Allenenes and Transition Metals: A Diverging Approach to Heterocycles

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General Methods

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available compounds were purchased from Aldrich Chemical Co., GFS Chemicals, Strem Chemicals, Acros Organics and Advanced Chemtech and used as received, unless otherwise specified. Carbon monoxide gas (99.9%) was purchased from Matheson Tri-Gas and used as received. ZnCl_2 (0.5 M in THF) was purchased from Aldrich Chemical Co. and stored over 4 Å molecular sieves. Tetrahydrofuran (THF), diethyl ether (Et_2O) and dichloromethane (CH_2Cl_2) were purified with alumina using the Sol-Tek ST-002 solvent purification system. Toluene and diisopropylamine were freshly distilled from CaH_2 prior to use. Purification of the compounds by flash chromatography was performed by using silica gel (32-63 μm particle size, 60 Å pore size) purchased from SAI.¹ TLC analyses were performed on EM Science Silica Gel 60 F₂₅₄ plates (250 μm thickness). HPLC purification was performed on a Varian-Prostar 210 instrument using a Varian Microsorb Dynamax 100-5 Si column (5 μm packing, 250 mm x 10 mm). All ^1H and ^{13}C spectra were obtained on Bruker Avance 300 MHz, and chemical shifts (δ) reported relative to residual solvent peak CHCl_3 , DMSO or C_6H_6 . All NMR spectra were obtained at room temperature unless otherwise specified. IR spectra were obtained using a Nicolet Avatar E.S.P. 360 FT-IR. EI mass spectrometry was performed on a Micromass Autospec high resolution mass spectrometer. Melting points were determined on a Mel-Temp instrument. The glassware was typically not oven-dried or flame-dried unless specified.

In some cases, mixtures of diastereomers were obtained and were not separated for characterization purposes. Consequently, the spectroscopic data has been reported as a mixture of diastereomers. Where possible resonances attributed to a single diastereomer are labeled accordingly: * denotes one diastereomer and ** denotes a second diastereomer. Where possible, the diastereomeric ratios were measured by integration of the resonances in the ^1H NMR.

¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

General procedure for the preparation of propargylic esters of N-carbamate protected amino acids.

To a solution of propargylic alcohol (5 mmol, 1 equiv.), in CH_2Cl_2 (5-10 mL), was added DMAP (0.5 mmol, 0.1 equiv.) and DCC (5.5 mmol, 1.1 equiv.) followed by N-protected-alanine (5.25 mmol, 1.05 equiv.) at room temperature under N_2 atmosphere. Precipitation of a white solid was observed within 1 min. The reaction mixture was stirred at room temperature for 1 h, then filtered through a plug of silica gel eluting with hexanes-EtOAc, 1 : 1, v/v, and the clear liquid concentrated under vacuum. Purification by flash chromatography (hexanes-EtOAc, 4 : 1, v/v) afforded the desired ester.

General procedure for the preparation of N-Cbz-allenic amino acid methyl esters via a three step reaction sequence.

R = Me, iPr

Preparation of LDA: To a flame dried 100 mL round bottomed flask, $i\text{-Pr}_2\text{NH}$ (10.0 mmol) was added followed by THF (10 mL) under N_2 atmosphere. The reaction flask was cooled to $-20\text{ }^\circ\text{C}$ and n-butyllithium (10.0 mmol of 1.6 M solution in hexanes) was added dropwise over 5 min. The colorless solution was then cooled to $-78\text{ }^\circ\text{C}$ and held at that temperature for 30 min.

Step 1. Ester-enolate Claisen rearrangement: The amino acid propargylic ester (4.0 mmol) was placed in a pear shaped flask as a solution in benzene and the solvent removed under high vacuum to azeotrope traces of water. The atmosphere was subsequently replaced with N_2 and THF (10 mL) was added. The resulting solution was added via a syringe to the freshly prepared solution of LDA at $-78\text{ }^\circ\text{C}$. After 3-5 min of stirring, ZnCl_2 (4.8 mmol of a 0.5 M solution in THF) was added at $-78\text{ }^\circ\text{C}$. The reaction

mixture was allowed to warm to room temperature over 12 h. Upon completion the reaction mixture was diluted with Et₂O (200 mL), and treated with 1M HCl (200 mL). The aqueous layer was extracted with Et₂O (2 x 100 mL), and the organic layers were combined and washed with brine. Concentration under vacuum afforded a yellow oil.

Step 2. Methyl ester formation: The yellow oil from step 1 was dissolved in DMF (10 mL). Pulverized KHCO₃ (10 mmol) was added at room temperature, followed by MeI (8 mmol). The reaction mixture was stirred for 2-4 h until complete based upon TLC, and then diluted with water (100 mL). The cloudy mixture was extracted (benzene-EtOAc, 1 : 9, v/v) (3 x 75 mL), the organic layers were combined, washed with brine (2 x 50 mL) and concentrated under vacuum to afford a dark-yellow oil.

Step 3. TMS removal: The dark yellow oil from step 2 was dissolved in THF (20 mL), and phosphate buffer solution in water (pH = 7, 1 mL) was added, followed by dropwise addition of TBAF (8 mmol of a 1.0 M solution in THF) at room temperature. The reaction mixture was stirred for 3 h at room temperature. Upon completion based upon TLC the reaction mixture was diluted with water (100 mL) and the aqueous layer extracted with Et₂O (3 x 100 mL). The organic layers were combined, dried over MgSO₄ and concentrated under vacuum. Purification of the crude residue by flash chromatography (hexanes-EtOAc, 4 : 1, v/v) afforded the title compound.

Reaction sequence for the preparation of **4** (Table 1, Entry a-d)

2-Benzyloxycarbonylamino-2-methyl-3-(trimethylsilyl)prop-2-ynyl

ester. Prepared by the general procedure for the preparation of propargylic esters of N-carbamate protected amino acids (page s3) from:

4-trimethylsilylbut-3-yn-2-ol (600 mg, 4.22 mmol), DMAP (51 mg, 0.42 mmol), DCC (956 mg, 4.64 mmol), *N*-Cbz-alanine (988 mg, 4.43 mmol)

Yield (1.35 g, 92%).

^1H NMR (300 MHz, CDCl_3) δ 7.36-7.27 (m, 5H), 5.50 (quin, $J = 6.8$ Hz, 1H), 5.33 (br s, 1H), 5.12 (s, 2H), 4.41 (sep, 7.3 Hz, 1H), 1.52-1.41 (m, 6H), 0.18 (s, 9H)*, 0.17 (s, 9H)**; ^{13}C NMR (75 MHz, CDCl_3) δ 171.8, 155.6, 136.3, 128.6, 128.2, 103.0, 102.8, 90.5, 90.2, 67.0, 62.0, 49.7, 21.4, 18.9, 18.6, -0.2; IR (thin film) ν 3341, 2960, 2178, 1727, 1251 cm^{-1} ; MS m/z (%) 348 (5), 270 (10), 178 (13), 134 (26), 91 (100); EI-HRMS calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_4\text{Si}$ m/z $[\text{M}^+]$ 347.1553; found 347.1541.

* from diastereomer 1, ** from diastereomer 2.

2-Benzyloxycarbonylamino-2-methylhexa-3,4-dienoic acid methyl ester. Prepared by the general procedure for the preparation of N-Cbz-allenic amino acid methyl esters via a three step reaction sequence (page s3):

Step 1: LDA (17 mmol), 2-benzyloxycarbonylamino-2-methyl-3-(trimethylsilyl)prop-2-ynyl ester (2.36 g, 6.80 mmol), ZnCl_2 (16.3 mL of a 0.5 M solution in THF, 8.16 mmol); Step 2: KHCO_3 (1.37 g, 13.6 mmol), MeI (0.67 mL, 11 mmol); Step 3: TBAF (6 mL of a 1.0 M solution in THF, 6 mmol).

Yield (970 mg, 49%, 3 steps).

^1H NMR (300 MHz, CDCl_3) δ 7.36-7.32 (m, 5H), 5.50 (bs, 1H), 5.44-5.36 (m, 2H), 5.13 (1/2 AB, $J = 12.5$ Hz, 1H), 5.08 (1/2 AB, $J = 12.3$ Hz, 1H), 3.74 (bs, 3H), 1.69-1.66 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 202.9, 173.2, 154.9, 136.5, 128.6, 128.3, 94.4, 91.9, 66.8, 58.6, 53.0, 23.6, 14.1; IR (thin film) ν 3348, 2951, 1966, 1724, 1267 cm^{-1} . MS m/z

Reaction sequence for the preparation of **4** (Table 1, Entry e)

Yield (1.65 g, 85%).

diastereomer 1, ** diastereomer 2

2-Benzyloxycarbonylamino-2,6-dimethylhepta-3,4-dienoic acid, methyl ester.

Prepared by following the general procedure the preparation of N-Cbz-allenic amino acid methyl esters via a three step reaction sequence (page s3):

Step 1: LDA (5.3 mmol), 2-benzyloxycarbonylamino-1-isopropyl-3-trimethylsilylprop-2-ynyl ester (800 mg, 2.13 mmol), ZnCl₂ (5.1 mL of a 0.5 M solution in THF, 2.6 mmol); Step 2: KHCO₃ (537 mg, 5.32 mmol), MeI (265 μ L, 4.26 mmol); Step 3: TBAF (2.1 mL of a 1.0 M solution in THF, 2.1 mmol).

Yield (325 mg, 48%, 3 steps).

¹H NMR (300 MHz, CDCl₃) δ 7.38-7.32 (m, 5H), 5.51-5.42 (m, 2H), 5.13 (1/2 AB, J = 12.3 Hz, 1H), 5.07 (1/2 AB, J = 12.2 Hz, 1H), 3.73 (bs, 3H), 2.39-2.24 (m, 1H), 1.67 (s, 3H), 1.01 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 200.5, 173.0, 154.8, 136.4, 128.5, 128.1, 104.5, 96.0, 66.6, 58.4, 52.7, 27.9, 23.4, 22.2, 22.1; IR (thin film) ν 3353, 2960, 1965, 1728, 1264 cm⁻¹; MS m/z (%) 318 (22), 317 (61), 302 (44), 274 (40), 258 (51), 91 (100); EI-HRMS calcd for C₁₈H₂₃NO₄ m/z [M⁺] 317.1627; found 317.1626.

4, Table 1, Entry n

2-tert-Butoxycarbonylamino-2-methylhexa-3,4-dienoic acid, methyl ester. This compound has been previously synthesized in the Curran group via a modified Claisen rearrangement procedure.²

These compounds have been synthesized previously by Castelhana.³ Comparable yields were obtained. Compound **4** (Entry f-i), was obtained as a mixture of diastereomers in

² Curran, D. P.; Werner, S.; Unpublished results.

ratio 1.7 : 1 resulting from the Claisen rearrangement. The diastereomeric ratio was retained in the subsequent alkylation, and rhodium catalyzed P-K reaction.

Reaction sequence for the preparation of **4** (Table 1, Entry l, m)

2-Benzoylamino-2-methylpenta-3,4-dienoic acid methyl ester. To a solution of propargyl alcohol (9.7 mL, 0.17 mol) in CH₂Cl₂ (400 mL) was added DMAP (100 mg, 0.820 mmol) and DCC (22.9 g, 0.111 mol) followed by *N*-benzoyl-alanine (21.4 g, 0.111 mol). A white precipitate forms immediately. After stirring for 36 h at room temperature the reaction mixture was filtered using a Büchner funnel to remove the solid. The resulting colorless solution was concentrated under vacuum and dissolved in EtOAc. Recrystallization (hexanes-EtOAc, 4 : 1, v/v) afforded the title compound (17.4 g, 68%).

mp range 94.5-97.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.78-7.76 (m, 2H), 7.75-7.35 (m, 3H), 6.98 (br d, *J* = 6.9 Hz, 1H), 4.79 (quin, *J* = 7.2 Hz, 1H), 4.76 (dd, *J* = 15.5, 2.5 Hz, 1H), 4.69 (dd, *J* = 15.5, 2.5 Hz, 1H), 2.51 (t, *J* = 2.4 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.3, 166.9, 133.6, 131.6, 128.4, 127.0, 76.9, 75.4, 52.7, 48.3, 18.0; IR (thin film) ν 3294, 2940, 2128, 1749, 1642, 1536, 1164 cm⁻¹; MS *m/z* (%) 231 (43), 176 (20), 148 (63), 105 (100); EI-HRMS calcd for C₁₃H₁₃NO₃ *m/z* [M⁺] 231.0895; found 231.0899.

2-Benzoylamino-2-methylpenta-3,4-dienoic acid methyl ester. To a solution of 2-benzoylamino-2-methylpenta-3,4-dienoic acid methyl ester (13 mmol), in acetonitrile (60 mL), were added successively Et₃N (54.6 mmol), CCl₄ (45.5 mmol), PPh₃ (40.3 mmol) all at room temperature. After 3 h the starting material was consumed based upon TLC, and hexanes

³ Castelhana, A. L.; Horne, S.; Taylor, G. J.; *Tetrahedron* **1988**, *44*, 5451.

2-*tert*-Butoxycarbonylamino-3-(*tert*-butyldimethylsilyloxy)-propionic acid 1-methylprop-2-ynyl ester. Prepared by following the general procedure for the preparation of propargylic esters of N-carbamate protected amino acids (page s3) from:

2-*tert*-Butoxycarbonylamino-3-(*tert*-butyldimethylsilyloxy)-propionic acid (220 mg, 0.689 mmol), 3-butyne-2-ol (53 μ L, 0.724 mmol), DCC (149 mg, 0.724 mmol), DMAP (8 mg, 0.007 mmol).

After flash chromatography (hexanes-EtOAc, 19 : 1, v/v), The title compound (187 mg, 73%) was obtained as a 1 : 1 mixture of diastereomers.

^1H NMR (300 MHz, CDCl_3) δ 5.52-5.42 (m, 1H), 5.32 (br d, $J = 7.4$ Hz, 1H), 4.36-4.30 (m, 1H), 4.08-4.03 (m, 1H), 3.81 (dd, $J = 10.0, 2.9$ Hz, 1H), 2.45 (d, $J = 2.1$ Hz, 1H)*, 2.41 (d, $J = 2.1$ Hz, 1H)**, 1.50 (d, $J = 6.7$ Hz, 3H)*, 1.49 (d, $J = 6.6$ Hz, 3H)**, 1.44 (s, 9H), 1.85 (s, 9H)**, 1.85 (s, 9H)*, 0.03-0.01 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 169.6, 155.4, 155.3, 81.6, 79.8, 73.3, 73.2, 63.6, 63.5, 61.1, 55.7, 55.6, 28.3, 25.7, 25.7, 21.3, 21.2, 18.1, -5.6; ; IR (thin film) ν 3451, 3314, 2932, 2122, 1750, 1720 cm^{-1} ; MS m/z (%) 372 (11), 316 (22), 258 (51), 206 (43), 57 (100); EI-HRMS calcd for $\text{C}_{18}\text{H}_{34}\text{NO}_5\text{Si}$ m/z $[\text{M}+1]^+$ 372.2206; found 372.2201.

*from diastereomer 1; ** from diastereomer 2.

2-Benzoylamino-3-(*tert*-butyldimethylsilyloxy)-propionic acid 1-methylprop-2-ynyl ester. 2-*tert*-Butoxycarbonylamino-3-(*tert*-butyldimethylsilyloxy)-propionic acid 1-methylprop-2-ynyl ester (1.48 g, 3.98 mmol) was dissolved in TFA (5 mL) and stirred for 5 min at room temperature, after which the excess TFA was removed under vacuum. The brown oil was purified by flash chromatography (hexanes-EtOAc, 3 : 1, v/v then EtOAc). After evaporation of the solvents the oil (1.54 g) was dissolved in CHCl_3 (20 mL) and Et_3N (1.65 mL, 12.0 mmol) was added followed by benzoyl chloride (444 μ L, 3.84 mmol) at 0 $^\circ\text{C}$ under N_2 . The reaction mixture was stirred for 1 h after which it was

diluted with CHCl_3 (120 mL). The organic phase was washed with acetic acid 5% (50 mL) and then sat. NaHCO_3 (50 mL), dried over MgSO_4 and concentrated under vacuum. Purification by flash chromatography (gradient elution, hexanes-EtOAc, 19 : 1 to 4 : 1, v/v) afforded the title compound (900 mg, 60%, 2 steps).

^1H NMR (300 MHz, CDCl_3) δ 7.84-7.81 (m, 2H), 7.62-7.44 (m, 3H), 6.98 (d, J = 7.5 Hz, 1H), 5.61-5.44 (m, 1H), 4.97-4.86 (m, 1H), 4.23-4.17 (m, 1H), 4.00-3.96 (m, 1H), 2.49 (d, J = 2.1 Hz, 1H)*, 2.46 (d, J = 2.1 Hz, 1H)**, 1.57 (d, J = 5.7 Hz, 3H)*, 1.55 (d, J = 5.7 Hz, 3H)**, 0.89 (s, 9H)*, 0.88 (s, 9H)**, 0.07 (s, 3H)*, 0.06 (s, 3H)*, 0.04 (s, 3H)**, 0.04 (s, 3H)**;

* from diastereomer 1

** from diastereomer 2

^{13}C NMR (75 MHz, CDCl_3) δ 169.5, 169.4, 167.0, 166.9, 134.0, 131.8, 128.7, 127.0, 81.5, 81.4, 73.6, 73.5, 63.5, 63.4, 61.5, 61.4, 54.7, 54.5, 25.8, 25.7, 21.3, 21.2, 18.2, 18.1, -5.5, -5.6; IR (thin film) ν 3442, 3310, 2930, 2121, 1747, 1665, 1109 cm^{-1} ; MS m/z (%) 360 (42), 318 (35), 105 (100); EI HRMS calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_4\text{Si}$ m/z [M^+] 375.1866, found 375.1852.

2-Benzoylamino-2-(tert-butyldimethylsilyloxymethyl)-hexa-3,4-dienoic acid methyl ester. To a solution of 2-Benzoylamino-3-(tert-butyldimethylsilyloxy)-propionic acid, 1-methylprop-2-ynyl ester (730 mg, 1.95 mmol) in MeCN (10 mL), were added in consecutive order Et_3N (758 μL , 5.45 mmol), CCl_4 (430 μL , 4.49 mmol) and PPh_3 (1.12 g, 4.29 mmol) at room temperature. After 3 h at room temperature, the solvent was evaporated under vacuum and MeOH (10 mL) was added followed by Et_3N (500 μL). After 3 h the solvents were evaporated and the crude mixture diluted with EtOAc (50 mL) and then hexanes (20 mL). The formed precipitate was removed by filtration through a plug of silica gel. After removal of the solvents under vacuum the residue was purified by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) to afford the title compound (660 mg, 87%).

^1H NMR (300 MHz, CDCl_3) δ 7.80-7.77 (m, 2H), 7.57-7.41 (m, 3H), 7.12 (br s, 1H), 5.54 (sex, $J = 3.2$ Hz, 1H)*, 5.44 (sex, $J = 3.1$ Hz, 1H)**, 5.38-5.30 (m, 1H), 4.40 (d, $J = 9.8$ Hz, 1H)**, 4.31 (d, $J = 9.8$ Hz, 1H)*, 4.09 (d, $J = 9.8$ Hz, 1H), 3.80 (s, 3H)**, 3.80 (s, 3H)*, 1.68-1.64 (m, 3H), 0.84 (s, 9H), 0.02 (s, 3H)**, 0.01 (s, 3H)*, 0.00 (s, 3H)*, -0.00 (s, 3H)**

* major diastereomer; ** minor diastereomer.

^{13}C NMR (75 MHz, CDCl_3) δ 204.0, 204.0, 171.1, 171.6, 166.3, 166.1, 134.8, 134.7, 131.3, 128.4, 126.8, 126.7, 90.7, 90.4, 89.9, 89.7, 64.6, 64.4, 64.1, 52.8, 52.7, 25.5, 17.9, 13.8, 13.8, -5.6, -5.7; IR (thin film) ν 3421, 3298, 2952, 1967, 1741, 1669, 1247 cm^{-1} ; MS m/z (%) 374 (10), 332 (92), 244 (90), 105 (100); EI HRMS calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_4\text{Si}$ m/z $[\text{M}^+]$ 389.2022, found 389.2020.

General procedure for N-alkylation of N-protected allenic amino acid methyl esters.

To a solution of the N-protected amino acid (1.0 mmol) in DMF (4 mL), was added NaH (2.0 mmol of a 60% dispersion in mineral oil) at 0 °C under N_2 atmosphere. After 2 min the alkyl bromide (1.5 – 2.0 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 15 - 45 min and upon completion as observed by TLC was quenched by cautiously pouring into water (50 mL). The mixture was extracted with EtOAc (3 x 50 mL), the organic layers were combined, washed with brine, dried with MgSO_4 , and concentrated under vacuum. Purification by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) afforded the desired alkylated products.

6, Table 1, Entry a

2-(Benzyloxycarbonylprop-2-ynylamino)-2-methylhexa-3,4-dienoic acid methyl ester (6, Table 1, Entry a). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzyloxycarbonylamino-2-methylhexa-3,4-dienoic acid methyl ester (240 mg, 0.83 mmol), NaH (60% dispersion in mineral oil, 70 mg, 1.8 mmol), propargyl bromide (80% wt. in toluene, 137 μ L, 1.25 mmol).

Purified by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) to afford the title compound (210 mg, 77%).

^1H NMR (300 MHz, C_6D_6 , 323K) δ 7.22-7.01 (m, 5H), 5.63 (sex, J = 3.1 Hz, 1H), 5.13-5.04 (m, 1H), 5.04 (s, 2H), 4.21 (d, J = 18.1 Hz, 1H), 4.04 (dd, J = 18.1, 2.0 Hz, 1H), 3.38 (br s, 3H), 1.88 (t, J = 2.4 Hz, 1H), 1.77 (s, 3H), 1.43 (dd, J = 7.1, 3.2 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6 , 323K) δ 205.5, 172.2, 155.3, 137.0, 93.8, 90.6, 81.3, 71.5, 67.8, 64.9, 52.1, 34.2, 21.3, 13.6; IR (thin film) ν 3288, 2950, 2115, 1966, 1745, 1704, 1254 cm^{-1} ; MS m/z (%) 312 (13), 268 (34), 91 (100); EI-HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_4$ m/z [$\text{M}-15^+$] 312.1236; found 312.1243.

6, Table 1, Entry b

2-(Benzyloxycarbonyl-but-2-ynyl-amino)-2-methylhexa-3,4-dienoic acid, methyl ester (6, Table 1, Entry b). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzyloxycarbonylamino-2-methylhexa-3,4-dienoic acid, methyl ester (400 mg, 1.38 mmol), NaH (110 mg of 60% dispersion in mineral oil, 2.76 mmol), 1-bromo-2-butyne (157 μ L, 1.79 mmol).

Purification by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) afforded the title compound (390 mg, 84%).

^1H NMR (300 MHz, $\text{DMSO}-d_6$, 323 K) δ 7.40-7.31 (m, 5H), 5.49-5.43 (m, 1H), 5.10 s, 2H), 4.22 (dq, J = 18.3, 2.3 Hz, 1H), 4.11 (dq, J = 18.2, 2.2 Hz, 1H), 3.50 (br s, 3H), 1.78 (d, J = 2.0 Hz, 3H), 1.66 (dd, J = 6.6, 3.4 Hz, 3H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, 323 K) δ 204.0, 171.5, 154.3, 136.1, 127.9, 127.5, 127.2, 92.5, 89.9, 78.5, 75.9, 66.5, 63.4, 51.6, 33.6, 20.5, 13.0, 2.6; IR (thin film) ν 2917, 1965, 1745, 1702, 1250 cm^{-1} ; MS m/z (%) 341 (5), 326 (7), 282 (15), 91 (100); EI-HRMS calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_4$ m/z [M^+] 341.1627; found 341.1630.

6, Table 1, Entry c

2-[Benzyloxycarbonyl-(3-trimethylsilylprop-2-ynyl)-amino]-2-methylhexa-3,4-dienoic acid, methyl ester (6, Table 1, Entry c). To a solution of 2-benzyloxycarbonylamino-2-methylhexa-3,4-dienoic acid, methyl ester (134 mg, 0.464 mmol), in dry THF (4 mL) was added KH (68 mg of 35% wt. dispersion in mineral oil, 0.51 mmol) at room temperature, followed by addition of (3-bromo-prop-1-ynyl)-trimethylsilane (131 μ L, 0.93 mmol). The reaction mixture was stirred at room temperature until TLC showed disappearance of the starting material (10 h). The reaction mixture was then poured into a beaker containing EtOAc (50 mL) and ice water (50 mL). The two layers were separated and the aqueous layer was extracted with EtOAc. The organic layers were then combined, washed with brine, dried over MgSO_4 , and concentrated under vacuum. Purified by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) to afford the title compound (128 mg, 86%).

^1H NMR (300 MHz, CDCl_3 , 310 K) δ 7.37-7.27 (m, 5H), 5.48 – 5.34 (m, 2H), 5.20 (1/2 AB, J = 12.5 Hz, 1H), 5.15 (1/2 AB, J = 12.7 Hz, 1H), 4.38 (1/2 AB, J = 18.3 Hz, 1H), 4.18 (1/2 AB, J = 18.4 Hz, 1H), 3.59 (br s, 3H), 1.73 (dd, J = 6.7, 2.9 Hz, 3H), 1.66 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3 , 310 K) δ 205.3, 172.5, 155.1, 136.3, 128.3, 127.9, 102.7, 92.9, 90.5, 88.0, 67.5, 64.5, 52.3, 34.8, 13.8, -0.3; IR (thin film) ν 2954, 2177, 1967, 1748, 1707, 1251 cm^{-1} ; MS m/z (%) 399 (5), 384 (9), 340 (25), 91 (100); EI-HRMS calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_4\text{Si}$ m/z [M^+] 399.1866; found 339.1875.

6, Table 1, Entry d

2-[Benzyloxycarbonyl-(3-phenylprop-2-ynyl)-amino]-2-methylhexa-3,4-dienoic acid, methyl ester (6, Table 1, Entry d). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzyloxycarbonylamino-2-methylhexa-3,4-dienoic acid, methyl ester (210 mg, 0.72 mmol), NaH (58 mg of 60% dispersion in mineral oil, 1.44 mmol), (3-bromoprop-1-ynyl)-benzene (281 mg, 1.44 mmol)

Purified by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) to afford the title compound (199 mg, 68%).

^1H NMR (300 MHz, DMSO- d_6 , 323 K) δ 7.39-7.31 (m, 10 H), 5.55-5.45 (m, 2H), 5.14 (s, 2H), 4.52 (1/2 AB, J = 18.6 Hz, 1H), 4.42 (1/2 AB, J = 18.6 Hz, 1H), 3.50 (bs, 3H), 1.61 (dd, J = 7.0, 3.3 Hz, 3H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6 , 323 K) δ 204.2, 171.6, 154.4, 136.2, 130.9, 128.4, 128.3, 128.1, 127.6, 127.3, 122.0, 92.6, 90.2, 86.6, 82.5, 66.7, 63.5, 51.9, 34.1, 13.2; IR (thin film) ν 2949, 1966, 1746, 1704, 1251 cm^{-1} ; MS m/z (%) 344 (39), 240 (40), 205 (49), 169 (61), 133 (84), 87 (100); EI-HRMS calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_4$ m/z [M^+] 403.1784, found 403.1788 and calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2$ m/z [$\text{M}-59^+$] 344.1651, found 344.1647.

6, Table 1, Entry e

2-(Benzyloxycarbonylbut-2-ynylamino)-2,6-dimethylhepta-3,4-dienoic acid, methyl ester (6, Table 1, Entry e). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzyloxycarbonylamino-2,6-dimethylhepta-3,4-dienoic acid, methyl ester (125 mg, 0.394 mmol), NaH (31 mg of a 60% dispersion in mineral oil, 0.79 mmol), 1-bromo-2-butyne (69 μL , 0.79 mmol).

Purification by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) afforded the title compound (125 mg, 86%).

^1H NMR (300 MHz, DMSO- d_6 , 323 K) δ 7.40-7.30 (m, 5H), 5.59-5.51 (m, 2H), 5.10 (s, 2H), 4.21 (dq, J = 18.2, 2.3 Hz, 1H), 4.11 (dq, J = 18.3, 2.4 Hz, 1H), 3.48 (s, 3H), 2.40-2.25 (m, 1H), 1.75 (t, J = 2.2 Hz, 3H), 1.52 (s, 3H), 1.01 (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, DMSO- d_6 , 323 K) δ 201.6, 171.3, 154.3, 136.0, 127.9, 127.4, 127.1, 102.4, 94.4, 78.5, 75.9, 66.5, 63.5, 51.6, 33.7, 27.0, 21.7, 21.5, 2.5; IR (thin film) ν 2959, 1964,

1746, 1704, 1253 cm^{-1} ; MS m/z (%) 369 (24), 326 (18), 167 (20), 91 (50), 83 (100); EI-HRMS calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_4$ m/z $[\text{M}^+]$ 369.1940; found 369.1957.

6, Table 1, Entry f

2-(Benzoylprop-2-ynylamino)-2-benzylhexa-3,4-dienoic acid, methyl ester (6, Table 1, Entry f). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzoylamino-2-benzyl-hexa-3,4-dienoic acid, methyl ester (175 mg, 0.521 mmol), NaH (60% dispersion in mineral oil) (42 mg, 1.0 mmol), propargyl bromide (80% wt. in toluene) (92 μL , 0.83 mmol).

Purification by flash chromatography (hexanes-EtOAc, 6 : 1, v/v) afforded the title compound (143 mg, 73%).

^1H NMR (300 MHz, CDCl_3) δ 7.67-7.62 (m, 2H), 7.49-7.39 (m, 3H), 7.28-7.23 (m, 5H), 5.85 (sex, $J = 3.1$ Hz, 1H), 5.56-5.41 (m, 1H), 3.97 (1/2 AB, $J = 13.5$ Hz, 1H)*, 3.96 (1/2 AB, $J = 13.6$ Hz, 1H)**, 3.76 (s, 3H)**, 3.76 (s, 3H)*, 3.76-3.75 (m, 1 H)**, 3.70-3.68 (m, 1H)*, 3.55-3.53 (m, 1H)*, 3.48-3.47 (m, 1H)**, 3.42 (1/2 AB, $J = 13.6$ Hz, 1H)*, 3.41 (1/2 AB, $J = 13.6$ Hz, 1H)**, 2.14 (t, $J = 2.4$ Hz, 1H)*, 2.12 (t, $J = 2.4$ Hz, 1H)**, 1.81 (dd, $J = 7.2, 3.2$ Hz, 3H)*, 1.75 (dd, $J = 7.1, 3.2$ Hz, 3H)**; ^{13}C NMR (75 MHz, CDCl_3) δ 205.0, 172.7, 171.7, 136.7, 136.6, 136.2, 131.4, 130.7, 128.7, 128.4, 127.5, 127.1, 91.1, 91.0, 90.7, 81.2, 72.9, 72.9, 69.2, 52.7, 52.7, 39.3, 39.2, 14.1, 13.8; IR (thin film) ν 2948, 2118, 1968, 1743, 1643 cm^{-1} ; MS m/z (%) 372 (50), 282 (40), 105 (100); EI-HRMS calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_3$ m/z $[\text{M}^+]$ 372.1600; found 372.1613.

*diastereomer 1; **diastereomer 2

6, Table 1, Entry g

2-(Benzoyl-but-2-ynyl-amino)-2-benzylhexa-3,4-dienoic acid methyl ester (6, Table 1, Entry g). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzoylamino-2-benzyl-hexa-3,4-dienoic acid methyl ester (330 mg, 0.982 mmol), NaH (95%) (60 mg, 2.5 mmol), 1-bromo-2-butyne (86 μ L, 0.98 mmol) .

Purification by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) afforded the title compound (315 mg, 83%).

^1H NMR (300 MHz, CDCl_3) δ 7.67-7.64 (m, 2H), 7.48-7.38 (m, 3H), 7.31-7.21 (m, 5H), 5.89-85 (m, 1H), 5.52-5.38 (m, 1H), 3.98 (1/2 AB, J = 13.6 Hz, 1H)*, 3.97 (1/2 AB, J = 13.5 Hz, 1H)**, 3.75 (s, 3H), 3.75-3.68 (m, 1H), 3.58-3.51 (m, 1H), 3.40 (1/2 AB, J = 13.6 Hz, 1H)*, 3.39 (1/2 AB, J = 13.5 Hz, 1H)**, 1.80 (dd, J = 7.1, 3.2 Hz, 3H)*, 1.74 (dd, J = 7.1, 3.1 Hz, 3H)**, 1.68 (s, 3H).

* from the major diastereomer

** from the minor diastereomer

^{13}C NMR (75 MHz, CDCl_3) δ 204.4, 172.5, 171.7, 136.5, 136.1, 131.3, 130.5, 128.4, 128.0, 127.5, 126.9, 91.0, 90.5, 90.3, 80.5, 76.2, 69.2, 68.0, 52.4, 39.6, 39.2, 25.7, 14.0, 13.8, 3.7; IR (thin film) ν 2948, 1967, 1744, 1642, 1393 cm^{-1} ; MS m/z (%) 386 (10), 328 (41), 296 (15), 105 (100); EI-HRMS calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_3$ m/z $[\text{M}-1]^+$ 386.1756; found 386.1745.

6, Table 1, Entry h

2-[Benzoyl-(3-trimethylsilylprop-2-ynyl)-amino]-2-benzylhexa-3,4-dienoic acid methyl ester (6, Table 1, Entry h). To a solution of 2-benzoylamino-2-benzyl-hexa-3,4-dienoic acid methyl ester (243 mg, 0.723 mmol), in dry THF (7 mL) was added KH (90 mg of 35% wt. dispersion in mineral oil, 0.8 mmol) at room temperature, followed by addition of (3-bromo-prop-1-ynyl)-trimethylsilane (203 μ L, 1.44 mmol). The reaction mixture was stirred at room temperature until TLC showed disappearance of the starting material (12 h). The reaction mixture was then carefully poured into a beaker containing EtOAc and water. The two layers were separated and the aqueous layer was extracted with EtOAc. The organic layers were then combined, washed with brine (20 mL), dried with MgSO_4 , and concentrated under vacuum. Purification by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) afforded the title compound (240 mg, 75%).

^1H NMR (300 MHz, CDCl_3) δ 7.68-7.64 (m, 2H), 7.46-7.38 (m, 3H), 7.33-7.21 (m, 5H), 5.83-5.80 (m, 1H), 5.57-5.41 (m, 1H), 3.98-3.91 (m, 1H), 3.76 (s, 3H)**, 3.75 (s, 3H)*, 3.67-3.65 (m, 1H), 3.52-3.41 (m, 2H), 1.81 (dd, $J = 7.2, 3.1$ Hz, 1H)*, 1.77 (dd, $J = 7.1, 3.1$ Hz, 1H)**, 0.16 (s, 9H)*, 0.15 (s, 9H)**

* from the major diastereomer

** from the minor diastereomer

^{13}C NMR (75 MHz, CDCl_3) δ 204.6, 172.6, 171.5, 136.4, 136.3, 135.8, 130.9, 130.3, 128.2, 128.0, 127.3, 126.8, 103.2, 90.9, 90.4, 89.4, 68.8, 52.4, 39.8, 38.8, 38.5, 13.9, 13.7, -0.3; IR (thin film) ν 2952, 2177, 1967, 1745, 1649 cm^{-1} ; MS m/z (%) 445 (21), 444 (36), 354 (50), 244 (74), 105 (100); EI-HRMS calcd for $\text{C}_{27}\text{H}_{30}\text{NO}_3\text{Si}$ m/z $[\text{M}-1]^+$ 444.1995; found 444.1984.

6, Table 1, Entry i

2-[Benzoyl-(3-phenylprop-2-ynyl)-amino]-2-benzylhexa-3,4-dienoic acid methyl ester (6, Table 1, Entry i). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzoylamino-2-benzyl-hexa-3,4-dienoic acid methyl ester (72 mg, 0.21 mmol), NaH (60% dispersion in mineral oil) (17 mg, 0.43 mmol), (3-bromo-prop-1-ynyl)-benzene (66 mg, 0.34 mmol).

Purification by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) afforded the title compound (86 mg, 89%).

^1H NMR (300 MHz, CDCl_3) δ 7.79-7.77 (m, 2H), 7.57-7.51 (m, 4H), 7.41-7.23 (m, 9H), 5.98 (sept, $J = 3.1$ Hz, 1H), 5.65-5.50 (m, 1H), 4.11 (1/2 AB, $J = 13.6$ Hz, 1H)*, 4.11-4.01 (m, 2H), 3.87 (s, 3H)**, 3.85 (s, 3H)*, 3.83-3.77 (m, 1H), 3.54 (d, $J = 13.5$, 1H), 1.89 (dd, $J = 7.2, 3.2$ Hz, 3H)*, 1.83 (dd, $J = 7.1, 3.2$ Hz, 3H)**.

* from the major diastereomer

** from the minor diastereomer

^{13}C NMR (75 MHz, CDCl_3) δ 204.6, 172.7, 172.6, 171.7, 171.6, 136.4, 136.3, 131.6, 131.5, 131.0, 130.4, 128.4, 128.3, 128.2, 128.0, 127.3, 126.9, 122.6, 90.9, 90.8, 90.4,

86.4, 86.3, 84.2, 69.0, 68.9, 52.4, 39.8, 39.0, 38.7, 13.9, 13.7; IR (thin film) ν 2948, 1967, 1743, 1645, 1392 cm^{-1} ; MS m/z (%) 448 (7), 390 (78), 358 (25), 105 (100); EI-HRMS calcd for $\text{C}_{30}\text{H}_{26}\text{NO}_3$ m/z $[\text{M}-1]^+$ 448.1913; found 448.1929.

6, Table 1, Entry j

2-(Benzoylbut-2-ynylamino)-2-benzylpenta-3,4-dienoic acid methyl ester (6, Table 1, Entry j). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzoylamino-2-benzyl-penta-3,4-dienoic acid methyl ester (450 mg, 1.40 mmol), NaH (60% dispersion in mineral oil) (123 mg, 3.08 mmol), 1-bromo-2-butyne (183 μL , 2.10 mmol).

Purification by flash chromatography (hexanes-EtOAc, 9 : 1, v/v) afforded the title compound (438 mg, 84%).

^1H NMR (300 MHz, CDCl_3) δ 7.68-7.65 (m, 2H), 7.46-7.41 (m, 3H), 7.32-7.22 (m, 5H), 5.97 (t, $J = 6.6$ Hz, 1H), 5.10 (dd, $J = 9.3, 6.6$ Hz, 1H), 5.05 (dd, $J = 9.3, 6.6$ Hz, 1H), 3.98 (1/2 AB, $J = 13.6$ Hz, 1H), 3.76 (s, 3H), 3.73 (dq, $J = 18.6, 2.3$ Hz, 1H), 3.55 (dq, $J = 18.6, 2.3$ Hz, 1H), 3.43 (1/2 AB, $J = 13.6$ Hz, 1H), 1.69 (t, $J = 2.3$ Hz, 3H); ^{13}C NMR (75MHz, CDCl_3) δ 207.6, 172.4, 171.3, 136.2, 135.9, 131.1, 130.3, 128.2, 128.2, 127.9, 127.3, 126.8, 90.8, 80.4, 79.2, 75.9, 68.7, 52.2, 39.4, 39.0, 3.5; IR (thin film) 2949, 2228, 1958, 1744, 1641 cm^{-1} ; MS m/z (%) 372 (45), 342 (10), 282 (31), 105 (100); EI-HRMS calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_3$ m/z $[\text{M}-1]^+$ 372.1600, found 372.1618.

6, Table 1, Entry k

2-(Benzoylprop-2-ynyl-amino)-2-benzylhexa-3,4-dienoic acid methyl ester (6, Table 1, Entry k). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzoylamino-2-benzyl-penta-3,4-dienoic acid methyl ester (495 mg, 1.54 mmol), NaH (60% dispersion in mineral oil) (154 mg, 3.85 mmol), propargyl bromide (80% wt. in toluene) (257 μ L, 2.31 mmol).

Purification by flash chromatography (gradient elution; hexanes-EtOAc, 9 : 1 to 4 : 1, v/v) afforded the title compound (364 mg, 66%).

^1H NMR (300 MHz, CDCl_3) δ 7.66-7.64 (m, 2H), 7.46-7.40 (m, 3H), 7.27-7.24 (m, 5H), 5.94 (t, J = 6.6 Hz, 1H), 5.10 (app dd, J = 6.6, 2.9 Hz, 2H), 3.96 (1/2 AB, J = 13.6 Hz, 1H), 3.76 (s, 3H), 3.73 (dd, J = 18.8, 1.8 Hz, 1H), 3.51 (dd, J = 18.8, 1.9 Hz, 1H), 3.45 (1/2 AB, J = 13.7 Hz, 1H), 2.18 (s, 1H); ^{13}C NMR (75MHz, CDCl_3) δ 207.7, 172.4, 171.1, 135.9, 135.5, 130.9, 130.4, 128.3, 128.1, 127.1, 126.9, 90.5, 80.5, 79.6, 72.8, 68.5, 52.3, 38.8, 38.6. IR (thin film) ν 3302, 2950, 2115, 1957, 1742, 1640, 1433, 1398, 1266, 1246 cm^{-1} ; MS m/z (%) 358 (35), 268 (42), 105 (100); EI HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_3$ m/z [M^+] 358.1443, found 358.1451.

6, Table 1, Entry I

2-(Benzoylbut-2-ynyl-amino)-2-methylpenta-3,4-dienoic acid methyl ester (6, Table 1, Entry I). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzoylamino-2-methyl-penta-3,4-dienoic acid methyl ester (200 mg, 0.816 mmol), NaH (65 mg of a 60% dispersion in mineral oil, 1.6 mmol), 1-bromo-2-butyne (142 μ L, 1.6 mmol).

Purification by flash chromatography (gradient elution; hexanes-EtOAc, 9 : 1 to 4 : 1, v/v) afforded the title compound (226 mg, 93%).

^1H NMR (300 MHz, CDCl_3) δ 7.60-7.57 (m, 2H), 7.40-7.34 (m, 3H), 5.79 (t, J = 6.6 Hz, 1H), 4.95 (d, J = 6.6 Hz, 1H), 3.96 (q, J = 2.2 Hz, 2H), 3.71 (s, 3H), 1.82 (t, J = 2.2 Hz, 3H), 1.72 (s, 3H); ^{13}C NMR (75MHz, CDCl_3) δ 208.2, 172.2, 171.8, 135.5, 130.2, 128.1, 128.1, 127.0, 92.5, 80.3, 78.9, 75.8, 63.4, 52.4, 43.0, 37.3, 20.5, 3.4; IR (thin film) ν 2949, 1957, 1742, 1637, 1398, 1264 cm^{-1} ; MS m/z (%) 297 (19), 258 (20), 238 (52), 105 (100); EI HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_3$ m/z [M^+] 297.1365, found 297.1359.

6, Table 1, Entry m

2-(Benzoylprop-2-ynylamino)-2-methylpenta-3,4-dienoic acid methyl ester (6, Table 1, Entry m). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzoylamino-2-methyl-penta-3,4-dienoic acid methyl ester (200 mg, 0.816 mmol), NaH (65 mg of a 60% dispersion in mineral oil, 1.6 mmol), propargyl bromide (80% wt. in toluene) (180 μ L, 1.6 mmol).

Purification by flash chromatography (gradient elution; hexanes-EtOAc, 9 : 1 to 4 : 1, v/v) afforded the title compound (217 mg, 94%).

^1H NMR (300 MHz, CDCl_3) δ 7.64-7.61 (m, 2H), 7.46-7.40 (m, 3H), 5.82 (t, J = 6.6 Hz, 1H), 5.01 (d, J = 6.5 Hz, 2H), 4.05 (d, J = 2.4 Hz, 2H), 3.76 (s, 3H), 2.39 (t, J = 2.4 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (75MHz, CDCl_3) δ 208.5, 172.2, 172.1, 135.5, 130.4, 128.4, 127.1, 92.6, 80.8, 79.2, 72.8, 63.8, 52.6, 37.1, 20.7; IR (thin film) ν 3256, 2950, 2115, 1956, 1740, 1640, 1397, 1264 cm^{-1} ; MS m/z (%) 283 (20), 252 (24), 244 (26), 224 (51), 105 (100); EI HRMS calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ m/z [M^+] 283.1208, found 283.1198.

6, Table 1, Entry n

2-(tert-Butoxycarbonyl-but-2-ynylamino)-2-methylhexa-3,4-dienoic acid methyl ester (6, Table 1, Entry n). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12) with the following modifications (KH was used as a base instead of NaH, and THF was used as solvent instead of DMF):

2-*tert*-butoxycarbonylamino-2-methyl-hexa-3,4-dienoic acid methyl ester (225 mg, 0.882 mmol), KH (233 mg of 30% wt. dispersion in mineral oil, 1.77 mmol), 1-bromo-2-butyne (155 μ L, 1.77 mmol), THF (10 mL). After addition of the reagents at 0 $^\circ\text{C}$, the reaction was stirred for 1 h followed by 2 h at room temperature.

Purification by flash chromatography (gradient elution; hexanes-EtOAc, 19 : 1 to 9 : 1, v/v) afforded the title compound (173 mg, 64%).

^1H NMR (300 MHz, CDCl_3) δ 5.46-5.39 (m, 1H), 5.36-5.27 (m, 1H), 4.18 (1/2 AB, J = 17.6 Hz, 1H), 4.00 (1/2 AB, J = 18.1, 1.9 Hz, 1H), 3.66 (s, 3H), 1.74 (t, J = 2.3 Hz, 3H), 1.68 (dd, J = 7.1, 3.2 Hz, 3H), 1.55 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (75MHz, CDCl_3) δ 204.9, 173.0, 154.3, 93.0, 90.1, 81.0, 78.1, 76.1, 63.6, 52.2, 33.9, 28.1, 13.7, 3.4; MS m/z (%) 251 (65), 192 (92), 154 (100), 148 (73); EI HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_4$ m/z [$\text{M}+1-\text{tBu}^+$] 251.1158, found 251.1169.

6, Table 1, Entry o

2-(Benzoyl-but-2-ynylamino)-2-(tert-butyldimethylsilyloxymethyl)-hexa-3,4-dienoic acid methyl ester (6, Table 1, Entry o). Followed general procedure for N-alkylation of N-protected allenic amino acid methyl esters (page s12):

2-Benzoylamino-2-(tert-butyl-dimethyl-silyloxymethyl)-hexa-3,4-dienoic acid methyl ester (245 mg, 0.629 mmol), NaH (60% dispersion in mineral oil) (50 mg of a 60% dispersion in mineral oil, 1.3 mmol), 1-bromo-2-butyne (88 μL , 1.1 mmol).

Purification by flash chromatography (gradient elution; hexanes-EtOAc, 19 : 1 to 9 : 1, v/v) afforded the title compound (237 mg, 85%).

^1H NMR (300 MHz, CDCl_3) δ 7.71-7.65 (m, 2H), 7.46-7.37 (m, 3H), 5.90-5.86 (m, 1H), 5.41-5.31 (m, 1H), 4.45 (d, J = 10.1 Hz, 1H)**, 4.44 (d, J = 10.1 Hz, 1H)*, 4.31-4.16 (m, 2H), 3.99 (dq, J = 18.5, 2.3 Hz, 1H), 3.74 (s, 3H)*, 3.73 (s, 3H)**, 1.90-1.87 (m, 3H), 1.71 (dd, J = 7.1, 3.2 Hz, 3H)*, 1.71 (dd, J = 7.1, 3.2 Hz, 3H)**, 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H).

* minor diastereomer, ** major diastereomer

^{13}C NMR (75 MHz, CDCl_3) δ 205.1, 205.0, 172.3, 172.2, 170.6, 136.1, 130.1, 128.1, 127.3, 127.3, 89.9, 89.8, 89.7, 79.8, 79.7, 77.2, 68.3, 68.2, 64.0, 63.9, 52.2, 52.1, 39.4, 39.3, 25.8, 25.7, 18.1, 14.0, 13.7, 3.6, -5.5, -5.6, -5.6, -5.7; IR (thin film) ν 2952, 1968, 1744, 1644 cm^{-1} ; MS m/z (%) 384 (35), 296 (31), 84 (100); EI-HRMS calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_4\text{Si}$ m/z [$\text{M}-57^+$] 384.1631; found 384.1630.

General procedure for the rhodium catalyzed formal Alder-ene reaction.

To a 10 mL test tube equipped with a magnetic stirring bar was added the alkynyl allene (0.1 mmol) as a solution in benzene. The solvent was removed under vacuum and the atmosphere replaced with N₂. Toluene (1 mL) was added followed by addition of [Rh(CO)₂Cl]₂ (0.005 mmol) at room temperature. Upon completion of the reaction based upon TLC (10 min) the solution was applied to a plug of silica gel. Elution with (hexanes-EtOAc, 9 : 1, v/v) afforded the title compound.

2-Methyl-5-methylene-4-vinyl-5,6-dihydro-2H-pyridine-1,2-dicarboxylic acid 1-benzyl ester 2-methyl ester (7, Table 2, Entry a). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-(Benzyloxycarbonylprop-2-ynylamino)-2-methylhexa-3,4-dienoic acid methyl ester (37 mg, 0.11 mmol), [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol).

Yield (31 mg, 84%).

¹H NMR (300 MHz, DMSO-*d*₆, 323 K) δ 7.35 (m, 5H), 6.43 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.68 (s, 1H), 5.48 (d, *J* = 17.3 Hz, 1H), 5.26-5.24 (m, 2H), 5.11 (s, 2H), 4.39 (1/2 AB, *J* = 14.2 Hz, 1H), 3.88 (1/2 AB, *J* = 14.2 Hz, 1H), 3.49 (br s, 3H), 1.55 (s, 3H); NMR (75 MHz, DMSO-*d*₆, 323 K) δ 171.3, 154.0, 136.1, 135.8, 134.2, 132.9, 128.1, 127.6, 127.4, 126.5, 117.3, 112.6, 66.5, 62.0, 52.0, 45.6, 21.5; IR (thin film) ν 2950, 1743, 1704, 1247 cm⁻¹; MS *m/z* (%) 327 (12), 268 (85), 224 (59), 91 (100); EI-HRMS calcd for C₁₉H₂₁NO₄ *m/z* [M⁺] 327.1471; found 327.1473.

5-Ethylidene-2-methyl-4-vinyl-5,6-dihydro-2H-pyridine-1,2-dicarboxylic acid 1-benzyl ester 2-methyl ester (7, Table 2, Entry b). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-(Benzyloxycarbonyl-but-2-ynyl-amino)-2-methylhexa-3,4-dienoic acid methyl ester (515 mg, 1.51 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (30 mg, 0.077 mmol).

Yield (420 mg, 81%).

^1H NMR (300 MHz, $\text{DMSO}-d_6$, 323 K) δ 7.37-7.33 (m, 5H), 6.40 (dd, $J = 17.2, 10.8$ Hz 1H), 5.76 (q, $J = 7.0$ Hz, 1H), 5.50 (br s, 1H), 5.40 (dd, $J = 17.2, 1.3$ Hz 1H), 5.19 (dd, $J = 10.8, 1.3$ Hz, 1H), 5.15 (1/2 AB, $J = 12.4$ Hz, 1H), 5.10 (1/2 AB, $J = 12.4$ Hz, 1H), 4.58 (1/2 AB, $J = 14.6$ Hz, 1H), 3.79 (1/2 AB, $J = 14.6$ Hz, 1H), 3.49 (s, 3H), 1.76 (d, $J = 7.0$ Hz, 3H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, 323K) δ 171.5, 154.1, 136.1, 135.3, 133.6, 128.9, 128.0, 127.5, 127.2, 123.9, 122.2, 117.0, 66.4, 61.6, 51.8, 12.7; IR (neat) ν 2949, 1743, 1704, 1404, 1243, 1110 cm^{-1} ; MS m/z (%) 341 (26), 282 (26), 238 (15), 91 (100); EI-HRMS calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_4$ $[\text{M}^+]$ m/z 341.1621, found 341.1627.

2-Methyl-5-trimethylsilylmethylene-4-vinyl-5,6-dihydro-2H-pyridine-1,2-dicarboxylic acid 1-benzyl ester 2-methyl ester (7, Table 2, Entry c). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-[Benzyloxycarbonyl-(3-trimethylsilylprop-2-ynyl)-amino]-2-methylhexa-3,4-dienoic acid methyl ester (30 mg, 0.075 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1.5 mg, 0.0037 mmol).

Yield (26 mg, 87%).

^1H NMR (300 MHz, $\text{DMSO}-d_6$, 323 K) δ 7.39-7.30 (m, 5H), 6.43 (dd, $J = 17.2, 10.8$ Hz, 1H), 5.76 (s, 1H), 5.66 (s, 1H), 5.41 (d, $J = 17.2$ Hz, 1H), 5.21 (dd, $J = 10.8, 0.7$ Hz, 1H), 5.13 (1/2 AB, $J = 13.4$ Hz, 1H), 5.07 (1/2 AB, $J = 13.4$ Hz, 1H), 4.54 (1/2 AB, $J = 14.4$ Hz, 1H), 3.94 (1/2 AB, $J = 14.4$ Hz, 1H), 3.52 (s, 3H), 1.57 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, 323K) δ 171.2, 153.9, 143.4, 136.1, 135.9, 123.3, 128.0, 127.6, 127.5, 126.9, 126.8, 126.1, 117.3, 66.6, 61.7, 51.9, 44.1, 21.2, -0.5; IR (neat) ν

2953, 1745, 1706, 1405, 1248, 1113 cm^{-1} ; MS m/z (%) 399 (25), 340 (34), 296 (15), 91 (100); EI-HRMS calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_4\text{Si} [\text{M}^+]$ m/z 399.1866, found 399.1843.

5-Benzylidene-2-methyl-4-vinyl-5,6-dihydro-2H-pyridine-1,2-dicarboxylic acid 1-benzyl ester 2-methyl ester (7, Table 2, Entry d). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-[Benzyloxycarbonyl-(3-phenylprop-2-ynyl)-amino]-2-methylhexa-3,4-dienoic acid methyl ester (25 mg, 0.062 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1.0 mg, 0.003 mmol).

Yield (25 mg, >95%).

^1H NMR (300 MHz, $\text{DMSO}-d_6$, 323 K) δ 7.46-7.21 (m, 10H), 6.76 (s, 1H), 6.57 (dd, $J = 17.1, 10.7$ Hz, 1H), 5.72 (s, 1H), 5.52 (d, $J = 17.2$ Hz, 1H), 5.29 (d, $J = 10.8$ Hz, 1H), 5.07 (1/2 AB, $J = 12.6$ Hz, 1H), 5.01 (1/2 AB, $J = 12.7$ Hz, 1H), 4.87 (1/2 AB, $J = 14.7$ Hz, 1H), 4.09 (1/2 AB, $J = 14.7$ Hz, 1H), 3.52 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, 323 K) δ 171.4, 153.9, 135.9, 135.9, 135.7, 133.7, 130.0, 128.8, 128.1, 127.6, 127.2, 127.1, 126.9, 126.0, 117.8, 66.4, 61.8, 52.1, 21.3; IR (thin film) ν 2949, 1742, 1704, 1408, 1248 cm^{-1} ; MS m/z (%) 403 (37), 344 (45), 300 (17), 91 (35), 84 (100); EI-HRMS calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_4$ m/z $[\text{M}^+]$ 403.1784, found 403.1789.

5-Ethylidene-2-methyl-4-(2-methylpropenyl)-5,6-dihydro-2H-pyridine-1,2-dicarboxylic acid 1-benzylester 2-methyl ester (7, Table 2, Entry e). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-(Benzyloxycarbonylbut-2-ynylamino)-2,6-dimethylhepta-3,4-dienoic acid methyl ester (40 mg, 0.11 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (2 mg, 0.005 mmol).

Yield (40 mg, >95%).

^1H NMR (300 MHz, $\text{DMSO-}d_6$, 323 K) δ 7.35 (s, 5H), 5.64 (s, 1H), 5.58 (q, J = 6.9 Hz, 1H), 5.12 (s, 3H), 4.65 (1/2 AB, J = 14.9 Hz, 1H), 3.71 (1/2 AB, J = 14.7 Hz, 1H), 3.47 (br s, 3H), 1.77 (s, 3H), 1.72 (d, J = 6.8 Hz, 3H), 1.58 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$, 323 K) δ 171.9, 154.2, 137.2, 136.2, 134.2, 130.2, 128.1, 128.1, 127.7, 127.4, 125.5, 122.0, 121.1, 66.5, 61.5, 51.8, 25.3, 18.5, 12.8; IR (thin film) ν 2930, 1742, 1687, 1424, 1253 cm^{-1} ; MS m/z (%) 369 (10), 310 (50), 266 (36), 91 (100); EI-HRMS calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_4$ m/z [M^+] 369.1940; found 369.1952.

1-Benzoyl-2-benzyl-5-methylene-4-vinyl-1,2,5,6-tetrahydropyridine-2-carboxylic acid methyl ester (7, Table 2, Entry f). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-(Benzoylprop-2-ynylamino)-2-benzylhexa-3,4-dienoic acid methyl ester (29 mg, 0.078 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1.5 mg, 0.0039 mmol).

Yield (21 mg, 74%).

^1H NMR (300 MHz, CDCl_3) δ 7.44-7.38 (m, 5 H), 7.25-7.20 (m, 5H), 6.37 (dd, J = 17.3, 10.8 Hz, 1H), 5.85 (s, 1H), 5.52 (dd, J = 17.3, 1.2 Hz, 1H), 5.28 (dd, J = 10.8, 1.1 Hz, 1H), 5.09 (s, 1H), 4.76 (s, 1H), 4.10 (1/2 AB, J = 13.7, 1H), 3.84 (1/2 AB, J = 13.9, 1H), 3.77 (s, 3H), 3.39 (1/2 AB, J = 13.7, 1H), 2.67 (1/2 AB, J = 14.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.6, 170.6, 137.9, 136.4, 136.0, 135.8, 133.3, 130.6, 129.9, 128.4, 128.0, 126.9, 126.8, 125.7, 117.8, 112.5, 66.5, 52.9, 50.6, 39.8; IR (thin film) ν 2949, 1739, 1638, 1410, 1242 cm^{-1} ; MS m/z (%) 373 (20), 342 (8), 314 (8), 282 (25), 105 (100); EI-HRMS calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_3$ m/z [M^+] 373.1678, found 373.1664.

1-Benzoyl-2-benzyl-5-ethylidene-4-vinyl-1,2,5,6-tetrahydropyridine-2-carboxylic acid methyl ester (7, Table 2, Entry g). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-(Benzoyl-but-2-ynyl-amino)-2-benzylhexa-3,4-dienoic acid methyl ester (20 mg, 0.052 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1.0 mg, 0.002 mmol)

Yield (16 mg, 80%).

^1H NMR (300 MHz, CDCl_3) δ 7.47-7.39 (m, 5H), 7.31-7.28 (m, 5H), 6.36 (dd, $J = 17.2$, 10.7 Hz, 1H), 5.75 (s, 1H), 5.63 (q, $J = 7.0$ Hz, 1H), 5.50 (dd, $J = 17.2$, 1.5 Hz, 1H), 5.27 (dd, $J = 10.7$, 1.5 Hz, 1H), 4.13 (1/2 AB, $J = 13.6$ Hz, 1H), 4.13 (1/2 AB, $J = 14.6$ Hz, 1H), 3.80 (s, 3H), 3.41 (1/2 AB, $J = 13.6$ Hz, 1H), 2.46 (1/2 AB, $J = 14.3$ Hz, 1H), 1.42 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.3, 171.3, 139.5, 137.0, 136.7, 134.6, 131.0, 130.1, 129.5, 128.8, 128.3, 127.2, 127.0, 123.5, 123.0, 117.9, 114.7, 67.0, 53.1, 44.7, 40.3, 13.4; IR (thin film) ν 2949, 1738, 1640, 1415 cm^{-1} ; MS m/z (%) 387 (8), 356 (7), 296 (25), 105 (100); EI-HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_3$ m/z $[\text{M}-91]^+$ 296.1287; found 296.1283.

1-Benzoyl-2-benzyl-5-trimethylsilylmethylene-4-vinyl-1,2,5,6-tetrahydropyridine-2-carboxylic acid methyl ester (7, Table 2, Entry h). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-[Benzoyl-(3-trimethylsilylprop-2-ynyl)-amino]-2-benzylhexa-3,4-dienoic acid methyl ester (46 mg, 0.10 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (2 mg, 0.005 mmol).

Yield (42 mg, 92%).

^1H NMR (300 MHz, CDCl_3) δ 7.38-7.18 (m, 10H), 6.32 (dd, $J = 17.3$, 10.8 Hz, 1H), 5.82 (s, 1H), 5.52 (s, 1H), 5.43 (dd, $J = 17.3$, 1.5 Hz, 1H), 5.21 (dd, $J = 10.8$, 1.5 Hz, 1H), 4.06 (1/2 AB, $J = 13.7$ Hz, 1H), 4.00 (1/2 AB, $J = 14.1$ Hz, 1H), 3.75 (s, 3H), 3.34 (1/2 AB, $J = 13.7$ Hz, 1H), 2.70 (1/2 AB, $J = 14.1$, 1.21 Hz, 1H), -0.35 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.8, 170.3, 142.5, 139.5, 136.5, 136.3, 134.0, 130.6, 129.7, 128.5, 128.0, 126.9, 126.7, 124.9, 117.7, 65.7, 52.8, 49.3, 39.7, -0.7; IR (neat) ν 3029, 2951, 1740, 1642, 1408, 1252, 1218 cm^{-1} ; MS m/z (%) 445 (5), 430 (5), 354 (40), 105 (100); EI-HRMS calcd for $\text{C}_{27}\text{H}_{31}\text{NO}_3\text{Si}$ $[\text{M}^+]$ m/z 445.2073, found 445.2076.

7, Table 2, Entry i

1-Benzoyl-2-benzyl-5-benzylidene-4-vinyl-1,2,5,6-tetrahydropyridine-2-carboxylic acid methyl ester (7, Table 2, Entry i). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-[Benzoyl-(3-phenylprop-2-ynyl)-amino]-2-benzylhexa-3,4-dienoic acid methyl ester (26 mg, 0.058 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1 mg, 0.003 mmol)

Yield (21 mg, 81 %).

^1H NMR (300 MHz, CDCl_3) δ 7.29-7.00 (m, 13 H), 6.82-6.79 (m, 2H), 6.61 (s, 1H), 6.43 (ddd, $J = 17.3, 10.7, 0.8$ Hz, 1H), 5.89 (s, 1H), 5.56 (dd, $J = 17.3, 1.5$ Hz, 1H), 5.33 (dd, $J = 10.7, 1.5$ Hz, 1H), 4.41 (1/2 AB, $J = 14.2$ Hz, 1H), 4.10 (1/2 AB, $J = 13.6$ Hz, 1H), 3.77 (s, 3H), 3.41 (1/2 AB, $J = 13.6$ Hz, 1H), 2.68 (1/2 AB, $J = 14.2, 1.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.1, 171.2, 139.8, 136.9, 136.1, 135.8, 134.5, 131.0, 130.5, 129.7, 128.8, 128.5, 128.4, 128.0, 127.5, 127.1, 127.0, 125.6, 118.5, 66.9, 53.2, 45.4, 40.3; IR (thin film) ν 2918, 1738, 1639, 1413, 1223 cm^{-1} ; MS m/z (%) 449 (10), 390 (15), 358 (50), 105 (100); EI-HRMS calcd for $\text{C}_{30}\text{H}_{27}\text{NO}_3$ m/z $[\text{M}^+]$ 449.1991; found 449.2011.

7, Table 2, Entry n

5-Ethylidene-2-methyl-4-vinyl-5,6-dihydro-2H-pyridine-1,2-dicarboxylic acid 1-tert-butyl ester 2-methyl ester (7, Table 2, Entry n). Compound has been previously synthesized in the Curran group via the same general procedure for the allenic Alder-ene reaction (page s23) in 79% yield.²

^1H NMR (300 MHz, CDCl_3) δ 6.31 (ddd, $J = 17.2, 10.7, 0.8$ Hz, 1H), 5.70 (q, $J = 7.1$ Hz, 1H), 5.39 (s, 1H), 5.34 (dd, $J = 17.2, 1.8$ Hz, 1H), 5.12 (dd, $J = 10.7, 1.7$ Hz, 1H), 4.66 (1/2 AB, $J = 14.0$ Hz, 1H), 3.65 (s, 3H), 3.59 (1/2 AB, $J = 14.0$ Hz, 1H), 1.78 (d, $J = 7.1$ Hz, 3H), 1.55 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 173.3, 154.4, 136.4, 134.4, 124.1, 122.9, 117.3, 81.0, 62.1, 52.4, 39.7, 28.3, 22.4, 13.5; MS m/z (%) 307 (26),

248 (47), 192 (100), 148 (56), 57 (60); EI-HRMS calcd for C₁₇H₂₅NO₄ m/z [M⁺] 307.1784; found 307.1783.

1-Benzoyl-2-(*tert*-butyldimethylsilyloxymethyl)-5-ethylidene-4-vinyl-1,2,5,6-tetrahydropyridine-2-carboxylic acid methyl ester (7, Table 2, Entry o). Followed general procedure for the rhodium catalyzed formal Alder-ene reaction (page s23):

2-(Benzoyl-but-2-ynylamino)-2-(*tert*-butyldimethylsilyloxymethyl)-hexa-3,4-dienoic acid methyl ester (36 mg, 0.082 mmol), [Rh(CO)₂Cl]₂ (1.5 mg, 0.0039 mmol).

Yield (32 mg, 89 %).

¹H NMR (300 MHz, CDCl₃) δ (7.47-7.40 (m, 5H), 6.38 (dd, J = 17.2, 10.7 Hz, 1H), 5.75 (q, J = 7.0 Hz, 1H), 5.57 (s, 1H), 5.44 (dd, J = 17.2, 1.5 Hz, 1H), 5.21 (dd, J = 10.7, 1.5 Hz, 1H), 4.70 (1/2 AB, J = 10.2 Hz, 1H), 4.51 (1/2 AB, J = 14.1 Hz, 1H), 4.19 (1/2 AB, J = 10.2 Hz, 1H), 3.99 (1/2 AB, J = 14.0 Hz, 1H), 3.69 (s, 3H), 1.58 (d, J = 7.1 Hz, 1H), 0.85 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 170.8, 139.6, 136.2, 134.4, 129.9, 129.7, 128.5, 127.0, 122.6, 122.4, 117.5, 66.3, 65.4, 52.5, 45.4, 25.8, 18.1, 13.4, -5.4, -5.5; IR (thin film) ν 2954, 2929, 2037, 1740, 1644 cm⁻¹; MS m/z (%) 441 (23), 411 (63), 384 (66), 296 (100); EI-HRMS calcd for C₂₅H₃₅NO₄Si m/z [M⁺] 441.2335; found 441.2333.

General procedure for rhodium catalyzed Pauson-Khand reaction for the preparation of [6,5] P-K products.

To a flame dried test tube equipped with a magnetic stirring bar was added $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.05 mmol) and DCE (1 mL). To this solution, PPh_3 (0.15 mmol) in DCE (1 mL) was added dropwise via a syringe at room temperature. The test tube was evacuated under vacuum by inserting a needle and charged with CO from a balloon 3 times. After 5 min AgBF_4 (0.1 mmol of a 0.05 M or 0.1 M solution in DCE) was added dropwise via a syringe. The mixture was stirred for an additional 5-10 min at room temperature and then the allenyne (0.5 mmol) in DCE (2 mL) was added via a syringe. The reaction was followed by TLC and upon completion (1-2 h at room temperature or 40 °C in some cases) it was directly applied to a silica gel column. Gradient elution (hexanes-EtOAc, 9 : 1 to 3 : 1, v/v) afforded the desired 4-alkylidene cyclopentenones.

Notes: $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and PPh_3 were both weighed in an open atmosphere. AgBF_4 was weighed in a glove box under N_2 atmosphere and caution was taken to limit exposure to light. DCE solution of AgBF_4 was prepared by sonication for 5 min.

8, Table 3, Entry b

3,5,7-Trimethyl-6-oxo-1,3,5,6-tetrahydro-[2]pyrindine-2,3-dicarboxylic acid 2-benzyl ester 3-methyl ester (8, Table 3, Entry b). Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-(Benzyloxycarbonyl-but-2-ynyl-amino)-2-methylhexa-3,4-dienoic acid methyl ester (25 mg, 0.07 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (3 mg, 0.01 mmol), PPh_3 (5 mg, 0.02 mmol), AgBF_4 (150 μL of 0.1 M solution in DCE, 0.02 mmol).

Yield (19 mg, 75%).

^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 7.41-7.30 (m, 5H), 5.72 (s, 1H), 5.15 (s, 2H), 4.86 (1/2 AB, J = 18.6 Hz, 1H), 4.34 (1/2 AB, J = 18.0 Hz, 1H), 3.48 (br s, 3H), 2.87 (q, J = 7.4

Hz, 1H), 1.73 (s, 3H), 1.57 (s, 3H), 1.07 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 206.4, 192.6, 172.7, 155.5, 154.9, 138.6, 137.0, 134.6, 129.2, 128.8, 128.5, 121.7, 67.7, 62.5, 53.1, 41.6, 40.7, 22.9, 14.1, 8.5; IR (thin film) ν 2916, 1744, 1700, 1234 cm^{-1} ; MS m/z (%) 369 (15), 310 (40), 266 (27), 91 (100); EI-HRMS calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_5$ m/z $[\text{M}^+]$ 369.1576; found 369.1581.

3,5-Dimethyl-6-oxo-7-trimethylsilyl-1,3,5,6-tetrahydro-[2]pyrindine-2,3-dicarboxylic acid 2-benzyl ester 3-methyl ester (8, Table 3, Entry c). Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-[Benzyloxycarbonyl-(3-trimethylsilylprop-2-ynyl)-amino]-2-methylhexa-3,4-dienoic acid methyl ester (30 mg, 0.075 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (3 mg, 0.01 mmol), PPh_3 (6 mg, 0.02 mmol), AgBF_4 (335 μL of 0.05 M solution in DCE, 0.02 mmol).

Yield (25 mg, 78%).

^1H NMR (300 MHz, DMSO- d_6 , 323 K) δ 7.37 (s, 5H), 5.80 (s, 1H), 5.18-5.09 (m, 2H), 5.01 (1/2 AB, $J = 18.6$ Hz, 1H), 4.46 (1/2 AB, $J = 18.6$ Hz, 1H), 3.53 (s, 3H), 2.84 (q, $J = 7.4$ Hz, 1H), 1.61 (s, 3H), 1.07 (d, $J = 7.4$ Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, DMSO- d_6 , 323 K) δ 209.5, 171.4, 166.2, 154.4, 139.7, 136.7, 135.9, 128.1, 127.8, 127.4, 122.9, 66.8, 61.3, 52.1, 41.7, 41.6, 21.3, 13.3, -1.3; IR (thin film) ν 2953, 1746, 1694, 1248 cm^{-1} ; MS m/z (%) 427 (11), 384 (30), 368 (32), 324 (27), 91 (100); EI-HRMS calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_5\text{Si}$ m/z $[\text{M}^+]$ 427.1815; found 427.1821.

3,5-Dimethyl-6-oxo-7-phenyl-1,3,5,6-tetrahydro-[2]pyrindine-2,3-dicarboxylic acid 2-benzyl ester 3-methyl ester (8, Table 3, Entry d). Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-[Benzyloxycarbonyl-(3-phenylprop-2-ynyl)-amino]-2-methylhexa-3,4-dienoic acid methyl ester (31 mg, 0.08 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (3 mg, 0.01 mmol), PPh_3 (6 mg, 0.02 mmol), AgBF_4 (340 μL of 0.05 M solution in DCE, 0.02 mmol).

Yield (25 mg, 75%).

^1H NMR (300 MHz, $\text{DMSO}-d_6$, 323 K) δ 7.47-7.32 (m, 10H), 5.90 (s, 1H), 5.16-5.08 (m, 2H), 4.99 (1/2 AB, $J = 18.6$ Hz, 1H), 4.66 (1/2 AB, $J = 18.6$ Hz, 1H), 3.51 (s, 3H), 3.09 (q, $J = 7.4$ Hz, 1H), 1.65 (s, 3H), 1.20 (d, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, 323 K) δ 203.7, 171.4, 154.4, 154.1, 137.7, 135.9, 134.3, 130.0, 128.4, 128.2, 128.1, 127.7, 127.3, 123.2, 66.7, 61.7, 52.1, 40.2, 21.4, 13.1; IR (thin film) ν 2931, 1745, 1703, 1241 cm^{-1} ; MS m/z (%) 431 (10), 372 (86), 328 (45), 91 (100); EI-HRMS calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_5$ m/z $[\text{M}^+]$ 431.1733; found 431.1735.

8, Table 3, Entry e

5-Isopropyl-3,7-dimethyl-6-oxo-1,3,5,6-tetrahydro-[2]pyrindine-2,3-dicarboxylic acid 2-benzyl ester 3-methyl ester (8, Table 3, Entry e). Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-(Benzyloxycarbonylbut-2-ynylamino)-2,6-dimethylhepta-3,4-dienoic acid methyl ester (98 mg, 0.265 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (5 mg, 0.01 mmol), PPh_3 (10 mg, 0.04 mmol), AgBF_4 (583 μL of 0.1 M solution in DCE, 0.0583 mmol).

The reaction mixture was heated to 35 $^\circ\text{C}$ for 2 h. Yield (78 mg, 74%).

^1H NMR (300 MHz, CDCl_3 , 320 K) δ 7.39-7.33 (m, 5H), 5.54 (s, 1H), 5.25 (d, $J = 12.2$ Hz, 1H), 5.17 (d, $J = 12.2$ Hz, 1H), 4.95 (1/2 AB, $J = 18.6$ Hz, 1H), 4.21 (1/2 AB, $J = 18.6$ Hz, 1H), 3.56 (br s, 3H), 2.77-2.76 (m, 1H), 2.30-2.17 (m, 1H), 1.81 (s, 3H), 1.69 (s, 3H), 0.93 (d, $J = 7.0$ Hz, 3H), 0.86 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , 320 K) δ 205.9, 172.5, 155.4, 155.3, 136.0, 135.9, 135.8, 128.5, 128.3, 121.6, 67.8, 62.3, 52.5, 52.1, 40.5, 29.8, 22.5, 19.7, 17.9, 7.9; IR (thin film) ν 2958, 1745, 1701, 1238 cm^{-1} . MS m/z (%) 397 (33), 338 (30), 294 (21), 91 (100); EI-HRMS calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_5$ m/z $[\text{M}^+]$ 397.1889; found 397.1888.

8, Table 3, Entry g

2-benzoyl-3-benzyl-5,7-dimethyl-6-oxo-2,3,5,6-tetrahydro-1H-[2]pyrindine-3-carboxylic acid methyl ester (8, Table 3, Entry g). Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-(Benzoyl-but-2-ynyl-amino)-2-benzylhexa-3,4-dienoic acid methyl ester (180 mg, 0.465 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (18 mg, 0.046 mmol), PPh_3 (54 mg, 0.14 mmol), AgBF_4 (2 mL of 0.05M solution in DCE, 0.1 mmol).

Yield (142 mg, 73%). The product was obtained in 1.7 : 1 diastereomeric ratio as determined by integration of resonances in the ^1H NMR.

IR (neat) ν 3027, 2918, 1740, 1704, 1644, 1384, 1250 cm^{-1} ; MS m/z (%) 415 (15), 384 (15), 324 (31), 105 (100); EI-HRMS calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_4$ $[\text{M}^+]$ m/z 415.1784, found 415.1802.

The diastereomers were separated by HPLC (hexanes:EtOAc 4 : 1).

Isomer 1 (R_f = 0.21 TLC hexanes : EtOAc, 2 : 1): ^1H NMR (300 MHz, CDCl_3) δ 7.46-6.98 (m, 10 H), 5.71 (s, 1 H), 4.34 (1/2 AB, J = 17.7 Hz, 1 H), 4.15 (1/2 AB, J = 13.7 Hz 1 H), 3.79 (s, 3H), 3.38 (1/2 AB, J = 13.7 Hz 1 H), 2.86 (1/2 AB, J = 17.7 Hz, 1 H), 2.84 (q, J = 7.4 Hz, 1H), 1.46 (s, 3H), 1.25 (d, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.5, 171.8, 171.6, 153.6, 140.8, 136.4, 135.9, 134.4, 130.6, 130.2, 128.9, 128.4, 127.4, 126.7, 119.9, 66.3, 53.2, 44.4, 42.0, 40.0, 13.6, 8.1;

Isomer 2 (R_f = 0.16 TLC hexanes : EtOAc, 2 : 1): ^1H NMR (300 MHz, CDCl_3) δ 7.47-6.89 (m, 10 H), 5.72 (s, 1 H), 4.34 (1/2 AB, J = 18.2 Hz, 1 H), 4.16 (1/2 AB, J = 13.8 Hz 1 H), 3.81 (s, 3H), 3.39 (1/2 AB, J = 13.8 Hz 1 H), 2.99 (1/2 AB, J = 18.2 Hz, 1 H), 2.86 (q, J = 7.6 Hz, 1H), 1.44 (s, 3H), 1.31 (d, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.6, 172.1, 171.9, 154.0, 140.5, 136.5, 134.5, 130.9, 130.3, 129.1, 128.4, 127.5, 126.8, 120.2, 66.3, 53.3, 44.9, 41.9, 40.2, 14.5, 8.1.

8, Table 3, Entry h

2-Benzoyl-3-benzyl-5-methyl-6-oxo-7-trimethylsilyl-2,3,5,6-tetrahydro-1H-

[2]pyridine-3-carboxylic acid methyl ester (8, Table 3, Entry h). Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-[Benzoyl-(3-trimethylsilylprop-2-ynyl)-amino]-2-benzylhexa-3,4-dienoic acid methyl ester (50 mg, 0.11 mmol), [Rh(CO)₂Cl]₂ (4 mg, 0.01 mmol), PPh₃ (9 mg, 0.03 mmol), AgBF₄ (250 μL of 0.1 M solution in DCE, 0.0250 mmol). The reaction was heated at 35 °C for 1 h.

Yield (52 mg, 98%) as a mixture of diastereomers in ratio 1.5 : 1. The diastereomers were separated by semi-preparative HPLC (hexanes-EtOAc, 4 : 1 v/v).

(major diastereomer – eluting first) ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.19 (m, 10H), 5.78 (s, 1H), 4.41 (1/2 AB, *J* = 18.1 Hz, 1H), 4.15 (1/2 AB, *J* = 13.7 Hz, 1H), 3.82 (s, 3H), 3.38 (1/2 AB, *J* = 13.7 Hz, 1H), 2.86-2.79 (m, 1H), 2.82 (1/2 AB, *J* = 16.8 Hz, 1H), 1.23 (d, *J* = 7.4 Hz, 1H), -0.14 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 210.2, 171.7, 171.6, 165.5, 142.8, 138.2, 136.3, 136.0, 130.6, 130.0, 128.9, 128.4, 127.3, 126.3, 121.5, 65.7, 53.2, 46.4, 42.9, 40.0, 13.8, -1.3; IR (thin film) ν 2952, 1742, 1694, 1647, 1250 cm⁻¹; MS *m/z* (%) 473 (5), 458 (22), 382 (45), 105 (100); EI-HRMS calcd for C₂₈H₃₁NO₄Si *m/z* [M⁺] 473.2022; found 473.2033.

(minor diastereomer – eluting second) ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.42 (m, 3H), 7.34-7.31 (m, 2H), 7.27-7.24 (m, 3H), 7.19-7.16 (m, 2H), 5.77 (d, *J* = 1.0 Hz, 1H), 4.39 (1/2 AB, *J* = 18.5, 1.2 Hz, 1H), 4.15 (1/2 AB, *J* = 13.7 Hz, 1H), 3.83 (s, 3H), 3.38 (1/2 AB, *J* = 13.7 Hz, 1H), 2.94 (1/2 AB, *J* = 18.5 Hz, 1H), 2.80 (q, *J* = 7.6 Hz, 1H), 1.29 (d, *J* = 7.5 Hz, 3H), -0.15 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 210.0, 171.7, 171.5, 165.8, 142.2, 138.0, 136.0, 130.7, 129.9, 128.8, 128.1, 127.2, 126.2, 121.5, 65.5, 53.0, 46.7, 42.5, 39.9, 14.2, -1.5; IR (thin film) ν 2953, 1742, 1695, 1649, 1250 cm⁻¹; MS *m/z* (%) 473 (5), 458 (22), 382 (45), 105 (100); EI-HRMS calcd for C₂₈H₃₁NO₄Si *m/z* [M⁺] 473.2022; found 473.2042.

2-Benzoyl-3-benzyl-5-methyl-6-oxo-7-phenyl-2,3,5,6-tetrahydro-1H-[2]pyrindine-3-carboxylic acid methyl ester (8, Table 3, Entry i). Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-[Benzoyl-(3-phenylprop-2-ynyl)-amino]-2-benzylhexa-3,4-dienoic acid methyl ester (37 mg, 0.082 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (3 mg, 0.008 mmol), PPh_3 (6 mg, 0.02 mmol), AgBF_4 (180 μL of 0.1 M solution in DCE, 0.0181 mmol).

Yield (29 mg, 74%). Diastereomer ratio 1.65 : 1. The diastereomers were separated by semi-preparative HPLC (hexanes-EtOAc, 4 : 1 v/v)

(major diastereomer R_t = 15 min HPLC, hexanes : EtOAc 5 : 1, v / v): ^1H NMR (300 MHz, CDCl_3) δ 7.42-7.17 (m, 13H), 7.04-7.00 (m, 2H), 5.88 (d, J = 1.1 Hz, 1H), 4.60 (1/2 AB, J = 17.7 Hz, 1H), 4.18 (1/2 AB, J = 13.7 Hz, 1H), 3.81 (s, 3H), 3.44 (1/2 AB, J = 13.8 Hz, 1H), 3.10-2.98 (m, 2H), 1.36 (d, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 171.8, 171.7, 153.6, 141.2, 136.6, 135.9, 135.5, 130.8, 130.3, 130.1, 128.9, 128.8, 128.7, 128.7, 128.6, 127.6, 126.8, 122.2, 66.6, 59.9, 53.3, 45.2, 42.9, 40.3, 13.9; IR (thin film) ν 2949, 1741, 1706, 1643 1259 cm^{-1} ; MS m/z (%) 477 (6), 418 (63), 386 (55), 105 (100); EI-HRMS calcd for $\text{C}_{31}\text{H}_{27}\text{NO}_4$ m/z [M^+] 477.1940; found 477.1954.

(minor diastereomer R_t = 18 min HPLC, hexanes : EtOAc 5 : 1): ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.20 (m, 13H), 7.03-6.99 (m, 2H), 5.90 (d, J = 0.9 Hz, 1H), 4.59 (1/2 AB, J = 18.2, 1.2 Hz, 1H), 4.19 (1/2 AB, J = 13.8 Hz, 1H), 3.83 (s, 3H), 3.45 (1/2 AB, J = 13.8 Hz, 1H), 3.17 (1/2 AB, J = 18.3 Hz, 1H), 3.03 (q, J = 7.5 Hz, 1H), 1.41 (d, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 204.9, 172.1, 171.7, 153.8, 140.7, 136.4, 136.0, 135.5, 130.9, 130.3, 130.1, 129.1, 128.8, 128.7, 128.6, 128.5, 127.6, 126.8, 122.5, 66.4, 53.3, 45.6, 42.6, 40.3, 14.9 ; IR (thin film) ν 2950, 1741, 1706, 1645, 1235 cm^{-1} ; MS m/z (%) 477 (10), 418 (15), 386 (25), 105 (100); EI-HRMS calcd for $\text{C}_{31}\text{H}_{27}\text{NO}_4$ m/z [M^+] 477.1940; found 477.1941.

8, Table 3, Entry I

2-Benzoyl-3,7-dimethyl-6-oxo-2,3,5,6-tetrahydro-1H-[2]pyrindine-3-carboxylic acid methyl ester (8, Table 3, Entry I). $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1.5 mg, 0.0038 mmol) was placed in a test tube and DCE (0.3 mL) was added. The test tube was sealed with a rubber septum,

the atmosphere evacuated by inserting a needle and replaced with CO (balloon) three times. 2-(Benzoyl-but-2-ynyl-amino)-2-methyl-penta-3,4-dienoic acid methyl ester (23 mg, 0.077 mmol) in DCE (0.7 mL) was added via syringe. After 2.5 h the reaction was complete based upon TLC and the light yellow solution was directly applied to a silica gel column. Elution (hexanes-EtOAc, 4 : 1 to 2 : 1, v/v) afforded the title compound (18 mg, 72%) after solvent removal.

^1H NMR (300 MHz, CDCl_3) δ 7.51-7.43 (m, 5H), 5.69 (s, 1H), 4.78 (1/2 AB, J = 17.6 Hz, 1H), 4.19 (1/2 AB, J = 17.6, 0.9 Hz, 1H), 3.74 (s, 3H), 3.02 (s, 1H), 1.79 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 203.5, 172.1, 171.8, 155.3, 136.2, 135.2, 133.0, 130.6, 128.8, 127.1, 123.0, 62.4, 52.9, 43.2, 37.4, 20.6, 8.0; IR (thin film) ν 2950, 1740, 1704, 1645, 1394 cm^{-1} . MS m/z (%) 325 (25), 294 (9), 266 (47), 105 (100); EI-HRMS calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_4$ m/z [M^+] 325.1314; found 325.1324.

8, Table 3, Entry n

3,5,7-Trimethyl-6-oxo-1,3,5,6-tetrahydro-[2]pyrindine-2,3-dicarboxylic acid 2-tert-butyl ester 3-methyl ester (8, Table 3, Entry n). Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-(*tert*-Butoxycarbonyl-but-2-ynylamino)-2-methylhexa-3,4-dienoic acid methyl ester (50 mg, 0.163 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (6.0 mg, 0.016 mmol), PPh_3 (13 mg, 0.049 mmol), AgBF_4 (360 μL of 0.1 M solution in DCE, 0.0359 mmol).

Upon disappearance of the starting material (TLC) the reaction mixture was applied to a small silica gel column and eluted (hexanes-EtOAc, 4 : 1 v/v) to afford a mixture of CO insertion products (40 mg, 73 %).

NMR analysis [6,5] : [5,5] = 5 : 1.

The two products were separated by flash chromatography (hexanes-EtOAc, 1 : 0 to 4 : 1 v/v).

[5,5] (R_f = 0.7, (hexanes-EtOAc, 3 : 1 v/v)) spectral data identical to **9** (Table 4, Entry n) formed via the Mo mediated P-K reaction.

[6,5] ($R_f = 0.66$, (hexanes-EtOAc, 3 : 1 v/v)) ^1H NMR (300 MHz, CDCl_3) δ 5.50 (s, 1H), 4.92 (1/2 AB, $J = 18.6$ Hz, 1H), 4.11 (1/2 AB, $J = 18.8$ Hz, 1H), 3.72 (s, 3H), 2.83 (q, $J = 7.5$ Hz, 1H), 1.84 (s, 3H), 1.66 (s, 3H), 1.48 (s, 9H), 1.21 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.7, 173.0, 154.8, 154.5, 138.4, 134.7, 121.0, 81.9, 62.0, 52.7, 41.6, 40.1, 28.2, 22.7, 13.7, 8.1; MS m/z (%) 335 (11), 276 (40), 220 (69), 176 (45), 57 (100); EI-HRMS calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_5$ m/z [M^+] 335.1733; found 335.1726.

8, Table 3, Entry o

2-Benzoyl-3-(*tert*-butyl-dimethyl-silyloxymethyl)-5,7-dimethyl-6-oxo-2,3,5,6-tetrahydro-1H-[2]pyrindine-3-carboxylic acid methyl ester (8, Table 3, Entry o).

Followed general procedure for the preparation of [6,5] P-K products (page s30):

2-(Benzoyl-but-2-ynylamino)-2-(*tert*-butyldimethylsilyloxymethyl)-hexa-3,4-dienoic acid methyl ester (50 mg, 0.11 mmol), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (4 mg, 0.01 mmol), PPh_3 (9 mg, 0.03 mmol), AgBF_4 (250 μL of 0.1 M solution in DCE, 0.0250 mmol).

Yield (43 mg, 81%). Diastereomer ratio 1.78 : 1. The diastereomers were separated by semi-preparative HPLC (hexanes-EtOAc, 6 : 1 v/v)

IR (thin film) ν 2953, 1741, 1708, 1648, 1258 cm^{-1}

(major diastereomer $R_t = 17$ min HPLC, EtOAc : Hex 1 : 6): ^1H NMR (300 MHz, CDCl_3) δ 7.49-7.43 (m, 5H), 5.56 (s, 1H), 4.75 (1/2 AB, $J = 17.1$ Hz, 1H), 4.74 (1/2 AB, $J = 10.4$ Hz, 1H), 4.45 (1/2 AB, $J = 17.4$ Hz, 1H), 4.15 (1/2 AB, $J = 10.3$ Hz, 1H), 3.74 (s, 3H), 2.89 (q, $J = 7.5$ Hz, 1H), 1.65 (s, 3H), 1.28 (d, $J = 7.5$ Hz, 3H), 0.81 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.5, 171.7, 170.5, 154.3, 144.3, 141.3, 135.9, 134.3, 130.0, 128.8, 126.5, 118.8, 66.1, 65.3, 52.6, 45.6, 41.9, 25.7, 18.0, 13.6, 7.9, -5.4, -5.6; MS m/z (%) 469 (37), 439 (30), 412 (30), 324 (20), 105 (100); EI-HRMS calcd for $\text{C}_{26}\text{H}_{35}\text{NO}_5\text{Si}$ m/z [M^+] 469.2285; found 469.2280.

(minor diastereomer $R_t = 26$ min HPLC, EtOAc : Hex 1 : 6): ^1H NMR (300 MHz, CDCl_3) δ 7.50-7.42 (m, 5H), 5.59 (s, 1H), 4.74 (1/2 AB, $J = 18.0$ Hz, 1H), 4.72 (1/2 AB, $J = 10.2$ Hz, 1H), 4.47 (1/2 AB, $J = 17.8$ Hz, 1H), 4.15 (1/2 AB, $J = 10.3$ Hz, 1H), 3.75 (s, 3H), 2.91 (q, $J = 7.6$ Hz, 1H), 1.64 (s, 3H), 1.27 (d, $J = 7.6$ Hz, 9H), 0.80 (s, 3H), 0.07 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.6, 171.9, 170.4, 154.6, 141.2, 135.9,

134.2, 130.0, 128.9, 126.5, 118.8, 65.9, 65.1, 52.6, 45.9, 41.6, 25.6, 17.9, 14.2, 7.9, -5.5, -5.7; MS m/z (%) 469 (7), 439 (30), 412 (35), 324 (22), 105 (100); EI-HRMS calcd for $C_{26}H_{35}NO_5Si$ m/z [M^+] 469.2285; found 469.2299.

General procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products.

To a solution of the allenyne (0.3 mmol) in toluene (3 mL) in a 10 mL round-bottomed flask was added DMSO (3 mmol) followed by $Mo(CO)_6$ (0.375 mmol) at room temperature under N_2 atmosphere. The flask was equipped with a reflux condenser and heated slowly to 80-90 °C in an oil bath. Stirring was continued at this temperature until TLC analysis showed absence of starting material. Upon completion the reaction mixture was directly applied on a small plug of silica gel and eluted (hexanes-EtOAc, 3 : 1 to 1 : 1, v/v). The collected fractions were combined and concentrated under vacuum, and NMR (or HPLC analysis) was performed to determine the product distribution.

Purification of the mixtures was performed by flash chromatography (gradient elution, hexanes-EtOAc v/v).

9, Table 4, Entry a

6-Ethylidene-1-methyl-5-oxo-3,5,6,6a-tetrahydro-1H-cyclopenta[c]pyrrole-1,2-dicarboxylic acid 2-benzyl ester 1-methyl ester (9, Table 4, Entry a). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(Benzyloxycarbonylprop-2-ynylamino)-2-methylhexa-3,4-dienoic acid methyl ester (80 mg, 0.25 mmol), DMSO (174 μ L, 2.45 mmol), $Mo(CO)_6$ (81 mg, 0.31 mmol). Heated to 80 °C for 30 min.

Elution (hexanes-EtOAc, 1 : 1 v/v) on a small silica gel plug afforded a mixture of compounds (82 mg, >95%). Product ratios determined by integration of the peaks in the HPLC trace (hexanes-EtOAc, 4 : 1 v/v): [5,5] Z / E = 7.6 : 1. Purification by flash chromatography (hexanes-EtOAc, 19 : 1 to 2 : 1 v/v) afforded the major Z isomer (48 mg, 55%).

(**Z**) : R_f = 0.4 (TLC, hexanes-EtOAc, 4 : 1 v/v) ^1H NMR (300 MHz, DMSO- d_6 353K) δ 7.40-7.32 (m, 5H), 6.29 (s, 1H), 5.98 (q, J = 7.24 Hz, 1H), 5.10 (s, 2H), 4.49 (1/2 AB, J = 16.2 Hz, 1H), 4.37 (1/2 AB, J = 16.1 Hz, 1H), 4.01 (s, 1H), 3.66 (br s, 3H), 2.17 (d, J = 7.3 Hz, 3H), 1.10 (s, 3H); IR (thin film) ν 2950, 1742, 1699, 1643, 1408 cm^{-1} ; MS m/z (%) 355 (10), 296 (18), 252 (19), 91 (100); EI-HRMS calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_5$ m/z [M^+] 355.1420; found 355.1427.

^{13}C NMR – Due to isomerization of the sample at 353K data was not collected

6-Ethylidene-1,4-dimethyl-5-oxo-3,5,6,6a-tetrahydro-1H-cyclopenta[c]pyrrole-1,2-dicarboxylic acid 2-benzyl ester 1-methyl ester (9, Table 4, Entry b). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(Benzyloxycarbonyl-but-2-ynyl-amino)-2-methylhexa-3,4-dienoic acid methyl ester (56 mg, 0.16 mmol), DMSO (116 μL , 1.64 mmol), $\text{Mo}(\text{CO})_6$ (54 mg, 0.20 mmol). Heated to 90 $^\circ\text{C}$ for 45 min.

Flash chromatography by gradient elution (hexanes-EtOAc, 9 : 1 to 4 : 1 v/v) afforded a mixture of compounds (60 mg, >95%). Product ratios determined by NMR: [5,5] : [6,5] > 20 : 1; [5,5] Z / E = 7 : 1. The major product was purified by semi-preparative HPLC (hexanes-EtOAc, 4 : 1 v/v).

(**Z**) : ^1H NMR (300 MHz, DMSO- d_6 353K) δ 7.38-7.33 (m, 5H), 5.98 (q, J = 7.3 Hz, 1H), 5.11 (s, 2H), 4.43 (1/2 AB, J = 16.2 Hz, 1H), 4.36 (1/2 AB, J = 16.3 Hz, 1H), 3.89 (s, 1H), 3.67 (s, 3H), 2.20 (d, J = 7.3 Hz, 3H), 1.75 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (75 MHz,

DMSO-*d*₆ 353K) δ 195.9, 172.0, 160.4, 152.7, 135.9, 135.8, 135.5, 132.0, 127.7, 127.3, 127.0, 66.0, 65.4, 53.7, 51.7, 44.8, 12.9, 12.7, 7.7; IR (thin film) ν 2951, 1743, 1698, 1646, 1408 cm^{-1} ; MS m/z (%) 369 (13), 310 (7), 266 (10), 91 (100); EI-HRMS calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_5$ m/z [M^+] 369.1576 found 369.1580.

6-Isobutylidene-1,4-dimethyl-5-oxo-3,5,6,6a-tetrahydro-1H-cyclopenta[c]pyrrole-1,2-dicarboxylic acid 2-benzyl ester 1-methyl ester (9, Table 4, Entry e). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(Benzyloxycarbonylbut-2-ynylamino)-2,6-dimethylhepta-3,4-dienoic acid methyl ester (47 mg, 0.13 mmol), DMSO (90 μL , 1.27 mmol), $\text{Mo}(\text{CO})_6$ (42 mg, 0.16 mmol). Heated to 80 $^\circ\text{C}$ for 1 h.

Gradient elution (hexanes-EtOAc, 9 : 1 to 4 : 1 v/v) on a small silica gel plug afforded a mixture of 2 compounds (50 mg, >95%). Product ratios determined by NMR: [5,5] Z / E = 6.4 : 1. Purification by flash chromatography afforded the major Z isomer (42 mg, 83%).

(**Z**) : R_f = 0.52 (TLC, hexanes-EtOAc, 4 : 1 v/v) ^1H NMR (300 MHz, DMSO-*d*₆ 353K) δ 7.38-7.31 (m, 5H), 5.67 (d, J = 9.8 Hz, 1H), 5.10 (s, 2H), 4.41 (1/2 AB, J = 17.5 Hz, 1H), 4.35 (1/2 AB, J = 17.5 Hz, 1H), 3.99-3.78 (m, 2H), 3.67 (br s, 3H), 1.76-1.75 (m, 3H), 1.06 (s, 3H), 0.99 (d, J = 5.5 Hz, 3H), 0.97 (d, J = 5.5 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-*d*₆ 353K) δ : 195.6, 172.2, 152.7, 147.7, 147.4, 136.0, 129.3, 127.9, 127.4, 127.2, 65.4, 51.9, 24.7, 21.9, 21.5, 21.2, 8.0; IR (thin film) ν 2955, 1744, 1699, 1643, 1407 cm^{-1} ; MS m/z (%) 397 (10), 262 (5), 149 (25), 91 (100); EI-HRMS calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_5$ m/z [M^+] 397.1889; found 397.1888.

2-Benzoyl-1-benzyl-4-methyl-6-methylene-5-oxo-1,2,3,5,6,6a-hexahydro-cyclopenta[c]pyrrole-1-carboxylic acid methyl ester (9, Table 4, Entry j). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(Benzoyl-but-2-ynyl-amino)-2-benzylhexa-3,4-dienoic acid methyl ester (338 mg, 0.906 mmol), DMSO (320 μ L, 4.53 mmol), Mo(CO)₆ (300 mg, 1.13 mmol). Heated to 90 °C for 45 min. Gradient elution (hexanes-EtOAc, 19 : 1 to 3 : 2, v/v) gave separation of the major component.

The ratio of products observed by ¹H NMR of the crude mixture after filtration on a small silica gel plug is: [5,5] : [6,5] = 5.7 : 1; Diastereomer ratio of [5,5] 6.4 : 1.

R_f = 0.3 (TLC, hexanes-EtOAc, 3 : 1 v/v) [5,5] major diastereomer (210 mg, 57%)

¹H NMR (300 MHz, CDCl₃) δ 7.60-7.28 (m, 10 H), 6.21 (s, 1H), 5.62 (s, 1H), 4.24 (1/2 AB, *J* = 14.6 Hz, 1H), 4.19 (1/2 AB, *J* = 14.3 Hz, 1H), 3.99 (1/2 AB, *J* = 14.6, 1.2 Hz, 1H), 3.90 (s, 1H), 3.61 (s, 3H), 3.38 (1/2 AB, *J* = 14.3 Hz, 1H), 1.69 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) 195.5, 171.0, 170.2, 162.6, 140.6, 136.1, 135.9, 134.7, 131.3, 131.1, 128.7, 128.5, 127.5, 127.3, 117.6, 71.0, 52.2, 50.5, 49.5, 37.9, 8.9. IR (thin film) ν 2950, 1741, 1707, 1644, 1378, 1340 cm⁻¹; MS *m/z* (%) 401 (40), 342 (22), 296 (35), 105 (100); EI-HRMS calcd for C₂₅H₂₃NO₄ *m/z* [M⁺] 401.1627 found 401.1641

R_f = 0.2 (TLC, hexanes-EtOAc, 3 : 1 v/v) mixture of [5,5] minor diastereomer and [6,5] (82 mg, 22%).

[5,5]-minor diastereomer : ¹H NMR (300 MHz, CDCl₃) δ 7.59-7.44 (m, 5H), 7.17-7.10 (m, 3H), 7.01-6.98 (m, 2H), 6.43 (d, *J* = 1.9 Hz, 1H), 5.66 (d, *J* = 1.3 Hz, 1H), 4.32 (d, *J* = 15.7, 1H), 4.01 (br s, 1H), 3.94 (s, 3H), 3.84 (d, *J* = 14.3 Hz, 1H), 3.59 (d, *J* = 15.6 Hz, 1H), 3.29 (d, *J* = 14.3 Hz, 1H), 1.22 (s, 3H).

Table 4, Entry j
[6,5] product

[6,5] : ¹H NMR (300 MHz, CDCl₃) δ 7.46-7.22 (m, 10 H), 5.77 (s, 1H), 4.34 (d, *J* = 17.8 Hz, 1H), 4.15 (d, *J* = 13.8 Hz, 1H), 3.80 (s, 3H), 3.37 (d, *J* = 13.7 Hz, 1H), 3.03 (s, 2H), 2.91 (d, *J* = 17.9 Hz, 1H), 1.45 (s, 3H).

9, Table 4, Entry k

2-Benzoyl-1-benzyl-6-methylene-5-oxo-1,2,3,5,6,6a-hexahydro-cyclopenta[c]pyrrole-1-carboxylic acid methyl ester (9, Table 4, Entry k). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(Benzoylprop-2-ynylamino)-2-benzylhexa-3,4-dienoic acid methyl ester (435 mg, 1.21 mmol), DMSO (429 μL , 6.06 mmol), Mo(CO)_6 (400 mg, 1.51 mmol). Heated to 90 $^\circ\text{C}$ for 20 min. The crude mixture was purified by flash chromatography (gradient elution, hexanes-EtOAc, 19 : 1 to 2 : 1, v/v).

Isolated two components:

$R_f = 0.3$ (TLC, hexanes-EtOAc, 3 : 1 v/v) [5,5] (260 mg, 55%).

^1H NMR (300 MHz, CDCl_3) δ : 7.52-7.27 (m, 10H), 6.19 (s, 1H), 6.07 (s, 1H), 5.63 (s, 1H), 4.24 (1/2 AB, $J = 14.9$ Hz, 1H), 4.23 (1/2 AB, $J = 14.2$ Hz, 1H), 4.03 (1/2 AB, $J = 15.0$ Hz, 1H), 3.98 (s, 1H), 3.62 (s, 3H), 3.39 (1/2 AB, $J = 14.3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ : 195.2, 170.9, 170.2, 170.1, 140.6, 135.7, 135.5, 131.1, 128.6, 128.5, 127.3, 126.2, 118.0, 70.8, 52.3, 51.5, 50.9, 37.7; IR (thin film) ν 3027, 1741, 1710, 1641, 1383 cm^{-1} ; MS m/z (%) 387 (15), 328 (10), 282 (22), 105 (100); EI-HRMS calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_4$ m/z [M^+] 387.1471 found 387.1470.

$R_f = 0.2$ (TLC, hexanes-EtOAc, 3 : 1 v/v) [6,5] (79 mg, 17%).

^1H NMR (300 MHz, CDCl_3) δ : 7.49-7.41 (m, 3H), 7.34-7.27 (m, 5H), 7.21-7.17 (m, 2H), 5.90 (s, 1H), 5.70 (s, 1H), 4.39 (1/2 AB, $J = 18.1$ Hz, 1H), 4.15 (1/2 AB, $J = 13.8$ Hz, 1H), 3.81 (s, 3H), 3.38 (1/2 AB, $J = 13.8$ Hz, 1H), 3.05 (s, 2H), 3.01 (1/2 AB, $J = 18.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ : 202.9, 171.3, 171.1, 161.1, 135.8, 135.4, 135.2, 130.3, 129.9, 128.7, 128.3, 127.4, 127.2, 126.3, 123.5, 65.9, 53.0, 45.1, 39.6, 37.7; IR (thin film) ν 2950, 1740, 1710, 1643, 1391 cm^{-1} ; MS m/z (%) 387 (47), 356 (15), 328 (12), 296 (30), 105 (100); EI-HRMS calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_4$ m/z [M^+] 387.1471 found 387.1489.

2-Benzoyl-1,4-dimethyl-6-methylene-5-oxo-1,2,3,5,6,6a-hexahydrocyclopenta[c]pyrrole-1-carboxylic acid methyl ester (9, Table 4, Entry l). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(Benzoylbut-2-ynylamino)-2-methylpenta-3,4-dienoic acid methyl ester (50 mg, 0.17 mmol), DMSO (120 μ L, 1.68 mmol), Mo(CO)₆ (55 mg, 0.21 mmol). Heated to 80 °C for 2 hours. After the initial filtration the crude mixture (53 mg, >95%) was purified by flash chromatography (gradient elution, hexanes-EtOAc, 9 : 1 to 2 : 1, v/v) to afford the major isomer (41 mg, 74 %).

Product ratios determined by ¹H NMR after the initial filtration: [5,5] : [6,5] = 14 : 1; Diastereomer ratio of [5,5] product : 10 : 1.

R_f = 0.23 (TLC, hexanes-EtOAc, 2 : 1, v/v) ¹H NMR (300 MHz, CDCl₃) δ : 7.54-7.44 (m, 5H), 6.26 (d, *J* = 1.9 Hz, 1H), 5.44 (s, 1H), 4.58 (1/2 AB, *J* = 15.7 Hz, 1H), 4.22 (1/2 AB, *J* = 15.7 Hz, 1H), 4.02 (s, 1H), 3.88 (s, 3H), 1.82 (s, 3H), 1.31 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ : 195.7, 172.6, 169.3, 162.4, 139.6, 136.0, 136.0, 130.2, 128.6, 126.5, 119.2, 66.5, 53.3, 52.9, 47.8, 14.6, 9.0; IR (thin film) ν 2950, 1740, 1707, 1689, 1642, 1404 cm⁻¹; MS *m/z* (%) 325 (30), 266 (28), 220 (15), 105 (100); EI-HRMS calcd for C₁₉H₁₉NO₄ *m/z* [M⁺] 325.1314; found 325.1305.

2-Benzoyl-1-methyl-6-methylene-5-oxo-1,2,3,5,6,6a-hexahydrocyclopenta[c]pyrrole-1-carboxylic acid methyl ester (9, Table 4, Entry m). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(Benzoylprop-2-ynylamino)-2-methylpenta-3,4-dienoic acid methyl ester (72 mg, 0.25 mmol), DMSO (180 μ L, 2.54 mmol), Mo(CO)₆ (84 mg, 0.32 mmol). Heated to 80 °C for 2 hours. After the initial filtration the crude mixture (80 mg, >95%) was purified by flash

chromatography (gradient elution, hexanes-EtOAc, 7 : 1 to 2 : 1, v/v) to afford the major isomer (49 mg, 62%).

Product ratios determined by ^1H NMR after the initial filtration: [5,5] : [6,5] = 14 : 1; Diastereomer ratio of [5,5] product : 11 : 1.

R_f = 0.15 (TLC, hexanes-EtOAc, 2 : 1, v/v) ^1H NMR (300 MHz, CDCl_3) δ : 7.51-7.41 (m, 5H), 6.26-6.25 (m, 2H), 5.46 (s, 1H), 4.66 (1/2 AB, J = 16.0 Hz, 1H), 4.29 (1/2 AB, J = 16.0 Hz, 1H), 4.13 (s, 1H), 3.88 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 195.6, 172.8, 170.4, 169.6, 140.2, 136.2, 130.6, 129.0, 127.9, 126.8, 120.0, 66.8, 55.4, 53.3, 49.2, 17.3, 15.0; IR (thin film) ν 2950, 1739, 1709, 1638, 1402 cm^{-1} ; MS m/z (%) 311 (18), 252 (22), 206 (9), 105 (100); EI-HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4$ m/z [M^+] 311.1158; found 311.1151.

6-Ethylidene-1,4-dimethyl-5-oxo-3,5,6,6a-tetrahydro-1H-cyclopenta[c]pyrrole-1,2-dicarboxylic acid 2-*tert*-butyl ester 1-methyl ester (9, Table 4, Entry n). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(*tert*-Butoxycarbonyl-but-2-ynylamino)-2-methylhexa-3,4-dienoic acid methyl ester (45 mg, 0.15 mmol), DMSO (106 μL , 1.49 mmol), $\text{Mo}(\text{CO})_6$ (49 mg, 0.19 mmol). Heated to 85 $^\circ\text{C}$ for 2.5 hours. After the initial filtration the crude mixture (45 mg, >90%) was purified by flash chromatography (gradient elution, hexanes-EtOAc, 9 : 1 to 4 : 1, v/v) to afford partial separation of the major from the minor isomer Z / E = 5 : 1 (NMR).

(**Z**) : R_f = 0.5 (TLC, hexanes-EtOAc, 4 : 1, v/v) ^1H NMR (300 MHz, $\text{DMSO}-d_6$ 353K) δ 5.99-5.91 (m, 1H), 4.31 (1/2 AB, J = 16.7 Hz, 1H), 4.23 (1/2 AB, J = 16.1 Hz, 1H), 3.84 (br s, 1H), 3.75 (s, 3H), 2.18 (d, J = 6.8 Hz, 3H), 1.75 (s, 3H), 1.39 (s, 9H), 1.04 (s, 3H); IR (thin film) ν 2977, 1744, 1696, 1647, 1390 cm^{-1} ; MS m/z (%) 335 (19), 279 (10), 235 (60), 220 (38), 57 (100) ; EI-HRMS calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_5$ m/z [M^+] 335.1733; found 335.1748.

N-Benzamide protected alkynyl allenes **6** (Table 1, Entry f, g and o) reacted in the Mo(CO)_6 mediated P-K reaction to afford products as complex mixture of diastereomers and Z / E isomers. Due to difficulties in purification no spectral data is available. The yields of crude mixtures are reported.

2-Benzoyl-1-benzyl-6-ethylidene-4-methyl-5-oxo-1,2,3,5,6,6a-hexahydro-cyclopenta[c]pyrrole-1-carboxylic acid methyl ester (9, Table 4, Entry f). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(Benzoylprop-2-ynylamino)-2-benzylhexa-3,4-dienoic acid methyl ester (42 mg, 0.11 mmol), DMSO (75 μL , 1.1 mmol), Mo(CO)_6 (37 mg, 0.14 mmol). Heated at 75 $^{\circ}\text{C}$ for 4 h. Weight of mixture after flash chromatography (26 mg, 57%). The starting material was recovered in 25%.

2-Benzoyl-1-benzyl-6-ethylidene-4-methyl-5-oxo-1,2,3,5,6,6a-hexahydro-cyclopenta[c]pyrrole-1-carboxylic acid methyl ester (9, Table 4, Entry g). Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38):

2-(benzoyl-but-2-ynyl-amino)-2-benzylhexa-3,4-dienoic acid methyl ester (36 mg, 0.093 mmol), DMSO (62 μL , 0.93 mmol), Mo(CO)_6 (31 mg, 0.12 mmol). Heated to 80 $^{\circ}\text{C}$ for 1 h. The reaction mixture was then cooled to room temperature, and applied to a silica gel column. Elution (hexanes-EtOAc, 2 : 1, v/v) afforded a mixture of compounds (29 mg, 77%).

9, Table 4, Entry o

2-Benzoyl-1-(*tert*-butyldimethylsilyloxymethyl)-6-ethylidene-4-methyl-5-oxo-1,2,3,5,6,6a-hexahydro-cyclopenta[c]pyrrole-1-carboxylic acid methyl ester (9**, Table 4, Entry o).** Followed general procedure for the molybdenum mediated allenic Pauson-Khand reaction for the formation of [5,5] P-K products (page s38): 2-(Benzoylbut-2-ynylamino)-2-(*tert*-butyldimethylsilyloxymethyl)-hexa-3,4-dienoic acid methyl ester (44 mg, 0.10 mmol), DMSO (70 μ L, 1.0 mmol), Mo(CO)₆ (33 mg, 0.12 mmol). Heated to 85 °C for 1 h. Weight of mixture after flash chromatography (50 mg, >95%).