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Synthesis of Indeno-Fused Derivatives of Quinolizinium Salts, Imidazo[1,2-*a*]pyridine, Pyrido[1,2-*a*]indole, and 4*H*-Quinolizin-4-one via Benzannulated Enyne−Allenes

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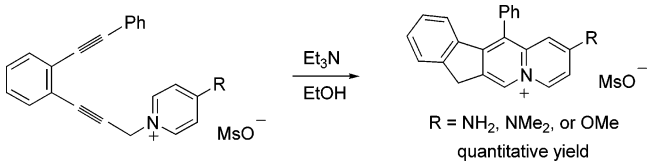
Received March 21, 2005

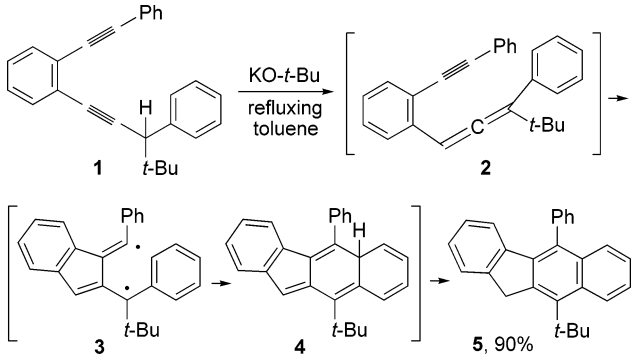


The benzannulated enediynyl propargylic alcohol **8** was prepared from 1-bromo-2-iodobenzene by two consecutive Sonogashira cross-coupling reactions. The subsequent transformation to mesylate **9** followed by treatment with 4-substituted pyridines **10** then furnished the benzannulated enediynes **11**. On exposure of **11** to triethylamine, the indeno-fused quinolizinium salts **15** were produced in quantitative yield. Presumably the reaction proceeded through a 1,3-prototropic rearrangement to form the benzannulated enyne−allenes **12**, which then underwent either a concerted Diels−Alder reaction or a two-step process involving a Schmittel cyclization reaction to form biradical **13** followed by an intramolecular radical−radical coupling to afford **14**. A subsequent prototropic rearrangement then produced **15**. Similarly, **21a** and **21b** were produced from **19a** and **19b**, respectively. The use of the Sonogashira reaction for cross-coupling between 1-iodo-2-(phenylethynyl)benzene (**7**) and 1-(2-propynyl)-1*H*-imidazole (**25**) followed by treatment of the resulting adduct with potassium *tert*-butoxide gave the indeno-fused imidazo[1,2-*a*]pyridine **24** in 98% yield. Similarly, the indeno-fused pyrido[1,2-*a*]indole **32** and 4*H*-quinolizin-4-one **35** were obtained by starting from **7** for cross-coupling with 1-(2-propynyl)-1*H*-indole (**30**) and 1-(2-propynyl)-2(1*H*)-pyridinone (**33**), respectively, followed by treatment with potassium *tert*-butoxide.

Introduction

Benzannulated enyne−allenes bearing an aryl substituent at the alkynyl terminus have been shown to undergo the Schmittel cyclization reaction to produce the corresponding benzofulvene biradicals under mild thermal conditions.[1] One such example involves a potassium *tert*-butoxide-promoted 1,3-prototropic rearrangement of the benzannulated enediyne **1** to produce in situ enyne−allene **2** for the subsequent Schmittel cyclization reaction to generate biradical **3** (Scheme 1).[2] The presence of a second phenyl substituent at the allenic terminus of **2**

SCHEME 1



permits an intramolecular radical−radical coupling to furnish the formal Diels−Alder adduct **4**, which in turn undergoes a prototropic rearrangement to afford **5** as a benzo[*b*]fluorene derivative. Several other synthetic meth-

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(1) (a) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999−1002. (b) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843−1845. (c) Schmittel, M.; Kiau, S.; Siebert, T.; Strittmatter, M. *Tetrahedron Lett.* **1996**, *37*, 7691−7694. (d) Schmittel, M.; Keller, M.; Kiau, S.; Strittmatter, M. *Chem. Eur. J.* **1997**, *3*, 807−816.

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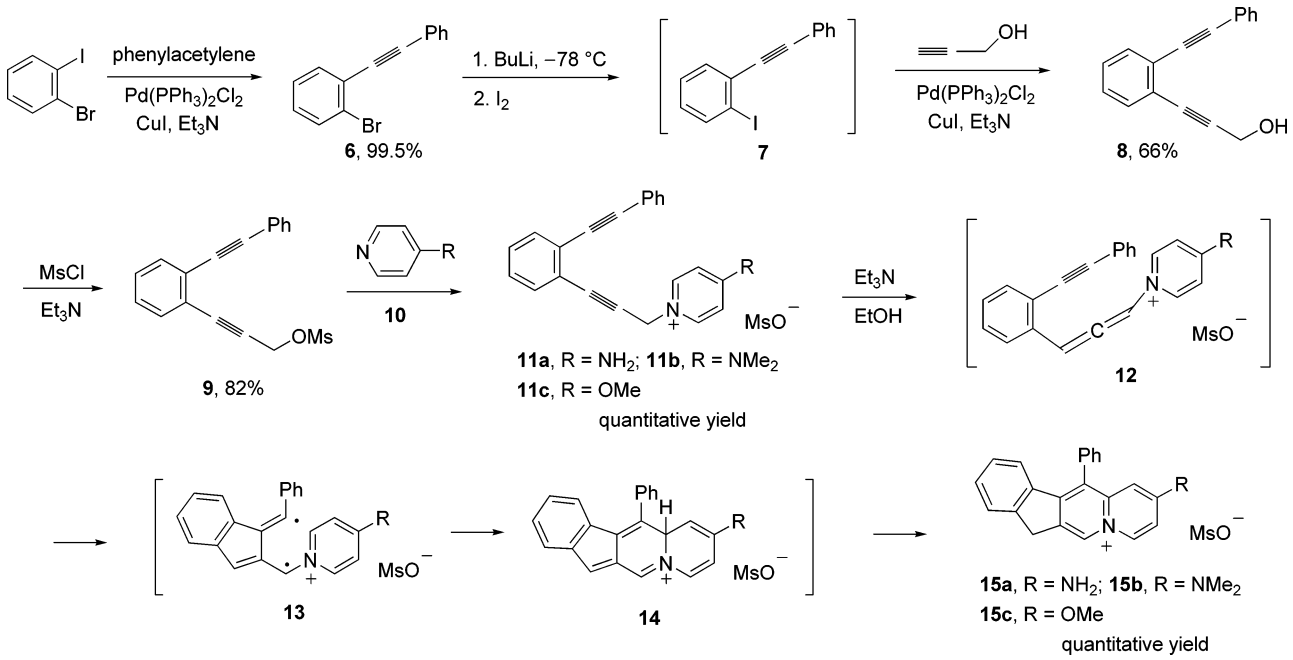
10.1021/jo0505730 CCC: $30.25
Published on Web 07/28/2005

SCHEME 2



ods have also been reported to furnish enyne−allenes for similar cascade transformations to a variety of benzo[*b*]-fluorenes and related polycyclic aromatic compounds.[3]

By placing a heteroaromatic substituent at the allenic terminus of the enyne−allene system, the cascade reaction sequence has been reported to lead to the derivatives of 10*H*-indeno[1,2-*g*]quinoline, 9*H*-fluoreno[2,3-*b*]furan, 9*H*-fluoreno[2,3-*b*]thiophene, and 5*H*- and 6*H*-indeno[2,1-*f*]indolizines.[1a,4] A similar strategy also finds success in the enyne−carbodiimide[5] and enallene−isonitrile systems,[6] producing a variety of novel heteroaromatic compounds. We have further applied this synthetic strategy to the preparation of the indeno-fused derivatives of quinolizinium salts, imidazo[1,2-*a*]pyridine, pyrido[1,2-*a*]indole, and 4*H*-quinolizin-4-one, taking advantage of the facile 1,3-prototropic rearrangements of the corresponding benzannulated enediynes to furnish the requisite enyne−allenes for subsequent cascade transformations to heteroaromatic ring systems.

Results and Discussion

The synthetic sequence outlined in Scheme 2 provides an efficient route to benzannulated enediynes **11a**−**c**. The palladium-catalyzed Sonogashira reaction between 1-bromo-2-iodobenzene and phenylacetylene produced **6** as reported previously.[3c] Treatment of **6** with butyllithium followed by iodine then afforded **7**, which was used for a second palladium-catalyzed coupling with propargyl alcohol to give **8** and subsequently, after treatment with methanesulfonyl chloride and triethylamine, mesylate **9**. Upon exposure of **9** to 4-aminopyridine, 4-(dimethylamino)pyridine, and 4-methoxypyridine, the benzannulated enediynes **11a**−**c** were obtained in essentially quantitative yield.[7] Efficient transformations of **11a**−**c** to the indeno-fused quinolizinium methanesulfonates **15a**−**c** were achieved also in essentially quantitative yield with triethylamine in ethanol. The products **15a**−**c** appeared to be free of other byproducts as judged by ^{1}H NMR spectra without the need for purification by column chromatography. The structures of **15a**−**c** were established by X-ray structure analyses. Presumably, a 1,3-prototropic rearrangement of **11** occurred to give the corresponding benzannulated enyne−allenes **12**, which then underwent either a concerted Diels−Alder reaction or a two-step process involving a Schmittel cyclization reaction to form biradical **13** followed by an intramolecular radical−radical coupling to afford **14**. A subsequent prototropic rearrangement then produced the indeno-fused quinolizinium methanesulfonates **15**. It is worth noting that several 2-amino-substituted quinolizinium salts and related compounds were reported to exhibit interesting biological activities and pronounced DNA-binding properties.[8]

It was reported earlier that placing a sterically demanding substituent, such as *tert*-butyl or trimethylsilyl, at the alkynyl terminus of the enyne−allene system also

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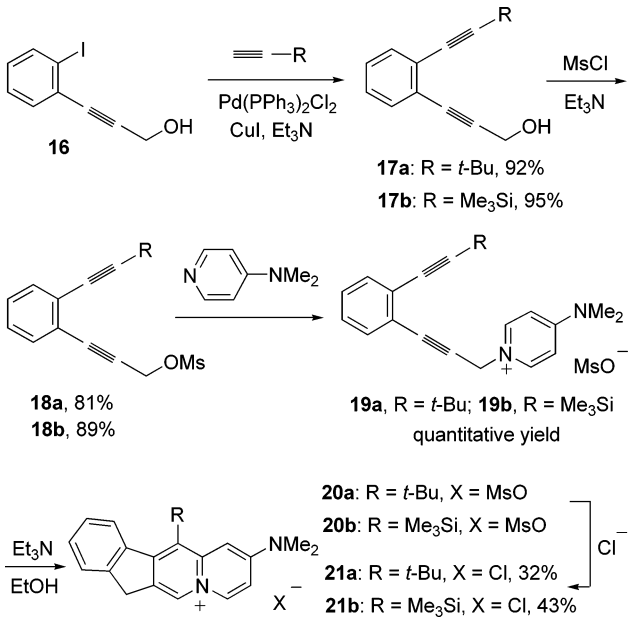
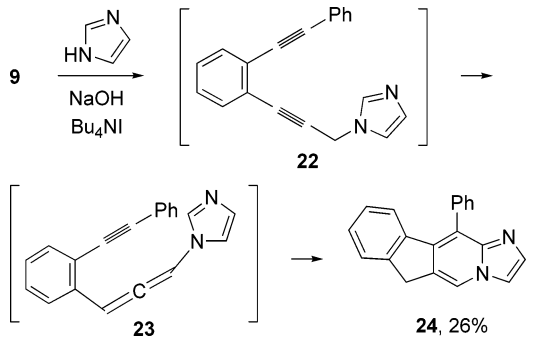
SCHEME 3



directed the biradical-forming reaction toward the Schmittel cyclization pathway.[1c] We have thus synthesized the benzannulated enediynes **19a** and **19b** bearing a *tert*-butyl group and a trimethylsilyl group at the alkynyl terminus, respectively, as outlined in Scheme 3. The starting iodide **16** was prepared by the palladium-catalyzed Sonogashira reaction between 1,2-diiodobenzene and propargyl alcohol as described previously.[9] Unlike **11b**, which underwent cyclization on exposure to triethylamine at room temperature to form **15b**, it was necessary to heat the reaction mixtures of **19a** and **19b** under refluxing ethanol to produce **20a** and **20b**. It was also necessary to purify the resulting products by column chromatography because significant amounts of unidentified byproducts were present as indicated by ^{1}H NMR spectra. Purification by column chromatography on neutral alumina resulted in an exchange of the mesylate anion by chloride to produce quinolizinium chlorides **21a** and **21b** in relatively low yields. The structure of **21a** was established by X-ray structure analysis.

An attempt to alkylate imidazole with **9** in a mixture containing sodium hydroxide and tetrabutylammonium iodide to produce **22** resulted in the formation of the indeno-fused imidazo[1,2-*a*]pyridine **24** directly albeit in relatively low yield (Scheme 4). Presumably **22** was formed initially, which then underwent a sodium hydroxide-promoted 1,3-prototropic rearrangement to the corresponding benzannulated enyne–allene **23** for the subsequent cascade reaction sequence to yield **24**. Alternatively, the palladium-catalyzed Sonogashira reaction between **7** and 1-(2-propynyl)-1*H*-imidazole (**25**)[10] was employed to produce **22**. Under the reaction condition, a mixture of the benzannulated enediyne **22** and the

SCHEME 4



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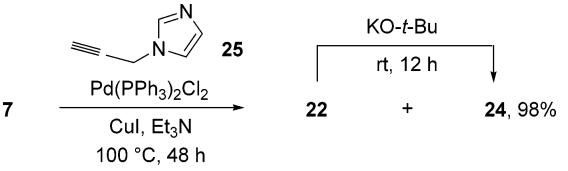
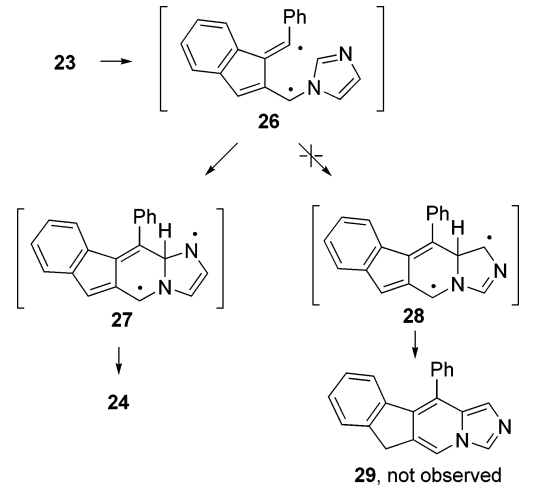


SCHEME 6



cyclized adduct **24** (**22**:**24** = 1:4) was produced in 98% combined yield (Scheme 5). Upon treatment of the mixture with potassium *tert*-butoxide, **22** was converted to **24** in essentially quantitative yield. The structure of **24** was established by X-ray structure analysis. A variety of imidazo[1,2-*a*]pyridine derivatives were also reported to exhibit useful pharmacological activities.[11]

Unlike biradicals **13**, a direct intramolecular radical–radical coupling involving a π bond of the imidazole substituent of biradical **26** could not be achieved (Scheme 6). Instead, a 6-*exo-trig* radical cyclization reaction involving the carbon–nitrogen double bond to form biradical **27** occurred and, after a prototropic rearrangement, produced **24**. This is reminiscent of what had been

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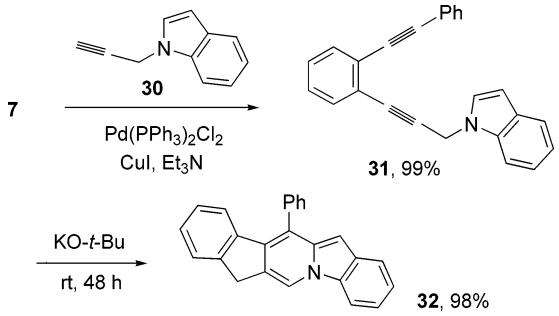
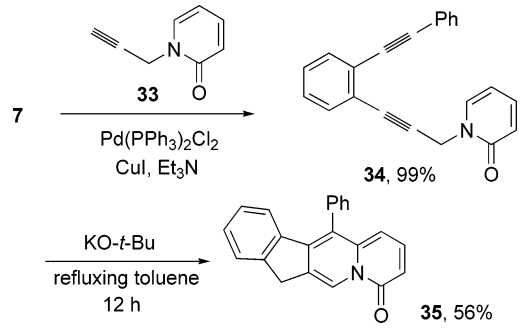
SCHEME 7



SCHEME 8



observed previously in a benzannulated enyne−allene system bearing a 1-pyrrolyl substituent at the allenic terminus.[4] It is also worth noting that because **29** was not observed the radical cyclization reaction did not appear to occur with the carbon−carbon double bond of the imidazole ring to give biradical **28**.

The palladium-catalyzed Sonogashira reaction between **7** and 1-(2-propynyl)-1*H*-indole (**30**)[12] was successful in producing **31** in excellent yield (Scheme 7). Treatment of **31** with potassium *tert*-butoxide at room temperature for 48 h produced the indeno-fused pyrido[1,2-*a*]indole **32** in 98% yield. It was reported that some pyrido[1,2-*a*]indole derivatives were unstable on exposure to air and decomposed to tarry materials in chloroform and methylene chloride solutions.[13] The ^{1}H NMR spectrum of **32** in $CDCl_3$, taken immediately after the solution was prepared, was found to be relatively clean. However, the solution gradually turned dark on standing at room temperature. Attempts to purify **32** by silica gel column chromatography also appeared to cause some decomposition.

Similarly, **34** was produced from coupling between **7** and 1-(2-propynyl)-2(1*H*)-pyridinone (**33**)[10] (Scheme 8). Treatment of **34** with potassium *tert*-butoxide under refluxing toluene for 12 h produced the indeno-fused 4*H*-quinolizin-4-one **35** in 56% yield. The structure of **35** was established by X-ray structure analysis. Development of new synthetic pathways to 4*H*-quinolizin-4-ones is an area of interest because these heteroaromatic compounds could serve as precursors to naturally occurring alkaloids possessing interesting biological activities.[14]

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Conclusions

Benzannulated enyne−allenes bearing a heteroaromatic substituent at the allenic terminus are excellent precursors of a variety of indeno-fused heteroaromatic ring systems. The use of the 1,3-prototropic rearrangement of the corresponding benzannulated enediynes to furnish enyne−allenes is especially attractive because of the simplicity of the procedure and ready availability of enediynes with diverse structural features. The resulting heteroaromatic compounds are of interest as potential candidates for pharmacological applications.

Experimental Section

Propargylic Alcohol 8. To a solution of **6** (480 mg, 1.87 mmol) in 20 mL of anhydrous diethyl ether at −78 °C was added dropwise 0.9 mL of a 2.5 M solution of *n*-butyllithium (2.25 mmol) in hexanes. After 1 h of stirring at −78 °C, a solution of 640 mg of iodine (2.52 mmol) in 30 mL of anhydrous diethyl ether was added dropwise via cannula. The reaction mixture was allowed to warm to room temperature before 15 mL of a 5% sodium thiosulfate solution was introduced. The organic layer was separated, washed with water, dried over sodium sulfate, and concentrated to give 477 mg of **7**. To a mixture of 477 mg of the crude iodide **7**, 55 mg (0.078 mmol) of $Pd(PPh_3)_2Cl_2$, and 29 mg (0.15 mmol) of copper(I) iodide in 25 mL of triethylamine under a nitrogen atmosphere was added dropwise via cannula a solution of 240 mg of propargyl alcohol (4.29 mmol) in 5 mL of triethylamine. The reaction mixture was stirred vigorously at 75 °C for 12 h before it was allowed to cool to room temperature. Then 50 mL of a saturated NH_4Cl solution and 50 mL of diethyl ether were introduced. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/diethyl ether:hexanes = 3:7) to give 286 mg (1.23 mmol, 66% overall yield) of **8** as a colorless liquid: IR 3334, 2217, 755, 690 cm^{-1}; ^{1}H δ 7.45−7.60 (4 H, m), 7.23−7.40 (5 H, m), 4.57 (2 H, d, J = 5.9 Hz), 1.75 (1 H, t, J = 6.2 Hz); ^{13}C δ 131.9, 131.7, 128.5, 128.4, 128.2, 127.9, 125.8, 125.0, 123.1, 93.5, 91.3, 88.0, 84.5, 51.8; MS *m/z* 232 (M^+), 231, 202, 101.

Propargyl Methanesulfonate 9. To a solution of **8** (322 mg, 1.39 mmol) and triethylamine (211 mg, 2.01 mmol) in 10 mL of methylene chloride at −50 °C under a nitrogen atmosphere was added dropwise methanesulfonyl chloride (207 mg, 1.81 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h before 5 mL of water was introduced. The organic layer was separated, and the aqueous layer was back extracted with methylene chloride. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/diethyl ether:hexanes = 3:7) to give 353 mg (1.14 mmol, 82%) of **9** as a colorless liquid: IR 2217, 1360 cm^{-1}; ^{1}H δ 7.48−7.61 (4 H, m), 7.28−7.42 (5 H, m), 5.18 (2 H, s), 3.12 (3 H, s); ^{13}C δ 132.3, 132.0, 131.7, 129.2, 128.8, 128.5, 128.1, 126.2, 123.5, 122.7, 93.9, 88.1, 87.5, 84.6, 58.5, 39.2.

Pyridinium Methanesulfonate 11a. To a solution of **9** (186 mg, 0.600 mmol) in 5 mL of methylene chloride was added dropwise a solution of 4-aminopyridine (56 mg, 0.60 mmol) in 5 mL of methylene chloride. The reaction mixture was stirred at room temperature for 24 h and concentrated. The residue was washed with diethyl ether to give 242 mg (0.599 mmol,

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100%) of **11a** as a colorless solid: mp 189−190 °C; IR 3330, 3120, 1197 cm^{-1}; ^1H δ 8.11 (2 H, s), 7.97 (2 H, d, J = 6.9 Hz), 7.22−7.52 (9 H, m), 6.96 (2 H, d, J = 6.9 Hz), 5.23 (2 H, s), 2.79 (3 H, s); ^{13}C δ 159.7, 140.9, 132.2, 132.0, 131.5, 129.2, 129.0, 128.6, 128.2, 126.0, 123.3, 122.4, 93.7, 88.0, 87.4, 83.6, 47.6, 39.7.

2-Amino-12-phenyl-7*H*-indeno[1,2-*b*]quinolizin-5-ium Methanesulfonate (15a). A solution of **11a** (45 mg, 0.11 mmol) and triethylamine (11 mg, 0.11 mmol) in 10 mL of ethanol was heated under reflux for 12 h. The solvent was removed and the residue was washed with diethyl ether to give 45 mg (0.11 mmol, 100%) of **15a** as a yellow solid: compound becomes black at 270 °C without melting; IR 3361, 1652, 1194 cm^{-1}; ^1H δ 8.67 (1 H, d, J = 7.4 Hz), 8.63 (1 H, s), 7.60−7.62 (3 H, m), 7.52 (1 H, d, J = 7.6 Hz), 7.28−7.39 (4 H, m), 7.05 (1 H, t, J = 7.6 Hz), 6.33−6.43 (2 H, m), 4.13 (2 H, s), 2.99 (2 H, s), 2.75 (3 H, s); ^{13}C (10% CD_3OD in $CDCl_3$) δ 153.9, 145.5, 145.1, 144.4, 136.9, 136.6, 133.4, 131.9, 131.0, 130.0, 129.4, 129.1, 128.5, 127.5, 126.7, 125.4, 125.2, 112.9, 101.6, 38.9, 33.8. Recrystallization of **15a** from a mixture of chloroform and methanol produced a crystal suitable for X-ray structure analysis.

Propargylic Alcohol 17a. To a mixture of 269 mg (1.04 mmol) of **16**, 22 mg (0.030 mmol) of $Pd(PPh_3)_2Cl_2$, and 11 mg (0.060 mmol) of copper(I) iodide in 20 mL of triethylamine under a nitrogen atmosphere was added dropwise via cannula a solution of 103 mg of 3,3-dimethyl-1-butyne (1.25 mmol) in 5 mL of triethylamine. The reaction mixture was stirred at room temperature for 12 h before 20 mL of a saturated NH_4Cl solution and 50 mL of diethyl ether were introduced. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/diethyl ether:hexanes = 1:2) to give 203 mg (0.96 mmol, 92%) of **17a** as a colorless liquid: IR 3331, 1025, 755 cm^{-1}; ^1H δ 7.33−7.42 (2 H, m), 7.14−7.25 (2 H, m), 4.52 (2 H, s), 1.97 (1 H, br), 1.33 (9 H, s); ^{13}C δ 131.6, 131.5, 128.1, 127.1, 126.6, 124.9, 103.0, 90.6, 84.6, 77.7, 51.6, 30.9, 28.1; MS m/z 212 (M^+), 197, 178, 165.

Propargyl Methanesulfonate 18a. To a solution of **17a** (68 mg, 0.32 mmol) and triethylamine (49 mg, 0.48 mmol) in 10 mL of methylene chloride at −50 °C under a nitrogen atmosphere was added dropwise methanesulfonyl chloride (48 mg, 0.42 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h before 5 mL of water was introduced. The organic layer was separated, and the aqueous layer was back extracted with methylene chloride. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/ethyl acetate:hexanes = 1:2) to give 76 mg (0.26 mmol, 81%) of **18a** as a colorless liquid: IR 2239, 1362, 1179 cm^{-1}; ^1H δ 7.35−7.44 (2 H, m), 7.28 (1 H, td, J = 7.6, 1.6 Hz), 7.21 (1 H, td, J = 7.4, 1.6 Hz), 5.11 (2 H, s), 3.16 (3 H, s), 1.34 (9 H, s); ^{13}C δ 132.0, 131.8, 129.0, 127.2, 127.1, 103.6, 88.3, 83.8, 77.3, 58.4, 39.2, 30.9, 28.1.

Pyridinium Methanesulfonate 19a. To a solution of **18a** (26 mg, 0.090 mmol) in 5 mL of methylene chloride was added dropwise a solution of 4-(dimethylamino)pyridine (11 mg, 0.090 mmol) in 5 mL of methylene chloride. The reaction mixture was stirred at room temperature for 24 h and concentrated. The residue was washed with diethyl ether to give 36 mg (0.087 mmol, 97%) of **19a** as a colorless solid: mp 127−128 °C; IR 2238, 1652, 1192 cm^{-1}; ^1H δ 8.56 (2 H, d, J = 7.4 Hz), 7.35−7.41 (2 H, m), 7.16−7.28 (2 H, m), 6.96 (2 H, d, J = 7.6 Hz), 5.44 (2 H, s), 3.22 (6 H, s), 2.75 (3 H, s), 1.25 (9 H, s); ^{13}C δ 156.5, 141.9, 132.3, 131.9, 129.0, 127.3, 126.8, 123.1, 108.1, 103.2, 88.6, 82.7, 47.7, 40.3, 39.5, 30.9, 28.1.

2-(Dimethylamino)-12-(1,1-dimethylethyl)-7*H*-indeno-[1,2-*b*]quinolizin-5-ium Chloride (21a). A solution of **19a** (26 mg, 0.063 mmol) and triethylamine (6 mg, 0.06 mmol) in 10 mL of ethanol was heated under reflux for 48 h. The solvent was removed in vacuo, and the residue was purified by column chromatography (neutral alumina/ethanol:methylene chloride = 1:10) to give 7 mg (0.020 mmol, 32%) of **21a** as a yellow solid: mp >360 °C; IR 1646, 1236, cm^{-1}; ^1H δ 10.14 (1 H, d, J = 7.6 Hz), 9.52 (1 H, s), 8.03 (1 H, dd, J = 6.9, 2.1 Hz), 7.60 (1 H, d, J = 6.6 Hz), 7.41−7.51 (2 H, m), 7.24 (1 H, dd, J = 7.6, 2.9 Hz), 7.11 (1 H, d, J = 2.6 Hz), 4.17 (2 H, s), 3.27 (6 H, s), 1.77 (9 H, s); ^{13}C δ 150.4, 148.1, 146.3, 143.5, 139.1, 138.6, 136.2, 133.7, 130.4, 129.7, 127.1, 126.7, 125.7, 109.1, 101.8, 40.1, 37.1, 34.7, 31.8. Recrystallization of **21a** from a mixture of dichloromethane and hexanes produced a crystal suitable for X-ray structure analysis.

11-Phenyl-6*H*-indeno[1,2-*d*]imidazo[1,2-*a*]pyridine (24). To a stirred mixture of imidazole (10 mg, 0.15 mmol), tetrabutylammonium iodide (27 mg, 0.073 mmol), and sodium hydroxide (50% aqueous solution, 0.52 mL) in toluene (0.41 mL) was added **9** (47 mg, 0.15 mmol). After 15 min at room temperature, toluene (0.5 mL) and water (0.5 mL) were added. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/diethyl ether:methanol = 100:3) to give 11 mg (0.039 mmol, 26%) of **24** as a pale yellow solid.

Alternatively, **24** was synthesized by treatment of a mixture of 15 mg (0.021 mmol) of $Pd(PPh_3)_2Cl_2$, 7.5 mg (0.039 mmol) of copper(I) iodide, and 200 mg (0.658 mmol) of **7** under a nitrogen atmosphere with 5 mL of DMF, 2 mL of triethylamine, and a solution of 85 mg (0.80 mmol) of **25** in 5 mL of DMF. The reaction mixture was heated at 100 °C for 48 h before it was allowed to cool to room temperature. The reaction mixture was then poured into a flask containing 40 mL of ethyl acetate and 5 mL of a saturated NH_4Cl solution. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/diethyl ether:methanol = 100:3) to give 181 mg (0.642 mmol, 98%) of a mixture of **22** and **24** (1:4) as a pale yellow solid. The ^1H NMR spectrum of the mixture exhibited a singlet at δ 5.02, attributable to the methylene hydrogens of **22**.

To a solution of 181 mg (0.642 mmol) of a mixture of **22** and **24** (1:4) in 5 mL of *tert*-butyl alcohol under a nitrogen atmosphere was added 0.64 mL of a 1.0 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol. The reaction mixture was stirred at room temperature for 12 h before 5 mL of water and 20 mL of ethyl acetate were introduced. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/diethyl ether:methanol = 100:3) to give 181 mg (0.642 mmol, 100%) of **24** as a pale yellow solid: mp 217−218 °C; IR 1301, 1234, 727, 699 cm^{-1}; ^1H δ 8.34 (1 H, s), 7.68 (1 H, d, J = 1.2 Hz), 7.47−7.64 (7 H, m), 7.29 (1 H, td, J = 7.4, 1.0 Hz), 7.08 (1 H, t, J = 7.9 Hz), 6.87 (1 H, d, J = 7.9 Hz), 4.07 (2 H, s); ^{13}C δ 145.7, 144.0, 139.3, 137.2, 134.9, 133.8, 129.6, 129.1, 128.6, 128.4, 128.1, 126.9, 125.1, 123.9, 120.0, 112.3, 33.6. Recrystallization of **24** from a mixture of dichloromethane and hexanes produced a crystal suitable for X-ray structure analysis.

Indole 31. To a mixture of 7 mg (0.010 mmol) of $Pd(PPh_3)_2Cl_2$, 4 mg (0.020 mmol) of copper(I) iodide, and 104 mg (0.34 mmol) of **7** under a nitrogen atmosphere was added in sequence 5 mL of DMF, 2 mL of triethylamine, and a solution of 58 mg (0.38 mmol) of **30** in 5 mL of DMF. After 4 h of stirring at room temperature, the reaction mixture was poured into a flask containing 40 mL of ethyl acetate and 5 mL of a saturated NH_4Cl solution. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes:methylene chloride = 95:5) to give 111 mg (0.335 mmol, 99%) of **31** as a white solid: mp 123−124 °C; IR 2216, 1494, 755, 742, 690 cm^{-1}; ^1H δ 7.67−7.71 (1 H, m), 7.48−7.58 (3 H, m), 7.39−7.46 (3 H, m), 7.28−7.38 (5 H, m), 7.14−7.26 (2 H, m), 6.52 (1 H, dd, J = 3.2, 0.8 Hz), 5.19 (2 H, s); ^{13}C δ 135.8, 132.1, 131.9,

131.7, 128.8, 128.4, 128.33, 128.28, 127.9, 127.3, 125.9, 124.7, 122.9, 121.8, 121.0, 119.7, 109.4, 101.8, 93.4, 87.9, 86.9, 84.0, 36.7.

12-Phenyl-7*H*-indeno[1′,2′:4,5]pyrido[1,2-*a*]indole (32). To a solution of 41 mg (0.12 mmol) of **31** in 5 mL of anhydrous toluene under a nitrogen atmosphere was added 0.1 mL of a 1.0 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol. After 48 h of stirring at room temperature, 5 mL of water and 20 mL of ethyl acetate were introduced. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes:methylene chloride = 95:5) to give 40 mg (0.12 mmol, 98%) of **32** as a pale yellow solid: mp 170−173 °C; IR 1459, 1323, 762, 724, 700 cm^{-1}; ^1H δ 8.44 (1 H, s), 7.90 (1 H, d, J = 7.6 Hz), 7.70 (1 H, d, J = 7.6 Hz),7.50−7.65 (5 H, m), 7.48 (1 H, d, J = 7.6 Hz), 7.22−7.35 (3 H, m), 7.05 (1 H, t, J = 7.5 Hz), 6.79 (1 H, d, J = 7.9 Hz), 6.31 (1 H, s), 4.09 (2 H, s); ^{13}C δ 144.4, 139.5, 138.5, 137.0, 134.5, 129.5, 129.1, 128.2, 127.8, 126.7, 125.2, 123.9, 123.7, 122.4, 120.3, 119.4, 118.1, 110.0, 91.9, 33.6.

2(1*H*)-Pyridinone 34. To a mixture of 12 mg (0.017 mmol) of $Pd(PPh_3)_2Cl_2$, 6.5 mg (0.034 mmol) of copper(I) iodide, and 171 mg (0.56 mmol) of **7** under a nitrogen atmosphere was added in sequence 5 mL of DMF, 2 mL of triethylamine, and a solution of 82 mg (0.62 mmol) of **33** in 5 mL of DMF. After 1 h of stirring at room temperature, the reaction mixture was poured into a flask containing 40 mL of ethyl acetate and 10 mL of a saturated NH_4Cl solution. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes:ethyl acetate = 1:1) to give 171 mg (0.553 mmol, 99%) of **34** as a colorless solid: mp 76−78 °C; IR 1660, 1588, 1538, 757 cm^{-1}; ^1H δ 7.91 (1 H, dt, J = 6.9, 0.9 Hz), 7.45−7.57 (4 H, m), 7.24−7.39 (6 H, m), 6.58 (1 H, dd, J = 9.2, 0.5 Hz), 5.93 (1 H, dt, J = 6.7, 0.8 Hz), 5.07 (2 H, s); ^{13}C δ 162.1, 139.7, 135.7, 132.0, 131.9, 131.7, 128.6, 128.4, 128.1, 125.9, 124.3, 122.8, 120.2, 106.4, 93.4, 87.8, 86.6, 85.6, 38.5.

4,7-Dihydro-12-phenylindeno[2,1-*g*]quinolizin-4-one (35). To a solution of 155 mg (0.502 mmol) of **34** in 30 mL of anhydrous toluene under a nitrogen atmosphere was added 0.5 mL of a 1.0 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol. The reaction mixture was heated under reflux for 12 h. After the reaction mixture was allowed to cool to room temperature, 20 mL of water and 50 mL of ethyl acetate were introduced. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/methanol:methylene chloride = 1:100) to give 87 mg (0.28 mmol, 56%) of **35** as a pale yellow solid: mp 205−207 °C; IR 1659, 1482 cm^{-1}; ^1H δ 9.44 (1 H, s), 7.59−7.72 (3 H, m), 7.50−7.59 (2 H, m), 7.32−7.43 (3 H, m), 7.08 (1 H, t, J = 7.9 Hz), 6.69 (1 H, d, J = 8.6 Hz), 6.46 (1 H, d, J = 7.9 Hz), 6.36 (1 H, d, J = 7.9 Hz), 4.18 (2 H, s); ^{13}C δ 145.5, 143.4, 141.9, 138.1, 137.0, 135.6, 130.5, 129.8, 129.7, 129.5, 129.0, 128.9, 127.3, 125.4, 124.8, 121.7, 107.4, 103.3, 34.4. Recrystallization of **35** from a mixture of dichloromethane and hexanes under a nitrogen atmosphere produced a crystal suitable for X-ray structure analysis.

Acknowledgment. K.K.W. thanks the Petroleum Research Fund (38169-AC1), administered by the American Chemical Society, and the National Science Foundation (CHE-0414063) for financial support. J.L.P. acknowledges the support (CHE-9120098) provided by the National Science Foundation for the acquisition of a Siemens P4 X-ray diffractometer.

Supporting Information Available: Experimental procedures and spectroscopic data for **11b**,**c**, **15b**,**c**, **18b**, **19b**, and **21b**; ^1H and ^{13}C NMR spectra of compounds **8**, **9**, **11a**−**c**, **15a**−**c**, **17a**, **18a**,**b**, **19a**,**b**, **21a**,**b**, **24**, **31**, **32**, **34**, and **35**; and ORTEP drawings of the crystal structures of **15a**−**c**, **21a**, **24**, and **35** in PDF format; and X-ray crystallographic data of **15a**−**c**, **21a**, **24**, and **35** as CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0505730