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Efficient synthesis of dihydrofurans and furans by rhodium(II)-catalyzed reactions of cyclic diazodicarbonyl compounds

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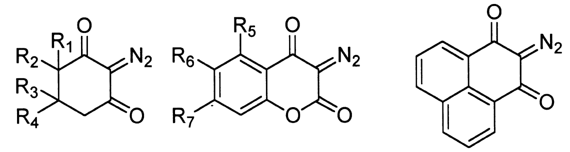
Abstract—An efficient synthesis of dihydrofurans and furans is achieved by rhodium-catalyzed reactions of cyclic diazodicarbonyl compounds with allyl halides. This method provides a rapid entry toward naturally occurring furocoumarin and furophenalenone derivatives.

Dihydrofurans and furans are two of the most important heterocycles with widespread occurrence in nature.[1] They are frequently found in many natural products arising from plants and marine organisms.[2] Possessing a variety of biological activities, they are used as pharmaceutical, flavor, insecticidal, and fish antifeedant agents.[3] Their important biological activities and usefulness as synthetic intermediates of natural products have prompted a search for better methods of synthesis of dihydrofurans and furans. Although a number of synthetic methods for the preparation of dihydrofurans and furans have been reported, simple and efficient approaches still remain scarce.[4]

The rhodium-mediated decomposition of diazocarbonyl compounds has become an important method in the synthesis of heterocyclic frameworks such as furans[5] and oxazoles.[6] We have been interested in rhodium-catalyzed reactions of diazodicarbonyl compounds with several substrates.[7] In particular, we have tried developing a new methodology utilizing rhodium catalyzed reactions of diazodicarbonyl compounds with halides such as acid halides and benzyl halides.[8] While continuing our studies in the development of new synthetic applications, we investigated the rhodium-catalyzed reactions of diazodicarbonyl compounds with allyl halides. We report here a new and efficient synthesis of dihydrofurans with *exo*-olefin and furans starting from diazodicarbonyl compounds (Fig. 1).



1 $R_1=R_2=R_3=R_4=H$
2 $R_1=R_2=R_3=H$, $R_4=CH_3$
3 $R_1=R_2=R_3=H$, $R_4=CH(CH_3)_2$
4 $R_1=R_2=CH_3$, $R_3=R_4=H$
5 $R_1=R_2=H$, $R_3=R_4=CH_3$

6 $R_5=R_6=R_7=H$
7 $R_5=CH_3$, $R_6=R_7=H$
8 $R_5=R_7=H$, $R_6=CH_3$
9 $R_5=R_6=H$, $R_7=CH_3$

10

Figure 1.

Diazodicarbonyl compounds **1**–**10** were prepared by the diazotransfer reaction of the corresponding 1,3-dicarbonyl compounds with mesyl azide according to Taber's method.[9] Reactions with allyl halides were first examined. When diazodicarbonyl compound **5** was treated with allyl chloride as a solvent and a reactant at room temperature for 5 h in the presence of 1 mol% of $Rh_2(OAc)_4$, the [2,3]-rearranged product **11** and the cycloaddition product **12** were obtained in 75 and 12% yields, respectively (Table 1, entry 1). The two isomers were easily separated by column chromatography and assigned by spectroscopic data. The ^{1}H NMR spectrum of **11** showed two peaks at δ 5.69 (multiplet) and δ 5.15 (double-doublet) which is associated with the vinyl group, whereas **12** showed peaks at δ 5.01 (multiplet), 3.64 (mutiplet), 2.95 (double-doublet), and 2.70 (double-doublet) associated with the dihydrofuran ring.

With allyl bromide, the [2,3]-rearranged product **13** and the cycloadduct **14** were also produced in 60 and 15% yields, respectively. However, reaction of **5** with allyl iodide only afforded cycloaddition product **15**, without the formation of the [2,3]-rearranged product, in a 92% yield. Reaction of another diazodicarbonyl compound **10** with allyl halides afforded similar results (entries 4–6). The results are summarized in Table 1.

Keywords: dihydrofurans and furans; rhodium(II)-catalyzed reaction; cyclic diazodicarbonyl.

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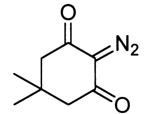
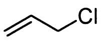
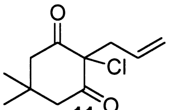
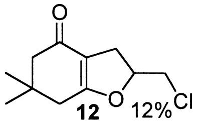
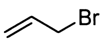
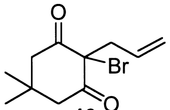
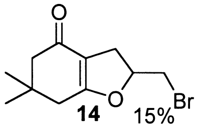
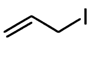
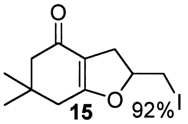
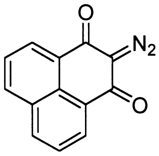
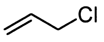
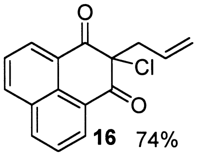
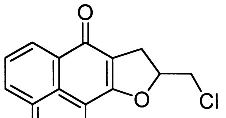
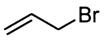
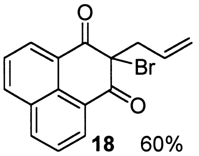
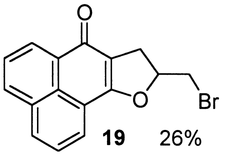
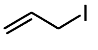
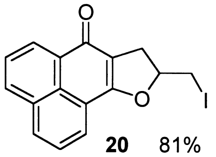
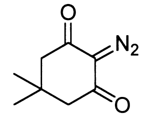
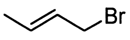
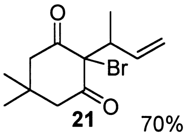
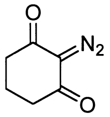
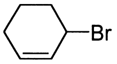
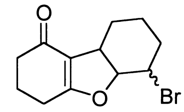
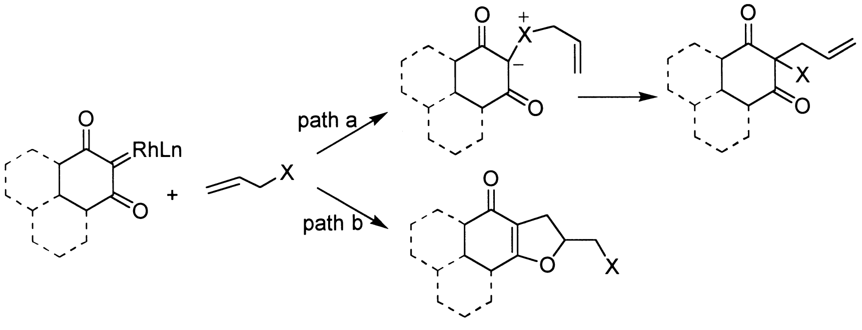
Table 1. Rhodium(II)-catalyzed reactions of diazodicarbonyl compounds with ally halides

Entry	Diazodicarbonyl compound	Allyl halide	Product	
1	 **5**		 **11** 75%	 **12** 12%
2			 **13** 60%	 **14** 15%
3				 **15** 92%
4	 **10**		 **16** 74%	 **17** 21%
5			 **18** 60%	 **19** 26%
6				 **20** 81%
7	 **5**		 **21** 70%	
8	 **1**		 **22** 58%	



Scheme 1.

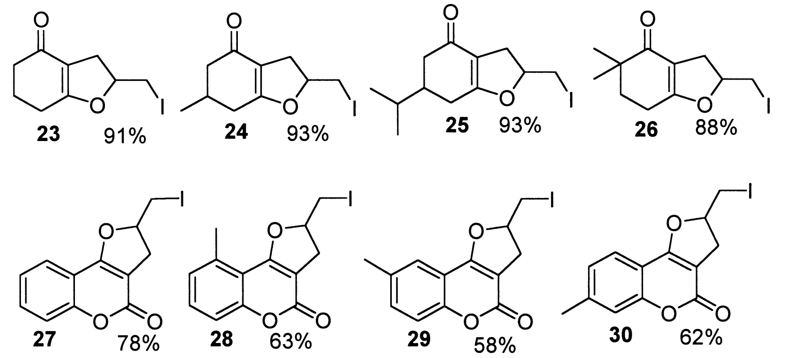


Figure 2.

Next, rhodium(II)-catalyzed reactions with other allyl halides such as crotyl bromide and 3-bromocyclohexene were examined. Treatment of **5** with crotyl bromide in the presence of 1 mol% of rhodium(II) acetate afforded the [2,3]-rearranged product **21** in 70% yield (entry 7). In this case, no cycloadducts were found. Interestingly, with 3-bromocyclohexene, cycloadduct **22** was obtained in 58% yield as a mixture of diastereomers of unassigned stereochemistry (entry 8). This reaction produces a dramatic reversal in the formation of product.

In view of our results, competition between ylide generation and 1,3-dipolar cycloaddition could be manipulated by varying the electronegativity of the halogen in allyl halides. Reactions with allyl chloride and allyl bromide resulted in [2,3]-rearranged products as a major component via ylide generation (path a), whereas reactions with allyl iodide afforded 1,3-dipolar cycloaddition products as a single compound (path b) as shown in Scheme 1. The decreased electronegativity of the halogen going from chlorine to iodine almost exclusively afforded 1,3-dipolar cycloaddition relative to the olefin. These results are in clear contrast to those of Doyle, who reported that the rhodium(II)-catalyzed reactions of ethyl diazoacetate with allyl iodide afforded the [2,3]-rearranged product as a single compound, whereas the cyclopropanation adduct occurred almost exclusively with allyl chloride and bromide.[10]

Additional reactions of a variety of cyclic diazodicarbonyl compounds with allyl iodide were next investigated. Treatment of diazodicarbonyl compounds **1–4** with allyl iodide gave the expected iodomethyldihydrofurans **23–26** in 88–93% yields after column chromatography. Extension to 3-diazo-2,4-chromenediones was also successful. Reactions of **6–9** with allyl iodide gave biologically interesting iodomethyldihydrofurocoumarin derivatives **27–30** in 58–78% yields. The results are collected in Fig. 2. These results seemed ideal for the synthesis of dihydrofurans with *exo*-olefin and 2-methylfurans by the reaction of cyclic diazodicarbonyl compounds with ally iodide in the presence of 1 mol% of $Rh_2(OAc)_4$.

Next, conversion of the halides to dihydrofurans with *exo*-olefin or 2-methylfurans was examined by two methods. Reaction of iodide **15** with 3 equiv. of DBU in benzene at room temperature for 20 h gave dihydrofuran **31** with *exo*-olefin in 94% yield, without the contamination of isomeric furans (method A). The dihydrofuran **31** is assigned by the chemical shifts associated with the *exo*-olefin group of the dihydrofuran ring. On the other hand, increasing the temperature influences the formation of products. Heating the iodide **15** at reflux with 3 equiv. of DBU in toluene for 2 h afforded furan **32** in 88% yield, possibly via both elimination and direct isomerization (method B). The structure of **32** is easily identified by the chemical shift of the vinylic proton in the furan ring. Similarly other results are also summarized in Table 2 (entries 1–4). These reactions are expected to be used as a rapid way of constructing dihydrofurans with *exo*-olefin and 2-methylfurans. On the other hand, treatment of **22** with 3 equiv. of DBU at reflux for 2 h in toluene gave **41** in 93% yield (entry 5) (Scheme 2).

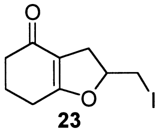
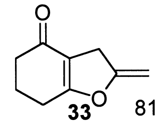
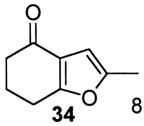
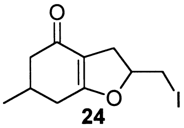
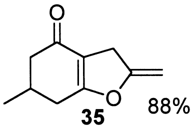
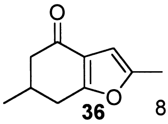
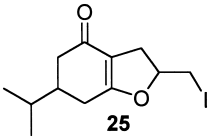
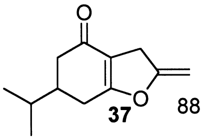
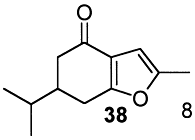
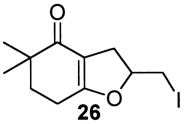
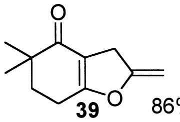
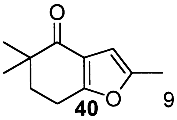
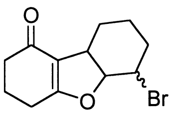
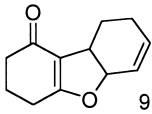
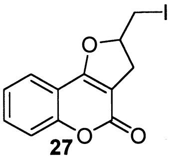
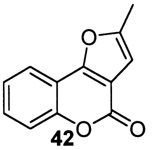
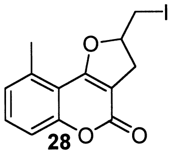
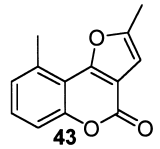
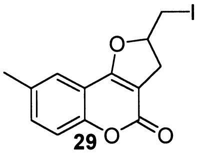
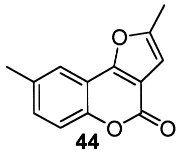
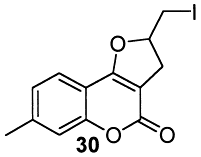
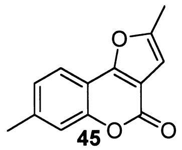
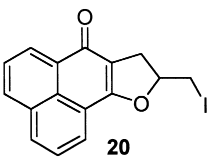
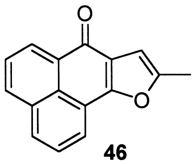
However, reaction of iodides **27–30** with DBU in benzene (method A) at room temperature for 20 h gave furocoumarins **42–45** in 80–98% yields (entries 6–9). In these cases, no expected dihydrofurocoumarins with *exo*-olefin were obtained. These reactions also provide a rapid synthetic route toward furocoumarin derivatives which are known to have such biological activities as anticoagulant, insecticide, anthelminthic, hypnotic, antifungal, and HIV protease inhibition.[11] Although there are currently several methods available for the synthesis of furocoumarins, their synthetic exploitation has been limited by the difficulties in controlling regiochemistry of the linear and angular adduct.[12] Our technique is experimentally simple and highly regioselective. Similarly, treatment of **20** with DBU in benzene (method A) afforded furophenalenone derivative **43** in 98% yield, which is reported to have important biological activities such as antibiotic, antimicrobial, and phytoalexin (entry 10).[13] The data are collected in Table 2.

In conclusion, the rhodium(II)-catalyzed reactions of cyclic diazodicarbonyl compounds with allyl halides are described. These reactions provide a rapid entry to the synthesis of dihydrofurans with *exo*-olefin and 2-methylfurans. This methodology is expected to be widely used in the synthesis of furocoumarin and furophenalenone natural products.

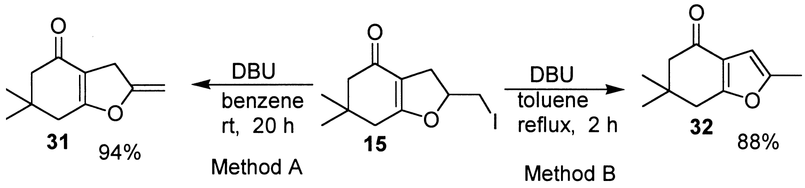
1. Experimental

All experiments were carried out under nitrogen atmosphere. Merck precoated silica gel plates (Art. 5554) with fluorescent indicator were used for analytical TLC.

Table 2. Synthesis of dihydrofurans and furans

Entry	Iodomethyldihydrofuran	Dihydrofuran, method A	2-Methylfuran, method B
1	 **23**	 **33** 81%	 **34** 83%
2	 **24**	 **35** 88%	 **36** 85%
3	 **25**	 **37** 88%	 **38** 81%
4	 **26**	 **39** 86%	 **40** 91%
5	 **22**		 **41** 93%
6	 **27**	 **42** 80%	
7	 **28**	 **43** 93%	
8	 **29**	 **44** 98%	
9	 **30**	 **45** 80%	
10	 **20**	 **46** 98%	

Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined with microcover glasses on a Fisher–Johns apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Model ARX (300 MHz) spectrometer. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. High resolution mass (HRMS) spectra were obtained on VG-MICROMASS Autospec at Yeungnam University and JEOL JMS-700 spectrometer at Korea Basic Science Institute.



Scheme 2.

1.1. General procedure for the reactions of diazodicarbonyl compounds and allyl halides

To a solution of diazodicarbonyl compound (1.0 mmol) and allyl halide (3 mL) was added rhodium acetate (5 mg, 0.01 mmol) at room temperature. The mixture was stirred for 5 h under nitrogen. Evaporation of allyl halide and purification by silica gel chromatography with 33% ethyl acetate in hexane as eluent afforded products.

1.1.1. 2-Ally-2-chloro-5,5-dimethylcyclohexane-1,3-dione (11) and 2-chloromethyl-6,6-dimethyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (12). Reaction of 5,5-dimethyl-2-diazocyclohexane-1,3-dione (166 mg, 1.0 mmol) with allyl chloride (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **11** (161 mg, 75%) and **12** (26 mg, 12%). **11**: mp 30–32°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (1H, m), 5.15 (2H, dd, J=17.2, 11.0 Hz), 3.10 (2H, d, J=14.0 Hz), 2.87 (2H, d, J=7.1 Hz), 2.42 (2H, d, J=14.5 Hz), 1.11 (3H, s), 0.84 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.40 (2CO), 132.06, 121.10, 70.76, 49.74, 37.09, 30.52, 29.65, 26.58 ($2CH_3$); IR (KBr) 3084, 2961, 2932, 2874, 1714, 1446, 1425, 1323, 1250, 1199, 1074, 1001, 932 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{11}H_{15}ClO_2$: 214.0757. Found: 214.0754. **12**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.01 (1H, m), 3.64 (2H, m), 2.95 (1H, dd, J=16.0, 8.6 Hz), 2.70 (1H, dd, J=16.0, 6.8 Hz), 2.29 (2H, s), 2.21 (2H, s), 1.08 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.46, 175.74, 111.27, 83.40, 50.68, 46.00, 37.36, 33.95, 29.19, 28.60, 28.27; IR (neat) 2959, 2872, 1636, 1404, 1369, 1260, 1221, 1168, 1145, 1099, 1044, 978 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{11}H_{15}ClO_2$: 214.0757. Found: 214.0756.

1.1.2. 2-Ally-2-bromo-5,5-dimethylcyclohexane-1,3-dione (13) and 2-bromomethyl-6,6-dimethyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (14). Reaction of 5,5-dimethyl-2-diazocyclohexane-1,3-dione (166 mg, 1.0 mmol) with allyl bromide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **13** (155 mg, 60%) and **14** (39 mg, 15%). **13**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.60 (1H, m), 5.11 (2H, dd, J=17.2, 10.1 Hz), 3.23 (2H, d, J=14.6 Hz), 2.97 (2H, d, J=7.1 Hz), 2.34 (2H, d, J=14.6 Hz), 1.09 (3H, s), 0.74 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.40 (2CO), 132.06, 121.10, 60.08, 49.35, 36.42, 30.86, 30.30, 25.58 ($2CH_3$); IR (neat) 3083, 2959, 2930, 2872, 1709, 1466, 1425, 1393, 1373, 1299, 1250, 1199, 1085, 1072, 1002, 931 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{11}H_{15}O_2$ Br: 258.0256. Found: 258.0255. **14**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.99 (1H, m), 3.50 (2H, m), 2.95 (1H, dd, J=14.2, 10.2 Hz), 2.69 (1H, dd, J=14.2, 6.7 Hz), 2.28 (2H, s), 2.20 (2H, s), 1.07 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.49, 175.60, 111.30, 83.06, 50.76, 37.44, 34.45, 34.01, 30.49, 28.69, 28.35; IR (neat) 2961, 2872, 1634, 1404, 1368, 1260, 1219, 1169, 1146, 1099, 1040, 961 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{11}H_{15}O_2Br$: 258.0256. Found: 258.0251.

1.1.3. 2-Iodomethyl-6,6-dimethyl-2,3,4,5,6,7-hexahydrobenzofuran-4-one (15). Reaction of 5,5-dimethyl-2-diazocyclohexane-1,3-dione (166 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **15** (282 mg, 92%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (1H, m), 3.29 (2H, d, J=5.3 Hz), 2.93 (1H, dd, J=14.6, 10.1 Hz), 2.54 (1H, dd, J=14.6, 6.7 Hz), 2.24 (2H, s), 2.16 (2H, s), 1.05 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.40, 175.40, 111.20, 83.19, 50.73, 37.46, 33.93, 32.25, 28.70, 28.37, 8.72; IR (neat) 2959, 2870, 1636, 1402, 1368, 1256, 1219, 1167, 1144, 1098, 1038, 947, 930 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{11}H_{15}O_2I$: 306.0117. Found: 306.0113.

1.1.4. 2-Allyl-2-chlorophenalene-1,3-dione (16) and 9-chloromethyl-8,9-dihydrophenaleno[1,2-*b*]furan-7-one (17). Reaction of 2-diazophenalene-1,3-dione (222 mg, 1.0 mmol) with allyl chloride (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **16** (200 mg, 74%) and **17** (57 mg, 21%). **16**: mp 142–144°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (2H, d, J=7.2 Hz), 8.25 (2H, d, J=8.2 Hz), 7.77 (2H, dd, J=8.2, 7.2 Hz), 5.73 (1H, m), 5.10 (2H, dd, J=17.4, 9.4 Hz), 3.19 (2H, d, J=6.9 Hz); IR (KBr) 3080, 2932, 2861, 1709, 1687, 1580, 1506, 1433, 1316, 1231, 1009, 930, 837 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{16}H_{11}ClO_2$: 270.0445. Found: 270.0448. **17**: mp 130–132°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (1H, d, J=7.5 Hz), 8.11 (1H, d, J=7.8 Hz), 8.05 (2H, m), 7.72 (1H, dd, J=7.8, 7.5 Hz), 7.60 (1H, dd, J=7.8, 7.5 Hz), 5.28 (1H, m), 3.81 (2H, d, J=5.3 Hz), 3.39 (1H, dd, J=15.9, 10.0 Hz), 3.14 (1H, dd, J=15.9, 6.5 Hz); IR (KBr) 3016, 2918, 2851, 1626, 1584, 1510, 1437, 1381, 1267, 1219, 1192, 1151, 1103, 1039, 1020, 889 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{16}H_{11}ClO_2$: 270.0445. Found: 270.0447.

1.1.5. 2-Allyl-2-bromophenalene-1,3-dione (18) and 9-bromomethyl-8,9-dihydrophenaleno[1,2-*b*]furan-7-one (19). Reaction of 2-diazo-phenalene-1,3-dione (222 mg, 1.0 mmol) with allyl bromide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **18** (188 mg, 60%) and **19** (82 mg, 26%). **18**: mp 53–55°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (2H, d, J=7.3 Hz), 8.24 (2H, d, J=8.3 Hz), 7.76 (2H, dd, J=8.3, 7.3 Hz), 5.74 (1H, m), 5.15 (2H, dd, J=17.2, 10.2 Hz), 3.48 (2H, d, J=7.0 Hz); IR (KBr) 3082, 3018, 2982, 1697, 1672, 1578, 1507, 1431, 1311, 1232, 1201, 1167, 999, 929 cm^{-1}; HRMS *m*/*z* (M^+)

calcd for $C_{16}H_{11}BrO_2$: 313.9939. Found: 313.9943. **19**: mp 45–47°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (1H, d, J=7.6 Hz), 8.11 (1H, d, J=7.8 Hz), 8.05 (2H, m), 7.71 (1H, dd, J=7.8, 7.6 Hz), 7.60 (1H, dd, J=7.8, 7.6 Hz), 5.28 (1H, m), 3.67 (2H, m), 3.40 (1H, dd, J=15.8, 10.0 Hz), 3.12 (1H, dd, J=15.8, 6.8 Hz); IR (KBr) 2920, 1628, 1584, 1510, 1422, 1381, 1262, 1219, 1192, 1150, 1101, 1032, 885 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_{16}H_{11}BrO_2$: 313.9939. Found: 313.9944.

1.1.6. 9-Iodomethyl-8,9-dihydro-phenaleno[1,2-*b*]furan-7-one (20). Reaction of 2-diazophenalene-1,3-dione (222 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **20** (293 mg, 81%) as a solid: mp 112–113°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (1H, d, J=7.3 Hz), 8.11 (1H, d, J=7.8 Hz), 8.06 (1H, d, J=7.6 Hz), 8.03 (1H, d, J=7.6 Hz), 7.71 (1H, dd, J=7.8, 7.6 Hz), 7.60 (1H, dd, J=7.8, 7.6 Hz), 5.13 (1H, m), 3.48 (3H, m), 3.02 (1H, dd, J=15.8, 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.48, 166.00, 134.13, 133.00, 131.83, 129.89, 126.85, 126.48, 125.94, 120.68, 114.63, 83.96, 33.67, 8.22; IR (KBr) 3051, 2951, 2853, 1622, 1582, 1564, 1510, 1422, 1381, 1258, 1217, 1186, 1150, 1018, 956 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_{16}H_{11}IO_2$: 361.9801. Found: 361.9804.

1.1.7. 2-Bromo-5,5-dimethyl-2-(1-methyl-allyl)-cyclohexane-1,3-dione (21). Reaction of 5,5-dimethyl-2-diazo-cyclohexane-1,3-dione (166 mg, 1.0 mmol) with crotyl bromide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **21** (191 mg, 70%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (1H, m), 5.08 (2H, dd, J=16.7, 11.0 Hz), 3.21 (3H, m), 2.45 (2H, d, J=14.7 Hz), 1.23 (3H, d, J=6.9 Hz), 1.06 (3H, s), 0.88 (3H, s); IR (neat) 3080, 2959, 2874, 1707, 1640, 1464, 1418, 1395, 1373, 1325, 1298, 1242, 1217, 1080, 925 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_{12}H_{17}$ BrO_2: 272.0407. Found: 272.0411.

1.1.8. 6-Bromo-3,4,5a,6,7,9,9a-octahydro-2*H*-dibenzofuran-1-one (22). Reaction of 2-diazocyclohexane-1,3-dione (138 mg, 1.0 mmol) with 3-bromocyclohexene (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **22** (157 mg, 58%) as a mixture of diastereomers. *Major isomer*: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.78 (1H, dd, J=8.3, 7.1 Hz), 4.21 (1H, m), 3.28 (1H, m), 2.39 (2H, m), 2.30 (2H, m), 2.04–1.50 (8H, m); IR (neat) 2946, 2868, 1626, 1454, 1421, 1399, 1179, 1136, 1059, 997, 972, 922 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_{12}H_{15}BrO_2$: 270.0251. Found: 270.0254. *Minor isomer*: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.91 (1H, m), 4.72 (1H, d, J=7.1, 3.5 Hz), 3.63 (1H, m), 2.39 (2H, m), 2.30 (2H, m), 2.04–1.50 (8H, m).

1.1.9. 2-Iodomethyl-2,3,4,5,6,7-hexahydrobenzofuran-4-one (23). Reaction of of 2-diazocyclohexane-1,3-dione (138 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **23** (252 mg, 91%) as a solid: mp 72–74°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.78 (1H, m), 3.28 (2H, d, J=5.6 Hz), 2.92 (1H, m), 2.92 (1H, dd, J=14.5, 10.7 Hz), 2.52 (1H, dd, J=14.5, 6.5 Hz), 2.38 (2H, m), 2.28 (2H, t, J=6.2 Hz), 1.98 (2H, m); IR (KBr) 2946, 2866, 1634, 1453, 1402, 1339, 1231, 1181, 1140, 1109, 1059, 1011, 976 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_9H_{11}O_2I$: 277.9804. Found: 277.9804.

1.1.10. 2-Iodomethyl-6-methyl-2,3,4,5,6,7-hexahydro-benzofuran-4-one (24). Reaction of 5-methyl-2-diazo-cyclohexane-1,3-dione (152 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **24** (286 mg, 93%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.78 (1H, m), 3.28 (2H, dd, J=7.0, 6.8 Hz), 2.91 (1H, m), 2.54 (1H, m), 2.37 (2H, m), 2.24 (1H, m), 2.05 (2H, m), 1.05 (3H, d, J=6.4 Hz); IR (neat) 2955, 2870, 1636, 1454, 1402, 1335, 1252, 1209, 1140, 1119, 1046, 1026, 937 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_{10}H_{13}O_2I$: 291.9960. Found: 291.9961.

1.1.11. 2-Iodomethyl-6-isopropyl-2,3,4,5,6,7-hexahydro-benzofuran-4-one (25). Reaction of 5-isopropyl-2-diazo-cyclohexane-1,3-dione (180 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (10 mg, 0.02 mmol) as a catalyst afforded **25** (297 mg, 93%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79 (1H, m), 3.27 (2H, dd, J=10.2, 5.9 Hz), 2.90 (1H, m), 2.52 (1H, m), 2.38 (2H, m), 2.06 (2H, m), 1.91 (1H, m), 1.56 (1H, m), 0.87 (6H, d, J=6.7 Hz); IR (neat) 2959, 2872, 1638, 1402, 1372, 1254, 1206, 1152, 1111, 1038, 939 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_{12}H_{17}O_2I$: 320.0273. Found: 320.0270.

1.1.12. 2-Iodomethyl-5,5-dimethyl-2,3,4,5,6,7-hexahydro-benzofuran-4-one (26). Reaction of 4,4-dimethyl-2-diazo-cyclohexane-1,3-dione (166 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **26** (269 mg, 88%) as a solid: mp 59–61°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70 (1H, m), 3.27 (2H, d, J=4.9 Hz), 2.90 (1H, dd, J=14.9, 10.1 Hz), 2.53 (1H, dd, J=14.9, 6.4 Hz), 2.34 (2H, t, J=6.0 Hz), 1.78 (2H, t, J=6.0 Hz), 1.19 (3H, s), 1.16 (3H, s); IR (KBr) 2965, 2930, 2865, 1651, 1628, 1472, 1400, 1341, 1292, 1248, 1198, 1157, 1119, 1065, 1005, 937 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_{11}H_{15}O_2I$: 306.0117. Found: 306.0114.

1.1.13. 2-Iodomethyl-2,3-dihydrofuro[3,2-*c*]chromen-4-one (27). Reaction of 3-diazo-chroman-2,4-dione (188 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **27** (256 mg, 78%) as a solid: mp 144–145°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (1H, d, J=7.8 Hz), 7.55 (1H, dd, J=8.4, 7.8 Hz), 7.36 (1H, d, J=8.4 Hz), 7.27 (1H, dd, J=8.4, 7.8 Hz), 5.14 (1H, m), 3.48 (2H, m), 3.34 (1H, dd, J=15.6, 9.9 Hz), 2.97 (1H, dd, J=15.6, 6.8 Hz); IR (KBr) 3061, 3019, 2959, 1724, 1644, 1603, 1566, 1495, 1443, 1414, 1343, 1300, 1273, 1252, 1211, 1150, 1094, 1030, 910 cm^{-1}; HRMS m/z (M$^+$) calcd for $C_{12}H_9O_3I$: 327.9597. Found: 327.9596.

1.1.14. 2-Iodomethyl-9-methyl-2,3-dihydro-furo[3,2-*c*]-chromen-4-one (28). Reaction of 3-diazo-5-methyl-chroman-2,4-dione (202 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **28** (215 mg, 63%) as a solid: mp 130–131°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (1H, dd, J=8.0, 7.8 Hz), 7.19 (1H, d, J=8.0 Hz), 7.03 (1H, d, J=7.8 Hz), 5.14 (1H, m), 3.46 (2H, m), 3.30 (1H, dd, J=15.6, 10.1 Hz), 2.91 (1H, dd, J=15.6, 6.7 Hz), 2.67 (3H, s); IR (KBr) 3057, 2961, 2856, 1709, 1632, 1601, 1483, 1447, 1418, 1393, 1254, 1223, 1142, 1049, 1026, 914 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{13}H_{11}IO_3$: 341.9750. Found: 341.9752.

1.1.15. 2-Iodomethyl-8-methyl-2,3-dihydrofuro[3,2-*c*]-chromen-4-one (29). Reaction of 3-diazo-6-methylchroman-2,4-dione (202 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **29** (198 mg, 58%) as a solid: mp 142–143°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (1H, s), 7.36 (1H, d, J=8.2 Hz), 7.25 (1H, d, J=8.2 Hz), 5.15 (1H, m), 3.48 (2H, m), 3.34 (1H, dd, J=15.6, 10.0 Hz), 2.96 (1H, dd, J=15.6, 6.8 Hz), 2.40 (3H, s); IR (KBr) 2961, 1720, 1649, 1612, 1578, 1500, 1441, 1400, 1346, 1298, 1273, 1252, 1206, 1100, 1042, 1009, 936 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{13}H_{11}IO_3$: 341.9750. Found: 341.9754.

1.1.16. 2-(Iodomethyl)-7-methyl-2,3-dihydro-4*H*-furo-[3,2-*c*]chromen-4-one (30). Reaction of 3-diazo-7-methylchroman-2,4-dione (202 mg, 1.0 mmol) with allyl iodide (3 mL) using rhodium acetate (5 mg, 0.01 mmol) as a catalyst afforded **30** (212 mg, 62%) as a solid: mp 105–106°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (1H, d, J=8.0 Hz), 7.15 (1H, s), 7.08 (1H, d, J=8.0 Hz), 5.15 (1H, m), 3.46 (2H, m), 3.32 (1H, dd, J=15.5, 9.9 Hz), 2.94 (1H, dd, J=15.5, 7.0 Hz), 2.43 (3H, s); IR (KBr) 3061, 2926, 1719, 1647, 1620, 1516, 1424, 1358, 1163, 1036, 912 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{13}H_{11}IO_3$: 341.9750. Found: 341.9751.

1.2. General procedure for the preparation of dihydrofurans with *exo*-olefin (method A)

DBU (0.9–3.9 mmol) was added to a stirred solution of the iodide (0.3–1.3 mmol) in benzene (5 mL). The solution was stirred at room temperature for 20 h. To the mixture, water (20 mL) was added and the solution was extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with saturated ammonium chloride solution and evaporated under reduced pressure to give the residue. The residue was purified by flash chromatography on silica gel with 33% ethyl acetate in hexane as eluent to give the product.

1.3. General procedure for the preparation of 2-methylfurans (method B)

DBU (1.2–3.0 mmol) was added to a stirred solution of the iodide (0.4–1.0 mmol) in toluene (5 mL). The solution was refluxed for 2 h. To the cold mixture, water (20 mL) was added and the solution was extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with saturated ammonium chloride solution and evaporated under reduced pressure to give residue. The residue was purified by flash chromatography on silica gel with 33% ethyl acetate in hexane as eluent to give the product.

1.3.1. 6,6-Dimethyl-2-methylene-2,3,4,5,6,7-hexahydrobenzofuran-4-one (31). Reaction of the iodide **15** (245 mg, 0.8 mmol) with DBU (365 mg, 2.4 mmol) in benzene (method A) afforded **31** (134 mg, 94%) as a solid: mp 61–62°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.75 (1H, dd, J=5.8, 2.7 Hz), 4.41 (1H, dd, J=5.3, 2.7 Hz), 3.48 (2H, m), 2.36 (2H, s), 2.25 (2H, s), 1.12 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.25, 173.88, 160.69, 112.63, 87.87, 50.63, 36.71, 33.83, 29.05, 28.41, 28.33; IR (KBr) 2959, 2924, 2886, 1640, 1466, 1402, 1372, 1346, 1402, 1372, 1346, 1296, 1231, 1204, 1165, 1148, 1092, 1032, 1019, 974, 926 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{11}H_{14}O_2$: 178.0994. Found: 178.0996.

1.3.2. 2,6,6-Trimethyl-4,5,6,7-tetrahydrobenzofuran-4-one (32). Reaction of the iodide **15** (141 mg, 0.5 mmol) with DBU (228 mg, 1.5 mmol) in toluene (method B) afforded **32** (72 mg, 88%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.16 (1H, s), 2.62 (2H, s), 2.27 (2H, s), 2.22 (3H, s), 1.06 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.76, 164.97, 152.73, 120.64, 101.69, 51.84, 37.20, 35.10, 28.51, 28.43, 13.29; IR (neat) 2961, 2874, 1680, 1605, 1584, 1433, 1387, 1346, 1302, 1248, 1227, 1184, 1115, 1933, 930 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{11}H_{14}O_2$: 178.0994. Found: 178.0991.

1.3.3. 2-Methylene-2,3,4,5,6,7-hexahydrobenzofuran-4-one (33). Reaction of the iodide **23** (355 mg, 1.3 mmol) with DBU (594 mg, 3.9 mmol) in benzene (method A) afforded **33** (156 mg, 81%) as a solid: mp 33–34°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (1H, dd, J=5.6, 2.7 Hz), 4.42 (1H, dd, J=5.3, 2.7 Hz), 3.47 (2H, m), 2.51 (2H, m), 2.38 (2H, t, J=6.6 Hz), 2.09 (2H, m); IR (KBr) 2943, 1653, 1456, 1402, 1362, 1256, 1235, 1206, 1181, 1144, 1101, 1057, 997, 922 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_9H_{10}O_2$: 150.0681. Found: 150.0685.

1.3.4. 2-Methyl-4,5,6,7-tetrahydrobenzofuran-4-one (34). Reaction of the iodide **23** (210 mg, 0.8 mmol) with DBU (365 mg, 2.4 mmol) in toluene (method B) afforded **34** (94 mg, 83%) as a solid: mp 36–37°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (1H, s), 2.82 (2H, t, J=6.3 Hz), 2.48 (2H, t, J=6.5 Hz), 2.29 (3H, s), 2.15 (2H, m); IR (KBr) 2951, 1674, 1582, 1458, 1433, 1383, 1358, 1433, 1383, 1358, 1316, 1238, 1192, 1163, 1123, 1057, 1011, 988, 938 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_9H_{10}O_2$: 150.0681. Found: 150.0683.

1.3.5. 6-Methyl-2-methylene-2,3,4,5,6,7-hexahydrobenzofuran-4-one (35). Reaction of the iodide **24** (215 mg, 0.74 mmol) with DBU (338 mg, 2.2 mmol) in benzene (method A) afforded **35** (107 mg, 88%) as a solid: mp 42–44°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (1H, dd, J=5.7, 2.7 Hz), 4.35 (1H, dd, J=5.3, 2.7 Hz), 3.40 (2H, m), 2.54 (1H, dd, J=16.8, 3.0 Hz), 2.42 (1H, dd, J=16.8, 3.0 Hz), 2.33 (1H, m), 2.20 (1H, m), 2.10 (2H, J=16.1, 10.0 Hz), 1.12 (3H, d, J=6.4 Hz); IR (KBr) 2955, 2874, 1640, 1456, 1399, 1323, 1226, 1196, 1140, 1109, 1040, 1019, 931 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{10}H_{12}O_2$: 164.0838. Found: 164.0839.

1.3.6. 2,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran-4-one (36). Reaction of the iodide **24** (200 mg, 0.7 mmol) with DBU (320 mg, 2.1 mmol) in toluene (method B) afforded **36** (95 mg, 85%) as a solid: mp 58–60°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (1H, s), 2.89 (1H, dd, J=15.7, 4.0 Hz), 2.86–2.38 (3H, m), 2.27 (3H, s), 2.20 (1H, dd, J=15.2, 9.9 Hz), 1.13 (3H, d, J=6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.14, 165.61, 152.61, 121.48, 101.71, 45.92, 31.26, 30.74, 20.94, 13.29; IR (KBr) 2951, 1674, 1582, 1458, 1433, 1358, 1238, 1123, 1057, 1011, 938 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{10}H_{12}O_2$: 164.0838. Found: 164.0840.

1.3.7. 6-Isopropyl-2-methylene-2,3,4,5,6,7-hexahydrobenzofuran-4-one (37). Reaction of the iodide **25** (270 mg, 0.84 mmol) with DBU (365 mg, 2.4 mmol) in benzene (method A) afforded **37** (143 mg, 88%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73 (1H, dd, *J*=5.9, 2.7 Hz), 4.38 (1H, *J*=5.5, 2.7 Hz), 3.43 (2H, br s), 2.50 (1H, dd, *J*=16.9, 3.0 Hz), 2.44 (1H, *J*=16.9, 3.0 Hz), 2.24 (1H, *J*=17.0, 11.0 Hz), 2.13 (1H, *J*=17.0, 11.5 Hz), 1.99 (1H, m), 1.63 (1H, m), 0.93 (6H, d, *J*=6.8 Hz); IR (neat) 2961, 2876, 1659, 1468, 1400, 1372, 1339, 1302, 1227, 1198, 1152, 1103, 1028, 920 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{12}H_{16}O_2$: 192.1150. Found: 192.1149.

1.3.8. 6-Isopropyl-2-methyl-4,5,6,7-tetrahydrobenzofuran-4-one (38). Reaction of the iodide **25** (119 mg, 0.37 mmol) with DBU (183 mg, 1.2 mmol) in toluene (method B) afforded **38** (58 mg, 81%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.15 (1H, s), 2.80 (1H, dd, *J*=17.0, 4.9 Hz), 2.49 (1H, dd, *J*=17.0, 4.9 Hz), 2.47 (1H, d, *J*=16.3 Hz), 2.22 (3H, s), 2.16 (1H, d, *J*=15.9 Hz), 2.03 (1H, m), 1.63 (1H, m), 0.91 (6H, d, *J*=6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.48, 166.23, 152.73, 121.59, 101.68, 42.12, 41.76, 31.91, 26.85, 19.76, 19.50, 13.32; IR (neat) 2961, 2876, 1678, 1586, 1460, 1433, 1389, 1370, 1337, 1244, 1217, 1179, 1127, 1042, 1003, 934 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{12}H_{16}O_2$: 192.1150. Found: 192.1152.

1.3.9. 5,5-Dimethyl-2-methylene-2,3,4,5,6,7-hexahydrobenzofuran-4-one (39). Reaction of the iodide **26** (100 mg, 0.3 mmol) with DBU (137 mg, 0.9 mmol) in benzene (method A) afforded **39** (50 mg, 86%) as a solid: mp 58–61°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70 (1H, dd, *J*=5.7, 2.7 Hz), 4.34 (1H, dd, *J*=5.2, 2.7 Hz), 3.40 (2H, m), 2.37 (2H, t, *J*=6.6 Hz), 1.82 (2H, t, *J*=6.6 Hz), 1.2 (6H, s); IR (KBr) 2968, 2932, 1661, 1634, 1474, 1401, 1329, 1306, 1231, 1202, 1148, 1119, 1065, 993 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{11}H_{14}O_2$: 178.0994. Found: 178.0993.

1.3.10. 2,5,5-Trimethyl-4,5,6,7-tetrahydrobenzofuran-4-one (40). Reaction of the iodide **26** (260 mg, 0.9 mmol) with DBU (411 mg, 2.7 mmol) in toluene (method B) afforded **40** (138 mg, 91%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (1H, s), 2.53 (2H, t, *J*=6.6 Hz), 2.28 (3H, s), 1.96 (2H, t, *J*=6.6 Hz), 1.35 (6H, s); IR (neat) 2967, 1680, 1578, 1472, 1433, 1383, 1364, 1327, 1304, 1258, 1227, 1202, 1150, 1227, 1150, 1088, 1038, 1005, 934 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{11}H_{14}O_2$: 178.0994. Found: 178.0991.

1.3.11. 3,4,5a,8,9,9a-Hexahydro-2*H*-dibenzofuran-1-one (41). Reaction of the iodide **22** (270 mg, 1.0 mmol) with DBU (457 mg, 3.0 mmol) in toluene (method B) afforded **41** (177 mg, 93%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (1H, m), 5.94 (1H, dd, *J*=7.8, 1.5 Hz), 4.86 (1H, dd, *J*=8.8, 1.5 Hz), 3.14 (1H, m), 2.42–2.30 (4H, m), 2.04–1.99 (6H, m); IR (neat) 2946, 1615, 1452, 1404, 1238, 1181, 1134, 1061, 1007, 959 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{12}H_{14}O_2$: 190.0990. Found: 190.0995.

1.3.12. 2-Methylfuro[3,2-*c*]chromen-4-one (42). Reaction of the iodide **27** (328 mg, 1.0 mmol) with DBU (457 mg, 3.0 mmol) in benzene (method A) afforded **42** (160 mg, 80%) as a solid: mp 166–168°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (1H, d, *J*=7.4 Hz), 7.44 (2H, m), 7.33 (1H, d, *J*=7.2 Hz), 6.56 (1H, s), 2.49 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.40, 156.70, 155.66, 152.23, 130.10, 124.37, 120.50, 117.22, 112.87, 111.58, 104.06, 13.76; IR (KBr) 3106, 2919, 1728, 1632, 1589, 1502, 1451, 1360, 1319, 1283, 1250, 1203, 1101, 1061, 1030, 974 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{12}H_8O_3$: 200.0471. Found: 200.0470.

1.3.13. 2,9-Dimethylfuro[3,2-*c*]chromen-4-one (43). Reaction of the iodide **28** (342 mg, 1.0 mmol) with DBU (457 mg, 3.0 mmol) in benzene (method A) afforded **43** (199 mg, 93%) as a solid: mp 175–177°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.22 (2H, m), 7.10 (1H, d, *J*=7.2 Hz), 6.58 (1H, s), 2.75 (3H, s), 2.49 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.46, 157.60, 155.42, 152.83, 133.56, 129.37, 126.36, 126.30, 114.88, 111.77, 103.74, 20.86, 13.89; IR (KBr) 3128, 3057, 2922, 1732, 1615, 1595, 1451, 1385, 1352, 1312, 1229, 1161, 1057, 1036, 956 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{13}H_{10}O_3$: 214.0627. Found: 214.0632.

1.3.14. 2,8-Dimethylfuro[3,2-*c*]chromen-4-one (44). Reaction of the iodide **29** (172 mg, 0.5 mmol) with DBU (229 mg, 1.5 mmol) in benzene (method A) afforded **44** (105 mg, 98%) as a solid: mp 157–159°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (1H, s), 7.28 (2H, *J*=8.2 Hz), 6.55 (1H, s), 2.47 (s, 3H), 2.43 (s, 3H); IR (KBr) 2926, 1728, 1634, 1589, 1572, 1437, 1377, 1352, 1314, 1281, 1200, 1155, 1117, 1059, 1007, 908 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{13}H_{10}O_3$: 214.0627. Found: 214.0630.

1.3.15. 2,7-Dimethylfuro[3,2-*c*]chromen-4-one (45). Reaction of the iodide **30** (212 mg, 1.0 mmol) with DBU (457 mg, 3.0 mmol) in benzene (method A) afforded **45** (171 mg, 80%) as a solid: mp 168–170°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (1H, d, *J*=8.0 Hz), 7.22 (1H, s), 7.13 (1H, d, *J*=8.0 Hz), 6.54 (s, 1H), 2.47 (3H, s), 2.44 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.62, 156.97, 155.13, 152.47, 141.12, 125.53, 120.17, 117.38, 110.67, 110.36, 103.90, 21.73, 13.72; IR (KBr) 3130, 3057, 2924, 1749, 1632, 1595, 1512, 1439, 1360, 1321, 1260, 1163, 1142, 1115, 1065, 976, 949 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{13}H_{10}O_3$: 214.0627. Found: 214.0632.

1.3.16. 9-Methylphenaleno[1,2-*b*]furan-7-one (46). Reaction of the iodide **20** (293 mg, 1.0 mmol) with DBU (457 mg, 3.0 mmol) in benzene (method A) afforded **46** (229 mg, 98%) as a solid: mp 129–132°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (1H, d, *J*=7.3 Hz), 8.12 (1H, dd, *J*=8.2, 7.8 Hz), 7.95 (1H, d, *J*=8.3 Hz), 7.73 (1H, dd, *J*=7.8, 7.6 Hz), 7.60 (1H, dd, *J*=7.9, 7.5 Hz), 6.62 (1H, s), 2.48 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.06, 157.60, 154.32, 134.55, 131.94, 130.26, 130.30, 129.47, 126.30, 125.94, 124.96, 122.66, 120.47, 103.60, 13.63; IR (KBr) 3124, 2916, 1644, 1580, 1549, 1507, 1506, 1466, 1435, 1377, 1323, 1273, 1197, 1151, 1101, 1024, 939 cm^{-1}; HRMS *m*/*z* (M$^+$) calcd for $C_{16}H_{10}O_2$: 234.0678. Found: 234.0682.

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