Angewandte Chemie

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z50890

69451 Weinheim, Germany

Vanadium-Catalyzed Anti -SelectiveAdditions of Allenols to Imines

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Experimental section:

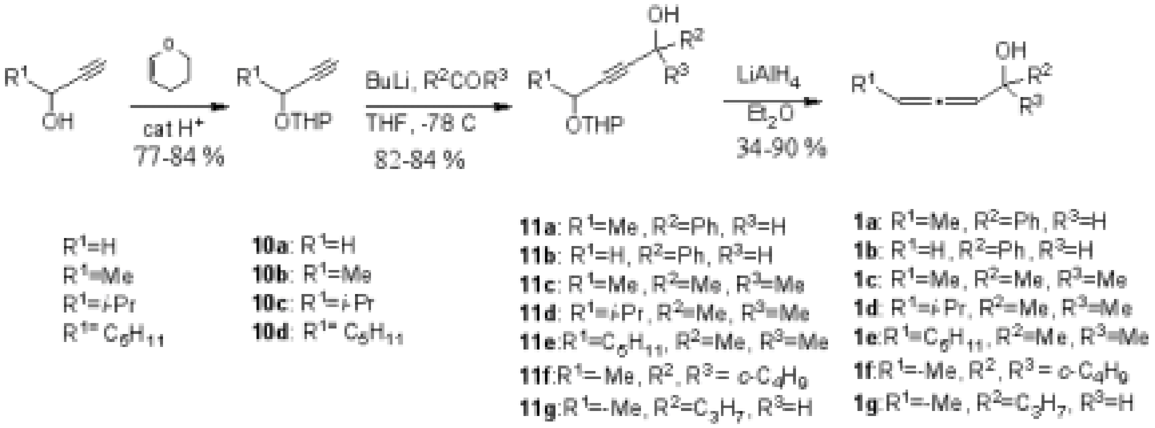
^1H NMR (300 or 500 MHz) and ^{13}C NMR (75 or 125 MHz) spectra were recorded on a Varian GEM-300 or on an Inova 500 spectrometer using the residual peak of $CHCl_3$ in $CDCl_3$ (7.26 ppm for ^1H and 77.0 ppm for ^{13}C) as the internal standard. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q; quartet; m, multiplet; br, broad peak. IR Spectra were obtained using a Perkin-Elmer 500 FT-IR instrument and the samples were examined as thin films or $CDCl_3$ solutions, (cm^{-1}). EM Science silica gel 60 (230-400 mesh) was used for flash chromatography and analytical thin-layer chromatography was performed on Merck precoated silica gel 60-F_{254} plates. Melting points (mp) were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. High-resolution mass spectroscopy were provided by the NIH Mass Spectroscopy Regional Centre of at UC- San Francesco on a Kratos MS9 instrument, Elemental analysis was performed by M-H-W laboratories of Phoenix, AZ. Gas chromatography were performed on a Hewlett-Packard 6890 Series gas chromatography using reported conditions. Analytical and preparative HPLC were performed on a Varian Prostar using silica Microsorb columns. Ethyl acetate and hexane was used as the eluent at 1ml//min for the analytical column and 10 ml/min for the preparative column. X-ray diffraction analysis were performed on a Bruker-Siemens SMART CCD area detector with graphite monochromated Mo-Kα radiation.

Tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl prior to use. Diethyl ether, and toluene were dried by pressing them through a column of activated alumina under argon. Dichlorometane (CH_2Cl_2) was distilled from calcium hydride. Petroleum ether refers to that fraction boiling in the range 35 – 60 °C. All reactions were run under an atmosphere of argon in flame-dried glassware. Anhydrous solvents were transferred by an oven-dried syringe or cannula. Unless otherwise noted, all material were obtained from commercial suppliers and used without further purification

Imines **2a**-**2c** were prepared from benzaldehyde and the corresponding amine according to literature procedures.[1] The *N*-moc imines **2e**-**2m** were prepared by acylation of the corresponding *N*-silylimines **12e-12m** in the presence of methyl chloroformate[2] (Scheme2).

Preparation of starting material:

The allenic alcohols **1a** to **1g** were prepared according to the procedure shown in Scheme 1.[3] The starting propargylic alcohols are commercially available. The propargylic alcohols were treated with dihydropyran to form the THP protected alcohols **10a-d**. The derivatives **11a-11g** were prepared by the reaction of the lithium acetylide of **10a-d** generated by treatment with butyllithium, with an appropriate aldehyde or ketone. Reaction of **11a-g** with $LiAlH_4$ gives the allenic alcohols in good yields.



Scheme 1

Preparation of tetrahydropyranyl ethers of propargylic alcohols (10a-d). All preparations were carried out according to the procedure by Landor[4]. The preparation of **1-methyl-2-propynyl tetrahydro-2*H*-2-pyranyl ether** (**10b**)[5] is representative.

To a mixture of 3-butyn-2-ol (30 g, 0.43 mol) and dihydropyran (39.2 g 0.47 mol) was added a few drops of concentrated hydrochloric acid, and the mixture was allowed to stir for 1.5 h. The mixture was then dried (K_2CO_3-$MgSO_4$), filtered and distilled to give the product **10b** in 84 % yield (55.6 g). Bp 98-101 ºC (20 mm Hg). The NMR spectra were complicated due to the presence of diastereomers. ^{1}H NMR[5] (300 MHz, $CDCl_3$): δ 4.92

(dd, *J* = 4.4, 2.9 Hz, 0.5 H), 4.75 (t, *J* = 3.2 Hz, 0.5 H), 4.53 (dq, *J* = 6.7, 2.0 Hz, 0.5 H), 4.44 (dq, *J* = 6.7, 2.0 Hz, 0.5 H), 3.97 (m, 0.5 H), 3.80 (m, 0.5 H), 3.51 (m, 1H), 2.41 (d, *J* = 2.0 Hz, 0.5 H), 2.36 (d, *J* = 2.0 Hz, 0.5 H), 1.89-1.62 (m, 2 H), 1.60-1.46 (m, 4 H), 1.46 (d, *J* = 6.7 Hz, 1.5 H), 1.42 (d, *J* = 6.7 Hz, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (97.1, 95.7), (84.6, 83.6), (72.4, 71.8), (62.4, 62.2), (62.1, 60.5), (30.46, 30.43), (25.37, 25.30), (21.9, 21.8), (19.4, 19.0); IR (neat): 3292, 2943, 2871, 2110, 1453, 1442, 1372, 1334, 1202, 1184, 1123, 1094, 1076, 1023, 984. cm^{-1}.

2-propynyl tetrahydro-2*H*-2-pyranyl ether (10a) was prepared from 2-propyn-1-ol according to the general procedure in 92% yield. Bp 78-80 ºC (20 mm Hg). NMR data were in accordance with previously reported data.[6]

1-isopropyl-2-propynyl tetrahydro-2*H*-2-pyranyl ether (10c) was prepared from 4-methyl-1-pentyn-3-ol according to the general procedure in 77% yield. Bp 55-58º C (1 mm Hg). The NMR spectra looked complicated due to the presence of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.98 (t, *J* = 3.3 Hz, 0.5 H), 4.70 (t, *J* = 3.4 Hz, 0.5 H), 4.18 (dd, *J* = 6.1, 2.0 Hz, 0.5 H), 4.06 (dd, *J* = 5.8, 2.0 Hz, 0.5 H), 4.02 (m, 0.5 H), 3.78 (m, 0.5 H), 3.52 (m, 1 H), 2.41 (d, *J* = 2.0 Hz, 0.5 H), 2.36 (d, *J* = 2.0 Hz, 0.5 H), 1.94 (m, 1H), 1.52-1.83 (m, 6 H), 1.04 (d, *J* = 6.8 Hz, 1.5 H), 1.02 (d, *J* = 6.7 Hz, 1.5 H), 1.00 (d, *J* = 6.8 Hz, 1.5 H), 0.98 (d, *J* = 6.7 Hz, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (98.8, 95.2), (82.5, 81.6), (73.8, 73.1), (72.6, 70.0), (62.2, 62.1), (32.9, 32.6), (30.38, 30.31), (25.4, 25.3), (19.2, 19.0), (18.5, 18.2), (17.9, 17.3); IR (neat): 3292, 2943, 2871, 2110, 1453, 1442, 1372, 1334, 1202, 1184, 1123, 1094, 1076, 1023, 984. cm^{-1}; Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95; Found: C, 72.38; H, 10.16.

1-pentyl-2-propynyl tetrahydro-2*H*-2-pyranyl ether (**10d**) was prepared from 1-octyn-3-ol according to Hickman *et al*.[7]

General Procedure[8] for the 4-(Tetrahydropyranyloxy)-butyn-1-ol Derivatives (11a-g). To a solution of the appropriate 3-(tetrahydro-2-pyranyloxy)-1-propyne derivative **10a-d** (38 mmol) in dry THF (38 mL) at –78 ºC was added BuLi (1.6 M in hexane 42.2 mmol) and the reaction mixture was stirred for 2h at the same temperature. An appropriate aldehyde or ketone (43.6 mmol) was added at – 78 ºC and the mixture was stirred at the same temperature for 2h. After allowing the solution to warm to room temperature, sat NH_4Cl (15 mL) was added and the mixture was extracted with ether (3 x 25 mL). The combined extracts were dried ($MgSO_4$), filtered and distilled to afford 4-(tetrahydropyranyloxy)-butyn-1-ol derivatives (**11a-g**).

1-phenyl-4-(tetrahydro-2*H*-2-pyranyloxy)-2-butyn-1-ol (11b).

Prepared from 3-(tetrahydro-2-pyranyloxy)-1-propyne derivative **10a** and benzaldehyde which after purification by flash chromatography (ether/petroleum ether 1:4) gave **11a** in 80 % yield. The NMR data were in accordance with previously reported values.[8]

1-phenyl-4-(tetrahydro-2*H*-2-pyranyloxy)-2-pentyn-1-ol (11a).

Prepared from 3-(tetrahydro-2-pyranyloxy)-1-propyne derivative **10b** and benzaldehyde which after purification by flash chromatography (ether/petroleum ether 1:5 gave **11a** in 84 % yield. The NMR spectra looked complicated due to the presence of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (m, 2 H), 7.41-7.28 (m, 3 H), 5.49 (m, 1 H), 4.95 (dd, *J* = 4.2, 2.8 Hz, 0.5 H), 4.78 (t, *J* = 3.3 Hz, 0.5 H), 4.64 (dq, *J* = 6.6, 1.5 Hz, 0.5 H), 4.52 (dq, *J* = 6.6, 1.5 Hz, 0.5 H), 3.96 (m, 0.5 H), 3.80 (m, 0.5 H), 3.49 (m, 1 H), 2.39 (br s, OH), 1.92-1.66 (m, 2 H), 1.65-1.45 (m, 4 H), 1.49 (dd, *J* = 6.6, 1.0 Hz, 1.5 H), 1.46 (dd, *J* = 6.6, 1.0 Hz, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (140.6, 140.5), (128.5, 128.4), (128.3, 128.2), (126.65, 126.62), (97.4, 95.8), (87.4, 86.4), (84.4, 83.6), (64.4, 64.9), (62.4, 62.1), 60.8, (30.5, 30.4), (25.34, 25.29), (21.9, 21.8), (19.3, 19.0); IR (neat): 3396, 3062, 2943, 2870, 2360, 1493, 1453, 1379, 1333, 1201, 1186, 1156, 1069, 994 cm^{-1}; Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74; Found: C, 73.76; H, 7.51.

2-methyl-5-(tetrahydro-2*H*-2-pyranyloxy)-3-hexyn-2-ol (11c).

Prepared from 3-(tetrahydro-2-pyranyloxy)-1-propyne derivative **10c** and acetone which after purification by flash chromatography (ether/petroleum ether 1:4) gave **11c** in 83 % yield. The NMR spectra looked complicated due to the presence of diastereomers.[9] ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.91 (dd, *J* = 4.1, 2.9 Hz, 0.5 H), 4.78 (t, *J* = 3.2 Hz, 0.5 H), 4.55 (dq, *J* = 6.7 Hz, 0.5 H) 4.46 (q, *J* = 6.7 Hz, 0.5 H), 3.98 (m, 0.5 H), 3.80 (m, 0.5 H), 3.52 (m, 1 H), 2.00 (br s, OH), 1.88-1.66 (m, 2 H), 1.65-1.45 (m, 4 H), 1.51 (s, 6 H), 1.44 (d, *J* = 6.7 Hz, 1.5 H), 1.41 (d, *J* = 6.7 Hz, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (100.2, 95.6), (97.1, 95.3), (89.6, 88.7), (82.5, 81.2), (64.77, 64.75), (62.9, 62.1), (61.8, 60.5), (31.35, 31.29), (30.5, 30.3), 25.3, 22.0, (19.1, 18.8); IR (neat): 3420, 2982, 2940, 2870, 2212, 1454, 1442, 1371, 1335, 1233, 1202, 1166, 1127, 1036, 993, 969. cm^{-1}.

2,6-dimethyl-5-(tetrahydro-2*H*-2-pyranyloxy)-3-heptyn-2-ol (11d)

Prepared from 3-(tetrahydro-2-pyranyloxy)-1-propyne derivative **10c** and benzaldehyde which after bulb to bulb distillation (1mm Hg) oven temperature: 160-180 ºC gave **11d** in 82 % yield. The NMR spectra looked complicated due to the presence of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.97 (t, *J* = 3.4 Hz, 0.5 H), 4.73 (t, *J* = 3.4 Hz, 0.5 H), 4.18 (d, *J* = 6.4 Hz, 0.5 H) 4.04 (d, *J* = 5.9 Hz, 0.5 H), 4.03 (m, 0.5 H), 3.78 (ddd, *J* = 11.2, 9.0, 3.2 Hz, 0.5 H), 3.53 (m, 1 H), 2.15 (br s, OH), 1.91 (m, 1 H), 1.85-1.53(m, 6 H), 1.51 (s, 6 H), 1.03 (d, *J* = 6.7 Hz, 1.5 H), 1.02 (d, *J* = 6.7 Hz, 1.5 H), 0.97 (d, *J* = 6.7 Hz, 1.5 H), 0.95 (d, *J* = 6.7 Hz, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (98.6, 95.0), (90.84, 90.89), (80.8, 79.6), (72.9, 70.0), 65.1, 61.9, (33.1, 32.8), (31.51, 31.49), (31.42, 31.41), (30.40, 30.35), (25.49, 25.44), (19.1, 18.9), (18.7, 18.4), (18.1, 17.6); IR (neat): 3415, 2872, 2360, 1469, 1455, 1367, 1233, 1202, 1168, 1020 cm^{-1}; Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06; Found: C, 69.96; H.9.88.

2-methyl-5-(tetrahydro-2*H*-2-pyranyloxy)-3-decyn-2-ol (11e)

Prepared from 1-pentyl-2-propynyl tetrahydro-2*H*-2-pyranyl ether **10d** and acetone which after purification by flash chromatography (ether/petroleum ether 1:4 → 3:2) gave **11e** in 62 % yield**.** The NMR spectra looked complicated due to the presence of diastereomers. Major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$): 4.94 (t, *J* = 3.2 Hz, 1 H), 4.40 (t, *J* = 6.9 Hz, 1 H), 3.78 (m, 1 H), 3.52 (m, 1 H), 1.87 (br s, 1 H), 1.77-1.44 (m, 13 H), 1.50 (s, 3 H), 1.31 (m, 4 H), 0.89 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 98.1, 95.2, 80.9, 65.1, 64.7, 62.1, 35.6, 31.5, 31.4 (2C), 30.4, 25.4, 25.1, 22.5, 19.2, 14.0; IR (neat): 3406, 2940, 2871, 1455, 1442, 1374, 1361, 1260, 1235, 1167, 1076 cm^{-1}; HRMS Calcd for $C_{16}H_{28}O_3$: 268.2038; Found: Submitted

1-[3-(tetrahydro-2*H*-2-pyranyloxy)-1-butynyl]-1-cyclopentanol (11f)

Prepared from 1-methyl-2-propynyl tetrahydro-2*H*-2-pyranyl ether (**10b**) and cyclopentanon which after purification by flash chromatography (ether/petroleum ether 1:10 → 1:3) gave **11f** in 75 % yield**.** The NMR spectra looked complicated due to the presence of diastereomers. Major diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.91 (dd, *J* = 3.6, 3.2 Hz, 1 H), 4.55 (q, *J* = 6.7 Hz, 1 H), 3.80 (m, 1 H), 3.51 (m, 1 H), 2.20 (br s, 1 H), 1.92-1.70 (m, 10 H), 1.52-1.60 (m, 4 H), 1.34 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 95.6, 88.5, 82.5, 74.3, 62.3, 60.7, 42.5, 42.4, 30.4, 25.4, 23.9 (2C), 22.1, 19.3; IR (neat): 3423, 2943, 2872, 1441, 1370, 1335, 1260, 1218, 1202, 1185, 1117, 1077.1035 cm^{-1}; Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30; Found: C, 70.43; H, 9.50.

7-(tetrahydro-2*H*-2-pyranyloxy)-5-octyn-4-ol (37) (11g).

Prepared from 3-(tetrahydro-2-pyranyloxy)-1-propyne derivative **10b** and butyraldehyde which after purification by flash chromatography (ether/petroleum ether 1:3) gave **11g** in 56 % yield The NMR spectra looked complicated due to the presence of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): 4.92 (dt, *J* = 4.1, 3.4 Hz, 0.5 H), 4.76 (t, *J* = 3.3 Hz, 0.5 H), 4.56 (dq, *J* = 6.6, 1.7 Hz, 0.5 H), 4.43 (dq, *J* = 6.6, 1.7 Hz, 0.5 H), 4.40 (t, *J* = 6.6 Hz, 1 H), 3.97 (m, 0.5 H), 3.81 (m, 0.5 H), 3.52 (m, 1 H), 1.86 (br s, OH), 1.84-1.47 (m, 10 H), 1.45 (d, *J* = 6.6 Hz, 1.5 H), 1.41 (d, *J* = 6.6 Hz, 1.5 H), 0.93 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (97.2, 95.6), (85.8, 85.4), (85.0, 84.2), (62.6, 62.4), (62.14, 60.67), 60.0, (39.77, 39.70), (30.51, 30.42), (25.35, 25.32) (22.07, 21.89), (19.37, 19.04), 18.4, 13.7; IR (neat): 3421, 2939, 2873, 1454, 1379, 1334, 1202, 1164, 1074 cm^{-1}. Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80; Found: C, 68.79; H, 9.68.

General Procedure for the preparation of 2,3-Butadienyl Alcohols 1a-g.[4] To a slurry of $LiAlH_4$ (1.12 g, 29.5 mmol) in dry diethylether (45 ml) at 0 ºC was added the appropriate derivative of 4-(tetrahydro-2-pyranyloxy)-2-butyn-1-ols **11a-g** (27 mmol) dissolved in dry ether (15 mL) over a period of 45 minutes. The mixture was refluxed for 4h and the excess $LiAlH_4$ was decomposed by adding aqueous THF dropwise until the gray slurry turned white. Water was then added and the phases were separated. The aqueous phase was extracted with ether (3x 50 mL) and the combined organic fractions were dried ($MgSO_4$) and filtered. After evaporation of the solvent the residue was purified by distillation or flash chromatography.

1-phenyl-2,3-pentadien-1-ol[10] (1a)

Purified by flash chromatography (EtOAc/petroleum ether, gradient 1:9→1:6), 90% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.43-7.28 (m, 5 H), 5.36 (m, 2 H), 5.22 (m, 1 H), 2.16 (br s, OH), 1.73 (dd, J = 6.7, 3.4 Hz, 1.5 H), 1.70 (dd, J = 6.7, 3.4 Hz, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.9, 143.0, 128.4, 127.7, 126.1, 95.5, (89.78, 89.68), (72.19, 72.11), (14.24, 14.37); IR (neat): 3362, 3062, 3029, 2926, 2859, 1968, 1492, 1452, 1407, 1371, 1278, 1194, 1073, 1030, 970. cm^{-1}; HRMS Calcd for $C_{11}H_{12}O$: 160.0888. Found: 160.0882.

1-Phenyl-2,3-butadienol (1b)

Purified by flash chromatography (Et_2O/petroleum ether, gradient 1:6→1:2), 75% yield. The NMR data were in accordance with previously reported data.[11]

2-methyl-3,4-hexadien-2-ol. (1c).

Purified by flash chromatography (Et_2O/Petroleumether 1:3), 34% yield[12]. The NMR data were in accordance with previously reported data[13]

2,6-dimethyl-3,4-heptadien-2-ol (1d).

Purified by distillation Bp 75 ºC (18 mmHg), 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.35 (m, 2 H), 2.31 (m, 1 H), 1.67 (br s, OH) 1.33 (s, 6 H), 1.02 (d, *J* = 6.7 Hz, 3 H), 1.01 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.7, 102.44, 102.41, 69.5, 30.0, 29.9, 27.9, 22.4, 22.3; IR (neat): 3361, 2965, 2290, 1960, 1464, 1363, 1299, 1237, 1150, 1069, 970. cm^{-1}.

2-methyl-3,4-decadien-2-ol (1e)

Purified by flash chromatography (Et_2O/petroleum ether, gradient 1:4→1:3) 79% yield ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.31 (m, 2 H), 2.00 (m, 2 H), 1.68 (br s, OH) 1.40 (m, 2 H), 1.33 (s, 6 H), 1.32-1.27 (m, 4 H), 0.88 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.2, 101.2, 95.1, 69.6, 31.3, 29.98, 29.94, 28.78, 28.76, 22.4, 13.9; IR (neat): 3363, 2962, 2857, 1961, 1463, 1408, 1375, 1217, 1149, 970. cm^{-1}; Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98;. Found: C, 78.36; H, 11.78.

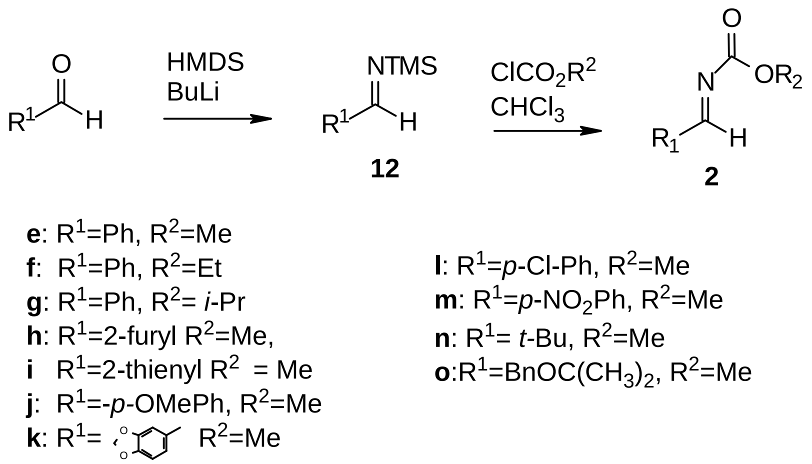
1-(1,2-butadienyl)-1-cyclopentanol (1f)

Purified by flash chromatography (Et_2O/petroleum ether, gradient (1:4→1:3); 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$):) ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.32 (dq, *J* = 6.3, 3.4 Hz, 1 H), 5.29 (dq, *J* = 6.8, 3.4 Hz, 1 H), 1.82-1.79 (m, 4 H), 1.77-1.61 (m, 4 H), 1.67 (dd, *J* = 6.8, 3.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.4, 98.8, 89.4, 80.0, 40.35, 40.32, 23.6, 23.5, 14.5; IR (neat): 3374, 2961, 2872, 1964, 1439, 1403, 1370, 1319, 1189, 1075, 994. cm^{-1}; HRMS Calcd for $C_9H_{14}O$: 138.1044, Found: 138.1041.

5,6-octadien-4-ol. (1g).

Purified by flash chromatography (Et_2O/petroleum ether, 1:3), 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.22 (m, 1 H), 5.16 (m, 1 H), 4.11 (m, 1 H), 1.78 (br s, OH, 1.69 (app dt *J* = 7.1, 3.2 Hz, 3 H), 1.51 (m, 2 H), 1.42 (m, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.8, (95.07, 95.00), (88.6, 88.4), (69.9, 69.6), (39.5, 39.48), 18.6, 14.3, 13.8; IR (neat): 3355, 2950, 2873, 1967, 1458, 1372, 1320, 1117, 1068, 1003. cm^{-1}; HRMS Calcd for $C_8H_{14}O$: 126.1044. Found: 126.1040.

Preparation of imines



e: R^1=Ph, R^2=Me
f: R^1=Ph, R^2=Et
g: R^1=Ph, R^2= *i*-Pr
h: R^1=2-furyl R^2=Me,
i R^1=2-thienyl R^2 = Me
j: R^1=-*p*-OMePh, R^2=Me
k: R^1= R^2=Me
l: R^1=*p*-Cl-Ph, R^2=Me
m: R^1=*p*-NO_2Ph, R^2=Me
n: R^1= *t*-Bu, R^2=Me
o:R^1=BnOC(CH_3)$_2$, R^2=Me

Scheme 2

N-[(*E*)-1-phenylmethylidene]-*N*-(1,1,1-trimethylsilyl)amine (12e)

Following the method of Hart et al[14] benzaldehyde (5.92g, 0.061 mmol) afforded **12e** (7.22 g, 73%); yellow oil, bp. 85° C/ 0.35 Torr). ^{1}HNMR was in accordance with previously reported data.[15]

Methyl *N*-[-1-phenylmethylidene]carbamate (2e)

Following the method of Vidal et al[15] silylimine **12e** (4.88g, 27.4 mmol) afforded **2e**(2.99 g, 67%); clear oil, b.p 100° C/ 0.7 Torr). ^{1}H and ^{13}CNMR was in accordance with previously reported data.[15]

Ethyl *N*-[-1-phenylmethylidene]carbamate (2f)

Ethylchloroformate (1.76g, 16.2 mmol) was added drop wise to a solution of silylimine **12e** (2.90 g, 16.2 mmol) in dry chloroform (25 mL) under nitrogen. The reaction mixture was refluxed for 1h until the yellow color had disappeared. After evaporation of the solvent (distillation under nitrogen) the crude product was distilled (B.p. 110 °C /1 Torr) to give **2f** in 52% yield (1.23 g) **.** The ^{1}H and ^{13}C NMR data were in accordance with previously reported data. [16]

Isopropyl *N*-[-1-phenylmethylidene]carbamate. (2g)

Isopropylchloroformate (1M solution in toluene) (16.8 mmol, 16.8 mL) was added dropwise to a solution of silylimine **12e** (3g, 16.8 mmol) in dry chloroform (25 mL) under nitrogen. The reaction mixture was refluxed for 1h until the yellow color had disappeared. After evaporation of the solvent (distillation under nitrogen) the crude product was distilled (B.p. 94-97 °C /0.25 Torr) to give **2f** in 62 % yield.^{1}H NMR (200 MHz, $CDCl_3$): δ 8.93 (s,1 H), 7.92 (m, 2 H), 7.56 (m, 1 H), 7.47 (m, 2 H), 5.10 (septet, J = 6.3 Hz, 1 H), 1.38 (d, J = 6.3 Hz, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9, 163.4, 133.9, 133.8, 130.4, 128.9, 70.9, 21.7 (2C); IR (neat): 3064, 2982, 1715, 1639, 1580, 1453, 1374, 1258, 1210, 1105, 995, 913, 791, 754 cm^{-1}; HRMS Calcd for M$^+$: $C_{11}H_{14}NO_2$: 192.1024. Found: 192.1018.

N-[-1-(2-furyl)methylidene]-*N*-(1,1,1-trimethylsilyl)amine (12h)

Following the method of Hart et al[14] 2-furaldehyde (2.68g, 0.028 mol) afforded **12h** (1.92 g, 41 %); Yellow liquid. Bp 55 °C/0.3 Torr. The. NMR data were in accordance with previously reported data .[17]

Methyl *N*-[(*E*)-1-(2-furyl)methylidene]carbamate (2h)

Following the method of Vidal et al[15] silylimine **12h** (1.92g, 0.011 mol) afforded **2h** (1.43 g, 81 %) after 3h at room temperature and recrystallization from THF/hexane.. Mp 42-44 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 (s,1 H), 7.69 (s, 1 H), 7.25 (m, 1 H), 6.59 (m, 1 H), 3.86 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.0, 158.7, 150.5, 148.5, 112.1, 113.1, 53.9; IR ($CDCl_3$): 3151, 3002, 2846, 1718, 1626, 1556, 1502, 1470, 1437, 1397, 1346, 1239, 1152, 1082 cm^{-1}; Anal. Calcd. for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.74; H, 4.80; N, 9.12.

N-[(*E*)-1-(2-thienyl)methylidene]-*N*-(1,1,1-trimethylsilyl)amine (12i)

Following the method of Hart et al [14] 2-thiophenecarboxaldehyde (5g, 0.044 mol) afforded **12i** (5.63 g, 69%); Yellow liquid. Bp 86 °C/0.02 Torr ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.97 (s,1 H), 7.43 (dq, *J* = 4.9, 1.2 Hz, 1 H), 7.41 (dt, *J* = 3.6, 1.2 Hz, 1 H), 7.10 (ddd, *J* = 4.9, 3.6, 1.2 Hz, 1 H), 0.23 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.6, 147.4, 131.3, 129.8, 127.6, -1.09.

Methyl *N*-[(*E*)-1-(2-thienyl)methylidene]carbamate (2i)

Following the method of Vidal et al[15] silylimine **12i** (5.63g, 0.031 mol) afforded **2i** (4.14 g, 80 %) after 3h reflux and recrystallization from THF/hexane. Yellow crystals. Mp 85-87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.12 (s,1H), 7.67 (m, 2 H), 7.16 (dd, *J* = 4.9, 3.8 Hz, 1 H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 163.8, 139.9, 137.7, 134.8, 128.5, 53.8; IR ($CDCl_3$): 2953, 1714, 1604, 1519, 1438, 1422, 1374, 1318, 1269, 1235, 1215, 1083 cm^{-1}; Anal. Calcd. for $C_7H_7NO_2S$: C, 49.69; H, 4.17; N, 8.28. Found: C, 49.49; H, 4.31; N, 8.35.

N-[-1-(4-methoxyphenyl)methylidene]-*N*-(1,1,1-trimethylsilyl)amine (12j)

Following the method of Hart et al[14] anisaldehyde (3.80g, 0.028 mol) afforded **12j** (4.69 g, 81%); yellow oil, b.p 95-96° C/ 0.3 Torr). ^{1}HNMR was in accordance with previously reported data.[18]

Methyl *N*-[-1-(4-methoxyphenyl)methylidene]carbamate. (2j)

Following the method of Vidal et al[15] silylimine **12j** (4.12g, 0.019 mmol) afforded **2j** (1.36 g, 35 %) after 1h reflux and recrystallization from THF/hexane. White crystals. Mp 43-46 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.95 (s,1 H), 7.89 (d, *J* = 9,0 Hz, 2 H), 6.97 (d, *J* = 9.0 Hz, 2 H), 3.90 (s, 3 H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0, 164.4, 164.3, 132.5, 126.5, 114.2, 55.3, 53.6; IR ($CDCl_3$): 3433, 3007, 2956, 1716, 1601, 1572, 1513, 1463, 1304, 1253, 1217, 1013 cm^{-1}; HRMS Calcd for $C_{10}H_{11}NO_3$: 193.0739. Found: 193.0741.

***N*-[(*E*)-1-(1,3-benzodioxol-5-yl)methylidene]-*N*-(1,1,1-trimethylsilyl)amine (12k).**

Following the method of Vidal et al[15] piperonal (5.0 g, 0.033 mol) afforded **12k** (3.82 g, 52%); yellow solid, bulb to bulb distillation (150 °C oven temperature / 0.3 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.84 (s,1 H), 7.41 (d, *J* = 1.5 Hz, 1 H), 7.23 (dd, *J* = 8.0,1.5 Hz, 1 H), 6.86 (d, *J* = 8.0 Hz, 1 H), 6.01 (s, 2 H); 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 150.4, 148.3, 134.2, 125.4, 107.9, 106.5, 101.4, -1.1.

Methyl *N*-[(*E*)-1-(1,3-benzodioxol-5-yl)methylidene]carbamate (2k)

Following the method of Vidal et al[15] silylimine **12k** (3.82g, 17.2 mmol) afforded **2k** (1.56 g, 44 %) after 3 h at room temperature. Pale yellow solid. Mp= 87-97 °C ^{1}H NMR (300 MHz, $CDCl_3$): δ δ 8.87 (s,1 H), 7.49 (d, *J* = 1.5 Hz, 1 H), 7.34 (dd, *J* = 8.0, 1.5 Hz, 1 H), 6.86 (d, *J* = 8.0 Hz, 1 H), 6.06 (s, 2 H), 3.89(s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0, 165.4, 152.9, 148.6, 129.4, 128.6, 108.4, 107.4, 102.1, 53.9; IR ($CDCl_3$): 3065, 2958, 1712, 1636, 1595, 1504, 1489, 1454, 1438, 1236, 1096 1041 cm^{-1} ; HRMS Calcd for $C_{10}H_9NO_4$: 207.0531, Found: 207.0537.

***N*-[- 1-(4-chlorophenyl)methylidene]-*N*-(1,1,1-trimethylsilyl)amine (12l)**

Following the method of Hart et al[14] 4-chloroaldehyde (3.91g, 0.027 mol) afforded **12l** (4.15 g, 71%); yellow liquid, bp 89 °C / 0.3 Torr). NMR data were in accordance with previously reported data.[15]

Methyl *N*-[- 1-(4-chlorophenyl)methylidene]carbamate (2l)

Following the method of Vidal et al[15] silylimine **12l** (4.1g, 0.019 mol) afforded **2l** (2.72 g, 71 %) after 1 night at room temperature and recrystallization from hexane. White crystals. Mp 82-85 °C (Litt value 84.5 °C)**.** NMR data were in accordance with previously reported data.[15]

***N*-[-1-(4-nitrophenyl)methylidene]-*N*-(1,1,1-trimethylsilyl)amine (12m)**

Following the method of Vidal et al[15] *p*-nitroaldehyde (2.55g, 0.016 mol) afforded **12m** (1.75 g, 47%); yellow solid, bulb to bulb distillation (180° C oven temperature / 0.3 Torr). ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.04 (s,1 H), 8.25 (d, *J* = 8.8 Hz, 2 H), 7.94 (d, *J* = 8.8 Hz, 2 H), 0.26 (s, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 165.6, 149.3, 143.4, 129.0, 123.8, -1.34.

Methyl *N*-[-1-(4-nitrophenyl)methylidene]carbamate (2m)

Following the method of Vidal et al[15] silylimine **12m** (3.0g, 0.013 mol) afforded **2m** (0.43 g, 16 %) after 3h reflux and recrystallization from THF/hexane. Yellow crystals. Mp 152-156 °C**.** ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.94 (s, 1 H), 8.32 (d, *J* = 8.8 Hz, 2 H), 8.09 (d, *J* = 8.8 Hz, 2 H), 3.93 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.0, 163.5, 150.7, 138.9, 130.9, 124.1, 54.3; IR (CDCl$_3$): 2958, 2922, 1727, 1635, 1603, 1528, 1438, 1349, 1259, 1212 cm^{-1}.

***N*-[-2,2-dimethylpropylidene]-*N*-(1,1,1-trimethylsilyl)amine.(12n)**

Following the method of Hart et al[14] isobutyraldehyde (2.39g, 0.028 mmol) afforded **12n** (1.13 g, 26%); yellow oil, b.p 39° C/ ca 20 Torr). ^{1}HNMR was in accordance with previously reported data.[19]

Methyl *N*-[-2,2-dimethylpropylidene]carbamate (2n)

Following the method of Vidal et al[15] silylimine **12n** (1.13g, 7.19 mmol) afforded **2n** (0.35 g, 34%); clear oil, b.p 78° C/ ca 20 Torr)**.** ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.18 (s,1

H), 3.83 (s, 3 H), 1.12 (s, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 182.6, 164.2, 53.8, 37.3, 25.8; IR (neat): 3388, 2904, 1735, 1659, 1480, 1437, 1365, 1242, 1028, 927, cm^{-1}.

N-((E)-2-(benzyloxy)-2-methylpropylidene)-N-(1,1,1-trimethylsilyl)amine (12o)

Following the method of Hart et al[14] 2-(benzyloxy)-2-methylpropanal[20] (1.91 g, 0.011 mol) afforded **12o** (1.69 g, 63 %); Clear liquid. Bp 83-86 °C/0.3 Torr. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.37 (s,1 H), 7.35-7.26 (m, 5 H), 4.42 (s, 2 H), 1.36 (s, 1 H), 0.17 (s, 9 H), ^{13}C NMR (75 MHz, CDCl$_3$): δ 177.4, 139.2, 128.3, 127.6, 79.1, 65.7, 23.1, -1.27.

Methyl N-((E)-2-(benzyloxy)-2-methylpropylidene)carbamate (2o)

Following the method of Vidal et al[15] silylimine **121** (1.60g, 6.41 mmol) afforded **122** (0.36 g, 25 %) after 12 h at room temperature. Clear liquid Bp 105-110 °C/0.03Torr ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.27 (s,1 H), 7.35-7.26 (m, 5 H), 4.49 (s, 2 H), 3.85 (s, 3 H), 2.46 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 178.6, 163.3, 138.3, 128.4, 127.6, 127.4, 77.3, 66.2, 53.9, 23.2; IR (CDCl$_3$): 3089, 3065, 2984, 1731, 1668, 1605, 1586, 1497, 1454, 1436, 1385, 1363, 1244, 1163, 1085 cm^{-1}.

Preparation of the catalyst.

Tris(triphenylsilyl)vanadate. [21]

To a solution of triphenyl silanol (9.66 g, 34.93 mmol), triethylamine (3.00 mL) and pyridine (2.00 mL) in toluene (200 mL) was added VOCl$_3$ (2.00 g, 1.20 mmol) slowly at room temperature under argon. The mixture was stirred for 16 h. The resulting suspension was heated to 60°C and filtered through a cannula with a cotton plug at the same temperature to remove precipitated triethylamine hydrochloride. The filtrate was concentrated in *vacuo* and 120 mL of diethyl ether was added. The precipitate was collected by filtration and washed with small amounts of diethyl ether. Acetonitrile (200 mL) was added to the solid and heated to reflux. Then THF (54 mL) was added to initiate the precipitation. After cooling to room temperature the precipitate was collected by filtration under argon, washed with acetonitrile and dried in *vacuo* to give $VO(OSiPh_3)_3$ (5.45 g, 51%) as a white solid. m.p.: 225 - 227 °C. (litt 224-226 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.50-7.44 (m, 2 H), 7.41-7.32 (m, 1 H), 7.16-7.25 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.2, 134.3, 130.1, 127.8. IR (KBr): 3068, 1589, 1429, 1118, 1005, 894, 740, 713, 698 cm^{-1}.

Tris(tri (*p*-chloro phenyl) silyl)vanadate. was prepared according to Pauling *et al.*[21] from *tri*(4-chlorophenyl)(hydroxy)silane and *tri*-isopropylvanadate. Mp=181-182 °C (Litt 181°C)

4.2.5 Reaction of Allenic Alcohols with Imines in the Presence of $VO(OSiPh_3)_3$

5-anilino-4-methyl-1,5-diphenyl-1-penten-3-one (3a)

The reactions were carried out in a flame dried 5 mL Screw-top V-vial sealed with a Miniert Syringe Valve under an Argon atmosphere. Allenic alcohol **1a** (100 mg, 0.62 mmol) and benzylidene-phenyl amine **2a** (135.9 mg, 0.75 mmol) was added to a solution of $VO(OSiPh_3)_3$ (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL). The mixture was stirred at room temperature for 24 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc/benzene/$CHCl_3$ (20/1/0.5/0.5) as the eluent to give **3a** (0.195 mg, 91%) as a mixture of *anti*- and *syn*-isomers (63/37). ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J* = 15.9 Hz, 0.5 H), 7.50-7.16 (m, 11.5 H), 7.05 (t, *J* = 7.8 Hz, 2 H), 6.74 (d, *J* = 15.9 Hz, 0.5 H), 6.62-6.51 (m, 2 H), 6.50 (d, *J* = 16.5 Hz, 0.5 H), 4.84 (br s, 0.5 H), 4.72 (d, *J* = 5.3 Hz, 0.5 H), 4.61 (d, *J* = 6.1 Hz, 0.5 H), 4.44 (br s, 1 H), 3.37 (m, 1 H), 1.23 (d, *J* = 7.1 Hz, 1.5 H), 1.17 (d, *J* = 7.1 Hz, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (202.8, 210.5), 147.0, (143.5, 143.4), 135.2, (134.9, 134.3), (130.6, 130.5), (129.0, 128.9), (128.9, 128.8), (128.5, 128.4), (127.9, 127.8), 127.3, (126.9, 126.6), 125.5, (117.6, 117.2), (113.7, 113.3), (60.8, 59.2), (50.7, 50.6), (15.8, 11.3); IR (neat): 3369, 3055, 2929, 1677, 1601, 1506, 1451, 1317, 1265, 1204, 1181, 1118, 1067, 1045, 870, 747, 701. cm^{-1}; Anal. Calcd. for $C_{24}H_{23}NO$: C, 84.42 ; H, 6.49; Found: C, 84.52; H.6.59.

5-(4-methoxyanilino)-4-methyl-1,5-diphenyl-1-penten-3-one (3b)

The reactions were carried out in a flame dried 5 mL Screw-top V-vial sealed with a Miniert Syringe Valve under an Argon atmosphere. Allenic alcohol **1a** (100 mg, 0.62 mmol) and *N*-(4-methoxyphenyl)-*N*-[(*E*)-1-phenylmethylidene]amine **2b** (138.4 mg, 0.66 mmol) was added to a solution of $VO(OSiPh_3)_3$ (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL). The mixture was stirred at room temperature for 24 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/ EtOAc (9:1) as the eluent to give **3b** (159.9 mg, 43%) as a mixture of *anti*- and *syn* -isomers (57:43). Yellow solid, Mp= 95-125 °C. *Anti*-**3b** : ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 16.0 Hz, 1 H), 7.53-7.20 (m, 10 H), 6.66 (m, 2H), 6.57 (d, *J* = 16.0 Hz, 1 H), 6.49 (m, 2 H), 4.39 (br s, 1 H), 4.56 (d, *J* = 6.7 Hz, 1 H), 3.67 (s, 3 H), 3.34 (m, 1 H), 1.22 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.7, 151.8, 143.2, 141.9, 141.2, 134.4, 130.5, 128.9, 128.8, 128.5, 127.3, 126.8, 125.4, 114.7, 114.6, 59.9, 55.6, 50.8, 15.7. *Syn*-**3b** : ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, *J* = 16.0 Hz, 1 H), 7.53-7.20 (m, 10 H), 6.75 (d, *J* = 16.0 Hz, 1 H), 6.66 (m, 2 H), 6.46 (m, 2 H), 4.39 (br s, 1 H), 4.66 (d, *J* = 5.2 Hz, 1 H), 3.67 (s, 3 H), 3.34 (m, 1 H), 1.19 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.7, 152.0, 143.4, 141.5, 141.3, 134.4, 130.6, 128.9, 128.8, 128.4, 127.1, 126.9, 124.7, 114.9, 114.6, 61.8, 60.3, 50.7, 11.5; IR ($CDCl_3$): 3411, 315, 2935, 1681, 1654, 1606, 1576, 1512, 1450, 1327, 1243, 1180, cm^{-1}; HRMS Calcd for $C_{25}H_{25}NO_2$: 371.1885. Found: 371.1892.

*N*1-[(*E*)-2-methyl-3-oxo-1,5-diphenyl-4-pentenyl]-1-benzenesulfonamide (3d)

The reactions were carried out in a flame dried 5 mL Screw-top V-vial sealed with a Miniert Syringe Valve under an Argon atmosphere. Allenic alcohol **1a** (100 mg, 0.62 mmol) and *N*1-[(*E*)-1-phenylmethylidene]-1-benzenesulfonamid **2d** (160.9 mg, 0.66 mmol) was added to a solution of $VO(OSiPh_3)_3$ (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL). The mixture was stirred at 35 °C for 24 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/ EtOAc (4:1) as the eluent to give **3d** (48.8 mg, 19%) as a mixture of *syn*- and *anti* -isomers (83:17). White solid, Mp= 147-149 °C. *Syn*-**3d** : ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.1 Hz, 2 H), 7.43-7.22 (m, 10 H), 7.03-7.08 (m, 4 H), 6.49 (d, *J* = 15.9 Hz, 1 H), 5.84 (d, *J* = 8.0 Hz, 1 H), 4.59 (t, *J* = 8.0 Hz, 1 H), 3.29 (dq, *J* = 8.0, 7.2 Hz, 1 H), 1.24 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 143.5, 139.9, 138.9, 134.1, 132.2, 130.6, 128.8, 128.6, 128.4, 128.2, 127.5, 127.1, 127.0, 124.4, 59.7, 50.1, 13.8; *Anti*-**3d** : ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (m, 2 H), 7.48-7.22 (m, 10 H), 7.00-7.05 (m, 4 H), 6.55 (d, *J* = 15.9 Hz, 1 H), 6.52 (d, *J* = 8.9 Hz, 1 H), 4.66 (dd, *J* = 8.9, 5.7 Hz, 1 H), 3.32 (dq, *J* = 5.7, 8.9 Hz, 1 H), 1.18 (d, *J* = 7.2 Hz, 3 H); IR ($CDCl_3$): 3274, 3065, 2976, 1684, 1655, 1608, 1576, 1495, 1449, 1327, 1163, 1093 cm^{-1}; Anal. Calcd. for $C_{24}H_{23}NO_3S$: C, 71.09 ; H, 5.72; N, 3.45. Found: C, 71.09; H.5.72; N, 3.48.

General Procedure for the reactions with metoxycarbonyl imines 3e-3o

The reactions were carried out in a flame dried 5 mL Screw-top V-vial sealed with a Miniert Syringe Valve under an Argon atmosphere. Allenic alcohol (1 equiv) was added slowly over 20 h (syringe pump) to a solution of $VO(OSiPh_3)_3$ (5 %) and the imine (1.05 equiv) in dichloromethane (2.5 M) at elevated temperature (35-45 °C). After the addition was complete the reaction was stirred for an additional 2h. The solvent was removed in *vacuo* and the residue purified by flash chromatography.

Methyl *N*-[-2-methyl-3-oxo-1,5-diphenyl-4-pentenyl]carbamate (3e)

Allenic alcohol **1a** (75 mg, 0.46 mmol)was added slowly over 20 (syringe pump) to a mixture of methyl *N*-[(*E*)-1-phenylmethylidene]carbamate (**2e**) (80.2 mg, 0.49 mmol) and $VO(OSiPh_3)_3$ (20.8 mg, 0.023 mmol) in dichloromethane (0.18 mL) at 35 °C. When the addition was complete the solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 6:1→3:1) as the eluent to give **3e** (0.13 mg, 85%) as a mixture of *anti*- and *syn*-isomers (90:10). White solid, Mp= 139-146 °C. *Anti*-**3e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (m, 2 H), 7.37 (m, 4 H), 7.28 (m, 4 H), 7.20 (m, 1 H), 6.55 (d, *J* = 16.0 Hz, 1 H), 6.33 (m, 1 H) , 4.98 (m, 1 H), 3.66 (s, 3 H), 3.45 (m, 1 H), 1.31 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 203.0, 156.7, 143.7, 141.1, 134.1, 130.6, 128.8, 128.4, 128.3, 127.2, 126.2, 125.2, 57.6, 52.1, 48.5, 15.8; *Syn*-**3e** ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.48-7.55 (m, 3 H), 7.20-7.38 (m, 8 H), 6.71 (d, *J* = 16.0 Hz, 1 H), 5.24 (m, 1 H) , 5.11 (m, 1 H), 3.64 (s, 3 H), 3.33 (m, 1 H), 1.21 (d, *J* = 7.0 Hz, 3 H); IR (CDCl$_3$) 3429, 3030, 2979, 1717, 1648, 1606, 1506, 1450, 1255 cm^{-1}; Anal. Calcd. for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33 Found: C, 74.15; H, 6.54; N, 4.35.

Ethyl *N*-[-2-methyl-3-oxo-1,5-diphenyl-4-pentenyl]carbamate (3f)

Allenic alcohol **1a** (100 mg, 0.62 mmol)was added slowly over 20 (syringe pump) to a mixture of methyl *N*-[(*E*)-1-phenylmethylidene]carbamate (**2f**) (116.2 mg, 0.66 mmol) and VO(OSiPh$_3$)$_3$ (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL) at 35 °C. When the addition was complete the solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 6:1→3:1) as the eluent to give **3f** (0.14 mg, 67 %) as a mixture of *anti*- and *syn*-isomers (88:12). White solid, Mp= 120-122 °C. *Anti*-**3f**: ^{1}H NMR (500 MHz, CDCl$_3$, 50 °C): δ 7.44 (m, 2 H), 7.41 (d, *J* = 16.0 Hz, 1 H), 7.35 (m, 3 H), 7.27 (m 4 H), 7.19 (m, 1 H), 6.56 (d, *J* = 16.0 Hz, 1 H), 6.11 (br s, 1 H) , 4.96 (dd, *J* = 9.2, 5.6 Hz, 1 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 3.43 (m, 1 H), 1.30 (d, *J* = 7.1 Hz, 3 H) 1.23 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 203.1, 156.4, 143.6, 141.2, 134.1, 130.6, 128.8, 128.45, 128.39, 127.2, 126.3, 125.3, 60.8, 57.6, 48.7, 15.8, 14.5. *Syn*-**3f** Characteristic peaks: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 6.71 (d, *J* = 16.0 Hz, 1 H), 5.31 (m, 1 H) , 5.11 (m, 1 H), 3.53 (m, 1 H); IR (CDCl$_3$) 3424, 2983, 1712, 1650, 1606, 1404, 1450, 1381, 1331, 1299, 1222, 1108, 1044, cm^{-1}; Anal. Calcd. for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15 Found: C, 75.03; H, 6.75; N, 4.26.

Iso-propyl *N*-[-2-methyl-3-oxo-1,5-diphenyl-4-pentenyl]carbamate (3g)

Allenic alcohol **1a** (100 mg, 0.62 mmol)was added slowly over 20 (syringe pump) to a mixture of isopropyl *N*-[(*E*)-1-phenylmethylidene]carbamate (**2g**) (119.9 mg, 0.65 mmol) and VO(OSiPh$_3$)$_3$ (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL) at 35 °C.

When the addition was complete the solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 5:1→3:1) as the eluent to give **3g** (0.18 mg, 86%) as a mixture of *syn*- and *anti*-isomers (88:12). White solid, Mp = 162-160°C. *Anti*-**3g**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (m, 2 H), 7.40 (d, *J* = 16.0 Hz, 1 H) 7.37 (m, 3 H), 7.28 (m, 4 H), 7.20 (m, 1 H), 6.55 (d, *J* = 16.0 Hz, 1 H), 6.16 (m, 1 H) , 4.97 (m, 1 H), 4.86 (septet, *J* = 6.3 Hz, 1 H), 3.44 (m, 1 H), 1.29 (d, *J* = 7.2 Hz, 3 H). 1.19 (d, *J* = 6.3 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.2, 156.1, 143.6, 141.4, 134.2, 130.7, 128.8, 128.5, 128.4, 127.2, 126.2, 125.3, 68.2, 57.6, 48.7, 22.1, 22.0, 15.8; IR ($CDCl_3$):3429, 2981, 2932, 1709, 1651, 1607, 1495, 1450, 1384, 1224, 1111 cm^{-1}; Anal. Calcd. for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99 Found: C,75.14; H,7.11; N, 3.70.

Methyl *N*-[(*E*)-1-(2-furyl)-2-methyl-3-oxo-5-phenyl-4-pentenyl]carbamate (3h)

Allenic alcohol **1a** (75 mg, 0.47 mmol) was added slowly over 20h (syringe pump) to a mixture of Methyl *N*-[(*E*)-1-(2-furyl)methylidene]carbamate (**2h**) (75.3 mg, 0.49 mmol) and $VO(OSiPh_3)_3$ (20.8 mg, 0.023 mmol) in dichloromethane (0.19 mL) at 35 °C. When the addition was complete the mixture was stirred for an additional 2h. The solvent was then removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 6:1→3:1) as the eluent to give **3h** (0.12 mg, 80%) as a mixture of *anti*- and *syn*-isomers (81:19). Pale yellow crystals, Mp 90-98 °C. Pure samples of the *syn*- and *anti* – isomers were obtained by preparative HPLC (Hexane /EtOAc 85:15). *Anti*-**3h**: ^{1}H NMR (500 MHz, $CDCl_3$, 45°C): δ 7.53 (d, *J* = 16.1 Hz, 1 H) 7.52 (m, 2 H), 7.38 (m, 3 H), 7.28 (m, 1 H), 6.66 (d, *J* = 16.1 Hz, 1 H), 6.25 (dd, *J* = 3.3, 1.8 Hz, 1 H), 6.16 (dt, *J* = 0.9, 3.3 Hz, 1 H), 6.09 (m, 1 H), 5.07 (dd, *J* = 9.3, 4.8 Hz, 1 H) , 3.69 (s, 3 H), 3.62 (m, 1 H), 1.26 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.5, 156.8, 153.6, 143.7, 141.7, 134.2, 130.7, 128.9, 128.5, 124.9, 110.3, 106.4, 52.3, 51.9, 45.8, 14.8; *Syn*-**3h**: ^{1}H NMR (500 MHz, $CDCl_3$, 45°C): δ 7.56 (d, *J* = 16.1 Hz, 1 H) 7.52 (m, 2 H), 7.38 (m, 3 H), 7.31 (dd, *J* = 1.8, 0.9 Hz 1 H), 6.75 (d, *J* = 16.1 Hz, 1 H), 6.26 (dd, *J* = 3.2, 1.8 Hz, 1 H), 6.18 (m, 1 H), 5.38 (t, *J*= 8.3 Hz, 1 H), 5.19 (m, 1 H), 3.67 (s, 3 H), 3.41 (m, 1 H), 1.25 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.2, 156.4, 153.2, 143.2, 141.9, 134.7, 130.5, 128.9, 128.4, 124.6, 110.4, 107.2, 51.3, 50.1, 48.2, 13.3; (*Syn* +*Anti* mixture); IR ($CDCl_3$):3429, 2979, 1720, 1655, 1608, 1577, 1504, 1450, 1381, 1263, 1192, 1110 cm^{-1}; Anal. Calcd. for $C_{18}H_{19}NO_4$: C, 69.00; H, 6.11; N, 4.47; Found: C,69.26; H, 6.09; N. 4.54.

Methyl *N*-[(*E*)-2-methyl-3-oxo-5-phenyl-1-(2-thienyl)-4-pentenyl]carbamate (3i)

Allenic alcohol **1a** (75 mg, 0.47 mmol) was added slowly over 20h (syringe pump) to a mixture of Methyl *N*-[(*E*)-1-(2-thienyl)methylidene]carbamate (**2i**) (75.3 mg, 0.49 mmol) and $VO(OSiPh_3)_3$ (20.8 mg, 0.023 mmol) in dichloromethane (0.19 mL) at 40 °C. When the addition was complete the mixture was stirred for an additional 2h. The solvent was then removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 6:1→3:1) as the eluent to give **3i** (0.126 mg, 81%) as a mixture of *syn*- and *anti*-isomers (76:24). White crystals, Mp = 102-105°C. Pure samples of the *syn*- and *anti* – isomers were obtained by preparative HPLC (Hexane /EtOAc 80:20). *Anti*-**3i**: ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.54 (d, *J* = 16.3 Hz, 1 H), 7.51 (m, 2 H), 7.40-7.35 (m, 3 H), 7.13 (dd, *J* = 4.9, 1.0 Hz, 1 H), 6.91 (dt, *J* = 3.5, 1.0 Hz, 1 H), 6.88 (dd, *J* = 4.9, 3.5 Hz, 1 H), 6.69 (d, *J* = 16.3 Hz, 1 H), 6.41 (br d, *J* =8.2. 1 H), 5.23 (m, 1 H) 3.68 (s, 3 H), 3.53 (m, 1 H), 1.32 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.9, 156.8, 145.2, 143.9, 134.0, 130.8, 128.9, 128.5, 126.7, 125.1, 124.2, 124.1, 53.7, 52.2, 48.6, 15.6; *Syn*-**3i**: ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.59 (d, *J* = 16.2 Hz, 1 H), 7.53 (m, 2 H), 7.40-7.35 (m, 3 H), 7.16 (dd, *J* = 5.2, 1.2 Hz, 1 H), 6.95 (m, 1 H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1 H), 6.77 (d, *J* = 16.2 Hz, 1 H), 5.38 (m, 1 H), 5.32 (m, 1H), 3.66 (s, 3 H), 3.41 (m, 1 H), 1.26 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.3, 156.2, 143.5, 143.6, 134.2, 130.7, 128.9, 128.5, 126.7, 125.5, 124.7, 124.2, 52.7, 52.3, 50.2, 13.9.; IR ($CDCl_3$):3415, 3331, 3062, 2975, 1719, 1607, 1516, 1498, 1450, 1379, 1263, 1194, 1110 cm^{-1}. Anal. Calcd. for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25 Found: C,65.78; H,6.03; N.4.23.

Methyl*N*-[(*E*)-1-(4-methoxyphenyl)-2-methyl-3-oxo-5-phenyl-4-pentenyl]carbamate (3j)

Allenic alcohol **1a** (75.0 mg, 0.47 mmol)was added slowly over 20 (syringe pump) to a mixture of Methyl *N*-[-1-(4-methoxyphenyl)methylidene]carbamate (**2j**) (95.0 mg, 0.49 mmol) and VO(OSiPh$_3$)$_3$ (20.8 mg, 0.023 mmol) in dichloromethane (0.19 mL) at 35 °C. When the addition was complete the solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 6:1→3:1) as the eluent to give **3j** (0.135 mg, 82%) as a mixture of *anti*- and *syn*-isomers (62:38).White solid, Mp= 165-167 °C. *Anti*-**3j**: ^{1}H NMR (500 MHz, CDCl$_3$, 45° C): δ 7.45 (m, 2 H), 7.38 (d, *J* = 16.0 Hz, 1 H), 7.37 (m, 3 H), 7.19 (d, *J* = 8.6 Hz, 2 H), 6.83 (d, *J* = 8.6 Hz, 2 H), 6.57 (d, *J* = 16.0 Hz, 1 H), 6.23 (m, 1 H) , 4.90 (dd, *J* = 8.5, 5.8 Hz, 1 H), 3.73 (s, 3 H), 3.64 (s, 3 H), 3.40 (m, 1 H), 1.27 (d, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 203.2, 158.7, 156.7, 143.7, 134.1, 133.4, 130.7, 128.8, 128.4, 127.4, 125.3, 113.8, 57.2, 55.2, 52.1, 48.7, 15.8; *Syn*-**3j**: ^{1}H NMR (500 MHz, CDCl$_3$, 45° C): δ 7.52 (d, *J* = 15.9 Hz, 1 H), 7.51 (m, 2 H), 7.38 (m, 3 H), 7.21 (d, *J* = 8.6 Hz, 2 H), 6.83 (d, *J* = 8.6 Hz, 2 H), 6.70 (d, *J* = 15.9 Hz, 1 H), 5.19 (m, 1 H), 5.02 (t, *J* = 8.6 Hz, 1 H), 3.74 (s, 3 H), 3.64 (s, 3 H), 3.32 (m, 1 H), 1.21 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 200.8, 158.8, 156.4, 143.2, 134.3, 133.4, 130.6, 128.8, 128.4, 127.9, 124.4, 113.8, 56.4, 55.2, 50.0, 48.8, 13.4; IR (CDCl$_3$) 3431, 2958, 1717, 1654, 1609, 1512, 1450, 1380, 1248, 1179 cm^{-1}; Anal. Calcd. for $C_{21}H_{23}NO_4$: C, 71.37; H, 6.56; N, 3.96, Found: C,71.50; H, 6.49; N, 3.96.

Methyl *N*-[(*E*)-1-(1,3-benzodioxol-5-yl)-2-methyl-3-oxo-5-phenyl-4-pentenyl] carbamate (3k)

The reactions were carried out in a flame dried 5 mL Screw-top V-vial sealed with a Miniert Syringe Valve under an Argon atmosphere. Allenic alcohol **1a** (75 mg, 0.46 mmol) and Methyl *N*-[(*E*)-1-(1,3-benzodioxol-5-yl)methylidene]carbamate **2k** (101.8 mg, 0.49 mmol) was added to a solution of VO(OSiPh$_3$)$_3$ (20.8 mg, 0.023 mmol) in dichloromethane (0.19 mL). The mixture was stirred at room temperature for 24 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/ EtOAc (gradient 9:1→ 3:1) as the eluent to give **3k** (134.2 mg, 79%) as a mixture of *anti*- and *syn* -isomers (60:40). Mp= 41-54 °C. *Anti*-**3k** : ^{1}H NMR

(500 MHz, $CDCl_3$, 50°C): δ 7.54-7.43 (m, 5 H), 6.80-6.67 (m, 4 H), 6.60 (d, *J* = 16.0 Hz, 1 H), 6.15 (br s, 1 H), 5.87 (m, 2 H), 4.86 (dd, *J* = 8.2, 5.5 Hz, 1 H), 3.65 (s, 3 H), 3.38 (dq, *J* = 7.2, 5.5 Hz, 1 H), 1.27 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 156.4, 147.7, 146.7, 143.8, 134.4, 130.8, 128.9, 128.44, 128.41, 125.2, 119.6, 108.1, 106.6, 100.9, 57.6, 52.2, 48.6, 15.8. *Syn*-**3k** ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.54-7.43 (m, 5 H), 6.80-6.67 (m, 4 H), 6.72 (d, *J* = 16.0 Hz, 1 H), 5.88 (m, 2 H), 5.17 (br s, 1 H), 4.98 (dd, *J* = 7.9, 7.2 Hz, 1 H), 3.65 (s, 3 H), 3.29 (quintet, *J* = 7.2 Hz, 1 H), 1.22 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 156.7, 146.8, 143.3, 135.5, 134.2, 130.6, 128.9, 128.44, 128.41, 124.3, 120.2, 108.2, 107.3, 100.9, 56.6, 52.2, 49.9, 13.4.. IR ($CDCl_3$): 3423, 2974, 2896, 1719, 1654, 1576, 1504, 1480, 1449, 1376, 1238, 1194,1042 cm^{-1}. HRMS Calcd for $C_{21}H_{21}NO_5$: 367.1419. Found: Submitted.

Methyl *N*-[(*E*)-1-(4-chlorophenyl)-2-methyl-3-oxo-5-phenyl-4-pentenyl]carbamate (3l)

Allenic alcohol **1a** (75 mg, 0.47 mmol)was added slowly over 20 (syringe pump) to a mixture of methyl *N*-[- 1-(4-chlorophenyl)methylidene]carbamate **(2l**) (97.3 mg, 0.49 mmol) and $VO(OSi(p\text{-}Cl\text{-}Ph)_3)_3$ (28.2 mg, 0.023 mmol) in dichloromethane (0.19 mL) at 45 °C. When the addition was complete the solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 9:1→3:1) as the eluent to give **3l** (0.116 g, 69 %) as a mixture of *anti*- and *syn*-isomers (86:14).White solid, Mp= 158-160 °C. *Anti*-**3l**: ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.45 (m, 2 H), 7.43 (d, *J* = 16.0 Hz, 1 H), 7.38 (m, 3 H), 7.25 (m, 4 H), 6.54 (d, *J* = 16.0 Hz, 1 H), 6.37 (m, 1 H) , 4.92 (dd, *J* = 8.5, 5.1 Hz, 1 H), 3.66 (s, 3 H), 3.40 (dq, *J* = 7.1, 5.1 Hz, 1 H), 1.31 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.9, 156.8, 143.7, 139.9, 133.9, 133.1, 130.0, 128.9, 128.6, 128.4, 127.7, 125.1, 57.2, 52.2, 48.4, 15.9. *Syn*-**3l** Characteristic peaks: ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 6.70 (d, *J* = 16.0 Hz, 1 H), 5.20 (br s, 1 H) , 5.04 (t, *J* = 7.7 Hz, 1 H), 3.31 (dq, *J* = 7.7, 7.2 Hz,1 H), 1.22 (d, *J* = 7.2 Hz, 3 H); IR ($CDCl_3$) 3425, 2976, 1718, 1654, 1605, 1506, 1494, 1450, 1381, 1329, 1255, 1093 cm^{-1}; Anal. Calcd. for $C_{20}H_{20}NO_3$: C, 67.13; H, 5.63; N, 3.91 Found: C, 66.96; H, 5.52; N, 3.86.

Methyl *N*-[(*E*)-2-methyl-1-(4-nitrophenyl)-3-oxo-5-phenyl-4-pentenyl]carbamate (3m)

Allenic alcohol **1a** (50 mg, 0.31 mmol)was added slowly over 20 (syringe pump) to a mixture of methyl *N*-[-1-(4-nitrophenyl)methylidene]carbamate (**2m**) (68.3 mg, 0.32 mmol) and VO(OSi(*p*-Cl-Ph)$_3$)$_3$ (18.2 mg, 0.015 mmol) in dichloromethane (0.13 mL) at 45 °C. When the addition was complete the solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 6:1→3:1) as the eluent to give **3m** (46.4 mg, 40 %) as a mixture of *anti*- and *syn*-isomers (86:14).White solid, Mp= 142-146 °C. *Anti*-**3m**: ^{1}H NMR (500 MHz, CDCl$_3$, 50°C): δ 7.14 (m, 2 H), 7.49-7.43 (m, 5 H), 7.40-7.33 (m, 3 H), 6.55 (d, *J* = 16.0 Hz, 1 H), 6.46 (br s, 1 H) , 5.04 (dd, *J* = 8.2, 4.7 Hz, 1 H), 3.65 (s, 3 H), 3.44 (dq, *J* = 7.2, 4.7 Hz, 1 H), 1.37 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 202.2, 156.9, 148.8, 147.4, 144.6, 133.9, 131.0, 129.0, 128.5, 127.4, 124.9, 123.8, 57.6, 52.3, 48.2, 16.0. *Syn*-**3m** Characteristic peaks: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 6.72 (d, *J* = 16.0 Hz, 1 H), 5.41 (br s, 1 H) , 5.14 (t, *J* = 7.7 Hz, 1 H), 3.65 (s, 3H), 3.36 (m,1 H), 1.25 (d, *J* = 7.2 Hz, 3 H); IR (CDCl$_3$) 3423, 2980, 1721, 1649, 1607, 1576, 1522, 1503, 1450, 1381, 1349, 1293, 1109 cm^{-1}; Anal. Calcd. for $C_{20}H_{20}N_2O_5$: C, 65.21; H, 5.47; N, 7.60 Found: Submitted. HRMS Calcd for $C_{20}H_{20}N_2O_5$: 368.1372. Found: Submitted.

Methyl *N*-[(*E*)-3-oxo-1,5-diphenyl-4-pentenyl]carbamate (7)

Allenic alcohol **1b** (91 mg, 0.62 mmol)was added slowly over 20 (syringe pump) to a mixture of methyl *N*-[(*E*)-1-phenylmethylidene]carbamate (**2e**) (106.9 mg, 0.65 mmol) and VO(OSiPh$_3$)$_3$ (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL) at 40 °C. When the addition was complete the solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 6:1→3:1) as the eluent to give **4** (0.15 mg, 78%). White crystals, Mp 124-125 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.53 (d, *J* = 16.2 Hz, 1 H), 7.51-7.47 (m, 2 H), 7.40-7.37 (m, 4 H), 7.31-7.36 (m, 3 H),7.24-7.22 (m, 1H), 6.66 (d, *J* = 16.2 Hz, 1 H), 5.88 (br s, 1 H), 5.22 (m, 1 H), 3.66 (s, 3 H), 3.34 (br d, *J* = 16.4 Hz, 1 H), 3.14 (br d, *J* = 16.4 Hz, 1 H); ^{13}C NMR (75

MHz, $CDCl_3$): δ 198.2, 156.6, 143.9, 141.6, 134.4, 131.0, 129.2, 128.9, 128.6, 127.7, 126.5, 126.2, 52.5, 52.0, 46.3; IR ($CDCl_3$) 3435, 3344, 3064, 2955, 1885, 1715, 1608, 1576, 1450, 1357, 1329, 1255 cm^{-1}; Anal. Calcd. for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53 Found: C, 73.90; H, 6.33; N, 4.56.

Methyl *N*-[2,5-dimethyl-3-oxo-1-(2-thienyl)-4-hexenyl]carbamate (5b)

Allenic alcohol **1c** (100.0 mg, 0.89 mmol) was added slowly over 20h (syringe pump) to a mixture of Methyl *N*-[(*E*)-1-(2-thienyl)methylidene]carbamate (**2i**) (158.2 mg, 0.93 mmol) and $VO(OSiPh_3)_3$ (39.7 mg, 0.044 mmol) in dichloromethane (0.35 mL) at 40 °C. When the addition was complete the mixture was stirred for an additional 2h. The solvent was then removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (6:1) as the eluent to give **5b** (205.0 mg, 82%) as a mixture of *anti*- and *syn*-isomers (83:17). White crystals; Mp 68-89 °C. *Anti*-**5b**: ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.13 (m, 1 H), 6.85 (m, 2 H), 6.27 (br s, 1 H), 6.01 (septet, *J* =1.3 Hz, 1 H), 5.11 (dd, , *J* = 8.8, 4.7 Hz, 1 H), 3.64 (s, 3 H), 3.11 (dq, *J* = 7.1, 4.7 Hz, 1 H), 2.08 (d, *J* = 1.3 Hz, 3 H), 1.86 (d, *J* = 1.3 Hz, 3 H), 1.23 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.2, 157.6, 156.7, 145.7, 126.6, 124.2, 123.9, 123.5, 54.1, 52.1, 51.2, 27.6, 20.8, 15.3; *Syn*-**5b**: ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.13 (m, 1 H), 6.85 (m, 2 H), 6.08 (septet, *J* =1.3 Hz, 1 H), 5.29 (dd, , *J* = 8.8, 4.7 Hz, 1 H), 5.23 (br s, 1 H), 3.62 (s, 3 H), 3.02 (quintet, *J* = 7.2 Hz, 1 H), 2.07 (d, *J* = 1.3 Hz, 3 H), 1.87 (d, *J* = 1.3 Hz, 3 H), 1.16 (d, *J* = 7.1 Hz, 3 H); IR ($CDCl_3$):3423, 2977, 2938, 1719, 1680, 1615, 1502, 1453, 1381, 1322, 1453, 1381, 1322, 1298, 1262, 1223, 1111.8, 1030, 981 cm^{-1}; Anal. Calcd. for $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98; Found: C, 59.90; H, 7.01; N, 4.89,

Methyl *N*-(2,5-dimethyl-3-oxo-1-phenyl-4-hexenyl)carbamate (5a)

Allenic alcohol **1c** (75 mg, 0.66 mmol) was added slowly over 20h (syringe pump) to a mixture of methyl *N*-[-1-phenylmethylidene]carbamate (**2e**) (114 mg, 0.70 mmol) and $VO(OSiPh_3)_3$ (29.8 mg, 0.033 mmol) in dichloromethane (0.28 mL) at 40 °C. When the addition was complete the mixture was stirred for an additional 2h. The solvent was then removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 9:1→3:1) as the eluent to give **5a** (128 mg, 70 %) as a mixture of *anti*- and *syn* -isomers (97:3). White crystals; Mp 160-162°C. *Anti*-**5a**: ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.31-7.20 (m, 5 H), 6.22 (br s, 1 H), 5.89 (septet, *J* = 1.3 Hz, 1 H), 4.86 (dd, *J* = 8.7, 5.7 Hz, 1 H), 3.66 (s, 3 H), 3.04 (dq, *J* = 7.2, 5.7 Hz, 1 H), 2.07 (d, *J* = 1.3 Hz, 3 H), 1.82 (d, *J* =1.3 Hz, 3 H), 1.22 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.7, 157.5, 156.8, 141.4, 128.3, 127.1, 126.3, 123.5, 57.5, 52.0, 51.0, 27.7, 20.8, 15.6; IR ($CDCl_3$): 3438, 2949, 2915, 1723, 1615, 1508, 1466, 1380, 1288, 1247, 1224, 1095 cm^{-1}; Anal. Calcd. for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.61; N, 5.09 Found: C, 69.83; H, 7.67; N,5.11.

Methyl *N*-(2-isopropyl-5-methyl-3-oxo-1-phenyl-4-hexenyl)carbamate (5d).

Allenic alcohol **1d** (87.5 mg, 0.63 mmol) was added slowly over 20h (syringe pump) to a mixture of methyl *N*-[-1-phenylmethylidene]carbamate (**2e**) (107 mg, 0.65 mmol) and $VO(OSiPh_3)_3$ (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL) at 40 °C. When the addition was complete the mixture was stirred for an additional 2h. The solvent was then removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (6:1) as the eluent to give *anti*-**5d** (81.4 mg, 43 %) and *syn*-**5d** (44.3 mg, 23%). *Anti/syn* ratio = 65:35 Total Yield 66%. *Anti*-**5d**: White crystals; Mp 96-98 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.26-7.18 (m, 5 H), 6.63 (br s, 1 H), 5.52 (s, 1 H), 5.01 (m, 1 H), 3.65 (s, 3 H), 2.61 (dd, *J* = 9.5, 3.2 Hz, 1 H), 2.12 (d septet *J* = 6.8, 3.2 Hz, 1 H), 1.97 (s, 3 H), 1.64 (s, 3 H), 1.10 (d, *J* = 6.8 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H);; ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6, 156.3, 155.6, 141.8, 128.2, 127.8, 126.8, 125.9, 60.4, 54.4, 51.9, 29.3,27.2, 21.1, 20.7, 20.55; *Syn*-**5d**: White crystals; Mp 162-164 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.26-7.15 (m, 5 H), 5.77 (s, 1 H), 5.07-5.05 (m, 2 H), 3.62 (s, 3 H), 2.89 (dd, *J* = 9.6, 5.3 Hz, 1 H), 2.14 (d septet *J* = 9.6, 5.3 Hz, 1 H), 1.86 (s, 3 H), 1.71 (s, 3 H), 1.04 (d, *J* = 6.8 Hz, 3 H), 0.99 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.8, 156.2, 154.5, 141.5, 128.3, 127.3, 126.1, 63.0, 55.1, 52.1, 28.3, 27.3, 21.6, 20.4, 18.5; IR ($CDCl_3$): 3438, 2949, 2915, 1723, 1615, 1508, 1466, 1380, 1288, 1247, 1224, 1095 cm^{-1}; HRMS Calcd for $C_{18}H_{25}NO_3$: 303.1834, Found: 303.1836.

Methyl *N*-(5-methyl-3-oxo-2-pentyl-1-phenyl-4-hexenyl)carbamate (5c)

Allenic alcohol **1e** (100.0 mg, 0.59 mmol) was added slowly over 20h (syringe pump) to a mixture of *N*-[(*E*)-1-phenylmethylidene]carbamate (**2e**) (101.9 mg, 0.62 mmol) and $VO(OSiPh_3)_3$ (26.5 mg, 0.029 mmol) in dichloromethane (0.24 mL) at 40 °C. When the addition was complete the mixture was stirred for an additional 2h. The solvent was then removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 9:1→ 6:1) as the eluent to give **5c** (0.168 g, 86 %) as a mixture of *anti*- and *syn*-isomers (96:4). White crystals; Mp 90-92 °C. *Anti*-**5c**: ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.28-7.25 (m, 2 H), 7.23-7.16 (m, 3 H), 6.34 (br s, 1 H), 5.74 (septet, *J* =1.3 Hz, 1 H), 4.89 (dd, , *J* = 8.6, 4.9 Hz, 1 H), 3.63 (s, 3 H), 2.92 (dt, *J* = 6.5, 6.3 Hz, 1 H), 2.03 (d, *J* = 1.3 Hz, 3 H), 1.76 (d, *J* = 1.3 Hz, 3 H), 1.67 (m, 1 H), 1.55 (m, 1 H), 1.38-1.24 (m, 6 H), 0.88 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.4, 156.9, 156.6, 141.6, 128.3, 126.9, 126.1, 124.6, 56.6, 56.1, 51.9, 31.6, 30.5, 27.5, 27.0, 22.3, 20.7,13.9; IR ($CDCl_3$):3418, 2957, 2859, 1716, 1673, 1613, 1504, 1467, 1383, 1286, 1218, 1099 cm^{-1}; Anal. Calcd. for $C_{20}H_{29}NO_3$: C, 72.47; H, 8.82; N, 4.23 Found: C, 72.28; H, 8.78; N, 4.39.

Methyl *N*-(4-cyclopentyliden-2-methyl-3-oxo-1-phenylbutyl)carbamate (7)

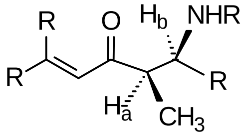
Allenic alcohol **1f** (100.0 mg, 0.72 mmol) was added slowly over 20h (syringe pump) to a mixture of *N*-[(*E*)-1-phenylmethylidene]carbamate (**2e**) (124.0 mg, 0.76 mmol) and $VO(OSiPh_3)_3$ (32.2 mg, 0.036 mmol) in dichloromethane (0.29 mL) at 40 °C. When the addition was complete the mixture was stirred for an additional 2h. The solvent was then removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 9:1→ 3:1) as the eluent to give **7** (173 mg, 79%) as a mixture of *anti*- and *syn*-isomers (93:7). White crystals; Mp 114-116 °C. *Anti*-**7** ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.30-7.16 (m, 5 H), 6.26 (br s, 1 H), 6.03 (quintet, *J* =2.1 Hz, 1 H), 4.82 (dd, *J* = 8.7, 5.2 Hz, 1 H), 3.61 (s, 3 H), 3.03 (m, 1 H), 2.68 (m, 2 H), 2.31 (m, 2 H), 1.70 (m, 2 H), 1.60 (m, 2 H), 1.18 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.3, 170.9, 156.7, 141.6, 128.2, 126.9, 126.3, 118.9, 57.8, 51.9, 50.7, 36.2, 33.5, 26.3, 25.1, 15.6; IR ($CDCl_3$):3421, 3030, 2964, 2874, 1718, 1674, 1612, 1505, 1455, 1379, 1360, 1301, 1255, 1106, 1080 cm^{-1}; Anal. Calcd. for $C_{18}H_{23}NO_3$: C, 71.74; H, 7.69; N, 4.65; Found: 71.72; H, 7.80; N, 4.87.

Methyl *N*-[(*E*)-2-methyl-3-oxo-1-phenyl-4-octenyl]carbamate (8)

Allenic alcohol **1f** (50.0 mg, 0.40 mmol) was added slowly over 20h (syringe pump) to a mixture of *N*-[(*E*)-1-phenylmethylidene]carbamate (**2e**) (67.7 mg, 0.41 mmol) and $VO(OSiPh_3)_3$ (23.8 mg, 0.020 mmol) in dichloromethane (0.16 mL) at 55 °C. When the addition was complete the mixture was stirred for an additional 2h. The solvent was then removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc (gradient 9:1→ 6:1) as the eluent to give **8** (51.4 mg, 45%) as a mixture of *anti*- and *syn*-isomers (83:17). White crystals; Mp 68-90 °C. *Anti*-**8** ^{1}H NMR (500 MHz, $CDCl_3$, 50°C): δ 7.30-7.17 (m, 5 H), 6.67 (dt, *J* = 15.9, 7.0 Hz, 1 H), 6.21 (br s, 1 H) , 5.93 (dt, *J* = 15.9, 1.5 Hz, 1 H), 4.89 (dd, *J* = 8.2, 5.4 Hz, 1 H), 3.65 (s, 3 H), 3.33 (dq, *J* = 7.2, 5.4 Hz, 1 H), 2.07 (m, 2 H), 1.37 (sextet, *J* = 7.3 Hz, 2 H), 1.23 (d, *J* = 7.2 Hz, 3 H), 0.85 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.6, 156.7, 149.0, 141.3, 129.7, 128.4, 127.2, 126.2, 57.6, 52.1, 47.2, 34.3, 21.2, 15.8, 13.5; *Syn*-**8** Characteristic peaks: ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 6.79 (dt, *J* = 15.9, 7.0 Hz, 1 H), 6.07 (d, *J* = 15.9 Hz, 1 H), 5.01 (t, *J* = 7.5 Hz, 1 H), 5.20 (br s, 1H), 3.63 (s, 3 H), 3.24 (m, 1 H), 2.14 (m, 2 H), 1.44 (sextet, *J* = 7.3 Hz, 2 H), 1.13 (d, *J* = 7.1 Hz, 3 H), 0.90 (t, *J* = 7.3 Hz, 3 H); IR ($CDCl_3$) 3419, 3339, 3031, 2962, 1718, 1659, 1623, 1507, 1456, 1380, 1289, 1255, 1193, 1080. 1042 cm^{-1}. HRMS Calcd for $C_{17}H_{23}NO_3$: 289.1677. Found: Submitted.

Determination of stereochemistry. Stereochemical assignments of major isomer of **7** was performed by X-ray crystal structure analysis. Crystal data, structure solution and refinement, and positional and thermal parameters are summarized in Tables **X-X**. Crystal structure is shown in Figure 1. The relative configuration of other products were deducted from the difference between both isomers in ^{1}HNMR data and ^{13}CNMR data. ^{13}C-spectroscopy may also be employed for the assignment of relative configuration.[22] The technique is particularly useful for *β*-aminoketones in which a methyl group is next to $H_{a.}$ The chemical shift of the methyl carbons of *syn* isomers are generally in the range 9-13 ppm and 12-18 ppm for the *anti* isomer.[23]. In the ^{1}HNMR the following relationships between both isomers were observed: *J*ab (*anti*) < *J*ab(*syn*). (Table 1)

Table 1. ^{1}H and ^{13}C- NMR data for selected *β*-amino ketones products.



Entry	**Product**	***Anti/Syn***	**^{13}C Me *Syn* (ppm)**	**^{13}C Me *Anti* (ppm)**	*J* AB ***Syn* (Hz)**	*J* AB ***Anti* (Hz)**
1	**3a**	63/37	11.3	15.8	6.1	5.3
2	**3d**	17/83	13.8	15.8	5.7	8.0
3	**3f**	88/12	-	15.8	-	5.6
4	**3j**	62/38	13.4	15.8	8.6	5.8
5	**3h**	81/19	13.3	14.8	8.3	4.8
6	**3k**	60/40	13.4	15.8	7.2	5.5
7	**3l**	86/14	-	15.9	7.7	5.1
8	**6a**	97/3	-	15.6	-	5.7
9	**6b**	65/35	-	-	5.3	3.1
10	**7**	93/7		15.6	7.5	5.2

Figure 1. X-ray structure of *anti*-**7**

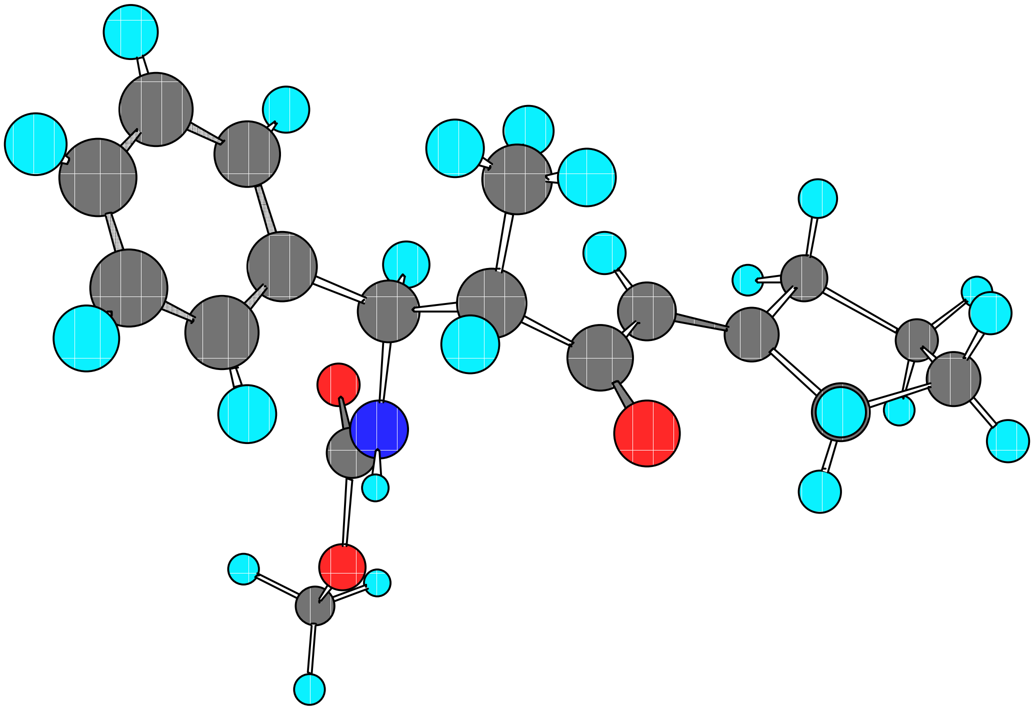


Table 2: Crystal data and Structure Refinement for *anti*-**7**

A. Crystal Data

Empirical Formula	$O_3NC_{18}H_{23}$
Formula Weight	301.38
Crystal Color, Habit	colorless rhombic
Crystal Dimensions	0.29 X 0.15 X 0.14 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	2486 ($4^{o} < 2\theta < 49.44^{o}$)

Lattice Parameters	a = 10.368(1) Å b = 9.541(1) Å c = 16.425(2) Å β = 93.077(2) ^{o} V = 1622.4(3) Å^{3}
Space Group	$P2_1/a$ (#14)
Z value	4
D_{calc}	1.234 g/cm^{3}
F_{000}	648.00
μ(MoKα)	0.83 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker-Siemens SMART CCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Temperature	-95^{o}C
Scan Type	ω(0.3^{o}/frame)
Scan Rate	10 sec Frame Exposure
$2\theta_{max}$	49.4^{o}
No. of Reflections Measured	Total: 7195 Unique: 2626 (R_{int} = 0.044)
Corrections	Absorption, Lorentz, polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(F_o^2 - F_c^2)^2$
Least Squares Weights	$1/\sigma^2(F_o^2) = 1/\sigma^2(F_o)/(4F_o^2)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>0.00\sigma(I)$)	2626
No. Variables	291
Reflection/Parameter Ratio	9.02
Residuals: R_1; wR_2	0.040 ; 0.099
Goodness of Fit Indicator	0.94
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.32 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.39 $e^-/Å^3$

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