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Tandem Inter [4 + 2]/Intra [3 + 2] Cycloadditions of Nitroalkenes. The Bridged Mode (β-Tether).

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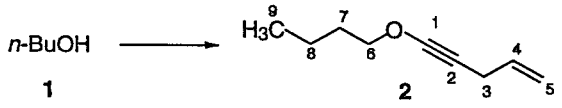
SUPPORTING INFORMATION

General. ^{1}H and ^{13}C NMR spectra were recorded on the Varian Unity-400 (400 MHz ^{1}H, 100 MHz ^{13}C), 500 (500 MHz ^{1}H, 125.7 MHz ^{13}C) and Varian Unity Inova 500 (500 MHz ^{1}H, 125.7 MHz ^{13}C) spectrometers in deuteriochloroform ($CDCl_3$), or deuteriobenzene (C_6D_6), with either chloroform (7.26 ppm ^{1}H, 77.0 ppm ^{13}C), or benzene (7.15 ppm ^{1}H, 128.0 ppm ^{13}C) as an internal reference. Data are reported in the following order: chemical shifts in ppm (δ); multiplicities are indicated b (broadened), s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet)); coupling constants, *J*, are reported (Hz). Infrared spectra (IR) were obtained either neat on NaCl discs or dissolved in $CHCl_3$ or CCl_4 on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67-100%), m (medium 33-67%), w (weak 0-33%), and (broad). Mass spectra were obtained through the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. Low-resolution electon impact (EI) mass spectra were obtained on a Finnigan-MAT CH-5 spectrometer with a typical ionization voltage of 70 or EI, 10 eV. Low-resolution chemical ionization (CI) mass spectra were obtained on a VG 70-VSE spectrometer using methane. Low-resolution fast atom bombardment (FAB) spectra were obtained on a VG ZAB-SE spectrometer in magic bullet (3/1, dithiothreitol/dithioerythitol) or 3-nitrobenzyl alcohol; high-resolution FAB spectra were obtained on a VG-SE-4F spectrometer. Data are reported in the form *m/z* (intensity relative to base peak = 100). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished by UV light, iodine, potassium permanganate solution, or *para*-anisaldehyde solution. Column chromatography was performed with 32-63 μm silica gel (Woelm) or alumina (neutral activity III or basic activity III), ~150 mesh, 58 Å (Aldrich).

Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. *n*-Butyllithium was titrated by the method of Gilman.[1] All reactions were performed under a dry nitrogen atmosphere in base-washed, flame-dried glassware.

Materials. Solvents for extraction were technical grade and distilled from the indicated drying agents: dichloromethane, pentane, hexane ($CaCl_2$); ethylacetate (K_2CO_3); tert-butyl methyl ether (MTBE) ($CaSO_4/FeSO_4$). Solvents for some column chromatography were reagent grade. Solvents for anhydrous reactions were reagent grade and distilled from the indicated drying agents; tetrahydrofuran (THF) (sodium and benzophenone), dichloromethane (P_2O_5), methanol (magnesium), pyridine (CaH_2), benzene (CaH_2), toluene (sodium). Brine refers to a saturated aqueous solution of NaCl. Tin(IV) chloride, titanium(IV) chloride and acetic anhydride were obtained from commercial sources and were distilled. Sodium borohydride, sodium bicarbonate, ethanol and trimethylaluminum (2.0 M in toluene, Aldrich) were obtained from commercial sources and used as received. (2-Nitro-1-propenyl)benzene (**4a**),[2] was prepared by a literature method.

1-Butyloxy-pent-4-ene-1-yne (2)



Data for **2**

^{1}H NMR: (400 MHz, $CDCl_3$)

5.83 (ddt, J = 16.8, 10.0, 5.0, 1 H, HC(4)), 5.29 (dq, J = 16.9, 2.0, 1 H, $H_aC(5)$), 5.06 (dq, J = 10.0, 1.8, 1 H, $H_bC(5)$), 4.00 (t, J = 6.2, 2 H, $H_2C(6)$), 2.90 (dt, J = 5.2, 2.0, 2 H, $H_2C(3)$), 1.74-1.67 (m, 2 H, $H_2C(7)$), 1.45-1.36 (m, 2 H, $H_2C(8)$), 0.94 (t, J = 7.4, 3 H, $H_3C(9)$).

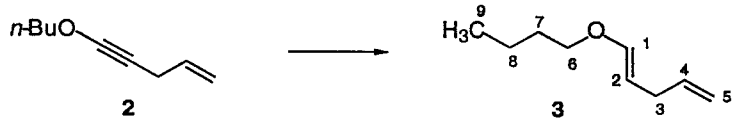
^{13}C NMR: (100.6 MHz, $CDCl_3$)

134.29 (C(4)), 114.94 (C(5), 91.82 (C(1)), 78.15 (C(6)), 33.59 (C(2)), 30.73 (C(3)), 21.63 (C(7)), 18.57 (C(8)), 13.61 (C(9)).

IR: (Neat)

2962 (s), 2937 (s), 2887 (m), 2876 (m), 2275 (s), 1642 (w), 1467 (w), 1237 (s), 1212 (s), 991 (m), 937 (s), 914 (s).

1-Butyloxy-1,4-pentadiene (3)



Data for **3**

^{1}H NMR: (400 MHz, $CDCl_3$)

6.25 (d, J = 12.7, 1 H, HC(1)), 5.87-5.77 (m, 1 H, HC(4)), 5.07-5.01 (m, 1 H, $H_aC(5)$), 4.98-4.94 (m, 1 H, $H_bC(5)$), 4.75 (dt, J = 12.7, 7.1, 1 H, HC(2)), 3.65 (t, J = 6.6, 2 H, $H_2C(6)$), 2.68-2.64 (m, 2 H, $H_2C(3)$), 1.65-1.58 (m, 2 H, $H_2C(7)$), 1.44-1.35 (m, 2 H, $H_2C(8)$), 0.93 (t, J = 7.5, 3 H, $H_3C(9)$).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

147.13 (C(1)), 138.17 (C(4)), 114.36 (C(5)), 101.19 (C(2)), 68.86 (C(6)), 31.94 (H_2C), 31.33 (H_2C), 19.16 (C(8)), 13.82 (C(9)).

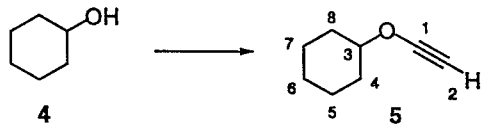
IR: (Neat)

3079 (w), 3004 (w), 2960 (s), 2935 (s), 2874 (s), 1672 (m), 1655 (s), 1416 (w), 1389 (w), 1218 (m), 1175 (s), 1131 (m), 994 (w), 935 (m), 914 (m).

MS: (70 eV)

140 (M^+, 45), 139 (M^+- 1, 61), 103 (31), 99 (42), 84 (100), 83 (100), 82 (50), 81 (67), 69 (46), 67 (40), 57 (100), 55 (100), 54 (62), 53 (82), 43 (71), 42 (56), 41 (100).

1-Cyclohexyloxy-acetylene (5)



Data for **5**

^{1}H NMR: (499.7 MHz, $CDCl_3$)

4.11-4.06 (m, 1 H, HC(3)), 1.99-1.96 (m, 2 H), 1.79-1.73 (m, 2 H), 1.65-1.58 (m, 2 H), 1.53-1.48 (m, 2 H, HC(2)), 1.37-1.25 (m, 3 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

89.89 (C(1)), 86.49 (C(3)), 30.74 (C(2)), 27.03 (C(8), C(4)), 25.04 (C(7), C(5)), 23.09 (C(6)).

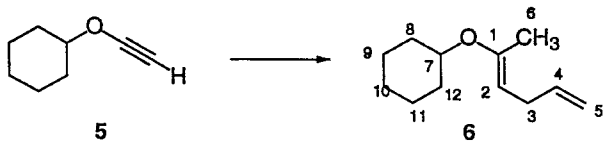
IR: (Neat)

3320 (s), 2942 (s), 2938 (s), 2862 (s), 2143 (s), 1451 (m), 1369 (w), 1162 (w), 1105 (s), 1086 (m), 1004 (m), 902 (m), 888 (m).

MS: (CI)

125 (M^++1, 0.2), 124 (M^+, 0.2), 123 (M^+-1, 0.6), 131 (74), 97 (2), 84 (7), 83 (100), 67 (6) 59 (2), 55 (14).

1-Cyclohexyloxy-1-methyl-1,4-pentadiene (6)



Data for **6**

^{1}H NMR: (499.7 MHz, $CDCl_3$)

5.86-5.78 (m, 1 H, HC(4)), 5.02 (dd, J = 17.0, 1.6, 1 H, $H_aC(5)$), 4.94 (dd, J = 10.0, 1.5, 1 H, $H_bC(5)$), 4.43 (t, J = 7.5, 1 H, HC(2)), 3.94-3.89 (m, 1 H, HC(7)), 2.72 (dd, J = 7.0, 6.6, 2 H, $H_2C(3)$), 1.93-1.90 (m, 2 H, $H_aC(8)$, $H_aC(12)$), 1.74-1.72 (m, 5 H, $H_3C(6)$, $H_aC(9)$, $H_aC(11)$), 1.55-1.53 (m, 1 H, $H_aC(10)$), 1.40-1.22 (m, 5 H, $H_bC(10)$, $H_bC(9)$, $H_bC(11)$, $H_bC(8)$, $H_aC(12)$).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

151.35 (C(1)), 138.23 (C(4)), 113.69 (C(5)), 95.92 (C(2)), 73.21 (C(7)), 31.75 (C(8), C(12)), 31.25 (C(3)), 25.77 (C(10)), 24.01 (C(9), C(11)), 16.39 (C(6)).

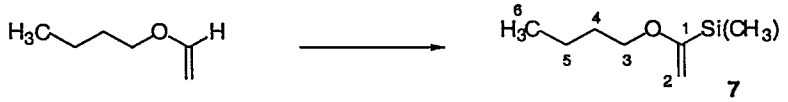
IR: (Neat)

2933 (s), 2859 (w), 1661 (m), 1469 (w), 1238 (m), 1181 (m), 1074 (w), 928 (w).

MS: (CI)

125 (M^++1, 0.6), 99 (14), 89 (11), 84 (7), 83 (100), 81 (19), 61 (22), 57 (9), 55 (10).

α-(Butoxyvinyl)-trimethylsilane (7)



7

Data for **7**

^{1}H NMR: (499.7 MHz, $CDCl_3$)

4.55 (d, J = 1.7 1 H, $H_aC(2)$), 4.26 (d, J = 1.7 1 H, $H_bC(2)$), 3.63 (t, J = 6.3, 2 H, $H_2C(3)$), 1.68-1.62 (m, 2 H, $H_2C(4)$), 1.46-1.38 (m, 2 H, $H_2C(5)$), 0.94 (t, J = 7.4, 3 H, $H_3C(6)$), 0.11 (s, 9 H, CH_3).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

170.15 (C(1)), 93.21 (C(2)), 66.13 (C(3)), 31.09 (C(4)), 19.42 (C(5)), 13.86 (C(6)), -2.38 (CH_3).

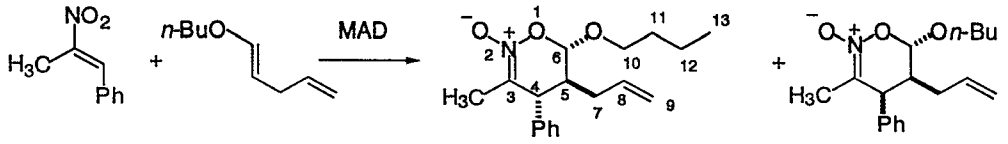
IR: (Neat)

2960 (s), 2936 (s), 2902 (m), 2874 (m), 1584 (s), 1467 (w), 1249 (s), 1216 (s), 1072 (w), 1030 (w).

MS: (CI)

173 (M^++1, 8), 171 (M^+, 2), 157 (14), 131 (74), 117 (12), 101 (14), 93 (15), 75 (50), 73 (65), 61 (17), 57 (100), 55 (15).

rel-(4_R_,5_S_,6_S_)-6-Butyloxy-3-methyl-4-phenyl-5-(2-propenyl)-5,6-dihydro-4_H_-[1,2]-oxazine _2_-Oxide (13a)



12 **3** **16a** **16c**

Data for **13a**

^{1}H NMR: (400 MHz, C_6D_6)

7.05-6.96 (m, 3 H, Ph), 6.89-6.86 (m, 2 H, Ph), 5.51-5.41 (m, 1 H, HC(8)), 4.95-4.86 (m, 2 H, H_2C(9)), 4.83 (d, J = 4.6, 1 H, HC(6)), 4.08 (dt, J = 9.5, 6.5, 1 H, H_aC(10)), 3.36 (dt, J = 9.5, 6.6, 1 H, H_bC(10)), 3.07 (dd, J = 7.3, 1.6, 1 H, HC(4)), 2.16-2.10 (m, 1 H, HC(5)), 2.04-1.97 (m, 1 H, H_aC(7)), 1.90-1.82 (m, 1 H, H_bC(7)), 1.68 (d, J = 1.7, 3 H, H_3C), 1.51-1.44 (m, 2 H, H_2C(11)), 1.34-1.20 (m, 2 H, H_2C(12)), 0.81 (t, J = 7.3, 3 H, H_3C(13)).

^{13}C NMR: (100.6 MHz, C_6D_6)

140.09 (Ph), 134.65 (C(8)), 129.11 (Ph), 128.94 (Ph), 127.47 (Ph), 120.88 (C(3)), 118.03 (C(9)), 105.62 (C(6)), 69.65 (C(10)), 47.80 (C(4)), 45.87 (C(5)), 35.14 (C(7)), 31.75 (C(11)), 19.45 (C(12)), 16.84 (CH_3), 13.91 (CH_3).

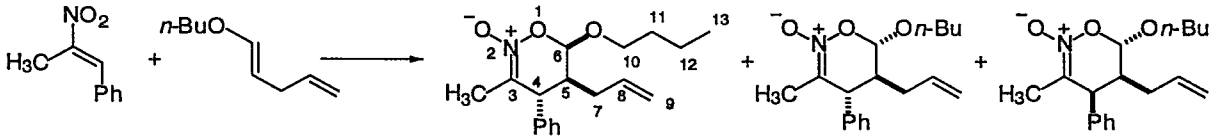
IR: (CCl_4)

3067 (w), 3003 (w), 2961 (s), 2935 (s), 2874 (m), 1641 (w), 1613 (s), 1495 (w), 1455 (m), 1379 (w), 1307 (m), 1273 (s), 1249 (s), 1174 (m), 1116 (s), 969 (w), 922 (s), 894 (s), 813 (w).

MS: (CI)

305 (M^++2, 23), 304 (M^++ 1, 100), 273 (12), 230 (22), 202 (12), 173 (15), 171 (16), 145 (34), 141 (12), 86 (52), 57 (40).

rel-(4_R_,5_S_,6_R_)-6-Butyloxy-3-methyl-4-phenyl-5-(2-propenyl)-5,6-dihydro-4_H_-[1,2]-oxazine _2_-Oxide (13b)



12 **3** **16b** **16a** **16c**

Data for **13b**

^{1}H NMR: (400 MHz, C_6D_6)

6.99-6.96 (m, 3 H, Ph), 6.70-6.78 (m, 2 H, Ph), 5.28-5.17 (m, 1 H, HC(8)), 5.02 (d, J = 1.7, 1 H, HC(6)), 4.89-4.81 (m, 2 H, H_2C(9)), 4.00 (dt, J = 9.8, 6.3, 1 H, H_aC(10)), 3.37 (dt, J = 9.8, 6.3, 1 H, H_bC(10)), 3.18-3.16 (m, 1 H, HC(4)), 2.00-1.90 (m, 3 H, H_2C(7),HC(5)), 1.69 (d, J = 1.7, 3 H, H_3C), 1.54-1.40 (m, 2 H, H_2C(11)), 1.38-1.20 (m, 2 H, H_2C(12)), 0.84 (t, J = 7.3, 3 H, H_3C(13)).

^{13}C NMR: (100.6 MHz, C_6D_6)

140.19 (Ph), 134.87 (C(8)), 129.13 (Ph), 128.80 (Ph), 127.63 (Ph), 119.05 (C(3)), 117.54 (C(9)), 102.16 (C(6)), 69.08 (C(10)), 47.37 (C(4)), 42.90 (C(5)), 33.69 (C(7)), 31.78 (C(11)), 19.51 (C(12)), 17.57 (CH_3), 13.89 (CH_3).

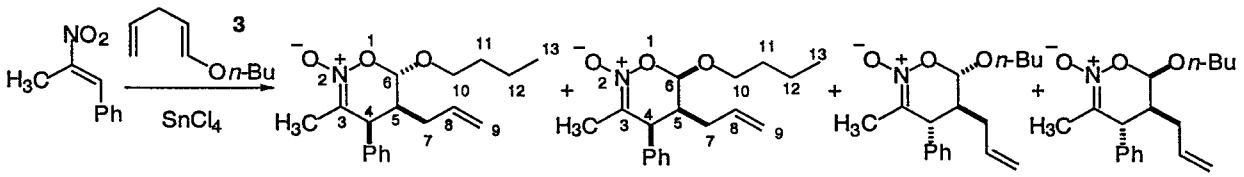
IR: (CCl_4)

3029 (w), 2961 (s), 2935 (s), 2875 (m), 1641 (w),1618 (s), 1455 (m), 1340 (w), 1277 (s), 1272 (s), 1238 (s), 1158 (m), 1074 (m), 934 (m), 921 (s), 897 (s).

MS: (CI)

305 (M^++2, 25), 304 (M^++ 1, 100)), 230 (11), 171 (17), 145 (15), 86 (15), 57 (10).

rel-(4_S_,5_S_,6_S_)-6-Butyloxy-3-methyl-4-phenyl-5-(2-propenyl)-5,6-dihydro-4_H_-[1,2]-oxazine _2_-Oxide (13c) and **_rel_-(4_S_,5_S_,6_R_)-6-Butyloxy-3-methyl-4-phenyl-5-(2-propenyl)-5,6-dihydro-4_H_-[1,2]-oxazine _2_-Oxide (13c)**



Data for **13c**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.36-7.26 (m, 3 H, Ph), 7.11-7.08 (m, 2 H, Ph), 5.54-5.43 (m, 1 H, HC(8)), 5.19 (d, J = 2.0, 1 H, HC(6)), 5.04-4.99 (m, 2 H, H_2C(9)), 4.17 (d, J = 6.6, 1 H, HC(4)), 4.01 (dt, J = 9.5, 6.6, 1 H, H_aC(10)), 3.64 (dt, J = 9.5, 6.3, 1 H, H_bC(10)), 2.11-1.97 (m, 2 H, HC(5), H_aC(7)), 1.92 (d, J = 1.6, 3 H, H_3C), 1.72-1.56 (m, 3 H, H_2C(11), H_bC(7)), 1.37 (sept, J = 7.3, 2 H, H_2C(12)), 0.92 (t, J = 7.4, 3 H, H_3C(13)).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

136.42 (Ph), 134.79 (C(8)), 129.31 (Ph), 128.71 (Ph), 127.51 (Ph), 122.55 (C(3)), 118.22 (C(9)), 103.23 (C(6)), 69.10 (C(10)), 44.75 (C(4)), 38.87 (C(5)), 32.11 (C(7)), 31.42 (C(11)), 19.12 (C(12)), 18.23 (CH_3), 13.74 (CH_3).

IR: (CCl_4)

3020 (m), 3004 (s), 2962 (s), 2935 (s), 2875 (m), 1613 (s), 1455 (w), 1281 (m), 1234 (m), 1120 (s), 881 (s), 824 (m).

MS: (CI)

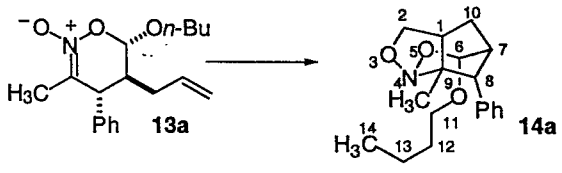
305 (M^++2, 21), 304 (M^++ 1, 100), 230 (22), 202 (18), 173 (13), 171 (17), 145 (32), 91 (13), 86 (29), 57 (53).

Data for **13d**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.31-7.25 (m, 5 H, Ph), 5.73-5.63 (m, 1 H, HC(8)), 5.17 (d, J = 2.9, 1 H, HC(6)), 5.04 (d, J = 10.0, 1 H, $H_aC(9)$), 4.95 (dd, J = 17.1, 12, 1 H, $H_bC(9)$), 4.06 (dt, J = 9.3, 6.4, 1 H, $H_aC(10)$), 3.70 (dd, J = 8.8, 1.2, 1 H, HC(4)), 3.47 (dt, J = 9.3, 6.7, 1 H, $H_bC(10)$), 2.54-2.47 (m, 1 H, HC(5)), 2.04-1.97 (m, 1 H, $H_aC(7)$), 1.87 (d, J = 1.2, 3 H, H_3C), 1.66-1.51 (m, 3 H, $H_2C(11)$, $H_bC(7)$), 1.38-1.24 (m, 2 H, $H_2C(12)$), 0.89 (t, J = 7.3, 3 H, $H_3C(13)$).

***rel*-(1*R*,6*S*,7*S*,8*R*,9*S*)-6-Butyloxy-9-methyl-8-phenyl-4-aza-3,5-dioxatricyclo[5.2.1.0^{4,9}]decane (14a)**



Data for **14a**

^{1}H NMR: (400 MHz, C_6D_6)

7.68-7.66 (m, 2 H, Ph), 7.26-7.22 (m, 2 H, Ph), 7.13-7.09 (m, 1 H, Ph), 4.69 (d, J = 1.0, 1 H, HC(6)), 4.05 (t, J = 8.3, 1 H, $H_aC(2)$), 3.79 (dd, J = 8.0, 3.7, 1 H, $H_bC(2)$), 3.72 (dt, J = 9.3, 6.5, 1 H, $H_aC(11)$), 3.06 (dt, J = 9.3, 6.4, 1 H, $H_bC(11)$), 2.70 (d, J = 4.5, 1 H, HC(8)), 2.33 (t, J = 5.2, 1 H, HC(7)), 1.95-1.90 (m, 1 H, HC(1)), 1.48 (ddd, J = 13.2, 10.3, 6.0, 1 H, $H_aC(10)$), 1.22-1.14 (m, 5 H, $H_2C(12)$, H_3C), 1.03-0.93 (m, 3 H, $H_2C(13)$, $H_bC(10)$), 0.71 (t, J = 7.5, 3 H, $H_3C(14)$).

^{13}C NMR: (100.6 MHz, C_6D_6)

138.43 (Ph), 130.94 (Ph), 128.48 (Ph), 126.35 (Ph), 106.32 (C(6)), 81.07 (C(9)), 77.68 (C(2)), 68.06 (C(11)), 51.50 (C(8)), 49.16 (CH)), 45.66 (CH), 35.45 (CH_2), 32.09 (CH_2), 22.59 (CH_3), 19.55 (C(13)), 14.17 (C(14)).

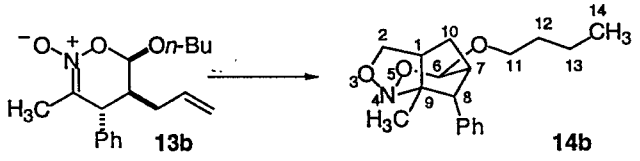
IR: (CCl_4)

2959 (s), 2935 (s), 2872 (s), 1606 (w), 1498 (w), 1457 (w), 1379 (w), 1360 (w), 1123 (m), 1106 (m), 1083 (w), 1004 (w), 922 (w), 877 (w), 841 (w).

MS: (CI)

305 (M^++2, 23), 304 (M^++ 1, 100), 231 (15), 230 (82), 212 (14), 202 (38), 171 (31).

rel-(1*R*,6*R*,7*S*,8*R*,9*S*)-6-Butyloxy-9-methyl-8-phenyl-4-aza-3,5-dioxatricyclo[5.2.1.0^{4,9}]decane (14b)



Data for **14b**

^{1}H NMR: (400 MHz, C_6D_6)

7.67 (d, J = 7.6, 2 H, Ph) 7.24-7.20 (m, 2 H, Ph), 7.12-7.08 (m, 1 H, Ph), 4.67 (d, J = 5.4, 1 H, HC(6)), 4.10 (d, J = 6.8, 2 H, $H_2C(2)$), 3.76 (dt, J = 9.5, 6.6, 1 H, $H_aC(11)$), 3.00 (dt, J = 9.5, 6.4, 1 H, $H_bC(11)$), 2.77 (d, J = 4.2, 1 H, HC(8)), 2.33 (q, J = 4.9, 1 H, HC(7)), 2.13-2.08 (m, 1 H, HC(1)), 1.98 (d, J = 12.7, 1 H, $H_aC(10)$), 1.42-1.30 (m, 3 H, $H_2C(12)$, $H_bC(10)$), 1.25-1.15 (m, 2 H, $H_2C(13)$), 0.77 (t, J = 7.3, 3 H, $H_3C(14)$).

^{13}C NMR: (100.6 MHz, C_6D_6)

137.00 (Ph), 130.46 (Ph), 128.44 (Ph), 126.78 (Ph), 101.40 (C(6)), 79.85 (C(9)), 77.27 (C(2)), 68.28 (C(11)), 53.27 (C(8)), 49.86 (CH)), 45.79 (CH), 32.06 (CH_2), 30.43 (CH_2), 22.06 (CH_3), 19.66 (C(13)), 13.95 (C(14)).

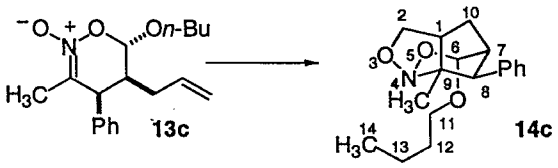
IR: (CCl_4)

2960 (s), 2935 (s), 2892 (m), 2875 (s), 1498 (w), 1456 (w), 1452 (w), 1128 (m), 1090 (s), 852 (m).

MS: (CI)

305 (M^++2, 24), 304 (M^++ 1, 100), 231 (13), 230 (67), 212 (14), 202 (29), 171 (49), 117 (17), 96 (12), 91 (15), 57 (24).

***rel*-(1*R*,6*S*,7*S*,8*S*,9*S*)-6-Butyloxy-9-methyl-8-phenyl-4-aza-3,5-dioxatricyclo[5.2.1.0^{4,9}]decane (14c)**



Data for **14c**

^{1}H NMR: (400 MHz, C_6D_6)

7.12-7.02 (m, 5 H, Ph), 4.67 (d, J = 2.4, 1 H, HC(6)), 4.26-4.24 (m, 2 H, HC(8), $H_aC(2)$), 4.11 (t, J = 7.8, 1 H, $H_bC(2)$), 4.04 (dt, J = 9.6, 6.7, 1 H, $H_aC(11)$), 3.39 (dt, J = 9.5, 6.6, 1 H, $H_bC(11)$), 2.14-2.07 (m, 3 H, HC(1), HC(7), $H_aC(10)$), 1.62-1.55 (m, 2 H, $H_2C(12)$), 1.43-1.24 (m, 3 H, $H_2C(13)$, $H_aC(10)$), 1.04 (s, 3 H, H_3C), 0.86 (t, J = 7.3, 3 H, $H_3C(14)$).

^{13}C NMR: (100.6 MHz, C_6D_6)

140.90 (Ph), 129.06 (Ph), 128.77 (Ph), 126.86 (Ph), 106.08 (C(6)), 87.92 (C(9)), 79.63 (C(2)), 67.70 (C(11)), 47.70 (CH), 46.04 (CH)), 44.66 (C(7)), 36.08 (CH_2), 32.14 (CH_2), 20.01 (CH_3), 19.77 (C(13)), 14.09 (C(14)).

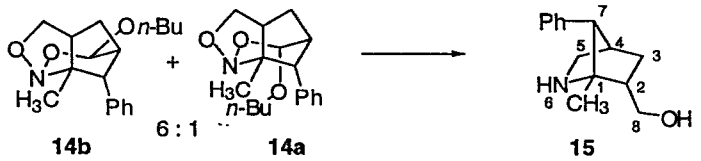
IR: (CCl_4)

3032 (w), 2959 (s), 2938 (s), 2874 (m), 1603 (w), 1468 (w), 1457 (w), 1378 (w), 1344 (w), 1247 (w), 1176 (m), 1111 (m), 1096 (s), 1078 (s), 1034 (m), 939 (m), 871 (w), 823 (w).

MS: (CI)

305 (M^++2, 19), 304 (M^++ 1, 89), 232 (16), 231 (18), 230 (100), 212 (20), 203 (17), 202 (91), 171 (16), 169 (12), 143 (11), 123 (27), 117 (46), 57 (89).

***rel*-(1*R*,2*S*,4*R*,7*S*)-2-Hydroxymethyl-1-methyl-7-phenyl-6-aza-bicyclo[2.2.1]hexane (15)**



14b 6 : 1 **14a** **15**

Data for **15**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.34-7.30 (m, 2 H, Ph), 7.25-7.21 (m, 3 H, Ph), 4.43 (s, *1* H, NH), 4.18 (dd, *J* = 11.6, 2.3, 1 H, $H_aC(8)$), 3.71 (dd, *J* = 11.6, 2.9, 1 H, $H_bC(8)$), 3.41 (dt, *J* = 10.3, 3.4, 1 H, $H_aC(5)$), 2.89 (d, *J* = 10.5, 1 H, $H_bC(5)$), 2.81 (s, 1 H, HC(7)), 2.66 (t, *J* = 3.9, 1 H, HC(4)), 2.04-1.96 (m, 1 H, $H_aC(3)$), 1.89-1.83 (m, 1 H, HC(2)), 1.78 (dd, *J* = 11.5, 5.1, 1 H, $H_aC(3)$), 1.35 (s, 3 H, H_3C).

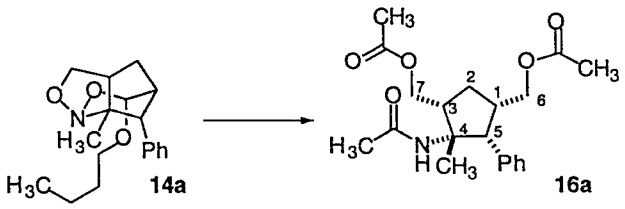
^{13}C NMR: (100.6 MHz, $CDCl_3$)

137.78 (Ph), 128.59 (Ph), 128.26 (Ph), 126.41 (Ph), 69.24 (C(1)), 62.25 (C(8)), 57.97 (C(7)), 51.54 (C(5)), 46.37 (C(2)), 42.05 (C(4)), 31.67 (C(3)), 16.59 (CH_3).

IR: ($CHCl_3$)

3689 (br), 3583 (br), 3011 (s), 2997 (s), 2966 (s), 2896 (s), 1603 (w), 1500 (m), 1474 (m), 1453 (s), 1395 (m), 1132 (m), 1102 (s), 980 (s), 830 (s).

[(1*S*,3*R*,4*S*,5*R*)-4-(Acetylamino)-4-methyl-5-phenyl]-1,3-cyclopentane-dimethanol Diacetate (16a)



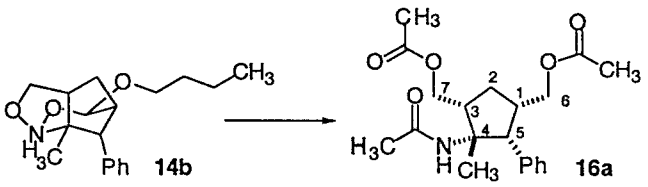
Data for **16a**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.34-7.30 (m, 2 H, Ph), 7.28-7.24 (m, 1 H, Ph), 7.21-7.19 (m, 2 H, Ph), 5.73 (s, 1 H, NH), 4.40 (dd, *J* = 11.3, 6.1, 1 H, $H_aC(7)$), 4.23 (dd, *J* = 11.5, 7.5, 1 H, $H_bC(7)$), 3.79 (d, *J* = 6.4, 2 H, $H_2C(6)$), 3.35 (d, *J* = 9.0, 1 H, HC(5)), 2.81-2.70

(m, 1 H, HC(1)), 2.49-2.41 (m, 1 H, HC(3)), 2.19-1.12 (m, 1 H, $H_aC(2)$), 2.10 (s, 3 H, H_3C), 1.79 (s, 3 H, H_3C), 1.71 (s, 3 H, H_3C), 1.71-1.64 (m, 1 H, $H_bC(2)$).

[(1*S*,3*R*,4*S*,5*R*)-4-(Acetylamino)-4-methyl-5-phenyl]-1,3-cyclopentane-dimethanol Diacetate (16a)



Data for **16a**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.34-7.30 (m, 2 H, Ph), 7.28-7.24 (m, 1 H, Ph), 7.21-7.19 (m, 2 H, Ph), 5.73 (s, 1 H, NH), 4.40 (dd, J = 11.3, 6.1, 1 H, $H_aC(7)$), 4.23 (dd, J = 11.5, 7.5, 1 H, $H_bC(7)$), 3.79 (d, J = 6.4, 2 H, $H_2C(6)$), 3.35 (d, J = 9.0, 1 H, HC(5)), 2.81-2.70 (m, 1 H, HC(1)), 2.49-2.41 (m, 1 H, HC(3)), 2.19-1.12 (m, 1 H, $H_aC(2)$), 2.10 (s, 3 H, H_3C), 1.79 (s, 3 H, H_3C), 1.71 (s, 3 H, H_3C), 1.71-1.64 (m, 1 H, $H_bC(2)$).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

170.80 (C=O), 170.34 (C=O), 169.34 (C=O), 136.69 (Ph), 129.91 (Ph), 128.37 (Ph), 127.11 (Ph), 65.10 (C(6)), 64.64 (C(7)), 63.73 (C(4)), 60.21 (C(5)), 49.11 (C(3)), 39.36 (C(1), 31.97 (C(2)), 28.10 (CH_3), 24.24 (CH_3), 20.90 (CH_3), 20.82 (CH_3).

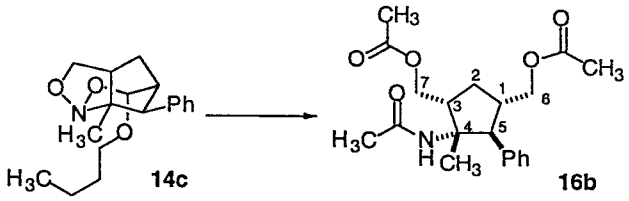
IR: (CCl_4)

3425 (w) 2966 (w), 2939 (w), 1745 (s), 1692 (m), 1521 (w), 1497 (m), 1440 (w), 1366 (m), 1274 (w), 1059 (m), 1235 (s), 1033 (m), 813 (w).

MS: (FAB)

363 (M^++2, 15), 362 (M^++1, 67), 303 (21), 302 (100), 183 (15), 155 (32), 153 (17), 152 (21), 135 (37), 121 (14), 119 (59), 103 (34).

[(1*S*,3*R*,4*S*,5*S*)-4-(Acetylamino)-4-methyl-5-phenyl]-1,3-cyclopentane-dimethanol Diacetate (16b)



Data for **16b**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.35-7.31 (m, 2 H, Ph), 7.28-7.24 (m, 1 H, Ph), 7.17-7.14 (m, 2 H, Ph), 5.43 (s, 1 H, NH), 4.16 (ABX, J_{ab} = 11.0, J_{ax} = 5.6, 1 H, $H_aC(7)$), 4.16 (ABX, J_{bx} = 7.4, 1 H, $H_bC(7)$), 4.07 (ABX, J_{ab} = 10.2, J_{ax} = 3.5, 1 H, $H_aC(6)$), 3.91 (ABX, J_{bx} = 6.3, 1 H, $H_bC(7)$), 3.42 (d, J = 11.2, 1 H, HC(5)), 2.73-2.63 (m, 1 H, HC), 2.58-2.51 (m, 1 H, HC), 2.23-2.15 (m, 1 H, $H_aC(2)$, 2.07 (s , 3 H, CH_3), 1.92 (s , 3 H, CH_3), 1.82 (s , 3 H, CH_3), 1.70-1.62 (m, 1 H, $H_bC(2)$), 1.06 (s , 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

171.03 (C=O), 171.00 (C=O), 169.90 (C=O), 138.11 (Ph), 128.95 (Ph), 128.50 (Ph), 127.19 (Ph), 66.95 (C(6)), 65.43 (C(7)), 63.86 (C(4)), 54.52 (C(5)), 46.59 (C(3)), 39.56 (C(1)), 30.20 (C(2)), 24.22 (CH_3), 23.47 (CH_3), 21.04 (CH_3), 20.60 (CH_3).

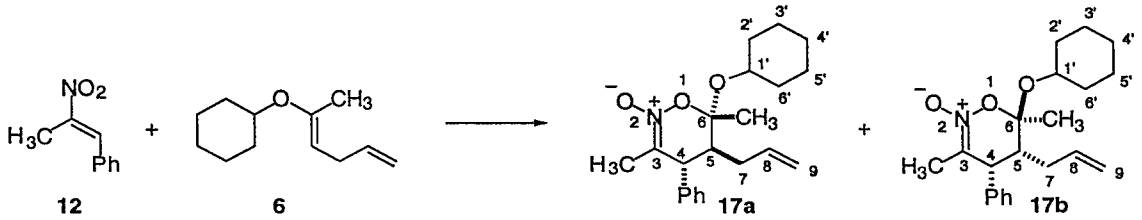
IR: (CCl_4)

3441 (w) 2954 (w), 1742 (s), 1686 (s), 1683 (s), 1499 (m), 1454 (m), 1366 (s), 1233 (s), 1033 (m).

MS: (FAB)

363 (M^++2, 18), 362 (M^++1, 78), 303 (20), 302 (100), 184 (17), 183 (81), 182 (19), 155 (13), 135 (12), 119 (18), 103 (14).

rel-(4_R_,5_S_,6_S_)-6-Cyclohexyloxy-3,6-dimethyl-4-phenyl-5-(2-propenyl)-5,6-dihydro-4_H_-[1,2]-oxazine _2_-Oxide (17a) and **_rel_-(4_R_,5_R_,6_R_)-6-Cyclohexyloxy-3,6-dimethyl-4-phenyl-5-(2-propenyl)-5,6-dihydro-4_H_-[1,2]-oxazine _2_-Oxide (17b)**



Data for **17a**

^{1}H NMR: (499.7 MHz, $CDCl_3$)

7.35-7.28 (m, 3 H, Ph), 7.20-7.18 (m, 2 H, Ph), 5.72-5.63 (m, 1 H, HC(8)), 4.94-4.90 (m, 2 H, H_2C(9)), 4.06-4.01 (m, 1 H, HC(1')), 3.47 (d, J = 10.2, 1 H, HC(4)), 2.25-2.12 (m, 3 H, H_2C(7),HC(5)), 1.83-1.68 (m, 7 H), 1.58-1.19 (m, 9 H).

^{13}C NMR: (125.7 MHz, $CDCl_3$)

139.47 (Ph), 136.07 (C(8)), 129.04 (Ph), 128.99 (Ph), 127.73 (Ph), 124.48 (C(3)), 116.69 (C(9)), 106.89 (C(6)), 70.87 (C(1')), 48.25 (C(5)), 47.69 (C(4)), 33.89 (CH_2), 33.57 (CH_2), 32.80 (C(7)), 25.51 (CH_2), 24.03 (CH_2, CH_2), 20.96 (CH_3), 17.24 (CH_3).

IR: (Neat)

2934 (s), 2856 (m), 1621 (s), 1453 (w), 1271 (s), 1237 (s), 1169 (w), 841 (m).

MS: (FAB)

345 (M^++2, 24), 344 (M^++ 1, 100)), 328 (8), 231 (24), 171 (8), 129 (16).

Data for **17b**

^{1}H NMR: (499.7 MHz, $CDCl_3$)

7.34-7.31 (m, 2 H, Ph), 7.28-7.26 (m, 1 H, Ph), 7.13-7.12 (m, 2 H, Ph), 5.30-5.22 (m, 1 H, HC(8)), 4.75-4.70 (m, 2 H, H_2C(9)), 4.42 (d, J = 6.0, 1 H, HC(4)), 4.07-4.02 (m, 1 H, HC(1')), 2.11-2.00 (m, 3 H, H_2C(7),HC(5)), 1.95 (d, J = 1.3, 3 H, H_3C), 1.79-1.67 (m, 4 H), 1.53-1.49 (m, 4 H), 1.41-1.15 (m, 5 H).

^{13}C NMR: (125.7 MHz, $CDCl_3$)

137.25 (Ph), 137.05 (C(8)), 129.70 (Ph), 128.67 (Ph), 127.33 (Ph), 123.29 (C(3)), 115.58 (C(9)), 107.37 (C(6)), 70.66 (C(1')), 46.27 (C(4)), 44.54 (C(5)), 34.31 (CH_2), 33.64 (CH_2), 30.68 (C(7)), 25.42 (CH_2), 24.30 (CH_2), 24.24 (CH_2), 20.49 (CH_3), 18.24 (CH_3).

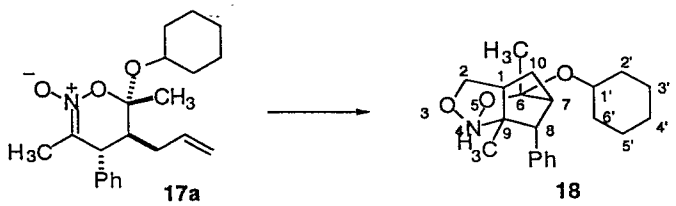
IR: (Neat)

2934 (s), 2856 (m), 1612 (m), 1453 (w), 1285 (w), 1244 (m), 1180 (m), 1024 (w), 913 (m), 830 (m).

MS: (FAB)

345 (M^++2, 25), 344 (M^++ 1, 100)), 362 (16), 244 (21), 231 (14), 202 (33), 201 (10), 171 (15), 129 (14), 119 (13), 117 (20), 107 (15).

***rel*-(1*R*,6*S*,7*S*,8*R*,9*S*)-6-Cyclohexyloxy-6,9-dimethyl-8-phenyl-4-aza-3,5-dioxatricyclo[5.3.1.0^{4,9}]decane (18)**



Data for **18**

^{1}H NMR: (499.7 MHz, C_6D_6)

7.61 (bs, 2 H, Ph), 7.21-7.18 (m, 2 H, Ph), 7.08-7.05 (m, 1 H, Ph), 4.28 (dd, J = 6.8, 3.5, 1 H, $H_aC(2)$), 4.09 (dd, J = 9.1, 6.8, 1 H, $H_bC(2)$), 3.86-3.80 (m, 1 H, HC(1')), 2.82 (d, J = 4.0, 1 H, HC(8)), 2.33-2.17 (m, 4 H, HC(7), $H_bC(2')$, $H_aC(6')$, HC(1)), 1.66-1.42 (m, 4 H, $H_aC(10)$, $H_bC(6')$), 1.35-1.24 (m, 6 H, $H_bC(10)$,$H_bC(2')$, H_3C), 1.19-1.03 (m, 3 H), 0.79 (s, 3 H, H_3C).

^{13}C NMR: (125.7 MHz, C_6D_6)

139.66 (Ph), 130.81 (Ph), 128.31 (Ph), 126.57 (Ph), 102.86 (C(6)), 78.36 (C(9)), 77.48 (C(2)), 70.59 (C(1')), 54.26 (C(8)), 51.85 (C(7)), 50.98 (C(1)), 35.07 (C(10)), 33.92 (C(2')), 31.26 (C(6')), 25.98 (CH_2), 25.88 (CH_3), 24.85 (CH_2), 24.68 (CH_2), 21.97 (CH_3).

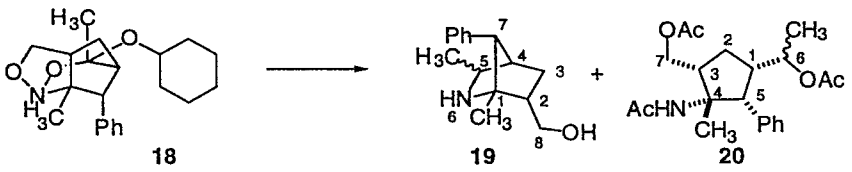
IR: (Neat)

3011 (w), 2994 (w), 2937 (s), 2858 (w), 1497 (w), 1450 (w), 1160 (m), 1142 (w), 1103 (m), 1047 (w), 823 (m).

MS: (FAB)

344 (M^++1, 68), 262 (64), 244 (56), 202 (51), 171 (100), 143 (14), 117 (32).

rel-(1_R_,2_S_,4_R_,5_R_,7_S_)-2-Hydroxymethyl-1,5-dimethyl-7-phenyl-6-aza-bicyclo[2.2.1]hexane and **_rel_-(1_R_,2_S_,4_S_,5_S_,7_S_)-2-Hydroxymethyl-1,5-dimethyl-7-phenyl-6-aza-bicyclo[2.2.1]hexane (19); _rel_-[(1_S_,3_R_,4_R_,5_R_,6_R_)-4-(Acetylamino)-4,6-dimethyl-5-phenyl]-1,3-cyclopentanedimethanol Diacetate** and**_rel_-[(1_S_,3_R_,4_S_,5_R_,6_S_)-4-(Acetylamino)-4,6-dimethyl-5-phenyl]-1,3-cyclopentanedimethanol Diacetate (20)**



Data for **19**

^{1}H NMR: (499.7 MHz, C_6D_6)

7.14-7.04 (m, 5 H, Ph), 4.51 (dd, J = 11.2, 6.6, 0.59 H, $H_aC(8)$), 4.31-4.21 (m, 1.41 H, $H_bC(8)$, $H_aC(8)$, HC(5)), 3.96 (dd, J = 11.2, 9.2, 0.41 H, $H_bC(8)$), 3.44-3.41 (m, 0.59 H, HC(5)), 2.46 (s, 0.59 H, HC(7)), 2.40 (s, 0.41 H, HC(7)), 2.09-2.03 (m, 0.59 H, HC(4)), 1.97 (s, 1.23 H, H_3C), 1.95-1.88 (m, 2.18 H, HC(4), H_3C), 1.78 (s, 1.77 H, H_3C), 1.72 (s, 1.77 H, H_3C), 1.64-1.57 (m, 1.82 H, $H_aC(3)$, H_3C), 1.49-1.31 (m, 2 H, $H_aC(3)$,$H_bC(3)$, $H_bC(3)$, HC(2)), 1.26 (d, ***J*** = , 1.77 H, H_3C), 1.10 (dd, J = 13.3, 4.8, 0.41 H, HC(2)), 0.79 (d, J = 6.2, 1.23 H, H_3C).

MS: (FAB)

317 (M^++2, 22), 316 (M^++1, 100), 214 (9), 119 (12).

Data for **20**

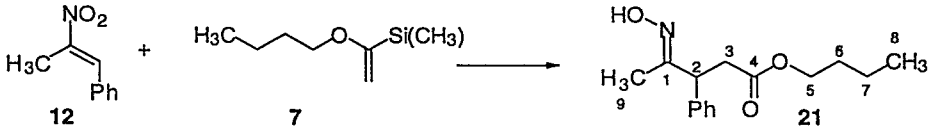
^{1}H NMR: (499.7 MHz, C_6D_6)

7.12-7.02 (m, 5 H, Ph), 5.74 (s, 0.12 H, N*H*), 5.25 (s, 0.88 H, N*H*), 4.91 (t, *J* = 6.6, 0.12 H, HC(6)), 4.54 (dd, *J* = 11.5, 6.0, .012 H, $H_aC(7)$), 4.47-4.41 (m, 1.76 H, HC(6), $H_aC(7)$), 4.29 (dd, *J* = 11.3, 7.3, 0.88 H, $H_bC(7)$), 4.25 (dd, *J* = 11.3, 7.5, 0.12 H, $H_bC(7)$), 3.34 (d, *J* = 7.9, 0.88 H, HC(5)), 2.92 (d, *J* = 9.5, 0.12 H, HC(5)), 2.32-2.24 (m, 1.76 H, HC(3), HC(1)), 2.15-2.08 (m, 0.24 H, HC(10), HC(1)), 1.89 (s, 0.36 H, H_3C), 1.79 (s, 2.64 H, H_3C), 1.72 (s, 2.64 H, H_3C), 1.64-1.54 (m, 1.36 H), 1.51 (s, 2.64 H, H_3C), 1.46-1.35 (m, 0.9 H), 1.26 (s, 2.64 H, H_3C), 1.02 (d, *J* = 6.0, 2.64 H, H_3C), 0.95 (d, *J* = 6.2, 0.36 H, H_3C), 0.91-0.86 (m, 0.88H, $H_bC(2)$).

MS: (FAB)

377 (M^++2, 11), 376 (M^++1, 42), 317 (22), 316 (100), 256 (16), 197 (19), 196 (10), 119 (15).

4-Hydroxyimino-3-phenyl-pentanoic Acid Butyl Ester (21)



Data for **21**

^{1}H NMR: (499.7 MHz, $CDCl_3$)

7.33-7.30 (m, 2 H, Ph), 7.27-7.23 (m, 2 H, Ph), 4.07-3.96 (M, 3 H, HC(2), $H_2C(5)$), 3.04 (dd, *J* = 15.9, 8.6, 1 H, $H_aC(3)$), 2.65 (dd, *J* = 15.9, 6.9, 1 H, $H_bC(3)$), 1.76 (s, 3 H, $H_3C(9)$), 1.56-1.50 (m, 2 H, $H_2C(6)$), 1.33-1.25 (m, 2 H, $H_2C(7)$), 0.88 (t, *J* = 7.5, 3 H, $H_3C(8)$).

^{13}C NMR: (125.7 MHz, $CDCl_3$)

172.06 (C=O), 158.37 (C(1)), 139.83 (Ph), 128.77 (Ph), 128.06 (Ph), 127.32 (Ph), 64.37 (C(5)), 48.02 (C(2)), 38.09 (C(3)), 30.55 (C(6)), 18.99 (C(7)), 13.63 (C(9)), 13.53 (C(8)).

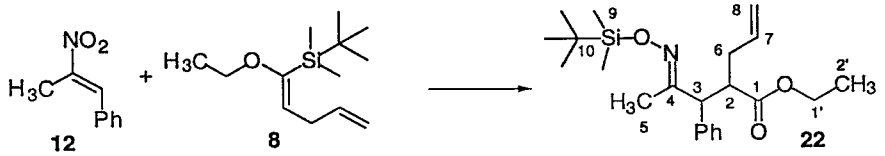
IR: ($CHCl_3$)

3504 (s), 3475 (s), 3420 (s), 3401 (s), 3361 (s), 2961 (w), 2934 (w), 2848 (w), 1726 (w), 1653 (w), 1636 (w), 1602 (w), 1288 (w), 1218 (w), 1211 (w), 1166 (w).

MS: (FAB)

265 (M^++2, 17), 264 (M^++ 1, 100)), 190 (35).

4-[Dimethyl-(1,1-dimethylethyl)]-silyloxyimino-2-(3-propenyl)-3-phenyl-pentanoic Acid Ethyl Ester (22)



Data for **22**

^{1}H NMR: (499.7 MHz, $CDCl_3$)

7.27-1.20 (m, 5 H, Ph), 5.81-5.73 (m, 1 H, HC(7)), 5.05 (dd, J = 17.0, 1.5, 1 H, $H_aC(8)$), 5.00 (dd, J = 11.2, 0.9, 1 H, $H_bC(8)$), 3.81-3.75 (m, 2 H, $H_2C(1')$), 3.61 (d, J = 11.5, 1 H, HC(3)), 3.32-3.27 (m, 1 H, HC(2)), 2.59-2.55 (m, 1 H, $H_aC(6)$), 3.39-3.33 (m, 1 H, $H_bC(6)$), 1.72 (s, 3 H, $H_3C(5)$), 0.96 (s, 9 H, $(H_3C)_3C(10)$), 0.87 (t, J = 7.1, 3 H, $H_3C(2')$) 0.19 (s, 3 H, $H_3C(9)$), 1.72 (s, 3 H, $H_3C(9)$).

^{13}C NMR: (125.7 MHz, $CDCl_3$)

173.98 (C(1)), 160,01 (C(4)), 138.79 (Ph), 135.19 (C(7)), 128.68 (Ph), 128.30 (Ph), 127.19 (Ph), 116.74 (C(8)), 59.91 (C(1')), 54.21 (C(2)), 48.41 (C(3)), 35.65 (C(6)), 26.17 ($H_3C)_3$C), 18.11 (C(10)), 14.13 (C(5)), 13.86 (C(2')), -5.07(C(9)).

IR: (Neat)

2980 (m), 2931 (m), 2856 (m), 1737 (s), 1456 (w), 1389 (w), 1253 (w), 1161 (m), 914 (m), 876 (s), 839 (s).

MS: (FAB)

391 (M^++2, 25), 390 (M^++ 1, 100)), 258 (34), 177 (43), 171, (42), 145 (39), 143 (67), 135 (72), 133 (48), 131 (46), 119, (58), 117 (60).

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