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A Convenient Synthesis of 7-Halo-1-indanones and 8-Halo-1-tetralones

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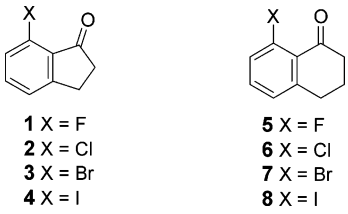
Abstract: A regioselective oxidation of *N*-indan-4-yl-acetamide or *N*-(5,6,7,8-tetrahydronaphthalen-1-yl)acetamide with potassium permanganate followed by acidic hydrolysis gave 7-aminoindan-1-one or 8-aminotetral-1-one in good yield. The amino ketones were converted to the corresponding 7-haloindanone or the 8-halotetralone. Another method to prepare 7-haloindan-1-ones was completed by a cyclization of 3-chloro-1-(2-halophenyl)propan-1-one under Friedel−Crafts conditions to produce the product in gram quantity.

The efficient preparation of functionalized cyclic structures is important in the search for bioactive small molecules. In the course of an ongoing project, we desired to synthesize indans and tetralins with substitution at the 7- or 8-position, respectively. In particular, we sought a concise, flexible method to produce 7-haloindanones and 8-halotetralones without the need for challenging conditions or difficult purifications. We wanted to include the fluoro group in our study due to its interesting properties and prominent use in pharmaceuticals and agrochemicals.[1] In this paper we report a general, divergent method for the convenient preparation of the entire family of 7-haloindanones and 8-halotetralones, and a linear 3-step synthesis of 7-haloindanones.

We were surprised to find no efficient method to prepare these particular compounds (Figure 1) and the preparation of most of these compounds has not been reported to date. The literature contains a few procedures for the preparation of the 7-chloroindanone (**2**)[2,3] and 7-bromoindanone (**3**)[4] but no accounts could be found for the preparation of the fluoro (**1**) or iodo (**4**) analogues. As for the 8-halotetralones, we found only the chloro analogue in the literature.[5] The known procedures for the preparation of these compounds are lengthy, not general, and relatively low yield. Published methods for the preparation of this family of compounds are summarized below. The classical cyclization with the Freidel−Crafts reaction gives the undesired 5-substituted product due to several factors as discussed in the literature.[6] For example, the cyclization of 3-(3-acetylaminophenyl)propionyl chloride with $AlCl_3$ gives predominately the 5-acetomido-1-indanone in a 40:1 ratio with the 7-substituted compound **13**.[7] Cyclization of 3-(3-bromophenyl)propionyl chloride under Friedel−Crafts conditions gave a 4.4:1 mixture of the 5-bromo- vs 7-bromoindanone (**3**).[4] A blocking/deblocking strategy is required to enforce the proper regiochemical outcome under these conditions. This protection/deprotection scheme requires at least 8 steps and is of moderate yield.[3,4a] Alternatively, one could employ a metalation tactic. The directed ortho-metalation[5] can be technically challenging on a preparative scale and purification of the product can be problematic. These difficulties are pronounced in the preparation of the fluorinated compounds. Another method that has been used is the acid-catalyzed cyclization of 1-(2-chlorophenyl)propenone in concentrated H_2SO_4. This reaction yields the 7-chloroindanone in a modest yield (14%).[2] The difficulties of these methods have limited the use of these desirable materials in structure−activity relationship studies and synthetic chemistry in general.



1 X = F
2 X = Cl
3 X = Br
4 X = I

5 X = F
6 X = Cl
7 X = Br
8 X = I

FIGURE 1. 7-Haloindanone and 8-halotetralone.

We directed our effort to find a common intermediate that could be used to generate any of the halogenated target compounds. Our preparation of this family of compounds took the following route. Indan-4-ylamine (**9**) was converted to *N*-indan-4-yl-acetamide (**11**) with acetic anhydride, which proved to be superior to the use of acetyl chloride/NEt_3.[8] The regioselective oxidation[9,10] of **11** with $KMnO_4$ in acetone/H_2O in the presence of $MgSO_4$ gives *N*-(3-oxo-indan-4-yl)acetamide (**13**) in 75% yield. None of the 4-amidoindanone was observed by ^1H NMR. This control is very useful and compliments the analogous oxidation of 4-nitroindan that produces 4-nitroindan-1-one as the major product.[11] This transformation was found to be very similar to the method for the oxidation of *N*-(5,6,7,8-tetrahydro-1-naphthyl)acetamide **12** as described in the literature.[9] Acidic hydrolysis of **13**

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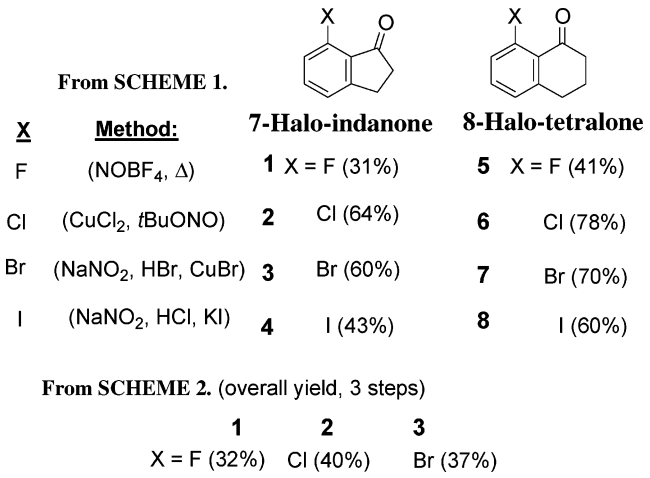
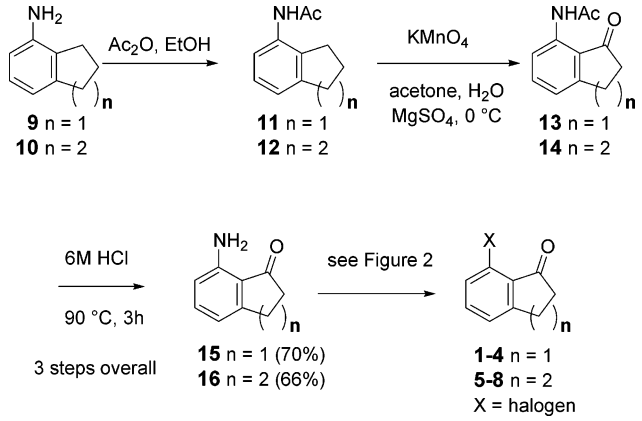
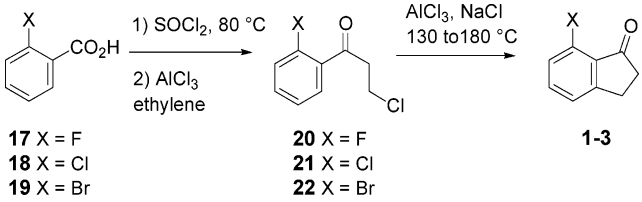


FIGURE 2. Summary of methods and yields.

SCHEME 1. A general and divergent regioselective oxidation method



SCHEME 2. A cyclization method for a linear synthesis of 7-haloindanones



gave 7-aminoindanone (**15**) in good yield. Amine **15** was employed in the synthesis[12,13] of the 7-haloindanones **1**−**4** (Figure 2). The same route that produced the amino indanone (**15**) was used for the preparation of aminotetralone (**16**).[9] The 8-halotetralones **5**−**8** were also prepared in a similar fashion (see Figure 2).

A complimentary route to efficiently synthesize 7-haloindanones (Scheme 2) was adapted from a method for the synthesis of 1-indanones.[14,15] Homologation of 2-halobenzoic acid (**17**−**19**) was followed by cyclization to the indanone product. The cyclization method with Freidel−Crafts conditions of 1-(2-halo-phenyl)-3-chloro-propan-1-one (**20**−**22**) is particularly useful in the preparation of gram quantities of haloindanones (**1**−**3**). It should be noted that this method is not applicable to formation of the tetralone system because the reaction of 1-(2-halophenyl)-4-chlorobutan-1-one readily forms the more favored 3-methylindanone.[14]

In regard of Figure 2, the successful preparation of the fluoro compounds **1** and **5** compared favorably with previously reported yields for fluorinations of this type. The limitation in yield (30−40%) of this particular Schiemann reaction is due to the presence and position of the carbonyl group as documented in the literature.[16] Conversion of the amines to the 7- or 8-chloro compounds **2** (64%) or **6** (78%) was accomplished in good yield with *t*BuONO and $CuCl_2$. During bromination, use of the method with *t*BuONO and $CuBr_2$ gave a 2:1 mixture of 4,7-dibromoindan-1-one and the desired compound **3**. Conversion of the 7- or 8-amino compound to the 7- or 8-bromo compound was accomplished with a Sandmeyer-type reaction, using $NaNO_2$, HBr, and CuBr: **3** (60% yield) and **7** (70% yield).[17] This method was also used to form the iodo compounds **4** (43%) and **8** (60%).

In conclusion, the facile preparation of 7-substituted indanones and 8-substituted tetralones is of interest to synthetic and medicinal chemists. This observation is illustrated by the variety of synthetic approaches appearing in several papers[2,3,6] and patents.[4,5a] In this paper, we have reported the regioselective oxidation of 7-amidoindans as applied to the preparation of 7-haloindanone. Also, we have included practical laboratory preparations of the 7-haloindanones and 8-halotetralones. We can now add these high-value intermediates to the synthetic chemist's toolbox.

Experimental Section

Preparation of 7-Aminoindan-1-one (15): *N*-Indan-4-yl-acetamide (11). Indan-4-ylamine (**9**; 13.5 g, 101 mmol) in EtOH (55 mL, anhydrous) was added to acetic anhydride (19 mL, 201 mmol) in EtOH (300 mL) at 0 °C.[8] The mixture was stirred for 16 h at room temperature. The solvent was removed under vacuum on a rotary evaporator to yield *N*-indan-4-yl-acetamide (**11**) as a white solid (~17 g) that was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 1H), 7.26 (br s, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 2.93 (t, J = 8.0 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H), 2.16 (s, 3H), 2.10−2.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 145.5, 134.8, 134.1, 127.3, 121.1, 119.6, 33.4, 30.4, 25.0, 24.5; HRMS *m*/*z* calcd for $C_{11}H_{13}NO$ 175.0997, obsd 175.1006.

***N*-(3-Oxo-indan-4-yl)acetamide (13).** *N*-Indan-4-yl-acetamide (**11**; ~17 g, 97 mmol) in acetone (600 mL) and 15% aqueous $MgSO_4$ (16 g in 90 mL of H_2O) at room temperature was treated with $KMnO_4$ (46 g, 228 mmol). The mixture was allowed to stir at room temperature for 16 h. The mixture was filtered through Celite and the solids were washed with $CHCl_3$ and water. The

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mother liquor was separated and the aqueous layer was extracted several times with $CHCl_3$. The organic fractions were washed with brine and dried over $MgSO_4$, filtered, and evaporated to give *N*-(3-oxo-indan-4-yl)acetamide (**13**) as a white solid, 14 g (73%, 2 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.43 (br s, 1H), 8.40 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.11 (dd, J = 7.5, 0.9 Hz, 1H), 3.12−3.09 (m, 2H), 2.74−2.70 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.2, 169.4, 155.8, 138.8, 136.9, 122.7, 120.5, 116.6, 36.4, 25.4, 25.1; HRMS *m*/*z* calcd for $C_{11}H_{11}NO_2$ 189.0790, obsd 189.0798. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.94; H, 5.84; N, 7.37.

7-Aminoindan-1-one (15). *N*-(3-Oxo-indan-4-yl)acetamide (**13**; 14 g, 74 mmol) in 6 N HCl (200 mL) was heated at 90 °C for 3 h. The mixture was cooled to room temperature and Na_2CO_3 was added in small portions followed by addition of 2 M NaOH until the mixture was at pH 8. The aqueous layer was extracted with EtOAc and the organic fractions were combined, washed with brine, dried, filtered, and concentrated to give 7-aminoindan-1-one (**15**) as a yellow solid, 9.95 g (91%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (t, J = 7.2 Hz, 1H), 6.65 (d, J = 7.2 Hz, 1H), 6.44 (dd, J = 8.4, 0.6 Hz, 1H), 5.70 (br s, 2H), 3.00 (t, J = 6.0 Hz, 2H), 2.64−2.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.2, 151.3, 142.5, 131.4, 115.8, 108.9, 107.2, 31.4, 21.0; HRMS *m*/*z* calcd for C_9H_9NO 147.0694, obsd 147.0684 Anal. Calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.24; H, 6.21; N, 9.49.

7-Fluoroindan-1-one (1). 7-Aminoindan-1-one (**15**, 0.78 g, 5.3 mmol) in acetone (12 mL, anhydrous) was added to a mixture of nitrosonium tetraborofluorate ($NOBF_4$; 0.72 g, 6.2 mmol) in acetone (10 mL) at −15 °C. After 30 min, more nitrosonium tetraborofluorate (∼0.3 g, 2.57 mmol) was added to the mixture. This was continued until the TLC showed the disappearance of the starting material. The mixture was poured into anhydrous $CHCl_3$ (50 mL) and stirred for 30 min. The mixture was cooled to 0 °C and the precipitate (diazonium borofluoride salt) was removed by filtration. The precipitate (mp 67−69 °C) was washed with hexane and dried under vacuum in a desiccator.[16d] The salt was added portion-wise to a solution of toluene at 84 °C. Heating continued for 5.5 h. The mixture was cooled to room temperature and loaded directly onto a column of silica gel. The product was eluted (10% EtOAc:hexane to 20% EtOAc:hexane) and 7-fluoroindan-1-one (**1**) was isolated as a yellow solid, 0.25 g (31%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dt, J = 5.1, 7.5 Hz, 3H), 7.22 (d, J = 7.8 Hz, 1H), 6.93 (t, J = 8.7 Hz, 1H), 3.12 (t, J = 6.0 Hz, 2H), 2.70−2.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.3, 160.9, 157.5, 136.6, 124.9, 122.6, 114.1, 36.9, 25.9; HRMS *m*/*z* calcd for C_9H_7FO 150.0481, obsd 150.0491 Anal. Calcd for C_9H_7FO: C, 77.99; H, 4.70. Found: C, 71.71; H, 4.61.

7-Chloro-indan-1-one (2). A mixture of $CuCl_2$ (0.55 g, 4.1 mmol) and *tert*-butyl nitrite (0.67 mL, 5.07 mmol) in acetonitrile (8 mL) at 65 °C was treated with 7-aminoindan-1-one (**15**; 0.46 g, 3.13 mmol) in acetonitrile (6 mL) over 10 min.[12] The mixture was concentrated onto silica gel (∼2 g) and purified by column chromatography with 10% EtOAc:hexane to give 7-chloroindan-1-one (**2**), 0.360 g (64%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.25 (d, J = 7.5 Hz, 1H), 3.07 (t, J = 6.0 Hz, 2H), 2.70−2.68 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 157.7, 135.2, 133.1, 132.05, 129.2, 125.4, 37.1, 25.3; HRMS *m*/*z* calcd for C_9H_7ClO 166.0185, obsd 166.0187. Anal. Calcd for C_9H_7ClO: C, 64.88; H, 4.23. Found: C, 64.77; H, 4.12.

7-Bromoindan-1-one (3). 7-Aminoindan-1-one (**15**; 0.5 g, 3.4 mmol) in HBr (48%, 1 mL) and EtOH (4 mL) at 0 °C was treated with an aqueous solution of $NaNO_2$ (0.31 g, 4.36 mmol in 0.54 mL of H_2O) for 15 min. This mixture was added to a solution of CuBr (0.27 g, 1.8 mmol) in HBr (∼5 mL) at 95 °C and kept at this temperature for 15 min.[17b] The solution was cooled to room temperature, diluted with water, and extracted with EtOAc. The organic layers were washed with sat. $NaHCO_3$, dried over $MgSO_4$, and purified by column chromatography with 40−50% EtOAc:hexane on silica gel. 7-Bromoindan-1-one (**3**) was isolated as a white solid, 0.42 g (60%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.45 (m, 1H), 7.41−7.33 (m, 2H), 3.06 (t, J = 6.0 Hz, 2H), 2.71−2.67 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 157.9, 135.1, 134.2, 132.4, 125.9, 119.5, 37.1, 25.0; HRMS *m*/*z* calcd for C_9H_7BrO 209.9680, obsd 209.9687. Anal. Calcd for C_9H_7BrO: C, 51.22; H, 3.34. Found: C, 51.23; H, 3.18.

7-Iodoindan-1-one (4). 7-Aminoindan-1-one (**15**; 0.68 g, 4.6 mmol) was dissolved in H_2O (5 mL), acetic acid (5 mL), and HCl (1.3 mL) at room temperature. A solution of $NaNO_2$ (0.36 g, 5 mmol) in H_2O (1.3 mL) was added at 0 °C for 5 min. A solution of KI (0.81 g, 4.9 mmol) in H_2O (1.3 mL) was added and the mixture was heated at 60 °C for 1 h.[17c] The mixture was cooled to room temperature and treated with solid $NaHSO_3$. The mixture was diluted with H_2O and extracted with CH_2Cl_2, and the organic solution was washed with sat. $NaHCO_3$ and brine and then dried over $MgSO_4$. The mixture was filtered and evaporated and the residue was purified on a column of silica gel eluting with 40−50% EtOAc:hexane. 7-Iodoindan-1-one (**4**) was obtained as a light yellow solid 0.5 g (43%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 3.03 (t, J = 6.0 Hz, 2H), 2.73−2.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.2, 157.9, 139.1, 136.2, 135.0, 126.7, 90.6, 37.2, 24.5; HRMS *m*/*z* calcd for C_9H_7IO 257.9542, obsd 257.9539. Anal. Calcd for C_9H_7IO: C, 41.89; H, 2.73. Found: C, 41.90; H, 2.68.

8-Fluoro-1-tetralone (5). 8-Amino-1-tetralone (**16**)[9] (see Supporting Information) (0.62 g, 3.85 mmol) in acetone (10 mL, anhydrous) was added to a mixture of $NOBF_4$ (0.59 g, 5.1 mmol) in acetone (10 mL) at −20 °C. After 45 min, more nitrosonium tetraborofluorate (∼0.67 g, 5.73 mmol) was added to the mixture. The reaction was continued (30 m) until TLC analysis showed no starting material. The mixture was poured into anhydrous $CHCl_3$ (50 mL) and stirred for 30 min. The mixture was dried over $MgSO_4$ and the solvent was removed under vacuum. The solids were added portion-wise to a solution of toluene at reflux. Heating was continued for 15 min whereupon the mixture was cooled to room temperature and filtered through Celite. The solids were flushed with $CHCl_3$ and the concentrated residue was purified on a column of silica gel. The product was eluted with 60% EtOAc:hexane to give 8-fluoro-1-tetralone (**5**) as a yellow oil, 0.26 g (41%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (dt, J = 7.8, 4.8 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.96 (dd, J = 8.7, 11.4 Hz, 1H), 2.95 (t, J = 5.7 Hz, 2H), 2.63 (t, J = 6.3 Hz, 2H), 2.13−2.05 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 164.1, 160.6, 147.0, 134.6, 124.6, 121.7, 115.3, 40.5, 30.2, 22.9; HRMS *m*/*z* calcd for $C_{10}H_9FO$ 164.0637, obsd 164.0646. Anal. Calcd for $C_{10}H_9FO$: C, 73.16; H, 5.53. Found: C, 73.08; H, 5.53.

8-Chloro-1-tetralone (6). A mixture of $CuCl_2$ (2.0 g, 14.8 mmol) and *tert*-butyl nitrite (2.3 mL, 17.4 mmol) in acetonitrile (830 mL) at 65 °C was treated with 8-amino-1-tetralone (**16**; 1.8 g, 11.1 mmol) in acetonitrile (15 mL). After 10 min, the mixture was cooled, concentrated onto silica gel, and purified by column chromatography with 10% EtOAc:hexane to give 8-chloro-1-tetralone (**6**), 1.58 g (78%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.21 (m, 2H), 7.11−7.08 (m, 1H), 2.90 (t, J = 6.0 Hz, 2H), 2.60 (t, J = 6.0 Hz, 2H), 2.06−1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 147.1, 134.1, 132.7, 130.3, 129.8, 127.6, 40.4, 30.7, 22.6; HRMS *m*/*z* calcd for $C_{10}H_9ClO$ 180.3342, obsd 180.0339. Anal. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02. Found: C, 66.24; H, 4.79.

8-Bromo-1-tetralone (7). 8-Amino-1-tetralone (**16**; 0.65 g, 41 mmol) in HBr (48%, 1.2 mL) and EtOH (4.8 mL) at 0 °C was treated with an aqueous solution of $NaNO_2$ (0.35 g, 4.39 mmol in 0.6 mL of H_2O) for 15 min. This mixture was added via pipet to a solution of CuBr (0.32 g, 2.2 mmol) in HBr (1.2 mL) at 95 °C and maintained at this temperature for 15 min. The solution was cooled to room temperature, diluted with water, and extracted with EtOAc. The organic layers were washed with sat. $NaHCO_3$, dried over $MgSO_4$, and purified by column chromatography with 10% EtOAc:hexane on silica gel. 8-Bromo-1-tetralone (**7**) was isolated as a white solid, 0.65 g (70%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.44 (m, 1H), 7.16−7.14 (m, 2H), 2.91 (t, J = 6.0 Hz, 2H), 2.62 (t, J = 6.3 Hz, 2H), 2.07−1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 147.2, 133.9, 132.9, 130.9, 128.3, 121.8, 40.0, 30.8, 22.4; HRMS *m*/*z* calcd for $C_{10}H_9BrO$ 223.9837, obsd 223.9828.

8-Iodo-1-tetralone (8). 8-Amino-1-tetralone (**16**; 0.51 g, 3.16 mmol) was dissolved in H_2O (4 mL), acetic acid (4 mL), and HCl (1 mL). A solution of $NaNO_2$ (0.25 g, 3.5 mmol) in H_2O (0.5 mL) was added at 0 °C for 5 min. A solution of KI (0.58 g, 3.5 mmol) in H_2O (1 mL) was added and the mixture was heated at 60 °C for 1 h. The mixture was cooled to room temperature. Solid $NaHSO_3$ was added and the mixture was diluted with H_2O and extracted with CH_2Cl_2. The organic solution was washed with sat. $NaHCO_3$ and brine and dried over $MgSO_4$. The mixture was filtered and evaporated and residue was purified on a column of silica gel eluting with 40% EtOAc:hexane. 8-Iodo-1-tetralone (**8**) was obtained as a light pink solid, 0.51 g (60%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 7.8 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 2.91 (t, J = 6.3 Hz, 2H), 2.64 (t, J = 6.6 Hz, 2H), 2.07−1.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 146.9, 141.6, 133.3, 132.5, 129.5, 93.2, 39.5, 31.2, 22.6; HRMS m/z calcd for $C_{10}H_9CIO$ 271.9698, obsd 271.9692. Anal. Calcd for $C_{10}H_9CIO$: C, 44.14; H, 3.33. Found: C, 43.88; H, 3.13.

Experimental for Scheme 2:[14,15] **7-Fluoro-indan-1-one (1).** 2-Fluorobenzoic acid (**17**; 20.0 g, 0.14 mol) and thionyl chloride (15.6 mL, 0.21 mol) in benzene were refluxed until no more gas evolution was observed. After being cooled to room temperature the mixture was concentrated under vacuum. The mixture was diluted with dichloroethane and added to a solution of $AlCl_3$ (19.0 g, 0.14 mol) in dichloroethane at room temperature. Ethylene was bubbled through the mixture for 4 h and the mixture was stirred overnight. The mixture was quenched with 4 M HCl. The resulting layers were separated and the aqueous layer was extracted with Et_2O (3 × 250 mL). The combined organic extracts were washed with H_2O (3 × 150 mL), sat. $NaHCO_3$ (3 × 150 mL), and brine (1 × 150 mL), dried over $MgSO_4$,and freed of solvent under reduced pressure. The material was added to a slurry of $AlCl_3$ (286 g, 2.14 mol) and NaCl (75 g, 1.28 mol) at 130 °C. The mixture was stirred at 180 °C for 2 h, cooled to room temperature, and quenched with ice followed by concentrated HCl. The resulting mixture was extracted with CH_2Cl_2 and the combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Column chromatography on silica gel with 25% EtOAc:hexane as eluant gave 7-fluoro-1-indanone (**1**), 6.85 g (32%, over three steps). See data for **1** above.

7-Chloroindan-1-one (2). 2-Chlorobenzoic acid (**18**; 10.0 g, 0.64 mol), $SOCl_2$ (7 mL, 0.096 mol), and $AlCl_3$ (8.5 g, 0.064 mol) were reacted with excess ethylene as above. This was followed by reaction with an additional amount of $AlCl_3$ (85 g, 0.64 mol) and NaCl (22 g, 0.38 mol) in the procedure above, to give 7-chloro-1-indanone (**2**), 4.13 g (39%, over three steps). See data for **2** above.

7-Bromoindan-1-one (3). 2-Bromobenzoic acid (**19**; 30.0 g, 0.15 mol), $SOCl_2$ (16.5 mL, 0.23 mol), and $AlCl_3$ (20.0 g, 0.150 mol) were reacted with excess ethylene as above. This was followed by reaction with an additional amount of $AlCl_3$ (200 g, 1.5 mol) and NaCl (52 g, 0.89 mol) in the procedure above to give 7-bromo-1-indanone (**3**), 9.68 g (31%, over three steps). See data for **3** above.

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Supporting Information Available: Experimental procedures for the preparation of 8-amino-1-tetralone (**16**)[9] and spectral data for **7** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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