Journal of Organometallic Chemistry 851 (2017) 218–224

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis of stemofurans C, L and T using organomanganese arene chemistry; Revised structure for stemofuran L

William H. Miles [a, *], Cassidy M. Madison [a], Christopher Y. Kim [a], Daniel J. Sweitzer [a], Shelby D. Valent [a], Dasan M. Thamattoor [b]

[a] Department of Chemistry, Lafayette College, Easton, PA 18042, USA
[b] Department of Chemistry, Colby College, Waterville, ME 04901, USA

ARTICLE INFO

Article history:
Received 28 June 2017
Received in revised form
19 September 2017
Accepted 21 September 2017
Available online 23 September 2017

Keywords:
Organomanganese arene
Stemofuran
Benzofuran
Nucleophile

ABSTRACT

The synthesis of stemofurans C, L and T was achieved using organomanganese arene complexes. The critical carbon-carbon bond between the C-2 position of benzofuran and the arene was established in a regioselective manner directed by the cationic manganese tricarbonyl moiety. Oxidation of the resulting dienyl complexes and cleavage of the methyl ethers gave the desired stemofuran products. The spectroscopic data for the originally proposed structure for stemofuran L did not match the synthesized material, which prompted the synthesis of an isomer that did match the spectroscopic data. This revised structure has been proposed as the correct structure for stemofuran L.

1. Introduction

Nucleophilic attack on arenes coordinated to transition metals is one of the most important modes of reactivity in organometallic chemistry [1]. Organomanganese arene complexes, which have been exploited in many studies [1b,2-7], are notable for their greater reactivity compared to the more extensively studied organochromium arene complexes [1a,1c]. The reactivity of nucleophiles with η^6-arene complexes, in which electron-donating groups such as alkoxy and amino groups direct the nucleophile to the *meta*-position, complements the standard electrophilic aromatic addition reactions to arenes [1–7]. The addition of carbon nucleophiles to organomanganese arene complexes possessing electron-donating substituents typically follows this pattern, but there are a couple of noteworthy exceptions [3b,6]. Steric repulsion inherent in more highly substituted arenes complexes (such as the (3-methoxyestrone)$Mn(CO)_3^+$) [3b] and/or the nature of the carbon nucleophile [6] leads to diminished selectivity. Even with these potential complications, the general selectivity of these reactions for nucleophilic attack at the *meta*-position to alkoxy groups suggested a straightforward method for the synthesis of some 2-arylbenzofurans, compounds that have become increasingly important [8–10].

Benzofurans represent a broad class of biologically important compounds [8]. 2-Arylbenzofurans, an important subset of benzofurans, have been isolated from various plants, and possess biological activity including antifungal, antibacterial, and anticancer properties [9,10]. The *Stemona* genus is a particularly rich source of 2-arylbenzofurans named stemofurans. The stemofurans are characterized by C-3′ and C-5′ oxygenation on the arene ring, and methylation on the arene and/or benzofuran rings, with additional oxygenation frequently occurring on the benzofuran moiety [9]. Some representative examples include stemofurans C (**1a**), T (**1b**), and L (**1c**; originally proposed structure). In the course of our synthetic studies, we suspected that **1c**, the originally proposed structure for stemofuran L, was incorrect based on the comparison between the literature values of the NMR peaks and compound **1c** that we synthesized, and that isomeric **1d** was the correct structure (Fig. 1).

There have been many synthetic strategies employed for the synthesis of 2-arylbenzofurans, in particular the Suzuki–Miyaura coupling of 2-(boronic acid)benzofurans with the appropriate aryl bromide [11,12]. This method depends on ready access to the necessary aryl bromide, which sometimes poses synthetic challenges with standard electrophilic aromatic substitution chemistry. We recognized that a subset of stemofurans and related 2-

* Corresponding author.
E-mail address: milesw@lafayette.edu (W.H. Miles).

https://doi.org/10.1016/j.jorganchem.2017.09.034
0022-328X/

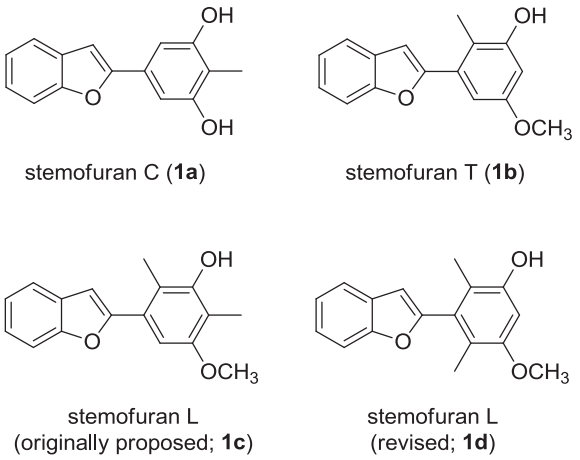
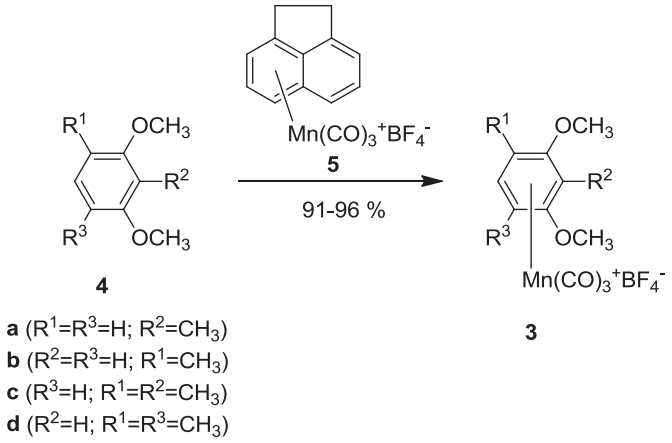


Fig. 1. Structure of stemofurans C, L and T.

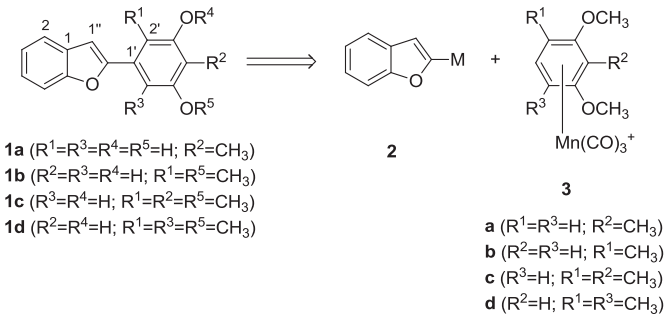


Scheme 2. Synthesis of complexes **3**.

arylbenzofurans, whose synthesis would be hampered due to the difficulty of preparing the necessary aryl bromide starting material, would be directly approachable using organomanganese arene chemistry. In employing this synthetic methodology, we envisioned the establishment of the critical carbon-carbon bond between C-2″ and C1′ by the addition of metallated benzofuran **2** to organomanganese arene complexes **3** (Scheme 1). Although we anticipated the addition would be directed *meta* by the two methoxy groups on the arene, we also recognized that the presence of additional methyl groups on the arene was a confounding variable. This paper describes the synthesis of 2-arylbenzofurans **1a-d** as a test for this synthetic methodology, and in doing so, has clarified the structure of stemofuran L.

2. Results and discussion

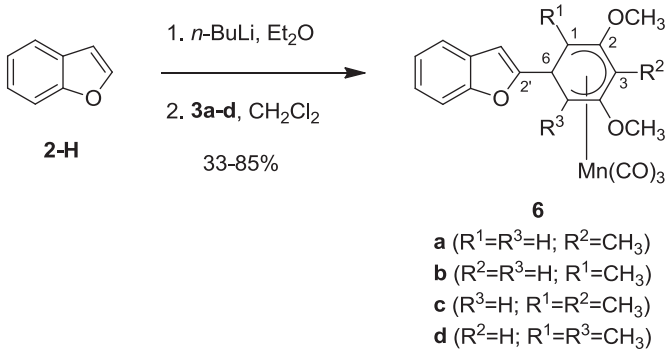
The required arenes were either commercially available (**4a** and **4b**) or were prepared according to literature procedures (**4c** [13] and **4d** [14]). In attempting to prepare η^6-organomanganese arene complexes **3a** and **3b** by the complexation of the arene (**4a** and **4b**) using the $AgBF_4/Mn(CO)_5Br$ method, our yields were low (10–30%). As an alternative approach, we investigated the utility of η^6-(polyarene)$Mn(CO)_3^+$ complexes as manganese tricarbonyl transfer reagents [15]. The reaction of acenaphthene complex **5** with 1.5 equivalents of arene **4** gave excellent yields (91–96%) of the corresponding organomanganese arene complexes **3** (Scheme 2) that were spectroscopically pure (>90%). Attempts to purify these complexes invariably led to small amounts of decomplexation and decomposition, so complexes **3** were used without purification in the next step.



Scheme 1. Retrosynthetic analysis.

Two primary variables were explored in the addition of metallated benzofuran **2** to arene complexes **3** to give η^5-dienyl complexes **6**: solvent (Et_2O, THF, CH_2Cl_2 and combinations thereof) and the nature of the metal (Li or Mg). When reactions were conducted in Et_2O or THF, there was a problem achieving full conversion of the starting material. In using the conditions we previously found most advantageous for the synthesis of stilbenes (lithiation followed by transmetallation with $Mg(OEt_2)_2$ [4b]), there was no reaction. The best yields were obtained using the procedure described for the addition of MeLi and PhLi to η^6-(3-methoxyestrone)$Mn(CO)_3^+$ [3b]. The addition of lithiated benzofuran prepared in Et_2O to a solution of the η^6-arene complexes **3** in CH_2Cl_2 gave fair to good yields (33–85% yield) of the η^5-dienyl complexes **6** (Scheme 3). Examination of the crude reaction mixtures indicated greater than 90% selectivity for *meta*-addition of the benzofuran moiety to the two methoxy substituents, although our analysis was hampered by the inherent broadness of the NMR peaks of these crude products (we were unable to isolate and characterize any other η^5-dienyl complexes besides **6**). The major competing pathway that accounted for some but not all of the yield loss was the decomplexation of the arene, which led to recovery of arenes **4**. Single crystal X-ray diffraction analysis of η^5-dienyl complexes **6a**, **6b**, and **6d** clearly showed the addition of the nucleophile occurred at the *meta*-position to the two methoxy substituents as well as *exo* to manganese (Fig. 2). The $Mn(CO)_3$ tripod eclipsed the two methoxy substituents and C6, an orientation typical of η^5-dienyl manganese complexes [3b,5c]. Selected bond lengths and angles for complexes **6a**, **6b**, and **6d** are given in Table 1.

Several oxidants have proved useful for the rearomatization and



Scheme 3. Synthesis of complexes **6**.

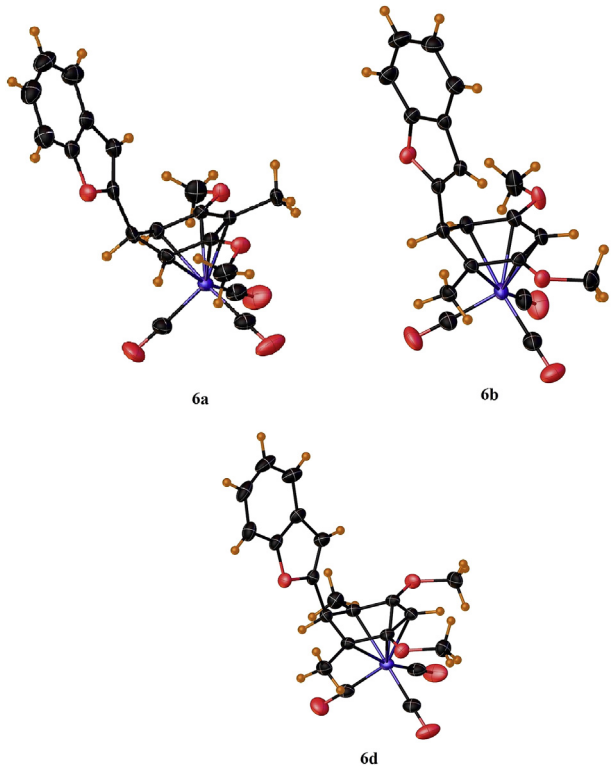


Fig. 2. X-ray crystal structures of complexes **6a**, **6b**, and **6d**. Thermal ellipsoids shown at 50% probability.

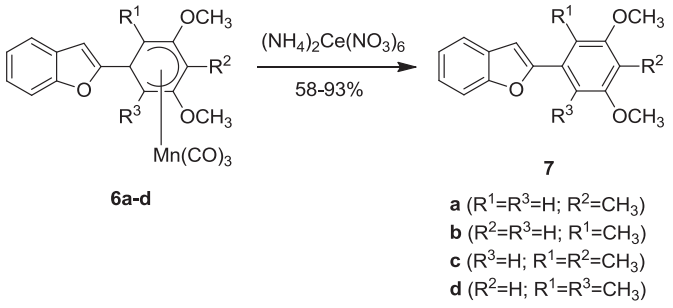
Table 1
Select bond lengths and angles for **6a**, **6b**, and **6d**.

	6a	6b	6d
Bond length (Å)			
C6-C1	1.505(2)	1.515(2)	1.5194(19)
C1-C2	1.396(2)	1.406(2)	1.396(2)
C2-C3	1.428(2)	1.422(2)	1.4272(19)
C1-Mn	2.1895(16)	2.2052(14)	2.2288(13)
C2-Mn	2.1807(15)	2.1890(14)	2.1870(13)
C3-Mn	2.1577(15)	2.1459(14)	2.1408(13)
Bond angle (°)			
C6-C1-C2	118.59(14)	116.94(12)	117.42(12)
C1-C2-C3	120.38(14)	120.33(13)	120.56(22)
C2′-C6-C1	115.66(14)	113.65(12)	115.93(11)
Torsional angle (°)			
C6-C1-C2-C3	30.6(2)	30.41(19)	28.60(18)

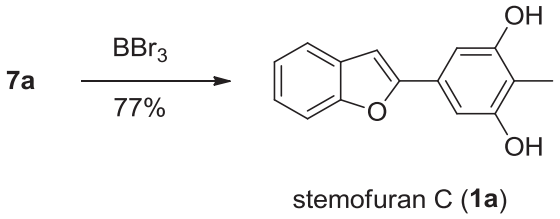
decomplexation of η^5-dienyl manganese complexes. In using either Jones reagent [3] or DDQ [4b], we obtained the desired products **7** but there were contamination issues that were difficult to resolve. The reaction of **6** with ceric ammonium nitrate (CAN) [5b], however, cleanly gave **7** in good yields (58–93%; Scheme 4).

The synthesis of stemofurans **1** from dialkoxyarenes **7** requires the cleavage of one or both of the methoxy groups to give phenolic group(s). Several reagents have been shown to be effective for this transformation including BBr_3, BCl_3, $LiPPh_2$, and Me_3SiI. In the case of **7a**, Lee [11a] used BBr_3 as the cleavage reagent for the conversion of **7a** to stemofuran C (**1a**; 92% yield), which we verified to be an effective reagent albeit under more vigorous conditions and in slightly lower yields (77% yield; Scheme 5).

The synthesis of stemofuran T [9e] required the cleavage of the methoxy group at the C-3′ position of **7b**, which we had hoped would be achieved employing reagents such as BCl_3 [13] and Me_3SiI



Scheme 4. Oxidation of complexes **6**.

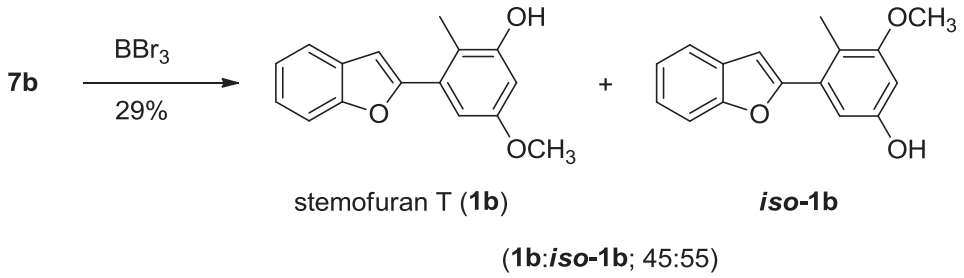


Scheme 5. Synthesis of stemofuran C (**1a**).

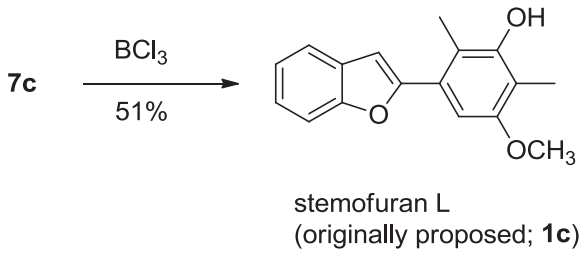
[16], known to effect selective cleavage of the more hindered alkoxy group. All of our attempts to selectively produce stemofuran T (**1b**) met with failure; we invariably produced equal or greater yields of ***iso*-1b**. Since there was also a balance between conversion and cleavage of both methoxy groups to yield the diphenolic compound, the best reaction conditions only gave a low yield of a mixture of **1b** and ***iso*-1b** (29% yield; Scheme 6). Unfortunately, we were unable to achieve separation of the mixture either by flash chromatography or recrystallization.

The synthesis of **1c**, reportedly isolated and identified from *Stemona curtisii* [9c], was achieved by the use of BCl_3, which has been reported to be a very selective cleavage reagent in a notable methodology study [13]. When **7c** was reacted with an excess of BCl_3 for 2 days, **1c** was isolated in 51% yield (Scheme 7). The crude reaction mixture contained only **1c** and unreacted **7c**, indicating a very high selectivity for the cleavage of the sterically hindered C-3′ methoxy group. In examining the ^1H and ^{13}C NMR spectra of **7c**, however, there were serious inconsistencies with the reported chemical shifts for stemofuran L as described in the original study [9c], indicating that the structural assignment was mistaken. In considering possible alternative structural assignments for stemofuran L, we hypothesized that **1d** was a likely candidate based on the spectroscopic evidence.

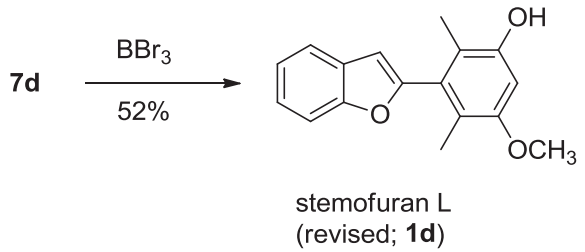
The synthesis of **1d** was readily accomplished by the reaction of **7d** with a slight excess of BBr_3, giving the desired compound **1d** (52% yield) as well as recovered **7d** and a compound tentatively identified as the diphenolic compound (Scheme 8). In examining the ^1H and ^{13}C NMR spectra of **1d**, there was good agreement between the reported spectra for stemofuran L [9c] and **1d** (Table 2). The chemical shifts that were most diagnostic were of the C-1″ proton, the arene proton, and the methyl groups on the 2-aryl ring. The C-1″ proton shifts for stemofuran L and **1d** were 0.2 ppm upfield from **1c**; the proton chemical shifts for the arene proton of stemofuran L and **1d** were 0.4 ppm upfield from **1c**. In the ^{13}C NMR, the methyl groups of the 2-aryl ring exhibited a significant 4–5 ppm difference depending on whether they were in the C-2′/C-6′ or C-4′ position, a comparison that held when looking at the carbon chemical shift of the methyl groups of **7c** and **7d** as well.



Scheme 6. Synthesis of stemofuran T (**1b**).



Scheme 7. Synthesis of **1c**.



Scheme 8. Synthesis of **1d** (revised structure of stemofuran L).

Table 2
Comparison of select ^{1}H and ^{13}C chemical shifts (ppm) of stemofuran L, **1c**, and **1d**.

C/H	Stemofuran L [9c]	**1c**	**1d**
C-1″ **H**	6.63	6.83	6.63
Ar**H**	6.51	6.92	6.52
OC**H**$_3$	3.82	3.78	3.88
ArC**H**$_3$'s	2.01, 1.98	2.40, 2.19	2.03, 1.99
OC**H**$_3$	55.9	55.7	55.9
ArC**H**$_3$	12.9, 12.6	13.2, 8.6	13.1, 12.7

3. Conclusion

The use of organomanganese arene complexes offers a simple synthetic strategy to prepare many naturally occurring 2-arylbenzofurans that is complementary to several current methods. The synthesis of **1c** and **1d**, which has clarified the structure of stemofuran L, exemplifies the power of organomanganese arene complexes to rapidly address issues in this field. Although our synthetic efforts focused on the stemofurans, the use of more substituted benzofurans and more elaborate arenes may provide access to functionally rich 2-arylbenzofurans such as the morusalfurans [10d] and lakoochins [10b]. The synthesis of stemofuran T (**1b**), in which we were unsuccessful in the selective cleavage of the methoxy groups of **7b**, underscores the need to distinguish between similar alkoxy groups earlier in the synthesis of **1b** and other related 2-arylbenzofurans.

4. Experimental

All reactions were carried out under Ar. All glassware were dried in the oven (110 °C) before use. IR spectra were obtained on a FT-IR spectrometer. The ^{1}H and ^{13}C NMR were recorded at 400 MHz and 100 MHz, respectively. All chemicals shifts in the ^{1}H NMR are reported in ppm relative to TMS ($\delta = 0.00$ ppm), $CHCl_3$ ($\delta = 7.26$ ppm), or CH_2Cl_2 ($\delta = 5.32$ ppm), and in the ^{13}C NMR are reported in ppm relative to $CDCl_3$ ($\delta = 77.16$ ppm) and CH_2Cl_2 ($\delta = 53.84$ ppm). Flash chromatography was performed on 60 Å silica gel (40–75 μm) or neutral alumina. Et_2O was distilled from sodium benzoketyl. Methylene chloride and THF were dried over molecular sieves. 2,6-dimethoxytoluene (**4a**) and 2,4-dimethoxytoluene (**4b**) were purchased from commercial sources. 1,5-dimethoxy-2,4-dimethylbenzene (**4d**) [14] and acenaphthene complex **5** [15b] were prepared according to the literature.

Crystals of **6a**, **6b**, and **6d** for X-ray diffraction analysis were prepared by slow evaporation from a heptane/Et_2O solution. X-ray data were acquired at 173 K on a Bruker D8 Quest Eco diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and PHOTON 50™ CMOS (**c**omplementary **m**etal-**o**xide **s**emiconductor) detector. The Bruker Apex 3 suite of programs was used to collect diffraction data [17]. The data reduction software package Bruker SAINT+ [18] was used for to integrate the frames with a narrow-frame algorithm and the multi-scan method (SADABS) [19] was used to correct the data for absorption effects. Processing of data was carried out with the Olex2 suite of programs [20]. The Bruker SHELXTL software package [21] was used to perform structure solution by direct methods, and refinement by full-matrix least-squares on F^2. All nonhydrogen atoms were refined anisotropically with suggested weighting factors and the hydrogens were calculated on a riding model. All cif files were validated with the checkCIF/Platon facility of IUCr that was accessed with Olex2 [20]. X-ray graphics were also produced with Olex2 [20].

4.1. 1,3-dimethoxy-2,4-dimethylbenzene (*4c*) [13]

To a stirred solution of 3-bromo-2,6-dimethoxytoluene [22] (8.68 g, 37.6 mmol) in ether (80 mL) at −78 °C was added *n*-BuLi (1.6 M in hexane, 26.0 mL, 41.4 mmol) over 5 min. The reaction mixture was stirred for 30 min at −78 °C and allowed to warm to ambient temperature over 30 min. The solution was cooled to −78 °C and methyl iodide (10 mL, 160 mmol) was added over 10 min. The solution was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was transferred with Et_2O (50 mL), washed with water (200 mL), brine (100 mL) and dried over Na_2SO_4. The volatiles were removed on the rotary evaporator to give 5.06 g (81%) of **4c** as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, $J = 8.1$ Hz, 1H), 6.56 (d, $J = 8.4$ Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 2.23 (s, 3H), 2.16 (s, 3H).

4.2. General procedure for the synthesis of **3a-d**

To a solution of acenaphthene complex **5** (3.80 g, 10.0 mmol) in CH_2Cl_2 (50 mL) at 22 °C was added arene **4** (15 mmol) in one portion. The reaction mixture was heated to reflux for 20 h, cooled to room temperature, and Et_2O (150 mL) was added, which precipitated **3**. Complex **3** was filtered and washed with Et_2O (2 × 50 mL) to give **3** as a yellow solid. Although the complexes were characterized by spectroscopic means, they gave unsatisfactory C,H microanalysis. Attempts to purify them by recrystallization invariably led to some decomposition, so they were used for the next reaction as isolated from the initial reaction.

4.2.1. η^6-(2,6-dimethoxytoluene)manganese tricarbonyl tetrafluoroborate (**3a**)

Yield: 3.63 g; 96%; IR (CH_2Cl_2) 2070, 2004 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 6.87 (t, $J = 6.8$ Hz, 1H), 5.99 (d, $J = 7.0$ Hz, 2H), 4.10 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 216.2, 149.4, 101.6, 89.4, 72.8, 59.0, 9.4.

4.2.2. η^6-(2,4-dimethoxytoluene)manganese tricarbonyl tetrafluoroborate (**3b**)

Yield: 3.58 g; 94%; IR (CH_2Cl_2) 2075 cm^{-1}, 1999 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 6.68 (d, $J = 7.0$ Hz, 1H), 5.92 (d, $J = 2.2$ Hz, 1H), 5.74 (dd, $J = 2.2$, 7.3 Hz, 1H), 4.10 (s, 3H), 4.06 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 215.5, 149.4, 148.9, 104.4, 104.3, 93.4, 72.7, 68.0, 58.6, 14.7.

4.2.3. η^6-(1,3-dimethoxy-2,4-dimethylbenzene)manganese tricarbonyl terafluoroborate (**3c**)

Yield: 3.67 g. 94%; IR (CH_2Cl_2) 2071, 2009 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 6.69 (d, $J = 7.3$ Hz, 1H), 6.03 (d, $J = 7.0$ Hz, 1H), 4.08 (s, 3H), 3.97 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 215.8, 147.7, 145.8, 101.8, 100.0, 96.6, 75.1, 62.6, 59.1, 15.6, 10.5.

4.2.4. η^6-(1,3-dimethoxy-2,6-dimethylbenzene)manganese tricarbonyl terafluoroborate (**3d**)

Yield: 3.56 g, 91%; IR (CH_2Cl_2) 2065, 2001 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 6.47 (s, 1H), 6.22 (s, 1H), 4.20 (s, 6H), 2.22 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 216.3, 147.8, 106.5, 91.5, 65.6, 59.1, 14.8.

4.3. General procedure for the synthesis of **6a, b and d**

A solution of benzofuran (0.63 mL, 0.68 g, 5.7 mmol) in Et_2O (20 mL) was cooled to 0 °C and *n*-BuLi (3.0 mL, 1.6 M, 4.8 mmol) was added dropwise over a few minutes and allowed to stir for 2 h at 0 °C. The solution of lithiated benzofuran was added to a solution of **3** (3.22 mmol) in CH_2Cl_2 (25 mL) cooled to −78 °C. After stirring for 45 min at −78 °C, the dry ice-acetone bath was removed and the reaction mixture was allowed to warm to room temperature over 1 h. The reaction mixture was quenched with saturated NH_4Cl (20 mL), transferred to a separatory funnel with additional EtOAc (50 mL), separated, the aqueous extracted with EtOAc (2 × 75 mL), and the combined organic phases were washed with brine (100 mL) and dried over Na_2SO_4. The volatiles were removed on the rotary evaporator to give the crude product, which was purified by column chromatography (hexanes → 25% EtOAc/hexanes) to give **6** as a yellow solid. Further purification by recrystallization with petroleum ether was necessary for **6b**.

4.3.1. 6-(2-benzofuranyl)-2,4-dimethoxy-3-methylcyclohexadienylmanganese tricarbonyl (**6a**)

Yield: yellow solid (0.737 g, 53% yield based on 1.266 g (3.22 mmol) of **3a**). IR (CH_2Cl_2) 2011, 1929 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, $J = 7.0$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.20 (t, $J = 7.0$ Hz, 1 H), 7.16 (t, $J = 7.2$ Hz, 1H), 6.02 (s, 1H), 3.95 (t, $J = 6.0$ Hz, 1H), 3.46 (s, 6H), 3.20 (d, $J = 6.2$ Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 220.9 (br), 162.5, 154.9, 141.1, 128.6, 124.1, 123.0, 121.1, 111.4, 100.7, 77.3, 55.3, 37.1, 36.6, 9.8; HRMS (DART-TOF, MH^+): found 409.0486. $C_{20}H_{18}MnO_6$ requires 409.0484.

4.3.2. 6-(2-benzofuranyl)-2,4-dimethoxy-1-methylcyclohexadienylmanganese tricarbonyl (**6b**)

Yield: yellow solid (0.915 g, 66% yield based on 1.27 g (3.23 mmol) of **3b**). IR (CH_2Cl_2) 2012, 1925 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.44 (m, 1H), 7.37 (d, $J = 8.0$ Hz, 1H) 7.23–7.13 (m, 2H), 6.13 (s, 1H), 5.75 (d, $J = 1.8$ Hz, 1H), 4.04 (d, $J = 6.2$ Hz, 1H), 3.84 (s, 3H), 3.50 (s, 3H), 3.32 (dd, $J = 2.2$, 6.2 Hz, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 220.1 (br), 160.8, 154.9, 140.3, 137.3, 128.6, 124.2, 123.0, 121.1, 111.4, 101.3, 56.1, 55.3, 55.1, 44.0, 39.1, 16.7; HRMS (DART-TOF, MH^+): found 409.0481. $C_{20}H_{18}MnO_6$ requires 409.0484.

4.3.3. 6-(2-benzofuranyl)-2,4-dimethoxy-1,3-dimethylcyclohexadienylmanganese tricarbonyl (**6d**)

Yield: yellow solid (0.450 g, 33% yield based on 1.313 g (3.23 mmol) of **3d**.) IR (CH_2Cl_2) 2007, 1925 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, $J = 7.9$ Hz, 1H), 7.36 (d, $J = 7.9$ Hz, 1H), 7.21–7.12 (m, 2H), 6.12 (s, 1H), 5.60 (s, 1H), 3.96 (s, 1H), 3.84 (s, 6H), 1.70 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 220.5 (br), 159.6, 154.9, 136.0, 128.6, 124.1, 121.0, 111.4, 101.7, 55.3, 54.9, 51.2, 50.5, 16.6; HRMS (DART-TOF, MH^+): found 423.0636. $C_{21}H_{20}MnO_6$ requires 423.0640.

4.3.4. 6-(2-benzofuranyl)-2,4-dimethoxy-3,5-dimethylcyclohexadienylmanganese tricarbonyl (**6c**)

To a solution of benzofuran (0.25 mL, 0.27 g, 2.3 mmol) in Et_2O (20 mL) was added *n*-BuLi (1.2 mL, 1.6 M, 1.9 mmol) over 5 min at 0 °C and stirred for 2 h at 0 °C. The lithiated benzofuran solution was added via a cannula to a solution of **3c** (0.511 g, 1.26 mmol) in CH_2Cl_2 (10 mL) cooled to −78 °C. The reaction was allowed to stir at −78 °C for 1 h, warmed to 0 °C, and stirred for 15 min. The reaction was quenched with water (5 mL), extracted with Et_2O (50 mL), the organic phase was washed with brine (50 mL), dried over Na_2SO_4, and the volatiles were removed on the rotary evaporator to give the crude product. The product was dissolved in Et_2O and filtered through a plug of silica gel. Further purification by recrystallization from petroleum ether gave **6c** as a yellow solid (0.45 g, 85% yield). IR (CH_2Cl_2) 2010, 1930 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 7.7$ Hz, 1H), 7.23–7.14 (m, 2H), 6.10 (s, 1H), 3.89 (d, $J = 5.9$ Hz, 1H), 3.63 (s, 3H), 3.42 (s, 3H), 3.14 (d, $J = 6.2$ Hz, 1H), 2.55 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 223.3, 160.8, 154.8, 139.3, 136.4, 128.6, 124.2, 123.1, 121.2, 111.3, 101.0, 78.7, 62.0, 59.7, 55.2, 43.3, 35.6, 17.3, 10.2. HRMS (DART-TOF, MH^+): found 423.0641. $C_{21}H_{20}MnO_6$ requires 423.0640.

4.4. General procedure for the synthesis of **7a-d**

A mixture of sodium acetate (1.20 g, 14.6 mmol) and **6a** (0.600 g, 1.47 mmol) in acetone (60 mL) was stirred rapidly as ceric ammonium nitrate (4.52 g, 8.24 mmol) was added in 0.2–0.4 g portions every 5 min. The reaction was stirred until TLC indicated that all of the starting material **6a** had reacted, usually within 15–30 min. The reaction was quenched with water (20 mL) and extracted with 1:1 mixture of hexanes:ethyl acetate (2 × 80 mL; hexanes were used for **7b**). The volatiles were removed on the rotary evaporator to give the crude product. The crude product was redissolved in a 1:1 mixture of hexanes:ether and filtered through a plug of silica gel to

give **7a** as a tan solid (0.353 g, 90% yield). Both compounds **7a** and **7b** required no further purification but flash chromatography was necessary for **7c** (hexanes→40% toluene/hexanes) and **7d** (hexanes→10% EtOAc/hexanes).

*4.4.1. 2-(3,5-dimethoxy-4-methylphenyl)benzofuran **7a** [11a]*

Yield: tan solid (0.353 g, 90% yield based on 0.600 g (1.25 mmol) of **6a**): mp 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.30–7.21 (m, 2H), 7.04 (s, 2H), 7.00 (s, 1H), 3.93 (s, 6H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 156.5, 154.8, 129.4, 128.8, 124.2, 123.0, 120.9, 115.7, 111.2, 101.0, 100.6, 56.0, 8.5.

*4.4.2. 2-(3,5-dimethoxy-2-methylphenyl)benzofuran (**7b**)*

Yield: yellow solid (0.312 g, 93% yield based on 0.511 g (1.25 mmol) of **6b**). IR (CH_2Cl_2) 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.3 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.32–7.22 (m, 2H), 6.94 (d, J = 2.6 Hz, 1H), 6.87 (s, 1H), 5.52 (d, J = 2.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.0, 158.4, 155.7, 154.4, 131.5, 129.2, 124.3, 122.9, 121.1, 117.7, 111.2, 105.9, 104.0, 99.3, 55.9, 55.4, 13.0; HRMS (DART-TOF, MH$^+$): found 269.1178. $C_{17}H_{17}O_3$ requires 269.1172.

*4.4.3. 2-(3,5-dimethoxy-2,4-dimethylphenyl)benzofuran (**7c**)*

Yield: white solid (0.157 g, 79% yield based on 0.300 g (0.711 mmol) of **6c)**; mp 93–94 °C. IR (CH_2Cl_2) 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.0 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.31–7.22 (m, 2H), 7.12 (s, 1H), 6.86 (s, 1H), 3.90 (s, 3H), 3.74 (s, 3H), 2.43 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 156.6, 155.8, 154.4, 129.3, 128.7, 124.3, 122.9, 121.7, 121.0, 120.7, 111.2, 106.1, 105.3, 60.3, 55.9, 13.8, 9.5; HRMS (DART-TOF, MH$^+$): found 283.1333. $C_{18}H_{19}O_3$ requires 283.1334.

*4.4.4. 2-(3,5-dimethoxy-2,6-dimethylphenyl)benzofuran (**7d**)*

Yield: yellow oil (0.116 g, 58% yield based on 0.300 g (0.711 mmol) of **6d**). IR (CH_2Cl_2) 1592 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.31–7.24 (m, 2H), 6.63 (d, J = 0.7 Hz, 1H), 6.58 (s, 1H), 3.87 (s, 6H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 154.9, 154.8, 132.5, 128.7, 123.9, 122.8, 120.9, 119.2, 111.4, 106.4, 96.9, 56.1, 13.0; HRMS (DART-TOF, MH$^+$): found 283.1333. $C_{18}H_{19}O_3$ requires 283.1334.

*4.5. Stemofuran C (**1a**) [9a]*

To a solution of **7a** (0.294 g, 1.10 mmol) in CH_2Cl_2 (15 mL) was added BBr_3 (5 mL, 1 M in CH_2Cl_2, 5 mmol) dropwise over 2 min at 0 °C. The reaction mixture was stirred for 5 min at 0 °C and then at 22 °C for 16 h. The reaction was quenched with ice water (15 mL), the aqueous phase was extracted with additional CH_2Cl_2 (3 × 30 mL), the combined organic phases were dried over Na_2SO_4, and the volatiles were removed on the rotary evaporator to give the crude product. Purification by flash chromatography (silica gel; hexanes→25% ethyl acetate/hexanes) gave **1a** as a beige solid (0.202 g, 77% yield): mp 200–201 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.39 (s, 2H), 7.59 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.28 (dt, J = 1.5, 7.7 Hz, 1H), 7.22 (dt, J = 1.1, 7.5 Hz, 1H), 7.04 (s, 1H), 7.01 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 157.6, 157.2, 155.4, 130.2, 129.1, 124.9, 123.8, 121.7, 113.1, 111.6, 104.1, 101.4, 8.7.

*4.6. Stemofuran T (**1b**) [9e]*

BBr_3 (2.2 mL, 1.0 M in CH_2Cl_2, 2.2 mmol) was added dropwise to a solution of **7b** (0.4894 g, 1.82 mmol) in CH_2Cl_2 (40 mL) at 0 °C. The reaction mixture was removed from the ice-water bath and stirred at 22 °C for 1 h, then re-cooled to 0 °C and stirred for 2 h. The reaction mixture was quenched with water (60 mL), the phases separated, and the aqueous phase was extracted with additional CH_2Cl_2 (50 mL). The organic layers were dried over Na_2SO_4 and the volatile solvents were removed on the rotary evaporator. The resulting crude product was purified by flash chromatography (toluene → 5% EtOAc/toluene) to give a 45:55 mixture of **1b** and ***iso*-1b** (0.131 g, 29% yield) as a white solid. For **1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.33–7.23 (m, 2H), 6.89 (d, J = 2.6 Hz, 1H), 6.87 (s, 1H), 6.48 (d, J = 2.6 Hz, 1H), 4.96 (s, 1H), 3.86 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.3, 155.5, 155.3, 154.4, 131.7, 129.2, 124.4, 123.0, 121.1, 117.5, 111.3, 106.8, 106.0, 99.4, 55.9, 13.0. For ***iso*-1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.33–7.23 (m, 2H), 6.95 (d, J = 2.6 Hz, 1H), 6.87 (s, 1H), 6.47 (d, J = 2.6 Hz,1H), 5.02 (s, 1H), 3.83 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.3, 155.1, 154.5, 154.2, 132.2, 129.1, 124.4, 123.9, 121.1, 114.8, 111.2, 106.3, 105.8, 102.5, 55.6, 12.8.

*4.7. Stemofuran L (originally proposed; **1c**)*

To a solution of 2-(3′,5′-dimethoxy-2′,4′-methylbenzene) benzofuran (**11b**) (62.8 mg, 0.22 mmol) in CH_2Cl_2 (0.5 mL) was added BCl_3 (1.0 mL, 1.0 M in CH_2Cl_2, 1.0 mmol). The reaction mixture was stirred at room temperature for 50 h, and then the reaction was quenched with water (10 mL). Et_2O (10 mL) and NaOH (4 mL, 0.25 M) were added, the phases separated, aqueous was extracted with additional Et_2O (5 mL). The combined organic layers were washed with HCl (5 mL, 1.0 M), dried over Na_2SO_4, and volatile solvents were removed on the rotary evaporator to afford a mixture of **1c** and starting material **7c**. The crude product was purified by column chromatography (hexanes → 20% EtOAc/hexanes) to give **1c** (30 mg, 51% yield) as a tan solid; mp 97–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.32–7.23 (m, 2H), 6.92 (s, 1H), 6.83 (d, J = 0.8 Hz, 1H), 4.84 (s, 1H), 3.88 (s, 3H), 2.40 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 156.0, 154.5, 153.1, 129.3, 128.6, 124.2, 122.9, 121.0, 114.7, 112.5, 111,2, 105.3, 103.3, 55.9, 13.2, 8.6; HRMS (DART-TOF, MH$^+$): found 269.1177. $C_{17}H_{17}O_3$ requires 269.1178.

*4.8. Stemofuran L (revised; **1d**) [9c]*

BBr_3 (1.0 M in THF, 1.0 mL, 1.0 mmol) was added to **7d** (0.266 g, 0.94 mmol) in CH_2Cl_2 (10 mL) at 0 °C over 15 min. The reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 15 min. Additional CH_2Cl_2 (40 mL) was added to the reaction mixture, which was quenched with water (20 mL), separated, and the organic phase was dried over Na_2SO_4. The volatile solvents were removed on the rotary evaporator, and the crude material was purified by column chromatography (hexanes→40% EtOAc/hexanes) to isolate **1d** (0.138 g, 52%); mp 61–63 °C. IR (CH_2Cl_2) 1599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.32–7.23 (m, 2H), 6.63 (s, 1H), 6.52 (s, 1H), 4.72 (s, 1H), 3.82 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 154.9, 154.6, 152.3, 132.5, 128.8, 124.0, 122.9, 121.0, 119.9, 115.4, 111.4, 106.5, 100.1, 55.9, 13.1, 12.7; HRMS (DART-TOF, MH$^+$): found 269.1176. $C_{17}H_{17}O_3$ requires 269.1178.

Acknowledgements

Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for support of this research. We gratefully acknowledge a grant from the Kresge Foundation for the purchase a 400 MHz NMR spectrometer.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2017.09.034.

References

[1] (a) M. Rosillo, G. Dominguez, J. Perez-Castells, Chromium arene complexes in organic synthesis, J. Chem. Soc. Rev. 36 (2007) 1589–1604;
(b) S.H. Sun, C.A. Dullaghan, D.A. Sweigart, The versatile chemistry of arene-manganese carbonyl complexes, J. Chem. Dalt. Trans. (1996) 4493–4507;
(c) F. Hu, M. Szostak, Pd-catalyzed C-H activation: expanding the portfolio of metal-catalyzed functionalization of unreactive C-H bonds by arene–chromium π-complexation, ChemCatChem 7 (2015) 1061–1063.

[2] P.L. Pauson, J.A. Segal, Formation of substituted cyclohexadienyl tricarbonylmanganese complexes by nucleophilic-addition reactions of functionally substituted (η-arene)tricarbonylmanganese cations, J. Chem. Dalt. Trans. (1975) 1683–1686.

[3] (a) Y.K. Chung, P.G. Williard, D.A. Sweigart, Addition of Grignard reagents and ketone enolates to the arene in (arene)manganese tricarbonyl cations, Organometallics 1 (1982) 1053–1056;
(b) Y. Cao, K. Woo, L.K. Yeung, G.B. Carpenter, D.A. Sweigart, Nucleophilic addition reactions and functionalization of (3-methoxyestrone)- and (3,17-dimethoxyestradiol)manganese tricarbonyl complexes, Organometallics 16 (1997) 178–183.

[4] (a) W.H. Miles, P.M. Smiley, H.R. Brinkman, The reaction of chiral nucleophiles with organomanganese arene complexes, J. Chem. Soc. Chem. Comm. (1989) 1897–1899;
(b) G.R. Krow, W.H. Miles, P.M. Smiley, W.S. Lester, Y.J. Kim, Synthesis of antibiotic stilbenes using organomanganese arene complexes, J. Org. Chem. 57 (1992) 4040–4043.

[5] (a) A.J. Pearson, P.R. Bruhn, F. Gouzoules, S.H. Lee, Stereoselective synthesis of arylglycine derivatives using arenemanganese tricarbonyl complexes, J. Chem. Soc. Chem. Comm. (1989) 659–661;
(b) A.J. Pearson, I.C. Richards, Preparation and reactivity of η^6-veratrolemanganese tricarbonyl tetrafluoroborate, J. Organomet. Chem. 258 (1983) C41–C44;
(c) A.J. Pearson, P.Y. Zhu, W.J. Youngs, J.D. Bradshaw, D.B. McConville, Chiral auxiliary-directed asymmetric nucleophile additions to arene-manganese tricarbonyl complexes, J. Am. Chem. Soc. 115 (1993) 10376–10377.

[6] R.P. Alexander, G.R. Stephenson, Reversal of regiocontrol in the alkylation of an arene π-complex, J. Organomet. Chem. 314 (1986) C73–C75.

[7] F. Rose-Munch, K. Aniss, Cationic arenetricarbonylmanganese complexes: nucleophilic aromatic addition, Tetrahedron Lett. 31 (1990) 6351–6354.

[8] (a) A. Hiremathad, M.R. Patil, K.R. Chethana, K. Chand, M.A. Santos, R.S. Keri, Benzofuran: an emerging scaffold for antimicrobial agents, RSC Adv. 5 (2015) 96809–96828;
(b) R.J. Nevagi, S.N. Dighe, Biological and medicinal significance of benzofuran, Eur. J. Med. Chem. 97 (2015) 561–581.

[9] (a) H. Greger, The diversity of *Stemona* stilbenoids as a result of storage and fungal infection, J. Nat. Prod. 75 (2012) 2261–2268;
(b) T. Pacher, C. Seger, D. Engelmeier, S. Vajrodaya, O. Hofer, H. Greger, Antifungal stilbenoids from *Stemona collinsae*, J. Nat. Prod. 65 (2002) 820–827;
c) S. Chaiyong, A. Jatisatienr, P. Mungkornasawakul, T. Sastraruji, S.G. Pyne, A.T. Ung, T. Urathamakul, W. Lie, Phytochemical investigations of *Stemona curtisii* and synthetic studies on stemocurtisine alkaloids, J. Nat. Prod. 73 (2010) 1833–1838;
(d) T. Sastraruji, S. Chaiyong, A. Jatisatienr, S.G. Pyne, A.T. Ung, W. Lie, Phytochemical studies on *Stemona aphylla*: isolation of a new stemofoline alkaloid and six new stemofurans, J. Nat. Prod. 74 (2011) 60–64;
(e) A. Zraunig, T. Pacher, L. Brecker, H. Greger, Phenylbenzofuran-type stilbenoids from *Stemona* species, Phytochem. Lett. 9 (2014) 33–36;
(f) L. Han, Y.M. Ma, L. An, Q. Zhang, C.L. Wang, Q.C. Zhao, Non-alkaloids extract from *Stemona sessilifolia* enhances the activity of chemotherapeutic agents through P-glycoprotein-mediated multidrug-resistant cancer cells, Nat. Prod. Res. 30 (2016) 1186–1189.

[10] (a) R. Naik, D.S. Harmalkar, X. Xu, K. Jang, K. Lee, Bioactive benzofuran derivatives: moracins A-Z in medicinal chemistry, Eur. J. Med. Chem. 90 (2015) 379–393;
(b) A. Puntumchai, P. Kittakoop, S. Rajviroongit, S. Vimuttipong, K. Likhitwitayawuid, Y. Thebtaranonth, Lakoochins A and B, new antimycobacterial stilbene derivatives from *Artocarpus lakoocha*, J. Nat. Prod. 67 (2004) 485–486;
(c) Z.G. Yang, K. Matsuzaki, S. Takamatsu, S. Kitanaka, Inhibitory effects of constituents from *Morus alba* var. *multicaulis* on differentiation of 3T3-L1 cells and nitric oxide production in RAW264.7 cells, Molecules 16 (2011) 6010–6022;
(d) M.T. Ha, M.H. Tran, K.J. Ah, K.J. Jo, J. Kim, W.D. Kim, W.J. Cheon, M.H. Woo, S.H. Ryu, B.S. Min, Potential pancreatic lipase inhibitory activity of phenolic constituents from the root bark of Morus alba L, Bioorg. Med. Chem. Lett. 26 (2016) 2788–2794.

[11] (a) H.J. Lee, S.H. Kim, Y.R. Lee, X. Wang, W.S. Lyoo, Concise synthesis of stemofurans a, C, and derivatives, Bull. Korean Chem. Soc. 31 (2010) 3027–3030;
(b) D.Y. Wu, H.B. Mei, P. Tan, W.Q. Lu, J. Zhu, W. Wang, J. Huang, J. Li, Total synthesis of the 2-arylbenzo[b]furan-containing natural products from *Artocarpus*, Tetrahedron Lett. 56 (2015) 4383–4387;
(c) K. Damodar, J.K. Kim, J.G. Jun, Unified syntheses of gramniphenols F and G, cicerfuran, morunigrol C and its derivative, Tetrahedron Lett. 57 (2016) 1183–1186;
(d) D.H. Dethe, R.D. Erande, S. Mahapatra, S. Das, B.V. Kumar, Protecting group free enantiospecific total syntheses of structurally diverse natural products of the tetrahydrocannabinoid family, Chem. Commun. 51 (2015) 2871–2873;
(e) I.S. Mann, D.A. Widdowson, J.M. Clough, Transition-metal directed synthesis of moracin M, a phytoalexin of *Morus alba* Linn, Tetrahedron 47 (1991) 7981–7990;
(f) I.S. Mann, D.A. Widdowson, J.M. Clough, Transition-metal mediated synthesis of some prenylated phytoalexins of morus-alba linn, Tetrahedron 47 (1991) 7991–8000.

[12] See also (a) A.A. More, C.V. Ramana, o-Quinone methides via oxone-mediated benzofuran oxidative dearomatization and their intramolecular cycloaddition with carbonyl groups: an expeditious construction of the central tetracyclic core of integrastatins, epicoccolide A, and epicocconigrone A, Org. Lett. 18 (2016) 612–615;
(b) I. Kim, K. Kim, J. Choi, A direct approach to 5-hydroxybenzofurans via a platinum-catalyzed domino rearrangement/5-*endo*-*dig* cyclization reaction of quinols, J. Org. Chem. 74 (2009) 8492–8495;
(c) J.J. Lee, S.R. Yun, J.G. Jun, Facile synthesis of natural moracin compounds using $Pd(OAc)_2/p(^tBu)_3$-HBF_4 as a Sonogashira coupling reagent, Bull. Korean Chem. Soc. 35 (2014) 3453–3458;
(d) H. Nambu, N. Ono, T. Yakura, Acid-catalyzed ring-opening cyclization of spirocyclopropanes for the construction of a 2-arylbenzofuran skeleton: total synthesis of cuspidan B, Synthesis 48 (2016) 1892–1901;
(e) J.A. Celaje, D. Zhang, A.M. Guerrero, M. Selke, Chemistry of *trans*-resveratrol with singlet oxygen: [2+2] addition, [4+2] addition, and formation of the phytoalexin moracin M, Org. Lett. 13 (2011) 4846–4849;
(f) R. Ghosh, E. Stridfeldt, B. Olofsson, Metal-free one-pot synthesis of benzofurans, Chem. Eur. J. 20 (2014) 8888–8892.

[13] C.F. Carvalho, A.V. Russo, M.V. Sargent, Boron-trichloride as a selective demethylating agent for hindered ethers, Aust. J. Chem. 38 (1985) 777–792.

[14] A. Bugarin, B.T. Connell, Chiral nickel(ii) and palladium(ii) NCN-pincer complexes based on substituted benzene: synthesis, structure, and Lewis acidity, Organometallics 27 (2008) 4357–4369.

[15] (a) M. Oh, J.A. Reingold, G.B. Carpenter, D.A. Sweigart, Manganese tricarbonyl transfer (MTT) reagents in the construction of novel organometallic systems, Coord. Chem. Rev. 248 (2004) 561–569;
(b) S.H. Sun, L.K. Yeung, D.A. Sweigart, T.Y. Lee, S.S. Lee, Y.K. Chung, S.R. Switzer, R.D. Pike, (η^6-Polyarene)$Mn(CO)_3^+$ complexes as manganese tricarbonyl transfer reagents - a convenient and general synthetic route to (arene)$Mn(CO)_3^+$ complexes, Organometallics 14 (1995) 2613–2615.

[16] M.E. Jung, M.A. Lyster, Quantitative dealkylation of alkyl ethers via treatment with trimethylsilyl iodide. A New Method for Ether Hydrolysis, J. Org. Chem. 42 (1977) 3761–3764.

[17] Bruker, APEX3. Version 2016.5-0, Bruker AXS, Inc, Madison, Wisconsin, USA, 2016.

[18] Bruker, SAINT+. Version 2016.5-0, Bruker AXS, Inc, Madison, Wisconsin, USA, 2015.

[19] L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D. Stalke, Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination, J. Appl. Crystallogr. 48 (2015) 3–10.

[20] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, J. Appl. Crystallogr. 42 (2009) 339–341.

[21] (a) G.M. Sheldrick, Crystal structure refinement with SHELXL, Acta Cryst. A 71 (2015) 3–8;
(b) G.M. Sheldrick, Crystal structure refinement with SHELXL, Acta Cryst. C 71 (2015) 3–8.

[22] D.C. Schlegel, C.D. Tipton, K.L. Rinehart, One-step monobromination of resorcinol ethers, J. Org. Chem. 35 (1970) 849.