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Electronic Supporting Information

Strong Green Chemiluminescence from Naphthalene Analogues of Luminol

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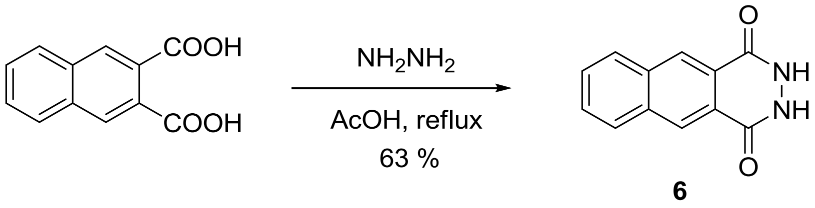
Contents

Materials and Methods

Materials and Instruments: Diethyl 6-nitro-naphthalene-2,3-dicarboxylate (**15**)[S2] was prepared following a published procedure. Hydrogen peroxide (30% in H_2O), potassium hexacyanoferrate (III), potassium persulfate, luminol (97%), 3-aminophthalic acid (3-APA, 90%), 3-nitrobenzaldehyde (99%), ethylene glycol (99.5%), chloromethyl phenylsulfone divinylbenzene (97%), 18-Crown-6 ether (99.5%), nitronium tetrafluoroborate (95%), hydrazine, (35 wt. % in water solution), iron powder (325 mesh, 97%), ammonium chloride (99.5%), 2,3-naphthalene dicarboxylic acid (95%), sodium hydride (95%), benzyl bromide (99%), DMSO (spectroscopic grade) and 4Å molecular sieves were purchased from Sigma Aldrich and distilled before used. All other reactants and spectroscopic solvents were purchase from Sigma Aldrich and used as received. Synthesis grade solvents were distilled and/or dried according standard procedures before used. Bi-distilled water was purified with the Millipore Milli-Q system. Flash column chromatography was performed with silica gel 60 (0.040-0.063 mm) purchased from Merck. NMR spectra were recorded on a Bruker Advanced II (300 or 400 MHz). Chemical shifts of ^{1}H NMR spectra are reported in ppm from the solvent resonance ($CDCl_3$ 7.26 ppm, CD_3SOCD_3 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Proton decoupled ^{13}C NMR spectra were also recorded in ppm from tetramethylsilane resonance ($CDCl_3$ 77.16, DMSO-d^6 39.5 ppm). Steady state fluorescence and chemiluminescence spectra were recorded on a Spex Fluorolog 1680 Double spectrometer.

Experimental Procedures for Compounds 1-20

2,3-dihydrobenzo[g]phthalazine-1,4-dione (6):



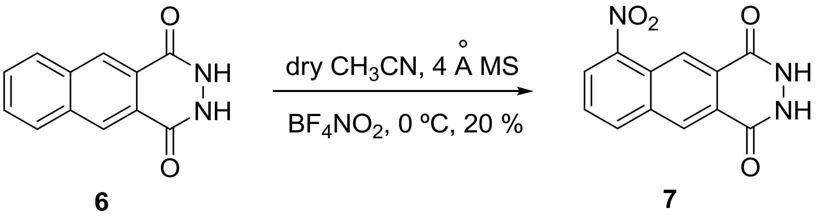
A suspension of acetic acid (20 mL) and naphthalene-2,3-dicarboxylic acid (4.0 g, 18.50 mmol) in a 250 mL round bottom flask was refluxed for 2h. The mixture was cooled to 25 °C and hydrazine (35% in H_2O) (2.09 mL, 23.12 mmol) was added dropwise. The reaction mixture was refluxed at 125 °C for another 2h and then, it was cooled to room temperature. The solid precipitated was removed by filtration and the crude product was dissolved in 5% NaOH (30 mL), acidified with AcOH (5 mL), and a yellow solid precipitate. The solid was filtered, washed with water (100 mL) and H_2O:MeOH (9:1) (20 mL) solution. The solid was recrystallized from hot methanol to afford **6** (2.45 g, 63 %) as gray white solid.

^{1}H NMR (300 MHz, dmso-d$_6$) δ/ppm: 7.85 – 7.87 (q, 2H), 8.39 – 8.41 (q, 2H), 8.85 (s, 2H) 11.60 (bs, 2H).

^{13}C-NMR (75 MHz, dmso-d$_6$) δ/ppm: 127.40, 129.77, 130.40, 135.32.

HRMS (ESI) calcd. for $C_{12}H_8N_2O_2$ $[M]^+$ 213.06585, found 213.06572.

6-nitro-2,3-dihydrobenzo[g]phthalazine-1,4-dione (7):



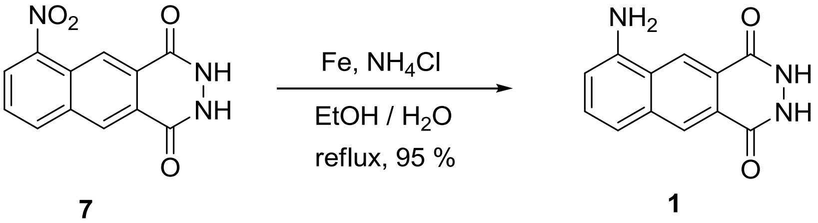
A suspension of **6** (2.0 g, 9.42 mmol) and 4 Å molecular sieves (2 g) in dry acetonitrile (15 mL) under argon atmosphere was cooled to 0 °C and nitronium tetrafluoroborate (1.26 g, 9.48 mmol) was added in small portions over 30-40 minutes. The magnetic stirring continued for another 30 minutes at 0 °C and the reaction mixture was poured into ice water (50 mL). It was neutralized with saturated $NaHCO_3$ solution and extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography using EtOAc :hexane (4:6) as eluent to obtain **7** (0.48 g, 20%) as light brown solid.

^{1}H NMR (500 MHz, dmso-d$_6$) δ/ppm: 7.91 (t, 1H), 8.52 (d, 1H), 8.63 (d, 1H), 8.66 (s, 2H), 11.78 (s, 2H, amide H)

^{13}C NMR (125 MHz, dmso-d$_6$) δ/ppm: 118.44, 124.96, 126.24, 127.03, 127.96, 129.74, 131.52, 136.02, 136.90, 147.39, 168.09, 168.25.

HRMS (ESI) calcd. for $C_{12}H_7N_3O_4$ $[M+H]^+$ 258.0518, found 213.0509.

6-amino-2,3-dihydrobenzo[g]phthalazine-1,4-dione (1):



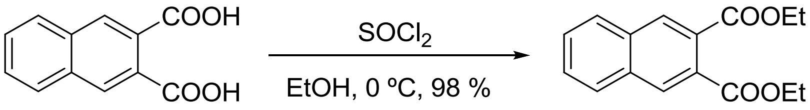
To a solution of **7** (1.0 g, 3.88 mmol) in ethanol (10.5 mL) and H_2O (3 mL), iron powder (325 mesh) (0.65 g, 11.64 mmol) and NH_4Cl (0.125 g, 2.33 mmol) were added at room temperature. The reaction mixture was stirred at 85 °C for 1h, cooled to room temperature, and filtered through celite. The solid was washed thoroughly with ethyl acetate (100 mL), and the filtrate was concentrated under reduced pressure, extract with ethyl acetate and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography with EtOAc:hexane (3: 7) as eluent affording **1** (0.83 g, 95%) as light brown colour amine.

^{1}H NMR (400 MHz, dmso-d$_6$) δ/ppm: 6.26 (s, 2H, *N*H2), 6.88 (d, 1H), 7.34 – 7.44 (m, 2H), 8.20 (s, 1H), 8.64 (s, 1H), 11.34 (bs, 2H, amide H).

^{13}C NMR (100 MHz, dmso-d$_6$) δ/ppm: 111.08, 117.56, 119.75, 123.29, 124.26, 125.98, 12830, 130.34, 136,38, 147.65, 169.14, 169.17.

HRMS (ESI) calcd. for $C_{12}H_{10}N_3O_2$ $[M+H]^+$ 228.0774, found 228.0774.

Diethyl naphthalene-2,3-dicarboxylate (8):[S2]



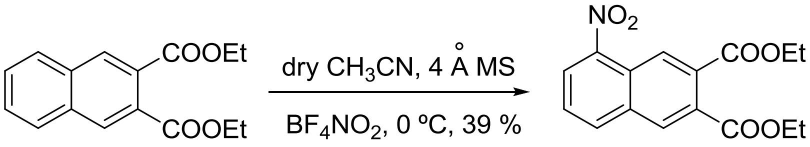
8

A solution of naphthalene 2,3-dicarboxylic acid (2.0 g, 9.25 mmol) in 100 mL ethanol was cooled to 0 ºC, and excess of $SOCl_2$ (10mL) was added drop wise. The reaction mixture was allowed to reach room temperature and then refluxed overnight. After completing the reaction, monitored my TLC, the reaction mixture was cooled to room temperature and the solvent was removed under reduced press. The crude was treated with $NaHCO_3$ and washed with dichlorormethane (3×50 mL). Diethyl naphthalene-2,3-dicarboxylate (**8**) was obtained as a yellow oil (2.46 g, 98 %), according to the literature,[S2] and was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 1.41-1.44 (t, 6H), 4.41-4.47 (q, 4H), 7.60-7.62 (m, 2H), 7.91-7.93 (m, 2H), 8.26 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 14.20, 61.65, 128.47, 128.62, 128.87, 130.02, 133.35, 167.75.

Diethyl 5-nitronaphthalene-2,3-dicarboxylate (9):



8 **9**

A suspension of **8** (1.0 g, 3.67 mmol) and 4 Å molecular sieves (2.0 g) in dry acetonitrile (15 mL) was cooled to 0 °C under argon atmosphere, and nitronium tetrafluoroborate (0.49 g, 3.68 mmol) was added in small portions over 30 min. The magnetic stirring continued for another 30 minutes at 0 °C and the reaction mixture was poured into ice water (50 mL). The solution was neutralized with saturated $NaHCO_3$ solution and extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous Na_2SO_4

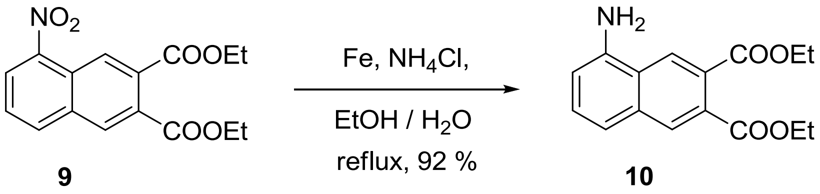
and concentrated under reduced pressure. The crude product was purified by flash chromatography using EtOAc :hexane (3:7) as eluent affording **9** (0.45 g, 39 %) as a pale yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 1.38 – 1.43 (m, 6H), 4.39 – 4.47 (m, 4H), 7.69 (t, 1H), 8.14 (d, 1H), 8.34 (s, 1H), 8.36 (d, 1H), 8.92 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 14.23, 62.17, 62.24, 125.12, 125.45, 126.41, 126.89, 130.24, 130.56, 132.66, 134.19, 135.26, 146.74, 166.64, 167.14.

HRMS (ESI) calcd. for $C_{16}H_{15}NO_6$ $[M]^+$ 318.09721, found 318.09684.

Diethyl 5-aminonaphthalene-2,3-dicarboxylate (10):



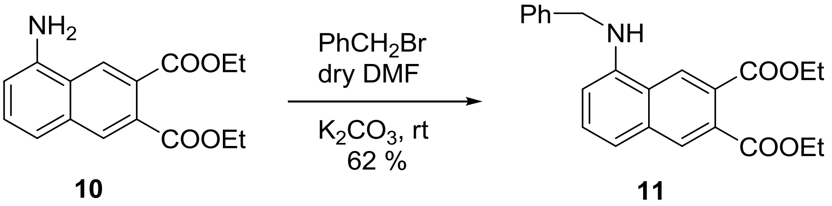
To a solution of **9** (1.0 g, 3.15 mmol) in EtOH (10.5 mL) and H_2O (3 mL), iron powder (320 mesh) (0.052 g, 0.93 mmol) and NH_4Cl (0.101 g, 1.88 mmol) were at room temperature. The reaction mixture was stirred at 85 °C for 1h, cooled to room temperature and filtered through celite. The solid was washed with ethyl acetate and the filtrate was concentrated under reduced pressure, extracted with ethyl acetate and washed with brine solution. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography with EtOAc:hexane (1:9) to give **10** (0.83 g, 92 %) as a light yellow solid

^{1}H NMR (300 MHz, dmso-d_6) δ/ppm: 1.28 – 1.34 (m, 6H), 4.27 – 4.34 (m, 4H), 6.13 (s, 2H, NH_2), 6.83 (d, 1H), 7.23 (d, 1H), 7.39 (t, 1H), 8.11 (s, 1H), 8.51 (s, 1H).

^{13}C NMR (75 MHz, dmso-d_6) δ/ppm: 14.02, 61.13, 61.19, 110.29, 115.75, 121.74, 125.05, 125.73, 128.10, 129.60, 129.99, 134.20, 146.11, 167.34, 167.39.

HRMS (ESI) calcd. for $C_{16}H_{17}NO_4$ $[M]^+$ 288.12303, found 288.12274.

Diethyl 5-(benzylamino)naphthalene-2,3-dicarboxylate (11):

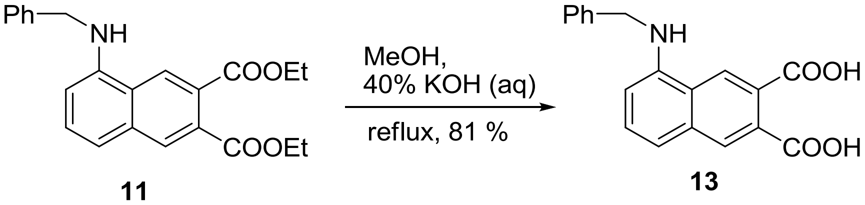


To a solution of **10** (1.0 g, 3.48 mmol) in dry DMF (5 mL), K_2CO_3 (0.529 g, 3.82 mmol) was added under argon atmosphere. After a few minutes of stirring at room temperature, benzyl bromide (0.595 g, 3.48 mmol) was added dropwise. The reaction mixture was allowed to stirrer for 2h and the reaction was monitored by TLC every 30 min. Initially, the mono benzylation occur and prolonged reaction time favor mixture of mono and dibenzylation products formation. To control the formation of dibenzylation, the reaction was stopped after 2h. The reaction mixture was filtered through celite and washed thoroughly with dichloromethane. The filtrated was extracted with dichloromethane and brine solution, and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The dark oily crude was purified by flash chromatography with EtOAc:hexane (3:7) affording **11** (0.81 g, 62 %) as a pale orange solid.

^{1}H NMR (300 MHz, dmso-d$_6$) δ/ppm: 1.39 – 1.45 (m, 6H), 4.39 – 4.47 (m, 4H), 4.50 (s, 2H), 5.01 (bs, 1H, *N*H), 6.71 (d, 1H), 7.27 – 7.47 (m, 7H, ArH), 8.17 (s, 1H), 8.33 (s, 1H).

^{13}C NMR (75 MHz, dmso-d$_6$) δ/ppm: 14.27, 48.37, 61.64, 61.72, 107.14, 117.73, 122.73, 126.97, 127.59, 127.66, 128.37, 128.56, 128.85, 129.00, 12971, 130.53, 134.67, 138.47, 144.13, 168.02, 168.06.

5-(benzylamino)naphthalene-2,3-dicarboxylic acid (13):



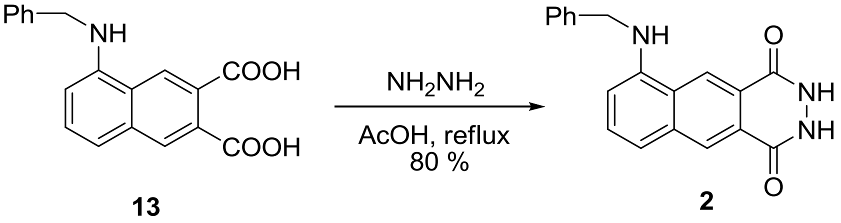
A mixture of **11** (1.0 g, 2.64 mmol) in MeOH:40% KOH (1:5, 25 mL) was refluxed for 5h. The reaction mixture was then poured over water (50 mL), acidified with 2 M HCl to pH 2. The precipitated was filtered and washed with 100 mL distilled water. The crude product was dried over calcium carbonate desiccator and recrystallized with hot methanol yielding the dicarboxylic acid **13** (0.68 g, 81 %) as a greenish yellow solid.

^{1}H NMR (300 MHz, dmso-d$_6$) δ/ppm: 4.49 (s, 2H), 6.48 (d, 1H), 7.18 – 7.41 (m, 8H, ArH), 8.06 (s, 1H), 8.67 (s, 1H), 12.98 (bs, 2H, COOH).

^{13}C NMR (75 MHz, dmso-d$_6$) δ/ppm: 46.27, 105.83, 115.59, 122.27, 123.66, 126.62, 126.94, 127.47, 128.30, 128.97, 129.38, 129.76, 134.12, 139.68, 144.57, 168.95.

HRMS (ESI) calcd. for $C_{19}H_{15}NO_4$ $[M+H]^+$ 322.1086, found 322.1074.

6-(benzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (2):



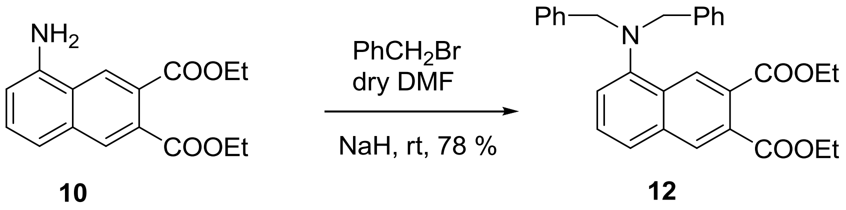
A suspension of acetic acid (20 mL) and **13** (1.0 g, 3.11 mmol) in a 250 mL round bottom flask was refluxed for 2h. The mixture was cooled to 25 °C and hydrazine (35% in H_2O) (0.35mL, 3.88 mmol) was added dropwise. The reaction mixture was refluxed at 125 °C for another 2h and then, it was cooled to room temperature. The solid precipitated was removed by filtration and the crude product was dissolved in 5% NaOH (30 mL), acidified with AcOH (5 mL), and a brown solid precipitate. The solid was filtered, washed with water (100 mL) and H_2O:MeOH (9:1, 20 mL) solution. The solid was recrystallized from hot methanol to afford **2** (0.79 g, 80 %) as pale brown solid.

^{1}H NMR (300 MHz, dmso-d$_6$) δ/ppm: 4.53 (s, 2H, benzylic H), 6.51 (s, 1H), 7.21 – 7.44 (m, 7H, ArH), 7.62 (bs, 1H), 8.49 (s, 1H), 9.11 (s, 1H), 11.40 (bs, 2H).

^{13}C NMR (75 MHz, dmso-d$_6$) δ/ppm: 46.34, 105.00, 116.00, 124.68, 126.65, 126.98, 128.32, 129.66, 135.51, 139.65, 144.90, 167.99.

HRMS (ESI) calcd. for $C_{19}H_{15}N_3O_2$ $[M]^+$ 318.12370, found 318.12344.

Diethyl 5-(dibenzylamino)naphthalene-2,3-dicarboxylate (12):



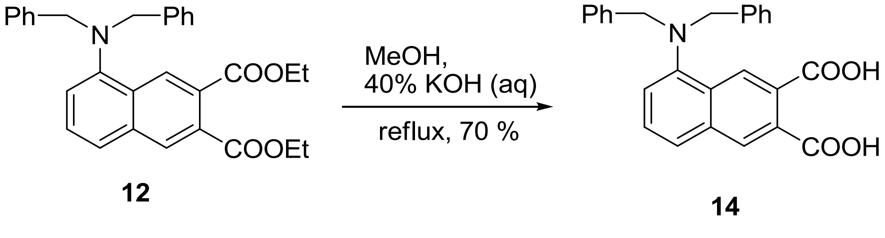
To a solution of **10** (1.0 g, 3.48 mmol) in dry DMF (5 mL), dried NaH (0.017 g, 0.71 mmol) was added under argon atmosphere. After 5 minutes stirring at room temperature, benzyl bromide (1.27 g, 7.42 mmol) was added dropwise. The reaction mixture was allowed to stirrer 2h at room temperature and the reaction was monitored by TLC for every 30 min. Once the starting material is completely disappeared, the reaction mixture was filtered through celite. The filtrate was extracted with dichloromethane and brine solution, and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The dark oily crude compound was purified by column chromatography with EtOAc :hexane (4:6) as eluent to afford **12** (1.26 g, 78 %) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 1.25 – 1.31 (m, 6H), 4.19 (s, 4H, benzylic H), 4.27 – 4.34 (m, 4H), 6.90 (d, 1H), 7.08 – 7.14 (m, 10H), 7.25 (t, 1H), 7.42 (d, 1H), 8.08 (s, 1H), 8.88 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.15, 57.57, 61.50, 61.57, 120.75, 123.73, 126.35, 127.13, 127.93, 128.26, 128.38, 129.22, 129.69, 130.28, 135.04, 137.57, 148.31, 167.70, 168.02.

HRMS (ESI) calcd. for $C_{30}H_{29}NO_4$ $[M]^+$ 468.21693, found 468.21660.

5-(dibenzylamino)naphthalene-2,3-dicarboxylic acid (14):



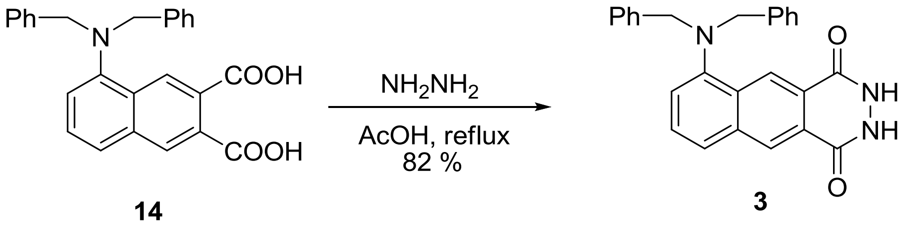
A mixture of **12** (1.0 g, 2.13 mmol) in MeOH:40% KOH (1:5, 5 mL) was refluxed for 5h. The reaction mixture was then poured over water (50 mL), acidified with 2 M HCl to pH 2. The precipitated was filtered and washed with 100 mL distilled water. The crude product was dried over calcium carbonate desiccator and recrystallized with hot methanol yielding the dicarboxylic acid **14** (0.61 g, 70 %) as a light yellow solid.

^{1}H NMR (300 MHz, dmso-d$_6$) δ/ppm: 4.30 (s, 4H, benzylic H), 7.19 – 7.31 (m, 11H), 7.45 (t, 1H), 7.71 (d, 1H), 8.22 (s, 1H), 8.85 (s, 1H), 13.01 (bs, 1H)

^{13}C NMR (75 MHz, dmso-d$_6$) δ/ppm: 57.24, 120.81, 123.87, 124.91, 127.10, 128.14, 128.30, 129.04, 129.46, 130.27, 134.50, 137.85, 147.24, 168.67, 168.92.

HRMS (ESI) calcd. for $C_{26}H_{21}NO_4$ $[M]^+$ 412.15433, found 412.15404.

6-(dibenzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (3):



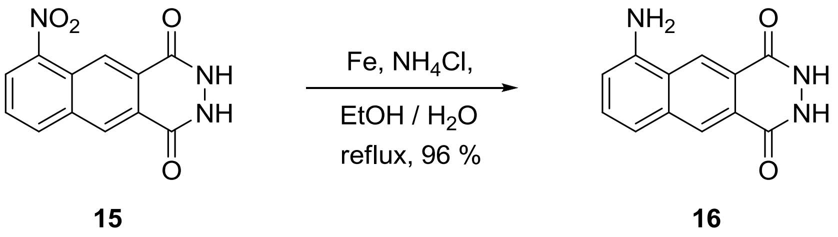
A suspension of acetic acid (20 mL) and **14** (2.0 g, 4.86 mmol) in a 250 mL round bottom flask was refluxed for 2h. The mixture was cooled to 25 °C and hydrazine (35% in H_2O) (0.55 mL, 6.07 mmol) was added dropwise. The reaction mixture was refluxed at 125 °C for another 2h and then, it was cooled to room temperature. The solid precipitated was removed by filtration and the crude product was dissolved in 5% NaOH (30 mL), acidified with AcOH (5 mL), and a brown solid precipitate. The solid was filtered, washed with water (100 mL) and H_2O:MeOH (9:1, 20 mL) solution. The solid was recrystallized from hot methanol to afford **3** (1.63 g, 82 %) as a yellow solid.

^{1}H NMR (300 MHz, dmso-d$_6$) δ/ppm: 4.33 (s, 4H, benzylic H), 7.16 – 7.33 (m, 11H, ArH), 7.51 (t, 1H), 7.90 (d, 1H), 8.68 (s, 1H), 9.32 (s, 1H), 11.49 (bs, 2H, amide H).

^{13}C NMR (75 MHz, dmso-d$_6$) δ/ppm: 57.10, 120.36, 121.82, 124.46, 124.77, 126.66, 127.08, 127.83, 128.26, 130.67, 135.62, 137.84, 147.38, 155.65, 156.01.

HRMS (ESI) calcd. for $C_{26}H_{21}N_3O_2$ $[M]^+$ 408.17065, found 408.17019.

Diethyl 6-amino-naphthalene-2,3-dicarboxylate (16):



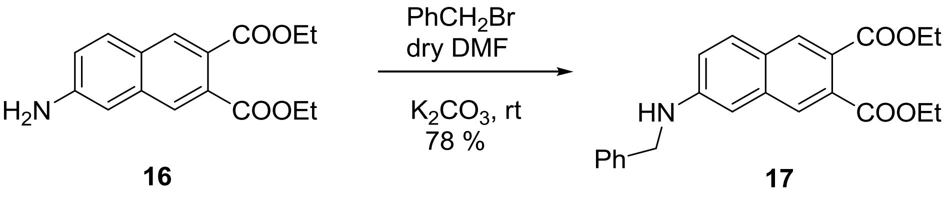
To a solution of **15** [S1] (3.0 g, 9.45 mmol) in EtOH (21 mL) and H_2O (6 mL), iron powder (320 mesh) (1.57 g, 28.13 mmol) and NH_4Cl (0.30 g, 5.60 mmol) were added at room temperature. The reaction mixture was stirred at 85 °C for 1h, cooled to room temperature and filtered through celite. The solid was washed with ethyl acetate and the filtrate was concentrated under reduced pressure, extracted with ethyl acetate and washed with brine solution. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography with EtOAc:hexane (2:8) to give **16** (2.60 g, 96 %) as a light yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 1.37 (dt, 6H), 4.37 (dq, 4H), 4.10 (s, 2H), 6.93 (s, 1H), 6.98 (d, 2H), 7.67 (d, 2H), 7.82 (s, 1H), 8.15 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.17, 14.23, 61.31, 61.55, 108.36, 120.16, 124.03, 127.08, 130.19, 130.23, 130.64, 135.56, 146.91, 167.54, 168.81.

HRMS (ESI) calcd. for $C_{16}H_{17}NO_4$ $[M]^+$ 288.12303, found 288.12279.

Diethyl 6-(benzylamino)naphthalene-2,3-dicarboxylate (17):



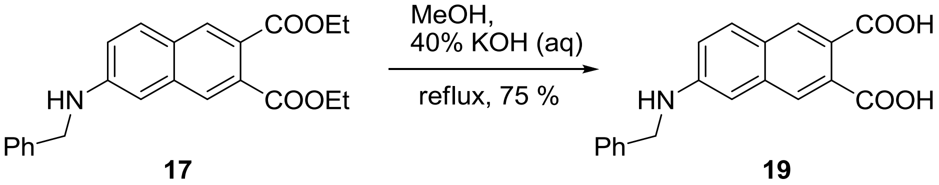
To a solution of **16** (2.0 g, 6.96 mmol) in dry DMF (5 mL), K_2CO_3 (1.16 g, 8.39 mmol) was added under argon atmosphere. After a few minutes of stirring at room temperature, benzyl bromide (1.31 g, 7.66 mmol) was added dropwise. The reaction mixture was allowed to stirrer for 2h and the reaction was monitored by TLC every 30 min. Initially, the mono benzylation occur and prolonged reaction time favor mixture of mono and dibenzylation products formation. To control the formation of dibenzylation, the reaction was stopped after 2h. The reaction mixture was filtered through celite and washed thoroughly with dichloromethane. The filtrated was extracted with dichloromethane and brine solution, and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The dark oily crude was purified by flash chromatography with EtOAc:hexane (3:7) affording **17** (2.05 g, 78 %) as a dark dense oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 1.40 (dt, 6H), 4.38 (dq, 4H), 4.45 (s, 2H, benzylic H), 6.83 (s, 1H), 7.00 (d, 1H), 7.02 – 7.42 (m, 6H, ArH), 7.69 (d, 1H), 7.85 (s, 1H), 8.17 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.28, 14.35, 48.08, 61.34, 61.58, 104.69, 119.95, 123.66, 126.74, 126.88, 127.28, 127.59, 127.64, 128.90, 129.08, 130.01, 130.51, 130.71, 136.04, 138.48, 148.07, 167.61, 168.98.

HRMS (ESI) calcd. for $C_{23}H_{23}NO_4$ $[M]^+$ 378.16998, found 378.17004.

6-(benzylamino)naphthalene-2,3-dicarboxylic acid (19):



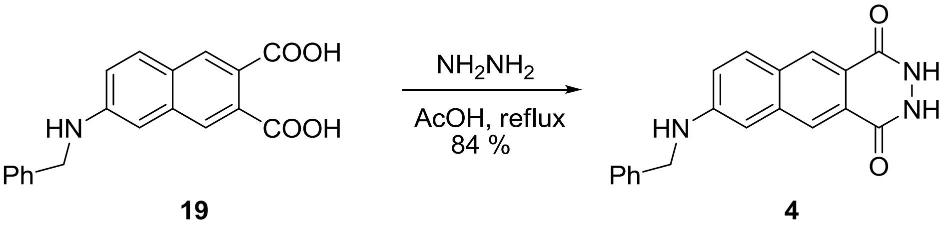
A mixture of **17** (1.0 g, 2.13 mmol) in MeOH:40% KOH (1:5, 25 mL) was refluxed for 5h. The reaction mixture was then poured over water (50 mL), acidified with 2 M HCl to pH 2. The precipitated was filtered and washed with 100 mL distilled water. The crude product was dried over calcium carbonate desiccator and recrystallized with hot EtOAc yielding the dicarboxylic acid **19** (1.27 g, 75 %) as a yellowish brown solid.

^{1}H NMR (300 MHz, dmso-d_6) δ/ppm: 4.39 (s, 2H, benzylic H), 6.98 (bs, 1H, *N*H), 6.83 – 8.09 (m, 10H, ArH), 12.74 (bs, 2H, COOH).

^{13}C NMR (75 MHz, dmso-d_6) δ/ppm: 46.25, 102.88, 120.09, 123.14, 125.33, 125.58, 126.88, 127.48, 128.40, 129.49, 129.87, 131.55, 135.64, 139.40, 148.80, 168.31, 169.80.

HRMS (ESI) calcd. for $C_{19}H_{15}NO_4$ $[M]^+$ 322.10738, found 322.10728.

7-(benzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (4):



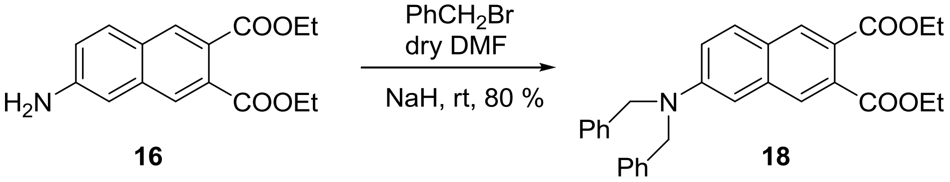
A suspension of acetic acid (20 mL) and **19** (1.0 g, 3.11 mmol) in a 250 mL round bottom flask was refluxed for 2h. The mixture was cooled to 25 °C and hydrazine (35% in H_2O) (0.35 mL, 3.88 mmol) was added dropwise. The reaction mixture was refluxed at 125 °C for another 2h and then, it was cooled to room temperature. The solid precipitated was removed by filtration and the crude product was dissolved in 5% NaOH (30 mL), acidified with AcOH (5 mL), and a brown solid precipitate. The solid was filtered, washed with water (100 mL) and H_2O:MeOH (9:1, 20 mL) solution. The solid was recrystallized from hot methanol to afford **4** (0.84 g, 84 %) as a yellow powder.

^{1}H NMR (300 MHz, dmso-d_6) δ/ppm: 4.42 (d, 2H, benzylic H), 6.95 (s, 1H), 7.11 – 7.96 (m, 8H, ArH & *N*H), 8.18 (s, 1H), 8.45 (s, 1H), 11.35 (bs, 2H).

^{13}C NMR (75 MHz, dmso-d_6) δ/ppm: 46.28, 102.08, 119.72, 121.82, 121.88, 124.11, 126.03, 126.96, 127.51, 127.58, 128.01, 128.45, 129.96, 136.96, 139.30, 148.58, 154.81, 156.01.

HRMS (ESI) calcd. for $C_{19}H_{15}N_3O_2$ $[M]^+$ 318.12370, found 318.12346.

Diethyl 6-(dibenzylamino)naphthalene-2,3-dicarboxylate (18):



To a solution of **16** (1.0 g, 3.48 mmol) in dry DMF (5 mL), dried NaH (0.017 g, 0.71 mmol) was added under argon atmosphere. After 5 minutes stirring at room temperature, benzyl bromide (1.27 g, 7.42 mmol) was added dropwise. The reaction mixture was allowed to stirrer

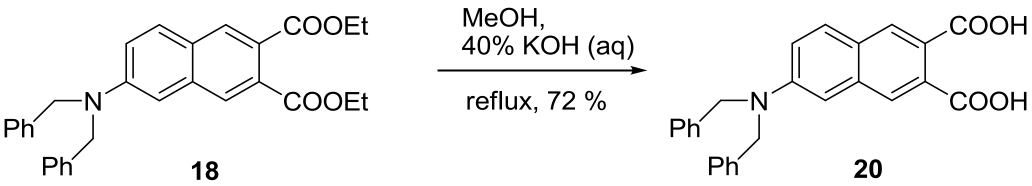
2h at room temperature and the reaction was monitored by TLC for every 30 min. Once the starting material is completely disappeared, the reaction mixture was filtered through celite. The filtrate was extracted with dichloromethane and brine solution, and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The dark oily crude compound was purified by column chromatography with EtOAc :hexane (4:6) as eluent to afford **18** (1.30 g, 80 %) as dark dense oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 1.39 – 1.44 (m, 6H, CH_3), 4.38 – 4.43 (m, 4H, OCH_2), 4.81 (s, 4H, benzylic H), 7.02 (s, 1H), 7.23 – 7.76 (m, 12H), 7.83 (s, 1H), 8.21 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.28, 14.34, 54.38, 61.29, 61.53, 106.50, 117.73, 123.59, 126.09, 126.64, 127.05, 127.36, 127.50, 128.63, 128.96, 130.21, 130.52, 130.62, 135.75, 137.68, 149.25, 167.53, 168.94

HRMS (ESI) calcd. for $C_{30}H_{29}NO_4$ $[M]^+$ 468.21693, found 468.21676.

6-(dibenzylamino)naphthalene-2,3-dicarboxylic acid (20):



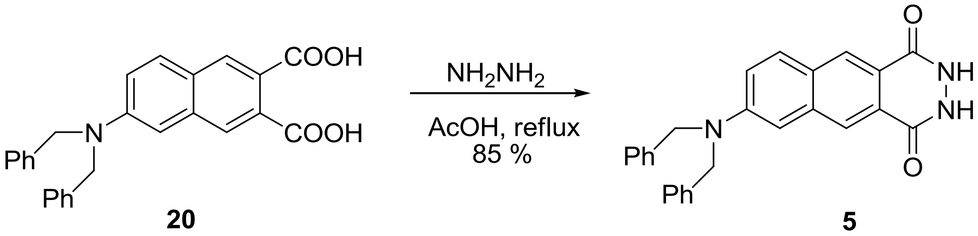
A mixture of **18** (1.0 g, 2.13 mmol) in MeOH:40% KOH (1:5, 30 mL) was refluxed for 5h. The reaction mixture was then poured over water (50 mL), acidified with 2 M HCl to pH 2. The precipitated was filtered and washed with 100 mL distilled water. The crude product was dried over calcium carbonate desiccator and recrystallized with hot methanol yielding the dicarboxylic acid **20** (0.62 g, 72%) as a pale yellow powder.

^{1}H NMR (300 MHz, dmso-d_6) δ/ppm 4.84 (s, 4H), 7.10 (s, 1H), 7.11 – 7.83 (m, 12H, ArH), 7.73 (1H, s), 8.11 (1H, s) 12.79 (bs, 2H, COOH).

^{13}C-NMR (75 MHz, dmso-d_6) δ/ppm: 53.99, 105.91, 117.74, 123.82, 124.94, 126.14, 126.76, 126.91, 128.58, 129.66, 129.75, 131.46, 135.00, 138.37, 148.27, 168.23, 169.59.

HRMS (ESI) calcd. for $C_{26}H_{21}NO_4$ $[M]^+$ 412.15433, found 412.15392.

7-(dibenzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (5):



A suspension of acetic acid (20 mL) and **20** (0.5 g, 1.21 mmol) in a 250 mL round bottom flask was refluxed for 2h. The mixture was cooled to 25 °C and hydrazine (35% in H_2O) (0.13 mL, 1.51 mmol) was added dropwise. The reaction mixture was refluxed at 125 °C for another 2h and then, it was cooled to room temperature. The solid precipitated was removed by filtration and the crude product was dissolved in 5% NaOH (30 mL), acidified with AcOH (5 mL), and a brown solid precipitate. The solid was filtered, washed with water (100 mL) and H_2O:MeOH (9:1, 20 mL) solution. The solid was recrystallized from hot methanol to afford **5** (0.42 g, 85 %) as yellow solid.

^{1}H NMR (300 MHz, dmso-d_6) δ/ppm: 4.88 (s, 4H, benzylic H), 7.22 – 7.39 (m, 11H, ArH), 7.42 (d, 1H), 8.00 (d, 1H), 8.19 (s, 1H), 8.46 (s, 1H), 11.25 (bs, 2H, amide H)

^{13}C NMR (75 MHz, dmso-d_6) δ/ppm: 54.06, 105.45, 119.14, 120.12, 122.52, 125.91, 126.78, 126.95, 127.40, 128.62, 130.24, 136.21, 138.35, 148.01.

HRMS (ESI) calcd. for $C_{26}H_{21}N_3O_2$ $[M]^+$ 408.17065, found 408.17033.

References

[S1] M. E. Vazquez, J. B. Blanco, B. Imperiali, *J. Am. Chem. Soc.* **2005**, *127*, 1300-1306.

[S2] Z.-Y. Wang, D.-M. Du, D. Wu, W.-T. Hua, *Synthetic Commun*. **2003**, *33*, 1275-1283.

NMR Data

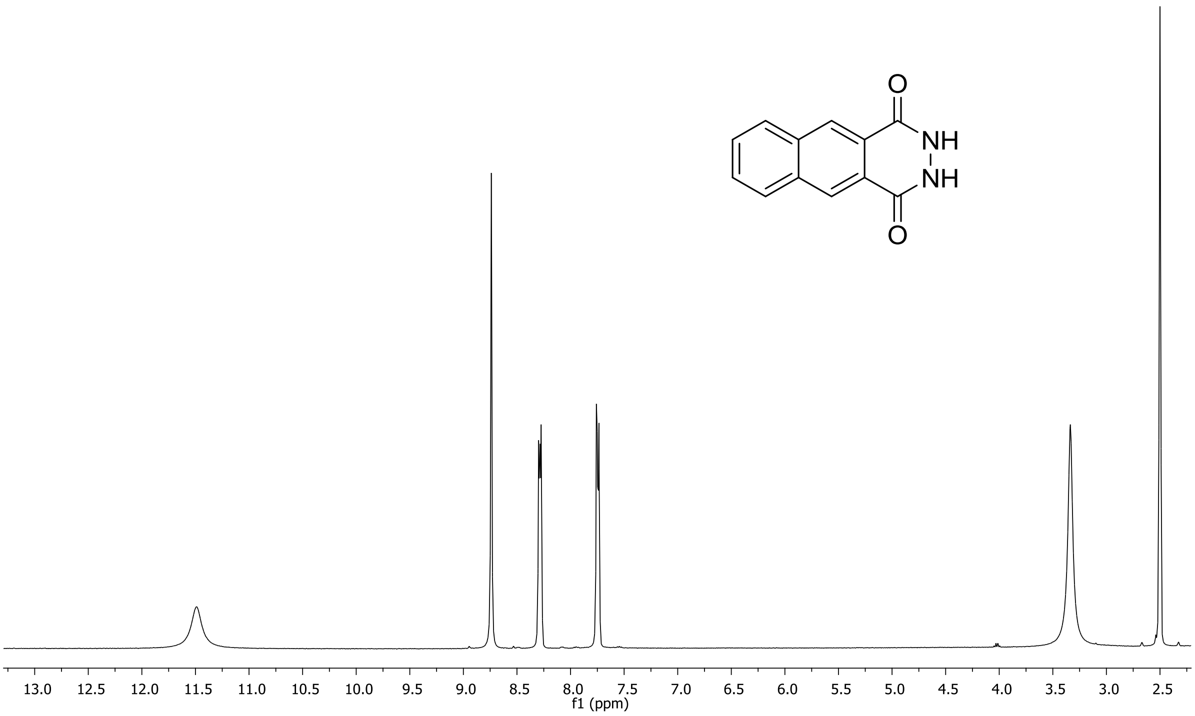


Figure S1-a: ^{1}H NMR spectrum of 2,3-dihydrobenzo[g]phthalazine-1,4-dione (**6**).

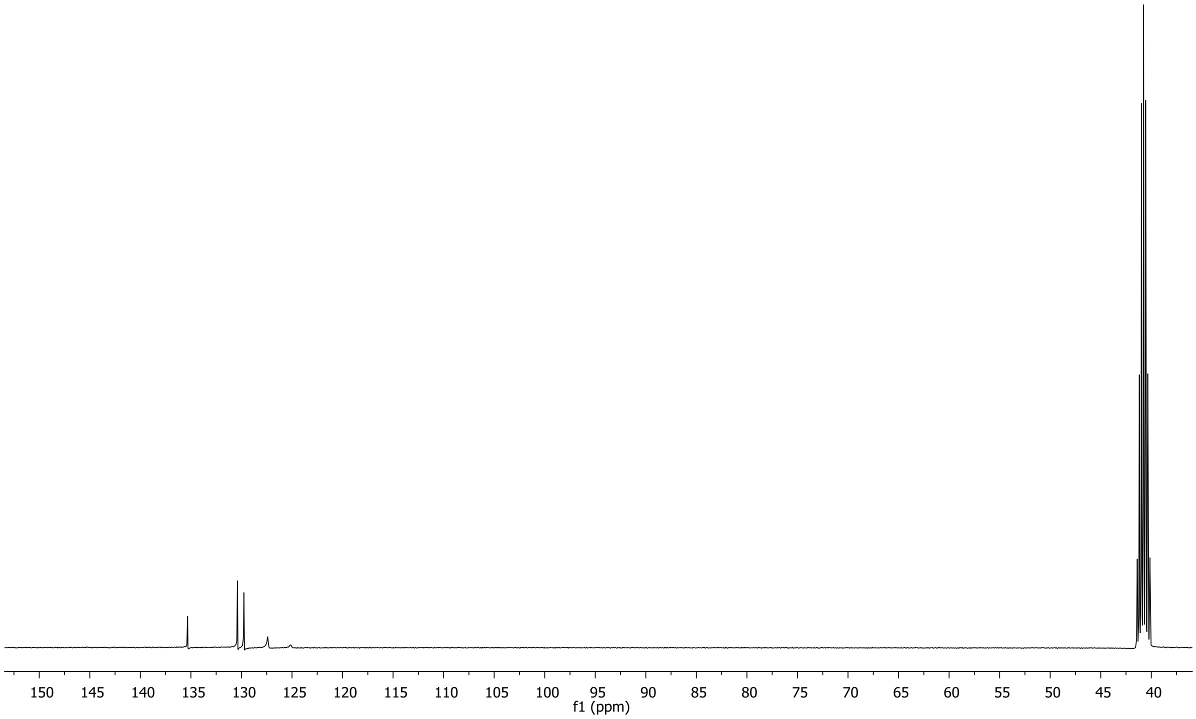


Figure S1-b: ^{13}C NMR spectrum of 2,3-dihydrobenzo[g]phthalazine-1,4-dione (**6**).

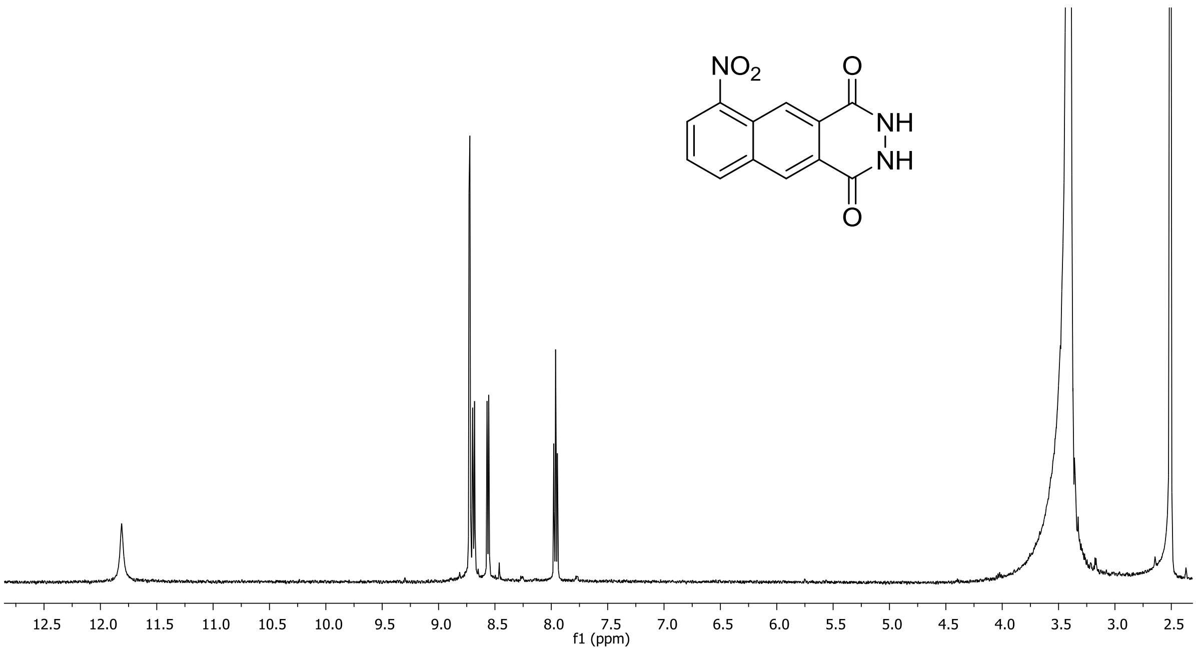


Figure S2-a: ^{1}H NMR spectrum of 6-nitro-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**7**).

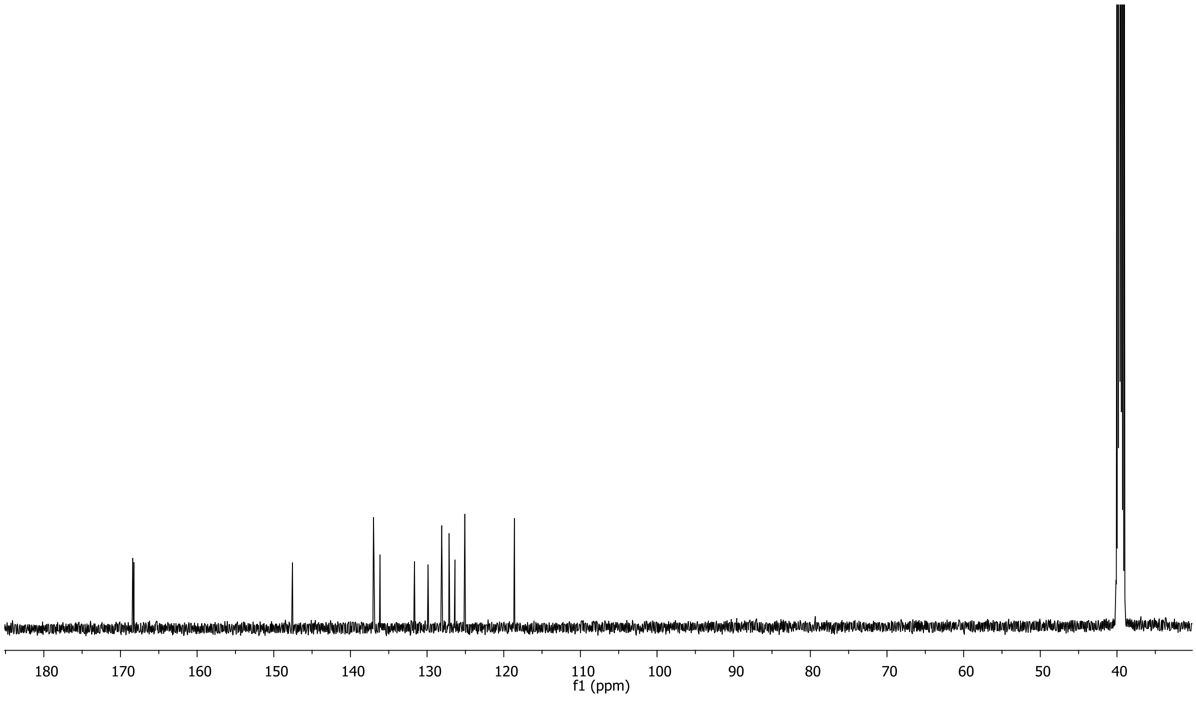


Figure S2-b: ^{13}C NMR spectrum of 6-nitro-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**7**).

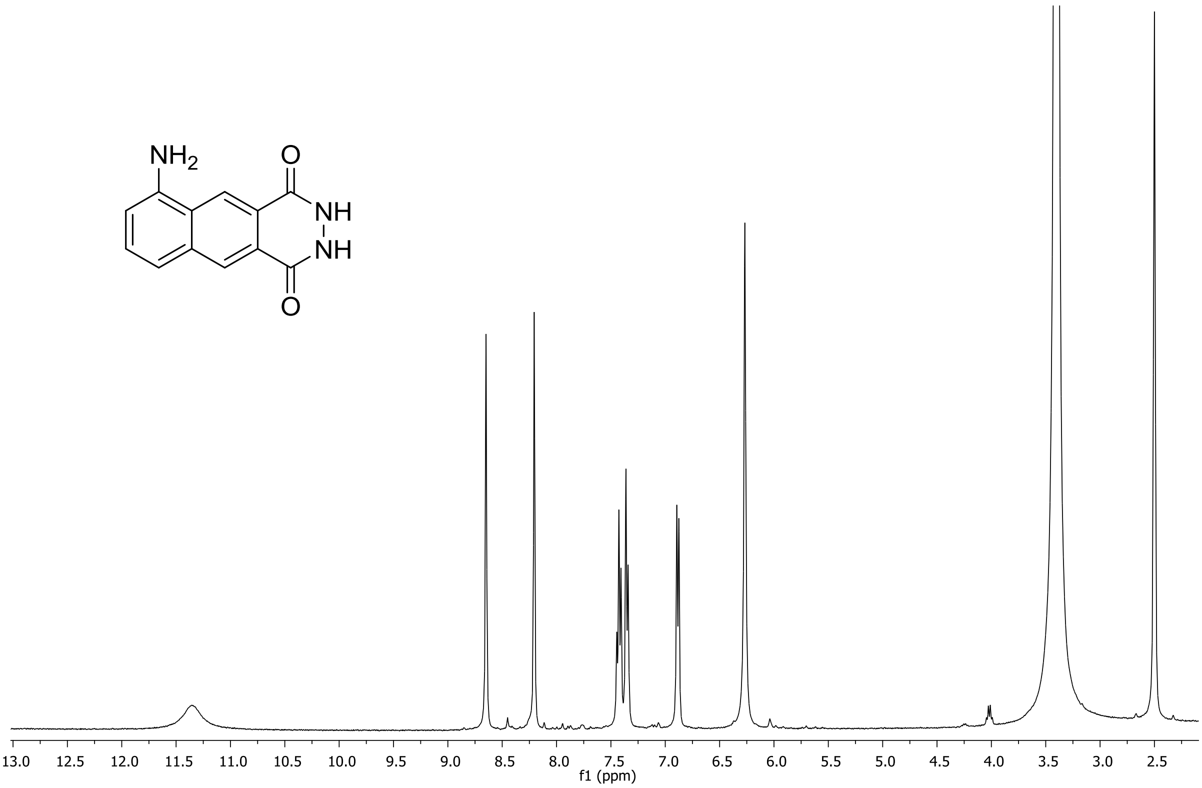


Figure S3-a: ^{1}H NMR spectrum of 6-amino-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**1**).

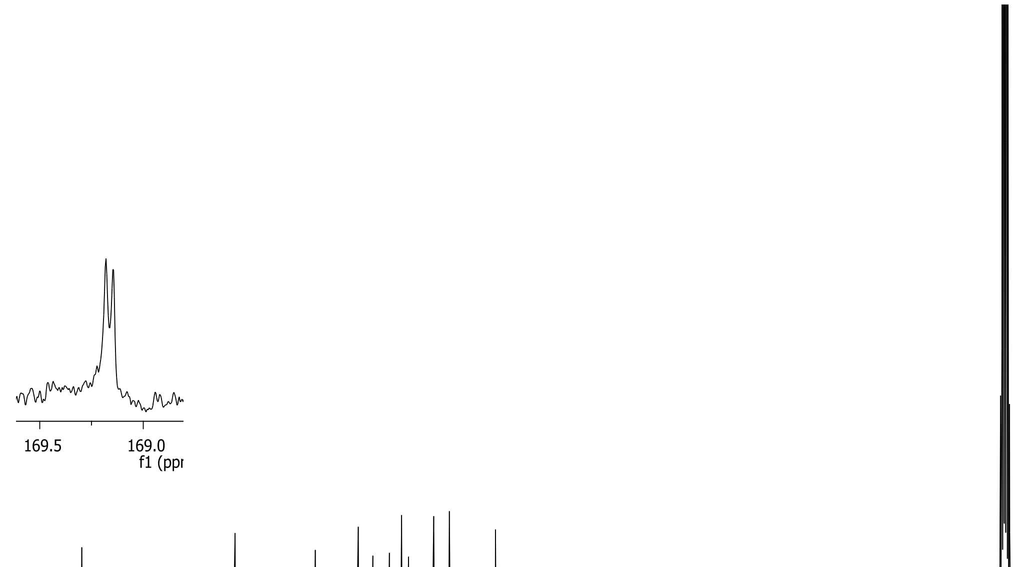


Figure S3-b: ^{13}C NMR spectrum of 6-amino-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**1**).

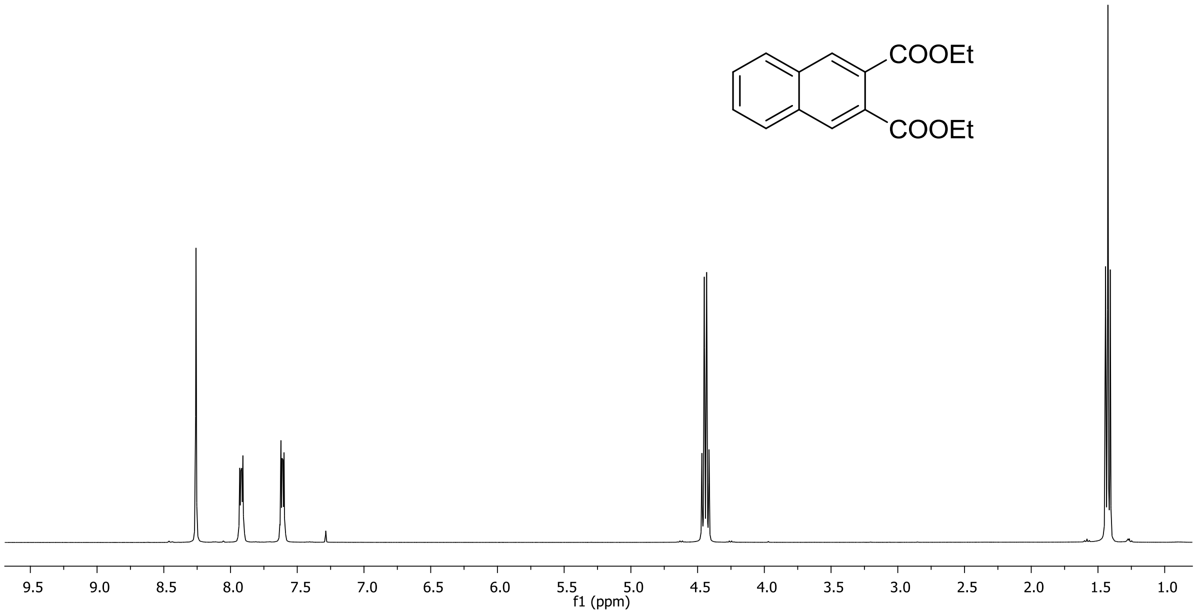


Figure 4-a: ^{1}H NMR spectrum of diethyl naphthalene-2,3-dicarboxylate (**8**).

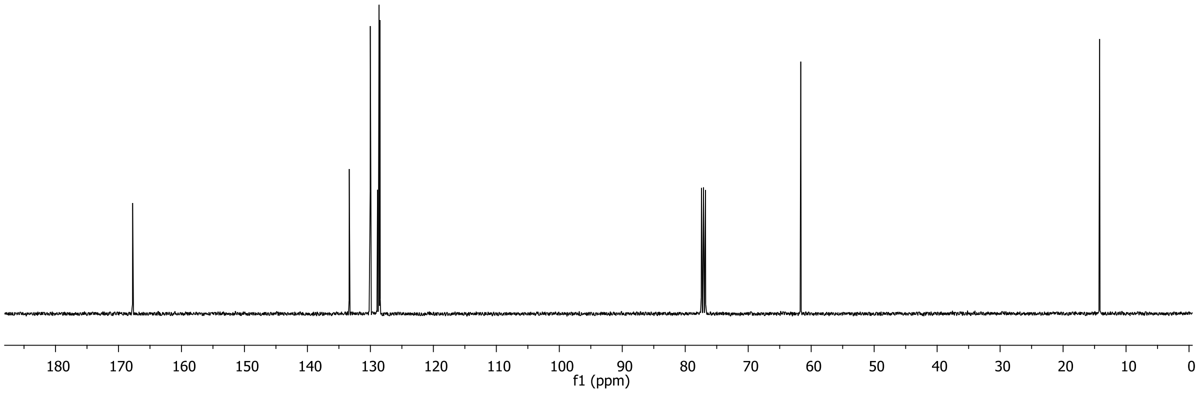


Figure 4-a: ^{13}C NMR spectrum of diethyl naphthalene-2,3-dicarboxylate (**8**).

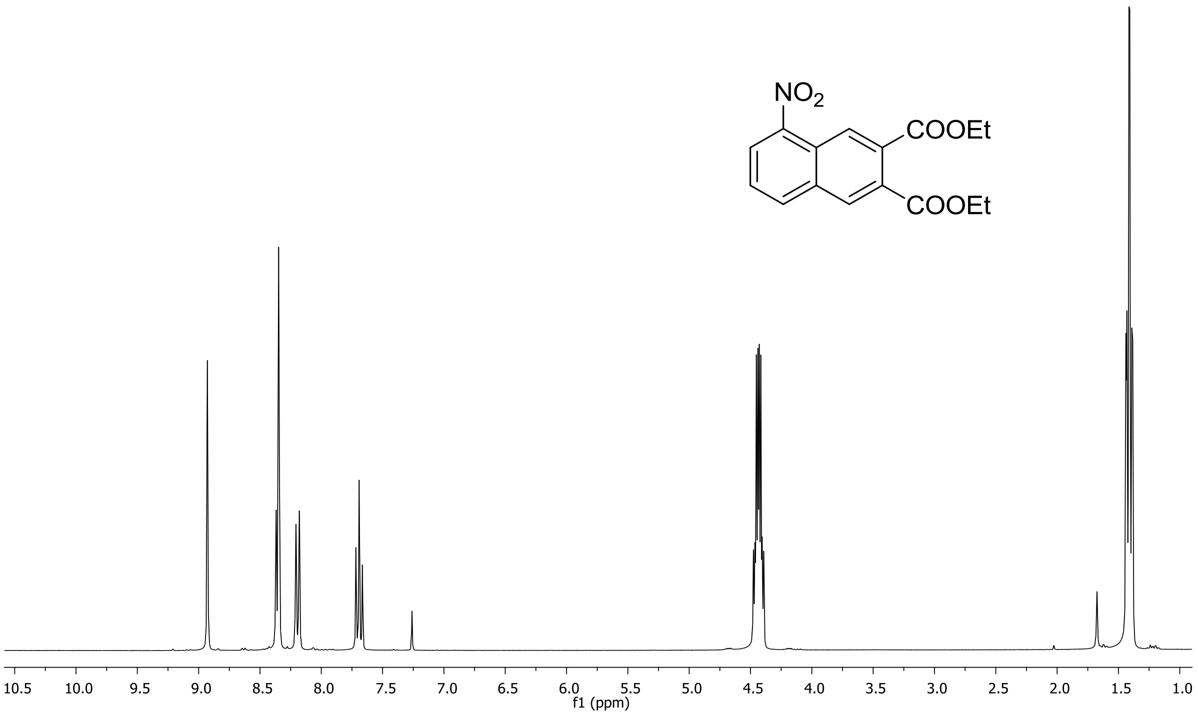


Figure S5-a: ^{1}H NMR spectrum of diethyl 5-nitronaphthalene-2,3-dicarboxylate (**9**).

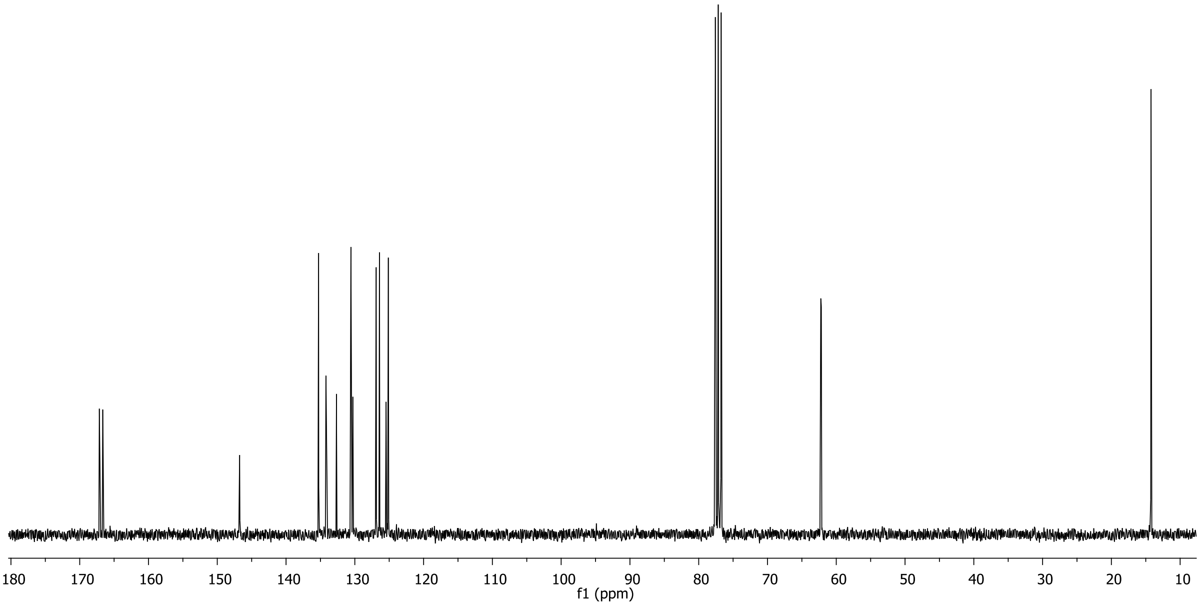


Figure S5-b: ^{13}C NMR spectrum of diethyl 5-nitronaphthalene-2,3-dicarboxylate (**9**).

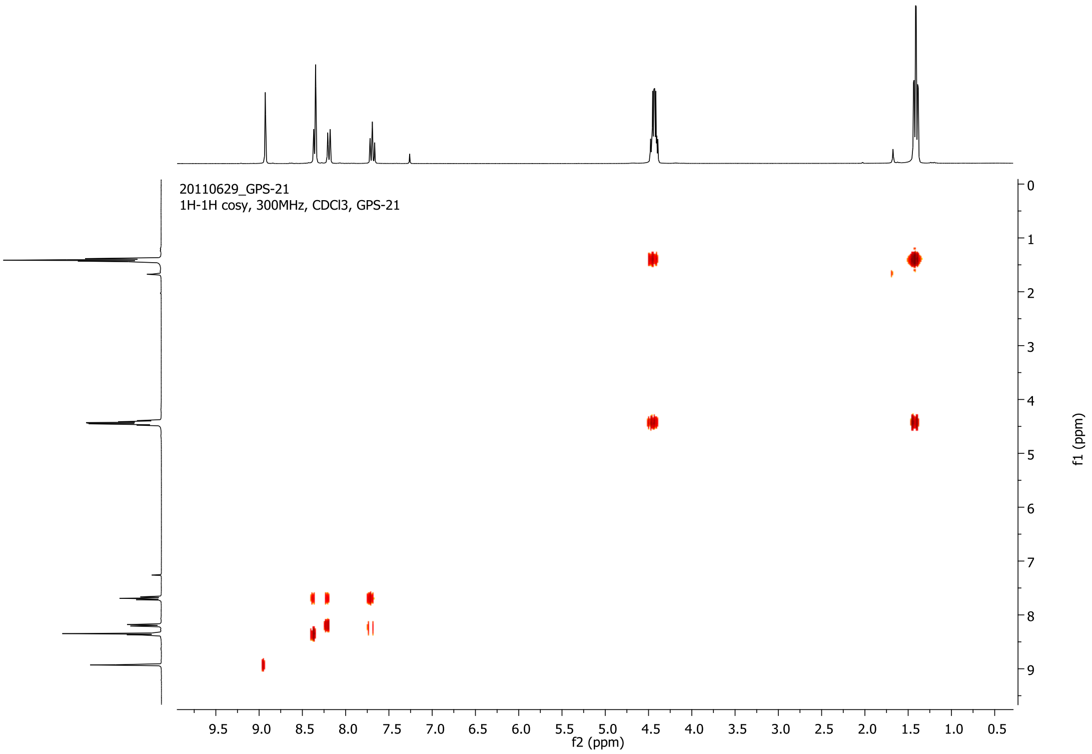


Figure S5-c: ^{1}H-^{1}H COSY NMR correlation spectrum of diethyl 5-nitronaphthalene-2,3-dicarboxylate (**9**).

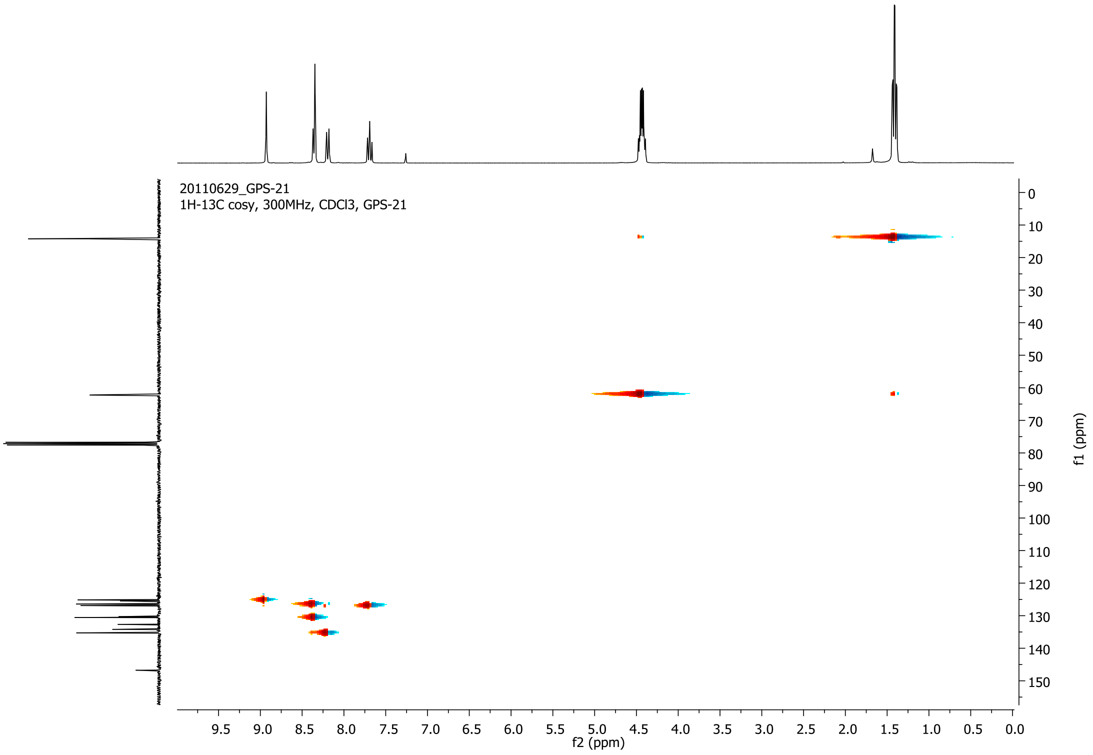


Figure S5-d: ^{1}H-^{13}C COSY NMR correlation spectrum of diethyl 5-nitronaphthalene-2,3-dicarboxylate (**9**).

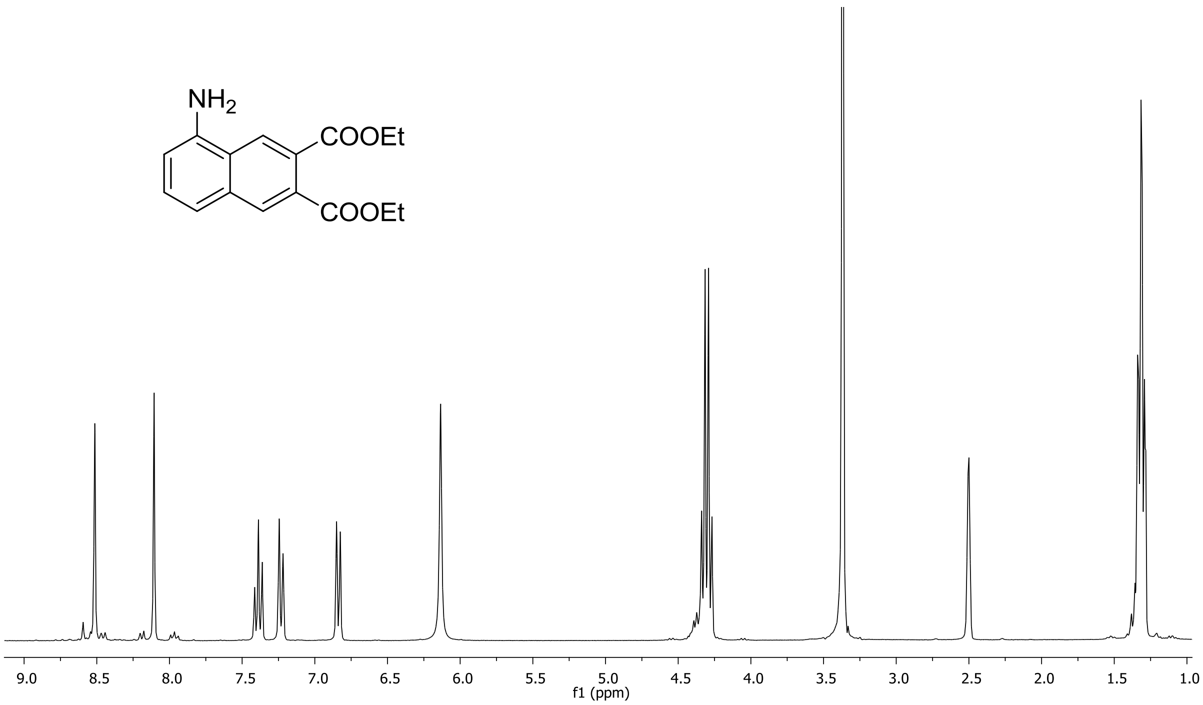


Figure S6-a: ^{1}H NMR spectrum of diethyl 5-aminonaphthalene-2,3-dicarboxylate (**10**).

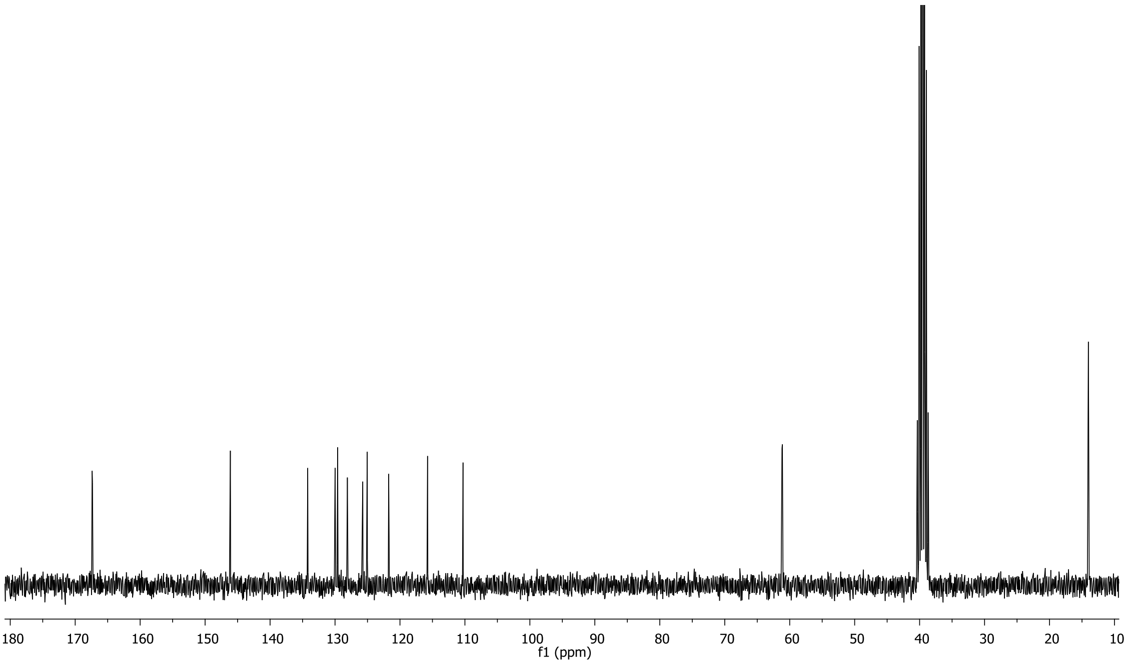


Figure S6-b: ^{13}C NMR spectrum of diethyl 5-aminonaphthalene-2,3-dicarboxylate (**10**).

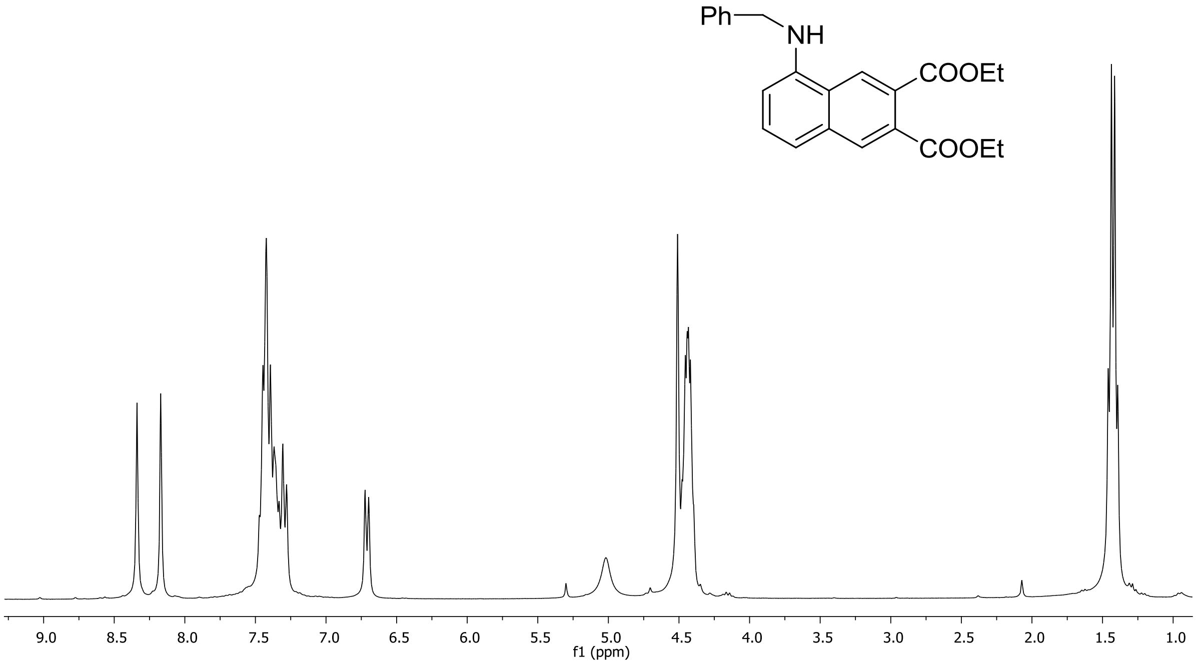


Figure S7-a: ^{1}H NMR spectrum of diethyl 5-(benzylamino)naphthalene-2,3-dicarboxylate (**11**).

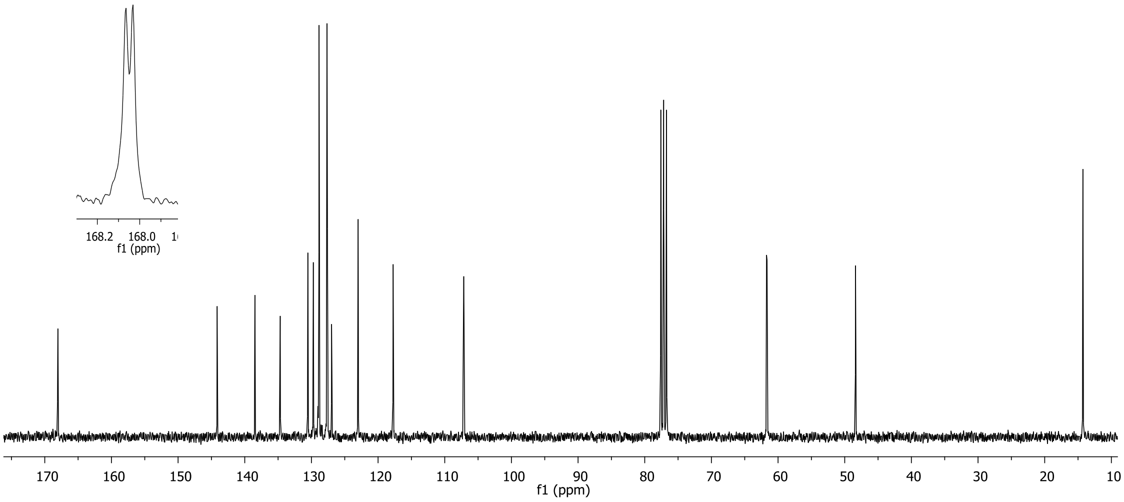


Figure S7-b: ^{13}C NMR spectrum of diethyl 5-(benzylamino)naphthalene-2,3-dicarboxylate (**11**).

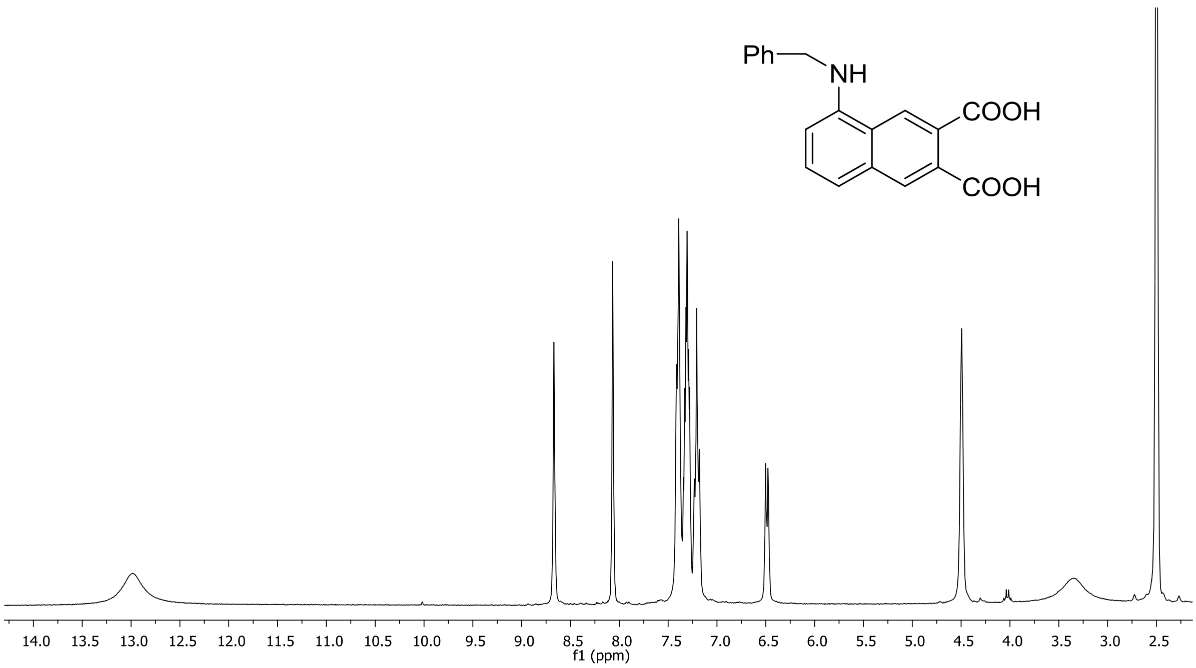


Figure S8-a: ^{1}H NMR spectrum of 5-(benzylamino)naphthalene-2,3-dicarboxylic acid (**13**).

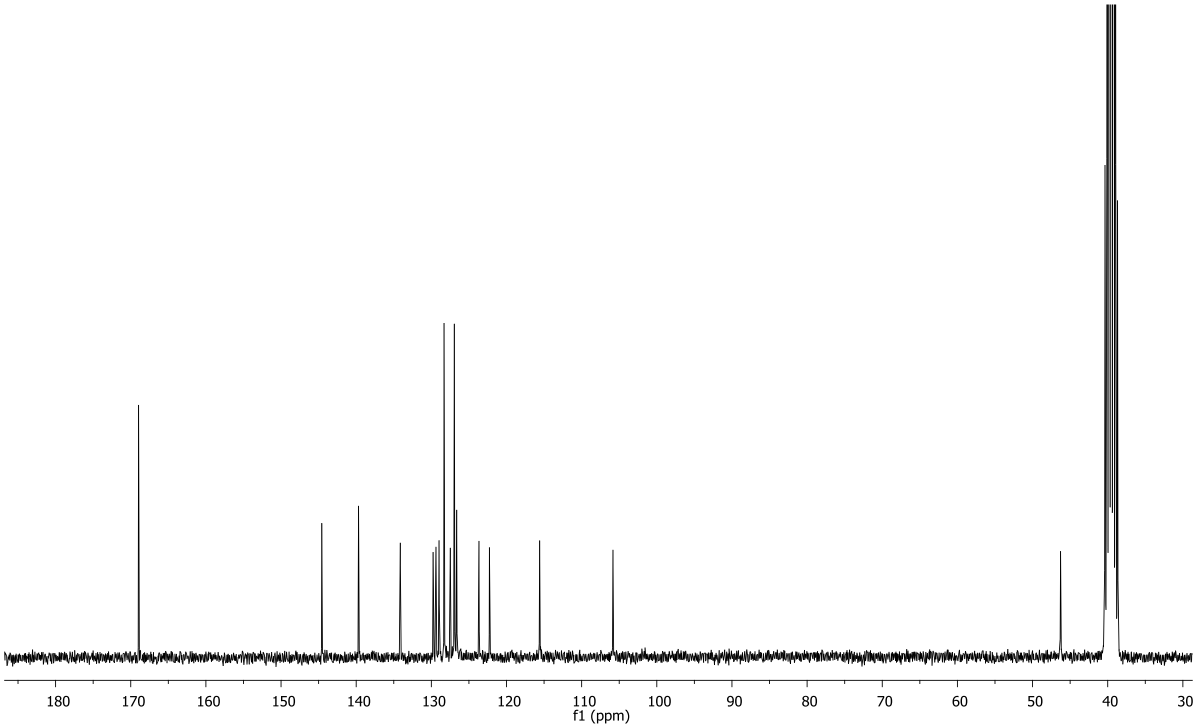


Figure S8-b: ^{13}C NMR spectrum of 5-(benzylamino)naphthalene-2,3-dicarboxylic acid (**13**).

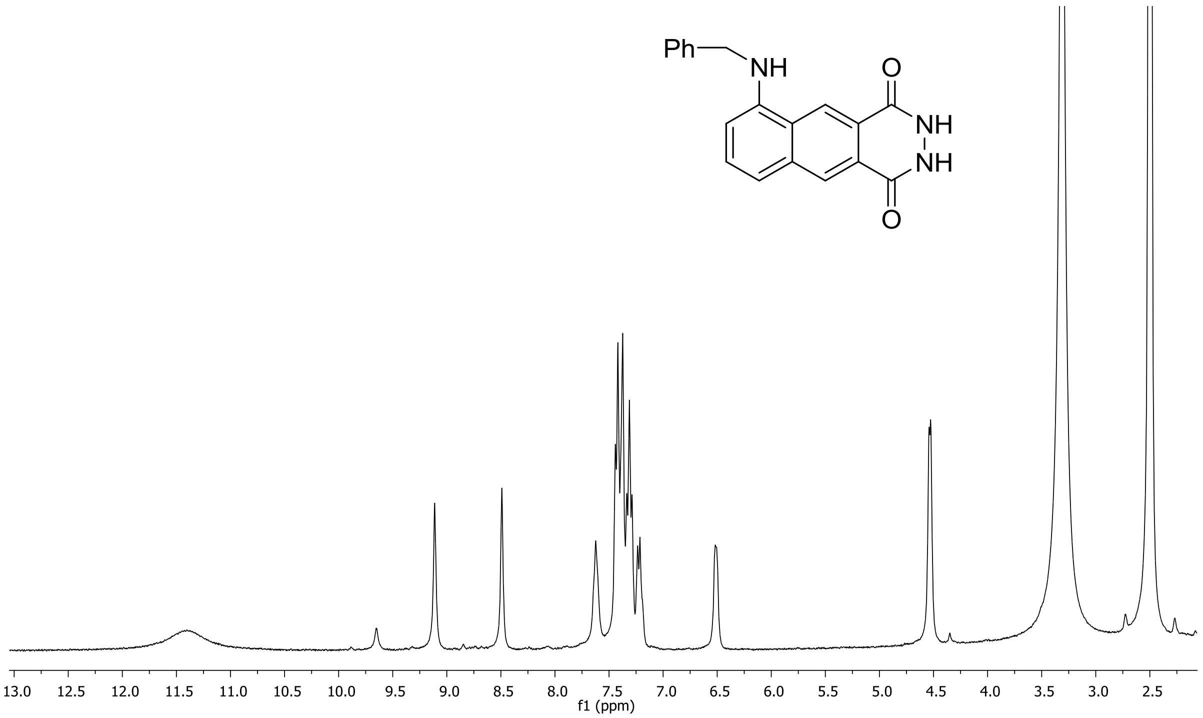


Figure S9-a: ^{1}H NMR spectrum of 6-(benzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**2**).

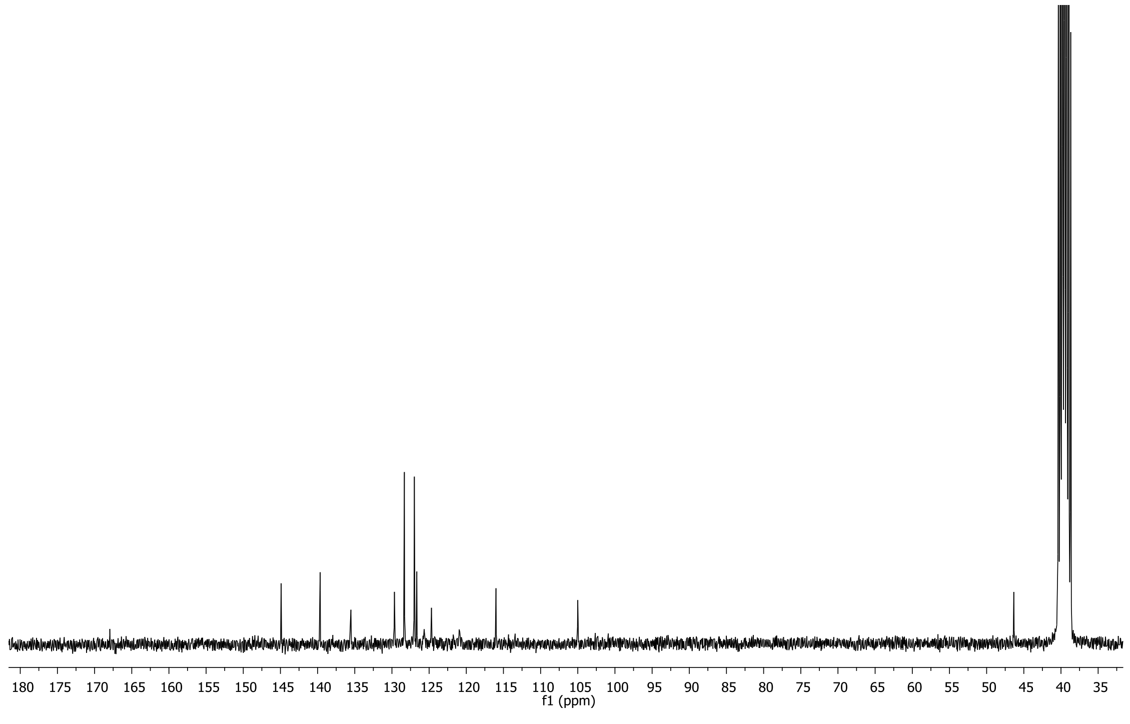


Figure S9-b: ^{13}C NMR spectrum of 6-(benzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**2**).

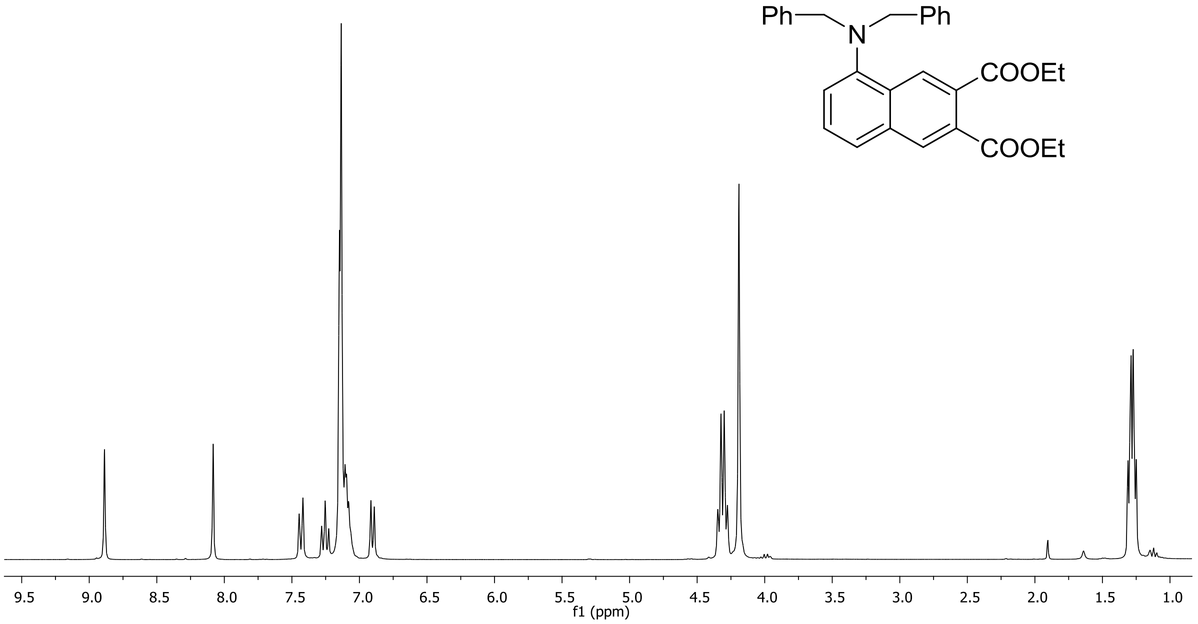


Figure S10-a: ^{1}H NMR spectrum of diethyl 5-(dibenzylamino)naphthalene-2,3-dicarboxylate (**12**).

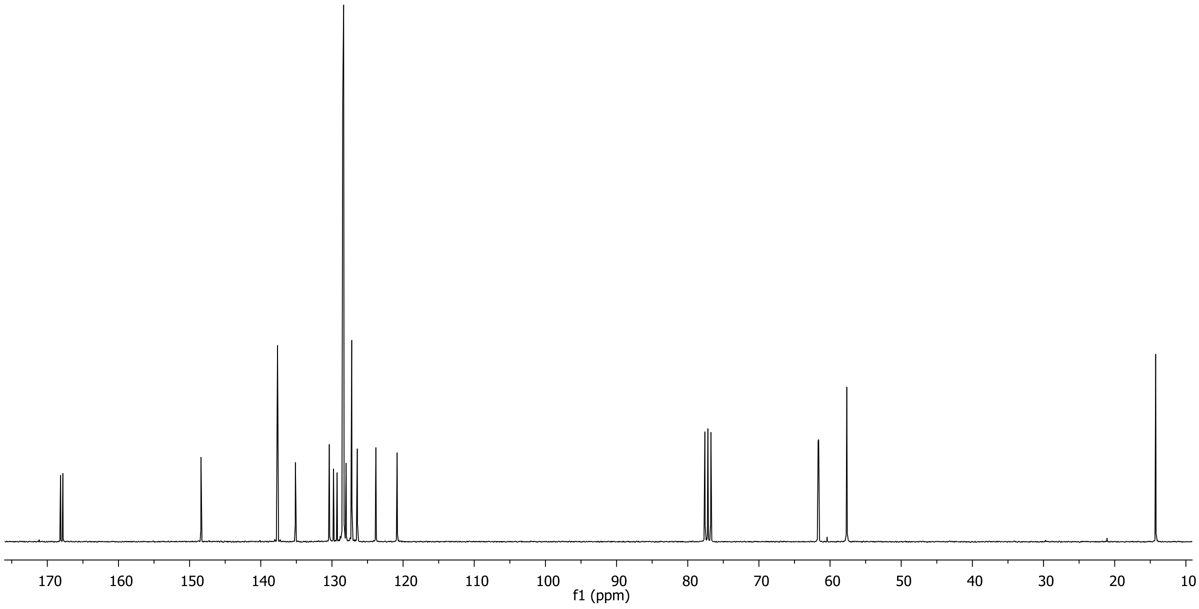


Figure S10-b: ^{13}C NMR spectrum of diethyl 5-(dibenzylamino)naphthalene-2,3-dicarboxylate (**12**).

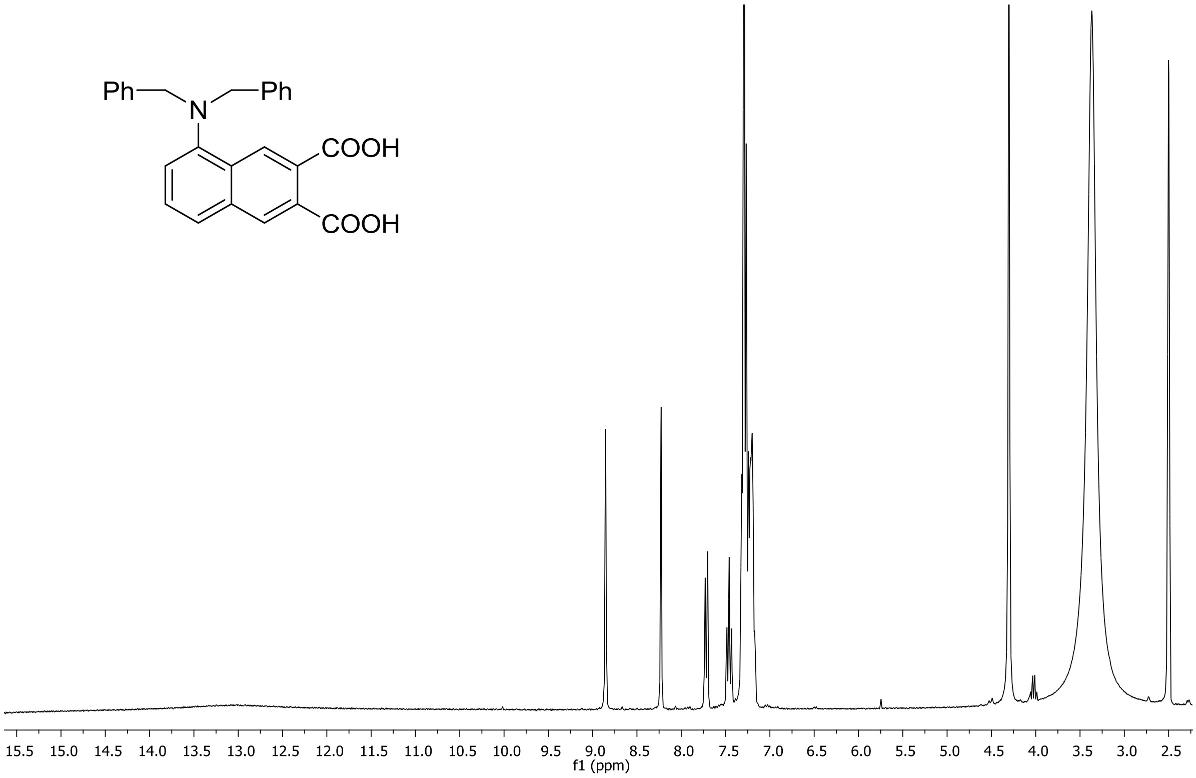


Figure S11-a: ^{1}H NMR spectrum of 5-(dibenzylamino)naphthalene-2,3-dicarboxylic acid (**14**).

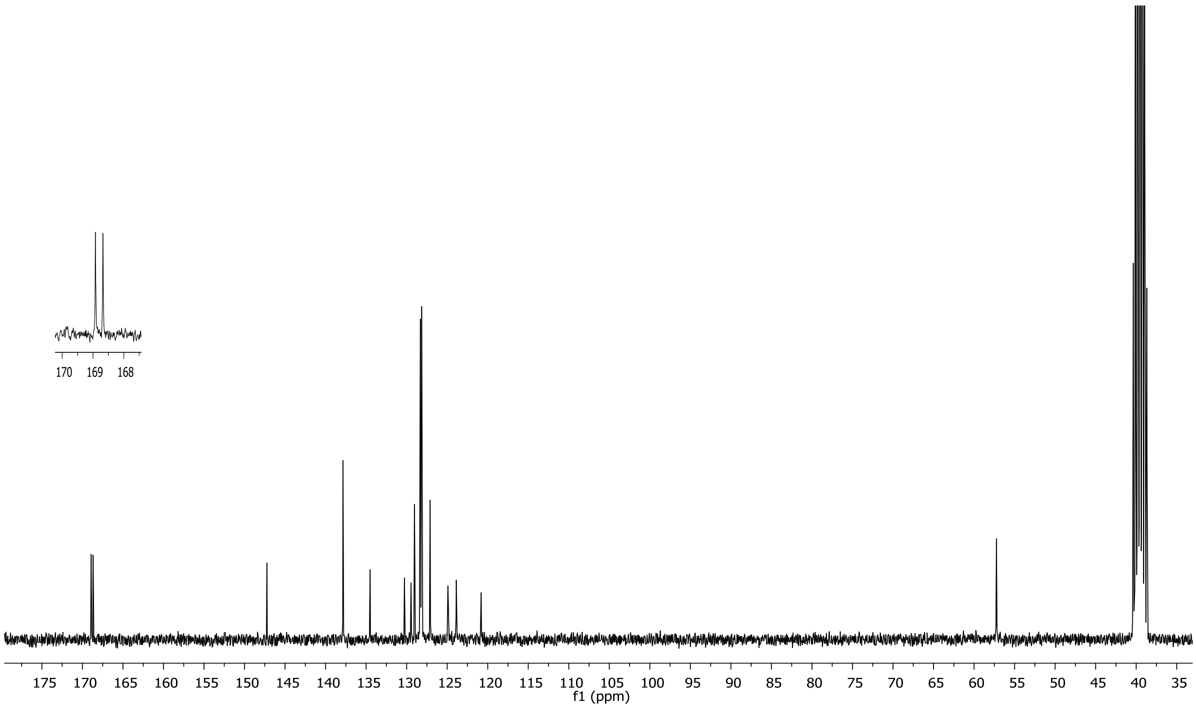


Figure S11-b: ^{13}C NMR spectrum of 5-(dibenzylamino)naphthalene-2,3-dicarboxylic acid (**14**).

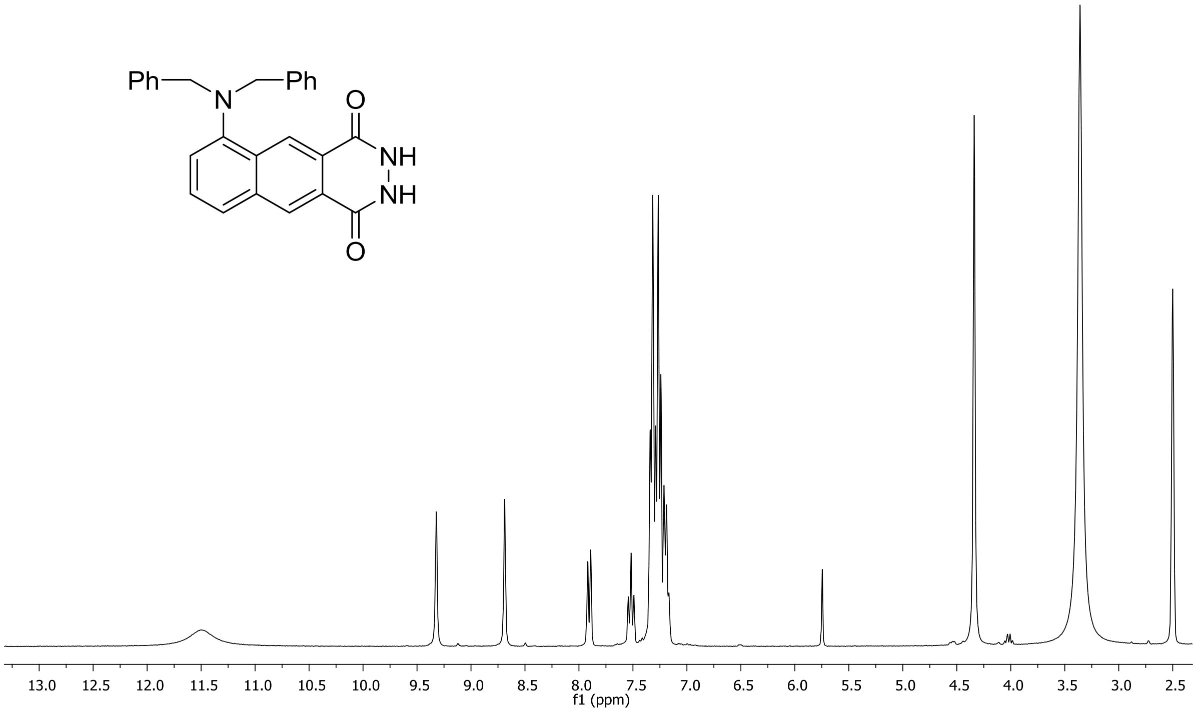


Figure S12-a: ^{1}H NMR spectrum of 6-(dibenzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**3**).

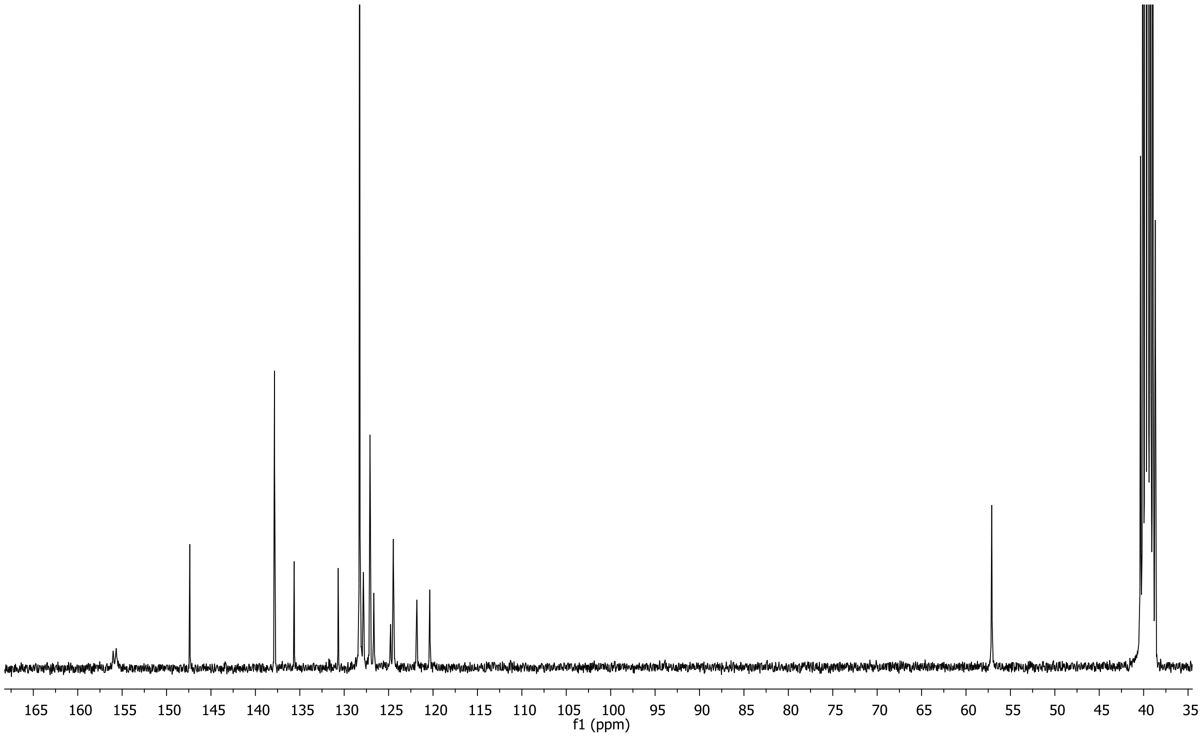


Figure S12-b: ^{13}C NMR spectrum of 6-(dibenzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**3**).

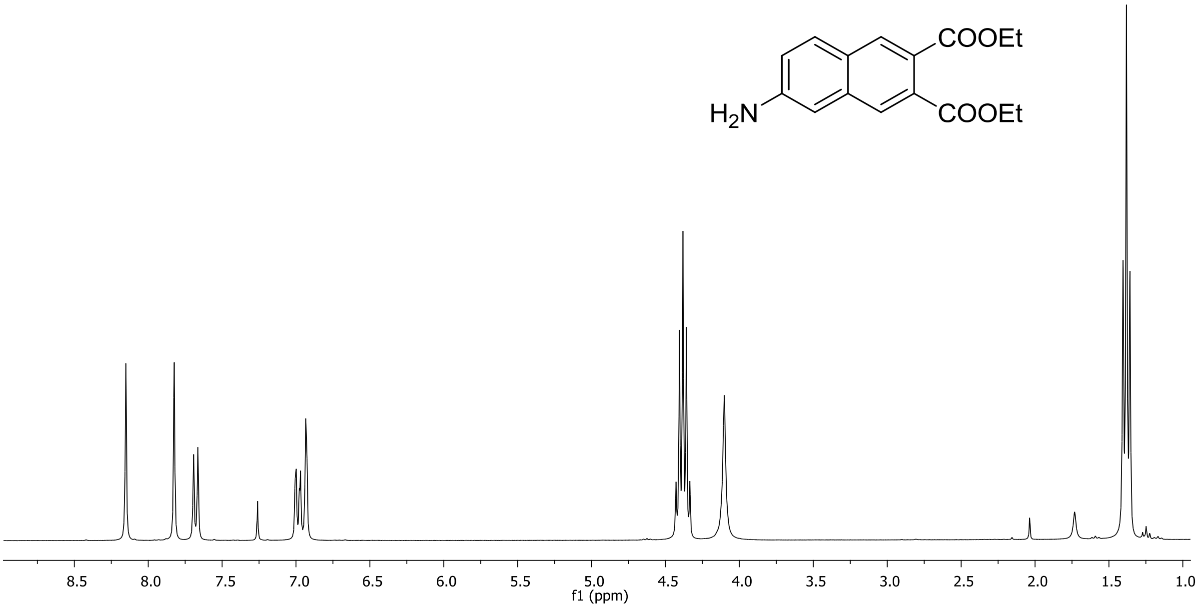


Figure S13-a: ^{1}H NMR spectrum of diethyl 6-aminonaphthalene-2,3-dicarboxylate (**16**).

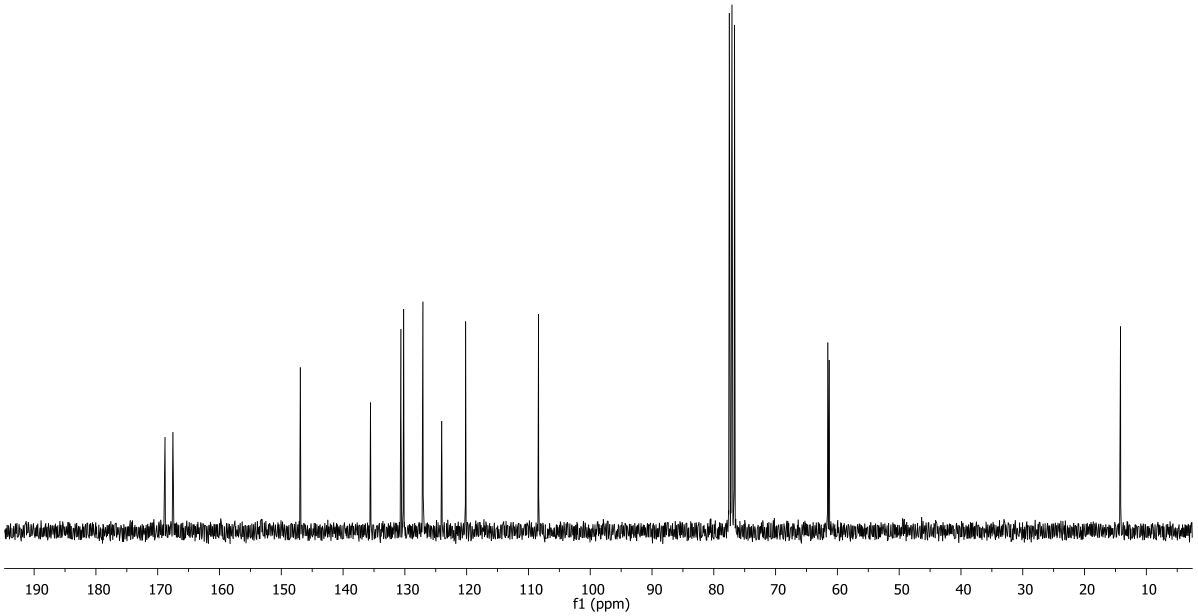


Figure S13-b: ^{13}C NMR spectrum of diethyl 6-aminonaphthalene-2,3-dicarboxylate (**16**).

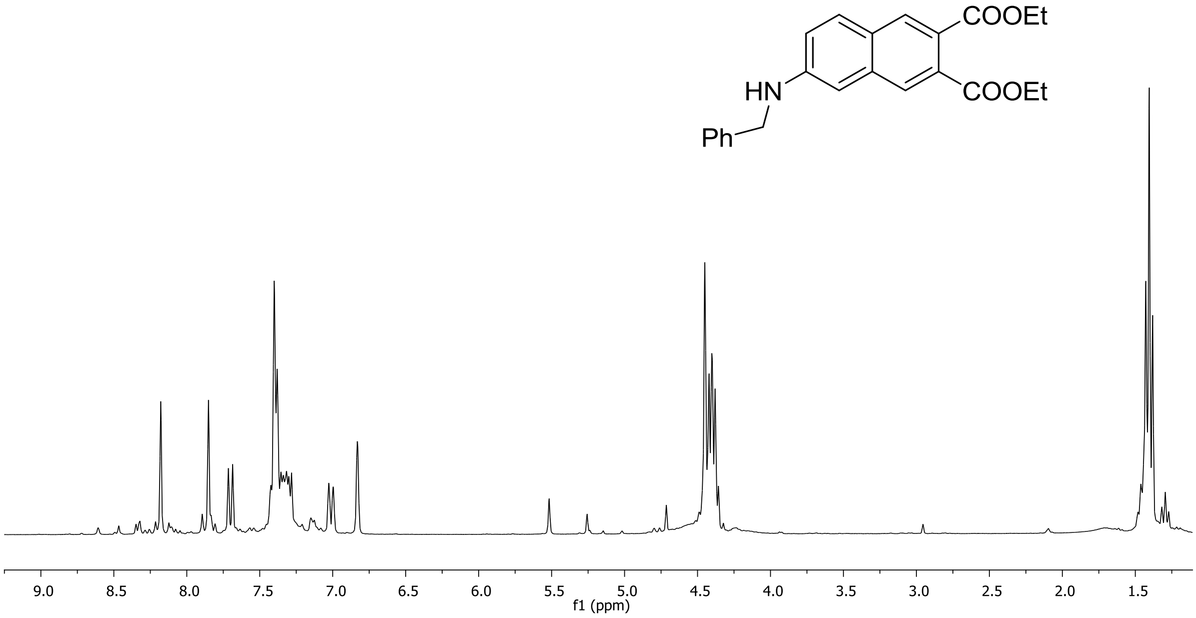


Figure S14-a: ^{1}H NMR spectrum of diethyl 6-(benzylamino)naphthalene-2,3-dicarboxylate (**17**).

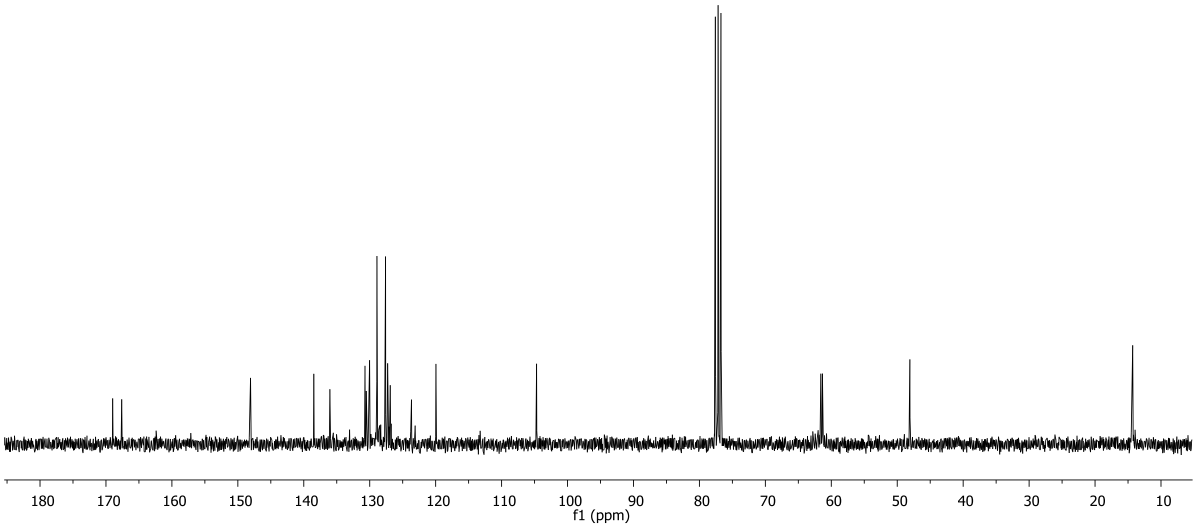


Figure S14-b: ^{13}C NMR spectrum of diethyl 6-(benzylamino)naphthalene-2,3-dicarboxylate (**17**).

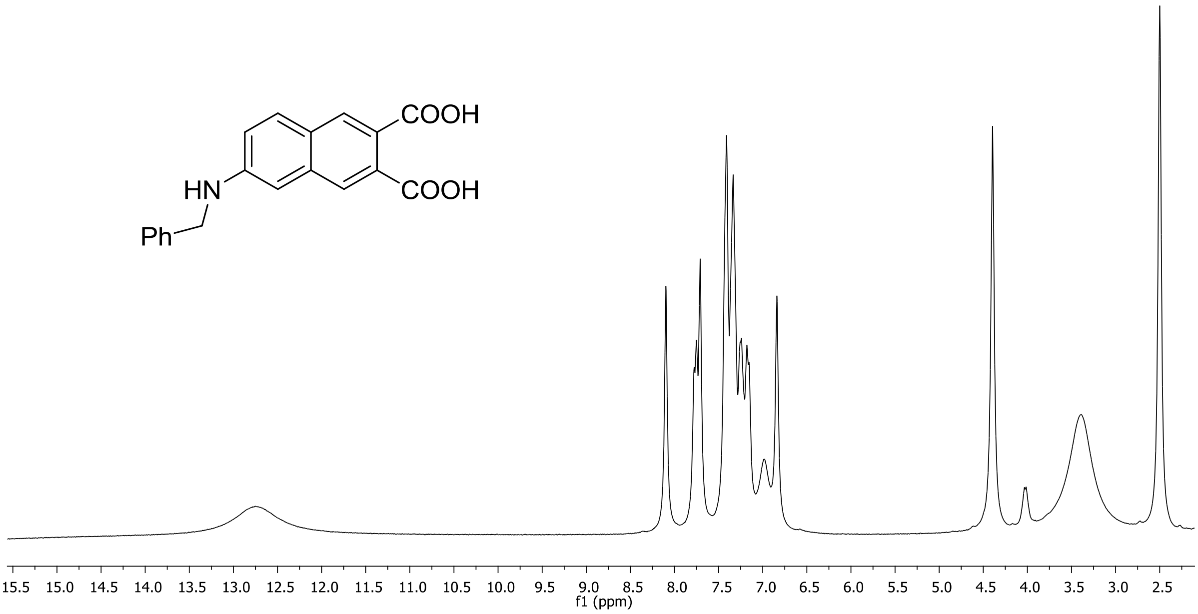


Figure S15-a: ^{1}H NMR spectrum of 6-(benzylamino)naphthalene-2,3-dicarboxylic acid (**19**).

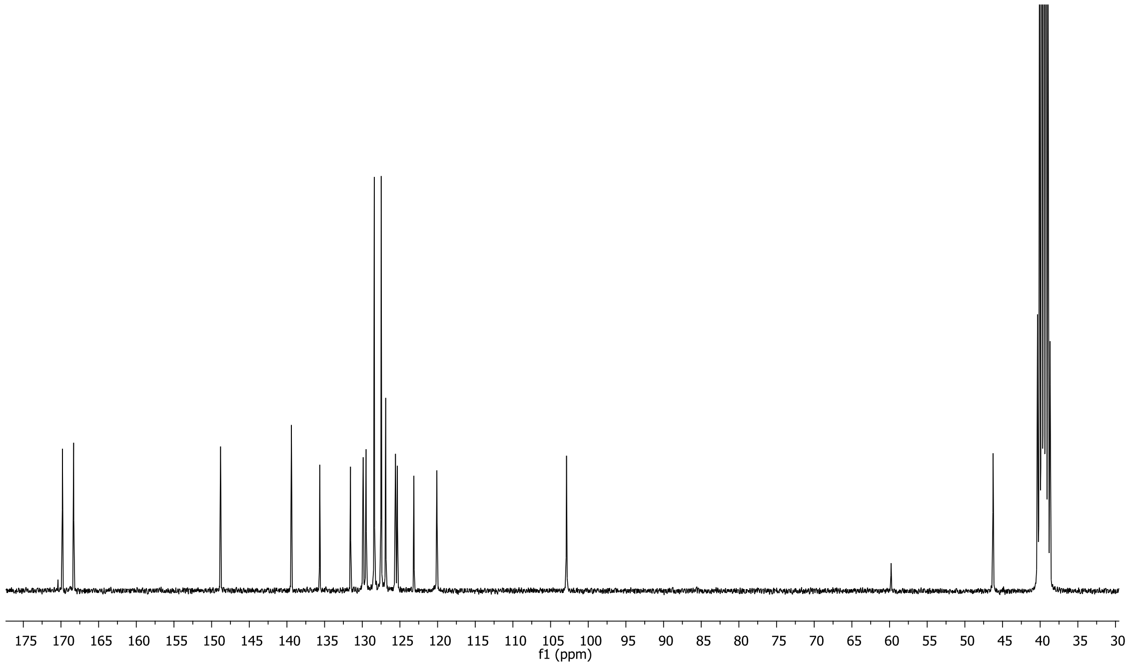


Figure S15-b: ^{13}C NMR spectrum of 6-(benzylamino)naphthalene-2,3-dicarboxylic acid (**19**).

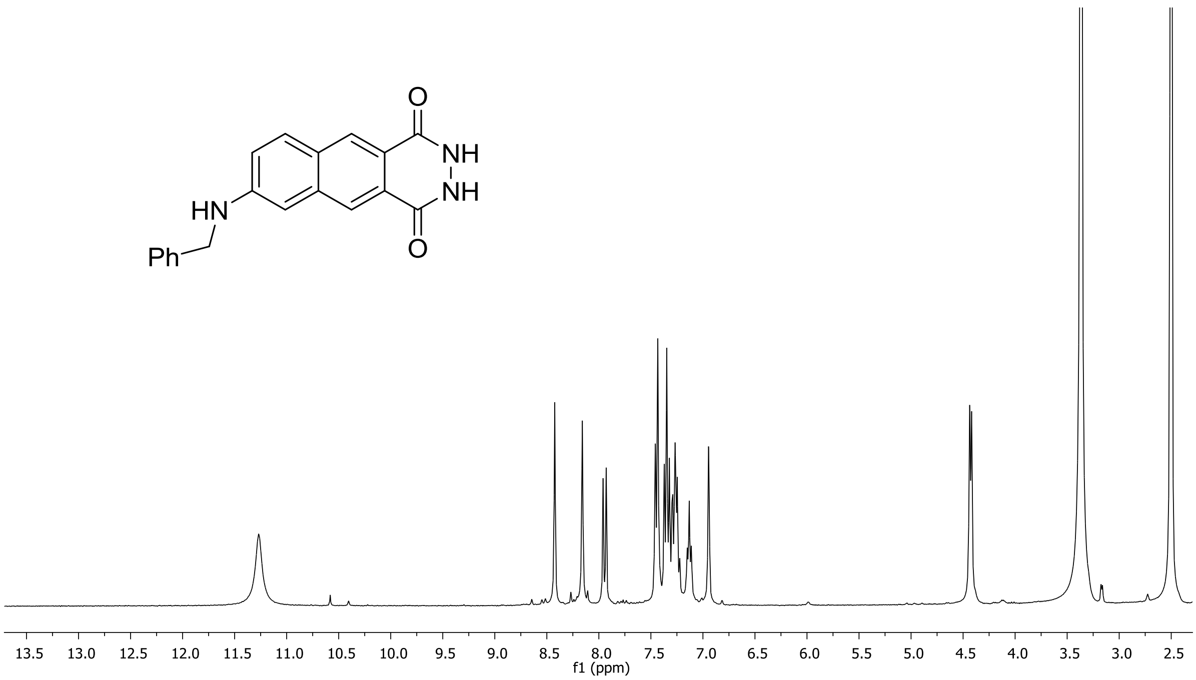


Figure S16-a: ^{1}H NMR spectrum of 7-(benzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**4**).

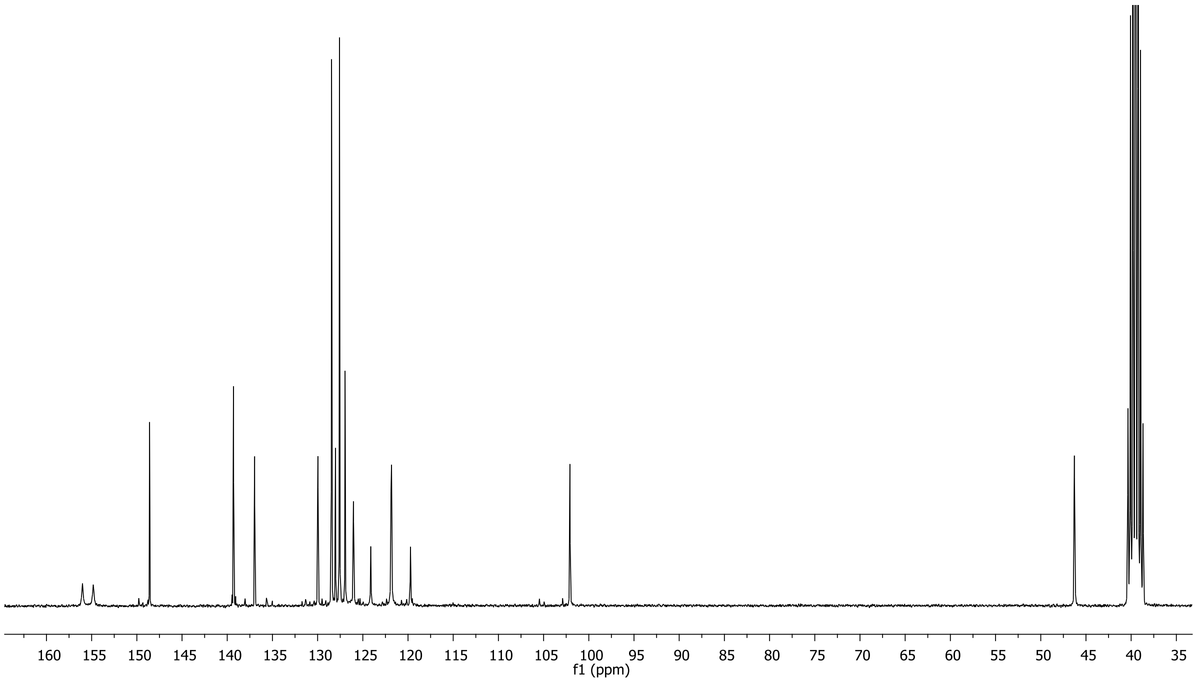


Figure S16-b: ^{13}C NMR spectrum of 7-(benzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**4**).

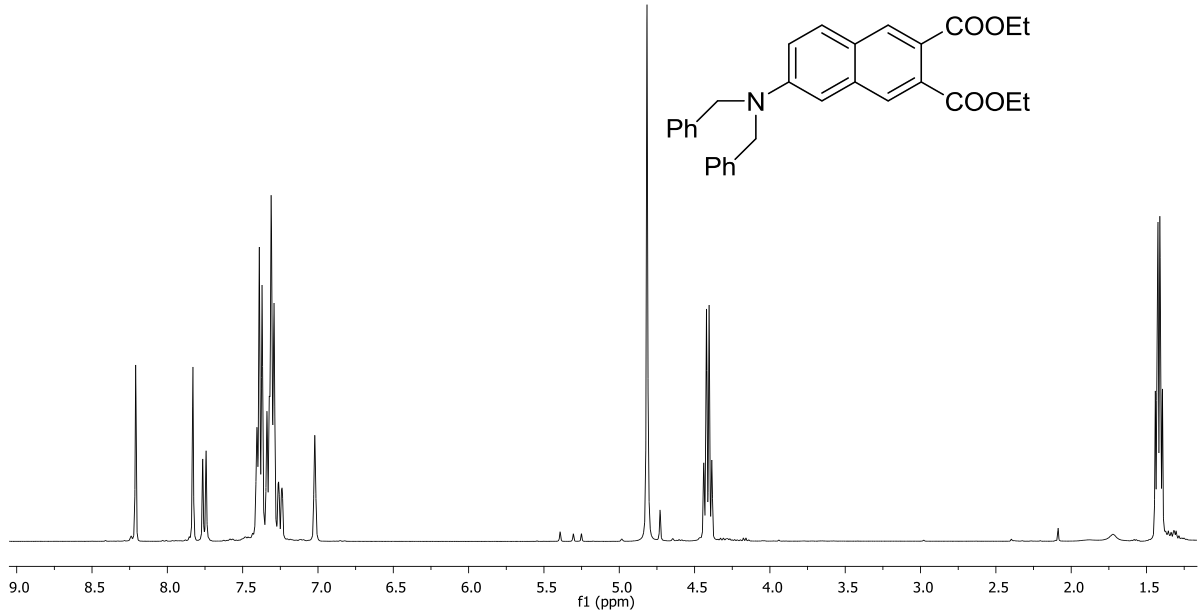


Figure S17-a: ^{1}H NMR spectrum of diethyl 6-(dibenzylamino)naphthalene-2,3-dicarboxylate (**18**).

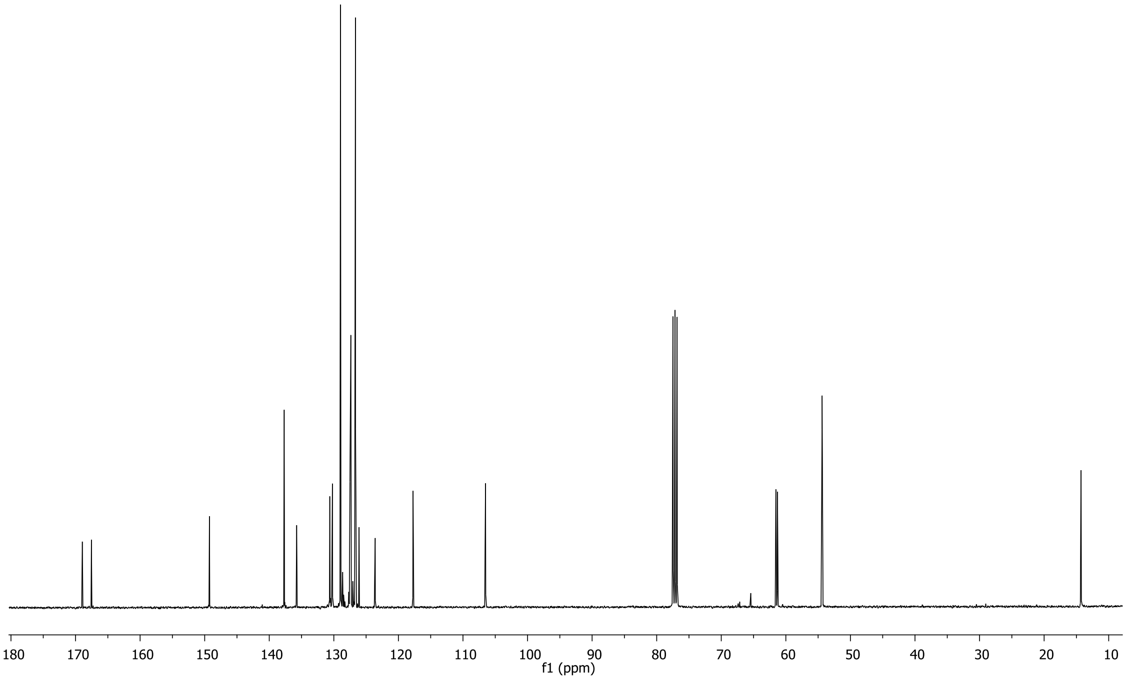


Figure S17-b: ^{13}C NMR spectrum of diethyl 6-(dibenzylamino)naphthalene-2,3-dicarboxylate (**18**).

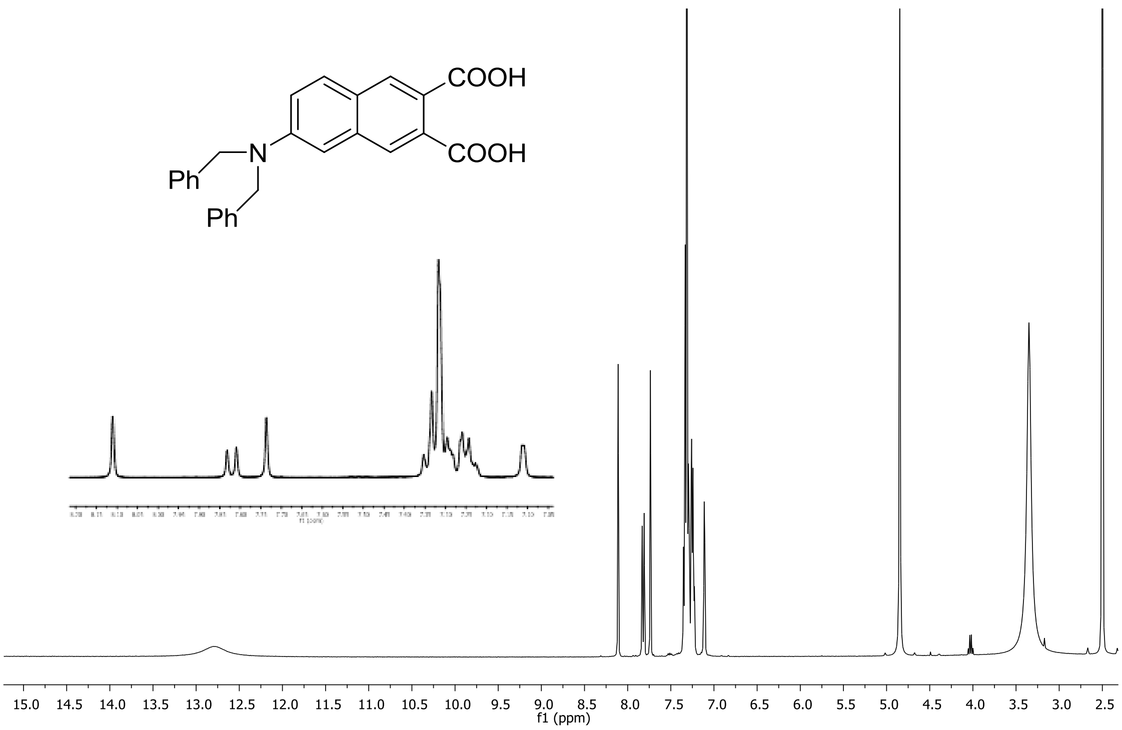


Figure S18-a: ^{1}H NMR spectrum of 6-(dibenzylamino)naphthalene-2,3-dicarboxylic acid (**20**).

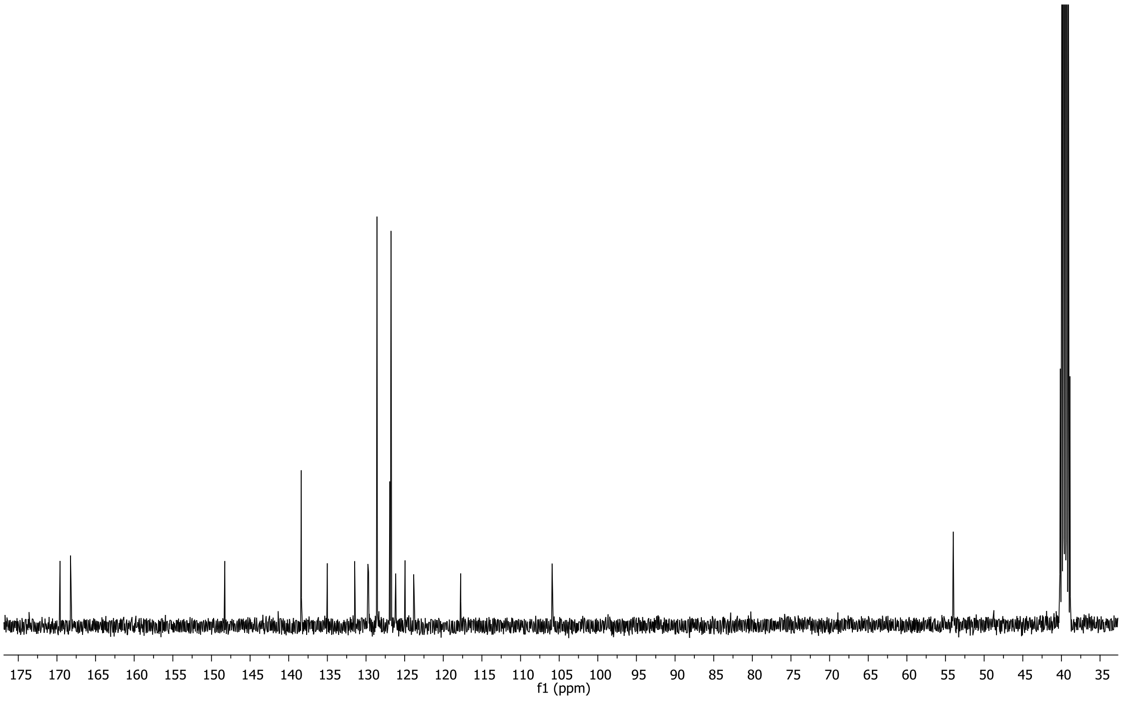


Figure S18-b: ^{13}C NMR spectrum of 6-(dibenzylamino)naphthalene-2,3-dicarboxylic acid (**20**).

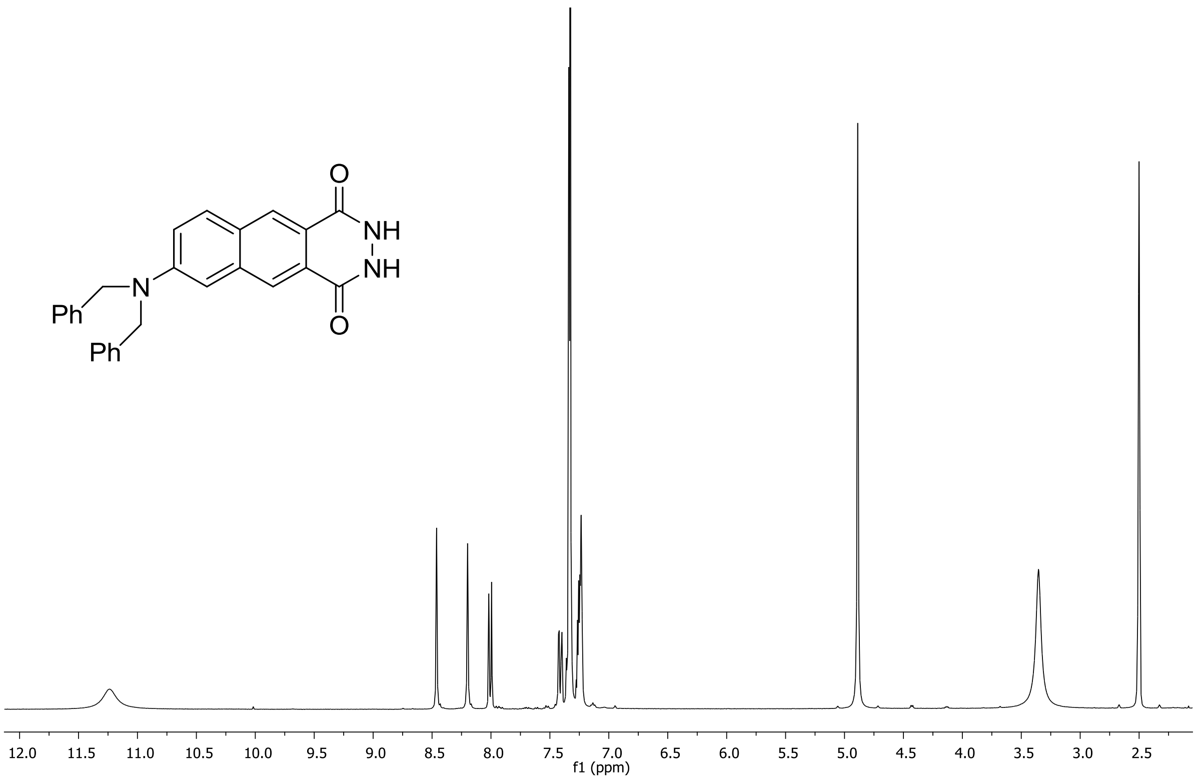


Figure S19-a: ^{1}H NMR spectrum of 7-(dibenzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**5**).

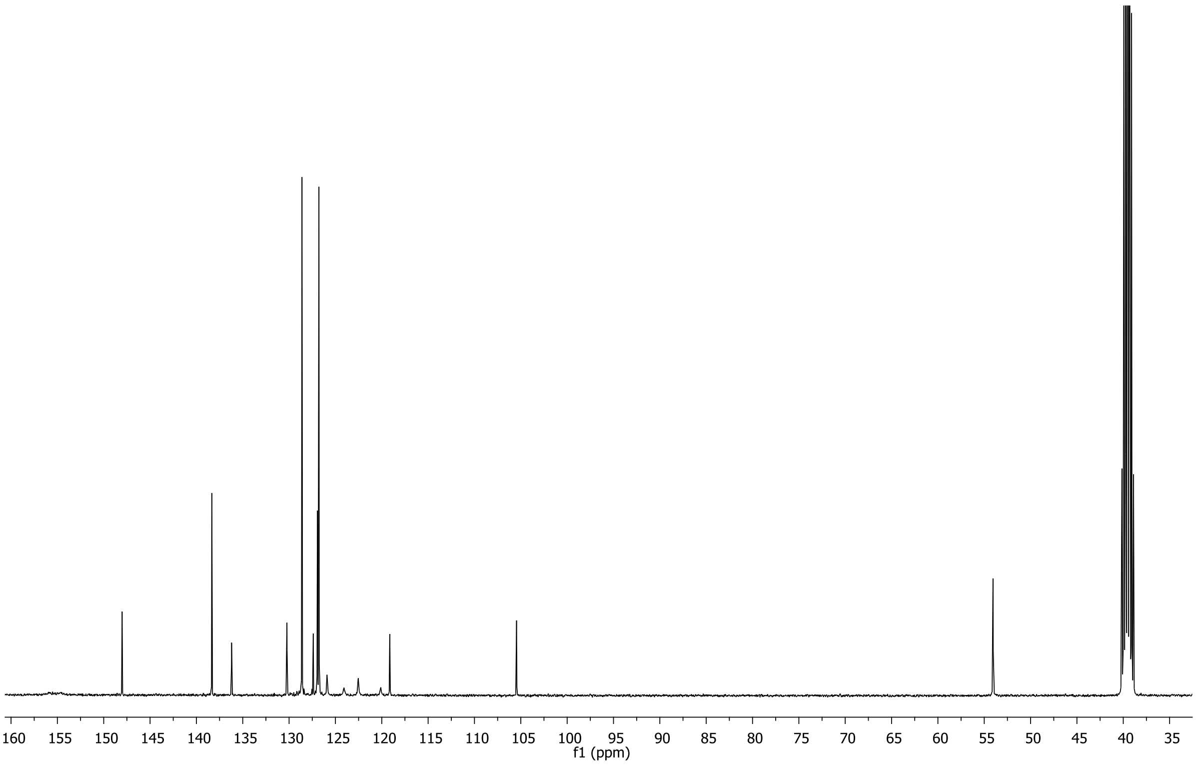


Figure S19-b: ^{13}C NMR spectrum of 7-(dibenzylamino)-2,3-dihydrobenzo[g]phthalazine-1,4-dione (**5**).