Selective Mono-Deactivating Nitrogen of Symmetrical Diamines *via* Complexation:

Application in the mono-Acylation of Symmetrical Diamines

Zhongxing Zhang, Zhiwei Yin, Nicholas A. Meanwell, John F. Kadow and Tao Wang*

Department of Chemistry, The Bristol-Myers Squibb Pharmaceutical Research Institute

5 Research Parkway, Wallingford, CT 06492

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General Procedure: Preparation of Compounds 8aa and 9aa

General procedure for the acylation of symmetrical diamines: 9-BBN (7.4 mL, ~ 0.5 M in hexane from Lancaster, 3.7 mmol) was added to a solution of ethylene diamine (222mg, 3.7 mmol) in dry THF (20 mL). After stirring for 1 h at room temperature, benzoyl chloride (492 mg, 3.5 mmol) was added and the mixture stirred for a further 2 h at room temperature. The reaction mixture was quenched with H₂O, the aqueous layer was extracted with EtOAc (3 x 100 mL) and the combined organic layers dried over MgSO₄. Concentration *in vacuo* afforded a residue which was purified by silica gel chromatography to provide *N*-benzoyl-ethylene diamine **8aa** (450 mg, 79% based on benzoyl chloride used) and *N,N'*-dibenzoyl-ethylene diamine **9aa** (80 mg, 17% based on benzoyl chloride used).

HRMS Results

Compound Number	Formula [M+H]	Theoretic m/z.	Observed m/z	Deviation in ppm
8aa	C ₉ H ₁₃ N ₂ O	165.1028	165.1030	-1.0
9aa	C ₁₆ H ₁₇ N ₂ O ₂	269.1290	269.1285	2.0
8ab	C ₁₀ H ₁₅ N ₂ O	179.1185	179.1180	2.2
9ab	C ₁₈ H ₂₁ N ₂ O ₂	297.1603	297.1612	-3.1

Supporting Material: Spectra

N-(2-Amino-ethyl)-benzamide, 8aa

^1H NMR (500 MHz, CD_3OD) δ 7.86 (d, 2H, $J = 7.00$ Hz), 7.54 (m, 1H), 7.45 (m, 2H), 3.68 (t, 2H, $J = 6.00$ Hz), 3.19 (t, 2H, $J = 6.00$ Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 171.3, 135.0, 133.1, 129.7, 128.5, 41.0, 38.9; HRMS m/z : $(\text{M}-\text{H})^+$ calcd. for $\text{C}_9\text{H}_{13}\text{N}_2\text{O}$: 165.1028. Found: 165.1030.

N, N'-Dibenzoyl-ethylenediamine, 9aa

^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.59 (s, 2H), 7.85 (d, 4H, $J = 7.00$ Hz), 7.48 (m, 6H), 3.46 (s, 4H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 166.5, 134.5, 131.0, 128.1, 127.1, 39.0; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_2$: 269.1290. Found 269.1285.

N-(2-Amino-ethyl)-2-phenyl-acetamide, 8ab

^1H NMR (500 MHz, CD_3OD) δ 7.29 (m, 5H), 3.55 (s, 2H), 3.44 (t, 2H, $J = 6.00$ Hz), 3.02 (t, 2H, $J = 6.00$ Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 175.4, 136.6, 130.4, 129.7, 128.1, 43.7, 40.8, 38.5; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}$: 179.1185. Found: 179.1180.

2-Phenyl-N-(2-phenylacetyl-amino-ethyl)-acetamide, 9ab

^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.04 (s, 2H), 7.26 (m, 10H), 3.38 (s, 4H), 3.11 (s, 4H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 170.2, 136.2, 128.9, 128.1, 126.2, 42.3, 38.4; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2$: 297.1603. Found 297.1612.