Synthesis of Functionalized Benzofurans by a Double Heck Reaction of 2,3-Dibromofurans and Subsequent 6π-Electrocyclization/Dehydrogenation

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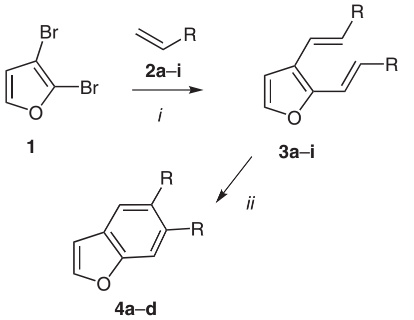
Abstract: The twofold Heck reaction of 2,3-dibromofurans afforded 2,3-di(alkenyl)furans which were transformed into functionalized benzofurans by a domino 6π-electrocyclization/dehydrogenation reaction.

Key words: catalysis, palladium, Heck reaction, electrocyclization, furans

Benzofurans are of considerable pharmacological relevance in medicinal chemistry and occur in many natural products.[1] For example, amiodarone represents a synthetic antiarrhythmic and antianginal drug.[2] The core structures of 7-alkanoylbenzofurans and 7-alkanoyl-2,3-dihydrobenzofurans are present in a number of natural products (e.g., longicaudatin,[3] the sessiliflorols A and B, flemistrictin E, tovophenone C, vismiaguianone C and piperaduncin B).[4]

Polyhalogenated compounds represent interesting substrates in palladium(0)-catalyzed cross-coupling reactions.[5,6] Bach and Krüger reported Sonogashira and Stille reactions of 2,3-dibromofuran.[7] These reactions proceed with very good site-selectivity in favor of position 2. de Meijere and co-workers reported that the combination of a twofold Heck reaction with 6π-electrocyclization provides a convenient approach to various carbocycles.[8] In recent years, we have studied the application of this methodology to heterocyclic systems.[9] Herein, we report what is, to the best of our knowledge, the first synthesis of functionalized benzofurans by a double Heck reaction of 2,3-dibromofurans and subsequent 6π-electrocyclization and dehydrogenation. This methodology provides a convenient approach to benzofurans containing substituents located at positions 5 and 6 which are not readily accessible by electrophilic substitution reactions.

The Heck reaction of 2,3-dibromofuran (**1**) with acrylates and styrenes **2a**–**i** (2.5 equiv) afforded the 2,3-di(alkenyl)furans **3a**–**i** in good yields (Scheme 1, Table 1). The reaction was thoroughly optimized for derivatives **3b** and **3f** (Table 2). The best yields were obtained when palladium(II) acetate (5 mol%) and the biaryl monophosphine ligands SPhos or XPhos[10] (10 mol%) were used. The employment of tetrakis(triphenylphosphine)palladium(0) resulted in considerably lower yields (Table 2, entry 1). The reactions were carried out in *N*,*N*-dimethylformamide at 120 °C. A relatively long reaction time (36 h) was necessary to achieve a complete conversion.



Scheme 1 Synthesis of **3a**–**i** and **4a**–**d**. *Reagents and conditions*: (i) **2a**–**i** (2.5 equiv), Pd(OAc)$_2$ (5 mol%), SPhos or XPhos (10 mol%), Et$_3$N, DMF, 120 °C, 36 h; (ii) (1) Ph$_2$O, 200 °C, 24 h; (2) Pd/C (10 mol%), Ph$_2$O, 200 °C, 24 h.

Table 1 Synthesis of **3a**–**i** and **4a**–**d**

3, **4**	R	Yield[a] (%) of **3**	Yield[a] (%) of **4**
a	CO$_2$Me	73[b]	90
b	CO$_2$Et	78[c]	93
c	CO$_2$*i*-Bu	93[b]	92
d	CO$_2$*n*-Bu	78[c]	95
e	CO$_2$(CH$_2$)$_5$Me	88[c]	–[d]
f	CO$_2$*t*-Bu	79[c]	–[e]
g	4-MeOC$_6$H$_4$	90[c]	–[e]
h	4-Tol	89[b]	–[e]
i	4-*t*-BuOC$_6$H$_4$	87[c]	–[e]

[a] Yields of isolated products.
[b] XPhos was used.
[c] SPhos was used.
[d] Reaction was not carried out.
[e] Decomposition.

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Table 2 Optimization of the Reaction Conditions for the Synthesis of **3b** and **3f**[a]

Entry	Catalyst	Yield[b] (%) of **3b**	Yield[b] (%) of **3f**
1	$Pd(PPh_3)_4$ (5 mol%)	35	41
2	$Pd(OAc)_2$ (5 mol%), XPhos (10 mol%)	73	72
3	**$Pd(OAc)_2$ (5 mol%), SPhos (10 mol%)**	**78**	**79**
4	$Pd(OAc)_2$ (3 mol%), Cy_3P (6 mol%)	65	59
5	$Pd(OAc)_2$ (2 mol%), $(HOCH_2CH_2)_3N$[c]	traces	traces

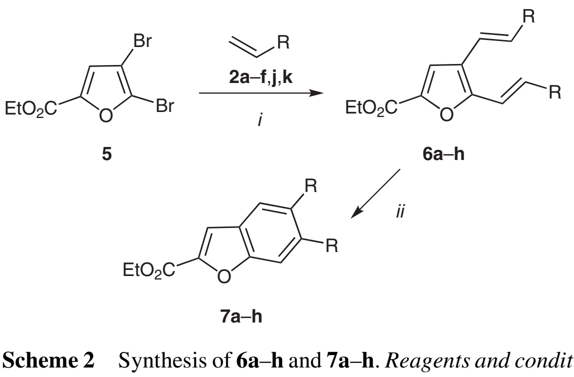
[a] Reactions were carried out in DMF using Et_3N as the base.

[b] Yields of isolated products.

[c] Triethanolamine was used as solvent, base and ligand.

Our next target was to find suitable conditions for a 6π-electrocyclization. In fact, 2,3-di(alkenyl)furans **3** proved to be rather reluctant to undergo the desired transformation. Stirring of a diphenyl ether solution of **3a–d** at 200 °C for 24 hours was required to induce the desired electrocyclization. To the reaction mixture was added palladium on carbon (10 mol%) and the mixture was stirred for an additional 24 hours at 200 °C to give benzofurans **4a–d** by dehydrogenation (see Table 1). Heating of **3f** resulted in decomposition of the *tert*-butyl ester moiety. Heating of the styrene-derived products **3g–i** also resulted in decomposition.

The twofold Heck reaction of 2,3-dibromo-5-(ethoxycarbonyl)furan (**5**) with acrylates and styrenes **2a–f**,**j**,**k** afforded the 2,3-di(alkenyl)furans **6a–h** (Scheme 2, Table 3). The reactions proceeded at slightly lower temperature (100 °C, 24 h) as compared to the synthesis of **3a–i**. The transformation of 2,3-di(alkenyl)furans **6a**,**b**,**d–h** to benzofurans **7a**,**b**,**d–h** required less drastic conditions (stirring at 170 °C, 2 × 12 h) as compared to the synthesis of **4a–d** (200 °C, 2 × 24 h). Similar to **3f**, heating of *tert*-butyl ester **6c** resulted in decomposition. In contrast to **3g–i**, electrocyclization of the styrene-derived 2,3-di(alkenyl)furan **6h** proved to be possible and afforded **7h** in good yield.



Scheme 2 Synthesis of **6a–h** and **7a–h**. *Reagents and conditions*: (i) **2a–f**,**j**,**k** (2.5 equiv), $Pd(OAc)_2$ (5 mol%), XPhos (10 mol%), Et_3N, DMF, 100 °C, 24 h; (ii) (1) Ph_2O, 170 °C, 12 h; (2) Pd/C (10 mol%), Ph_2O, 170 °C, 12 h.

Table 3 Synthesis of **6a–h** and **7a–h**

2	**6**, **7**	R	Yield[a] (%) of **6**	Yield[a] (%) of **7**
c	**a**	CO_2i-Bu	81	95
e	**b**	$CO_2(CH_2)_5Me$	85	97
f	**c**	CO_2t-Bu	83	–[b]
j	**d**	$CO_2(CH_2)_5CHMe_2$	85	88
d	**e**	CO_2n-Bu	88	90
a	**f**	CO_2Me	84	93
b	**g**	CO_2Et	94	94
k	**h**	$4\text{-}ClC_6H_4$	83	90

[a] Yields of isolated products.

[b] Decomposition.

It was noted above that Sonogashira and Stille reactions of 2,3-dibromofurans are known to proceed with excellent site-selectivity in favor of position 2. The site-selectivity of palladium(0)-catalyzed reactions of polyhalogenated substrates is generally controlled by steric and electronic effects. More electron-deficient carbon atoms are usually more reactive than electron-rich atoms; however, all attempts to carry out site-selective mono-Heck reactions of dibromofuran **1** or **5** failed. All reactions resulted in the isolation of double-Heck products **3** and **6** and of unreacted starting material. This might be explained by a proximity effect. The first attack occurs at carbon atom C-2 of the furan. The palladium catalyst is coordinated by the alkene and the reactivity of the neighbored carbon atom C-3 might thus be increased. In the case of products **3a–f** and **6a–g**, the increased reactivity of C-3 might alternatively be explained by the electron-withdrawing effect of the acrylate moiety located at carbon C-2.

In conclusion, functionalized benzofurans were prepared by a twofold Heck reaction of 2,3-dibromofurans and a subsequent domino 6π-electrocyclization/dehydrogenation reaction. The products are not readily available by other methods.

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra, the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative-scale chromatography, silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used. Melting points are uncorrected.

2,3-Di(alkenyl)furans 3a–i and 6a–h; General Procedure

In a pressure tube (glass bomb), a suspension of $Pd(OAc)_2$ (12 mg, 5 mol%) and XPhos or SPhos (10 mol%) in DMF (5 mL) was purged with argon and stirred at 20 °C to give a yellowish or brownish clear solution. To the stirred solution were added dibromofuran **1** (0.12 mL, 1.0 mmol) or **5** (300 mg, 1.0 mmol), Et_3N (1.1 mL, 8.0

mmol) and the acrylate or styrene **2a–i** (2.5 mmol). The reaction mixture was stirred at 120 °C for 36 h (for **3a–i**) or at 100 °C for 24 h (for **6a–h**). The solution was cooled to 20 °C, poured into H_2O (25 mL) and CH_2Cl_2 (25 mL), and the organic layer and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography (heptanes–EtOAc).

Dimethyl (2*E*,2′*E*)-3,3′-(Furan-2,3-diyl)diacrylate (3a)

Yield: 172 mg (73%); light yellow oil.

IR (KBr): 3100 (w), 2850 (m), 1711 (s), 1676 (w), 1631 (m), 1510 (w), 1445, 1292 (m), 1275, 1245, 1178 (s), 1035, 970, 872, 749 (m), 861, 756 (w), 721 (m), 530 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.72 (s, 3 H, CH_3O), 3.74 (s, 3 H, CH_3O), 6.16 (d, J = 15.8 Hz, 1 H, CH), 6.34 (d, J = 15.8 Hz, 1 H, CH), 6.57 (d, J = 2.2 Hz, 1 H, ArH), 7.38 (d, J = 1.7 Hz, 1 H, ArH), 7.55 (d, J = 15.8 Hz, 1 H, CH), 7.62 (d, J = 15.8 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 51.79, 51.85 (CH_3O), 109.4, 117.8, 119.8 (CH), 124.8 (C), 127.4, 132.7, 145.2 (CH), 150.5 (C), 166.9, 167.0 (CO).

GC-MS (EI, 70 eV): m/z (%) = 236 (11) [M$^+$], 230 (14), 213 (29), 187 (100), 173 (5), 151 (6), 111 (4).

HRMS (EI, 70 eV): m/z calcd for $C_{12}H_{12}O_5$: 236.06847; found: 236.06801.

Diethyl (2*E*,2′*E*)-3,3′-(Furan-2,3-diyl)diacrylate (3b)

Compound **3b** was directly transformed into **4b** without characterization.

Diisobutyl (2*E*,2′*E*)-3,3′-(Furan-2,3-diyl)diacrylate (3c)

Yield: 297 mg (93%); light yellow oil.

IR (KBr): 3119 (w), 2935 (s), 2852 (m), 1711 (s), 1631 (m), 1579, 1509 (w), 1290 (m), 1272, 1257 (s), 1045, 832, 740 (m), 658, 606 (w), 530 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (d, J = 6.8 Hz, 12 H, 4 CH_3), 1.86–1.97 (m, 2 H, 2 CH), 3.90 (d, J = 6.7 Hz, 2 H, CH_2O), 3.91 (d, J = 6.7 Hz, 2 H, CH_2O), 6.17 (d, J = 15.6 Hz, 1 H, CH), 6.35 (d, J = 15.6 Hz, 1 H, CH), 6.58 (d, J = 1.8 Hz, 1 H, ArH), 7.37 (d, J = 2.0 Hz, 1 H, ArH), 7.55 (d, J = 15.6 Hz, 1 H, CH), 7.59 (d, J = 15.6 Hz, 1 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.1 (4 CH_3), 27.8 (2 CH), 70.7, 70.8 (CH_2O), 109.3, 118.2, 120.3 (CH), 124.7 (C), 127.2, 132.4, 145.1 (CH), 150.5 (C), 166.4, 166.5 (CO).

GC-MS (EI, 70 eV): m/z (%) = 320 (71) [M$^+$], 305 (18), 290 (11), 262 (11), 249 (20), 189 (17), 153 (19), 147 (100).

HRMS (EI, 70 eV): m/z calcd for $C_{18}H_{24}O_5$: 320.16237; found: 320.16360.

Dibutyl (2*E*,2′*E*)-3,3′-(Furan-2,3-diyl)diacrylate (3d)

Yield: 249 mg (78%); light yellow oil.

IR (KBr): 3133, 3118 (w), 2925 (s), 2850 (m), 1711 (s), 1676 (w), 1631 (m), 1549, 1500 (w), 1445 (m), 1290 (m), 1275, 1255, 1168 (s), 1035, 969, 862, 749 (m), 746 (w), 720 (m), 648, 606 (w), 539 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.3 Hz, 6 H, 2 CH_3), 1.28–1.40 (m, 4 H, 2 CH_2), 1.56–1.65 (m, 4 H, 2 CH_2), 4.10–4.15 (m, 4 H, 2 CH_2O), 6.14 (d, J = 15.6 Hz, 1 H, CH), 6.32 (d, J = 15.6 Hz, 1 H, CH), 6.56 (d, J = 1.9 Hz, 1 H, ArH), 7.36 (d, J = 2.0 Hz, 1 H, ArH), 7.52 (d, J = 15.6 Hz, 1 H, CH), 7.57 (d, J = 15.5 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.6 (2 CH_3), 19.1 (2 CH_2), 30.7 (2 CH_2), 64.4, 64.5 (CH_2O), 109.3, 118.2, 120.3 (CH), 124.7 (C), 127.2, 132.3, 145.1 (CH), 150.5 (C), 166.5, 166.6 (CO).

GC-MS (EI, 70 eV): m/z (%) = 320 (71) [M$^+$], 264 (8), 247 (23), 190 (17), 163 (86), 147 (100), 134 (11), 119 (53).

HRMS (EI, 70 eV): m/z calcd for $C_{18}H_{24}O_5$: 320.16238; found: 320.16236.

Dihexyl (2*E*,2′*E*)-3,3′-(Furan-2,3-diyl)diacrylate (3e)

Yield: 331 mg (88%); light yellow oil.

IR (KBr): 3122, 3108 (w), 2921, 1711 (s), 1631 (m), 1549, 1500 (w), 1445 (m), 1377 (w), 1292 (m), 1275, 1255, 1167 (s), 1069 (w), 1035 (m), 1018 (w), 959 (m), 933 (w), 862 (m), 825 (w), 749 (m), 746 (w), 721 (m), 648, 607 (w), 538 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.86 (m, 6 H, 2 CH_3), 1.16–1.34 (m, 12 H, 6 CH_2), 1.58–1.68 (m, 4 H, 2 CH_2), 4.13 (t, J = 6.8 Hz, 2 H, CH_2O), 4.14 (t, J = 6.7 Hz, 2 H, CH_2O), 6.16 (d, J = 15.5 Hz, 1 H, CH), 6.35 (d, J = 15.5 Hz, 1 H, CH), 6.57 (d, J = 2.4 Hz, 1 H, ArH), 7.37 (d, J = 1.9 Hz, 1 H, ArH), 7.55 (d, J = 15.5 Hz, 1 H, CH), 7.60 (d, J = 15.6 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0 (2 CH_3), 22.5, 22.6, 28.7, 31.4 (2 CH_2), 64.9, 65.0 (CH_2O), 109.4, 118.3, 120.3 (CH), 124.7 (C), 127.2, 132.4, 145.1 (CH), 150.5 (C), 166.5, 166.6 (CO).

GC-MS (EI, 70 eV): m/z (%) = 376 (1) [M$^+$], 345 (8), 291 (3), 206 (10), 189 (100), 162 (8).

HRMS (EI, 70 eV): m/z calcd for $C_{22}H_{32}O_5$: 376.22497; found: 376.22397.

Di-*tert*-butyl (2*E*,2′*E*)-3,3′-(Furan-2,3-diyl)diacrylate (3f)

Yield: 252 mg (79%); light yellow oil.

IR (KBr): 2976, 2931 (m), 1705 (s), 1636, 1454, 1392, 1367, 1313, 1283, 1253 (m), 1146 (s), 1018, 977, 844, 767 (m), 711, 685, 594, 574 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 18 H, 6 CH_3), 6.03 (d, J = 16.1 Hz, 1 H, CH), 6.27 (d, J = 15.5 Hz, 1 H, CH), 6.54 (d, J = 2.3 Hz, 1 H, ArH), 7.34 (d, J = 2.3 Hz, 1 H, ArH), 7.44 (d, J = 15.5 Hz, 1 H, CH), 7.45 (d, J = 15.7 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.2 (6 CH_3), 80.7, 80.8 (C), 109.4, 120.1, 122.1 (CH), 124.4 (C), 126.5, 131.6, 144.8 (CH), 150.5 (C), 165.8, 165.9 (CO).

GC-MS (EI, 70 eV): m/z (%) = 320 (15) [M$^+$], 247 (11), 208 (100), 163 (31), 147 (21), 119 (26).

HRMS (EI, 70 eV): m/z calcd for $C_{18}H_{24}O_5$: 320.16237; found: 320.16232.

2,3-Bis(4-methoxystyryl)furan (3g)

Yield: 299 mg (90%); light yellow oil.

IR (KBr): 3030, 2996, 2992, 2930, 2833 (w), 1599, 1571, 1508, 1497, 1456, 1436, 1417, 1298, 1290, 1267 (m), 1246 (s), 1174, 1145, 1109, 1061, 958, 934, 895, 852, 845 (m), 815 (s), 740, 720 (m), 696, 659, 637, 610, 561, 547 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 6 H, 2 CH_3O), 6.56 (d, J = 2.1 Hz, 1 H, ArH), 6.71 (d, J = 16.2 Hz, 1 H, CH), 6.82 (d, J = 8.8 Hz, 4 H, ArH), 6.87–6.92 (m, 3 H), 7.25 (d, J = 2.0 Hz, 1 H, ArH), 7.34 (d, J = 8.6 Hz, 2 H, ArH), 7.38 (d, J = 8.7 Hz, 2 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.3 (CH_3O), 108.7, 112.1, 114.1, 114.2, 116.0 (CH), 121.6 (C), 126.8, 127.4, 127.7, 128.1 (CH), 130.0, 130.3 (C), 142.1 (CH), 150.0, 159.2, 159.4 (C).

GC-MS (EI, 70 eV): m/z (%) = 332 (100) [M$^+$], 207 (20), 166 (10), 121 (17).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{22}H_{20}O_3$: 332.14070; found: 332.14073.

2,3-Bis(4-methylstyryl)furan (3h)
Yield: 270 mg (89%); light yellow oil.

IR (KBr): 3020, 2992, 2963, 2833 (w), 1599, 1571, 1508, 1498, 1456, 1436, 1418, 1298, 1290 (m), 1246, 1174 (s), 1029, 959, 815, 740, 720 (m), 659, 638, 610, 562, 548 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 6 H, 2 CH_3), 6.54 (d, *J* = 2.0 Hz, 1 H, ArH), 6.68 (d, *J* = 16.2 Hz, 1 H, CH), 6.97 (m, 3 H), 7.05 (d, *J* = 7.9 Hz, 4 H, ArH), 7.22 (d, *J* = 2.0 Hz, 1 H, ArH), 7.28 (d, *J* = 7.9 Hz, 2 H, ArH), 7.29 (d, *J* = 8.2 Hz, 2 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.3, 21.4 (CH_3), 108.8, 113.1, 117.1 (CH), 122.0 (C), 126.2, 126.5, 127.4, 128.7, 129.4, 129.5 (CH), 134.4, 134.8, 137.3, 137.7 (C), 142.3 (CH), 150.1 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 300 (100) [M^+], 281 (33), 245 (8), 216 (10), 204 (8), 198 (10).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{22}H_{20}O$: 300.15142; found: 300.15133.

2,3-Bis(4-*tert*-butoxystyryl)furan (3i)
Yield: 361 mg (87%); light yellow oil.

IR (KBr): 3033, 2972, 2929, 2872, 1623 (w), 1503, 1362, 1271 (m), 1159 (s), 1102, 1060, 1029, 968, 959, 947 (w), 891, 864, 832, 743, 690, 677, 591 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.37 (s, 18 H, 6 CH_3), 6.54 (d, *J* = 2.0 Hz, 1 H, ArH), 6.67 (d, *J* = 16.1 Hz, 1 H, CH), 6.80–6.94 (m, 7 H), 7.23 (d, *J* = 2.0 Hz, 1 H, ArH), 7.30 (d, *J* = 8.5 Hz, 2 H, ArH), 7.31 (d, *J* = 8.6 Hz, 2 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 28.9 (6 CH_3), 78.7, 78.8 (CO), 108.8, 112.9, 116.9 (CH), 121.8 (C), 124.2, 124.3, 126.7, 126.9, 127.0, 128.3 (CH), 132.4, 132.7 (C), 142.3 (CH), 150.1, 155.0, 155.3 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 416 (14) [M^+], 360 (7), 304 (100), 210 (7).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{28}H_{32}O_3$: 416.23460; found: 416.23516.

Diisobutyl (2*E*,2′*E*)-3,3′-[5-(Ethoxycarbonyl)furan-2,3-diyl]diacrylate (6a)
Yield: 318 mg (81%); light yellow solid; mp 152–154 °C.

IR (KBr): 3109, 2958, 2874 (w), 1709 (s), 1633, 1578, 1515, 1469 (m), 1394 (w), 1368 (m), 1343 (w), 1318 (s), 1300, 1270 (w), 1255 (m), 1239 (w), 1220 (m), 1171 (s), 1114 (m), 1080 (w), 1008, 962 (s), 875, 861, 837 (w), 765, 748, 720, 693, 657 (m), 609, 595, 542 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 6.7 Hz, 12 H, 4 CH_3), 1.40 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.96–2.01 (m, 2 H, 2 CH), 4.01 (d, *J* = 3.6 Hz, 2 H, CH_2O), 4.03 (d, *J* = 3.5 Hz, 2 H, CH_2O), 4.41 (q, *J* = 7.1 Hz, 2 H, CH_2O), 6.34 (d, *J* = 15.8 Hz, 1 H, CH), 6.71 (d, *J* = 15.8 Hz, 1 H, CH), 7.37 (s, 1 H, ArH), 7.62 (d, *J* = 8.6 Hz, 1 H, CH), 7.67 (d, *J* = 8.4 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.1 (4 CH_3), 27.8 (2 CH), 61.7, 71.0, 71.1 (CH_2O), 115.8, 121.5, 121.6 (CH), 125.2 (C), 126.5, 131.5 (CH), 145.5, 152.4 (C), 158.0, 166.2, 166.5 (CO).

GC-MS (EI, 70 eV): *m*/*z* (%) = 393 (22), 392 (80) [M^+], 347 (22), 336 (18), 320 (10), 319 (49), 280 (53), 263 (16), 235 (72), 219 (100), 206 (44).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{21}H_{28}O_7$: 392.18295; found: 392.18259.

Dihexyl (2*E*,2′*E*)-3,3′-[5-(Ethoxycarbonyl)furan-2,3-diyl]diacrylate (6b)
Yield: 382 mg (85%); yellow solid; mp 162–164 °C.

IR (KBr): 3107, 2953, 2929, 2857 (w), 1715, 1632 (s), 1579, 1518, 1467 (m), 1453, 1392, 1368, 1346 (w), 1321 (s), 1301, 1265, 1252, 1240 (w), 1223 (m), 1175 (s), 1123, 1107, 1052, 1038 (w), 1024, 977, 961 (m), 910 (w), 875, 860 (m), 822, 799 (w), 764, 724, 661, 596 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.86 (m, 6 H, 2 CH_3), 1.23–1.28 (m, 12 H, 6 CH_2), 1.38 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.59–1.68 (m, 4 H, 2 CH_2), 4.02 (d, *J* = 3.7 Hz, 2 H, CH_2O), 4.05 (d, *J* = 3.6 Hz, 2 H, CH_2O), 4.32 (q, *J* = 7.1 Hz, 2 H, CH_2O), 6.23 (d, *J* = 15.7 Hz, 1 H, CH), 6.61 (d, *J* = 15.8 Hz, 1 H, CH), 7.27 (s, 1 H, ArH), 7.53 (d, *J* = 8.0 Hz, 1 H, CH), 7.58 (d, *J* = 8.0 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0 (2 CH_3), 14.3 (CH_3), 22.5, 25.6, 28.6, 31.4 (2 CH_2), 61.7, 65.0, 65.2 (CH_2O), 115.8, 121.6, 121.7 (CH), 125.2 (C), 126.5, 131.5 (CH), 145.8, 152.4 (C), 158.0, 166.2, 166.5 (CO).

GC-MS (EI, 70 eV): *m*/*z* (%) = 449 (14), 448 (49) [M^+], 403 (17), 347 (18), 320 (10), 291 (7), 280 (19), 246 (22), 235 (100).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{25}H_{36}O_7$: 448.24555; found: 448.24519.

Di-*tert*-butyl (2*E*,2′*E*)-3,3′-[5-(Ethoxycarbonyl)furan-2,3-diyl]diacrylate (6c)
Yield: 326 mg (83%); orange solid; mp 158–160 °C.

IR (KBr): 3109, 2979, 2930 (w), 1714, 1699 (s), 1633 (m), 1575, 1509, 1475, 1455, 1391 (w), 1367, 1322, 1280, 1256, 1220 (m), 1141 (s), 1079, 1019 (w), 975, 958 (m), 885, 863, 844 (w), 763, 750, 722, 653 (m), 607, 579 (w) cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.46 (s, 18 H, 6 CH_3), 4.31 (q, *J* = 7.2 Hz, 2 H, CH_2O), 6.14 (d, *J* = 15.4 Hz, 1 H, CH), 6.53 (d, *J* = 15.7 Hz, 1 H, CH), 7.24 (s, 1 H, ArH), 7.42 (d, *J* = 4.3 Hz, 1 H, CH), 7.48 (d, *J* = 4.3 Hz, 1 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.3 (CH_3), 28.1 (6 CH_3), 61.5 (CH_2), 81.1, 81.2 (C), 115.9, 123.4, 123.5 (CH), 124.9 (C), 125.7, 130.5 (CH), 145.6, 152.3 (C), 158.1, 165.3, 165.4 (CO).

GC-MS (EI, 70 eV): *m*/*z* (%) = 392 (11) [M^+], 336 (9), 280 (100), 235 (23), 219 (17), 206 (34).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{21}H_{28}O_7$: 392.18295; found: 392.18307.

Bis(6-methylheptyl) (2*E*,2′*E*)-3,3′-[5-(Ethoxycarbonyl)furan-2,3-diyl]diacrylate (6d)
Yield: 430 mg (85%); yellow solid; mp 153–155 °C.

IR (KBr): 3107, 2956, 2948, 2857 (w), 1717, 1635 (s), 1579, 1517, 1469 (m), 1457, 1392, 1368, 1346 (w), 1323 (s), 1311, 1266, 1253, 1242 (w), 1224 (m), 1178 (s), 1125, 1105, 1053, 1039 (w), 1021, 978, 962 (m), 910 (w), 875, 861 (m), 823, 798 (w), 764, 723, 663, 598 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.72–0.87 (m, 12 H, 4 CH_3), 0.89–0.90 (m, 2 H, 2 CH), 1.10–1.23 (m, 8 H, 4 CH_2), 1.32 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.36–1.39 (m, 8 H, 4 CH_2), 4.10–4.22 (m, 4 H, 2 CH_2O), 4.32 (q, *J* = 7.1 Hz, 2 H, CH_2O), 6.23 (dd, *J* = 2.8, 15.8 Hz, 1 H, CH), 6.61 (dd, *J* = 2.8, 15.8 Hz, 1 H, CH), 7.27 (s, 1 H, ArH), 7.53 (d, *J* = 8.2 Hz, 1 H, CH), 7.58 (d, *J* = 8.2 Hz, 1 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.5 (4 CH_3), 23.4, 25.7, 28.6, 31.4 (2 CH_2), 27.7 (2 CH), 61.6, 65.1, 65.4 (CH_2O), 115.7, 121.4, 121.8 (CH), 125.2 (C), 126.7, 131.8 (CH), 145.7, 152.6 (C), 158.4, 166.2, 166.4 (CO).

GC-MS (EI, 70 eV): m/z (%) = 504 (40) [M$^+$], 459 (30), 457 (60), 392 (35), 376 (100), 348 (53), 317 (33), 280 (26), 246 (50), 219 (72).

HRMS (EI, 70 eV): m/z calcd for $C_{29}H_{44}O_7$: 504.30816; found: 504.30782.

Dibutyl (2*E*,2′*E*)-3,3′-[5-(Ethoxycarbonyl)furan-2,3-diyl]diacrylate (6e)
Yield: 346 mg (88%); light yellow solid; mp 158–160 °C.

IR (KBr): 3107, 2953, 2929, 2857 (w), 1715, 1632 (s), 1579, 1518, 1467 (m), 1453, 1392, 1368, 1346 (w), 1321 (s), 1301, 1265, 1252, 1240 (w), 1223 (m), 1175 (s), 1123, 1107, 1052, 1038 (w), 1024, 977, 961 (m), 910 (w), 875, 860 (m), 822, 799 (w), 764, 724, 661, 596 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.4 Hz, 6 H, 2 CH_3), 1.32 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.35–1.42 (m, 4 H, 2 CH_2), 1.57–1.67 (m, 4 H, 2 CH_2), 4.12–4.18 (m, 4 H, 2 CH_2O), 4.32 (q, *J* = 7.1 Hz, 2 H, CH_2O), 6.23 (d, *J* = 15.8 Hz, 1 H, CH), 6.61 (d, *J* = 15.5 Hz, 1 H, CH), 7.27 (s, 1 H, ArH), 7.53 (d, *J* = 8.1 Hz, 1 H, CH), 7.58 (d, *J* = 8.1 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7 (2 CH_3), 14.3 (CH_3), 19.1 (2 CH_2), 30.7 (2 CH_2), 61.6, 64.8, 64.9 (CH_2O), 115.8, 121.6, 121.7 (CH), 125.2 (C), 126.5, 131.4 (CH), 145.9, 152.3 (C), 158.0, 166.1, 166.2 (CO).

GC-MS (EI, 70 eV): m/z (%) = 392 (43) [M$^+$], 347 (9), 336 (11), 319 (23), 291 (16), 263 (15), 235 (60), 219 (49), 191 (100).

HRMS (EI, 70 eV): m/z calcd for $C_{21}H_{28}O_7$: 392.18295; found: 392.18324.

Dimethyl (2*E*,2′*E*)-3,3′-[5-(Ethoxycarbonyl)furan-2,3-diyl]diacrylate (6f)
Yield: 259 mg (84%); orange solid; mp 150–152 °C.

IR (KBr): 3397, 3109, 2985 (w), 1708 (s), 1639 (m), 1580, 1517, 1443, 1395 (w), 1367, 1321 (m), 1267, 1256, 1234, 1223 (w), 1182 (s), 1117, 1083 (w), 1036, 968, 957 (s), 893, 874, 863, 810 (w), 763, 746, 722, 656 (m), 607, 585 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.74 (s, 3 H, CH_3O), 3.76 (s, 3 H, CH_3O), 4.32 (q, *J* = 7.3 Hz, 2 H, CH_2O), 6.23 (d, *J* = 15.9 Hz, 1 H, CH), 6.59 (d, *J* = 15.9 Hz, 1 H, CH), 7.27 (s, 1 H, ArH), 7.54 (d, *J* = 8.7 Hz, 1 H, CH), 7.59 (d, *J* = 8.7 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.2 (CH_3), 50.9, 51.1 (CH_3O), 60.7 (CH_2O), 114.7, 120.1, 120.2 (CH), 124.2 (C), 125.7, 130.7 (CH), 145.0, 151.3 (C), 157.0, 165.4, 165.5 (CO).

GC-MS (EI, 70 eV): m/z (%) = 308 (100) [M$^+$], 277 (36), 263 (20), 249 (63), 235 (91), 217 (31), 205 (55), 177 (44), 162 (30), 145 (92).

HRMS (EI, 70 eV): m/z calcd for $C_{15}H_{16}O_7$: 308.08905; found: 308.08870.

Diethyl (2*E*,2′*E*)-3,3′-[5-(Ethoxycarbonyl)furan-2,3-diyl]diacrylate (6g)
Yield: 317 mg (94%); yellow solid; mp 168–170 °C.

IR (KBr): 3399, 3108, 2983 (w), 1705 (s), 1637 (m), 1579, 1515, 1444, 1392 (w), 1366, 1320 (m), 1268, 1255, 1234, 1221 (w), 1180 (s), 1116, 1081 (w), 1037, 969, 958 (s), 893, 874, 863, 810 (w), 763, 746, 722, 656 (m), 607, 585 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.35 (m, 9 H, 3 CH_3), 4.17–4.25 (m, 4 H, 2 CH_2O), 4.32 (q, *J* = 7.3 Hz, 2 H, CH_2O), 6.23 (d, *J* = 15.7 Hz, 1 H, CH), 6.60 (d, *J* = 15.7 Hz, 1 H, CH), 7.27 (s, 1 H, ArH), 7.54 (d, *J* = 8.1 Hz, 1 H, CH), 7.59 (d, *J* = 8.1 Hz, 1 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.2 (2 CH_3), 14.3 (CH_3), 60.8, 61.0, 61.6 (CH_2O), 115.7, 121.6, 121.7 (CH), 125.2 (C), 126.5, 131.4 (CH), 145.9, 152.3 (C), 158.0, 166.0, 166.1 (CO).

GC-MS (EI, 70 eV): m/z (%) = 336 (100) [M$^+$], 291 (53), 263 (89), 235 (45), 219 (46), 217 (35), 191 (70).

HRMS (EI, 70 eV): m/z calcd for $C_{17}H_{20}O_7$: 336.12035; found: 336.11988.

Ethyl 4,5-Bis(4-chlorostyryl)furan-2-carboxylate (6h)
Compound **6h** was directly transformed into **7h** without characterization.

Functionalized Benzofurans 4a–d and 7a–h; General Procedure
A diphenyl ether solution (3 mL) of a 2,3-di(alkenyl)furan **3a**–**d** or **6a**–**h** (0.5 mmol) was stirred at 200 °C for 24 h (for **3a**–**d**) or at 170 °C for 12 h (for **6a**–**h**) in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (10 mol%) was added. The solution was stirred at 200 °C for 24 h (for **3a**–**d**) or at 170 °C for 12 h (for **6a**–**h**) under argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash silica gel chromatography (heptanes–EtOAc).

Dimethyl Benzofuran-5,6-dicarboxylate (4a)
Yield: 105 mg (90%); light yellow oil.

IR (KBr): 3010, 2850 (w), 1723, 1716 (s), 1583, 1486, 1435 (w), 1229, 1202, 1165, 1071, 1021, 981, 865, 797, 750, 692, 666 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CH_3O), 3.82 (s, 3 H, CH_3O), 6.75 (d, *J* = 2.1 Hz, 1 H, ArH), 7.63 (d, *J* = 2.2 Hz, 1 H, ArH), 7.80 (s, 1 H, ArH), 7.90 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 52.6, 52.7 (CH_3O), 107.0, 112.6, 122.6 (CH), 127.4, 128.2, 129.6 (C), 148.3 (CH), 155.2 (C), 167.9, 168.4 (CO).

GC-MS (EI, 70 eV): m/z (%) = 234 (10) [M$^+$], 204 (4), 187 (100), 171 (5), 149 (6), 111 (4).

HRMS (EI, 70 eV): m/z calcd for $C_{12}H_{10}O_5$: 234.05282; found: 234.05277.

Diethyl Benzofuran-5,6-dicarboxylate (4b)
Yield: 122 mg (93%); light yellow oil.

IR (KBr): 3411, 3120, 2931, 2872 (w), 1715 (s), 1619, 1586, 1529 (w), 1488, 1465 (m), 1391 (w), 1367 (m), 1300, 1219, 1149, 1125, 1102, 1039 (s), 896, 859, 772, 691, 588 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.5 Hz, 6 H, 2 CH_3), 4.30–4.35 (m, 4 H, 2 CH_2O), 6.77 (d, *J* = 2.2 Hz, 1 H, ArH), 7.69 (d, *J* = 2.2 Hz, 1 H, ArH), 7.81 (s, 1 H, ArH), 7.91 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.1 (2 CH_3), 61.6, 61.7 (CH_2O), 107.3, 112.4, 122.5 (CH), 127.8, 128.8, 129.5 (C), 148.2 (CH), 155.2 (C), 167.6, 168.0 (CO).

GC-MS (EI, 70 eV): m/z (%) = 262 (18) [M$^+$], 234 (4), 217 (19), 189 (100), 175 (5), 145 (6), 133 (4), 116 (7).

HRMS (EI, 70 eV): m/z calcd for $C_{14}H_{14}O_5$: 262.08458; found: 262.08413.

Diisobutyl Benzofuran-5,6-dicarboxylate (4c)
Yield: 146 mg (92%); light yellow oil.

IR (KBr): 3434 (w), 2959, 2874 (m), 1769 (w), 1716 (s), 1614, 1585, 1529 (w), 1468, 1377 (m), 1305, 1218 (s), 1125 (m), 1103, 1035, 938 (s), 893, 773 (m), 691, 632 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.7 Hz, 6 H, 2 CH_3), 0.93 (d, *J* = 6.8 Hz, 6 H, 2 CH_3), 1.96–2.01 (m, 2 H, 2 CH), 4.02 (d,

J = 6.7 Hz, 2 H, CH_2O), 4.03 (d, J = 6.7 Hz, 2 H, CH_2O), 6.76 (d, J = 2.2 Hz, 1 H, ArH), 7.71 (d, J = 2.1 Hz, 1 H, ArH), 7.81 (s, 1 H, ArH), 7.91 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.1 (4 CH_3), 27.5 (2 CH), 71.8, 71.9 (CH_2O), 107.0, 112.6, 122.6 (CH), 127.9, 128.8, 129.5 (C), 148.2 (CH), 155.2 (C), 167.6, 168.0 (CO).

GC-MS (EI, 70 eV): m/z (%) = 318 (1) [M^+], 263 (3), 189 (100), 162 (9), 144 (4), 133 (2), 116 (6).

HRMS (ESI$^+$): m/z calcd for $C_{18}H_{22}O_5$: 318.14674; found: 318.14664.

Dibutyl Benzofuran-5,6-dicarboxylate (4d)
Yield: 151 mg (95%); light yellow, highly viscous oil.

IR (KBr): 3144, 3117 (w), 2959, 2921, 2852 (m), 1711 (s), 1631, 1462, 1446, 1377, 1292 (w), 1275, 1255, 1223, 1169 (m), 1036, 969, 862, 794, 721, 539 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.3 Hz, 6 H, 2 CH_3), 1.30–1.43 (m, 4 H, 2 CH_2), 1.60–1.69 (m, 4 H, 2 CH_2), 4.24 (t, J = 6.7 Hz, 2 H, CH_2O), 4.25 (t, J = 6.7 Hz, 2 H, CH_2O), 6.74 (d, J = 2.2 Hz, 1 H, ArH), 6.67 (d, J = 2.2 Hz, 1 H, ArH), 7.78 (s, 1 H, ArH), 7.88 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7 (2 CH_3), 19.2 (2 CH_2), 30.6 (2 CH_2), 65.5, 65.6 (CH_2O), 107.0, 112.5, 122.5 (CH), 127.8, 128.7, 129.4 (C), 148.1 (CH), 155.1 (C), 167.5, 168.0 (CO).

GC-MS (EI, 70 eV): m/z (%) = 318 (5) [M^+], 245 (5), 189 (100), 116 (10).

HRMS (ESI$^+$): m/z calcd for $C_{18}H_{22}O_5$: 318.14623; found: 318.14626.

2-Ethyl 5,6-Diisobutyl Benzofuran-2,5,6-tricarboxylate (7a)
Yield: 185 mg (95%); light yellow oil.

IR (KBr): 2874 (w), 1719 (s), 1621 (w), 1583, 1467 (m), 1442, 1394 (w), 1369, 1345 (m), 1309 (s), 1259 (m), 1194, 1155, 1100 (s), 1038, 982, 943 (m), 901, 846 (w), 765, 740, 690 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, J = 6.5 Hz, 12 H, 4 CH_3), 1.37 (t, J = 7.1 Hz, 3 H, CH_3), 1.96–2.01 (m, 2 H, 2 CH), 4.03 (d, J = 3.4 Hz, 2 H, CH_2O), 4.05 (d, J = 3.3 Hz, 2 H, CH_2O), 4.40 (q, J = 7.1 Hz, 2 H, CH_2O), 7.49 (s, 1 H, ArH), 7.87 (s, 1 H, ArH), 8.01 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.1, 19.2 (4 CH_3), 27.7 (2 CH), 62.0, 72.0, 72.1 (CH_2O), 113.4, 113.5, 124.3 (CH), 128.6, 128.8, 131.9, 148.7, 155.7 (C), 158.8, 167.1, 167.1 (CO).

GC-MS (EI, 70 eV): m/z (%) = 390 (5) [M^+], 345 (20), 278 (30), 261 (100), 233 (16).

HRMS (EI, 70 eV): m/z calcd for $C_{21}H_{26}O_7$: 390.16730; found: 390.16659.

2-Ethyl 5,6-Dihexyl Benzofuran-2,5,6-tricarboxylate (7b)
Yield: 216 mg (97%); light yellow oil.

IR (KBr): 2955, 2928, 2857 (w), 1720 (s), 1621, 1582 (w), 1462 (m), 1369, 1344 (w), 1302 (s), 1258 (m), 1193, 1156, 1101 (s), 1017 (m), 944, 900, 836 (w), 765 (m), 740, 690, 574 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.85 (m, 6 H, 2 CH_3), 1.24–1.28 (m, 12 H, 6 CH_2), 1.37 (t, J = 7.2 Hz, 3 H, CH_3), 1.63–1.72 (m, 4 H, 2 CH_2), 4.22–4.28 (m, 4 H, 2 CH_2O), 4.40 (q, J = 7.4 Hz, 2 H, CH_2O), 7.50 (s, 1 H, ArH), 7.86 (s, 1 H, ArH), 8.01 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0 (2 CH_3), 14.3 (CH_3), 22.5, 25.6, 28.5, 31.5 (2 CH_2), 62.0, 66.1, 66.2 (CH_2O), 113.4, 113.5, 124.3 (CH), 128.5, 128.7, 131.9, 148.7, 155.7 (C), 158.8, 167.1, 167.3 (CO).

GC-MS (EI, 70 eV): m/z (%) = 446 (20) [M^+], 401 (20), 363 (20), 345 (10), 278 (14), 261 (100), 233 (12).

HRMS (EI, 70 eV): m/z calcd for $C_{25}H_{34}O_7$: 446.22990; found: 446.22914.

2-Ethyl 5,6-Bis(6-methylheptyl) Benzofuran-2,5,6-tricarboxylate (7d)
Yield: 221 mg (88%); light yellow oil.

IR (KBr): 3109, 2958, 2874 (w), 1709 (s), 1633, 1578, 1515, 1469 (m), 1394 (w), 1368 (m), 1343 (w), 1318 (s), 1300, 1270 (w), 1255 (m), 1239 (w), 1220 (m), 1171 (s), 1114 (m), 1080 (w), 1008, 962 (s), 875, 861, 837 (w), 765, 748, 720, 693, 657 (m), 609, 595, 542 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.74–0.89 (m, 12 H, 4 CH_3), 0.90–0.91 (m, 2 H, 2 CH), 1.11–1.23 (m, 8 H, 4 CH_2), 1.33 (t, J = 7.3 Hz, 3 H, CH_3), 1.37–1.41 (m, 8 H, 4 CH_2), 4.12–4.24 (m, 4 H, 2 CH_2O), 4.34 (q, J = 7.1 Hz, 2 H, CH_2O), 7.49 (s, 1 H, ArH), 7.85 (s, 1 H, ArH), 8.00 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.4 (CH_3), 19.8 (4 CH_3), 23.5, 25.8, 28.7, 31.6 (2 CH_2), 27.3 (2 CH), 61.7, 65.2, 65.5 (CH_2O), 113.6, 113.7, 124.5 (CH), 128.7, 128.9, 131.7, 148.4, 155.8 (C), 158.6, 166.3, 166.5 (CO).

GC-MS (EI, 70 eV): m/z (%) = 502 (20) [M^+], 457 (30), 391 (28), 279 (21), 261 (100), 233 (15).

HRMS (EI, 70 eV): m/z calcd for $C_{29}H_{42}O_7$: 502.29251; found: 502.29179.

5,6-Dibutyl 2-Ethyl Benzofuran-2,5,6-tricarboxylate (7e)
Yield: 176 mg (90%); highly viscous, yellow oil.

IR (KBr): 2873 (w), 1719 (s), 1621 (w), 1583 (m), 1563, 1508, 1488 (w), 1462 (m), 1369, 1344 (w), 1302 (s), 1257, 1242 (w), 1193, 1156, 1100 (s), 1060, 1037, 1015, 961 (w), 941 (m), 901, 840 (w), 765, 740, 691 (m), 643, 603, 579 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.3 Hz, 6 H, 2 CH_3), 1.32 (t, J = 7.2 Hz, 3 H, CH_3), 1.35–1.45 (m, 4 H, 2 CH_2), 1.62–1.71 (m, 4 H, 2 CH_2), 4.12–4.18 (m, 4 H, 2 CH_2O), 4.40 (q, J = 7.2 Hz, 2 H, CH_2O), 7.49 (s, 1 H, ArH), 7.86 (s, 1 H, ArH), 8.00 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7 (2 CH_3), 14.3 (CH_3), 19.2 (2 CH_2), 30.5, 30.6 (CH_2), 62.0, 65.8, 65.9 (CH_2O), 113.4, 113.5, 124.3 (CH), 128.5, 128.7, 131.9, 148.7, 155.7 (C), 158.8, 167.1, 167.3 (CO).

GC-MS (EI, 70 eV): m/z (%) = 390 (43) [M^+], 345 (30), 335 (11), 317 (40), 278 (18), 261 (100), 233 (17).

HRMS (EI, 70 eV): m/z calcd for $C_{21}H_{26}O_7$: 390.16730; found: 390.16658.

2-Ethyl 5,6-Dimethyl Benzofuran-2,5,6-tricarboxylate (7f)
Yield: 142 mg (93%); light yellow oil.

IR (KBr): 2951, 2925, 2853 (w), 1721 (s), 1620, 1578 (w), 1564 (m), 1535, 1488, 1475, 1465 (w), 1431, 1372, 1347 (m), 1310 (s), 1265, 1242 (m), 1207, 1156, 1100 (s), 1043, 1019, 966 (m), 934, 919, 876 (w), 854, 825, 785 (m), 765 (s), 742, 690, 667, 641, 568 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.1 Hz, 3 H, CH_3), 3.86 (s, 3 H, CH_3O), 3.88 (s, 3 H, CH_3O), 4.40 (q, J = 7.3 Hz, 2 H, CH_2O), 7.49 (s, 1 H, ArH), 7.86 (s, 1 H, ArH), 8.03 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.3 (CH_3), 52.8, 53.0 (CH_3O), 62.1 (CH_2O), 113.4, 113.5, 124.4 (CH), 128.0, 128.9, 131.5, 148.8, 155.8 (C), 158.8, 167.6, 167.7 (CO).

GC-MS (EI, 70 eV): m/z (%) = 306 (40) [M^+], 276 (15), 275 (100), 261 (8), 247 (44), 217 (5).

HRMS (EI, 70 eV): m/z calcd for $C_{15}H_{14}O_7$: 306.07340; found: 306.07314.

Triethyl Benzofuran-2,5,6-tricarboxylate (7g)
Yield: 157 mg (94%); highly viscous, orange oil.

IR (KBr): 3055, 2981, 2929 (w), 1714 (s), 1622 (w), 1581, 1564 (m), 1536, 1504 (w), 1488, 1474, 1445, 1396 (m), 1368 (s), 1345 (w), 1305, 1238, 1198, 1156, 1102 (s), 1043, 1020, 906, 868, 837, 785 (m), 765 (s), 740, 691, 671, 643, 562 (w) cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.29–1.40 (m, 9 H, 3 CH_3), 4.18–4.45 (m, 6 H, 3 CH_2O), 7.49 (s, 1 H, ArH), 7.86 (s, 1 H, ArH), 8.03 (s, 1 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.0, 14.1, 14.3 (CH_3), 61.8, 61.9, 62.0 (CH_2O), 113.3, 113.4, 124.3 (CH), 128.4, 128.7, 131.8, 148.7, 155.7 (C), 158.8, 167.1, 167.2 (CO).

GC-MS (EI, 70 eV): m/z (%) = 334 (25) [M^+], 306 (4), 289 (26), 261 (100), 247 (7), 233 (32), 217 (6).

HRMS (EI, 70 eV): m/z calcd for $C_{17}H_{18}O_7$: 334.10470; found: 334.10407.

Ethyl 5,6-Bis(4-chlorophenyl)benzofuran-2-carboxylate (7h)
Yield: 185 mg (90%); light brown, highly viscous oil.

IR (KBr): 2957, 2922, 2852 (w), 1720 (s), 1657, 1622, 1581, 1566, 1555 (w), 1494, 1455 (m), 1434, 1392 (w), 1368, 1328, 1301, 1285, 1261, 1240, 1228 (m), 1183, 1152, 1089, 1012 (s), 953 (m), 934, 889, 871, 854 (w), 827 (s), 765, 756, 743, 728 (m), 697, 682, 646, 636, 625, 590, 537 (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.1 Hz, 3 H, CH_3), 4.39 (q, J = 7.1 Hz, 2 H, CH_2O), 6.96–7.00 (dd, J = 2.3, 8.6 Hz, 4 H, ArH), 7.13–7.17 (dd, J = 2.0, 8.5 Hz, 4 H, ArH), 7.48 (s, 1 H, ArH), 7.51 (s, 1 H, ArH), 7.59 (s, 1 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.3 (CH_3), 60.6 (CH_2O), 112.5, 112.7, 123.3 (CH), 125.6 (C), 127.2, 127.3, 130.1, 130.2 (CH), 131.9, 132.2, 135.0, 138.2, 138.3, 138.5, 145.8, 154.2 (C), 158.3 (CO).

GC-MS (EI, 70 eV): m/z (%) = 412 (68), 411 (26), 410 (100) [M^+], 382 (5), 367 (4), 365 (5), 347 (4), 312 (14), 302 (10).

HRMS (ESI^+): m/z calcd for $C_{23}H_{16}O_3Cl_2$: 410.04710; found: 410.04713.

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