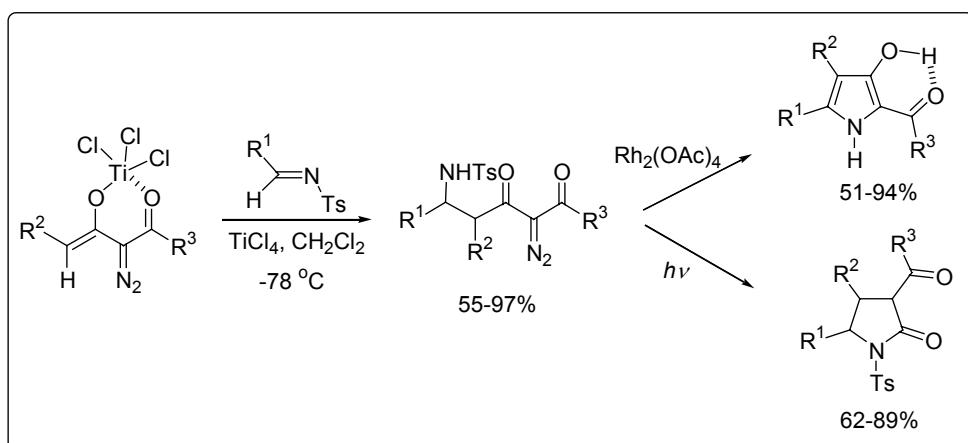


*Supporting Information*

**New Approaches to Polysubstituted Pyrroles and  $\gamma$ -Lactams based on Nucleophilic Addition of Ti(IV) Enolates derived from  $\alpha$ -Diazo- $\beta$ -keto Carbonyl Compounds to *N*-Tosylimines**

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**Ethyl 2-Diazo-3-oxo-5-(*N*-tosyl)amino-5-phenylpentanoate (**3a**).** mp 140-142 °C; IR (KBr) 3223, 2152, 1748, 1625 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.32 (t, *J* = 7.2 Hz, 3H), 2.37 (s, 3H), 3.19 (dd, *J* = 15.6, 5.4 Hz, 1H), 3.36 (dd, *J* = 15.6, 8.0 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.76-4.86 (m, 1H), 5.69 (d, *J* = 7.8 Hz, 1H), 7.14-7.20 (m, 7H), 7.58 (d, *J* = 8.2 Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 14.2, 21.4, 46.3, 54.5, 61.6, 76.2, 126.3, 127.0, 127.4, 128.4, 129.2, 137.4, 140.1, 143.0, 161.1, 189.8; MS *m/z* (FAB) 416 [(M+H)<sup>+</sup>, 13], 388 (3), 344 (2), 261 (11), 245 (69), 219 (20), 181(12), 171 (49), 139 (23), 115 (38), 91 (100), 77 (22), 59 (38), 41 (53). Anal. Calcd for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>5</sub>S: C, 57.82; H, 5.09; N, 10.11. Found: C, 57.85; H, 5.09; N, 10.01.

**Ethyl 2-Diazo-3-oxo-5-(*N*-tosyl)amino-5-(2-methylphenyl)pentanoate (**3b**).** mp 112-114 °C; IR (KBr) 3212, 2151, 1715, 1626 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.31 (t, *J* = 7.2 Hz, 3H), 2.26 (s, 3H), 2.34 (s, 3H), 3.17 (dd, *J* = 15.6, 5.6 Hz, 1H), 3.38 (dd, *J* = 15.6, 8.0 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.76-4.86 (m, 1H), 5.69 (d, *J* = 7.8 Hz, 1H), 7.02-7.18 (m, 6H), 7.53 (d, *J* = 8.2 Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 14.1, 18.8, 21.2, 45.5, 50.6, 61.5, 76.6, 126.0, 126.7, 127.1, 129.0, 130.1, 134.8, 137.3, 138.2, 142.7, 161.0, 189.6; MS *m/z* (FAB) 430 [(M+H)<sup>+</sup>, 16], 402 (21), 274 (99), 259 (62), 185 (71), 155 (97), 129 (48), 118 (55), 91 (100), 77 (46), 45 (66). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>N<sub>3</sub>O<sub>5</sub>S: C, 58.73; H, 5.40; N, 9.78. Found: C, 58.63; H, 5.43; N, 9.67.

**Ethyl 2-Diazo-3-oxo-5-(*N*-tosyl)amino-5-(4-fluorophenyl)pentanoate (**3c**).** mp 143 °C (dec.); IR (KBr) 3235, 2146, 1708, 1629 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.32 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 3.18 (dd, *J* = 15.4, 5.4 Hz, 1H), 3.30 (dd, *J* = 15.5, 7.7 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.74-4.85 (m, 1H), 5.81 (d, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 8.7 Hz, 2H), 7.14 -7.21 (m, 4H), 7.57 (d, *J* = 8.6 Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 14.3, 21.4, 46.2, 54.0, 61.8, 115.0, 115.5, 127.1, 128.1, 128.3, 129.3, 136.0, 137.5, 143.2, 159.6, 161.1, 164.5, 189.8; MS *m/z* (FAB) 434 [(M+H)<sup>+</sup>, 4], 263 (60), 251 (4), 237 (10), 204 (7), 189 (43), 156 (49), 139 (29), 124 (26), 91 (100), 77 (18), 45 (68). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>FN<sub>3</sub>O<sub>5</sub>S: C, 55.42; H, 4.65; N, 9.69. Found: C, 55.44; H, 4.60; N, 9.68.

**Ethyl 2-Diazo-3-oxo-5-(*N*-tosyl)amino-5-(4-chlorophenyl)pentanoate (**3d**).** mp 149-152 °C (dec.); IR (KBr) 3214, 2157, 1719, 1625 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.32 (t, *J* = 7 Hz, 3H), 2.39 (s, 3H), 3.17 (dd, *J* = 15.6, 5.4 Hz, 1H), 3.29 (dd, *J* = 15.6, 7.8 Hz, 1H), 4.28 (q, *J* = 7.0 Hz, 2H), 4.73-4.83 (m, 1H), 5.85 (d, *J* = 7.8 Hz, 1H), 7.15-7.19 (m, 6H), 7.56 (d, *J* = 8.2 Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 14.3, 21.4, 46.0, 54.0, 61.8, 127.1, 127.9, 128.5, 129.3, 133.3, 137.3, 138.6, 143.3, 161.1, 189.7; MS *m/z* (FAB) 450 [(M+H)<sup>+</sup>, 7], 422 (3), 378 (2), 294 (52), 279 (65), 253 (19), 237 (2), 222 (12), 205 (50), 192 (7), 179 (16), 155 (87), 139 (63), 125 (12), 115 (35), 91 (100), 77 (33), 59 (48), 45 (80). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>5</sub>S: C, 53.39; H, 4.48; N, 9.34. Found: C, 53.53; H, 4.48; N, 9.12.

**Ethyl 2-Diazo-3-oxo-5-(*N*-tosyl)amino-5-(3-cyanophenyl)pentanoate (**3e**).** mp 120-121 °C; IR (KBr) 3193, 2232, 2157, 1714, 1619 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 3H), 3.24 (d, *J* = 6.4 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.79-4.89 (m, 1H), 6.03 (d, *J*

= 7.2Hz, 1H), 7.18 (d,  $J$  = 8.2 Hz, 2H), 7.27-7.58 (m, 6H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  14.2, 21.4, 46.1, 53.8, 61.9, 76.8, 112.3, 118.4, 127.0, 129.2, 129.4, 131.0, 131.2, 137.1, 141.7, 143.5, 161.0, 189.3; MS  $m/z$  (FAB) 441[(M+H) $^+$ , 3], 413 (3), 285 (16), 270 (6), 258 (4), 196 (14), 181 (3), 155 (57), 139 (29), 115 (8), 91 (100), 77 (21), 45 (65). Anal. Calcd for  $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$ : C, 57.26; H, 4.58; N, 12.72. Found: C, 57.13; H, 4.61; N, 12.70.

**Ethyl 2-Diazo-3-oxo-5-(*N*-tosyl)amino-5-(4-methoxyphenyl)pentanoate (3f).** mp 107-110 °C; IR (KBr) 3236, 2361, 2143, 1713, 1626  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.32 (t,  $J$  = 7 Hz, 3H), 2.38 (s, 3H), 3.19 (dd,  $J$  = 15.7, 5.5 Hz, 1H), 3.34 (dd,  $J$  = 15.7, 7.8 Hz, 1H), 3.75(s, 3H), 4.28 (q,  $J$  = 7 Hz, 2H), 4.70-4.81 (m, 1H), 5.59 (d,  $J$  = 7.6 Hz, 1H), 6.72(d,  $J$  = 8.4 Hz, 2H), 7.10 (d,  $J$  = 8.4 Hz, 2H), 7.17 (d,  $J$  = 8.3 Hz, 2H), 7.58 (d,  $J$  = 8.3 Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  14.2, 21.3, 46.3, 54.1, 55.1, 61.6, 76.8, 113.7, 127.0, 127.6, 129.2, 132.2, 137.5, 142.9, 158.8, 161.0, 189.9; MS  $m/z$  (FAB) 452 [(M+Li) $^+$ , 20], 275 (56), 249 (11), 201 (27), 155 (23), 91 (100), 47 (66). Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_6\text{S}$ : C, 56.62; H, 5.20; N, 9.43. Found: C, 56.61; H, 5.09; N, 9.49.

**Ethyl 2-Diazo-3-oxo-5-(*N*-tosyl)amino-5-[(E)-cinnamyl]pentanoate (3h).** mp 99-101 °C; IR (KBr) 3231, 2361, 2152, 1710, 1653  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.26 (t,  $J$  = 7.2 Hz, 3H), 2.23 (s, 3H), 3.15-3.19 (m, 2H), 4.23 (q,  $J$  = 7.2 Hz, 2H), 4.35-4.50 (m, 1H), 5.87-5.99 (m, 2H), 6.28 (d,  $J$  = 16.2 Hz, 1H), 7.07-7.25 (m, 7H), 7.72 (d,  $J$  = 8.2 Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 20.9, 44.8, 52.5, 61.3, 76.4, 126.0, 126.9, 127.3, 127.5, 127.9, 129.1, 131.1, 135.7, 137.6, 142.8, 160.7, 189.7; MS  $m/z$  (FAB) 448 [(M+Li) $^+$ , 6], 420 (2), 286 (6), 266 (12), 169 (10), 115 (47), 91 (100), 45 (36). Anal. Calcd for  $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_5\text{S}$ : C, 59.85; H, 5.25; N, 9.52. Found: C, 59.61; H, 5.27; N, 9.42.

**Ethyl 2-Diazo-3-oxo-5-(*N*-tosyl)amino-5-(2-furyl)pentanoate (3i).** mp 120-122 °C; IR (KBr) 3259, 2140, 1710, 1644  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.33 (t,  $J$  = 7.2 Hz, 3H), 2.43 (s, 3H), 3.21 (dd,  $J$  = 16.5, 5.7 Hz, 1H), 3.53 (dd,  $J$  = 16.5, 6.6 Hz, 1H), 4.29 (q,  $J$  = 7.2 Hz, 2H), 4.87-4.98 (m, 1H), 5.61 (d,  $J$  = 9 Hz, 1H), 6.01-6.03 (m, 1H), 6.15-6.18 (m, 1H), 7.16-7.18 (m, 1H), 7.22 (d,  $J$  = 8.0 Hz, 2H), 7.65 (d,  $J$  = 8.0 Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 21.1, 43.4, 48.0, 61.4, 76.5, 106.7, 110.0, 126.7, 129.1, 137.4, 141.5, 142.8, 152.2, 160.8, 189.0; MS  $m/z$  (FAB) 412 [(M+Li) $^+$ , 10], 386 (9), 340 (4), 265 (10), 256 (7), 229 (25), 205 (11), 184 (7), 157 (24), 115 (100), 91 (17), 81 (8), 47 (25), 43 (13). Anal. Calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_6\text{S}$ : C, 53.33; H, 4.72; N, 10.36. Found: C, 53.41; H, 4.64; N, 10.20.

**2-Diazo-1,5-diphenyl-5-(*N*-tosyl)amino-1,3-pentanedione (3j).** oil; IR (film) 3276, 2125, 1642  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3H), 3.32 (dd,  $J$  = 12.0, 5.4 Hz, 1H), 3.46 (dd,  $J$  = 12.0, 8.4 Hz, 1H), 4.93~4.91 (m, 2H), 6.02 (d,  $J$  = 8.1 Hz, 1H), 7.27~7.11 (m, 7H), 7.62~7.46 (m, 7H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.3, 47.3, 54.8, 126.4, 127.0, 127.3, 127.4, 128.4, 128.9, 129.2, 132.9, 136.8, 137.5, 140.1, 142.9, 185.1, 190.7; EI-MS ( $m/z$ , relative intensity): 419

$[(M-28)^+]$ , 6.9], 264 (38), 155 (21), 105 (100), 91 (69), 77 (51). Anal. Calcd for  $C_{24}H_{21}N_3O_4S$ : C, 64.41; H, 4.73; N, 9.39. Found: C, 64.47; H, 4.64; N, 9.19.

**2-Diazo-5-furyl-1-phenyl-5-(*N*-tosyl)amino-1,3-pentanedione (**3k**)**. mp 120-121 °C; IR (KBr) 3281, 2127, 1655, 1636  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  2.36 (s, 3H), 3.33 (dd,  $J = 16.3, 5.2$  Hz, 1H), 3.63 (dd,  $J = 16.3, 7.2$  Hz, 1H), 4.97-5.04 (m, 1H), 5.64-5.71 (br, m, 1H), 6.04 (d,  $J = 2.8$  Hz, 1H), 6.16-6.18 (m, 1H), 7.17 (s, 1H), 7.21 (d,  $J = 8.2$  Hz, 2H), 7.46-7.68 (m, 7H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  21.1, 44.5, 48.2, 83.8, 106.7, 110.0, 126.7, 127.1, 128.7, 129.1, 132.6, 136.6, 137.4, 141.6, 142.8, 152.2, 184.7, 189.9; MS  $m/z$  (FAB) 444  $[(M+Li)^+, 4]$ , 295 (3), 263 (14), 205 (12), 157 (9), 115 (100), 91 (40), 57 (21), 47 (31). Anal. Calcd for  $C_{22}H_{19}N_3O_5S$ : C, 60.40; H, 4.38; N, 9.61. Found: C, 60.39; H, 4.32; N, 9.43.

**(E)-2-Diazo-1,7-diphenyl-5-(*N*-tosyl)aminohept-6-en-1,3-dione (**3l**)**. mp 78-82 °C (decomposed); IR (KBr) 3255, 2240, 1661, 1630  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  2.26 (s, 3H), 3.22 (dd,  $J = 16.3, 4.9$  Hz, 1H), 3.37 (dd,  $J = 16.3, 6.7$  Hz, 1H), 4.39-4.52 (m, 1H), 5.67 (d,  $J = 8.8$  Hz, 1H), 5.95 (dd,  $J = 16, 7$  Hz, 1H), 6.63 (d,  $J = 16$  Hz, 1H), 7.11-7.28 (m, 7 H), 7.24-7.62 (m, 5H), 7.72 (d,  $J = 8.2$  Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  21.0, 46.1, 52.9, 84.0, 126.2, 127.0, 127.1, 127.5, 128.1, 128.7, 129.2, 131.3, 132.6, 135.9, 136.7, 137.7, 142.9, 184.8, 190.6; MS  $m/z$  (FAB) 480  $[(M+Li)^+, 5]$ , 452 (7), 297 (5), 263 (6), 223 (7), 205 (6), 157 (9), 147 (14), 115 (100), 91 (46), 47 (24). Anal. Calcd for  $C_{26}H_{23}N_3O_4S$ : C, 65.95; H, 4.90; N, 8.87. Found: C, 66.01; H, 4.72; N, 8.91.

**3-Diazo-6-phenyl-6-(*N*-tosyl)amino-2,4-hexanedione (**3m**)**. mp 131-132 °C; IR (KBr) 3294, 2362, 2132, 1665, 1628  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  2.33 (s, 3H), 2.37 (s, 3H), 3.17 (dd,  $J = 15.6, 5.5$  Hz, 1H), 3.34 (dd,  $J = 15.6, 7.4$  Hz, 1H), 4.76-4.86 (m, 1H), 5.71 (d,  $J = 7.8$  Hz, 1H), 7.13-7.17 (m, 7H), 7.57 (d,  $J = 8.2$  Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  21.4, 28.0, 47.1, 54.4, 85.0, 126.4, 127.0, 127.6, 128.5, 129.3, 137.3, 139.8, 143.1, 187.2, 189.1; MS  $m/z$  (FAB) 392  $[(M+Li)^+, 28]$ , 372 (14), 366 (25), 349 (14), 315 (12), 307 (32), 285 (4), 265 (18), 247 (2), 223 (28), 205 (10), 189 (4), 157 (27), 121 (39), 115 (100), 91 (10), 59 (9), 47 (24). Anal. Calcd for  $C_{19}H_{19}N_3O_4S$ : C, 59.21; H, 4.97; N, 10.90. Found: C, 59.01; H, 4.80; N, 10.76.

**3-Diazo-6-(4-methoxyphenyl)-6-(*N*-tosyl)amino-2,4-hexanedione (**3n**)**. mp 136-138 °C; IR (KBr) 3193, 2361, 2150, 1676, 1626  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  2.33 (s, 3H), 2.38 (s, 3H), 3.16 (dd,  $J = 15.5, 5.8$  Hz, 1H), 3.31 (dd,  $J = 15.5, 7.2$  Hz, 1H), 3.74 (s, 3H), 4.71-4.81 (m, 1H), 5.71 (d,  $J = 7.4$  Hz, 1H), 6.69 (d,  $J = 9.6$  Hz, 2H), 6.78 (d,  $J = 9.6$  Hz, 2H), 7.16 (d,  $J = 8.4$  Hz, 2H), 7.57 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  21.4, 28.0, 47.1, 54.0, 55.2, 85.0, 113.8, 127.1, 127.6, 129.3, 131.8, 137.4, 143.0, 158.9, 187.3, 189.1; MS  $m/z$  (FAB) 422  $[(M+Li)^+, 20]$ , 365 (18), 223 (28), 157 (30), 115 (100), 47 (23), 45 (15). Anal. Calcd for  $C_{20}H_{21}N_3O_5S$ : C, 57.82; H, 5.09; N, 10.11. Found: C, 57.89; H, 5.03; N, 10.21.

**3-Diazo-6-(3-bromophenyl)-6-(*N*-tosyl)amino-2,4-hexanedione (3o).** mp 125-127 °C; IR (KBr) 3209, 2151, 1669, 1622 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 2.34 (s, 3H), 2.38 (s, 3H), 3.16 (dd, *J* = 15.8, 5.5 Hz, 1H), 3.30 (dd, *J* = 15.8, 7.6 Hz, 1H), 4.72-4.83 (m, 1H), 5.74 (d, *J* = 8 Hz, 1H), 7.02-7.30 (m, 6H), 7.54 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 21.4, 27.8, 46.9, 53.9, 85.1, 122.4, 125.2, 127.0, 129.3, 129.6, 130.0, 130.5, 137.2, 142.0, 143.3, 187.0, 188.9; MS *m/z* (FAB) 472 [(M+Li)<sup>+</sup>, 10], 444 (17), 265 (12), 223 (20), 157 (24), 115 (100), 47 (19), 45 (13); Anal. Calcd for C<sub>19</sub>H<sub>18</sub>BrN<sub>3</sub>O<sub>4</sub>S: C, 49.15; H, 3.91; N, 9.05. Found: C, 49.16; H, 3.87; N, 8.97.

**Ethyl 2-Diazo-4-methyl-3-oxo-5-phenyl-5-(*N*-tosyl)aminopentanoate (3p).** The major isomer: IR (film) 3287, 2983, 2140, 1715, 1654, 1160 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.01 (d, *J* = 6.9, 3H), 1.30 (t, *J* = 7.2, 3H), 2.32 (s, 3H), 4.03-4.23 (m, 1H), 4.27 (q, *J* = 7.2, 2H), 4.48-4.54 (m, 1H), 7.04-7.14 (m, 7H), 7.45-7.48 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.2, 15.3, 21.3, 46.1, 61.1, 61.7, 126.7, 127.2, 128.2, 129.0, 137.9, 139.3, 142.6, 161.5, 195.0; EI-MS (*m/z*, relative intensity): 401 [(M-28)<sup>+</sup>, 5], 337 (33), 260 (65), 155 (57), 91 (100). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>N<sub>3</sub>O<sub>5</sub>S: C, 58.73; H, 5.40; N, 9.78. Found: C, 58.72; H, 5.39; N, 9.57.

**Ethyl 2-Diazo-4-methyl-5-(4-methoxyphenyl)-3-oxo-5-(*N*-tosyl)aminopentanoate (3q).** The major isomer: IR (film) 3278, 2982, 2140, 1715, 1654, 1160 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.98 (d, *J* = 6.9 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.74 (s, 3H), 4.00-4.09 (m, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.46 (t, *J* = 8.4 Hz, 1H), 6.02 (d, *J* = 9.6 Hz, 1H), 6.65 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.1, 15.2, 21.3, 46.2, 55.1, 60.6, 61.6, 113.6, 126.7, 127.9, 129.0, 131.5, 138.0, 142.5, 158.7, 161.6, 195.0; EI-MS (*m/z*, relative intensity): 459 (M<sup>+</sup>, 3), 431 (23), 290 (38), 276 (45), 222 (82), 176 (79), 91 (100). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub>S: C, 57.50; H, 5.48; N, 9.14. Found: C, 57.39; H, 5.50; N, 9.09.

**Ethyl 2-Diazo-3-oxo-4,5-diphenyl-5-(*N*-tosyl)aminopentanoate (3r).** The major isomer: IR (film) 3274, 2142, 1715, 1651 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.24 (t, *J* = 7.2 Hz, 3H), 2.30 (s, 3H), 4.14-4.22 (m, 2H), 4.93-4.99 (m, 1H), 5.33-5.39 (m, 1H), 6.09 (d, *J* = 9.6 Hz, 1H), 6.97-7.38 (m, 14H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 191.1, 160.8, 142.7, 139.0, 137.6, 136.6, 134.4, 129.3, 129.1, 128.3, 128.1, 128.0, 127.5, 127.0; EI-MS (*m/z*, relative intensity): 463 [(M-28)<sup>+</sup>, 6], 399 (61), 308 (64), 260 (44), 176 (100), 131 (57), 91 (50); Anal. Calcd for C<sub>26</sub>H<sub>25</sub>N<sub>3</sub>O<sub>5</sub>S: C, 63.53; H, 5.13; N, 8.55. Found: C, 63.69; H, 5.35; N, 8.21.

**Ethyl 2-Diazo-5-(2-methylphenyl)-3-oxo-4-phenyl-5-(*N*-tosyl)aminopentanoate (3s).** The major isomer: mp 130-131 °C; IR (film) 3276, 2982, 2142, 1716, 1650 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.22 (t, *J* = 7.2 Hz, 3H), 2.15 (s, 3H), 2.29 (s, 3H), 4.10-4.21 (m, 2H), 5.19-5.25 (m, 1H), 5.31-5.34 (d, *J* = 8.1 Hz, 1H), 6.26 (d, *J* = 8.7 Hz, 1H), 6.79-6.82 (m, 1H), 6.92-6.98 (m, 4H), 7.10-7.23 (m, 6H), 7.36 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.1, 19.1, 21.3, 56.6, 56.9, 61.5, 126.0, 126.5, 126.6, 127.6, 128.2, 128.8, 129.3, 130.0, 134.2, 134.9, 137.1,

137.6, 142.4, 160.8, 191.2; EI-MS (*m/z*, relative intensity): 477 [(M-28)<sup>+</sup>, 7], 413 (13), 274 (57), 176 (80), 155 (24), 118 (74), 91 (100). Anal. Calcd for C<sub>27</sub>H<sub>27</sub>N<sub>3</sub>O<sub>5</sub>S: C, 64.14; H, 5.38; N, 8.31. Found: C, 64.11; H, 5.39; N, 8.08.

The minor product: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.22 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 2.47 (s, 3H), 4.15-4.22 (m, 2H), 5.27-5.32 (m, 1H), 5.49 (d, *J* = 10.8 Hz, 1H), 6.96-7.04 (m, 5H), 7.18-7.30 (m, 6H), 7.39-7.41 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.4, 19.4, 21.4, 29.7, 57.7, 61.43, 125.9, 126.9, 127.5, 128.3, 128.9, 129.0, 129.4, 130.4, 134.3, 136.9, 142.5, 160.5, 189.4.

**Ethyl 5-(4-Chlorophenyl)-2-diazo-3-oxo-4-phenyl-5-(N-tosyl)aminopentanoate (3t).** The major product: mp 136-137 °C; IR (film) 3292, 2957, 2137, 1716, 1649 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.22 (t, *J* = 7.2, 3H), 2.40 (s, 3H), 4.72 (d, *J* = 4.5, 1H), 4.96-4.91 (m, 1H), 5.30 (d, *J* = 10.8, 1H), 7.33~7.06 (m, 13H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.1, 21.5, 57.9, 58.9, 61.5, 127.2, 128.3, 128.5, 129.1, 129.2, 129.3, 129.6, 133.5, 136.4, 137.5, 143.1, 160.3, 189.2; EI-MS (*m/z*, relative intensity): 498 [(M-28)<sup>+</sup>, 5], 433 (8), 342 (32), 294 (22), 176 (100), 131 (64), 91 (46); Anal. Calcd for C<sub>26</sub>H<sub>24</sub>ClN<sub>3</sub>O<sub>5</sub>S: C, 59.37; H, 4.60; N, 7.99. Found: C, 59.06; H, 4.72; N, 7.71.

**Ethyl 2-Diazo-7-methyl-3-oxo-5-(N-tosyl)aminoctanoate (3u).** mp 83-84 °C; IR (film) 3292, 2957, 2137, 1716, 1649 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.76 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H), 1.22-1.31 (m, 1H), 1.32 (t, *J* = 7.2, 3H), 1.42-1.52 (m, 1H), 1.53-1.64 (m, 1H), 2.41 (s, 3H), 2.82 (dd, *J* = 6.0, 5.4 Hz, 1H), 3.01 (dd, *J* = 6.0, 16.5 Hz, 1H), 3.65-3.76 (m, 1H), 4.27 (q, *J* = 7.2, 2H), 5.28 (d, *J* = 9.0 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.2, 21.3, 21.8, 22.5, 24.4, 43.9, 44.9, 49.3, 61.5, 127.0, 129.4, 138.1, 143.0, 160.9, 190.9; EI-MS (*m/z*, relative intensity): 395 (M<sup>+</sup>, 4), 338 (6), 310 (4), 240 (24), 155 (65), 91 (100). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>N<sub>3</sub>O<sub>5</sub>S: C, 54.67; H, 6.37; N, 10.63. Found: C, 54.66; H, 6.24; N, 10.63.

**Ethyl 2-Diazo-3-oxo-5-(N-tosyl)aminoundecanoate (3v).** mp 66-67 °C; IR (film) 3293, 2929, 2858, 2137, 1716, 1650 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.85 (t, *J* = 7.2 Hz, 3H), 1.11-1.25 (m, 8H), 1.33 (t, *J* = 7.2, 3H), 1.46-1.52 (m, 2H), 2.41 (s, 3H), 2.82 (dd, *J* = 6.6, 4.8 Hz, 1H), 3.03 (dd, *J* = 6.6, 15.9 Hz, 1H), 3.59-3.66 (m, 1H), 4.27 (q, *J* = 7.2, 2H), 5.15 (d, *J* = 8.7 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.0, 14.2, 22.3, 22.4, 25.4, 28.7, 31.5, 35.7, 43.7, 51.3, 61.5, 127.0, 129.4, 138.1, 143.0, 161.1, 190.9; EI-MS (*m/z*, relative intensity): 423 (M<sup>+</sup>, 3), 338 (23), 268 (31), 310 (11), 155 (100), 91 (98). Anal. Calcd for C<sub>20</sub>H<sub>29</sub>N<sub>3</sub>O<sub>5</sub>S: C, 56.72; H, 6.90; N, 9.92. Found: C, 56.75; H, 7.00; N, 9.83.

**2-Carboethoxy-3-hydroxy-5-phenylpyrrole (6a).** mp 138-140 °C; IR (KBr) 3453, 3304, 3278, 1692 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.37 (t, *J* = 7.2 Hz, 3H), 4.37 (q, *J* = 7.2 Hz, 2H), 6.16 (d, *J* = 3.2 Hz, 1H), 7.25-7.52 (m, 5H), 7.91 (br, s, 1H), 8.76 (br, d, 1H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 14.6, 61.2, 95.9, 106.2, 124.9, 128.2, 128.6, 131.1, 136.0, 155.2, 162.0; MS *m/z* (EI)

231 ( $M^+$ , 91), 203 (3), 185 (100), 156 (18), 129 (12), 102 (72), 77 (14), 51 (6). Anal. Calcd for  $C_{13}H_{13}NO_3$ : C, 67.52; H, 5.67; N, 6.06. Found: C, 67.45; H, 5.59; N, 5.91.

**2-Carboethoxy-3-hydroxy-5-(2-methylphenyl)pyrrole (6b).** mp 91-93 °C; IR (KBr) 3489, 3310, 1696, 1677  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.37 (t,  $J = 7.2$  Hz, 3H), 2.43 (s, 3H), 4.35 (q,  $J = 7.2$  Hz, 2H), 5.98 (d,  $J = 2.6$  Hz, 1H), 7.23-7.37 (m, 4H), 7.76 (br, s, 1H), 8.11 (br, s, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  14.5, 20.7, 60.0, 98.8, 105.5, 126.0, 128.3, 128.4, 130.9, 131.5, 135.7, 135.9, 153.7 (br), 162.0 (br); MS  $m/z$  (EI) 245 ( $M^+$ , 100), 222 (3), 199 (93), 193 (28), 171 (12), 144 (12), 134 (12), 123 (28), 116 (63), 95 (7), 91 (6), 77 (6), 57 (6), 43 (7). Anal. Calcd for  $C_{14}H_{15}NO_3$ : C, 68.56; H, 6.16; N, 5.71. Found: C, 68.45; H, 6.18; N, 5.61.

**2-Carboethoxy-3-hydroxy-5-(3-cyanophenyl)pyrrole (6c).** mp 203 °C; IR (KBr) 3501, 3337, 2227, 1669  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3/d_6\text{-DMSO}$ )  $\delta$  1.41 (t,  $J = 7.2$  Hz, 3H), 4.39 (q,  $J = 7.2$  Hz, 2H), 6.17 (d,  $J = 2.8$  Hz, 1H), 7.44-7.56 (m, 2H), 7.89-7.95 (m, 2H), 8.15 (s, 1H), 10.91 (br, s, 1H);  $^{13}\text{C}$  NMR (50MHz,  $\text{CDCl}_3/d_6\text{-DMSO}$ )  $\delta$  14.1, 59.4, 95.7, 106.9, 112.0, 118.1, 128.0, 128.9, 129.9, 132.2, 132.5, 152.7, 161.4; MS  $m/z$  (EI) 348 ( $M^+$ , 4), 284 (6), 256 (14), 241 (2), 210 (20), 178 (5), 171 (43), 155 (57), 127 (14), 107 (22), 91 (100), 65 (39), 57 (31), 39 (18). Anal. Calcd for  $C_{14}H_{12}N_2O_3$ : C, 65.62; H, 4.72; N, 10.93. Found: C, 65.81; H, 4.59; N, 10.83.

**2-Carboethoxy-3-hydroxy-5-[(E)-cinnamyl]pyrrole (6d).** mp 150-152 °C; IR (KBr) 3269, 1680, 1661  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3/d_6\text{-DMSO}$ )  $\delta$  1.37 (t,  $J = 7.2$  Hz, 3H), 4.34 (q,  $J = 7.2$  Hz, 2H), 5.94 (d,  $J = 2.8$  Hz, 1H), 6.88 (d,  $J = 16.4$  Hz, 1H), 7.06 (d,  $J = 16.4$  Hz, 1H), 7.21-7.44 (m, 5H), 7.91 (s, 1H), 11.0 (br, s, 1H);  $^{13}\text{C}$  NMR (50MHz,  $\text{CDCl}_3/d_6\text{-DMSO}$ )  $\delta$  14.0, 58.9, 94.8, 105.2, 117.6, 125.4, 126.9, 127.9, 128.3, 133.8, 136.2, 152.6, 161.1; MS  $m/z$  (EI) 257 ( $M^+$ , 100), 210 (88), 183 (11), 182 (6), 167 (8), 154 (28), 128 (46), 102 (5), 77 (6), 51 (5), 29 (5). Anal. Calcd for  $C_{15}H_{15}NO_3$ : C, 70.02; H, 5.88; N, 5.44. Found: C, 70.22; H, 6.08; N, 5.29.

**2-Carboethoxy-3-hydroxy-5-(2-furyl)pyrrole (6e).** mp 131-133 °C; IR (KBr) 3306, 1667, 1564  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.38 (t,  $J = 7.2$  Hz, 3H), 4.38 (q,  $J = 7.2$  Hz, 2H), 6.06 (d,  $J = 2.6$  Hz, 1H), 6.45-6.47 (m, 1H), 6.56 (d,  $J = 3.4$  Hz, 1H), 7.41-7.42 (m, 1H), 7.92 (br, s, 1H), 8.59 (br, s, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  14.5, 60.1, 94.6, 105.4, 106.2, 111.7, 126.8, 142.0, 146.5, 154.4, 162.1; MS  $m/z$  (EI) 221 ( $M^+$ , 95), 193.3 (4), 175 (100), 147 (26), 139 (2), 119 (15), 92 (52), 91 (8), 63 (15), 39 (12). Anal. Calcd for  $C_{11}H_{11}NO_4$ : C, 59.73; H, 5.01; N, 6.33. Found: C, 59.65; H, 4.97; N, 6.13.

**2-Benzoyl-3-hydroxy-5-(2-furyl)pyrrole (6f).** mp 139-142 °C; IR (KBr) 3320, 1590, 1567  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  6.14 (d,  $J = 2.4$  Hz, 1H), 6.50 (dd,  $J = 3.5, 1.7$  Hz, 1H), 6.66 (d,  $J = 3.5$  Hz, 1H), 7.44 (d,  $J = 1.7$  Hz, 1H), 7.50-7.59 (m, 3H), 7.77-7.82 (m, 2H), 8.26 (br, s, 1H), 10.43 (br, s, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  94.8, 108.2, 112.1, 116.0, 127.5, 129.0, 129.8, 131.6, 137.7, 142.7, 145.9, 159.3, 184.0; MS  $m/z$  (EI) 253 ( $M^+$ , 100), 236 (5), 224 (4), 196

(4), 176 (30), 147 (7), 120 (9), 105 (37), 92 (24), 91 (3), 77 (49), 65 (20), 51 (17), 39 (15). Anal. Calcd for C<sub>15</sub>H<sub>11</sub>NO<sub>3</sub>: C, 71.14; H, 4.38; N, 5.53. Found: C, 70.98; H, 4.37; N, 5.46.

**2-Benzoyl-3-hydroxy-5-[(E)-cinnamyl]pyrrole (6g).** mp 159-161 °C; IR (KBr) 3322, 2261, 1626, 1592, 1550, 1503 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 6.10 (d, *J* = 2 Hz, 1H), 6.79 (d, *J* = 16.5 Hz, 1H), 7.00 (d, *J* = 16.5 Hz, 1H), 7.28-7.54 (m, 8H), 7.68-7.72 (m, 2H), 8.41 (br, s, 1H), 10.40 (br, s, 1H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 96.3, 116.6, 117.3, 126.6, 127.5, 128.5, 128.8, 128.9, 131.6, 132.0, 135.9, 137.7, 138.0, 159.5, 183.8; MS *m/z* (EI) 289 (M<sup>+</sup>, 100), 288 (27), 270 (10), 212 (13), 156 (6), 128 (23), 105 (49), 77 (31), 51 (7). Anal. Calcd for C<sub>19</sub>H<sub>15</sub>NO<sub>2</sub>: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.80; H, 5.21; N, 4.74.

**2-Acetyl-3-hydroxy-5-(4-methoxyphenyl)pyrrole (6h).** mp 178-180 °C (decomposed); IR (KBr) 3272, 1614, 1585, 1534 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 2.48 (s, 3H), 3.85 (s, 3H), 6.01 (d, *J* = 2.8 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 9.47 (br, s, 1H), 10.59 (br, s, 1H); MS *m/z* (EI) 231 (M<sup>+</sup>, 100), 216 (93), 202 (9), 188 (5), 174 (8), 161 (15), 146 (4), 133 (18), 118 (7), 117 (8), 102 (3), 89 (12), 77 (4), 63 (6), 43 (13). Anal. Calcd for C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub>: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.41; H, 5.71; N, 6.01.

**2-Carboethoxy-3-hydroxy-4-methyl-5-phenylpyrrole (6i).** mp 94-95 °C; IR (film) 3306, 2980, 1676 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.36 (t, *J* = 7.2 Hz, 3H), 2.14 (s, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 7.26-7.51 (m, 5H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 7.9, 14.6, 60.0, 105.2, 127.0, 127.9, 128.8, 132.2; EI-MS (*m/z*, relative intensity): 245 (M<sup>+</sup>, 76), 199 (100), 171 (26), 116 (81). Anal. Calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub>: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.47; H, 6.30; N, 5.55.

**2-Carboethoxy-3-hydroxy-4-methyl-5-(4-methoxyphenyl)pyrrole (6j).** mp 77-78 °C; IR (film) 3313, 2980, 1672 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.47 (br, s, 1H), 7.88 (br, d, *J* = 18.3), 7.42 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.11 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.3, 128.3, 124.8, 114.2, 104.5, 59.90, 55.30, 14.62, 7.84; EI-MS (*m/z*, relative intensity): 275 (M<sup>+</sup>, 88.8), 229 (100), 199 (35.5), 146 (66.4); Anal. Calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>4</sub>: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.43; H, 6.18; N, 4.79.

**2-Carboethoxy-3-hydroxy-5-(2-methylphenyl)-4-phenylpyrrole (6k).** mp 179-180 °C; IR (film) 3288, 2981, 1677, 1655, 1303 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.36 (t, *J* = 7.2 Hz, 3H), 1.99 (s, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 7.10-7.34 (m, 9H), 8.13 (br, d, 1H), 8.66 (br, s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.6, 19.8, 60.2, 111.8, 125.9, 126.0, 128.0, 128.2, 129.0, 130.2, 130.5, 132.0, 132.8, 137.5; EI-MS (*m/z*, relative intensity): 321 (M<sup>+</sup>, 72), 275 (100), 260 (30), 191 (33); Anal. Calcd for C<sub>20</sub>H<sub>19</sub>NO<sub>3</sub>: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.83; H, 5.91; N, 4.13.

**2-Carboethoxy-5-(4-chlorophenyl)-3-hydroxy-4-phenylpyrrole (6l).** mp 136-137 °C; IR (film) 3292, 2982, 1678 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.39 (t, *J* = 7.2 Hz, 3H), 4.39 (q, *J* =

7.2 Hz, 2H), 7.22-7.34 (m, 9H), 8.10 (br, s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.6, 34.2, 60.4, 126.6, 128.4, 129.0, 129.5, 130.2, 131.8; EI-MS ( $m/z$ , relative intensity): 341 ( $M^+$ , 82), 295 (100), 260 (20), 212 (36), 176 (18). Anal. Calcd for  $\text{C}_{20}\text{H}_{19}\text{NO}_3$ : C, 66.77; H, 4.72; N, 4.10. Found: C, 66.59; H, 4.80; N, 3.83.

**2-Carboethoxy-3-hydroxy-5-isobutylpyrrole (6m).** mp 95-96 °C; IR (film) 3289, 2951, 1676, 1659  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (d,  $J = 7.2$  Hz, 6H), 1.36 (br, s, 3H), 1.88 (m, 1H), 2.39 (d,  $J = 7.2$  Hz, 2H), 4.34 (br, s, 2H), 5.62 (d,  $J = 2.4$ , 1H), 6.58 (br, 0.5H), 7.92 (br, 1H), 8.93 (br, 0.5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.6, 22.3, 28.8, 37.7, 59.7, 97.0, 103.7, 137.2, 155.2, 162.4; EI-MS ( $m/z$ , relative intensity): 211 ( $M^+$ , 48), 168 (100), 140 (41), 122 (67), 28 (43). Anal. Calcd for  $\text{C}_{11}\text{H}_{17}\text{NO}_3$ : C, 62.54; H, 8.11; N, 6.63. Found: C, 62.53; H, 8.06; N, 6.35.

**2-Carboethoxy-5-hexyl-3-hydroxypyrrrole (6n).** mp 69-70 °C; IR (film) 3448, 3301, 2955, 2922, 2856, 1677  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 6.6$  Hz, 3H), 1.29-1.37 (m, 9H), 1.55~1.65 (m, 2H), 2.52 (t,  $J = 7.2$  Hz, 2H), 4.33 (br, s, 2H), 5.62 (d,  $J = 2.7$ , 1H), 6.57 (br, 0.5H), 7.90 (br, 1H), 8.74 (br, 0.5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 14.5, 155.3, 22.5, 28.3, 28.8, 28.9, 31.4, 59.7, 96.2; EI-MS ( $m/z$ , relative intensity): 239 ( $M^+$ , 34), 194 (14), 168 (34), 122 (58), 67 (58) 41 (64), 29 (100). Anal. Calcd for  $\text{C}_{13}\text{H}_{21}\text{NO}_3$ : C, 65.25; H, 8.84; N, 5.85. Found: C, 65.38; H, 8.57; N, 5.68.

### S-p-tolyl-p-toluenesulfonothioate (11).<sup>1</sup>

M.p. 88-90 °C; IR (KBr) 1590, 1487, 1323, 1140, 804, 652, 585  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  2.83 (s, 3H), 2.42 (s, 3H), 7.12-7.23 (m, 6H), 7.46 (d,  $J = 8.8$  Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 142.0, 140.4, 136.5, 130.2, 129.3, 127.6, 124.5, 21.63, 21.46; MS (EI) ( $m/z$ , relative intensity) 278 ( $M^+$ , 52), 155 (32), 139 (100), 123 (44), 91 (82), 65 (23), 45 (19).

**3-Carboethoxy-5-phenyl-N-tosyl-2-pyrrolidinone (7a).** Amorphous solid; the major isomer: IR (film) 2976, 1728, 1367, 1170  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.22-1.29 (m, 3H), 2.15-2.22 (m, 1H), 2.40 (s, 3H), 2.93-3.04 (m, 1H), 3.70-3.76 (m, 1H), 4.13-4.25 (m, 2H), 5.49-5.52 (m, 1H), 7.11-7.32 (m, 7H), 7.50-7.62 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 21.6, 32.3, 47.8, 61.2, 62.1, 125.9, 127.0, 128.3, 128.5, 128.9, 134.8, 139.8, 145.2, 167.6, 168.5; EI-MS ( $m/z$ , relative intensity): 388 [( $M+1$ )<sup>+</sup>, 6], 323 (89), 250 (31), 232 (38), 186 (47), 155 (25), 91 (100). Anal. Calcd for  $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{S}$ : C, 62.00; H, 5.46; N, 3.62. Found: C, 62.11; H, 5.57; N, 3.44.

**3-Carboethoxy-5-(2-methylphenyl)-N-tosyl-2-pyrrolidinone (7b).** Amorphous solid; the major isomer: IR (film) 2981, 1747, 1729, 1170  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.27 (t,  $J = 7.2$  Hz, 3H), 2.42 (s, 6H), 2.04-2.12 (m, 1H), 2.92-3.03 (m, 1H), 3.65-3.72 (m, 1H), 4.21 (q,  $J = 7.2$  Hz, 2H), 5.74-5.77 (m, 1H), 6.78 (d,  $J = 7.8$  Hz, 1H), 6.98-7.04 (m, 1H), 7.20-7.27 (m, 4H), 7.69 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 19.1, 21.6, 31.3, 47.5, 57.7, 62.1,

124.2, 126.2, 127.9, 128.8, 129.2, 131.2, 134.5, 134.7, 137.7, 145.3, 167.6, 168.7. EI-MS (*m/z*, relative intensity): 401 (M<sup>+</sup>, 26), 337 (28), 264 (45), 246 (45), 200 (47), 91 (100). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>5</sub>S: C, 62.82; H, 5.77; N, 3.49. Found: C, 62.54; H, 5.74; N, 3.25.

**3-Carboethoxy-5-(4-chlorophenyl)-N-tosyl-2-pyrrolidinone (7c).** Amorphous solid; the major isomer: IR (film) 1729, 1729, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.23-1.28 (m, 3H), 2.10-2.18 (m, 1H), 2.42 (s, 3H), 2.92-3.02 (m, 1H), 3.61-3.72 (m, 1H), 4.13-4.24 (m, 2H), 5.45-5.49 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.71-8.31 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 13.9, 21.6, 32.2, 47.7, 60.6, 62.2, 127.3, 128.4, 128.7, 129.0, 134.1, 134.7, 138.5, 145.5, 167.4, 168.3; EI-MS (*m/z*, relative intensity): 422 [(M+1)<sup>+</sup>, 5], 357 (58), 266 (40), 220 (42), 155(29), 91 (100). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>ClNO<sub>5</sub>S: C, 56.94; H, 4.78; N, 3.32. Found: C, 56.85; H, 4.87; N, 3.22.

**3-Carboethoxy-5-(3-cyanophenyl)-N-tosyl-2-pyrrolidinone (7d).** Amorphous solid; the major isomer: IR (film) 2231, 1729, 1560, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.27 (t, *J* = 7.2, 3H), 2.10-2.18 (m, 1H), 2.45 (s, 3H), 2.95-3.06 (m, 1H), 3.64-3.70 (m, 1H), 4.15-4.26 (m, 2H), 5.50-5.53 (m, 1H), 7.20-7.68 (m, 8H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 13.9, 21.7, 32.1, 47.6, 60.5, 62.4, 113.1, 117.9, 128.4, 129.4, 129.9, 130.5, 131.4, 131.9, 134.5, 141.6, 146.0, 167.2, 168.1; EI-MS (*m/z*, relative intensity): 413 [(M+1)<sup>+</sup>, 3], 258 (100), 212 (53), 184 (45), 105 (29), 91 (51); Anal. Calcd for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>S: C, 61.15; H, 4.89; N, 6.79. Found: C, 61.07; H, 5.03; N, 6.65.

**3-Carboethoxy-5-furyl-N-tosyl-2-pyrrolidinone (7e).** Amorphous solid; the major isomer: IR (film) 1730, 1171 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.27-1.32 (m, 3H), 2.31-2.40 (m, 1H), 2.38 (s, 3H), 2.89-3.00 (m, 1H), 3.91-3.98 (m, 1H), 4.20-4.28 (m, 2H), 5.52 (d, *J* = 8.4 Hz, 1H), 6.37-6.49 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.0, 21.6, 29.0, 48.5, 53.8, 62.1, 110.0, 110.4, 128.3, 129.2, 134.4, 142.6, 145.0, 151.5, 167.5, 168.0; EI-MS (*m/z*, relative intensity): 377 (M<sup>+</sup>, 2), 222 (100), 176 (96), 148 (28), 91 (47). Anal. Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>6</sub>S: C, 57.28; H, 5.07; N, 3.71. Found: C, 57.28; H, 5.10; N, 3.58.

**3-Carboethoxy-4-methyl-5-phenyl-N-tosyl-2-pyrrolidinone (7h).** Amorphous solid; the major isomer: IR (film) 2979, 1748, 1730, 1172 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.21 (t, *J* = 7.2 Hz, 3H), 2.00 (s, 3H), 2.43 (s, 3H), 3.79 (m, 1H), 3.90 (d, *J* = 9.9 Hz, 1H), 4.08-4.23 (m, 2H), 5.53 (d, *J* = 6.9 Hz, 1H), 5.74-5.77 (m, 1H), 7.04-7.31 (m, 11H), 7.56 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.0, 16.8, 21.6, 40.8, 56.1, 62.0, 68.9, 126.3, 127.3, 128.3, 128.4, 128.5, 128.6, 128.7, 129.1, 129.2, 135.3, 138.8, 145.0, 167.6, 168.6; EI-MS (*m/z*, relative intensity): 402 [(M+1)<sup>+</sup>, 3], 337 (91), 264 (35), 200 (27), 155 (33), 132 (34), 91 (100); Anal. Calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>6</sub>S: C, 62.84; H, 5.74; N, 3.49. Found: C, 63.24; H, 6.04; N, 3.34; HRMS calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>5</sub>S: 401.1296, found: 401.1308.

**3-Carboethoxy-4-methyl-5-(4-methoxyphenyl)-N-tosyl-2-pyrrolidinone (7i).** Amorphous solid; the major isomer: IR (film) 2922, 1750, 1731, 1204 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.21 (t, *J* = 7.2 Hz, 3H), 2.00 (s, 3H), 2.43 (s, 3H), 3.79 (m, 1H), 3.90 (d, *J* = 9.9 Hz, 1H), 4.08-4.23 (m, 2H), 5.74-5.77 (m, 1H), 5.53 (d, *J* = 6.9 Hz, 1H), 7.04-7.31 (m, 11H), 7.56 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.0, 16.6, 21.6, 40.8, 55.2, 56.1, 61.9, 68.6, 113.7, 114.0, 127.7, 128.2, 128.5, 128.7, 129.1, 129.2, 130.6, 135.4, 144.9, 159.5, 167.7, 168.5; EI-MS (*m/z*, relative intensity): 431 (M<sup>+</sup>, 44), 276 (100), 230 (90), 202 (34), 162 (47), 134 (35), 91 (71). HRMS calcd for C<sub>22</sub>H<sub>25</sub>NO<sub>6</sub>S: 431.1402, found: 431.1394.

**3-Carboethoxy-5-(2-methylphenyl)-4-phenyl-N-tosyl-2-pyrrolidinone (7j).** The major isomer: M.p. 179-180 °C; IR (film) 2982, 1730, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.21 (t, *J* = 7.2 Hz, 3H), 2.00 (s, 3H), 2.43 (s, 3H), 3.79 (m, 1H), 3.90 (d, *J* = 9.9 Hz, 1H), 4.08-4.23 (m, 2H), 5.74-5.77 (m, 1H), 5.53 (d, *J* = 6.9 Hz, 1H), 7.04-7.31 (m, 11H), 7.56 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 13.9, 19.1, 21.7, 51.2, 56.0, 62.2, 64.4, 126.0, 126.3, 127.2, 168.3, 127.9, 128.1, 128.6, 129.1, 129.2, 130.4, 135.2, 136.2, 137.2, 137.8, 145.2, 167.3; EI-MS (*m/z*, relative intensity): 477 (M<sup>+</sup>, 7), 404 (16), 322 (33), 274 (36), 176 (100), 146 (70), 131 (80), 118 (55), 91 (85); Anal. Calcd for C<sub>27</sub>H<sub>27</sub>NO<sub>5</sub>S: C, 67.90; H, 5.70; N, 2.93. Found: C, 67.77; H, 5.87; N, 2.70.

One of the minor isomers: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.19 (t, *J* = 7.2 Hz, 3H), 1.77 (s, 3H), 2.42 (s, 3H), 4.04 (d, *J* = 13.5 Hz, 1H), 4.05-4.21 (m, 2H), 4.38-4.51 (m, 1H), 5.97 (d, *J* = 8.1 Hz, 1H), 6.66-6.73 (m, 3H), 6.89-7.27 (m, 8H), 7.63 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 13.9, 19.0, 21.7, 48.5, 53.1, 61.1, 62.1, 125.4, 125.6, 127.9, 128.0, 128.2, 128.6, 129.0, 129.2, 130.8, 133.1, 133.5, 134.6, 137.0, 145.4, 166.7, 168.0.

**3-Carboethoxy-5-(4-chlorophenyl)-4-phenyl-N-tosyl-2-pyrrolidinone (7k).** Amorphous solid; the major isomer: IR (film) 2982, 1730, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.20 (t, *J* = 7.2 Hz, 3H), 2.44 (s, 3H), 4.03 (d, *J* = 13.2 Hz, 1H), 4.08-4.22 (m, 2H), 4.44-5.51 (m, 1H), 5.62 (d, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 6.76 -6.80 (m, 2H), 7.01-7.31 (m, 7H), 7.72 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 13.9, 21.6, 47.9, 51.3, 62.3, 64.9, 126.8, 127.2, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5, 128.7, 129.2, 129.4, 133.3, 133.5, 134.1, 134.2, 134.6, 137.3, 145.6, 166.6, 167.7; EI-MS (*m/z*, relative intensity): 498 [(M+1)<sup>+</sup>, 5], 433 (8), 342 (31), 294 (22), 176 (100), 166 (31), 131 (62), 91 (45). HRMS calcd for C<sub>26</sub>H<sub>24</sub>ClNO<sub>5</sub>S: 497.1063, found: 497.1063.

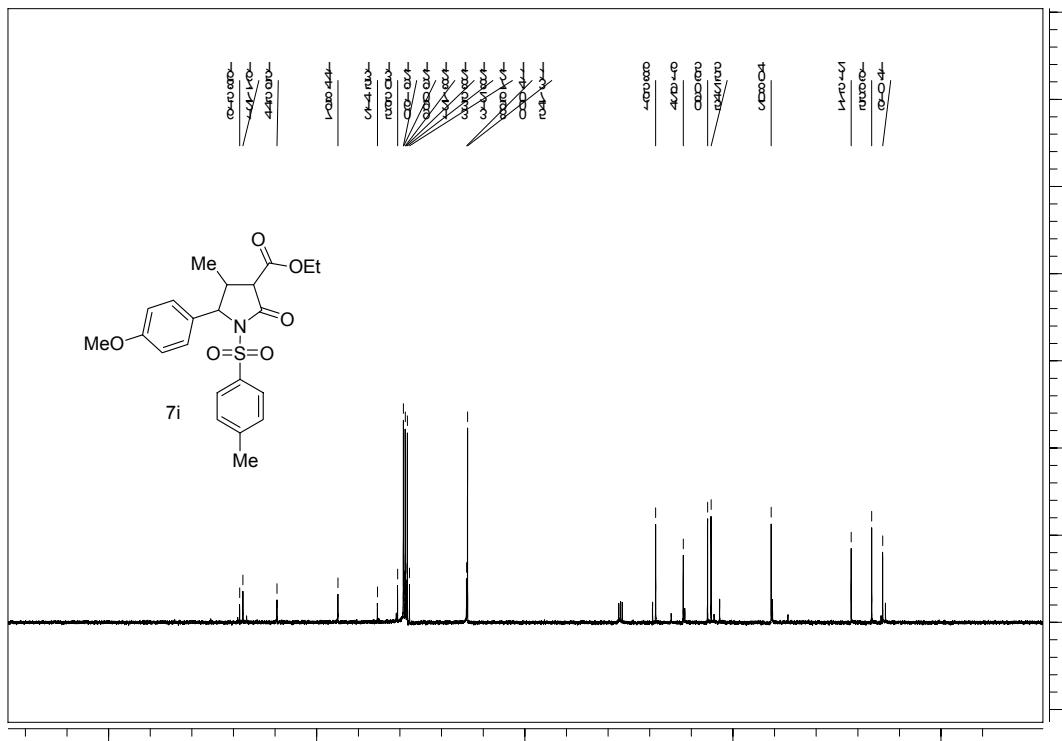
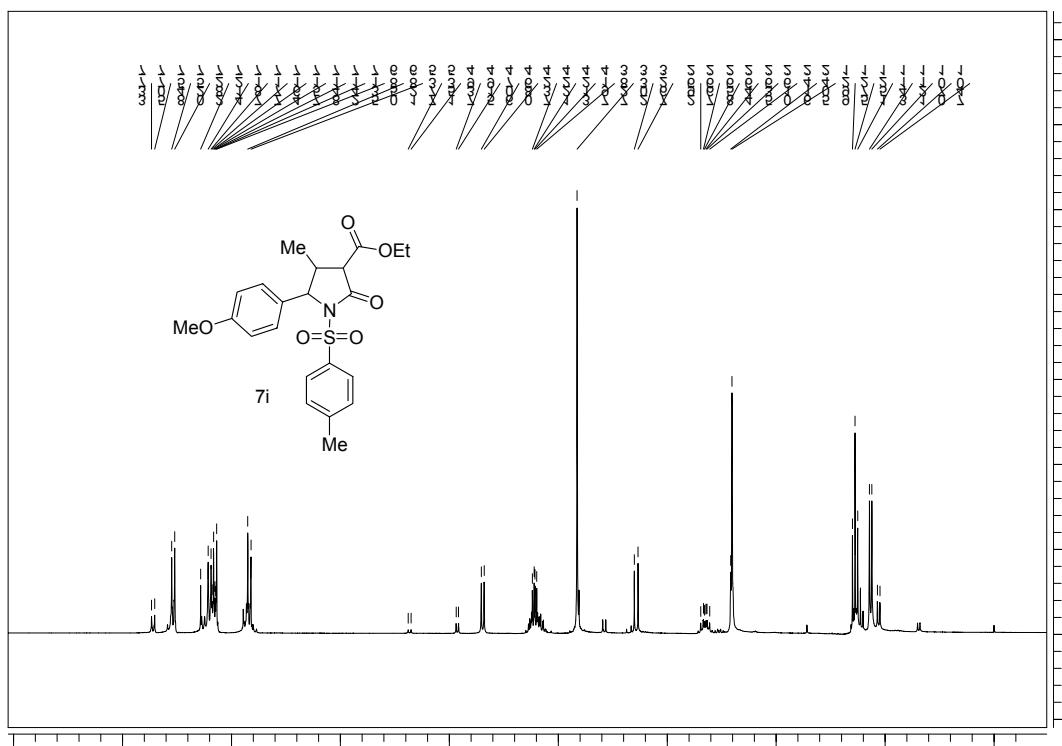
**3-Carboethoxy-5-isobutyl-N-tosyl-2-pyrrolidinone (7l).** Amorphous solid; the major isomer: IR (film) 2960, 1748, 1729, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.97-1.03 (m, 6H), 1.21-1.27 (m, 3H), 1.40-1.96 (m, 3H), 2.44 (s, 3H), 2.21-2.72 (m, 2H), 3.54-3.60 (m, 1H), 4.13-4.22 (m, 2H), 4.34-4.56 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 13.9, 21.2, 21.6, 23.7, 25.4, 27.9, 44.2, 47.7, 57.2, 61.9, 128.4, 129.5, 135.5, 145.2, 167.8, 168.3; EI-MS (*m/z*, relative intensity): 368 [M+1]<sup>+</sup>, 6], 303 (20), 230 (26),

155 (80), 91 (100). Anal. Calcd for  $C_{18}H_{25}NO_5S$ : C, 58.83; H, 6.86; N, 3.81. Found: C, 59.11; H, 6.89; N, 3.66.

**3-Carboethoxy-5-hexyl-N-tosyl-2-pyrrolidinone (7m).** Amorphous solid; the major isomer: IR (film) 2929, 2859, 1729, 1169  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86-0.91 (m, 3H), 1.18-1.32 (m, 11H), 1.49-1.79 (m, 1H), 1.95-2.13 (m, 1H), 2.20-2.28 (m, 1H), 2.44 (s, 3H), 2.54-2.65 (m, 1H), 3.52-3.59 (m, 1H), 4.13-4.22 (m, 2H), 4.40-4.48 (m, 1H), 7.33 (d,  $J = 8.4$  Hz, 2H), 7.94 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 21.6, 22.5, 24.9, 26.7, 27.6, 28.9, 31.6, 34.6, 48.1, 58.5, 61.9, 128.4, 129.5, 135.4, 145.2, 167.8, 168.4; EI-MS ( $m/z$ , relative intensity): 396 [ $(M+1)^+$ , 5], 331 (32), 310 (28), 258 (30), 155 (88), 91 (100). HRMS calcd for  $C_{20}H_{29}NO_5S$ : 395.1766, found: 395.1787;  $C_{20}H_{30}NO_5S$ : 396.1844, found: 396.1835. Anal. Calcd for  $C_{20}H_{29}NO_5S$ : C, 60.76; H, 7.39; N, 3.54. Found: C, 61.17; H, 7.37; N, 3.48.

(1) (a) Noguchi, Y.; Kurogi, K.; Sekioka, M.; Furukawa, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 349-350. (b) Sas, W. *J. Chem. Res. Synop.* **1993**, 160-161.

*Diastereomeric mixtures*



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