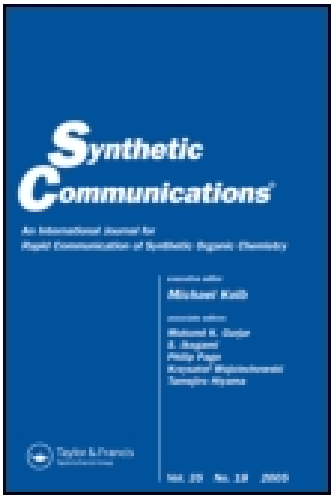

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Cycloaddition of Zirconacyclopentadiene with 2-Bromoacrylate, 2-Bromoacrylaldehyde, and 3-Bromofuran-2,5-dione in the Presence of CuCl: A New Pathway for the Formation of Benzene Derivatives and Isobenzofuran-1,3-dione

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CYCLOADDITION OF ZIRCONACYCLOPENTADIENE WITH 2-BROMOACRYLATE, 2-BROMOACRYLALDEHYDE, AND 3-BROMOFURAN-2,5-DIONE IN THE PRESENCE OF CuCl: A NEW PATHWAY FOR THE FORMATION OF BENZENE DERIVATIVES AND ISOBENZOFURAN-1,3-DIONE

Chao Chen, Xiaoyu Yan, and Chanjuan Xi

Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing, China

Reaction of zirconacyclopentadienes with 2-bromoalkenes in the presence of CuCl afforded multisubstituted benzene derivatives. The reactions of 2-bromoacrylate and 2-bromo-3-phenylacrylaldehyde afforded penta- and hexasubstituted benzenes in good yields. The reaction of 3-bromofuran-2,5-dione with zirconacyclopentadienes gave isobenzofuran-1,3-diones in good yields.

Keywords: 2-Bromoacrylaldehyde; 2-bromoacrylate; 3-bromofuran-2,5-dione; cuprous chloride; zirconacyclopentadiene

INTRODUCTION

Transformation of metallacycles to carbocyclic compounds is of general synthetic interest, and special attention has been devoted to the preparation of benzene derivatives. In this regard, zirconacyclopentadienes, which can be easily prepared by reductive coupling of two alkynes on zirconocene(II) species[1–6] and can participate in a number of organic reactions,[7,8] are especially attractive. Takahashi et al. have reported several reactions of zirconacyclopentadienes with various alkynes, affording benzene derivatives in good yields.[9–11] These reactions have opened new avenues for highly selective one-pot formation of benzene derivatives by coupling three different alkynes. Alternatively, reactions of zirconacyclopentadienes with other simple and readily available substrates for the formation of benzene derivatives in a new pathway remain to be developed. Herein, we report the reaction of zirconacyclopentadienes with 2-bromoacrylate, 2-bromoacrylaldehyde, and 3-bromofuran-2,5-dione in the presence of CuCl. This reaction provided a new method for the preparation of benzene derivatives and isobenzofuran-1,3-dione (Scheme 1).

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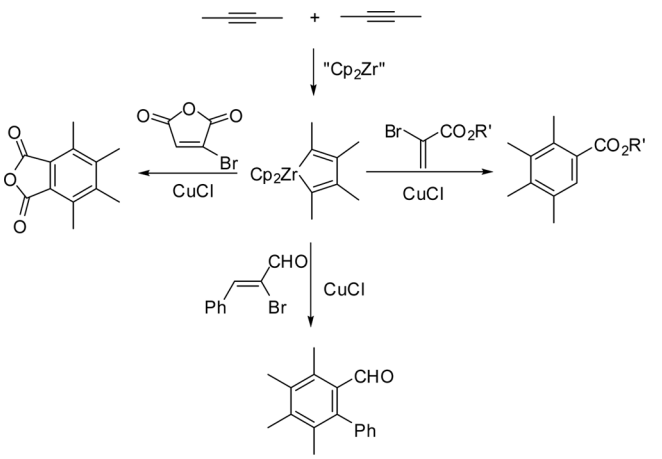
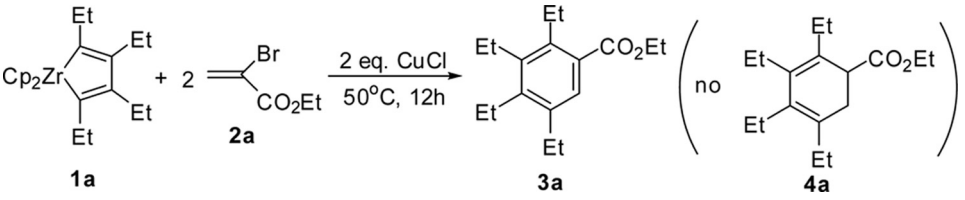


Scheme 1. Reaction of zirconacyclopentadiene with bromoethylene derivative.

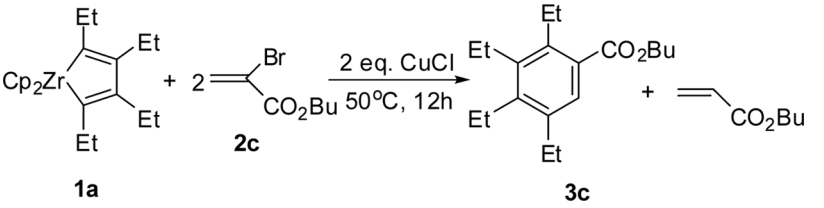
RESULTS AND DISCUSSION

Reaction of zirconacyclopentadienes with 3-iodopropenoate and 3-iodocycloenones in the presence of CuCl afforded cyclopentadienes and spirocyclic compounds.[12,13] In this case, the reaction proceeded through a cross-coupling–conjugate addition reaction sequence. Analogously, the reaction of zirconacyclopentadiene with 2-bromoacrylate in the presence of CuCl was envisioned to be given cyclohexdiene through cross-coupling–conjugate addition reaction in sequence. However, it is interesting that reaction of zirconacyclopentadiene **1a** with 2 equiv. of ethyl 2-bromoacrylate **2a** in the presence of 2 equiv. of CuCl took place at 50°C in 12 h. Only benzene derivative **3a** was obtained in 63% isolated yield rather than the expected cyclohexadiene **4a** (Scheme 2). At first, we tested the reaction of zirconacyclopentadiene **1a** with 1 equiv. of 2-bromoacrylate **2a** in the presence of 2 equiv. of CuCl at 50°C for 12 h. About 50% of starting **1a** remained. Addition of 2 equiv. of 2-bromoacrylate **2a** to this mixture consumed essentially all of **1a**. The best yield of the benzene derivative was obtained when zirconacyclopentadiene **1a** and 2-bromoacrylate **2a** were in 1:2 ratio at 50°C for 12 h.

Examination of 1:2 reaction mixture based on the reaction of zirconacyclopentadiene **1a** with 2 equiv. of butyl 2-bromoacrylate **2c** in the presence of 2 equiv. of



Scheme 2. Reaction of zirconacyclopentadiene with fethyl 2-bromoacrylate.

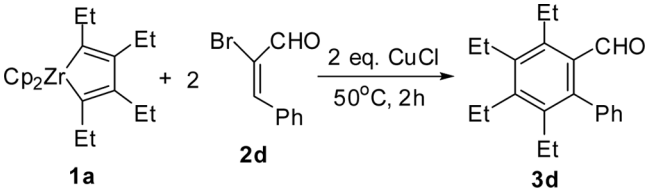


Scheme 3. Reaction of zirconacyclopentadiene with butyl 2-bromoacrylate.

CuCl gave the benzene derivative **3c** in 67% isolated yield together with nearly 1 equiv. of butyl acrylate (Scheme 3). This has provided a possible explanation for the requirement for 2 equiv. of 2-bromoacrylate.

Further reaction with 2-bromo-3-phenylacrylaldehyde **2d** under the identical conditions afforded hexasubstituted benzene **3d** in 66% isolated yield (Scheme 4). The structure of **3d** was unequivocally confirmed by single-crystal analysis (Fig. 1). (Crystal data for compound **3d**: $C_{21}H_{26}O$, MW = 294.42, monoclinic, space group $P2_1/n$, R1 = 0.0602, wR2 = 0.1048, a = 9.0946(17) Å, b = 9.0952(16) Å, c = 22.213(4) Å, $\alpha = 90°$, $\beta = 97.408(16)°$, $\gamma = 90°$, V = 1822.0(6) $Å^3$, T = 295 ± 2 K, Z = 4.)

The results concerning the formation of benzene derivatives are presented in Table 1. Generally, various zirconacyclopentadienes, including monocyclic and



Scheme 4. Reaction of zirconacyclopentadiene with 2-bromo-3-phenylacrylaldehyde.

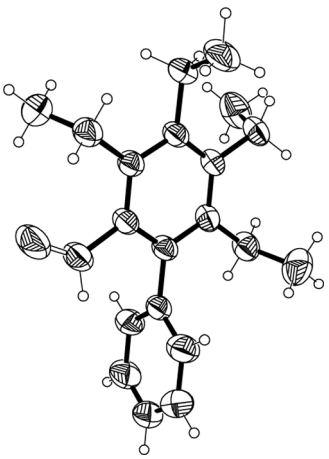
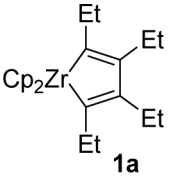
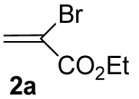
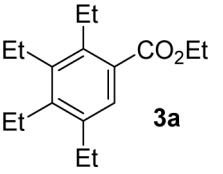
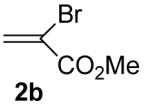
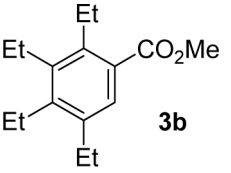
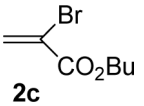
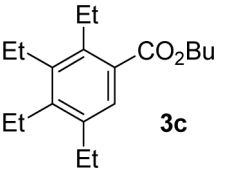
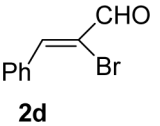
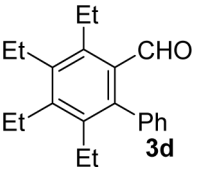
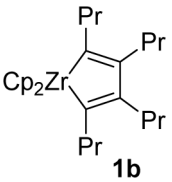
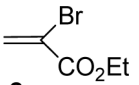
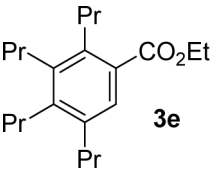
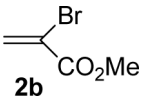
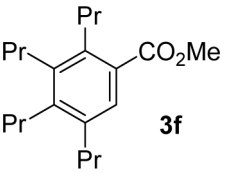
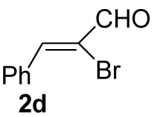
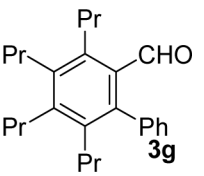


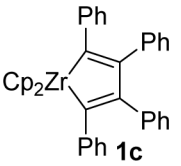
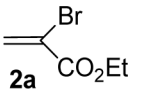
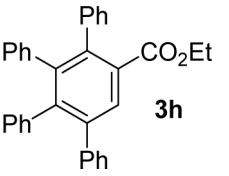
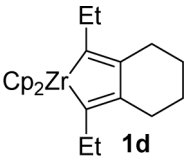
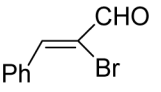
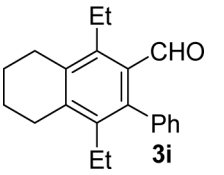
Figure 1. Structure of **3d**.

Table 1. Cycloaddition reactions of zirconacyclopentadienes with 2-bromoacrylate and 2-bromo-phenylacrylaldehyde

Zirconacyclopentadiene	Substrate	Time (h)	Product	Yield (%)[a]
 **1a**	 **2a**	12	 **3a**	70 (63)
	 **2b**	12	 **3b**	55 (48)
	 **2c**	12	 **3c**	75 (67)
	 **2d**	2	 **3d**	75 (66)
 **1b**	 **2a**	12	 **3e**	67 (57)
	 **2b**	12	 **3f**	64 (52)
	 **2d**	2	 **3g**	67 (57)

(*Continued*)

Table 1. Continued

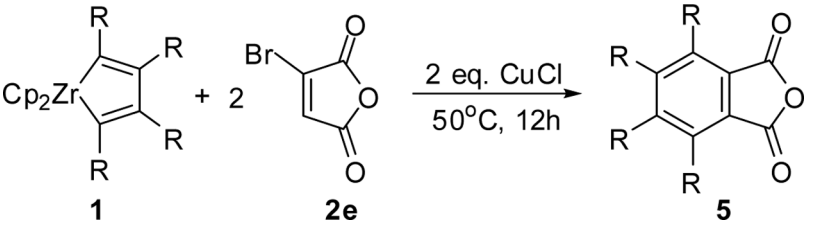
Zirconacyclopentadiene	Substrate	Time (h)	Product	Yield (%)[a]
 **1c**	 **2a**	12	 **3h**	— (46)
 **1d**	 **2d**	2	 **3i**	72 (65)

[a]GC yields; isolated yields are given in parentheses.

bicyclic zirconacyclopentadienes bearing alkyl or aryl substituents, could react with **2a**, **2b**, **2c**, and **2d** in the presence of CuCl. In all cases, the corresponding products were obtained in good yields.

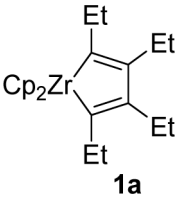
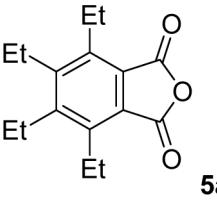
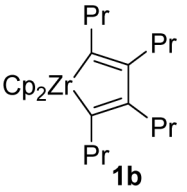
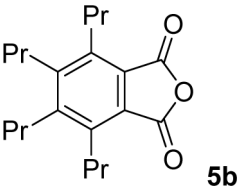
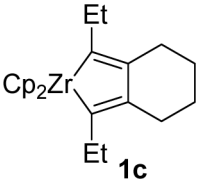
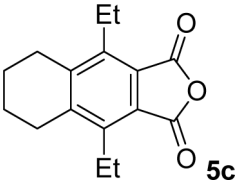
Furthermore, when 3-bromofuran-2,5-dione **2e** was applied, the reaction under the identical conditions gave isobenzofuran-1,3-dione **5** (Scheme 5). In all cases, the corresponding products were obtained in good yields. Results are summarized in Table 2. The structure of **5a** was also confirmed by single-crystal analysis (Fig. 2). (Crystal data for compound **5a**: $C_{16}H_{20}O_3$, MW = 260.32, monoclinic, space group C2/c, R1 = 0.0382, wR2 = 0.0705, a = 14.363(3) Å, b = 12.634(3) Å, c = 7.8445(17) Å, $\alpha = 90°$, $\beta = 102.948(19)°$, $\gamma = 90°$, V = 1387.3(5) $Å^3$, T = 295 ± 2 K, Z = 4.)

With these results, we propose the following reaction mechanism (Scheme 6). In the first step, the transmetallation of the Zr-C bond in zirconacyclopentadiene to the Cu-C bond affords bis(cuprate) **6**,[14] which reacts with 2-bromoacrylate via Diels–Alder reaction to give the intermediate **7**. Then, elimination of CuBr affords cyclohexadiene derivative **8**. Finally, elimination of the CuH drives the formation of aromatic ring **3**. The CuH reacts with the second molecular 2-bromoacrylate to form acrylate and CuBr.



Scheme 5. Reaction of zirconacyclopentadiene with 3-bromofuran-2,5-dione.

Table 2. Cycloaddition reactions of zirconacyclopentadienes with 3-bromofuran-2,5-dione

Zirconacyclopentadine	Product	Yield (%)[a]
 **1a**	 **5a**	80 (74)
 **1b**	 **5b**	87 (82)
 **1c**	 **5c**	82 (76)

[a]GC yields; isolated yields are given in parentheses.

In summary, we have reported a new and simple method to synthesize penta- and hexasubstituted benzenes from two alkynes and 2-bromoalkene via zirconacyclopentadienes in the presence of CuCl.

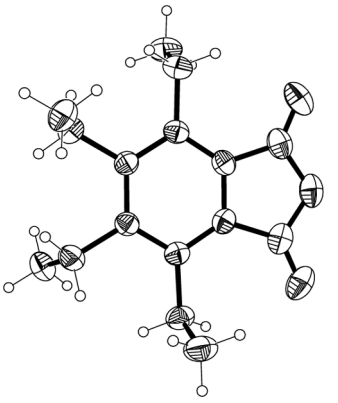
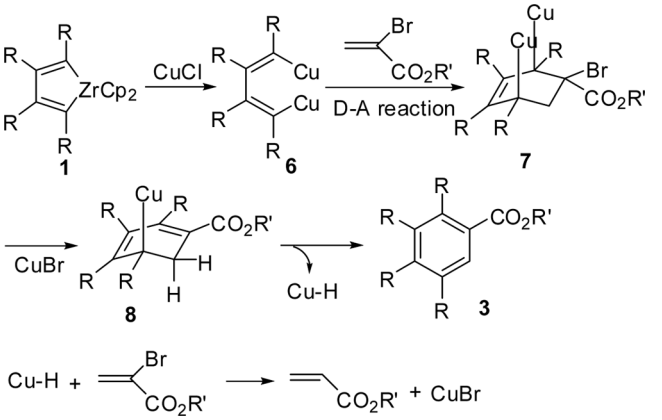


Figure 2. Structure of **5a**.



Scheme 6. Proposed reaction mechanism.

EXPERIMENTAL SECTION

General

All reactions were carried out in a predried Schlenk tube and under nitrogen with slightly positive pressure. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Methyl 2-bromoacrylate, ethyl 2-bromoacrylate, butyl 2-bromoacrylate, 2-bromo-3-phenylacrylaldehyde, and 3-bromofuran-2,5-dione were prepared according to the procedure reported in the literature.[15,16] Tetrahydrofuran (THF) was refluxed and distilled from sodium and benzophenone under a nitrogen atmosphere. Gas Chromatographic (GC) analysis was performed on a gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector using a fused silica capillary column (CBP1-M25-025) and Shimadzu CR6A-Chromatopac integrator. GC yields were determined using suitable hydrocarbons as internal standards. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Joel 300 NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as internal standard. Flash-column chromatography was performed using silica gel (200–300 mesh).

Representative Procedure for the Preparation of Ethyl 2,3,4,5-Tetraethylbenzoate (3a)

n-BuLi (1.6 M in hexane, 2.4 mmol) at −78°C was added to a solution of Cp_2ZrCl_2 (1.2 mmol, 0.352 g) in THF (5.0 mL), and the mixture was stirred for 1 h. After addition of 3-hexyne (2.0 mmol, 228 μL), the mixture was warmed to room temperature and stirred for 1 h. Before CuCl (2.0 mmol, 196 mg) was added, the mixture was cooled to 0°C using an ice bath and maintained at this temperature for 5 min. Ethyl 2-bromoacrylate (2.0 mmol, 270 μL) was added to the mixture. The mixture was warmed up to 50°C, kept for 12 h, and quenched with 3 N HCl. Then, aqueous layers were extracted with 15 mL of Et_2O five times. The combined organic layers were dried over Na_2SO_4. The solvent was evaporated, and the product

was purified by column chromatography with petroleum ether/diethyl ether 20/1 as elution to afford the target compound as a light yellow liquid (165 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.13–1.26 (m, 12H), 1.38 (t, $J = 7.2$ Hz, 3H), 2.61–2.75 (m, 6H), 2.88 (q, $J = 7.5$ Hz, 2H), 4.32 (q, $J = 7.2$ Hz, 2H), 7.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 15.42, 15.35, 15.53, 15.84, 16.22, 21.79, 22.18, 22.99, 25.71, 60.71, 127.91, 129.29, 139.59, 140.20, 141.00, 143.97, 169.30. Calcd. for $C_{17}H_{26}O_2$ 262.1933; found 262.1929.

Selected Data

Methyl 2,3,4,5-tetraethylbenzoate (3b). A light yellow liquid (119 mg, isolated yield 48%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.15–1.26 (m, 12H), 2.62–2.74 (m, 6H), 2.91 (q, $J = 7.5$ Hz, 2H), 3.87 (s, 3H), 7.45 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 15.91, 15.98, 16.02, 16.53, 22.35, 22.74, 23.70, 26.17, 52.05, 128.34, 128.89, 139.95, 141.01, 141.75, 144.50, 169.72. Calcd. for $C_{16}H_{24}O_2$ 248.1776; found 248.1779.

Butyl 2,3,4,5-tetraethylbenzoate (3c). A light yellow liquid (195 mg, isolated yield 67%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.97 (t, $J = 7.5$ Hz, 3H), 1.12–1.26 (m, 12H), 1.41–1.48 (m, 2H), 1.65–1.1.74 (m, 2H), 2.60–2.74 (m, 6H), 2.91 (q, $J = 7.5$ Hz, 2H), 4.26 (t, $J = 7.5$ Hz, 2H), 7.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.8, 15.3, 15.4, 15.8, 16.2, 19.4, 21.8, 22.2, 23.0, 25.7, 30.9, 64.7, 128.0, 130.5, 139.6, 140.3, 141.0, 144.0, 169.5. Calcd. for $C_{19}H_{30}O_2$ 290.2246; found 290.2249.

3,4,5,6-Tetraethylbiphenyl-2-carbaldehyde (3d). A light yellow liquid (195 mg, isolated 66%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.91–1.04 (m, 6H), 1.20–1.25 (m, 6H), 2.39–2.45 (m, 2H), 2.74–2.81 (m, 4H), 2.95–3.00 (m, 2H), 7.21–7.23 (m, 2H), 7.34–7.39 (m, 3H), 9.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 15.52, 15.67, 15.97, 16.05, 21.42, 21.96, 22.63, 22.80, 127.16, 127.97, 130.08, 132.03, 138.66, 138.95, 140.83, 144.42, 145.72, 195.50. Calcd. for $C_{21}H_{26}O$ 294.1984; found 294.1980.

Ethyl 2,3,4,5-tetrapropylbenzoate (3e). A light yellow liquid (181 mg, isolated yield 57%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.98–1.08 (m, 12H), 1.38 (t, $J = 7.2$ Hz, 3H), 1.49–1.69 (m, 8H), 2.53–2.78 (m, 6H), 2.81 (q, $J = 8.1$ Hz, 2H), 4.32 (q, $J = 7.2$ Hz, 2H), 7.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.81, 14.88, 15.00, 15.04, 15.08, 24.60, 24.67, 24.96, 25.35, 31.61, 31.89, 32.19, 35.23, 60.69, 128.61, 129.12, 138.26, 138.98, 140.10, 142.90, 169.36. Calcd. for $C_{21}H_{34}O_2$ 318.2559; found 318.2563.

Methyl 2,3,4,5-tetrapropylbenzoate (3f). A light yellow liquid (158 mg, isolated yield 52%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.96–1.06 (m, 12H), 1.25–1.37 (m, 8H), 2.56–2.60 (m, 6H), 2.80–2.83 (m, 2H), 3.85 (s, 3H), 7.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.97, 14.37, 14.82, 14.97, 24.50, 24.55, 24.87, 25.26, 31.83, 32.07, 32.45, 35.13, 51.76, 128.44, 128.73, 138.17, 139.33, 140.11, 143.08, 169.51. Calcd. for $C_{20}H_{32}O_2$ 304.2402; found 304.2402.

3,4,5,6-Tetrapropylbiphenyl-2-carbaldehyde (3g). A light yellow solid (200 mg, isolated 57%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.78 (t, $J = 7.2$ Hz, 3H), 1.10–1.18 (m, 9H), 1.36–1.44 (m, 2H), 1.64–1.66 (m, 6H), 2.36–2.41 (m, 2H), 2.74–2.76 (m, 4H), 2.97–3.00 (m, 2H), 7.25–7.27 (m, 2H), 7.37–7.42 (m, 3H), 9.78 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.70, 14.88, 15.05, 15.12, 24.72, 24.82, 24.89, 25.32, 31.32, 32.15, 32.68, 127.16, 127.96, 128.22, 130.09, 132.12, 137.55, 139.06, 139.73, 139.80, 144.37, 144.57, 195.41. Calcd. for $C_{25}H_{34}O$ 350.2610; found 350.2615.

Ethyl 2,3,4,5-tetraphenylbenzoate (3h). A light yellow solid (118 mg, isolated yield 26%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.96 (t, $J = 7.2$ Hz, 3H), 4.07 (q, $J = 7.2$ Hz, 2H), 6.77–6.95 (m, 10H), 7.07–7.19 (m, 10H), 7.93 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.79, 61.10, 125.78, 126.07, 126.44, 126.67, 126.85, 127.12, 127.26, 127.79, 129.96, 131.23, 131.38, 132.21, 139.35, 139.45, 140.10, 140.21, 141.09, 142.36, 143.08, 168.90. Calcd. for $C_{33}H_{26}O_2$ 454.1933; found 454.1938.

1,4-Diethyl-3-phenyl-5,6,7,8-tetrahydronaphthalene-2-carbaldehyde (3i). A light yellow solid (190 mg, isolated yield 65%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.94 (t, $J = 7.5$ Hz, 3H), 1.23 (t, $J = 7.5$ Hz, 3H), 1.85–1.88 (m, 4H), 2.41 (q, $J = 7.5$ Hz, 2H), 2.85–2.90 (m, 4H), 2.97 (q, $J = 7.5$ Hz, 2H), 7.21–7.25 (m, 2H), 7.37–7.42 (m, 3H), 9.73 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.39, 14.78, 21.86, 22.34, 22.77, 22.99, 26.47, 27.84, 127.33, 128.17, 130.20, 131.47, 136.23, 138.75, 138.95, 141.22, 141.35, 143.44, 195.64. Calcd. for $C_{21}H_{24}O$ 292.1827; found 292.1830.

4,5,6,7-Tetraethylisobenzofuran-1,3-dione (5a). White solid (192 mg, isolated 74%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.16–1.21 (m, 12H), 2.78 (q, $J = 7.5$ Hz, 4H), 3.05 (q, $J = 7.2$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 15.27, 15.44, 21.33, 22.21, 126.40, 142.93, 150.17, 163.41. Calcd. for $C_{16}H_{20}O_3$ 260.1412; found 260.1412.

4,5,6,7-Tetrapropylisobenzofuran-1,3-dione (5b). White solid (249 mg, isolated yield 65%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.00–1.10 (m, 12H), 1.47–1.58 (m, 8H), 2.66–2.71 (m, 4H), 2.96–3.01 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.58, 14.91, 24.64, 24.76, 30.19, 31.72, 126.50, 141.49, 149.06, 163.50. Calcd. for $C_{20}H_{28}O_2$ 316.2038; found 316.2034.

4,9-Diethyl-5,6,7,8-tetrahydronaphtho[2,3-c]furan-1,3-dione (5c). A light yellow liquid (196 mg, isolated yield 76%) ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.12 (t, $J = 7.5$ Hz, 6H), 1.82 (b, 4H), 2.84 (b, 4H), 3.03 (q, $J = 7.5$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.90, 20.67, 21.98, 26.87, 125.07, 142.86, 145.41, 163.52. Calcd. for $C_{16}H_{18}O_3$ 258.1256; found 258.1253.

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