Supporting Information

Experimental Descriptions of all compounds S1-S15

Tables of Reaction Conditions attempted in cycloadditions S-16-S-18

Selected NMR and IR Spectra S-19-S27

An Ortho-Iminothio Quinone: Its Cycloaddition to Produce an Indologlycoside and its Self-dimerization to Form a Dithio-Diazocycloctane, the Structure Assignment of which is Based on the DFT Prediction of its IR Spectrum

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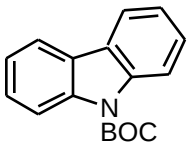
Experimental

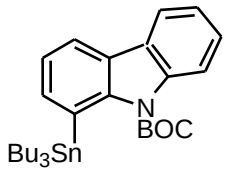
All reactions were carried out under a dry argon/nitrogen atmosphere at ambient temperature unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} (E. Merck) plates unless otherwise stated, and short/long wave ultraviolet (UV) light was used to visualize the spots. Flash column chromatography was carried out on silica gel 60 (230-400 mesh). Chromatotron (radial chromatography) plates were prepared by using Kiesegel 60 F_{254} gipshaltig (E. Merck). Petroleum ether, dichloromethane, and ethyl acetate used as eluting solvents were ACS reagent grade. Molecular sieves (Aldrich Chemical Co.) were activated by heating in an oven (>100 ^{o}C) overnight or by heating them with a Bunsen burner under high vacuum. The following reaction solvents were purified and dried by using standard distillation procedures: tetrahydrofuran (THF, refluxing over sodium metal with benzophenone as indicator), ether (refluxing over sodium metal with benzophenone as indicator), and

[%] Taken in part from doctoral thesis submitted by V.D. to the Graduate School of CUNY in 2002.

methylene chloride (CH_2Cl_2, refluxing over P_2O_5. NMR spectra were measured at 300 MHz with $CDCl_3$ as the solvent unless otherwise stated. Infrared spectra were recorded on a Perkin-Elmer 1310 spectrophotometer. Melting points were determined on a Fisher-Johns melting point apparatus.

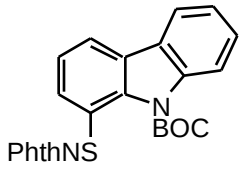


***tert*-Butylcarbazole-9-carboxylate**. Carbazole (1.00 g, 5.99 mmol, 1.0 eq) was dissolved in dry acetonitrile(25 mL). Di-*tert*-butyldicarbonate (2.60 mL, 11.32 mmol, 1.9 eq) was added as a neat liquid. DMAP (0.735 g, 6.01 mmol, 1.0 eq) was added in one portion. The reaction mixture was stirred for 1h 45min. After column chromatography (2% ethyl acetate/ pet. ether), a colorless oil was obtained in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) __1.76 (9H, s, t-Bu), 7.34 (2H, t, J = 7.5 Hz), 7.46 (2H, t, J = 7.8 Hz), 7.96 (2H, d, J = 7.8 Hz), 8.30 (2H, d, J = 8.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) __28.7, 84.1, 116.4, 119.7, 123.1, 125.9, 127.2, 138.7, 151.2.



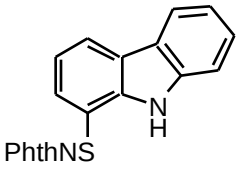
***tert*-Butyl-1-(1,1-dibutyl-1-stannapentyl)carbazole-9-carboxylate.** Under an argon atmosphere, a 1.3 M solution of *s*-BuLi in cyclohexane (1.35 mL, 1.76 mmol, 1.57 eq) was added dropwise to a stirred solution of *tert*-butylcarbazole-9-carboxylate 0.298 g, 1.12 mmol, 1.0 eq) and TMEDA (0.22 mL, 1.47 mmol, 1.3 eq) in 5 mL of ether at -78 ^{o}C. After stirring for 1 hour, Bu_3SnCl (0.46 mL, 1.6 mmol, 1.5 eq) was added as a neat liquid *via* a syringe. After stirring for another 30 minutes at -78 ^{o}C, the reaction mixture was removed from the dry ice-acetone bath and was allowed to stir for an additional 1 hour. The reaction mixture was quenched with water and the products were extracted with ether (3 x 15 mL). The combined ether extracts were washed with water (25 mL) and then with saturated NaCl solution (25 mL), dried over Na_2SO_4, and evaporated. This compound was purified by basic alumina column chromatography (petroleum ether) to give a colorless oil (10%). ^{1}H NMR (300 MHz, $CDCl_3$) __0.87 (9H, t, J = 7.05 Hz), 1.08 (6H, t, J = 8.25 Hz), 1.33 (6H, sextet, J = 7.32 Hz), 1.55 (6H, quintet, J = 7.51 Hz), 1.72 (9H, singlet), 7.32 (2H, t, J = 7.46 Hz), 7.40 (1H, t, J = 7.87 Hz), 7.64 (1H, d, J = 6.95 Hz), 7.93 (2H, t, J = 7.69 Hz), 8.07 (1H, d, J = 8.43 Hz); ^{13}C NMR (300 MHz, $CDCl_3$)

__13.9, 14.0, 27.9, 28.8, 29.5, 84.3, 117.1, 119.4, 119.5, 123.3 (2), 126.0, 126.7, 126.7, 131.4, 137.2, 138.4, 146.1, 152.2.



***tert*-Butyl-1-(1,3-dioxoisointolin-2-ylthio)carbazole-9-carboxylate.** To a stirred solution of *tert*-butyl-1-(1,1-dibutyl-1-stannapentyl)carbazole-9-carboxylate, 69.8 mg, 0.125 mmol, 1.0 eq) and 2,6-lutidine (0.0145 mL, 0.124 mmol, 1.0 eq) in methylene chloride (1 mL, dry) under reflux was added phthalimide-N-sulfenyl chloride (115 mg, 0.54 mmol, 4.35 eq, in 3 mL of dry methylene chloride). After stirring for 1.5 hours with reflux, the reaction mixture was quenched with saturated aqueous ammonium chloride solution (10 mL), separated, and the aqueous layer was washed with CH_2Cl_2 (3 x 10 mL). The CH_2Cl_2 layers were combined, washed with potassium fluoride solution (10 g KF/100 mL H_2O solution), dried over anhydrous Na_2SO_4, and concentrated with a rotary evaporator. Purification was done using silica gel column chromatography (25% ethyl acetate/petroleum ether) to give 38.1 mg (68%) of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) __1.75 (9H, s), 7.22 (2H, m), 7.35 (1H, t, J = 7.51 Hz), 7.48 (1H, t, J = 8.43

Hz), 7.76 (3H, t of d, J = 2.93 Hz, J = 5.86 Hz), 7.91 (3H, m), 8.08 (1H, d, J = 8.05 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) __28.5, 85.6, 116.5, 118.6, 120.1, 123.7, 124.1, 124.8, 125.4, 126.0, 126.3, 127.5, 127.6, 132.3, 134.7, 136.8, 139.4, 152.5, 168.3.



2-Carbazolylthioisoindoline-1,3-dione 30. To a solution of *tert*-butyl-1-(1,3-dioxoisointolin-2-ylthio)carbazole-9-carboxylate, 26.7 mg, 0.060 mmol, 1.0 eq) in methylene chloride (1 mL) was added trifluoroacetic acid (0.50 mL, 0.65 mmol, 11 eq). After stirring for 23 hours at room temperature, the reaction mixture was quenched with saturated sodium carbonate solution. The aqueous layer was washed 3 times with methylene chloride and the organic layers were combined, dried over anhydrous sodium sulfate, concentrated, and after column chromatography (10% ethyl acetate/petroleum ether), the desired product was obtained (13.8 mg, 67%). R_f 0.33 (20% ethyl acetate/pet. ether); ^{1}H NMR (300 MHz, $CDCl_3$) __7.20 (1H, t, J = 7.69 Hz), 7.26 (1H, t, J = 3.45 Hz), 7.48 (1H, t of d, J = 8.1 Hz, J = 1.2 Hz), 7.64 (1H, d, J = 8.1 Hz), 7.71 (2H, dd, J = 5.4

Hz, J = 3.0 Hz), 7.87 (2H, dd, J = 5.4 Hz, J = 3.0 Hz), 7.99 (1H, dd, J = 7.69 Hz, J = 1.10 Hz), 8.03 (1H, d, J = 7.8 Hz), 8.15 (1H, d, J = 7.69 Hz or 7.8 Hz), 9.92 (1H, s, N-H).

1-(*tert*-Butoxycarbonyl)indoline 18. To a stirred solution of indoline (1.7 mL, 15 mmol1.0 eq) in THF (18 mL) was added di-*tert*-butyldicarbonate (3.7 mL, 16 mmol, 1.1 eq). The reaction mixture was stirred overnight (25 1/3 h) at room temperature and the solvent was removed with a rotary evaporator. The residual liquid was distilled under reduced pressure (Kugelrohr distillation) to give the product as a colorless oil (3.14 g, 94%), bp 148 ^{o}C (oven temperature)/0.20-0.15 mmHg, which on standing solidifies. R_f 0.5 (20% ethyl acetate/petroleum ether); mp 44-45 ^{o}C (lit. 42-45 ^{o}C)[9]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (9H, s, *t*-Bu), 3.09 (2H, t, J = 8.7 Hz, H-3), 3.97 (2H, t, J = 8.7 Hz, H-2), 6.92 (1H, t, J = 7.5 Hz, H-5), 7.13-7.18 (2H, m, H-4, H-6), 7.3-7.8 (1H, broad, H-7); ^{13}C NMR (300 MHz, $CDCl_3$) δ 27.4, 28.6, 47.7, 80.7, 114.7, 122.1, 124.7, 127.3, 131.2, 142.5, 152.6; IR (KBr, cm^{-1}) 1703.7.

1-(*tert*-Butoxycarbonyl)-7-phenylthioindoline 19. Under an argon (or nitrogen) atmosphere, a 1.3 M solution of *s*-BuLi in cyclohexane (1.2 mL, 1.6 mmol, 1.3 eq) was added dropwise to a stirred solution of 1-(*tert*-butoxycarbonyl)indoline (*tert*-butylindoline carboxylate, 0.27 g, 1.2 mmol, 1.0 eq) and TMEDA (0.25 mL, 1.7 mmol, 1.4 eq, dry) in 6 mL of ether at -78 ^{o}C. A yellow-orange mixture was formed. After stirring for 1 hour, phenyl disulfide (0.40 g, 1.8 mmol, 1.5 eq) was added as an ether (2

mL) solution *via* a syringe. The reaction mixture was stirred for 30 minutes at -78 ^{o}C, then the dry ice-acetone bath was removed and the reaction mixture was stirred for an additional 1 hour. The reaction mixture was quenched with water and the products were extracted with ether (4 x 10 mL). The combined ether extracts were washed with water (50 mL) and then with saturated NaCl solution (50 mL), dried over Na_2SO_4, and evaporated. Separation was performed using a 2-mm chromatotron plate (2-10% ethyl acetate in petroleum ether) to give a white solid after removal of the solvent (0.24 g, 60%). R_f 0.29 (10% ethyl acetate in petroleum ether; 0.55 in CH_2Cl_2); mp 114-116 ^{o}C (lit. 114-115 ^{o}C)[9]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (9H, s, *t*-Bu), 3.04 (2H, t, J = 7.8 Hz, H-3), 4.14 (2H, t, J = 7.8 Hz, H-2), 6.87 (1H, dd, J = 7.8 Hz, 7.0 Hz, H-5), 6.92 (1H, dd, J = 7.8 Hz, 0.9 Hz, H-6), 7.02 (1H, dd, J = 7.0 Hz, 0.9 Hz, H-4), 7.20-7.30 (3H, m, SPh), 7.30-7.36 (2H, m, SPh); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.6, 29.9, 51.0, 81.7, 122.5, 124.9, 127.2, 129.1, 130.5, 132.4, 134.7, 137.3, 142.6, 154.0.

1-(*tert*-Butoxycarbonyl)-7-tributylstannylindoline 20. Under an argon atmosphere, a 1.3 M solution of *s*-BuLi in cyclohexane (3.0 mL, 3.9 mmol, 1.3 eq) was added dropwise to a stirred solution of 1-(*tert*-butoxycarbonyl)indoline **18** (0.66 g, 3.0 mmol, 1.0 eq) and TMEDA (0.59 mL, 3.9 mmol, 1.3 eq, dry) in 15 mL of ether at -78 ^{o}C. After stirring for 1 hour, Bu_3SnCl (4.6 mmol, 1.5 eq) was added as a neat liquid *via* a syringe. After stirring for another 30 minutes at -78 ^{o}C, the reaction mixture was removed from the dry ice-acetone bath and was allowed to stir for an additional 1 hour. The reaction mixture was

quenched with water and the products were extracted with ether. The combined ether extracts were washed with water and then with saturated NaCl solution, dried over anhydrous sodium sulfate, and evaporated. This compound was purified by basic alumina column chromatography (petroleum ether) to give a colorless oil (73%). R_f 0.58 (petroleum ether, on neutral alumina), ^{1}H NMR (300 MHz, $CDCl_3$) δ_0.87(9H, t, J= 7.2 Hz) , 0.97 (6H, m, -CH_2- of Bu), 1.32 (6 H, sextet, J = 7.2 Hz, -CH_2- of Bu), 1.4-1.6 (6H, m), 1.51 (9H, s, *t*-Bu), 3.00 (2H, t, J = 8.4 Hz, H-3), 3.96 (2H, t, J = 8.4 Hz, H-2), 6.93 (1H, t, J = 7.2 Hz, H-5), 7.10 (1H, dd, J = 7.5 Hz, 1.2 Hz, H-4), 7.32 (1H, dd, J = 6.6 Hz, 1.2 Hz, H-6); ^{13}C NMR (300 MHz, $CDCl_3$) δ13.2, 14.0, 27.9, 28.2, 28.8, 29.6, 48.2, 80.7, 122.8, 124.5, 130.5, 131.5, 136.6, 149.2, 153.7; IR (KBr, cm^{-1}) 1693.8; MS Calcd for $C_{25}H_{43}NO_2Sn$: 507.2312. Found *m/z* 506.1 (36), 507.2 (31), 508.1 (71), 509.1 (38), 510.2 (98), 511.2 (25), 512.2 (15), 513.2 (6), 514.2 (14).

***tert*-Butyl-7-(1,3-dioxoisoindolin-2-ylthio)indoline carboxylate 21.** To a stirred solution of 1-(*tert*-butoxycarbonyl)-7-tributylstannyl indoline **20** (0.27 g, 0.53 mmol, 1.0 eq) and 2,6-lutidine (0.1 mL, 0.86 mmol, 1.6 eq) in methylene chloride (1 mL, dry) was added phthalimide-N-sulfenyl chloride (0.57 g, 2.3 mmol, 4.3 eq). After stirring for 2.5 hours at room temperature, the reaction mixture was quenched with saturated aqueous ammonium chloride solution, separated, and the aqueous layer was washed with CH_2Cl_2. The CH_2Cl_2 layers were combined, washed with potassium fluoride solution (10 g KF/100 mL H_2O solution), dried over anhydrous sodium sulfate, and concentrated with a

rotary evaporator. Purification was done using silica gel column chromatography (20% ethyl acetate/petroleum ether) (0.20 g, 94%). R_f 0.37 (30% ethyl acetate/petroleum ether); mp ~140 ^oC (decomposition); ^1H NMR (300 MHz, $CDCl_3$) δ 1.57 (9H, s, *t*-Bu), 3.07 (2H, t, J = 8.1 Hz, H-3), 4.15 (2H, t, J = 8.1 Hz, H-2), 6.86 (1H, t, J = 7.5 Hz, H-5), 6.93 (1H, d, J = 7.5 Hz, H-4), 6.99 (1H, d, J = 6.9 Hz, H-6), 7.76-7.79 (4H, m, Phth-H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.5, 29.4, 49.5, 82.3, 123.3, 125.5, 124.0, 125.2, 126.1, 132.5, 133.7, 134.5, 140.5, 154.7, 168.6; IR (KBr, cm^{-1}) 1734.8; MS Calcd for $C_{21}H_{20}N_2O_4S$: 396.1144. Found: *m/z* 397 ($M+H^+$), 414 ($M+NH_4^+$); *Anal*. Calcd for $C_{21}H_{20}N_2O_4S$: C, 63.62; H, 5.08; N, 7.07; S, 8.09. Found: C, 62.85; H, 5.05; N, 6.80; S, 8.00.

2-Indolin-7-ylthioindoline-1,3-dione 14. To a solution of *tert*-butyl-7-(1,3-dioxoisoindolin-2-ylthio)indolinecarboxylate (**21**, 1.35 g, 3.40 mmol, 1.0 eq) in methylene chloride (25 mL) was added trifluoroacetic acid (2.6 mL, 34 mmol, 10 eq). After stirring for 2 hours at room temperature, the reaction mixture was quenched with saturated sodium carbonate solution. The aqueous layer was washed 4 times with methylene chloride and the organic layers were combined, dried over anhydrous sodium sulfate, concentrated, and after column chromatography (15% ethyl acetate/petroleum ether), the desired product was obtained (0.703 g, 70%). R_f 0.48 (20% ethyl acetate/petroleum ether); mp 160-170 ^oC (decomposition); ^1H NMR (300 MHz, $CDCl_3$) δ 3.06 (2H, t, J = 8.5 Hz, H-3), 3.66 (2H, t, J = 8.5 Hz, H-2), 5.69 (1H, broad singlet, N-

H), 6.52 (1H , t, J = 7.35 Hz, H-5), 7.08 (1H, d, J = 7.2 Hz, H-6), 7.47 (1H, d, J = 8.1 Hz, H-4), 7.72-7.89 (4H, m, Phth-H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 30.8, 46.9, 110.8, 117.6, 124.1, 128.1, 130.5, 132.4, 134.7, 136.0, 156.7, 168.8; IR (KBr, cm-1) 3357.8 (broad), 1728.1, 1703.1; MS Calcd for $C_{16}H_{12}N2O_2S$: 296.0619. Found *m/z* 297 ($M+H^+$); *Anal*. Calcd for $C_{16}H_{12}N_2O_2S$: C, 64.85; H, 4.08; N, 9.45; S, 10.82. Found: C, 64.97; H, 4.24; N, 9.35; S, 10.83.

Cycloaddition to form N-glycoside 22 Method A-In a typical experiment, heterodiene precursor **21** and 3,4,6-tri-*O*-benzyl-D-glucal **7**(1-5 eq) were dissolved in dry CH_2Cl_2. The appropriate silica gel (10 x mass of 3,4,6-Tri-*O*-benzyl-D-glucal) was then added. The solvent was then removed to dryness using a rotary evaporator. The flask containing the dry mixture of diene precursor **21**, 3,4,6-tri-*O*-benzyl-D-glucal **7**, and silica gel was subject to low pressure by attaching it to a vacuum pump and heated to 50-55 ^{o}C for the desired reaction time.(see Table in Supporting Information for sets of other conditions)

Method B Cycloaddition between 2-indolin-7-ylthioindoline-1,3-dione (**14**) and 3,4,6-tri-*O*-benzyl-D- glucal (**7**). When silica gel was used, the procedure was the same as that for the cycloaddtition between **21** and glucal. When no silica gel was used, a typical procedure was as follows: 2-Indolin-7-ylthioindoline-1,3-dione (**14**, 45 mg, 0.15 mmol, 1.0 eq) and 3,4,6-tri-*O*-benzyl glucal **7** (127 mg, 0.31 mmol, 2.0 eq) were dissolved in methylene chloride (1 mL, dry) and stirred at room temperature for 3 days. The reaction mixture was concentrated and after separation on a 1-mm chromatotron plate, 8.1 mg

(9%) of the cycloadduct was obtained .(see Table in Supporting Information for sets of other conditions). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.93 (2H, t, J = 9.5 Hz), 3.14 (1H, quartet, J = 10.1 Hz), 3.35 (1H, dd, J = 10.8 Hz, 3.6 Hz), 3.58 (1H, m), 3.73 (3H, m), 3.91 (1H, m), 4.11 (1H, m), 4.52 (2H, t, J = 11.1 Hz), 4.65 (1H, d, J = 12.3 Hz), 4.78 (1H, d, J = 10.5 Hz), 4.84 (1H, d, J = 10.8 Hz), 4.90 (1H, d, J = 3.6 Hz), 5.00 (1H, d, J = 10.2 Hz), 6.66 (1H, t, J = 7.5 Hz), 6.86 (2H, t, J = 8.7 Hz), 7.12-7.73 (15 H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.4, 46.4, 51.2, 69.1, 69.8, 71.8, 73.8, 75.3, 79.6, 81.4, 82.3, 112.2, 120.4, 121.2, 123.6, 127.9, 128.0, 128.1, 128.1, 128.2, 128.3, 128.6, 129.2, 130.2, 138.3, 138.4, 145.1; MS Calcd for $C_{35}H_{35}NO_4S$: 565.2282. Found m/z 566 ($M+H^+$), 434 (TBG + NH_4^+); *Anal*. Calcd for $C_{35}H_{35}NO_4S$: C, 74.31; H, 6.24; N, 2.48; S, 5.67. Found: C, 74.03; H, 6.28; N, 2.35; S, 5.60.

Dimer 31 ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.83 (2H, m), 3.06 (2H, m), 3.69 (4H, m), 6.64 (2H, t, J = 7.5 Hz), 7.03 (2H, d, J = 7.2 Hz), 7.23 (2H, d, J = 7.8 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 29.1, 58.1, 118.6, 119.4, 127.2, 132.3, 135.9, 151.4; IR (KBr, cm-1) 739.1, 768.0, 948.8, 1057.7, 1216.9, 1244.2, 1418.2, 1592.1; MS Calcd for $C_{16}H_{14}N_2S_2$: 298.0598. Found *m/z* 299 ($M+H^+$).

1-(*tert*-Butoxycarbonyl)-7-tributylstannyl-5-chloroindoline 25. Under an inert (N_2) atmosphere, a 1.3 M solution of *s*-BuLi in cyclohexane (2.0 mL, 2.6 mmol, 1.7 eq) was added dropwise to a stirred solution of 1-(*tert*-butoxycarbonyl)-5-chloroindoline **24** (0.38

g, 1.5 mmol, 1.0 eq) and TMEDA (0.30 mL, 2.0 mmol, 1.3 eq, dry) in 15 mL of THF at -78 ^{o}C. After stirring for 1 hour, Bu_3SnCl (0.81 mL, 3.0 mmol, 2.0 eq) was added as a neat liquid *via* a syringe. After stirring for another 30 minutes at -78 ^{o}C, the reaction mixture was allowed to warm to room temperature and stirred for an additional 1 hour. The reaction mixture was quenched with water and the products were extracted with ether. The combined ether extracts were washed with water and then with saturated NaCl solution, dried over anhydrous sodium sulfate, and evaporated. This compound was purified by basic alumina column chromatography (petroleum ether) to give a colorless oil (75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (9H, t, J = 7.2 Hz, CH_3 of Bu), 0.98 (6H, t, J = 8.2 Hz, -CH_2- of Bu), 1.31 (6 H, sextet, J = 7.2 Hz, -CH_2- of Bu), 1.4-1.6 (6H, m, -CH_2- of Bu), 1.51 (9H, s, CH_3 of *t*-Bu), 2.97 (2H, t, J = 8.4 Hz, H-3), 3.96 (2H, t, J = 8.4 Hz, H-2), 7.05 (1H, d, J = 1.5 Hz, H-4), 7.24 (1H, d, J = 2.1 Hz, H-6). ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.3, 13.9, 27.7, 28.0, 28.7, 29.4, 48.3, 81.1, 124.5, 128.4, 132.7, 133.5, 135.8, 147.8, 153.7. IR (KBr, cm^{-1}) 1694.0.

***tert*-Butyl-7-(1,3-dioxoisoindolin-2-ylthio)-5-chloroindolinecarboxylate 26.** To a stirred solution of 1-(*tert*-butoxycarbonyl)-5-chloro-7-tributylstannylindoline **25**, 0.18 g, 0.32 mmol, 1.0 eq) and 2,6-lutidine (0.38 mL, 0.33 mmol, 1.0 eq) in methylene chloride (2 mL, dry) under reflux was added phthalimide-N-sulfenyl chloride (0.19 g, 75% pure, 0.67 mmol, 2.1 eq, in 3 mL of dry methylene chloride). After stirring for 1 hour with

reflux, the reaction mixture was quenched with saturated aqueous ammonium chloride solution, separated, and the aqueous layer was washed with CH_2Cl_2. The CH_2Cl_2 layers were combined, washed with potassium fluoride solution (10 g KF/100 mL H_2O solution), dried over anhydrous sodium sulfate, and concentrated with a rotary evaporator. Purification was done using silica gel column chromatography (20% ethyl acetate/petroleum ether) (0.11 g, 82%). R_f 0.54 (1:1 ethyl acetate/pet. ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (9H, s, *t*-Bu), 3.06 (2H, t, J = 8.1 Hz, H-3), 4.15 (2H, t, J = 8.1 Hz, H-2), 6.88 (1H, d, J = 1.5 Hz, H-4), 6.97 (1H, d, J = 1.5 Hz, H-6), 7.77-7.95 (4H, m, Phth-H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.6, 29.4, 49.7, 82.7, 123.6, 124.2, 124.9, 127.4, 130.0, 132.3, 134.8, 135.4, 139.2, 154.5, 168.2; MS Calcd for $C_{21}H_{19}ClN_2O_4S$: 430.0754. Found *m/z* 453 ($M+Na^+$).

2-(5-Chloroindolin-7-ylthio)isoindoline-1,3-dione 27. To a solution of *tert*-butyl-7-(1,3-dioxoisoindolin-2-ylthio)-5-chloroindolinecarboxylate **26**, 0.43 g, 0.99 mmol, 1.0 eq) in methylene chloride (18 mL) was added trifluoroacetic acid (1.5 mL, 19 mmol, 19 eq) *via* a syringe in one portion. After stirring for 1.5 hours at room temperature, the reaction mixture was quenched with saturated aqueous sodium carbonate solution (saturated). The aqueous layer was washed 3 times with methylene chloride and the organic layers were combined, dried over anhydrous sodium sulfate, concentrated, and after column chromatography (20-25% ethyl acetate/pet. ether), quantitative yield of the

desired product was obtained; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.05 (2H, t, J = 8.5 Hz. H-3), 3.68 (2H, t, J = 8.5 Hz, H-2), 5.67 (1H, s, N-H), 7.01 (1H , s, H-4), 7.45 (1H, s, H-6), 7.73-7.90 (4H, m, Phth-H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 30.2, 47.2, 110.9, 121.2, 124.1, 128.3, 132.2, 132.3, 134.4, 134.7, 155.3, 168.5; *Anal*. Calcd for $C_{16}H_{11}ClN_2O_2S$: C, 58.09; H, 3.35; Cl, 10.72; N, 8.47; S, 9.69. Found: C, 57.89; H, 3.36; Cl, 11.14; N, 8.28; S, 9.29; MS Calcd for $C_{16}H_{11}ClN_2O_2S$: 330.0230. Found m/z 331 ($M+H^+$), 353 ($M+Na^+$).

Cycloaddition to form N-glycoside 28). A typical experiment: 2-(5-chloroindolin-7-ylthio)isoindoline-1,3-dione **27**, 66.5 mg, 0.201 mmol, 1.0 eq) and 3,4,6-tri-*O*-benzyl-D-glucal **7** (168.8 mg, 0.405 mmol, 2.0 eq) were dissolved in methylene chloride (2 mL, dry) and stirred under reflux for 1 day. The reaction mixture was concentrated and after silica gel column chromatography (pet ether to 5% ethyl acetate/pet ether), 70.4 mg (58%) of the cycloadduct was obtained. R_f 0.41 (20% ethyl acetate/pet. ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.90 (2H, t, J = 10.4 Hz), 3.15 (1H, quartet, J = 10.3 Hz), 3.33 (1H, dd, J = 10.8 Hz, 3.5 Hz), 3.58 (1H, t, J = 8.25 Hz), 3.72 (3H, m), 3.86 (1H, t, J = 9.7 Hz), 4.09 (1H, t, J = 7.8 Hz), 4.51 (1H, d, J = 10.7 Hz), 4.55 (1H, d, J = 12.4 Hz), 4.64 (1H, d, J = 12.1 Hz), 4.79 (1H, d, J = 10.5 Hz), 4.83 (1H, d, J = 10.8 Hz), 4.87 (1H, d, J = 3.5 Hz), 4.96 (1H, d, J = 10.2 Hz), 6.81-7.41 (17 H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.23, 46.35, 51.31, 69.04, 71.94, 73.87, 75.34, 76.74, 79.62, 81.31, 82.10, 113.41,

121.48, 122.94, 124.85, 127.88, 127.99, 128.14, 128.26, 128.56, 128.63, 128.97, 131.50, 138.13, 138.18, 138.37, 143.68; *Anal*. Calcd for $C_{35}H_{34}NO_4S$: C, 70.04; H, 5.71; N, 2.33. Found: C, 69.10; H, 5.66; N, 2.14.

1-(*tert*-Butoxycarbonyl)-5-chloroindoline 24. A mixture of 5-chloroindoline (0.21 g, 1.4 mmol, 1.0 eq) and di-*tert*-butyl dicarbonate (0.38 mL, 1.7 mmol, 1.2 eq) in ether (5 mL) was stirred overnight at room temperature for 2 days. After silica gel column chromatography (2.5 % ethyl acetate/petroleum ether), 0.34 g (96%) of the desired product was obtained. R_f 0.58 (20% ethyl acetate/petroleum ether); mp 129-130 ^oC (lit. 130-130.5 ^oC)[9]; ^1H NMR (300 MHz, $CDCl_3$) δ 1.55 (9H, s, *t*-Boc), 3.05 (2H, t, J = 8.7 Hz, H-3), 3.97 (2H, t, J = 8.7 Hz, H-2), 7.08 (1H, s, H-6), 7.09 (1H, d, J = 8.4 Hz, H-4), 7.73 (1H, broad singlet, H-7); ^{13}C NMR (300 MHz, $CDCl_3$) δ 27.4, 28.7, 48.0, 81.0, 115.6, 124.9, 127.1, 127.3, 133.0, 142.0, 152.4; IR (KBr, cm^{-1}) 1707.8, 1479.8, 1390.0, 1329.9, 1255.6, 1142.0, 1019.5, 873.6, 823.2, 762.5.