

Supporting Information for:

Sequential Diels-Alder Reaction of *in situ* Generated 2,3-dimethylene Pyrrole and Carbodienophiles: The Rapid Synthesis of 2,3,6,7-Tetrasubstituted Carbazoles.

Jeffrey T. Vessels, Slawomir Z. Janicki and Peter A. Petillo

*Roger Adams Laboratory, Department of Chemistry, University of Illinois
Urbana, IL 61801*

Submitted to *Organic Letters*

Address correspondence to:

Professor Peter A. Petillo
261 Roger Adams Laboratory, Box 43
Department of Chemistry
University of Illinois
600 South Matthews Avenue
Urbana, IL 61801

Tel no: (217) 333-0695

FAX no: (217) 244-8559

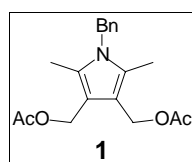
E-Mail: alchmist@alchmist.scs.uiuc.edu

Experimental

General Methods. Varian Unity-400, Varian Unity-500, or a Varian Inova-500 FT NMR spectrometers was utilized for ^1H and ^{13}C NMR spectra. Proton and carbon chemical shifts are reported in delta (δ) units, parts per million (ppm) referenced to residual solvent, CDCl_3 (7.27 ppm ^1H , 77.23 ppm ^{13}C), and DMSO-d_6 (2.50 ppm ^1H , 39.51 ppm ^{13}C). Mass spectra were obtained by the University of Illinois Mass Spectrometry Center either on a 70-VSE for high- and low-resolution electron impact (EI), a ZAB-SE for low-resolution fast atom bombardment (FAB), or a 70-SE-4F for high-resolution FAB.

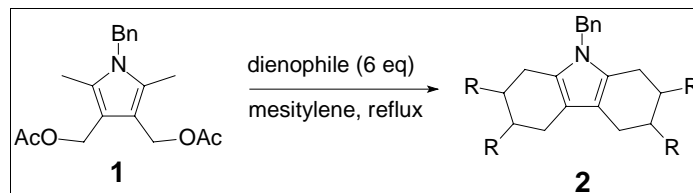
Analytical thin-layer chromatography was performed using Merck silica gel 60 F_{254} precoated plates with a fluorescent indicator. Visualization was achieved using UV light, iodine, or phosphomolybdic acid dip. Flash column chromatography was performed using 230-400 mesh silica gel from Merck. All chromatography solvents were ACS reagent grade except THF, which was Fisher's Optima grade.

All reactions were performed in oven dried flasks cooled under vacuum (0.2 torr). Reflux condensers were flame dried and cooled under vacuum (0.2 torr). Unless other wise noted, all reactions were performed under Ar atmosphere. The reaction solvents (1,4 dioxane, mesitylene, and toluene) were distilled from Na° under N_2 .

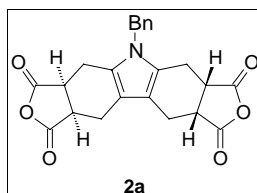


1-Benzyl-2,5-dimethyl-3,4-bisacetoxymethylpyrrole (1). Dry pyridine (3.4 mL, 42 mmol), acetic anhydride (4.0 mL, 42 mmol) and a few crystals of 4-dimethylaminopyridine were added to a solution of **5** (2.58 g, 11 mmol) in dry methylene chloride (50 mL) under N_2 . The mixture was stirred at rt for 20 h, quenched with water (50 mL) and stirred at rt for 15 min. The layers were separated, the aqueous layer was washed with methylene chloride (10 mL), and the combined organic layers were dried (MgSO_4) and

concentrated *in vacuo*. The crude residue (3.4 g) was recrystallized from ethyl acetate/hexane mixture to afford 2.93 g (9 mmol, 85% yield) of **1** as large off-white crystals. *The product is sensitive to acids stronger than acetic acid.* mp 113-114 °C. ¹H NMR (400 MHz, CDCl₃) 2.05 (s, 6 H), 2.15 (s, 6 H), 5.01 (s, 2 H), 5.06 (s, 4 H), 6.85-6.90 (m, 2 H), 7.18-7.29 (m, 3 H). ¹³C NMR (100 MHz, CDCl₃) 9.6, 46.8, 56.0, 118.0, 125.5, 125.5, 127.0, 128.7, 137.9.



General procedure for **9a-j**: A solution of **1** (50 mg, 0.151 mmol) and dienophile (0.81 mmol, free of acid) in mesitylene (4 mL, distilled from Na^o) was refluxed in a dry round bottom flask fitted with an air cooled reflux condenser under Ar for 45 min to 25 h. The solution was cooled, and the solvent was removed *in vacuo*.

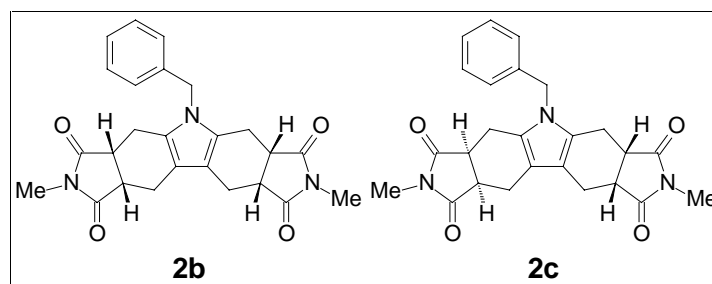


9-benzyl-cis-2,3;cis-6,7-trans-2,7;trans-3,6-1,2,3,4,5,6,7,8-octahydrocarbazole-tetracarboxylic acid

3,4;6,7-dianhydride (2a) A solution of **1** (52 mg, 0.158 mmol) and acid free maleic anhydride (91 mg, 0.93 mmol freshly recrystallized from dry CH₂Cl₂) in mesitylene (4 mL) was refluxed under Ar for 2 h.

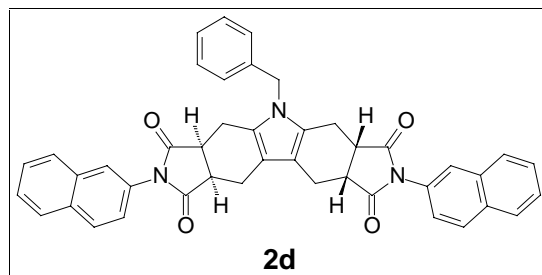
The solvent was removed *in vacuo* to afford a yellow solid, which was triturated with CH₂Cl₂ (2 x 2 mL) to afford 58 mg (0.141 mmol, 90%) of **2a** as an off-white solid. mp 254-256 °C with decomp. ¹H NMR (399.95 MHz, DMSO-d₆) 2.65 (dd, *J* = 15.3, 7.49 Hz; 2H), 2.70 (dd, *J* = 15.82, 7.86 Hz; 2H), 2.82 (dd, *J* = 15.3, 2.18 Hz; 2H), 2.95 (dd, *J* = 15.82, 1.91 Hz; 2H), 3.66 (ddABq, *J* = 9.86, 7.49, 2.18 Hz; 2H), 3.73 (ddABq, *J* = 9.86, 7.86, 1.91 Hz; 2 H), 4.95 (ABq, *J* = 16.77 Hz, 1H), 5.08 (ABq, *J* = 16.77 Hz, 1H), 6.88-

6.93 (m, 2 H), 7.20-7.32 (m, 3 H). ^{13}C NMR (100.58 MHz, DMSO- d_6) 20.47, 20.68, 40.20, 40.39, 45.82, 111.79, 124.25, 126.28, 127.20, 128.60, 138.29, 175.39, 175.57. MS (EI, 70 eV) exact mass calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_6$ 405.1204, found 405.1212.

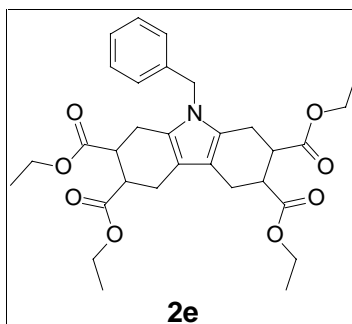


Bis-N-methyl 9-benzyl-*cis*-2,3;*cis*-6,7-*trans*-2,7;*trans*-3,6-1,2,3,4,5,6,7,8-octahydrocarbazole-2,3,6,7-tetracarboxylic acid 2,3;6,7-diimide (2b) and **bis-N-methyl 9-benzyl-*cis*-2,3;*cis*-6,7-*cis*-2,7;*cis*-3,6-1,2,3,4,5,6,7,8-octahydrocarbazole-2,3,6,7-tetracarboxylic acid 2,3;6,7-diimide (2c)** A solution of **1** (100 mg, 0.304 mmol) and N-methylmaleimide (205 mg, 1.86 mmol) in mesitylene (8 mL) was refluxed under Ar for 2 h. The solvent was removed *in vacuo* affording a brown solid, which was purified by flash chromatography (SiO_2 , CHCl_3 :EtOAc, 1:1) to afford 34 mg (0.08 mmol, 25%, $R_f = 0.42$) of **2b** as a light yellow solid. mp 214-245 °C. ^1H NMR (499.70, CHCl_3) 2.73 (ABCDEF, $J_{AB} = 15.5$ Hz, $J_{AC} = 7.8$ Hz; 2H), 2.74 (ABCDEF, $J_{FE} = 16.2$ Hz, $J_{FD} = 8.7$ Hz; 2H), 2.87 (s, 6H), 2.94 (ABCDE, $J_{BA} = 15.5$ Hz, $J_{BC} = 3.0$ Hz; 2H), 2.98 (ABCDEF, $J_{EF} = 16.2$ Hz, $J_{ED} = 3.0$ Hz; 2H), 3.19 (ABCDEF, $J_{CD} = 9.55$ Hz, $J_{CA} = 8.0$ Hz, $J_{CB} = 2.5$ Hz; 2H), 3.20 (ABCDEF, $J_{DC} = 9.55$ Hz, $J_{DF} = 8.0$, $J_{DE} = 2.6$ Hz; 2H), 4.93 (s, 2H), 6.81-6.82 (m, 2H), 7.21-7.28 (m, 3H). ^{13}C NMR (125.66 MHz, CDCl_3) 20.93, 21.27, 25.14, 40.08, 40.38, 46.73, 112.79, 124.60, 126.15, 127.64, 128.98, 138.10, 179.97, 180.02. MS (EI, 70 eV) exact mass calcd for $\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_4$ 431.1845, found 431.1842. Compound **2c** 69 mg (0.16 mmol, 52%, $R_f = 0.49$) was obtained as a light yellow solid. mp 142-150 °C. ^1H NMR (500.08 MHz, CHCl_3) 2.67 (ABCDEF, $J_{AB} = 13.7$ Hz, $J_{AC} = 8.0$ Hz; 2H), 2.69 (ABCDEF, $J_{FE} = 13.2$ Hz, $J_{FD} = 8.0$ Hz; 2H), 2.94 (s, 6H), 3.12 (ABCDEF, $J_{BA} = 13.7$ Hz, J_{BC}

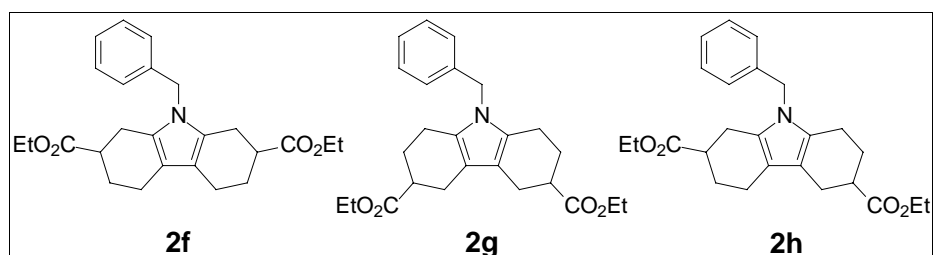
= 2.5 Hz; 2H), 3.15 (ABCDEF, $J_{EF} = 13.2$ Hz, $J_{ED} = 2.6$ Hz; 2H), 3.27 (ABCDEF, $J_{CD} = 8.7$ Hz, $J_{CA} = 8.0$ Hz, $J_{CB} = 2.5$ Hz; 2H), 3.27 (ABCDEF, $J_{DC} = 8.7$ Hz, $J_{DF} = 8.0$ Hz, $J_{DE} = 2.6$ Hz; 2H), 4.94 (ABq, $J = 16.5$ Hz, 1H), 4.98 (ABq, $J = 16.5$ Hz, 1H), 6.84 (m, 2H), 7.30 (m, 3H). ^{13}C NMR (125.66 MHz, CDCl_3) 21.1, 21.2, 25.4, 40.1, 40.3, 46.8, 112.9, 124.5, 126.4, 127.7, 127.0, 138.2, 180.4, 180.6. MS (EI, 70 eV) exact mass calcd for $\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_4$ 431.1845, found 431.1839.



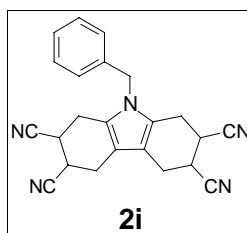
Bis-N-2'-naphthyl 9-benzyl-cis-2,3;cis-6,7-trans-2,7;trans-3,6-1,2,3,4,5,6,7,8-octahydrocarbazole-2,3,6,7-tetracarboxylic acid 2,3,6,7-diimide (2d) A solution of **1** (49 mg, 0.15 mmol) and N-2-naphthylmaleimide (205 mg, 0.908 mmol) in mesitylene (4 mL) was refluxed under Ar for 4 h. The solvent was removed *in vacuo* affording a yellow solid, which was purified by flash chromatography (SiO_2 , CH_2Cl_2 :EtOAc, 200:10) to afford 89 mg (0.136 mmol, 89%) mmol) of **2d** as a light yellow solid. mp 135-145 °C. ^1H NMR (499.70 MHz, CDCl_3) 2.78 (ABCDEF, $J_{AB} = 15.6$ Hz, $J_{AC} = 5.2$ Hz; 2H), 2.81 (ABCDEF, $J_{FE} = 16.0$ Hz, $J_{FD} = 5.2$ Hz; 2H), 3.25 (ABCDEF, $J_{BA} = 15.6$ Hz, $J_{BC} = 2.4$ Hz; 2H), 3.27 (ABCDEF, $J_{EF} = 16.0$ Hz, $J_{ED} = 2.4$ Hz; 2H), 3.46 (ABCDEF, $J_{CD} = 10.0$ Hz, $J_{CA} = 5.2$ Hz, $J_{CB} = 2.4$ Hz; 2H), 3.47 (ABCDEF, $J_{DC} = 10.0$ Hz, $J_{DF} = 5.2$ Hz, $J_{DE} = 2.4$ Hz; 2H), 4.98 (ABq, $J = 16.5$ Hz, 1H), 5.03 (ABq, $J = 16.5$ Hz, 1H), 6.89-6.90 (m, 2H), 7.20 (dd, $J = 5.2, 2.0$ Hz; 2H), 7.23 (dd, $J = 8.8, 2.0$ Hz; 2H), 7.49-7.54 (m, 5H), 7.68 (d, $J = 2.0$ Hz, 2H), 7.82-7.86 (m, 4H), 7.89 (d, $J = 9.2$ Hz, 2H). ^{13}C NMR (125.66 MHz, CDCl_3) 21.49, 21.60, 40.31, 40.55, 46.88, 112.97, 123.89, 124.58, 125.47, 126.31, 126.80, 127.03, 127.69, 127.95, 128.35, 129.05, 129.10, 129.62, 132.96, 133.30, 138.15, 179.39, 179.60. MS (EI, 70 eV) exact mass calcd for $\text{C}_{43}\text{H}_{33}\text{N}_3\text{O}_4$ 655.2471, found 655.2482.



Tetraethyl ester of 9-benzyl-1,2,3,4,5,6,7,8-octahydrocarbazole-2,3,6,7-tetracarboxylic acid (2e) A solution of **1** (50 mg, 0.15 mmol) and ethyl maleate (150 μ L, 0.93 mmol, freshly distilled under reduced pressure) in mesitylene (4 mL) was refluxed under Ar for 5 h. The solvent was removed *in vacuo* affording a dark brown oil, which was purified by flash chromatography (SiO_2 , CHCl_3) to afford 57 mg (0.10 mmol, 68%) of a mixture of 6 stereoisomers **2e** as a dark brown oil. ^1H NMR (499.70 MHz, CDCl_3) 1.15-1.28 (m, 12H), 2.46-2.59 (m, 2H), 2.66-2.77 (m, 2H), 2.80-3.05 (m, 6H), 3.14-3.21 (m, 2H), 4.03-4.16 (m, 8H), 4.87-4.92 (m, 2H), 6.82-6.87 (m, 2H), 7.18-7.29 (m, 3H). ^{13}C NMR (125.66 MHz, CDCl_3) 14.35, 14.28, 14.23, 22.64, 22.73, 24.75, 24.97, 41.16, 41.21, 41.31, 42.62, 42.66, 42.70, 42.80, 42.84, 42.90, 43.04, 46.61, 60.73, 60.76, 60.80, 60.85, 60.88, 60.91, 60.93, 112.62, 112.67, 112.79, 112.83, 112.90, 112.97, 113.14, 124.48, 124.54, 124.66, 124.71, 125.01, 125.21, 125.30, 125.36, 125.83, 125.86, 125.96, 126.02, 126.11, 127.24, 127.38, 127.50, 128.75, 128.79, 128.91, 129.04, 138.12, 138.15, 138.36, 138.57, 138.67, 173.13, 173.16, 173.28, 173.42, 173.57, 174.72, 174.83, 174.88, 175.04, 175.13, 175.25. MS (EI, 70 eV) exact mass calcd for $\text{C}_{31}\text{H}_{39}\text{NO}_8$ 553.2676, found 553.2686.

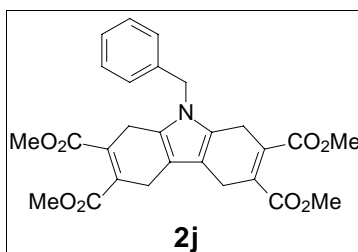


Diethyl ester of 9-benzyl-1,2,3,4,5,6,7,8-octahydrocarbazole-2,7-dicarboxylic acid (2f), diethyl ester of 9-benzyl-1,2,3,4,5,6,7,8-octahydrocarbazole-3,6-dicarboxylic acid (2h), and diethyl ester of 9-benzyl-1,2,3,4,5,6,7,8-octahydrocarbazole-3,7-dicarboxylic acid (2g) A solution of **1** (50 mg, 0.152 mmol) and ethyl acrylate (150 μ L, 1.38 mmol) in mesitylene (4 mL) was refluxed under Ar for 20 h. The solvent was removed *in vacuo* affording a brown oil, which was purified by flash chromatography (SiO_2 , CHCl_3) to afford 42 mg (0.102 mmol, 67%) of a mixture of **2f**, **2g**, and **2h** as a brown oil. ^1H NMR (499.70 MHz, CDCl_3) 1.23-1.30 (m, 6H), 1.74-1.88 (m, 2H), 2.17-2.23 (m, 2H), 2.46-2.75 (m, 10H), 4.12-4.19 (m, 4H), 4.90-4.98 (m, 2H), 6.91-6.95 (m, 2H), 7.22-7.31 (m, 3H). ^{13}C NMR (125.66 MHz, CDCl_3) 14.38, 14.41, 20.80, 20.84, 20.89, 21.24, 21.26, 21.32, 24.42, 24.45, 24.50, 24.53, 26.20, 26.27, 26.30, 26.78, 26.82, 40.76, 40.83, 40.87, 40.90, 46.44, 46.52, 46.55, 46.59, 46.65, 46.79, 60.48, 60.61, 113.30, 113.41, 114.21, 114.35, 125.15, 125.25, 125.31, 126.12, 126.15, 127.26, 128.88, 138.61, 138.65, 138.69, 175.72, 176.06, 176.10. MS (EI, 70 eV) exact mass calcd for $\text{C}_{25}\text{H}_{31}\text{NO}_4$ 409.2253, found 409.2250.

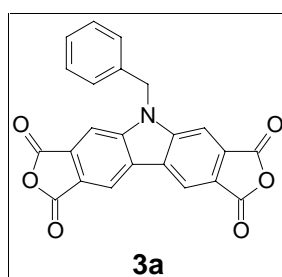


9-Benzyl-1,2,3,4,5,6,7,8-octahydrocarbazole-2,3,6,7-tetraniitrile (2e) A solution of **1** (53.8 mg, 0.16 mmol) and fumaronitrile (73.3 mg, 0.93 mmol) in mesitylene (4 mL) was refluxed under Ar for 24 h. The solvent was removed *in vacuo* affording a brown solid, which was purified by flash chromatography (SiO_2 , CHCl_3 :EtOAc 200:20) to afford 41 mg (0.11 mmol, 67%) of a mixture of 2 diastereomers of **2i** as a light brown brown solid. mp 244-249 $^\circ\text{C}$. ^1H NMR (500.08 MHz, CDCl_3) 2.81-2.91 (m, 4H), 3.03-3.11 (m, 4H), 3.29-3.35 (m, 4H), 4.94 (s, 2H), 2.83-2.84 (m, 2H), 7.28-7.35 (m, 2H). ^{13}C NMR (100.58 MHz, CDCl_3) 23.75, 23.79, 24.00, 24.04, 28.60, 28.63, 28.67, 47.07, 47.08, 110.76, 118.41, 118.69, 123.08,

125.55, 128.22, 129.49, 136.50. MS (EI, 70 eV) exact mass calcd for $C_{31}H_{39}NO_8$ 365.1640, found 365.1636.

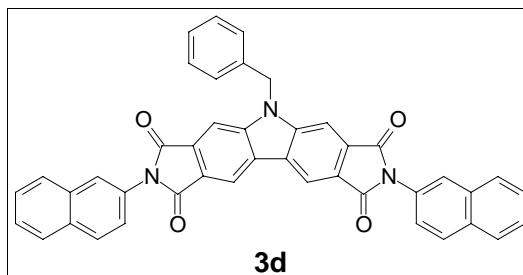


Tetramethyl ester of 9-benzyl-1,4,5,8-tetrahydrocarbazole-2,3,6,7-tetracarboxylic acid (2j) A solution of **1** (50 mg, 0.152 mmol) and dimethyl acetylenedicarboxylate (110 μ L, 0.89 mmol) in mesitylene (4 mL) was refluxed under Ar for 2 h. The solvent was removed *in vacuo* affording a brown solid, which was purified by flash chromatography (SiO_2 , $CHCl_3$:EtOAc, 150:10) to afford 52 mg of **2j** as a yellow solid. mp 195-197 $^{\circ}C$. 1H NMR (499.70 MHz, $CDCl_3$) 3.46 (A_2B_2 , $J_{AB} = 7.2$ Hz, 4H), 3.54 (A_2B_2 , $J_{BA}=7.2$ Hz, 4H), 3.75 (s, 6H), 3.82 (s, 6H), 4.99 (s, 2H), 6.85, (m, 2H), 7.30 (m, 3H). ^{13}C NMR (125.66 MHz, $CDCl_3$) 24.93, 26.55, 47.09, 52.57, 52.61, 109.43, 123.11, 125.69, 127.68, 129.19, 130.63, 136.16, 137.97, 168.24, 169.50. MS (EI, 70 eV) exact mass calcd for $C_{27}H_{27}NO_8$ 493.1737, found 493.1728.

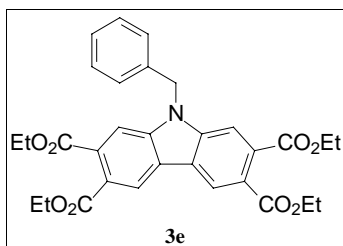


9-Benylcarbazole-2,3,6,7-tetracarboxylic acid 2,3;6,7-dianhydride (3a) A solution of **2a** (50 mg, 0.122 mmol) and DDQ (112 mg, 0.49 mmol) in 1,4 dioxane (8.5 mL) was stirred at rt under Ar for 23 h. The precipitated 4,5-dichloro-3,6-dihydroxy-phthalonitrile was removed by filtration, and the dioxane was removed *in vacuo* affording a brown solid, which was purified by flash chromatography (SiO_2 ,

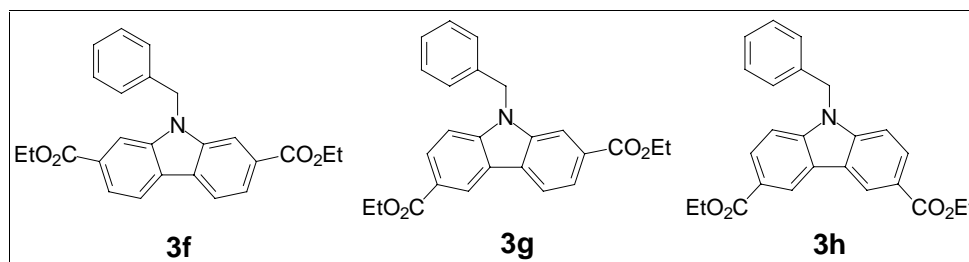
THF:CH₂Cl₂, 1:1) to afford 42.6 mg (0.11 mmol, 87%) of **3a** as a yellow solid. mp >310 °C. ¹H NMR (499.70 MHz, DMSO-d₆) 6.04 (s, 1H), 7.18-7.20 (m, 2H), 7.25-7.30 (m, 3H), 8.55 (s, 2H), 9.26 (s, 2H). ¹³C NMR (125.7 MHz, d₆-DMSO) 46.65, 108.67, 120.98, 122.71, 126.80, 127.27, 127.92, 128.88, 130.44, 136.16, 145.53, 163.31, 163.45. MS (EI, 70 eV) exact mass calcd for C₂₃H₁₁NO₆ 397.0586, found 397.0581.



Bis-N-2'-naphthyl 9-benzylcarbazole-2,3,6,7-tetracarboxylic acid 2,3;6,7-diimide (3d) A solution of **2d** (69.3 mg, 0.105 mmol) and DDQ (120 mg, 0.53 mmol) in 1,4 dioxane (11.1 mL) was refluxed under Ar for 1.5 h. The solution was cooled, the precipitated 4,5-dichloro-3,6-dihydroxy-phthalonitrile was removed by filtration, and the dioxane was removed *in vacuo* to afford a brown solid, which was purified by flash chromatography (SiO₂, CH₂Cl₂:EtOAc, 200:5) to afford 22 mg (0.033 mmol, 32%) of **3d** as a yellow solid. mp 115-140 °C. ¹H NMR (499.70 MHz, DMSO-d₆) 6.16 (s, 2H), 7.19-7.21 (m, 2H), 7.25-7.32 (m, 3H), 7.55-7.60 (m, 4H), 7.60 (dd, *J* = 8.6, 2 Hz; 2H), 7.93-8.00 (m, 4H), 8.01 (d, *J* = 1.8 Hz, 2H), 8.04 (d, *J* = 9 Hz, 2H). ¹³C NMR (125.66 Mhz, DMSO-d₆) 46.5, 107.06, 118.77, 123.51, 125.30, 125.92, 126.38, 126.68, 126.76, 127.71, 127.92, 128.40, 128.86, 129.68, 130.81, 132.08, 132.68, 136.70, 144.49, 167.07, 167.15. MS (FAB) exact mass calcd for C₄₃H₂₅N₃O₄ 648.1917 (M+1), found 648.1923 (M+1).



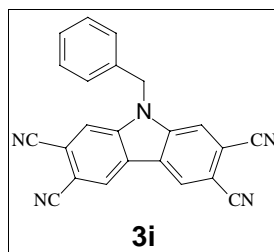
Tetraethyl ester of 9-benzylcarbazole-2,3,6,7-tetracarboxylic acid (3e) A solution of **2e** (57 mg, 0.10 mmol) in 1,4 dioxane (5.5 mL) was slowly added to a solution of DDQ (95 mg, 0.418 mmol) in 1,4-dioxane (4.0 mL) under Ar and was stirred for 20 h. The precipitate which formed was removed by filtration, and the solvent was removed *in vacuo* to afford a brown semi-solid, which was purified by flash chromatography (SiO₂, EtOAc:Hex, 2:3) to afford 34 mg (0.062 mmol, 60%) of **3e** as a brown semi-solid. ¹H NMR (500 MHz, CDCl₃) 1.88 (t, *J* = 7.2 Hz, 6H), 1.93 (t, *J* = 7.2 Hz, 6H), 4.90 (q, *J* = 7.2 Hz, 4H), 4.93 (q, *J* = 7.2 Hz, 4H), 6.09 (s, 2H), 7.55 (m, 3H), 7.74 (m, 3H), 8.16 (s), 9.14 (s). ¹³C NMR (125.7 MHz, CDCl₃) 14.26, 14.44, 47.24, 61.77, 62.12, 110.33, 123.39, 123.59, 123.69, 126.33, 128.33, 129.34, 132.77, 135.40, 142.72, 167.43, 168.78. MS (EI, 70 eV) exact mass calcd for C₃₁H₃₁NO₈ m/z 545.2049, found 545.2041.



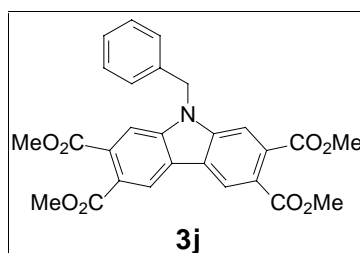
Diethyl ester of 9-benzylcarbazole-2,7-dicarboxylic acid (3f), diethyl ester of 9-benzylcarbazole-3,7-dicarboxylic acid (3g), and diethyl ester of 9-benzylcarbazole-3,6-dicarboxylic acid (3h) A solution of crude **3f**, **3g**, and **3h** (114 mg, 0.278 mmol), DDQ (255 mg, 1.12 mmol), and 1,4 dioxane (19 mL) was stirred at rt under Ar for 12 h. The precipitated 4,5-dichloro-3,6-dihydroxy-phthalonitrile was removed by filtration, and the dioxane was removed *in vacuo* affording a brown solid, which was purified by flash

chromatography (SiO₂, CH₂Cl₂) to afford three isomers: 21 mg (0.052 mmol, 19%) of **3f** as a white solid, 32 mg (0.080 mmol, 29%) of **3g** as a white solid, and 18 mg (0.045 mmol, 16.1%) of **3h** as a white solid.

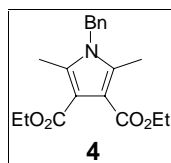
3f: mp 174-176 °C ¹H NMR (499.70 MHz, CDCl₃) 1.34 (t, *J* = 7.2 Hz, 6H), 4.33 (q, *J* = 7.2 Hz, 4H), 5.54 (s, 2H), 7.04-7.05 (m, 2H), 7.16-7.20 (m, 3H), 7.89 (dd, *J* = 8.0, 1.2 Hz; 2H), 8.05 (d, *J* = 1.2 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (126.76 MHz, CDCl₃) 14.64, 46.92, 61.38, 111.25, 121.00, 121.02, 125.99, 126.57, 127.97, 129.14, 136.63, 141.52, 167.21. MS (EI, 70 eV) exact mass calcd for C₂₅H₂₃NO₄ m/z 401.1627, found 401.1623. **3g**: mp 164-165 °C. ¹H NMR (500.80 MHz, CDCl₃) 1.34 (t, *J* = 7.0 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 4.34 (q, *J* = 7.0 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 5.50 (s, 2H), 7.02-7.04 (m, 2H), 7.16-7.20 (m, 3H), 7.29 (dd, *J* = 8.7, 0.7 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.07 (dd, *J* = 1.3, 0.6 Hz, 1H), 8.10 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.12 (dd, *J* = 8.2, 0.6 Hz, 1H), 8.80 (dd, *J* = 1.7, 0.7 Hz, 1H). ¹³C NMR (125.66 MHz, CDCl₃) 14.64, 14.73, 47.08, 61.09, 61.37, 109.21, 111.24, 120.62, 121.06, 121.64, 122.36, 122.38, 123.92, 126.60, 127.07, 128.10, 128.71, 128.89, 129.22, 136.39, 141.07, 144.64, 167.28, 167.35. MS (EI, 70 eV) exact mass calcd for C₂₅H₂₃NO₄ m/z 401.1627, found 401.1632. **3h**: mp 125-137 °C. ¹H NMR (500.80 MHz, CDCl₃) 1.39 (t, *J* = 7.1 Hz, 6H), 4.37 (q, *J* = 7.1 Hz, 4H), 5.49 (s, 2H), 7.03-7.04 (m, 2H), 7.18-7.20 (m, 3H), 7.33 (d, *J* = 8.6 Hz, 2H), 8.11 (dd, *J* = 8.6, 1.5 Hz, 2H), 8.83 (d, *J* = 1.5 Hz, 2H). ¹³C NMR (125.66 MHz, CDCl₃) 14.74, 47.25, 61.11, 109.19, 122.86, 123.22, 123.32, 126.59, 128.18, 128.43, 129.27, 136.16, 144.19, 167.35. MS (EI, 70 eV) exact mass calcd for C₂₅H₂₃NO₄ m/z 401.1627, found 401.1625.



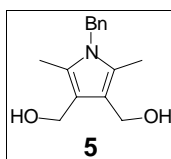
9-Benzylcarbazole-2,3,6,7-tetranitrile (3i) A solution of **2i** (27 mg, 0.07 mmol) in 1,4-dioxane (2.4ml) was slowly added to a solution of DDQ (69.7mg, 0.31 mmol) in 1,4-dioxane (2.0 ml) under Ar, and was refluxed for 24 hr. The precipitate which formed was removed by filtration and the solvent was removed *in vacuo*, to afford a brown solid, which was purified by flash chromatography (SiO₂, CHCl₃:EtOAc, 200:60) to afford 7.7 mg (0.021 mmol, 29%) of **3e** as a white solid. mp 254-260 °C ¹H NMR (399.95 MHz, DMSO-d₆) 5.89 (s, 2H), 7.22-7.30 (m, 5H), 8.83 (s, 2H), 9.21 (s, 2H). ¹³C NMR (100.58 MHz, DMSO-d₆) 46.6, 105.7, 112.7, 116.5, 116.8, 118.1, 123.7, 127.1, 128.1, 129.2, 129.5, 135.6, 142.2. MS (EI, 70 eV) exact mass calcd for C₂₃H₁₁N₅ m/z 357.1014, found 357.1018.



Tetramethyl ester of 9-benzylcarbazole-2,3,6,7-tetracarboxylic acid (3j) A solution of **2j** (52 mg, 0.105 mmol) in 1,4-dioxane (4.3 ml) was slowly added to a solution of DDQ (50 mg, 0.220 mmol) in 1,4-dioxane (4.0 ml) under Ar. After 1 h, the precipitated 4,5-dichloro-3,6-dihydroxy-phthalonitrile was removed by filtration, and the dioxane was removed *in vacuo* affording a brown solid, which was purified by flash chromatography (SiO₂, EtOAc:Hexane, 1:1) to afford 36 mg (0.07 mmol, 70%) of **3j** as a yellow solid. mp 161-169 °C ¹H NMR (499.70 MHz, CDCl₃) 3.93 (s, 6H), 3.96 (s, 6H), 5.59 (s, 2H), 7.05 (m, 2H), 7.28 (m, 3H), 7.67 (s, 2H), 8.65 (s, 2H); ¹³C NMR (125.66 MHz, CDCl₃) 47.32, 52.89, 53.16, 110.43, 123.41, 123.56, 123.73, 126.34, 128.45, 129.45, 132.61, 135.32, 142.87, 167.86, 169.22; MS (EI, 70 eV) exact mass calcd for C₂₇H₂₃NO₈ 489.1424, found 489.1421.



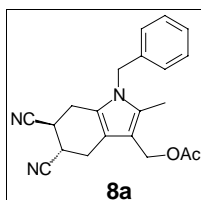
Diethyl 1-benzyl-2,5-dimethylpyrrole-3,4-dicarboxylate (4). Using a modified procedure 3,4-carbethoxy-2,5-hexanedione (**10**) (7.53 g, 0.03 mol), benzylamine (11.5 mL, 0.11 mol), and acetic acid (5 mL) were stirred under N₂ at rt.¹ The mixture solidified quickly and was left at ambient temperature overnight. The solid mixture was partitioned between methylene chloride and satd. NaHCO₃. The organic layer was separated, washed (satd. NaHCO₃), dried (K₂CO₃), and concentrated *in vacuo*. The semisolid residue was purified by column chromatography (SiO₂ ether:hexane 1:2, then 1:1) to afford 7.53 g (0.23 mol, 78% yield) of **10** as colorless crystals. mp 63-64 °C. lit.² 61.5-63 °C ¹H NMR (400 MHz, CDCl₃) 1.331 (t, *J* = 7.2 Hz, 6H), 2.309 (s, 6H), 4.281 (q, *J* = 7.2 Hz, 4H), 5.036 (s, 2H), 6.89-6.93 (m, 2H), 7.22-7.33 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) 10.7, 14.1, 46.7, 59.9, 112.4, 125.4, 127.4, 128.8, 133.3, 135.8, 165.5. GC-MS (M⁺) calc. for C₁₉H₂₃NO₄, 329, found 329.



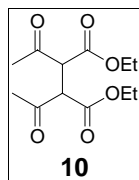
1-Benzyl-2,5-dimethylpyrrole-3,4-dimethanol (5). Lithium aluminum hydride (1.35 g, 35 mmol) was suspended in dry ether (30 mL) under N₂. A solution of **4** (4.45 g, 13 mmol) in 20 mL of dry ether was added dropwise over a period of 10 min. After the strongly exothermic reaction ceased, the mixture was stirred at rt overnight. Water (1 mL) was added dropwise followed by 10% aq. NaOH (2 mL) and water (4.5 mL). The resulting suspension was stirred for 2 h; the precipitate removed by filtration and washed with ether and the combined filtrates were concentrated *in vacuo*. The residue was recrystallized from ethyl acetate/hexane mixture to afford 2.94 g (12 mmol, 89%) as large off-white crystals. The product was

(1) Broadbent, H. S.; Burnham, W. S.; Olsen, R. K.; Sheeley, R. M. *J. Heterocyclic Chem.* **1968**, *5*, 757-767.

sensitive to acid, light, and oxygen. ^1H NMR (400 MHz, CDCl_3) 2.11 (s, 6H), 3.28 (t, $J = 4.9$ Hz, 2H), 4.55 (d, $J = 4.5$ Hz, 4H), 5.00 (s, 2H), 6.86-6.90 (m, 2H), 7.18-7.30 (m, 3H), ^{13}C NMR (100 MHz, CDCl_3) 9.6, 46.8, 56.0, 118.0, 125.5, 125.5, 127.0, 128.7, 137.9.



9-benzyl-2-methyl-3-acetoxymethyl-4,5,6,7-tetrahydroindole-*trans*-5,6-dinitrile (8a) A solution of **1** (50 mg, 0.15 mmol) and fumaronitrile (73.3 mg, 0.93 mmol) in mesitylene (4 mL) was refluxed under Ar for 7 h. The solvent was removed *in vacuo* affording a brown solid, which was purified by flash chromatography (SiO_2 , CHCl_3 :EtOAc 200:20) to afford 13 mg (0.035 mmol, 24%) of **2i** and 12 mg (0.035 mmol, 22%) of **8a** as a light brown brown solid. **8a**: mp 171-175 °C. ^1H NMR (500.08 MHz, CDCl_3) 2.09 (s, 3H), 2.19 (s, 3H), 2.82 (ABCDEF, $J = 15.7, 5.6$; 1H), 2.99 (ABCDEF, $J = 15.7, 5.8$, 1H), 3.03 (ABCDEF, $J = 15.6, 5.5$; 1H), 3.18 (ABCDEF, $J = 15.6, 5.4$; 1H), 3.27 (ABCDEF, $J = 7.1, 5.6, 5.8$; 1H), 3.29 (ABCDEF, $J = 7.1, 5.5, 5.4$; 1H), 4.98 (ABq, $J = 12.7$, 1H), 4.99 (ABq, $J = 12.7$, 1H), 5.00 (s, 1H), 6.89-6.90 (m, 2H), 7.29-7.36 (m, 3H). ^{13}C NMR (125.76 MHz, CDCl_3) 9.87, 21.42, 24.13, 24.37, 28.89, 29.01, 47.18, 57.90, 112.37, 112.58, 118.72, 119.00, 121.11, 125.76, 127.91, 129.31, 130.01, 137.15, 171.44. MS (EI, 70 eV) exact mass calcd for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_2$ 347.1633, found 367.1629.



3,4-Carboethoxy-2,5-hexanedione (10).³ Ethyl acetoacetate (76.5 mL, 0.6 mol) and THF (300 mL) were placed in a 2 L flask under nitrogen with a magnetic stirrer and a thermometer. The flask was cooled in an ice-water bath to 0 °C. Potassium *tert*-butoxide (680 mL of a 0.88 M solution in THF, 0.6 mol) was added slowly through a transfer needle at 0 to 5 °C. The mixture was stirred for 15 min at 0 °C. Solid iodine (78.0g, 0.3 mol) was added in portions while the reaction mixture was kept below 30 °C. The solution became yellow, and a fine white precipitate formed. The suspension was stirred at 0 °C for an additional 15 min and concentrated *in vacuo*. The residue was partitioned between ether (0.5 L) and water (0.5 L). The layers were separated and the aqueous phase was washed with ether. Combined organic layers were washed with brine, dried (MgSO₄), and concentrated *in vacuo*. The semisolid residue was recrystallized from hexane. Two crops of white crystals were collected, for a total of 49.7 g (64% yield). mp 91-92 °C lit.⁴ 90 °C. The purity by GC-MS was about 90%. ¹H NMR (400 MHz, CDCl₃) 1.26 (t, *J* = 7.1 Hz, 6H), 2.44 (s, 6H), 4.16 (quartet, *J* = 7.2 Hz, 4H), 4.49 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) 13.9, 30.8, 57.7, 62.7, 167.0, 201.6. GC-MS (M⁺) calc. for C₁₂H₁₈O₆, 258, found 258.

(3) Two additional method for the synthesis of **11**. (a) Gabel, N. W. *J. Org. Chem.* **1962**, 27, 301-303. (b) Acheson, R. M.; Vernon, J. M. *J. Chem. Soc.* **1961**, 457-459.

(4) Wiley, R. H.; Harrell, J. R. *J. Org. Chem.* **1960**, 25, 903.

Table 1. Crystal data and structure refinement for **2d**:

Identification code	2d		
Empirical formula	C ₄₇ H ₃₇ N ₃ O ₆ S ₂		
Formula weight	803.92		
Temperature	193(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a: = 9.2659(7)	• = 95.004(2)°	
	b: = 11.7692(9)	• = 95.602(2)°	
	c: = 17.9388(14)	• = 94.332(2)°	
Volume,	1932.5(3) Å ³		
Density (calculated)	1.382 Mg/m ³		
Absorption coefficient	0.195 mm ⁻¹		
F(000)	840		
Crystal size	0.16 x 0.11 x 0.08 mm		
range for data collection	1.15 to 25.05°		
Limiting indices	-8 < h < 11, -14 < k < 12, -20 < l < 21		
Reflections collected	10368		
Independent reflections	6695 (R _{int} = 0.0502)		
Completeness to =	25.05° 98.1 %		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	6695 / 0 / 523		
Goodness-of-fit on F ²	0.895		
Final R indices [I>2•(I)] =	0.0498, wR2 = 0.0981		
R indices (all data) =	0.1413, wR2 = 0.1339		
Largest diff. peak and hole	0.330 and -0.291 Å ³		

Table 2. Atomic coordinates [x 10⁴] and equivalent isotropic displacement parameters [x 10³] for **2d**. U_(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U _(eq)
C(1)	7370(4)	6851(3)	43(2)	33(1)
C(2)	7932(4)	6147(3)	-488(2)	30(1)
C(3)	7864(4)	4952(3)	-481(2)	31(1)
C(4)	7191(4)	4383(3)	48(2)	33(1)
C(5)	6604(4)	5069(3)	599(2)	30(1)
C(6)	5873(4)	4819(3)	1242(2)	29(1)
C(7)	5405(4)	3792(3)	1514(2)	31(1)
C(8)	4749(4)	3884(3)	2173(2)	31(1)
C(9)	4594(4)	4958(3)	2556(2)	30(1)
C(10)	4988(4)	5987(3)	2294(2)	31(1)
C(11)	5625(4)	5893(3)	1620(2)	28(1)
C(12)	6725(4)	6284(3)	599(2)	30(1)
C(13)	6060(4)	7982(3)	1401(2)	31(1)

C(14)	7510(4)	8623(3)	1686(2)	29(1)
C(15)	8784(4)	8093(3)	1816(2)	36(1)
C(16)	10097(4)	8719(3)	2046(2)	37(1)
C(17)	10163(5)	9898(3)	2156(2)	40(1)
C(18)	8901(5)	10432(3)	2044(2)	44(1)
C(19)	7589(4)	9807(3)	1817(2)	38(1)
C(20)	8658(4)	6456(3)	-1149(2)	34(1)
C(21)	8601(4)	4478(3)	-1116(2)	34(1)
C(22)	4135(4)	2985(3)	2599(2)	34(1)
C(23)	3965(4)	4751(3)	3265(2)	33(1)
C(24)	9745(4)	5333(3)	-2184(2)	34(1)
C(25)	10818(4)	6133(3)	-2307(2)	35(1)
C(26)	11387(4)	6106(3)	-3009(2)	34(1)
C(27)	12438(4)	6960(3)	-3179(2)	40(1)
C(28)	12937(4)	6921(3)	-3873(2)	46(1)
C(29)	12446(5)	6029(4)	-4426(2)	50(1)
C(30)	11431(4)	5194(3)	-4285(2)	46(1)
C(31)	10877(4)	5222(3)	-3573(2)	37(1)
C(32)	9803(4)	4386(3)	-3414(2)	40(1)
C(33)	9227(4)	4438(3)	-2739(2)	39(1)
C(34)	2891(4)	2993(3)	3781(2)	33(1)
C(35)	1606(4)	2315(3)	3523(2)	37(1)
C(36)	835(4)	1781(3)	4022(2)	42(1)
C(37)	1308(4)	1915(3)	4797(2)	35(1)
C(38)	515(4)	1394(3)	5334(2)	45(1)
C(39)	1013(5)	1536(3)	6076(2)	54(1)
C(40)	2298(5)	2212(3)	6330(2)	52(1)
C(41)	3095(4)	2752(3)	5832(2)	43(1)
C(42)	2611(4)	2604(3)	5057(2)	32(1)
C(43)	3397(4)	3150(3)	4524(2)	34(1)
C(44)	6666(4)	-56(3)	-994(2)	52(1)
C(45)	8868(4)	1231(3)	-178(2)	56(1)
C(46)	3292(6)	8437(4)	4203(3)	93(2)
C(47)	4856(6)	10158(3)	3738(3)	90(2)
N(1)	9073(3)	5419(2)	-1498(2)	34(1)
N(2)	6116(3)	6762(2)	1212(2)	30(1)
N(3)	3641(3)	3560(2)	3241(2)	33(1)
O(1)	8873(3)	7390(2)	-1371(1)	39(1)
O(2)	8810(3)	3496(2)	-1293(1)	52(1)
O(3)	4049(3)	1953(2)	2465(1)	42(1)
O(4)	3765(3)	5436(2)	3783(1)	39(1)
O(5)	6193(3)	1392(2)	159(2)	59(1)
O(6)	3824(4)	8407(2)	2792(2)	73(1)
S(1)	7188(1)	480(1)	-43(1)	46(1)
S(2)	3344(2)	9202(1)	3386(1)	76(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **2d**.

C(1)-C(2)	1.374(4)
C(1)-C(12)	1.403(4)
C(2)-C(3)	1.404(4)
C(2)-C(20)	1.479(5)
C(3)-C(4)	1.379(4)
C(3)-C(21)	1.474(4)
C(4)-C(5)	1.399(4)
C(5)-C(12)	1.427(4)
C(5)-C(6)	1.435(4)
C(6)-C(7)	1.397(4)
C(6)-C(11)	1.427(4)
C(7)-C(8)	1.380(4)
C(8)-C(9)	1.410(4)
C(8)-C(22)	1.471(4)
C(9)-C(10)	1.372(4)
C(9)-C(23)	1.481(5)
C(10)-C(11)	1.396(4)
C(11)-N(2)	1.383(4)
C(12)-N(2)	1.380(4)
C(13)-N(2)	1.453(4)
C(13)-C(14)	1.510(5)
C(14)-C(15)	1.385(5)
C(14)-C(19)	1.388(4)
C(15)-C(16)	1.382(5)
C(16)-C(17)	1.380(5)
C(17)-C(18)	1.374(5)
C(18)-C(19)	1.380(5)
C(20)-O(1)	1.210(4)
C(20)-N(1)	1.419(4)
C(21)-O(2)	1.207(4)
C(21)-N(1)	1.417(4)
C(22)-O(3)	1.212(4)
C(22)-N(3)	1.417(4)
C(23)-O(4)	1.215(4)
C(23)-N(3)	1.407(4)
C(24)-C(25)	1.364(4)
C(24)-C(33)	1.407(5)
C(24)-N(1)	1.432(4)
C(25)-C(26)	1.410(4)
C(26)-C(31)	1.406(5)
C(26)-C(27)	1.419(5)
C(27)-C(28)	1.368(5)
C(28)-C(29)	1.397(5)
C(29)-C(30)	1.366(5)
C(30)-C(31)	1.420(5)
C(31)-C(32)	1.414(5)
C(32)-C(33)	1.369(5)
C(34)-C(43)	1.362(5)
C(34)-C(35)	1.398(5)
C(34)-N(3)	1.429(4)
C(35)-C(36)	1.364(5)
C(36)-C(37)	1.408(5)
C(37)-C(42)	1.417(5)

C(37)-C(38)	1.420(5)
C(38)-C(39)	1.358(5)
C(39)-C(40)	1.395(5)
C(40)-C(41)	1.379(5)
C(41)-C(42)	1.411(5)
C(42)-C(43)	1.424(4)
C(44)-S(1)	1.774(4)
C(45)-S(1)	1.780(4)
C(46)-S(2)	1.788(5)
C(47)-S(2)	1.758(5)
O(5)-S(1)	1.510(3)
O(6)-S(2)	1.480(3)
C(2)-C(1)-C(12)	114.8(3)
C(1)-C(2)-C(3)	123.0(3)
C(1)-C(2)-C(20)	128.8(3)
C(3)-C(2)-C(20)	108.2(3)
C(4)-C(3)-C(2)	122.7(3)
C(4)-C(3)-C(21)	128.9(3)
C(2)-C(3)-C(21)	108.4(3)
C(3)-C(4)-C(5)	116.1(3)
C(4)-C(5)-C(12)	120.4(3)
C(4)-C(5)-C(6)	133.1(3)
C(12)-C(5)-C(6)	106.4(3)
C(7)-C(6)-C(11)	120.8(3)
C(7)-C(6)-C(5)	132.6(3)
C(11)-C(6)-C(5)	106.6(3)
C(8)-C(7)-C(6)	116.4(3)
C(7)-C(8)-C(9)	121.4(3)
C(7)-C(8)-C(22)	130.0(3)
C(9)-C(8)-C(22)	108.6(3)
C(10)-C(9)-C(8)	124.0(3)
C(10)-C(9)-C(23)	128.3(3)
C(8)-C(9)-C(23)	107.6(3)
C(9)-C(10)-C(11)	114.4(3)
N(2)-C(11)-C(10)	128.3(3)
N(2)-C(11)-C(6)	108.9(3)
C(10)-C(11)-C(6)	122.8(3)
N(2)-C(12)-C(1)	128.0(3)
N(2)-C(12)-C(5)	109.2(3)
C(1)-C(12)-C(5)	122.9(3)
N(2)-C(13)-C(14)	114.6(3)
C(15)-C(14)-C(19)	117.7(3)
C(15)-C(14)-C(13)	123.5(3)
C(19)-C(14)-C(13)	118.8(3)
C(16)-C(15)-C(14)	121.4(3)
C(17)-C(16)-C(15)	120.2(4)
C(18)-C(17)-C(16)	119.0(4)
C(17)-C(18)-C(19)	120.8(3)
C(18)-C(19)-C(14)	120.9(4)
O(1)-C(20)-N(1)	125.0(3)
O(1)-C(20)-C(2)	128.8(3)
N(1)-C(20)-C(2)	106.2(3)
O(2)-C(21)-N(1)	124.5(3)
O(2)-C(21)-C(3)	129.0(3)

N(1)-C(21)-C(3)	106.5(3)
O(3)-C(22)-N(3)	124.2(3)
O(3)-C(22)-C(8)	129.7(3)
N(3)-C(22)-C(8)	106.1(3)
O(4)-C(23)-N(3)	124.7(3)
O(4)-C(23)-C(9)	129.0(3)
N(3)-C(23)-C(9)	106.3(3)
C(25)-C(24)-C(33)	120.9(3)
C(25)-C(24)-N(1)	120.5(3)
C(33)-C(24)-N(1)	118.5(3)
C(24)-C(25)-C(26)	120.5(3)
C(31)-C(26)-C(25)	119.5(3)
C(31)-C(26)-C(27)	118.1(3)
C(25)-C(26)-C(27)	122.4(3)
C(28)-C(27)-C(26)	120.7(4)
C(27)-C(28)-C(29)	120.9(4)
C(30)-C(29)-C(28)	120.1(4)
C(29)-C(30)-C(31)	120.3(4)
C(26)-C(31)-C(32)	118.4(3)
C(26)-C(31)-C(30)	119.9(4)
C(32)-C(31)-C(30)	121.7(4)
C(33)-C(32)-C(31)	121.7(3)
C(32)-C(33)-C(24)	119.0(3)
C(43)-C(34)-C(35)	121.7(3)
C(43)-C(34)-N(3)	120.4(3)
C(35)-C(34)-N(3)	117.8(3)
C(36)-C(35)-C(34)	119.8(3)
C(35)-C(36)-C(37)	120.8(4)
C(36)-C(37)-C(42)	119.3(3)
C(36)-C(37)-C(38)	122.3(4)
C(42)-C(37)-C(38)	118.4(3)
C(39)-C(38)-C(37)	120.6(4)
C(38)-C(39)-C(40)	120.9(4)
C(41)-C(40)-C(39)	120.8(4)
C(40)-C(41)-C(42)	119.4(4)
C(41)-C(42)-C(37)	119.9(3)
C(41)-C(42)-C(43)	121.3(3)
C(37)-C(42)-C(43)	118.8(3)
C(34)-C(43)-C(42)	119.6(3)
C(21)-N(1)-C(20)	110.6(3)
C(21)-N(1)-C(24)	124.9(3)
C(20)-N(1)-C(24)	124.2(3)
C(12)-N(2)-C(11)	108.8(2)
C(12)-N(2)-C(13)	124.7(3)
C(11)-N(2)-C(13)	126.5(3)
C(23)-N(3)-C(22)	111.1(3)
C(23)-N(3)-C(34)	125.1(3)
C(22)-N(3)-C(34)	123.8(3)
O(5)-S(1)-C(44)	107.56(17)
O(5)-S(1)-C(45)	105.54(17)
C(44)-S(1)-C(45)	97.70(19)
O(6)-S(2)-C(47)	107.1(2)
O(6)-S(2)-C(46)	106.4(2)
C(47)-S(2)-C(46)	96.4(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for **2d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	42(2)	24(2)	33(2)	3(2)	7(2)	3(2)
C(2)	34(2)	27(2)	30(2)	5(2)	4(2)	1(2)
C(3)	38(2)	25(2)	30(2)	1(2)	6(2)	2(2)
C(4)	41(2)	26(2)	32(2)	5(2)	4(2)	6(2)
C(5)	34(2)	28(2)	28(2)	3(2)	3(2)	3(2)
C(6)	33(2)	28(2)	24(2)	1(2)	2(2)	2(2)
C(7)	38(2)	27(2)	26(2)	0(2)	1(2)	2(2)
C(8)	34(2)	28(2)	29(2)	3(2)	4(2)	0(2)
C(9)	31(2)	29(2)	28(2)	-1(2)	3(2)	1(2)
C(10)	41(2)	25(2)	27(2)	-1(2)	6(2)	3(2)
C(11)	32(2)	24(2)	27(2)	2(2)	3(2)	-1(2)
C(12)	30(2)	28(2)	30(2)	-1(2)	4(2)	0(2)
C(13)	38(2)	26(2)	31(2)	2(2)	9(2)	7(2)
C(14)	38(2)	26(2)	24(2)	1(2)	6(2)	4(2)
C(15)	46(3)	28(2)	34(2)	2(2)	12(2)	6(2)
C(16)	32(2)	39(2)	39(2)	-6(2)	2(2)	4(2)
C(17)	47(3)	35(2)	37(2)	-5(2)	6(2)	-4(2)
C(18)	55(3)	25(2)	51(3)	-1(2)	7(2)	1(2)
C(19)	43(3)	25(2)	44(2)	4(2)	0(2)	6(2)
C(20)	36(2)	31(2)	33(2)	0(2)	6(2)	3(2)
C(21)	42(3)	30(2)	32(2)	5(2)	7(2)	9(2)
C(22)	37(2)	33(2)	30(2)	4(2)	1(2)	1(2)
C(23)	37(2)	31(2)	30(2)	-1(2)	3(2)	0(2)
C(24)	40(3)	32(2)	32(2)	2(2)	10(2)	7(2)
C(25)	43(3)	32(2)	32(2)	-1(2)	6(2)	9(2)
C(26)	36(2)	36(2)	33(2)	3(2)	10(2)	11(2)
C(27)	38(3)	42(2)	41(2)	5(2)	7(2)	6(2)
C(28)	44(3)	55(3)	45(3)	18(2)	19(2)	7(2)
C(29)	55(3)	63(3)	36(3)	5(2)	17(2)	15(2)
C(30)	52(3)	51(3)	36(2)	1(2)	13(2)	15(2)
C(31)	38(3)	39(2)	35(2)	4(2)	8(2)	12(2)
C(32)	45(3)	36(2)	37(2)	-7(2)	4(2)	3(2)
C(33)	40(3)	35(2)	43(3)	5(2)	11(2)	3(2)
C(34)	38(3)	28(2)	34(2)	5(2)	10(2)	3(2)
C(35)	37(3)	38(2)	33(2)	1(2)	-1(2)	-1(2)

C(36)	39(3)	40(2)	44(3)	1(2)	6(2)	-8(2)
C(37)	40(3)	30(2)	36(2)	1(2)	11(2)	-1(2)
C(38)	48(3)	37(2)	50(3)	0(2)	15(2)	-8(2)
C(39)	62(3)	52(3)	51(3)	15(2)	22(3)	-6(2)
C(40)	63(3)	59(3)	35(2)	8(2)	12(2)	0(3)
C(41)	47(3)	46(2)	34(2)	1(2)	5(2)	-6(2)
C(42)	35(2)	31(2)	31(2)	4(2)	6(2)	5(2)
C(43)	36(2)	32(2)	35(2)	3(2)	7(2)	-2(2)
C(44)	51(3)	59(3)	45(3)	-6(2)	5(2)	13(2)
C(45)	57(3)	53(3)	57(3)	8(2)	3(2)	3(2)
C(46)	90(4)	108(4)	82(4)	0(3)	33(3)	-7(4)
C(47)	136(5)	47(3)	77(4)	0(3)	-24(4)	-9(3)
N(1)	43(2)	29(2)	32(2)	3(1)	14(2)	7(2)
N(2)	38(2)	22(2)	30(2)	-3(1)	10(2)	1(1)
N(3)	42(2)	29(2)	29(2)	1(1)	8(2)	-2(2)
O(1)	47(2)	30(1)	42(2)	8(1)	15(1)	5(1)
O(2)	81(2)	33(2)	47(2)	7(1)	31(2)	18(2)
O(3)	61(2)	28(2)	35(2)	0(1)	11(1)	-4(1)
O(4)	50(2)	34(1)	33(2)	-5(1)	14(1)	-2(1)
O(5)	70(2)	56(2)	55(2)	-3(1)	24(2)	16(2)
O(6)	92(3)	61(2)	65(2)	-22(2)	5(2)	25(2)
S(1)	58(1)	44(1)	38(1)	8(1)	7(1)	7(1)
S(2)	75(1)	72(1)	72(1)	-27(1)	-19(1)	33(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2d**.

	x	y	z	U(eq)
H(1A)	7416	7659	34	39
H(4A)	7129	3572	38	39
H(7A)	5532	3070	1260	37
H(10A)	4839	6703	2551	38
H(13A)	5383	8094	1790	37
H(13B)	5655	8322	948	37
H(15A)	8753	7282	1744	43
H(16A)	10958	8337	2129	45
H(17A)	11065	10333	2307	48
H(18A)	8934	11243	2125	53
H(19A)	6727	10191	1748	45
H(25A)	11184	6712	-1918	43
H(27A)	12798	7565	-2807	48
H(28A)	13626	7508	-3980	55
H(29A)	12819	6003	-4902	60
H(30A)	11094	4592	-4664	55
H(32A)	9472	3771	-3785	48
H(33A)	8489	3878	-2646	46

H(35A)	1270	2226	3002	44
H(36A)	-31	1312	3845	50
H(38A)	-372	942	5172	55
H(39A)	479	1171	6427	64
H(40A)	2629	2301	6852	62
H(41A)	3962	3219	6010	51
H(43A)	4269	3620	4687	41
H(44A)	5724	-506	-1032	78
H(44B)	7401	-543	-1170	78
H(44C)	6587	585	-1305	78
H(45A)	9331	1600	306	84
H(45B)	8687	1815	-525	84
H(45C)	9511	692	-389	84
H(46A)	2491	7832	4118	140
H(46B)	3141	8965	4636	140
H(46C)	4215	8095	4303	140
H(47A)	5068	10682	3360	135
H(47B)	5701	9726	3852	135
H(47C)	4640	10597	4197	135

Table 6. Torsion angles [$^{\circ}$] for **2d**.

C(12)-C(1)-C(2)-C(3)	0.3(5)
C(12)-C(1)-C(2)-C(20)	179.0(3)
C(1)-C(2)-C(3)-C(4)	1.9(6)
C(20)-C(2)-C(3)-C(4)	-177.1(3)
C(1)-C(2)-C(3)-C(21)	-178.5(4)
C(20)-C(2)-C(3)-C(21)	2.5(4)
C(2)-C(3)-C(4)-C(5)	-1.8(6)
C(21)-C(3)-C(4)-C(5)	178.7(4)
C(3)-C(4)-C(5)-C(12)	-0.4(5)
C(3)-C(4)-C(5)-C(6)	-178.0(4)
C(4)-C(5)-C(6)-C(7)	-5.0(7)
C(12)-C(5)-C(6)-C(7)	177.1(4)
C(4)-C(5)-C(6)-C(11)	175.9(4)
C(12)-C(5)-C(6)-C(11)	-2.0(4)
C(11)-C(6)-C(7)-C(8)	-2.2(5)
C(5)-C(6)-C(7)-C(8)	178.8(4)
C(6)-C(7)-C(8)-C(9)	-1.4(5)
C(6)-C(7)-C(8)-C(22)	179.5(4)
C(7)-C(8)-C(9)-C(10)	4.1(6)
C(22)-C(8)-C(9)-C(10)	-176.7(3)
C(7)-C(8)-C(9)-C(23)	-175.4(3)
C(22)-C(8)-C(9)-C(23)	3.9(4)
C(8)-C(9)-C(10)-C(11)	-2.6(5)
C(23)-C(9)-C(10)-C(11)	176.7(3)
C(9)-C(10)-C(11)-N(2)	179.1(3)
C(9)-C(10)-C(11)-C(6)	-1.2(5)
C(7)-C(6)-C(11)-N(2)	-176.6(3)

C(5)-C(6)-C(11)-N(2)	2.7(4)
C(7)-C(6)-C(11)-C(10)	3.7(6)
C(5)-C(6)-C(11)-C(10)	-177.1(3)
C(2)-C(1)-C(12)-N(2)	177.8(4)
C(2)-C(1)-C(12)-C(5)	-2.4(5)
C(4)-C(5)-C(12)-N(2)	-177.6(3)
C(6)-C(5)-C(12)-N(2)	0.6(4)
C(4)-C(5)-C(12)-C(1)	2.5(6)
C(6)-C(5)-C(12)-C(1)	-179.2(3)
N(2)-C(13)-C(14)-C(15)	-4.7(4)
N(2)-C(13)-C(14)-C(19)	174.3(3)
C(19)-C(14)-C(15)-C(16)	-1.8(5)
C(13)-C(14)-C(15)-C(16)	177.2(3)
C(14)-C(15)-C(16)-C(17)	0.3(5)
C(15)-C(16)-C(17)-C(18)	1.0(5)
C(16)-C(17)-C(18)-C(19)	-0.8(5)
C(17)-C(18)-C(19)-C(14)	-0.7(5)
C(15)-C(14)-C(19)-C(18)	2.0(5)
C(13)-C(14)-C(19)-C(18)	-177.0(3)
C(1)-C(2)-C(20)-O(1)	-2.2(7)
C(3)-C(2)-C(20)-O(1)	176.7(4)
C(1)-C(2)-C(20)-N(1)	178.1(4)
C(3)-C(2)-C(20)-N(1)	-3.0(4)
C(4)-C(3)-C(21)-O(2)	-2.5(7)
C(2)-C(3)-C(21)-O(2)	177.9(4)
C(4)-C(3)-C(21)-N(1)	178.5(4)
C(2)-C(3)-C(21)-N(1)	-1.0(4)
C(7)-C(8)-C(22)-O(3)	-0.9(7)
C(9)-C(8)-C(22)-O(3)	179.9(4)
C(7)-C(8)-C(22)-N(3)	178.4(4)
C(9)-C(8)-C(22)-N(3)	-0.8(4)
C(10)-C(9)-C(23)-O(4)	-5.8(7)
C(8)-C(9)-C(23)-O(4)	173.6(4)
C(10)-C(9)-C(23)-N(3)	175.1(4)
C(8)-C(9)-C(23)-N(3)	-5.5(4)
C(33)-C(24)-C(25)-C(26)	2.8(5)
N(1)-C(24)-C(25)-C(26)	-174.2(3)
C(24)-C(25)-C(26)-C(31)	-2.3(5)
C(24)-C(25)-C(26)-C(27)	176.0(3)
C(31)-C(26)-C(27)-C(28)	0.0(5)
C(25)-C(26)-C(27)-C(28)	-178.3(3)
C(26)-C(27)-C(28)-C(29)	-1.2(6)
C(27)-C(28)-C(29)-C(30)	1.5(6)
C(28)-C(29)-C(30)-C(31)	-0.5(6)
C(25)-C(26)-C(31)-C(32)	0.0(5)
C(27)-C(26)-C(31)-C(32)	-178.4(3)
C(25)-C(26)-C(31)-C(30)	179.3(3)
C(27)-C(26)-C(31)-C(30)	0.9(5)
C(29)-C(30)-C(31)-C(26)	-0.7(6)
C(29)-C(30)-C(31)-C(32)	178.6(4)
C(26)-C(31)-C(32)-C(33)	1.9(5)
C(30)-C(31)-C(32)-C(33)	-177.4(3)
C(31)-C(32)-C(33)-C(24)	-1.5(5)
C(25)-C(24)-C(33)-C(32)	-0.8(5)

N(1)-C(24)-C(33)-C(32)	176.2(3)
C(43)-C(34)-C(35)-C(36)	-0.8(5)
N(3)-C(34)-C(35)-C(36)	-178.3(3)
C(34)-C(35)-C(36)-C(37)	0.8(5)
C(35)-C(36)-C(37)-C(42)	-0.7(5)
C(35)-C(36)-C(37)-C(38)	178.5(3)
C(36)-C(37)-C(38)-C(39)	179.5(4)
C(42)-C(37)-C(38)-C(39)	-1.4(5)
C(37)-C(38)-C(39)-C(40)	1.1(6)
C(38)-C(39)-C(40)-C(41)	0.0(6)
C(39)-C(40)-C(41)-C(42)	-0.9(6)
C(40)-C(41)-C(42)-C(37)	0.6(5)
C(40)-C(41)-C(42)-C(43)	179.8(3)
C(36)-C(37)-C(42)-C(41)	179.7(3)
C(38)-C(37)-C(42)-C(41)	0.5(5)
C(36)-C(37)-C(42)-C(43)	0.5(5)
C(38)-C(37)-C(42)-C(43)	-178.7(3)
C(35)-C(34)-C(43)-C(42)	0.6(5)
N(3)-C(34)-C(43)-C(42)	178.1(3)
C(41)-C(42)-C(43)-C(34)	-179.6(3)
C(37)-C(42)-C(43)-C(34)	-0.5(5)
O(2)-C(21)-N(1)-C(20)	-180.0(4)
C(3)-C(21)-N(1)-C(20)	-0.9(4)
O(2)-C(21)-N(1)-C(24)	5.9(6)
C(3)-C(21)-N(1)-C(24)	-175.0(3)
O(1)-C(20)-N(1)-C(21)	-177.3(4)
C(2)-C(20)-N(1)-C(21)	2.4(4)
O(1)-C(20)-N(1)-C(24)	-3.1(6)
C(2)-C(20)-N(1)-C(24)	176.6(3)
C(25)-C(24)-N(1)-C(21)	-144.2(4)
C(33)-C(24)-N(1)-C(21)	38.7(5)
C(25)-C(24)-N(1)-C(20)	42.4(5)
C(33)-C(24)-N(1)-C(20)	-134.6(4)
C(1)-C(12)-N(2)-C(11)	-179.1(3)
C(5)-C(12)-N(2)-C(11)	1.0(4)
C(1)-C(12)-N(2)-C(13)	-1.1(6)
C(5)-C(12)-N(2)-C(13)	179.1(3)
C(10)-C(11)-N(2)-C(12)	177.4(4)
C(6)-C(11)-N(2)-C(12)	-2.3(4)
C(10)-C(11)-N(2)-C(13)	-0.6(6)
C(6)-C(11)-N(2)-C(13)	179.7(3)
C(14)-C(13)-N(2)-C(12)	-71.1(4)
C(14)-C(13)-N(2)-C(11)	106.6(4)
O(4)-C(23)-N(3)-C(22)	-174.0(4)
C(9)-C(23)-N(3)-C(22)	5.2(4)
O(4)-C(23)-N(3)-C(34)	7.0(6)
C(9)-C(23)-N(3)-C(34)	-173.9(3)
O(3)-C(22)-N(3)-C(23)	176.5(4)
C(8)-C(22)-N(3)-C(23)	-2.8(4)
O(3)-C(22)-N(3)-C(34)	-4.5(6)
C(8)-C(22)-N(3)-C(34)	176.2(3)
C(43)-C(34)-N(3)-C(23)	-56.0(5)
C(35)-C(34)-N(3)-C(23)	121.6(4)
C(43)-C(34)-N(3)-C(22)	125.1(4)

C(35)-C(34)-N(3)-C(22)

-57.3(5)

Symmetry transformations used to generate equivalent atoms:

