Rhodium-Mediated Dipolar Cycloaddition of Diazoquinolinediones

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As an entry to furoquinoline structures of natural origin, the rhodium-mediated dipolar cycloaddition of diazoquinolinediones with alkenes and alkynes has been examined. Because of the unsymmetrical nature of the diazo compounds, both linear and angular furoquinoline products are possible. For the most part, a mixture of regioisomers is generated in moderate to good yields, though in a few cases dominant products are obtained in high yields. The products can be further converted to naturally occurring alkaloids such as isodictamnine. A novel observation in this work is that catalytic quantities of acid enhance the yield and regiochemical control in the cycloaddition.

Introduction

The furoquinoline alkaloids are an extremely diverse set of natural products that are the most widely distributed of quinoline alkaloids.[1] They are primarily isolated from Rutaceae and often incorporate a terpenoid fragment. Members of the group have vasoconstrictive, antidiuretic, antiarrhythmic, spasmolytic, sedative, and hypothermic effects.[2] Biological properties also include photosensitization for DNA damage and mutation[3] and antineoplastic[4]/antimicrobial[5]/antimalarial[6] activity. Most of the known alkaloids in the group are linearly fused and O-alkylated and fall into the dictamnine class. A few alkaloids in the isodictamnine class are instead alkylated at the N-1 position. In rare cases, related angularly fused furo[3,4-*d*]quinoline structures have been found in Nature.

While they are of relatively modest complexity by today's standards of organic synthesis, a number of synthetic approaches to the furoquinoline alkaloids have been reported, primarily by Grundon.[7] Other workers have achieved total syntheses of dictamnine[8] and isoplatydesmine,[9] inter alia.

The method we have developed for the synthesis of complex polyheterocyclic systems using the dipolar cycloaddition of rhodium carbenoids to polar olefins[10] seemed ideal for the preparation of furoquinoline alkaloids (eq 1) and, with the available asymmetric rhodium catalysts,[11] might be able to provide access to single enantiomers of the natural products. The mechanism that we have proposed for the production of dipolar

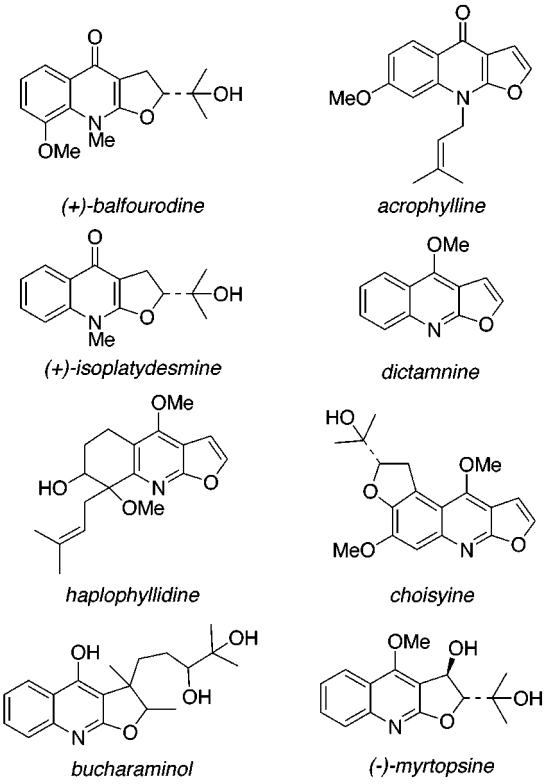

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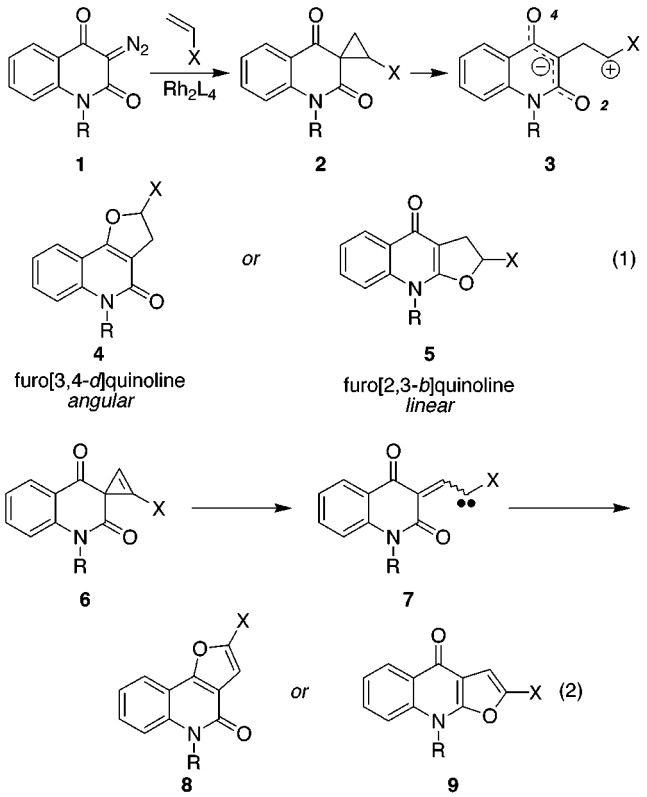
Table 1. AM1-Calculated Atomic Charges of Quinolinedione Anions

	$R_1 = H$, $R_2 = H$	$R_1 = Me$, $R_2 = H$	$R_1 = MOM$, $R_2 = H$	$R_1 = Bz$, $R_2 = H$	$R_1 = Me$, $R_2 = OMe$
			(a) Mulliken Charges		
N1	−0.326	−0.344	−0.308	−0.276	−0.271
C2	0.358	0.358	0.367	0.341	0.365
O2	−0.495	−0.454	−0.499	−0.471	−0.484
C3	−0.526	−0.558	−0.525	−0.566	−0.524
H3	0.136	0.146	0.138	0.145	0.138
C4	0.317	0.295	0.319	0.291	0.316
O4	−0.479	−0.449	−0.472	−0.449	−0.478
O4−O2	0.016	0.005	0.027	0.022	0.006
sum	−1.015	−1.006	−0.980	−0.985	−0.938
			(b) Atomic Charges from Electrostatic Potential		
N1	−0.614	−0.558	−0.496	−0.506	−0.371
C2	0.785	0.783	0.773	0.763	0.727
O2	−0.668	−0.619	−0.658	−0.635	−0.641
C3	−0.914	−0.971	−0.937	−0.694	−0.897
H3	0.205	0.236	0.211	0.228	0.206
C4	0.699	0.656	0.723	0.669	0.687
O4	−0.647	−0.606	−0.643	−0.619	−0.646
O4− O2	0.021	0.013	0.015	0.016	−0.005
sum	−1.154	−1.079	−1.027	−0.794	−0.935

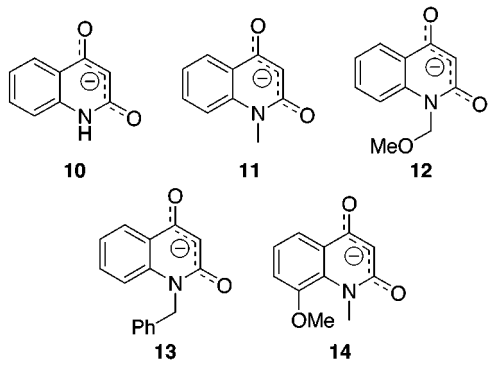
cycloadducts in the reactions of cyclic rhodium carbenoids with olefins involves initial cyclopropanation, ring opening to a zwitterion, and ring closure. It is also possible that the zwitterion is formed directly. In the case of a diazoquinolinedione (**1**), it is readily seen that regiochemical issues arise. Since most of our earlier studies have not addressed regiochemistry, the behavior of such unsymmetrical diones might yield further mechanistic insight. Likewise, with acetylenic dipolarophiles, we have provided a mechanistic explanation that could be further amplified by consideration of regiochemistry (eq 2).



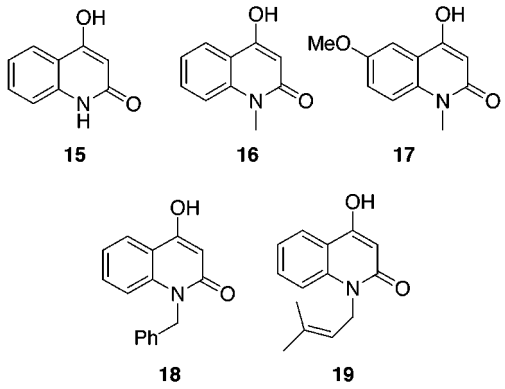
This report describes the rhodium-mediated dipolar cycloaddition of diazoquinolinediones and its application to the preparation of furoquinoline alkaloids, including a synthesis of isodictamnine. It includes a provocative, novel observation that acid can influence the course of these reactions.

Results

We first aimed to predict the regiochemical outcome of the dipolar cycloaddition with alkenes (based on the mechanistic rationale in eq 1) using theoretical methods. Reasoning that ring closure of a zwitterion such as **3** would likely occur at the site of highest electron density, we performed Spartan AM1 calculations on a range of substituted quinolinedione anions. In the synthetic study, the R group could presumably be introduced for the purpose of controlling regiochemistry. Collected in Table 1 is the charge distribution in the quinolone portion of these zwitterions, expressed either as the Mulliken charges or the atomic charges from an electrostatic potential map. In all cases but **14**, the O2 position is more negative, suggesting that the linear isomer should be favored.



Several novel 4-hydroxy-2-quinolones (= quinolinediones) were needed to investigate the influence of substituents on reactivity and regiochemistry. The parent compound **15** is commercially available. The *N*-methyl-



4-hydroxy-2-quinolones **16** and **17** were prepared by cyclization of the corresponding anthranilic acids with acetic anhydride in acetic acid (70% and 39%, respectively).[12] The *N*-prenyl-4-hydroxy-2-quinolone **19** was prepared by the method of Coppola,[13] wherein an N-alkylated isatoic anhydride participates in a Dieckmann-like condensation (eq 3). The *N*-benzyl-4-hydroxy-2-

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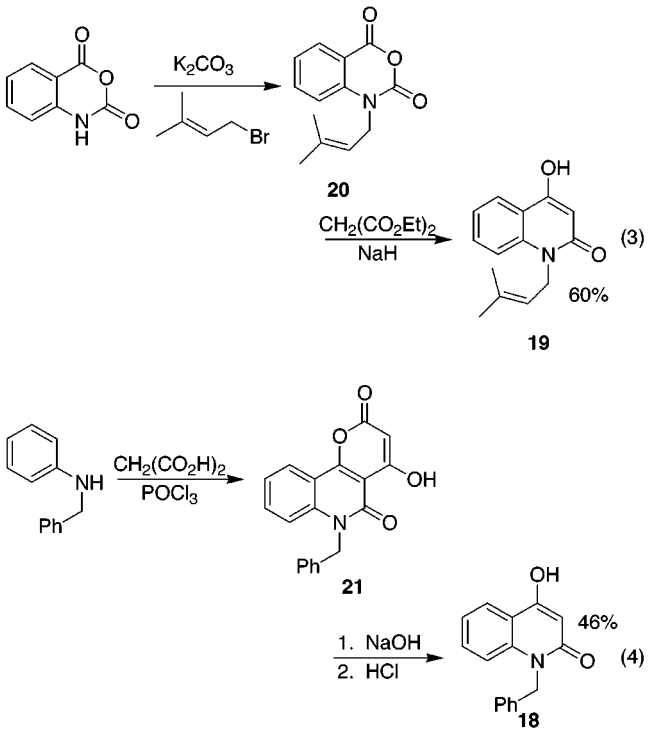
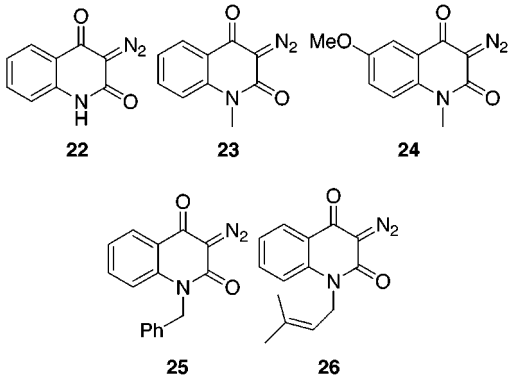


quinolone **18** was prepared by condensation of *N*-benzylaniline with malonic acid (eq 4).[14] The poor solubility properties of these compounds make them resistant to conventional purification schemes (recrystallization, chromatography). In our hands, the best choice has been precipitation by centrifugation.

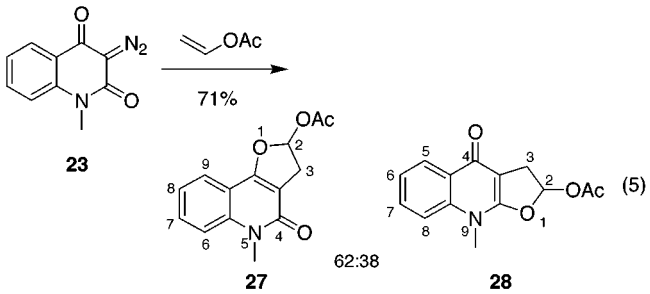
Diazotransfer[15] with mesyl azide in ethanol results in the conversion of these 4-hydroxy-2-quinolones in 63−90% yields to the diazoquinolinediones **22**−**26**, which precipitate from solution. Small quantities of azo compounds are also formed, which can be removed by filtration through silica gel (THF).

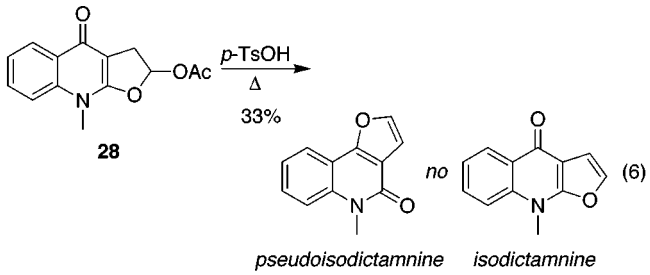


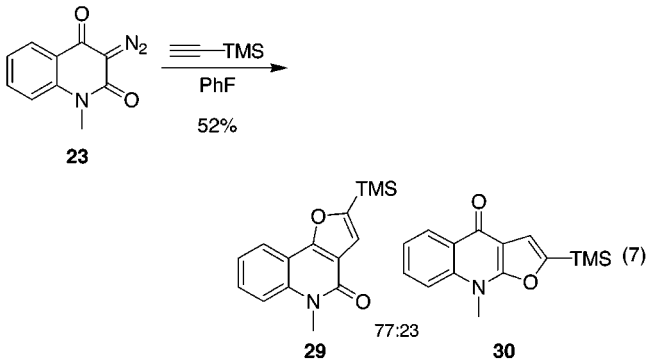
Because of low solubility of the diazoquinolinediones in most solvents usually employed for rhodium-based carbenoid chemistry, decomposition reactions were conducted at 55 °C by slow addition of **22**−**26** in *powder* form to the neat alkene (vinyl acetate) or alkyne (trimethylsilylacetylene (20-fold excess) in fluorobenzene) over 2−3 d. Other olefins examined included phenyl vinyl sulfide and phenyl vinyl sulfoxide, which complex with the catalyst (as evidenced by a color change) and thereby prevent reaction. Isoprene and vinyltrimethoxysilane also do not give cycloadducts. The catalysts examined in this study include rhodium anisoate, pivalate, adamantanoate, tricyanoacetate, and acetate. Only the first three electron-rich catalysts show any catalytic activity.

Diazo compound **22** showed no reaction under any of a wide variety of reaction/catalyst conditions examined. It could also be converted to an *N*-acetyl derivative that readily evolved nitrogen (even at 0 °C) with rhodium pivalate, but no dipolar cycloadducts could be isolated.

The *N*-methyl diazoquinolinedione **23** undergoes cycloaddition with vinyl acetate under rhodium pivalate catalysis to give a mixture of regioisomers (eq 5). The







assignment of the structures of these products is readily made on the basis of spectral properties, primarily NMR, and particularly the downfield shift (δ >8.0 ppm) of the peri hydrogen at the 5-position of the linear isomer. With rhodium adamantanoate, only the angular isomer **27** is formed, but in lower yield. The aromatization of the linear **28** yields a surprising result: formation of the angular isomer, a known but unnatural product called pseudoisodictamnine (eq 6). Presumably, its formation involves prior acid-catalyzed equilibration of **27** and **28**, though no direct evidence for this process could be garnered. Thermal equilibration of isodictamnine and pseudoisodictamnine has also been reported.[16] With trimethylsilylacetylene as the dipolarophile, regiochemi-

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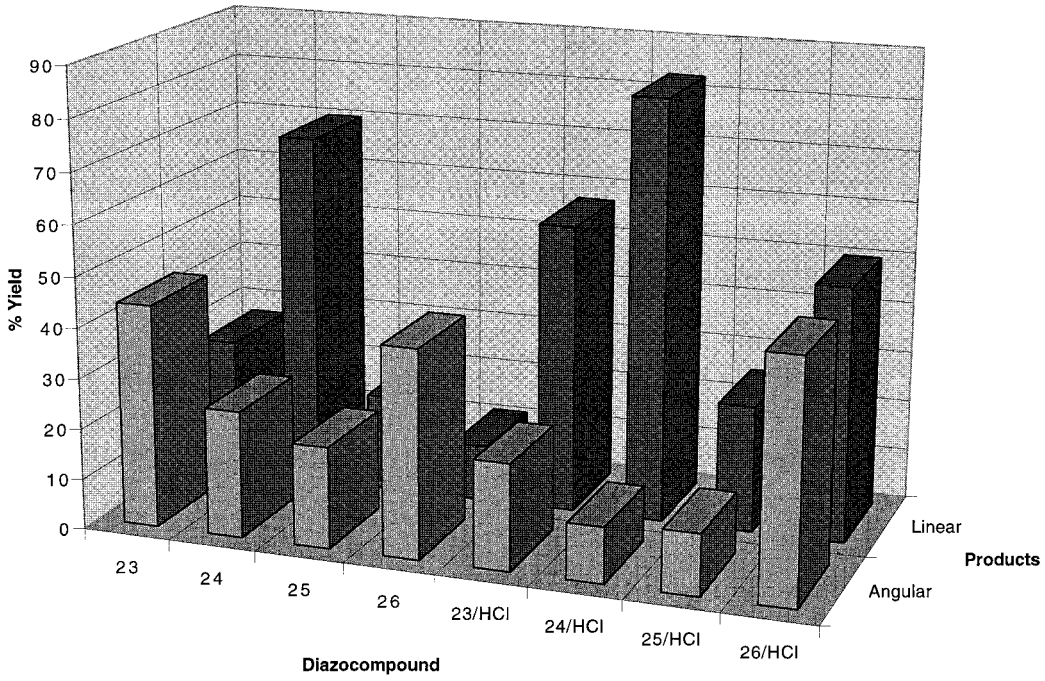
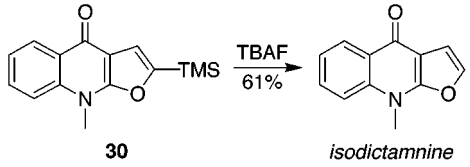
Chart 1. Reaction of Diazoquinolinediones with Vinyl Acetate



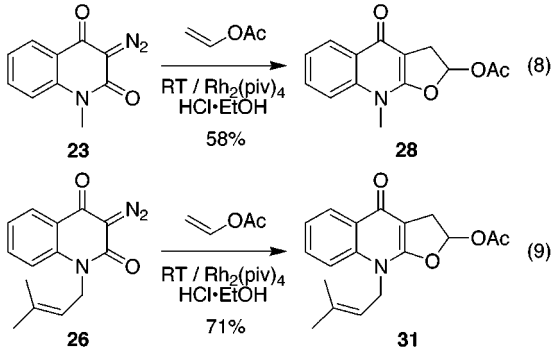
cal control and yield are diminished, but the separable products **29** and **30** are readily desilylated with tetra-*n*-butylammonium fluoride to provide the isodictamnine isomers, which gave data identical to literature reports.



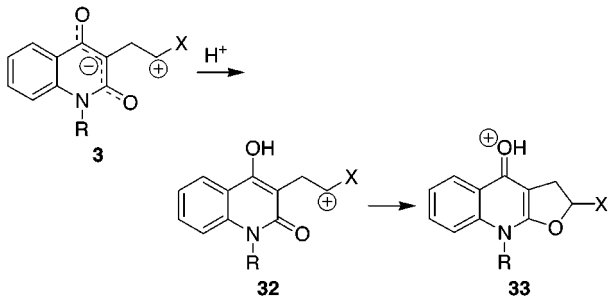
The influence of substitution on the diazoquinolinedione (i.e., **23**−**26**) on dipolar cycloadditions with vinyl acetate and trimethylsilylacetylene catalyzed by rhodium pivalate is summarized in Charts 1 and 2. Late in this investigation, it was discovered that the addition of a few drops of HCl ethanolate to the reaction mixture affects both the efficiency and selectivity of the reaction, generally in favor of the linear isomer, in reactions with vinyl acetate. Notable is the cycloaddition of **24**, favoring the linear isomer by a margin of ~7:1 (95% combined yield). Furthermore, this additive enables cycloadditions with vinyl acetate to be conducted at room temperature with enhanced selectivity (eqs 8 and 9), though requiring longer reaction times. This acid effect is less dramatic with trimethylsilylacetylene, primarily increasing the yield but not affecting the favored regioisomer. Control experiments show that acid alone does not affect any of the starting materials or products.

Discussion

Any explanation for the regiochemical outcome in the dipolar cycloaddition of diazoquinolinediones must be tempered by the modest levels of selectivity and seemingly spurious divergence of reactivity with small changes in structure and conditions. Nevertheless, it seems likely that balanced electron density at oxygen in the putative zwitterions **3** is reflected in the production of similar



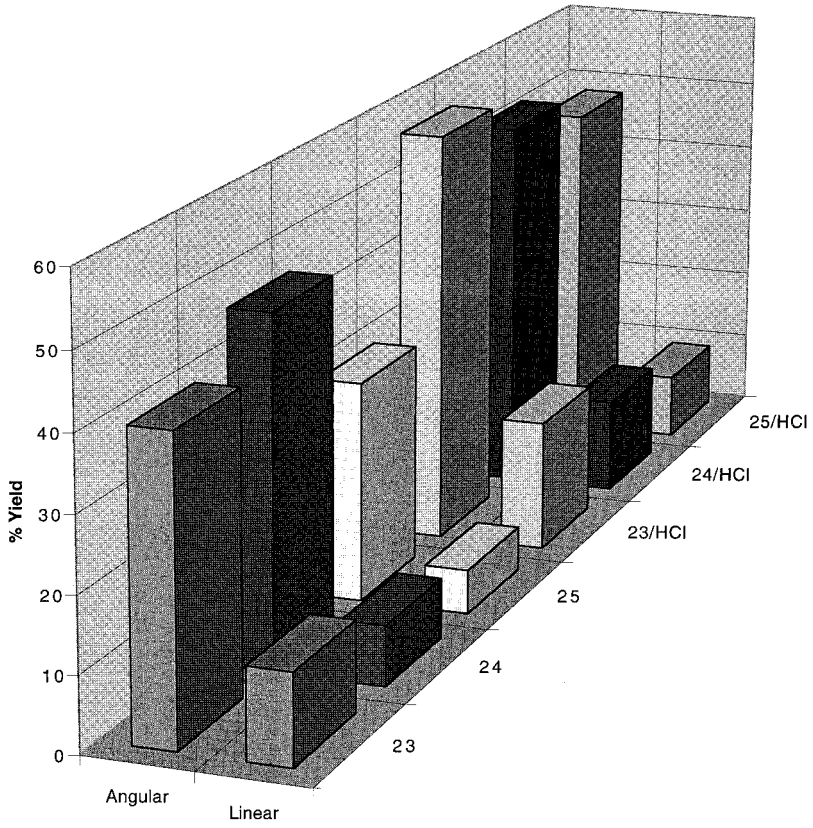
amounts of the regioisomers in cycloadditions to vinyl acetate. As no change in the product distributions was observed over time, we believe this reaction is under kinetic control. Sterics seem to have little, if any, influence on the product ratios. On the other hand, in cycloadditions with trimethylsilylacetylene, the angular furoquinoline, which is known to be more thermodynamically stable, is invariably favored. We suggest this regiochemistry is under thermodynamic control, with equilibration occurring among intermediates such as **7**.



The rationale for the addition of acid to the dipolar cycloaddition reaction was that protonation of zwitterion **3** would likely favor tautomer **32**, as is the case with the 4-hydroxy-2-quinolones. Such a cation would be expected to close on O2 to generate the linear isomer. The

(16) Tuppy, H.; Boehm, F. *Mh. Chem.* **1956**, *87*, 735−740.

Chart 2. Reaction of Diazoquinolinediones with Trimethylsilylacetylene



enhancement of the production of linear isomers in the presence of acid supports this theory.

In summary, the methodology developed here may be useful in the preparation of polyheterocyclic ring systems based on quinolones. The results also support previously proposed mechanisms for the dipolar cycloaddition.

Experimental Section

General Methods. All purchased chemicals were used without further purification unless noted otherwise. Chemical suppliers used were Aldrich and VWR. All flash chromatography was done using silica gel 60 (230−400 mesh ASTM). Chromatographic analyses were performed on precoated aluminum TLC silica gel plates. Indicators used: UV short wave light, phosphomolybdic acid dip (in EtOH). All reported R_f values are from TLC in 1:1 pentane/ethyl acetate. All rhodium(II) carboxylate catalysts were synthesized from commercially available carboxylic acids by exchange with rhodium acetate. All reactions were performed under argon atmosphere.

General Procedure for Diazo Transfer of 4-Hydroxy-2-quinolones. The 4-hydroxy-2-quinolone was suspended in a minimum amount of cold ethanol (usually about 3 M). The suspension was cooled in an ice bath, and 2 equiv of Et_3N was added. After 0.5 h, mesyl azide (1.1 equiv) was added, and the reaction mixture was allowed to slowly warm to room temperature. After 12 h, the solid product was filtered and washed with ether. The crude product was, if necessary, purified by recrystallization from ethanol or acetone or by passing it through a plug of silica (THF).

General Procedures for 1,3-Dipolar Addition of Diazoquinolinediones. A. To a solution of olefin (20 mmol) in 1 mL of fluorobenzene kept at 55 °C was added 6.1 mg (0.01 mol %) rhodium(II)pivalate and, in small portions, 1 mmol of the diazo compound. The reaction was followed to completion by TLC. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel using a ether/pentane gradient with concentrations of ether increasing from 0% to 100%.

Table 2. Reactions of Diazoquinolinediones with Vinyl Acetate

diazo compd	angular	yield (%)	linear	yield (%)
23	**27**	44	**28**	27
24	**34**	25	**35**	70
25	**36**	20	**37**	19
26	**38**	41	**31**	11
23/HCl	**27**	21	**28**	57
24/HCl	**34**	11	**35**	83
25/HCl	**36**	12	**37**	25
26/HCl	**38**	47	**31**	50

Table 3. Reactions of Diazoquinolinediones with Trimethylsilylacetylene

diazo compd	angular	yield (%)	linear	yield (%)
23	**29**	40	**30**	12
24	**39**	47	**40**	8
25	**41**	30	**42**	6
23/HCl	**29**	57	**30**	18
24/HCl	**39**	52	**40**	13
25/HCl	**41**	48	**42**	9

B. To a solution of 6.1 mg (0.01 mol %) of rhodium(II)-pivalate in 2 mL of vinyl acetate kept at 55 °C was added, in small portions, 1 mmol of diazo compound over a period of 48 h. Addition of 0.01 mol % of 1 M HCl−etherate (0.02 mL) increased the total yield and favored the linear furoquinoline adducts.

Results are summarized in Tables 2 and 3.

1-Methyl-4-hydroxy-2-quinolone (16). According to a literature procedure,[17] a solution of *N*-methylanthranilic acid (9.1 g, 60 mmol) in 30 mL acetic anhydride and 30 mL acetic acid was refluxed for 5 h. The reaction mixture was poured with stirring onto 300 mL of ice/water. The solid was filtered and dissolved in a minimum amount of warm aqueous NaOH. Solids were removed by filtration, and the filtrate was acidified

(17) Lutz, R. F.; Codington, J. F.; Rowlett, R. J. *J. Am. Chem. Soc.* **1946**, *68*, 1810.

to pH 4 with concentrated HCl. The product was filtered, washed with copious amounts of water, and dried in vacuo: $R_f = 0.06$, white powder, 7.35 g, 70%; mp 263−264 °C (ethanol). Spectral/physical data were consistent with literature data.[18]

1-Methyl-4-hydroxy-6-methoxy-2-quinolone (17). To a mixture of 2.40 g (17.5 mmol) of *N*-methyl-*p*-anisidine and 3.65 g (35 mmol) of malonic acid was added 15 mL of $POCl_3$. The solution was heated at 90 °C for 1 h and then poured onto ice/water. The solution was brought to pH 14, filtered, and acidified to pH 4−5. Filtration afforded **17**: $R_f = 0.10$, yellow powder, 39%; mp 293 °C (ethanol); ^{1}H NMR (DMSO-d_6) δ 3.49 (s, 3H), 3.79 (s, 3H), 5.86 (s, 1H), 7.25 (dd, J = 6.1, 9.1 Hz, 1H), 7.31 (d, J = 2.9 Hz, 1H), 7.41 (d, J = 9.1 Hz, 1H), 11.33 (s, 1H); ^{13}C NMR δ 28.5, 40.1, 40.3, 55.4, 98.4, 104.8, 116.1, 116.7, 119.7, 134.5, 153.8, 160.4, 162.1. Spectral/physical data were consistent with literature data.[19]

1-Benzyl-4-hydroxy-2-quinolone (18). A solution of *N*-benzylaniline (3.66 g, 20 mmol) and malonic acid (2.60 g, 25 mmol) in 20 mL of $POCl_3$ was heated for 1 h at 90 °C. The black syrup was poured onto ice−water and basified to pH 14 with NaOH pellets. After filtration, the liquid was acidified to pH 4−5 with concentrated HCl. Filtration through a plug of silica (THF) gives **18**: $R_f = 0.01$, pale ochre solid, 46%; mp 288 °C (ethanol); ^{1}H NMR (DMSO-d_6) δ 5.44 (s, 2H), 5.98 (s, 1H), 7.15−7.28 (m, 7H), 7.48 (t, J = 7.7 Hz, 1H), 7.90 (d, J = 7.7 Hz, 1H), 11.60 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 44.3, 79.4, 116.1, 120.0, 122.6, 125.4, 126.2, 127.0, 128.4, 135.0, 140.1, 158.8, 174.5; IR 2558 (broad), 1540, 1245 cm^{-1}. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.23; H, 5.38; N, 5.58. Spectral/physical data were consistent with literature data.[14]

1-(3′-Methyl-2′-butenyl)isatoic Anhydride (20). To a suspension of isatoic anhydride (1.63 g, 10 mmol) in DMF was added K_2CO_3 (0.83 g, 0.06 mol). After 1 h, 1-bromo-3-methyl-2-butene (1.25 g, 0.012 mol) was added, and the reaction was stirred for 20 h. Most of the DMF was removed in vacuo. The oily mixture was then poured onto 20 mL of ice/water. The solid product was filtered, washed with copious amounts of water, and dried in vacuo to give pale brown crystals: R_f = 0.55, 93%; mp 119 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 1.74 (s, 3H), 1.85 (s, 3H), 4.67 (d, J = 6.2, 2H), 5.17 (dt, J = 1.2, 6.2 Hz, 1H), 7.12 (d, J = 8.5, 1H), 7.28 (d, J = 7.5, 1H), 7.72 (dt, J = 8.6, 1.4, 1H), 8.14 (dd, J = 7.9, 1.2). Anal. Calcd For $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.29; H, 5.69; N, 6.10.

1-(3′-Methyl-2′-butenyl)-4-hydroxy-2-quinolone (19). To NaH (0.17 g, 0.007 mol, 60% in mineral oil, pentane washed) in 4 mL of DMF was added in portions diethyl malonate (1.12 g, 0.007 mol). When the evolution of H_2 ceased, the solution was stirred for 15 min and was placed in an oil bath at 80 °C. To this solution 1.15 g (0.005 mol) of **20** in 3 mL of DMF was added dropwise over a period of 15 min. The mixture was heated for 18 h at 120 °C and cooled and the solid removed by filtration to give a white powder: $R_f = 0.06$, 63%; mp 257 °C (ethanol); ^{1}H NMR (DMSO-d_6) δ 1.64 (s, 3H), 1.80 (s, 3H), 4.78 (s, 2H), 5.02 (s, 1H), 5.93 (s, 1H), 7.18−7.89 (m, 4H), 11.50 (s, 1H); ^{13}C NMR δ 17.8, 25.0, 97.7, 114.3, 116.0, 120.0, 120.8, 123.0, 130.9, 134.6, 138.9, 160.9, 162.0; IR (KBr) 2550, 1641, 1596 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.18; H, 6.64; N, 6.05.

3-Diazo-1*H*-quinolin-2,4-dione (22). By the general procedure: 3.22 g (20 mmol) **15**; 4.04 g (40 mmol) Et_3N; 2.66 g (22 mmol) MsN_3; $R_f = 0.36$, pale pink needles, 2.88 g, 72%; mp 236 °C (ethanol); ^{1}H NMR (DMSO-d_6) δ 7.17 (t, J = 7.8 Hz, 2H), 7.63 (t, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 11.37 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 78.4, 115.5, 118.3, 122.2, 124.8, 134.8, 140.0, 158.8, 175.6; IR (KBr) 3192, 2161, 1669, 1636, 1610 cm^{-1}. Spectral/physical data were consistent with literature data.[20,21]

1-Methyl-3-diazoquinoline-2,4-dione (23). By the general procedure: 3.50 g (20 mmol) **16**; 4.04 g (40 mmol) Et_3N; 2.66 g (22 mmol) MsN_3. $R_f = 0.56$, pale yellow needles, 3.62 g, 90%; mp 164 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 3.53 (s, 3H), 7.22−7.27 (m, 2H), 7.65 (dt, J = 1.6, 7.3 Hz, 1H), 8.17 (dd, J = 1.5, 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.3, 115.0, 120.7, 123.0, 126.7, 135.2, 141.5, 159.2, 174.5, 174.8; IR 2169, 1634, 1602 cm^{-1}; LR MS 202 (MH^+). Anal. Calcd for $C_{10}H_7N_3O_2$: C, 59.70; H, 3.51; N, 20.89. Found: C, 59.81; H, 3.53; N, 20.85. Spectral/physical data were consistent with literature data.[22]

1-Methyl-6-methoxy-3-diazoquinoline-2,4-dione (24). By the general procedure: 1.37 g (6.68 mmol) **17**; 5 mL EtOH; $R_f = 0.6$, yellow needles, 73%; mp 162 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 3.56 (s, 3H), 3.88 (s, 3H), 7.18−7.27 (m, 2H), 7.62 (d, J = 2.8 Hz, 1H); ^{13}C NMR δ 29.4, 55.9, 107.9, 108.2, 111.9, 112.1, 116.6, 121.3, 123.7, 135.7, 155.5; IR 2152 cm^{-1}. Anal. Calcd for $C_{11}H_9N_3O_2$: C, 57.14; H, 3.92; N, 18.17. Found: C, 57.23; H, 4.01; N, 18.07.

1-Benzyl-3-diazoquinoline-2,4-dione (25). By the general procedure: 251 mg (1.0 mmol) of **18**; 3 mL of EtOH; $R_f = 0.65$, orange needles, 63%; mp 151 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 5.40 (s, 2H), 7.14−7.36 (m, 7H), 7.50 (dt, J = 1.5, 7.9 Hz, 1H), 8.18 (dd, J = 1.3, 7.9 Hz, 1H); ^{13}C NMR δ 45.8, 115.9, 120.8, 123.1, 126.7, 127.6, 128.9, 135.1, 135.6, 140.8; IR 2144, 1659, 1638, 1601, 1373 cm^{-1}. Anal. Calcd for $C_{16}H_{11}N_3O_2$: C, 69.31; H, 4.00; N, 15.15. Found: C, 69.37; H, 4.10; N, 15.06.

1-(3′-Methyl-2′-butenyl)-3-diazoquinoline-2,4-dione (26). By the general procedure: $R_f = 0.72$, pink needles, 69%; mp 105 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3H), 1.75 (s, 3H), 4.75 (d, J = 5.9 Hz, 2H), 5.12 (t, J = 5.9 Hz, 1H), 7.18−7.24 (m, 2H), 7.59 (t, J = 11.6, 1H), 8.16 (dd, J = 1.5, 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.6, 25.0, 40.0, 114.8, 117.9, 120.2, 122.1, 126.0, 134.4, 136.2, 140.1, 158.3, 174.9; IR (KBr) 2965, 2142, 1658, 1637, 1601, 1376 cm^{-1}. Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.94; H, 5.18; N, 16.35.

1-Acetoxy-5-methyl-2,3-dihydrofuro[3,4-*d*]quinolin-4-one (27). General procedure B: 201 mg of **23**; $R_f = 0.51$, yellow solid; mp 135 °C (ether/pentane), 44% (w/o HCl) or 21% (w/HCl). At room temperature with HCl−etherate 2% of this product was formed: ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 3H), 3.21 (dd, J = 2.2, 7.1 Hz, 1H), 3.50 (dd, J = 7.2, 17.1 Hz, 1H), 3.72 (s, 3H), 7.00 (dd, J = 2.2, 17.1 Hz, 1H), 7.28 (obscured by $CDCl_3$), 7.40 (d, J = 8.6, 1H), 7.61 (dt, J = 1.3, 8.6 Hz, 1H), 7.80 (dd, J = 1.3, 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.3, 28.5, 33.5, 98.5, 106.2, 111.3, 113.9, 121.2, 122.5, 130.6, 139.9, 160.0, 160.2, 168.9; IR 2989, 1745, 1665, 1634, 1595, 1247 cm^{-1}; LR MS 260 (MH^+); HR MS calcd for $C_{14}H_{13}NO_4$ 259.0844, found 259.0853 (M^+). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.82; H, 5.10; N, 5.38.

2-Acetoxy-9-methyl-2,3-dihydrofuro[2,3-*b*]quinolin-4-one (28). General procedure B (same as for **27**): $R_f = 0.02$, colorless needles; mp 183 °C (THF/pentane), 27% (w/o HCl) or 57% (w/HCl), 58% (at rt w/HCl); ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3H), 3.29 (dd, J = 2.2, 16.0 Hz, 1H), 3.55 (dd, J = 7.2, 16.0 Hz, 1H), 3.74 (s, 3H), 6.93 (dd, J = 2.2, 7.2 Hz, 1H), 7.40−7.45 (m, 2H), 7.65 (t, J = 1.2 Hz, 1H), 8.48 (dd, J = 1.3, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.3, 28.5, 33.5, 98.4, 106.1, 111.2, 113.9, 121.2, 122.4, 130.6, 139.9, 160.0, 160.1, 168.8; IR (KBr) 1763, 1630, 1588, 1517, 942 cm^{-1}; FAB MS 260.09 (MH^+); HR MS calculated for $C_{14}H_{13}NO_4$ 259.0844, found 259.0844 (M^+). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 62.94; H, 5.29; N, 5.27.

5-Methyl-2-trimethylsilylfuro[3,4-*d*]quinolin-4-one (29). General procedure A: 201 mg of **23**, 1.96 g of trimethylsilylacetylene; R_f = 0.58, colorless needles; mp 80 °C (ether/pentane), 40% (w/o HCl), 57% (w/HCl); ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 9H), 3.79 (s, 3H), 7.26 (s, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.56 (dt, J = 7.3, 1.3 Hz, 1H), 8.08 (dd, J = 6.8, 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −2.4, 28.7, 112.7, 114.3, 114.9, 117.0, 120.8, 121.4, 128.7, 137.4, 157.8, 159.0, 162.6; LR MS 272 (MH^+); HR MS calcd for $C_{15}H_{17}NO_2Si$ 271.1028,

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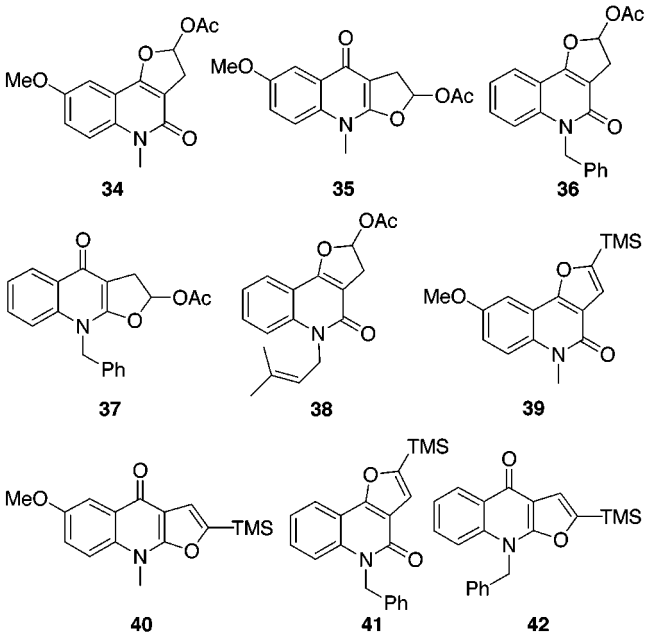
found 271.1033 (M^+). Anal. Calcd for $C_{15}H_{17}NO_2Si$: C, 66.39; H, 6.31; N, 5.16. Found: C, 66.44; H, 6.34; N, 5.22.

9-Methyl-2-trimethylsilylfuro[2,3-*b*]quinolin-4-one (30). General procedure A (same as for **29**): $R_f = 0.33$, white solid, mp 160 °C (THF/pentane), 12% (w/o HCl) 18% (w/HCl); ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H), 3.95 (s, 3H), 7.28 (s, 1H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.69 (dt, $J = 1.0$, 8.3 Hz, 1H), 8.55 (dd, $J = 1.0$, 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ −2.5, 30.7, 106.7, 113.3, 116.9, 121.7, 124.6, 126.8, 131.3, 137.5, 155.8, 158.3, 172.6; LR MS 272 (MH^+). Anal. Calcd for $C_{15}H_{17}NO_2Si$: C, 66.39; H, 6.31; N, 5.16. Found: C, 66.45; H, 6.26; N, 5.13.

2-Acetoxy-9-(3′-methyl-2′-butenyl)-2,3-dihydrofuro[2,3-*b*]quinolin-4-one (31). General procedure B: 255 mg of **26**; $R_f = 0.01$, pale yellow powder; mp 190 °C (THF/pentane), 11% (w/o HCl), 50% (w/HCl) or 71% (at room temperature w/HCl); ^{1}H NMR ($CDCl_3$) δ 1.74 (s, 3H), 1.84 (s, 3H), 2.14 (s, 3H), 3.28 (dd, $J = 2.1$, 15.9 Hz, 1H), 3.54 (dd, 7.0, 15.9 Hz, 1H), 4.78 (d, $J = 6.4$ Hz), 5.22 (t, $J = 6.4$ Hz, 1H), 6.93 (dd, 2.1, 7.0 Hz, 1H), 7.35−7.43 (m, 2H), 7.59 (t, $J = 8.4$ Hz, 1H), 8.47 (dd, $J = 1.3$, 8 Hz); ^{13}C NMR ($CDCl_3$) δ 17.5, 20.2, 25.0, 32.0, 42.5, 96.1, 97.6, 114.3, 117.0, 122.7, 126.0, 130.6, 136.9, 137.2, 158.8, 168.6; HR MS calcd for $C_{18}H_{19}NO_4$ 313.1314, found 313.1301 (M^+). Anal. Calcd for $C_{18}H_{19}NO_4$: C, 69.00; H, 6.11; N, 4.47. Found: C, 66.96; H, 6.31; N, 4.33.



2-Acetoxy-8-methoxy-5-methyl-2,3-dihydrofuro[3,4-*d*]-quinolin-4-one (34). General procedure B: 231 mg of **24**; $R_f = 0.12$, white powder, 25% (w/o HCl) 11% (w/HCl), mp 130 °C (ether/pentane); ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3H), 3.22 (dd, $J = 2.3$, 17.4 Hz, 1H), 3.51 (dd, $J = 7.2$, 17.4 Hz, 1H), 3.70 (s, 3H), 3.87 (s, 3H), 7.01 (dd, $J = 2.3$, 7.2 Hz, 1H), 7.17−7.34 (m, 3H); ^{13}C NMR δ 21.1, 29.4, 34.3, 55.9, 99.1, 104.0, 107.4, 108.2, 112.5, 116.2, 120.9, 135.4, 154.6, 160.4, 169.6; LR MS 290 (MH^+); HR MS calcd for $C_{15}H_{15}NO_5$ 289.0950, found 289.0945 (M^+). Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.01; H, 5.28; N, 4.84.

2-Acetoxy-6-methoxy-9-methyl-2,3-dihydrofuro[2,3-*b*]-quinolin-4-one (35). General procedure B (same as for **34**): $R_f = 0.01$, yellow solid; mp 205 °C (THF/pentane), 70% (w/o HCl) or 83% (w/HCl); ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3H), 3.28 (dd, $J = 2.1$, 15.9 Hz, 1H), 3.54 (dd, $J = 6.9$, 15.9 Hz, 1H), 3.72 (s, 3H), 3.94 (s, 3H), 6.92 (dd, $J = 2.1$, 6.9 Hz, 1H), 7.24 (1H, obscured by $CHCl_3$), 7.37 (d, $J = 9.1$ Hz, 1H), 7.89 (d, $J = 2.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.0, 31.8, 32.8, 55.8, 96.4, 98.3, 106.5, 115.9, 121.2, 127.7, 133.0, 156.2, 159.2, 169.4, 173.2; IR 2923, 1763, 1588, 1556, 1519 cm^{-1}; HR MS calcd for $C_{15}H_{15}NO_5$ 289.0950, found 289.0938 (M^+). Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.22; H, 5.30; N, 4.80.

2-Acetoxy-5-benzyl-2,3-dihydrofuro[3,4-*d*]quinolin-4-one (36). General procedure B: 277 mg of **25**; $R_f = 0.39$, white powder; mp 133 °C (ether/pentane), 20% (w/o HCl) or 12% (w/HCl); ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H), 3.29 (dd, $J = 1.4$, 17.1 Hz, 1H), 3.57 (dd, $J = 7.1$, 17.1 Hz, 1H), 4.12 (s (br), 2H), 7.05 (dd, $J = 1.4$, 7.1 Hz, 1H), 7.18−7.31 (m, 7H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.81 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.4, 33.6, 44.9, 98.5, 106.0, 111.6, 114.8, 121.3, 122.6, 125.8, 126.5, 128.1, 130.6, 136.0, 139.5, 160.2, 160.6, 168.8; IR 2922, 1767, 1666 cm^{-1}; FAB MS 336.12; HR MS calcd for $C_{20}H_{17}NO_4$ 335.1157, found 335.1158 (MH^+). Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.51; H, 5.18; N, 4.15.

2-Acetoxy-9-benzyl-2,3-dihydrofuro[2,3-*b*]quinolin-4-one (37). General procedure B (same as for **36**): $R_f = 0.01$, white solid; mp 195 °C (THF/pentane), 19% (w/o HCl) or 25% (w/HCl); ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3H), 3.33 (d, $J = 5.5$ Hz, 1H), 3.59 (dd, $J = 6.7$, 15.6 Hz), 5.41 (s, 2H), 6.95 (d, $J = 6.0$ Hz, 1H), 7.14−7.37 (m, 7H), 7.51 (t, $J = 7.3$ Hz, 1H), 8.48 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.2, 32.1, 47.4, 96.1, 97.6, 114.6, 122.9, 125.5, 126.2, 127.3, 130.7, 134.3, 137.4, 159.2, 168.6, 173.3. LR MS 335.12. HR MS calcd for $C_{20}H_{17}NO_4$ 335.1157, found 335.1154 (MH^+). Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.65; H, 5.23; N, 4.14.

2-Acetoxy-5-(3′-methyl-2′-butenyl)-2,3-dihydrofuro[3,4-*d*]quinolin-4-one (38). General procedure B: 255 mg of **26**; $R_f = 0.36$, pale brown solid; mp 116 °C (ether/pentane), 41% (w/o HCl), 47% (w/HCl) or 4% (at room temperature w/HCl); ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3H), 1.91 (s, 3H), 2.13 (s, 3H), 3.22 (dd, $J = 1.9$, 17.1 Hz, 1H), 3.50 (dd, 7.2, 17.1 Hz, 1H), 4.95 (d, $J = 5.3$ Hz, 2H), 5.14 (t, $J = 5.3$ Hz, 1H), 7.00 (dd, 1.9, 7.2 Hz, 1H), 7.21−7.37 (m, 2H), 7.57 (t, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR δ 17.6, 20.3, 25.0, 33.5, 39.8, 98.5, 106.2, 111.5, 114.4, 118.8, 121.0, 122.6, 130.5, 135.3, 139.4, 159.7, 160.2, 168.8. Anal. Calcd for $C_{18}H_{19}NO_4$: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.88; H, 6.18; N, 4.45.

8-Methoxy-5-methyl-2-trimethylsilylfuro[3,4-*d*]quinolin-4-one (39). General procedure A: 231 mg of **24**, 1.96 g of trimethylsilylacetylene; $R_f = 0.50$, colorless needles, mp 138 °C (ether/pentane), 47% (w/o HCl) or 52% (w/HCl); ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 9H), 3.78 (s, 3H), 3.96 (s, 3H), 7.16 (dd, $J = 2.9$, 9.2 Hz, 1H), 7.27 (s, 1H), 7.38 (d, $J = 9.2$ Hz), 7.49 (d, $J = 2.9$ Hz); ^{13}C NMR ($CDCl_3$) δ −2.4, 28.8, 55.1, 102.6, 113.2, 115.4, 115.8, 117.2, 117.3, 132.0, 154.1, 157.4, 158.5, 162.6; HR MS calcd for $C_{16}H_{19}NO_3Si$ 301.1134, found 301.1121 (M^+).

6-Methoxy-9-methyl-2-trimethylsilylfuro[2,3-*b*]quinolin-4-one (40). General procedure A (same as for **39**): $R_f = 0.25$, colorless needles; mp 166 °C (THF/pentane), 8% (w/o HCl) or 13% (w/HCl); ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 9H), 3.95 (s, 6H), 7.27−7.33 (m, 2H), 7.99 (d, $J = 2.8$ Hz, 1H); ^{13}C NMR δ −2.6, 30.8, 54.9, 106.1, 115.0, 116.4, 121.3, 125.1, 131.8, 137.3, 154.5, 155.9, 157.7, 171.4; HR MS calcd for $C_{16}H_{19}NO_3Si$ 301.1134, found 301.1138 (M^+).

5-Benzyl-2-trimethylsilylfuro[3,4-*d*]quinolin-4-one (41). General procedure A (277 mg of **25**, 1.96 g of trimethylsilylacetylene; $R_f = 0.80$, colorless needles; mp 142 °C (ether/pentane), 30% (w/o HCl), 48% (w/HCl); ^{1}H NMR ($CDCl_3$) δ 0.45 (s, 9H), 5.70 (s, 2H), 7.27−7.45 (m, 10H), 8.14 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −2.4, 45.0, 113.1, 114.8, 115.2, 117.1, 120.9, 121.5, 125.8, 126.5, 128.0, 128.8, 136.1, 136.9, 158.1, 159.2, 162.8; HR MS calcd for $C_{21}H_{21}NO_2Si$ 347.1325, found 347.1327 (M^+). Anal. Calcd for $C_{21}H_{21}NO_2Si$: C, 72.59; H, 6.09; N, 4.03. Found: C, 72.37; H, 6.16; N, 4.00.

9-Benzyl-2-trimethylsilylfuro[2,3-*b*]quinolin-4-one (42). General procedure A (same as for **41**): 6% (w/o HCl) or 9% (w/HCl), orange solid; mp 171 °C (THF/pentane); ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H), 5.66 (s (2H), 7.16−7.62 (m, 9H), 8.58 (dd, $J = 1.5$, 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.8, 48.3, 114.9, 117.6, 122.6, 126.5, 127.7, 128.1, 129.1, 132.0, 135.15; LR MS

270 (MH^+); HR MS calcd for $C_{21}H_{21}NO_2Si$ 347.1325, found 347.1330 (M^+).

Pseudoisodictamnine. (A) Refluxing 96 mg (0.37 mmol) of **28** in 2 mL benzene with a catalytic amount of *p*-toluenesulfonic acid and subsequent chromatography with a gradient of ether/pentane gave 33% (24 mg) of pseudoisodictamnine. (B) To 285 mg (1.1 mmol) of **29** in 2 mL of THF was added 1.1 mL (1.1 mmol) of a 1 M solution of TBAF in THF. Immediate reaction with a change in color to red gave pseudoisodictamnine in 87% yield (182 mg) after column chromatography: R_f = 0.34, pale orange crystals; mp 133 °C (ether/pentane); ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 7.09 (d, J = 1.9 Hz, 1H), 7.33 (dt, J = 0.7, 17.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.57 (dt, J = 1.4, 7.3 Hz, 1H), 7.64 (d, J = 1.9, 1H), 8.03 (dd, J = 1.3, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.8, 107.7, 112.5, 114.4, 114.7, 120.5, 121.6, 128.8, 137.4, 143.3, 154.4, 158.8; IR 1659, 1650 cm^{-1}; HR MS calcd for $C_{12}H_8NO_2$ 198.0841, found 198.0547 (MH^+). Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.23; H, 4.63; N, 7.00.

Isodictamnine. To 61 mg (0.23 mmol) of **30** in 2 mL of THF was added 0.23 mL (0.23 mmol) of a 1 M solution of TBAF in THF. Reaction was complete after 10 min. Column chromatography yielded 27 mg (61%) of isodictamnine: R_f = 0.15, pale orange powder; mp 185−187 °C (THF/pentane) (lit.[23] mp 187 °C); ^{1}H NMR ($CDCl_3$) δ 3.96 (s, 3H), 7.14 (d, J = 1.0 Hz, 1H), 7.32 (d, J = 1.0 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.74 (t, J = 7.3 Hz, 1H), 8.59 (dd, J = 7.9, Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 30.7, 105.7, 107.2, 113.3,121.9, 124.5, 126.7, 131.4, 132.1, 137.2, 137.5, 172.6; LR MS 200 (MH^+); HR MS calcd for $C_{12}H_9NO_2$ 199.0633, found 199.0638 (M^+). Spectral/physical data consistent with literature data.[23]

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