Iodine-Catalyzed One-Pot Synthesis of 2*H*-Pyrans by Domino Knoevenagel/6π-Electrocylization

Ene Jin Jung, Yong Rok Lee,* and Ha-Jin Lee†

*School of Chemical Engineering and Technology, Yeungnam University, Kyongsan 712-749, Korea. *E-mail: yrlee@yu.ac.kr*
†Korea Basic Science Institute, Jeonju Center, Jeonju 561-756, Korea
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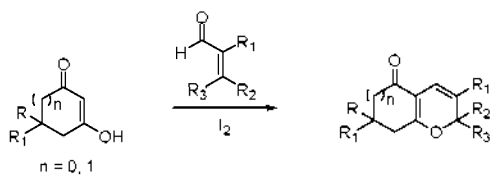
2*H*-Pyrans are important core units in a number of natural products[1] and also in photochromic materials.[2] The molecules bearing 2*H*-pyrans have a variety of interesting biological activities and potential medical applications.[3] 2*H*-Pyrans were prepared earlier using piperidine or BF_3-Et_2O as a catalyst.[4] We have been developed the methodologies for the synthesis of 2*H*-pyrans through indium(III) chloride- or EDDA-catalyzed formal [3+3] cycloaddition as a Lewis acid[5] or a Bronsted acid and base catalyst.[6] Later, novel approaches for the synthesis of 2*H*-pyrans were also developed by other groups using $TiCl_4$ and $In(OTf)_3$ Lewis acids as a catalyst[7] and phosphoric acid as a Bronsted acid catalyst.[8] Although several synthetic approaches for constructing 2*H*-pyrans derivatives have been reported by us[5,6] and other groups,[7,8] more simple and cost-effective approaches are still demand because of their importance.

Recently, iodine has been received considerable attention as an inexpensive and readily available catalyst for various organic reactions.[9] Iodine-catalyzed Suzuki-Miyaura coupling reaction,[10] delhydration of tertiary alcohols to alkenes,[11] esterifications,[12] transesterification,[13] acetylation,[14] protection[15] or deprotection[16] of acetals, *N*-Boc protection of amines,[17] and Michael addition[18] were described by many groups. Iodine-catalyzed and -mediated syntheses of benzyl alkyl ethers,[19] benzothiophenes,[20] bis-indols,[21] β-keto enol ethers,[22] chalcones,[23] quinolines,[24] and isoquinolines[25] were already reported. However, iodine-catalyzed formal [3+3] cycloadditon of 1,3-carbonyls to α,β-unsaturated aldehydes to afford 2*H*-pyrans has not been examined. We report herein a convenient and efficient one-pot synthesis of 2*H*-pyrans by a domino Knoevenagel/6π-electrocyclic reaction. As shown in Scheme 1, the crucial strategy that we have developed begins with reactions of cyclic 1,3-dicarbonyls to α,β-unsaturated aldehydes in the presence of iodine as an inexpensive and readily available mild catalyst.

Reaction of dimedone (**1**) with 3-methyl-2-butenal in the presence of 20 mol% of iodine using several solvents first investigated (Table 1). The best yield (94%) was obtained in refluxing methylene chloride for 24 h. Other solvents included in toluene (reflux, 24 h, 75%), DMF (100 °C, 24 h, 47%), and acetonitrile (reflux, 24 h, 40%). In this reaction, we found that iodine (94%) was the much superior catalyst for this cyclization than indium (III) chloride (53%),[5] phosphoric acid (73%),[8] and PPTS (59%).[8] The formation of **2** was readily confirmed by the observation of a carbonyl absorption of enone in the IR spectrum at 1651 cm^{-1} and the expected chemical shifts associated with two vinylic protons on 2*H*-pyranyl ring at 6.40 (10.0 Hz) and 5.24 (10.0 Hz) ppm in the ^1H NMR spectrum.

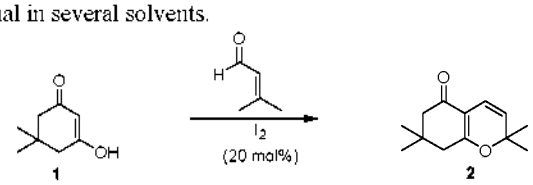


Scheme 1

Next, additional reactions of cyclic 1,3-dicarbonyls with 3-metyl-2-butenal and 1-cyclohexene-1-carboxaldehyde were attempted. The results are summarized in Figure 1. Reactions of 1,3-cyclopentanedione and 1,3-indandione with 3-methyl-2-butenal in the presence of 20 mol% of iodine afforded 2*H*-pyrans **3** and **4** in 66 and 84% yields, respectively. Treatment of 1,3-cyclohexanedione and 5-phenyl-1,3-cyclohexanedione with 3-methyl-2-butenal gave **5** and **6** in 70 and 90% yields, respectively. Similarly, reactions of 3-hydroxy-1*H*-phenalen-1-one, 4-hydroxycoumarin, and 4-hydroxy-6,7-dimethylcoumarin with 3-methyl-2-butenal afforded **7** ~ **9** in 90, 99, and 60% yields, respectively. Compounds **8** and **9** have been clearly shown to be angular by their spectral analysis and by comparison with reported data in the literature.[26] In addition, in the case of 1-cyclohexene-1-carboxaldehyde with a ring system, the expected pyrans **10** ~ **13** were also produced in 61, 70, 99, and 80% yields, respectively.

Although the exact mechanism of the reaction is still not clear, it is best described as shown in Scheme 2. Iodine first activates carbonyl oxygen of 3-methyl-2-butenal to give iodine-aldehyde

Table 1. Iodine-catalyzed reaction of dimedone (1) with 3-methyl-2-butenal in several solvents.



1 **2**

solvent	condition	yield (%)
CH_3CN	reflux, 24 h	40
DMF	100 °C, 24 h	47
toluene	reflux, 24 h	75
CH_2Cl_2	reflux, 24 h	94

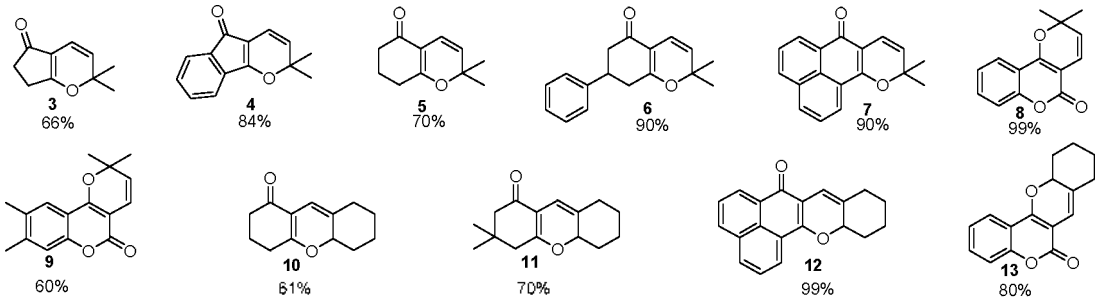
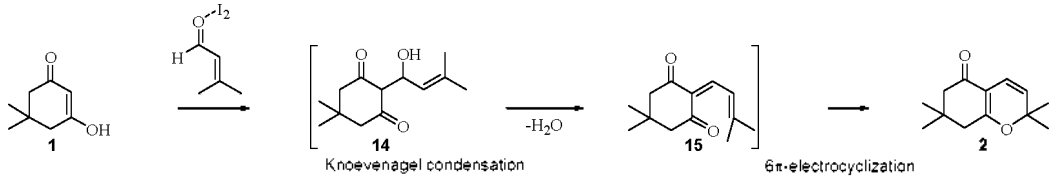
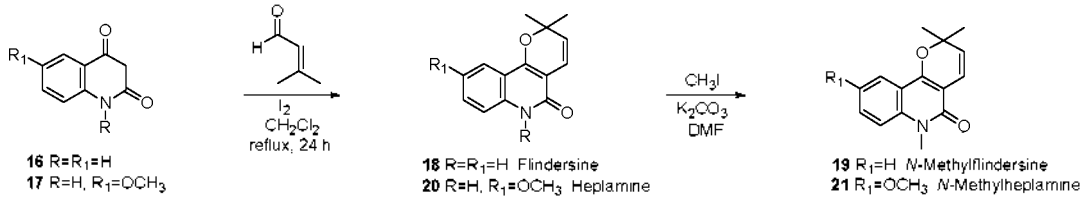


Figure 1. Synthesis of a variety of 2*H*-pyrans (**3-13**) by iodine-catlyzed reactions.



Scheme 2



Scheme 3

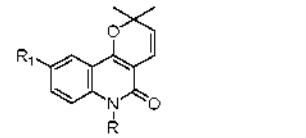


Figure 2

complex and thus increase the electrophilicity of carbonyl carbon of aldehyde.[27] The dimedone (**1**) then attacks activated aldehyde to yield intermediate **14**, which is dehydrated on heating to give other intermediate **15**.[27] The intermediate **15** further undergoes 6π-electrocyclization to give cycloadduct **2**.[7]

As an application of this methodology, the syntheses of pyranoquinolinone alkaloids such as flindersine (**18**), *N*-methylflindersine (**19**), haplamine (**20**), and *N*-methylhaplamine (**21**) were investigated. Flindersine (**18**) and *N*-methylflindersine (**19**) have been primarily isolated from Rutaceous plants, *Fagara heitzii*,[28] *Geijera balansae*,[29] *Haplophyllum saveolens*,[30] *Atalantia roxburghiana*,[31] *Micromelum minutum*,[32] and *Zanthoxylum coco*.[33] Haplamine (**20**) was isolated from *Haplophyllum acutifolium*,[34] *H. perforatum*,[35] and *H. sieversii*.[36] The extracts of this plant have shown to possess cytotoxic,[35] antifungal,[36] and antimicrobial[37] activities. *N*-Methylhaplamine (**21**) was isolated from *Agathosma barosmaefolia*.[38]

As shown in Scheme 3, reaction of 4-hydroxy-2(1*H*)-quinolone (**16**) with 3-methyl-2-butenal in the presence of 20 mol% of iodine at reflux in methylene chloride for 24 h gave flindersine (**18**) in 65% yield. Similarly, treatment of **17** with 3-methyl-2-butenal afforded heplamine (**20**) in 70% yield. Spectral data of synthetic **18** and **20** are in agreement with those reported in the literature.[36] Treatment of **18** and **20** with methyl iodide under K_2CO_3 in DMF gave *N*-methylflindersine (**19**) and *N*-methylheplamine (**21**) in 89 and 90% yields, respectively.[34,38]

In summary, iodine-catalyzed reactions of a variety of cyclic 1,3-dicarbonyls with 3-metyl-2-butenal and 1-cyclohexene-1-carboxaldehyde are carried out in refluxing methylene chloride to yield the 2*H*-pyrans. This methodology has been applied to the synthesis of biologically interesting and naturally occurring pyranoquinolinone alkaloids such as flindersine (**18**), *N*-methylflindersine (**19**), haplamine (**20**), and *N*-methylhaplamine (**21**) in moderate yields.

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Experimental

General Procedure for the Synthesis of 2*H*-Pyrans. To a solution of cyclic 1,3-dicarbonyl compound (1.0 mmol) with 3-metyl-2-butenal or 1-cyclohexene-1-carboxaldehyde (2.0 mmol) in methlene chloride (10 mL) was added iodine (51 mg, 0.2 mmol) at room temperature. The reaction mixture was refluxed for 24 h and then cooled to room temperature. Evaporation of solvent

and purification by column chromatography on silica gel give products.

2,2,7,7-Tetramethyl-2,6,7,8-tetrahydrochromen-5-one (2): Yield 94%; mp 38 ~ 40 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (1H, d, J = 9.9 Hz), 5.19 (1H, d, J = 9.9 Hz), 2.23 (2H, s), 2.21 (2H, s), 1.35 (6H, s), 1.03 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 170.1, 122.7, 115.8, 109.6, 79.8, 50.4, 42.5, 32.2, 28.4, 28.3; IR (KBr) 2959, 2870, 1645, 1633, 1586, 1454, 1416, 1351, 1324, 1299, 1251, 1206, 1131, 1090, 1047, 976, 928 cm^{-1}; HRMS m/z (M^-) calcd for $C_{13}H_{18}O_2$: 206.1307. Found: 206.1310.

2,2-Dimethyl-6,7-dihydro-2*H*-cypenta[*b*]pyran-5-one (3): Yield 66%; mp 145 ~ 147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.37 (1H, d, J = 9.9 Hz), 5.20 (1H, d, J = 9.9 Hz), 2.34 (2H, t, J = 6.9 Hz), 1.93 (2H, t, J = 6.9 Hz), 1.36 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 170.1, 122.7, 115.8, 109.6, 79.8, 34.4, 28.3, 27.8; IR (KBr) 2944, 1643, 1587, 1460, 1414, 1338, 1305, 1268, 1188, 1137, 1090, 1017, 847, 798 cm^{-1}; HRMS m/z (M^+) calcd for $C_{10}H_{12}O_2$: 164.0837. Found: 164.0837.

2,2-Dimethyl-2*H*-indeno[1,2-*b*]pyran-5-one4 (4): Yield 84 %; mp 158 ~ 159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (1H, d, J = 7.8 Hz), δ 7.45 (1H, t, J = 7.8 Hz), 7.24-7.17 (2H, m), 6.37 (1H, d, J = 10.0 Hz), 5.20 (1H, d, J = 10.0 Hz), 1.37 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.0, 160.9, 158.8, 153.1, 132.0, 126.1, 123.9, 122.7, 116.7, 115.6, 100.2, 80.5, 28.5; IR (KBr) 3064, 2926, 1725, 1640, 1458, 1364, 1284, 1215, 1159, 1114, 1037, 908 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{12}O_2$: 212.0837. Found: 212.0837.

2,2-Dimethyl-2,6,7,8-tetrahydrochromen-5-one (5): Yield 70%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (1H, d, J = 10.0 Hz), 5.21 (1H, d, J = 10.0 Hz), 2.38-2.33 (2H, m), 1.95-1.91 (2H, m), 1.36 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.8, 171.5, 122.9, 115.8, 110.6, 79.7, 36.4, 28.6, 28.4, 20.6; IR (neat) 2926, 1645, 1611, 1455, 1399, 1375, 1266, 1188, 1130, 1010, 905 cm^{-1}; HRMS m/z (M^-) calcd for $C_{11}H_{14}O_2$: 178.0994. Found: 178.0991.

2,2-Dimethyl-7-phenyl-2,6,7,8-tetrahydro-chromen-5-one (6): Yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$) 7.35- 7.30 (2H, m), 7.26-7.21 (3H, m), 6.43 (1H, d, J = 9.9 Hz), 5.26 (1H, J = 9.9 Hz), 3.39-3.28 (1H, m), 2.65-2.57 (4H, m), 1.44 (3H, s), 1.37 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 170.7, 142.6, 128.7, 126.9, 126.6, 123.0, 115.0, 110.2, 80.2, 43.5, 38.7, 36.1, 28.6, 28.2; IR (neat) 3487, 3056, 2971, 2925, 1723, 1644, 1590, 1454, 1415, 1330, 1252, 1203, 1142, 1090, 1048, 919, 887, 819, 673, 604 cm^{-1}; HRMS m/z (M^-) calcd for $C_{17}H_{18}O_2$: 254.1307. Found: 254.1304.

10,10-Dimethyl-10*H*-11-oxa-benzo[de]anthracen-7-one (7): Yield 90%; mp 87 ~ 88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (1H, dd, J = 7.3, 1.2 Hz), 8.21 (1H, dd, J = 7.3, 1.2 Hz), 8.10 (1H, dd, J = 8.1, 1.1 Hz), 8.01 (1H, dd, J = 8.1, 1.1 Hz), 7.69 (1H, dd, J = 8.1, 7.3 Hz), 7.60 (1H, dd, J = 8.1, 7.3 Hz), 6.83 (1H, d, J = 9.9 Hz), 5.56 (1H, d, J = 9.9 Hz), 1.54 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.3, 159.3, 134.0, 132.2, 131.7, 129.7, 128.5, 126.7, 126.2, 126.1, 125.8, 124.3, 117.0, 112.0, 79.3, 28.3; IR (KBr) 2975, 2927, 1632, 1578, 1506, 1458, 1425, 1387, 1331, 1259, 1152, 1127, 898 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{14}O_2$: 262.0994. Found: 262.0995.

2,2-Dimethyl-2*H*-pyrano[3,2-*c*]chromen-5-one (8): Yield 99%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (1H, dd, J = 7.8, 1.6 Hz), 7.50 (1H, m), 7.30-7.23 (2H, m), 6.53 (1H, d, J = 9.9 Hz), 5.52 (1H, d, J = 9.9 Hz), 1.47 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 158.8, 153.1, 132.0, 126.1, 123.9, 122.7, 116.7, 115.5, 100.2, 80.5, 28.5; IR (neat) 3073, 2978, 2930, 1715, 1642, 1566, 1493, 1458, 1416, 1362, 1327, 1281, 1217, 1192, 1157, 1115, 1038, 992, 909 cm^{-1}; HRMS m/z (M^-) calcd for $C_{14}H_{12}O_3$: 228.0786. Found: 228.0785.

2,2,8,9-Tetramethyl-2*H*-pyrano[3,2-*c*]chromen-5-one (9): Yield 60%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (1H, s), 7.03 (1H, s), 6.50 (1H, d, J = 10.0 Hz), 5.46 (1H, d, J = 10.0 Hz), 2.30 (3H, s), 2.29 (3H, s), 1.51 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.1, 151.6, 142.2, 132.8, 125.5, 122.6, 117.2, 116.9, 113.0, 99.4, 80.3, 28.5, 20.3, 19.2; IR (neat) 2924, 1716, 1641, 1573, 1491, 1424, 1359, 1279, 1209, 1125, 1042, 1018, 820 cm^{-1}; HRMS m/z (M^-) calcd for $C_{16}H_{16}O_3$: 256.1099. Found: 256.1099.

2,3,4,5,6,7,8,10a-Octahydro-xanthen-1-one (10): Yield 61 %; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (1H, s), 4.91 (1H, dd, J = 10.9, 4.9 Hz), 2.35-2.30 (6H, m), 1.95-1.24 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.8, 171.5, 141.3, 122.9, 115.8, 79.7, 36.6, 36.4, 33.3, 31.0, 28.6, 28.4, 20.6; IR (neat) 2942, 1645, 1518, 1404, 1171, 1073, 1019, 939, 869 cm^{-1}; HRMS m/z (M^+) calcd for $C_{13}H_{16}O_2$: 204.1150. Found: 204.1150.

3,3-Dimethyl-2,3,4,5,6,7,8,10a-octahydro-xanthen-1-one (11): Reaction of 5.5-dimethyl-1.3-cyclohexanedione (140 mg, 1.0 mmol) with 1-cylohexene-1-carboxaldehyde (220 mg, 2.0 mmol) afforded **11** (163 mg, 70%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (1H, s), 4.92 (1H, dd, J = 10.9, 4.9 Hz), 2.37-2.05 (6H, m), 1.95-1.20 (6H, m), 1.04 (3H, s), 1.03 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 170.1, 122.7, 115.8, 109.6, 79.8, 50.4, 42.5, 35.1, 33.0, 32.2, 28.3, 26.8, 24.3; IR (neat) 2955, 1644, 1630, 1617, 1404, 1258, 1231, 1146, 1074, 1041, 1008, 945 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{20}O_2$: 232.1463. Found: 232.1464.

10,11,12,12a-Tetrahydro-9*H*-13-oxa-benzo[de]naphthacen-7-one (12): Yield 99%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (1H, d, J = 7.3 Hz), 8.13 (1H, d, J = 7.3 Hz), 8.07 (1H, d, J = 8.1 Hz), 7.97 (1H, d, J = 8.1 Hz), 7.67 (1H, dd, J = 8.1, 7.3 Hz), 7.57 (1H, dd, J = 8.1, 7.3 Hz), 6.51 (1H, s), 5.17 (1H, dd, J = 11.1, 5.1 Hz), 2.51-1.34 (8H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 180.7, 158.3, 133.7, 133.6, 131.6, 131.3, 129.3, 128.1, 126.3, 126.0, 125.9, 125.6, 123.5, 111.1, 109.9, 79.1, 35.1, 33.0, 26.8, 24.4; IR (neat) 3060, 2933, 2857, 1632, 1577, 1422, 1383, 1296, 1198, 1026, 941, 861 cm^{-1}; HRMS m/z (M^-) calcd for $C_{20}H_{16}O_2$: 288.1150. Found: 288.1147.

9,10,11,11a-Tetrahydro-8*H*-chromeno[4,3-*b*]chromen-6-one (13): Yield 80%; mp 135 ~ 137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (1H, d, J = 7.5 Hz), 7.43 (1H, t, J = 7.5 Hz), 7.26-7.17 (2H, m), 6.17 (1H, s), 5.18 (1H, dd, J = 11.1, 5.1 Hz), 2.47-1.33 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 157.5, 152.5, 134.5, 131.3, 133.6, 122.2, 116.3, 114.9, 109.4, 99.5, 79.8, 35.1, 33.0, 26.8, 24.3; IR (KBr) 2933, 2858, 1697, 1609, 1488, 1412, 1326, 1272, 1186, 1048, 990, 755 cm^{-1}; HRMS m/z (M^-) calcd for $C_{16}H_{14}O_3$: 254.0943. Found: 254.0942.

Flindersine (18):[35] Reaction of 4-hydroxy-2(1*H*)-quinolone (161 mg, 1.0 mmol) with 3-methyl-2-butenal (168 mg, 2.0 mmol) afforded **18** (148 mg, 65%) as a solid: mp 195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.5 (1H, s), 7.87 (1H, d, J = 8.1 Hz), 7.46 (1H, dd, J = 8.2, 7.4 Hz), 7.31 (1H, d, J = 8.2 Hz), 7.17 (1H, dd, J = 8.1, 7.4 Hz), 6.75 (1H, d, J = 9.9 Hz), 5.54 (1H, d, J = 9.9

Hz), 1.53 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 157.5, 137.9, 130.9, 126.2, 122.5, 122.2, 117.0, 116.2, 115.3, 105.5, 79.2, 28.3; IR (KBr) 3152, 2975, 1651, 1630, 1599, 1499, 1433, 1411, 1361, 1278, 1132, 872 cm^{-1}.

***N*-Methylflindersine (19):**[35] Methyl iodide (85 mg, 0.6 mmol) in DMF (1 mL) was added to a solution of **18** (114 mg, 0.5 mmol) and potassium carbonate (345 mg, 2.5 mmol) in DMF (10 mL). The reaction mixture was stirred at room temperature for 10 h. The solvent was evaporated under reduced pressure. The residue was treated with water (30 mL), acidified with 2 N HCl solution (20 mL), and extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **19** (107 mg, 89%) as a solid: mp 80 ~ 81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (1H, d, J = 8.0 Hz), δ 7.51 (1H, dd, J = 8.3, 7.3 Hz), 7.28 (1H, d, J = 8.3 Hz), δ 7.19 (1H, dd, J = 8.0, 7.3 Hz), 6.73 (1H, d, J = 10.0 Hz), 5.51 (1H, d, J = 10.0 Hz), 3.67 (3H, s), 1.49 (6H, s); IR (KBr) 2976, 1645, 1505, 1464, 1418, 1360, 1325, 1211, 1154, 1123, 1092, 1044, 1005, 987, 895 cm^{-1}.

Heplamine (20): Reaction of 6-methoxyl-1*H*-quinoline-2,4-dione (190 mg, 1.0 mmol) with 3-methyl-2-butenal (168 mg, 2.0 mmol) afforded **20** (179 mg, 70%) as a solid: mp 202 ~ 203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.89 (1H, s), 7.33 (1H, d, J = 9.0 Hz), 7.25 (1H, d, J= 3.0 Hz), 7.10 (1H, dd, J = 9.0, 3.0 Hz), 6.75 (1H, d, J = 10.0 Hz), 5.54 (1H, d, J = 10.0 Hz), 3.86 (3H, s), 1.23 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 156.8, 154.9, 132.7, 126.3, 120.6, 117.6, 117.2, 115.6, 105.8, 103.2, 79.0, 55.6, 28.3; IR (KBr) 3448, 2927, 2846, 2353, 1660, 1498, 1347, 1220, 1122, 1033, 905, 833, 717 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{15}NO_3$: 257.1052. Found: 257.1054.

***N*-Methylheplamine (21):** Methyl iodide (85 mg, 0.6 mmol) in DMF (1.0 mL) was added to a solution of compound **20** (113 mg, 0.5 mmol) and potassium carbonate (345 mg, 2.5 mmol) in DMF (10 mL). The reaction mixture was stirred at room temperature for 10 h. The solvent was evaporated under reduced pressure. The residue was treated with water (30 mL), acidified with 2 N HCl solution (20 mL), and extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **21** (108 mg, 90%) as a solid: mp 136 ~ 138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (1H, d, J = 3.0 Hz), 7.25 (1H, d, J = 9.0 Hz), 7.15 (1H, dd, J = 9.0, 3.0 Hz), 6.76 (1H, d, J = 9.9 Hz), 5.53 (1H, d, J = 9.9 Hz), 3.89 (3H, s), 3.68 (3H, s), 1.15 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 154.5, 154.4, 133.8, 126.3, 119.4, 117.9, 116.5, 115.3, 106.1, 104.5, 78.6, 55.5, 29.2, 28.0; IR (KBr) 3461, 2963, 1624, 1509, 1459, 1327, 1216, 1035, 817, 727 cm^{-1}; HRMS *m/z* (M^-) calcd for $C_{16}H_{17}NO_3$: 271.1208. Found: 271.1205.

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