Supporting Information

"Expanding Dendrons. The Photoisomerism of Folded Azobenzene Dendrons"

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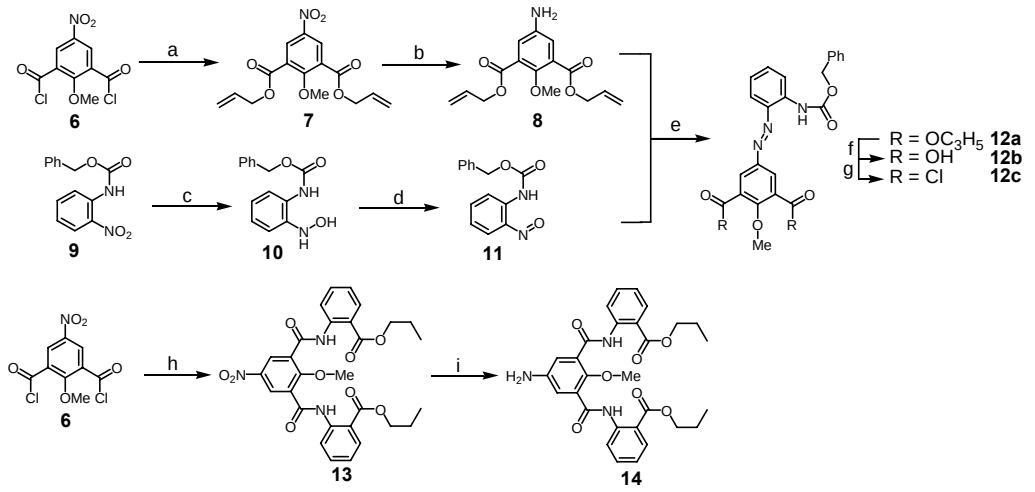
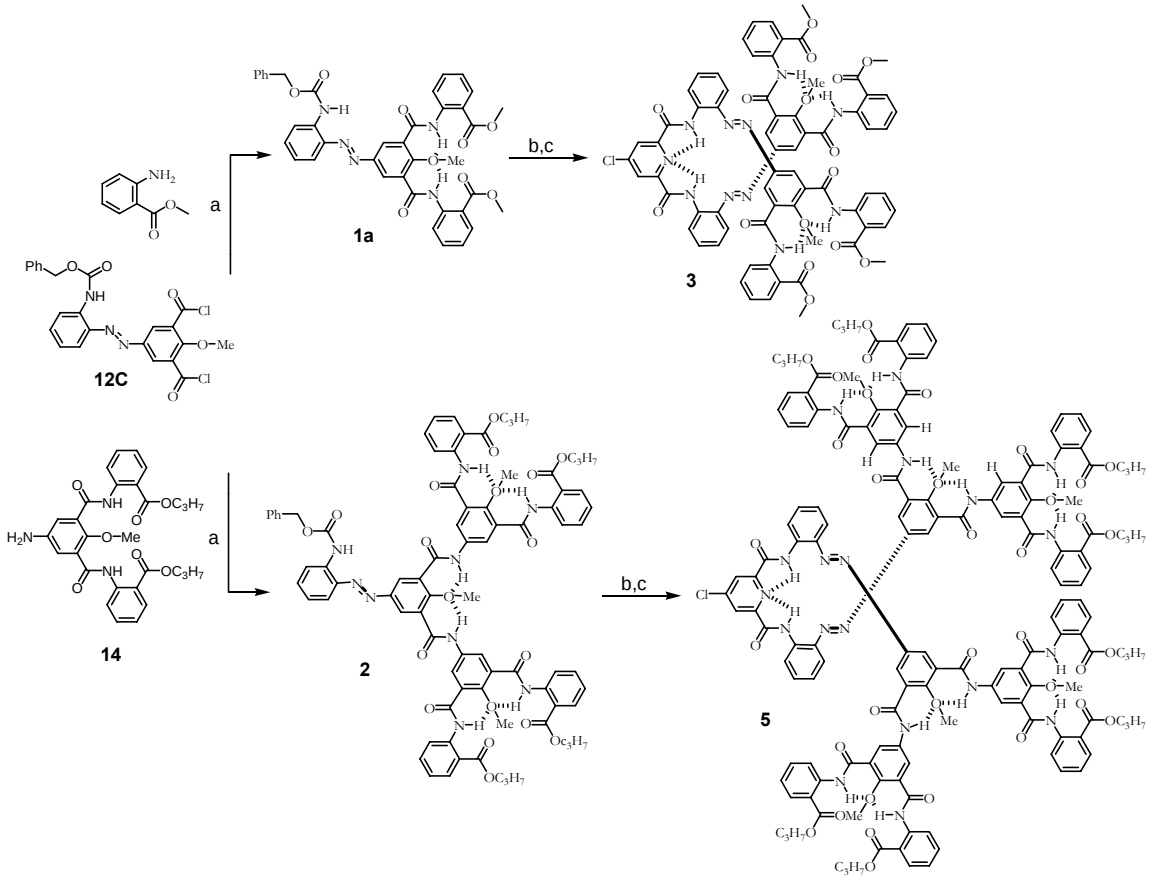
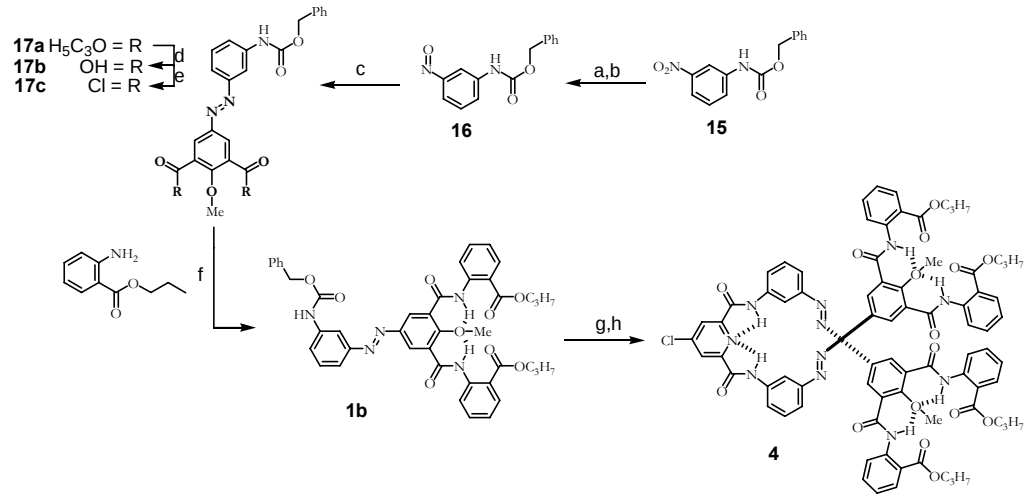


Scheme 1. K*ey*. (a) ally alcohol, THF-pyridine, 89%; (b) $SnCl_2$, EtOAc / MeOH, reflux, 92%; (c) Rh/C, NH_2NH_2, THF, quant.; (d) *t*-butyl hypochlorite, THF, -78 °C, 68%; (e) AcOH, 80 °C, 90%; (f) $Pd_2(dba)_3$•$CHCl_3$, PPh_3, THF, 98%; (g) $(COCl)_2$, DMF (cat.), THF, quant.; (h) propyl anthranilate, DMAP, THF-pyridine, 82%; (i) $SnCl_2$, EtOAc / MeOH, reflux, 97%.



Scheme 2. K*ey*. (a) $CHCl_3$-pyridine, DMAP, 85% (for **1**), 98% (for **2**); (b) HF-pyridine, 94% (for **1a**), thioanisole, TFA, 50% (for **2**); (c) 4-chloropyridine-2,6-dicarbonyl chloride, CH_2Cl_2-pyridine, DMAP, 85% (for **3**), 88% (for **5**).



Scheme 3. K*ey*. (a) Rh/C NH_2NH_2, THF, crude, quant; (b) *t*-C_4H_9OCl, -78 °C, 40%; (c) **8,** 10% AcOH / CH_2Cl_2, 90%; (d) $PdOAc_2$, PPh_3, Et_3N, formic acid, THF, 54%; (e) $(COCl)_2$, DMF (cat.), THF, quant.; (f) CH_2Cl_2, pyridine, 74%; (g) HF-pyridine, 93%; (h) 4-chloro-2,6-pyridine dicarbonyl chloride, DMAP, THF, pyridine, 81%.

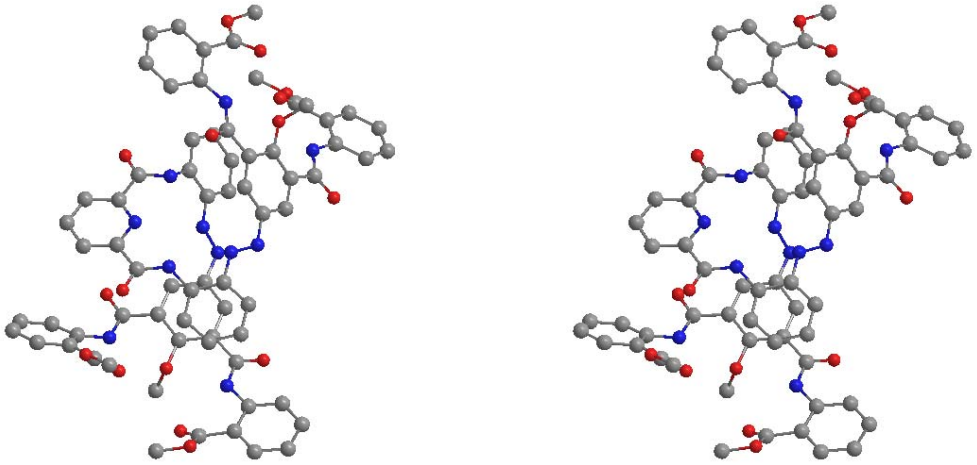


Figure 1. Stereodepiction of the lowest energy conformer of **3** as determined by Monte Carlo conformational searching.

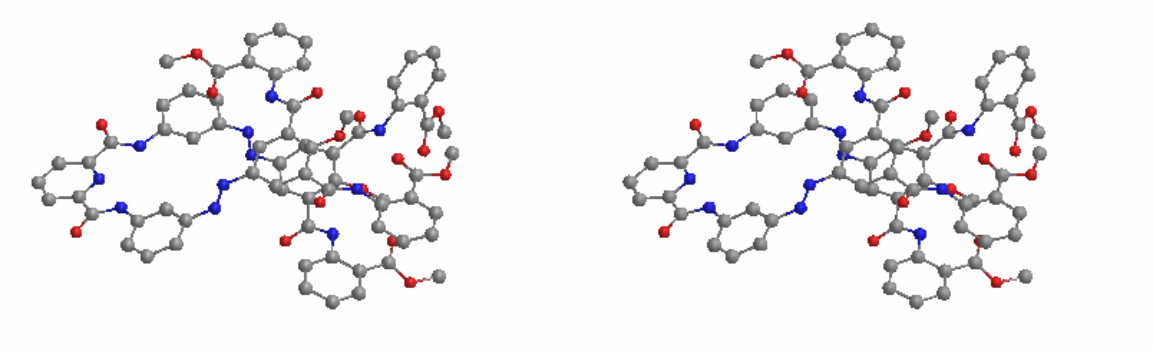


Figure 2. Stereodepiction of the lowest energy conformer of **4** as determined by Monte Carlo conformational searching.

Experimental Section.

General Methods. Melting Points were determined in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1600 instrument. ^{1}H NMR were recorded at 400 or 500 MHz and ^{13}C NMR spectra at 100 or 125 MHz on a Bruker DPX-400 or DPX-500 instrument as indicated. EI or FAB mass spectra were recorded at The Ohio State University Chemical Instrumentation Center. MALDI-TOF spectrometry was performed using 2,5-dihydroxybenzoic acid as the matrix in tetrahydrofuran (THF). All reactions were performed under an argon or nitrogen atmosphere. Dimethylformamide (DMF) was dried by distillation from $MgSO_4$; Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl; dichloromethane was distilled from calcium hydride; pyridine was distilled from calcium hydride; chloroform was distilled from calcium carbonate. Chromatographic separations were performed on silica gel 60 (230-400 mesh, 60 Å) using the indicated solvents.

DOSY-NMR Experiments. Diffusion ordered 2D-NMR (DOSY) spectra were obtained for **1a**, **1b**, **2, 3, 4** and **5** in $CDCl_3$ after filtration of the solvent through basic alumina. Diffusion coefficients, ***D***, were calculated from DOSY-NMR spectra recorded on a Bruker DPX-500. Effective hydrodynamic radii were calculated using the Stokes-

Einstein equation, $R_H = k_B T/(D6\pi\eta)$, where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent.

Allyl 2-methoxy-5-nitroisophthalate (7) To the flask containing 2-methoxy-5-nitroisophthaloyl dichloride[1] (**6**) (5.76 g, 20.73 mmol 100 mol%) was added freshly distilled THF (50 mL), and pyridine (3.3 mL). Allyl alcohol (3.61 g, 4.23 mL, 62.19 mmol, 300 mol%) was added dropwise and the mixture was stirred for 2 h. The solvent was removed under reduced pressure (40 mm Hg) to give a crude brown oil. Purification by flash chromatography (SiO_2) with CH_2Cl_2 afforded the product as a light yellow oil (2.17g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 3H), 4.87 (dd, J = 3.6 Hz, J = 1.2 Hz 4H), 5.35 (dd, J = 8.4 Hz, J = 1.2 Hz, 2H), 5.45 (dd, J = 14.4 Hz, J = 1.6 Hz, 2H), 6.04 (m, 2H), 8.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.2, 66.7, 119.5, 127.4, 129.7, 131.2, 142.4, 163.3, 164.2; IR (solution cell, $CHCl_3$) υ 3092, 3037, 2953, 1749, 1609, 1534, 1468, 1419, 1350, 1306 cm^{-1}; HRMS (ES) calcd. for $C_{15}H_{15}NO_7Na^+$: 344.0741 Observed: 344.0759.

Allyl 5-amino-2-methoxyisophthalate (8) Allyl 2-methoxy-5-nitroisophthalate (**7**) (3.83 g, 11.92 mmol, 100 mol%) was dissolved in ethyl acetate (90 mL) and methanol (10 mL) in a 250 round bottomed flask. $SnCl_2$ (18.83 g, 83.45 mmol, 700 mol%) was added and the mixture was heated at reflux for 2 h. The solution was cooled and transferred to a 1000 mL erhlenmeyer flask. Ethyl acetate (300 mL) and saturated $NaHCO_3$ (300 mL) were added giving a milky white precipitate. The reaction was filtered through a pad of celite, the filtrate was transferred to a separatory funnel and the product was extracted with ethyl acetate (3 x 300 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure (40 mm Hg) to

give a crude yellow oil. Purification by flash chromatography (SiO_2) with 5:1 CH_2Cl_2 / ethyl acetate afforded product as a light yellow oil (3.21 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 3H), 4.99 (dd, *J* = 5.2, 1.2 Hz 4H), 5.47 (dd, *J* = 10.4 Hz, *J* = 1.3 Hz, 2H), 5.60 (dd, *J* = 17.2, 1.6 Hz, 2H), 6.19 (m, 2H), 7.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.6, 65.7, 118.6, 120.6, 126.9, 131.8, 142.1, 151.4, 165.3; IR (solution cell, $CHCl_3$) υ 3485, 3398, 3086, 2948, 1725, 1623, 1475, 1425, 1367, 1265 cm^{-1}; HRMS (ES) Calcd. for $C_{15}H_{17}NO_5Na^+$: 314.0999 Observed: 314.0997.

2-Hydroxylamino-*N*-carbobenzyloxyaniline (10) 2-Nitro-*N*-carbobenzyloxyaniline[2] (**9**) (4.0 g, 14.69 mmol, 100 mol%) was dissolved in THF (40 mL) to give a yellow solution. Rhodium on carbon (0.300 g, 7.5% w/w) was added and the heterogeneous mixture was cooled to 0 °C using an ice-water bath. Anhydrous hydrazine (0.570g, 0.558 mL, 17.63 mmol, 120 mol%) was added dropwise via syringe and the mixture was stirred for 1 h. The solution was filtered through a pad of celite and the filter cake was washed with THF (3 x 10 mL). The THF was evaporated under reduced pressure (40 mm Hg) to give the product as a yellow oil which was used without further purification (3.79g, 100%). ^{1}H NMR (400 MHz, DMSO) δ 5.17 (s, 2H), 6.84 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.09 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.22 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.33-7.46 (m, 6H), 7.91 (s, 1H), 8.73 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.4, 115.1, 120.3, 125.6, 126.9, 127.1, 128.4, 137.4, 144.4, 154.5; IR (solution cell, $CHCl_3$) υ 3485, 3398, 3086, 2948, 1725, 1623, 1475, 1425, 1367, 1265 cm^{-1}; HRMS (ES) Calcd. for $C_{15}H_{17}NO_5Na^+$: 314.0999 Observed: 314.0997.

2-nitroso-*N*-carbobenzyloxyaniline (11) 2-Hydroxylamino-*N*-carbobenzyloxyaniline (3.79 g, 14.69 mmol, 100 mol%) was dissolved in THF (500 mL) in a 1000 mL round-

bottomed flask. The solution was cooled to -78 °C using a dry ice-acetone bath and *t*-butylhypochlorite[3] (1.59g, 1.75 mL, 14.69 mmol, 100 mol%) was added via syringe. The clear yellow solution immediately turned green. The solution was allowed to stir for 1 h while the reaction was warmed to room temperature. The solvent was evaporated under reduced pressure (40 mm Hg) to give crude green oil. Purification by flash chromatography (SiO_2) with 10:1 hexanes / ethyl acetate afforded the product as a bright green solid (2.56g, 68%). mp: 44-45 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO) δ 5.30 (s, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.35-7.48 (m, 6H), 7.68 (t, *J* = 7.6 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 10.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.64, 119.7, 121.8, 128.4, 128.6, 128.7, 135.6, 138.8, 153.1, 156.1 ; IR (solution cell, $CHCl_3$) υ 3391, 3286, 2957, 2253, 1745, 1593, 1488, 1420, 1319, 1240 cm^{-1}; HRMS (ES) Calcd. for $C_{14}H_{12}N_2O_3Na^+$: 279.0740 Observed: 279.0747.

5-(2-Benzyloxycarbonylaminophenylazo)-2-methoxyisophthalic acid diallylester (12a) Allyl 5-amino-2-methoxyisophthalate (**8**) (1.98 g, 6.81 mmol, 100 mol%) was dissolved in glacial acetic acid (30 mL) and heated to 80 °C. 2-(Nitrosophenyl)-carbamic acid benzyl ester (**11**) (1.66 g, 6.49 mmol, 95 mol%) was added and the mixture was stirred for 12 h. The acetic acid was evaporated and the resulting brown residue was dissolved in CH_2Cl_2 (50 mL) and transferred to a separatory funnel. The solution was washed with sat. $NaHCO_3$ (30 mL) and the product was extracted with CH_2Cl_2 (3 x 50 mL). The organic extracts were dried ($MgSO_4$), filtered and evaporated to reveal a black oil. Purification by flash chromatography (SiO_2) with 5:1 hexanes / ethyl acetate afforded the product as an orange solid (3.32 g, 90%). mp: 61-63 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (s, 3H), 4.87 (dt, *J* = 5.5, 2.5, 1.0, Hz, 4H), 5.28 (s, 2H), 5.32

(dd, *J* = 7.0, 1.0 Hz, 2H), 5.45 (dddd, *J* = 16.0, 4.0, 3.0, 1.5, Hz, 2H), 6.05 (m, 2H), 7.13 (td, *J* = 8.5, 1.5 Hz, 1H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.41 (t, *J* = 3.0 Hz, 2H), 7.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.39 (s, 2H), 8.44 (d, *J* = 8.5 Hz), 9.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.0, 66.2, 67.0, 118.9, 119.0, 120.3, 122.6, 127.5, 128.2, 128.3, 128.5, 128.71, 131.5, 133.4, 136.0, 136.5, 138.6, 147.2, 152.9, 161.4, 164.6, ; IR (solution cell, $CHCl_3$) υ 3402, 3155, 2254, 1815, 1794, 1732, 1646, 1595, 1466, 1300 cm^{-1}; HRMS (ES) Calcd. for $C_{29}H_{27}N_3O_7Na^+$: 552.1746 Observed: 552.1513.

5-(2-Benzyloxycarbonylaminophenylazo)-2-methoxyisophthalic acid (12b) To a stirring solution of **12a** (1.00 g, 1.89 mmol, 100 mol%) and *N,N*-dimethylbarbituric acid (0.620 g, 3.97 mmol, 210 mol%) in dry THF (10 mL), a solution of Pd (0)-catalyst (prepared from $Pd_2(dba)_3 \cdot CHCl_3$ (0.098 g, triphenylphosphine (0.095 g, in THF (10 mL)) (10 mL, 0.095 mmol, 5 mol%) was added and the mixture was stirred for 30 min. The solvent was evaporated under reduced pressure (40 mm Hg) to give an orange solid. The solid was suspended in diethyl ether (30 mL), stirred for 5 min. and the orange product was collected via vacuum filtration (0.830 g, 98%). mp: 145-149 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, DMSO) δ 3.90 (s, 3H), 5.22 (s, 2H), 7.21 (td, *J* = 8.0, 1.0 Hz, 1H), 7.34 (td, *J* = 7.5, 5.0 Hz, 1H), 7.40 (td, *J* = 7.0, 1.5 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.55 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.68 (dd, *J* = 8.0 Hz, 1.9 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 8.39 (s, 2H), 9.94 (s, 1H), 13.45 (bs, 2H); ^{13}C NMR (125 MHz, DMSO) δ 63.6, 66.7, 117.0, 122.6, 124.2, 127.8, 128.5, 128.6, 128.9, 129.1, 133.1, 136.9, 137.7, 141.9, 147.5, 154.1, 159.8, 167.0; IR (solution cell, $CHCl_3$) υ 3413, 3255, 1824, 1742, 1722, 1653, 1605, 1479, 1310 cm^{-1};HRMS (ES) Calcd. for $C_{23}H_{19}N_3O_7Na^+$: 472.1152 Observed: 472.1112.

5-(2-Benzyloxycarbonylaminophenylazo)-2-methoxyisophthalic diacid chloride (12c) 12b (0.200 g, 0.445 mmol, 100 mol%) was dissolved in THF (5 mL) and DMF (5 μL). Oxalyl chloride (0.155 mL, 1.78 mmol, 400 mmol) was added dropwise and the orange solution was stirred under nitrogen at room temperature for 3h. The solvent was removed by blowing a stream of N_2 through the flask and the resultant orange solid was placed under vacuum for 1h and used without further purification (0.215 g, 100%).

2-CBzN-$C_6H_4N_2$-[G1] (**1a**) Methyl 2-aminobenzoate (0.336 g, 2.22 mmol, 200 mol%) and DMAP (0.027 g, 0.222 mmol, 20 mol%) were dissolved in $CHCl_3$ (5 mL) and pyridine (0.5 mL) in a flame dried 25 mL round bottom flask equipped with a stir bar and activated 4 Å molecular sieves. **12c** (0.539 g, 1.11 mmol, 100 mol%) was dissolved in $CHCl_3$ (1 mL) and added dropwise. The orange solution was stirred at room temperature for 3h. The molecular sieves were removed via filtration and the solvent was evaporated under reduced pressure (40 mm Hg) to reveal a crude orange oil which was purified by flash chromatography (SiO_2) with 3:1 hexanes / ethyl acetate to afford the product as an orange solid (0.675 g, 85%). mp: 73-76 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 6H), 4.14 (s, 3H), 5.26 (s, 2H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 7.19 (td, *J* = 8.5, 1.0 Hz, 2H), 7.29 (d, *J* = 6.0 Hz, 1H), 7.35 (t, *J* =7.0, 1.5 Hz, 2H), 7.44 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.47 (td, *J* = 9.0, 1.5 Hz, 1H), 7.64 (td, *J* = 8.0, 1.0 Hz, 2H), 7.86 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.09 (dd, *J* = 9.0, 1.5 Hz, 2H), 8.43 (d, *J* = 8.5 Hz, 1H), 8.56 (s, 2H), 8.93 (d, *J* = 8.0 Hz, 2H), 9.46 (s, 1H), 11.96 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 64.0, 66.9, 116.5, 119.0, 120.9, 121.4, 122.6, 123.3, 127.8, 128.2, 128.5, 130.6, 131.0, 133.2, 134.4, 136.1, 136.4, 138.9, 140.8, 148.2, 153.2, 157.9, 163.9, 168.0; IR (solution cell,

$CHCl_3$) υ 3999, 3267, 2954, 1731, 1701, 1676, 1588, 1518, 1448, 1308 cm^{-1}; HRMS (ES) calcd. for $C_{39}H_{33}N_5O_9Na^+$: 738.2170 Observed: 738.2160.

2-NH_2-$C_6H_4N_2$-[G1] (1a-NH_2) 2-CBzN-$C_6H_4N_2$-[G1] (**1a**) (0.250 g, 0.350 mmol, 100 mol%) was dissolved in HF · pyridine(1 mL) and the solution was stirred at room temperature for 3 h. Sat. $NaHCO_3$ was added (100 mL) and the solution was extracted with CH_2Cl_2 (3 x 50 mL). The solvent was evaporated under reduced pressure (40 mm Hg) to reveal a crude orange foam which was purified by flash chromatography (SiO_2) with 1:1 hexanes / ethyl acetate to afford the product as an orange solid (0.191 g, 94%). mp: 86-89 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 6H), 4.11 (s, 3H), 6.01 (s, 2H), 6.77 (d, *J* = 6.8 Hz, 1H), 7.17-7.23 (m, 4H) 7.64 (td, *J* = 9.0, 1.5 Hz, 2H), 7.85 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.55 (s, 2H), 8.93 (d, *J* = 8.5 Hz, 2H), 11.95 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 64.0, 116.6, 1 117.0, 117.3, 121.5, 123.2, 127.3, 128.1, 130.4, 131.0, 132.7, 134.4, 136.8, 140.8, 143.2 140.8, 143.2, 148.8, 156.9, 164.1, 168.0 ; IR (solution cell, $CHCl_3$) υ 3688, 3269, 1674, 1587, 1519, 1448, 1309, 1265, 1232 cm^{-1}; HRMS (ES) calcd. for $C_{31}H_{27}N_5O_7Na^+$: 604.1802 Observed: 604.1813

Cl-I-(N_2)$_2$-[G2] (3) 2-NH_2-$C_6H_4N_2$-[G1] (**1a-NH_2**) (0.336 g, 2.22 mmol, 200 mol%) and DMAP (0.027 g, 0.222 mmol, 20 mol%) were dissolved in $CHCl_3$ (5 mL) and pyridine (0.5 mL) in a flame dried 25 mL round bottom flask equipped with a stir bar and activated 4 Å molecular sieves. 4-Chloropyridine-2,6-dicarbonyl chloride[4] (0.539 g, 1.11 mmol, 100 mol%) was dissolved in $CHCl_3$ (1 mL) and added dropwise and the orange solution was stirred at room temperature for 3 h. The molecular sieves were removed via filtration and the solvent was evaporated under reduced pressure (40 mm Hg) to reveal a

crude orange oil which was purified by flash chromatography (SiO_2) with 3:1 hexanes / ethyl acetate to afford the product as an orange solid (0.675 g, 85%). mp: 73-76 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.93 (s, 12H), 3.96 (s, 6H), 7.10 (td, *J* = 8.0, 1.0 Hz, 2H), 7.18-7.26 (m, 8H), 7.59 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.68 (td, *J* = 8.5, 1.5 Hz, 4H), 8.03 (dd, *J* = 8.0, 1.5 Hz, 4H), 8.50 (s, 4H), 8.54 (s, 2H), 8.64 (d, *J* = 8.0 Hz, 4H), 8.92 (d, *J* = 8.5 Hz, 4H), 11.79 (s, 4H), 12.13 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.4, 63.6, 116.4, 120.1, 121.6, 123.1, 123.8, 125.9, 127.8, 128.6, 129.3, 130.9, 133.0, 134.5, 135.3, 139.1, 140.8, 147.7, 148.3, 151.2, 157.8, 160.4, 163.3, 167.9; IR (solution cell, $CHCl_3$) υ 3690, 3263, 2953, 1696, 1586, 1522, 1447, 1312, 1264, 1231 cm^{-1}; HRMS (ES) calcd. for $C_{69}H_{54}ClN_{11}O_{16}Na^+$: 1350.3330 Observed: 1350.3379

NO_2-[G1] (13) 2-Methoxy-5-nitroisophthaloyl dichloride (**6**) (1.15 g, 4.15 mmol, 100 mol%) was dissolved in THF (5mL) and was added dropwise to a stirring solution of propyl 2-aminobenzoate[5] (1.49, 8.3 mmol, 200 mol%) and DMAP (0.101 g, 0.83 mmol, 20 mol%) in THF (20 mL) and pyridine (1 mL). The yellow solution was stirred for 2 h and the solvent was evaporated under reduced pressure (40 mm Hg) to reveal a crude yellow product which was purified by flash chromatography (SiO_2) with 5:1 hexanes / ethyl acetate followed by CH_2Cl_2 to afford a white solid (1.91 g, 82%). mp: 160-163 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7.5 Hz, 6H), 1.80 (sextet, *J* = 7.5 Hz, 4H), 4.20 (s, 3H), 4.29 (t, *J* = 6.5 Hz, 4H), 7.20 (td, *J* = 8.5, 1.0 Hz, 2H), 7.64 (td, *J* = 9.0, 1.5 Hz, 2H), 8.11 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.87 (obscured d, 2H), 8.88 (s, 2H), 12.06 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4, 21.9, 63.7, 67.0, 116.7, 121.3, 123.6, 128.7, 130.3, 130.9, 134.4, 140.6, 143.1, 160.5, 162.5, 167.8; IR (solution cell, $CHCl_3$) υ

3252, 3040, 1677, 1589, 1605, 1589, 1527, 1448, 1349, 1303 cm^{-1}; HRMS (ES) calcd. for $C_{29}H_{29}N_3O_9Na^+$: 586.1796 Observed: 586.1778

NH_2-[G1] (14) NO_2-[G1] (**13**) (1.91 g, 3.39 mmol, 100 mol%) was dissolved in ethyl acetate (30 mL) and methanol (5 mL) in a 100 mL round bottom flask. $SnCl_2 \cdot 2H_2O$ (5.35 g, 23.7 mmol, 700 mol%) was added and the mixture was heated to reflux for 1 h. The solution was cooled and transferred to a 500 mL erhlenmeyer flask. Saturated $NaHCO_3$ (200 mL) was added and the solution was filtered through a pad of celite to remove the white precipitate. The filtrate was transferred to a separatory funnel and the product was extracted with ethyl acetate (3 x 300 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure (40 mm Hg) to give a crude yellow oil. Purification by flash chromatography (SiO_2) with 8:1 CH_2Cl_2 / ethyl acetate and 4:1 CH_2Cl_2 / ethyl acetate afforded the product as a light yellow solid (1.75 g, 97%). mp 147-150 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.5 Hz, 6H), 1.76 (sextet, *J* = 7.0 Hz, 4H), 3.88 (bs, 6H), 4.27 (t, *J* = 6.5 Hz, 4H), 7.12 (td, *J* = 7.0, 0.50 Hz, 2H), 7.37(s, 2H), 7.57 (td, *J* = 8.5, 1.0 Hz, 2H), 8.05 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.84 (d, *J* = 8.5 Hz, 2H), 11.84 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4, 21.9, 64.1, 66.8, 117.0, 119.7, 121.6, 123.0, 130.2, 130.8, 134.0, 140.9, 143.3, 148.1, 164.6, 167.4; IR (solution cell, $CHCl_3$) υ 3374, 3263, 3043, 2970, 1697, 1673, 1586, 1522, 1467, 1448 cm^{-1}; HRMS (ES) calcd. for $C_{29}H_{31}N_3O_7Na^+$: 556.2054 Observed: 556.2069.

2-CBzN-$C_6H_4N_2$-[G2] (2) NH_2-[G1] (**14**) (0.138 g, 450 mmol, 200 mol%) and DMAP (0.005 g, 0.045 mmol, 20 mol%) were dissolved in THF (2 mL) and pyridine (0.125 mL) in a flame dried 25 mL round bottom flask equipped with a stir bar and activated 4 Å molecular sieves. **12c** (0.108 g, 2.23 mmol, 100 mol%) was dissolved in THF (2 mL)

and added dropwise. The orange solution was stirred at room temperature for 3 h. The molecular sieves were removed via filtration and the solvent was evaporated under reduced pressure (40 mm Hg) to afford a crude orange solid which was purified by flash chromatography (SiO_2) with 8:1 CH_2Cl_2 / ethyl acetate to afford the product as an orange solid (0.318 g, 98%). mp: 112-117 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.5 Hz, 12H), 1.76 (sextet, *J* = 7.5 Hz, 8H), 4.04 (s, 6H), 4.16 (s, 3H), 4.26 (t, *J* = 6.5 Hz, 8H), 5.21 (s, 2H), 7.05 (td, *J* = 8.0, 1.0 Hz, 1H), 7.13 (td, *J* = 7.5, 0.5 Hz, 4H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.36-7.39 (m, 3H), 7.56 (td, *J* = 8.5, 1.5 Hz, 4H), 7.76 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.5 Hz, 4H), 8.35 (d, *J* = 8.5 Hz, 1H), 8.45 (s, 4H), 8.53 (s, 2H), 8.83 (d, *J* = 8.5 Hz, 4H), 9.49 (s, 1H), 9.62 (s, 2H), 11.92 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4, 21.9, 64.1, 64.3, 66.8, 67.0, 116.7, 118.9, 121.4, 122.6, 123.0, 124.9, 128.2, 128.4, 128.5, 129.0, 130.5, 130.8, 133.3, 134.2, 134.4, 136.0, 136.3, 138.7, 140.8, 148.5, 152.5, 153.2, 156.9, 162.4, 163.9, 167.6,; IR (solution cell, $CHCl_3$) υ 3264, 2971, 1681, 1603, 1587, 1516, 1466, 1447, 1298 cm^{-1}; HRMS (ES) calcd. for $C_{81}H_{77}N_9O_{19}Na^+$: 1502.5233 Observed: 1502.5115

2-NH_2-$C_6H_4N_2$-[G2] (2-NH_2) 2-CBzN-$C_6H_4N_2$-[G2] **(2)** (0.500 g, 0.345 mmol, 100 mol%) was dissolved in thioanisole (2.14 g, 17.24 mmol, 500 mol%) and TFA (7.43 mL, 93.15 mmol, 2700) and the solution was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure (40 mm Hg) to reveal a crude brown oil which was purified by flash chromatography (SiO_2) with 15:1 CH_2Cl_2 / ethyl acetate to afford the product as an orange solid (0.230 g, 50%). mp: 125-127 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.5 Hz, 12H), 1.77 (sextet, *J* = 7.0 Hz, 8H), 4.03 (s, 6H), 4.17 (s, 3H), 4.28 (t, *J* = 6.5 Hz, 8H), 6.74 (t, *J* = 7.0 Hz, 2H), 7.14 (t, *J* = 7.5 Hz,

5H), 7.57 (t, *J* = 8.5 Hz, 4H), 7.73 (d, *J* = 8.0, Hz, 1H), 8.06 (dd, *J* = 8.0, 1.0 Hz, 4H), 8.46 (s, 4H), 8.54 (s, 2H), 8.84 (d, *J* = 8.5 Hz, 4H), 9.70 (s, 2H), 11.91 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.5, 21.9, 64.1, 64.2, 66.8, 116.8 116.8, 121.5, 123.0, 125.0, 128.6, 130.4, 130.8, 134.1, 134.5, 140.9, 152.5, 162.7, 164.0, 167.6; IR (solution cell, $CHCl_3$) υ 3490, 3265, 2969, 1678, 1605, 1587, 1518, 1467, 1447, 1424, 1296, 1264, 1165 cm^{-1}; HRMS (ES) calcd. for $C_{73}H_{69}N_7O_{17}Na^+$: 1368.4860 Observed: 1368.4747

Cl-I-(N_2)$_2$-[G3] (5) 2-NH_2-$C_6H_4N_2$-[G2] (**2-NH_2**) (0.148 g, 0.113 mmol, 200 mol%) and DMAP (0.0014 g, 0.0114 mmol, 20 mol%) were dissolved in THF (0.5 mL) and pyridine (0.017 mL) in a flame dried 10 mL round bottom flask equipped with a stir bar. 4-Chloropyridine-2,6-dicarbonyl chloride (0.014 g, 0.057 mmol, 100 mol%) was dissolved in THF (0.250 mL) and added dropwise to a stirring solution of the amine. The solution was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure (40 mm Hg) to reveal a crude orange solid. Purification by flash chromatography (SiO_2) using 10:1 CH_2Cl_2 / ethyl acetate and 5:1 CH_2Cl_2 / ethyl acetate afforded the product as an orange solid (0.071 g, 88%). mp: 149-152°C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.5 Hz, 24H), 1.77 (sextet, *J* = 7.0 Hz, 16H), 3.97 (s, 6H), 4.11 (s, 12H), 4.28 (t, *J* = 7.0 Hz, 16H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 8H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5, Hz, 2H), 7.62(d, *J* = 8.0, 8H), 8.09 (d, *J* = 8.0 Hz, 8H), 8.21 (s, 2H), 8.41 (s, 4H), 8.47 (s, 8H), 8.68 (d, *J* = 8.5 Hz, 2H), 8.92 (d, *J* = 8.5 Hz, 8H), 9.23 (s, 4H), 11.71 (s, 2H), 11.96 (s, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.5, 21.9, 64.1, 64.3, 66.8, 117.0, 121.5, 123.1, 123.2, 125.1, 126.0, 128.2, 130.7, 130.8, 133.5, 134.1, 134.2, 136.8, 138.8, 140.9, 148.5, 149.1, 150.7, 152.7, 156.6, 160.1, 161.35, 164.1, 167.6; IR (solution cell, $CHCl_3$) υ 3368, 3265, 16181, 1587, 1525, 1462,

1447, 1315, 1297, 1265, 1165 cm^{-1}; HRMS (ES) calcd. for $C_{153}H_{142}ClN_{19}O_{36}Na_2^{2+}$: 1451.4685 Observed: 1451.4724

3-Nitroso-*N*-carbobenzyloxyaniline (16) A. 3-Nitro-*N*-carbobenzyloxyaniline[6] (**15**) (1.0 g, 3.89 mmol, 100 mol%) was dissolved in THF (20 mL) to give a clear colorless solution. Rh-C (0.1 g, 7.5% w/w) was added and the heterogeneous mixture was cooled to 0 °C using an ice bath. Anhydrous hydrazine (0.0.131g, 0.128 mL, 4.08 mmol, 105 mol%) was added dropwise via syringe and the mixture was stirred for 20 min. The solution was filtered through a pad of celite and washed with THF (3 x 10 mL). The THF was evaporated under reduced pressure (40 mm Hg) to give the product as a white solid which was used without further purification (0.946 g, 100%). ^{1}H NMR (500 MHz, DMSO) δ 5.14 (s, 2H), 6.47 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.85 (d, *J* = 8.0, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 7.33 (td, *J* = 7.0, 2.5 Hz, 1H), 7.38-7.43 (m, 4H), 8.23 (d, *J* = 2.0 Hz, 2H), 9.58 (s, 1H) ; ^{13}C NMR (100 MHz, DMSO) δ 65.9, 103.5, 107.9, 109.9, 128.4, 128.5, 128.9, 129.0, 137.3, 139.8, 153.1, 153.7; IR (solution cell, $CHCl_3$) ν 3569, 3432, 3155, 2254, 1796, 1733, 1608, 1530, 1462, 1381, 1214, 1095, 898 cm^{-1}.

B. Crude 3-hydroxylamino-*N*-carbobenzyloxyaniline (0.946 g, 3.89 mmol, 100 mol%) was dissolved in THF (300 mL) in a 500 mL round-bottomed flask. The solution was cooled to -78 °C using a dry ice-acetone bath and *t*-butylhypochlorite (0.443 g, 0.487 mL, 4.08 mmol, 105 mol%) was added via syringe. The clear colorless solution instantly turned bright green in color and was allowed to stir for 1 h. SiO_2 (50 g) was added the solvent was evaporated under reduced pressure (40 mm Hg) to give a crude red solid. Purification by flash chromatography (SiO_2) with CH_2Cl_2 afforded the product as a bright

green solid (0.375 g, 40%). mp: 98-100 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24 (s, 2H), 7.08 (s, 1H), 7.35-7.42 (m, 5H), 7.57 (t, *J* = 8.0Hz, 1H), 7.72 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.4, 108.9, 118.2, 125.1, 128.4, 128.5, 128.7, 130.1, 135.6, 139.1, 153.2, 165.8; IR (solution cell, $CHCl_3$) ν 3689, 3429, 3068, 3035, 2959, 2257, 1736, 1604, 1530, 1503, 1425, 1320, 1206, 1097, 1063 cm^{-1}; HRMS (ES) Calcd. for $C_{14}H_{12}N_2O_3Na^+$: 279.0740 Observed: 279.0740.

5-(3-Benzyloxycarbonylaminophenylazo)-2-methoxyisophthalic acid diallylester (17a) Allyl 5-amino-2-methoxyisophthalate (**8**) (0.309 g, 1.06 mmol, 100 mol%) was dissolved in glacial acetic acid (2 mL) and CH_2Cl_2 (20 mL) and 3-nitroso-*N*-carbobenzyloxy-aniline (0.256 g, 1.06 mmol, 100 mol%) was added and the mixture was stirred for 12 h. The solvent was evaporated and the resulting brown residue was dissolved in CH_2Cl_2 (20 mL) and transferred to a separatory funnel. The solution was washed with sat. $NaHCO_3$ (20 mL) and the product was extracted with CH_2Cl_2 (3 x 20 mL). The organic extracts were dried ($MgSO_4$), filtered and evaporated to reveal a dark red oil. Purification by flash chromatography (SiO_2) with 4:1 hexanes / ethyl acetate afforded the product as an orange solid (0.505 g, 90%). mp: 103-106 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.01 (s, 3H), 4.88 (d, *J* = 7.05 Hz, 4H), 5.24 (s, 2H), 5.32 (dd, *J* = 13.0, 1.0 Hz, 2H), 5.47 (dd, *J* = 21.5, 2.0 Hz, 2H), 6.06 (m, 2H), 6.89 (s, 1H), 7.36-7.48 (m, 6H), 7.54 (d, *J* = 5.0 Hz, 1H), 7.66 (d, *J* = 10.0 Hz, 1H), 7.98 (s, 1H), 8.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.0, 66.2, 67.2, 112.1, 119.1, 119.2, 127.3, 128.3, 128.4, 128.6, 129.1, 129.7, 131.7, 135.8, 138.8, 147.3, 152.9, 153.2, 161.5, 164.7 ; IR

(solution cell, $CHCl_3$) ν 3431, 3156, 2254, 1732, 1598, 1527, 1466, 1380, 1230, 1205, 1093, 900 cm^{-1}; HRMS (ES) Calcd. for $C_{29}H_{27}N_3O_7Na^+$: 552.1746 Observed: 552.1767.

5-(3-Benzyloxycarbonylaminophenylazo)-2-methoxyisophthalic acid (17b)

To a stirring solution of **17a** (0.297 g, 0.561 mmol, 100 mol%) in dry THF (5 mL), a solution of Pd (0)-catalyst (prepared from $PdOAc_2$, (0.012 g (0.056 mmol), PPh_3 (0.030 g, 0.112 mmol), formic acid (0.169 mL, 4.49 mmol), Et_3N (0.630 mL, 4.49 mmol)) in THF (2 mL) was added and the mixture was stirred for 30 min. The solvent was evaporated under reduced pressure (40 mm Hg) to give an orange solid. The solid was suspended in diethyl ether (30 mL) and stirred for 5 min. and the orange product was collected by vacuum filtration (0.221 g, 88%). mp: 103-106 °C (Et_2O); ^1H NMR (500 MHz, DMSO) δ 3.91 (s, 3H), 5.19 (s, 2H), 7.35 (td, *J* = 6.0, 1.0 Hz, 1H), 7.34 (td, *J* = 7.5, 5.0 Hz, 1H), 7.40 (td, *J* = 7.0, 1.5 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 8.12 (s, 1H), 8.28 (s, 2H), 10.03 (s, 2H), 13.36, (bs, 2H); ^{13}C NMR (125 MHz, DMSO) δ 63.7, 66.4, 111.7, 118.4, 121.9, 127.5, 128.5, 128.6, 128.9, 129.1, 130.2, 136.9, 140.7, 147.0, 152.7, 153.9, 160.4, 166.7; IR (solution cell, $CHCl_3$) ν 3413, 3255, 1824, 1742, 1722, 1653, 1605, 1479, 1310 cm^{-1}; HRMS (ES) Calcd. for $C_{23}H_{19}N_3O_7Na^+$: 472.1121 Observed: 472.1118.

3-CBzN-$C_6H_4N_2$-[G1] (**1b**) Propyl 2-aminobenzoate (0.163 g, 0.908 mmol, 200 mol%) and DMAP (0.005 g, 0.045 mmol, 10 mol%) were dissolved in CH_2Cl_2 (2 mL) and pyridine (0.150 mL) in a flame dried 10 mL round bottom flask equipped with a stir bar and activated 4 Å molecular sieves. **1** (0.220 g, 0.454 mmol, 100 mol%) was dissolved in

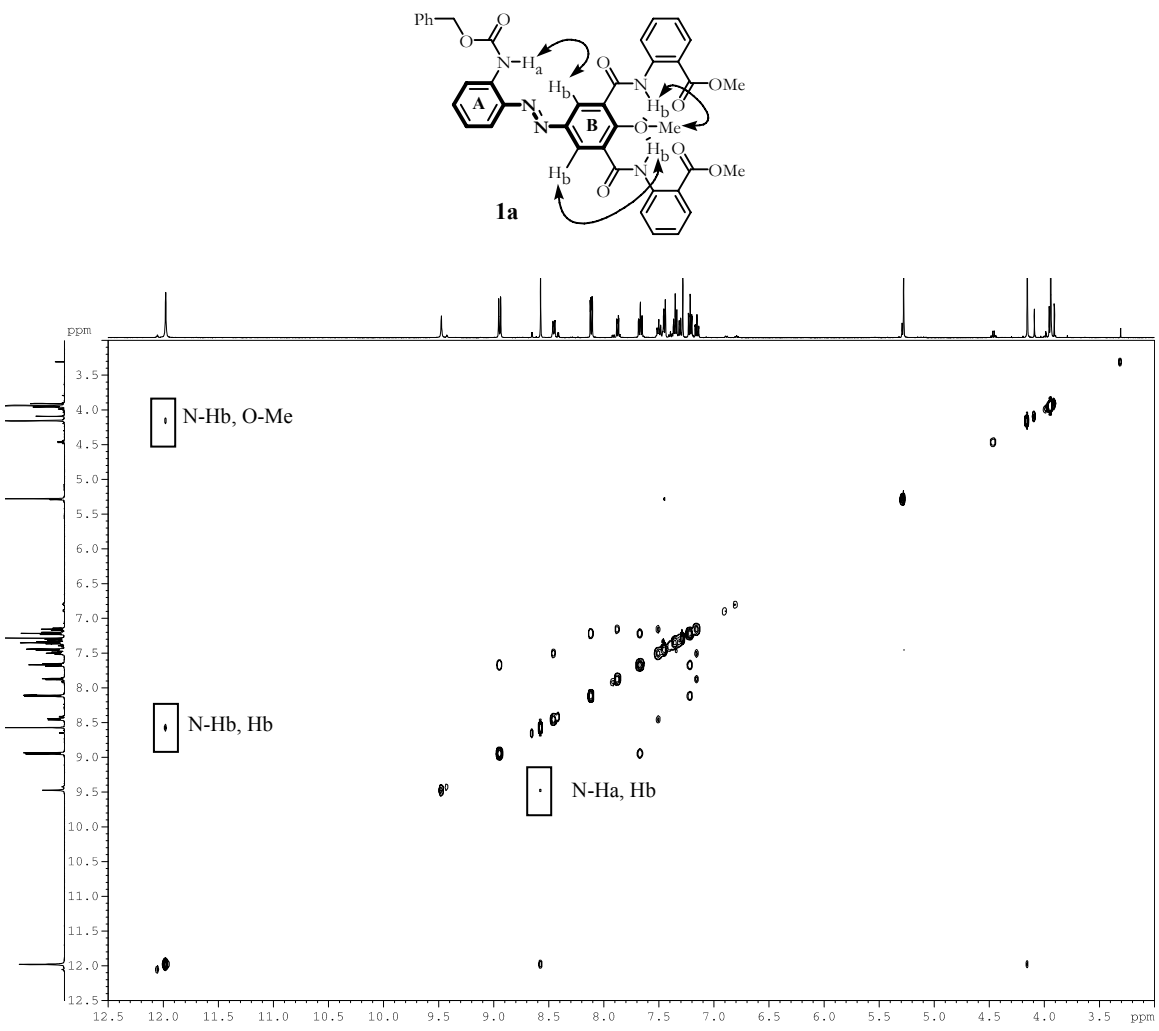
THF (2 mL) and added dropwise. The orange solution was stirred at room temperature for 3h. The molecular sieves were removed via filtration and the solvent was evaporated under reduced pressure (40 mm Hg) to reveal a crude orange oil which was purified by flash chromatography (SiO_2) with 15:1 CH_2Cl_2 / ethyl acetate to afford the product as an orange solid (0.259 g, 74%). 139-142 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.5 Hz, 6H), 1.78 (sextet, *J* = 7.05 Hz, 4H), 4.13 (s, 3H), 4.29 (t, *J* = 6.5 Hz, 4H), 5.23 (s, 2H), 6.93, (s, 1H), 7.18 (td, *J* = 8.5, 1.0 Hz, 2H), 7.32-7.41 (m, 5H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.63 (td, *J* = 8.0, 1.5 Hz, 2H) 7.66 (d, *J* = 8.5 Hz, 2H), 7.92 (s, 1H), 8.11 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.59 (s, 2H), 8.93 (d, *J* = 8.5 Hz, 2H), 11.99 (s, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.5, 21.9, 63.9, 66.9, 67.1, 116.8, 121.5, 123.2, 128.0, 128.3, 128.4, 128.6, 129.7, 130.5, 130.9, 134.3, 136.0, 138.8, 140.9, 148.2, 152.9, 153.3, 157.9, 164.1, 167.6; IR (solution cell, $CHCl_3$) υ 3432, 3262, 2970, 1733, 1679, 1589, 1521, 1450, 1304, 1260, 1213, 1087, 918 cm^{-1}; HRMS (ES) calcd. for $C_{43}H_{41}N_5O_9Na^+$: 794.2802 Observed: 794.2855.

3-NH_2-$C_6H_4N_2$-[G1] (1b-NH_2) 3-CBzN-$C_6H_4N_2$-[G1] (**1b**) (0.034 g, 0.044, mmol, 100 mol%) was dissolved in HF · pyridine(0.259 mL) in a polyethylene centrifuge tube and the solution was stirred at room temperature for 10 min. Sat. $NaHCO_3$ was added (30 mL) and the solution was extracted with CH_2Cl_2 (3 x 5 mL). The solvent was evaporated under reduced pressure (40 mm Hg) to reveal a crude orange solid which was purified by flash chromatography (SiO_2) with 15:1 CH_2Cl_2 / ethyl acetate to afford the product as an orange solid (0.026 g, 93%). mp: 125-129 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.5 Hz, 6H), 1.78 (sextet, *J* = 7.0 Hz, 4H), 4.13 (s, 3H), 4.30 (t, *J* = 6.5 Hz,

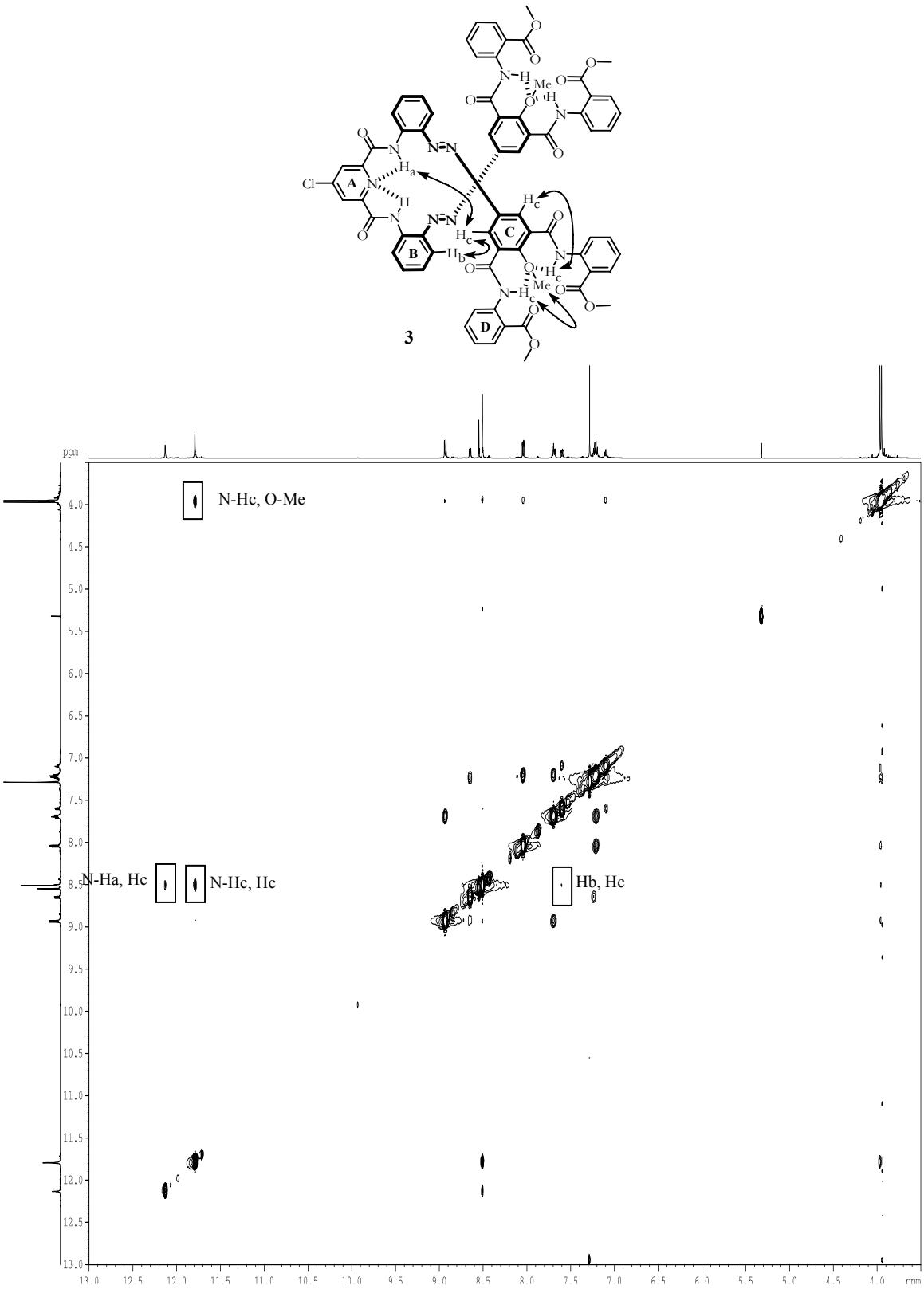
4H), 6.93, (dd, *J* = 7.0, 1.0 Hz, 1H), 7.18 (td, *J* = 8.5, 1.0 Hz, 2H), 7.26 (buried t, J = 0.5 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 7.63 (td, *J* = 6.5, 1.5 Hz, 2H), 8.10 (dd, J = 8.0, 1.5 Hz, 2H), 8.58 (s, 2H), 8.93 (dd, J = 8.5, 0.5 Hz, 2H), 11.96 (s, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4, 21.9, 63.8, 66.9, 107.8, 115.4, 116.8, 118.3, 121.5, 123.1, 127.8, 129.8, 130.5, 130.8, 134.2, 140.9, 146.9, 148.4, 153.5, 157.7, 164.1, 167.6; IR (solution cell, $CHCl_3$) υ 3261, 3156, 2940, 2254, 1796, 1677, 1589, 1517, 1450, 1382, 1304, 1259, 1212, 1145, 1009, 900 cm^{-1}; HRMS (ES) calcd. for $C_{35}H_{35}N_5O_7Na^+$: 660.2434 Observed: 660.2434.

***Meta*-Cl-I-(N_2)$_2$-[G2] (4)** 3-NH_2-$C_6H_4N_2$-[G1] (**1b-NH_2**) (0.028 g, 0.044 mmol, 200 mol%) and DMAP (0.0027 g, 0.002 mmol, 10 mol%) were dissolved in CH_2Cl_2 (0.10 mL) and pyridine (0.007 mL) in a flame dried 5 mL pear-shaped flask equipped with a stir bar and activated 4 Å molecular sieves. 4-Chloropyridine-2,6-dicarbonyl chloride (0.005 g, 0.022 mmol, 100 mol%) was dissolved in CH_2Cl_2 (0.230 mL) and added dropwise and the orange solution was stirred at room temperature for 7 h. The molecular sieves were removed via filtration and the solvent was evaporated under reduced pressure (40 mm Hg) to reveal a crude orange solid which was purified by flash chromatography (SiO_2) with 15:1 CH_2Cl_2 / ethyl acetate to afford the product as an orange solid (0.025 g, 81%). mp: 126-130 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.5 Hz, 12H), 1.76 (sextet, *J* = 7.0 Hz, 8H), 4.06 (s, 6H), 4.23 (t, J = 7.0 Hz, 8 H), 7.14 (td, J = 8.0, 1.0 Hz, 4H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.56 (td, *J* = 8.5, 1.5 Hz, 4H), 7.64 (d, *J* = 8.0 Hz, 2H), 8.04 (dd, *J* = 8.0, 1.5 Hz, 4H), 8.24 (s, 2H), 8.39 (bt, *J* = 2.0 Hz, 2H), 8.41 (s, 4H), 8.82 (d, *J* = 8.5 Hz, 4H), 10.26 (s, 2H), 11.89 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 10.5, 21.9, 63.8, 66.9, 114.8, 116.8, 120.0, 121.5, 123.2, 123.4, 125.6, 128.0, 129.3, 129.9, 130.8, 134.1, 138.1, 140.7, 147.6, 147.8, 150.2, 152.6, 158.0, 160.5, 164.0, 167.5; IR (solution cell, $CHCl_3$) υ 3258, 2949, 2230, 1684, 1599, 1565, 1463, 1286, 1256, 907 cm^{-1}; MS (MALDI) calcd. for $C_{77}H_{70}ClN_{11}O_{16}Na^+$: 1462.469 Observed: 1462.487



2D $^{1}H - {}^{1}H$ NOESY spectrum of 2-CBzN-$C_6H_4\mathbf{N_2}$-[G1] **(1a)** in $CDCl_3$



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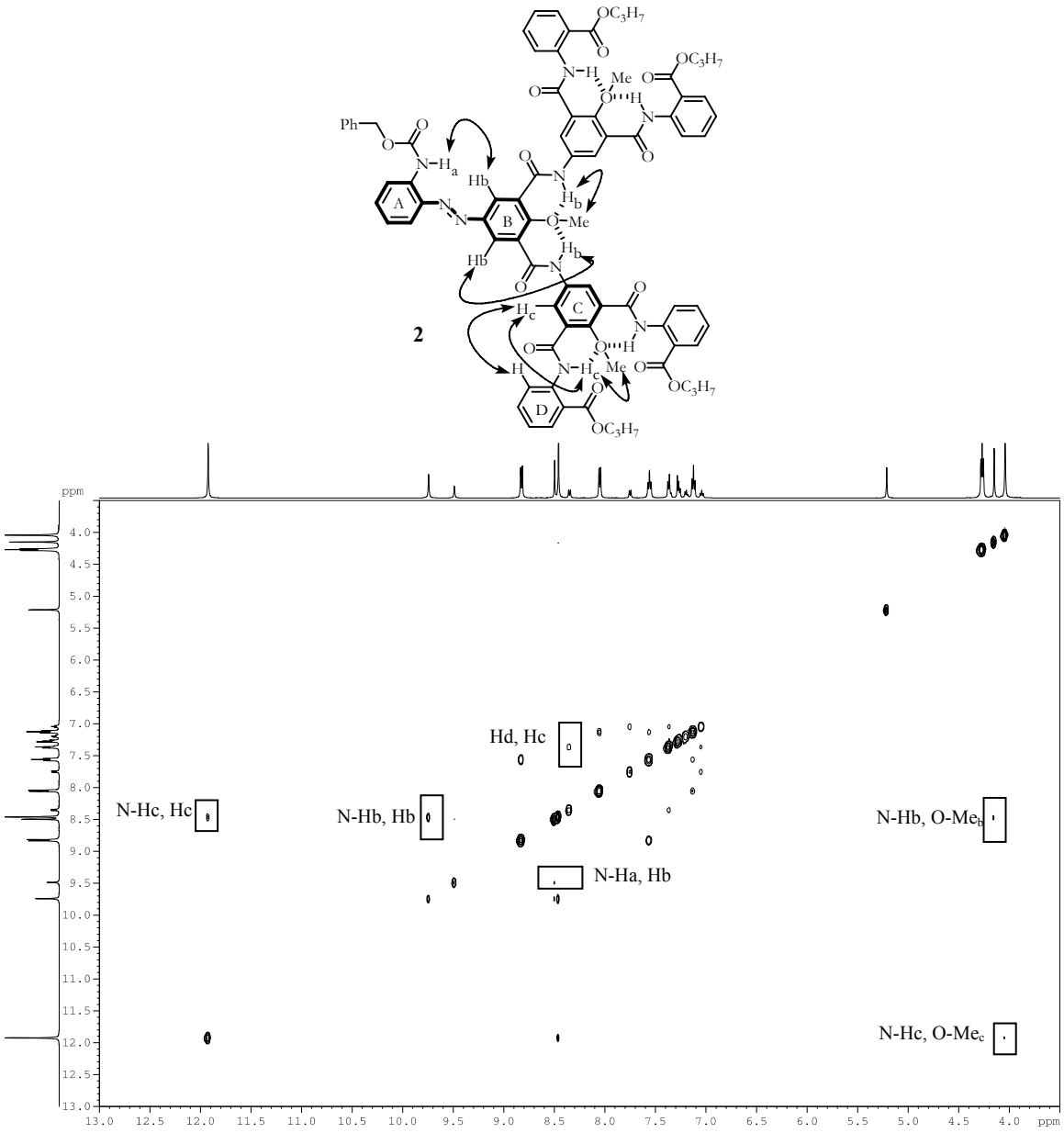

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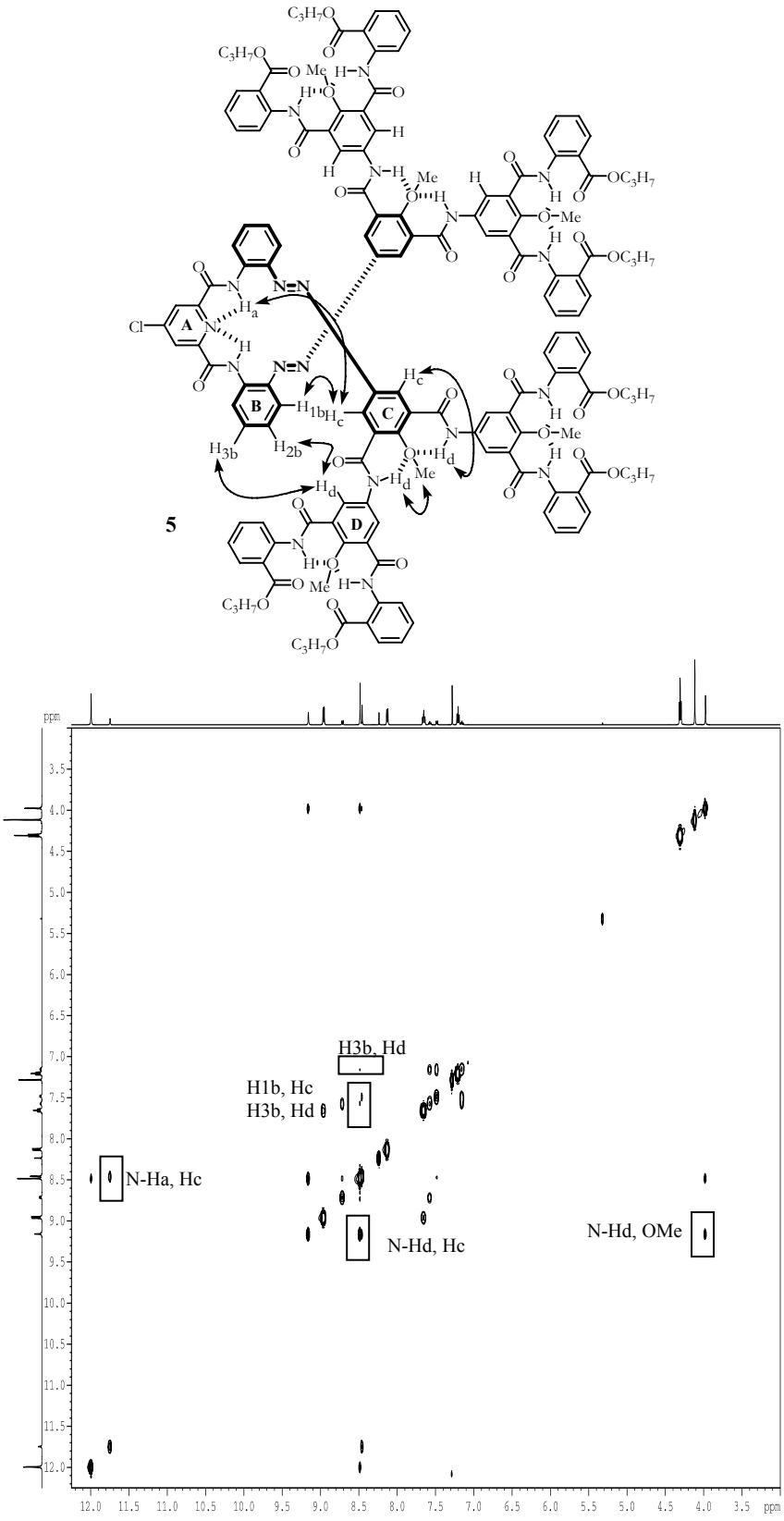
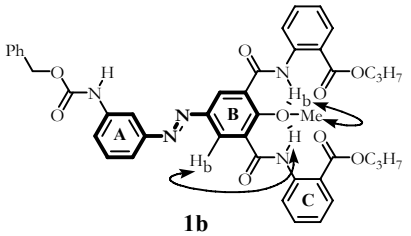
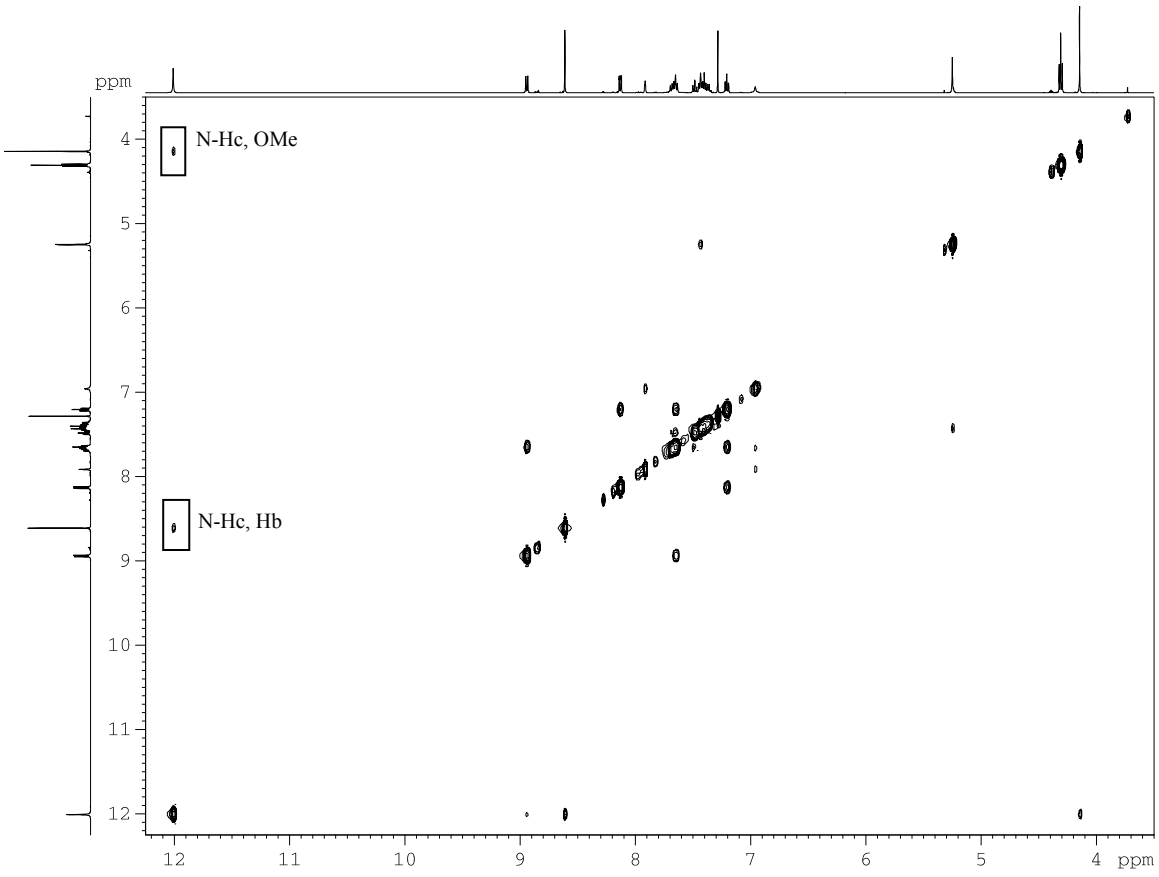


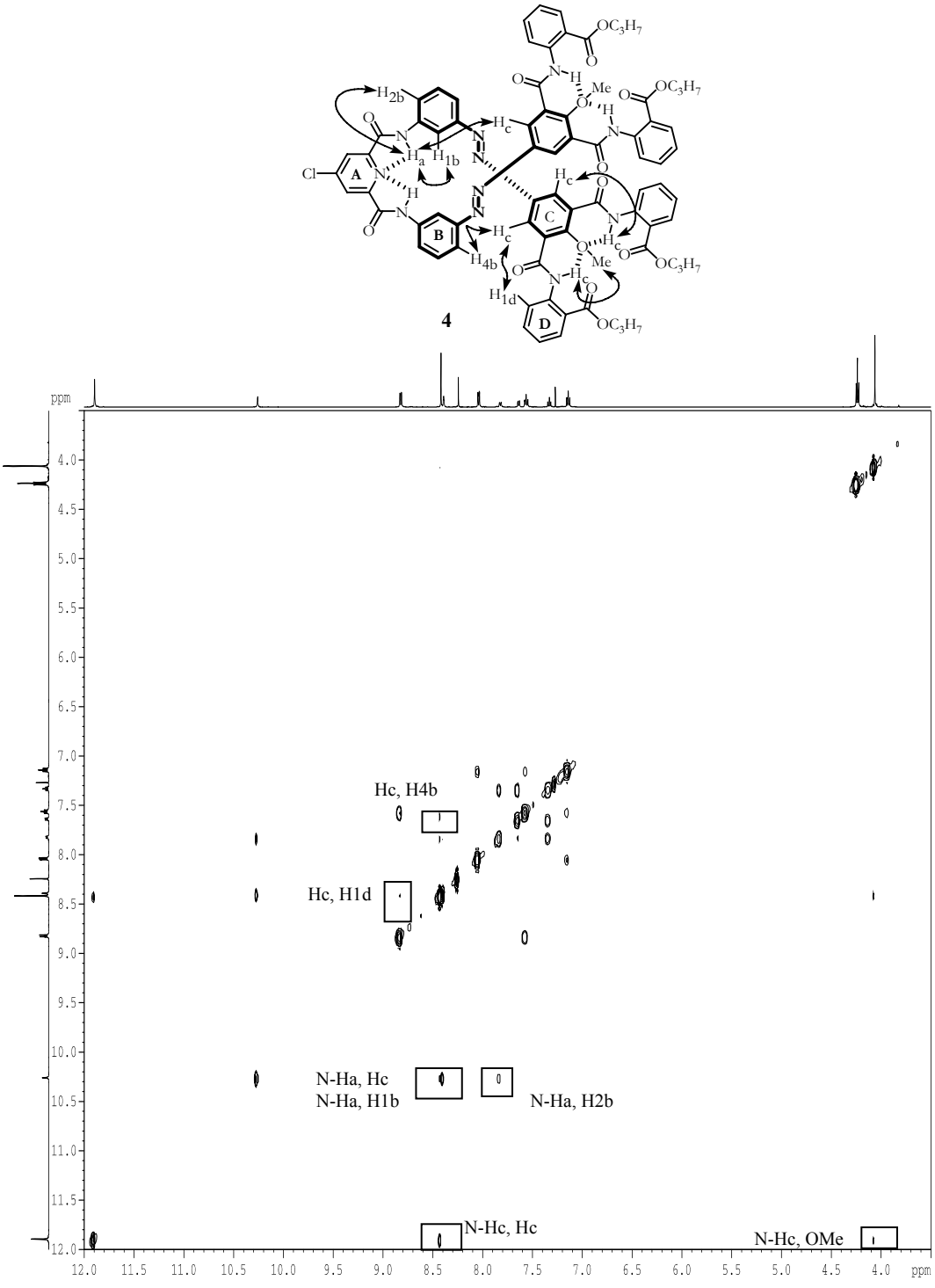
2D $^{1}H - {}^{1}H$ NOESY spectrum of Cl-I-$(\mathbf{N_2})_2$-[G3] **(5)** in $CDCl_3$



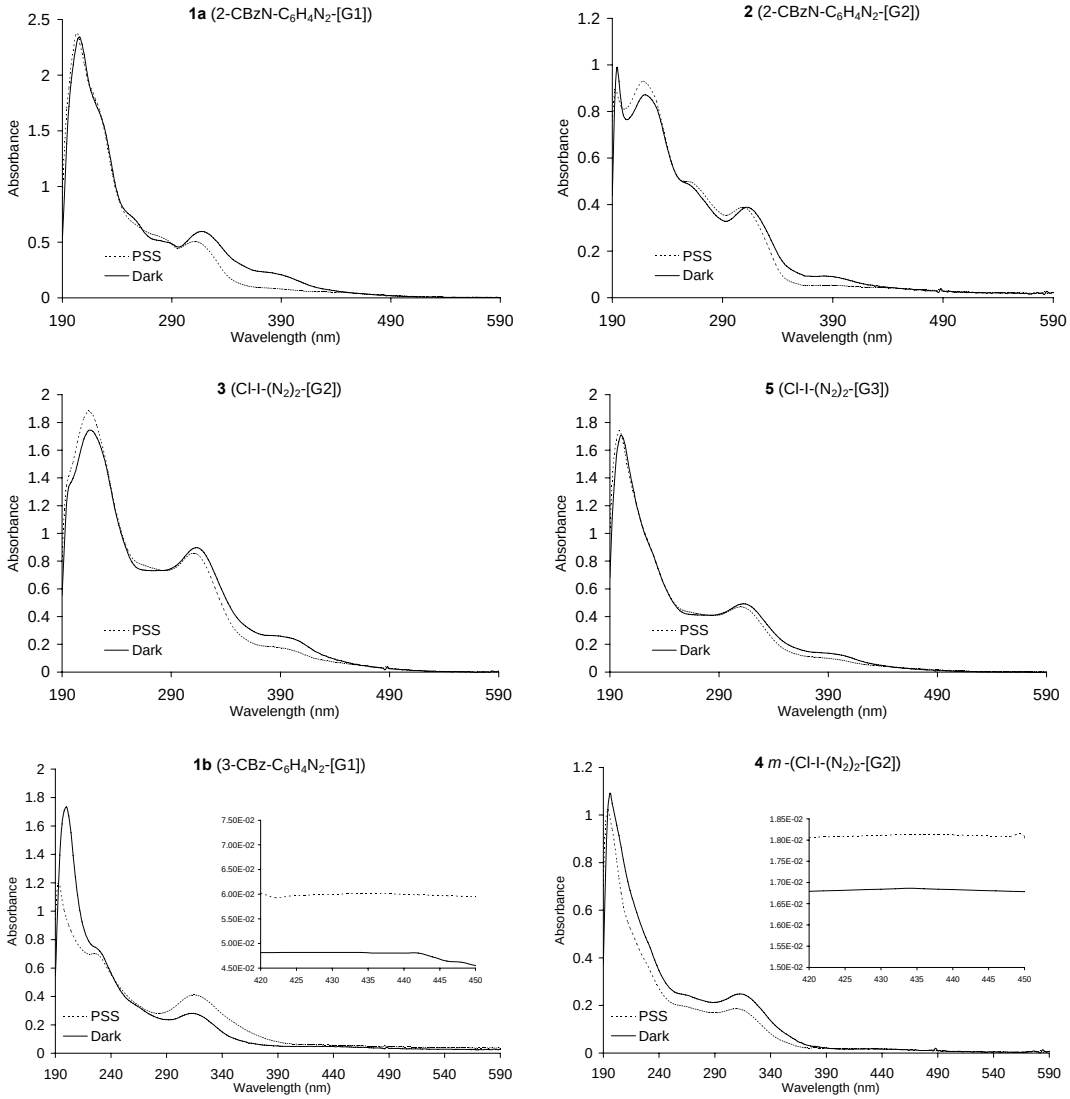
1b



2D ^{1}H – ^{1}H NOESY spectrum of 3-CBzN-C_6H_4**N_2**-[G1] **(1b)** in $CDCl_3$



2D ^{1}H – ^{1}H NOESY spectrum of *m*-Cl-I-**(N_2)$_2$**-[G2] **(4)** in $CDCl_3$



UV-Vis spectra of compounds before and after irradiation at 350 nm for 1 h

Table 1. Temperature-dependent rates of the thermal *Z*→*E* isomerization[a]

	Temp. (K) / Rate (s^{-1})			
Cmpd.	**313 K**	**323 K**	**333 K**	**343 K**
1a	2.17E-4	3.00E-4	7.94E-4	1.60E-3
1a-NH_2	6.21E-3	1.02E-3	1.76E-3	3.65E-3
1b	3.64E-5	8.25E-5	2.56E-4	6.33E-4
1b-NH_2	1.80E-5	4.22E-5	1.19E-4	6.70E-4
2	4.11E-5	1.12E-4	2.69E-4	1.19E-3
3	2.59E-4	3.55E-4	9.02E-4	1.92E-3
4	2.88E-5	6.73E-5	1.78E-4	6.34E-4
5	2.70E-4	2.84E-4	9.66E-4	1.66E-3

[a] Rate constants were determined by measuring the apparent first-order rate constants by UV spectroscopy in CH_3CN (10^{-5} M).

Table 2. Activation parameters of the thermal *Z*→*E* isomerization[a]

Cmpd.	**$\Delta H^{\neq}$** (kcal mol^{-1})	**$\Delta S^{\neq}$** (cal $mol^{-1}K^{-1}$)	**$\Delta G^{\neq}$ (298 K)** (kcal/mol)
1a	7.80	-49.40	22.50
1a-NH_2	11.79	-35.76	22.45
1b	20.02	-15.13	24.53
1b-NH_2	24.58	-2.24	25.25
2	22.70	-6.50	24.60
3	14.10	-30.3	23.10
4	21.14	-12.10	24.75
5	13.50	-32.30	23.20

[a] Activation parameters were determined by plotting the Eyring equation using the rate constants from table 1.

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