Supplementary Information

(Tables S1 – S10 and Figures S1 – S10)

For

Catalytic C–H amination driven by intramolecular ligand-to-nitrene one-electron transfer through a rhodium(III) centre

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General. Reagents and solvents used in this study except for the ligand and complexes were commercial products of the highest available purity and further purified by standard methods, if necessary. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECP 400 or a JEOL ECS 400 spectrometer. EPR spectra were taken on a BLUKER X−band spectrometer under non-saturating microwave power conditions operating at 9.4 GHz. Cyclic voltammetry measurements were performed in CH_2Cl_2 (1.0 mM) containing $(n\text{−Bu})_4NPF_6$ (0.1 M) at room temperature using a glassy carbon electrode. All redox potentials are referenced to Fc/Fc^+ redox potential. The ligand LH_3, $[Rh^ICl(cod)]_2$, and xanthene-d_2 were synthesized by following the literature methods.[1, 2, 3]

X-ray Structure Determination. Each single crystal was mounted on a loop. Data from X-ray diffraction were collected at −170 °C by a VariMax with RAPID imaging plate two-dimensional area detector using graphite –monochromated Mo Kα radiation($\lambda = 0.71069$ Å) to $2\theta_{max}$ of 55°. All of the crystallographic calculations were performed using the Crystal Structure software package of Molecular Structure Corp. [Crystal Structure, Crystal Structure Analysis Package, version 3.8.1, Molecular Structure Corp. and Rigaku Corp.(2005)]. Structures were solved by a direct method (SIR 2008) and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically by full-matrix least-squres on F^2. Hydrogen atoms were attached at idealized positions on carbon atoms and not refined. CCDC-1535694, 1535696, and 1535697 contain the supplementary crystallographic data for $[Rh^I(LH_2^-)(cod)]$, $\mathbf{1^H}$, and $\mathbf{[1^H]SbF_6}$.

Synthesis. *$[Rh^I(LH_2^-)(cod)]$*. LH_3 (200 mg, 0.382 mmol) and $[Rh^I(cod)Cl]_2$ (94.2 mg, 0.191 mmol) were dissolved in THF (4 ml). One equivalent of triethylamine (53.2 µl, 0.382 mmol) was added to the solution and the resultant solution was stirred for 2 h at room temperature. Slow diffusion of methanol to the solution produced yellow crystals of $[Rh^I(LH_2^-)(cod)]$ (267 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): (isomer A) δ 8.86 (s, 2H), 7.17 (d, 2H, J = 1.6 Hz), 6.77 (d, 2H, J = 2.0 Hz), 5.76 (s, 2H), 4.04 (t, 2H, J = 6.8 Hz), 3.58 (s, 2H), 3.18 (q, 2H, J = 6.8 Hz), 2.61−2.48 (m, 2H), 2.10−2.00 (m, 2H), 1.98−1.82 (m, 2H), 1.44 (s, 18H), 1.32 (s, 18H); (isomer B) δ 8.79 (s, 2H), 7.17 (d, 2H, J = 1.6 Hz), 6.87 (d, 2H, J = 2.0 Hz), 5.98 (s, 2H), 3.49 (s, 4H), 2.27 (s, 4H), 1.81−1.71 (m, 4H), 1.44 (s, 18H), 1.32 (s, 18H). ^{13}C NMR ($CDCl_3$, 400 MHz): 158.35, 158.23, 144.25, 144.17, 142.85, 142.56, 139.56, 139.45, 136.12, 136.08, 122.11, 122.09, 121.95, 118.82, 87.62, 87.50, 84.93, 84.80, 80.87, 80.74, 58.67, 53.58, 35.28, 35.25, 34.61, 33.17, 31.70, 30.15, 29.50, 27.45, 18.60. Anal. Calcd for $[Rh^I(LH_2^-)(cod)]\cdot THF\cdot CH_3OH$ ($C_{44}H_{68}RhN_3O_6$): C, 63.07; H, 8.18; N, 5.01; Found: C, 63.21; H, 8.50; N, 5.04. MS (FAB^+): m/z = 734 ($[M]^+$) .

$[Rh^{III}L^{3-}(PhNH_2)_2]$ ($\mathbf{1^H}$). $Rh^{I}(LH_2^-)(cod)$ (36.7 mg, 50.0 μmol) was dissolved in THF (3 ml) and stirred at room temperature for 10 min. Triethylamine (14μl, 100μmol) and then aniline (9.2 μl, 100 μmol) were added to the solution. The reaction mixture was stirred at room temperature for 3 h under air. Precipitated material was removed by filtration and the filtrate was evaporated in vacuo. The residue was dissolved in dichloromethane (CH_2Cl_2). Slow diffusion of ethanol into the CH_2Cl_2 solution gave orange needle crystals (28.3 mg, 70 %). ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.84 (d, J = 2.0 Hz, 2H), 7.33 (d, J = 1.6 Hz, 2H), 7.23 (d, J = 2.0Hz, 2H), 6.94, 6.92 (dd, J = 7.2 Hz, 7.6 Hz, 2H), 6.81, 6.79 (dd, J = 8.0 Hz, 7.6 Hz, 2H), 6.09 (d, J = 7.6 Hz, 2H), 4.07 (br s, 4H) 1.67 (s, 18H), 1.38 (s, 18H). ^{13}C NMR ($CDCl_3$, 400 MHz): 162.82, 140.11, 138.12, 137.34, 137.29, 131.78, 128.57, 126.24, 122.43, 120.36, 109.28, 35.81, 34.61, 32.07, 29.96. Anal. Calcd for $\mathbf{1}^{H}\cdot 0.5H_2O$ ($C_{43}H_{57}RhN_5O_{4.5}$): C, 63.07; H, 7.02; N, 8.55; Found: C, 63.10; H, 7.19; N, 8.53. MS (FAB$^+$) m/z = 809 ([M]$^+$).

$[Rh^{III}(L^{3-})(p\text{-methoxyaniline})_2]$ ($\mathbf{1^{OMe}}$). $\mathbf{1^{OMe}}$ was prepared by the same method described for the synthesis of $[Rh^{III}(L^{3-})(PhNH_2)_2]$($\mathbf{1^H}$) except the use of *p*-methoxy-aniline instead of aniline. The crude product was purified by silica gel column chromatography (eluent; $AcOCH_3$: *n*-hexane = 1 : 5, 20.4 mg, 47%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (d, J = 2.0 Hz, 2H), 7.33 (d, J = 1.6 Hz, 2H), 7.20 (d, J = 2.0 Hz, 2H), 6.30 (d, J = 8.4 Hz, 4H), 6.01 (d, J = 8.8 Hz, 4H), 3.99 (br s, 4H), 3.60 (s, 6H), 1.65 (s, 18H), 1.30 (s, 18H). ^{13}C NMR ($CDCl_3$, 400 MHz): 162.80, 157.67, 140.06, 138.08, 137.26, 137.09, 130.03, 127.38, 122.41,121.44, 113.75,109.23, 55.49, 35.79, 34.60, 32.07, 29.96. Anal. Calcd for $\mathbf{1^{OMe}}\cdot 1.5H_2O$ ($C_{45}H_{63}RhN_5O_{7.5}$): C, 60.26; H, 7.08; N, 7.81; Found: C, 60.28; H, 7.18; N, 7.75. MS (FAB$^+$): m/z = 869 ([M]$^+$).

$[Rh^{III}(L^{3-})(p\text{-chroloaniine})_2]$ ($\mathbf{1^{Cl}}$). $\mathbf{1^{Cl}}$ was prepared by the same method described for the synthesis of $[Rh^{III}(L^{3-})(PhNH_2)_2]$($\mathbf{1^H}$) except the use of *p*-chloro-aniline instead of aniline. The crude product was purified by silica gel column chromatography (eluent; $AcOCH_3$: *n*-hexane = 1 : 6, 11.4 mg, 26%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.98 (d, J = 1.6 Hz, 2H), 7.32 (d, J = 2.4 Hz, 2H), 7.21 (d, J = 2.0 Hz, 2H), 6.78 (d, J = 8.4 Hz, 4H), 6.10 (d, J = 8.8 Hz, 4H), 4.09 (br 4H), 1.64 (s, 18H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$, 400 MHz): 162.86, 140.30, 138.39, 137.26, 136.76, 136.16, 131.78, 128.72, 127.24, 122.81, 121.94, 109.05, 35.79, 34.60, 32.08, 29.91. Anal. Calcd for $\mathbf{1^{Cl}}\cdot 0.5H_2O$ ($C_{43}H_{55}RhN_5O_{4.5}Cl_2$): C, 58.18; H, 6.25; N, 7.89; Found: C, 58.36; H, 6.62; N, 7.79. MS (FAB$^+$): m/z = 877 ([M]$^+$).

$[Rh^{III}L^{2-}(PhNH_2)_2]SbF_6$ ($\mathbf{[1^H]SbF_6}$). A CH_2Cl_2 (2 ml) solution of $AgSbF_6$ (21.5 mg, 62.6 μmol) was added to complex $\mathbf{1^H}$ (35.0 mg, 43.2 μmol) in CH_2Cl_2 (2 ml) with stirring at room temperature. The reaction mixture was added dropwise to *n*-hexane (50 mL) with vigorous stirring. After reducing the volume of the

solvent to 5 mL, generated dark red precipitates were collected by filtration. Dark red crystals were obtained by slow diffusion of cyclohexane into a CH_2Cl_2 solution containing the complex (37.5 mg, 83%). Anal. Calcd for **[1^{H}]SbF$_6$**·H_2O ($C_{43}H_{58}RhN_5O_5SbF_6$): C, 48.56; H, 5.50; N, 6.58; Found: C, 48.54; H, 5.53; N, 6.63.

Amination of Xanthene by TsN_3. A solution of tosylazide (6.91 mg, 35.0 μmol) and Boc_2O (7.64 mg, 35.0 μmol) in toluene (1 ml) was added to **1^{x}** (3.50 μmol) and xanthene (6.38 mg, 35.0 μmol) in a 50 ml Schlenk tube. After removing dioxygen in the solvent by freeze–pump–thaw cycle (three times), the mixture was stirred at 100 ℃ for 24 h under dinitrogen atmosphere. All volatiles were evaporated in vacuo and the crude products were analyzed by ^{1}H NMR spectroscopy ($CDCl_3$, 400 MHz, Internal Standard; 1,1,2,2-tetracroloethane (14.5 mg, 86.4 μmol)).

Kinetic Isotope Effect Measurement. A 1 mL of toluene solution of tosylazide (6.9 mg, 35.0 μmol) and Boc_2O (7.6 mg, 35.0 μmol) was added to a mixture of **1^{H}** (2.8 mg, 3.50 μmol), xanthene (3.19 mg, 17.5 μmol), and xanthene−d_2 (3.22 mg, 17.5 μmol) in a 50 ml Schlenk tube. After purge of dioxygen in the solvent by freeze−pump−thaw cycle (three times), the mixture was stirred at 100 ℃ for 24 h under dinitrogen atmosphere. All volatiles were evaporated in vacuo and the crude products were analyzed by a ^{1}H NMR spectroscopy (DMSO−d_6, 400 MHz, Internal Standard; 1,1,2,2−tetracroloethane (14.5 mg, 86.4 μmol)).

Computational method. Energy calculations in the triplet and singlet states were performed using unrestricted density functional theory implemented with the Gaussian09 program package.[4] The open-shell singlet state was computed using the broken-symmetry approach. Geometry optimizations were performed with the B3LYP functional.[5,6] For the Rh atom, the SDD basis set[7] and for the other atoms, D95** basis set[8] were used. The computed kinetic isotope effect (k_H/k_D) was obtained by transition state theory[9] with the Wigner tunneling correction.

KIE calculations. We consider the kinetic isotope effects (KIE) in the C-H amination of xanthene by 3^{H}-T. The values of KIE were obtained by transition state theory with the following expression.

$$\frac{k_H}{k_D} = \left(\frac{m_D^R m_H^\#}{m_H^R m_D^\#}\right)^{3/2} \left(\frac{I_{xD}^R I_{yD}^R I_{zD}^R}{I_{xH}^R I_{yH}^R I_{zH}^R}\right)^{1/2} \left(\frac{I_{xH}^\# I_{yH}^\# I_{zH}^\#}{I_{xD}^\# I_{yD}^\# I_{zD}^\#}\right)^{1/2} \frac{q_{vD}^R q_{vH}^\#}{q_{vH}^R q_{vD}^\#} \exp\left(-\frac{E_H^\# - E_D^\#}{RT}\right)$$

Here *m, I, q*, and *E* indicate the molecular mass, the moment of inertia, the vibrational partition function, and the activation energy, respectively. The superscript *R* specifies the reactant complex 3H-T, and the

superscript # indicates the transition state. The subscript *H* means the species including xanthene and the subscript *D* means the species including dideuterated-xanthene. Table S2 summarizes computed values of k_H/k_D.

References.

1 J. Takaichi, K. Ohkubo, H. Sugimoto, M. Nakano, D. Usa, H. Maekawa, N. Fujieda, N. Nishiwaki, S. Seki, S. Fukuzumi and S. Itoh, *Dalton Trans*., 2013, **42**, 2438.

2 G. Giordano and R. H. Crabtree, *Inorg. Syn.*, 1990, **28**, 88.

3 A. Lewandowska-Andralojc, D. C. Grills, J. Zhang, R. M. Bullock, A. Miyazawa, Y. Kawanishi and E. Fujita, *J. Am. Chem. Soc.*, 2014, **136**, 3572.

1 Gaussian 09, *Revision D01*; Gaussian, Inc.: Wallingford, CT, 2009.

2 A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648.

3 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

4 M. Dolg, H. Stoll, H. Preuss and R.M. Pitzer, *J. Phys. Chem.*, 1993, **97**, 5852.

5 T. H. Dunning, Jr., P. J. Hay, *In Modern Theoretical Chemistry*, Vol. 3; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976; pp 1.

6 D. A. McQuarrie, Statistical Thermodynamics; University Science Book: Mill Valley, 1973.

Table S1. Selected Bond Lengths (Å) of $\mathbf{1^H}$ and [$\mathbf{1^H}$]SbF_6.

Ring A	$\mathbf{1^H}$	[$\mathbf{1^H}$]$\mathbf{SbF_6}$
Rh1−O1	2.0190(11)	2.0402(19)
Rh1−N1	1.9817(13)	1.989(2)
C1−C2	1.396(2)	1.404(4)
C2−C3	1.385(2)	1.380(4)
C3−C4	1.410(2)	1.435(4)
C4−C5	1.385(2)	1.370(4)
C5−C6	1.428(2)	1.449(4)
C6−C1	1.421(2)	1.446(4)
O1−C6	1.3332(19)	1.295(3)
N1−C1	1.4273(19)	1.385(4)
Ring B	$\mathbf{1^H}$	[$\mathbf{1^H}$]SbF_6
Rh1−O2	2.0072(12)	2.0075(18)
Rh1−N2	1.9763(13)	1.973(2)
C10−C11	1.400(2)	1.392(4)
C11−C12	1.384(2)	1.375(4)
C12−C13	1.405(2)	1.413(4)
C13−C14	1.389(2)	1.382(4)
C14−C15	1.420(2)	1.426(4)
C15−C10	1.418(2)	1.416(4)
O2−C15	1.3362(18)	1.325(3)
N2−C10	1.428(2)	1.418(3)

Table S2. Calculated kinetic isotope effects for the C-H amination of xanthene by $\mathbf{3^H}$**-T**.

Temperature (K)	k_H/k_D	k_H/k_D[a]
300	5.616	8.345
325	4.980	7.234
350	4.490	6.383
375	4.102	5.713
400	3.788	5.173

[a] Wigner tunneling correction

Table S3. Cartesian coordinates of $\mathbf{1^H}$ in the singlet state.

C	-1.928083	-2.306338	-2.914962
C	-0.555664	-2.429592	-2.662986
C	-0.006355	-3.575597	-2.071492
C	-0.864961	-4.617266	-1.716205
C	-2.253685	-4.520175	-1.926965
C	-2.767390	-3.358282	-2.536578
S	0.552404	-1.137616	-3.171663
O	0.211294	-0.638050	-4.511218
C	-3.164907	-5.634705	-1.473487
N	0.033449	0.255735	-2.057487
Rh	0.161248	0.704454	0.060342
N	-1.436606	-0.434130	0.496325
C	-1.321489	-1.684616	0.879861
C	-0.091439	-2.385963	1.017989
N	-0.207702	-3.774131	1.377025
O	0.829560	-4.469907	1.447388
C	1.237500	-1.907661	0.824425
N	1.551861	-0.693949	0.435202
C	2.873366	-0.198863	0.284332
C	2.944128	1.158080	-0.128636
C	4.227859	1.759338	-0.316485
C	5.349442	0.962629	-0.071036
C	5.295064	-0.389384	0.346481
C	4.035379	-0.956990	0.520675
O	1.806329	1.846259	-0.320092
C	6.602637	-1.168374	0.578414
C	6.347261	-2.620510	1.027720
C	4.357523	3.223017	-0.784497
C	3.680786	3.391126	-2.168009
O	-1.345825	-4.255645	1.581626
C	7.420584	-1.210227	-0.736337
C	7.439931	-0.467302	1.676828

C	3.685191	4.171316	0.240462
C	5.829719	3.661855	-0.927107
N	0.290701	1.521693	1.968810
C	0.262971	0.746083	3.191662
C	1.465004	0.286111	3.745515
C	1.433179	-0.453239	4.934133
C	0.210806	-0.731201	5.563395
C	-0.985524	-0.267234	4.996711
C	-0.965330	0.471281	3.807367
O	-1.287816	2.122996	-0.225390
C	-2.517399	1.636940	0.012024
C	-2.661826	0.272664	0.383336
C	-3.927667	-0.294247	0.623626
C	-5.081180	0.479858	0.514989
C	-4.919885	1.842609	0.168507
C	-3.687695	2.454838	-0.082364
C	-6.492575	-0.085049	0.760368
C	-7.350954	0.085021	-0.517512
C	-3.588774	3.952496	-0.439577
C	-2.962598	4.123175	-1.845204
O	1.926849	-1.477640	-2.798430
C	-6.468798	-1.583259	1.121670
C	-7.163806	0.678707	1.928773
C	-4.969360	4.641548	-0.455343
C	-2.713688	4.687489	0.607389
H	-3.998692	-1.341893	0.893586
H	-5.812398	2.453459	0.093926
H	6.327757	1.407882	-0.212587
H	-2.208906	-2.263858	1.115849
H	2.022101	-2.631971	1.021142
H	1.063189	-3.644616	-1.898401
H	-0.451895	-5.504052	-1.240703
H	-3.836957	-3.271603	-2.715012
H	-2.332585	-1.416154	-3.389565

H	-1.893101	0.826040	3.361418
H	-1.937259	-0.480631	5.478112
H	0.190398	-1.306551	6.486099
H	2.364725	-0.811345	5.366580
H	2.411881	0.499067	3.252029
H	-7.436082	1.135812	-0.814159
H	-6.911457	-0.463415	-1.359282
H	-8.365925	-0.298706	-0.352550
H	-6.028949	-2.188679	0.319831
H	-5.905888	-1.774130	2.043151
H	-7.492477	-1.941775	1.281112
H	-8.174652	0.291782	2.110301
H	-6.584365	0.565983	2.852773
H	-7.250701	1.750160	1.718609
H	-1.953099	3.709724	-1.876844
H	-3.570908	3.620255	-2.607060
H	-2.906517	5.187723	-2.106020
H	-4.839419	5.700884	-0.705749
H	-5.638983	4.207930	-1.207735
H	-5.467639	4.593298	0.520489
H	-3.139395	4.583363	1.613636
H	-1.694591	4.293174	0.610466
H	-2.664499	5.758235	0.372253
H	5.787996	-3.188625	0.274948
H	7.303642	-3.133378	1.183225
H	5.793510	-2.665416	1.973449
H	7.677684	-0.205115	-1.087740
H	8.357760	-1.761509	-0.587329
H	6.853715	-1.706061	-1.532762
H	8.382939	-1.004073	1.841443
H	7.687706	0.564261	1.404222
H	6.893248	-0.439055	2.627095
H	3.777677	4.429026	-2.511531
H	4.155035	2.741187	-2.913373

H	2.618352	3.143870	-2.117260
H	4.154756	4.074027	1.227803
H	3.794923	5.214453	-0.082581
H	2.618412	3.954003	0.333153
H	6.368269	3.062568	-1.670748
H	5.863181	4.705569	-1.260689
H	6.373010	3.603406	0.023939
H	1.161637	2.053093	1.879336
H	-0.480710	2.194178	1.933591
H	3.944010	-1.991322	0.832624
H	-4.204348	-5.451400	-1.761413
H	-2.853862	-6.595908	-1.899076
H	-3.117444	-5.730257	-0.381723
N	-0.049955	1.319890	-2.737355
N	-0.143940	2.279715	-3.340426

Table S4. Cartesian coordinates of TS1 in the singlet state.

C	3.636139	-2.455376	-0.029753
C	2.474873	-1.620936	0.047548
C	2.639002	-0.254024	0.402607
C	3.909400	0.295379	0.659263
C	5.050364	-0.499316	0.582602
C	4.872293	-1.862117	0.240470
O	1.244140	-2.096113	-0.188679
Rh	-0.180001	-0.637311	0.006084
N	-0.303700	-1.380129	2.035566
C	-0.218650	-0.560546	3.223357
C	-1.384963	-0.004525	3.767350
C	-1.297416	0.792748	4.915077
C	-0.054034	1.036063	5.516750
C	1.106421	0.476746	4.962159
C	1.029789	-0.321371	3.814140
N	1.428795	0.481148	0.478695
C	1.318893	1.737777	0.837529
C	0.093608	2.457459	0.939666
C	-1.234795	1.992453	0.745454
N	-1.557819	0.776510	0.367239
C	-2.878335	0.289528	0.227762
C	-2.960772	-1.085425	-0.126947
C	-4.243752	-1.708911	-0.228485
C	-5.360443	-0.897145	-0.014361
C	-5.297077	0.480917	0.306306
C	-4.035123	1.058702	0.434341
O	-1.820165	-1.766983	-0.337206
C	-4.385948	-3.209544	-0.553343
C	-5.860533	-3.662534	-0.578526
C	-6.599612	1.277920	0.495798
C	-7.431132	0.653466	1.643807
C	6.465891	0.042379	0.853456

C	7.100653	-0.729046	2.037109
C	3.520069	-3.948385	-0.399509
C	2.615080	-4.680482	0.623667
N	0.088120	-0.284869	-1.928836
N	-0.524512	-1.692827	-2.658451
N	-0.265715	-2.647583	-3.185468
S	-0.624867	0.966005	-2.986907
O	-1.925722	1.478330	-2.523097
C	0.639854	2.197212	-2.696543
C	1.967347	1.929277	-3.061510
C	2.926912	2.929023	-2.874974
C	2.577315	4.185734	-2.344244
C	1.231114	4.427235	-2.006648
C	0.257088	3.440759	-2.173385
C	3.616585	5.261539	-2.132520
O	-0.500798	0.410006	-4.347739
N	0.220516	3.852006	1.285441
O	1.361442	4.321506	1.487435
O	-0.811991	4.552723	1.351233
C	-6.337264	2.756290	0.844131
C	-7.422939	1.232264	-0.815776
C	-3.778894	-3.513086	-1.945070
C	-3.657171	-4.051764	0.524694
C	7.345389	-0.147031	-0.407214
C	6.460469	1.542011	1.209560
C	2.918103	-4.090847	-1.818942
C	4.889544	-4.659316	-0.398073
H	3.992987	1.345175	0.916858
H	5.756140	-2.487403	0.183327
H	-6.341070	-1.350597	-0.099728
H	2.208252	2.309626	1.084969
H	-2.013359	2.725167	0.934601
H	-0.781872	3.627497	-1.919139
H	0.943749	5.391989	-1.593553

H	3.961066	2.727791	-3.146484
H	2.241398	0.963970	-3.477662
H	1.931305	-0.751142	3.380398
H	2.075117	0.660863	5.421520
H	0.010047	1.657062	6.407236
H	-2.202491	1.223742	5.337398
H	-2.349715	-0.190351	3.297937
H	7.418457	-1.200284	-0.698399
H	6.930935	0.405475	-1.258872
H	8.363275	0.220374	-0.224199
H	6.048700	2.152563	0.396881
H	5.881433	1.745663	2.118291
H	7.486631	1.883044	1.389929
H	8.114051	-0.358553	2.237459
H	6.505045	-0.603646	2.949139
H	7.173704	-1.802514	1.831855
H	1.924756	-3.641231	-1.868722
H	3.558526	-3.603234	-2.564080
H	2.831511	-5.151329	-2.088050
H	4.747214	-5.713651	-0.662546
H	5.579647	-4.228632	-1.133364
H	5.370323	-4.629718	0.587265
H	3.024809	-4.593803	1.638197
H	1.602550	-4.270133	0.614945
H	2.554258	-5.747866	0.376105
H	-5.780685	3.269907	0.051508
H	-7.291680	3.280784	0.968397
H	-5.779464	2.863891	1.782289
H	-7.683834	0.206560	-1.097807
H	-8.357980	1.794400	-0.698440
H	-6.859277	1.673377	-1.645857
H	-8.369131	1.206381	1.779282
H	-7.688241	-0.391764	1.441071
H	-6.877943	0.684157	2.590166

H	-3.919259	-4.572695	-2.193830
H	-4.266814	-2.914250	-2.723389
H	-2.710033	-3.297225	-1.961218
H	-4.079229	-3.860794	1.519659
H	-3.774611	-5.121201	0.309376
H	-2.588030	-3.826115	0.543643
H	-6.437492	-3.147109	-1.355443
H	-5.901654	-4.735297	-0.799347
H	-6.359671	-3.506386	0.385433
H	-1.187860	-1.890834	2.003194
H	0.448694	-2.071919	2.001523
H	-3.940907	2.109111	0.683593
H	4.619997	4.909298	-2.389724
H	3.397643	6.142685	-2.748098
H	3.622899	5.589531	-1.086301

Table S5. Cartesian coordinates of $\mathbf{2^H}$ in the singlet state.

C	1.503342	3.921971	0.326649
C	0.344095	3.473044	-0.325256
C	-0.876393	4.140243	-0.139590
C	-0.931547	5.262906	0.695422
C	0.222748	5.722285	1.346471
C	1.437599	5.046594	1.158125
N	0.402605	2.305747	-1.165695
Rh	0.062018	0.236642	-0.383363
S	0.680609	-2.840501	-0.290297
C	-0.313060	-4.086976	0.552918
C	-0.183571	-4.249661	1.936978
C	-0.951013	-5.226799	2.583007
C	-1.846161	-6.039583	1.864581
C	-1.955537	-5.851919	0.471749
C	-1.196335	-4.882977	-0.190015
O	-1.505725	0.371217	-1.769776
C	-2.655035	0.566544	-1.164872
C	-2.666630	0.864362	0.237875
C	-3.861538	1.224340	0.902484
C	-5.065333	1.234200	0.215062
C	-5.046936	0.867197	-1.164840
C	-3.906194	0.519014	-1.876235
N	-1.419607	0.737437	0.861386
C	-1.241093	0.814672	2.169507
C	0.009313	0.667617	2.810136
C	1.289346	0.499965	2.245408
N	1.518380	0.376008	0.944997
C	2.803166	0.346159	0.382204
C	3.994577	0.592039	1.098880
C	5.220221	0.494609	0.457633
C	5.217168	0.155930	-0.927362
C	4.076898	-0.086297	-1.686958

C	2.815537	0.022911	-1.009515
C	-6.404388	1.599010	0.877062
C	-7.034650	2.807179	0.139704
C	-3.949629	0.108905	-3.359925
C	-3.124471	1.103591	-4.215580
C	6.560934	0.729862	1.172776
C	7.322755	1.891006	0.486215
C	4.146346	-0.441320	-3.184173
C	5.597323	-0.449304	-3.708497
O	1.663285	-0.144337	-1.634615
C	-7.367178	0.388014	0.791813
C	-6.240351	1.976860	2.361858
C	-3.369811	-1.319958	-3.514984
C	-5.389422	0.099684	-3.913789
C	6.375846	1.091775	2.659344
C	7.415760	-0.560046	1.095016
C	3.547865	-1.850926	-3.412476
C	3.356775	0.602618	-4.015037
N	-0.023343	0.758871	4.276032
O	1.045587	0.642715	4.895525
O	-1.118990	0.947169	4.828747
H	-3.834484	1.483988	1.954122
H	-5.993996	0.861529	-1.692360
O	0.928565	-3.323237	-1.670135
H	6.177333	0.089107	-1.426118
H	-2.089359	0.982400	2.823967
H	2.120423	0.469785	2.941125
H	0.518672	-3.630854	2.489547
H	-0.849619	-5.358913	3.658801
C	-2.654708	-7.111788	2.560792
H	-2.641055	-6.474977	-0.100837
H	-1.270268	-4.748652	-1.265895
H	-1.774554	3.785971	-0.642747
H	-1.878821	5.779864	0.833160

H	0.176510	6.596131	1.992188
H	2.339169	5.394705	1.657678
H	2.446323	3.396632	0.184593
H	-7.560685	0.089384	-0.244085
H	-6.951032	-0.479376	1.317188
H	-8.331579	0.636412	1.252018
H	-5.836471	1.146783	2.953470
H	-5.583855	2.845543	2.492945
H	-7.216913	2.236455	2.786234
H	-7.999255	3.067005	0.593041
H	-6.382438	3.686571	0.199163
H	-7.212957	2.594352	-0.919812
H	-2.341315	-1.377972	-3.152343
H	-3.974157	-2.044816	-2.956025
H	-3.381064	-1.612941	-4.572418
H	-5.367943	-0.220696	-4.961575
H	-6.035314	-0.600762	-3.370767
H	-5.853298	1.093584	-3.885447
H	-3.509862	2.125865	-4.109744
H	-2.071271	1.091162	-3.926741
H	-3.190680	0.827201	-5.275180
H	5.873046	0.291770	3.215467
H	7.355510	1.249173	3.124968
H	5.799556	2.016249	2.787440
H	7.623540	-0.851601	0.059922
H	8.379033	-0.408804	1.598126
H	6.902606	-1.398115	1.580282
H	8.286474	2.059973	0.982701
H	7.526471	1.680679	-0.569237
H	6.746214	2.822538	0.536415
H	3.578807	-2.096674	-4.481977
H	4.128037	-2.609344	-2.873636
H	2.513617	-1.920400	-3.071642
H	3.754669	1.614098	-3.856981

H	3.445782	0.371209	-5.083637
H	2.296058	0.591207	-3.754232
H	6.216367	-1.195596	-3.196390
H	5.590284	-0.709422	-4.773052
H	6.082423	0.530506	-3.612857
O	1.838992	-2.530428	0.590773
H	1.305428	2.211075	-1.631398
H	-0.325478	2.313328	-1.882561
H	3.947441	0.855626	2.148920
H	-3.682410	-7.144729	2.181830
H	-2.212923	-8.102652	2.391811
H	-2.693236	-6.945852	3.642009
N	-0.440540	-1.596013	-0.325425

Table S6. Cartesian coordinates of **3^{H}-T** in the triplet state.

C	2.981637	-2.794824	0.407333
C	1.530448	-2.797988	0.370405
C	0.812127	-4.009851	0.292349
C	1.489667	-5.218524	0.252374
C	2.924563	-5.199057	0.309306
C	3.694980	-4.054569	0.387139
N	0.966495	-1.534358	0.427067
C	-0.340001	-1.294255	0.394424
C	-0.912974	-0.011604	0.479449
N	-2.373984	0.013451	0.424158
O	-2.949863	1.113619	0.510414
C	0.770250	-6.570236	0.143658
C	1.231964	-7.288733	-1.150161
C	5.232660	-4.088812	0.428622
C	5.744568	-3.397174	1.718859
O	3.601341	-1.657068	0.475820
Rh	2.311388	-0.039302	0.537611
N	2.151169	0.302738	-1.414989
S	3.153897	-0.537835	-2.457908
O	2.677020	-1.947418	-2.529048
N	2.571754	-0.217289	2.739658
C	1.462106	-0.318174	3.654028
C	0.969653	-1.580227	4.018103
C	-0.124009	-1.673050	4.888108
C	-0.728651	-0.513750	5.395231
C	-0.230423	0.744015	5.024619
C	0.862060	0.846910	4.154769
O	3.649759	1.492492	0.776309
C	3.048867	2.665038	0.811747
C	1.617311	2.722468	0.789545
C	0.928786	3.953935	0.861706
C	1.634829	5.144622	0.946903

C	3.060478	5.072519	0.949494
C	3.793650	3.894127	0.879677
N	0.997828	1.470015	0.686924
C	-0.297820	1.270539	0.613348
C	0.950782	6.519986	1.018452
C	-0.586127	6.410210	1.020702
C	5.333396	3.878904	0.847724
C	5.926477	5.300700	0.923484
C	2.768095	0.237573	-4.040597
C	1.671615	-0.216466	-4.784938
C	1.382661	0.392916	-6.009786
C	2.174441	1.448556	-6.503635
C	3.270272	1.879982	-5.735815
C	3.574274	1.280858	-4.505954
C	1.861516	2.082138	-7.841747
O	4.586055	-0.265898	-2.178078
C	1.383121	7.248740	2.315397
C	1.371119	7.367486	-0.208804
C	5.886021	3.075908	2.052769
C	5.815932	3.231370	-0.476060
C	1.126340	-7.444357	1.373148
C	-0.762039	-6.419072	0.088306
C	5.770422	-5.534639	0.430321
C	5.807344	-3.364314	-0.815229
O	-2.985580	-1.062570	0.295598
H	-0.154767	3.963307	0.841604
H	3.608098	6.006960	1.001713
H	3.435187	-6.154523	0.281770
H	-0.981701	2.111677	0.649632
H	-1.041399	-2.116087	0.299600
H	1.068585	-1.040195	-4.412017
H	0.531698	0.042649	-6.592239
H	3.896693	2.691535	-6.102281
H	4.428913	1.604892	-3.917873

H	1.245464	1.824637	3.866868
H	-0.691676	1.649651	5.412601
H	-1.578260	-0.589222	6.069769
H	-0.501257	-2.653701	5.170159
H	1.437241	-2.482584	3.626748
H	2.455280	7.517644	-0.250287
H	1.065345	6.881071	-1.142345
H	0.899113	8.357146	-0.167764
H	-0.963994	5.940618	0.104840
H	-0.953837	5.836015	1.879697
H	-1.027733	7.411535	1.081739
H	0.914629	8.239318	2.368700
H	1.081219	6.680968	3.203532
H	2.467902	7.392307	2.363559
H	5.450743	2.207803	-0.584438
H	5.470050	3.815534	-1.338044
H	6.913028	3.210858	-0.501398
H	7.019793	5.234039	0.890190
H	5.611473	5.924653	0.078493
H	5.656496	5.814510	1.854547
H	5.546376	3.509352	3.002416
H	5.570524	2.031242	2.006443
H	6.982881	3.100688	2.045513
H	-1.084157	-5.835715	-0.782142
H	-1.225804	-7.408780	0.009413
H	-1.160685	-5.941752	0.991561
H	2.311282	-7.473877	-1.156551
H	0.727630	-8.258518	-1.240959
H	0.990114	-6.691884	-2.036817
H	0.630716	-8.419849	1.296829
H	2.203455	-7.625467	1.452958
H	0.795750	-6.966782	2.303155
H	6.903649	-3.412291	-0.789908
H	5.466748	-3.847865	-1.737935

H	5.508697	-2.315657	-0.857630
H	5.333574	-3.878816	2.615980
H	6.837547	-3.473374	1.769192
H	5.481616	-2.336954	1.729370
H	5.490967	-6.079203	-0.479479
H	6.864974	-5.507008	0.468159
H	5.425117	-6.107819	1.300135
H	3.194766	-1.021547	2.819799
H	3.129506	0.620960	2.911141
H	-0.270028	-3.991517	0.254142
H	2.407946	3.020745	-7.977076
H	2.139662	1.412216	-8.665724
H	0.790476	2.292883	-7.941031
C	-10.152748	1.660634	-0.155838
C	-8.888618	0.827389	-0.107395
C	-11.390735	0.816164	-0.375642
H	-10.256687	2.228072	0.780340
H	-10.071360	2.410200	-0.956013
C	-12.663308	1.403877	-0.467333
C	-13.815819	0.636377	-0.667445
C	-13.703302	-0.759212	-0.780376
C	-12.448314	-1.367071	-0.693190
C	-11.303166	-0.579773	-0.492300
H	-12.745319	2.487056	-0.379298
H	-14.789107	1.117061	-0.735031
H	-14.589338	-1.371215	-0.936271
H	-12.331512	-2.444756	-0.777621
O	-10.113767	-1.267873	-0.419768
C	-8.935603	-0.567569	-0.237908
C	-7.769298	-1.346304	-0.189899
C	-6.529263	-0.727682	-0.008934
C	-6.455162	0.669320	0.123371
C	-7.630120	1.426541	0.072389
H	-7.857414	-2.424948	-0.296283

H	-5.617409	-1.318682	0.029751
H	-5.487932	1.144843	0.263351
H	-7.578492	2.510624	0.173752

Table S7. Cartesian coordinates of **TS2** in the triplet state.

C	-2.325546	3.724199	0.916694
C	-0.943600	3.849461	0.711492
C	-0.402426	5.028354	0.195005
C	-1.258112	6.092586	-0.131521
C	-2.645993	5.991120	0.054221
C	-3.164193	4.790916	0.584746
S	0.163302	2.500979	1.208956
O	1.539468	2.932979	0.825988
C	-3.570103	7.136023	-0.299048
N	-0.404801	1.221890	0.301391
Rh	0.132558	-0.647966	0.929332
O	-1.469692	-0.630505	2.219729
C	-2.595894	-0.895421	1.598896
C	-2.563454	-1.268044	0.212288
C	-3.747328	-1.569025	-0.496615
C	-4.975677	-1.523693	0.145151
C	-4.992415	-1.163138	1.527176
C	-3.866500	-0.846620	2.276404
N	-1.277448	-1.312439	-0.333979
C	-0.986486	-1.753160	-1.540170
C	0.329508	-1.798446	-2.082794
C	1.555132	-1.370579	-1.535972
N	1.692575	-0.839447	-0.325938
C	2.912846	-0.480168	0.228625
C	2.830503	-0.093286	1.621680
C	4.045322	0.233128	2.337404
C	5.224329	0.169761	1.617182
C	5.319763	-0.193168	0.232306
C	4.154422	-0.515480	-0.443776
O	1.667603	-0.086897	2.202111
C	4.003808	0.628998	3.824209
C	5.415457	0.913031	4.377560

C	6.701448	-0.202780	-0.438492
C	7.632660	-1.189734	0.310142
C	-6.304492	-1.822585	-0.568336
C	-7.027073	-2.992479	0.145234
C	-3.947516	-0.440715	3.760042
C	-3.118418	-1.423842	4.625339
O	-0.116191	2.243509	2.645084
N	0.454587	-2.629197	1.841255
C	0.606501	-3.846146	1.084443
C	1.885526	-4.270036	0.694493
C	2.027021	-5.441122	-0.060134
C	0.899490	-6.189738	-0.427824
C	-0.375529	-5.758159	-0.033628
C	-0.526948	-4.588194	0.720616
N	0.429016	-2.424481	-3.404364
O	-0.615442	-2.825386	-3.946738
O	1.552363	-2.542535	-3.922887
C	6.635348	-0.635214	-1.915826
C	7.307855	1.222187	-0.376872
C	3.149565	1.908118	4.008974
C	3.396401	-0.527725	4.659646
C	-7.205822	-0.562868	-0.524771
C	-6.100423	-2.215571	-2.044295
C	-3.398429	0.997488	3.939767
C	-5.397161	-0.465743	4.286743
C	-0.067988	2.113951	-2.211894
C	-1.239287	1.620486	-2.973094
C	-1.056758	0.772407	-4.083539
O	0.193414	0.423044	-4.540090
C	1.306037	1.034726	-4.006795
C	1.234396	1.868295	-2.873129
C	-2.562035	1.947598	-2.610573
C	-3.653670	1.443536	-3.319771
C	-3.441785	0.584002	-4.414114

C	-2.140946	0.246997	-4.798562
C	2.517059	0.784621	-4.665014
C	3.687460	1.387107	-4.194536
C	3.643931	2.224918	-3.064284
C	2.431461	2.452898	-2.410873
H	-3.690152	-1.812972	-1.550868
H	-5.956667	-1.124199	2.021535
H	6.146344	0.416453	2.130868
H	-1.770342	-2.133009	-2.186547
H	2.425678	-1.521301	-2.164713
H	0.673167	5.109748	0.063093
H	-0.835129	7.012126	-0.532472
H	-4.237582	4.695000	0.743894
H	-2.730725	2.805404	1.331705
H	-1.518039	-4.253826	1.023414
H	-1.256829	-6.331278	-0.313400
H	1.012868	-7.097162	-1.016243
H	3.020474	-5.766811	-0.360859
H	2.762660	-3.690448	0.978467
H	-7.422981	-0.250243	0.502313
H	-6.722491	0.278712	-1.034918
H	-8.163319	-0.761226	-1.022370
H	-5.620317	-1.414123	-2.618072
H	-5.490697	-3.121495	-2.144630
H	-7.071774	-2.419450	-2.509636
H	-7.982010	-3.208460	-0.350025
H	-6.416716	-3.902935	0.119736
H	-7.242201	-2.763899	1.194580
H	-2.362298	1.086348	3.605770
H	-4.010331	1.714797	3.377471
H	-3.442913	1.282388	4.998767
H	-5.400089	-0.168900	5.341685
H	-6.044125	0.237922	3.748929
H	-5.845370	-1.465423	4.225631

H	-3.481403	-2.453068	4.506997
H	-2.060944	-1.385868	4.355074
H	-3.208244	-1.154659	5.685070
H	6.011063	0.039994	-2.511844
H	7.642937	-0.622779	-2.347297
H	6.242648	-1.653050	-2.026713
H	7.420402	1.576801	0.653123
H	8.300475	1.231151	-0.843920
H	6.672240	1.939901	-0.908340
H	8.628780	-1.190361	-0.149275
H	7.754782	-0.923736	1.365387
H	7.236610	-2.211169	0.265405
H	3.157137	2.200978	5.067039
H	3.560009	2.738176	3.422402
H	2.114061	1.760329	3.698766
H	3.975026	-1.452564	4.534413
H	3.412337	-0.263465	5.724098
H	2.357850	-0.713445	4.376186
H	5.897558	1.752549	3.862247
H	5.335066	1.184815	5.435905
H	6.074696	0.038115	4.311871
H	1.264540	-2.456798	2.437974
H	-0.370654	-2.657455	2.443041
H	4.186987	-0.777987	-1.493798
H	-4.143550	7.464461	0.576505
H	-3.012115	7.997215	-0.679363
H	-4.293343	6.836692	-1.067813
H	-0.183587	3.147057	-1.873217
H	-1.944483	-0.411118	-5.640717
H	-4.287064	0.184853	-4.971107
H	-4.665135	1.713739	-3.024636
H	-2.719889	2.601324	-1.755585
H	2.517271	0.129537	-5.532075
H	4.628712	1.207238	-4.710352

H	4.553814	2.692479	-2.694478
H	2.394258	3.065544	-1.512815
H	-0.132003	1.563512	-1.059989

Table S8. Cartesian coordinates of $\mathbf{4^H}$ in the triplet state.

C	3.125279	-2.680716	0.064510
C	1.772001	-2.694438	0.601995
C	1.146247	-3.910681	0.941837
C	1.812257	-5.112271	0.754755
C	3.148056	-5.081863	0.224529
C	3.829233	-3.933576	-0.126813
N	1.212213	-1.437951	0.732996
C	-0.040676	-1.221349	1.123354
C	-0.602979	0.053088	1.300431
N	-2.000380	0.059111	1.719285
O	-2.561040	1.157270	1.895109
C	1.177511	-6.471179	1.079327
C	1.113597	-7.320873	-0.216021
C	5.249616	-3.955174	-0.716128
C	6.209235	-3.117255	0.168270
O	3.668375	-1.540281	-0.216552
Rh	2.437388	0.072082	0.226725
N	1.563945	0.265609	-1.632066
S	1.738509	-0.905411	-2.805853
O	1.251750	-2.185217	-2.231063
N	3.499342	0.074482	2.140419
C	2.821412	0.102228	3.415162
C	2.528912	-1.099628	4.075715
C	1.857176	-1.068828	5.304507
C	1.476121	0.154581	5.874289
C	1.771660	1.351336	5.204920
C	2.442540	1.330618	3.976038
O	3.687959	1.633435	-0.205466
C	3.116673	2.805383	0.038046
C	1.790043	2.839298	0.565140
C	1.140916	4.059123	0.855683
C	1.786487	5.266734	0.628454

C	3.105574	5.217980	0.094737
C	3.793390	4.047024	-0.213415
N	1.212835	1.567410	0.745712
C	-0.018130	1.350016	1.136788
C	1.137678	6.631134	0.918794
C	-0.288306	6.492477	1.486723
C	5.214223	4.061682	-0.810084
C	5.748350	5.495929	-0.999946
C	0.537789	-0.354310	-4.042630
C	-0.831694	-0.387561	-3.741880
C	-1.752614	0.011007	-4.713343
C	-1.327643	0.443854	-5.986603
C	0.049874	0.468524	-6.259567
C	0.988289	0.069127	-5.295610
C	-2.339588	0.850239	-7.035664
O	3.064106	-0.893730	-3.477046
C	1.994499	7.402525	1.953275
C	1.054289	7.453122	-0.391609
C	6.193532	3.316884	0.132291
C	5.203188	3.371927	-2.198113
C	2.042118	-7.204659	2.136145
C	-0.252797	-6.336398	1.636431
C	5.814675	-5.388732	-0.787283
C	5.220277	-3.378173	-2.154398
O	-2.581358	-1.030184	1.884326
H	0.132908	4.047214	1.254262
H	3.607235	6.162086	-0.086420
H	3.648567	-6.033254	0.089176
H	-0.675874	2.184671	1.355014
H	-0.701171	-2.058421	1.322181
H	-1.164456	-0.722376	-2.762838
H	-2.816598	-0.012889	-4.482136
H	0.397739	0.799280	-7.236833
H	2.054405	0.076017	-5.505991

H	2.667702	2.260266	3.456019
H	1.480896	2.305631	5.638701
H	0.955052	0.175364	6.828571
H	1.634774	-2.002684	5.816281
H	2.824662	-2.051250	3.636359
H	2.042608	7.621768	-0.832778
H	0.439405	6.936801	-1.137909
H	0.604639	8.434931	-0.197751
H	-0.960129	5.983318	0.785523
H	-0.300449	5.943339	2.436064
H	-0.706999	7.487073	1.678689
H	1.551336	8.384752	2.159998
H	2.056391	6.850812	2.898930
H	3.016657	7.568005	1.596025
H	4.877531	2.332091	-2.124895
H	4.532862	3.899805	-2.887675
H	6.211499	3.386884	-2.631206
H	6.756050	5.449180	-1.428358
H	5.126913	6.079629	-1.689565
H	5.819609	6.041133	-0.050720
H	6.218671	3.788551	1.123111
H	5.906620	2.268810	0.245012
H	7.209186	3.349560	-0.281461
H	-0.927439	-5.855569	0.918687
H	-0.657565	-7.331896	1.850443
H	-0.278188	-5.764995	2.572173
H	2.106311	-7.497365	-0.643336
H	0.665521	-8.298385	-0.000301
H	0.504297	-6.824529	-0.979553
H	1.604522	-8.184112	2.364179
H	3.066800	-7.373028	1.788274
H	2.093600	-6.630049	3.068612
H	6.236148	-3.382867	-2.569981
H	4.584270	-3.989885	-2.804409

H	4.837406	-2.356897	-2.185960
H	6.224147	-3.491917	1.200427
H	7.229619	-3.187497	-0.227379
H	5.923305	-2.063227	0.175057
H	5.214778	-6.035842	-1.438077
H	6.824877	-5.352614	-1.209877
H	5.887598	-5.858416	0.201856
H	4.109797	-0.740638	2.068800
H	4.084104	0.902287	2.008476
H	0.138409	-3.903571	1.337832
H	-1.862704	1.374061	-7.870132
H	-2.853151	-0.030025	-7.443711
H	-3.108290	1.507718	-6.613401
C	-9.656484	1.479815	0.332676
C	-8.421181	0.866766	0.691281
C	-10.775970	0.661574	0.009334
H	-9.743415	2.562833	0.306028
C	-12.050177	1.170263	-0.361610
C	-13.107969	0.315728	-0.666965
C	-12.928949	-1.080390	-0.612099
C	-11.683254	-1.614855	-0.249455
C	-10.627635	-0.754789	0.055090
H	-12.186271	2.249533	-0.402890
H	-14.074933	0.727276	-0.948419
H	-13.753455	-1.748431	-0.850055
H	-11.518613	-2.688352	-0.199709
O	-9.432074	-1.337544	0.402978
C	-8.341828	-0.554289	0.716574
C	-7.164260	-1.220319	1.057262
C	-6.020298	-0.477757	1.384993
C	-6.065805	0.931143	1.369589
C	-7.245264	1.589908	1.029319
H	-7.156152	-2.307589	1.061137
H	-5.093675	-0.980363	1.649867

H	-5.169464	1.491219	1.624122
H	-7.284132	2.677933	1.016306
H	1.972350	1.115529	-2.034310

Table S9. Cartesian coordinates of **TS3** in the singlet state.

O	-0.129010	0.115704	4.334420
C	1.113739	0.437119	3.892062
C	1.323711	1.433620	2.909627
C	0.182911	2.052994	2.279723
C	-1.118022	1.715745	2.794616
C	-1.221747	0.749410	3.824688
C	-2.453701	0.426775	4.410541
C	-3.597437	1.083498	3.964028
C	-3.524598	2.054303	2.938288
C	-2.303274	2.364141	2.359638
C	2.185769	-0.227706	4.508767
C	3.485203	0.131146	4.164800
C	3.727445	1.154464	3.218025
C	2.661776	1.792168	2.600669
N	0.366440	1.410124	0.144062
S	0.123035	2.825063	-0.826804
O	0.362449	2.573487	-2.256728
Rh	-0.218885	-0.424382	-0.801839
N	1.138876	-1.398014	0.329756
C	0.816818	-1.995896	1.454337
C	-0.489187	-2.028478	2.016555
N	-0.604194	-2.706365	3.278654
O	-1.730439	-2.796961	3.819608
C	-1.704868	-1.514196	1.475594
N	-1.803659	-0.808372	0.374819
C	-3.029708	-0.369370	-0.189650
C	-2.887572	0.274528	-1.447898
C	-4.066035	0.714188	-2.136519
C	-5.292848	0.501880	-1.503876
C	-5.447162	-0.125273	-0.242344
C	-4.292573	-0.562787	0.401871
O	-1.669337	0.429690	-1.966242

C	-6.856138	-0.299951	0.353585
C	-6.831221	-1.015532	1.718666
C	-3.971201	1.383466	-3.522249
C	-3.141158	2.686812	-3.426277
O	0.428234	-3.171570	3.816031
C	-7.512863	1.088720	0.553076
C	-7.733063	-1.140201	-0.607939
C	-3.293962	0.416813	-4.527398
C	-5.360054	1.744759	-4.089486
N	-0.628259	-2.125400	-2.016334
C	-0.885648	-3.452920	-1.511345
C	-2.202343	-3.850892	-1.239965
C	-2.444910	-5.138443	-0.746077
C	-1.381496	-6.024811	-0.520781
C	-0.067749	-5.614730	-0.792054
C	0.185446	-4.329416	-1.286132
O	1.413542	-0.252995	-2.046908
C	2.504404	-0.824749	-1.535280
C	2.434231	-1.429364	-0.249464
C	3.564662	-2.014449	0.351851
C	4.788874	-2.034322	-0.313856
C	4.837331	-1.461022	-1.608280
C	3.747128	-0.865322	-2.248916
C	6.059936	-2.658039	0.291673
C	7.172022	-1.584728	0.392598
C	3.856493	-0.291015	-3.675786
C	3.531326	1.223052	-3.668936
O	-1.153862	3.425163	-0.376652
C	1.450994	3.943411	-0.290892
C	1.141741	5.061814	0.489460
C	2.166119	5.947660	0.852881
C	3.493166	5.732905	0.441334
C	3.772606	4.603795	-0.354965
C	2.761580	3.714960	-0.733614

C	4.589155	6.709857	0.804275
C	5.818629	-3.227109	1.703611
C	6.553754	-3.816099	-0.610850
C	5.268835	-0.468297	-4.271147
C	2.860025	-1.020920	-4.612166
H	3.476000	-2.450777	1.340466
H	5.782728	-1.491194	-2.138642
H	-6.189615	0.835615	-2.013778
H	1.572585	-2.532551	2.019551
H	-2.596745	-1.753373	2.046005
H	0.111355	5.246262	0.783519
H	1.925113	6.820770	1.456672
H	4.790890	4.426683	-0.697258
H	2.983062	2.870808	-1.381471
H	1.205474	-4.007605	-1.489900
H	0.763769	-6.294306	-0.618095
H	-1.574100	-7.023492	-0.135370
H	-3.466896	-5.446617	-0.536169
H	-3.026430	-3.159204	-1.406833
H	7.423284	-1.165632	-0.587583
H	6.855537	-0.755705	1.037377
H	8.087926	-2.017140	0.815618
H	5.485579	-2.451769	2.404626
H	5.068846	-4.027075	1.699262
H	6.750243	-3.651094	2.096862
H	7.463832	-4.267896	-0.195372
H	5.790426	-4.598903	-0.691930
H	6.785445	-3.471110	-1.624215
H	2.523130	1.411520	-3.292817
H	4.258894	1.765743	-3.049672
H	3.597319	1.627618	-4.687269
H	5.287515	-0.045552	-5.282381
H	6.034094	0.053834	-3.683793
H	5.555555	-1.524021	-4.350670

H	3.061220	-2.099725	-4.631944
H	1.830522	-0.854816	-4.286385
H	2.958037	-0.640621	-5.636928
H	-6.248410	-0.456430	2.460870
H	-7.852324	-1.113377	2.106064
H	-6.408483	-2.024623	1.644444
H	-7.593790	1.639773	-0.390035
H	-8.524204	0.982567	0.966489
H	-6.923550	1.702661	1.245237
H	-8.744353	-1.263070	-0.199044
H	-7.826529	-0.667678	-1.591504
H	-7.301702	-2.137141	-0.757341
H	-3.098124	3.172887	-4.410068
H	-3.599245	3.388738	-2.718987
H	-2.121472	2.485705	-3.095479
H	-3.856617	-0.522802	-4.608048
H	-3.259228	0.875027	-5.524072
H	-2.268951	0.195912	-4.220508
H	-5.890262	2.463516	-3.452885
H	-5.235023	2.210541	-5.073959
H	-5.998747	0.862329	-4.221499
H	-1.413129	-1.766086	-2.565195
H	0.201415	-2.099886	-2.614250
H	-4.360479	-1.053409	1.366343
H	5.532216	6.193316	1.013419
H	4.774853	7.405562	-0.024358
H	4.321276	7.305796	1.682438
H	1.385777	1.284389	0.156786
H	0.310268	3.034874	1.849661
H	1.971482	-1.008443	5.232943
H	4.322611	-0.378041	4.636917
H	4.748209	1.432524	2.969007
H	2.842189	2.572599	1.865163
H	-2.486445	-0.335749	5.182963

H	-4.559043	0.839957	4.411111
H	-4.429731	2.544005	2.589191
H	-2.232540	3.069790	1.537176

Table S10. Cartesian coordinates of $\mathbf{5^H}$ in the singlet state.

C	2.977902	0.249331	1.252496
C	3.076448	-0.492016	0.046732
C	4.314151	-0.714084	-0.584581
C	5.491262	-0.236856	-0.012547
C	5.384725	0.446455	1.223000
C	4.180540	0.699732	1.886106
N	1.835794	-0.993753	-0.426953
C	1.718099	-1.871105	-1.395857
C	0.497507	-2.465917	-1.821617
N	0.604345	-3.398155	-2.918437
O	-0.430564	-3.960141	-3.336658
C	6.873971	-0.425030	-0.663086
C	7.505640	0.960986	-0.945602
C	4.146037	1.420952	3.249428
C	3.478820	0.505596	4.307759
O	1.767650	0.481834	1.775843
Rh	0.271379	-0.419771	0.700393
N	-0.359821	1.500312	-0.371315
S	0.273894	2.961511	0.499670
O	1.638297	3.179534	-0.003464
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C	1.237604	-6.025520	1.130309
C	-0.063051	-5.550964	1.354750
C	-0.280056	-4.203719	1.667414
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C	-3.798005	0.304842	3.481430
C	-5.210834	0.257770	4.098893
C	-0.737298	4.349638	-0.059775
C	-0.264764	5.191174	-1.075572
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C	-3.464864	1.786390	3.172534
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H	-5.728233	-1.185720	2.229210
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H	6.176105	-0.667845	-2.734380
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H	3.367067	3.268188	4.105147
H	3.785459	3.401054	2.382881

H	2.307721	2.552535	2.871375
H	4.022492	-0.443272	4.405138
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H	-4.103520	7.714250	-0.892743
H	-2.648586	8.705263	-0.716774
H	-3.027991	7.975591	-2.280782
H	-1.300360	1.402692	0.031811
C	-0.538064	1.732758	-1.889420
H	-0.481741	2.818362	-2.017727
C	0.531021	1.114679	-2.767557
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C	-2.117921	0.302882	-3.280039
C	-3.404257	-0.103364	-3.670097
C	-4.523721	0.502367	-3.101179
C	-4.362268	1.522261	-2.147743
C	-3.076613	1.908039	-1.766540
H	-3.494452	-0.881897	-4.423303
H	-5.519877	0.189725	-3.407073
H	-5.229676	2.007498	-1.707596
H	-2.961016	2.710931	-1.041223
C	0.195732	0.161332	-3.741678
C	1.156021	-0.371180	-4.613194
C	2.478288	0.062147	-4.527647
C	2.836869	1.029991	-3.573981
C	1.869414	1.546913	-2.710855
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H	0.845602	-1.120511	-5.336405

H	3.223894	-0.353554	-5.201554
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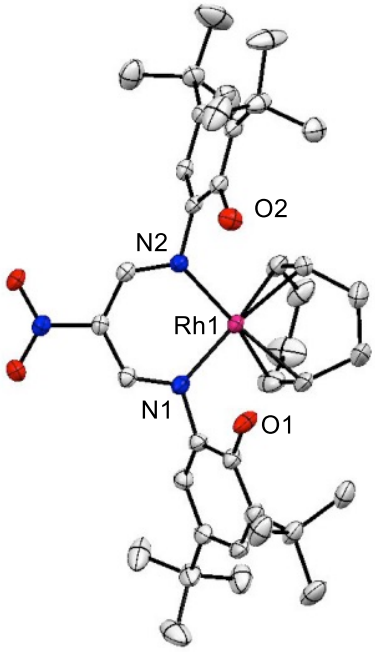

Figure S1. Crystal structure of $Rh^{I}(LH_2^{-})$(cod) (cod = 1,5-cyclooctadiene). The solvent molecule (methanol) and hydrogen atoms are omitted for clarity.

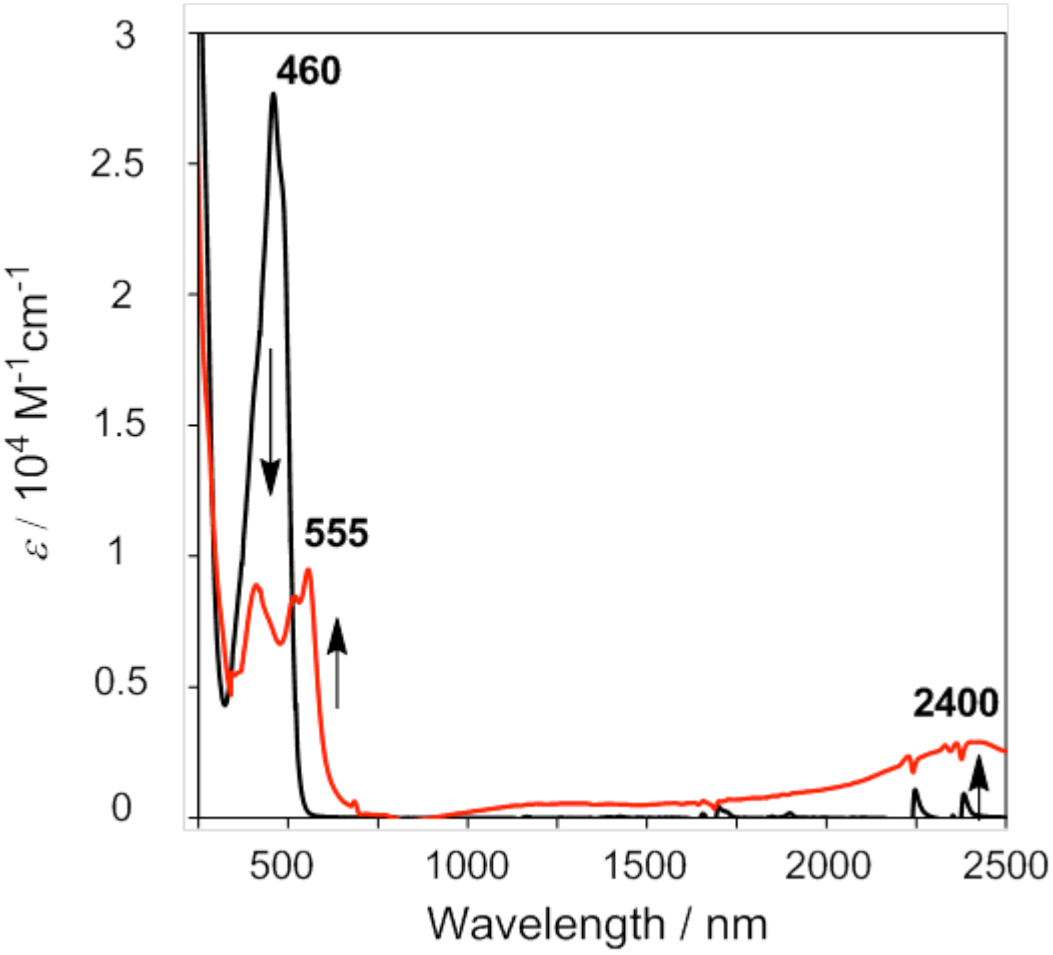

Figure S2. Absorption spectra of $\mathbf{1^H}$ (black) and $\mathbf{[1^H]SbF_6}$ (red) in CH_2Cl_2.

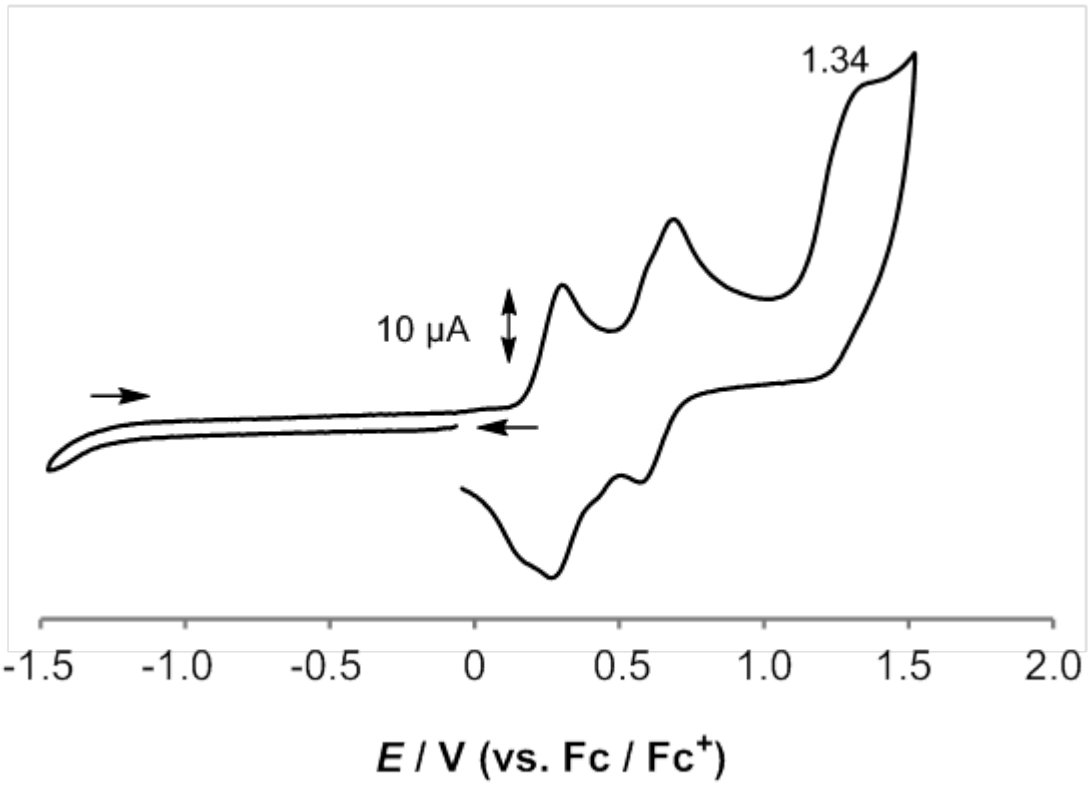

Figure S3. Cyclic voltammogram of $\mathbf{1^H}$ (1.0 mM) in a CH_2Cl_2 solution containing 0.10 M $^nBu_4NPF_6$ (working electrode = GC, counter electrode = Pt, scan rate = 0.1 V s^{-1}).

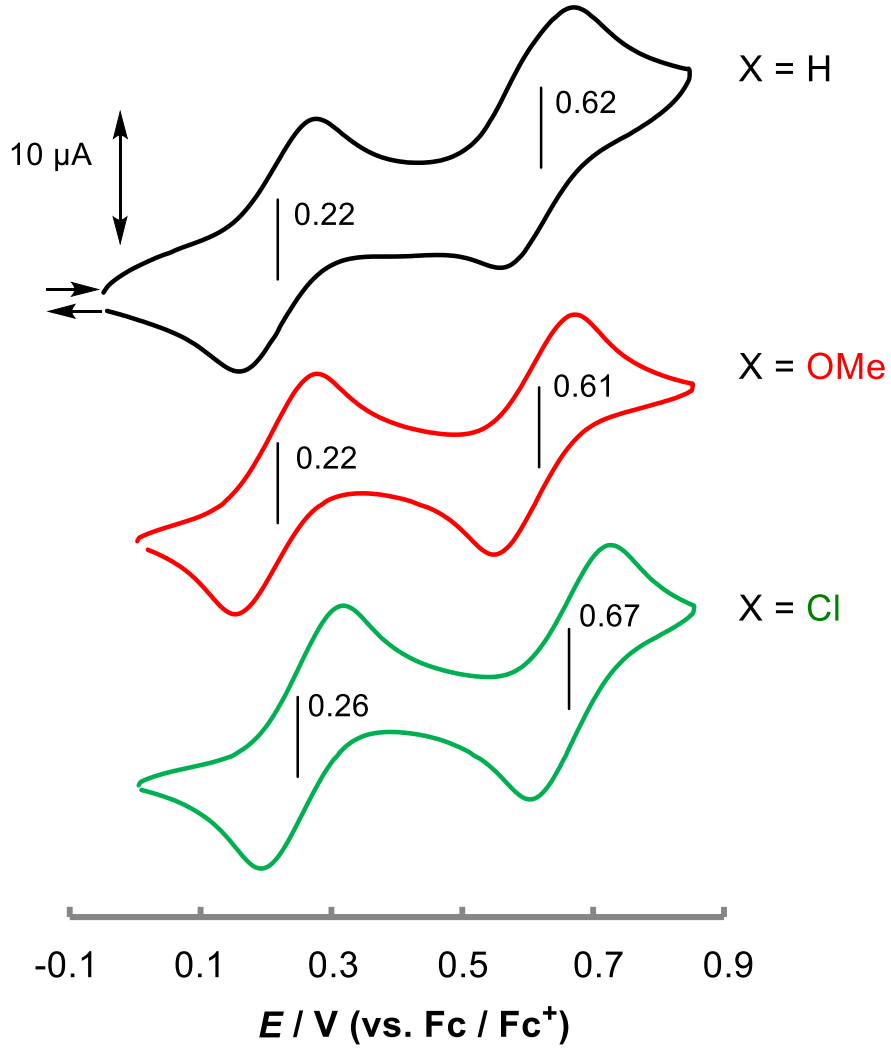

Figure S4. Cyclic voltammogram of $\mathbf{1}^{X}$ (X = H, OMe, Cl) (1.0 mM) in a 0.10 M $^{n}Bu_4NPF_6$ containing CH_2Cl_2 solution (working electrode = GC, counter electrode = Pt, scan rate = 100 mV s^{-1}).

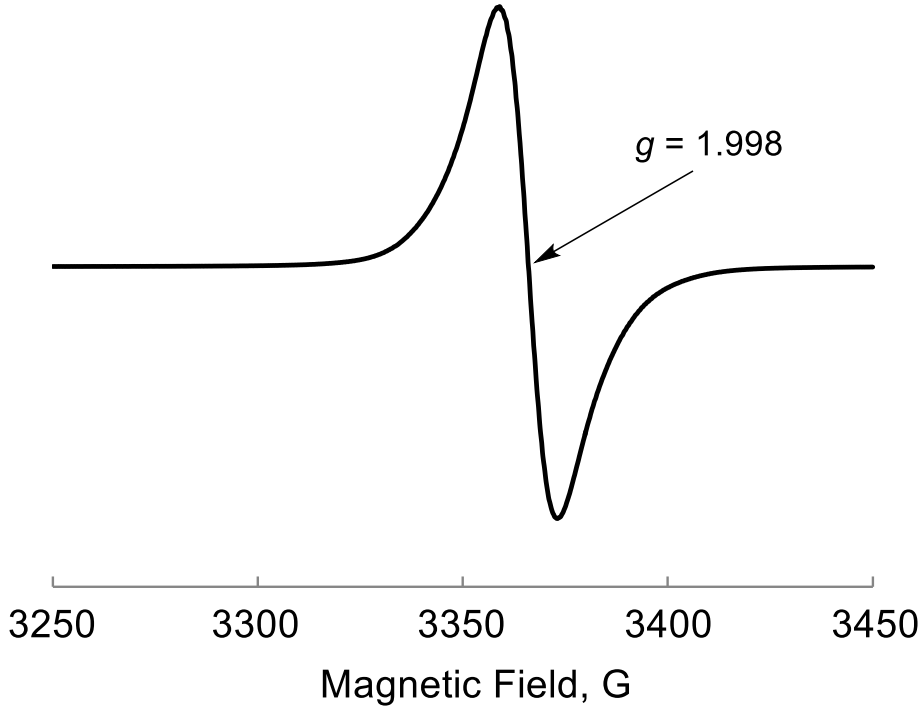

Figure S5. EPR spectrum of **[1^{H}]**SbF_6 (2.0 mM) in CH_2Cl_2 at 100K.

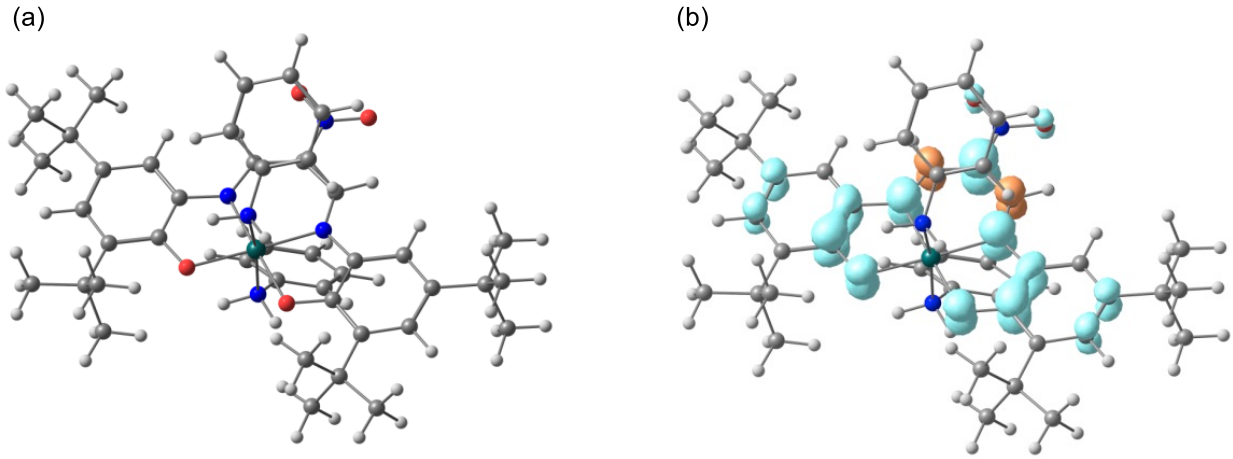

Figure S6. (a) DFT optimized structure of **[1^{H}]**$^{+}$. (b) Spin density plot of **[1^{H}]**$^{+}$

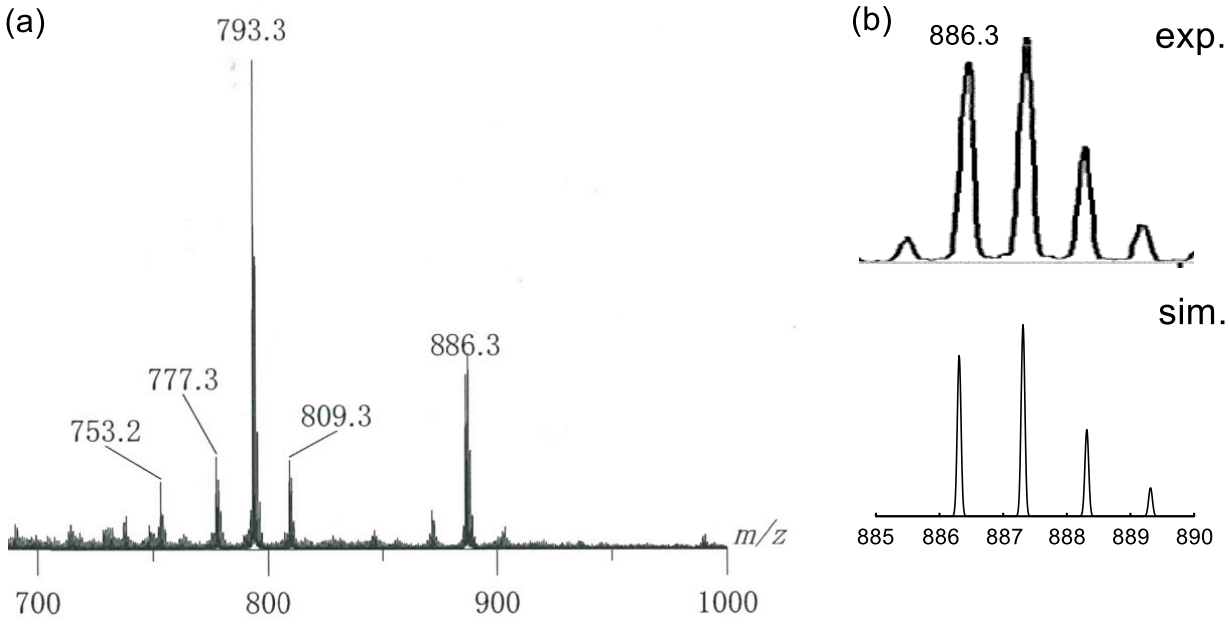

Figure S7. (a) FAB−MS (positive ion mode) spectrum of a reaction solution of $\mathbf{1^H}$ with TsN_3. (b) Enlarged view of the peaks at m/z =887.3. This isotope distribution patterns correspond to a 2:3 mixture of $[Rh+L+NTs+A^H+H]^+$ and $[Rh+L+NTs+ A^H+2H]^+$.

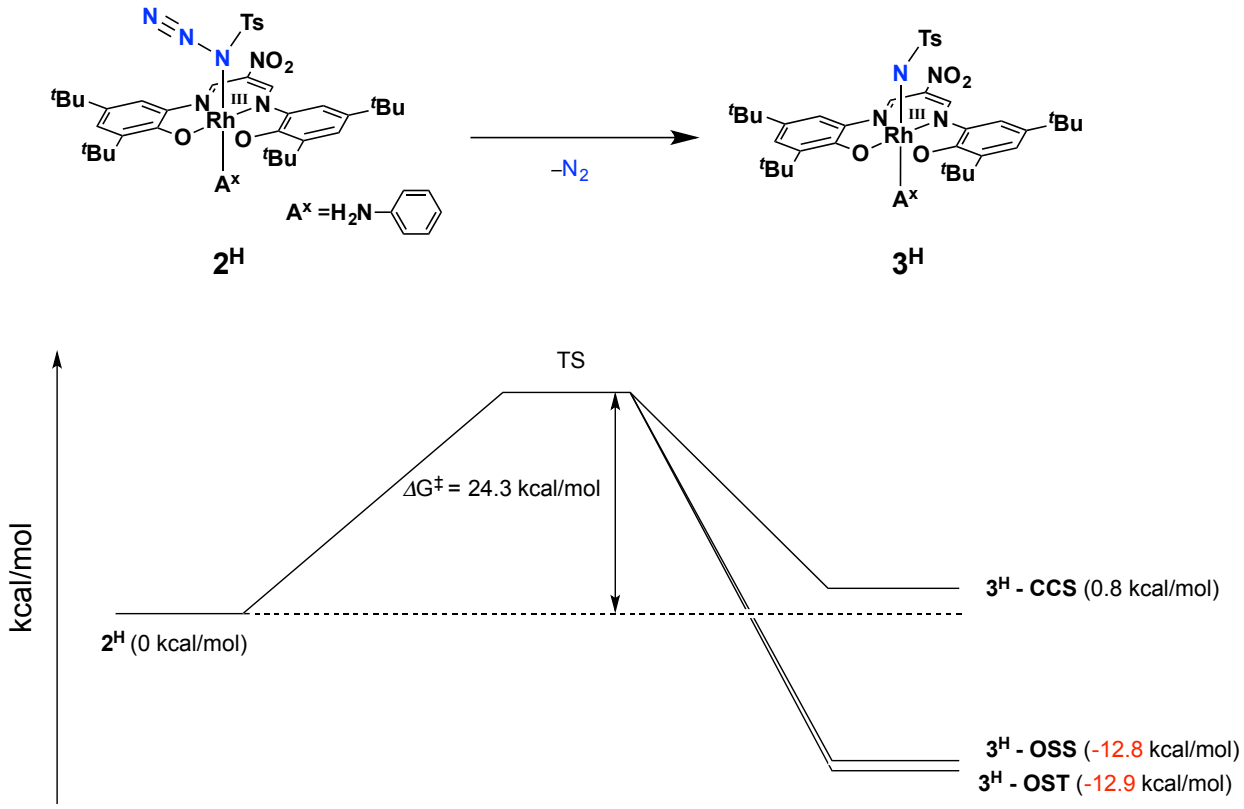

Figure S8−1. Free energy profile for the formation of $\mathbf{3^H}$.

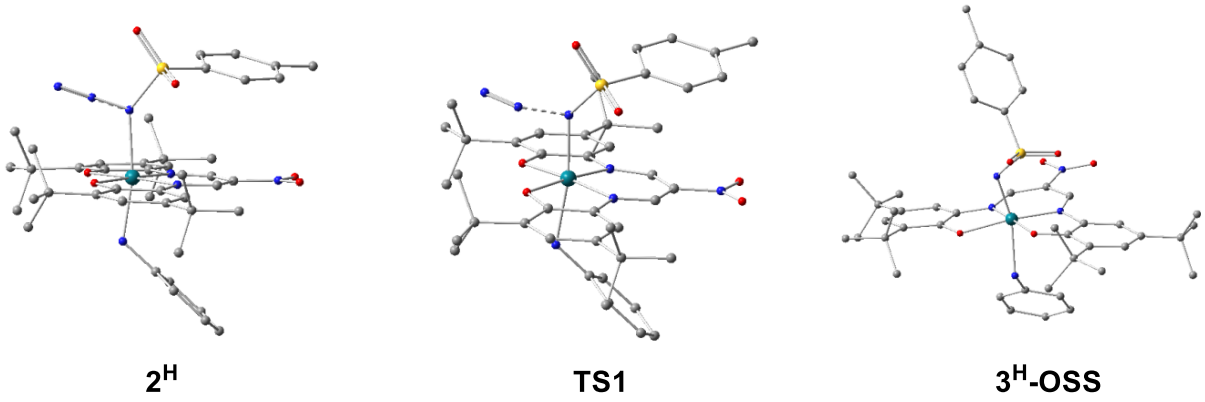

Figure S8−2. DFT optimized structures (B3LYP/SDD) of intermediates and transition states in the formation of $\mathbf{3^H}$.

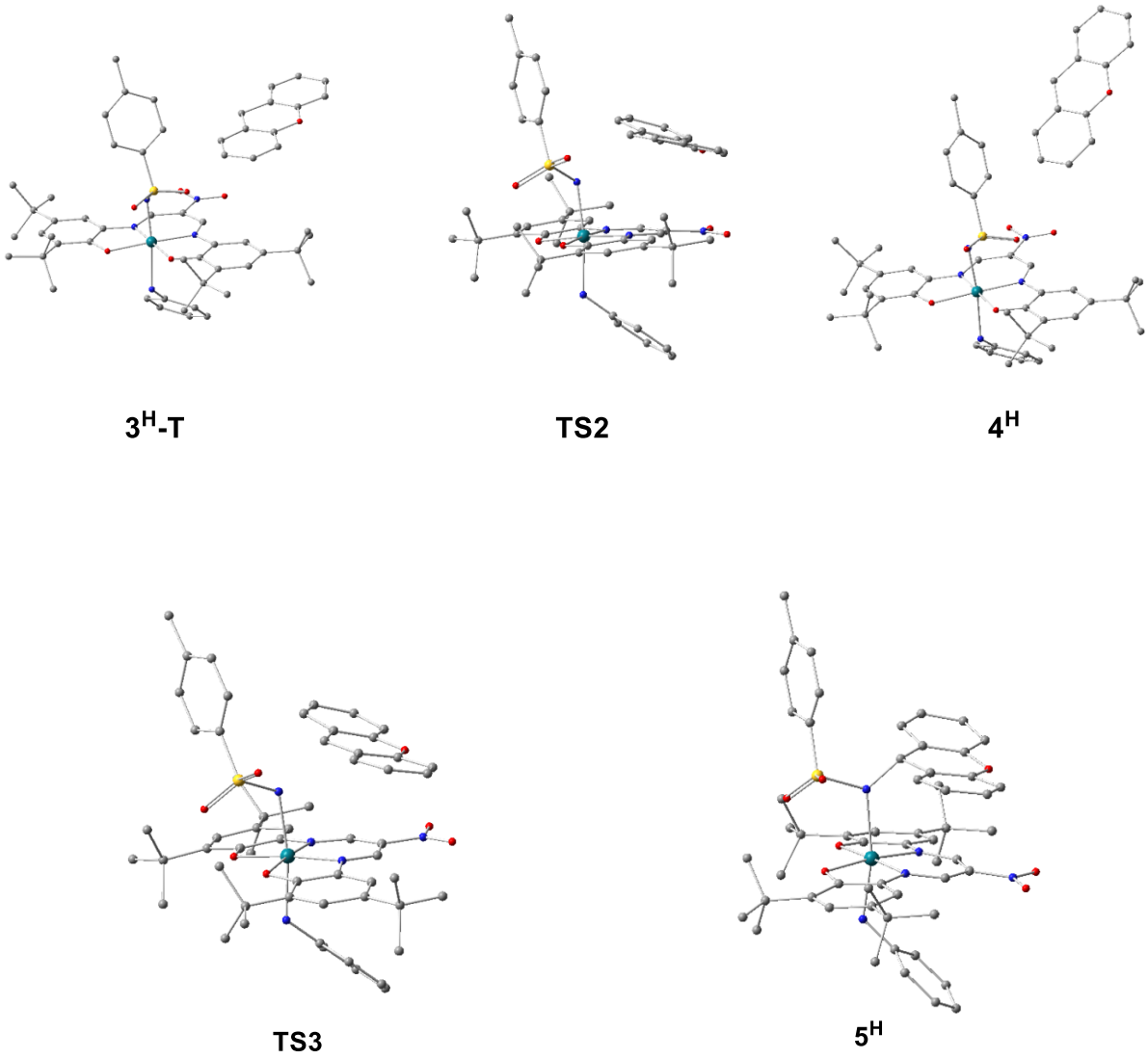

Figure S9. DFT optimized structures (B3LYP/SDD) of intermediates and transition states in the amination reaction of xanthene.

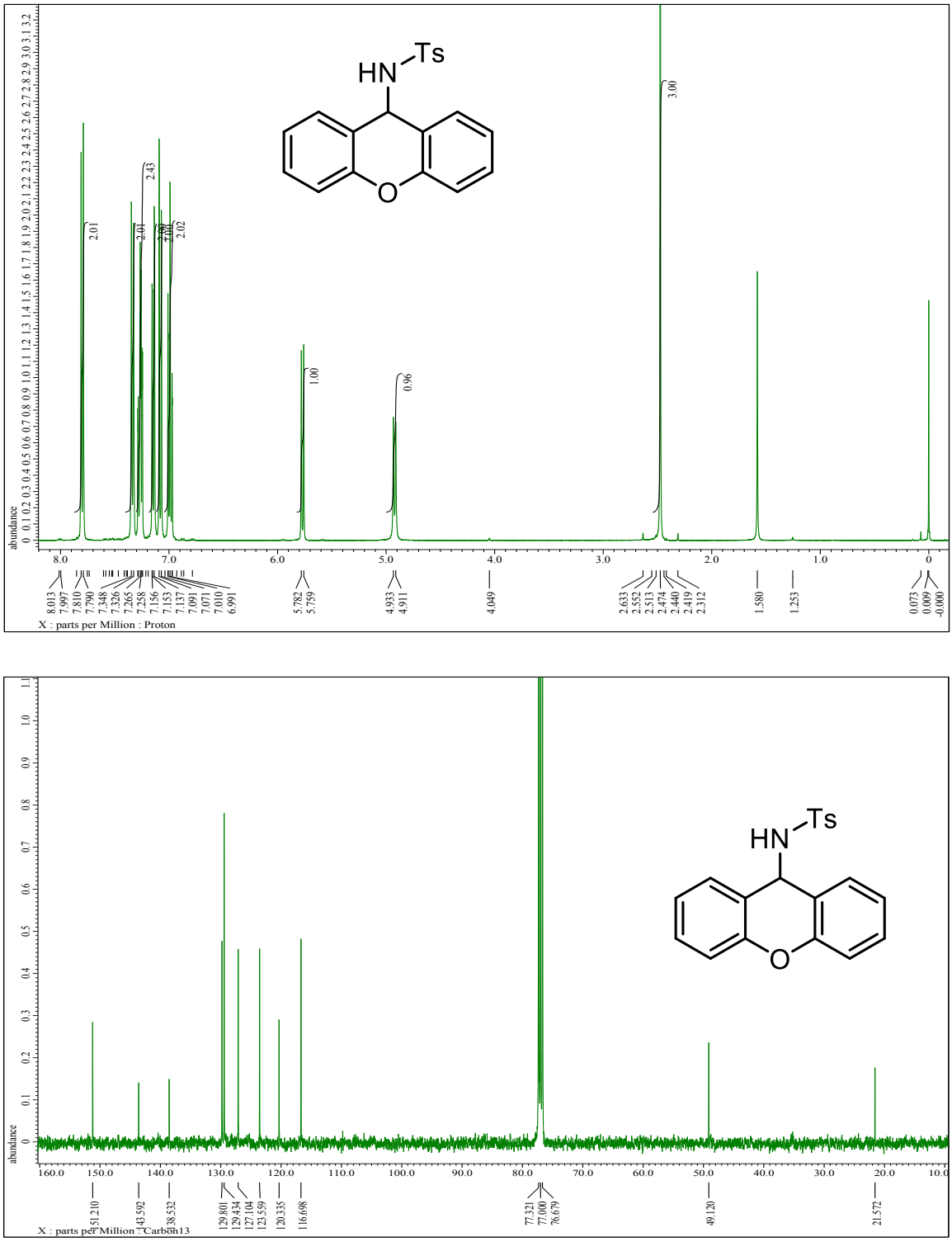

Figure S10−1. ^{1}H NMR (top) and ^{13}C NMR (bottom) chart of *N*-xanthyl-*p*-toluenesulfonamide (Solvent: $CDCl_3$).

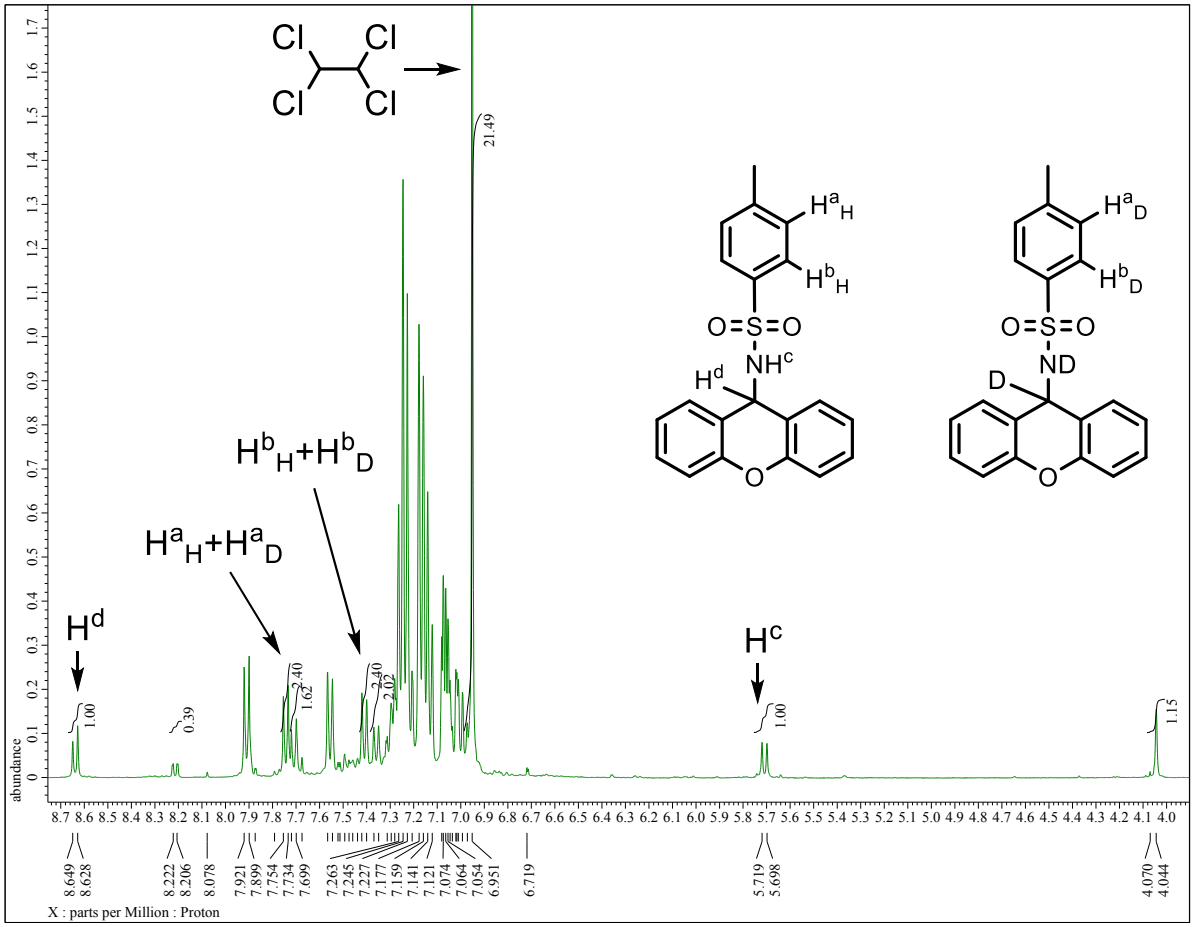

Figure S10–2. ^{1}H NMR chart of kinetic isotope effect experiment (Solvent: DMSO-d_6).