Supplementary Information

Iron-Catalyzed Synthesis of Glycine Derivatives via Carbon-Nitrogen Bond Cleavage Using Diazoacetate

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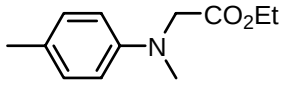
General. All reactions were carried out in dry solvent under an argon atmosphere. Ethanol was purchased from Wako Pure Chemical Industries and was dried before use. $FeCl_3$ was purchased from Nacalai Tesque Inc. $MnBr_2$ was purchased from Kishida Chemical Co. Anilines (**1a**, **1e**, **1g**, **1h**, **1j**, **1k**), ethyl diazoacetate (**2**), thioanisole (**5**), and 2,2,2-trifluoroethanol were purchased from Aldrich Co., Kanto Kagaku Reagent Division, Nacalai Tesque Inc., Tokyo Kasei Kogyo Co., and Wako Pure Chemical Industries. *N*,*N*-dialkylanilines (**1b**, **1c**, **1d**, **1f**, **1i**, **1k**, **1m**) were prepared by standard *N*-alkylation methods from corresponding anilines and iodoalkanes using K_2CO_3 as a base. Ammonium salt **4** was prepared according to the literature method from **3a** and methyl iodide.[1]

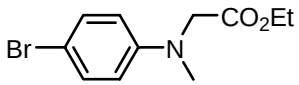
^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to Me_4Si ($CDCl_3$) at δ 0.00 ppm or residual solvent peak ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm. IR spectra were recorded on a SHIMADZU IRAFFINITY-1 100V J.

Glycine derivatives (**3a**, **3b**, **3d** and **3f**) and ethyl 2-(phenylthio)acetate (**6**) were already known. The structures of these reaction products were determined by comparing the spectrum data of these products with those of **3a**,[2] **3b**,[2] **3d**,[3] **3f**[2] and **6**.[4]

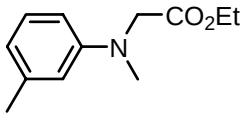
***N*-(4-Methylphenyl)-*N*-methylglycine ethyl ester (3c).** ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 2.24 (s, 3H), 3.03 (s, 3H), 4.02 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 6.62 (d, *J* =



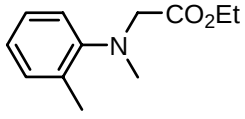
8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 20.2, 39.6, 54.7, 60.7, 112.6, 126.5, 129.7, 146.8, 171.1; IR (nujol, ν / cm^{-1}) 1749, 1618, 1521, 1364, 1251, 1190, 1117, 1030, 949, 804; HRMS (EI^+) Calcd for $C_{12}H_{17}NO_2Na$ ($[M+Na]^+$) 230.1157, Found 230.1153.

***N*-(4-Bromophenyl)-*N*-methylglycine ethyl ester (3e).** 

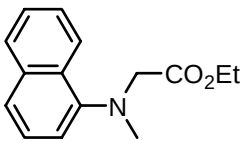
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 3.04 (s, 3H), 4.02 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.55 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 39.6, 54.4, 61.0, 109.4, 113.9, 131.8, 147.9, 170.5; IR (nujol, ν / cm^{-1}) 1765, 1587, 1489, 1277, 1178, 1041, 1009, 905, 818; HRMS (EI^+) Calcd for $C_{11}H_{14}BrNO_2Na$ ($[M+Na]^+$) 294.0106, Found 294.0115.

***N*-(3-Methylphenyl)-*N*-methylglycine ethyl ester (3g).** 

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 2.30 (s, 3H), 3.05 (s, 3H), 4.04 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.48-6.53 (m, 2H), 6.57 (d, *J* = 7.2 Hz, 1H), 7.11 (t, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.9, 39.5, 54.5, 60.8, 109.5, 113.1, 118.3, 129.0, 138.8, 149.0, 171.1; IR (nujol, ν / cm^{-1}) 1749, 1734, 1653, 1604, 1583, 1560, 1499, 1182, 1121, 1031, 953, 765; HRMS (EI^+) Calcd for $C_{12}H_{17}NO_2Na$ ($[M+Na]^+$) 230.1157, Found 230.1155.

***N*-(2-Methylphenyl)-*N*-methylglycine ethyl ester (3h).** 

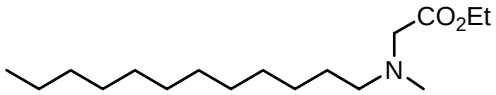
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 2.87 (s, 3H), 3.72 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 7.08-7.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 18.3, 41.4, 57.4, 60.5, 120.2, 123.0, 126.3, 131.2, 132.0, 150.7, 170.9; IR (nujol, ν / cm^{-1}) 1751, 1734, 1654, 1599, 1560, 1493, 1449, 1375, 1261, 1186, 1101, 1031, 947, 766, 725; HRMS (EI^+) Calcd for $C_{12}H_{17}NO_2Na$ ($[M+Na]^+$) 230.1157, Found 230.1149.

***N*-(2-Naphthyl)-*N*-methylglycine ethyl ester (3i).** 

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H), 3.03 (s, 3H), 3.92 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* =

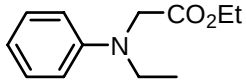
7.5 Hz, 1H), 7.43-7.52 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 41.7, 58.7, 60.6, 123.4, 123.6, 125.46, 125,50, 125.7, 128.4, 128.6, 134.8, 148.7, 170.8; IR (neat, ν / cm^{-1}) 3524, 3049, 2937, 2792, 1747, 1717, 1575, 1558, 1506, 1456, 1396, 1192, 1051, 1028, 937, 802, 775; HRMS (EI^+) ($[M+Na]^+$) Calcd for $C_{15}H_{17}NO_2Na$ (M^+) 266.1157, Found 266.1154.

***N*-Dodecyl-*N*-methylglycine ethyl ester (3j).**



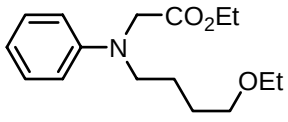
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.20-1.35 (m, 18H), 1.40-1.54 (m 2H), 2.36 (s, 3H), 2.46 (t, 2H) 3.23 (s, 2H) 4.19 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.3, 22.7, 25.7, 27.4, 31.9, 32.8, 42.5, 57.4, 58.6, 60.4, 171.0; IR (nujol, ν / cm^{-1}) 2926, 2854, 1867, 1843, 1748, 1732, 1717, 1697, 1681, 1557, 1541, 1506, 1472, 1456, 1435, 1394, 1182, 1034, 721; HRMS (EI^+) Calcd for $C_{17}H_{35}NO_2Na$ ($[M+Na]^+$) 308.2566, Found 308.2568.

***N*-Ethyl-*N*-phenylglycine ethyl ester (3k).**



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 3.48 (q, *J* = 7.2 Hz, 2H), 4.01 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 14.2, 46.0, 52.3, 60.9, 112.0, 116.8, 129.2, 147.8, 171.4; IR (neat, ν / cm^{-1}) 2976, 2930, 1748, 1732, 1697, 1682, 1601, 1558, 1506, 1456, 1394, 1373, 1271, 1186, 1128, 1030, 988, 746, 691; HRMS (EI^+) Calcd for $C_{12}H_{17}NO_2Na$ ($[M+Na]^+$) 230.1157, found 230.1153.

***N*-(4-Ethoxybutyl)-*N*-phenylglycine ethyl ester (3l).**



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.60-1.67 (m, 2H), 1.67-1.76 (m, 2H), 3.40-3.50 (m, 6H), 4.02 (s, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 6.64 (d, *J* = 8.1 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 7.21 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.2, 24.3, 27.2, 51.9, 52.9, 60.9, 66.2, 70.4, 112.1, 116.9, 129.2, 147.9, 171.3; IR (neat, ν / cm^{-1}) 2976, 2930, 2859, 1751, 1734, 1655, 1601, 1560, 1501, 1458, 1375, 1261, 1180, 1114, 1029, 746; HRMS (EI^+) Calcd for $C_{16}H_{25}NO_3Na$ ($[M+Na]^+$) 302.1732, Found 302.1722.

References

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