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Supplemental Experimental Section

***trans*-*N*-Methyl-5-phenyl-4-pentenamine** was prepared in four steps from 5-bromopentanoic acid. Reduction of 5-bromopentanoic acid with BH_3/Me_2S followed by oxidation with pyridinium chlorochromate gave 5-bromopentanal[1] in 86% yield. Reaction of 5-bromopentanal with phenylmagnesium bromide in ether gave 5-bromo-1-phenyl-1-pentanol[2] in 61% yield. Dehydration of 5-bromo-1-phenyl-1-pentanol with *p*-toluenesulfonic acid in refluxing benzene gave 5-bromo-1-phenyl-1-pentene[3] as a 96/4 *trans/cis* mixture in 99% yield. The pure *trans* isomer was obtained by column chromatography on silica (80/20, hexanes--EtOAc). Reaction of 5-bromo-1-phenyl-1-pentene with a 30-fold excess of methylamine (40% aqueous solution) in THF overnight at room temperature gave the known *trans*-*N*-methyl-5-phenyl-4-pentenamine[4] in 81% yield. Spectral properties of these compounds were in agreement with those reported.

***trans*-*N*-*t*-Butoxylcarbonyl-2-phenylcyclobutylamine.** *trans*-2-Phenylcyclobutylamine was prepared by the method of Beard and Burger.[5] To a stirred solution of this amine (1.87 g, 12.72 mmol) in CH_2Cl_2 (30 mL) under nitrogen, was added triethylamine (4.43 mL, 31.8 mmol) dropwise via an addition funnel, followed by a solution of di-*t*-butyl carbonate (2.16 g, 14.4 mmol) in CH_2Cl_2 (20 mL). After stirring at room temperature for 10 h, 50 mL of an aqueous saturated $NaHCO_3$ solution was added. The organic layer was separated, washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the desired product was purified by chromatography on silica gel (80/20, hexanes--EtOAc) to yield the desired product as a white solid (2.98 g, 12.1 mmol, 95%). Mp 85-86 °C. ^{1}H NMR: δ 1.4 (s, 9 H), 1.8 (m, 2 H), 2.1 (m, 1 H), 2.3 (m, 1 H), 3.2 (broad m, 1 H), 4.2 (broad m, 1 H), 4.8 (broad s, 1 H), 7.1-7.3 (m, 5 H). ^{13}C NMR: δ 21.870, 22.153, 28.034, 28.298, 49.255, 51.505, 79.235, 126.262, 126.485, 128.301, 142.578, 154.705. Mass spectrum: *m/e* (relative intensity), 219 (2.6), 191 (15), 163 (18) 143 (4.3), 104 (28), 57 (100).

***trans*-*N*-*t*-Butyloxycarbonyl-*N*-methyl-2-phenylcyclobutylamine.** The methylation procedure of Olsen was followed.[6] The above protected amine (2.6 g, 10.53 mmol)

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was dissolved in anhydrous dimethylformamide (40 mL). To this solution were added methyl iodide (6.2 mL, 99.6 mmol) and silver oxide (11.49 g, 49.6 mmol). After stirring at 45 °C overnight, the reaction mixture was cooled and filtered. The solid was washed with of dimethylformamide (5 mL). Chloroform (150 mL) was added to the resulting filtrate. After washing twice with 5% aqueous KCN solution and 10 times with water, the chloroform phase was dried over $MgSO_4$. After filtration and solvent removal under reduced pressure, the crude product was purified by column chromatography on silica gel (90/10, hexanes-- EtOAc) to afford the desired product as a light yellow (2.5 g, 9.6 mmol, 91%). ^{1}H NMR: δ 1.4 (s, 9 H), 1.7 (m, 1 H), 2.1 (m, 3 H), 2.9 (s, 3 H), 3.5 (m, 1 H), 4.6 (broad s, 1 H), 7.1-7.3 (m, 5 H). ^{13}C NMR: δ 21.907 (broad), 23.937, 28.154, 28.929, 45.203, 56.398 (very broad), 79.267, 126.044, 126.403, 128.141, 142.781, 155.219. Mass spectrum: *m/z* (relative intensity), 205 (7.6), 157 (21), 131 (11), 101 (46), 57 (100).

***trans*-*N*-Methyl-2-phenylcyclobutylamine** was prepared following the procedure described by Olsen.[6] *trans*-*N*-*t*-Butyloxycarbonyl-*N*-methyl-2-phenylcyclobutylamine (2.5 g, 9.6 mmol) was stirred overnight at room temperature in a solution of 3 M hydrochloric acid in EtOAc (50 mL). The solvent was removed in vacuum, and the residue was redissolved in water. The aqueous layer was washed once with ether then made basic with 10% aqueous sodium hydroxide solution. The organic layer was extracted with ether, and the ether extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the product as a light yellow oil (1.33 g, 8.26 mmol, 86%). ^{1}H NMR: δ 1.2 (broad s, 1 H), 1.6-1.8 (m, 2 H), 2.1-2.3 (m, 2 H), 2.3 (s, 3 H), 3.16 (q, J = 8.0 Hz, 1 H), 3.2-3.3 (q, J = 8.0 Hz, 1 H), 7.1-7.3 (m, 5 H). ^{13}C NMR: δ 22.078, 26.547, 33.109, 49.400, 62.755, 125.966, 126.652, 128.220, 144.048. Mass spectrum: *m/e* (relative intensity), 161 (M^+, 1.3), 133 (21), 104 (10), 57 (100). HRMS: calcd for $C_{11}H_{15}N$, 161.1205; found, 161.1207.

***trans*-*N*-*t*-Butyloxycarbonyl-2-phenylcyclopopylamine.** *trans*-2-Phenylcyclopropylisocyanate[5] (2.4 g, 15.07 mmol) in *t*-butanol (60 mL) was heated at reflux under nitrogen for 12 h. The solvent was removed under reduced pressure, and the product was purified by

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chromatography on silica gel (80/20, hexanes--EtOAc) to yield a white solid (2.92 g, 12.53 mmol, 83%). Mp 76-77 °C. ^{1}H NMR: δ 1.2 (m, 2 H), 1.4 (s, 9 H), 2.0 (m, 1 H), 2.7 (broad s, 1 H), 4.8 (broad s, 1 H), 7.1-7.3 (m, 5 H). ^{13}C NMR: δ 16.32, 26.0 (broad), 28.35, 32.46 (broad), 80.0, 125.979, 126.453, 128.291, 140.702. Mass spectrum: *m/e* (relative intensity), 233 (M^+, 0.002), 177 (17.5), 133 (41.8), 116 (35.7), 57 (100).

***trans*-*N*-*t*-Butyloxycarbonyl-*N*-methyl-2-phenylcyclopropylamine.** The methylation procedure of Olsen was followed.[6] *trans*-*N*-*t*-Butyloxycarbonyl-2-phenylcyclopropylamine (2.8 g, 12 mmol) was dissolved in anhydrous dimethylformamide (40 mL). To this solution were added methyl iodide (6 mL, 96 mmol) and silver oxide (11.12 g, 48 mmol). After stirring at 45 °C overnight, the reaction mixture was cooled and filtered. The solid was washed with dimethylformamide (10 mL). Chloroform (150 mL) was added to the resulting filtrate. After washing twice with 5% aqueous KCN solution and ten times with water, the chloroform phase was dried over $MgSO_4$. After filtration and solvent removal under reduced pressure, the crude product was purified by column chromatography on silica gel (90/10, hexanes--EtOAc) to afford the desired product as a light yellow oil (2.18 g, 8.83 mmol, 74%). ^{1}H NMR: δ 1.1 (m, 1 H), 1.2 (m, 1 H), 1.3 (s, 9 H), 2.0 (m, 1 H), 2.6 (m, 1 H), 2.8 (s, 3 H), 7.0-7.2 (m, 5 H). ^{13}C NMR: δ 17.458, 26.066 (broad), 28.432, 34.424 (broad), 39.958, 79.536, 125.881, 126.109, 128.202, 140.962. Mass spectrum: *m/e* (relative intensity), 248 ($(M+1)^+$, 17), 192 (100), 147 (19.), 116 (11). HRMS: calcd for $C_{11}H_{12}NO_2$ (M-C_4H_8), 191.0946; found, 191.0950.

***trans*-*N*-Methyl-2-phenylcyclopropylamine.** The compound was prepared from *trans*-*N*-*t*-Butyloxycarbonyl-*N*-methyl-2-phenylcyclopropylamine by the same procedure as described above for the preparation of *trans*-*N*-methyl-2-phenylcyclobutylamine. The product was obtained as a light yellow oil in 71% yield. ^{1}H NMR: δ 1.0 (dt, J = 6.7, 5.9 Hz, 1 H), 1.1 (dt, J = 9.4, 4.7 Hz, 1 H), 1.6 (broad s, 1 H), 1.9 (ddd, J = 9.2, 5.9, 3.0 Hz, 1 H), 2.3 (ddd, J = 6.9, 4.0, 3.3 Hz, 1 H), 2.5 (s, 3 H), 7.0-7.3 (m, 5 H). ^{13}C NMR: δ 16.876, 24.766, 35.613, 43.145, 125.283, 125.718, 128.065, 142.280. Mass spectrum: *m/e* (relative intensity), 147

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(M^+, 100), 132 (52), 115 (40), 91 (41), 77 (19), 70 (67). HRMS: calcd for $C_{10}H_{13}N$, 147.1048; found, 147.1046. This amine was prepared previously by a different route.[7]

2-Benzyl-*N*-methylpyrrolidine. A flame dried 25 mL round-bottomed flask containing a stir bar and septum seal and flushed with nitrogen was wrapped in aluminum foil and placed in a –78 °C bath. A solution of PTOC carbamate **3P** (0.14 g, 0.43 mmol) in 5 mL of THF was transferred *via* syringe into the reaction flask, and Bu_3SnH (0.582 g, 2 mmol) was added in 5 mL of THF *via* syringe. The reaction was allowed to equilibrate at room temperature. The aluminum foil was removed, and the reaction was irradiated with a 150 W tungsten filament lamp. After 1 h, a solution of I_2 in CH_2Cl_2 was added until a red color persisted. Then the organic solution was washed with aqueous solution of KF and a 1 M aqueous solution of $Na_2S_2O_3$. The ethereal layer was treated with 50 mL of 10% aqueous HCl solution, and the aqueous layer was separated and neutralized with 10% aqueous NaOH solution. Diethyl ether (50 mL) was added, and the organic layer was separated, washed with brine and dried over $MgSO_4$.. The solvent was removed under reduced pressure, and the product was purified by column chromatography on neutral alumina (20:80, hexanes--ethyl acetate) to give the known pyrrolidine[4] as a yellow oil (0.061 g, 0.35 mmol, 81%). ^1H NMR: δ 1.4-1.7 (m, 4 H), 2-2.4 (m, 6 H), 3 (m, 2 H), 7.1-7.3 (m, 5 H). ^{13}C NMR: δ 21.603, 29.647, 30.789, 40.553, 57.259, 67.744, 125.878, 128.178, 129.034, 140.01. Mass spectrum: *m/e* (relative intensity), 174 (0.3), 84 (80.2), 58 (45.4), 43 (100).

4-Phenylbutanal was prepared in 94% yield by PCC oxidation of 4-phenyl-1-butanol.[8] The ^1H and ^{13}C NMR spectra were consistent with those previously reported for this compound.[9]

3-Phenylpropanal was prepared in 92% yield by PCC oxidation of 3-phenyl-1-propanol.[8] The ^1H and ^{13}C NMR spectra were consistent with those previously reported for this compound.[10]

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Table S1. Observed rate constants for cyclizations of radicals **2•**, **3•** and **4•**.

Radical	temp (°C)[a]	k_{obs} (s^{-1})[b]
2•	20.0	1.31×10^4
	30.0	2.14×10^4
	40.0	3.31×10^4
	50.0	4.70×10^4
3•	0.0	0.86×10^5
	10.0	1.28×10^5
	20.0	1.90×10^5
	30.0	2.63×10^5
	40.0	3.54×10^5
	50.0	4.56×10^5
4•	0.0	1.69×10^5
	0.0	1.67×10^5
	10.0	2.25×10^5
	10.0	2.32×10^5
	20.0	3.04×10^5
	20.0	3.10×10^5
	30.0	4.51×10^5
	40.0	6.03×10^5
	40.0	6.13×10^5
	50.0	7.96×10^5
	50.0	7.61×10^5
	50.0	7.62×10^5
	60.0	9.40×10^5

[a]± 0.2 °C. [b]Random errors in direct measurements at 2σ are ca. 2-3%.

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Table S2. k_{obs} for 5-exo cyclization of **4•** at 20.0 ± 0.2 °C at varied concentrations of **4P**.

[**4P**] (M)	k_{obs} (s^{-1})
1×10^{-5}	3.13×10^{5}
2×10^{-5}	3.26×10^{5}
4×10^{-5}	3.08×10^{5}
5×10^{-5}	2.91×10^{5}

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Table S3. Results from indirect kinetic studies of radical **5•**.[a]

temp (°C)[b]	[PhSH][c] (M)	%A[d]	%C[d]	A/C[e]	k_r/k_T[f] (M)
50	0.49	88.0	5.9	14.9	7.3
25	0.49	83.4	8.3	10.0	4.9
25	0.98	75.9	14.9	5.1	5.0
1	0.49	75.2	10.9	6.9	3.4
–23	0.49	67.1	15.6	4.3	2.1
–46	0.49	60.3	19.5	3.1	1.5

[a]Reactions run in THF. [b]± 0.5 °C. [c]Mean concentration of PhSH. [d]Absolute % yields. [d]Ratio of acyclic to cyclic product. [f]Ratio of rate constants for rearrangement and trapping.

This data gives a relative Arrhenius function of

$\log ((k_r/k_T) \times M^{-1}) = (2.48 \pm 0.19) - (2.42 \pm 0.24)/\theta$

where $\theta = 2.3RT$ in kcal/mol.

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Table S4. Results from indirect kinetic studies of radical **6•**.[a]

temp (°C)[b]	[PhSeH][c] (M)	%A[d]	%C[d]	A/C[e]	k_r/k_T[f] (M)
50	3.8	89.8	0.93	96.6	367
25	3.8	88.5	0.94	94.1	357
1	3.8	87.6	0.96	91.3	347
–23	3.8	87.1	0.98	88.9	338
–46	3.8	85.1	1.02	83.4	317

[a]Reactions run in THF. [b]± 0.5 °C. [c]Mean concentration of PhSeH. [d]Absolute % yields. [e]Ratio of acyclic to cyclic product. [f]Ratio of rate constants for rearrangement and trapping.

This data gives a relative Arrhenius function of

$\log ((k_r/k_T) \times M^{-1}) = (2.71 \pm 0.03) - (0.21 \pm 0.03)/\theta$

where $\theta = 2.3RT$ in kcal/mol.

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Table S5. Observed rate constants for cyclization of **4•** in THF as a function of temperature and *t*-BuSH concentration.

temp (°C)[a]	[*t*-BuSH] (M)	$10^{-5} \times k_{obs}$ (s^{-1})[b]
10	0.10	7.85 ± 0.07
10	0.075	7.33 ± 0.05
10	0.063	6.63 ± 0.05
10	0.050	6.52 ± 0.06
10	0.050	6.60 ± 0.05
10	0.038	5.16 ± 0.04
10	0.025	4.76 ± 0.03
10	0.013	3.63 ± 0.01
25	0.10	10.4 ± 0.08
25	0.075	9.20 ± 0.06
25	0.063	8.52 ± 0.05
25	0.050	8.13 ± 0.04
25	0.038	7.03 ± 0.03
25	0.025	6.46 ± 0.03
25	0.025	6.57 ± 0.03
25	0.013	5.34 ± 0.02
40	0.10	13.6 ± 0.07
40	0.07	11.8 ± 0.06
40	0.063	11.2 ± 0.05
40	0.050	10.5 ± 0.08
40	0.038	9.26 ± 0.04
40	0.025	8.56 ± 0.03
40	0.025	8.44 ± 0.03
40	0.013	7.40 ± 0.03

[a]Temperatures are believed to be accurate to ± 1 °C. [b]Each rate constant is the least squares weighted average of 8 to 15 measurements.

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Table S6. Product ratios from reactions of **4•** in the presence of Bu_3SnH.[a]

temp (°C)[b]	$[Bu_3SnH]$[c] (M)	C/A[d]	k_T/k_r (M^{-1})[e]
40	1.18	0.68	1.25
25	1.00	0.77	1.30
15	1.27	0.61	1.29
0	0.89	0.76	1.48
–23	1.10	0.55	1.65

[a]Reactions conducted in benzene-d_6 and analyzed by 500 MHz NMR spectroscopy; no products other than the cyclic and acyclic amine were apparent in >5% yield. [b]± 1 °C. [c]Mean concentration of tin hydride. [d]Ratio of cyclic to acyclic product determined from integrals of the vinyl proton from the acyclic amine and the diphenylalkyl proton from the cyclic amine. [e]Ratio of rate constants.

This data gives

$\log ((k_T/k_r) \times M) = (-0.43 \pm 0.16) + (0.74 \pm 0.20)/\theta$

where $\theta = 2.3RT$ in kcal/mol.

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Table S7. Product ratios from reactions of **3•** and **4•** in THF in the presence of PhSH.

radical	temp (°C)[a]	[PhSH][b] (M)	C/A[c]	k_T/k_r (M^{-1})[d]
3•	50	0.015	6.7	444
	25	0.015	9.1	606
	1	0.015	12.5	831
	–23	0.015	20	1330
	–46	0.015	33	2200
4•	50	0.015	3.27	218
	25	0.015	3.71	248
	1	0.015	4.68	312
	–23	0.015	7.37	492
	–46	0.015	10.4	695

[a]± 1 °C. [b]Mean concentration of thiophenol. [c]Ratio of cyclic to acyclic product; the absolute yields determined against an internal standard by GC were 81-99%. [d]Ratio of rate constants.

The data for radical **3•** gives

$\log ((k_T/k_r) \times M) = (1.00 \pm 0.08) + (2.43 \pm 0.09)/\theta$

The data for radical **4•** gives

$\log ((k_T/k_r) \times M) = (1.06 \pm 0.23) + (1.84 \pm 0.28)/\theta$

where $\theta = 2.3\ RT$ in kcal/mol.

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Table S8. Product ratios from reactions of **5•** in THF in the presence of PhSeH.

temp (°C)[a]	[PhSeH][b] (M)	R/U[c]	k_T/k_r (M^{-1})[d]
50	0.49	0.76	2.68
25	0.49	0.55	3.71
1	0.49	0.37	5.52
–23	0.49	0.25	8.16
–46	0.49	0.14	14.58

[a]± 1 °C. [b]Mean concentration of benzeneselenol. [c]Ratio of rearranged to unrearranged product; the absolute yields determined against an internal standard by GC were 77-96%. [d]Ratio of rate constants.

This data gives

$\log ((k_T/k_r) \times M) = (-1.30 \pm 0.09) + (2.54 \pm 0.11)/\theta$

where $\theta = 2.3\ RT$ in kcal/mol.