Supporting Information

Scandium-Catalyzed Intermolecular Hydroaminoalkylation of Olefins with Aliphatic Tertiary Amines

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1. General Methods

All manipulations were performed under a nitrogen atmosphere by use of standard Schlenk techniques or in an mBRAUN Labmaster glovebox. Nitrogen was purified by passing through a Dryclean column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). Hexane, THF, toluene and benzene (dehydrated, stabilizer-free) were obtained from Kanto Chemical Co. and purified by use of an MBraun SPS-800 solvent purification system. Silica gel column chromatography was performed with Silica Gel 60 N (spherical, neutral, 40-50 mm) obtained from Kanto Chemical Co. [Ln(CH₂C₆H₄NMe₂-o)₃] (Ln = Sc, Y, Lu, Gd, Sm)¹ and [(C₅Me₅)Sc(CH₂C₆H₄NMe₂-o)₂]² were prepared according to the literature methods. N,N-dimethylbutylamine (1a), N,N-dimethylcyclohexylamine (1c), N,N-dibutylmethylamine (1e), N-methylpyrrolidine (1f), d₃-N-methylpyrrolidine (1f₃), N-methylpiperidine (1h) and tropane (1j) were commercially available. N-methyl,N-ethylbutylamine (1d), N-methyl,4-methylpiperidine (1i), N-methylhexamethylenimine (1g), and N,N-dimethyladamantylamine (1k), were prepared via the literature method.³ All olefins were commercially available, except 4-dimethylaminostyrene (2e) which was synthesized via the literature method.⁴ Amines and olefins were all distilled from appropriate drying agents such as CaH₂ and Na. All ¹H NMR and ¹³C NMR spectra were recorded on either a JEOL AL-400 MHz instrument or a Bruker AVANCE III HD 500 NMR spectrometer in C₆D₆ with tetramethylishilane as an internal standard otherwise mentioned. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sep = septet, m = multiplet, br = broad signal), coupling constant (Hz), integration. Gas chromatography analysis was performed on Shimadzu GC2014 using a capillary column (Agilent J&W GC columns DB-1, 30m, 0.32 mm i.d., 0.25 mm film thickness. High-resolution MS were obtained on a Bruker microTOF-Q III (ESI+).
2. Catalyst Screening

In a glovebox, [Sc(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_3] (6 mg, 0.013 mmol) was dissolved in \text{C}_6\text{D}_6 (1.0 mL). To this solution, ferrocene (19 mg, 0.1 mmol), \text{N,N-}dimethylbutylamine (25 mg, 0.25 mmol), norbornene (26 mg, 0.28 mmol) and [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] (16 mg, 0.013 mmol) were added sequentially. The biphasic mixture was transferred to a J Young NMR tube, sealed and a baseline \(^1\text{H} \) NMR spectrum taken. The tube was then heated at 70 °C for 24 hours, and the yield calculated from the internal standard (ferrocene). For entries 5 and 6, the sample was quenched with \text{EtOAc} (2 mL) after 24 h at 70 °C, filtered and the volatiles removed \textit{in vacuo} to remove the paramagnetic catalyst.

Table S1. Catalyst Dependant Hydroaminoalkylation of Norbornene with \text{N,N-}dimethylbutylamine

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Co-catalyst</th>
<th>Yield, %(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})}_3]_2]</td>
<td>[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>[(\text{C}_5\text{H}_5)\text{Sc(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})}_3]_2</td>
<td>[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>[\text{Y(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})}_3]_3</td>
<td>[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>[\text{Lu(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})}_3]_3</td>
<td>[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>[\text{Gd(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})}_3]_3</td>
<td>[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>[\text{Sm(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})}_3]_3</td>
<td>[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>[\text{Sc(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})}_3]_3</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>\text{N/A}</td>
<td>[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]</td>
<td>0</td>
</tr>
<tr>
<td>9(^c)</td>
<td>[\text{Sc(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})}_3]_3</td>
<td>[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

\(^a\) Reactions were carried out with 0.25 mmol amine and 0.275 mmol norbornene in 1 mL of \text{C}_6\text{D}_6. \(^b\) NMR yield calculated against \text{Cp}_2\text{Fe} as an internal standard. \(^c\) 10 mol% [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] used.
3. Typical Procedure for the Catalytic Alkylation of Amines with Olefins

In a glovebox, [Sc(CH₂C₆H₄NMe₂-ο)]₂ (22 mg, 0.05 mmol) was dissolved in toluene (2.0 mL). To this solution N-methylpiperidine (99 mg, 1 mmol), styrene (115 mg, 1.1 mmol) and [Ph₃C][B(C₆F₅)₃] (46 mg, 0.05 mmol) were added sequentially. The biphasic mixture was transferred to a Schlenk ampoule, sealed and heated at 70 °C for 24 hours. EtOAc (5 mL) was added to the crude mixture and the volatiles removed in vacuo. The compound was purified by silica gel column chromatography (hexane/EtOAc), to afford 4a as colourless oil (173 mg, 0.851 mmol, 85 % yield).

4. Analytical Data

**3a:** ¹H NMR (500 MHz, C₆D₆): δ 2.30 – 2.25 (m, 2H), 2.22 (br, 1H), 2.16 (br, 1H), 2.16 – 2.12 (m, 1H), 2.14 (s, 3H), 1.94 (dd, J = 7.5 Hz, 4.5 Hz, 1H), 1.64 – 1.58 (m, 1H), 1.52 – 1.40 (m, 4H), 1.37 – 1.27 (m, 4H), 1.18 – 1.13 (m, 1H), 1.05 (d, J = 9.5 Hz, 1H), 0.91 (t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, C₆D₆): δ 64.3, 58.3, 42.7, 40.7, 39.9, 36.9, 36.5, 35.6, 30.5, 30.2, 29.5, 20.9, 14.3. HR MS (ESI+): Found 196.2066 [M+H]+, calcd. for C₁₃H₂₆N⁺ 196.2065.

**3b:** ¹H NMR (500 MHz, C₆D₆): δ 2.32 – 2.27 (m, 2H), 2.23 (br, 1H), 2.18 – 2.14 (m, 2H), 2.16 (s, 3H), 1.96 (dd, J = 7.0 Hz, 5.0 Hz, 1H), 1.66 – 1.60 (m, 1H), 1.50 – 1.45 (m, 4H), 1.38 – 1.25 (br m, 12H), 1.18 – 1.13 (m, 3H), 1.05 (d, J = 9.5 Hz, 1H), 0.90 (t, J = 8.0 Hz, 3H). ¹³C NMR (125 MHz, C₆D₆): δ 64.3, 58.7, 42.7, 40.7, 39.9, 37.0, 36.5, 35.6, 32.4, 30.5, 30.1, 29.9, 29.5, 28.1, 27.9, 23.1, 14.4. HR MS (ESI+): Found 252.2692 [M+H]+, calcd. for C₁₃H₃₄N⁺ 252.2691.

**3c:** ¹H NMR (500 MHz, C₆D₆): δ 2.35 – 2.17 (m, 4H), 2.21 (s, 3H), 2.05 (dd, J = 12.3 Hz, 7.2 Hz, 1H), 1.81 – 1.67 (m, 4H), 1.66 – 1.58 (m, 1H), 1.58 – 1.44 (m, 3H), 1.40 – 1.33 (m, 1H), 1.32 – 1.27 (m, 1H), 1.23 – 1.10 (m, 7H), 1.06 (d, J = 9.7 Hz, 1H), 1.04 – 0.96 (m, 1H). ¹³C NMR (125 MHz, C₆D₆): δ 63.7, 59.7, 41.1, 39.9, 38.1, 37.0, 36.3, 35.6, 30.5, 29.6, 29.1, 28.9, 26.9, 26.5. HR MS (ESI+): Found 222.2221 [M+H]+, calcd. for C₁₃H₃₈N⁺ 222.2222.

**3d:** ¹H NMR (500 MHz, C₆D₆): δ 2.50 – 2.31 (m, 4H), 2.24 (br, 1H), 2.21 – 2.17 (m, 2H), 2.03 (dd, J = 12.5 Hz, 7.1 Hz, 1H), 1.65 – 1.58 (m, 1H), 1.55 – 1.27 (m, 8H), 1.20 – 1.12 (m, 3H), 1.06 (d, J = 9.7 Hz, 1H), 0.98 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H). ¹³C NMR (125 MHz, C₆D₆): δ 60.3, 54.0, 48.2, 41.0, 39.9, 36.9, 36.5, 35.6, 30.5, 30.2, 29.5, 21.0, 14.4, 12.4. HR MS (ESI+): Found: 210.2222 [M+H]+, calcd. for C₁₄H₂₉N⁺ 210.2222.

**3e:** ¹H NMR (500 MHz, C₆D₆): δ 2.44 – 2.31 (m, 4H), 2.26 (br, 1H), 2.23 – 2.18 (m, 2H), 2.04 (dd, J = 12.5 Hz, 7.0 Hz, 1H), 1.67 – 1.60 (m, 1H), 1.56 – 1.41 (m, 6H), 1.39 – 1.29 (m, 6H), 1.21 – 1.11 (m, 3H), 1.06 (d, J = 9.7 Hz, 1H), 0.92 (t, J = 7.2 Hz, 6H). ¹³C NMR (125 MHz, C₆D₆): δ 61.0, 54.7, 41.0, 39.9, 36.9, 36.5, 35.5, 30.5, 30.2, 29.5, 21.0, 14.4. HR MS (ESI+): Found: 238.2536 [M+H]+, calcd. for C₁₅H₃₂N⁺ 238.2535.

**3f:** ¹H NMR (400 MHz, C₆D₆): δ 2.46 - 2.36 (m, 4H), 2.32 (dd, J = 11.6 Hz, 8.8 Hz, 1H), 2.28 (br, 1H), 2.17 (br, 1H), 2.07 (dd, J = 11.6 Hz, 7.3 Hz, 1H), 1.67 – 1.60 (m, 5H), 1.51 – 1.44 (m, 2H), 1.41 – 1.35 (m, 1H), 1.30 (ddt, J = 9.7 Hz, 3.8 Hz, 1.9 Hz, 1H),
1.22 – 1.10 (m, 3H), 1.07 – 1.03 (m, 1H). 13C NMR (100 MHz, C6D6): δ 62.6, 54.6, 41.9, 39.9, 36.9, 36.7, 35.6, 30.5, 29.5, 24.0. HR MS (ESI+): Found 180.1755 [M+H]+, calcd. for C12H23N+ 180.1752.

3g: 1H NMR (500 MHz, C6D6): δ 2.55 (br, 4H), 2.27 (dd, J = 12.1 Hz, 8.5 Hz, 1H), 2.21 – 2.18 (m, 2H), 2.11 (dd, J = 12.1 Hz, 7.4 Hz, 1H), 1.57 (br, 9H), 1.51 – 1.44 (m, 2H), 1.37 – 1.30 (m, 1H), 1.28 (d, J = 9.5 Hz, 1H), 1.15 (br, 3H), 1.05 (d, J = 9.4 Hz, 1H). 13C NMR (125 MHz, C6D6): δ 64.5, 56.0, 41.3, 39.9, 37.0, 36.4, 35.7, 30.5, 29.5, 29.3, 27.6. HR MS (ESI+): Found: 208.2066 [M+H]+, calcd. for C13H26N+ 208.2065.

3h: 1H NMR (500 MHz, C6D6): δ 2.30 (br, 4H), 2.21 (br, 1H), 2.16 (br, 1H), 2.12 (dd, J = 12.2 Hz, 8.6 Hz, 1H), 1.93 (dd, J = 12.1 Hz, 7.4 Hz, 1H), 1.66 – 1.61 (m, 1H), 1.56 (s, 2H), 1.56 – 1.51 (m, 4H), 1.48 – 1.44 (m, 1H), 1.35 – 1.27 (m, 4H), 1.18 – 1.10 (m, 3H), 1.03 (d, J = 9.7 Hz, 1H). 13C NMR (125 MHz, C6D6): δ 65.8, 55.4, 40.0, 37.0, 36.6, 35.6, 30.5, 30.1, 29.5, 26.7, 25.2. HR MS (ESI+): Found 194.1904 [M+H]+, calcd. for C13H23N+ 194.1909.

3i: 1H NMR (500 MHz, C6D6): δ 2.80 – 2.73 (m, 2H), 2.22 (d, J = 9.0 Hz, 1H), 2.17 – 2.12 (m, 2H), 1.99 – 1.91 (m, 1H), 1.77 (m, 1H), 1.71 – 1.63 (m, 2H), 1.61 – 1.42 (m, 7H), 1.40 – 1.27 (m, 2H), 1.20 – 1.10 (m, 3H), 1.05 (d, J = 9.7 Hz, 1H), 0.83 (d, J = 6.6 Hz, 3H). 13C NMR (125 MHz, C6D6): δ 65.5 (x2), 63.2, 62.8, 55.0, 54.6, 40.1, 40.0 (x3), 37.0, 36.6 (x2), 35.6 (x2), 33.7, 31.6, 31.5, 30.5, 29.5, 26.1, 20.0. HR MS (ESI+): Found 208.2065 [M+H]+, calcd. for C14H28N+ 208.2065.

3j: 1H NMR (500 MHz, C6D6): δ 3.06 (s, 2H), 2.32 (s, 1H), 2.20 (s, 1H), 2.11 (dd, J = 12.1 Hz, 8.5 Hz, 1H), 1.99 (dd, J = 12.1 Hz, 7.2 Hz, 1H), 1.85 – 1.78 (m, 4H), 1.58 – 1.47 (m, 3H), 1.44 – 1.35 (m, 5H), 1.32 – 1.30 (m, 1H), 1.22 – 1.13 (m, 5H), 1.07 (d, J = 9.1 Hz, 1H). 13C NMR (125 MHz, C6D6): δ 57.9, 57.8, 56.7, 39.5, 37.4, 34.5, 34.3, 33.9, 29.1, 29.0, 28.1, 27.1, 24.5, 24.3, 15.0. HR MS (ESI+): Found 220.2065 [M+H]+, calcd. for C15H25N+ 220.2065.

3k: 1H NMR (500 MHz, C6D6): δ 2.72 (d, J = 3.9 Hz, 1H), 2.53 (t, J = 12.5 Hz, 1H), 2.25 (s, 3H), 2.22 – 2.17 (m, 4H), 2.00 (br, 3H), 1.77 (d, J = 11.7 Hz, 3H), 1.73 – 1.71 (m, 1H), 1.67 (d, J = 11.7 Hz, 3H), 1.61 – 1.45 (m, 12H), 1.43 – 1.40 (m, 1H), 1.35 – 1.17 (m, 5H), 1.15 (d, J = 7.5 Hz, 2H), 1.01 (d, J = 9.5 Hz, 2H). 13C NMR (125 MHz, C6D6): δ 54.0, 52.8, 49.3, 46.0, 43.5, 41.8, 41.4, 41.3, 40.4, 39.3, 37.5, 37.3, 35.4, 34.5, 33.3, 31.8, 30.6, 30.2, 29.7 (x2). HR MS (ESI+): Found 368.3317 [M+H]+, calcd. for C20H24N+ 368.3317.

4a: 1H NMR (500 MHz, C6D6): δ 7.19 – 7.16 (m, 2H), 7.12 (d, J = 7.6 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 2.58 (t, J = 7.7 Hz, 2H), 2.25 (br, 4H), 2.20 (t, J = 7.1 Hz, 2H), 1.73 (quin, J = 7.5 Hz, 2H), 1.52 (quin, J = 5.5 Hz, 4H), 1.33 (br, 2H). 13C NMR (125 MHz, C6D6): δ 142.9, 128.9, 128.6, 126.0, 58.6, 54.9, 33.3, 29.3, 26.6, 25.1. HR MS (ESI+): Found 204.1753 [M+H]+, calcd. for C14H19N+ 204.1752.

4b: 1H NMR (500 MHz, C6D6): δ 7.07 (d, J = 7.7 Hz, 2H), 7.02 (d, J = 7.7 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.27 (br, 4H), 2.23 (t, J = 7.2 Hz, 2H), 2.16 (s, 3H), 1.76 (quin, J = 7.5 Hz, 2H), 1.53 (quin, J = 6.0 Hz, 4H), 1.33 (br,
$^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 139.9, 135.1, 129.3, 128.8, 58.7, 55.0, 33.5, 29.4, 26.7, 25.2, 21.1. HR MS (ESI+): Found 218.1906 [M+H]$^+$, calcd. for C$_{15}$H$_{24}$N$^+$ 218.1909.

![Image](ESI+): $^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 148.1, 139.5, 128.2, 125.1, 58.4, 54.6, 34.0, 33.1, 31.2, 29.0, 26.3, 24.8. HR MS (ESI+): Found 260.2373 [M+H]$^+$, calcd. for C$_{18}$H$_{30}$N$^+$ 260.2373.

$^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 149.5, 131.1, 129.4, 113.5, 55.8, 55.0, 40.7, 33.1, 29.8, 26.7, 25.2. HR MS (ESI+): Found 247.2177 [M+H]$^+$, calcd. for C$_{16}$H$_{27}$N$_2^+$ 247.2174.

$^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 159.8 ($J = 242.8$ Hz), 136.5 ($J = 3.2$ Hz), 128.2 ($J = 7.7$ Hz), 113.3 ($J = 21.0$ Hz), 56.4, 53.0, 31.0, 27.3, 24.7, 23.2. HR MS (ESI+): Found 222.1657 [M+H]$^+$, calcd. for C$_{14}$H$_{21}$FN$^+$ 222.1658.

$^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 141.3, 131.8, 130.2, 128.7, 58.3, 54.9, 37.0, 29.0, 26.6, 25.1. HR MS (ESI+): Found 238.1357 [M+H]$^+$, calcd. for C$_{18}$H$_{25}$ClN$^+$ 238.1363.

$^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 142.0, 141.8, 139.2, 129.3, 129.0, 127.4 (x2), 127.2, 58.6, 55.0, 33.5, 29.3, 26.7, 25.2. HR MS (ESI+): Found 280.2060 [M+H]$^+$, calcd. for C$_{20}$H$_{26}$N$^+$ 280.2065.

$^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 63.2, 55.1, 26.7, 25.2, 22.1, 14.5 HR MS (ESI+): Found 200.1834 [M+H]$^+$, calcd. for C$_{14}$H$_{20}$NSiN$^+$ 200.1835.

$^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 132.9, 130.7, 65.9, 55.3, 53.1, 44.7, 42.9, 40.4, 38.7, 32.5, 32.2,
31.3, 26.7, 25.2. 5a: δ 132.7, 131.4, 65.6, 55.4, 54.1, 43.1, 42.5, 41.5, 38.8, 34.3, 32.7, 29.0, 26.7, 25.2; HR MS (ESI+): Found 232.2070 [M+H]+, calcd. for C16H28N1 232.2065.

5b: 1H NMR (500 MHz, C6D6): δ 2.30 (br, 4H), 2.04 (ddd, J = 28.9 Hz, 12.0 Hz, 7.3 Hz, 2H), 1.81 (td, J = 13.7 Hz, 6.8 Hz, 1H), 1.53 (quin, J = 6.0 Hz, 4H), 1.34 (br, 2H), 1.02 (d, J = 6.5 Hz, 3H), 0.84 (dd, J = 14.7 Hz, 4.5 Hz, 1H), 0.36 – 0.28 (m, 1H), 0.07 (s, 9H). 13C NMR (125 MHz, C6D6): δ 69.8, 55.5, 27.6, 26.7, 25.1, 23.3, 21.8, -0.37. HR MS (ESI+): Found 214.1987 [M+H]+, calcd. for C12H28NSi+ 214.1991.

5c: 1H NMR (500 MHz, C6D6): δ 7.19 (t, J = 7.4 Hz, 2H), 7.13 – 7.08 (m, 3H), 2.84 (dd, J = 13.3 Hz, 4.7 Hz, 1H), 2.31 – 2.26 (br m, 5H), 2.09 (dd, J = 12.0 Hz, 7.6 Hz, 1H), 1.99 (dd, J = 12.0 Hz, 7.1 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.52 (quin, J = 6.0 Hz, 4H), 1.33 (br, 2H), 0.87 (d, J = 6.5 Hz, 3H). 13C NMR (125 MHz, C6D6): δ 141.6, 129.7, 128.4 (x2), 126.0, 66.0, 55.3, 41.6, 33.0, 26.7, 25.1, 18.2. HR MS (ESI+): Found 218.1904 [M+H]+, calcd. for C15H24N1 218.1909.

5d: 1H NMR (500 MHz, C6D6): δ 6.88 - 6.81 (m, 4H), 2.69 (dd, J = 13.4 Hz, 4.7 Hz, 1H), 2.24 (br, 4H), 2.17 (dd, J = 13.4 Hz, 8.4 Hz, 1H), 2.02 (dd, J = 12.51 Hz, 7.9 Hz, 1H), 1.95 (dd, J = 12.2 Hz, 6.9 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.52 (quin, J = 5.5 Hz, 4H), 1.33 (br, 2H), 0.80 (d, J = 6.6 Hz, 3H). 13C NMR (125 MHz, C6D6): δ 161.8 (d, J = 242.9 Hz), 137.1 (d, J = 3.2 Hz), 131.0 (d, J = 7.6 Hz), 115.1 (d, J = 20.9 Hz), 65.8, 55.3, 40.5, 32.9, 26.6, 25.1, 18.0. HR MS (ESI+): Found 236.1817 [M+H]+, calcd. for C15H23FN1 236.1815.

5e: 1H NMR (500 MHz, C6D6): δ 8.29 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.23 (d, J = 6.9 Hz, 1H), 3.60 (dd, J = 13.5 Hz, 8.5 Hz, 1H), 2.46 (dd, J = 13.5 Hz, 8.9 Hz, 1H), 2.35 (br, 2H), 2.24 (br, 2H), 2.17 – 1.98 (m, 3H), 1.56 (quin, J = 5.5 Hz, 4H), 1.35 (br, 2H), 0.85 (d, J = 6.4 Hz, 3H). 13C NMR (125 MHz, C6D6): δ 138.4, 134.8, 133.0, 129.2, 127.5, 127.0, 125.8, 125.6 (x2), 124.9, 67.0, 55.7, 39.3, 32.8, 26.7, 25.1, 18.7. HR MS (ESI+): Found 268.2063 [M+H]+, calcd. for C15H26N1 268.2065.

5f: 1H NMR (500 MHz, C6D6): δ 2.29 (br, 4H), 2.10 (dd, J = 12.1 Hz, 6.7 Hz, 1H), 2.00 (dd, J = 12.1 Hz, 7.9 Hz, 1H), 1.68 – 1.59 (m, 1H), 1.54 (quin, J = 5.5 Hz, 4H), 1.51 – 1.45 (m, 1H), 1.38 – 1.22 (m, 6H), 1.12 – 1.05 (m, 1H), 0.97 (d, J = 6.6 Hz, 3H), 0.92 (q, J = 7.0 Hz, 3H). 13C NMR (125 MHz, C6D6): δ 67.0, 55.5, 35.4, 30.9, 29.7, 26.7, 25.2, 23.5, 18.7, 14.4. HR MS (ESI+): Found 184.2064 [M+H]+, calcd. for C12H18N1 184.2065.

5g: 1H NMR (500 MHz, C6D6): δ 2.32 (br m 2H), 2.25 (br, 2H), 2.20 (dd, J = 12.1 Hz, 6.2 Hz, 1H), 2.01 (dd, J = 12.1 Hz, 8.6 Hz, 1H), 1.75 – 1.72 (m, 2H), 1.68 – 1.65 (m, 1H), 1.60 – 1.51 (m, 7H), 1.36 – 1.31 (m, 3H), 1.27 – 1.20 (m, 2H), 1.17 – 1.08 (m, 2H), 1.06 -0.97 (m, 1H), 0.94 (d, J = 6.8 Hz, 3H). 13C NMR (125 MHz, C6D6): δ 64.4, 55.6, 41.3, 35.8, 31.5, 28.7, 27.4, 27.3, 27.2, 26.7, 25.2, 15.1. HR MS (ESI+): Found 210.2224 [M+H]+, calcd. for C10H23N1 210.2222.
5h: $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 2.31 – 2.28 (br, 4H), 2.09 (dd, $J = 12.0$ Hz, 6.7 Hz, 1H), 2.00 (dd, $J = 12.0$ Hz, 7.9 Hz, 1H), 1.89 – 1.64 (m, 6H), 1.54 (quin, $J = 6.0$ Hz, 4H), 1.44 – 1.30 (m, 4H), 1.27 – 1.10 (m, 3H), 0.99 – 0.79 (m, 3H), 0.96 (d, $J = 6.5$ Hz, 3H). $^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 67.4, 55.5, 44.0, 35.4, 34.8, 33.5, 27.7, 27.2, 26.9, 26.8, 26.7, 25.2, 19.2. HR MS (ESI+): Found 224.2378 [M+H]$^+$, calcd. for C$_{15}$H$_{30}$N$^+$ 224.2378.

6a: $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 7.18 (d, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 7.3$ Hz, 2H), 7.08 (t, $J = 7.3$ Hz, 1H), 2.61 (t, $J = 7.6$ Hz, 2H), 2.35 – 2.32 (m, 6H), 1.74 (quin, $J = 7.5$ Hz, 2H), 1.61 – 1.55 (m, 4H). $^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ 142.7, 128.8, 128.7, 126.1, 55.7, 54.2, 33.9, 30.9, 23.9. HR MS (ESI+): Found 190.1599 [M+H]$^+$, calcd. for C$_{13}$H$_{20}$N$^+$ 190.1596.
5. Kinetic Isotope Effect Experiments

\[
\begin{align*}
\text{1f} + \text{2b} & \rightarrow [\text{Sc(CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_3]\text{, (5 mol\%)} \\
& [\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]\text{, (5 mol\%) }]
\end{align*}
\]

Toluene, 70 °C, 24 h

\[
\begin{align*}
\text{N} - \text{CH}_3 & \rightarrow \text{N} - \text{CH}_2\text{-phenyl}
\end{align*}
\]

Compound 6a could be synthesized following the general procedure above in an 81% isolated yield.

**Intermolecular Competition Experiment**

\[
\begin{align*}
\text{N} \text{CD}_3 + \text{N} \text{CH}_3 & \rightarrow [\text{Sc(CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_3]\text{, (5 mol\%)} \\
& [\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]\text{, (5 mol\%) }]
\end{align*}
\]

Toluene, 70 °C, 8 h

\[
\begin{align*}
\text{D/H} & \rightarrow \text{H/D} \\
k_{D} / k_{D} = 2.70 & \text{6a/6ad3}
\end{align*}
\]

In a glovebox, [Sc(CH\text{2}C\text{6}H\text{4}NMe\text{2-o})\text{3}] (6 mg, 0.013 mmol) was dissolved in toluene (1.0 mL). To this solution 1f\text{d3} (22 mg, 0.25 mmol), 1f (21 mg, 0.25 mmol), styrene (26 mg, 0.25 mmol) and [Ph\text{3}C][B(C\text{6}F\text{5})\text{4}] (16 mg, 0.013 mmol) were added sequentially. The biphasic mixture was transferred to a Schlenk ampoule, sealed and heated at 70 °C for 8 hours. EtOAc (5 mL) was added to the crude mixture and the volatiles removed in vacuo. The compound was purified by silica gel column chromatography (hexane/EtOAc), to afford a mixture of 6a and 6ad3 as a colorless oil (12 mg, 25% yield). A \(k_{D}/k_{D}\) value of 2.70 was found by comparison of the relative ratios of 6a and 6ad3 by \(^1\text{H NMR}\) spectroscopy using the integration values for the benzylic proton(s). No deuterium scrambling was observed when this mixture of 6a and 6ad3 was exposed to the standard reaction conditions.

**Fig. S1. The \(^1\text{H NMR Spectrum of an Isolated Mixture of 6a and 6ad3}**
Comparison of Initial Rates

In a glovebox, \([\text{Sc}((\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2-\text{o})_3])\) (6 mg, 0.013 mmol) was dissolved in \(\text{C}_7\text{D}_8\) (1.0 mL). To this solution, ferrocene (19 mg, 0.1 mmol), \(N\)-methylpyrrolidine (21 mg, 0.25 mmol), styrene (29 mg, 0.28 mmol) and \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\) (16 mg, 0.013 mmol) were added sequentially. The biphasic mixture was transferred to a J Young NMR tube, sealed and the reaction monitored by \(^1\text{H}\) NMR at 70 °C for 12 h. The reaction with \(\text{d}_3-N\)-methylpyrrolidine was performed and monitored under exactly the same conditions. Initial rates were extracted by comparing the \(^1\text{H}\) NMR integration of the benzylic proton(s) of 6a and 6a\(_{d3}\) against the internal standard. A \(k_H/k_D\) value of 1.97 ± 0.03 was found by comparison of the initial rates of reaction.

![Fig. S2. Initial Rates of C–H/C–D Addition of N-methylpyrrolidine to Styrene](image)

**Fig. S2.** Initial Rates of C–H/C–D Addition of N-methylpyrrolidine to Styrene

- $y = 7.28145 + 0.1661x$
  - $R^2 = 0.99822$

- $y = -2.64113 + 0.08437x$
  - $R^2 = 0.99852$
6. Dialkylation of 1k to give 3k

**Scheme S1. A Plausible Mechanism for the Formation of 3k**
7. References


8. $^1$H and $^{13}$C NMR spectra of products
3d

C\textsubscript{2}H\textsubscript{5}N

$\text{Et}$

$\text{Et}$