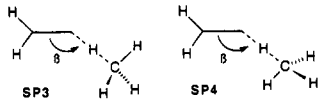
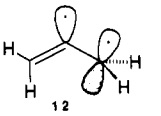
1,2-cyclodecadiene[7a] must proceed through a substantially nonlinear geometry. Estimates of saddle point "flexibility" are available for 1 and 2. Initial attempts to locate the saddle point for 1 with a UHF/STO-3G wavefunction gave two geometries, SP3 and SP4, both with β = ca. 150°.



With the 3-21G basis set, both SP3 and SP4 collapsed to the linear SP2 geometry, however, both were only 1.3 kcal/mol (UHF/3-21G) higher than SP1. This result indicates that *substantial out-of-plane bending will have a very small effect on the saddle point energy.* Indeed, entropic differences might cancel these small differences in enthalpy. As a consequence, intramolecular hydrogen abstraction or abstraction in matrices may be insensitive to modest geometric changes. We are exploring the generality of this observation for other triplet carbenes. For planar triplet allene (2), we performed similar calculations in which β was systematically varied while the C1–H distance was fixed at the SP2 value. At the UHF/3-21G//STO-3G level, relative energetics were as follows: β = 180°, 0.0 kcal/mol; 170°, 1.6; 160°, 5.3; 150°, 10.6; 140°, 25.1. These data indicate that hydrogen abstraction by 2 should be much more sensitive to geometry. These differences presumably arise because the half-filled out-of-plane orbital in 1 is concentrated at C1, while in 2, there is a node at this site.

Predicted activation and reaction energies (Table II) are not strongly dependent on the level of calculation. It is remarkable that the HF/3-21G calculation compares well to UMP3/6-31G*, which requires ca. 50 times the computational effort for a single point.

One additional question is the existence of other triplet C_3H_4 species. We conducted a limited search using triplet MCSCF or UHF wavefunctions. Intermediates with D_{2h}, D_2, or C_2 symmetry all collapsed to 2. In addition to π bond twisting ($D_{2d} \rightarrow C_2$ or $D_{2d} \rightarrow D_2$), inplane bending ($D_{2d} \rightarrow C_s$) leads to substantial stabilization of the lowest triplet state of allene.[19] MCSCF or UHF geometry optimization, with restriction to C_s symmetry, gives a $^3A'$ species, best characterized as 12. Energetics of this species



are summarized in Table I. This structure is 18–24 kcal/mol above 2, and UHF/3-21G vibrational analysis gave a single imaginary frequency. We thus conclude that 12 is a saddle point for rotation of 2, rather than an intermediate. Martin, Yates, and Csizmadia recently reported calculations on a $^3A''$ (C_s) allene triplet state; this is predicted to be much higher energy than 12 and hence seems an unlikely intermediate.[20] We find no computational evidence for low-energy triplet C_3H_4 intermediates other than 1 and 2.

Conclusions

Hydrogen abstractions by triplet cyclopropylidene (1) and planar triplet allene (2) are predicted to have nearly identical activation energies of <19 kcal/mol. Because of limitations in the quantum mechanical model, these numbers are likely to be somewhat high. Both reactions are slightly exothermic. Predicted barriers are similar to those of other free radicals and triplet carbenes. Our results support previous conclusions that intermediates like both 1 and 2 are involved in triplet allene photoreactions. Both saddle points are predicted to have linear C--H--C geometries; however, abstraction by cyclopropylidene is found to be quite insensitive to out-of-plane bending. This saddle point flexibility may explain the facility and remarkably *unselective* intramolecular hydrogen abstraction in reactions of cyclic allenes.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. 1, 2143-70-6; 2, 463-49-0; CH_4, 74-82-8; hydrogen, 1333-74-0.

Supplementary Material Available: Z matrix input and cartesian coordinates for saddle points SP1 and SP2 (6 pages). Ordering information is given on any current masthead page.

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Synthesis of Quinolinequinones and 1,2,3,4-Tetrahydroquinolinequinones via Cyclobutenediones

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N-Benzyl-1,2,3,4-tetrahydrocyclobuta[*b*]pyridine-5,6-dione is easily synthesized and functions as a synthetic equivalent of the unstable pyridiocyclobutenedione. Regiospecific introduction of unsaturated nucleophiles at the more reactive carbonyl group, followed by thermolysis in xylene in vessels open to air, rapidly establishes the tetrahydroquinolinequinone system which can be oxidized to the corresponding quinolinequinone with 2,3-dichloro-5,6-dicyanoquinone.

Within the last few years, cyclobutenediones (1) have emerged as versatile reagents for the construction of highly substituted quinones.[1-7] Addition of an unsaturated nucleophilic reagent to 1 followed by thermolysis leads to

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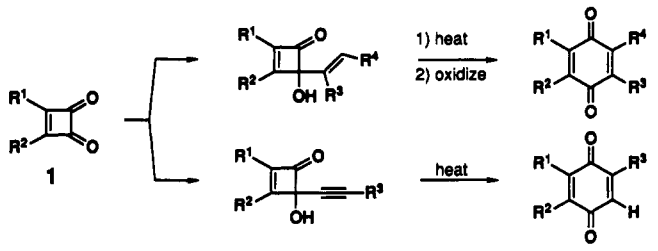
Scheme I

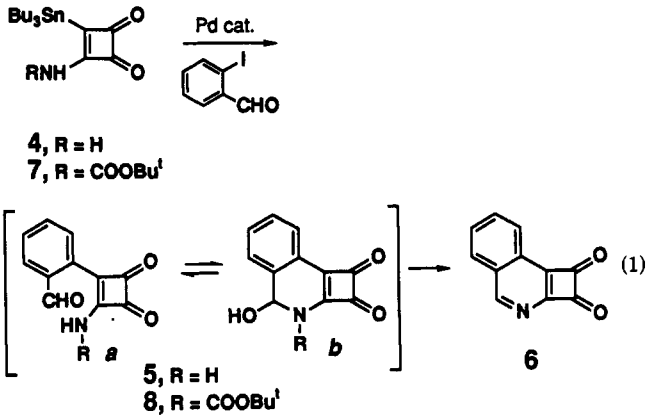


quinones directly, when the entering nucleophile is an alkynyl anion, or after oxidation, when the entering nucleophile is a vinyl, aryl, or heteroaryl anion (Scheme I). In order to expand the utility of this process, we have been involved in a continuing effort to broaden the range of synthetically useful transformations available to the cyclobutenedione family of molecules.[8-10] Reported herein are studies directed toward the synthesis and subsequent transformations of 1,2,3,4-tetrahydrocyclobuta[*b*]-pyridine-5,6-dione (**2**) the tetrahydro version of the (unstable) pyridine analogue of benzocyclobutenedione (**3**).[11,12] The former serves as a useful vehicle for the

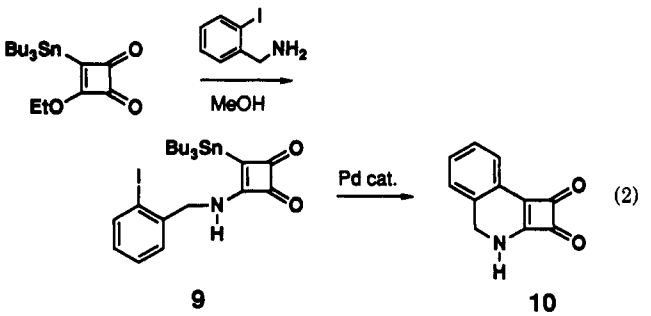
construction of a variety of azabenzoquinones bearing or formally derived from the 1,2,3,4-tetrahydroquinoline-quinone and quinolinequinone ring systems, substructures found in a variety of biologically active, naturally occurring compounds.[13-27]

Results and Discussion

McOmie[11] and Jones[12] and their co-workers have previously reported attempts to prepare pyridine-fused cyclobutenediones, but the molecules could not be fully characterized due to their instability. An attempted preparation of the related molecule, cyclobuta[*c*]isoquinoline-7,8-dione (**6**) confirmed the instability of the pyridine-fused cyclobutenedione ring system. Palladium-catalyzed cross-coupling of 3-amino-4-(tri-*n*-butylstannyl)cyclobutene-1,2-dione (**4**) with 2-iodobenzaldehyde provided the unstable product **5** in 92% yield (eq 1). ^1H



NMR spectra suggested that **5** exists in the open form (**5a**). Dehydration of **5a** to **6** proceeded spontaneously in CH_2Cl_2 in the presence of Na_2SO_4, but the product was very unstable and easily underwent cleavage of the cyclobutenedione ring in the presence of water or alcohol. Inhibition of the dehydration process was achieved by prior conversion of **4** into the N-protected variant **7**, which underwent palladium-catalyzed cross-coupling with 2-iodobenzaldehyde directly providing the stable aminol **8b** in 68% yield. Interestingly, intramolecular palladium-catalyzed cross-coupling of **9**, the condensation product between 2-iodobenzylamine and 3-ethoxy-4-(tri-*n*-butylstannyl)cyclobutene-1,2-dione, gave the stable cyclized product **10**[28] in 61% yield (eq 2). In contrast to the instability of the pyridine and isoquinoline fused cyclobutenediones, the stability of compounds **8** and **10** suggested that reduced forms of pyridiocyclobutenedione would be more amenable to study.



N-Benzyl-1,2,3,4-tetrahydrocyclobuta[*b*]pyridine-5,6-dione (**11**) was chosen as a functional equivalent of the

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Scheme II

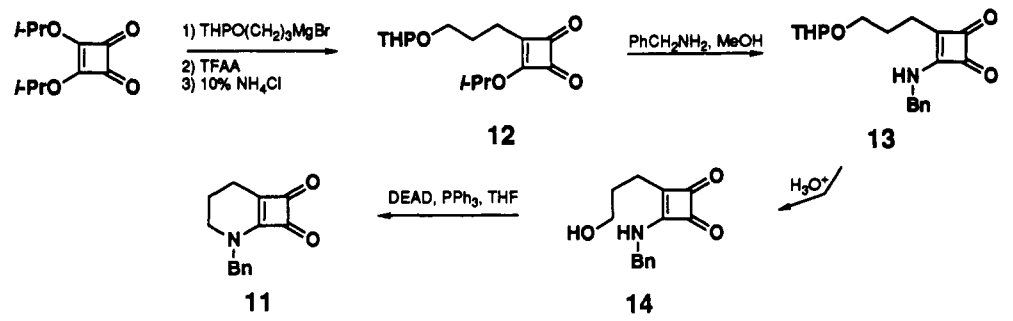
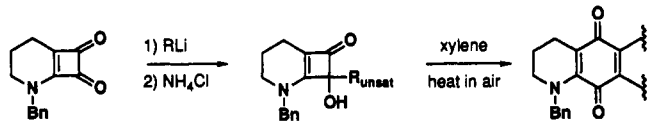
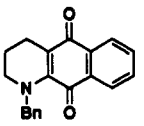
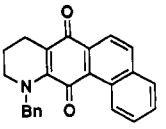
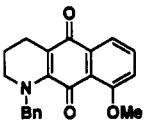
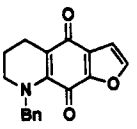
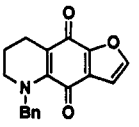
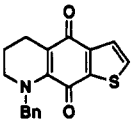
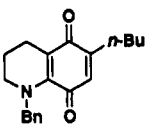


Table I. *N*-Benzyltetrahydroquinolinequinones



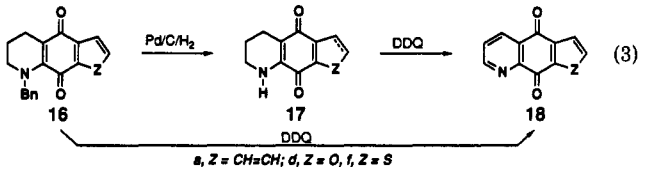
entry	R	compd, yield (%)	structure	compd no.	yield (%)
1	phenyl	**15a**, 70		**16a**	89
2	1-naphthyl	**15b**, 79		**16b**	91
3	2-anisyl	**15c**, 80		**16c**	71
4	2-furyl	**15d**, 76		**16d**	76
5	3-furyl	**15e**, 85		**16e**	83
6	2-thienyl	**15f**, 77		**16f**	84
7	1-hexynyl	**15g**, 67		**16g**	87

pyridine-fused cyclobutenedione **3**. Addition of the Grignard reagent derived from 1-(tetrahydropyranyloxy)-3-bromopropane to diisopropyl squarate provided, after a quench with trifluoroacetic anhydride, the cyclobutenedione **12** in 57% yield (Scheme II). Addition of benzylamine in MeOH gave the benzylamino derivative **13** (95%), which was hydrolyzed with dilute HCl to the primary alcohol **14** (95%) and then subjected to Mitsunobu dehydration to give the (tetrahydropyridio)cyclobutenedione **11** in 65% yield.

Cyclobutenedione **11** was treated with a variety of carbon nucleophiles, and the adducts **15** were isolated in good yield after quenching the reaction with 10% aqueous NH_4Cl (Table I). Thermolysis in *o*-xylene at 120–160 °C in vessels open to the air led to disappearance of the adducts **15** and formation of reaction mixtures that directly provided the red to purple tetrahydroquinolinequinones **16** shown in Table I. Comparison of entries 4 and 5 highlights the ease with which regioisomeric compounds can be prepared via this procedure. Entry 7 in Table I shows the use of the Moore reaction, the direct conversion of alkyne adducts of cyclobutenediones into quinones on thermolysis.[5]

Conversion of the tetrahydroquinolinequinone **16** into quinoline quinones was investigated next. Three systems, **16a**, **16d**, and **16f** were chosen for study, and of these only

16a underwent debenzylation in a straightforward fashion (eq 3). After debenzylation to 17a (94%), the tetra-



(3)

hydroquinoline ring was oxidized to the quinolinequinone 18a (69%) on treatment with DDQ in benzene. On attempted debenzylation, the furan derivative 16d suffered overreduction and the quinone product dihydro-17d was obtained in 89% yield. Debenzylation of the thiophene analogue (16f) proceeded to 17f in low yield only, even using 1 equiv of palladium. The difficulties encountered with the latter two substrates were easily remedied by direct oxidation of the N-benzylated compounds 16 with DDQ in benzene (eq 3). Substrates 16a, 16d, and 16f were treated with 3 equiv of DDQ and underwent debenzylation under the reaction conditions directly providing the desired quinoline quinones 18a (42%), 18d (37%), and 18f (35%).

Conclusions

In summary, *N*-benzyl-1,2,3,4-tetrahydrocyclobuta[*b*]-pyridine-5,6-dione (11) is easily synthesized and functions as an equivalent of the unstable pyridiocyclobutenedione 2. Reaction of 11 with unsaturated nucleophiles followed by thermolysis in xylene rapidly establishes the tetrahydroquinolinequinone system which can be oxidized to the corresponding quinolinequinone.

Experimental Section

Materials and Methods. Separations were done either by standard flash chromatography techniques using Baker silica gel (40 μm) or via radial chromatography using a 7924T Chromatotron from Harrison Research. The rotor was coated with Merck PF254 silica gel. THF and ether were distilled from sodium benzophenone ketyl solutions. All other solvents were of reagent grade and were used without purification. Squaric acid was purchased from Aldrich Chemical Co. 3-(Tri-*n*-butylstannyl)-4-(1-methylethoxy)-3-cyclobutene-1,2-dione was prepared according to the literature procedure.[9] 1-Bromo-3-(tetrahydropyranyloxy)propane was purchased from Sigma Chemical Co.

Cyclobuta[*c*]quinoline-7,8-dione (6) Studies. Synthesis of 3-(Tri-*n*-butylstannyl)-4-amino-3-cyclobutene-1,2-dione (4). A solution of 3-(tri-*n*-butylstannyl)-4-isopropoxy-3-cyclobutene-1,2-dione[9] (0.458 g, 1.103 mmol) in 5 mL of dry MeOH was added to a solution of 50 mL of dry MeOH saturated with gaseous ammonia at 0 °C. After the addition was complete, the solution was stirred at rt for 2 h, TLC (SiO_2, 1:4 EtOAc/hexanes, UV, product R_f = 0.15). The solvent was evaporated, and the residue was passed through a small plug of SiO_2 with $CHCl_3$ giving 0.361 g (85%) of product as a pale yellow solid: mp 80–81 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.80 (s br, 2 H), 1.54 (m, 6 H), 1.32 (m, 6 H), 1.16 (m, 6 H), 0.89 (t, J = 7.2 Hz, 9 H); IR (CH_2Cl_2, cm^{-1}) 3500, 3400, 2960, 2930, 1772, 1740, 1625, 1550; MS (LREI) m/z (relative intensity) 330 [$(M - C_4H_9)^+$, 9], 291 (21), 235 (52), 177 (100). Anal. Calcd for $C_{16}H_{29}NO_2Sn$: C, 49.77; H, 7.57; N, 3.63. Found: C, 49.83; H, 7.59; N, 3.68.

Synthesis of 3-(2-Formylphenyl)-4-amino-3-cyclobutene-1,2-dione (5a). A solution of 2-iodobenzaldehyde (24 mg, 0.1 mmol), 3-(tri-*n*-butylstannyl)-4-amino-3-cyclobutene-1,2-dione (35 mg, 0.09 mmol), and Pd(benzyl)Cl(PPh_3)$_2$/CuI (1:1 mol mixture) (5.6 mg, 6.5 mol %) in 3.5 mL of dry benzene was stirred at rt. A white solid formed within 1 h. After 20 h the solid was collected by filtration, washed with benzene, and dried under vacuum to give 17 mg (92%) of product as a white-grey solid. Solution instability of the compound precluded the acquisition of a good ^1H NMR spectrum. Apparently, it undergoes dehydration to form the unstable product 6 which very easily suffers opening of the cyclobutenedione ring: mp 160–163 °C dec; ^1H NMR (acetone-d_6, 300 MHz) δ 10.20 (s, 1 H), 8.01–7.52 (m, 4 H); IR (KBr, cm^{-1}) 3410, 3340, 3270, 2890, 1788, 1732, 1675, 1584, 1405, 1310, 1235, 827, 780, 755; MS (HREI) Calcd for $C_{11}H_5NO_2$ ($M - H_2O$)$^+$ 183.0320, found 183.0319.

Dehydration of 3-(2-Formylphenyl)-4-amino-3-cyclobutene-1,2-dione (5a) to 6. As mentioned previously, the coupling product very easily dehydrates to 6 with simultaneous decomposition. Dehydration, however, was effectively achieved at rt by suspension of the coupling product 5a in CH_2Cl_2 with anhydrous Na_2SO_4. The product was always contaminated with decomposition impurities, and attempts to obtain analytically pure material were not successful: TLC (SiO_2, 1:2 EtOAc/hexanes, UV) showed R_f = 0.13; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.55 (s, 1 H), 8.48 (d, 1 H, J = 8.1 Hz), 8.34 (d, 1 H, J = 7.5 Hz), 8.10 (m, 2 H); IR ($CDCl_3$, cm^{-1}) 1800, 1790. Apparently, the instability of compound 6 is associated with very facile opening of the cyclobutenedione ring. Dissolution of 6 in MeOH produces a pair of new products that show no cyclobutenedione bands in the IR (1800 and 1790). TLC shows R_f = 0.47 (19%) and R_f = 0.31 (44%) (SiO_2, 1:2 EtOAc/hexanes, UV). Less polar isomer: ^1H NMR ($CDCl_3$, 300 MHz) δ 9.30 (s, 1 H), 8.58 (s, 1 H), 8.04 (m, 2 H), 7.81 (m, 2 H), 4.03 (s, 3 H); IR ($CDCl_3$, cm^{-1}) 1745, 1705, 1265, 1168, 1132, 1027. More polar isomer: ^1H NMR ($CDCl_3$, 300 MHz) δ 9.41 (s, 1 H), 8.98 (s, 1 H), 8.95 (d, J = 8.7 Hz, 1 H), 8.06 (d, J = 8.1 Hz, 1 H), 7.90 (t, J = 8.0 Hz, 1 H), 7.73 (t, J = 7.5 Hz, 1 H), 4.01 (s, 3 H); IR ($CDCl_3$, cm^{-1}) 1745, 1688, 1507, 1250, 1235, 1160, 1098. These compounds were not characterized in greater detail, but the spectra are consistent with those anticipated for 3-carbomethoxy-4-formylisoquinoline and 3-formyl-4-carbomethoxyisoquinoline.

Synthesis of 3-(Tri-*n*-butylstannyl)-4-[*N*-(*tert*-butoxycarbonyl)amino]-3-cyclobutene-1,2-dione (7). To a stirred solution of 3-(tri-*n*-butylstannyl)-4-amino-3-cyclobutene-1,2-dione (4; 432 mg, 1.12 mmol), $(Boc)_2O$ (261 mg, 1.20 mmol), and 0.2 mL of triethylamine in 7 mL of acetonitrile was added a few mg of DMAP as a catalyst, and the mixture was stirred at rt: TLC (SiO_2, 1:1 EtOAc/hexanes, product R_f = 0.2). After 4 h, solvents were removed on a rotary evaporator and the residue was chromatographed on silica gel (20 g, 1:7 EtOAc/hexanes) to give 7 (492 mg, 91%) as a yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.84 (s, 1 H), 1.52 (s, 9 H), 1.6–1.1 (m, 18 H), 0.87 (t, J = 7.2 Hz, 9 H); IR (CH_2Cl_2, cm^{-1}) 3380, 2960, 2930, 2880, 2860, 1790, 1774, 1750, 1560, 1507, 1152; MS (LRFAB) 488 $(M + H)^+$, 494 $(M + Li)^+$.

Synthesis of Compound 8. A solution of 2-iodobenzaldehyde (117 mg, 0.487 mmol), 3-(tri-*n*-butylstannyl)-4-[*N*-(*tert*-butoxycarbonyl)amino]-3-cyclobutene-1,2-dione (7; 248 mg, 0.51 mmol), and Pd(benzyl)Cl(PPh_3)$_2$/CuI (1:1 mol mixture) (12 mg, 2.5 mol %) in 5 mL of dry THF was heated at gentle reflux for 20 h, TLC (SiO_2, 1:4 EtOAc/hexanes, UV, R_f = 0.1). The solvent was evaporated and the residue purified by chromatography on silica gel (15 g, 1:5 EtOAc/hexanes) to give 100 mg (68%) of product as a yellow solid: mp 127–128 dec; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, J = 7.5 Hz, 1 H), 7.66–7.54 (m, 3 H), 6.86 (s, 1 H), 4.23 (s br, 1 H), 1.65 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 188.2, 183.6, 180.3, 166.7, 149.7, 132.7, 131.0, 128.3, 125.4, 122.1, 86.4, 79.2 27.4; IR (CH_2Cl_2, cm^{-1}) 3550, 1792, 1770, 1735, 1619, 1594, 1318, 1145; MS (LRFAB) 302 $(M + H)^+$, 308 $(M + Li)^+$. Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.76; H, 5.03; N, 4.66.

5,6-Dihydrocyclobuta[*c*]quinoline-7,8-dione (10).[28] Synthesis of 3-(Tri-*n*-butylstannyl)-4-[*N*-(2-iodobenzyl)-amino]-3-cyclobutene-1,2-dione (9). A solution of 2-iodobenzylamine (47 mg, 0.2 mmol) and 3-ethoxy-4-(tri-*n*-butylstannyl)-3-cyclobutene-1,2-dione (94.5 mg, 0.23 mmol) in 5 mL of dry MeOH under nitrogen was stirred at rt for 2 h, TLC (SiO_2, 1:4 EtOAc/hexanes, UV, R_f = 0.22). The product was purified by preparative layer chromatography (0.5 mm SiO_2, 1:4, EtOAc/hexanes) to give 103 mg (86%) of product as a low melting solid (about 1:1 mixture of s-trans and s-cis isomers as determined by ^1H NMR): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.9–7.0 (m, 4 H), 6.86 (s br, 0.5 H), 6.38 (s br, 0.5 H), 4.90 (d, J = 6.6 Hz, 1 H), 4.52 (d, J = 5.7 Hz, 1 H), 1.54–1.05 (m, 18 H), 0.84 (t, J = 7.2 Hz, 9 H); IR (CH_2Cl_2, cm^{-1}) 3390, 2960, 2930, 2880, 2860, 1767, 1735, 1584. Anal. Calcd for $C_{23}H_{34}INO_2Sn$: C, 45.88; H, 5.69; N, 2.33. Found: C, 46.38; H, 5.83; N, 2.21.

Synthesis of 5,6-Dihydrocyclobuta[*c*]quinoline-7,8-dione (10). A solution of compound **9** (278 mg, 0.461 mmol) and Pd(PPh_3)$_4$ (26 mg, 4.9 mol %) in 5 mL of dry THF was refluxed under nitrogen for 20 h. The product, which was insoluble in THF, was collected by filtration and washed with CH_2Cl_2 to give 52 mg (61%) of a beige solid which was recrystallized from DMSO and water to provide a yellow crystalline solid, mp 235–236 °C dec; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 9.36 (s, 1 H), 7.42–7.16 (m, 4 H), 4.88 (s, 2 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 190.3, 183.9, 182.7, 161.0, 131.7, 129.9, 128.2, 127.0, 124.8, 124.5, 46.8; IR (KBr, cm^{-1}) 3225, 3100, 3040, 2960, 2858, 1790, 1740, 1625, 1555, 1470, 1364, 1251, 1158, 1060, 794; MS (LREI) *m/z* (relative intensity) 185 (M^+, 12), 157 (87), 129 (74), 102 (100), 76 (36). Anal. Calcd for $C_{11}H_7NO_2$: C, 71.35; H, 3.81; N, 7.56. Found: C, 71.07; H, 3.78; N, 7.50.

***N*-Benzyl-1,2,3,4-tetrahydrocyclobuta[*b*]pyridine-5,6-dione (11). Preparation of 3-Isopropoxy-4-[3-(tetrahydropyranyloxy)propyl]-3-cyclobutene-1,2-dione (12).** To Mg (0.491 g, 20.2 g atoms) and a small piece of iodine under N_2 at rt was added a solution of 1-bromo-3-(tetrahydropyranyloxy)-propane (4.53 g, 20.3 mmol) in 100 mL of dry THF. The resulting Grignard reagent was stirred for 1 h at rt, and then the solution was added via cannula into a solution of diisopropyl squarate (2.31 g, 11.7 mmol) in 50 mL of dry THF at −78 °C. After the addition, the mixture was stirred for 1 h at −78 °C and 1 h at −20 °C, TLC (SiO_2, 1:2 EtOAc/hexanes, UV, R_f = 0.22). The reaction was quenched by trifluoroacetic anhydride (3 mL, 21.2 mmol) followed by 20 mL of 10% NH_4Cl solution at −20 °C. After the mixture reached rt, it was extracted with 100 mL of ether and twice with 30 mL of CH_2Cl_2. The organic layers were combined and dried over $MgSO_4$. The solvent was evaporated on a rotary evaporator, and the residue was chromatographed on silica gel (250 g, 1:4 EtOAc: hexanes). After evaporation of solvent, the product (1.87 g, 57%) was isolated as a yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.39 (hept, J = 6 Hz, 1 H), 4.55 (t, J = 3 Hz, 1 H), 3.84–3.74 (m, 2 H), 3.52–3.37 (m, 2 H), 2.70 (t, J = 7.5 Hz, 2 H), 1.99 (hept, J = 6.6 Hz, 2 H), 1.78–1.49 (m, 6 H), 1.44 (d, J = 6.3 Hz, 6 H); IR (CH_2Cl_2, cm^{-1}) 2943, 2872, 1789, 1589, 1383, 1105; MS (LRFAB) 283 (M + H)$^+$, 289 (M + Li)$^+$. Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.50; H, 8.17.

Preparation of 3-(Benzylamino)-4-[3-(tetrahydropyranyloxy)propyl]-3-cyclobutene-1,2-dione (13). Benzylamine (0.314 g, 2.93 mmol) was added by syringe to a solution of 3-isopropoxy-4-[3-(tetrahydropyranyloxy)propyl]-3-cyclobutene-1,2-dione (**12**; 0.827 g, 2.93 mmol) in 30 mL of MeOH at 0 °C, and the mixture was stirred at 0 °C for 0.5 h, TLC (SiO_2, 4:1 EtOAc/hexanes, UV, R_f = 0.60). The MeOH was removed on a rotary evaporator, and the residue was chromatographed on silica gel (50 g, 1:1 EtOAc/hexanes). After evaporation of solvent, the product (0.92 g, 95%) was obtained as a white solid: mp 96–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.28 (m, 5 H), 7.22 (s br, 1 H), 4.90 (dd, J = 6.3 Hz, 14.7 Hz, 1 H), 4.79 (dd, J = 6.0 Hz, 14.7 Hz, 1 H), 4.40 (dd, J = 2.1 Hz, 5.3 Hz, 1 H), 3.77–3.33 (m, 4 H), 2.70 (m, 2 H), 1.99–1.62 (m, 4 H), 1.45–1.31 (m, 4 H); IR (CH_2Cl_2, cm^{-1}) 3380, 3280, 2940, 2860, 1760, 1735, 1605, 1445, 1350, 1130, 1270, 1230; MS (LREI) *m/z* (relative intensity) 329 (M^+, 0.23), 244 (12), 216 (33), 154 (31), 91 (100). Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.37; H, 7.10; N, 4.15.

Preparation of 3-(Benzylamino)-4-(3-hydroxypropyl)-3-cyclobutene-1,2-dione (14). To a suspension of 3-(benzylamino)-4-[3-(tetrahydropyranyloxy)propyl]-3-cyclobutene-1,2-dione (**13**; 0.193 g, 0.587 mmol) in 10 mL of water was added 4 drops of concd HCl. The mixture was heated at 60 °C until the solid went into solution (about 1.5 h). The solution was neutralized with $NaHCO_3$, and then extracted three times with 15 mL of CH_2Cl_2. The extract was dried over $MgSO_4$ and purified by radial chromatography (2-mm SiO_2 plate, 4:1 EtOAc/hexanes). After evaporation of solvent, the product (0.137 g, 95%) was isolated as a colorless oil, R_f = 0.27 (SiO_2, 4:1 EtOAc/hexanes, UV), which appeared to be a mixture of two conformers (about 2:1 ratio from ^{1}H NMR): ^{1}H NMR (300 MHz, $CDCl_3$) (major isomer including the peaks which are overlapping) δ 7.42–7.28 (m, 6 H), 4.84 (d, J = 6.3 Hz, 2 H), 4.64 (m, 2 H), 2.68 (t, J = 6.7 Hz, 2 H), 2.29 (s br, 1 H), 1.85 (hept, J = 6.3 Hz, 2 H), (peaks for minor isomer which are separated from the major one) 6.57 (s br, 1 H), 4.64 (d, J = 5.7 Hz, 2 H), 2.71 (t, J = 7.2 Hz, 2 H), 2.19 (s br, 1 H), 1.80 (hept, J = 6.3 Hz, 2 H); IR (CH_2Cl_2, cm^{-1}) 3380, 3280, 3130, 2930, 1780, 1730, 1610, 1450, 1410, 1350, 1070; MS (LREI) *m/z* (relative intensity) 245 (M^+, 1.6) 216 (11), 91 (100). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.51; H, 6.17; N, 5.66.

Preparation of *N*-Benzyl-1,2,3,4-tetrahydrocyclobuta[*b*]pyridine-5,6-dione (11). To a solution of DEAD (0.508 g, 2.92 mmol) and triphenylphosphine (0.766 g, 2.92 mmol) in 20 mL of THF was added a solution of 3-(benzylamino)-4-(3-hydroxypropyl)-3-cyclobutene-1,2-dione (**14**; 0.700 g, 2.86 mmol) in 10 mL of THF by syringe at rt under N_2, TLC (1 h, SiO_2, 4:1 EtOAc/hexanes, UV, R_f = 0.31). The reaction mixture was concentrated under reduced pressure, and the residue was purified by chromatography on SiO_2 (50 g, 4:1 EtOAc/hexanes) to give 65% (0.420 g) of product as a low-melting white solid, mp 50–52 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.19 (m, 5 H), 4.61 (s, 2 H), 3.22 (t, J = 5.6 Hz, 2 H), 2.62 (t, J = 6.2 Hz, 2 H), 1.83 (hept, J = 5.7 Hz, 2 H); IR ($CDCl_3$, cm^{-1}) 2860, 1780, 1725, 1610, 1445, 1345, 1240, 1170; MS (LREI) *m/z* (relative intensity) 227 (M^+, 2.6), 198 (100). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.42; H, 5.82; N, 6.09.

Tetrahydroquinolinequinones 16. Addition of Organolithium Reagents to *N*-Benzyl-1,2,3,4-tetrahydrocyclobuta[*b*]pyridine-5,6-dione. General Experimental Procedure. A solution of *N*-benzyl-1,2,3,4-tetrahydrocyclobuta[*b*]pyridine-5,6-dione (**11**) in dry THF was cooled to −78 °C under N_2, and the organolithium reagent was added. This mixture was stirred until compound **11** was consumed (0.5–1 h) as detected by TLC. When complete, the reaction was quenched with 10% aqueous NH_4Cl and extracted with ether and twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, the solvent was removed on a rotary evaporator, and the residue was chromatographed on SiO_2 by elution with a mixture of EtOAc and hexanes to give the product.

***N*-Benzyl-1,2,3,4-tetrahydro-6-hydroxy-6-phenylcyclobuta[*b*]pyridin-5-one (15a).** Reaction of **11** (180 mg, 0.79 mmol) with 1.06 equiv of PhLi for 0.5 h gave 70% of **15a** (170 mg) as a white solid: R_f = 0.19 (SiO_2, 4:1 EtOAc/hexanes, UV); mp 173–175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 6 Hz, 2 H), 7.31 (t, J = 6 Hz, 2 H), 7.24 (d, J = 5.7 Hz, 1 H), 7.20–6.96 (m, 5 H), 4.69 (s br, 1 H), 4.28 (d, J = 12.3 Hz, 1 H), 4.16 (d, J = 12.3 Hz, 1 H), 3.08 (m, 2 H), 2.20 (t, J = 4.2 Hz, 2 H), 1.82 (m, 2 H); IR ($CDCl_3$, cm^{-1}) 3270, 2960, 2950, 2860, 1745, 1575, 1496, 1455, 1445, 1350, 1260, 1190, 1170, 930, 900, 740, 710, 660; MS (LREI) *m/z* (relative intensity) 305 (M^+, 32), 214 (54), 91 (100). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.21; N, 4.59. Found: C, 78.39; H, 6.21; N, 4.51.

***N*-Benzyl-1,2,3,4-tetrahydro-6-hydroxy-6-(1-naphthyl)-cyclobuta[*b*]pyridin-5-one (15b).** Reaction of **11** (201 mg, 0.885 mmol) with 1.1 equiv of 1-lithionaphthalene (generated by addition of 1.0 equiv of *n*-BuLi to a THF solution of 1-bromonaphthalene at −78 °C and stirring at −78 °C for 15 min) for 0.5 h gave a 79% yield of **15b** (249 mg) as white crystals: R_f = 0.46 (SiO_2, 4:1 EtOAc/hexanes); mp 173–175 °C (CH_3CN); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.85 (dd, J = 3.3 Hz, 6.3 Hz, 1 H), 7.82 (dd, J = 3.3 Hz, 6.3 Hz, 1 H), 7.79 (d, J = 8.4 Hz, 1 H), 7.45–7.27 (m, 9 H), 6.92 (s, 1 H), 4.70 (d, J = 14.7 Hz, 1 H), 4.47 (d, J = 14.7 Hz, 1 H), 3.02 (m, 2 H), 2.01 (m, 2 H), 1.87–1.75 (m, 2 H); IR (KBr, cm^{-1}) 3420, 3240, 3050, 2960, 2860, 1740, 1575, 1455, 1440, 1355, 1250, 1190, 785; MS (LREI) *m/z* (relative intensity) 355 (M^+, 4.1), 339 (11), 263 (25), 91 (100). Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94. Found: C, 80.92; H, 5.89; N, 3.88.

***N*-Benzyl-1,2,3,4-tetrahydro-6-hydroxy-6-(2-methoxyphenyl)cyclobuta[*b*]pyridin-5-one (15c).** Reaction of **11** (209 mg, 0.92 mmol) with 1-lithio-2-methoxybenzene (generated by addition of 1.0 equiv of PhLi to an ether solution of 2-bromoanisole at rt and stirring at rt for 1 h) for 1 h gave an 80% yield of **15c** (247 mg) as a pale yellow foam: R_f = 0.31 (SiO_2, 4:1 EtOAc/hexanes); mp 53–55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 7.2 Hz, 1 H), 7.21 (m, 3 H), 7.14 (m, 2 H), 6.92 (t, J = 7.5 Hz, 1 H), 6.86 (d, J = 8.4 Hz, 1 H), 5.50 (s br, 1 H), 4.47 (d, J = 14.7 Hz, 1 H), 4.26 (d, J = 15 Hz, 1 H), 3.78 (s, 3 H), 3.10 (m, 2 H), 2.15 (m, 1 H), 1.81 (m, 2 H); IR (CH_2Cl_2, cm^{-1}) 3510, 3050, 2960, 2870, 1750, 1595, 1495, 1455, 1440, 1355, 1245, 1195, 1115, 1030; MS (HREI) calcd for $C_{21}H_{21}NO_3$ 335.1521, found 335.1519.

N-Benzyl-1,2,3,4-tetrahydro-6-hydroxy-6-(2-furyl)cyclobuta[b]pyridin-5-one (15d). Reaction of **11** (225 mg) with 2-lithiofuran (generated by addition of 1.0 equiv of *n*-BuLi to an ether solution of furan and 1.0 equiv of tetramethylethylenediamine at −78 °C and stirring at rt for 4 h) for 1 h gave a 76% yield of **15d** (223 mg) as an off-white solid: R_f = 0.22 (SiO_2, 4:1 EtOAc/hexanes); mp 147–148 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (s, 1 H), 7.29–7.08 (m, 5 H), 6.53 (d, *J* = 3 Hz, 1 H), 6.36 (t, *J* = 2.4 Hz, 1 H), 4.63 (s br, 1 H), 4.44 (s, 2 H), 3.13 (t, *J* = 5.6 Hz, 2 H), 2.21 (m, 2 H), 1.84 (hept, *J* = 5.9 Hz, 2 H); IR (CH_2Cl_2, cm^{-1}) 3300, 2950, 2860, 1750, 1605, 1585, 1350; MS (HREI) calcd for $C_{18}H_{17}NO_3$ 295.1208, found 295.1202.

N-Benzyl-1,2,3,4-tetrahydro-6-hydroxy-6-(3-furyl)cyclobuta[b]pyridin-5-one (15e). Reaction of **11** (214 mg, 0.943 mmol) with 3-lithiofuran (generated by addition of 1.0 equiv of *n*-BuLi to an ether solution of 3-bromofuran at −78 °C and stirring at rt for 15 min) for 0.5 h gave an 85% yield of **15e** (235 mg) as a white foam which acquires a purple color (quinone) on handling: R_f = 0.26 (SiO_2, 4:1 EtOAc/hexanes, UV); mp 57–59 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (2, 1 H), 7.34 (s, 1 H), 7.24 (m, 3 H), 7.11 (m, 2 H), 6.34 (s, 1 H), 4.40 (d, *J* = 14.7 Hz, 1 H), 4.33 (d, *J* = 15 Hz, 1 H), 3.07 (m, 2 H), 2.15 (t, *J* = 5.2 Hz, 2 H), 1.80 (hept, *J* = 5.7 Hz, 2 H); IR (CH_2Cl_2, cm^{-1}) 3270, 2960, 2870, 1750, 1595, 1585, 1500, 1455, 1440, 1355, 1190, 1170, 1160; MS (HREI) calcd for $C_{18}H_{17}NO_3$ 295.1208, found 295.1204.

N-Benzyl-1,2,3,4-tetrahydro-6-hydroxy-6-(2-thienyl)-cyclobuta[b]pyridin-5-one (15f). Reaction of **11** (421 mg, 1.85 mmol) with 2-lithiothiophene (generated by addition of 1.0 equiv of *n*-BuLi to a THF solution of thiophene at −78 °C and stirring at −78 °C for 15 min and then −23 °C for 30 min) for 1 h gave a 77% yield of **15f** (443 mg) as a white foam: R_f = 0.33 (SiO_2, 4:1 EtOAc/hexanes); mp 52–54 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 4 H), 7.10 (d, *J* = 3.3 Hz, 1 H), 7.05 (m, 2 H), 6.98 (d, *J* = 4.2 Hz, 1 H), 4.43 (d, *J* = 15 Hz, 1 H), 4.34 (d, *J* = 15 Hz, 1 H), 3.10 (m, 2 H), 2.20 (m, 2 H), 1.82 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.0, 173.6, 142.8, 134.3, 128.1, 127.8, 127.4, 126.6, 124.8, 123.8, 117.1, 90.7, 54.3, 45.4, 21.5, 17.2; IR ($CDCl_3$, cm^{-1}) 3260, 2970, 2875, 1750, 1590, 1460, 1445, 1355, 1260, 1140, 1050; MS *m/z* (relative intensity) 311 (M^+, 76), 293 (77), 91 (100). Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.43; H, 5.50; N, 4.50. Found: C, 69.49; H, 5.55; N, 4.51.

N-Benzyl-1,2,3,4-tetrahydro-6-hydroxy-6-(1-hexynyl)-cyclobuta[b]pyridin-5-one (15g). Reaction of **11** (436 mg, 1.92 mmol) with 1-lithiohexyne (generated by addition of 1.0 equiv of *n*-BuLi to a THF solution of 1-hexyne at −78 °C and stirring at −78 °C for 1 h and then 0 °C for 1 h) for 1 h gave a 67% yield of **15g** (400 mg) as a white solid which rapidly acquires a purple color (quinone) on handling; rapid conversion to the quinone precluded determination of an accurate mp: R_f = 0.24 (SiO_2, 4:1 EtOAc/hexanes); ^1H NMR (360 MHz, $CDCl_3$) δ 7.36 (m, 5 H), 4.62 (d, *J* = 14.8 Hz, 1 H), 4.52 (d, *J* = 14.8 Hz, 1 H), 3.18 (br s, 1 H), 3.14 (t, *J* = 5.4 Hz, 2 H), 2.24 (t, *J* = 7.2 Hz, 2 H), 2.16 (q, *J* = 7.2 Hz, 2 H), 1.82 (hept, *J* = 5.8 Hz, 2 H), 1.48–1.31 (m, 4 H), 0.85 (t, *J* = 7.2 Hz, 3 H); IR (CH_2Cl_2, cm^{-1}) 3560, 2960, 2940, 2860, 1755, 1605, 1450, 1350, 1190, 1110. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.59; H, 7.51; N, 4.48.

Thermolysis of Compound 15 To Form N-Benzyl-1,2,3,4-tetrahydroquinolinequinones (16). General Experimental Procedure. A solution of compound **15** in *o*-xylene (THF for **15g**) was heated under air until compound **15** was consumed (0.5–3.5 h) as monitored by TLC. When the reaction was complete, the solution was cooled to rt and the product was purified by chromatography on flash SiO_2 (elution with a mixture of EtOAc and hexanes) and recrystallization. In parentheses following each of the compounds shown below is an indication of the scale of the reaction, the reaction temperature and time, and the yield of the product.

N-Benzyl-1,2,3,4-tetrahydroquinolinequinone-5,8-dione (16a) (0.236 mmol, 160 °C, 2 h, 89%): red needles; R_f = 0.38 (SiO_2, 1:4 EtOAc/hexanes); mp 103–104 °C (CH_2Cl_2/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 1 H), 7.90 (d, *J* = 7.8 Hz, 1 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.55 (t, *J* = 7.5 Hz, 1 H), 7.37–7.27 (m, 5 H), 4.85 (s, 2 H), 3.25 (t, *J* = 5.3 Hz, 2 H), 2.67 (t, *J* = 6.2 Hz, 2 H), 1.86 (hept, *J* = 5.9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.5, 180.8, 148.1, 137.4, 133.0, 132.1, 131.8, 131.1, 128.0, 126.7, 125.4, 124.7, 117.2, 56.2, 49.5, 20.5, 19.6; IR ($CDCl_3$, cm^{-1}) 2970, 2940, 1675, 1618, 1600, 1580, 1387, 1364, 1295, 1285; MS (LREI) *m/z* (relative intensity) 303 (M^+, 65), 212 (64), 91 (100). Anal. Cald for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.00; H, 5.69; N, 4.56.

Preparation of 16b (0.28 mmol, 140 °C, 0.5 h, 91%): red crystals; R_f = 0.70 (SiO_2, 1:2 EtOAc/hexanes); mp 152–153 °C (ether/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.7 Hz, 1 H), 8.18 (d, *J* = 10.2 Hz, 1 H), 8.07 (d, *J* = 8.4 Hz, 1 H), 7.85 (dd, *J* = 1.2 Hz, 8.4 Hz, 1 H), 7.56, 7.55 (two overlapping hept, *J* = 7.8 Hz, 2 H), 7.38–7.27 (m, 5 H), 4.81 (s, 1 H), 3.27 (t, *J* = 5.4 Hz, 2 H), 2.66 (t, *J* = 6 Hz, 2 H), 1.89 (hept, *J* = 5.9 Hz, 2 H); IR (CH_2Cl_2, cm^{-1}) 3020, 2960, 1660, 1605, 1590, 1545, 1385, 1350, 1305, 1175, 1115; MS (LREI) *m/z* (relative intensity) 353 (M^+, 41), 263 (43), 91 (100). Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.44; H, 5.45; N, 3.92.

Preparation of 16c (0.30 mmol, 140 °C, 2 h, 71%): red crystals; R_f = 0.22 (SiO_2, 1:2 EtOAc/hexanes); mp 125–126 °C (ether/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1 H), 7.56 (t, *J* = 7.9 Hz, 1 H), 7.33–7.27 (m, 5 H), 7.10 (d, *J* = 8.4 Hz, 1 H), 4.74 (s, 2 H), 3.91 (s, 3 H), 3.19 (t, *J* = 5.4 Hz, 2 H), 2.60 (t, *J* = 6.3 Hz, 2 H), 1.82 (hept, *J* = 6 Hz, 2 H); IR (CH_2Cl_2, cm^{-1}) 3040, 2940, 2840, 1665, 1580, 1550, 1390, 1355, 1195, 1065, 950; MS (LREI) *m/z* (relative intensity) 333 (M^+, 18), 243 (37), 91 (68), 77 (100). Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.43; H, 5.79; N, 4.10.

Preparation of 16d (0.149 mmol, 120 °C, 0.5 h, 76%): dark violet crystals; R_f = 0.41 (SiO_2, 1:2 EtOAc/hexanes); mp 151–152 °C (ether/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 0.9 Hz, 1 H), 7.36–7.26 (m, 5 H), 6.77 (d, *J* = 0.9 Hz, 1 H), 4.88 (s, 2 H), 3.21 (t, *J* = 5.3 Hz, 2 H), 2.56 (t, *J* = 6.3 Hz, 2 H), 1.78 (hept, *J* = 5.7 Hz, 2 H); IR ($CDCl_3$, cm^{-1}) 2860, 2850, 1675, 1625, 1535, 1480, 1375, 1360, 1235, 1145; MS (HREI) calcd for $C_{18}H_{15}NO_3$ 293.1052, found 293.1055. Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.52; H, 5.17; N, 4.72.

Preparation of 16e (0.627 mmol, 130 °C, 0.5 h, 83%): dark purple crystals; R_f = 0.39 (SiO_2, 1:2 EtOAc/hexanes); mp 155–156 °C (CH_2Cl_2/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 0.9 Hz, 1 H), 7.36–7.26 (m, 5 H), 6.77 (d, *J* = 0.9 Hz, 1 H), 4.88 (s, 2 H), 3.21 (t, *J* = 5.3 Hz, 2 H), 2.56 (t, *J* = 6.3 Hz, 2 H), 1.78 (hept, *J* = 5.7 Hz, 2 H); IR (CH_2Cl_2, cm^{-1}) 3040, 2960, 1675, 1635, 1540, 1490, 1385, 1360, 1240, 1200, 1130; MS (HREI) calcd for $C_{18}H_{15}NO_3$ 293.1052, found 293.1051. Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.86; H, 5.21; N, 4.75.

Preparation of 16f (1.4 mmol, 130 °C, 0.5 h, 84%): purple crystals; R_f = 0.22 (SiO_2, 1:2 EtOAc/hexanes); mp 98–99 °C (ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 4.8 Hz, 1 H), 7.44 (d, *J* = 5.1 Hz, 1 H), 7.35–7.26 (m, 5 H), 4.86 (s, 2 H), 3.21 (t, *J* = 5.4 Hz, 2 H), 2.59 (t, *J* = 6.3 Hz, 2 H), 1.80 (hept, *J* = 5.9 Hz, 2 H); IR (CH_2Cl_2, cm^{-1}) 2980, 2970, 1640, 1605, 1570, 1520, 1400, 1360, 1300; MS (HREI) calcd for $C_{18}H_{15}NO_2S$ 309.0823, found 309.0827. Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.88; H, 4.89; N, 4.53. Found: C, 69.70; H, 4.96; N, 4.52.

Preparation of 16g (0.197 mmol, THF, 75 °C, 3.5 h, 87%): purple solid: R_f = 0.72 (SiO_2, 1:1 EtOAc/hexanes); mp 43–45 °C (ether/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.22 (m, 5 H), 6.22 (s, 1 H), 4.78 (s, 2 H), 3.17 (t, *J* = 5.3 Hz, 2 H), 2.48 (t, *J* = 6 Hz, 2 H), 2.40 (t, *J* = 7.2 Hz, 2 H), 1.78 (hept, *J* = 5.4 Hz, 2 H), 1.50–1.33 (m, 4 H), 0.91 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.8, 183.2 149.9, 145.5, 137.4, 129.1, 127.9, 126.7, 120.7, 114.3, 55.8, 49.4, 29.5, 28.2, 21.9, 20.0, 19.7, 13.3; IR ($CDCl_3$, cm^{-1}) 2950, 2930, 1655, 1630, 1550, 1350, 1185; MS (HREI) calcd for $C_{20}H_{23}NO_2$ 309.1728, found 309.1722. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.46; H, 7.54; N, 4.46.

Quinolinequinones 18. A. Debenzylation of N-Benzyl-1,2,3,4-tetrahydroquinolinequinones by Hydrogenolysis. General Experimental Procedure. A solution of *N*-benzyl-1,2,3,4-tetrahydroquinolinequinone **16** and 10% Pd/C in ethanol was heated while being sparged with H_2 gas. The reaction was monitored by TLC until completion, filtered through a pad of Celite 545 with CH_2Cl_2, and concentrated under reduced pressure. The residue was purified by chromatography on flash SiO_2 (hexanes/EtOAc gradient). In parentheses following each of the compounds shown below is an indication of the scale of the reaction, the percentage of palladium catalyst used, the reaction

temperature and time, and the yield of the product.

B. Debenzylation of *N*-benzyl-1,2,3,4-tetrahydroquinoline-5,8-dione (16a) to give 17a (0.44 mmol, 7.7 mol %, 40 °C, 2 h, 94%): red needles; R_f = 0.45 (SiO_2, 1:2 EtOAc/hexanes, red spot); mp 179–180 °C (EtOH) (lit.[29] mp 182–183 °C (MeOH)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 1 H), 7.93 (d, J = 7.5 Hz, 1 H), 7.63 (t, J = 7.7 Hz, 1 H), 7.52 (t, J = 7.7 Hz, 1 H), 5.78 (s br, 1 H), 3.39 (s br, 2 H), 2.61 (t, J = 6 Hz, 2 H), 1.87 (hept, J = 6 Hz, 2 H); IR ($CDCl_3$, cm^{-1}) 3420, 2960, 2935, 2880, 2860, 1670, 1610, 1570, 1510, 1435, 1385, 1335, 1310, 1260, 1230; MS (HREI) calcd for $C_{13}H_{11}NO_2$ 213.0790, found 213.0786.

Debenzylation of 16d to give 17d (0.23 mmol, 10 mol %, 50 °C, 1 h, 89%): dark blue needles; R_f = 0.33 (SiO_2, 1:2 EtOAc/hexanes); mp 217–220 °C (CH_2Cl_2/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.25 (s br, 1 H), 4.62 (t, J = 9.9 Hz, 2 H), 3.32 (appeared s br, 2 H), 3.02 (t, J = 9.9 Hz, 2 H), 2.44 (t, J = 6.1 Hz, 2 H), 1.81 (hept, J = 5.9 Hz, 2 H); IR (CH_2Cl_2, cm^{-1}) 3420, 2960, 2860, 1680, 1645, 1610, 1590, 1500, 1380, 1130; MS (LREI) m/z (relative intensity) 205 (M^+, 100), 190 (12), 176 (16), 149 (19), 108 (43). Anal. Calcd for $C_{11}H_9NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.10; H, 5.42; N, 6.77.

Debenzylation of 16f to give 17f (0.75 mmol, 100 mol %, 85 °C, 16 h, 27%): bright purple crystals; R_f = 0.49 (SiO_2, 1:2 EtOAc/hexanes); mp 185–186 °C (CH_2Cl_2/hexanes) and with 40 mg (17%) of starting material recovered: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 4.8 Hz, 1 H), 7.49 (d, J = 5.1 Hz, 1 H), 5.72 (s br, 1 H), 3.40 (m, 2 H), 2.56 (t, J = 6.1 Hz, 2 H), 1.87 (hept, J = 5.9 Hz, 2 H), IR (CH_2Cl_2, cm^{-1}) 3410, 2960, 1655, 1590, 1515, 1505, 1390, 1320, 830; MS (LREI) m/z (relative intensity) 219 (M^+, 100), 204 (27), 162 (20), 111 (41). Anal. Calcd for $C_{11}H_9NO_2S$: C, 60.26; H, 4.14; N, 6.39. Found: C, 59.99; H, 4.09; N, 6.31.

General Experimental Procedure for DDQ Oxidation of Tetrahydropyridine Ring. A solution of tetrahydropyridine ring compound (16 or 17) and 3 equiv of DDQ in dry benzene was heated at 80 °C under N_2 until compound 16 or 17 was consumed (15 min–3 h) as monitored by TLC. When the reaction was complete, the product was purified by chromatography on flash SiO_2 (elution with a mixture of EtOAc and hexanes). In parentheses following each of the compounds shown below is an indication of the scale of the reaction, the reaction time, and the yield of the product.

1-Azaanthraquinone (18a) by the oxidation of 17a (0.216 mmol, 1.5 h, 69%): yellow needles. Analysis as shown below.

Preparation of 18f by the oxidation of 17f (0.059 mmol, 1 h, 63%): yellow solid. Analysis as shown below.

Direct oxidation of *N*-benzyl-1,2,3,4-tetrahydro-1-azaanthraquinone (16a) to form 1-azaanthraquinone (18a) (0.149 mmol, 3 h, 42%): yellow needles; mp 275–276 °C (CH_2Cl_2/hexanes) (lit.[29] mp 273–275 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.12 (d, J = 4 Hz, 1 H), 8.65 (d, J = 7.5 Hz, 1 H), 8.41 (m, 1 H), 8.32 (m, 1 H), 7.83 (m, 2 H), 7.74 (dd, J = 7.8 Hz, 4.5 Hz, 1 H).

Direct oxidation of 16d to form 18d (0.287 mmol, 45 min, 37%): yellow needles; mp 273 °C (sublimation) (CH_2Cl_2/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (dd, J = 1.5 Hz, 4.8 Hz, 1 H), 8.52 (dd, J = 1.5 Hz, 7.8 Hz, 1 H), 7.83 (d, J = 1.5 Hz, 1 H), 7.69 (dd, J = 4.8 Hz, 7.8 Hz, 1 H), 7.03 (d, J = 1.5 Hz, 1 H); IR (CH_2Cl_2, cm^{-1}) 1698, 1683, 1365, 1110; MS (HREI) calcd for $C_{11}H_5NO_3$ 199.0269, found 199.0272.

Direct oxidation of 16f to form 18f (0.337 mmol, 15 min, 35%): yellow needles; mp 262–263 °C (CH_2Cl_2/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (dd, J = 1.6 Hz, 4.7 Hz, 1 H), 8.53 (dd, J = 1.6 Hz, 8.0 Hz, 1 H), 7.83 (d, J = 5.1 Hz, 1 H), 7.70 (d, J = 5.1 Hz, 1 H), 7.70 (dd, J = 4.6 Hz, 8.0 Hz, 1 H); IR (CH_2Cl_2, cm^{-1}) 1680, 1585, 1520, 1400, 1320, 1290, 885; MS (HREI) calcd for $C_{11}H_5NO_2S$ 215.0041, found 215.0027.

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Registry No. 4, 135831-74-2; **5a**, 135865-28-0; **6**, 135831-75-3; **7**, 135831-76-4; **8**, 135831-77-5; **9**, 135831-78-6; **10**, 135831-79-7; **11**, 135831-80-0; **12**, 135831-81-1; **13**, 135831-82-2; **14**, 135831-83-3; **15a**, 135831-84-4; **15b**, 135831-85-5; **15c**, 135831-86-6; **15d**, 135831-87-7; **15e**, 135831-88-8; **15f**, 135831-89-9; **15g**, 135831-90-2; **16a**, 135831-91-3; **16b**, 135831-92-4; **16c**, 135831-93-5; **16d**, 135831-94-6; **16e**, 135831-95-7; **16f**, 135831-96-8; **16g**, 135831-97-9; **17a**, 18710-11-7; **17d**, 135831-98-0; **17f**, 135831-99-1; **18a**, 3712-09-2; **18d**, 135832-00-7; **18f**, 135832-01-8; DDQ, 84-58-2; PhLi, 591-51-5; *o*-LiC_6H_4OMe, 31600-86-9; $LiC{\equiv}C(CH_2)_3CH_3$, 17689-03-1; Pd(benzyl)Cl(PPh_3)$_2$, 86633-24-1; CuI, 7681-65-4; $(BOC)_2O$, 24424-99-5; $Pd(PPh_3)_4$, 14221-01-3; 3-carbomethoxy-4-formylisoquinoline, 135832-02-9; 3-formyl-4-carbomethoxyisoquinoline, 135832-03-0; 3-(tri-*n*-butylstannyl)-4-isopropoxy-3-cyclobutene-1,2-dione, 129034-70-4; 1-lithionaphthalene, 14474-59-0; 2-lithiofuran, 2786-02-9; 3-lithiofuran, 53101-93-2; 2-lithiothiophene, 2786-07-4; 2-iodobenzaldehyde, 26260-02-6; 2-iodobenzylamine, 39959-51-8; 3-ethoxy-4-(tri-*n*-butylstannyl)-3-cyclobutene-1,2-dione, 135832-04-1; 1-bromo-3-(tetrahydropyranyloxy)propane, 33821-94-2; diisopropyl squarate, 61699-62-5.

(29) Birch, A. J.; Butler, D. N.; Siddall, J. B. *J. Chem. Soc.* **1964**, 2941.