Supporting Information

1,6-Naphthodione-Based Monomers and Polymers

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Experimental section

Materials. 4-Bromomandelic acid, 1.5-dihydroxynaphthalene, 1.5-diaminonaphthalene, 2,5-bis-(trimethylstannyl)thiophene (**M3**), tetrakis(triphenyl-phosphino) palladium(0), potassium carbonate and nitrobenzene were obtained from Aldrich and Fluka, and used without further purification. Solvents were of analytical grade and used without further purification.

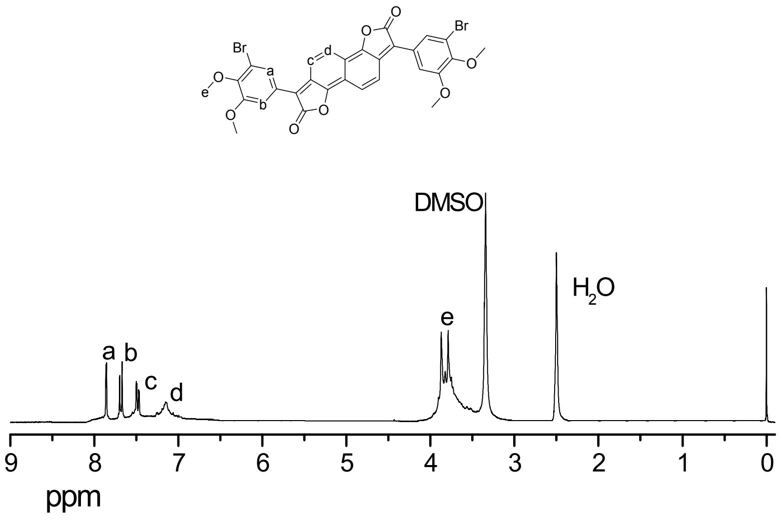
3,8-Bis(4-bromophenyl)naphtho[1,2-*b*:5,6-*b*']difuran-2,7-dione (**M1a**).

Using a Dean-Stark apparatus, 1,5-dihydroxynaphthalene (0.8 g, 5 mmol), and 4-bromomandelic acid (2.31 g, 10 mmol) are dissolved in 1,2,4-trichlorobenzene (10 ml). The reaction mixture is stirred for 4 hours at 160 ^{o}C allowing formed water to distil off, before it is cooled to room temperature. Then nitrobenzene (0.67 g, 5 mmol) is added. The mixture is stirred for another half an hour at 200 ^{o}C and allowed to cool. A precipitate is formed, which is filtered off, and washed with methanol. The crude product is dissolved in 1,2,4-trichlorobenzene at 200 ^{o}C, precipitated at room temperature, digested in hot acetic acid, and filtered. The product is subjected to Soxhlet extraction with methanol for 6 h giving a deep purple solid (1.69 g, yield: 62 %). The product is poorly soluble. NMR spectra cannot be measured. Microanalysis found C, 56.93 %, H, 2.59 % (C, 56.97 %; H, 2.21 %). UV/Vis (DMF): 560 nm.

3,8-Bis(3-bromo-4,5-dimethoxyphenyl)naphtho[1,2-*b*:5,6-*b*']difuran-2,7-dione (**M1b**).

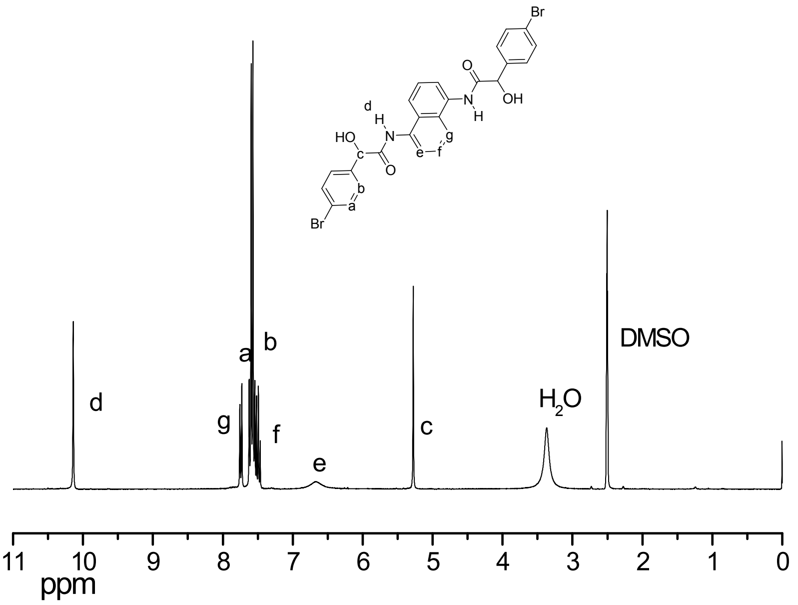
Using a Dean-Stark apparatus, 1,5-dihydroxynaphthalene (0.8 g, 5 mmol) and 3-bromo-4,5-dimethoxymandelic acid (2.92 g, 10 mmol) are dissolved in 1,2,4-trichlorobenzene (10 ml). The reaction mixture is stirred for 4 hours at 200 ^{o}C allowing formed water to distil off, before it is cooled to room temperature.

Nitrobenzene (1.23 g, 10 mmol) is added and the mixture is stirred for another hour at 160 °C. After cooling to room temperature, 50 ml methanol are added. A precipitate is formed, which is filtered off, and washed with methanol. The crude product is dissolved in 1,2,4-trichlorobenzene at 200 °C, precipitated at room temperature, digested in hot acetic acid, and filtered. The product is subjected to Soxhlet extraction with methanol for 6 h giving a dark solid (1.57 g, yield: 47 %). ^{1}H NMR (500 MHz, DMSO): δ ppm 7.85 (d, J=9 Hz, 2H), 7.68 (d, J=9 Hz, 2H), 7.46-7.50 (m, 2H), 7.14 (s, 2H), 4.01 (d, J=8Hz, 12H). ^{13}C NMR cannot be measured. Microanalysis found C, 52.01 %; H, 3.98 % (C, 53.92 %; H, 3.02 %). UV/Vis (DCM): 588 nm. ε (588) /L mol^{-1}cm^{-1}: 2.6*10^{4}.



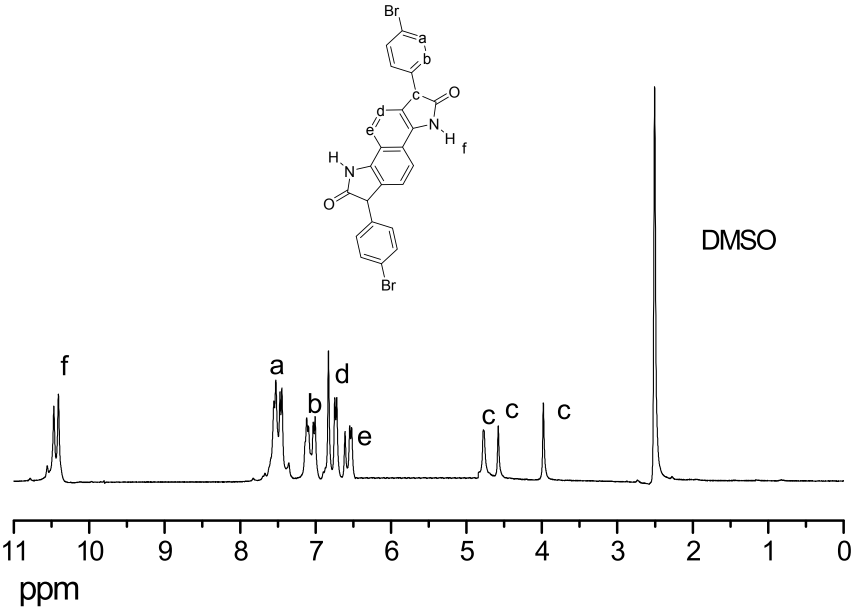
1,4-Bis(α-hydroxy(4-bromophenyl)acetylamino)naphthalene (**1**).

A mixture of 1,5-diaminonaphthalene (1.582 g, 10 mmol) and 4-bromomandelic acid (6.93 g, 30 mmol) in chlorobenzene (40 ml) is heated at 135 °C for 21 hours. On cooling to room temperature, the precipitate is filtered, washed with ethanol and dried in vacuo to yield the crude product (5.19 g, yield: 89 %). The crude product is suspended in chlorobenzene (20 ml), heated to 135 °C and stirred for 20 minutes, and then is cooled to room temperature. The precipitated product is filtered off and washed with methanol. The product is dried in air giving a white solid (4.23 g, yield: 72 %). ^{1}H NMR (300 MHz, DMSO): δ ppm 10.13 (s, 2H), 7.74 (d, J=8.1 Hz, 2H), 7.60 (d, J=8.4 Hz, 4H), 7.55 (d, J=8.4 Hz, 4H), 7.49 (t, J=8.0 Hz, 2H), 6.67 (d, J=4.8 Hz, 2H), 5.27 (d, J=4.5 Hz, 2H). ^{13}C NMR, (300MHz, $CDCl_3$): δ ppm 171.90, 140.89, 133.70, 131.56, 129.39, 129.31, 125.95, 122.80, 121.29, 120.72, 73.73. Microanalysis found C, 53.21 %; H, 3.68 %, N, 4.89 % (C, 53.45 %, H, 3.45 %, N, 4.79 %).



3,8-Di(4-bromophenyl)-2,7-dioxo-1,2,3,6,7,8-hexahydronaphtho[1,2-*b*:5,6-*b*’]dipyrrole (**2**).

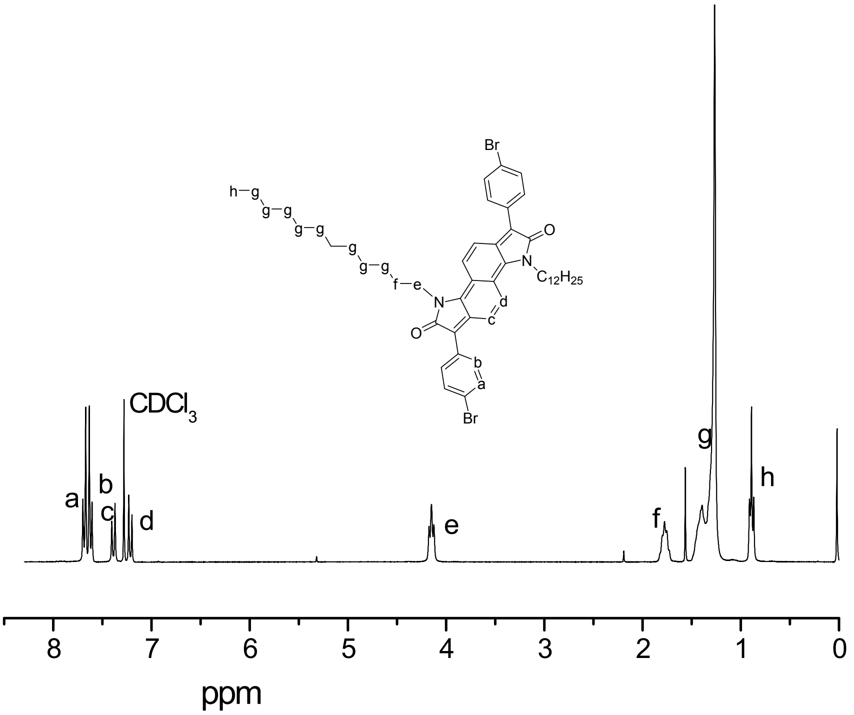
1 (3,56 g, 6.1 mmol) is added to sulfuric acid (20 ml). After stirring at room temperature for 18 hours, the mixture is poured into ice water. The precipitate is filtered, washed with water and dried to yield the product (3.16 g, yield: 95 %). ^{1}H NMR (300 MHz, DMSO): δ ppm 11.27-11.58 (m, 2H), 7.44-7.55 (m, 4H), 7.00-7.12 (m, 4H), 6.72-6.83 (t, 2H), 6.52-6.61 (t, 2H), 3.98-4.78 (t, 2H). ^{13}C NMR, (300MHz, $CDCl_3$): δ ppm 176.31, 175.48, 131.56, 130.74, 130.54, 130.26, 129.77, 129.64, 120.40, 108.78, 106.69. Microanalysis found C, 60.11 %; H, 2.98 %, N, 5.01 % (C, 59.96 %, H, 2.94 %, N, 5.11 %).



3,8-Di(4-bromophenyl)-2,7-dioxo-1,2,6,7-tetrahydronaphtho[1,2-*b*:5,6-*b*']dipyrrole (**3**). An aqueous solution of sodium hydroxide (2.11 ml, 5 N) is dropwisely added to a suspension of **2** (3.16 g, 5.8 mmol) in ethanol (18 ml). Then potassium persulfate (4.22 g, 15.7 mmol) in water (14 ml) is added. The resulting mixture is heated at reflux for 3 hours. The precipitate in the mixture is filtered, washed with water and ethanol, and dried to yield the product (2.88 g, yield: 91 %). The product is poorly soluble. NMR spectra cannot be measured. Microanalysis found C, 58.01 %; H, 2.98 %, N, 9.89 % (C, 57.17 %, H, 2.58 %, N, 5.13 %). UV/Vis (DMF): 567 nm.

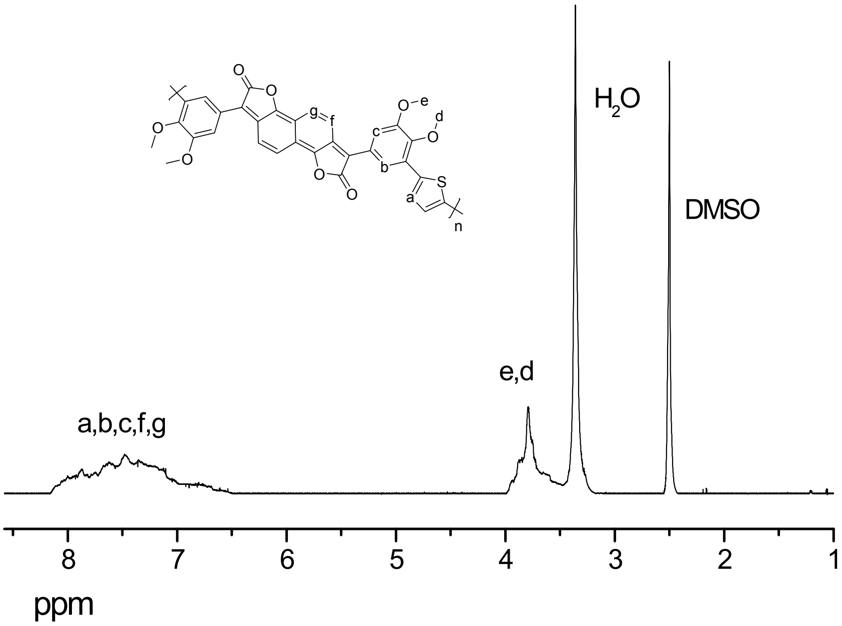
3,8-Di(4-bromophenyl)-1.6-bisdodecyl-2,7-dioxo-1,2,6,7-tetrahydronaphtho[1,2-*b*:5,6-*b*']dipyrrole (**M2**).

2 (1.5 g, 2.75 mmol) is dissolved in anhydrous dimethylformamide (40 ml) and then potassium carbonate (2.66 g, 19.25 mmol) and 1-iodododecane (3.39 g, 10.98 mmol) are added. After stirring for 12 hours at 50 ^{o}C, the mixture is poured into water and extracted with DCM. The organic layer is washed with brine and dried over anhydrous $MgSO_4$. On removal of the solvent, the crude solid product is obtained. Then the crude product is dissolved in a minimal amount of DCM and precipitated in methanol. The crude product is obtained as a dark solid (1.41 g, yield: 52 %), and purified by column chromatography on silica gel with hexane:DCM=1:2 as eluent to yield **M2** (0.54 g, 20%).^{1}H NMR (300 MHz, DMSO): δ ppm 7.65 (d, J=8.7 Hz, 4 H), 7.60 (d, J=8.7 Hz, 4 H), 7.40 (d, J=9.6 Hz, 2H), 7.15 (d, J=9.6 Hz, 2H), 4.07 (t, 4H), 1.77 (m, 4H), 1.15-1.35 (br, 36 H), 0.87-0.91 (t, 6 H). ^{13}C NMR, (300MHz, $CDCl_3$): δ ppm 131.52, 131.47, 130.6, 130.55, 123.44, 123.37, 122.70, 121.49, 119.08, 114.84, 41.96, 41.76, 31.47, 29.21, 29.13, 29.06, 28.96, 28.90, 28.80, 26.33, 22.25, 13.68. Microanalysis found C, 67.95 %; H, 7.12 %, N, 3.19 % (C, 68.02 %, H, 7.08 %, N, 3.17 %). UV/Vis (DCM): 567 nm; ε (567) /L mol^{-1}cm^{-1}: 4.6*10^{4}.



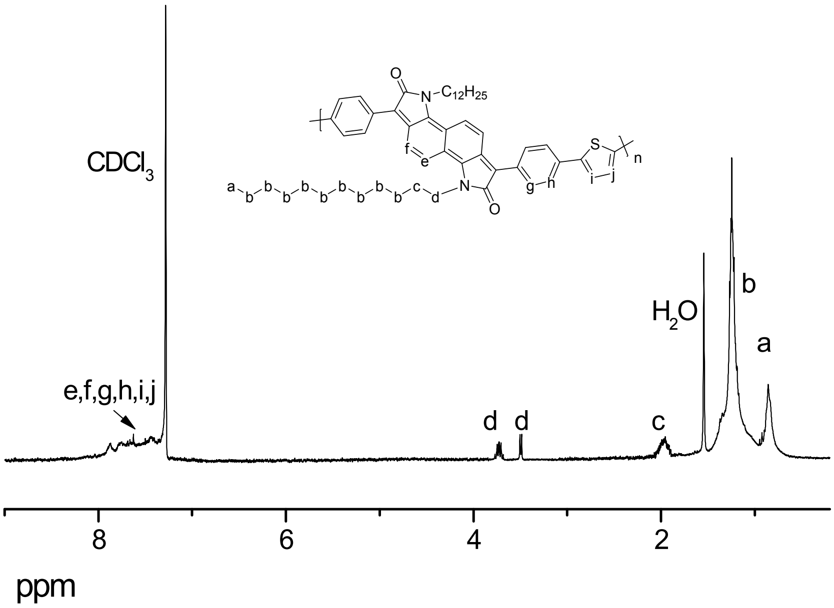
Polymer **P1**.

In a Schlenk flask, **M1b** (200.0 mg, 0.30 mmol), **M3** (122.6 mg, 0.30 mmol) and tetrakis(triphenylphosphine)palladium(0) (17.3 mg, 0.015 mmol), are dissolved in dry toluene/DMF(4/1, 10 ml). Then the mixture is heated and kept at 100 °C under nitrogen for 18 hours. After cooling to room temperature, methanol is added and a precipitate is formed. The precipitate is collected by filtration. Then the product is purified upon Soxhlet extraction with methanol and hexane. A dark solid is obtained (123 mg, yield: 45 %). ^{1}H NMR (300 MHz, DMSO): δ ppm 7.01-8.08 (br, 10 H), 3.59-3.91 (br, 12H). M_w:7.9 kDa, PDI: 1.5. UV/Vis (1,2,4-trichlorobenzene): 644 nm. ε (644) /L mol^{-1}cm^{-1}: 1.9*10^{4}. UV/Vis (thin film): 692 nm. ε (692) /cm^{-1}: 4.2*10^{5} cm^{-1}.



Polymer **P2**.

In a Schlenk flask, **M2** (200.0 mg, 0.23), **M3** (92.8 mg, 0.23 mmol) and tetrakis(triphenylphosphine)palladium(0) (10.4 mg, 0.009 mmol) are dissolved in dry DMF (10 ml). Then the mixture is heated and kept under nitrogen at 100 ^{o}C for 18 hours. After cooling to room temperature, methanol is added and a precipitate is formed. The precipitate is collected by filtration. Then the product is purified upon Soxhlet extraction with methanol and hexane. A dark solid is obtained (96.3 mg, yield: 52 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 7.02-8.04 (br, 14 H), 3.66-3.79 (m, 3H), 3.51 (d, J=6 Hz, 1H), 1.87-2.08 (s, 4H), 0.99-1.49 (s, 36H), 0.77-0.99 (s, 6H).M_w:16.7 kDa, PDI: 2.2. UV/Vis (DCM): 615 nm. ε (615) /L mol^{-1}cm^{-1}: 2.8*10^{4}. UV/Vis (thin film): 678 nm. ε (678) /cm^{-1}: 7.6*10^{5}.



Methods.

Instrumentation. UV/vis absorption spectra were recorded using a Perkin-Elmer Lambda 14 spectrometer. The polymer concentration in solution was 50 mg/L. ^{1}H-NMR spectra were recorded using a Bruker DPX 300/500 spectrometer operating at 300 or 500 MHz. Molecular weights were determined using size exclusion chromatography (SEC). A Water/Millipore UV detector 481 and a mixed gel column (Latek/Styragel 50/1000 nm pore size) were used. All measurements were carried out in tetrahydrofuran at 45 ^{o}C. The column was calibrated using commercially available polystyrene standards. The film thickness was measured using a Veeco Dektak 150. Cyclic voltammograms were recorded with a potentiostat PG 390 from Heka Company. The thin films of the polymers were cast on an ITO electrode and cycled in acetonitrile (saturated with nitrogen) containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte salt. Reference and counter electrodes were platinum. The voltage data were calculated for the standard calomel electrode (SCE). Scan rate: 100 mV s^{-1}; temperature: 20 ^{o}C. The single crystal structure of **M2** was determined with a Nonius Kappa CCD-Diffractometer Mo-K_{α} (λ=0.71073 Å) controlled by COLLECT (Nonius). The structure was solved and refined using Shelx197.

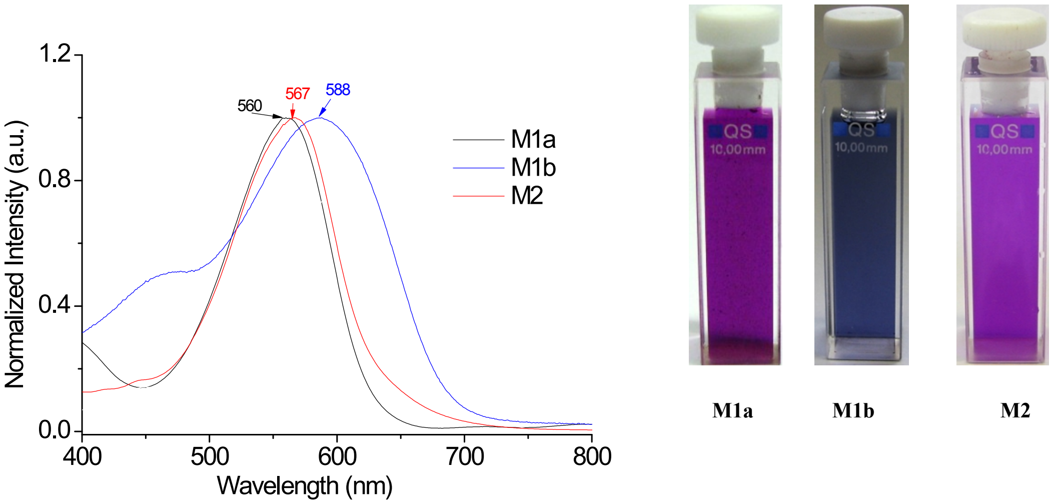


Figure S1. UV/vis absorption spectra and photographs of **M1a**, **M1b** and **M2** in dichloromethane.

Table S2. Single Crystal Structure Data of **M2**.

Bond Lengths (Angstrom).

Br(1)	-	C(1)	1.902	O(1)	-	C(6)	1.230
N(1)	-	C(6)	1.398	N(1)	-	C(7)	1.391
N(1)	-	C(25)	1.461	C(1)	-	C(2)	1.395
C(1)	-	C(23)	1.373	C(2)	-	C(3)	1.374
C(3)	-	C(4)	1.402	C(4)	-	C(5)	1.459
C(4)	-	C(24)	1.415	C(5)	-	C(6)	1.472
C(5)	-	C(8)	1.371	C(7)	-	C(8)	1.457
C(7)	-	C(11)	1.394	C(8)	-	C(9)	1.425
C(9)	-	C(10)	1.346	C(10)	-	C(11)a	1.430
C(11)	>	C(11)a	1.493	C(23)	-	C(24)	1.373
C(25)	-	C(26)	1.525	C(26)	-	C(27)	1.527
C(27)	-	C(28)	1.528	C(28)	-	C(29)	1.531
C(29)	-	C(30)	1.520	C(30)	-	C(31)	1.528
C(31)	-	C(32)	1.524	C(32)	-	C(33)	1.522
C(33)	-	C(34)	1.504	C(34)	-	C(47)	1.534
C(47)	-	C(48)	1.516	C(48)	-	H(48C)	0.96
C(2)	-	H(2)	0.93	C(3)	-	H(3)	0.93
C(9)	-	H(9)	0.93	C(10)	-	H(10)	0.93
C(23)	-	H(23)	0.93	C(24)	-	H(24)	0.93
C(25)	-	H(25A)	0.97	C(25)	-	H(25B)	0.97

C(26)	-	H(26A)	0.97	C(26)	-	H(26B)	0.97
C(27)	-	H(27A)	0.97	C(27)	-	H(27B)	0.97
C(28)	-	H(28A)	0.97	C(28)	-	H(28B)	0.97
C(29)	-	H(29A)	0.97	C(29)	-	H(29B)	0.97
C(30)	-	H(30A)	0.97	C(30)	-	H(30B)	0.97
C(31)	-	H(31A)	0.97	C(31)	-	H(31B)	0.97
C(32)	-	H(32A)	0.97	C(32)	-	H(32B)	0.97
C(33)	-	H(33A)	0.97	C(33)	-	H(33B)	0.97
C(34)	-	H(34A)	0.97	C(34)	-	H(34B)	0.97
C(47)	-	H(47A)	0.97	C(47)	-	H(47B)	0.97
C(48)	-	H(48A)	0.96	C(48)	-	H(48B)	0.96

Bond/Valence Angles (Degrees)

C(6) -N(1) -C(7)	109.9	C(6) -N(1) -C(25)	119.8
C(7) -N(1) -C(25)	130.2	C(2) -C(1) -C(23)	121.7
C(1) -C(2) -C(3)	118.3	C(2) -C(3) -C(4)	122.5
C(3) -C(4) -C(5)	123.0	C(3) -C(4) -C(24)	116.5
C(5) -C(4) -C(24)	120.4	C(4) -C(5) -C(6)	123.4
C(4) -C(5) -C(8)	129.6	C(6) -C(5) -C(8)	106.9
O(1) -C(6) -N(1)	123.5	O(1) -C(6) -C(5)	129.4
N(1) -C(6) -C(5)	107.1	N(1) -C(7) -C(8)	106.6
N(1) -C(7) -C(11)	130.5	C(8) -C(7) -C(11)	123.0
C(5) -C(8) -C(7)	109.4	C(5) -C(8) -C(9)	132.4
C(7) -C(8) -C(9)	118.2	C(8) -C(9) -C(10)	121.5
C(9) -C(10)-C(11)a	121.3	C(7) -C(11)-C(10)a	124.0
C(7) -C(11)-C(11)a	115.5	C(1) -C(23)-C(24)	119.2
C(4) -C(24)-C(23)	121.9	N(1) -C(25)-C(26)	114.2
C(25)-C(26)-C(27)	112.3	C(26)-C(27)-C(28)	112.4
C(27)-C(28)-C(29)	114.0	C(28)-C(29)-C(30)	113.4
C(29)-C(30)-C(31)	114.9	C(30)-C(31)-C(32)	111.6
C(31)-C(32)-C(33)	115.1	C(32)-C(33)-C(34)	115.6
Br(1)-C(1) -C(2)	118.7	Br(1)-C(1) -C(23)	119.6
C(10)a-C(11)-C(11)a	120.5		

Torsion/Dihedral Angles (Degrees)

C(24)-C(4)-C(5)-C(8)	24.9	C(3)-C(4)-C(5)-C(6)	26.6
C(3)-C(4)-C(5)-C(8)	-159.2	C(24)-C(4)-C(5)-C(6)	-149.4