Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Electronic Supplementary Information

Convenient Preparations of Azo-Dye Labelled Amino Acids and Amines

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Experimental Section

General Methods:

Melting points were determined on Fisher melting apparatus. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a 300 MHz NMR spectrometer in $CDCl_3$ or DMSO-d_6. HPLC analyses were performed on Beckman system gold programmable solvent module 126, using Chirobiotic T column (4.6 × 250 mm), detection at 254 nm, flow rate of 1.0 mL/min and MeOH as eluting solvent. Elemental analyses were performed on a Carlo Erba-1106 instrument. Optical rotation values were measured with the use of sodium D line. Arylazobenzoic acids, amino acids, and amines were purchased from Fisher or Aldrich chemical company.

General procedure for preparation of *N*-(4-arylazo)benzoyl-benzotriazoles (3a-b): Arylazobenzoic acid **1** (7.43 mmol, 2.0 g for **1a**, 1.68 g for **1b**), 1-(methylsulfonyl)-1*H*-benzotriazole **2**[9d] (1.46 g, 7.43 mmol), Et_3N (1.5 mL, 10.4 mmol) were mixed in THF at room temperature. After refluxing for 5h, the reaction mixture was cooled to room temperature and kept overnight at room temperature, then solid was precipitated. After filtration and drying under vacuum, the corresponding product, *N*-(4-arylazobenzoyl)-benzotriazoles **3a-b**, were obtained.

4-[(4-Dimethylamino)phenylazo]benzoyl-1H-benzotriazole (3a). (2.24 g, 81%). Red microcrystal; mp 210.0–212.0°C (from THF); (Found: C, 68.27; H, 4.77; N, 22.59. Calc. for $C_{21}H_{18}N_6O$: C, 68.09; H, 4.90; N, 22.69%); δ_H(300 MHz; $CDCl_3$) 8.42 (1H, d, *J* 8.4 , Ar*H*), 8.38 (2H, d, *J* 8.7, Ar*H*), 8.19 (1H, d, *J* 8.1, Ar*H*), 7.97 (4H, dd, $J_1 = J_2$ 8.4, Ar*H*), 7.72 (1H, t, *J* 7.2, Ar*H*), 7.56 (1H, t, *J* 8.4, Ar*H*), 6.77 (2H, d, *J* 9.0, Ar*H*) and 3.13 (6H, s, 2 × NCH_3,); δ_C(75 MHz, $CDCl_3$) 170.0, 166.3, 156.4, 153.2, 145.9, 143.9, 133.1, 132.6, 131.1, 130.5, 126.5, 125.8, 122.1, 120.3, 115.0, 111.6 and 40.4.

4-Phenylazobenzoyl-1*H*-benzotriazole (3b). (2.2 g, 84%). Red microcrystal; mp 203.0–204.0 °C (from THF) (Found: C, 70.06; H, 3.80; N, 21.37. Calc. for $C_{19}H_{13}N_5O$: C, 69.71; H, 4.00; N, 21.39%); δ_H(300 MHz; $CDCl_3$) 8.44-8.39 (3H, m, Ar*H*), 8.20 (1H, d, *J* 8.4, Ar*H*), 8.09 (2H, d, *J* 8.4, Ar*H*), 8.01-7.98 (2H, m, Ar*H*), 7.77-7.72 (1H, m, Ar*H*), 7.61-7.51 (4H, m, Ar*H*); δ_C(75 MHz, $CDCl_3$) 166.2, 155.4, 152.7, 145.9, 133.0, 132.5, 132.1, 130.7, 129.4, 126.6, 123.4, 122.8, 120.4, 115.0.

General method for the preparation of carboxylic azo-dye labeled amino acids 5a-m: *N*-(4-Arylazobenzoyl)benzotriazole **3** (200 mg, 0.54 mmol for **3a** and 0.611 mmol for **3b**, 1eq.) and amino acid **4**

(1eq.) were added to a mixture of DMF and water (3:1,v/v), and stirred at room temperature for 24h. After the evaporation of solvent, washed with CH_2Cl_2 and drying under vacuum, the corresponding pure products **5** were obtained with high yield of 81-99%; For **5k-m**, after the evaporation of solvent, the residue was dissolved in CH_2Cl_2 and washed with 4N HCl.

4-[(4-Dimethylamino)phenylazo]benzoylglycine (5a). (175 mg, 99%). Red microcrystal; mp 238.0–240.0°C (from CH_2Cl_2) (lit.,[4b,10] mp 232-233°C); δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.94 (1H, t, *J* 5.7, N*H*), 8.02 (2H, d, *J* 8.7, Ar*H*), 7.84 (2H, d, *J* 8.7, Ar*H*), 7.83 (2H, d, *J* 9.3, Ar*H*), 6.85 (2H, d, *J* 9.3, Ar*H*), 3.95 (2H, d, *J* 6.0, CH_2) and 3.08 (6H, s, 2 × CH_3); δ_C(75 MHz, DMSO-d_6) 171.4, 165.9, 154.1, 152.9, 142.7, 134.1, 128.4, 125.1, 121.6, 111.6, 41.4 and 39.8.

4-[4-(Dimethylamino)phenylazo]benzoyl-L-alanine (**5b**). (200 mg, 81%). Red microcrystal; mp 205–207°C (from CH_2Cl_2); $[\alpha]_D^{25}$ +73.3 (c 2.6 in MeOH); found: C, 63.29; H, 6.05; N, 16.19. Calc. for $C_{18}H_{20}N_4O_3$: C, 63.51; H, 5.92; N, 16.46%; δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.62 (1H, d, *J* 7.2, N*H*), 8.01 (2H, d, *J* 8.1 Hz, Ar*H*), 7.82 (4H, d, *J* 8.7, Ar*H*), 6.85 (2H, d, *J* 9.3, Ar*H*), 4.4–4.25 (1H, m, C*H*CH_3), 3.08 (6H, s, 2 × CH_3) and 1.39 (3H, d, *J* 7.5, CHCH_3); δ_C(75 MHz, DMSO-d_6; Me_4Si) 174.9, 165.2, 154.0, 152.8, 142.5, 134.4, 128.5, 125.1, 121.5, 111.6, 48.8, 39.8 and 17.4.

4-[4-(Dimethylamino)phenylazo]benzoyl-L-phenylalaine (**5c**). (180 mg, 80%). Red microcrystal; mp 202.0–203.0 °C (from CH_2Cl_2); $[\alpha]_D^{25}$ +119.4 (c 1.8 in MeOH); found: C, 69.00; H, 5.90; N, 13.28. Calc. for $C_{24}H_{24}N_4O_3$: C, 69.21; H, 5.81; N, 13.45%; δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.80 (1H, d, *J* 7.8, N*H*), 7.94 (2H, d, *J* 8.4, Ar*H*), 7.83-7.78 (4H, m, Ar*H*), 7.34-7.18 (5H, m, Ar*H*), 6.85 (2H, d, *J* 9.3, Ar*H*), 4.66-4.59 (1H, m, C*H*CH_2), 3.24–3.18 (2H, m, CHCH_2) and 3.08 (6H, s, 2 × CH_3); δ_C(75 MHz, DMSO-d_6; Me_4Si) 173.3, 165.8, 154.1, 152.8, 142.6, 138.2, 134.1, 129.1, 128.5, 128.2, 126.3, 125.1, 121.5, 111.6, 54.4, 39.8 and 36.3.

4-[4-(Dimethylamino)phenylazo]benzoyl-L-typtophan (**5d**). (220 mg, 90%). Red microcrystal; mp 220.0–222.0°C (from CH_2Cl_2); $[\alpha]_D^{25}$ +112.1 (c 2.6 in MeOH); found: C, 67.13; H, 5.57; N, 15.42. Calc. for $C_{26}H_{25}N_5O_3 \cdot 1/2H_2O$: C, 67.23; H, 5.64; N, 15.08%; δ_H(300 MHz, DMSO-d_6; Me_4Si) 10.80 (1H, s, COO*H*), 8.53 (1H, s, N*H*CO), 7.95 (2H, d, *J* 8.4, Ar*H*), 7.80 (4H, t, *J* 7.8, Ar*H*), 7.60 (1H, d, *J* 7.8, Ar*H*), 7.31 (1H, d, *J* 8.1, Ar*H*), 7.21 (1H, s, =C*H*NH), 7.04 (1H, t, *J* 7.2, Ar*H*), 6.96 (1H, t, *J* 7.5, Ar*H*), 6.84 (2H, d, *J* 9.3, Ar*H*), 4.68-

4.58 (1H, m, C*H*CH_2), 3.41–3.19 (3H, m, CHCH_2 and N*H*CH=) and 3.07 (6H, s, 2 × CH_3); δ_C(75 MHz, DMSO-d_6; Me_4Si) 165.7, 154.1, 152.9, 142.7, 136.2, 134.7, 128.6, 127.5, 125.2, 123.6, 121.5, 120.9, 118.3, 111.6, 111.4, 111.1, 55.0, 54.6, 39.9 and 27.1.

4-[4-(Dimethylamino)phenylazo]benzoyl-L-isoleucine (**5e**). (220 mg, 87%). Red microcrystal; mp 232.0–234.0°C (from CH_2Cl_2); $[\alpha]_D^{25}$ +52.2 (c 2.5 in MeOH); found: C, 60.29; H, 7.43; N, 13.18. Calc. for $C_{21}H_{26}N_4O_3 \cdot 2H_2O$: C, 60.27; H, 7.23; N, 13.39%; δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.43 (1H, d, *J* 6.6, N*H*), 8.02 (2H, d, *J* 8.4, Ar*H*), 7.82 (4H, d, *J* 8.4, Ar*H*), 6.85 (2H, d, *J* 9.0, Ar*H*), 4.33 (1H, t, *J* 7.2, NHC*H*), 3.07 (6H, s, 2 × CH_3), 2.05–1.90 (1H, m, C*H*CH_2), 1.59-1.51 (1H, m, CHCH_2), 1.33-1.22 (1H, m, CHCH_2), 0.94 (3H, d, *J* 6.9, CHCH_3) and 0.88 (3H, t, *J* 7.2, CH_2CH_3); δ_C(75 MHz, DMSO-d_6; Me_4Si) 166.0, 154.1, 152.8, 142.6, 134.5, 128.7, 125.1, 121.4, 111.6, 57.7, 39.8, 36.0, 15.7 and 11.2.

4-[4-(Dimethylamino)phenylazo]benzoyl-L-methionine (**5f**). (175 mg, 81%). Red microcrystal; mp 205.0–207.0°C (from CH_2Cl_2); $[\alpha]_D^{25}$ +31.1 (c 2.6 in MeOH); found: C, 59.96; H, 6.19; N, 13.65. Calc. for $C_{20}H_{24}N_4O_3S$: C, 59.98; H, 6.04; N, 13.99%; δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.75 (1H, d, *J* 7.8, N*H*), 8.03 (2H, d, *J* 8.7, Ar*H*), 7.83 (4H, d, *J* 8.4 , Ar*H*), 6.85 (2H, d, *J* 9.3, Ar*H*), 4.57-4.50(1H, m, NHC*H*), 3.08 (6H, s, 2 × CH_3), 2.64-2.50 (2H, m, CH_2S), 2.11-2.05 (2H, m, CHCH_2) and 2.07 (3H, s, SCH_3); δ_C(75 MHz, DMSO-d_6; Me_4Si) 173.5, 166.1, 154.1, 152.9, 142.6, 134.2, 128.7, 125.1, 121.5, 111.6, 51.8, 39.8, 30.3, 30.1 and 14.6.

4-[4-(Dimethylamino)phenylazo]benzoyl-L-serine (**5g**). (170 mg, 88%). Red microcrystal; mp 205.0–207.0°C (from CH_2Cl_2); $[\alpha]_D^{25}$ +60.0 (c2.8 in MeOH); found: C, 59.49; H, 5.69; N, 15.22. Calc. for $C_{18}H_{20}N_4O_4 \cdot 1/3H_2O$: C, 59.66; H, 5.75; N, 15.46%; δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.53 (1H, d, *J* 7.5, N*H*), 8.05 (2H, d, *J* 8.4, Ar*H*), 7.86-7.82 (4H, m, Ar*H*), 6.85 (2H, d, *J* 7.5, Ar*H*), 4.58-4.45 (1H, m, NHC*H*), 3.82 (2H, d, *J* 5.1, CHCH_2) and 3.08 (6H, s, 2 × CH_3); δ_C(75 MHz, DMSO-d_6; Me_4Si) 172.0, 165.8, 154.1, 152.8, 142.7, 134.2, 128.6, 125.1, 121.5, 111.6, 61.2, 55.8 and 39.8.

4-[4-(Dimethylamino)phenylazo]benzoyl-DL-phenylalaine (**5h**). (185 mg, 82%). Red microcrystal; mp 203.0–204.0°C (from CH_2Cl_2); found: C, 69.02; H, 5.96; N, 13.23. Calc. for $C_{24}H_{24}N_4O_3$: C, 69.21; H, 5.81; N, 13.45%; δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.82 (1H, d, *J* 8.1, N*H*), 7.94 (2H, d, *J* 8.4, Ar*H*), 7.83-7.79 (4H, m, Ar*H*), 7.34-7.16 (5H, m, Ar*H*), 6.85 (2H, d, *J* 9.3, Ar*H*), 4.68-4.58 (1H, m, NHC*H*), 3.24-3.05 (2H, m, CHCH_2)

and 3.08 (6H, s, 2 × C*H*$_3$); δ_C(75 MHz, DMSO-d_6; Me_4Si) 173.2, 165.8, 154.1, 152.8, 142.7, 138.3, 134.1, 129.1, 128.5, 128.2, 126.4, 125.1, 121.5, 111.6, 54.4, 39.8 and 36.3.

4-[(4-Dimethylamino)phenylazo]benzoyl-DL-phenylglycine (5i). (190 mg, 88%). Red microcrystal; mp 189–191°C (from CH_2Cl_2) (lit., [7-8] 188-190°C); δ_H(300 MHz, DMSO-d_6; Me_4Si) 9.17 (1H, d, *J* 7.5 Hz, N*H*), 8.09 (2H, d, *J* 8.4, Ar*H*), 7.92 (1H, br s, COO*H*), 7.84 (4H, d, *J* 9.0, Ar*H*), 7.55-7.32 (5H, m, Ar*H*), 6.85 (2H, d, *J* 9.0, Ar*H*), 5.64 (1H, d, *J* 7.2, NHC*H*) and 3.08 (6H, s, 2 × C*H*$_3$); δ_C(75 MHz, DMSO-d_6; Me_4Si) 171.9, 165.7, 154.1, 152.8, 142.7, 137.2, 134.0, 130.5, 128.9, 128.4, 128.2, 127.9, 125.3, 125.1, 121.7, 121.4, 111.6, 57.0 and 39.8.

4-[4-(Dimethylamino)phenylazo]benzoyl-6-aminocaproic acid (5j). (197 mg, 95%). Red microcrystal; mp 208.0–210.0°C (from CH_2Cl_2); found: C, 65.57; H, 6.85; N, 14.55. Calc. for $C_{21}H_{26}N_4O_3$: C, 65.95; H, 6.85; N, 14.65%; δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.56 (1H, t, *J* 5.7, N*H*), 7.98 (2H, d, *J* 8.4, Ar*H*), 7.84-7.80 (4H, m, Ar*H*), 6.85 (2H, d, *J* 9.3, Ar*H*), 3.34-3.23 (2H, m, NHC*H*$_2$), 3.08 (6H, s, 2 × C*H*$_3$), 2.22 (2H, t, *J* 7.2, C*H*$_2$CO), 1.59-1.49 (4H, m, NHCH$_2$C*H*$_2$ and C*H*$_2$CH$_2$CO) and 1.37-1.28 (2H, m, NHCH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$CO); δ_C(75 MHz, DMSO-d_6; Me_4Si) 174.5, 165.5, 153.9, 152.8, 142.6, 135.0, 128.3, 125.1, 121.5, 111.6, 39.8, 39.2, 33.7, 28.9, 26.1 and 24.3.

4-Phenylazobenzoyl-L-leucine (**5k**). (170 mg, 86%). Off red microcrystal; mp 120.0–122.0°C (from CH_2Cl_2/Hexane) (lit.,[8c] mp 173°C); $[\alpha]_D^{25}$ 9.0 (c 2.5 in MeOH); found: C, 65.59; H, 6.21; N, 12.08. Calc. for $C_{19}H_{21}N_3O_3.1/2H_2O$: C, 65.50; H, 6.36; N, 12.06; δ_H(300 MHz, $CDCl_3$) 7.95-7.90 (6H, m, Ar*H*), 7.56-7.51 (3H, m, Ar*H*), 6.73 (1H, d, *J* 7.8, N*H*), 4.91-4.84 (1H, m, NHC*H*), 1.88-1.72 (3H, m, C*H*$_2$C*H*CH$_3$) and 1.01 (6H, d, *J* 4.5, 2 × C*H*$_3$); δ_C(75 MHz, $CDCl_3$) 176.7, 167.6, 154.5, 152.5, 135.3, 131.7, 129.2, 128.4, 123.2, 123.0, 51.6, 41.2, 25.1, 23.0 and 22.0.

4-Phenylazobenzoyl-L-phenylalanine (**5l**). (216 mg, 95%). Off red microcrystal; mp 185–186°C (from CH_2Cl_2/Hexane) (lit.,[7] mp 183-184°C); $[\alpha]_D^{25}$ +103.0 (c 2.4 in MeOH); δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.93 (1H, d, *J* 7.8, N*H*), 8.03-7.94 (6H, m, Ar*H*), 7.62 (3H, br s, Ar*H*), 7.33-7.19 (6H, m, Ar*H*), 4.68-4.60 (1H, m, NHC*H*) and 3.26-3.06 (2H, m, CHC*H*$_2$); δ_C(75 MHz, DMSO-d_6; Me_4Si) 173.2, 165.6, 153.4, 151.9, 138.2, 136.1, 132.1, 129.6, 129.1, 128.7, 128.2, 126.4, 122.8, 122.4, 54.5 and 36.3.

4-Phenylazobenzoyl-L-alanine (**5m**). (158 mg, 87%). Off red microcrystal; mp 222–224°C (from CH_2Cl_2/Hexane) (lit.,[8c] 220°C); $[\alpha]_D^{25}$ +29.3 (c 2.5 in MeOH); δ_H(300 MHz, DMSO-d_6; Me_4Si) 8.89 (1H, d, *J* 7.2, N*H*), 8.12 (2H, d, *J* 8.4, Ar*H*), 7.99-7.94 (4H, m, Ar*H*), 7.64-7.62 (3H, m, Ar*H*), 4.50-4.44 (1H, m, NHC*H*) and 1.43 (3H, d, *J* 7.5, CH_3); δ_C(75 MHz, DMSO-d_6; Me_4Si) 174.2, 165.4, 153.4, 151.9, 136.1, 132.1, 129.6, 128.8, 122.8, 122.4, 48.3 and 16.9.

Gerenal procedure for the preparation of 7a-f: Procedure A: *N*-[[4-(*p*-Dimethylaminophenylazo)]benzoyl]benzotriazole **(3)** (200 mg, 0.54 mmol for **3a** and 0.611 mmol for **3b**) and corresponding amines (1-3eq.) were mixed in THF (10mL) and stirred for 1-48 hours at room temperature (monitored by TLC). After the evaporation of solvent, pure products **7** were obtained from the residues after simple purification procedures with high yield of 85-100%.

4-[4-(Dimethylamino)phenylazo]benzoyl-morpholine (**7a**). 1eq. **6a**; purified with column on silica gel eluting with ethyl acetate/hexane (1:2, v/v) to give **7a** as red microcrystal (184 mg, 100%); mp 212.0–215.0°C (from EtOAc/Hexane); found: C, 67.57; H, 6.66; N, 16.57. Calc. for $C_{19}H_{22}N_4O_2$: C, 67.44; H, 6.55; N, 15.56%; δ_H(300 MHz, $CDCl_3$) 7.88 (4H, t, *J* 8.1, Ar*H*), 7.52 (2H, d, *J* 8.1, Ar*H*), 6.76 (2H, d, *J* 9.0, Ar*H*), 3.85-3.40 (8H, br s, CH_2CH_2) and 3.11 (6H, s, 2 × CH_3); δ_C(75 MHz, $CDCl_3$) 170.1, 154.0, 152.8, 143.6, 135.6, 128.1, 125.4, 122.3, 111.5, 66.9, 40.3 and 29.8.

4-[4-(Dimethylamino)phenylazo]benzoyl-*n*-butylamine (**7b**). 1eq. **6b**; worked up with MeOH to give **7b** as red microcrystal (180 mg, 93%); mp 212.0–214.0°C (from MeOH); found: C, 70.58; H, 7.64; N, 17.37. Calc. for $C_{19}H_{24}N_4O$: C, 70.34; H, 7.46; N, 17.27%; δ_H(300 MHz, $CDCl_3$) 7.89 (2H, d, *J* 9.3, Ar*H*), 7.86 (4H, s, Ar*H*), 6.75 (2H, d, *J* 8.7, Ar*H*), 6.18 (1H, br s, N*H*), 3.48 (2H, q, *J* 6.6, NHCH_2), 3.10 (6H, s, 2 × NCH_3), 1.67-1.58 (2H, m, NHCH$_2$CH_2), 1.49-1.37 (2H, m, CH_2CH$_3$) and 0.97 (3H, t, *J* 7.2, CH_3); δ_C(75 MHz, $CDCl_3$) 167.2, 155.1, 152.9, 143.7, 134.9, 127.9, 125.5, 122.3, 111.6, 40.4, 40.0, 31.9, 29.8, 20.3 and 13.9.

4-[4-(Dimethylamino)phenylazo]benzoyl-*tert*-butylamine (**7c**). 3eq. **6c**; worked up with MeOH to give **7c** as red microcrystal (148 mg, 85 %); mp 228.0–230.0°C (from MeOH); found: C, 7.48; H, 7.85; N, 17.12. Calc. for $C_{19}H_{24}N_4O$: C, 70.34; H, 7.46; N, 17.27%; δ_H(300 MHz, $CDCl_3$) 7.91-7.80 (6H, m, Ar*H*), 6.76 (2H, d, *J* 9.3, Ar*H*), 5.98 (1H, s, N*H*), 3.10 (6H, s, 2 × NCH_3) and 1.50 (9H, s, 3 × CCH_3); δ_C(75 MHz, $CDCl_3$) 166.5, 154.9,

152.8, 143.7, 136.0, 127.7, 125.4, 122.2, 111.5, 51.8, 40.4 and 29.0.

4-[4-(Dimethylamino)phenylazo]benzoyl-*2*-(ethylamino)-ethanol (**7d**).[3i] 1eq. **6d**; purified with column on silica gel eluting with CH_2Cl_2/MeOH (10:1, v/v) to give **7d** as red microcrystal (180 mg, 94%); mp 176.0–178.0°C (from MeOH); found: C, 64.38; H, 6.94; N, 15.85. Calc. for $C_{19}H_{24}N_4O_3$: C, 64.03; H, 6.79; N, 15.72%; δ_H(300 MHz, $CDCl_3$) 7.89-7.82 (6H, m, Ar*H*), 6.92 (1H, s, N*H*), 6.74 (2H, d, *J* 8.7, Ar*H*), 3.75 (2H, br s, NHCH_2), 3.67 (4H, br s, CH_2OCH_2), 3.62-3.59 (2H, m, CH_2OH), 3.09 (6H, s, 2 × CH_3) and 2.66 (br s, 1H, O*H*); δ_C(75 MHz, $CDCl_3$) 167.4, 155.1, 152.9, 143.7, 134.6, 128.0, 125.5, 122.3, 111.6, 72.4, 70.0, 61.9, 40.4 and 40.0.

4-[4-(Dimethylamino)phenylazo]benzoyl-*6*-amino-*1*-hexanol (**7e**). 1.1eq. **6e**; worked up with CH_2Cl_2 to give **7e** as red microcrystal (93%); mp 150.0–152.0°C (from CH_2Cl_2); found: C, 64.00; H, 7.49; N, 14.21. Calc. for $C_{21}H_{28}N_4O_2$·4/3H_2O C, 64.26; H, 7.88; N, 14.27; δ_H(300 MHz; DMSO-d_6; Me_4Si) 8.57 (1H, t, *J* 5.1, N*H*), 7.98 (2H, d, *J* 8.4, Ar*H*), 7.84-7.80 (4H, m, Ar*H*), 6.85 (2H, d, *J* 9.0, Ar*H*), 4.38 (1H, br s, O*H*), 3.30-3.24 (4H, m, NHCH_2 and CH_2OH), 3.08 (6H, s, 2 × CH_3) and 1.54-1.32 (8H, m, $CH_2(CH_2)_4CH_2$); δ_C(75 MHz; DMSO-d_6; Me_4Si) 165.5, 153.9, 152.8, 142.6, 135.0, 128.3, 125.1, 121.5, 111.6, 60.7, 39.8, 39.3, 32.5, 29.2, 26.5 and 25.3.

4-[4-(Dimethylamino)phenylazo]benzoyl-L-*α*-**methylbenzyl-amine** (**7f**).[13] 1.3eq **6f**; worked up with MeOH to give **7f** as red microcrystal (176 mg, 88%); mp 222–224°C (from MeOH); $[\alpha]_D^{25}$ +250.0 (c 2.3 in MeOH); retention time: 3.45; found: C, 72.99; H, 6.46; N, 14.81. Calc. for $C_{23}H_{24}N_4O$.1/3H_2O: C, 72.99; H, 6.57; N, 14.80%; δ_H(300 MHz, $CDCl_3$) 7.91-7.87 (6H, m, Ar*H*), 7.43-7.29 (5H, m, Ar*H*), 6.76 (2H, d, *J* 9.3, Ar*H*), 6.37 (1H, d, *J* 7.5, N*H*), 5.41-5.32 (1H, m, C*H*CH_3), 3.11 (6H, s, 2 × NCH_3) and 1.63 (3H, d, *J* 6.9, CHCH_3); δ_C(75 MHz, $CDCl_3$) 166.2, 155.1, 152.8, 143.6, 143.2, 134.6, 128.8, 127.9, 127.5, 126.3, 125.4, 122.3, 111.5, 49.3, 40.3 and 21.8.

The preparation of 7g, 7h: Procedure B. 4-[(4-Dimethylamino)phenylazo]benzoyl-1*H*-benzotriazole (**3a**) (200 mg, 0.54 mmol) was added to the solution of amine (1-3eq.) and Et_3N (3.0 eq.) in THF (10ml) at room temperature. The mixture was heated under reflux for 24 hours. After filtration, the solvent was evaporated under reduced pressure. Pure products were obtained from the residues after simple purification procedures.

4-[4-(Dimethylamino)phenylazo]benzoyl-L-valine methyl ester (**7g**). 1.0eq. **6g**; purified with column on silica

gel eluting with ethyl acetate/hexanes (1:3, v/v) to give **7g** as red microcrystal (188 mg, 90%); mp 156.0–158.0°C (from EtOAc/Hexane); $[\alpha]_D^{25}$ +59.6 (c 2.8 in MeOH); retention time: 3.29; found: C, 66.05; H, 6.94; N, 14.37. Calc. for $C_{21}H_{26}N_4O_3$: C, 69.95; H, 6.85; N, 14.65%; δ_H(300 MHz, $CDCl_3$) 7.90 (6H, m, Ar*H*), 6.76 (2H, d, *J* 9.0, Ar*H*), 6.67 (1H , d, *J* 8.4, N*H*), 4.83-4.79 (1H, m, *J* 5.1, 3.6, NHC*H*), 3.79 (3H, s, OCH_3), 3.12 (6H, s, 2 × NCH_3), 2.33-2.27 (1H, m, C*H*CH_3) and 1.02 (6H, t, *J* 6.6, 2 × CHCH_3); δ_C(75 MHz, $CDCl_3$) 172.8, 167.0, 155.4, 152.9, 143.7, 134.2, 128.1, 125.6, 122.4, 111.6, 57.6, 52.4, 40.4, 31.8, 19.2 and 18.2.

4-[4-(Dimethylamino)phenylazo]benzoyl-*p*-toluidine (**7h**). 3.0eq. **6h**; worked up with MeOH to give **7h** as red microcrystal (166 mg, 86%); mp 263.0–265.0°C (from MeOH); found: C, 73.94; H, 6.40; N, 15.57. Calc. for $C_{22}H_{22}N_4O$: C, 73.72; H, 6.19; N, 15.63%; δ_H(300 MHz; DMSO-d_6; Me_4Si) 10.28 (1H, s, N*H*), 8.11 (2H, d, *J* 8.4, Ar*H*), 7.86 (4H, t, *J* 8.7, 10.2, Ar*H*), 7.69 (2H, d, *J* 8.1, Ar*H*), 7.17 (2H, d, *J* 8.1, Ar*H*), 6.86 (2H, d, *J* 9.0, Ar*H*), 3.09 (6H, s, 2 × NCH_3) and 2.29 (3H, s, PhCH_3); δ_C(75 MHz; DMSO-d_6; Me_4Si) 164.7, 154.1, 152.9, 142.6, 136.6, 135.1, 132.7, 129.0, 128.8, 125.2, 121.6, 120.4, 111.6, 39.8 and 20.5.

Gerenal procedure for the preparation of 7i-k: Procedure C: *N*-[[4-(p-Dimethylaminophenylazo)]benzoyl]benzotriazole (**3a**) (200 mg, 0.54 mmol) and corresponding amine (2.0-3.0 eq.), Et_3N (0.23mL, 1.62 mmol) were mixed in DMF (10mL). The mixture was heated at 150°C for 5-10 hours. After the evaporation of solvent under reduced pressure, the residue was worked up with MeOH and the products were obtained as red solids.

4-[4-(Dimethylamino)phenylazo]benzoyl-*N*-methylaniline (**7i**). 3eq. **6i**; worked up with MeOH to give **7i** as red microcrystal (140 mg, 74%); mp 185.0–187.0°C (from MeOH); found: C, 73.38; H, 6.35; N, 15.71. Calc. for $C_{22}H_{22}N_4O$: C, 73.72; H, 6.19; N, 15.63%; δ_H(300 MHz; DMSO-d_6; Me_4Si) 7.75 (2H, d, *J* 7.5, Ar*H*), 7.57 (2H, d, *J* 6.9, Ar*H*), 7.38 (2H, d, *J* 7.8, Ar*H*), 7.27 (2H, d, *J* 6.6, Ar*H*), 7. 20 (3H, d, *J* 6.3, Ar*H*), 6.82 (2H, d, *J* 7.8, Ar*H*), 3.40 (3H, s, CONCH_3) and 3.06 (6H, s, 2 × NCH_3); δ_C(75 MHz; DMSO-d_6; Me_4Si) 168.9, 152.7, 152.4, 144.4, 142.6, 136.8, 129.3, 129.1, 127.1, 126.5, 125.0, 121.0, 111.5, 39.8 and 37.8.

4-[4-(Dimethylamino)phenylazo]benzoyl-2-aminopyridine (**7j**). 3 eq. **6j**; worked up with MeOH to give **7j** as red microcrystal (157 mg, 84%); mp190.0–192.0°C (from MeOH); found: C, 69.34; H, 5.64; N, 20.30. Calc. for $C_{20}H_{19}N_5O$: C, 69.55; H, 5.54; N, 20.28; δ_H(300 MHz; DMSO-d_6; Me_4Si) 10.90 (1H, s, N*H*), 8.42-8.40 (1H, m, Ar*H*), 8.22 (1H, d, *J* 8.4, Ar*H*), 8.18 (2H, d, *J* 8.7, Ar*H*), 7.89-7.83 (5H, m, Ar*H*), 7.20-7.16 (1H, m, Ar*H*), 6.87

(2H, d, *J* 9.3, Ar*H*) and 3.09 (6H, s, 2 × CH_3); δ_C(75 MHz; DMSO-d_6; Me_4Si) 165.4, 154.4, 152.9, 152.2, 148.0, 142.7, 138.1, 134.2, 129.3, 125.2, 121.5, 119.9, 114.8, 111.6 and 39.8.

4-[4-(Dimethylamino)phenylazo]benzoyl-carbazole (**7k**). 2eq. **6k**; worked up with MeOH to give **7k** as red microcrystal (183 mg, 81%); mp 204.0–206.0°C (from MeOH); found: C, 77.12; H, 5.20; N, 13.35. Calc. for $C_{27}H_{22}N_4O$: C, 77.49; H, 5.30; N, 13.39%; δ_H(300 MHz; DMSO-d_6; Me_4Si) 8.25-8.22 (2H, m, Ar*H*), 7.94 (2H, d, *J* 8.7, Ar*H*), 7.87 (4H, d, *J* 9.0, Ar*H*), 7.50-7.46 (2H, m, Ar*H*), 7.43-7.39 (4H, m, Ar*H*), 6.87 (2H, d, *J* 9.3 , Ar*H*) and 3.01 (6H, s, 2 × CH_3); δ_C(75 MHz; DMSO-d_6; Me_4Si) 168.5, 154.7, 153.1, 142.7, 138.5, 135.2, 130.2, 127.0, 125.4, 123.6, 122.2, 120.4, 115.3, 111.6 and 39.9.

The preparation of 7l-n.

In the preparation of **7l-n,** 200 mg (0.611mmol) of 4-phenylazobenzoyl-1*H*-benzotriazole **3b** was used.

4-Phenylazobenzoyl-benzylamine (**7l**). Procedure A; 1.2 eq. **6l**; worked up with MeOH; to give **7l** as off red microcrystal (175 mg, 91%); mp 192–193°C (from MeOH) (lit.,[8b], 194–194.5°C); δ_H(300 MHz; DMSO-d_6; Me_4Si) 7.99-7.93 (6H, m, Ar*H*), 7.57-7.50 (3H, m, Ar*H*), 7.39-7.31 (5H, m, Ar*H*), 6.53 (1H, br s, N*H*) and 4.68 (2H, d, *J* 5.4, NHCH_2); δ_C(75 MHz; DMSO-d_6; Me_4Si) 166.8, 154.4, 152.6, 138.1, 136.2, 131.7, 129.3, 128.9, 128.1, 127.8, 123.2, 123.0 and 44.4.

4-Phenylazobenzoyl-m-toluidine (7m). Procedure D; 3 eq. **6m**; worked up with MeOH to give **7m** as off red microcrystal (165 mg, 86%); mp168.0–169.0°C (from MeOH) (lit.,[8b] 168.5–170.0°C); δ_H(300 MHz; $CDCl_3$) 7.98-7.89 (7H, m, Ar*H*), 7.55-7.51 (4H, m, Ar*H*), 7.43 (1H, d, *J* 8.1, Ar*H*), 7.27-7.22 (1H, m, Ar*H*), 6.97 (1H, d, *J* 7.2, Ar*H*) and 2.36 (3H, s, CH_3); δ_C(75 MHz; DMSO-d_6; Me_4Si) 165.2, 154.4, 152.6, 139.2, 137.8, 136.8, 131.8, 129.3, 129.0, 128.2, 125.7, 123.2, 123.2, 121.2, 117.6 and 21.6.

4-Phenylazobenzoyl-DL-valine methyl ester (**7n**). Procedure D; 1eq **6n**; purified with column on silica gel eluting with ethyl acetate/hexanes (1:3, v/v) to give **7n** as off red microcrystal (189 mg, 91%); mp 131–132°C (from EtOAc/Hexane) (lit.,[14] 130–131°C); retention time: 0/3.08, 3.25; δ_H(300 MHz; $CDCl_3$) 8.00-7.94 (6H, m, Ar*H*), 7.57-7.48 (3H, m, Ar*H*), 6.72 (1H, d, *J* 8.4 , N*H*), 4.83-4.79 (1H, m, NHC*H*), 3.78 (3H, s, OCH_3), 2.36-2.26 (1H, m, C*H*CH_3) and 1.03 (6H, t, *J* 6.9, 2 × CHCH_3); δ_C(75 MHz; DMSO-d_6; Me_4Si) 172.7, 166.7, 154.5, 152.6, 135.9, 131.7, 129.2, 128.2, 123.2, 123.0, 57.7, 52.4, 31.7, 19.1 and 18.1.