

Supporting Information

Rare-earth metal diisopropylamide- catalyzed intramolecular hydroamination

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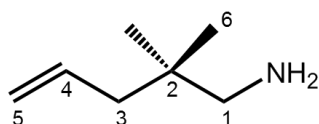
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Experimental Section

Synthesis and characterization of aminoalkene substrates **S1**, **S2**, and **S3**

All aminoalkenes were prepared according to literature procedures.¹

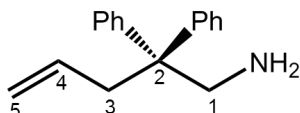
1-Amino-2,2-dimethyl-4-pentene (**S1**)



Isolated product: 8.3 g, 0.073 mol, 59% based on 0.124 mol of dimethylacetonitrile.

¹H NMR (C₆D₆, 26 °C, 400.11 MHz): 0.59 (broad s, 2H, NH₂), 0.75 (s, 6H; Me₂), 1.89 (dt, 2H, J = 7.4 and 1.3 Hz, CH₂CH=), 2.27 (s, 2H, NCH₂), 5.00 (m, 2H, J = 11.5 and 1.4 Hz, CH₂=), 5.75 (m, 1H, J = 17.8 and 7.5 Hz, CH₂=CH). ¹³C{¹H} NMR (CDCl₃, 26 °C, 100.61 MHz): 24.50 (C6), 34.79 (C2), 43.92 (C3), 52.55 (C1), 116.79 (C5), 135.21 (C4).

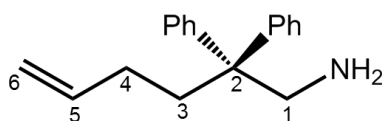
1-Amino-2,2-diphenyl-4-pentene (**S2**)



Isolated product: 14.7 g, 0.062 mol, 50% based on 0.124 mol of diphenylacetonitrile.

¹H NMR (C₆D₆, 26 °C, 400.11 MHz): 0.40 (broad s, 2H, NH₂), 2.87 (dt, 2H, CH₂CH=), 3.17 (s, 2H, NCH₂), 4.96 (m, 2H, J = 17.3, 10.3, and 1.4 Hz, CH₂=), 5.45 (dm, 1H, J = 10.1 Hz, CH₂=CH), 7.07 (m, 10H, Ph₂). ¹³C{¹H} NMR (CDCl₃, 26 °C, 100.61 MHz): 41.1 (C3), 48.7 (C1), 51.5 (C2), 117.7 (C5), 126.1 + 128.3 + 128.6 (C-Ph), 135.3 (C4), and 147.2 (C-Ph).

1-Amino-2,2-diphenyl-5-hexene (S3)



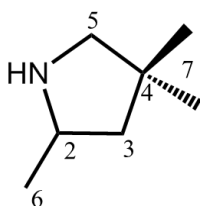
Isolated product: 15.4 g, 0.061 mol, 49% based on 0.124 mol of diphenylacetonitrile.

^1H NMR (C_6D_6 , 26 °C, 400.11 MHz): 0.37 (broad s, 2H, NH_2), 1.90 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}=\text{}$), 2.32 (m, 2H, $J = 8.35$ and 1.1 Hz, $\text{CH}_2\text{CH}=\text{}$), 3.24 (s, 2H, NCH_2), 5.03 (m, 2H, $J = 1.8$ and 1.1 , $\text{CH}_2=\text{}$), 5.85 (dm, 1H, $J = 6.6$ and 2.9 Hz, $\text{CH}_2=\text{CH}$), 7.00 (m, 10H, Ph_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 26 °C, 100.61 MHz): 29.1 (C3), 35.9 (C4), 49.1 (C1), 51.8 (C2), 114.3 (C6), 126.1 + 128.2 + 128.6 (C-Ph), 139.3 (C5), 147.3 (C-Ph).

Characterization of the cyclized amines **P1**, **P2**, and **P3**

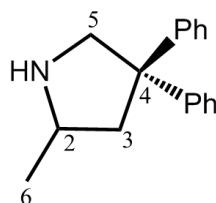
The NMR resonances of the cyclized amines were assigned by comparison with literature data.²

2,4,4-Trimethylpyrrolidine (P1)



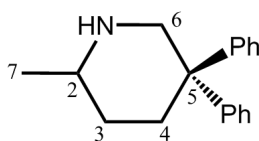
^1H NMR (C_6D_6 , 26 °C, 500.13 MHz): 0.94 (s, 3H, H-7), 0.98 (m, 1H, H-3), 1.02 (s, 3H, H-7), 1.07 (s, 3H, H-6), 1.20 (broad s, 1H, NH), 1.51 (dd, 1H, H-3), 2.53 (d, 1H, H-5), 2.66 (d, 1H, H-5), 3.13 (m, 1H, H-2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 26 °C, 100.61 MHz): 18.9 (C6), 27.5 (C7), 39.4 (C4), 47.3 (C3), 49.9 (C2), 56.7 (C5).

2-Methyl-4,4-diphenylpyrrolidine (P2)



^1H NMR (C_6D_6 , 60 °C, 500.13 MHz): 1.02 (d, 3H, *H*-6), 1.31 (broad s, 1H, *NH*), 1.84 (m, 1H, *H*-3), 2.43 (m, 1H, *H*-3), 3.17 (m, 1H, *H*-2), 3.39 (m, 1H, *H*-5), 3.51 (m, 1H, *H*-5), 7.12 (m, 10H, *Ph*-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 26 °C, 100.61 MHz): 22.7 (C6), 47.3 (C3), 53.8 (C2), 57.4 (C4), 58.3 (C5), 126.3 + 126.4 + 127.6 + 127.7 + 128.7 + 128.8 + 148.0 + 148.3 (C-*Ph*).

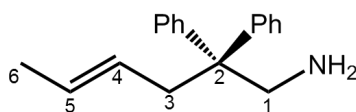
2-Methyl-5,5-diphenylpiperidine (P3)



^1H NMR (C_6D_6 , 60 °C, 500.13 MHz): 0.96 (d, 3H, *H*-7), 1.18 - 1.24 (ddt, 1H, *H*-3), 1.45 (dq, 1H, *H*-3), 1.54 (broad s, *NH*), 2.16 (dm, 1H, *H*-4), 2.54 (m, 1H, *H*-4), 2.65 (m, 1H, *H*-2), 3.03 (dd, 1H, *H*-6), 3.86 (dm, 1H, *H*-6), 7.07 - 7.28 (m, 8H, *Ph*-*H*), 7.53 (dm, 2H, *Ph*-*H*). NMR (C_6D_6 , 26 °C, 100.61 MHz): 22.8 (C7), 31.5 (C3), 36.4 (C4), 45.8 (C5), 52.4 (C2), 56.8 (C6), 126.9 + 128.7 + 129.2 + 149.7 (C-*Ph*).

Isomerized product: 1-Amino-2,2-diphenyl-4-hexene (P4)

The NMR resonances were assigned by comparison with literature data.^{1b}



^1H NMR (C_6D_6 , 60 °C, 500.13 MHz): 1.59 (d, 3H, *H*-6, $J = 6.75$ Hz), 2.92 (d, 2H, *H*-3, $J = 7.0$ Hz), 3.31 (m, 2H, *H*-1), 5.31 (m, 1H, *H*-4), 5.52 (m, 1H, *H*-5), 7.2 (m, 10H, *Ph*-*H*).

NMR Spectroscopic and Catalytic Data

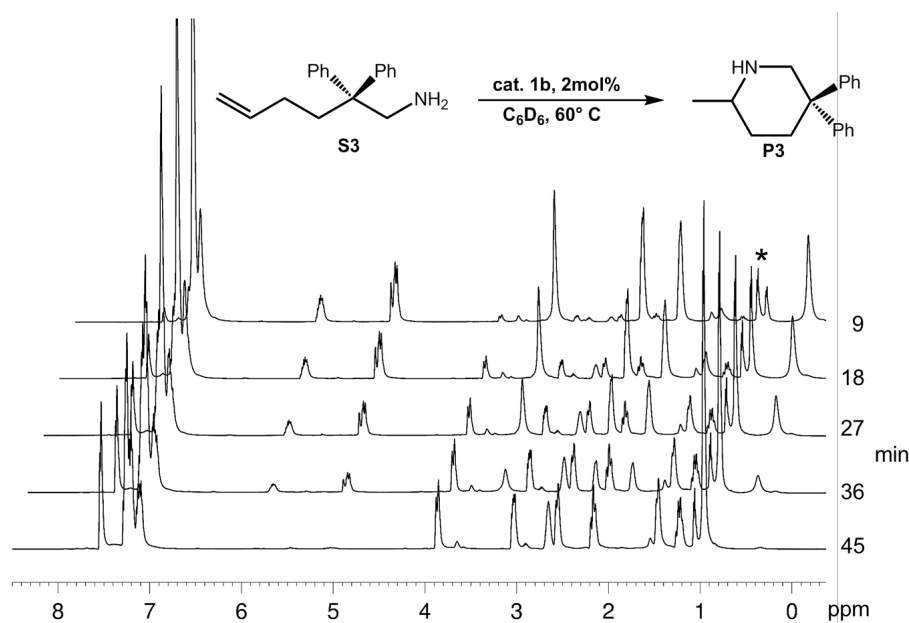


Figure S1. ^1H NMR monitoring (500.13 MHz) of the IHC reaction of substrate **S3** using 2 mol% $\text{LiY}(\text{NiPr}_2)_4(\text{THF})$ (**1b**) as a precatalyst at 60 °C in C_6D_6 (cf., Table 1, entry 14). * Signal of liberated HNiPr_2 .

Table S1. IHC of aminoalkenes catalyzed by 4 mol% $\text{NaLn}(\text{NiPr}_2)_4(\text{THF})$ ($\text{Ln} = \text{Sc}$ (**3a**), Y (**3b**)) at 60 °C in C_6D_6 .

entry	aminoalkene	product	catalyst	t/h	conv./ % ^a	N_t/h^{-1} ^b
1			3a	24	traces	-
2			3b	3	37	3.1
3			3a	24	traces	-
4			3b	3	15	1.25

^a All conversion data were derived from ^1H NMR spectra referring to the corresponding duration of reaction; ^b N_t at time t given in this table.

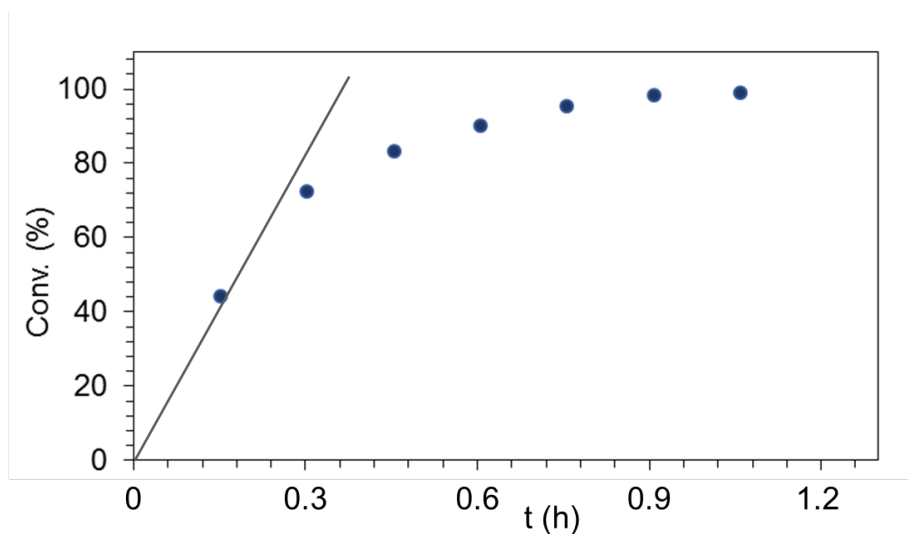


Figure S2. Experimental conversion/time data plot for the IHC of aminoalkenes **S2** at 26°C using 4 mol% $[\text{LiY}(\text{NiPr}_2)_4]_n$ (**2**) as precatalyst and tetrakis(p-tolyl)silane as an internal standard, initial $N_t = 62.4 \text{ h}^{-1}$, overall N_t at 80% conversion = 45.9 h^{-1} .

References

- (a) Y. Tamaru, M. Hojo, H. Higashimura and Z. Yoshida, *J. Am. Chem. Soc.*, 1988, **110**, 3994;
 (b) M. R. Crimmin, M. Arrowsmith, A. G. M. Barrett, I. J. Casely, M. S. Hill and P. A. Procopiou, *J. Am. Chem. Soc.*, 2009, **131**, 9670.
- M. Arrowsmith, M. R. Crimmin, A. G. M. Barrett, M. S. Hill, G. Kociok-Köhn and P. A. Procopiou, *Organometallics*, 2011, **30**, 1493.