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Supporting Information

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Radical-mediated γ–Funtionalizations of α,β–Unsaturated Carboxylic Imides

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General. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 spectrometers. The chemical shifts in $CDCl_3$ or benzene-d_6 reported in δ(ppm) relative to $CDCl_3$ or Me_4Si as an internal reference. Splitting patterns are designated as follows: br s; broad singlet, s; singlet, d; doublet, t; triplet, m; multiplet, dt; double of triplet, td; triple of doublet, dd; double of doublet. IR spectra were measured on a BOMEM MB-100 Fourier Transform spectrometer. High resolution mass spectra were obtained on a VG AUTOSPEC Ultma GC/MS system using direct insertion probe (DIP) and electron impact (EI) (70 eV) method. Flash chromatography was carried out on Merck silica 60 (230-400 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel 60 F_{254} plates. All reagents were purchased from Aldrich Co. All dry solvents were freshly distilled under nitrogen from the appropriate drying agent before use. The photochemical reactor was RAYONET purchased from the southern new England ultraviolet company.

Preparation of benzyl but-2-enoyl-*tert*-butyldiphenylsilyloxy-carbamate (8a)

To a solution of *tert*-butyldiphenylsilyloxy-carbamic acid benzyl ester **7**(4.06 g, 10 mmol) and crotonyl chloride **6a**(1.15 ml, 12 mmol) in dichloromethane (20 ml) was added triethylamine (1.67 ml, 12 mmol) and 4-dimethylaminopyridine (244 mg, 2 mmol) at 0 ^{o}C. After being stirried for 30 min at room temperature, the reaction mixture was diluted with dichloromethane (50 ml), quenched with aqueous NH_4Cl solution and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by passing through a short column of silica gel (ethyl acetate : *n*-hexane = 1 : 10) to yield **8a** (3.69 g, 7.8 mmol, 78%).

MW: $C_{28}H_{31}NO_4Si$ = 473.64; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.10 (s, 9H), 1.76 (dd, *J* = 6.9 Hz, 1.7 Hz, 3H), 4.88 (s, 2H), 6.44-6.50 (m, 1H), 6.76-6.85 (m, 1H), 7.09-7.61 (m, 15H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 18.3, 19.8, 26.9, 68.6, 123.5, 127.3, 127.7, 128.4, 128.6, 129.0, 130.0, 131.3, 136.2, 144.3, 153.1, 164.9; **IR** (polymer) 1736, 1702, 1429, 1284, 1205, 1115, 1055, 742, 701, 509 cm^{-1}; **HRMS** (M^+) calcd for $C_{28}H_{31}NO_4Si$: 473.2022, found 473.2022.

Benzyl pent-2-enoyl-*tert*-butyldiphenylsilyloxy-carbamate (8b)

MW: $C_{29}H_{33}NO_4Si$ = 487.66; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.97 (t, *J*= 7.4 Hz, 3H), 1.13 (s, 9H), 2.08-2.14 (m, 2H), 4.92 (s, 2H), 6.47 (dt, *J*= 15.3 Hz, 1.6 Hz, 1H), 6.86 (dt, *J*= 15.4 Hz, 6.5 Hz, 1H), 7.14-7.65 (m, 15H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 12.1, 19.8, 25.5, 27.0, 68.6, 121.3, 127.3, 128.4, 128.6, 129.0, 129.9, 131.4, 134.4, 136.3, 150.5, 153.1, 165.1; **IR** (polymer) 2962, 2858, 1736, 1702, 1655, 1638, 1474, 1429, 1279, 1196, 1115, 744, 702, 609, 507 cm^{-1}; **HRMS** (M^+) calcd for $C_{29}H_{33}NO_4Si$: 487.2179, found 487.2176.

Benzyl 3-methylbut-2-enoyl-*tert*-butyldiphenylsilyloxy-carbamate (8c)

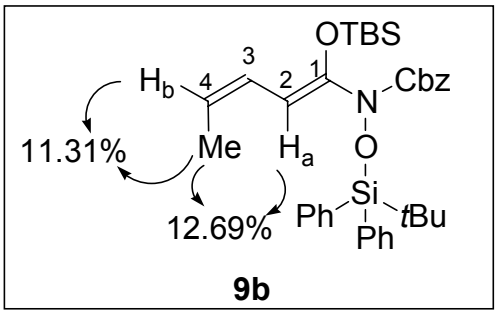
MW: $C_{29}H_{33}NO_4Si$ = 487.66; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.14 (s, 9H), 1.78 (s, 3H), 1.90 (s, 3H), 4.88 (s, 2H), 6.08 (t, *J*= 1.1 Hz, 1H), 7.12-7.65 (m, 15H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.7, 20.7, 26.9, 27.2, 68.4, 117.9, 127.2, 128.4, 128.5, 128.9, 129.9, 131.5, 134.5, 136.2, 153.1, 154.6, 164.7; **IR** (polymer) 2982, 2869, 1735, 1702, 1459, 1297, 1231, 1143, 1026, 749, 701 cm^{-1}; **HRMS** (M^+) calcd for $C_{29}H_{33}NO_4Si$: 487.2179, found 487.2093.

Benzyl 1-*tert*-butyldimethylsilyloxybuta-1,3-dienyl-*tert*-butyldiphenylsilyloxy-carbamate (9a)

To a mixture of **8a** (947 mg, 2 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 919 μl, 4 mmol) in THF (6 ml) at -40 ^{o}C was slowly added a lithium *bis*(trimethylsilyl)amide (LHMDS, 1.0 M solution in THF, 3 ml, 3 mmol). After being stirred for 30 min at -40 ^{o}C, the reaction mixture was diluted with diethyl ether (10 ml), quenched with aqueous sodium bicarbonate and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by passing through a short column of silica gel (ethyl acetate : *n*-hexane =1:50) to give benzyl 1-*tert*-butyldimethylsilyloxybuta-1,3-dienyl-*tert*–butyldiphenyl silyloxy- carbamate (**9a**, 1.12 g, 1.9 mmol, 95%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.14 (s, 6H), 0.96 (s, 9H), 1.08 (s, 9H), 4.79 (d, J = 11.0 Hz, 1H), 4.85-4.90 (m, 2H), 4.91 (s, 2H), 6.36 (dt, J = 17.0 Hz, 6.2 Hz, 1H), 7.14-7.65 (m, 15H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.7, 18.2, 19.4, 25.6, 26.9, 67.7, 111.9, 116.0, 127.2, 128.0, 128.3 (C2), 129.9, 130.4, 131.9, 134.9, 136.3, 141.8, 155.4; **IR** (polymer) 2957, 2859, 1720, 1655, 1427, 1321, 1258, 1115, 824, 741, 700, 505 cm^{-1}; **HRMS** (M^+) calcd for $C_{34}H_{45}NO_4Si_2$: 587.2887, found 587.2924.

Benzyl 1-*tert*-butyldimethylsilyloxypenta-1,3-dienyl-*tert*-butyldiphenylsilyloxy-carbamate (9b)

MW: $C_{35}H_{47}NO_4Si_2$ = 601.92; (1*Z*, 3*Z*) : (1*Z*, 3*E*) = 4.1 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.15 (s, 6H), 0.85 (s, 9H), 1.08 (s, 9H), 1.40 (dd, J= 7.0 Hz, 1.6 Hz, 3H), 4.91-4.98 (m, 3H), 5.33-5.37 (m, 1H), 5.97-6.03 (m, 1H), 7.13-7.66 (m, 15H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.7, 13.3, 18.2, 19.4, 25.7, 26.9, 67.6, 107.2, 122.7, 125.8, 127.2, 127.4, 128.0, 128.3, 129.8, 132.0, 134.9, 136.3, 141.3, 155.4; **IR** (polymer) 2933, 1719, 1665, 1617, 1364, 1256, 1223, 1119, 1059, 844, 743, 700 cm^{-1}; **HRMS** (M^+) calcd for $C_{35}H_{47}NO_4Si_2$: 601.3044, found 601.3059.

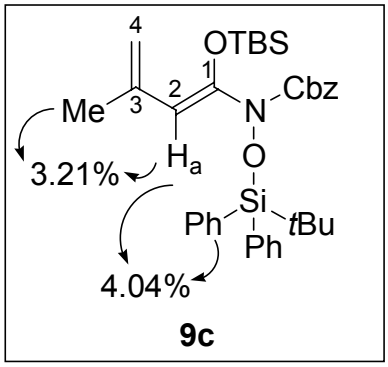


9b

From the ^{1}H-^{1}H COSY NMR spectrum and the decoupling technique, an NOE experiment of **9b** showed 12.69% NOE between Me (1.40 ppm) and H_a (4.91-4.98 ppm) and 11.31% NOE between Me (4.79 ppm) and H_b (5.33-5.37 ppm), indicating that the stereochemistry of a major isomer is (1*Z*, 3*Z*) form.

Benzyl *tert*-butyldimethylsilyloxy-3-methylbuta-1,3-dienyl-*tert*-butyldiphenylsilyloxy-carbamate (9c)

MW: $C_{35}H_{47}NO_4Si_2$ = 601.92; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.10 (s, 6H), 0.90 (s, 9H), 1.02 (s, 9H), 1.69 (s, 3H), 4.49 (s, 1H), 4.69-4.70 (m, 2H), 4.88 (s, 2H), 7.10-7.60 (m, 15H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.5, 18.0, 19.4, 22.6, 25.8, 26.9, 67.6, 112.8, 115.3, 127.2, 128.0, 128.3 (C2), 129.9, 131.9, 135.7, 136.2, 138.4, 140.2, 154.7; **IR** (polymer) 2931, 2859, 1736, 1654, 1340, 1258, 1087, 824, 699 cm^{-1}; **HRMS** (M^+) calcd for $C_{35}H_{47}NO_4Si_2$: 601.3044, found 601.3043.



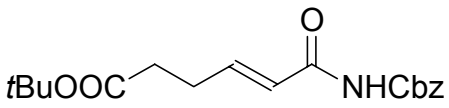
9c

From the ^{1}H-^{1}H COSY NMR spectrum and the decoupling technique, an NOE experiment of **9c** showed 3.21% NOE between H_a (4.49 ppm) and Me (1.69 ppm) and 4.04% NOE between H_a (4.49 ppm) and Ph (7.10-7.60 ppm), indicating that the stereochemistry of **9c** is (1*Z*)-form.

(4-Methyl-6-oxo-6-phenyl-hex-2-enoyl)-carbamic acid benzyl ester (10b)

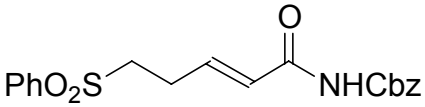
MW: $C_{21}H_{21}NO_4$ = 351.40; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.15 (d, J = 6.6 Hz, 3H), 2.95-3.16 (m, 3H), 5.16 (s, 2H), 6.83 (d, J = 15.5 Hz, 1H), 7.12 (dd, J = 15.5 Hz, 6.8 Hz, 1H), 7.32-7.92 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.1, 32.3, 44.1, 67.8, 120.1, 127.9, 128.0, 128.4, 128.6, 128.7, 133.2, 134.3, 134.9, 136.8, 151.4, 154.6, 165.7, 198.0; **IR** (polymer) 2988, 2871, 1763, 1686, 1638, 1509, 1377, 1276, 1199, 1143, 750 cm^{-1}; **HRMS** (M^+) calcd for $C_{21}H_{21}NO_4$: 351.1471, found 351.1471.

6-Benzyloxycarbonylamino-6-oxo-hex-4-enoic acid *tert*-butyl ester



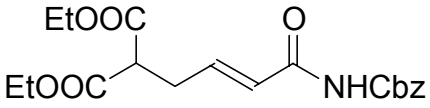
MW: $C_{18}H_{23}NO_5$ = 333.38; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.42 (s, 9H), 2.36-2.40 (m, 2H), 2.49-2.54 (m, 2H), 5.16 (s, 2H), 6.83 (d, J = 15.5 Hz, 1H), 7.09 (dt, J = 15.4 Hz, 6.6 Hz, 1H), 7.32-7.37 (m, 5H), 7.51 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 27.8, 28.0, 33.6, 67.9, 80.8, 121.8, 128.4, 128.7, 134.9, 149.1, 151.5, 165.5, 171.5; **IR** (polymer) 3277, 2979, 1763, 1729, 1698, 1520, 1369, 1196, 1152, 1049 cm^{-1}; **HRMS** (M^+) calcd for $C_{18}H_{23}NO_5$: 333.1576 found 331.1602.

(5-Benzenesulfonyl-pent-2-enoyl)-carbamic acid benzyl ester



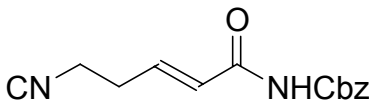
MW: $C_{19}H_{19}NO_5S$ = 373.42; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.63-2.69 (m, 2H), 3.19-3.23 (m, 2H), 5.15 (s, 2H), 6.85 (d, J = 15.5 Hz, 1H), 6.94 (dt, J = 15.4 Hz, 6.3 Hz, 1H), 7.33-7.90 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.7, 54.2, 68.0, 123.1, 128.1, 128.4, 128.7, 128.8, 129.5, 134.0, 134.8, 138.6, 145.1, 151.5, 165.0; **IR** (polymer) 1769, 1695, 1651, 1517, 1307, 1151, 739 cm^{-1}; **HRMS** (M^+) calcd for $C_{19}H_{19}NO_5S$: 373.0984, found 373.0970.

2-(4-Benzyloxycarbonylamino-4-oxo-but-2-enyl)-malonic acid diethyl ester



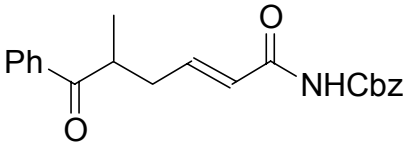
MW: $C_{19}H_{23}NO_7$ = 377.39; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.23-1.27 (m, 6H), 2.82 (td, J = 7.4 Hz, 1.1Hz, 2H), 3.48 (t, J = 7.4 Hz, 1H), 4.15-4.21 (m, 4H), 5.16 (s, 2H), 6.88 (d, J = 15.5 Hz, 1H), 7.02 (dt, J = 15.4 Hz, 6.9 Hz, 1H), 7.32-7.37 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.0, 31.3, 50.6, 61.8, 67.9, 123.6, 128.4, 128.7, 134.9, 145.8, 151.4, 165.1, 168.3; **IR** (polymer) 1751, 1649, 1524, 1372, 1030, 737, 702 cm^{-1}; **HRMS** (M^+) calcd for $C_{19}H_{23}NO_7$: 377.1475, found 337.1482.

(5-Cyano-pent-2-enoyl)-carbamic acid benzyl ester



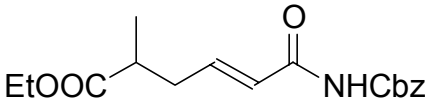
MW: $C_{14}H_{14}N_2O_3$ = 258.27; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.50 (td, J = 6.9 Hz, 1.8 Hz, 2H), 2.57-2.62 (m, 2H), 5.17 (s, 2H), 6.97 (d, J = 15.6 Hz, 1H), 7.03 (dt, J = 15.5 Hz, 5.5 Hz, 1H), 7.33-7.38 (m, 5H), 7.68 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 16.0, 28.0, 68.0, 118.3, 123.7, 128.4, 128.7 (C2), 134.8, 144.9, 151.5, 166.4 ; **IR** (polymer) 1768, 1693, 1651, 1519, 1197, 1050, 739, 702 cm^{-1}; **HRMS** (M^+) calcd for $C_{14}H_{14}N_2O_3$: 258.1004, found 258.1003.

(5-Methyl-6-oxo-6-phenyl-hex-2-enoyl)-carbamic acid benzyl ester



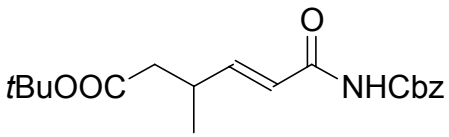
MW: $C_{21}H_{21}NO_4$ = 351.40; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.22 (d, J = 7.0 Hz, 3H), 2.36-2.42 (m, 1H), 2.72-2.77 (m, 1H), 3.57-3.62 (m, 1H), 5.15 (s, 2H), 6.86 (d, J = 15.3 Hz, 1H), 7.03-7.11 (m, 1H), 7.33-7.93 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 17.6, 35.8, 39.8, 67.8, 123.2, 128.3, 128.4, 128.7 (C2), 133.2, 134.3, 134.9, 135.8, 148.1, 151.4, 165.3, 202.5; **IR** (polymer) 1763, 1678, 1648, 1523, 1450, 1199, 1127, 974, 742, 701 cm^{-1}; **HRMS** (M^+) calcd for $C_{21}H_{21}NO_4$: 351.1471, found 351.1475.

6-Benzyloxycarbonylamino-2-methyl-6-oxo-hex-4-enoic acid ethyl ester



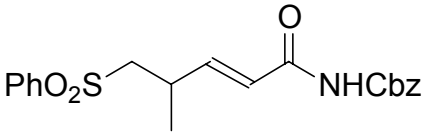
MW: $C_{17}H_{21}NO_5$ = 319.35; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.17 (d, J = 6.8 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 2.33-2.37 (m, 1H), 2.56-2.63 (m, 2H), 4.08-4.14 (m, 2H), 5.16 (s, 2H), 6.83 (d, J = 15.3 Hz, 1H), 7.03 (dt, J = 15.4 Hz, 6.8 Hz, 1H), 7.31-7.37 (m, 5H), 7.58 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.2, 16.8, 36.1, 38.5, 60.6, 67.8, 123.1, 128.4, 128.7, 134.9, 147.7, 151.5, 165.4, 175.3; **IR** (polymer) 3284, 2979, 1762, 1732, 1648, 1519, 1198 cm^{-1}; **HRMS** (M^+) calcd for $C_{17}H_{21}NO_5$: 319.1420, found 319.1415.

6-Benzyloxycarbonylamino-3-methyl-6-oxo-hex-4-enoic acid *tert*-butyl ester



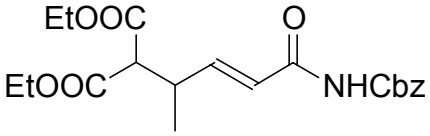
MW: $C_{19}H_{25}NO_5$ = 347.41; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.10 (d, J = 6.8 Hz, 3H), 1.41 (s, 9H), 2.22 (dd, J = 15.3 Hz, 7.6 Hz, 1H), 2.34 (dd, J = 15.1 Hz, 6.8 Hz, 1H), 2.81-2.86 (m, 1H), 5.16 (s, 2H), 6.80 (dd, J = 15.4 Hz, 1.0 Hz, 1H), 7.04 (dd, J = 15.4 Hz, 7.1 Hz, 1H), 7.33-7.37 (m, 5H), 7.52 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 18.9, 28.1, 33.6, 41.5, 67.8, 80.7, 120.0, 128.4, 128.7, 134.3, 135.0, 151.5, 154.2, 165.7, 171.0; **IR** (polymer) 3286, 2977, 1763, 1727, 1701, 1647, 1523, 1369, 1198, 1157, 1039, 749, 699 cm^{-1}; **HRMS** (M^+) calcd for $C_{19}H_{25}NO_5$: 347.1733, found 347.1779.

(5-Benzenesulfonyl-4-methyl-pent-2-enoyl)-carbamic acid benzyl ester



MW: $C_{20}H_{21}NO_5S$ = 387.45; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.22 (d, J = 6.8 Hz, 3H), 2.96-3.03 (m, 1H), 3.08 (dd, J = 14.1 Hz, 6.4 Hz, 1H), 3.21 (dd, J = 14.1 Hz, 6.5 Hz, 1H), 5.16 (s, 2H), 6.75 (d, J = 15.5 Hz, 1H), 6.85 (dd, J = 15.4 Hz, 7.4 Hz, 1H), 7.34-7.88 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.6, 31.9, 60.9, 67.9, 121.2, 128.0, 128.4, 128.7 (C2), 129.4, 133.9, 134.9, 139.4, 151.1, 151.4, 165.2; **IR** (polymer) 1769, 1694, 1645, 1519, 1304, 1196, 1149, 1085, 741 cm^{-1}; **HRMS** (M^+) calcd for $C_{20}H_{21}NO_5S$: 387.1140, found 387.1132.

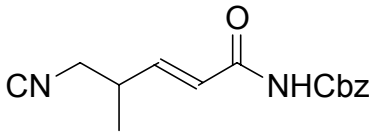
2-(4-Benzyloxycarbonylamino-1-methyl-4-oxo-but-2-enyl)-malonic acid diethyl ester



MW: $C_{20}H_{25}NO_7$ = 391.42; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.15 (d, J = 6.8 Hz, 3H), 1.17-1.33 (m, 6H), 3.12-3.18 (m, 1H), 3.34 (d, J = 8.5 Hz, 1H), 4.11-4.21 (m, 4H), 5.16 (s, 2H), 6.82 (d, J = 15.4 Hz, 1H), 7.03 (dd, J = 15.5 Hz, 8.0 Hz, 1H), 7.31-7.36 (m, 5H), 7.62 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.0 (C2), 17.2, 36.5, 56.7, 61.5, 61.6, 67.8, 121.8, 128.4, 128.6, 134.9, 150.9, 151.4, 165.3,

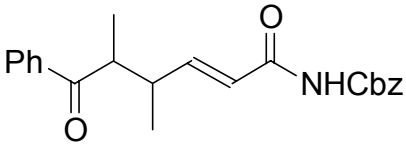
167.7(C2); **IR** (polymer) 1755, 1651, 1519, 1371, 1197, 1029, 739, 701 cm^{-1}; **HRMS** (M^+) calcd for $C_{20}H_{25}NO_7$: 391.1631, found 391.1633.

(5-Cyano-4-methyl-pent-2-enoyl)-carbamic acid benzyl ester



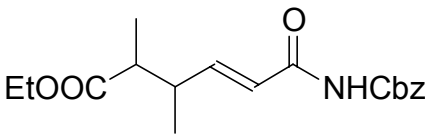
MW: $C_{15}H_{16}N_2O_3$ = 272.30; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.25 (d, J = 6.8 Hz, 3H), 2.36-2.50 (m, 2H), 2.75-2.81 (m, 1H), 5.17 (s, 2H), 6.93 (d, J = 15.5 Hz, 1H), 6.98 (dd, J = 15.4 Hz, 5.9 Hz, 1H), 7.33-7.37 (m, 5H), 7.69 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 18.7, 23.6, 33.4, 68.0, 117.6, 121.9, 128.4, 128.7 (C2), 134.8, 150.3, 151.5, 165.3; **IR** (polymer) 1763, 1687, 1655, 1523, 1210, 1174, 1116, 1027, 777, 736, 700 cm^{-1}; **HRMS** (M^+) calcd for $C_{15}H_{16}N_2O_3$: 272.1161, found 272.1161.

(4,5-Dimethyl-6-oxo-6-phenyl-hex-2-enoyl)-carbamic acid benzyl ester



MW: $C_{22}H_{23}NO_4$ = 365.42; *syn* : *anti* = 2.5 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ *syn* : 1.06 (d, J = 7.0 Hz, 3H), 1.16 (d, J = 6.9 Hz, 3H), 2.86-2.91 (m, 1H), 3.49-3.58 (m, 1H), 5.15 (s, 2H), 6.78 (d, J = 15.4 Hz, 1H), 7.10 (dd, J = 15.4 Hz, 7.3 Hz, 1H), 7.34-7.94 (m, 11H); *anti*: 1.04 (d, J = 7.0 Hz, 3H), 1.12 (d, J = 7.0 Hz, 3H), 2.86-2.91 (m, 1H), 3.40-3.45 (m, 1H), 5.17 (s, 2H), 6.83 (d, J = 15.4 Hz, 1H), 7.02 (dd, J = 15.4 Hz, 6.5 Hz, 1H), 7.34-7.94 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 13.3, 14.8, 38.5, 44.6, 67.8, 120.9, 127.9, 128.2, 128.4, 128.7 (C2), 133.1, 134.3, 136.4, 151.4, 153.6, 165.5, 202.6; **IR** (polymer) 1763, 1685, 1523, 1222, 1048, 701 cm^{-1}; **HRMS** (M^+) calcd for $C_{22}H_{23}NO_4$: 365.1627, found 365.1611.

6-Benzyloxycarbonylamino-2,3-dimethyl-6-oxo-hex-4-enoic acid ethyl ester



MW: $C_{18}H_{23}NO_5$ = 333.38; *syn* : *anti* = 1 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ *syn* : 1.07 (d, *J* = 6.7 Hz, 3H), 1.11 (d, *J* = 6.2 Hz, 3H), 1.18-1.61 (m, 3H), 2.46-2.55 (m, 1H), 2.71-2.76 (m, 1H), 4.08-4.14 (m, 2H), 5.16 (s, 2H), 6.79 (d, *J* = 15.5 Hz, 1H), 7.04 (dd, *J* = 15.5 Hz, 7.7 Hz, 1H), 7.33-7.36 (m, 5H), 7.45 (br s, 1H); *anti* : 1.06 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.1 Hz, 3H), 1.18-1.61 (m, 3H), 2.35-2.43 (m, 1H), 2.64-2.70 (m, 1H), 4.08-4.14 (m, 2H), 5.17 (s, 2H), 6.83 (d, *J* = 15.5 Hz, 1H), 6.96 (dd, *J* = 15.4 Hz, 8.4 Hz, 1H), 7.33-7.36 (m, 5H), 7.45 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 13.3, 14.2, 15.0, 15.5, 17.7, 39.1, 39.9, 43.9, 44.6, 60.5, 67.9 (C2), 121.0, 121.6, 128.4, 128.7, 134.9 (C2), 151.5, 152.8, 153.3, 165.5, 174.8, 175.1; **IR** (polymer) 1767, 1732, 1645, 1520, 1195, 1119, 740, 702 cm^{-1}; **HRMS** (M^+) calcd for $C_{18}H_{23}NO_5$: 333.1576, found 333.1566.

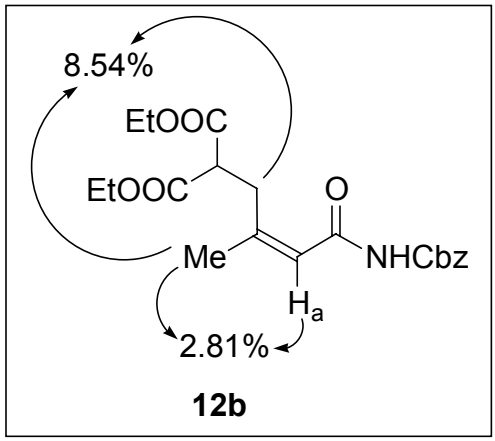
(3-Methyl-6-oxo-6-phenyl-hex-2-enoyl)-carbamic acid benzyl ester (12a)

MW: $C_{21}H_{21}NO_4$ = 351.40; *Z* : *E* = 5.1 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ *Z* : 2.20 (d, *J* = 1.2 Hz, 3H), 2.62 (t, *J* = 7.5 Hz, 2H), 3.16 (t, *J* = 7.8 Hz, 2H), 5.14 (s, 2H), 6.54 (s, 1H), 7.32-7.95 (m, 11H); *E* : 1.98 (d, J = 1.2 Hz, 3H), 2.91 (t, *J* = 7.3 Hz, 2H), 3.16 (d, *J* = 7.8 Hz, 2H), 5.15 (s, 2H), 6.48 (s, 1H), 7.32-7.95 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.9, 35.1, 36.2, 67.6, 116.3, 128.0, 128.3, 128.5, 128.6, 133.2, 134.4, 135.1, 136.6, 151.5, 160.9, 165.7, 198.5; **IR** (polymer) 1762, 1686, 1634, 1509, 1207, 744, 699 cm^{-1}; **HRMS** (M^+) calcd for $C_{21}H_{21}NO_4$: 351.1471, found 351.1454.

2-(4-Benzyloxycarbonylamino-2-methyl-4-oxo-but-2-enyl)-malonic acid diethyl ester (12b)

MW: $C_{20}H_{25}NO_7$ = 391.42; *Z* : *E* = 4.5 : 1 (from ^{1}H NMR ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ *Z* : 1.20-1.25 (m, 6H), 2.15 (d, *J* = 0.6 Hz, 3H), 2.76 (d, *J* = 3.9 Hz, 2H), 3.60 (t, *J* = 7.6 Hz, 1H), 4.14-4.20 (m, 4H), 5.13 (s, 2H), 6.47 (s, 1H), 7.30-7.35 (m, 5H), 7.50 (br s, 1H); *E* : 1.20-1.25 (m, 6H), 1.93 (d, *J* = 0.7 Hz, 3H), 3.10 (d, *J* = 3.9 Hz, 2H), 3.73 (t, *J* = 7.7 Hz, 1H), 4.14-4.20 (m, 4H), 5.14 (s, 2H), 6.52 (s, 1H), 7.30-7.35 (m, 5H), 7.62 (br s, 1H) ; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.0, 19.5, 39.5,

50.0, 61.7, 67.6, 117.8, 128.4, 128.6 (C2), 135.1, 151.3, 157.0, 168.5; **IR** (polymer) 1752, 1510, 1371, 1200, 745, 702 cm^{-1}; **HRMS** (M^+) calcd for $C_{20}H_{25}NO_7$: 391.1631, found 391.1634.



12b

From the ^1H-^1H COSY NMR spectrum and the decoupling technique, an NOE experiment of **12b** showed 2.81% NOE between Me (2.15 ppm) and H_a (6.47 ppm), indicating that the stereochemistry of a major isomer is *Z*-form.

(4-Phenylsulfanyl-but-2-enoyl)-carbamic acid benzyl ester (14)

MW: $C_{18}H_{17}NO_3S$ = 327.40; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.64 (dd, J = 7.14 Hz, 1.3 Hz, 2H), 5.14 (s, 2H), 6.80 (d, J = 15.2 Hz, 1H), 7.06 (dt, J = 15.2 Hz, 7.2 Hz, 1H), 7.16-7.38 (m, 10H), 7.47 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 36.0, 67.9, 123.0, 127.0, 128.4, 128.7 (C2), 129.0, 130.7, 134.9, 144.6, 151.3, 165.1; **IR** (polymer) 1768, 1692, 1646, 1523, 1196, 1027, 746 cm^{-1}; **HRMS** (M^+) calcd for $C_{18}H_{17}NO_3S$: 327.0929, found 327.0921.

(3,4-Bis-phenylsulfanyl-butyryl)-carbamic acid benzyl ester (15)

MW: $C_{24}H_{23}NO_3S_2$ = 437.58; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.02 (dd, J = 13.9 Hz, 9.4 Hz, 1H), 3.17 (dd, J = 18.3 Hz, 7.9 Hz, 1H), 3.27-3.37 (m, 2H), 3.63-3.70 (m, 1H), 5.15 (s, 2H), 7.15-7.37 (m, 15H), 7.57 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 38.8, 39.3, 43.5, 68.0, 126.5, 127.7, 128.5, 128.7, 128.8, 129.0 (C2), 129.9, 133.0, 133.3, 134.8, 135.0, 151.3, 171.6; **IR** (polymer) 1764, 1708, 1482, 1201, 744, 696 cm^{-1}; **HRMS** (M^+) calcd for $C_{24}H_{23}NO_3S_2$: 437.1119, found 437.1124.

Typical procedure : A dichloromethane solution (1 ml) of diene *O*,*N*-acetal (**9a**, 118 mg, 0.2 mmol), phenylsulfonyl bromide (88 mg, 0.4 mmol), and V-70 (12 mg, 0.04 mmol) was degassed with nitrogen for 10 min and then the solution was heated at 30°C under nitrogen for 10 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate and *n*-hexane (1:3) as eluant to give (4-benzenesulfonyl-but-2-enoyl)-carbamic acid benzyl ester (**16a**, 51 mg, 71%).

MW: $C_{18}H_{17}NO_5S$ = 359.40; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.96 (d, J = 3.3 Hz, 2H), 5.13 (s, 2H), 6.82-6.93 (m, 2H), 7.30-7.85 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 59.3, 68.1, 128.3, 128.4, 128.7, 128.8, 129.1, 129.3, 134.2 (C2), 134.7, 151.3, 164.0; **IR** (polymer) 1768, 1694, 1651, 1519, 1310, 1195, 1153, 1086, 1028, 748 cm^{-1}; **HRMS** (M^+) calcd for $C_{18}H_{17}NO_5S$: 359.0827, found 359.0823.

(4-Phenylselanyl-but-2-enoyl)-carbamic acid benzyl ester (16b)

MW: $C_{18}H_{17}NO_3Se$ = 374.29; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.58 (dd, J = 8.1 Hz, 1.1 Hz, 2H), 5.14 (s, 2H), 6.55 (d, J= 15.1 Hz, 1H), 7.05-7.49 (m, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 28.9, 67.9, 121.8, 127.6, 127.9, 128.4, 128.7, 129.1, 134.3, 134.4, 134.5, 145.2, 151.3, 165.1; **IR** (polymer) 1764, 1691, 1640, 1518, 1195, 1128, 1025, 741, 700 cm^{-1}; **HRMS** (M^+) calcd for $C_{18}H_{17}NO_3Se$: 375.0374, found 375.0374.

(4-Tris(trimethylsilyl)-but-2-enoyl)-carbamic acid benzyl ester (16c)

MW: $C_{21}H_{39}NO_3Si_4$ = 465.88; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.17 (s, 27H), 2.02 (dd, J = 9.1 Hz, 1.2 Hz, 2H), 5.16 (s, 2H), 6.74 (d, J = 15.0 Hz, 1H), 7.24-7.36 (m, 6H), 7.41 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 0.9, 16.0, 67.6, 117.3, 128.3, 128.6 (C2), 135.1, 151.6, 153.6, 165.7; **IR** (polymer) 2952, 1760, 1693, 1615, 1503, 1246, 1199, 837, 697 cm^{-1}; **HRMS** (M^+) calcd for $C_{21}H_{39}NO_3Si_4$: 465.2007, found 465.2041.