was synthesized from **3c**, as described for **5a**: yield 32%; TGA 350 °C dec; UV/vis and IR (KBr) as for **5a**; ^{1}H NMR (CD_3OD) δ 3.7–4.5 (m, 96 H, CH_2O), 9.4 (br s, 8 H, ArH) ppm. Anal. Calcd for $C_{80}H_{106}N_8O_{30}Si$: C, 58.69; H, 6.07; N, 6.37. Found: C, 57.9; H, 6.2; N, 6.5 (different samples gave varying results with a maximum variation of about 1.5% for all elements).

Polycondensation of 5c To Give 1c. This compound was synthesized from **5c** as described for **1a**: yield 71%, TGA 285 °C dec. Anal. Calcd for $(C_{86}H_{104}N_8O_{29}Si)_n$: C, 59.30; H, 6.02; N, 6.43. Found: C, 60.4; H, 6.2; N, 6.3 (different samples gave varying results with a maximum variation of about 1.5% for all elements).

Dimeric, Trimeric, and Oligomeric Products of 5a–c. Soluble dimeric and trimeric compounds of **5a–c** were obtained by heating the monomers in freshly distilled quinoline at 200 °C with a catalytic amount of $CaCl_2$, under an atmosphere of N_2, for 2 and 5 h, respectively. The reaction mixture was filtered, and the solid product was obtained as a black precipitate by slowly evaporating ether into the reaction mixture. The solid was filtered off, dissolved in chloroform, and washed with water. The products were separated by gel permeation chromatography (Sephadex LH 60, eluent $CHCl_3$/MeOH 1:1). Their molecular weights were estimated by ^{1}H NMR by using the integral ratio ArH/SiOH. Soluble oligomeric **5c** was prepared in a similar way but with a reaction time of 30 h.

Determination of K_a and $\Delta G°$ Values. The K_a values were determined by the picrate extraction technique from H_2O into $CHCl_3$ at 25 °C as described in the literature.[8] The $\Delta G°$ values were calculated from the K_a values by using the expression $\Delta G° = -RT \ln K_a$.

Saturation Experiments. The complex stoichiometries of Na^+ in compounds **1a–c** were determined by shaking the powdered solid polymers (~4 mg) with picrate solutions (10^{-3} M) for 7 h at 25 °C with a Griffin flask shaker. From the decrease of picrate concentrations, measured spectrophotometrically, the complexed cation to crown ether ratio was determined by plotting the molar ratio of the complexed sodium ions (Na^+_{compl}) to host (CE) vs the molar ratio of the total amount of sodium present (Na^+_{tot}) and host (CE). Solid H_2Pc was used as a reference compound to measure the adsorption of picrate salts to solid material.

Acknowledgment. We thank Prof. J. H. van der Maas for recording and discussing the infrared spectra, Mr. C. Versluis for recording the FAB Mass spectra, Mrs. G. Nagtegaal, and Mr. A. Kentgens for helping recording and discussing the CPMAS spectra, and Mr. A. Swolfs for running the 400-MHz NMR spectra. Part of this work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Foundation for Scientific Research (NWO).

Registry No. 1a (homopolymer), 118443-49-5; **1b** (homopolymer), 125541-37-9; **1c** (homopolymer), 125541-39-1; **2a**, 110682-73-0; **2b**, 108695-56-3; **2c**, 108695-57-4; **3a**, 116285-46-2; **3b**, 125541-32-4; **3c**, 125541-33-5; **5a**, 118342-88-4; **5b**, 125541-41-5; **5c**, 125541-42-6; $SiCl_4$, 10026-04-7; Li^+, 7439-93-2; Na^+, 7440-23-5; K^+, 7440-09-7; Rb^+, 7440-17-7; Cs^+, 7440-46-2; ammonia, 7664-41-7.

An Annulation Method for the Synthesis of Highly Substituted Polycyclic Aromatic and Heteroaromatic Compounds

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Abstract: A general strategy for the synthesis of highly substituted polycyclic aromatic and heteroaromatic compounds has been developed. The new aromatic annulation is achieved simply by the irradiation of a dichloroethane solution of an acetylene derivative and a vinyl or aryl α-diazo ketone. Mechanistically, the reaction proceeds via the photochemical Wolff rearrangement of the diazo ketone to generate an aryl- or vinylketene, followed by a cascade of three pericyclic reactions. A variety of substituted phenols, naphthalenes, benzofurans, benzothiophenes, indoles, and carbazoles can be prepared by using the method. The application of the aromatic annulation to the total synthesis of the marine alkaloid hyellazole demonstrates the synthetic utility of the method.

The invention of efficient methods for the synthesis of substituted aromatic compounds has commanded the interest of chemists since the time of the earliest synthetic organic investigations in the 19th century. Classical approaches to aromatic compounds exploited readily available benzene derivatives and relied heavily on electrophilic and nucleophilic substitution reactions. In recent years, directed metalation reactions have joined the classical substitution methods as another vehicle for the introduction of substituents onto preexisting aromatic rings.

A second approach to highly substituted aromatic compounds involves the application of *annulation methods*: convergent strategies in which the aromatic system is assembled from acyclic precursors in a single step, with all (or most) substituents already in place. Annulation strategies enjoy several advantages over classical linear substitution strategies, especially when applied to the preparation of highly substituted target molecules. For example, annulation routes frequently avoid the regiochemical ambiguities associated with aromatic substitution reactions and provide access to substitution patterns that cannot be obtained via the more conventional routes. The intrinsic convergent nature of annulation strategies facilitates the efficient assembly of highly substituted aromatics that would require long, multistep routes using classical substitution methodology.

Particularly noteworthy aromatic annulations[1] which have been developed recently include methods based on Diels–Alder chemistry,[2] carbonyl condensation reactions,[3] and transition-metal-mediated processes. Prominent among the last class of reactions are the cobalt-mediated [2 + 2 + 2] acetylene cycloadditions investigated by Vollhardt[4] and the Dötz reaction of Fischer carbene complexes.[5] We have recently shown that addition of vinylketenes

(1) For reviews, see: (a) Bamfield, P.; Gordon, P. F. *Chem. Soc. Rev.* **1984**, *13*, 441. (b) Wedenmeyer, K. F. In *Methoden der organischen Chemie (Houben-Weyl)*; Muller, E., Ed.; George Theime: Stuttgart, 1976; Vol. 6/1c, pp 853–924.

(2) Recent examples: (a) Snowden, R. L.; Wüst, M. *Tetrahedron Lett.* **1986**, *27*, 703. (b) Boger, D. L.; Mullican, M. D. *Organic Syntheses* **1987**, *65*, 98. (c) Ziegler, T.; Layh, M.; Effenberger, F. *Chem. Ber.* **1987**, *120*, 1347 and references cited therein.

(3) Recent examples: (a) Tius, M. A.; Gomez-Galeno, J. *Tetrahedron Lett.* **1986**, *27*, 2571. (b) Chan, T. H.; Prasad, C. V. C. *J. Org. Chem.* **1986**, *51*, 3012.

(4) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(5) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kriessel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie International: Deerfield Beach, FL, 1984. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1.

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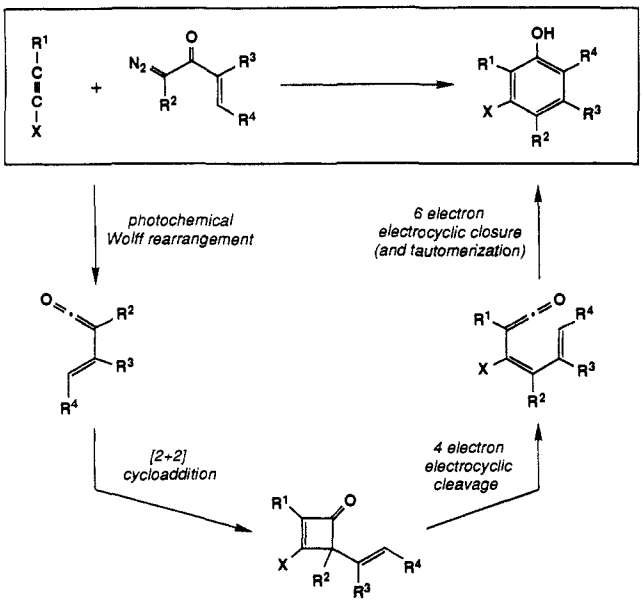
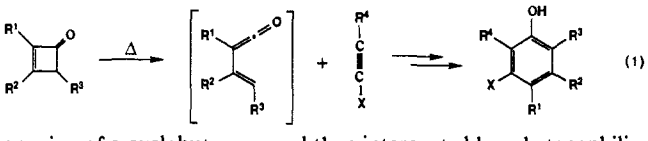
Scheme I



to activated (heterosubstituted)[6] and unactivated[7] acetylenes provides another efficient annulation route to highly substituted aromatic systems. In our original version of this annulation strategy (eq 1), the vinylketene is generated by the 4π electrocyclic



(1)

opening of a cyclobutenone and then intercepted by a ketenophilic acetylene to afford a 4-vinylcyclobutenone derivative. Subsequent electrocyclic cleavage of this intermediate then leads to a dienylketene, which undergoes 6π electrocyclic closure to furnish (after tautomerization) a substituted phenol. Liebeskind[8] and Moore[9] have recently employed a related strategy for the synthesis of highly substituted quinones. In this case, a 4-aryl- or 4-vinyl-4-hydroxycyclobutenone is generated by the addition of an aryl- or vinyllithium reagent to a cyclobutenedione derivative; thermolysis and oxidation then produce a 1,4-benzoquinone.

In this paper we describe a "second-generation" version of our annulation strategy which significantly expands the scope of the method. In particular, this new variant provides access to a variety of important *polycyclic* aromatic and heteroaromatic systems which are not available by using the cyclobutenone-based reaction. The new annulation method is based on the initial generation of the key vinyl- or arylketene intermediate via the *photochemical Wolff rearrangement* of an unsaturated α-diazo ketone. Scheme I outlines the overall mechanistic course of the reaction, which features a cascade of pericyclic reactions similar to that involved in our earlier method. Thus, irradiation of the α-diazo ketone induces Wolff rearrangement[10] to produce an aryl- or vinylketene intermediate which then combines with the acetylene in a regiospecific [2 + 2] cycloaddition.[11] Further irradiation (or thermolysis, vide infra) brings about the 4π electrocyclic cleavage of the resulting 4-substituted cyclobutenone, producing a dienylketene which undergoes 6π electrocyclization to afford a 2,4-cyclohexadienone. Tautomerization then furnishes the desired aromatic product.

Table I delineates the scope of the new aromatic annulation strategy. One of the attractive features of the method is the availability of a wide variety of functionalized aryl and vinyl α-diazo ketones in one step from simple ketones and carboxylic acid derivatives. For example, the synthesis of aryl diazo ketones is conveniently achieved by the addition of diazomethane to acid chlorides or, alternatively, from the corresponding ketones by using the diazo group transfer strategy pioneered by Regitz.[12] The vinyl diazo ketones employed in entries 1–4 are best prepared via the latter (diazo transfer) route, since the addition of diazomethane to α,β-unsaturated acyl chlorides is often complicated by competing 1,3-dipolar cycloaddition to the carbon–carbon double bond. In the course of these studies we have also found that the efficiency of the diazo transfer reaction can be improved, sometimes dramatically, by employing a "detrifluoroacetylative" procedure[13] in place of the original "deformylative" method of Regitz. As indicated in Table I, under these conditions a variety of sensitive heteroaromatic and α,β-unsaturated diazo ketone derivatives can be prepared in good to excellent yield.

The reaction of α-diazoacetophenone with 1-methoxybutyne was initially examined to optimize conditions for the aromatic annulation. Best results were obtained by irradiation of solutions of the annulation components in vycor tubes with a low-pressure mercury lamp (254 nm) in a standard photochemical reactor. Methylene chloride, chloroform, 1,2-dichloromethane, and acetonitrile all proved to be suitable solvents for the reaction. However, complex mixtures of products were obtained from annulations carried out in THF, and hexane was found to be unsuitable due to the low solubility of most diazo ketones in this solvent.

Two protocols were developed for effecting the aromatic annulation. In the first procedure, a 0.3 M solution of diazo ketone in 1,2-dichloroethane containing 3.0 equiv of the acetylene is simply irradiated at room temperature until formation of the desired annulation product is complete (generally 6 h) as determined by TLC analysis. This procedure is particularly preferred for the synthesis of thermally labile compounds such as the benzocyclobutene **5**. In other cases, we generally employed an alternative procedure which allows the annulation to be carried out with more concentrated solutions. In a typical reaction, a 0.7 M solution of diazo ketone in 1,2-dichloroethane containing 1.0–1.2 equiv of the acetylene component is irradiated until TLC analysis indicates that consumption of the diazo ketone is complete (usually 5–8 h). At this point, the reaction solution contains a mixture of the desired aromatic product and varying amounts of the intermediate 4-aryl- or 4-vinylcyclobutenone. In most cases the further transformation of the cyclobutenone intermediate to final product by continued irradiation was found to be inefficient due to the accumulation of colored polymers on the walls of the reaction vessel. To complete the annulation, the reaction solution

(6) (a) Danheiser, R. L.; Gee, S. K. *J. Org. Chem.* **1984**, *49*, 1672 and references cited therein. (b) Danheiser, R. L.; Gee, S. K.; Perez, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 806. (c) Danheiser, R. L.; Nishida, A.; Savariar, S.; Trova, M. P. *Tetrahedron Lett.* **1988**, *29*, 4917. See, also: Kowalski, C. J.; Lal, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 3693.

(7) Kowalczyk, J. J. Ph.D. Thesis, Massachusetts Institute of Technology, 1988.

(8) Liebeskind, L. S.; Iyer, S.; Jewell, C. F., Jr. *J. Org. Chem.* **1986**, *51*, 3065.

(9) (a) Perri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 3067. (b) Perri, S. T.; Moore, H. W. *Tetrahedron Lett.* **1987**, *28*, 4507. (c) Moore, H. W.; Perri, S. T. *J. Org. Chem.* **1988**, *53*, 996. (d) Reed, M. W.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 4166.

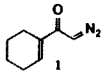
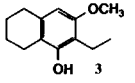
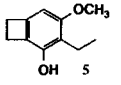
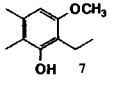
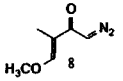
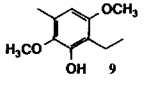
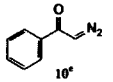
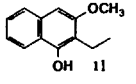
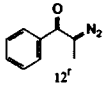
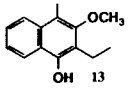
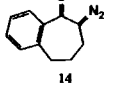
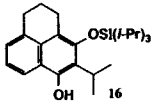
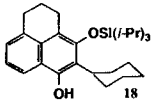
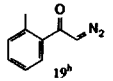
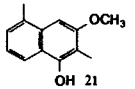
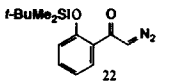
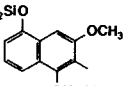
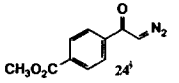
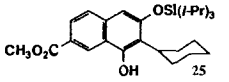
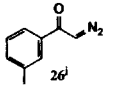
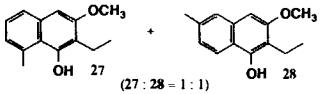
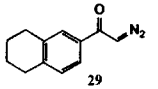
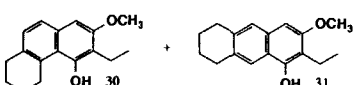
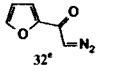
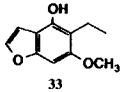
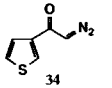
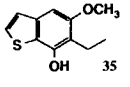
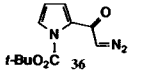
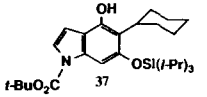
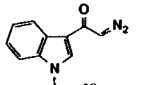
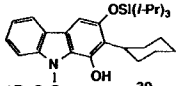
(10) For reviews of the photochemical Wolff rearrangement, see: (a) Meier, H.; Zeller, K. P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32. (b) Ando, W. In *The Chemistry of the Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Part 1, p 458. (c) Regitz, M.; Maas, G. *Diazo Compounds: Properties and Synthesis*; Academic Press: Orlando, FL, 1986; p 185.

(11) For previous examples of [2 + 2] cycloadditions of alkenes with ketenes generated by photochemical Wolff rearrangement, see: (a) Masamune, S.; Castellucci, N. T. *Proc. Chem. Soc.* **1964**, 298. (b) Masamune, S.; Fukumoto, K. *Tetrahedron Lett.* **1965**, 4647. (c) Yates, P.; Fallis, A. G. *Tetrahedron Lett.* **1968**, 2493. (d) DoMinh, T.; Strauz, O. P. *J. Am. Chem. Soc.* **1970**, *92*, 1766. (e) Becker, D.; Nagler, M.; Birnbaum, D. *J. Am. Chem. Soc.* **1972**, *94*, 4771. (f) Geisel, M.; Grob, C. A.; Santi, W.; Tschudi, W. *Helv. Chim. Acta* **1973**, *56*, 1046. (g) Becker, D.; Harel, Z.; Birnbaum, D. *J. Chem. Soc., Chem. Commun.* **1975**, 377. (h) Becker, D.; Birnbaum, D. *J. Org. Chem.* **1980**, *45*, 570. (i) Stevens, R. V.; Bisacchi, G. S.; Goldsmith, L.; Strouse, C. E. *J. Org. Chem.* **1980**, *45*, 2708. (j) Ireland, R. E.; Dow, W. C.; Godfrey, J. D.; Thaisrivongs, S. *J. Org. Chem.* **1984**, *49*, 1001.

(12) For reviews, see: (a) Chapter 13 in ref 10c. (b) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 733. (c) Regitz, M. *Synthesis* **1972**, 351.

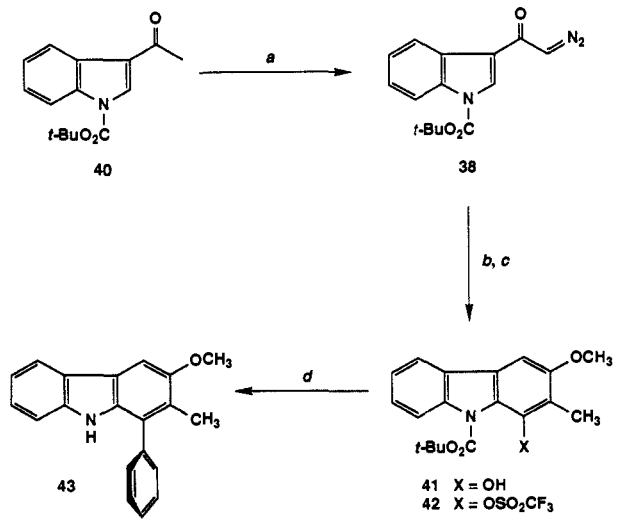
(13) (a) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. Manuscript in preparation. (b) Doyle, M. P.; Dorrow, R. L.; Terpstra, J. W.; Rodenhouse, R. A. *J. Org. Chem.* **1985**, *50*, 1663.

Table I. Synthesis of Polycyclic Aromatic and Heteroaromatic Compounds

entry	diazoketone[a]	method of preparation (yield, %)[b,c]	acetylene	annulation product(s)[a]	yield, %[c]
1	 1	A (87)	Et–C≡C–OCH$_3$ 2[d]	 3	50
2	 4	B (42)	2	 5	56
3	 6	B (74)	2	 7	46
4	 8	B (46)	2	 9	31
5	 10[e]	A (95)	2	 11	49
6	 12[f]	A (63)	2	 13	51
7	 14	B (74)	*i*-Pr–C≡C–OSi(*i*-Pr)$_3$ 15[g]	 16	60
8	14		Cyh–C≡C–OSi(*i*-Pr)$_3$ 17[g]	 18	62
9	 19[h]	A (81)	Me–C≡C–OCH$_3$ 20[d]	 21	57
10	 22	B (58)	20	 23	52
11	 24[i]	C (93)	17	 25	49
12	 26[j]	C (92)	2	 27 + 28 (27 : 28 = 1 : 1)	64
13	 29	B (93)	2	 30 + 31 (30 : 31 = 3 : 1)	57
14	 32[e]	A (71)	2	 33	44
15	 34	A (92)	2	 35	46
16	 36	B (74)	17	 37	42
17	 38	A (90)	17	 39	42

[a] IR, UV, ^{1}H NMR, and ^{13}C NMR spectral data were fully consistent with the assigned structures. High-resolution mass spectral data and/or elemental analyses were obtained for all new compounds. [b] Method A: The diazo ketone was prepared by the sequential treatment of the corresponding ketone with LiHMDS and then $CF_3CO_2CH_2CF_3$ in THF, followed by MsN_3 and Et_3N in aqueous CH_3CN. Method B: The diazo ketone was synthesized employing the procedure of Doyle, M. P.; Dorow, R. L.; Terpstra, J. W.; Rodenhouse, R. A. *J. Org. Chem.* **1985**, *50*, 1663. Method C: These diazo ketones were prepared by treating the corresponding acid chloride with 3–4 equiv of diazomethane in Et_2O at 0 °C. [c] Isolated yields of products purified by column chromatography on silica gel. [d] These acetylenes were prepared by the method of Newman, M. S.; Geib, J. R.; Stalick, W. N. *Org. Prep. Proc. Int.* **1972**, *4*, 89. [e] Regitz, M.; Menz, F. *Chem. Ber.* **1968**, *101*, 2622. [f] Taber, D. F.; Ruckle, R. E., Jr.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077. [g] Substituted siloxyacetylenes were prepared via the method of Kowalski, C. J.; Lal, C. S.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 7127. [h] Steinberg, G. M.; Lieske, C. N.; Ash, A. B.; Blumbergs, P. U.S. Patent 3 729 558. [i] Firestone, R. A.; Maciejewicz, N. S.; Christensen, B. G. *J. Org. Chem.* **1974**, *39*, 3384. [j] Tsuno, Y.; Ibata, J.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 960.

Scheme II. Synthesis of Hyellazole[a]



[a] Reagents and conditions: (a) LiHMDS, THF, −78 °C; $CF_3CO_2CH_2CF_3$; $CH_3SO_2N_3$, Et_3N, H_2O, CH_3CN, 86%; (b) CH_3-C≡C-O-CH_3, $ClCH_2CH_2Cl$, hv, 19.5 h, reflux, 5 h, 56%; (c) $(CF_3SO_2)_2O$, DMAP, pyridine, 0 °C to rt, 78%; (d) Me_3SnPh, LiCl, 10 mol % $PdPh_4$, dioxane, 94 to 150 °C, 63%.

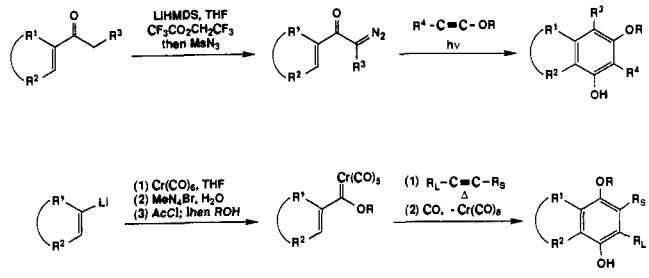
was therefore transferred (with the aid of additional solvent) to a second reaction flask and heated at reflux (83 °C), generally for 2–4 h, to effect the electrocyclic cleavage of the cyclobutenone intermediate thermally and thus complete the annulation.

As indicated in Table I, a variety of both vinyl and aryl α-diazo ketones participate in the aromatic annulation. Particularly notable is the smooth reaction of diazoacetylcyclobutene (**4**) to produce the benzocyclobutene derivative **5**. Benzocyclobutenes have found considerable use lately as synthetic intermediates;[14] in particular, their application as *o*-quinodimethane precursors for Diels–Alder reactions is now well documented.[15] Among the several classes of *vinyl* diazo ketones investigated to date, the only systems which have failed to undergo efficient aromatic annulation are the α-diazo derivatives of α′-alkylidenecycloalkanones. For example, the reaction of 1-methoxybutyne with 6-diazo-2-ethylidenecyclohexanone and cycloheptanone produced the desired hydrindane and tetralin derivatives in only 15–20% yield.

A wide range of *aryl* and *heteroaryl* diazo ketones participate smoothly in the annulation, providing an efficient route to substituted naphthalenes, benzofurans, benzothiophenes, indoles, and carbazoles. Several substituted aromatic diazo ketones have also been successfully employed in the annulation, although aryl *alkyl* ether derivatives such as 2-diazo-2′-methoxyacetophenone were found to react in disappointingly low yield. Fortunately, however, the corresponding silyl ether derivatives react smoothly without complication as indicated by the conversion of **22** to the naphthol **23** in 52% yield.

As illustrated with entries 12 and 13, the application of the aromatic annulation to meta-substituted benzene derivatives generally leads to the formation of mixtures of regioisomeric products. The regiochemical outcome of the reaction of the tetralin **29** is intersting in that the electrocyclization of the dienylketene intermediate proceeds predominantly at the more sterically congested position of the aromatic ring. This result is consistent with the previous suggestion[16] that these electrocyclic reactions proceed via polar transition states and can be viewed as involving an electrophilic addition of the ketene carbonyl group to the aromatic ring. Note that electrophilic substitution reactions of 2-substituted

Scheme III



tetralin derivatives are well-known to occur preferentially at the C-1 carbon.[17]

Among the acetylene derivatives tested to date, alkynyl ethers and siloxyacetylenes have proven to be the most effective ketenophile components for the aromatic annulation. Both classes of acetylenes are readily available by methods discussed previously.[18,19] Efforts to employ "unactivated" acetylenes such as 1-phenylpropyne and 1-hexyne in this version of our annulation strategy have to date proved unsuccessful.

The application of the new annulation strategy to the synthesis of the marine carbazole alkaloid hyellazole illustrates the utility of this methodology for the synthesis of aromatic natural products. Hyellazole (**43**) was isolated from the Hawaiian blue-green alga *Hyella caespitosa* by Moore and co-workers in 1979[20] and has since been the objective of several synthetic studies.[21] Scheme II summarizes our approach. The requisite α-diazo ketone (**38**) was conveniently prepared by the application of our modified diazo transfer procedure to the *t*-BOC derivative of 3-acetylindole. Irradiation of a 1,2-dichloroethane solution of **38** and 1.5 equiv of 1-methoxypropyne for 19.5 h followed by heating at reflux for 5 h furnished the expected carbazole annulation product in 56% yield. The installation of the C-1 phenyl group was then accomplished by using the Stille cross coupling reaction.[22] Thus, the triflate derivative of **41** and 1.2 equiv of phenyltrimethylstannane was heated in dioxane in the presence of a catalytic amount of $(Ph_3P)_4Pd$ at 94 °C for 38 h and then at 150 °C for 6 h. Under these conditions, coupling and concomitant cleavage of the *t*-BOC protective group occurs,[23] thus affording hyellazole as white crystals with physical and spectroscopic properties identical with those reported previously.

In summary, this second-generation version of our annulation strategy provides a convenient two-step method for the preparation of polycyclic aromatic and heteroaromatic compounds starting from readily available aryl and vinyl ketones. As outlined in Scheme III, the most efficient current version of the aromatic annulation produces aromatic rings which are substituted as 3-alkoxy phenol derivatives. In this respect the annulation may be viewed as complementing the Dötz reaction, which as indicated in Scheme III results in the formation of 4-alkoxy phenol derivatives.

Further studies are underway in our laboratory aimed at the application of this methodology to the total synthesis of biologically

(14) For reviews on the synthesis and chemistry of benzocyclobutenes, see: (a) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471. (b) Thummel, R. P. *Acc. Chem. Res.* **1980**, *13*, 70.

(15) For a review, see: Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873.

(16) (a) Dötz, K. H.; Deitz, R. *Chem. Ber.* **1978**, *111*, 2517. (b) Also see ref 9a.

(17) For example, see: (a) Arnold, R. T.; Zaugg, H. E.; Sprung, J. *J. Am. Chem. Soc.* **1941**, *63*, 1134. (b) Prieto, J.; Vega, A.; Moragues, J. *J. Heterocycl. Chem.* **1976**, *13*, 813. (c) Einhorn, J.; Demerseman, P.; Rene, L.; Royer, R.; Cavier, R. *Eur. J. Med. Chem.-Chim. Ther.* **1983**, *18*, 79. (d) Gaude, D.; LeGoaller, R.; Pierre, J. L. *Synth. Commun.* **1986**, *16*, 63.

(18) Newman, M. S.; Geib, J. R.; Stalick, W. N. *Org. Prep. Proc. Int.* **1972**, *4*, 89.

(19) Kowalski, C. J.; Lal, G. S.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 7127.

(20) Cardellina, J. H., II; Kirkup, M. P.; Moore, R. E.; Mynderse, J. S.; Seff, K.; Simmons, C. J. *Tetrahedron Lett.* **1979**, 4915.

(21) (a) Kano, S.; Sugino, E.; Shibuya, S.; Hibino, S. *J. Org. Chem.* **1981**, *46*, 3856. (b) Takano, S.; Suzuki, Y.; Ogasawara, K. *Heterocycles* **1981**, *16*, 1479. (c) Kawasaki, T.; Nonaka, Y.; Sakamoto, M. *J. Chem. Soc., Chem. Commun.* **1989**, 43. (d) Moody, C. J.; Shah, P. *J. Chem. Soc., Perkin Trans. 1* **1989**, 376.

(22) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

(23) (a) Rawal, V. H.; Cava, M. P. *Tetrahedron Lett.* **1985**, *26*, 6141. (b) Wasserman, H. H.; Berger, G. B.; Cho, K. R. *Tetrahedron Lett.* **1982**, *23*, 465.

interesting aromatic natural products.

Experimental Section

General Procedures. All reactions were performed in flame-dried glassware under a positive pressure of argon or nitrogen. Reaction mixtures were stirred magnetically unless otherwise indicated. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or cannula into the reaction vessels through rubber septa. Reaction product solutions and chromatography fractions were concentrated by using a Büchi rotary evaporator at ca. 20 mmHg. Column chromatography was performed by using Baker silica gel (230–400 mesh).

Materials. Reagent grade solvents were used without further purification except as indicated below. Tetrahydrofuran and dioxane were distilled from sodium benzophenone dianion. 1,2-Dichloroethane, acetonitrile, diisopropylamine, 1,1,1,3,3,3-hexamethyldisilazane, 2,2,2-trifluoroethyl trifluoroacetate, and triethylamine were distilled from calcium hydride. Pyridine was distilled from KOH. All ketones were purified by distillation or column chromatography prior to use except for 3-acetylthiophene and 3-acetylindole which were used as received from Aldrich. Trifluoromethylsulfonic anhydride (Aldrich), potassium *tert*-butoxide (Gallery), lithium chloride (Mallinckrodt), tetrakis(triphenylphosphine)palladium(0) (Aldrich), di-*tert*-butyl dicarbonate (Aldrich), and 4-(dimethylamino)pyridine (DMAP, Sigma) were used as received. 2-Diazo-4'-(methoxycarbonyl)acetophenone[24] (**24**) and 2-diazo-3'-methylacetophenone[25] (**26**) were prepared by the reaction of the appropriate acid chloride with 3–4 equiv of diazomethane in ether at 0 °C. Phenyltrimethylstannane ($PhMe_3Sn$) was prepared according to the procedure of Eaborn and Waters.[26] The petroleum ether used for column chromatography had a boiling range of 35–60 °C.

Instrumentation. Photolyses were carried out in a Rayonet photochemical reactor Model RPR-100 containing 16 253.7-nm, low-pressure mercury vapor bulbs (Southern New England Ultraviolet Company). Melting points were determined with a Fischer–Johns melting point apparatus and are uncorrected. Infrared spectra were obtained by using a Perkin-Elmer 1320 grating spectrophotometer. Ultraviolet–visible spectra were measured on a Varian DMS 100 spectrophotometer. ^1H NMR spectra were recorded with Bruker WM-250 (250 MHz) and Varian XL-300 (300 MHz), XL-400 (400 MHz), and VXR-500 (500 MHz) spectrophotometers. ^{13}C NMR spectra were recorded on Bruker WM-270 (68 MHz), Varian XL-300 (75 MHz) and XL-400 (100 MHz) spectrophotometers. Chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane. High resolution mass spectra were obtained on a Finnegan Matt-8200 spectrometer. Elemental analyses were performed by Robertson Laboratory, Inc., of Madison, NJ.

General Procedure A for Aromatic Annulation. 2-Ethyl-3-methoxy-5,6,7,8-tetrahydro-1-naphthol (3). A solution of diazo ketone **1** (0.862 g, 5.74 mmol) and 1-methoxybutyne (0.70 mL, 0.579 g, 6.89 mmol) in 8.2 mL of 1,2-dichloroethane was distributed evenly between three 25-cm vycor tubes (9 mm o.d., 7 mm i.d.) fitted with rubber septa. A second rubber septum (inverted) was secured with wire to each tube to insure a good seal, and the reaction mixtures were degassed (three freeze–thaw cycles at −196 °C, ≤0.5 mmHg) and then irradiated with 253.7 nm light for 10 h in a Rayonet reactor. The resulting solutions were combined in a threaded tube sealed with a Teflon screwcap, diluted with 8 mL of additional 1,2-dichloroethane, and then heated at reflux for 4 h in a 90 °C oil bath (the level of the oil should not be higher than the level of the reaction solution). Concentration afforded 1.2 g of an orange-brown oil. Column chromatography on silica gel (elution with 10% Et_2O–petroleum ether) provided 0.473 g (40%) of **3** as off-white crystals as well as 0.056 g of an ester derivative which could be converted to **3** by saponification with 4 mL of 10% aqueous NaOH in 4 mL of CH_3OH at reflux for 5 h. Workup and purification by column chromatography as described above furnished 0.034 g of additional **3** as off-white crystals (total yield: 43%):[27] mp 56.5–57.5 °C; IR (CCl_4) 3620, 3055, 2935, 2860, 2819, 1740, 1619, 1495, 1462, 1446, 1243, 1352, 1315, 1292, 1265, 1228, 1195, 1160, 1126, 1086, and 1046 cm^{-1}; UV max (CH_3CN) 274 (ϵ = 1200) and 205 (37 000) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1 H), 4.70 (s, 1 H), 3.97 (s, 3 H), 2.74 (t, J = 5.9 Hz, 2 H), 2.65 (q, J = 7.2 Hz, 2 H), 2.57 (t, J = 5.9 Hz, 2 H), 1.82–1.88 (m, 2 H), 1.75–1.80 (m, 2 H), and 1.14 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 151.8, 135.6, 115.3 (2-C), 103.5, 55.6, 29.9, 22.9 (2-C), 22.5, 16.3, and 13.8. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.57; H, 8.80.

General Procedure B for Aromatic Annulation. 4-Ethyl-3-hydroxy-5-methoxybenzocyclobutene (5). A 25-cm vycor tube (9 mm o.d., 7 mm i.d.) fitted with a rubber septum was charged with a solution of the diazo ketone **4** (0.156 g, 1.28 mmol) in 2 mL of 1,2-dichloroethane. 1-Methoxybutyne (0.39 mL, 0.323 g, 3.84 mmol) and 2 mL of additional 1,2-dichloroethane were then added, and a second rubber septum (inverted) was secured with wire over the first to insure a good seal. The reaction mixture was degassed (three freeze–thaw cycles at −196 °C, ≤0.5 mmHg) and then irradiated with 253.7-nm light for 5 h in a Rayonet reactor. Concentration afforded 0.2 g of an orange-brown oil. Column chromatography on silica gel (elution with 10% Et_2O–petroleum ether) provided 0.128 g (56%) of **5** as white crystals: mp 65–66 °C; IR ($CHCl_3$) 3600, 2970, 2935, 2875, 2841, 1599, 1435, 1330, 1312, 1278, 1260, 1239, 1220, 1205, 1126, and 1058 cm^{-1}; UV max (CH_3CN) 272 (ϵ = 1200) and 203 (31 000) nm; ^1H NMR (250 MHz, $CDCl_3$) δ 6.32 (s, 1 H), 5.04 (s, 1 H), 3.76 (s, 3 H), 3.02 (m, 4 H), 2.64 (q, J = 7.5 Hz, 2 H), and 1.09 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 148.1, 143.5, 120.8, 117.5, 99.7, 56.2, 28.8, 26.3, 16.4, and 14.1. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.29; H, 8.18.

5,6-Dimethyl-2-ethyl-3-methoxyphenol (7). Reaction of diazo ketone **6** (0.144 g, 1.16 mmol) with 1-methoxybutyne (0.14 mL, 0.118 g, 1.40 mmol) according to general procedure A (irradiation for 6 h, heating for 3.5 h) gave 0.19 g of an orange-brown oil. Column chromatography on silica gel (elution with 10% Et_2O–petroleum ether) furnished 0.094 g (46%) of **7** as off-white crystals: mp 57–57.5 °C; IR (CCl_4) 3630, 3070, 2980, 2950, 2880, 2790, 1625, 1585, 1505, 1470, 1425, 1385, 1335, 1320, 1280, 1235, 1210, 1135, 1095, and 1060 cm^{-1}; UV max (CH_3OH) 273 (ϵ = 1300) and 205 (25 000) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 6.33 (s, 1 H), 4.72 (s, 1 H), 3.78 (s, 3 H), 2.62 (q, J = 7.1 Hz, 2 H), 2.25 (s, 3 H), 2.11 (s, 3 H), and 1.12 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 151.9, 134.8, 115.3, 114.3, 104.9, 55.6, 20.4, 16.6, 13.8, and 11.3. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.23; H, 8.66.

2,5-Dimethoxy-6-ethyl-3-methylphenol (9). Reaction of diazo ketone **8** (0.164 g, 1.17 mmol) with 1-methoxybutyne (0.14 mL, 0.118 g, 1.40 mmol) according to general procedure A (irradiation for 10 h, heating for 4 h) gave 0.3 g of an orange-brown oil. Column chromatography on silica gel (elution with 10% Et_2O–petroleum ether) provided 0.070 g (31%) of **9** as white crystals: mp 44.5–45 °C; IR (CCl_4) 3530, 2930, 2840, 1615, 1585, 1440, 1412, 1355, 1305, 1122, 1084, and 985 cm^{-1}; UV max (CH_3CN) 279 (ϵ = 1500) and 203 (38 000) nm; ^1H NMR (250 MHz, $CDCl_3$) δ 6.20 (s, 1 H), 5.95 (s, 1 H), 3.77 (s, 3 H), 3.75 (s, 3 H), 2.64 (q, J = 7.4 Hz, 2 H), 2.27 (s, 3 H), and 1.11 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 147.1, 139.3, 126.9, 116.9, 103.9, 60.8, 55.7, 16.7, 15.9, and 13.7. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.44; H, 8.26.

2-Ethyl-3-methoxy-1-naphthol (11). Reaction of diazo ketone **10**[28] (0.144 g, 0.985 mmol) with 1-methoxybutyne (0.10 mL, 0.083 g, 0.98 mmol) according to general procedure A (irradiation for 5 h, heating for 3 h) gave 0.25 g of a brown oil. Column chromatography on silica gel (elution with 40% petroleum ether–benzene) provided 0.097 g (49%) of **11** as off-white crystals: mp 74–76 °C; IR (CCl_4) 3610, 3060, 3000, 2970, 2940, 2910, 2870, 2830, 1630, 1600, 1580, 1500, 1460, 1430, 1405, 1380, 1340, 1290, 1250, 1230, 1220, 1200, 1150, 1130, 1100, 1050, and 850 cm^{-1}; UV max (CH_3CN) 330 (ϵ = 2000), 312 (2100), 284 (4500), 238 (51 000), and 219 (26 000) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 1 H), 7.66 (d, J = 8.1 Hz, 1 H), 7.30–7.34 (m, 2 H), 6.76 (s, 1 H), 5.27 (s, 1 H), 3.90 (s, 3 H), 2.79 (q, J = 7.5 Hz, 2 H), and 1.18 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 148.8, 133.2, 126.4, 126.0, 122.9, 120.9, 120.3, 115.8, 98.2, 55.4, 16.8, and 13.7; HRMS, m/e calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0995.

2-Ethyl-3-methoxy-4-methyl-1-naphthol (13). Reaction of diazo ketone **12**[29] (0.159 g, 0.985 mmol) with 1-methoxybutyne (0.12 mL, 0.099 g, 1.18 mmol) according to general procedure A (irradiation for 5 h, heating for 8 h) gave 0.2 g of a brown oil. Column chromatography on silica gel (elution with 0–10% Et_2O–petroleum ether) provided 0.109 g (51%) of **13** as off-white crystals: IR (CCl_4) 3615, 3070, 2965, 2935, 2870, 1625, 1450, 1412, 1383, 1369, 1320, 1278, 1240, 1152, 1110, 1055, 1025, and 921 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 1 H), 7.88 (d, J = 8.7 Hz, 1 H), 7.42 (m, 2 H), 5.35 (s, 1 H), 3.78 (s, 3 H), 2.82 (q, J = 7.5 Hz, 2 H), 2.53 (s, 3 H), and 1.24 (t, J = 7.5 Hz, 3 H). Because of the propensity of this naphthol to undergo oxidation, full characterization was obtained for the acetate derivative which was prepared by the treatment of crude **13** with acetic anhydride and DMAP according to the procedure of Steglich and Höfle[30] (47% overall yield from diazoketone **12**). For 2-ethyl-3-methoxy-4-methyl-1-naphthyl acetate: IR (neat) 3060, 2960, 2935, 2870, 1758, 1668, 1620, 1595, 1575, 1500, 1450, 1365, 1320, 1270, 1238, 1202, 1155, 1110, 1028, 1005, 925, 895, 855, 762, 700, and 645 cm^{-1}; UV max (CH_3CN) 324 (ϵ = 700), 282 (4500), and 226 (32 000) nm; ^1H NMR (250 MHz, $CDCl_3$) δ 7.92 (dd, J = 1.9 and 6.9 Hz, 1 H), 7.65 (dd, J = 1.9 and 6.9 Hz, 1 H), 7.43 (m, 2 H), 3.97 (s, 3 H), 2.71 (m, 2 H), 2.58 (s, 3 H), 2.46 (s, 3 H), and

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1.22 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5, 154.7, 143.3, 132.5, 128.6, 125.8, 125.1, 124.5, 124.1, 123.2, 121.3, 61.5, 20.56, 18.9, 14.2, and 11.6. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.80; H, 7.05.

2,3-Dihydro-5-isopropyl-4-(triisopropylsiloxy)-6-phenalenol (16). Reaction of diazo ketone **14** (0.085 g, 0.454 mmol) with 2-isopropyl-1-(triisopropylsiloxy)ethyne (0.111 g, 0.461 mmol) according to general procedure A (irradiation for 7 h, heating for 5 h) gave 0.2 g of a brown oil. Column chromatography on silica gel (elution with 10% Et_2O–petroleum ether) provided 0.108 g (60%) of **16** as a yellow oil: IR (neat) 3640, 3580, 2950, 2880, 1620, 1600, 1500, 1470, 1420, 1410, 1375, 1340, 1330, 1270, 1210, 1190, 1150, 1125, 1090, 1080, 1030, 1020, 930, 900, 890, 825, 810, 760, and 685 cm^{-1}; UV max (CH_3CN) 335 (ϵ = 2100), 306 (4300), and 243 (52 000) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 1 H), 7.21 (d, J = 8.3 Hz, 1 H), 7.13 (dd, J = 2.1 and 8.2 Hz, 1 H), 5.16 (s, 1 H), 3.63 (septet, J = 7.4 Hz, 1 H), 2.95–3.02 (m, 4 H), 1.98 (appar quintet, 2 H), 1.45 (d, J = 7.4 Hz, 6 H), 1.27–1.39 (m, 3 H), and 1.14 (d, J = 7.4 Hz, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 148.8, 135.5, 129.7, 123.8, 122.7, 122.2, 121.2, 117.6, 115.3, 31.3, 26.0, 25.0, 22.8, 21.2, 18.2, and 14.4; HRMS, m/e calcd for $C_{25}H_{38}O_2Si$ 398.2641, found 398.2642.

5-Cyclohexyl-2,3-dihydro-4-(triisopropylsiloxy)-6-phenalenol (18). Reaction of diazo ketone **14** (0.090 g, 0.485 mmol) with 2-cyclohexyl-1-(triisopropylsiloxy)ethyne (0.141 g, 0.504 mmol) according to general procedure A (irradiation for 7 h, heating for 7 h) gave 0.2 g of a brown oil. Column chromatography on silica gel (elution with 5% EtOAc–hexane) provided 0.131 g (62%) of **18** as a viscous, slightly yellow oil: IR (neat) 3620, 3570, 2940, 2870, 1620, 1595, 1585, 1495, 1465, 1450, 1410, 1360, 1345, 1330, 1315, 1270, 1240, 1230, 1200, 1180, 1140, 1110, 1090, 1070, 1025, 925, 905, 890, 850, 820, 800, 760, 680, and 655 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 1 H), 7.10–7.23 (m, 2 H), 5.23 (s, 1 H), 3.22–3.32 (m, 1 H), 2.94–3.00 (m, 4 H), 1.60–2.15 (m, 8 H), 1.30–1.50 (m, 3 H), 1.16 (d, J = 7.4 Hz, 18 H), and 1.02–1.30 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 148.7, 135.5, 129.7, 123.8, 122.7, 121.4, 121.2, 117.7, 115.3, 35.7, 31.3, 30.8, 27.2, 26.3, 26.1, 22.8, 18.3, and 14.5; HRMS, m/e calcd for $C_{28}H_{42}O_2Si$ 438.2954, found 438.2955.

2,5-Dimethyl-3-methoxy-1-naphthol (21). Reaction of diazo ketone **19**[31] (0.172 g, 1.08 mmol) with 1-methoxypropyne (0.11 mL, 0.09 g, 1.28 mmol) according to general procedure A (irradiation for 9 h, heating for 3.5 h) gave 0.225 g of a maroon oil. Column chromatography on silica gel (elution with 10% Et_2O–hexane) furnished 0.124 g (57%) of **21** as off-white crystals: mp 77–78 °C; IR (CCl_4) 3610, 3000, 2970, 2830, 2810, 1635, 1505, 1465, 1430, 1330, 1280, 1250, 1130, 1080, 980, 910, and 880 cm^{-1}; UV max (CH_3CN) 286 (ϵ = 9900) and 237 (12 500) nm; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.90 (br d, J = 7.2 Hz, 1 H), 7.23 (m, 2 H), 6.81 (s, 1 H), 5.25 (s, 1 H), 3.93 (s, 3 H), 2.61 (s, 3 H), and 2.26 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 149.7, 132.6, 132.1, 126.8, 122.6, 120.0, 119.1, 109.0, 94.6, 55.4, 19.8, and 8.4. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.79; H, 6.84.

5-(*tert*-Butyldimethylsiloxy)-3-methoxy-2-methyl-1-naphthol (23). Reaction of diazo ketone **22** (0.174 g, 0.63 mmol) with 1-methoxypropyne (0.07 mL, 0.053 g, 0.76 mmol) according to general procedure A (irradiation for 6 h, heating for 3 h) gave 0.198 g of a maroon oil. Column chromatography on silica gel (gradient elution with 0–10% Et_2O–hexane) furnished 0.104 g (52%) of **23** as a pale yellow oil: IR (CCl_4) 3610, 2940, 2860, 1630, 1470, 1430, 1400, 1380, 1270, 1220, 1130, and 960 cm^{-1}; UV max (CH_3CN) 332 (ϵ = 800), 297 (1900), 287 (1900), 235 (14 700), and 203 (6700) nm; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1 H), 7.18 (m, 1 H), 7.13 (s, 1 H), 6.82 (d, J = 8.0 Hz, 1 H), 5.13 (s, 1 H), 3.92 (s, 3 H), 2.27 (s, 3 H), 1.11 (s, 9 H), 0.27 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 150.6, 149.3, 127.3, 122.8, 121.6, 113.8, 113.2, 109.6, 93.1, 55.4, 25.9, 18.4, 8.5, and −4.3; HRMA, m/e calcd for $C_{18}H_{26}O_3Si$ 318.1651, found 318.1650.

2-Cyclohexyl-7-(methoxycarbonyl)-3-(triisopropylsiloxy)-1-naphthol (25). Reaction of diazo ketone **24**[24] (0.200 g, 0.98 mmol) with 2-cyclohexyl-1-(triisopropylsiloxy)ethyne (0.29 g, 1.03 mmol) according to general procedure A (irradiation for 21 h, heating for 2 h) gave 0.434 g of a maroon oil. Column chromatography on silica gel (gradient elution with 0–20% Et_2O–hexane) furnished 0.218 g (49%) of **25** as off-white crystals: mp 141–142 °C; IR (CCl_4) 3700, 3620, 3430 (br), 2940, 2875, 1720, 1700, 1625, 1450, 1405, 1390, 1320, 1295, 1280, 1230, 1195, 1170, 1140, 1105, 1010, 930, 910, 850, and 670 cm^{-1}; UV max (CH_3CN) 317 (ϵ = 3900), 260 (37 000), and 225 (11 000) nm; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.90 (br s, 1 H), 7.93 (dd, J = 1.5, 9.0 Hz, 1 H), 7.58 (d, J = 9 Hz, 1 H), 6.78 (s, 1 H), 6.22 (s, 1 H), 3.96 (s, 3 H), 3.40–3.52 (m, 1 H), 2.00–2.21 (m, 2 H), 1.71–1.95 (m, 4 H), 1.32–1.53 (m, 7 H), and 1.16 (d, J = 7.2 Hz, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 155.8, 152.0, 135.4, 126.1, 125.3, 124.5, 124.1, 121.8, 120.0, 106.0, 52.1, 35.8, 30.6, 27.5, 26.3, 18.1, and 13.2. Anal. Calcd for $C_{27}H_{40}O_4Si$: C, 71.01; H, 8.83. Found: C, 70.85; H, 8.56.

2-Ethyl-3-methoxy-8-methyl-1-naphthol (27) and 2-Ethyl-3-methoxy-6-methyl-1-naphthol (28). Reaction of diazo ketone **26**[25] (0.117 g, 0.730 mmol) with 1-methoxybutyne (0.08 mL, 0.074 g, 0.876 mmol) according to general procedure A (irradiation for 7 h, heating for 3 h) gave 0.2 g of a brown oil. ^{1}H NMR analysis of the crude product indicated the presence of a 1:1 mixture of regioisomers. Column chromatography on silica gel (elution with 10% Et_2O–petroleum ether) provided 0.051 g (32%) of **27** and 0.052 g (32%) of **28** as off-white crystals. For **27**: IR ($CHCl_3$) 3600, 3030, 3005, 2964, 2935, 2870, 2835, 1620, 1579, 1500, 1430, 1350, 1323, 1284, 1253, 1220, 1207, 1195, 1150, 1129, and 1039 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.1 Hz, 1 H), 7.20 (appar t, 1 H), 7.01 (d, J = 7.0 Hz, 1 H), 6.73 (s, 1 H), 5.39 (s, 1 H), 3.88 (s, 3 H), 2.92 (s, 3 H), 2.74 (q, J = 7.6 Hz, 2 H), and 1.17 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 151.5, 134.8, 134.1, 126.1, 125.5, 125.1, 119.7, 115.7, 99.0, 55.3, 24.6, 16.5, and 13.5. For **28**: IR ($CHCl_3$) 3600, 3060, 3000, 2960, 2930, 2865, 1630, 1609, 1578, 1500, 1447, 1401, 1339, 1283, 1244, 1226, 1198, 1131, 1101, and 1043; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 1 H), 7.43 (s, 1 H), 7.13 (d, J = 8.5 Hz, 1 H), 6.68 (s, 1 H), 5.23 (s, 1 H), 3.88 (s, 3 H), 2.76 (q, J = 7.5 Hz, 2 H), 2.4k (s, 3 H), and 1.17 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 148.8, 135.6, 133.4, 125.6, 125.0, 120.8, 118.4, 114.9, 97.7, 55.4, 21.6, 16.7, and 13.7. Due to the propensity of these naphthols to undergo oxidation, further characterization was performed on the acetate derivatives (prepared by using the procedure of Steglich and Höfle[30]). For 2-ethyl-3-methoxy-8-methyl-1-naphthyl acetate (white solid): mp 83.5–85 °C; IR ($CHCl_3$) 2930, 2870, 2830, 1752, 1620, 1600, 1576, 1445, 1420, 1366, 1330, 1156, 1105, 1035, and 895 cm^{-1}; UV max (CH_3CN) 330 (ϵ = 1800), 316 (1400), 279 (5300), 269 (4700), and 229 (28 000) nm; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.56 (δ, J = 8.1 Hz, 1 H), 7.24 (appar t, 1 H), 7.08 (d, J = 7.0 Hz, 1 H), 7.03 (s, 1 H), 3.92 (s, 3 H), 2.65–2.85 (m, 2 H), 2.71 (s, 3 H), 2.41 (s, 3 H), and 1.15 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 155.5, 145.5, 134.5, 131.9, 127.5, 126.3, 125.7, 125.6, 122.3, 104.7, 55.5, 23.3, 21.4, 18.4, and 13.4. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.19; H, 7.03. For 2-ethyl-3-methoxy-6-methyl-1-naphthyl acetate (colorless oil): IR (neat) 3065, 2970, 2955, 2875, 1760, 1632, 1610, 1575, 1500, 1460, 1400, 1368, 1330, 1275, 1235, 1200, 1172, 1132, 1100, 1060, 1048, 1015, 885, 860, 818, 810, 770, 728, and 655 cm^{-1}; UV max (CH_3CN) 327 (ϵ = 1900), 312 (1400), 279 (4400), 269 (4200), and 225 (30 000) nm; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49 and 7.47 (overlapping d and s, 2 H total), 7.1 (dd, J = 1.2 and 8.6 Hz, 1 H), 6.94 (s, 1 H), 3.89 (s, 3 H), 2.67 (q, J = 7.4 Hz, 2 H), 2.4k (s, 3 H), 2.44 (s, 3 H), and 1.15 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 156.3, 144.7, 135.7, 133.4, 126.2, 125.8, 124.7, 120.8, 120.7, 102.9, 55.5, 21.5, 20.6, 18.2, and 13.4. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.63; H, 7.23.

3-Ethyl-2-methoxy-5,6,7,8-tetrahydro-4-phenanthrol (30) and 2-Ethyl-3-methoxy-5,6,7,8-tetrahydro-1-anthrol (31). Reaction of diazo ketone **29** (0.295 g, 1.47 mmol) with 1-methoxybutyne (0.45 mL, 0.371 g, 4.41 mmol) according to general procedure B (irradiation for 6 h) produced 0.167 g (57%) of a 3:1 mixture of unstable compounds **30** and **31**. Due to the propensity of these compounds to undergo oxidation, full characterization was performed on the acetate derivatives (prepared by using the procedure of Steglich and Höfle[30]). For 3-ethyl-2-methoxy-5,6,7,8-tetrahydro-4-phenanthryl acetate (white solid): mp 104–105.5 °C; IR ($CHCl_3$) 2910, 2860, 2830, 1748, 1620, 1608, 1560, 1495, 1450, 1368, 1348, 1290, 1145, 1108, 1022, 905, 880, and 845 cm^{-1}; UV max (CH_3CN) 335 (ϵ = 2000), 320 (1700), 278 (5200), 268 (5100), and 227 (28 000) nm; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.43 (d, J = 8.3 Hz, 1 H), 7.05 (d, J = 8.3 Hz, 1 H), 6.97 (s, 1 H), 3.89 (s, 3 H), 2.70–2.95 (m, 4 H), 2.42–2.60 (m, 2 H), 2.39 (s, 3 H), 1.60–2.05 (m, 4 H), and 1.14 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 154.8, 145.3, 133.2, 132.9, 130.3, 128.6, 126.2, 125.0, 122.4, 104.9, 55.3, 30.9, 28.5, 23.9, 22.1, 21.3, 18.4, and 13.4. Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.25; H, 7.30. For 2-ethyl-3-methoxy-5,6,7,8-tetrahydro-1-anthryl acetate (pale yellow solid): mp 100.5–102 °C; IR ($CHCl_3$) 2910, 2860, 2830, 1752, 1630, 1605, 1562, 1490, 1450, 1400, 1368, 1348, 1320, 1135, 1105, 1035, 960, 800, and 862 cm^{-1}; UV max (CH_3CN) 334 (ϵ = 2000), 320 (1600), 283 (4200), 234 (30 000) nm; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40 (s, 1 H), 7.25 (s, 1 H), 6.90 (s, 1 H), 3.89 (s, 3 H), 2.89 (m, 4 H), 2.65 (appar q, 2 H), 2.4m (s, 3 H), 1.82 (m, 4 H), and 1.1j (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 155.8, 144.4, 136.7, 134.5, 131.9, 125.9, 124.9, 121.4, 120.0, 102.7, 55.4, 29.6, 29.5, 23.2, 23.1, 20.5, 18.0, and 13.3; HRMS, m/e calcd for $C_{19}H_{22}O_3$ 298.1569, found 298.1570.

5-Ethyl-4-hydroxy-6-methoxybenzofuran (33). Reaction of diazo ketone **32**[28] (0.229 g, 1.68 mmol) with 1-methoxybutyne (0.21 mL, 0.173

(27) In other runs the yield for this reaction ranged from 50 to 54%.

g, 2.02 mmol) according to general procedure A (irradiation for 46 h, heating for 3.5 h) gave 0.25 g of a brown oil. Column chromatography on silica gel (gradient elution with 0–50% benzene–petroleum ether) provided 0.143 g (44%) of **33** as pale yellow crystals: mp 69–71 °C; IR (CCl_4) 3620, 3000, 2970, 2940, 2880, 2840, 1640, 1610, 1480, 1460, 1440, 1375, 1340, 1310, 1260, 1240, 1230, 1200, 1140, 1080, 1045, 850, and 730 cm^{-1}; UV max (CH_3CN) 327 (ϵ = 200), 286 (sh, 700), 273 (sh, 1000), 252 (7100), 217 (17 000), and 212 (16 000) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 2.8 Hz, 1 H), 6.73 (d, J = 2.8 Hz, 1 H), 6.69 (s, 1 H), 5.13 (s, 1 H), 3.84 (s, 3 H), 2.72 (q, J = 7.5 Hz, 2 H), 1.15 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 154.8, 146.3, 142.3, 112.7, 110.0, 102.9, 87.7, 55.9, 16.4, and 14.0; HRMS, m/e calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0787.

6-Ethyl-7-hydroxy-5-methoxybenzothiophene (35). Reaction of diazo ketone **34** (0.171 g, 1.12 mmol) with 1-methoxybutyne (0.14 mL, 0.116 g, 1.35 mmol) according to general procedure A (irradiation for 48 h, heating for 12 h) gave 0.25 g of a brown oil. Column chromatography on silica gel (gradient elution with 0–50% benzene–petroleum ether) provided 0.107 g (46%) of **35** as pale yellow crystals: mp 54–56 °C; IR (CCl_4) 3610, 3000, 2970, 2940, 2910, 2870, 2840, 1620, 1565, 1500, 1460, 1410, 1400, 1365, 1280, 1255, 1225, 1205, 1195, 1160, 1140, 1130, 1035, and 660 cm^{-1}; UV max (CH_3CN) 312 (ϵ = 2600), 302 (2600), 269 (7300), 261 (7400), 226 (23 000), and 209 (21 000) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, J = 5.5 Hz, 1 H), 7.22 (d, J = 5.5 Hz, 1 H), 6.92 (s, 1 H), 5.06 (s, 1 H), 3.86 (s, 3 H), 2.74 (q, J = 7.5 Hz, 2 H), and 1.17 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 147.7, 138.9, 125.7, 124.1, 120.8, 114.7, 97.4, 55.8, 16.7, and 13.9; HRMS, m/e calcd for $C_{11}H_{12}O_2S$ 208.0558, found 208.0558.

1-(*tert*-Butoxycarbonyl)-5-cyclohexyl-4-hydroxy-6-(triisopropylsiloxy)indole (37). Reaction of diazo ketone **36** (0.200 g, 0.85 mmol) with 2-cyclohexyl-1-(triisopropylsiloxy)ethyne (0.263 g, 0.936 mmol) according to general procedure A (irradiation for 4.5 h, heating for 2 h) gave 0.393 g of a brown oil. Column chromatography on silica gel (gradient elution with 0–10% EtOAc–hexane) furnished 0.173 g (42%) of **37** as off-white crystals: mp 177–178 °C; IR (CCl_4) 3620, 3330, 3580, 2920, 2860, 1730, 1630, 1450, 1395, 1345, 1315, 1290, 1260, 1220, 1170, 1140, 1085, 1015, 920, 880, and 680 cm^{-1}; UV max (CH_3CN) 306 (ϵ = 7000), 295 (6400), 270 (13 000), and 237 (32 000) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 3.7 Hz, 1 H), 7.23 (br s, 1 H), 6.46 (d, J = 3.7 Hz, 1 H), 4.96 (s, 1 H), 3.30–3.45 (m, 1 H), 1.92–2.11 (m, 2 H), 1.80–1.90 (m, 2 H), 1.70–1.78 (m, 2 H), 1.64 s, 9 H), 1.50–1.20 (m, 7 H), and 1.15 (d, J = 7.2 H, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 149.8, 147.4, 134.1, 123.2, 117.8, 114.3, 102.6, 98.2, 83.2, 35.5, 30.9, 28.2, 27.6, 26.4, 18.2, and 13.2. Anal. Calcd for $C_{28}H_{45}NO_4Si$: C, 68.95; H, 9.30; N, 2.87. Found: C, 69.21; H, 9.42; N, 2.94.

9-(*tert*-Butoxycarbonyl)-2-cyclohexyl-1-hydroxy-3-(triisopropylsiloxy)carbazole (39). Reaction of diazo ketone **38** (0.144 g, 0.51 mmol) with 2-cyclohexyl-1-(triisopropylsiloxy)ethyne (0.156 g, 0.56 mmol) according to general procedure A (irradiation for 8 h, heating for 2.5 h) gave 0.317 g of a brown oil. Column chromatography on silica gel (gradient elution with 0–15% EtOAc–hexane) furnished 0.115 g (42%) of **39** as off-white crystals: mp 156.5–157 °C; IR (CCl_4) 3120 (br) 2970, 2930, 2870, 2860, 1685, 1625, 1595, 1575, 1475, 1435, 1380, 1375, 1320, 1290, 1230, 1210, 1160, 1130, 1085, 1015, 890, 860, 840, and 690 cm^{-1}; UV max (CH_3CN) 330 (ϵ = 5000), 315 (5000), 300 (12 000), 276 (13 000), 231 (13 000), and 210 (24 000) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 11.15 (br s, 1 H), 8.01 (d, J = 7.6 Hz, 1 H), 7.78 (dd, J = 1.7, 7.2 Hz, 1 H), 7.29–7.36 (m, 2 H), 6.87 (s, 1 H), 3.40–3.52 (m, 1 H), 2.28–2.40 (m, 2 H), 1.75–1.90 (m, 2 H), 1.73 (s, 9 H), 1.60–1.68 (m, 2 H), 1.25–1.45 (m, 7 H), and 1.17 (d, J = 6.9 Hz, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 152.2, 145.4, 138.4, 127.3, 126.6, 125.7, 125.0, 123.5, 121.9, 119.3, 116.9, 99.4, 86.2, 36.8, 29.6, 28.3, 27.6, 26.4, 18.2, and 13.2; HRMS, m/e calcd for $C_{32}H_{47}NO_4Si$ 537.3274, found 537.3274.

1-(3-(1-*tert*-Butoxycarbonyl)indolyl)-1-ethanone (40). A 250-mL, three-necked, round-bottomed flask equipped with a glass stopper, a rubber septum, and a nitrogen inlet adapter was charged with 3-acetylindole (2.0 g, 12.6 mmol), di-*tert*-butyl dicarbonate (3.01 g, 3.17 mL, 13.8 mmol), potassium *tert*-butoxide (0.140 g, 1.25 mmol), and 50 mL of THF, and the resulting orange mixture was stirred at room temperature for 18 h. The reaction mixture was then diluted with 30 mL of Et_2O, washed with 20 mL of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated to yield 4.94 g of a yellow solid. Column chromatography on silica gel (elution with 10% EtOAc–hexane) furnished 3.06 g (94%) of **40** as white crystals: mp 143–144 °C; IR (CCl_4) 3150, 3060, 2990, 2940, 1750, 1675, 1480, 1455, 1390, 1375, 1365, 1340, 1310, 1275, 1245, 1200, 1155, 1115, 1065, 1020, and 925 cm^{-1}; UV max (CH_3CN) 285 (ϵ = 12 800) and 213 (36 700) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 8.36–8.39 (m, 1 H), 8.23 (s, 1 H), 8.10–8.13 (m, 1 H), 7.34–7.41 (m, 2 H), 2.57 (s, 3 H), and 1.72 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 149.1, 135.5, 132.4, 127.3, 125.4, 124.3, 122.7, 120.6, 114.9, 85.4, 28.1, and 27.7. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.21; H, 6.42; N, 5.33.

2-Diazo-1-(3-(1-*tert*-butoxycarbonyl)indolyl)-1-ethanone (38). A 250-mL, three-necked, round-bottomed flask equipped with a rubber septum, nitrogen inlet adapter, and a glass stopper was charged with a solution of 1,1,1,3,3,3-hexamethyldisilazane (1.05 mL, 1.14 g, 7.09 mmol) in 20 mL of THF and then cooled at 0 °C in an ice–water bath, while a solution of *n*-butyllithium (2.20 M in hexane, 3.22 mL, 7.09 mmol) was added dropwise over 2 min. The resulting solution was stirred at 0 °C for 10 min, cooled to −78 °C in a dry ice–acetone bath, and then treated dropwise over 15 min with a solution of **40** (1.53 g, 5.91 mmol, in 15 mL of THF). The resulting mixture was stirred at −78 °C for 30 min and then was treated with 2,2,2-trifluoroethyl trifluoroacetate (0.95 mL, 1.39 g, 7.09 mmol) in one portion. After 10 min, the reaction mixture was poured into a separatory funnel containing 25 mL of 5% aqueous HCl solution and 30 mL of Et_2O. The aqueous phase was separated and extracted with two 20-mL portions of Et_2O, and the combined organic phases were then washed with 25 mL of saturated NaCl solution and concentrated at reduced pressure to give 2.22 g of a tan solid that was immediately dissolved in 20 mL of CH_3CN and transferred to a 100-mL, three-necked, round-bottomed flask equipped with a glass stopper, a rubber septum, and an argon inlet adapter. Deionized H_2O (0.11 mL, 0.11 g, 5.91 mmol) and Et_3N (1.23 mL, 0.896 g, 8.86 mmol) were added, and then a solution of methanesulfonyl azide (0.77 mL, 1.07 g, 8.86 mmol) in 20 mL of CH_3CN was added dropwise over 30 min. The resulting solution was stirred at room temperature for 2.5 h and was then concentrated to a volume of ca. 10 mL. The residue was diluted with 30 mL of Et_2O, washed with three 20-mL portions of 10% aqueous NaOH solution and 25 mL of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated to afford 1.52 g of a bright yellow solid. Column chromatography on silica gel (elution with 20% EtOAc–hexane) provided 1.45 g (86%) of the diazo ketone **38** as yellow solid: mp 119–122 °C; IR (CCl_4) 2970, 2930, 2860, 2100, 1740, 1625, 1450, 1390, 1370, 1360, 1330, 1310, 1260, 1235, 1185, 1150, 1100, and 1045 cm^{-1}; UV max (CH_3CN) 308 (ϵ = 18 000), 245 (19 000), and 217 (28 000) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28–8.30 (m, 1 H), 8.10–8.13 (m, 1 H), 8.02 (s, 1 H), 7.34–7.41 (m, 2 H), 5.79 (s, 1 H), and 1.70 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.7, 149.0, 135.5, 128.5, 127.3, 125.4, 124.2, 122.1, 119.3, 115.0, 85.3, 54.3, and 28.0. Anal. Calcd for $C_{15}H_{15}N_3O_3$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.37, H, 5.40, N, 14.79.

9-(*tert*-Butoxycarbonyl)-1-hydroxy-3-methoxy-2-methylcarbazole (41). Reaction of diazo ketone **38** (0.453 g, 1.59 mmol) with methoxypropyne (0.167 g, 2.39 mmol) according to general procedure A (irradiation for 19.5 h, heating for 5 h) gave 0.631 g of a maroon oil. Column chromatography on silica gel (elution with 20% EtOAc–hexane) furnished 0.289 g (56%) of **41** as off-white crystals: mp 137–138 °C; IR (CCl_4) 3120, 2900, 2700, 1680, 1620, 1590, 1480, 1450, 1430, 1390, 1360, 1290, 1230, 1210, 1160, 1150, 1060, 1030, 1005, 935, 910, 800 (br), 690, and 670 cm^{-1}; UV max (CH_3CN) 326 (ϵ = 7800), 314 (8100), 292 (20 100), 275 (20 900), 228 (53 900), and 209 (46 500) nm; ^1H NMR (250 MHz, $CDCl_3$) δ 11.36 (s, 1 H), 8.05 (br d, J = 7.8 Hz, 1 H), 7.90 (br d, J = 7.9 Hz, 1 H), 7.38 (m, 2 H), 6.94 (s, 1 H), 3.94 (s, 3 H), 2.27 (s, 3 H), 1.76 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 154.3, 143.8, 138.0, 127.3, 126.5, 125.6, 123.5, 121.0, 119.2, 116.9, 114.2, 91.8, 86.4, 55.8, 28.2, and 9.4. Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.68; H, 6.58; N, 4.15.

9-(*tert*-Butoxycarbonyl)-3-methoxy-2-methyl-1-((trifluoromethyl)sulfonyl)carbazole (42). A 25-mL, two-necked flask equipped with a nitrogen inlet adapter and a rubber septum was charged with carbazole **41** (0.264 g, 0.81 mmol), DMAP (0.098 g, 0.81 mmol), and 2 mL of pyridine. The resulting orange solution was cooled at 0 °C, while trifluoromethanesulfonic anhydride (0.341 g, 0.203 mL, 1.21 mmol) was added dropwise over 1 min. Pyridine (1 mL) was added to dissolve the small amount of white precipitate which had formed, and the resulting brown solution was allowed to slowly warm to room temperature. After 18.5 h, the reaction mixture was diluted with 15 mL of Et_2O and 15 mL of H_2O, and the aqueous layer was separated and extracted with three 10-mL portions of Et_2O. The combined organic layers were washed with five 10-mL portions of dilute aqueous $CuSO_4$ solution, 10 mL of H_2O, and 10 mL of saturated NaCl solution, dried over Na_2SO_4, filtered, and

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concentrated to yield 0.542 g of a light orange solid. Column chromatography on silica gel (elution with 5% EtOAc-hexane) furnished 0.289 g (78%) of **42** as yellow crystals: mp 112-113 °C; IR (CCl_4) 3060, 2990, 2940, 2880, 2840, 1945, 1910, 1740, 1630, 1480, 1455, 1430, 1380, 1350, 1330, 1300, 1200, 1150, 1130, 1090, 1040, 935, 845, and 655 cm^{-1}; UV max (CH_3CN) 325 (ϵ = 5600), 314 (5200), 293 (17 000), 263 (13 000), 230 (38 200), and 208 (29 200) nm; ^1H NMR (250 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.0 and 1.0 Hz, 1 H), 7.91 (dd, J = 8.0 and 1.0 Hz, 1 H), 7.46 (m, 1 H), 7.35 (m, 1 H), 7.40 (s, 1 H), 3.99 (s, 3 H), 2.38 (s, 3 H), and 1.72 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 150.2, 139.9, 135.4, 127.5, 125.4, 124.8, 123.2, 121.0, 120.7, 119.4, 116.5, 116.0, 100.2, 84.7, 56.2, 28.0, and 10.8. Anal. Calcd for $C_{20}H_{20}F_3NO_6S$: C, 52.29; H, 4.39; N, 3.05. Found: C, 52.58; H, 4.53; N, 2.73.

Hyellazole (43). A threaded Pyrex tube (2.5 cm o.d., 1.8 cm i.d., 17 cm in length) fitted with a rubber septa was charged with the triflate **42** (0.416 g, 0.91 mmol), LiCl (0.114 g, 2.72 mmol), 4 mL of dioxane, $PhMe_3Sn$ (0.262 g, 1.09 mmol), and $Pd(PPh_3)_4$ (0.052 g, 0.045 mmol). The resulting yellow suspension was degassed by two freeze-pump-thaw cycles (-196 °C, <0.5 mmHg) and then sealed with a threaded Teflon cap. The yellow reaction mixture was heated at 94 °C for 24 h during which time the color changed to black. The reaction mixture was then allowed to cool to room temperature, and an additional portion of $Pd(PPh_3)_4$ (0.052 g, 0.045 mmol) was added. The mixture was degassed by one freeze-pump-thaw cycle (-196 °C, <0.5 mmHg) and was heated at 94 °C for 14 h and then at 150 °C for 6 h. The resulting mixture was allowed to cool to room temperature, diluted with 10 mL of Et_2O, and washed with two 10-mL portions of 10% NH_4OH solution. The combined aqueous layers were extracted with two 4-mL portions of Et_2O, and the combined organic layers were washed with 10 mL of H_2O, 10 mL of 10% HCl solution, and 10 mL of saturated NaCl solution. The organic phase was dried over Na_2SO_4, filtered, and concentrated to yield 1.02 g of a brown solid. Column chromatography on silica gel (elution with 30% benzene-hexane) furnished 0.163 g (63%) of **43** as white crystals (mp 132-133 °C, lit. mp 133-134 °C) with spectroscopic data fully consistent with that previously reported[20] for hyellazole: IR (CCl_4) 3485, 3065, 3040, 3000, 2945, 2840, 1550, 1495, 1460, 1425, 1380, 1350, 1310, 1295, 1210, 1160, 1150, 1080, 1050, 1030, 1005, 985, 805, 720, 660, 640, and 610 cm^{-1}; ^1H NMR (250 MHz, acetone-d_6) δ 9.55 (br s, 1 H), 8.11 (br d, J = 8.0 Hz, 1 H), 7.71 (s, 1 H), 7.40-7.56 (m, 6 H), 7.30 (dt, J = 7.0 and 1.0 Hz, 1 H), 7.13 (dt, J = 7.0 and 1.0 Hz, 1 H), 3.99 (s, 3 H), and 2.16 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 139.5, 137.5, 133.3, 129.9, 128.9, 127.6, 125.5, 125.1, 123.8, 123.7, 120.3, 119.9, 118.8, 110.6, 100.3, 56.1, and 13.7; HRMS, m/e calcd for $C_{20}H_{17}NO$ 287.1310, found 287.1311. Anal. Calcd for $C_{20}H_{17}NO$: C, 83.60; H, 5.96; N, 4.87. Found: C, 83.20; H, 5.90; N, 5.04.

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Registry No. 1, 124687-96-3; **2**, 13279-94-2; **3**, 125569-58-6; **4**, 125569-59-7; **5**, 125569-60-0; **6**, 125569-61-1; **7**, 125569-62-2; **8**, 125569-63-3; **9**, 125569-64-4; **10**, 3282-32-4; **11**, 125569-65-5; **12**, 14088-57-4; **13**, 125569-66-6; **14**, 125569-67-7; **15**, 122760-68-3; **16**, 125569-68-8; **17**, 104875-64-1; **18**, 125569-69-9; **19**, 41441-74-1; **20**, 13169-01-2; **21**, 125569-70-2; **22**, 125569-71-3; **23**, 125569-72-4; **24**, 22744-13-4; **25**, 125569-73-5; **26**, 7023-80-5; **27**, 125569-74-6; **28**, 125569-75-7; **29**, 125569-76-8; **30**, 125569-77-9; **31**, 125569-78-0; **32**, 21443-46-9; **33**, 125569-79-1; **34**, 72676-21-2; **35**, 125569-80-4; **36**, 125569-81-5; **37**, 125569-82-6; **38**, 124687-95-2; **39**, 125569-83-7; **40**, 124688-00-2; **41**, 125569-84-8; **42**, 125569-85-9; **43**, 74364-11-7; 2-ethyl-3-methoxy-4-methyl-1-naphthyl acetate, 125569-86-0; 2-ethyl-3-methoxy-8-methyl-1-naphthyl acetate, 125569-87-1; 2-ethyl-3-methoxy-6-methyl-1-naphthyl acetate, 125569-88-2; 3-ethyl-2-methoxy-5,6,7,8-tetrahydro-4-phenanthryl acetate, 125569-89-3; 2-ethyl-3-methoxy-5,6,7,8-tetrahydro-1-anthryl acetate, 125569-90-6; 3-acetylindole, 703-80-0; 6-diazo-2-ethylidenecyclohexanone, 125569-91-7; 6-diazo-2-ethylidenecycloheptanone, 125569-92-8; 6-ethyl-7-methoxy-4-methyl-5-indanol, 125569-93-9; 3-ethyl-4-methoxy-1-methyl-5,6,7,8-tetrahydro-2-naphthol, 125569-94-0; 1-acetylcyclohexene, 932-66-1; acetophenone, 98-86-2; propiophenone, 93-55-0; 2-methylacetophenone, 577-16-2; *p*-(carbomethoxy)benzoyl chloride, 7377-26-6; *m*-toluoyl chloride, 1711-06-4; 2-acetylfuran, 1192-62-7; 3-acetylthiophene, 1468-83-3.

Tandem Cyclization-Cycloaddition Reaction of Rhodium Carbenoids. Scope and Mechanistic Details of the Process

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Abstract: Treatment of 1-diazo-2,5-pentanediones with rhodium(II) carboxylates affords cyclic six-ring carbonyl ylide dipoles. These species undergo facile 1,3-dipolar cycloaddition with both electron-deficient and electron-rich dipolarophiles. In certain cases 2:1 cycloadducts are formed. The higher order cycloadducts are derived by further dipolar cycloaddition of the carbonyl ylide across the keto group of the initially formed 1:1 cycloadduct. Attempts to obtain a cycloadduct from the reaction of the diazo dione with nonactivated olefins led to 6-substituted 2*H*-pyran-3(4*H*)-ones. The formation of this ring system proceeds via a 1,4-hydrogen shift from the intermediate carbonyl ylide dipole. The observed regioselectivity in these cycloadditions can be nicely accommodated in terms of frontier molecular orbital theory. A type II FMO interaction is suggested since carbonyl ylides possess one of the smallest HOMO-LUMO energy gaps of the common 1,3-dipoles. The HOMO of the dipole is dominant for reactions with electron-deficient dipolarophiles such as methyl propiolate, while the LUMO becomes important for cycloaddition to more electron-rich species such as propargyl ethers. MNDO calculations indicate that the largest coefficient in the HOMO resides on the enolate carbon, whereas the γ-carbon bears the largest coefficient in the LUMO.

The stereoselective preparation of highly substituted oxygen heterocycles, especially structurally complex tetrahydrofurans and tetrahydropyrans, has attracted considerable attention in recent years.[1,2] These medium size cyclic ethers are becoming increasingly recognized as common structural units in naturally occurring compounds such as the ionophores,[3] the brevetoxins,[4]

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