$^+$ C$_{23}$H$_{21}$BF$_2$N$_3$S: 420.15173; found: 420.15155. Based on the HPLC-MS UV detection, at 30 minutes 3c was formed as a minor product (24%) and 4c as major product (57%). The product ratio at 8h was found 3c (17%) and 4c (61 %) respectively. Trace amounts of the homodimerization product 2c were observed at 8h (7%).
Sulfone (1d) and 2-methyl-2-butene (1S) cross-metathesis:

Following the general procedure II, after 8h reaction time compound 4d was isolated by column chromatography eluting with EtOAc/hexane (15:85) to yield an orange solid (44 mg, 0.098 mmol, 98%). Rf = 0.22 (30:70, EtOAc/ hexane; 1H NMR (300 MHz, CDCl3): δ 8.94 (d, J = 7.78 Hz, 1H), 8.38 (d, J = 7.63 Hz, 1H), 8.06 (d, J = 1.32 Hz, 1H), 7.66 (dd, J = 9.54, 2.05 Hz,1H), 7.59-7.55 (m, 2H), 7.50-7.30 (m, 4H), 6.87 (d, J = 9.54Hz, 1H), 5.28 (tt, J = 7.78, 1.47 Hz, 1H), 3.81 (d, J = 8.07 Hz, 2H), 1.81 (s, 3H), 1.50 (s, 3H); 13C NMR (75 MHz, CDCl3) 160.0, 154.9, 143.9, 142.5, 142.4, 140.3, 137.9, 133.7, 132.9, 132.0, 130.6, 128.9, 128.8, 127.3 (t, J = 9.26 Hz, 1C), 124.5, 120.8, 120.3, 120.0, 113.2, 110.3, 56.3, 25.8, 18.0; 19F NMR (282 MHz, CDCl3); δ -148.55 (q, J = 28.61 Hz, 2F). UV-Vis (octanol) λmax: 537 nm, ε= 40100 M⁻¹cm⁻¹; λem: 572 nm; Φf = 0.80. Log Po/w = 0.79. HRMS/(m/z): calcd for [M+H]⁺ C23H20BF2N3O2S: 452.14156; found: 452.14091. Based on the HPLC-MS UV detection, at 30 minutes 3d was formed as a minor product (25%) and 4d as major (72%). The product distribution at 8h contained trace amounts of 3d (1%) and the major produce 4d (98 %) respectively. No homodimerization product 2d was detected at 8h.
Figure S9. HPLC-UV-MS chromatogram of allyl sulfone (1d) and 2-methyl-2-butene (1S) cross-metathesis reaction products after 30 min and 8h reaction times. UV detection at 525 nm was used for relative quantitation of reaction products and HRMS detection was used to identify the reaction products.

Figure S10. Relative abundance of total peak area for allylic sulfone (1d) and 2-methyl-2-butene (1S) cross-metathesis reaction products after 30 min and 8h reaction times. UV detection at 525 nm was used for relative quantitation of reaction products and HRMS detection was used to identify the reaction products.
Secondary cross-metathesis of sulfone homodimer (2d) with 2-methyl-2-butene (2S)

The homodimer 2d (10 mg, 0.012 mmol), 2-methyl-2-butene 2S (142 μL, 1.22 mmol), HG(II) catalyst (0.4 mg, 0.0006 mmol) and dichloromethane (2 mL, 0.006M) were combined and heated at 40 °C. The aliquot at 30 min and 8h were analyzed.

Figure S11. Relative abundance of total peak area for allylic sulfone homodimer (2d) and 2-methyl-2-butene (1S) cross-metathesis reaction products after 30 min and 8h reaction times. UV detection at 525 nm was used for relative quantitation of reaction products and HRMS detection was used to identify the reaction products

Sulfone (1d) and citral (2S) cross-metathesis:

The allylic sulfone 1d (21 mg, 0.05 mmol), citral (94 μL, 0.05 mmol), HG(II) catalyst (1.5 mg, 0.0025 mmol) and dichloromethane (1 mL, 0.05M) were combined and heated to reflux at 40 °C for 1h. An aliquot of the reaction mixture was passed through a short column of silica gel (800 mg) and the colored fractions were collected and analyzed by HPLC-MS. The product distribution was quantified as shown in the Scheme 4. The remaining reaction mixture was purified by flash chromatography to isolate 5d (11 mg, 43%), 4d (7.5 mg, 24 %) and 2d (6.7 mg, 24 %) as orange solids. The spectral properties of 5d are as follows: R\textsubscript{f} = 0.44 (5:95, MeOH:DCM); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ = 9.98 (d, J = 7.8 Hz, 1 H), 8.94 (d, J = 7.8 Hz, 1 H), 8.36 (d, J = 7.9 Hz, 1 H), 8.19 - 7.98 (m, 1 H), 7.65 - 7.25 (m, 6 H), 6.88 (d, J = 9.5 Hz, 1 H), 5.87 (dd, J = 6.0, 12.8 Hz, 1 H), 5.79 - 5.49 (m, 2 H), 3.78 (d, J = 7.0 Hz, 2 H), 2.65 (t, J = 7.8 Hz, 1 H), 2.42 - 2.19 (m, 3 H), 2.19 - 2.10 (m, 2 H), 1.96 (s, 1 H); \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) δ = -149.83-149.52(m, 2F); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) δ = 191.1, 190.3, 162.1, 162.0, 160.0, 155.2, 142.6, 142.5, 140.5, 140.2, 139.9, 138.2, 137.7, 137.6, 133.9, 133.0, 132.0, 130.6, 128.9, 128.9, 128.7, 127.4(t, J = 8.83Hz, 1C), 120.6, 120.3, 120.0, 117.7, 117.3, 116.2, 113.5, 60.0, 59.9, 39.2, 31.6, 31.4, 29.9, 29.7, 24.9, 17.5.

None of the possible cross-metathesis products from reaction at the electron deficient α-β unsaturated alkene were detected. For comparison, an authentic sample of 6d was synthesized by an alternative route. The allylic sulfone 1d (21 mg, 0.05 mmol), acrolein (16.6 μL, 0.25 mmol), HG(II) catalyst (1.5 mg, 0.0025 mmol) and dichloromethane (1 mL, 0.05M) were heated to refluxed at 40 °C for 2h. The reaction mixture was passed through a pad of celite, volatiles were removed under reduced pressure, and the residue was purified by column chromatography. The compound 6d (17 mg, 75%) was isolated as an orange solid. R\textsubscript{f} = 0.51 (5.95, MeOH:DCM); \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) δ = 9.68 - 9.58 (m, 1 H), 8.97 - 8.83 (m, 1 H), 8.35 (d, J = 7.8 Hz, 1 H), 8.20 - 8.07 (m, 1 H), 7.64 - 7.22 (m, 9 H), 6.91 - 6.70 (m, 2 H), 6.37 - 6.18 (m, 1 H), 4.11 (d, J = 7.4 Hz, 2 H); \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) δ = -150.05-149.74 (m, 2F) ; \textsuperscript{13}C NMR (50MHz, CDCl\textsubscript{3}) δ = 191.7, 159.9, 156.0, 142.6, 142.6, 142.5, 140.7, 139.7, 139.3, 137.6, 137.0, 134.0, 133.8, 133.2, 133.2, 131.9, 130.5, 128.9, 128.9, 127.7, 127.5, 127.3, 126.8, 120.5, 120.4, 120.0, 113.9, 59.6
Figure S12. Cross-metathesis of 1d with citral. A) Cross-metathesis reactions were conducted using 1.0 equiv citral (2S), 1.0 equiv of 1d in dichloromethane (0.05M), 5 mol% HG(II) at 40 °C, monitored for 1h; B) HPLC chromatogram of reaction mixture; C) quantification of product distribution (%) by integration of UV chromatographic peaks at 505 nm. Product identities for chromatographic peaks were determined by accurate mass measurement and isotopic fine structure analysis provided by in-line high resolution mass spectrometry after UV detection.

**Sulfone (1d) and squalene (3S) cross-metathesis:**

The allylic sulfone (1d) (21 mg, 0.05 mmol), squalene (120 µL, 0.25 mmol), HG(II) catalyst (1.5 mg, 0.0025 mmol) and dichloromethane (1 mL, 0.05M) were combined and heated to refluxed at 40 °C for one hour. An aliquot of the reaction mixture was passed through a short column of silica gel and the colored fractions were collected and analyzed by HPLC-MS. The products were quantified as shown in Scheme 5. The remaining reaction mixture was concentrated and purified by column chromatography to isolate 4d (9 mg, 0.02 mmol, 40%).
General procedure (III) for cross-metathesis reactions with tetrasubstituted alkene 4S:

Each of the metathesis probes (0.05 mmol) were treated with 2,3-dimethyl-2-butene (4S) (177 µL, 1.5 mmol), HG(II) catalyst (1.5 mg, 0.0025 mmol), in 1,2-dichloroethane and heated at 60 °C for 4h. An aliquot of the reaction mixture was passed through a short column of silica gel and the colored fractions were collected and analyzed by HPLC-MS. The respective quantification histogram and the HPLC chromatogram are shown below.

Sulfide probe (1c) and 2,3-dimethyl-2-butene (4S) cross-metathesis:

Following the general procedure (III), the reaction of 1c and tetrasubstituted alkene 4S was carried out and the product 4c (5 mg, 0.011 mmol, 24.4%) and homodimer 2c (6 mg, 0.007 mmol, 31.3%) were detected.
Figure S15. Relative abundance of total peak area for allylic sulfide (1c) and 2,3-dimethyl-2-butene (4S) cross-metathesis reaction products after 30 min and 8h reaction times. UV detection at 525 nm was used for relative quantitation of reaction products and HRMS detection was used to identify the reaction products.

Sulfone probe (1d) and 2,3-dimethyl-2-butene (4S) cross-metathesis:

Following the general procedure (III), the reaction of 1d and 4S was carried out and the product 4d (59%) and homodimer 2d (31%) were detected. The reaction mixture was purified by flash chromatography to isolate 4d (12 mg, 0.027 mmol, 54%), and 2d (5 mg, 0.006 mmol, 30%) respectively. The chromatogram and the histogram associated with the products are shown below.

Figure S16. HPLC-MS chromatogram of the cross-metathesis reaction products from allylic sulfone (1d) and 2,3-dimethyl-2-butene (4S) after 30 min and 8h reaction times. UV detection at 525 nm was used for quantitation of reaction products and HRMS detection was used to identify the reaction products.
Figure S17. Relative abundance of total peak area for allylic sulfone (1d) and 2,3-dimethyl-2-butene (4S) cross-metathesis reaction products after 30 min and 8h reaction times. UV detection at 525 nm was used for relative quantitation of reaction products and HRMS detection was used to identify the reaction products.

Methyl allyl sulfone (12) and 2,3-dimethyl-2-butene (4S) cross-metathesis:

Following the general procedure (III), the methyl allyl sulfone (12) and the tetrasubstituted alkene (4S) cross-metathesis was carried out and the products 13 (3.7 mg, 0.025 mmol, 50%) and 14 (2.1 mg, 0.01 mmol, 40%) were isolated. The spectral data for each product are shown below.

3-methyl-1-(methylsulfonyl)but-2-ene (13)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 5.41 – 5.27 (m, 1H), 3.71 (ddt, $J = 8.1, 1.7, 0.9$ Hz, 2H), 2.81 (t, $J = 0.8$ Hz, 3H), 1.84 (q, $J = 1.1$ Hz, 3H), 1.75 (t, $J = 1.0$ Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 142.98, 110.92, 65.99, 39.30, 26.16, 18.50.

1,4-bis(methylsulfonyl)but-2-ene (14)

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 5.97 – 5.88 (m, 2H), 4.03 – 3.95 (m, 4H), 2.93 (s, 6H); $^{13}$C NMR (50 MHz, DMSO-d$_6$) $\delta$ 126.96, 57.06, 39.52.

Phenyl allyl sulfone (15) and 2,3-dimethyl-2-butene (4S) cross-metathesis:

Following the general procedure (III), the phenyl allyl sulfone (15) and the tetrasubstituted alkene (4S) cross-metathesis was carried out and the products 16 (5.2 mg, 0.025 mmol, 50%) and 17 (3.3 mg, 0.01 mmol, 40%) were isolated.

((3-methylbut-2-en-1-yl)sulfonyl)benzene (16)

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 7.87 – 7.45 (m, 2H), 7.75 - 7.45 (m, 3H), 5.20 (t, $J = 7.6$ Hz, 1H), 3.79 (d, $J = 8.0$ Hz, 2H), 1.72 (s, 3H), 1.31 (s, 3H) 

$^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 142.9, 138.7, 133.5, 128.9, 128.5, 110.4, 56.2, 25.8, 17.7.

1,4-bis(phenylsulfonyl)but-2-ene (17)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 7.4$ Hz, 4H), 7.62 (dt, $J = 32.5, 7.4$ Hz, 6H), 5.62 (d, $J = 5.0$ Hz, 2H), 3.82 – 3.73 (m, 4H).

The spectral properties of compound 17 were identical to the published values.$^{[2]}$
SUPPORTING INFORMATION

Phenylvinyl sulfone (18) and 2,3-dimethyl-2-butene (4S) cross-metathesis:

Following the general procedure (III), phenylvinyl sulfone 18 and tetrasubstituted alkene (4S) were subjected to the cross-metathesis reaction conditions and monitored over an extended 12 h period. Analysis of the composition of the reaction mixture by 300 MHz $^1$H-NMR showed only unreacted 18, and no trisubstituted cross metathesis product was detected.

1-(allyloxy)-4-methoxybenzene (19) and 2,3-dimethyl-2-butene (4S) cross-metathesis:

The allylic ether 1-(allyloxy)-4-methoxybenzene (19) was synthesized following the reported procedure,[9] and used as an additional model chalcogenide substrate for the cross metathesis with 2,3-dimethyl-2-butene (4S). The reaction was conducted following the general procedure III. The reaction mixture was purified by silica gel chromatography eluted with hexanes to remove the homodimerization product, catalyst and other impurities. The resulting major fraction consisted of unreacted 19 and trace amounts (~7%) of the trisubstituted cross metathesis product determined by integration of the characteristic peak for the methyl groups that appear as singlet at δ1.8 in the 300 MHz $^1$H-NMR (CDCl$_3$) (see spectrum page 70).[8]

Computational details

Electronic structure calculations were performed with the Gaussian 09 package, revision D01 or E01.[7] For the density functional theory (DFT) calculations, we used M06-L functional[9] and def2-SV(P) basis set[9] (for Ru, the 28 core electrons were treated using the effective core potential approach).[11] Solvent effects were evaluated using the implicit integral equation formalism polarizable continuum model (IEF-PCM, referred in the text as PCM)[11] with the dichloromethane solvent parameters. In all DFT calculations, ultrafine Lebedev’s grid was used with 99 radial shells per atom and 590 angular points in each shell. The wave function stability tests[12] were performed to ensure that the closed-shell singlet states were the solutions with the lowest energy. Tight cutoffs on forces and atomic displacement were used to determine convergence in geometry optimization procedure. Hessian matrices were calculated for the optimized structures to confirm absence of imaginary frequencies or presence of a single imaginary frequency for minima and transition states, respectively. The M06-L functional with def2-SV(P) basis was found to be effective for the HG(II) catalyst as shown by the small differences between the computed and X-ray data shown in Figure S15 and Table S3.

Results from the DFT calculations were further refined by the single-point calculations at the DLPNO-CCSD(T)/def2-TZVP level[13] using Orca v4.0 program[14] according to the following scheme[15]:

\[ H_{\text{DLPNO-CCSD(T)}} = E_{\text{DLPNO-CCSD(T)}} + (E_{\text{M06L}} - E_{\text{M06L}}) + H_{\text{M06L}} \tag{Eq. S1} \]

\[ G_{\text{DLPNO-CCSD(T)}} = E_{\text{DLPNO-CCSD(T)}} + (E_{\text{M06L}} - E_{\text{M06L}}) + G_{\text{M06L}} \tag{Eq. S2} \]

where $E_{\text{gas}}$ and $G_{\text{gas}}$ are the electronic energies in gas- and solvent phase from the DFT calculations, and enthalpic/entropic corrections $H_{\text{corr}}$ and $G_{\text{corr}}$ were calculated by DFT using the standard approximations of quantum harmonic oscillator (for the vibrational component of the partition functions), rigid rotor (for the rotational component), and particle-in-the box (for the translational component) for $T = 298.15$ K and $P = 1$ atm.

The reaction complex approach was used for the evaluation of the enthalpy/free energy changes along reaction coordinate in order to minimize the error in the calculated entropy contribution.[15,16]
Validation of the computational model

Figure S18. Equilibrium geometry of the HG(II) catalyst, calculated at the M06-L/def2-SV(P)+PCM(Dichloromethane) level of theory

Table S3. Comparison of the structural parameters of HG(II) pre-catalyst, obtained by X-ray crystallography and DFT calculations

| Structural parameter | X-ray a | DFT b | % Error |
|----------------------|---------|-------|---------|
| Bond lengths (Å)     |         |       |         |
| Ru(1) C(1)           | 1.82    | 1.84  | 1.09    |
| Ru(1) C(2)           | 1.98    | 1.97  | 0.50    |
| Ru(1) O(1)           | 2.26    | 2.34  | 3.50    |
| Ru(1) Cl(1)          | 2.32    | 2.4   | 3.40    |
| Ru(1) Cl(2)          | 2.34    | 2.41  | 2.90    |
| C(2) N(1)            | 1.35    | 1.35(6)| 0.44    |
| C(2) N(2)            | 1.35    | 1.36  | 0.74    |
| Bond angles (°)      |         |       |         |
| C(1) Ru(1) O(1)      | 79.3    | 77.9  | 1.7     |
| C(1) Ru(1) C(2)      | 101.6   | 102.7 | 1.1     |
| C(2) Ru(1) O(1)      | 176.2   | 179   | 1.5     |
| C(1) Ru(1) Cl(1)     | 100.16  | 99.9  | 0.3     |
| C(1) Ru(1) Cl(2)     | 100.16  | 97.5  | 2.6     |
| O(1) Ru(1) Cl(1)     | 86.8    | 85.4  | 1.7     |
| O(1) Ru(1) Cl(2)     | 85.3    | 84.2  | 1.3     |
| C(2) Ru(1) Cl(1)     | 90.9    | 93.7  | 3.1     |
| C(2) Ru(1) Cl(2)     | 96.6    | 96.5  | 0.0     |
Crystallographic data obtained from Garber et al.\textsuperscript{[7]}

Calculated at the M06-L/def2-SV(P)+PCM(MeCN) level of theory.

### Archive entries from the calculation files

The archive entries, formerly intended for the Browse Quantum Chemistry Database System, are organized as a simple list of data fields separated by backslash symbols, which is wrapped in 70-char text lines. The script ‘Parse.Archive.pl’, written in Perl, converts archive entry into human readable format. To use this script,

Check if Perl interpreter is installed on the system. To do this, run the command ‘perl –v’ in console. If console returns a message like ‘command not found’, please obtain and install a Perl interpreter (\texttt{www.perl.org/get.html}; Perl is Open Source software licensed under GNU GPL).

Save the script code, listed below, as a file named ‘Parse.Archive.pl’.

Select an archive entry of interest and save it as another file (e.g. ‘B-Xb.txt’).

Run the command ‘perl Parse.Archive.pl B-Xb.txt > B-Xb-parsed.txt’ in console. The parsed archive entry will be stored in the file ‘B-Xb-parsed.txt’ in this example. In some cases, absolute path to the Perl interpreter might need to be provided.

```
# --- Parse.Archive.pl ---
# Merge all strings in one line
my $s='';
while (<>) {chomp;$s .= $_}
$_ = $s;

# Some PDF viewers (like Mac OS’s Preview) might substitute
# 'end of line' symbols by the white space symbols,
# To remove these extra white spaces, please uncomment the following lines:
# my $str_length = 70;
# my $index = $str_length;
# while (length($_) > $index) {
#     substr $_,$index,1,'';
#     $index += $str_length;
# }

# Replace all backslashes by new-line symbols
s\:\:\n: g;

# Print the resulting output
print;
# --- END ---
```
HG(II) – 2,3-dimethyl-2-butene (4S) initiation reaction evaluation

Scheme 3 Reaction of HG(II) and 2,3-dimethyl-2-butene (4S) (tetrastubstituted alkene)

01. Initial complex

02.ts

03.pi

04.ts

05.MCB

06.ts

07.pi

09.finalcomplex

01.initialcomplex
null
Reaction of allylsulfone carbene and 2,3-dimethyl-2-butene (4S)
**01. initial complex chelated**

01. initial complex non-chelated

02. ts

03. pcomplex

06. MCB

04. ts

07. pl

09. final complex

Scheme 4 Reaction of allylsulfonecarbene and 2,3-dimethyl-2-butene(4S) (tetrasubstituted alkene)
Reaction of allylsulfide carbene and 2,3-dimethyl-2-butene (4S)
Scheme 5 Reaction of allylsulfidecarbene and 2,3-dimethyl-2-butene (tetrasubstituted alkene)

01.initialcomplex

02.ts

03.picomplex

04.ts

05.MCB

06.ts

07.pi

08.09.finalcomplex

- SUPPORTING INFORMATION -

01.initialcomplex

1/1\GINC-C01\Stability\RM06L\Gen\C30H44Cl2N2Ru1S1\RISHIRAMT\25-Nov-2017\#\# M06/L/chkbasis stable(opt) pop(nbo) scrf(check) guess(read) geo (allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)

Title

\C,0,-6.1619632257,-3.512273171,6.6916802107\C,0,-5.128424697,-3.4693872899,7.6346869668\C,0,-4.1578576638,-2.4693203086,7.5079731141\N,0,-5.243097132,-0.7122034515,4.4370688337\C,0,-4.5440753757,-0.75114408,1.2730366855\N,0,-4.8218560838,0.403590647,2.6032710968\C,0,-5.6171849671,3.3901243965\N,0,-6.1203595199,0.461146231,4.5217409196\Ru,0,-3.3833459442,-2.081466987,2.440034566\C,0,-3.6425363273,-3.4672089777,3.592824637\C,0,-4.1512510662,0.8214920441,1.4156519415\C,0,-2.8647846962,1.3928072687,1.5180952254\C,0,-2.2009302717,1.7346036666,0.3361311174\C,0,-2.7918415491,1.5695020293,-0.921235961\C,0,-4.1072216297,1.098013281,-0.974376761\C,0,-4.8119562196,0.7268853375,0.1752482251\C,0,-2.2575226388,1.7422768294,2.8419910547\C,0,-2.0244102399,1.8662025792,-2.1716344985\C,0,-6.2466649005,0.3144559013,0.0714673343\C,0,-7.3023443787,-2.7156502117,4.5869738698\C,0,-5.0327868854,-4.4954617097,8.7207833927\C,0,-3.135220552,-0.4837359717,6.3350529296\C,0,-1.2324944577,-1.3758061733,3.211459055\C,0,-5.0825224066,-2.7096024407,0.8745386881\H,0,-6.0354137788,0.9323546597,5.515280433\H,0,-7.1762270943,0.1581697406,4.3840909314\H,0,-4.981956846,2.1766463419,3.74728
SUPPORTING INFORMATION

74106V,H,0,-6.4280734355,1.774700977,2.7798714645\h,0,-1.188822005,2.1
55749753,0.403420648V,H,0,-4.6041795761,0.004019217,-1.949489926V,H,0,-3.
345075288,-2.4133940347,8.2447128452\h,0,-6.9328038969,-4.2896566733,
6.7749166522\h,0,-6.893063473,1.2046199475,6.1856031584\h,0,-6.417101
47146,-0.3335341566,-0.8041292224\h,0,-6.592410754,-0.223982974,0.962
7314166V,H,0,-1.1590251439,1.6650513698,2.8152298766\h,0,-2.5029460072,
.7904144745,3.1073375818\h,0,-2.6113923742,1.0127242592,3.665233222V,H,0,-2.
5183092896,-0.6227588279,5.4237826863\h,0,-3.5728665331,0.528406
8056,6.2260952628,5.7874830713,0.7003264695,3.9710504402,5.19100859
58\h,0,-0.9899039333,-4.1950932545,6.8509829593\h,0,-1.0923240055,-3.9
114105862,0.255288076V,C,0,-1.1502545475,-2.6616495902,-0.7545459797
V,C,0,-2.6062786738,-5.8089760033,-0.0732142977,0.0459166577,-4.335571
3047,1.1148672258\h,0,-2.2040323181,-2.1805990192,-1.2665546526\h,0,-0.
619617914,-1.6329826454,-0.0324943701,0.0,0.1921744338,-3.6456398667,
3.4998858211\h,0,0.1,0.012702895,4.3828751373,0.6075485299\h,0,-1.0265
48511,-5.3433266178,1.5664971015\h,0,0.6534317499,-1.9197632449,0.729
564034\h,0,-0.5291239793,-0.6689397986,0.2840126981\h,0,0.4644897629,
-1.42444894,-0.9731848094\h,0,-2.9092178242,-4.6942983718,-0.6972089125
\h,0,-2.4791571132,-5.4674046043,0.8431030436\h,0,-1.5431395542,-5.834
882730,0.6032227904\h,0,-3.0201235959,-2.8590596433,-1.4065561899\h,0,
-1.7535048917,-1.92529691,2.3795749313,2.5967225389,2.7554628547\h,0,-4.
0504207671,-3.5684718846,4.2774397427\h,0\nVersio
n=ES64-G16RevA.03VFH=269.12589984\RMSD=4.302e-09\Dipole=-1.6484772
.0403376,1.1160786\Quadropole=7.1922812,17.27719510,0.084139,-14.755
9909,-21.0556622,3.30930668\PG=CO1\X[C(30044CL2NuR1s1)]"
SUPPORTING INFORMATION

44,-4.7985348579,1.0939037695\ C,0,-2.4221501549,-1.804287031,0.8223311824,0,-1.486673051,-4.8467933798,-0.3807087485\ C,0,0.1531635895,-4.5391438145,1.5390878839\ C,0,-3.1386001213,-1.7053157705,-0.4858272548\ C ,0,-0.9626574263,-1.4953936429,0.6566180295\ H,0,0.1981177262,-3.9782910118,2.4890289593\ H,0,0.720194925,-3.9734336532,0.7804011761\ H,0,0.692509681,-5.4946748262,1.6912144624\ H,0,-0.3345488345,1.7747112071,1.5129986474\ H,0,-0.8596692941,-0.400710673,0.5062269901\ H,0,-0.5564260002,-1.9449886042,-0.2725771117\ H,0,-2.5560586027,4.9388680864,-0.6334908986\ H,0,-0.9625329917,-5.7241899109,-0.809071614\ H,0,-1.0655186991,3.9698146522,-0.9040151055\ H,0,-4.2323573959,-1.6902804362,-0.4125736522\ H,0,-2.8663193734,-2.59661908,-1.0880026671\ H,0,-2.7826400508,-0.8294870015,-1.0654243379\ H,0,-3.2265333256,-5.4031742806,1.5135581196\ Ve rsion=ES641-G09RevE.01\ HF=-2691.2653359\ RMSD=4.127e-09\ Dipole=0.2545124,1.4543827,0.2768673\ Quadrupole=-9.9551198,-5.0324962,14.987616,-23.4448856,-12.96445,-0.7594326\ PG=C01 [X{C30H44Cl2N2Ru1S1}]\@
NMR Spectra of the compounds

Compound 1
1a, HNMR
**SUPPORTING INFORMATION**

2d, HNMR

![HNMR Spectrum](image)

Chemical Shift (ppm)

2d, 19FCNMR

![19FCNMR Spectrum](image)

Chemical Shift (ppm)
**Supporting Information**

4c, HNMR

4c, 19F NMR

Chemical Shift (ppm)

Normalized Intensity
**Chemical Shift (ppm)**

**Normalized Intensity**

-150.5214
-150.6166
-150.7363
-150.8376
-162.9000

4c, 19FNMR

**Normalized Intensity**

-150.5214
-150.6166
-150.7363
-150.8376
-162.9000

4c, 13CNMR

**Normalized Intensity**

-150.5214
-150.6166
-150.7363
-150.8376
-162.9000

**Normalized Intensity**

-150.5214
-150.6166
-150.7363
-150.8376
-162.9000
Supporting Information

4d,HNMR

4d,19FNMR
4d,19FNMR

Chemical Shift (ppm)

-149.6575
-149.7542
-149.8647
-149.9737
-162.9015

4d,19FNMR

Normalized Intensity

C6F6

Chemical Shift (ppm)

0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Normalized Intensity

4d,13CNMR

Chemical Shift (ppm)

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

Chemical Shift (ppm)

0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Normalized Intensity

C6F6
5d,HNMR

5d,13CNMR

Normalized Intensity

Chemical Shift (ppm)

Normailzed Intensity

Chemical Shift (ppm)
Supplemental Information

5d,19F NMR

Normalized Intensity

Chemical Shift (ppm)

Normalized Intensity

Chemical Shift (ppm)
13, HNMR

13, 13CNMR
14, HNMR

14, 13CNMR
References:

[1] S. Hapuarachchige, G. Montano, C. Ramesh, D. Rodriguez, L. Henson, C. Williams, S. Kadavakkollu, D. Johnson, C. Shuster, J. Arterburn, *Journal of the American Chemical Society* **2011**, *133*, 6780-6790.

[2] B. Tao, D. Boykin, *Journal of Organic Chemistry* **2004**, *69*, 4330-4335.

[3] T. Okauchi, K. Kuramoto, M. Kitamura, *Synlett* **2010**, 2891-2894.

[4] B. Trost, D. Curran, *Tetrahedron Letters* **1981**, *22*, 1287-1290.

[5] Y. Masahiro, H. Mariko, S. Kozo, *Organic Letters* **2009**, *11*, 4752-4755.

[6] S. Bernd, R. Martin, *Synthesis* **2016**, *48*, 1399-1406.

[7] H. Blackwell, D. O'Leary, A. Chatterjee, R. Washenfelder, D. Bussmann, R. Grubbs, *Journal of the American Chemical Society* **2000**, *122*, 58-71.

[8] Y. Zhao, D. Truhlar, *Journal of Chemical Physics* **2006**, *125*.

[9] F. Weigend, R. Ahrlich, *Physical Chemistry Chemical Physics* **2005**, *7*, 3297-3305.

[10] D. Andrae, U. Haussermann, M. Dolg, H. Stoll, H. Preuss, *Theoretica Chimica Acta* **1990**, *77*, 123-141.

[11] S. Miertus, E. Scrocco, J. Tomasi, *Chemical Physics* **1981**, *55*, 117-129; E. Cances, B. Mennucci, J. Tomasi, *Journal of Chemical Physics* **1997**, *107*, 3032-3041; J. Tomasi, B. Mennucci, R. Cammi, *Chemical Reviews* **2005**, *105*, 2999-3093; R. Ribeiro, A. Marenich, C. Cramer, D. Truhlar, *Journal of Physical Chemistry B* **2011**, *115*, 14556-14562; M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chemical Physics Letters* **1998**, *286*, 253-260.

[12] R. Seeger, J. Pople, *Journal of Chemical Physics* **1977**, *66*, 3045-3050.

[13] C. Riplinger, F. Neese, *Journal of Chemical Physics* **2013**, *138*.

[14] F. Neese, *Wiley Interdisciplinary Reviews-Computational Molecular Science* **2012**, *2*, 73-78.

[15] B. Mondal, F. Neese, S. Ye, *Inorganic Chemistry* **2015**, *54*, 7192-7198.

[16] S. Ye, C. Riplinger, A. Hansen, C. Krebs, J. Bollinger, F. Neese, *Chemistry-a European Journal* **2012**, *18*, 6555-6567; G. Xue, C. Geng, S. Ye, A. Fiedler, F. Neese, L. Que, *Inorganic Chemistry* **2013**, *52*, 3976-3984; J. Song, E. Klein, F. Neese, S. Ye, *Inorganic Chemistry* **2014**, *53*, 7500-7507; S. Cao, X. Liu, Y. Yuan, Z. Zhang, J. Fang, S. Loo, J. Barber, T. Sum, C. Xue, *Physical Chemistry Chemical Physics* **2013**, *15*, 18363-18366.

[17] S. Garber, J. Kingsbury, B. Gray, A. Hoveyda, *Journal of the American Chemical Society* **2000**, *122*, 8168-8179.