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Synthesis of dibenzofuran-1,4-diones using the Dötz benzannulation

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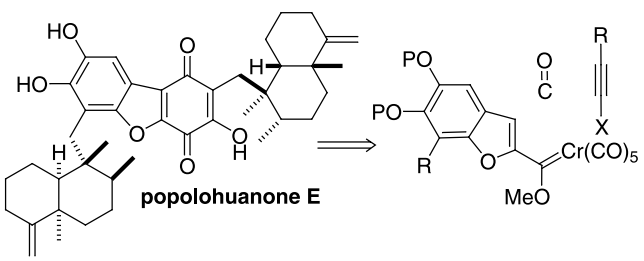
Abstract—The chromium Fischer carbene complexes of benzofuran and benzothiophene have been prepared and can be used in Dötz benzannulations with alkynes for the regioselective and converg ent synthesis of dibenzofuran-1,4-dione heterocycles. The use of alkynylboronates led to model systems of the tricyclic ring system of popolohuanone E after oxidation. It would appear that the combination of alkynyl boronates with furan type Fischer carbene complexes leads to substantial amounts (~50%) of protodeboronated products.

1. Introduction

The dibenzofuran-1,4-dione heterocycle is the central structural element of popolohuanone E (Scheme 1), a marine natural product isolated from the Pohnpei marine sponge *Dysidea* sp which exhibits potent topoisomerase-II inhibition and is cytotoxic against non-small cell lung cancer cells.[1] Access to this heterocyclic ring system has classically relied upon the cyclisation of bisquinones using acidic,[2] photochemical,[3] or oxidative[4] methods. The bisquinones were formed from the dimerisation of oxygenated phenyl rings, or the photochemical oxidative dimerisation of certain quinones.[5] Aside from often mediocre to low yields and harsh reaction conditions these classical methods restricted the structure of the final dibenzofuran-1,4-dione due to the precursors being derived from the homodimerisation of aromatic systems. The convergent synthesis of dibenzofuran-1,4-diones from two different aromatic systems has been achieved by the phenol–chloranil reaction,[6] but gave complex mixtures with low yields of products.[7] However, this last approach has been used in a more modern and ingenious setting by Terashima et.al. to prepare various model compounds of the central tricyclic ring system of popolohuanone E.[8] This strategy was then used in an enantioselective synthesis of popolohuanone E, but faltered at the removal of the 8-*O*-methyl group.[9] We decided to pursue a regioselective synthesis of dibenzofuran-1,4-dione heterocycles using a Dötz benzannulation strategy (Scheme 1). We recognised the potential for this strategy to be divergent due to the convergence of two different reaction partners.

The reaction between chromium Fischer carbene complexes and alkynes, first reported by Dötz in 1975,[10] is renowned for it's ability to construct highly substituted benzenoid compounds from simple starting materials in one step with a high degree of regiochemical control.[11] We envisaged that the development of this route would enable the synthesis of diverse dibenzofuran-1,4-dione **2** systems currently inaccessible from existing classical methods (Scheme 2). For a synthesis of more oxygenated heterocycles we would require the alkynyl substituent X to be oxygen (Schemes 1 and 2). Although alkynylethers have been shown to react with Fischer carbenes with good regioselectivities, they are often low yielding.[11e] A masked oxygen function could be introduced with the use of alkynylsilanes (X=SiR_3), but in general these substrates show low regioselectivity.[12,13] The recent development by Harrity of alkynylboronic esters as partners in the Dötz benzannulation has shown these substrates to provide excellent yields of regioisomerically pure products.[14] The boron substituent can be oxidised to a hydroxyl group in the presence of basic hydrogen peroxide to give high yields of hydroxyquinone (Scheme 2).[15] We



Scheme 1.

Keywords: Dibenzofuran-1,4-diones; Chromium carbenes; Dötz benzannulation; Alkynyl boronates; Popolohuanone E.
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† Corresponding author for X-ray crystal structures.

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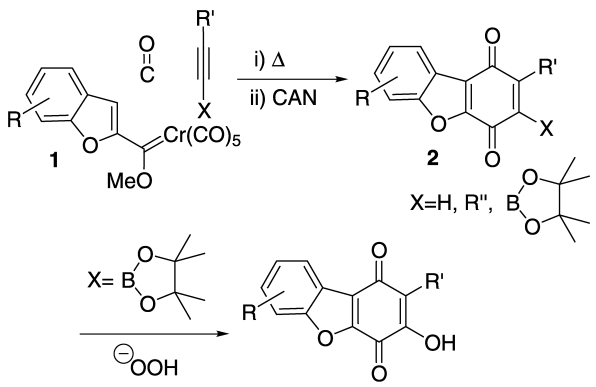


Scheme 2.

report here our results for the synthesis of dibenzofuran-1,4-diones using the Dötz benzannulation of benzofuran chromium Fischer carbene complex **1** with both terminal and symmetrical alkynes and alkynylboronic esters.

The Dötz benzannulation chemistry of 2-furyl **3**[16] and 2-(*N*-methyl)indole **4**[17] chromium Fischer carbene complexes (Fig. 1) are known, but the corresponding reactions of benzofuran complex **1** to the best of our knowledge has not been reported. We also report Dötz benzannulation studies with the sulfur analogue of **1**.

2. Results and discussion

The chromium Fischer carbene complex **5** of benzofuran was prepared in the standard way (Scheme 3).[18] We found the use of *t*-BuLi instead of *n*-BuLi avoided the formation of small quantities of [(butyl)methoxycarbene]pentacarbonyl–chromium impurity. Reaction with symmetrical and terminal acetylenes **6a-c** gave different results depending on whether solution or solid state conditions[19] were employed (Table 1). Good yields of simple dibenzofuran-1,4-diones were obtained from reaction in THF. The moderate yield with *t*-butylethyne (**6c**) highlights the sensitivity of the Dötz benzannulation to steric hindrance around the acetylene, no cyclobutenone products were detected. In reactions with terminal acetylenes **6b**+**c** only one regioisomeric product was observed. The regiochemistry of strutures **7b**,**c** were assigned (Scheme 3) based on extensive literature precedent[11] and was corroborated through the single crystal X-ray structure determination of **7c**.[20]

Treatment of **5** with alkynylboronic ester **6d**[21] under solution state conditions led to the dibenzofuran-1,4-dione boronic ester **7d** in 47% yield as a single regioisomer. The regiochemistry was assigned based on literature precedent[14] and by analogy to a similar product which was characterised by single crystal X-ray structure determination (**14**, vide supra). The mediocre yield of this reaction compared to those with terminal acetylenes **6a** and **6b** is due to the

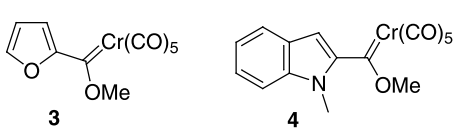
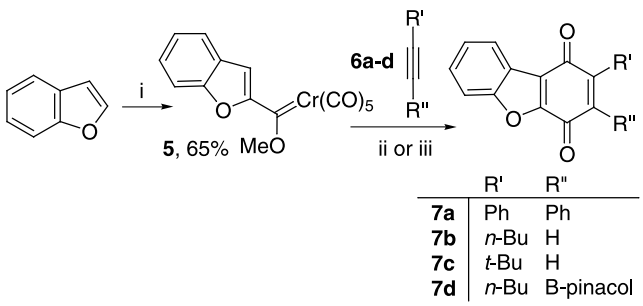


Figure 1.



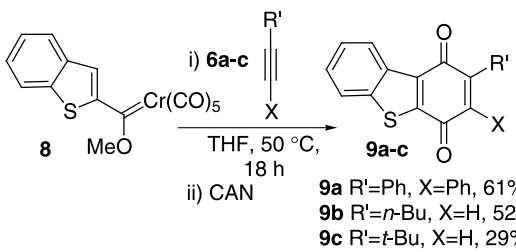
Scheme 3. Reagents: (i) *t*-BuLi; $Cr(CO)_6$, Et_2O; Me_3OBF_4, CH_2Cl_2; (ii) 0.05 M **5**, 2 equiv. **6**, THF, 50 °C, 18 h; 8 equiv. CAN, 0.5 M in 0.1 M HNO_3; (iii) 2 equiv. **6**, 10 g SiO_2 per mmol **6**, 50 °C, 3 h; 8 equiv. CAN, 0.5 M in 0.1 M HNO_3.

Table 1. Dötz benzannulation of **5** with **6a-d**

Product	Conditions	R′	R″	Yield (%)
7a	ii	Ph	Ph	81
7b	ii	*n*-Bu	H	71
7c	ii	*t*-Bu	H	41
7d	ii	*n*-Bu	B-pinacol	47
7a	iii	Ph	Ph	61
7b	iii	*n*-Bu	H	35
7c	iii	*t*-Bu	H	29

formation of 31% of the corresponding protodeboronated product of **7d** (R′=H). Evidence suggests that the substantial amount of protodeboronated product is formed via protodeboronation of the acid labile alkynylboronic acid by the acidic phenolic proton from the initial chromium arene complex formed from the Dötz reaction.[14] The terminal acetylene thus formed (**6b**) then reacts in preference to the alkynylboronic ester (**6d**) with **5**. It is interesting to note that a high level of protodeboronation has been noted by Harrity for the 2-furyl chromium Fischer carbene complex **3**.[14] This, coupled with our result, points towards this problem being characteristic of these types of furyl complexes or intermediates derived from them.

For comparison it was decided to prepare the analogous and novel sulfur containing Fischer carbene complex **8**, which was derived from benzothiophene as before in 69% yield. Reaction with the same set of acetylenes **6a-c** under solution state conditions gave slightly lower yields of benzannulated products **9a-c** (Eq. 1), but with the same trend in yields across the series. We assume the regioselectivity had proceeded in line with literature precedent and by analogy to the products from **5**.

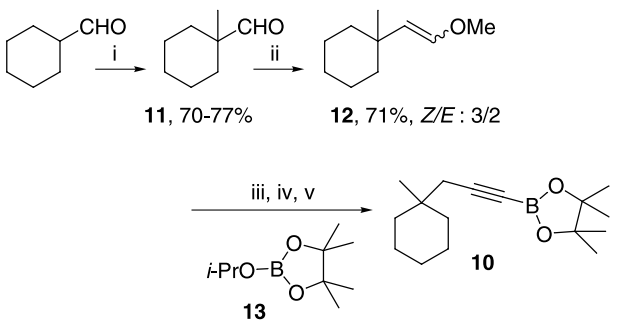


(1)

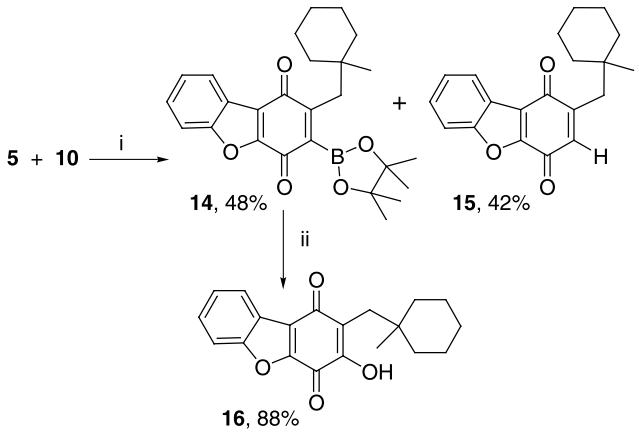
Having demonstrated that the Dötz benzannulation could be used for the regioselective synthesis of certain dibenzofuran-1,4-diones we turned our attention to model studies closer to the central dibenzofuran-1,4-dione core required for the synthesis of popolohuanone E. One of the difficult

bond constructions in the synthesis of this molecule and related members of this family is the formation of the aryl-*neo*-pentyl bond.[9,22] In the synthesis of model acetylene **10** we encountered a similar problem in the construction of the alkyne-*neo*-pentyl bond. This key bond was prepared through homologation of an aldehyde in order to avoid displacement reactions adjacent to the *neo*-pentyl centre. Methylation of the enolate of commercially available cyclohexane carboxaldehyde was not a trivial transformation and a variety of standard reaction conditions led to low yields, byproducts and difficulties upon scale up.[23] We reasoned that a base that was only sparingly soluble in the reaction solvent could minimise the formation of byproducts. After a series of optimisation experiments we found that a one pot procedure whereby the aldehyde was added to reagent grade KO*t*-Bu in CH_2Cl_2 at 0 °C followed by methyl iodide and warming to rt overnight led to **11** in 70–77% yield (Scheme 4). This procedure seems to be one of very few examples of the direct alkylation of the potassium enolates of secondary alkyl substituted aldehydes[24] and does not require pre-drying or purification of KO*t*-Bu or CH_2Cl_2. In order to simplify purification problems from using excess ylid, aldehyde **11** was added to 1 equiv. of (methoxymethyl)triphenylphosphoniumylide to give **12** in 67% yield. Hydrolysis of **12** (96%) was followed by Corey–Fuchs alkynation, quenching with boronic ester **13**,[25] to give the model alkynylboronic ester **10**.

Treatment of chromium Fischer carbene complex **5** with the model acetylene **10** initially gave low yields of desired product with substantial amounts of protodeboronated product. Optimisation of reaction conditions in line with Harrity's original observation that good yields of quinone products were formed using 3 equiv. of alkyne,[14] led to the isolation of dibenzofuran-1,4-dione boronic ester **14** as a single regioisomer in 48% yield along with 42% of protodeboronated product **15** (Scheme 5). The structure of **14** was verified by single crystal X-ray structure determination.[20] The yield was similar to that observed for the simpler system **7d**. Protodeboronation is reportedly due to the detrimental acidic proton from the phenolic reaction intermediate.[14] Wulff has isolated chromium arene (phenolic) intermediates from Dötz benzannulation reactions by conducting the reaction in the presence of TBDMS-Cl.[26] In an effort to sequester the detrimental proton from the reaction intermediate we conducted an identical benzannulation of **10** with **5** in the presence of TBDMS-Cl and *i*-Pr_2EtN. Analysis of the crude reaction mixture by ^{1}H



Scheme 4. Reagents: (i) KO*t*-Bu, MeI, CH_2Cl_2, 70–77%; (ii) $Ph_3P{=}CHOCH_3$, Et_2O, 71%; (iii) CF_3CO_2H, CH_2Cl_2, 96%; (iv) PPh_3, CBr_4, Zn, CH_2Cl_2, 77%; (v) *n*-BuLi, **13**; HCl, 65%.

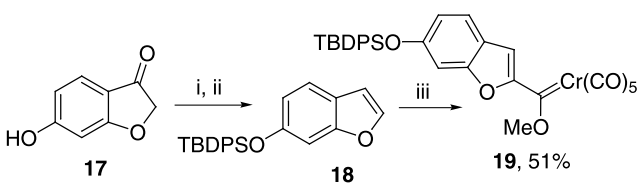


Scheme 5. Reagents: (i) 0.05 M **5**, 3 equiv. **10**, THF, 50 °C, 16 h; 8 equiv. CAN, 0.5 M in 0.1 M HNO_3; (ii) H_2O_2, Na_2CO_3, EtOH.

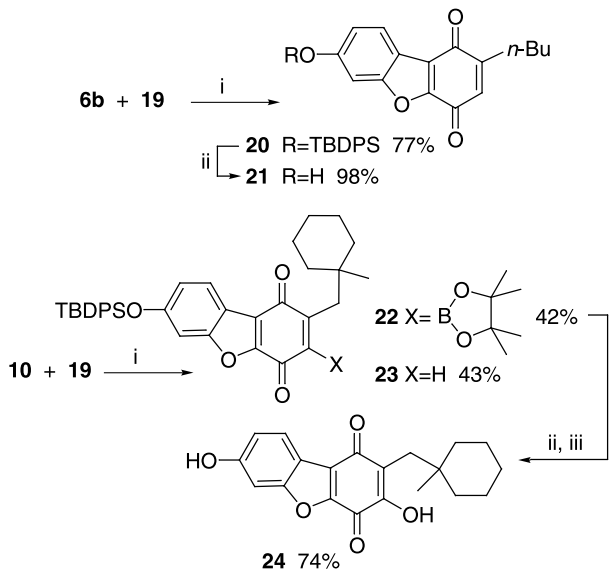
NMR revealed a ~1:1:1:1 mixture of silylated and unsilylated, boronated/protodeboronated products. Conducting a similar experiment in the presence of excess MeI and K_2CO_3 led to a similar distribution of products. These two attempts at trying to sequester the phenolic proton before protodeboronation of **10** did not alter the ratio of boronated to deboronated product probably because proton transfer will be much faster than protection of the phenolic hydroxyl group. Attempts at buffering reactions with heterogeneous and homogeneous bases were similarly ineffective. The boronic ester **14** was oxidised with basic hydrogen peroxide to give hydroxy dibenzofuran-1,4-dione **16** in 88% yield.

In a final study we wished to explore the reactivity of benzofuran chromium Fischer carbene complexes that bore oxygen substituents on the aryl ring as these would more closely mimic the types of dibenzofuran-1,4-diones needed for the synthesis of polopolohuanone E. Due to the lack of commercially available benzofurans[27] we opted to prepare complex **19**. Without conducting the actual synthesis of the popolohuanone E core, this complex would probe what effect this more influential oxy substituent would have on the reaction. The position of this particular oxygen substituent (along with that at C-5) allows participation in conjugation with the empty p-orbital of the carbene centre in addition to its *-I* effect. We wanted to determine the effect this substitution would have on the benzannulation reaction. Protection of the hydroxyl group of commercially available **17** as its TBDPS silyl ether (94%), followed by reduction with $NaBH_4$ and an acidic workup provided benzofuran **18** in 81% yield (Scheme 6). Formation of the chromium Fischer carbene as before gave the complex **19** in 51% yield.

Reaction of **19** with acetylene **6b** gave one regioisomeric



Scheme 6. Reagents: (i) *t*-$BuPh_2SiCl$, imidazole, CH_2Cl_2, 94%; (ii) $NaBH_4$, EtOH; 1 M HCl, 81%; (iii) *t*-BuLi; $Cr(CO)_6$, Et_2O; Me_3OBF_4, CH_2Cl_2, 51%.



Scheme 7. Reagents: (i) 0.05 M **19**, 3 equiv. **6b** or **10**, THF, 55 °C, 24 h; 8 equiv. CAN, 0.5 M in 0.1 M HNO_3; (ii) 5 equiv. HF·Py, THF, rt, 1.5 h; (iii) H_2O_2, Na_2CO_3, EtOH.

product **20** (Scheme 7) under solution or solid state conditions with the highest yield of 77% being obtained using solution state conditions. It is noteworthy that conjugation of the ether substituent reduces the reactivity of the carbene complex which is reflected in the longer reaction time required for consumption of **19** when compared to the identical reactions with **5** (~24 h versus ~16 h). The regiochemistry was assumed from previous experiments. Deprotection of the silyl group was quantitative with HF·Py complex giving **21** as a deep purple solid. The use of TBAF caused degradation, possibly due to ring opening of the furan ring by hydroxide ion, to give a deep purple coloured solution.[3a]

Benzannulation of model acetylene **10** with **19** gave the typical ratio (~1:1) of boronated **22** to protodeboronated product **23** in isolated yields of 42 and 43%, respectively. The sequential deprotection of the phenolic hydroxyl group followed by oxidation of the boronate ester proceeded smoothly to give **24** in 74% yield over the two steps as a dark purple solid.

3. Conclusion

The chromium Fischer carbene complexes of benzofuran and benzothiophene have been prepared and shown to be useful for the regioselective and convergent synthesis of dibenzofuran-1,4-dione heterocycles. The methodology works well for simple alkynes and although further substitution on the benzo-ring of the chromium Fischer carbenes would appear to be tolerated, the availability of the parent benzofurans may pose a limitation to the structural diversity of the products which would be easily available. With alkynyl boronate partners the synthesis of model systems of the tricyclic ring system of popolohuanone E can be accomplished after oxidation of the product arylboronate esters. It would appear that the combination of alkynyl boronates with furan type Fischer carbene complexes leads to substantial amounts (~50%) of protodeboronated products. Further use of this strategy for the synthesis of popolohuanone E is ongoing and will be reported in due course.

4. Experimental

4.1. General

Our general experimental details have been reported.[28]

4.1.1. [(2-Benzofuryl)methoxycarbene]pentacarbonylchromium (5). To a stirred solution of benzofuran (901 mg, 7.60 mmol) in Et_2O (20 mL) under argon at −78 °C was added *t*-butyl lithium (4.47 mL of a 1.70 M solution in pentane, 7.60 mmol) dropwise over 2 min. After 45 min the light yellow solution was added via cannula to a stirred suspension of $Cr(CO)_6$ (1.65 g, 7.60 mmol) in Et_2O at −78 °C. The reaction was then allowed to warm to rt over 1 h. After which time the solvent was removed from the dark red reaction mixture in vacuo affording a foamy dark red solid to which was added CH_2Cl_2 (20 mL) and Meerweins salt (1.46 g, 9.88 mmol, 1.3 equiv.) portionwise over 5 min. The reaction was then stirred vigorously for a further 20 min. After which time the blood red reaction mixture was washed with saturated $NaHCO_3$ (2×25 mL). The combined organics were then dried ($MgSO_4$) and filtered. The filter cake was washed with CH_2Cl_2 until white. The solvent was then removed in vacuo leaving a dark red solid. Purification by flash column chromatography (silica 10% EtOAc/pet. ether) gave a dark red metallic solid **5** (1.89 g 71%). Mp 110–111 °C. IR (solid) ν_{max} 2957, 2060, 1993, 1950, 1611, 1522, 1436, 1220 cm^{-1}; ^1H NMR (400 MHz) δ 4.93 (3H, s, OCH_3), 7.25 (1H, s, ArH), 7.30 (1H, t, J=7.2 Hz, ArH), 7.52 (1H, t, J=7.1 Hz, ArH), 7.65 (1H, d, J=8.1 Hz, ArH), 7.76 (1H, d, J=7.4 Hz, ArH); ^{13}C NMR (100 MHz) δ 66.4 (OCH_3), 106.7 (CH), 112.4 (CH), 124.3 (CH), 124.6 (CH), 127.2 (Cq), 129.0 (CH), 157.4 (Cq), 162.7 (Cq), 216.7 (CO), 224.4 (CO); *m/z* (EI^+) 352 (13%, M^+), 324 (31%, M^+-CO), 296 (20%, $M^+-(CO)_2$), 212 (100%, $M^+-(CO)_5$); HRMS $C_{15}H_8O_7^{52}Cr$ calcd 351.9675, found 351.9650. Anal. calcd for $C_{15}H_8O_7Cr$, C, 51.15; H, 2.29. Found C, 51.32; H, 2.52.

4.1.2. 2,3-Diphenyldibenzofuran-1-4-dione (7a). Representative solution state procedure. To a stirred solution of Fischer carbene **5** (86 mg, 0.24 mmol) in THF (2 mL) was added diphenylacetylene (**6a**, 85 mg, 0.48 mmol, 2.0 equiv.). The reaction was then heated to 50 °C for 18 h, after which time the black reaction mixture was concentrated in vacuo. The residue was diluted with Et_2O (2 mL) and aq. CAN (3.84 mL, 1.92 mmol, 8 equiv. of a 0.5 M soltn. in 0.1 M HNO_3) was added via syringe in one portion and the reaction was exposed to the air and stirred vigorously for 30 min. The organic layer was then separated and the aqueous layer extracted with Et_2O (2×2 mL). The combined organics were then washed with brine (5 mL) and dried ($MgSO_4$) and the solvent removed in vacuo to give a deep orange powdery solid. Purification by flash column chromatography (silica, 30% EtOAc/pet. ether) gave **7a** as a deep orange powder (63 mg, 81%).

Representative procedure for dry state conditions. To a stirred solution of Fischer carbene **5** (70 mg, 0.20 mmol) in Et_2O (1 mL) was added silica (4.0 g). After stirring for 5 min, the solvent was removed in vacuo. The flask was then purged with nitrogen and dipheynlacetylene (**6a**, 71 mg, 0.40 mmol, 2.0 equiv.) was added. The mixture was then heated at 50 °C for 3 h. After which time the cream solid was suspended in Et_2O (2 mL) and filtered. The filtrate was then treated with aq. CAN, worked up and purified as above to give **7a** as a deep orange powder (41 mg, 61%).

Mp >230 °C. IR (solid) ν_{max} 1662, 1567, 1482, 1312, 1114, 1096, 1060, 852 cm^{-1}; ^1H NMR (400 MHz) δ 7.08–7.10 (4H, m, phenyl), 7.22–7.26 (6H, m, phenyl), 7.50 (1H, t, J=7.2 Hz, ArH), 7.61 (1H, t, J=8.4 Hz, ArH), 7.72 (1H, d, J=8.1 Hz, ArH), 8.21 (1H, d, J=7.7 Hz, ArH); ^{13}C NMR (100 MHz) 113.0 (CH), 122.0 (Cq), 122.6 (Cq), 123.7 (CH), 126.2 (2×CH), 127.8 (CH), 127.8 (CH), 128.5 (CH), 128.5 (CH), 129.4 (CH), 130.8 (CH), 132.2 (Cq), 132.6 (Cq), 143.1 (Cq), 144.4 (Cq), 151.7 (Cq), 156.5 (Cq), 177.3 (CO), 183.4 (CO); HRMS $C_{24}H_{14}O_3$ calcd 350.0943, found 350.0935. Anal. calcd for $C_{24}H_{14}O_3$, C, 82.27; H, 4.03. Found C, 82.35; H, 3.88.

4.1.3. 2-Butyldibenzofuran-1,4-dione (7b). Purification by flash column chromatography (silica, 20% EtOAc/pet. ether) gave **7b** as a yellow solid, 66 mg, 71% by solution state and 45 mg, 35% by solid state. Mp 89–90 °C. IR (solid) ν_{max} 2960, 1660, 1602, 1572, 1318 cm^{-1}; ^1H NMR (400 MHz) δ 0.97 (2H, t, J=7.3 Hz, $CH_2CH_2CH_2CH_2$), 1.44 (2H, ap sex, J=7.3 Hz, $CH_2CH_2CH_2CH_2$), 1.57 (2H, ap quin J=7.5 Hz, $CH_2CH_2CH_2CH_2$), 2.57 (2H, td, J=7.7, 1.3 Hz, $CH_2CH_2CH_2CH_2$), 6.58 (1H, t, J=1.3 Hz, ArH), 7.31 (1H, t, J=7.8, 7.6 Hz, ArH), 7.55 (1H, t, J=8.4, 7.6 Hz, ArH), 7.67 (1H, d, J=8.4 Hz, ArH), 8.18 (1H, d, J=8.4 Hz, ArH); ^{13}C NMR (100 MHz) δ 13.9 (CH_3), 22.5 (CH_2), 28.8 (CH_2), 30.6 (CH_2), 112.9 (CH_2), 122.4 (Cq), 122.5 (Cq), 123.4 (CH), 126.0 (CH), 129.2 (CH), 131.4 (CH), 151.2 (Cq), 156.0 (Cq), 177.7 (CO), 183.8 (CO); m/z (EI^+) 254 (62%, M^+), 212 (100%, $M^+-C_3H_6$), 184 (27%, $M^+-C_4H_6O$); HRMS $C_{16}H_{14}O_3$ calcd 254.0943, found 254.0931.

4.1.4. 2-*t*-Butyldibenzofuran-1-4-dione (7c). Purification by flash column chromatography (silica, 20% EtOAc/pet. ether) gave **7c** as a yellow solid, 26 mg, 41% by solution state and 31 mg, 29% by solid state. Mp sublimed at 182 °C. IR (solid) ν_{max} 2971, 1660, 1750, 1124, 753 cm^{-1}; ^1H NMR (400 MHz) δ 1.40 (9H, s, $C(CH_3)_3$), 6.57 (1H, s, C3-H), 7.28 (1H, ddd, J=8.0, 7.0, 1.0 Hz, ArH), 7.55 (1H, ddd, J=8.4, 7.2, 1.3 Hz, ArH), 7.67 (1H, d, J=7.7 Hz, ArH), 8.20 (1H, d, J=8.0 Hz, ArH). ^{13}C NMR (100 MHz) δ 29.8 (CH_3), 35.8 (Cq), 112.9 (CH), 122.9 (Cq), 123.5 (Cq), 126.0 (CH), 129.2 (CH), 130.8 (CH), 151.2 (Cq), 156.2 (Cq), 157.3 (Cq), 178.0 (C=O), 184.0 (C=O); m/z (EI^+) 254 (100%, M^+), 198 (17%, $M^+-(CH_3)_3$); HRMS $C_{16}H_{14}O_3$ calcd 254.0943, found 254.0951.

4.1.5. 2-Butyl-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)dibenzofuran-1-4-dione (7d). Purification by flash column chromatography (silica, 10% EtOAc/pet. ether) gave **7d** as dark yellow needles (32 mg, 47%) and **7b** a yellow solid (14 mg, 31%). Data for **7d**. Mp 127–129 °C. IR (solid) ν_{max} 2970, 1658, 1574, 1372, 1138, 753 cm^{-1}; ^1H NMR (400 MHz) δ 0.96 (3H, t, J=7.3 Hz, $CH_2CH_2CH_2CH_3$), 1.48 (9H, s, ^{t}Bu), 1.44–1.57 (4H, m, $CH_2CH_2CH_2CH_3$), 2.58 (2H, t, J=7.2 Hz, $CH_2CH_2CH_2CH_3$), 7.46 (1H, t, J=7.6 Hz, ArH), 7.53 (1H, t, J=7.8 Hz, ArH), 7.65 (1H, d, J=8.4 Hz, ArH), 8.17 (1H, d, J=8.4 Hz, ArH); ^{13}C NMR (100 MHz) δ 14.0 (CH_3), 23.3 (CH_2), 24.89 (CH_3), 29.9 (CH_2), 32.8 (CH_2), 85.2 (Cq), 112.9 (CH), 121.9 (Cq), 122.6 (Cq), 123.4 (CH), 125.9 (CH), 129.9 (CH), 152.1 (Cq), 155.3 (Cq), 155.9 (Cq), 180.6 (CO), 183.7 (CO); m/z (EI^+) 380 (75%, M^+), 323 (71%, $M^+-CH_2CH_2CH_2CH_3$); HRMS $C_{22}H_{25}BO_5$ calcd 380.1795, found 380.1796. Anal. calcd for $C_{22}H_{25}BO_5$, C, 69.49; H 6.63. Found C, 69.36; H, 6.47.

4.1.6. [(2-Benzothiophene)methoxycarbene]pentacarbonylchromium (8). Prepared in an identical manner to **5**. Purification by flash column chromatography (silica 10% EtOAc/pet. ether) gave a dark red metallic solid (1.44 g 69%). Mp 114–115 °C. IR (solid) ν_{max} 2051, 1984, 1904, 1500, 1208, 1157; ^1H NMR (400 MHz) δ 4.92 (3H, s, OCH_3), 7.43 (1H, t, J=7.5 Hz, ArH), 7.49, (1H, t, J=7.1 Hz, ArH), 7.82 (1H, d, J=7.9 Hz, ArH), 8.00 (1H, d, J=8.0 Hz, ArH), 8.71 (1H, s, ArH); ^{13}C NMR (100 MHz) δ 66.7 (CH_3), 122.9 (CH), 125.2 (CH), 126.8 (CH), 129.0 (CH), 139.2 (CH), 142.0 (Cq), 153.8 (Cq), 217.0 (C≡O), 223.4 (C≡O); m/z (EI^+) 339 ($M^+-(CO)$), 283 ($M^+-(CO)_3$), 227 ($M^+-(CO)_5$); HRMS $C_{15}H_8O_6^{52}CrS$ calcd 367.9447, found 367.9441. Anal. calcd for $C_{15}H_8O_6CrS$, C, 48.92; H 2.19. Found C, 49.25; H, 2.21.

4.1.7. 2,3-Diphenyldibenzothiophene-1-4-dione (9a). Prepared using solution state method. Purification by flash column chromatography (silica 30% EtOAc/pet. ether) gave **9a** as a deep orange powder (77 mg, 61%). Mp >230 °C. IR (solid) ν_{max} 1654, 1601, 1463, 1382, 1090, 944 cm^{-1}; ^1H NMR (400 MHz) δ 7.18 (4H, m, phenyl), 7.23 (6H, m, phenyl), 7.65 (2H, m, ArH), 8.04 (1H, d, J=7.0 Hz, ArH), 8.85 (1H, d, J=6.5 Hz, ArH); ^{13}C NMR (125 MHz) δ 123.07 (CH), 126.97 (CH), 127.29 (CH), 127.77 (CH), 128.21 (CH), 128.42 (CH), 132.66 (Cq), 133.05 (Cq), 133.62 (Cq), 136.18 (Cq), 142.04 (Cq, 144.30 (Cq), 145.55 (Cq), 181.55 (C≡O), 182.27 (C≡O); m/z (EI^+) 366 (100%, M^+); HRMS $C_{24}H_{14}O_2S$ calcd 366.0711, found 366.0717.

4.1.8. 2-Butyldibenzothiophene-1,4-dione (9b). Prepared using solution state method. Purification by flash column chromatography (silica 20% EtOAc/pet. ether) gave **9b** as orange needles (63 mg, 52%). Mp 86–87 °C. IR (solid) ν_{max} 2959, 1613, 1463, 1332, 1293, 1082, 890 cm^{-1}; ^1H NMR (400 MHz) δ 0.98 (3H, t, J=7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.45 (2H, sex, J=7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.69 (2H, quin, J=7.1 Hz, $CH_2CH_2CH_2CH_3$), 2.57 (2H, td, J=7.0 Hz, 1.2, $CH_2CH_2CH_2CH_3$), 6.85 (1H, t, J=1.3 Hz, ArH), 7.52–7.55 (2H, m, ArH), 7.92 (1H, d, J=7.2 Hz, ArH), 8.75 (1H, d, J=7.1 Hz, ArH); ^{13}C NMR (100 MHz) δ 13.9 (CH_3), 22.6 (CH_2), 29.0 (CH_2), 30.5 (CH_2), 123.1 (CH), 125.5 (CH), 127.4 (CH), 128.0 (CH), 132.8 (CH), 133.9 (Cq), 135.1 (Cq), 141.5 (Cq), 145.5 (Cq), 152.1 (Cq), 182.0 (C≡O), 182.5 (C≡O); m/z (EI^+) 270 (100%, M^+), 241 (21%, $M^+-CH_2CH_3$), 228 (96%, $M^+-CH_2CH_2CH_3$); HRMS $C_{16}H_{13}O_2S$ calcd 270.0714, found 270.0709.

4.1.9. 2-*t*-Butyldibenzothiophene-1,4-dione (9c). Prepared using solution state method. Purification by flash column chromatography (silica 10% EtOAc/pet. ether) gave **9c** as a dark yellow needles (20 mg, 29%). Mp 172–174 °C. IR (solid) ν_{max} 2965, 2358, 1726, 1654, 1521, 1459, 1094, 749 cm^{-1}; ^1H NMR (400 MHz) δ 1.41 (9H, s, ^{t}Bu), 6.75 (1H, s, ArH), 7.52–7.57 (2H, m, ArH), 7.92 (1H, d, J=8.0 Hz, ArH), 8.81 (1H, d, J=7.8 Hz, ArH); ^{13}C NMR (100 MHz) δ 29.8 (CH_3), 35.9 (Cq), 123.1 (CH), 126.8 (CH), 127.1 (CH), 128.0 (CH), 132.1 (CH), 135.1 (Cq)136.4 (Cq), 141.7 (Cq), 144.3 (Cq), 158.4 (Cq), 182.5 (Cq), 182.8 (Cq); *m/z* (EI^+) 270 (100%, M^+), 213 (21% $M^+-{}^t$Bu); HRMS $C_{16}H_{14}O_2S$ calcd 270.0714, found 270.0703.

4.1.10. 1-Methylcyclohexanecarboxaldehyde (11). To a well stirred solution of cyclohexylcarboxaldehyde (15.0 g, 133 mmol) in CH_2Cl_2 (665 mL) at 0 °C was added KO^{t}Bu (19.4 g, 172 mmol, 1.30 equiv.) in one portion followed by MeI (25.0 mL, 399 mmol, 3.0 equiv.) in one portion. After 30 min the cloudy reaction mixture was brought to rt and stirred for a further 1.5 h. The reaction mixture was then poured into brine (500 mL) and the layers were separated. The organic layer was then dried ($MgSO_4$) and the solvent removed in vacuo affording a light yellow oil. Purification by a silica plug eluting with petrol gave a colourless oil (13.9 g, 81%). IR ($CHCl_3$) ν_{max} 2905, 2852, 1714 cm^{-1}; ^1H NMR (400 MHz) δ 1.00 (3H, s, CH_3), 1.23–1.33 (2H, m, Cy), 1.33–1.45 (2H, m, Cy), 1.45–1.54 (2H, m, Cy), 1.54–1.63 (2H, m, Cy), 1.80–1.88 (2H, m, Cy), 9.44 (1H, s, CHO)); ^{13}C NMR (67.8 MHz) δ 21.7 (CH_3), 22.4 (CH_2), 25.5 (CH_2), 32.4 (CH_2), 46.2 (Cq), 206.7 (CHO); *m/z* (EI^+) 126 (5%, M^+), 97 (80%, M^+-CHO); HRMS $C_8H_{14}O$ calcd 126.1045, found 126.1050.

4.1.11. 1-(2-Methoxyvinyl)-1-methylcyclohexane (12). To a well stirred suspension of methoxymethylphosphonium chloride (15.7 g, 38.7 mmol) in Et_2O (175 mL) at 0 °C was added KO^{t}Bu (4.33 g, 38.7 mmol, 1.30 equiv.) in one portion. The reaction was then stirred at 0 °C for 45 min. After which time **11** (4.47 g, 35.2 mmol, 1.0 equiv.) was added as a solution in Et_2O (10 mL+5 mL wash) via cannula to the deep red coloured reaction mixture. After 1 h the now chalky coloured reaction mixture was poured into brine (200 mL) and the organic layer was separated and washed again with brine (100 mL). The organic layer was then dried ($MgSO_4$) and concentrated in vacuo. Purification by flash column chromatography (silica, 5% EtOAc/pet. ether) afforded a colourless oil (3.56 g, 71%, 3:2, *Z*:*E* by ^1H NMR). The mixture of geometric isomers was not separated and used directly in the next reaction.

A small sample was partially separated on silica (hexane) and gave in order of elution, *Z*-isomer. IR ($CHCl_3$) ν_{max} 2903, 2851, 1652, 1456, 1103 cm^{-1}; ^1H NMR (400 MHz) δ 0.98 (3H, s, CH_3), 1.21–1.82 (10H, m, Cy), 3.53 (3H, s, OCH_3), 4.13 (1H, d, J=7.1 Hz, CHC*H*O), 5.77 (1H, d, J=7.1 Hz, C*H*CHO); ^{13}C NMR (67.8 MHz) δ 23.0 (CH_2), 26.3 (CH_2), 28.6 (CH_3), 35.2 (Cq), 38.9 (CH_2), 59.5 (OCH_3), 114.9 (CH*C*HO), 145.2 (*C*HCHO).

E-isomer. IR ($CHCl_3$) ν_{max} 2914, 2854, 1650, 1455, 1104 cm^{-1}; ^1H NMR (400 MHz) δ 0.97 (3H, s, CH_3), 1.10–1.52 (10H, m, Cy), 3.51 (3H, s, OCH_3), 4.78 (1H, d, J=12.9 Hz, CHC*H*O), 6.22(1H, d, J=12.9 Hz, C*H*CHO); ^{13}C NMR (125 MHz) δ 22.4 (CH_2), 26.4 (CH_2), 28.5 (CH_3), 33.5 (Cq), 39.0 (CH_2), 56.0 (OCH_3), 114.2 (CH), 145.6 (CH); *m/z* (EI^+) 154 (2%, M^+), 96 (98%, CH_7CH_{12}); HRMS $C_{10}H_{18}O$ calcd 154.1358, found 154.1359.

4.1.12. 4,4,5,5-Tetramethyl-2-[3-(1-methylcyclohexyl)-prop-1-ynyl]-[1,3,2]-dioxaborolane (10). To a solution of **12** (2.81 g, 18.0 mmol) in CH_2Cl_2 (90 mL) at 0 °C was added TFA (5.54 mL, 72 mmol, 4 equiv.). After 1 h the reaction was brought to rt and stirred for a further 30 min. Saturated aq. $NaHCO_3$ (50 mL) was then added and stirring continued until effervescence ceased. The aqueous layer was then separated and extracted with CH_2Cl_2 (50 mL). The combined organics were then washed with brine (40 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to give a pale yellow liquid, which was purified by flash column chromatography (silica 10% EtOAc/pet. ether) to afford the homologated aldehyde as a colourless liquid (2.35, 92%). Spectroscopic data was identical to the literature.[29]

To a stirred suspension of Ph_3P (10.5 g, 40.0 mmol, 2.0 equiv.) and Zn dust (2.61 g, 40.0 mmol, 2.0 equiv.) in CH_2Cl_2 (90 mL) at 0 °C was added CBr_4 (13.3 g, 40.0 mmol, 2.0 equiv.). The reaction was warmed to rt and stirred for a further 15 h. The homologated aldehyde from above (2.83 g, 20.0 mmol, 1.0 equiv.) was added to the purple solution via cannula as a solution in CH_2Cl_2 (5 mL+3 mL wash). After 1 h the reaction was concentrated in vacuo to give a dark purple foam which was suspended in CH_2Cl_2 (5 mL) and extracted with petrol (5×15 mL). The resulting cream solution was concentrated in vacuo and purified immediately by flash column chromatography (neutral alumina, pet. ether) and the vicinal vinyl dibromide was obtained as a colourless liquid (4.49 g, 78%), which was stored under nitrogen, protected from light and in a freezer to avoid decomposition. IR ($CHCl_3$) ν_{max} 2925, 2847, 1613, 1449 cm^{-1}; ^1H NMR (400 MHz) δ 0.91 (3H, s, CH_3), 1.20–1.38 (5H, m, Cy), 1.38–1.52 (5H, m, Cy), 2.04 (2H, d, J=7.6 Hz, CH_2CHCBr$_2$), 6.43 (1H, t, J=7.6 Hz, CH$_2$C*H*CBr$_2$); ^{13}C NMR (100 MHz) δ 22.1 (CH_2), 25.1 (CH_3) 26.2 (CH_2), 34.0 (Cq), 37.6 (CH_2), 45.1 (*C*H$_2$CHBr$_2$), 89.0 (CH$_2$*C*HCBr$_2$); *m/z* (EI^+) 295 (3%, M^+), 215 (5%, $C_4H_5^{81}Br_2$), 213 (10%, $C_4H_5^{79}Br^{81}Br$), 211 (5%, $C_4H_5^{79}Br_2$), 97 (100%, C_7H_{13}); HRMS $C_{10}H_{15}^{79}Br^{81}Br$ calcd 294.9520, found 294.9520. Anal. calcd for $C_{10}H_{16}Br_2$, C, 40.57; H, 5.45. Found C, 40.68; H, 5.37.

To a stirred solution of the vicinal vinyl dibromide from above (1.09 g, 3.61 mmol) in Et_2O (15 mL) at −78 °C was added *n*-butyl lithium (3.11 mL of a 2.35 M solution in hexanes, 7.32 mmol, 2.0 equiv.) dropwise over 2 min under an atmosphere of argon. After 1 h the resultant light yellow solution was added to a solution of boronic ester **13**[24] (504 mg, 3.66 mmol 1 equiv.) in Et_2O (2 mL) at −78 °C via cannula over 5 min. The reaction was stirred for 3 h at −78 °C. After which time anhydrous HCl (8.06 mL of a 2.35 M solution in Et_2O, 40.3 mmol, 1 equiv.) was added to the reaction mixture which contained a voluminous white precipitate and the reaction mixture was warmed to rt over 1 h. The reaction was then concentrated in vacuo. The resultant pale orange liquid was filtered through a celite pad.

The filtrate was then concentrated in vacuo to give a colourless liquid which was distilled at reduced pressure (142–143 °C at 0.1 mm/Hg) to give a colourless liquid which immediately solidified to give **10** as a colourless solid (591 mg, 68%). Mp 58 °C. IR ($CHCl_3$) ν_{max} 2980, 2854, 2204, 1449, 1382, 1343 cm^{-1}; ^1H NMR (500 MHz) δ 0.98 (3H, s, CH_3), 1.23–1.58 (10H, m, Cy), 1.28 (12H, s, $((CH_3)_2CC(CH_3)_2)$, 2.19 (2H, s, CH_2CC); ^{13}C NMR (125 MHz) δ 22.1 (CH_2), 24.6 (CH_3), 24.9 (CH_3), 26.2 (CH_2), 32.7 (CH_2), 33.4 (Cq), 37.1 (CH_2), 83.2 (C≡C), 84.1 (Cq), 103.0 (C≡C); *m/z* (EI^+) 262 (3%, M^+), 166 (17%, $M^+-C_7H_{12}$), 151 (33%, $M^+-C_8H_{15}$); HRMS $C_{16}H_{27}BO_2$ calcd 262.2104, found 262.2111.

4.1.13. 2-(1-Methylcyclohexylmethyl)-3-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)dibenzofuran-1,4-dione (14) and 2-(1-methylcyclohexylmethyl)dibenzofuran-1,4-dione (15). To a stirred solution of Fischer carbene **5** (35 mg, 0.10 mmol, azeotroped from PhMe) in THF (1.9 mL) was added acetylene **10** (80 mg, 0.30 mmol, 3 equiv., azeotroped from PhMe) and the reaction performed in an identical manner to **7a** to give a crude yellow solid. Purification by flash column chromatography (silica, 10% EtOAc/pet. ether) afforded, in order of elution: **15** as yellow needles (13 mg, 42%). Mp 191–192 °C. IR ($CHCl_3$) ν_{max} 2928, 2851, 1665, 1570, 1446, 1374, 1313, 1142 cm^{-1}; ^1H NMR (400 MHz) δ 0.91 (3H, s, CH_3), 1.15–1.62 (10H, m, Cy), 2.52 (2H, s, CH_2Cy), 6.58 (1H, s, Ar), 7.47 (1H, m, Ar), 7.55 (1H, m, Ar), 7.66 (1H, d, *J*=8.4 Hz, Ar), 8.19 (1H, d, *J*=7.6 Hz, Ar); ^{13}C NMR (125 MHz) δ 22.1 (CH_2), 24.7 (CH_3), 26.3 (CH_2), 35.2 (CH_2), 38.0 (CH_2), 40.0 (Cq), 112.9 (CH), 122.3 (Cq), 122.7 (Cq), 123.5 (CH), 126.0 (CH), 129.2 (CH), 134.1 (CH), 148.4 (Cq), 151.8 (Cq), 156.1 (Cq), 177.4 (CO), 184.0 (CO); *m/z* (EI^+) 308 (14%, M^+), 212 (100%, $M^+-C_7H_{12}$), 97 (52%, C_7H_{13}); HRMS $C_{20}H_{20}O_3$ calcd 308.1412, found 308.1402.

Compound **14** as yellow needles (22 mg, 48%). Mp 191–192 °C. IR (solid) ν_{max} 2931, 1657, 1602, 1348, 1141 cm^{-1}; ^1H NMR (500 MHz) δ 0.97 (3H, s, $CyCH_3$), 1.39–1.41 (6H, m, Cy), 1.50 (12H, s, $(CH_3)_2CC(CH_3)_3$), 1.60–1.69 (4H, m, Cy), 2.69 (2H, s, CH_2), 7.54 (1H, t, *J*=7.7 Hz, ArH), 7.60 (1H, t, *J*=7.6 Hz, ArH), 7.72 (1H, d, *J*=8.4 Hz, ArH), 8.26 (1H, d, *J*=7.7 Hz, ArH); ^{13}C NMR (125 MHz) δ 22.3 (CH_2), 24.9 (CH_3), 25.1 (CH_3), 26.4 (CH_2), 85.1 (Cq), 113.0 (CH), 122.0 (Cq), 122.7 (Cq), 123.5 (CH), 125.8 (CH), 128.9 (CH), 152.0 (Cq), 153.7 (Cq), 156.0 (Cq), 180.3 (C=O), 184.4 (C=O); *m/z* (EI^+) 434 (5%, M^+), 338 (100%, $M^+-C_7H_{12}$), 97 (52%, C_7H_{13}); HRMS $C_{26}H_{31}^{11}BO_5$ calcd 434.2264, found 434.2281.

4.1.14. 3-Hydroxy-2-(1-methylcyclohexylmethyl)dibenzofuran-1,4-dione (16). To a stirred solution of quinone **14** (28 mg, 0.06 mmol) in EtOH (2.4 mL) was added excess H_2O_2 (2.4 mL of a 30% aq. soltn.) followed by solid Na_2CO_3 (6 mg, 0.06 mmol). The reaction mixture was allowed to stir at rt for 30 min. After this time H_2O (10 mL) was added to the dark blue reaction. The product was extracted with CH_2Cl_2 (2×3 mL) the combined organics were then washed with brine (5 mL) and dried ($MgSO_4$) and the solvent removed in vacuo. Purification by flash chromatography (silica 20% EtOAc/hex) afforded **16** as a dark red solid (17 mg, 88%). Mp 162–164 °C. IR ($CHCl_3$) ν_{max} 3422, 3156, 2927, 2855, 2253, 1794, 1672, 1650, 1571, 1461, 1381, 1348, 1319, 1265, 1094, 895 cm^{-1}; ^1H NMR (500 MHz) δ 0.93 (3H, s, $CyCH_3$), 1.26–1.57 (10H, m, Cy), 2.53 (2H, s, CH_2), 7.47 (1H, t, *J*=8.2 Hz, ArH), 7.57 (1H, t, *J*=8.5 Hz, ArH), 7.64 (1H, d, *J*=8.5 Hz, ArH), 8.20 (1H, d, ArH); ^{13}C NMR (500 MHz) δ 22.3 (CH_2, CH_3), 26.4 (CH_2), 33.52 (Cq), 35.5 (CH_2), 38.50 (CH_2), 112.9 (CH), 119.8 (Cq), 124.1 (CH), 124.5 (Cq), 126.2 (CH), 149.0 (Cq), 152.7 (Cq), 157.3 (Cq), 172.7 (C=O), 184.1 (C=O); *m/z* (EI^+) 324 (25%, M^+), 228 (73%, $C_{13}H_8O_4$), 97 (100%, C_7H_{13}); HRMS $C_{20}H_{20}O_4$ calcd 324.1362, found 324.1346.

4.1.15. 6-*t*-Butyldiphenylsilyloxybenzofuran (18). To a stirred solution of alcohol **17** (624 mg, 4.14 mmol) in CH_2Cl_2 (20 mL) was added *t*-butyldiphenylsilylchloride (1.14 g, 4.14 mmol) and imidazole (281 mg, 4.14 mmol). The reaction was then left to stir for 18 h at rt. After which time the reaction was poured into brine (30 mL) and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined organics were dried ($MgSO_4$) and the solvent removed in vacuo. Purification by column chromatography (silica, 10% EtOAc/pet. ether) gave silyl protected **17** as a white solid (1.52 g, 94%). Mp 100 °C. IR ($CHCl_3$) ν_{max} 2933, 2860, 1763, 1612, 1449, 1324, 1149, 1106, 1006, 956 cm^{-1}; ^1H NMR (400 MHz) δ 1.12 (9H, s, $(CH_3)_3$), 4.53 (2H, s, CH_2), 6.40 (1H, d, *J*=2.0 Hz, ArH), 6.55 (1H, dd, *J*=8.3, 1.8 Hz, ArH), 7.9–7.47 (7H, m, phenyl, ArH), 7.7 (4H, m, phenyl); ^{13}C NMR (100 MHz) δ 26.38 (CH_3), 60.48 (Cq), 75.38 (CH_2), 103.74 (CH), 114.99 (Cq), 115.91 (CH), 124.97 (CH), 128.95 (CH), 130.43 (CH), 131.64 (Cq), 135.42 (CH), 164.65 (Cq), 175.86 (Cq), 197.88 (C=O); *m/z* (EI^+) HRMS $C_{24}H_{24}O_3Si$ calcd 388.1495, found 388.1477. Anal. calcd for $C_{24}H_{24}O_3Si$, C, 74.19; H, 6.23. Found C, 74.49; H, 6.08.

To a stirred solution of silyl protected **17** from above (980 mg, 2.52 mmol) in EtOH (12 mL) was added $NaBH_4$ (48 mg, 1.26 mmol, 0.5 equiv.) portionwise over 5 min. The reaction was then stirred at rt for 1 h. After which time 1 M HCl (10 mL) was added. The product was extracted with Et_2O (2×10 mL) and the organics washed with brine (15 mL). The combined organics were then dried ($MgSO_4$) and the solvent removed in vacuo. Purification by column chromatography (silica, 20% EtOAc/pet. ether) gave the benzofuran **18** (759 mg, 81%) as a colourless viscous oil. IR ($CHCl_3$) ν_{max} 2933, 2894, 1619, 1589, 1291, 1154, 1106, 1103, 966 cm^{-1}; ^1H NMR (400 MHz) δ 1.18 (9H, s, $(CH_3)_3$), 6.67 (1H, d, *J*=2.2 Hz, ArH), 6.88 (1H, dd, *J*=8.5, 2.2 Hz, ArH), 7.01 (1H, s, ArH), 7.42–7.81 (7H, m, phenyl, ArH), 7.85 (4H, m, phenyl); ^{13}C NMR (400 MHz) δ 19.59 (Cq), 26.64 (CH_3), 102.71 (CH), 106.34 (CH), 116.23 (CH), 120.76 (CH), 121.76 (CH), 127.88 (CH), 127.88 (CH), 130.01 (CH), 132.93 (Cq), 135.63 (CH), 144.18 (CH), 153 (Cq), 155.58 (Cq); *m/z* (EI^+) 372 (51%, M^+), 315 (100%, $M^+-{}^tBu$); HRMS $C_{24}H_{24}O_2Si$ calcd 372.1554, found 372.1546.

4.1.16. [(2-(6-*t*-Butyldiphenylsilyloxybenzofuryl))-methoxycarbene]pentacarbonylchromium (19). Prepared in an identical manner to **5**. Purification by flash column chromatography (silica 7% EtOAc/pet. ether) followed by recrystallisation from petrol gave **19** as dark red plates (615 mg, 55%). Mp >230 °C. IR ($CHCl_3$) ν_{max} 2055, 1988, 1620, 1493, 1257, 1204, 1166, 1121, 990 cm^{-1}; ^1H NMR (400 MHz) δ 1.13 (9H, s, $(CH_3)_3$), 4.84 (3H, s, OCH_3), 6.77

(1H, dd, *J*=8.7, 2.1 Hz, ArH), 6.94 (1H, br s, ArH), 7.27 (1H, d, *J*=5.7 Hz, ArH), 7.38–7.54 (7H, m, phenyl, ArH), 7.75 (4H, d, *J*=7.3 Hz, phenyl); ^{13}C NMR (100 MHz) δ 19.91 (Cq), 26.85 (CH_3), 66.49 (CH_3), 103.17 (CH), 111.10 (Cq), 119.17 (CH), 121.68 (Cq), 130.60 (CH), 132.50 (CH), 135.87 (CH), 158.26 (Cq), 158.68 (Cq), 163.13 (Cq), 217.26 (C≡O), 224.57 (C≡O); *m/z* meaningful data could not be obtained. Anal. calcd for $C_{31}H_{28}OSiCr$, C, 60.48; H, 4.32. Found C, 60.86; H, 4.37.

4.1.17. 2-Butyl-7-(*t*-Butyldiphenylsilyloxy)dibenzofuran-1,4-dione (20). To a stirred solution of Fischer carbene **19** (100 mg, 0.16 mmol) in THF (3 mL) was added acetylene **6b** (0.035 mL, 0.37 mmol, 2.0 equiv.) and the reaction performed in an identical manner to **7a**, but heated for 24 h, to give an orange solid. Purification by flash column chromatography (silica, 10% EtOAc/pet. ether) gave **20** as a yellow solid (64 mg, 55%). Mp >230 °C; ν_{max} ($CHCl_3$) 2399, 1662, 1602, 1521, 1424, 1232, 1016, 927 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.95 (3H, t, *J*=7.2 Hz, $CH_2CH_2CH_2$-CH_3), 1.14 (9H, s, $(CH_3)_3$); 1.42 (2H, sext, *J*=7.3 Hz, $CH_2CH_2CH_2CH_3$), 1.50 (2H, quin. *J*=7.3 Hz, CH_2CH_2-CH_2CH_3), 2.50 (1H, td, *J*=7.1, 1.1 Hz, $CH_2CH_2CH_2CH_3$), 6.47 (1H, t, *J*=1.1 Hz, ArH), 7.01 (1H, dd, *J*=8.9, 2.1 Hz, ArH), 7.37–7.45 (6H, m, phenyl), 7.71 (4H, d, *J*=7.2 Hz, phenyl), 7.88 (1H, d, *J*=8.7 Hz, ArH); ^{13}C NMR (400 MHz) δ 13.9 (CH_3), 19.6 (Cq), 22.51 (CH_2), 26.5 (CH_3), 28.8 (CH_2), 30.6 (CH_2), 103.5 (CH), 116.3 (Cq), 120.3 (CH), 122.6 (Cq), 123.4 (CH), 128.1 (CH), 130.4 (CH), 131.3 (CH), 132.0 (Cq), 135.5 (CH), 150.4 (Cq), 151.4 (Cq), 157.2 (Cq), 157.5 (Cq), 177.2 (C═O), 184.1 (C═O); *m/z* (EI^+) HRMS $C_{32}H_{32}O_4Si$ calcd 508.2070, found 508.2071.

4.1.18. 2-Butyl-7-hydroxydibenzofuran-1,4-dione (21). To a stirred solution of silyl ether **20** (13 mg, 0.025 mmol) in THF (0.1 mL) was added HF·py (1.7 μL of a ~70% soltn. of HF in pyridine, 0.025 mmol). The reaction was stirred at rt for 1.5 h after which time satd. aq. $NaHCO_3$ (2 mL) was added. The organic layer was separated and the aqueous layer extracted with Et_2O (3×1 mL). The combined organics were then washed with brine (3 mL) and dried ($MgSO_4$). Purification by flash column chromatography (silica, 30% EtOAc/pet. ether) afforded a dark purple solid (6.5 mg, 97%). Mp 170–171 °C. IR ($CHCl_3$) ν_{max} 3685, 3156, 3012, 1974, 1661, 1571, 1097, 945, 897 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.97 (3H, t, *J*=7.3 Hz, $CH_2CH_2CH_2CH_3$), 1.44 (2H, sex, *J*=7.0 Hz, $CH_2CH_2CH_2CH_3$), 1.54, (2H, quin. *J*=7.3 Hz, $CH_2CH_2CH_2CH_3$), 2.54 (2H, td, *J*=7.6, 1.0 Hz, $CH_2CH_2CH_2CH_3$), 6.53, (1H, t, *J*=1.4 Hz, ArH), 7.02 (1H, dd, *J*=8.6, 2.1 Hz, ArH), 7.13 (1H, d, *J*=2.4 Hz, ArH), 8.01 (1H, d, *J*=8.8 Hz); ^{13}C NMR (100 MHz) δ 13.9 (CH_3), 22.5 (CH_3), 28.8 (CH_3), 30.6 (CH_3), 99.2 (CH), 115.0 (Cq), 116.1 (CH), 122.8 (Cq), 124.1 (CH), 131.4 (CH), 150.5 (Cq), 151.3 (Cq), 157.6 (Cq), 157.7 (Cq), 177.4 (CO), 184.1 (CO); *m/z* (EI^+) 270 (100%, M^+), 228 (83%, $M^+-CH_2CH_2CH_3$), 213 (28%, $M^+-CH_2CH_2CH_2CH_3$); HRMS $C_{16}H_{14}O_4$ calcd 270.0892, found 270.0895.

4.1.19. 7-(*t*-Butyldiphenylsilyloxy)-2-(1-methylcyclohexylmethyl)-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)dibenzofuran-1,4-dione (22) and 7-(*t*-butyldiphenylsilyloxy)-2-(1-methylcyclohexylmethyl)dibenzofuran-1,4-dione (23). To a stirred solution of Fischer carbene **19** (74 mg, 0.12 mmol, azeotroped from PhMe) in THF (2 mL) was added acetylene **10** (95 mg, 0.36 mmol, 3 equiv., azeotroped from PhMe) and the reaction performed in an identical manner to **7a**, but heated for 24 h, to give a dark orange oil. Purification by flash column chromatography (silica, 30% EtOAc/pet. ether) gave, in order of elution, **23** (22 mg, 43%) as a dark orange viscous oil. IR ($CHCl_3$) ν_{max} 2927, 2873, 1662, 1621, 1562, 1199, 987, 822 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.87 (3H, s, CH_3 cHexyl), 1.14 (9H, s, CH_3, ^{t}Bu), 1.29–1.56 (10H, m, cHexyl), 2.47, (2H, CH_2 cHexyl), 6.47 (1H, s, ArH), 6.90 (1H, d, *J*=2.1 Hz, ArH), 7.01 (1H, dd, *J*=8.0, 2,2 Hz, ArH), 7.26.7.45 (6H, m, ArH), 7.72 (4H, m, ArH), 7.89 (1H, d, *J*=8.7 Hz, ArH); ^{13}C NMR (100 MHz) δ 19.6 (Cq), 22.1 (CH_2), 24.6 (CH_3), 26.2 (CH_2), 26.5 (CH_3), 35.1 (Cq), 38.0 (CH_2), 39.9 (CH_2), 103.5 (Cq), 116.4 (Cq), 120.2 (CH), 122.5 (Cq), 123.5 (CH), 128.1 (CH), 130.4 (CH), 132.0 (CH), 134.0 (CH), 135.6 (CH), 147.7 (Cq), 151.2 (Cq), 157.2 (Cq), 157.5 (Cq), 176.9 (Cq), 184.2 (Cq); *m/z* (EI^+) 562 (19%, M^+), 505 (100%, $M^+-{}^t$Bu); HRMS $C_{36}H_{38}O_4Si$ calcd 562.2540, found 562.2535.

Compound **22** (35 mg, 42%) as a dark orange viscous oil. IR ($CHCl_3$) ν_{max} 3019, 2399, 1709, 1600, 1519, 1420, 1362, 1219, 1016 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.92 (3H, s, CH_3 cHexyl), 1.12 (9H, s, CH_3, ^{t}Bu), 1.40 (12H, s, CH_3 boronate), 1.26–1.57 (10H, m, cHexyl), 2.56, (2H, CH_2 cHexyl), 6.91 (1H, d, *J*=2.1 Hz, ArH), 6.97 (1H, dd, *J*=8.6, 2.1 Hz, ArH), 7.36.7.40 (6H, m, ArH), 7.70–7.81 (4H, m, ArH), 7.85 (1H, d, *J*=8.7 Hz, ArH); ^{13}C NMR (100 MHz) δ 19.6 (Cq), 22.3 (CH_2), 24.1 (CH_3), 25.0 (CH_3), 26.3 (CH_2), 26.5 (CH_3), 35.6 (Cq), 38.0 (CH_2), 42.8 (CH_2), 85.1 (Cq), 103.5 (CH), 116.4 (Cq), 119.9 (CH), 122.2 (Cq), 123.4 (CH), 128.1 (CH), 130.3 (CH), 132.1 (Cq), 135.5 (CH), 151.5 (Cq), 153.0 (Cq), 157.1 (Cq), 157.3 (Cq), 179.8 (CO), 184.5 (CO); *m/z* (EI^+) 690 (12%, MH_2^+); HRMS $C_{42}H_{51}BO_6Si$ calcd 690.3548, found 690.3562.

4.1.20. 7-Hydroxy-2-(1-methylcyclohexylmethyl)-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)dibenzofuran-1,4-dione (24). To a stirred solution of quinone 22 (18 mg, 0.026 mmol) in THF (0.2 mL) was added HF.py (1.48 μL of a ~70% soltn of HF in pyridine, 0.052 mmol, 2.0 equiv.) the reaction was then stirred for 1 h at rt after which time satd. aq. $NaHCO_3$ (1 mL) was added and stirring continued until effervescence ceased. The organic layer was then separated and the aqueous layer extracted with Et_2O (2×1 mL) the combined organic layers dried ($MgSO_4$) and the solvents removed in vacuo to give the alcohol as a dark red oil, which was used directly without purification in the next step.

To a stirred solution of the crude alcohol (11 mg) in EtOH (0.1 mL) was added aq. H_2O_2 (0.2 mL, excess, of a 20 volumes aq. soltn.) followed by solid Na_2CO_3 (2 mg, 0.02 mmol, 1 equiv.) and the reaction was stirred at rt for 1.5 h, after which time water (1 mL) followed by Et_2O (1 mL) were added and the purple organic layer separated. The aqueous layer was then extracted a further three times with Et_2O (1 mL). The combined organics where then dried ($MgSO_4$) and the solvent removed in vacuo to give a dark purple solid which was purified by flash column chromatography (silica, 30% EtOAc/pet. ether) to give 24 (6 mg,

74%) as a purple solid. Mp 176–179 °C. IR ($CHCl_3$) ν_{max} 3697, 3420, 2901, 1667, 1649, 1620, 1570, 1448, 1340, 1117, 1045, 972 cm^{-1}; ^1H NMR (400 MHz) δ 0.90 (3H, s, CH_3), 1.21–1.44 (10H, m, chexyl), 5.89 (1H, br s, OH), 7.00 (1H, dd, J=7.0, 2.2 Hz, ArH), 7.06 (1H, d, J=1.9 Hz, ArH), 7.11 (1H, s, OH), 8.04 (1H, d, J=8.4 Hz); ^{13}C NMR (125 MHz) CD_3OD δ 22.0 (CH_2), 24.1 (CH_3), 26.9 (CH_2), 34.4 (Cq), 35.7 (CH_2). 38.2 (CH_2), 97.1 (CH), 113.9 (Cq), 115.4 (Cq), 115.7 (CH), 117.1 (Cq), 123.0 (CH), 123.7 (Cq), 148.2 (Cq), 158.9 (Cq), 160.0 (Cq), 172.7 (Cq), 184.5 (Cq); m/z (EI^+) 340 (2%, M^+), 244 (100%, $M^+-C_7H_{13}$); HRMS $C_{20}H_{20}O_5$ calcd 340.13107, found 340.12940.

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