Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Tuning Rh(II)-Catalysed Cyclopropanation with Tethered Thioether Ligands

*Derek Cressy, Cristian Zavala, Anthony Abshire, William Sheffield, and Ampofo Darko**

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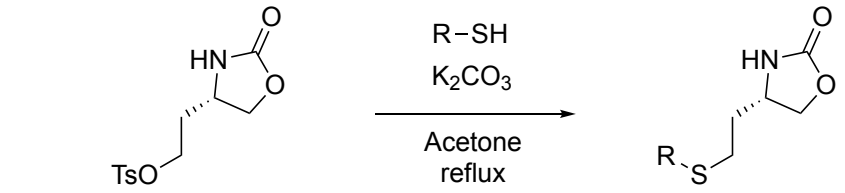
General Methods

Unless otherwise noted, all reagents were purchased and used as received from the manufacturer without further purification. Ligand **1a** and **1d** were synthesized via established literature procedures.[1, 2] Methyl phenyl diazoacetate was prepared from benzylic acid according to established procedures.[3] Hexanes, tetrahydrofuran (THF), diethyl ether, CH_2Cl_2, and acetonitrile (ACN) were dried with columns packed with alumina using an Inert® PureSolv Micro Solvent Purification System and stored over molecular sieves. Reactions were monitored using thin layer chromatography (TLC) on Sorbent Technologies Silica XG TLC Plates. Column chromatography was performed using 60 Å, 40-63 μm silica from Sorbent Technologies. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Vx 300 MHz, Varian VNMRS 500 MHz, or Varian VNMRS 600 MHz spectrometers. All NMR chemical shifts are reported in ppm on the δ scale. Signals were referenced by residual solvent signal for ^1H NMR ($CHCl_3$ = 7.26 ppm, acetone = 2.05 ppm, acetonitrile = 1.94 ppm) and ^{13}C NMR ($CHCl_3$ = 77.16 ppm, acetone = 206.26 ppm, acetonitrile = 1.32 ppm). HPLC analysis was performed on a Shimadzu LC-2030 Prominence-I instrument using a C_{18} column. The mass spectra for all compounds, unless otherwise specified, were obtained using an AccuTOF Mass spectrometer equipped with a DART ionization apparatus. UV-Visible data was obtained in a 10mm quartz cell using a Cary 5000 spectrophotometer.

Experimental Procedures

Ligand Synthesis



(*S*)-2-(2-oxooxazolidin-4-yl)ethyl 4-methylbenzenesulfonate

R = ^{t}Bu (**1b**)
R = Ph (**1c**)

(S)-4-(2-(*tert*-butylthio)ethyl)oxazolidine-2-one (1b)

To a flame dried 5 mL flask equipped with a stir bar was (S)-2-(2-oxooxazolidin-4-yl)ethyl 4-methylbenzenesulfonate[4] (0.43 g, 1.5 mmol) followed by 2-methyl-2-propanethiol (1.5 mL, 13 mmol). The reagents were then dissolved in 6 mL acetone and refluxed at 45 °C for 24 hours. The reaction was allowed to cool to room temperature, then concentrated *in vacuo*. The resulting mixture was dissolved in 10 mL DI water and extracted twice with 5 mL dichloromethane. The combined organic layers were then washed with 5 mL brine solution, followed by 5 mL saturated sodium bicarbonate solution. The organics were separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was then purified by column chromatography (25% EtOAc/Hexanes to 50% EtOAc/Hexanes) to afford **1b** as a pale-yellow oil (0.1181 g, 0.58 mmol, 39% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.81 (s, 1H), 4.56 – 4.47 (m, 1H), 4.07 – 3.96 (m, 2H), 2.63 – 2.54 (m, 2H), 1.93 – 1.81 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.46, 70.24, 52.29, 42.69, 35.05, 30.97, 24.62. Calculated *m/z*: $[M+H]^+$ = 204.1014, found m/z: $[M+H]^+$ = 204.1069

(*S*)-4-(2-(phenylthiol)oxazolidin-2-one (1c)

To a flame dried 5 mL flask equipped with a stir bar was added (S)-2-(2-oxooxazolidin-4-yl)ethyl 4-methylbenzenesulfonate[4] (0.10 g, 0.36 mmol) followed by thiophenol (0.5 mL, 0.54 mmol). The reagents were then dissolved in 1 mL acetone and refluxed for 4 hours. The reaction was allowed to cool to room temperature, then concentrated *in vacuo*. The resulting mixture was dissolved in 2 mL DI water and extracted twice with 2 mL dichloromethane. The organics were combined and washed with 1 mL brine solution, followed by 1 mL saturated sodium bicarbonate solution. The organics were separated, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was then purified by column chromatography (2.5% MeOH/DCM) to afford **1c** as a yellow oil (68 mg, 0.29 mmol, 84% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.21 (m, 4H), 5.73 – 5.65 (m, 1H), 4.55 – 4.47 (m, 1H), 4.09 – 3.99 (m, 2H), 2.97 (td, *J* = 7.0, 2.5 Hz, 2H), 1.99 – 1.83 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.18, 134.88, 129.88, 129.20, 126.79, 51.63, 34.33, 30.21. Calculated *m/z*: $[M+H]^+$ = 224.0701, found m/z: $[M+H]^+$ = 224.0691

General Microwave Conditions

All microwave reactions were conducted in sealed reaction vials with a Biotage Initiator+ equipped with an IR sensor for determination of reaction temperature. Power input was adjusted by the instrument achieve and maintain the desired reaction temperature. Reaction times are presented as hold times, not total reaction time. Synthesis of $Rh_2(OAc)_3$(MeTOX) (**2**), $Rh_2(OAc)_2$(MeTOX)$_2$ (**3a/b**), and $Rh_2(OAc)_3$(OX) were confirmed by comparison of NMR spectra from our previous work.[5, 6]

General Procedure for Microwave Reactions

A 2-5 mL microwave vial equipped with a magnetic stir bar was charged with dirhodium acetate (15 mg, 34 mmol) and the desired ligand (34 mmol). The edges of the flask were rinsed with 4 mL 1,2-dichloroethane (DCE). The vial was then capped and heated at 190°C for 10 minutes. The mixture was allowed to cool to RT, transferred to a round-bottom flask using DCM, and concentrated *in vacuo*. The crude mixture was then purified by column chromatography using a 1:1 toluene/MeCN mobile phase. Bis substituted products eluted first as a mixture of *cis* and *trans* isomers. The bis fractions were then recrystallised in MeCN to remove excess oxazolidinone starting material. Mono products eluted next with no further purification needed. Dirhodium(II) acetate eluted last.. The product distribution for the ligand exchange reaction with ligand **1a** was quantified via HPLC using 75% 1:1 MeCN:MeOH with 0.1% TFA/25% water with 0.1%TFA on a C_{18} column. Calibration curves were generated for **2a**, **3a/b**, and $Rh_2(OAc)_4$. The yields for complexes **4-9** were determined by isolated material.

$Rh_2(OAc)_3$(^{t}BuTOX) (4)

R_f: 0.46. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.45 – 4.39 (m, 1H), 3.76 – 3.65 (m, 1H), 3.11 (ddd, *J* = 12.7, 5.4, 2.7 Hz, 1H), 2.97 (td, *J* = 12.4, 3.0 Hz, 1H), 2.11 (dddd, *J* = 14.7, 5.4, 3.0, 1.3 Hz, 1H), 1.99 (s, 3H), 1.87 (s, 3H), 1.84 (s, 3H), 1.84 – 1.76 (m, 1H), 1.66 (s, 10H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.82, 190.79, 189.00, 167.23, 70.04, 58.95, 49.59, 31.96, 29.15, 29.03, 24.07, 23.90, 23.34. Calculated *m/z*: $[M+H]^+$ = 585.9489 , found m/z: $[M+H]^+$ 585.9444. Anal. Calcd for $C_{15}H_{25}NO_8Rh_2S$: C, 30.79; H, 4.31; N, 2.39; S, 5.48. Found: C, 32.80; H, 4.79; N, 2.42; S, 5.18.

$Rh_2(OAc)_2$(^{t}BuTOX)$_2$ (5a/b)

R_f: 0.93. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.31 – 4.25 (m, 1H), 3.74 – 3.54 (m, 2H), 3.19 (m, *J* = 13.1, 5.7, 2.5 Hz, 1H), 2.97 (m, *J* = 12.2, 9.1, 2.8 Hz, 1H), 1.99 (m, *J* = 17.5, 5.6, 2.8, 1.3 Hz, 1H), 1.90 (s, 2H), 1.85 (s, 1H), 1.81 – 1.72 (m, 1H), 1.65 (s, 10H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 189.25, 69.62, 59.84, 59.74, 48.19, 48.01, 32.70, 32.64, 29.84, 29.78, 29.75, 28.95, 23.94, 23.71. Calculated *m/z*: $[M+H]^+$ = 729.0257, found m/z: $[M+H]^+$ = 729.0233. Anal. Calcd for $C_{22}H_{38}N_2O_8Rh_2S_2$: C, 36.27; H, 5.27; N, 3.85; S, 8.81. Found: C, 39.08; H, 5.88; N, 3.62; S, 8.04.

$Rh_2(OAc)_3$(PhTOX) (6)

R_f: 0.46. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 – 7.89 (m, 2H), 7.44 – 7.40 (m, 3H), 4.45 – 4.38 (m, 1H), 3.83 – 3.73 (m, 2H), 3.55 (ddd, *J* = 13.1, 5.8, 2.3 Hz, 1H), 3.37 (ddd, *J* = 13.1, 11.8, 2.5 Hz, 1H), 2.18 (dddd, *J* = 14.8, 6.0, 2.6, 1.4 Hz, 1H), 2.02 (dddd, *J* = 14.6, 12.1, 9.9, 2.4 Hz, 1H), 1.96 (s, 3H), 1.88 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.27, 190.97, 189.55, 167.73, 133.00, 131.05, 129.04, 128.54, 69.89, 59.09, 37.26, 31.16, 23.94, 23.91, 23.35 Calculated *m/z*: $[M+H]^+$ = 605.9176 , found m/z: $[M+H]^+$ 605.9180. Anal. Calcd for $C_{17}H_{21}NO_8Rh_2S$: C, 33.74; H, 3.50; N,2.32; S, 5.30. Found: C, 37.79; H, 4.40; N, 2.51.

$Rh_2(OAc)_2(PhTOX)_2$ (7a/b)

R_f: 0.85. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.84 (m, 2H), 7.42 – 7.29 (m, 3H), 4.41 – 4.07 (m, 2H), 3.77 – 3.61 (m, 3H), 3.43 – 3.30 (m, 1H), 2.12 – 1.93 (m, 3H), 1.89 (s, 1H), 1.86 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 189.65, 168.30, 131.41, 131.06, 128.91, 127.86, 69.39, 59.67, 37.09, 31.53, 23.64 Calculated *m/z*: $[M+H]^+$ = 768.9632, found m/z: $[M+H]^+$ = Anal. Calcd for $C_{26}H_{30}N_2O_8Rh_2S_2$: C, 40.64; H, 3.94; N, 3.65; S, 8.35. Found: C, 41.49; H, 4.24; N, 3.45; S, 7.73.

$Rh_2(OAc)_3(SerMeTOX)$ (8)

R_f: 0.63. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.69 (t, *J* = 8.0 Hz, 1H), 4.11 (m, *J* = 11.4, 10.2, 7.8, 3.5 Hz, 1H), 3.98 (dd, *J* = 10.4, 8.2 Hz, 1H), 2.86 (dd, *J* = 12.2, 3.5 Hz, 1H), 2.55 (s, 3H), 2.26 (t, *J* = 12.0 Hz, 1H), 2.03 (s, 3H), 1.84 (d, *J* = 5.4 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.49, 192.22, 191.04, 72.96, 59.70, 41.16, 24.27, 24.18, 23.77, 16.27. Calculated *m/z*: $[M+H]^+$ = 529.8863, found m/z: $[M+H]^+$= 529.3375. Anal. Calcd for $C_{11}H_{17}NO_8Rh_2S$: C, 24.97; H, 3.25; N,2.65; S, 6.06. Found: C, 29.71; H, 4.26; N, 2.74.

$Rh_2(OAc)_2(SerMeTOX)_2$ (9a/b)

R_f: 0.95. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.71 – 4.59 (m, 1H), 4.00 – 3.89 (m, 1H), 2.84 (m, *J* = 12.2, 5.8, 3.4 Hz, 1H), 2.59 (d, *J* = 9.2 Hz, 1H), 2.52 (d, *J* = 5.8 Hz, 2H), 2.31 – 2.18 (m, 1H), 1.97 – 1.90 (m, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.32, 167.65, 72.29, 59.69, 23.72, 15.76. Calculated *m/z*: $[M+H]^+$ = 616.9006 , found m/z: $[M+H]^+$ = 616.8975. Anal. Calcd for $C_{14}H_{22}N_2O_8Rh_2S_2$: C, 27.29; H, 3.61; N, 4.45; S, 10.41. Found: C, 28.92; H, 3.91; N, 4.33; S, 9.95.

General Procedure for the Cyclopropanation of Styrene

Under an atmosphere of N_2, a 25 mL Schlenk flask equipped with a magnetic stir bar was flame dried and charged with styrene (0.19 mL, 1.7 mmol, 1.0 equiv.), catalyst (2 mol%), and DCE (0.5 mL). The solution was then brought to the desired temperature, followed by slow addition of ethyl diazoacetate (1.7 mL, 0.17 mmol, 1.0 equiv.) by syringe pump (1 mL/hr). Once addition was complete, 16.54 μL of mesitylene standard was added to the reaction mixture and stirred. The solution was then eluted through a Nylon66 0.2 μm syringe filter into a 2 mL glass GC vial. Yields and diastereoselectivity were determined

by gas chromatography using a multiple point internal standard of the cyclopropyl product and mesitylene as the internal standard.[7]

General Procedure for the Cyclopropanation of Olefin Substrates with $Rh_2(OAc)_3$(PhTOX) **(6)**

Under an atmosphere of N_2, a 25 mL Schlenk flask equipped with a magnetic stir bar was flame dried and charged with olefin (1.0 or 5.0 equiv. with respect to ethyl diazoacetate), **3a** (2 mol%), and DCE (0.5 mL). The solution was then heated to 80°C, followed by slow addition of ethyl diazoacetate (1.7 mL, 0.17 mmol, 1.0 equiv.) by syringe pump (1 mL/hr). After addition was complete, the reaction solution was filtered through 1.5-inch silica plug and eluted with 4 mL of DCM. The eluent was then concentrated *in vacuo* with a rotary evaporator. 10 μL of mesitylene was then added as an internal standard for ^{1}H NMR determination of cyclopropane product yield and diastereoselectivity.

Cyclopropanation of Olefin Substrates: ^{1}H NMR Yield Calculations

Yield and diastereoselectivity for each cyclopropanation reaction was calculated by ^{1}H NMR using mesitylene as an internal standard. Normalised integration of the methyl protons of mesitylene (2.26 ppm) was compared to the integration of the diastereotopic protons of the methylene unit of the cyclopropane for the *cis* (2.06 ppm) and *trans* (1.90 ppm) isomers to give the total yield of the cyclopropane product.

Cyclic Voltammetry

Both DCM and MeCN were freeze-pumped-thawed before introduction into a glovebox under an inert N_2 atmosphere. The electrolyte solution used was 0.1 M [nBu$_4$N] [PF_6] in the respective solvent. Electrochemical grade [nBu$_4$N] [PF_6] was purchased from Sigma-Aldrich and used as received. Cyclic voltammetry measurements were made inside a dry glovebox using a BASi Epsilon electrochemical analyzer with a platinum working electrode, platinum wire counter electrode, and a silver wire reference electrode.

As stated in the manuscript, solvents effects were observed when electrochemical experiments were conducted in MeCN (Figure S1). The $E_{1/2}$ potentials are affected since MeCN is able to coordinate to open axial sites, especially when the tethered thioether is a weak coordinating group. $Rh_2(OAc)_3$(OX), $Rh_2(OAc)_3$(PhTOX) (**6**), and $Rh_2(OAc)_3$(^{t}BuTOX) (**4**) shift to lower potentials in MeCN compared to DCM, while $Rh_2(OAc)_3$(SerMeTOX) (**8**) shifts to slightly higher potentials in MeCN. The order by increasing $E_{1/2}$ remains the same when comparing tethered complexes for both solvents (**6** < **4** < **8**), but $Rh_2(OAc)_3$(OX) has the lowest $E_{1/2}$ in DCM and the highest $E_{1/2}$ in MeCN. In addition to perturbing the position of the $E_{1/2}$ potentials, CVs in MeCN displayed further oxidation events or loss of reversibility in some complexes. $Rh_2(OAc)_3$(PhTOX) (**6**) demonstrated further oxidation events after the $Rh_2^{4+/5+}$ wave, but does not prevent the reformation of the neutral Rh complex (Figure S1, brown trace). It is plausible that these further oxidation events are centered on the ligand, possibly from oxidation of the sulphur. When scanned at lower scan rates (100 mV/s) two peaks can be observed at the higher oxidation regions,

while only one peak is observed at higher scan rates (500 mV/s, Figure S2). The $Rh_2^{4+/5+}$ wave in $Rh_2(OAc)_3(^tBuTOX)$ (**4**) appears quasi-reversible in MeCN (Figure S1, green trace) and loses reversibility with further scans (Figure S3). This loss of reversibility is not observed in DCM (Figure S4).

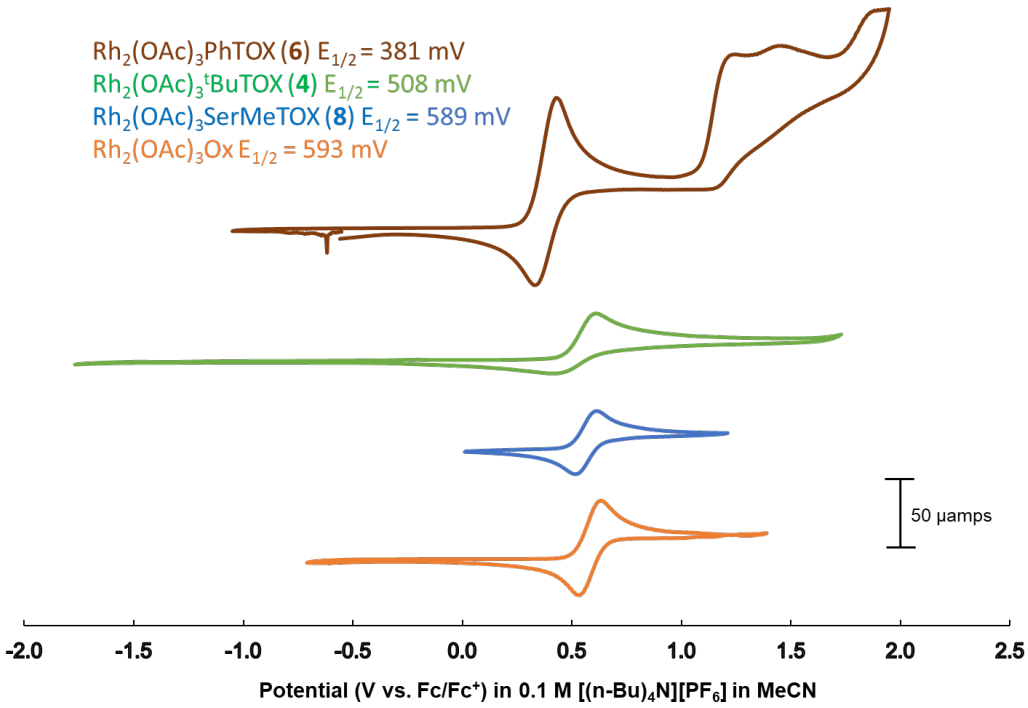


Figure S1. CV traces of the novel Rh^{II} complexes in MeCN

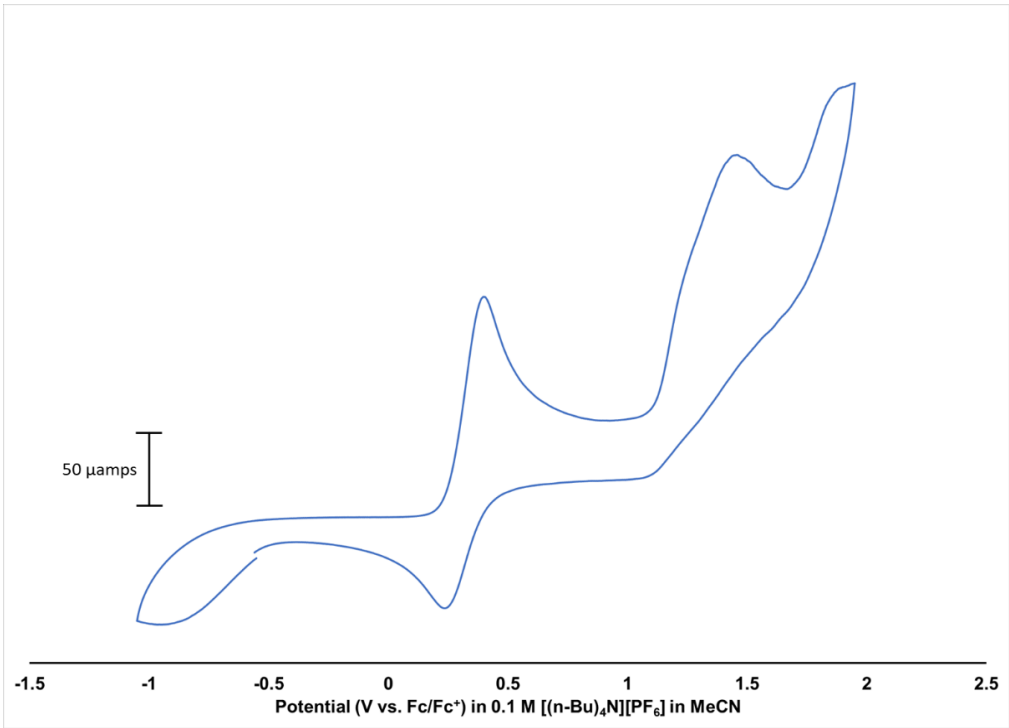


Figure S2. CV trace of complex **6** at 500 mV/s showing coalescence of the two unknown oxidation events.

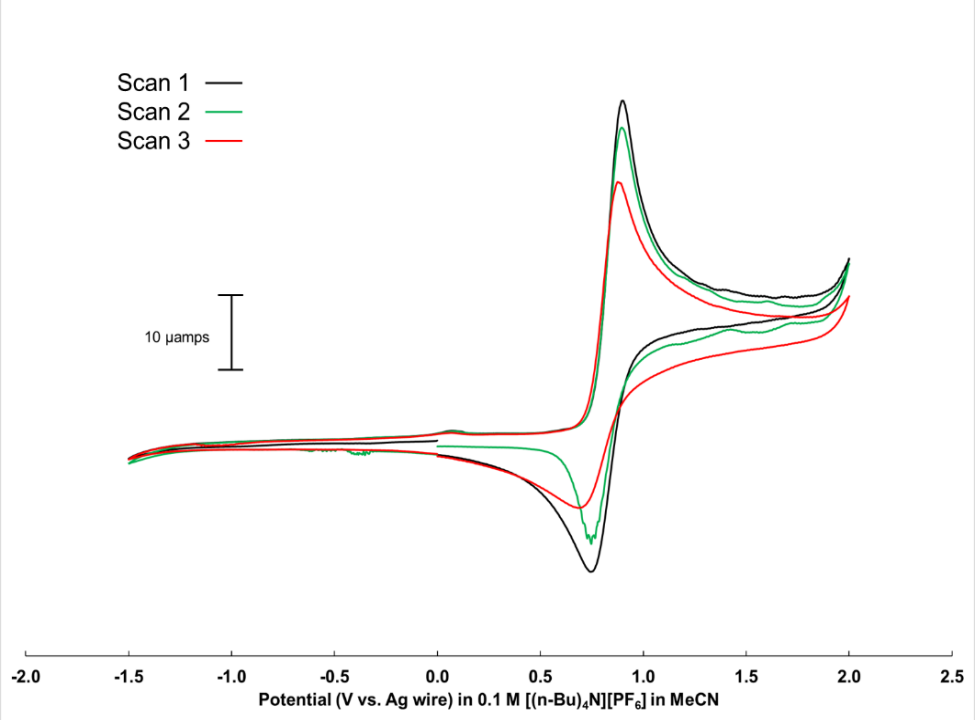


Figure S3. CV traces showing diminished reversibility of the Rh oxidation over multiple scans for complex **4** in MeCN.

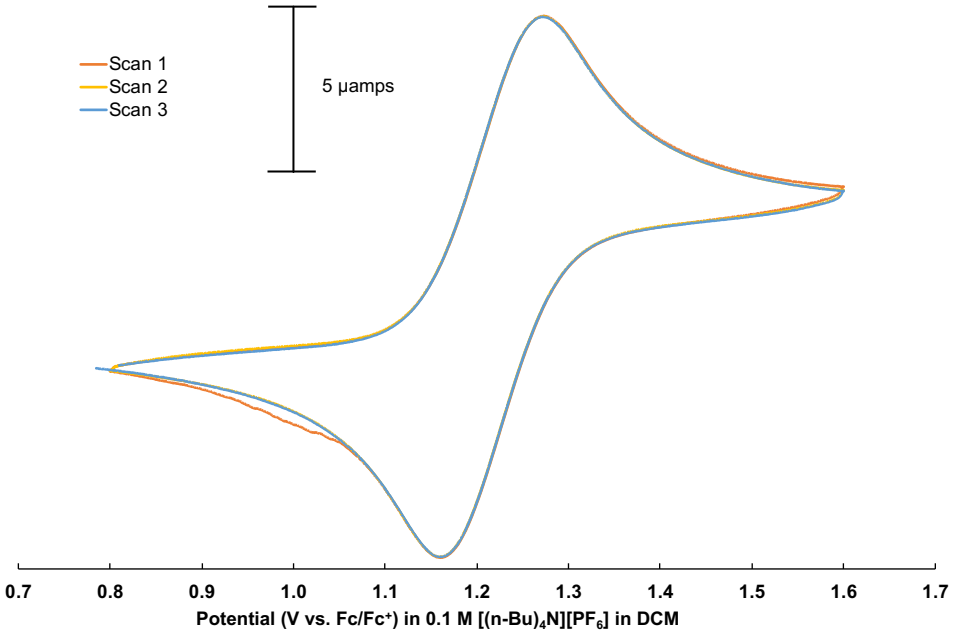


Figure S4. CV traces showing diminished reversibility of the Rh oxidation over multiple scans for complex **4** in DCM.

Computational studies

All geometry optimisations were completed on Gaussian 09[8] and implemented the density functional theory M06-2X[9] functional with the def2-TZVPP[10] basis set. An ultrafine integration grid was utilised as well as tight convergence criteria. Frequency calculations were performed to verify the stationary points on the potential energy surface were in fact ground state minima. Negative frequencies were calculated for $Rh_2(OAc)_3(Ox)$ at -20.1475 cm^{-1}, $Rh_2(OAc)_3(PhTOX)$ at -4.6272 cm^{-1}, $Rh_2(OAc)_4C(H)(CO_2Et)$ at -19.8149 cm^{-1}, $Rh_2(OAc)_3(OX)C(H)(CO_2Et)$ at -10.6252 cm^{-1}, and $Rh_2(OAc)_3(MeTOX)C(H)(CO_2Et)$ at -3.5171 cm^{-1} but is still believed to be the ground state structure. Orbital visualisations were completed with ChemCraft.[11]

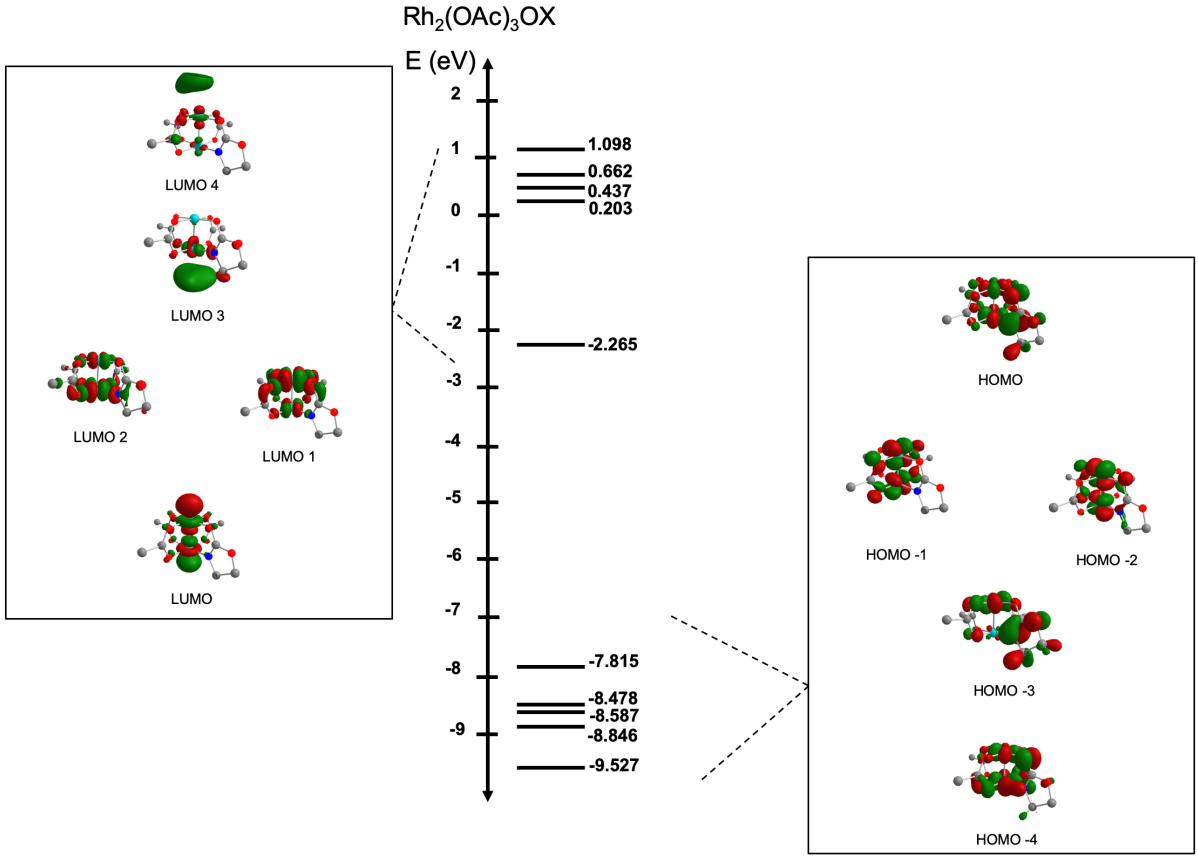


Figure S5. Calculated molecular orbitals of $Rh_2(OAc)_3(OX)$ at the MO6-2X/def2-TZVPP level of theory.

$Rh_2(OAc)_3(OX)$ at M06-2X/def2-TZVPP level of theory

45	-0.016540000	0.010927000	-1.085971000
45	-0.461287000	0.008315000	1.221577000
8	-0.178051000	2.054805000	-1.059935000
8	-0.581628000	2.050158000	1.143115000
8	0.115171000	-2.036900000	-1.017678000
8	-0.317547000	-2.037103000	1.179889000
8	-2.063913000	-0.128340000	-1.417267000
8	-2.449473000	-0.121272000	0.783541000
8	1.548456000	0.135808000	1.658400000
8	3.631169000	0.067521000	0.851913000
7	1.945972000	0.140641000	-0.605575000
6	-0.411801000	2.630517000	0.037264000

6	-0.066790000	-2.615069000	0.088843000
6	-0.470341000	4.132644000	0.037102000
6	0.003832000	-4.116727000	0.114843000
6	-2.827920000	-0.165159000	-0.420789000
6	-4.305137000	-0.299217000	-0.666722000
6	2.300040000	0.120479000	0.656534000
6	4.256077000	0.199229000	-0.430500000
6	3.121333000	-0.052125000	-1.436997000
1	0.492541000	4.507973000	0.384835000
1	-1.234223000	4.473030000	0.730807000
1	-0.655647000	4.505478000	-0.965225000
1	0.629869000	-4.434737000	0.945439000
1	0.384838000	-4.498843000	-0.826403000
1	-0.999322000	-4.505008000	0.289008000
1	-4.564779000	-1.356014000	-0.597035000
1	-4.555732000	0.058286000	-1.660564000
1	-4.860975000	0.237281000	0.097030000
1	5.067030000	-0.520629000	-0.492536000
1	4.655284000	1.210042000	-0.511842000
1	3.143422000	-1.066342000	-1.844520000
1	3.148861000	0.654227000	-2.265510000

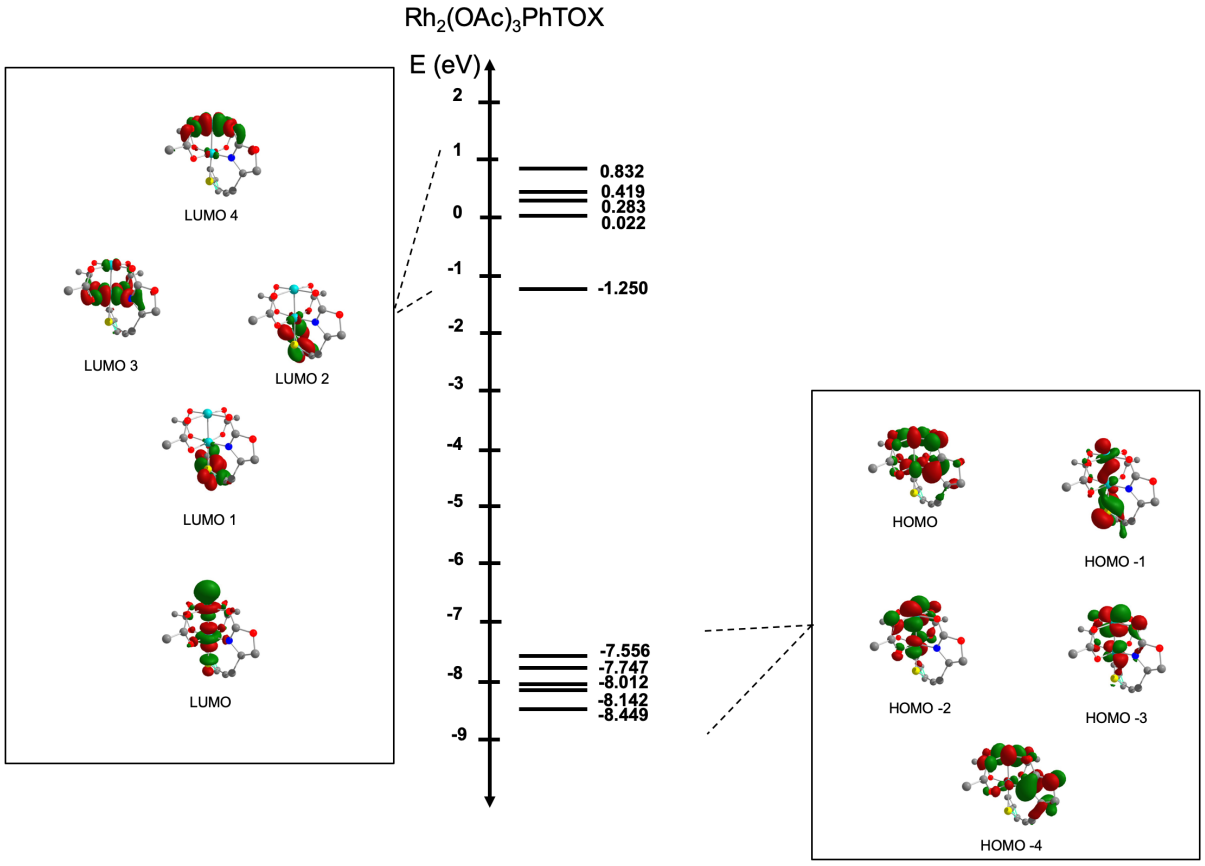


Figure S6. Calculated molecular orbitals of $Rh_2(OAc)_3$(PhTOX) (**6**) at the MO6-2X/def2-TZVPP level of theory.

$Rh_2(OAc)_3$(PhTOX) (**6**) at M06-2x/def2-TZVPP level of theory

45	0.096236000	0.000964000	-0.284224000
45	2.175964000	-0.839876000	0.532697000
16	-2.036302000	0.932053000	-1.312345000
8	2.738273000	1.069085000	1.138261000
8	2.099617000	3.197541000	1.410073000
8	-0.302514000	-1.934458000	-0.988050000
8	1.599190000	-2.704696000	-0.098792000
8	1.051920000	0.437341000	-2.056343000
8	2.972277000	-0.462960000	-1.330312000
8	1.232679000	-1.158761000	2.341569000
8	-0.746679000	-0.485699000	1.529849000
7	0.663519000	1.787374000	0.456355000
6	1.856289000	1.935113000	0.988501000
6	1.023966000	4.007029000	0.933420000
6	-0.098775000	3.009466000	0.614070000
6	-0.916134000	3.393328000	-0.612146000
6	-2.240606000	2.645060000	-0.725885000
6	-3.472416000	0.153181000	-0.613331000
6	0.525182000	-2.851513000	-0.734381000
6	0.210296000	-4.227194000	-1.258382000
6	2.263259000	0.104341000	-2.197485000
6	2.912608000	0.443997000	-3.512335000
6	0.003186000	-0.931356000	2.446739000
6	-0.638911000	-1.182642000	3.784975000
6	-4.692593000	0.820582000	-0.559881000
6	-5.809927000	0.174080000	-0.052877000
6	-5.718403000	-1.139185000	0.385296000
6	-4.501909000	-1.803319000	0.315655000
6	-3.374078000	-1.163688000	-0.177544000
1	1.353545000	4.528088000	0.030484000
1	0.764053000	4.731073000	1.700811000
1	-0.779397000	2.912694000	1.470167000
1	-0.305534000	3.253485000	-1.507825000
1	-1.155761000	4.458264000	-0.546185000
1	-2.896765000	3.149404000	-1.432609000
1	-2.738489000	2.602442000	0.242744000
1	0.505007000	-4.264467000	-2.307521000
1	-0.859212000	-4.412939000	-1.203420000
1	0.767848000	-4.979262000	-0.709107000
1	3.304393000	1.459419000	-3.443106000
1	2.180077000	0.411850000	-4.313673000
1	3.739607000	-0.231995000	-3.707302000
1	-0.115599000	-1.977692000	4.307775000
1	-1.691885000	-1.418211000	3.659987000
1	-0.556068000	-0.269851000	4.376061000
1	-4.780915000	1.836841000	-0.918642000
1	-4.422953000	-2.826752000	0.656917000
1	-2.422633000	-1.675060000	-0.218939000
1	-6.754892000	0.698531000	-0.009082000
1	-6.591543000	-1.642159000	0.777758000

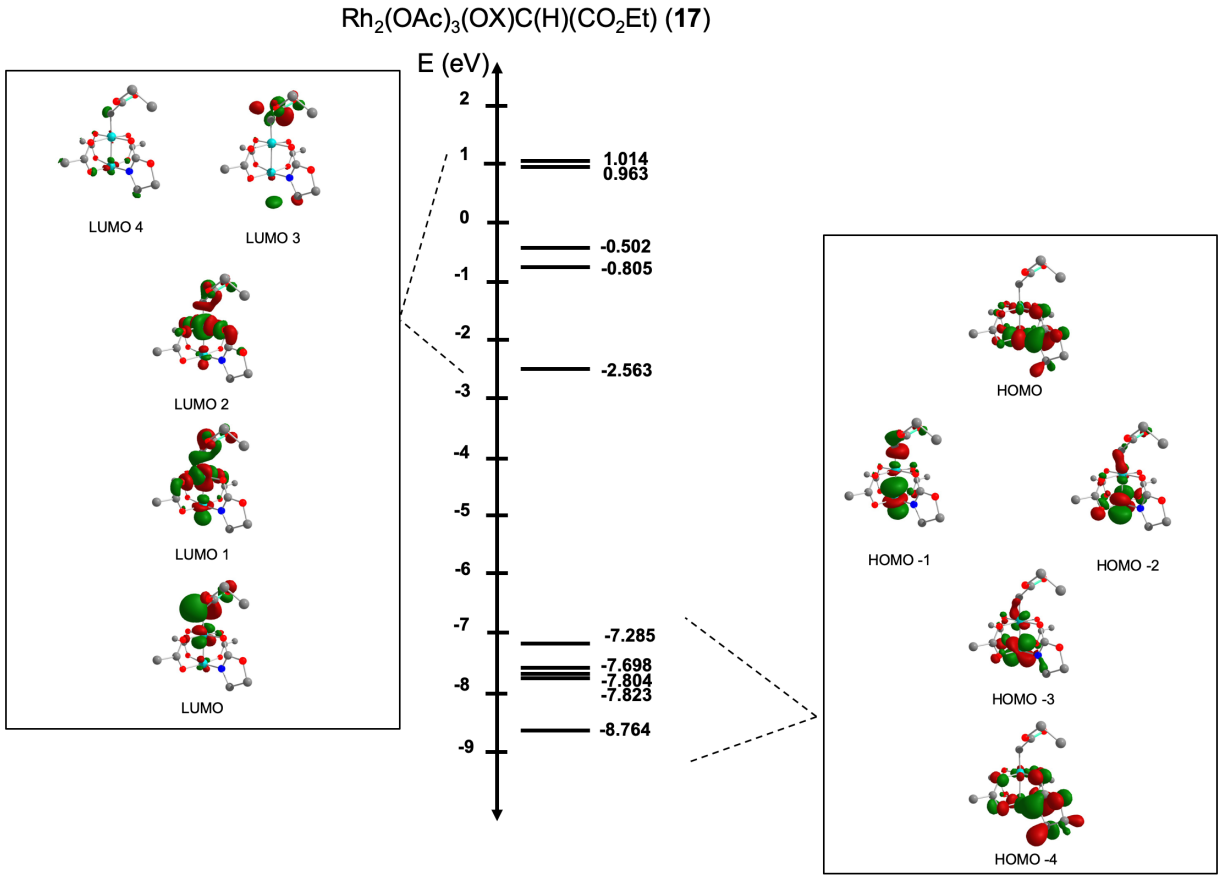


Figure S7. Calculated molecular orbitals of $Rh_2(OAc)_3(OX)C(H)(CO_2Et)$ (**17**) at the MO6-2X/def2-TZVPP level of theory.

$Rh_2(OAc)_3(OX)C(H)(CO_2Et)$ (**17**) at M06-2X/def2-TZVPP level of theory

45	-0.036316000	-0.834992000	-0.082787000
45	1.636119000	0.971797000	0.149102000
8	-3.382567000	-1.583402000	0.677922000
8	-3.137060000	-2.202011000	-1.483275000
8	-2.140747000	2.691254000	-0.326857000
8	-1.522545000	0.551671000	-0.374706000
8	1.454652000	-2.183427000	0.207644000
8	3.033234000	-0.596523000	0.389756000
8	-0.270021000	-0.659930000	1.947559000
8	1.271135000	0.955550000	2.194675000
8	0.382981000	-0.799350000	-2.073566000
8	1.891526000	0.855961000	-1.909676000
7	0.036721000	2.235044000	-0.105816000
6	-4.817566000	0.203598000	-0.123981000
6	-4.756854000	-1.192435000	0.452273000
6	-2.717389000	-2.001300000	-0.374394000
6	-1.270615000	-2.218174000	-0.156862000
6	-0.048962000	3.675489000	0.075257000
6	-1.498877000	3.972999000	-0.341199000

6	-1.163314000	1.760733000	-0.271060000
6	3.676501000	-2.875371000	0.545215000
6	2.656285000	-1.781411000	0.369650000
6	0.136083000	0.148849000	4.114670000
6	1.414659000	-0.056187000	-4.047585000
6	0.414056000	0.163929000	2.634629000
6	1.228505000	0.021245000	-2.555995000
1	-4.333616000	0.237756000	-1.097916000
1	-5.859827000	0.502717000	-0.236074000
1	-4.311734000	0.910813000	0.530303000
1	-5.221338000	-1.924099000	-0.206668000
1	-5.213302000	-1.249974000	1.436645000
1	-0.946676000	-3.258148000	-0.077332000
1	0.672860000	4.195845000	-0.552258000
1	0.149498000	3.938698000	1.117003000
1	-1.561600000	4.372178000	-1.353369000
1	-2.029007000	4.629742000	0.342934000
1	3.687941000	-3.495596000	-0.349872000
1	4.658985000	-2.449268000	0.718141000
1	3.383906000	-3.508800000	1.380728000
1	0.375016000	-0.837703000	4.508887000
1	0.728451000	0.905995000	4.617530000
1	-0.925751000	0.320984000	4.280978000
1	2.162514000	0.659978000	-4.371315000
1	1.714577000	-1.067106000	-4.317834000
1	0.461157000	0.144292000	-4.533487000

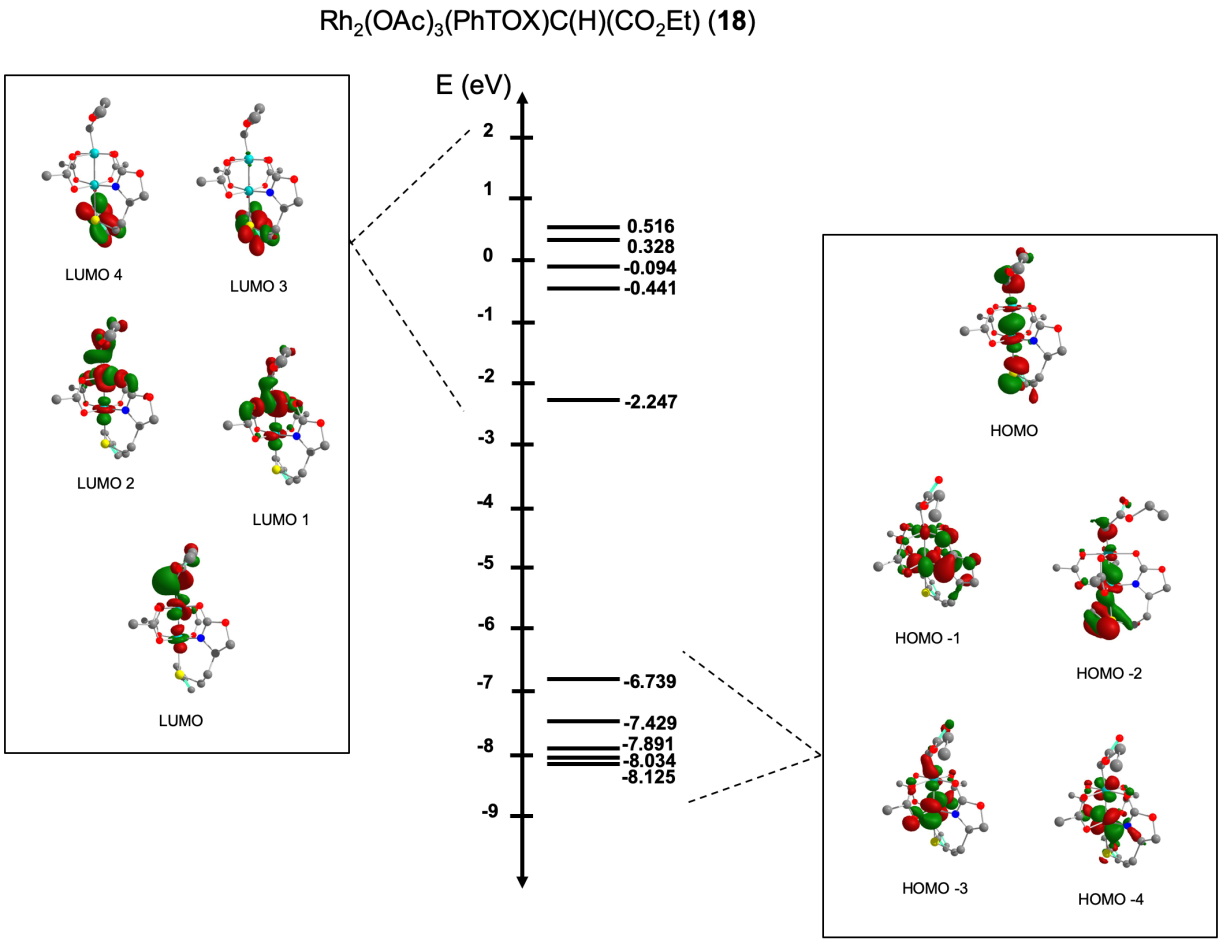


Figure S8. Calculated molecular orbitals of $Rh_2(OAc)_3(PhTOX)C(H)(CO_2Et)$ (**18**) at the MO6-2X/def2-TZVPP level of theory.

$Rh_2(OAc)_3(PhTOX)C(H)(CO_2Et)$ (**18**) at M06-2x/def2-TZVPP level of theory

45	0.672712000	-0.008420000	0.399110000
45	-1.489370000	-0.947899000	-0.287879000
16	3.022220000	1.218597000	1.179596000
8	-4.705153000	0.117309000	0.131508000
8	-5.088479000	-1.161791000	-1.684773000
8	-2.098265000	0.923224000	-0.926237000
8	-1.512536000	3.015952000	-1.441473000
8	1.090665000	-1.934478000	1.171840000
8	-0.835547000	-2.761659000	0.376748000
8	-0.182040000	0.535844000	2.209283000
8	-2.087008000	-0.496724000	1.632973000
8	-0.647803000	-1.301266000	-2.111664000
8	1.386274000	-0.619536000	-1.457651000
7	0.008379000	1.724479000	-0.440099000
6	-5.709412000	2.187012000	0.695188000
6	-5.734189000	1.036103000	-0.278980000
6	-4.458047000	-0.875303000	-0.696832000
6	-3.249043000	-1.669244000	-0.434063000
6	-1.207807000	1.810071000	-0.909388000

6	-0.417283000	3.880975000	-1.132142000
6	0.739878000	2.930198000	-0.796202000
6	1.657171000	3.474884000	0.293753000
6	3.042768000	2.832057000	0.340007000
6	4.384588000	0.385080000	0.417131000
6	0.278662000	-2.863293000	0.978000000
6	0.614916000	-4.237642000	1.494747000
6	-1.352962000	0.161324000	2.430344000
6	-1.980690000	0.503604000	3.755589000
6	0.589534000	-1.097994000	-2.296727000
6	1.117792000	-1.467590000	-3.656946000
6	5.547328000	1.051604000	0.041337000
6	6.599530000	0.342964000	-0.520630000
6	6.506256000	-1.030653000	-0.692139000
6	5.349242000	-1.693344000	-0.304656000
6	4.284530000	-0.992758000	0.241060000
1	-4.735316000	2.673374000	0.673628000
1	-6.471537000	2.916685000	0.424516000
1	-5.905917000	1.838979000	1.708301000
1	-5.515650000	1.356875000	-1.296794000
1	-6.690646000	0.513343000	-0.281739000
1	-3.438689000	-2.683713000	-0.078352000
1	-0.688493000	4.488714000	-0.264569000
1	-0.227585000	4.524231000	-1.987111000
1	1.343186000	2.733024000	-1.691592000
1	1.151917000	3.391398000	1.259561000
1	1.805876000	4.541662000	0.102568000
1	3.736600000	3.482625000	0.869654000
1	3.420969000	2.675110000	-0.670486000
1	-0.110194000	-4.511360000	2.260134000
1	1.616262000	-4.251932000	1.912275000
1	0.526192000	-4.959148000	0.684926000
1	-2.880681000	1.090350000	3.577805000
1	-1.282428000	1.056573000	4.375018000
1	-2.281187000	-0.416226000	4.254392000
1	0.879763000	-2.509563000	-3.862205000
1	2.189540000	-1.304601000	-3.704008000
1	0.610694000	-0.862162000	-4.406941000
1	5.640418000	2.118413000	0.193664000
1	5.265988000	-2.763285000	-0.441122000
1	3.370793000	-1.504241000	0.516665000
1	7.498405000	0.867966000	-0.815274000
1	7.329722000	-1.580986000	-1.126284000

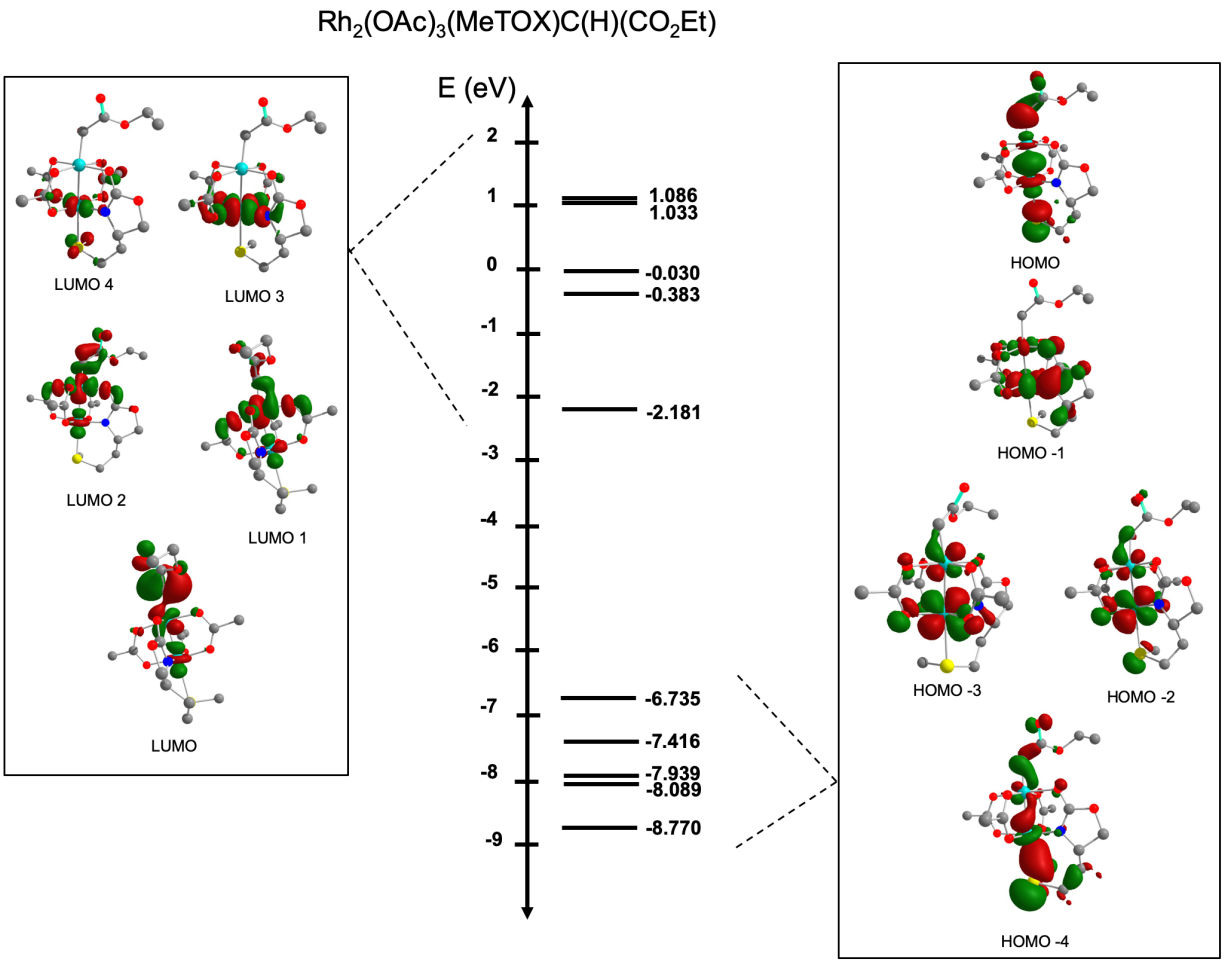


Figure S9. Calculated molecular orbitals of $Rh_2(OAc)_3(MeTOX)C(H)(CO_2Et)$ at the MO6-2X/def2-TZVPP level of theory.

$Rh_2(OAc)_3(MeTOX)C(H)(CO_2Et)$ at M06-2x/def2-TZVPP level of theory

45	1.313385000	-0.320864000	0.013653000
45	-1.080616000	-0.830147000	0.201109000
16	3.978540000	0.342861000	-0.135018000
8	-1.475160000	1.159081000	0.618566000
8	-0.659574000	3.205033000	0.997048000
8	1.561822000	-2.344284000	-0.534775000
8	-0.618796000	-2.770543000	-0.226447000
8	1.444353000	-0.843651000	2.022879000
8	-0.766761000	-1.180612000	2.181080000
8	-1.132977000	-0.427739000	-1.825911000
8	1.021467000	0.168820000	-1.987217000
8	-4.923890000	-0.400300000	0.625378000
8	-3.882320000	0.699697000	-1.049325000
7	0.790499000	1.572562000	0.536567000
6	-0.462567000	1.898825000	0.700893000
6	0.602159000	3.854638000	0.821956000
6	1.634074000	2.715809000	0.842711000

6	2.780008000	2.930722000	-0.141986000
6	4.043581000	2.129996000	0.163457000
6	4.121002000	0.325930000	-1.930472000
6	0.573307000	-3.105681000	-0.514079000
6	0.772108000	-4.559246000	-0.856402000
6	0.406835000	-1.136377000	2.658300000
6	0.529818000	-1.470280000	4.120895000
6	-0.124704000	-0.005177000	-2.460590000
6	-0.353356000	0.300488000	-3.917703000
6	-2.929525000	-1.245373000	-0.065966000
6	-4.017472000	-0.263723000	-0.161238000
6	-4.846157000	1.769382000	-0.976826000
6	-4.470893000	2.744574000	0.116732000
1	0.733105000	4.583585000	1.617127000
1	0.598578000	4.361990000	-0.146442000
1	2.053050000	2.597378000	1.850061000
1	3.055875000	3.989903000	-0.113681000
1	2.415949000	2.721324000	-1.151275000
1	4.303395000	2.234883000	1.217630000
1	4.885167000	2.514198000	-0.414090000
1	4.012685000	-0.712220000	-2.237405000
1	5.096904000	0.700473000	-2.233647000
1	3.318368000	0.899034000	-2.387385000
1	1.819017000	-4.762139000	-1.055724000
1	0.167738000	-4.804618000	-1.728398000
1	0.418139000	-5.171571000	-0.028894000
1	-0.098909000	-0.790767000	4.693776000
1	1.563228000	-1.393628000	4.442218000
1	0.156584000	-2.479658000	4.285772000
1	0.545179000	0.708855000	-4.368749000
1	-1.180860000	1.001524000	-4.008951000
1	-0.642263000	-0.617305000	-4.427793000
1	-5.834402000	1.342094000	-0.814304000
1	-4.809547000	2.229199000	-1.961152000
1	-4.508611000	2.257652000	1.089341000
1	-5.171429000	3.579903000	0.116736000
1	-3.462065000	3.122505000	-0.038210000
1	-3.194203000	-2.241842000	-0.424833000

Crystallographic Data

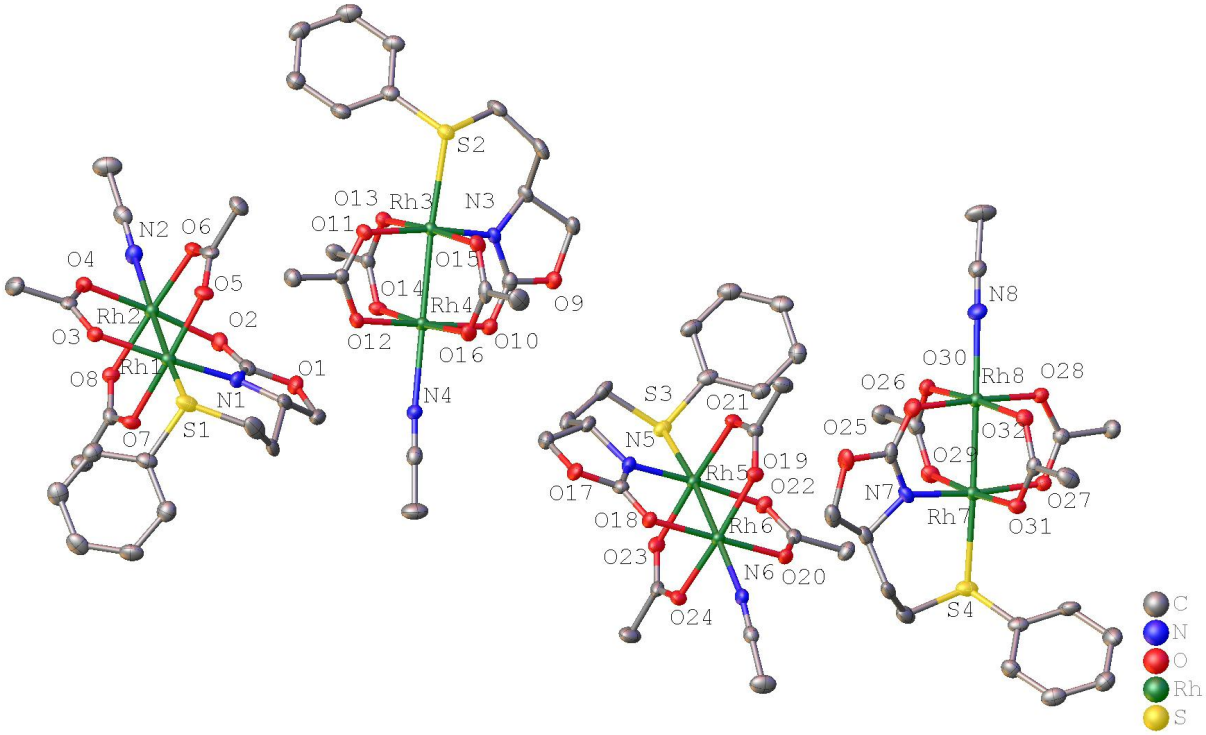


Figure S10. Asymmetric unit of $Rh_2(OAc)_3PhTOX{\cdot}CH_3CN$ (**6**·CH_3CN) with ellipsoids shown at 50% probability level and protons omitted for clarity

Table S1. Selected bond lengths (Å) and bond angles (º) for $Rh_2(OAc)_3PhTOX{\cdot}CH_3CN$ (**6**·CH_3CN)

Rh(1)–Rh(2)	2.4246(5)
Rh(3)–Rh(4)	2.4200(5)
Rh(5)–Rh(6)	2.4182(4)
Rh(7)–Rh(8)	2.4243(4)
Rh(1)–S(1)	2.4730(12)
Rh(3)–S(2)	2.5102(11)
Rh(5)–S(3)	2.5195(11)
Rh(7)–S(4)	2.5004(12)
Rh(2)–N(2)	2.244(4)
Rh(4)–N(4)	2.232(3)
Rh(6)–N(6)	2.233(3)
Rh(8)–N(8)	2.234(4)
Rh(2)–Rh(1)–S(1)	176.08(3)
Rh(4)–Rh(3)–S(2)	175.12(3)
Rh(6)–Rh(5)–S(3)	174.60(3)
Rh(8)–Rh(7)–S(4)	176.20(3)
Rh(1)–Rh(2)–N(2)	171.00(10)
Rh(3)–Rh(4)–N(4)	174.99(9)
Rh(5)–Rh(6)–N(6)	175.00(9)

Rh(7)–Rh(8)–N(8)	171.90(10)
N(1)–Rh(1)–Rh(2)–O(2)	6.68(12)
N(3)–Rh(3)–Rh(4)–O(10)	2.22(12)
N(5)–Rh(5)–Rh(6)–O(18)	1.19(12)
N(7)–Rh(7)–Rh(8)–O(26)	6.85(12)
O(5)–Rh(1)–Rh(2)–O(6)	4.21(3)
O(13)–Rh(3)–Rh(4)–O(14)	1.90(11)
O(21)–Rh(5)–Rh(6)–O(22)	0.82(12)
O(29)–Rh(7)–Rh(8)–O(30)	4.86(12)
O(7)–Rh(1)–Rh(2)–O(8)	3.88(12)
O(15)–Rh(3)–Rh(4)–O(16)	0.54(12)
O(23)–Rh(5)–Rh(6)–O(24)	0.91(12)
O(31)–Rh(7)–Rh(8)–O(32)	4.27(12)
O(3)–Rh(1)–Rh(2)–O(4)	4.42(12)
O(11)–Rh(3)–Rh(4)–O(12)	1.69(12)
O(19)–Rh(5)–Rh(6)–O(20)	0.76(12)
O(27)–Rh(7)–Rh(8)–O(28)	4.86(12)

Table S2. Crystal data and structure refinement for $Rh_2(OAc)_3PhTOX \cdot CH_3CN$.

Identification code	MonoAspPhTOX
Empirical formula	$C_{19}H_{24}N_2O_8Rh_2S$
Formula weight	646.29
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.9230(9)
b/Å	28.185(3)
c/Å	14.6929(13)
α/°	90
β/°	90.176(2)
γ/°	90
Volume/Å^3	4523.3(7)
Z	8
ρ_{calc}g/cm^3	1.8979
μ/mm^{-1}	1.600
F(000)	2560.3
Crystal size/mm^3	0.222 × 0.131 × 0.079
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.64 to 55.04
Index ranges	$-14 \leq h \leq 14$, $-36 \leq k \leq 36$, $-19 \leq l \leq 19$
Reflections collected	119747
Independent reflections	20769 [R_{int} = 0.0506, R_{sigma} = 0.0308]
Data/restraints/parameters	20769/1/1169
Goodness-of-fit on F^2	1.061

Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0640
Final R indexes [all data]	R_1 = 0.0311, wR_2 = 0.0660
Largest diff. peak/hole / e Å^{-3}	2.22/-0.64
Flack parameter	0.032(17)

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for MonoAspPhTOX. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Rh5	6783.4(3)	3772.05(7)	2456.3(2)	15.76(7)
Rh2	1756.6(3)	5888.67(7)	10512.8(2)	16.17(6)
Rh3	1796.9(3)	6227.28(7)	5061.3(2)	14.49(6)
Rh4	3709.3(3)	5902.21(7)	5624.5(2)	15.31(6)
Rh1	3538.0(3)	6323.40(7)	10007.4(2)	16.74(7)
Rh7	8599.2(3)	3649.33(7)	-2497.2(2)	15.75(7)
Rh8	6797.2(3)	4070.08(7)	-3017.8(2)	16.20(7)
Rh6	8696.2(3)	4098.97(7)	1906.0(2)	15.93(6)
S3	4902.0(10)	3411.7(3)	3163.6(7)	21.0(2)
S2	-86.8(10)	6584.3(3)	4357.9(7)	19.7(2)
S4	10372.3(10)	3185.8(4)	-1886.6(8)	25.2(2)
S1	5264.1(10)	6804.9(4)	9434.1(8)	26.4(2)
O20	8878(3)	3511.4(10)	1119(2)	19.0(6)
O28	6426(3)	3495.1(10)	-3808(2)	19.4(6)
O18	8492(3)	4688.3(10)	2714(2)	21.6(7)
O5	2464(3)	6626.6(11)	9028(2)	22.4(7)
O10	3511(3)	5311.5(10)	4812(2)	21.5(6)
O14	2704(3)	5580.7(10)	6619(2)	19.6(6)
O15	2791(3)	6536.0(11)	4039(2)	21.8(7)
O12	3885(3)	6489.6(10)	6408(2)	18.7(6)
O27	8174(3)	3121.0(10)	-3428(2)	18.8(6)
O16	4571(3)	6236.8(11)	4577(2)	20.7(6)
O19	7120(3)	3188.9(10)	1624(2)	20.0(6)
O13	923(3)	5903.0(10)	6121.8(19)	18.2(6)
O22	7699(3)	4415.6(10)	898(2)	20.8(6)
O11	2141(3)	6817.2(10)	5875(2)	18.4(6)
O2	2273(3)	5311.3(10)	9737(2)	22.9(7)
O3	3079(3)	6851.4(10)	10934(2)	19.7(6)
O7	4495(3)	5994.9(10)	11023(2)	19.6(6)
O23	7763(3)	3451.1(10)	3472(2)	22.8(7)
O31	9551(3)	3989.4(10)	-3501(2)	19.7(6)
O4	1354(3)	6456.6(10)	11304(2)	19.6(6)
O9	2314(3)	4919.8(10)	3828(2)	23.6(7)
O26	7266(3)	4652.1(10)	-2248(2)	23.9(7)
O17	7304(3)	5075.3(11)	3707(2)	24.8(7)
O24	9542(3)	3767.9(11)	2964(2)	21.8(6)

O32	7835(3)	4339.8(10)	-4046(2)	21.2(6)
O6	834(3)	6182.0(10)	9434(2)	21.4(6)
O25	8466(3)	4933.1(11)	-1132(2)	27.7(7)
O8	2801(3)	5626.1(10)	11552(2)	19.9(6)
O1	3488(3)	5047.6(11)	8622(2)	26.5(7)
O30	5875(3)	3768.9(10)	-1954(2)	21.3(6)
O29	7519(3)	3331.9(11)	-1545(2)	22.4(7)
O21	5915(3)	4102.6(11)	1398.6(19)	20.6(6)
N7	8845(3)	4200.4(12)	-1658(2)	20.3(8)
N1	3833(3)	5778.9(13)	9168(2)	21.1(8)
C39	7512(4)	4689.3(15)	3172(3)	20.4(9)
N3	1657(3)	5627.1(12)	4338(2)	17.6(7)
C33	1560(4)	5645.8(15)	6660(3)	18.2(8)
N5	6656(3)	4367.8(12)	3196(2)	19.2(8)
C20	2526(4)	5308.0(15)	4359(3)	20.1(9)
C58	8161(4)	4575.1(15)	-1714(3)	21.5(9)
C50	8067(4)	3188.7(14)	1143(3)	17.6(8)
N2	-62(4)	5588.5(13)	10925(3)	23.4(8)
C54	8911(4)	3513.8(15)	3505(3)	21.9(9)
C13	1791(5)	7177.7(16)	12069(3)	29.1(11)
N6	10533(3)	4339.2(13)	1427(2)	21.5(8)
C35	3945(5)	6482.1(15)	4026(3)	23.3(10)
N8	4984(4)	4372.4(13)	-3419(3)	25.5(8)
C31	3094(4)	6822.6(14)	6370(3)	16.2(8)
C11	7668(5)	6697.1(17)	10086(3)	28.2(11)
N4	5549(3)	5661.2(12)	6101(2)	19.1(7)
C12	2102(4)	6801.1(14)	11381(3)	18.4(8)
C16	3925(4)	5729.0(15)	11578(3)	19.4(9)
C32	3314(4)	7248.6(15)	6970(3)	23.6(9)
C69	7173(4)	3156.4(14)	-3871(3)	18.6(8)
C14	1352(4)	6484.4(15)	8933(3)	22.0(9)
C70	6874(4)	2778.1(16)	-4546(3)	25.6(10)
C51	8275(4)	2769.9(15)	508(3)	24.0(9)
C52	6547(4)	4349.2(15)	852(3)	19.3(9)
C67	13591(5)	3227.0(16)	-3273(4)	29.1(11)
C34	871(4)	5388.2(17)	7401(3)	24.9(10)
C71	6410(4)	3460.4(16)	-1467(3)	23.2(9)
C57	12875(4)	4405.8(18)	1170(4)	32.5(12)
C23	11(5)	5807.1(16)	3196(3)	26.6(10)
C1	3166(4)	5392.5(15)	9222(3)	22.4(9)
C61	10941(4)	4064.9(18)	-1052(3)	27.1(10)
C56	11556(4)	4370.3(14)	1315(3)	19.4(9)
C73	8977(4)	4245.7(15)	-4056(3)	19.3(9)
C4	5896(4)	5954.1(18)	8542(3)	27.8(10)
C22	622(4)	5444.8(15)	3808(3)	19.3(8)

C21	1227(4)	5035.0(15)	3294(3)	22.2(9)
C9	8236(5)	6958.2(16)	11585(3)	29.6(11)
C30	-778(4)	6985.3(16)	5950(3)	25.1(10)
C25	-1188(4)	6750.8(15)	5179(3)	21.3(9)
C43	4127(4)	3858.2(16)	3854(3)	26.0(10)
C74	9701(5)	4469.3(17)	-4804(3)	30.6(11)
C2	4595(4)	5220.3(18)	8166(3)	30.0(11)
C17	4655(4)	5509.9(17)	12330(3)	28.6(10)
C10	8548(4)	6767.1(17)	10756(4)	30.5(11)
C47	2050(4)	2956.6(16)	1071(4)	27.8(10)
C53	5875(4)	4597.2(17)	96(3)	28.1(10)
C45	4155(4)	3046.4(15)	1557(3)	22.2(9)
C42	5031(5)	4180.0(16)	4348(3)	27.5(10)
C49	2519(4)	3326.3(17)	2501(3)	27.8(10)
C60	9668(4)	4242.9(16)	-871(3)	25.0(10)
C44	3744(4)	3257.3(15)	2350(3)	22.4(9)
C63	11525(4)	3152.8(15)	-2724(3)	21.8(9)
C41	5622(4)	4547.2(16)	3731(3)	22.4(9)
C46	3288(5)	2897.7(16)	917(3)	26.0(10)
C6	6450(4)	6819.1(16)	10262(3)	23.6(10)
C66	13270(5)	3008.9(16)	-4082(3)	29.3(10)
C40	6224(4)	4954.6(16)	4249(3)	26.8(10)
C26	-2449(4)	6682.9(16)	5066(3)	25.7(10)
C18	-1080(4)	5591.8(15)	11046(3)	23.8(10)
C76	2645(5)	4414.6(19)	-3702(4)	40.1(14)
C72	5660(5)	3226.6(18)	-731(3)	31.6(11)
C55	9595(5)	3259.9(18)	4261(3)	32.6(12)
C68	12732(4)	3302.1(16)	-2606(3)	25.2(10)
C59	9574(5)	4769.3(17)	-668(3)	29.4(11)
C8	7018(5)	7076.8(17)	11762(4)	30.3(11)
C37	6577(4)	5621.0(15)	6213(3)	21.8(9)
C48	1679(5)	3174.8(17)	1848(4)	30.5(11)
C62	11038(4)	3531.5(18)	-956(3)	31.8(11)
C65	12065(5)	2863.3(17)	-4208(4)	30.5(11)
C75	3957(4)	4388.4(16)	-3517(3)	24.6(10)
C28	-2845(5)	7104.1(17)	6462(4)	28.8(10)
C15	621(5)	6701.8(18)	8175(3)	31.1(11)
C7	6136(5)	7007.2(16)	11101(3)	27.2(10)
C24	-875(4)	6131.5(16)	3690(3)	26.2(10)
C64	11194(4)	2937.9(17)	-3532(4)	28.6(11)
C38	7874(5)	5569.9(19)	6355(4)	36.1(12)
C3	4627(4)	5750.7(17)	8372(3)	25.9(10)
C29	-1595(5)	7163.4(17)	6584(3)	29.2(11)
C36	4612(5)	6727.3(18)	3270(3)	30.6(11)
C27	-3268(5)	6858.6(17)	5701(4)	33.1(12)

C19	-2375(5)	5583.4(18)	11238(4)	38.9(13)
C5	5915(5)	6490.4(19)	8468(3)	36.8(13)

Table S4. Anisotropic Displacement Parameters ($Å^2×10^3$) for MonoAspPhTOX. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh5	14.40(15)	19.43(15)	13.46(15)	2.98(12)	1.50(12)	0.83(12)
Rh2	14.91(15)	17.67(15)	15.93(15)	-0.10(13)	-0.16(12)	-1.24(13)
Rh3	13.96(15)	17.21(15)	12.30(14)	-1.62(12)	-1.09(11)	-0.11(11)
Rh4	12.27(14)	19.52(15)	14.15(14)	-0.94(13)	0.08(11)	-1.27(12)
Rh1	15.20(15)	19.84(16)	15.18(15)	0.36(12)	-0.70(12)	2.31(12)
Rh7	14.45(15)	18.70(15)	14.09(15)	-0.37(12)	0.07(12)	1.38(12)
Rh8	15.12(15)	17.56(15)	15.93(15)	0.82(13)	-0.06(12)	-1.14(12)
Rh6	13.03(14)	20.66(16)	14.09(14)	1.30(13)	0.12(11)	-1.40(12)
S3	19.4(5)	22.9(5)	20.7(5)	4.1(4)	5.2(4)	4.6(4)
S2	18.7(5)	21.3(5)	18.9(5)	-0.6(4)	-2.9(4)	2.2(4)
S4	18.3(5)	30.0(6)	27.4(6)	2.3(5)	-0.3(4)	9.6(5)
S1	19.1(5)	34.1(6)	26.0(6)	-4.2(5)	-3.5(4)	11.0(5)
O20	13.5(14)	26.6(16)	16.8(14)	-0.1(12)	2.6(11)	-2.5(12)
O28	16.0(15)	22.0(15)	20.3(15)	1.4(12)	1.0(12)	-1.9(12)
O18	18.0(15)	26.2(16)	20.7(15)	2.7(13)	0.1(12)	-7.7(13)
O5	19.1(16)	25.8(16)	22.4(16)	3.9(13)	-3.9(13)	4.4(13)
O10	16.5(15)	25.2(16)	22.9(16)	0.0(12)	0.1(12)	-6.3(13)
O14	13.7(15)	24.7(16)	20.5(15)	0.7(12)	-1.4(12)	3.5(12)
O15	21.0(16)	30.6(17)	13.8(14)	-3.7(13)	0.9(12)	2.7(12)
O12	17.6(15)	23.2(16)	15.4(14)	-0.5(12)	-2.4(12)	-3.3(12)
O27	17.0(15)	18.9(15)	20.4(15)	0.7(12)	0.4(12)	-0.2(12)
O16	14.8(14)	30.3(17)	17.0(14)	-3.6(13)	3.7(11)	-0.1(13)
O19	18.2(15)	20.3(15)	21.4(15)	-0.6(12)	4.5(12)	-1.6(12)
O13	16.4(14)	23.1(14)	15.0(13)	-0.9(13)	1.0(11)	3.6(12)
O22	17.0(15)	27.4(16)	18.0(15)	3.1(13)	1.3(12)	3.2(13)
O11	17.5(15)	19.5(15)	18.2(14)	-2.3(12)	-2.9(12)	-1.3(12)
O2	26.8(18)	19.6(16)	22.2(16)	0.8(13)	-1.7(13)	-3.9(13)
O3	16.3(15)	21.3(15)	21.4(15)	1.5(12)	-2.3(12)	-4.0(12)
O7	13.1(14)	26.0(16)	19.7(15)	0.8(12)	-0.3(11)	5.4(12)
O23	23.6(16)	29.7(17)	15.2(14)	7.3(13)	3.2(12)	5.7(12)
O31	15.5(14)	24.3(16)	19.4(15)	-0.3(12)	1.4(12)	3.9(12)
O4	15.7(14)	21.2(15)	21.8(15)	-0.3(12)	-1.7(12)	-4.2(12)
O9	19.8(16)	25.8(16)	25.1(16)	-0.6(13)	-0.6(13)	-8.8(13)
O26	25.0(17)	21.9(16)	25.0(17)	1.0(13)	1.0(13)	-4.8(13)
O17	21.8(17)	26.1(17)	26.4(17)	5.4(13)	-0.2(13)	-11.4(13)
O24	18.8(15)	31.3(17)	15.2(14)	5.7(13)	-1.0(12)	2.3(13)
O32	22.1(16)	23.1(16)	18.4(15)	-0.1(13)	0.8(12)	3.5(12)
O6	16.6(14)	26.9(16)	20.8(15)	3.6(13)	-5.2(12)	-0.5(13)

O25	26.2(17)	31.6(18)	25.4(17)	-10.2(14)	1.3(14)	-11.4(14)
O8	18.2(15)	22.2(16)	19.2(15)	0.8(12)	1.5(12)	3.4(12)
O1	27.4(18)	29.5(17)	22.6(16)	7.2(14)	0.4(14)	-7.4(13)
O30	17.8(15)	28.4(16)	17.6(14)	-0.8(13)	3.3(12)	-0.6(13)
O29	18.2(16)	27.4(17)	21.6(16)	-4.8(13)	0.9(12)	4.4(13)
O21	15.4(14)	31.4(16)	15.1(14)	4.6(13)	-0.2(11)	3.6(13)
N7	19.8(18)	25(2)	15.6(17)	-3.6(15)	-4.7(14)	-0.8(14)
N1	17.8(18)	29(2)	16.3(17)	2.8(15)	2.9(14)	-1.2(15)
C39	17(2)	23(2)	21(2)	4.8(17)	-3.1(17)	-2.1(17)
N3	15.5(17)	21.8(18)	15.5(17)	-3.5(14)	-1.8(14)	-3.8(14)
C33	17(2)	25(2)	12.5(19)	-2.8(17)	0.6(16)	0.1(16)
N5	18.5(18)	22.7(19)	16.4(17)	3.9(15)	1.6(14)	-3.0(14)
C20	22(2)	20(2)	19(2)	-4.2(17)	3.0(17)	-2.8(16)
C58	25(2)	24(2)	15(2)	-7.7(18)	6.5(17)	-3.9(16)
C50	20(2)	18(2)	15.1(19)	3.2(16)	-2.6(16)	0.6(15)
N2	23(2)	23.7(19)	23.0(19)	-4.1(16)	2.3(16)	-2.9(15)
C54	25(2)	26(2)	14(2)	11.2(18)	0.0(17)	-2.4(17)
C13	26(3)	27(2)	34(3)	2.9(19)	-2(2)	-10(2)
N6	20.0(19)	26(2)	18.0(18)	3.3(15)	-2.0(15)	-7.5(15)
C35	32(3)	22(2)	16(2)	-8.7(19)	4.0(19)	-4.0(17)
N8	23(2)	24(2)	30(2)	6.5(16)	-1.4(16)	-2.9(16)
C31	13.4(19)	20(2)	15.4(19)	-2.9(16)	1.1(15)	0.7(15)
C11	30(3)	26(3)	29(3)	-1(2)	2(2)	-1.8(19)
N4	17.1(18)	21.1(18)	19.1(17)	2.5(14)	-0.5(14)	-3.2(14)
C12	18(2)	19(2)	19(2)	6.7(16)	-3.0(16)	3.1(16)
C16	24(2)	21(2)	13.9(19)	1.8(17)	-0.7(17)	0.5(16)
C32	25(2)	23(2)	23(2)	-1.1(18)	-2.5(18)	-2.0(17)
C69	19(2)	18(2)	19(2)	-1.1(17)	0.2(16)	2.1(16)
C14	19(2)	23(2)	24(2)	8.4(17)	-3.9(18)	-1.2(18)
C70	25(2)	24(2)	27(2)	0.4(19)	-1.1(19)	-6.5(19)
C51	27(2)	21(2)	24(2)	4.8(18)	5.1(19)	-1.7(17)
C52	16(2)	25(2)	17(2)	3.2(17)	0.7(16)	1.4(17)
C67	21(2)	23(2)	42(3)	-1.9(19)	3(2)	7(2)
C34	16(2)	38(3)	21(2)	-7.3(19)	0.2(17)	7.6(19)
C71	23(2)	28(2)	18(2)	-4.7(19)	-1.3(18)	3.0(18)
C57	21(2)	35(3)	41(3)	-4(2)	2(2)	12(2)
C23	33(2)	31(3)	16(2)	-7(2)	-9.0(18)	-1.2(18)
C1	25(2)	25(2)	18(2)	6.5(18)	-6.7(18)	-0.9(17)
C61	16(2)	52(3)	13.7(19)	-2(2)	-0.9(16)	-5(2)
C56	24(2)	17(2)	17(2)	0.1(17)	-2.2(17)	-0.3(16)
C73	21(2)	19(2)	17(2)	-4.7(17)	3.4(17)	-2.0(16)
C4	18(2)	53(3)	11.6(19)	0(2)	-0.4(16)	-6(2)
C22	18(2)	23(2)	17(2)	-5.7(17)	-3.0(16)	-2.5(16)
C21	20(2)	28(2)	18(2)	-4.1(18)	0.3(17)	-5.8(17)
C9	27(3)	30(3)	31(3)	-13(2)	-5(2)	4(2)

C30	21(2)	27(2)	27(2)	2.7(18)	-8.1(19)	1.3(19)
C25	20(2)	20(2)	24(2)	2.3(17)	-3.6(18)	2.5(17)
C43	25(2)	27(2)	26(2)	4.6(19)	14.6(19)	1.1(19)
C74	29(3)	38(3)	26(2)	-6(2)	-3(2)	11(2)
C2	24(2)	48(3)	18(2)	15(2)	-0.8(18)	-3(2)
C17	24(2)	35(3)	27(2)	5(2)	-2.2(19)	8(2)
C10	18(2)	32(3)	41(3)	-1.9(19)	-5(2)	3(2)
C47	24(2)	22(2)	38(3)	2.5(19)	-5(2)	5(2)
C53	19(2)	43(3)	23(2)	2(2)	-0.1(18)	8(2)
C45	17(2)	23(2)	27(2)	1.0(17)	3.0(18)	1.6(18)
C42	34(3)	33(3)	16(2)	11(2)	6.2(18)	1.6(18)
C49	21(2)	33(3)	30(3)	6(2)	8.2(19)	7(2)
C60	24(2)	38(3)	12.7(19)	-5(2)	-1.3(17)	-0.5(18)
C44	19(2)	20(2)	28(2)	3.3(17)	4.5(18)	8.1(18)
C63	18(2)	19(2)	28(2)	2.9(17)	-0.2(18)	7.1(18)
C41	22(2)	29(2)	16(2)	10.0(18)	4.2(17)	0.3(17)
C46	30(3)	25(2)	23(2)	-1.7(19)	2.4(19)	-0.6(18)
C6	20(2)	25(2)	26(2)	-0.5(18)	-3.6(18)	7.5(18)
C66	28(3)	28(2)	32(3)	4(2)	4(2)	-1(2)
C40	26(2)	34(3)	21(2)	7(2)	-1.0(19)	-6.9(19)
C26	19(2)	24(2)	34(3)	-2.4(18)	-3.1(19)	1.6(19)
C18	28(3)	19(2)	24(2)	-3.2(18)	-4.4(19)	0.7(17)
C76	17(2)	42(3)	61(4)	0(2)	6(2)	17(3)
C72	23(2)	46(3)	26(2)	-2(2)	4(2)	10(2)
C55	24(2)	49(3)	24(2)	9(2)	-3(2)	10(2)
C68	22(2)	28(2)	26(2)	-4.1(19)	-3.6(19)	-0.0(19)
C59	26(2)	43(3)	19(2)	-12(2)	3.4(19)	-6(2)
C8	31(3)	30(3)	30(3)	-10(2)	3(2)	2(2)
C37	29(3)	19(2)	18(2)	1.4(18)	2.1(18)	1.0(16)
C48	20(2)	32(3)	40(3)	1(2)	0(2)	5(2)
C62	24(2)	55(3)	16(2)	4(2)	-1.6(18)	6(2)
C65	33(3)	27(2)	32(3)	8(2)	-5(2)	-5(2)
C75	25(2)	25(2)	24(2)	4.0(19)	1.3(19)	-0.3(18)
C28	24(2)	29(2)	33(3)	3(2)	9(2)	4(2)
C15	32(3)	39(3)	21(2)	3(2)	-8(2)	2(2)
C7	26(2)	27(2)	28(2)	1(2)	5(2)	4.7(19)
C24	24(2)	28(2)	27(2)	-0.1(19)	-13.3(19)	-1.4(19)
C64	14(2)	31(3)	41(3)	2.8(19)	-3(2)	-3(2)
C38	23(3)	39(3)	46(3)	7(2)	-3(2)	9(2)
C3	20(2)	46(3)	12.2(19)	6(2)	-1.4(17)	-1.1(18)
C29	28(3)	35(3)	25(2)	6(2)	-4(2)	-1(2)
C36	25(2)	43(3)	24(2)	-9(2)	7.3(19)	7(2)
C27	21(2)	30(3)	48(3)	-2(2)	0(2)	3(2)
C19	24(3)	35(3)	58(4)	-5(2)	-1(2)	8(3)
C5	23(2)	67(4)	20(2)	-14(2)	3.7(19)	7(2)

Table S5. Bond Lengths for MonoAspPhTOX.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rh5	Rh6	2.4247(5)	O17	C40	1.466(6)
Rh5	S3	2.5195(11)	O24	C54	1.273(6)
Rh5	O19	2.082(3)	O32	C73	1.275(5)
Rh5	O23	2.045(3)	O6	C14	1.261(6)
Rh5	O21	2.043(3)	O25	C58	1.363(5)
Rh5	N5	2.005(3)	O25	C59	1.462(6)
Rh2	Rh1	2.4182(4)	O8	C16	1.262(5)
Rh2	O2	2.066(3)	O1	C1	1.360(5)
Rh2	O4	2.027(3)	O1	C2	1.468(6)
Rh2	O6	2.050(3)	O30	C71	1.268(5)
Rh2	O8	2.042(3)	O29	C71	1.270(6)
Rh2	N2	2.244(4)	O21	C52	1.268(5)
Rh3	Rh4	2.4243(4)	N7	C58	1.296(6)
Rh3	S2	2.5102(11)	N7	C60	1.467(5)
Rh3	O15	2.050(3)	N1	C1	1.313(6)
Rh3	O13	2.046(3)	N1	C3	1.460(6)
Rh3	O11	2.081(3)	C39	N5	1.303(6)
Rh3	N3	2.003(3)	N3	C20	1.308(6)
Rh4	O10	2.060(3)	N3	C22	1.464(5)
Rh4	O14	2.043(3)	C33	C34	1.511(6)
Rh4	O12	2.025(3)	N5	C41	1.469(5)
Rh4	O16	2.038(3)	C50	C51	1.522(6)
Rh4	N4	2.232(4)	N2	C18	1.127(6)
Rh1	S1	2.4729(11)	C54	C55	1.516(6)
Rh1	O5	2.041(3)	C13	C12	1.505(6)
Rh1	O3	2.080(3)	N6	C56	1.133(6)
Rh1	O7	2.041(3)	C35	C36	1.499(6)
Rh1	N1	1.995(4)	N8	C75	1.131(6)
Rh7	Rh8	2.4201(4)	C31	C32	1.508(6)
Rh7	S4	2.5004(11)	C11	C10	1.389(7)
Rh7	O27	2.074(3)	C11	C6	1.399(7)
Rh7	O31	2.046(3)	N4	C37	1.140(6)
Rh7	O29	2.040(3)	C16	C17	1.494(6)
Rh7	N7	2.000(3)	C69	C70	1.492(6)
Rh8	O28	2.034(3)	C14	C15	1.499(6)
Rh8	O26	2.056(3)	C52	C53	1.502(6)
Rh8	O32	2.039(3)	C67	C66	1.382(7)
Rh8	O30	2.046(3)	C67	C68	1.376(7)
Rh8	N8	2.234(4)	C71	C72	1.510(6)
Rh6	O20	2.030(3)	C57	C56	1.460(7)
Rh6	O18	2.054(3)	C23	C22	1.515(6)

Rh6	O22	2.041(3)	C23	C24	1.518(7)
Rh6	O24	2.033(3)	C61	C60	1.503(6)
Rh6	N6	2.233(4)	C61	C62	1.514(7)
S3	C43	1.827(4)	C73	C74	1.495(6)
S3	C44	1.791(5)	C4	C3	1.520(6)
S2	C25	1.770(5)	C4	C5	1.516(7)
S2	C24	1.824(4)	C22	C21	1.531(6)
S4	C63	1.766(5)	C9	C10	1.376(7)
S4	C62	1.827(5)	C9	C8	1.398(7)
S1	C6	1.774(5)	C30	C25	1.384(6)
S1	C5	1.820(5)	C30	C29	1.387(7)
O20	C50	1.270(5)	C25	C26	1.401(6)
O28	C69	1.259(5)	C43	C42	1.523(7)
O18	C39	1.266(5)	C2	C3	1.526(7)
O5	C14	1.286(5)	C47	C46	1.382(7)
O10	C20	1.264(5)	C47	C48	1.360(7)
O14	C33	1.265(5)	C45	C44	1.383(6)
O15	C35	1.271(6)	C45	C46	1.397(6)
O12	C31	1.277(5)	C42	C41	1.520(6)
O27	C69	1.274(5)	C49	C44	1.371(6)
O16	C35	1.263(6)	C49	C48	1.392(7)
O19	C50	1.255(5)	C60	C59	1.517(7)
O13	C33	1.277(5)	C63	C68	1.394(6)
O22	C52	1.274(5)	C63	C64	1.380(7)
O11	C31	1.269(5)	C41	C40	1.525(6)
O2	C1	1.257(6)	C6	C7	1.386(7)
O3	C12	1.263(5)	C66	C65	1.390(7)
O7	C16	1.272(5)	C26	C27	1.386(7)
O23	C54	1.267(6)	C18	C19	1.443(7)
O31	C73	1.256(5)	C76	C75	1.459(7)
O4	C12	1.274(5)	C8	C7	1.379(7)
O9	C20	1.363(5)	C37	C38	1.439(7)
O9	C21	1.458(5)	C65	C64	1.393(7)
O26	C58	1.270(6)	C28	C29	1.387(7)
O17	C39	1.362(5)	C28	C27	1.392(7)

Table S6. Bond Angles for MonoAspPhTOX.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S3	Rh5	Rh6	174.60(3)	C52	O22	Rh6	119.9(3)
O19	Rh5	Rh6	87.14(8)	C31	O11	Rh3	119.0(3)
O19	Rh5	S3	94.01(9)	C1	O2	Rh2	113.7(3)
O23	Rh5	Rh6	87.81(9)	C12	O3	Rh1	117.8(3)
O23	Rh5	S3	86.93(9)	C16	O7	Rh1	119.1(3)

O23	Rh5	O19	89.23(12)	C54	O23	Rh5	118.8(3)
O21	Rh5	Rh6	88.38(8)	C73	O31	Rh7	119.0(3)
O21	Rh5	S3	96.89(9)	C12	O4	Rh2	120.8(3)
O21	Rh5	O19	89.75(12)	C21	O9	C20	105.4(3)
O21	Rh5	O23	176.10(12)	C58	O26	Rh8	113.2(3)
N5	Rh5	Rh6	85.63(11)	C40	O17	C39	105.3(3)
N5	Rh5	S3	93.21(11)	C54	O24	Rh6	119.3(3)
N5	Rh5	O19	172.77(14)	C73	O32	Rh8	118.5(3)
N5	Rh5	O23	90.69(13)	C14	O6	Rh2	120.2(3)
N5	Rh5	O21	89.85(13)	C59	O25	C58	105.0(3)
O2	Rh2	Rh1	90.48(9)	C16	O8	Rh2	118.7(3)
O4	Rh2	Rh1	87.26(9)	C2	O1	C1	105.9(4)
O4	Rh2	O2	176.56(12)	C71	O30	Rh8	119.2(3)
O6	Rh2	Rh1	87.27(9)	C71	O29	Rh7	119.4(3)
O6	Rh2	O2	91.44(12)	C52	O21	Rh5	118.6(3)
O6	Rh2	O4	91.04(12)	C58	N7	Rh7	121.2(3)
O8	Rh2	Rh1	87.99(8)	C60	N7	Rh7	129.0(3)
O8	Rh2	O2	88.52(12)	C60	N7	C58	109.6(4)
O8	Rh2	O4	88.80(12)	C1	N1	Rh1	120.7(3)
O8	Rh2	O6	175.26(12)	C3	N1	Rh1	129.4(3)
N2	Rh2	Rh1	171.00(10)	C3	N1	C1	109.5(4)
N2	Rh2	O2	95.48(13)	O17	C39	O18	116.9(4)
N2	Rh2	O4	87.08(13)	N5	C39	O18	128.4(4)
N2	Rh2	O6	85.84(13)	N5	C39	O17	114.8(4)
N2	Rh2	O8	98.88(13)	C20	N3	Rh3	121.0(3)
S2	Rh3	Rh4	175.11(3)	C22	N3	Rh3	129.5(3)
O15	Rh3	Rh4	87.30(9)	C22	N3	C20	109.3(3)
O15	Rh3	S2	87.90(9)	O13	C33	O14	126.1(4)
O13	Rh3	Rh4	88.56(8)	C34	C33	O14	117.3(4)
O13	Rh3	S2	96.25(8)	C34	C33	O13	116.6(4)
O13	Rh3	O15	175.84(12)	C39	N5	Rh5	121.1(3)
O11	Rh3	Rh4	87.25(8)	C41	N5	Rh5	129.3(3)
O11	Rh3	S2	93.59(8)	C41	N5	C39	109.2(4)
O11	Rh3	O15	89.24(12)	O9	C20	O10	116.8(4)
O11	Rh3	O13	90.19(12)	N3	C20	O10	128.6(4)
N3	Rh3	Rh4	85.76(10)	N3	C20	O9	114.6(4)
N3	Rh3	S2	93.39(10)	O25	C58	O26	116.5(4)
N3	Rh3	O15	90.55(13)	N7	C58	O26	128.4(4)
N3	Rh3	O13	89.51(13)	N7	C58	O25	115.1(4)
N3	Rh3	O11	173.01(13)	O19	C50	O20	126.2(4)
O10	Rh4	Rh3	91.08(8)	C51	C50	O20	115.7(4)
O14	Rh4	Rh3	86.97(8)	C51	C50	O19	118.1(4)
O14	Rh4	O10	90.02(12)	C18	N2	Rh2	156.1(4)
O12	Rh4	Rh3	88.01(8)	O24	C54	O23	126.3(4)
O12	Rh4	O10	179.00(12)	C55	C54	O23	116.6(4)

O12	Rh4	O14	90.33(12)	C55	C54	O24	117.2(4)
O16	Rh4	Rh3	88.09(8)	C56	N6	Rh6	163.0(3)
O16	Rh4	O10	89.09(12)	O16	C35	O15	126.2(4)
O16	Rh4	O14	174.96(12)	C36	C35	O15	116.1(4)
O16	Rh4	O12	90.47(12)	C36	C35	O16	117.7(4)
N4	Rh4	Rh3	174.99(9)	C75	N8	Rh8	158.0(4)
N4	Rh4	O10	91.64(12)	O11	C31	O12	124.8(4)
N4	Rh4	O14	97.24(12)	C32	C31	O12	116.9(4)
N4	Rh4	O12	89.24(12)	C32	C31	O11	118.3(4)
N4	Rh4	O16	87.74(13)	C6	C11	C10	119.4(5)
S1	Rh1	Rh2	176.08(3)	C37	N4	Rh4	163.9(3)
O5	Rh1	Rh2	88.13(9)	O4	C12	O3	125.6(4)
O5	Rh1	S1	88.12(9)	C13	C12	O3	117.6(4)
O3	Rh1	Rh2	88.03(8)	C13	C12	O4	116.8(4)
O3	Rh1	S1	90.91(9)	O8	C16	O7	126.4(4)
O3	Rh1	O5	91.30(12)	C17	C16	O7	117.2(4)
O7	Rh1	Rh2	87.50(8)	C17	C16	O8	116.4(4)
O7	Rh1	S1	96.24(9)	O27	C69	O28	125.3(4)
O7	Rh1	O5	175.62(12)	C70	C69	O28	116.7(4)
O7	Rh1	O3	88.27(12)	C70	C69	O27	118.0(4)
N1	Rh1	Rh2	86.08(11)	O6	C14	O5	125.0(4)
N1	Rh1	S1	94.98(11)	C15	C14	O5	117.0(4)
N1	Rh1	O5	88.84(14)	C15	C14	O6	118.0(4)
N1	Rh1	O3	174.11(14)	O21	C52	O22	125.9(4)
N1	Rh1	O7	91.13(13)	C53	C52	O22	116.8(4)
S4	Rh7	Rh8	176.20(3)	C53	C52	O21	117.2(4)
O27	Rh7	Rh8	87.88(8)	C68	C67	C66	120.7(5)
O27	Rh7	S4	91.90(8)	O29	C71	O30	125.6(4)
O31	Rh7	Rh8	87.54(8)	C72	C71	O30	117.0(4)
O31	Rh7	S4	96.24(9)	C72	C71	O29	117.4(4)
O31	Rh7	O27	88.51(12)	C24	C23	C22	113.7(4)
O29	Rh7	Rh8	87.72(9)	O1	C1	O2	117.5(4)
O29	Rh7	S4	88.49(9)	N1	C1	O2	128.3(4)
O29	Rh7	O27	90.50(12)	N1	C1	O1	114.2(4)
O29	Rh7	O31	175.20(12)	C62	C61	C60	112.3(4)
N7	Rh7	Rh8	85.51(10)	C57	C56	N6	179.5(5)
N7	Rh7	S4	94.72(11)	O32	C73	O31	126.7(4)
N7	Rh7	O27	173.38(13)	C74	C73	O31	117.1(4)
N7	Rh7	O31	90.75(13)	C74	C73	O32	116.1(4)
N7	Rh7	O29	89.69(14)	C5	C4	C3	112.2(4)
O28	Rh8	Rh7	87.16(8)	C23	C22	N3	114.7(3)
O26	Rh8	Rh7	90.91(9)	C21	C22	N3	101.1(3)
O26	Rh8	O28	176.89(13)	C21	C22	C23	113.9(4)
O32	Rh8	Rh7	87.90(8)	C22	C21	O9	104.7(3)
O32	Rh8	O28	89.10(12)	C8	C9	C10	119.8(5)

O32	Rh8	O26	88.38(12)	C29	C30	C25	121.0(4)
O30	Rh8	Rh7	87.55(8)	C30	C25	S2	117.7(4)
O30	Rh8	O28	90.45(12)	C26	C25	S2	123.6(4)
O30	Rh8	O26	91.91(13)	C26	C25	C30	118.6(4)
O30	Rh8	O32	175.44(12)	C42	C43	S3	111.9(3)
N8	Rh8	Rh7	171.90(10)	C3	C2	O1	104.6(4)
N8	Rh8	O28	88.76(13)	C9	C10	C11	120.7(5)
N8	Rh8	O26	93.45(13)	C48	C47	C46	119.0(5)
N8	Rh8	O32	99.04(14)	C46	C45	C44	118.4(4)
N8	Rh8	O30	85.49(14)	C41	C42	C43	113.4(4)
O20	Rh6	Rh5	88.04(8)	C48	C49	C44	119.1(5)
O18	Rh6	Rh5	91.11(9)	C61	C60	N7	113.5(4)
O18	Rh6	O20	179.12(12)	C59	C60	N7	101.1(4)
O22	Rh6	Rh5	87.11(9)	C59	C60	C61	115.1(4)
O22	Rh6	O20	89.80(12)	C45	C44	S3	115.9(3)
O22	Rh6	O18	90.40(12)	C49	C44	S3	123.0(4)
O24	Rh6	Rh5	87.73(9)	C49	C44	C45	121.1(5)
O24	Rh6	O20	90.92(12)	C68	C63	S4	125.0(4)
O24	Rh6	O18	88.80(12)	C64	C63	S4	115.9(4)
O24	Rh6	O22	174.77(12)	C64	C63	C68	119.0(4)
N6	Rh6	Rh5	175.00(9)	C42	C41	N5	114.4(4)
N6	Rh6	O20	88.76(12)	C40	C41	N5	101.3(4)
N6	Rh6	O18	92.07(12)	C40	C41	C42	113.5(4)
N6	Rh6	O22	96.72(13)	C45	C46	C47	121.0(4)
N6	Rh6	O24	88.48(13)	C11	C6	S1	124.1(4)
C43	S3	Rh5	109.36(15)	C7	C6	S1	115.9(4)
C44	S3	Rh5	113.44(15)	C7	C6	C11	119.8(4)
C44	S3	C43	102.2(2)	C65	C66	C67	118.8(5)
C25	S2	Rh3	112.55(15)	C41	C40	O17	104.5(3)
C24	S2	Rh3	109.02(14)	C27	C26	C25	120.5(5)
C24	S2	C25	103.4(2)	C19	C18	N2	177.3(5)
C63	S4	Rh7	109.32(14)	C63	C68	C67	120.8(5)
C62	S4	Rh7	107.20(16)	C60	C59	O25	105.9(4)
C62	S4	C63	105.4(2)	C7	C8	C9	119.9(5)
C6	S1	Rh1	109.54(16)	C38	C37	N4	179.9(5)
C5	S1	Rh1	107.37(16)	C49	C48	C47	121.4(5)
C5	S1	C6	105.0(2)	C61	C62	S4	115.6(3)
C50	O20	Rh6	120.0(3)	C64	C65	C66	120.6(5)
C69	O28	Rh8	121.2(3)	C76	C75	N8	176.6(5)
C39	O18	Rh6	113.7(3)	C27	C28	C29	119.2(5)
C14	O5	Rh1	119.1(3)	C8	C7	C6	120.4(5)
C20	O10	Rh4	113.5(3)	C23	C24	S2	112.3(3)
C33	O14	Rh4	120.2(3)	C65	C64	C63	120.1(4)
C35	O15	Rh3	119.2(3)	C4	C3	N1	113.1(4)
C31	O12	Rh4	120.9(3)	C2	C3	N1	101.5(4)

C69	O27	Rh7	118.1(3)	C2	C3	C4	115.0(4)
C35	O16	Rh4	119.1(3)	C28	C29	C30	120.3(5)
C50	O19	Rh5	118.6(3)	C28	C27	C26	120.4(5)
C33	O13	Rh3	118.1(3)	C4	C5	S1	115.1(3)

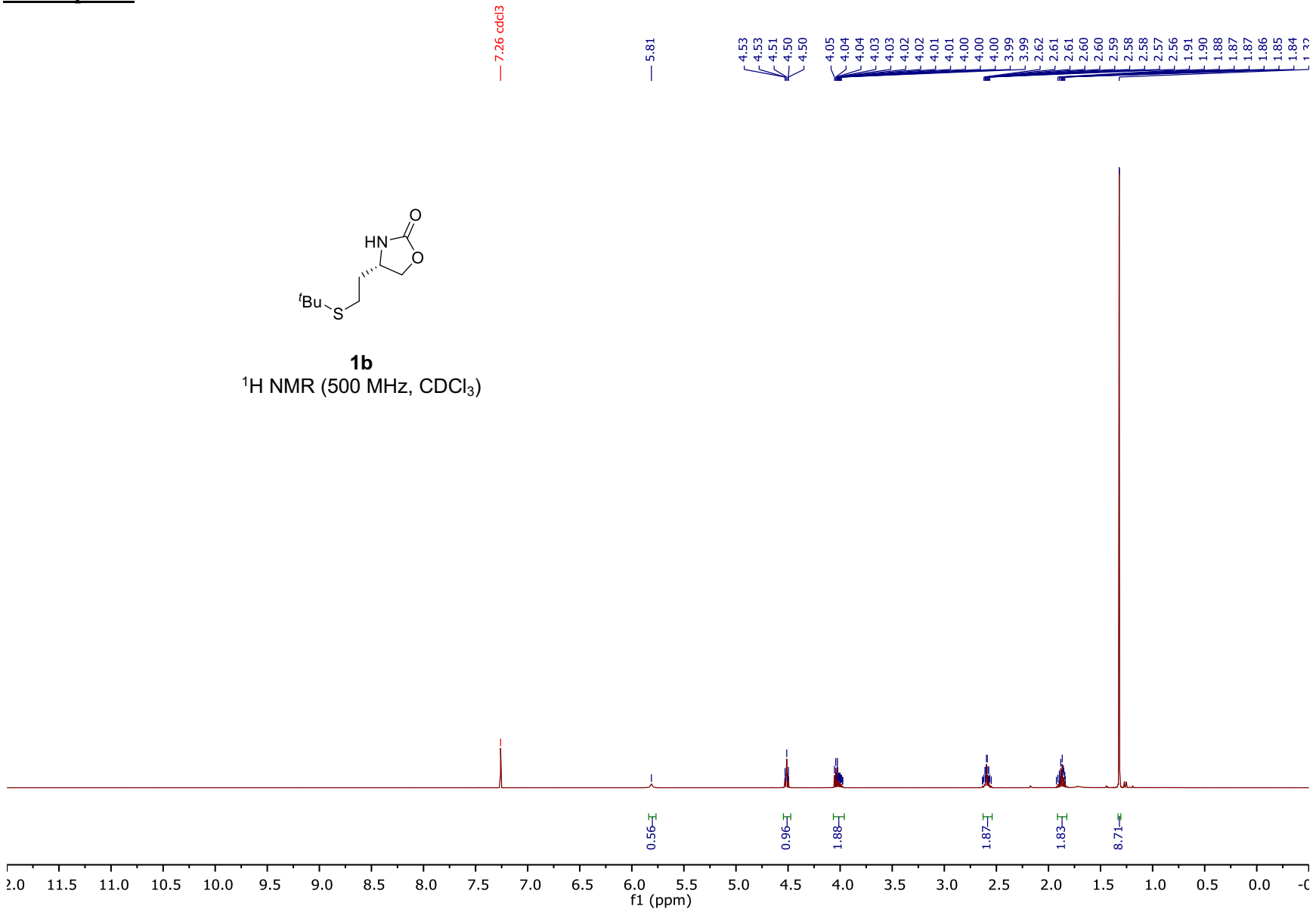
Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for MonoAspPhTOX.

Atom	*x*	*y*	*z*	U(eq)
H01d	942(11)	7281(9)	11979(15)	34.9(13)
H01e	1890(30)	7048(4)	12684(4)	34.9(13)
H01f	2340(20)	7449(5)	11992(15)	34.9(13)
H01P	7890(5)	6567.5(17)	9513(3)	33.8(13)
H01g	3200(30)	7159(3)	7608(4)	35.5(14)
H01h	4154(11)	7362(7)	6885(17)	35.5(14)
H01i	2740(20)	7501(5)	6806(16)	35.5(14)
H01j	6031(12)	2670(9)	-4452(16)	38.4(15)
H01k	6960(30)	2905(4)	-5163(3)	38.4(15)
H01l	7440(20)	2511(5)	-4465(16)	38.4(15)
H01a	8170(30)	2873(3)	-124(3)	36.0(14)
H01b	9109(11)	2649(8)	592(17)	36.0(14)
H01c	7690(20)	2518(5)	648(16)	36.0(14)
H01Z	14413(5)	3325.9(16)	-3177(4)	34.9(13)
H02	410(30)	5123(8)	7135(5)	37.4(15)
H	1453(5)	5267(11)	7854(13)	37.4(15)
Ha	300(20)	5608(4)	7695(16)	37.4(15)
H02a	13031(4)	4567(12)	590(13)	48.8(17)
H02b	13247(6)	4588(11)	1667(14)	48.8(17)
H02c	13232(7)	4086.9(18)	1150(30)	48.8(17)
H0aa	651(5)	6003.3(16)	2904(3)	31.9(12)
Hb	-437(5)	5638.1(16)	2707(3)	31.9(12)
H4aa	11185(4)	4157.1(18)	-1676(3)	32.6(12)
Hc	11517(4)	4217.6(18)	-621(3)	32.6(12)
H02p	6177(4)	5859.8(18)	9157(3)	33.4(12)
H02q	6473(4)	5818.5(18)	8093(3)	33.4(12)
H029	-3(4)	5312.4(15)	4235(3)	23.2(10)
H1aa	1454(4)	5133.5(15)	2670(3)	26.7(11)
Hd	670(4)	4758.7(15)	3255(3)	26.7(11)
H02t	8847(5)	7009.3(16)	12036(3)	35.5(13)
H2aa	77(4)	7024.8(16)	6045(3)	30.1(12)
H02d	3593(4)	4053.5(16)	3458(3)	31.2(12)
H02e	3601(4)	3697.6(16)	4307(3)	31.2(12)
H5aa	10040(30)	4771(7)	-4591(9)	45.9(16)
He	10370(20)	4256(6)	-4983(18)	45.9(16)
Hf	9166(9)	4528(12)	-5329(10)	45.9(16)

H02u	5333(4)	5060.6(18)	8409(3)	36.0(13)
H02v	4547(4)	5163.5(18)	7502(3)	36.0(13)
H02w	4940(30)	5195(6)	12142(10)	42.9(16)
H02x	5364(19)	5711(7)	12467(17)	42.9(16)
H02y	4143(11)	5481(12)	12874(8)	42.9(16)
H02z	9375(4)	6682.3(17)	10641(4)	36.6(13)
H02J	1466(4)	2846.4(16)	639(4)	33.4(12)
H02f	5340(20)	4842(9)	353(4)	42.2(16)
H02g	6467(4)	4745(11)	-316(14)	42.2(16)
H02h	5380(30)	4366(3)	-242(15)	42.2(16)
H02L	5005(4)	3003.8(15)	1451(3)	26.6(11)
H02i	4599(5)	4345.8(16)	4847(3)	33.0(12)
H02k	5681(5)	3982.0(16)	4625(3)	33.0(12)
H02N	2247(4)	3475.5(17)	3044(3)	33.4(13)
H6aa	9314(4)	4060.9(16)	-350(3)	29.9(12)
H02R	4987(4)	4678.7(16)	3309(3)	26.9(11)
H02S	3554(5)	2753.8(16)	368(3)	31.2(12)
H7aa	13863(5)	2959.5(16)	-4545(3)	35.2(13)
H02m	6464(4)	4853.7(16)	4870(3)	32.2(12)
H02o	5662(4)	5229.1(16)	4296(3)	32.2(12)
H3aa	-2747(4)	6515.4(16)	4549(3)	30.8(12)
H8aa	2510(5)	4562(14)	-4297(13)	60(2)
Hg	2298(8)	4094(2)	-3700(30)	60(2)
Hh	2247(7)	4605(13)	-3230(16)	60(2)
H9aa	5850(30)	3373(9)	-143(5)	47.5(17)
Hi	4787(5)	3268(12)	-866(14)	47.5(17)
Hj	5850(30)	2887(3)	-707(17)	47.5(17)
H03a	9280(20)	3365(10)	4851(3)	48.9(17)
H03b	9480(30)	2917(2)	4198(16)	48.9(17)
H03c	10470(7)	3334(11)	4221(16)	48.9(17)
H031	12964(4)	3457.4(16)	-2058(3)	30.3(12)
H03x	10302(5)	4939.5(17)	-899(3)	35.3(13)
H03y	9511(5)	4823.9(17)	-4(3)	35.3(13)
H033	6797(5)	7205.1(17)	12336(4)	36.4(13)
H035	830(5)	3224.7(17)	1948(4)	36.7(13)
H03z	10632(4)	3437.0(18)	-383(3)	38.1(14)
Hk	11914(4)	3446.4(18)	-900(3)	38.1(14)
H037	11834(5)	2711.5(17)	-4759(4)	36.6(13)
H039	-3406(5)	7229.5(17)	6892(4)	34.6(12)
H03d	930(20)	7022(5)	8052(17)	46.6(17)
H03e	700(30)	6507(7)	7626(8)	46.6(17)
H03f	-242(7)	6718(12)	8352(10)	46.6(17)
H03g	5308(5)	7088.8(16)	11222(3)	32.6(12)
H03n	-1395(4)	5939.0(16)	4099(3)	31.4(12)
H03o	-1416(4)	6288.0(16)	3239(3)	31.4(12)

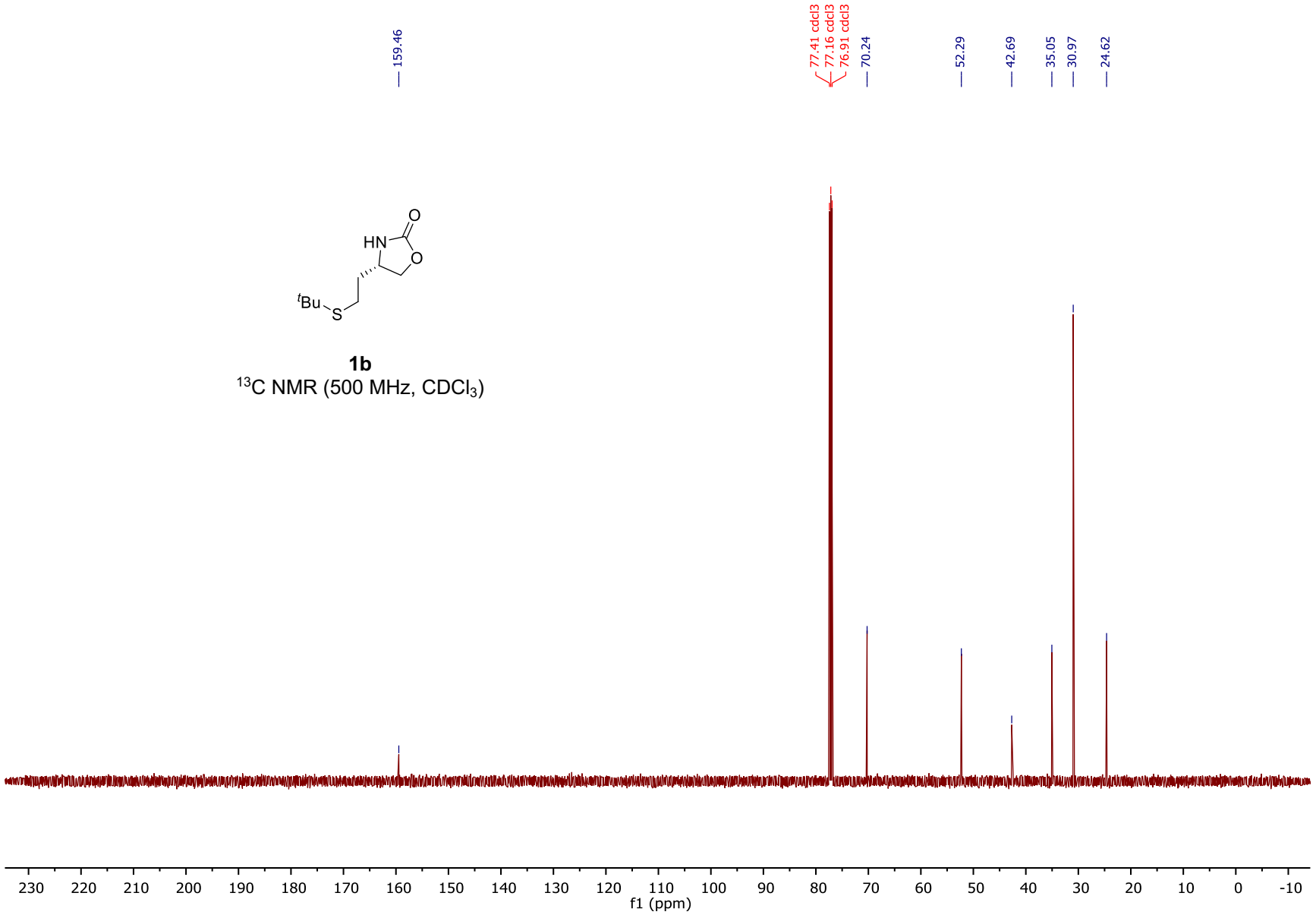
H03	10371(4)	2840.6(17)	-3628(4)	34.3(13)
H03p	8244(7)	5423(13)	5817(11)	54.1(19)
H03q	8241(7)	5883(2)	6460(30)	54.1(19)
H03r	8022(5)	5369(11)	6888(16)	54.1(19)
H03h	4235(4)	5926.4(17)	7857(3)	31.1(12)
H03s	-1297(5)	7326.9(17)	7105(3)	35.0(13)
H03t	4340(30)	6600(9)	2684(3)	45.9(16)
H03u	4440(30)	7068(2)	3293(16)	45.9(16)
H03v	5494(5)	6674(11)	3338(15)	45.9(16)
H03w	-4122(5)	6811.1(17)	5618(4)	39.7(14)
H03i	-2836(5)	5573(15)	10666(4)	58(2)
H03j	-2568(8)	5302(8)	11600(20)	58(2)
H03k	-2599(8)	5869(7)	11580(20)	58(2)
H03l	5461(5)	6583.9(19)	7912(3)	44.2(16)
H03m	6774(5)	6594.4(19)	8392(3)	44.2(16)

NMR Spectra



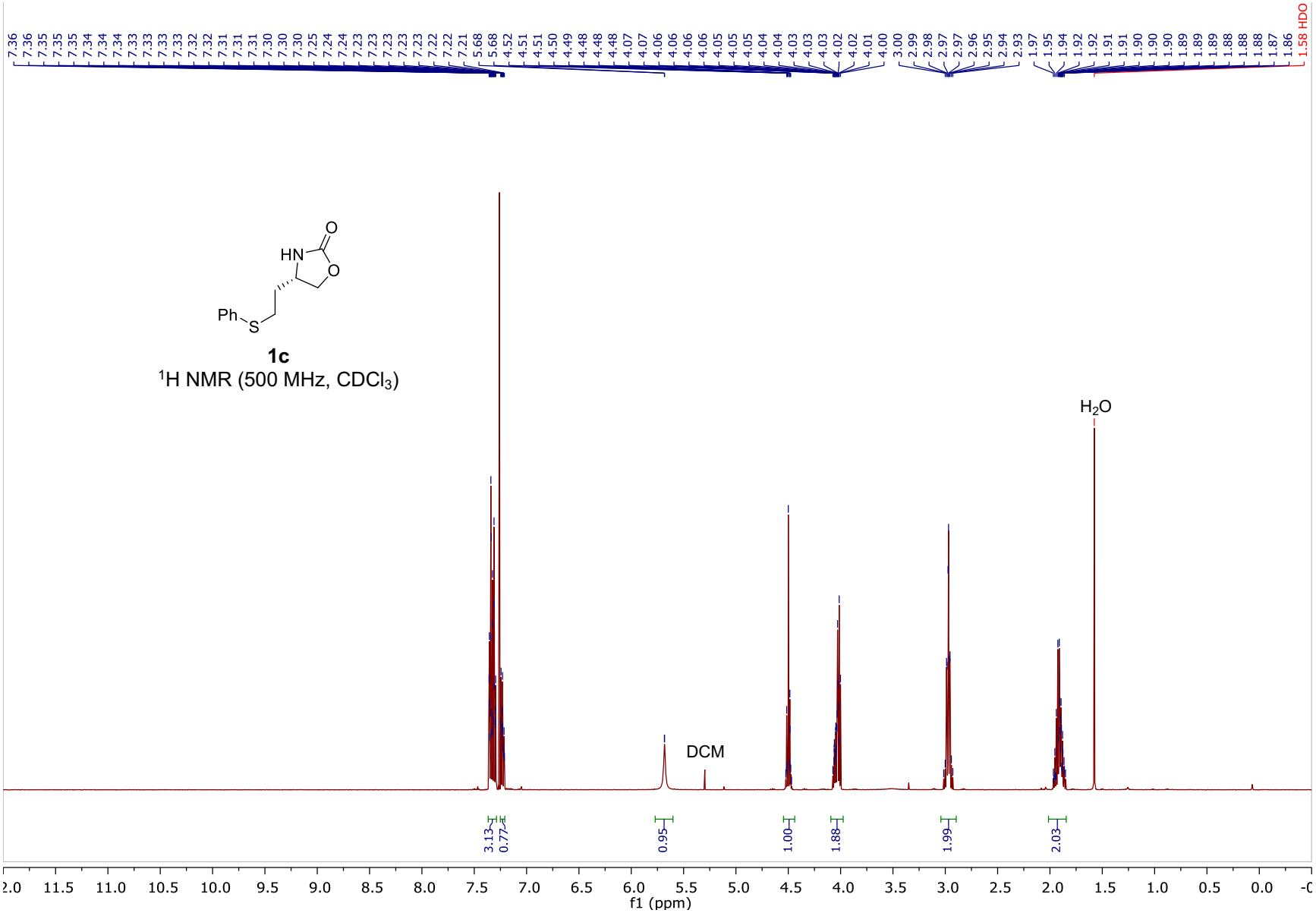
1b

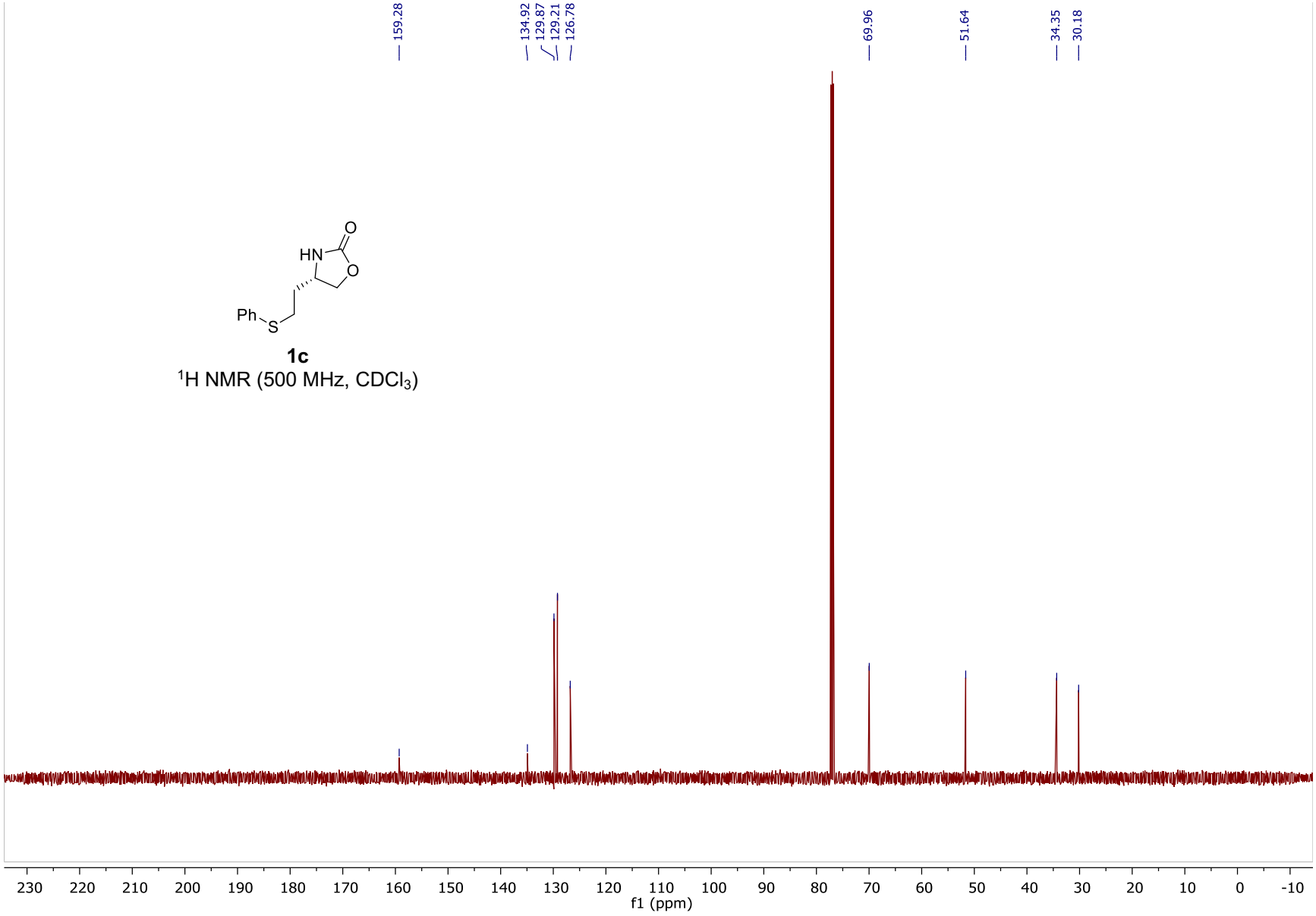
^{1}H NMR (500 MHz, $CDCl_3$)

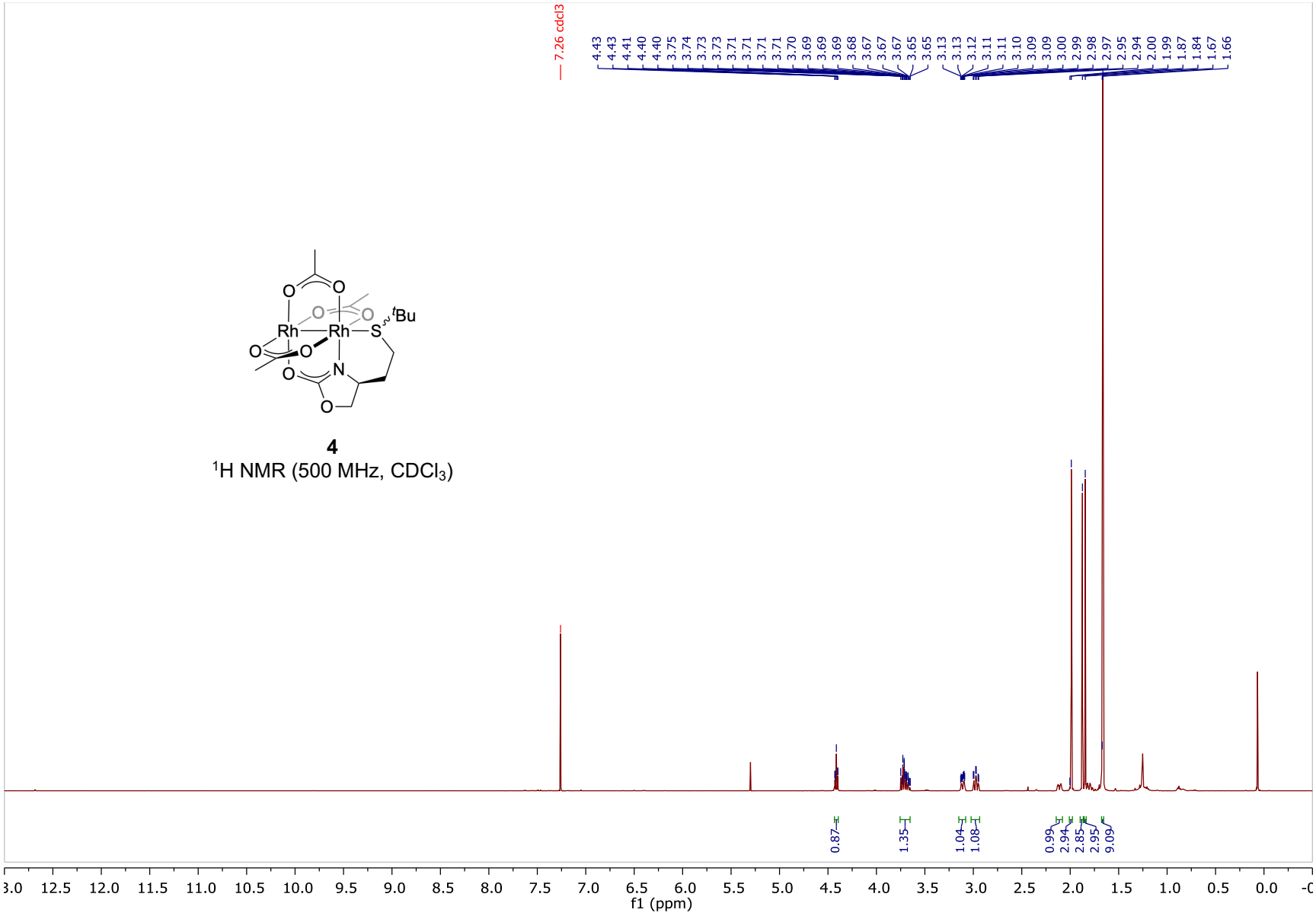


1b

^{13}C NMR (500 MHz, $CDCl_3$)

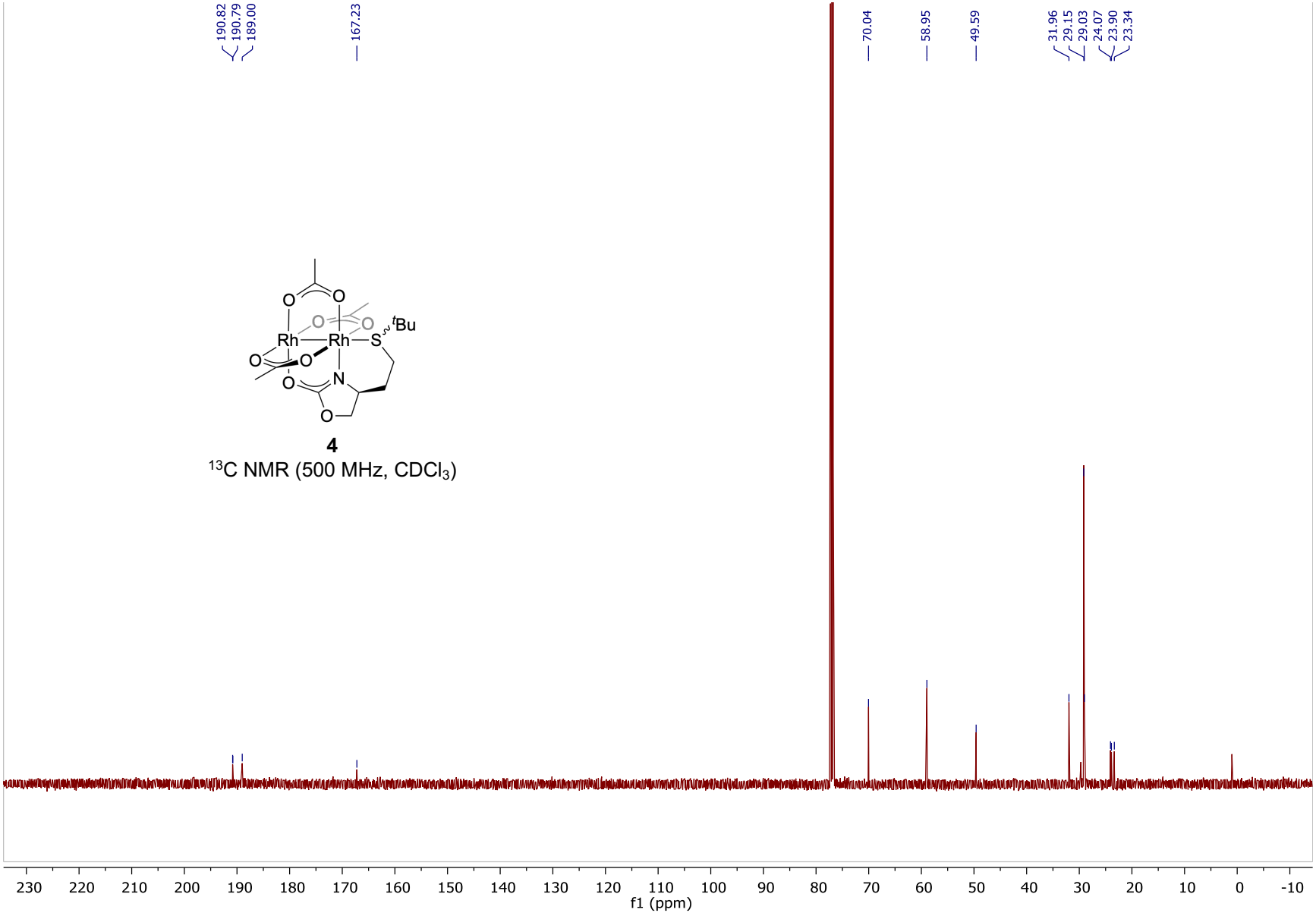

7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.25 7.24 7.24 7.23 7.23 7.23 7.23 7.23 7.22 7.22 7.21 5.68 5.68 4.52 4.51 4.51 4.50 4.49 4.48 4.48 4.48 4.07 4.07 4.06 4.06 4.06 4.06 4.05 4.05 4.05 4.04 4.04 4.03 4.03 4.03 4.02 4.02 4.01 4.00 3.00 2.99 2.98 2.97 2.97 2.96 2.95 2.94 2.93 1.97 1.95 1.94 1.92 1.92 1.91 1.91 1.90 1.90 1.90 1.89 1.89 1.89 1.88 1.88 1.88 1.87 1.86 1.58 HDO
HN
O
O
O
Ph
S
1c
1H NMR (500 MHz, CDCl3)
H2O
DCM
3.13
0.77
0.95
1.00
1.88
1.99
2.03
f1 (ppm)


159.28
134.92
129.87
129.21
126.78
69.96
51.64
34.35
30.18
HN
O
O
Ph
S
1c
1H NMR (500 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



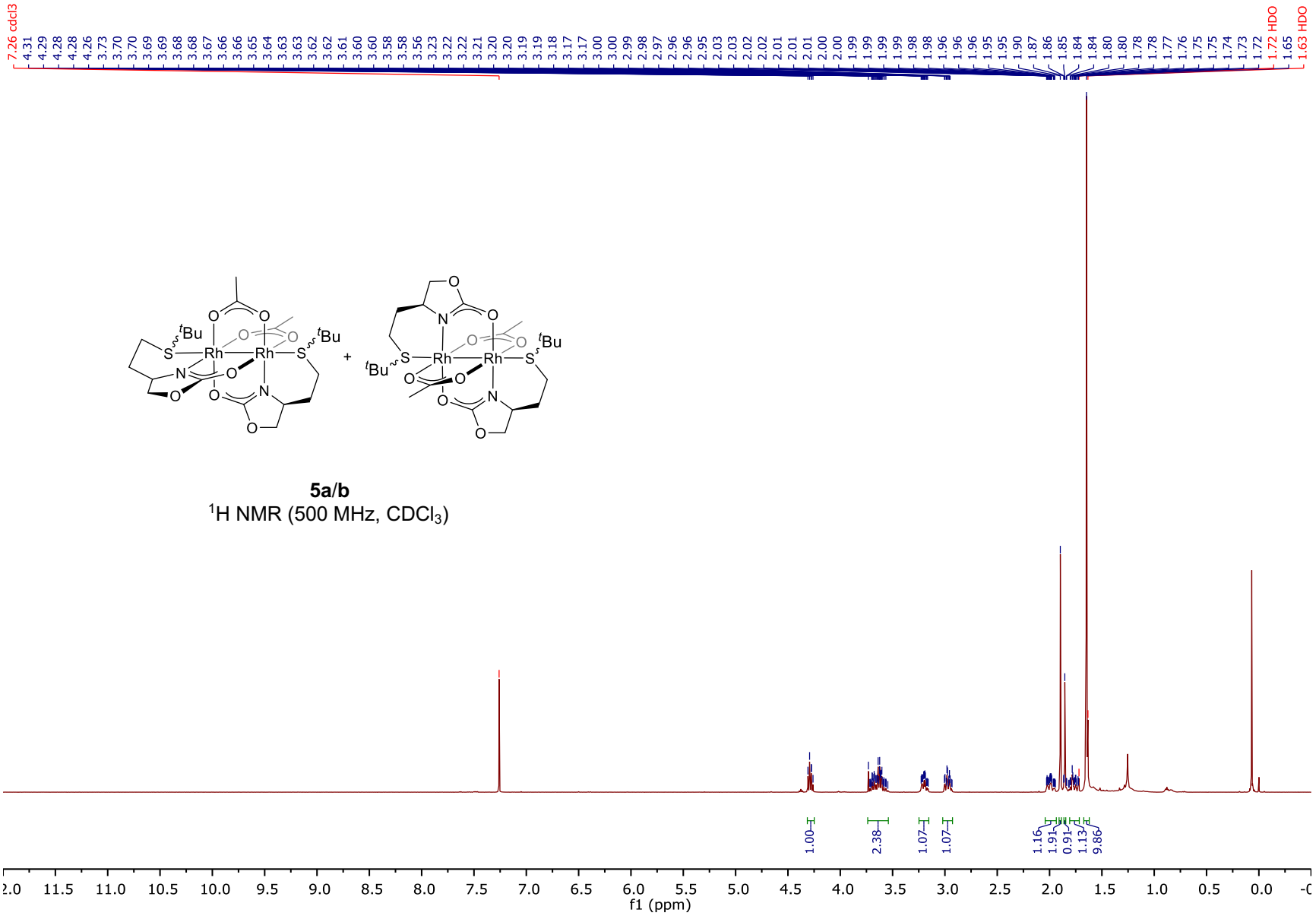
4

^{1}H NMR (500 MHz, $CDCl_3$)



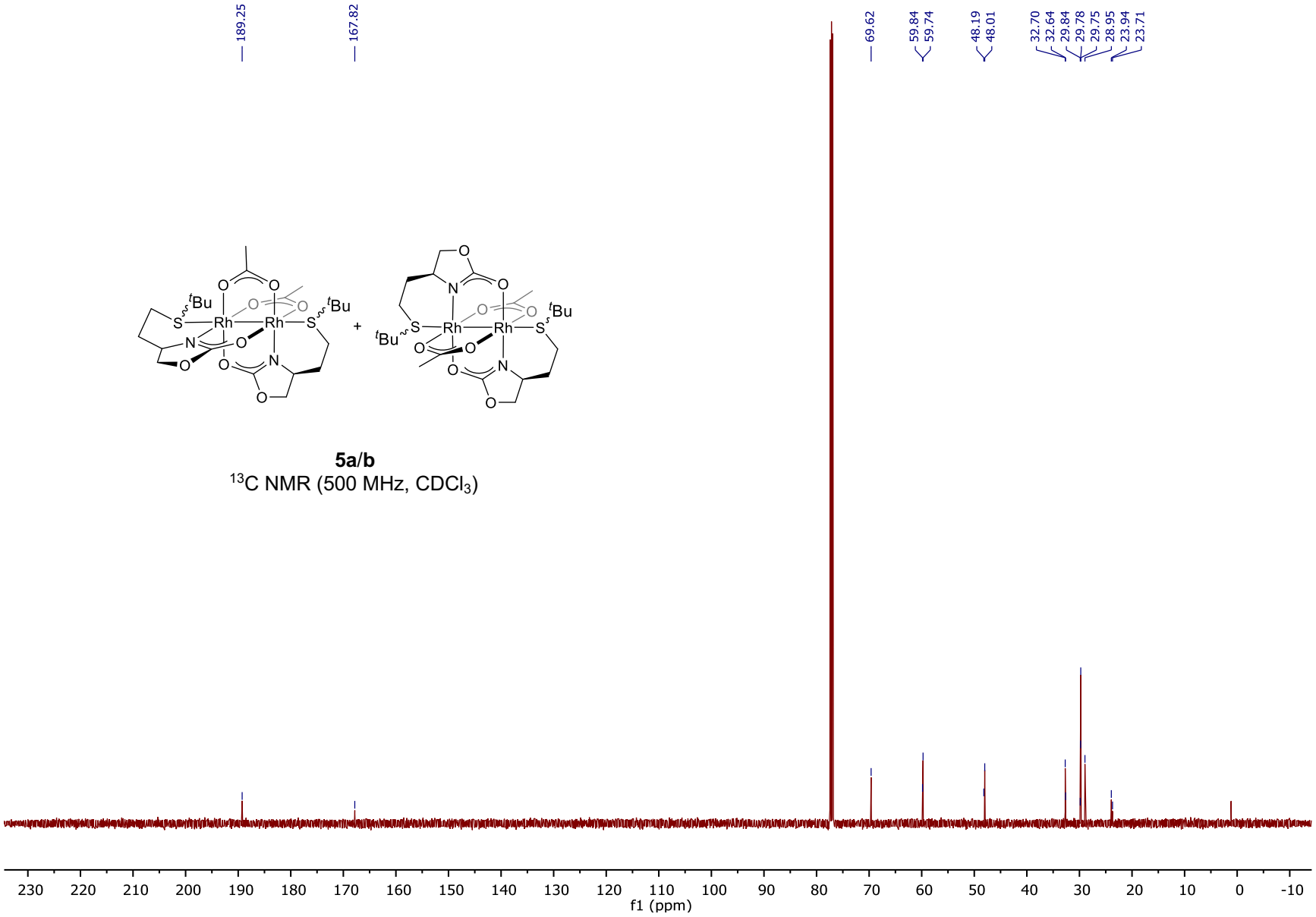
4

^{13}C NMR (500 MHz, $CDCl_3$)



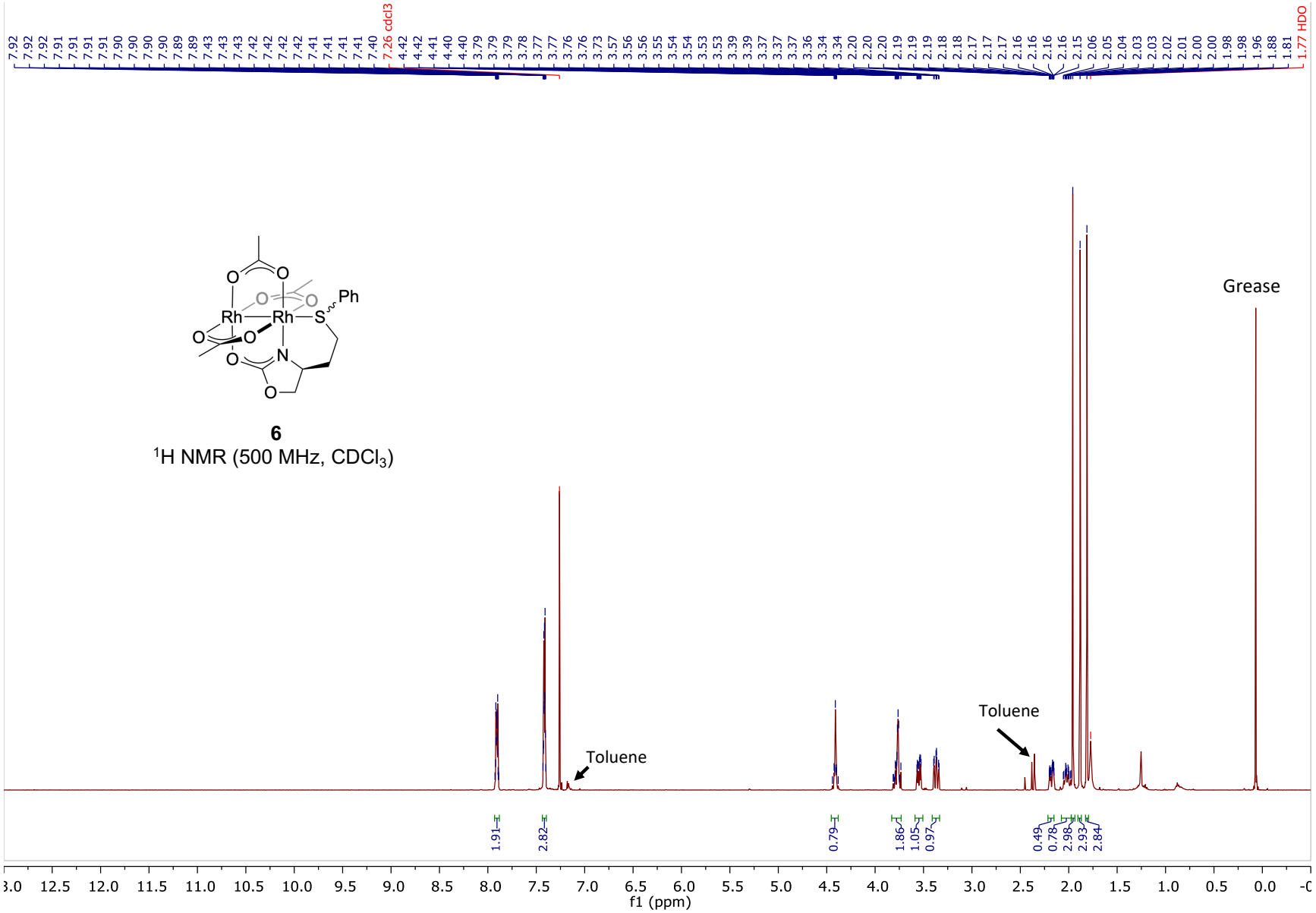
5a/b

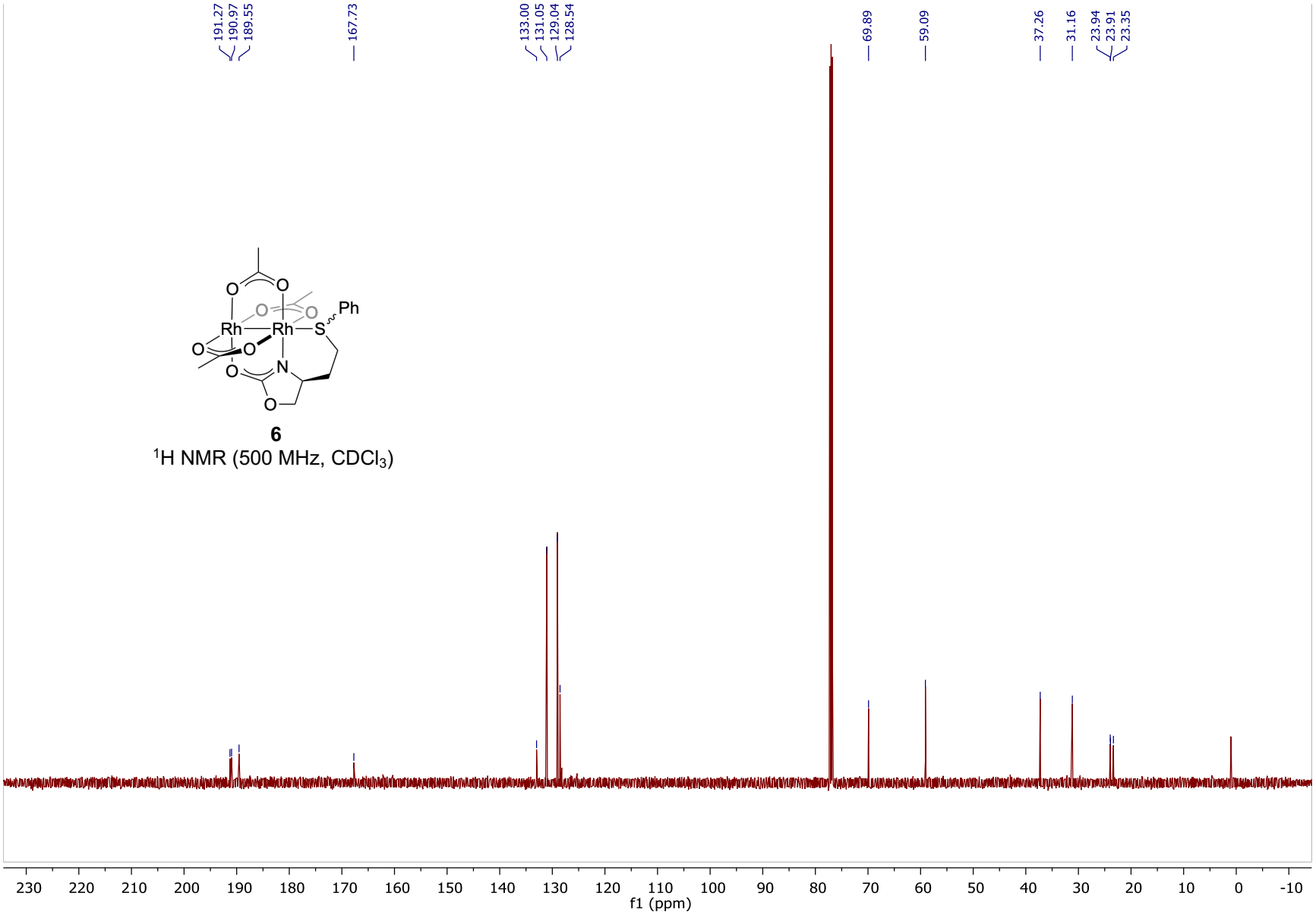
^{1}H NMR (500 MHz, $CDCl_3$)



5a/b

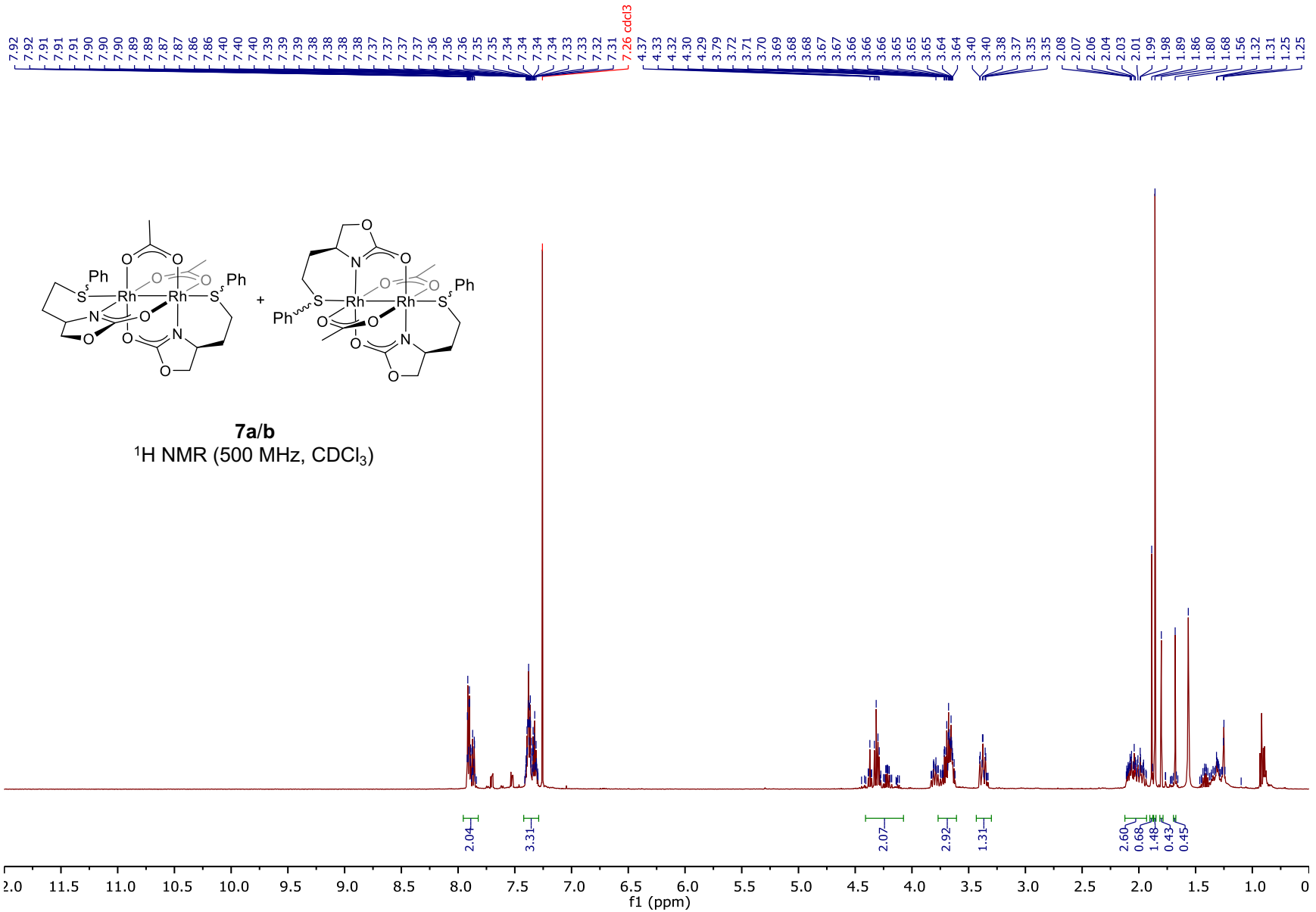
^{13}C NMR (500 MHz, $CDCl_3$)


Ph
Rh
Rh
S
N
O
6
^{1}H NMR (500 MHz, $CDCl_3$)
Grease
Toluene
Toluene
f1 (ppm)



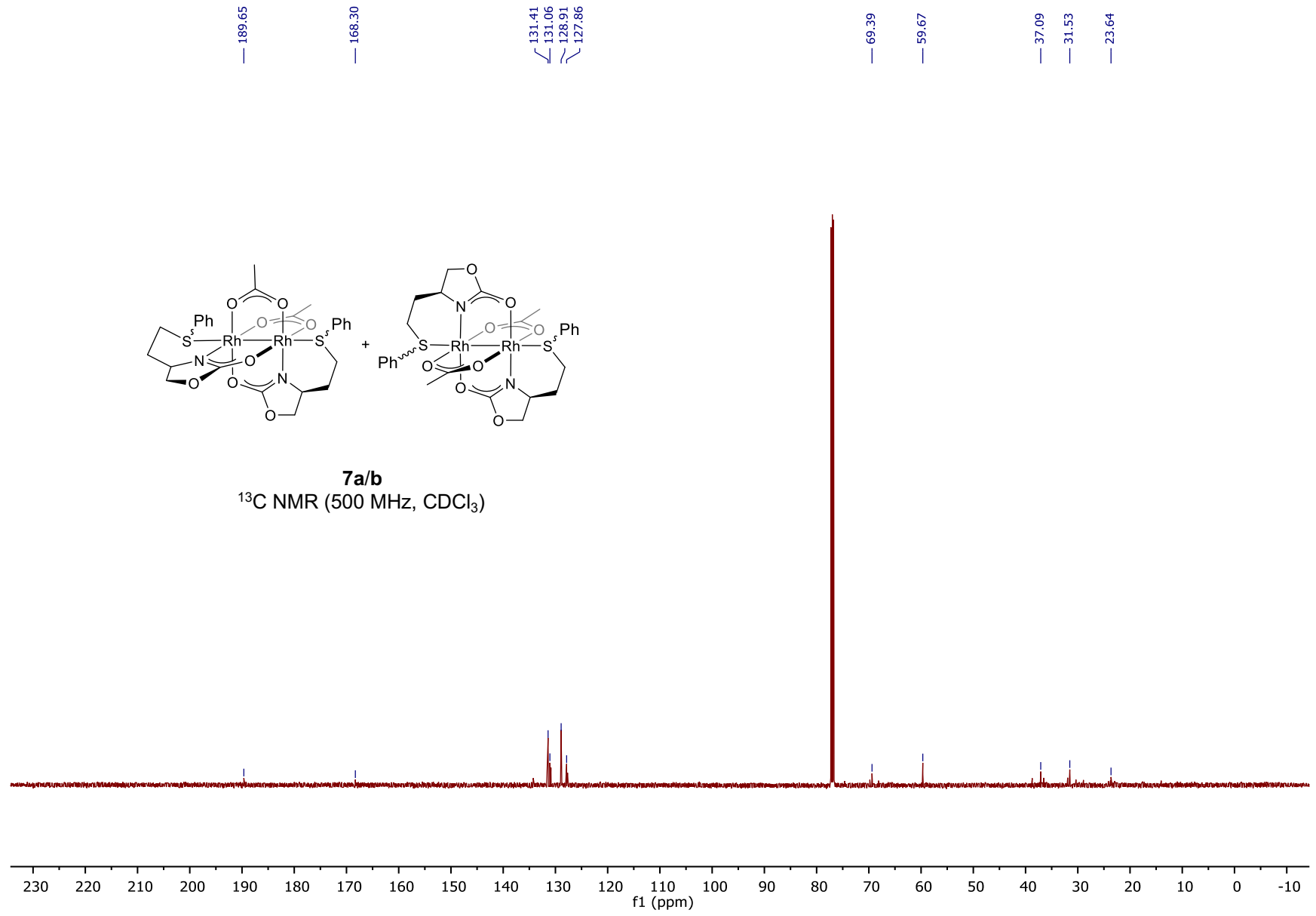
6

^{1}H NMR (500 MHz, $CDCl_3$)



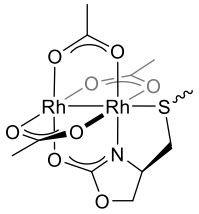
7a/b

^{1}H NMR (500 MHz, $CDCl_3$)



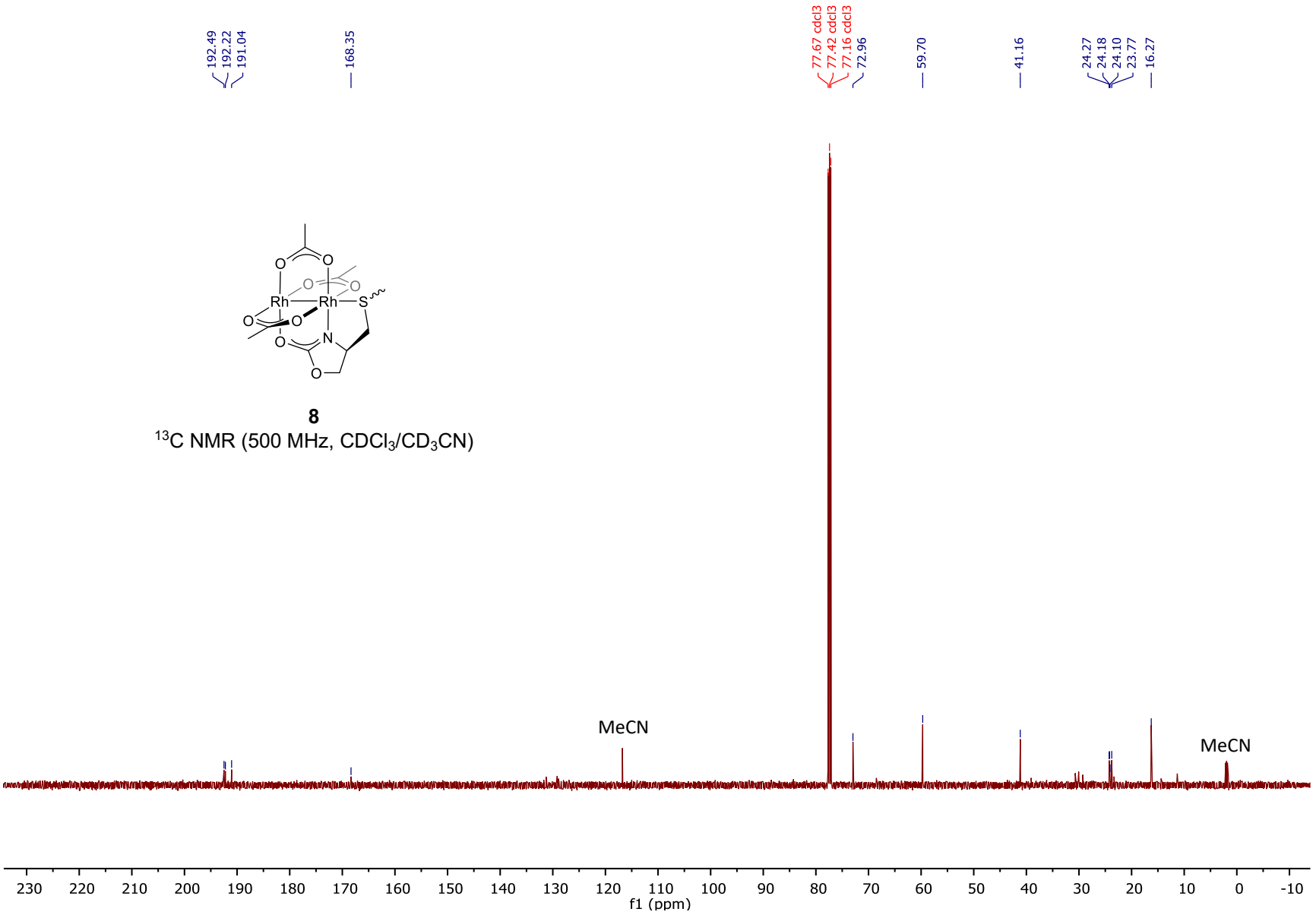
7a/b

^{13}C NMR (500 MHz, $CDCl_3$)



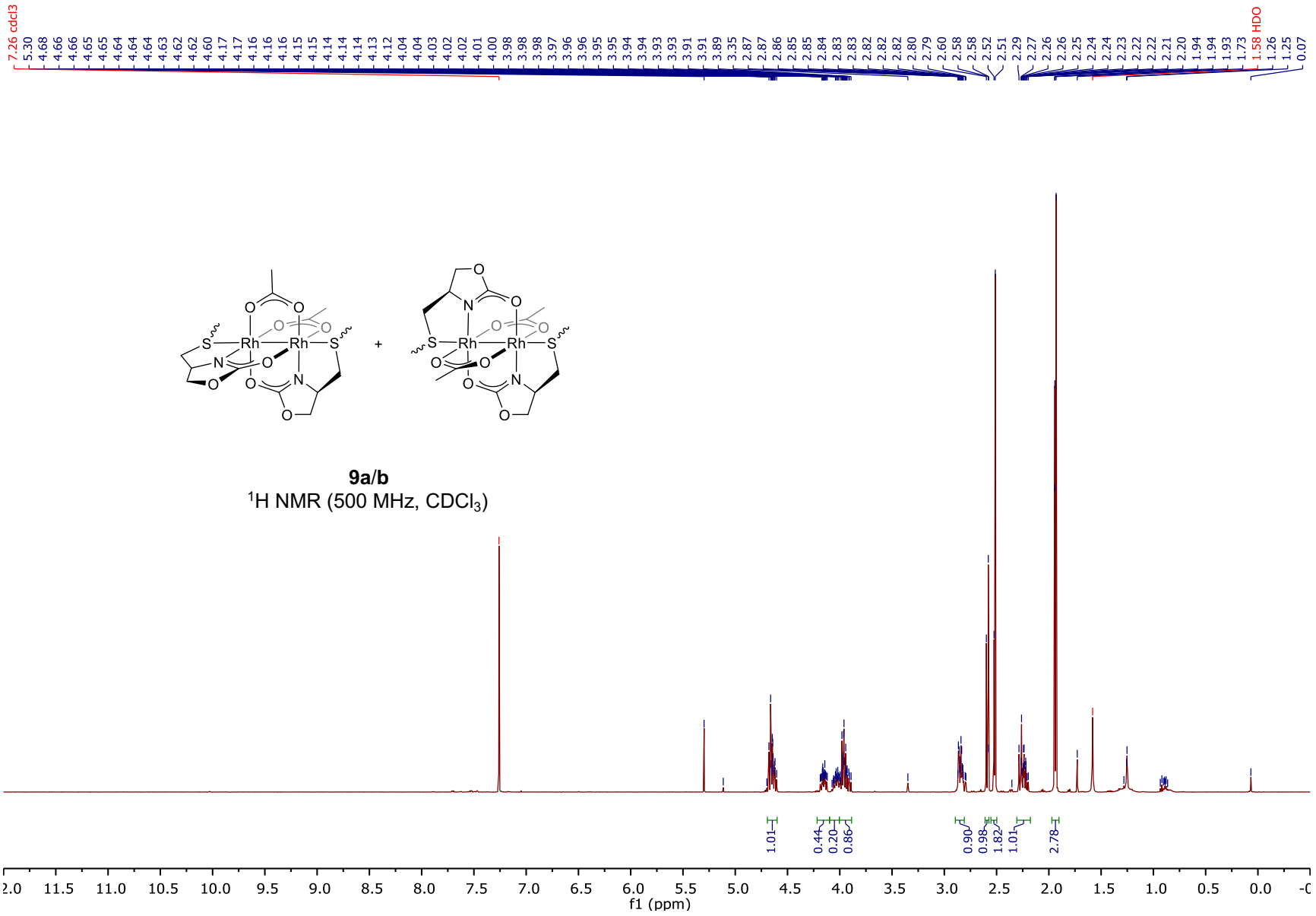
8

^{1}H NMR (500 MHz, $CDCl_3/CD_3CN$)



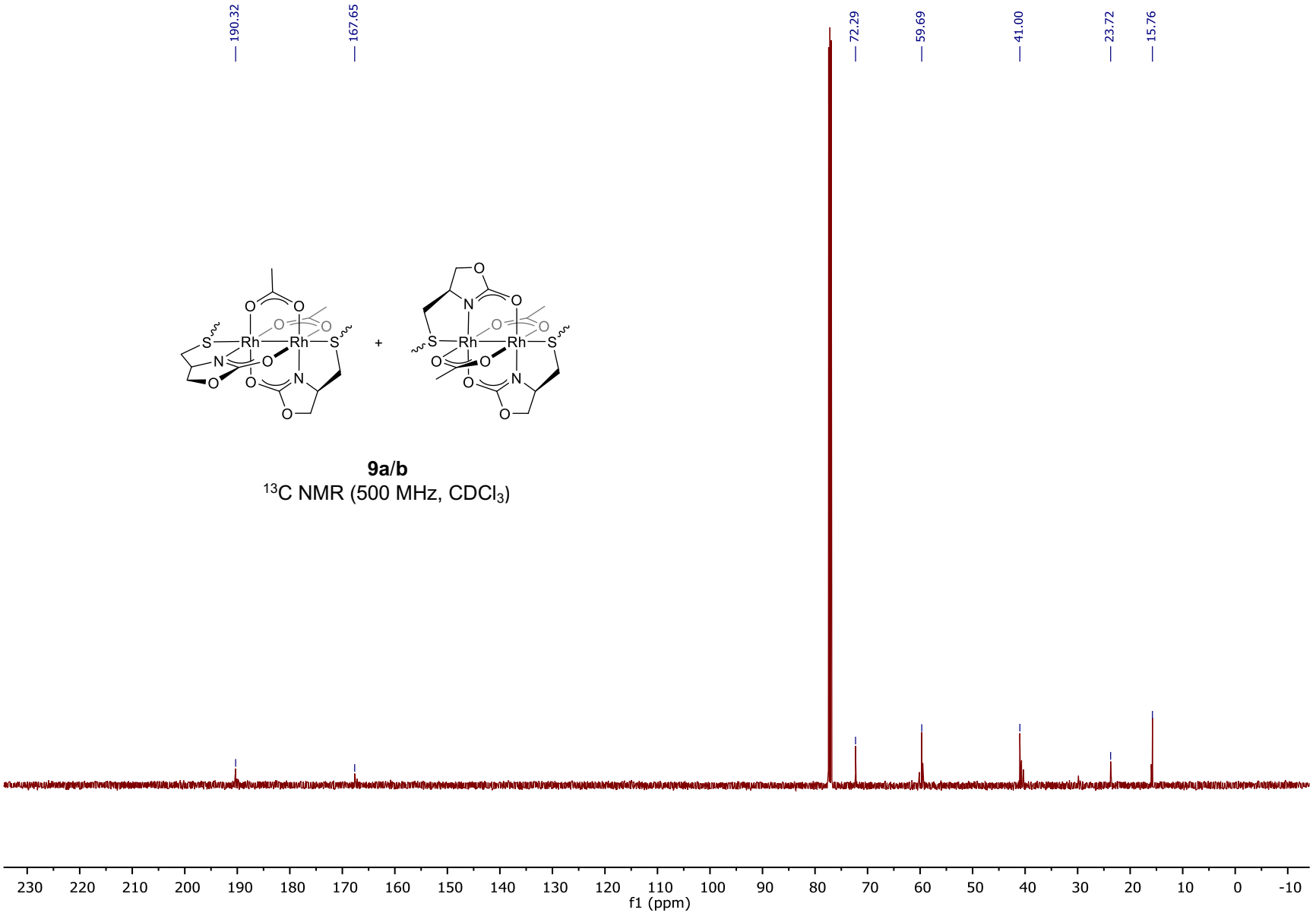
8

^{13}C NMR (500 MHz, $CDCl_3/CD_3CN$)



9a/b

^{1}H NMR (500 MHz, $CDCl_3$)



9a/b

^{13}C NMR (500 MHz, $CDCl_3$)

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