Supporting Information

Encapsulation of Protonated Diamines in a Water-Soluble Chiral, Supramolecular Assembly Allows for Measurement of Hydrogen-Bond Breaking Followed by Nitrogen Inversion/Rotation (NIR)

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Experimental

General Procedures. All NMR spectra were obtained using a Bruker AV-500 MHz spectrometer at the indicated frequencies. Chemical shifts are reported as parts per million (δ) and referenced to residual protic solvent peaks. The following abbreviations are used in describing NMR couplings: (s) singlet, (d) doublet, (t) triplet, (q) quartet, b (broad), m (multiplet). The temperature of all variable temperature NMR experiments was calibrated with methanol or ethylene glycol standards.[1] Selective Inversion Recovery (SIR)[2] experiments were performed at constant temperature using a 10 second delay time between experiments. Data points for each Selective Inversion Recovery experiment were measured from 0.0005 seconds to 18 seconds in 42 increments. In all cases, the efficiency of the inversion pulse was greater than 70%.

Determination of $\Delta G^{\ddagger}_{inv}$ using the coalescence temperature method. Analysis of coalescence data using lineshape analysis was not possible due to both encapsulation and guest exhange effecting the peak width of encapsulated substrates. Activation energies for inversion were determined using the coalescence method by determining the coalescence temperature (T_c) and chemical shift difference at the slow exchange limit ($\Delta\upsilon$) using the equation 2 from the manuscript:[7] The uncertainty in $\Delta G^{\ddagger}_{inv}$ was calculated using differential error analysis by the following equation:

$$\sigma(\Delta G^{\ddagger}_{inv}) = \sqrt{\left(\frac{\partial(\Delta G^{\ddagger}_{inv})}{\partial(\delta\upsilon)}\right)^2 \sigma^2(\Delta\upsilon) + \left(\frac{\partial(\Delta G^{\ddagger}_{inv})}{\partial(T_c)}\right)^2 \sigma^2(T_c)}$$

The uncertainty in $\Delta G^{\ddagger}_{exch}$ was calculated using differential error analysis by the following equation using the uncertainty for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the least-squares linear fit:

$$\sigma(\Delta G^{\ddagger}_{exch}) = \sqrt{\left(\frac{\partial(\Delta G^{\ddagger}_{exch})}{\partial(\Delta H^{\ddagger})}\right)^2 \sigma^2(\Delta H^{\ddagger}) + \left(\frac{\partial(\Delta G^{\ddagger}_{exch})}{\partial(\Delta S^{\ddagger})}\right)^2 \sigma^2(\Delta S^{\ddagger}) + 2\left(\frac{\partial(\Delta G^{\ddagger}_{exch})}{\partial(\Delta H^{\ddagger})}\right)\left(\frac{\partial(\Delta G^{\ddagger}_{exch})}{\partial(\Delta S^{\ddagger})}\right)\sigma(\Delta H^{\ddagger})\sigma(\Delta S^{\ddagger}) + \left(\frac{\partial(\Delta G^{\ddagger}_{exch})}{\partial(T_c)}\right)^2 \sigma^2(T_c)}$$

***N,N,N′,N′*-tetramethyl-2,2-dimethyl-1,3-propanediamine (7)** A 100 mL round bottom flask containing 2,2-dimethyl-1,3-propanediamine (5.1 mL, 42.5 mmol) was cooled to 0 °C in an ice bath and formic acid (24.2 mL, 510 mmol) was added cautiously followed by a 37% solution of formaldehyde in water (20.7 mL, 255 mmol). The reaction mixture was heated to reflux overnight and cooled to room temperature at which point 10 mL of concentrated HCl was added and the solvent removed under vacuum to afford a brown solid. The solid was redissolved in 20 mL of H_2O and KOH pellets were added with cooling in an ice bath until the pH of the solution was greater than 12. The basic solution was extracted with ether (3 x 50 mL) and the extracts were dried over $MgSO_4$. The solvents were removed by rotary evaporator to leave a light yellow oil which was distilled under vacuum to afford 4.8 g (72%) of the title compound. ^{1}H NMR (500MHz, $CDCl_3$): δ 2.24 (s, 12H, 4x NCH_3), 2.13 (s, 4H, 2x CH_2), 0.92 (s, 6H, 2x CH_3). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$): δ 67.1 (*C*H_2), 49.4 (N*C*H_3), 31.4 (*C*$(CH_2)_2$), 25.0 (*C*H_3). MS (ES+): m/z = 159 ($[M + H]^+$).

[*N,N,N′,N′*-tetramethylethylenediamine-H^+ ⊂ Ga_4L_6]$^{11-}$ ([2-H^+ ⊂ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD): δ 8.19 (d, *J* = 7.8 Hz, 12H, *aryl*), 7.88 (d, *J* = 8.5 Hz, 12H, *aryl*), 7.32 (dd, *J* = 8.0 Hz, 1.2Hz, 12H, *aryl*), 7.13 (t, *J* = 8.0 Hz, 12H, *aryl*), 6.68 (dd, *J* = 7.0 Hz, 1.2Hz, 12H, *aryl*), 6.38 (t, *J* = 8.0 Hz, 12H, *aryl*). Guest: -0.35 (s, 12H, N-CH_3), -0.58 (m, 4H, CH_2). Below T_c: ^{1}H NMR (500MHz, MeOD, 220K): δ 8.23 (bs, 12H, *aryl*), 7.84 (d, *J* = 7.5 Hz, 12H, *aryl*), 7.33 (d, *J* = 8.5Hz, 12H, *aryl*), 7.12 (bs, 12H, *aryl*), 6.72 (d, *J* = 7.5 Hz, 12H, *aryl*),

6.41 (t, *J* = 7.6Hz, 12H, *aryl*). Guest: -0.11 (s, 6H, N-CH_3), -0.44 (bs, 2H, CH_2), -0.74 (s, 6H, N-CH_3), -0.81 (bs, 2H, CH_2).

[*N,N,N′,N′*-tetramethyl-1,3-propanediamine-H^+ ⊂ Ga_4L_6]$^{11-}$ ([3-H^+ ⊂ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD): δ 8.17 (d, *J* = 7.8 Hz, 12H, *aryl*), 7.91 (d, *J* = 9.5 Hz, 12H, *aryl*), 7.31 (dd, *J* = 6.6 Hz, 1.5 Hz, 12H, *aryl*), 7.16 (t, *J* = 8.1 Hz, 12H, *aryl*), 6.68 (dd, *J* = 6.6 Hz, 1.5 Hz, 12H, *aryl*), 6.39 (t, *J* = 7.6 Hz, 12H, *aryl*). Guest: -0.46 (s, 12H, N-CH_3), -0.55 (dm, *J* = 16.8 Hz, 6.4 Hz, 4H, N-CH_2), -1.39 (quintet, *J* = 5.4 Hz, 2H, $NCH_2CH_2CH_2N$). Below T_c: ^{1}H NMR (500MHz, MeOD, 200K): δ 8.21 (bs, 12H, *aryl*), 7.83 (bs, 12H, *aryl*), 7.31 (bs, 12H, *aryl*), 7.09 (bs, 12H, *aryl*), 6.71 (bs, 12H, *aryl*), 6.39 (bs, 12H, *aryl*). Guest: -0.37 (s, 6H, N-CH_3), -0.50 (s, 6H, N-CH_3), -0.62 (bd, 4H, CH_2 (partially overlapping CH_3 resonance), -1.38 (bs, 2H, $NCH_2CH_2CH_2N$).

[*N,N,N′,N′*-tetramethyl-1,4-butanediamine-H^+ ⊂ Ga_4L_6]$^{11-}$ ([4-H^+ ⊂ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD): δ 8.17 (d, *J* = 7.6 Hz, 12H, *aryl*), 7.91 (d, *J* = 11.5 Hz, 12H, *aryl*), 7.31 (dd, *J* = 11.4 Hz, 1.5 Hz, 12H, *aryl*), 7.18 (t, *J*= 8.0 Hz, 12H, *aryl*), 6.67 (dd, *J* = 7.4 Hz, 1.6 Hz, 12H, *aryl*), 6.37 (t, *J* = 8.0 Hz, 12H, *aryl*). Guest: -0.31 (bs, 12H, N-CH_3), -0.72 (bm, 8H, CH_2), -1.07 (s, 4H, CH_2), -1.26 (bm, 2H, CH_2), -1.38 (bm, 2H, CH_2). Below T_c: ^{1}H NMR (500MHz, MeOD, 273K): δ 7.98 (bs, 12H, *aryl*), 7.84 (d, *J* = 7.5 Hz, 12H, *aryl*), 7.33 (d, *J* = 8.5 Hz, 12H, *aryl*), 7.06 (bs, 12H, *aryl*), 6.80 (d, *J* = 7.5 Hz, 12H, *aryl*), 6.64 (bs, 12H, *aryl*).

[*N,N,N′,N′*-tetramethyl-1,5-pentanediamine-H^+ ⊂ Ga_4L_6]$^{11-}$ ([5-H^+ ⊂ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD): δ 8.07 (bs, 12H, *aryl*), 7.78 (bs, 12H, *aryl*), 7.20 (d, *J* = 8.0 Hz, 12H, *aryl*), 7.03 (bs, 12H, *aryl*), 6.55 (d, *J* = 7.0 Hz, 12H, *aryl*), 6.29 (t, *J* = 8.0 Hz, 12H, *aryl*). Guest: -0.46 (bs, 12H, N-CH_3), -1.01 (bs, 4H, CH_2), -1.41 (bm, 4H, CH_2), -1.78 (bs, 4H, CH_2). Below T_c: ^{1}H NMR (500MHz, MeOD, 235K): δ 8.21 (d, *J* = 7.5 Hz, 12H, *aryl*), 7.87 (d, *J* = 8.5

Hz, 12H, *aryl*), 7.33 (d, J = 7.0 Hz, 12H, *aryl*), 7.15 (t, J = 8.0 Hz, 12H, *aryl*), 6.68 (d, J = 8.5 Hz, 12H, *aryl*), 6.41 (t, J = 7.5 Hz, 12H, *aryl*). Guest: -0.20 (s, 6H, N-CH_3), -0.66 (s, 6H, N-CH_3), -1.03 (dm, J = 46 Hz, 4H, CH_2), -1.16 (m, 2H, CH_2), -1.26 (m, 2H, CH_2), -1.73 (m, 2H, CH_2).

[*N,N,N′,N′*-tetramethyl-1,6-hexanediamine-$H^+ \subset Ga_4L_6]^{11-}$ ([6-$H^+ \subset$ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD): δ 8.18 (d, J = 7.6 Hz, 12H, *aryl*), 7.86 (d, J = 8.2 Hz, 12H, *aryl*), 7.33 (d, J = 8.2 Hz, 12H, *aryl*), 7.10 (bs, 12H, *aryl*), 6.68 (d, J = 6.8 Hz, 12H, *aryl*), 6.39 (t, J = 7.8 Hz, 12H, *aryl*). Guest: -0.40 (bs, 12H, N-CH_3), -0.75 (bm, 8H, CH_2), -1.95 (bs, 4H, CH_2). Below T_c: ^{1}H NMR (500MHz, MeOD, 273K): δ 8.19 (d, J = 7.6 Hz, 12H, *aryl*), 7.86 (d, J = 8.2 Hz, 12H, *aryl*), 7.34 (d, J = 8.2 Hz, 12H, *aryl*), 7.10 (t, J = 8.0 Hz, 12H, *aryl*), 6.68 (d, J = 6.8 Hz, 12H, *aryl*), 6.39 (t, J = 7.8 Hz, 12H, *aryl*). Guest: -0.31 (s, 6H, N-CH_3), -0.54 (s, 6H, N-CH_3), -0.67 (s, 2H, CH_2), -0.80 (s, 4H, CH_2), -0.86 (s, 2H, CH_2), -1.98 (bs, 4H, CH_2).

[*N,N,N′,N′*-tetramethyl-2,2-dimethyl-1,3-propanediamine-$H^+ \subset Ga_4L_6]^{11-}$ ([7-$H^+ \subset$ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD): δ 8.17 (d, J = 7.5 Hz, 12H, *aryl*), 7.90 (d, J = 7.4 Hz, 12H, *aryl*), 7.30 (d, J = 7.5 Hz, 12H, *aryl*), 7.14 (t, J = 8.0 Hz, 12H, *aryl*), 6.66 (d, J = 6.5 Hz, 12H, *aryl*), 6.39 (t, J = 8.0 Hz, 12H, *aryl*). Guest: -0.09 (s, 6H, N-CH_3), -0.13 (s, 6H, N-CH_3), -0.87 (dd, J = 19.0 Hz, J = 14.0 Hz, 4H, CH_2), -1.74 (s, 6H, CH_3). Above T_c: ^{1}H NMR (500MHz, MeOD, 340K): δ 8.16 (d, J = 7.5 Hz, 12H, *aryl*), 7.92 (d, J = 7.5 Hz, 12H, *aryl*), 7.48 (d, J = 6.5 Hz, 12H, *aryl*), 7.14 (t, J = 8.0 Hz, 12H, *aryl*), 6.51 (d, J = 7.5 Hz, 12H, *aryl*), 6.38 (t, J = 7.5 Hz, 12H, *aryl*). Guest: -0.06 (s, 12H, N-CH_3), -0.77 (d, J = 8.5 Hz, 2H, CH_2), -0.85 (d, J = 8.5 Hz, 2H, CH_2), -1.69 (s, 6H, CH_3).

[*N,N*-dimethylbenzylamine-$H^+ \subset Ga_4L_6]^{11-}$ ([8-$H^+ \subset$ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD, 334K): δ 8.12 (bs, 12H, *aryl*), 7.85 (d, *J* = 7.4 Hz, 12H, *aryl*), 7.40 (overlapping with free amine), 7.08 (t, *J* = 7.0 Hz, 12H, *aryl*), 6.73 (d, *J* = 7.0 Hz, 12H, *aryl*), 6.38 (t, *J* = 7.5 Hz, 12H, *aryl*). Guest: 6.17 (s, 1H, *aryl*), 5.48 (m, 1H, *aryl*), 4.69 (m, 1H, *aryl*), 4.44 (m, 1H, *aryl*), 4.32 (m, 1H, *aryl*), 0.98 (bs, 6H, CH_3), 0.86 (m, 1H, C-H), 0.48 (m, 1H, C-H). Below T_c: ^{1}H NMR (500MHz, MeOD, 245K): δ 8.19 (bs, 12H, *aryl*), 7.83 (d, *J* = 7.0 Hz, 12H, *aryl*), 7.40 (overlapping with free amine), 7.04 (t, *J* = 7.5 Hz, 12H, *aryl*), 6.70 (d, *J* = 7.0 Hz, 12H, *aryl*), 6.42 (t, *J* = 7.5 Hz, 12H, *aryl*). Guest: 6.14 (s, 1H, *aryl*), 5.50 (m, 1H, *aryl*), 4.65 (m, 1H, *aryl*), 4.41 (m, 1H, *aryl*), 4.37 (m, 1H, *aryl*), 1.34 (s, 3H, CH_3), 0.89 (m, 1H, C-H), 0.43 (m, 1H, C-H), -0.73 (s, 3H, CH_3).

[*N*,*N*-dimethylcyclohexylamine-H^+ ⊂ Ga_4L_6]$^{11-}$ ([9-H^+ ⊂ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD, 329 K): δ 8.12 (d, *J* = 7.8 Hz, 12H, *aryl*), 7.84 (d, *J* = 8.0 Hz, 12H, *aryl*), 7.30 (d, *J* = 7.5 Hz, 12H, *aryl*), 7.04 (t, *J* = 8.0 Hz, 12H, *aryl*), 6.66 (d, *J* = 7.6 Hz, 12H, *aryl*), 6.39 (t, *J* = 7.5 Hz, 12H, *aryl*). Guest: 0.17 (bs, 6H, N-CH_3), -0.43 – -0.99 (broad overlapping, 3H, CH_2, CH), -1.12 – -1.60 (broad overlapping, 6H, 3x CH_2), -1.78 – -1.98 (broad multiplet, 2H, 2x CH). Below T_c: ^{1}H NMR (500MHz, MeOD, 268K): δ 8.16 (d, *J* = 7.0 Hz, 12H, *aryl*), 7.83 (d, *J* = 7.4 Hz, 12H, *aryl*), 7.29 (d, *J* = 7.5 Hz, 12H, *aryl*), 7.06 (t, *J* = 7.0 Hz, 12H, *aryl*), 6.68 (d, *J* = 8.5 Hz, 12H, *aryl*), 6.41 (t, *J* = 7.5 Hz, 12H, *aryl*). Guest: 0.38 (s, 3H, N-CH_3), -0.13 (s, 3H, N-CH_3), -0.43 – -0.61 (broad overlapping, CH_2, CH), -0.84 (bs, 1H, CH), -1.18 (bs, 1H, CH), -1.24 – -1.36 (broad overlapping, 2x CH), -1.41 – -1.56 (broad overlapping, 2x CH), -1.76 (bs, 1H, CH), -2.12 (bs, 1H, CH).

[*N*,*N*-diisopropylethylamine-H^+ ⊂ Ga_4L_6]$^{11-}$ ([10-H^+ ⊂ 1]$^{11-}$)

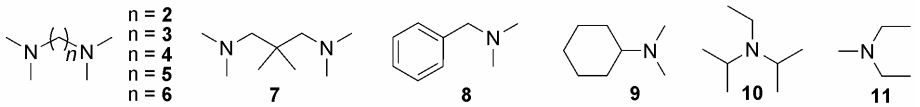
^{1}H NMR (500MHz, MeOD, 330K): δ 8.38 (d, *J* = 7.0 Hz, 12H, *aryl*), 7.90 (d, *J* = 7.5 Hz, 12H, *aryl*), 7.30 (d, *J* = 7.0 Hz, 12H, *aryl*), 7.15 (t, *J* = 7.5 Hz, 12H, *aryl*), 6.80 (d, *J* = 7.5 Hz, 12H,

aryl), 6.38 (t, *J* = 7.6 Hz, 12H, *aryl*). Guest: -0.27 (bm, 2H, C-H), -0.36 (m, 2H, CH_2), -0.99 (d, *J* = 5.5 Hz, 3H, CH_3), -1.13 (d, *J* = 5.5 Hz, 3H, CH_3), 1.20 (t, *J* = 6.5 Hz, 3H, CH_3), -1.49 (d, *J* = 6.0 Hz, 3H, CH_3), -1.95 (d, *J* = 6 Hz, 3H, CH_3). Below T_c: ^{1}H NMR (500MHz, MeOD, 273K): δ 8.21 (d, *J* = 7.6 Hz, 12H, *aryl*), 7.76 (d, *J* = 8.0 Hz, 12H, *aryl*), 7.33 (d, *J* = 7.6 Hz, 12H, *aryl*), 7.15 (t, *J* = 8.0 Hz, 12H, *aryl*), 6.68 (d, *J* = 7.0 Hz, 12H, *aryl*), 6.40 (t, *J* = 7.6 Hz, 12H, *aryl*). Guest: -0.28 (s, 1H, C-H), -0.39 (m, 2H, CH_2), -0.57 (m, 1H, C-H), -0.69 (d, *J* = 5.5 Hz, 3H, CH_3), -1.08 (d, *J* = 6.0 Hz, 3H, CH_3), -1.28 (t, *J* = 7.0 Hz, 3H, CH_3), -1.61 (overlapping, 2x CH_3).

[*N*,*N*-diethylmethylamine-H^+ ⊂ Ga_4L_6]$^{11-}$ ([11-H^+ ⊂ 1]$^{11-}$)

^{1}H NMR (500MHz, MeOD, 273K): δ 8.15 (d, *J* = 7.5 Hz, 12H, *aryl*), 7.87 (d, *J* = 7.0 Hz, 12H, *aryl*), 7.30 (d, *J* = 8.0 Hz, 12H, *aryl*), 7.11 (t, *J* = 7.5 Hz, 12H, *aryl*), 6.68 (d, *J* = 7.8 Hz, 12H, *aryl*), 6.40 (t, *J* = 7.0 Hz, 12H, *aryl*). Guest: -0.36 – -0.50 (overlapping 2x CH_2, CH_3, 7H), -0.96 (s, 3H, CH_3), -1.19 (s, 3H, CH_3). Below T_c: ^{1}H NMR (500MHz, MeOD, 237K): δ 8.20 (d, *J* = 7.5 Hz, 12H, *aryl*), 7.84 (d, *J* = 7.0 Hz, 12H, *aryl*), 7.31 (d, *J* = 8.0 Hz, 12H, *aryl*), 7.09 (t, *J* = 8.0 Hz, 12H, *aryl*), 6.70 (d, *J* = 6.5 Hz, 12H, *aryl*), 6.42 (t, *J* = 7.5 Hz, 12H, *aryl*). Guest: -0.41 (m, 2H, CH_2), -0.48 (s, 3H, CH_3), -0.72 (m, 2H, CH_2), -0.92 (t, *J* = 7.5 Hz, 3H, CH_3), -1.26 (t, *J* = 6.0 Hz, 3H, CH_3).

Table S1 Comparison of activation parameters for guest exchange ($\Delta G^{\ddagger}_{exch}$) and energy barriers for hydrogen-bond breaking followed by NIR in **1** ($\Delta G^{\ddagger}_{coal}$).



Guest	$\Delta G^{\ddagger}_{exch}$ [a] (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	T_c [b] (K)	$\Delta\nu$ [c] (Hz)	$\Delta G^{\ddagger}_{coal}$ (kcal mol^{-1})	$\Delta\Delta G^{\ddagger}$ [d] (kcal mol^{-1})
2	17.2 ± 0.8	20.8 ± 0.8	14.8 ± 0.8	244	311	11.0 ± 0.2	6.2 ± 0.8
3	16.9 ± 1.0	15.9 ± 1.0	-3.8 ± 0.4	231	344	10.3 ± 0.2	6.6 ± 1.0
4	19.1 ± 0.8	18.4 ± 0.8	-2.1 ± 0.4	344[e]	321	15.7 ± 0.2	3.4 ± 0.8
5	15.1 ± 0.3	10.3 ± 0.3	-16.4 ± 0.5	293	244	13.5 ± 0.2	1.6 ± 0.4
6	15.0 ± 0.8	16.2 ± 0.8	4.2 ± 0.3	288	323	13.1 ± 0.2	1.9 ± 0.8
7	19.7 ± 0.9	20.1 ± 0.9	1.3 ± 0.1	339[e]	109	16.2 ± 0.2	3.5 ± 0.9
8	14.8 ± 1.0	15.1 ± 1.0	0.5 ± 0.1	328	1130	14.2 ± 0.2	0.6 ± 1.0
9	14.2 ± 0.5	15.9 ± 0.5	5.4 ± 0.3	326	313	14.9 ± 0.2	-0.7 ± 0.6
10	17.5 ± 1.0	19.2 ± 1.0	4.3 ± 0.2	347[e]	89	16.8 ± 0.2	0.7 ± 0.9
11	13.3 ± 1.0	17.9 ± 1.0	15.9 ± 1.0	293	124	13.8 ± 0.2	-0.5 ± 1.0

[a] Calculated at T_c. [b] ± 2 K. [c] ± 4 Hz. [d] $\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}_{exch} - \Delta G^{\ddagger}_{NIR}$ [e] Measured in a sealed NMR tube

In comparing the activation barriers for guests exchange ($\Delta G^{\ddagger}_{exch}$), for the monoprotonated amines, a strong correlation between the size of the amine is observed. Smaller substrates require a smaller dilation of the aperture of **1** to allow for guest exchange and would be expected to have lower activation barriers. Interestingly, for **5** and **6** this trend is broken. One possible explanation of this is that chelating amines **2-4** are still chelating the bound proton during guest ejection. However, as the alkyl chain between the two nitrogens is increased, as in the case of **5** and **6**, the amines may exit **1** in an un-chelated linear form thereby requiring a smaller dilation of the aperture of **1** and lowering the activation barrier for guest exchange. We surmise that the lack of trends for the hydrogen-bond breaking / NIR process in **1** is due to steric considerations. For smaller chelating amines, the proton is likely chelated more tightly thereby increasing the barrier for hydrogen-bond breaking. However, once the hydrogen bond is broken, the smaller amines have more space inside the cavity of **1** for the NIR process to occur. Conversely, for larger chelating amines, the hydrogen-bond breaking is likely more facile, but the NIR process is encumbered by the increased steric interactions with the interior of **1**.

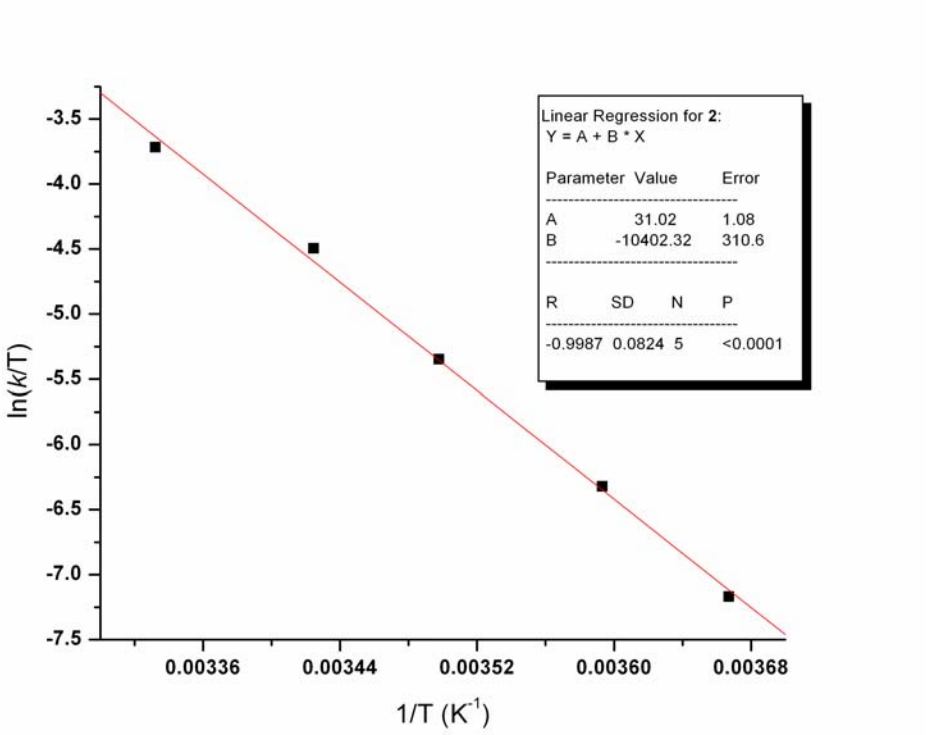


Figure S1. Eyring plot for the self exchange of **2**

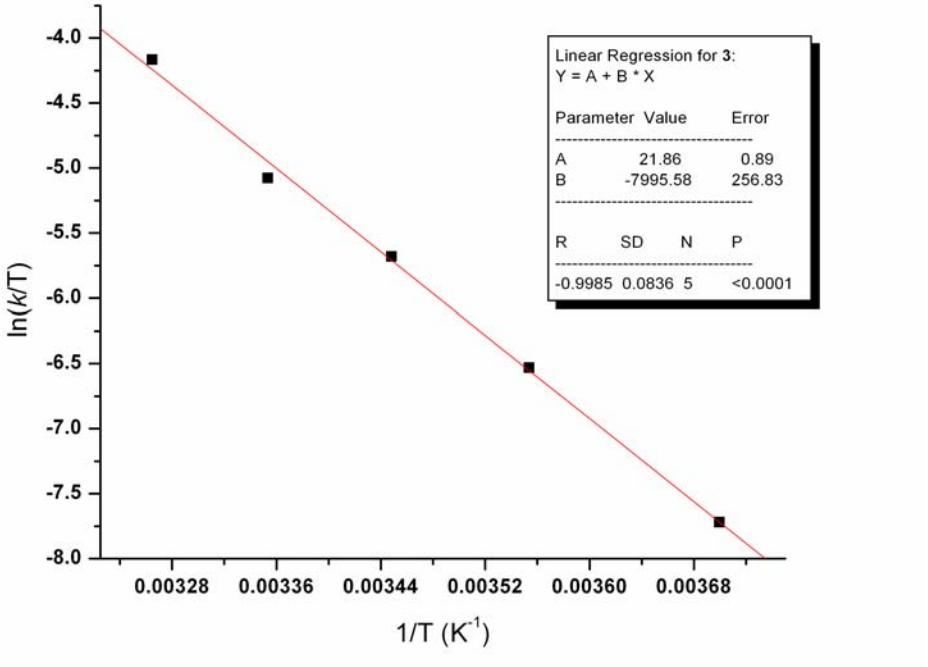


Figure S2. Eyring plot for the self exchange of **3**

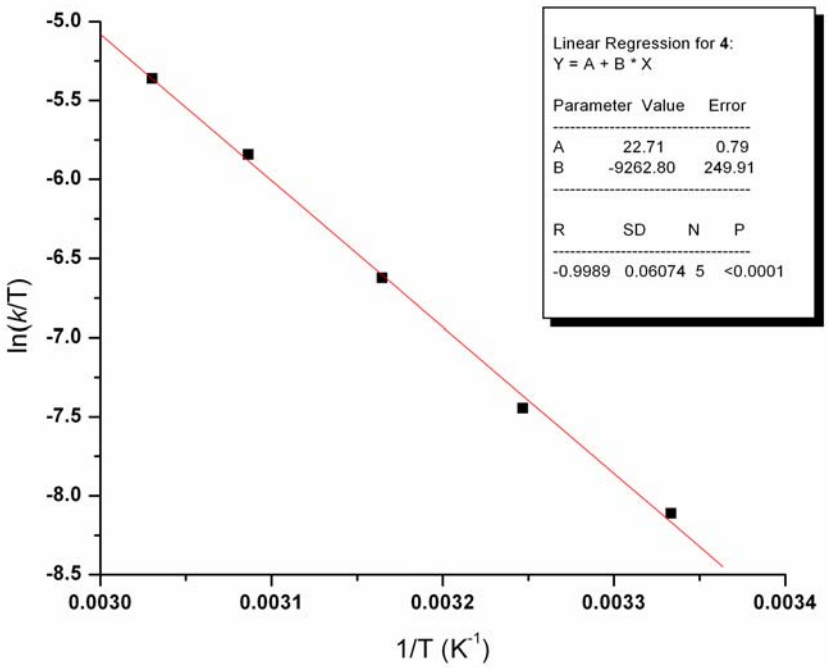


Figure S3. Eyring plot for the self exchange of **4**

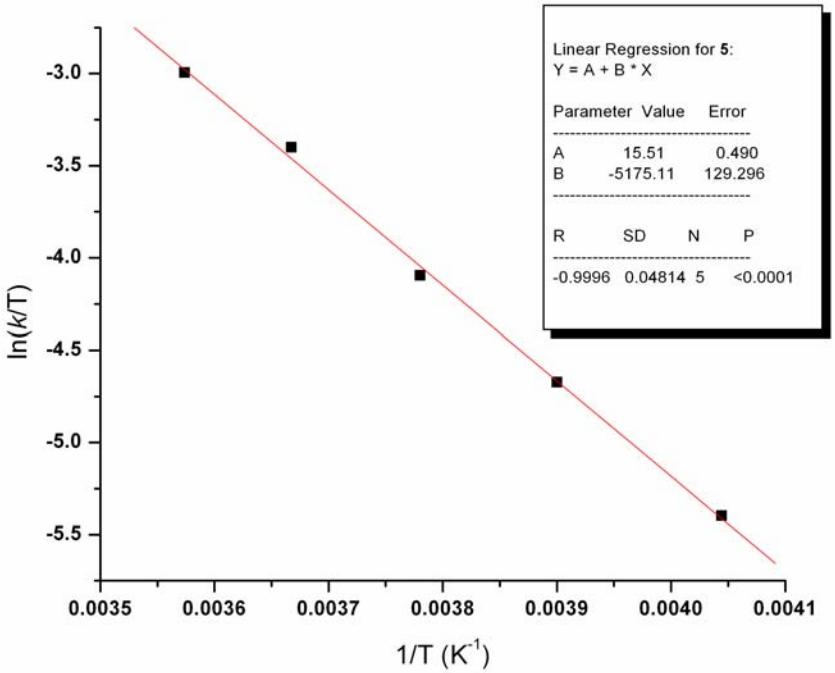


Figure S4. Eyring plot for the self exchange of **5**

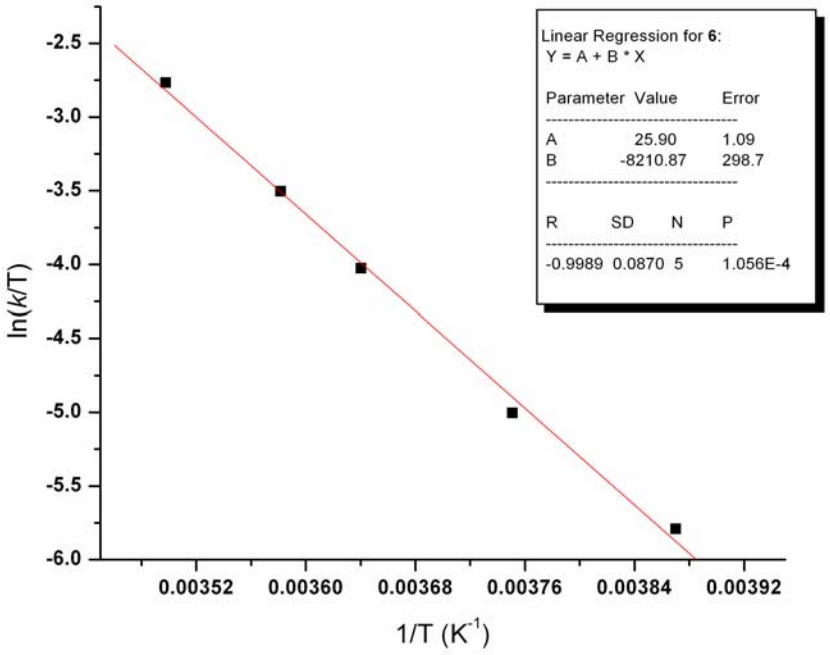


Figure S5. Eyring plot for the self exchange of **6**

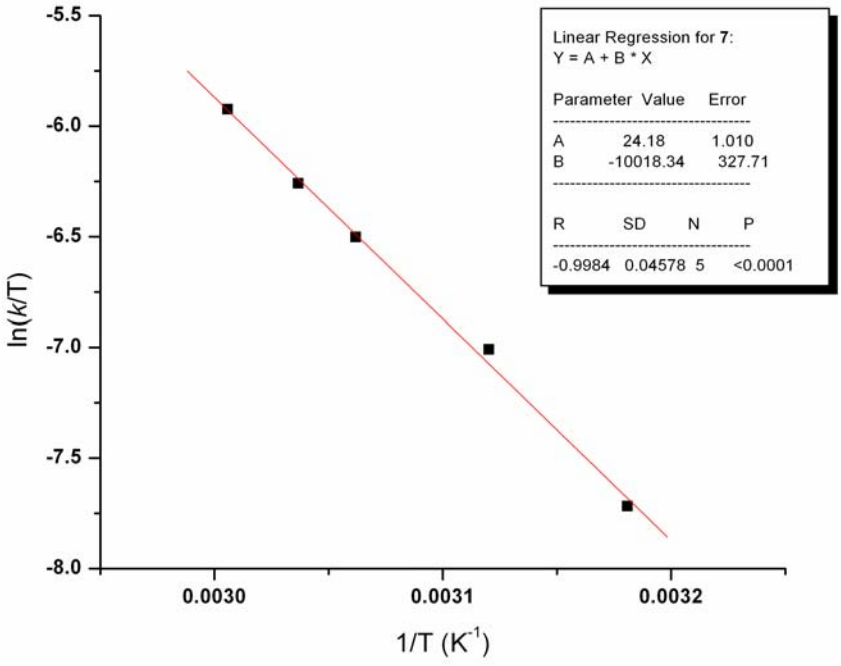


Figure S6. Eyring plot for the self exchange of **7**

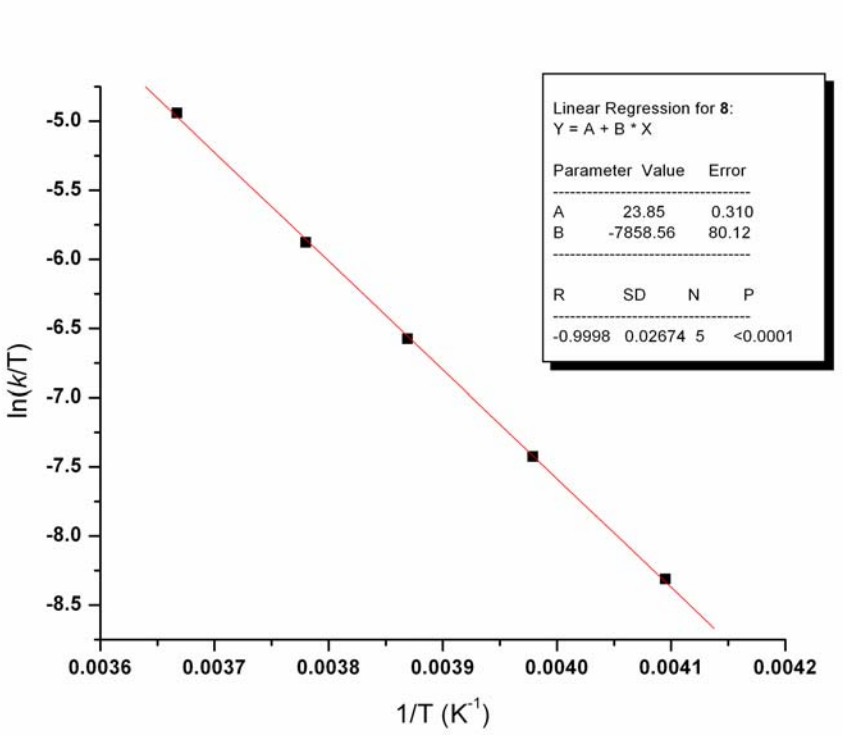


Figure S7. Eyring plot for the self exchange of **8**

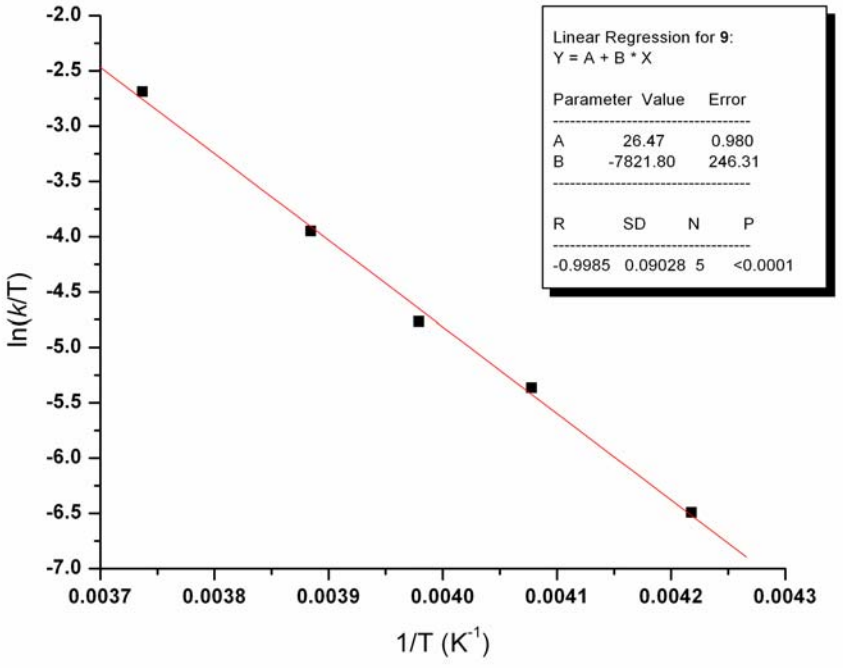


Figure S8. Eyring plot for the self exchange of **9**

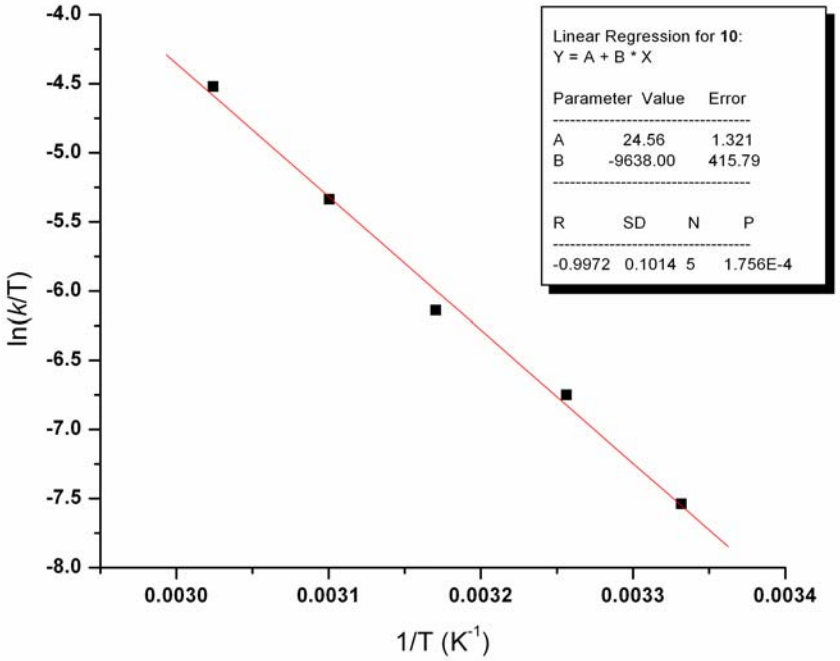


Figure S9. Eyring plot for the self exchange of **10**

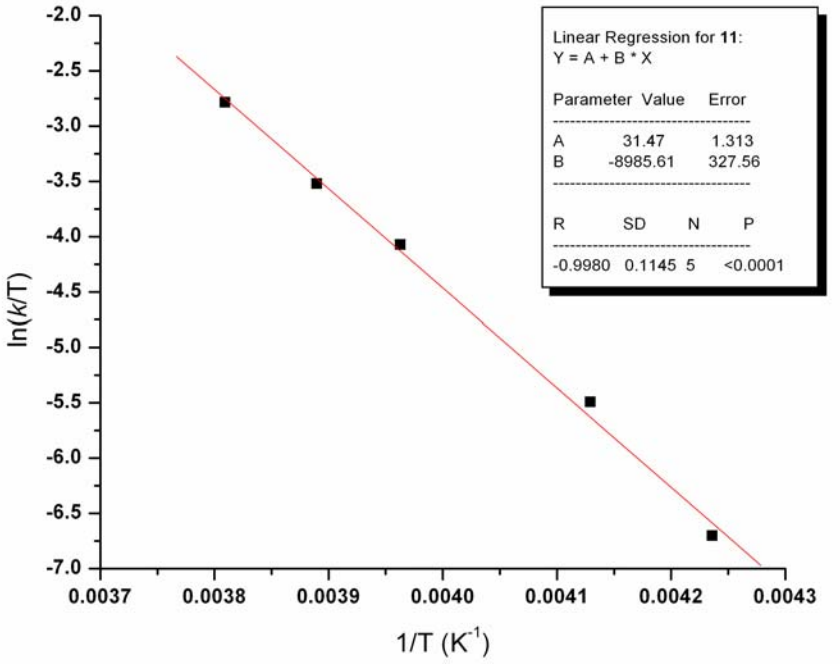


Figure S10. Eyring plot for the self exchange of **11**

Table S2. Unscaled frequencies for the located transition states.

Transition State	ν_{min} (cm^{-1})
TS1	-1097.3
TS2	-179.8
TS3	-118.2
TS4	-69.5
TS5	-202.6
TS6	-56.2

Table S3. Raw energies for the calculated ground states, intermediates, and transition states.

Structure	Energy (hartree)
2	-347.498254
2a	-347.498258
12	-347.481101
13	-347.482606
14	-347.479627
TS1	-347.494449
TS2	-347.480671
TS3	-347.472350
TS4	-347.481790
TS5	-347.473904
TS6	-347.477850

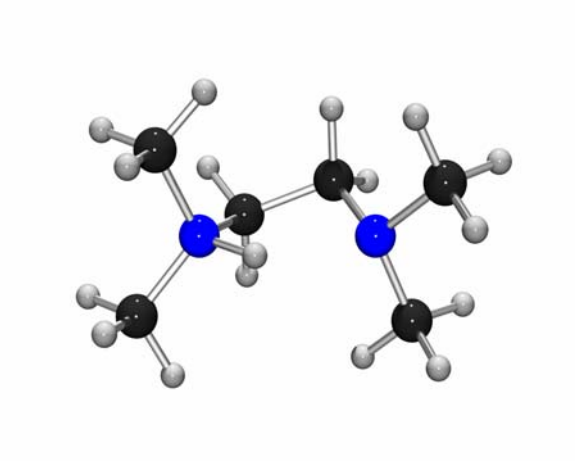


Figure S11. Calculated structure for **2**

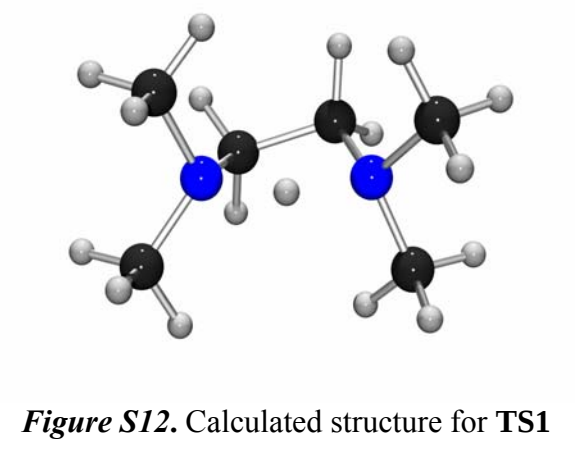


Figure S12. Calculated structure for **TS1**

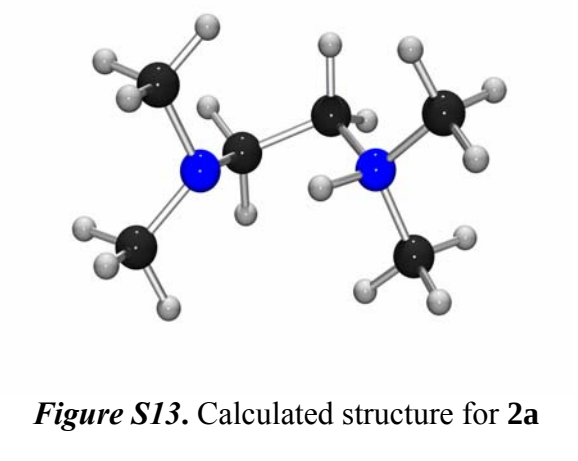


Figure S13. Calculated structure for **2a**

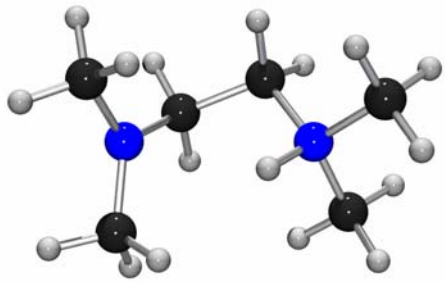


Figure S14. Calculated structure for **TS2**

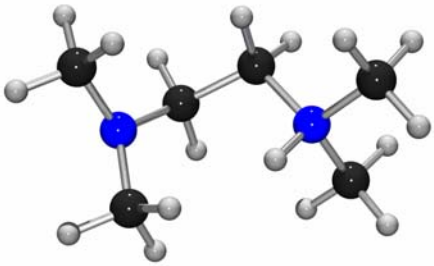


Figure S15. Calculated structure for **12**

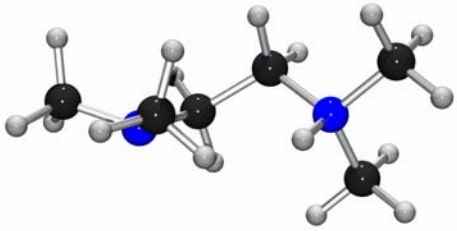


Figure S16. Calculated structure for **TS3**

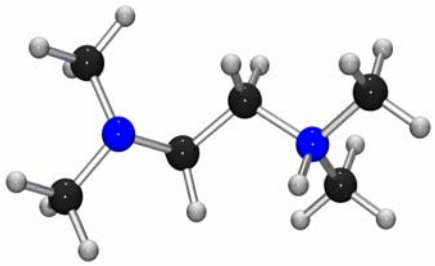


Figure S17. Calculated structure for **TS4**

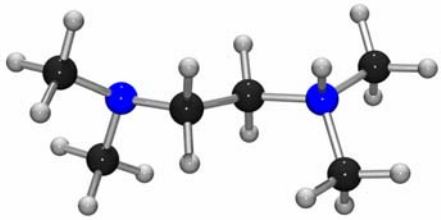


Figure S18. Calculated structure for **13**

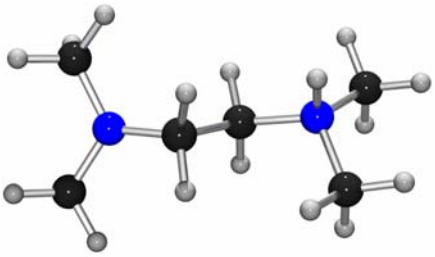


Figure S19. Calculated structure for **TS5**

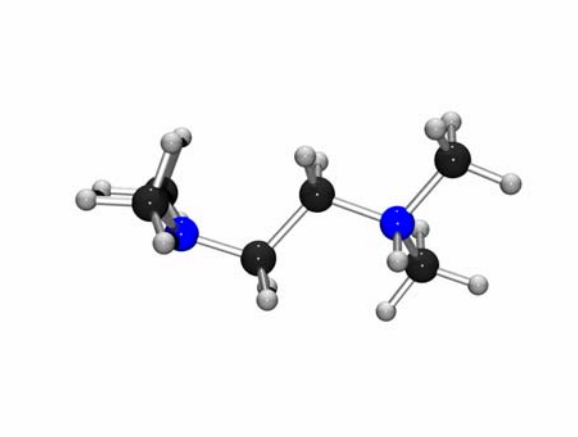


Figure S20 Calculated structure for **14**

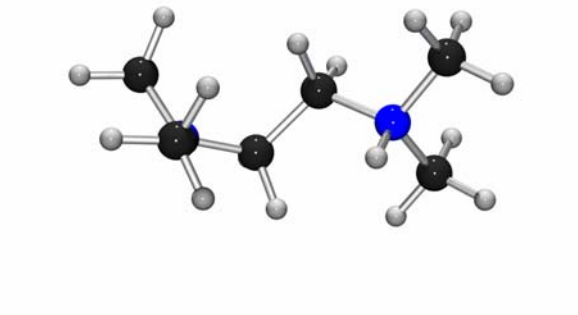


Figure S21 Calculated structure for **TS6**

Calculated Geometries

2

Atom	x	y	z
N	1.34075900	-0.00625000	-0.20296900
C	0.73843800	-0.31683700	1.10216800
H	0.69406000	-1.40388900	1.21675300
H	1.31755900	0.07087700	1.95296300
C	-0.68348000	0.27551600	1.15519100
H	-1.29071400	-0.15620300	1.95337200
H	-0.65841800	1.35918800	1.28367900
N	-1.33951400	0.00337300	-0.18150500
C	1.93649300	1.34218200	-0.24025500
H	2.27077700	1.56270100	-1.25654000
H	1.20057800	2.10017900	0.04337000
H	2.79828900	1.42824800	0.43912500
C	2.32127800	-1.01965000	-0.63214000
H	1.85396200	-2.00758800	-0.65671400
H	2.66604500	-0.77923700	-1.64049600
H	3.19625200	-1.06033600	0.03392200
C	-2.29732200	1.07168700	-0.60718400
H	-1.77391300	2.02752300	-0.64014300
H	-2.68202900	0.82802900	-1.59842800
H	-3.12022300	1.12159400	0.10820400
C	-1.96031500	-1.35880300	-0.26115100
H	-2.82199200	-1.39563600	0.40755500
H	-2.27730000	-1.54295500	-1.28831100
H	-1.22694100	-2.10871900	0.03377000
H	-0.48526000	0.01179000	-0.80053600

2a

Atom	x	y	z
N	-1.33947300	0.00339600	-0.18152000
C	-0.68346200	0.27545800	1.15517100
H	-0.65838200	1.35912100	1.28383300
H	-1.29069500	-0.15633900	1.95330800
C	0.73837100	-0.31699800	1.10205900
H	1.31757800	0.07034600	1.95297400
H	0.69386900	-1.40408600	1.21635100
N	1.34083000	-0.00625000	-0.20296300
C	-1.96063300	-1.35867400	-0.26109100
H	-2.27539900	-1.54380400	-1.28875700
H	-1.22823700	-2.10855600	0.03633900
H	-2.82379600	-1.39440200	0.40575200
C	-2.29715050	1.07186700	-0.60724200
H	-1.77333500	2.02743400	-0.64126600
H	-2.68270200	0.82763000	-1.59800800
H	-3.11946300	1.12258700	0.10875900
C	2.32124000	-1.01968000	-0.63227700
H	1.85372600	-2.00750500	-0.65729700
H	2.66627000	-0.77897200	-1.64046700
H	3.19605200	-1.06076700	0.03395700
C	1.93665400	1.34212700	-0.24001000
H	2.79834700	1.42807100	0.43950600
H	2.27111600	1.56271700	-1.25621300
H	1.20076500	2.10016800	0.04355800
H	-0.48531300	0.01173100	-0.80060100

12

Atom	x	y	z
N	1.38240100	-0.02272300	-0.21556300
C	0.48297100	-0.69709200	0.81855900
H	0.21332500	-1.66722100	0.39508900
H	1.10617600	-0.86744700	1.70159400
C	-0.78829700	0.10648200	1.17580000
H	-1.22012000	-0.42496700	2.03345400
H	-0.52133600	1.10241600	1.54736800
N	-1.81278900	0.24492500	0.16314300
C	2.11492300	1.16983600	0.33629800
H	2.67440800	1.64394700	-0.47077000
H	1.39980300	1.87590800	0.75438800
H	2.79882900	0.82404900	1.11271700
C	2.34139700	-1.00264900	-0.83694200
H	1.77275700	-1.80119500	-1.31398700
H	2.95236200	-0.48399000	-1.57658000
H	2.97459500	-1.41281000	-0.04916600
C	-2.45175400	-0.98794300	-0.27673000
H	-2.71202800	-1.60230700	0.59027600
H	-3.37848000	-0.74612500	-0.80439600
H	-1.83295600	-1.59772200	-0.96263000
C	-1.58859100	1.21423600	-0.89350200
H	-0.92003500	0.86604200	-1.71539900
H	-2.53898000	1.45894900	-1.37706600
H	-1.18348100	2.14284200	-0.47856000
H	0.76398300	0.31700500	-0.96028800

13

Atom	x	y	z
N	1.88466800	-0.23206200	-0.22621900
C	0.52329500	-0.22801000	0.45914300
H	0.43457500	-1.17530900	0.99384000
H	0.55386100	0.58376200	1.18906800
C	-0.65151100	-0.09778900	-0.52206500
H	-0.59266900	0.84258800	-1.10130200
H	-0.59581600	-0.92471100	-1.24118200
N	-1.89691900	-0.21585900	0.22048300
C	2.26431600	1.10836900	-0.80015900
H	3.22966700	1.01670100	-1.29909600
H	1.50489600	1.42543500	-1.51265300
H	2.33308600	1.82375600	0.02036700
C	2.95909900	-0.74901700	0.69489100
H	2.69393200	-1.75560800	1.01861600
H	3.90946000	-0.76311500	0.16016600
H	3.02327000	-0.08340800	1.55649100
C	-2.98106700	-0.78660000	-0.58668300
H	-2.68406800	-1.76566900	-0.97279500
H	-3.85886400	-0.92932300	0.04790300
H	-3.27072400	-0.14229800	-1.43514100
C	-2.30617700	1.04473100	0.84674400
H	-2.55066800	1.82603500	0.10494000
H	-3.18974300	0.86850900	1.46424100
H	-1.52149100	1.42740300	1.50609700
H	1.81931200	-0.88940100	-1.01063600

14

Atom	x	y	z
N	-1.81652100	0.17393400	-0.22649600
C	-0.39446300	0.20830700	0.31708400
H	-0.16162900	1.26292300	0.48076100
H	-0.42447900	-0.29722200	1.28535100
C	0.63764700	-0.42845000	-0.65242800
H	0.48076100	-1.51178400	-0.70072600
H	0.46366100	-0.02493000	-1.66169300
N	2.01844500	-0.19276800	-0.30573100
C	-2.36443900	-1.22413300	-0.34922600
H	-3.37460200	-1.17105700	-0.75629800
H	-1.72761800	-1.80658900	-1.01278700
H	-2.38404200	-1.67250500	0.64497800
C	-2.74273600	1.05088400	0.57541400
H	-2.35222400	2.06870700	0.57821200
H	-3.73464100	1.02996700	0.12211400
H	-2.78768300	0.66385200	1.59405000
H	-1.77678500	0.56478600	-1.17420500
C	2.48033100	1.18446900	-0.43762000
H	2.17963100	1.58509900	-1.41114100
H	2.11505500	1.86546800	0.35319200
H	3.57274100	1.19812800	-0.39760100
C	2.48615600	-0.86682800	0.90212100
H	3.57838200	-0.83017400	0.93068500
H	2.11509300	-0.41798500	1.84155600
H	2.18994200	-1.92032200	0.87707100

TS1

Atom	x	y	z
N	1.23408000	0.00841900	0.14799000
C	0.73900700	0.24533700	-1.23908500
H	0.79436000	1.31578700	-1.44838500
H	1.34004800	-0.27950600	-1.98560300
C	-0.73904200	-0.24546800	-1.23906200
H	-1.34010000	0.27931300	-1.98561300
H	-0.79443300	-1.31594200	-1.44822800
N	-1.23405900	-0.00840000	0.14800600
C	1.86424900	-1.32646200	0.31568800
H	2.04251600	-1.50943700	1.37708200
H	1.20011200	-2.10315000	-0.06946100
H	2.81604000	-1.37219900	-0.22385200
C	2.09751700	1.08968400	0.68184300
H	1.57195700	2.04453200	0.62074300
H	2.32550100	0.87786600	1.72845000
H	3.03394900	1.15640200	0.11780900
C	-2.09750300	-1.08962300	0.68192400
H	-1.57156100	-2.04432900	0.62185400
H	-2.32635050	-0.87720400	1.72821800
H	-3.03348000	-1.15701900	0.11722000
C	-1.86423800	1.32650200	0.31561600
H	-2.81659600	1.37179900	-0.22295800
H	-2.04141200	1.51003800	1.37709700
H	-1.20061300	2.10304700	-0.07069400
H	-0.00001700	0.00004700	0.59279800

TS2

Atom	x	y	z
N	1.31102200	-0.02373400	-0.20378800
C	0.58708100	-0.65753500	0.97282600
H	0.44221600	-1.70726500	0.70736500
H	1.25332700	-0.60464800	1.83873100
C	-0.77957600	0.01953500	1.23317400
H	-1.24344300	-0.57005100	2.03766200
H	-0.63571100	1.02597100	1.63970500
N	-1.65756600	0.09347700	0.09566300
C	1.92480400	1.30691900	0.13579400
H	2.33368700	1.74938900	-0.77311200
H	1.16236000	1.96123500	0.55484600
H	2.72090400	1.14277500	0.86309200
C	2.32672500	-0.94959900	-0.81515700
H	1.82537700	-1.86242400	-1.13731700
H	2.79130200	-0.45578300	-1.66947600
H	3.08067900	-1.18229000	-0.06205900
C	-2.18847200	-1.13713000	-0.46367000
H	-2.36980800	-1.86314300	0.33611800
H	-3.14797900	-0.93709300	-0.95068900
H	-1.53638000	-1.61757100	-1.21676100
C	-1.76666900	1.30739400	-0.69359600
H	-1.08493600	1.36624700	-1.56764300
H	-2.78215900	1.39970700	-1.09340200
H	-1.58391100	2.18377200	-0.06414700
H	0.57691900	0.14546500	-0.90226200

TS3

Atom	x	y	z
N	-1.53378100	0.12691500	-0.12080400
C	-0.49844900	-0.35487600	0.89576800
H	-0.27656100	0.50330100	1.53285500
H	-1.01295900	-1.10715800	1.49938100
C	0.77359900	-0.95727700	0.29224800
H	1.24779400	-1.46120200	1.14477300
H	0.49993800	-1.76723300	-0.40008000
N	1.74669100	-0.05809300	-0.33871900
C	-2.14330400	-0.99170100	-0.92194300
H	-2.83643200	-0.56361600	-1.64671000
H	-1.35787700	-1.53820200	-1.44114700
H	-2.67724900	-1.65453300	-0.23949100
C	-2.59684000	0.96058500	0.54185700
H	-2.12519100	1.81207400	1.03287100
H	-3.29989800	1.30801700	-0.21584000
H	-3.11447100	0.34316500	1.27719200
C	3.10261700	-0.22471200	0.19175800
H	3.37903300	-1.28231200	0.17137800
H	3.80995800	0.30957700	-0.44695600
H	3.21660300	0.14713900	1.22546300
C	1.38800400	1.32882800	-0.57711000
H	1.11616700	1.91421800	0.32134900
H	2.24145300	1.83480400	-1.03364000
H	0.58078000	1.41768900	-1.32295900
H	-1.03520900	0.73743300	-0.77723700

TS4

Atom	x	y	z
N	-1.78783200	-0.09373000	-0.28527800
C	-0.53518100	0.51417700	0.32808300
H	-0.27442000	1.36533600	-0.30370700
H	-0.83043000	0.87347500	1.31679800
C	0.64845900	-0.47731400	0.35259400
H	0.84856000	-0.79909700	1.39205900
H	0.38214800	-1.38536100	-0.20447600
N	1.81678600	0.10093100	-0.29761800
C	-2.38689600	-1.17434700	0.57510100
H	-3.22745000	-1.62408900	0.04556300
H	-1.63119500	-1.93020200	0.78532200
H	-2.72957500	-0.71895100	1.50519000
C	-2.80821500	0.96005200	-0.62579200
H	-2.36267300	1.67010900	-1.32274900
H	-3.67599400	0.48030300	-1.07981900
H	-3.10022000	1.46897100	0.29360000
C	2.80158600	-0.92682400	-0.65405500
H	2.34539300	-1.66691200	-1.31833100
H	3.62816600	-0.45651100	-1.19153800
H	3.21532000	-1.44917800	0.22591800
C	2.43222000	1.15674800	0.51451500
H	2.81545400	0.77824200	1.47888500
H	3.26393600	1.59835800	-0.03874800
H	1.71483900	1.95756800	0.72156900
H	-1.49637500	-0.52741700	-1.16794500

TS5

Atom	x	y	z
N	1.88839900	-0.15023300	-0.23092400
C	0.48074800	-0.25051700	0.35439400
H	0.29881400	-1.31360400	0.52681000
H	0.50536500	0.26306600	1.31873300
C	-0.62662400	0.32088000	-0.57213200
H	-0.50871100	1.40601500	-0.66952500
H	-0.49152100	-0.10791500	-1.58117800
N	-1.92853700	0.02873700	-0.06970800
C	2.37118700	1.27063500	-0.35034600
H	3.36678700	1.26920100	-0.79538200
H	1.68496200	1.83466500	-0.97994600
H	2.40857800	1.70478300	0.64964300
C	2.87274800	-0.99720400	0.53122800
H	2.52819600	-2.03149700	0.52643500
H	3.85123100	-0.92447600	0.05447300
H	2.92617000	-0.62583000	1.55530100
C	-2.58068200	-1.23194600	-0.37712000
H	-1.99215800	-1.79503100	-1.10845200
H	-2.71719100	-1.86835100	0.50988500
H	-3.57308400	-1.05831700	-0.81591100
C	-2.70164700	1.01525000	0.66593100
H	-3.66693700	1.20431600	0.17491500
H	-2.90924600	0.69764100	1.69798100
H	-2.15936700	1.96385500	0.71110500
H	1.83470800	-0.53062900	-1.18220100

TS6

Atom	x	y	z
N	-1.65512300	0.16991400	-0.15100400
C	-0.40109500	-0.18398400	0.63736900
H	-0.01379300	0.75929000	1.02851700
H	-0.74110900	-0.78947000	1.48072300
C	0.68336200	-0.90046900	-0.23422900
H	0.83537300	-1.91101600	0.15693300
H	0.30467000	-1.01860100	-1.26059900
N	1.96696000	-0.24347200	-0.31279400
C	-2.46597400	-1.04845900	-0.50661300
H	-3.29472300	-0.74827500	-1.14865600
H	-1.83228400	-1.76562900	-1.02703000
H	-2.84613400	-1.48593200	0.41746200
C	-2.49885700	1.19701700	0.55612000
H	-1.90121500	2.09436300	0.71805700
H	-3.36798400	1.43067700	-0.06024000
H	-2.81889800	0.78199500	1.51254100
C	2.73419000	-0.24129500	0.93017900
H	2.78377100	-1.25638100	1.33514300
H	3.75532400	0.08671700	0.71988500
H	2.32408400	0.42774100	1.70961600
C	1.95736400	1.03855500	-1.00093700
H	1.43799800	1.84829400	-0.44908000
H	2.98563500	1.37289500	-1.16015100
H	1.49077600	0.92903500	-1.98689500
H	-1.33829800	0.59102200	-1.03096900

References

(1) Amman, C.; Meier, P.; Merbach, A. E., *J. Magn. Reson. A* **1982,** 46, 319.

(2) a.) Perrin, C. L.; Dwyer, T. J., *Chem. Rev.* **1990,** 90, 935; b.) Bain, A. D.; Cramer, J. A., *J. Magn. Reson. A* **1996,** 118, 21; c.) Bain, A.; Cramer, J. A., *J. Magn. Reson. A* **1993,** 103, 217.

(3) Halpern, A. M.; Legenza, M. W.; Ramachandran, B. R., *J. Am. Chem. Soc.* **1979,** 101, 5736.

(4) Clarke, H. T.; Gillespie, H. B.; Weisshaus, S. Z., *J. Am. Chem. Soc.* **1933,** 55, 4571.

(5) Cope, A. C.; LeBel, N. A.; Lee, H. H.; Moore, W. R., *J. Am. Chem. Soc.* **1957,** 79, 4720.

(6) Caulder, D. L.; Powers, R. E.; Parac, T. N.; Raymond, K. N., *Angew. Chem. Int. Ed.* **1998,** 37, 1840.

(7) a.) Allerhand, A.; Gutowsky, H. S.; Jonas, J.; Meinzer, R. A., *J. Am. Chem. Soc.* **1966,** 88, 3185; b.) Lambert, J. B.; Mazzola, E. P., *Nuclear Magnetic Resonance Spectroscopy*. Pearson Education: Upper Saddle River, NJ, 2004; p 341.

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