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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo3022988 • Publication Date (Web): 28 Dec 2012

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Synthesis of Fused Bromofurans via Mg Mediated Dibromocyclopropanation of Cycloalkanone Derived Chalcones and Cloke-Wilson Rearrangement

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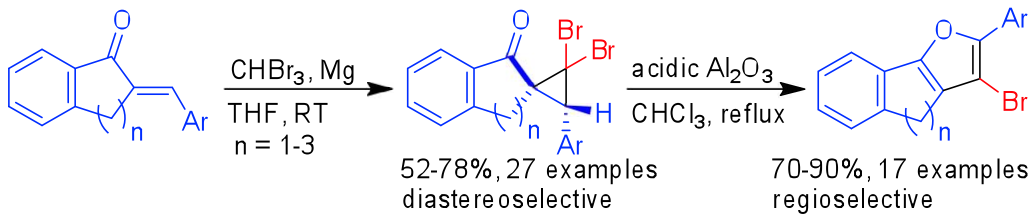


Abstract. A convenient two step sequence for the conversion of alkylidenecycloalkanones to bromofurans is reported. The steps involve Mg mediated diastereoselective dibromocyclopropanation of alkylidenecycloalkanone followed by acidic alumina mediated regioselective ring expansion of the cyclopropyl ketone. The scope of the reaction was investigated using alkylidenecycloalkanones derived from tetralone, indanone and benzosuberone to afford 2-aryl-3-bromofurans fused to various benzocycloalkanes. Representative examples of stereoconvergent dibromocyclopropanation and total aromatization of the furobenzocycloalkane are also reported.

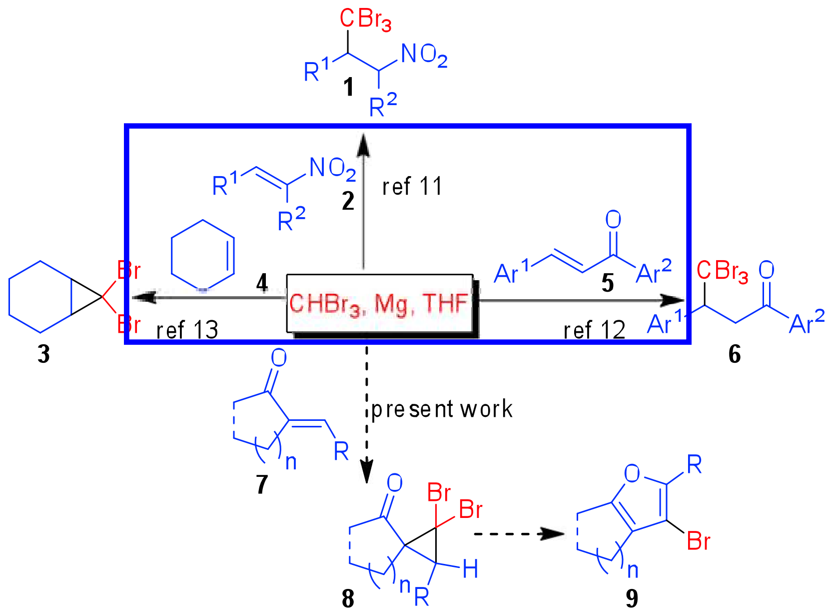
Introduction

Cyclopropane ring is an integral part of many natural products and drug molecules such as plant hormone precursor 1-aminocyclopropane-1-carboxylic acid (ACC), anticancer agent (+)-ptaquiloside, insecticide (+)-trans-chrysanthemic acid and renal dehydropeptidase inhibitor Cilastatin, to name a few.[1] Methods involving dihalocarbenes, diazoalkanes or sulfonium ylides are frequently used for the synthesis of cyclopropanes.[2] Cyclopropane derivatives have been employed as key scaffolds in the synthesis of complex heterocycles, for instance, pyrrolidine alkaloids.[3] Ring expansion of vinylcyclopropane to cyclopentene and cyclopropyl ketone to furan (Cloke-Wilson rearrangement) emerged as some of the elegant applications of the cyclopropane scaffold in natural product synthesis.[4] However, spirocyclopropanes, to which illudin class of anticancer natural products belong, have received less attention presumably due to inherent strain and poor stereoselectivity in the ring formation.[5]

Among the cyclopropanation methods, *gem*-dihalocyclopropanation, normally using haloform and a base, often under PTC conditions, has found applications in total synthesis and in a multitude of synthetic transformations such as chain elongation, ring cleavage, ring expansion etc.[6-7] However, ring expansion of dihalocyclopropyl ketones to (halo)furans has received only limited attention.[8] These include Banwell's base mediated conversion of alkoxydichlorocyclopropane to furan, Chen's Bronsted acid catalyzed transformation of difluorocyclopropyl ketone and carboxaldehyde to 3-fluorofuran, and Tanabe's and Dolbier's Lewis acid catalyzed ring expansion of dihalocyclopropyl ketones to 3-halofurans.[8] Furthermore, ring expansion of spirodihalocyclopropyl ketones to 3-halofurans remains unreported, to our knowledge. Owing to the synthetic and biological significance of furans,[9] such a regioselective ring expansion appeared an attractive approach to access functionalized and fused 3-halofurans.[10]

Recently, we reported the Mg mediated conjugate addition of bromoform to electron deficient alkenes such as nitroalkenes **2** and chalcones **5** (Scheme 1).[11-12] The Michael adducts **1** were transformed via HBr elimination to dibromomethylenated nitroalkanes which in turn were excellent partners in Suzuki coupling.[11] The Michael adducts **6**, on the other hand, were valuable precursors to dialkoxydihydrofurans and γ-ketoesters.[12] Herein, we report an efficient dibromocyclopropanation of α-substituted enones of type **7** under the above conditions to generate novel spirodibromocyclopropanes of type **8** and subsequent rearrangement of **8** to fused 3-bromofurans **9**.

Scheme 1



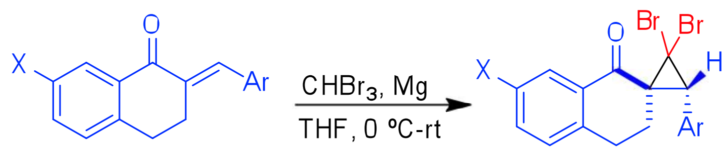
Results and Discussion

The optimized conditions for the conjugate addition of bromoform to nitroalkenes **2** and enones **5**, viz 22 equiv bromoform and 8 equiv Mg in THF, appeared suitable for the addition of bromoform to α-substituted enones of type **7** as well. Interestingly, when tetralone derivative **10a** was treated with bromoform in the presence of Mg in THF, we isolated dibromocyclopropane **11a** in 62% yield as the only product (Table 1, entry 1). We were pleased by this new product profile that emerged because although unactivated alkenes, e.g. **4**, were reported to give dibromocyclopropanes, e.g. **3**,[13] conjugated electron deficient alkenes such as **2** and **5**, including α-substituted nitroalkenes **2** ($R^2 \neq$ H) afforded exclusively the Michael adducts **1** and **6**, respectively (see Scheme 1).[11-12, 14]

In light of the above, we desired to investigate this Mg mediated dibromocyclopropanation in detail by screening different tetralone derivatives **10b-p** (Table 1, entries 2-17). In general, the cyclopropanation was complete in less than 5 h and the products were isolated in moderate to good yield (52-75%). Substrates with single and multiple electron donating groups on the aromatic ring β to carbonyl reacted with bromoform to afford cyclopropanes **11b-h** and **11p** in 60-73% yield (entries 2-8 and 17). Similarly, cyclopropanes were isolated in good yield when substrates with electron withdrawing β-aryl groups were reacted with bromoform (69-75%, entries 9-10). The products were isolated in good yield in the presence of unsubstituted β-aryl groups as well (Ph and naphthyl, 62-71%, entries 1 and 11). However, the reaction of bromoform with a β-heteroaryl enone **10l** (entries 12-13) and β-styrenyl enones **10m-o** (entries 14-16), could not be generalized. But nevertheless, these reactions gave us valuable insights into the mechanism of the dibromocyclopropanation as well as the potential of the dibromocyclopropyl ketones of type **8** to undergo ring expansion to afford synthetically and biologically relevant furans of type **9** (see Scheme 1).

First of all, when enone **10l** was treated with bromoform for a limited time (1.5 h) under our optimized conditions, the product isolated was not cyclopropane, but 1,4-adduct **12l** in 65% yield (Table 1, entry 12 and Figure 1). However, when the reaction was prolonged for 12 h in another experiment, we were pleased to isolate the cyclopropane **11l** in 60% yield (entry 13). This observation confirmed that dibromocyclopropanation of enones of type **7** took place via initial Michael addition followed by intramolecular cyclization.

Table 1. Mg Mediated Dibromocyclopropanation of Tetralones[a]



entry	**10**	X	Ar	**11**	time (h)	% yield[b]
1	**10a**	H	Ph	**11a**	1.5	62
2	**10b**	H	4-MePh	**11b**	1.5	73
3	**10c**	H	4-MeOPh	**11c**	1.5	68
4	**10d**	H	3-MeOPh	**11d**	1.5	71
5	**10e**	H	2,4-$(MeO)_2$Ph	**11e**	4	60
6	**10f**	H	3,4-$(MeO)_2$Ph	**11f**	1.5	65
7	**10g**	H	2,3,4-$(MeO)_3$Ph	**11g**	1.5	70
8	**10h**	H	3,4,5-$(MeO)_3$Ph	**11h**	1.5	71
9	**10i**	H	4-CF_3Ph	**11i**	1.5	69
10	**10j**	H	4-FPh	**11j**	1.5	75

11	**10k**	H	1-Naphthyl	**11k**	3.5	71
12	**10l**	H	2-furyl	**11l**	1.5	-[c]
13	**10l**	H	2-furyl	**11l**	12	60
14	**10m**	H	PhCH=CH	**11m**	4	69
15	**10n**	H	2-MeOPhCH=CH	**11n**	4.5	-[d]
16	**10o**	H	2-NO_2PhCH=CH	**11o**	4	52
17	**10p**	OMe	3,4-$(MeO)_2$Ph	**11p**	1.5	65

[a]Mg and bromoform were used in excess (8 atom g and 22 equiv, respectively). [b]Isolated yield after purification by silica gel column chromatography. [c] Michael adduct **12l** was isolated in 65% yield as a nearly single diastereomer (>95:5, inseparable), see Figure 1.[d] Rearranged product **13n** was isolated in 70% yield, see Figure 1.

While addition of bromoform to β-styrenyl enones **10m** and **10o** afforded the expected cyclopropanes in 69% and 52%, respectively (entries 14 and 16), we were pleasantly surprised to isolate the rearranged product **13n** in 70% yield when enone **10n** was treated with bromoform under our experimental conditions. This suggested that other dibromocyclopropyl ketones with electron donating aromatic rings would be amenable for rearrangement upon appropriate activation, for instance, by a Lewis acid. Thus, selected dibromocyclopropyl ketones **11e-f**, **11h** and **11p** were refluxed with acidic alumina to afford fused bromofurans **13e-f**, **13h** and **13p** in excellent yield (Table 2, entries 1-3 and 5).

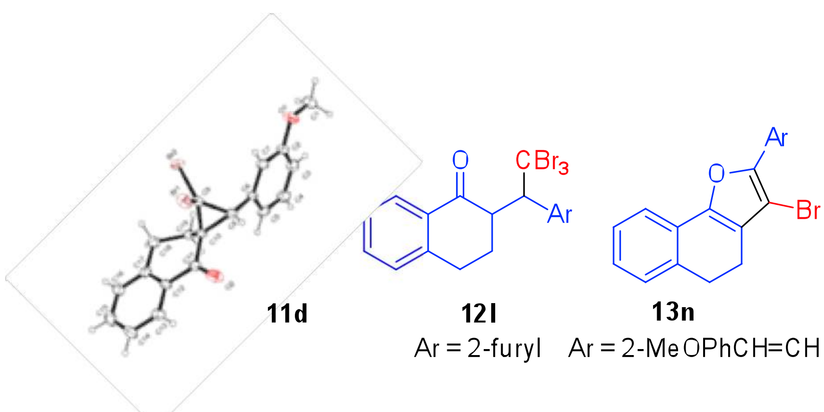
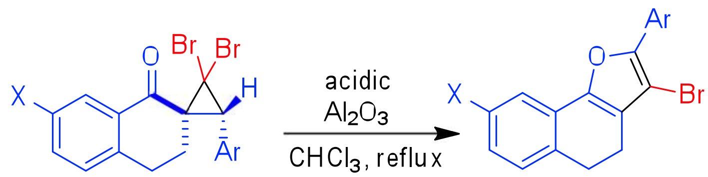


Figure 1. X-ray Structure of **11d** and Chemical Structures of **12l** and **13n**

Table 2. Alumina Mediated Cloke-Wilson Rearrangement of Dibromocyclopropanes[a]



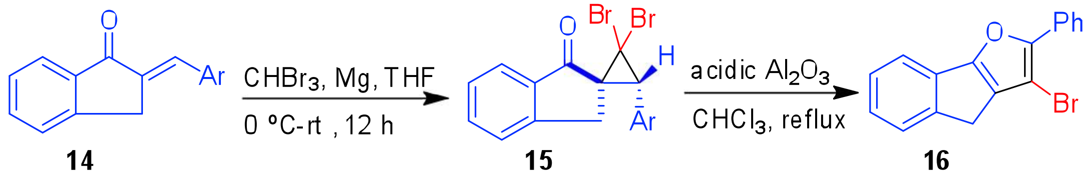
11 → **13**

entry	**11**	X	Ar	**13**	time (h)	% yield[b]
1	**11e**	H	2,4-$(OMe)_2$Ph	**13e**	2	83
2	**11f**	H	3,4-$(OMe)_2$Ph	**13f**	5	85
3	**11h**	H	3,4,5-$(OMe)_3$Ph	**13h**	15	87
4	**11n**	H	2-MeOPhCH=CH	**13n**	4.5[c]	70
5	**11p**	OMe	3,4-$(OMe)_2$Ph	**13p**	4	84

[a]Mg, bromoform and acidic Al_2O_3 were used in excess (8 atom g, 22 equiv and 25 equiv, respectively). [b] Isolated yield after purification by silica gel column chromatography. [c] For direct transformation of **10n** to **13n**; **11n** was not isolable in this case; see also Table 1 and Figure 1.

The above results encouraged us to expand the scope of our methodology to other enones, viz easily accessible indanone derivatives **14** (Table 3). Thus, selected indanone derived enones **14a-f** were subjected to Mg mediated dibromocyclopropanation to afford the products **15a-f** in moderate to good yield (53-78%, entries 1-6). Although these reactions required longer time (~ 12 h), as compared to dibromocyclopropanation of tetralone derived enones **10** (see Table 1), we were gratified to note that subsequent ring expansion via Cloke-Wilson rearrangement took place smoothly in all the cases. Thus, cyclopropyl ketones **15a-f** when refluxed with acidic alumina in $CHCl_3$ for 2.5 to 4 h, the desired bromofurans **16a-f** were isolated in excellent yield (82-89%, entries 1-6). Quite remarkably and unlike in the case of tetralone derived cyclopropanes **11** (see Tables 1-2), the rearrangement of indanone derived cyclopropanes **15** took place regardless of the nature of β-aryl substituent (Table 3).

Table 3. Dibromocyclopropanation-Cloke-Wilson Rearrangement of Indanones[a]

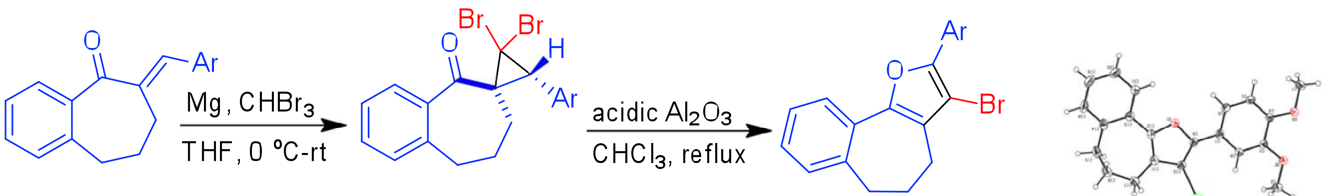


entry	14	Ar	15	% yield[b]	16	time (h)	% yield[b]
1	**14a**	Ph	**15a**	68	**16a**	3	84
2	**14b**	4-MePh	**15b**	68	**16b**	3	89
3	**14c**	3,4-Me_2Ph	**15c**	72	**16c**	2.5	85
4	**14d**	4-FPh	**15d**	53	**16d**	4	82
5	**14e**	1-Naphthyl	**15e**	78	**16e**	4	87
6	**14f**	4-OMePh	**15f**	-[c]	**16f**	1	76[d]

[a] Mg, bromoform and acidic Al_2O_3 were used in excess (8 atom g, 22 equiv and 25 equiv, respectively). [b] Isolated yield after purification by silica gel column chromatography. [c] Crude product was directly subjected to the next step due to instability. [d] For two steps.

Finally, the scope of our methodology was further extended by converting benzosuberone derived enones **17** to bromofuran **19** via Mg mediated dibromocyclopropanation and subsequent alumina mediated Cloke-Wilson rearrangement (Table 4). In these cases, the dibromocyclopropanation was complete in 4 h or less to afford the products in good yield (65-74%, entries 1-3 and 5). Since cyclopropane **18d** was not amenable for purification, the crude residue obtained after workup was directly subjected to alumina mediated rearrangement to bromofuran **19d** (84% yield, entry 4). Cyclopropanes **18a-c** and **18e** also underwent facile rearrangement to deliver bromofurans **19a-c** and **19e**, respectively, in excellent yields (81-90%, entries 1-3 and 5).

Table 4. Dibromocyclopropanation-Cloke-Wilson Rearrangement of Benzosuberones[a]

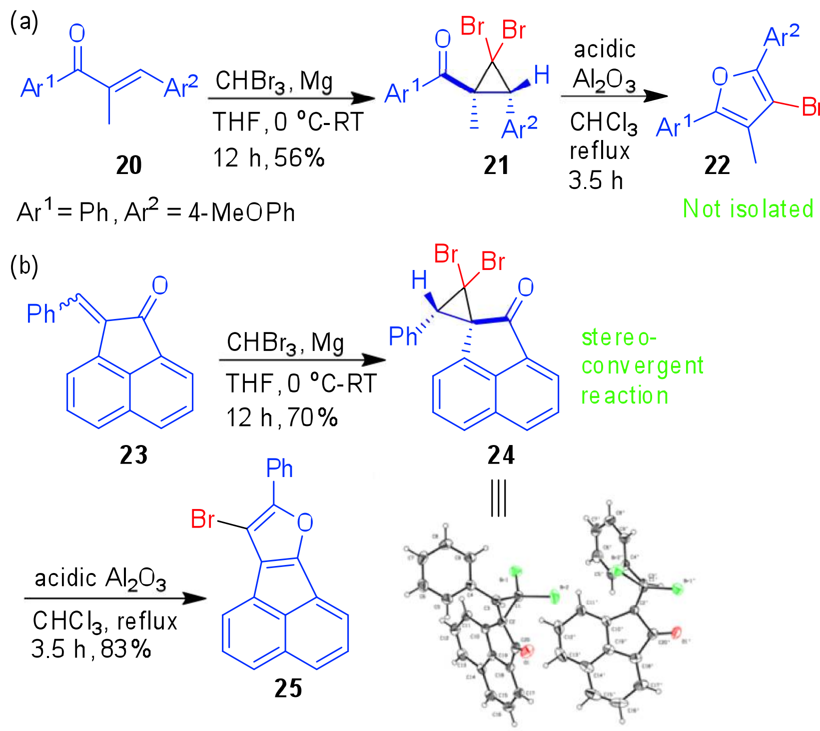


entry	17	Ar	18	time (h)	% yield[b]	19	time (h)	% yield[b]
1	**17a**	Ph	**18a**	3	65	**19a**	12	88
2	**17b**	4-MePh	**18b**	3	69	**19b**	4	88
3	**17c**	4-FPh	**18c**	2.5	70	**19c**	6	81
4	**17d**	4-MeOPh	**18d**	3	-[c]	**19d**	3	84[d]
5	**17e**	3,4-(MeO)$_2$Ph	**18e**	4	74	**19e**	2	90

[a]Mg, bromoform and acidic Al_2O_3 were used in excess (8 atom g, 22 equiv and 25 equiv, respectively). [b] Isolated yield after purification by silica gel column chromatography. [c]Crude product was directly subjected to next step due to instability. [d] For two steps.

Later on, a representative open chain α,β-disubstituted enone **20** underwent bromoform addition satisfactorily to give cyclopropane **21** in 56% yield (Scheme 2a). However, attempted transformation of **21** to the desired bromofuran **22** afforded only an intractable mixture. Reactivity of enones derived from highly fused cycloalkanones was subsequently investigated taking enone **23** as a model substrate (Scheme 2b). This mono-Wittig product of acenaphthaquinone, prepared as a 1:1 mixture of E/Z isomers, underwent smooth reaction with bromoform under our conditions to afford cyclopropane **24** as a single diastereomer in 70% yield. Subsequent alumina mediated rearrangement of **24** to bromofuran **25** took place in excellent (83%) yield.

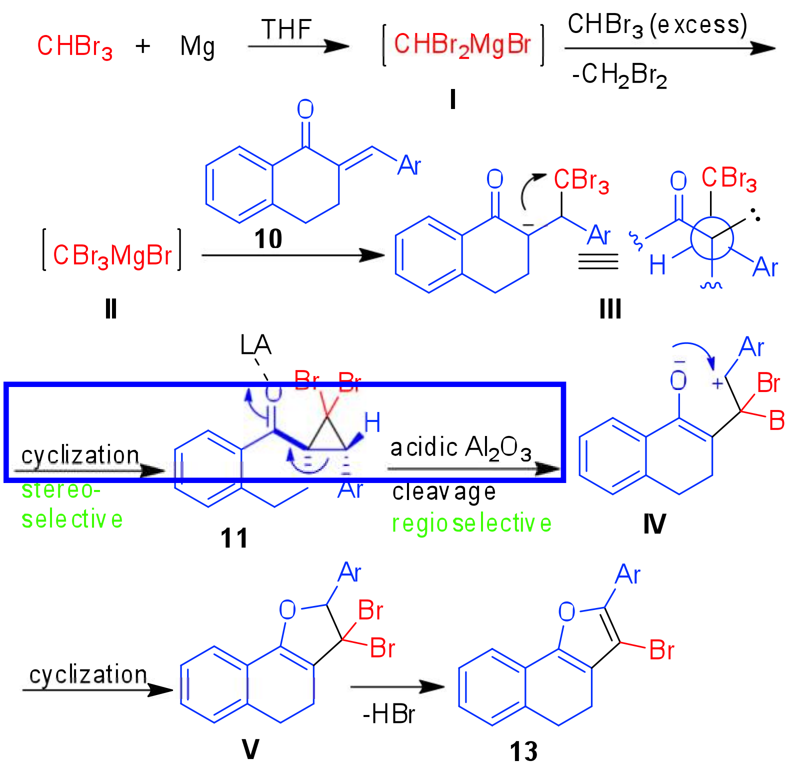
Scheme 2



The formation of a single diastereomer of cyclopropane **24** from a 1:1 *E*/*Z* mixture of **23** further confirmed the stepwise nature of the dibromocyclopropanation. It is obvious that both *E* and *Z* isomers of **23** give rise to the same enolate of the intermediate Michael adduct that cyclizes to give cyclopropane **24** as a single diastereomer. This stereoconvergence, though at the expense of stereospecificity, is remarkable.

The structure and stereo/regiochemistry of the products were determined by detailed NMR analysis and further unambiguously established by single crystal X-ray analysis of representative compounds. A positive NOE between the protons ortho to methoxy group in 4-methoxyphenyl with the methylene protons β to carbonyl of tetralone moiety in cyclopropane **11c** suggested their cis relationship and, therefore, the trans relationship of the aromatic ring and the C=O group. Finally, the structure was unambiguously established by X-ray analysis of cyclopropane **11d** (see Figure 1) and **24** (vide infra, also see Scheme 3, the experimental section and the Supporting Information). In the bromofuran series, while the benzylic methylene protons in **13f** showed positive NOE with one of the protons of benzo group, there was no NOE between either of the methylene protons with the 3,4-dimethoxyphenyl protons suggesting that it could be 3-bromofuran and not 2-bromofuran. The possibility of 2-bromofuran was ruled out also based on the ^{13}C NMR chemical shift of C-Br (δ 97.8). The structure was later unequivocally established by X-ray analysis of an analog **19e** (see Table 4 and also the experimental section and the Supporting Information).

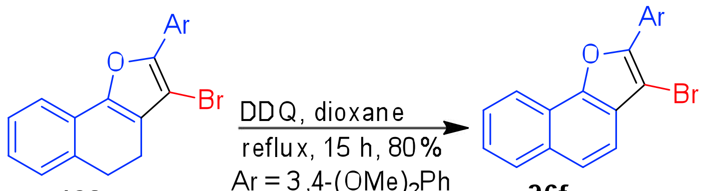
Scheme 3



The proposed mechanism of cyclopropanation and rearrangement taking chalcone **10** as a representative example is presented in Scheme 3. The cyclopropanation step involves formation of tribromomethyl magnesium bromide **II** from Mg and excess bromoform and its addition to chalcone **10** in a 1,4-fashion. The resulting enolate cyclizes spontaneously in most cases to give cyclopropyl ketone **11** as a single diastereomer. Examination of the X-ray data confirms that the C=O group and the Ar group avoid each other (dihedral angle 142.6° in **11d** and 137° in **24**) during cyclization to afford a single diastereomer of the spirocyclopropane (see the Supporting Information).[15] This also explains the stereoconvergence observed in the transformation of **23** to **24** as both *E* and *Z* isomers of **23** give rise to the same enolate which eventually cyclizes to cyclopropane **24** (Scheme 2). In the rearrangement step, the Lewis acid mediated activation of carbonyl *with or without* the electron donating ability of the β-aryl substituent triggers the regioselective cleavage of cyclopropane in **11**. The resulting enolate **IV** then cyclizes intramolecularly to dihydrofuran **V**. Spontaneous elimination of HBr from **V** completes the process to deliver fused 3-bromofuran **13**.

Possible transformation of tetraline fused bromofurans **13** to angularly fused naphthofurans **26** was demonstrated via complete aromatization of a representative example **13f** using DDQ in dioxane (Scheme 4).

Scheme 4



Conclusions

Treatment of cycloalkanone derived chalcones with Mg and $CHBr_3$ in THF affords spirodibromocyclopropanated products, rather than Michael adducts, as single stereoisomers. These adducts undergo facile regioselective ring expansion in the presence of acidic Al_2O_3 to afford 2-aryl-3-halofurans fused to benzocycloalkanes as single regioisomers. The stereoconvergence in the cyclopropanation of mixture of *E* and *Z* chalcones and complete aromatization of tetralone derived 3-bromofurans via DDQ dehydrogenation have been demonstrated with representative examples.

Experimental Section

General. The melting points recorded are uncorrected. NMR spectra (^{1}H, ^{1}H decoupled ^{13}C, ^{13}C-APT, ^{1}H-^{1}H-COSY and ^{1}H-^{1}H-NOESY) were recorded with TMS and ^{19}F spectra with $CFCl_3$ as the internal standard. The coupling constants (*J* values) are given in Hz. High resolution mass spectra were recorded under ESI Q-TOF conditions. X-ray data were collected on a diffractometer equipped with graphite monochromated Mo Kα radiation. The structure was solved by direct methods shelxs97 and refined by full-matrix least squares against F^2 using shelxl97 software. Chalcones **10, 14, 17** and **20** were prepared via condensation of ketones with aromatic aldehydes.[16] Chalcone **23** was prepared as a 1:1 mixture of isomers via Wittig reaction of acenaphthaquinone with benzyl bromide.[17] Mg turnings were activated by washing with 1% dil HCl, water and acetone followed by drying in an oven overnight. Bromoform was commercially available and was used as such.

General Procedure for Addition of Bromoform to Chalcones 10, 14, 17, 20 and **23.** To a stirred solution of magnesium (196 mg, 8 atom g) and chalcone **10, 14, 17, 20** or **23** (1 mmol) in THF (20 mL) was added bromoform (5.4 g, 2 mL, 22 mmol) dropwise over a period of 10 min at 0 °C. The reaction mixture was gradually brought to room temperature over a period of 1.5 h during which the solution turned dark brown. The reaction mixture was subsequently quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with ethyl acetate (5 × 20 mL) and the combined organic layers were washed with H_2O (3 × 10 mL), dried (anhyd Na_2SO_4), and concentrated in vacuo to afford the crude product, which was subjected to silica gel column chromatography (ethyl acetate/hexane mixture, 5-15%, gradient elution) to afford product **11, 15, 18, 21** or **24**.

2, 2-Dibromo-3-phenyl-3', 4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11a). Colorless solid; Yield 62%, 251 mg; mp 88-90 °C; IR (KBr, cm^{-1}) 2929 (m), 2852 (w), 1676 (vs), 1599 (m), 1300 (s), 1215 (m), 757 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.58 (td, *J* = 7.5, 1.4 Hz, 1H), 7.43–7.35 (m, 4H), 7.35 – 7.31 (m, 3H), 4.02 (s, 1H), 3.52 (ddd, *J* = 16.9, 13.1, 4.2 Hz, 1H), 2.96 (ddd collapsed to dt, *J* = 16.9, 3.0 Hz, 1H), 2.61 (ddd, *J* = 14.1, 13.1, 4.2 Hz, 1H), 2.03 (ddd, *J* = 14.1, 4.2, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 144.1, 134.3, 133.3, 131.5, 130.1, 129.1, 128.6, 128.4, 127.7, 127.2, 42.9, 39.2, 36.1, 29.7, 27.0; MS (ES+, Ar) m/z (rel intensity) 328 ($[(MH+2)-Br]^+$, 25), 327 ($[(M+2)-Br]^+$, 100), 326 ($[MH-Br]^+$, 25), 325 ($[M-Br]^+$, 98); HRMS (ES+, Ar) calcd for $C_{18}H_{14}OBr$ ($[M-Br]^+$) 325.0228, found 325.0238.

2, 2-Dibromo-3-(p-tolyl)-3', 4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11b). Colorless solid; Yield 73%, 306 mg; mp 156-158 °C; IR (KBr, cm^{-1}) 3057 (w), 2971 (w), 2910 (w), 1680 (vs), 1297 (s), 1223 (m), 780 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.55 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (td, *J* = 7.7, 0.8 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.19

(unresolved m, 4H), 3.95 (s, 1H), 3.50 (ddd, *J* = 16.9, 13.9, 4.1 Hz, 1H), 2.93 (ddd collapsed to dt, *J* = 16.9, 3.0 Hz, 1H), 2.58 (ddd collapsed to td, *J* = 13.9, 4.1 Hz, 1H), 2.36 (s, 3H), 2.01 (ddd, *J* = 13.9, 4.1, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 144.1, 137.5, 134.3, 131.6, 130.3, 130.0, 129.4, 129.1, 128.4, 127.2, 42.9, 39.0, 36.4, 29.7, 27.0, 21.4; MS (ES+, Ar) m/z (rel intensity) 342 ([(MH+2)-Br]$^+$, 25), 341 ([(M+2)-Br]$^+$, 98), 340 (MH-Br]$^+$, 25), 339 ([M-Br]$^+$, 100); HRMS (ES+, Ar) calcd for $C_{19}H_{16}OBr$ ([M-Br]$^+$) 339.0385, found 339.0395.

2, 2-Dibromo-3-(4-methoxyphenyl)-3', 4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11c). Colorless solid; Yield 68%, 296 mg; mp 110-112 °C; IR (KBr, cm^{-1}) 2928 (vs), 2857 (m), 1683 (m), 1600 (m), 1515 (m), 1248 (m), 1023 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.55 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38 (td, *J* = 7.8, 1.2 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 1H), 3.82 (s, 3H), 3.49 (ddd, *J* = 16.9, 13.9, 4.2 Hz, 1H), 2.94 (ddd collapsed to dt, *J* = 16.9, 3.0 Hz, 1H), 2.55 (ddd collapsed to td, *J* = 13.9, 4.2 Hz, 1H), 2.00 (ddd, *J* = 13.9, 4.2, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 159.1, 144.1, 134.3, 131.6, 131.2, 129.1, 128.4, 127.2, 125.3, 114.1, 55.4, 42.9, 38.7, 36.7, 29.7, 27.0; MS (ES+, Ar) m/z (rel intensity) 358 ([(MH+2)-Br]$^+$, 21), 357 ([(M+2)-Br]$^+$, 98), 356 (MH-Br]$^+$, 21), 355 ([M-Br]$^+$, 100); HRMS (ES+, Ar) calcd for $C_{19}H_{16}O_2Br$ ([M-Br]$^+$) 355.0334, found 355.0348. Confirmed by ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY experiments.

2,2-Dibromo-3-(3-methoxyphenyl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11d). Colorless solid; Yield 71%, 309 mg; mp 130-132 °C; IR (KBr, cm^{-1}) 2937 (m), 2840 (s), 2739 (m), 1696 (vs), 1599 (s), 1578 (s), 1511 (s), 1316 (s), 1260 (s), 1161 (s), 1027 (s), 834 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.56 (td, *J* = 7.4, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.30 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.26 (s, 1H), 6.90–6.84 (m, 3H), 3.97 (s, 1H), 3.82 (s, 3H), 3.50 (ddd, *J* = 16.9, 13.0, 4.2 Hz, 1H), 2.95 (ddd collapsed to dt, *J* = 16.9, 3.0 Hz, 1H), 2.58 (ddd, *J* = 14.1, 13.0, 4.2 Hz, 1H), 2.03 (ddd, *J* = 14.1, 4.2, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 159.7, 144.0, 134.7, 134.3, 131.5, 129.6, 129.1, 128.4, 127.2, 122.3, 115.8, 113.2, 55.4, 42.9, 39.3, 36.0, 29.8, 27.0; MS (ES+, Ar) m/z (rel intensity) 358 ([(MH+2)-Br]$^+$, 25), 357 ([(M+2)-Br]$^+$, 100), 356 ([(MH-Br]$^+$, 21), 355 ([M-Br]$^+$, 98); HRMS (ES+, Ar) calcd for $C_{19}H_{16}O_2Br$ ([M-Br]$^+$) 355.0334, found

355.0327. Selected X-ray Data: $C_{19}H_{16}Br_2O_2$, *M* = 436.14, Triclinic, space group *P-1*, *a* = 7.0570(2)Å, *b* = 11.2036(2) Å, *c* = 12.3063(3) Å, α = 63.4440(10) °, β = 84.1330(10)°, γ = 71.8540(10)°, *V* = 826.26(3) Å^3, D_c = 1.753Mg/m^3, *Z* = 2, F(000) = 432, λ = 0.71073 Å, μ = 4.912 mm^{-1}, Total/ unique reflections = 12706 / 2829 [R(int) = 0.0541], *T* = 293(2) K, θ range = 1.85 to 25.00°, Final *R* [I>2σ(I)]: R1 = 0.0461, wR2 = 0.1094, *R* (all data): R1 = 0.0738, wR2 = 0.1239.

2, 2-Dibromo-3-(2,4-dimethoxyphenyl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphtha-len]-1'-one (11e). Colorless solid; Yield 60%, 279 mg; mp 88-90 °C; IR (KBr, cm^{-1}) 3001 (w), 2938 (m), 2836 (w), 1614 (vs), 1583 (s), 1500 (vs), 1465 (s), 1382 (m), 1291 (vs), 1210 (vs), 1160 (vs), 1033 (s), 820 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.54 (td, *J* = 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.7, 1.1 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.15 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.50 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.46 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.74 (s, 1H), 3.49 (ddd, *J* = 16.8, 13.6, 4.1 Hz, 1H), 2.91 (ddd collapsed to dt, *J* = 16.8, 3.0 Hz, 1H), 2.60 (ddd collapsed to td, *J* = 13.6, 4.1 Hz, 1H), 2.09 (ddd, *J* = 13.6, 4.1, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 160.7, 160.2, 144.2, 134.1, 131.7, 130.7, 129.1, 128.4, 127.1, 114.9, 103.8, 98.8, 55.7, 55.5, 43.1, 37.7, 36.3, 29.6, 27.0; MS (ES+, Ar) m/z (rel intensity) 388 ([(MH+2)-Br]$^+$, 28), 387 ([(M+2)-Br]$^+$, 100), 386 ([(MH-Br]$^+$, 28), 385 ([M-Br]$^+$, 98); HRMS (ES+, Ar) calcd for $C_{20}H_{18}O_3Br$ ([M-Br]$^+$) 385.0439, found 385.0450.

2, 2-Dibromo-3-(3,4-dimethoxyphenyl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphtha-len]-1'-one (11f). Colorless solid; Yield 65 %, 302 mg; mp 154-156 °C; IR (KBr, cm^{-1}) 2930 (m), 2857 (w), 1679 (s), 1599 (m), 1510 (vs), 1455 (m), 1259 (m), 1241 (s), 1223 (m), 1138 (m), 1026 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.55 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (td, *J* = 7.8, 0.9 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.88–6.80 (m, 3H), 3.94 (s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.50 (ddd, *J* = 16.9, 13.9, 4.1 Hz, 1H), 2.95 (ddd collapsed to dt, *J* = 16.9, 3.0 Hz, 1H), 2.56 (ddd collapsed to td, *J* = 13.9, 4.1 Hz, 1H), 2.02 (ddd, *J* = 13.9, 4.1, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 149.0, 148.6, 144.1, 134.4, 131.6, 129.1, 128.5, 127.2, 125.7, 122.2, 113.3, 111.1, 56.2, 56.0, 43.0, 39.1, 36.6, 29.8, 27.1; MS (ES+, Ar) m/z (rel intensity) 388 ([(MH+2)-Br]$^+$, 28), 387 ([(M+2)-Br]$^+$, 100), 386

([MH-Br]$^+$, 28), 385 ([M-Br]$^+$, 98); HRMS (ES+, Ar) calcd for $C_{20}H_{18}O_3Br$ ([M-Br]$^+$) 385.0439, found 385.0454.

2,2-Dibromo-3-(2,3,4-trimethoxyphenyl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naph-thalen]-1'-one (11g). Colorless solid; Yield 70%, 347 mg; mp 94-96 ^{o}C; IR (KBr, cm^{-1}) 2935 (w), 1681 (m), 1600 (w), 1497 (m), 1466 (m), 1300 (m), 1222 (m), 1098 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.54 (td, *J* = 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.95 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.82 (s, 1H), 3.49 (ddd, *J* = 16.9, 13.6, 4.2 Hz, 1H), 2.92 (ddd collapsed to dt, *J* = 16.9, 3.0 Hz, 1H), 2.67 (td, *J* = 13.6, 4.2 Hz, 1H), 2.10 (ddd, *J* = 13.6, 4.2, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 153.7, 153.6, 144.2, 142.5, 134.2, 131.6, 129.1, 128.4, 127.1, 124.5, 120.1, 106.6, 61.1, 61.0, 56.1, 43.2, 37.1, 36.4, 29.6, 27.0; MS (ES+, Ar) m/z (rel intensity) 418 ([(MH+2)-Br]$^+$, 25), 417 ([(M+2)-Br]$^+$, 100), 416 ([(MH-Br]$^+$, 25), 415 ([M-Br]$^+$, 98); HRMS (ES+, Ar) calcd for $C_{21}H_{20}O_4Br$ ([M-Br]$^+$) 415.0545, found 415.0546.

2,2-Dibromo-3-(3,4,5-trimethoxyphenyl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naph-thalen]-1'-one (11h). Colorles ssolid; Yield 71%, 352 mg; mp 118-120 ^{o}C; IR (KBr, cm^{-1}) 2930 (br m), 1680 (m), 1586 (m), 1508 (m), 1292 (m), 1241 (m), 1127 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.56 (td, *J* = 7.6, 1.4 Hz, 1H), 7.39 (td, *J* = 7.7, 1.1 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.48 (d, *J* = 0.8 Hz, 2H), 3.94 (s, 1H), 3.86 (s, 9H), 3.51 (ddd, *J* = 16.9, 13.6, 4.1 Hz, 1H), 2.97 (ddd collapsed to dt, *J* = 16.9, 3.0 Hz, 1H), 2.55 (ddd collapsed to td, *J* = 13.6, 4.2 Hz, 1H), 2.03 (ddd, *J* = 13.6, 4.1, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 153.4, 144.0, 137.6, 134.4, 131.5, 129.1, 128.6, 128.4, 127.2, 107.1, 61.1, 56.4, 43.0, 39.5, 36.1, 29.9, 27.1; MS (ES+, Ar) m/z (rel intensity) 418 ([(MH+2)-Br]$^+$, 25), 417 ([(M+2)-Br]$^+$, 100), 416 ([(MH-Br]$^+$, 25), 415 ([M-Br]$^+$, 100); HRMS (ES+, Ar) calcd for $C_{21}H_{20}O_4Br$ ([M-Br]$^+$) 415.0545, found 415.0557.

2, 2-Dibromo-3-(4-(trifluoromethyl)phenyl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11i). Colorless solid; Yield 69%, 327 mg; mp 182-184 ^{o}C; IR (KBr, cm^{-1}) 2938 (w), 1675 (m), 1328 (s), 1302 (m), 1160 (m), 1126 (s), 751 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.57 (td, *J* = 7.6, 1.3 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.40 (td, J = 8.1, 0.9 Hz, 1H), 7.32 (dd, J = 7.6, 1.3 Hz, 1H), 4.01 (s, 1H), 3.51 (ddd, J = 16.9, 13.6, 4.2 Hz, 1H), 2.97 (ddd collapsed to dt, J = 16.9, 2.9 Hz, 1H), 2.59 (ddd collapsed to td, J = 13.6, 4.2 Hz, 1H), 1.96 (ddd, J = 13.6, 4.1, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 144.0, 137.4, 134.6, 131.4, 130.6, 130.2, 129.8, 129.2, 128.5, 127.3, 125.6 (q, J = 16 Hz) 43.1, 38.8, 34.9, 29.7, 26.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; MS (ES+, Ar) m/z (rel intensity) 396 ([(MH+2)-Br]$^+$, 25), 395 ([(M+2)-Br]$^+$, 100), 394 ([MH-Br]$^+$, 25), 393 ([M-Br]$^+$, 100); HRMS (ES+, Ar) calcd for $C_{19}H_{13}OBrF_3$ ([M-Br]$^+$) 393.0102, found 393.0104.

2, 2-Dibromo-3-(4-fluorophenyl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11j). Colorless solid; Yield 75%, 318 mg; mp 144-146 °C; IR (KBr, cm^{-1}) 2978 (w), 2915 (w), 1682 (vs), 1599 (m), 1512 (s), 1300 (s), 1300 (s), 1224 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 7.7, 0.9 Hz, 1H), 7.56 (td, J = 7.6, 1.3 Hz, 1H), 7.38 (td, J = 7.7, 0.9 Hz, 1H), 7.31 (dd, J = 7.6, 1.3 Hz, 1H), 7.29–7.24 (m, 2H), 7.12–7.03 (m, 2H), 3.93 (s, 1H), 3.50 (ddd, J = 16.9, 13.6, 4.2 Hz, 1H), 2.95 (ddd collapsed to dt, J = 16.9, 2.9 Hz, 1H), 2.56 (ddd collapsed to td, J = 13.6, 4.2 Hz, 1H), 1.97 (ddd, J = 13.6, 4.1, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 162.3 (d, $J_{C\text{-}F}$ = 246.0 Hz), 144.0, 134.4, 131.8, 131.5, 129.2, 129.1 (d, $J_{C\text{-}F}$ = 6.0 Hz), 128.5, 127.2, 115.8, 115.6, 42.9, 38.5, 35.8, 29.6, 26.9; ^{19}F NMR ($CDCl_3$) δ -114.0 (dtt, J = 11.3, 7.5, 3.8 Hz, 1F); MS (ES+, Ar) m/z (rel intensity) 346 ([(MH+2)-Br]$^+$, 25), 345 ([(M+2)-Br]$^+$, 100), 344 ([MH-Br]$^+$, 25), 343 ([M-Br]$^+$, 100); HRMS (ES+, Ar) calcd for $C_{18}H_{13}OBrF$ ([M-Br]$^+$) 343.0134, found 343.0131.

2,2-Dibromo-3-(naphthalen-1-yl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11k). Colorless solid; Yield 71%, 322 mg; mp 182-184 °C; IR (KBr, cm^{-1}) 2923 (m), 2851 (w), 1678 (vs), 1457 (w), 1298 (w), 1262 (w), 1021 (w), 757 (s), 741 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.87–7.81 (m, 1H), 7.64-7.52 (m, 3H), 7.46–7.39 (m, 3H), 7.33 (d, J = 7.8 Hz, 1H), 4.32 (s, 1H), 3.55 (ddd, J = 16.9, 13.5, 4.2 Hz, 1H), 2.95 (ddd collapsed to dt, J = 16.9, 3.0 Hz, 1H), 2.74 (ddd collapsed to td, J = 13.5, 4.2 Hz, 1H), 2.18 (ddd, J = 13.5, 4.1, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 144.1, 134.5, 134.0, 133.2, 131.6, 130.7, 129.2, 128.8, 128.6 (× 2), 127.3, 127.1, 126.8, 126.3, 125.2, 125.1, 43.4, 38.4, 36.8, 30.3, 27.2; MS

(ES+, Ar) m/z (rel intensity) 378 ([(MH+2)-Br]$^+$, 25), 377 ([(M+2)-Br]$^+$, 100), 376 ([MH-Br]$^+$, 25), 375 ([M-Br]$^+$, 100); HRMS (ES+, Ar) calcd for $C_{22}H_{16}OBr$ ([M-Br]$^+$) 375.0385, found 375.0378.

2, 2-Dibromo-3-(furan-2-yl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11l). Colorless solid; Yield 60%, 237 mg; mp 114-116 °C; IR (KBr, cm^{-1}) 2926 (m), 2856 (w), 1686 (vs), 1600 (s), 1455 (m), 1365 (m), 1299 (s), 1225 (s), 1023 (m), 786 (m), 737 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.55 (td, *J* = 7.7, 1.3 Hz, 1H), 7.43-7.45 (m, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 6.39 (d, *J* = 1.3 Hz, 2H), 3.92 (s, 1H), 3.49 (ddd, *J* = 16.9, 12.9, 4.5 Hz, 1H), 2.98 (dt, *J* = 16.9, 3.2 Hz, 1H), 2.50 (ABq, *J* = 14.3 Hz, the upper half is further split into dd, *J* = 4.5, 2.7 Hz, the lower half is further split into dd, *J* = 12.9, 4.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 147.8, 143.9, 142.7, 134.4, 131.4, 129.1, 128.5, 127.2, 110.6, 110.0, 43.5, 34.4, 34.3, 29.1, 27.1; MS (ES+, Ar) m/z (rel intensity) 318 ([(MH+2)-Br]$^+$, 20), 317 ([(M+2)-Br]$^+$, 100), 316 ([MH-Br]$^+$, 20), 315 ([M-Br]$^+$, 98), 236 (48); HRMS (ES+, Ar) calcd for $C_{16}H_{12}O_2Br$ ([M-Br]$^+$) 315.0021, found 315.0024.

(E)-2,2-Dibromo-3-styryl-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11m). Dark green solid; Yield 69%, 298 mg; mp 96-98 °C; IR (KBr, cm^{-1}) 3019 (w), 1684 (m), 1600 (w), 1301 (w), 1216 (s), 757 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44–7.24 (m, 7H), 6.85 (d, *J* = 15.8 Hz, 1H), 5.95 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.54 (d, *J* = 8.8 Hz, 1H), 3.51–3.44 (m, 1H), 2.99 (dt, *J* = 16.8, 3.4 Hz, 1H), 2.42–2.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 143.8, 137.0, 136.7, 134.3, 131.6, 129.1, 128.8, 128.4, 128.2, 127.2, 126.4, 122.2, 43.7, 38.8, 38.0, 28.3, 26.9; MS (ES+, Ar) m/z (rel intensity) 354 ([(MH+2)-Br]$^+$, 31), 353 ([(M+2)-Br]$^+$, 100), 352 ([MH-Br]$^+$, 31), 351 ([M-Br]$^+$, 100); HRMS (ES+, Ar) calcd for $C_{20}H_{16}OBr$ ([M-Br]$^+$) 351.0385, found 351.0388.

(E)-2,2-Dibromo-3-(2-nitrostyryl)-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11o). Dark Green solid; Yield 52%, 247 mg; mp 126-128 °C; IR (KBr, cm^{-1}) 3027 (w), 2967 (w), 1683 (m), 1600 (w), 1454 (w), 1300 (m), 1223 (m), 761 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.99–7.91 (m, 1H), 7.62–7.58 (m, 2H), 7.53 (td, *J* = 7.7, 1.3 Hz, 1H), 7.46–7.41 (m, 1H), 7.39-7.29 (m, 3H), 5.94 (dd, *J* = 15.7, 8.5 Hz, 1H), 3.58 (d, *J* = 8.5 Hz, 1H), 3.49 (ddd, *J* = 16.9, 14.2, 4.5 Hz, 1H), 3.00 (dt, J = 16.9, 3.1 Hz, 1H), 2.45 (td, J = 14.2, 4.5 Hz, 1H), 2.34 (ddd, J = 14.2, 4.5, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 147.5, 143.6, 134.4, 133.4, 132.4, 132.1, 131.4, 129.1, 129.0, 128.7, 128.4, 128.0, 127.2, 124.9, 44.0, 38.3, 37.2, 28.4, 26.9; MS (ES+, Ar) m/z (rel intensity) 399 ($[(MH+2)-Br]^+$, 25), 398 ($[(M+2)-Br]^+$, 100), 397 ($[MH-Br]^+$, 25), 396 ($[M-Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{20}H_{15}NO_3Br$ ($[M-Br]^+$) 396.0235, found 396.0223.

2,2-Dibromo-3-(3,4-dimethoxyphenyl)-7'-methoxy-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one (11p). Colorless solid; Yield 65%, 323 mg; mp 104-106 °C; IR (KBr, cm^{-1}) 2934 (m), 2837 (w), 1682 (s), 1609 (m), 1518 (s), 1498 (s), 1421 (m), 1323 (m), 1261 (vs), 1242 (vs), 1030 (vs), 733 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 2.8 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.13 (dd, J = 8.4, 2.8 Hz, 1H), 6.87–6.77 (m, 3H), 3.93 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.41 (ddd, J = 16.6, 13.4, 4.1 Hz, 1H), 2.89 (dd, J = 16.6, 3.3 Hz, 1H), 2.53 (td, J = 13.4, 4.1 Hz, 1H), 2.00 (dt, J = 13.4, 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 158.7, 149.0, 148.6, 136.7, 132.2, 130.3, 125.6, 122.8, 122.2, 113.2, 111.1, 110.2, 56.1, 56.0, 55.7, 42.8, 39.1, 36.5, 30.1, 26.2; MS (ES+, Ar) m/z (rel intensity) 418 ($[(MH+2)-Br]^+$, 25), 417 ($[(M+2)-Br]^+$, 100), 416 ($[MH-Br]^+$, 25), 415 ($[M-Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{21}H_{20}O_4Br$ ($[M-Br]^+$) 415.0545, found 415.0557.

2-(2, 2,2-Tribromo-1-(cyclopenta-1,3-dien-1-yl)ethyl)-3,4-dihydronaphthalen-1(2H)-one (12l). Colorless solid; Yield 65% (dr > 95:5, inseparable), 309 mg; mp 124-126 °C; IR (KBr, cm^{-1}) 2928 (w), 1676 (vs), 1600 (m), 1455 (w), 1286 (m), 1235 (m), 1223 (m), 1017 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.8, 1.2 Hz, 1H), 7.45 (td, J = 7.6, 1.3 Hz, 1H), 7.36 (dd, J = 2.2, 0.8 Hz, 1H), 7.24 (td, J = 7.8, 1.2 Hz, 1H), 7.22 (dd, J = 7.6, 1.3 Hz, 1H), 6.55 (d, J = 3.2, 0.8 Hz, 1H), 6.32 (dd, J = 3.2, 2.2 Hz, 1H), 5.35 (d, J = 2.9 Hz, 1H), 3.27 (ddd, J = 10.9, 4.1, 3.0 Hz, 1H), 3.17 (dt, J = 16.7, 5.1 Hz, 1H), 3.07–3.00 (m, 1H), 2.99–2.90 (m, 1H), 2.73–2.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 152.4, 143.1, 142.0, 133.6, 132.4, 128.6, 128.1, 126.9, 110.9, 110.7, 58.9, 53.4, 43.8, 28.7, 27.0; MS (ES+, Ar) m/z (rel intensity) 481 ($[(MH+6)]^+$, 35), 479 ($[(MH+4)]^+$, 98), 477 ($[(MH+2)]^+$, 100), 475 ($[MH]^+$, 35), 399 ($[(M+4)-Br]^+$, 35), 397 ($[(M+2)-Br]^+$, 70), 395 ($[M-Br]^+$, 35), 317 ($[(MH+2)-Br_2]^+$, 35), 315 ($[MH-Br_2]^+$, 35); HRMS (ES+, Ar) calcd for $C_{16}H_{14}O_2Br_3$ ($[MH]^+$) 474.8544, found 474.8552.

2,2-Dibromo-3-phenylspiro[cyclopropane-1,2'-inden]-1'(3'H)-one (15a). Colorless solid; Yield 68%, 267; mp 106-108 °C; IR (KBr, cm^{-1}) 3063 (w), 2980 (w), 2917 (w), 1678 (vs), 1596 (m), 1296 (s), 1221 (m), 806 (m), 786 (vs), 775 (vs), 760 (s), 746 (s), 736 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H), 7.54 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.48 (td, *J* = 7.6, 0.8 Hz, 1H), 7.43–7.35 (m, 3H), 7.34-7.30 (m, 2H), 3.64 (s, 1H), 3.44 (ABq, *J* = 18.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 151.6, 136.5, 135.2, 133.3, 130.0, 128.7, 128.2, 128.1, 126.2, 124.4, 44.7, 44.5, 37.5, 34.0; MS (ES+, Ar) m/z (rel intensity) 314 ($[(M+3)-Br]^+$, 25), 313 ($[(M+2)-Br]^+$, 100), 312 ($[MH-Br]^+$, 25), 311 ($[M-Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{17}H_{12}OBr$ ($[M-Br]^+$) 311.0072, found 311.0079.

2,2-Dibromo-3-(p-tolyl)spiro[cyclopropane-1,2'-inden]-1'(3'H)-one (15b). Colorless solid; Yield 68%, 276 mg; mp 104-106 °C; IR (KBr, cm^{-1}) 3016 (w), 2918 (w), 1713 (m), 1607 (w), 1467 (w), 1279 (w), 1217 (w), 1037 (w), 769 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.18 (unresolved m, 4H), 3.58 (s, 1H), 3.41 (ABq, *J* = 18.3 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 151.6, 137.9, 136.6, 135.1, 130.2, 129.8, 129.4, 128.1, 126.1, 124.3, 44.6, 44.4, 37.9, 33.9, 21.4; MS (ES+, Ar) m/z (rel intensity) 328 ($[(M+3)-Br]^+$, 21), 327 ($[(M+2)-Br]^+$, 100), 326 ($[MH-Br]^+$, 18), 325 ($[M-Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{18}H_{14}OBr$ ($[M-Br]^+$) 325.0228, found 325.0227.

2,2-Dibromo-3-(3,4-dimethylphenyl)spiro[cyclopropane-1,2'-inden]-1'(3'H)-one (15c). Colorless solid; Yield 72%, 302 mg; mp 112-114 °C; IR (KBr, cm^{-1}) 3053 (w), 2920 (w), 1713 (vs), 1606 (s), 1517 (m), 1466 (m), 1278 (s), 1203 (m), 1036 (s), 1022 (m), 770 (s), 737 (s), 714 (m), 515 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.66 (td, *J* = 7.7, 1.0 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.07 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 3.57 (s, 1H), 3.50 (d, *J* = 18.3 Hz, 1H), 3.43 (ABq, *J* = 18.3 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 151.7, 137.0, 136.6, 135.1, 131.1, 130.6, 129.9, 128.1, 127.1, 126.1, 124.4, 44.6, 44.5, 38.0, 34.0, 20.0, 19.7; MS (ES+, Ar) m/z (rel intensity) 342 ($[(M+3)-Br]^+$, 25), 341 ($[(M+2)-Br]^+$, 100), 340 ($[MH-Br]^+$, 25), 339 ($[M-Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{19}H_{16}OBr$ ($[M-Br]^+$) 339.0385, found 339.0373.

2,2-Dibromo-3-(4-fluorophenyl)spiro[cyclopropane-1,2'-inden]-1'(3'H)-one (15d). Colorless solid; Yield 53%, 217 mg; mp 126-128 °C; IR (KBr, cm^{-1}) 2925 (s), 2863 (m), 1714 (vs), 1604 (m), 1512 (s), 1276 (m), 1225 (m), 1157 (m), 1035 (m), 1015 (m), 771 (s), 738 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.67 (td, *J* = 7.7, 1.1 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.32–7.24 (m, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 3.57 (s, 1H), 3.40 (ABq, *J* = 18.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 162.5 (d, J_{C-F} = 247.0 Hz), 151.4, 136.5, 135.3, 131.7 (d, J_{C-F} = 9.0 Hz), 129.1, 129.0, 128.2, 126.1, 124.4, 115.9, 115.7, 44.4, 43.9, 37.3, 33.9; MS (ES+, Ar) m/z (rel intensity) 332 ($[(M+3)-Br]^+$, 21), 331 ($[(M+2)-Br]^+$, 100), 330 ($[MH-Br]^+$, 23), 329 ($[M-Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{17}H_{11}OBrF$ ($[M-Br]^+$) 328.9977, found 328.9977.

2,2-Dibromo-3-(naphthalen-1-yl)spiro[cyclopropane-1,2'-inden]-1'(3'H)-one (15e). Colorless solid; Yield 78%, 345 mg; mp 144-146 °C; IR (KBr, cm^{-1}) 3019 (m), 1712 (w), 1606 (w), 1279 (w), 1216 (s), 759 (s), 669 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.90–7.83 (m, 3H), 7.67 (td, *J* = 7.6, 1.0 Hz, 1H), 7.54–7.42 (m, 6H), 3.93 (s, 1H), 3.46 (ABq, *J* = 18.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 151.9, 136.6, 135.3, 133.9, 132.5, 130.3, 129.0, 128.9, 128.2, 127.6, 126.9, 126.4, 126.2, 125.1, 124.5, 124.4, 44.7, 43.5, 38.4, 34.8; MS (ES+, Ar) m/z (rel intensity) 364 ($[(M+3)-Br]^+$, 24), 363 ($[(M+2)-Br]^+$, 100), 362 ($[(MH-Br]^+$, 24), 361 ($[M-Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{21}H_{14}OBr$ ($[M-Br]^+$) 361.0228, found 361.0217.

2',2'-Dibromo-3'-phenyl-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopropan]-5(7H)-one (18a). Colorless solid; Yield 65%, 225 mg; mp 124-126 °C; IR (KBr, cm^{-1}) 3060 (w), 3026 (w), 2946 (m), 2867 (w), 1667 (vs), 1598 (m), 1447 (m), 1293 (m), 1252 (s), 1209 (m), 964 (m), 776 (m), 755 (vs), 701 (m), 559 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 7.40–7.36 (m, 3H), 7.34–7.25 (m, 4H), 4.11 (s, 1H), 3.38 (td, *J* = 13.6, 5.1 Hz, 1H), 2.95 (dt, *J* = 13.6 Hz, 3.7 Hz, 1H), 2.61–2.51 (m, 1H), 2.19 (dt, *J* = 15.5, 8.9 Hz, 1H), 1.81 (ddd, *J* = 15.5, 8.4, 1.4 Hz, 1H), 1.76–1.68 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 141.7, 136.4, 134.0, 133.8, 130.6, 130.2, 129.8, 128.5, 127.6, 127.1, 45.9, 42.1, 37.8, 32.7, 26.4, 23.4; MS (ES+, Ar) m/z (rel intensity) 342 ($[(M+3)-Br]^+$, 21), 341 ($[(M+2)-Br]^+$, 100), 340 ($[MH-Br]^+$, 21), 339 ($[M-Br]^+$, 93); HRMS (ES+, Ar) calcd for $C_{19}H_{16}OBr$ ($[M-Br]^+$) 339.0385, found 339.0375.

2',2'-Dibromo-3'-(p-tolyl)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopropan]-5(7H)-one (18b). Colorless solid; Yield 69%, 299 mg; mp 110-112 °C; IR (KBr, cm^{-1}) 2932 (m), 2865 (w), 1668 (vs), 1598 (m), 1515 (w), 1450 (m), 1293 (m), 1251 (s), 1208 (w), 1029 (w), 964 (w), 769 (m), 742 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.19 (unresolved, 4H), 4.05 (s, 1H), 3.37 (td, *J* = 13.8, 5.0 Hz, 1H), 2.94 (dt, *J* = 13.8, 3.4 Hz, 1H), 2.59–2.51 (m, 1H), 2.36 (s, 3H), 2.18 (dt, *J* = 15.5, 8.9 Hz, 1H), 1.80 (dd, *J* = 15.5, 8.4 Hz, 1H), 1.76-1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 141.7, 137.4, 136.5, 133.7, 131.0, 130.6, 130.1, 129.7, 129.3, 127.1, 45.8, 42.0, 38.2, 32.7, 26.4, 23.4, 21.4; MS (ES+, Ar) m/z (rel intensity) 356 ($[(M+3)\text{-}Br]^+$, 20), 355 ($[(M+2)\text{-}Br]^+$, 93), 354 ($[MH\text{-}Br]^+$, 22), 353 ($[M\text{-}Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{20}H_{18}OBr$ ($[M\text{-}Br]^+$) 353.0541, found 353.0536.

2',2'-Dibromo-3'-(4-fluorophenyl)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopropan]-5(7H)-one (18c). Colorless solid; Yield 70%, 306 mg; mp 128-130 °C; IR (KBr, cm^{-1}) 3068 (w), 2949 (m), 2868 (w), 1667 (s), 1598 (s), 1512 (s), 1450 (m), 1295 (s), 1253 (s), 1226 (s), 1158 (m), 964 (m), 896 (m), 773 (m), 739 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.53 (td, *J* = 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.6, 0.9 Hz, 1H), 7.26-7.25 (m, 3H), 7.09–7.03 (m, 2H), 4.03 (s, 1H), 3.36 (td, *J* = 14.0, 5.1 Hz, 1H), 2.95 (dt, *J* = 14.0, 3.6 Hz, 1H), 2.56–2.50 (m, 1H), 2.16 (dt, *J* = 15.4, 8.9 Hz, 1H), 1.78–1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 162.3 (d, $J_{C\text{-}F}$ = 250.0 Hz), 141.7, 136.3, 133.9, 132.0, 131.9, 130.6, 129.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.5 (d, $J_{C\text{-}F}$ = 26.4 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.0 Hz), 45.9, 41.4, 37.6, 32.7, 26.3, 23.4; MS (ES+, Ar) m/z (rel intensity) 360 ($[(M+3)\text{-}Br]^+$, 22), 359 ($[(M+2)\text{-}Br]^+$, 100), 358 ($[MH\text{-}Br]^+$, 22), 357 ($[M\text{-}Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{19}H_{15}OBrF$ ($[M\text{-}Br]^+$) 357.0290, found 357.0292.

2',2'-Dibromo-3'-(3,4-dimethoxyphenyl)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopropan]-5(7H)-one (18e). Colorless solid; Yield 74%, 355 mg; mp 98-100 °C; IR (KBr, cm^{-1}) 2933 (vw), 2835 (w), 1667 (s), 1597 (m), 1517 (s), 1450 (m), 1251 (vs), 1140 (m), 1027 (s), 767 (m), 739 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.26-7.28 (m, 1H), 6.80-6.87 (m, 3H), 4.04 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.37 (td, *J* = 14.0, 5.1 Hz, 1H), 2.95 (dt, *J* = 14.0, 3.6 Hz, 1H), 2.63–2.49 (m, 1H), 2.16 (dt, *J* = 15.5, 9.1 Hz, 1H), 1.83 (dd, *J* = 15.5, 8.3 Hz, 1H), 1.79–1.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 148.9, 148.5, 141.8, 136.5, 133.8, 130.6, 129.8, 127.2, 126.4, 122.4, 113.3, 111.1, 56.2, 56.0, 46.0, 41.9, 38.3, 32.7, 26.4, 23.5; MS (ES+, Ar) m/z (rel intensity) 402 ($[(M+3)-Br]^+$, 23), 401 ($[(M+2)-Br]^+$, 100), 400 ($[MH-Br]^+$, 23), 399 ($[M-Br]^+$, 93); HRMS (ES+, Ar) calcd for $C_{21}H_{20}O_3Br$ ($[M-Br]^+$) 399.0596, found 399.0598.

(2, 2-Dibromo-1-methyl-3-phenylcyclopropyl)(phenyl)methanone (21). Colorless solid; Yield 56%, 237 mg; mp 124-126 °C; IR (KBr, cm^{-1}) 2928 (w), 1683 (s), 1610 (m), 1514 (m), 1450 (w), 1248 (s), 1173 (w), 1033 (w), 972 (w), 745 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.03 (m, 2H), 7.66–7.61 (m, 1H), 7.59–7.55 (m, 2H), 7.30 (dd, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.53 (s, 1H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 159.1, 134.4, 133.7, 131.4, 130.2, 128.9, 125.5, 114.1, 55.4, 43.6, 38.9, 36.9, 19.8; MS (ES+, Ar) m/z (rel intensity) 346 ($[(M+3)-Br]^+$, 8), 345 ($[(M+2)-Br]^+$, 40), 344 ($[(MH-Br]^+$, 8), 343 ($[M-Br]^+$, 40), 264 (100); HRMS (ES+, Ar) calcd for $C_{18}H_{16}O_2Br$ ($[M-Br]^+$) 343.0334, found 343.0350.

2',2'-Dibromo-3'-phenyl-2H-spiro[acenaphthylene-1,1'-cyclopropan]-2-one (24). Colorless solid; Yield 70%, 300 mg; mp 132-134 °C; IR (KBr, cm^{-1}) 3055 (w), 2924 (w), 2852 (w), 1722 (vs), 1599 (w), 1492 (w), 1429 (w), 1373 (w), 1252 (m), 1089 (w), 780 (m), 749 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 7.1 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.79 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.46 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.38–7.30 (m, 3H), 7.18-7.22 (m, 2H), 6.73 (d, *J* = 7.1 Hz, 1H), 4.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 142.9, 133.2, 132.4, 132.2, 131.7, 130.6, 130.5, 128.4, 128.2, 127.8, 125.1, 122.9, 47.8, 45.6, 37.6; MS (ES+, Ar) m/z (rel intensity) 350 ($[(M+3)-Br]^+$, 25), 349 ($[(M+2)-Br]^+$, 100), 348 ($[MH-Br]^+$, 25), 347 ($[M-Br]^+$, 100); HRMS (ES+, Ar) calcd for $C_{20}H_{12}OBr$ ($[M-Br]^+$) 347.0072, found 347.0078. Selected X-ray Data: $C_{20}H_{12}Br_2O$, M = 428.12, Triclinic, space group P -1, a = 11.7848(4) Å, b = 12.5578(8) Å, c = 12.5773(4) Å, α = 97.749(3) °, β = 117.692(2)°, γ = 92.803(3) °, V = 1619.82(13) Å^3, D_c = 1.756 Mg/m^3, Z = 4, F(000) = 840, λ = 0.71073 Å, μ = 5.01 mm^{-1}, Total/ unique reflections = 27307 / 8087 [R(int) = 0.0618], T = 293(2) K, θ range = 1.7–28.5°, Final R [I>2σ(I)]: R1 = 0.0375, wR2 = 0.0801, R (all data): R1 = 0.0768, wR2 = 0.0925.

General Procedure for the Acidic Al_2O_3 Mediated Conversion of Dibromocyclopropanes 11/15/18/21/24 to Bromofurans 13/16/19/22/25. To a stirred the solution of dibromocyclopropane **11/15/18/21/24** (0.1 mmol) in chloroform (5 mL) was added activated acidic Al_2O_3 (250 mg, 25 equiv, excess) and the reaction mixture was refluxed. After completion (monitored by TLC), the reaction mixture was concentrated in vacuo and the crude residue was subjected to silica gel column chromatography (EtOAc/hexane mixture, gradient elution) to afford bromofuran **13/16/19/22/25**.

3-Bromo-2-(2,4-dimethoxyphenyl)-4,5-dihydronaphtho[1,2-b]furan (13e). Colorless liquid; Yield 83%, 32 mg; IR (KBr, cm^{-1}) 2933 (m), 2835 (w), 1605 (w), 1505 (s), 1268 (s), 1251 (s), 1027 (s), 1222 (m), 1144 (m), 1027 (m), 763 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.21-7.25 (m, 2H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 6.57-6.61 (m, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 3.04 (t, *J* = 7.9 Hz, 2H), 2.75 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 158.7, 149.2, 147.5, 134.8, 132.1, 128.2, 127.7, 126.9, 121.5, 119.4, 111.9, 104.8, 101.0, 99.2, 55.8, 55.6, 28.8, 20.2; MS (ES+, Ar) m/z (rel intensity) 387 ($[M+3]^+$, 95), 386 ($[M+2]^+$, 25), 385 (MH^+, 100), 388 (25); HRMS (ES+, Ar) calcd for $C_{20}H_{18}O_3Br$ ($[MH]^+$) 385.0439, found 385.0456.

3-Bromo-2-(3,4-dimethoxyphenyl)-4,5-dihydronaphtho[1,2-b]furan (13f). Colorless solid; Yield 85%, 33 mg; mp 126-128 °C; IR (KBr, cm^{-1}) 2926 (s), 2852 (w), 1662 (vs), 1597 (s), 1454 (w), 1268 (vs), 1048 (s), 740 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.56–7.52 (m, 1H), 7.28–7.23 (m, 1H), 7.22–7.18 (m, 1H), 7.15 (td, *J* = 7.4, 1.3 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.02 (t, *J* = 7.9 Hz, 2H), 2.72 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 148.5, 147.9, 134.9, 128.3, 127.3, 127.1, 127.0, 123.2, 122.5, 119.4, 118.6, 111.2, 108.8, 97.8, 56.1 (× 2), 28.6, 20.1; MS (ES+, Ar) m/z (rel intensity) 387 ($[M+3]^+$, 100), 386 ($[M+2]^+$, 32), 385 (MH^+, 98), 384 (M^+, 15), 337 (17), 300 (16), 291 (40), 265 (85), 263 (88); HRMS (ES+, Ar) calcd for $C_{20}H_{18}O_3Br$ ($[MH]^+$) 385.0439, found 385.0429. Confirmed by ^1H-^1H 2D-NOESY experiment.

3-Bromo-2-(3,4,5-trimethoxyphenyl)-4,5-dihydronaphtho[1,2-b]furan (13h). Yellow solid; Yield 87%, 36 mg; mp 116-118 °C; IR (KBr, cm^{-1}) 2923 (s), 2851 (m), 1655 (w), 1484 (m), 1464 (m), 1288 (m), 1096 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.54 (m, 1H), 7.29 (s, 2H), 7.27–7.20 (m, 2H), 7.19–7.14 (td, J = 7.3, 1.2 Hz, 1H), 3.96 (s, 6H), 3.91 (s, 3H), 3.03 (t, J = 8.0 Hz, 2H), 2.73 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 148.9, 147.7, 138.1, 135.0, 128.3, 127.4, 127.2, 127.0, 125.7, 122.6, 119.5, 103.0, 98.7, 61.1, 56.4, 28.6, 20.0; MS (ES+, Ar) m/z (rel intensity) 418 ($[M+4]^+$, 18), 417 ($[M+3]^+$, 100), 416 ($[M+2]^+$, 25), 415 (MH^+, 100), 400 (15); HRMS (ES+, Ar) calcd for $C_{21}H_{20}O_4Br$ ($[MH]^+$) 415.0545, found 415.0564.

(E)-3-Bromo-2-(2-methoxystyryl)-4,5-dihydronaphtho[1,2-b]furan (13n). Yellow solid; Yield 70%, 266 mg; mp 148-150 °C; IR (KBr, cm^{-1}) 2961 (w), 2929 (w), 2840 (w), 1659 (br, w), 1480 (w), 1466 (w), 1244 (s), 1030 (m), 959 (m), 749 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.5, 1.2 Hz, 2H), 7.53 (d, J = 16.4 Hz, 1H), 7.30–7.24 (m, 2H), 7.21 (dd, J = 7.5, 1.2 Hz, 1H), 7.16 (td, J = 7.5, 1.2 Hz, 1H), 7.07 (d, J = 16.4 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H), 3.01 (t, J = 7.9 Hz, 2H), 2.71 (t, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 149.8, 149.4, 135.1, 129.0, 128.2, 127.3, 127.2, 127.0, 126.9, 126.2, 123.0, 122.0, 120.9, 119.8, 114.5, 111.2, 101.9, 55.7, 28.6, 19.9; MS (ES+, Ar) m/z (rel intensity) 384 ($[M+4]^+$, 30), 383 ($[M+3]^+$, 100), 382 ($[M+2]^+$, 25), 381 (MH^+, 100); HRMS (ES+, Ar) calcd for $C_{21}H_{18}O_2Br$ (MH^+) 381.0490, found 381.0501.

3-Bromo-2-(3,4-dimethoxyphenyl)-8-methoxy-4,5-dihydronaphtho[1,2-b]furan (13p). Colorless solid; Yield 84%, 35 mg; mp 114-116 °C; IR (KBr, cm^{-1}) 2923 (m), 2846 (w), 1651 (vs), 1495 (w), 1262 (m), 1223 (m), 1026 (m), 752 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.5, 2.0 Hz, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H), 7.09 (d, J = 2.6 Hz, 1H), 6.95 (d, J = 8.5 Hz, 1H), 6.70 (dd, J = 8.3, 2.6 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.85 (s, 3H), 2.95 (t, J = 7.9 Hz, 2H), 2.70 (t, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 149.0, 148.9, 148.5, 148.0, 129.1, 128.2, 127.1, 123.2, 123.1, 118.7, 112.1, 111.2, 108.9, 105.4, 97.9, 56.2, 56.1, 55.6, 27.8, 20.4; MS (ES+, Ar) m/z (rel intensity) 418 ($[M+4]^+$, 25), 417 ($[M+3]^+$, 100), 416 ($[M+2]^+$, 25), 415 (MH^+, 100); HRMS (ES+, Ar) calcd for $C_{21}H_{20}O_4Br$ ($[MH]^+$) 415.0545, found 415.0565.

3-Bromo-2-phenyl-4H-indeno[1,2-b]furan (16a). Colorless solid; Yield 84%, 26 mg; mp 104-106 °C; IR (KBr, cm^{-1}) 2923 (s), 2857 (m), 1712 (m), 1605 (m), 1438 (br, m), 1259 (br, m), 1023 (w), 944 (m), 757 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.04 (m, 2H), 7.54–7.47 (m, 2H), 7.47–7.44 (m, 2H), 7.37-7.31 (m, 2H), 7.22 (td, J = 7.5, 1.1 Hz, 1H), 3.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 151.8, 145.4, 133.0, 131.7, 130.7, 128.7, 127.9, 127.3, 125.8, 125.5, 125.3, 117.2, 96.2, 29.6; MS (ES+, Ar) m/z (rel intensity) 330 (17), 329 (100), 328 (17), 327 (100), 313 ($[(M+2)H]^+$, 17), 311 (MH^+, 17); HRMS (ES+, Ar) calcd for $C_{17}H_{12}OBr$ ($[MH]^+$) 311.0072, found 311.0057.

3-Bromo-2-(p-tolyl)-4H-indeno[1,2-b]furan (16b). Colorless solid; Yield 89%, 29 mg; mp 100-102 °C; IR (KBr, cm^{-1}) 2925 (vs), 2852 (m), 1709 (m), 1605 (m), 1457 (m), 1259 (m), 1023 (m), 752 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.21 (td, J = 7.5, 1.1 Hz, 1H), 3.51 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 152.1, 145.3, 137.9, 133.1, 131.6, 129.4, 127.9, 127.2, 125.8, 125.5, 125.2, 117.1, 95.5, 29.6, 21.6; MS (ES+, Ar) m/z (rel intensity) 343 (86), 341 (100), 327 ($[(M+2)H]^+$, 18), 325 (MH^+, 19); HRMS (ES+, Ar) calcd for $C_{18}H_{14}OBr$ ($[MH]^+$) 325.0228, found 325.0226.

3-Bromo-2-(3,4-dimethylphenyl)-4H-indeno[1,2-b]furan (16c). Colorless solid; Yield 85%, 29 mg; mp 94-96 °C; IR (KBr, cm^{-1}) 2921 (vs), 2852 (m), 1706 (s), 1646 (s), 1432 (w), 1402 (w), 1259 (w), 1023 (m), 966 (w), 883 (w), 749 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81–7.78 (m, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.18-7.22 (m, 2H), 3.51 (s, 2H), 2.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 152.2, 145.3, 136.9, 136.7, 133.1, 131.6, 129.9, 128.3, 127.2, 126.7, 125.8, 125.1, 123.2, 117.0, 95.4, 29.6, 20.1, 19.9; MS (ES+, Ar) m/z (rel intensity) 341 ($[M+3]^+$, 100), 340 ($[M+2]^+$, 38), 339 (MH^+, 98), 338 (M^+, 39); HRMS (ES+, Ar) calcd for $C_{19}H_{16}OBr$ ($[MH]^+$) 339.0385, found 339.0388.

3-Bromo-2-(4-fluorophenyl)-4H-indeno[1,2-b]furan (16d). Pale yellow solid; Yield 82%, 27 mg; mp 114-116 °C; IR (KBr, cm^{-1}) 2928 (s), 2868 (m), 1712 (m), 1605 (m), 1487 (br, w), 1236 (s), 1158 (w), 1065 (m), 947 (m), 840 (m), 757 (vs); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05–7.99 (m, 2H), 7.51-7.47 (m, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.22 (td, J = 7.4, 1.1 Hz, 1H), 7.17–7.11 (m, 2H), 3.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 247.0 Hz), 158.0, 151.0, 145.3, 132.9, 131.5, 127.5, 127.4 (d, J_{C-F} = 8.0 Hz), 126.9 (d, J_{C-F} = 3.0 Hz), 125.8, 125.4, 117.1, 115.8 (d, J_{C-F} = 22.0 Hz), 95.9, 29.5; MS (ES+, Ar) m/z (rel intensity) 331 ($[(M+2)H]^+$, 25), 329 ($[MH]^+$, 25), 248 (100), 250 (81), 265 (43), 281 (69); HRMS (ES+, Ar) calcd for $C_{17}H_{11}OBrF$ ($[MH]^+$) 328.9977, found 328.9971.

3-Bromo-2-(naphthalen-1-yl)-4H-indeno[1,2-b]furan (16e). Colorless viscous liquid; Yield 87%, 32 mg; IR (KBr, cm^{-1}) 2918 (s), 2857 (m), 1602 (w), 1432 (m), 1289 (m), 1265 (m), 1128 (w), 1021 (m), 933 (w), 798 (m), 774 (s), 755 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.09 (m, 1H), 7.97–7.92 (m, 2H), 7.80 (d, J = 7.1 Hz, 1H), 7.60–7.54 (m, 5H), 7.37 (t, J = 7.5 Hz, 1H), 7.27–7.23 (m, 1H), 3.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 153.0, 145.3, 134.0, 133.2, 131.8, 130.5, 130.0, 129.3, 128.6, 127.3, 126.9, 126.4, 126.3, 125.9, 125.4, 125.2, 117.2, 99.2, 29.7; MS (ES+, Ar) m/z (rel intensity) 364 ($[M+4]^+$, 25), 363 ($[M+3]^+$, 100), 362 ($[M+2]^+$, 30), 361 (MH^+, 100); HRMS (ES+, Ar) calcd for $C_{21}H_{14}OBr$ (MH^+) 361.0228, found 361.0234.

3-Bromo-2-(4-methoxyphenyl)-4H-indeno[1,2-b]furan (16f). Pale yellow solid; Yield 76%, 259 mg; mp 198-200 °C; IR (KBr, cm^{-1}) 3050 (w), 2995 (w), 2963 (w), 2935 (w), 2855 (w), 1656 (br, s), 1608 (s), 1486 (s), 1255 (vs), 1241 (s), 1177 (s), 1027 (vs), 946 (m), 831 (s), 755 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.20 (td, J = 7.5, 1.1 Hz, 1H), 6.99 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H), 3.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 157.4, 152.0, 145.2, 133.2, 131.6, 127.2 (× 2), 125.7, 125.0, 123.5, 116.9, 114.2, 94.7, 55.5, 29.6; MS (ES+, Ar) m/z (rel intensity) 344 ($[MH+3]^+$, 15), 343 ($[(MH+2)]^+$, 93), 342 ($[MH+1]^+$, 34), 341 (MH^+, 100); HRMS (ES+, Ar) calcd for $C_{18}H_{14}O_2Br$ (MH^+) 341.0177, found 341.0177.

3-Bromo-2-phenyl-5,6-dihydro-4H-benzo[6,7]cyclohepta[1,2-b]furan (19a). Colorless liquid; Yield 88%, 30 mg; IR (KBr, cm^{-1}) 2931 (w), 1680 (vs), 1599 (s), 1582 (m), 1490 (m), 1455 (m), 1432 (m), 1300 (s), 1288 (m), 1222 (m), 1052 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (m, 2H), 7.96 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.38–7.28 (m, 2H), 7.20-7.15 (m, 2H), 2.94 (t, J = 10.5 Hz, 2H), 2.75 (t, J = 6.5 Hz, 2H), 2.06 (tt, J = 10.5, 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 146.9, 139.4, 129.9, 129.6, 129.3, 128.6, 127.9, 127.2, 126.4, 125.5, 125.1, 124.4, 101.6, 35.7, 27.6, 24.4; MS (ES+, Ar) m/z (rel intensity) 342 ($[MH+3]^+$, 24), 341 ($[(MH+2)]^+$, 100), 340 ($[MH+1]^+$, 24), 339 ($[MH]^+$, 100); HRMS (ES+, Ar) calcd for $C_{19}H_{16}OBr$ ($[MH]^+$) 339.0393, found 339.0385.

3-Bromo-2-(p-tolyl)-5,6-dihydro-4H-benzo[6,7]cyclohepta[1,2-b]furan (19b). Colorless liquid; Yield 88%, 31 mg; IR (KBr, cm^{-1}) 3025 (w), 2926 (vs), 2851 (m), 1646 (br, s), 1498 (s), 1446 (m), 1266 (m), 1109 (m), 819 (s), 761 (vs), 737 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.7 Hz, 2H), 7.94 (d, J = 7.8 Hz, 1H), 7.33–7.26 (m, 3H), 7.23–7.14 (m, 2H), 2.93–2.90 (m, 2H), 2.74 (t, J = 6.4 Hz, 2H), 2.41 (s, 3H), 2.06 (quintet, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 146.6, 139.4, 138.0, 129.6, 129.5, 129.4, 127.3, 127.2, 126.5, 125.7, 125.1, 124.5, 101.0, 35.9, 27.7, 24.5, 21.6; MS (ES+, Ar) m/z (rel intensity) 356 ($[M+4]^+$, 23), 355 ($(M+3)^+$, 100), 354 ($[M+2]^+$, 22), 353 ($[MH]^+$, 82); HRMS (ES+, Ar) calcd for $C_{20}H_{18}OBr$ (MH^+) 353.0541, found 353.0555.

3-Bromo-2-(4-fluorophenyl)-5,6-dihydro-4H-benzo[6,7]cyclohepta[1,2-b]furan (19c). Colorless liquid; Yield 81%, 29 mg; IR (KBr, cm^{-1}) 3069 (w), 2928 (s), 2861 (m), 1604 (m), 1557 (w), 1497 (s), 1447 (m), 1234 (s), 1159 (m), 835 (s), 761 (s), 737 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–8.03 (m, 2H), 7.91 (d, J = 7.7 Hz, 1H), 7.32–7.28 (m, 1H), 7.21–7.12 (m, 4H), 2.93–2.90 (m, 2H), 2.73 (t, J = 6.5 Hz, 2H), 2.05 (quintet, J = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 248.6 Hz), 147.0, 146.4, 139.5, 129.70, 129.4, 127.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 127.4, 126.6, 126.4 (d, $J_{C\text{-}F}$ = 3.3 Hz), 125.1, 124.5, 115.8 (d, $J_{C\text{-}F}$ = 21.8 Hz), 101.3, 35.8, 27.7, 24.5; MS (ES+, Ar) m/z (rel intensity) 359 ($[M+4]^+$, 22), 359 ($[M+3]^+$, 100), 358 ($[M+2]^+$, 22), 357 (MH^+, 100); HRMS (ES+, Ar) calcd for $C_{19}H_{15}OBrF$ (MH^+) 357.0290, found 357.0292.

3-Bromo-2-(4-methoxyphenyl)-5,6-dihydro-4H-benzo[6,7]cyclohepta[1,2-b]furan (19d). Colorless liquid; Yield 84%, 310 mg (from reaction at 1 mmol scale); IR (KBr, cm^{-1}) 3054 (s), 2987 (m), 1607 (m), 1500 (s), 1442 (m), 1422 (m), 1266 (vs), 1180 (m), 896 (m), 739 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, J = 9.0, 2.1 Hz, 2H), 7.91 (dd, J = 8.2, 1.0 Hz, 1H), 7.29 (ddd, J = 8.2, 6.7, 2.1 Hz, 1H), 7.19–7.12 (m, 2H), 6.98 (dt, J = 9.0, 2.1 Hz, 2H), 3.86 (s, 2H), 2.92 (t, J = 10.5 Hz, 2H), 2.72 (t, J = 6.5 Hz, 2H), 2.04 (tt, J = 10.5, 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 147.3, 146.4, 139.3, 129.6 (× 2), 127.2, 127.1, 126.5, 125.0, 124.4, 122.9, 114.1, 100.1, 55.5, 35.9, 27.8, 24.5; MS (ES+, Ar) m/z (rel intensity) 371 ($[(MH+2)]^+$, 100), 370 ($[(MH+1)]^+$, 50), 369 (MH^+, 100), 368 (M^+, 45); HRMS (ES+, Ar) calcd for $C_{20}H_{18}O_2Br$ (MH^+) 369.0490, found 369.0482.

3-Bromo-2-(3,4-dimethoxyphenyl)-5,6-dihydro-4H-benzo[6,7]cyclohepta[1,2-b]furan (19e). Pale yellow solid; Yield 90%, 36 mg; mp 96-98°C; IR (KBr, cm^{-1}) 2929 (m), 2835 (w), 1647 (vs), 1503 (vs), 1462 (m), 1440 (m), 1252 (s), 1027 (s), 762 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.5, 0.9 Hz, 1H), 7.63 (ABq, J = 8.4 Hz, the lower half further split into d, J = 2.1 Hz, 2H), 7.33–7.27 (td, J = 6.9, 1.9 Hz, 1H), 7.20–7.13 (m, 2H), 6.95 (d, J = 8.4 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 2.92 (t, J = 10.5 Hz, 2H), 2.73 (t, J = 6.5 Hz, 2H), 2.05 (tt, J = 10.5, 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 148.9, 147.2, 146.4, 139.4, 129.7, 129.5, 127.2, 126.5, 125.0, 124.4, 123.1, 118.8, 111.2, 109.0, 100.4, 56.1 (× 2), 35.8, 27.7, 24.5; MS (ES+, Ar) m/z (rel intensity) 401 ($[MH+1]^+$, 75), 399 (MH^+, 100), 359 (60), 357 (60); HRMS (ES+, Ar) calcd for $C_{21}H_{20}O_3Br$ (MH^+) 399.0596, found 399.0596; Selected X-ray Data: $C_{21}H_{19}BrO_3$, M = 399.27, Orthorhombic, space group $P2_12_12_1$, a = 7.9204 (3) Å, b = 8.6133 (3) Å, c = 25.5389 (11) Å, α = 90.00 °, β = 90.00 °, γ = 90.00 °, V = 1742.28 (12) Å^3, D_c = 1.756 Mg/m^3, Z = 4, F(000) = 840, λ = 0.71073 Å, μ = 5.01 mm^{-1}, Total/ unique reflections = 27307 / 8087 [R(int) = 0.0618], T = 293(2) K, θ range = 1.7–28.5°, Final R [I>2σ(I)]: R1 = 0.0375, wR2 = 0.0801, R (all data): R1 = 0.0768, wR2 = 0.0925.

9-Bromo-8-phenylacenaphtho[1,2-b]furan (25). Yellow solid; Yield 83%, 29 mg; mp 112-114 °C; IR (KBr, cm^{-1}) 2922 (m), 2846 (w), 1602 (m), 1435 (w), 1410 (w), 1259 (w), 1240 (w), 760 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.08 (m, 2H), 7.86 (d, J = 6.9 Hz, 1H), 7.76 (t, J = 7.6 Hz, 3H), 7.56 (d, J = 6.9 Hz, 1H), 7.54 (d, J = 6.9 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.38–7.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 152.9, 131.0, 130.9, 130.5, 129.6, 129.4, 128.8, 128.1, 127.8, 127.7, 127.6, 127.4, 126.6, 125.6, 122.1, 120.0, 94.2; MS (ES+, Ar) m/z (rel intensity) 350 ($[M+4]^+$, 26), 349 ($[M+3]^+$, 100), 348 ($[M+2]^+$, 25), 347 (MH^+, 100); HRMS (ES+, Ar) calcd for $C_{20}H_{12}OBr$ (MH^+) 347.0072, found 347.0078.

3-Bromo-2-(3,4-dimethoxyphenyl)naphtho[1,2-b]furan 26f (via DDQ dehydrogenation of 13f). A suspension of dihydronaphthofuran **13f** (0.2 mmol, 77 mg) and DDQ (0.28 mmol, 64 mg) in dioxane (5 mL) was refluxed with stirring for 15 h (monitored by TLC). The solvent was removed in vacuo and the residue was purified by silica gel column chromatography using 5% ethyl acetate-pet ether as eluent. Colorless solid; Yield 80%, 61 mg; mp 88-90 °C; IR (KBr, cm^{-1}) 3058 (w), 2929 (s), 2834 (w), 1645 (s), 1505 (m), 1381 (m), 1248 (m), 1267 (s), 1222 (m), 1094 (m), 1027 (s), 811 (m), 749 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.81 (dd, J = 8.4, 2.0 Hz, 1H), 7.77

(d, J = 2.0 Hz, 1H), 7.73–7.71 (m, 1H), 7.64–7.62 (m, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.53–7.49 (m, 1H), 7.00 (d, J = 8.5 Hz, 1H), 4.03 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.7, 149.0, 148.7, 132.1, 128.7, 126.8, 125.7, 125.5, 124.4, 122.8, 121.0, 120.0, 119.9, 117.9, 111.3, 109.7, 93.6, 56.2, 56.1; MS (ES+, Ar) m/z (rel intensity) 386 ([M+4]$^+$, 23), 385 ((M+3)$^+$, 100), 384 ([M+2]$^+$, 22), 383 (MH$^+$, 100); HRMS (ES+, Ar) calcd for $C_{20}H_{16}O_3Br$ ([MH]$^+$) 383.0283, found 383.0275.

Acknowledgment. INNN thanks DST India for financial assistance. EG thanks CSIR India for a senior research fellowship. The authors thank SAIF, IIT Madras, and University of Madras for X-ray data and Dr. G. N. Gururaja for helpful discussions.

Supporting Information Available. Complete characterization data and copies of NMR spectra for all the new compounds as well as CIF for compounds **11d, 19e** and **24**. This material is available free of charge via the internet at http://pubs.acs.org.

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