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The efficient synthesis of substituted 2-methylbenzofurans

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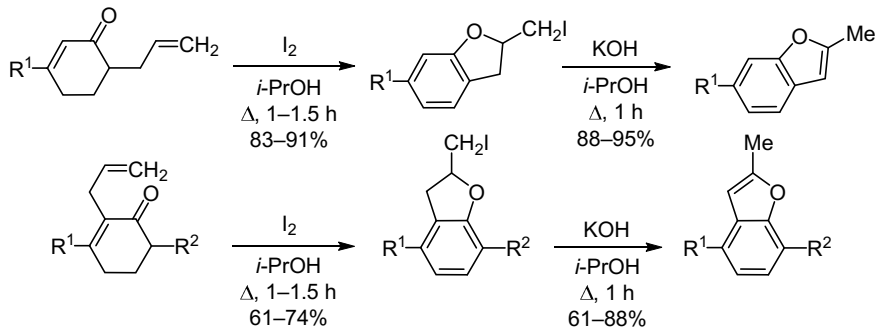


R^1 = Me, Br, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 6-MeO-naphthalen-2-yl, 4-(*trans*-4-ethylcyclohexyl)phenyl; R^2 = H, Et

The efficient synthesis of substituted 2-methylbenzofurans by aromatization of accessible allyl-substituted cyclohex-2-enones in the presence of iodine followed by dehydroiodination of the 2-iodomethyl-2,3-dihydrobenzofuran intermediate is described.

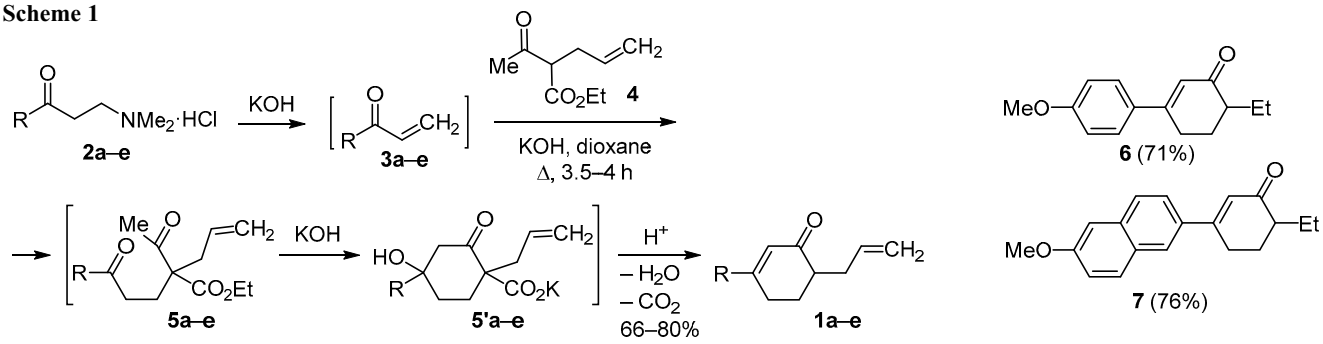
Keywords: aryl vinyl ketones, benzofurans, cyclohexenones, aromatization, iodocyclization.

Benzofuran is a fundamental structural unit in a variety of biologically active natural products as well as synthetic materials. Benzofuran derivatives, including substituted 2,3-dihydrobenzofurans and methylbenzofurans are of great interest because of their application in pharmacology and wide distribution in nature.[1–6] Substituted dihydrobenzofurans and methylbenzofurans have been used in the pharmaceutical industry for the preparation of drugs with antimicrobial, antiviral, antioxidative, antifungal, antineoplastic, and other properties.[7,8] The unique structural features of benzofuran and wide array of its biological activity made it privileged structure in drug discovery.

Due to the great biological importance of this scaffold, investigation of various synthesis methods and structural modifications of benzofuran derivatives have now become an important goal for several research groups. As a result, various methods for the synthesis of substituted 2,3-dihydrobenzofurans and methylbenzofurans have been described.[1–6,9–11] Typically, the routes leading to these compounds include cyclization of substituted *o*-allylphenols, using various catalysts or solid-phase synthesis,[12] or dehydrohalogenation of substituted 2-iodomethyl-2,3-dihydrobenzofurans, formed by the treatment of substituted *o*-allylphenols with I_2,[13] or iodo- and bromoenolcyclization of 2-(2-propenyl)cyclohexanediones and 2-(2-propenyl)-cyclohexenone derivatives using I_2 in MeOH.[14] Unfortunately, the utilization of expensive catalysts, sophisticated reagents, long reaction times, and low yields of the desired products limit the application of these methods for the preparation of substituted dihydrobenzofurans and methylbenzofurans.

It is known that *o*-alkylphenols can be synthesized by aromatization of the corresponding 6-substituted cyclohex-2-enones with high yields.[15,16] 3,6-Disubstituted cyclohex-2-enones can be easily prepared by condensation of the corresponding Mannich salt with the 2-substituted acetoacetic ester (or substituted methyl benzyl ketones) and are accessible intermediates for further chemical transformations into various substituted benzenes and biphenyls as earlier reported by us.[17–19] In continuation of these investigations and our quest to develop an effective route for the preparation of substituted 2-methylbenzofurans we were interested in the synthesis of allyl-substituted cyclohex-2-enones and their aromatization in the presence of I_2.

Scheme 1



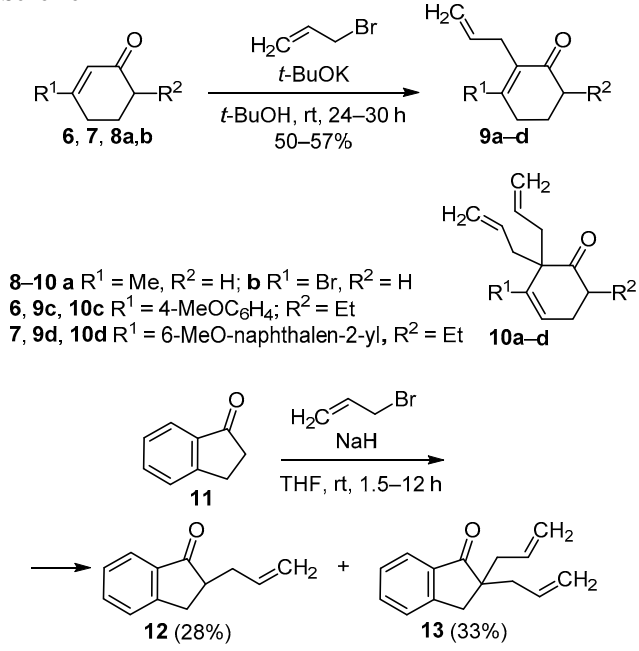
a R = Ph, **b** R = 4-MeC_6H_4, **c** R = 4-$MeOC_6H_4$, **d** R = 4-(*trans*-4-ethylcyclohexyl)phenyl, **e** R = 6-MeO-naphthalen-2-yl

Starting 6-allyl-3-arylcyclohex-2-enones **1a**–**e** were synthesized by Michael addition of aryl vinyl ketones **3a**–**e**, generated *in situ* from the corresponding Mannich salts **2a**–**e**, to 2-allylacetoacetic ester **4** in boiling dioxane in the presence of a base (Scheme 1).[17–19] Intermediate 1,5-diketones **5a**–**e** undergo intramolecular aldol condensation to cyclic compounds **5'a**–**e**, leading to the corresponding substituted cyclohex-2-enones **1a**–**e**. The similar transformations were also used for the preparation of 6-ethyl-3-(4-methoxyphenyl)cyclohex-2-enone **6** and 6-ethyl-3-(6-methoxy-2-naphthyl)cyclohex-2-enone **7**. The realization of this process in the presence of KOH in dioxane allowed us to prepare the desired products **1a**–**e**, **6**, **7** in 66–80% yield without isolation of intermediates or use of any auxiliary agents or phase-transfer catalysts.

The alkylation of substituted cyclohex-2-enones **6**, **7**, **8a**,**b** and indan-1-one (**11**) by allyl bromide at room temperature in the presence of *t*-BuOK[20] or NaH[21] was used for regioselective preparation of 2-allyl-substituted cyclohex-2-enones **9a**–**d** and 2-allylindan-1-one **12** (Scheme 2). It should be noted that in contrast to the alkylation of indan-1-one (**11**), when bisallylation product 2,2-bisallylindan-1-one **13** is formed, and similar investigations reported earlier[22,23] the interaction of 3,6-disubstituted cyclohex-2-enones **6**, **7**, **8a**,**b** with allyl bromide in these conditions didn't lead to the formation of bis-allylated byproducts **10a**–**d** (Scheme 2). 2-Allyl-3,6-disubstituted cyclohex-2-enones **9a**–**d** were prepared in 50–57% yield.

We continued with the transformation of 2-allyl-substituted cyclohex-2-enones **1a**–**e** and **9a**–**d** to the corresponding benzofurans through the stage of aromatization of cyclohexenone fragment and investigation of the possibility to use saturated cyclic allyl ketones for the preparation analogous furan derivatives. The aromatization of 6-allyl-3-arylcyclohex-2-enones **1a**–**e**, 2-allyl-substituted cyclohex-2-enones **9a**–**d** was carried out under previously reported conditions.[14,15,17] The conversion of 6-allyl-3-arylcyclohex-2-enones **1a**–**e** and 2-allyl-substituted cyclohex-2-enones **9a**–**d** in the presence of I_2 proceeded smoothly through the formation of the possible intermediate *o*-allylphenol, which *in situ* in reaction with of I_2 gave the required products – substituted 2-iodomethyl-2,3-dihydrobenzofurans **14a**–**e**, **16a**–**d** in up to 91% yield (Scheme 3). Further investigations have shown that 2-iodomethyl-

Scheme 2



Scheme 3

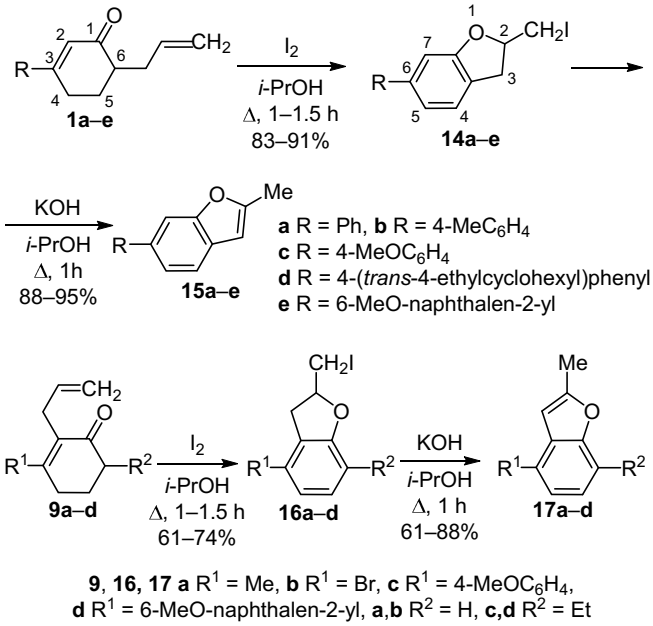
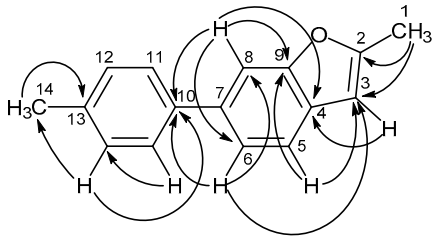


Table 1. Important correlations in ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC spectra of compound **15b**



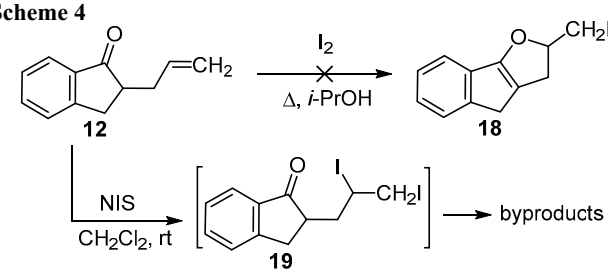
Atom	δ_C, ppm	Correlation with H atoms in ^{1}H–^{13}C HSQC spectrum	Correlations with H atoms in ^{1}H–^{13}C HMBC spectrum
C-1	14.2	H-1	–
C-2	155.9	–	1-CH_3
C-3	102.4	H-3	1-CH_3, H-5
C-4	128.2	–	H-3, H-6, H-8
C-5	120.0	H-5	–
C-6	121.8	H-6	H-8
C-7	136.7 (2C)	–	–
C-8	109.0	H-8	H-6
C-9	155.4	–	H-3, H-5, H-8
C-10	138.7	–	H-6, H-8, H-12
C-11	127.1	H-11	H-12
C-12	129.5	H-12	H-11, 14-CH_3
C-13	136.7 (2C)	–	–
C-14	21.1	H-14	H-12

2,3-dihydrobenzofurans **14a**–**e**, **16a**–**d** can be easily converted to the corresponding substituted 2-methylbenzofurans **15a**–**e**, **17a**–**d** in the presence of KOH in boiling *i*-PrOH in 61–95% yield (Scheme 3). The transformations of compounds **1a**–**e**, **9a**–**d** can be interpreted as the domino process, which includes: (a) formation of the furan ring, (b) dehydroiodination of 2-iodomethyl-2,3-dihydrobenzofurans **14a**–**e**, **16a**–**d**, (c) 1,3-sigmatropic shift in the allylic system.

The structures of all synthesized compounds were confirmed by ^{1}H and ^{13}C spectral data. Although some of the compounds were reported earlier, analytical data were in good correlation with the literature reported. The structure of compound **15b** was also confirmed by two-dimensional ^{1}H–^{13}C HMBC and ^{1}H–^{13}C HSQC experiments. (Table 1).

Unfortunately, treatment of 2-allylindan-1-one **12** with 1 equiv of I_2 in boiling *i*-PrOH does not give furan derivative **18** and interaction with 2 equiv of *N*-iodosuccinimide in CH_2Cl_2 at room temperature leads to unsaturated byproducts, possibly through the formation of unstable bisiodo intermediate **19** and its further dehydroiodination (Scheme 4).

Scheme 4



In summary, an efficient and effective method for the preparation of substituted 2,3-dihydrobenzofurans and 2-methylbenzofurans using aromatization of accessible allyl-substuted cyclohex-2-enones in the presence of iodine, followed by dehydroiodination of the intermediate 2-iodomethyl-2,3-dihydrobenzofurans has been developed. The method is simple and economical, has several advantages over the other routes and can be used for the preparation of diverse substituted 2,3-dihydrobenzofurans and benzofurans possessing biological or pharmacological activity.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 (400 and 100 MHz, respectively) and Bruker Avance 500 (500 and 126 MHz, respectively) spectrometers in $CDCl_3$, residual solvent peaks were used as internal standards (7.26 ppm for ^{1}H nuclei, 77.2 ppm for ^{13}C nuclei). Elemental analysis was performed on a PerkinElmer 2400 Series II CHNS/O analyzer, halogens were determined by published methods.[24] Melting points were determined on a BÜCHI B-540 digital melting point apparatus.

Synthesis of 6-allylcyclohex-2-enones 1a–e and 6-ethylcyclohex-2-enones 6, 7 (General method). A mixture of 1-aryl-3-(*N*,*N*-dimethylamino)propan-1-one hydrochloride **2a**–**e** (0.1 mol), ethyl 2-acetylpent-4-enoate (**4**) (0.11 mol) and KOH (0.35 mol) was stirred in dioxane (100 ml) at reflux for 3.5–4 h. The reaction mixture was cooled, acidified with 5% aqueous H_2SO_4 to pH 5–6. The precipitate was filtered off, washed with H_2O, and crystallized from *i*-PrOH.

6-Allyl-3-phenylcyclohex-2-en-1-one (1a). Yield 15.4 g (73%), white solid, mp 66.3–67.9°C (mp 49°C[25]). ^{1}H NMR spectrum (400 MHz), δ, ppm: 7.53 (2H, d, *J* = 7.9, H Ph); 7.44–7.33 (3H, m, H Ph); 6.42 (1H, s, 2-CH); 5.85–5.79 (1H, m, C<u>H</u>=CH_2); 5.13–5.05 (2H, m, CH=C<u>H</u>$_2$); 2.90–2.68 (2H, m, 4-CH_2); 2.44–2.35 (1H, m, 6-CH); 2.28–2.12 (2H, m, C<u>H</u>$_2$CH=CH_2); 1.94–1.82 (2H, m, 5-CH_2). ^{13}C NMR spectrum (100 MHz), δ, ppm: 200.7; 158.8; 138.6; 136.2; 129.7; 129.0; 126.7; 125.1; 116.7; 45.6; 33.7; 27.5; 27.4. Found, %: C 84.80; H 7.52. $C_{15}H_{16}O$. Calculated, %: C 84.87; H 7.60.

6-Allyl-3-(4-methyphenyl)cyclohex-2-en-1-one (1b). Yield 15.82 g (70%), white solid, mp 47.0–51.6°C. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.44 (2H, d, *J* = 8.2, H Ar); 7.21 (2H, d, *J* = 8.2, H Ar); 6.41 (1H, s, 2-CH); 5.86–5.79 (1H, m, C<u>H</u>=CH_2); 5.15–5.02 (2H, m, CH=C<u>H</u>$_2$); 2.89–2.63 (3H, m, 4-CH_2); 2.45–2.38 (1H, m, 6-CH); 2.38 (3H, s, CH_3); 2.29–2.12 (2H, m, C<u>H</u>$_2$CH=CH_2); 1.91–1.76 (1H, m, 5-CH_2). ^{13}C NMR spectrum (126 MHz), δ, ppm: 201.0; 158.6; 140.3; 136.2; 135.5; 129.4; 125.9; 124.2; 116.7; 45.2; 33.8; 27.4; 27.2; 21.3. Found, %: C 84.85; H 7.99. $C_{16}H_{18}O$. Calculated, %: C 84.91; H 8.02.

6-Allyl-3-(4-methoxyphenyl)cyclohex-2-en-1-one (1c).[26] Yield 17.18 g (71%), white solid, mp 72.5–73.7°C. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.43 (2H, d, *J* = 7.9, H Ar); 6.93 (2H, d, *J* = 7.9, H Ar); 6.42 (1H, s, 2-CH); 5.86–5.78 (1H, m, C<u>H</u>=CH_2); 5.13–5.05 (2H, m, CH=C<u>H</u>$_2$); 3.84 (3H, s, OCH_3); 2.90–2.68 (2H, m, 4-CH_2);

2.40 (1H, m, 6-CH); 2.28–2.12 (2H, m, C$\underline{H}_2$CH=CH$_2$); 1.94–1.82 (2H, m, 5-CH$_2$). ^{13}C NMR spectrum (100 MHz), δ, ppm: 200.8; 161.1; 158.0; 136.2; 130.5; 127.5; 123.2; 116.6; 114.0; 55.3; 45.1; 33.8; 27.3; 27.0. Found, %: C 79.23; H 7.32. $C_{16}H_{18}O_2$. Calculated, %: C 79.31; H 7.49.

6-Allyl-3-[4-(*trans*-4-ethylcyclohexyl)phenyl]cyclohex-2-en-1-one (1d). Yield 25.76 g (80%), white solid, mp 76.4–77.9°C. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.47 (2H, d, *J* = 7.9, H Ar); 7.25 (2H, d, *J* = 7.9, H Ar); 6.42 (1H, s, 2-CH); 5.84–5.79 (1H, m, C$\underline{H}$=CH$_2$); 5.13–5.05 (2H, m, CH=C$\underline{H}_2$); 2.90–2.68 (2H, m, 4-CH$_2$); 2.50 (1H, t, *J* = 12.3, 1-CH Cy); 2.40–2.37 (1H, m, 6-CH); 2.28–2.12 (2H, m, C$\underline{H}_2$CH=CH$_2$); 1.94–1.82 (6H, m, 5-CH$_2$, 2,6-CH$_2$ Cy); 1.52–1.06 (7H, m, C$\underline{H}_2$CH$_3$, 3,5-CH$_2$ Cy, 4-CH Cy); 0.91 (3H, t, *J* = 7.2, CH$_2$C$\underline{H}_3$). ^{13}C NMR spectrum (100 MHz), δ, ppm: 200.9; 158.6; 147.7; 136.2; 135.6; 128.9; 126.0; 124.2; 116.7; 45.2; 43.7; 33.8; 31.2; 29.9; 29.0; 27.4; 27.2; 24.9; 11.5. Found, %: C 85.57; H 9.29. $C_{23}H_{30}O$. Calculated, %: C 85.66; H 9.38.

6-Allyl-3-(6-methoxynaphthalen-2-yl)cyclohex-2-en-1-one (1e). Yield 19.27 g (66%), white solid, mp 111.3–114.0°C. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.93 (1H, d, *J* = 1.6, H-1); 7.75 (1H, d, *J* = 9.0, H Ar); 7.71 (1H, d, *J* = 8.7, H Ar); 7.62 (1H, dd, *J* = 8.7, *J* = 1.6, H-3); 7.17 (1H, dd, *J* = 9.0, *J* = 2.2, H-7); 7.11 (1H, d, *J* = 2.2, H-5); 6.54 (1H, d, *J* = 1.6, 2-CH); 5.90–5.80 (1H, m, CH$_2$C$\underline{H}$=CH$_2$); 5.11 (1H, d, *J* = 17.9, CH$_2$CH=C$\underline{H}_2$); 5.08 (1H, d, *J* = 10.9, CH$_2$CH=C$\underline{H}_2$); 3.93 (3H, s, OCH$_3$); 2.96 (1H, dt, *J* = 18.0, *J* = 4.8, CH$_2$ enone); 2.88–2.80 (1H, m, CH$_2$ enone); 2.75–2.67 (1H, m, CH$_2$ enone); 2.47–2.39 (1H, m, 6-CH); 2.31–2.16 (2H, m, C$\underline{H}_2$CH=CH$_2$); 1.93–1.84 (1H, m, CH$_2$ enone). ^{13}C NMR spectrum (126 MHz), δ, ppm: 200.9; 158.7; 158.4; 136.2; 135.3; 133.3; 130.2; 128.4; 127.2; 125.9; 124.4; 123.8; 119.5; 116.8; 105.6; 55.3; 45.3; 33.8; 27.4; 27.1. Found, %: C 82.11; H 6.95. $C_{20}H_{20}O$. Calculated, %: C 82.16; H 6.90.

6-Ethyl-3-(4-methoxyphenyl)cyclohex-2-en-1-one (6). Yield 16.33 g (71%), white solid, mp 72.5–73.7°C. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.52 (2H, d, *J* = 8.6, H Ar); 6.92 (2H, d, *J* = 8.6, H Ar); 6.37 (1H, s, 2-CH); 3.84 (3H, s, OCH$_3$); 2.82 (1H, dt, *J* = 18.2, *J* = 5.1, 4-CH$_2$); 2.71 (1H, dddd, *J* = 18.2, *J* = 9.1, *J* = 4.5, *J* = 1.5, 4-CH$_2$); 2.27–2.18 (2H, m, 5-CH$_2$); 1.98–1.80 (2H, m, C$\underline{H}_2$CH$_3$); 1.55–1.43 (1H, m, 6-CH); 0.98 (3H, t, *J* = 7.2, CH$_2$C$\underline{H}_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 202.0; 161.1; 157.8; 130.6; 127.5; 123.2; 114.0; 55.3; 46.9; 27.1; 26.8; 22.2; 11.4. Found, %: C 78.15; H 7.74. $C_{15}H_{18}O_2$. Calculated, %: C 78.23; H 7.88.

6-Ethyl-3-(6-methoxynaphthalen-2-yl)cyclohex-2-en-1-one (7). Yield 21.28 g (76%), white solid, mp 108.9–109.9°C. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.93 (1H, s, H-1); 7.75 (1H, d, *J* = 8.9, H Ar); 7.72 (1H, d, *J* = 8.9, H Ar); 7.62 (1H, dd, *J* = 8.5, *J* = 1.8, H-3); 7.17 (1H, dd, *J* = 8.9, *J* = 2.5, H-7); 7.12 (1H, d, *J* = 2.5, H-5); 6.52 (1H, d, *J* = 1.0, 2-CH enone); 3.92 (3H, s, OCH$_3$); 2.95 (1H, dt, *J* = 18.0, *J* = 4.4, CH$_2$ enone); 2.87–2.78 (1H, m, CH$_2$ enone); 2.32–2.22 (2H, m, CH$_2$ enone); 1.90–1.85 (2H, m, C$\underline{H}_2$CH$_3$); 1.57–1.46 (1H, m, 6-CH); 1.00 (3H, t, *J* = 7.5, CH$_2$C$\underline{H}_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 201.9; 158.6; 158.0; 135.3; 133.3; 130.2; 128.4; 127.1; 125.8; 124.4; 123.7; 119.4; 105.6; 55.3; 47.0; 27.2; 26.9; 22.2; 11.4. Found, %: C 81.35; H 7.08. $C_{19}H_{20}O_2$. Calculated, %: C 81.40; H 7.19.

3-Bromocyclohex-2-en-1-one (8b) was prepared according to the literature procedure.[27] Yield 5.6 g (86%), yellow oil, bp 65–66°C (2.0 mm). ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 6.47 (1H, t, *J* = 1.1, 2-CH); 2.83 (2H, dt, *J* = 6.1, *J* = 1.6, CH$_2$); 2.42 (2H, t, *J* = 6.1, CH$_2$); 2.15–2.05 (2H, m, CH$_2$). Found, %: C 41.06; H 3.90; Br 45.44. C_6H_7BrO. Calculated, %: C 41.17; H 4.03; Br 45.65.

Synthesis of 2-allylcyclohex-2-enones 9a–d (General method). A solution of *t*-BuOK (536 mg, 4.78 mmol, 1.1 equiv) in *t*-BuOH (10 ml) was stirred under N$_2$ for a few minutes, then a solution of the respective cyclohex-2-enone **6**, **7**, **8a**,**b** (4.34 mmol) in *t*-BuOH was added, and stirring at room temperature was continued for 1 h. Then allyl bromide (0.41 ml, 4.78 mmol, 1.1 equiv) was added, and the formation of 2-allyl-substituted cyclohex-2-en-1-one was controlled by TLC, eluent petroleum ether – EtOAc. 1% HCl (50 ml) was added after 24–30 h to the resultant reaction mixture and the solution was extracted with CH_2Cl_2 (3×25 ml). The organic extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The resultant crude was purified by column chromatography, eluent petroleum ether – EtOAc.

2-Allyl-3-methylcyclohex-2-en-1-one (9a).[28] Yield 0.33 g (50%), colorless oil. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 5.80–5.71 (1H, m, C$\underline{H}$=CH$_2$); 4.94 (1H, d, *J* = 16.0, CH=C$\underline{H}_2$); 4.93 (1H, d, *J* = 10.0, CH=C$\underline{H}_2$); 3.07 (2H, d, *J* = 6.1, C$\underline{H}_2$CH=CH$_2$); 2.38 (2H, t, *J* = 6.8, 4(6)-CH$_2$ enone); 2.35 (2H, t, *J* = 6.8, 6(4)-CH$_2$ enone); 1.95 (2H, quint, *J* = 6.8, 5-CH$_2$ enone); 1.94 (3H, s, CH$_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 198.1; 156.8; 135.7; 133.0; 114.2; 37.6; 32.8; 29.1; 22.2; 21.1. Found, %: C 79.85; H 9.33. $C_{10}H_{14}O$. Calculated, %: C 79.96; H 9.39.

2-Allyl-3-bromocyclohex-2-en-1-one (9b).[29] Yield 0.47 g (50%), colorless oil. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 5.81–5.72 (1H, m, C$\underline{H}$=CH$_2$); 5.08 (1H, dd, *J* = 16.7, *J* = 1.3, CH=C$\underline{H}_2$); 5.01 (1H, dd, *J* = 10.3, *J* = 1.3, CH=C$\underline{H}_2$); 3.22 (2H, d, *J* = 6.4, C$\underline{H}_2$CH=CH$_2$); 2.93 (2H, t, *J* = 6.7, CH$_2$); 2.47 (2H, t, *J* = 6.7, CH$_2$ enone); 2.04 (2H, quin, *J* = 6.7, 5-CH$_2$ enone). ^{13}C NMR spectrum (126 MHz), δ, ppm: 194.6; 147.9; 138.1; 133.5; 115.9; 37.8; 37.4; 33.7; 22.8. Found, %: C 50.15; H 5.09; Br 36.99. $C_9H_{11}BrO$. Calculated, %: C 50.26; H 5.16; Br 37.15.

2-Allyl-6-ethyl-3-(4-methoxyphenyl)cyclohex-2-en-1-one (9c). Yield 0.63 g (54%), colorless oil. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7,18 (2H, d, *J* = 8.7, H Ar); 6,90 (2H, d, *J* = 8.7, H Ar); 5.87–5.77 (1H, m, C$\underline{H}$=CH$_2$); 4.91 (1H, d, *J* = 10.3, CH=C$\underline{H}_2$); 4.85 (1H, dd, *J* = 17.3, *J* = 1.9, CH=C$\underline{H}_2$); 3.82 (3H, s, OC$\underline{H}_3$); 2.94 (2H, s, CH$_2$); 2.65 (2H, t, *J* = 6.0, CH$_2$); 2.30–2.22 (1H, m, CH$_2$ enone); 2.20–2.13 (1H, m, CH$_2$ enone); 1.96–1.79 (2H, m, CH$_2$ enone); 1.53–1.43 (1H, m, CH$_2$ enone); 0.97 (3H, t, *J* = 7.4, CH$_2$C$\underline{H}_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 201.1; 159.3; 156.3; 137.3; 133.4; 133.2; 128.3; 114.5; 113.6; 55.2; 47.4; 32.1; 31.3; 27.0; 22.5; 11.4. Found, %: C 79.86; H 8.07. $C_{18}H_{22}O_2$. Calculated, %: C 79.96; H 8.20.

2-Allyl-6-ethyl-3-(6-methoxynaphthalen-2-yl)cyclohex-2-en-1-one (9d). Yield 0.79 g (57%), colorless oil. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.74 (1H, d, *J* = 8.4, H Ar); 7.72 (1H, d, *J* = 8.4, H Ar); 7.65 (1H, s, H-1); 7.31 (1H, dd, *J* = 8.4, *J* = 1.6, H-3); 7.17 (1H, dd, *J* = 8.8, *J* = 2.5, H-7); 7.15 (1H, dd, *J* = 2.5, H-5); 5.90–5.81 (1H, m, C<u>H</u>=CH$_2$); 4.95 (1H, dd, *J* = 10.1, *J* = 1.7, CH=C<u>H$_2$</u>); 4.95 (1H, dd, *J* = 17.0, *J* = 1.7, CH=C<u>H$_2$</u>); 3.93 (3H, s, OCH$_3$); 3.03–2.92 (2H, m, CH$_2$); 2.77–2.72 (2H, m, CH$_2$); 2.36–2.28 (1H, m, CH$_2$ enone); 2.26–2.18 (1H, m, CH$_2$ enone); 2.01–1.86 (2H, m, CH$_2$ enone); 1.58–1.48 (1H, m, CH$_2$ enone); 1.00 (3H, t, *J* = 7.5, CH$_2$CH$_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 201.1; 158.1; 156.7; 137.2; 136.2; 134.0; 133.6; 129.6; 128.3; 126.7; 125.7; 125.5; 119.3; 114.6; 105.6; 55.3; 47.5; 32.1; 31.4; 27.2; 22.5; 11.5. Found, %: C 82.29; H 7.44. $C_{22}H_{24}O_2$. Calculated, %: C 82.46; H 7.55.

Compounds **12** and **13** were prepared according to the literature procedure.[21a]

2-Allyl-2,3-dihydro-1*H*-inden-1-one (12).[21b] Purified by column chromatography, eluent petroleum ether – EtOAc, 17:1. Yield 0.73 g (28%), colorless oil. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.75 (1H, d, *J* = 7.4, H-7); 7.58 (1H, dt, *J* = 7.4, *J* = 1.1, H-6); 7.45 (1H, d, *J* = 7.4, H-4); 7.36 (1H, t, *J* = 7.4, H-5); 5.85–5.75 (1H, m, C<u>H</u>=CH$_2$); 5.14–5.09 (1H, m, CH=C<u>H$_2$</u>); 5.06–5.03 (1H, m, CH=C<u>H$_2$</u>); 3.28 (1H, dd, *J* = 17.4, *J* = 7.8, CH$_2$); 2.86 (1H, dd, *J* = 17.4, *J* = 3.9, CH$_2$); 2.80–2.67 (2H, m, CH$_2$); 2.30–2.21 (1H, m, CH$_2$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 208.1; 153.8; 136.7; 135.5; 134.8; 127.3; 126.6; 123.9; 116.9; 46.5; 35.5; 32.0. Found, %: C 83.66; H 6.97. $C_{12}H_{12}O$. Calculated, %: C 83.69; H 7.02.

2,2-Diallyl-2,3-dihydro-1*H*-inden-1-one (13).[30] Purified by column chromatography, eluent petroleum ether – EtOAc, 17:1. Yield 1.06 g (33%), colorless oil. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.72 (1H, d, *J* = 7.7, H-7); 7.57 (1H, dt, *J* = 7.7, *J* = 1.1, H-6); 7.41 (1H, d, *J* = 7.7, H-4); 7.34 (1H, t, *J* = 7.7, H-5); 5.63–5.54 (1H, m, C<u>H</u>=CH$_2$); 5.06 (2H, dd, *J* = 17.1, *J* = 1.7, CH=C<u>H$_2$</u>); 4.97 (2H, d, *J* = 10.6, CH=C<u>H$_2$</u>); 3.02 (2H, s, CH$_2$); 2.44 (2H, dd, , *J* = 13.7, *J* = 6.9, C<u>H$_2$</u>CH=CH$_2$); 2.31 (2H, dd, *J* = 13.7, *J* = 8.0, C<u>H$_2$</u>CH=CH$_2$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 210.0; 153.0; 136.7; 134.9; 133.3; 127.3; 126.4; 123.8; 118.5; 52.2; 41.7; 36.0. Found, %: C 84.80; H 7.57. $C_{15}H_{16}O$. Calculated, %: C 84.87; H 7.60.

Synthesis of 6-aryl-2-iodomethyl-2,3-dihydro-1-benzofurans 14a–e and 2-iodomethyl-2,3-dihydro-1-benzofurans 16a,c (General method). A mixture of allyl-substituted cyclohex-2-enones **1a**–**e**, **9a**–**d** (7 mmol), I_2 (2.2 g, mmol, 1.2 equiv) was stirred in *i*-PrOH (10 ml) under reflux for 1–1.5 h, cooled, diluted with H_2O (100 ml). If solid products were crystallized in the reaction mixture they were filtered off, washed with cold H_2O, and recrystallized from *i*-PrOH. In case of liquid products, reaction mixture was extracted with CH_2Cl_2 (3×15 ml). The organic extracts were combined, dried over $MgSO_4$, and concentrated. The resulting crude was purified by column chromatography, eluent petroleum ether – EtOAc, 20:1.

2-(Iodomethyl)-6-phenyl-2,3-dihydro-1-benzofuran (14a). Yield 2.0 g (85%), white solid, decomposes upon heating. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.53 (2H, d, *J* = 7.7, H Ph); 7.41–7.35 (3H, m, H Ph); 7.18 (1H, d, *J* = 7.4, H-5 dihydrobenzofuran); 7.09 (1H, d, *J* = 7.4, H-4 dihydrobenzofuran); 7.00 (1H, s, H-7 dihydrobenzofuran); 4.92 (1H, quin, *J* = 5.1, 2-CH dihydrobenzofuran); 3.50–3.30 (3H, m, 3-CH$_2$ dihydrobenzofuran, CH$_2$I); 3.06 (1H, dd, *J* = 9.7, *J* = 6.1, 3-CH$_2$ dihydrobenzofuran). ^{13}C NMR spectrum (100 MHz), δ, ppm: 159.8; 143.4; 142.1; 129.4; 129.2; 128.1; 127.6; 124.5; 119.7; 108.1; 82.0; 35.8; 8.9. Found, %: C 53.46; H 3.81; I 37.52. $C_{15}H_{13}IO$. Calculated, %: C 53.59; H 3.90; I 37.75.

2-(Iodomethyl)-6-(*p*-tolyl)-2,3-dihydro-1-benzofuran (14b). Yield 2.21 g (90%), white solid, decomposes upon heating. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.44 (2H, d, *J* = 7.6, H Ar); 7.26–7.17 (3H, m, H Ar); 7.09 (1H, d, *J* = 8.0, H Ar); 7.00 (1H, s, H Ar); 4.97–4.89 (1H, m, 2-CH dihydrobenzofuran); 3.49–3.32 (3H, m, 3-CH$_2$ dihydrobenzofuran, CH$_2$I); 3.07 (1H, dd, *J* = 16.0, *J* = 6.4, 3-CH$_2$ dihydrobenzofuran); 2.38 (3H, s, CH$_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 159.7; 141.9; 138.2; 137.1; 129.4; 126.9; 125.0; 124.5; 119.8; 108.1; 82.0; 35.8; 21.1; 8.9. Found, %: C 54.80; H 4.30; I 36.30. $C_{16}H_{15}IO$. Calculated, %: C 54.88; H 4.32; I 36.24.

2-Iodomethyl-6-(4-methoxyphenyl)-2,3-dihydro-1-benzofuran (14c). Yield 2.13 g (83%), white solid, decomposes upon heating. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.43 (2H, d *J* = 7.7, H Ar); 6.93 (2H, d, *J* = 7.9, H Ar); 7.18 (1H, d, *J* = 7.4, H-5 dihydrobenzofuran); 7.09 (1H, d, *J* = 7.4, H-4 dihydrobenzofuran); 7.00 (1H, s, H-7 dihydrobenzofuran); 4.92 (1H, quin, *J* = 5.1, 2-CH dihydrobenzofuran); 3.84 (3H, s, OCH$_3$); 3.50–3.30 (3H, m, 3-CH$_2$ dihydrobenzofuran, CH$_2$I); 3.06 (1H, dd, *J* = 9.7, *J* = 6.1, 3-CH$_2$ dihydrobenzofuran). ^{13}C NMR spectrum (100 MHz), δ, ppm: 159.8; 159.2; 141.5; 133.6; 128.0; 125.0; 124.2; 119.6; 114.1; 107.9; 82.0; 55.3; 35.8; 8.9. Found, %: C 52.35; H 4.04; I 34.48. $C_{16}H_{15}IO_2$. Calculated, %: C 52.48; H 4.13; I 34.65.

6-[4-(*trans*-4-Ethylcyclohexyl)phenyl]-2-iodomethyl-2,3-dihydro-1-benzofuran (14d). Yield 2.81 g (90%), white solid, decomposes upon heating. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.47 (2H, d, *J* = 7.9, H Ar); 7.25 (2H, d, *J* = 7.9, H Ar); 7.18 (1H, d, *J* = 7.4, H-5 dihydrobenzofuran); 7.09 (1H, d, *J* = 7.4, H-4 dihydrobenzofuran); 7.00 (1H, s, H-7 dihydrobenzofuran); 4.92 (1H, quin, *J* = 5.1, 2-CH dihydrobenzofuran); 3.50–3.30 (3H, m, 3-CH2 dihydrobenzofuran, CH$_2$I); 3.06 (1H, dd, *J* = 9.7, *J* = 6.1, 3-CH$_2$ dihydrobenzofuran); 2.50 (1H, t, *J* = 12.3, 1-CH Cy); 1.94–1.82 (4H, m, 2,6-CH$_2$ Cy); 1.52–1.06 (7H, m, C<u>H$_2$</u>CH$_3$, 3,5-CH$_2$ Cy, 4-CH Cy); 0.91 (3H, t, *J* = 7.2, CH$_2$C<u>H$_3$</u>). ^{13}C NMR spectrum (100 MHz), δ, ppm: 159.8; 146.1; 143.8; 138.8; 129.4; 128.5; 127.9; 124.7; 119.8; 108.8; 82.1; 44.4; 39.0; 35.9; 34.2; 33.4; 30.2; 11.6; 9.0. Found, %: C 61.74; H 6.02; I 28.30. $C_{23}H_{27}IO$. Calculated, %: C 61.89; H 6.10; I 28.43.

2-(Iodomethyl)-6-(6-methoxynaphthalen-2-yl)-2,3-dihydro-1-benzofuran (14e). Yield 2.65 g (91%), white solid, decomposes upon heating. ^{1}H NMR spectrum

(500 MHz), δ, ppm (*J*, Hz): 7.92 (1H, s, H-1 naphthalene); 7.77 (1H, d, *J* = 9.0, H-8 naphthalene); 7.75 (1H, d, *J* = 8.7, H-4 naphthalene); 7.65 (1H, dd, *J* = 8.7, *J* = 1.9, H-3 naphthalene); 7.23 (1H, s, H-7(4) dihydrobenzofuran); 7.21 (1H, dd, *J* = 7.7, *J* = 1.3, H-5 dihydrobenzofuran); 7.16 (1H, dd, *J* = 9.0, *J* = 2.6, H-7 naphthalene); 7.14 (1H, d, *J* = 2.6, H-5 naphthalene); 7.12 (1H, s, H-4(7) dihydrobenzofuran); 4.97–4.93 (1H, m, 2-CH dihydrobenzofuran); 3.93 (3H, s, OCH_3); 3.48 (1H, dd, *J* = 10.3, *J* = 4.8, CH_2I); 3.44 (1H, dd, *J* = 16.0, *J* = 9.0, 3-CH_2 dihydrobenzofuran); 3.38 (1H, dd, *J* = 10.3, *J* = 7.7, CH_2I); 3.09 (1H, dd, *J* = 16.0, *J* = 6.4, 3-CH_2 dihydrobenzofuran). ^{13}C NMR spectrum (126 MHz), δ, ppm: 159.8; 155.7; 144.0; 134.4; 131.0; 130.7; 130.1; 129.2; 128.5; 128.0; 126.6; 124.6; 119.9; 119.6; 110.9; 106.9; 82.0; 55.5; 35.8; 8.9. Found, %: C 57.61; H 4.03; I 30.37. $C_{20}H_{17}IO_2$. Calculated, %: C 57.71; H 4.12; I 30.49.

2-(Iodomethyl)-4-methyl-2,3-dihydro-1-benzofuran (16a). Yield 1.17 g (61%), yellow oil. ^1H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.03 (1H, t, *J* = 7.7, H-6 dihydrobenzofuran); 6.68 (1H, d, *J* = 7.7, H-5 dihydrobenzofuran); 6.61 (1H, d, *J* = 7.7, H-7 dihydrobenzofuran); 4.95–4.85 (1H, m, 2-CH dihydrobenzofuran); 3.44 (1H, dd, *J* = 10.0, *J* = 4.8, CH_2I); 3.32 (1H, dd, *J* = 10.0, *J* = 8.0, CH_2I); 3.30 (1H, dd, *J* = 16.0, *J* = 9.0, 3-CH_2 dihydrobenzofuran); 2.93 (1H, dd, *J* = 16.0, *J* = 6.4, 3-CH_2 dihydrobenzofuran); 2.24 (3H, s, CH_3). ^{13}C NMR spectrum (126 MHz), δ, ppm: 159.8; 136.9; 129.6; 128.8; 122.1; 109.9; 82.0; 35.8; 19.3; 9.0. Found, %: C 43.70; H 3.98; I 46.17. $C_{10}H_{11}IO$. Calculated, %: C 43.82; H 4.05; I 46.30.

7-Ethyl-2-(iodomethyl)-4-(4-methoxyphenyl)-2,3-dihydro-1-benzofuran (16c). Yield 2.04 g (74%), colorless oil. ^1H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.39 (2H, d, *J* = 8.7, H Ar); 7.06 (1H, d, *J* = 7.7, H-6 dihydrobenzofuran); 6.97 (2H, d, *J* = 8.7, H Ar); 6.88 (1H, d, *J* = 7.7, H-5 dihydrobenzofuran); 4.96–4.85 (1H, m, 2-CH dihydrobenzofuran); 3.82 (3H, s, OCH_3); 3.47 (1H, dd, *J* = 16.0, *J* = 9.0, 3-CH_2 dihydrobenzofuran); 3.44 (1H, dd, *J* = 4.5, *J* = 9.9, CH_2I); 3.33 (1H, dd, *J* = 9.9, *J* = 7.7, CH_2I); 3.10 (1H, dd, *J* = 16.0, *J* = 6.4, 3-CH_2 dihydrobenzofuran); 2.62 (2H, q, *J* = 7.4, C<u>H</u>$_2$CH$_3$); 1.24 (3H, t, *J* = 7.4, CH_2C<u>H</u>$_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 159.4; 159.0; 135.8; 131.4; 130.6; 128.9; 126.1; 125.5; 123.9; 114.7; 82.5; 55.8; 36.3; 22.8; 14.9; 9.0. Found, %: C 54.73; H 4.80; I 32.04. $C_{18}H_{19}IO_2$. Calculated, %: C 54.84; H 4.86; I 32.19.

Synthesis of 6-aryl-2-methyl-1-benzofurans 15a–e and 2-methyl-1-benzofurans 17a–d (General method). A mixture of 2-iodomethyl-2,3-dihydro-1-benzofurans **14a–e** or **16a**,**c** (5 mmol), KOH (1 g, 17.5 mmol, 3.5 equiv) in *i*-PrOH (10 ml) was refluxed for 1 h, cooled, diluted with H_2O (50 ml). If solid products were crystallized in the reaction mixture they were filtered off, washed with cold H_2O, and recrystallized from *i*-PrOH. In case of liquid products, reaction mixture was extracted with CH_2Cl_2 (3×15 ml). The organic extracts were combined, dried over $MgSO_4$, and concentrated. The resulting crude was purified by column chromatography, eluent petroleum ether – EtOAc 20:1. Benzofurans **17b**,**d** were prepared from cyclohexenones **9b**,**d** in one-pot manner without isolation of the intermediate 2-iodomethyl derivatives **16b**,**d**.

2-Methyl-6-phenyl-1-benzofuran (15a).[31] Yield 0.93 g (89%), white solid, mp 52.1–54.1°C. ^1H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.61 (1H, s, H-7 benzofuran); 7.57 (2H, d, *J* = 7.9, H Ph); 7.47 (1H, d, *J* = 7.9, H-4 benzofuran); 7.41 (1H, d, *J* = 7.9, H-5 benzofuran); 7.46–7.38 (3H, m, H Ph); 6.38 (1H, s, H-3 benzofuran); 2.46 (3H, s, CH_3). ^{13}C NMR spectrum (100 MHz), δ, ppm: 156.1; 155.4; 141.6; 136.8; 128.8; 128.4; 127.9; 127.0; 122.0; 120.1; 109.2; 102.5; 14.2. Found, %: C 86.43; H 5.72. $C_{15}H_{12}O$. Calculated, %: C 86.51; H 5.81.

2-Methyl-6-(*p*-tolyl)-1-benzofuran (15b). Yield 0.98 g (88%), white solid, mp 49.4–50.9°C. ^1H NMR spectrum (500 MH), δ, ppm (*J*, Hz): 7.60 (1H, s, H-7 benzofuran); 7.52 (2H, d, *J* = 8.1, H Ar); 7.49 (1H, d, *J* = 8.0, H Ar); 7.42 (1H, dd, *J* = 8.0, *J* = 1.5, H-5 benzofuran); 7.26 (2H, d, *J* = 8.1, H Ar); 6.37 (1H, s H-3 benzofuran); 2.47 (3H, d, *J* = 1.0, CH_3 benzofuran); 2.40 (1H, s, $CH_3C_6H_4$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 155.9 (C-2); 155.4 (C-9); 138.7 (C-10); 136.7 (C-7,13); 129.5 (C-12); 128.2 (C-4); 127.1 (C-11); 121.8 (C-6); 120.0 (C-5); 109.0 (C-8); 102.4 (C-3); 21.1 (C-14); 14.2 (C-1). Found, %: C 86.37; H 6.21. $C_{16}H_{14}O$. Calculated, %: C 86.45; H 6.35.

6-(4-Methoxyphenyl)-2-methyl-1-benzofuran (15c). Yield 1.05 g (88%), white solid, mp 63.2–65.2°C. ^1H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.61 (1H, s, H-7 benzofuran); 7.43 (2H, d, *J* = 7.9, H Ar); 7.47 (1H, d, *J* = 7.9, H-4 benzofuran); 7.39 (1H, d, *J* = 7.9, H-5 benzofuran); 6.98 (2H, d, *J* = 7.9, H Ar); 6.38 (1H, s, H-3 benzofuran); 3.84 (3H, s, OCH_3); 2.46 (3H, c, CH_3). ^{13}C NMR spectrum (100 MHz), δ, ppm (*J*, Hz): 160.0; 156.0; 155.5; 138.1; 133.3; 130.1; 128.6; 127.5; 126.9; 119.6; 114.2; 108.9; 55.4; 14.3. Found, %: C 80.51; H 5.85. $C_{16}H_{14}O_2$. Calculated, %: C 80.65; H 5.92.

6-[4-(*trans*-4-Ethylcyclohexyl)phenyl]-2-methyl-1-benzofuran (15d). Yield 1.51 g (95%), white solid, mp 113.8–115.8°C. ^1H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.61 (1H, s, H-7 benzofuran); 7.54 (2H, d, *J* = 7.9, H Ar); 7.47 (1H, d, *J* = 7.9, H-4 benzofuran); 7.41 (1H, d, *J* = 7.9, H-5 benzofuran); 7.28 (2H, d, *J* = 7.9, H Ar); 6.38 (1H, s, H-3 benzofuran); 2.51 (1H, t, *J* = 12.3, 1-CH Cy); 2.46 (3H, s, CH_3 benzofuran); 1.94–1.82 (4H, m, 2,6-CH_2 Cy); 1.52–1.06 (7H, m, C<u>H</u>$_2$CH$_3$, 3,5-CH_2 Cy, 4-CH Cy); 0.91 (3H, t, *J* = 7.2, CH_2CH_3). ^{13}C NMR spectrum (100 MHz), δ, ppm (*J*, Hz): 155.9; 155.4; 146.7; 139.1; 136.8; 128.2; 127.2; 127.1; 121.9; 120.0; 109.0; 102.5; 44.3; 39.1; 34.3; 33.2; 30.0; 14.1; 11.5. Found, %: C 86.59; H 8.11. $C_{23}H_{26}O$. Calculated, %: C 86.75; H 8.23.

6-(6-Methoxynaphthalen-2-yl)-2-methyl-1-benzofuran (15e). Yield 1.27 g (88%), white solid. ^1H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.99 (1H, d, *J* = 1.3, H-1 naphthalene); 7.79 (2H, d, *J* = 8.5, H-4,8 naphthalene); 7.74 (1H, dd, *J* = 8.5, *J* = 1.9, H-3 naphthalene); 7.72 (1H, s, H-7 benzofuran); 7.54 (1H, dd, *J* = 8.0, *J* = 1.2, H-5 benzofuran); 7.53 (1H, d, *J* = 8.0, H-4 benzofuran); 7.17 (1H, dd, *J* = 8.5, *J* = 2.6, H-7 naphthalene); 7.15 (1H, d, *J* = 2.6, H-5 naphthalene); 6.40 (1H, s, H-3 benzofuran); 3.93 (3H, s, OCH_3); 2.49 (3H, d, *J* = 1.0, CH_3). ^{13}C NMR

spectrum (126 MHz), δ, ppm: 155.9; 155.6; 155.4; 144.8; 133.8; 131.0; 130.2; 130.0; 129.6; 128.7; 128.1; 127.6; 126.5; 125.9; 119.7; 118.9; 106.8; 102.5; 55.5; 14.2. Found, %: C 83.32; H 5.55. $C_{20}H_{16}O_2$. Calculated, %: C 83.31; H 5.59.

2,4-Dimethyl-1-benzofuran (17a). Yield 0.45 g (61%), colorless oil. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.23 (1H, d, *J* = 8.0, H-7 benzofuran); 7.09 (1H, t, *J* = 8.0, H-6 benzofuran); 6.96 (1H, d, *J* = 8.0, H-5 benzofuran); 6.38 (1H, s, H- benzofuran); 2.46 (3H, s, CH_3); 2.45 (3H, s, CH_3). ^{13}C NMR spectrum (126 MHz), δ, ppm: 156.0; 155.4; 130.7; 130.5; 123.8; 123.5; 108.5; 102.7; 19.5; 14.2. Found, %: C 82.07; H 6.81. $C_{10}H_{10}O$. Calculated, %: C 82.16; H 6.90.

4-Bromo-2-methyl-1-benzofuran (17b). Yield 0.73 g (69%), yellow oil. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.23 (1H, d, *J* = 8.0, H-7 benzofuran); 7.09 (1H, t, *J* = 8.0, H-6 benzofuran); 6.96 (1H, d, *J* = 8.0, H-5 benzofuran); 6.38 (1H, s, H-3 benzofuran); 2.47 (3H, s, CH_3). ^{13}C NMR spectrum (126 MHz), δ, ppm: 156.2; 154.4; 130.6; 125.4; 124.0; 112.9; 109.7; 102.8; 14.2. Found, %: C 51.30; H 3.30; Br 37.88. C_9H_7BrO. Calculated, %: C 51.22; H 3.34; Br 37.86.

7-Ethyl-4-(4-methoxyphenyl)-2-methyl-1-benzofuran (17c). Yield 1.17 g (88%), white solid. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.53 (2H, d, *J* = 8.8, H Ar); 7.16 (1H, d, *J* = 7.7, H-5 benzofuran); 7.08 (1H, d, *J* = 7.7, H-6 benzofuran); 7.00 (2H, d, *J* = 8.8, H Ar); 6.54 (1H, s, H-3 benzofuran); 3.86 (3H, s, CH_3O); 2.94 (2H, q, *J* = 7.7, $C\underline{H}_2CH_3$); 2.50 (3H, s, CH_3); 1.37 (3H, t, *J* = 7.7, $CH_2C\underline{H}_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 159.7; 155.0; 152.9; 133.1; 129.3; 127.4; 127.3; 124.8; 122.9; 122.0; 114.6; 101.9; 55.8; 22.4; 14.9; 14.2. Found, %: C 81.03; H 6.74. $C_{18}H_{18}O_2$. Calculated, %: C 81.17; H 6.81.

7-Ethyl-4-(6-methoxynaphthalen-2-yl)-2-methyl-1-benzofuran (17d). Yield 1.14 g (72%), white solid, mp 102.2–103.5°C. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 7.98 (1H, s, H-1 naphthalene); 7.83 (1H, d, *J* = 8.5, H Ar); 7.80 (1H, d, *J* = 9.5, H Ar); 7.73 (1H, dd, *J* = 8.5, *J* = 1.7, H Ar); 7.31 (1H, d, *J* = 7.5, H-5(6) benzofuran); 7.21–7.17 (2H, m, H Ar); 7.15 (1H, d, *J* = 7.5, H-6(5) benzofuran); 6.63 (1H, d, *J* = 1.0, H-3 benzofuran); 3.86 (3H, s, CH_3O); 2.98 (2H, q, *J* = 7.5, $C\underline{H}_2CH_3$); 2.50 (3H, s, CH_3); 1.40 (3H, t, *J* = 7.5, $CH_2C\underline{H}_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 157.7; 155.4; 153.5; 135.9; 133.5; 131.8; 129.6; 129.1; 127.4; 127.1; 126.9; 126.7; 126.1; 122.7; 122.3; 119.0; 105.6; 102.4; 55.3; 22.8; 14.3; 14.2. Found %: C 83.61; H 6.37. $C_{22}H_{20}O_2$. Calculated, %: C 83.52; H 6.37.

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