Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of air using reagent grade solvents. All commercially obtained reagents were used as received. Reaction temperatures were controlled using an Heidolph temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde and potassium permanganate. Flash column chromatography was performed using normal phase silica gel (60 Å, 0.040 – 0.063 mm, Geduran). $^1$H NMR spectra were recorded on Varian spectrometers (at 500 or 600 MHz) and are reported
relative to deuterated solvent signals. Data for $^1$H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. $^{13}$C NMR spectra were recorded on Varian Spectrometers (125 or 150 MHz). Data for $^{13}$C NMR spectra are reported in terms of chemical shift (δ ppm), multiplicity, coupling constant (Hz). IR spectra were recorded on a Perkin Elmer Spectrum 100 FT/IR spectrometer and are reported in terms of frequency of absorption (cm$^{-1}$). Mass spectra were obtained from the UC Santa Barbara Mass Spectrometry Facility on a (Waters Corp.) Micromass QTOF2 with an electrospray ionization source. X-ray data were obtained from the UC Santa Barbara X-ray Facility.

**General Procedure for the Synthesis of Hydroxylamines:** Hydroxylamines were synthesized following published procedures.$^1$

\[
\begin{align*}
\text{Bn} & \equiv \text{Benzyl} \\
\text{N} & \equiv \text{Nitrogen} \\
\text{O} & \equiv \text{Oxygen} \\
\text{Bn} & \equiv \text{Benzyl}
\end{align*}
\]

$N,O$-Dibenzylhydroxylamine (2):
Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.27 (m, 10H), 5.74 (s, 1H), 4.67 (s, 2H), 4.07 (s, 2H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.0, 137.7, 129.1, 128.6, 128.5, 127.9, 127.6, 76.5, 56.7 ppm; IR (thin film) 3260, 3087, 3019, 2912, 2858, 1895, 1877, 1810, 1604, 1495, 1453, 1275, 1260, 988 cm$^{-1}$; MS (ESI) $m/z$ 214.1219 (214.1232 calcd for C$_{14}$H$_{16}$NO$^+$ [MH$^+$]).

\[
\begin{align*}
\text{Bn} & \equiv \text{Benzyl} \\
\text{N} & \equiv \text{Nitrogen} \\
\text{O} & \equiv \text{Oxygen} \\
\text{Bn} & \equiv \text{Benzyl}
\end{align*}
\]

$N$-Benzyl-$O$-methylhydroxylamine (S-1):
Colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.38 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 5.73 (s, 1H), 4.06 (s, 2H), 3.52 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 137.7, 129.0, 128.6, 127.6, 62.0, 56.4 ppm; IR (thin film) 3259, 3030, 2937, 2894, 2808, 1604, 1454, 1275, 1260, 992 cm$^{-1}$; MS (ESI) $m/z$ 160.0737 (160.0738 calcd for C$_8$H$_{11}$NNaO$^+$ [MNa$^+$]).
N-Benzyl-O-(tert-butyl)hydroxylamine (S-2):
Colorless oil. $^{1} \text{H NMR}$ (500 MHz, CDCl$_3$) $\delta$ 7.41 – 7.27 (m, 5H), 4.00 (s, 2H), 1.18 (s, 9H) ppm; $^{13} \text{C NMR}$ (150 MHz, CDCl$_3$) $\delta$ 129.4, 128.5, 127.6, 57.8, 26.9 ppm; $\text{IR}$ (thin film) 3255, 2975, 2929, 2863, 1947, 1876, 1806, 1603, 1454, 1360 cm$^{-1}$; $\text{MS}$ (ESI) $m/z$ 180.1362 (180.1383 calcd for C$_{11}$H$_{18}$NO$^+$ [MH]$^+$).

Methyl 4-(((benzyl)oxy(amino)methyl)benzoate (S-3):
Colorless oil. $^{1} \text{H NMR}$ (600 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J$ = 8.2 Hz, 2H), 7.43 (d, $J$ = 8.0 Hz, 2H), 7.38 – 7.27 (m, 5H), 4.63 (s, 2H), 4.09 (s, 2H), 3.92 (s, 3H) ppm; $^{13} \text{C NMR}$ (150 MHz, CDCl$_3$) $\delta$ 167.1, 143.3, 137.8, 129.8, 129.9, 128.9, 128.6, 128.5, 76.6, 56.3, 52.2 ppm; $\text{IR}$ (thin film) 3267, 3031, 2951, 1937, 1721, 1612 cm$^{-1}$; $\text{MS}$ (ESI) $m/z$ 294.1096 (294.1106 calcd for C$_{16}$H$_{17}$NNaO$_3$$^+$ [MNa]$^+$).

O-Benzyl-N-(4-methoxybenzyl)hydroxylamine (S-4):
Colorless oil. $^{1} \text{H NMR}$ (600 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J$ = 3.0 Hz, 4H), 7.30 – 7.32 (m, 1H), 7.30 (d, $J$ = 8.5 Hz, 2H), 6.91 (d, $J$ = 8.6 Hz, 2H), 5.68 (bs, 1H) 4.70 (s, 2H), 4.03 (s, 2H), 3.83 (s, 3H) ppm; $^{13} \text{C NMR}$ (150 MHz, CDCl$_3$) $\delta$ 159.1, 138.0, 130.3, 129.7, 128.5, 128.4, 127.8, 113.9, 76.3, 56.0, 55.3 ppm; $\text{IR}$ (thin film) 3261, 3031, 2910, 2859, 2060, 1883, 1612, 1513 cm$^{-1}$; $\text{MS}$ (ESI) $m/z$ 244.1319 (244.1332 calcd for C$_{15}$H$_{18}$NO$_2$$^+$ [MH]$^+$).

O-Benzyl-N-cinnamylhydroxylamine (S-5):
Colorless oil; $^{1} \text{H NMR}$ (600 MHz, CDCl$_3$) $\delta$ 7.41 – 7.29 (m, 9H), 7.27 – 7.21 (m, 1H), 6.58 (d, $J$ = 16.0 Hz, 1H), 6.30 (dt, $J$ = 15.9, 6.6 Hz, 1H), 5.61 (s, 1H), 4.76 (s, 2H), 3.72 (dd, $J$ = 6.6, 1.3 Hz, 2H) ppm; $^{13} \text{C NMR}$ (125 MHz, CDCl$_3$) $\delta$ 138.0, 137.1, 133.3,
128.7, 128.6, 128.5, 128.0, 127.7, 126.5, 125.7, 76.5, 54.6 ppm; **IR** (thin film) 3258, 3061, 3028, 2910, 2853, 1877, 1598, 1494, 1453, 1361, 1275, 1260, 965 cm\(^{-1}\); **MS** (ESI) \(m/z\) 240.1381 (240.1388 calcd for \(C_{16}H_{18}NO^+ [MH]^+\)).

\[
\text{O-allyl-\(N\)-benzylhydroxylamine (S-6):}
\]

Colorless oil; **\(^1\)H NMR** (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.30 (m, 4H), 7.32 – 7.25 (m, 1H), 5.91 (ddt, \(J = 17.3, 10.4, 5.9\) Hz, 1H), 5.72 (s, 1H), 5.26 (ddt, \(J = 17.3, 1.6, 1.6\) Hz, 1H), 5.18 (ddt, \(J = 10.4, 2.0, 1.2\) Hz, 1H), 4.17 (ddd, \(J = 6.0, 1.3, 1.3\) Hz, 2H), 4.07 (s, 2H) ppm; **\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)) \(\delta\) 137.6, 134.6, 129.1, 128.5, 127.6, 117.7, 75.2, 56.7 ppm; **IR** (thin film) 3254, 3065, 3030, 2907, 2858, 1807, 1645, 1454, 1421, 1343, 1239, 988, 923 cm\(^{-1}\); **MS** (ESI) \(m/z\) 186.0873 (186.0895 calcd for \(C_{10}H_{13}NNaO^+ [MNa]^+\)).

\[
\text{O-benzyl-\(N\)-neopentylhydroxylamine (S-7):}
\]

Colorless oil; **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 5.60 (s, 1H), 4.70 (s, 2H), 2.75 (s, 2H), 0.93 (s, 9H) ppm; **\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)) \(\delta\) 138.1, 128.6, 128.4, 127.8, 75.9, 63.6, 31.1, 28.3 ppm; **IR** (thin film) 3276, 3031, 2953, 2906, 2865, 1476, 1454, 1363, 1275, 1259, 978 cm\(^{-1}\); **MS** (ESI) \(m/z\) 194.1523 (194.1545 calcd for \(C_{12}H_{20}NO^+ [MH]^+\)).

\[
\text{O-benzyl-\(N\)-pentylhydroxylamine (S-8):}
\]

Colorless oil; **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 5.54 (s, 1H), 4.71 (s, 2H), 2.93 (dd, \(J = 7.3, 7.3\) Hz, 2H), 1.52 (ddd, \(J = 7.4, 7.4, 7.4\) Hz, 2H), 1.36 – 1.25 (m, 4H), 0.90 (dd, \(J = 6.8, 6.8\) Hz, 3H) ppm; **\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)) \(\delta\) 138.2, 128.5, 128.5, 127.9, 76.3, 52.4, 29.5, 27.2, 22.7, 14.2 ppm; **IR** (thin
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Film) 3265, 3031, 2955, 2930, 1857, 1454, 1362, 1275, 1206, 998 cm\(^{-1}\); **MS** (ESI) \(m/z\) 194.1535 (194.1545 calcd for C\(_{12}\)H\(_{20}\)NO\(^+\) [MH\(^+\)].

**Ethyl (trans)-5-phenyloxazolidine-4-carboxylate (S-9):**
Prepared according to literature procedure.\(^2\) Colorless oil. \(^1\)H NMR (600 MHz, Chloroform-d) \(\delta\) 7.39 – 7.32 (m, 4H), 7.32 – 7.28 (m, 1H), 5.72 (s, 1H), 5.08 (d, \(J = 5.7\) Hz, 1H), 4.27 – 4.12 (m, 2H), 3.57 (dd, \(J = 11.8, 3.3\) Hz, 1H), 3.47 (dd, \(J = 11.8, 8.4\) Hz, 1H), 3.35 – 3.20 (m, 1H), 1.27 (t, \(J = 7.2\) Hz, 3H) ppm; \(^{13}\)C NMR (151 MHz, Chloroform-d) \(\delta\) 173.2, 139.2, 128.7, 128.3, 126.2, 86.8, 61.4, 56.6, 53.7, 14.2 ppm; IR (thin film) 3229, 3065, 3034, 2983, 2942, 2906, 1886, 1813, 1729 cm\(^{-1}\); **MS** (ESI) \(m/z\) 244.0942 (244.0950 calcd for C\(_{12}\)H\(_{15}\)NO\(_3\)\(^+\) [MH\(^+\)].

\[\text{HN}\overset{\text{O}}{\text{Ph}}\overset{\text{CO}_2\text{Et}}{\text{S-9}}\]

**O-Benzoyl-N-propylhydroxylamine (S-10):**
Colorless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.03 (dd, \(J = 8.5, 1.4\) Hz, 2H), 7.58 (t, \(J = 7.5\) Hz, 1H), 7.46 (t, \(J = 7.8\) Hz, 2H), 3.12 (t, \(J = 7.1\) Hz, 2H), 1.66 (h, \(J = 7.4\) Hz, 2H), 1.01 (t, \(J = 7.4\) Hz, 3H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.1, 133.4, 129.5, 128.7, 128.6, 54.5, 20.7, 11.7 ppm; IR (thin film) 3239, 2963, 2936, 2876, 1765, 1716 cm\(^{-1}\); **MS** (ESI) \(m/z\) 180.0997 (180.1019 calcd for C\(_{10}\)H\(_{14}\)NO\(_2\)\(^+\) [MH\(^+\)].

\[\text{HN}^\text{O}^\text{Ph}\overset{\text{O}}{\text{Ph}}\overset{\text{S-10}}{\text{O}}\]

**General Procedure for the Synthesis of Furylecarbinols:** Furylecarbinols 1 and S-12 – S-19 were prepared using standard synthetic chemistry from readily available commercial starting materials.

\[\text{Ph}^\text{OH}\overset{\text{S-19}}{\text{O}}\]

**Furan-2-yl(phenyl)methanol (1):**
Light yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 3H), 7.36 – 7.30 (m, 1H), 6.32 (dd, \(J = 3.2, 1.8\) Hz, 1H), 6.12 (d, \(J = 3.3\) Hz, 1H), 5.83 (d,
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J = 4.0 Hz, 1H), 2.42 (d, J = 4.3 Hz, 1H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$) δ 156.1, 142.7, 140.9, 128.6, 128.2, 126.7, 110.4, 107.6, 70.3 ppm; IR (thin film) 3362, 3063, 3031, 2897, 1957, 1888, 1810, 1492, 1452, 1141, 1007 cm$^{-1}$; MS (EI$^+$) m/z 174.0685 (174.0681 calcd for C$_{11}$H$_{10}$O$_2$ $^{[M]^+}$).

(5-(3-((Benzyloxy)amino)propyl)furan-2-yl)(phenyl)methanol (S-11):
Light yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.47 – 7.42 (m, 2H), 7.39 – 7.28 (m, 8H), 5.94 (d, J = 3.1 Hz, 1H), 5.90 (d, J = 3.1 Hz, 1H), 5.76 (s, 1H), 4.70 (s, 2H), 2.95 (t, J = 7.0 Hz, 2H), 2.65 (t, J = 7.5 Hz, 2H), 1.85 (tt J = 7.3, 7.3 Hz, 2H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 156.0, 154.5, 141.1, 138.0, 128.5, 128.5, 128.5, 128.0, 127.9, 126.7, 108.4, 105.8, 76.4, 70.2, 51.5, 25.8 ppm; IR (thin film) 3382, 3087, 3062, 3030, 2910, 2858, 1955, 1885, 1453, 1190, 1010, 961 cm$^{-1}$; MS (ESI) m/z 360.1574 (360.1576 calcd for C$_{21}$H$_{23}$NNaO$_3$ $^{[MNa]^+}$).

4-(Furan-2-yl(hydroxy)methyl)benzonitrile (S-12):
Yellow solid; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.69 – 7.63 (m, 2H), 7.59 – 7.54 (m, 2H), 7.42 – 7.38 (m, 1H), 6.36 – 6.31 (m, 1H), 6.15 (d, J = 3.3 Hz, 1H), 5.88 (s, 1H), 2.69 (s, 1H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$) δ 154.7, 146.0, 143.2, 132.4, 127.3, 118.8, 111.8, 110.6, 108.1, 69.4 ppm; IR (thin film) 3418, 3122, 2879, 2228, 1927, 1808, 1609, 1504, 1410, 1141, 1009 cm$^{-1}$; MS (EI$^+$) m/z 199.0628 (199.0633 calcd for C$_{12}$H$_9$O$_2$ $^{[M]^+}$).

Furan-2-yl(4-methoxyphenyl)methanol (S-13):
Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.38 (d, J = 0.8 Hz, 1H), 7.34 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.31 (dd, J = 3.2, 1.8 Hz, 1H), 6.11 (d, J = 3.2 Hz, 1H), 5.76 (s, 1H), 3.80 (s, 3H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$) δ 159.5, 156.3, 142.5,
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133.2, 128.1, 113.9, 110.3, 107.3, 69.9, 55.4 ppm; IR (thin film) 3402, 3001, 2935, 2910, 2837, 1610, 1586, 1510 cm⁻¹; MS (EI) m/z 204.0776 (204.0786 calcd for C₁₂H₁₂O₃⁺ [M⁺]).

Furan-2-yl(thiophen-2-yl)methanol (S-14):
Yellow oil. 
\(^1\)H NMR (600 MHz, CDCl₃) δ 7.69 (d, J = 3.3 Hz, 1H), 7.38 (dd, J = 1.5, 0.7 Hz, 1H), 7.32 (d, J = 3.2 Hz, 1H), 6.35 – 6.30 (m, 2H), 6.08 (s, 1H), 4.79 (s, 1H) ppm; 
\(^{13}\)C NMR (150 MHz, CDCl₃) δ 171.7, 153.3, 143.1, 142.3, 119.9, 110.6, 108.4, 67.6 ppm; IR (thin film) 3119, 2852, 1766, 1621, 1503, 1432 cm⁻¹; MS (EI) m/z 180.0247 (180.0245 calcd for C₉H₈O₂S⁺ [M⁺]).

Furan-2-yl(2,4,6-triisopropylphenyl)methanol (S-15):
Brown solid; 
\(^1\)H NMR (500 MHz, CDCl₃) δ 7.39 (ddd, J = 1.8, 0.8, 0.8 Hz, 1H), 7.05 (s, 2H), 6.41 (d, J = 2.9 Hz, 1H), 6.31 (dd, J = 3.3, 1.8 Hz, 1H), 6.00 (ddd, J = 3.3, 1.1, 1.1 Hz, 1H), 3.35 (hept, J = 6.8 Hz, 2H), 2.89 (hept, J = 6.9 Hz, 1H), 2.32 (d, J = 3.5 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.8 Hz, 6H), 1.15 (d, J = 6.8 Hz, 6H) ppm; 
\(^{13}\)C NMR (150 MHz, CDCl₃) δ 156.4, 148.8, 142.0, 131.7, 122.2, 110.5, 106.6, 65.8, 34.3, 29.8, 25.1, 24.1, 24.1 ppm; IR (thin film) 3408, 2959, 2928, 2868, 1768, 1607, 1460, 1362, 1142, 1004 cm⁻¹; MS (EI⁺) m/z 300.2096 (300.2089 calcd for C₂₀H₂₆O₂⁺ [M⁺]).

Furan-2-yldiphenylmethanol (S-16):
Yellow oil. 
\(^1\)H NMR (600 MHz, CDCl₃) δ 7.46 (s, 1H), 7.40 – 7.27 (m, 10H), 6.34 (d, J = 1.5 Hz, 1H), 5.94 (d, J = 3.2 Hz, 1H), 3.11 (s, 1H) ppm; 
\(^{13}\)C NMR (150 MHz, CDCl₃) δ 158.0, 144.7, 142.8, 128.1, 127.8, 127.3, 110.2, 109.8, 78.1 ppm; IR (thin film) 3410,
3061, 3028, 1957, 1888, 1813, 1725, 1598, 1554, 1490, 1447 cm\(^{-1}\); **MS** (EI) \(m/z\) 250.0991 (250.0994 calcd for C\(_{17}\)H\(_{14}\)O\(_2\) \([\text{M}]^+\)).

1-(Furan-2-yl)pentan-1-ol (S-18):
Colorless oil; \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.37 (m, 1H), 6.32 (dd, \(J = 3.3, 1.8\) Hz, 1H), 6.22 (d, \(J = 3.2\) Hz, 1H), 4.66 (td, \(J = 6.7, 3.8\) Hz, 1H), 1.91 (s, 1H), 1.88 – 1.80 (m, 2H), 1.47 – 1.23 (m, 4H), 0.90 (t, \(J = 7.1\) Hz, 3H) ppm; \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 157.1, 142.0, 110.2, 105.9, 68.0, 35.4, 27.8, 22.6, 14.1 ppm; **IR** (thin film) 3360, 2956, 2932, 2861, 1597, 1505, 1466, 1149, 1007 cm\(^{-1}\); **MS** (EI\(^+\)) \(m/z\) 154.0998 (154.0994 calcd for C\(_9\)H\(_{14}\)O\(_2\) \([\text{M}]^+\)).

1-(Furan-2-yl)-2-methylpropan-1-ol (S-19):
Yellow oil; \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.37 (dd, \(J = 1.8, 0.9\) Hz, 1H), 6.33 (dd, \(J = 3.2, 1.8\) Hz, 1H), 6.23 (d, \(J = 3.2\) Hz, 1H), 4.38 (d, \(J = 7.0\) Hz, 1H), 2.11 (h, \(J = 6.8\) Hz, 1H), 1.84 (s, 1H), 1.02 (d, \(J = 6.7\) Hz, 3H), 0.86 (d, \(J = 6.8\) Hz, 3H) ppm; \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 156.3, 141.8, 110.2, 106.6, 73.7, 33.5, 18.9, 18.4 ppm; **IR** (thin film) 3392, 2961, 2933, 2873, 1665, 1505, 1468 cm\(^{-1}\); **MS** (EI) \(m/z\) 140.0840 (140.0837 calcd for C\(_8\)H\(_{12}\)O\(_2\) \([\text{M}]^+\)).

Synthesis of Substituted Cyclopentenones:

General Procedure for the Synthesis of Substituted Cyclopentenones: Furylcarbinol (17) and hydroxylamine (4) were stirred as a solution in MeNO\(_2\) at rt. 5-10 mol %
Dy(OTf)$_3$ was added to the reaction mixture, and the flask placed in an oil bath preheated at 80 °C. The reactions were monitored by TLC. Upon completion, the reaction was quenched with saturated NaHCO$_3$ at rt and extracted with EtOAc (3x). The combined organic layers were dried over MgSO$_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenones (18).

**Table S1.** A small solvent screen was performed.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time</th>
<th>Temp.</th>
<th>Cyclopentenone Yield</th>
<th>Substitution Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>4 days</td>
<td>80 °C</td>
<td>71%</td>
<td>11%</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>4 days</td>
<td>40 °C</td>
<td>40%</td>
<td>41%</td>
</tr>
<tr>
<td>MeCN</td>
<td>18 h</td>
<td>80 °C</td>
<td>87%</td>
<td>0%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>1 h</td>
<td>80 °C</td>
<td>88%</td>
<td>0%</td>
</tr>
</tbody>
</table>

**Table S2.** Optimization of the rearrangement conditions.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Catalyst</th>
<th>Time</th>
<th>Cyclopentenone Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>Dy(OTf)$_3$</td>
<td>18 h</td>
<td>87%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>Dy(OTf)$_3$</td>
<td>30 min</td>
<td>88%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>Sc(OTf)$_3$</td>
<td>20 min</td>
<td>76%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>La(OTf)$_3$</td>
<td>40 min</td>
<td>91%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>Gd(OTf)$_3$</td>
<td>30 min</td>
<td>88%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>Yb(OTf)$_3$</td>
<td>40 min</td>
<td>94%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>DyCl$_3$</td>
<td>10 h</td>
<td>54%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>PMA$^b$</td>
<td>5 min</td>
<td>Decomp</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>TsOH$^c$</td>
<td>15 min</td>
<td>35%</td>
</tr>
<tr>
<td>MeNO$_2$</td>
<td>Amberlyst$^c$</td>
<td>6 h</td>
<td>35%</td>
</tr>
</tbody>
</table>

[a] Isolated yields. [b] PMA = phosphomolybdic acid. [c] 100 mol % of catalyst was used.
**General Procedure for Table 1 optimization study:** Furylcarbinol (1) and hydroxylamine (2) were stirred as a solution in MeCN or MeNO₂ at rt. The catalyst was added to the reaction mixture, and the flask placed in an oil bath pre-heated at 80 °C. The reactions were monitored by TLC. Upon completion, the reaction was quenched with saturated NaHCO₃ at rt and extracted with EtOAc (3x). The combined organic layers were dried over MgSO₄, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenones (3).

4-(Benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-one (3):

According to the general procedure, furan-2-yl(phenyl)methanol (38.2 mg, 0.220 mmol) and *N*,*O*-dibenzylhydroxylamine (2) (46.8 mg, 0.220 mmol) were treated with Dy(OTf)₃ (6.7 mg, 0.011 mmol) in MeNO₂ (2.2 mL). The resulting reaction mixture was heated to 80 °C for 30 min. The reaction was then quenched at 23 °C with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone 3 (71.6 mg, 88%) as a light orange/yellow solid. **¹H NMR** (600 MHz, CDCl₃) δ 7.61 (s, 1H), 7.36 – 7.20 (m, 9H), 7.15 – 7.04 (m, 6H), 6.33 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 10.2 Hz, 1H), 4.24 (ddd, *J* = 2.3, 2.3, 2.3 Hz, 1H), 4.01 (d, *J* = 12.6 Hz, 1H), 3.93 (s, 1H), 3.80 (d, *J* = 12.6 Hz, 1H) ppm; **¹³C NMR** (125 MHz, CDCl₃) δ 207.1, 162.4, 139.0, 136.7, 136.6, 134.9, 129.9, 129.2, 129.1, 128.5, 128.4, 128.3, 128.3, 127.7, 127.2, 76.9, 73.9, 61.3, 52.7 ppm; **IR** (thin film) 3063, 3031, 2919, 1709, 1595, 1454, 1265, 1029, 975 cm⁻¹; **MS** (ESI) *m/z* 392.1636 (392.1626 calcd for C₂₅H₂₃NNaO₂⁺ [MNa]⁺).
4-(Benzyl(methoxy)amino)-5-phenylcyclopent-2-en-1-one (6):

According to the general procedure, furan-2-yl(phenyl)methanol (30.0 mg, 0.172 mmol) and N-benzyl-O-methylhydroxylamine (S-1) (23.6 mg, 0.172 mmol) were treated with Dy(OTf)₃ (5.2 mg, 0.0086 mmol) in MeNO₂ (1.8 mL). The resulting reaction mixture was heated to 80 °C for 30 min. The reaction was then quenched at 23 °C with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 6 (46.2 mg, 91%) as an orange/brown solid. $^1$H NMR (600 MHz, CDCl₃) δ 7.76 (dd, $J = 5.7$, 2.3 Hz, 1H), 7.33 (dd, $J = 7.4$, 7.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.21 (m, 3H), 7.12 (d, $J = 7.2$ Hz, 2H), 7.08 (s, 2H), 6.36 (dd, $J = 5.7$, 1.9 Hz, 1H), 4.21 (ddd, $J = 2.3$, 2.3, 2.3 Hz, 1H), 3.99 (d, $J = 12.7$ Hz, 1H), 3.87 (s, 1H), 3.74 (d, $J = 12.7$ Hz, 1H), 3.32 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl₃) δ 207.1, 162.1, 138.9, 136.7, 135.0, 129.7, 129.1, 128.5, 128.3, 127.6, 127.2, 73.9, 62.4, 60.9, 52.9 ppm; IR (thin film) 3062, 3030, 2934, 2812, 1709, 1595, 1454, 1266, 1040, 978 cm⁻¹; MS (ESI) m/z 316.1309 (316.1313 calcd for C₁₉H₁₉NNaO₂⁺ [MNa⁺]).

$\text{O} \quad \text{N} \quad \text{Ph}$

$\text{Bn} \quad \text{N} \quad \text{O} \quad \text{tBu}$

$\text{Bn} \quad \text{N} \quad \text{H} \quad \text{O} \quad \text{tBu}$

4 mol % Dy(OTf)₃ MeNO₂, 80 °C

4-(Benzyl(tert-butoxy)amino)-5-phenylcyclopent-2-en-1-one (7):

According to the general procedure, furan-2-yl(phenyl)methanol (31.7 mg, 0.182 mmol) and N-benzyl-O-(tert-butyl)hydroxylamine (S-2) (32.7 mg, 0.182 mmol) were treated with Dy(OTf)₃ (5.54 mg, 0.0091 mmol) in MeNO₂ (1.8 mL). The resulting reaction mixture was heated to 80 °C for 1 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 7 (46.2 mg, 76%) as a colorless oil. $^1$H NMR (600 MHz, CDCl₃) δ 7.68 – 7.63 (m, 1H), 7.35 – 7.25 (m, 3H), 7.19 – 7.03 (m, 5H), 6.79 (d, $J = 7.5$ Hz, 2H), 6.28 (d, $J = 3.6$ Hz, 1H), 4.19 – 4.08 (m, 3H), 3.80 (d, $J = 12.7$ Hz, 1H), 1.22 (s, 9H) ppm; $^{13}$C NMR (150 MHz, CDCl₃) δ 207.9, 164.9, 140.0, 136.9, 134.1, 129.4, 129.1, 128.7, 128.3, 127.5,
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127.1, 78.0, 72.0, 62.8, 51.1, 28.1 ppm; IR (thin film) 3062, 3029, 2975, 2928, 2867, 1712, 1602 cm⁻¹; MS (ESI) m/z 358.1774 (358.1783 calcd for C₂₂H₂₅NNaO₂⁺ [MNa]+).

Methyl 4-(((benzyloxy)(4-oxo-5-phenylcyclopent-2-en-1-yl)amino)methyl)benzoate (8):

According to the general procedure, furan-2-yl(phenyl)methanol (28.8 mg, 0.166 mmol) and methyl 4-(((benzyloxy)amino)methyl)benzoate (S-3) (44.9 mg, 0.166 mmol) were treated with Dy(OTf)₃ (5.1 mg, 0.0084 mmol) in MeNO₂ (1.6 mL). The resulting reaction mixture was heated to 80 ºC for 1 h. The reaction was then quenched at 23 ºC with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 8 (57.4 mg, 82%) as a white solid.

1H NMR (600 MHz, CDCl₃) δ 7.92 (d, J = 7.8 Hz, 2H), 7.62 (s, 1H), 7.33 (t, J = 7.3 Hz, 2H), 7.31 – 7.27 (m, 4H), 7.18 – 7.13 (m, 2H), 7.13 – 7.08 (m, 4H), 6.35 (dd, J = 5.8, 1.9 Hz, 1H), 4.47 – 4.37 (m, 2H), 4.24 (d, J = 2.3 Hz, 1H), 4.04 (d, J = 12.8 Hz, 1H), 3.94 (s, 1H), 3.91 (s, 3H), 3.84 (d, J = 12.8 Hz, 1H) ppm;

13C NMR (150 MHz, CDCl₃) δ 206.8, 167.0, 162.0, 141.9, 138.8, 136.5, 135.1, 129.8, 129.6, 129.2, 129.2, 128.5, 128.5, 128.4, 127.3, 77.0, 74.1, 61.0, 52.7, 52.2 ppm;

IR (thin film) 3084, 3031, 2950, 2910, 2874, 2275, 1738, 1718, 1701 cm⁻¹; MS (ESI) m/z 450.1665 (450.1682 calcd for C₂₇H₂₅NNaO₄⁺ [MNa]+).

4-((Benzyloxy)(4-methoxybenzyl)amino)-5-phenylcyclopent-2-en-1-one (9):
According to the general procedure, furan-2-yl(phenyl)methanol (19.7 mg, 0.113 mmol) and O-benzyl-N-(4-methoxybenzyl)hydroxylamine (S-4) (27.6 mg, 0.113 mmol) were treated with Dy(OTf)$_3$ (3.4 mg, 0.0057 mmol) in MeNO$_2$ (1.1 mL). The resulting reaction mixture was heated to 80 °C for 2h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO$_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO$_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 9 (34.4 mg, 76%) as a white solid. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.59 (s, 1H), 7.36 – 7.26 (m, 6H), 7.20 – 7.14 (m, 2H), 7.11 (d, $J$ = 7.5 Hz, 2H), 6.95 (s, 2H), 6.76 (d, $J$ = 8.1 Hz, 2H), 6.33 (dd, $J$ = 5.8, 2.1 Hz, 1H), 4.44 (s, 2H), 4.24 (d, $J$ = 2.5 Hz, 1H), 3.96 (d, $J$ = 12.5 Hz, 1H), 3.94 (s, 1H), 3.78 (s, 3H), 3.74 (d, $J$ = 12.6 Hz, 1H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$) δ 207.2, 162.6, 159.2, 139.1, 136.8, 134.9, 131.1, 129.3, 129.1, 128.7, 128.6, 128.4, 128.3, 127.2, 113.7, 76.8, 73.6, 60.6, 55.4, 52.8 ppm; IR (thin film) 3030, 2930, 2837, 1884, 1712, 1611 cm$^{-1}$; MS (ESI) m/z 422.1716 (422.1732 calcd for C$_{26}$H$_{25}$NNaO$_3$ $^+$ [MNa$^+$]).

4-((Benzyloxy)(cinnamyl)amino)-5-phenycyclopent-2-en-1-one (10):

According to the general procedure, furan-2-yl(phenyl)methanol (15.0 mg, 0.086 mmol) and O-benzyl-N-cinnamylhydroxylamine (S-5) (20.6 mg, 0.086 mmol) were treated with Dy(OTf)$_3$ (5.2 mg, 0.0086 mmol) in MeNO$_2$ (1.8 mL). The resulting reaction mixture was heated to 80 °C for 1.5 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO$_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO$_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 10 (29.3 mg, 86%) as a light orange oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.63 (s, 1H), 7.35 – 7.19 (m, 11H), 7.16 (d, $J$ = 7.4 Hz, 2H), 7.11 (d, $J$ = 7.2 Hz, 2H), 6.33 (dd, $J$ = 5.8, 2.0 Hz, 1H), 6.12 (ddd, $J$ = 14.7, 6.6, 6.6 Hz, 1H), 5.90 (d, $J$ = 15.9 Hz, 1H), 4.69 (d, $J$ = 10.7 Hz, 1H), 4.63 (d, $J$ = 10.8 Hz, 1H), 4.37 (s, 1H), 3.87 (s, 1H), 3.69 (dd, $J$ = 12.8, 6.1 Hz, 1H), 3.48 (dd, $J$ = 13.0, 8.1 Hz, 1H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 207.1, 162.5, 139.0,
136.8, 136.7, 134.9, 129.2, 129.1, 128.6, 128.5, 128.3, 127.9, 127.2, 126.5, 123.9, 76.8, 73.6, 59.3, 52.4 ppm; IR (thin film) 3061, 3029, 2822, 2854, 1950, 1709, 1495, 1453, 1165, 1028, 968 cm⁻¹; MS (ESI) m/z 418.1766 (418.1783 calcd for C₂₇H₂₅NNaO₂⁺ [MNa⁺]).

4-(((Allyloxy)(benzyl)amino)-5-phenylcyclopent-2-en-1-one (11):

According to the general procedure, furan-2-yl(phenyl)methanol (100.0 mg, 0.57 mmol) and O-allyl-N-benzylhydroxylamine (S-6) (93.8 mg, 0.57 mmol) were treated with Dy(OTf)₃ (17.5 mg, 0.029 mmol) in MeNO₂ (5.7 mL). The resulting reaction mixture was heated to 80 ºC for 45 min. The reaction was then quenched at 23 ºC with saturated aqueous NaHCO₃ (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 11 (173.5 mg, 95%) as an orange oil. ¹H NMR (600 MHz, CDCl₃) δ 7.75 (dd, J = 6.0, 2.5 Hz, 1H), 7.33 (t, J = 7.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.18 (m, 3H), 7.12 (d, J = 7.3 Hz, 2H), 7.07 (s, 2H), 6.36 (dd, J = 5.8, 2.0 Hz, 1H), 5.70 (dddd, J = 16.8, 10.3, 6.2, 6.2 Hz, 1H), 5.15 – 5.07 (m, 2H), 4.25 – 4.19 (m, 1H), 4.02 (d, J = 12.7 Hz, 1H), 4.00 – 3.89 (m, 3H), 3.78 (d, J = 12.7 Hz, 1H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 207.1, 162.3, 138.9, 136.6, 135.0, 133.5, 129.8, 129.1, 128.5, 128.3, 127.6, 127.2, 118.3, 75.9, 73.8, 61.4, 52.8 ppm; IR (thin film) 3063, 3029, 2916, 2858, 1708, 1495, 1454, 1165, 1029, 980 cm⁻¹; MS (ESI) m/z 342.1466 (342.1470 calcd for C₂₁H₂₁NNaO₂⁺ [MNa⁺]).

4-(((Benzzyloxy)(neopentyl)amino)-5-phenylcyclopent-2-en-1-one (12):

According to the general procedure, furan-2-yl(phenyl)methanol (30.0 mg, 0.172 mmol) and O-benzyl-N-neopentylhydroxylamine (S-7) (33.3 mg, 0.172 mmol) were treated with
Dy(OTf)$_3$ (5.2 mg, 0.0085 mmol) in MeNO$_2$ (1.8 mL). The resulting reaction mixture was heated to 80 ºC for 45 min. The reaction was then quenched at 23 ºC with saturated aqueous NaHCO$_3$ (5 mL) and extracted with ethyl acetate ($3 \times 5$ mL). The combined organic layers were dried over MgSO$_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 12 (52.6 mg, 81%) as an orange oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 (dd, $J = 5.8$, 2.3 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.22 (m, 4H), 7.17 – 7.09 (m, 4H), 6.40 (dd, $J = 5.8$, 1.9 Hz, 1H), 4.70 (d, $J = 10.5$ Hz, 1H), 4.62 (d, $J = 10.5$ Hz, 1H), 4.38 (ddd, $J = 2.3$, 2.3, 2.3 Hz, 1H), 3.72 (d, $J = 2.8$ Hz, 1H), 2.65 (d, $J = 14.1$ Hz, 1H), 2.58 (d, $J = 14.1$ Hz, 1H), 0.94 (s, 9H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 207.3, 162.2, 139.2, 136.6, 135.4, 129.0, 128.7, 128.5, 128.3, 128.1, 127.1, 76.5, 75.1, 67.8, 53.5, 31.7, 28.5 ppm; IR (thin film) 3063, 3030, 2952, 2866, 1711, 1601, 1453, 1362, 1026, 981 cm$^{-1}$; MS (ESI) m/z 372.1932 (372.1939 calcd for C$_{23}$H$_{27}$NNaO$_2^+$ [MNa$^+$]).

4-((Benzyloxy)(pentyl)amino)-5-phenylcyclopent-2-en-1-one (13):

According to the general procedure, furan-2-yl(phenyl)methanol (15.0 mg, 0.086 mmol) and O-benzyl-N-pentylhydroxylamine (S-8) (16.7 mg, 0.086 mmol) were treated with Dy(OTf)$_3$ (5.2 mg, 0.0086 mmol) in MeNO$_2$ (0.9 mL). The resulting reaction mixture was heated to 80 ºC for 1 h. The reaction was then quenched at 23 ºC with saturated aqueous NaHCO$_3$ (5 mL) and extracted with ethyl acetate ($3 \times 5$ mL). The combined organic layers were dried over MgSO$_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 13 (22.8 mg, 76%) as an orange oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.73 (dd, $J = 5.8$, 2.3 Hz, 1H), 7.32 (ddd, $J = 7.7$, 4.1 Hz, 5H), 7.27 – 7.22 (m, 3H), 7.13 – 7.08 (m, 2H), 6.36 (dd, $J = 5.8$, 1.9 Hz, 1H), 4.69 (d, $J = 10.6$ Hz, 1H), 4.64 (d, $J = 10.7$ Hz, 1H), 4.27 (ddd, $J = 2.3$, 2.3, 2.3 Hz, 1H), 3.77 (s, 1H), 2.87 (ddd, $J = 12.5$, 8.9, 5.6 Hz, 1H), 2.67 (ddd, $J = 12.5$, 8.8, 5.9 Hz, 1H), 1.57 – 1.41 (m, 2H), 1.29 – 1.20 (m, 4H), 0.89 – 0.81 (m, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 207.3, 162.2, 139.1, 136.8, 135.0, 129.1, 128.9, 128.5, 128.3, 128.3,
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127.1, 77.2, 75.1, 57.4, 52.8, 29.5, 27.1, 22.6, 14.1 ppm; IR (thin film) 3062, 3029, 2954, 2982, 2858, 1711, 1496, 1453, 1165, 1029, 982 cm\(^{-1}\); MS (ESI) \(m/z\) 372.1937 (372.1939 calcd for \(\text{C}_{23}\text{H}_{27}\text{NNaO}_{2}\)\(^{+} \left[\text{MNa}\right]^{+}\)).

Ethyl 2-(4-oxo-5-phenylcyclopent-2-en-1-yl)-5-phenylisoxazolidine-4-carboxylate (14):

According to the general procedure, furan-2-yl(phenyl)methanol (33.7 mg, 0.194 mmol) and ethyl 5-phenylisoxazolidine-4-carboxylate (made according to literature procedure)\(^2\) \(\text{S-9}\) (42.9 mg, 0.194 mmol) were treated with \(\text{Dy(OTf)}_3\) (5.9 mg, 0.0097 mmol) in \(\text{MeNO}_2\) (1.9 mL). The resulting reaction mixture was heated to 80 °C for 1.25 h. The reaction was then quenched at 23 °C with saturated aqueous \(\text{NaHCO}_3\) (5 mL) and extracted with ethyl acetate (3 \(\times\) 5 mL). The combined organic layers were dried over \(\text{MgSO}_4\), filtered and then concentrated \(\text{in vacuo}\). The residue was purified by flash column chromatography to afford cyclopentenone 14 (46.0 mg, 63%, 1:1 mixture of diastereomers) as a brown oil. Higher RF diastereomer \(^1\text{H NMR}\) (500 MHz, Toluene-\(d_8\), 90 °C) \(\delta\) 7.45 – 7.30 (m, 3H), 7.21 – 6.94 (m, 8H), 6.02 (d, \(J = 5.8\) Hz, 1H), 5.33 (d, \(J = 5.9\) Hz, 1H), 4.09 (s, 1H), 3.94 – 3.75 (m, 2H), 3.52 (s, 1H), 3.19 – 3.08 (m, 2H), 3.08 – 3.00 (m, 1H), 3.04 (t, \(J = 8.1\) Hz, 1H), 0.88 (t, \(J = 7.1\) Hz, 3H) ppm; \(^{13}\text{C NMR}\) (200 MHz, Toluene-\(d_8\), 70 °C) 204.0, 171.6, 170.0, 159.8, 135.4, 129.2, 129.1, 128.6, 127.5, 126.8, 125.7, 81.8, 74.3, 61.3, 60.2, 57.0, 56.8, 56.1, 14.3 ppm; IR (thin film) 3063, 3030, 2981, 2927, 2852, 1714, 1597 cm\(^{-1}\); MS (ESI) \(m/z\) 400.1516 (400.1525 calcd for \(\text{C}_{23}\text{H}_{23}\text{NNaO}_{4}\)\(^{+} \left[\text{MNa}\right]^{+}\)).

Lower RF diastereomer \(^1\text{H NMR}\) (500 MHz, Toluene-\(d_8\), 90 °C) \(\delta\) 7.32 (d, \(J = 7.1\) Hz, 3H), 7.19 – 7.10 (m, 2H), 7.10 – 6.95 (m, 6H), 6.02 (dd, \(J = 5.8\) Hz, 1H), 5.18 (d, \(J = 6.5\) Hz, 1H), 4.06 (q, \(J = 2.5\) Hz, 1H), 3.90 (dddd, \(J = 17.9, 10.8, 7.1, 3.7\) Hz, 2H), 3.58 (d, \(J = 3.1\) Hz, 1H), 3.37 (dd, \(J = 9.4, 5.2\) Hz, 1H), 3.06 (ddd, \(J = 8.7, 6.5, 5.1\) Hz, 1H), 2.78 (t, \(J = 9.1\) Hz, 1H), 0.92 (t, \(J = 7.1\) Hz, 3H) ppm; \(^{13}\text{C NMR}\) (125 MHz, Toluene-\(d_8\),
90 °C) 203.9, 171.5, 159.5, 159.3, 141.2, 139.4, 135.6, 135.6, 127.4, 127.0, 100.8, 82.1, 74.9, 61.3, 57.0, 56.5, 56.2, 24.5, 14.4 ppm; IR (thin film) 3063, 3030, 2981, 2925, 2852, 1714, 1597 cm⁻¹; MS (ESI) m/z 400.1508 (400.1525 calcd for C_{23}H_{23}NNaO_{4}^+ [MNa]^+).

4-((Benzoyloxy)(propyl)amino)-5-phenylcyclopent-2-en-1-one (15):
According to the general procedure, furan-2-yl(phenyl)methanol (28.3 mg, 0.163 mmol) and O-benzoyl-N-propylhydroxylamine (S-10) (29.1 mg, 0.163 mmol) were treated with 30 mol % Dy(OTf)₃ (29.8 mg, 0.0489 mmol) in MeCN (1.6 mL). The resulting reaction mixture was stirred at room temperature for 58 h. The reaction was then quenched with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 15 (27.1 mg, 50%) as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (dd, J = 8.3, 1.4 Hz, 2H), 7.84 (dd, J = 5.8, 2.4 Hz, 1H), 7.58 (dddd, J = 7.1, 7.1, 1.3, 1.3 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 7.20 – 7.14 (m, 2H), 6.36 (dd, J = 5.8, 1.9 Hz, 1H), 4.56 (dd, J = 4.6, 2.3 Hz, 1H), 3.89 (d, J = 2.8 Hz, 1H), 3.16 – 3.09 (m, 1H), 2.91 (ddd, J = 12.7, 8.2, 6.8 Hz, 1H), 1.61 – 1.48 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 206.2, 165.7, 160.9, 138.4, 135.7, 133.6, 129.6, 129.3, 128.7, 128.5, 128.2, 127.5, 76.0, 59.6, 52.7, 20.6, 11.6 ppm; IR (thin film) 3063, 3030, 2964, 2935, 2876, 1743, 1712 cm⁻¹; MS (ESI) m/z 358.1406 (358.1419 calcd for C_{21}H_{21}NNaO_{3}^+ [MNa]^+).

1-(Benzyloxy)-6-phenyl-1-azaspiro[4.4]non-8-en-7-one (16):
According to the general procedure, (5-(3-((benzyloxy)amino)propyl)furan-2-yl)(phenyl)methanol (S-11) (240 mg, 0.71 mmol) was treated with Dy(OTf)₃ (21.6 mg,
0.036 mmol) in MeNO₂ (7 mL). The resulting reaction mixture was heated to 80 °C for 1 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 16 (185.6 mg, 82%) as a yellow oil. \(^1\)H NMR (500 MHz, CDCl₃) δ 7.54 (d, \(J = 5.8\) Hz, 1H), 7.38 – 7.21 (m, 8H), 7.06 – 7.00 (m, 2H), 6.34 (d, \(J = 5.8\) Hz, 1H), 4.73 (d, \(J = 11.4\) Hz, 1H), 4.70 (d, \(J = 11.4\) Hz, 1H), 4.00 (s, 1H), 3.28 – 3.20 (m, 1H), 3.10 (ddd, \(J = 10.2, 8.0, 4.3\) Hz, 1H), 1.71 – 1.59 (m, 2H), 1.60 – 1.50 (m, 1H), 1.28 – 1.13 (m, 1H) ppm; \(^1\)C NMR (125 MHz, CDCl₃) δ 208.2, 165.5, 137.8, 137.6, 134.5, 130.2, 129.0, 128.6, 128.5, 128.2, 127.1, 78.5, 76.8, 56.6, 53.5, 29.5, 18.9 ppm; IR (thin film) 3061, 3029, 2940, 2865, 1707, 1594, 1496, 1453, 1342, 1208, 1032, 977, 918 cm⁻¹; MS (ESI) m/z 342.1477 (342.1470 calcd for C₂₁H₂₁NNaO₂⁺ [MNa⁺]).

4-(2-(Benzyl(benzyloxy)amino)-5-oxocyclopent-3-en-1-yl)benzonitrile (19):
According to the general procedure, 4-(furan-2-yl(hydroxy)methyl)benzonitrile (34.4 mg, 0.172 mmol) and N,O-dibenzylhydroxylamine (2) (36.8 mg, 0.172 mmol) were treated with Dy(OTf)₃ (5.2 mg, 0.0086 mmol) in MeNO₂ (1.8 mL). The resulting reaction mixture was heated to 80 °C for 17 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 19 (57.0 mg, 84%) as an orange oil. \(^1\)H NMR (500 MHz, CDCl₃) δ 7.63 – 7.56 (m, 3H), 7.32 – 7.22 (m, 6H), 7.16 (d, \(J = 8.1\) Hz, 2H), 7.15 – 7.10 (m, 2H), 7.07 (s, 2H), 6.32 (dd, \(J = 5.8, 2.0\) Hz, 1H), 4.45 (d, \(J = 10.9\) Hz, 1H), 4.43 (d, \(J = 10.9\) Hz, 1H), 4.22 (ddd, \(J = 2.3\) Hz, 1H), 4.00 (d, \(J = 12.6\) Hz, 1H), 3.95 (s, 1H), 3.78 (d, \(J = 12.5\) Hz, 1H) ppm; \(^1\)C NMR (125 MHz, CDCl₃) δ 205.3, 162.3, 144.3, 136.5, 136.2, 134.7, 132.7, 129.6, 129.4, 129.5, 128.4, 128.0, 118.8, 111.1, 76.8, 73.1, 61.1, 52.6 ppm; IR (thin film)
4-(Benzyl(benzyloxy)amino)-5-(4-methoxyphenyl)cyclopent-2-en-1-one (20):
According to the general procedure, furan-2-yl(4-methoxyphenyl)methanol (23.1 mg, 0.113 mmol) and \( \text{H}_{\text{O}} \) dibenzylhydroxylamine (2) (24.1 mg, 0.113 mmol) were treated with Dy(OTf)\(_3\) (3.4 mg, 0.0057 mmol) in MeNO\(_2\) (1.1 mL). The resulting reaction mixture was heated to 80 °C for 30 min. The reaction was then quenched at 23 °C with saturated aqueous NaHCO\(_3\) (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO\(_4\), filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 20 (36.7 mg, 81%) as a yellow waxy solid. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.61 (s, 1H), 7.31 – 7.27 (m, 3H), 7.28 – 7.23 (m, 3H), 7.15 – 7.09 (m, 4H), 7.02 (d, \( J = 8.6 \) Hz, 2H), 6.87 (d, \( J = 8.6 \) Hz, 2H), 6.32 (dd, \( J = 5.8, 1.9 \) Hz, 1H), 4.41 (s, 2H), 4.21 (dd, \( J = 4.2, 2.1 \) Hz, 1H), 4.01 (d, \( J = 12.6 \) Hz, 1H), 3.88 (s, 1H), 3.81 (d, \( J = 12.6 \) Hz, 1H), 3.80 (s, 3H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 207.4, 162.2, 158.8, 136.7, 136.7, 134.9, 130.9, 130.0, 129.5, 129.3, 128.4, 128.4, 128.3, 127.7, 114.6, 77.0, 73.9, 61.4, 55.5, 52.0 ppm; IR (thin film) 3030, 2921, 2854, 1883, 1708, 1611, 1511 cm\(^{-1}\); MS (ESI) \( m/z \) 422.1717 (422.1732 calcd for C\(_{26}\)H\(_{25}\)N\(_2\)NaO\(_3\)\(^+\) [MNa\(^+\)].

4-(Benzyl(benzyloxy)amino)-5-(thiophen-2-yl)cyclopent-2-en-1-one (21):
According to the general procedure, furan-2-yl(thiophen-2-yl)methanol (31.1 mg, 0.172 mmol) and \( \text{H}_{\text{O}} \) dibenzylhydroxylamine (2) (36.8 mg, 0.172 mmol) were treated with Dy(OTf)\(_3\) (5.2 mg, 0.0086 mmol) in MeNO\(_2\) (1.8 mL). The resulting reaction mixture was heated to 80 °C for 30 min. The reaction was then quenched at 23 °C with saturated
aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 21 (59.2 mg, 92%) as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.59 (s, 1H), 7.32 – 7.27 (m, 6H), 7.14 – 7.10 (m, 2H), 7.00 – 6.96 (m, 1H), 6.90 (d, J = 3.3 Hz, 1H), 6.31 (dd, J = 6.0, 1.8 Hz, 1H), 4.43 (d, J = 10.6 Hz, 1H), 4.40 (d, J = 10.6 Hz, 1H), 4.34 (ddd, J = 2.4, 2.4, 2.4 Hz, 1H), 4.20 (s, 1H), 4.06 (d, J = 12.7 Hz, 1H), 3.95 (d, J = 12.7 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 204.7, 161.4, 140.1, 136.7, 136.5, 134.1, 129.9, 129.2, 128.6, 128.4, 128.3, 127.8, 127.2, 125.9, 124.7, 77.0, 74.1, 61.4, 47.6 ppm; IR (thin film) 3064, 3030, 2919, 2867, 1954, 1712, 1454, 1343, 1167, 1028, 972 cm⁻¹; MS (ESI) m/z 398.1188 (398.1191 calcd for C₂₃H₂₁NNaO₂S⁺ [MNa]⁺).

(4R,5S)-4-(Benzyl(benzyloxy)amino)-5-(2,4,6-triisopropylphenyl)cyclopent-2-en-1-one (22): According to the general procedure, furan-2-yl(2,4,6-triisopropylphenyl)methanol (32.0 mg, 0.105 mmol) and N,O-dibenzylhydroxylamine (2) (22.5 mg, 0.105 mmol) were treated with Dy(OTf)₃ (3.2 mg, 0.0053 mmol) in MeNO₂ (1.0 mL). The resulting reaction mixture was heated to 80 ºC for 40 min. The reaction was then quenched at 23 ºC with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 22 (41.7 mg, 80%) as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 7.39 – 7.30 (m, 4H), 7.28 (d, J = 7.3 Hz, 2H), 7.17 – 7.13 (m, 1H), 7.11 (t, J = 7.4 Hz, 2H), 7.07 (d, J = 1.9 Hz, 1H), 6.90 (d, J = 1.9 Hz, 1H), 6.67 (s, 2H), 6.31 (d, J = 4.7 Hz, 1H), 4.66 (d, J = 11.2 Hz, 1H), 4.63 – 4.53 (m, 2H), 4.03 (s, 1H), 3.99 (d, J = 12.2 Hz, 1H), 3.65 (d, J = 12.2 Hz, 1H), 3.57 (p, J = 6.8 Hz, 1H), 2.91 (hept, J = 6.9 Hz, 1H), 1.83 (hept, J = 6.7 Hz, 1H), 1.44 (d, J = 6.6 Hz, 3H), 1.29 (t, J = 7.1 Hz, 6H), 1.25 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.5 Hz, 3H), 0.65 (d, J = 5.6 Hz, 3H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 207.4, 160.9, 147.9, 147.7, 137.3, 136.3, 134.4, 130.7, 129.7, 129.2, 128.4, 128.3, 128.2, 127.5, 122.5,
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121.4, 76.2, 72.6, 60.1, 48.3, 34.4, 30.7, 30.3, 29.9, 26.5, 24.4, 24.3, 24.2, 24.1, 22.2 ppm; IR (thin film) 3063, 3032, 2960, 2926, 2868, 1710, 1607 cm⁻¹; MS (ESI) m/z 518.3011 (518.3035 calcd for C₃₄H₄₁NNaO₂⁺ [MNa⁺]).

4-(Benzyl(benzyloxy)amino)-5,5-diphenylcyclopent-2-en-1-one (23):
According to the general procedure, furan-2-yldiphenylmethanol (43.2 mg, 0.173 mmol) and N,O-dibenzylhydroxylamine (2) (36.8 mg, 0.173 mmol) were treated with Dy(OTf)₃ (5.3 mg, 0.0087 mmol) in MeNO₂ (1.7 mL). The resulting reaction mixture was heated to 80 °C for 4 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 23 (58.4 mg, 76%) as a yellow oil. ¹H NMR (500 MHz, Toluene-d₈, 90 °C) δ 7.58 (dd, J = 6.1, 2.8 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.30 – 7.19 (m, 2H), 7.13 – 7.09 (m, 2H), 7.08 – 6.89 (m, 11H), 6.79 (d, J = 6.7 Hz, 2H), 6.32 (s, 1H), 6.02 (dd, J = 6.0, 1.4 Hz, 1H), 4.96 (s, 1H), 3.95 (d, J = 11.0 Hz, 1H), 3.76 (d, J = 10.9 Hz, 1H), 3.49 (dd, J = 20.3, 12.9 Hz, 2H) ppm; ¹³C NMR (125 MHz, Toluene-d₈, 90 °C) δ 205.0, 143.5, 142.1, 138.3, 135.3, 132.0, 131.8, 130.5, 130.4, 130.4, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.3, 127.0, 75.8, 75.5, 63.6, 60.7 ppm; IR (thin film) 3087, 3060, 3030, 2922, 2858, 1952, 1883, 1808, 1709 cm⁻¹; MS (ESI) m/z 468.1920 (468.1940 calcd for C₃₁H₂₇NNaO₂⁺ [MNa⁺]).

4-((Benzyloxy)(neopentyl)amino)-5,5-diphenylcyclopent-2-en-1-one (24):
According to the general procedure, furan-2-yldiphenylmethanol (100.0 mg, 0.40 mmol) and O-benzyl-N-neopentylhydroxylamine (S-7) (77.2 mg, 0.40 mmol) were treated with Dy(OTf)₃ (12.2 mg, 0.020 mmol) in MeNO₂ (4.0 mL). The resulting reaction mixture was
heated to 80 °C for 18 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 24 (142.0 mg, 83%) as a brown/orange solid. 

\[ ^1H \text{ NMR} (500 \text{ MHz, toluene-}d_8, 80 \degree \text{C}) \delta 7.58 (dd, J = 6.1, 2.7 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.18 (d, J = 7.5 Hz, 2H), 7.03 (m, 11H) 6.02 (dd, J = 6.0, 1.4 Hz, 1H), 4.92 (s, 1H), 4.28 (d, J = 11.1 Hz, 1H), 3.86 (s, 1H), 2.55 (d, J = 13.9 Hz, 1H), 2.25 (d, J = 13.8 Hz, 1H), 0.71 (s, 9H) ppm; \]

\[ ^{13}C \text{ NMR} (125 \text{ MHz, toluene-}d_8, 80 \degree \text{C}) \delta 204.5, 158.1, 143.9, 141.3, 138.0, 135.0, 131.8, 131.6, 128.5, 128.4, 128.2, 127.6, 126.9, 126.7, 77.2, 73.2, 67.7, 62.9, 31.7, 28.7, 24.2 ppm; IR (thin film) 3059, 2953, 2868, 1707, 1494, 1444, 1265, 1037, 1029, 949 \text{ cm}^{-1}; MS (ESI) m/z 448.2231 (448.2252 \text{ calcd for C}_{29}\text{H}_{31}\text{NNaO}_2^+ [MNa]^+) \]

4-(Benzyl(benzyloxy)amino)-5-butylcyclopent-2-en-1-one (25):

According to the general procedure, 1- (furan-2-yl)pentan-1-ol (26.5 mg, 0.172 mmol) and \(N,N\)-dibenzylhydroxylamine (2) (36.7 mg, 0.172 mmol) were treated with Dy(OTf)₃ (10.5 mg, 0.0172 mmol) in MeNO₂ (1.8 mL). The resulting reaction mixture was heated to 80 °C for 48 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 25 (31.8 mg, 53%) as a dark yellow oil. 

\[ ^1H \text{ NMR} (500 \text{ MHz, CDCl}_3) \delta 7.66 (dd, J = 5.9, 2.0 Hz, 1H), 7.42 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.29 – 7.24 (m, 3H), 7.11 – 7.05 (m, 2H), 6.26 (dd, J = 5.8, 1.4 Hz, 1H), 4.34 (s, 2H), 3.98 (d, J = 12.9 Hz, 1H), 3.95 (d, J = 13.1 Hz, 1H), 3.91 (s, 1H), 2.53 (s, 1H), 1.76 – 1.65 (m, 1H), 1.63 – 1.51 (m, 1H), 1.35 – 1.23 (m, 4H), 0.88 (dd, J = 6.9 Hz, 3H) ppm; \]

\[ ^{13}C \text{ NMR} (125 \text{ MHz, CDCl}_3) \delta 209.9, 160.8, 137.4, 136.7, 135.7, 129.8, 129.1, 128.5, 128.4, 128.2, 127.8, 76.9, 71.7, 60.7, 47.2, 30.0, 28.9, 23.0, 14.0 ppm; IR (thin film) 3063, 3031, 2955, 2928, 2858, 2816, 2714, 1699, 1639, 1550, 1474, 1444, 1365, 1265, 1230, 1192, 1019, 949 \text{ cm}^{-1}; MS (ESI) m/z 488.2252 (488.2260 \text{ calcd for C}_{30}\text{H}_{33}\text{NNaO}_2^+ [MNa]^+) \]
1707, 1454, 1359, 1176, 1028, 976 cm$^{-1}$; $\text{MS (ESI) } m/z$ 372.1941 (372.1939 calcd for C$_{23}$H$_{27}$NNaO$_2^+$ [MNa$^+$]).

(4-(Benzyl(benzyloxy)amino)-5-isopropylcyclopent-2-en-1-one (26):
According to the general procedure, 1-(furan-2-yl)-2-methylpropan-1-ol (12.1 mg, 0.086 mmol) and N,O-dibenzylhydroxylamine (2) (18.4 mg, 0.086 mmol) were treated with Dy(OTf)$_3$ (5.2 mg, 0.0086 mmol) in MeNO$_2$ (0.9 mL). The resulting reaction mixture was heated to 80 °C for 24 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO$_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over MgSO$_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford cyclopentenone 26 (14.4 mg, 50%) as a light orange oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.74 (dd, $J = 5.7$, 2.1 Hz, 1H), 7.36 (m, 5H), 7.28 – 7.22 (m, 3H), 7.09 – 7.01 (m, 2H), 6.26 (dd, $J = 5.8$, 1.3 Hz, 1H), 4.33 (s, 2H), 4.00 – 3.87 (m, 3H), 2.41 (s, 1H), 2.19 (dqq, $J = 13.9$, 6.9, 4.5 Hz, 1H), 0.94 (d, $J = 6.9$ Hz, 3H), 0.83 (d, $J = 6.8$ Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 209.7, 160.8, 137.5, 136.7, 136.6, 129.8, 129.1, 128.5, 128.4, 128.2, 127.8, 77.0, 68.9, 60.5, 52.9, 29.0, 20.2, 18.8 ppm; IR (thin film) 3063, 3031, 2957, 2928, 2872, 1703, 1454, 1367, 1181, 1028, 963 cm$^{-1}$; $\text{MS (ESI) } m/z$ 358.1787 (358.1783 calcd for C$_{22}$H$_{25}$NNaO$_2^+$ [MNa$^+$]).

4-((Benzyloxy)(neopentyl)amino)-5-isopropylcyclopent-2-en-1-one (27):
According to the general procedure, 1-(furan-2-yl)-2-methylpropan-1-ol (20.0 mg, 0.140 mmol) and O-benzyl-N-neopentylhydroxylamine (S-7) (27.6 mg, 0.140 mmol) were treated with Dy(OTf)$_3$ (8.7 mg, 0.014 mmol) in MeNO$_2$ (1.4 mL). The resulting reaction mixture was heated to 80 °C for 96 h. The reaction was then quenched at 23 °C with saturated aqueous NaHCO$_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The
combined organic layers were dried over MgSO₄, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone 27 (22.6 mg, 51%) as an orange oil. \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.80 (dd, \(J = 5.8, 2.1\) Hz, 1H), 7.36 – 7.27 (m, 5H), 6.27 (dd, \(J = 5.9, 1.6\) Hz, 1H), 4.79 (d, \(J = 10.6\) Hz, 1H), 4.73 (d, \(J = 10.6\) Hz, 1H), 4.15 (s, 1H), 2.55 (d, \(J = 14.3\) Hz, 1H), 2.34 (d, \(J = 14.0\) Hz, 1H), 2.27 (dqq, \(J = 13.8, 6.9, 4.1\) Hz, 1H), 2.15 (s, 1H), 1.04 (d, \(J = 7.0\) Hz, 3H), 0.97 (s, 9H), 0.87 (d, \(J = 6.8\) Hz, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl₃) \(\delta\) 209.5, 161.9, 137.0, 136.8, 128.6, 128.5, 128.1, 74.6, 69.1, 66.0, 53.4, 31.6, 28.8, 28.6, 20.5, 18.6 ppm; IR (thin film) 3065, 3032, 2955, 2870, 1705, 1463, 1362, 1027, 976 cm⁻¹; MS (ESI) \(\text{m/z}\) 338.2093 (338.2096 calcd for C₂₀H₂₉NNaO₂⁺ [MNa]+).

### Selected Functionalization of the Cyclopentenone Scaffold:

\[
\begin{align*}
\text{O} & \phantom{\text{MeMgBr}} \phantom{\text{LaCl₃(LiCl)}} \phantom{\text{THF}, 0{^\circ}\text{C}, 1\text{h}} \phantom{16:1 \text{dr}} \phantom{\text{PCC, 4Å MS}} \phantom{\text{CH₂Cl₂, rt, 2h}} \text{O} \\
\text{N} & \phantom{\text{MeMgBr}} \phantom{\text{LaCl₃(LiCl)}} \phantom{\text{THF}, 0{^\circ}\text{C}, 1\text{h}} \phantom{16:1 \text{dr}} \phantom{\text{PCC, 4Å MS}} \phantom{\text{CH₂Cl₂, rt, 2h}} \\
\text{Ph} & \phantom{\text{MeMgBr}} \phantom{\text{LaCl₃(LiCl)}} \phantom{\text{THF}, 0{^\circ}\text{C}, 1\text{h}} \phantom{16:1 \text{dr}} \phantom{\text{PCC, 4Å MS}} \phantom{\text{CH₂Cl₂, rt, 2h}} \text{Ph} \\
\text{Bn} & \phantom{\text{MeMgBr}} \phantom{\text{LaCl₃(LiCl)}} \phantom{\text{THF}, 0{^\circ}\text{C}, 1\text{h}} \phantom{16:1 \text{dr}} \phantom{\text{PCC, 4Å MS}} \phantom{\text{CH₂Cl₂, rt, 2h}} \\
\text{OBn} & \phantom{\text{MeMgBr}} \phantom{\text{LaCl₃(LiCl)}} \phantom{\text{THF}, 0{^\circ}\text{C}, 1\text{h}} \phantom{16:1 \text{dr}} \phantom{\text{PCC, 4Å MS}} \phantom{\text{CH₂Cl₂, rt, 2h}} \\
\text{HO} & \phantom{\text{MeMgBr}} \phantom{\text{LaCl₃(LiCl)}} \phantom{\text{THF}, 0{^\circ}\text{C}, 1\text{h}} \phantom{16:1 \text{dr}} \phantom{\text{PCC, 4Å MS}} \phantom{\text{CH₂Cl₂, rt, 2h}} \\
\text{Me} & \phantom{\text{MeMgBr}} \phantom{\text{LaCl₃(LiCl)}} \phantom{\text{THF}, 0{^\circ}\text{C}, 1\text{h}} \phantom{16:1 \text{dr}} \phantom{\text{PCC, 4Å MS}} \phantom{\text{CH₂Cl₂, rt, 2h}} \\
\end{align*}
\]

5-(Benzyl(benzyloxy)amino)-3-methyl-4-phenylcyclopent-2-en-1-one (29):

Adapted from literature procedure.\(^3\) In a flame dried round bottom flask with magnetic stirrer under \(N_2\) atmosphere, 4-(benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-one 3 was dissolved in 0.5 mL dry THF followed by the addition of 0.6 M \(\text{LaCl₃(LiCl)}\) in THF (0.0939 mmol, 157 \(\mu\)L) and stirring at room temperature for 1 hour. The reaction mixture was cooled to 0 \(°\)C and 3.0 M methylmagnesium bromide in diethyl ether (0.188 mmol, 63 \(\mu\)L) was added. Stirring at 0 \(°\)C continued until complete as determined by thin layer chromatography. Upon completion, the reaction was quenched with saturated aqueous \(\text{NH}_₄\text{Cl}\) (5 mL) then extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated *in vacuo*. The crude reaction mixture contained allylic alcohol 28 in 16:1 dr as determined by \(^1\)H NMR spectroscopy. The crude reaction mixture was passed through a silica gel plug using 3:1 hexanes : ethyl acetate and used as is for the subsequent reaction. 80% Yield of crude material.
Adapted from literature procedure. In a 10 mL round bottom flask containing a magnetic stir bar under N\textsubscript{2} atmosphere, 4Å mol sieves (500 mg) and pyridinium chlorochromate (PCC) (27.2 mg, 0.126 mmol) were added to anhydrous CH\textsubscript{2}Cl\textsubscript{2} (1 mL) followed by addition of 4-(benzyl(benzyloxy)amino)-1-methyl-5-phenylcyclopent-2-en-1-ol 28 (24.3 mg, 0.063 mmol). Reaction was stirred until complete (2 h) as determined by thin layer chromatography. Upon completion, 5 mL Et\textsubscript{2}O was added, and the residual solids were decanted off (3 x). The decanted liquid was transferred to a separatory funnel containing 5 mL 2M NaOH and extracted with Et\textsubscript{2}O (3 x 5 mL). The combined organic layers were dried over MgSO\textsubscript{4}, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography (1% EtOAc in toluene) to afford cyclopentenone 29 (18.4 mg, 70%) (56% yield over 2 steps) as a colorless oil. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.36 – 7.30 (m, 2H), 7.31 – 7.24 (m, 3H), 7.21 – 7.16 (m, 3H), 7.14 – 7.08 (m, 7H), 6.16 (s, 1H), 4.65 (d, \(J = 10.3\) Hz, 1H), 4.42 (d, \(J = 10.3\) Hz, 1H), 4.33 (s, 1H), 4.10 (d, \(J = 12.4\) Hz, 1H), 3.93 (d, \(J = 12.4\) Hz, 1H), 3.62 (d, \(J = 2.7\) Hz, 1H), 1.85 (s, 3H) ppm; \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 205.3, 179.1, 141.0, 137.0, 136.5, 130.7, 130.0, 129.3, 129.3, 128.4, 128.2, 128.1, 128.1, 127.6, 127.4, 76.5, 76.5, 60.8, 51.4, 18.2 ppm; IR (thin film) 3405, 3063, 3030, 2924, 2857, 1953, 1880, 1810, 1711, 1623 cm\textsuperscript{-1}; MS (ESI) \(m/z\) 406.1795 (406.1783 calcd for C\textsubscript{26}H\textsubscript{25}NNaO\textsubscript{2}\textsuperscript{+} [MNa]\textsuperscript{+}).

\[ \text{4-(Benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-ol (30 and 30m):}\]

4-(Benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-one (18) (231 mg, 0.63 mmol) and YbCl\textsubscript{3}·6H\textsubscript{2}O (387.5 mg, 1.25 mmol) was dissolved in 3 mL THF, then 23 mL MeOH was added and the solution stirred while cooling to -78 °C. NaBH\textsubscript{4} (47.3 mg, 1.25 mmol) was added in one portion and the reaction was stirred at -78 °C until complete (1 h) as determined by thin layer chromatography (2:1 hexanes:ethyl acetate, stained with
The reaction was then quenched with saturated aqueous NH₄Cl (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over MgSO₄, filtered and then concentrated in vacuo. The residue (20:1 dr as determined by ¹H NMR of crude mixture) was purified by flash column chromatography (15:1 → 9:1 → 6:1 hexanes:ethyl acetate) to afford cyclopentenone 30 (174 mg, 78%) as a colorless oil. **Major Diastereomer:** ¹H NMR (600 MHz, CDCl₃)  δ 7.36 – 7.27 (m, 10H), 7.23 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 7.2 Hz, 2H), 7.15 – 7.09 (m, 2H), 6.24 – 6.19 (m, 1H), 6.19 – 6.14 (m, 1H), 4.48 (s, 1H), 4.43 (d, J = 9.8 Hz, 1H), 4.29 (d, J = 9.8 Hz, 1H), 4.06 (d, J = 12.7 Hz, 1H), 3.96 (q, J = 2.1 Hz, 1H), 3.85 (d, J = 12.7 Hz, 1H), 3.44 (s, 1H), 2.49 (s, 1H) ppm; ¹³C NMR (150 MHz, CDCl₃)  δ 144.5, 137.4, 137.0, 136.1, 134.4, 130.1, 129.5, 128.9, 128.5, 128.4, 128.3, 127.6, 127.0, 126.4, 83.4, 78.2, 77.3, 61.4, 53.1 ppm; IR (thin film) 3414, 3062, 2978, 2928, 2878, 1602, 1454 cm⁻¹; MS (ESI) m/z 394.1785 (394.1783 calcd for C₂₅H₂₅NNaO₂⁺ [MNa⁺]).

**Minor Diastereomer:** ¹H NMR (600 MHz, Chloroform-d)  δ 7.37 – 7.31 (m, 2H), 7.32 – 7.21 (m, 12H), 7.03 (s, 2H), 6.31 (d, J = 6.4 Hz, 1H), 6.12 (d, J = 5.8 Hz, 1H), 4.96 (d, J = 6.8 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.40 – 4.24 (m, 2H), 3.89 (d, J = 12.9 Hz, 1H), 3.82 – 3.71 (m, 2H) ppm; ¹³C NMR (150 MHz, Chloroform-d)  δ 139.0, 137.0, 135.8, 135.4, 130.0, 129.4, 129.1, 128.8, 128.3, 128.2, 128.0, 127.4, 127.1, 77.7, 77.0, 76.5, 61.6 ppm; IR (thin film) 3413, 3062, 3003, 2919, 1602, 1495, 1454, 1361 cm⁻¹; MS (ESI) m/z 394.1769 (394.1783 calcd for C₂₅H₂₅NNaO₂⁺ [MNa⁺]).

3-Amino-2,2-diphenylcyclopentan-1-one (31): In a 20 mL vial, 4-(benzyl(benzyloxy)amino)-5,5-diphenylcyclopent-2-en-1-one 23 (13.4 mg, 0.0301 mmol) was dissolved in MeOH (1.5 mL), followed by addition of Palladium on carbon (10 wt%) (1.6 mg, 0.0015 mmol). One drop of 12M HCl from an 18 gauge needle was added prior to placing the vial into the pressure vessel. The reaction mixture was placed under H₂ gas at 70 bar for 48h. The reaction mixture was filtered over Celite. The Celite
pad was rinsed with ethyl acetate (3 x 5mL). The organic layer was then quenched with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 x 5 ml). The combined organic layers were dried with Na₂SO₄, filtered and then concentrated in vacuo to afford 31 (7.6 mg, quantitative yield) as a clear oil. 

**1H NMR** (600 MHz, CDCl₃) δ 7.41 (d, J = 7.6 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 3H), 7.24 – 7.19 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 4.37 (t, J = 4.5 Hz, 1H), 2.75 – 2.60 (m, 1H), 2.46 – 2.29 (m, 2H), 1.83 – 1.74 (m, 1H), 1.69 (bs, 2H) ppm; 

**13C NMR** (150 MHz, CDCl₃) δ 216.3, 140.5, 139.8, 129.7, 128.8, 128.6, 128.2, 127.3, 127.0, 66.7, 56.4, 36.0, 27.5 ppm; 

**IR** (thin film) 3372, 3302, 3086, 3057, 3032, 2925, 2855, 1763, 1672 cm⁻¹; 

**MS** (EI) m/z 251.1305 (251.1310 calcd for C₁₇H₁₇NO⁺ [M⁺]).

3-(Neopentylamino)-2,2-diphenylcyclopentan-1-one (32): 

In a 20 mL vial, 4-((benzyloxy)(neopentyl)amino)-5,5-diphenylcyclopent-2-en-1-one 24 (41.5 mg, 0.098 mmol) was dissolved in MeOH (1.5 mL), followed by addition of Palladium on carbon (10 wt%) (5.2 mg, 0.0049 mmol). One drop of 12M HCl from an 18 gauge needle was added prior to placing the vial into the pressure vessel. The reaction mixture was placed under H₂ gas at 70 bar for 48h. The reaction mixture was filtered over Celite. The Celite pad was rinsed with ethyl acetate (3 x 5mL). The organic layer was then quenched with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over Na₂SO₄, filtered and then concentrated in vacuo to afford 32 (31.3 mg, quantitative yield) as a brown oil.

**1H NMR** (600 MHz, CDCl₃) δ 7.45 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.20 (d, J = 7.5 Hz, 3H), 3.94 (t, J = 4.3 Hz, 1H), 2.63 (ddd, J = 18.9, 9.0, 7.2 Hz, 1H), 2.46 (d, J = 11.1 Hz, 1H), 2.28 (ddd, J = 18.8, 9.1, 4.5 Hz, 1H), 2.22 (d, J = 11.0 Hz, 1H), 2.19 (dddd, J = 11.5, 9.1, 5.9, 3.5 Hz, 1H), 1.89 (dddd, J = 13.4, 9.1, 4.4, 4.4 Hz, 1H), 1.29 (s, 1H), 0.76 (s, 9H) ppm; 

**13C NMR** (150 MHz, CDCl₃) δ 216.6, 140.4, 140.0, 66.3, 63.4, 59.8, 35.5, 31.7, 29.8, 27.7, 23.8 ppm; 

**IR** (thin film) 3347, 3087, 3058, 3032, 2925, 2855, 1763, 1672 cm⁻¹;
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3031, 2951, 2864, 1737, 1599 cm⁻¹; MS (EI) m/z 321.2096 (321.2093 calcd for C_{22}H_{27}NO⁺ [M⁺]).

Synthesis of Allylic Alcohols:

4-((Allyloxy)(benzyl)amino)-5-phenylcyclopent-2-en-1-ol (S-20):
A solution of 11 (300.0 mg, 0.94 mmol) in MeOH (22 mL) was treated with CeCl₃•7H₂O (384.9 mg, 1.03 mmol) and stirred at rt for 20 min. The solution was cooled to –78 °C and subsequently treated with NaBH₄ (46.2 mg, 1.22 mmol) and stirred at this temperature until the reaction was complete by TLC. The reaction was quenched with H₂O, and allowed to come to rt before removal of the solvent and extracting with EtOAc (3 x 10 mL). The combined organic phases were dried over MgSO₄, filtered and then concentrated in vacuo. ¹H NMR analysis of the crude reaction mixture indicated a 5:1 mixture of diastereomers. The residue was purified by flash column chromatography to afford the separated allylic alcohols S-20 and S-20m (286.8 mg, 95% combined yield) as yellow oils. Major diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (m, 2H), 7.27 – 7.24 (m, 5H), 7.25 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 6.19 (ddd, J = 5.7, 1.9, 1.9 Hz, 1H), 6.11 (dd, J = 5.7, 2.3 Hz, 1H), 5.70 (dddd, J = 16.8, 10.3, 6.3, 6.3 Hz, 1H), 5.17 – 5.08 (m, 1H), 5.13–5.11 (m, 1H), 4.48 (d, J = 6.1 Hz, 1H), 4.04 (d, J = 12.7 Hz, 1H), 3.96 – 3.90 (m, 1H), 3.90 – 3.83 (m, 2H), 3.81 (d, J = 12.8 Hz, 1H), 3.43 (s, 1H), 2.65 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 144.4, 137.3, 137.1, 134.4, 133.0, 130.0, 128.9, 128.3, 127.5, 127.0, 126.5, 119.0, 83.3, 78.0, 76.0, 61.4, 53.3 ppm; IR (thin film) 3413, 3061, 3029, 2918, 2851, 1601, 1494, 1453, 1344, 1080, 1027, 995, 925 cm⁻¹; MS (ESI) m/z 344.1605 (344.1626 calcd for C_{21}H_{23}NNaO₂ [MNa⁺]). Minor diastereomer: ¹H NMR (600 MHz, CDCl₃) δ 7.33 (t, J = 7.5 Hz, 2H), 7.29 – 7.18 (m, 8H), 6.27 (d, J = 4.3 Hz, 1H), 6.11 – 6.05 (m, 1H), 5.63 (dddd, J = 16.7, 10.4, 6.3, 6.3 Hz, 1H), 5.07 – 5.00 (m, 2H), 4.92 (d, J = 5.9 Hz, 1H), 4.40 – 4.36 (m, 1H), 3.90 – 3.82 (m, 3H), 3.76 – 3.68 (m,
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2H), 1.25 (d, $J = 12.8$ Hz, 1H) ppm; $^{13}$C NMR (125 MHz, CHCl$_3$) $\delta$ 139.0, 137.7, 135.9, 135.2, 133.8, 129.8, 129.4, 128.8, 128.2, 127.4, 127.1, 117.9, 77.6, 76.2, 75.9, 61.6, 50.8 ppm; IR (thin film) 3425, 3061, 3029, 2917, 2865, 1602, 1494, 1453, 1342, 1069, 1029, 994 cm$^{-1}$; MS (ESI) $m/z$ 344.1636 (344.1626 calcd for C$_{21}$H$_{23}$NNaO$_2$ [MNa]$^+$).

4-((Benzyloxy)(neopentyl)amino)-5-phenylcyclopent-2-en-1-ol (S-21 and S-21m):

A solution of 12 (52.6 mg, 0.15 mmol) in MeOH (3.6 mL) was treated with CeCl$_3$·7H$_2$O (61.7 mg, 0.17 mmol) and stirred at rt for 20 min. The solution was cooled to –78 °C and subsequently treated with NaBH$_4$ (7.4 mg, 0.20 mmol) and stirred at this temperature until the reaction was complete as judged by TLC. The reaction was quenched with H$_2$O and allowed to come to rt before extracting with EtOAc (3x 6 mL). The combined organic phases were dried over MgSO$_4$, filtered and then concentrated in vacuo. $^1$H NMR analysis of the crude reaction mixture indicated a 2:1 mixture of diastereomers. The residue was purified by flash column chromatography to afford the separated allylic alcohols S-21 and S-21m (37.1 mg, 70% combined yield) as yellow oils. 

**Major diastereomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.33 – 7.27 (m, 5H), 7.23 – 7.19 (m, 3H), 7.16 – 7.11 (m, 2H), 6.18 (dd, $J = 5.7$, 2.1 Hz, 1H), 6.15 (ddd, $J = 5.7$, 1.8, 1.8 Hz, 1H), 4.76 (d, $J = 10.0$ Hz, 1H), 4.58 (d, $J = 9.9$ Hz, 1H), 4.45 (s, 1H), 3.95 (s, 1H), 3.25 (dd, $J = 2.6$, 2.6 Hz, 1H), 2.82 (d, $J = 14.1$ Hz, 1H), 2.60 (d, $J = 14.1$ Hz, 1H), 2.33 (s, 1H), 0.95 (s, 9H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.9, 136.7, 136.2, 134.6, 129.1, 128.9, 128.6, 128.3, 127.0, 126.3, 83.3, 80.9, 75.6, 69.0, 53.9, 31.7, 28.7 ppm; IR (thin film) 3408, 3086, 3061, 3029, 2951, 2903, 2866, 1945, 1804, 1602, 1453, 1360, 1209, 1020, 1011, 909 cm$^{-1}$; MS (ESI) $m/z$ 374.2069 (374.2096 calcd for C$_{23}$H$_{29}$NNaO$_2$ [MNa]$^+$).

**Minor Diastereomer:** $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.34 (t, $J = 7.5$ Hz, 2H), 7.30 – 7.24 (m, 6H), 7.14 (d, $J = 6.0$ Hz, 2H), 6.30 (d, $J = 5.6$ Hz, 1H), 6.13 – 6.04 (m, 1H), 4.92 (d, $J = 6.5$ Hz, 1H), 4.66 – 4.60 (m, 2H), 4.56 (s, 1H), 3.53 (dd, $J = 6.2$ Hz, 1H), 2.61 (d, $J = 14.2$ Hz, 1H), 2.48 (d, $J = 14.2$ Hz, 1H), 1.25 (s, 1H), 0.89 (s, 9H) ppm; $^{13}$C NMR (125
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MHz, CDCl$_3$) $\delta$ 139.3, 137.2, 136.1, 135.5, 129.4, 128.8, 128.6, 128.4, 127.9, 127.0, 78.4, 77.4, 74.8, 67.6, 50.4, 31.6, 28.6 ppm; IR (thin film) 3412, 3086, 3061, 3030, 2951, 2904, 2865, 1947, 1807, 1602, 1453, 1361, 1208, 1027, 910 cm$^{-1}$; MS (ESI) $m/z$ 374.2097 (374.2096 calcd for C$_{23}$H$_{29}$NNaO$_2$ $^{[\text{MNa}]}^+$).

**4-(Benzyl(benzyloxy)amino)-5-butylcyclopent-2-en-1-ol (S-22 and S-22m):**

A solution of 25 (145.5 mg, 0.42 mmol) in MeOH (10 mL) was treated with CeCl$_3$•7H$_2$O (170.6 mg, 0.45 mmol) and stirred at rt for 20 min. The solution was cooled to –30 °C and subsequently treated with NaBH$_4$ (20.5 mg, 0.54 mmol) and stirred at this temperature until the reaction was complete by TLC. The reaction was quenched with H$_2$O and allowed to come to rt before extracting with EtOAc (3x 10 mL). The combined organic phases were dried over MgSO$_4$, filtered and then concentrated in vacuo. $^1$H NMR analysis of the crude reaction mixture indicated a 1.3:1 mixture of diastereomers. The residue was purified by flash column chromatography to afford the separated allylic alcohols S-22 and S-22m (132.6 mg, 90% combined yield) as a yellow oil (major) and light orange solid (minor). **Major diastereomer:** $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J$ = 7.2 Hz, 2H), 7.36 (t, $J$ = 7.4 Hz, 2H), 7.31 (t, $J$ = 7.3 Hz, 1H), 7.25 (d, $J$ = 5.9 Hz, 3H), 7.08 – 7.05 (m, 2H), 6.03 (d, $J$ = 5.3 Hz, 1H), 5.99 – 5.95 (m, 1H), 4.35 (d, $J$ = 9.7 Hz, 1H), 4.24 – 4.18 (m, 1H), 4.15 (d, $J$ = 8.4 Hz, 1H), 3.96 (d, $J$ = 12.8 Hz, 1H), 3.86 (d, $J$ = 12.8 Hz, 1H), 3.51 (s, 1H), 2.28 (s, 1H), 2.15 (s, 1H), 1.42 – 1.27 (m, 6H), 0.90 (dd, $J$ = 7.0, 7.0 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 137.9, 136.7, 136.1, 133.0, 130.0, 129.5, 128.5, 128.4, 128.3, 127.6, 80.9, 77.2, 76.1, 61.3, 46.9, 33.6, 30.1, 23.0, 14.2 ppm; IR (thin film) 3422, 3087, 3062, 3031, 2955, 2926, 2856, 1496, 1454, 1359, 1209, 1028, 1000 cm$^{-1}$; MS (ESI) $m/z$ 374.2010 (374.2096 calcd for C$_{23}$H$_{29}$NNaO$_2$ [MNa]$^+$).

**Minor Diastereomer:** $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J$ = 7.2 Hz, 2H), 7.33 (t, $J$ = 7.3 Hz, 2H), 7.29 (d, $J$ = 7.2 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.11 – 7.02 (m, 2H), 6.24 (d, $J$ = 5.2 Hz, 1H), 6.06 (ddd, $J$ = 5.8, 2.1, 2.1 Hz, 1H), 4.78 (d, $J$ = 5.6 Hz, 1H), 4.34 (s, 2H),...
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3.93 (d, J = 13.0 Hz, 1H), 3.85 (d, J = 13.0 Hz, 1H), 3.80 (s, 1H), 2.13 (ddddd, J = 12.5, 6.1, 6.1, 6.1 Hz, 1H), 1.64 – 1.54 (m, 1H), 1.52 – 1.45 (m, 1H), 1.45 – 1.38 (m, 1H), 1.37 – 1.28 (m, 3H), 1.14 (s, 1H), 0.91 (dd, J = 7.1, 7.1 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.3, 137.2, 136.0, 134.7, 129.8, 129.1, 128.3, 127.9, 127.4, 76.7, 76.2, 76.1, 60.3, 44.6, 31.0, 27.5, 23.2, 14.3 ppm; IR (thin film) 3376, 3089, 3064, 3033, 2956, 2930, 2872, 2859, 1606, 1496, 1454, 1362, 1265, 1210, 1028, 906 cm$^{-1}$; MS (ESI) m/z 374.2087 (374.2096 calcd for C$_{23}$H$_{29}$NNaO$_2$ [MNa]$^+$).

1-(Benzyloxy)-6-phenyl-1-azaspiro[4.4]non-8-en-7-ol (S-23):
A solution of 16 (85.0 mg, 0.27 mmol) in MeOH (3.6 mL) and THF (0.4 mL) was treated with YbCl$_3$$\cdot$6H$_2$O (206.4 mg, 0.53 mmol) and stirred at rt for 20 min. The solution was subsequently treated with NaBH$_4$ (20.1 mg, 0.53 mmol) and stirred at this temperature until the reaction was complete by TLC. The reaction was quenched with saturated NH$_4$Cl and extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over MgSO$_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography to afford allylic alcohol S-23 (66.5 mg, 77%, isolated as an inseparable mixture of diastereomers with 8:1 d.r.) as a light yellow oil. Major: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39 – 7.28 (m, 8H), 7.27 – 7.22 (m, 2H), 6.18 (dd, J = 5.7, 1.9 Hz, 1H), 6.02 (d, J = 5.3 Hz, 1H), 5.19 (dd, J = 6.3, 6.3 Hz, 1H), 4.80 – 4.67 (m, 2H), 3.68 (d, J = 7.0 Hz, 1H), 3.17 – 2.99 (m, 2H), 1.70 – 1.60 (m, 2H), 1.59 – 1.49 (m, 1H), 1.49 – 1.38 (m, 1H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.3, 137.9, 137.6, 137.2, 130.6, 128.9, 128.5, 128.4, 127.9, 127.1, 83.0, 78.3, 76.6, 54.7, 53.3, 30.6, 19.3 ppm; IR (thin film) 3413, 3086, 3059, 3029, 2940, 2866, 1601, 1494, 1453, 1362, 1208, 1080, 1026, 974 cm$^{-1}$; MS (ESI) m/z 344.1640 (344.1626 calcd for C$_{21}$H$_{23}$NNaO$_2$ [MNa]$^+$).

Reductive N–O bond cleavage:

\[
\begin{array}{c}
\text{Ph} \quad \text{N} \\
\text{BnO} \quad \text{16} \\
\uparrow \\
\text{NaBH}_4 \\
\text{MeOH/THF (8:1), rt} \\
\downarrow \\
\text{Ph} \quad \text{N} \\
\text{BnO} \quad \text{S-23} \\
\end{array}
\]

8:1 d.r.
4-(Benzylamino)-5-phenylcyclopent-2-en-1-ol (35):

4-(Benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-ol 30 (13.3 mg, 0.036 mmol) was dissolved in 0.5 mL THF, followed by addition of 6-9 micron Zn powder (46.8 mg, 0.716 mmol). Next, 2M HCl (1 mL) in H₂O was added and the solution was heated to 70 °C. Reaction was stirred until complete (2 h) as determined by thin layer chromatography. The reaction was then quenched by the addition of 4M NaOH (aq) until pH 14 was reached and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over Na₂SO₄, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography (3% MeOH in CH₂Cl₂) to afford the free amine 35 (9.5 mg, quantitative yield) as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.32 (t, J = 7.5 Hz, 2H), 7.28 – 7.22 (m, 4H), 7.19 (t, J = 7.2 Hz, 4H), 6.00 (t, J = 7.0 Hz, 2H), 4.64 (d, J = 4.5 Hz, 1H), 3.84 – 3.77 (m, 2H), 3.73 (d, J = 13.1 Hz, 1H), 3.18 (s, 2H), 3.00 (t, J = 4.9 Hz, 1H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 143.0, 138.9, 135.6, 134.5, 128.9, 128.6, 127.6, 127.4, 126.8, 83.9, 69.6, 62.0, 51.3 ppm; IR (thin film) 3294, 3061, 3028, 2922, 1951, 1877, 1810, 1734, 1602, 1495 cm⁻¹; MS (ESI) m/z 288.1371 (288.1371 calcd for C₁₈H₁₉NNaO⁺ [MNa⁺]).

4-(Benzylamino)-5-phenylcyclopent-2-en-1-ol (36):

A solution of S-30m (20.0 mg, 0.062 mmol) in THF (1.9 mL) was treated with Zn (81.4 mg, 1.2 mmol), followed by slow addition of 3.7 mL 2M HCl. The reaction was placed in an oil bath at 70 °C and stirred until no starting material was observed by TLC. The reaction was then cooled to rt, quenched with saturated NaHCO₃, then the pH was adjusted to 9 using 3 M NaOH before extraction with EtOAc (3 x 5 mL). The combined
Supporting Information

Veits, Wenz, Palmer, St. Amant, Hein and Read de Alaniz*

Organic phases were dried over Na$_2$SO$_4$, filtered, and solvent removed in vacuo. The residue was purified by flash column chromatography to afford 36 (11.7 mg, 98%) as a light yellow solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 3H), 7.27 – 7.24 (m, 2H), 7.24 – 7.18 (m, 3H), 6.21 (dd, $J = 5.8, 1.7$ Hz, 1H), 6.04 (ddd, $J = 5.8, 2.2, 2.2$ Hz, 1H), 4.84 (ddd, $J = 6.3, 2.1, 2.1$ Hz, 1H), 4.31 (dddd, $J = 6.6, 1.8, 1.8$, 1.8 Hz, 1H), 3.77 (s, 2H), 3.23 (dd, $J = 6.4, 6.4$ Hz, 1H), 1.57 (s, 2H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 140.1, 138.7, 138.2, 133.2, 129.4, 128.8, 128.5, 128.3, 127.2, 127.2, 77.3, 67.2, 57.8, 52.4 ppm; IR (thin film) 3302, 3059, 3027, 2901, 2851, 1601, 1553, 1493, 1453, 1319, 1094, 1070, 1028 cm$^{-1}$; MS (ESI) $m/z$ 288.1354 (288.1364 calcd for C$_{18}$H$_{19}$NNaO [MNa$^+$]).

4-(Neopentylamino)-5-phenylcyclopent-2-en-1-ol (37):

A solution of S-21 (7.6 mg, 0.022 mmol) in THF (0.7 mL) was treated with Zn (28.3 mg, 0.43 mmol), followed by slow addition of 1.3 mL 2M HCl. The reaction was placed in an oil bath at 70 °C and stirred until no starting material was observed by TLC. The reaction was then cooled to rt, quenched with saturated NaHCO$_3$, then the pH was adjusted to ~10 using 3 M NaOH before extraction with EtOAc (3 x 5 mL). The combined organic phases were dried over Na$_2$SO$_4$, filtered, and solvent removed in vacuo. The residue was purified by flash column chromatography to afford 37 (3.1 mg, 58%) as a yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.32 (t, $J = 7.3$ Hz, 2H), 7.27 – 7.20 (m, 3H), 6.08 (d, $J = 5.7$ Hz, 1H), 6.01 (d, $J = 5.2$ Hz, 1H), 4.68 (s, 1H), 3.80 – 3.75 (m, 1H), 2.99 – 2.94 (m, 1H), 2.39 (s, 2H), 1.28 (s, 1H), 1.25 (s, 1H), 0.89 (s, 9H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.0, 136.7, 133.9, 129.0, 127.4, 126.9, 84.1, 71.4, 59.2, 31.4, 29.9, 27.9 ppm; IR (thin film) 3293, 3061, 3028, 2953, 2926, 2855, 1555, 1467, 1453, 1363, 1079, 1013, 906 cm$^{-1}$; MS (ESI) $m/z$ 246.1853 (246.1858 calcd for C$_{16}$H$_{24}$NO [MH$^+$]).
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4-(Benzylamino)-5-butylcyclopent-2-en-1-ol (38):  
A solution of S-22 (30.2 mg, 0.086 mmol) in THF (2.6 mL) was treated with Zn (112.4 mg, 1.7 mmol), followed by slow addition of 5.2 mL 2M HCl. The reaction was placed in an oil bath at 70 °C and stirred for 40 min, until no starting material was observed by TLC. The reaction was then cooled to rt, quenched with saturated NaHCO₃, then the pH was adjusted to ~10 using 3 M NaOH before extraction with EtOAc (3 × 5 mL). The combined organic phases were dried over Na₂SO₄, filtered, and solvent removed *in vacuo*. The residue was purified by flash column chromatography to afford 38 (17.3 mg, 82%) as a yellow oil.  

$$\text{H NMR (500 MHz, CDCl}_3\delta 7.37 – 7.30 \text{ (m, 4H), 7.28 – 7.23 \text{ (m, 1H), 5.97 – 5.91 \text{ (m, 1H), 5.89 \text{ (ddd, } J = 5.7, 1.7, 1.7 \text{ Hz, 1H), 4.32 – 4.27 \text{ (m, 1H), 3.84 \text{ (d, } J = 2.0 \text{ Hz, 2H), 3.34 – 3.28 \text{ (m, 1H), 2.53 \text{ (s, 2H), 1.79 \text{ (ddd, } J = 10.0, 3.6, 3.6, 3.6 \text{ Hz, 1H), 1.56 – 1.28 \text{ (m, 6H), 0.91 \text{ (dd, } J = 7.1, 7.1 \text{ Hz, 3H) ppm; 13C NMR (125 MHz, CDCl}_3\delta 139.5, 135.7, 134.4, 128.6, 128.5, 127.4, 81.6, 67.9, 54.7, 51.8, 33.1, 30.1, 23.1, 14.2 \text{ ppm; IR (thin film) 3290, 3059, 2039, 2955, 2924, 2855, 1454, 1354, 1073, 1027, 996 \text{ cm}^{-1}; MS (ESI) m/z 268.1662 (268.1677 \text{ calcd for C}_{16}H_{23}NNaO [MNa]^+).}}$$

6-Phenyl-1-azaspiro[4.4]non-8-en-7-ol (39):  
A solution of (S-23) (66.5 mg, 0.21 mmol, as an 8:1 mixture of diastereomers) in 6.4 mL THF was treated with zinc (274.7 mg, 4.2 mmol), followed by dropwise addition of 2M HCl (12.7 mL). The reaction was placed in an oil bath heated to 70 °C and stirred for 2 hours. The reaction was then cooled to rt, quenched with saturated NaHCO₃, then the pH
was adjusted to ~10 using 3M NaOH before extraction with EtOAc (3 x 10 mL). The combined organic phases were dried over Na$_2$SO$_4$, filtered, and solvent removed in vacuo. The residue was purified by flash column chromatography to afford 39 (34.3 mg, 77%) as a yellow oil and an inseparable 7:1 mixture of diastereomers. Major: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32 – 7.23 (m, 5H), 6.04 (d, $J = 5.8$ Hz, 1H), 6.01 (dd, $J = 5.8$, 1.9 Hz, 1H), 5.13 (ddd, $J = 6.4$, 1.6, 1.6 Hz, 1H), 3.37 (d, $J = 6.4$ Hz, 1H), 2.94 (ddd, $J = 10.4$, 7.9, 5.0 Hz, 1H), 2.84 (ddd, $J = 10.6$, 6.8, 6.8 Hz, 1H), 2.14 (bs, 3H), 1.73 – 1.46 (m, 5H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 140.6, 138.0, 134.7, 130.7, 128.4, 127.2, 77.7, 76.6, 61.0, 45.7, 34.8, 25.7 ppm; IR (thin film) 3363, 3060, 3029, 2922, 2852, 1600, 1554, 1455, 1387, 1104, 1083, 1033 cm$^{-1}$; MS (ESI) $m/z$ 216.1393 (216.1388 calcd for C$_{14}$H$_{18}$NO [MH]$^+$).

**Allylic Oxidation:**

4-(Benzylamino)-5-phenylcyclopent-2-en-1-one (40):

A solution of (35) (50.0 mg, 0.19 mmol) in 1.9 mL dry DMF was treated with pyridinium dichromate (PDC) (354 mg, 0.94 mmol) and stirred at rt for 2 h. The reaction was quenched with water (20 mL) and diluted with EtOAc (5 mL). The phases were separated, and the aqueous phase extracted with EtOAc (3 x 5 mL). Subsequently, the combined organic phases were washed with H$_2$O (5 x 5 mL) and brine (2 x 5 mL). The organic layer was dried over MgSO$_4$, filtered and solvent removed in vacuo to give the crude, desired product 40 (35 mg, 70%) as a yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.68 (s, 1H), 7.42 – 7.03 (m, 10H), 6.31 (s, 1H), 4.13 (s, 1H), 3.91 (d, $J = 12.8$ Hz, 1H), 3.82 (d, $J = 12.3$ Hz, 1H), 3.41 (s, 1H), 2.19 (bs, 1H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 207.1, 163.3, 139.4, 138.4, 134.0, 129.0, 128.6, 128.3, 127.4, 127.3, 67.3, 60.6, 51.9 ppm; IR (thin film) 3085, 3061, 3029, 2925, 2853, 1705, 1494, 1453, 1265 cm$^{-1}$; MS (ESI) $m/z$ 264.1376 (264.1388 calcd for C$_{18}$H$_{18}$NO [MH]$^+$).
4-(Benzylamino)-2-phenylcyclopent-2-en-1-one (41):
Upon purification on silica, exposure to base, or standing at rt, 40 isomerizes to the more thermodynamically stable cyclopentenone 41. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J = 2.6$ Hz, 1H), 7.71 – 7.65 (m, 2H), 7.41 – 7.32 (m, 7H), 7.32 – 7.27 (m, 1H), 4.08 (ddd, $J = 5.9, 2.5, 2.5$ Hz, 1H), 3.95 (d, $J = 13.0$ Hz, 1H), 3.91 (d, $J = 13.0$ Hz, 1H), 2.91 (dd, $J = 18.5, 6.2$ Hz, 1H), 2.43 (dd, $J = 18.5, 2.4$ Hz, 1H), 1.63 (bs, 2H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.2, 157.9, 143.9, 139.7, 139.7, 131.1, 129.0, 128.8, 128.6, 128.4, 127.5, 55.3, 52.1, 44.3 ppm; IR (thin film) 3086, 3059, 3029, 2925, 2851, 1704, 1598, 1577, 1494, 1452, 1265 cm$^{-1}$; MS (ESI) $m/z$ 264.1374 (264.1388 calcd for C$_{18}$H$_{18}$NO [MH]$^+$).

Crystallographic Experimental Section
A colorless crystal of approximate dimensions 0.3*0.1*0.1 mm was mounted on a glass fiber and transferred to a Bruker Kappa Apex II diffractometer. The APEX2 program was used to determine the unit cell parameters and data collection (15 sec / frame, 0.3 deg./frame)$^2$ The data were collected at 100K. The raw frame data were processed using APEX2 program.$^2$ The absorption correction was applied using program SADABS.$^3$ Subsequent calculations were carried out using SHELXTL program.$^4$ The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. Hydrogen atomic positions were theoretically calculated. At convergence, wR2 = 0.1517 and GOF = 0.957 for 274 variables refined against 4375 reflections, while R1 = 0.0620 for 3625 reflections with I>2$\sigma$(I). All ORTEP diagrams have been drawn with 50% probability ellipsoids.

Crystals were prepared by slow vapor diffusion using hexanes and ethyl acetate.

The crystal structure data can be obtained free of charge from the Cambridge Crystallographic Data Centre [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)
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Compound # 30 CCDC 986010

References:

S48
higher rf diastereomer
higher rf diastereomer
lower rf diastereomer
1:1
lower rf diastereomer

\[
\begin{align*}
\text{Ph} & \quad \text{CO}_2\text{Et} \\
\text{Ph} & \quad \text{CO}_2\text{Et}
\end{align*}
\]
S69

![Chemical Structure](image)

- 52.6
- 61.1
- 73.1
- 76.8
- 76.9
- 77.2
- 77.4
- 111.1
- 118.8
- 128.0
- 128.4
- 128.5
- 129.4
- 129.6
- 132.7
- 134.7
- 136.2
- 136.5
- 144.3
- 162.3

(ppm)
The image contains a graph with ppm values on the x-axis and various chemical shifts on the y-axis. A chemical structure is also present in the image, depicting a compound with the notation "Ph" and "Bn." The structure is labeled as 23.
S103
major diastereomer

39
major diastereomer

39
S113
Ph\(\text{C}^{\text{O}}\text{Bn}\)

S-5
$\text{Bn-O-CH} = \text{S-6}$

S122
S123
S125

\[
\begin{align*}
\text{S-7}
\end{align*}
\]
S133

![Chemical Structure](image)

The diagram shows a 1H NMR spectrum with assignments for various peaks at different ppm values. The peaks are labeled with the corresponding chemical shifts, such as 156.0, 154.4, 144.1, etc., indicating the position of protons in the molecule.
S153

- The image contains a 1D NMR spectrum with chemical shift values ranging from 28.7 to 144.9 ppm.
- The spectrum shows peaks at various chemical shifts, indicating the presence of different chemical environments.
- The diagram includes a chemical structure with labels indicating the positions of hydroxyl (OH), phenyl (Ph), and N-OBn groups.
- The structure is labeled S-21.
8:1 d.r.

S 23