Steric and electronic effects in latent S-chelated olefin metathesis catalysts

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Table of Contents

Part I. General information

All commercially available solvents and reagents were of reagent grade and used without further purification unless otherwise stated. The ruthenium complexes, **Ru(SIMes)(=CHPhSPh)Cl_2**, **Ru(SIMes)(=CHPhSPh)I_2** and **Ru(SIMes)(=CHPhSCF_3)I_2** were prepared according to the previously reported procedures.[1] Purification by column chromatography was performed on Fluka silica gel 60 (40-60 μm). TLC analyses were performed using Merck pre-coated silica gel (0.2 mm) aluminum sheets.

All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker AVANCE III 400 MHz spectrometer, chemical shifts, given in ppm are relative to Me_4Si as the internal standard, or to the residual solvent peak. HRMS analyses were done on a Q Exactive™ Focus by Thermo Fisher with an ESI probe.

Irradiation experiments were carried out using a Luzchem LZC-ORG photoreactor with 510 nm lamps (green LED) and were carried out in 5mm NMR tubes at room temperature.

X-ray experimental data: Single crystals of **SIMes-SPh-Br_2** and **SIMes-SCF_3-Br_2** were obtained by slow diffusion of pentane into dichloromethane and acetone solutions of the complexes, respectively, at 5 °C. A suitable crystal was selected and mounted on a on a Bruker APEXII DUO CCD diffractometer equipped with Cu-microsource, and data was collected using Mo-K_α radiation (λ =0.71073). The crystal was kept at 200.15 K during data collection. Using Olex2,[2] the structure was solved with the olex2.solve[3] structure solution program using Charge Flipping and refined with the SHELXL[4] refinement package using Least Squares minimization. Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically.

Part II. Synthesis and characterization of new complexes

Ru(SIMes)(=CHPhSPh)Br_2 A solution of lithium bromide(64 mg, 0.74 mmol, 5.0 equiv) in dry acetone (1 mL) was added to SIMes-SPh-Cl_2 (50 mg, 0.074 mmol, 1.0 equiv) in acetone (0.5 mL). The reaction mixture was stirred for 15 min, during which the color turned to bright green. The crude was filtered over celite with DCM as an eluent. Solvents were removed under vacuum. A minimal amount of acetone was added, followed by addition of hexane to obtain green crystals. Filtration over Büchner and washing with hexane produced dark green crystals (40 mg, 52.2 μmol, 70%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane to a DCM solution at −20 °C.

^{1}H NMR (Acetone-d_6, 400 MHz): δ (ppm) 17.05 (S, 1H), 7.55−7.51 (m, 1H), 7.36−7.31 (m, 2H), 7.29−7.22 (m, 3H), 7.11−7.08 (m, 2H), 7.01−6.99 (m, 2H), 6.92 (s, 2H), 6.05(s, 1H), 4.24−4.06 (m, 4H), 2.72 (S, 3H), 2.63 (S, 3H), 2.53 (S, 3H), 2.24 (S, 3H), 2.18 (S, 3H), 1.86 (S, 3H). ^{13}C NMR (acetone-d_6, 100 MHz): δ (ppm) 17.2, 18.7, 19.2, 20.1, 20.3, 20.4, 51.3, 51.7, 123.3, 128.0, 128.9, 129.1, 129.2, 129.3, 129.4, 129.5, 130.2, 132.4, 133.9, 135.5, 135.9, 136.5, 137.3, 138.0, 138.1, 138.9, 139.9, 155.1, 212.7, 280.6. HRMS m/z: calcd for $[C_{34}H_{36}BrN_2RuS]^+$, 685.08306; found, 685.08307.

Ru(SIMes)(=CHPhSCF_3)Cl_2 The complex was synthesized according to the following modified procedure. A SMes 3rd generation Grubbs (250.0 mg, 0.31 mmol, 1.0 equiv) was dissolved in dry DCM (12 mL) followed by addition of the styrene ligand (75.6 mg, 0.37 mmol, 1.2 equiv) the reaction mixture was refluxed overnight. The solvent was removed under vacuum. The crude was purified by precipitations to give blue solid (190mg, 0.25 mmol, 82%). NMR spectra and HRMS matched the reported characterization.[1b]

Ru(SIMes)(=CHPhSCF_3)Br_2 A solution of lithium bromide(64 mg, 0.75 mmol, 5.0 equiv) in dry acetone (1 mL) was added to SIMes-SCF_3-Cl_2 (50 mg, 0.075 mmol, 1.0 equiv) in acetone (0.5 mL). The reaction mixture was stirred for 15 min, during which the color turned to bright green. The crude was filtered over celite with DCM as an eluent. Solvents were removed under vacuum. A minimal amount of

acetone was added, followed by addition of hexane to obtain green crystals. Filtration over Büchner and washing with hexane produced dark green crystals (40 mg, 52.8 μmol, 70%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane to a DCM solution at −20 °C.

^{1}H NMR (Acetone-d_6, 400 MHz): δ (ppm) 16.82 (S, 1H), 7.89−7.87 (d, 1H), 7.78−7.35 (m, 1H), 7.49−7.45 (m, 1H), 7.09−7.00 (m, 4H), 6.88 (s, 1H), 4.29−4.06 (m, 4H), 2.65 (S, 3H), 2.63 (S, 3H), 2.45 (S, 3H), 2.30 (S, 3H), 2.15 (S, 3H), 1.78 (S, 3H). ^{13}C NMR (DCM-d_2, 100 MHz): δ (ppm) 17.9, 19.5, 19.6, 21.2, 21.4, 21.5, 52.1, 52.3, 124.8, 129.5, 129.9, 130.1, 130.2, 131.0, 131.7, 135.4, 136.7, 137.9, 139.2, 141.1, 155.5, 209.6, 284.1 HRMS m/z: calcd for $[C_{29}H_{31}BrF_3N_2RuS]$+, 677.03814; found,677.03784.

Ru(SIPr)(=CHPhSPh)Cl_2 A SIPr Grubbs (250.0 mg, 0.27 mmol, 1.0 equiv) was dissolved in dry DCM (15 mL) followed by addition of the styrene ligand (68.3 mg, 0.32 mmol, 1.2 equiv) the reaction mixture was refluxed for 4 days. The solvent was removed under vacuum. The crude was purified by flash chromatography using 3:7 to 5:5 acetone/hexane as eluent to give a green solid after solvent evaporation (113.6 mg, 0.15 mmol, 55%).

^{1}H NMR (Acetone-d_6, 400 MHz): δ (ppm) 17.01 (S, 1H), 7.59−7.50 (m, 3H), 7.43−7.41 (m, 1H), 7.35−7.22 (m, 5H), 7.13 (t, 2H), 6.89−7.87 (m, 1H), 6.84−6.82 (m, 2H), 6.64−6.62 (m, 1H), 4.37−4.10 (m, 4H), 3.48 (m, 1H), 2.55 (m, 1H), 1.73−1.72 (d, 3H), 1.66−1.64 (d, 3H), 1.54−1.52 (d, 3H), 1.32−1.30 (d, 3H), 1.19 (t, 6H), 1.04−1.03 (d, 3H), 0.42−0.40(d, 3H). ^{13}C NMR (DCM-d_2, 100 MHz): δ (ppm) 21.5, 22.8, 23.2, 24.9, 26.5, 27.1, 28.2, 28.3, 28.9, 29.1, 29.4, 29.6, 31.2, 124.0, 125.0, 125.6, 126.3, 128.5, 129.4, 129.8, 129.9, 130.7, 131.2, 131.4, 132.4, 133.9, 136.8, 139.0, 146.1, 147.9, 149.8, 151.4, 155.9, 217.3, 285.5. HRMS m/z: calcd for $[C_{40}H_{48}BrN_2RuS]^+$, 725.22647; found, 725.22681.

Ru(SIPr)(=CHPhSPh)Br_2 A solution of lithium bromide (45.7 mg, 0.53 mmol, 5.0 equiv) in dry acetone (1 mL) was added to SIPr-SPh-Cl_2 (40.0 mg, 0.0053 mmol, 1.0 equiv) in acetone (0.5 mL). The reaction mixture was stirred for 15 min, during which the color turned to bright green. The crude was filtered over celite with DCM as an eluent. Solvents were removed under vacuum. A minimal amount of acetone was added, followed by addition of hexane to obtain green crystals. Filtration over Büchner and washing with hexane produced dark green crystals (31.0 mg, 36.5 μmol, 69%).

^{1}H NMR (Acetone-d_6, 400 MHz): δ (ppm) 16.96 (S, 1H), 7.60−7.51 (m, 3H), 7.40−7.38 (m, 1H), 7.35−7.24 (m, 5H), 7.18−7.14 (m, 2H), 6.92−6.86 (m, 3H), 6.61−6.59 (m, 1H), 4.38−4.32 (m, 4H), 3.49 (m, 1H), 2.62 (m, 1H), 1.71−1.69 (d, 3H), 1.64−1.63 (d, 3H), 1.54−1.52 (d, 3H), 1.30−1.29 (d, 3H), 1.18 (t, 6H), 1.04−1.02 (d, 3H), 0.49−0.47(d, 3H). ^{13}C NMR (Acetone-d_6, 100 MHz): δ (ppm) 20.9, 21.9, 22.7, 24.4, 25.9, 26.2, 27.2, 27.5, 53.7, 54.2, 123.4, 124.2, 124.6, 124.9, 125.6, 127.8, 128.7, 129.2, 129.3, 130.2, 130.4, 130.7, 132.3, 133.6, 136.8, 137.6, 145.7, 147.3, 148.9, 150.4, 155.4, 216.3, 282.7. HRMS m/z: calcd for $[C_{40}H_{48}BrN_2RuS]$+, 769.17596; found, 771.175542.

Ru(SIPr)(=CHPhSPh)I_2

A solution of sodium iodide (78.9 mg, 0.53 mmol, 5.0 equiv) in dry acetone (1 mL) was added to SIPr-SPh-Cl_2 (40.0 mg, 0.0053 mmol, 1.0 equiv) in acetone (0.5 mL). The reaction mixture was stirred for 15 min, during which the color turned to bright brown. The crude was filtered over celite with DCM as an eluent. Solvents were removed under vacuum. A minimal amount of acetone was added, followed by addition of hexane to obtain brown crystals. Filtration over Büchner and washing with hexane produced dark brown crystals (29.8 mg, 31.58 μmol, 60%).

^{1}H NMR (Acetone-d_6, 400 MHz): δ (ppm) 16.74 (S, 1H), 7.62−7.58 (dt, 3H), 7.50 (S, 1H), 7.49−7.48 (d, 1H), 7.35−7.23 (m, 5H), 7.17 (t, H), 7.05−7.02 (m, 3H), 6.97−6.95 (dd, 1H), 6.57−6.54 (dd, 1H), 4.38−4.18 (m, 4H), 3.53 (m, 1H), 2.87 (m, 1H), 1.60−1.59 (d, 3H), 1.57−1.54 (m, 6H), 1.27−1.25 (d, 3H),

1.17 (t, 6H), 1.04−1.03 (d, 3H), 0.69−0.67(d, 3H). ^{13}C NMR (DCM-d_2, 100 MHz): δ (ppm) 21.9, 22.7, 23.8, 24.4, 25.1, 25.4, 25.7, 27.0, 27.3, 28.1, 29.2, 29.3, 29.5, 30.0, 123.9, 125.0, 125.3, 125.5, 125.6, 125.8, 126.4, 128.4, 129.9, 130.5, 130.7, 131.0, 133.0, 137.1, 146.1, 146.7, 147.7, 149.5, 150.9, 156.4, 158.4, 216.8, 283.7. HRMS m/z: calcd for $[C_{40}H_{48}IN_2RuS]$+, 817.16209; found, 817.16400.

Ru(SIPr)(=CHPhSCF$_3$)Cl$_2$ The complex was synthesized according to the following modified procedure. A SIPr 3rd generation Grubbs (140.0 mg, 0.17 mmol, 1.0 equiv) was dissolved in dry DCM (2 mL) followed by addition of the styrene ligand (42.3 mg, 0.21 mmol, 1.2 equiv) the reaction mixture was stirred at R.T. overnight. The solvent was removed under vacuum. The crude was purified by precipitations to give green solid (94.3 mg, 0.12 mmol, 72%). NMR spectra and HRMS matched the reported characterization.[5]

Ru(SIPr)(=CHPhSCF$_3$)Br$_2$ A solution of lithium bromide (46.2 mg, 0.53 mmol, 5.0 equiv) in dry acetone (1 mL) was added to SIPr-SCF$_3$-Cl$_2$ (40.0 mg, 0.053 mmol, 1.0 equiv) in acetone (0.5 mL). The reaction mixture was stirred for 15 min, during which the color turned to bright green. The crude was filtered over celite with DCM as an eluent. Solvents were removed under vacuum. A minimal amount of acetone was added, followed by addition of hexane to obtain green crystals. Filtration over Büchner and washing with hexane produced dark green crystals (31.0 mg, 36.8 μmol, 69%).

^{1}H NMR (DCM-d_2, 400 MHz): δ (ppm) 16.70 (S, 1H), 7.69−7.67 (d, 1H), 7.62−7.58 (m, 1H), 7.54 (t, 1H), 7.45−7.42 (m, 1H), 7.36−7.34 (m, 1H), 7.32−7.29 (m, 1H), 7.28−7.26 (m, 1H), 7.18 (t, 1H), 6.89−6.87 (m, 1H), 6.47−6.45 (m, 1H), 4.31−4.08 (m, 4H), 3.38 (m, 1H), 2.38 (m, 1H), 1.64−1.63 (d, 3H), 1.60−1.58 (m,6H), 1.24−1.21 (m, 6H), 1.19−1.17 (d, 3H), 0.98−0.96 (d, 3H), 0.51−0.49 (d, 3H). ^{13}C NMR (Acetone-d_6, 100 MHz): δ (ppm) 21.9, 22.4, 23.6, 25.5, 26.9, 28.0, 28.5, 54.7, 55.3, 124.1, 125.2, 125.7, 125.9, 126.5, 130.5, 130.8, 131.6, 131.9, 132.9, 146.5, 148.1, 150.0,151.3, 155.4, 213.4, 283.9. HRMS m/z: calcd for $[C_{35}H_{43}BrF_3N_2RuS]^+$, 761.13204; found, 763.13171.

Ru(SIPr)(=CHPhSCF$_3$)I$_2$ A solution of sodium iodide (49.85 mg, 0.33 mmol, 5.0 equiv) in dry acetone (1 mL) was added to SIPr-SCF$_3$-Cl$_2$ (25.0 mg, 0.033 mmol, 1.0 equiv) in acetone (0.5 mL). The reaction mixture was stirred for 15 min, during which the color turned to bright brown. The crude was filtered over celite with DCM as an eluent. Solvents were removed under vacuum. A minimal amount of acetone was added, followed by addition of hexane to obtain brown crystals. Filtration over Büchner and washing with hexane produced dark green crystals (18.4 mg, 59.13 μmol, 59%).

^{1}H NMR (DCM-d_2, 400 MHz): δ (ppm) 16.45 (S, 1H), 7.71−7.67 (d, 1H), 7.63-7.60 (td, 1H), 7.51 (t, 1H), 7.39−7.32 (m, 4H), 7.27−7.23 (m, 2H), 7.11 (t, 1H), 6.91−6.88 (dd, 1H), 6.44−6.42 (dd, 1H), 4.32−4.06 (m, 4H), 3.48 (m, 1H), 2.57 (m, 1H), 1.61−1.60 (d, 3H), 1.59−1.58 (d, 3H), 1.45−1.43 (d, 3H), 1.22−1.18 (m, 6H), 1.16−1.15 (d, 3H), 0.98−1.96 (d, 3H), 0.67−0.65 (d, 3H). ^{13}C NMR (DCM-d_2, 100 MHz): δ (ppm) 21.9, 22.1, 23.7, 24.4, 25.1, 25.7, 26.8, 27.2, 28.2, 28.8, 29.2, 29.8, 30.3, 31.2, 123.7, 124.9, 125.6, 125.8, 126.3, 128.4, 129.7, 130.2, 131.1, 131.7, 132.0, 132.4, 136.5, 146.0, 146.7, 147.6, 149.8, 150.8, 207.0, 256.1. HRMS m/z: calcd for $[C_{35}H_{41}F_3BrN_2RuS]$+, 809.11817; found, 809.12634.

Part III. NMR data of new complexes

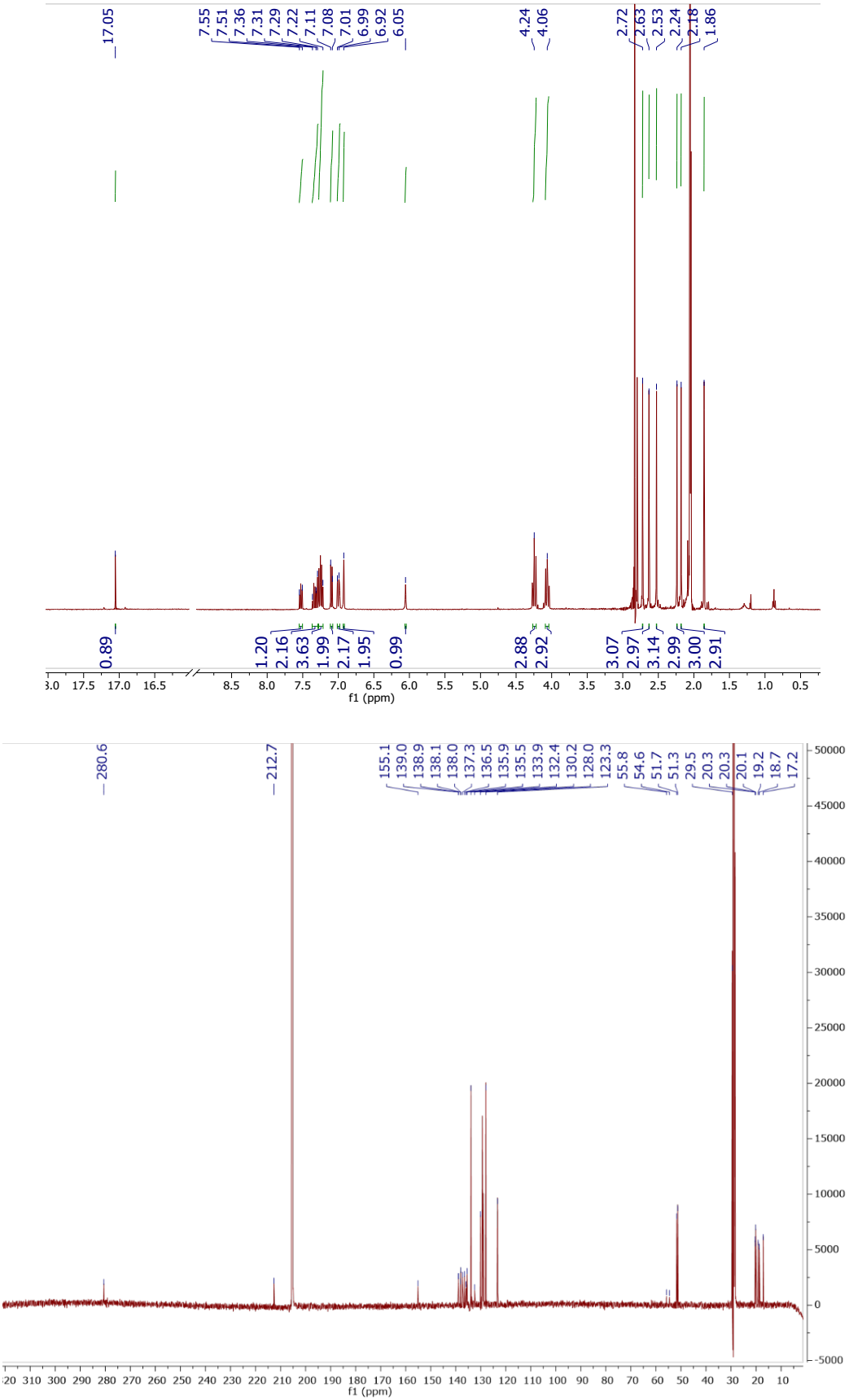


Figure S1. NMR spectra of **SIMes-SPh-Br$_2$**. *Top:* ^{1}H-NMR (400MHz, Acetone-d$_6$), Bottom: ^{13}C-NMR (400MHz, Acetone-d$_6$).

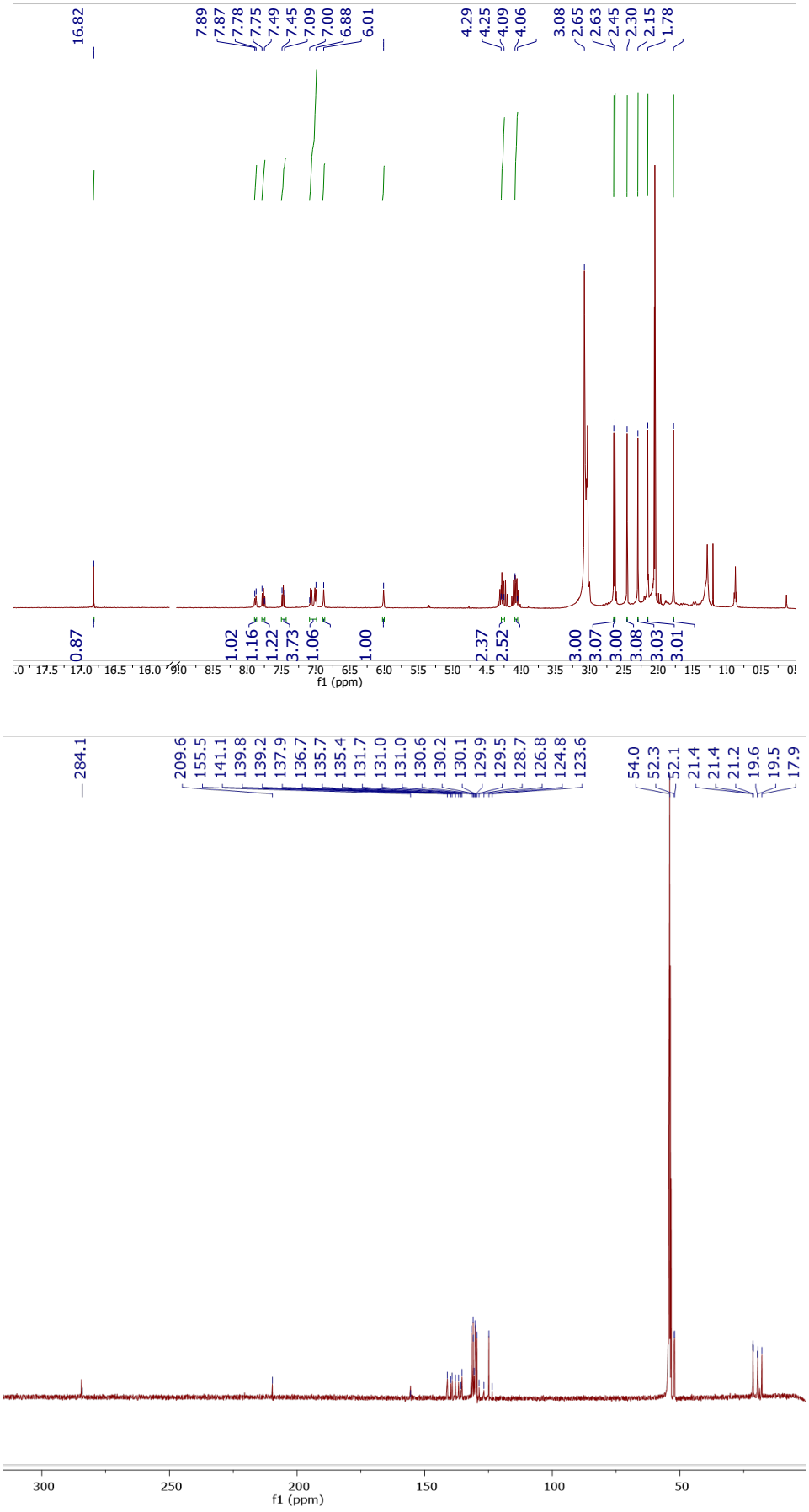


Figure S2. NMR spectra of **SIMes-SCF$_3$-Br$_2$**. *Top:* ^{1}H-NMR (400MHz, Acetone-d$_6$), Bottom: ^{13}C-NMR (400MHz, DCM-d$_2$).

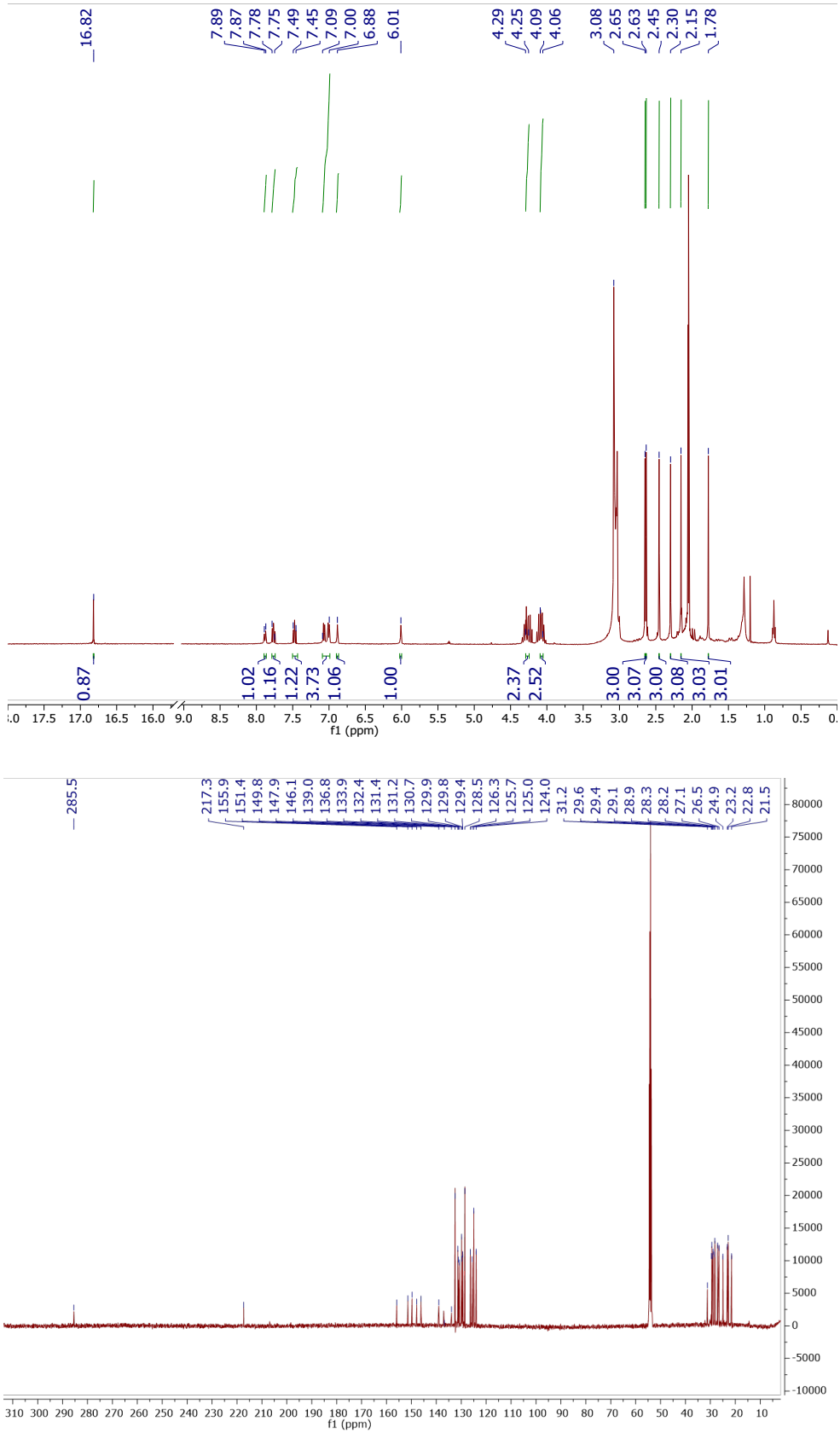


Figure S3. NMR spectra of **SIPr-SPh-Cl$_2$**. *Top:* ^{1}H-NMR (400MHz, Acetone-d$_6$), Bottom: ^{13}C-NMR (400MHz, DCM-d$_2$).

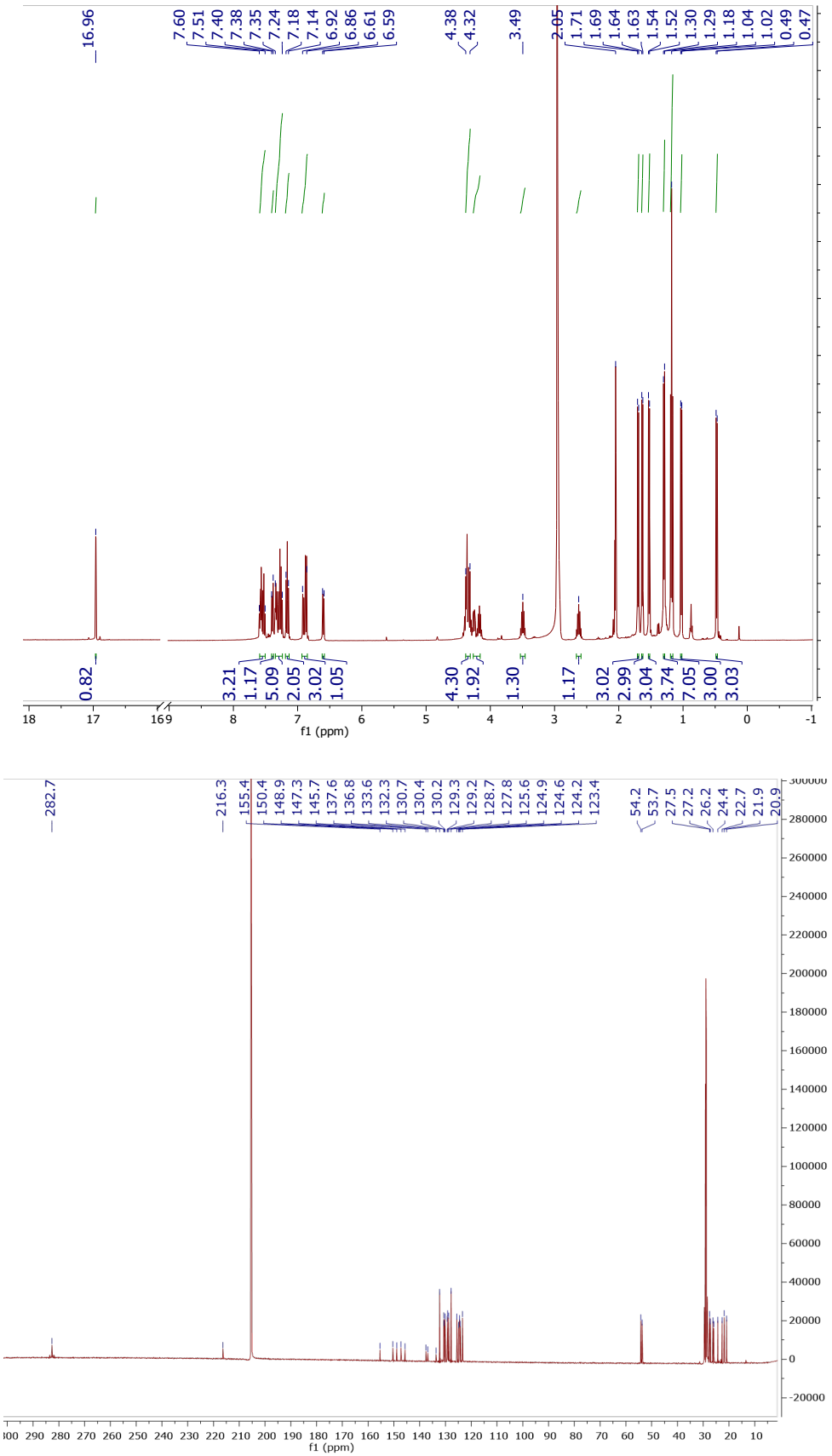


Figure S4. NMR spectra of **SIPr-SPh-Br$_2$**. *Top:* ^{1}H-NMR (400MHz, Acetone-d$_6$), Bottom: ^{13}C-NMR (400MHz, Acetone-d$_6$).

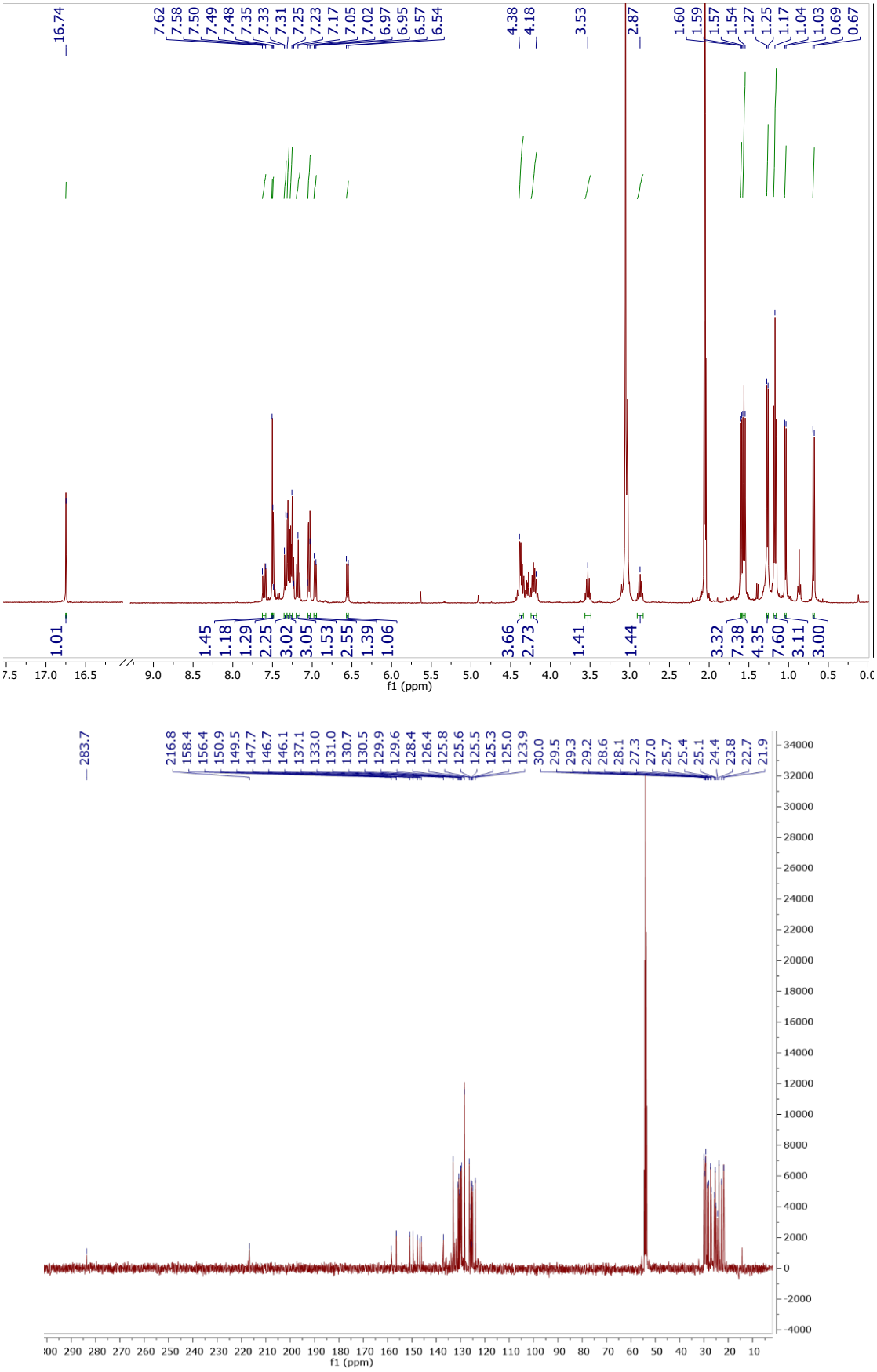


Figure S5. NMR spectra of **SIPr-SPh-I$_2$**. *Top:* ^{1}H-NMR (400MHz, Acetone-d$_6$), Bottom: ^{13}C-NMR (400MHz, DCM-d$_2$).

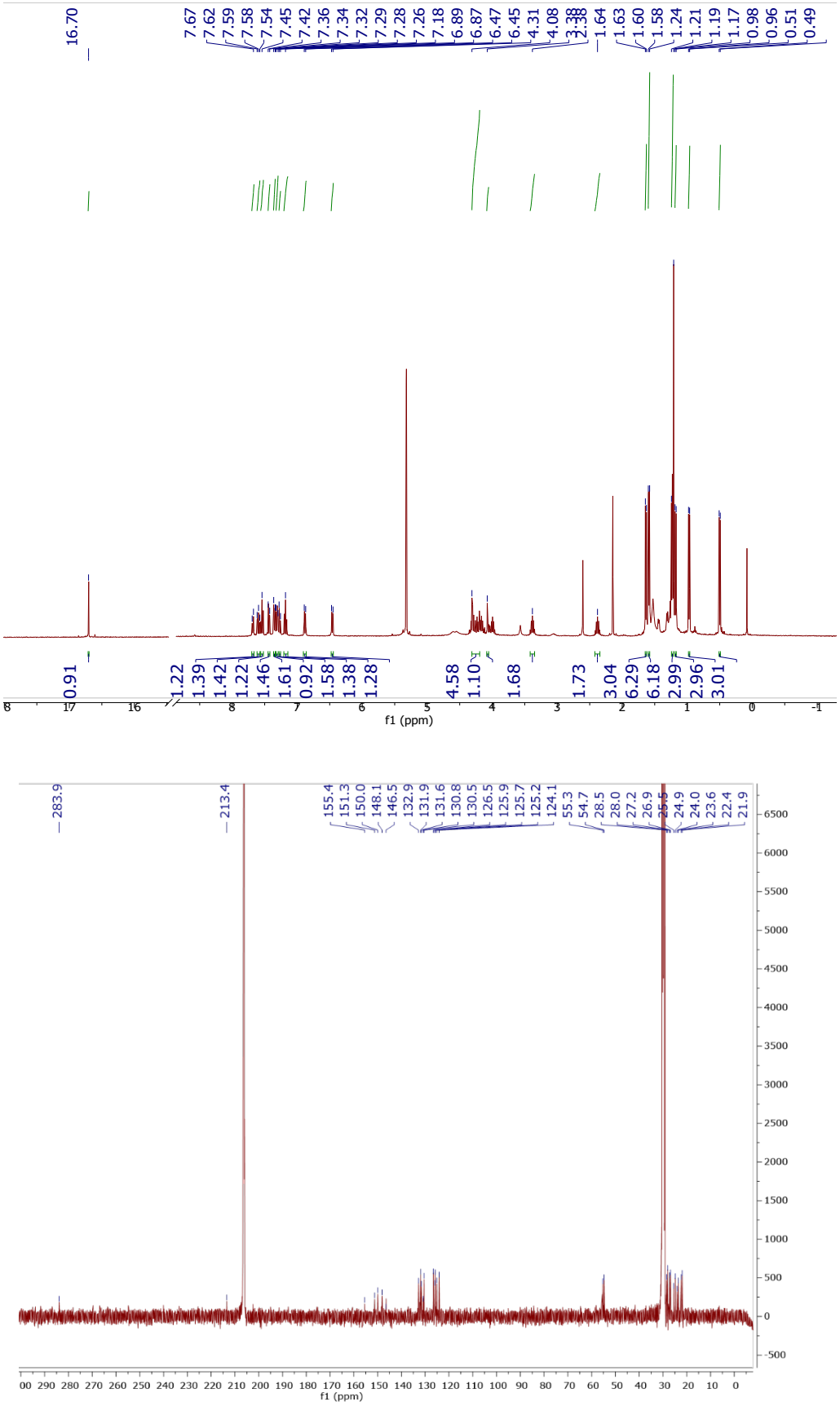


Figure S6. NMR spectra of **SIPr- SCF_3-Br_2**. *Top:* ^{1}H-NMR (400MHz, Acetone-d_6), Bottom: ^{13}C-NMR (400MHz, Acetone-d_6)

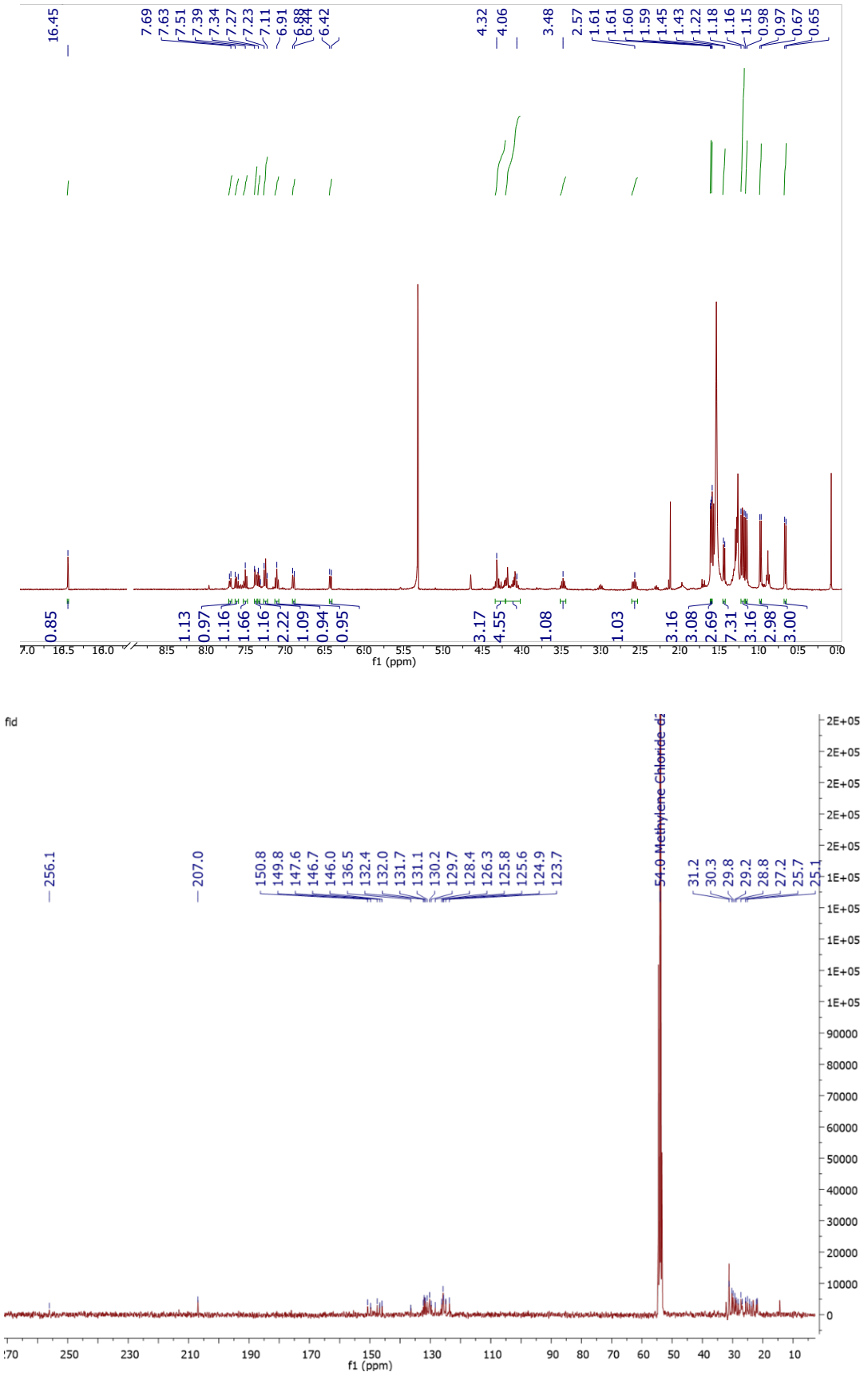


Figure S7. NMR spectra of **SIPr- SCF_3-I_2**. *Top:* ^{1}H-NMR (400MHz, DCM-d_2), Bottom: ^{13}C-NMR (400MHz, DCM-d_2)

Part IV. HRMS data of new complexes

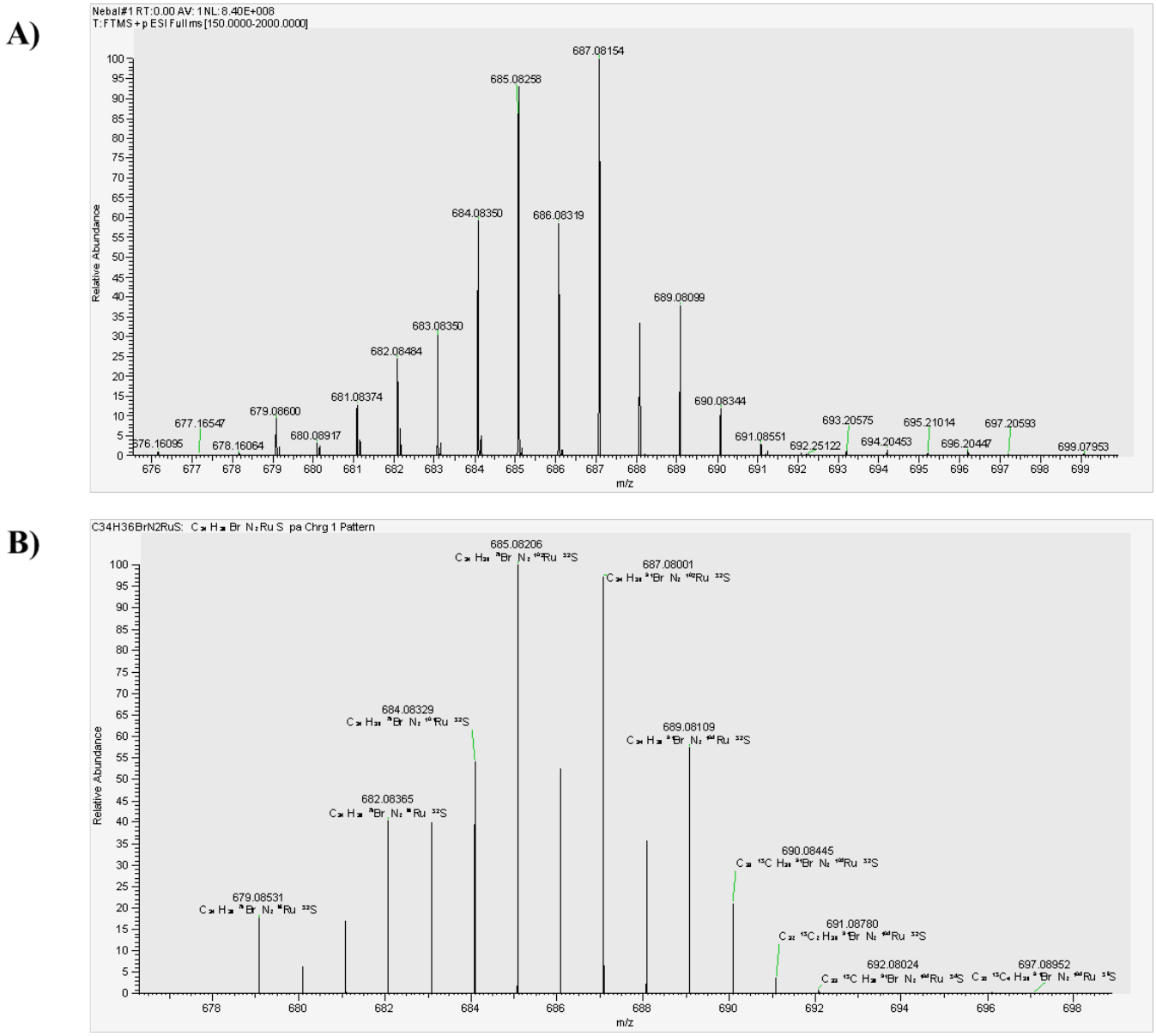


Figure S8. Experimental (A) and simulated (B) HRMS chromatogram of **SIMes-SPh-Br$_2$**

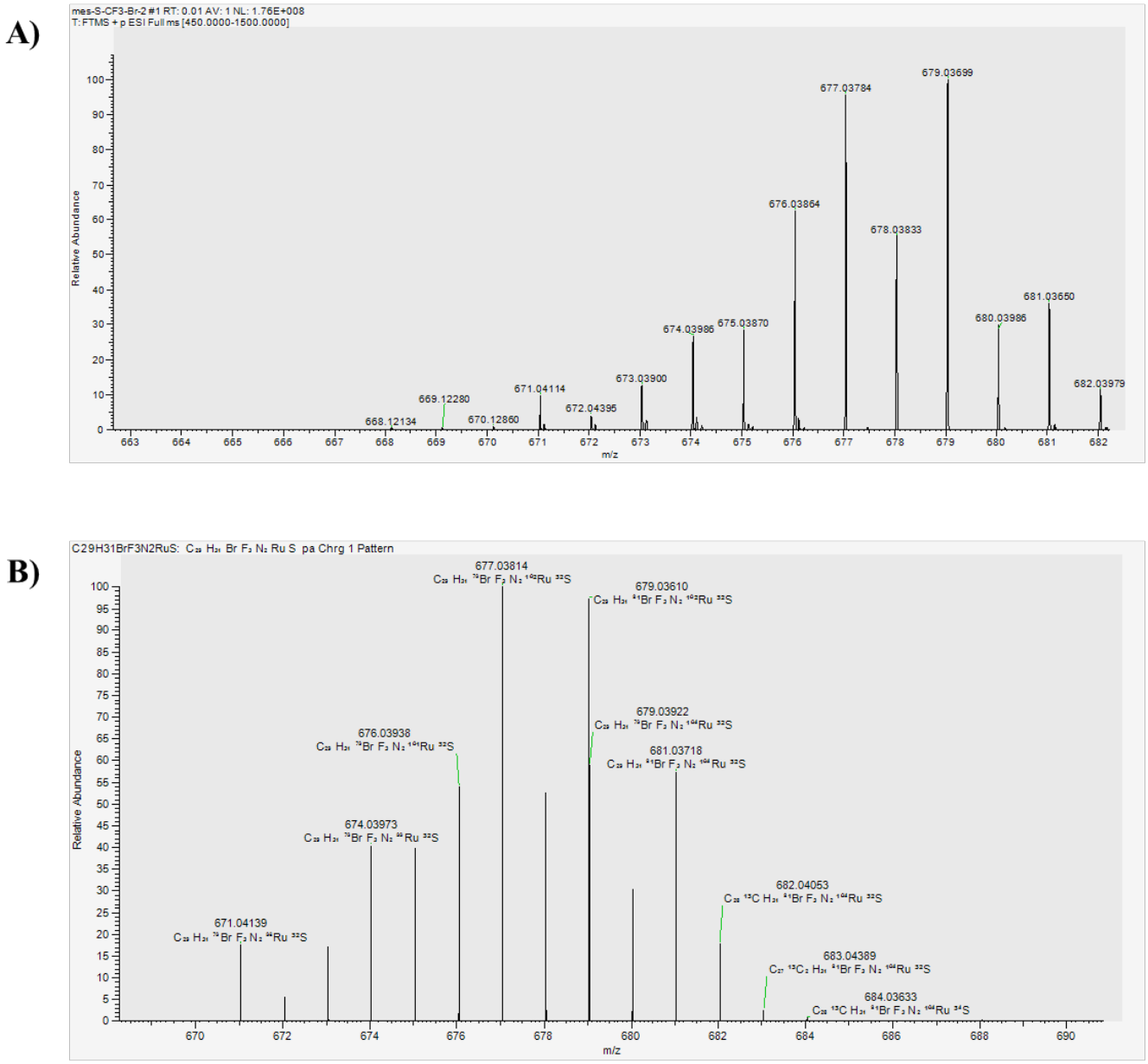
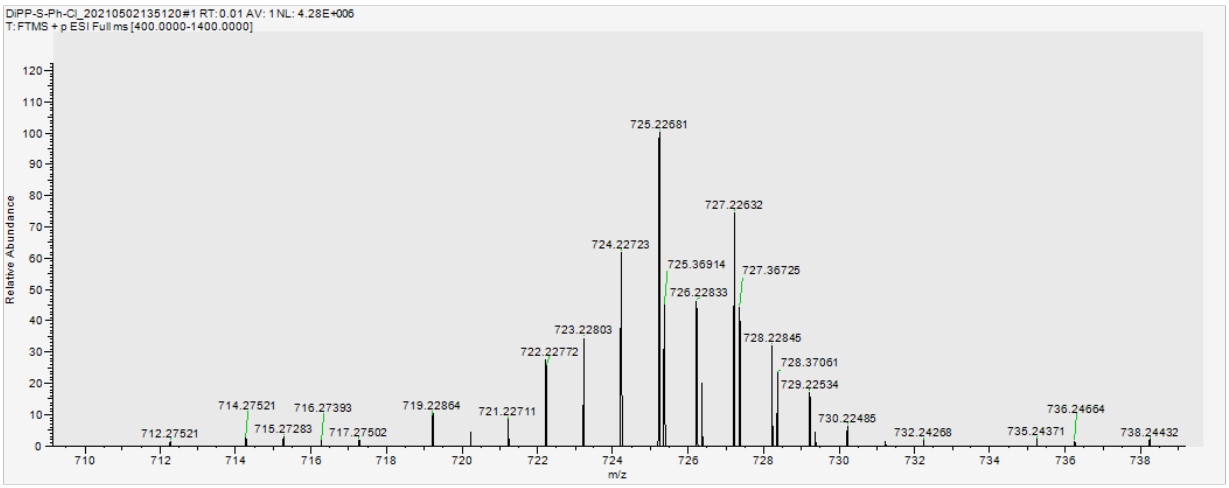


Figure S9. Experimental (A) and simulated (B) HRMS chromatogram of **SIMes-SCF$_3$-Br$_2$**

A)



B)

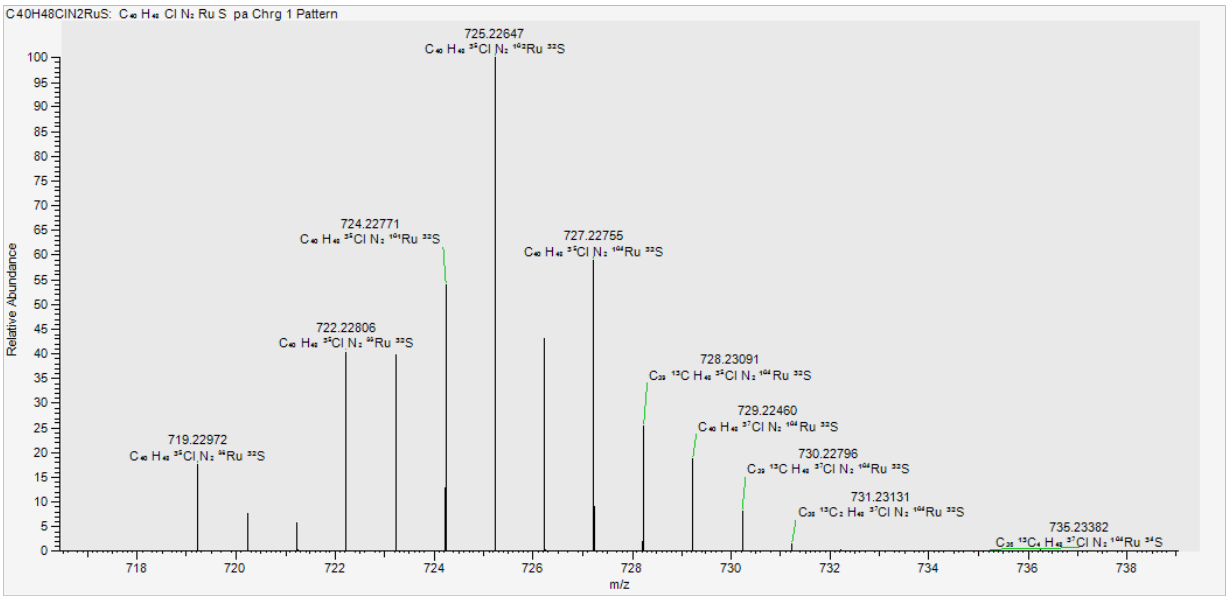
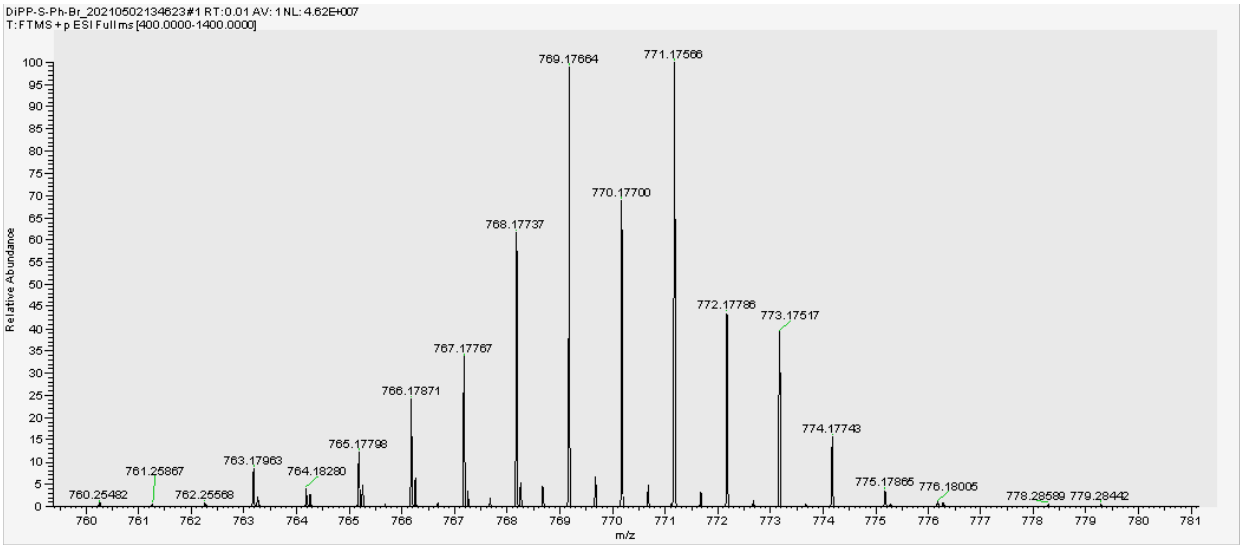


Figure S10. Experimental (A) and simulated (B) HRMS chromatogram of **SIPr-SPh-Cl$_2$**

A)



B)

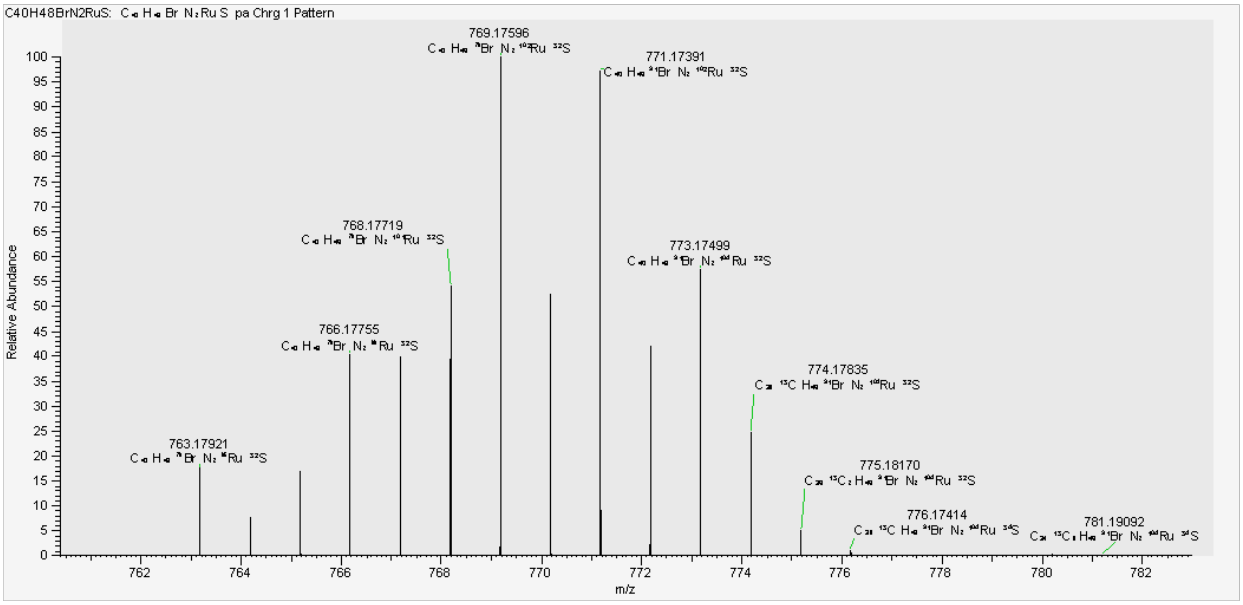


Figure S11. Experimental (A) and simulated (B) HRMS chromatogram of **SIPr-SPh-Br$_2$**

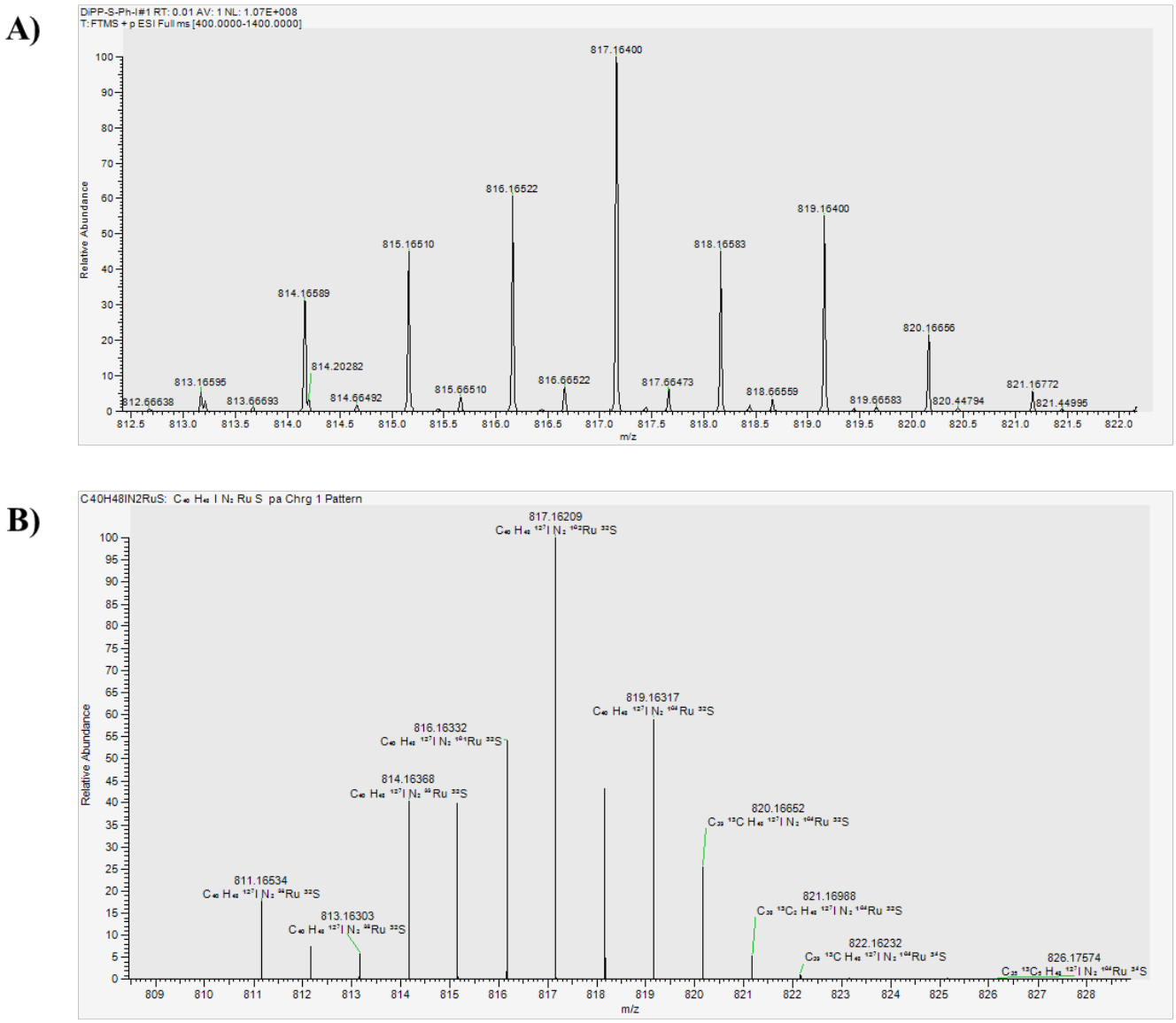


Figure S12. Experimental (A) and simulated (B) HRMS chromatogram of **SIPr-SPh-I$_2$**

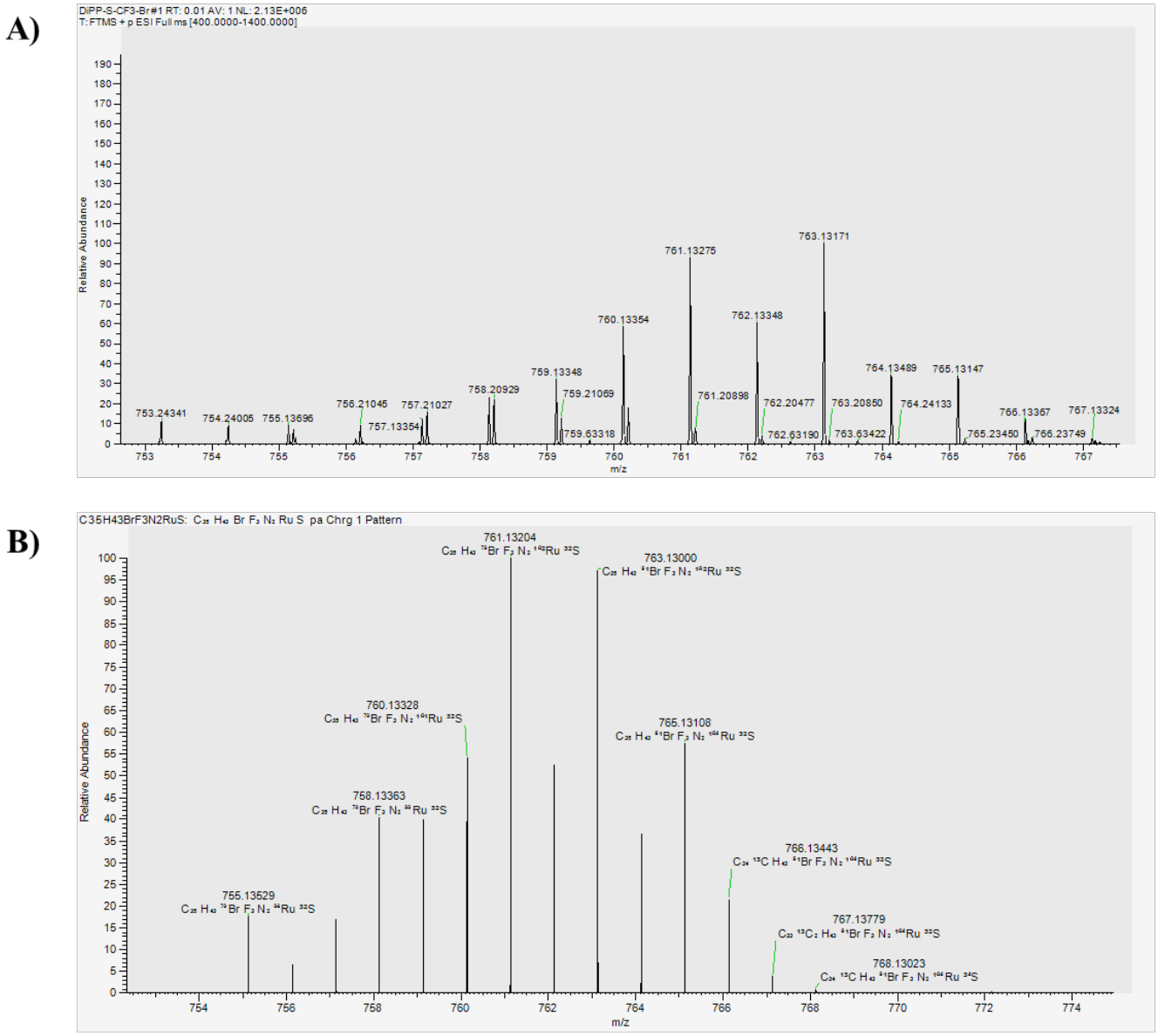


Figure S13. Experimental (A) and simulated (B) HRMS chromatogram of **SIPr-SCF$_3$-Br$_2$**

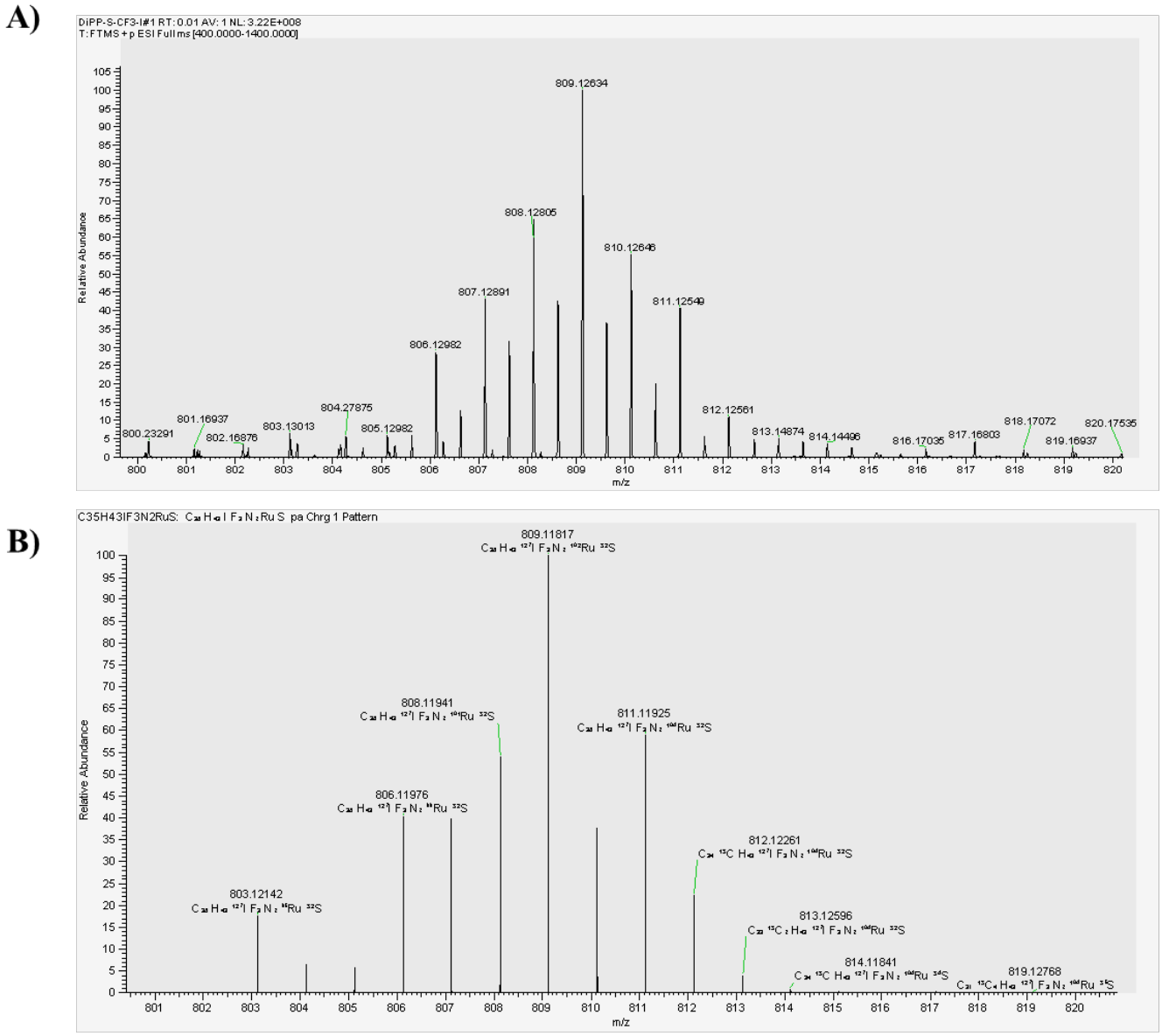


Figure S14. Experimental (A) and simulated (B) HRMS chromatogram of **SIPr-SCF$_3$-I$_2$**

Part V. X-ray data

CCDC 2141615 and 2141616 of **SIMes-SPh-Br$_2$** and **SIMes-SCF$_3$-Br$_2$** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S1. Crystallographic data of **SIMes-SPh-Br$_2$** and **SIMes-SCF$_3$-Br$_2$**

	SIMes-SPh-Br$_2$	**SIMes-SCF$_3$-Br$_2$**
Chemical formula	$C_{34}H_{37}Br_2N_2RuS$	$C_{29}H_{32}F_3Br_2N_2RuS$
Formula Weight	766.6	758.5
Temperature (K)	200.15	200.15
Crystal size (mm^3)	0.09×0.06×0.06	0.33×0.06×0.06
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a (Å)	10.261(2)	8.3337(15)
b (Å)	11.332(3)	30.607(6)
c (Å)	14.623(3)	40.881(8)
α (°)	102.134(6)	90
β (°)	104.895(5)	95.485(5)
γ (°)	96.574(6)	90
Volume (Å^3)	1580.6(6)	10380(3)
Z	2	12
ρ (g cm^{-3})	1.611	1.456
μ (mm^{-1})	3.116	2.858
F(000)	770.0	4524.0
Radiation	MoKα (λ=0.71073)	MoKα (λ=0.71073)
hkl range	$-12 \le h \le 8$	$-9 \le h \le 9$
	$-13 \le k \le 13$	$35 \le k \le 33$
	$-13 \le l \le 17$	$-45 \le l \le 45$
No. of reflections collected	9689	47529
Independent reflections	5417 [R_{int} = 0.1553, R_σ = 0.2445]	15831 [R_{int} = 0.2217, R_σ = 0.4019]
No. of parameters	361	1003
Goodness-of-fit on F^2	0.863	0.908
Final R indexes [I≥2σ (I)]	R_1 = 0.0608, wR_2 = 0.1159	R_1 = 0.0793, wR_2 = 0.1283

Part VI. *Cis-trans* Isomerization studies following heating at 80 °C

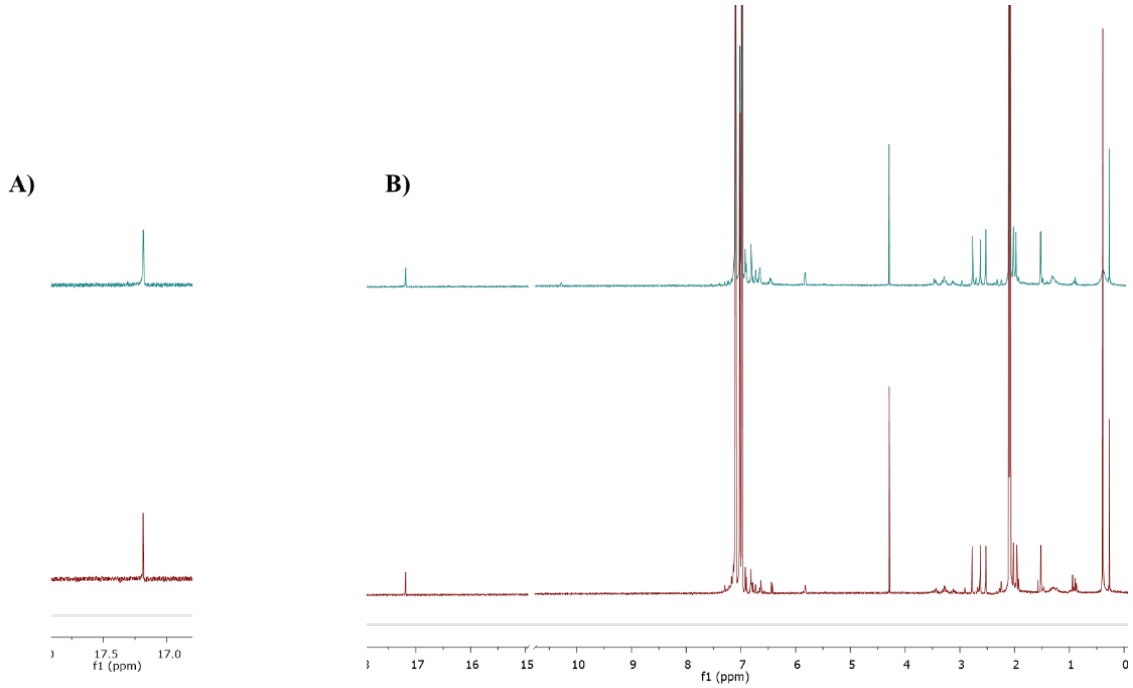


Figure S15. ^{1}H NMR analysis following isomerization of **SIMes-SPh-Cl$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 4 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization < 1), B) the full spectra.

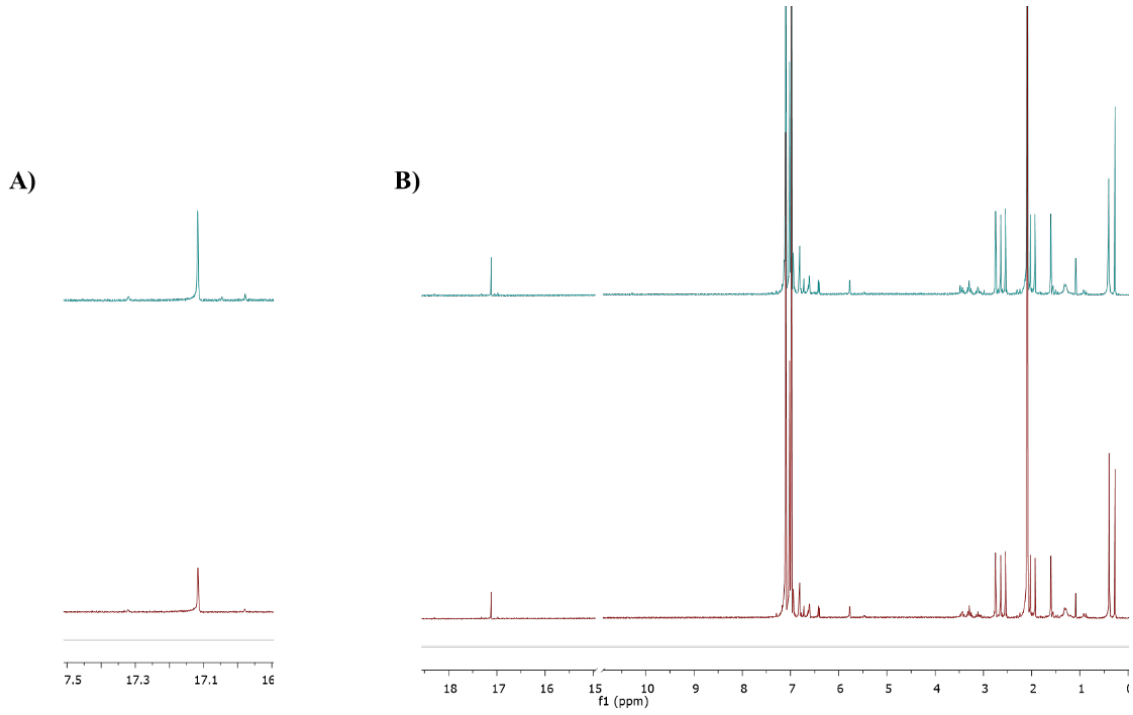


Figure S16. ^{1}H NMR analysis following isomerization of **SIMes-SPh-Br$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 4 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization < 1), B) the full spectra.

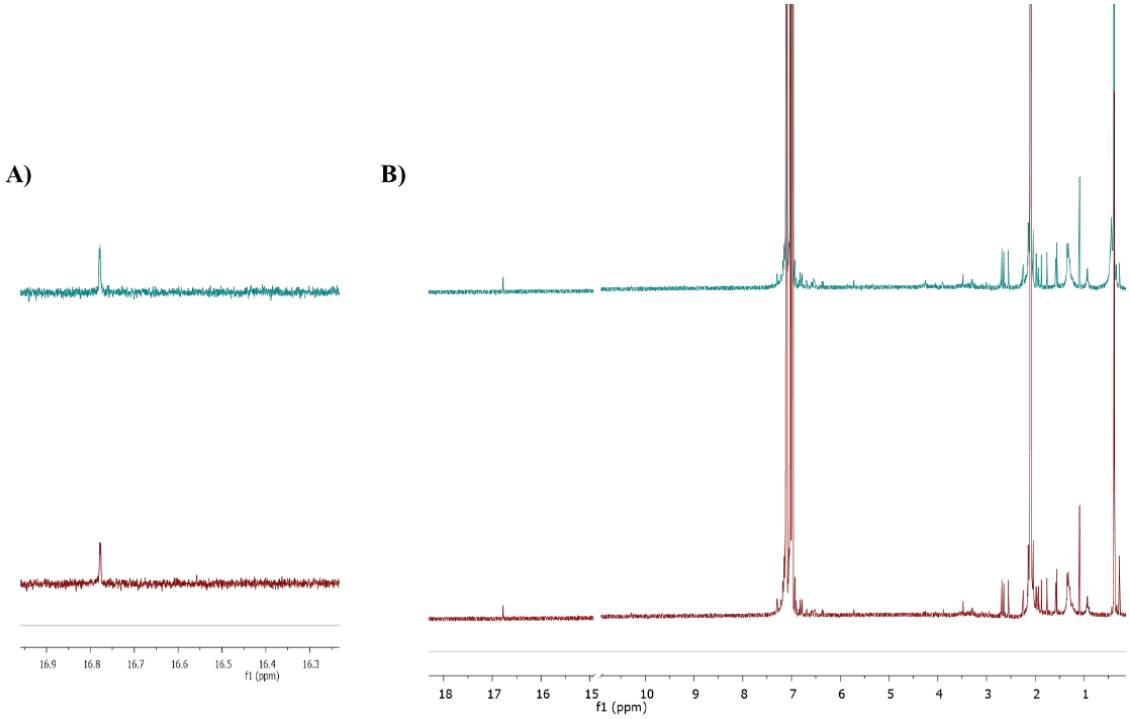


Figure S17. ^{1}H NMR analysis following isomerization of **SIMes-SPh-I$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 4 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization < 1) B) the full spectra.

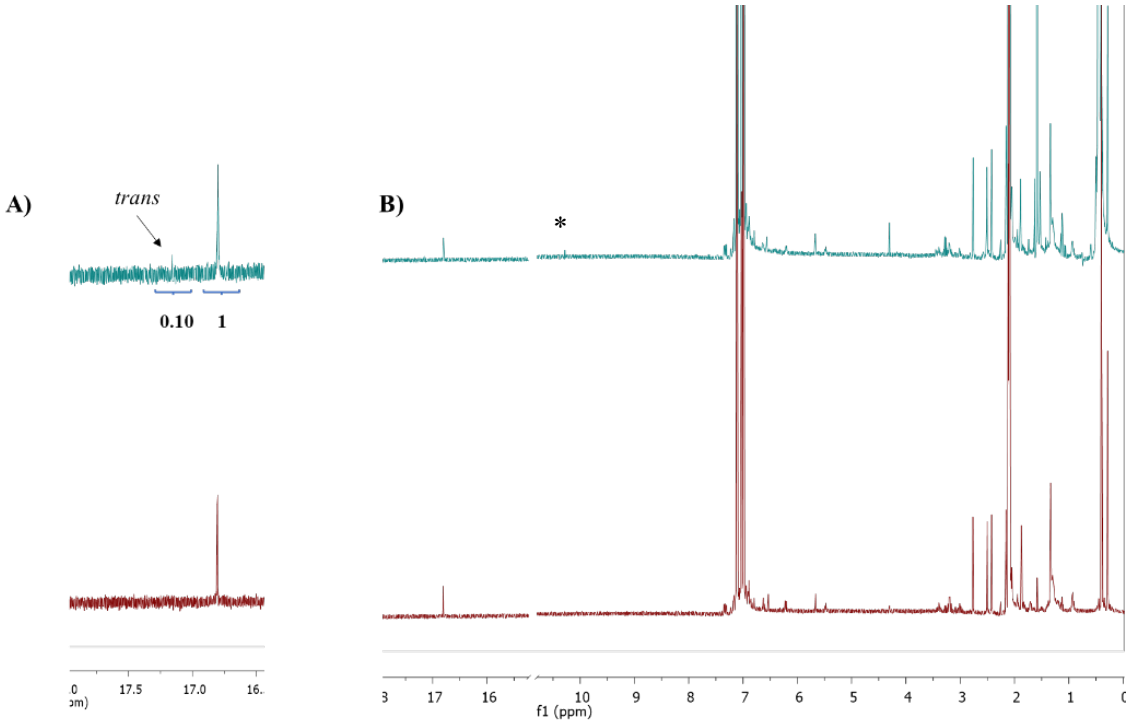


Figure S18. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-Cl$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 3 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 9) B) the full spectra.

*9% decomposition

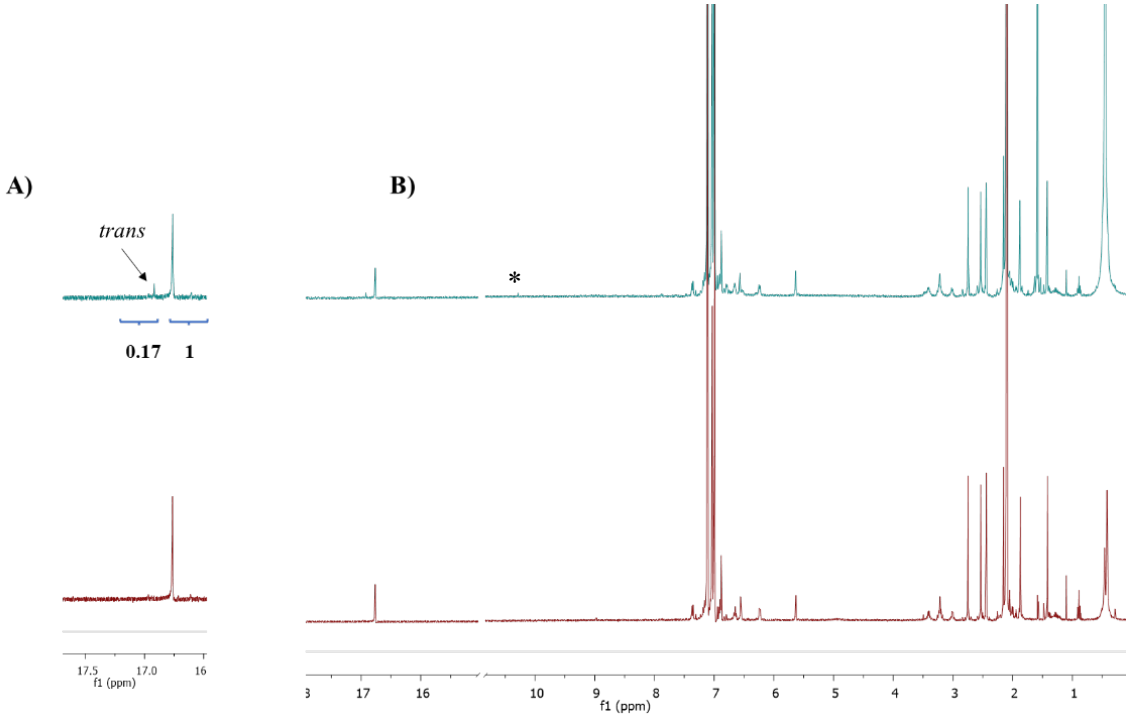


Figure S19. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-Br$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 1.5 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 17) B) the full spectra.

*7% decomposition

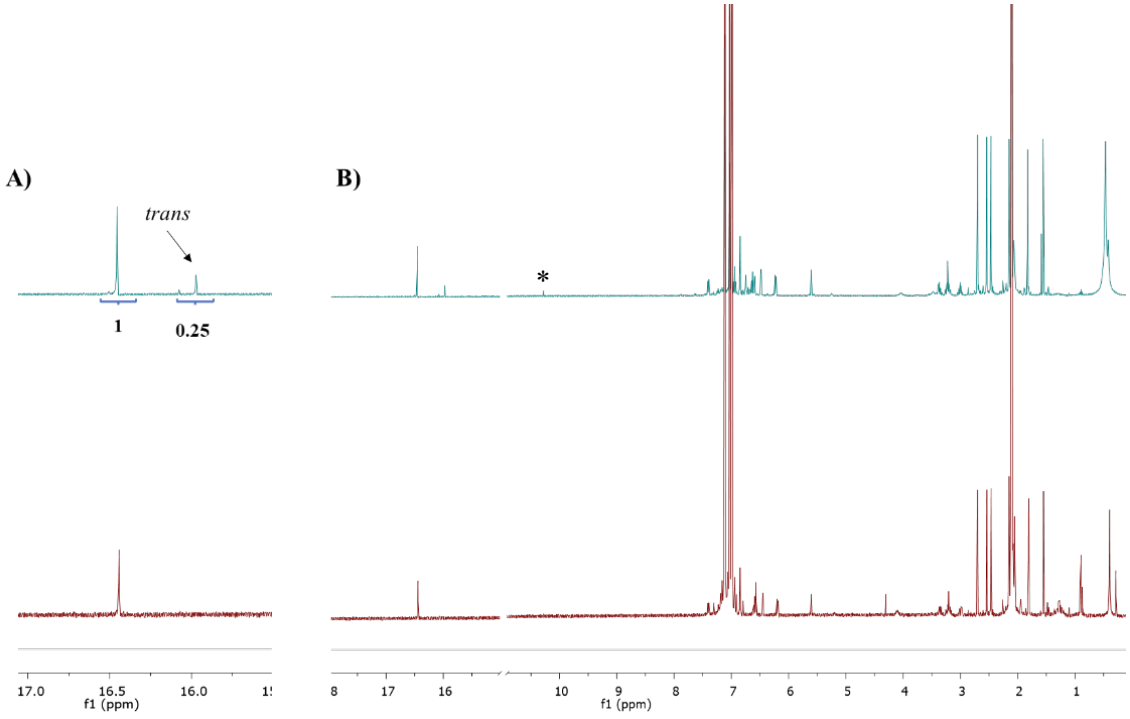


Figure S20. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-I$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 15 min. at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 20) B) the full spectra.

*7% decomposition

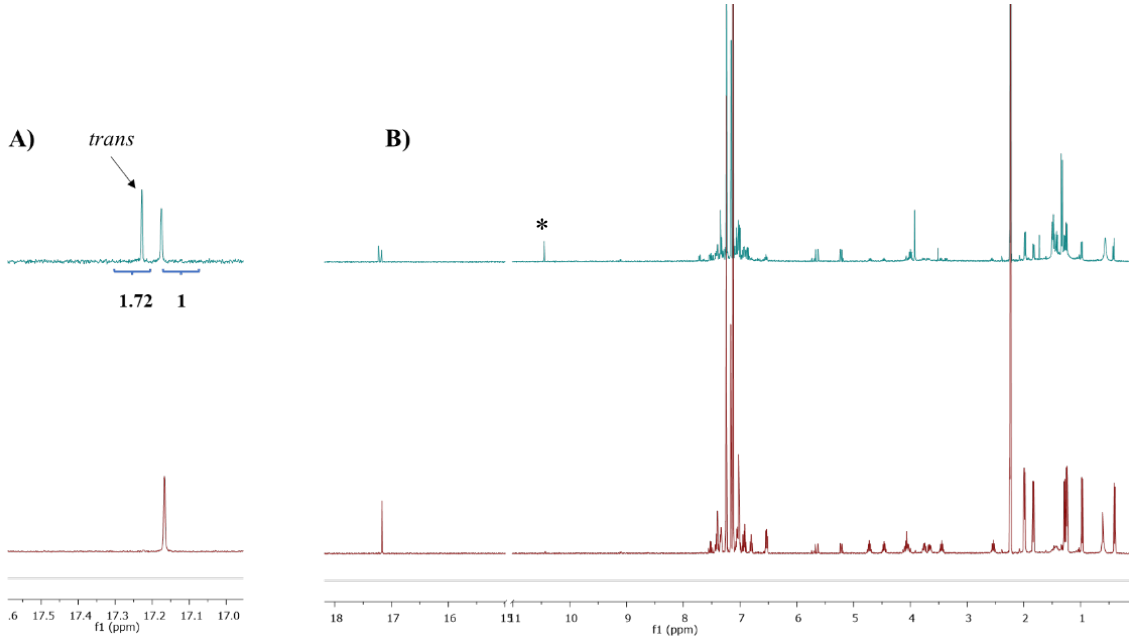


Figure S21. ^{1}H NMR analysis following isomerization of **SIPr-SPh-Cl$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 3 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 63) B) the full spectra.

*29% decomposition

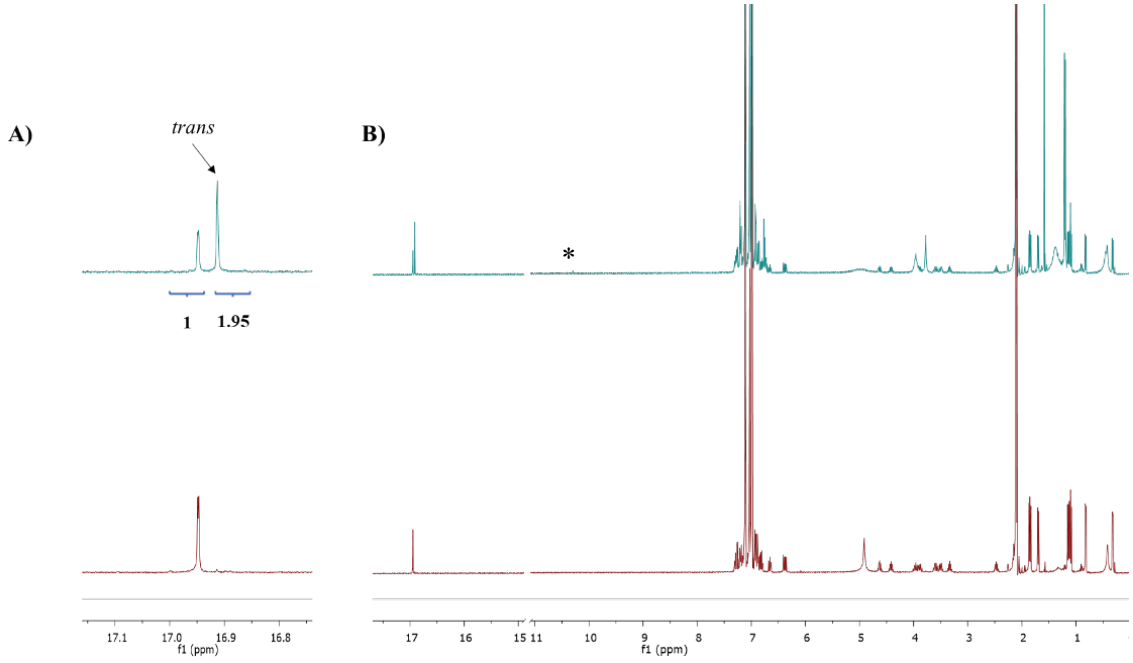


Figure S22. ^{1}H NMR analysis following isomerization of **SIPr-SPh-Br$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 1.5 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 66) B) the full spectra.

*1% decomposition

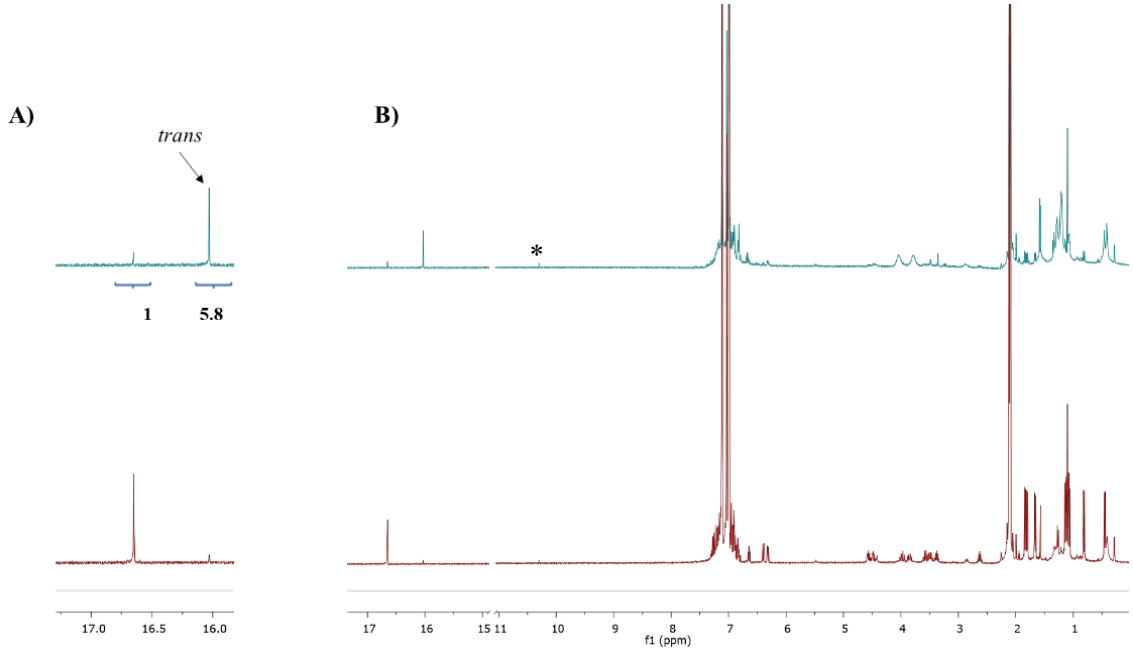


Figure S23. ^{1}H NMR analysis following isomerization of **SIPr-SPh-I$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 15 min. at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 85) B) the full spectra.

*4% decomposition

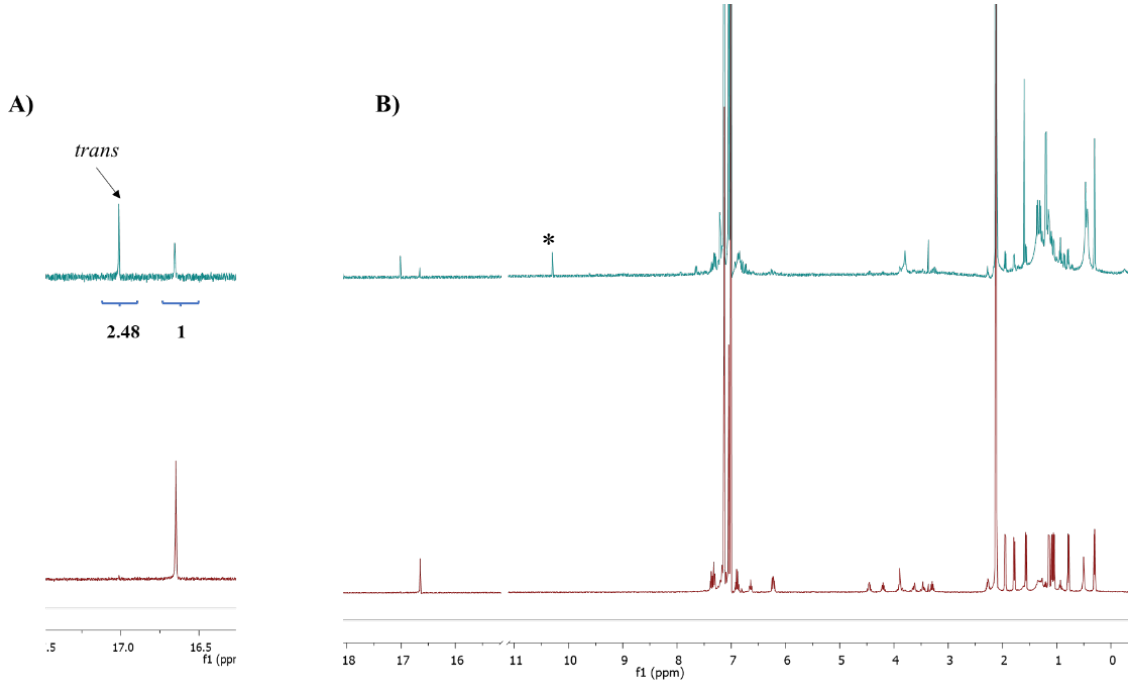


Figure S24. ^{1}H NMR analysis following isomerization of **SIPr-SCF$_3$-Cl$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 2 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 71) B) the full spectra.

*30% decomposition

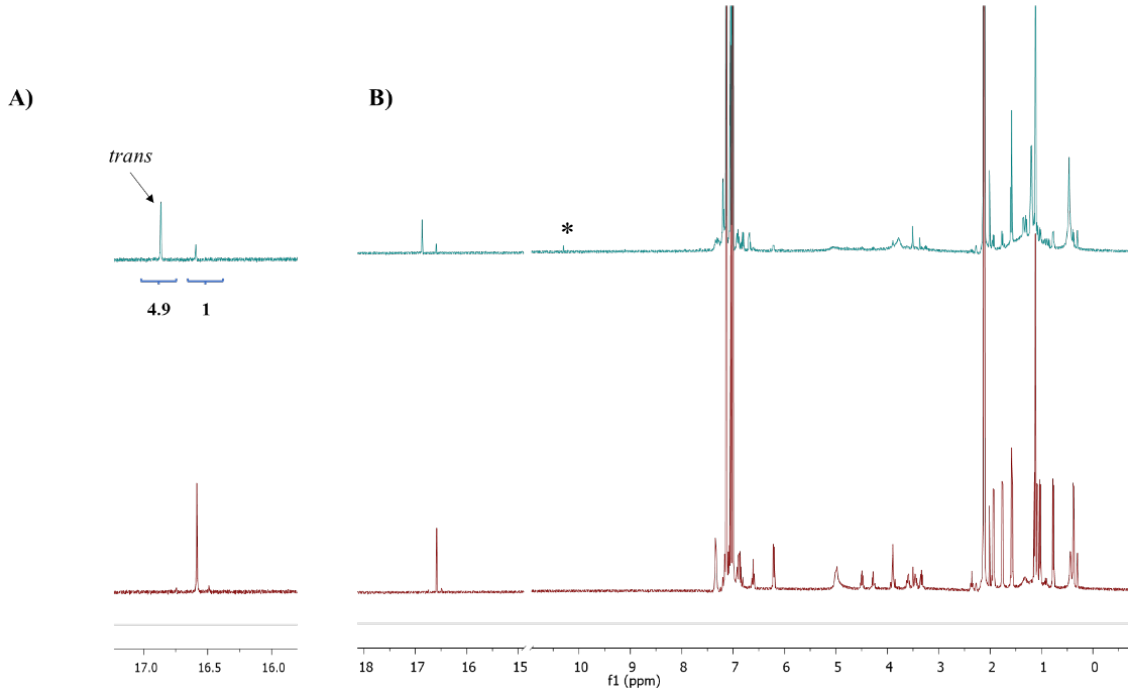


Figure S25. ^{1}H NMR analysis following isomerization of **SIPr-SCF$_3$-Br$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 1.5 h at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 80) B) the full spectra.

*6% decomposition

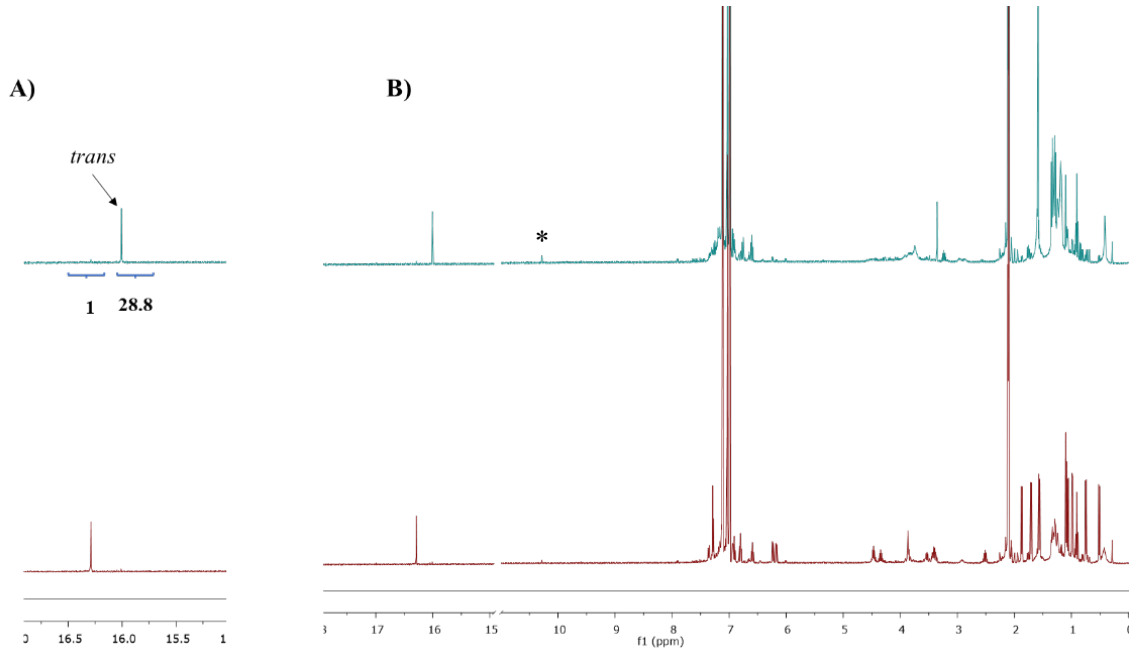


Figure S26. ^{1}H NMR analysis following isomerization of **SIPr-SCF$_3$-I$_2$** at 80°C in toluene-d$_8$ at t = 0 (bottom) and t = 15 min. at equilibrium (top): A) Zoom-in of the carbene region (% isomerization = 97) B) the full spectra.

*6% decomposition

Part VII. *cis-trans* photoisomerization studies following irradiation at 350 nm

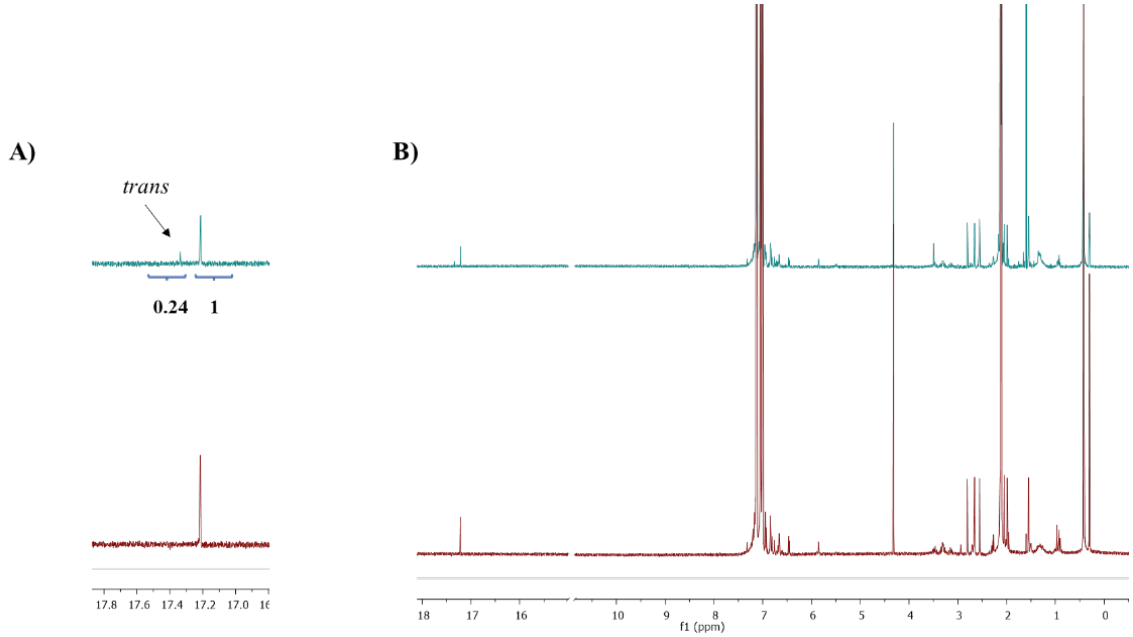


Figure S27. ^{1}H NMR analysis following isomerization of **SIMes-SPh-Cl$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 19); B) the full spectra.

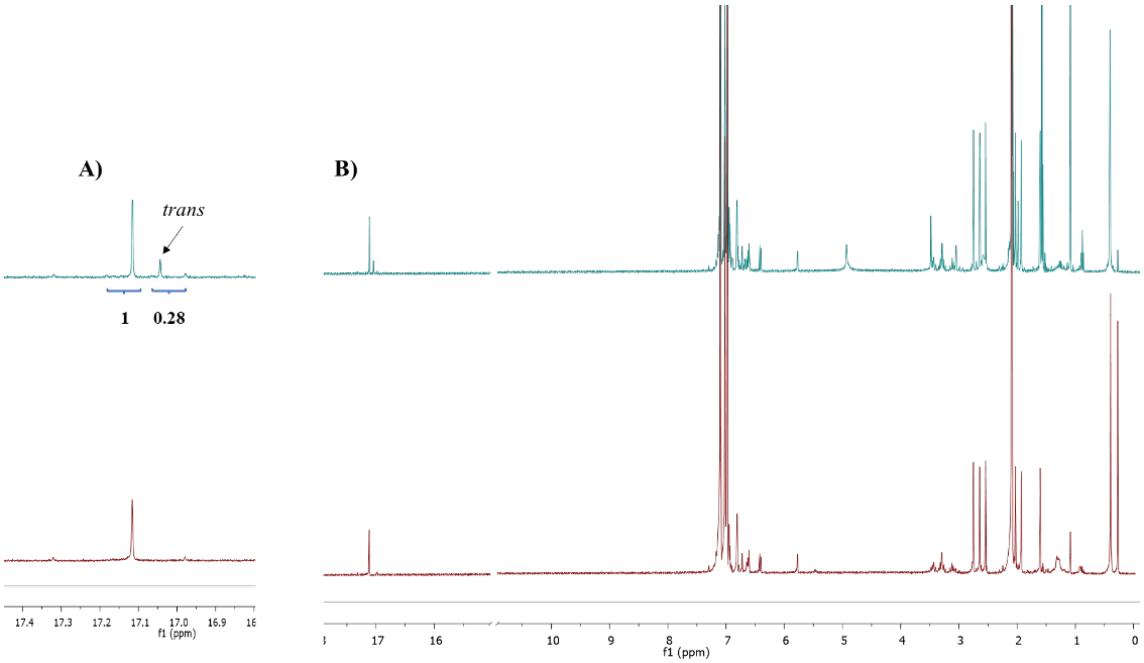


Figure S28. ^{1}H NMR analysis following isomerization of **SIMes-SPh-Br$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 22); B) the full spectra.

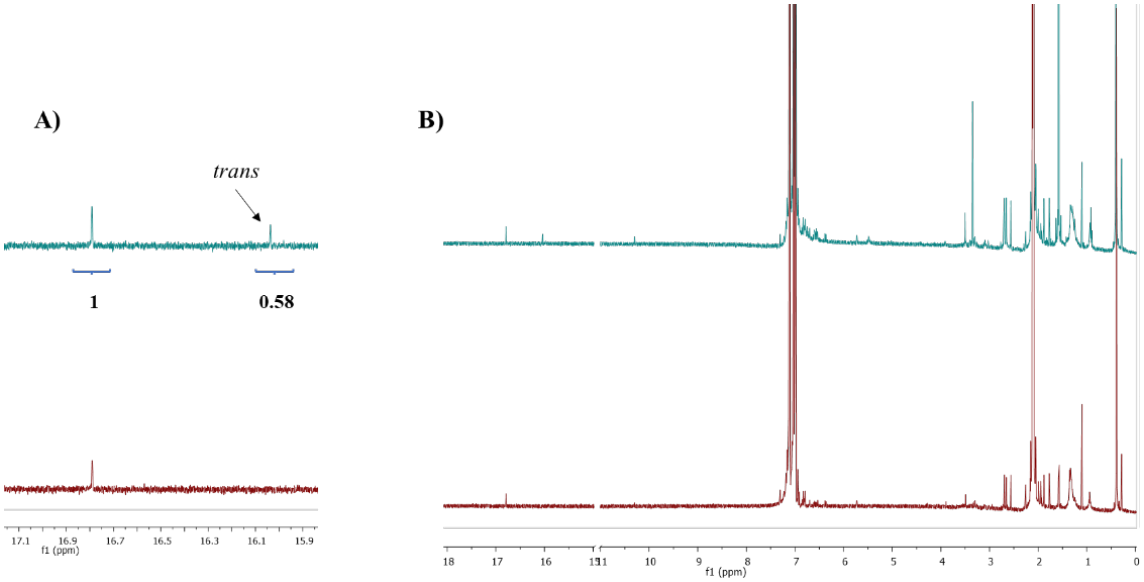


Figure S29. ^{1}H NMR analysis following isomerization of **SIMes-SPh-I$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 37); B) the full spectra.

*10% decomposition

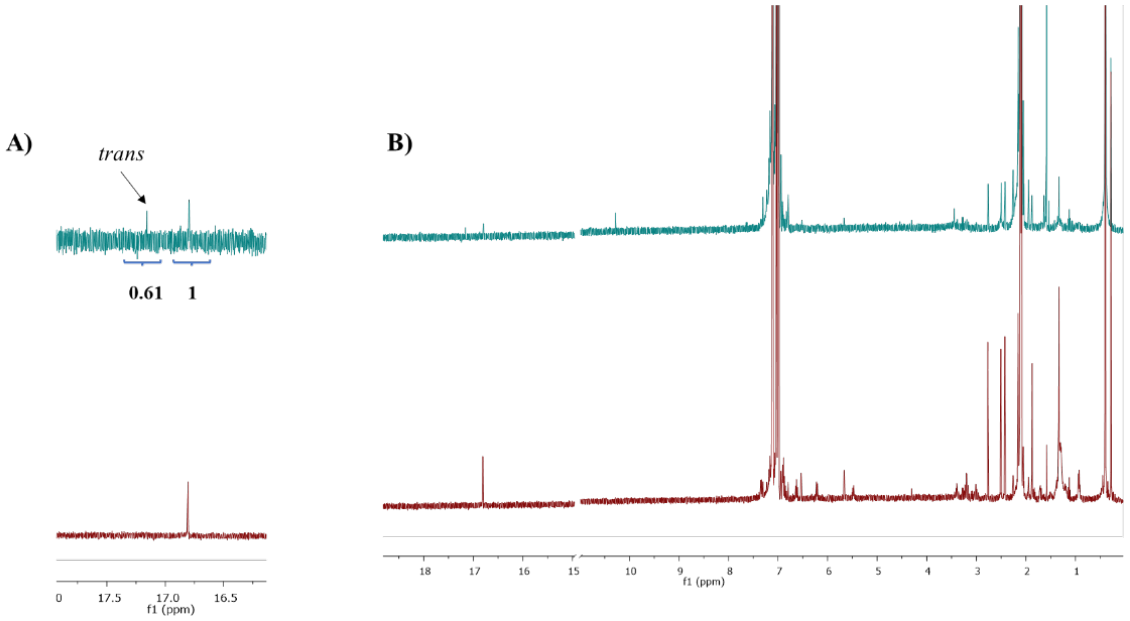


Figure S30. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-Cl$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 38); B) the full spectra.

*35% decomposition

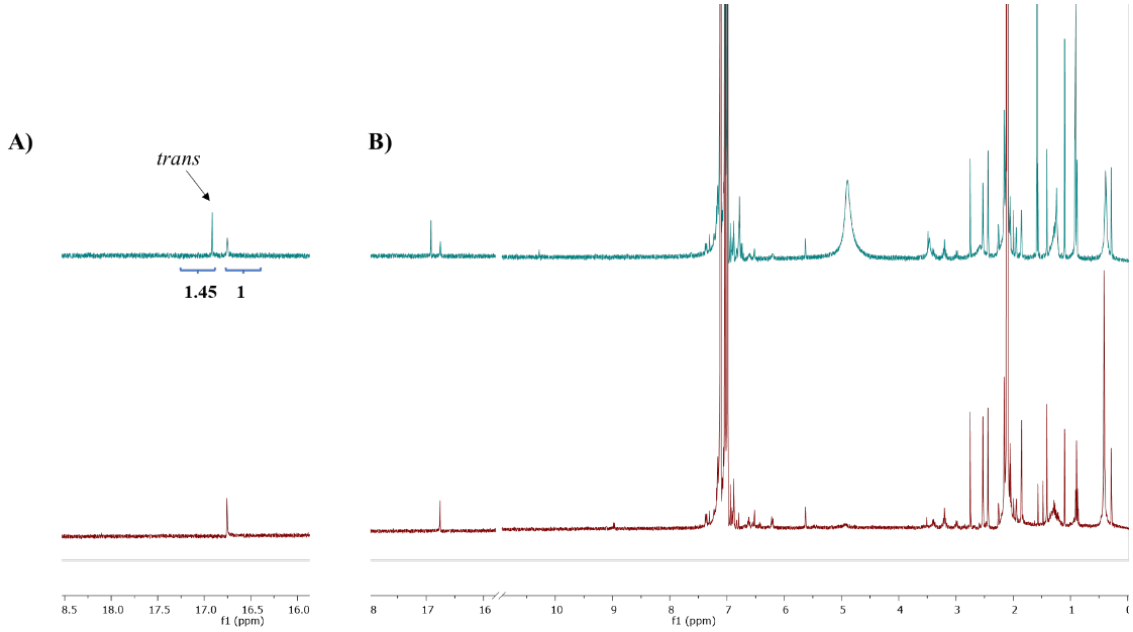


Figure S31. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-Br$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 59); B) the full spectra.

*4% decomposition

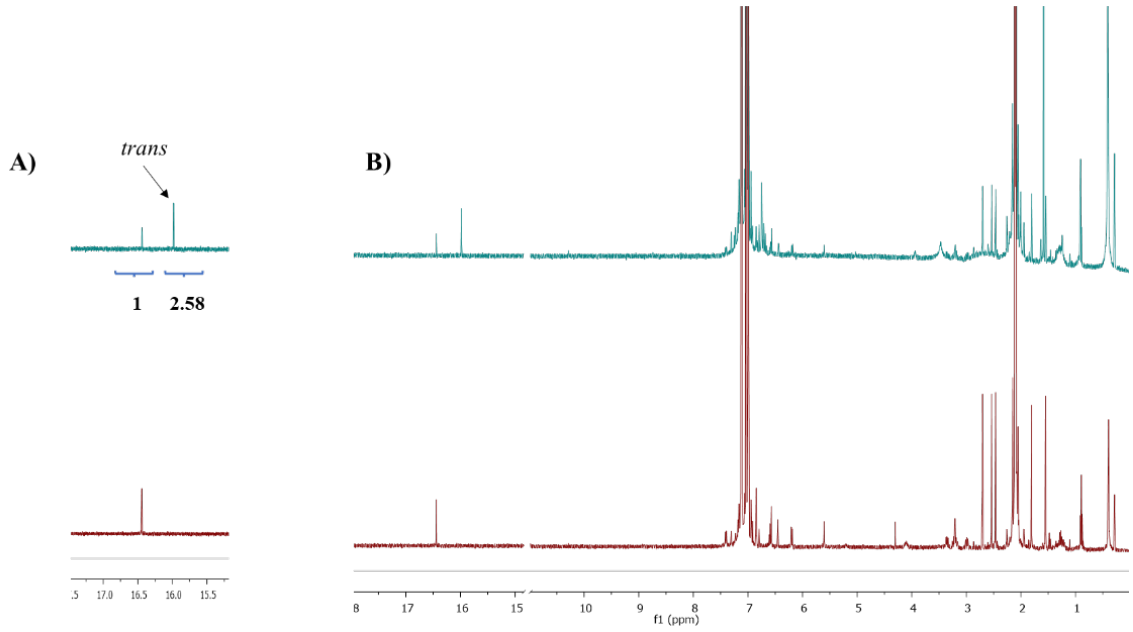


Figure S32. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-I$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 72); B) the full spectra.

*6% decomposition

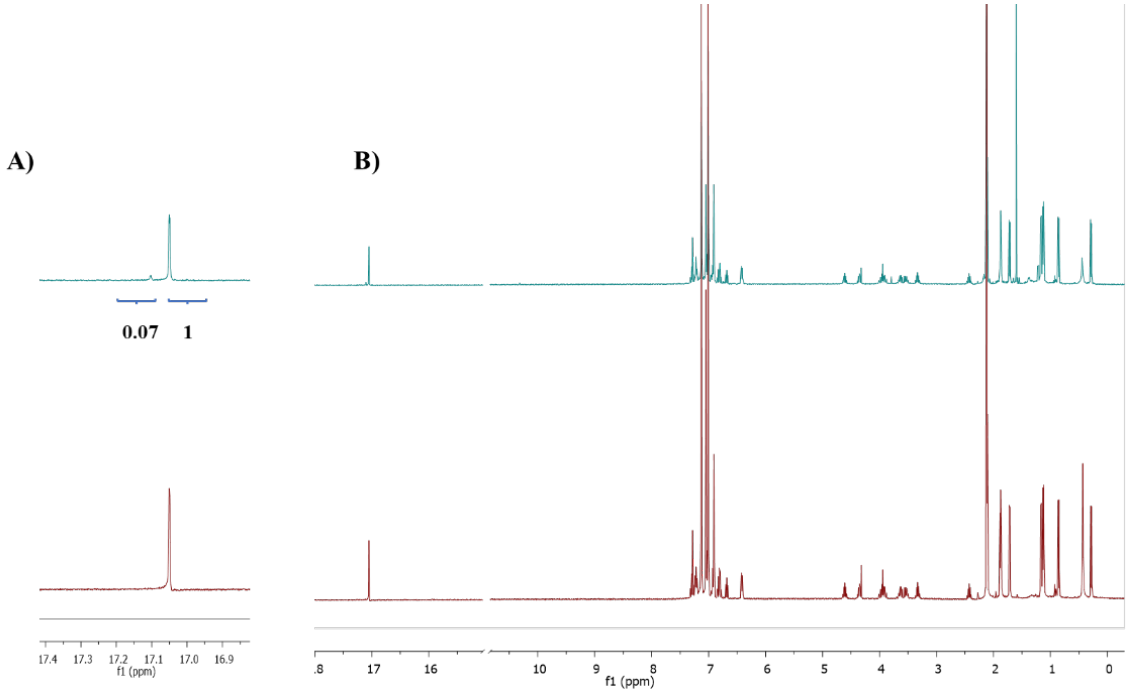


Figure S33. ^{1}H NMR analysis following isomerization of **SIPr-SPh-Cl$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 7); B) the full spectra.

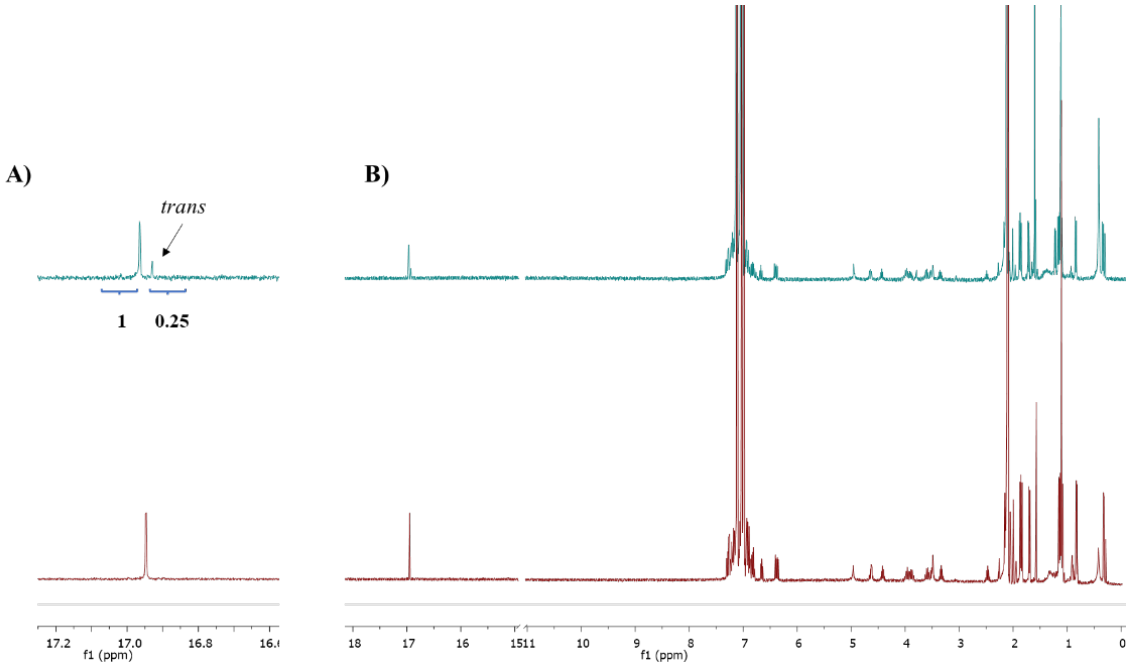


Figure S34. ^{1}H NMR analysis following isomerization of **SIPr-SPh-Br$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 20); B) the full spectra**.**

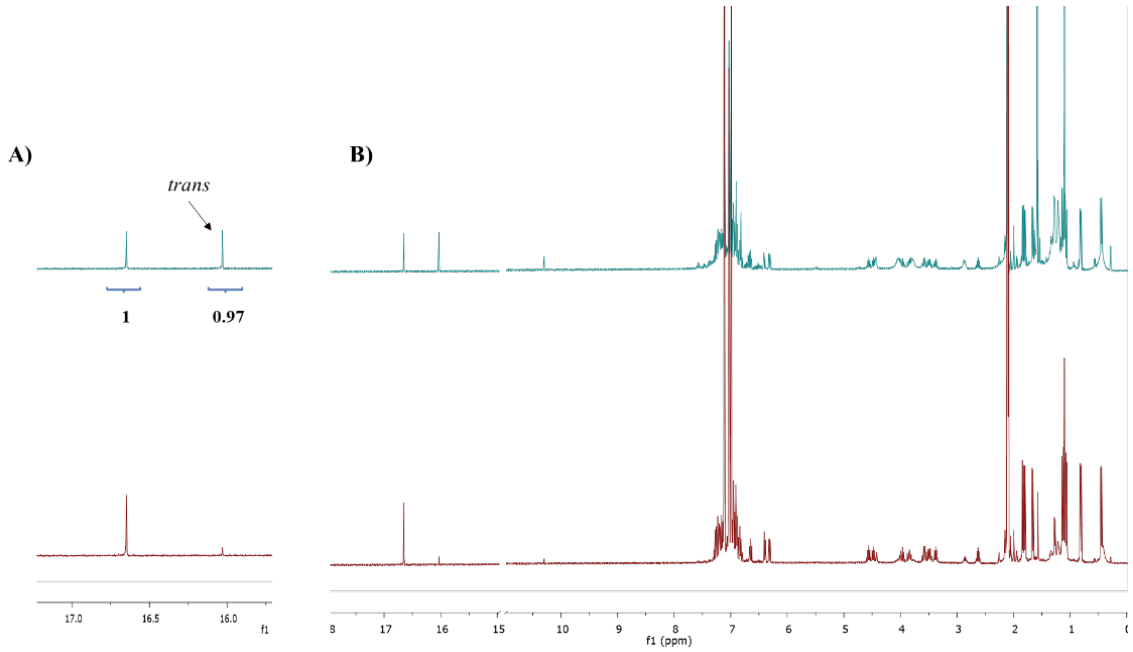


Figure S35. ^{1}H NMR analysis following isomerization of **SIPr-SPh-I$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 49); B) the full spectra

*8% decomposition

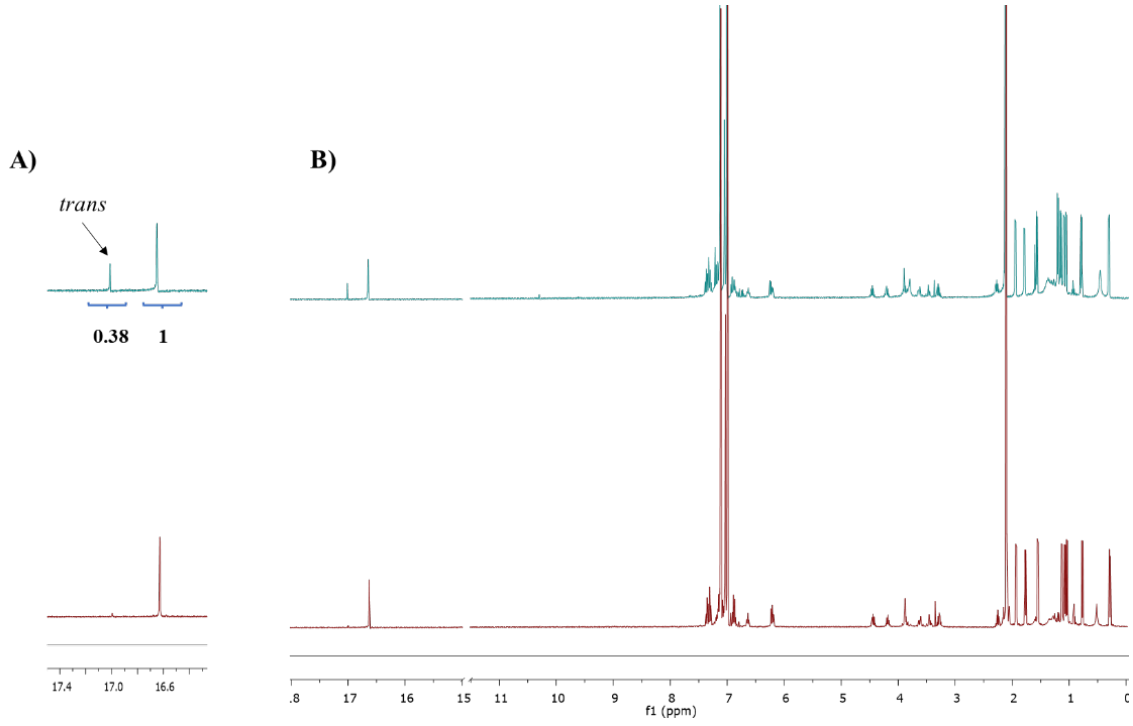


Figure S36. ^{1}H NMR analysis following isomerization of **SIPr-SCF$_3$-Cl$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 28); B) the full spectra

*6% decomposition

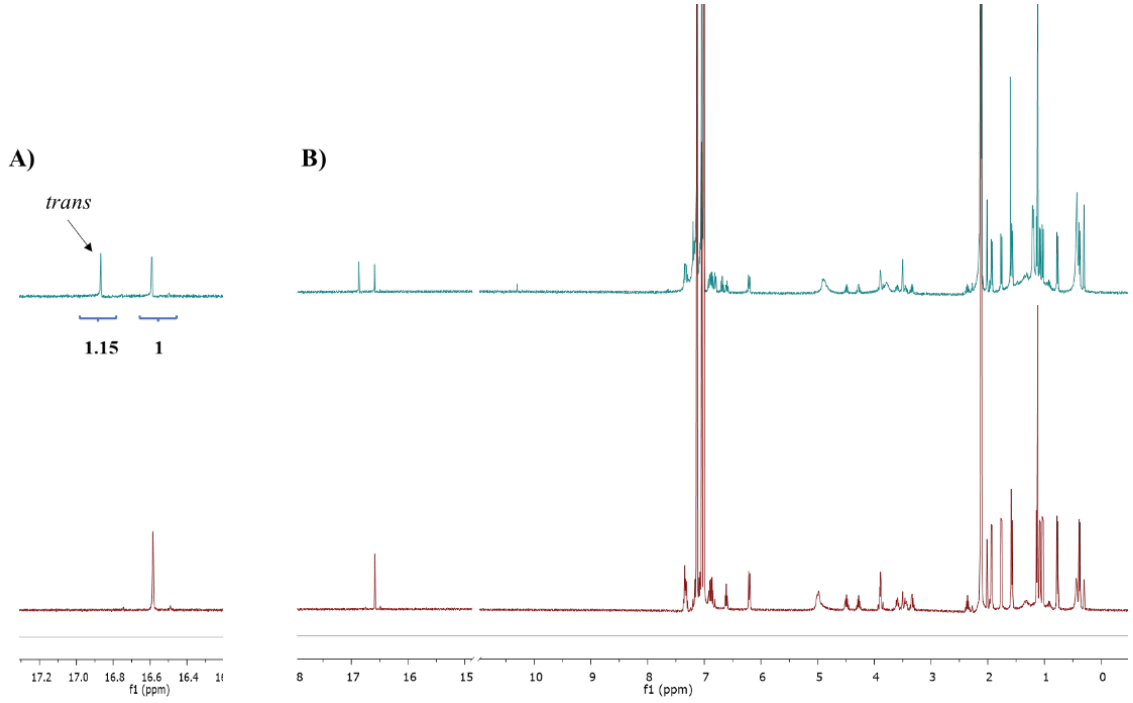


Figure S37. ^{1}H NMR analysis following isomerization of **SIPr-SPh-Br$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 54); B) the full spectra

*8% decomposition

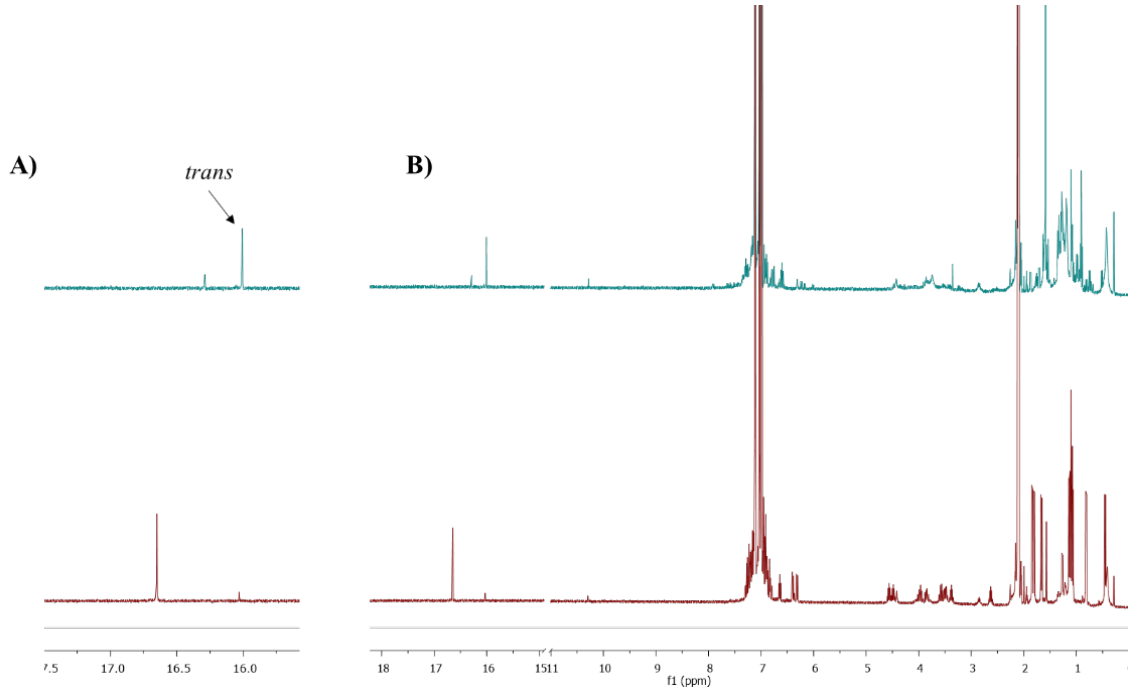


Figure S38. ^{1}H NMR analysis following isomerization of **SIPr-SPh-I$_2$** before (bottom) and after irradiation at 350 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization > 99); B) the full spectra.

*8% decomposition.

Part VIII. *cis-trans* photoisomerization studies following irradiation at 510 nm

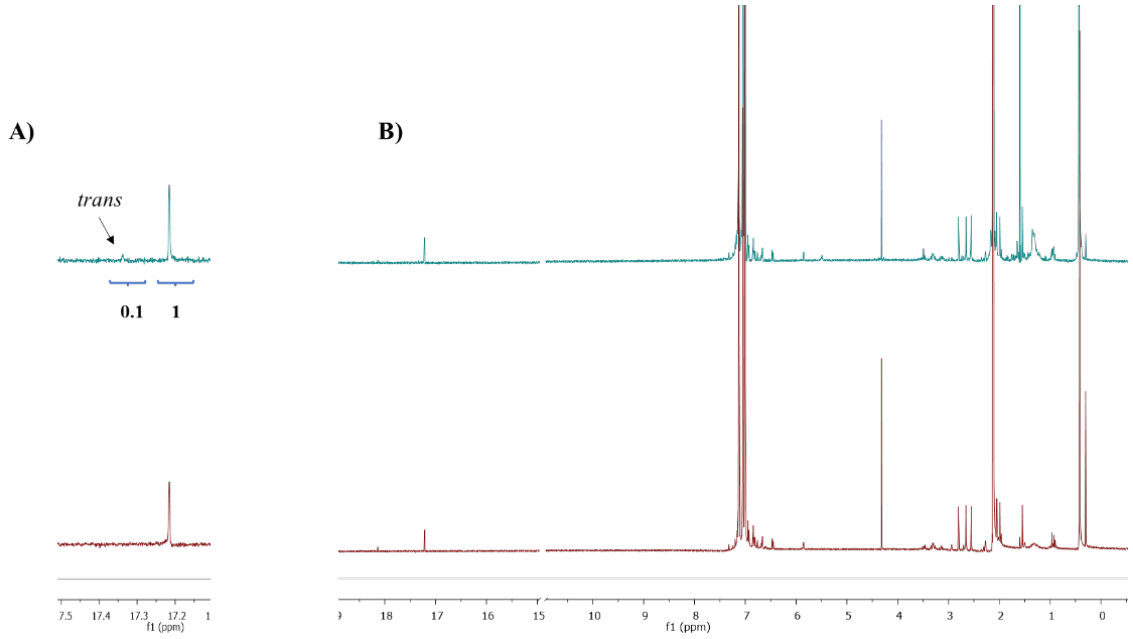


Figure S39. ^{1}H NMR analysis following isomerization of **SIMes-SPh-Cl$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 9); B) the full spectra.

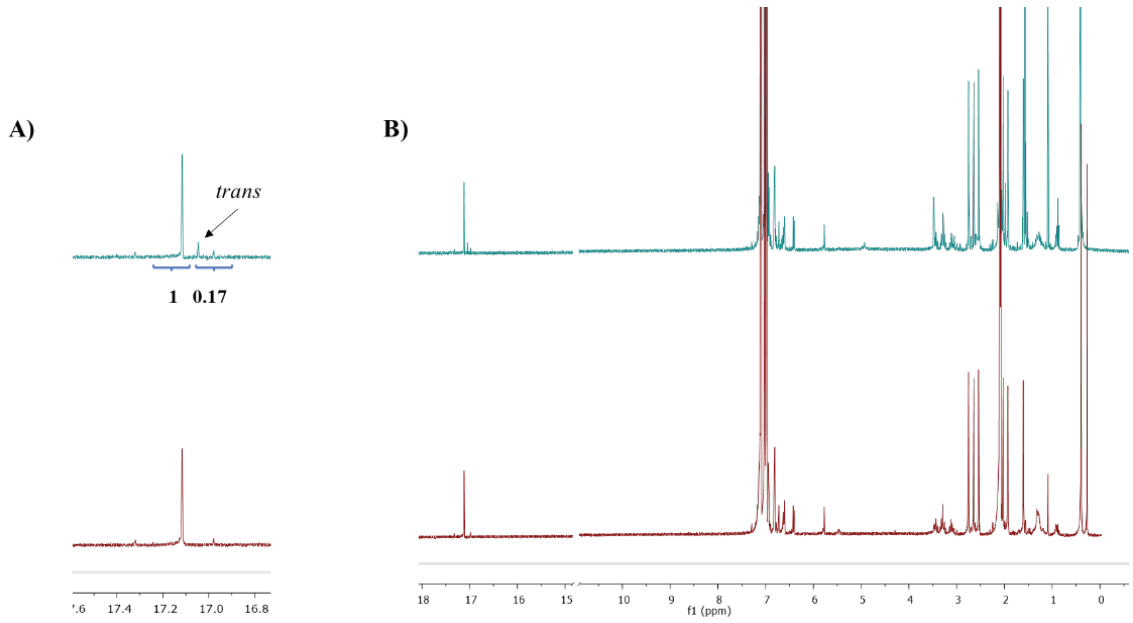


Figure S40. ^{1}H NMR analysis following isomerization of **SIMes-SPh-Br$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 15); B) the full spectra..

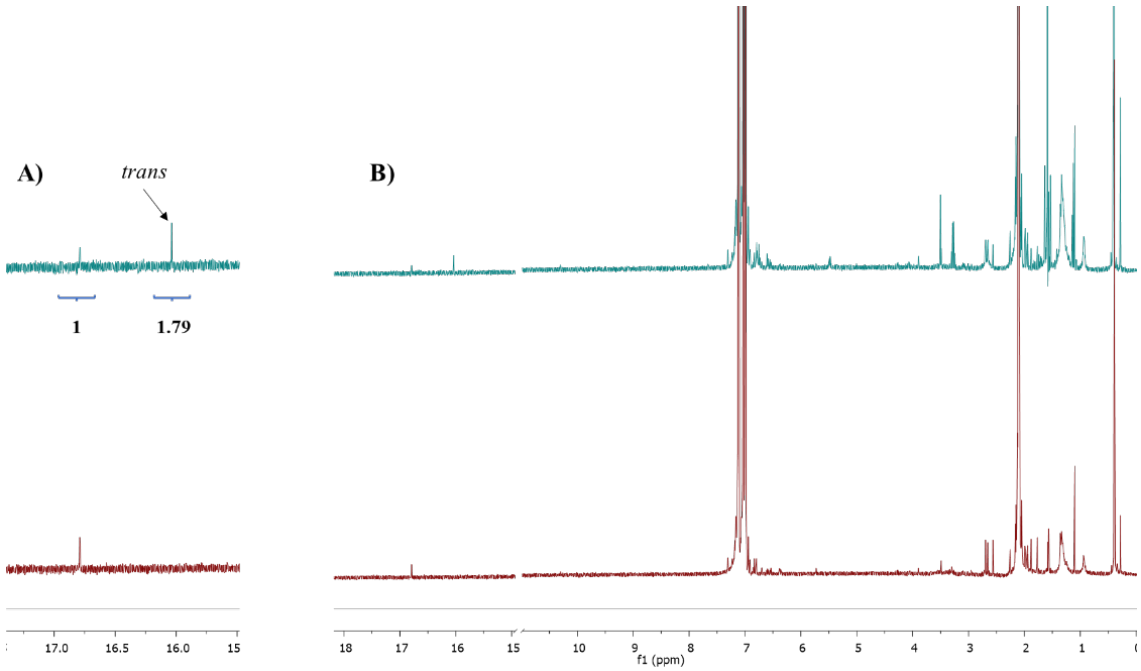


Figure S41. ^{1}H NMR analysis following isomerization of **SIMes-SPh-I$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 64); B) the full spectra.

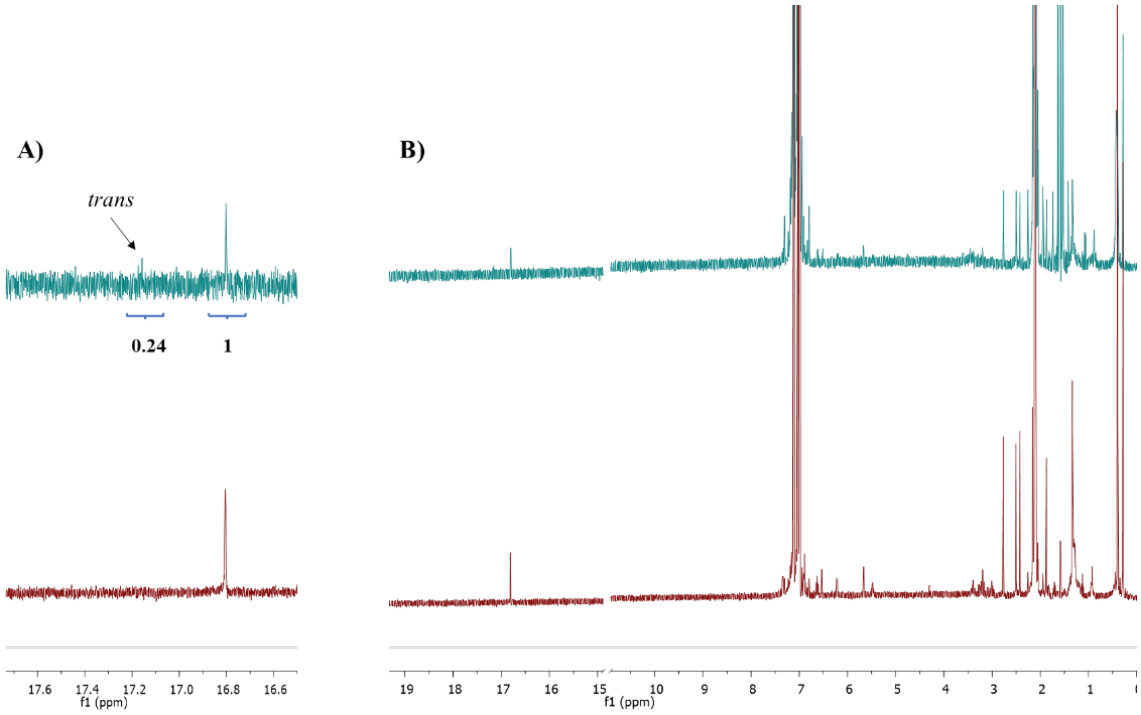


Figure S42. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-Cl$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 19); B) the full spectra.

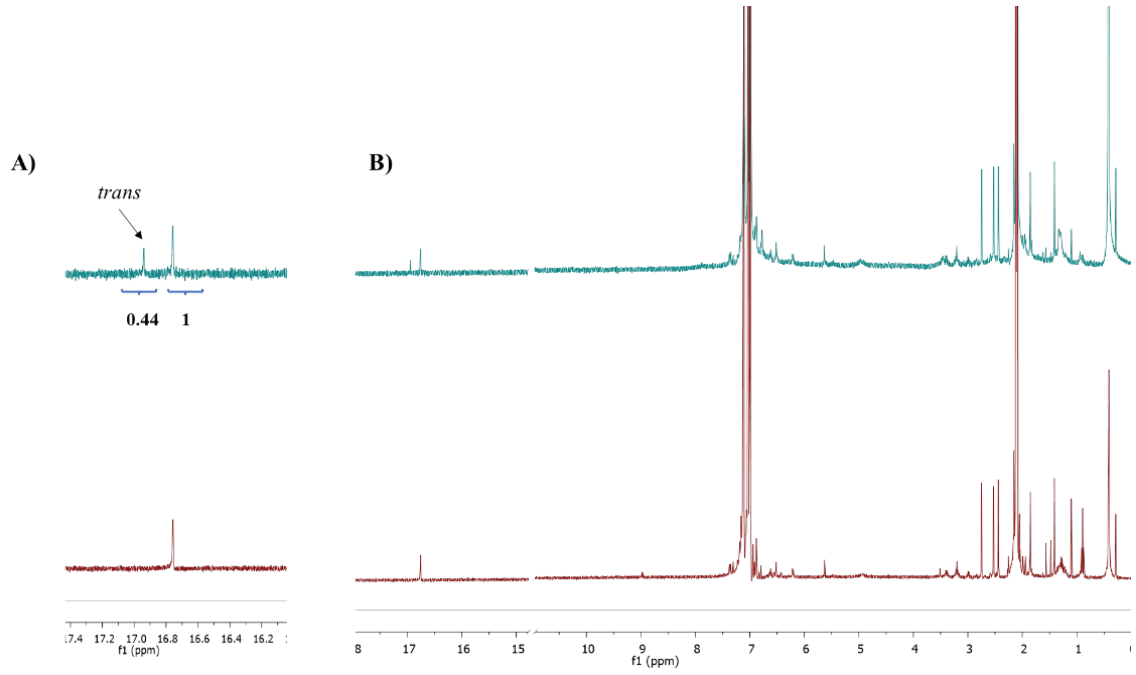


Figure S43. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-Br$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 31); B) the full spectra..

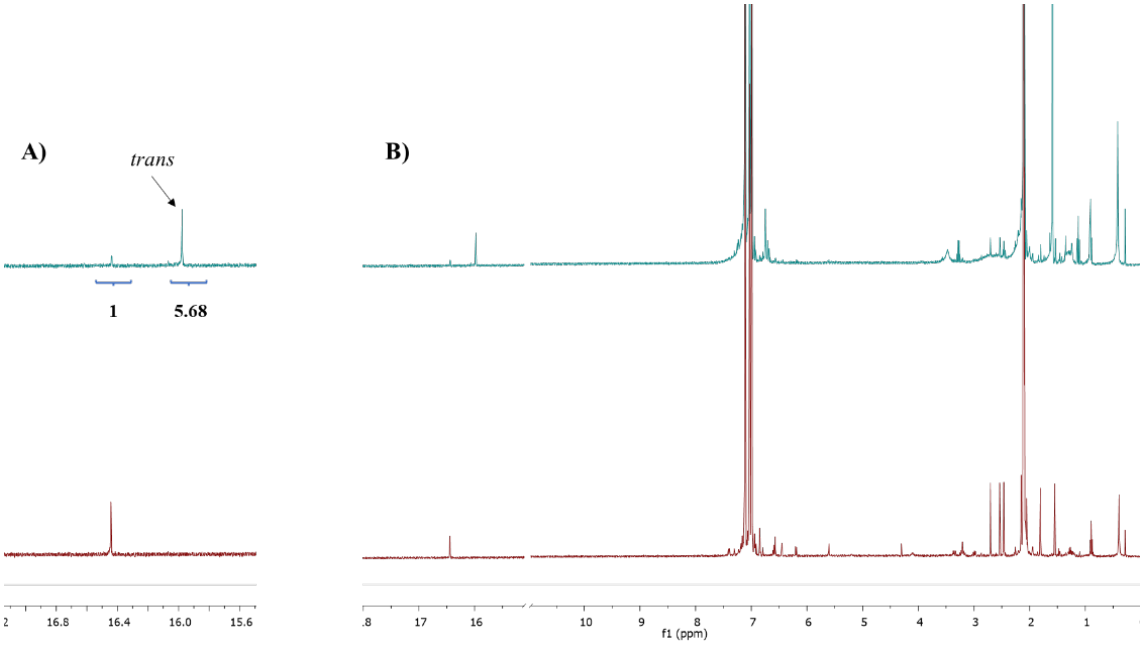


Figure S44. ^{1}H NMR analysis following isomerization of **SIMes-SCF$_3$-I$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 85); B) the full spectra.

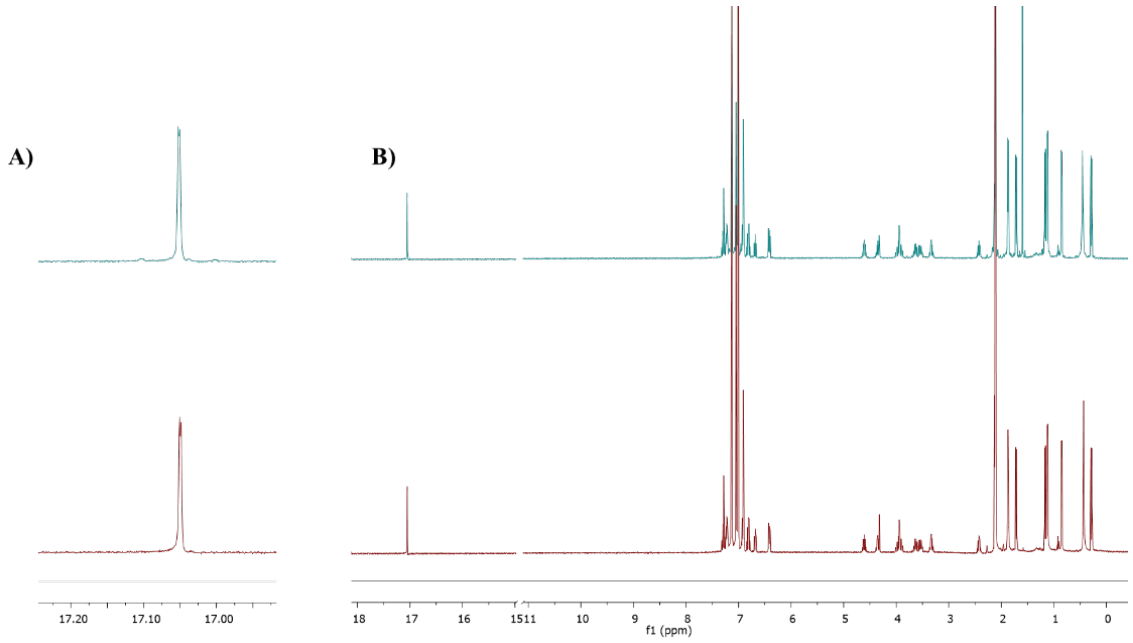


Figure S45. ^{1}H NMR analysis following isomerization of **SIPr-SPh-Cl$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 4); B) the full spectra.

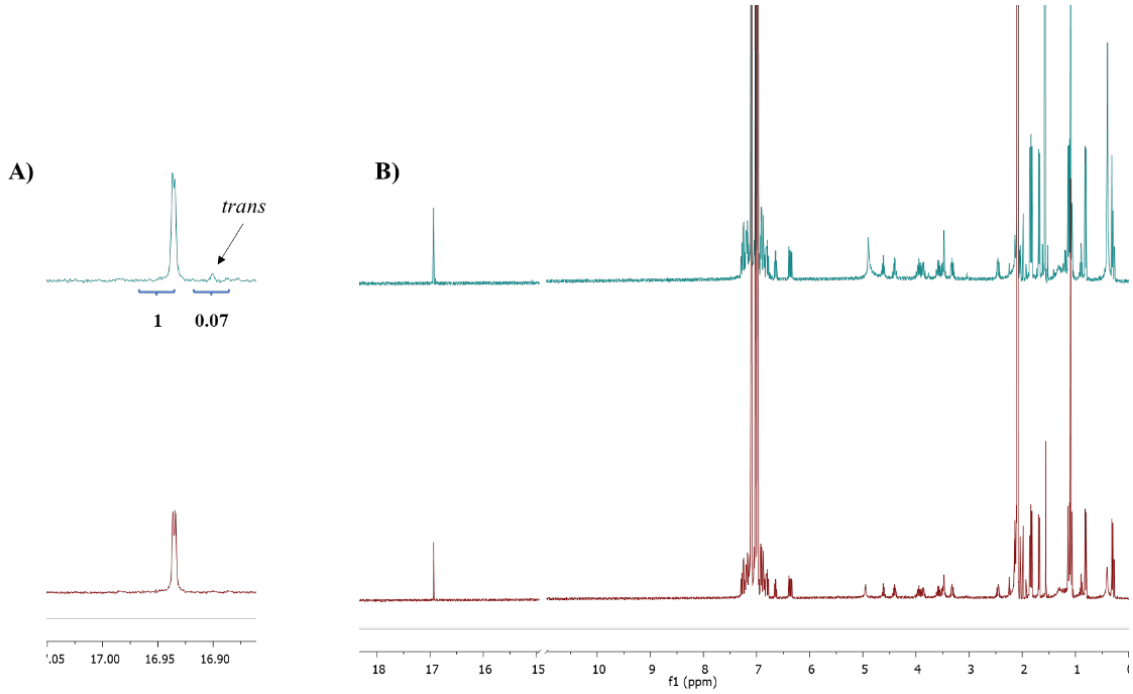


Figure S46. ^{1}H NMR analysis following isomerization of **SIPr-SPh-Br$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 7); B) the full spectra.

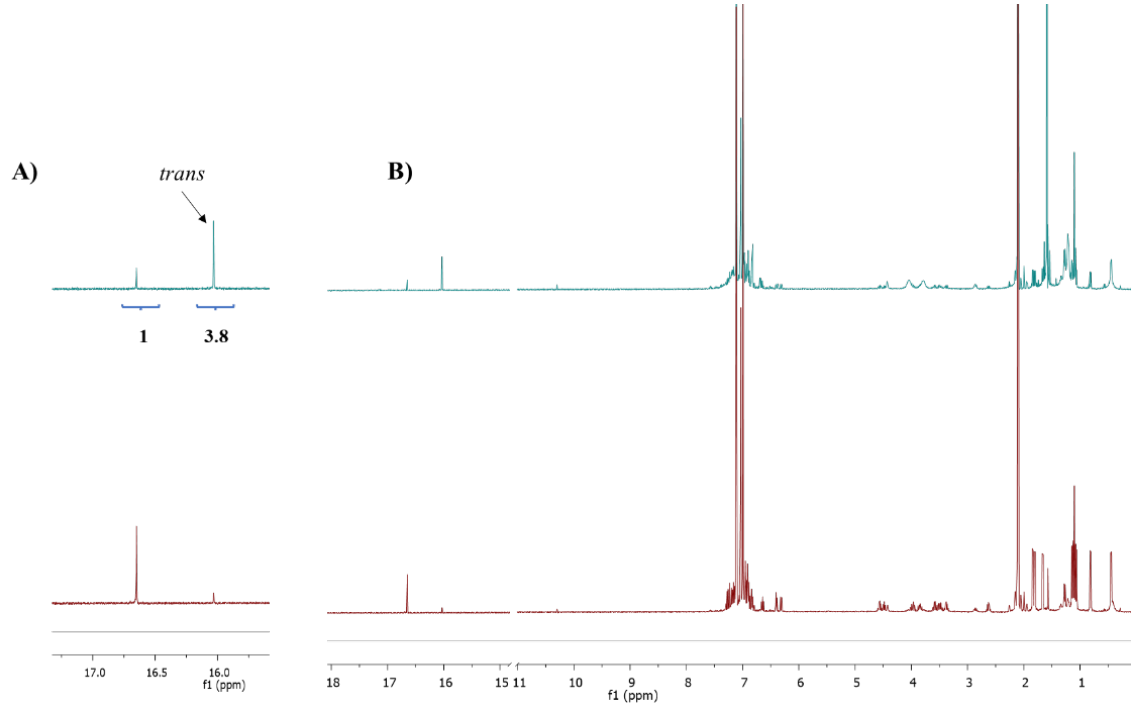


Figure S47. ^{1}H NMR analysis following isomerization of **SIPr-SPh-I$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 79); B) the full spectra.

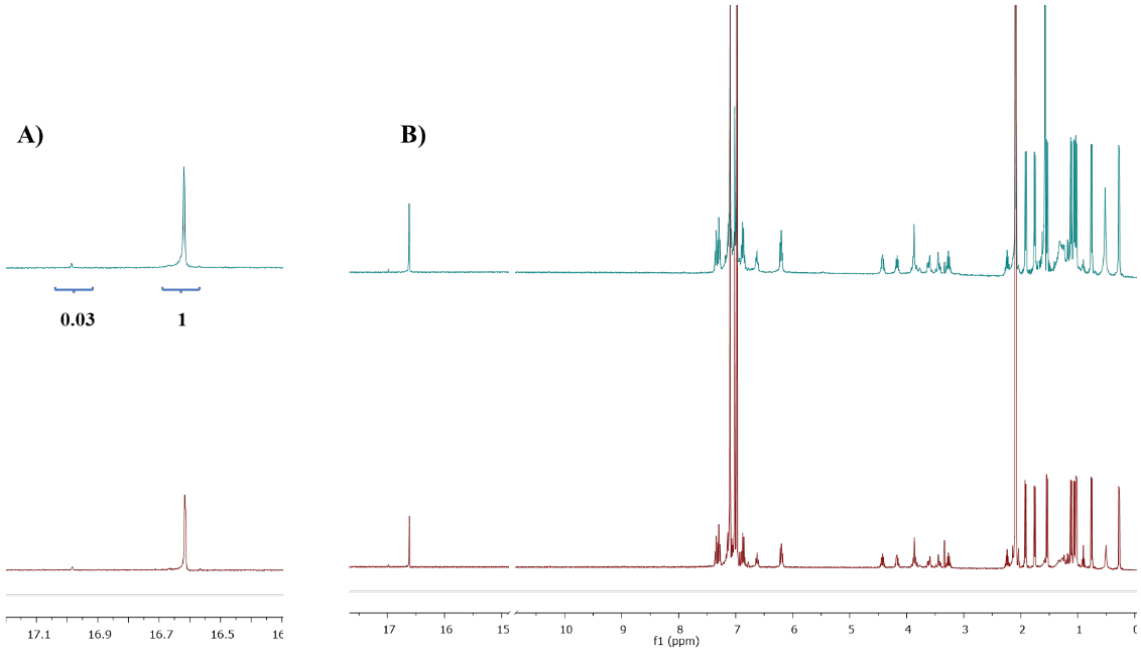


Figure S48. ^{1}H NMR analysis following isomerization of **SIPr-SCF$_3$Cl$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 3); B) the full spectra.

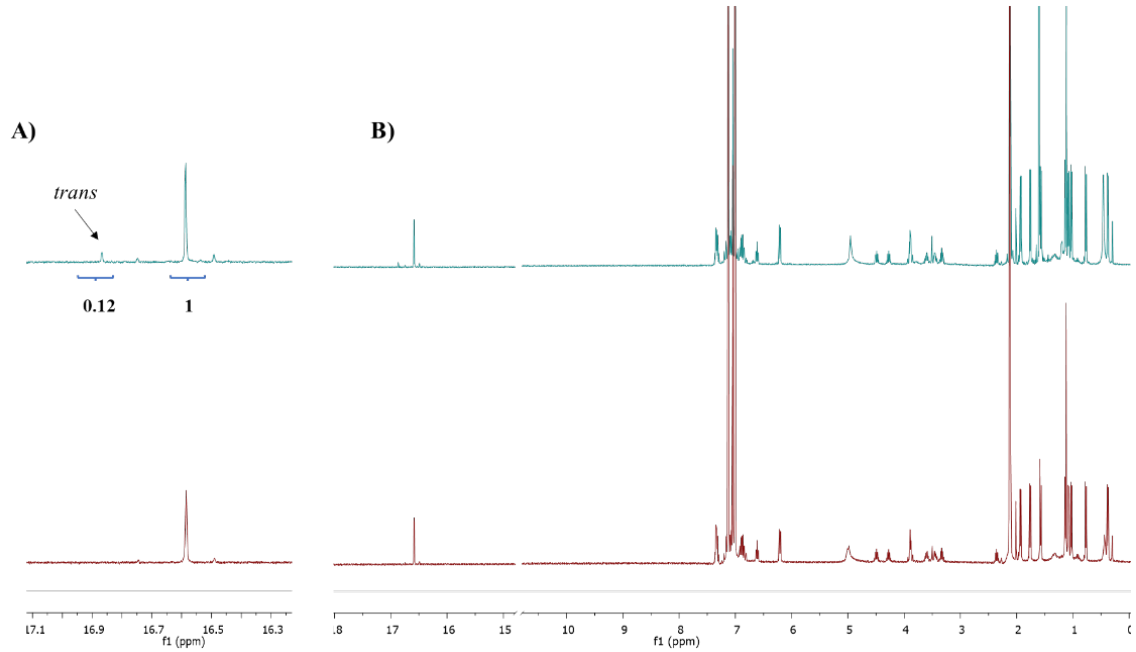


Figure S49. ^{1}H NMR analysis following isomerization of **SIPr-SCF$_3$Br$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization = 11); B) the full spectra.

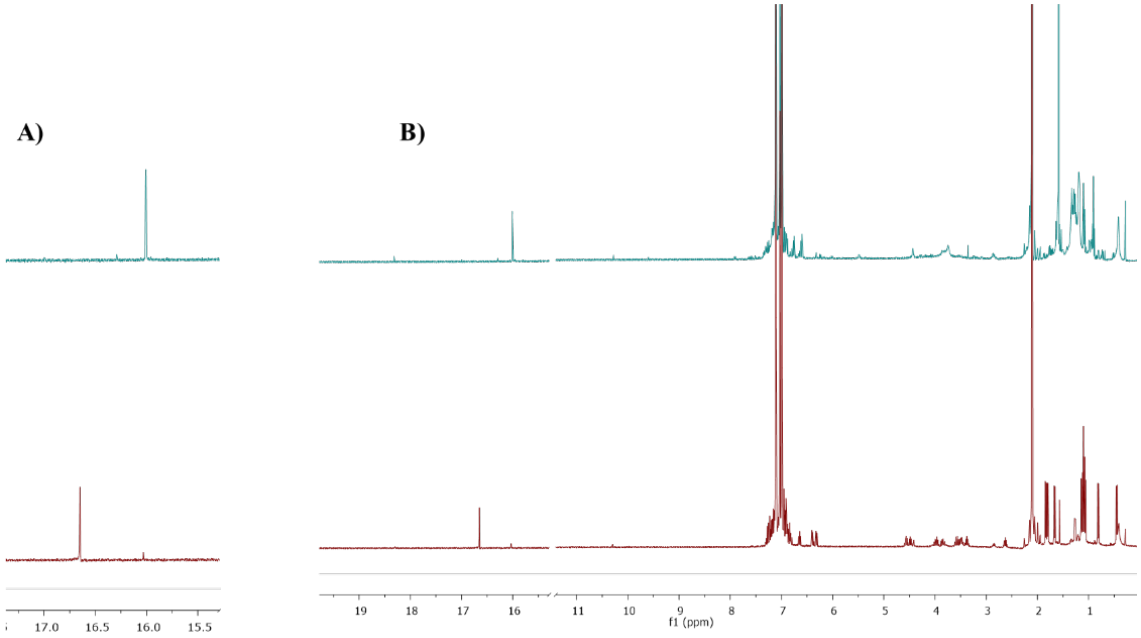


Figure S50. ^{1}H NMR analysis following isomerization of **SIPr-SCF$_3$I$_2$** before (bottom) and after irradiation at 510 nm in toluene-d$_8$ for 2 h (top): A) Zoom-in of the carbene region (% isomerization > 99); B) the full spectra.

Part IX. Reactivity of equilibrated Ru complexes at *RT*

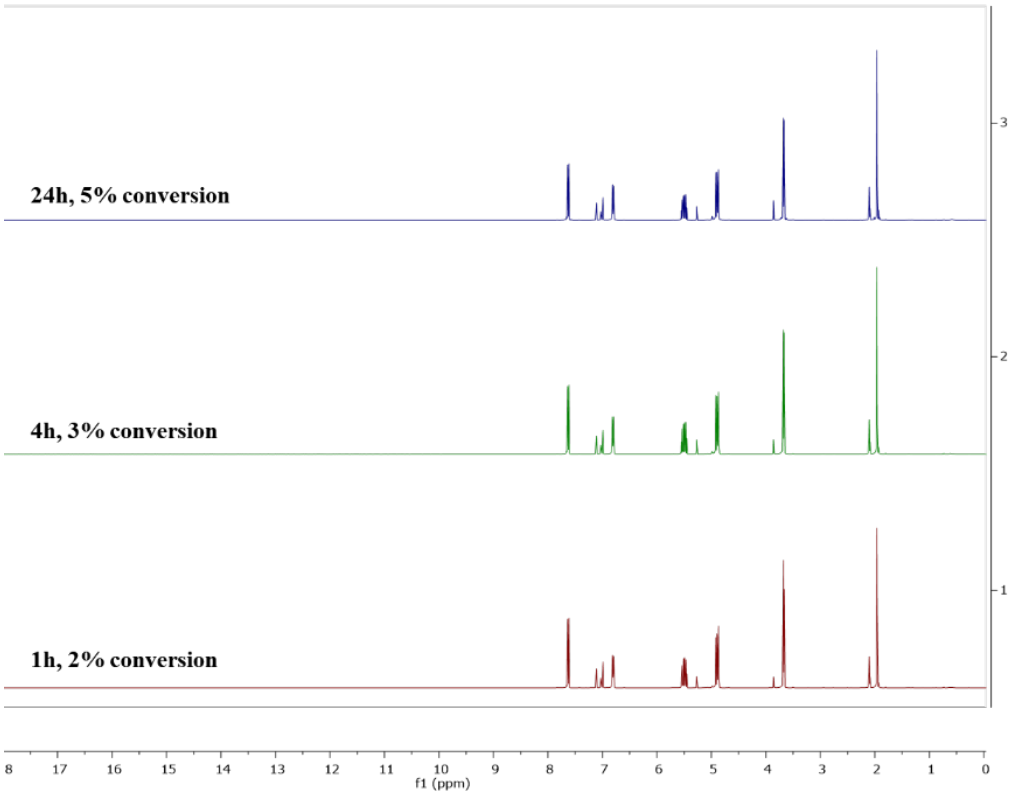


Figure S51. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIMes-SCF$_3$-Cl$_2$**.

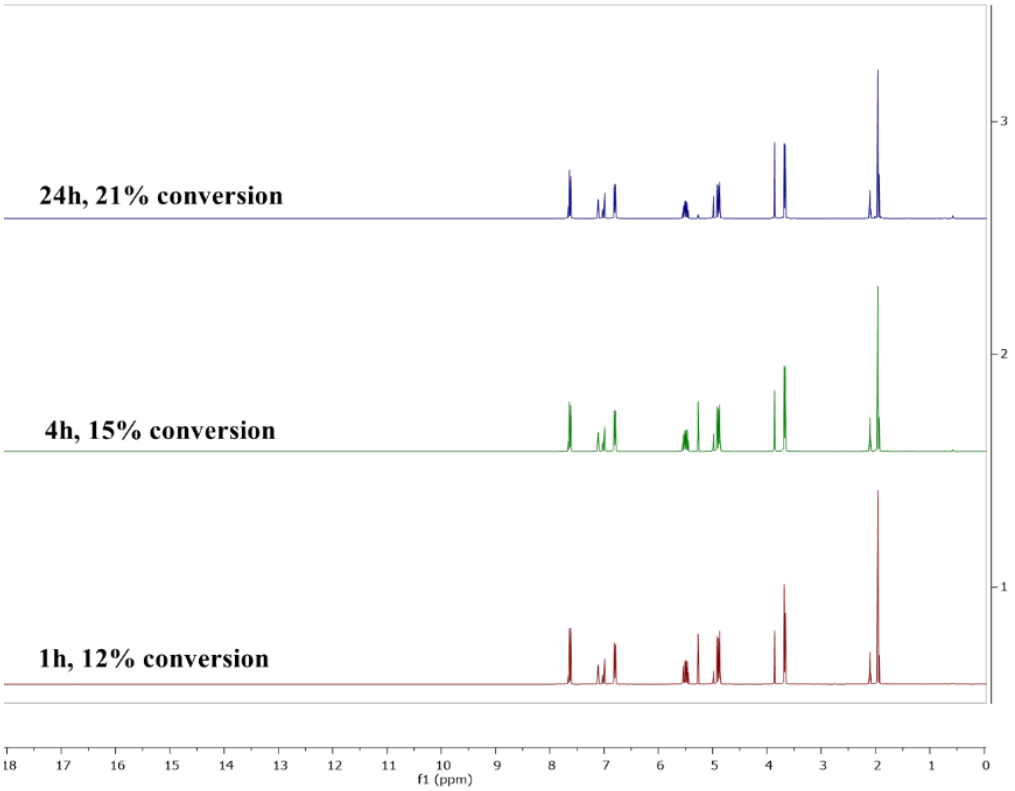


Figure S52. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIMes-SCF$_3$-Br$_2$**.

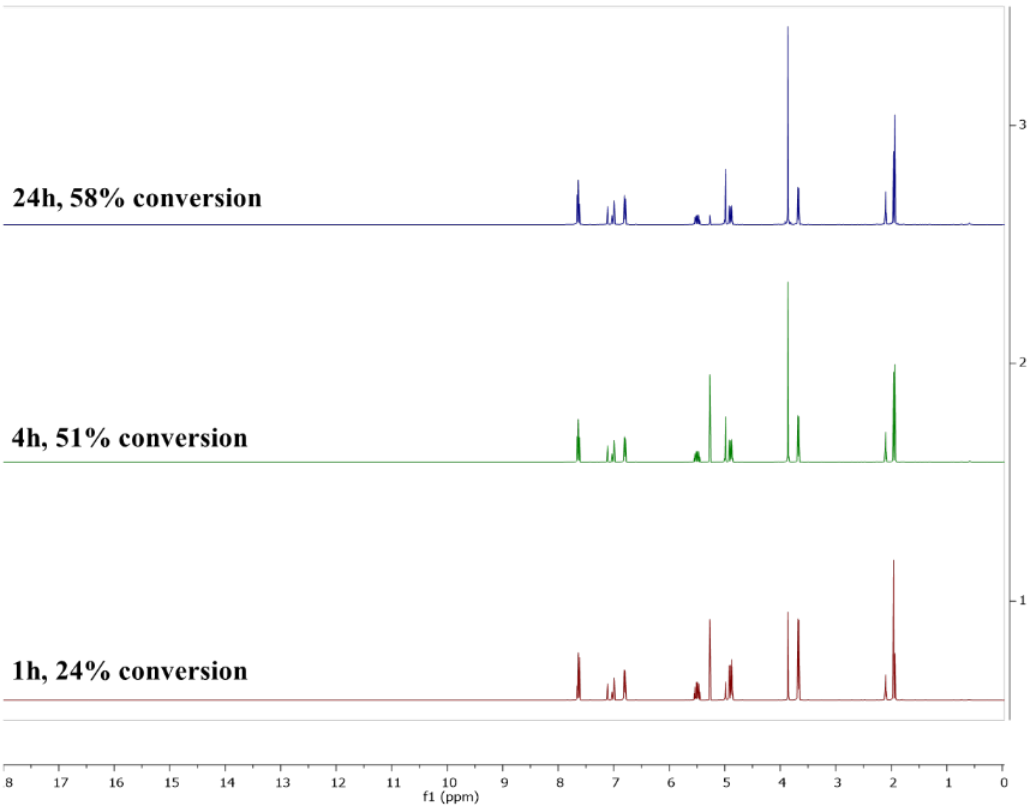


Figure S53. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIMes-SCF$_3$-I$_2$**.

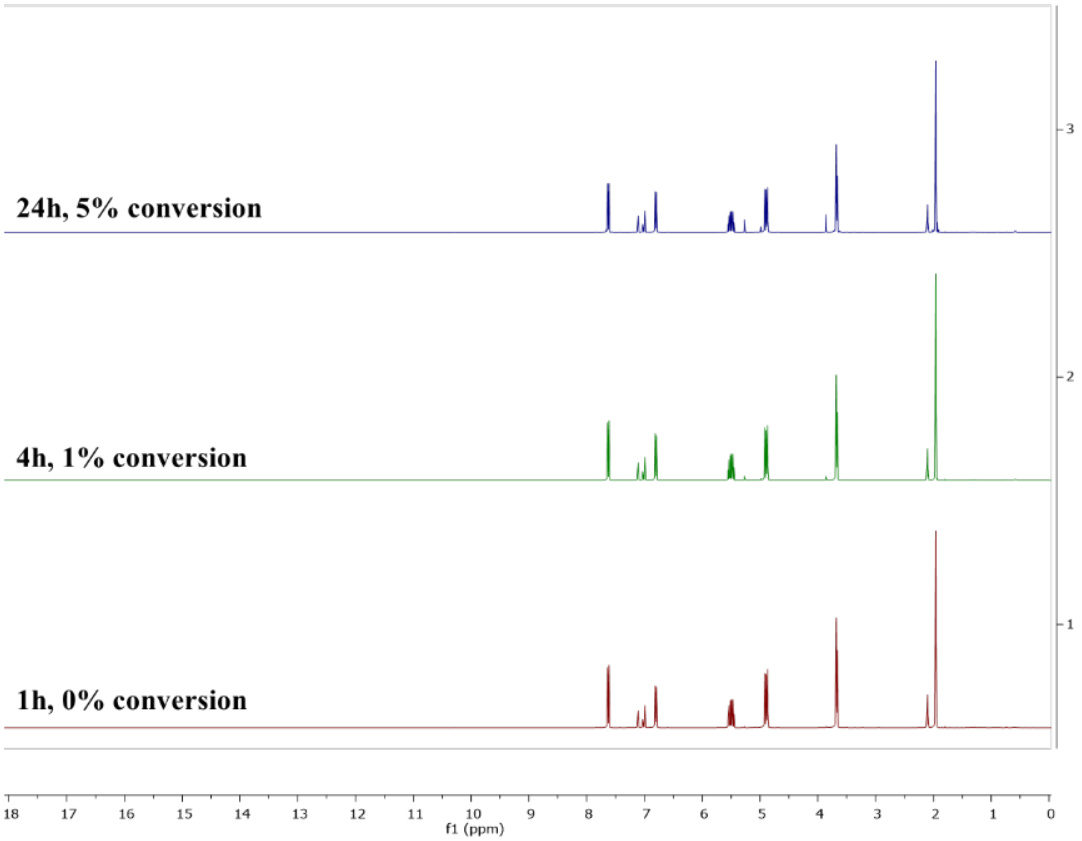


Figure S54. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIPr-SPh-Cl$_2$**.

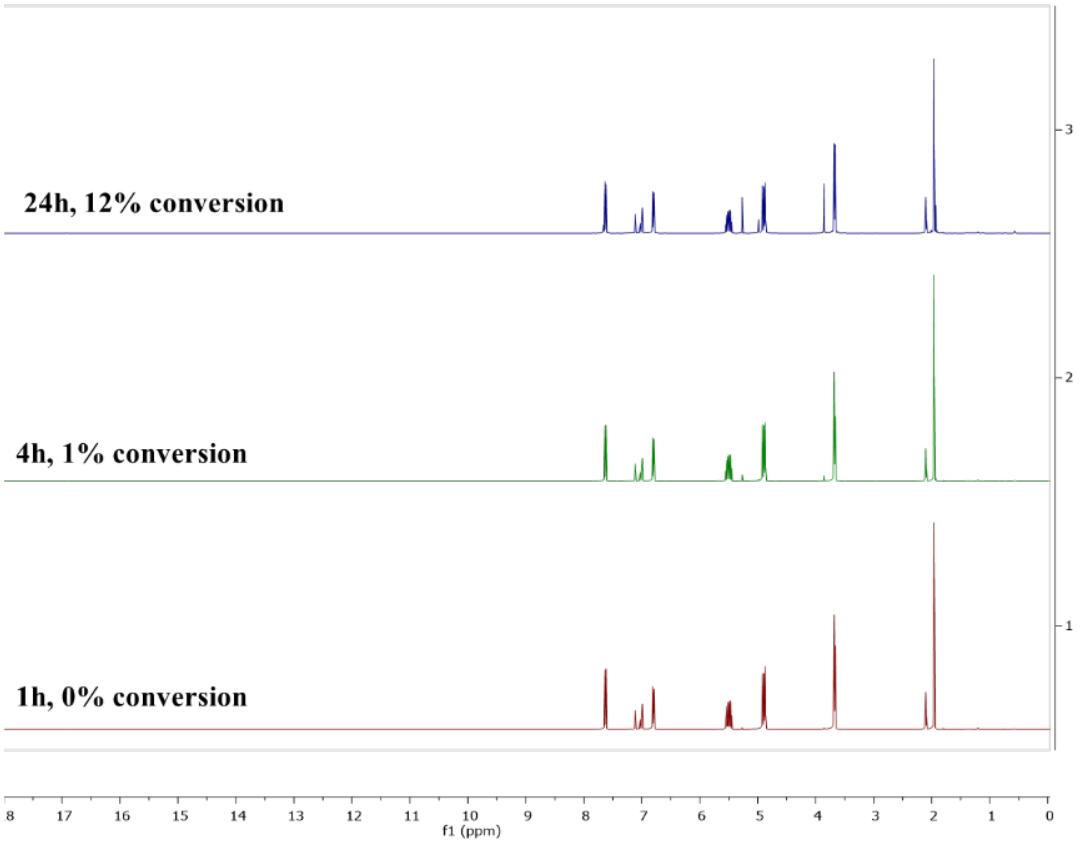


Figure S55. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIPr-SPh-Br$_2$**.

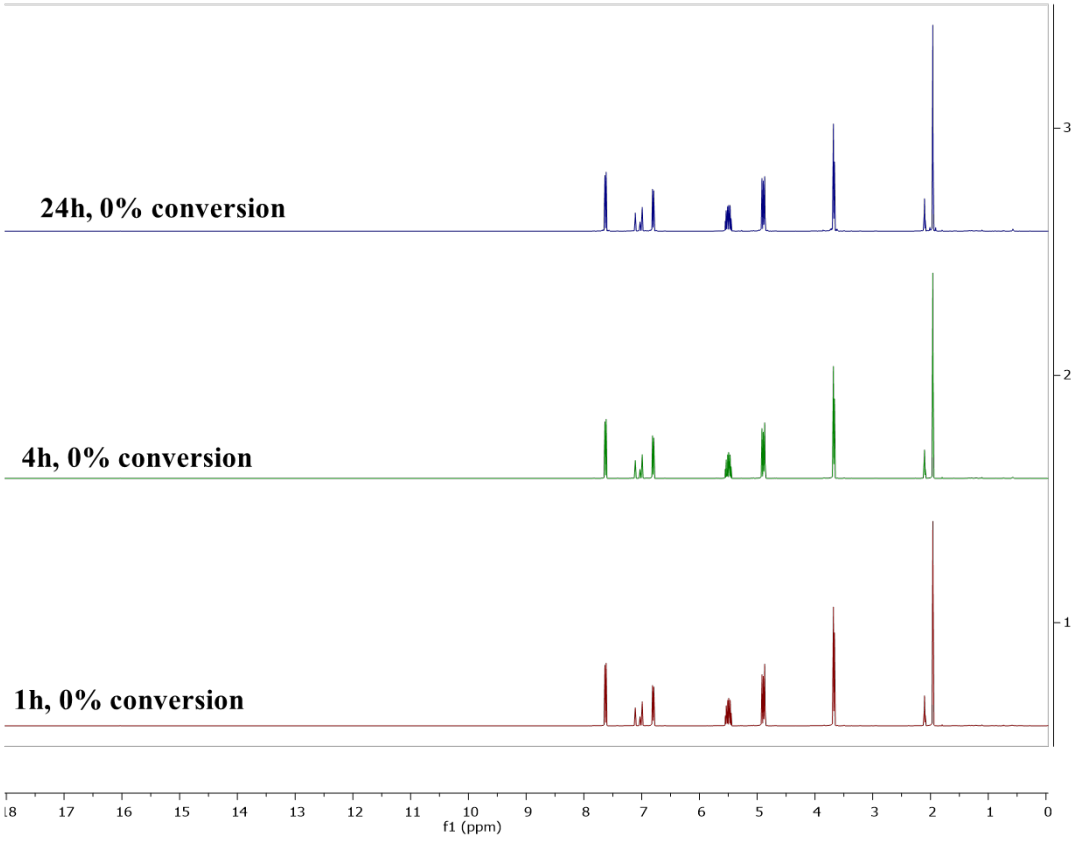


Figure S56. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIPr-SPh-I**.

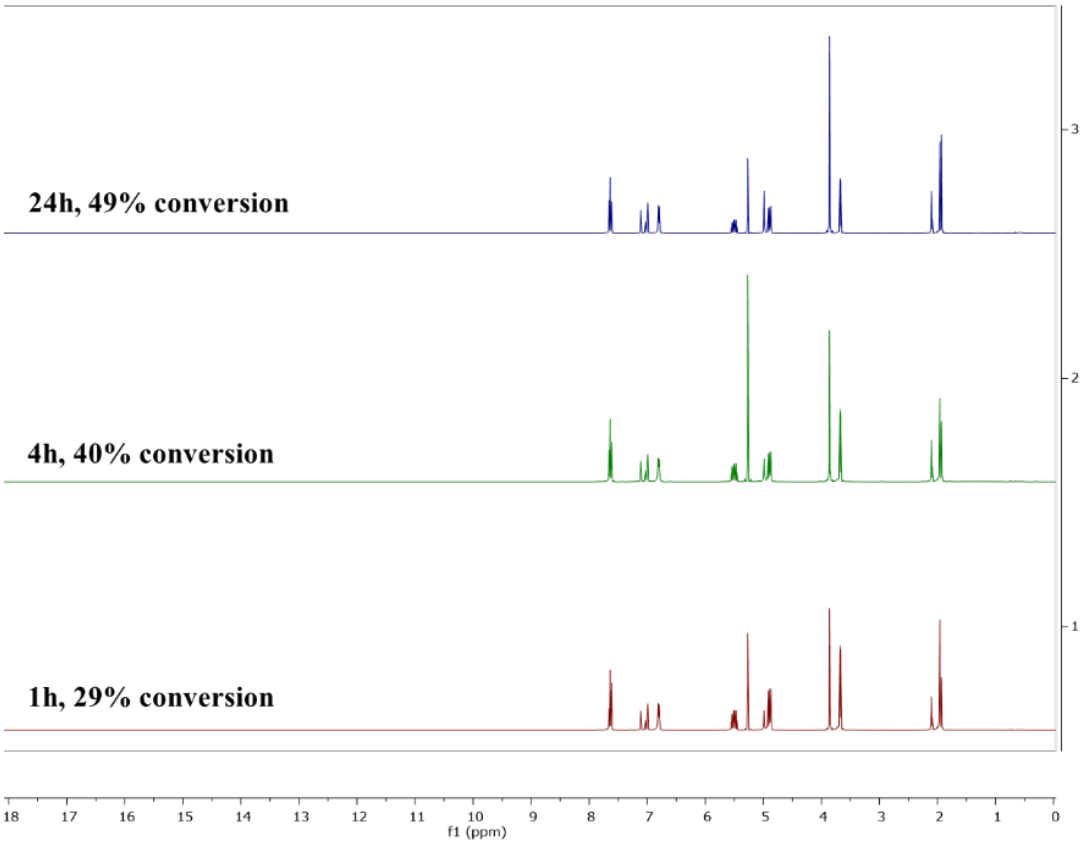


Figure S57. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIPr-SCF$_3$-Cl$_2$**.

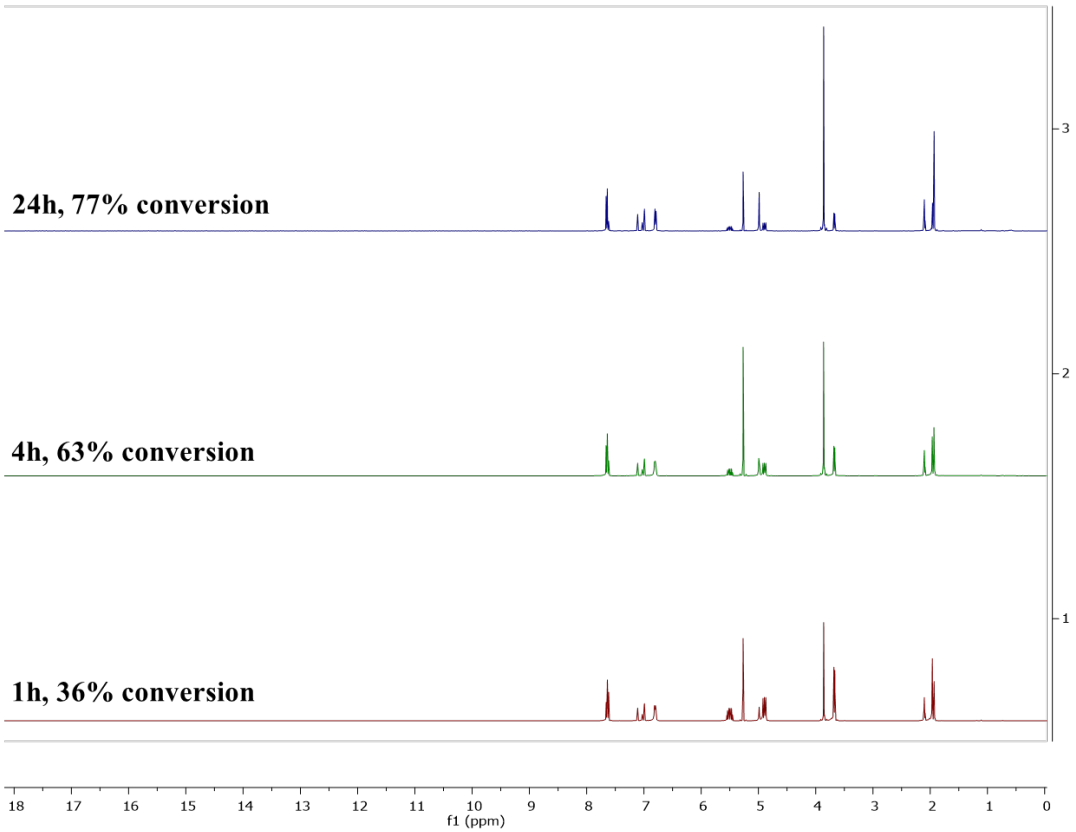


Figure S58. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIPr-SCF$_3$-Br$_2$**.

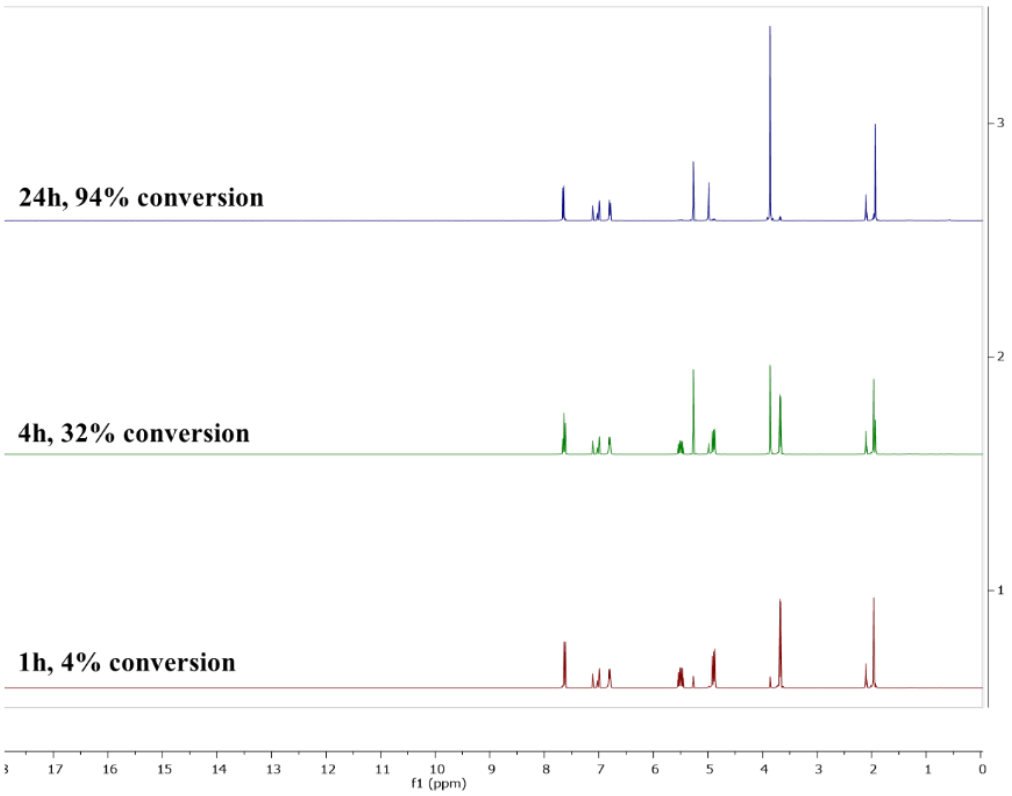


Figure S59. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIPr-SCF$_3$-I$_2$**.

Part X. *cis-trans* Isomerization of **SIPr-SPh-I$_2$** at room temperature

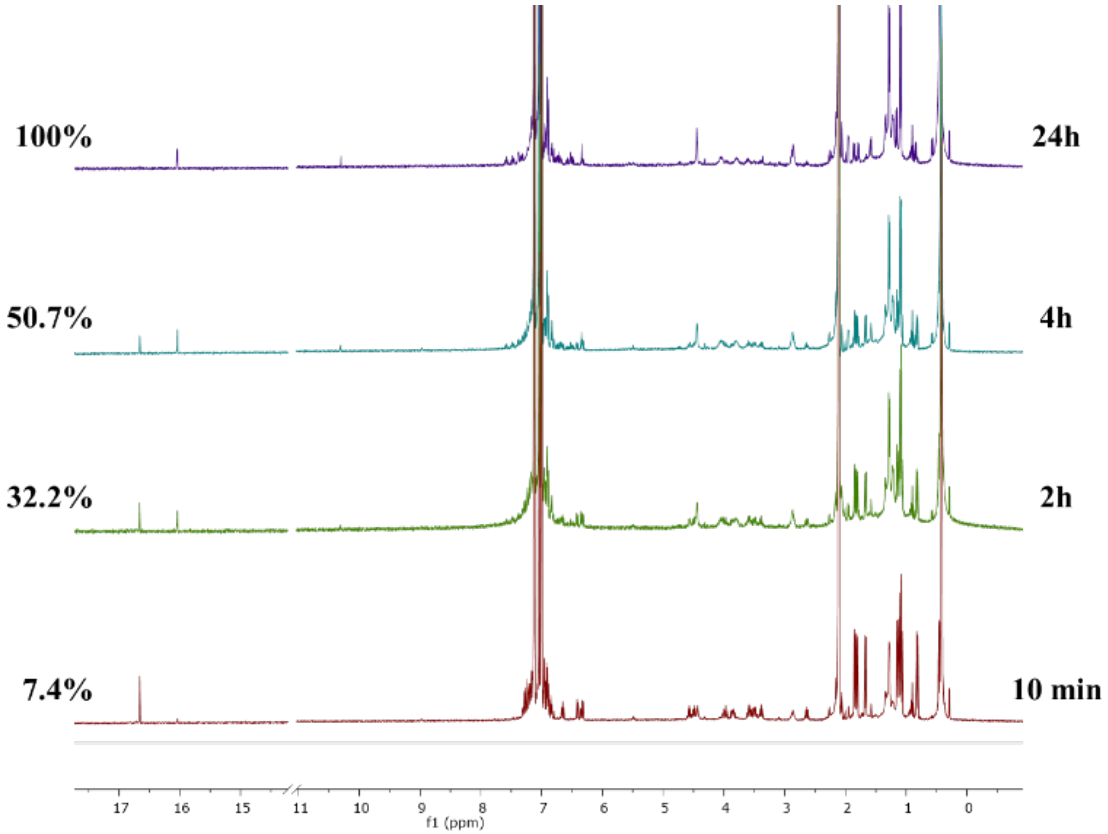


Figure S60. SIPr-SPh-I$_2$ in tolunene-d_8 at *RT*.

Part XI. Reactivity under irradiation for SIPr-SPh complexes after isomerization

Table S2. Reactivity of the SIPr-SPh complexes (1 mol-%) with 0.1M of *N,N*-diallyl-4-methylbenzenesulfonamide in toluene-d_8, under different conditions.

Entry	Precatalyst	% Conversion[a]	% Conversion[b]	% Conversion[c]
1	**SIPr-SPh-Cl_2**	0	0	0
2	**SIPr-SPh-Br_2**	0	0	1
3	**SIPr-SPh-I_2**	0	0	0

[a] Irradiating the precatalyst at 350 nm for 1 h, and then addition of the RCM substrate at *RT* for 1h.

[b] Heating the precatalyst at 100 °C for 30 min, and then addition of the RCM substrate followed by irradiation at 350 nm for 1 h at *RT*.

[c] Irradiating the mixture of both precatalyst and RCM substrate at 350 nm for 1h.

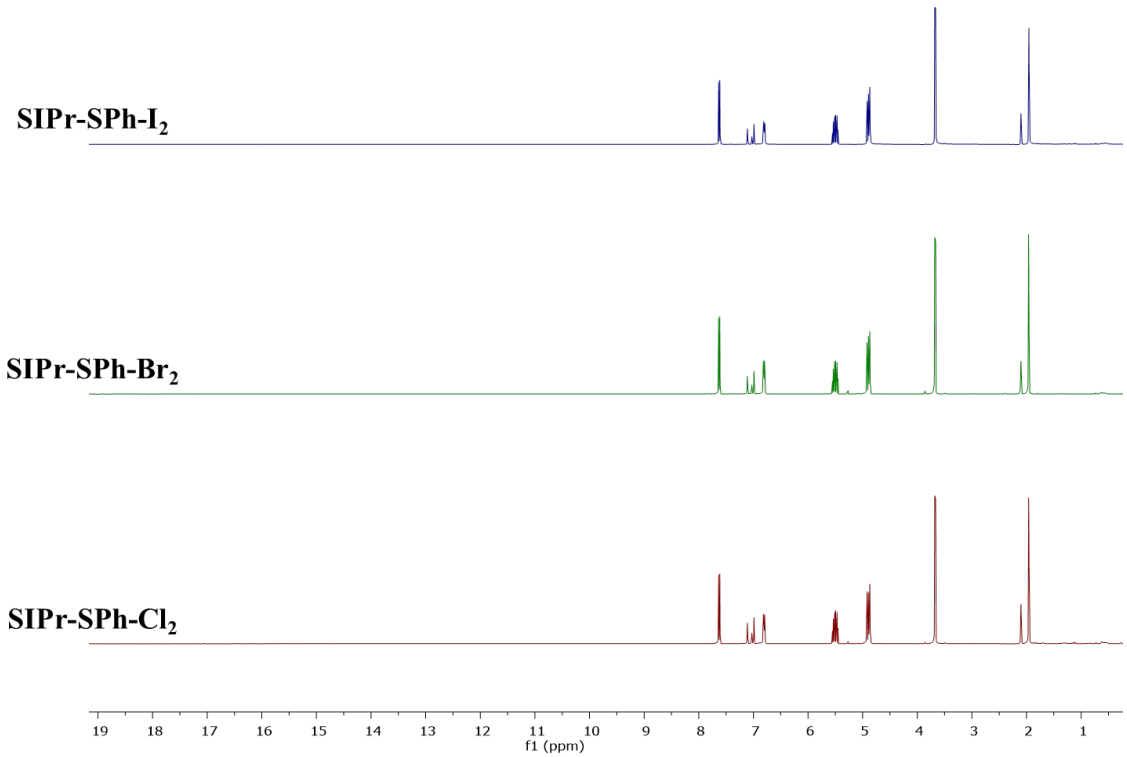


Figure S61. ^{1}H NMR spectra of *N,N*-diallyl-4-methylbenzenesulfonamide in toluene-d_8, following irradiation of different precatalysts (1 mol-%) at 350 nm for 1 h and then addition of the RCM substrate at *RT* for 1h (Route a in Table S2).

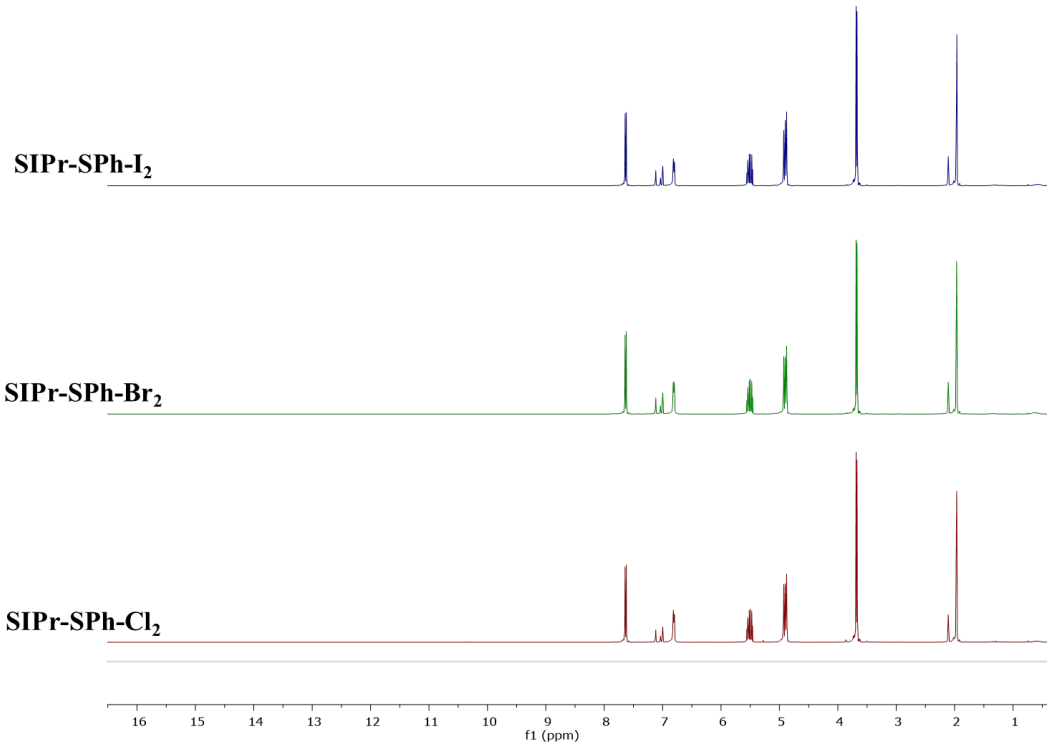


Figure S62. ^{1}H NMR spectra of *N,N*-diallyl-4-methylbenzenesulfonamide in toluene-d_8, following heating the different precatalysts (1 mol-%) to 100 °C for 30 min. and then addition of the RCM substrate followed by irradiation at 350 nm for 1h (Route b in Table S2).

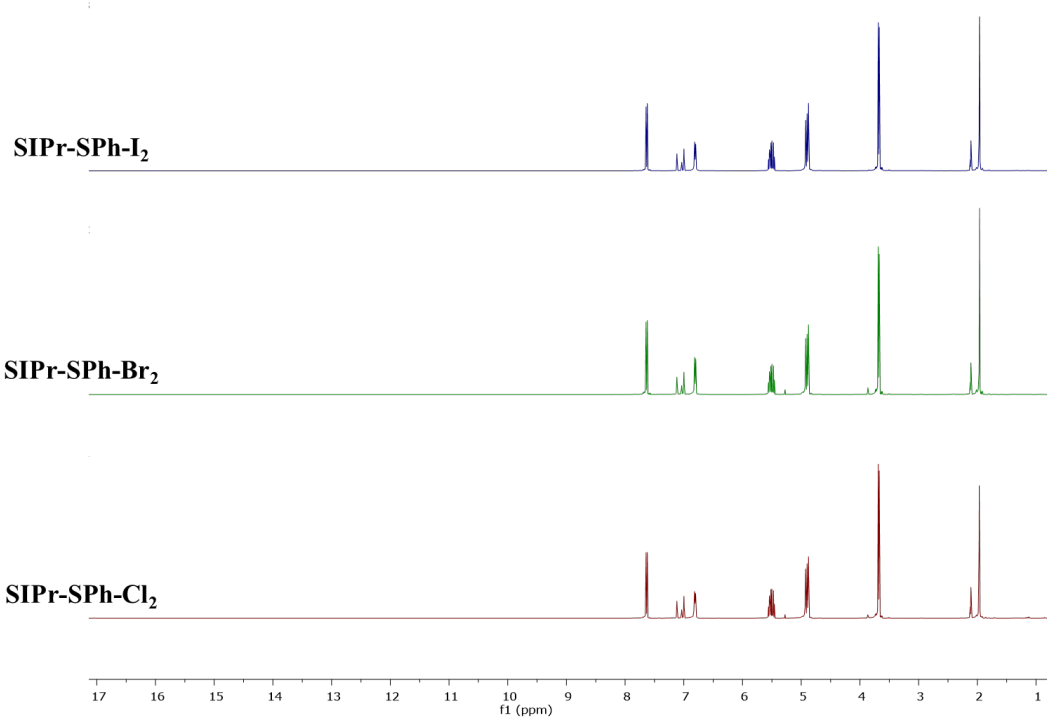


Figure S63. ^{1}H NMR spectra with *N,N*-diallyl-4-methylbenzenesulfonamide in toluene-d_8, following irradiation of different precatalysts (1 mol-%) and the RCM substrate at 350 nm for 1h (Route c in Table S2).

Table S3. Reactivity of the SIPr-SPh complexes (1 mol-%) with 0.1M of *N,N*-diallyl-4-methylbenzenesulfonamide in toluene-d_8 under irradiation at 510 nm in different conditions

Entry	Precatalyst	% Conversion[a]	% Conversion[b]
1	**SIPr-SPh-Cl_2**	0	0
2	**SIPr-SPh-Br_2**	0	1
3	**SIPr-SPh-I_2**	0	0

[a] Heating the precatalyst at 100 °C for 30 min. and then addition of the RCM substrate at *RT* followed by irradiation at 510 nm for 1 h.

[b] Irradiating both precatalyst and RCM substrate at 510 nm for 1 h.

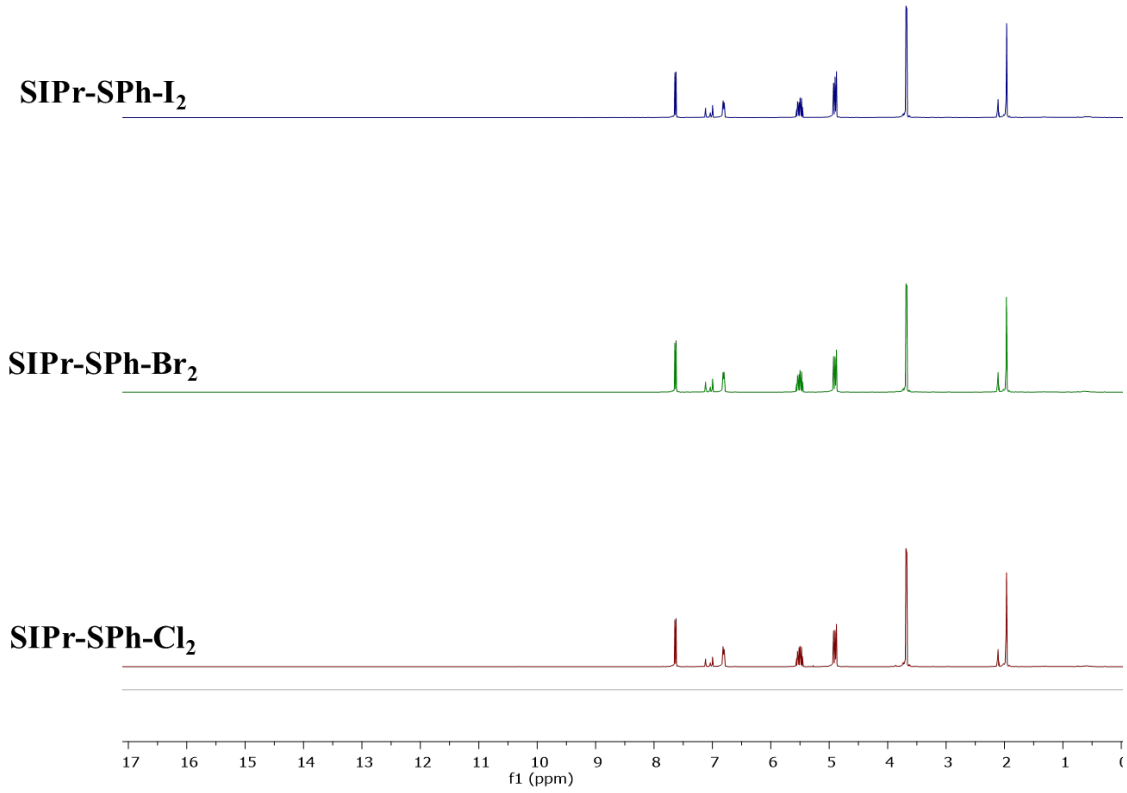


Figure S64. ^{1}H NMR spectra of *N,N*-diallyl-4-methylbenzenesulfonamide in toluene-d_8, following heating the different precatalysts (1 mol-%) to 100 °C for 30 min. and then addition of the RCM substrate followed by irradiation at 510 nm for 1h (Route a in Table S3).

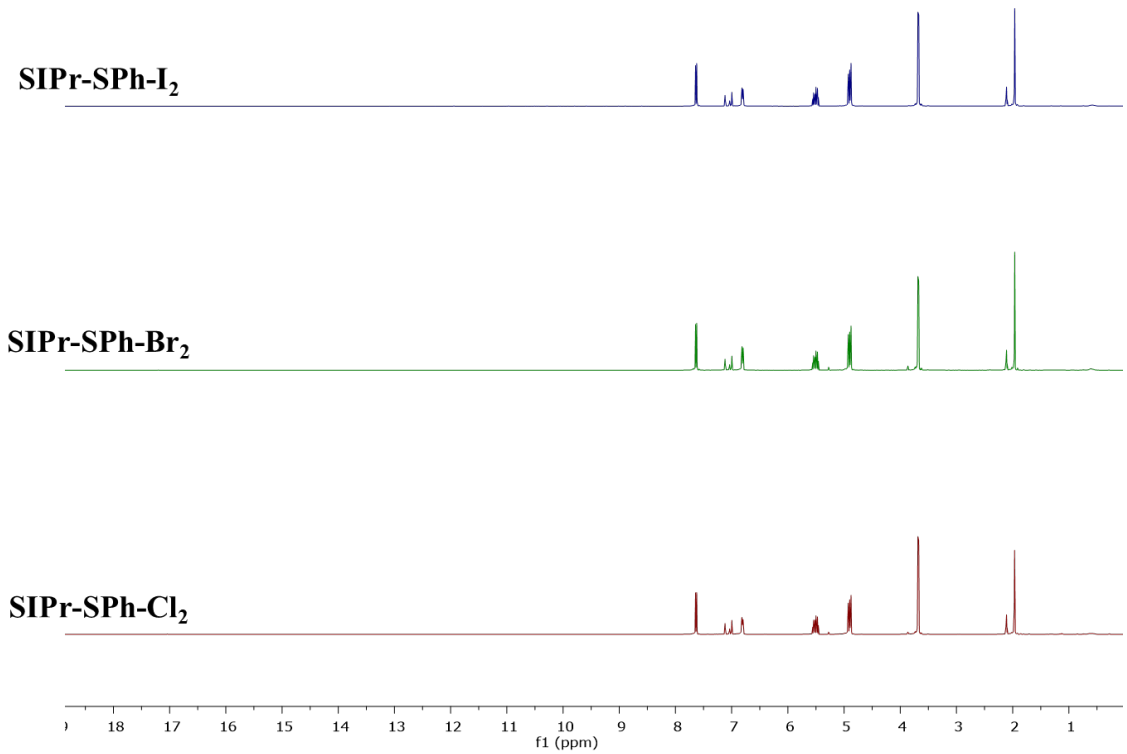


Figure S65. ^{1}H NMR spectra of *N,N*-diallyl-4-methylbenzenesulfonamide in toluene-d_8, following irradiation of different precatalysts (1 mol-%) and the RCM substrate at 510 nm for 1h (Route c in Table S3).

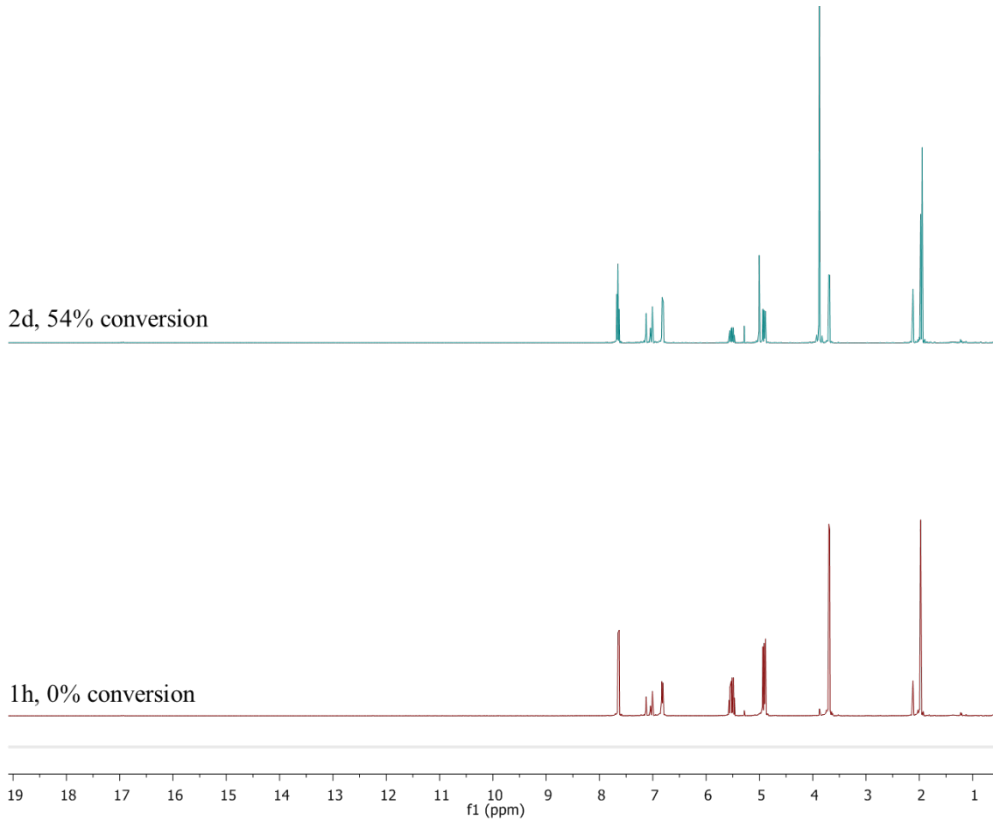


Figure S66. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIPr-SPh-Br$_2$** at *RT*.

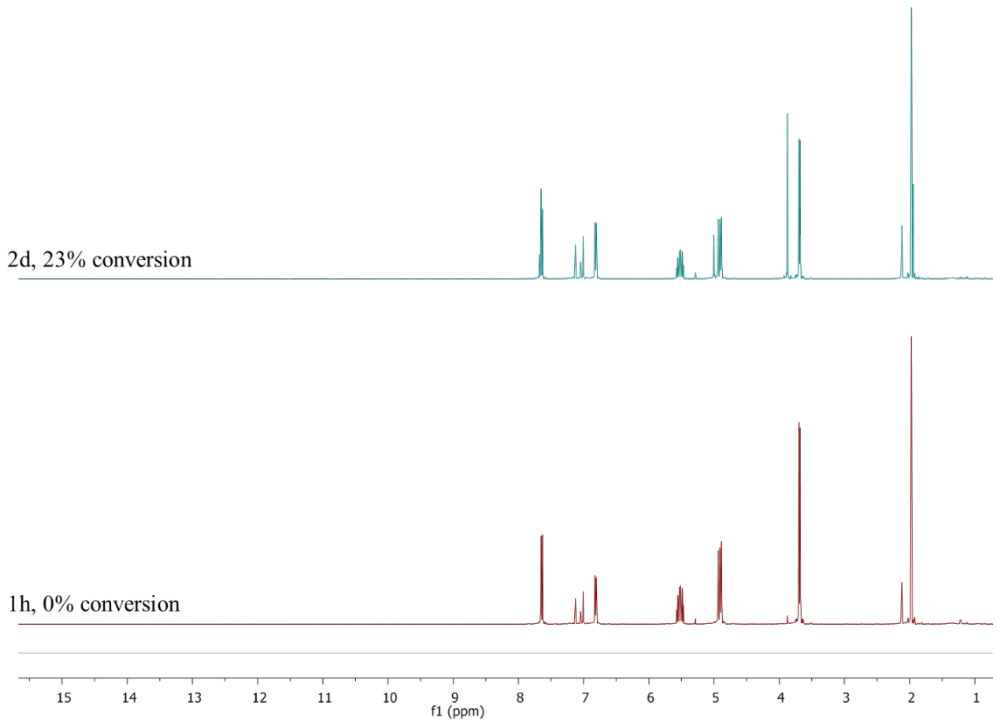


Figure S67. RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-d_8, 0.1M of substrate, 1 mol-% **SIPr-SPh-Br$_2$** at 510 nm.

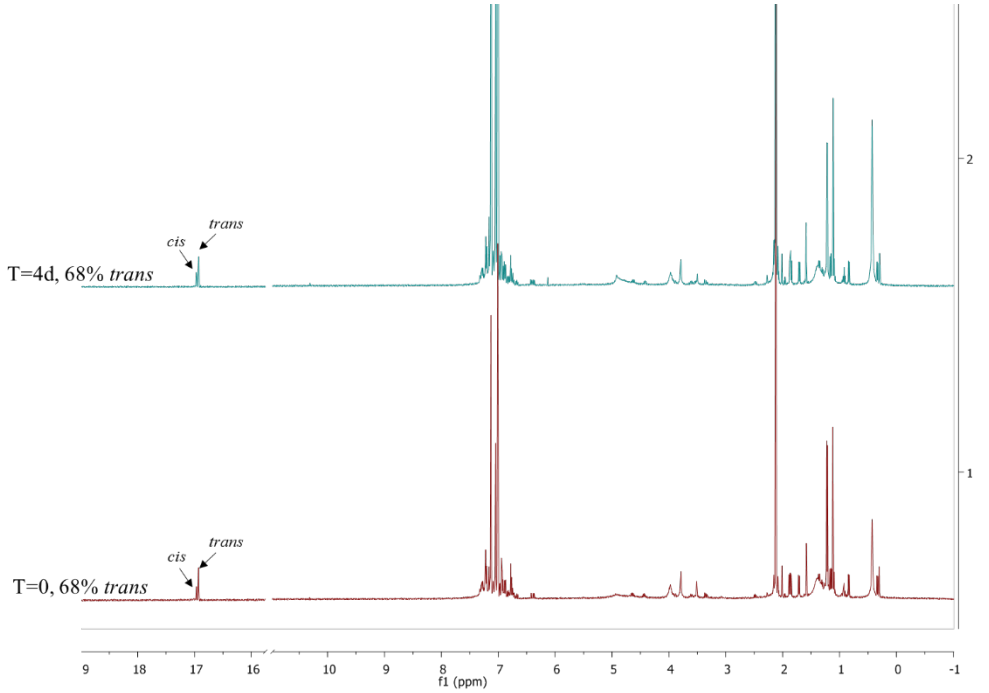


Figure S68. Isomerization 68% ***trans*-SIPr-SPh-Br$_2$** at *RT*

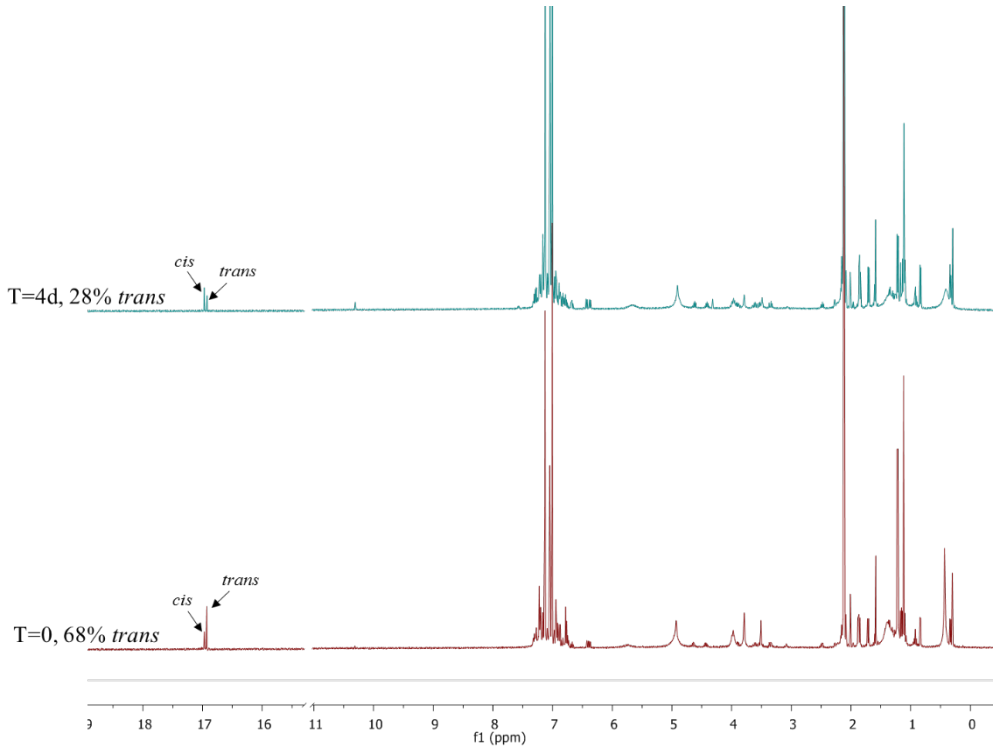


Figure S69. Isomerization 68% ***trans*-SIPr-SPh-Br$_2$** at 510nm

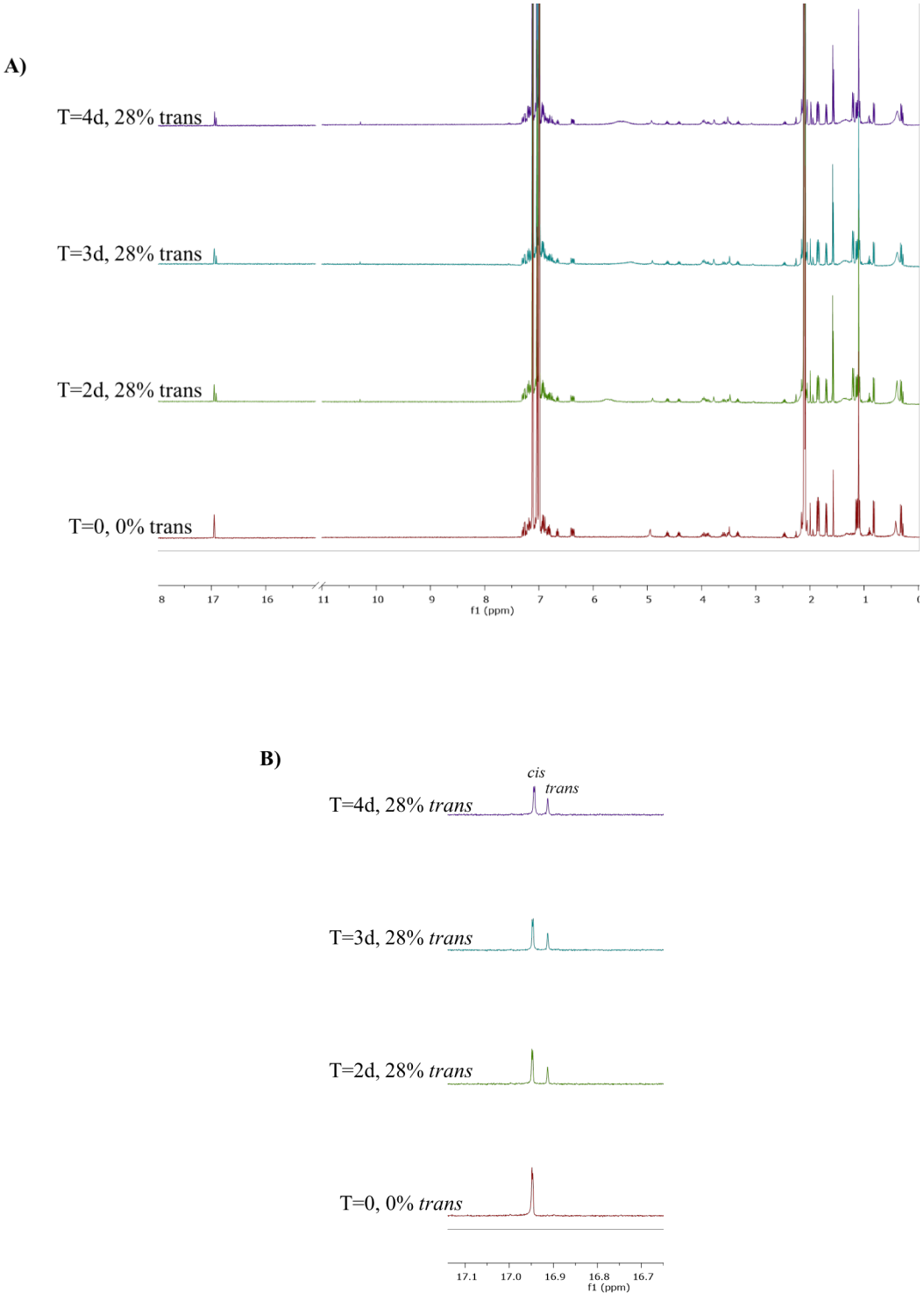
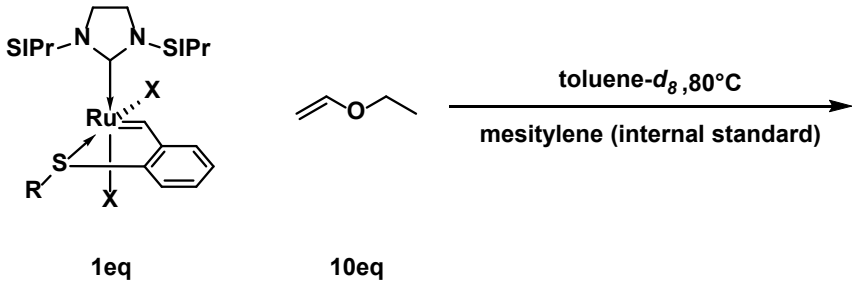


Figure S71. A) Isomerization of **SIPr-SPh-Br$_2$** at 510nm for longer time. B) Zoom-in of the carbene region.

Part XII. Kinetic analysis of initiation of **SIPr-SPh** complexes

1 mg of the complex was dissolved in 0.5 mL toluene-d_8 in an NMR tube, mesitylene was added as internal standard, and 10 eq of ethylvinyl ether was added. Then, the NMR tube was heated inside the NMR instrument to 80ºC, and the ^{1}H-NMR was recorded every one minute (the measuring can start only from the 5th minute, this is the time it takes to add the reagents, heat the solution inside the NMR, shim and record).



1eq 10eq

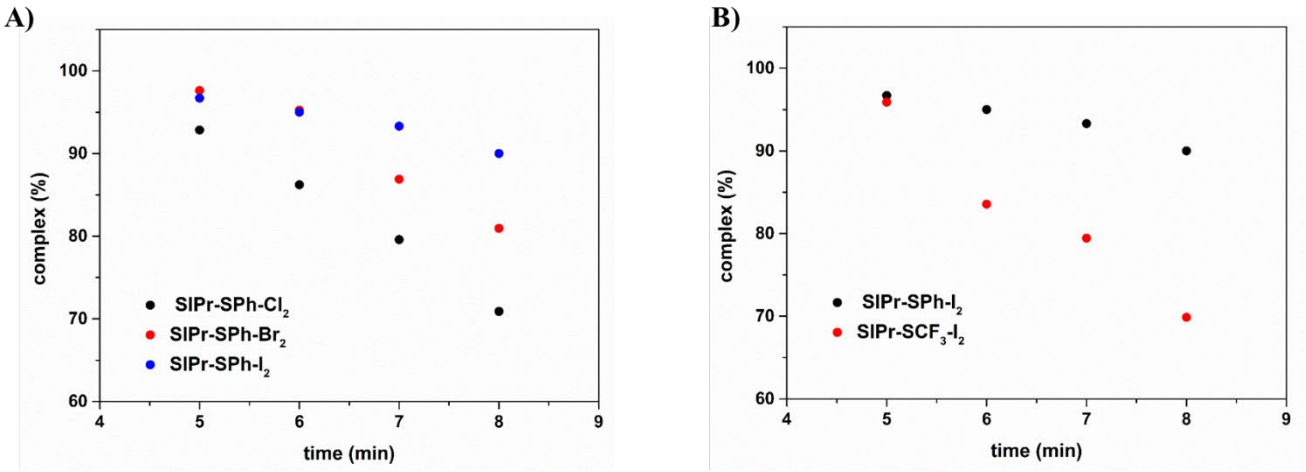


Figure S71. A) Kinetic profile of initiation of **SIPr-SPh-X$_2$** complexes. B) Kinetic profile of initiation of **SIPr-SPh-I$_2$** and **SIPr-SCF$_3$-I$_2$** complexes.

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