Supplementary Information

Rhodium(II)/Rhodium(III) Redox Couple for C–H Bond Amination with Alkylazides: a Rhodium(III)-nitrenoid Intermediate with a Tetradentate [14]-Macrocyclic Ligand

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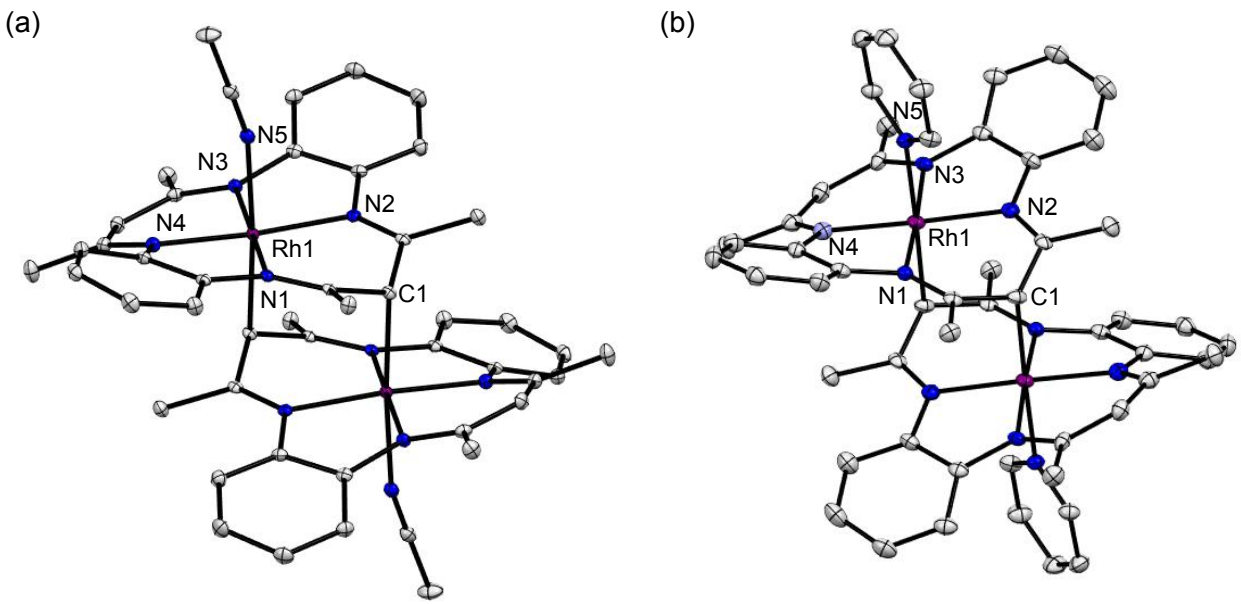

Fig. S1 Intermolecular interaction of $\mathbf{2}^{CH_3CN}$ (a) and $\mathbf{2}^{Py}$ (b). Hydrogen atoms, counter anions, and solvent molecules are omitted for clarity.

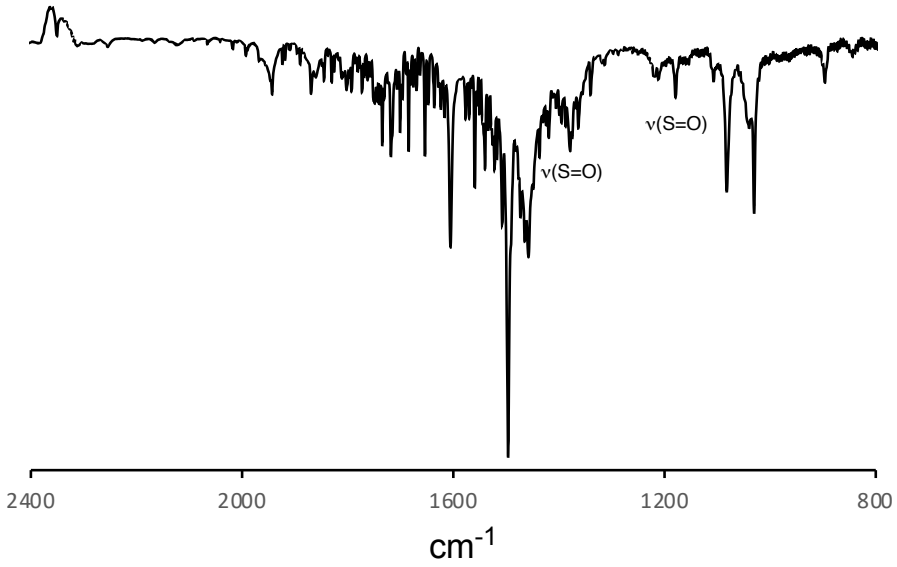

Fig. S2 IR spectrum of a reaction solution of $[Rh(TMAA)]_2$ and 2 equiv of N_3-Trs in toluene.

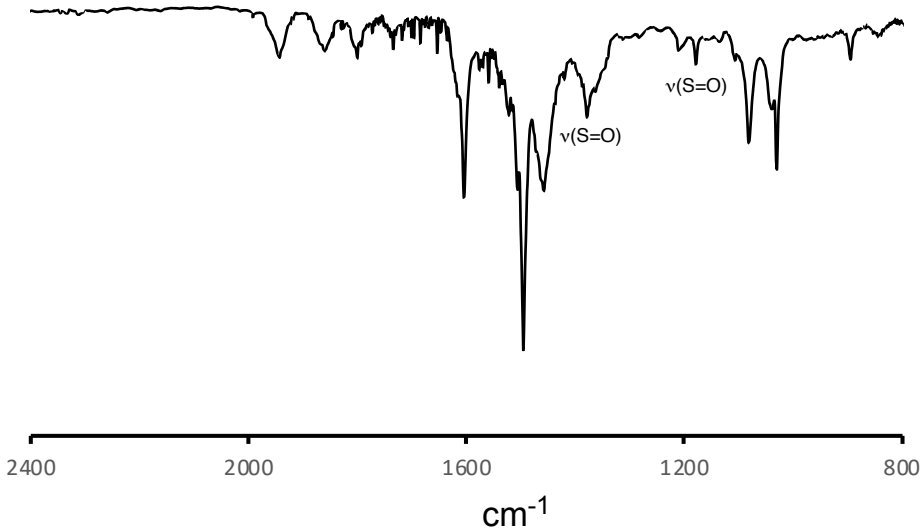

Fig. S3 IR spectrum of a reaction solution of $[Rh(TMAA)]_2$ and 2 equiv of N_3-Ns in toluene.

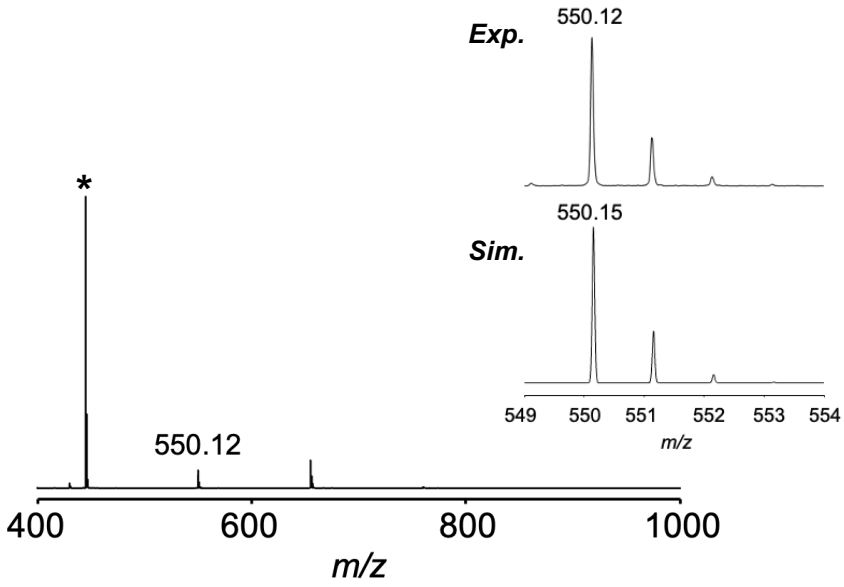

Fig. S4 An ESI-mass spectrum of a reaction solution of $[Rh(TMAA)]_2$ with N_3-CH_2Ph in toluene. Inset: an expanded spectrum at around *m*/*z* = 550.12 and a simulation spectrum for [Rh(N-CH_2Ph)(TMAA)]. A peak cluster marked with * corresponds to [Rh(TMAA)].

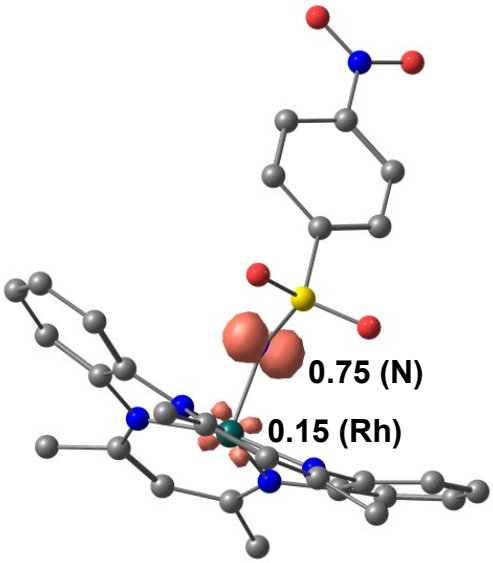

Fig. S5 DFT calculated structure of [Rh(N•Ns)(TMAA)] (2N•Ns) and the spin density plot.

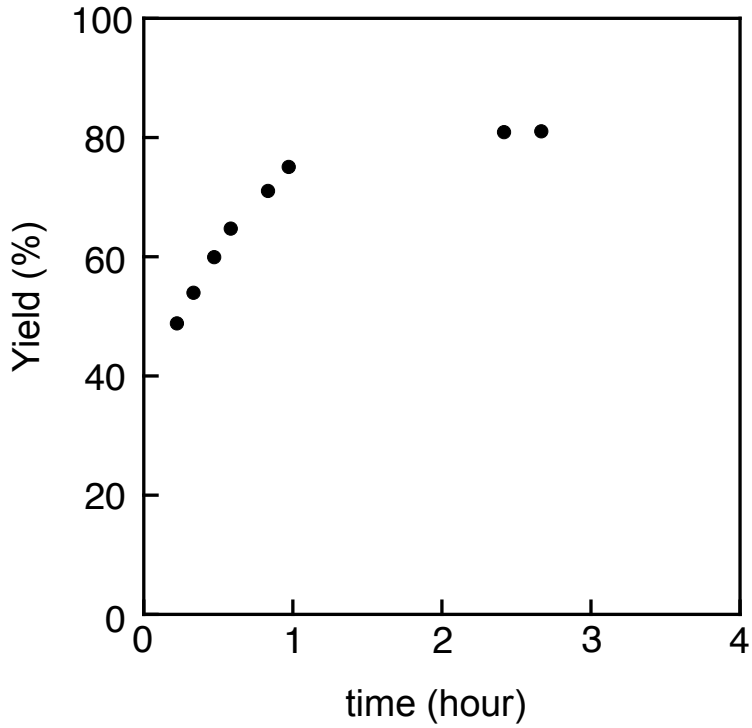

Fig. S6 Plot of yields of sultam against reaction times in a catalytic amination of N_3-Trs (70 μmol)) in the presence of $[Rh(TMAA)]_2$ (3.5 μmol) in toluene.

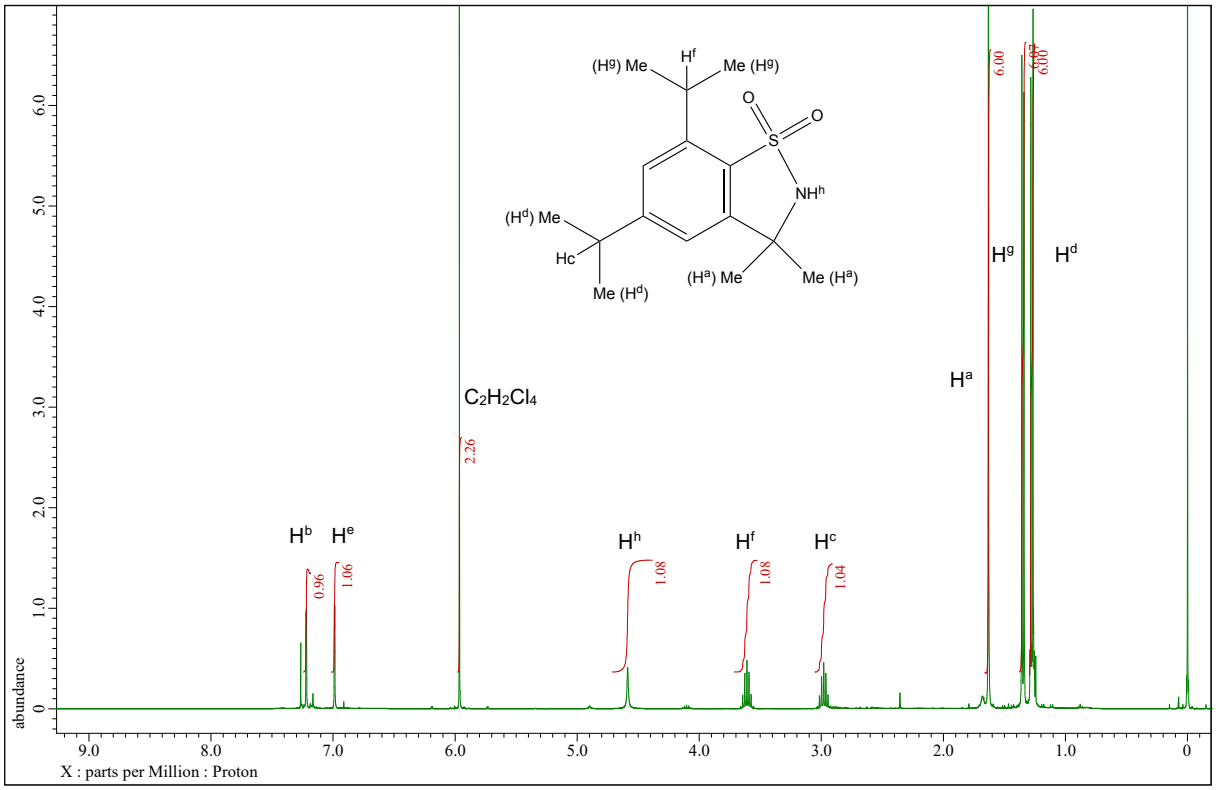

Fig. S7 ^{1}H-NMR spectrum of sultam obtained from trisylazide in the presence of $[Rh(TAMM)]_2$ (5% mol) at 100 ºC for 24 h. A peak around 6 ppm is due to the internal standard (1,1,2,2-tetrachloroethane). Ha ~ Hh were assigned by comparing chemical shifts of those reported in literature (J. V. Ruppel, R. M. Kamble and X. P. Zhang, *Org. Lett.*, 2007, **9**, 4889).

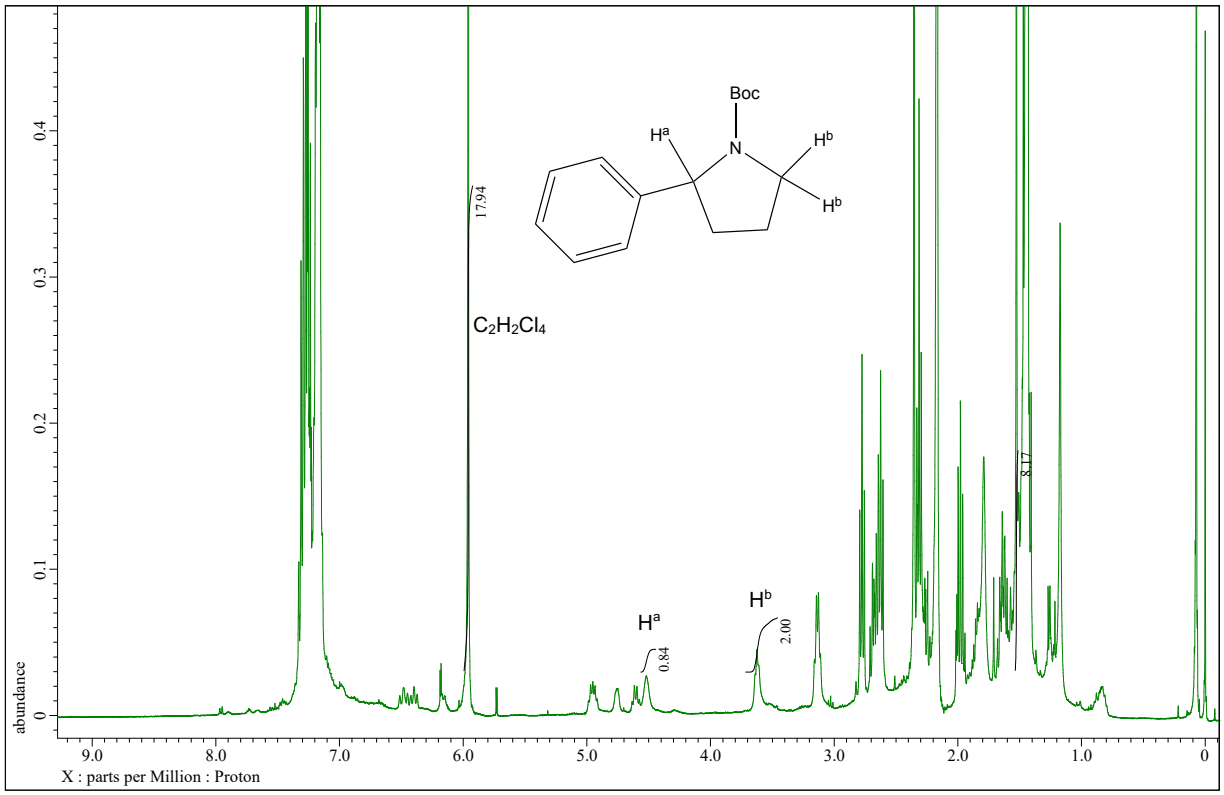

Fig. S8 ^{1}H-NMR spectrum of obtained solid by a reaction of 1-azido-4-phenylbutane and $(Boc)_2O$ in the presence of $[Rh(TAMM)]_2$ (5% mol) at 100 ºC for 24 h. A peak around 6 ppm is due to the internal standard (1,1,2,2-tetrachloroethane). Ha and Hb were assigned by comparing chemical shifts of those reported in literature (E. T. Hennessy and T. A. Betley, *Science*, 2013, **340**, 591).

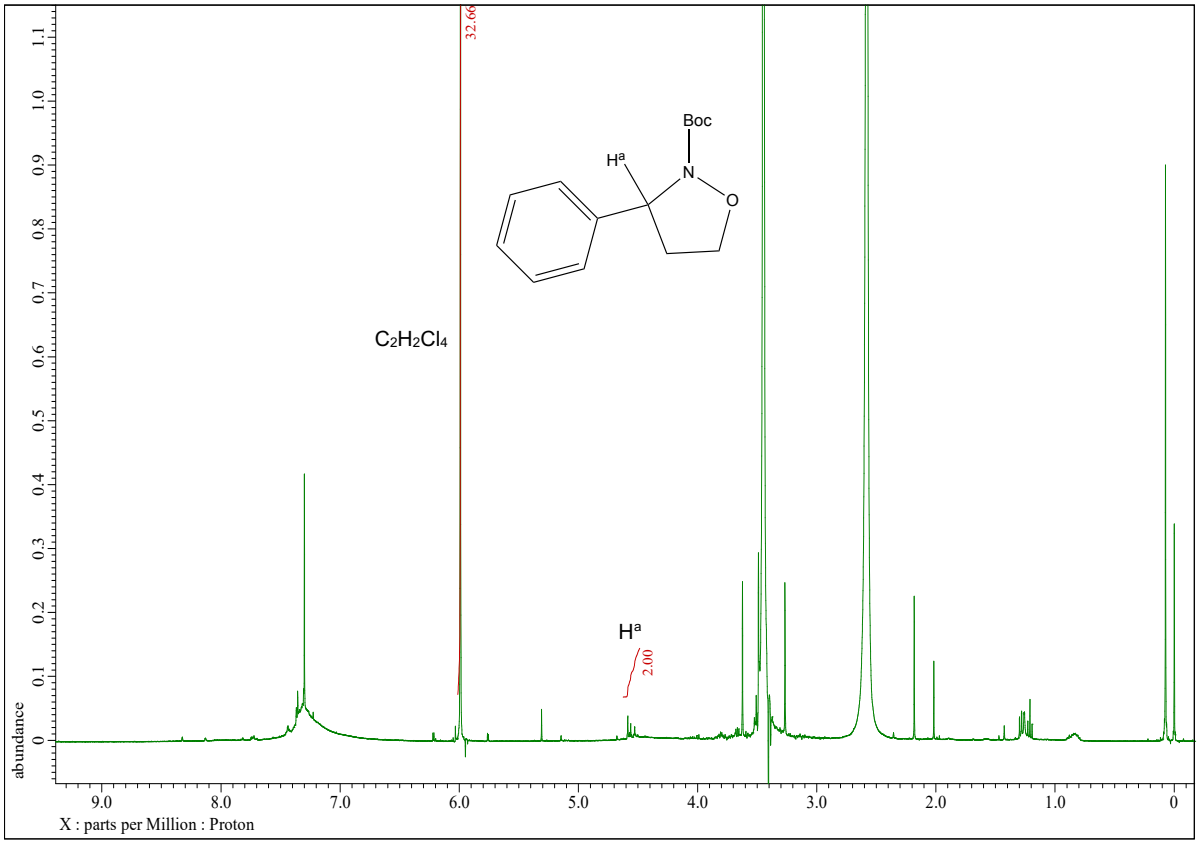

Fig. S9 ^{1}H-NMR spectrum of obtained solid by a reaction of benzyl-2-azidoethyl-ether and $(Boc)_2O$ in the presence of $[Rh(TAMM)]_2$ (5% mol) at 100 ºC for 24 h. A peak around 6 ppm is due to the internal standard (1,1,2,2-tetrachloroethane). Ha was assigned by comparing a chemical shift of that reported in literature (E. T. Hennessy and T. A. Betley, *Science*, 2013, **340**, 591).

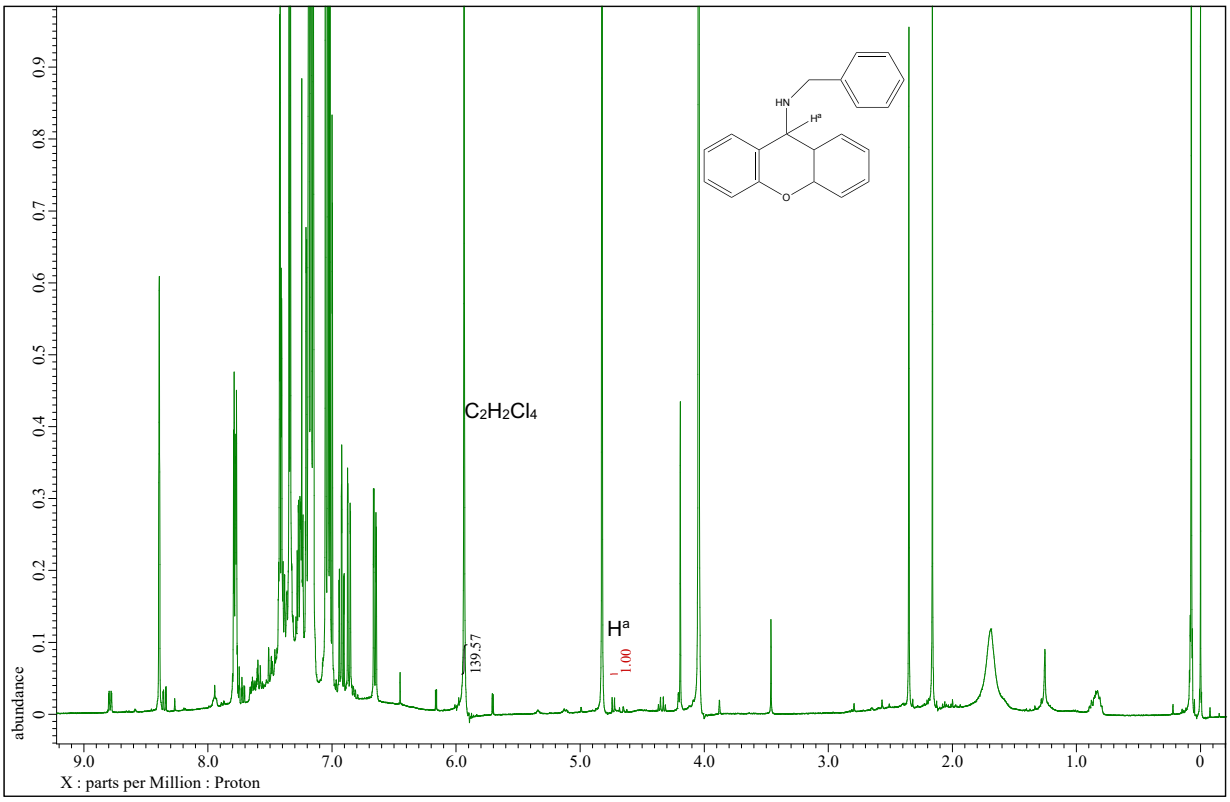

Fig. S10 ^{1}H-NM R spectrum of obtained solid by a reaction of xanthene and benzylazide in the presence of $[Rh(TAMM)]_2$ (5% mol) at 100 ºC for 24 h. A peak around 6 ppm is due to the internal standard (1,1,2,2-tetrachloroethane). Ha was assigned by comparing a chemical shift of methine proton of *N*-(diphenylmethyl)methylamine reported in literature (S. Cicchi, M. Bonanni, F. Cardona and J. Revuelta, *Org. Lett.*, 2003, **5**, 1773).

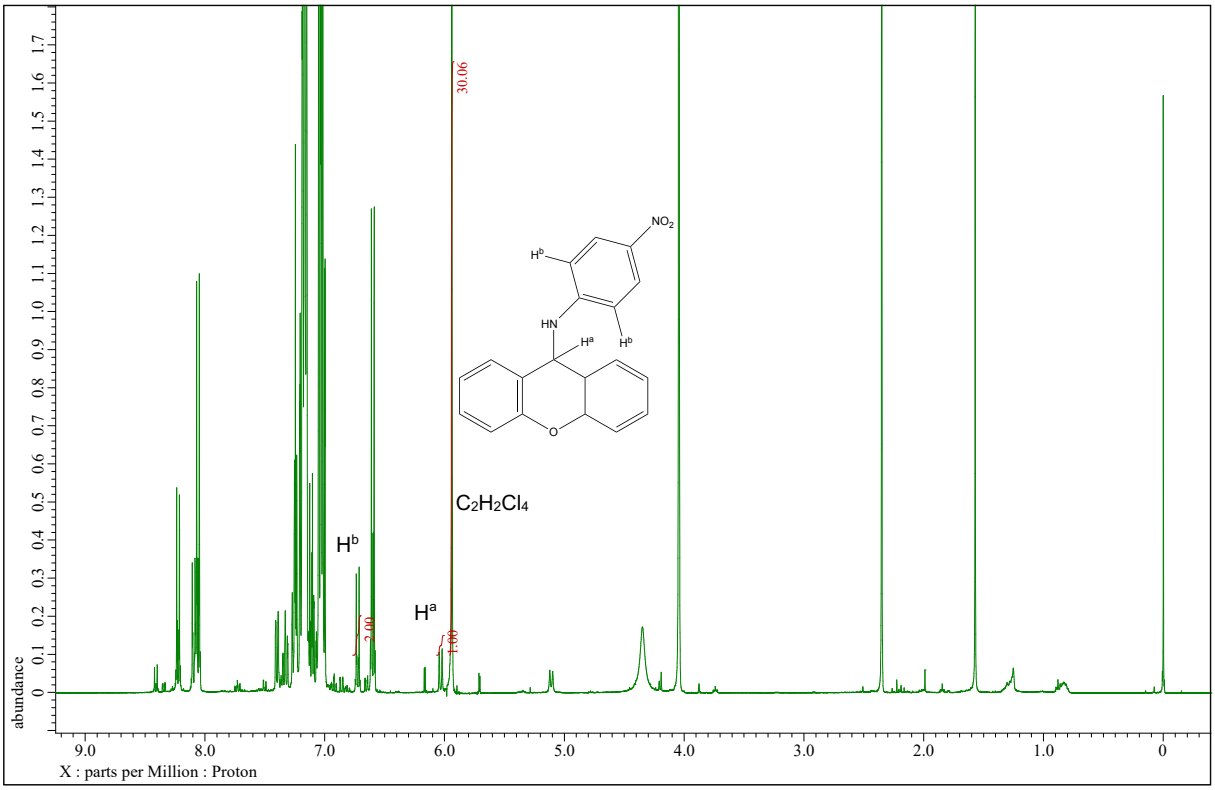

Fig. S11 ^{1}H-NMR spectrum of obtained solid by a reaction of xanthene and 4-nitro-phenylazide in the presence of $[Rh(TAMM)]_2$ (5% mol) at 100 ºC for 24 h. A peak around 6 ppm is due to the internal standard (1,1,2,2-tetrachloroethane). Ha and Hb were assigned by comparing chemical shifts of those reported in literature (Y. Liu and C.-M. Che, *Chem. Eur. J*, 2010, **16**, 10494).

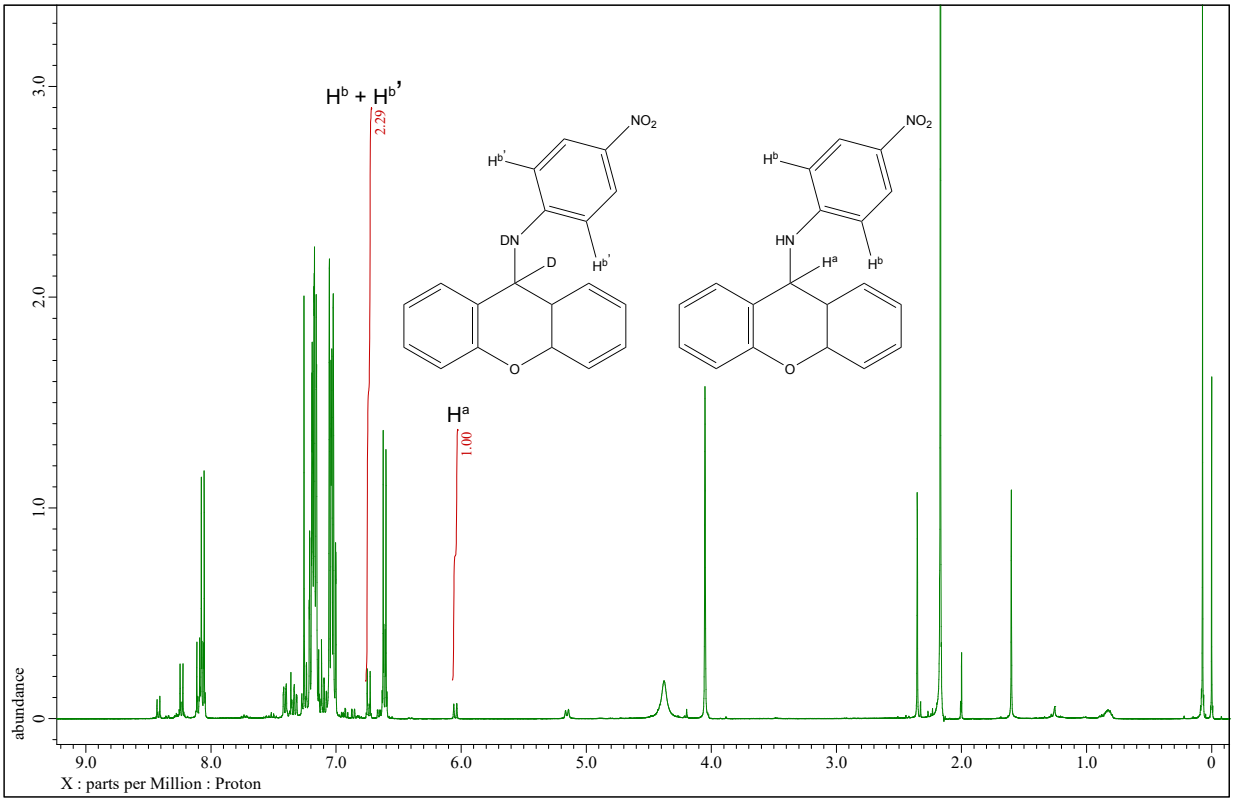

Fig. S12 ^{1}H-NMR spectrum of obtained solid by a reaction of xanthene, xanthene-d_2 (1 : 1), and 4-nitro-phenylazide in the presence of [Rh(TAMM)]$_2$ (5% mol) at 100 ºC for 24 h. Ha and Hb were assigned by comparing chemical shifts of those reported in literature (Y. Liu and C.-M. Che, *Chem. Eur. J*, 2010, **16**, 10494).

Table S1. Crystallographic Data for $[Rh^{III}(TMAA)(CH_3CN)]PF_6 \bullet CH_3CN$ ($2^{CH3CN} \bullet CH_3CN$) and $[Rh^{III}(TMAA)(py)]PF_6$ (2^{py})

	$2^{CH3CN} \bullet CH_3CN$	2^{py}
formula	$C_{26}H_{28}F_6N_6PRh$	$C_{27}H_{27}F_6N_5PRh$
fw	672.42	669.41
cryst system	Triclinic	Monoclinic
space group	*P*-1 (#2)	*C*2/c (#15)
a, Å	8.6913(8)	13.4897(13)
b, Å	11.5969(12)	20.8788(18)
c, Å	13.7677(14)	18.4267(19)
α, deg	71.972(5)	90
β, deg	85.744(6)	98.183(7)
γ, deg	74.916(5)	90
V, Å^3	1274.1(2)	5137.0(9)
Z	2	8
ρ, g cm^{-3}	1.753	1.731
μ, cm^{-1}	8.07	8.00
reflns. obsd	12505	23608
parameters	367	365
*R*1[a]	0.0280	0.0618
*wR*2[b]	0.0638	0.1365
GOF	1.039	1.112

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = (\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(F_o^2)^2)^{1/2}$.

Table S2. Optimized structure of 1.

Atom	X	Y	Z
Rh	-0.000006	0.000011	0.018567
N	-1.492378	1.330589	-0.079702
N	1.492339	-1.330584	-0.079611
N	-1.492341	-1.330643	-0.079578
C	2.737562	-0.717155	0.233011
C	-2.737617	0.717138	0.232899
C	1.293591	-2.591364	-0.497948
C	-1.293543	-2.591463	-0.497748
C	0.000042	-3.133966	-0.695763
H	0.000062	-4.151748	-1.070782
C	-2.737574	-0.717182	0.233021
C	3.884248	-1.393325	0.678062
H	3.878627	-2.471069	0.766649
C	2.437708	-3.520294	-0.880040
H	3.271962	-2.971347	-1.324414
H	2.078012	-4.251020	-1.608666
H	2.817238	-4.081060	-0.016984
C	-5.032905	-0.697384	1.086458
H	-5.900989	-1.253132	1.433888
C	-3.884314	-1.393283	0.678037
H	-3.878764	-2.471013	0.766676
N	1.492380	1.330609	-0.079666
C	-1.293567	2.591460	-0.497760
C	2.737622	0.717152	0.232961
C	-3.884485	1.393207	0.677645
C	-2.437596	-3.520655	-0.879384
C	5.032821	-0.697462	1.086587
C	-5.032994	0.697263	1.086232
C	1.293597	2.591456	-0.497729
C	-2.437593	3.520647	-0.879545
C	0.000010	3.134019	-0.695561
C	3.884459	1.393187	0.677834

H	-3.879122	2.470952	0.766023
H	-2.817154	-4.080928	-0.016024
H	-3.271850	-2.971994	-1.324126
H	-2.077846	-4.251795	-1.607560
H	5.900882	-1.253231	1.434043
C	5.032927	0.697191	1.086450
H	-5.901166	1.253008	1.433453
C	2.437624	3.520637	-0.879527
H	-3.271778	2.972006	-1.324430
H	-2.817284	4.080938	-0.016233
H	-2.077720	4.251803	-1.607652
H	0.000020	4.151874	-1.070412
H	3.879095	2.470934	0.766284
H	5.901093	1.252887	1.433761
H	2.077787	4.251681	-1.607770
H	2.817186	4.081058	-0.016238
H	3.271876	2.971985	-1.324255

Table S3. Optimized structure of $2^{N•Ns}$.

Atom	X	Y	Z
C	-3.538926	-1.225787	-0.584170
C	-2.890436	-0.001857	-0.791032
C	-3.539822	1.221711	-0.584805
C	-4.869163	1.225320	-0.151952
C	-5.507973	-0.002590	0.060690
C	-4.868267	-1.230141	-0.151309
N	-0.405995	-0.000323	0.141879
Rh	1.525787	0.000863	0.221547
N	1.896441	1.519146	-1.052779
C	2.449050	1.297148	-2.253807
C	2.917140	2.434397	-3.146137
N	1.898622	-1.516896	-1.052800
C	2.450927	-1.294099	-2.253811
C	2.712289	0.001721	-2.758382

N	1.603538	1.522186	1.561859
C	1.885714	1.298261	2.851902
C	2.172314	2.434339	3.822572
N	1.605954	-1.520310	1.561864
C	1.346791	-2.756177	0.929564
C	1.500554	-2.752656	-0.495647
C	1.128753	-3.896977	-1.223389
C	0.662458	-5.044787	-0.575133
C	0.519370	-5.052308	0.817480
C	0.840431	-3.909618	1.557532
C	1.342403	2.757605	0.929490
C	0.834047	3.910237	1.557337
C	0.511168	5.052360	0.817201
C	0.654412	5.045013	-0.575394
C	1.122673	3.897945	-1.223548
C	1.496312	2.754275	-0.495716
C	1.887819	-1.295926	2.851895
C	2.176290	-2.431579	3.822512
C	2.024075	0.001274	3.403786
C	2.920705	-2.430667	-3.146122
H	2.291413	0.001486	4.454559
H	0.631614	3.907838	2.619782
H	2.661622	3.275572	3.325420
H	2.826514	2.072261	4.619326
H	1.253487	2.801887	4.295186
H	0.119661	-5.926077	1.327230
H	0.638148	-3.907509	2.620011
H	1.133064	-3.876848	-2.304114
H	1.258098	-2.800526	4.295271
H	2.666779	-3.272067	3.325264
H	2.830075	-2.068524	4.619162
H	0.109944	5.925483	1.326868
H	0.370691	-5.911070	-1.164490
H	3.280587	-3.282441	-2.563804

H	2.112341	-2.775984	-3.801583
H	3.733144	-2.076464	-3.785257
H	3.191491	0.002072	-3.730781
H	1.127121	3.877775	-2.304271
H	0.361265	5.910781	-1.164824
H	3.730107	2.081381	-3.785261
H	2.108264	2.778486	-3.801613
H	3.275763	3.286718	-2.563846
H	-5.409478	-2.154513	0.019889
H	-5.411052	2.149386	0.018755
S	-1.166899	-0.001385	-1.366766
O	-0.960839	1.275655	-2.094564
O	-0.959734	-1.278936	-2.093350
H	-3.011522	2.151722	-0.775288
H	-3.009933	-2.155501	-0.774180
N	-6.912449	-0.002981	0.521070
O	-7.459422	1.091705	0.700732
O	-7.458584	-1.097971	0.701425

Table S4. Optimized structure of 1^{N3Trs}.

Atom	X	Y	Z
C	-1.741654	-2.867288	-0.854508
C	-1.878702	-2.984266	0.574930
C	-1.385578	-4.139610	1.209463
C	-0.798362	-5.183338	0.481137
C	-0.659900	-5.067706	-0.905063
C	-1.111914	-3.912279	-1.556749
N	-2.401965	-1.847986	1.231355
C	-2.982610	-1.785677	2.436464
C	-3.411026	-0.568427	3.029603
C	-3.350119	0.786419	2.606886
C	-3.998442	1.776643	3.565286
N	-2.157759	-1.638093	-1.408612
C	-2.485951	-1.374438	-2.680070

C	-2.819709	-0.075374	-3.141835
C	-2.857344	1.194406	-2.508841
C	-3.308864	2.334973	-3.410466
Rh	-2.354002	-0.219139	0.022364
N	-2.832300	1.162657	1.430726
C	-2.661012	2.477010	0.935007
C	-2.524449	2.588174	-0.493314
C	-2.218102	3.846469	-1.043933
C	-2.084233	4.985376	-0.240062
C	-2.219583	4.877781	1.147297
C	-2.486826	3.629421	1.723984
N	-2.588027	1.372158	-1.209605
N	0.176856	0.171793	0.346132
S	1.253013	0.620473	-1.042181
O	0.933300	2.011683	-1.388737
C	-2.608446	-2.466850	-3.733364
C	-3.313151	-3.032079	3.247463
C	2.928750	0.448369	-0.345259
C	3.763067	1.586943	-0.154243
C	5.094435	1.331505	0.216328
C	5.601363	0.046206	0.424100
C	4.721888	-1.034893	0.290212
C	3.381101	-0.878087	-0.082132
C	3.363995	3.057976	-0.333958
C	3.759079	3.549564	-1.744377
C	2.528577	-2.151219	-0.153286
C	2.946380	-3.021626	-1.356786
C	7.060570	-0.159030	0.805048
C	7.812144	-0.992547	-0.253936
C	3.959669	3.977671	0.751795
C	7.200488	-0.786556	2.208006
C	2.594230	-2.950142	1.165968
O	0.992659	-0.437099	-2.021767
H	-3.892042	-0.700741	3.992790

H	-1.410021	-4.215151	2.288352
H	-3.590520	-3.869246	2.601389
H	-4.151080	-2.817185	3.915136
H	-2.469775	-3.349053	3.873546
H	-2.081029	5.746128	1.787871
H	-2.503182	3.553282	2.802997
H	-2.016921	3.936888	-2.102509
H	-3.264285	2.229554	4.243051
H	-4.506409	2.581474	3.027354
H	-4.733162	1.254120	4.182788
H	-0.425766	-6.060775	1.005575
H	-1.835120	5.939228	-0.700194
H	-3.920116	3.060769	-2.867578
H	-2.454431	2.865507	-3.848411
H	-3.900408	1.931165	-4.235843
H	-3.094300	-0.044903	-4.190649
H	-0.918752	-3.809780	-2.615736
H	-0.175394	-5.853019	-1.481702
H	-3.296950	-2.139202	-4.516122
H	-1.643527	-2.674536	-4.212160
H	-2.987420	-3.399437	-3.306823
H	5.761516	2.178231	0.351010
H	5.084217	-2.041143	0.482218
H	7.529464	0.833257	0.838995
H	1.482198	-1.893555	-0.301456
H	8.873157	-1.077649	0.009550
H	7.404277	-2.007890	-0.325311
H	7.741382	-0.532557	-1.245933
H	8.258087	-0.868735	2.485753
H	6.693222	-0.180654	2.967135
H	6.768862	-1.794089	2.239304
H	3.506197	4.971635	0.662650
H	3.750358	3.601991	1.759880
H	5.043254	4.109820	0.653521

H	2.282703	3.144305	-0.256434
H	3.459484	4.596114	-1.875848
H	4.844012	3.484945	-1.894652
H	3.266252	2.958952	-2.522620
H	1.885680	-3.783882	1.114746
H	3.590113	-3.367397	1.355544
H	2.319598	-2.326461	2.024791
H	2.313162	-3.914758	-1.402322
H	2.826306	-2.470026	-2.294330
H	3.991048	-3.346672	-1.275741
N	0.417428	0.857832	1.369094
N	0.558870	1.424109	2.354942

Table S5. Optimized structure of TS($^{NTrs-N2}$).

Atom	X	Y	Z
C	3.296826	0.846727	0.079252
C	2.642308	-0.403265	0.255777
C	3.309422	-1.632136	0.006814
C	4.685289	-1.566878	-0.273602
C	5.390731	-0.364170	-0.359618
C	4.668162	0.825609	-0.211545
S	0.952563	-0.398540	0.982891
O	0.846384	0.732280	1.932492
C	2.669719	-3.025595	-0.021640
C	2.998173	-3.772468	-1.332052
C	6.887382	-0.359218	-0.639269
C	7.216317	0.313905	-1.988416
C	2.620837	2.220831	0.131712
C	2.846974	2.996417	-1.184132
N	-0.086288	0.036190	-0.352034
N	0.414354	-0.866586	-1.534901
N	-0.138360	-1.009230	-2.547365
O	0.649988	-1.737967	1.536401
C	3.087659	-3.850915	1.212661

C	3.098776	3.033695	1.351402
C	7.679914	0.293114	0.512685
Rh	-2.090481	0.233242	0.014422
N	-2.355298	-1.254262	1.353201
C	-2.342510	-2.514658	0.717088
C	-2.574730	-2.482889	-0.696824
C	-2.456911	-3.674705	-1.436464
C	-2.158652	-4.886788	-0.806685
C	-1.931231	-4.917488	0.575060
C	-2.002709	-3.738327	1.322106
N	-2.773604	-1.195728	-1.241922
C	-3.381630	-0.882158	-2.395181
C	-4.129923	-1.918420	-3.219090
C	-3.449630	0.437154	-2.902417
C	-2.944373	1.670105	-2.426128
C	-3.308154	2.877162	-3.278042
N	-2.271911	1.789051	-1.272346
C	-1.694292	2.954103	-0.728901
C	-1.498390	2.931151	0.693055
C	-0.825808	4.008199	1.301240
C	-0.392260	5.106755	0.552692
C	-0.585767	5.129700	-0.834044
C	-1.212140	4.051562	-1.466963
N	-1.911158	1.746295	1.335640
C	-2.169369	1.566839	2.640310
C	-2.244696	2.729104	3.617201
C	-2.471179	0.305970	3.202316
C	-2.544541	-0.997442	2.654435
C	-2.944010	-2.079992	3.643651
H	-3.999377	0.519206	-3.833375
H	-1.272998	4.047620	-2.547091
H	-3.508852	3.758986	-2.664240
H	-4.202142	2.649921	-3.863669
H	-2.508189	3.127384	-3.985357

H	-2.062204	-5.791421	-1.402940
H	-2.536670	-3.654262	-2.515038
H	-1.716761	-3.766131	2.364014
H	-3.466211	-2.408722	-3.941530
H	-4.579869	-2.689485	-2.588894
H	-4.923001	-1.424669	-3.786050
H	-0.217279	5.961610	-1.430160
H	-1.651141	-5.846209	1.067137
H	-3.582493	-2.837157	3.181629
H	-2.060469	-2.579577	4.058570
H	-3.487607	-1.627397	4.476503
H	-2.677621	0.342068	4.266082
H	-0.580005	3.969461	2.353009
H	0.130616	5.920401	1.050573
H	-2.903698	2.461835	4.446834
H	-1.258165	2.953650	4.040204
H	-2.632441	3.634695	3.143911
H	5.223339	-2.497603	-0.438446
H	5.181891	1.776581	-0.328870
H	7.207318	-1.407641	-0.707838
H	1.546154	2.090056	0.234521
H	8.758167	0.233927	0.319884
H	7.418546	1.352203	0.624943
H	7.473938	-0.204574	1.466947
H	8.291358	0.251438	-2.197387
H	6.677929	-0.167056	-2.812818
H	6.939287	1.374918	-1.981734
H	2.434145	-4.712676	-1.364001
H	2.714569	-3.178822	-2.208360
H	4.061009	-4.025399	-1.422225
H	1.588795	-2.921036	0.018463
H	2.616703	-4.841349	1.182498
H	4.174749	-3.995852	1.250761
H	2.771328	-3.351891	2.133619

H	2.270666	3.928465	-1.160248
H	3.900043	3.257965	-1.341881
H	2.510243	2.412755	-2.048679
H	2.595354	4.007852	1.372920
H	2.862430	2.504327	2.279407
H	4.180613	3.214212	1.319430

Table S6. Optimized structure of 2 ^{NTrs}.

Atom	X	Y	Z
C	2.317079	2.824400	-0.138529
C	3.080177	1.494868	-0.143206
C	2.515982	0.216562	-0.392766
C	3.257838	-0.974246	-0.158902
C	4.617598	-0.840134	0.157985
C	5.243807	0.404860	0.294214
C	4.448604	1.547305	0.172737
N	-0.100038	0.022169	0.283593
Rh	-2.025609	-0.117024	0.147115
N	-2.153160	-1.639296	-1.169911
C	-2.594851	-1.438865	-2.419324
C	-2.888423	-2.591880	-3.364724
N	-2.374170	1.389299	-1.148078
C	-2.783472	1.144862	-2.400635
C	-2.897416	-0.158386	-2.939011
N	-2.134272	-1.661346	1.462096
C	-2.568023	-1.475881	2.715162
C	-2.878267	-2.642242	3.642247
N	-2.355341	1.376214	1.483871
C	-2.133113	2.638068	0.890235
C	-2.136640	2.643461	-0.543537
C	-1.787550	3.825971	-1.219678
C	-1.490484	4.999239	-0.518634
C	-1.495856	4.997579	0.880934
C	-1.794461	3.820074	1.574985

C	-1.732387	-2.869145	0.850735
C	-1.226420	-3.999833	1.518837
C	-0.761254	-5.111654	0.808290
C	-0.756329	-5.092186	-0.591136
C	-1.220250	-3.964127	-1.275615
C	-1.736101	-2.854339	-0.583002
C	-2.756683	1.112146	2.733584
C	-3.232016	2.207968	3.676685
C	-2.855061	-0.199728	3.258850
C	-3.242386	2.256565	-3.329623
H	-3.231810	-0.234443	4.274946
H	-1.136909	-4.000863	2.596626
H	-3.259682	-3.505004	3.090370
H	-3.631951	-2.334112	4.370894
H	-1.990585	-2.958889	4.203078
H	-1.228764	5.893918	1.436357
H	-1.704069	3.818242	2.652695
H	-1.676345	3.822060	-2.294767
H	-2.399285	2.641404	4.243656
H	-3.734315	3.014459	3.136622
H	-3.933040	1.783586	4.399449
H	-0.367377	-5.968058	1.351149
H	-1.213784	5.895710	-1.068952
H	-3.727297	3.069339	-2.783244
H	-2.397757	2.672528	-3.891715
H	-3.952243	1.851568	-4.054954
H	-3.272575	-0.178432	-3.955875
H	-1.111650	-3.928661	-2.350406
H	-0.353400	-5.931236	-1.153915
H	-3.650130	-2.283826	-4.085091
H	-1.992849	-2.872804	-3.931659
H	-3.249774	-3.474146	-2.830596
H	4.906459	2.520685	0.335831
C	6.730686	0.521398	0.601271

H	5.200022	-1.745645	0.310328
C	2.686477	-2.397062	-0.173577
S	0.836110	0.101713	-1.135254
O	0.746313	-1.156179	-1.921638
O	0.565140	1.346866	-1.900007
C	7.088494	-0.107790	1.964131
C	7.593462	-0.078854	-0.528420
H	6.965509	1.592685	0.661721
C	2.977457	-3.128319	1.154683
H	1.604602	-2.347464	-0.272170
C	3.210055	-3.200342	-1.381079
H	8.660234	0.067079	-0.318084
H	7.417679	-1.156319	-0.632118
H	7.365954	0.390477	-1.492109
H	8.151419	0.042149	2.190411
H	6.499029	0.338288	2.773146
H	6.896553	-1.187470	1.966599
C	2.506910	3.569805	1.200187
H	1.862908	4.457458	1.215645
H	2.227809	2.934020	2.048450
H	3.539236	3.905674	1.353746
C	2.722896	3.709114	-1.334405
H	1.252413	2.626135	-0.238045
H	2.159836	4.650600	-1.315723
H	3.792075	3.955067	-1.309796
H	2.504472	3.199187	-2.277364
H	2.460691	-4.095706	1.157231
H	4.046106	-3.322694	1.304531
H	2.615330	-2.548399	2.011539
H	2.782887	-4.210934	-1.376317
H	2.922700	-2.712511	-2.317201
H	4.303042	-3.296215	-1.358557

Table S7. Optimized structure of TS1.

Atom	X	Y	Z
C	3.749224	-0.023612	1.015287
C	2.571720	-0.358607	0.299158
C	2.624963	-0.813956	-1.037617
C	3.874584	-0.879888	-1.675543
C	5.057159	-0.533031	-1.014690
C	4.967305	-0.119980	0.322636
S	0.911997	-0.287335	1.091235
O	0.636631	-1.655261	1.611960
C	1.394762	-1.276440	-1.781918
C	1.241167	-0.749529	-3.201156
C	6.398413	-0.613728	-1.732321
C	7.344954	-1.635416	-1.068091
C	3.759370	0.350737	2.499969
C	3.704322	-0.934543	3.360499
N	-0.007145	0.181651	-0.243895
O	0.836787	0.817839	2.081650
C	1.097621	-2.760757	-1.608869
C	7.070073	0.770973	-1.844666
C	4.952697	1.227251	2.919513
Rh	-2.000653	0.311310	-0.054189
N	-1.999204	1.687244	-1.545135
C	-1.394961	2.885301	-1.108298
C	-1.309274	3.038573	0.315327
C	-0.597041	4.133628	0.837731
C	-0.020226	5.090027	-0.003889
C	-0.112644	4.946223	-1.393161
C	-0.777890	3.841744	-1.935622
N	-1.852692	1.977465	1.068370
C	-2.207286	1.982509	2.360157
C	-2.288595	3.266589	3.169677
C	-2.613912	0.819587	3.054229

C	-2.693888	-0.541331	2.676373
C	-3.228118	-1.466220	3.758821
N	-2.400084	-0.979560	1.442234
C	-2.401300	-2.315658	0.984677
C	-2.179728	-3.453563	1.780922
C	-2.135686	-4.733278	1.220676
C	-2.274510	-4.894893	-0.162694
C	-2.443858	-3.772905	-0.979921
C	-2.521597	-2.477370	-0.433952
N	-2.584175	-1.273736	-1.173720
C	-3.061361	-1.100592	-2.417504
C	-3.787292	-2.209846	-3.166893
C	-3.013903	0.136106	-3.104667
C	-2.527486	1.419631	-2.742892
C	-2.744239	2.499690	-3.793166
H	-2.905765	1.005040	4.081839
H	-1.965690	-3.342049	2.834402
H	-3.859969	-2.255452	3.343730
H	-3.819300	-0.885070	4.470648
H	-2.410382	-1.937681	4.316833
H	0.535939	5.918381	0.429373
H	-0.429973	4.212395	1.902850
H	-0.760481	3.703484	-3.008415
H	-1.329529	3.489612	3.652421
H	-2.571050	4.121735	2.550635
H	-3.033433	3.147820	3.960638
H	-1.948138	-5.592183	1.861070
H	0.366004	5.663355	-2.056392
H	-2.966143	3.466851	-3.335159
H	-1.865285	2.620388	-4.438077
H	-3.582879	2.217411	-4.434541
H	-3.460668	0.103119	-4.092258
H	-2.460047	-3.915154	-2.051960
H	-2.206896	-5.882137	-0.614381

H	-4.471606	-1.765989	-3.893770
H	-3.092738	-2.852637	-3.721298
H	-4.364921	-2.841104	-2.486854
H	3.922027	-1.219239	-2.708524
H	5.878905	0.140813	0.851771
H	6.198181	-0.966280	-2.753258
H	2.850529	0.917250	2.706088
H	8.279322	-1.721075	-1.636441
H	7.603212	-1.332413	-0.046348
H	6.882958	-2.627724	-1.015380
H	8.003998	0.701130	-2.415952
H	6.413128	1.490150	-2.346767
H	7.313540	1.175522	-0.854976
H	0.149516	-3.029174	-2.087108
H	1.893572	-3.361797	-2.076332
H	1.040390	-3.035933	-0.551512
H	4.803338	1.568478	3.950638
H	5.904870	0.682393	2.898972
H	5.050166	2.114535	2.282871
H	3.672974	-0.673260	4.425578
H	2.816044	-1.531379	3.130900
H	4.591990	-1.557182	3.188733
H	0.451502	-0.600523	-1.114552
H	0.233016	-0.958094	-3.579036
H	1.410056	0.331790	-3.244778
H	1.951658	-1.232353	-3.889790

Table S8. Optimized structure of Int.

Atom	X	Y	Z
C	-3.305042	-0.676049	0.894489
C	-2.616915	-0.250790	-0.267997
C	-3.307417	0.429559	-1.335993
C	-4.732280	0.434217	-1.261903
C	-5.436422	-0.042308	-0.161274

C	-4.702865	-0.544395	0.927883
S	-0.923100	-0.889625	-0.565283
O	-0.857805	-2.241462	0.048897
C	-2.703082	1.166191	-2.417031
C	-3.459927	1.401176	-3.701031
C	-6.957984	0.020641	-0.129576
C	-7.583204	-1.386132	-0.024233
C	-2.635788	-1.244726	2.151956
C	-3.059490	-2.702464	2.418554
N	0.039736	0.241065	0.240596
Rh	2.078927	0.179810	0.098978
N	2.425202	-0.949066	-1.534469
C	2.291218	-2.328729	-1.251296
C	2.316482	-2.672162	0.138186
C	2.073138	-4.004418	0.515454
C	1.841157	-4.995911	-0.441630
C	1.804399	-4.658665	-1.798898
C	2.006667	-3.333358	-2.193481
N	2.455324	-1.578936	1.026355
C	2.880777	-1.612518	2.295513
C	3.440625	-2.876553	2.932445
C	2.932605	-0.465595	3.131889
C	2.598670	0.891929	2.919426
C	2.890198	1.812629	4.096254
N	2.141891	1.357602	1.746799
C	1.669909	2.653622	1.453070
C	1.643340	2.992683	0.057749
C	1.071939	4.220774	-0.327940
C	0.570584	5.119335	0.618882
C	0.596780	4.788136	1.978691
C	1.124483	3.558126	2.384455
N	2.094255	1.983312	-0.815663
C	2.486229	2.113862	-2.091456
C	2.720332	3.474462	-2.732567

C	2.803927	1.010559	-2.915755
C	2.778481	-0.390365	-2.699855
C	3.277129	-1.213491	-3.877910
O	-0.622598	-0.803622	-2.009921
C	-1.417331	1.932538	-2.296646
C	-2.913589	-0.340149	3.372601
C	-7.473716	0.940567	0.996733
H	3.326737	-0.667430	4.121759
H	1.059531	3.287969	3.429913
H	3.229910	2.796351	3.762282
H	3.671924	1.367226	4.716498
H	2.008499	1.953267	4.733279
H	1.637888	-6.014759	-0.119512
H	1.989076	-4.268307	1.560543
H	1.866719	-3.078314	-3.234166
H	2.649069	-3.489474	3.380114
H	3.975158	-3.490951	2.203796
H	4.133423	-2.601630	3.731473
H	0.174003	5.461902	2.720604
H	1.568641	-5.410373	-2.548819
H	3.832866	-2.095448	-3.550292
H	2.446001	-1.546063	-4.511173
H	3.935029	-0.597662	-4.496067
H	3.143679	1.290889	-3.906683
H	0.960505	4.461717	-1.376138
H	0.124984	6.054365	0.286699
H	3.461382	3.374558	-3.529452
H	1.804271	3.871655	-3.186452
H	3.087544	4.204898	-2.007073
H	-5.288384	0.897452	-2.072085
H	-5.232263	-0.870463	1.819746
H	-7.283524	0.455240	-1.084342
H	-1.555729	-1.270468	2.007681
H	-8.567579	1.016282	0.961895

H	-7.198718	0.552768	1.984998
H	-7.056595	1.949910	0.905870
H	-8.677841	-1.325748	-0.065750
H	-7.243306	-2.031975	-0.841544
H	-7.311314	-1.872455	0.920342
H	-2.748920	1.503258	-4.530284
H	-4.147370	0.585523	-3.945509
H	-4.041310	2.338017	-3.672398
H	-0.658566	1.547298	-2.990682
H	-1.610188	2.983729	-2.567279
H	-2.552562	-3.086635	3.312771
H	-4.140140	-2.787742	2.584572
H	-2.784219	-3.334428	1.569408
H	-2.364469	-0.713273	4.246297
H	-2.596314	0.692499	3.183578
H	-3.977369	-0.318150	3.635655
H	-0.175212	0.114480	1.235321
H	-0.992772	1.902523	-1.292535

Table S9. Optimized structure of TS2.

Atom	X	Y	Z
C	-3.482063	-1.561635	0.228938
C	-2.356542	-1.089625	-0.478395
C	-2.477255	-0.253289	-1.604928
C	-3.756667	0.221623	-1.947982
C	-4.896690	-0.170311	-1.234782
C	-4.737567	-1.076563	-0.174748
C	-1.312589	0.068299	-2.459085
N	0.267053	-0.287301	-0.686368
S	-0.670610	-1.497353	0.085280
Rh	1.882954	0.575590	0.360437
N	3.100355	0.241683	-1.228932
C	3.483134	-1.117539	-1.294671
C	3.273512	-1.871405	-0.088496

C	3.498712	-3.260396	-0.112793
C	3.959622	-3.903076	-1.266404
C	4.170273	-3.168974	-2.438817
C	3.914080	-1.793326	-2.453006
N	2.728193	-1.144708	0.991691
C	2.785506	-1.445621	2.298474
C	3.613952	-2.608193	2.823476
O	-0.318070	-2.840748	-0.449707
O	-0.639167	-1.294206	1.551296
C	-1.070835	1.496601	-2.855642
C	-0.820095	-1.006739	-3.397555
C	-6.270517	0.361038	-1.623671
C	-6.906584	1.183736	-0.483667
C	-3.406755	-2.555571	1.388903
C	-3.738855	-1.866374	2.728198
C	2.157070	-0.668393	3.299461
C	1.321615	0.473976	3.242873
C	0.869708	0.997156	4.597628
N	1.007294	1.094766	2.099614
C	0.105089	2.161575	1.913796
C	-1.000668	2.453331	2.732740
C	-1.892828	3.482885	2.409544
C	-1.711050	4.221059	1.235447
C	-0.639016	3.923843	0.384658
C	0.287656	2.914299	0.703847
N	1.338035	2.467563	-0.125768
C	1.976868	3.146539	-1.083947
C	1.771365	4.640581	-1.293606
C	2.954495	2.559993	-1.930923
C	3.484225	1.247758	-2.026721
C	4.600033	1.087287	-3.050361
C	-7.215284	-0.768158	-2.085357
C	-4.312638	-3.779932	1.143486
H	2.333314	-1.029562	4.306757

H	-1.208612	1.839096	3.598405
H	0.787617	2.086976	4.606841
H	1.592049	0.696135	5.360637
H	-0.102150	0.575484	4.882218
H	4.107278	-4.980613	-1.255520
H	3.250158	-3.862980	0.749936
H	4.005848	-1.260411	-3.390087
H	3.040306	-3.542993	2.814669
H	4.522547	-2.758321	2.234411
H	3.900040	-2.409844	3.859237
H	-2.745882	3.674991	3.056616
H	4.491356	-3.664556	-3.352328
H	5.363882	0.386330	-2.703805
H	4.222126	0.729579	-4.016077
H	5.072528	2.057047	-3.224912
H	3.403392	3.261126	-2.626312
H	-0.562232	4.454462	-0.555345
H	-2.417338	4.999992	0.956485
H	2.674102	5.072790	-1.732486
H	0.942671	4.844521	-1.983048
H	1.563324	5.153195	-0.350953
H	-3.861570	0.888004	-2.802381
H	-5.617643	-1.413721	0.368391
H	-6.125730	1.038043	-2.476461
H	-2.383931	-2.927299	1.466714
H	-7.865076	1.609970	-0.804606
H	-7.097370	0.559787	0.397717
H	-6.250585	2.005514	-0.175275
H	-8.176199	-0.355111	-2.416015
H	-6.780413	-1.333782	-2.917137
H	-7.418873	-1.474381	-1.271557
H	-0.019223	1.648046	-3.127817
H	-1.674128	1.773952	-3.737857
H	-1.321751	2.182723	-2.041456

H	-4.177226	-4.508429	1.952016
H	-5.375656	-3.512121	1.117019
H	-4.063343	-4.273412	0.197433
H	-3.655426	-2.582912	3.554639
H	-3.040665	-1.044726	2.914974
H	-4.760096	-1.465051	2.730904
H	0.764191	-0.821055	-1.405606
H	0.199323	-0.796952	-3.747770
H	-0.840021	-2.001082	-2.939910
H	-1.461222	-1.045488	-4.295301

Table S10. Optimized structure of PC.

Atom	X	Y	Z
C	-0.184361	2.893045	0.639837
C	-0.757321	1.962668	1.578069
C	-2.098189	2.143128	1.965987
C	-2.864432	3.213935	1.487250
C	-2.309949	4.113114	0.572645
C	-0.987239	3.937066	0.143808
N	0.065397	0.873546	1.938661
C	-0.029060	0.091488	3.023994
C	0.814955	-1.024875	3.251478
C	1.868517	-1.612196	2.498467
C	2.515738	-2.820948	3.158999
N	1.126583	2.590675	0.204854
C	2.034053	3.428844	-0.315844
C	3.307742	3.004045	-0.777951
C	3.939760	1.732666	-0.835619
C	5.368598	1.759979	-1.361756
Rh	1.636794	0.683383	0.676156
N	2.306006	-1.107423	1.341229
C	3.282349	-1.643747	0.472046
C	3.860347	-0.714198	-0.462800
C	4.747987	-1.198425	-1.442805

C	5.102023	-2.552489	-1.502967
C	4.537115	-3.455893	-0.598072
C	3.625118	-3.004178	0.363381
N	3.360632	0.609569	-0.393221
N	0.513002	-0.479072	-1.610163
S	-0.349672	-1.964288	-1.715523
O	-0.390911	-2.453642	-3.113131
C	1.809945	4.934165	-0.382749
C	-1.006781	0.382217	4.154912
C	-1.980141	-1.329497	-1.269538
C	-2.312408	-0.101580	-1.894810
C	-3.525557	0.497131	-1.547518
C	-4.413702	-0.103675	-0.639806
C	-4.064971	-1.340867	-0.089496
C	-2.850712	-1.990216	-0.382155
C	-1.408319	0.464999	-2.987288
C	0.078692	0.576056	-2.562827
C	-2.589288	-3.361453	0.244728
C	-2.404031	-3.245329	1.772224
C	-5.747364	0.564101	-0.328226
C	-6.044084	0.638967	1.181744
C	-1.853102	1.816520	-3.561272
C	-6.901033	-0.135897	-1.080599
C	-3.709505	-4.361815	-0.111529
O	0.248992	-2.835505	-0.686653
H	0.620084	-1.531628	4.190525
H	-2.576535	1.414413	2.606143
H	-1.137293	1.456900	4.307753
H	-0.628388	-0.055451	5.081778
H	-1.993171	-0.058589	3.964065
H	4.763345	-4.517836	-0.662858
H	3.128063	-3.736369	0.984010
H	5.133473	-0.529852	-2.201311
H	2.078157	-3.759077	2.796190

H	3.593042	-2.852882	2.976268
H	2.348322	-2.777571	4.238065
H	-3.899148	3.318022	1.807659
H	5.781046	-2.896180	-2.280117
H	6.000638	1.034227	-0.843349
H	5.414573	1.545305	-2.436729
H	5.789897	2.757009	-1.211340
H	3.930267	3.814514	-1.141696
H	-0.599413	4.602071	-0.616659
H	-2.902013	4.931240	0.168071
H	2.776688	5.443417	-0.384938
H	1.282758	5.231432	-1.297924
H	1.231743	5.291740	0.473358
H	-3.796310	1.450886	-1.990910
H	-4.756314	-1.832523	0.590308
H	-5.686294	1.594199	-0.703769
H	-1.658835	-3.761234	-0.156775
H	-6.965507	1.205859	1.361268
H	-6.183869	-0.358259	1.615727
H	-5.227403	1.131076	1.720951
H	-7.849802	0.385902	-0.904667
H	-6.716435	-0.156830	-2.160506
H	-7.018171	-1.172384	-0.741584
H	-1.143274	2.142604	-4.330812
H	-2.838551	1.749579	-4.034111
H	-1.890138	2.590704	-2.785909
H	-1.443540	-0.272173	-3.799890
H	0.693068	0.553652	-3.471366
H	0.247856	1.529884	-2.054586
H	-3.456259	-5.355061	0.278141
H	-4.675467	-4.074579	0.320714
H	-3.837040	-4.446500	-1.196701
H	-2.205424	-4.234213	2.203354
H	-1.558541	-2.593013	2.015244

H	-3.302758	-2.843794	2.257430
H	1.497567	-0.721289	-1.742039

Table S11. Optimized structure of trisylazide.

Atom	X	Y	Z
N	3.559271	-0.061354	-2.617168
N	3.086069	-0.585292	-1.714297
N	2.585692	-1.244545	-0.776283
S	2.164301	-0.208284	0.635816
O	2.376447	-1.083454	1.792579
O	2.959181	1.021581	0.484053
C	0.385732	0.062760	0.362284
C	-0.147508	1.378409	0.289377
C	-1.519198	1.482623	-0.000520
C	-2.351562	0.375400	-0.182437
C	-1.787259	-0.899083	-0.043527
C	-0.428591	-1.098383	0.230078
C	0.622857	2.689395	0.496515
H	-1.954530	2.475353	-0.076083
C	-3.828206	0.560115	-0.502725
H	-2.422184	-1.774776	-0.149465
C	0.040480	-2.548922	0.402828
H	1.120658	-2.584019	0.521068
C	-0.554172	-3.145010	1.697269
C	-0.295452	-3.414629	-0.828141
H	0.111042	-4.423461	-0.690692
H	-1.375266	-3.514748	-0.987423
H	0.145992	-2.993631	-1.737895
H	-0.193697	-4.171314	1.835367
H	-0.250689	-2.559135	2.571188
H	-1.649883	-3.173978	1.666547
C	-4.730075	-0.015095	0.609522
H	-4.015812	1.640790	-0.553579
C	-4.190674	-0.039680	-1.877532

H	-5.243339	0.155885	-2.114279
H	-3.574792	0.391571	-2.674677
H	-4.042847	-1.126161	-1.890052
H	-5.785069	0.184574	0.387096
H	-4.609320	-1.101247	0.699722
H	-4.495004	0.430536	1.582562
C	1.014488	3.304051	-0.865311
H	1.546180	2.477905	1.030826
C	-0.157924	3.708041	1.352672
H	1.571756	4.235890	-0.712762
H	1.651309	2.624134	-1.439999
H	0.125579	3.534500	-1.465623
H	0.500360	4.550852	1.593595
H	-1.031094	4.120933	0.834770
H	-0.498031	3.265455	2.295792