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**Methyl 4-*p*-toluenesulfonylamino-2*E*-butenoate (2a)**

To a solution of *p*-toluenesulfonamide (85 mg, 0.5 mmol), triphenylphosphine (12 mg, 0.05 mmol), and sodium acetate (21 mg, 0.25 mmol) in toluene (1 mL) at 85°C was sequentially added 15 mg of acetic acid (0.25 mmol) and 50 mg of methyl 2-butynoate (0.5 mmol). After 18 hours, the reaction mixture was cooled to rt and chromatographed directly (1/1 EtOAc-hexanes) to yield 97 mg (72%) of a white solid (Mp: 100-102°C).

IR ($CDCl_3$): 3396, 3276, 3150, 2957, 1795, 1716, 1663, 1470, 1437, 1384, 1331, 1291, 1158, 1098 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.74 (d,*J* =8.24 Hz, 2H); 7.31 (d,*J* =7.97 Hz, 2H); 6.75 (dt, *J* =15.7, 5.19 Hz, 1H); 5.94(dt, *J* =15.7, 1.86 Hz, 1H); 5.12 (bs, 1H); 3.70 (s, 3H); 3.73-3.68 (m, 2H); 2.42 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 166.1, 143.8, 142.6, 136.6, 129.8, 127.1, 122.54, 122.5. 122.4, 51.7, 43.7, 21.5. Anal. Calc'd for $C_{12}H_{15}NO_4S$: C 53.52, H 5.61, N 5.20. Found: C 53.68, H 5.78, N 5.12.

**Methyl 4-phthalimido-2*E*-butenoate (2b)**

To a solution of phthalimide (53 mg, 0.36 mmol), dppp (31mg, 0.075 mmol), and sodium acetate (21 mg, 0.25 mmol) in toluene (1 mL) at 85°C was sequentially added 15 mg of acetic acid (0.25 mmol) and 50 mg of methyl 2-butynoate (0.5 mmol). After two hours, the reaction mixture was cooled to rt and chromatographed directly (3/1 ether-hexanes) to yield 79 mg (88%) of a white solid (Mp: 104-105°C).

IR ($CDCl_3$): 1718, 1392 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.88-7.85 (m, 2H), 7.77-7.74 (m, 2H), 6.92 (dt, J=15.72, 5.28 Hz, 1H), 5.90 (dt, J=15.72, 1.71 Hz, 1H), 4.44 (dd, J=1.77, 5.28 Hz, 2H), 3.70 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 167.4, 165.9, 140.9, 134.2, 131.2, 131.8, 123.4, 122.6, 51.6, 38.1. Anal. Calc'd for $C_{13}H_{11}NO_4$: C 63.67, H 4.52, N 5.51. Found: C 63.49, H 4.70, N 5.56.

**Methyl 4-tetrahydrophthalimido-2*E*-butenoate (2c)**

(Mp: 71.5-73°C) IR ($CDCl_3$): 2950, 1782, 1704, 1420, 1396, 1333, 1310, 1279, 1196, 1170 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.75 (dt, J=15.78, 5.10 Hz, 1H), 5.92 (t,

J=3.3 Hz, 2H), 5.74 (dt, J=15.72, 1.80 Hz, 1H), 4.19 (dd, J=1.85, 5.16 Hz, 2H), 3.68 (s, 3H), 3.12 Z(t, J=3.02 Hz, 2H), 2.65-2.58 (m, 2H), 2.25-2.17 (m, 2H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 179.3, 165.9, 160.2, 140.1, 127.9, 127.6, 122.4, 51.6, 40.2, 39.1, 39.1, 23.4, 23.2. HRMS: Calc'd for $C_{13}H_{15}NO_4$: 249.1001. Found: 249.1001.

**5-phthalimido-3*E*-pentene-2-one (5a)**

(Mp=74-76°C). IR (film): 1774, 1718, 1682, 1392, 1421, 1361 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.89-7.84 (m, 2H), 7.78-7.73 (m, 2H), 6.74 (dt, J=15.99, 5.22 Hz, 1H), 6.10 (dt, J=16.05, 1.65 Hz, 1H), 4.46 (dd, J=1.74, 5.16 Hz, 2H), 2.24 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 197.5, 167.5, 139.5, 134.3, 131.8, 131.8, 123.5, 38.3, 27.1. HRMS: Calc'd for $C_{13}H_{11}NO_3$: 229.0737. Found: 229.0739.

**5-tetrahydrophthalimido-3*E*-pentene-2-one (5b)**

(Mp: 77-78°C) IR (film): 1776, 1705, 1648, 1636, 1421, 1395, 1361, 1334, 1253, 1170 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.59 (dt, J=16.14, 4.95 Hz, 1H), 5.97 (dt, J=16.08, 1.71 Hz, 1H), 5.94 (t, J=3.17 Hz, 2H), 4.22 (dd, J=1.77, 5.04 Hz, 2H), 3.15 (t, J=2.96 Hz, 2H), 2.67-2.60 (m, 2H), 2.27-2.19 (m, 2H), 2.21 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 197.6, 179.5, 138.6, 131.6, 128.1, 77.2, 39.1, 27.1, 23.4. HRMS: Calc'd for $C_{13}H_{15}NO_3$: 233.1060. Found: 223.1052.

**Methyl 4-N-methoxy-N-pentanamido-2*E*-butenoate (7a)**

IR (film): 2957, 2937, 2873, 1727, 1668, 1437, 1395, 1349, 1309, 1276, 1195, 1175 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.86 (dt, J=15.69, 5.68 Hz, 1H), 5.93 (dt, J=15.72, 1.62 Hz, 1H), 4.34 (dd, J=1.62, 5.56 Hz, 2H), 3.71 (s, 3H), 3.67 (s, 3H) 2.44 (t, J=7.41 Hz, 2H), 1.61 (dt, J=7.36, 5.44 Hz, 2H), 1.35 (ses, J=7.42 Hz, 2H), 0.91 (t, J=7.20 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 175.0, 166.2, 141.9, 123.1, 62.2, 51.6, 46.3, 31.7, 26.5, 22.4, 13.8. HRMS: Calc'd for $C_{11}H_{20}NO_4$ ($MH^+$): 230.1392. Found: 230.1392.

**Methyl 4-N-methoxy-N-isobutanamido-2*E*-butenoate (7b)**

IR (film): 2973, 1726, 1664, 1437, 1307, 1276, 1195, 1174, 998 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.86 (dt, J=15.71, 5.59 Hz, 1H), 5.94 (dt, J=15.72, 1.65 Hz, 1H), 4.34 (dd, J=5.59, 1.68 Hz, 2H), 3.71 (s, 3H), 3.68 (s, 3H) 2.95 (m, 1H), 1.13 (d, J=6.84 Hz, 6H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 178.9, 166.4, 142.1, 123.0, 62.3, 51.6, 46.1, 29.9, 18.9. Anal. Calc'd for $C_9H_{17}NO_4$: C 55.76, H 7.96, N 6.51. Found: C 55.58, H 7.74, N 6.38.

**Alanine derivative 7c**

(Mp=74-75°C).$[\alpha]_D^{22}$ = -21.30 (c=1.07, $CH_2Cl_2$) IR (film): 3355, 2977, 2926, 1717, 1669, 1456, 1367, 1277, 1248, 1172 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.85 (dt, J=15.75, 5.62 Hz, 1H), 5.97 (dt, J=15.74, 1.62 Hz, 1H), 5.20 (d, J=8.09 Hz, 1H), 4.73 (m, 1H), 4.53 (dd, J=17.24, 4.45 Hz, 1H), 4.21 (dd, J=17.25, 5.00 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 1.43 (s, 9H), 1.33 (d, J=6.93 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 174.2, 166.2, 155.3, 141.2, 123.5, 79.6, 62.5, 51.6, 46.6, 45.8, 29.6, 28.2, 18.4. HRMS: Calc'd for $C_{14}H_{25}N_2O_6$ ($MH^+$): 317.1703. Found: 317.1712.

**Valine derivative 9a**

$[\alpha]_D^{22}$ = -11.34 (c=1.07, $CH_2Cl_2$) IR (film): 3349, 2969, 1717, 1662, 1505, 1390, 1275, 1242, 1172, 1040, 1014 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.86 (dt, J=15.70, 5.74 Hz, 1H), 5.99 (dt, J=15.70, 1.55 Hz, 1H), 5.10 (d, J=9.89 Hz, 1H), 4.61-4.54 (m, 2H), 4.20 (dd, J=5.43, 16.69 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 2.02 (ses, J=6.54 Hz, 1H), 1.44 (s, 9H), 0.97 (d, J=6.72 Hz, 3H), 0.90 (d, J=6.87Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 173.3, 166.2, 155.9, 141.3, 123.6, 79.6, 62.4, 55.0, 51.6, 45.7, 30.9, 28.2, 19.4, 17.2. HRMS: Calc'd for $C_{16}H_{29}N_2O_6$ ($MH^+$): 345.2037. Found: 345.2027.

**Tryptophan derivative 9b**

To a solution of 66 mg (0.2 mmol) of the methyl hydroxamic acid ester of N-tBoc-tryptophan, 5 mg (0.02 mmol) of triphenylphosphine, 8 mg (0.1 mmol) of sodium acetate in toluene at 110°C was sequentially added 6 mg of acetic acid (0.1 mmol) and 20 mg of

methyl 2-butynoate (0.2 mmol). After 2h, the reaction mixture was cooled and chromatographed directly on silica (4/1 ether-hexane) to yield 65 mg (76%) of a white solid (mp 135-136°, $[\alpha]_D^{25}$= -4.37 (c=0.88, $CH_2Cl_2$))

IR (film): 3346, 2977, 2955, 1755, 1680, 1458, 1438, 1172, 741 $cm^{-1}$ $^1H$ NMR (300 MHz, $CDCl_3$) δ: 8.25 (bs, 1H), 7.63 (d, J = 7.69 Hz, 1H), 7.34 (d, J = 7.90 Hz, 1H), 7.18-7.11 (m, 2H), 7.00 (d, J = 2.05 Hz, 1H), 6.72-6.67 (m, 1H), 5.84 (d, J = 15.3 Hz, 1H), 5.21 (d, J =8.58 Hz, 1H), 5.07 (d, J =7.36 Hz, 1H), 4.48 (dd, J =4.67, 17.04 Hz, 1H), 4.08 (dd, J =4.88, 16.81 Hz, 1H), 3.74 (s, 3H), 3.57 (s, 3H), 3.21-3.19 (m, 2H), 1.48 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 173.3, 166.4, 155.4, 141.4, 136.2, 127.7, 123.3, 122.1, 119.5, 118.7, 111.2, 110.4, 79.7, 62.2, 51.6, 50.7, 45.8, 45.7, 28.5, 28.4, 28.2, 28.1. Anal. Calc'd for $C_{22}H_{29}N_3O_6$: C, 61.24; H, 6.77; N, 9.74. Found: C, 61.03; H, 7.03; N, 9.48.

**Methionine derivative 9c**

($[\alpha]_D^{25}$= -26.90 (c=3.99, $CH_2Cl_2$)) IR (film): 3342, 2976, 2922, 1715, 1667, 1515, 1436, 1171 $cm^{-1}$ $^1H$ NMR (300 MHz, $CDCl_3$) δ: 6.83 (dt, J =15.7, 5.77 Hz, 1H), 5.96 (dt, J =15.1, 1.49 Hz, 1H), 5.20 (d, J =9.12 Hz, 1H), 4.81-4.76 (m, 1H), 4.51 (dd, J =16.9, 4.67 Hz, 1H), 4.20 (dd, J =17.0, 5.1 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.57-2.53 (m, 2H), 2.07 (s, 3H), 2.05-1.57 (m, 2H), 1.41 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 173.1, 166.1, 155.6, 141.0, 123.7, 79.8, 62.6, 51.6, 49.8, 46.0, 32.0, 30.0, 29.5, 28.2, 15.3. Anal. Calc'd for $C_{16}H_{28}N_2O_6S$: C, 51.05; H, 7.50; N, 7.44. Found: C, 51.27; H, 7.54; N, 7.65.

**Valine derivative 10a**

Mp = 72-74°C. ($[\alpha]_D^{25}$= -8.88 (c=0.88, $CH_2Cl_2$)) IR (tf): 3309, 2955, 2934, 1725, 1677, 1640, 1580, 1366, 1173, 1042, 1018 $cm^{-1}$ $^1H$ NMR (300 MHz, $CDCl_3$) δ: 6.89 (dt, J =15.69, 4.97 Hz, 1H), 6.46 (t, J =4.95 Hz, 1H), 5.91 (dt, J =15.75, 1.80 Hz, 1H), 5.05 (d, J =7.76 Hz, 1H), 4.06-4.04 (m, 2H), 3.90 (dd, J =8.57, 6.59 Hz, 1H), 3.72 (s, 3H), 2.19-2.14 (m, 1H), 1.44 (s, 9H), 0.97 (d, J =6.87 Hz, 3H), 0.93 (d, J =6.07 Hz, 3H).

$^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 172.0, 166.5, 156.1, 144.0, 121.5, 60.2, 51.6, 39.9, 30.3, 29.6, 28.2, 19.3, 17.7. HRMS: Calc'd for $C_{15}H_{26}N_2O_5$: 314.1841. Found: 314.1835.

**Methionine derivative 10c**

($[\alpha]_D^{25}$= -6.88 (c=1.2, $CH_2Cl_2$)) IR (tf): 3315, 2963, 2924, 1715, 1661, 1525, 1261, 1168, 1095, 1024, 800 $cm^{-1}$ $^1H$ NMR (300 MHz, $CDCl_3$) δ: 6.89 (dt, J =15.8, 4.86 Hz, 1H), 6.63 (bs, 1H), 5.92 (dt, J =15.7, 1.86 Hz, 1H), 4.29-4.27 (m, 2H), 4.07-4.04 (m, 2H), 3.72 (s, 3H), 2.61-2.52 (m, 2H), 2.11 (s, 3H), 1.98-1.92 (m, 2H), 1.44 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 171.8, 166.5, 143.9, 121.5, 51.6, 39.9, 30.9, 30.2, 29.6, 28.2, 15.2. HRMS: Calc'd for $C_{15}H_{26}N_2O_5S$: 346.1562. Found: 346.1561.