Reactions of Sodium Diisopropylamide:

Liquid-Phase and Solid-Liquid Phase-Transfer Catalysis

by *N,N,N',N'',N''*-Pentamethyldiethylenetriamine

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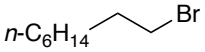
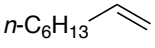
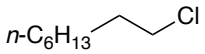
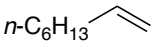
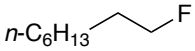
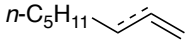
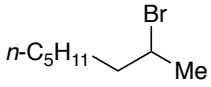
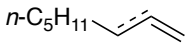
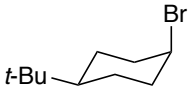
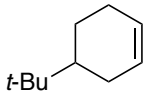
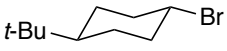
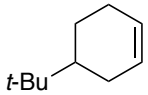
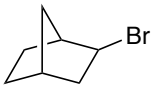
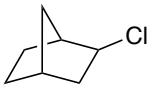
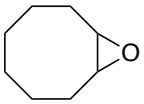
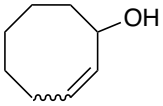
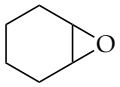
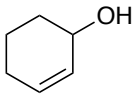
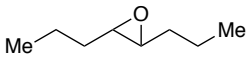
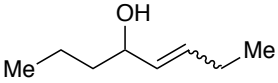
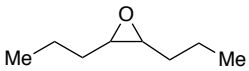
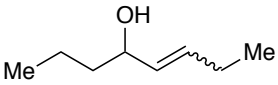
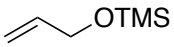
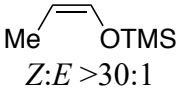
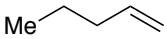
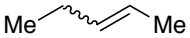
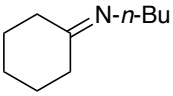
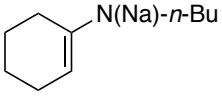
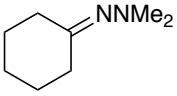
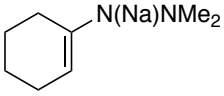
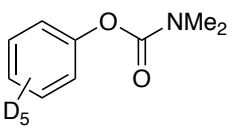
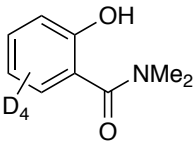
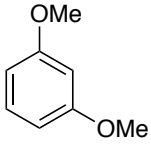
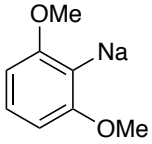
NMR and Kinetic Data:

substrate $\xrightarrow[\text{10 mol \% PMDTA or TMEDA}]{\text{i-Pr}_2\text{NNa (1.2 equiv) neat Me}_2\text{NEt (DMEA)}}$ product (7)

$$k_{rel} = (k_{DMEA} + k_{PMDTA}/10)/k_{DMEA} \quad (8)$$

Table S1. PMDTA-dependent relative rate constants (eq 8 of text) for NaDA-mediated metalations (eq 7 of text).

entry	substrate	product	temperature (°C)	yield	k_{PMDTA}
1	 **9**	 **10**	–30	82%	300
2		 **10**	0	86%	220
3			25	—	>200
4	 **11**	 **10** 9:1	0	90%	340
5	 **12**		–30	95%	150
6	 **13**		25	86%	230
7			–80	95%	350
8			0	93%	330

9	 **15**	 **16** (5:1 Z:E)	25	84%	35
10			25	90%	40
11	 *trans*-**17**	 **18**; *E*/*Z* = 2:1	25	89%	70
12	 *cis*-**17**	 **18**; *E*/*Z* > 30:1	25	91%	20
13	 **19**	 *Z*:*E* >30:1 **20**	0	—	20
14			25	85%	85
15			–78	—	45
16			–78	—	35
17			–78	92%	<1
18			–78	—	15

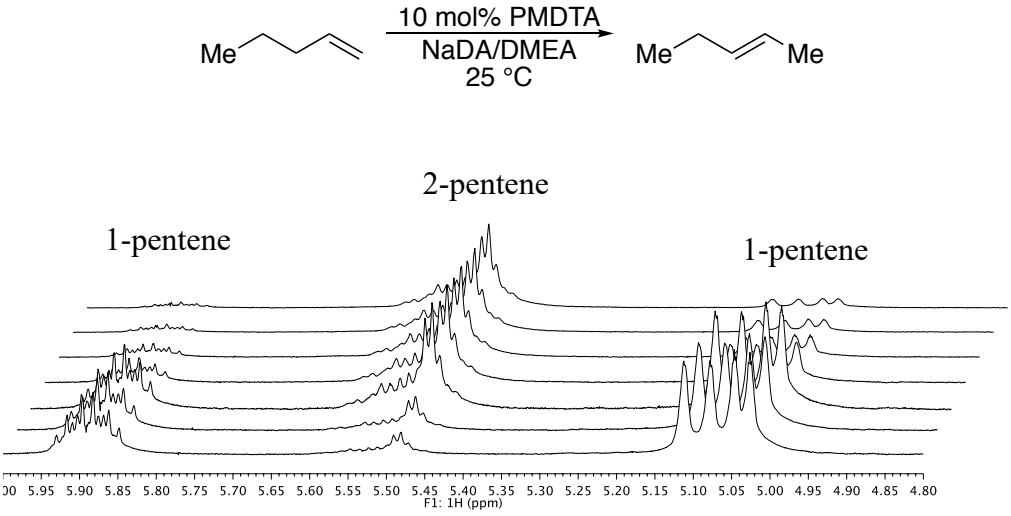


Figure S1. Representative stack plot showing loss of 1-pentene and formation of 2-pentene versus time measured with ^{1}H NMR spectroscopy for the isomerization of 0.050 M 1-pentene with 0.10 M NaDA in neat DMEA in the presence of 10 mol% PMDTA at 25 °C. Each interval represents 180 s.

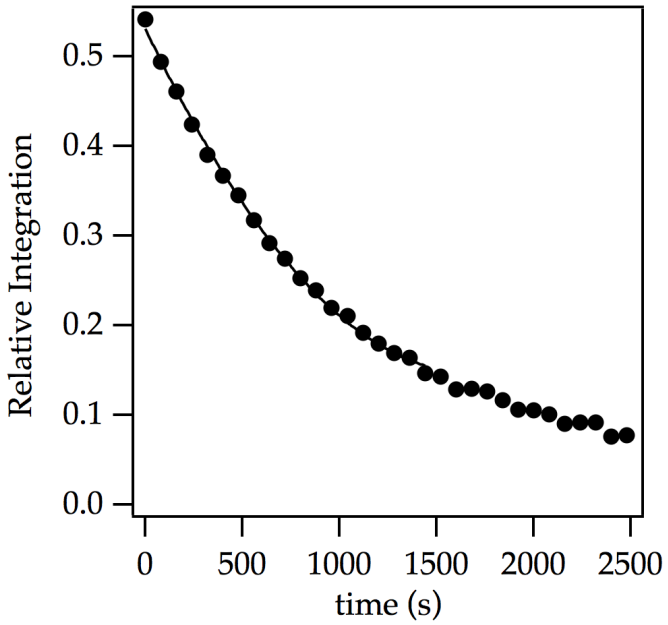


Figure S2. Plot of alkene concentration versus time measured with ^{1}H NMR spectroscopy for the isomerization of 0.050 M 1-pentene with 0.10 M NaDA in neat DMEA in the presence of 10 mol% PMDTA at 25 °C.

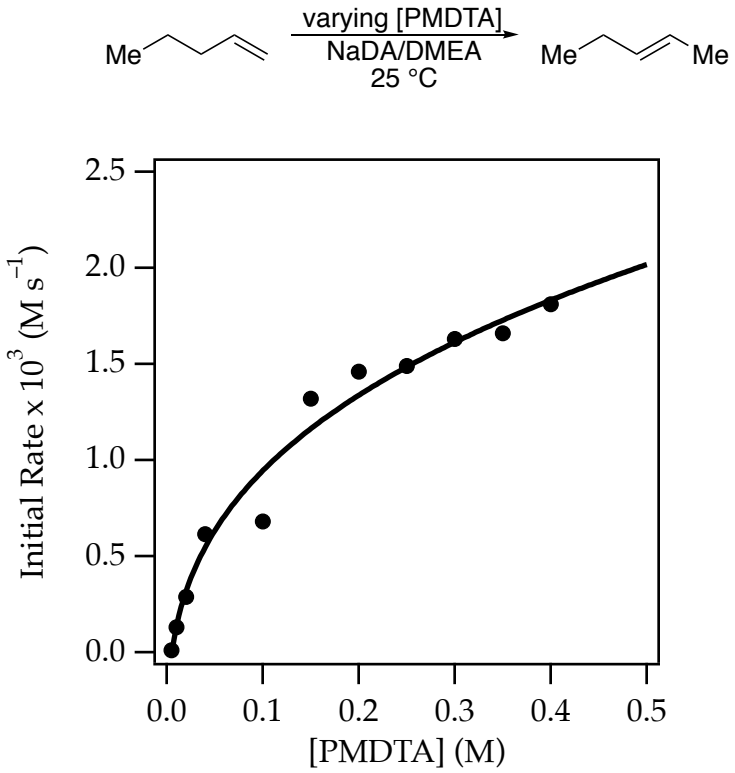


Figure S3. Plot of initial rate versus [PMDTA] in DMEA for the isomerization of 1-pentene (0.050 M) at 25 °C. The curve depicts an unweighted lease-squares fit to $y = ax^n$ ($a = (7.0 \pm 0.2) \times 10^4$, $n = 0.55 \pm 0.06$

[PMDTA] (%)	$y_1 \times 10^3$ (s^{-1})
0.0	0.0101
5	0.0933
10	0.130
20	0.3
40	0.62
100	0.68
150	1.32
200	1.46
250	1.49
300	1.63
350	1.66
400	1.81

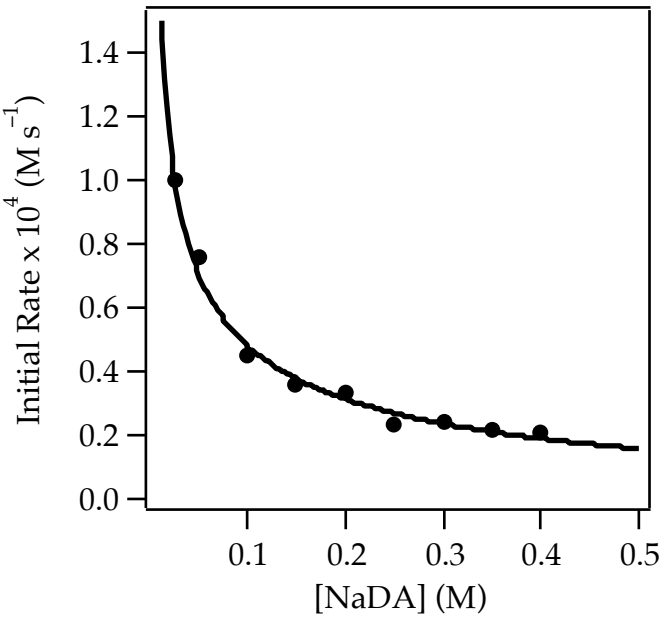


Figure S4. Plot of initial rate versus [NaDA] in DMEA for the isomerization of 1-pentene (0.050 M) in the presence of 10% PMDTA at 25 °C. The curve depicts an unweighted least-squares fit to $y = ax^n + c$ (a = (2.3 ± 1.0) x 10^5, c = (1.9 ± 0.4), n = (–0.48 ± 0.11).

[NaDA] (M)	y_1 x 10^5(s^{-1})
0.025	10.0
0.05	7.64
0.10	4.56
0.15	3.60
0.20	2.38
0.25	2.14
0.30	2.38
0.35	2.15
0.40	2.11

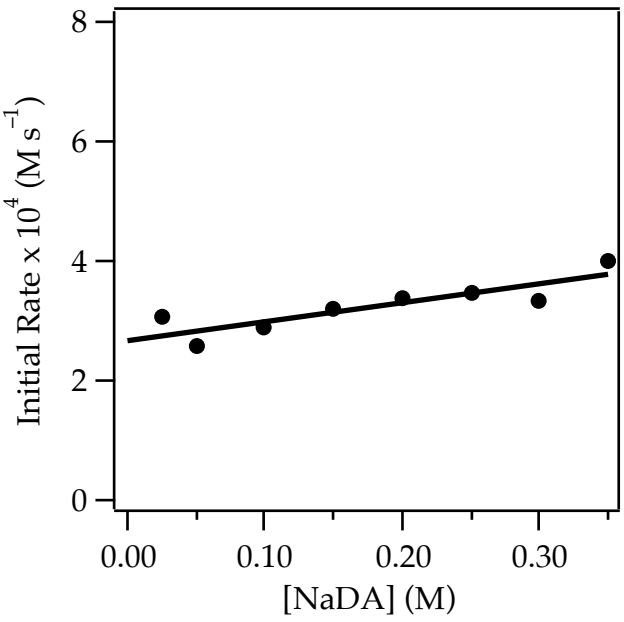


Figure S5. Plot of initial rate versus [NaDA] in neat DMEA for the isomerization of pentene (0.050 M) in the presence of 10 mol% PMDTA relative to NaDA at 25 °C. The curve depicts an unweighted least-squares fit to $y = ax + b$ ($a = (2.7 \pm 0.1) \times 10^4$, $b = (3.0 \pm 0.6) \times 10^4$).

[NaDA] (M)	$y_1 \times 10^4 (s^{-1})$
0.025	3.06
0.05	2.59
0.10	2.90
0.15	3.21
0.20	3.37
0.25	3.47
0.30	3.34
0.35	4.02

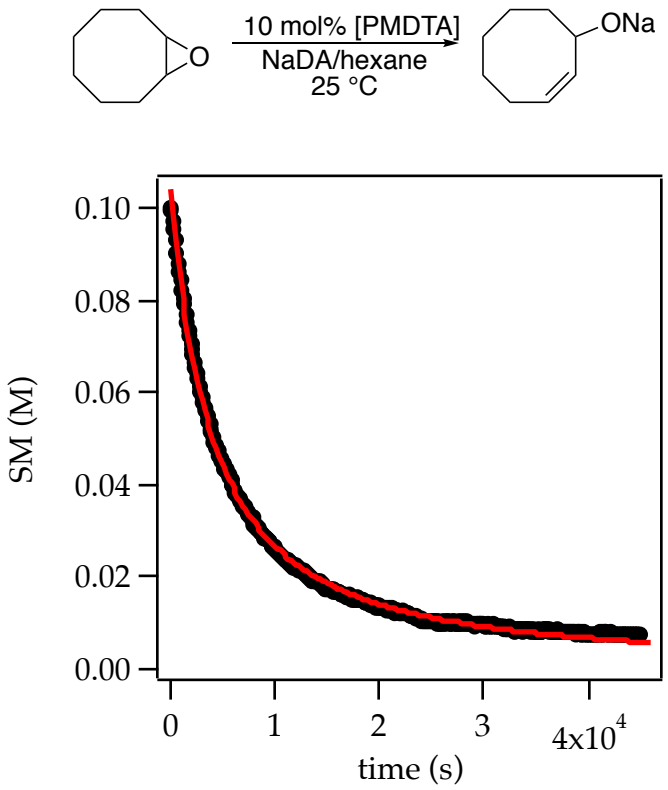


Figure S6. Plot of cyclooctene oxide concentration versus time for the elimination of 0.10 M cyclooctene oxide with 0.12 M NaDA in neat DMEA in the presence of 10 mol% PMDTA at 25 °C. The curve depicts an unweighted least-squares fit to $y = ((n–1)k_{obsd}t + [A_0]^{-(n-1)})^{-1/n-1}$ (n = 1.78 ± 0.01, k_{obsd} = 0.0015 ± 0.0003, $[A]_0$ = 0.10 ± 0.0003).

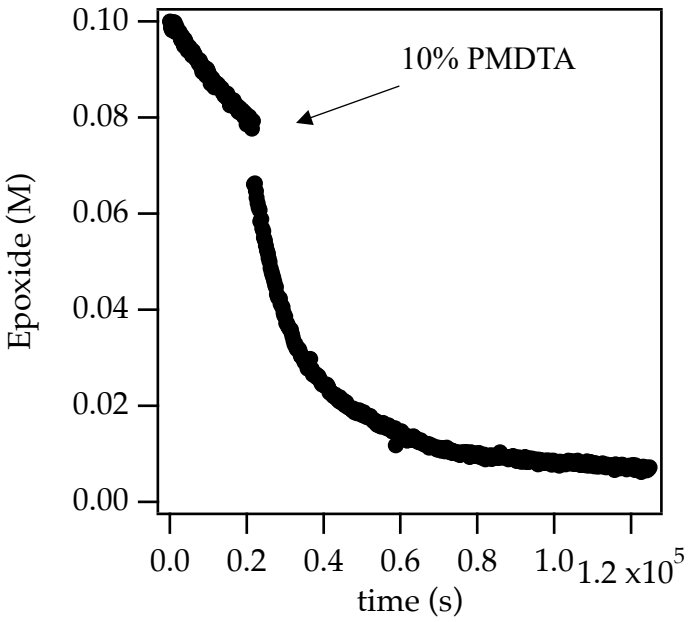


Figure S7. Metalation of 0.010 M cyclooctene epoxide (**15**) with 0.12 M NaDA in 1.0 M DMEA at 25 °C monitored by ^{1}H NMR spectroscopy. PMDTA (0.10 equiv, 10 mol %) was injected (arrow).

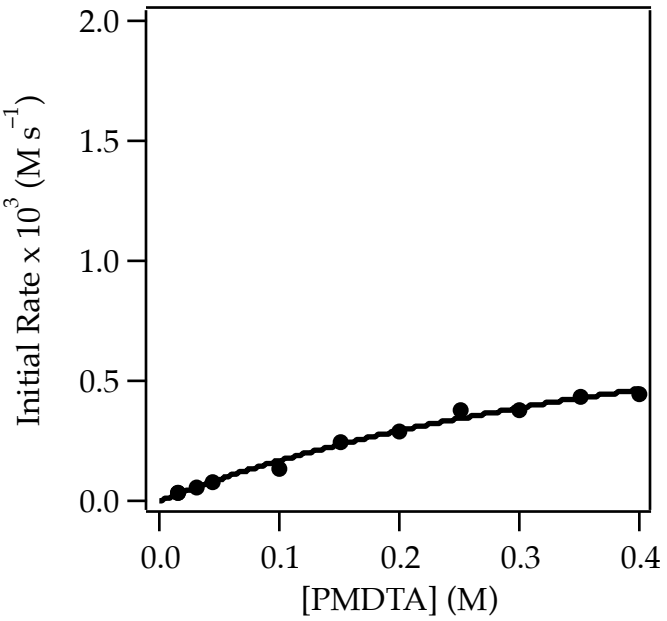


Figure S8. Plot of initial rates versus [PMDTA] in neat DMEA for the elimination of cyclooctene oxide (0.067 M) with 0.10 M NaDA at 25 °C. The curve depicts an unweighted least-squares fit to $y = ax/(1 + bx)$ ($a = (2.0 \pm 0.2) \times 10^3$, $b = (1.7 \pm 0.4) \times 10^3$).

[PMDTA] (M)	$y_1 \times 10^3 (s^{-1})$
0015	0.034
0.03	0.055
0.045	0.075
0.10	0.14
0.15	0.25
0.20	0.29
0.25	0.38
0.30	0.38
0.35	0.43
0.40	0.45

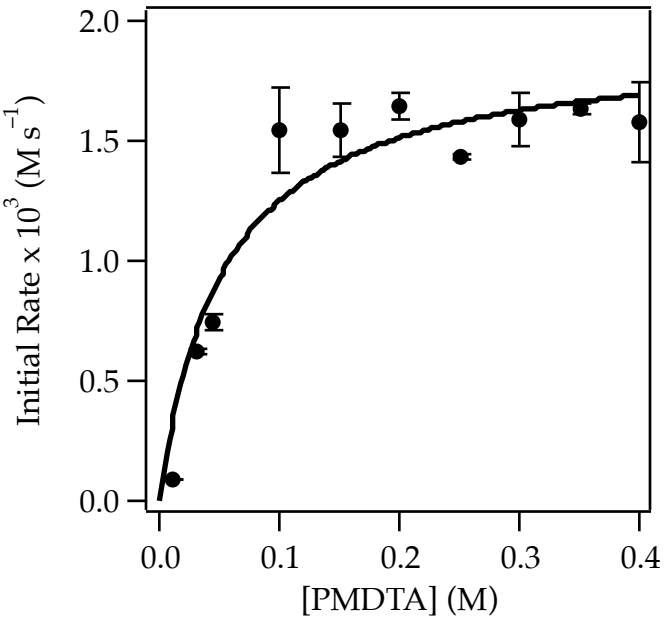


Figure S9. Plot of initial rates versus [PMDTA] in 1.0 M DMEA/hexanes for the elimination of cyclooctene oxide (0.067 M) in the presence of 0.10 M NaDA at 25 °C. The curve depicts an unweighted least-squares fit to y = *a*x/(1 + *b*x) (*a* = (3.5 ± 0.9) x 10^4, *b* = (1.9 ± 0.6) x 10^4).

[PMDTA] (M)	y_1 x 10^3(s^{-1})	y_1 x 10^3(s^{-1})	$y_{av.}$ x 10^3(s^{-1})
0.01	0.093	0.089	0.091
0.03	0.63	0.61	0.62
0.045	0.77	0.73	0.75
0.10	1.67	1.42	1.55
0.15	1.63	1.47	1.55
0.20	1.68	1.60	1.64
0.25	1.44	1.42	1.43
0.30	1.51	1.67	1.59
0.35	1.65	1.62	1.64
0.40	1.62	1.46	1.58

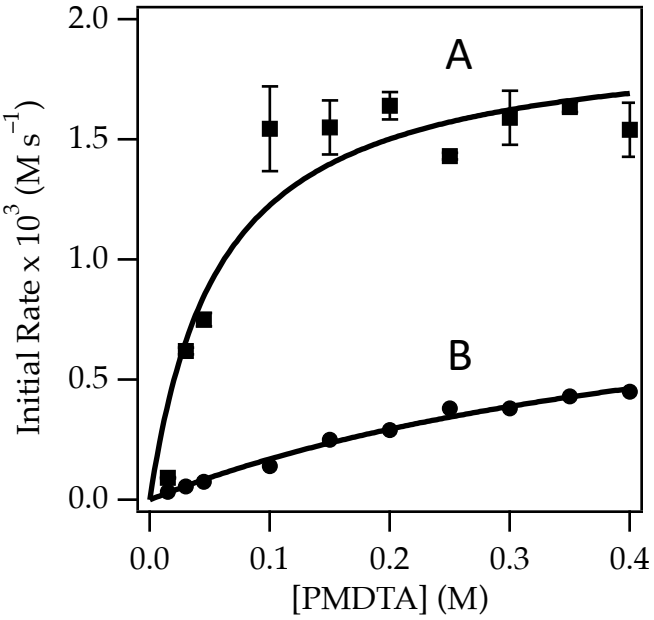


Figure S10. Plot of initial rates versus [PMDTA] in DMEA/hexanes for the elimination of cyclooctene oxide (0.067 M) in the presence of 0.10 M NaDA at 25 °C. A: 1.0 M DMEA; B: neat DMEA.

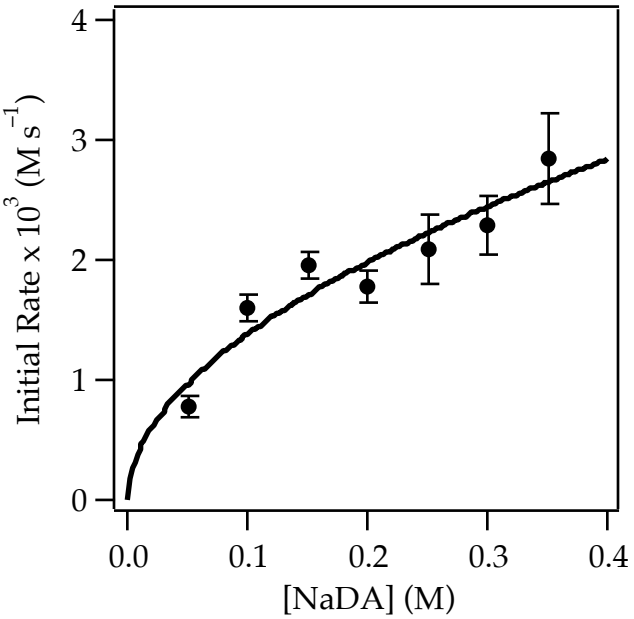


Figure S11. Plot of initial rate versus [NaDA] in 1.0 M DMEA/hexanes for the elimination of cyclooctene oxide (0.067 M) in the presence of 2.0 M PMDTA at 25 °C. The curve depicts an unweighted least-squares fit to $y = ax^n$ ($a = (4.6 \pm 0.7) \times 10^3$, $n = 0.5 \pm 0.1$).

[NaDA] (M)	$y_1 \times 10^3 (s^{-1})$	$y_2 \times 10^3 (s^{-1})$	$y_{av.} \times 10^3 (s^{-1})$
0.05	0.84	0.70	0.77
0.10	1.50	1.67	1.59
0.15	2.05	1.88	1.97
0.20	1.69	1.87	1.78
0.25	1.89	2.30	2.10
0.30	2.46	2.11	2.29
0.35	3.2	2.68	2.84

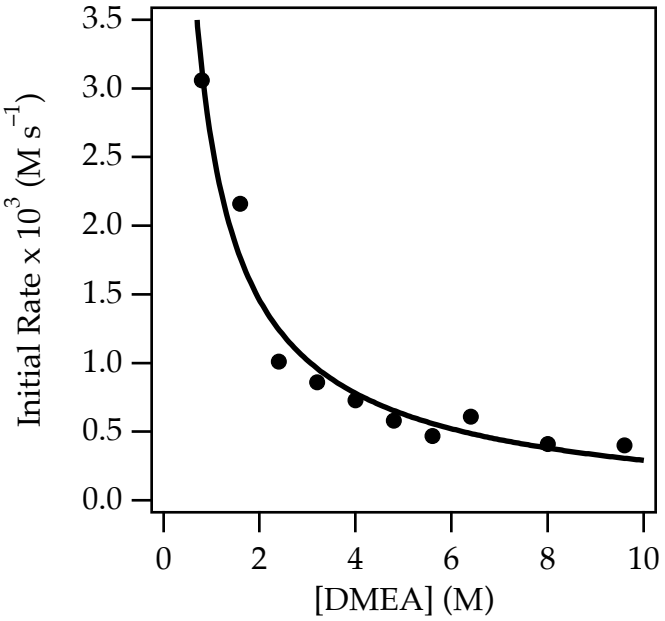


Figure S12. Plot of initial rates versus [DMEA] in hexanes for the elimination of cyclooctene oxide with NaDA (0.10 M) in the presence of 1.5 M PMDTA at 25 °C. The curve depicts an unweighted least-squares fit to $y = ax^n + c$ (a = (2.8 ± 0.5) x 10^3, c = (–1.8 ± 0.7) x 10^3, n = –0.8 ± 0.2).

[DMEA] (M)	y_1 x 10^3(s^{-1})
0.8	3.06
1.6	2.16
2.4	1.01
3.2	0.86
4.0	0.73
4.8	0.58
5.6	0.47
6.4	0.61
8.0	0.41
9.6	0.40

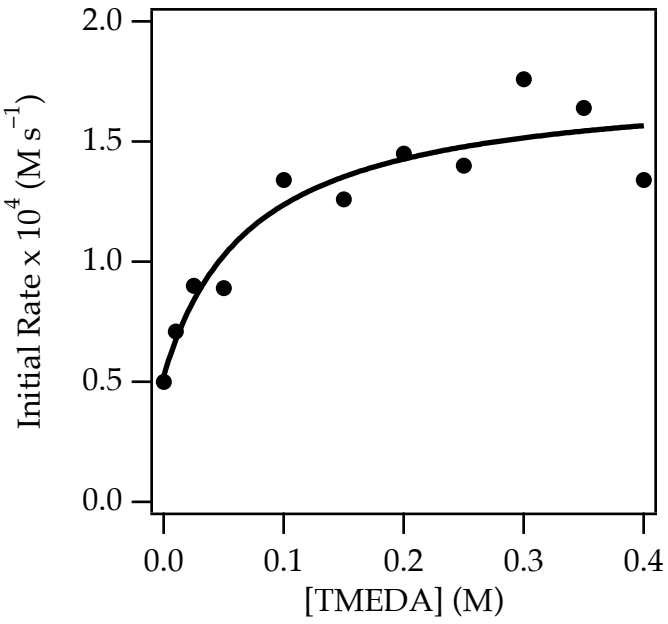


Figure S13. Plot of initial rates versus [TMEDA] in 1.0 M DMEA/hexanes for the elimination of cyclooctene oxide (0.067 M) in the presence of 0.10 M NaDA at 25 °C. Curves depict unweighted least-squares fits to $y = ax/(1 + bx) + c$: $a = (1.7 \pm 0.9) \times 10^5$; $b = (1.4 \pm 0.8) \times 10^{5,}$; $c = 0.53$ (set by measurement).

[TMEDA] (M)	$y_1 \times 10^3 (s^{-1})$
0.0	0.05
0.01	0.071
0.025	0.090
0.05	0.089
0.10	0.134
0.15	0.126
0.20	0.133
0.25	0.133
0.30	0.165
0.35	0.176
0.40	0.134

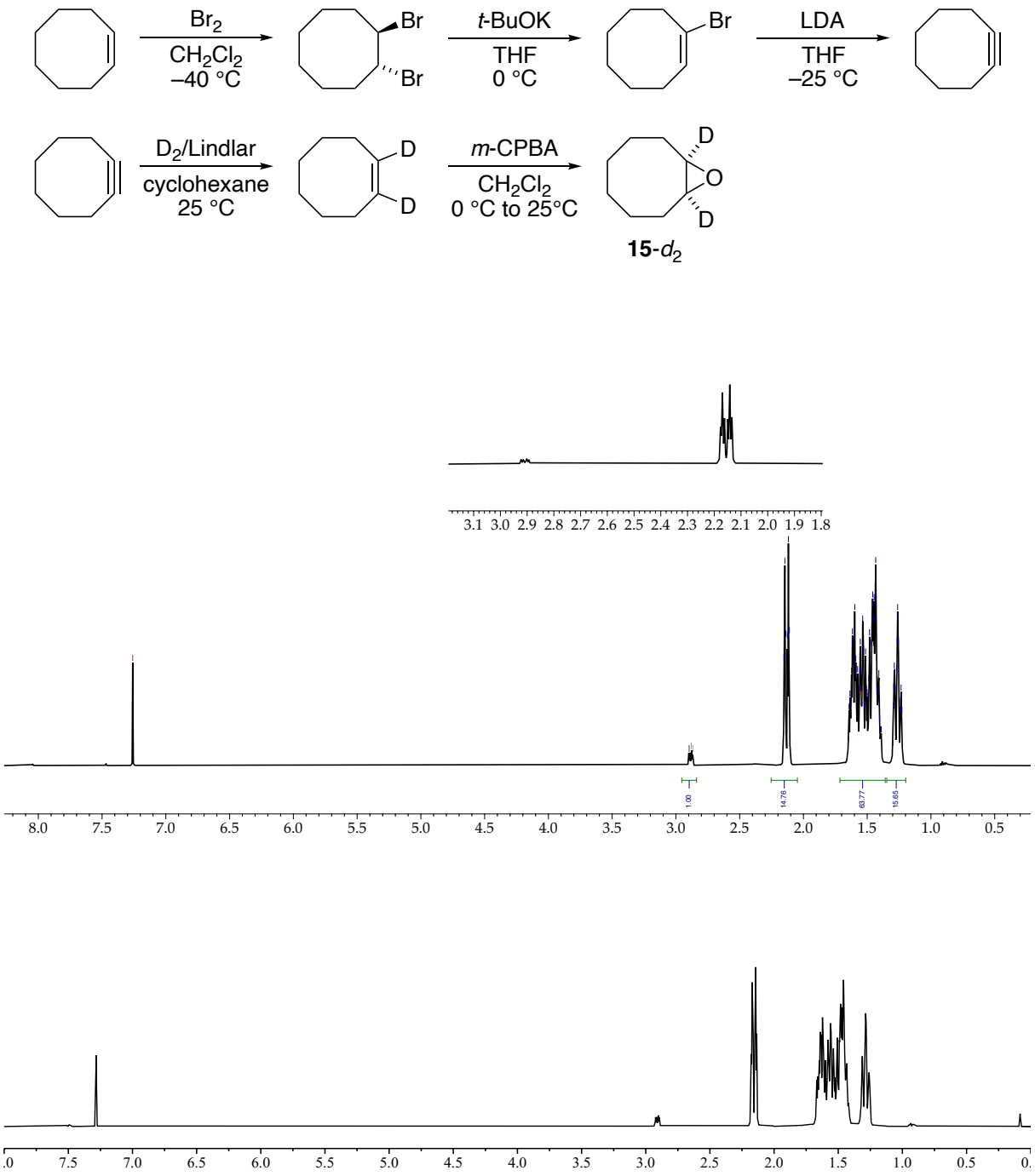


Figure S14. ^{1}H NMR spectrum of **15**-d_2 in $CDCl_3$.

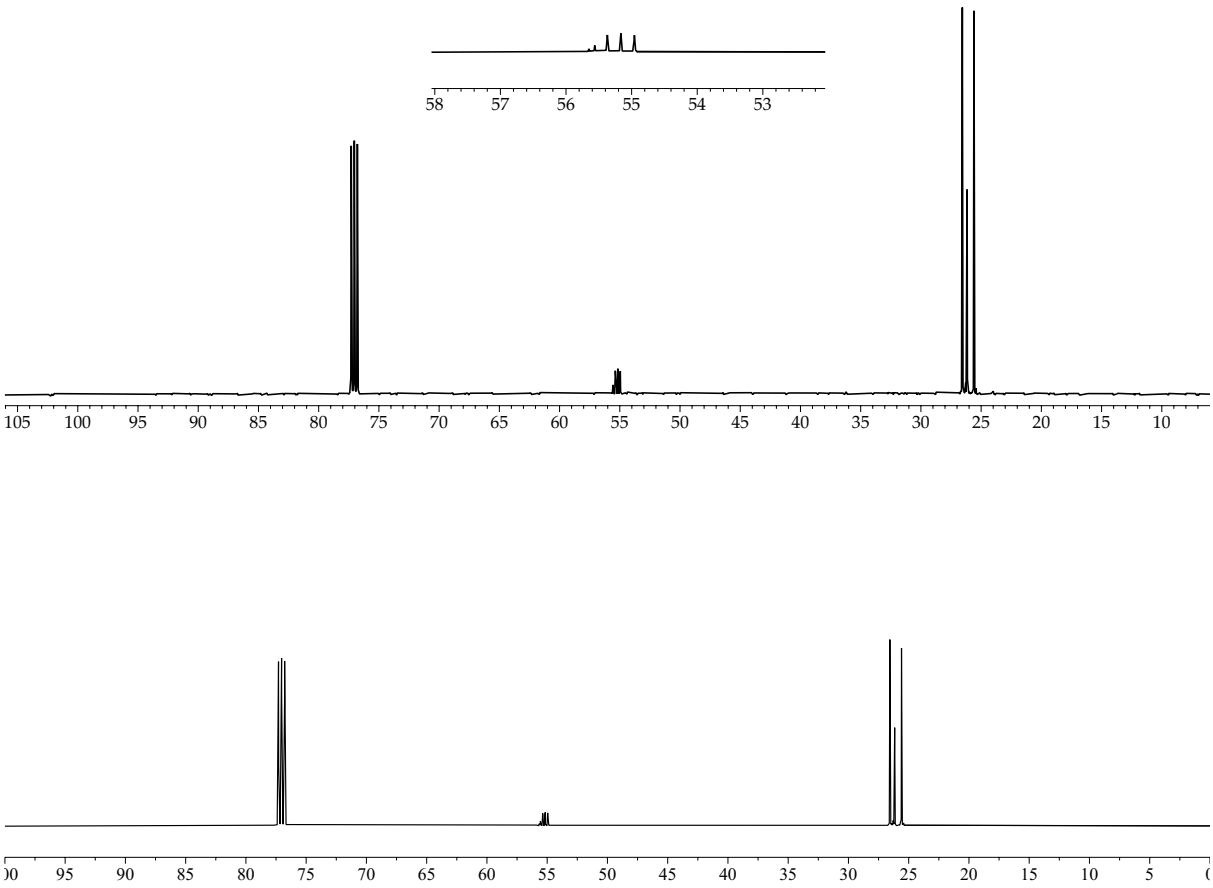


Figure S15. ^{13}C NMR spectrum of **15**-d_2 in $CDCl_3$.

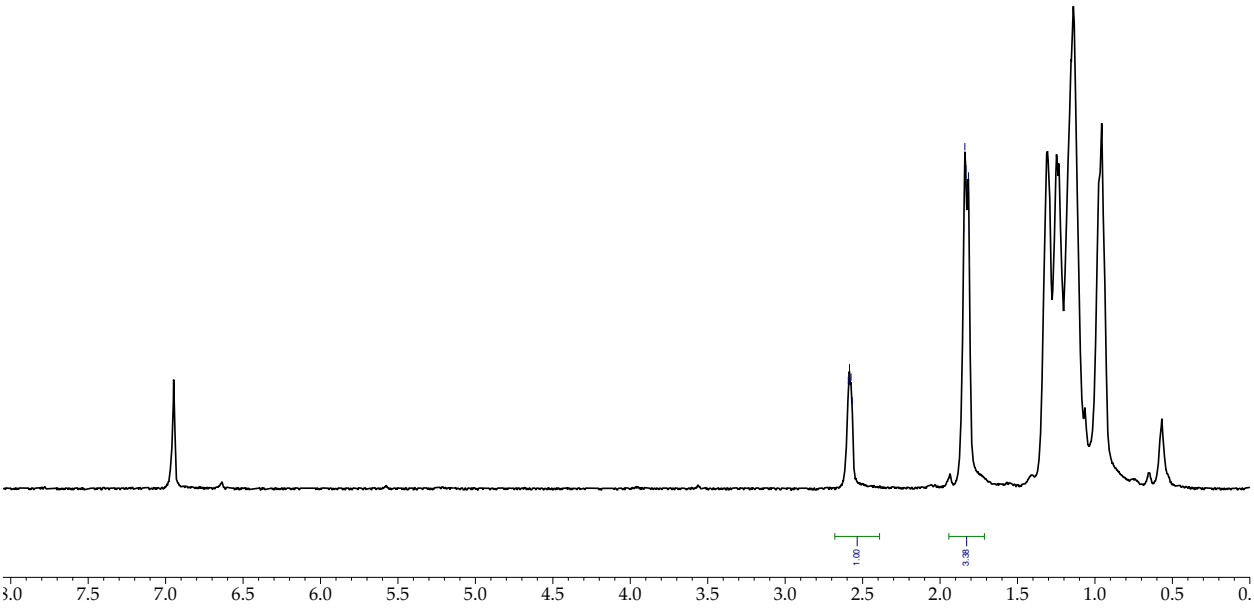


Figure S16. Isolated starting material ^{1}H NMR spectrum for metalation of 0.10 M d_2-cyclooctene oxide (**15**-d_2) with 0.040 M NaDA in 2.0 ml hexane and 1.0 equiv PMDTA at 25 ºC after work up.

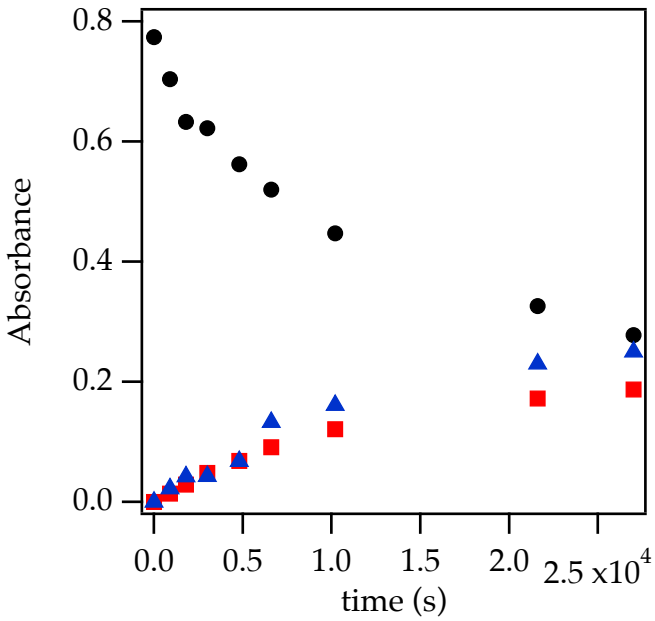


Figure S17. Plot of GC absorbance versus time for the elimination of 0.15 M cyclooctene oxide with 0.16 M NaDA in hexanes at 25 °C. Black = **15**; blue = **39**; red = *Z*-**16**+*E*-**16**.

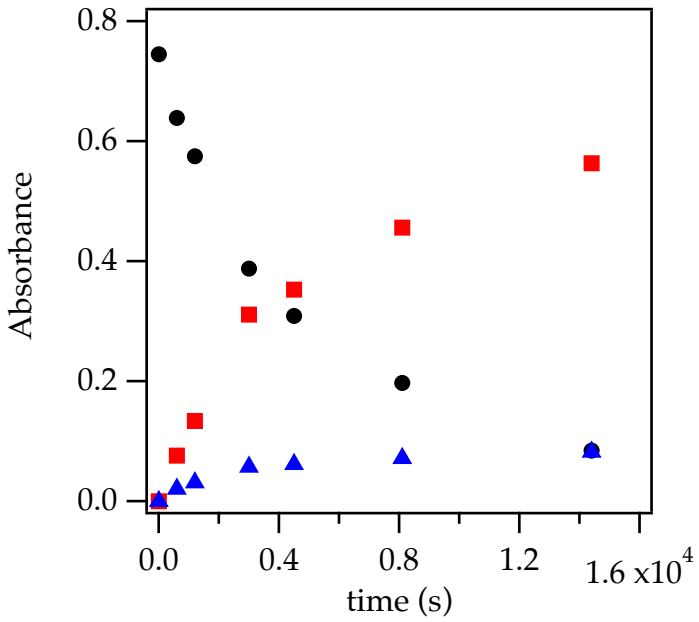


Figure S18. Plot of GC absorbance versus time for the elimination of 0.15 M cyclooctene oxide with 0.16 M NaDA in hexanes in the presence of 5 mol % PMDTA at 25 °C. Black = **15**; blue = **39**; red = *Z*-**16**+*E*-**16**.

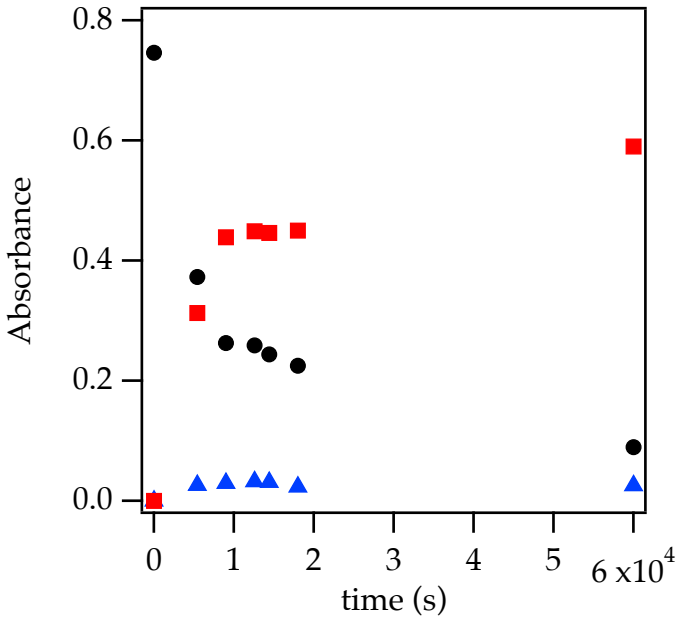


Figure S19. Plot of GC absorbance versus time for the elimination of 0.15 M cyclooctene oxide (added *via* syringe pump) with 0.16 M NaDA in hexanes in the presence of 5 mol % PMDTA at 25 °C. Black = **15**; blue = **39**; red = *Z*-**16**+*E*-**16**.

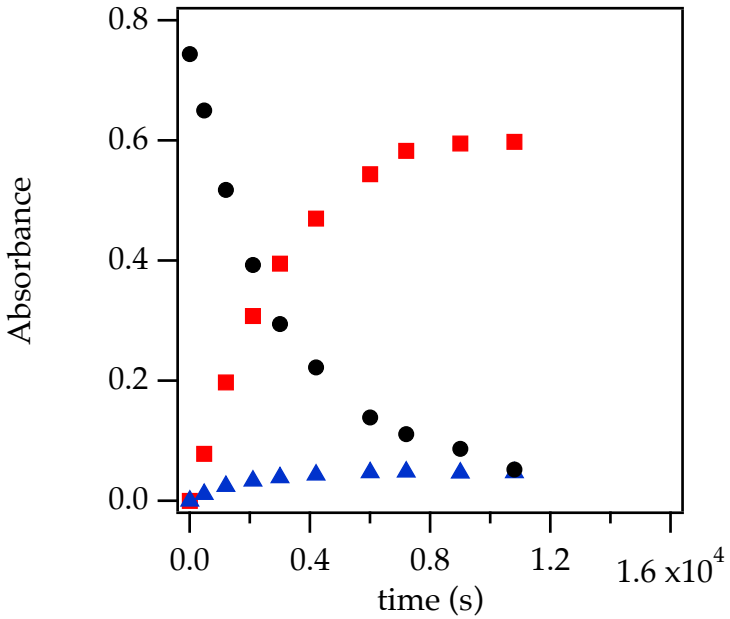


Figure S20. Plot of GC absorbance versus time for the elimination of 0.15 M cyclooctene oxide with 0.16 M NaDA in hexanes in the presence of 10 mol % PMDTA at 25 °C. Black = **15**; blue = **39**; red = *Z*-**16**+*E*-**16**.

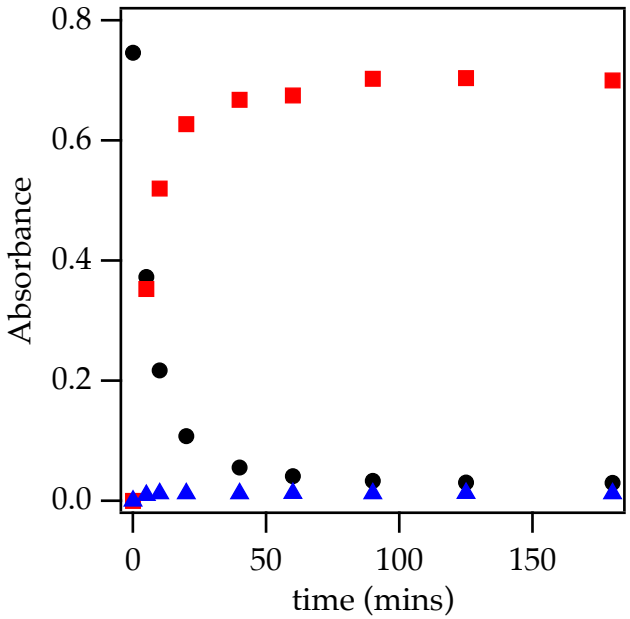


Figure S21. Plot of GC absorbance versus time for the elimination of 0.15 M cyclooctene oxide with 0.16 M NaDA in hexanes in the presence of 1.0 equiv PMDTA at 25 °C. Black = **15**; blue = **39**; ref = *Z*-**16**+*E*-**16**.

Table S2. Product ratios for the elimination of cyclooctene oxide with NaDA in hexanes in the presence of PMDTA.[a]

PMDTA (mol %)	**(*E*-16** + ***Z*-16)/39**
0	0.7
5	7
10	12
5*	14
100	50

[a]Conditions: 0.15 M cyclooctene oxide with 0.16 M NaDA in hexanes in the presence of PMDTA.

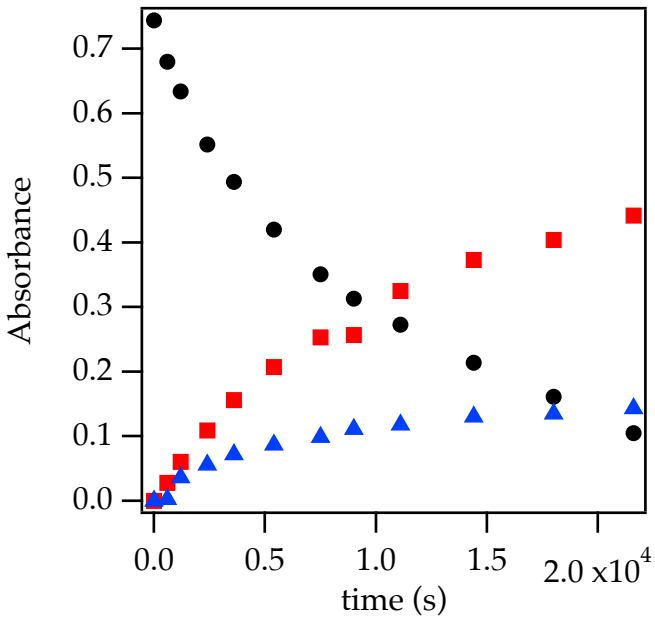


Figure S22. Plot of GC absorbance versus time for the elimination of 0.15 M cyclooctene oxide with 0.16 M NaDA in hexanes in the presence of 10 mol% TMEDA at 25 °C. Black = **15**; blue = **39**; red = *Z*-**16**+*E*-**16**.

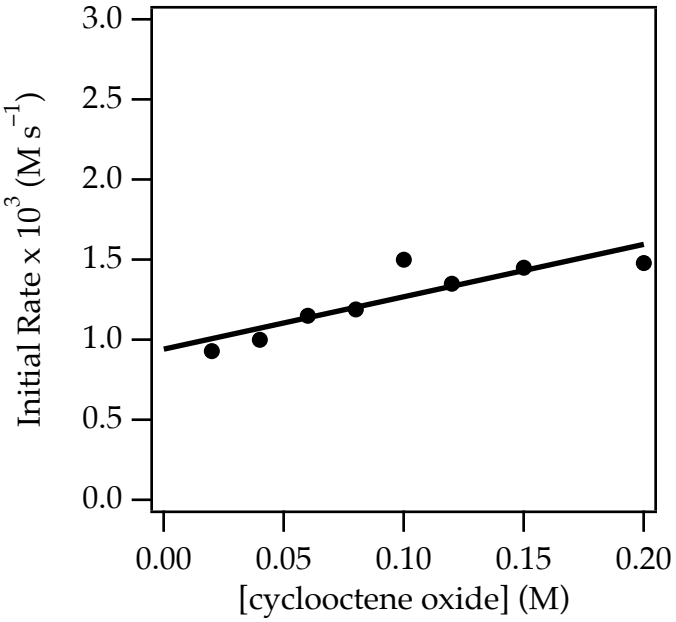


Figure S23. Plot of initial rates versus [cyclooctene oxide] in hexanes for the elimination of cyclooctene oxide in the presence of 0.15 M NaDA at 25 °C. Curves depict unweighted least-squares fits to y = *a* + *b*x. *a* = (9.4 ± 0.7) x 10^4; *b* = (3.5 ± 0.6) x 10^4.

[cyclooctene oxide] (M)	y_1 $10^3(s^{-1})$
0.02	0.99
0.04	1.16
0.08	1.19
0.10	1.51
0.12	1.32
0.15	1.52
0.20	1.58

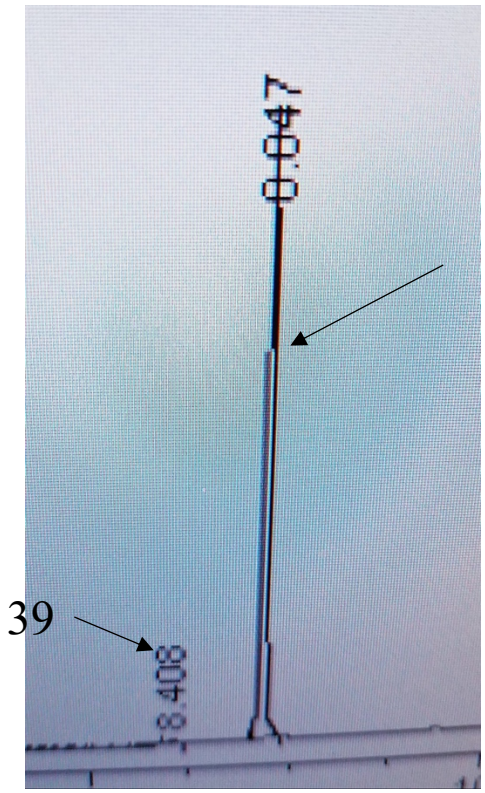


Figure S24. Plot of GC absorbance versus time for the elimination of 0.15 M cyclooctene oxide with 0.16 M NaDA in hexanes in the presence of 1.0 equiv PMDTA.

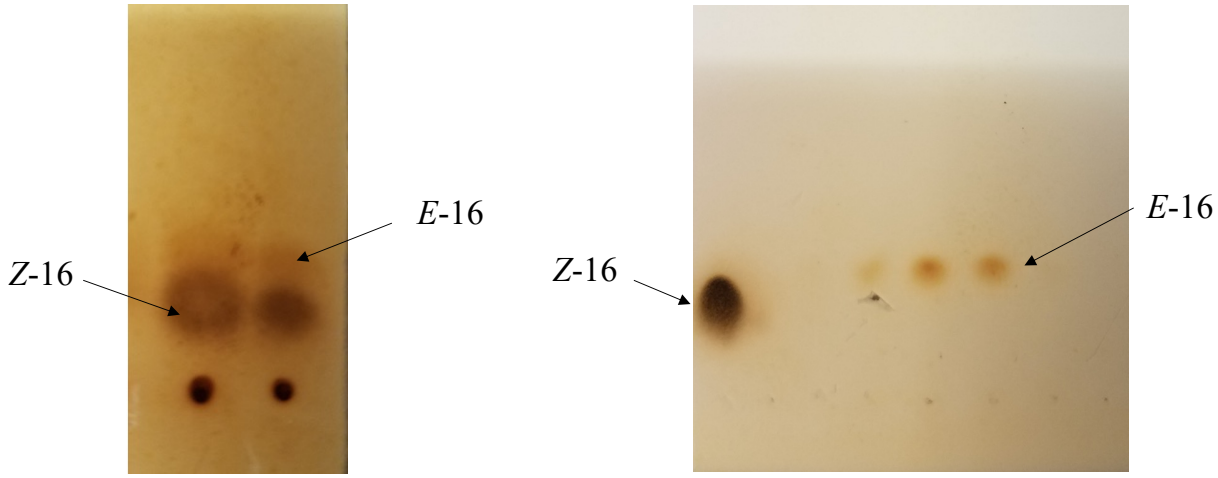


Figure S25. TLC of crude products (left) and purified products (right)

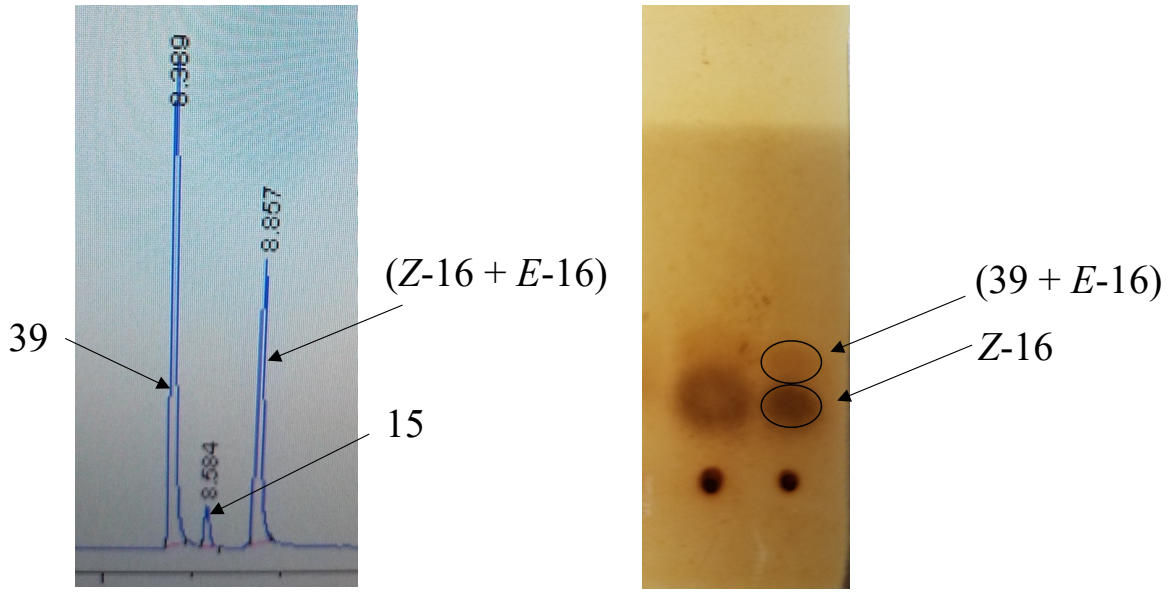


Figure S26. Plot of GC absorbance versus time for the elimination of 0.15 M cyclooctene oxide with 0.16 M NaDA in hexanes (left). TLC of crude products (right)

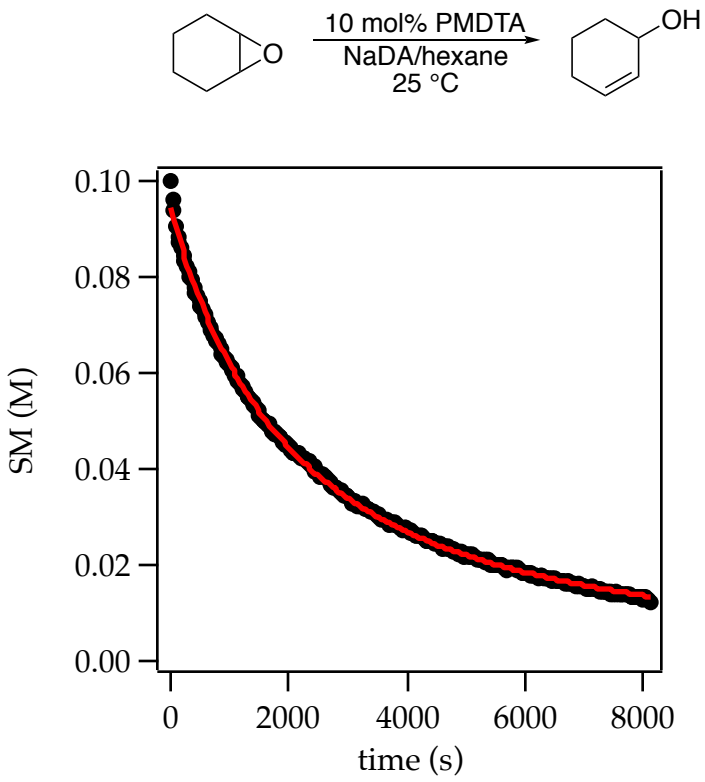


Figure S27. Plot of cyclohexene oxide concentration versus time for the elimination of 0.10 M cyclohexene oxide with 0.12 M NaDA in neat DMEA in the presence of 10 mol% PMDTA at 25 °C. The curve depicts an unweighted least-squares fit to $y = ((n–1)\ k_{obsd}t + [A_0]^{-(n-1)})^{-1/n-1}$ (n = 1.65 ± 0.01, k_{obsd}= 0.0023 ± 0.0001, $[A]_0$ = 0.0940 ± 0.0002).

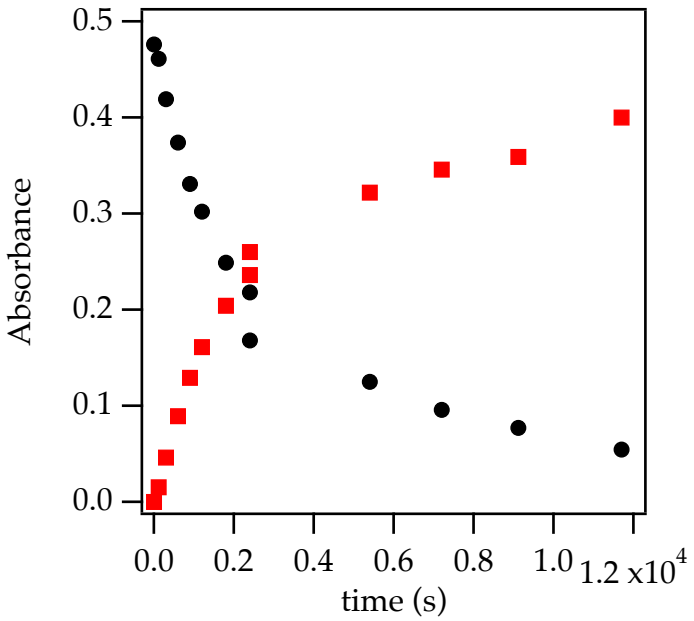


Figure S28. Plot of GC absorbance versus time for the elimination of 0.15 M cyclohexene oxide with 0.16 M NaDA in hexanes at 25 °C. Black = cyclohexene epoxide; red = 2-cyclohexen-1-ol.

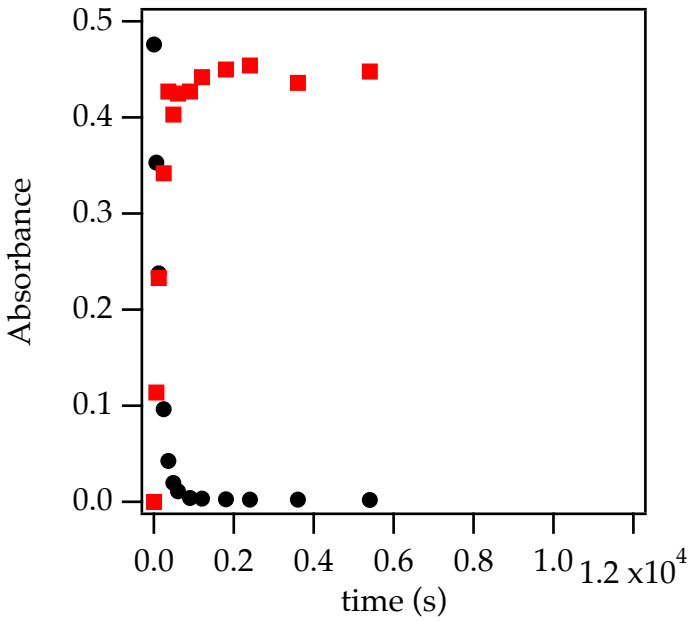


Figure S29. Plot of GC absorbance versus time for the elimination of 0.15 M cyclohexene oxide with 0.16 M NaDA in hexanes in the presence of 10 mol % PMDTA at 25 °C. Black: cyclohexene epoxide**;** red: 2-cyclohexen-1-ol.

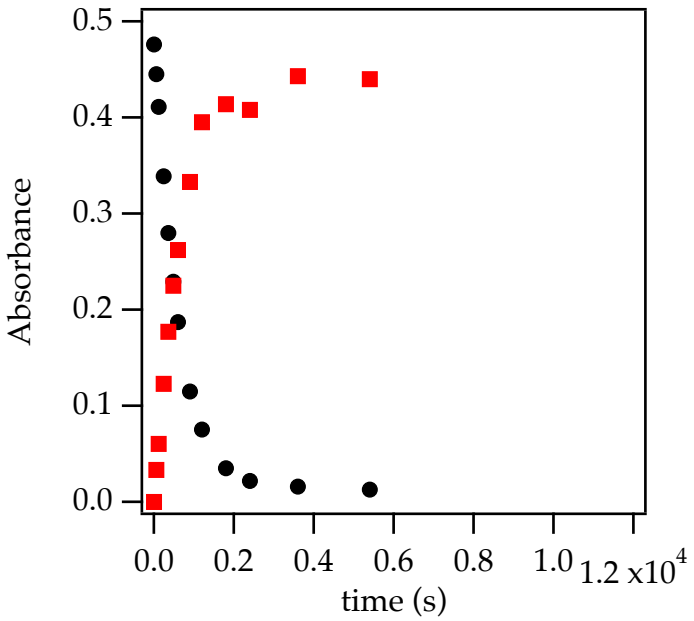


Figure S30. Plot of GC absorbance versus time for the elimination of 0.15 M cyclohexene oxide with 0.16 M NaDA in hexanes in the presence of 10 mol % TMEDA at 25 °C. Black = cyclohexene epoxide**;** red = 2-cyclohexen-1-ol.

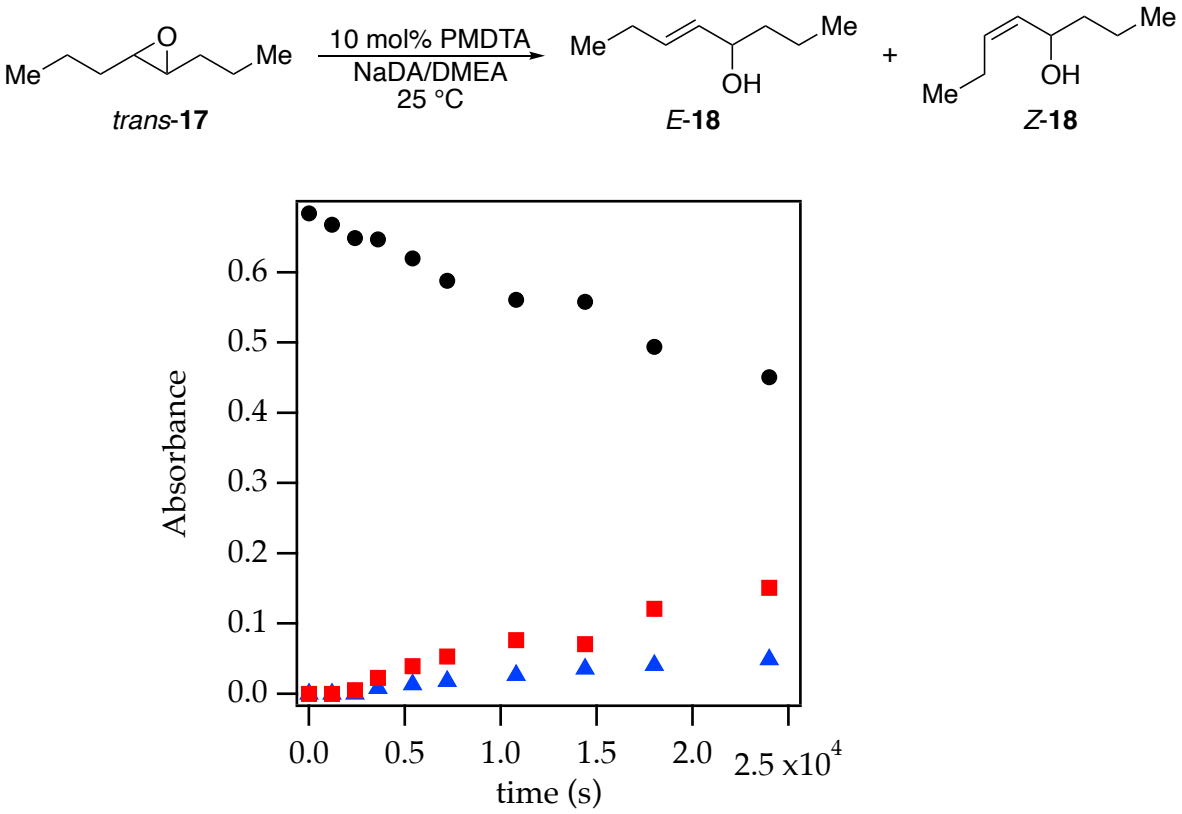


Figure S31. Plot of GC absorbance versus time for the elimination of 0.15 M *trans*-4-octene epoxide (*trans*-**17**) with 0.16 M NaDA in hexanes at 25 °C. Black: *trans*-**17;** red: *E*-**18**; blue = *Z*-**18**.

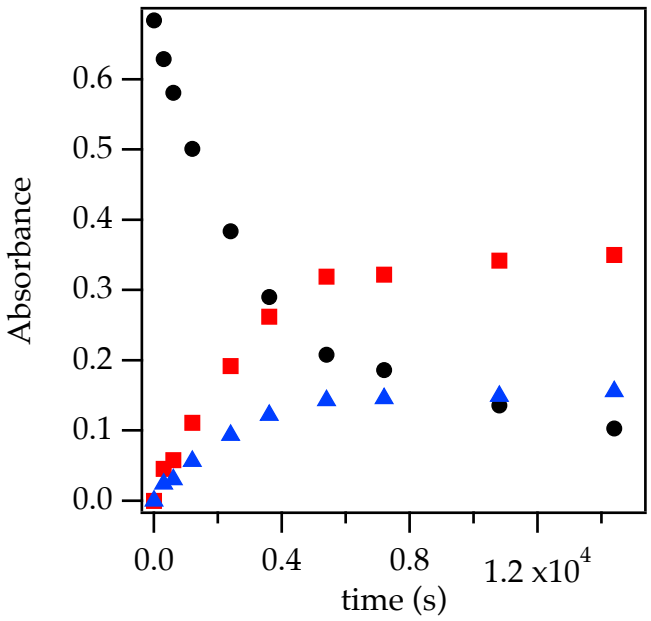


Figure S32. Plot of GC absorbance versus time for the elimination of 0.15 M *trans*-4-octene epoxide (*trans*-**17**) with 0.16 M NaDA in hexanes in the presence of 10 mol % PMDTA at 25 °C. Black = *trans*-**17;** red = *E*-**18**; blue = *Z*-**18**.

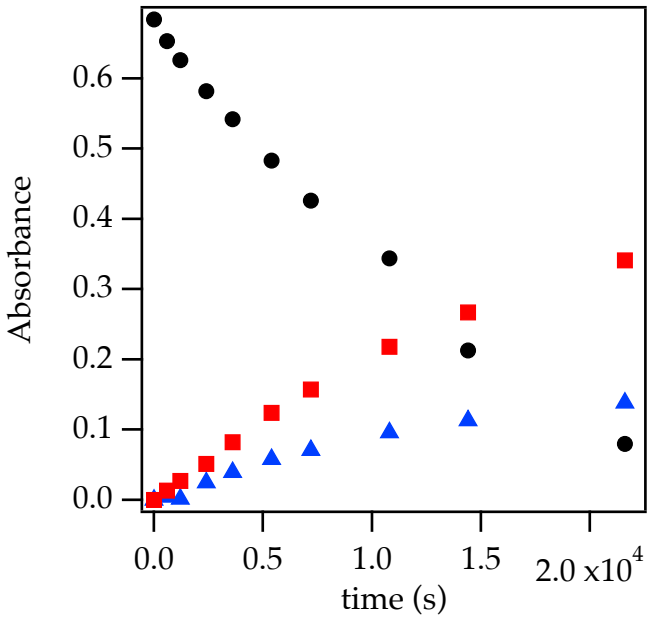


Figure S33. Plot of GC absorbance versus time for the elimination of 0.15 M *trans*-4-octene epoxide (*trans*-**17**) with 0.16 M NaDA in hexanes in the presence of 10 mol % TMEDA at 25 °C. *trans*-**17;** red = *E*-**18**; blue = *Z*-**18**.

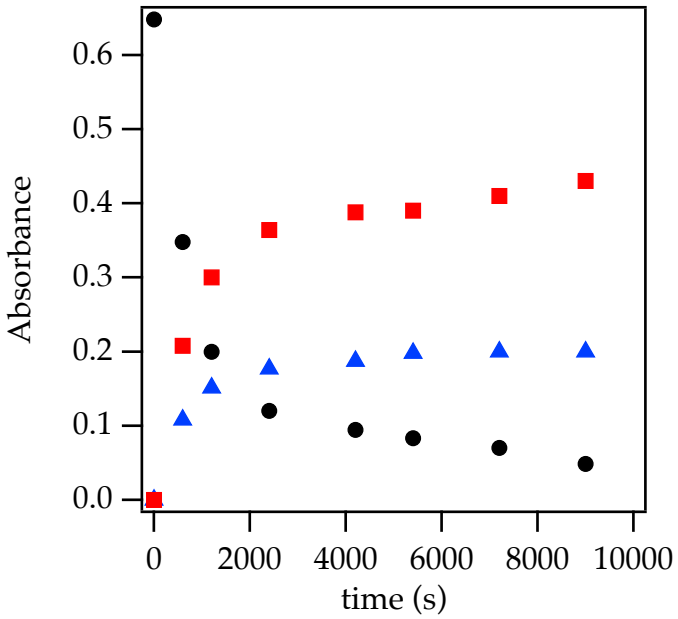


Figure S34. Plot of GC absorbance versus time for the elimination of 0.15 M *trans*-4-octene epoxide (*trans*-**17**) with 0.16 M NaDA in hexanes in the presence of 1.0 equiv PMDTA at 25 °C. *trans*-**17;** red = *E*-**18**; blue = *Z*-**18**.

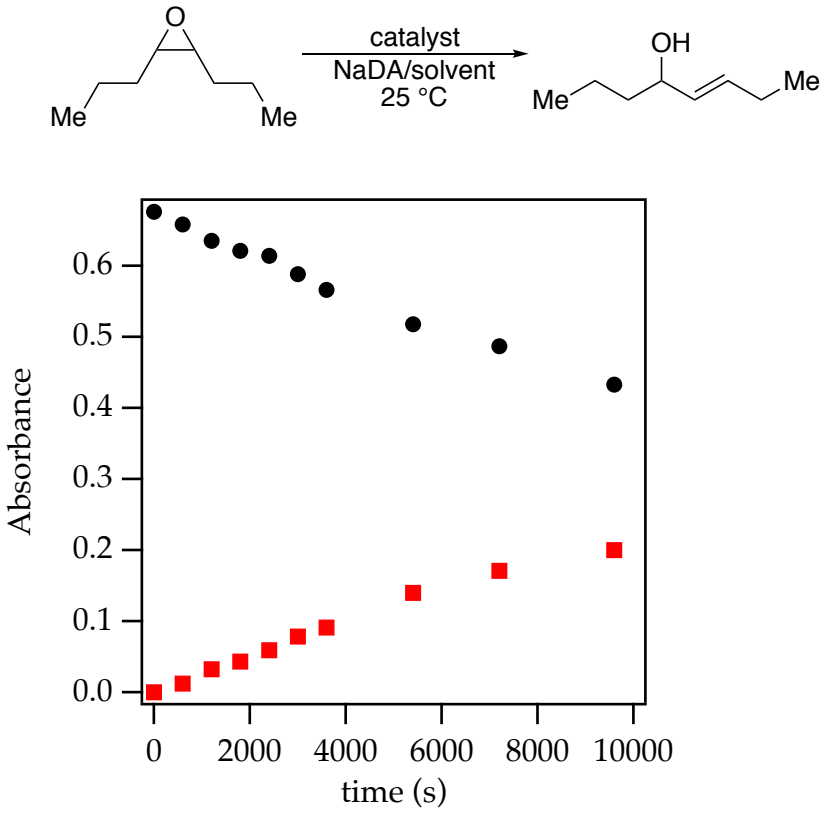


Figure S35. Plot of GC absorbance versus time for the elimination of 0.15 M *cis*-4-octene epoxide (*cis*-**17**) with 0.16 M NaDA in hexanes at 25 °C. *cis*-**17;** red = *E*-**18**.

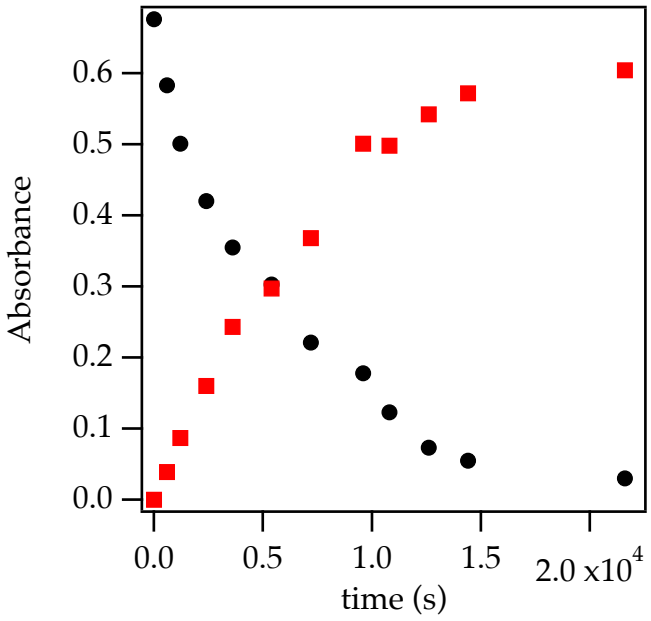


Figure S36. Plot of GC absorbance versus time for the elimination of 0.15 M *cis*-4-octene epoxide (*cis*-**17**) with 0.16 M NaDA in hexanes in the presence of 10 mol % PMDTA at 25 °C. *cis*-**17;** red = *E*-**18**.

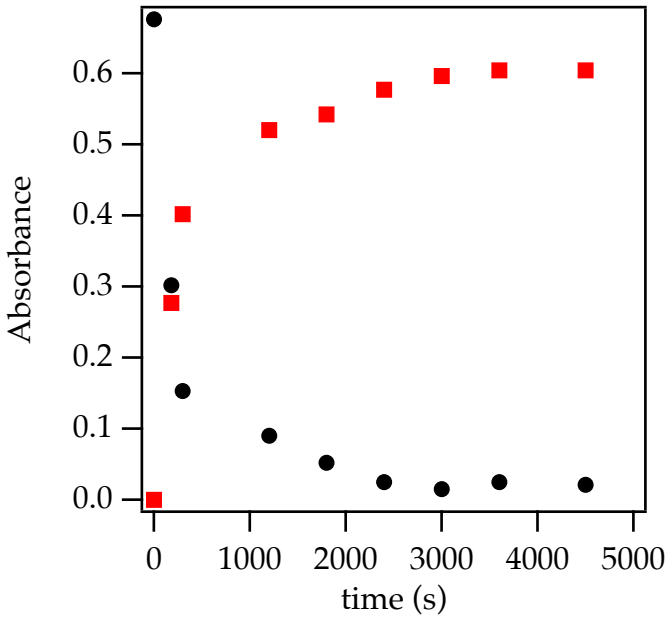


Figure S37. Plot of GC absorbance versus time for the elimination of 0.15 M *cis*-4-octene epoxide (*cis*-**17**) with 0.16 M NaDA in hexanes in the presence of 1.0 equiv PMDTA at 25 °C. Black = *cis*-**17**; red = *E*-**18**.

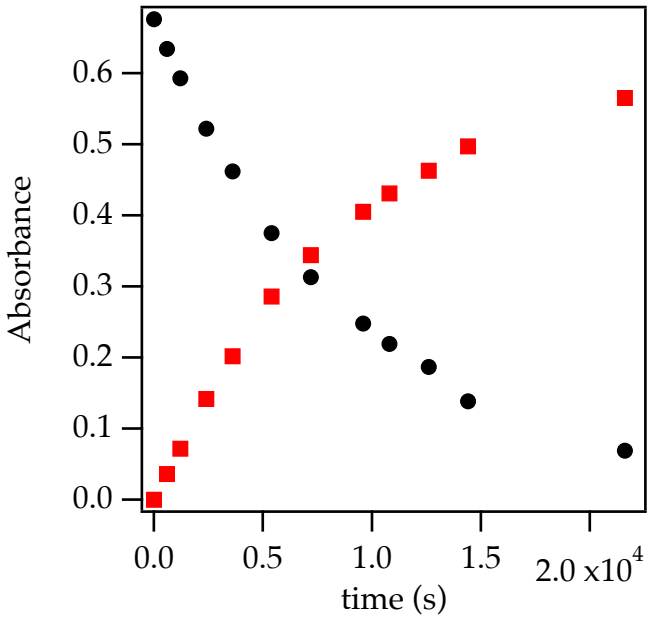


Figure S38. Plot of GC absorbance versus time for the elimination of 0.15 M *cis*-4-octene epoxide (*cis*-**17**) with 0.16 M NaDA in hexanes in the presence of 10 mol % TMEDA at 25 °C. Black = *cis*-**17**; red = *E*-**18**.

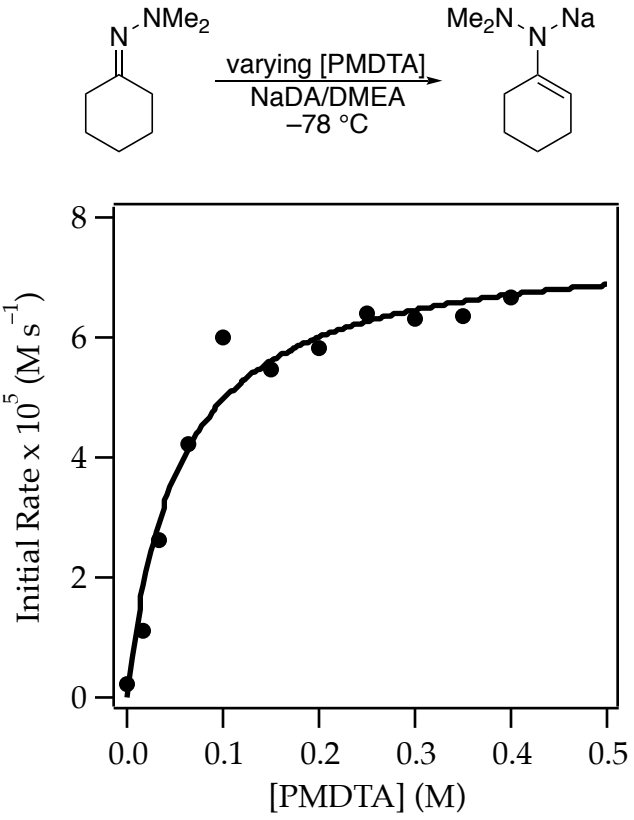


Figure S39. Plot of initial rate versus [PMDTA] in neat DMEA for the deprotonation of NaDA (0.10 M) with 2-cyclohexliden-1,1-dimethylhydrazine (0.050 M) at –78 °C. The curve depicts an unweighted least-squares fit to y = *a*x/(1 + *b*x) (*a* = (1.4 ± 0.2) x 10^4, *b* = (1.9 ± 0.4) x 10^4).

[PMDTA] (M)	y_1 x 10^5(s^{-1})
0.0	0.24
0016	1.13
0.03	2.61
0.064	4.23
0.10	6.02
0.15	5.48
0.20	5.82
0.25	6.40
0.30	6.32
0.35	6.35
0.40	6.68

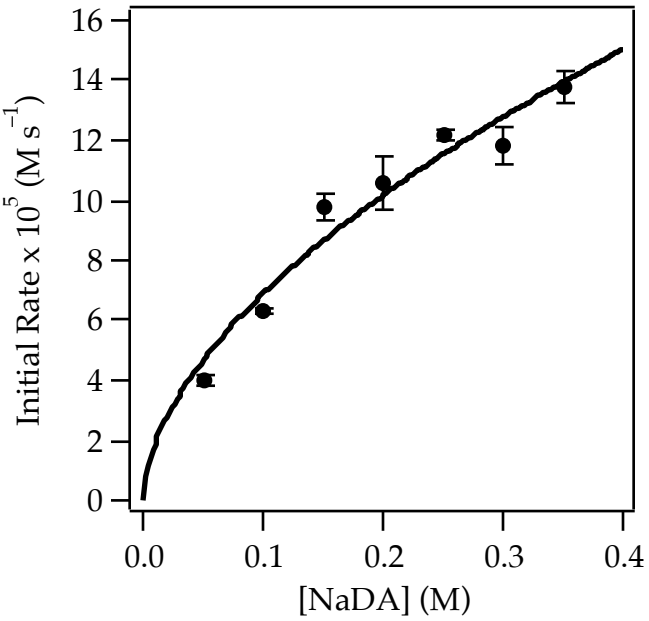


Figure S40. Plot of initial rate versus [NaDA] in neat DMEA for the deprotonation of 2-cyclohexliden-1,1-dimethylhydrazine (0.050 M) in the presence of 2.0 M PMDTA at –78 °C. The curve depicts an unweighted least-squares fit to $y = ax^n$ ($a = (2.5 \pm 0.3) \times 10^3$, $n = 0.56 \pm 0.07$).

[NaDA] (M)	$y_1 \times 10^3 (s^{-1})$	$y_1 \times 10^3 (s^{-1})$	$y_{av} \times 10^3 (s^{-1})$
0.05	3.83	4.10	3.97
0.10	6.41	6.31	6.36
0.15	9.80	9.05	9.75
0.20	9.89	11.20	10.55
0.25	12.29	12.10	12.20
0.30	12.24	11.38	11.81
0.35	13.42	14.20	13.81

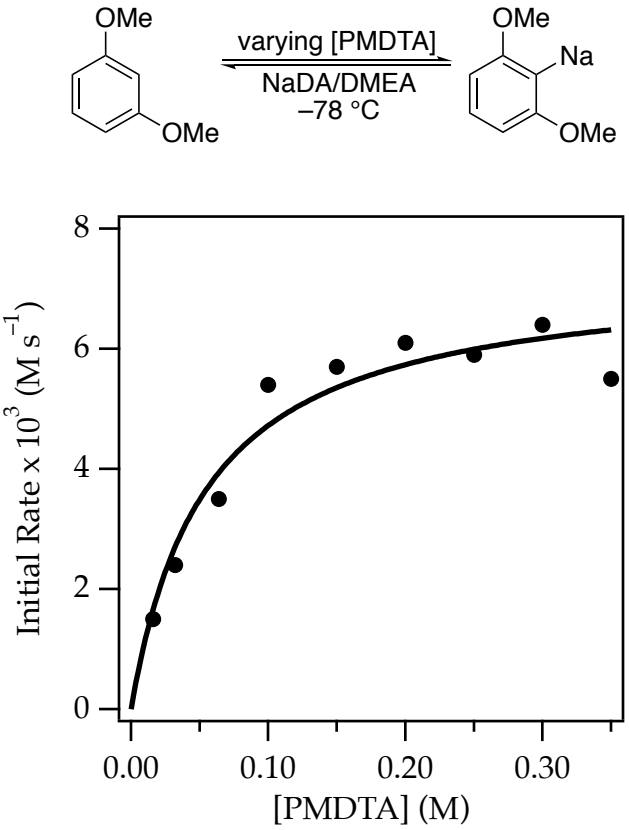


Figure S41. Plot of initial rate versus [PMDTA] in neat DMEA for the deprotonation of NaDA (0.10 M) with 1,3-dimethoxybenzene (0.050 M) at –78 °C. The curve depicts an unweighted least-squares fit to y = *a*x/(1 + *b*x) (*a* = (1.3 ± 0.0.3) x 10^4, *b* = (1.8 ± 0.5) x 10^4).

[PMDTA] (M)	y_1 x 10^5(s^{-1})
0015	1.5
0.032	2.4
0.064	3.5
0.10	5.4
0.15	5.7
0.20	6.1
0.25	5.9
0.30	6.4
0.35	5.5

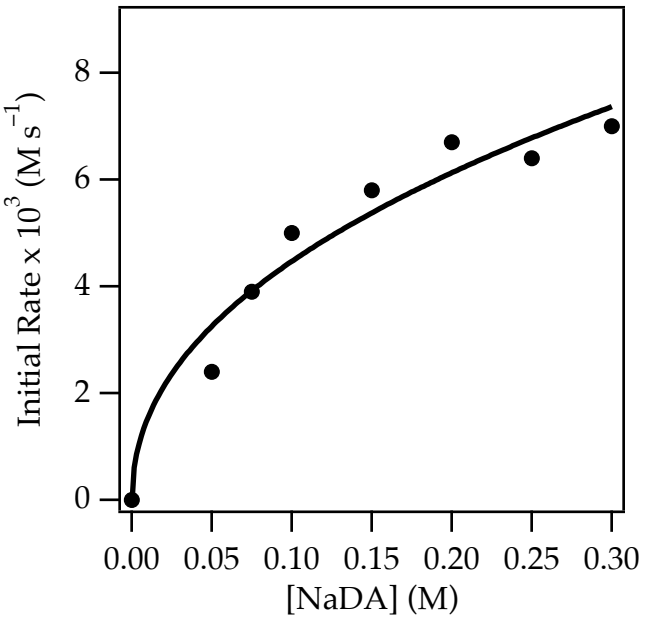


Figure S42. Plot of initial rate versus [NaDA] in neat DMEA for the deprotonation of 1,3-dimethoxybenzene (0.050 M) in the presence of 2.0 M PMDTA at –78 °C. The curve depicts an unweighted least-squares fit to $y = ax^n$ ($a = (1.3 \pm 0.2) \times 10^4$, $n = 0.45 \pm 0.08$).

[NaDA] (M)	$y_1 \times 10^3 (s^{-1})$
0.05	2.4
0.075	3.9
0.10	5.0
0.15	5.8
0.20	6.7
0.25	6.4
0.30	7.1

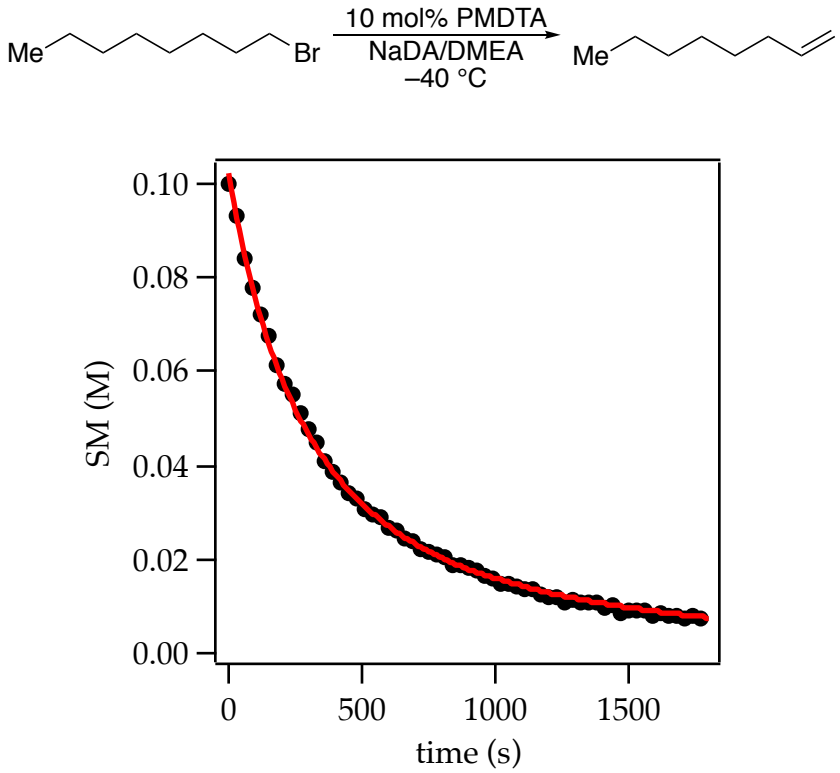


Figure S43. Plot of 1-bromooctane concentration versus time measured with ^{1}H NMR spectroscopy for the debromination of 0.10 M 1-bromooctane with 0.12 M NaDA in neat DMEA in the presence of 10% PMDTA at –40 °C. The curve depicts an unweighted least-squares fit to $y = ((n–1)\ k_{obsd}t + [A_0]^{-(n-1)})^{-1/n-1}$ (n = 1.56 ± 0.01, k_{obsd} = 0.012 ± 0.009, $[A]_0$ = 0.10 ± 0.0015).

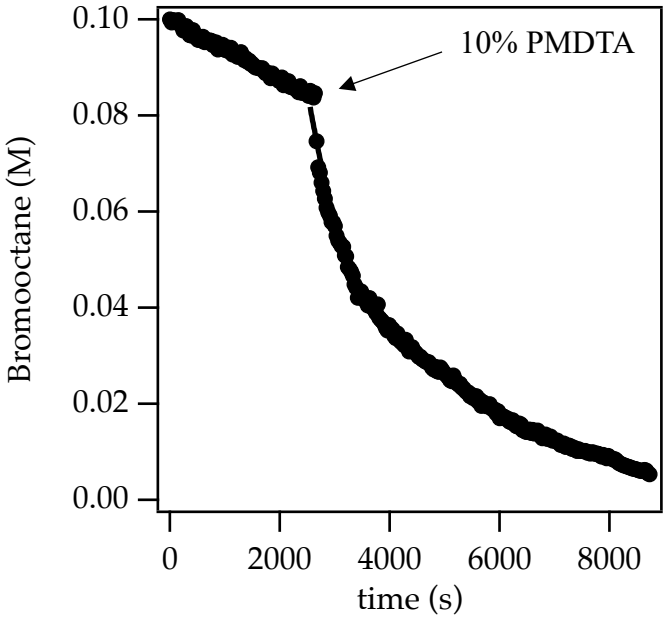


Figure S44. Metalation of 0.10 M **9** with 0.12 M NaDA in neat DMEA at –40 °C monitored by ^{1}H NMR spectroscopy. PMDTA (0.010 M, 0.10 equiv) was injected (see arrow).

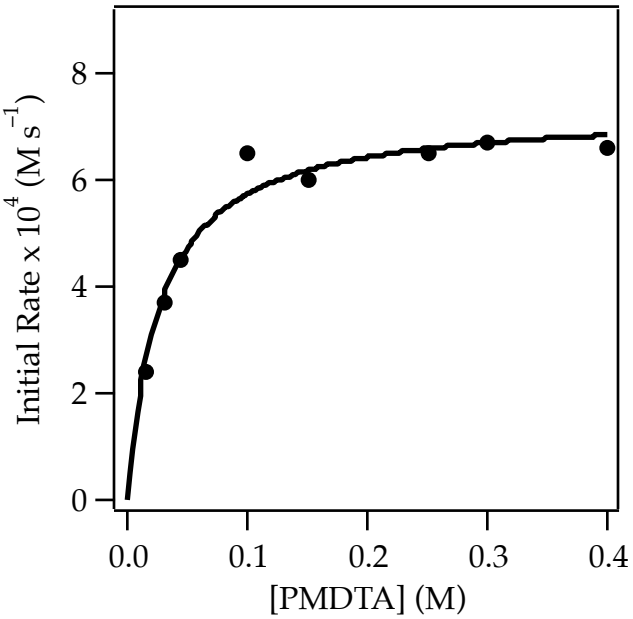


Figure S45. Plot of initial rate versus [PMDTA] in neat DMEA for the debromination of NaDA (0.10 M) with 1-bromooctane (0.033 M) at –60 °C. The curve depicts an unweighted least-squares fit to $y = ax/(1 + bx)$ ($a = (1.60 \pm 0.08) \times 10^4$, $b = (9.7 \pm 0.2) \times 10^5$).

[PMDTA] (M)	$y_1 \times 10^4 (s^{-1})$
0.015	2.3
0.030	3.8
0.045	4.2
0.10	5.4
0.15	5.7
0.25	6.4
0.30	6.8
0.40	6.6

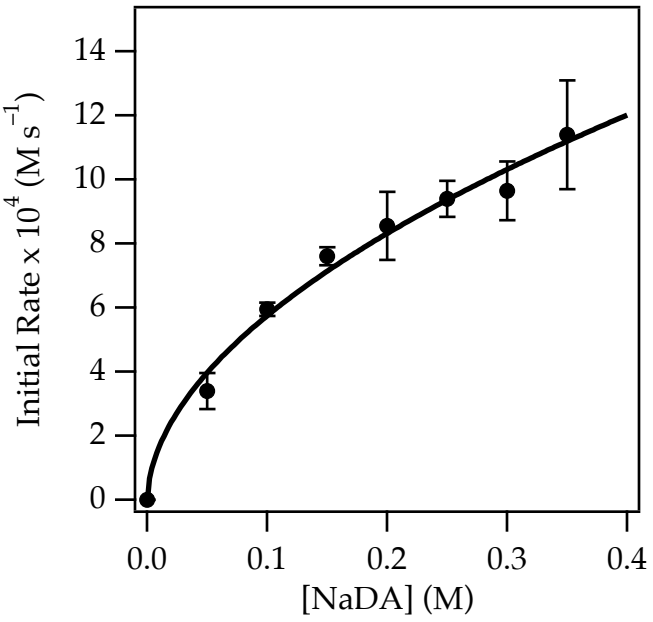
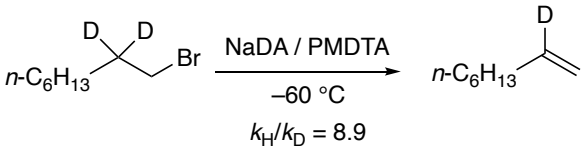


Figure S46. Plot of initial rate versus [NaDA] in neat DMEA for the deprotonation of 1-bromooctane (0.050 M) in the presence of 2.0 M PMDTA at –60 °C. The curve depicts an unweighted least-squares fit to $y = ax^n$ (a = (20 ± 1) x 10^4, n = 0.52 ± 0.06).

[NaDA] (M)	y_1 x $10^3(s^{-1})$	y_2 x $10^3(s^{-1})$	$y_{av.}$ x $10^3(s^{-1})$
0.05	3.8	3.0	3.4
0.10	5.8	6.1	6.4
0.15	7.4	7.8	7.6
0.20	9.3	7.8	8.6
0.25	9.8	9.0	9.4
0.30	9.0	10.3	9.7
0.35	10.2	12.6	11.4



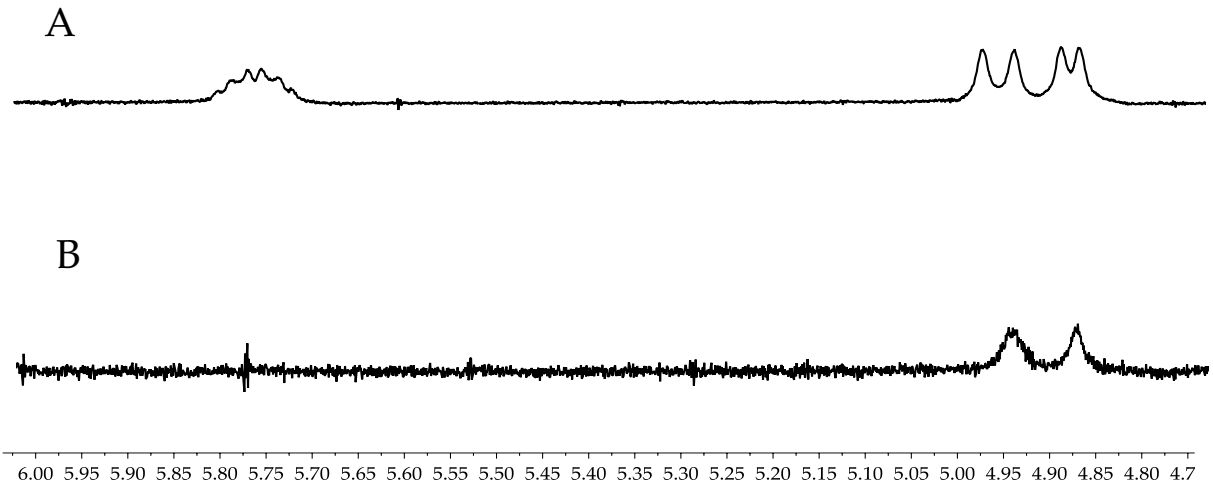
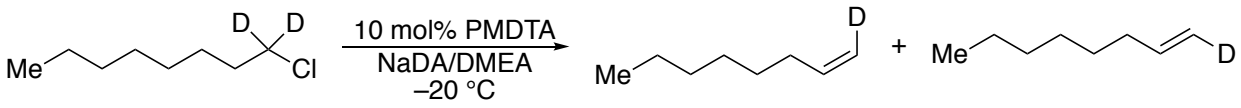


Figure S47. ^{1}H NMR spectra of NaDA (0.12 M) with the following substrates (0.08 M) in 0.15 M PMDTA/DMEA at at –60 °C: 1-bromooctane-2,2-d_2.



$k_H/k_D = 2$

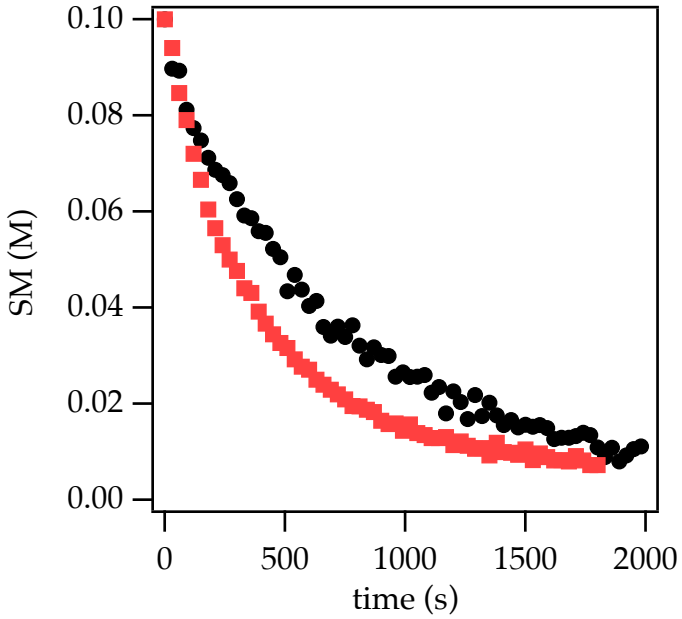


Figure S48. Plot of ^{1}H NMR spectra versus time for the elimination of 0.10 M Chlorooctane with 0.12 M NaDA in DMEA in the presence of 0.20 M PMDTA at –25 °C. Black = 1-chlorooctane; red = 1-chloro-1,1-dideuterio-chlorooctane: k_H/k_D = 2.0.

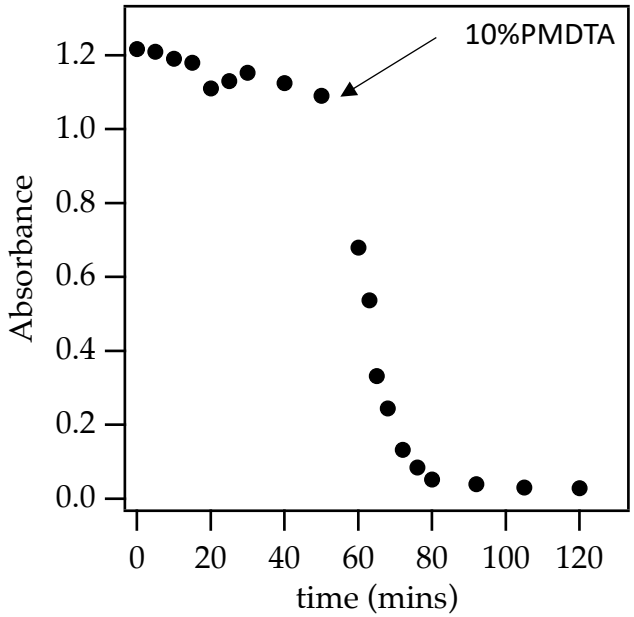


Figure S49. Elimination of 0.15 M 1-bromooctane (**9**) with solid NaDA (equiv of 0.16 M) suspended in hexane at –15 °C monitored by GC analysis of quenched aliquots. PMDTA (0.016 M, 0.10 equiv) was injected. (See arrow.)

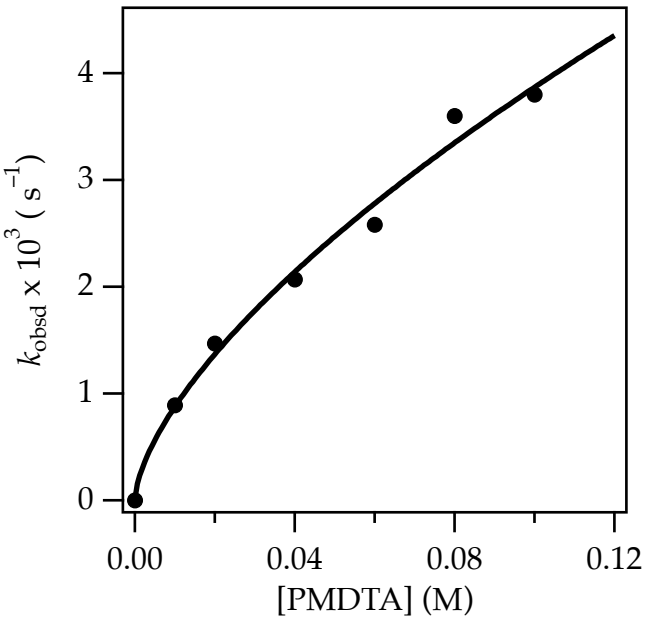


Figure S50. Plot of initial rates versus [PMDTA] in hexanes for the elimination of 1-bromooctane (**9**; 0.050 M) in the presence of 0.10 M NaDA at –40 °C. The curve depicts an unweighted least-squares fit to $y = ax^n$ (a = (1.7 ± 0.03) x 10^2, n = 0.65 ± 0.08).

[PMDTA] (M)	y_1 x 10^3(s^{-1})
10	2.5
20	3.7
40	5.5
60	6.0
80	7.9
100	9.6

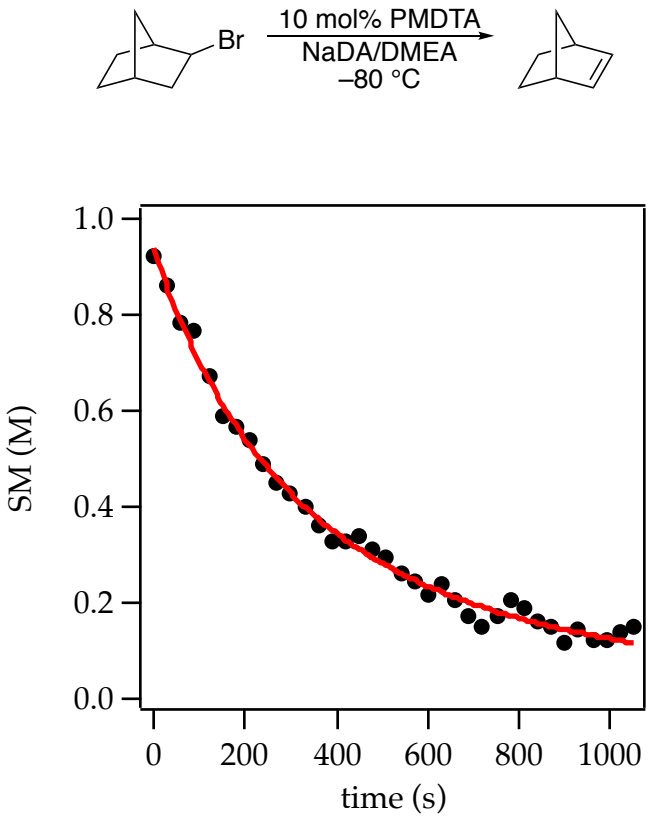


Figure S51. Plot of *exo*-2-bromonorbornane concentration versus time measured with ^{1}H NMR spectroscopy for the debromination of 0.10 M *exo*-2-bromonorbornane with 0.12 M NaDA in neat DMEA in the presence of 10% PMDTA at –78 °C. The curve depicts an unweighted least-squares fit to $y = ((n-1)k_{obsd}t + [A_0]^{-(n-1)})^{-1/n-1}$ ($n = 1.40 \pm 0.05$, $k_{obsd} = 0.0031 \pm 0.0002$, $[A]_0 = 0.93 \pm 0.01$).

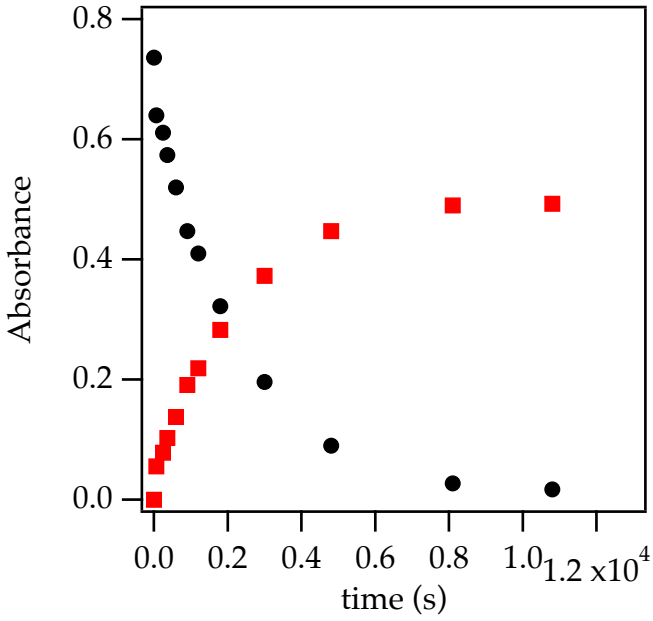


Figure S52. Plot of concentration versus time measured with GC for the debromination of 0.15 M *exo*-2-bromonorbornane with 0.16 M NaDA in hexanes in the presence of 10 mol% PMDTA at –30 °C. Black = *exo*-2-bromonorbornane; red = norbornene.

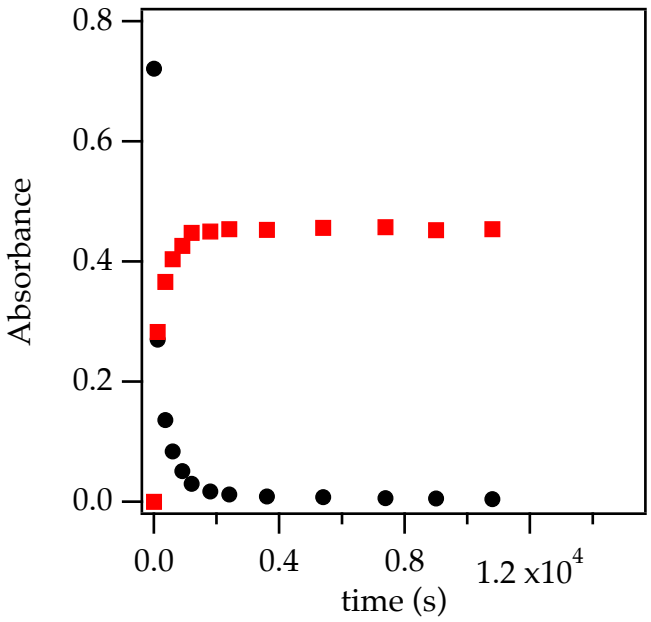


Figure S53. Plot of *exo*-2-bromonorbornane concentration versus time measured with GC spectroscopy for the debromination of 0.15 M *exo*-2-bromonorbornane with 0.16 M NaDA in hexanes in the presence of 1.0 equiv PMDTA at –30 °C. Black = *exo*-2-bromonorbornane; red = norbornene.

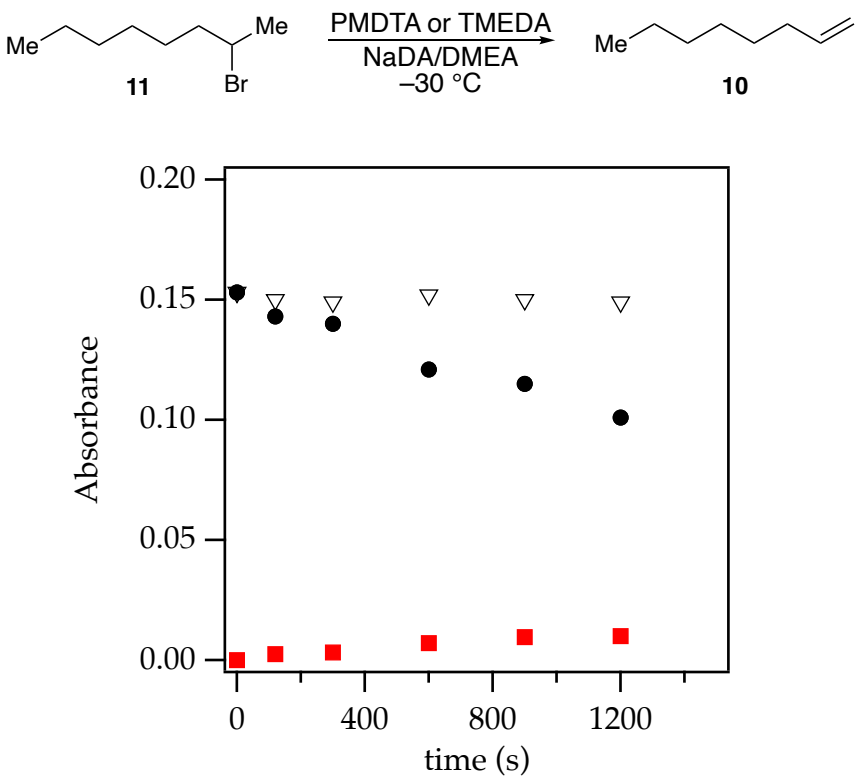


Figure S54. Plot of 2-bromooctane absorbance versus time measured with GC for the debromination of 0.15 M 2-bromooctane with 0.16 M NaDA in hexanes at –30 °C. Black = **11** and red = **10**. White triangles correspond to the elimination of **11** with no added PMDTA.

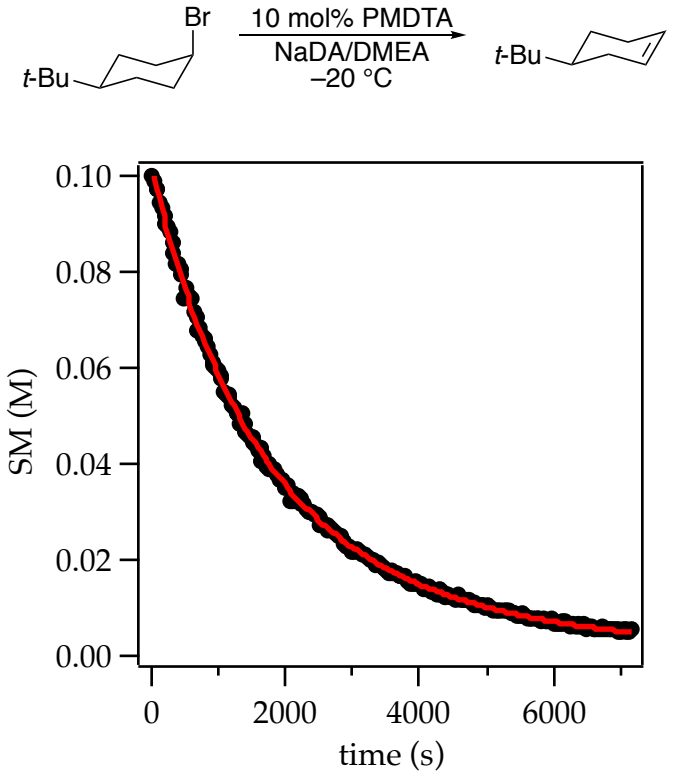


Figure S55. Plot of concentration versus time measured with ^{1}H NMR spectroscopy for the debromination of 0.10 M *cis*-*t*-butycyclohexanebromide (**12**) with 0.12 M NaDA in neat DMEA in the presence of 10 mol% PMDTA at–30 °C. The curve depicts an unweighted least-squares fit to $y = ((n–1)\ k_{obsd}t + [A_0]^{-(n-1)})^{-1/n-1}$ (n = 1.240 ± 0.005, k_{obsd} = 0.00093 ± 0.00001, $[A]_0$ = 0.100 ± 0.0001).

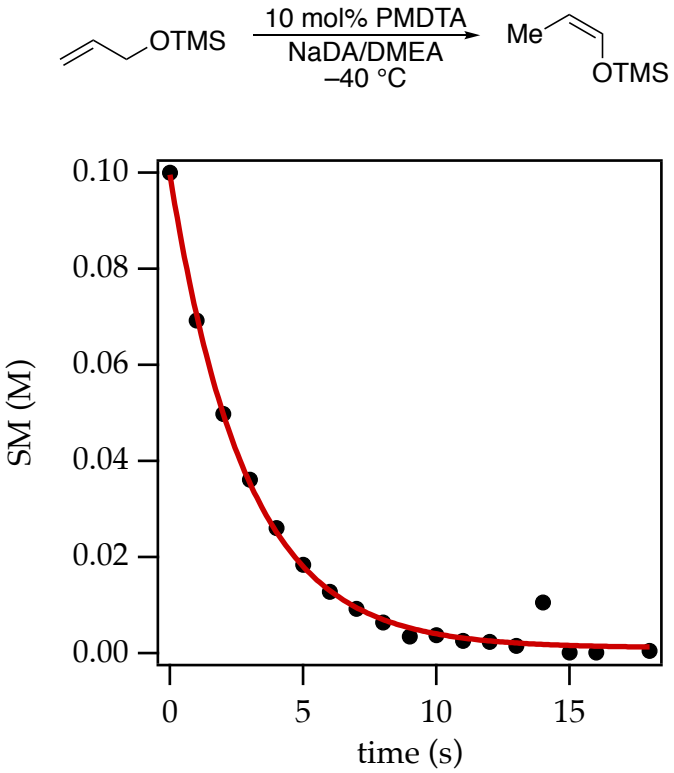


Figure S56. Plot of (allyloxy)trimethylsilane concentration versus time in neat DMEA, measured with ^{1}H NMR spectroscopy for the isomerization of 0.10 M (allyloxy)trimethylsilane with 0.12 M NaDA in neat DMEA in the presence of 10% PMDTA at –40 °C. The curve depicts an unweighted least-squares fit to y = $((n–1)k_{obsd}t + [A_0]^{-(n-1)})^{-1/n-1}$ (n = 1.88 ± 0.01, k_{obsd}= 0.0082 ± 0.0001, $[A]_0$ = 0.10 ± 0.01).

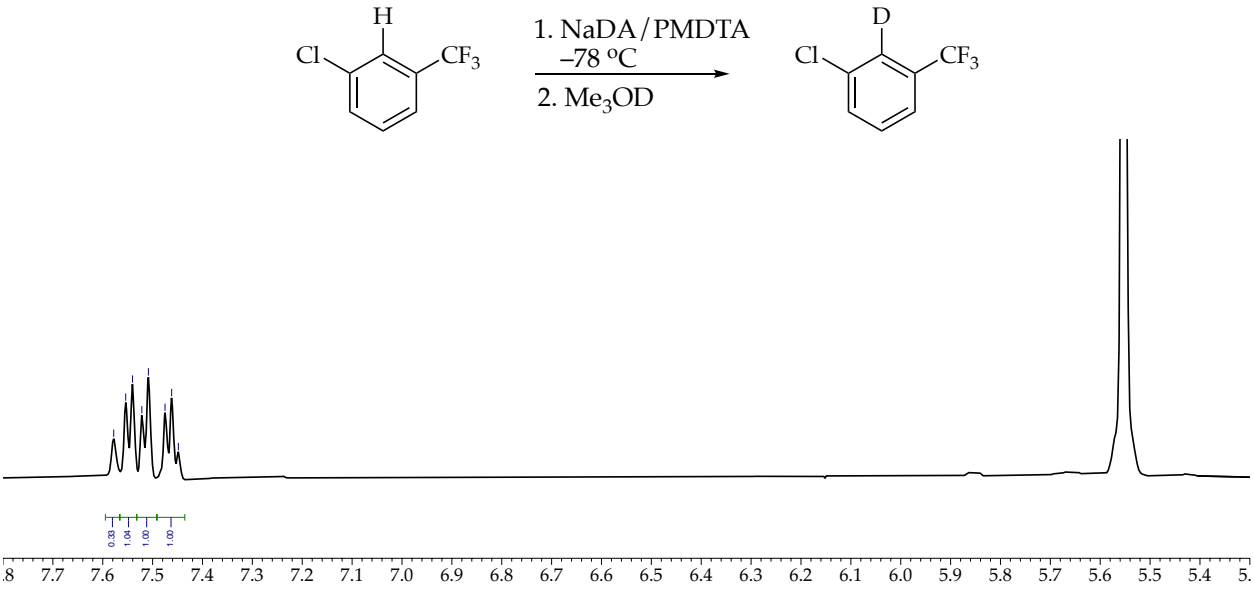
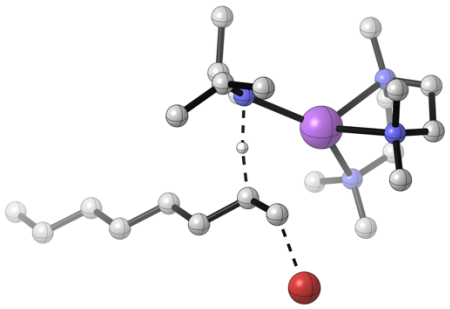


Figure S57. ^{1}H NMR spectrum for metalation of 0.40 M 3-chlorobenzotrifluoride with 0.40 M NaDA in 2.0 ml DMEA and 1.0 equiv PMDTA at –78 ºC after quenching by 200 µL MeOD with 100 µl cyclohexene as internal standard at 5.5 ppm. Loss of the resonance at 6.70 ppm indicates orthometalation at the two position.

Computations

DFT calculations were performed with the Gaussian 09 program package. Geometry optimizations and single point energies were computed at the M06-2X/def2-SVP level of theory and M06-2X/def2-TZVP level of theory respectively. A pruned (99,590) integration grid was used for all computations as well. CYLview Visualization Software was used for all ball-and-stick structures. Goodvibes (v3.0.1) was also used to streamline the extraction of thermochemical data. Thermal corrected single point energies (denoted as G(T)_SPC) are listed as well as other thermochemical data extracted using Goodvibes. For computed transition structures, the single imaginary frequency for each structure was extracted using Goodvibes and is included in the table as proof of a legitimate saddle point. All energies are in Hartrees and thermal corrections correspond to frequency calculations conducted at T = 195 K.

Table S3. Geometric coordinates and thermal corrected single point energies for NaDA/PMDTA-mediated anti elimination of 1-bromooctane via a monomer transition structure.



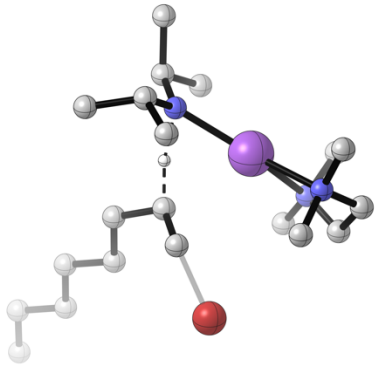
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-3864.2758	-3862.65	0.756823	-3863.4992	0.058019	0.05468	-3863.5572	-3863.5539

Imaginary frequency: -1365.46 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-1.3752810	-0.5772330	0.0494570	H	0.6834640	-0.2775950	0.9474350
N	0.2285620	-1.5126870	1.4686880	N	-3.1600140	-1.8746890	-1.0215670
C	0.3757510	-1.3992440	2.9111540	N	-3.5149370	0.5140540	0.8552340
H	0.3992050	-2.4025460	3.3793740	N	-1.3667210	0.1158460	-2.4745120
C	1.6727580	-0.6863920	3.3332810	C	-4.3167230	0.2760830	-0.3390540
H	2.5463420	-1.1305210	2.8312730	C	-2.5391550	-0.5415530	-3.0491770
H	1.6341010	0.3781440	3.0555830	C	-2.8152550	-1.9096910	-2.4415100
H	1.8368940	-0.7488190	4.4202080	C	-4.0511370	-0.1930920	2.0097480
C	-0.8368240	-0.6818140	3.4993050	H	-3.5113000	0.1183810	2.9118020
H	-1.7426190	-1.2795200	3.3226700	H	-5.1310770	0.0202870	2.1554440
H	-0.7325570	-0.5082170	4.5815980	H	-3.9181260	-1.2789400	1.9051290
H	-0.9711170	0.2991460	3.0109690	C	-3.4651870	1.9476320	1.1246980
C	0.9716010	-2.6168660	0.8944230	H	-4.4794320	2.3695230	1.2777970
H	2.0528450	-2.5778760	1.1706660	H	-2.8731220	2.1385470	2.0298830
C	0.4636550	-4.0016140	1.3201670	H	-2.9829370	2.4828510	0.2932720
H	1.0287930	-4.8028330	0.8183010	C	-4.4290900	-1.1880680	-0.7607180
H	0.5527900	-4.1652650	2.4024580	C	-3.1586950	-3.2260340	-0.4721380

H	-0.6012130	-4.1005760	1.0531860	H	-3.3088040	-3.1934170	0.6160350
C	0.9033370	-2.5134520	-0.6277200	H	-3.9467840	-3.8635040	-0.9213020
H	1.2681340	-1.5358530	-0.9709340	H	-2.1852180	-3.7005390	-0.6562710
H	1.4952370	-3.2968790	-1.1239700	C	-1.4432210	1.5662900	-2.6157580
H	-0.1460170	-2.6303980	-0.9598520	H	-0.5588300	2.0387280	-2.1662140
C	7.1903790	-0.1634360	-0.6640880	H	-1.5070250	1.8732580	-3.6796300
H	7.3693060	0.8008570	-1.1686300	H	-2.3246490	1.9607990	-2.0896350
H	7.4675230	-0.0081140	0.3920210	C	-0.1541660	-0.3659980	-3.1279320
C	5.7042680	-0.4994830	-0.7442190	H	-0.1445770	-0.0892420	-4.2020220
H	5.4230380	-0.6558330	-1.8009440	H	0.7335130	0.0714780	-2.6514710
H	5.5204900	-1.4633990	-0.2374030	H	-0.0754190	-1.4580800	-3.0504130
C	4.8030670	0.5693010	-0.1351480	H	-5.0879930	-1.2344550	-1.6502430
H	4.9804490	1.5326580	-0.6445250	H	-5.3530280	0.6531180	-0.1878890
H	5.0876940	0.7281090	0.9198270	H	-4.9646680	-1.7367070	0.0276020
C	3.3187540	0.2273960	-0.2039760	H	-3.8822510	0.8791100	-1.1474760
H	3.1376550	-0.7305750	0.3151040	H	-3.4173670	0.1053550	-2.9151230
H	3.0360580	0.0592650	-1.2603260	H	-2.4239250	-0.6613780	-4.1461140
C	2.4157000	1.3003280	0.3954350	H	-3.6231130	-2.3994880	-3.0266730
H	2.5984980	2.2626590	-0.1217370	H	-1.9202980	-2.5418940	-2.5530400
H	2.7154660	1.4680480	1.4462110	C	8.0799720	-1.2388100	-1.2770650
C	0.9411720	0.9402770	0.3504160	H	9.1447840	-0.9756630	-1.2073240
H	0.6204310	0.7789190	-0.6965050	H	7.9380710	-2.2038630	-0.7674200
C	0.0565410	1.8944060	1.0160700	H	7.8397640	-1.3888890	-2.3405930
H	0.3710250	2.1628170	2.0323960				
H	-1.0065710	1.6289620	1.0186390				
Br	-0.0847620	3.7972790	0.1512200				

Table S4. Geometric coordinates and thermal corrected single point energies for NaDA/TMEDA-mediated anti elimination of 1-bromooctane via a monomer transition structure.



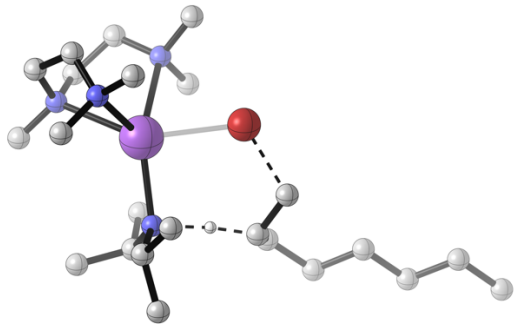
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-3691.0101	-3689.5786	0.652632	-3690.3392	0.056006	0.052163	-3690.3952	-3690.3914

Imaginary frequency: -1344.52 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-2.0658480	0.3319240	0.4409970	H	7.9093170	-0.9952270	1.7578350
N	-1.4133950	2.4364220	-0.0777210	H	8.1373630	-1.3735720	0.0395210
C	-1.7026200	3.1439680	-1.3103400	H	-0.3378890	1.5150160	-0.3464320
H	-2.4924000	3.9083420	-1.1528290	N	-3.6266170	-1.3724300	-0.3325360
C	-0.4834550	3.8706130	-1.8984660	N	-1.6369870	-1.5149060	1.9643350
H	-0.7288390	4.3753500	-2.8455540	C	-2.2129510	-2.6683610	1.2718770
H	-0.0992520	4.6323530	-1.2036830	C	-3.5998630	-2.4157350	0.6942030
H	0.3299520	3.1509060	-2.0877790	C	-4.9658650	-0.8170780	-0.4821510
C	-2.2630200	2.1537070	-2.3312020	H	-4.9592280	-0.0313050	-1.2502410
H	-3.1572360	1.6528120	-1.9234710	H	-5.7028900	-1.5881600	-0.7840290
H	-2.5505770	2.6514320	-3.2690150	H	-5.3008970	-0.3694010	0.4647310
H	-1.5133750	1.3850170	-2.5780160	C	-0.2620860	-1.8141300	2.3535590
C	-0.9782720	3.2704660	1.0282880	H	0.1997530	-0.9247380	2.8058160
H	0.0355850	3.6985910	0.8473800	H	-0.2221880	-2.6419210	3.0904650
C	-1.9062360	4.4537460	1.3214640	H	0.3222420	-2.0994950	1.4678620

H	-1.5933710	4.9819020	2.2351140	C	-2.4136900	-1.1248910	3.1330490
H	-1.9121760	5.1857210	0.5014420	H	-2.5588420	-1.9704210	3.8369940
H	-2.9385780	4.0916080	1.4600690	H	-1.8895250	-0.3200900	3.6664310
C	-0.8615080	2.4012830	2.2828540	H	-3.4058300	-0.7432740	2.8484250
H	-0.2076630	1.5323130	2.1058130	H	-1.5133630	-2.9521020	0.4692330
H	-0.4455960	2.9626070	3.1323720	H	-2.2809690	-3.5376070	1.9609900
H	-1.8633430	2.0409490	2.5806610	H	-3.9904850	-3.3712350	0.2888030
C	6.9740850	0.4282220	0.4040700	H	-4.2909010	-2.1241740	1.4991260
H	7.1854710	0.8846930	-0.5774860	C	-3.1551410	-1.8901020	-1.6149320
H	6.9588040	1.2605970	1.1276880	H	-3.8427800	-2.6642200	-2.0113310
C	5.5950280	-0.2233270	0.3636560	H	-3.0958540	-1.0727100	-2.3484240
H	5.6055660	-1.0559260	-0.3613660	H	-2.1549210	-2.3362570	-1.5168120
H	5.3798160	-0.6815600	1.3452680	H	2.1770410	1.4947790	-1.4029120
C	4.4725920	0.7438480	0.0025310	H	2.0253460	1.9294720	0.2925160
H	4.6891290	1.2019270	-0.9788620	C	0.5635540	0.5081390	-0.3787010
H	4.4611610	1.5772610	0.7275490	H	0.3586950	0.0301490	0.5965490
C	3.0949260	0.0907100	-0.0419270	C	0.1613790	-0.3628790	-1.4787240
H	2.8722480	-0.3648080	0.9404420	H	0.5455870	-0.0604020	-2.4607390
H	3.1042340	-0.7442390	-0.7611010	H	-0.9137760	-0.5638930	-1.5578850
C	1.9758330	1.0706900	-0.4018200	Br	0.7813970	-2.3888180	-1.4084790
				C	8.0857650	-0.5495540	0.7671210
				H	9.0691390	-0.0591960	0.7896830

Table S5. Geometric coordinates and thermal corrected single point energies for NaDA/PMDTA-mediated syn elimination of 1-bromooctane via a monomer transition structure.



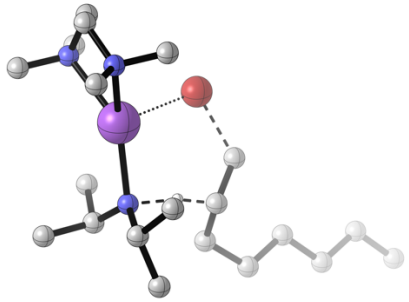
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-3864.2778	-3862.6531	0.756805	-3863.5015	0.057376	0.054151	-3863.5588	-3863.5556

Imaginary frequency: -1035.64 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-7.5275250	-1.1554400	0.1175860	Na	1.5714810	-0.0303230	0.0002170
H	-7.1876470	-2.1869110	-0.0752040	H	-1.1182350	1.2473750	0.1236110
H	-7.3217220	-0.9633490	1.1839590	N	1.9622350	-2.4003180	-0.9845180
C	-6.7025300	-0.1921910	-0.7305630	N	3.3151780	-0.1352920	1.6724190
H	-6.9088990	-0.3792390	-1.7992040	N	3.8573910	-0.0420670	-1.3160570
H	-7.0354130	0.8425790	-0.5355640	C	4.3304050	-0.9406000	1.0118220
C	-5.2007570	-0.2919990	-0.4801570	C	3.2283600	-2.4523160	-1.7010640
H	-4.8659580	-1.3244620	-0.6891930	C	3.6744670	-1.1208710	-2.2852470
H	-5.0061290	-0.1161030	0.5919850	C	4.8609030	-0.3546430	-0.2937120
C	-4.3870350	0.6886780	-1.3186500	C	4.2352560	1.1676500	-2.0374690
H	-4.6934650	1.7168050	-1.0563700	H	3.4633680	1.4267090	-2.7747090
H	-4.6566580	0.5538050	-2.3806920	H	4.3309290	2.0115730	-1.3414270
C	-2.8649750	0.5801840	-1.1731370	H	5.1988520	1.0443380	-2.5737550
H	-2.4112300	1.2970460	-1.8752050	C	0.8334390	-2.2899740	-1.9000690
H	-2.5343770	-0.4209660	-1.5106360	H	0.7456770	-3.1863700	-2.5490540
C	-2.3199720	0.8295610	0.2318020	H	-0.0944040	-2.1775880	-1.3209310

H	-2.7765970	1.7176800	0.6982380	H	0.9398820	-1.4086280	-2.5461120
C	-2.3955100	-0.2979380	1.1451890	C	1.7988120	-3.5818830	-0.1503030
H	-2.9022220	-1.2052760	0.8073140	H	1.8228840	-4.5139430	-0.7528070
H	-2.6017770	-0.0800130	2.1960250	H	2.6046840	-3.6381460	0.5967380
Br	-0.4820770	-1.3364090	1.4977560	H	0.8395420	-3.5286910	0.3804720
C	-9.0252880	-1.0494150	-0.1450930	C	2.8810500	-0.7927190	2.8951500
H	-9.5985830	-1.7511620	0.4767590	H	3.7076960	-0.8867840	3.6302420
H	-9.3911510	-0.0339150	0.0693130	H	2.0575510	-0.2307730	3.3554340
H	-9.2562650	-1.2677700	-1.1987190	H	2.5023520	-1.7983600	2.6606350
N	0.2607160	1.9019460	-0.0425340	C	3.7489470	1.2291240	1.9240950
C	0.3130050	2.8750830	1.0372470	H	4.7114740	1.2686820	2.4776030
H	1.3050710	3.3854220	1.0581780	H	3.8592150	1.7829950	0.9802030
C	-0.7372920	3.9992530	0.9661040	H	2.9858560	1.7506580	2.5160590
H	-0.6337320	4.6793440	1.8257250	H	5.2102810	-1.0863790	1.6792480
H	-0.6414320	4.6026190	0.0521040	H	3.8945260	-1.9347460	0.8431760
H	-1.7559550	3.5843720	0.9840940	H	5.6291950	-1.0468830	-0.6949930
C	0.1676760	2.1485500	2.3734570	H	5.4010210	0.5726480	-0.0552310
H	0.8735640	1.3080510	2.4369180	H	4.6209340	-1.3022530	-2.8409670
H	0.3393070	2.8272050	3.2233120	H	2.9421140	-0.7756270	-3.0324100
H	-0.8414590	1.7188040	2.4739140	H	4.0022740	-2.8253060	-1.0135170
C	0.2481720	2.4897190	-1.3671130	H	3.1839450	-3.1903580	-2.5312040
H	-0.7140010	3.0167310	-1.5812440	H	2.3361450	3.0622320	-1.3477930
C	1.3660760	3.5134140	-1.6110460	H	1.3994550	3.8258870	-2.6669240
H	1.2453400	4.4170060	-0.9978790	C	0.3706250	1.3675700	-2.3986860
				H	-0.3586520	0.5715020	-2.1879040
				H	0.2086780	1.7254650	-3.4270330
				H	1.3840650	0.9276840	-2.3544680

Table S6. Geometric coordinates and thermal corrected single point energies for NaDA/TMEDA-mediated syn elimination of 1-bromooctane via a monomer transition structure.



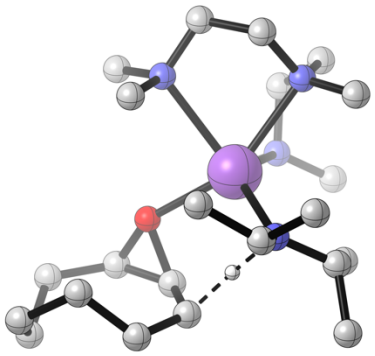
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-3691.0154	-3689.5836	0.652437	-3690.3448	0.055758	0.051908	-3690.4006	-3690.3968

Imaginary frequency: -814 cm^{-1}

Atom	X	Y	Z	Atom	X	Y	Z
C	-7.0569670	-1.5879480	0.1067710	H	-0.7482080	0.9921720	0.1833120
H	-6.8476710	-2.1366820	-0.8268420	N	3.4216040	-1.1567730	-1.4324320
H	-6.5693660	-2.1631430	0.9117220	N	3.8726860	-0.4658770	1.4835430
C	-6.4186990	-0.2045260	0.0253440	C	4.0699930	-2.0306490	-0.4598600
H	-6.9063220	0.3750400	-0.7781640	C	4.7674370	-1.2926150	0.6762130
H	-6.6211490	0.3466490	0.9606390	C	3.1363550	-1.2712830	2.4522850
C	-4.9132840	-0.2407730	-0.2203300	C	4.6074860	0.5926250	2.1605300
H	-4.7114060	-0.7809130	-1.1631260	H	5.0917110	1.2492480	1.4237530
H	-4.4373030	-0.8333290	0.5803930	H	3.9176030	1.2023470	2.7596620
C	-4.2791940	1.1450020	-0.2829330	H	5.3871420	0.1885720	2.8381900
H	-4.4331620	1.6535850	0.6854350	C	4.3457940	-0.2285610	-2.0635960
H	-4.8207680	1.7479810	-1.0322810	H	4.7380130	0.4975080	-1.3369030
C	-2.7856380	1.1631720	-0.6180860	H	5.2044380	-0.7477930	-2.5392270
H	-2.4678280	2.2132260	-0.7122660	H	3.8154120	0.3389240	-2.8409200
H	-2.6267180	0.7092790	-1.6133990	C	2.7293160	-1.9568740	-2.4336890
C	-1.8741480	0.4712500	0.4002890	H	2.1839850	-1.3006410	-3.1257380
H	-2.0853130	0.8136300	1.4267650	H	3.4366900	-2.5786530	-3.0203760

C	-1.8602970	-0.9787920	0.3377400	H	1.9969430	-2.6120200	-1.9431050
H	-2.2318910	-1.4375090	-0.5829950	H	3.8167560	-1.7314640	3.1978540
H	-2.1333910	-1.5514250	1.2257820	H	2.4069580	-0.6432290	2.9838520
Br	0.1566480	-1.9248580	0.2210980	H	5.2895180	-2.0397290	1.3091520
C	-8.5611630	-1.5377890	0.3483320	H	5.5546650	-0.6458350	0.2622240
H	-8.9985710	-2.5444970	0.4030330	H	3.2947700	-2.7016080	-0.0543990
H	-8.7908990	-1.0195100	1.2915500	H	4.8240430	-2.6792160	-0.9575560
H	-9.0713790	-0.9929750	-0.4603180	H	2.5729780	-2.0676330	1.9478690
N	0.5176260	1.8718150	-0.0884120	H	-0.6101240	2.8676310	-1.6071760
C	0.5277850	2.8772700	0.9555870	C	1.4370370	3.4120010	-1.8349630
H	1.3657220	3.5954590	0.8084740	H	1.3518800	4.3347210	-1.2429660
C	-0.7490530	3.7299710	1.0453410	H	2.4468200	2.9967850	-1.6670970
H	-0.6533330	4.5092640	1.8173250	H	1.3463110	3.6879630	-2.8971720
H	-0.9592620	4.2334460	0.0892750	C	0.4385820	1.1907490	-2.4037590
H	-1.6206030	3.1055990	1.2975770	H	-0.2399400	0.3859210	-2.0807530
C	0.7877160	2.1813960	2.2920770	H	0.1812490	1.4811500	-3.4333560
H	1.7685970	1.6776560	2.2764690	H	1.4627720	0.7748610	-2.4236830
H	0.7857480	2.8885050	3.1350710	Na	1.9826330	0.1540850	0.0278460
H	0.0194690	1.4139230	2.4776690				
C	0.3758350	2.3759890	-1.4394360				

Table S7. Geometric coordinates and thermal corrected single point energies for NaDA/PMDTA-mediated pro-cis opening of cyclooctene oxide via a monomer transition structure.



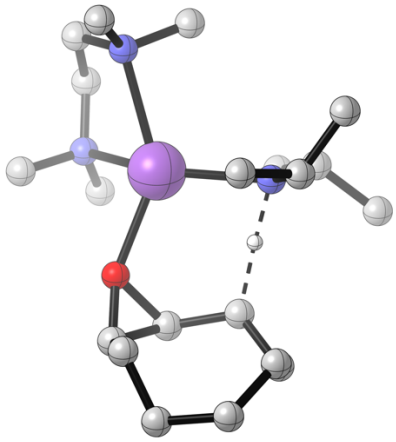
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1363.4563	-1362.0594	0.729768	-1362.7094	0.050567	0.048771	-1362.7599	-1362.7581

Imaginary frequency: -1203.56 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-1.7868490	-0.5963300	1.3993680	C	1.1993040	-2.5126020	2.0843840
C	-2.1639150	-2.0166900	1.1447890	C	2.6107180	-0.8248030	2.9999520
C	-3.7140080	0.0826840	-1.0093430	H	3.1145190	-2.3371800	-1.8734580
C	-3.3961300	-2.5980420	0.4694330	H	2.4831170	-1.7747700	-3.4210010
C	-4.8508300	-0.9124680	-0.7929340	H	1.5190810	-3.7272490	-1.0247870
C	-4.6828900	-1.7619430	0.4623420	H	-0.2092030	-3.3097670	-1.1693580
H	-1.7245530	-2.7292200	1.8607960	H	0.7373850	-3.7491120	-2.6305740
H	-3.1212270	-2.8695600	-0.5653450	H	0.0304760	-1.6258750	-3.6429200
H	-2.7798550	-0.4677310	-1.2077100	H	-0.8971010	-1.2678870	-2.1429700
H	-4.9324800	-1.5828460	-1.6664160	H	0.2949450	-0.1033710	-2.7457070
H	-1.1113320	-0.5389660	2.2699870	H	3.9847370	-0.1184430	-2.5036520
H	-3.9275400	0.6616210	-1.9213330	H	2.3460750	0.5501660	-2.5748370
H	-5.8049530	-0.3630280	-0.7322150	H	4.6964220	-1.0869210	-0.4238080
H	-5.5462380	-2.4397010	0.5464660	H	4.3434690	-0.0345680	0.9396150
H	-4.7039630	-1.1228920	1.3597440	H	2.5302320	2.1972250	-0.9931240
C	-2.2794930	0.7600460	1.0598270	H	3.3274220	1.8856600	0.5508480

H	-1.1386850	1.4922590	0.4979480	H	4.3023120	1.8598770	-0.9535540
H	-2.3830720	1.2961320	2.0184860	H	3.8917740	-2.4348830	1.4035420
C	-3.5133940	1.0225550	0.1943120	H	2.6756690	-2.4628270	0.1143190
H	-4.4498850	1.0096920	0.7868590	H	1.7466200	-3.3471320	2.5715350
H	-3.4353140	2.0598730	-0.1736350	H	0.4058290	-2.1792760	2.7690260
O	-1.1525580	-1.4161460	0.3470090	H	0.7186910	-2.8764090	1.1660830
N	-0.1189950	2.1995880	0.0374930	H	3.2595380	0.0345250	2.7848590
C	-0.6656450	3.0602270	-1.0027410	H	1.7880150	-0.4646360	3.6328470
C	0.4105900	2.9389010	1.1757530	H	3.1990220	-1.5706480	3.5748770
H	-1.5882980	3.5720020	-0.6452470	H	1.6226860	1.2535400	1.8174280
H	1.3092200	3.5216280	0.8742180	H	-3.6033270	-3.5494140	0.9804820
C	-1.0705970	2.2124810	-2.2027680	Na	0.6595750	-0.0872490	0.0367290
H	-1.6164340	1.3152450	-1.8797810	N	1.0955810	-1.8137910	-1.8057690
H	-1.7068620	2.7765300	-2.9018120	N	3.0026910	0.1858980	-0.6432190
H	-0.1677620	1.8950110	-2.7508520	N	2.0773680	-1.3944570	1.7744960
C	0.2827930	4.1668770	-1.4779900	C	2.4380190	-1.5957890	-2.3254200
H	0.5347460	4.8818900	-0.6821400	C	0.7734460	-3.2206610	-1.6551050
H	1.2233430	3.7279640	-1.8503430	C	0.0829610	-1.1725700	-2.6308260
H	-0.1737590	4.7345530	-2.3033330	C	2.9709170	-0.1915990	-2.0519520
C	-0.5737110	3.9370400	1.8080230	C	3.8641720	-0.6637730	0.1751300
H	-0.1319310	4.4136110	2.6966520	C	3.3182030	1.6025860	-0.5106460
H	-0.8551700	4.7366330	1.1083210	C	3.1373400	-1.8161000	0.8683810
H	-1.4961910	3.4199240	2.1137460				
C	0.8789570	1.9464870	2.2369540				
H	1.3401360	2.4555390	3.0967390				
H	0.0285360	1.3523830	2.6098510				

Table S8. Geometric coordinates and thermal corrected single point energies for NaDA/TMEDA-mediated pro-cis opening of cyclooctene oxide via a monomer transition structure.



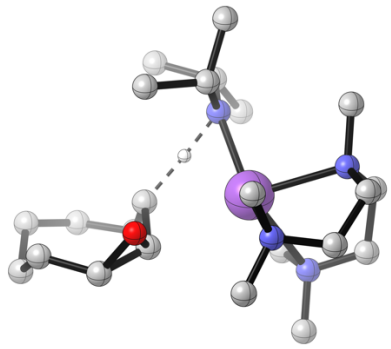
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1190.1967	-1188.9934	0.625598	-1189.5556	0.048091	0.045978	-1189.6037	-1189.6015

Imaginary frequency: -1135.79 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-1.6170550	-1.5980980	1.0791130	H	2.8649890	-2.8383470	2.6156590
C	-1.8517520	-2.4994860	-0.0642870	C	2.3899320	-2.9344310	-0.0239120
C	-4.0106290	0.4436890	-0.4229250	H	3.1777280	-3.6860230	0.1938550
C	-2.6569520	-2.1013400	-1.2742200	H	1.4019760	-3.3775600	0.1486230
C	-4.7981260	-0.6997880	-1.0739360	H	2.4470490	-2.6706620	-1.0903340
C	-4.1613850	-2.0860600	-0.9459780	H	3.1634800	1.5296370	0.3968850
H	-1.9067560	-3.5748750	0.1615090	H	-1.8908700	2.6038970	-0.5384760
H	-2.3223890	-1.1075050	-1.5977510	H	0.8844200	3.2282390	1.2335960
H	-3.1501570	0.7161620	-1.0518150	C	-0.7773050	1.5749140	-2.0461790
H	-4.9422020	-0.4627970	-2.1417840	H	-1.1443700	0.5578360	-1.8412610
H	-1.3859060	-2.1482440	2.0027600	H	-1.3919380	2.0008220	-2.8536250
H	-4.6646730	1.3306340	-0.4345170	H	0.2627300	1.4977190	-2.4098900
H	-5.8082060	-0.7432100	-0.6340520	C	-0.1974750	3.7931180	-1.0624190
H	-4.7092960	-2.7935270	-1.5859350	H	-0.2919220	4.4822120	-0.2118080

H	-4.3003240	-2.4470210	0.0864600	H	0.8749250	3.6964730	-1.2982580
C	-2.0332180	-0.1776670	1.2366510	H	-0.6928440	4.2606380	-1.9267320
H	-1.0596110	0.7887640	0.6544940	C	-1.0280900	3.0625090	2.1884630
H	-1.8311370	0.0603650	2.2953590	H	-0.7070190	3.6484490	3.0635420
C	-3.5129100	0.1946460	1.0157580	H	-1.5722240	3.7390600	1.5128340
H	-4.2101120	-0.5188170	1.5035460	H	-1.7361210	2.2916980	2.5284970
H	-3.6554430	1.1367970	1.5695240	C	0.9004780	1.4762290	2.4498720
O	-0.5551110	-1.9642720	0.0871930	H	0.2553580	0.6229880	2.7116310
N	-0.1713300	1.6631500	0.2850480	H	1.8189730	1.0771450	1.9883420
C	-0.8155360	2.4225240	-0.7744370	H	1.1848860	1.9904770	3.3799430
C	0.1730380	2.4122560	1.4825680	H	-2.4327890	-2.7946440	-2.0993650
Na	0.9008150	-0.2974100	-0.2558040	C	3.2334210	1.5746730	-0.6977310
N	3.1349640	0.2399370	-1.2748290	H	4.1912340	2.0651420	-0.9688560
N	2.5235360	-1.7500710	0.8107950	H	2.3946160	2.1935180	-1.0423520
C	3.8337020	-1.1294330	0.6935390	C	3.2371390	0.3117580	-2.7236680
H	3.8692670	-0.2799990	1.3945810	H	3.0898270	-0.6844870	-3.1647060
H	4.6410930	-1.8276300	1.0068810	H	2.4613870	0.9824030	-3.1185340
C	4.1461250	-0.6559650	-0.7225810	H	4.2237260	0.6977000	-3.0535710
H	5.1465860	-0.1740190	-0.7213590	C	2.1969150	-2.0596640	2.1924990
H	4.2295350	-1.5281380	-1.3874950	H	2.2835690	-1.1555160	2.8110240
				H	1.1587960	-2.4174820	2.2450010

Table S9. Geometric coordinates and thermal corrected single point energies for NaDA/PMDTA-mediated pro-trans opening of cyclooctene oxide via a monomer transition structure.



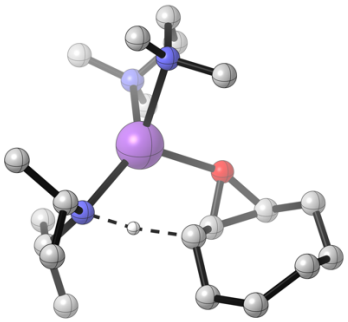
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1363.4441	-1362.0472	0.729815	-1362.697	0.05132	0.049185	-1362.7483	-1362.7461

Imaginary frequency: -1234.89 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	2.3785260	-2.3538000	-0.9154640	H	-1.3862500	3.8866440	-1.5456270
C	1.5165850	-1.4035800	-0.1853430	C	0.3995930	3.0338650	2.0200270
C	4.9718990	-0.4236050	0.4374010	H	0.7448540	3.9136960	2.5831300
C	1.9319900	-0.0413620	0.2844920	H	-0.6647930	2.8716890	2.2509120
C	4.1549740	0.0759260	1.6380610	H	0.9693510	2.1593480	2.3724620
C	2.6421790	-0.2065350	1.6395370	C	2.0617550	3.5937580	0.2385240
H	0.7331310	-1.9052870	0.4205110	H	2.7197350	2.7450290	0.4869940
H	2.6525050	0.3418370	-0.4554150	H	2.2205500	3.8434670	-0.8199880
H	4.8172970	0.2526410	-0.4182160	H	2.3758600	4.4634910	0.8372780
H	4.3129250	1.1657480	1.7008650	Na	-0.8216090	-0.0988240	-0.0461790
H	2.1590890	-3.4258460	-0.8055620	N	-3.1441410	0.5812680	0.0359800
H	6.0329350	-0.3060320	0.7087890	N	-1.7263150	-1.1743520	2.0539440
H	0.9808510	1.0461570	0.1046440	N	-1.9712180	-1.7750260	-1.3732820
H	4.5883580	-0.3376190	2.5648330	C	-3.0870800	-0.6787050	2.2206280
H	2.2038970	0.4341970	2.4279200	H	-3.7859930	-1.4589840	1.8849540
H	2.4914110	-1.2402860	2.0102980	H	-3.3152670	-0.5092120	3.2952710

C	3.8094160	-2.0190060	-1.2666360	C	-3.3765270	0.6184180	1.4757980
H	3.8131760	-1.0897780	-1.8549160	H	-4.4299790	0.9001760	1.6949980
H	4.1921210	-2.8073900	-1.9323860	H	-2.7485370	1.4265990	1.8829780
C	4.7466030	-1.8705750	-0.0478460	C	-3.9591740	-0.3938430	-0.6833060
H	4.3822870	-2.5005830	0.7826520	H	-4.9532970	-0.5226880	-0.2066500
H	5.7248120	-2.2893290	-0.3257450	H	-4.1630060	0.0132170	-1.6842690
O	1.3376920	-1.6424430	-1.5808710	C	-3.3261610	-1.7784020	-0.8434900
N	0.1326840	2.0317680	-0.1801940	H	-4.0021010	-2.3814140	-1.4907180
C	0.5942350	3.2193050	0.5163170	H	-3.2851840	-2.2936150	0.1251570
H	-0.0193420	4.0992400	0.2363820	C	-3.2807240	1.9290240	-0.5021740
C	-0.0516600	2.1460630	-1.6285450	H	-2.5133100	2.5704520	-0.0455140
H	-0.8817480	1.4548070	-1.9069200	H	-3.1007310	1.9216150	-1.5861760
C	1.1442490	1.6797880	-2.4830690	H	-4.2876830	2.3556470	-0.3155530
H	0.9091220	1.7739790	-3.5558910	C	-1.4049180	-3.1136740	-1.2998320
H	2.0400260	2.2837330	-2.2763940	H	-1.9979280	-3.8446320	-1.8886450
H	1.3918600	0.6282930	-2.2837230	H	-0.3764750	-3.0909630	-1.6806340
C	-0.5190100	3.5222970	-2.1151800	H	-1.3868990	-3.4494090	-0.2522110
H	0.2814490	4.2720050	-2.0215040	C	-1.8884320	-1.2578420	-2.7304050
H	-0.8010760	3.4715440	-3.1775600	H	-2.2506150	-0.2203670	-2.7730680
H	-1.8334350	-2.6686060	3.5733110	H	-0.8361800	-1.2623740	-3.0488250
C	-0.7605840	-0.3470580	2.7666170	H	-2.4846640	-1.8646610	-3.4444860
H	-0.9703430	-0.3130440	3.8560600	C	-1.6189070	-2.5552160	2.4902680
H	0.2515440	-0.7478670	2.6181170	H	-2.3271600	-3.1886480	1.9360970
H	-0.7594690	0.6812390	2.3805770	H	-0.6015560	-2.9282880	2.3029030

Table S10. Geometric coordinates and thermal corrected single point energies for NaDA/TMEDA-mediated pro-trans opening of cyclooctene oxide via a monomer transition structure.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1190.1927	-1188.9894	0.624781	-1189.5518	0.050398	0.04738	-1189.6022	-1189.5992

Imaginary frequency: -1039.11 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	1.6598610	-2.1576770	1.4077980	H	3.3178150	1.6928230	0.1431170
C	1.4163840	-0.7116740	1.2665990	H	3.5689870	0.3894680	1.2765650
C	4.1125150	-1.5297990	-1.0301810	C	2.3949320	-2.9345950	0.3396700
C	1.7822870	0.1186650	0.0798230	H	1.8544200	-2.8250180	-0.6116620
C	4.2523570	-0.0302460	-0.7240760	H	2.3554630	-4.0036680	0.5984060
C	3.2325390	0.5943510	0.2424650	C	3.8651540	-2.4974180	0.1464890
H	1.3383550	-0.1616170	2.2192600	H	4.2502700	-2.0641890	1.0857000
H	1.6892790	-0.5124670	-0.8212080	H	4.4638940	-3.4033300	-0.0265830
H	3.3075170	-1.6788460	-1.7679750	O	0.3435550	-1.6765020	1.1200290
H	4.1976450	0.4983870	-1.6906700	N	-0.0740710	2.1398960	0.0167570
H	1.7401980	-2.5670840	2.4233000	C	-0.1239300	3.0702000	1.1302820
H	5.0352790	-1.8356100	-1.5481460	H	-0.5136240	4.0541430	0.7991750
H	0.8709500	1.2697360	0.0676290	C	-0.0488380	2.6981960	-1.3203240
H	5.2675700	0.1653330	-0.3388420	H	0.1805330	1.8383540	-1.9870580
H	1.1998030	4.0078100	2.6165940	C	1.0543760	3.7369250	-1.5711380
Na	-0.9216080	0.0021150	0.0912670	H	1.0689350	4.0589890	-2.6238180

N	-1.9029700	-1.2489450	-1.7592610	H	0.8997900	4.6343860	-0.9507940
N	-2.8444750	-1.0202790	1.1034970	H	2.0402140	3.3150960	-1.3245500
C	-2.9052340	-2.2387440	0.3028970	C	-1.4110130	3.2542190	-1.7524200
H	-1.9868390	-2.8101940	0.5113770	H	-1.6989630	4.1082470	-1.1181180
H	-3.7619080	-2.8737670	0.6188040	H	-1.4035270	3.6034120	-2.7972420
C	-3.0296890	-1.9886470	-1.1967110	H	-2.1893850	2.4827670	-1.6437070
H	-3.1550290	-2.9667120	-1.7057060	C	-1.0934830	2.5437230	2.1935610
H	-3.9502750	-1.4222990	-1.3988040	H	-1.1539170	3.2007590	3.0752190
C	-0.7607900	-2.1205620	-2.0039010	H	-2.1011970	2.4332170	1.7643640
H	-0.9896810	-2.8880760	-2.7718860	H	-0.7542280	1.5506280	2.5399400
H	0.0949890	-1.5227040	-2.3511330	C	1.2545050	3.3098760	1.7661800
C	-2.2725740	-0.5358140	-2.9717230	H	1.6674680	2.3548610	2.1312440
H	-3.0999510	0.1574280	-2.7656800	H	1.9632070	3.7138860	1.0306270
H	-1.4173090	0.0536390	-3.3308750	H	-3.3985660	-1.9621990	2.9373050
H	-2.5854820	-1.2251050	-3.7828860	C	-4.0323070	-0.1939870	0.9681500
C	-2.5865650	-1.3457770	2.4988650	H	-4.9615980	-0.7533410	1.2062880
H	-1.6361250	-1.8909440	2.5731610	H	-3.9598870	0.6603790	1.6542810
H	-2.5017880	-0.4196580	3.0846270	H	-4.1190020	0.2103090	-0.0502590
				H	-0.4573490	-2.6204660	-1.0743370