Novel Intramolecular Cyclocarbonylations Involving π-Alkene-Hydridoiron Intermediates: From [η^5-$C_5H_5(CO)_2Fe$]-Substituted (*Z*)-Enals to α,β-Butenolides and γ-Butyrolactones

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Abstract: In order to broaden the application of [η^5-$C_5H_5(CO)_2Fe$]-substituted enals, reaction cascades were developed for the construction of five-membered lactone skeletons, initiated by the regioselective reduction of the aldehyde functionality with sodium borohydride or K-Selectride. Depending on the iron compound and the reagent employed, α,β-butenolides or γ-lactones were obtained. The key steps in the reaction cascade for the formation of α,β-butenolides involve carbonylation and reductive elimination. Labeling experiments, which were carried out to provide mechanistic details of the subsequent γ-lactone formation, are in agreement with a reduction step which involves a π-alkene hydridoiron intermediate. Proposed reaction pathways are given.

Keywords: carbonylations · domino reactions · enals · iron · lactones

Introduction

Well-defined carbonylation reactions have been developed for use in organic synthesis in recent years.[1] Various concepts and strategies rely on intramolecular cyclocarbonylations. For instance, titanium-catalyzed[2] and iron-promoted syntheses[3] of bicyclic ring systems from enynes have been recently reported. During the last two decades, many efforts have been directed towards the development of catalytical and stoichiometric palladium-mediated carbonylation methodologies.[1, 4] Whereas the synthesis of lactones could be achieved starting from hydroxyvinyl iodides,[5] triflates,[6] allyl alcohols, or *ortho*-halogeno-substituted benzylalcohols, the construction of lactams was accomplished, for example, from allylamines or the appropriately substituted benzylamines as the starting materials.[1, 6b] Higher temperatures and pressures of carbon monoxide are usually required for these transformations. In addition, stoichiometric multicomponent carbonylations have also attracted considerable interest. For example, hydroxybutenolides have been obtained from the cobalt-mediated reaction of [$(CO)_4Co$]Na, MeI, HC≡CR, H_2O, and 2 CO in a sequential insertion cascade.[7, 8] More recently, other teams have applied a related methodology to the synthesis of α,β-butenolides by the use of organomanganese pentacarbonyl complexes.[9] The sequential insertion of carbon monoxide and alkynes into alkylmanganese pentacarbonyl complexes at high pressure (2 – 10 kbar) gives acyl-coordinated manganese complexes, which, upon treatment with the diisobutylaluminiumhydride-butyllithium complex, furnish α,β-butenolides by an intramolecular version of the Reppe reaction.[10]

We recently reported the synthesis of α,β-unsaturated γ-lactams from titanium tetrachloride-mediated transformations of analogous (*Z*)-configured vinyl iron formyl complexes **2** with electron-rich primary amines.[11] These iron compounds are readily available from the corresponding 3-halogeno (*Z*)-alkenals[11, 12] **1** and the sodium ferrate complex [η^5-C_5H_5-$(CO)_2Fe$]Na by an addition – elimination process. In order to promote the practical application of the iron compounds **2** and to gain further insight into the mechanism of γ-lactam formation,[11, 12] reactions with other nucleophiles were investigated. In this paper reaction cascades initiated by the attack of hydride at the aldehyde group of **2** to give either α,β-butenolides **3** or the saturated γ-lactones **4** (Scheme 1) are presented.

In the course of our investigations, differences in the reactivity of the iron compounds as well as in the progress of the reaction cascades, initiated by a series of hydride donors, were observed. Labeling studies provided mechanistic details and thereby a basis on which to establish a reasonable working hypothesis regarding the reaction mechanism. Thus, the reduction to the saturated γ-lactones **4** can be traced back to the formation of a π-alkene-hydridoiron intermediate after ring closure to produce the butenolide framework during reductive elimination.

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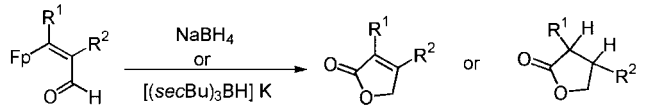


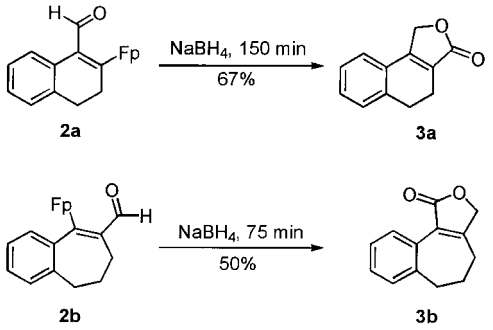
2 3 4

Scheme 1. Synthesis of α,β-butenolides **3** and γ-butyrolactones **4** from the reactions of $[\eta^5\text{-}C_5H_5(CO)_2Fe]$-substituted enals **2** with reducing reagents.

Results and Discussion

The iron compounds **2** are available from the reaction of ferrates and the corresponding β-halogeno vinyl aldehydes **1**, as described previously.[11, 12] The latter can be prepared, for example, from the appropriate α-methylene ketones and Vilsmeier–Haack reagents.[13] For instance, the compounds **2e** and **2f** (Table 1) were synthesized in a two-step sequence starting from thiochromanone and 4-*tert*-butyl-cyclohexanone: the corresponding ketones were treated with DMF/PBr_3 to give the desired β-bromo enals **1e** and **1f** (see the Experimental Section), which were then treated with the sodium ferrate complex to yield the fairly air-stable iron compounds **2e** (66%) and **2f** (70%) after column chromatography.

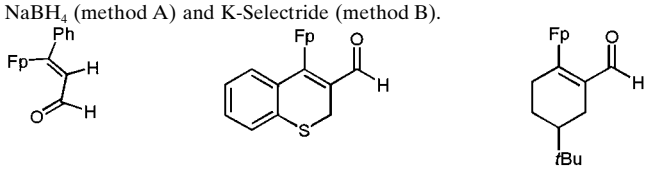
During an attempt to utilize iron derivatives **2** in reaction cascades leading to five-membered lactone skeletons, reactions with hydride donors were examined. Fortunately, sodium borohydride, the reducing reagent which was examined first, was found to work well. The treatment of **2a** and **2b** with 1.1–1.4 equivalents of $NaBH_4$ in ethanol or ethanol/dichloromethane at room temperature afforded the α,β-butenolides **3a** and **3b**, exclusively, as indicated by IR and NMR spectroscopy of the crude products obtained (Scheme 2).



2a 3a 2b 3b

Scheme 2. Fp = $[\eta^5\text{-}C_5H_5(CO)_2Fe]$.

Table 1. Reactions of $[\eta^5\text{-}C_5H_5(CO)_2Fe]$-substituted (*Z*)-enals **2d**-**2f** with $NaBH_4$ (method A) and K-Selectride (method B).



	Reactant	Method	Time [h]	Yield [%][a] **3**	**4**	Ratio[b] [**3**:**4**]
1	**2d**	A	3	54 (**3**+**4**)		63:37
2	**2d**	A	5.25	–	**4d**: 57	0:100
3	**2d**	B	3	–	**4d**: 27	0:100
4	**2e**	A	4.5	**3e**: 23	**4e**: 28	45:55
5	**2e**	A	20	–	**4e**: 38	0:100
6	**2f**	A	2.7	**3f**: 38	***trans*-4f**: 31[c]	55:45
7	**2f**	A	20	**3f**: 34	***trans*-4f**: 28[c]	55:45
8	**2f**	B	0.8	–	***cis*-4f**: 36	0:100

[a] Isolated yield. [b] ^{1}H NMR spectroscopy of the crude reaction mixture. [c] Ratio *trans*:*cis* = 86:14 for **4f**.

Abstract in German: *Fünfringlactone können aus β-Cyclopentadienyl(dicarbonyl)eisen-substituierten (Z)-Enalen über intramolekulare Reaktionskaskaden unter Carbonylierung durch den Einsatz von Reduktionsmitteln, wie Natriumborhydrid oder K-Selectride, hergestellt werden. In Abhängigkeit vom Reduktionsmittel und der Reaktivität der eingesetzten eisenorganischen Verbindung sind α,β-Butenolide oder gesättigte γ-Lactone isolierbar. Die Ergebnisse mit deuterierten Reagenzien beweisen, daß die Bildung der gesättigten γ-Lactone durch Reduktion der Doppelbindung nach Carbonylierung und reduktiver Eliminierung über den intermediär gebildeten π-Olefinhydridoeisenkomplex bewirkt wird.*

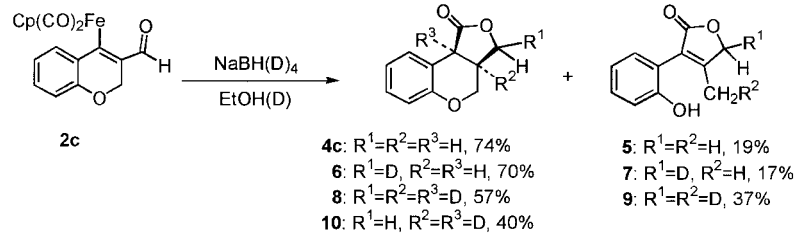
The characteristic $\tilde{\nu}$(C=O) band of these compounds is observed at $\approx$1750 cm^{-1} in dichloromethane. In general, after complete consumption of the starting materials (TLC monitoring) the reaction mixtures were immediately hydrolyzed by the addition of saturated aqueous NH_4Cl solution. The crude products were purified by flash chromatography on Florisil to furnish **3a** and **3b** in 67% and 50% yield. This also separated the ferrocene byproduct that stems from the iron fragment. Iron oxide and hydroxide residues can be removed by precipitation and filtration, as described in detail in the Experimental Section.

In the case of compound **2c**, the treatment with $NaBH_4$ was complete within 30 min and gave two new products. After acidic workup and purification by chromatography, the main product was found to be the saturated γ-lactone **4c** ($\tilde{\nu}$ = 1773 cm^{-1}), which was isolated in 74% yield along with the minor product lactone **5** in 19% yield (Scheme 3).

In contrast, the $NaBH_4$-mediated reactions of the iron compounds listed in Table 1 (method A) gave mixtures of the corresponding α,β-butenolides **3** and γ-lactones **4**, which were isolated upon hydrolysis of the reaction mixtures immediately after complete consumption of the starting materials (see Scheme 1 and Table 1, entries 1, 4 and 6).

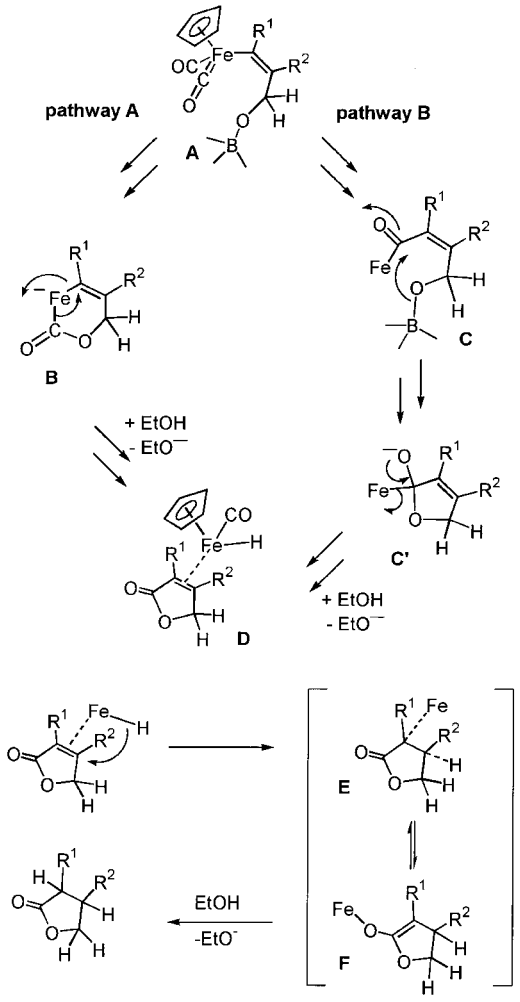
However, if the reaction time for the iron compounds **2d** and **2e** was prolonged, then only the saturated γ-lactones **4d** and **4e** were obtained. Compound **4e** was isolated in significantly lower yield (Table 1, entries 2 and 5). For the γ-lactones **4c** (Scheme 3) and **4e** the *cis*-configuration was assigned, in accordance with the coupling constants ($J \approx$ 8.3 Hz) in the ^{1}H NMR spectra.[14] In contrast, for the aliphatic γ-lactone **4f** (Table 1, entries 6 and 7), obtained from **2f** and $NaBH_4$, the predominant formation of the *trans*-isomer (ratio *trans*:*cis* = 86:14) was ascertained by ^{1}H NMR spectroscopy.[15]

Evidently, the outcome of the reaction cascade depends on the reactivity of the β-cyclopentadienyl(dicarbonyl)iron-substituted (*Z*)-enals **2** and the reaction time. Variation of the



Scheme 3. Labeling experiments with **2c**.

amount of $NaBH_4$ from 1.0 to 2.0 equivalents did not result in any change. Thus, the reactivity of the iron compounds **2** and consequently of the corresponding intermediates involved in the reaction cascades (Scheme 4) is strongly influenced by the



Scheme 4. Proposed mechanism for the formation of γ-lactone that involves a π-alkene-hydridoiron intermediate.

electronic properties of the substituents at the alkene unit. In the case of the chromanone derivative **2c**, activation of the aryl-substituted α,β-unsaturated moiety by the alkoxy substituent in the *ortho*-position at the aryl residue has to be considered. So far, only the five-membered iron compound **2g** (R^1, $R^2 = (CH_2)_3$, Scheme 1) did not form a lactone framework upon reduction of the aldehyde group with $NaBH_4$ to the boron alkoxide, possibly for steric reasons.[12]

Labeling experiments were undertaken to clarify the formation of the saturated γ-lactones. The treatment of the iron compound **2c** with $NaBD_4$ in ethanol gave the γ-lactone **6** in $\approx$70% yield and, according to ^{1}H NMR spectroscopy, exclusively deuterated at C5 of the lactone skeleton (Scheme 3). In addition, the side product **7** was isolated in 17% yield, with deuterium incorporated in position 5 (see the Experimental Section). This proves that $NaBH_4$ does not bring about the reduction of the α,β-unsaturated lactone moiety in the course of the reaction cascade.

In an alternative procedure, compound **2c** was treated with $NaBD_4$ in [D_1]ethanol to furnish **8** in 57% yield, along with the deuterated side product **9** (37%). In product **8** the incorporation of deuterium was detected by ^{1}H NMR spectroscopy at positions 3, 4, and 5 (100% deuteration) on the lactone moiety. These results led us to envision the working hypothesis shown in Scheme 4.

The formation of the α,β-butenolides can be rationalized by the reaction cascades shown, starting with the attack of the hydride at the aldehyde group to give the boron alkoxide **A**. The latter would then undergo an intramolecular carbonylation reaction by nucleophilic attack at one of the CO ligands (pathway A) to give the ferrilactone intermediate **B**, as previously discussed for the formation of α,β-unsaturated γ-lactams.[12] In analogy, a vinyl migration step followed by intramolecular nucleophilic attack of the alkoxide at the acyl iron intermediate **C** (pathway B) also has to be considered.[11, 12] However, after reductive elimination the stabilization of the remaining iron moiety with vacant coordination sites by η^2-coordination to the double bond of the α,β-butenolide framework seems to be reasonable. Proton transfer from the solvent to an electron-rich or even charged iron intermediate (structure **B**) during the carbonylation or the reductive elimination step would furnish a π-alkene hydridoiron species **D**, as outlined in Scheme 4. This intermediate would be responsible for the subsequent reduction step that yields the α-iron-substituted lactone compound **E** or its iron enolate **F** by conjugate addition to the α,β-unsaturated lactone moiety. Thus, the transfer of a proton from the solvent to either intermediate **E** or **F** yields the saturated lactone. The reactions performed with deuterated reagents underline this hypothesis. Evidently, the formation of the byproducts **5**, **7**, and **9** takes place by an alternative pathway, as depicted in Scheme 5. An attack by the hydride function (structure **G**) or by the negatively charged iron center (structure **H**) on the methylene group next to the ring oxygen in an internal S_N2 process would result in the opening of the chromanone ring with the phenol residue functioning as a leaving group. Pathway B would give an allyliron intermediate **I** prior to protonation to yield **5**. The deuterium incorporation determined for **7** and **9** also supports these assumptions.

Additional reducing reagents were examined for certain iron complexes; $LiAlH_4$ proved to be less efficient compared

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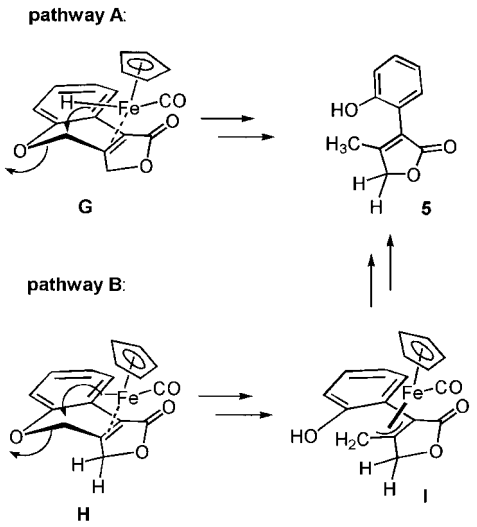

Scheme 5. Proposed mechanism for the formation of byproduct **5**.

with $NaBH_4$. For instance, in the range of 0 °C to room temperature the reaction of **2c** with $LiAlH_4$ (0.5 equiv) in THF for 18 hours gave unsatisfactorily results: the γ-lactone **4c** was isolated in 7% yield. The formation of **5** was detected by ^{1}H NMR spectroscopy of the crude product. Attempts to employ diisobutylaluminiumhydride (DIBALH) in THF at −78 °C as the reagent for lactone formation were completely unsuccessful. Although the reduction of the aldehyde moiety of **2c** was nearly quantitative (IR monitoring), additional reaction steps were not observed.

The application of K-Selectride as the reagent was also investigated; these reactions were studied in THF at −30 °C to room temperature (method B in Table 1, Scheme 1). Only the iron compound **2b** gave the corresponding α,β-butenolide **3b** (19%), as ascertained by the ^{1}H NMR spectra of the crude reaction product. As can be seen in Table 1, for all other examples only the saturated γ-lactones were detected by TLC or ^{1}H NMR spectroscopy after hydrolysis and were isolated in yields of 27–65%. The reaction of **2f** and K-Selectride only gave ***cis*-4f**, in contrast to the results of the $NaBH_4$-mediated domino process (Table 1, entries 6, 7, and 8). The latter was isolated in 36% yield after flash chromatography. Upon treatment of compound **2c** with K-Selectride, the formation of the ring-opened byproduct **5** (see Scheme 3) was detected only in isolated cases, possibly depending upon the hydrolysis procedure employed.

Much attention was devoted to the improvement of the hydrolysis procedure and thus the yield. However, significantly lower yields were observed under a variety of acidic and alkaline conditions. It is possible that undesirable side reactions can occur during hydrolysis because of the presence of the borane. In all the examples presented in Table 1 (method B) the turnover was monitored by IR spectroscopy. Thus, the disappearance of the characteristic ν(CO) stretching frequencies of the starting materials and the appearance of two new absorptions at $\tilde{\nu} = 1970-1960\ cm^{-1}$ and 1820–1810 cm^{-1}, as well as a shoulder at $\approx 1850-1830\ cm^{-1}$ was observed, in addition to a new absorption at $\tilde{\nu} = 1690-1670\ cm^{-1}$. Evidently, unlike the domino process which furnishes α,β-unsaturated γ-lactams[11, 12] and the $NaBH_4$-mediated process described above, K-Selectride gives rise to a sequential transformation[16] that leads to a ferrilactone intermediate (Scheme 4, pathway A, structure **B**). The IR data are in agreement with the bands expected for such electron-rich or even anionic intermediates, with the characteristic ν(CO) absorptions shifted to lower frequencies compared with the reported neutral, stable complexes of related structures.[4, 17, 18] These intermediates decompose only upon the addition of water, evidently by a well-defined reaction sequence, to afford the γ-lactone derivatives **4**. In contrast to the $NaBH_4$ reaction, here the addition of water is necessary for the reaction cascade to proceed after the carbonylation step. However, the latter should indeed proceed according to pathway A, Scheme 4, as supported by the IR data. When the reaction of **2c** with K-Selectride was hydrolyzed with D_2O the incorporation of deuterium at positions 3 and 4 was observed for **10** (see Scheme 3 and the Experimental Section).

Conclusions

So far, a considerable amount of progress has been achieved in the development of reaction cascades that lead to five-membered lactone skeletons starting from iron-substituted enals **2** and the appropriate hydride donors. Efforts will be continued to improve the yields and the selectivity of α,β-butenolide versus γ-lactone formation reaction. Furthermore, additional reducing reagents will be examined to clarify the reaction pathway and the factors which influence the carbonylation step, the reductive elimination sequence, and the formation of π-alkene-hydridoiron intermediates during the course of the reaction cascades. Our current interest is directed towards the development of reaction cascades initialized by the addition of C-nucleophiles to furnish 5-substituted α,β-butenolides.

Experimental Section

All reactions were carried out under an atmosphere of argon in oven-dried glassware by standard needle/syringe techniques. THF was dried and distilled from potassium/benzophenone under argon and degassed (ultrasound) before use. Solvents for chromatography were of technical quality and were purified as follows: petroleum ether (40–60 °C) was distilled from P_2O_5, ethyl acetate from K_2CO_3, and diethyl ether from KOH/Cu(I)Cl. K-Selectride (1M in THF) was purchased from Aldrich, sodium amalgam (2%) from Lancaster, and [{Cp(CO)$_2$Fe}$_2$] from Fluka. Buffer solutions were used as indicated (pH 6: 7.86 g citric acid monohydrate + 22.28 g $Na_2HPO_4 \cdot 2H_2O$ in 1.0 L of water; pH 7: 3.99 g citric acid monohydrate + 28.84 g $Na_2HPO_4 \cdot 2H_2O$ in 1.0 L of water). All reactions were monitored by analytical thin-layer chromatography (TLC, silica gel, Merck 60 F_{254} plates) and visualized by UV light, basic potassium permanganate, or acidic phosphomolybdic acid/cerium(IV)sulfate. The products were purified by column chromatography on Baker silica gel (0.06–0.2 mm) and by flash chromatography on Merck silica gel 60 (230–400 mesh) or Florisil (140–200 mesh, supplied by Fluka), unless otherwise stated. Melting points were measured on a Büchi apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer FT IR-Spectrometer 1760X. NaCl cells were used for IR monitoring. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200, or a Bruker AM400 in $CDCl_3$, unless otherwise stated. For some signal assignments, standard techniques such as homo- and heteronuclear decoupling experiments,

2D COSY or heterocorrelation were employed. Mass spectra were obtained on a Varian MAT CH 7a or a Finnigan MAT 95. The elemental analyses were performed by the Microanalytical Division of the Institute of Organic Chemistry, Johannes Gutenberg-Universität, Mainz (Germany).

4-Bromo-2*H*-1-benzothiopyran-3-carbaldehyde (**1e**): To a solution of DMF (12.7 mL, 165 mmol) in chloroform (70 mL) was added PBr_3 (12.5 mL, 132 mmol) dropwise at 0 °C, as described in the literature,[11, 12] the mixture was stirred for 90 min. A solution of thiochroman-4-one (5.41 g, 32.9 mmol) in chloroform (50 mL) was added and the reaction mixture was heated to reflux for 45 min (TLC monitoring), cooled to 0 °C, and then hydrolyzed by careful addition of saturated aqueous $NaHCO_3$ (200 mL), solid $NaHCO_3$, and water (300 mL). The aqueous layer was separated and extracted repeatedly with chloroform. The combined organic phases were washed with brine (100 mL) and dried ($MgSO_4$), and the solvent evaporated. Column chromatography on silica gel (petroleum ether/ether 5:1) gave 6.19 g (74 %) of **1e**, as a yellow oil, which solidified on cooling; $R_f = 0.64$ (petroleum ether/ether 2:1); m.p. 60 – 61 °C; ^{1}H NMR (200 MHz): $\delta = 10.18$ (s, 1H, CHO), 7.96 – 7.91 (m, 1H, arom CH), 7.33 – 7.23 (m, 3H, arom CH), 3.66 (s, 2H); ^{13}C NMR (100.6 MHz): $\delta =$ 191.3, 139.2, 137.6, 132.9, 131.4, 131.2, 129.1, 127.6, 126.1, 24.5; IR (KBr): $\tilde{\nu} =$ 2987, 2911, 2865, 1662, 1629, 1582, 1544, 1455, 1431, 1417, 1298, 1265, 1232, 1209, 1159, 1135, 1071, 1042, 938, 887, 866, 776, 724, 706, 620 cm^{-1}; MS (EI, 70 eV): m/z (%) = 256 (51), 227 (49), 175 (89), 147 (100), 102 (40), 77 (14), 75 (15), 69 (26), 45 (21); $C_{10}H_7BrOS$ (255.1): calcd C 47.08, H 2.77; found C 47.17, H 2.70.

2-Bromo-5-*tert*-butyl-1-cyclohexen-1-carbaldehyde (**1f**): To a solution of DMF (20.0 mL, 258 mmol) in chloroform (120 mL) PBr_3 (18.6 mL, 196 mmol) was added dropwise at 0 °C. The mixture was stirred for 60 min, then a solution of 4-*tert*-butylcyclohexanone (10.0 g, 64.8 mmol) in chloroform (100 mL) was added. The mixture was heated to reflux for 45 min (TLC monitoring), cooled to 0 °C, and then hydrolyzed by careful addition of saturated aqueous $NaHCO_3$ (250 mL), solid $NaHCO_3$, and water (600 mL). The aqueous layer was separated and extracted repeatedly with CH_2Cl_2. The combined organic phases were washed with brine, dried ($MgSO_4$), and the solvent evaporated. Column chromatography on silica gel (petroleum ether/ether 20:1) gave 13.3 g (83 %) of **1f** as a pale yellow liquid; $R_f = 0.69$ (petroleum ether/ether 4:1); ^{1}H NMR (400 MHz): $\delta = 9.98$ (s, 1H, CHO), 2.77 – 2.71 (m, 2H), 2.53 – 2.46 (m, 1H), 1.88 – 1.75 (m, 2H), 1.39 – 1.21 (m, 2H), 0.85 (s, 9H); ^{13}C NMR (100.6 MHz): $\delta = 193.7$ (CHO), 143.2 (C2), 135.3 (C1), 43.0 (C5), 40.0 (C3), 32.2 ($C(CH_3)_3$), 27.1 ($C(CH_3)_3$), 26.7 (C6), 25.7 (C4); IR (film): $\tilde{\nu} =$ 2962, 2901, 2867, 1620, 1471, 1422, 1396, 1384, 1367, 1230, 1211, 1009 cm^{-1}; $C_{11}H_{17}BrO$ (245.2): calcd C 53.89, H 6.99; found C 53.99, H 7.01.

4-[Cyclopentadienyl(dicarbonyl)iron]-2*H*-1-benzothiopyran-3-carbaldehyde (**2e**): To the aldehyde **1e** (2.00 g, 7.84 mmol) dissolved in THF (70 mL), a solution of [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (1.53 g, 4.31 mmol) and sodium amalgam (12.6 g, 11.0 mmol) in THF (60 mL),[11, 12] was added by means of a cannula at −78 °C over a period of 30 min. The reaction mixture was stirred for 15 min at −78 °C and then warmed to room temperature over a period of 1 h (IR monitoring). The solution was concentrated in vacuo (bath temperature 5 °C) and the residue purified by column chromatography on silica gel with i) petroleum ether/ether (2:1) to separate [{Cp(CO)$_2$Fe}$_2$], ii) ether/acetone (1:1) to yield 1.81 g (66 %) of **2e** as a green-brown foam, sufficiently pure for further transformations, but too unstable to be stored for a prolonged time at low temperature. $R_f = 0.33$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta = 10.02$ (s, 1H, CHO), 7.85 (dd, $J = 1.0$, 7.8 Hz, 1H, arom CH), 7.33 – 7.20 (m, 2H, arom CH), 7.12 (dt, $J = 7.3$ Hz, 1H, arom CH), 5.47 (s, 5H, C_5H_5), 3.34 (s, 2H, CH_2S); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 10.26$ (br s, 1H, CHO), 7.55 – 6.89 (m, 4H, arom CH), 4.12 (s, 5H, C_5H_5), 1.62 (s, 2H, CH_2S); ^{13}C NMR (50.3 MHz, [D$_5$]pyridine, selected data): $\delta =$ 194.7, 179.5, 148.8, 146.5, 136.6, 128.0, 127.8, 125.2, 87.7, 25.9; IR (CH_2Cl_2): = 2028, 1978, 1638 cm^{-1}; IR (THF): $\tilde{\nu} =$ 2023, 1973, 1645 cm^{-1}; MS (FAB): m/z (%) = 353.7 (11), 352.7 (43), 324.7 (32), 323.7 (48), 296.7 (53), 295.7 (100).

2-[Cyclopentadienyl(dicarbonyl)iron]-5-*tert*-butyl-1-cyclohexen-1-carbaldehyde (**2f**): The iron complex was synthesized according to the procedure described for **2e** starting from **1f** (1.50 g, 6.12 mmol) dissolved in THF (60 mL) and [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (1.20 g, 3.39 mmol) and sodium amalgam (10.0 g, 8.7 mmol) in THF (50 mL). Column chromatography performed under the same conditions as described above gave 1.47 g (70 %) of **2f** as a dark yellow, amorphous solid. M.p. 151 °C; $R_f = 0.47$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 10.07$ (s, 1H, CHO), 3.91 (s, 5H, C_5H_5), 3.06 – 2.93 (m, 1H), 2.66 – 2.59 (m, 2H), 2.33 – 2.19 (m, 1H), 1.64 – 1.56 (m, 1H), 1.26 – 1.05 (m, 2H), 0.94 (s, 9H); ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta = 9.71$ (s, 1H, CHO), 5.15 (s, 5H, C_5H_5), 3.00 – 2.91 (m, $J = 7.9$ Hz, 1H), 2.66 – 2.57 (m, 1H), 2.42 – 2.33 (m, $J = 3.9$, 7.3 Hz, 1H,), 1.81 – 1.59 (m, $J = 7.4$ Hz, 2H), 1.23 – 1.12 (m, $J = 3.4$ Hz, 1H), 0.92 – 0.89 (m, 1H, overlayed by the adjacent singlet), 0.82 (s, 9H); ^{13}C NMR (^{13}C{^{1}H} DEPT 135 NMR, 50.3 MHz): $\delta =$ 216.3 (s), 215.8 (s), 196.9 (d), 146.1 (s), 87.2 (d), 51.9 (t), 43.5 (d), 32.0 (s), 29.0 (t), 27.4 (t), 27.0 (q); IR (KBr): $\tilde{\nu} =$ 3115, 2958, 2934, 2865, 2838, 1997, 1951, 1756, 1716, 1683, 1634, 1544, 1364 cm^{-1}; IR (CH_2Cl_2): = 2018, 1965, 1635 cm^{-1}; MS (FAB): m/z (%) = 342.9 (18), 313.9 (18), 286.8 (43), 285.8 (100); $C_{18}H_{22}FeO_3$ (342.2): calcd C 63.00, H 6.42; found C 63.01, H 6.37.

4,5-Dihydronaphtho[1,2-c]furan-3(1*H*)-one (**3a**):

Method A and general workup procedure: A stirred solution of **2a**[11, 12] (510 mg, 1.53 mmol) in ethanol/dichloromethane (30 mL, 2:1) was cooled to 0 °C, and neat $NaBH_4$ (65 mg, 1.72 mmol) was added. After 150 min (TLC monitoring), saturated aqueous NH_4Cl solution (60 mL) was added, and the mixture was then concentrated in vacuo to 20 % of the original solvent volume. The mixture was diluted with dichloromethane (100 mL) and 2 N HCl (100 mL). The separated aqueous layer was extracted with CH_2Cl_2 (100 mL). The combined organic phases were washed with 2 N HCl (100 mL), brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash chromatography (Florisil, petroleum ether/ethyl acetate 8:1) to afford **3a** (189 mg, 67 %) as a beige amorphous solid. $R_f = 0.68$ (petroleum ether/ethyl acetate 2:1); m.p. 103 – 105 °C; ^{1}H NMR (400 MHz): $\delta = 7.33$ (t, $J = 7.5$ Hz, 1H, arom CH), 7.26 – 7.22 (m, 2H, arom CH), 7.10 (d, $J = 7.3$ Hz, 1H, arom CH), 5.10 (s, 2H, CH_2O), 2.98 (t, $J = 8.2$ Hz, 2H), 2.56 (t, $J = 8.2$ Hz, 2H); ^{13}C NMR (100.6 MHz): $\delta =$ 173.3, 156.0, 137.3, 130.9, 128.5, 127.9, 126.9, 124.7, 123.4, 68.7, 27.7, 18.1; IR (CH_2Cl_2): $\tilde{\nu} = 1751$ cm^{-1}; $C_{12}H_{10}O_2$ (186.2): calcd C 77.40, H 5.41; found C 76.90, H 5.36.

3,4,5,6-Tetrahydro-1*H*-benzo[3,4]cyclohepta[1,2-c]furan-1-one (**3b**): To a solution of **2b**[11, 12] (0.60 g, 1.72 mmol) in ethanol/dichloromethane (45 mL, 2:1) was added $NaBH_4$ (78 mg, 2.1 mmol) at 0 °C and the reaction mixture was stirred for 75 min (TLC monitoring). Then a solution of saturated aqueous NH_4Cl (30 mL) was added, and the mixture was subsequently concentrated in vacuo to 20 % of the original solvent volume. After dilution with CH_2Cl_2 (80 mL), the combined organic phases were washed with saturated aqueous $NaHCO_3$ solution (80 mL) and brine (80 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was analyzed by ^{1}H NMR spectroscopy and then purified by flash chromatography on Florisil with petroleum ether/ethyl acetate (20:1 to 5:1) to furnish **3b** (174 mg, 50 %) as a pale yellow oil, which solidified on standing (−22 °C). M.p. 82 °C, pale yellow crystals; $R_f = 0.36$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): $\delta = 8.20$ (dd, $J = 1.5$, 7.6 Hz, 1H, H10), 7.28 (dt, $J = 1.5$, 7.6 Hz, 1H, H9), 7.22 (dt, $J = 1.5$, 7.6 Hz, 1H, H8), 7.13 (dd, $J = 1.2$, 7.6 Hz, 1H, H7), 4.73 (s, 2H, OCH_2), 2.80 (m, 2H, H6a/b), 2.68 (t, $J =$ 7.0 Hz, 2H, H4a/b), 2.06 (m, 2H, H5a/b); ^{13}C NMR (100.6 MHz): $\delta = 173.4$ (s), 161.4 (s, C3a), 142.6 (s, C6a), 128.9 and 128.8 (d, C10 and C10a), 128.4 (d, C8), 126.3 (d, C9), 123.8 (s, C10b), 71.5 (t, C3), 34.8 (t, C6), 29.8 (t, C4), 26.1 (t, C5); IR (CH_2Cl_2): = 1753 cm^{-1}; IR (KBr): $\tilde{\nu} =$ 3456 (broad), 3064, 3026, 2957, 2943, 2917, 2896, 2862, 1735, 1697, 1639, 1599, 1493, 1456, 1446, 1418, 1390, 1351, 1300, 1279, 1219, 1167, 1162 cm^{-1}; $C_{13}H_{12}O_2$ (200.2) · 0.5 H_2O: calcd C 74.62, H 6.26; found C 74.32, H 5.96.

Method B: A solution of **2b** (1.24 g, 3.56 mmol) in THF (60 mL) was treated with K-Selectride (3.9 mL, 1 M solution in THF) at −30 °C. The mixture was stirred for 40 min (TLC monitoring), buffer (pH 6, 150 mL) added, and the reaction mixture then diluted with ether (100 mL). The aqueous layer was washed twice with ether (50 mL). The organic phases were combined and washed with brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash chromatography on Florisil with petroleum ether/ethyl acetate (20:1 to 12:1) to yield **3b** (137 mg, 19 %).

3-Phenyl-tetrahydro-2-furanone (**4d**):

Method A: To the iron complex **2d**[11, 12] (0.50 g, 1.62 mmol) dissolved in ethanol (30 mL) was added $NaBH_4$ (92 mg, 2.43 mmol) at 0 °C. The solution was stirred for 3 h (TLC monitoring). Then a saturated aqueous NH_4Cl solution (50 mL) was added, and the reaction mixture concentrated

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in vacuo, as described for **3a**. The residue was diluted with ether (50 mL), and the separated aqueous layer was extracted repeatedly with ether (5 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography (Florisil, petroleum ether/ethyl acetate 18:1 to 8:1) afforded a mixture of **3d** and **4d** (63:37; 140 mg, 54%), as indicated by ^{1}H NMR spectroscopy. Selected data for **2,5-Dihydro-3-phenyl-2-furanone** (**3d**): ^{1}H NMR (200 MHz): 7.84 (t, J = 3.9 Hz, 2H), 7.63 (s, 1H), 4.91 (s, 2H); IR (CH_2Cl_2): = 1760 cm^{-1}.

Following the procedure given above, the iron compound **2d** (1.13 g, 3.67 mmol) dissolved in ethanol/dichloromethane (66 mL, 2:1) was treated with $NaBH_4$ (153 mg, 4.04 mmol). The reaction mixture was worked up after 5 h to afford **4d** (338 mg, 57%), exclusively, as a pale yellow liquid; R_f = 0.36 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz): δ = 7.33–7.26 (m, 5H), 4.51–4.27 (m, 2H), 3.80 (t, J = 9.5 Hz, 1H), 2.79–2.62 (m, 1H), 2.53–2.33 (m, 1H); ^{13}C NMR (50.3 MHz): δ = 177.6, 136.8, 128.9, 128.0, 127.6, 66.6, 45.5, 31.6; IR (CH_2Cl_2): $\tilde{\nu}$ = 1773 cm^{-1}; MS (EI, 70 eV): m/z (%) = 162 (34), 117 (100), 104 (14), 103 (20), 91 (34), 77 (14); $C_{10}H_{10}O_2$ (162.2): calcd C 74.06, H 6.21; found C 74.14, H 6.20.

Method B: A stirred solution of **2d** (635 mg, 2.06 mmol) dissolved in THF (40 mL) was cooled to 0 °C and K-Selectride (2.1 mL, 1M, THF) was added. The mixture was stirred for 3 h (IR monitoring) until TLC indicated complete turnover. The mixture was diluted with saturated aqueous NH_4Cl solution (80 mL) and concentrated in vacuo. The mixture was partitioned between CH_2Cl_2 (100 mL) and 2N HCl (50 mL). The aqueous layer was separated, diluted with water (200 mL), and extracted with CH_2Cl_2 (4 × 50 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography on Florisil with petroleum ether/ethyl acetate (25:1 to 10:1) gave **4d** (89 mg, 27%).

1,3a,4,9b-Tetrahydro-3*H*-[1]benzothiopyrano[3,4-c]furan-1-one (**4e**): A solution of **2e** (2.10 g, 5.96 mmol) in ethanol (120 mL) was treated with $NaBH_4$ (338 mg, 8.94 mmol) at 0 °C. The reaction mixture stirred for 255 min (TLC monitoring), diluted with saturated aqueous NH_4Cl solution (30 mL), and then worked up as described for compound **3a**. The crude, solid product obtained was separated by flash chromatography (Florisil, petroleum ether/ethyl acetate 15:1 to 7:1) to afford firstly **3e** (281 mg, 23%) and secondly **4e** (340 mg, 28%), as pale yellow amorphous solids. Under the same conditions as described above, a solution of **2e** (1.61 g, 4.57 mmol) in ethanol (100 mL) was treated with $NaBH_4$ (260 mg, 6.87 mmol) for 20 h to yield **4e** (354 mg, 38%), exclusively.

4e: R_f = 0.66 (petroleum ether/ethyl acetate 1:2); m.p. 104–105 °C; ^{1}H NMR (200 MHz): δ = 7.48 (t, J = 3.5 Hz, 1H), 7.23–7.14 (m, 3H), 4.53 (dd, J = 9.8, 6.4 Hz, 1H), 4.32 (dd, J = 9.3, 2.4 Hz, 1H), 3.82 (d, J = 8.3 Hz, 1H), 3.23–3.12 (m, 1H), 2.92–2.81 (m, 2H); ^{13}C NMR (50.3 MHz): δ = 175.8, 133.0, 132.0, 127.9, 127.8, 127.7, 125.8, 71.4, 43.3, 36.0, 29.5; IR (CH_2Cl_2): $\tilde{\nu}$ = 1777 cm^{-1}; MS (FD): m/z (%) = 206.0 (100); $C_{11}H_{10}O_2S$ (206.3): calcd C 64.05, H 4.89; found C 64.15, H 4.94.

1,4-Dihydro-3*H*-[1]benzothiopyrano[3,4-c]furan-1-one (**3e**): R_f = 0.71 (petroleum ether/ethyl acetate 1:2); m.p. 139–140 °C; ^{1}H NMR (200 MHz): δ = 8.21 (q, 1H), 7.31–7.16 (m, 3H), 4.87 (s, 2H), 3.76 (s, 2H); ^{13}C NMR (50.3 MHz): δ = 170.5, 152.5, 130.9, 129.4, 126.7, 126.3, 125.9, 125.3, 124.3, 69.7, 24.0; IR (CH_2Cl_2): $\tilde{\nu}$ = 1760 cm^{-1}; MS (FD): m/z (%) = 204 (100); $C_{11}H_8O_2S$ (204.3): calcd C 64.69, H 3.95; found C 64.62, H 3.92.

5-*tert*-Butyl-perhydro-isobenzofuranone (**4f**): A solution of the iron compound **2f** (1.45 g, 4.24 mmol) in ethanol/dichloromethane (75 mL, 2:1) was treated with $NaBH_4$ (176 mg, 4.65 mmol) for 160 min (TLC monitoring). Then saturated aqueous NH_4Cl solution (75 mL) was added, and the reaction mixture was worked up according to the general procedure given for compound **3a**, except that the combined CH_2Cl_2 phases were washed with water (3 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was dissolved in petroleum ether/ether (30 mL, 1:1) and stored overnight at room temperature. The fluffy precipitate (iron oxide and hydroxide) was removed by filtration over a plug of Celite with ether. The filtrate was concentrated and the crude product was separated by flash chromatography (Florisil, petroleum ether/ether 10:1 to 2:1) to afford firstly **4f** (260 mg, 31%; mixture of *trans*- and *cis*-isomers, ratio: 86:14), as a orange-yellow foam, and secondly **3f** (316 mg, 38%) as a red-orange oil.

***trans*-4f**: R_f = 0.54 (petroleum ether/ether 2:1); ^{1}H NMR {400 MHz, *trans*-isomer [ratio: 86:14]}: δ = 4.29–4.20 (dd, J = 8.3, 8.4 Hz, 1H), 4.14–4.05 (dd, J = 10.7, 8.3 Hz, 1H), 2.84–2.70 (m, 1H), 2.48–2.34 (m, 1H), 2.12–1.97 (m, 1H), 1.87–1.74 (m, 1H), 1.69–1.56 (m, 1H), 1.48–1.26 (m, 2H), 1.19–0.99 (m, 1H), 0.98–0.80 (m, 1H overlayed by the adjacent singlet), 0.80 (s, 9H); ^{13}C NMR (50.3 MHz): δ = 180.0, 69.9, 42.3, 39.0, 35.1, 32.4, 27.3, 24.6, 24.5, 23.9; IR (CH_2Cl_2): $\tilde{\nu}$ = 1768 cm^{-1}; MS (EI): m/z (%) = 196 (7), 140 (53), 95 (23), 86 (7), 80 (9), 67 (7), 57 (100); $C_{12}H_{20}O_2$ (196.3): calcd C 73.43, H 10.27; found C 73.30, H 10.28.

5-*tert*-Butyl-4,5,6,7-tetrahydro-1(3*H*)isobenzofuranone (**3f**): R_f = 0.35 (petroleum ether/ether 2:1); ^{1}H NMR (400 MHz): δ = 4.65 (d, J = 17.4 Hz, 1H, CH_2O), 4.58 (d, J = 17.5 Hz, 1H, CH_2O), 2.35–2.27 (m, 2H, $H4_{eq}$ and $H7_{eq}$), 2.04–1.96 (m, 3H, $H6_{eq}$, $H4_{ax}$ and $H7_{ax}$), 1.41–1.34 (m, 1H, H5), 1.19–1.09 (m, 1H, H6), 0.87 (s, 9H); ^{13}C NMR (100.6 MHz): δ = 174.0 (C1), 161.9 (C3a), 126.2 (C7a), 71.8 (C3), 43.9 (C5), 32.2 ($C(CH_3)_3$), 27.1 ($C(CH_3)_3$), 25.2 (C4), 23.3 (C6), 20.9 (C7); IR (CH_2Cl_2): $\tilde{\nu}$ = 1749 cm^{-1}; IR (film): $\tilde{\nu}$ = 3441, 2961, 2869, 1756, 1685, 1471, 1440, 1396, 1367, 1348, 1258, 1227, 1160, 1110, 1088, 1035 cm^{-1}; MS (EI, 70 eV): m/z (%) = 194 (19), 138 (82), 93 (14), 69 (10), 57 (100), 41 (23); $C_{12}H_{18}O_2$ (194.3) · 0.25 H_2O: calcd C 72.51, H 9.38; found C 72.41, H 9.36.

***cis*-4f**: Method B: To a solution of **2f** (1.42 g, 4.15 mmol) in THF (70 mL) was added K-Selectride (4.5 mL, 1M, THF) at 0 °C. The reaction mixture was stirred for 50 min (TLC monitoring) before a buffer solution (pH 6, 150 mL) was added. The reaction mixture was diluted with ether (100 mL) and worked up as described above for compound **4d**. After evaporation of the solvent, the reminder was dissolved in ether (20 mL) and stored at room temperature for 18 h. The fluffy precipitate (iron oxide and iron hydroxide) was removed by filtration over a plug of Celite with ether. The filtrate was concentrated and the crude product purified by flash chromatography on Florisil with petroleum ether/ether (12:1 to 6:1 to 3:1) to yield ***cis*-4f** (290 mg, 36%), exclusively, as colorless crystals (petroleum ether/ether). M.p. 94–95 °C; R_f = 0.38 (petroleum ether/ether 1:1); ^{1}H NMR (200 MHz): δ = 4.20 (dd, J = 8.8, 4.4 Hz, 1H), 3.92 (d, J = 8.8 Hz, 1H), 2.63–2.60 (m, 1H), 2.47–2.39 (m, 1H), 2.29–2.20 (m, 1H), 1.88–1.79 (m, 1H), 1.70–1.46 (m, 2H), 0.93–0.80 (m, 3H, overlayed by the adjacent singlet), 0.80 (s, 9H); ^{13}C NMR (100.6 MHz): δ = 178.4, 72.1, 45.7, 39.4, 36.6, 32.2, 29.2, 27.3, 23.8, 23.6; IR (KBr): $\tilde{\nu}$ = 3000, 2956, 2942, 2900, 2881, 2866, 2856, 1762, 1474, 1438, 1382, 1364, 1289, 1236, 1214, 1171, 1151 cm^{-1}; $C_{12}H_{20}O_2$ (196.3): calcd C 73.43, H 10.27; found C 73.49, H 10.25.

Reaction of 2c with $NaBH_4$ in ethanol (Method A): To a solution of **2c** (1 g, 3 mmol) in ethanol (40 mL) was added $NaBH_4$ (135 mg, 2.6 mmol) at 0 °C, and the reaction mixture was stirred for 1 h at room temperature (TLC monitoring). Then saturated aqueous NH_4Cl solution (50 mL) was added, and the solution was concentrated as described for **3a**. The mixture was diluted with CH_2Cl_2 (80 mL) and water (80 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 × 80 mL). The combined organic phases were washed with water (80 mL) and brine (80 mL) and dried ($MgSO_4$), and the solvent evaporated. The crude, solid product was purified by flash chromatography on Florisil with petroleum ether/ethyl acetate (9:1 to 5:1) to give firstly **4c** (420 mg, 74%) and secondly **5** (107 mg, 19%).

Reaction of 2c with K-Selectride/H_2O (Method B): To a solution of **2c** (0.50 g, 1.49 mmol) in THF (30 mL) was added K-Selectride (1.5 mL, 1M, THF) at 0 °C. The reaction mixture was stirred for 90 min (TLC monitoring), diluted with saturated aqueous NH_4Cl solution (20 mL), and then worked up as described for **4d**, except that ether was used for extraction instead of CH_2Cl_2. Flash chromatography on Florisil with petroleum ether/ethyl acetate (18:1 to 8:1) gave **4c** (184 mg, 65%).

1,3a,4,9b-Tetrahydro-3*H*-furo[3,4-c][1]benzopyran-1-one (**4c**): beige amorphous solid; m.p. 92–93 °C; R_f = 0.35 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): δ = 7.51 (d, J = 7.3 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.9 Hz, 1H), 4.48 (dd, J = 9.2, 6.8 Hz, 1H), 4.24 (dd, J = 11.4, 4.1 Hz, 1H), 4.18 (dd, J = 9.5, 3.9 Hz, 1H), 3.78 (dd, J = 11.5, 8.8 Hz, 1H), 3.73 (d, J = 8.2 Hz, 1H), 3.06 (m, 1H);^{13}C NMR (^{13}C{^{1}H} DEPT 135 NMR, 100.6 MHz): δ = 175.5 (s), 154.3 (s), 130.4 (d), 128.8 (d), 121.9 (d), 117.1 (d), 115.9 (s), 67.5 (t), 64.2 (t), 38.5 (d), 33.6 (d); IR (CH_2Cl_2): $\tilde{\nu}$ = 1773 cm^{-1}; IR (KBr): $\tilde{\nu}$ = 3519, 2991, 2973, 2907, 2869, 1781, 1772, 1612, 1584, 1496, 1470, 1456, 1389, 1365, 1333, 1307, 1290, 1270, 1245, 1238, 1224, 1205, 1187, 1164, 1157, 1133, 1116 cm^{-1}; MS (EI, 70 eV): m/z (%) = 190 (48); $C_{11}H_{10}O_3$ (190.2) · 2 H_2O: calcd C 58.40, H 6.24; found C 58.39, H 5.87.

1,3-Dihydro-4-methyl-5-(2′-hydroxyphenyl)-1-furanone (**5**): Beige, amorphous solid, m.p. 98–100 °C; R_f = 0.18 (petroleum ether/ethyl acetate 2:1);

^{1}H NMR (400 MHz): $\delta = 7.56$ (br s, 1H), 7.26 (t, $J = 7.3$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 8.2$ Hz, 1H), 6.95 (t, $J = 7.7$ Hz, 1H), 4.88 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100.6 MHz): $\delta = 175.8$, 160.7, 154.6, 130.6, 130.5, 125.8, 120.6, 118.9, 117.1, 74.4, 13; IR (CH_2Cl_2): $\tilde{\nu} = 1721$ cm^{-1}; MS (EI): m/z (%) = 191.1 (8), 190.1 (100), 161.1 (17), 147.0 (11), 145.1 (17), 133.1 (45), 131.0 (24), 115.0 (17), 105.0 (17), 105.0 (28); $C_{11}H_{10}O_3$ (190.2): calcd C 69.48, H 5.30; found C 69.44, H 5.35.

Reaction of 2c with $NaBD_4$ in ethanol: As outlined above, the iron compound **2c** (1 g, 3 mmol) dissolved in ethanol (40 mL) was treated with $NaBD_4$ (139 mg, 3.3 mmol) at room temperature for 30 min (TLC monitoring). Then saturated aqueous NH_4Cl solution (50 mL) was added, and the reaction mixture was worked up. The crude solid product was purified by flash chromatography on Florisil with i) petroleum ether/ethyl acetate (8:1 to 4:1) to yield firstly **6** (400 mg, 70%), ii) ethyl acetate as eluent to yield secondly **7** (95 mg, 17%).

Compound 6: Pale yellow, amorphous solid; ^{1}H NMR (400 MHz, deuteration rate 100% at position 3): $\delta = 7.51$ (dd, $J = 7.6$, 0.9 Hz, 1H), 7.18 (dt, $J = 8.5$, 1.5 Hz, 1H), 6.99 (dt, $J = 7.6$, 1.2 Hz, 1H), 6.87 (dd, $J = 7.6$, 0.9 Hz, 1H), 4.46 (d, $J = 6.8$ Hz), 4.23 (dd, $J = 11.5$, 4.1 Hz, 1H), 4.16 (d, $J = 3.5$ Hz), 3.78 (dd, $J = 11.5$, 8.8 Hz, 1H), 3.73 (d, $J = 8.2$ Hz, 1H), 3.06 (m, 1H); ^{13}C NMR (100.6 MHz): $\delta = 175.8$, 154.3, 130.4, 128.8, 121.9, 117.2, 116.0, (67.8, 67.6, 67.3), 64.3, 38.9, 33.6; IR (CH_2Cl_2): $\tilde{\nu} = 1780$ cm^{-1}; MS (FD): m/z (%) = 191.7 (19), 190.7 (100).

Compound 7: Pale yellow, amorphous solid; ^{1}H NMR (400 MHz, deuteration rate 50% at position 5): $\delta = 7.55$ (br s, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 7.3$ Hz, 1H), 6.99 (d, $J = 7.9$ Hz, 1H), 6.95 (t, $J = 7.3$ Hz, 1H), 4.89 (s), 4.88 (s), 2.18 (s, 3H); ^{13}C NMR (100.6 MHz): $\delta = 175.8$, (160.6, 160.5), 154.7, 130.6, 130.5, (125.94, 125.90), 120.7, 119.0, 117.1, [74.5, (74.4, 74.2, 73.9)] 13.9; IR (CH_2Cl_2): $\tilde{\nu} = 3292$ broad, 1764, 1723 cm^{-1}; MS (EI, 70 eV): m/z (%) = 190.1 (100), 161.1 (30), 147.1 (30), 133.1 (80), 115.0 (24), 105.0 (50), 91.0 (19), 77.0 (47).

Reaction of 2c with $NaBD_4$ in [D_1]ethanol: To a solution of **2c** (0.98 g, 2.9 mmol) in [D_1]ethanol (CH_3CH_2OD, 40 mL) was added $NaBD_4$ (135 mg, 3.2 mmol) at room temperature. The mixture was stirred for 1 h (TLC monitoring), then a saturated aqueous NH_4Cl solution (50 mL) was added, and the reaction mixture was worked up as described above. Flash chromatography on Florisil with petroleum ether/ethyl acetate (8:1 to 4:1) gave firstly **8** (320 mg, 57%) and secondly **9** (210 mg, 37%).

Compound 8: Pale yellow, amorphous solid; ^{1}H NMR (400 MHz, deuteration rate 100% at positions 9b, 3a, and 3-Ha/3-Hb): $\delta = 7.52$ (d, $J = 7.3$ Hz, 1H), 7.18 (t, $J = 7.6$ Hz, 1H), 6.99 (t, $J = 7.3$ Hz, 1H), 6.87 (d, $J = 7.9$ Hz, 1H), 4.47 (s, 0.5H), 4.24 (d, $J = 11.4$ Hz, 1H), 4.17 (s, 0.5H), 3.80 (d, $J = 11.4$ Hz, 1H); ^{13}C NMR (100.6 MHz): $\delta = 171.3$, 150.0, 126.0, 124.5, 117.6, 112.8, 111.5, (63.1, 62.9, 62.6), 59.8 (m, 33.8), (m, 28.8); MS (EI): m/z (%) = 194.1 (16), 193.2 (56), 148.1 (51), 132.1 (100), 120.1 (18), 104.1 (11.5), 78.0 (22).

Compound 9: Pale yellow, amorphous solid: ^{1}H NMR (400 MHz, deuteration rate 100% at 4-CH_3 and 95% at position 5-Ha/5-Hb): $\delta = 7.56$ (br s, 1H), 7.28–7.26 (m, 1H), 7.13–7.11 (m, 1H), 7.00–6.93 (m, 2H), 4.87 {br s, CD(D/H)}, 2.16 (s, 2H); ^{13}C NMR (100.6 MHz): $\delta = 171.6$, 156.2, 150.4, 126.3, 126.2, 121.7, 116.4, 114.7, 112.8, (69.7, 69.5, 69.3), (9.5, 9.3, 9.1); MS (FD): m/z (%) = 194.1 (15), 193.1 (100), 192.1 (15), 163.1 (23.4), 149.0 (19), 135.1 (68.4), 117.1 (15), 107.0 (41), 93.0 (11), 78.0 (17).

Reaction of 2c with K-Selectride/D_2O: As outlined above, a solution of the iron compound **2c** (0.50 g, 1.49 mmol) in THF (30 mL) was treated with K-Selectride (1.5 mL) at 0 °C. The mixture was stirred for 75 min, then D_2O (10 mL) was added, and the reaction mixture was worked up as described above, except that ether was used for extraction. The crude solid product was purified by flash chromatography on Florisil with petroleum ether/ethyl acetate (18:1 to 10:1) to yield **10** (114 mg, 40%) as a pale-yellow, amorphous solid. ^{1}H NMR (200 MHz, deuteration rate 100% at positions 9b and 3a): $\delta = 7.52$ (d, $J = 7.8$ Hz, 1H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.03 (t, $J = 7.8$ Hz, 1H), 6.87 (d, $J = 8.3$ Hz, 1H), 4.49 (d, $J = 9.8$ Hz, 1H), 4.21 (t, $J = 9.7$ Hz, 1H), 3.79 (d, $J = 9.8$ Hz, 2H); ^{13}C NMR (50.3 MHz): $\delta = 175.6$, 154.3, 130.3, 128.8, 121.8, 117.1, 115.9, 67.5, 64.1, (38.4, 38.2, 38.0), (33.2, 33.0, 32.8); MS (FD): $m/z = 191.7$ (100).

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