Supporting Information

*In-Situ* Generation of *N*-Boc-Protected Alkenyl Imines: Controlling the *E/Z* Geometry of Alkenyl Moieties in the Mukaiyama–Mannich Reaction

Jian-Fei Bai, Hajime Sasagawa, Taiga Yurino, Taichi Kano* and Keiji Maruoka*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

**General Information:** Infrared (IR) spectra were recorded on a Thermo SCIENTIFIC Nicolet iS5 spectrometer. $^1$H NMR spectra were measured on JEOL JNM-FX400 (400 MHz) spectrometer. Chemical shifts were reported in ppm from tetramethylsilane (in the case of CDCl$_3$) as an internal standard. Data were reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and app = apparent), and coupling constants (Hz). $^{13}$C NMR spectra were recorded on JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. $^{19}$F NMR spectra were measured on JEOL JNM-ECA500 (470 MHz) spectrometer. $^{31}$P NMR spectra were measured on JEOL JNM-ECA500 (202 MHz) spectrometer. High performance liquid chromatography (HPLC) was performed on Shimadzu 20A instruments using Daicel Chiralcel OD3, Chiralpak OD, Chiralpak AD-H, and Chiralpak IC column. The high-resolution mass spectra (HRMS) were performed on Bruker microTOF or Thermo Scientific EXACTIVE PLUS. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 F$_{254}$, 0.25 mm) were used. The products were purified by flash column chromatography on neutral silica gel 60N (Kanto Chemical Co. Inc., 40-50μm). tert-Butyl methyl ether (TBME) and propionitrile (EtCN) were dried over activated 4 Å molecular sieves for 48 h before used. Tetrahydrofuran (THF) and Dichloromethane (CH$_2$Cl$_2$) were purchased from Kanto Chemical Co. Inc. as “Dehydrated”. 

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Preparation of Alkynyl N-Boc-Protected Aminals 4

General Procedure for Synthesis of Aminals 4: The reported procedure for synthesis of N-Boc-protected aminals 4 was modified. To a mixture of a 2-alkynynal and tert-butyl carbamate in acetic anhydride was added trifluoroacetic acid, and the mixture was stirred for 30 min. The product was solidified in acetic anhydride solvent as white solid. The solid was filtered in vacuum, and the obtained powder was washed with hexane (10 mL).

Spectra data of 4a, 4b, 4d, 4e and 4g are in accordance with the literature.

Di-tert-butyl (3-phenyl-prop-2-yn-1,1-diyl)dicarbamate (4a)

Following the general procedure, to a mixture of 3-phenylpropynal (232 μL, 1.9 mmol) and tert-butyl carbamate (410 mg, 3.5 mmol) in acetic anhydride (480 μL) was added trifluoroacetic acid (13 μL, 17 μmol). White powder. 86% yield (507 mg, 1.5 mmol). ¹H-NMR (400 MHz, CDCl₃): δ 7.42 (2H, d, J = 7.7, 2.2 Hz, Ph), 7.33-7.26 (3H, m, Ph), 5.98 (1H, t, J = 8.2 Hz, CH(NHBoc)₂), 5.53 (2H, br s, NH), 1.47 (18H, s, C(CH₃)₃). ¹³C-NMR (100 MHz, CDCl₃): δ 154.1, 131.8, 128.7, 128.3, 122.1, 85.4, 82.8, 80.5, 51.5, 28.3. IR (neat): 3308, 2980, 1698, 1540, 1501, 1369, 1251, 1172, 1014 cm⁻¹. HRMS (ESI): calcd. for C₁₉H₂₆N₂O₄Na⁺ (M+Na)⁺: 369.1785, found: 369.1784.

Di-tert-butyl (3-(4-methoxyphenyl)-prop-2-yn-1,1-diyl)dicarbamate (4b)

Following the general procedure, to a mixture of 3-(4-methoxyphenyl)propynal (419 mg, 2.6 mmol) and tert-butyl carbamate (522 mg, 4.5 mmol) in acetic anhydride (610 μL) was added trifluoroacetic acid (17 μL, 0.23 mmol). Light yellow powder. 67% yield (576 mg, 1.5 mmol). ¹H-NMR (400 MHz, CDCl₃): δ 7.36 (2H, d, J = 8.8 Hz, Ar), 6.83
(2H, d, J = 8.8 Hz, Ar), 5.96 (1H, t, J = 8.0 Hz, CH(NHBoc)2), 5.46 (2H, br s, NH), 3.81 (3H, s, MeO), 1.47 (18H, s, C(CH3)3). 13C-NMR (100 MHz, CDCl3): δ 159.9, 54.1, 133.3, 114.1, 113.9, 84.0, 82.9, 80.5, 55.3, 51.6, 28.3. IR (neat): 3314, 2978, 1697, 1539, 1506, 1499, 1278, 1169, 1032, 1013 cm⁻¹. HRMS (ESI): calcd. for C20H28N2NaO5+(M+Na)+: 399.1890, found: 399.1896.

Di-tert-butyl (3-(4-fluorophenyl)-prop-2-yne-1,1-diyl)dicarbamate (4c)

Following the general procedure, to a mixture of 3-(4-fluorophenyl)propionaldehyde (0.45 g, 3 mmol) and tert-butyl carbamate (0.6 g, 5.16 mmol) in acetic anhydride (1.0 mL) was added trifluoroacetic acid (20 μL, 0.255 mmol). White powder. 86% yield (0.81g, 2.2 mmol). 1H-NMR (400 MHz, CDCl3): δ 7.42-7.38 (2H, m, Ar), 6.99 (2H, t, J = 8.7 Hz, Ar), 5.95 (1H, t, J = 8.1 Hz, CH(NHBoc)2), 5.55 (2H, br s, NH), 1.47 (18H, s, C(CH3)3). 13C-NMR (100 MHz, CDCl3): δ 162.8 (JCF = 251 Hz), 154.1, 133.2, 131.6, 123.0, 121.1, 86.5, 81.8, 80.7, 51.5, 28.3. IR (neat): 3315, 2979, 1700, 1538, 1507, 1368, 1246, 1172, 1155, 1014 cm⁻¹. HRMS (ESI): calcd. for C19H25N2O4FNa+(M+Na)+: 387.1691, found: 387.1693.

Di-tert-butyl (3-(4-bromophenyl)-prop-2-yne-1,1-diyl)dicarbamate (4d)

Following the general procedure, to a mixture of 3-(4-bromophenyl)propynal (125 mg, 0.6 mmol) and tert-butyl carbamate (117 mg, 0.5 mmol) in acetic anhydride (187 μL) was added trifluoroacetic acid (3.7 μL, 0.05 mmol). White powder. 99% yield (0.109g, 0.26 mmol). 1H-NMR (400 MHz, CDCl3): δ 7.43 (2H, d, J = 8.8 Hz, ArH), 7.27 (2H, d, J = 8.8 Hz, ArH), 5.94 (1H, t, J = 8.0 Hz, CH(NHBoc)2), 5.59 (2H, br s, NH), 1.47 (18H, s, C(CH3)3). 13C-NMR (100 MHz, CDCl3): δ 154.1, 133.2, 131.6, 123.0, 121.1, 86.5, 81.8, 80.7, 51.5, 28.3. IR (neat): 3318, 2978, 1701, 1537, 1493, 1368, 1250, 1171, 1138, 1013 cm⁻¹. HRMS (ESI): calcd. for C19H25N2O4BrNa+(M+Na)+: 447.0890, found: 447.0903.
Di-tert-butyl (oct-2-yne-1,1-diyl)dicarbamate (4e)

Following the general procedure, to a mixture of 2-octynal (855 μL, 6.0 mmol) and tert-butyl carbamate (1.17 g, 10.0 mmol) in acetic anhydride (1.4 mL) was added trifluoroacetic acid (37 μL, 0.05 mmol). White powder. 84% yield (1.44 g, 4.2 mmol).

\begin{align*}
\text{H}^1\text{NMR} & \text{ (400 MHz, CDCl}_3\text{): } \delta 5.72 (1H, \text{ br t, } J = 8.0 \text{ Hz, CH(NHBoc)}_2), 5.42 (2H, \text{ br s, NH}), 2.17 (2H, \text{ td, } J = 7.1, 1.9 \text{ Hz, CH}_2\text{C≡C}), 1.51-1.46 (2H, \text{ m, CH}_2), 1.45 (18H, \text{ s, C(CH}_3)_3), 1.38-1.23 (4H, \text{ m, CH}_2), 0.89 (3H, \text{ t, } J = 7.0 \text{ Hz, CH}_3). \text{ \textsuperscript{13}C-NMR (100 MHz, CDCl}_3\text{): } \delta 154.1, 83.8, 80.2, 76.5, 51.2, 30.9, 28.3, 28.0, 22.1, 18.5, 13.9. \text{ IR (neat): } 3318, 2978, 2931, 1699, 1539, 1499, 1366, 1246, 1173, 1013 \text{ cm}^{-1}. \text{ HRMS (ESI): calcd. for C}_{18}\text{H}_{32}\text{N}_2\text{O}_4\text{Na}^+ (M+Na)^+: 363.2254, \text{ found: 363.2222.}
\end{align*}

Di-tert-butyl (but-2-yne-1,1-diyl)dicarbamate (4f)

Following the general procedure, to a mixture of 2-butynal (620 μL, 3.0 mmol) and tert-butyl carbamate (586 mg, 5.0 mmol) in acetic anhydride (685 μL) was added trifluoroacetic acid (18 μL, 25 μmol). White powder. 77% yield (545 mg, 1.9 mmol).

\begin{align*}
\text{H}^1\text{NMR} & \text{ (400 MHz, CDCl}_3\text{): } \delta 5.69 (1H, \text{ br t, } J = 7.5 \text{ Hz, CH(NHBoc)}_2), 5.39 (2H, \text{ br s, NH}), 1.82 (3H, \text{ d, } J = 1.9 \text{ Hz, CH}_3), 1.45 (18H, \text{ s, C(CH}_3)_3). \text{ \textsuperscript{13}C-NMR (100 MHz, CDCl}_3\text{): } \delta 154.1, 80.3, 79.4, 75.7, 51.1, 28.3, 3.4. \text{ IR (neat): } 3313, 2979, 1698, 1540, 1509, 1369, 1250, 1170, 1014 \text{ cm}^{-1}. \text{ HRMS (ESI): calcd. for C}_{14}\text{H}_{24}\text{N}_2\text{O}_4\text{Na}^+ (M+Na)^+: 307.1628, \text{ found: 307.1628.}
\end{align*}

Di-tert-butyl (3-(cyclohexyl)-prop-2-yne-1,1-diyl)dicarbamate (4g)

Following the general procedure, to a mixture of 3-cyclohexylpropiolaldehyde (490 mg, 3.6 mmol) and tert-butyl carbamate (703 mg, 6.0 mmol) in acetic anhydride (822 μL) was added trifluoroacetic acid (22 μL, 0.30 mmol). White powder. 78% yield (0.83 g, 2.35 mmol).

\begin{align*}
\text{H}^1\text{NMR} & \text{ (400 MHz, CDCl}_3\text{): } \delta 5.73 (1H, \text{ t, } J = 7.6 \text{ Hz, CH(NHBoc)}_2),
\end{align*}
5.30 (2H, br s, NHBoc), 2.37 (1H, app t, J = 9.2 Hz, Cy), 1.76-1.61 (5H, m, Cy), 1.45 (18H, s, C(CH$_3$)$_3$), 1.45-1.40 (2H, m, Cy), 1.31-1.26 (3H, m, Cy).

$^{13}$C-NMR (100 MHz, CDCl$_3$): δ 154.0, 87.6, 80.2, 76.6, 51.1, 32.2, 28.7, 28.3, 25.8, 24.6. **IR** (neat): 3321, 2936, 1701, 1537, 1499, 1337, 11246, 1163, 1130, 1009 cm$^{-1}$. **HRMS** (ESI): calcd. for C$_{19}$H$_{32}$N$_2$O$_4$Na$^+$ (M+Na)$^+$: 375.2254, found: 375.2255.

Di-tert-butyl (3-(3,5-dimethoxyphenyl)-prop-2-yn-1,1-diyl)dicarbamate (4h)

Following the general procedure, to a mixture of 3-(3,5-dimethoxyphenyl)propynal (646 mg, 3.4 mmol) and tert-butyl carbamate (715 mg, 6.1 mmol) in acetic anhydride (840 μL) was added trifluoroacetic acid (23 μL, 0.31 mmol). Light brown powder. 88% yield (1.09 g, 2.7 mmol). **$^1$H-NMR** (400 MHz, CDCl$_3$): δ 6.58 (2H, d, J = 2.2 Hz, 2-H-Ar), 6.45 (1H, t, J = 2.3 Hz, 4-H-Ar), 5.96 (1H, t, J = 8.1 Hz, CH(NHBoc)$_2$), 5.48 (2H, br s, NH), 3.77 (6H, s, MeO), 1.47 (18H, s, C(CH$_3$)$_3$). **$^{13}$C-NMR** (100 MHz, CDCl$_3$): δ 160.6, 154.1, 123.3, 109.7, 102.3, 84.9, 82.9, 80.6, 55.4, 51.5, 28.3. **IR** (neat): 3293, 2977, 1695, 1587, 1544, 1505, 1251, 1207, 1160, 1066, 1014 cm$^{-1}$. **HRMS** (ESI): calcd. for C$_{21}$H$_{30}$N$_2$O$_6$Na$^+$ (M+Na)$^+$: 429.1996, found: 429.2003.

**Preparation of N-Boc-Protected Z-Alkenyl Aminals Z-2**

**General Procedure for Synthesis of Z-alkenyl Aminals Z-2:** A mixture of an alkenyl aminal 4, Lindlar’s catalyst, ethylenediamine$^2$ and activated powdered 5 Å molecular sieves in dichloromethane or ethyl acetate was flushed with Ar, then stirred under H$_2$ at room temperature. The mixture was stirred for 30 min-6 h. The reaction was monitored by TLC (CH$_2$Cl$_2$/AcOEt = 29/1). After all the substrate was consumed, the flask was purged with Ar. The reaction mixture was filtered through celite, and the solvent was removed in vacuo. The crude solid was recrystallized from acetonitrile to give the desired N-Boc-protected Z-alkenyl aminal Z-2.

Di-tert-butyl ((Z)-3-phenyl-prop-2-ene-1,1-diyl)dicarbamate (Z-2a)
The title compound was prepared from 4a (693 mg, 2.0 mmol) using Lindlar’s catalyst (139 mg, 20 wt%), ethylenediamine (160 μL, 2.4 mmol) and activated powdered 5 Å molecular sieves (ca. 100 mg) in ethyl acetate (50 mL). White powder. 85% yield (576 mg, 1.7 mmol). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.36-7.22 (5H, m, Ph), 6.51 (1H, d, \(J = 11.4\) Hz, PhCH=CH), 6.05 (1H, br s, PhCH=CH), 5.68 (1H, br s, CH(NHBoc)\(_2\)), 5.63 (2H, br s, NH), 1.43 (18H, s, C(CH\(_3\))\(_3\)). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 154.7, 135.8, 130.9, 128.7, 128.4, 127.5, 79.9, 57.3, 28.3. IR (neat): 3333, 2979, 1703, 1542, 1506, 1366, 1306, 1249, 1175, 1013 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{19}\)H\(_{28}\)N\(_2\)O\(_4\)Na\(^+\) (M+Na\(^+\)): 371.1941, found: 371.1947.

Di-tert-butyl ((Z)-3-(4-methoxyphenyl)-prop-2-ene-1,1-diyl)dicarbamate (Z-2b)

The title compound was prepared from 4b (75 mg, 0.20 mmol) using Lindlar’s catalyst (37 mg, 50 wt%), ethylenediamine (16 μL, 0.24 mmol) and activated powdered 5 Å molecular sieves (ca. 40 mg) in dichloromethane (10 mL). White powder. 71% yield (54 mg, 0.14 mmol). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.22 (2H, d, \(J = 8.8\) Hz, 2-H-Ar), 6.87 (2H, d, \(J = 8.8\) Hz, 3-H-Ar), 6.46 (1H, d, \(J = 11.6\) Hz, ArCH=CH), 5.94 (1H, m, ArCH=CH), 5.68 (1H, br s, CH(NHBoc)\(_2\)), 5.46 (2H, br s, NH), 3.81 (3H, s, MeO), 1.44 (18H, s, C(CH\(_3\))\(_3\)). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 159.1, 154.7, 130.6, 130.1, 128.5, 126.8, 114.0, 80.0, 57.5, 55.2, 28.4. IR (neat): 3329, 2979, 1709, 1542, 1506, 1366, 1306, 1249, 1175, 1013 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{20}\)H\(_{30}\)N\(_2\)O\(_5\)Na\(^+\) (M+Na\(^+\)): 401.2047, found: 401.2048.

Di-tert-butyl ((Z)-3-(4-fluorophenyl)-prop-2-ene-1,1-diyl)dicarbamate (Z-2c)
The title compound was prepared from 4c (364 mg, 1.0 mmol) using Lindlar’s catalyst (73 mg, 20 wt%), ethylenediamine (80 μL, 1.2 mmol) and activated powdered 5 Å molecular sieves (ca. 100 mg) in dichloromethane (20 mL). White powder. 87% yield (320 mg, 0.87 mmol). 1H-NMR (400 MHz, CDCl3): δ 7.27-7.23 (2H, m, ArH), 7.02 (2H, t, J = 8.7 Hz, 2.3 Hz, ArH), 6.48 (1H, d, J = 11.6 Hz, ArCH=CH), 6.03 (1H, br s, ArCH=CH), 5.62 (1H, br s, CH(NHBoc)2), 5.48 (2H, br s, NH), 1.44 (18H, s, C(CH3)3).

13C-NMR (100 MHz, CDCl3): δ 162.2 (JCF = 249 Hz), 154.8, 131.9 (JCF = 3.3 Hz), 130.5 (JCF = 7.4 Hz), 129.9, 128.4, 115.5 (JCF = 21.4 Hz), 80.7, 57.2, 28.3. IR (neat): 3323, 2978, 1699, 1541, 1506, 1252, 1173, 1014 cm⁻¹. HRMS (ESI): calcd. for C19H27N2O4FNa+ (M+Na)+: 389.1847, found: 389.1847.

Di-tert-butyl ((Z)-3-(4-bromophenyl)-prop-2-ene-1,1-diyl)dicarbamate (Z-2d)

Di-tert-butyl ((Z)-oct-2-ene-1,1-diyl)dicarbamate (Z-2e)
The title compound was prepared from 4e (341 mg, 1.0 mmol) using Lindlar’s catalyst (68 mg, 20 wt%), ethylenediamine (80 µL, 1.2 mmol) and activated powdered 5 Å molecular sieves (ca. 100 mg) in dichloromethane (10 mL) and ethyl acetate (10 mL). White powder. 99% yield (340 mg, 0.99 mmol). ¹H-NMR (400 MHz, CDCl₃): δ 5.68 (1H, br s, CH(NHBoc)₂), 5.58 (1H, d, J = 5.8 Hz, CH₂CH=CH), 5.49 (1H, dt, J = 9.9, 7.5 Hz, CH₂CH=CH), 5.41 (2H, br s, NH), 2.11 (2H, app q, J = 7.0 Hz, CH₂CH), 1.44 (18H, s, C(CH₃)₃), 1.40-1.25 (6H, m, CH₂), 0.88 (3H, t, J = 6.8 Hz, CH₃).

¹³C-NMR (100 MHz, CDCl₃): δ 154.7, 133.3, 127.3, 79.8, 56.6, 31.3, 28.9, 28.3, 27.7, 22.5, 13.9. IR (neat): 3327, 2964, 2928, 2858, 1694, 1544, 1501, 1366, 1247, 1173, 1011 cm⁻¹. HRMS (ESI): calcd. for C₁₈H₃₄N₂O₄Na⁺ (M+Na)⁺: 365.2411, found: 365.2379.

Di-tert-butyl ((Z)-but-2-ene-1,1-diyl)dicarbamate (Z-2f)

The title compound was prepared from 4f (569 mg, 2.0 mmol) using Lindlar’s catalyst (114 mg, 20 wt%), ethylenediamine (160 µL, 2.4 mmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in dichloromethane (20 mL). White powder. 48% yield (275 mg, 0.96 mmol). ¹H-NMR (400 MHz, CDCl₃): δ 5.69 (1H, br s, CH(NHBoc)₂), 5.79-5.54 (2H, m, CH₃CH=CH), 5.37 (2H, br s, NH), 1.71 (3H, d, J = 5.3 Hz, CH₃CH=CH), 1.45 (18H, s, C(CH₃)₃). ¹³C-NMR (100 MHz, CDCl₃): δ 154.7, 133.3, 127.3, 79.8, 56.4, 31.3, 28.9, 28.3, 27.7, 22.5, 13.9. IR (neat): 3317, 2977, 1695, 1547, 1510, 1364, 1250, 1178, 1012 cm⁻¹. HRMS (ESI): calcd. for C₁₄H₂₆N₂O₄Na⁺ (M+Na)⁺: 309.1785, found: 309.1788.

Di-tert-butyl ((Z)-3-(cyclohexyl)-prop-2-ene-1,1-diyl)dicarbamate (Z-2g)

The title compound was prepared from 4g (352 mg, 1.0 mmol) using Lindlar’s catalyst (70 mg, 20 wt%) and activated powdered 5 Å molecular sieves (ca. 100 mg) in dichloromethane (10 mL) and ethyl acetate (10 mL). White powder. 97% yield (342 mg, 0.97 mmol). ¹H-NMR (400 MHz, CDCl₃): δ 5.65-5.55 (2H, m), 5.42-5.17 (2H, m), 5.32 (1H, t, J = 10.0 Hz), 2.32 (1H, app t, J = 14.0 Hz, Cy), 1.70-1.60 (4H, m, Cy), 1.44 (18H, s, C(CH₃)₃), 1.35-1.12 (4H, m, Cy), 1.05 (2H, m, Cy). ¹³C-NMR (100 MHz,
CDCl₃): δ 154.7, 138.9, 125.3, 79.9, 56.7, 36.9, 32.9, 28.4, 25.9, 25.6. IR (neat): 3325, 2926, 1696, 1541, 1505, 1366, 1246, 1175, 1009 cm⁻¹. HRMS (ESI): calcd. for C₁₉H₃₄N₂O₄Na⁺ (M+Na)⁺: 377.2411, found: 377.2414.

Di-tert-butyl ((Z)-3-(3,5-dimethoxyphenyl)-prop-2-ene-1,1-diyl)dicarbamate (Z-2h)

The title compound was prepared from 4h (163 mg, 0.40 mmol) using Lindlar’s catalyst (81 mg, 50 wt%), ethylenediamine (32 μL, 0.48 mmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in dichloromethane (20 mL). White powder. 68% yield (110 mg, 0.27 mmol). ¹H-NMR (400 MHz, CDCl₃): δ 6.47 (1H, d, J = 12 Hz, ArCH=CH), 6.45 (2H, d, J = 2.4 Hz, 2-H-Ar), 6.38 (1H, t, J = 2.2 Hz, 4-H-Ar), 6.05 (1H, br s, ArCH=CH), 5.71 (1H, br s, CH(NHBoc)₂), 5.51 (2H, br s, NH), 3.79 (6H, s, MeO), 1.43 (18H, s, C(CH₃)₃). ¹³C-NMR (100 MHz, CDCl₃): δ 160.8, 154.7, 137.7, 131.0, 128.4, 106.7, 100.4, 80.0, 57.3, 55.4, 28.3. IR (neat): 3356, 2977, 1705, 1591, 1537, 1491, 1305, 1240, 1158, 1005 cm⁻¹. HRMS (ESI): calcd. for C₂₁H₃₂N₂O₆Na⁺ (M+Na)⁺: 431.2153, found: 431.2155.

**General Procedure for Mannich-Type Reaction**

In the presence of a catalyst, a mixture of an N-Boc-protected alkenyl aminal Z-2, 1-phenyl-1-trimethylsilyloxyethylene, and activated powdered 5 Å molecular sieves in a solvent was stirred at room temperature under Ar atmosphere. The reaction was monitored by TLC (CH₂Cl₂/AcOEt = 49/1). After all the substrate was consumed, the reaction mixture was passed through a silica gel short-column (Hexane/AcOEt = 1/1 as eluent), and the solvent was removed in vacuo. The ¹H-NMR spectrum of crude material was measured with 1,2-dichloroethane as an internal standard. The pure target material was isolated by a silica gel column chromatography (CH₂Cl₂/AcOEt as eluent).

tert-Butyl ((Z)-5-oxo-1,5-diphenylpent-1-en-3-yl)carbamate (Z-6a)

The title compound was prepared from Z-2a (17 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene (10 µL, 0.05 mmol), copper(II) triflate (0.9 mg,
2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 20 mg) in dichloromethane (1.0 mL). Colorless oil. 94% yield (0.047 mmol). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.87 (2H, dd, \(J = 8.2, 1.0\) Hz, COPh), 7.54 (1H, tt, \(J = 7.4, 1.2\) Hz, COPh), 7.42 (2H, tt, \(J = 7.7, 1.5\) Hz, COPh), 7.36-7.22 (5H, m, Ph), 6.49 (1H, d, \(J = 11.6\) Hz, PhCH=CH), 5.88 (1H, app t, \(J = 10.3\) Hz, PhCH=CH), 5.34 (1H, br s, NH), 5.13 (1H, m, CH(NHBoc)), 3.40 (1H, dd, \(J = 16.4, 3.9\) Hz, PhCOCH\(_3\)), 3.21 (1H, dd, \(J = 16.7, 5.1\) Hz, PhCOCH\(_3\)), 1.40 (9H, s, C(CH\(_3\))\(_3\)). \(^1\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.6, 155.0, 136.9, 136.4, 133.3, 131.5, 130.7, 128.6, 128.5, 128.2, 127.3, 79.5, 46.0, 43.6, 28.4. IR (neat): 3360, 2976, 1683, 1494, 1449, 1365, 1248, 1166, 1019 cm\(^{-1}\). HRMS (ESI): calcd. for \(\text{C}_{22}\text{H}_{25}\text{NO}_3\text{Na}^+ (M+Na)^+\): 374.1727, found: 374.1725.

tert-Butyl ((\(Z\))-1-(4-methoxyphenyl)-5-oxo-5-phenylpent-1-en-3-yl)-carbamate (\(Z\)-6b)

![tert-Butyl ((\(Z\))-1-(4-methoxyphenyl)-5-oxo-5-phenylpent-1-en-3-yl)-carbamate (\(Z\)-6b)](image)

The title compound was prepared from Z-2b (19 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene (10 µL, 0.05 mmol), copper(II) triflate (0.9 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 20 mg) in dichloromethane (1.0 mL). Colorless oil. 92% yield (0.046 mmol). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.88 (2H, d, \(J = 7.0\) Hz, Ph), 7.54 (1H, tt, \(J = 7.5, 1.2\) Hz, Ph), 7.42 (2H, t, \(J = 7.5\) Hz, Ph), 7.26 (2H, d, \(J = 8.9\) Hz, ArH), 6.86 (2H, dt, \(J = 8.7, 2.4\) Hz, ArH), 6.41 (1H, d, \(J = 11.8\) Hz, ArCH=CH), 5.76 (1H, app t, \(J = 10.4\) Hz, PhCH=CH), 5.32 (1H, br s, NH), 5.14 (1H, m, CH(NHBoc)), 3.81 (3H, s, MeO), 3.42 (1H, dd, \(J = 16.7, 4.6\) Hz, PhCOCH\(_3\)), 3.21 (1H, dd, \(J = 16.7, 5.3\) Hz, PhCOCH\(_3\)), 1.41 (9H, s, C(CH\(_3\))\(_3\)). \(^1\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.6, 155.8, 155.1, 137.0, 133.2, 130.3, 130.0, 129.8, 129.0, 128.6, 128.2, 113.9, 79.5, 55.2, 46.0, 43.7, 28.4. IR (neat): 3380, 2932, 1708, 1511, 1449, 1347, 1248, 1166, 1139, 1036 cm\(^{-1}\). HRMS (ESI): calcd. for \(\text{C}_{22}\text{H}_{27}\text{NO}_3\text{Na}^+ (M+Na)^+\): 404.1832, found: 404.1794.

tert-Butyl ((\(Z\))-1-(4-fluorophenyl)-5-oxo-5-phenylpent-1-en-3-yl)-carbamate (6c)
The title compound was prepared from \(Z-2c\) (18.3 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene (10 µL, 0.05 mmol), copper(II) triflate (0.9 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in dichloromethane (1.0 mL). White solid. 52% yield (0.026 mmol). \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 (2H, d, \(J = 8.0\) Hz, Ph), 7.55 (1H, t, \(J = 7.4\) Hz, Ph), 7.42 (2H, t, \(J = 7.7\) Hz, Ph), 7.30-7.26 (2H, m, ArH), 7.01 (2H, t, \(J = 8.7\) Hz, ArH), 6.44 (1H, d, \(J = 11.8\) Hz, ArCH=CH), 5.84 (1H, t, \(J = 10.4\) Hz, ArCH=CH), 5.32 (1H, br s, NH), 5.11-5.04 (1H, m, CH(NHBoc)), 3.39 (1H, dd, \(J = 16.6, 4.5\) Hz, PhCOCH\(_2\)H), 3.19 (1H, dd, \(J = 16.2, 5.8\) Hz, PhCOCH\(_2\)H), 1.41 (9H, s, C(CH\(_3\))\(_3\)). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) 198.5, 162.0 (\(J_{CF} = 246\) Hz), 155.0, 136.8, 133.4, 132.4 (\(J_{CF} = 3.3\) Hz), 131.4, 130.4 (\(J_{CF} = 8.2\) Hz), 129.7, 128.7, 128.1, 115.5 (\(J_{CF} = 21.4\) Hz), 79.7, 45.4, 43.7, 28.4. IR (neat): 3358, 2977, 1687, 1508, 1392, 1225, 1168 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{22}\)H\(_{24}\)FNO\(_3\)Na\(^+\) (M+Na\(^+\)): 392.1632, found 392.1637.

tert-Butyl ((Z)-1-oxo-1-phenyldec-4-en-3-yl)carbamate (Z-6e)

The title compound was prepared from \(Z-2e\) (17 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene (10 µL, 0.05 mmol), copper(II) triflate (0.9 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 20 mg) in dichloromethane (1.0 mL). Colorless oil. 85% yield (0.043 mmol). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.95 (2H, d, \(J = 8.0\) Hz, Ph), 7.56 (1H, t, \(J = 7.3\) Hz, Ph), 7.46 (2H, t, \(J = 7.5\) Hz, Ph), 5.63-5.40 (2H, m, CH=CH), 5.17 (1H, br s, NH), 4.88 (1H, m, CH(NHBoc)), 3.39 (1H, dd, \(J = 16.0, 3.6\) Hz, PhCOCH\(_2\)H), 3.16 (1H, dd, \(J = 16.2, 5.8\) Hz, PhCOCH\(_2\)H), 2.18-1.93 (2H, m, CH\(_2\)CH=CH), 1.53-1.07 (6H, m, CH\(_2\)), 1.43 (9H, s, C(CH\(_3\))\(_3\)), 0.86 (3H, t, \(J = 6.6\) Hz, CH\(_3\)). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.5, 155.1, 137.1, 133.2, 132.9, 128.9, 128.6, 128.2, 79.3, 45.4, 44.1, 31.5, 29.2, 28.4, 27.7, 22.5, 14.0. IR (neat): 3362, 2960, 2928, 1684, 1496, 1449, 1366, 1246, 1170, 1019 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{21}\)H\(_{31}\)NO\(_3\)Na\(^+\) (M+Na\(^+\)): 368.2196, found: 368.2155.
tert-Butyl ((Z)-1-oxo-1-phenylhex-4-en-3-yl)carbamate (Z-6f)

The title compound was prepared from Z-2f (14 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene (10 µL, 0.05 mmol), copper(II) triflate (0.9 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 20 mg) in dichloromethane (1.0 mL). Colorless oil. 63% yield (0.032 mmol). 1H-NMR (400 MHz, CDCl3): δ 7.95 (2H, d, J = 8.2 Hz, Ph), 7.57 (1H, td, J = 7.4, 1.2 Hz, Ph), 7.46 (2H, t, J = 7.4 Hz, Ph), 5.67-5.48 (2H, m, CH=CH), 5.19 (1H, br s, NH), 4.90 (1H, m, CH(NHBoc)), 3.39 (1H, dd, J = 16.2, 4.6 Hz, PhCOCH2), 3.18 (1H, dd, J = 16.4, 6.0 Hz, PhCOCHH), 1.68 (3H, dd, J = 5.1, 1.0 Hz, CH2CH=CH), 1.43 (9H, s, C(CH3)3). 13C-NMR (100 MHz, CDCl3): δ 198.6, 155.1, 137.0, 133.2, 130.1, 128.6, 128.1, 126.7, 79.4, 45.0, 43.8, 28.4, 13.2. IR (neat): 3376, 2976, 2930, 1706, 1497, 1449, 1365, 1245, 1164, 1016 cm⁻¹. HRMS (ESI): calcd. for C17H23NO3Na+ (M+Na)+: 312.1570, found: 312.1572.

tert-Butyl ((E)-5-oxo-1,5-diphenylpent-1-en-3-yl)carbamate (E-6a)

The title compound was prepared from Z-2a (17 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene (15 µL, 0.075 mmol), TsOH·H2O in THF (25 mM, 100 µL, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL). Colorless oil. 90% yield (0.045 mmol). 1H-NMR (400 MHz, CDCl3): δ 7.95 (2H, d, J = 7.3 Hz, COPh), 7.57 (1H, t, J = 7.4, Hz, COPh), 7.46 (2H, t, J = 7.9 Hz, COPh), 7.34-7.17 (5H, m, Ph), 6.55 (1H, d, J = 16.0 Hz, PhCH=CH), 6.32 (1H, dd, J = 16.0, 6.5 Hz, PhCH=CH), 5.45 (1H, br s, NH), 4.82 (1H, m, CH(NHBoc)), 3.47 (1H, dd, J = 17.2, 3.6 Hz, PhCOCHH), 3.32 (1H, dd, J = 16.9, 5.8 Hz, PhCOCHH), 1.44 (9H, s, C(CH3)3). 13C-NMR (100 MHz, CDCl3): δ 198.3, 155.2, 136.9, 136.6, 133.3, 130.8, 129.2, 128.7, 128.5, 128.1, 127.6, 126.5, 79.4, 49.7, 43.4, 28.4. IR (neat): 3352, 2976, 2930, 1706, 1497, 1449, 1365, 1245, 1164, 1016 cm⁻¹. HRMS (ESI): calcd. for C22H25NO3Na+ (M+Na)+: 374.1727, found: 374.1716.

tert-Butyl ((E)-1-(4-methoxyphenyl)-5-oxo-5-phenylpent-1-en-3-yl)-carbamate (E-6b)
The title compound was prepared from Z-2b (19 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene (15 µL, 0.075 mmol), TsOH·H2O in THF (25 mM, 100 µL, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) and dichloromethane (1.6 mL). White powder. 65% yield (0.033 mmol). ¹H-NMR (400 MHz, CDCl₃): δ 7.95 (2H, d, J = 7.6 Hz, Ph), 7.57 (1H, tt, J = 7.8, 1.2 Hz, Ph), 7.46 (2H, t, J = 7.4 Hz, Ph), 7.26 (2H, d, J = 9.2 Hz, ArH), 6.81 (2H, d, J = 8.8 Hz, ArH), 6.50 (1H, d, J = 16.0 Hz, ArC=CH), 6.17 (1H, dd, J = 16.0, 6.6 Hz, PhCH=CH), 5.38 (1H, br s, NH), 4.78 (1H, m, C(H(NHBoc)), 3.79 (3H, s, MeO), 3.46 (1H, dd, J = 17.4, 4.2 Hz, PhCOCH/H), 3.31 (1H, dd, J = 17.0, 5.8 Hz, PhCOCH/H), 1.44 (9H, s, C(CH₃)₃).

⁰¹C-NMR (100 MHz, CDCl₃): δ 198.4, 159.3, 155.2, 137.0, 133.4, 130.4, 129.4, 128.7, 128.2, 127.7, 127.0, 114.0, 79.5, 55.3, 49.8, 43.6, 28.4. IR (neat): 3360, 2976, 1685, 1511, 1366, 1249, 1173, 1033 cm⁻¹. HRMS (ESI): calcd. for C₂₃H₂₇NO₄Na⁺ (M+Na)⁺: 404.1832, found: 404.1840.

tert-Butyl ((E)-1-(4-fluorophenyl)-5-oxo-5-phenylpent-1-en-3-yl)-carbamate (E-6c)

The title compound was prepared from Z-2c (18 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene (15 µL, 0.075 mmol), TsOH·H₂O in THF (25 mM, 100 µL, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at 55 °C. White powder. 52% yield (0.026 mmol). ¹H-NMR (400 MHz, CDCl₃): δ 7.95 (2H, d, J = 7.3 Hz, Ph), 7.58 (1H, tt, J = 7.4, 1.5 Hz, Ph), 7.47 (2H, t, J = 7.6 Hz, Ph), 7.30-7.26 (2H, m, ArH), 6.96 (2H, tt, J = 8.7, 2.3 Hz, ArH), 6.52 (1H, d, J = 16.0 Hz, ArCH=CH), 6.24 (1H, dd, J = 16.0, 6.5 Hz, ArCH=CH), 5.44 (1H, br s, NH), 4.81 (1H, m, CH(NHBoc)), 3.47 (1H, dd, J = 16.8, 4.0 Hz, PhCOCH/H), 3.32 (1H, dd, J = 16.8, 6.0 Hz, PhCOCH/H), 1.44 (9H, s, C(CH₃)₃). ¹³C-NMR (100 MHz, CDCl₃): δ 198.5, 162.5 (J_C-F = 248 Hz), 155.3, 137.0, 133.6, 132.9 (J_C-F = 4.1 Hz), 129.8, 129.1, 128.9, 128.3, 128.2 (J_C-F = 8.3 Hz), 115.6 (J_C-F = 21.4 Hz), 79.8, 49.7, 43.5, 28.6. IR (neat): 3351, 2924, 1689, 1508, 1391, 1229, 1158, 1024 cm⁻¹. HRMS (ESI): calcd. for C₂₂H₂₉FNO₃Na⁺ (M+Na)⁺: 392.1632, found: 392.1638.
tert-Butyl (\((E)-1\)-oxo-1-phenyldec-4-en-3-yl)carbamate (\(E-6e\))

The title compound was prepared from \(Z-2e\) (17 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloyxyethylene (30 \(\mu\)L, 0.15 mmol), 4-nitrobenzenesulfonic acid (0.5 mg, 2.5 \(\mu\)mol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL). White powder. 65% yield (0.033 mmol). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.94 (2H, d, \(J = 7.0\) Hz, Ph), 7.57 (1H, tt, \(J = 7.5, 1.2\) Hz, Ph), 7.46 (2H, t, \(J = 7.6\) Hz, Ph), 5.65-5.46 (2H, m, CH=CH), 5.23 (1H, br s, NH), 4.58 (1H, m, C\(\text{H}(\text{NHBoc})\)), 3.38 (1H, dd, \(J = 16.0, 4.0\) Hz, PhCOCH\(_2\)), 3.17 (1H, dd, \(J = 16.4, 4.0\) Hz, PhCOCH\(_2\)). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.6, 155.2, 137.0, 133.2, 132.3, 129.1, 128.6, 128.1, 79.3, 49.6, 43.5, 32.1, 31.3, 28.7, 28.4, 22.5, 14.0. IR (neat): 3349, 2960, 2928, 1689, 1596, 1508, 1365, 1271, 1171 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{17}\)H\(_{31}\)NO\(_3\)Na\(^+\) (M+Na): 368.2196, found: 368.2199.

tert-Butyl (\((E)-1\)-oxo-1-phenylhex-4-en-3-yl)carbamate (\(E-6f\))

The title compound was prepared from \(Z-2f\) (14 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloyxyethylene (30 \(\mu\)L, 0.15 mmol), 4-nitrobenzenesulfonic acid (0.5 mg, 2.5 \(\mu\)mol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL). Colorless oil. 51% yield (0.026 mmol). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.94 (2H, d, \(J = 6.8\) Hz, Ph), 7.57 (1H, tt, \(J = 7.4, 1.2\) Hz, Ph), 7.46 (2H, t, \(J = 7.8\) Hz, Ph), 5.68-5.53 (2H, m, CH=CH), 5.24 (1H, br s, NH), 4.58 (1H, m, CH(NHBoc)), 3.37 (1H, dd, \(J = 16.4, 4.0\) Hz, PhCOCH\(_2\)), 3.18 (1H, dd, \(J = 16.4, 6.0\) Hz, PhCOCH\(_2\)). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.6, 155.2, 137.0, 133.2, 130.6, 128.6, 128.1, 126.8, 79.3, 46.3, 43.5, 28.4, 17.6. IR (neat): 3361, 2976, 1686, 1507, 1449, 1366, 1247, 1169, 1022 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{17}\)H\(_{23}\)NO\(_3\)Na\(^+\) (M+Na): 312.1570, found: 312.1570.

Intramolecular Friedel-Crafts-Type Cyclization

In the presence of copper(II) triflate (2.2 mg, 6 \(\mu\)mol), a mixture of \(Z-2h\) (25 mg,
0.06 mmol), and activated powdered 5 Å molecular sieves (ca. 30 mg) in dichloromethane (2.0 mL) was stirred at room temperature under Ar atmosphere for 3 h. The reaction mixture was passed through a silica gel short-column (Hexane/AcOEt = 2/1 as eluent), and the solvent was removed in vacuo. The pure target material was isolated by a silica gel column chromatography (Hexane/AcOEt as eluent).

tert-Butyl (5,7-dimethoxy-1H-inden-1-yl)carbamate (7)

White solid. 99% yield (0.06 mmol). 1H-NMR (400 MHz, CDCl₃): δ 6.62 (1H, dd, J = 5.6, 1.7 Hz, CH=CH), 6.50-6.45 (2H, m, CH=CCH, ArH), 6.31 (1H, d, J = 1.9 Hz, ArH), 5.37 (1H, br s, CH(NHBoc)), 4.52 (1H, br s, NH), 3.82 (3H, s, MeO), 3.81 (3H, s, MeO), 1.50 (9H, s, C(CH₃)₃). 13C-NMR (100 MHz, CDCl₃): δ 162.0, 156.4, 156.1, 148.8, 138.4, 131.7, 122.1, 99.4, 96.5, 79.4, 57.1, 55.6, 55.3, 28.4. IR (neat): 3356, 2975, 1706, 1601, 1507, 1292, 1168, 1045 cm⁻¹. HRMS (ESI): calcd. for C₁₆H₂₁NO₄Na⁺ (M+Na)⁺: 314.1363, found: 314.1359.

Asymmetric Mannich-Type Reaction

Preparation of silyl enol ether 5 was carried out following the same general procedure described in the literature.³ Catalyst (R)-8 was prepared from (R)-5,5',6,6',7,7',8,8'-octahydro-[1,1'-binaphthalene]-2,2'-diol and pyren-1-ylboronic acid following the same general procedure described in the literature.⁴

61% yield (4 steps). White solid. [α]₀²⁰ = −478.7 (c 1.5 in CHCl₃). 1H-NMR (500 MHz, CD₃CN) δ 8.26-8.17 (6H, m, ArH), 8.11-8.08 (6H, m, ArH), 8.05-8.01 (4H, m, ArH), 7.84 (2H, dd, J = 13.9, 9.4 Hz, ArH), 7.44-7.31 (2H, m, ArH), 3.08-2.96 (6H, m, CH₂), 2.78-2.56 (6H, m, CH₂), 2.08-1.95 (4H, m, CH₂). 13C-NMR (125 MHz, CDCl₃) δ 138.2, 136.0, 133.0, 132.8, 132.7, 131.3, 131.1, 130.9, 130.84, 130.82, 130.74, 130.71, 130.69, 130.37, 130.5, 130.3, 128.95, 128.92, 128.89, 128.85, 128.83, 128.78, 128.0,
127.9, 127.79, 127.77, 127.5, 127.44, 127.35, 127.2, 127.12, 127.09, 127.06, 127.0, 125.81, 125.77, 125.7, 125.2, 125.1, 125.0, 124.9, 124.7, 124.6, 124.4, 124.0, 29.4, 29.3, 28.2, 28.1, 22.7, 22.6 (2C), 22.5. 19F-NMR (470 MHz, CDCl₃): δ = –79.4. 31P-NMR (202 MHz, CDCl₃): δ = –4.7. IR (neat): 3444, 2931, 1449, 1289, 1198, 1098, 960, 906, 831, 819, 791, 730 cm⁻¹. HRMS (ESI): calcd. for C₁₃₃H₃₆F₃NO₅PS (M–H)⁻: 886.1998, found 886.2018.

Catalyst (S)-9 was prepared following a literature procedure.⁵

81% yield (2 steps). Green solid. [α]²⁰_D = 54.5 (c 0.5 in CHCl₃). IR (neat): 2925, 1456, 1312, 1185, 1090, 969, 842, 751 cm⁻¹. HRMS (ESI): calcd. for C₁₀₆H₅₇CuF₆N₂O₁₀P₂S₂ (M+H)⁺: 1820.2130, found 1820.2084. Due to the paramagnetic nature of the Cu(II)-catalyst, ¹H, ¹³C and ³¹P-NMR cannot be obtained.

**General Procedure for Asymmetric Mannich-Type Reaction**

Unless otherwise specified, all reactions were carried out following the general procedure. In the presence of 5 mol% catalyst (R)-8, a mixture of an N-Boc-protected alkenyl aminal Z-2, silyl enol ether 5, and activated powdered 5 Å molecular sieves in anhydrous TBME was stirred under Ar atmosphere. The reaction was monitored by TLC (CH₂Cl₂/AcOEt = 49/1). After all substrates were consumed, the reaction mixture was passed through a silica gel short-column (Hexane/AcOEt = 1/1 as eluent), and the solvent was removed in vacuo. The ¹H-NMR spectrum of crude material was measured with 1,2-dichloroethane as an internal standard. The pure target material was isolated by a silica gel column chromatography (Hexane /AcOEt as eluent).

**tert-Butyl (R,E)-(5-oxo-1,5-diphenylpent-1-en-3-yl)carbamate (E-6a)**

The title compound was prepared from Z-2a (17 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene³ (15 µL, 0.075 mmol), catalyst (R)-8 (2.2 mg, 2.5 µmol) and
activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at –20 °C for 50 h. Colorless oil. 58% yield (0.029 mmol). [α]_D^20 = −11.0 (c 0.7 in CHCl₃). HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, λ = 264 nm, retention time: t (minor) = 21.3 min, t (major) = 29.7 min, 84% ee.

tert-Butyl (R,E)-(5-oxo-1-phenyl-5-(p-tolyl)pent-1-en-3-yl)carbamate (E-6g)

![Chemical Structure](image)

The title compound was prepared from Z-2a (17 mg, 0.05 mmol), trimethyl((1-(p-tolyl)vinyl)oxy)trimethylsilyl)vinyl)oxy)silane\(^3\a\) (16 mg, 0.075 mmol), catalyst (R)-8 (2.2 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at –20 °C for 72 h. Colorless oil. 66% yield (0.033 mmol). [α]_D^20 = −9.9 (c 0.6 in CHCl₃). \(^1\)H-NMR (500 MHz, CDCl₃) δ 7.85 (2H, d, J = 8.2 Hz, ArH), 7.33 (2H, d, J = 8.5 Hz, ArH), 7.28-7.25 (4H, m, Ph), 7.22-7.19 (1H, m, Ph), 6.55 (1H, d, J = 15.9 Hz, PhCH=CH), 6.32 (1H, dd, J = 15.9, 6.5 Hz, PhCH=CH), 5.49 (1H, br s, NH), 4.82-4.77 (1H, m, CH(NHBoc)), 3.45 (1H, d, J = 16.0 Hz, ArCOCH), 3.30 (1H, dd, J = 16.7 Hz, 5.7 Hz, ArCOCH), 2.41 (3H, s, CH₃), 1.44 (9H, s, C(CH₃)₃). \(^13\)C-NMR (100 MHz, CDCl₃) δ 198.2, 155.2, 144.3, 136.6, 134.4, 130.7, 129.4, 129.3, 128.5, 128.3, 127.6, 126.5, 79.6, 49.7, 43.2, 28.4, 21.7. IR (neat): 3355, 2977, 1684, 1606, 1494, 1391, 1248, 1168, 1045 cm\(^{-1}\). HRMS (ESI): calcd. for C₂₅H₂₉NO₃Na⁺ (M+Na)⁺: 388.1883, found 388.1888. HPLC analysis: Daicel Chiralpak AD-H, Hexane/iPrOH = 10/1, flow rate = 0.5 mL/min, λ = 240 nm, retention time: t (major) = 32.0 min, t (minor) = 35.3 min, 83% ee.

tert-Butyl (R,E)-(5-(4-chlorophenyl)-5-oxo-1-phenylpent-1-en-3-yl)carbamate (E-6h)

![Chemical Structure](image)

The title compound was prepared from Z-2a (17 mg, 0.05 mmol), ((1-(4-chlorophenyl)vinyl)oxy)trimethylsilyl)vinyl)oxy)silane\(^3\a\) (17 mg, 0.075 mmol), catalyst (R)-8 (2.2 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at –20 °C for 72 h. Colorless oil. 70% yield (0.035 mmol). [α]_D^20 = −9.5 (c 0.7 in CHCl₃). \(^1\)H-NMR (500 MHz, CDCl₃) δ 7.90 (2H, dt, J = 9.1, 2.2 Hz, ArH),
7.44 (2H, dt, J = 9.0, 2.3 Hz, ArH), 7.34-7.32 (2H, m, Ph), 7.30-7.26 (2H, m, Ph), 7.23-7.20 (1H, m, Ph), 6.55 (1H, d, J = 15.9 Hz, PhCH=CH), 6.30 (1H, dd, J = 15.9, 6.5 Hz, PhCH=CH), 5.37 (1H, br s, NH), 4.82-4.77 (1H, m, CH(NHBoc)), 3.45 (1H, d, J = 14.2 Hz, ArCOH), 3.29 (1H, dd, J = 16.9, 5.8 Hz, ArCOH), 1.44 (9H, s, C(\text{CH}_3)_3).

\[^{13}\text{C-NMR}\] (100 MHz, CDCl\textsubscript{3}) \(\delta\) 197.2, 155.2, 139.9, 136.5, 135.1, 131.0, 129.5, 129.0, 128.8, 128.5, 127.7, 126.5, 79.7, 49.6, 43.5, 28.4. \(\text{IR}\) (neat): 3351, 2977, 1685, 1589, 1494, 1365, 1248, 1166, 1026 cm\(^{-1}\). \(\text{HRMS}\) (ESI): calcd. for C\textsubscript{22}H\textsubscript{24}NO\textsubscript{3}ClNa\textsuperscript{+} (M+Na): 408.1337, found 408.1342. \(\text{HPLC}\) analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.9 mL/min, \(\lambda = 260\) nm, retention time: t (minor) = 19.7 min, t (major) = 47.4 min, 78% ee.

**tert-Butyl (R,E)-(5-(naphthalen-1-yl)-5-oxo-1-phenylpent-1-en-3-yl)carbamate (E-6i)**

![tert-Butyl (R,E)-(5-(naphthalen-1-yl)-5-oxo-1-phenylpent-1-en-3-yl)carbamate (E-6i)](image)

The title compound was prepared from Z-2a (17 mg, 0.05 mmol), trimethyl(1-(naphthalen-1-yl)vinyl)oxy)silane\(^{3a}\) (18 mg, 0.075 mmol), catalyst (R)-8 (2.2 mg, 2.5 \(\mu\)mol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at 0 \(^\circ\)C for 50 h. Colorless oil. 83% yield (0.042 mmol). \([\alpha]_D^{20} = -17.7\) (c 0.6 in CHCl\textsubscript{3}). \(\text{^1H-NMR}\) (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.56 (1H, d, J = 8.2 Hz, ArH), 7.99 (1H, d, J = 8.2 Hz, ArH), 7.88-7.84 (2H, m, ArH), 7.56-7.43 (3H, m, ArH), 7.31-7.26 (4H, m, Ph), 7.22-7.18 (1H, m, Ph), 6.55 (1H, d, J = 16.0 Hz, PhCH=CH), 6.33 (1H, dd, J = 16.0, 6.5 Hz, PhCH=CH), 5.39 (1H, br s, NH), 4.86-4.80 (1H, m, CH(NHBoc)), 3.55 (1H, dd, J = 16.6, 4.7 Hz, ArCOH), 3.40 (1H, dd, J = 16.4, 5.8 Hz, ArCOH), 1.43 (9H, s, C(\text{CH}_3)_3). \(\[^{13}\text{C-NMR}\] (100 MHz, CDCl\textsubscript{3}) \(\delta\) 202.7, 155.2, 136.6, 135.8, 134.1, 133.0, 131.0, 129.1, 128.5, 128.4, 128.1, 127.8, 127.7, 126.6, 126.5, 125.8, 124.4, 79.7, 50.3, 46.7, 28.4. \(\text{IR}\) (neat): 3343, 2976, 1685, 1507, 1391, 1274, 1165, 1095 cm\(^{-1}\). \(\text{HRMS}\) (ESI): calcd. for C\textsubscript{26}H\textsubscript{27}NO\textsubscript{3}Na\textsuperscript{+} (M+Na): 424.1883, found 424.1888. \(\text{HPLC}\) analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, \(\lambda = 264\) nm, retention time: t (minor) = 46.1 min, t (major) = 55.5 min, 94% ee.

**tert-Butyl(R,E)-(1-(4-methoxyphenyl)-5-(naphthalen-1-yl)-5-oxopent-1-en-3-yl)carbamate (E-6j)**

S18
The title compound was prepared from Z-2b (19 mg, 0.05 mmol), trimethyl((1-(naphthalen-1-yl)vinyl)oxy)silane\(^3\) (18 mg, 0.075 mmol), catalyst \((R)-8\) (2.2 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at −20 °C for 70 h. Colorless oil. 92% yield (0.046 mmol). \([\alpha]_D^{20} = -12.4 \) (c 0.6 in CHCl\(_3\)). \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta 8.56\) (1H, dd, \(J = 7.9, 1.3\) Hz, ArH), 7.99 (1H, d, \(J = 8.2\) Hz, ArH), 7.87 (2H, dt, \(J = 9.4, 2.9\) Hz, ArH), 7.57-7.48 (3H, m, ArH), 7.24 (2H, dt, \(J = 8.9, 2.1\) Hz, ArH), 6.81 (2H, dt, \(J = 9.3, 2.4\) Hz, ArH), 6.49 (1H, d, \(J = 16.0\) Hz, ArCH=CH), 6.19 (1H, dd, \(J = 15.7, 6.5\) Hz, ArCH=CH), 5.38 (1H, br s, NH), 4.84-4.77 (1H, m, CH(NHBoc)), 3.79 (3H, s, OMe), 3.55 (1H, dd, \(J = 16.4, 4.6\) Hz, ArCOH), 3.38 (1H, dd, \(J = 16.4, 6.0\) Hz, ArCOH), 1.43 (9H, s, C(CH\(_3\))\(_3\)). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta 202.8, 159.3, 155.2, 135.8, 134.0, 133.0, 130.5, 130.0, 129.3, 128.4, 128.0, 127.8, 127.7, 126.8, 126.5, 125.7, 124.4, 113.9, 79.7, 55.3, 50.2, 46.8, 28.4. IR (neat): 3357, 2976, 1694, 1511, 1391, 1248, 1172, 1030 cm\(^{-1}\).

HRMS (ESI): calcd. for C\(_{37}\)H\(_{30}\)NO\(_3\)Na\(^+\) (M+Na\(^+\)): 454.1989, found 454.1990. HPLC analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9/1, flow rate = 1.0 mL/min, \(\lambda = 264\) nm, retention time: t (minor) = 31.4 min, t (major) = 67.6 min, 92% ee.

tert-Butyl(R,E)-(1-(4-bromophenyl)-5-(naphthalen-1-yl)-5-oxopent-1-en-3-yl)carbamate (E-6k)

The title compound was prepared from Z-2d (21 mg, 0.05 mmol), trimethyl((1-(naphthalen-1-yl)vinyl)oxy)silane\(^3\) (18 mg, 0.075 mmol), catalyst \((R)-8\) (2.2 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at rt for 72 h. Colorless oil. 77% yield (0.039 mmol). \([\alpha]_D^{20} = -14.5 \) (c 0.6 in CHCl\(_3\)). \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta 8.57\) (1H, d, \(J = 8.9\) Hz, ArH), 8.01 (1H, d, \(J = 8.2\) Hz, ArH), 7.90-7.87 (2H, m, ArH), 7.57-7.49 (3H, m, ArH), 7.40 (2H, dd, \(J = 8.9\) Hz, 2.1 Hz, ArH), 7.17 (2H, d, \(J = 8.5\) Hz, ArH), 6.49 (1H, d, \(J = 16.0\) Hz, ArCH=CH), 6.33 (1H, dd, \(J = 16.2, 6.3\) Hz, ArCH=CH), 5.42 (1H, br s, NH), 4.87-4.79 (1H, m, CH(NHBoc)), 3.57 (1H, dd, \(J = 17.0, 4.7\) Hz, ArCOH), 3.40 (1H,
dd, J = 16.6, 5.9 Hz, ArCOHH), 1.44 (9H, s, C(CH₃)₃). ¹³C-NMR (125 MHz, CDCl₃) δ 202.7, 155.1, 135.5, 135.0, 134.0, 133.2, 131.6, 130.1, 129.9, 129.8, 128.5, 128.1, 128.0, 127.9, 126.6, 125.7, 124.4, 121.4, 79.8, 50.0, 46.5, 28.4. IR (neat): 3348, 2976, 1690, 1508, 1488, 1392, 1246, 1167, 1072, 1045 cm⁻¹. HRMS (ESI): calcd. for C_{26}H_{26}BrNO_{3}Na⁺ (M+Na)⁺: 502.0988, found 502.0990. HPLC analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9/1, flow rate = 0.5 mL/min, λ = 264 nm, retention time: t (minor) = 36.4 min, t (major) = 85.0 min, 92% ee.

tert-Butyl (R,E)-(1-(naphthalen-1-yl)-1-oxodec-4-en-3-yl)carbamate (E-6l)

The title compound was prepared from Z-2f (14 mg, 0.05 mmol), trimethyl((1-(naphthalen-1-yl)vinyl)oxy)silane³ (18 mg, 0.075 mmol), catalyst (R)-8 (2.2 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at −20 °C for 70 h. Colorless oil. 52% yield (0.026 mmol). [α]ₐ = −11.5 (c 0.6 in CHCl₃). ¹H-NMR (500 MHz, CDCl₃) δ 8.55 (1H, d, J = 8.5 Hz, ArH), 7.99 (1H, d, J = 8.5 Hz, ArH), 7.87 (2H, d, J = 7.9 Hz, ArH), 7.60-7.56 (1H, m, ArH), 7.55-7.48 (2H, m, ArH), 5.67-5.56 (2H, m, CH=CH), 5.22 (1H, br s, NH), 4.63-4.57 (1H, m, CH(NHBoc)), 3.46 (1H, dd, J = 15.4, 4.1 Hz, ArCOH), 3.26 (1H, dd, J = 16.2, 6.2 Hz, ArCOHH), 1.63 (3H, d, J = 6.0 Hz, CH₃CH=CH), 1.42 (9H, s, C(CH₃)₃). ¹³C-NMR (125 MHz, CDCl₃) δ 203.0, 155.3, 136.0, 134.1, 133.0, 130.5, 130.2, 128.6, 128.1, 127.9, 127.3, 126.6, 125.9, 124.5, 79.8, 50.1, 47.1, 28.5, 17.8. IR (neat): 3357, 2965, 1699, 1507, 1391, 1285, 1170, 1094 cm⁻¹. HRMS (ESI): calcd. for C_{21}H_{25}NO_{3}Na⁺ (M+Na)⁺: 362.1727, found 362.1731. HPLC analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9/1, flow rate = 1.0 mL/min, λ = 220 nm, retention time: t (minor) = 14.0 min, t (major) = 30.9 min, 95% ee.

tert-Butyl (R,E)-(1-(naphthalen-1-yl)-1-oxohex-4-en-3-yl)carbamate (E-6m)

The title compound was prepared from Z-2e (17 mg, 0.05 mmol), trimethyl((1-(naphthalen-1-yl)vinyl)oxy)silane³ (18 mg, 0.075 mmol), catalyst (R)-8
(2.2 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at –20 °C for 70 h. Colorless oil. 63% yield (0.032 mmol). 

$[\alpha]_D^{20} = -12.9$ (c 0.6 in CHCl$_3$). $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.55 (1H, d, $J = 8.8$ Hz, ArH), 7.99 (1H, d, $J = 8.2$ Hz, ArH), 7.87 (2H, d, $J = 7.9$ Hz, ArH), 7.59-7.49 (3H, m, ArH), 5.62 (1H, dt, $J = 15.5$, 6.3 Hz, CH=CH), 5.54 (1H, dd, $J = 15.9$, 6.0 Hz, CH=CH), 5.23 (1H, br s, NH), 4.64-4.58 (1H, m, CH(NHBoc)), 3.48 (1H, dd, $J = 16.9$, 3.8 Hz, ArCOH), 3.26 (1H, dd, $J = 16.9$, 6.5 Hz, ArCOH), 1.96 (2H, app q, $J = 7.0$ Hz, CH$_2$CH=CH), 1.44 (9H, s, C(CH$_3$)$_3$), 1.32-1.20 (6H, m, CH$_2$), 0.84 (3H, t, $J = 7.1$ Hz, CH$_3$). $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 202.9, 155.1, 135.9, 134.0, 132.8, 132.5, 130.1, 129.0, 128.4, 127.9, 127.8, 126.5, 125.8, 124.4, 79.4, 50.0, 46.8, 32.2, 31.3, 28.7, 28.4, 22.5, 14.0. IR (neat): 3349, 2927, 1695, 1507, 1390, 1245, 1170, 1045 cm$^{-1}$. HRMS (ESI): calcd. for C$_{25}$H$_{33}$NO$_3$Na$^+$ (M+Na)$^+$: 418.2353, found 418.2355. HPLC analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9:1, flow rate = 1.0 mL/min, $\lambda = 220$ nm, retention time: $t$ (minor) = 10.5 min, $t$ (major) = 18.8 min, 93% ee.

** tert-Butyl (R,E)-(1-cyclohexyl-5-(naphthalen-1-yl)-5-oxopent-1-en-3-yl)carbamate (E-6n)**

![ tert-Butyl (R,E)-(1-cyclohexyl-5-(naphthalen-1-yl)-5-oxopent-1-en-3-yl)carbamate (E-6n) ](image)

The title compound was prepared from Z-2g (18 mg, 0.05 mmol), trimethyl(1-(naphthalen-1-yl)vinyl)oxy)silane$^{3a}$ (18 mg, 0.075 mmol), catalyst (R)-8 (2.2 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at –20 °C for 70 h. Colorless oil. 64% yield (0.032 mmol). 

$[\alpha]_D^{20} = -20$ (c 0.6 in CHCl$_3$). $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.55 (1H, d, $J = 8.5$ Hz, ArH), 8.00 (1H, d, $J = 8.5$ Hz, ArH), 7.88 (2H, dd, $J = 5.8$, 2.7 Hz, ArH), 7.60-7.50 (3H, m, ArH), 5.57 (1H, dd, $J = 15.6$, 6.2 Hz, CH=CH), 5.53 (1H, dd, $J = 15.9$, 5.7 Hz, CH=CH), 5.20 (1H, br s, NH), 4.64-4.58 (1H, m, CH(NHBoc)), 3.49 (1H, d, $J = 14.2$ Hz, ArCOH), 3.25 (1H, dd, $J = 16.0$, 6.4 Hz, ArCOH), 1.94-1.86 (1H, m, Cy), 1.70-1.60 (3H, m, Cy), 1.44 (9H, s, C(CH$_3$)$_3$), 1.27-1.06 (5H, m, Cy), 1.03-0.95 (2H, m, Cy). $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 203.0, 155.1, 138.1, 136.0, 134.0, 132.8, 130.1, 128.4, 127.9, 127.7, 126.6, 126.5, 125.8, 124.4, 79.4, 50.0, 47.0, 40.3, 32.7, 28.4, 26.1, 25.9. IR (neat): 3350, 2923, 1698, 1507, 1391, 1245, 1158, 1020 cm$^{-1}$. HRMS (ESI): calcd. for C$_{26}$H$_{33}$NO$_3$Na$^+$ (M+Na)$^+$: 430.2353, found 430.2357. HPLC analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9:1, flow rate = 1.0 mL/min, $\lambda = 220$ nm, retention time:
t (minor) = 12.4 min, t (major) = 28.8 min, 93% ee.

**S-tert-Butyl (R,E)-3-(((tert-butoxycarbonyl)amino)-5-phenylpent-4-enethioate (E-6o)**

\[
\text{Ph} \overset{(E)}{\text{NH}} \overset{(R)}{\text{S}}
\]

Under Ar atmosphere, ((1-(tert-butythio)vinyl)oxy)trimethylsilane\(^{3b}\) (20 mg, 0.1 mmol) in 2.0 mL TBME was added dropwise to a mixture of an N-Boc-protected alkenyl aminal \(Z\)-2a (17 mg, 0.05 mmol), catalyst (R)-8 (2.2 mg, 2.5 µmol), and activated powdered 5 Å molecular sieves (100 mg) in anhydrous TBME (1.0 mL) for 20 min. The mixture was stirred at rt for 20 h. Colorless oil. 78% yield (0.039 mmol). \([\alpha]_D^{20} = 33.0 (c 0.7 \text{ in CHCl}_3)\). \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.34 (2H, d, \(J = 7.1 \text{ Hz, Ph}\)), 7.30 (2H, t, \(J = 7.5 \text{ Hz, Ph}\)), 7.23 (1H, t, \(J = 7.1 \text{ Hz, Ph}\)), 6.53 (1H, d, \(J = 15.9 \text{ Hz, PhCH=CH}\)), 6.16 (1H, dd, \(J = 15.7, 6.1 \text{ Hz, PhCH=CH}\)), 5.21 (1H, br s, NH), 4.65 (1H, m, \(\text{CH}_2\text{(NHBoc)}\)), 2.84-2.75 (2H, m, \(\text{CH}_2\)), 1.45 (9H, s, C(CH\(_3\))\(_3\)), 1.44 (9H, s, C(CH\(_3\))\(_3\)).

\(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 198.2, 155.0, 136.6, 130.8, 128.5, 128.4, 79.7, 50.2, 48.8, 48.6, 29.7, 28.4 \(^1\)IR (neat): 3346, 2965, 1689, 1496, 1391, 1247, 1168, 1042 cm\(^{-1}\) HRMS (ESI): calcd. for \(\text{C}_{20}\text{H}_{29}\text{NO}_3\text{SNa}^+ (M+Na)^+\): 386.1760, found 386.1764. HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, \(\lambda = 240 \text{ nm, retention time: t (minor) = 12.5 min, t (major) = 18.0 min, 91\% ee.}\)

**S-tert-Butyl (R,E)-3-(((tert-butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-enethioate (E-6p)**

\[
\text{MeO} \overset{(E)}{\text{NH}} \overset{(R)}{\text{S}}
\]

Under Ar atmosphere, ((1-(tert-butythio)vinyl)oxy)trimethylsilane\(^{3b}\) (15 mg, 0.075 mmol) in 2.0 mL TBME was added dropwise to a mixture of an N-Boc-protected alkenyl aminal \(Z\)-2b (19 mg, 0.05 mmol), catalyst (R)-8 (2.2 mg, 2.5 µmol), and activated powdered 5 Å molecular sieves (100 mg) in anhydrous TBME (1.0 mL) for 20 min. The mixture was stirred at rt for 20 h. Colorless oil. 66% yield (0.033 mmol). \([\alpha]_D^{20} = 43.2 (c 0.6 \text{ in CHCl}_3)\). \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.29-7.27 (2H, m, ArH), 6.84 (2H, dt, \(J = 9.4, 2.4 \text{ Hz, ArH}\)), 6.47 (1H, d, \(J = 15.9 \text{ Hz, ArCH=CH}\)), 6.01 (1H, dd, \(J = 15.9, 6.2 \text{ Hz, ArCH=CH}\)), 5.18 (1H, br s, NH), 4.64-4.60 (1H, m, \(\text{CH(NHBoc)}\)), 3.80
(3H, s, OMe), 2.84-2.75 (2H, m, CH2), 1.45 (9H, s, C(CH3)3), 1.44 (9H, s, C(CH3)3).

\(^{13}\text{C-NMR}\) (125 MHz, CDCl3) \(\delta\) 198.2, 159.3, 155.0, 130.3, 129.3, 127.7, 126.2, 113.9, 79.6, 55.3, 50.3, 49.0, 48.5, 29.7, 28.4. IR (neat): 3351, 2923, 1689, 1512, 1391, 1302, 1249, 1173, 1037 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{21}\)H\(_{31}\)NO\(_3\)Na\(^+\) (M+Na\(^+\))\(^+\): 416.1866, found 416.1870. HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, \(\lambda = 250\) nm, retention time: t (minor) = 12.5 min, t (major) = 14.3 min, 91% ee.

**S-tert-Butyl (R,E)-3-(((tert-butoxycarbonyl)amino)hex-4-enethioate (E-6q)**

\[
\begin{align*}
\text{Me} & \quad \text{Boc} \quad \text{NH} \\
& \quad \text{O} \quad \text{S}
\end{align*}
\]

The title compound was prepared from Z-2f (14 mg, 0.05 mmol), ((1-(tert-butythio)vinyl)oxy) (isopropyl)dimethylsilane\(^{3b}\) (17 mg, 0.075 mmol), catalyst (R)-8 (2.2 mg, 2.5 \(\mu\)mol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at 0 °C for 36 h. Colorless oil. 66% yield (0.033 mmol). \([\alpha]_D^0 = 26.3\) (c 0.6 in CHCl3). \(^{1}\text{H-NMR}\) (400 MHz, CDCl3) \(\delta\) 5.67-5.58 (1H, m, CH=CH), 5.42 (1H, ddd, \(J = 15.3, 6.2, 1.6\) Hz, CH=CH), 5.02 (1H, br s, NH), 4.45-4.38 (1H, m, CH(NHBoc)), 2.74-2.62 (2H, m, CH2), 1.67 (3H, dt, \(J = 6.5, 1.5\) Hz, CH\(_2\)CH=CH), 1.45 (9H, s, C(CH\(_3\))\(_3\)). \(^{13}\text{C-NMR}\) (125 MHz, CDCl3) \(\delta\) 198.1, 155.0, 129.8, 126.9, 79.4, 50.0, 49.1, 48.4, 29.7, 28.4, 17.6. IR (neat): 3351, 2965, 1689, 1506, 1391, 1365, 1248, 1170, 1040 cm\(^{-1}\). HRMS (ESI): calcd. for C\(_{15}\)H\(_{22}\)NO\(_3\)Na\(^+\) (M+Na\(^+\))\(^+\): 324.1604, found 324.1612. HPLC analysis: Daicel Chiralpak AD-H, Hexane/iPrOH = 20/1, flow rate = 0.5 mL/min, \(\lambda = 230\) nm, retention time: t (major) = 18.4 min, t (minor) = 27.1 min, 90% ee.

**S-tert-Butyl (R,E)-3-(((tert-butoxycarbonyl)amino)dec-4-enethioate (E-6r)**

\[
\begin{align*}
\text{Boc} & \quad \text{NH} \\
& \quad \text{O} \quad \text{S}
\end{align*}
\]

The title compound was prepared from Z-2e (17 mg, 0.05 mmol), ((1-(tert-butythio)vinyl)oxy) (isopropyl)dimethylsilane\(^{3b}\) (17 mg, 0.075 mmol), catalyst (R)-8 (2.2 mg, 2.5 \(\mu\)mol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous TBME (1.0 mL) at 0 °C for 36 h. Colorless oil. 68% yield (0.034 mmol). \([\alpha]_D^0 = 28.0\) (c 0.6 in CHCl3). \(^{1}\text{H-NMR}\) (500 MHz, CDCl3) \(\delta\) 5.64-5.58 (1H, m, CH=CH), 5.39 (1H, dd, \(J = 15.3, 6.0\) Hz, CH=CH), 5.05 (1H, br s, NH), 4.44-4.42 (1H,
m, CH(NHBoc)), 2.73 (1H, dd, J = 15.0, 6.5 Hz, CHCHH), 2.66 (1H, dd, J = 15.0, 5.5 Hz, CHCHH), 2.00 (2H, app q, J = 7.1 Hz, CH₂CH=CH), 1.44 (9H, s, C(CH₃)₃), 1.43 (9H, s, C(CH₃)₃), 1.37-1.21 (6H, m, CH₂), 0.88 (3H, t, J = 6.8 Hz, CH₃). ¹³C-NMR (125 MHz, CDCl₃) δ 198.4, 155.0, 132.3, 128.4, 79.4, 50.0, 49.0, 48.4, 32.1, 31.3, 29.7, 28.8, 28.4, 22.5, 14.0. IR (neat): 3352, 2926, 1691, 1495, 1391, 1365, 1247, 1169, 1042 cm⁻¹. HRMS (ESI): calcd. for C₁₉H₃₅NO₃SNa⁺ (M+Na)⁺: 380.2230, found 380.2234. HPLC analysis: Daicel Chiralpak AD-H, Hexane/iPrOH = 20/1, flow rate = 0.5 mL/min, λ = 230 nm, retention time: t (major) = 14.4 min, t (minor) = 25.6 min, 84% ee.

tert-Butyl (S,Z)-(5-oxo-1,5-diphenylpent-1-en-3-yl)carbamate (Z-6a)

The title compound was prepared from Z-2a (17 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene³a (15 µL, 0.075 mmol), Cu(II)-catalyst (4.6 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous CH₂Cl₂ (1.0 mL) at −20 °C for 48 h. Colorless oil. 78% yield (0.039 mmol). [α]ᵡ° = 15.4 (c 0.7 in CHCl₃). HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, λ = 254 nm, retention time: t (minor) = 14.1 min, t (major) = 15.2 min, 82% ee.

tert-Butyl (S,Z)-(1-oxo-1-phenyldec-4-en-3-yl)carbamate (Z-6e)

The title compound was prepared from Z-2e (17 mg, 0.05 mmol), 1-phenyl-1-trimethylsilyloxyethylene³a (15 µL, 0.075 mmol), Cu(II)-catalyst (4.6 mg, 2.5 µmol) and activated powdered 5 Å molecular sieves (ca. 50 mg) in anhydrous CH₂Cl₂ (1.0 mL) at −40 °C for 60 h. Colorless oil. 71% yield (0.036 mmol). [α]ᵡ° = 10.9 (c 0.7 in CHCl₃). HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, λ = 254 nm, retention time: t (minor) = 8.7 min, t (major) = 9.8 min, 80% ee.
Determination of Stereochemistry

The absolute stereochemistry C-3 of the E-6 was confirmed as (3R) by converting the E-6i and E-6o to the known compound for comparison of optical rotation values. The absolute stereochemistry C-3 of the Z-6a was confirmed as (3S) by converting the Z-6a to the known compound for comparison of optical rotation values.

Determination of Relative and Absolute Configuration of E-6i

Ozone was bubbled to a mixture of E-6i (20 mg, 0.05 mmol) and 0.2 mL of NaOH soln. in MeOH (2.5M, 0.5 mmol) in 4 mL of CH₂Cl₂ at -78 °C until the starting material was totally consumed as indicated by TLC. After addition of H₂O, the organic layer was separated, and washed with Brine, the organic layer was then dried over Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by a silica gel column chromatography (Hex/AcOEt as eluent). Colorless oil, 40% yield. [α]D = -22 (c 0.3 in CH₂Cl₂). The absolute configuration was determined by comparison with optical rotation of the literature data (lit [α]D = 18 (c 0.3 in CH₂Cl₂)).

1H-NMR (400 MHz, CDCl₃) δ 8.70 (1H, d, J = 8.5 Hz, ArH), 8.02 (1H, d, J = 8.2 Hz, ArH), 7.95 (1H, d, J = 7.0 Hz, ArH), 7.88 (1H, d, J = 8.0 Hz, ArH), 7.62-7.49 (3H, m, ArH), 5.70 (1H, d, J = 8.0 Hz, NH), 4.76-4.71 (1H, m, CH(NHboc)), 3.84 (1H, dd, J = 18.0, 4.0 Hz, CHH), 3.78 (3H, s, OCH₃), 3.63 (1H, dd, J = 17.9, 3.9 Hz, CHH), 1.46 (9H, s, C(CH₃)₃).

13C-NMR (125 MHz, CDCl₃) δ 201.8, 172.2, 155.7, 134.2, 134.0, 133.6, 130.2, 128.8, 128.5, 128.3, 126.6, 125.8, 124.4, 80.1, 52.7, 50.1, 43.8, 28.3. IR (neat): 3385, 2921, 1716, 1506, 1392, 1287, 1168, 1098 cm⁻¹. HRMS (ESI): calcd. for C₂₀H₂₃NO₅Na⁺ (M+Na)⁺: 380.1468, found 380.1475. HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.9 mL/min, λ = 230 nm, retention time: t (major) = 15.5 min, t (minor) = 20.8 min, 93% ee.
Determination of Relative and Absolute Configuration of E-60

To a solution of E-60 (18 mg, 0.05 mmol) in 2.0 mL CH₃OH was added 0.2 mL 50% aqueous KOH at 0 °C, and the mixture stirred at 0 °C for 30 min. The solution was concentrated under reduced pressure, diluted with water (3.0 mL), acidified to pH 2 with 1N HCl and extract with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated. The residue was purified by flash silica column chromatography (Hexane/AcOEt) to give the title compound. White solid, 82% yield. \([\alpha]^{20}_{D} = 21 \quad (c = 0.7 \text{ in CHCl}_3)\).

The absolute configuration was determined by comparison with optical rotation of the literature data.⁶ (lit \([\alpha]^{20}_{D} = 36.6 \quad (c = 1.1 \text{ in CHCl}_3))\).

¹H-NMR (500 MHz, CDCl₃) \(\delta 7.35 \quad (2H, d, J = 7.4 \text{ Hz, Ph}), \quad 7.30 \quad (2H, t, J = 7.7 \text{ Hz, Ph}), \quad 7.23 \quad (1H, t, J = 7.2 \text{ Hz, Ph}), \quad 6.56 \quad (1H, d, J = 15.9 \text{ Hz, PhCH=CH}), \quad 6.20 \quad (1H, dd, J = 15.9, 6.0 \text{ Hz, PhCH=CH}), \quad 5.26 \quad (1H, br s, NH), \quad 4.81-4.60 \quad (1H, m, CH(NHBoc)), \quad 2.84-2.59 \quad (2H, m, \text{ CH}_2), \quad 1.45 \quad (9H, s, C(CH}_3)_3)\).

¹³C-NMR (125 MHz, CDCl₃) \(\delta 176.0, 155.2, 136.4, 131.1, 128.5, 128.2, 127.8, 126.5, 79.9, 48.9, 39.4, 28.4\). IR (neat): 2962, 1715, 1496, 1393, 1259, 1167, 1045 cm⁻¹. HRMS (ESI): calcd. for C₁₆H₂₀N₄ (M–H)⁻: 290.1387, found 290.1399. HPLC analysis: Daicel Chiralcel OD, Hexane/iPrOH = 10/1 (with 0.1% TFA), flow rate = 1.0 mL/min, \(\lambda = 230 \text{ nm, retention time: t (major) = 8.2 min, t (minor) = 13.1 min, 86% ee}\).

Determination of Relative and Absolute Configuration of Z-6a

Ozone was bubbled to a mixture of Z-6a (21 mg, 0.06 mmol) and 0.24 mL of NaOH soln. in MeOH (2.5M, 0.6 mmol) in 4 mL of CH₂Cl₂ at −78 °C until the starting material was totally consumed as indicated by TLC. After addition of H₂O, the organic layer was separated, and washed with Brine, the organic layer was then dried over Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by a silica
gel column chromatography (Hex/AcOEt as eluent). Colorless oil, 38% yield. $[\alpha]_D^{20} = 16.4 \ (c \ 0.6 \ \text{in} \ \text{CH}_2\text{Cl}_2)$. The NMR spectral data of the obtained methyl ester are in accordance with the literature.\textsuperscript{6a} \textbf{H-NMR} (400 MHz, CDCl$^3$) δ 7.94 (2H, dt, $J = 7.5$, 1.4 Hz, Ph), 7.59 (1H, tt, $J = 7.4$, 1.4 Hz, Ph), 7.48 (2H, tt, $J = 7.7$, 1.6 Hz, Ph), 5.61 (1H, d, $J = 8.5$ Hz, NH), 4.72-4.68 (1H, m, $CH(NH\text{Boc})$), 3.78 (3H, s, OCH$_3$), 3.73 (1H, dd, $J = 18.0$, 4.4 Hz, $CHH$), 3.55 (1H, dd, $J = 18.1$, 4.4 Hz, $CHH$), 1.44 (9H, s, C(CH$_3$)$_3$). The absolute configuration was determined by comparison with optical rotation of the literature data.\textsuperscript{6a} (lit $[\alpha]_D^{20} = 28.2 \ (c \ 1.2 \ \text{in} \ \text{CH}_2\text{Cl}_2)$).
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Diagram: Structure of NHBoc

Diagram: NMR spectrum with peaks at various PPM values.
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HPLC Charts

tert-Butyl \((R,E)-(5\text{-}\text{oxo}\text{-}1\text{-}5\text{-}\text{diphenylpent}1\text{-}en}3\text{-yl})\text{carbamate}

\[
\text{HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, } \lambda = 264 \text{ nm, retention time: } t (\text{minor}) = 21.3 \text{ min, } t (\text{major}) = 29.7 \text{ min, } 84\% \text{ ee}
\]

![HPLC Chart 1](image)


tert-Butyl \((R,E)-(5\text{-}\text{oxo}\text{-}1\text{-}phenyl}5\text{-}(p\text{-tolyl)pent}1\text{-en}3\text{-yl})\text{carbamate}

\[
\text{HPLC analysis: Daicel Chiralpak AD-H, hexane/iPrOH = 10/1, flow rate = 0.5 mL/min, } \lambda = 240 \text{ nm, retention time: } t (\text{major}) = 32.0 \text{ min, } t (\text{minor}) = 35.3 \text{ min, } 83\% \text{ ee}
\]

![HPLC Chart 2](image)
**tert-Butyl (R,E)-(5-(4-chlorophenyl)-5-oxo-1-phenylpent-1-en-3-yl)carbamate**

Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.9 mL/min, λ = 260 nm, retention time: t (minor) = 19.7 min, t (major) = 47.4 min, 78% ee

**tert-Butyl (R,E)-(5-(naphthalen-1-yl)-5-oxo-1-phenylpent-1-en-3-yl)carbamate**

**HPLC analysis:** Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, λ = 264 nm, retention time: t (minor) = 46.1 min, t (major) = 55.5 min, 94% ee
**tert-Butyl(R,E)-(1-(4-methoxyphenyl)-5-(naphthalen-1-yl)-5-oxopent-1-en-3-yl)carbamate**

HPLC analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9/1, flow rate = 1.0 mL/min, \( \lambda = 264 \) nm, retention time: \( t \) (minor) = 31.4 min, \( t \) (major) = 67.6 min, 92% ee

**tert-Butyl(R,E)-(1-(4-bromophenyl)-5-(naphthalen-1-yl)-5-oxopent-1-en-3-yl)carbamate**

HPLC analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9/1, flow rate = 0.5 mL/min, \( \lambda = 264 \) nm, retention time: \( t \) (minor) = 36.4 min, \( t \) (major) = 85.0 min, 92% ee
**tert-Butyl (R,E)-(1-(naphthalen-1-yl)-1-oxohex-4-en-3-yl)carbamate**

![Chemical structure](image)

**HPLC** analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9/1, flow rate = 1.0 mL/min, λ = 220 nm, retention time: t (minor) = 14.0 min, t (major) = 30.9 min, 95% ee

![HPLC chromatograms](image)

**tert-Butyl (R,E)-(1-(naphthalen-1-yl)-1-oxodec-4-en-3-yl)carbamate**

![Chemical structure](image)

**HPLC** analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9/1, flow rate = 1.0 mL/min, λ = 220 nm, retention time: t (minor) = 10.5 min, t (major) = 18.8 min, 93% ee

![HPLC chromatograms](image)
**tert-Butyl (R,E)-(1-cyclohexyl-5-(naphthalen-1-yl)-5-oxopent-1-en-3-yl)carbamate**

![Chemical structure of tert-Butyl (R,E)-(1-cyclohexyl-5-(naphthalen-1-yl)-5-oxopent-1-en-3-yl)carbamate]

**HPLC** analysis: Daicel Chiralpak IC, Hexane/iPrOH = 9/1, flow rate = 1.0 mL/min, λ = 220 nm, retention time: t (minor) = 12.4 min, t (major) = 28.8 min, 93% ee

**S-tert-butyl (R,E)-3-((tert-butoxycarbonyl)amino)-5-phenylpent-4-enethioate**

![Chemical structure of S-tert-butyl (R,E)-3-((tert-butoxycarbonyl)amino)-5-phenylpent-4-enethioate]

**HPLC** analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, λ = 240 nm, retention time: t (minor) = 12.5 min, t (major) = 18.0 min, 91% ee.
**S-tert-butyl (R,E)-3-((tert-butoxycarbonyl)amino)-5-(4-methoxyphenyl)pent-4-enethioate**

![Chemical structure]

**HPLC analysis:** Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, λ = 250 nm, retention time: t (minor) = 12.5 min, t (major) = 14.3 min, 91% ee

---

**S-tert-butyl (R,E)-3-((tert-butoxycarbonyl)amino)hex-4-enethioate**

![Chemical structure]

**HPLC analysis:** Daicel Chiralpak AD-H, Hexane/iPrOH = 20/1, flow rate = 0.5 mL/min, λ = 230 nm, retention time: t (major) = 18.4 min, t (minor) = 27.1 min, 90% ee
**S-tert-butyl (R,E)-3-((tert-butoxycarbonyl)amino)dec-4-enethioate**

![Chemical Structure](image)

**HPLC** analysis: Daicel Chiralpak AD-H, Hexane/iPrOH = 20/1, flow rate = 0.5 mL/min, λ = 230 nm, retention time: t (major) = 14.4 min, t (minor) = 25.6 min, 84% ee

**tert-Butyl (S,Z)-(5-oxo-1,5-diphenylpent-1-en-3-yl)carbamate**

![Chemical Structure](image)

**HPLC** analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, λ = 254 nm, retention time: t (minor) = 14.1 min, t (major) = 15.2 min, 82% ee
**tert-Butyl (S,Z)-(1-oxo-1-phenyldec-4-en-3-yl)carbamate**

HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: $t$ (minor) = 8.7 min, $t$ (major) = 9.8 min, 80% ee

**Methyl (R)-2-((tert-butoxycarbonyl)amino)-4-(naphthalen-1-yl)-4-oxobutanoate**

HPLC analysis: Daicel Chiralcel OD3, Hexane/EtOH = 20/1, flow rate = 0.9 mL/min, $\lambda = 230$ nm, retention time: $t$ (major) = 15.5 min, $t$ (minor) = 20.8 min, 93% ee
\((R,E)-3-((\text{tert-butoxycarbonyl})\text{amino})-5\text{-phenylpent-4-enoic acid}\)

**HPLC** analysis: Daicel Chiralpak OD, Hexane/\(i\)PrOH = 10/1 (with 0.1% TFA), flow rate = 1.0 mL/min, \(\lambda = 230\) nm, retention time: \(t\) (major) = 8.2 min, \(t\) (minor) = 13.1 min, 86% ee