SUPPLEMENTARY MATERIAL

for
the full article
entitled

A Highly Stereoselective Synthesis of Novel *E*-α-Haloenamides via a Mild and Efficient Hydrohalogenation of Ynamides

authored
by

Jason A. Mulder, Kimberly, C. M. Kurtz, Richard P. Hsung,* Heather A. Coverdale, Michael O. Frederick, Lichun Shen, and Craig A. Zificsak

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

Revised Experimental Procedures and Characterization Data

General Procedure for the Hydrohalogenation of Ynamides:

To a solution of ynamide (0.1 mmol) in wet dichloromethane (2-3 mL) was added MgX_2 (1 equiv). The heterogeneous reaction mixture was capped and stirred vigorously at room temperature for 3-48 h until TLC indicated the disappearance of starting material. The reaction mixture was washed (2 mL x 2) with saturated aqueous $Na_2S_2O_3$ solution and then dried over Na_2SO_4. After being filtered through a short column of alumina, the organic phase was concentrated *in vacuo*. The crude product was in general very pure and could be used without further purification. When necessary the crude product was purified by silica gel chromatography (eluent EtOAc in hexanes 0-25%). Most α-haloenamide products are quite stable and can be stored in the refrigerator for months. Some α-iodoenamides are less stable and decompose upon storage in the refrigerator. Careful washing with $Na_2S_2O_3$ and storage over copper metal in the freezer retards α-iodoenamide decomposition.

General Procedure for Sonagashira Coupling of α-Haloenamides with Alkynes:

To a solution of α-bromo- or α-iodoenamide (0.1 mmol) in 0.6 mL distilled toluene and 0.4 mL distilled diisopropylamine was added $Pd(PPh_3)_4$ (0.01 mmol, 11.6 mg). The mixture was stirred at room temperature under $N_{2(g)}$ atmosphere for 2 hours, then alkyne (0.12 mmol) and CuI (0.007 mmol, 1.3 mg) are both added to the reaction. The mixture is then stirred at room temperature for 12 hours. The reaction mixture was washed (1 mL x 2) with saturated aqueous $Na_2S_2O_3$ solution and then dried over Na_2SO_4. After being filtered through a short column of alumina, the organic phase was concentrated *in vacuo*. The crude product was in general very pure and could be used without further purification. When necessary the crude product was purified by silica gel chromatography (eluent EtOAc in Hexanes 0-25%).

α-Bromoenamide 3:

R_f = 0.34 (25% EtOAc in hexanes); orange oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.5 Hz, 3 H), 1.20-1.32 (m, 6 H), 1.35 (m, 2 H), 1.96 (ddd, *J* = 7.5, 7.5, 7.5 Hz, 2 H), 2.14 (dddd, *J* = 7.5, 7.5, 8.0, 8.0 Hz, 2 H), 2.44 (t, *J* = 8.0 Hz, 2 H), 3.54 (br m, 2 H), 5.96 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 18.1, 22.4, 28.3, 28.8, 29.4, 30.6, 31.4, 48.0, 113.4, 135.4, 173.5; IR (thin film) cm^{-1} 2955m, 2926s, 2856m, 1726s, 1384m, 1253m; mass spectrum (LCMS) for $C_{12}H_{21}BrNO$: *m/e* (%relative intensity) 274 (35) $(M+H)^+$, 226 (80), 194 (85), 149 (100).

α-Chloroenamide 4:

R_f = 0.32 (25% EtOAc in hexanes); clear oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3 H), 1.20-1.32 (m, 6 H), 1.35 (m, 2 H), 1.97 (ddd, *J* = 7.5, 7.5, 7.5 Hz, 2 H), 2.13 (dddd, , *J* = 7.5,

7.5, 8.0, 8.0 Hz, 2 H), 2.45 (dd, *J* = 8.0, 8.0 Hz, 2 H), 3.58 (dd, *J* = 7.5, 7.5 Hz, 2 H), 5.74 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 18.3, 22.5, 28.4, 28.8, 30.6, 31.4, 47.4, 123.8, 130.2, 173.7 (missing 1 signal due to overlap); IR (thin film) cm^{-1} 2955m, 2927s, 2857m, 1728s, 1379m, 1251m; mass spectrum (LCMS) for $C_{12}H_{21}ClNO$: *m/e* (%relative intensity) 230 (57) $(M+H)^+$, 194 (43), 168 (22), 105 (100), 73 (68).

α-Iodoenamide 5:

R_f = 0.55 (50% EtOAc in hexanes); clear oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3 H), 1.20-1.30 (m, 6 H), 1.35 (m, 2 H), 1.96 (ddd, *J* = 7.5, 7.5, 7.5 Hz, 2 H), 2.14 (dddd, , *J* = 7.0, 7.0, 7.5, 7.5 Hz, 2 H), 2.38 (dd, *J* = 7.5, 7.5 Hz, 2 H), 3.38 (br m, 2 H), 6.23 (t, *J* = 7.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 17.9, 22.5, 28.3, 28.9, 30.8, 31.0, 31.5, 49.0, 112.4, 145.0, 173.5; IR (thin film) cm^{-1} 2926s, 2855w, 1719s, 1376m, 1250m; mass spectrum (LCMS) for $C_{12}H_{20}INO$: *m/e* (%relative intensity) 322 (70) $(M+H)^+$, 226 (100), 197 (70), 86 (35).

α-Iodoenamide 15:

R_f = 0.75 (50% EtOAc in hexanes); $[\alpha]_D^{23}$ = -36.9 (*c* 0.25, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (dd, *J* = 8.7, 9.6 Hz, 1 H), 4.70 (dd, *J* = 8.7, 8.7 Hz, 1 H), 4.84 (dd, *J* = 8.7, 9.6 Hz, 1H) 7.04-7.07 (m, 1 H), 7.17-7.38 (m, 10 H); ^{13}C (75 MHz, $CDCl_3$) δ 63.2, 69.7, 127.9, 128.0, 128.3, 128.4, 128.6, 129.1, 135.2, 145.4, 155.7 (missing 6 signals due to overlap); IR (thin film) cm^{-1} 2986m, 2305m, 1768 s, 1422m, 1264s; mass spectrum for $C_{17}H_{15}INO_2$ (LCMS) *m/e* (% relative intensity) 392 (35) $(M+H)^+$, 296 (90), 265 (60), 252 (75), 238 (100), 231 (72), 220 (75), 120 (75), 104 (60), 91 (25); HRMS *m/e* calcd. for $C_{17}H_{15}INO_2$ 392.0148, found 392.0136.

α-Iodoenamide 16:

R_f = 0.77 (50% EtOAC in hexanes); $[\alpha]_D^{23}$ = -29.6 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.55 (dd, *J* = 9.9, 13.5 Hz, 1 H), 3.14 (dd, *J* = 3.6, 13.5 Hz, 1 H), 4.02-4.12 (dddd, *J* = 3.6, 8.1, 8.1, 9.0 Hz, 1 H), 4.16 (dd, *J* = 8.1, 9.0 Hz, 1 H), 4.30-4.40 (m, 1 H), 7.10 (m, 1 H), 7.30-7.50 (m, 10 H); ^{13}C (75 MHz, $CDCl_3$) δ 38.0, 59.7, 68.3, 127.9, 128.0, 128.3, 128.4, 128.6, 129.1, 134.7, 145.3, 155.2 (missing 6 signals due to overlap); IR (thin film) cm^{-1} 3054m, 2987m, 2928w, 2305m, 1768m, 1712m, 1422m, 1264s; mass spectrum (LCMS) for $C_{18}H_{17}INO_2$ *m/e* (% relative intensity) 406 (15) $(M+H)^+$, 362 (15), 278 (80), 252 (100), 117 (32); HRMS *m/e* calcd. for $C_{18}H_{17}INO_2$ 406.0309, found 406.0309.

α-Iodoenamide 17:

R_f = 0.71 (50% EtOAc in hexanes) $[\alpha]_D^{23}$ = + 8.2 (*c* 0.073, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.0 Hz, 3 H), 0.95-1.00 (m, 6H), 1.28 (d, *J* = 18.5 Hz, 6 H), 1.48 (m, 2H), 2.15 (m, 1H), 3.77 (dt, *J* = 4.5, 8.0, 8.5 Hz, 1 H), 4.13 (t, *J* = 9 Hz, 1 H), 4.35 (t, *J* = 10.5 Hz, 1 H), 6.29 (dd, *J* =

4.5, 7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 15.6, 18.1, 22.3, 27.9, 29.6, 31.3, 62.2, 63.7, 105.4, 146.2, 153.8 (missing 1 signal due to overlap); IR (thin film) cm^{-1} 2958s, 1773s, 1639w, 1464w, 1391m, 1374m, 1219s. mass spectrum (LCMS) for $C_{13}H_{23}INO_2$ *m/e* (% relative intensity) 352 (20) $(M+H)^+$, 257 (20), 256 (100), 224 (20), 212 (23), 198 (50), 180 (22).

α-Bromoenamide 18:

R_f = 0.39 (25% EtOAc in hexanes); clear oil; $[\alpha]_D^{23}$ = + 34.6 (*c* 0.78, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3 H), 1.06-1.10 (m, 1 H), 1.20-1.31 (m, 3 H), 1.55-1.63 (m, 1 H), 1.95-2.03 (m, 1 H), 4.10-4.13 (m, 2 H), 4.33 (t, *J* = 8.5 Hz, 1 H), 4.98 (ddd, *J* = 6.5, 8.5, 9.5 Hz, 1 H), 5.53 (t, *J* = 7.0 Hz, 1 H), 7.22-7.39 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.3, 29.6, 30.4, 56.4, 58.1, 66.9, 113.4, 127.3, 127.4, 127.6, 127.7, 128.3, 129.1, 137.3, 139.6, 139.7, 155.1 (missing 4 signals due to overlap); IR (thin film) cm^{-1} 3028m, 2955w, 1773s, 1659m, 1494m; mass spectrum (LCMS) for $C_{22}H_{25}BrNO_2$: *m/e* (%relative intensity) 416 (5) $(M+H)^+$, 366 (15), 334 (100), 308 (15), 254 (10), 193 (10).

α-Iodoenamide 19:

R_f = 0.39 (25% EtOAc in hexanes); clear oil; $[\alpha]_D^{23}$ = + 22.4 (*c* 0.85, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.5 Hz, 3 H), 1.04-1.09 (m, 1 H), 1.19-1.29 (m, 3 H), 1.60-1.64 (m, 1 H), 1.98-2.05 (m, 1 H), 4.10 (d, *J* = 9.0 Hz, 1 H), 4.13 (t, *J* = 9.0, 1 H), 4.31 (t, *J* = 9.0 Hz, 1 H), 4.74 (dd, *J* = 9.0, 16.0 Hz, 1 H), 5.82 (t, *J* = 7.0 Hz, 1 H), 7.23-7.40 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 22.3, 30.0, 31.0, 56.0, 59.7, 66.6, 127.3, 127.4, 127.7, 128.0, 128.3, 129.0, 139.5, 139.6, 146.4, 154.8 (missing 5 signals due to overlap); IR (thin film) cm^{-1} 3027w, 2956s, 1770s, 1636m, 1493m; mass spectrum (LCMS) for $C_{22}H_{25}INO_2$: *m/e* (%relative intensity) 462 (12) $(M+H)^+$, 366 (17), 334 (100), 308 (28), 194 (10).

α-Iodoenamide 20:

R_f = 0.46 (25% EtOAc in hexanes); brown oil, $[\alpha]_D^{23}$ = - 43.5 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76 (t, *J* = 7.5 Hz, 3 H), 0.85-1.00 (m, 3 H), 1.00-1.10 (m, 2 H), 1.10-1.20 (m, 1 H), 1.40-1.50 (m, 1 H), 1.70-1.80 (m, 1 H), 3.34 (dd, *J* = 3.0, 18.0 Hz, 1 H), 3.56 (dd, *J* = 8.0, 18.0 Hz, 1 H), 5.12 (d, *J* = 7.5 Hz, 1 H), 5.40 (ddd, , *J* = 3.0, 7.5, 8.0 Hz, 1 H), 6.30 (dd, *J* = 6.0, 9.0 Hz, 1 H), 7.20-7.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.2, 27.6, 30.9, 31.1, 39.5, 65.0, 77.6, 85.3, 125.4, 125.5, 127.6, 130.0, 137.1, 140.4, 147.8, 153.0; IR (thin film) cm^{-1} 2953m, 2927m, 2856w, 1768s, 1371m, 1199m, 1041m; mass spectrum (LCMS) for $C_{17}H_{21}INO_2$: *m/e* (%relative intensity) 398 (20) $(M+H)^+$, 354 (100), 302 (45), 270 (65), 226 (95), 176 (45).

α-Bromoenamide 21:

R_f = 0.46 (25% EtOAc in hexanes); orange oil, $[\alpha]_D^{23}$ = - 56.7 (*c* 0.12, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76 (t, *J* = 7.0 Hz, 3 H), 0.85-1.02 (m, 3 H), 1.02-1.10 (m, 2 H), 1.10-1.20 (m, 1 H), 1.35-1.50 (m, 1 H), 1.70-1.80 (m, 1 H), 3.32 (dd, *J* = 3.0, 18.0 Hz, 1 H), 3.54 (dd, *J* = 8.0, 18.0 Hz, 1 H), 5.32 (d, *J* = 7.5 Hz, 1 H), 5.41 (ddd, , *J* = 3.0, 8.0, 8.0 Hz, 1 H), 6.01 (dd, *J* = 6.0, 9.0 Hz, 1 H), 7.22-7.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.2, 27.7, 29.4, 31.2, 39.4, 63.9, 77.8, 111.5, 125.4, 125.5, 127.6, 130.0, 137.4, 138.4, 140.2, 153.5; IR (thin film) cm^{-1} 2956m, 2926m, 2858m, 1770s, 1375m, 1200m; mass spectrum (LCMS) for $C_{17}H_{21}BrNO_2$: *m/e* (%relative intensity) 350 (30) $(M+H)^+$, 302 (74), 270 (100), 244 (30), 176 (25).

α-Bromoenamide 24:

R_f = 0.39 (25% EtOAc in hexanes); yellow oil; $[\alpha]_D^{23}$ = – 262 (*c* 0.78, CH_2Cl_2); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 3.23 (dd, *J* = 3.0, 18.0 Hz, 1 H), 3.62 (m, 1 H), 5.43 (br m, 1 H), 5.60 (br m, 1 H), 6.90-7.40 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.4, 64.6, 78.0, 114.8, 125.4, 125.6, 127.4, 127.8, 128.4, 130.2, 133.7, 135.9, 136.7, 140.2, 153.4 (missing 3 signals due to overlap); IR (thin film) cm^{-1} 3037w, 2919w, 1769s, 1541m, 1458m, 1373m, 1199m; mass spectrum (LCMS) for $C_{18}H_{15}BrNO_2$: *m/e* (% relative intensity) 358 (9), 356 (9) $M+H^+$, 308 (100), 250 (21).

α-Bromoenamide 25:

R_f = 0.39 (25% EtOAc in hexanes); $[\alpha]_D^{23}$ = – 210 (*c* 0.93, CH_2Cl_2); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 3.20 (dd, *J* = 3.6, 12.0 Hz, 1 H), 3.61 (br m, 1 H), 5.25 (d, *J* = 13.0 Hz, 1 H), 5.56 (br m, 1 H), 6.90-7.40 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.5, 65.7, 77.7, 125.4, 127.3, 127.8, 128.2, 130.2, 135.0, 136.3, 140.3, 144.9, 153.2 (missing 5 signals due to overlap); IR (thin film) cm^{-1} 3047w, 2918w, 1761s, 1541m, 1458m, 1368m, 1197m; mass spectrum (LCMS) for $C_{18}H_{15}INO_2$: *m/e* (%relative intensity) 404 (68) $(M+H)^+$, 308 (100), 250 (28) 176 (11).

α-Bromoenamide 26:

R_f = 0.39 (25% EtOAc in hexanes); mp = 134-138 °C; $[\alpha]_D^{23}$ = - 53.1 (*c* 0.14, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.50 (d, *J* = 6.7 Hz, 3 H), 0.93 (d, *J* = 6.7 Hz, 3 H), 1.91 (m, 1 H), 3.34 (dd, *J* = 3.3, 18.0 Hz, 1 H), 3.57 (dd, *J* = 7.8, 18.0 Hz, 1 H), 5.30 (d, *J* = 7.9 Hz, 1 H), 5.43 (dt, *J* = 3.4, 7.8 Hz, 1 H), 5.86 (d, *J* = 10.5 Hz, 1 H), 7.23-7.39 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 21.5, 29.8, 39.4, 63.8, 77.6, 110.2, 125.4, 125.5, 127.4, 130.0, 137.3, 140.1, 144.9, 153.8; IR (thin film) cm^{-1} 1758s, 1650w, 1382s, 1359m, 763m; mass spectrum (LCMS) for $C_{15}H_{17}BrNO_2$: *m/e* (% relative intensity) 322 (6) $(M+H)^+$, 274 (100), 230 (97), 198 (47), 176 (78); HRMS *m/e* calcd for $C_{15}H_{17}BrNO_2$ $(M + H)^+$ 322.0443, found 322.0459.

α-Bromoenamide 27:

R_f = 0.43 (25% EtOAc in hexanes); mp = 96-100 °C; $[\alpha]_D^{23}$ = - 46.7 (*c* 0.19, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 0.52 (d, *J* = 6.7 Hz, 3 H), 0.96 (d, *J* = 6.7 Hz, 3 H), 1.99 (m, 1 H), 3.38 (dd, *J* = 3.5, 18.0 Hz, 1 H), 3.63 (dd, *J* = 8.0, 18.0 Hz, 1 H), 5.40 (d, *J* = 8.0 Hz, 1 H), 5.60 (dt, *J* = 3.5, 8.0 Hz, 1 H), 6.19 (d, *J* = 10.4 Hz, 1 H), 7.28-7.46 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 21.3, 31.1, 39.4, 64.8, 84.1, 125.4, 125.4, 127.4, 130.0, 137.0, 140.3, 148.3, 153.4, 154.2; IR (thin film) cm^{-1} 1760s, 1634m, 1372s, 757w; mass spectrum (LCMS) for $C_{15}H_{17}INO_2$: *m/e* (% relative intensity) 370 (25) $(M + H)^+$, 326 (43), 274 (93), 230 (87), 199 (100), 176 (58); HRMS *m/e* calcd for $C_{15}H_{17}INO_2$ $(M + H)^+$ 370.0304, found 370.0301.

α-Iodoenamide 28:

R_f = 0.77 (50% EtOAc/hexanes); yellow oil; $[\alpha]_D^{23}$ = - 19.7 (*c* 0.48, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) major rotomer: δ 0.84 (t, *J* = 7.0 Hz, 3 H), 1.79 (d, *J* = 7.0 Hz, 3 H), 2.34–2.61 (m, 4 H), 4.99 (m, 1 H), 5.10 (m, 1 H), 5.87 (m, 1 H), 5.98 (q, *J* = 7.0 Hz, 1 H), 6.22 (q, *J* = 7.0 Hz, 1 H), 7.26-7.47 (m, 5 H); minor rotomer: δ 1.54 (d, *J* = 7.0 Hz, 3 H), 1.62 (d, *J* = 7.0 Hz, 3 H), 2.34–2.61 (m, 4 H), 4.99 (m, 1 H), 5.10 (m, 1 H), 5.65 (q, *J* = 7.0 Hz, 1 H), 5.87 (m, 1 H), 6.44 (q, *J* = 7.0 Hz, 1 H), 7.26-7.47 (m, 5 H); IR (thin film) cm^{-1} 3065m, 2979s, 2934s, 1674s, 1638s, 915m; mass spectrum (LCMS) for $C_{16}H_{21}INO$: *m/e* (% relative abundance) 370(30) $(M+H)^+$, 266(100), 242(35), 160(45), 138(60), 105(90), 87(60).

α-Iodoenamide 29:

R_f = 0.55 (50% EtOAc/hexanes); yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (quintet, *J* = 7 Hz, 2 H), 1.54 (d, *J* = 7.0 Hz, 3 H / 2), 1.55 (m, 2 H / 2), 1.65 (m, 2 H / 2), 1.74 (d, *J* = 7.0 Hz, 3 H / 2), 2.08 (quintet, *J* = 7.5 Hz, 2 H), 2.88 (s, 3 H), 2.90 (s, 3 H), 3.23 (t, *J* = 7.5 Hz, 2 H), 4.95 (m, 1 H), 5.01 (m, 1 H), 5.47 (q, *J* = 7.0 Hz, 1 H / 2), 5.81 (m, 1 H), 5.96 (q, *J* = 7.0 Hz, 1 H / 2); IR (thin film) cm^{-1} 3074w, 2974m, 2929s, 2856s, 1662s.

Trimethylsilyl Enyne 30:

R_f = 0.44 (25% EtOAc/hexanes); yellow oil; $[\alpha]_D^{23}$ = -40.0 (*c* 0.07, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 0.24 (s, 9H), 0.76 (t, *J* = 7.0 Hz, 3 H), 0.88-1.10 (m, 5 H), 1.16-1.26 (m, 1 H), 1.55-1.65 (m, 1 H), 1.98 (dddd, *J* = 6.0, 6.0, 8.0, 16.0 Hz, 1 H), 3.35 (dd, *J* = 2.0, 18.0 Hz, 1 H), 3.47-3.56 (m, 1 H), 5.40-5.44 (m, 2 H), 6.04 (dd, *J* = 6.0, 9.5 Hz, 1 H), 7.20-7.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.1, 13.8, 22.2, 27.7, 28.2, 31.2, 39.4, 64.0, 77.3, 94.0, 100.1, 115.6, 125.3, 127.3, 129.5, 138.3, 140.0, 141.1, 154.0 (missing 3 signals due to overlap); IR (thin film) cm^{-1} 2956m, 2924m, 2857w, 1392m, 844s, 758m; mass spectrum (LCMS) for $C_{22}H_{30}NO_2Si$: *m/e* (%relative intensity) 368 (100) $(M+H)^+$, 324 (5), 296 (8), 252 (20), 205 (10).

Phenyl Enyne 31:

R_f = 0.33 (25% EtOAc/hexanes); orange oil; $[\alpha]_D^{23}$ = - 33.3 (*c* 0.03, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7.5 Hz, 3 H), 0.90-1.32 (m, 6 H), 1.66 (dddd, *J* = 7.0, 8.5, 9.5, 16.0 Hz, 1 H), 2.02 (dddd, *J* = 6.0, 6.0, 8.0, 15.5 Hz, 1 H), 3.38 (dd, *J* = 3.0, 18.0 Hz, 1 H), 3.54 (dd, *J* = 7.0, 18.0 Hz, 1 H), 5.46 (ddd, *J* = 3.0, 8.0, 8.0 Hz, 1 H), 5.51 (d, *J* = 8.0 Hz, 1 H), 6.12 (dd, *J* = 6.0, 9.5 Hz, 1 H), 7.21-7.25 (m, 1 H), 7.28-7.37 (m, 5 H), 7.40-7.43 (br d, *J* = 7.0 Hz 1 H), 7.47-7.52 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.3, 27.9, 28.4, 31.3, 39.6, 64.3, 77.6, 85.0, 88.6, 115.6, 122.4, 125.4, 125.5, 127.5, 128.4, 128.7, 129.7, 131.7, 138.4, 140.2, 141.1, 154.4 (missing 2 signals due to overlap); IR (thin film) cm^{-1} 2954m, 2925m, 2856m, 1759s, 1393m, 1202m, 1042m; mass spectrum (LCMS) for $C_{25}H_{26}NO_2$: *m/e* (%relative intensity) 372 (100) $(M+H)^+$, 341 (1), 328 (40).

Enyne 32:

R_f = 0.19 (25% EtOAc/hexanes); brown oil; $[\alpha]_D^{23}$ = -3.5 (*c* 0.40, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7.5 Hz, 3 H), 0.85-1.80 (m, 6 H), 1.95-2.10 (m, 2 H), 3.36 (dd, *J* = 3.0, 20.5 Hz, 1 H), 3.56 (dd, *J* = 7.5, 20.5 Hz, 1 H), 3.83 (s, 3 H), 5.41 (d, *J* = 9.0 Hz, 1 H), 5.46 (ddd, *J* = 3.0, 9.0, 9.0 Hz, 1 H), 6.38 (dd, *J* = 6.0, 10.5 Hz, 1 H), 7.18-7.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.1, 27.3, 28.7, 31.1, 39.3, 52.8, 64.0, 77.6, 79.9, 81.9, 113.6, 125.0, 125.4, 127.4, 129.7, 137.8, 139.9, 147.3, 148.1, 154.0; IR (thin film) cm^{-1} 2955w, 2927s, 2855m, 2214w, 1761s, 1717m, 1396m, 1262m; ass spectrum (LCMS) for $C_{21}H_{24}NO_4$: *m/e* (%relative intensity) 354 (50) $(M+H)^+$, 322 (100), 294 (18), 252 (24), 115 (50).