

Supporting Information

General. All reactions with air- and moisture-sensitive components were performed under a nitrogen atmosphere in a flame-dried reaction flask, and the components were added via syringe. All solvents were distilled prior to use. The boiling point of petroleum ether is between 30 and 60 °C. THF was distilled from sodium prior to use. For chromatography, 100-200 mesh silica gel (Qingdao, China) was employed. For preparative TLC, 10-40 μ m silica gel GF₂₅₄ (Qingdao, China) was used. Recrystallization was from petroleum ether-ethyl acetate. ¹H and ¹³C NMR spectra were recorded at 200 MHz and 50 MHz with Varian Mercury 200 spectrometer, or at 400 MHz and 100.6 MHz with Bruker ARX400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. Mass spectra were obtained on a VG ZAB-HS mass spectrometer.

General procedure for the copper complex catalyzed diazo decomposition of *N*-tosyl diazoketamine **3a**: A solution of **3a** (30 mg, 0.08 mmol) in 20 ml CH₂Cl₂ was stirred at room temperature under N₂, and then copper catalyst (10 % mmol) was added. The reaction mixture was stirred at room temperature until the disappearance of the starting material. The solvent was removed under vacuum, and the residue was analyzed by ¹H NMR and purified by column chromatography.

Diazo decomposition of **3a** catalyzed by AgO₂CPh:

To a solution of **3a** (100 mg, 0.26 mmol) in anhydrous THF (50 mL), was added a solution of AgO₂CPh (10 mg) in Et₃N (0.2 mL). The mixture was heated under gentle reflux for 4 h.. The solvent was removed under vacuum, and the residue was analyzed by ¹H NMR and purified by column chromatography.

Photolysis of *N*-tosyl diazoketamine **3a**:

A solution of **3a** (200 mg, mmol) in anhydrous benzene (300 mL) was irradiated at room temperature with high pressure mercury lamp for 12 h. The solvent was removed under vacuum, and the residue was analyzed by ¹H NMR and purified by column chromatography.

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-phenylpropanoate (3a): IR 3207, 3057, 2112, 1679 cm⁻¹; ¹H NMR (200 MHz) δ 1.16 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H, Me), 4.06 (q, *J* = 7.2 Hz, 2H), 5.34 (d, *J* = 6.0 Hz, 1H), 5.62 (s, 1H), 7.22-7.31(m, 7H), 7.74 (d, *J* = 8.2Hz, 2H); MS *m/z* (FAB) 380 [(M+Li)⁺, 30], 354 (58), 268 (17), 197 (38), 184 (33), 169 (21), 147 (17), 125 (23), 115 (100), 91 (57), 77 (22), 59 (20), 49 (51).

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-(*p*-methoxy)phenylpropanoate (3b): IR 3234, 2108, 1675 cm⁻¹; ¹H NMR (200 MHz) δ 1.18 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 3.78 (s, 3H), 4.07 (q, *J* = 7.2 Hz, 2H), 5.27 (d, *J* = 7.2 Hz, 1H), 5.45 (s, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H); MS *m/z* (FAB) 410 [(M+Li)⁺, 58], 384 (18), 290 (17), 263 (11), 205 (88), 177 (63), 133 (37), 115 (100), 45 (54).

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-(*p*-chloro)phenylpropanoate (3c): IR 3432, 3211, 2108, 1679 cm⁻¹; ¹H NMR (200 MHz) δ 1.17 (t, *J* = 7.2 Hz, 3H), 2.44 (s, 3H), 4.06 (q, *J* = 7.2 Hz, 2H), 5.30 (d, *J* =

8.0 Hz, 1H), 5.61(s, 1H), 7.20-7.32 (m, 6H), 7.72 (d, $J = 8.4$ Hz, 2H); MS m/z (FAB): 414 [(M+Li)⁺, 27], 388 (14), 263 (14), 181 (26), 115 (100), 47 (46).

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-(*p*-phenyl)phenylpropanoate (3d): IR 3448, 3226, 2110, 1678cm⁻¹; ¹H NMR (200 MHz) δ 1.19 (t, $J = 7.0$ Hz, 3H), 2.43 (s, 3H), 4.10 (q, $J = 7.0$ Hz, 2H), 5.38 (d, $J = 7.6$ Hz, 1H), 5.56 (s,1H),7.29-7.57 (m, 12H), 7.76 (d, $J = 8.4$ Hz, 2H); MS m/z (FAB): 456 [(M+Li)⁺, 36], 430 (6), 263 (13), 223 (29), 157 (46), 115 (100), 49 (93), 45 (36)

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-(3-bromo)phenylpropanoate (3e): IR 3238, 2977, 2103, 1670 cm⁻¹; ¹H NMR (200 MHz) δ 1.18 (t, $J = 7.2$ Hz, 3H), 2.44 (s, 3H), 4.08 (q, $J = 7.2$ Hz 2H), 5.30 (d, $J = 8.2$ Hz, 1H), 5.60 (s, 1H), 7.18-7.43 (m, 6H), 7.71(d, $J = 8.2$ Hz, 2H); MS m/z (FAB): 452 [M+Li]⁺, 11], 358 (6), 205 (7), 184 (10), 157 (9), 115 (100), 91 (12), 49 (25), 43 (10).

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-(2-methyl)phenylpropanoate (3f): IR 3242, 2987, 2092, 1693 cm⁻¹; ¹H NMR δ 1.20 (t, $J = 7.2$ Hz, 3H), 2.23 (s, 3H), 2.42 (s, 3H), 4.02-4.16 (m, 2H), 5.25 (d, $J = 5.8$ Hz, 1H), 5.51 (d, $J = 5.8$ Hz, 1H), 7.11-7.7.30 (m, 6H), 7.73 (d, $J = 7.8$ Hz, 2H); MS m/z (FAB): 394 [(M+Li)⁺, 28], 372 (13), 368 (42), 211 (17), 184 (29), 161 (18), 121 (43), 115 (100), 91 (59), 63 (22), 51 (30).

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-(2,4-dichloro)phenylpropanoate (3g): IR 3392, 3238, 2982, 2098, 1701cm⁻¹; ¹H NMR δ 1.16 (t, $J = 7.2$ Hz, 3H), 2.42 (s, 3H), 4.05 (q, $J = 7.2$ Hz, 2H), 5.55 (d, $J = 7.6$ Hz, 1H), 5.88 (s, 1H), 7.13-7.41 (m, 5H), 7.70 (d, $J = 8.2$ Hz, 2H); MS m/z (FAB): 448 [(M+Li)⁺, 43], 422 (27), 265 (26), 243 (16), 215 (28), 178 (25), 155 (40), 115 (43), 91 (100), 59 (22), 45 (37).

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-(3,5-dimethoxy)phenylpropanoate (3h): IR 3214, 2964, 2108, 1675 cm⁻¹; ¹H NMR δ 1.19 (t, $J = 7.2$ Hz, 3H), 2.43 (s, 3H), 3.73 (s, 6H), 4.08 (q, $J = 7.2$ Hz, 2H), 5.25 (d, $J = 7.2$ Hz, 1H), 6.51(d, $J = 7.2$ Hz, 1H), 6.34-6.39 (m, 3H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 8.2$ Hz, 2H); MS m/z (FAB): 440 [(M+Li)⁺, 45], 414 (47), 366 (19), 257 (38), 178 (29), 163 (24), 115 (100), 49 (30), 43 (29).

Ethyl 2-Diazo-3-(*N*-Tosyl)amino-3-phenylbutanoate (3i): IR 3242, 2987, 2092, 1693 cm⁻¹; ¹H NMR δ 1.19 (t, $J = 7.2$ Hz, 3H), 2.42 (s, 3H), 4.05-4.12(m, 2H), 5.28(d, $J = 5.8$ Hz, 1H), 5.51 (d, $J = 5.8$ Hz, 1H), 7.14-7.29 (m, 7H), 7.73 (d, $J = 8.2$ Hz, 2H); MS m/z (FAB): 394 [(M+Li)⁺, 59], 368 (26), 320 (18), 274 (15), 211 (21), 189 (39), 161 (35), 115 (68), 91 (100), 45 (44).

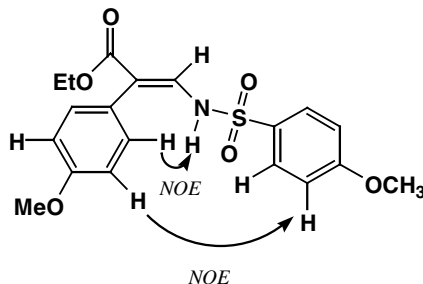
(*E*)-Ethyl 2-Phenyl-3-(*N*-tosyl)amine-2-propenoate (4a): IR 3178, 2984, 1700 cm⁻¹; ¹H NMR δ 1.23 (t, $J = 7.0$ Hz, 3H), 2.44 (s, 3H), 4.20 (q, $J = 7.0$ Hz, 2H), 6.80 (d, $J = 12.6$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 2H), 7.30-7.39 (m, 5H), 7.71(d, $J = 12.6$ Hz, 1H); ¹³C NMR (50 MHz) δ 14.21, 21.52, 60.62, 114.24, 126.72, 128.28, 129.06, 129.61, 130.08, 131.89, 134.28, 136.41, 144.62, 166.17; MS m/z (EI): 345 (M⁺, 100), 299 (48), 235 (31), 207 (9), 155 (20), 118 (91), 91 (89)..

(*Z*)-Ethyl 3-Phenyl-3-(*N*-tosyl)amine-2-propenoate (5a): IR 3132, 2927, 1660 cm⁻¹; ¹H NMR δ 1.26 (t, $J = 7.2$ Hz, 3H), 2.40(s, 3H), 4.17(q, $J = 7.2$ Hz, 2H), 5.20(s, 1H), 7.18 (d, $J = 8.2$ Hz, 2H),7.29-7.30

(m, 4H), 7.40 (d, $J = 8.2$ Hz, 2H), 10.68 (s, 1H); ^{13}C NMR (50 MHz) δ 14.14, 21.55, 60.48, 102.17, 127.54, 127.82, 128.82, 129.30, 130.45, 134.02, 136.47, 143.97, 154.92, 168.35; MS m/z (EI): 345 (M^+ , 68), 299 (30), 279 (9), 235 (15), 207 (6), 167 (21), 149 (100), 118 (63), 91 (78).

(Z)-Ethyl 2-Phenyl-3-(N-tosyl)amine-2-propenoate (6a): IR 3223, 2933, 1673 cm^{-1} ; ^1H NMR δ 1.23 (t, $J = 7.0$ Hz, 3H), 2.43 (s, 3H), 4.20 (q, $J = 7.0$ Hz, 2H), 7.11 (d, $J = 11.2$ Hz, 1H), 7.23-7.33 (m, 7H), 7.77 (d, $J = 8.2$ Hz, 2H), 10.53 (d, $J = 11.2$ Hz, 1H); ^{13}C NMR (50 MHz) δ 14.06, 21.55, 60.90, 110.69, 126.68, 127.20, 128.01, 129.38, 130.01, 135.633, 137.10, 139.39, 144.35, 168.37; MS m/z (EI): 345 (M^+ , 100), 299 (42), 235 (23), 207 (7), 162 (11), 144 (67), 118 (79), 91 (99).

(E)-Ethyl 2-(4-Methoxyphenyl)-3-(N-tosyl)amine-2-propenoate (4b): IR 3267, 2972, 1696 cm^{-1} ; ^1H NMR δ 1.25 (t, $J = 7.1$ Hz, 3H), 2.44 (s, 3H), 3.80 (s, 3H), 4.17 (q, $J = 7.1$ Hz, 2H), 6.80 (d, $J = 12.4$ Hz, 1H), 6.88 (d, $J = 8.7$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.68 (d, $J = 12.4$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (50 MHz) δ 14.19, 21.49, 55.11, 60.62, 113.83, 114.39, 123.81, 126.65, 129.99, 130.76, 134.11, 136.45, 144.50, 159.24, 166.38; MS m/z (EI): 375 (M^+ , 74), 329 (36), 365 (20), 220 (17), 192 (26), 147 (100), 132 (69), 91 (67), 65 (29), 29 (48).



(E)-Ethyl 2-(4-Chlorophenyl)-3-(N-tosyl)amine-2-propenoate (4c): IR 3229, 2987, 1707 cm^{-1} ; ^1H NMR δ 1.23 (t, $J = 7.0$ Hz, 3H), 2.44 (s, 3H), 4.13-4.19 (m, 2H), 6.87 (1H), 6.99-7.02 (m, 2H), 7.30-7.35 (m, 5H), 7.70 (d, $J = 6.3$ Hz, 1H), 7.71 (d, $J = 12.4$ Hz, 2H); ^{13}C NMR (50 MHz) δ 14.19, 21.58, 60.85, 112.83, 126.72, 129.24, 130.11, 130.33, 131.10, 134.22, 134.76, 136.29, 144.75, 165.89; MS m/z (EI): 379 (M^+ , 68), 333 (15), 178 (25), 152 (39), 123 (13), 117 (34), 91 (100), 77 (11), 65 (32), 39 (15), 29 (57).

(E)-Ethyl 2-(4-Phenylphenyl)-3-(N-tosyl)amine-2-propenoate (4d): IR 3449, 3171, 1698 cm^{-1} ; ^1H NMR δ 1.25 (t, $J = 7.0$ Hz, 3H), 2.41 (s, 3H), 4.18 (q, $J = 7.0$ Hz, 2H), 7.03 (d, $J = 12.4$ Hz, 1H), 7.13 (d, $J = 8.2$ Hz, 2H), 7.30-7.44 (m, 5H), 7.56 (d, $J = 8.2$ Hz, 4H), 7.72 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 12.4$ Hz, 1H); ^{13}C NMR (50 MHz) δ 14.24, 21.52, 60.78, 113.80, 126.74, 127.00, 127.51, 127.72, 128.77, 130.04, 130.07, 130.80, 134.46, 136.46, 140.31, 141.05, 144.62, 166.19; MS m/z (EI): 421 (M^+ , 100), 375 (64), 311 (16), 220 (49), 193 (82), 165 (46), 139 (12), 91 (54), 65 (13), 29 (8).

(E)-Ethyl 2-(3-Bromophenyl)-3-(N-tosyl)amine-2-propenoate (4e): IR 3129, 2982, 1677 cm^{-1} ; ^1H NMR δ 1.25 (t, $J = 7.0$ Hz, 3H), 2.41 (s, 3H), 4.18 (q, $J = 7.0$ Hz, 2H), 6.74 (d, $J = 12.4$ Hz, 1H), 7.26-7.37 (m, 4H), 7.49-7.6 (m, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 12.4$ Hz, 1H); ^{13}C NMR (50 MHz) δ 14.18, 21.30, 60.45, 103.04, 123.08, 126.54, 128.53, 129.98, 130.11, 130.45, 132.14, 134.13, 136.01, 143.19, 150.87, 164.45; MS m/z (EI): 424 (M^+ , 3), 276 (18), 178 (100), 155 (76), 91 (83), 65 (49), 29 (70).

(Z)-Ethyl 3-(3-Bromophenyl)-3-(N-tosyl)amine-2-propenoate (5e): IR 3152, 2927, 1673 cm^{-1} ; ^1H NMR δ 1.26 (t, $J = 7.0$ Hz, 3H), 2.42 (s, 3H), 4.18 (q, $J = 7.0$ Hz, 2H), 5.19 (s, 1H), 7.20-7.23 (m, 3H), 7.30-7.32 (m, 1H), 7.42 (d, $J = 8.4$ Hz, 2H), 10.65 (s, 1H); ^{13}C NMR (50 MHz) δ 14.11, 21.58, 60.67, 102.67, 121.81, 127.49, 127.63, 129.45, 129.50, 131.35, 133.24, 135.96, 136.44, 144.31, 153.07, 168.10; MS m/z (EI): 424 (4), 380 (3), 359 (6), 315 (3), 286 (5), 224 (3), 196 (4), 178 (68), 157 (3), 155 (27), 132 (22), 106 (6), 91 (100).

(E)-Ethyl 2-(2-Methylphenyl)-3-(N-tosyl)amine-2-propenoate (4f): IR 3155, 2984, 1697 cm^{-1} ; ^1H NMR δ 1.20 (t, $J = 7.0$ Hz, 1H), 1.98 (s, 3H), 2.44 (s, 3H), 4.09-4.20 (m, 2H), 6.55 (d, $J = 12.4$ Hz, 1H), 7.13-7.22 (m, 3H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 12.4$ Hz, 1H); ^{13}C NMR (50 MHz) δ 14.16, 19.06, 21.46, 60.53, 113.96, 126.38, 126.60, 128.68, 129.86, 129.95, 130.57, 131.05, 134.57, 136.50, 137.36, 144.49, 166.01; MS m/z (EI): 359 (M^+ , 88), 313 (21), 204 (19), 158 (63), 155 (21), 130 (94), 115 (18), 91 (100), 77 (25), 65 (32), 39 (15), 29 (42).

(E)-Ethyl 2-(2,4-Dichlorophenyl)-3-(N-tosyl)amine-2-propenoate (4g): IR 3449, 3240, 2975, 1711 cm^{-1} ; ^1H NMR δ 1.20 (t, $J = 7.2$ Hz, 3H), 2.45 (s, 3H), 4.14-4.22 (m, 2H), 6.68 (s, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 7.23-7.41 (m, 4H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.76 (s, 1H); ^{13}C NMR (50 MHz) δ 14.19, 21.60, 60.96, 110.55, 115.99, 126.85, 127.81, 129.40, 129.99, 130.09, 132.69, 135.30, 135.35, 135.92, 144.83, 165.31; MS m/z (EI): 413 (48), 378 (36), 368 (6), 332 (24), 212 (11), 178 (20), 155 (61), 123 (21), 91 (100), 65 (46), 29 (41).

(E)-Ethyl 2-(3,5-Dimethoxyphenyl)-3-(N-tosyl)amine-2-propenoate (4h): IR 3218, 2970, 1703 cm^{-1} ; ^1H NMR δ 1.25 (t, $J = 7.0$ Hz, 3H), 2.43 (s, 3H), 3.69 (s, 6H), 4.18 (q, $J = 7.0$ Hz, 2H), 6.19 (d, $J = 2.2$ Hz, 2H), 6.34 (t, $J = 2.2$ Hz, 1H), 7.06 (d, $J = 12.4$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 12.4$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (50 MHz) δ 14.24, 21.49, 55.17, 60.68, 100.28, 107.45, 114.02, 126.72, 130.03, 133.72, 134.50, 136.52, 144.55, 161.05, 165.97; MS m/z (EI): 405 (M^+ , 100), 359 (12), 250 (73), 205 (77), 204 (100), 162 (41), 91 (92), 65 (36), 29 (21).

(E)-Ethyl 2-phenyl-3-(N-tosyl)amine-2-butenate (4i): IR 3268, 2975, 1697 cm^{-1} ; ^1H NMR δ 1.20 (t, $J = 7.0$ Hz, 3H), 1.98 (s, 3H), 2.43 (s, 3H), 4.07-4.21 (m, 2H), 6.54 (s, 1H), 6.87 (d, $J = 7.4$ Hz, 1H), 7.12-7.24 (m, 3H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.67-7.71 (t, 3H); ^{13}C NMR (50 MHz) δ 14.17, 19.07, 21.47, 60.53, 113.99, 126.40, 126.61, 128.70, 129.85, 125.96, 130.59, 131.05, 134.55, 136.51, 137.36, 144.50, 165.98; MS m/z (EI): 359 (M^+ , 71), 313 (19), 204 (21), 188 (13), 158 (66), 155 (22), 130 (100), 115 (17), 91 (91), 77 (27), 65 (31), 39 (17), 29 (40).