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Supplementary Material

Experimental and computational studies of the mechanisms of hydroamination/cyclization of unactivated, α,ω-amino-alkenes with CCC-NHC pincer Zr complexes

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^{1}H NMR,^{13}C NMR, and HRMS Spectra of Imidazolium Salts

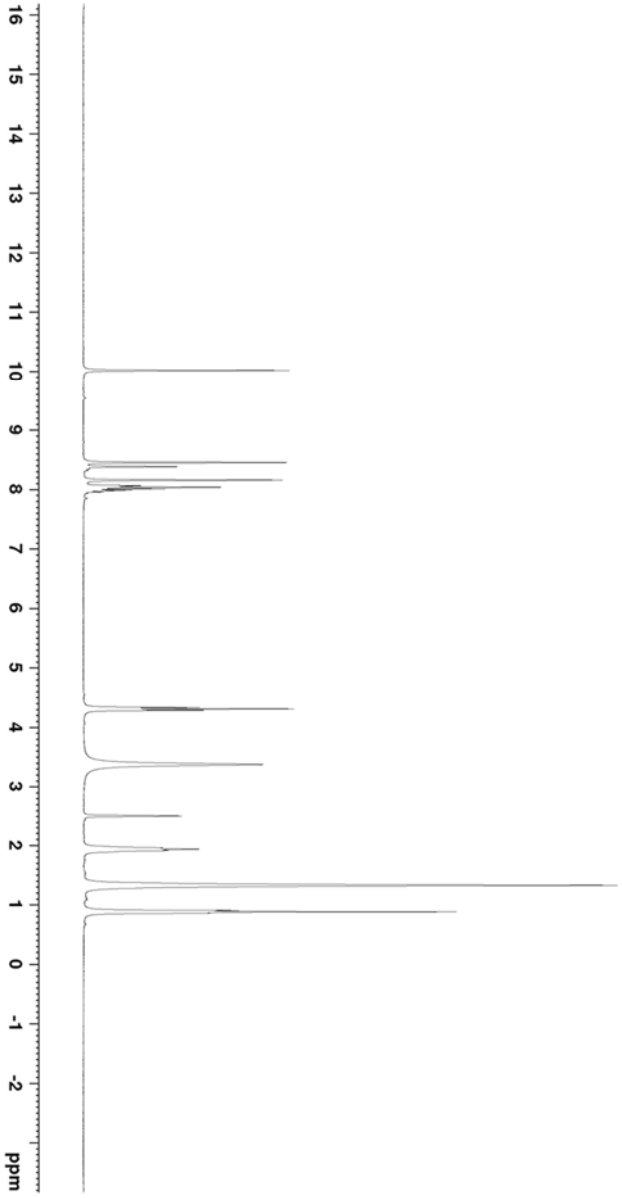


Figure S1. ^{1}H NMR spectrum of hexyl diiodo salt **1b** in DMSO-d_6.

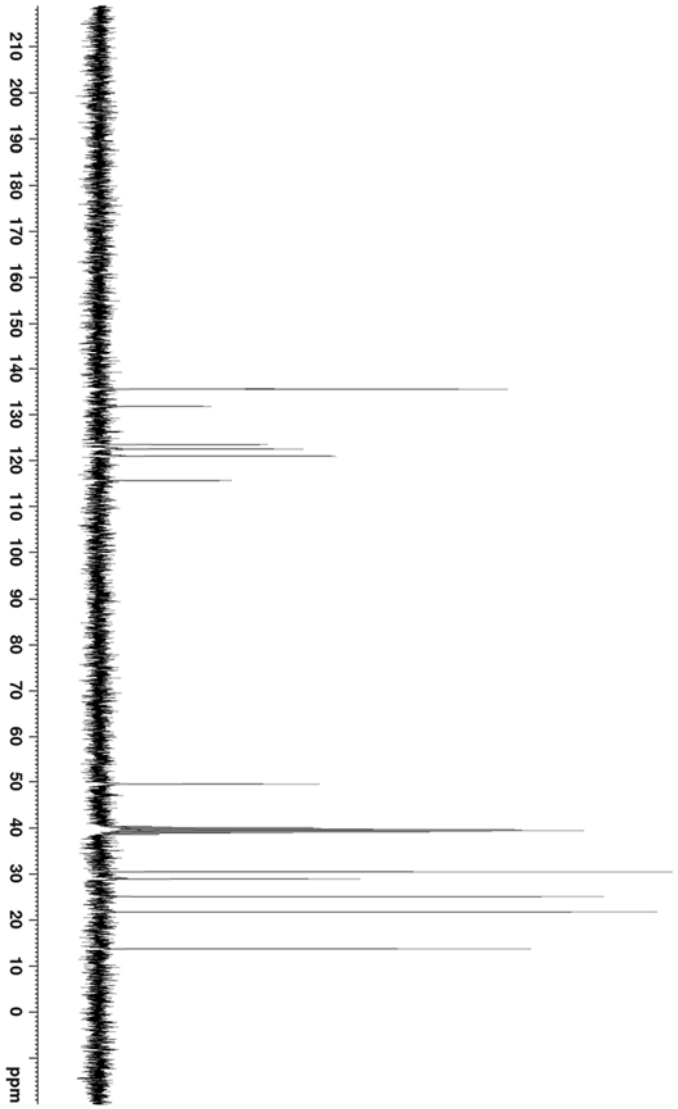


Figure S2. ^{13}C NMR spectrum of hexyl diiodo salt **1b** in DMSO-d_6.

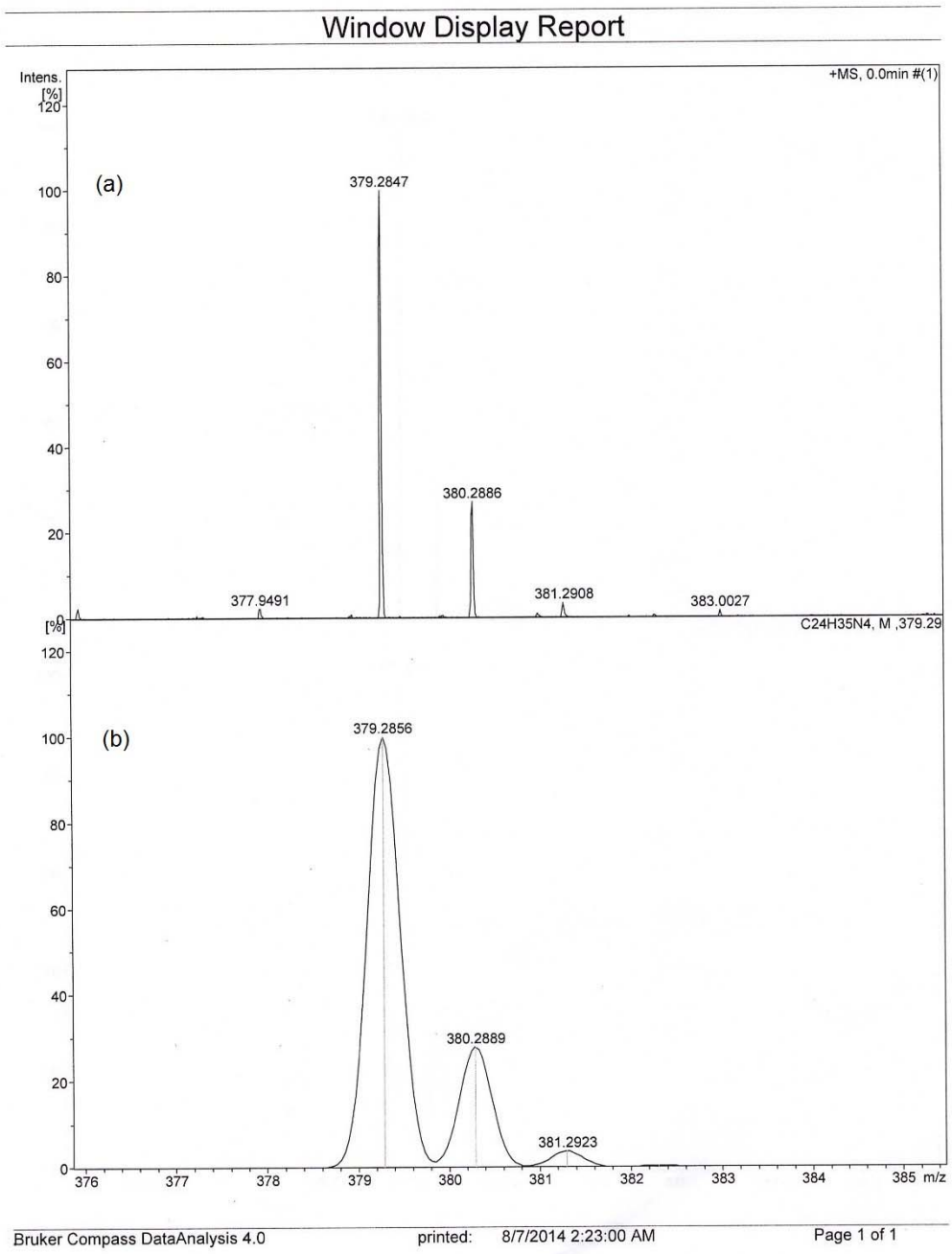


Figure S3. HRMS of hexyl diiodo salt **1b** in MeOH. (a) Observed spectrum $[M\text{-}2I\text{-}H]^+$ (b) Calculated spectrum for $C_{24}H_{35}N_4$.

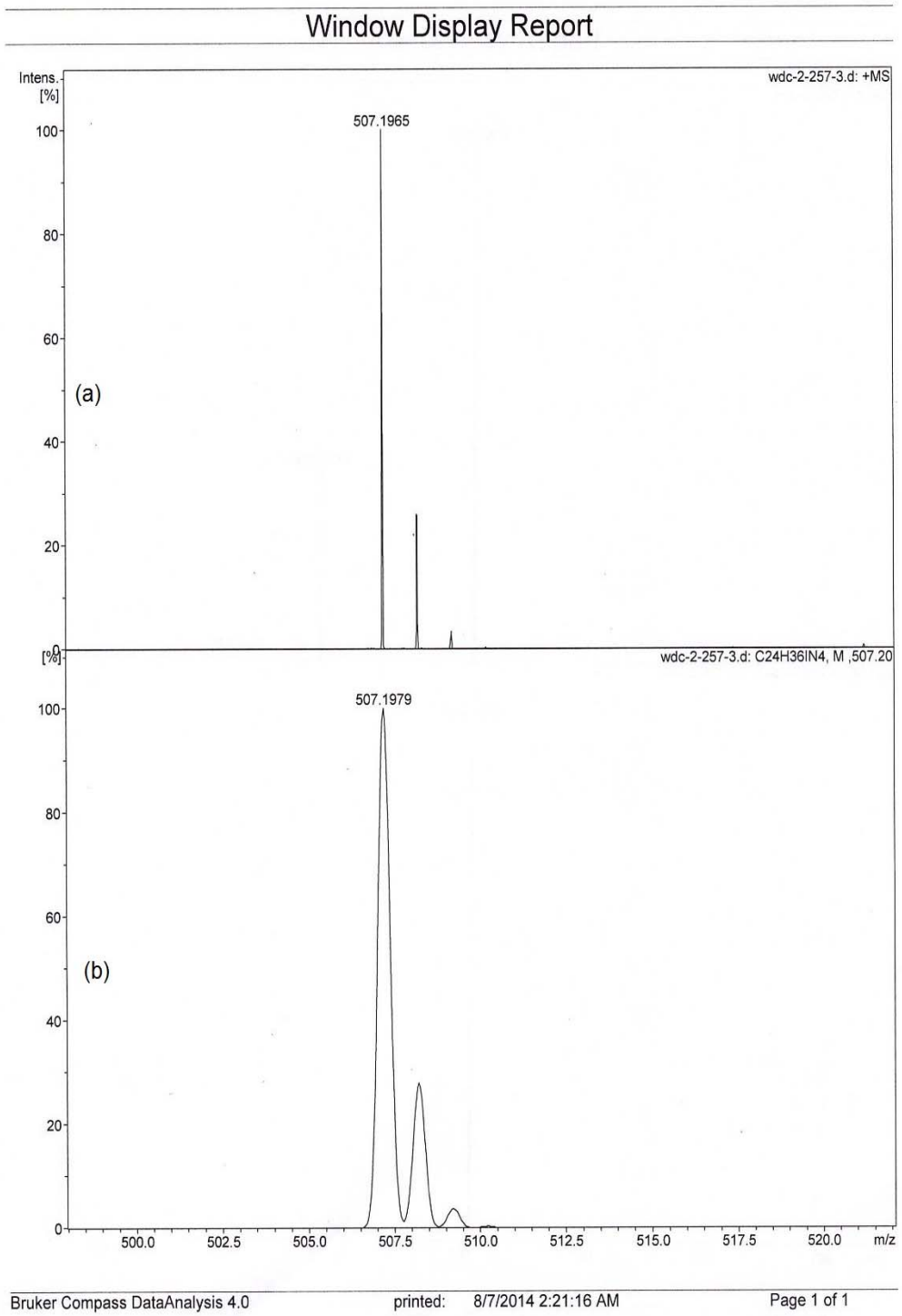


Figure S4. HRMS of hexyl diiodo salt **1b** in MeOH. (a) Observed spectrum $[M\text{-}I]^+$. (b) Calculated spectrum for $C_{24}H_{36}IN_4$

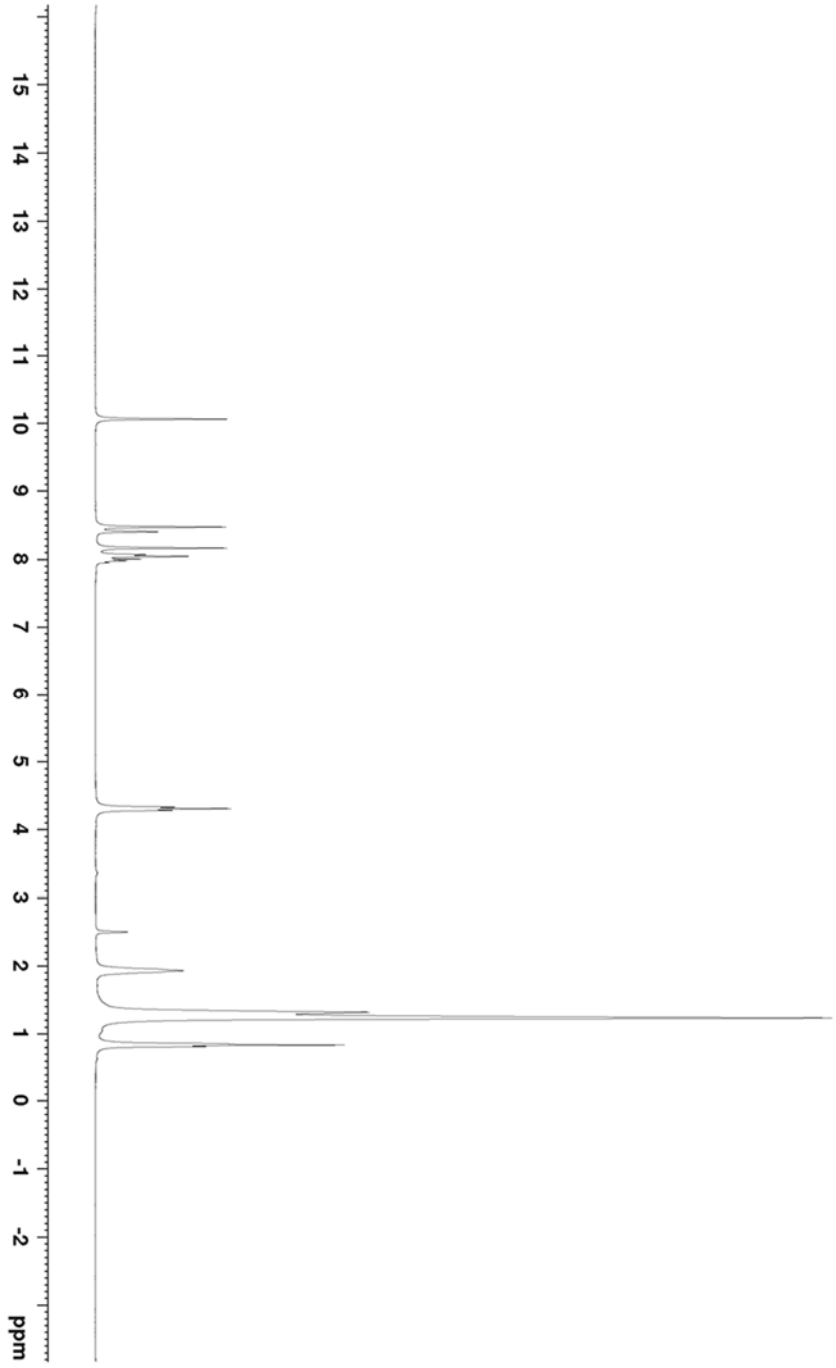


Figure S5. ^{1}H NMR spectrum of undecyl diiodo salt **1c** in DMSO-d_6.

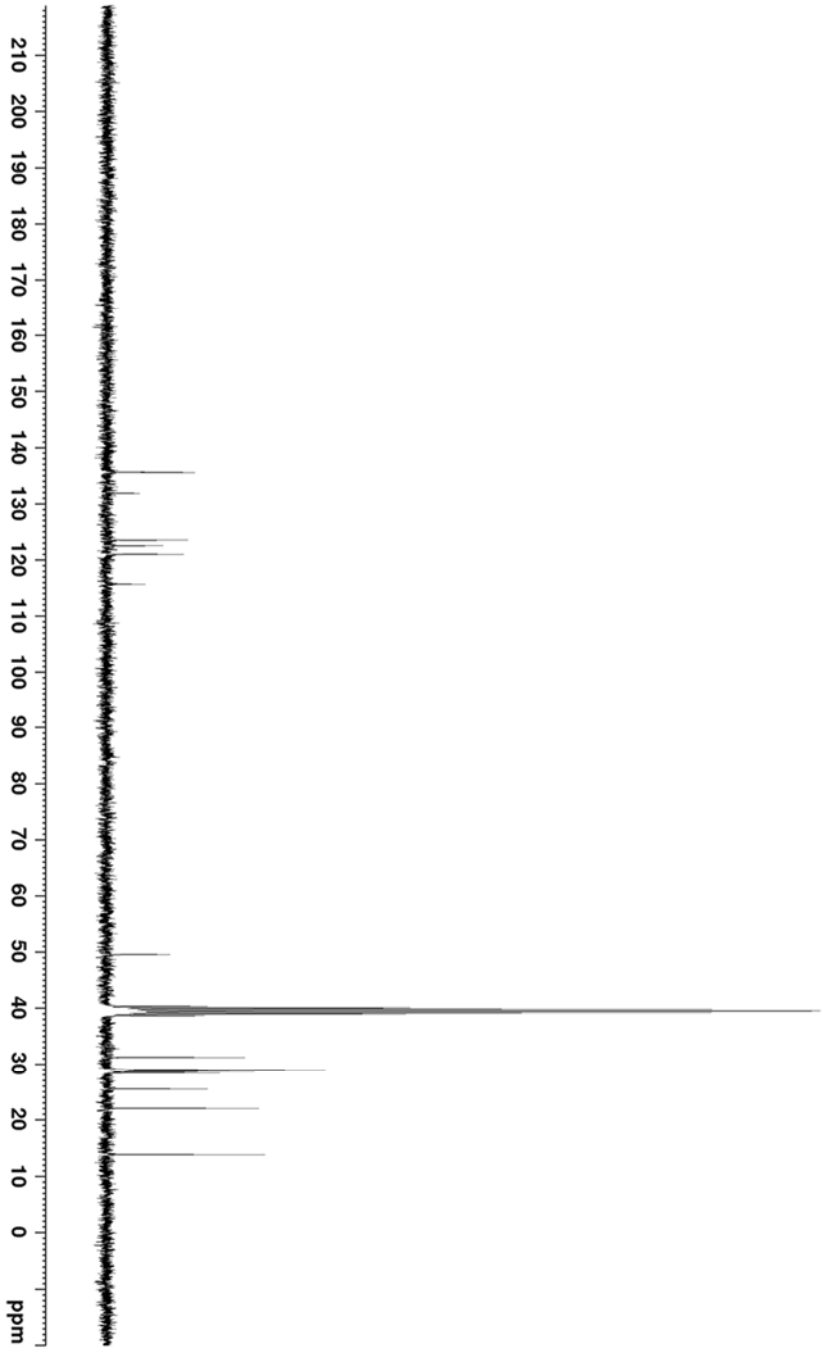


Figure S6. ^{13}C NMR spectrum of undecyl diiodo salt **1c** in DMSO-d_6.

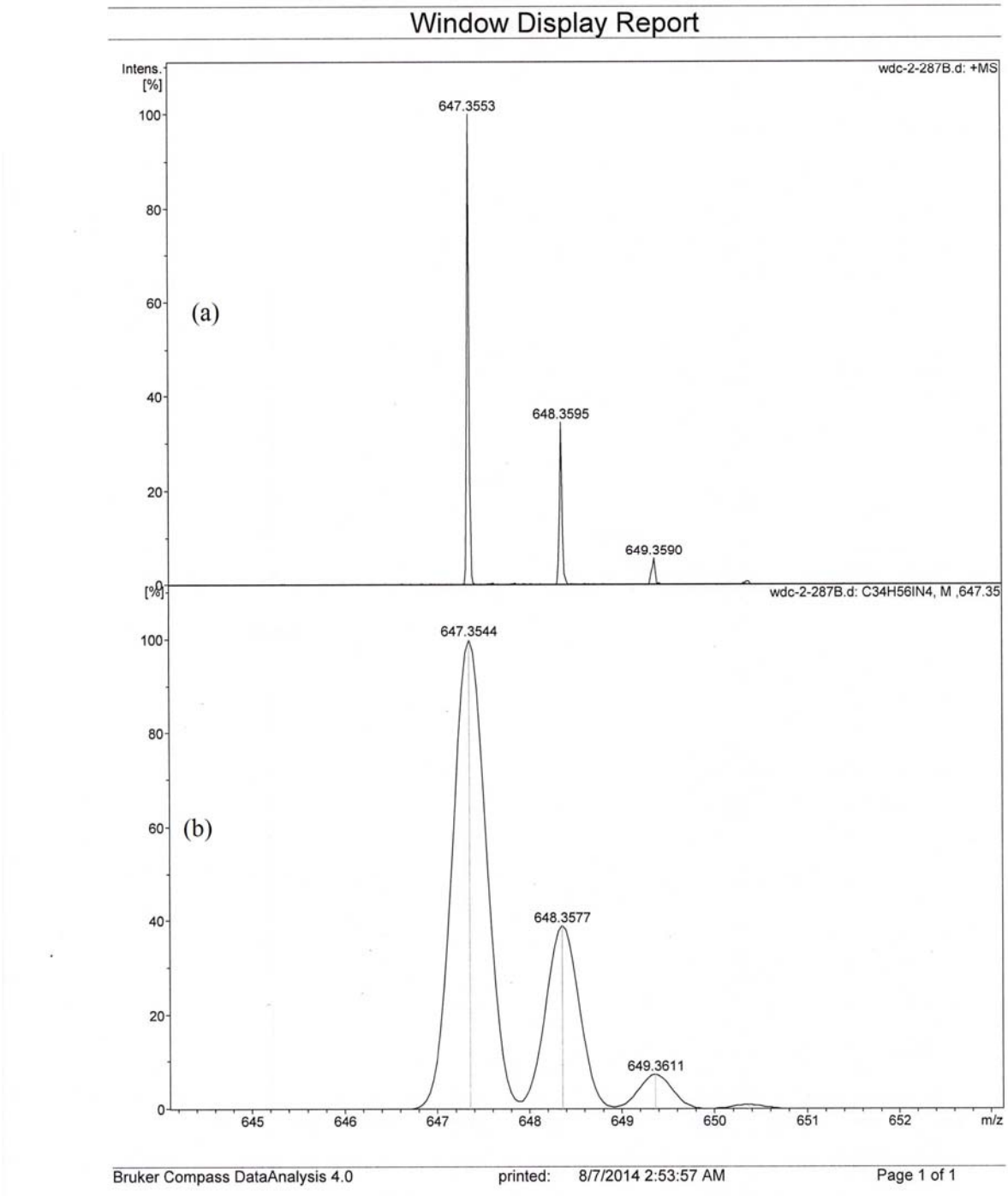


Figure S7. HRMS of undecyl diiodo salt **1c** in MeOH. (a) Observed spectrum $[M\text{-}I]^+$. (b) Calculated spectrum for $C_{34}H_{56}IN_4$.

^{1}H NMR and ^{13}C NMR spectra of CCC-NHC Zr complexes

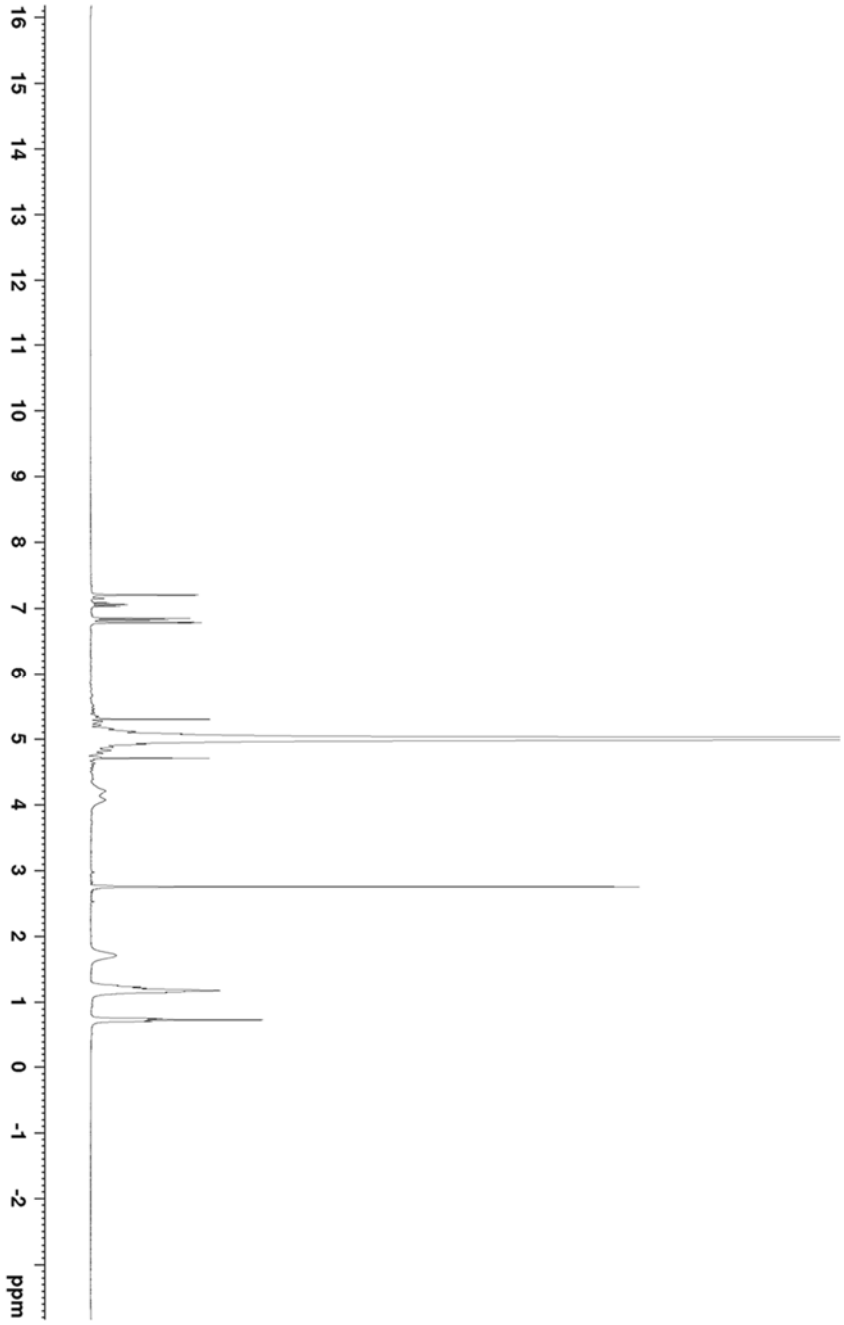


Figure S8. ^{1}H NMR spectrum of hexyl diiodo complex **2a** in CH_2Cl_2/C_6D_6.

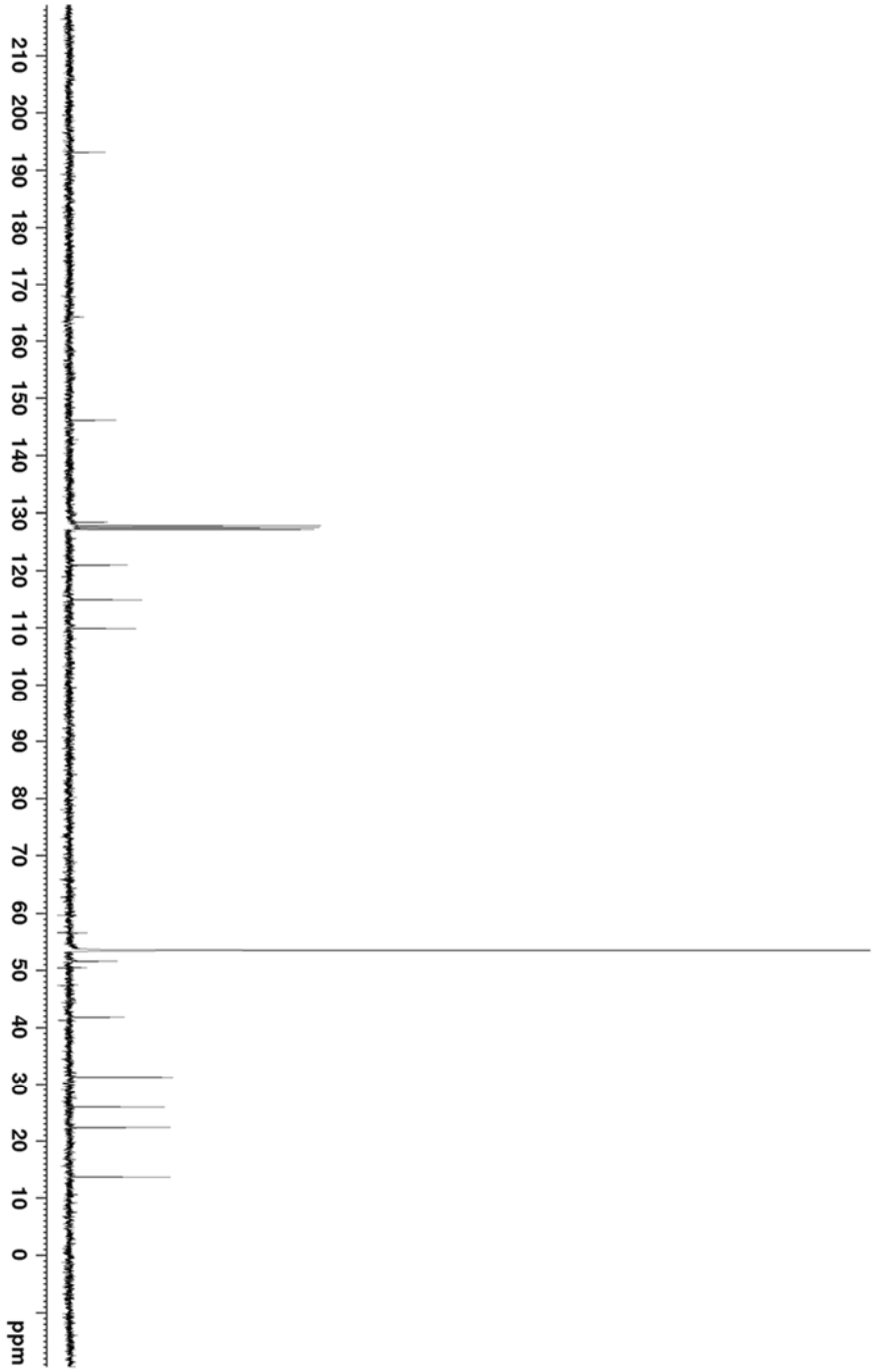


Figure S9. ^{13}C NMR spectrum of hexyl diiodo complex **2a** in CH_2Cl_2/C_6D_6.

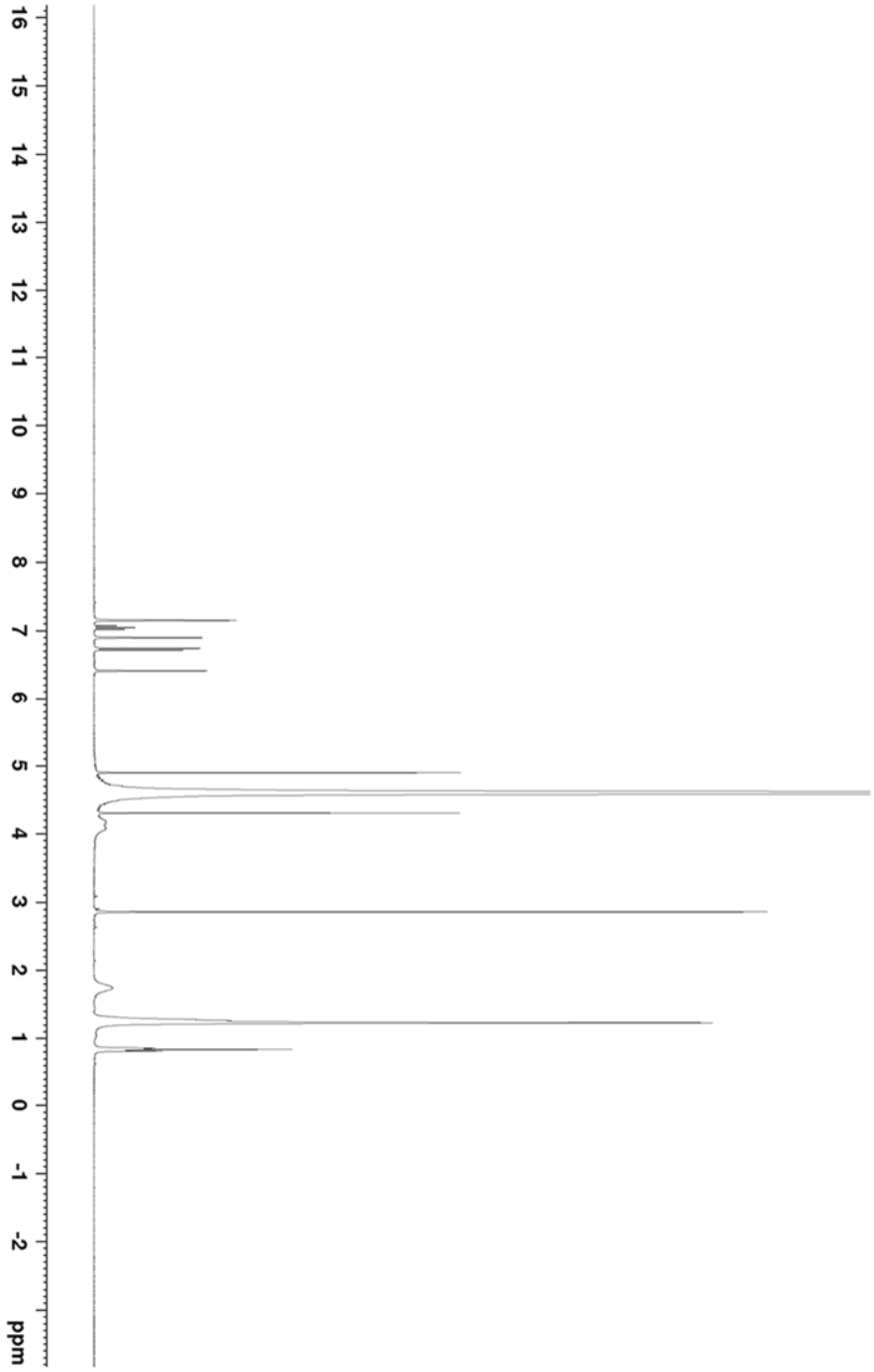


Figure S10. ^{1}H NMR spectrum of undecyl diiodo complex **2b** in CH_2Cl_2/C_6D_6.

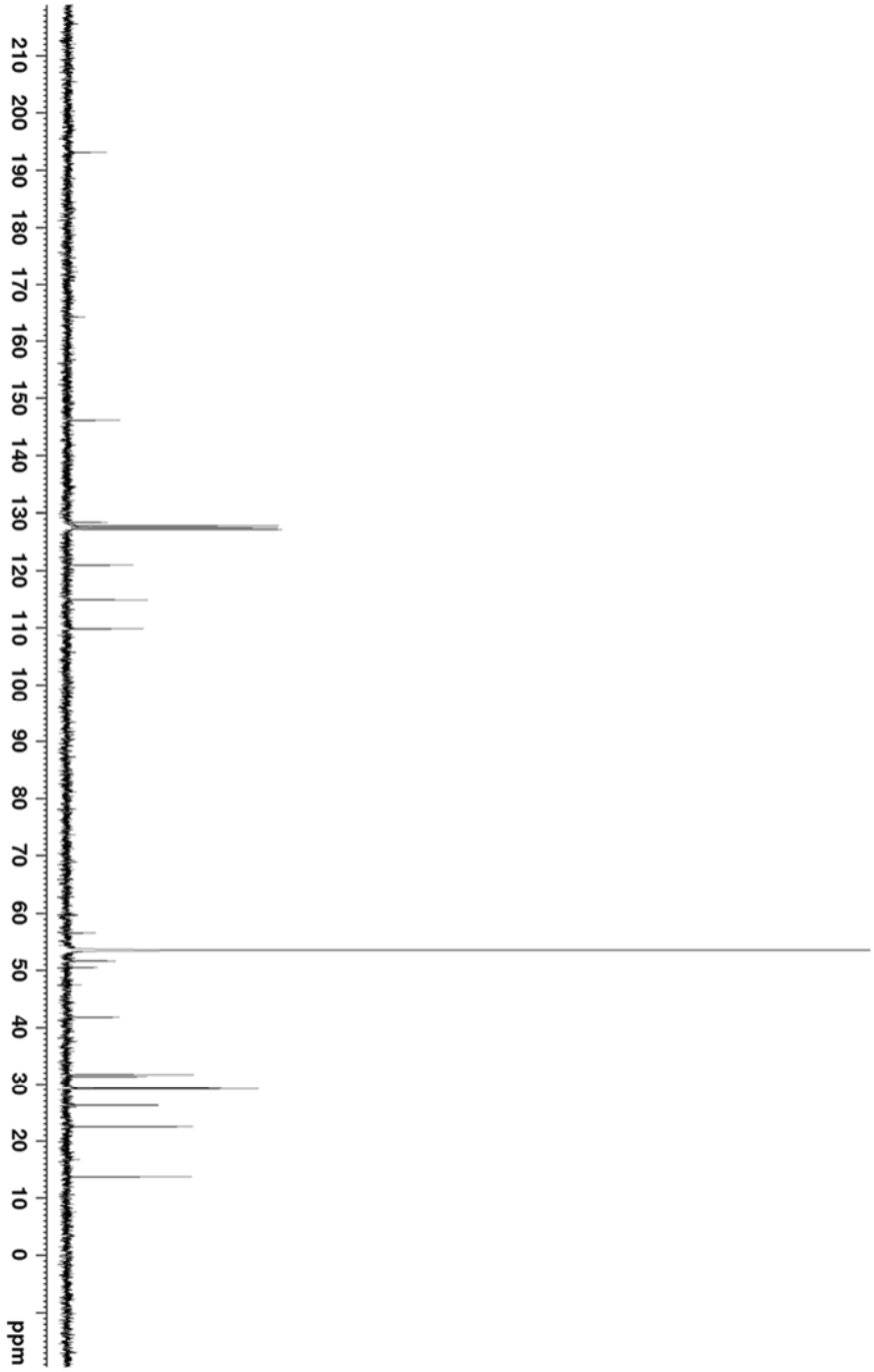


Figure S11. ^{13}C NMR spectrum of hexyl diiodo complex **2b** in CH_2Cl_2/C_6D_6.

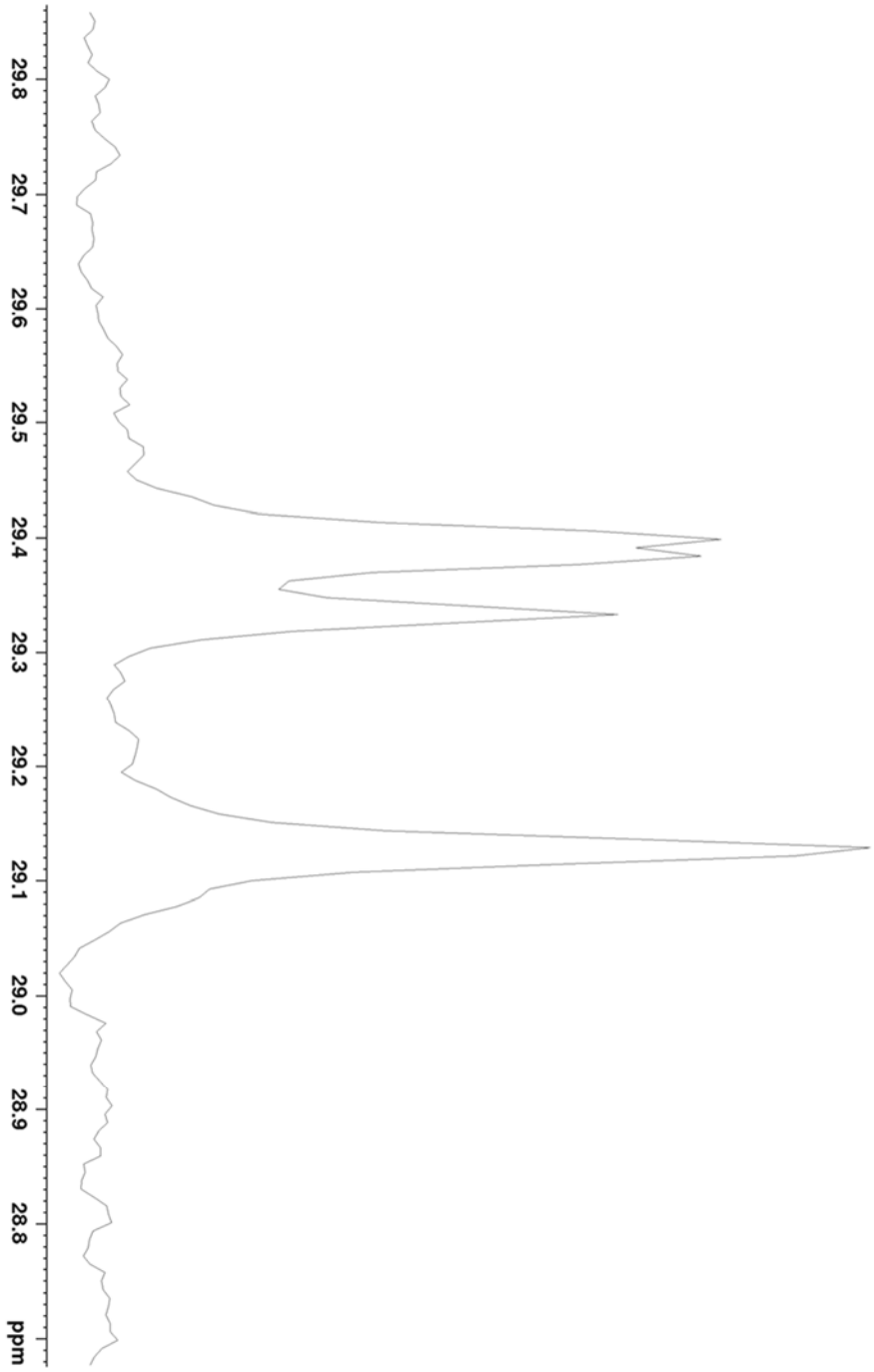


Figure S12. Excerpt of the ^{13}C NMR spectrum of hexyl diiodo complex **2b** in CH_2Cl_2/C_6D_6.

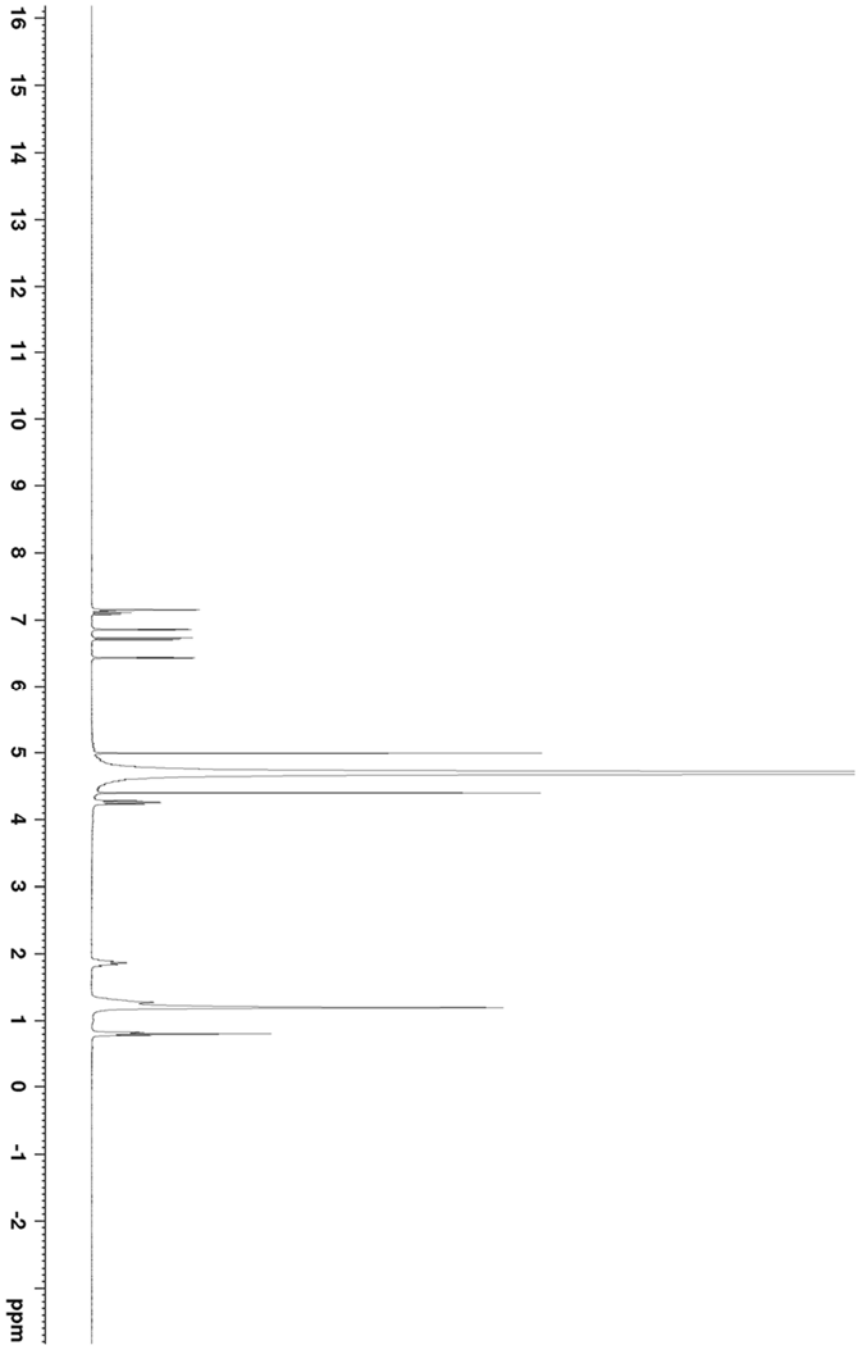


Figure S13. ^{1}H NMR spectrum of undecyl triiodo complex **3a** in CH_2Cl_2/C_6D_6.

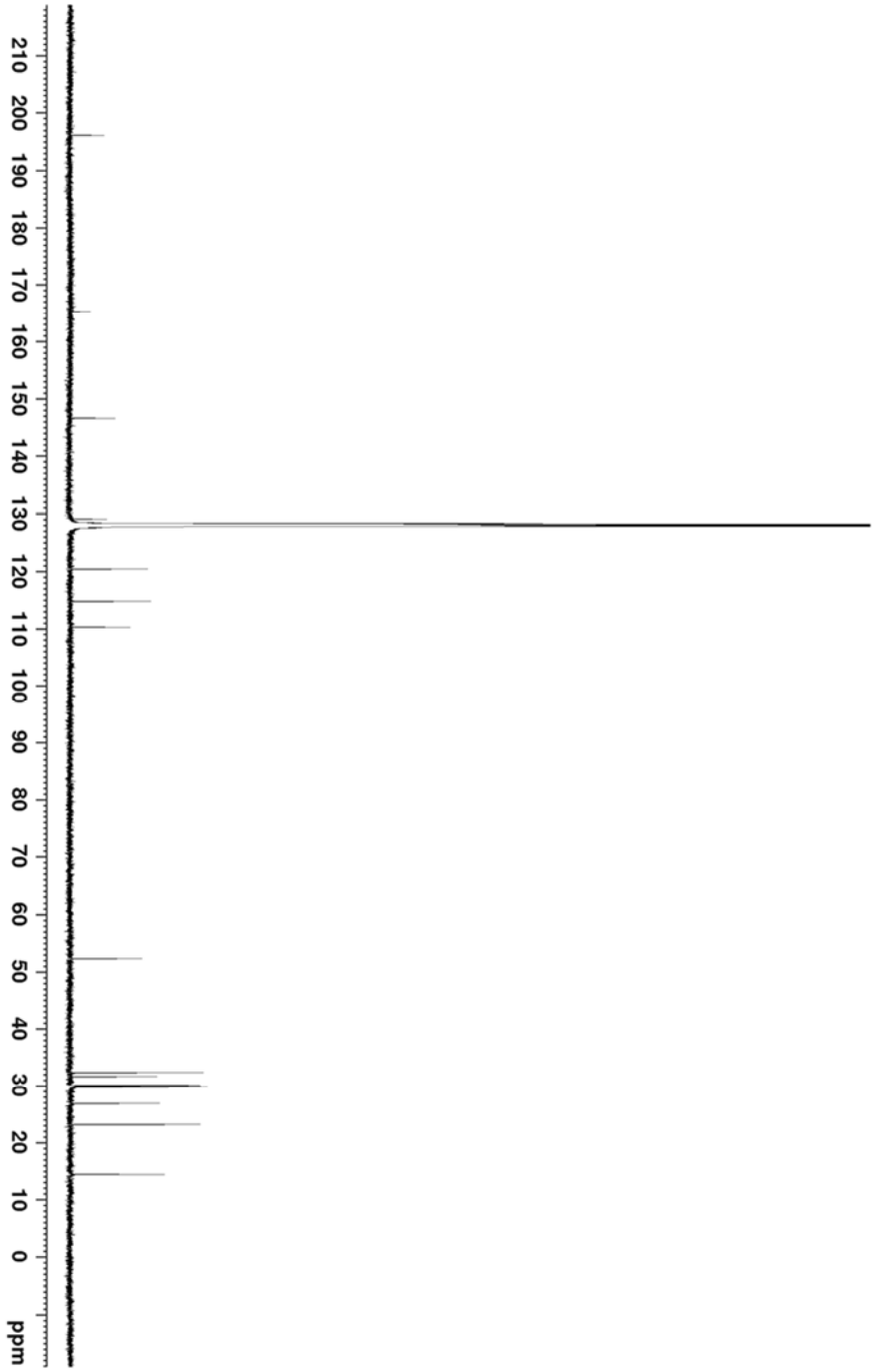


Figure S14. ^{13}C NMR spectrum of undecyl triiodo complex **3a** in C_6D_6.

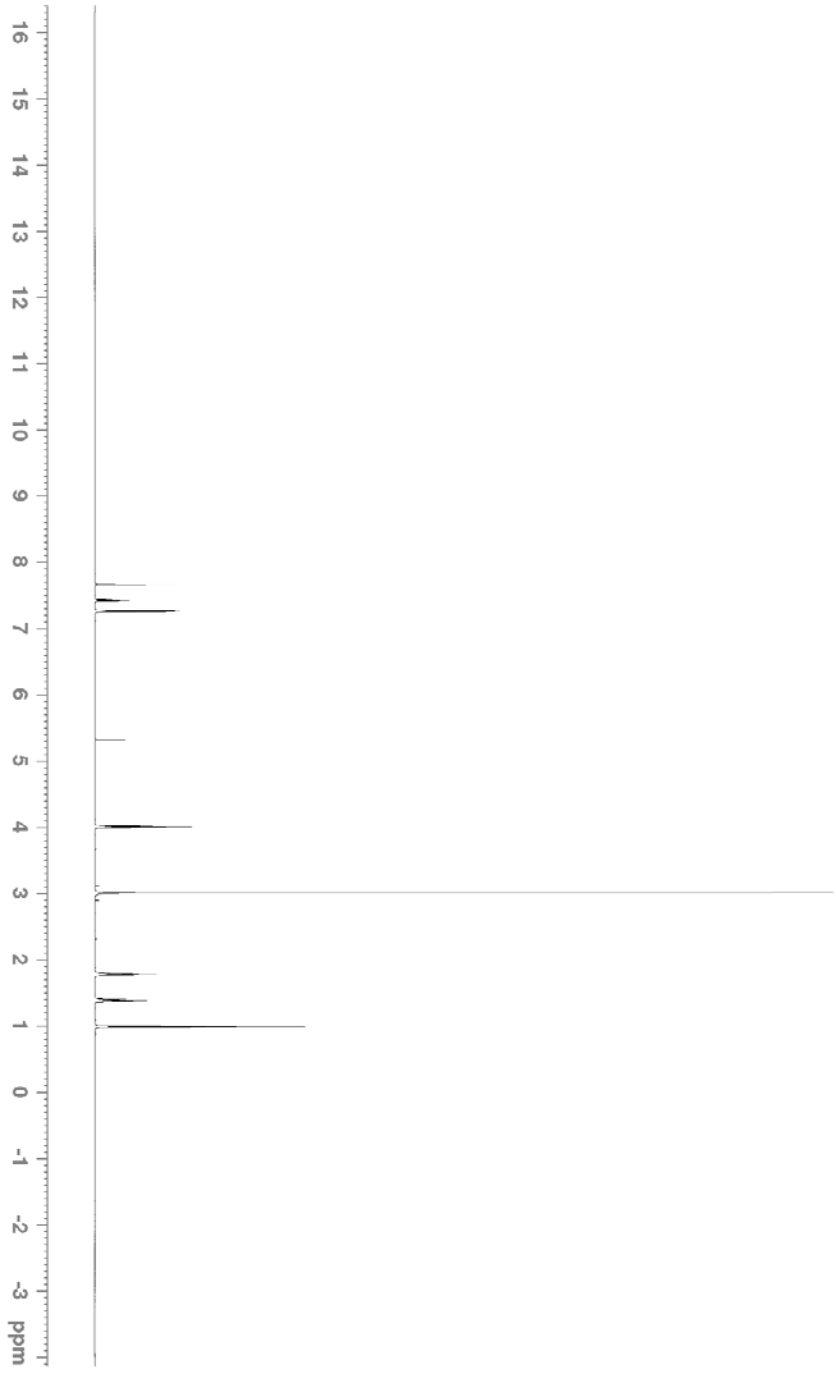


Figure S15. ^{1}H NMR spectrum of diamido complex **4a** in CD_2Cl_2.

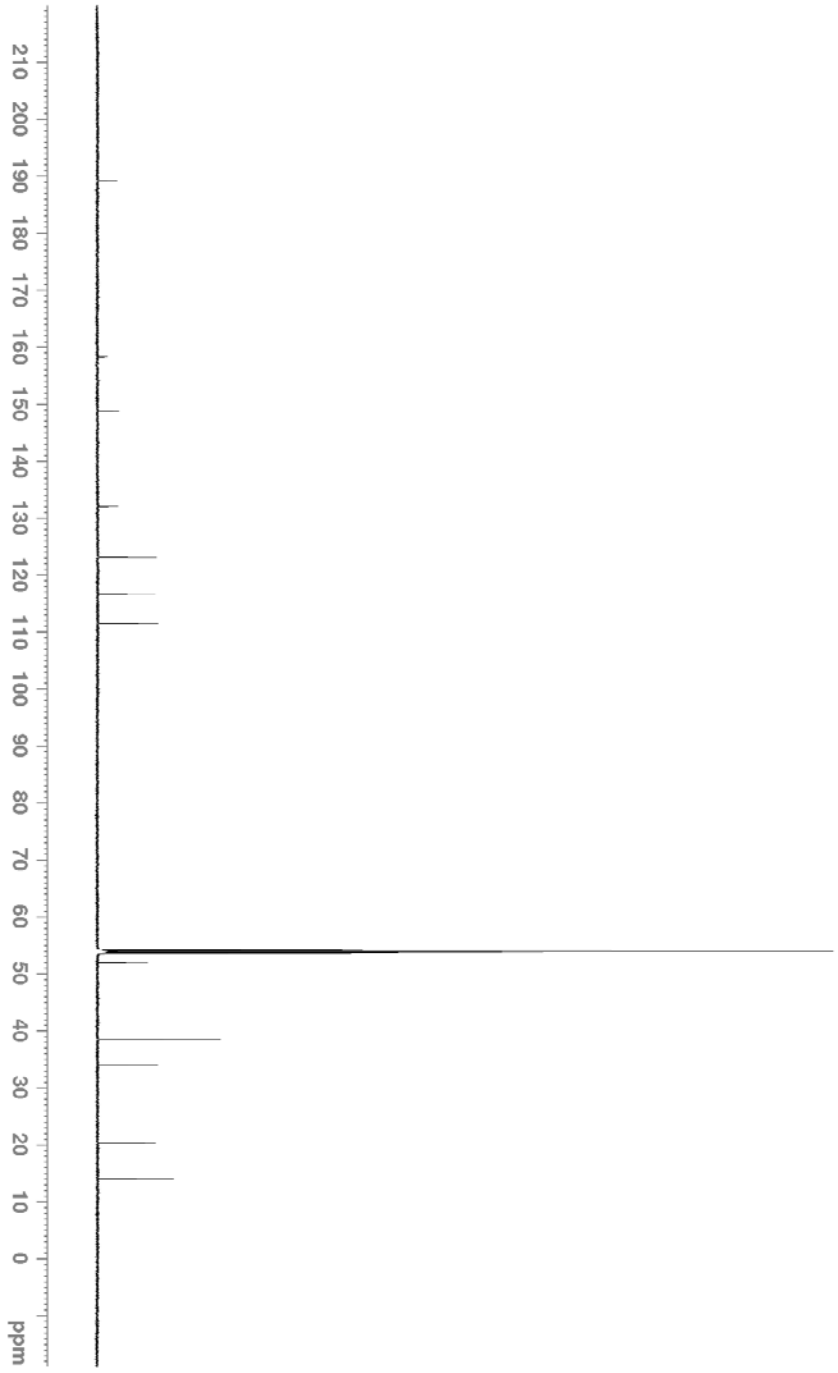
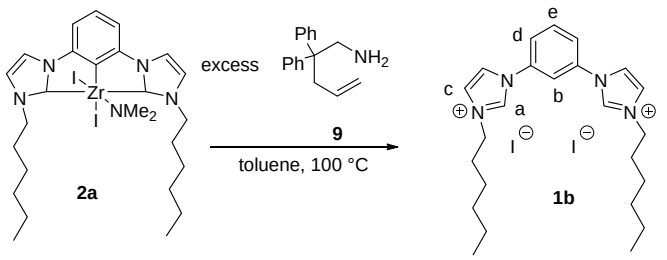


Figure S16. ^{13}C NMR spectrum of complex **4a** in CD_2Cl_2.



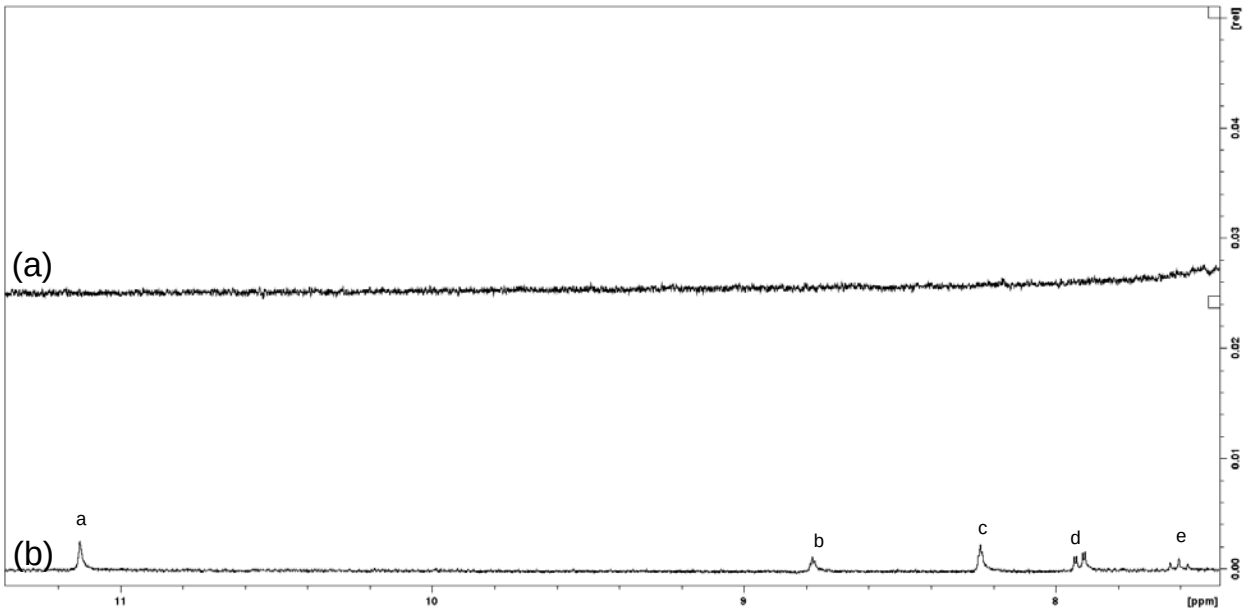
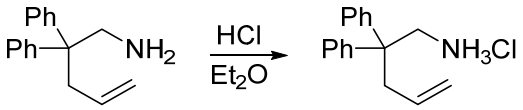


Figure S17. (a) ^{1}H NMR spectrum of the homogenous reaction mixture with complex **2a**, substrate and d-toluene only at room temperature. (b) ^{1}H NMR spectrum of the mixture after heating for 20 minutes (solid forms), cooling to room temperature, and adding CH_2Cl_2 to dissolve the solid. Several signals consistent with imidazolium salt formation were observed.

Synthesis and characterization of Ammonium salts

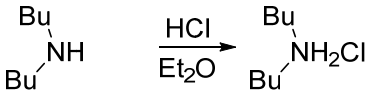
2,2-diphenylpent-4-en-1-amine hydrochloride



5 **5·HCl**

HCl (saturated in Et_2O, 5 mL), precooled to -30 °C, was added to a solution of Substrate **5** (312 mg, 1.315 mmol) and Et_2O (5 mL) at room temperature. A white solid immediately formed and the mixture was stirred for 1 minute. Volatiles were removed in vacuo and the white solid was dried under reduced pressure. 341 mg, 95%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.31-7.29 (m, 4 H), 7.26-7.23 (m, 2H), 7.13 (d, 2H, J=7.8 Hz), 5.91 (bs, 3H, J=6.2 Hz), 5.32 (m, 1H), 5.21 (d, 1H, J=17 Hz), 5.03 (d, 1H, 10.0 Hz), 3.45 (s, 2H), 3.01 (d, 2H, J=6.8 Hz). ^{13}C NMR ($CDCl_3$,, 151 MHz): δ 144.5, 133.3, 128.5, 127.9, 126.8, 119.5, 49.6, 46.7, 40.6. *m/z* 238.1584 $[M\text{-}Cl]^+$, calcd for $C_{17}H_{20}N^+$ 238.1590.

Dibutylamine hydrochloride



A solution of Dibutylamine (0.68g, 5.3 mmol) and 5 mL Et_2O was added to HCl (saturated in Et_2O, 5 mL) precooled to -30 °C. A white solid formed immediately. Volatiles were removed in vacuo and the white solid was dried under reduced pressure. 0.81 g, 92 %. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.50 (s, 2H), 2.92 (bs, 4H), 1.93-1.88 (m, 4H), 1.45-1.38 (m, 4H), 0.95 (t, 6H, J=7.4 Hz). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 47.8, 28.0, 20.3, 13.7. *m/z* 130.1595 $[M\text{-}Cl]^+$, calcd for $C_8H_{20}N^+$ 130.1590.

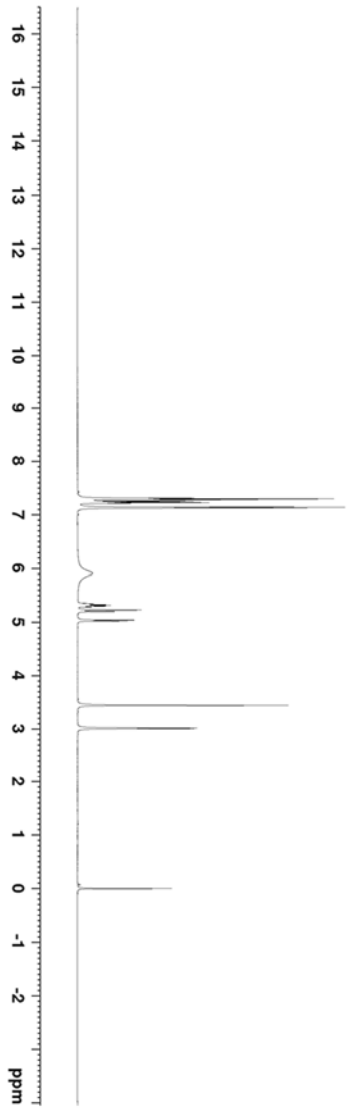


Figure S18. ^{1}H NMR spectrum of 2,2-diphenylpent-4-en-1-amine hydrochloride in $CDCl_3$.

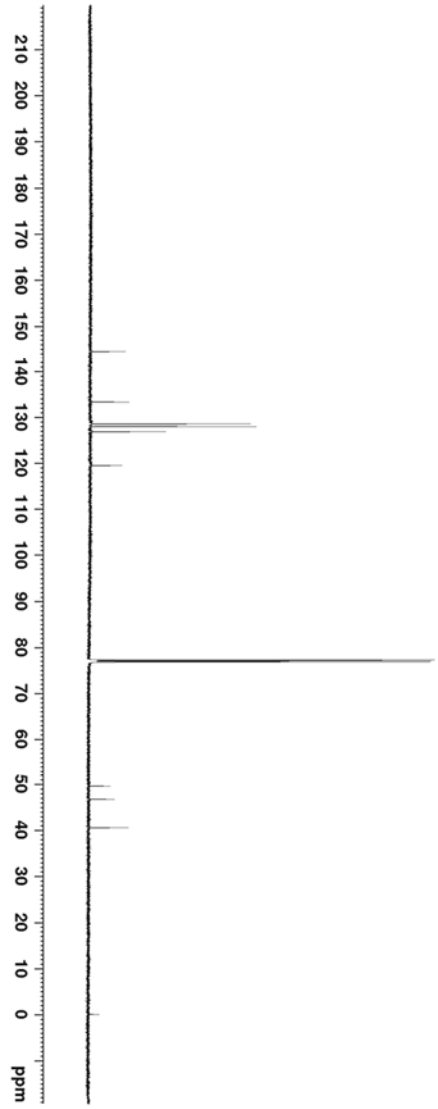


Figure S19. ^{13}C NMR spectrum of 2,2-diphenylpent-4-en-1-amine hydrochloride in $CDCl_3$.

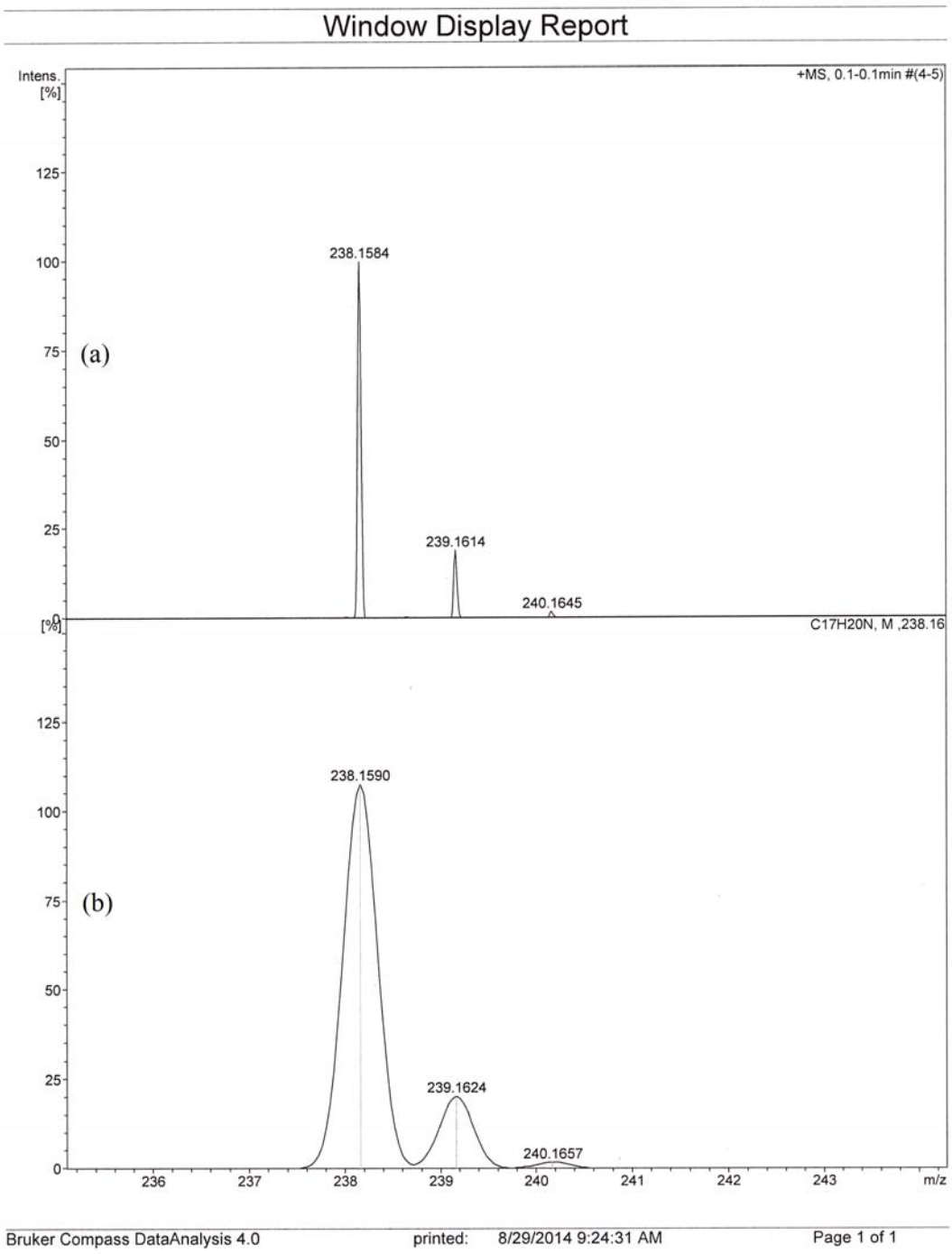


Figure S20. HRMS of 2,2-diphenylpent-4-en-1-amine hydrochloride. (a) Observed spectrum $[M-Cl]^+$ (b) Calculated spectrum for $C_{17}H_{20}N$.

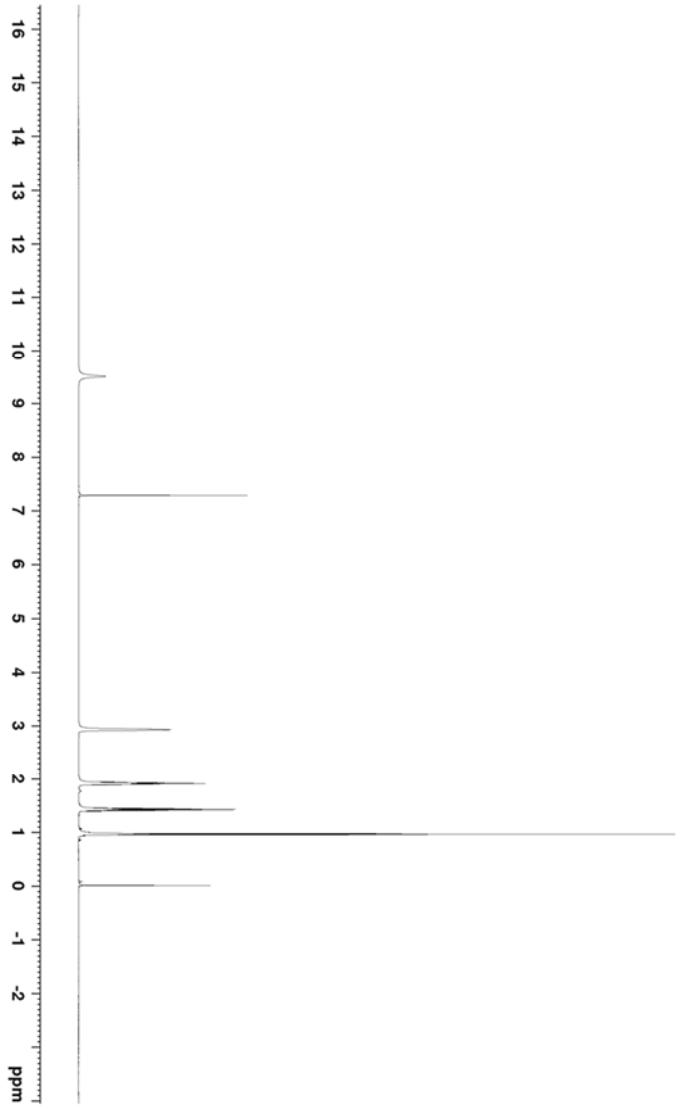


Figure S21. ^{1}H NMR spectrum of dibutylamine hydrochloride in $CDCl_3$.

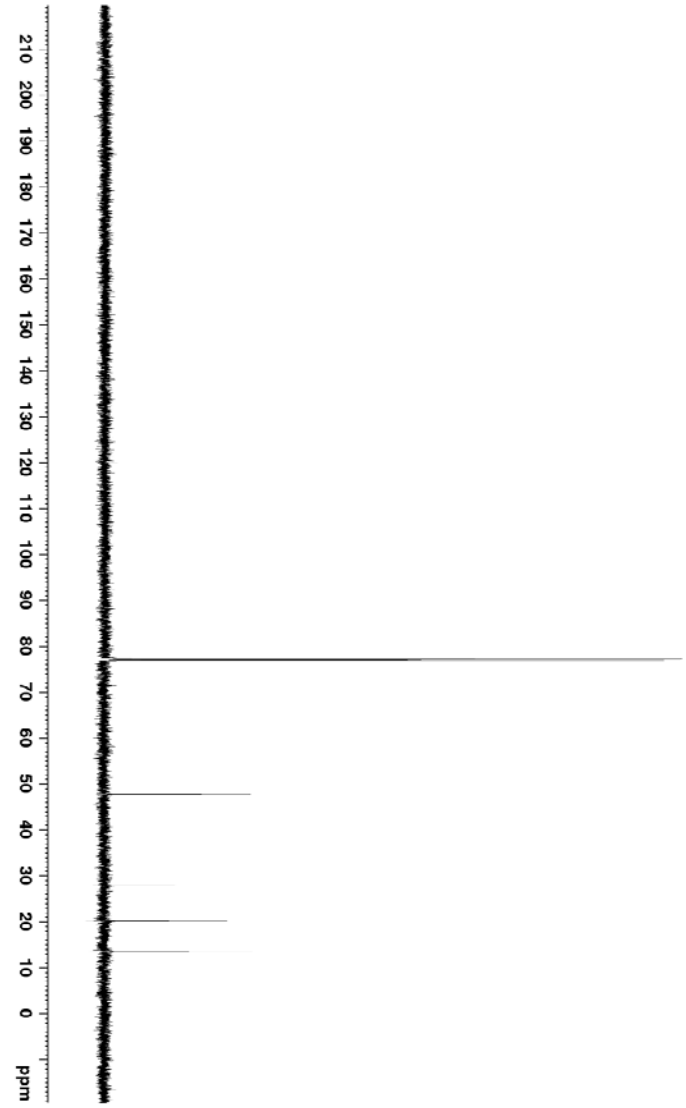


Figure S22. ^{13}C NMR spectrum of dibutylamine hydrochloride in $CDCl_3$.

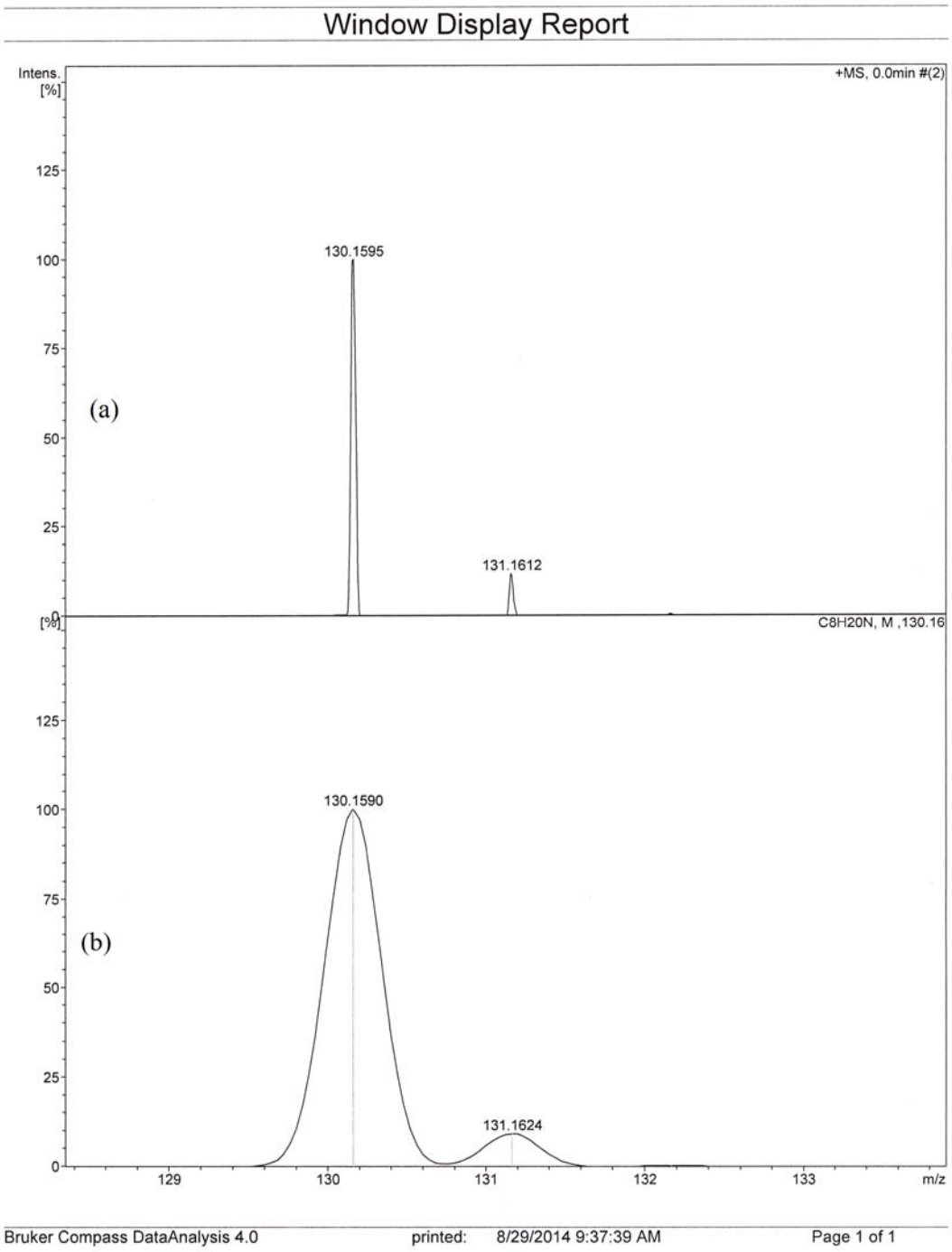
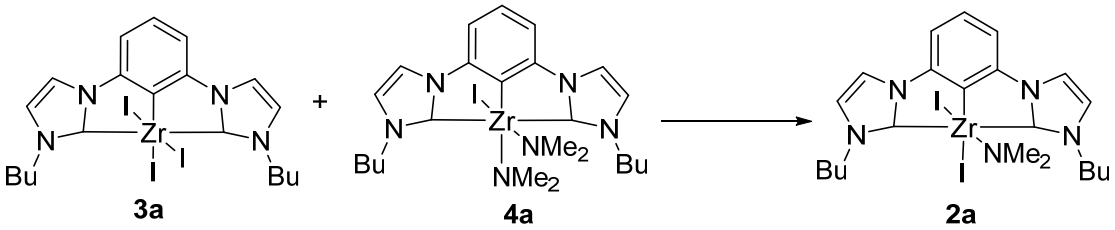


Figure S23. HRMS of dibutylamine hydrochloride. (a) Observed spectrum for $[M\text{-}Cl]^+$. (b) Calculated spectrum for $C_8H_{20}N$.

Conproportionation Results



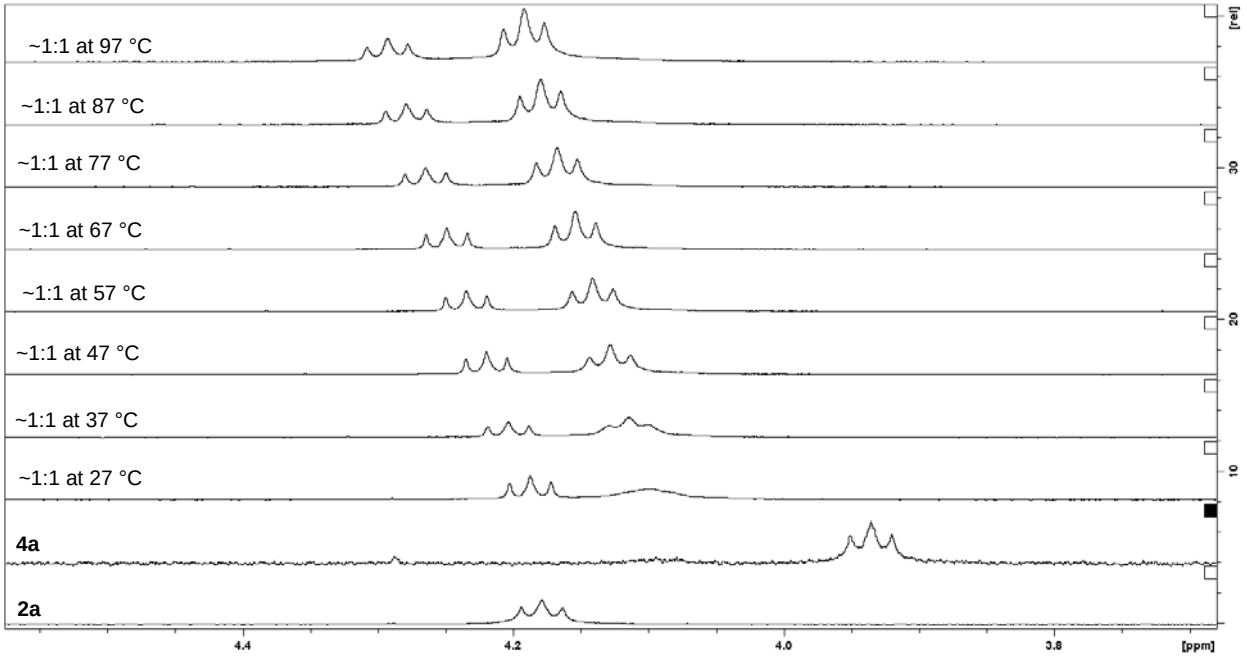


Figure S24. ^{1}H NMR spectrum of the methylene group bound to the imidazolium nitrogen for the conproportionation experiment. The signal for diamido **4a** is clearly no longer present upon mixing, and the new signal corresponds to the mono amido complex **2a** (see Figure S25, [Zr]I_2NMe_2 (Standard Spectra in d-Toluene, 97 °C)).

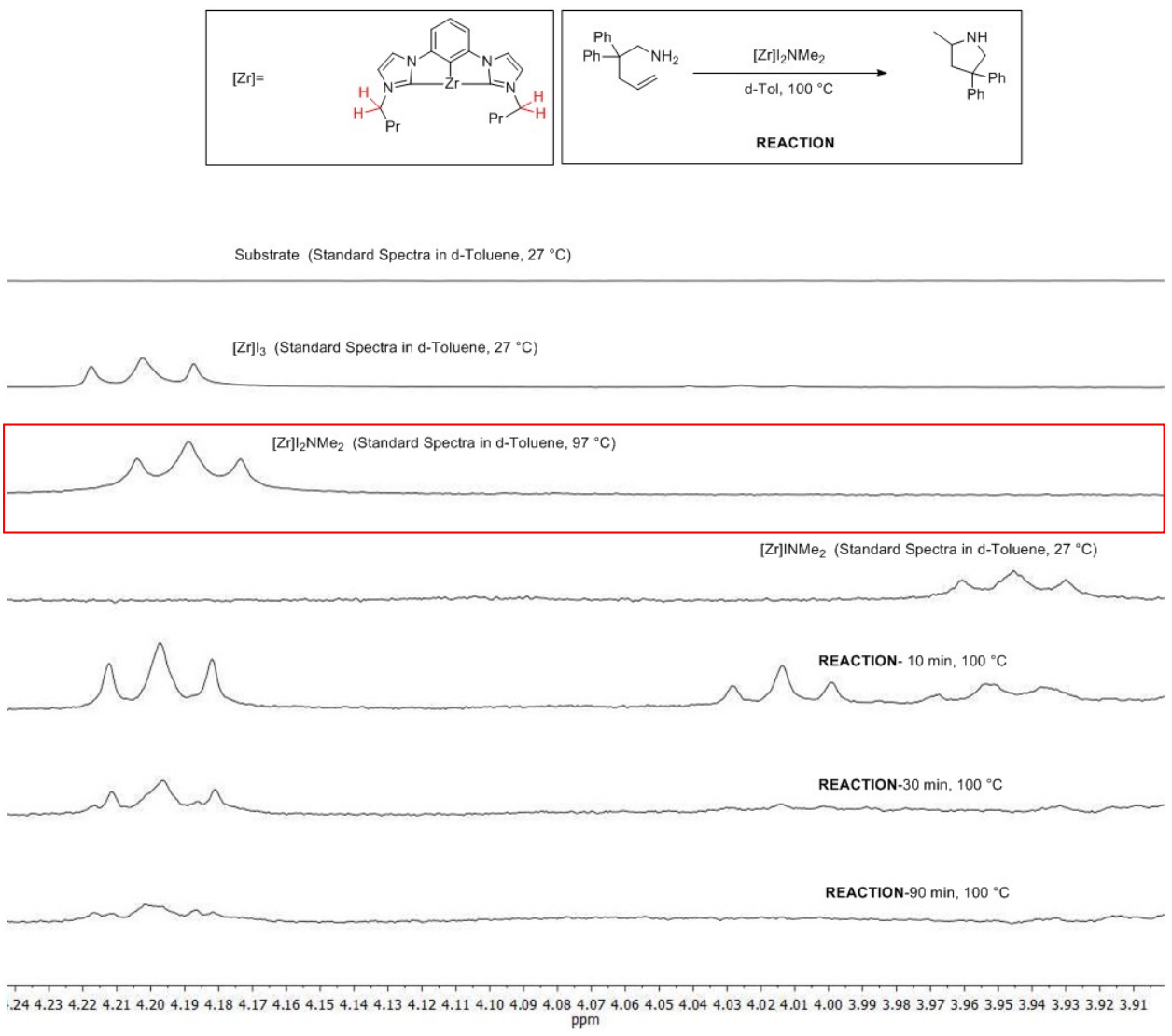


Figure S25. Spectral data on complexes of the key methylene region and observations during the catalytic run.

Evaluation of Precatalyst Activity

General comments

All reactions were performed in screw cap NMR tubes with 1, 2-dichlorobenzene and C_6D_6 as solvent. The reaction mixtures were set up in an Ar glovebox, heated in oil baths, and monitored with ^{1}H NMR spectroscopy at regular time intervals.

Evaluation with 2,2-diphenylpent-4-en-1-amine

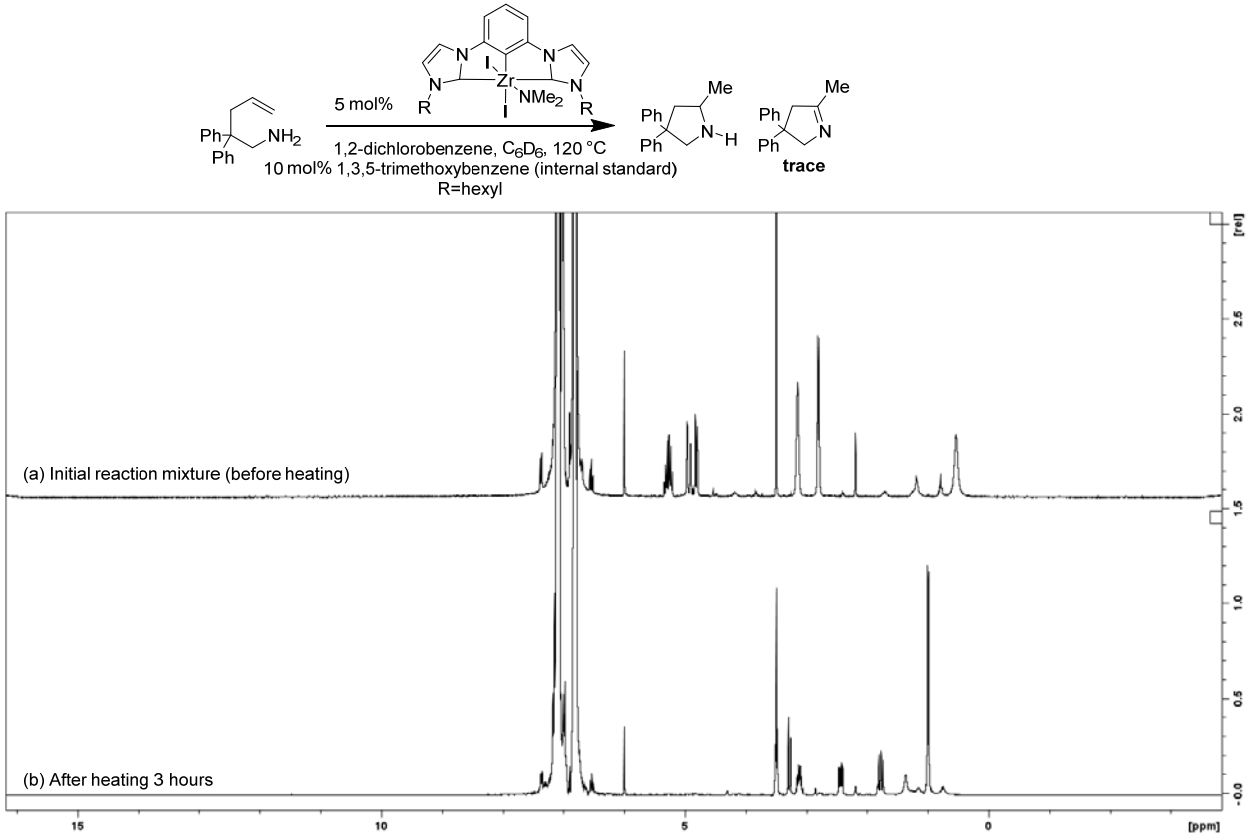


Figure S26. ^{1}H NMR spectra of reaction mixture evaluating 1° aminoalkenes.

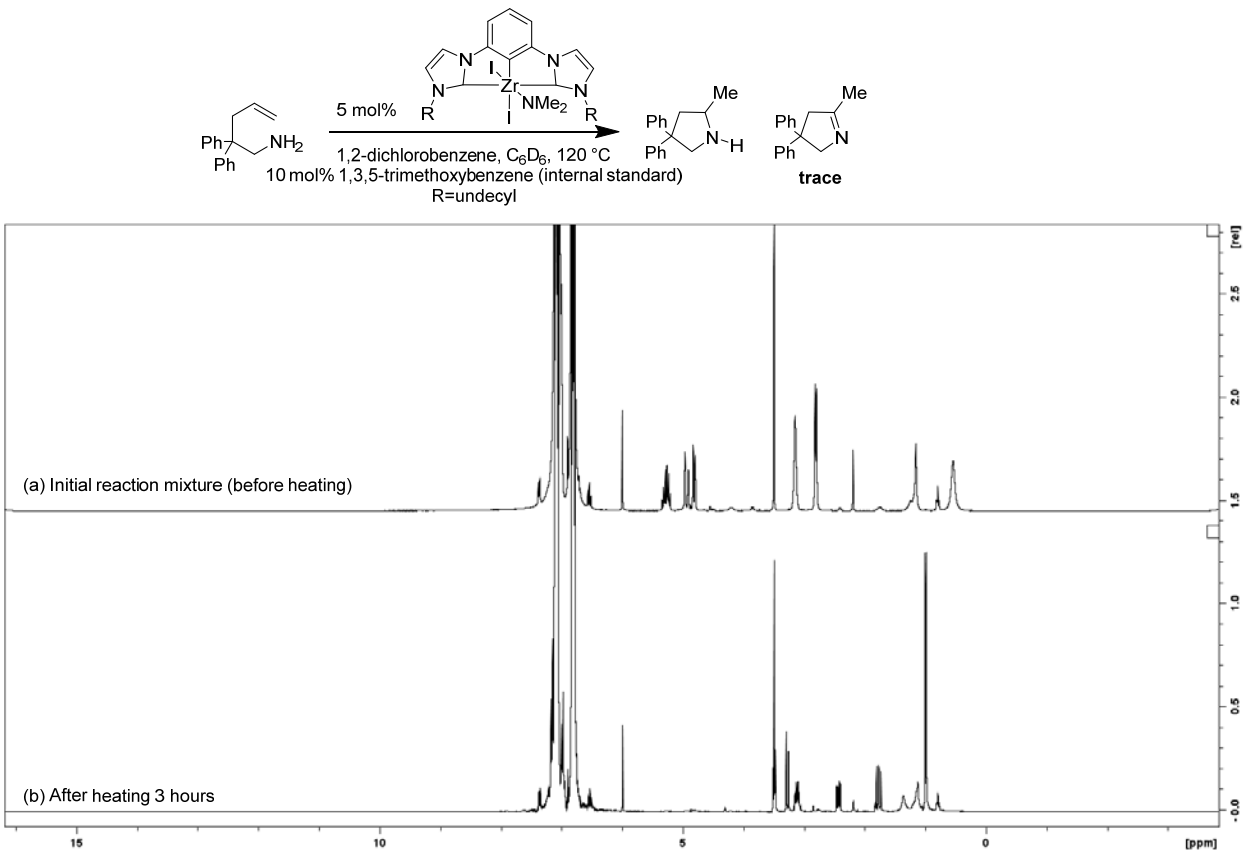


Figure S27. ^{1}H NMR spectra of reaction mixture evaluating 1° aminoalkenes.

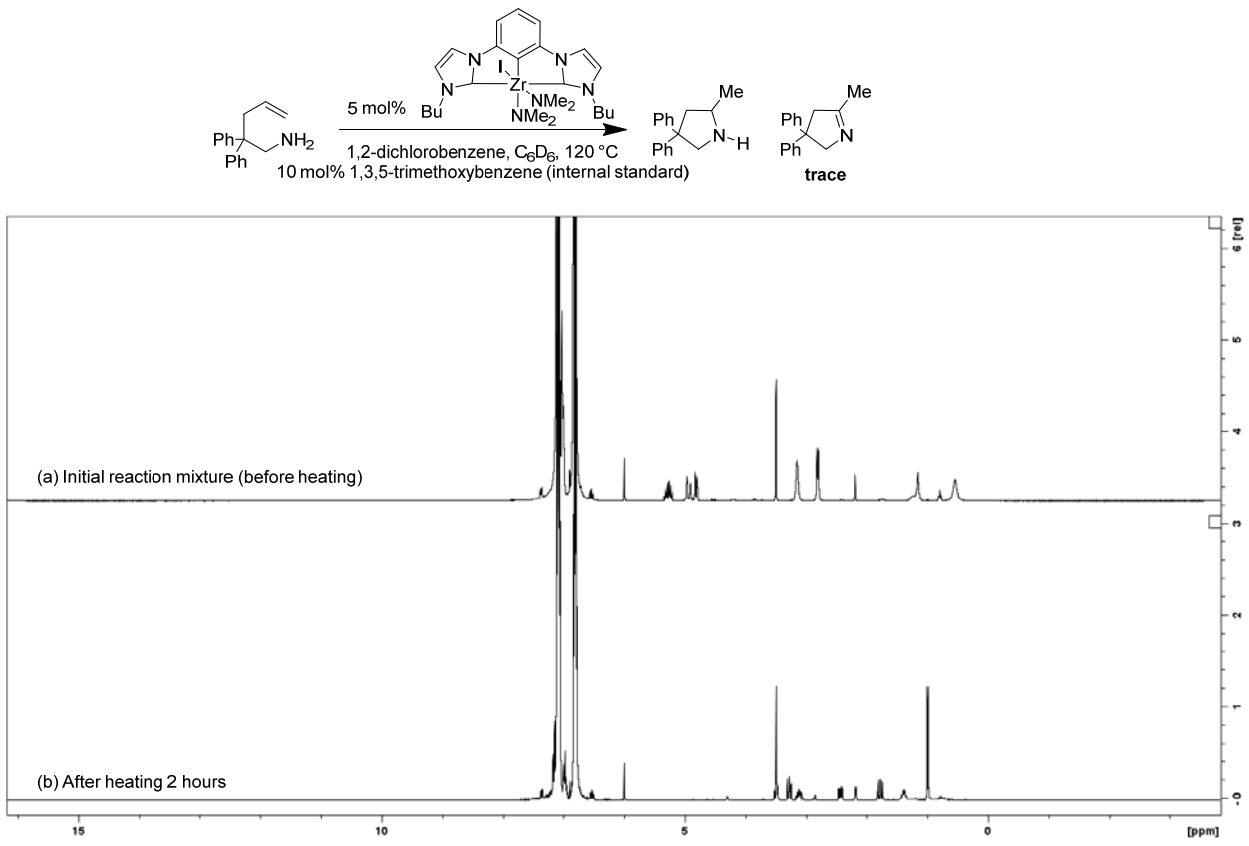


Figure S28. ^{1}H NMR spectra of reaction mixture evaluating 1° aminoalkenes.

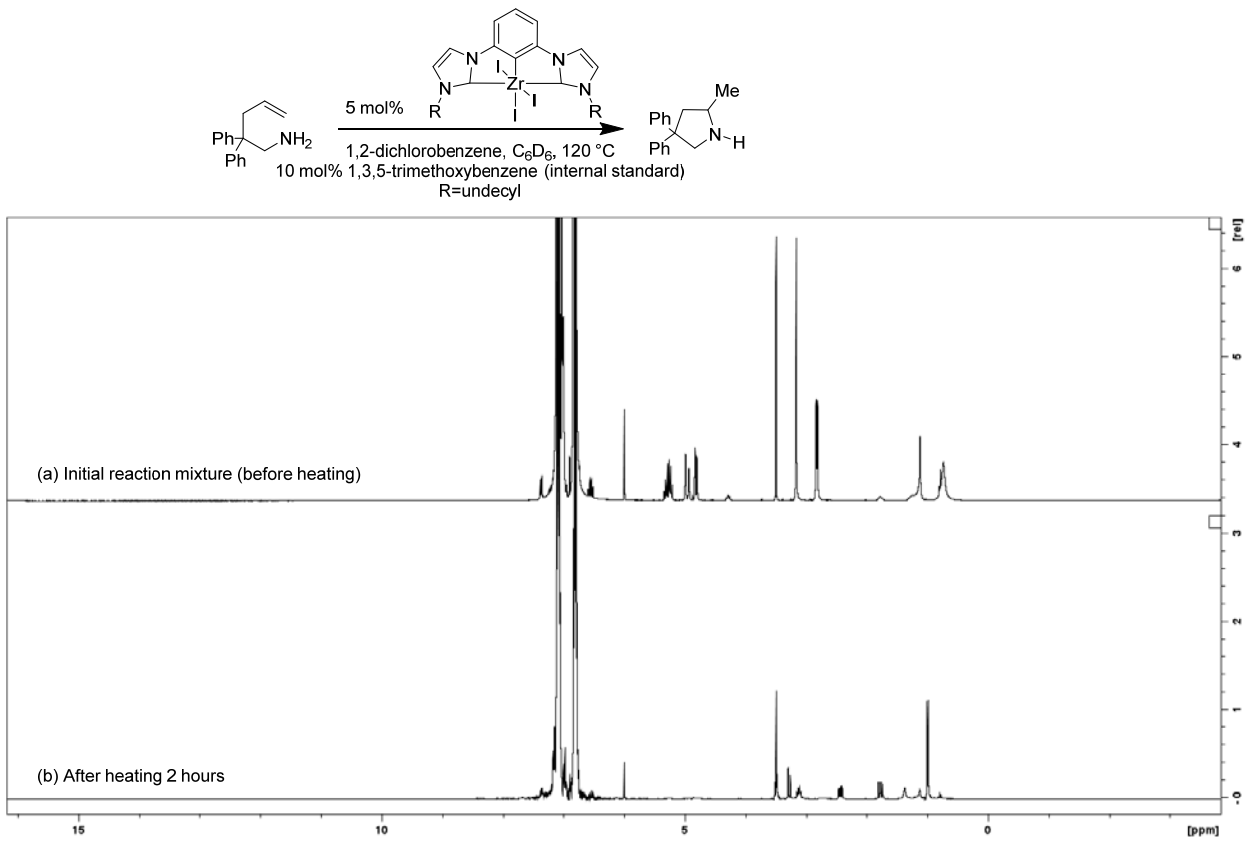


Figure S29. ^{1}H NMR spectra of reaction mixture evaluating 1° aminoalkenes.

Evaluation with N-benzyl-2,2-diphenylpent-4-en-1-amine

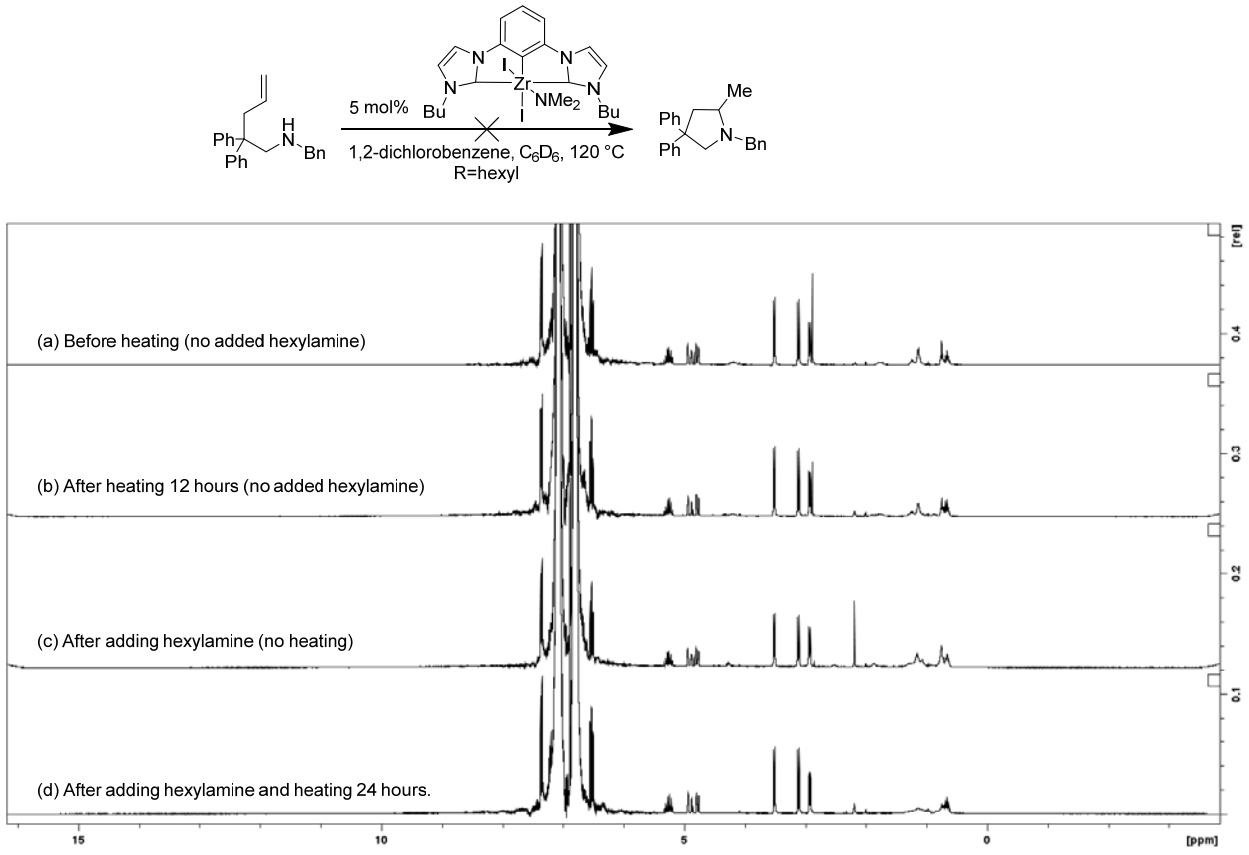


Figure S30. ^{1}H NMR spectra of reaction mixture evaluating 2° aminoalkenes.

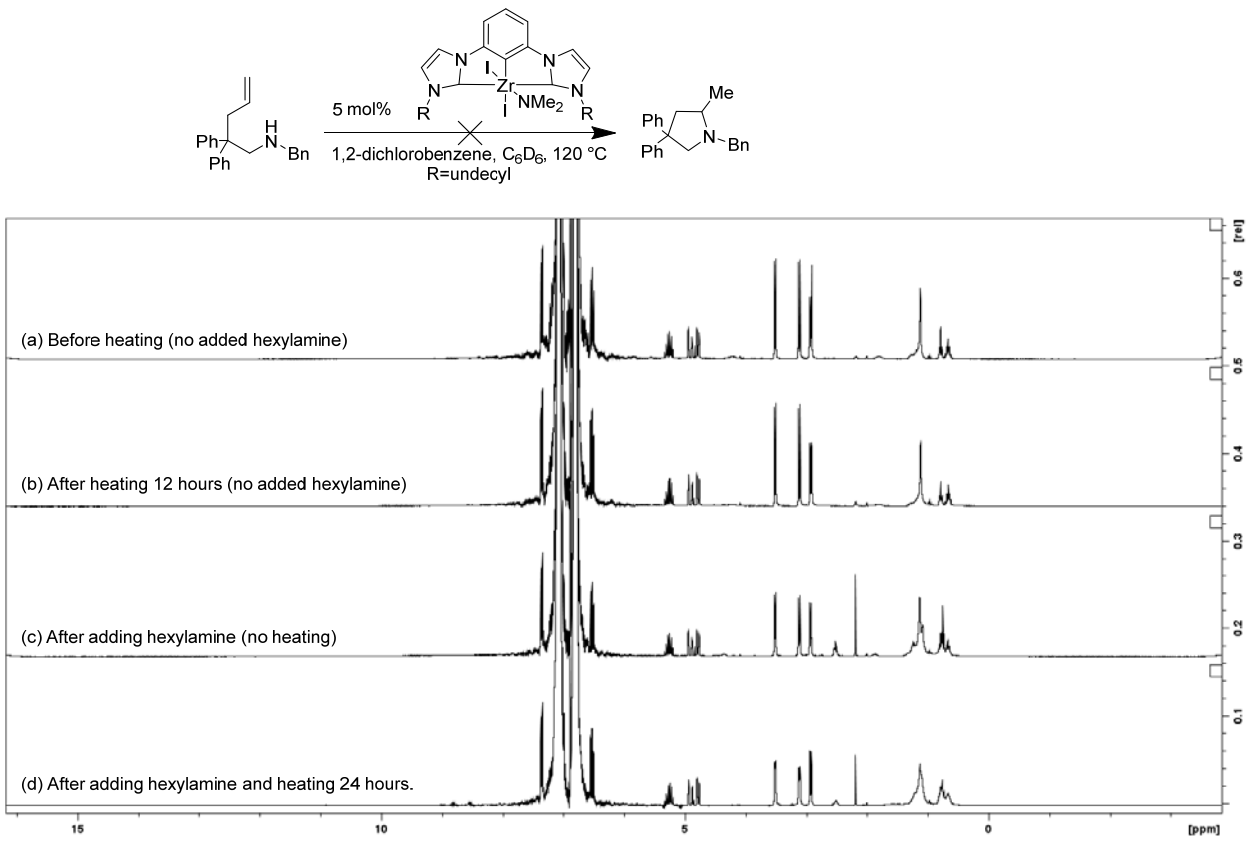


Figure S31. ^{1}H NMR spectra of reaction mixture evaluating 2° aminoalkenes.

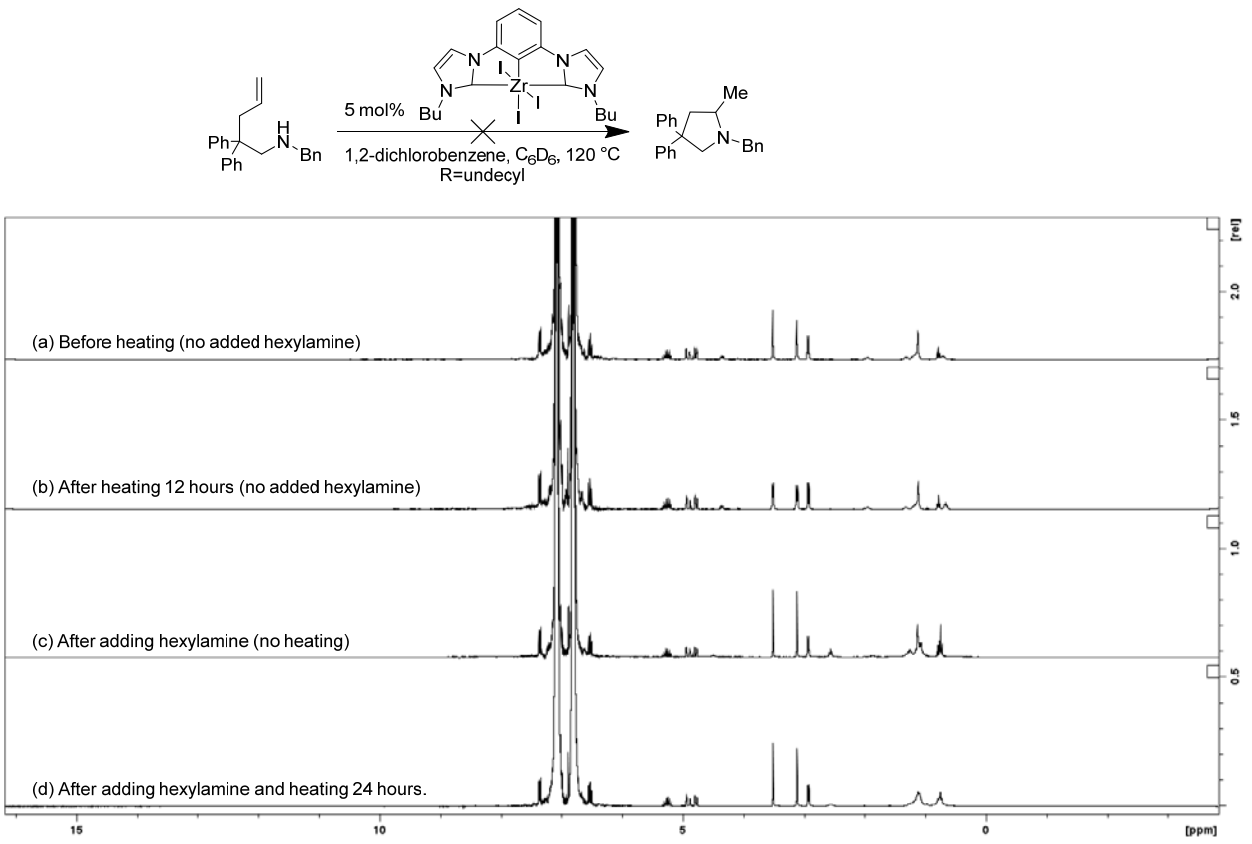


Figure S32. ^{1}H NMR spectra of reaction mixture evaluating 2° aminoalkenes.

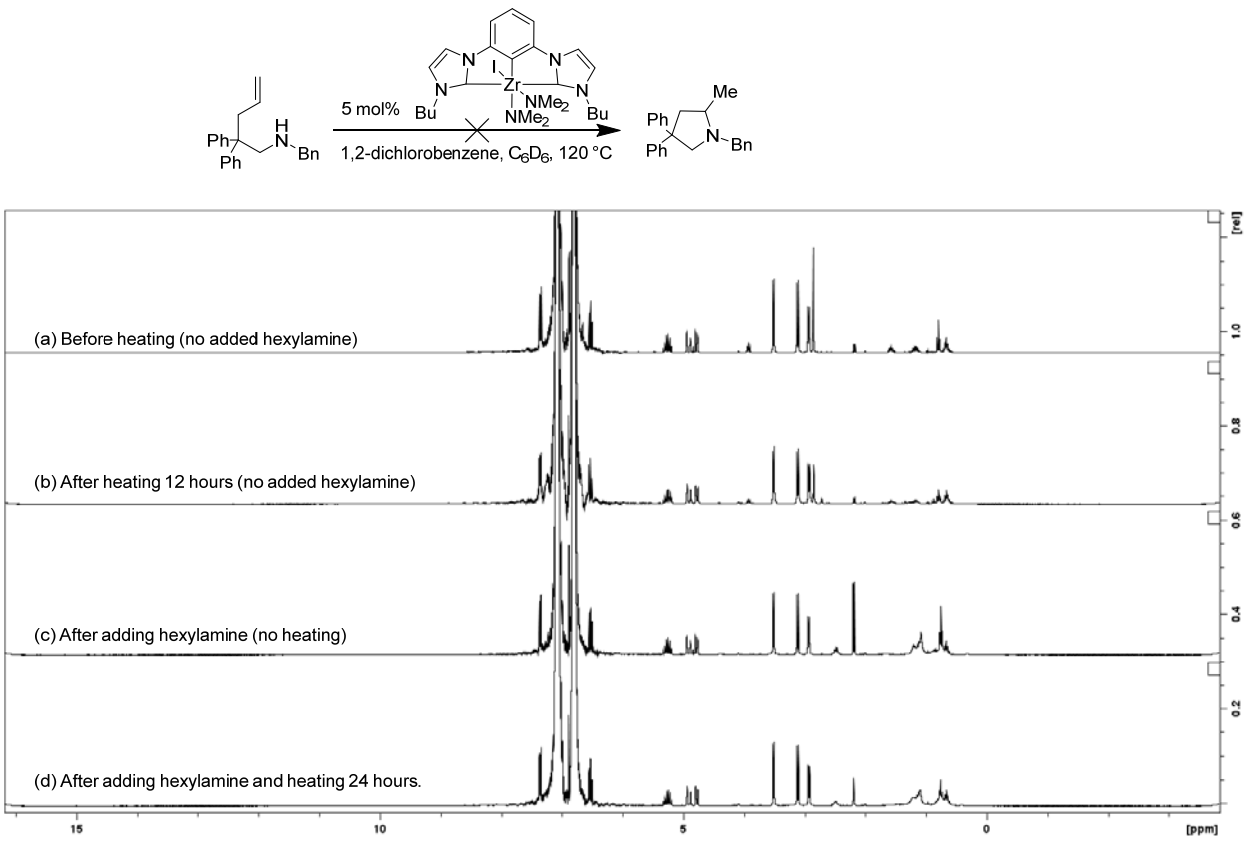


Figure S33. ^{1}H NMR spectra of reaction mixture evaluating 2° aminoalkenes.

Observations from Kinetic Studies

Characterization of substrate adduct

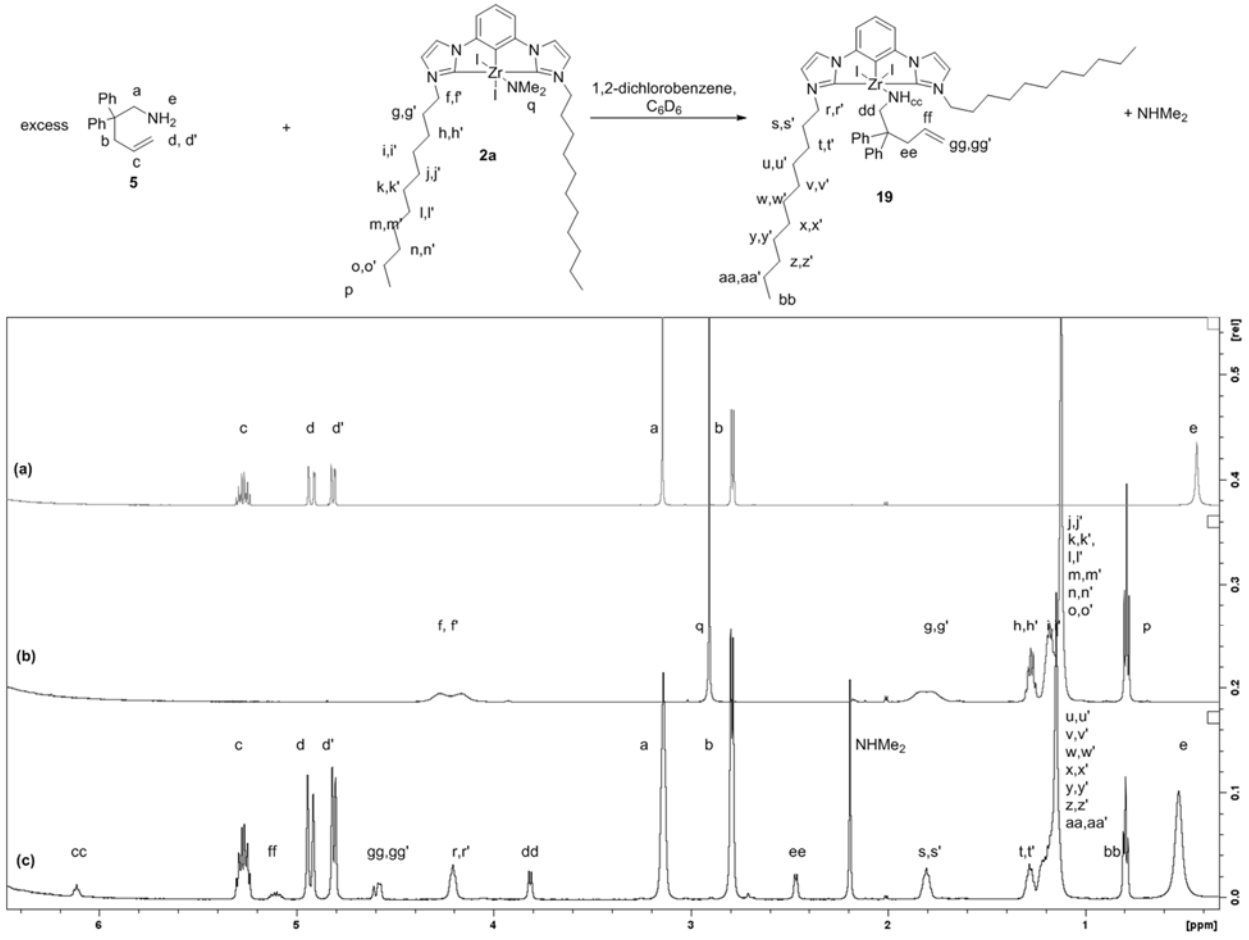


Figure S34. ^{1}H NMR spectra of (a) Substrate only (b) Diiodo complex **2b** only (c) Diiodo complex **2b** + excess substrate. All spectra were collected at 25 °C in 10:1 1,2-dichlorobenzene, C_6D_6. The aromatic region is obscured by signals from 1,2-dichlorobenzene.

Observations from the addition of Substrate·HCl to reaction conditions

Substrate **5** (8.4 mg, 0.035 mmol) was added to a solution of diiodo complex **2b** (13.0 mg, 0.014 mmol) and 1,2-dichlorobenzene:C_6D_6 (8:1, 0.65 mL). The homogenous solution was placed in a preheated NMR probe and an ^{1}H NMR spectrum taken (Figure S35a). The sample was ejected from the NMR probe, cooled to room temperature and substrate **5**·HCl was added (1.0 mg, 0.0037 mmol). The still homogenous solution was again placed in the NMR probe and ^{1}H NMR spectra collected at regular intervals. Peaks at δ 11.50, 9.09, and 8.42 appeared, which are consistent with the formation of imidazolium salt **1c**.

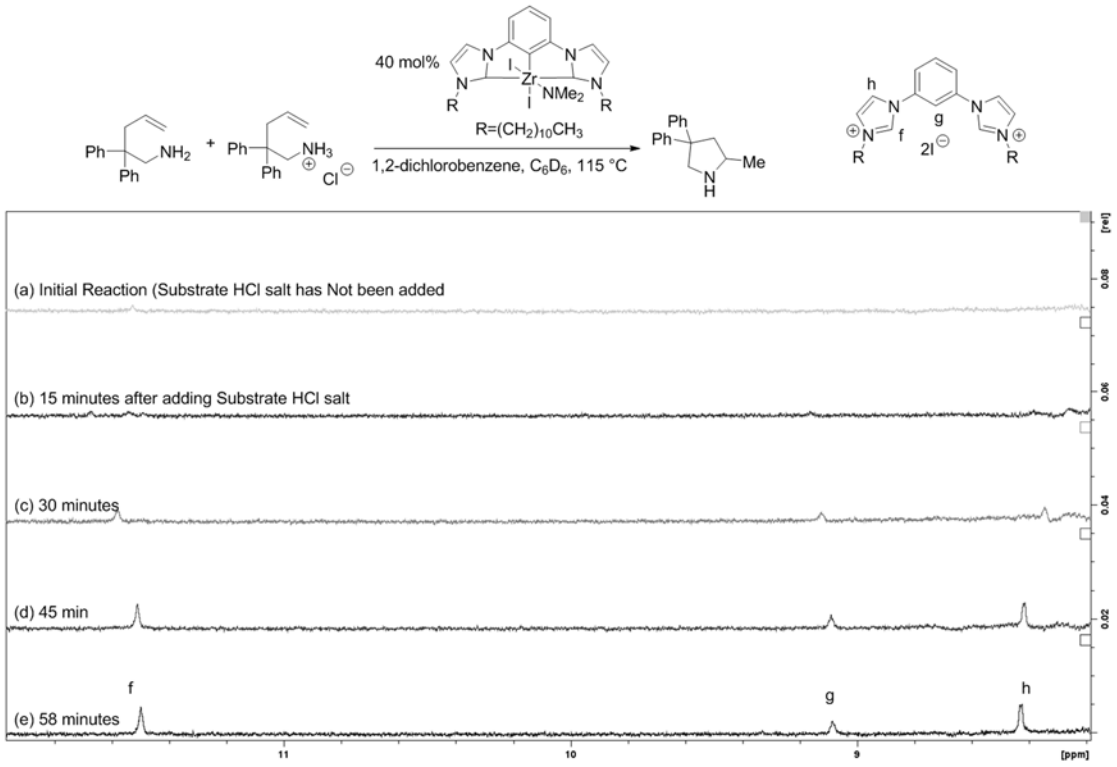
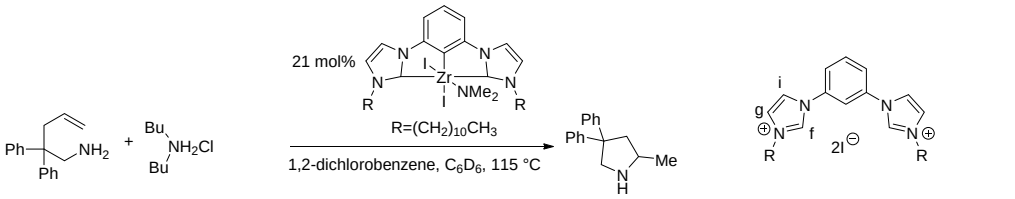


Figure S35. ^{1}H NMR spectra of (a) Mixture of substrate and 40 mol % diiodo complex **2b** (The Substrate HCl salt has not been added). (b) Mixture 15 min after adding Substrate HCl salt (c) Mixture 30 min after adding Substrate HCl salt (d) Mixture 45 min after adding Substrate HCl salt (e) Mixture 58 min after adding Substrate HCl salt. ^{1}H NMR spectra were taken at 115 °C.

Observations from the addition of butylamine hydrochloride to reaction conditions

Solid diiodo complex **2b** (6.7 mg, 0.0074 mmol) was added to a solution of Substrate **5** (8.6 mg, 0.036 mmol) and 1,2-dichlorobenzene/C_6D_6 (0.72 mL). The homogenous solution was placed in a preheated NMR probe and a ^{1}H NMR spectrum was obtained (Figure S36a). The sample was allowed to cool to room temperature and butylamine hydrochloride (1.1 mg, 0.0066 mmol) was added. The still homogenous sample was returned to the preheated NMR probe and spectra were collected at regular time intervals. Peaks at δ 11.50, 9.09, and 8.37 appeared, which are consistent with the formation of imidazolium salt **1c**.



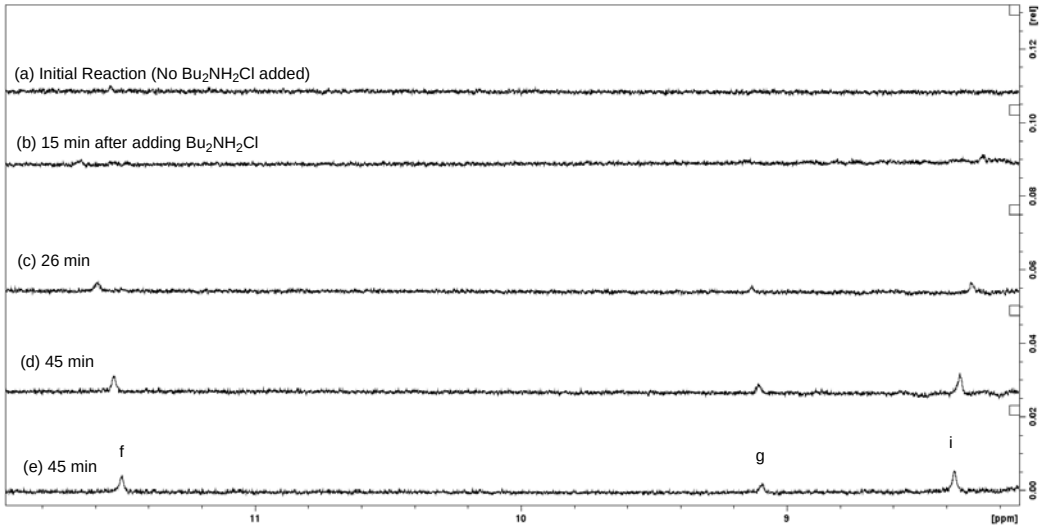


Figure S36. ^{1}H NMR spectra of (a) Mixture of substrate and 21 mol % diiodo complex **2b** (The $Bu_2NH{\cdot}HCl$ salt has not been added). (b) Mixture 15 min after adding $Bu_2NH{\cdot}HCl$ salt (c) Mixture 26 min after adding $Bu_2NH{\cdot}HCl$ salt (d) Mixture 45 min after adding $Bu_2NH{\cdot}HCl$ salt (e) Mixture 90 min after adding $Bu_2NH{\cdot}HCl$ salt. ^{1}H NMR spectra were taken at 115 °C.

Observations from spiking the reaction conditions with imidazolium salt

A standard solution of substrate (0.2104 M, 0.700 mL, 0.147 mmol) was added to solid precatalyst **2b** (8.5 mg, 0.0094 mmol) resulting in a homogenous yellow solution. The sample was placed in a preheated NMR probe and a ^{1}H NMR spectrum was collected (Figure S37a). The sample was cooled to room temperature and solid imidazolium salt **1c** was added (2.0 mg, 0.0026 mmol). The sample was again placed in a preheated NMR probe and a ^{1}H NMR spectrum was collected. When ejected, the sample was homogenous.

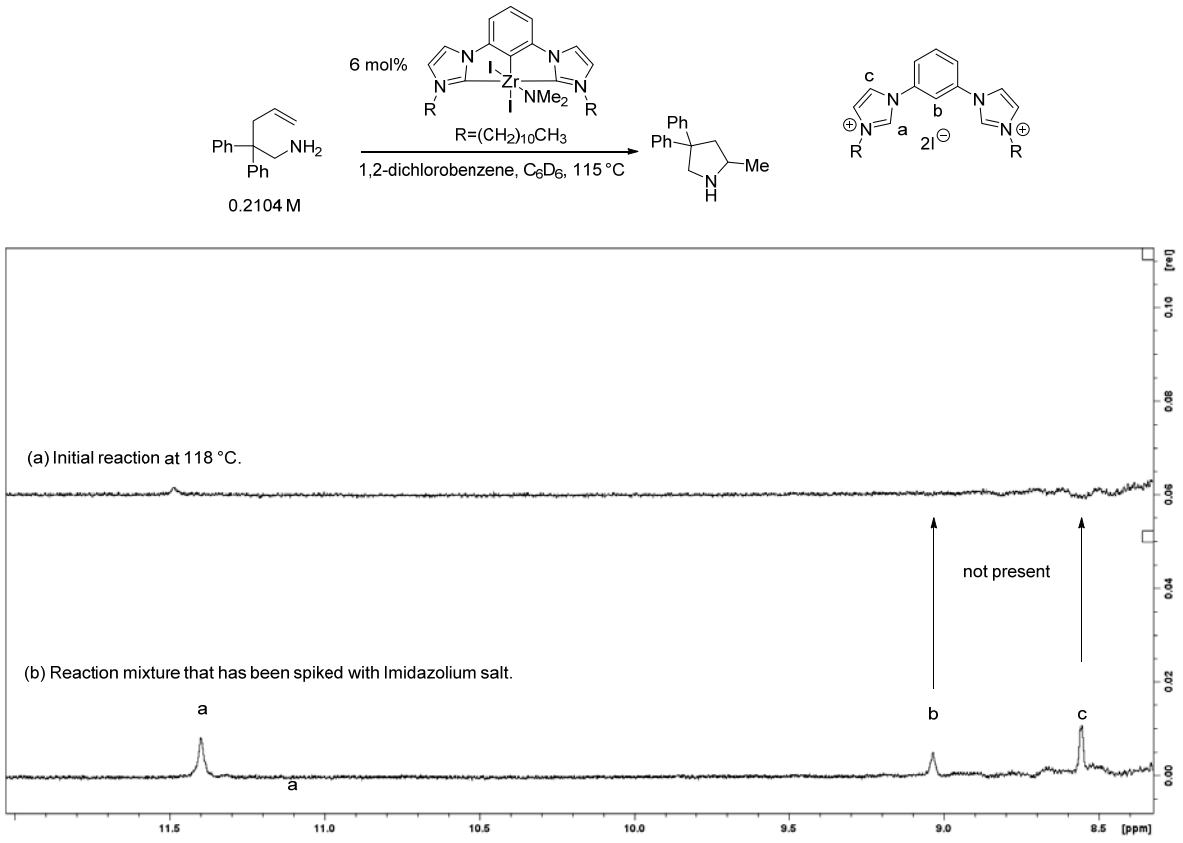


Figure S37. ^{1}H NMR spectra of (a) Initial reaction mixture at 118 °C (b) Initial reaction mixture that has been spiked with imidazolium salt indicating peaks for protons b and c are not present in the initial reaction mixture.

*Observation of imidazolium salt formation in homogenous conditions with complex **3a***

Solid triiodo complex **3a** (1.0 mg, 0.00010 mmol) and 1,2-dichlorobenzene:C_6D_6 (10:1, 0.63 mL) were combined in a screw cap NMR tube resulting in a homogenous yellow solution. The sample was placed inside a preheated and calibrated NMR probe (110 °C) and a ^{1}H NMR spectrum collected. No resonances > δ 8.5 were observed. The sample was allowed to cool to room temperature and substrate **5** was added (27.2 mg, 0.115 mmol). The sample was placed in the preheated NMR probe and a ^{1}H NMR spectrum collected. Three resonances were observed above δ 8.5 ppm (δ 11.55, 9.09, and 8.46). The sample was allowed to cool to room temperature and imidazolium salt **1c** (1.2 mg, 0.0015 mmol) was added. The sample was again placed in the preheated NMR probe and a ^{1}H NMR spectrum was collected. Three resonances > δ 8.5 ppm were observed (δ 11.48, 9.06, 8.51). See Figure S38 for spectra.

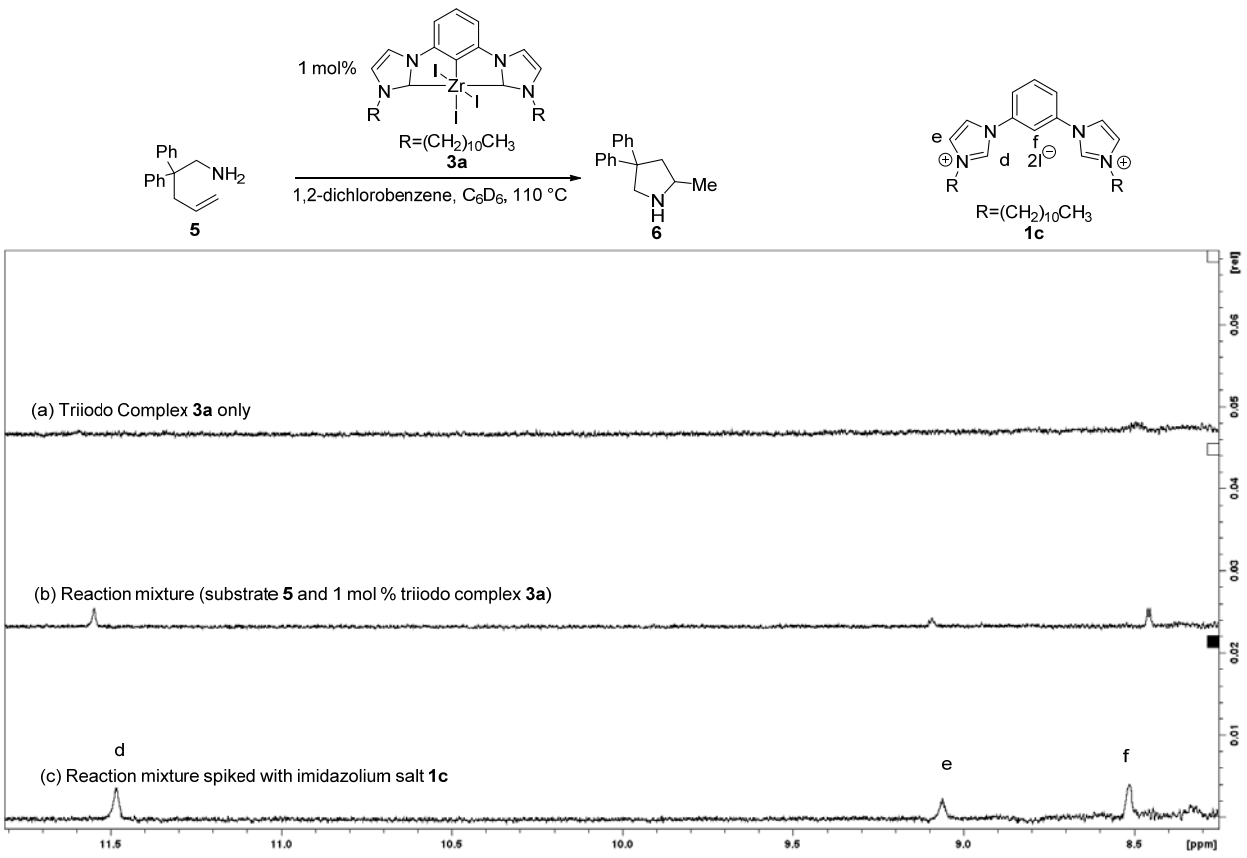


Figure S38. ^{1}H NMR spectra of (a) triiodo complex **3a** only (b) Substrate 9 and 1 mol % triiodo complex **3a** (c) Reaction mixture spiked with imidazolium salt **1c**. All spectra were taken at 110 °C in 10:1 1,2-dichlorobenzene:C_6D_6

Table S1. Selected resonances and differences from spectra shown in Figure S38.

Spectra	δ (ppm)		
(a)	–	–	–
(b)	11.55	9.09	8.46
(c)	11.48	9.06	8.51
Δ δ	0.07	0.03	-0.05

Observation of imidazolium salt formation from heterogeneous reaction conditions

CCC-NHC Zr complex **2a** (0.0067 g, 0.011 mmol), substrate **5** (0.0651 g, 0.274 mmol), and d-toluene (0.72 ml) were combined at room temperature yielding a yellow, homogenous solution. The solution was placed in a 100 °C oil bath for 20 minutes, during which time a fine solid had formed. CH_2Cl_2 (2 mL) was added yielding a homogenous solution and the mixture was immediately characterized with ^{1}H NMR spectroscopy. Several signals, consistent with the formation of imidazolium salt **1b**, were observed. ^{1}H NMR (CH_2Cl_2/C_6D_6): Imidazolium salt **1b** δ11.13 (2 H, s), 8.78 (t, J=2.1 Hz, 1 H), 8.24 (t, J=1.9 Hz, 2H), 7.92 (dd, J_1=8.29 Hz, J_2=2.3 Hz, 2H), 7.60 (t, J=8.3 Hz, 1H).

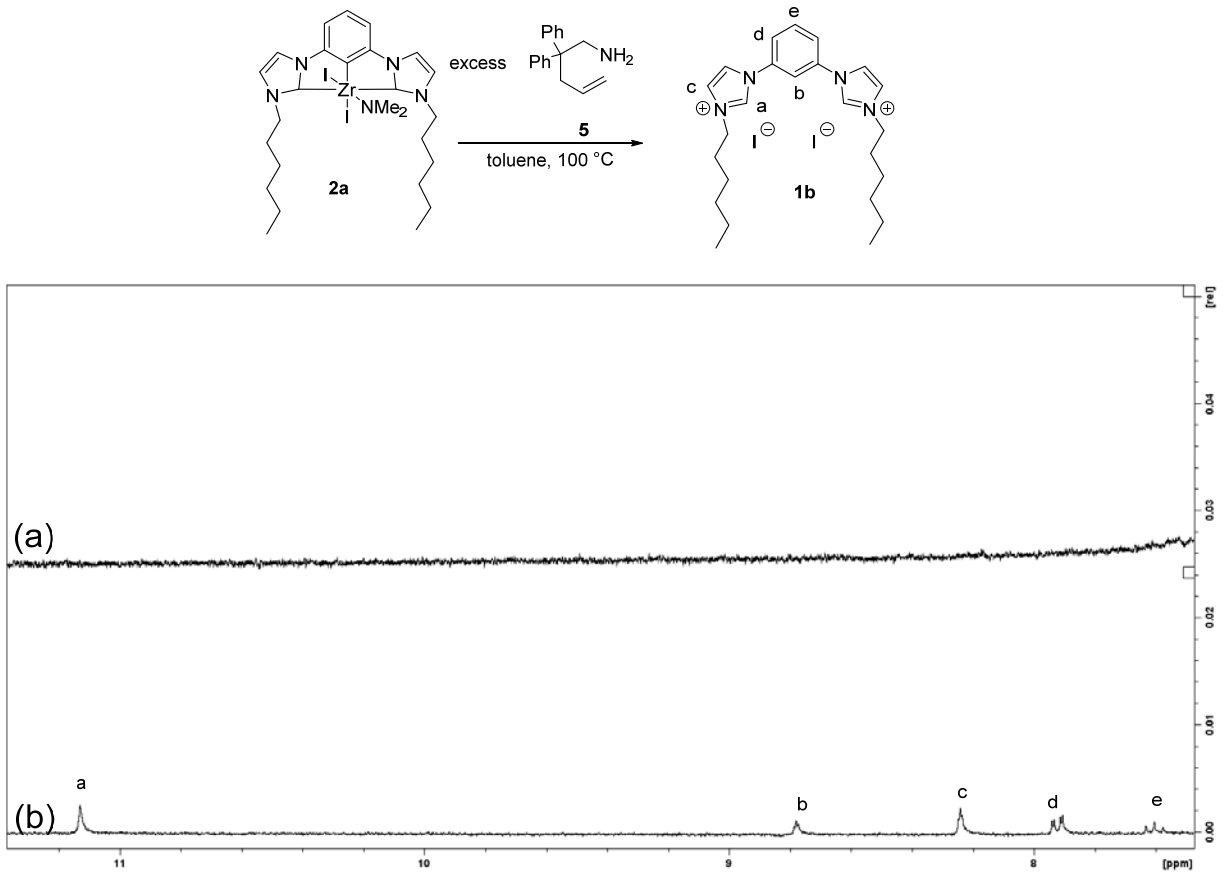


Figure S39. (a) ^{1}H NMR spectrum of the reaction mixture before heating. (b) ^{1}H NMR spectrum of the reaction mixture after heating (solid forms), cooling to room temperature, and adding CH_2Cl_2.

Time elapsed plot of oxidative product formation.

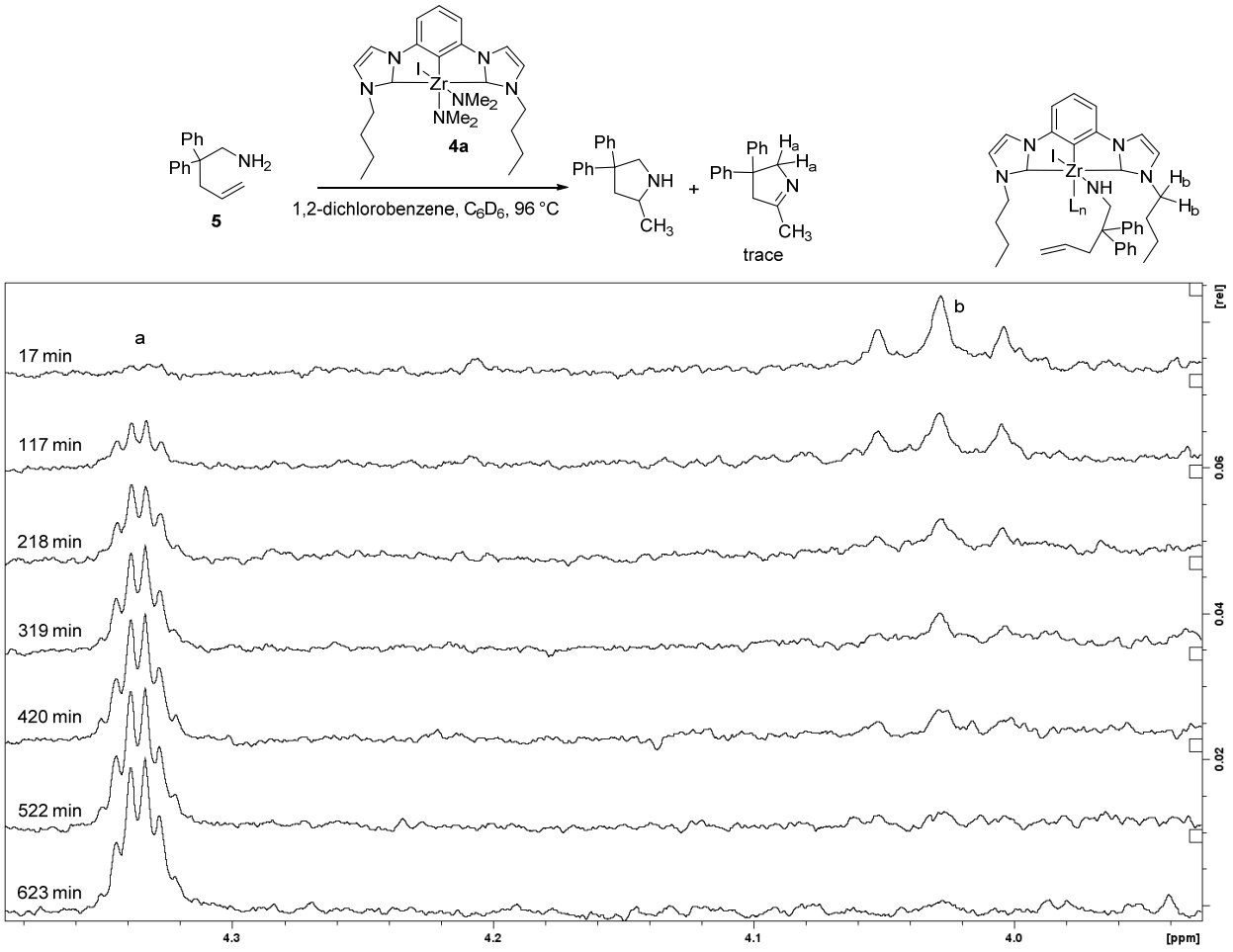
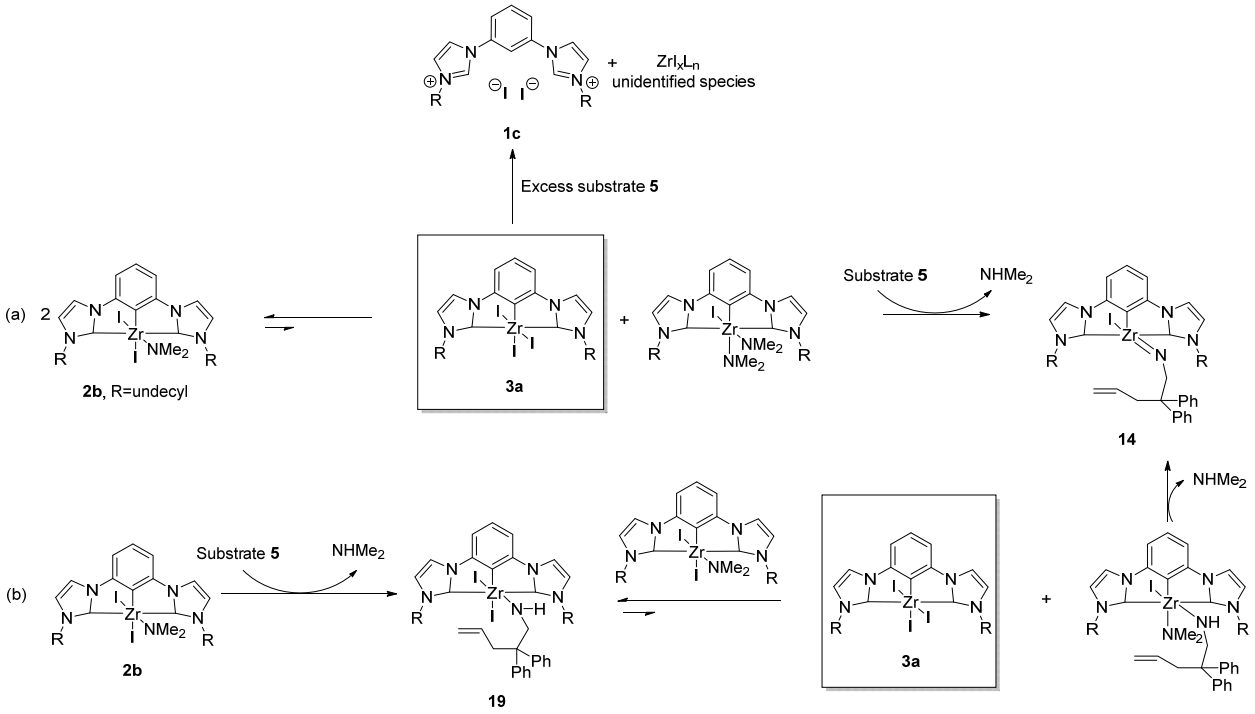


Figure S40. Time elapsed plot showing rise of oxidative amination product signal (δ 4.34) and decay of triplet (δ 4.03) indicative of CCC-NHC Zr pincer complexes.

Disproportionation reactions considered in proposing mechanism



Scheme S1. Reactions considered in determining source of intermediate **14**. (a) Disproportionation of two diiodo complexes and subsequent double deprotonation of a substrate molecule. (b) Ligand exchange to form the substrate adduct **9**, then ligand exchange to form

When triiodo complex **3a** is in solution with the substrate **5**, it decomposes to imidazolium salt **1c**, which is observed with peaks at δ 11.55, 9.09 and 8.46 (Figure S38). Therefore, if triiodo complex **3a** was formed at observable concentrations in the reaction conditions, it would react with the substrate and form the imidazolium salt **1c** (which is observable at δ 11.48, 9.06, and 8.51). These signals were not observed in reactions involving complex **2b** (Figure S37).

Representative Kinetic Run

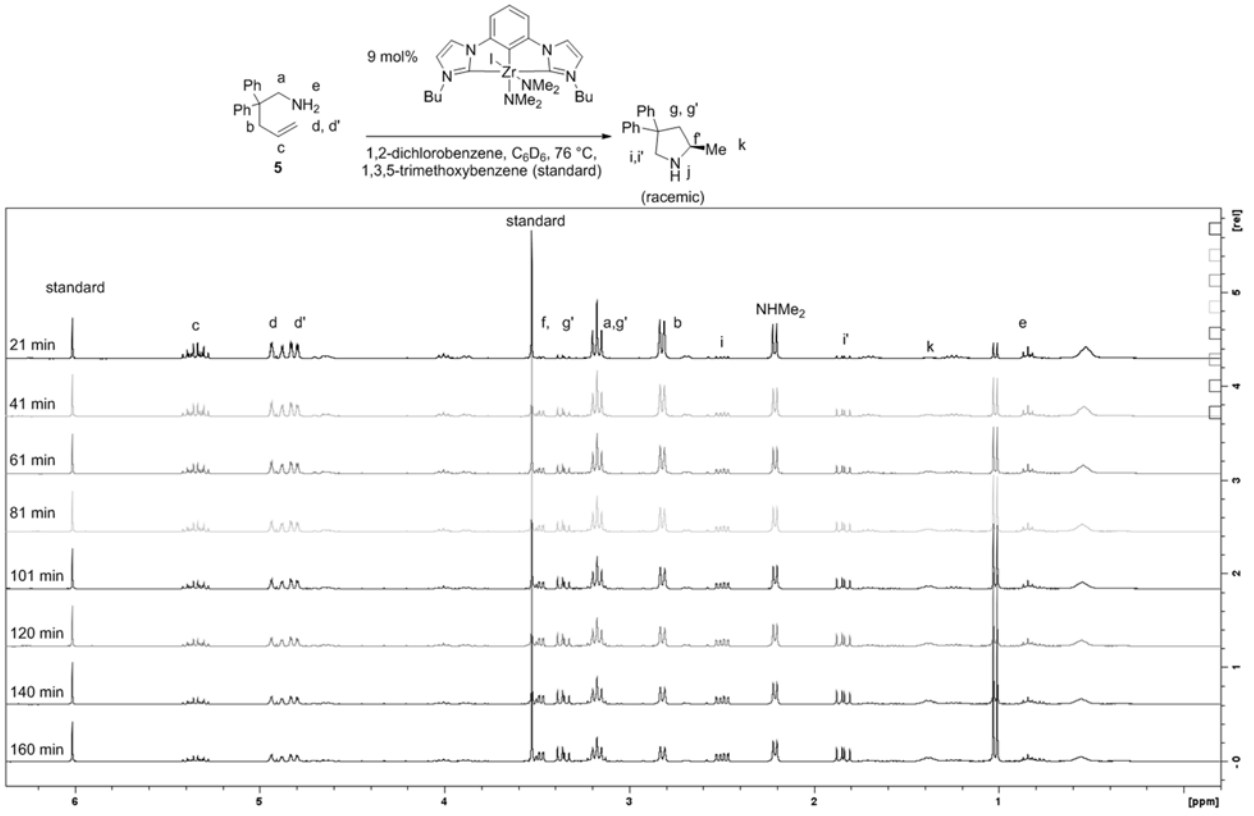


Figure S41. ^{1}H NMR spectra from a representative kinetic run.

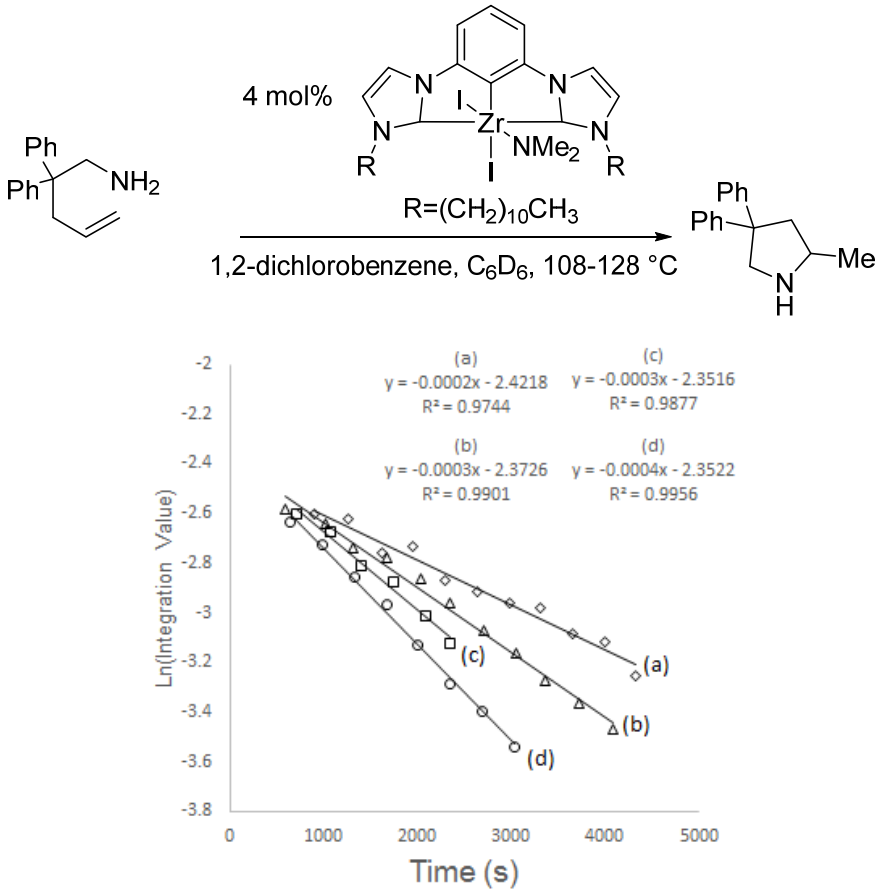


Figure S42. Data from Erying plot analysis using substrate **5** (0.282 M) and 4 mol % diiodo complex **2b**. (a) 108 °C (b) 117 °C (c) 123 °C (d) 128 °C. See Error Analysis for Eyring Plots using Complex **2b** as a precatalyst for detailed slope values.

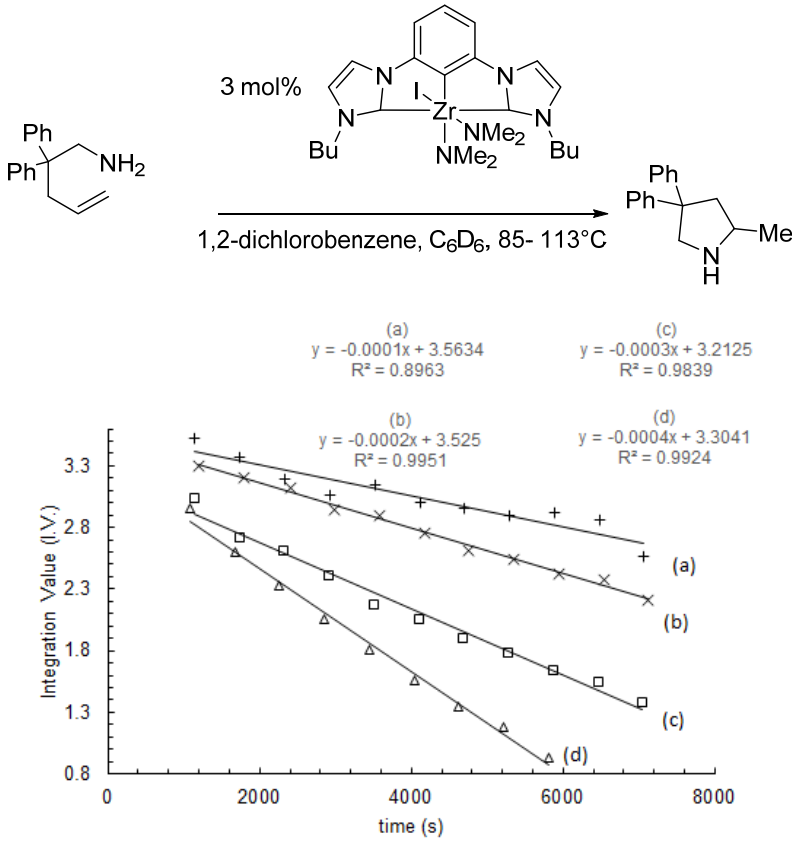


Figure S43. Data from Erying plot analysis using substrate **5** (0.282 M) and 3 mol % diamido complex **4a**. (a) 85°C (b) 93 °C (c) 104 °C (d) 113 °C. See Error Analysis for Eyring Plots using Complex **4a** as a precatalyst for detailed slope values.

Initial Rate Plots for Substrate and Precatalyst Order of Reaction Determination

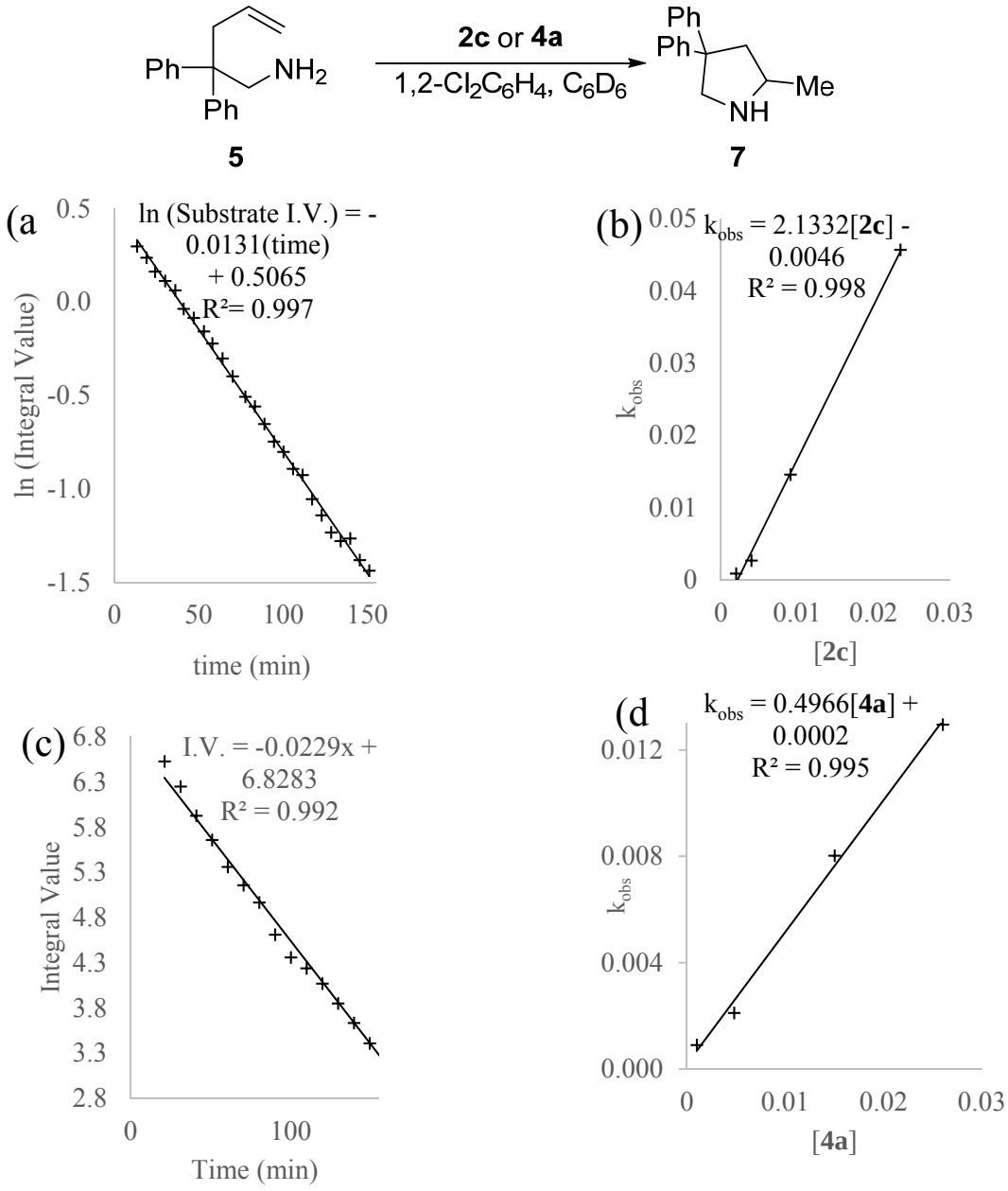
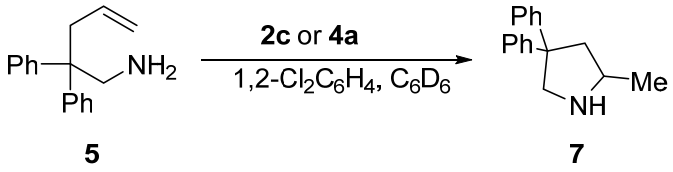
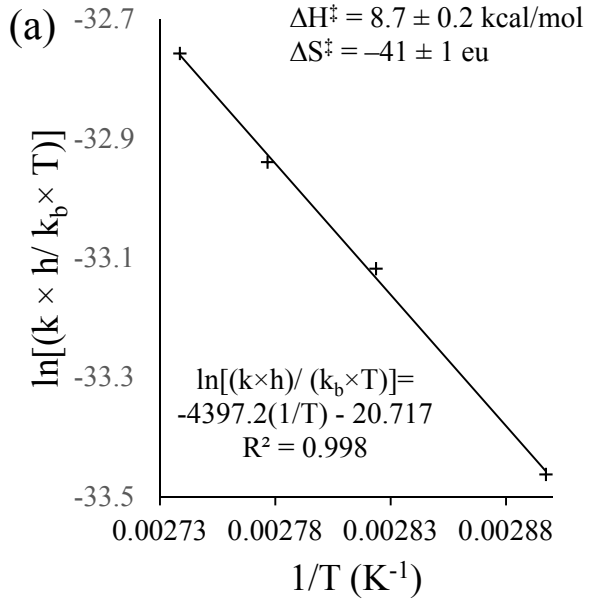


Figure S44. Plots showing substrate and precatalysts order. (a) Plot of ln(substrate integration) vs time using 3.2 mol% precatalyst **2c** ($[Zr]_0$ = 0.0091 M) at 112 °C with $[substrate]_0$ = 0.282 M. At 150 min the reaction was at 83% conversion. (b) Plot of k_{obs} vs [**2c**] at 112 °C (c) Plot of product integration vs time using 8.8 mol% diamido complex **4a** ($[Zr]_0$ = 0.00263 M) at 76 °C with $[substrate]_0$ = 0.298 M. At 179 min the reaction was at 59% conversion and still linear. (d) Plot of k_{obs} vs [complex **4a**] when at 76 °C.

Eyring Plots for Activation Parameter Determinations



5 **7**



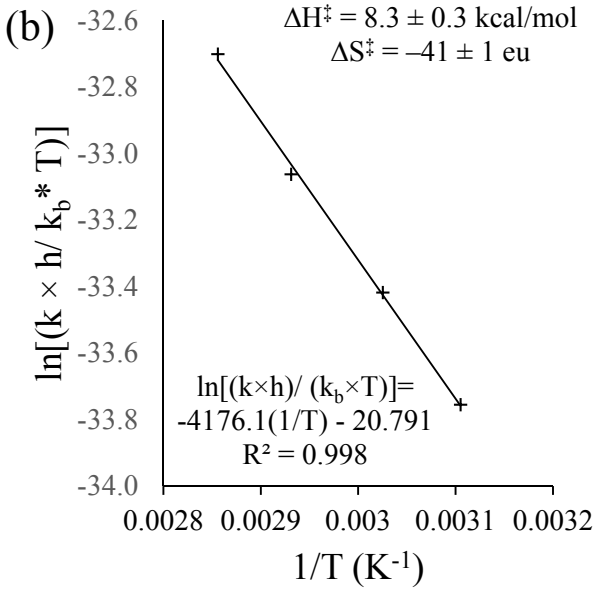


Figure S45. (a) Erying plot for diiodo complex **2c** in the temperature range 108 - 128 °C (b) Erying plot for diamido complex **4a** in the temperature range 76-104 °C.

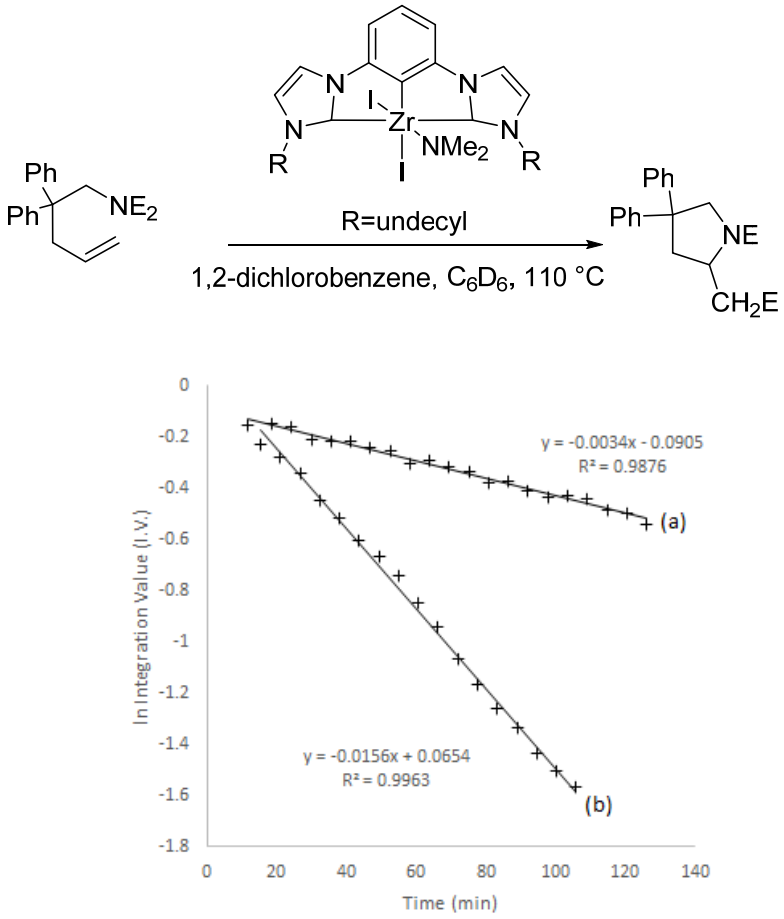


Figure S46. Plot of substrate integration vs time for (a) **6-D** (ND_2) and (b) **6** (NH_2).

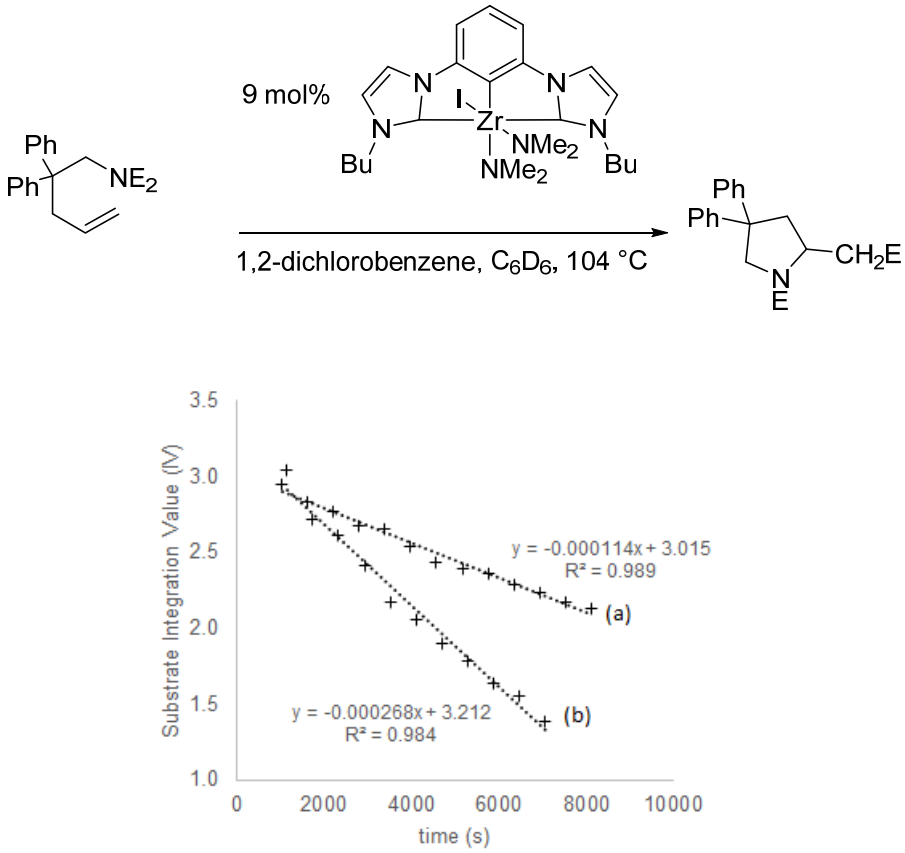


Figure S47. Plot of substrate integration vs time for (a) **5-D** (ND_2) and (b) **5** (NH_2)

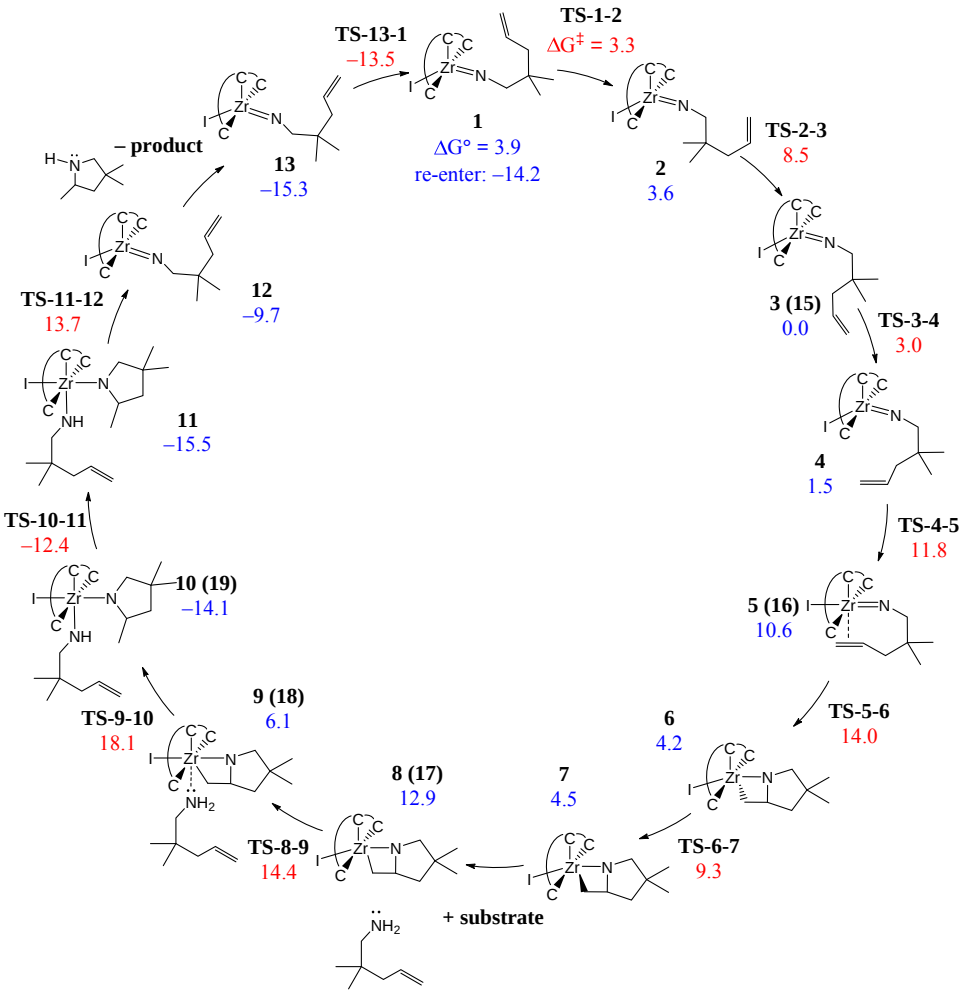


Figure S48. Final proposed free energy diagram following the principle of microscopic reversibility for the imido [2+2] cycloaddition mechanism of CCC-NHC pincer Zr complexes. The numbers in parentheses correspond to the numbering the main text.

Computational Details

Table S2. Electronic energies and free energies (absolute energies in Hartrees, relative energies in kcal mol^{-1}). $\Delta G_{gas}°$ are gas-phase relative free energies. ΔG_{conc} are relative free energies including the 1.77 kcal mol^{-1} concentration correction.

Numbering article	Numbering in SI	E	G		
2		-963.31011904	-963.047710		
4		-1086.24947362	-1085.907688		
substrate, 5	**substrate**	-330.02912501	-329.858123		
$HNMe_2$		-134.96934811	-134.904375		
$(H_2NMe_2)I$		-146.99007904	-146.920386		
product, 7	**product**	-330.06184032	-329.886971		
		E	**G**	$\Delta G_{gas}°$ (kcal mol^{-1}) relative to **4**	ΔG_{conc} (kcal mol^{-1}) relative to **3**
	1	-1146.31598705	-1145.953511	2.23	3.9
	TS-1-2	-1146.31682818	-1145.952817	2.66	4.3
	2	-1146.31571451	-1145.953874	2.00	3.6
	TS-2-3	-1146.30860772	-1145.946113	6.87	8.5
15	**3**	-1146.32137499	-1145.959674	-1.64	0.0
	TS-3-4	-1146.31752064	-1145.954941	1.33	3.0
	4	-1146.31948395	-1145.957362	-0.19	1.5
	TS-4-5	-1146.30603697	-1145.940893	10.15	11.8
16	**5**	-1146.30767423	-1145.942829	8.93	10.6
	TS-5-6	-1146.30146095	-1145.937432	12.32	14.0
	6	-1146.31827274	-1145.952910	2.60	4.2
	TS-6-7	-1146.31137550	-1145.944839	7.67	9.3
	7	-1146.31584231	-1145.952554	2.83	4.5
17	**8**	-1476.35335164	-1475.797229	11.27	12.9
	TS-8-9	-1476.35324844	-1475.794901	12.73	14.4
18	**9**	-1476.37001904	-1475.808107	4.44	6.1
	TS-9-10	-1476.34595680	-1475.788993	16.44	18.1
19	**10**	-1476.39892586	-1475.840296	-15.76	-14.1
	TS-10-11	-1476.39705869	-1475.837628	-14.08	-12.4
	11	-1476.40184881	-1475.842493	-17.14	-15.5
	TS-11-12	-1476.35119467	-1475.795991	12.04	13.7
	12	-1476.38817112	-1475.833275	-11.35	-9.7
	13	-1146.31594797	-1145.955287	-16.99	-15.3
	TS-13-1	-1146.31579294	-1145.952275	-15.10	-13.5

Table S2 (cont.). Electronic energies and free energies (absolute energies in Hartrees, relative energies in kcal mol^{-1}). $\Delta G_{gas}°$ are gas-phase relative free energies. ΔG_{conc} are relative free energies including the 1.77 kcal mol^{-1} concentration correction.

Numbering article	Numbering in SI	E	G	$\Delta G_{gas}°$ (kcal mol^{-1}) relative to **4**	ΔG_{conc} (kcal mol^{-1}) relative to **3**
	21	-1476.36625725	-1475.809720	3.43	5.1
	TS-21-22	-1476.32623607	-1475.776825	24.07	25.7
9	**22**	-1476.36854268	-1475.816238	-0.66	1.0
	22B	-1476.35527908	-1475.795516	12.34	14.0
TS-9-10	**TS-22-23**	-1476.34276858	-1475.782323	20.62	22.3
10	**23**	-1476.36437684	-1475.803148	7.55	9.2
TS-10-11	**TS-23-24**	-1476.33033663	-1475.772822	26.58	28.2
11	**24**	-1476.38121338	-1475.824240	-5.68	-4.0
12	**25**	-1416.28399371	-1415.746583	12.07	13.7
TS-12-13	**TS-25-26**	-1416.24770917	-1415.715307	31.69	33.3
13	**26**	-1416.28762665	-1415.751643	8.89	10.5
TS-13-14	**TS-26-27**	-1416.23972029	-1415.699451	41.64	43.3
14	**27**	-1416.31547882	-1415.774460	-5.43	-3.8

Included in the Cartesian coordinates section is one species, **22B**, that is not included in Scheme 4. **22B** is a conformer of **22** (**9** in Scheme 4). **TS-22-23** connects **22B** to **23** (**10** in Scheme 4), not **22** to **23**.

Numbering in the coordinates sections corresponds to the numbering of the complexes in Figure S48 and "Appendix B- excerpted from the dissertation of Katie Leigh".

substrate

N	-0.062900	2.053890	-0.065258
C	0.654067	1.012861	-0.820926
H	0.061535	0.781753	-1.727398
C	0.833404	-0.300791	-0.010990
C	1.332680	0.014448	1.412885
C	1.878135	-1.177091	-0.732996
C	-0.503695	-1.105213	0.040657
H	-0.337169	-1.963839	0.727980
H	-0.686955	-1.548382	-0.959468
C	-1.745197	-0.368430	0.472321
H	-1.693584	0.178283	1.422817
C	-2.900311	-0.373865	-0.217398
H	-3.793706	0.148703	0.144720
H	-2.995602	-0.903229	-1.175419
H	1.657307	1.343361	-1.179967
H	-0.516351	2.701748	-0.715040
H	0.604830	2.609327	0.478070
H	1.980931	-2.161694	-0.239749
H	1.591809	-1.359415	-1.786689
H	2.874122	-0.695456	-0.732958
H	1.491957	-0.915571	1.989968
H	2.299045	0.555597	1.386530
H	0.607630	0.640080	1.962089

el energy= -330.025215751
zpe= -329.819613
th energy= -329.809034
th enthalpy= -329.808090
free energy= -329.854476

uncatalyzed intramolecular hydroamination TS

N	-1.010523	1.164607	-0.371751
C	0.296676	0.840553	-1.000125
H	0.077917	0.293594	-1.936993
C	1.014162	-0.106026	-0.001131
C	1.581301	0.688688	1.193478
C	2.141926	-0.888372	-0.692666
C	-0.161936	-1.017884	0.444207
H	0.064083	-1.537356	1.394009
H	-0.331509	-1.794135	-0.327033
C	-1.438791	-0.168306	0.572123
H	-1.551378	0.280444	1.579285
C	-2.659244	-0.585935	-0.144282
H	-3.602705	-0.410954	0.395306
H	-2.615589	-1.600139	-0.571537
H	0.875903	1.746089	-1.253781
H	-1.969720	0.818649	-0.921142
H	-1.023108	2.083176	0.104459
H	2.613080	-1.601611	0.008202
H	1.758377	-1.465477	-1.554544
H	2.936435	-0.212449	-1.061999
H	2.060452	0.008432	1.921595
H	2.345175	1.418461	0.864426
H	0.791682	1.244717	1.732387

el energy= -329.957260152
zpe= -329.755779
th energy= -329.746668
th enthalpy= -329.745724
free energy= -329.788469

product

N	-0.982695	1.167533	-0.488324
C	0.318979	0.770287	-1.053678
H	0.152358	0.175018	-1.976675
C	1.033096	-0.118485	0.003097
C	1.661627	0.754264	1.108330
C	2.100103	-1.031411	-0.618790
C	-0.189383	-0.901962	0.547140
H	-0.031070	-1.279403	1.574258
H	-0.377778	-1.784102	-0.096638
C	-1.396497	0.080255	0.452893
H	-1.598066	0.525998	1.447782
C	-2.680467	-0.604012	-0.035154
H	-3.513448	0.118520	-0.093861
H	-2.977879	-1.427234	0.642012
H	0.902981	1.663283	-1.346326
H	-2.529603	-1.026220	-1.045834
H	-0.854440	2.031396	0.045435
H	2.537747	-1.714883	0.132929
H	1.672203	-1.651259	-1.429151
H	2.930363	-0.439609	-1.049281
H	2.060071	0.131657	1.930973
H	2.497585	1.360179	0.710390
H	0.923094	1.450311	1.549235

el energy= -330.061760626
zpe= -329.853296
th energy= -329.844091
th enthalpy= -329.843146
free energy= -329.886787

[Zr]I

Zr	0.290665	-0.592037	0.428214
C	2.442123	0.408165	-0.013994
C	0.148084	1.719172	0.062690
C	-1.925828	0.289565	0.928900
N	-3.158459	-0.189562	1.265542
N	-2.155050	1.619548	0.645380
C	-3.501509	1.941239	0.760217
C	-4.138506	0.791619	1.148642
N	3.754832	0.024516	-0.052689
N	2.480355	1.742367	-0.351327
C	3.773520	2.172172	-0.600486
C	4.583718	1.081378	-0.410158
C	1.255805	2.490427	-0.314951
C	1.197843	3.865029	-0.592917
C	-0.042807	4.509881	-0.455584
C	-1.058607	2.424804	0.209936
C	-1.182181	3.802602	-0.039258
H	-5.188912	0.595104	1.356888
H	-3.894772	2.936598	0.567815
H	5.663913	0.972372	-0.493850
H	4.016782	3.193333	-0.884964
H	2.078820	4.438285	-0.904952
H	-0.119613	5.582712	-0.664236
H	-2.133925	4.332252	0.085293
C	4.234166	-1.306517	0.311040
C	-3.420466	-1.601373	1.513732
H	4.803583	-1.256889	1.255978
H	3.351063	-1.955124	0.434254
H	4.883653	-1.704671	-0.487411
H	-3.542387	-2.135131	0.553126
H	-2.565961	-2.030720	2.061431
H	-4.333163	-1.707441	2.122832
I	-1.483953	-0.887555	-2.055264
N	0.577286	-0.906314	2.495582
C	0.045253	-0.046399	3.546697
H	-0.643444	-0.601324	4.226686
H	0.685529	-2.645915	3.739173
C	1.325729	-2.011472	3.081564
H	2.162983	-1.640577	3.716442
H	1.753461	-2.651647	2.290222
H	0.861726	0.366295	4.181534
H	-0.510303	0.803119	3.113166
N	1.122563	-2.374129	-0.362488
C	1.810088	-2.660597	-1.609378
H	1.081465	-2.860794	-2.427974
H	2.473448	-3.553007	-1.522472
H	-0.398345	-3.828699	-0.759016
C	0.308128	-3.516057	0.043244
H	0.934611	-4.396203	0.318380
H	-0.301301	-3.269638	0.942174
H	2.425972	-1.797177	-1.919737

el energy= -1086.24947362
zpe= -1085.846735
th energy= -1085.817358
th enthalpy= -1085.816414
free energy= -1085.907688

[Zr]I$_2$

Zr	0.348626	-0.011289	0.423490
C	-0.969016	-1.993485	0.484247
C	-1.936677	0.443183	0.296848
C	-0.081225	2.303380	0.066466
N	0.638924	3.446211	-0.144119
N	-1.393063	2.725961	0.042857
C	-1.483224	4.090415	-0.180743
C	-0.195701	4.546899	-0.298361
N	-0.738988	-3.337199	0.471147
N	-2.339714	-1.881061	0.438995
C	-2.946124	-3.126474	0.375440
C	-1.931144	-4.049372	0.394792
C	-2.906155	-0.568046	0.368577
C	-4.287570	-0.323381	0.340572
C	-4.719958	1.010373	0.233140
C	-2.428054	1.748734	0.173063
C	-3.796683	2.064993	0.142982
H	0.191485	5.547319	-0.484214
H	-2.431215	4.618701	-0.249923
H	-1.956646	-5.137247	0.361003
H	-4.024004	-3.260021	0.319866
H	-5.024989	-1.132880	0.395319
H	-5.793044	1.229334	0.211408
H	-4.156593	3.096343	0.049034
C	0.588570	-3.945773	0.419785
C	2.095900	3.514947	-0.233739
H	0.789569	-4.328711	-0.595920
H	1.343335	-3.181564	0.663883
H	0.650679	-4.770593	1.149735
H	2.505598	4.085877	0.618021
H	2.503738	2.491586	-0.220608
H	2.386582	4.003999	-1.178983
I	3.233472	-0.453676	0.231882
I	-0.010577	-0.496720	-2.457529
N	0.202023	0.140663	2.506818
C	1.236774	0.888591	3.222476
C	-0.831999	-0.294868	3.432946
H	-1.613959	-0.867003	2.908731
H	-0.403252	-0.935853	4.235786
H	-1.316986	0.573666	3.932209
H	2.035691	1.223901	2.536294
H	0.806647	1.784196	3.724267
H	1.718311	0.258746	4.002966

el energy= -963.310119038
zpe= -962.986307
th energy= -962.959378
th enthalpy= -962.958434
free energy= -963.047710

[Zr]I$_3$

Zr	0.334378	-0.000506	0.007365
C	-0.553878	-2.188303	-0.012777
C	-1.992406	0.003300	-0.008028
C	-0.546674	2.190168	-0.018764
N	-0.046310	3.459661	-0.040436
N	-1.911403	2.359645	-0.020686
C	-2.252624	3.701190	-0.043136
C	-1.070340	4.398147	-0.056918
N	-0.057608	-3.459454	-0.031496
N	-1.919146	-2.353355	-0.014420
C	-2.264699	-3.693858	-0.033988
C	-1.084676	-4.394658	-0.046036
C	-2.738239	-1.182812	-0.007587
C	-4.141259	-1.216599	-0.006148
C	-4.830906	0.007959	-0.006208
C	-2.734335	1.191842	-0.010709
C	-4.137229	1.230236	-0.009379
H	-0.874969	5.468944	-0.075888
H	-3.282010	4.051859	-0.043719
H	-0.892813	-5.466132	-0.062471
H	-3.295211	-4.041214	-0.034012
H	-4.702504	-2.158193	-0.005452
H	-5.926186	0.009776	-0.005013
H	-4.695403	2.173653	-0.011222
C	1.362456	-3.802961	-0.079145
C	1.374813	3.798574	-0.089284
H	1.587131	-4.560662	0.690119
H	1.957854	-2.897499	0.118125
H	1.623767	-4.194385	-1.077702
H	1.601836	4.558166	0.677412
H	1.637309	4.185765	-1.089182
H	1.967366	2.891937	0.111074
I	3.216120	-0.003258	0.064823
I	0.058403	0.003549	2.832613
I	0.142835	-0.005962	-2.825148

el energy= -840.366486622
zpe= -840.121173
th energy= -840.097430
th enthalpy= -840.096485
free energy= -840.180461

1

Zr	0.659672	-0.225827	-0.037322
C	1.609543	1.889419	0.577436
C	-0.522513	1.573028	-0.963300
C	-1.076646	-0.959161	-1.539991
N	-1.585854	-2.135125	-2.010544
N	-1.878313	0.003167	-2.114499
C	-2.865814	-0.562741	-2.906030
C	-2.680602	-1.920446	-2.840454
N	2.634245	2.351116	1.351896
N	0.968172	3.035327	0.157824
C	1.575358	4.174331	0.666523
C	2.632630	3.740307	1.425055
C	-0.168847	2.905462	-0.708339
C	-0.845917	4.008278	-1.255305
C	-1.927902	3.755900	-2.115787
C	-1.593683	1.384846	-1.848399
C	-2.312940	2.441394	-2.432685
H	-3.225684	-2.737544	-3.310188
H	-3.603154	0.024626	-3.448274
H	3.374460	4.295397	1.997034
H	1.223805	5.181378	0.453862
H	-0.554500	5.042573	-1.036931
H	-2.473357	4.597653	-2.556494
H	-3.148485	2.271214	-3.122153
C	3.581661	1.484196	2.048504
C	-1.067785	-3.450924	-1.641509
H	4.600796	1.894661	1.951483
H	3.316156	1.402910	3.117289

H	3.549356	0.484640	1.586288
H	-1.133556	-4.128019	-2.509095
H	-0.011752	-3.344727	-1.344273
H	-1.645705	-3.868372	-0.798367
I	2.938983	-1.901471	-0.681978
N	-0.139665	-0.569684	1.618512
C	-0.751475	-0.832884	2.885864
C	-2.254057	-1.285824	2.916037
C	-3.236362	-0.083800	2.755529
C	-3.239470	0.636136	1.433703
C	-4.320659	0.764639	0.642837
H	-5.289802	0.322478	0.913687
H	-4.279020	1.326274	-0.298787
H	-2.288570	1.088728	1.121806
H	-4.263578	-0.445253	2.969272
H	-2.992390	0.645198	3.559206
C	-2.528345	-2.358440	1.850715
C	-2.500662	-1.881413	4.320678
H	-0.173891	-1.633316	3.405970
H	-0.668147	0.065968	3.541450
H	-3.560228	-2.171235	4.450566
H	-1.880748	-2.782306	4.485678
H	-2.252331	-1.151776	5.115720
H	-1.847518	-3.221608	1.979738
H	-3.568902	-2.728783	1.926352
H	-2.379381	-1.947165	0.838079

el energy= -1146.31598705
zpe= -1145.889646
th energy= -1145.859230
th enthalpy= -1145.858286
free energy= -1145.953511

TS-1-2

Zr	0.446317	-0.321595	-0.197104
C	2.392705	0.576245	0.873187
C	0.501856	2.012325	-0.300160
C	-1.348010	0.565151	-1.545506
N	-2.400329	0.102641	-2.281598
N	-1.450576	1.936193	-1.645930
C	-2.542159	2.310581	-2.415875
C	-3.146422	1.145895	-2.816965
N	3.462493	0.109306	1.580607
N	2.509798	1.946431	0.957618
C	3.618567	2.317436	1.704520
C	4.222597	1.151445	2.101527
C	1.526716	2.758695	0.299091
C	1.599601	4.160347	0.248346
C	0.591951	4.847745	-0.449941
C	-0.458441	2.752220	-1.004363
C	-0.447939	4.154401	-1.092354
H	-4.028413	0.976140	-3.432380
H	-2.794905	3.347411	-2.625514
H	5.118559	0.980120	2.696076
H	3.891585	3.353914	1.889348
H	2.411221	4.722483	0.725548
H	0.624198	5.941500	-0.504347
H	-1.214692	4.713095	-1.642094
C	3.729059	-1.309526	1.803952
C	-2.734495	-1.312058	-2.429365
H	4.815626	-1.492974	1.762674
H	3.337941	-1.624870	2.787464
H	3.232914	-1.891036	1.009719
H	-3.122506	-1.493776	-3.445331
H	-1.821605	-1.911162	-2.279712
H	-3.493993	-1.604396	-1.683293
I	1.448731	-2.590750	-1.701060
N	-0.449482	-0.688271	1.404452
C	-0.944960	-1.171270	2.658621
C	-2.486617	-1.421060	2.779594
C	-3.291776	-0.086009	2.865513
C	-3.274962	0.806398	1.652697
C	-4.366938	1.136301	0.937708
H	-5.363218	0.751792	1.198219
H	-4.310926	1.807364	0.071413
H	-2.294148	1.205579	1.362305
H	-4.344009	-0.336352	3.112985
H	-2.894079	0.482493	3.734217
C	-2.984273	-2.282770	1.609038
C	-2.712424	-2.174565	4.108960
H	-0.447326	-2.138786	2.904049
H	-0.661180	-0.467333	3.476525
H	-3.788950	-2.357102	4.286070
H	-2.200915	-3.155193	4.102589
H	-2.324157	-1.596234	4.969790
H	-2.460560	-3.257029	1.585692
H	-4.070219	-2.479852	1.694442
H	-2.796814	-1.773932	0.648465

el energy= -1146.31682818
zpe= -1145.890600
th energy= -1145.861014
th enthalpy= -1145.860070
free energy= -1145.952817

2

Zr	0.345756	-0.330448	-0.198509
C	2.532231	-0.265031	0.783311
C	1.148680	1.857659	0.007878
C	-1.111406	1.274664	-1.263118
N	-2.263537	1.280456	-1.993814
N	-0.766069	2.606991	-1.176491
C	-1.685979	3.414527	-1.828061
C	-2.638556	2.572063	-2.344529
N	3.430996	-1.147093	1.309724
N	3.082903	0.969739	1.050851
C	4.287017	0.854354	1.730453
C	4.507594	-0.489094	1.896148
C	2.382770	2.141822	0.609621
C	2.899887	3.440574	0.747550
C	2.139719	4.509698	0.243133
C	0.453845	2.961423	-0.505823
C	0.909727	4.285925	-0.398815
H	-3.532274	2.780832	-2.930392
H	-1.591598	4.496404	-1.887025
H	5.330260	-1.023238	2.368936
H	4.883354	1.711922	2.033544
H	3.867712	3.638223	1.223713
H	2.518767	5.533097	0.339613
H	0.342859	5.135249	-0.798352
C	3.249996	-2.596523	1.303788
C	-3.047992	0.082150	-2.284251
H	4.203288	-3.089026	1.048267
H	2.907699	-2.945320	2.294099
H	2.495119	-2.854622	0.544104
H	-3.536021	0.192646	-3.266558
H	-2.370733	-0.786982	-2.312069
H	-3.808543	-0.062112	-1.496582
I	0.515191	-2.513019	-2.108253
N	-0.522359	-0.673124	1.424145
C	-1.185545	-0.934499	2.665547
C	-2.729170	-1.237048	2.639946
C	-3.572024	0.073365	2.698292
C	-3.411906	1.052512	1.567566
C	-4.433313	1.547381	0.841979
H	-5.470862	1.233566	1.023187
H	-4.275752	2.300897	0.060111
H	-2.386682	1.392286	1.363574
H	-4.643678	-0.197700	2.793812
H	-3.300214	0.590821	3.644791
C	-3.109262	-2.082052	1.414973
C	-3.048175	-2.028304	3.928601
H	-0.702516	-1.818470	3.144877
H	-1.023029	-0.089026	3.374738
H	-4.135972	-2.198937	4.036089
H	-2.550734	-3.015885	3.919644
H	-2.703353	-1.484168	4.829407
H	-2.534357	-3.026084	1.390585
H	-4.186603	-2.336053	1.432300
H	-2.893858	-1.542568	0.477310

el energy= -1146.31571451
zpe= -1145.889437
th energy= -1145.858984
th enthalpy= -1145.858040
free energy= -1145.953874

TS-2-3

Zr	0.202874	-0.259420	-0.294647
C	2.275442	-1.207946	0.472062
C	1.803091	1.381401	0.153399
C	-0.523892	1.922651	-0.999888
N	-1.601875	2.487726	-1.614958
N	0.288518	2.994902	-0.698661
C	-0.281433	4.193350	-1.101974
C	-1.483035	3.871006	-1.681043
N	2.787895	-2.441850	0.753999
N	3.264235	-0.337759	0.878360
C	4.353815	-1.014771	1.405742
C	4.051669	-2.350417	1.328165
C	3.054755	1.071480	0.702191
C	4.018225	2.037733	1.035768
C	3.707338	3.387490	0.797499
C	1.561071	2.741601	-0.085050
C	2.477438	3.759395	0.227974
H	-2.246340	4.500251	-2.135847
H	0.202089	5.157954	-0.965279
H	4.624262	-3.228949	1.621254
H	5.242331	-0.511330	1.779810
H	4.990729	1.771866	1.467141
H	4.440176	4.161763	1.050079
H	2.262795	4.818436	0.041359
C	2.074943	-3.694659	0.516379
C	-2.762533	1.731460	-2.079967
H	2.774380	-4.448652	0.118017
H	1.625687	-4.067718	1.453717
H	1.279699	-3.512598	-0.224521
H	-3.161827	2.198336	-2.995578
H	-2.445252	0.700377	-2.306920
H	-3.535400	1.716293	-1.291953
I	-0.672624	-2.062650	-2.407206
N	-0.656994	-0.400667	1.359546
C	-1.235593	-0.680545	2.635381
C	-2.760320	-1.024662	2.659334
C	-3.694486	0.176359	2.252872
C	-3.083010	1.529477	1.955525
C	-3.718049	2.512577	1.288045
H	-4.731256	2.377521	0.882417
H	-3.256911	3.496520	1.139736
H	-2.080464	1.735139	2.351526
H	-4.317559	-0.120317	1.386831
H	-4.420852	0.323865	3.080115
C	-3.022049	-2.215003	1.716728
C	-3.096716	-1.441945	4.109533
H	-0.713071	-1.551990	3.094441
H	-1.055796	0.166654	3.338150
H	-4.160448	-1.731018	4.202197
H	-2.485714	-2.306076	4.432466
H	-2.910493	-0.612378	4.818895
H	-2.436847	-3.102499	2.026304
H	-4.091818	-2.498771	1.723523
H	-2.730437	-1.968093	0.679847

el energy= -1146.30860772
zpe= -1145.882547
th energy= -1145.852919
th enthalpy= -1145.851975
free energy= -1145.946113

3

Zr	0.279984	-0.228814	-0.283151
C	2.259869	-1.319224	0.539075
C	1.969797	1.300724	0.233619
C	-0.326972	2.019269	-0.894348
N	-1.388832	2.676572	-1.446106
N	0.557097	3.027483	-0.572738
C	0.050606	4.274654	-0.906753
C	-1.184968	4.052063	-1.459695
N	2.676645	-2.585706	0.831543
N	3.303903	-0.521546	0.955861
C	4.334025	-1.274294	1.500021
C	3.936344	-2.584730	1.421970
C	3.193756	0.900137	0.786310
C	4.217510	1.795396	1.138119
C	3.998910	3.165940	0.915977
C	1.816588	2.677609	0.021225
C	2.797831	3.627532	0.350666
H	-1.921682	4.746113	-1.860975
H	0.594248	5.201722	-0.739845
H	4.438800	-3.501224	1.727234
H	5.250442	-0.835555	1.888208
H	5.166564	1.459725	1.572983
H	4.780724	3.886036	1.181689
H	2.654629	4.701376	0.181128
C	1.875644	-3.783424	0.590921
C	-2.609049	2.017213	-1.910891
H	2.501629	-4.563198	0.124994
H	1.457331	-4.164115	1.539348
H	1.053019	-3.524341	-0.094688
H	-2.976375	2.525122	-2.818127
H	-2.371971	0.969138	-2.155802
H	-3.383776	2.047018	-1.123453
I	-0.672365	-1.897012	-2.465039
N	-0.691778	-0.332794	1.307419
C	-1.435792	-0.412590	2.525503
C	-2.883682	-0.990167	2.389186
C	-3.688955	-0.211542	1.306279
C	-3.770576	1.277686	1.505170
C	-4.907539	1.989791	1.625020
H	-5.893692	1.506416	1.599209
H	-4.899263	3.078861	1.757662
H	-2.806259	1.808061	1.536587
H	-3.196925	-0.412896	0.332278
H	-4.710488	-0.637353	1.244195
C	-2.806353	-2.468009	1.962596
C	-3.580452	-0.872455	3.758119
H	-0.894922	-1.051363	3.261945
H	-1.502578	0.594555	2.996819
H	-4.583408	-1.339254	3.733999
H	-2.992879	-1.381773	4.545762
H	-3.710059	0.184457	4.055980
H	-2.299455	-3.074609	2.737837
H	-3.815815	-2.894562	1.809260
H	-2.240376	-2.571666	1.018527

el energy= -1146.32137499
zpe= -1145.894857
th energy= -1145.864495
th enthalpy= -1145.863551
free energy= -1145.959674

TS-3-4

Zr	0.217226	-0.088198	-0.288263
C	1.825888	-1.834794	0.109100
C	2.302071	0.763609	0.345726
C	0.277738	2.305421	-0.390000
N	-0.580685	3.325464	-0.679364
N	1.421359	2.942847	0.040042
C	1.270753	4.321512	0.026694
C	-0.000986	4.563871	-0.428854

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N     1.870190 -3.199303  0.095901
N     3.075794 -1.466952  0.558351
C     3.867823 -2.573984  0.824637
C     3.102377 -3.674276  0.532229
C     3.378292 -0.068557  0.681274
C     4.632722  0.410839  1.093905
C     4.814630  1.802610  1.165864
C     2.548947  2.141442  0.422353
C     3.777674  2.688877  0.827109
H    -0.530204  5.500089 -0.598801
H     2.058106  5.009245  0.326398
H     3.330599 -4.737296  0.590887
H     4.891782 -2.500090  1.183776
H     5.459712 -0.259883  1.356104
H     5.783272  2.203434  1.484461
H     3.947231  3.770845  0.883001
C     0.739863 -4.045559 -0.279662
C    -1.953825  3.120506 -1.141480
H     0.184185 -4.370197  0.617848
H     0.068395 -3.467451 -0.934856
H     1.107123 -4.929592 -0.826953
H    -2.303624  4.034145 -1.648662
H    -1.971236  2.278233 -1.852723
H    -2.618508  2.884226 -0.290809
I    -1.243968 -0.943894 -2.654055
N    -0.697774 -0.206808  1.335336
C    -1.444609 -0.306115  2.549063
C    -2.816746 -1.049644  2.441739
C    -3.748744 -0.339520  1.425527
C    -4.123105  1.092816  1.746761
C    -4.877761  1.889688  0.966056
H    -5.287524  1.541573  0.007693
H    -5.133979  2.913335  1.266017
H    -3.756524  1.507540  2.698034
H    -3.260133 -0.376497  0.431326
H    -4.676517 -0.941139  1.327504
C    -2.578689 -2.492317  1.955857
C    -3.458083 -1.090749  3.843953
H    -0.841081 -0.833477  3.324424
H    -1.631003  0.713087  2.959837
H    -4.427002 -1.624382  3.820853
H    -2.800584 -1.619138  4.560298
H    -3.643459 -0.079607  4.251660
H    -3.532074 -3.046420  1.863651
H    -2.081911 -2.492795  0.968807
H    -1.933369 -3.044280  2.666672
   el energy= -1146.31752064
        zpe= -1145.891616
   th energy= -1145.861854
  th enthalpy= -1145.860910
  free energy= -1145.954941

4
Zr    0.152445  0.022012 -0.298202
C     1.356185 -2.068082 -0.267161
C     2.382298  0.306502  0.341495
C     0.722510  2.331178 -0.040395
N     0.085005  3.536050 -0.097450
N     1.983521  2.641436  0.418606
C     2.120475  4.002654  0.648491
C     0.914326  4.570200  0.322017
N     1.119486 -3.389671 -0.517006
N     2.666481 -2.041585  0.160601
C     3.220263 -3.313009  0.185091
C     2.238399 -4.169333 -0.243813
C     3.262420 -0.774927  0.482133
C     4.600745 -0.639057  0.887700
C     5.081035  0.654703  1.153791
C     2.923114  1.572619  0.606846
C     4.251824  1.780706  1.011706
H     0.585469  5.607844  0.346921
H     3.040068  4.455219  1.012224
H     2.244867 -5.249430 -0.381198
H     4.246397 -3.509161  0.487632
H     5.270364 -1.500309  0.999288
H     6.121654  0.788355  1.469422
H     4.652908  2.781144  1.213659
C    -0.162715 -3.916161 -0.978919
C    -1.315146  3.686095 -0.492164
H    -0.734004 -4.340194 -0.134228
H    -0.738312 -3.094459 -1.435376
H     0.010598 -4.698360 -1.736846
H    -1.505068  4.737307 -0.761906
H    -1.515445  3.040392 -1.363081
H    -1.982386  3.383312  0.334070
I    -1.486425 -0.099863 -2.700608
N    -0.734012 -0.093729  1.341291
C    -1.463987 -0.085743  2.570405
C    -2.681947 -1.061826  2.642973
C    -3.725398 -0.709527  1.541360
C    -4.318651  0.673728  1.609302
C    -4.296257  1.567175  0.601920
H    -3.816456  1.332261 -0.358153
H    -4.779970  2.548574  0.691741
H    -4.831762  0.947139  2.544522
H    -3.251907 -0.850861  0.551218
H    -4.548355 -1.453605  1.615306
C    -2.204171 -2.508231  2.416784
C    -3.302749 -0.947955  4.050086
H    -0.783416 -0.334633  3.417880
H    -1.848474  0.940334  2.771935
H    -4.198480 -1.590929  4.144597
H    -2.579113 -1.266882  4.823898
H    -3.603379  0.089218  4.288290
H    -3.051823 -3.219550  2.439514
H    -1.696941 -2.596182  1.439085
H    -1.483091 -2.812082  3.199691
   el energy= -1146.31948395
        zpe= -1145.892949
   th energy= -1145.862572
  th enthalpy= -1145.861628
  free energy= -1145.957362

TS-4-5
Zr   -0.102075 -0.176123  0.071191
C     0.131128  2.170305 -0.343275
C     1.988030  0.348699 -0.800484
C     1.360588 -2.114364 -0.008514
N     1.343737 -3.447274  0.300556
N     2.609929 -1.926704 -0.556987
C     3.342685 -3.103646 -0.587189
C     2.539696 -4.069849 -0.039423
N    -0.611731  3.306579 -0.195688
N     1.295933  2.610964 -0.927424
C     1.277123  3.982952 -1.139459
C     0.065016  4.423949 -0.675569
C     2.329105  1.655359 -1.183458
C     3.565934  2.003324 -1.750217
C     4.519078  0.988199 -1.935651
C     2.986512 -0.614773 -0.995918
C     4.244485 -0.335565 -1.555636
H     2.715947 -5.129946  0.135155
H     4.350792 -3.166039 -0.989618
H    -0.363015  5.424303 -0.638234
H     2.107972  4.528850 -1.579907
H     3.803019  3.032795 -2.043757
H     5.492374  1.233859 -2.374561
H     5.006134 -1.111145 -1.698496
C    -1.940874  3.333421  0.408218
C     0.225039 -4.121221  0.951179
H    -2.703074  2.992027 -0.314633
H    -1.941128  2.673319  1.292922
H    -2.173513  4.362808  0.724731
H     0.365281 -5.211082  0.873387
H     0.167724 -3.834665  2.015627
H    -0.713428 -3.840845  0.447589
I    -0.268092  0.587888  2.968372
N    -1.046101 -0.531869 -1.520897
C    -1.971104 -0.974875 -2.510067
C    -3.473128 -0.666754 -2.185613
C    -3.756130 -0.805138 -0.657141
C    -2.950062 -1.839770  0.092428
C    -2.629263 -1.750827  1.405108
H    -2.904243 -0.878553  2.009680
H    -2.118815 -2.558885  1.940780
H    -2.683157 -2.752112 -0.464378
H    -3.615921  0.171458 -0.154783
H    -4.834968 -1.044561 -0.537691
C    -3.803122  0.777236 -2.611129
C    -4.352923 -1.652924 -2.980830
H    -1.742295 -0.530165 -3.506655
H    -1.866272 -2.077139 -2.652608
H    -5.425292 -1.390674 -2.904056
H    -4.081505 -1.647556 -4.053670
H    -4.232066 -2.690133 -2.613642
H    -4.815729  1.078379 -2.279721
H    -3.070060  1.481590 -2.174651
H    -3.762140  0.886689 -3.711238
   el energy= -1146.30603697
        zpe= -1145.879304
   th energy= -1145.850037
  th enthalpy= -1145.849093
  free energy= -1145.940893

5
Zr    0.251488  0.215802  0.074666
C    -0.039304 -2.077601 -0.559023
C    -1.765509 -0.132083 -1.049937
C    -1.125420  2.241592 -0.010143
N    -1.111092  3.545888  0.412471
N    -2.317681  2.144728 -0.694897
C    -3.017219  3.341239 -0.693041
C    -2.253051  4.231588  0.013275
N     0.611551 -3.266468 -0.393800
N    -1.156756 -2.411288 -1.287615
C    -1.204298 -3.772170 -1.560299
C    -0.081345 -4.314693 -0.992364
C    -2.108752 -1.384825 -1.581706
C    -3.280460 -1.624583 -2.317819
C    -4.164270 -0.552670 -2.524941
C    -2.692299  0.890697 -1.281183
C    -3.885091  0.721153 -2.004262
H    -2.422171  5.277633  0.263263
H    -3.978382  3.467857 -1.184875
H     0.274597 -5.342937 -0.957328
H    -2.016419 -4.240833 -2.110733
H    -3.519425 -2.613475 -2.726719
H    -5.086369 -0.714069 -3.094158
H    -4.592941  1.542023 -2.168912
C     1.837587 -3.414149  0.384146
C    -0.068514  4.144423  1.237974
H     2.692876 -2.964489 -0.150352
H     1.702850 -2.919057  1.362089
H     2.035843 -4.485601  0.545403
H    -0.118626  5.241060  1.142333
H    -0.200678  3.867050  2.298696
H     0.917547  3.802548  0.890185
I    -0.570845 -0.981383  2.745156
N     1.442298  0.639638 -1.347271
C     2.552168  1.063388 -2.130019
C     3.938701  0.704466 -1.487992
C     3.813393  0.717740  0.069939
C     2.689931  1.547002  0.648468
C     2.054943  1.255055  1.829064
H     2.293297  0.347360  2.396578
H     1.399679  1.968469  2.340715
H     2.523236  2.527667  0.177321
H     3.711058 -0.314793  0.457209
H     4.768562  1.096582  0.492589
C     4.366562 -0.706742 -1.936621
C     4.985736  1.734590 -1.957886
H     2.516314  0.621709 -3.151863
H     2.510367  2.168717 -2.284871
H     6.005810  1.455756 -1.632115
H     4.995710  1.810196 -3.061901
H     4.766433  2.743270 -1.558416
H     5.267909 -1.048657 -1.392567
H     3.551911 -1.431583 -1.749117
H     4.597104 -0.729180 -3.018340
   el energy= -1146.30767423
        zpe= -1145.880697
   th energy= -1145.851012
  th enthalpy= -1145.850068
  free energy= -1145.942829

TS-5-6
Zr    0.268372  0.254156  0.131665
C    -0.063105 -1.986322 -0.662702
C    -1.754369  0.020836 -1.051434
C    -1.007989  2.349347  0.016249
N    -0.942164  3.643257  0.464738
N    -2.210007  2.311102 -0.658823
C    -2.866864  3.529649 -0.622153
C    -2.062933  4.376576  0.094304
N     0.551114 -3.198969 -0.541043
N    -1.205312 -2.263907 -1.379514
C    -1.309119 -3.617498 -1.671494
C    -0.196318 -4.211155 -1.135045
C    -2.123585 -1.198951 -1.640234
C    -3.288399 -1.370956 -2.406479
C    -4.132350 -0.262776 -2.587618
C    -2.632989  1.085667 -1.275044
C    -3.817594  0.984373 -2.023323
H    -2.191091  5.422642  0.367516
H    -3.829334  3.700432 -1.098024
H     0.122233 -5.252125 -1.125766
H    -2.142921 -4.044893 -2.223128
H    -3.550516 -2.333871 -2.860737
H    -5.048391 -0.372348 -3.178603
H    -4.491147  1.835682 -2.177353
C     1.734710 -3.412636  0.283772
C     0.131735  4.195272  1.284345
H     2.478254 -2.629003  0.064029
H     1.455200 -3.358614  1.351784
H     2.169134 -4.398689  0.053373
H     0.130353  5.292674  1.183862
H    -0.010109  3.926117  2.345455
H     1.098091  3.804202  0.935366
I    -0.879875 -1.206362  2.523519
N     1.773633  0.694475 -1.037464
C     2.888026  0.912383 -1.910519
C     4.236152  0.548403 -1.192265
C     3.898726  0.617076  0.325941
C     2.598220  1.369477  0.572465
C     1.811323  1.120146  1.753522
H     2.101602  0.272290  2.390240
H     1.389094  1.962789  2.312259
H     2.636347  2.419096  0.230897
H     3.796788 -0.399021  0.754776
H     4.714182  1.112116  0.890800
C     4.687680 -0.871322 -1.581911
C     5.330267  1.563499 -1.574312
H     2.759471  0.315681 -2.836669
H     2.924012  1.981946 -2.227036
H     6.306312  1.291673 -1.129986
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H     5.464173  1.610497 -2.671990
H     5.072457  2.582095 -1.226897
H     5.547716 -1.203055 -0.969417
H     3.864862 -1.596131 -1.435336
H     4.993574 -0.919475 -2.644195
    el energy= -1146.30146095
          zpe= -1145.875108
    th energy= -1145.846180
  th enthalpy= -1145.845236
  free energy= -1145.937432
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6

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Zr   -0.220506 -0.407578  0.170943
C     1.287089  0.308853 -1.636475
C    -0.895461  1.623381 -0.748229
C    -2.380526  0.278441  0.969808
N    -3.401729 -0.225210  1.726666
N    -2.828215  1.534710  0.613625
C    -4.077333  1.806479  1.148729
C    -4.442859  0.687090  1.852313
N     2.408374 -0.095913 -2.299773
N     1.023228  1.553742 -2.168164
C     1.956857  1.905784 -3.133856
C     2.837754  0.858560 -3.216429
C    -0.123753  2.289614 -1.712123
C    -0.444078  3.565636 -2.207128
C    -1.590649  4.205129 -1.706514
C    -2.041646  2.300229 -0.308704
C    -2.410145  3.580661 -0.751216
H    -5.348452  0.464030  2.414424
H    -4.605132  2.743381  0.985204
H     3.714124  0.711974 -3.845702
H     1.918828  2.840765 -3.687814
H     0.169015  4.069833 -2.963259
H    -1.854089  5.203186 -2.073778
H    -3.304150  4.095106 -0.379434
C     3.089361 -1.362262 -2.042605
C    -3.441710 -1.584696  2.260735
H     3.900230 -1.222958 -1.305002
H     2.351567 -2.081993 -1.653754
H     3.512299 -1.749598 -2.984210
H    -4.332030 -2.108540  1.871976
H    -2.531535 -2.107120  1.932847
H    -3.478780 -1.561886  3.363891
I    -0.701343 -2.881921 -1.265170
N     1.250840  0.500148  1.328490
C     2.519764  1.206344  1.359811
C     3.354015  0.620665  2.564306
C     2.454818 -0.544509  3.070715
C     1.024088 -0.155736  2.635882
C    -0.000814 -1.261826  2.344666
H     0.512892 -2.240964  2.231612
H    -0.760285 -1.363880  3.138225
H     0.611168  0.581760  3.365343
H     2.730972 -1.488892  2.560921
H     2.547376 -0.710176  4.160932
C     4.732454  0.121854  2.097008
C     3.533002  1.689465  3.661925
H     3.053014  1.093278  0.393493
H     2.363170  2.299926  1.504340
H     4.107795  1.289963  4.518789
H     4.074191  2.574362  3.275584
H     2.555278  2.037893  4.044078
H     5.293369 -0.349892  2.926239
H     4.628494 -0.633254  1.293788
H     5.353198  0.951365  1.705916
    el energy= -1146.31827274
          zpe= -1145.890583
    th energy= -1145.861455
  th enthalpy= -1145.860511
  free energy= -1145.952910
```

TS-6-7

```
Zr    0.490060 -0.269992 -0.326897
C    -0.959324 -1.428744  1.174117
C    -0.408240  1.144204  1.341656
C     1.548698  1.875085 -0.274747
N     2.530395  2.520803 -0.969438
N     1.043840  2.842293  0.567504
C     1.691581  4.055474  0.392736
C     2.633540  3.853100 -0.584336
N    -1.432351 -2.701228  1.313123
N    -1.656272 -0.707419  2.119206
C    -2.544819 -1.511022  2.817115
C    -2.406352 -2.776193  2.303094
C    -1.351502  0.689200  2.269883
C    -1.912725  1.501864  3.268898
C    -1.490565  2.841837  3.337826
C     0.003570  2.473091  1.486433
C    -0.517541  3.345827  2.457004
H     3.361578  4.532762 -1.024222
H     1.448897  4.945988  0.968173
H    -2.903973 -3.709355  2.561847
H    -3.184720 -1.136511  3.612816
H    -2.649441  1.125849  3.989221
H    -1.913803  3.499729  4.105005
H    -0.185989  4.386998  2.551676
C    -0.982707 -3.822765  0.491345
C     3.346939  1.886765 -2.002327
H    -1.038995 -4.753052  1.079766
H    -1.611438 -3.917691 -0.411850
H     0.064501 -3.643008  0.195606
H     4.379803  2.267532 -1.938964
H     3.353622  0.798554 -1.827076
H     2.937385  2.098046 -3.005895
I     2.849165 -1.920021  0.119057
N    -1.199237  0.513005 -1.349525
C    -2.491489  1.163120 -1.262255
C    -3.477711  0.318137 -2.164721
C    -2.521306 -0.685945 -2.889059
C    -1.105364 -0.102869 -2.672416
C     0.107393 -1.023601 -2.504483
H    -0.188949 -2.094610 -2.464381
H     0.880337 -0.929826 -3.290392
H    -0.924249  0.681337 -3.451372
H    -2.571457 -1.679375 -2.399567
H    -2.783266 -0.825566 -3.954987
C    -4.511807 -0.419023 -1.294240
C    -4.201776  1.227847 -3.175465
H    -2.833962  1.243117 -0.213194
H    -2.430865  2.203794 -1.660431
H    -4.914874  0.652318 -3.796041
H    -4.772117  2.026038 -2.662227
H    -3.481722  1.718937 -3.857039
H    -5.135612 -1.102435 -1.902198
H    -4.011647 -1.024761 -0.514378
H    -5.192776  0.291464 -0.786484
    el energy= -1146.31137550
          zpe= -1145.884395
    th energy= -1145.856007
  th enthalpy= -1145.855063
  free energy= -1145.944839
```

7

```
Zr   -0.478727  0.178878 -0.331888
C     0.375356  2.206784  0.622357
C     0.760082 -0.206993  1.603851
C    -0.743754 -2.126780  0.456912
N    -1.381472 -3.285184  0.125066
N     0.073063 -2.490964  1.507540
C    -0.055904 -3.839796  1.811646
C    -0.978591 -4.344532  0.932512
N     0.276518  3.552707  0.411161
N     1.251649  2.104171  1.683325
C     1.696033  3.348077  2.103304
C     1.074170  4.267849  1.297220
C     1.493668  0.804328  2.238288
C     2.348601  0.578910  3.329237
C     2.452983 -0.734358  3.818494
C     0.886205 -1.493260  2.148345
C     1.717256 -1.785090  3.244048
H    -1.382059 -5.349689  0.821365
H     0.489608 -4.324740  2.617770
H     1.124399  5.355565  1.288302
H     2.392571  3.485089  2.927458
H     2.922852  1.384610  3.801697
H     3.110777 -0.941372  4.669915
H     1.803143 -2.795712  3.660121
C    -0.603991  4.167548 -0.579725
C    -2.341859 -3.397534 -0.970455
H    -1.305802  4.854793 -0.076604
H    -0.009564  4.725362 -1.324281
H    -1.166891  3.366791 -1.081991
H    -3.088414 -4.169971 -0.723244
H    -2.850267 -2.427220 -1.092926
H    -1.827889 -3.670303 -1.909313
I    -3.365825  0.566955 -0.295596
N     1.059966 -0.659448 -1.447920
C     2.211456 -1.522430 -1.575817
C     3.298566 -0.667961 -2.341261
C     2.470566  0.537769 -2.902878
C     0.989117  0.153726 -2.677351
C    -0.048823  1.251829 -2.381299
H     0.426491  2.249393 -2.406584
H    -0.886963  1.255636 -3.104422
H     0.661683 -0.494925 -3.528498
H     2.690373  1.455430 -2.322698
H     2.699953  0.748711 -3.964713
C     4.379380 -0.184089 -1.357050
C     3.942968 -1.492133 -3.470421
H     2.566155 -1.868746 -0.586071
H     1.965886 -2.429683 -2.178570
H     4.725983 -0.912417 -3.995022
H     4.416152 -2.412768 -3.077080
H     3.189306 -1.797166 -4.220901
H     5.075879  0.525039 -1.844319
H     3.916355  0.333105 -0.495318
H     4.979105 -1.028709 -0.965927
    el energy= -1146.31584231
          zpe= -1145.888436
    th energy= -1145.859115
  th enthalpy= -1145.858171
  free energy= -1145.952554
```

8

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Zr   -0.647963 -0.375657 -0.279482
C    -2.287740  0.287888 -1.893464
C    -2.799635 -0.328220  0.609228
C    -0.725443 -1.436760  1.918751
N     0.076949 -2.113822  2.786437
N    -1.932693 -1.348168  2.583040
C    -1.874344 -1.955854  3.829301
C    -0.598924 -2.444175  3.955668
N    -2.350482  0.558787 -3.231411
N    -3.571636  0.532330 -1.449740
C    -4.396889  0.963696 -2.476611
C    -3.621697  0.977771 -3.608259
C    -3.884127  0.222686 -0.086015
C    -5.154860  0.415827  0.479733
C    -5.345644  0.011504  1.812171
C    -3.053115 -0.733090  1.927835
C    -4.304263 -0.576807  2.550423
H    -0.123904 -2.993737  4.766649
H    -2.719170 -1.998844  4.512738
H    -3.869053  1.233740 -4.637364
H    -5.447955  1.204853 -2.334695
H    -5.985016  0.862822 -0.079977
H    -6.326419  0.148198  2.281183
H    -4.487296 -0.897709  3.582663
C    -1.238650  0.379706 -4.162236
C     1.452253 -2.512188  2.479081
H    -0.440506 -0.172615 -3.644477
H    -1.582907 -0.199993 -5.035614
H    -0.853584  1.358884 -4.497321
H     1.977548 -1.679436  1.969508
H     1.967391 -2.757600  3.422725
H     1.443498 -3.396774  1.818473
I     0.406608 -2.796210 -1.527983
N    -0.305163  1.407739  0.742650
C    -0.670738  2.359646  1.769108
C    -0.744987  3.766015  1.045289
C    -0.135757  3.467153 -0.364209
C     0.581352  2.110521 -0.199205
C     0.711432  1.175590 -1.413360
H     0.427385  1.690220 -2.347816
H     2.965238  0.720710  0.575611
H     1.569581  2.310015  0.297340
H    -0.943271  3.343783 -1.112993
H     0.535497  4.274739 -0.714575
C    -2.204359  4.242898  0.936293
C     0.093465  4.811745  1.804717
H    -1.627540  2.080068  2.250236
H     0.104394  2.400100  2.570969
H     0.019893  5.808010  1.328697
H    -0.245972  4.915336  2.853438
H     1.162489  4.526134  1.826899
H    -2.280408  5.163805  0.326461
H    -2.835736  3.468945  0.460986
H    -2.632681  4.465575  1.932672
H     1.737813  0.777846 -1.553248
N     3.330220 -0.067693  1.118182
C     4.415817 -0.737878  0.385087
H     4.669872 -1.656214  0.953823
C     5.749111  0.032071  0.123462
C     6.787760 -1.006075 -0.353402
C     6.249975  0.692588  1.421989
C     5.616310  1.108438 -1.007339
H     5.413151  0.572552 -1.957001
H     6.610255  1.586030 -1.122171
C     4.573570  2.183658 -0.821142
H     3.545419  1.933618 -1.126202
C     4.814842  3.424954 -0.358396
H     5.825220  3.748358 -0.072763
H     4.013279  4.166673 -0.255246
H     3.995972 -1.087875 -0.578430
H     3.694887  0.336352  1.988253
H     7.745870 -0.522654 -0.621096
H     6.996766 -1.751916  0.436439
H     6.426207 -1.553375 -1.244767
H     7.260812  1.119257  1.281331
H     5.589048  1.518007  1.744079
H     6.313567 -0.044532  2.245860
    el energy= -1476.35335164
          zpe= -1475.718438
    th energy= -1475.677027
  th enthalpy= -1475.676083
  free energy= -1475.797229
```

TS-8-9

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Zr   -0.523714 -0.331187 -0.225303
C    -2.104766  0.204567 -1.941242
C    -2.721692 -0.413922  0.534873
C    -0.676208 -1.425698  1.963584
N     0.092991 -2.107543  2.857903
N    -1.923042 -1.396039  2.555792
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C	-1.920017	-2.042440	3.784005
C	-0.640125	-2.496458	3.973764
N	-2.109002	0.446939	-3.286081
N	-3.422386	0.386159	-1.572582
C	-4.213182	0.751418	-2.651432
C	-3.379032	0.787311	-3.739457
C	-3.792360	0.077045	-0.224223
C	-5.100127	0.211749	0.269332
C	-5.344583	-0.189305	1.593943
C	-3.029473	-0.824223	1.839946
C	-4.318433	-0.722253	2.392902
H	-0.197642	-3.058251	4.794744
H	-2.803363	-2.134562	4.411651
H	-3.583000	1.008942	-4.785875
H	-5.282552	0.933410	-2.571732
H	-5.918640	0.611966	-0.340616
H	-6.354795	-0.095479	2.007704
H	-4.541482	-1.044245	3.416911
C	-0.940099	0.318095	-4.152922
C	1.487338	-2.472975	2.611632
H	-0.165837	-0.244425	-3.610174
H	-1.223796	-0.233475	-5.065216
H	-0.550200	1.313556	-4.429204
H	1.947865	-1.698256	1.969727
H	2.019815	-2.531465	3.576241
H	1.534358	-3.450501	2.100044
I	0.555037	-2.749697	-1.473365
N	-0.401451	1.491409	0.781348
C	-0.899622	2.429984	1.761279
C	-1.060680	3.805235	0.997770
C	-0.295605	3.552579	-0.343972
C	0.494060	2.243951	-0.114821
C	0.759187	1.314779	-1.313488
H	0.450869	1.794184	-2.258765
H	2.805790	0.883877	0.608099
H	1.435914	2.507720	0.439234
H	-1.014148	3.382814	-1.169824
H	0.353131	4.403096	-0.628498
C	-2.549151	4.104205	0.743445
C	-0.422858	4.952411	1.803060
H	-1.849908	2.076329	2.205121
H	-0.170418	2.558387	2.596939
H	-0.558441	5.925640	1.294235
H	-0.873598	5.035571	2.810899
H	0.663640	4.789426	1.936100
H	-2.674712	4.991268	0.093038
H	-3.039859	3.245803	0.247234
H	-3.089070	4.303205	1.689336
H	1.823361	1.023318	-1.424441
N	3.097134	-0.002110	1.031541
C	4.146415	-0.641040	0.219824
H	4.320346	-1.647839	0.652194
C	5.536391	0.056680	0.085242
C	6.498809	-0.974450	-0.543596
C	6.069315	0.468340	1.470651
C	5.504703	1.298931	-0.868946
H	5.269993	0.931035	-1.888803
H	6.535869	1.704056	-0.911133
C	4.553832	2.420010	-0.525537
H	3.509245	2.297897	-0.851583
C	4.897277	3.562218	0.099231
H	5.930934	3.759035	0.415278
H	4.161157	4.347442	0.310407
H	3.721733	-0.820043	-0.787091
H	3.473287	0.242414	1.954835
H	7.495131	-0.531703	-0.729825
H	6.637197	-1.846602	0.122518
H	6.109602	-1.348734	-1.509531
H	7.112235	0.830049	1.399330
H	5.471184	1.284210	1.915898
H	6.064804	-0.389816	2.170534

el energy= -1476.35324844
zpe= -1475.718381
th energy= -1475.677870
th enthalpy= -1475.676926
free energy= -1475.794901

9

Zr	-0.131972	-0.174954	-0.214877
C	-1.713472	-0.726913	-1.920254
C	-2.303173	-0.433407	0.625405
C	-0.188702	-0.478554	2.300887
N	0.600265	-0.728640	3.393871
N	-1.452613	-0.378263	2.848749
C	-1.440648	-0.550202	4.226660
C	-0.136287	-0.772434	4.574890
N	-1.701174	-1.071392	-3.242107
N	-3.054099	-0.701874	-1.600419
C	-3.849702	-1.013720	-2.694278
C	-2.989200	-1.255233	-3.734461
C	-3.413003	-0.483037	-0.233372
C	-4.743459	-0.365305	0.200469
C	-4.976052	-0.202237	1.576857
C	-2.600839	-0.306587	1.987655
C	-3.909061	-0.181456	2.489989
H	0.321672	-0.970023	5.542769
H	-2.341288	-0.535068	4.835470
H	-3.182505	-1.546846	-4.765584
H	-4.935856	-1.048562	-2.649787
H	-5.589753	-0.395449	-0.496491
H	-6.003490	-0.102163	1.944092
H	-4.116061	-0.071317	3.561143
C	-0.478875	-1.341266	-3.990952
C	2.024918	-1.030983	3.331895
H	0.324970	-0.719816	-3.566088
H	-0.200293	-2.405455	-3.893861
H	-0.632321	-1.086371	-5.053068
H	2.225797	-1.598681	2.407968
H	2.637364	-0.110384	3.369009
H	2.297329	-1.662997	4.192996
I	0.608960	-3.076653	-0.256133
N	-0.547656	1.835870	0.160198
C	-1.229958	2.879365	0.892870
C	-1.654877	3.974590	-0.163462
C	-0.946839	3.494612	-1.469397
C	0.107642	2.463752	-1.003193
C	0.518948	1.324262	-1.961713
H	-0.111828	1.369815	-2.868869
H	2.291644	1.343748	0.022421
H	1.012545	3.033659	-0.651347
H	-1.669168	2.976720	-2.129860
H	-0.504661	4.330071	-2.045460
C	-3.185253	4.003243	-0.330039
C	-1.148740	5.365150	0.265566
H	-2.094702	2.464915	1.446969
H	-0.551959	3.343344	1.649850
H	-1.457154	6.145601	-0.455728
H	-1.547940	5.648780	1.258522
H	-0.044004	5.384865	0.332481
H	-3.487039	4.677003	-1.155102
H	-3.574890	2.992712	-0.555616
H	-3.684680	4.359547	0.591710
H	1.571780	1.421216	-2.296890
N	2.270368	0.333861	0.213825
C	3.340112	-0.338602	-0.568808
H	3.273442	-1.415880	-0.327626
C	4.804883	0.144079	-0.356145
C	5.722365	-0.935612	-0.971531
C	5.127648	0.285167	1.144054
C	5.113350	1.490793	-1.096592
H	5.087970	1.286458	-2.186206
H	6.157835	1.769671	-0.852122
C	4.205243	2.659000	-0.801633
H	3.257768	2.696809	-1.362804
C	4.474790	3.658849	0.059424
H	5.417328	3.697489	0.622402
H	3.770459	4.483592	0.222167
H	3.062834	-0.248097	-1.635661
H	2.482086	0.241570	1.211742
H	6.782710	-0.623676	-0.934384
H	5.630911	-1.894088	-0.427978
H	5.463490	-1.124368	-2.030483
H	6.207503	0.472074	1.293157
H	4.584596	1.130400	1.606468
H	4.875367	-0.640890	1.696212

el energy= -1476.37001904
zpe= -1475.733338
th energy= -1475.692984
th enthalpy= -1475.692039
free energy= -1475.808107

TS-9-10

Zr	-0.071541	-0.100284	-0.119010
C	-1.560172	-0.506609	-1.961572
C	-2.274616	-0.454343	0.587635
C	-0.252080	-0.514336	2.280028
N	0.560806	-0.740214	3.354312
N	-1.518522	-0.526801	2.825361
C	-1.489846	-0.750033	4.193661
C	-0.168361	-0.885162	4.530559
N	-1.482862	-0.745398	-3.304827
N	-2.910204	-0.562660	-1.692189
C	-3.648737	-0.832062	-2.836567
C	-2.743105	-0.951945	-3.858115
C	-3.336356	-0.484184	-0.328763
C	-4.690305	-0.482671	0.048461
C	-4.994567	-0.462259	1.419513
C	-2.642525	-0.463985	1.939111
C	-3.974006	-0.463224	2.386257
H	0.307614	-1.082468	5.489723
H	-2.387424	-0.815317	4.804286
H	-2.885812	-1.170809	-4.915040
H	-4.732223	-0.925025	-2.835641
H	-5.501650	-0.496360	-0.689003
H	-6.042124	-0.457111	1.740452
H	-4.233296	-0.467501	3.451708
C	-0.231066	-0.951450	-4.026750
C	2.007759	-0.908715	3.268741
H	0.576424	-0.418370	-3.502598
H	0.014406	-2.027789	-4.054708
H	-0.325168	-0.558557	-5.053119
H	2.272159	-0.980622	2.203648
H	2.529598	-0.050122	3.729163
H	2.302085	-1.835966	3.789244
I	0.333096	-3.026253	-0.408734
N	-0.542725	1.902392	0.240582
C	-1.384751	2.830733	0.970517
C	-1.787265	3.968042	-0.040537
C	-0.773143	3.766559	-1.215025
C	0.244801	2.715850	-0.707147
C	0.903436	1.760094	-1.713732
H	0.182221	1.512559	-2.517812
H	1.727921	0.936500	-0.873593
H	1.050144	3.248961	-0.138644
H	-1.290944	3.360392	-2.105346
H	-0.284512	4.711574	-1.519396
C	-3.235025	3.764265	-0.523971
C	-1.639190	5.355357	0.610644
H	-2.262123	2.311243	1.398853
H	-0.817462	3.279538	1.820565
H	-1.938811	6.160786	-0.086205
H	-2.271791	5.443271	1.515005
H	-0.592519	5.544850	0.915774
H	-3.489066	4.471061	-1.337084
H	-3.374124	2.736658	-0.908868
H	-3.960516	3.920446	0.297307
H	1.778229	2.221120	-2.213087
N	2.239585	0.213874	0.123969
C	3.320801	-0.648616	-0.364809
H	3.296726	-1.643478	0.135233
C	4.779894	-0.114937	-0.259980
C	5.684947	-1.196604	-0.892859
C	5.189063	0.068864	1.214653
C	5.005818	1.209316	-1.065435
H	4.551430	1.071074	-2.069463
H	6.096737	1.319758	-1.230065
C	4.494105	2.490446	-0.456021
H	3.403869	2.616051	-0.406458
C	5.281036	3.476966	0.011106
H	6.376785	3.403162	-0.022519
H	4.864897	4.397687	0.437784
H	3.113003	-0.865279	-1.436262
H	2.543527	0.810512	0.899009
H	6.753837	-0.931871	-0.789985
H	5.531037	-2.178641	-0.408075
H	5.468927	-1.318137	-1.971218
H	6.240676	0.403108	1.294973
H	4.577639	0.831681	1.730958
H	5.095410	-0.886312	1.765736

el energy= -1476.34595680
zpe= -1475.714793
th energy= -1475.674695
th enthalpy= -1475.673750
free energy= -1475.788993

10

Zr	0.040254	0.060350	-0.267862
C	0.568099	0.842717	1.972128
C	2.110283	-0.767685	0.494777
C	1.019411	-1.513188	-1.791748
N	0.678685	-2.120952	-2.966932
N	2.244949	-2.060457	-1.479056
C	2.642631	-2.991724	-2.424189
C	1.648923	-3.030226	-3.369876
N	-0.021988	1.520284	3.002176
N	1.804024	0.490365	2.481701
C	1.960875	0.925967	3.790250
C	0.804753	1.581942	4.119141
C	2.664695	-0.357208	1.714299
C	3.926588	-0.777396	2.168412
C	4.661279	-1.662376	1.361232
C	2.886144	-1.655775	-0.261685
C	4.149533	-2.121180	0.134531
H	1.550489	-3.624894	-4.276599
H	3.571067	-3.553277	-2.349989
H	0.499476	2.071162	5.042544
H	2.850427	0.721219	4.380990
H	4.346966	-0.442117	3.123995
H	5.646507	-2.005161	1.696198
H	4.736316	-2.819888	-0.473798
C	-1.367229	2.079920	2.956345
C	-0.558970	-1.856133	-3.692553
H	-1.966430	1.514760	2.228344
H	-1.837874	1.983982	3.948651
H	-1.343499	3.146187	2.666398
H	-1.172428	-1.189325	-3.066108
H	-0.340912	-1.371570	-4.660973
H	-1.101252	-2.801067	-3.867792
I	-0.745142	-2.342760	1.456838
N	0.621959	1.800922	-1.315952
C	1.990092	1.828272	-1.865301
C	2.579987	3.246471	-1.558250
C	1.288718	4.088544	-1.317111
C	0.105147	3.138968	-1.640462
C	-1.186584	3.520636	-0.919090

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H    -1.050863  3.448728  0.176999
H    -2.037026  2.877114 -1.205405
H    -0.082127  3.187137 -2.742147
H     1.221536  4.399453 -0.256308
H     1.257813  5.007951 -1.932039
C     3.459885  3.205905 -0.295180
C     3.396611  3.768911 -2.753939
H     2.613844  1.017508 -1.443079
H     1.954768  1.677306 -2.970265
H     3.832209  4.762745 -2.538721
H     4.232012  3.084513 -2.996897
H     2.768042  3.864180 -3.659594
H     3.772113  4.224064  0.006550
H     2.908594  2.754374  0.550497
H     4.375443  2.607131 -0.461815
H    -1.466544  4.562354 -1.160436
N    -1.980946 -0.053004 -0.927694
C    -3.123668 -0.961802 -1.010479
H    -3.117485 -1.506416 -1.986399
C    -4.562494 -0.377982 -0.853322
C    -5.526448 -1.581045 -0.964358
C    -4.886528  0.622726 -1.979486
C    -4.780978  0.265748  0.554435
H    -4.273568 -0.386020  1.296900
H    -5.862327  0.237742  0.798044
C    -4.290934  1.679622  0.714536
H    -3.241351  1.850311  0.442098
C    -5.034147  2.713670  1.149517
H    -6.091103  2.588393  1.422249
H    -4.619101  3.724421  1.250462
H    -2.977406 -1.732256 -0.229813
H    -2.116034  0.716825 -1.604453
H    -6.580896 -1.249654 -0.921724
H    -5.382097 -2.124085 -1.917632
H    -5.362683 -2.300715 -0.140199
H    -5.916551  1.014358 -1.881843
H    -4.213472  1.500479 -1.969400
H    -4.803068  0.136454 -2.970596
   el energy= -1476.39892586
        zpe= -1475.763757
   th energy= -1475.722594
  th enthalpy= -1475.721650
  free energy= -1475.840296
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TS-10-11

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Zr    0.061603  0.146961 -0.103817
C     0.303853 -0.314484  2.270581
C     2.008644 -1.093220  0.356302
C     1.208720 -0.544203 -2.098347
N     1.021033 -0.462206 -3.449077
N     2.389242 -1.244311 -1.970820
C     2.905879 -1.601096 -3.205524
C     2.037816 -1.104505 -4.145206
N    -0.401611 -0.187701  3.435382
N     1.463622 -0.957082  2.661578
C     1.464739 -1.225643  4.022996
C     0.283908 -0.735761  4.514194
C     2.408340 -1.373205  1.669353
C     3.603181 -2.042320  1.987380
C     4.431534 -2.457360  0.931160
C     2.873231 -1.536397 -0.652933
C     4.076645 -2.215097 -0.407893
H     2.056224 -1.159701 -5.232461
H     3.822621 -2.174590 -3.322061
H    -0.126345 -0.740501  5.522594
H     2.273802 -1.752979  4.522567
H     3.901961 -2.249096  3.021951
H     5.366768 -2.982673  1.154256
H     4.734736 -2.557031 -1.215815
C    -1.733013  0.399057  3.534338
C    -0.123026  0.193154 -4.073026
H    -2.232038  0.324971  2.557809
H    -2.326613 -0.162820  4.274129
H    -1.677904  1.459711  3.839348
H    -0.762084  0.578695 -3.263352
H     0.216191  1.022917 -4.718190
H    -0.693182 -0.533933 -4.676926
I    -0.995134 -2.709982 -0.002195
N     0.969732  2.056967 -0.117512
C     2.378152  2.249428 -0.549218
C     2.807456  3.714450 -0.194415
C     1.670929  4.160189  0.752855
C     0.437640  3.379636  0.261451
C    -0.681479  3.311854  1.304689
H    -0.308714  2.836173  2.230866
H    -1.547930  2.729622  0.940753
H     0.028043  3.896709 -0.641690
H     1.896441  3.850029  1.792860
H     1.513283  5.255526  0.751201
C     4.187676  3.751608  0.483281
C     2.830444  4.593348 -1.463105
H     3.033099  1.512072 -0.045145
H     2.488597  2.079166 -1.641630
H     3.094534  5.639614 -1.218128
H     3.575450  4.219413 -2.190499
H     1.847314  4.602825 -1.969735
H     4.465639  4.782953  0.772622
H     4.199606  3.128183  1.396821
H     4.977334  3.373971 -0.193947
H    -1.046192  4.326052  1.551744
N    -1.847913  0.640591 -0.938825
C    -2.964581  0.008211 -1.640669
H    -2.876915  0.169097 -2.742914
C    -4.420610  0.417755 -1.259191
C    -5.354632 -0.493425 -2.086439
C    -4.699077  1.886598 -1.634638
C    -4.711063  0.144200  0.254752
H    -4.130763 -0.758289  0.543356
H    -5.781542 -0.116238  0.377391
C    -4.388818  1.270705  1.199271
H    -3.369468  1.674823  1.131081
C    -5.242895  1.803886  2.092101
H    -6.274502  1.438748  2.188933
H    -4.949027  2.623694  2.759494
H    -2.863513 -1.081222 -1.476614
H    -1.889578  1.662095 -1.095875
H    -6.415549 -0.224931 -1.925861
H    -5.145228 -0.404766 -3.169652
H    -5.225710 -1.555374 -1.804571
H    -5.729395  2.184421 -1.364001
H    -4.018635  2.587873 -1.116597
H    -4.579119  2.037436 -2.724795
   el energy= -1476.39705869
        zpe= -1475.762199
   th energy= -1475.721705
  th enthalpy= -1475.720761
  free energy= -1475.837628
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11

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Zr    0.101393  0.092124 -0.002457
C     0.356635 -1.273943  1.985276
C     2.264287 -0.838001  0.168706
C     1.467849  0.582115 -1.915242
N     1.318337  1.189977 -3.129442
N     2.769628  0.129473 -1.929809
C     3.404004  0.442089 -3.120985
C     2.483418  1.117330 -3.882719
N    -0.413856 -1.776398  2.995093
N     1.604538 -1.815866  2.225386
C     1.596566 -2.640723  3.341619
C     0.317321 -2.614032  3.831005
C     2.659589 -1.586875  1.284834
C     3.958367 -2.097832  1.450970
C     4.902584 -1.847244  0.440737
C     3.248116 -0.623852 -0.804515
C     4.561797 -1.108165 -0.706192
H     2.557043  1.535695 -4.885225
H     4.429760  0.154591 -3.340430
H    -0.130323 -3.119881  4.684844
H     2.472868 -3.187328  3.681697
H     4.250764 -2.680027  2.332958
H     5.920959 -2.237285  0.546914
H     5.314710 -0.930443 -1.483531
C    -1.837638 -1.501984  3.153238
C     0.079125  1.817490 -3.575643
H    -2.264746 -1.249442  2.171688
H    -2.343686 -2.403030  3.537297
H    -2.003771 -0.662856  3.852333
H    -0.705291  1.546855 -2.850437
H     0.195182  2.915549 -3.616929
H    -0.192868  1.438378 -4.575411
I    -0.396945 -2.696030 -1.102551
N     0.283083  1.939578  0.993087
C     1.618185  2.439941  1.360489
C     1.582989  3.961242  1.044668
C     0.137586  4.310712  1.497406
C    -0.673039  2.975338  1.438609
C    -1.315215  2.641987  2.799909
H    -0.536530  2.517753  3.575560
H    -1.898430  1.705507  2.746138
H    -1.490835  3.052814  0.690108
H     0.147789  4.698226  2.534572
H    -0.312554  5.098675  0.865832
C     2.651610  4.740128  1.827395
C     1.756377  4.196933 -0.468393
H     1.822028  2.294033  2.447123
H     2.414960  1.903991  0.808749
H     1.601090  5.261846 -0.725309
H     2.772947  3.913638 -0.802142
H     1.030877  3.592019 -1.042181
H     2.567713  5.828107  1.645341
H     2.554156  4.572154  2.916409
H     3.671451  4.432545  1.527649
H    -1.994953  3.453473  3.123133
N    -1.816242  0.525658 -0.819031
C    -2.832349  0.044202 -1.750857
H    -2.719970  0.532817 -2.750024
C    -4.333374  0.203995 -1.354447
C    -5.148334 -0.521459 -2.448132
C    -4.746562  1.689351 -1.330277
C    -4.646521 -0.491121  0.010980
H    -4.049057 -1.426787  0.047398
H    -5.711494 -0.799051  0.023612
C    -4.372336  0.327875  1.244763
H    -3.364751  0.760302  1.312683
C    -5.254335  0.560236  2.233989
H    -6.275447  0.156018  2.201774
H    -4.993221  1.162912  3.112977
H    -2.626737 -1.031153 -1.912242
H    -2.012048  1.516519 -0.591037
H    -6.234753 -0.384280 -2.291990
H    -4.900823 -0.133393 -3.454542
H    -4.938011 -1.607415 -2.446281
H    -5.810234  1.804315 -1.048870
H    -4.160733  2.277466 -0.599153
H    -4.609287  2.149448 -2.327689
   el energy= -1476.40184881
        zpe= -1475.766610
   th energy= -1475.725485
  th enthalpy= -1475.724541
  free energy= -1475.842493
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TS-11-12

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Zr    0.067001 -0.660851 -0.298868
C     0.323762 -1.301168  2.014988
C     2.268503 -0.371432  0.440253
C     1.523913 -0.012264 -2.072842
N     1.428372  0.251268 -3.409194
N     2.848455  0.227657 -1.777063
C     3.551274  0.633218 -2.899845
C     2.650768  0.644037 -3.937305
N    -0.418614 -1.858789  3.017396
N     1.589255 -1.197625  2.558462
C     1.620685 -1.662929  3.864059
C     0.346806 -2.082605  4.154151
C     2.663621 -0.705591  1.742301
C     3.985941 -0.595111  2.203230
C     4.966201 -0.149576  1.298758
C     3.297052  0.021022 -0.427354
C     4.639459  0.151606 -0.034939
H     2.779447  0.895172 -4.988934
H     4.608842  0.886471 -2.879618
H    -0.069192 -2.522622  5.059007
H     2.524423 -1.674981  4.468602
H     4.271935 -0.846472  3.231596
H     6.004470 -0.052325  1.634540
H     5.427423  0.465321 -0.730341
C    -1.833757 -2.207572  2.891669
C     0.191800  0.088421 -4.169413
H    -2.026791 -2.524565  1.853964
H    -2.057727 -3.045706  3.571267
H    -2.480117 -1.346145  3.134276
H    -0.655519  0.253788 -3.485308
H     0.161084  0.828870 -4.985659
H     0.127448 -0.931319 -4.588246
I    -0.598894 -3.306153 -1.144191
N     0.140097  1.785053  0.477227
C     0.989163  2.723754 -0.262119
C     0.497194  4.168420  0.095795
C    -0.316849  3.932125  1.408978
C    -0.092435  2.437509  1.782951
C     1.043060  2.280458  2.814278
H     2.015092  2.612077  2.405285
H     1.151968  1.230067  3.129237
H    -1.013621  2.005870  2.225562
H    -0.006577  4.619636  2.218968
H    -1.393191  4.112443  1.227260
C     1.683376  5.127106  0.311950
C    -0.413325  4.716071 -1.019943
H     2.067852  2.615792 -0.001309
H     0.905510  2.523393 -1.349667
H    -0.888564  5.669846 -0.719827
H     0.157368  4.903150 -1.950395
H    -1.220423  3.996236 -1.251987
H     1.337424  6.149483  0.557471
H     2.333706  4.784866  1.138706
H     2.310266  5.198566 -0.598266
H     0.833338  2.886119  3.716823
N    -1.552048  0.472616 -0.729228
C    -2.775314  0.414449 -1.503247
H    -2.649341  1.001850 -2.446428
C    -4.084304  0.963688 -0.842660
C    -5.223451  0.724148 -1.858000
C    -3.961772  2.472596 -0.565857
C    -4.443602  0.180122  0.461668
H    -4.226365 -0.893737  0.273710
H    -5.537001  0.251722  0.633254
C    -3.731102  0.625996  1.710626
H    -2.634543  0.631701  1.651941
C    -4.337976  1.020139  2.846151
H    -5.432864  1.041956  2.937576
H    -3.766685  1.346490  3.724566
H    -2.991674 -0.630867 -1.826753
H    -0.978172  1.455350 -0.192374
H    -6.175699  1.154483 -1.495471
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H    -4.992670  1.192794 -2.833742
H    -5.385395 -0.356548 -2.033742
H    -4.869725  2.864435 -0.069592
H    -3.101363  2.694531  0.089216
H    -3.823790  3.031872 -1.511219
   el energy= -1476.35119467
         zpe= -1475.720645
    th energy= -1475.679948
  th enthalpy= -1475.679003
  free energy= -1475.795991
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12

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Zr   -1.909810 -0.081355 -0.132044
C    -0.280705 -1.301799 -1.430174
C    -0.313460  1.333840 -1.079953
C    -2.456122  2.232794  0.198908
N    -3.422086  2.971674  0.819873
N    -1.553057  3.174339 -0.245997
C    -1.945986  4.459497  0.097393
C    -3.132062  4.331520  0.774231
N     0.006846 -2.595625 -1.756373
N     0.783321 -0.587842 -1.939984
C     1.714935 -1.417293 -2.548180
C     1.221122 -2.692388 -2.430603
C     0.777694  0.842519 -1.810443
C     1.761135  1.666328 -2.386660
C     1.635855  3.056942 -2.218804
C    -0.394128  2.728606 -0.966262
C     0.553655  3.609841 -1.512847
H    -3.785592  5.082527  1.215237
H    -1.372066  5.345980 -0.162826
H     1.623223 -3.645526 -2.770665
H     2.667113 -1.051843 -2.929597
H     2.610037  1.255452 -2.944170
H     2.387428  3.721409 -2.659921
H     0.468840  4.698428 -1.411417
C    -0.821018 -3.739101 -1.377329
C    -4.591549  2.397489  1.480966
H    -1.838303 -3.380347 -1.151832
H    -0.867962 -4.454734 -2.215009
H    -0.398046 -4.236298 -0.486096
H    -4.714145  1.357236  1.139186
H    -4.460541  2.411669  2.577365
H    -5.491968  2.974555  1.210618
I    -4.468628 -1.309003 -0.735532
N     4.370810 -0.014825 -1.143311
C     5.385572  1.055160 -1.166443
C     6.051753  1.085908  0.237921
C     6.100386 -0.435305  0.550877
C     4.917860 -1.080373 -0.242995
C     5.362868 -2.301503 -1.058995
H     6.121975 -2.015199 -1.811226
H     4.505437 -2.750110 -1.591918
H     4.110036 -1.397658  0.443629
H     7.062606 -0.858509  0.200473
H     6.036624 -0.638108  1.635788
C     7.444879  1.733245  0.211097
C     5.147204  1.823991  1.246644
H     6.151265  0.813760 -1.933134
H     4.919235  2.016231 -1.454866
H     5.561185  1.759039  2.270076
H     5.053460  2.895883  0.988341
H     4.127324  1.396073  1.278153
H     7.936083  1.675528  1.200454
H     8.105199  1.232474 -0.522040
H     7.383797  2.803297 -0.064806
H     5.807473 -3.074019 -0.403762
N    -1.258756 -0.340766  1.604552
C    -1.024196 -0.446009  3.014291
H    -1.278321  0.528645  3.493038
C     0.425450 -0.804890  3.494231
C     0.438112 -0.624722  5.027890
C     1.452534  0.143877  2.853138
C     0.777635 -2.297866  3.204637
H    -0.083485 -2.911404  3.549370
H     1.638275 -2.594105  3.839305
C     1.086584 -2.645739  1.773734
H     0.349290 -2.301268  1.037024
C     2.176807 -3.324219  1.367631
H     2.937193 -3.673657  2.080330
H     2.351782 -3.561073  0.310383
H    -1.714249 -1.195564  3.468736
H     3.530100  0.371256 -0.699380
H     1.436188 -0.853184  5.446164
H     0.184269  0.414463  5.309776
H    -0.293718 -1.295606  5.517955
H     2.483625 -0.116172  3.161312
H     1.392356  0.100853  1.751635
H     1.260254  1.190181  3.158579
   el energy= -1476.38817112
         zpe= -1475.752459
    th energy= -1475.710629
  th enthalpy= -1475.709684
  free energy= -1475.833275
```

13

```
Zr   -0.508669 -0.391838 -0.102440
C     1.381802 -0.522714 -1.598899
C    -0.100365  1.642504 -1.181145
C    -2.197297  1.238045  0.391520
N    -3.318923  1.335208  1.163966
N    -2.033739  2.508615 -0.117312
C    -3.022967  3.369649  0.334813
C    -3.838773  2.625513  1.148407
N     2.305809 -1.444911 -2.000471
N     1.760212  0.631356 -2.250490
C     2.892129  0.430951 -3.025606
C     3.240123 -0.886811 -2.866210
C     0.973480  1.818729 -2.064360
C     1.253712  3.031794 -2.715057
C     0.400252  4.121896 -2.472908
C    -0.927376  2.759306 -0.996301
C    -0.707006  4.000408 -1.616028
H    -4.734101  2.900860  1.703551
H    -3.075169  4.417788  0.049109
H     4.055825 -1.465875 -3.296183
H     3.349923  1.215545 -3.623644
H     2.105878  3.149456 -3.394950
H     0.596302  5.079681 -2.967407
H    -1.366151  4.861677 -1.454381
C     2.345638 -2.823427 -1.515043
C    -3.874377  0.227872  1.937874
H     1.330581 -3.118880 -1.203108
H     2.682641 -3.489242 -2.326508
H     3.036109 -2.903072 -0.656387
H    -3.426709 -0.711768  1.577084
H    -3.646927  0.355254  3.010900
H    -4.967511  0.184647  1.795689
I    -1.984912 -2.852177 -0.514138
N     0.349853 -0.229138  1.552533
C     0.746614 -0.220159  2.929822
H    -0.014526  0.347257  3.515230
C     2.137605  0.406278  3.291231
C     2.189045  0.501495  4.832043
C     2.272643  1.811460  2.681784
C     3.318484 -0.513741  2.848267
H     3.093965 -1.537896  3.219623
H     4.239972 -0.190352  3.374711
C     3.595809 -0.574112  1.370525
H     2.728649 -0.808763  0.739925
C     4.794505 -0.347077  0.802724
H     5.677783 -0.087773  1.403110
H     4.939709 -0.402289 -0.283780
H     0.735584 -1.256292  3.343041
H     3.147986  0.936591  5.170425
H     1.374170  1.141781  5.219262
H     2.086764 -0.495554  5.302747
H     3.253031  2.259511  2.932425
H     2.175729  1.779262  1.583152
H     1.483008  2.482283  3.070953
   el energy= -1146.31594797
         zpe= -1145.889899
    th energy= -1145.859267
  th enthalpy= -1145.858323
  free energy= -1145.955287
```

TS-13-1

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Zr   -0.696991 -0.210259  0.021147
C     0.687033 -2.018950 -0.759544
C     0.804790  0.487639 -1.627172
C    -1.070307  2.070806 -0.625192
N    -1.892604  3.102768 -0.275296
N    -0.197074  2.633807 -1.530476
C    -0.465337  3.980610 -1.726530
C    -1.541253  4.279041 -0.929728
N     0.869246 -3.348341 -0.504201
N     1.665697 -1.721432 -1.683582
C     2.437881 -2.834197 -1.983320
C     1.933114 -3.866808 -1.234060
C     1.748867 -0.380686 -2.191867
C     2.680196  0.012113 -3.167169
C     2.653752  1.347777 -3.603537
C     0.815204  1.801501 -2.115956
C     1.717442  2.261150 -3.089492
H    -2.080777  5.213069 -0.781289
H     0.109173  4.608629 -2.403622
H     2.235140 -4.910556 -1.164537
H     3.259536 -2.813431 -2.695577
H     3.414821 -0.683034 -3.590878
H     3.369989  1.680442 -4.362911
H     1.709491  3.295084 -3.454585
C     0.074735 -4.108656  0.458068
C    -2.972526  2.986475  0.701190
H    -0.125010 -5.116500  0.057592
H     0.611291 -4.193855  1.419619
H    -0.883146 -3.587428  0.617216
H    -3.869301  3.509816  0.328911
H    -3.208741  1.918815  0.837614
H    -2.666443  3.422282  1.668714
I    -3.359232 -1.338571  0.268009
N     0.185167  0.190658  1.620749
C     0.620006  0.554865  2.935660
C     2.080031  1.107088  3.090924
C     3.143517 -0.033756  3.018943
C     3.309156 -0.726246  1.692819
C     4.465210 -0.800515  1.008811
H     5.387381 -0.332365  1.380502
H     4.535893 -1.329600  0.050234
H     2.405135 -1.193311  1.280673
H     4.123564  0.381772  3.332046
H     2.867062 -0.787827  3.788614
C     2.367252  2.188111  2.036550
C     2.170639  1.723144  4.504461
H    -0.061230  1.342244  3.335164
H     0.515569 -0.309558  3.633136
H     3.190589  2.097987  4.711391
H     1.471206  2.573381  4.613146
H     1.920482  0.979708  5.286106
H     1.639345  3.017991  2.119422
H     3.381011  2.611306  2.172721
H     2.297493  1.774321  1.016744
   el energy= -1146.31579294
         zpe= -1145.889685
    th energy= -1145.860030
  th enthalpy= -1145.859086
  free energy= -1145.952275
```

TS2-5-6

```
Zr    0.299859 -0.155832  0.085564
C    -0.947776 -2.168964 -0.258466
C    -1.809959  0.246510 -0.914662
C    -0.082182  2.191302 -0.339681
N     0.528614  3.387295 -0.081662
N    -1.283439  2.553819 -0.918487
C    -1.407858  3.931987 -1.006913
C    -0.260556  4.462133 -0.473960
N    -0.804893 -3.496647  0.031323
N    -2.194937 -2.085218 -0.842244
C    -2.804517 -3.327668 -0.907512
C    -1.925012 -4.223703 -0.350915
C    -2.683519 -0.794686 -1.249422
C    -3.907595 -0.605574 -1.911575
C    -4.268573  0.709339 -2.257646
C    -2.221935  1.530903 -1.287040
C    -3.430841  1.796997 -1.952732
H     0.050855  5.496656 -0.338447
H    -2.285290  4.421137 -1.423801
H    -2.007270 -5.298098 -0.194017
H    -3.796483 -3.479082 -1.327362
H    -4.578224 -1.436744 -2.162811
H    -5.217563  0.889035 -2.774921
H    -3.735455  2.811166 -2.239676
C     0.358641 -4.047318  0.719998
C     1.808715  3.509582  0.605746
H     0.086172 -4.353521  1.745282
H     0.750065 -4.918366  0.166244
H     1.124009 -3.254932  0.771341
H     1.659214  3.876004  1.636719
H     2.272761  2.511443  0.643953
H     2.469209  4.204418  0.058498
I    -0.879358  0.253916  2.706626
N     2.195735 -0.731812  0.283949
C     3.558518 -1.174995  0.310969
C     4.416876 -0.421138 -0.762051
C     3.395379 -0.041109 -1.877140
C     2.088569 -0.796407 -1.713997
C     0.857058 -0.296953 -2.252535
H     0.853743  0.709743 -2.692701
H     0.160719 -1.006252 -2.715302
H     2.202656 -1.893135 -1.744138
H     3.177274  1.044332 -1.864645
H     3.810298 -0.266129 -2.880877
C     5.049025  0.843180 -0.152325
C     5.525364 -1.345439 -1.300029
H     3.977189 -1.016931  1.326704
H     3.627807 -2.273266  0.111048
H     6.185254 -0.813926 -2.011597
H     6.160046 -1.725251 -0.476490
H     5.098689 -2.221720 -1.824187
H     5.821977  0.584324  0.595854
H     5.528360  1.467642 -0.930341
H     4.281089  1.457196  0.353132
   el energy= -1146.30003861
         zpe= -1145.873522
    th energy= -1145.844873
  th enthalpy= -1145.843929
  free energy= -1145.934461
```

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```
Zr   -0.062396 -0.022770 -0.241470
C    -1.448314 -1.503408 -1.521912
C    -2.144777 -0.392881  0.768962
C    -0.163448  0.902372  2.100094
N     0.561451  1.618172  3.019115
N    -1.404314  0.801785  2.696211
```

```
C    -1.438786  1.419432  3.939703
C    -0.190256  1.937207  4.147218
N    -1.329324 -2.310273 -2.619794
N    -2.745114 -1.710180 -1.103386
C    -3.409590 -2.616354 -1.917518
C    -2.508922 -3.000976 -2.876676
C    -3.167124 -1.104372  0.121329
C    -4.463516 -1.260345  0.638215
C    -4.744260 -0.696671  1.893644
C    -2.479743  0.127566  2.025344
C    -3.752224 -0.008034  2.609644
H     0.222503  2.494299  4.986636
H    -2.326560  1.446342  4.566124
H    -2.604232 -3.703866 -3.702803
H    -4.441350 -2.918220 -1.753209
H    -5.245947 -1.807436  0.098679
H    -5.745200 -0.806319  2.325565
H    -3.988676  0.397931  3.600202
C    -0.077464 -2.535355 -3.332040
C     1.957252  2.004849  2.861420
H    -0.257052 -2.530944 -4.421187
H     0.612284 -1.720109 -3.065241
H     0.361425 -3.503356 -3.031348
H     2.626551  1.133627  2.977875
H     2.113363  2.465382  1.872667
H     2.212842  2.747163  3.634403
I     0.685543 -2.655972  1.106462
N    -0.766831  1.895507 -0.638818
C    -1.686701  2.975251 -0.360286
C    -2.389115  3.323215 -1.731662
C    -1.527478  2.538165 -2.774056
C    -0.256811  2.102611 -2.007667
C     0.451209  0.794417 -2.425205
H    -0.062839  0.364367 -3.305099
H     1.499526  0.988584 -2.731786
H     0.463472  2.962243 -2.001187
H    -2.063553  1.626132 -3.102168
H    -1.301276  3.139199 -3.675757
C    -3.846867  2.827429 -1.726770
C    -2.350054  4.840150 -1.994337
H    -2.411666  2.685649  0.424317
H    -1.141478  3.877311  0.009280
H    -2.867203  5.098539 -2.937964
H    -2.842928  5.402600 -1.177709
H    -1.308294  5.206097 -2.070228
H    -4.312944  2.939883 -2.724738
H    -3.893850  1.757980 -1.447595
H    -4.464308  3.393894 -1.002899
H     2.626064  1.172903  0.086172
N     2.363495  0.179163  0.074059
C     3.284559 -0.553784 -0.835501
H     3.072609 -1.627241 -0.674229
C     4.803631 -0.284124 -0.638894
C     5.564962 -1.405744 -1.377791
C     5.181651 -0.316724  0.855028
C     5.243067  1.081065 -1.274456
H     5.237923  0.955484 -2.376191
H     6.295983  1.263932 -0.981945
C     4.409675  2.293468 -0.935142
H     3.478394  2.418690 -1.511827
C     4.729174  3.232459 -0.022467
H     5.660265  3.176379  0.557376
H     4.087641  4.103471  0.159566
H     2.986873 -0.317244 -1.873105
H     2.499056 -0.185853  1.025546
H     6.655345 -1.221534 -1.363476
H     5.380602 -2.387877 -0.904846
H     5.249034 -1.474446 -2.436095
H     6.280860 -0.303177  0.976085
H     4.782331  0.556693  1.403758
H     4.802542 -1.234394  1.343664
   el energy= -1476.37183263
        zpe= -1475.734827
    th energy= -1475.694451
  th enthalpy= -1475.693507
  free energy= -1475.809819

TS-14-15
Zr   -0.429030 -0.458889 -0.090709
C    -2.406924 -1.372983 -1.122574
C    -2.338647  0.737174  0.497600
C    -0.136968  0.862542  1.988163
N     0.790478  1.121570  2.960547
N    -1.135251  1.778806  2.252548
C    -0.831126  2.582524  3.342515
C     0.393443  2.166151  3.790887
N    -2.737179 -2.362860 -2.000252
N    -3.545876 -0.598823 -1.053535
C    -4.551144 -1.092564 -1.875921
C    -4.036380 -2.211011 -2.477700
C    -3.557468  0.527224 -0.167734
C    -4.701297  1.312095  0.052207
C    -4.623082  2.341062  1.006582
C    -2.343392  1.730167  1.485269
C    -3.450933  2.553842  1.750875
H     1.000321  2.507176  4.628064
H    -1.496182  3.357048  3.716785
H    -4.482879 -2.910960 -3.182006
H    -5.534457 -0.634991 -1.955382
H    -5.642679  1.135996 -0.481305
H    -5.500732  2.970065  1.192908
H    -3.430017  3.334746  2.519752
C    -1.814799 -3.412654 -2.423087
C     2.029554  0.371450  3.154198
H    -2.387521 -4.316137 -2.688938
H    -1.224282 -3.079421 -3.295140
H    -1.139116 -3.644883 -1.583558
H     1.833784 -0.694857  2.953984
H     2.827991  0.745195  2.487792
H     2.352287  0.480889  4.202269
I    -0.234186 -3.009963  1.334639
N     0.687834  1.556285 -0.722925
C     0.599188  2.984588 -0.387958
C     0.570198  3.769185 -1.737215
C    -0.061066  2.712191 -2.680567
C     0.531341  1.377774 -2.197443
C    -0.311886  0.105252 -2.357553
H    -1.311634  0.349991 -2.767502
H     0.136514 -0.657547 -3.027423
H     1.536295  1.245875 -2.666650
H    -1.160480  2.696540 -2.534545
H     0.135849  2.913245 -3.750709
C    -0.272934  5.049739 -1.630684
C     2.001118  4.127047 -2.191105
H    -0.325859  3.206391  0.186200
H     1.451831  3.311666  0.247548
H     1.994790  4.605746 -3.188955
H     2.475146  4.832831 -1.482669
H     2.649972  3.234184 -2.251869
H    -0.311339  5.588562 -2.596418
H    -1.311760  4.817812 -1.329895
H     0.149087  5.747121 -0.881225
H     1.633188  0.717885 -0.348543
N     1.942108 -0.509087 -0.074685
C     2.686955 -1.325900 -1.039925
H     2.368568 -2.392794 -0.971438
C     4.240969 -1.316644 -0.917803
C     4.783602 -2.288335 -1.989313
C     4.677785 -1.819908  0.471830
C     4.866206  0.089068 -1.206007
H     4.574318  0.380275 -2.236880
H     5.967861 -0.039030 -1.218017
C     4.525590  1.218872 -0.265372
H     3.543778  1.691162 -0.401162
C     5.347640  1.694723  0.690407
H     6.344956  1.265934  0.859965
H     5.063318  2.540094  1.329618
H     2.413680 -0.985479 -2.058762
H     2.300504 -0.696593  0.864657
H     5.888535 -2.332760 -1.965779
H     4.402416 -3.313297 -1.824417
H     4.480671 -1.975073 -3.006712
H     5.776965 -1.940599  0.517884
H     4.400804 -1.114134  1.275723
H     4.220482 -2.801547  0.697904
   el energy= -1476.34105087
        zpe= -1475.710661
    th energy= -1475.670311
  th enthalpy= -1475.669367
  free energy= -1475.785077

15
Zr   -0.036164 -0.334967 -0.058837
C    -1.295228 -1.442540 -1.777467
C    -2.301335  0.284143 -0.017333
C    -0.769558  0.574023  2.110802
N    -0.291702  0.745155  3.380183
N    -2.009966  1.178480  2.151535
C    -2.286251  1.710203  3.404018
C    -1.194614  1.436198  4.185550
N    -1.086591 -2.341244 -2.781750
N    -2.576769 -0.982371 -2.007396
C    -3.141776 -1.583837 -3.128319
C    -2.196165 -2.443874 -3.619269
C    -3.161572 -0.077042 -1.066276
C    -4.500120  0.348108 -1.144773
C    -5.002627  1.151378 -0.107226
C    -2.881564  1.022456  1.021285
C    -4.208030  1.484689  1.004077
H    -0.995445  1.652015  5.234171
H    -3.223328  2.206112  3.646577
H    -2.221863 -3.121101 -4.471360
H    -4.152954 -1.374820 -3.469308
H    -5.158152  0.056330 -1.971944
H    -6.041766  1.496851 -0.148901
H    -4.638744  2.068600  1.826303
C     0.147204 -3.105328 -2.924982
C     0.957039  0.163714  3.865045
H    -0.048455 -4.001836 -3.535134
H     0.930342 -2.495675 -3.410957
H     0.484046 -3.417719 -1.921529
H     1.177187 -0.729273  3.258561
H     1.788805  0.889220  3.795729
H     0.831456 -0.136125  4.918499
I    -0.512912 -2.997800  1.193423
N     0.415501  2.104712 -0.129399
C    -0.433273  3.314010  0.003874
C     0.070886  4.314892 -1.067747
C     0.364859  3.333462 -2.230184
C     0.931267  2.048929 -1.572576
C     0.487512  0.701679 -2.131387
H    -0.386518  0.820239 -2.800523
H     1.282294  0.193109 -2.713239
H     2.033949  2.107132 -1.520623
H    -0.580716  3.091171 -2.754043
H     1.059314  3.753392 -2.980938
C    -0.998067  5.360192 -1.420179
C     1.362653  5.017255 -0.599322
H    -1.484229  3.037529 -0.201533
H    -0.384824  3.708268  1.036079
H     1.754269  5.685860 -1.388243
H     1.178477  5.633289  0.301437
H     2.165016  4.294797 -0.358257
H    -0.652865  6.025828 -2.233130
H    -1.935289  4.877111 -1.753929
H    -1.238505  5.999974 -0.549396
H     1.216155  2.180287  0.505197
N     1.983242 -0.353197  0.661400
C     2.809284 -1.406127  0.078992
H     2.779409 -2.337163  0.696098
C     4.313080 -1.088307 -0.208634
C     4.879255 -2.282014 -1.007445
C     5.087255 -0.965709  1.118835
C     4.484242  0.198640 -1.078767
H     3.688626  0.183085 -1.853699
H     5.449920  0.138210 -1.620495
C     4.433812  1.513376 -0.344165
H     3.534260  1.679665  0.265296
C     5.390437  2.458497 -0.384950
H     6.306738  2.323491 -0.975807
H     5.297100  3.403735  0.163881
H     2.350441 -1.695609 -0.897507
H     2.386217 -0.045025  1.550897
H     5.972477 -2.187926 -1.147066
H     4.686044 -3.238281 -0.485666
H     4.416319 -2.346444 -2.011134
H     6.154168 -0.736800  0.937938
H     4.691346 -0.155298  1.758425
H     5.032566 -1.911261  1.690449
   el energy= -1476.36544861
        zpe= -1475.729845
    th energy= -1475.689204
  th enthalpy= -1475.688260
  free energy= -1475.804637

16
Zr   -0.136516 -0.040031 -0.272926
C    -1.455531 -1.242954 -1.851728
C    -2.439475  0.482794 -0.124050
C    -0.722444  1.180959  1.776169
N    -0.137410  1.549407  2.955432
N    -2.012335  1.653768  1.890617
C    -2.222303  2.278433  3.111558
C    -1.031856  2.213891  3.788659
N    -1.251902 -2.191701 -2.813461
N    -2.786974 -0.908689 -1.999162
C    -3.389570 -1.638914 -3.016578
C    -2.416352 -2.452336 -3.532937
C    -3.357582  0.021737 -1.078768
C    -4.713581  0.389751 -1.093371
C    -5.172526  1.260971 -0.090885
C    -2.966102  1.316379  0.870679
C    -4.307614  1.730391  0.913665
H    -0.755877  2.564747  4.781839
H    -3.183885  2.690076  3.409351
H    -2.454467 -3.191610 -4.331440
H    -4.438968 -1.533031 -3.281816
H    -5.414187  0.012080 -1.847952
H    -6.224906  1.566288 -0.081747
H    -4.694212  2.391622  1.698779
C     0.013172 -2.887498 -3.006271
C     1.231607  1.209952  3.319784
H     0.377521 -2.746507 -4.039992
H     0.732807 -2.462733 -2.288473
H    -0.111086 -3.966171 -2.804256
H     1.251848  0.780191  4.335883
H     1.598075  0.454058  2.609078
H     1.882586  2.103576  3.290419
I    -1.145900 -2.298567  1.488881
N     1.661767 -1.177328 -0.301480
C     2.324469 -2.436893  0.001005
H     1.641491 -2.998314  0.668112
C     3.726900 -2.353935  0.684078
C     4.059713 -3.760927  1.225182
C     3.714390 -1.353346  1.850825
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C     4.864541 -1.974501 -0.328362
H     5.006855 -2.837712 -1.010476
H     5.805132 -1.871552  0.249295
C     4.668578 -0.738051 -1.170368
H     4.041736 -0.856989 -2.068987
C     5.228699  0.467229 -0.941636
H     5.892482  0.638510 -0.083767
H     5.071926  1.316167 -1.619345
H     2.448003 -3.071413 -0.912230
H     2.298178 -0.605522 -0.883736
H     5.085575 -3.802489  1.637931
H     3.357458 -4.048558  2.028965
H     3.986900 -4.523693  0.426250
H     4.665697 -1.395695  2.415869
H     3.575376 -0.319061  1.489002
H     2.888606 -1.584136  2.548615
N     1.371980  1.914171 -0.439726
C     1.078753  3.300746 -0.003201
H    -0.019227  3.434450  0.036338
C     1.688598  4.231535 -1.083200
C     3.216258  4.349276 -0.899464
C     1.049314  5.628607 -1.059967
C     1.342362  3.435966 -2.371182
H     2.053800  3.643696 -3.191610
H     0.337055  3.725390 -2.731781
C     1.321452  1.927693 -1.975213
H     2.244880  1.422563 -2.321126
C     0.098791  1.096130 -2.342570
H    -0.796664  1.736335 -2.484190
H     0.238196  0.510826 -3.268310
H     1.473123  3.476650  1.014358
H     2.318604  1.664011 -0.127071
H     3.662820  4.951658 -1.711974
H     3.468819  4.840105  0.059724
H     3.716699  3.362057 -0.912746
H     1.264787  6.156794 -0.111577
H     1.436964  6.256461 -1.883339
H    -0.049002  5.566237 -1.172163
    el energy= -1476.36977317
         zpe= -1475.734416
    th energy= -1475.693721
  th enthalpy= -1475.692777
  free energy= -1475.808755
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TS-16-17

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C    -2.231517 -0.053941 -0.013791
C    -0.621773  0.541617  2.030339
N    -0.103376  0.819915  3.262425
N    -1.965349  0.843962  2.164807
C    -2.261803  1.281282  3.449505
C    -1.081175  1.266967  4.145508
N    -0.668680 -2.469862 -2.766264
N    -2.367527 -1.418799 -1.937373
C    -2.859945 -2.202168 -2.973122
C    -1.783484 -2.869220 -3.497674
C    -3.076530 -0.624087 -0.974406
C    -4.477506 -0.523409 -0.936297
C    -5.055762  0.157831  0.150323
C    -2.869218  0.520597  1.092292
C    -4.264376  0.665110  1.196714
H    -0.861115  1.518027  5.181953
H    -3.268576  1.537201  3.771104
H    -1.718824 -3.588928 -4.312211
H    -3.911969 -2.228989 -3.248022
H    -5.123121 -0.973563 -1.700339
H    -6.145747  0.257966  0.203803
H    -4.747841  1.130072  2.064560
C     0.675848 -3.004446 -2.949233
C     1.290017  0.575361  3.619009
H     0.963307 -2.948571 -4.013726
H     1.365125 -2.401558 -2.338490
H     0.718701 -4.053337 -2.606252
H     1.345501  0.250775  4.671172
H     1.673472 -0.229887  2.972966
H     1.901877  1.485727  3.484867
I    -0.205618 -2.803006  1.365655
N     2.079237 -0.583139 -0.488947
C     3.383911 -1.112212 -0.779795
H     3.381895 -2.188564 -0.488280
C     4.607078 -0.461196 -0.049479
C     5.790737 -1.445115 -0.170593
C     4.284179 -0.226170  1.433918
C     5.057155  0.880304 -0.714979
H     5.469333  0.633572 -1.716610
H     5.900300  1.288951 -0.121992
C     4.012758  1.948481 -0.891683
H     3.259632  1.757527 -1.668364
C     3.970738  3.118338 -0.222876
H     4.709902  3.366919  0.550333
H     3.215121  3.885613 -0.440220
H     3.603700 -1.097301 -1.877315
H     1.549795  0.072522 -1.542065
H     6.718215 -1.011565  0.248986
H     5.580358 -2.384275  0.373503
H     5.989870 -1.704755 -1.228546
H     5.184287  0.111320  1.983614
H     3.498885  0.540321  1.543519
H     3.919140 -1.156305  1.907873
N     0.452463  2.188338 -0.333408
C    -0.449994  3.256138  0.202371
H    -1.281001  2.783471  0.750602
C    -0.994034  4.061213 -1.014702
C    -0.147363  5.328591 -1.259622
C    -2.466800  4.454341 -0.809051
C    -0.810732  3.038269 -2.163318
H    -0.795437  3.507929 -3.163327
H    -1.638631  2.301489 -2.142831
C     0.504643  2.314522 -1.849778
H     1.352850  2.980819 -2.112922
C     0.684450  0.921766 -2.452608
H    -0.215165  0.590911 -3.000213
H     1.513867  0.889726 -3.186148
H     0.094480  3.903318  0.916725
H     1.405150  2.294431  0.039762
H    -0.489091  5.864228 -2.164985
H    -0.227347  6.027478 -0.405782
H     0.925058  5.094210 -1.395629
H    -2.585757  5.124758  0.063603
H    -2.861081  4.990052 -1.692662
H    -3.097143  3.561712 -0.640365
    el energy= -1476.32979139
         zpe= -1475.697983
    th energy= -1475.657901
  th enthalpy= -1475.656957
  free energy= -1475.772042
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17

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C    -1.006086 -1.110124 -2.095904
C    -2.287484 -0.022780 -0.035263
C    -0.720637  0.375090  2.120027
N    -0.260571  0.492010  3.403069
N    -2.078777  0.627321  2.238739
C    -2.434872  0.876810  3.556326
C    -1.283745  0.790094  4.295589
N    -0.660151 -1.795409 -3.225727
N    -2.370787 -0.930389 -2.220664
C    -2.849055 -1.499845 -3.390087
C    -1.764245 -2.048721 -4.028945
C    -3.100008 -0.324680 -1.132810
C    -4.489607 -0.120997 -1.155569
C    -5.089742  0.410152  0.001913
C    -2.945621  0.460011  1.100154
C    -4.331576  0.698961  1.150733
H    -1.113072  0.901732  5.365231
H    -3.459077  1.072680  3.865484
H    -1.693195 -2.598176 -4.966399
H    -3.900684 -1.487865 -3.668237
H    -5.112723 -0.365899 -2.025057
H    -6.171353  0.585919  0.013969
H    -4.834799  1.087589  2.045038
C     0.699051 -2.253765 -3.496822
C     1.111246  0.196959  3.799943
H     1.058897 -1.841446 -4.456395
H     1.334412 -1.904837 -2.665573
H     0.724448 -3.356671 -3.536523
H     1.133081 -0.708763  4.431129
H     1.699411  0.004555  2.890177
H     1.543576  1.046807  4.357548
I    -0.501805 -3.014070  1.047924
N     1.952598 -0.816791 -0.315661
C     3.184421 -1.532376 -0.468463
H     3.046249 -2.553168 -0.034548
C     4.483033 -0.948282  0.188451
C     5.535733 -2.077190  0.203766
C     4.209484 -0.485408  1.626992
C     5.080934  0.226101 -0.647891
H     5.382964 -0.191441 -1.632915
H     6.013896  0.571237 -0.156491
C     4.185038  1.408969 -0.894309
H     3.285169  1.203372 -1.491050
C     4.428768  2.661227 -0.460758
H     5.314969  2.897916  0.143452
H     3.773277  3.506894 -0.708308
H     3.431569 -1.705155 -1.547835
H     1.105668  0.873991 -2.888676
H     6.514282 -1.713383  0.570794
H     5.214692 -2.906784  0.860437
H     5.690239 -2.492923 -0.810975
H     5.146816 -0.178847  2.130962
H     3.517656  0.374450  1.632231
H     3.751365 -1.300175  2.218655
N     0.478784  2.096591 -0.419546
C    -0.440903  3.027192  0.312716
H    -1.472898  2.647063  0.202793
C    -0.306654  4.421349 -0.342837
C     0.936873  5.164096  0.189209
C    -1.562322  5.278951 -0.122649
C    -0.122271  4.002354 -1.819893
H     0.339782  4.792457 -2.439712
H    -1.110505  3.769001 -2.263894
C     0.742285  2.723479 -1.785010
H     1.812054  3.003934 -1.811315
C     0.472341  1.776954 -2.952803
H    -0.585580  1.458899 -2.968072
H     0.693468  2.287721 -3.908855
H    -0.194536  3.021287  1.388697
H     1.386692  2.082721  0.064643
H     1.104131  6.106813 -0.364233
H     0.813233  5.420328  1.258059
H     1.858222  4.558560  0.100295
H    -1.713512  5.497492  0.951230
H    -1.480289  6.248214 -0.648756
H    -2.468663  4.766118 -0.494449
    el energy= -1476.37469487
         zpe= -1475.738246
    th energy= -1475.697264
  th enthalpy= -1475.696320
  free energy= -1475.814058
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Zr    0.704131  0.029070 -0.709389
C     0.046423 -2.136427  0.097558
C    -0.455018  0.164511  1.335352
C     0.434273  2.283028  0.019777
N     0.789217  3.531720 -0.409091
N    -0.212702  2.516768  1.219810
C    -0.255682  3.870610  1.517577
C     0.383791  4.514087  0.486456
N     0.219522 -3.442523 -0.257919
N    -0.534564 -2.207616  1.349905
C    -0.711649 -3.523383  1.752272
C    -0.228231 -4.307346  0.733628
C    -0.847268 -0.982361  2.037359
C    -1.478908 -0.942040  3.293026
C    -1.717576  0.318533  3.869280
C    -0.697509  1.390543  1.967899
C    -1.327978  1.503532  3.219551
H     0.584115  5.572216  0.325045
H    -0.723396  4.267843  2.415881
H    -0.164024 -5.390279  0.639525
H    -1.151056 -3.799632  2.708319
H    -1.782489 -1.850026  3.828386
H    -2.209417  0.378331  4.846633
H    -1.513408  2.472365  3.699480
C     0.855394 -3.843089 -1.510313
C     1.522875  3.761183 -1.651213
H     0.343172 -4.729740 -1.921479
H     0.771930 -2.995151 -2.213039
H     1.922839 -4.071185 -1.343934
H     2.603799  3.860005 -1.449831
H     1.349912  2.881017 -2.300271
H     1.150932  4.679446 -2.137203
I     3.481333 -0.424050 -0.052499
N    -1.707940  0.259560 -1.178521
C    -2.698643 -0.836974 -1.114601
C    -4.111387 -0.191502 -1.246609
C    -3.765718  1.159873 -1.938762
C    -2.300367  1.316838 -1.628200
C     0.514346  0.163973 -2.752227
H     1.577343 -0.040593 -3.059054
H    -0.141926  0.277069 -3.634365
H    -1.718863  2.231790 -1.795085
H    -3.912490  1.117632 -3.039047
H    -4.375934  2.008259 -1.572733
C    -5.076939 -1.059939 -2.067070
C    -4.687502  0.076626  0.158950
H    -2.469711 -1.532683 -1.945784
H    -2.573988 -1.396834 -0.171804
H    -5.643510  0.630094  0.098058
H    -4.879836 -0.872329  0.693429
H    -3.984493  0.669551  0.773452
H    -6.063351 -0.571054 -2.173848
H    -4.682112 -1.253220 -3.081780
H    -5.245038 -2.038031 -1.578390
    el energy= -1146.26631003
         zpe= -1145.842423
    th energy= -1145.812261
  th enthalpy= -1145.811317
  free energy= -1145.905791
```

19

```
Zr   -0.183238 -0.169836 -0.342365
C    -2.156070 -1.449210 -0.621076
C    -2.105048  1.177470 -0.365424
C     0.251604  2.142862  0.383570
N     1.229339  2.872996  1.005574
N    -0.783105  3.045547  0.249005
C    -0.450444  4.293823  0.750933
C     0.828030  4.186049  1.231972
N    -2.483549 -2.760650 -0.827694
N    -3.354906 -0.783373 -0.802505
C    -4.384320 -1.657281 -1.136305
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```
C    -3.829780 -2.909102 -1.153901
C    -3.364297  0.634836 -0.670356
C    -4.523786  1.416734 -0.819942
C    -4.412436  2.807484 -0.661221
C    -2.067522  2.564317 -0.179993
C    -3.182821  3.404307 -0.332323
H     1.469179  4.914730  1.725516
H    -1.137754  5.136657  0.750869
H    -4.275819 -3.882772 -1.350108
H    -5.406569 -1.332283 -1.314582
H    -5.498979  0.971449 -1.049912
H    -5.301360  3.436825 -0.781883
H    -3.122203  4.491031 -0.199699
C    -1.502526 -3.838552 -0.809796
C     2.484267  2.322198  1.507243
H    -0.825234 -3.742316 -1.678636
H    -0.912699 -3.779719  0.120858
H    -2.025518 -4.807265 -0.854918
H     2.568165  2.524325  2.589043
H     2.472107  1.233947  1.346460
H     3.346706  2.773805  0.985135
I     0.247023 -1.698339  2.180769
N     2.323612 -0.352126 -0.471515
C     3.101594  0.466357 -1.436632
C     4.559777 -0.086869 -1.447664
C     4.341413 -1.524925 -0.892235
C     3.014868 -1.411937 -0.191361
C     0.088425 -0.378635 -2.338278
H    -0.565995  0.537120 -2.468608
H     0.382319 -0.774788 -3.325903
H     2.596644 -2.160584  0.495961
H     4.264535 -2.279944 -1.703462
H     5.150842 -1.869187 -0.220351
C     5.169343 -0.072832 -2.858574
C     5.451354  0.712457 -0.475815
H     2.593043  0.368664 -2.412534
H     3.037744  1.533867 -1.153113
H     6.472976  0.290202 -0.434378
H     5.537200  1.768380 -0.794631
H     5.041400  0.698367  0.551457
H     6.183742 -0.513747 -2.860651
H     4.547034 -0.645530 -3.570569
H     5.256283  0.960092 -3.244514
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    th energy= -1145.813493
  th enthalpy= -1145.812549
  free energy= -1145.906650

20
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C    -0.310483  2.342808  0.338904
C    -1.988695  0.617301 -0.662867
C    -0.713497 -1.549281 -1.341594
N    -0.334151 -2.785683 -1.864372
N    -2.099019 -1.527412 -1.594548
C    -2.532339 -2.698090 -2.208232
C    -1.423221 -3.485270 -2.372122
N     0.313703  3.485925  0.834389
N    -1.657506  2.743821  0.260912
C    -1.835476  4.050134  0.702849
C    -0.597328  4.510184  1.066294
C    -2.590774  1.822422 -0.270522
C    -3.976846  2.061648 -0.409464
C    -4.761153  1.036649 -0.969077
C    -2.816823 -0.367884 -1.222854
C    -4.209922 -0.188454 -1.384778
H    -1.316083 -4.471762 -2.821701
H    -3.567202 -2.864798 -2.498789
H    -0.288749  5.480586  1.453361
H    -2.802543  4.548165  0.701441
H    -4.442182  3.005351 -0.102224
H    -5.839413  1.199746 -1.087674
H    -4.852975 -0.962121 -1.820102
C     1.732793  3.559362  1.127951
C     1.024040 -3.291373 -1.804227
H     1.964867  3.122894  2.120828
H     2.292661  3.004748  0.354715
H     2.058845  4.612811  1.118750
H     1.124328 -4.160213 -2.475052
H     1.728361 -2.502904 -2.121700
H     1.287868 -3.602788 -0.772207
I     2.960217  0.414994 -1.483602
N     0.920662 -0.572821  1.726162
C    -0.326713 -0.665672  2.547649
C    -0.383331 -2.103586  3.141329
C     1.128957 -2.477644  3.278416
C     1.845730 -1.665104  2.205652
C     2.151619 -0.232965  2.493294
H     1.999859  0.137934  3.516801
H     2.912195  0.287114  1.898046
H     2.409250 -2.169481  1.411331
H     1.509086 -2.221602  4.286255
H     1.286087 -3.561593  3.138904
C    -1.118583 -2.129545  4.490772
C    -1.066806 -3.054168  2.137817
H    -0.312274  0.112678  3.332698
H    -1.196144 -0.458313  1.887330
H    -1.019687 -4.100486  2.492490
H    -2.130825 -2.786036  2.003213
H    -0.589188 -2.994264  1.141807
H    -1.128333 -3.150783  4.914221
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H    -2.170771 -1.809423  4.377194
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    th energy= -1145.793043
  th enthalpy= -1145.792099
  free energy= -1145.885153

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C     0.415041  1.554016 -1.704755
N    -0.177909  2.742127 -2.052364
N     1.371560  1.385729 -2.684918
C     1.364427  2.420537 -3.607042
C     0.379251  3.284196 -3.206380
N     2.136327 -2.513667  2.011195
N     3.013279 -2.089079  0.087702
C     3.833896 -3.038286  0.683601
C     3.273404 -3.309949  1.904308
C     3.150151 -1.409919 -1.161301
C     4.154917 -1.723670 -2.091777
C     4.208654 -0.985152 -3.285447
C     2.317787  0.313084 -2.556825
C     3.290984  0.047804 -3.535392
H     0.041430  4.229017 -3.629283
H     2.062182  2.479786 -4.438934
H     3.588271 -3.984443  2.698944
H     4.740536 -3.418955  0.219220
H     4.881932 -2.524752 -1.913302
H     4.977853 -1.216894 -4.030566
H     3.350394  0.613458 -4.472820
C     1.198315 -2.557642  3.127269
C    -1.200484  3.418713 -1.264767
H     0.766552 -1.554108  3.263577
H     0.384581 -3.272428  2.909701
H     1.735175 -2.856311  4.042908
H    -2.215377  3.137929 -1.599527
H    -1.054166  3.151994 -0.207455
H    -1.073457  4.508831 -1.363017
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N     0.680318  0.910519  1.567465
C     1.037805  1.356907  2.882299
H     0.399762  0.844684  3.644971
C     0.931023  2.885960  3.207321
C     1.207342  3.041860  4.719284
C    -0.482389  3.403798  2.897777
C     2.011406  3.725646  2.456530
H     3.000158  3.286935  2.713195
H     2.008779  4.751843  2.879239
C     1.902707  3.813998  0.957323
H     1.963574  2.859637  0.417915
C     1.758092  4.964535  0.272772
H     1.691174  5.936171  0.782490
H     1.725456  4.982479 -0.824430
H     2.086306  1.052544  3.117910
H    -2.221650  1.305969  0.309257
H     1.155506  4.102727  5.027984
H     0.467264  2.479761  5.319547
H     2.213339  2.662926  4.983652
H    -0.570440  4.486600  3.108368
H    -0.731868  3.240985  1.835627
H    -1.237415  2.874773  3.510541
N    -2.104353  0.341760 -0.021681
C    -2.906453  0.125848 -1.254694
H    -2.496212  0.809088 -2.022975
C    -4.447460  0.323828 -1.164702
C    -4.973082  0.358800 -2.616881
C    -4.809003  1.646965 -0.463484
C    -5.161068 -0.871637 -0.443973
H    -5.029337 -1.771530 -1.077188
H    -6.245623 -0.642664 -0.435864
C    -4.711240 -1.200977  0.960009
H    -3.837066 -1.867377  1.044198
C    -5.316829 -0.775349  2.085428
H    -6.213488 -0.140959  2.055186
H    -4.950511 -1.059477  3.079357
H    -2.685224 -0.902568 -1.596209
H    -2.482532 -0.255271  0.726561
H    -6.076952  0.418579 -2.636924
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H    -5.898414  1.829725 -0.519536
H    -4.536752  1.638542  0.607628
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  th enthalpy= -1475.688536
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TS-21-22
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N    -2.212701  0.525354  2.562436
C    -2.448194  0.973403  3.852308
C    -1.215710  1.130660  4.433355
N    -1.008245 -1.992994 -2.919583
N    -2.713549 -1.422163 -1.726102
C    -3.226023 -1.981107 -2.889366
C    -2.141804 -2.343786 -3.646432
C    -3.391879 -0.878357 -0.588517
C    -4.791681 -0.814746 -0.492973
C    -5.350937 -0.260333  0.670711
C    -3.144026  0.108915  1.556207
C    -4.536160  0.208735  1.714501
H    -0.935234  1.453441  5.434658
H    -3.446224  1.127431  4.256163
H    -2.082018 -2.820318 -4.623443
H    -4.291194 -2.082981 -3.082929
H    -5.448503 -1.180222 -1.290970
H    -6.440391 -0.195361  0.766733
H    -4.994729  0.635352  2.614199
C     0.369248 -2.209597 -3.357054
C     1.166828  0.743631  3.706583
H     0.852640 -1.244066 -3.587332
H     0.927069 -2.716240 -2.550785
H     0.365571 -2.842356 -4.258486
H     1.385993  0.155145  4.614056
H     1.629853  0.270851  2.826476
H     1.559301  1.768676  3.826255
I     0.831189 -3.145438  0.572269
N     0.098261  1.137763 -1.039688
C     0.123920  1.991117 -2.201990
H     1.126557  1.935487 -2.688362
C    -0.181085  3.513249 -1.982037
C     0.214157  4.235292 -3.289452
C     0.645381  4.073970 -0.813784
C    -1.701863  3.782815 -1.751126
H    -2.248681  3.350987 -2.617566
H    -1.863769  4.879354 -1.797564
C    -2.307640  3.255400 -0.477874
H    -2.304727  2.165007 -0.353426
C    -2.849958  4.025808  0.482677
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H    -3.298104  3.590106  1.384625
H    -0.603959  1.618611 -2.958897
H     1.270007  0.857289 -0.598615
H    -0.012967  5.316192 -3.232118
H     1.296421  4.129079 -3.492645
H    -0.334238  3.823511 -4.158905
H     0.440524  5.151565 -0.666635
H     0.404662  3.546756  0.125452
H     1.729701  3.961238 -1.007019
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C     3.012338  1.281997  0.842454
H     2.461470  2.244738  0.811810
C     4.355114  1.463264  0.058544
C     4.929933  2.843896  0.441297
C     4.135109  1.405606 -1.462646
C     5.414980  0.390287  0.484983
H     5.702714  0.607510  1.535197
H     6.323486  0.550457 -0.130009
C     4.999960 -1.055957  0.388173
H     4.309829 -1.423603  1.163403
C     5.421367 -1.923181 -0.551481
H     6.126094 -1.620727 -1.338216
H     5.081557 -2.965678 -0.565079
H     3.301123  1.137002  1.912893
H     2.624690 -0.614757  0.162762
H     5.939344  2.994234  0.013874
H     4.281626  3.660292  0.070912
H     5.012896  2.951637  1.540401
H     5.074904  1.636152 -2.000174
H     3.793772  0.407251 -1.786401
H     3.375356  2.143725 -1.782022
    el energy= -1476.32623607
         zpe= -1475.697651
    th energy= -1475.655892
  th enthalpy= -1475.654947
  free energy= -1475.776825

22
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C    -2.282985 -0.781496  0.092529
C    -1.034210  0.487213  2.048452
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N    -1.969386 -2.105020 -1.851791
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C    -0.975879 -3.234189 -3.468963
C    -2.893954 -1.566140 -0.893864
C    -4.273145 -1.836804 -0.920089
C    -5.068931 -1.301639  0.108152
C    -3.119343 -0.312740  1.111182
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H    -0.697432 -3.855678 -4.318408
H    -3.198152 -3.281256 -3.218762
H    -4.737487 -2.452596 -1.699719
H    -6.147123 -1.497182  0.109711
H    -5.144296 -0.163571  1.955048
C     1.413499 -2.624680 -2.882556
C     0.705224  1.504781  3.513923
H     1.821491 -1.620028 -3.085831
H     1.873551 -3.022811 -1.961299
H     1.640026 -3.290622 -3.729967
H     1.014240  0.960285  4.423377
H     1.337919  1.198555  2.664127
H     0.797980  2.591912  3.682294
I     0.967533 -2.929150  1.338747
N    -0.345734  1.250730 -1.153458
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H    -2.520724  4.833541 -0.569474
C    -0.892608  3.959103  0.502194
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H    -2.385671  1.276285 -1.570922
H     0.526155  1.704420 -1.457551
H    -3.118812  4.679788 -2.878012
H    -2.760345  3.208214 -3.825977
H    -3.830205  3.111808 -2.397861
H    -0.655358  5.155301 -2.498881
H     0.431254  3.907454 -1.859934
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N     1.994423  0.483981  0.295729
C     2.704427  1.748893  0.195688
H     1.991865  2.499207 -0.207725
C     3.989062  1.785088 -0.695651
C     4.302000  3.266737 -0.995546
C     3.765000  1.032624 -2.018600
C     5.233003  1.195747  0.053355
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H     4.527267 -0.314124  1.535965
C     5.664392 -1.302637  0.068663
H     6.274532 -1.249020 -0.843354
H     5.536370 -2.293328  0.520631
H     2.997820  2.145729  1.200032
H     2.639351 -0.256364  0.608257
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H     3.505188  3.724600 -1.611759
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H     4.633345  1.162124 -2.692814
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H     2.870007  1.416971 -2.544550
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  th enthalpy= -1475.692880
  free energy= -1475.816238
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22B

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N     0.681217 -3.523359 -1.212335
N     2.371688 -2.225230 -1.535773
C     2.749557 -3.475716 -2.007944
C     1.675721 -4.299222 -1.802782
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C     3.413991  2.766784  1.713277
C     2.427907  3.178361  2.573298
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C     4.796323  1.029120 -0.414918
C     5.335854  0.042669 -1.256451
C     3.205116 -1.084381 -1.283012
C     4.553022 -1.042029 -1.682351
H     1.542999 -5.361212 -2.003613
H     3.736427 -3.688815 -2.411704
H     2.447354  3.908313  3.381096
H     4.454816  3.071604  1.631658
H     5.436693  1.837679 -0.042944
H     6.388177  0.101774 -1.555858
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H    -0.173454  3.558100  3.295220
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H    -0.867780 -3.500381  0.191357
H    -1.360489 -4.089865 -1.448981
I     0.381423 -1.430672  2.534068
N    -1.041744  1.678015 -0.087149
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C    -1.138511  3.567334 -1.794838
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H    -4.815984 -0.072693  2.138978
C    -6.577410  0.748006  1.324762
H    -7.364035  0.710613  0.558884
H    -6.659730  1.544373  2.074265
H    -2.905841 -0.123282  0.831323
H    -1.590545 -1.859205 -1.141786
H    -5.118829 -2.547245 -2.027784
H    -3.364688 -2.369182 -2.258959
H    -3.995166 -3.327152 -0.878383
H    -5.218222 -0.010142 -2.188462
H    -4.492405  1.002900 -0.911923
H    -3.442839  0.223407 -2.142499
    el energy= -1476.35527908
         zpe= -1475.721258
    th energy= -1475.680186
  th enthalpy= -1475.679242
  free energy= -1475.795516
```

TS-22-23

```
Zr    0.282903 -0.088470 -0.158354
C     1.167876  1.694471  1.257121
C     2.606907  0.295795 -0.459477
C     1.484482 -1.998981 -1.160496
N     1.274428 -3.313117 -1.487014
N     2.771567 -1.766052 -1.610474
C     3.329031 -2.891675 -2.203757
C     2.378864 -3.873035 -2.125693
N     0.739461  2.456429  2.306119
N     2.457607  2.126422  1.041421
C     2.825172  3.114813  1.944512
C     1.734305  3.321490  2.750247
C     3.260453  1.409454  0.091624
C     4.596168  1.749300 -0.180288
C     5.329894  0.907489 -1.033403
C     3.415098 -0.542940 -1.241121
C     4.755805 -0.261948 -1.558624
H     2.399635 -4.913373 -2.446665
H     4.341393 -2.917055 -2.599781
H     1.587684  3.995842  3.592470
H     3.808804  3.578887  1.952038
H     5.076154  2.631724  0.259925
H     6.372271  1.150553 -1.267858
H     5.361268 -0.931437 -2.181167
C    -0.535154  2.238448  2.982165
C     0.107858 -4.094035 -1.083951
H    -1.249910  1.841204  2.245336
H    -0.407975  1.496931  3.790793
H    -0.905898  3.192312  3.393532
H     0.424367 -5.133086 -0.893814
H    -0.295677 -3.663770 -0.154142
H    -0.667499 -4.097965 -1.872441
I     0.762893 -1.585465  2.357730
N    -1.240065  1.566087 -0.411062
C    -1.553609  2.986488 -0.333419
H    -0.673157  3.516370  0.078633
C    -1.919064  3.549859 -1.754791
C    -1.308893  4.952089 -1.943496
C    -3.447734  3.623292 -1.932559
C    -1.305404  2.525528 -2.753397
H    -2.063126  1.799353 -3.108252
H    -0.927245  3.043345 -3.658441
C    -0.153302  1.771029 -2.117876
H     0.602622  2.449483 -1.680123
C     0.381980  0.531192 -2.567378
H    -0.242181 -0.098425 -3.216515
H     1.458559  0.495480 -2.761984
H    -2.395377  3.162772  0.369558
H    -2.044901  1.073126 -0.822046
H    -1.618449  5.401522 -2.905630
H    -1.633008  5.636934 -1.136569
H    -0.202930  4.916894 -1.925844
H    -3.716600  3.894256 -2.971049
H    -3.926320  2.650959 -1.708034
H    -3.893647  4.381700 -1.261328
N    -1.455801 -1.265561 -0.593114
C    -2.635854 -1.411216  0.247510
H    -2.489187 -2.223358  1.003666
C    -3.986549 -1.685868 -0.487005
C    -3.881072 -2.977343 -1.324688
C    -4.352359 -0.508422 -1.409092
C    -5.114253 -1.905718  0.573458
H    -4.868041 -2.828404  1.140466
H    -6.061935 -2.108384  0.035169
C    -5.329744 -0.778907  1.550566
H    -4.536904 -0.618525  2.296396
C    -6.413682  0.017680  1.581336
H    -7.239635 -0.109235  0.868342
H    -6.524627  0.818573  2.322423
H    -2.744651 -0.482288  0.845376
H    -1.389710 -2.054274 -1.240373
H    -4.858137 -3.240295 -1.772408
H    -3.164968 -2.862249 -2.160347
H    -3.554545 -3.834166 -0.703794
H    -5.261952 -0.725488 -2.001258
H    -4.550844  0.408302 -0.822347
H    -3.526864 -0.305696 -2.116758
    el energy= -1476.34276858
         zpe= -1475.708685
    th energy= -1475.668595
  th enthalpy= -1475.667651
  free energy= -1475.782323
```

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```
Zr    0.283061 -0.209029 -0.211808
C     0.591454  1.425025  1.569954
C     2.463045  0.678205 -0.162301
C     1.883270 -1.554795 -1.414053
N     1.935636 -2.767593 -2.047505
N     3.132257 -1.013991 -1.658243
C     3.920200 -1.857174 -2.430593
C     3.161588 -2.969316 -2.678406
N    -0.088873  1.891833  2.658977
N     1.781221  2.116797  1.600181
C     1.845661  2.971881  2.691510
C     0.660175  2.826323  3.366743
C     2.808490  1.763331  0.656224
C     4.060344  2.400196  0.622525
C     5.027915  1.903744 -0.268736
C     3.490007  0.191138 -0.982243
C     4.762341  0.780942 -1.071007
H     3.390698 -3.882153 -3.225990
H     4.941945 -1.618356 -2.716279
H     0.295713  3.297583  4.278078
H     2.710064  3.595668  2.906509
H     4.303211  3.251293  1.270461
H     6.011852  2.383269 -0.319063
H     5.546550  0.384451 -1.727306
C    -1.356482  1.323669  3.107652
C     0.890688 -3.781597 -1.965696
H    -2.069574  1.293421  2.267105
H    -1.187849  0.296156  3.477514
H    -1.772660  1.950602  3.912343
H     1.357573 -4.780568 -1.953279
H     0.336499 -3.625948 -1.026907
H     0.202929 -3.718512 -2.829763
I     0.997607 -1.995562  2.069853
N    -1.329832  1.558482 -0.831815
C    -2.075380  2.760215 -0.413048
H    -1.520920  3.237258  0.417622
C    -2.136114  3.719834 -1.664284
C    -1.739839  5.151136 -1.256117
C    -3.549458  3.720106 -2.277537
```

```
C    -1.091360  3.092444 -2.647640
H    -1.599738  2.542065 -3.464493
H    -0.445600  3.856448 -3.117783
C    -0.286176  2.085637 -1.790143
H     0.419575  2.665317 -1.154354
C     0.439580  0.873011 -2.339303
H    -0.166405  0.357158 -3.111802
H     1.426816  1.123874 -2.758699
H    -3.079146  2.483617 -0.040746
H    -1.953522  0.954397 -1.386507
H    -1.805239  5.845202 -2.114430
H    -2.403969  5.539883 -0.460139
H    -0.702397  5.184217 -0.872798
H    -3.573376  4.296769 -3.221067
H    -3.886741  2.691345 -2.508342
H    -4.289276  4.171239 -1.588709
N    -1.264559 -1.517116 -0.905666
C    -2.367071 -1.858749 -0.016958
H    -2.167778 -2.809198  0.537951
C    -3.780282 -1.981334 -0.672056
C    -3.771142 -3.125956 -1.706600
C    -4.184060 -0.669891 -1.368107
C    -4.829421 -2.348726  0.428153
H    -4.566136 -3.352356  0.823331
H    -5.819456 -2.450769 -0.059908
C    -4.940766 -1.386200  1.582581
H    -4.104810 -1.381213  2.298213
C    -5.981264 -0.561850  1.803069
H    -6.849322 -0.540007  1.130301
H    -6.015900  0.110887  2.668739
H    -2.421336 -1.075919  0.773311
H    -1.208865 -2.180676 -1.682115
H    -4.778356 -3.280316 -2.137645
H    -3.088357 -2.906510 -2.549122
H    -3.451841 -4.080196 -1.245358
H    -5.166647 -0.767084 -1.868007
H    -4.262053  0.162016 -0.643179
H    -3.438381 -0.404764 -2.140600
   el energy= -1476.36437684
        zpe= -1475.728052
   th energy= -1475.687642
  th enthalpy= -1475.686698
  free energy= -1475.803148
```

TS-23-24

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Zr    0.088368 -0.244313 -0.159785
C    -1.106835 -1.549211 -1.778674
C    -2.281934  0.026112 -0.008776
C    -0.639825  0.653799  2.002925
N    -0.100625  0.987225  3.212936
N    -1.975114  0.987262  2.137859
C    -2.247285  1.497524  3.400310
C    -1.058775  1.499065  4.082711
N    -0.806287 -2.457511 -2.753316
N    -2.469544 -1.360754 -1.913026
C    -2.994758 -2.149697 -2.927916
C    -1.940776 -2.845766 -3.459719
C    -3.149490 -0.541092 -0.950904
C    -4.547661 -0.413332 -0.898765
C    -5.101304  0.294142  0.183647
C    -2.897015  0.639833  1.089485
C    -4.288061  0.808416  1.209002
H    -0.821482  1.800451  5.101819
H    -3.244665  1.791680  3.718665
H    -1.903547 -3.578451 -4.264336
H    -4.051456 -2.159216 -3.185238
H    -5.209973 -0.861912 -1.649298
H    -6.188768  0.412813  0.249093
H    -4.752377  1.297949  2.073767
C     0.520516 -3.030164 -2.948333
C     1.292961  0.744575  3.566971
H     0.782488 -3.018632 -4.020723
H     1.239316 -2.424530 -2.376541
H     0.546475 -4.067408 -2.569816
H     1.347505  0.319990  4.583531
H     1.705124  0.016023  2.852578
H     1.881895  1.679400  3.529941
I    -0.382756 -2.752782  1.393637
N     1.998462 -0.697209 -0.478547
C     3.243721 -1.363222 -0.755469
H     3.120207 -2.437667 -0.483198
C     4.519665 -0.865842  0.005111
C     5.590104 -1.970630 -0.125802
C     4.201921 -0.630593  1.489221
C     5.120656  0.432868 -0.622562
H     5.508953  0.168068 -1.629314
H     6.000274  0.732394 -0.017215
C     4.196221  1.609245 -0.771844
H     3.414429  1.503129 -1.535530
C     4.281585  2.765449 -0.085102
H     5.052191  2.926921  0.680552
H     3.603173  3.607739 -0.278017
H     3.484354 -1.354062 -1.848798
H     1.516906 -0.017401 -1.548186
H     6.552826 -1.650046  0.315093
H     5.271403 -2.893201  0.393395
H     5.775470 -2.226688 -1.187143
H     5.127733 -0.436659  2.064930
H     3.533430  0.238525  1.604401
H     3.697640 -1.511089  1.929113
N     0.492976  2.170127 -0.361280
C    -0.476662  3.234742  0.042097
H    -1.465758  2.769452  0.197635
C    -0.553318  4.246581 -1.129928
C     0.578700  5.290951 -1.039043
C    -1.915589  4.956601 -1.172027
C    -0.340292  3.291226 -2.330554
H    -0.038704  3.815698 -3.255335
H    -1.283758  2.751253 -2.546400
C     0.732304  2.286352 -1.868894
H     1.732201  2.741340 -2.010613
C     0.697806  0.881683 -2.464336
H    -0.274475  0.662050 -2.942516
H     1.463158  0.740568 -3.251942
H    -0.166941  3.696592  0.997658
H     1.389889  2.301925  0.122809
H     0.578393  5.953000 -1.924809
H     0.457022  5.928400 -0.143210
H     1.577775  4.820192 -0.978097
H    -2.080328  5.563710 -0.261592
H    -1.981461  5.638191 -2.040271
H    -2.743751  4.227790 -1.247600
   el energy= -1476.33033663
        zpe= -1475.698557
   th energy= -1475.658385
  th enthalpy= -1475.657441
  free energy= -1475.772822
```

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```
Zr    0.033384 -0.419548 -0.004120
C    -1.172415 -1.207971 -1.950217
C    -2.349158 -0.353784  0.289188
C    -0.621149  0.381420  2.191088
N    -0.006948  0.693653  3.370977
N    -1.969236  0.414117  2.500431
C    -2.172345  0.730363  3.834742
C    -0.928373  0.905294  4.388856
N    -0.871717 -1.806461 -3.141205
N    -2.553056 -1.245458 -1.898567
C    -3.082782 -1.854016 -3.025830
C    -2.017232 -2.211282 -3.814722
C    -3.227625 -0.767843 -0.715858
C    -4.626676 -0.756049 -0.578147
C    -5.159608 -0.314399  0.647189
C    -2.935670  0.055253  1.489859
C    -4.324533  0.092015  1.704251
H    -0.630683  1.150380  5.407275
H    -3.160618  0.794943  4.284767
H    -1.982992 -2.719346 -4.777235
H    -4.150665 -1.997661 -3.175497
H    -5.305215 -1.079849 -1.377414
H    -6.246694 -0.295255  0.784056
H    -4.771985  0.415799  2.652497
C     0.496696 -2.034577 -3.596879
C     1.443546  0.693657  3.542796
H     0.631313 -1.628947 -4.615105
H     1.175006 -1.523662 -2.893198
H     0.722619 -3.115127 -3.597020
H     1.768693  1.627859  4.033184
H     1.752680 -0.172237  4.153874
H     1.903544  0.606121  2.544819
I     0.235544 -3.125511  1.006872
N    -0.378842  2.020059 -0.575689
C    -1.554354  2.833032 -0.171617
C    -1.244928  4.310400 -0.565825
C    -0.161675  4.153332 -1.689266
C     0.051819  2.625233 -1.882059
C    -0.749258  2.068181 -3.063339
H    -1.828418  2.293001 -2.978134
H    -0.632306  0.974229 -3.133620
H     1.115176  2.363548 -2.020368
H    -0.474400  4.638079 -2.632275
H     0.783789  4.637314 -1.379600
C    -2.510314  5.027497 -1.070422
C    -0.663603  5.074228  0.642001
H    -2.440279  2.448100 -0.706383
H    -1.742285  2.701920  0.907335
H    -0.327954  6.086945  0.350312
H    -1.414938  5.185497  1.446473
H     0.212525  4.548568  1.070140
H    -2.293018  6.076161 -1.346557
H    -2.929706  4.523957 -1.961342
H    -3.297374  5.043942 -0.292721
H    -0.388669  2.524070 -4.003252
N     1.837936  0.098049 -0.412721
C     3.102671  0.678373 -0.752574
H     3.133810  0.984696 -1.830083
C     4.333034 -0.262272 -0.512713
C     4.164741 -1.544972 -1.348725
C     4.423114 -0.632486  0.978103
C     5.641818  0.452951 -0.979770
H     5.553903  0.635348 -2.072861
H     6.486112 -0.253204 -0.847120
C     5.976563  1.752570 -0.295206
H     5.310581  2.603765 -0.503558
C     7.021622  1.945661  0.529972
H     7.722931  1.133874  0.766065
H     7.221720  2.917754  0.997128
H     3.282705  1.614556 -0.168918
H     0.384514  2.237399  0.082521
H     5.028171 -2.224088 -1.212973
H     3.249259 -2.081924 -1.044723
H     4.089272 -1.309187 -2.429294
H     5.263105 -1.328951  1.165140
H     4.589764  0.264201  1.605006
H     3.487327 -1.125133  1.297414
   el energy= -1476.38121338
        zpe= -1475.744896
   th energy= -1475.703707
  th enthalpy= -1475.702762
  free energy= -1475.824240
```

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```
Zr    0.658995  0.124113  0.836242
C    -0.767340  2.116410  1.019795
C     0.808165  1.572637 -1.055807
C     2.567258 -0.413045 -0.616065
N     3.623178 -1.281442 -0.670436
N     2.691091  0.316915 -1.783911
C     3.774740 -0.109107 -2.544474
C     4.363232 -1.121811 -1.837682
N    -1.725351  2.595885  1.871289
N    -0.855821  2.951895 -0.072336
C    -1.829955  3.925875  0.102232
C    -2.383550  3.700421  1.336869
C     0.036025  2.735733 -1.183343
C     0.141050  3.645695 -2.248389
C     1.104288  3.382520 -3.237033
C     1.800789  1.407697 -2.034604
C     1.959261  2.272894 -3.132897
H     5.231527 -1.738614 -2.063788
H     4.034480  0.325841 -3.506461
H    -3.172561  4.226610  1.872217
H    -2.056810  4.680586 -0.647710
H    -0.479332  4.547455 -2.319215
H     1.209662  4.067598 -4.085719
H     2.733161  2.116234 -3.893752
C    -2.000040  2.021648  3.186360
C     3.918463 -2.301745  0.329044
H    -3.085702  1.861362  3.306967
H    -1.462959  1.060490  3.241612
H    -1.640844  2.694925  3.984615
H     4.049461 -3.278135 -0.167297
H     4.834512 -2.039323  0.888733
H     3.062373 -2.382598  1.014526
I     0.357128 -2.861966 -0.457092
N     0.124568 -0.756480  2.774648
C     0.589631 -0.278435  4.074185
C    -0.784249 -1.874000  3.016110
H    -1.120402 -2.336886  2.072477
H    -0.290156 -2.681055  3.605378
H    -1.684879 -1.563648  3.603533
H     1.216390  0.620812  3.952690
H    -0.255139 -0.023024  4.763376
H     1.183808 -1.058425  4.605873
N     2.102878  1.357310  1.776051
C     3.299932  0.692394  2.276604
C     2.267739  2.795922  1.856016
H     3.104433  3.151147  1.209549
H     1.351870  3.316243  1.532759
H     2.506058  3.123030  2.895842
H     4.189925  0.881816  1.631873
H     3.554201  1.040637  3.304768
H     3.147828 -0.401860  2.338216
N    -1.721992 -0.313731  0.085864
C    -2.168739 -0.085968 -1.312197
C    -3.678474 -0.289226 -1.623945
C    -4.100757 -1.797367 -1.678306
C    -3.858105 -2.628840 -0.442273
C    -4.791012 -2.927452  0.481902
H    -4.557447 -3.547999  1.355542
H    -5.828617 -2.576879  0.390726
H    -2.842976 -3.039946 -0.321638
H    -3.567198 -2.262989 -2.531292
H    -5.180960 -1.822946 -1.926633
C    -3.915781  0.299494 -3.033206
C    -4.556727  0.469257 -0.608416
H    -1.550038 -0.746945 -1.946897
H    -1.896186  0.951159 -1.577239
H    -2.359461  0.165362  0.731724
H    -1.794533 -1.319536  0.292701
H    -5.609569  0.492632 -0.947103
H    -4.552058 -0.016375  0.385171
H    -4.221924  1.518673 -0.490476
H    -4.958748  0.133243 -3.360976
```

```
H    -3.725228  1.389144 -3.049431
H    -3.248464 -0.170193 -3.780119
    el energy= -1416.28399371
         zpe= -1415.672514
    th energy= -1415.631779
  th enthalpy= -1415.630835
  free energy= -1415.746583
```

TS-25-26

```
Zr   -0.501987 -0.313244  0.749506
C     1.277883 -2.086888  0.656684
C    -0.616348 -1.649981 -1.175114
C    -2.775613 -0.390354 -0.220512
N    -4.045648  0.079625  0.004233
N    -2.858385 -0.933841 -1.485636
C    -4.118451 -0.766606 -2.043939
C    -4.867877 -0.122814 -1.098574
N     2.379216 -2.526619  1.349554
N     1.399446 -2.732392 -0.555040
C     2.530243 -3.533025 -0.616691
C     3.154654 -3.401794  0.593444
C     0.390755 -2.549110 -1.552048
C     0.385147 -3.283647 -2.750285
C    -0.716918 -3.139352 -3.606766
C    -1.739287 -1.638906 -2.019371
C    -1.808353 -2.337982 -3.236627
H    -5.907569  0.199402 -1.111069
H    -4.380688 -1.116755 -3.038752
H     4.066631 -3.853830  0.979914
H     2.797642 -4.120541 -1.491259
H     1.195808 -3.970302 -3.019970
H    -0.744542 -3.689791 -4.553653
H    -2.690225 -2.289732 -3.885430
C     2.752830 -2.108679  2.696809
C    -4.468816  0.842465  1.173507
H     3.657556 -2.660051  2.998162
H     2.960821 -1.027237  2.717060
H     1.940587 -2.336004  3.405316
H    -5.454269  1.288373  0.965996
H    -4.546153  0.193522  2.060794
H    -3.740393  1.654347  1.349394
I    -1.467502  2.475565 -0.343891
N     0.824052  1.101235  2.276724
C     0.993739  0.615260  3.646896
C     0.885098  2.569962  2.319011
H     0.935812  2.989596  1.300577
H    -0.008174  3.006759  2.814122
H     1.784848  2.911497  2.881128
H     0.836679 -0.473504  3.700363
H     1.998828  0.862312  4.064242
H     0.250466  1.085046  4.329901
N    -1.131797 -1.502467  2.352161
C    -2.051449 -0.713969  3.156855
C    -0.916205 -2.815232  2.917683
H    -1.868967 -3.387436  2.995794
H    -0.226050 -3.394907  2.282245
H    -0.496342 -2.762595  3.952437
H    -3.067001 -1.167965  3.214324
H    -1.677418 -0.575438  4.197461
H    -2.169732  0.311086  2.735799
N     1.521319  0.596042 -0.087069
C     2.686486  0.136182 -0.842365
C     3.851683  1.153591 -1.058833
C     3.532921  2.226657 -2.154974
C     2.341535  3.121205 -1.924205
C     2.405339  4.397980 -1.502690
H     1.498048  4.993473 -1.346013
H     3.366167  4.890400 -1.298286
H     1.347370  2.697370 -2.132489
H     3.401536  1.689925 -3.117760
H     4.437788  2.857933 -2.267950
C     5.061161  0.341060 -1.573805
C     4.228862  1.838267  0.266524
H     2.385806 -0.257062 -1.841516
H     3.128204 -0.722341 -0.301132
H     1.550603  0.820784  1.234386
H     1.162635  1.455758 -0.524365
H     5.131259  2.467055  0.141555
H     3.414043  2.482199  0.637858
H     4.451675  1.085681  1.048039
H     5.916449  1.001899 -1.808901
H     5.399954 -0.391586 -0.816631
H     4.805848 -0.219349 -2.493899
    el energy= -1416.24770917
         zpe= -1415.641343
    th energy= -1415.601146
  th enthalpy= -1415.600202
  free energy= -1415.715307
```

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```
Zr    0.149410 -0.735688  0.271875
C    -0.087341  0.597828  2.306946
C     2.074434  0.506973  0.792519
C     2.204833 -1.639221 -0.706693
N     2.651838 -2.797699 -1.277769
N     3.314879 -0.823715 -0.717649
C     4.409744 -1.448192 -1.294697
C     3.988670 -2.703934 -1.652141
N    -0.971322  0.801025  3.327276
N     0.843329  1.606120  2.484091
C     0.524960  2.422915  3.559674
C    -0.627658  1.911304  4.093568
C     2.015702  1.596988  1.672701
C     3.039339  2.554211  1.785643
C     4.181042  2.406614  0.979289
C     3.257464  0.389552  0.050877
C     4.314223  1.312979  0.106536
H     4.523286 -3.529829 -2.118878
H     5.386188 -0.976471 -1.381304
H    -1.220264  2.231152  4.949129
H     1.133759  3.270296  3.866557
H     2.969799  3.399971  2.479612
H     4.987044  3.145829  1.044963
H     5.221989  1.201122 -0.498283
C    -2.112353 -0.059545  3.631818
C     1.857576 -4.020164 -1.353185
H    -3.051200  0.408038  3.292077
H    -1.986347 -1.005706  3.087649
H    -2.142664 -0.241426  4.720457
H     0.975746 -3.876352 -0.707928
H     1.541528 -4.225371 -2.391012
H     2.456932 -4.869759 -0.983567
I    -3.201776 -0.568678  0.232323
N    -0.813213 -1.789754 -1.998130
C    -0.037917 -1.488435 -3.215611
C    -1.533070 -3.071852 -2.125643
H    -2.258298 -3.152785 -1.300520
H    -2.084684 -3.140407 -3.088108
H    -0.828724 -3.919452 -2.074438
H     0.403372 -0.483473 -3.125454
H     0.780528 -2.220748 -3.334776
H    -0.667012 -1.525636 -4.131232
N    -0.225580 -2.561921  1.317976
C     0.858070 -2.654672  2.288618
C    -1.234595 -3.570909  1.562093
H    -2.099306 -3.417669  0.896284
H    -0.838820 -4.603386  1.407006
H    -1.611007 -3.535784  2.612968
H     0.493269 -2.607614  3.342155
H     1.452967 -3.592371  2.178562
H     1.581442 -1.812506  2.159478
N    -0.372090  0.981786 -0.877543
C     0.332081  1.914136 -1.749130
H     1.410896  1.910919 -1.491275
C    -0.174596  3.389845 -1.702840
C    -0.053565  3.963216 -0.278720
C     0.699463  4.222158 -2.663262
C    -1.675070  3.466731 -2.134553
H    -1.957950  4.541241 -2.146445
H    -2.305814  2.997966 -1.353560
C    -2.006441  2.851962 -3.470608
H    -1.536804  3.310810 -4.354700
C    -2.832219  1.803210 -3.646728
H    -3.047306  1.401655 -4.645047
H    -3.330412  1.313183 -2.798160
H     0.264461  1.602044 -2.819996
H    -1.542246 -1.064298 -1.908252
H    -1.383020  1.156113 -0.929737
H     0.369645  5.278181 -2.689677
H     1.757200  4.210357 -2.338163
H     0.666370  3.831216 -3.697348
H    -0.446205  4.997138 -0.231980
H    -0.616066  3.343378  0.442014
H     1.003891  3.984775  0.046222
    el energy= -1416.28762665
         zpe= -1415.677144
    th energy= -1415.635945
  th enthalpy= -1415.635001
  free energy= -1415.751643
```

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```
Zr    0.522924 -0.511710  0.191272
C    -0.726042  0.531645  2.065736
C     1.158379  1.701265  0.628847
C     2.848254 -0.013401 -0.360512
N     4.007697 -0.686374 -0.637580
N     3.204914  1.311908 -0.490091
C     4.536713  1.456261 -0.853180
C     5.046026  0.186560 -0.949145
N    -1.627166  0.215685  3.047124
N    -0.646100  1.913102  2.147174
C    -1.488045  2.429124  3.123278
C    -2.110802  1.350229  3.691019
C     0.376047  2.575442  1.402423
C     0.619058  3.956501  1.500529
C     1.714286  4.492421  0.803368
C     2.293775  2.285249  0.040115
C     2.584203  3.657495  0.080149
H     6.048363 -0.162667 -1.192487
H     5.016785  2.423450 -0.984762
H    -2.839162  1.292011  4.498409
H    -1.565170  3.490716  3.346276
H    -0.012201  4.614700  2.108837
H     1.914243  5.568360  0.854189
H     3.468128  4.081509 -0.410986
C    -1.987879 -1.139853  3.456444
C     4.152742 -2.134209 -0.521851
H    -2.941516 -1.447994  2.995881
H    -1.205051 -1.828479  3.110613
H    -2.063050 -1.167621  4.557449
H     3.282435 -2.506655  0.042705
H     4.190454 -2.611530 -1.517348
H     5.081844 -2.367461  0.025722
I    -2.102785 -2.346175  0.128521
N     0.732277 -1.642382 -1.910049
C     1.615690 -1.033286 -2.928898
C     0.855539 -3.114912 -1.975933
H     0.110974 -3.569421 -1.301688
H     0.658907 -3.476944 -3.008192
H     1.868819 -3.439422 -1.679974
H     1.527606  0.066813 -2.897409
H     2.670709 -1.304517 -2.756266
H     1.333858 -1.377939 -3.946546
N     1.307027 -1.925526  1.573783
C     2.064367 -1.312591  2.661700
C     1.135616 -3.348032  1.808907
H     0.530374 -3.805733  1.010126
H     2.117907 -3.876332  1.862182
H     0.618742 -3.548063  2.777214
H     1.587396 -1.493202  3.653552
H     3.105462 -1.710455  2.718777
H     2.138749 -0.215040  2.521380
N    -1.085283  0.678652 -1.146208
C    -1.411715  2.111651 -1.176131
H    -1.507290  2.534910 -0.157851
C    -2.740274  2.341279 -1.967164
C    -3.930419  2.446182 -0.993372
C    -2.641638  3.629140 -2.806174
C    -2.881652  1.081640 -2.865810
H    -3.241485  1.353228 -3.878319
H    -3.626174  0.372346 -2.452957
C    -1.546971  0.358240 -2.992073
H    -0.756641  1.009297 -3.407551
C    -1.482618 -0.991931 -3.431845
H    -0.844831 -1.223342 -4.295856
H    -2.367926 -1.629353 -3.315043
H    -0.570044  2.646275 -1.659554
H    -0.295592 -1.447813 -2.371124
H    -1.910061  0.194615 -0.749977
H    -3.596157  3.852170 -3.319634
H    -2.391979  4.501137 -2.170733
H    -1.853820  3.543377 -3.578732
H    -4.891428  2.487373 -1.540543
H    -3.971127  1.569634 -0.318425
H    -3.859786  3.355596 -0.365471
    el energy= -1416.23972029
         zpe= -1415.630440
    th energy= -1415.591590
  th enthalpy= -1415.590646
  free energy= -1415.699451
```

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```
Zr    0.747826 -0.516078  0.145107
C    -0.763952  0.267842  2.058310
C     0.950035  1.783758  0.665429
C     2.940724  0.405361 -0.286908
N     4.146076 -0.066363 -0.719032
N     3.070252  1.772698 -0.384325
C     4.318182  2.140911 -0.869994
C     5.000705  0.969591 -1.083418
N    -1.637241 -0.200124  3.001389
N    -0.877527  1.641945  2.184839
C    -1.808400  2.005657  3.148894
C    -2.290796  0.832988  3.665745
C     0.036178  2.480990  1.473213
C     0.067721  3.876450  1.656696
C     1.091406  4.609892  1.036238
C     2.011216  2.563122  0.169880
C     2.099876  3.957708  0.307755
H     6.012526  0.791699 -1.444862
H     4.623689  3.175045 -1.013305
H    -3.021763  0.648001  4.451544
H    -2.038869  3.037607  3.403011
H    -0.668638  4.396282  2.280276
H     1.128337  5.698055  1.159011
H     2.935753  4.532569 -0.108076
C    -1.829316 -1.606968  3.349604
C     4.476158 -1.487518 -0.773150
H    -2.746546 -2.001228  2.881926
H    -0.977144 -2.182929  2.964721
H    -1.887692 -1.694823  4.448708
H     3.739813 -2.021477 -0.154070
H     4.422719 -1.859889 -1.811071
H     5.493547 -1.646299 -0.376641
I    -1.673593 -2.712552 -0.034296
```

N	1.241826	-1.302348	-1.801308
C	1.731486	-0.458746	-2.881388
C	1.253103	-2.690579	-2.238568
H	0.857882	-3.358345	-1.456388
H	0.625256	-2.845345	-3.147649
H	2.284955	-3.025064	-2.504089
H	1.655941	0.614485	-2.623744
H	2.805226	-0.660127	-3.119192
H	1.166159	-0.619475	-3.827726
N	1.665590	-1.802410	1.519131
C	2.200302	-1.184120	2.725452
C	1.777120	-3.249093	1.569640
H	1.348946	-3.705070	0.662232
H	2.840073	-3.575327	1.665707
H	1.231238	-3.673438	2.444070
H	1.689650	-1.554636	3.644817
H	3.289538	-1.390903	2.845592
H	2.075597	-0.083561	2.689907
N	-1.440754	0.572254	-1.207418
C	-2.354993	1.563094	-0.588611
H	-2.809332	1.132833	0.321510
C	-3.401005	1.964246	-1.657642
C	-4.525573	0.910620	-1.744237
C	-4.009030	3.346631	-1.369526
C	-2.508462	1.965709	-2.926164
H	-2.046057	2.963781	-3.048828
H	-3.086482	1.760367	-3.846454
C	-1.407446	0.889200	-2.683335
H	-0.416777	1.321919	-2.913264
C	-1.606199	-0.375919	-3.526314
H	-1.392168	-0.167331	-4.590542
H	-2.646065	-0.743438	-3.455892
H	-1.772044	2.456252	-0.292172
H	-0.942191	-1.185050	-3.179417
H	-1.880459	-0.358650	-1.105067
H	-4.713922	3.648751	-2.166768
H	-4.571847	3.344600	-0.416434
H	-3.224839	4.124031	-1.299498
H	-5.181969	1.101292	-2.613895
H	-4.130932	-0.117306	-1.838229
H	-5.155527	0.936016	-0.834915

el energy= -1416.31547882
zpe= -1415.702405
th energy= -1415.662479
th enthalpy= -1415.661535
free energy= -1415.774460

Appendix A – excerpted from the dissertation of WDC

Error analysis for KIE experiments

For Complex **2b:** From the linear regression analysis plots of plots of ln(integration value) vs time (Figure S46).

Table S2. Linear regression analysis.

	NH_2
	Slope
Value	-0.0155737
±	0.0002453

Table S3. Linear regression analysis.

	ND_2
	Slope
Value	-0.0033733
±	8.659E-05

k_{obs}^{H}/k_{obs}^{D}= -0.0155737/-0.0033733=4.6

$$\delta\left\{\frac{k^H}{k^D}\right\} \approx \left[\left(\frac{\delta k^H}{k^H}\right)^2 + \left(\frac{\delta k^D}{k^D}\right)^2\right]^{\frac{1}{2}} \times \frac{k^H}{k^D}$$

$$= \left[\left(\frac{0.0002453}{-0.0155737}\right)^2 + \left(\frac{8.659\text{E}-05}{-0.0033733}\right)^2\right]^{\frac{1}{2}} \times \frac{-0.0155737}{-0.0033733} = 0.14$$

k_{obs}^{H}/k_{obs}^{D}=4.6 ± 0.1

For complex **4a**: From the linear regression analysis plots of plots of Integration value vs time (Figure S47).

Table S4. Linear regression analysis.

	NH_2
	Slope
Value	-0.000268
±	1.14E-05

Table S5. Linear regression analysis.

	ND_2
	Slope
Value	-0.00011385
±	3.68305E-06

k_{obs}^{H}/k_{obs}^{D}= -0.00027/-0.00011385=2.4

$$\delta\left\{\frac{k^H}{k^D}\right\} \approx \left[\left(\frac{\delta k^H}{k^H}\right)^2 + \left(\frac{\delta k^D}{k^D}\right)^2\right]^{\frac{1}{2}} \times \frac{k^H}{k^D}$$

$$= \left[\left(\frac{1.14 \times 10^{-5}}{-0.000268}\right)^2 + \left(\frac{3.68 \times 10^{-6}}{-0.00011385}\right)^2\right]^{\frac{1}{2}} \times \frac{-0.000268}{-0.00011385} = 0.13$$

k_{obs}^{H}/k_{obs}^{D}=2.4 ± 0.1

*Error Analysis for Eyring Plots using Complex **2b** as a precatalyst*

Linear regression from ln[Sub **5** (I.V.)] vs time (s)

Table S6. Linear regression analysis.

	108 °C
	Slope
Value	-0.00018
±	9.81E-06

Table S7. Linear regression analysis.

	117 °C
	Slope
Value	-0.00026
±	8.77E-06

Table S8. Linear regression analysis.

	123 °C
	Slope
Value	-0.00032
±	1.78E-05

Table S9. Linear regression analysis.

	128 °C
	Slope
Value	-0.00039
±	1.05E-05

Table S10. Data for Eyring Analysis.

Temperature	k_{obs}	k	Ln(k × h/(κ *k_b*T)	1/T (K^{-1})
108 °C	-0.0001814	0.021097	-33.4626	0.002897291
117 °C	-0.0002628	0.030555	-33.1179	0.002823662
123 °C	-0.0003195	0.037154	-32.9392	0.002776621
128 °C	-0.0003887	0.045192	-32.7571	0.002738601

Table S11. Linear Regression analysis for Ln(k × h/(κ ×k_b×T) vs 1/T (K^{-1})

	Slope	Intercept
Value	-4397.16	-20.7174
±	124.2371	0.349065

Using standard Eyring analysis of a Ln(k × h/(κ ×k_b×T) vs 1/T (K^{-1}) plot:

$$\Delta H^{\ddagger} = -Slope \times R = -4397.16\ K \times \frac{1.99\ \times\ 10^{-3} kcal}{K \times mol} = 8.7 \frac{kcal}{mol}$$

$$\delta\{\Delta H^{\ddagger}\} \approx -\delta\{Slope\} \times R = 124.2371\ K \times \frac{1.99\ \times\ 10^{-3} kcal}{K \times mol} = 0.2 \frac{kcal}{mol}$$

$$\Delta H^{\ddagger} = 8.7\ \pm 0.2\ kcal/mol$$

$$\Delta S^{\ddagger} = -Intercept \times R = -20.7174\ \times \frac{1.99 cal}{K \times mol} = -41 \frac{cal}{K \times mol} = -41\ eu$$

$$\delta\{\Delta S^{\ddagger}\} \approx -\delta\{Intercept\} \times R = 0.349065\ K \times \frac{1.99 cal}{K \times mol} = -1 \frac{cal}{K \times mol} = -1\ eu$$

$$\Delta S^{\ddagger} = -41 \pm 1\ eu$$

*Error Analysis for Eyring Plots using Complex **4a** as a precatalyst*

Linear regression from Sub (I.V.) vs time (s)

Table S12. Linear regression analysis.

	85 °C
	Slope
Value	-0.000126398
±	1.43284E-05

Table S13. Linear regression analysis.

	93 °C
	Slope
Value	-0.000181833
±	4.27795E-06

Table S14. Linear regression analysis.

	104 °C
	Slope
Value	-0.000267844
±	1.14029E-05

Table S15. Linear regression analysis.

	113 °C
	Slope
Value	-0.000394645
±	1.7725E-05

Table S16. Data for Eyring Analysis.

Temperature	k_{obs}	k	$Ln(k \times h/(\kappa \times k_b \times T)$	1/T (K^{-1})
85 °C	-0.000126398	0.014697	-33.7548	0.003105
93 °C	-0.000181833	0.021143	-33.4172	0.003025
104 °C	-0.000267844	0.031145	-33.0614	0.002931
113 °C	-0.000394645	0.045889	-32.6999	0.002856

Table S17. Linear Regression analysis for $Ln(k \times h/(\kappa \times k_b \times T)$ vs 1/T (K^{-1})

	Slope	Intercept
Value	-4176.08326	-20.791
±	131.971212	0.3934

Using standard Eyring analysis of a $Ln(k \times h/(\kappa \times k_b \times T)$ vs 1/T (K^{-1}) plot:

$$\Delta H^{\ddagger} = -Slope \times R = -4176.08326\ K \times \frac{1.99\ \times\ 10^{-3} kcal}{K \times mol} = 8.3 \frac{kcal}{mol}$$

$$\delta\{\Delta H^{\ddagger}\} = -\delta\{Slope\} \times R = 131.971212\ K \times \frac{1.99\ \times\ 10^{-3} kcal}{K \times mol} = 0.3 \frac{kcal}{mol}$$

$$\Delta H^{\ddagger} = 8.3\ \pm 0.3\ kcal/mol$$

$$\Delta S^{\ddagger} = -Intercept \times R = -20.791\ \times \frac{1.99 cal}{K \times mol} = -41 \frac{cal}{K \times mol} = -41\ eu$$

$$\delta\{\Delta S^{\ddagger}\} = -\delta\{Intercept\} \times R = 0.3934\ K \times \frac{1.99 cal}{K \times mol} = -1 \frac{cal}{K \times mol} = -1\ eu$$

$$\Delta S^{\ddagger} = -41 \pm 1\ eu$$

*Derivation of Rate Law for Monoamido complex **2b***

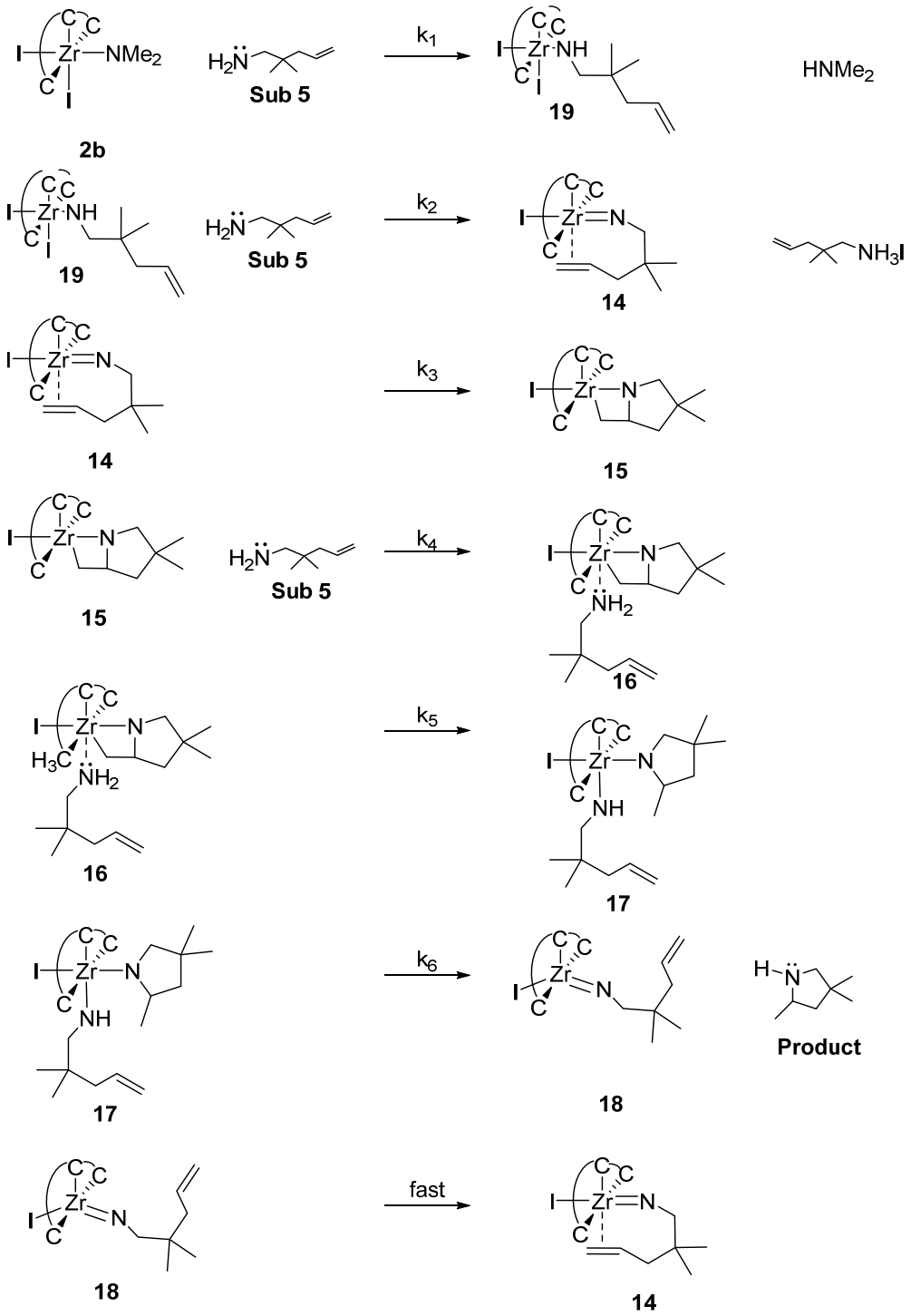


Figure S48. The mechanism of hydroamination/cyclization with complex **2b** written out in individual steps for clarity.

The rate can be written in terms of the formation of product, namely

$$Rate = \frac{\delta[Product]}{dt} = k_6[17] \quad \text{(S1)}$$

Now solving for the concentrations of the intermediates while applying the steady state assumption yields:

$$\frac{\delta[17]}{\delta dt} = -\mathrm{k_6}[17] + \mathrm{k_5}[16] = 0 \ \therefore [17] = \frac{\mathrm{k_5}[16]}{\mathrm{k_6}} \quad \text{(S2)}$$

$$\frac{\delta[16]}{\delta dt} = -\mathrm{k_5}[16] + \mathrm{k_4}[15][\text{Substrate } \mathbf{5}] = 0 \ \therefore \ [16] = \frac{\mathrm{k_4}[15][\text{Substrate } \mathbf{5}]}{\mathrm{k_5}} \quad \text{(S3)}$$

$$\frac{\delta[15]}{\delta dt} = \mathrm{k_3}[14] - \mathrm{k_4}[15][\text{Substrate } \mathbf{5}] = 0 \ \therefore \ [15] = \frac{\mathrm{k_3}[14]}{\mathrm{k_4}[\text{Substrate } \mathbf{5}]} \quad \text{(S4)}$$

$$\frac{\delta[14]}{\delta dt} = \mathrm{k_2}[19][\text{Substrate } \mathbf{5}] - \mathrm{k_3}[14] = 0 \ \therefore \ [14] = \frac{\mathrm{k_2}[19][\text{Substrate } \mathbf{5}]}{\mathrm{k_3}} \quad \text{(S5)}$$

$$\frac{\delta[19]}{\delta dt} = \mathrm{k_1}[2\mathrm{b}][\text{Substrate } \mathbf{5}] - \mathrm{k_2}[19][\text{Substrate } \mathbf{5}] = 0 \ \therefore \ [9] = \frac{\mathrm{k_1}[2\mathrm{b}]}{\mathrm{k_2}} \quad \text{(S6)}$$

The concentrations of the intermediates are defined in terms of the initial precatalyst concentration,

$$[2\mathrm{b}]_0 = [2\mathrm{b}] + [19] + [14] + [15] + [16] + [17] \quad \text{(S7)}$$

Solving these equations simultaneously (with the aid of Mathematica 9.0.1) gives:

$$Rate = \frac{k_6([2b]_0\, k_1\, k_2\, k_3\, k_4\, k_5\, k_6\, [Substrate\ 5])}{k_2k_3k_4k_5k_6 + k_1\,(k_3\, k_4\, k_5\, k_6 + k_2(k_3k_5k_6 + k_3k_4k_5\, [Substrate\ 5] + k_3k_4k_6[Substrate\ 6] + k_4k_5k_6[Substrate\ 5]))} \quad \text{(S8)}$$

Fully expanding the Rate equation gives:

$$Rate = \frac{[3\mathrm{b}]_0\mathrm{k_1k_2k_3k_4k_5k_6[Sub]}}{\mathrm{k_1k_2k_3k_5k_6 + k_1k_3k_4k_5k_6 + k_2k_3k_4k_5k_6 + k_1k_2k_3k_4k_5[Sub] + k_1k_2k_3k_4k_6[Sub] + k_1k_2k_4k_5k_6[Sub]}} \quad \text{(S9)}$$

Assuming that

$$k_1k_2k_3k_5k_6 + k_1k_3k_4k_5k_6 + k_2k_3k_4k_5k_6 \gg k_1k_2k_3k_4k_5[\mathrm{Sub}] + k_1k_2k_3k_4k_6[\mathrm{Sub}] + k_1k_2k_4k_5k_6[\mathrm{Sub}] \quad \text{(S10)}$$

The rate law simplifies to:

$$Rate \approx \frac{k_1k_2k_4[2b]_0[\mathrm{Sub}]}{k_2k_4+k_1(k_2+k_4)} = k'[2b]_0[Sub] \quad \text{(S11)}$$

*Derivation of Rate Law for Diamido complex **4a***

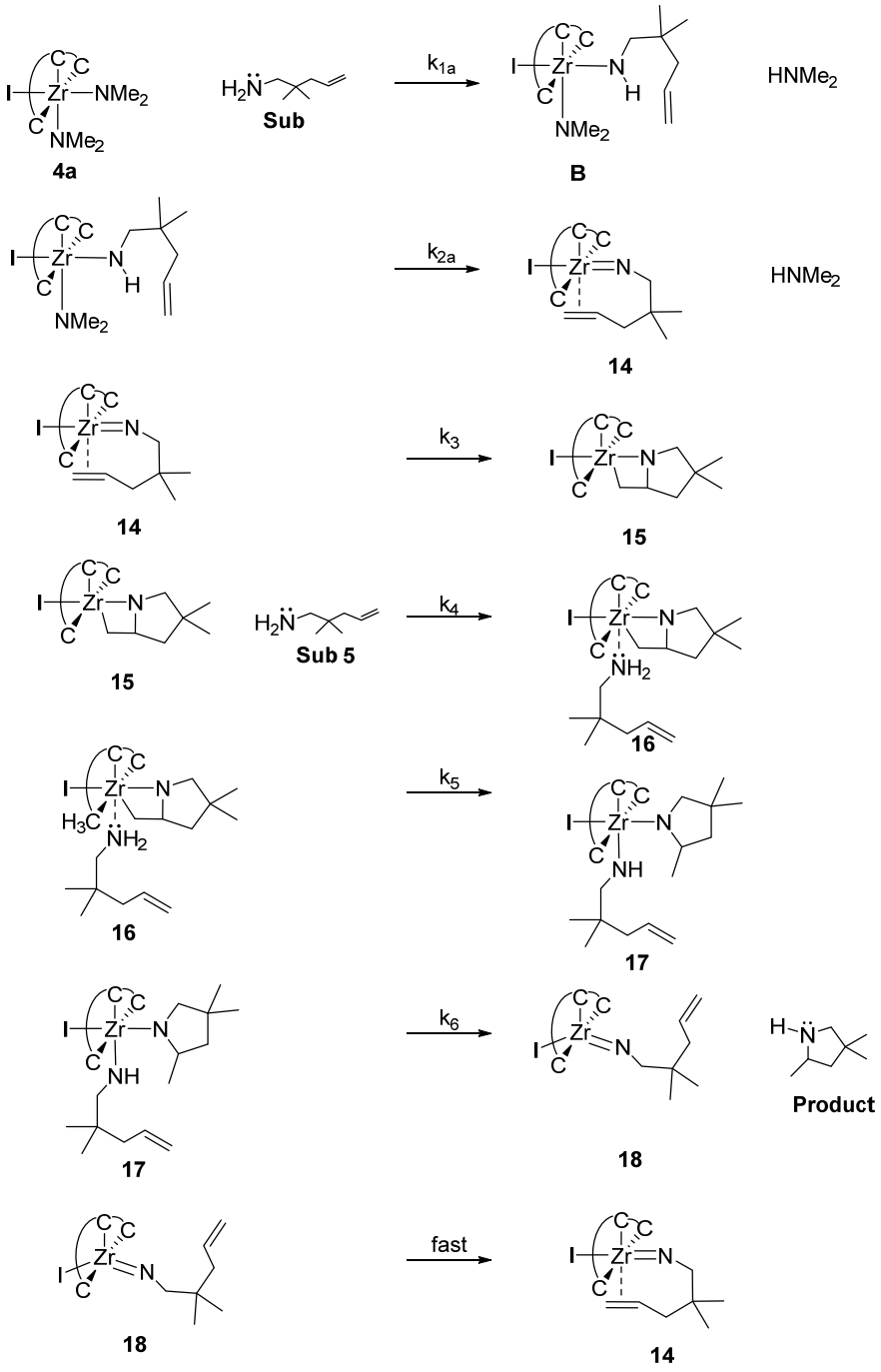


Figure S49. The mechanism of hydroamination/cyclization with complex **4a** written out in individual steps for clarity.

The rate can be written in terms of the formation of product, namely

$$\text{Rate} = \frac{\delta[\text{Product}]}{\text{dt}} = \text{k}_6[17] \quad \text{(S1)}$$

Now solving for the concentrations of the intermediates while applying the steady state assumption yields:

$$\frac{\delta[17]}{\delta\text{dt}} = \text{-k}_6[17] + \text{k}_5[16] = 0 \ \therefore [17] = \frac{\text{k}_5[16]}{\text{k}_6} \quad \text{(S2)}$$

$$\frac{\delta[16]}{\delta\text{dt}} = \text{-k}_5[16] + \text{k}_4[15][\text{Substrate 5}] = 0 \therefore \ [16] = \frac{\text{k}_4[15][\text{Substrate 5}]}{\text{k}_5} \quad \text{(S3)}$$

$$\frac{\delta[15]}{\delta\text{dt}} = \text{k}_3[14]\text{-k}_4[15][\text{Substrate 5}] = 0 \therefore \ [15] = \frac{\text{k}_3[14]}{\text{k}_4[\text{Substrate 5}]} \quad \text{(S4)}$$

$$\frac{\delta[17]}{\delta dt} = \text{k}_2[\text{B}][\text{Substrate } \mathbf{5}] - \text{k}_3[17] = 0 \therefore \ [17] = \frac{\text{k}_{2\text{a}}[\text{B}]}{\text{k}_3} \quad \text{(S12)}$$

$$\frac{\delta[B]}{\delta dt} = \text{k}_{1\text{a}}[2\text{b}][\text{Substrate } \mathbf{5}] - \text{k}_{2\text{a}}[\text{B}] = 0 \therefore \ [\text{B}] = \frac{\text{k}_{1\text{a}}[2\text{b}][Substrate\ 5]}{\text{k}_{2\text{a}}} \quad \text{(S13)}$$

The concentrations of the intermediates are defined in terms of the initial precatalyst concentration,

$$[\mathbf{4a}]_0 = [\mathbf{4a}] + [\text{B}] + [17] + [18] + [19] + \text{gggg} \quad \text{(S14)}$$

Solving these equations simultaneously (with the aid of Mathematica 9.0.1) gives:

$$Rate = \frac{\delta[Product]}{dt} = \frac{([4\text{a}]_0\text{k}_{1\text{a}}\text{k}_{2\text{a}}\text{k}_3\text{k}_4\text{k}_5\text{k}_6[\text{Sub}])}{(\text{k}_{2\text{a}}\text{k}_3\text{k}_4\text{k}_5\text{k}_6 + \text{k}_{1\text{a}}\left(\text{k}_3\text{k}_4\text{k}_5\text{k}_{6[\text{Sub}]} + \text{k}_{2\text{a}}(\text{k}_3\text{k}_5\text{k}_6 + \text{k}_3\text{k}_4\text{k}_5[\text{Sub}] + \text{k}_3\text{k}_4\text{k}_6[\text{Sub}] + \text{k}_4\text{k}_5\text{k}_6[\text{Sub}])\right))} \quad \text{(S15)}$$

Fully expanding the Rate equation gives:

$$Rate = \frac{[4\text{a}]_0\text{k}_{1\text{a}}\text{k}_2\text{k}_3\text{k}_4\text{k}_5\text{k}_6[\text{Sub}]}{(\text{k}_{1\text{a}}\text{k}_{2\text{a}}\text{k}_3\text{k}_5\text{k}_6 + \text{k}_{2\text{a}}\text{k}_3\text{k}_4\text{k}_5\text{k}_6 + \text{k}_{1\text{a}}\text{k}_{2\text{a}}\text{k}_3\text{k}_4\text{k}_5[\text{Sub}] + \text{k}_{1\text{a}}\text{k}_{2\text{a}}\text{k}_3\text{k}_4\text{k}_6[\text{Sub}] + \text{k}_{1\text{a}}\text{k}_{2\text{a}}\text{k}_4\text{k}_5\text{k}_6[\text{Sub}] + \text{k}_{1\text{a}}\text{k}_3\text{k}_4\text{k}_5\text{k}_6[\text{Sub}])} \quad \text{(S16)}$$

Assuming that

$$k_{1a}k_{2a}k_3k_4k_5[\mathrm{Sub}] + k_{1a}k_{2a}k_3k_4k_6[\mathrm{Sub}] + k_{1a}k_{2a}k_4k_5k_6[\mathrm{Sub}] + k_{1a}k_3k_4k_5k_6[\mathrm{Sub}] \gg$$

$$k_{1a}k_{2a}k_3k_5k_6 + k_{2a}k_3k_4k_5k_6 \qquad \text{(S17)}$$

The rate law simplifies to:

$$Rate \approx \frac{[4a]_0 k_{2a}k_3k_5k_6}{k_3k_5k_6 + k_{2a}(k_5k_6 + k_3(k_5 + k_6))} = k''[5a]_0 \qquad \text{(S18)}$$

Appendix B- excerpted from the dissertation of Katie Leigh

Energetics of the [Zr]I, [Zr]I_2, and [Zr]I_3 species

Beginning with the diiodo species, [Zr]I_2, both the [Zr]I_3 and [Zr]I species can be produced (Figure B1) from hypothetical reactions. From [Zr]I_2, the addition of HI and loss of $HNMe_2$ produces [Zr]I_3, a process which is favored by 24.9 kcal mol^{-1}. Also from [Zr]I_2, the addition of $HNMe_2$ and loss of HI produces [Zr]I, a process disfavored by 25.3 kcal mol^{-1}. The general trend of stability increasing with increased iodide substitution is consistent in the gas-phase and in toluene at both 298 K and 433 K.

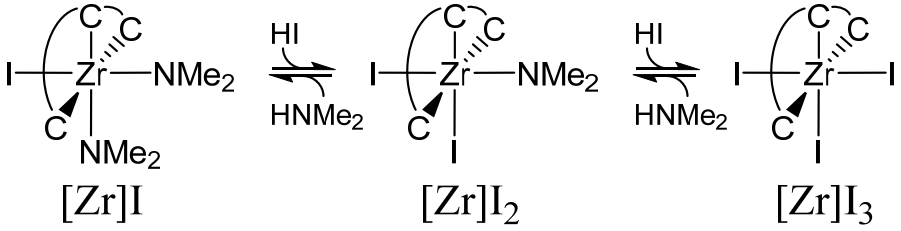


Figure B1. Hypothetical reactions to convert between [Zr]I, [Zr]I_2, and [Zr]I_3.

Computed [2+2] cycloaddition mechanism (the long version)

The proposed cycloaddition mechanism begins from the [Zr]I catalytic complex. Substrate enters the system and binds to Zr in a position *cis* to the phenyl carbon of the pincer through the amine lone pair. One of the substrate amine protons is transferred to an amide ligand, followed by the exit of the newly-formed dimethyl amine. The remaining substrate amine proton is then transferred to the remaining amide ligand, followed by the exit of this dimethyl amine. What remains is substrate bound to the Zr of the catalytic complex through an imido nitrogen.

The imido complex has a highly distorted trigonal bipyramidal geometry around the Zr ion with the phenyl carbon, iodide, and imide in the equatorial positions (**1**). The remaining pincer

carbons are in axial positions, creating a C–Zr–C angle of 135.5°, far from the idealized 180°. This rough trigonal bipyramidal geometry is retained as the substrate reorients prior to cyclization. Rotation along the Zr–N–CH_2 axis (**TS-1-2**) is followed by rotation of the tertiary C–CH_2 bond (**TS-2-3**), and rotation of the alkene (**TS-3-4**). As a result of these rotations, the π electrons of the alkene are positioned below the Zr ion (**4**), and can coordinate in the position *trans* to the phenyl carbon of the pincer (**TS-4-5**). The catalyst now has a pseudo-octahedral geometry around Zr, with the imido nitrogen and coordinated alkene positioned *cis* to one another (**5**).

Cyclization occurs by a [2+2] cycloaddition mechanism (**TS-5-6** and Figure B2). The two π electrons of the Zr–N bond attack the secondary carbon of the alkene as the two π electrons of the alkene attack the Zr ion. With a free energy of activation of 28.5 kcal mol^{-1}, cyclization is the turnover-limiting step for the proposed mechanism. The result is a bicyclic structure: a four-membered ring consisting of the alkene carbons, Zr, and N bound to a five-membered nitrogen-containing heterocycle (**6**). An alternative cyclization transition state with the alkene bound *cis* and the imide bound *trans* to the phenyl carbon has also been calculated (**TS2-5-6**), but it has a higher energy of activation at 30.5 kcal mol^{-1} (see Figure B3).

After cyclization, the bicyclic structure undergoes a rotation of the Zr–N and Zr–C bonds (**TS-6-7**) prior to the entrance of a second substrate to the system (**8**). The amine of this substrate coordinates to the Zr *trans* to the phenyl carbon (**TS-8-9**). One amine proton is transferred to the methylene carbon of the four-membered ring (**TS-9-10**), a process with a free energy of activation of 25.2 kcal mol^{-1}. The resulting complex (**10**) contains the amide substrate bound *trans* to the phenyl carbon and the amide product bound *cis* which is very low in energy at –8.0 kcal mol^{-1}. After a reorientation of the ring (**TS-10-11**), the remaining substrate proton is then transferred to the nitrogen of the ring (**TS-11-12**) with a free energy of activation of 20.3 kcal mol^{-1}. The cyclized

product is then released, leaving a distorted trigonal bipyramidal catalyst complex (**13**). After rotation along the Zr–N–CH_2 axis (**TS-13-1**), complex **1** is reformed, which can then begin the catalytic cycle again. Alternatively, protonation of the bicyclic structure has been computed in the reverse order (Figure B4). Initial protonation of the amide (**14**) is comparable with a free energy of activation of 27.5 kcal mol^{-1} (**TS-14-15**) to produce **15**. However, subsequent protonation of the methylene unit (**16**) requires more energy, with a free energy of activation of 35.8 kcal mol^{-1} (**TS-16-17**) to produce **17**.

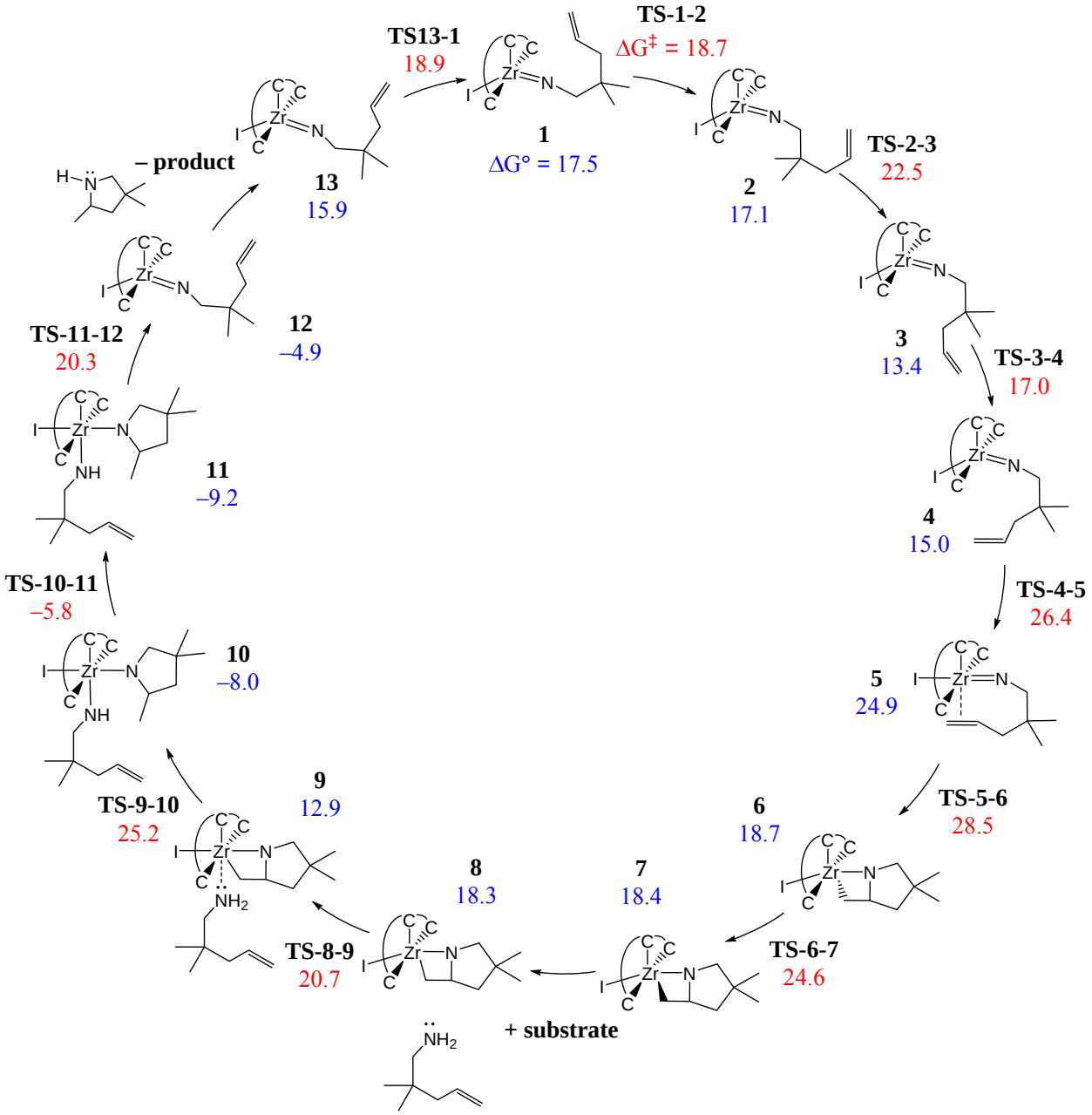


Figure B2. Proposed mechanism for [2+2] cycloaddition. Gas-phase free energies (kcal mol^{-1}) are relative to $[Zr]I_2$ and two infinitely separated substrate molecules.

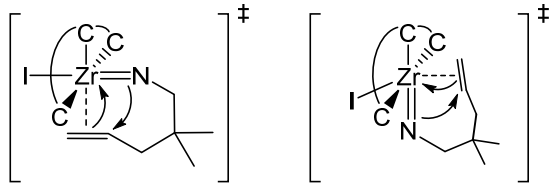


Figure B3. [2+2] cycloaddition transition states. Left, imido *cis*/alkene *trans* to phenyl carbon. Right, alkene *cis*/imido *trans* to phenyl carbon. Gas-phase free energies (kcal mol^{-1}) are relative to $[Zr]I_2$ and two infinitely separated substrate molecules.

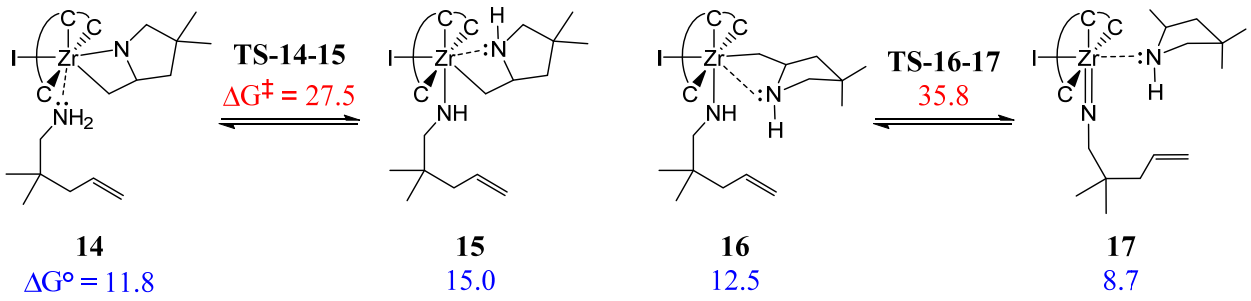


Figure B4. Alternate protonations of bicyclic structure. Gas-phase free energies (kcal mol^{-1}) are relative to $[Zr]I_2$ and two infinitely separated substrate molecules.

Computed [2+2] cycloaddition mechanism (the short version)

The amine of the substrate binds to the Zr of the [Zr]I catalytic complex system and transfers its two protons to the bound amides. Two equivalents of dimethyl amine are produced as well as an imido-substrate complex with a distorted trigonal bipyramidal geometry (not shown). After a series of rotations, the alkene portion of the substrate coordinates to Zr *trans* to the phenyl

carbon of the pincer (**5**, Figure B5). Cyclization then occurs through a [2+2] cycloaddition mechanism, where two π electrons of the Zr–N bond attack the secondary carbon of the alkene as the two π electrons of the alkene attack the Zr ion (**TS-5-6**). The resulting bicyclic structure consists of a four-membered ring (the alkene carbons, Zr, and N) bound to a five-membered nitrogen-containing heterocycle (**6**). A second substrate is introduced into the system, with the amine binding to Zr *trans* to the phenyl carbon of the pincer (**9**). The two substrate amine protons serve to first protonate the methylene carbon bound to Zr (**TS-9-10**), followed by protonation of the nitrogen (**TS-11-12**). The product is released, and the resulting imido substrate can then reenter the cycle.

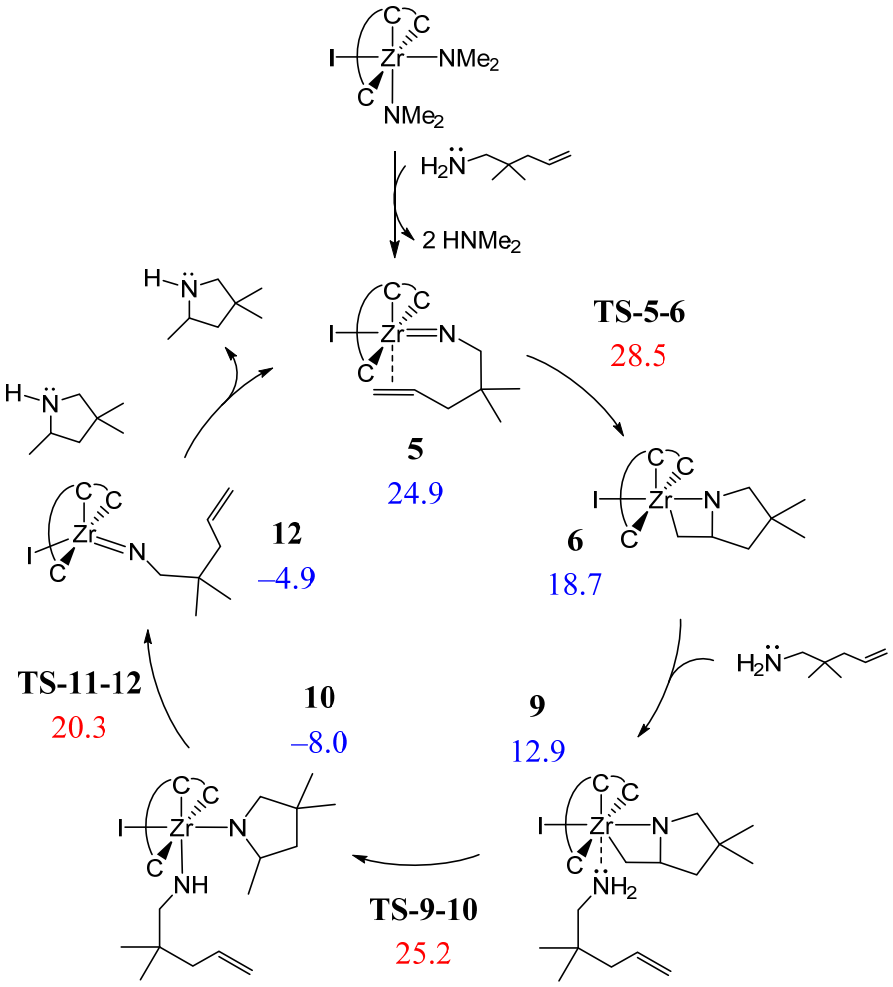
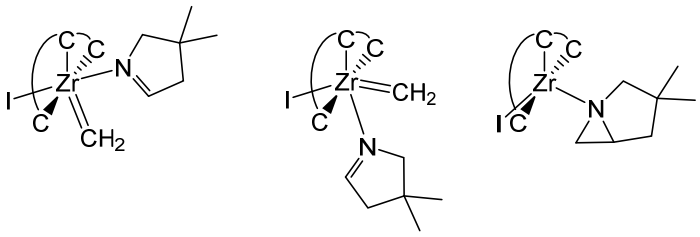


Figure B5. Simplified proposed mechanism for [2+2] cycloaddition. Gas-phase free energies (kcal mol^{-1}) are relative to $[Zr]I_2$ and two infinitely separated substrate molecules.

Formation of alternative high-energy compounds

In addition to the bicyclic structure formed by [2+2] cycloaddition, formation of alternative structures were also investigated. Methylidene and an unsaturated N-substituted cyclopentane can be formed when the π electrons of the Zr–N bond attack the substrate carbon adjacent to the alkene. Transfer of a proton from that carbon to the secondary carbon of the alkene creates the separate methylidene and ring. The process could occur with the imido nitrogen either *cis* or *trans* to the phenyl carbon of the pincer (**18** and **19**, Figure 6XX), but both orientations are quite high in energy (47.6 and 47.2 kcal mol^{-1}, respectively). Alternatively, a bicyclic azacyclopropane structure could be formed (**20**, Figure B6). The π electrons of the Zr–N bond attack the secondary carbon of the alkene as in [2+2] cycloaddition, but instead of the π electrons of the alkene attacking the Zr ion and forming a C–Zr bond, the π electrons attack the nitrogen. The nitrogen-substituted cyclopropane is formed at an angle approximately 120° from the five-membered ring. At 61.0 kcal mol^{-1}, this azacyclopropane is much less stable than the bicyclic structure formed from [2+2] cycloaddition. As the energies of all three compounds are higher than the energy of activation for [2+2] cycloaddition (28.5 kcal mol^{-1}), their formation is not expected.



18 47.6 **19** 47.2 **20** 61.0

Figure 6. Alternative high-energy Zr complexes. Left, *cis*-bound imido; center, *trans*-bound imido; right, azacyclopropane. Gas-phase free energies (kcal mol^{-1}) are relative to $[Zr]I_2$ and two infinitely separated substrate molecules.

Other hydroamination mechanisms

It has been suggested that intramolecular hydroamination may occur by mechanisms other than [2+2] cycloaddition, and these have been investigated computationally. In the insertion-type mechanism (Figure B7), substrate enters the system and, through protonation, creates two equivalents of dimethyl amine and an imido-bound substrate. A second substrate binds *trans* to the phenyl carbon of the pincer (**21**) and protonates the imido substrate using an amine proton (**TS-21-22**), producing two amido-bound substrates *cis* to one another (**22**). Cyclization then occurs through a 1,2-insertion step, where the carbons of the alkene are inserted between the Zr ion and N atom (**TS-22-23**, 29.5 kcal mol^{-1}). The methylene unit between Zr and the five-membered ring is then protonated by the substrate (**TS-23-24**), forming the amine-coordinated product. At 35.3 kcal mol^{-1}, the final protonation is the turnover-limiting step of the 1,2-insertion mechanism.

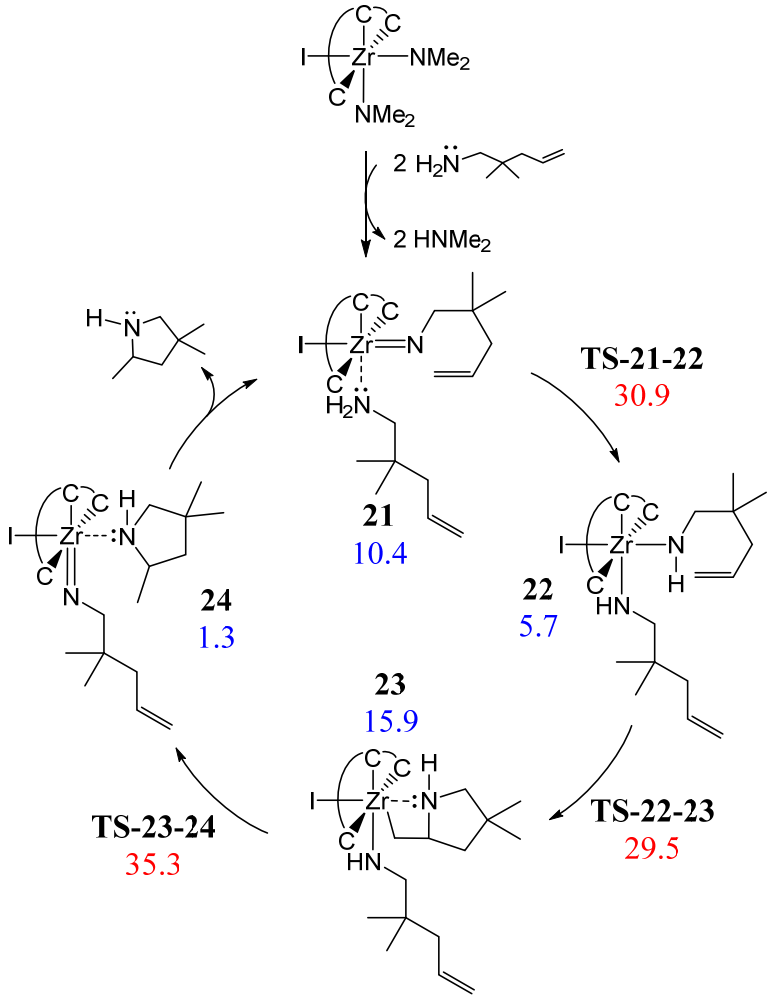


Figure B7. Proposed mechanism for 1,2-insertion. Gas-phase free energies (kcal mol^{-1}) are relative to [Zr]I_2 and two infinitely separated substrate molecules.

In the concerted-type mechanism, cyclization and protonation of the terminal alkene carbon occurs in one step (Figure B8). Substrate enters the system and bind to Zr through the amine in a position *cis* to the phenyl carbon of the pincer (**25**). One amine proton serves to protonate the amide *cis* to the substrate (**TS-25-26**, 49.3 kcal mol^{-1}), and the newly-formed amine remains coordinated to the Zr (**26**). Cyclization then occurs as the substrate nitrogen attacks the

secondary alkene carbon of the substrate, while at the same time the proton of the amine is transferred to the terminal alkene carbon (**TS-26-27**, 61.1 kcal mol^{-1}), forming the desired product. The turnover-limiting step is the concerted cyclization; however, both it and the initial protonation are much higher in energy than the turnover-limiting step of the proposed [2+2] cyclization mechanism (**TS-5-6**, 28.5 kcal mol^{-1}).

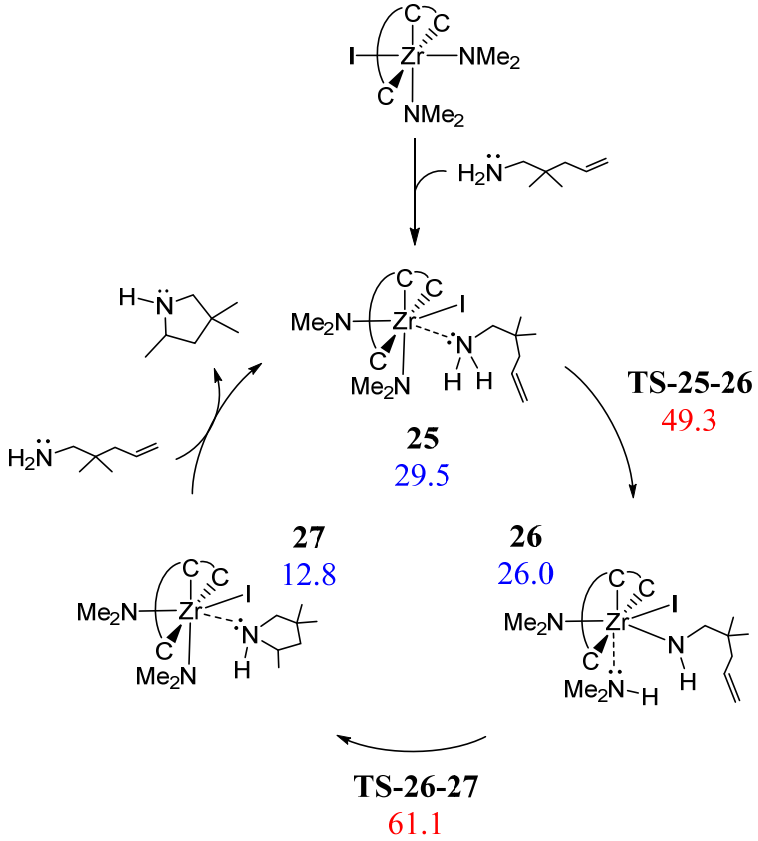


Figure B8. Proposed mechanism for concerted cyclization. Gas-phase free energies (kcal mol^{-1}) are relative to [Zr]I_2 and two infinitely separated substrate molecules.

Effect of halogens on cyclization

Experimental results have shown the Hollis catalyst to be active with bromine and chlorine in the place of the iodine ligand. For the dimethyl-substituted substrate studied here, the iodine version of the catalyst showed 88% conversion, but catalysts with the other halides were much less robust (Br 20%, Cl 6%).[14] The turnover-limiting step of the proposed [2+2] cycloaddition mechanism (**TS-5-6**) was computed with bromine and chlorine versions of the catalyst (Table B1). There is an increase in the computed free energy of activation from iodine (28.5 kcal mol^{-1}) to bromine (32.4 kcal mol^{-1}) to chlorine (33.3 kcal mol^{-1}), a trend that follows experiment. The increasing free energy of activation may explain the decreasing rates of conversion for the catalysts.

Table B1. Computed free energies for [2+2] cyclization of dimethyl-substituted substrate with [Zr]–I, [Zr]–Br, and [Zr]–Cl catalyst species. Gas-phase free energies (kcal mol^{-1}) are relative to $[Zr]X_2$ and two infinitely separated substrate molecules.

species	[Zr]–I	[Zr]–Br	[Zr]–Cl
5	24.9	26.6	27.5
TS-5-6	28.5	32.4	33.3
6	18.7	19.2	19.1

References – Appendix B

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