**Biradicals/Zwitterions from Enallene-Isonitriles. Formal [4 + 1] Cycloadditions
Leading to 11*H*-Indeno[1,2-*b*]quinolines and Related Compounds**

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7-(Dimethylamino)-11*H*-indolizino[1,2-*b*]quinolin-10-ium Chloride (**21**).

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. 2-Iodoaniline, 3-phenyl-1-propyne, Pd(PPh₃)₂Cl₂, copper(I) iodide, triethylamine, POCl₃, diisopropylamine, 1.0 M solution of potassium *t*-butoxide in *t*-butyl alcohol, 2-propyn-1-ol, methanesulfonyl chloride, 3-methoxy-1-propyne, 4-(dimethylamino)pyridine, and 4-methoxypyridine were purchased from chemical suppliers and were used without further purification. 2-Iodoformanilide²⁰ was prepared from 2-iodoaniline in 98% yield according to a reported procedure.²¹ 2-(3-Hydroxy-1-propynyl)formanilide (**7**)²² was prepared from 2-iodoformanilide in 96% yield according to the procedure described for **1**. Melting points were uncorrected. ¹H (270 MHz) and ¹³C (67.9 MHz) NMR spectra were recorded in CDCl₃ using CHCl₃ (¹H δ 7.26) and CDCl₃ (¹³C δ 77.00) as internal standards unless otherwise indicated.

2-(3-Phenyl-1-propynyl)formanilide (1). To a mixture of 0.028 g (0.040 mmol) of Pd(PPh₃)₂Cl₂, 0.015 g (0.080 mmol) of copper(I) iodide, and 0.494 g (2.00 mmol) of 2-iodoformanilide were added in sequence 2 mL of DMF, 10 mL of triethylamine, and a solution of 0.256 g (2.20 mmol) of 3-phenyl-1-propyne in 5 mL of triethylamine. After 12 h of stirring at room temperature, the reaction mixture was poured into a flask containing 40 mL of ethyl acetate and 20 mL of a saturated NH₄Cl solution. The organic layer was separated, washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography (silica gel, hexanes:ethyl acetate = 5:3) to give 0.470 g (1.99 mmol, 99%) of **1** as a brown yellow viscous liquid: IR (neat) 3298, 2193, 1689, 756, 698 cm⁻¹; ¹H δ 8.79 (0.3 H, d, *J* = 11.3 Hz), 8.45–8.38 (1.4 H, m), 7.97 (1 H, br s), 7.49–7.13 (7.3 H, m), 7.06 (1 H, t, *J* = 7.6 Hz), 3.91 (1.4 H, s), 3.89 (0.6 H, s); ¹³C δ 161.2, 158.8, 137.9, 137.6, 136.1, 135.8, 132.9, 131.8, 129.1, 128.8, 128.7, 128.6, 127.8, 127.7, 126.9, 126.8, 124.3, 123.7, 119.7, 115.7, 113.6, 112.3, 95.4, 95.3, 25.9, 25.8; MS *m/z* 235 (M⁺), 206, 130.

11*H*-Indeno[1,2-*b*]quinoline (6).^{16b,23} To a solution of 0.165 g (0.70 mmol) of **1** in 5 mL of dichloromethane at 0 °C was added 0.57 mL (4.08 mmol) of diisopropylamine followed by dropwise addition of 0.14 mL (1.48 mmol) of POCl₃. After 1 h of stirring at 0 °C, 5 mL of *t*-butyl alcohol was introduced. Dichloromethane was removed in vacuo before 3.5 mL of a 1.0 M solution of potassium *t*-butoxide in *t*-butyl alcohol was introduced. After 5 h at room temperature, 25 mL of water and 25 mL of ethyl acetate were added, and the organic layer was separated, washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography (silica gel, hexanes:ethyl acetate = 10:1) to give 0.079 g (0.363 mmol, 52%) of **6** as a white solid: mp: 165–166 °C (lit.²³ mp 167–169 °C); IR 1623, 1396, 769, 737 cm⁻¹; ¹H δ 8.31 (1 H, dd, *J* = 5.9, 2.0 Hz), 8.21 (1 H, d, *J* = 8.4 Hz), 8.11 (1 H, s), 7.78 (1 H, d, *J* = 8.2 Hz), 7.70 (1 H, td, *J* = 7.1, 1.6 Hz), 7.59–7.44 (4 H, m), 3.97 (2 H, s); ¹³C δ 161.6, 148.0, 145.0, 140.3, 134.5, 131.0, 129.9, 129.0, 128.7, 127.7, 127.4, 127.3, 125.5, 125.4, 121.9, 33.9; MS *m/z* 217 (M⁺), 189.

Mesylate 8. To a mixture of 0.875 g (5.00 mmol) of **7** and 1.04 mL of triethylamine in 40 mL of dichloromethane was added dropwise a solution of 0.745 g (6.50 mmol) of methanesulfonyl chloride in 30 mL of dichloromethane at –50 °C for 1 h. The reaction mixture was stirred for an additional 1 h before it was allowed to warm to room temperature. The reaction mixture was then poured into a flask containing 100 mL of water. The organic layer was separated, washed with water and brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography (silica gel, hexanes:ethyl acetate = 5:3) to afford **8** (0.944 g, 3.73 mmol, 75%) as a pale yellow liquid: IR (neat) 3350, 2231, 1694 cm⁻¹; ¹H δ 8.78 (0.3 H, d, *J* = 11.0 Hz), 8.46–8.38 (1.4 H, m), 8.32 (0.7 H, br), 8.17 (0.3 H, br), 7.46 (0.3 H, d, *J* = 7.9 Hz), 7.41–7.33 (1.7 H, m), 7.25 (0.3 H, d, *J* = 8 Hz), 7.13 (0.3 H, t, *J* = 7.6 Hz), 7.05 (0.7 H, td, *J* = 7.6, 1.1 Hz), 5.11 (2

H, s), 3.14 (3 H, s); ^{13}C δ 161.4, 159.4, 139.1, 133.1, 131.4, 130.7, 130.5, 124.4, 123.5, 120.0, 116.5, 111.4, 109.8, 88.1, 87.9, 84.6, 57.3, 56.9, 38.6; MS m/z 253 (M^+), 223.

2-(3-Chloro-1-propynyl)formanilide (9). A mixture of 0.116 g (0.460 mmol) of the mesylate **8**, 0.779 g (18.4 mmol) of anhydrous LiCl, and 10 mL of THF was stirred at room temperature for 4 h. To the reaction mixture were then added 20 mL of water and 20 mL of ethyl acetate. The organic layer was separated, washed with water, dried over Na_2SO_4 , and concentrated. The residue was purified by column chromatography (silica gel, hexanes:ethyl acetate = 5:3) to give 0.815 g (4.31 mmol, 91%) of **9** as a white solid: mp 72.0–72.5 °C; IR 3327, 2226, 1694 cm^{-1} ; ^1H δ 8.77 (0.33 H, d, J = 11.3 Hz), 8.47 (0.66 H, d, J = 1.6 Hz), 8.36 (0.66 H, d, J = 8.2 Hz), 8.07 (1 H, br), 7.45–7.28 (2 H, m), 7.19 (0.33 H, d, J = 7.9 Hz), 7.12–7.00 (1 H, m), 4.41 (1.33 H, s), 4.39 (0.66 H, s); ^{13}C δ 161.5, 159.1, 138.2, 138.0, 133.2, 132.1, 130.2, 124.4, 123.8, 120.0, 116.4, 112.2, 110.8, 91.1, 90.9, 81.2, 80.9, 30.8, 30.6; MS m/z 193 (M^+), 158, 130.

2-(3-Methoxy-1-propynyl)formanilide (10). The same procedure was repeated as described for **1** except that 0.066 g (0.095 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.036 g (0.189 mmol) of copper(I) iodide, 1.168 g (4.73 mmol) of 2-iodoformanilide, 5 mL of DMF, 10 mL of triethylamine, and a solution of 0.410 g (5.67 mmol) of 3-methoxy-1-propyne in 10 mL of triethylamine were used to give 0.815 g (4.31 mmol, 91%) of **10** as a yellow liquid: IR (neat) 3310, 1700, 758 cm^{-1} ; ^1H δ 8.76 (0.5 H, d, J = 11.4 Hz), 8.45 (0.66 H, s), 8.36 (0.66 H, d, J = 8.4 Hz), 8.04 (0.66 H, br s), 7.88 (0.33 H, br s), 7.45–7.27 (2 H, m), 7.19 (0.33 H, d, J = 7.9 Hz), 7.1–6.96 (1 H, m), 4.34 (1.33 H, s), 4.32 (0.66 H, s), 3.43 (1 H, s), 3.41 (2 H, s); ^{13}C δ 168.2, 161.3, 159.0, 139.0, 138.0, 137.8, 133.1, 132.1, 131.8, 129.8, 124.4, 123.7, 123.2, 119.9, 119.3, 116.1, 112.7, 111.3, 92.3, 92.2, 81.1, 80.9, 60.3, 60.2, 57.8, 57.7; MS m/z 189 (M^+), 160, 130.

2-Chloro-3-(chloromethyl)quinoline (14)²⁴ and 3-(Chloromethyl)-2,4-dichloroquinoline

(15). To a solution of 0.066 g (0.341 mmol) of **9** in 5 mL of THF at 0 °C were added in sequence 0.28 mL (2.05 mmol) of triethylamine, 0.072 g (1.70 mmol) of LiCl in 10 mL of THF, and 0.157 g (1.02 mmol) of POCl₃ in 5 mL of THF. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for an additional 2 h before 20 mL of water and 20 mL of ethyl acetate were introduced. The organic layer was separated, washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography (silica gel, hexanes:ethyl acetate = 10:1) to give 0.030 g (0.14 mmol, 41%) of **14** as a white solid and 0.0052 g (0.021 mmol, 6%) of **15** as a white solid. Compound **14**: recrystallization from hexanes afforded colorless needles; mp 112.5–113.5 °C (lit.²⁴ mp 111–113 °C); IR 1564, 780, 757, 722 cm⁻¹; ¹H δ 8.27 (1 H, s), 8.02 (1 H, d, *J* = 8.4 Hz), 7.83 (1 H, d, *J* = 8.2 Hz), 7.75 (1 H, ddd, *J* = 8.6, 7.1, 1.6 Hz), 7.58 (1 H, ddd, *J* = 8.2, 7.1, 1.1 Hz), 4.83 (2 H, s); ¹³C δ 149.6, 147.3, 138.7, 131.0, 129.0, 128.3, 127.6, 127.5, 127.1, 43.1; MS *m/z* 211 (*M*⁺, 215:213:211 = 1:6:9), 176, 140. The structure of **14** was established by X-ray structure analysis. Without the presence of LiCl, **14** was obtained in only 17% yield. Compound **15**: mp 109–110 °C; IR 1570, 1484, 770 cm⁻¹; ¹H δ 8.24 (1 H, dd, *J* = 8.4, 0.8 Hz), 8.03 (1 H, d, *J* = 8.4 Hz), 7.82 (1 H, ddd, *J* = 8.3, 7.1, 1.3 Hz), 7.69 (1 H, ddd, *J* = 8.4, 7.1, 1.1 Hz), 5.06 (2 H, s); ¹³C δ 150.4, 147.2, 145.0, 132.0, 128.9, 128.4, 127.3, 125.5, 124.9, 40.9; MS *m/z* 245 (*M*⁺), 210, 174.

2-Chloro-3-(methoxymethyl)quinoline (16).²⁵ The same procedure was repeated as described for **14** except that 0.182 g (0.960 mmol) of **10**, 0.77 mL (5.56 mmol) of triethylamine, 0.270 g (6.37 mmol) of LiCl in 10 mL of THF, and 0.157 g (1.023 mmol) of POCl₃ in 5 mL of THF were used to give 0.073 g (0.353 mmol, 37%, alumina, hexanes:ethyl acetate = 10:1) of **16**²⁵ as a colorless liquid: IR (neat) 1116, 780, 753 cm⁻¹; ¹H δ 8.25 (1 H, s), 8.01 (1 H, d, *J* = 8.4 Hz), 7.84

(1 H, dd, $J = 7.9, 1.1$ Hz), 7.71 (1 H, ddd, $J = 8.4, 6.9, 1.6$ Hz), 7.56 (1 H, ddd, $J = 8.1, 6.9, 1.1$ Hz), 4.67 (2 H, d, $J = 0.8$ Hz), 3.57 (3 H, s); ^{13}C δ 148.9, 146.8, 136.2, 130.2, 130.0, 128.1, 127.4, 127.2, 127.0, 70.9, 58.9; MS m/z 207 (M^+ , 209:207 = 1:3), 176, 140. Without the presence of LiCl, **16** was obtained in only 15% yield. A trace amount of a dichloride attributable to **17** was also detected by GC/MS. **17**: MS m/z 241 (M^+ , 245:243:241 = 1:6:9), 206, 176.

4-(Dimethylamino)pyridinium Mesylate 18. A mixture of 0.944 g (3.73 mmol) of the mesylate **8** and 0.456 g (3.73 mmol) of 4-(dimethylamino)pyridine in 30 mL of dichloromethane was stirred at room temperature for 12 h. The solution was then concentrated, and the residue was washed with 10 mL of ethyl acetate three times to give 1.389 g (3.70 mmol, 99%) of **18** as a viscous liquid: IR (neat) 3420, 2234, 1684, 1652 cm^{-1} ; ^1H δ 9.68 (1 H, s), 8.57 (1 H, s), 8.51 (2 H, d, $J = 6.9$ Hz), 8.26 (1 H, d, $J = 8.2$ Hz), 7.28 (1 H, d, $J = 8.2$ Hz), 7.22 (1 H, t, $J = 8.2$ Hz), 6.91 (1 H, t, $J = 7.6$ Hz), 6.71 (2 H, d, $J = 6.9$ Hz), 5.56 (2 H, s), 3.04 (6 H, s), 2.73 (3 H, s). ^{13}C δ 161.7, 156.1, 142.2, 140.0, 132.4, 130.1, 123.2, 120.3, 110.6, 107.7, 88.3, 83.4, 47.7, 40.0, 39.6.

The chloride **9** was also used for reaction with 4-(dimethylamino)pyridine. A mixture of 0.125 g (0.648 mmol) of the chloride **9**, 0.0792 g (0.648 mmol) of 4-(dimethylamino)pyridine in 10 mL of dichloromethane was stirred at room temperature for 48 h. The precipitate was filtered and washed with 10 mL of dichloromethane twice to yield 0.181 g (0.573 mmol, 88%) of the corresponding pyridinium chloride as a white solid: mp 147–148 $^{\circ}\text{C}$; IR (KBr) 3412, 2230, 1682, 1652 cm^{-1} ; ^1H δ 10.14 (1 H, s), 8.81 (2 H, d, $J = 7.1$ Hz), 8.76 (1 H, s), 8.33 (1 H, d, $J = 8.2$ Hz), 7.30 (1 H, d, $J = 7.4$ Hz), 7.27 (1 H, t, $J = 7.4$ Hz), 6.94 (1 H, t, $J = 7.4$ Hz), 6.74 (2 H, d, $J = 7.7$ Hz), 5.81 (2 H, s), 3.10 (6 H, s); ^{13}C δ 162.3, 156.4, 142.4, 140.7, 132.3, 130.4, 123.2, 120.6, 110.6, 107.7, 88.2, 84.7, 48.6, 40.2.

7-(Dimethylamino)-11*H*-indolizino[1,2-*b*]quinolin-10-ium Chloride (21). To a solution of 0.159 g (0.42 mmol) of **18** in 15 mL of dichloromethane at $-20\text{ }^{\circ}\text{C}$ was added 1.1 mL (7.65 mmol) of diisopropylamine followed by dropwise addition of a solution of 0.294 g (1.91 mmol) of POCl_3 in 15 mL of dichloromethane. After 0.5 h of stirring at $-20\text{ }^{\circ}\text{C}$, the reaction mixture was quenched with 3 mL of 95% ethanol and then concentrated. The residue was purified by column chromatography (neutral alumina, $\text{CH}_2\text{Cl}_2\text{:EtOH}$ (95%) = 20:1 to 10:1) to give 0.086 g (0.29 mmol, 68%) of **21** as a white solid. Recrystallization from a mixture of dichloromethane and absolute ethanol (19:1) afforded **21** as colorless needles: a sample of the crystals turns black at $270\text{ }^{\circ}\text{C}$ and melts at $318\text{ }^{\circ}\text{C}$; IR (KBr) 1652, 1579 cm^{-1} ; ^1H (6% CD_3OD in CDCl_3) δ 9.11 (1 H, d, $J = 7.1\text{ Hz}$), 8.54 (1 H, s), 8.16 (1 H, d, $J = 8.4\text{ Hz}$), 7.98 (1 H, d, $J = 8.2\text{ Hz}$), 7.84 (1 H, td, $J = 7.1, 1.3\text{ Hz}$), 7.68 (1 H, t, $J = 7.9\text{ Hz}$), 7.62 (1 H, m), 7.08 (1 H, dd, $J = 7.4, 2.9\text{ Hz}$), 5.93 (2 H, s), 3.37 (3 H, s), 3.33 (3 H, s); ^{13}C (6% CD_3OD in CDCl_3) δ 157.3, 150.1, 149.8, 148.5, 140.8, 132.1, 131.1, 129.3, 129.2, 128.7, 128.5, 108.4, 99.7, 56.1, 40.7, 40.5. The structure of **21** was established by X-ray structure analysis.

4-Methoxypyridinium Mesylate 22. A mixture of 0.390 g (1.54 mmol) of the mesylate **8** and 0.168 g (1.54 mmol) of 4-methoxypyridine in 20 mL of dichloromethane was stirred at room temperature for 14 h. The reaction was ca. 70% complete at this stage. The solvent was then removed in vacuo, and 10 mL of 1,2-dichloroethane was added to the residue. Then the mixture was heated under reflux for 3 h before it was allowed to cool to room temperature. The reaction mixture was concentrated, and the residue was washed with 10 mL of ethyl acetate three times to give 0.540 g (1.49 mmol, 97 %) of **22** as a viscous liquid: IR (neat) 3426, 2235, 1690 cm^{-1} ; ^1H δ 9.69 (1 H, s), 9.14 (2 H, d, $J = 7.1\text{ Hz}$), 8.56 (1 H, s), 8.25 (1 H, d, $J = 8.2\text{ Hz}$), 7.29–7.21 (4 H, m), 6.91 (1 H, t, $J = 7.7\text{ Hz}$), 5.89 (2 H, s), 3.92 (6 H, s), 2.71 (3 H, s); ^{13}C δ 171.1, 161.5, 146.2,

140.0, 132.5, 130.5, 123.3, 120.5, 113.2, 110.2, 87.2, 84.8, 57.7, 49.8, 39.6.

Indole 25. The same procedure was repeated as described for **21** except that 0.021 g (0.057 mmol) of **22**, 0.14 mL (1.02 mmol) of diisopropylamine, 0.039 g (0.25 mmol) of POCl₃, and 2 mL of *t*-butyl alcohol were used. The reaction mixture was stirred at room temperature for 7 h before it was concentrated in vacuo. The residue was washed with 2 mL of ethyl acetate three times to give 0.018 g (0.054 mmol, 95%) of **25** as a viscous liquid: IR (neat) 3403, 1643, 1520 cm⁻¹; ¹H δ 11.3 (1 H, br s), 8.88 (2 H, d, *J* = 7.4 Hz), 7.47 (1 H, d, *J* = 7.7 Hz), 7.39 (1 H, d, *J* = 8.4 Hz), 7.11 (1 H, td, *J* = 7.1, 1.1 Hz), 7.04–6.98 (3 H, m), 6.68 (1 H, s), 5.83 (2 H, s), 3.84 (3 H, s), 2.84 (3 H, s); ¹³C δ 170.6, 145.8, 137.3, 129.7, 127.4, 123.0, 120.7, 120.0, 113.0, 112.3, 104.6, 57.6, 55.9, 39.8. A similar result but with lower yield was obtained when the reaction was conducted in dichloromethane.

Indole 27. A mixture of 0.039 g (0.104 mmol) of **18**, 0.01 mL (0.099 mmol) of triethylamine and 1 mL of absolute ethanol was stirred at room temperature for 7 h. The reaction mixture was then concentrated in vacuo, and the residue was washed with 2 mL of ethyl acetate three times to give 0.035 g (0.095 mmol, 99%) of **27** as a viscous liquid: IR (neat) 3432, 1650, 1570 cm⁻¹; ¹H δ 8.31 (2 H, d, *J* = 7.4 Hz), 7.39 (1 H, d, *J* = 7.6 Hz), 7.36 (1 H, d, *J* = 7.9 Hz), 7.00 (1 H, td, *J* = 7.1, 1.1 Hz), 6.91 (1 H, t, *J* = 7.9 Hz), 6.55 (1 H, s), 6.29 (2 H, d, *J* = 7.4 Hz), 5.38 (2 H, s), 2.85 (3 H, s), 2.78 (6 H, s); ¹³C δ 155.2, 141.6, 136.5, 131.0, 127.2, 122.1, 120.2, 119.3, 111.7, 106.9, 103.0, 53.3, 39.6, 39.4.

2-(3-Phenyl-1-propynyl)aniline (28). The same procedure was repeated as described for **1** except that 0.014 g (0.02 mmol) of Pd(PPh₃)₂Cl₂, 0.008 g (0.04 mmol) of copper(I) iodide, 0.219 g (1.00 mmol) of 2-iodoaniline, 2 mL of DMF, 10 mL of triethylamine, and a solution of 0.128 g (1.10 mmol) of 3-phenyl-1-propyne in 5 mL of triethylamine were used to give 0.149 g (0.721

mmol, 72%) of **28** as a yellow liquid: IR (neat) 3473, 3375, 1612, 1492, 748, 701 cm^{-1} ; ^1H δ 7.48–7.25 (6 H, m), 7.14 (1 H, tt, $J = 7.7, 1.6$ Hz), 6.75–6.69 (2 H, m), 4.20 (2 H, br s), 3.93 (2 H, s); ^{13}C δ 147.8, 136.8, 132.1, 129.1, 128.5, 127.8, 126.6, 117.8, 114.1, 108.3, 92.8, 79.2, 25.9; MS m/z 207 (M^+), 206, 130.

2-(Phenylmethyl)indole (31).²⁶ To a solution of 0.0854 g (0.363 mmol) of **1** in 5 mL of *t*-butyl alcohol was added 1.8 mL of a 1.0 M solution of potassium *t*-butoxide in *t*-butyl alcohol. After 2 h of stirring at room temperature, 20 mL of water and 20 mL of ethyl acetate were added. The organic layer was then separated, washed with water, dried over Na_2SO_4 , and concentrated. The residue was purified by column chromatography (alumina, hexanes:ethyl acetate = 10:1) to give 0.045 g (0.216 mmol, 60%) of **31** as a white solid: mp: 84–85 °C (lit.²⁶ mp 85–86 °C); IR 3384, 1455, 748, 701 cm^{-1} ; ^1H δ 7.73 (1 H, br s), 7.62–7.59 (1 H, m), 7.41–7.25 (6 H, m), 7.20–7.10 (2 H, m), 6.38 (1 H, m, $J = 1.1$ Hz), 4.15 (2 H, s); ^{13}C δ 138.5, 137.7, 136.2, 128.8, 128.7, 126.7, 121.3, 120.0, 119.7, 110.4, 101.0, 34.6; MS m/z 207 (M^+), 206, 130.

The indole **31** was also obtained from **28**. A solution of 0.068 g (0.329 mmol) of **28**, 5 mL of *t*-butyl alcohol, and 1.6 mL of a 1.0 M solution of potassium *t*-butoxide in *t*-butyl alcohol was stirred at room temperature for 24 h to yield 0.053 g (0.254 mmol, 77 %) of **31**.

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