

2,6-Di-*tert*-butyl-4-(3,3-diarylpropadienylidene)-2,5-cyclohexadien-1-ones, the First Stable *p*-Quinopropadienes

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Treatment of 2,6-di-*tert*-butyl-4-ethynylphenol with 2 equivalents of *n*BuLi, followed by addition of diaryl ketones, afforded the corresponding *p*-quinopropadienes **2a–f** upon appropriate dehydrative treatments. These compounds are fairly stable, orange to purple, crystalline substances, exhibiting intense absorptions at longer wavelengths. In particular, the bis(dimethylamino) derivative **2a** absorbs across the whole of the visible spectrum and into the near infrared. Unlike the quinone methides **1**, compounds **2** exhibited irreversible oxidation waves together with irreversible reduction waves on cyclic voltammetry. The very small E_{sum}^1 value of

2a also indicates the highly amphoteric redox properties of **2a**; however, both the anion and cation radicals of **2** are highly reactive. The molecular structures of **2a** and **2e** exhibit relatively small dihedral angles between two aromatic ring planes (**2a** for 47° and **2e** for 52°), and each has a short central double bond and long side double bonds. The short central double bond (**2a** for 1.228 Å and **2e** for 1.235 Å) indicates the importance of the resonance contribution of the dipolar structure with an acetylenic bond.

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Introduction

Intensely colored organic compounds have attracted considerable attention in relation to development of new materials.^[1] The extension of conjugation by schematic insertion of π units into a simple π system has been regarded as the most effective methods for designing new dyes, and in this context a number of conjugated systems possessing inserted π units such as 1,4-phenylene, 2,5-thienylene, and 1,2-ethynyl groups have been prepared.^[2] Although 7,7-diaryl-*p*-quinone methides **1**, which are appreciably dipolar and colored compounds, have been fairly extensively studied,^[3,4] the novel extended *p*-quinone methides (quinopropadienes) **2**, in which a *p*-quinone methide is united with 1,1-diarylbutatriene, are little known. The quinopropadienes **2** would be intriguing molecules because the extended conjugation and the cumulene structure should decrease their HOMO–LUMO energy gaps and enhance their dipolarities.^[5] Although the quinopropadiene derivative **3** was studied as a reactive intermediate by G. Cevasco and his co-workers,^[6] no stable derivatives have been prepared so far. Recently we reported the generation and reaction behavior of lithium 2,6-di-*tert*-butyl-4-lithiophenoxide as a key synthon for *p*-quinone methides **1**.^[7] As an extension of this finding, we expected that lithium 2,6-di-*tert*-butyl-4-lithioethynylphenoxide (**4**) should be a promising synthon

for **2**. Here we report the syntheses, structures, and properties of **2a–f** (Figure 1).

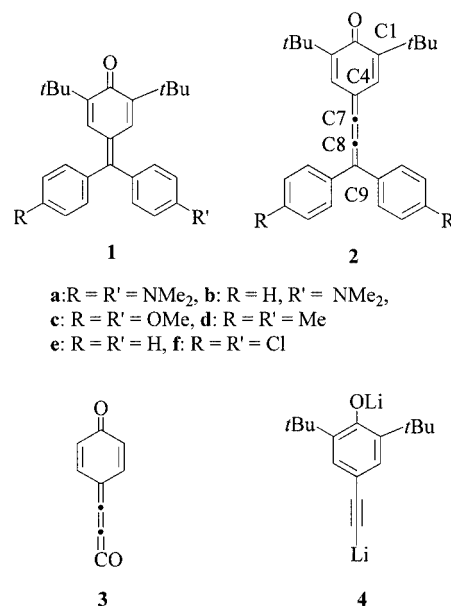


Figure 1. Chemical structures of **1–4**

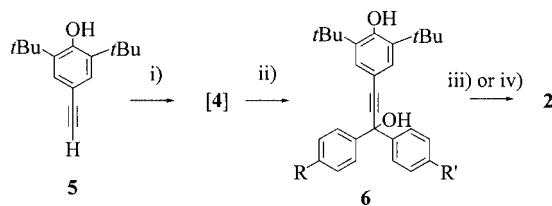
Results and Discussion

Synthesis of Quinopropadienes **2a–f**

Di-*tert*-butyl-4-ethynylphenol (**5**), a precursor of **4**, had previously been prepared from 2,6-di-*tert*-butylphenol in

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36% total yield in four steps including a Vilsmeier reaction.^[8a] To increase the availability of **5**, we modified the synthesis by using the Sonogashira reaction as a key step; treatment of 2,6-di-*tert*-butyl-4-bromo(trimethylsiloxy)benzene, which was obtained from bromination and silylation of di-*tert*-butylphenol,^[8b] with (trimethylsilyl)acetylene and subsequent desilylation with *n*Bu₄NF afforded **5** in 64% total yield. Treatment of a THF solution of **5** with 2 equivalents of *n*-butyllithium at -78°C , followed by addition of diaryl ketones and conventional workup, afforded the corresponding alkynol **6a–f** (Scheme 1). The colorless nature of the products of these reactions indicated the formation of **6**. The alcohols **6e** and **6f** were obtained in good yields (**6e**: 70%; **6f**: 71%) by chromatography on silica gel as colorless crystals. On the other hand, **6a** and **6b** were dehydrated on the column even at 0°C , to afford the quinopropadienes **2a** (34%) and **2b** (35%), respectively, as the sole isolated products. Compounds **2a** and **2b** are also sensitive to silica gel, and chromatography at ambient temperature drastically decreased the yields of products. On the other hand, similar chromatographic treatment of **6c** and **6d** afforded mixtures of the corresponding quinopropadiene and unchanged **6a**. Upon loading of the alcohols onto silica gel at room temp. for appropriate periods (3 h for **6c**; 12 h for **6d**), pure **2c** and **2d** were eluted from the column (**2c**: 67%, **2d**: 67%). However, similar dehydration of **6e** and **6f** to **2e** and **2f** on silica gel ended in failure. Dehydrative treatments with anhydrous CuSO₄ were then examined; we have reported that the reagent is effective for dehydration of acid-sensitive alcohols.^[9] However, treatment of **6e** and **6f** with anhydrous CuSO₄ (10 equiv.) in THF at reflux for 16 h gave **2e** and **2f** only in poor yields (28% for **2e**, and 19% for **2f**). The most successful results were achieved by heating with anhydrous CuSO₄ in THF in the presence of ZnCl₂, giving good yields (**2e**: 70%; **2f**: 71%). The Lewis-acidic properties of ZnCl₂ appears to play an important role in the synthesis.



Scheme 1. Reagents and conditions: i) 2.2 equiv. *n*BuLi, THF, -78°C , ii) diaryl ketone, -78°C then to room temp., iii) silica gel for **2a–d**, iv) 6 equiv. ZnCl₂, 5 equiv. CuSO₄, THF, reflux for **2e–f**

Spectral Properties

The thus obtained quinopropadienes **2a–f** are fairly stable, orange to purple, crystalline substances, exhibiting intense absorptions at longer wavelengths than the corresponding *p*-quinone methides. For example, the longest-absorption band of **2a** ($\lambda_{\text{max.}} = 641 \text{ nm/CH}_2\text{Cl}_2$) is ca. 150 nm longer than that of **1a** ($\lambda_{\text{max.}} = 495 \text{ nm/CH}_2\text{Cl}_2$). In particular, the fact that **2a** absorbs across the whole of the visible

spectrum and into the near infrared could have useful technical implications (Figure 2). Moreover, the intensely colored **2a** shows appreciably large positive solvatochromism: $\lambda_{\text{max.}} = 579 \text{ nm}$ in cyclohexane, 631 nm in chloroform, 654 and 720 (shoulder) nm in acetonitrile, and 668 and 731 nm in methanol. The new band at long wavelength in the polar solvents may be attributable to twisted intramolecular charge transfer (TICT), because the band appears even in the polar aprotic solvent acetonitrile.^[10]

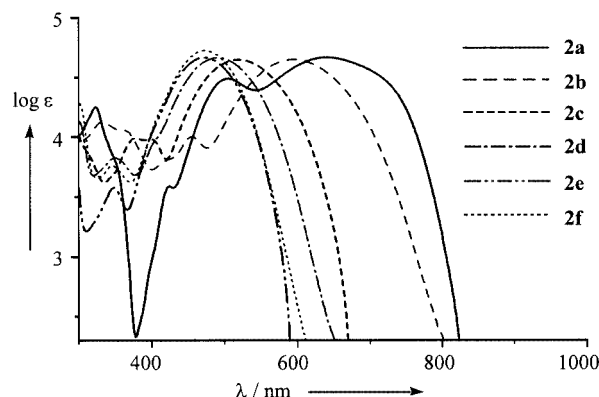


Figure 2. UV/Vis spectra of **2a–2f** in CH₂Cl₂ solution

The selective IR stretching frequencies and ¹³C NMR chemical shifts of **2a–f** are summarized in Table 1, together with those of **1a** and **1d**. The extended conjugation would be expected to enhance the dipolarity of **2a–f**; actually, the carbonyl stretching absorptions of **2a–f** in the IR spectra ($\tilde{\nu} = 1551\text{--}1598 \text{ cm}^{-1}$) are at frequencies 15 to 50 cm^{-1} lower than those of the corresponding quinone methides.^[7] Moreover, **2a–c**, **2f**, and **1a** each exhibit two CO vibrations, whereas **2d–e** and **1e** each have one. The splits become larger with stronger electron-donating properties of the substituents, probably due to the large contribution of the highly polarized zwitterionic forms in the solid state. The ¹³C NMR chemical shifts also indicate the dipolar character of **2**, through large difference in the chemical shifts between C4 and C7 of **1a** and **1e** shift in opposite directions ($\Delta\delta$ of C4 = -0.9 ppm and $\Delta\delta$ of C7 = 3.3 ppm), suggesting increasing dipolar properties. On the other hand, the chemical shifts of all the butatriene carbon atoms (C4, C7–C9) of **2** monotonically change with the electronic properties of the substituents on aromatic rings. The electron-donating substituents of **2** should increase the electron density of all the butatriene carbon atoms but not the dipolar character of the molecule.

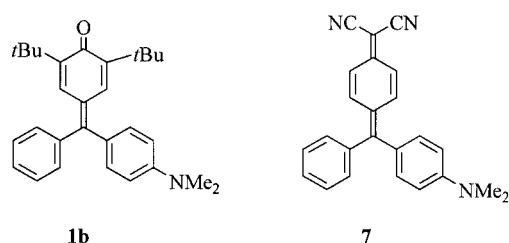
Variable temperature ¹H NMR spectra of unsymmetrical **2b** in [D₆]DMSO show broadening of the *tert*-butyl protons ($\delta = 1.33$ and 1.36 ppm at 30°C) at 60°C , and the signals coalesce at about 85°C , indicating fairly easy rotation of the butatriene bond, probably at the C4–C7 double bond ($\Delta G^{\ddagger} = 18.5 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$). The energy barrier is considerably lower than that in the *p*-quinone methide **1b** (no broadening of the *tert*-butyl signals at 120°C), but higher than that of the quinodimethane **7**^[11] ($T_c = -10^{\circ}\text{C}$; $\Delta G^{\ddagger} =$

Table 1. Selected spectroscopic data of **2a–f**, and quinone methide **1a** and **1e**

Compound	IR stretching (cm ⁻¹) ^[a]		C1	¹³ C NMR chemical shifts (δ ppm) ^[b]			
	C=O	C=C=C=C		C4	C7	C8	C9
2a	1594 s, 1551 s	2043 m	184.72	109.09	153.73	137.27	130.40
2b	1598 m, 1571 s	2037 m	185.21	111.95	155.68	138.70	131.23
2c	1595 m, 1579 s	2040 m	185.39	113.04	156.73	137.36	133.39
2d	1585 s	2033 m	185.52	114.38	157.76	139.77	135.65
2e	1588 s	2027 m	185.64	115.54	158.27	141.60	138.27
2f	1590 s, 1585 s	2027 m	185.62	116.42	157.09	141.63	136.40
1a	1601 s, 1587 s		185.9	128.8			159.2 ^[c]
1e	1604 s		186.1	129.7			155.9 ^[c]

^[a] KBr disk. ^[b] δ in CDCl₃. Based on C–H COSY (HMQC and HMBC) spectra. ^[c] Diarylmethylene carbon (C7).

11.5 ± 0.5 kcal·mol⁻¹ in [D₇]DMF). Thus, **2b** has a substantial dipolar property, intermediate between **1b** and **7**.



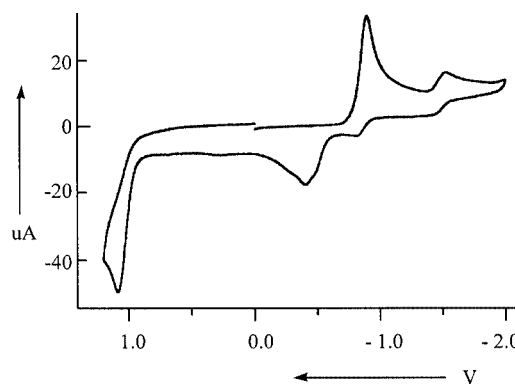
Electrochemical Properties

The quinopropadienes **2** have higher electron affinity than the *p*-quinone methides **1**, as exemplified by the lower first reduction potential of **2e** ($E_{\text{red}}^1 = -0.85$ V) in relation to **1e** ($E_{\text{red}}^1 = -1.14$ V) (Table 2, Figure 3). However, while the first reduction wave of **1e** is reversible, that of **2e** is almost irreversible. The results indicate the transient nature of the anion radical **2e^{-•}**. The second weak reduction wave probably corresponds to the formation of the dianion **2e²⁻**. On the other hand, **2a–f** also each exhibited an irreversible oxidation wave in the measurable range (< +1.5 V), unlike the corresponding quinone methides. In particular, the electron-releasing properties of **2a** are significantly high, so **2a** can be regarded as a highly amphoteric redox system ($E_{\text{sum}}^1 = 1.37$ V). This ability of **2a** is quite similar to that of **8**, the best amphoteric redox system containing a butatriene moiety.^[12]

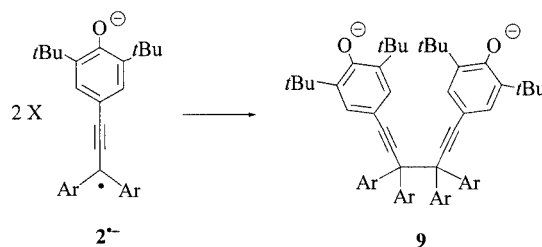
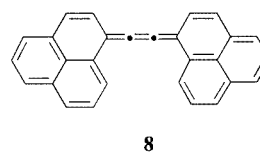
Table 2. Electrochemical data of **2a–f**, **1a**, and **1e**

Compound	Redox potentials (V) ^[a]		
	E_{ox}^1	E_{red}^1	E_{red}^2
2a	0.36	-1.07	-1.76
2b	0.51	-0.96	-1.61
2c	0.85	-0.95	
2d	1.01	-0.88	
2e	1.08	-0.85	
2f	1.13	-0.80	
1a		-1.42	-1.98
1e		-1.14	-1.73

^[a] V vs. Ag/Ag⁺ (ferrocene/ferrocenium cation = +0.24 V) in 0.1 mol·dm⁻³ *n*Bu₄NClO₄, 25 °C, sweep rate 100 mV·sec⁻¹.

Figure 3. Cyclic voltammogram of **2e** in DMF

Notably, a common re-oxidation wave at about -0.40 V is observed for each of the compounds **2a–f**. These observations are best explained in terms of easy coupling of the anion radical of **2a–f** at the C-9 position to form the dimer dianion **9** (Scheme 2). The substituents on the aryl group in this dimer should have little effect on the oxidation potential of the 4-ethynylphenoxide parts.

Scheme 2. Coupling of radical anions of **2** to generate the dimer **9****8**

Molecular Structures of **2a** and **2e**

Good single crystals of **2a** and **2e** suitable for X-ray analysis were obtained from hexane and benzene-hexane solutions, respectively. Figure 4 shows the molecular structures. Both molecules have almost planar butatriene moieties, and the aryl rings are inclined from the butatriene plane propeller fashion. However, the dihedral angles between two aromatic ring planes (**2a** for 47° and **2e** for 52°) are appreciably smaller than those of the known *p*-quinone methides (ca. 95°),^[13] probably due to the low steric hindrance around the central carbon of diarylmethylidenes. The structural properties account for the higher reactivity of radical anions **2^{•-}** relative to **1^{•-}**. The characteristic points of each of these structures are the short central double bond (C7–C8) and the long side double bonds (C4–C7 and C8–C9); the central double bond of **2a** (1.228 Å) is the second shortest among the known butatrienes, the shortest one being the highly polarized 1,1-dicyano-4,4-bis(dimethylamino)butatriene (**10**) (1.201 Å).^[14] In those structures of low symmetry, the lengths of the side double bonds are different; the quinone methide double bonds (C4–C7) are 0.24 Å for **2a** and 0.27 Å longer than the diarylmethylene double bonds (C8–C9). These structural characteristics should indicate a large resonance contribution by the dipolar structure possessing an acetylenic bond **11**. The other interesting feature in each molecular structures is that the butatriene part is strongly bent, the bond angles around the sp carbon atoms being 171.9 and 170.5° for **2a** and 175.2 and 175.7° for **2e**. The electron-rich **2a** is thus more bent than **2e** and the other butatrienes reported so far.^[14] Although spectroscopic data such as variable-temperature NMR and theoretical calculations on **2a** tell little about its bent structure, the larger bending of **2a** in the crystal might be associated with the higher electron density at the butatriene carbon atoms, as indicated by the ¹³C chemical shifts. Both molecules form head-to-tail dimeric structure in the crystals, as shown in Figure 5. The molecules are stacked in a parallel-displaced manner, probably due to the presence of bulky *tert*-butyl groups.

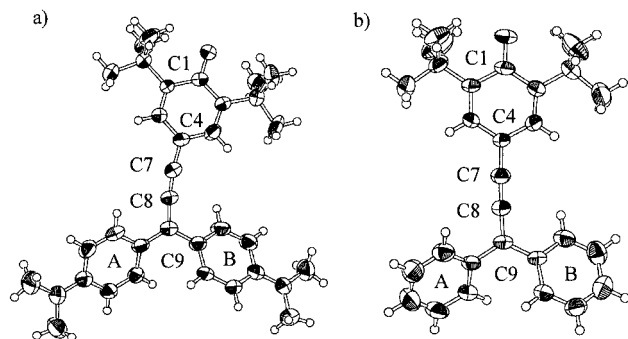


Figure 4. Molecular structures of: a) **2a**, and b) **2e** in the crystal; selected bond lengths (Å) and angles (°): **2a**: O1–C1 1.252(4), C4–C7 1.380(5), C7–C8 1.228(5), C8–C9 1.356(5); C4–C7–C8 171.9(5), C7–C8–C9 170.5(5), dihedral angle of least-squares planes A and B 52°; **2e**: O1–C1 1.232(4), C4–C7 1.375(4), C7–C8 1.235(4), C8–C9 1.348(4); C4–C7–C8 175.2(4), C7–C8–C9 175.7(5), dihedral angle of least-squares planes A and B 47°

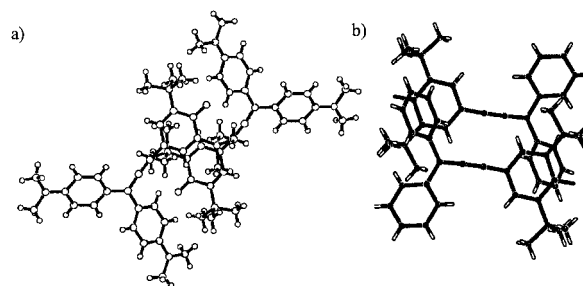
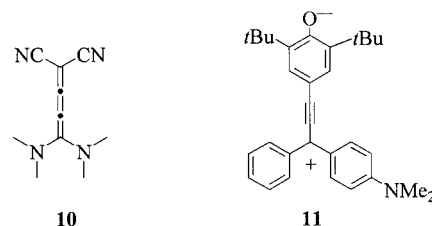


Figure 5. Dimeric structures of: a) **2a**, and b) **2e** in the crystals



Conclusion

We have provided a synthetic route to *p*-quinopropadienes **2**, using lithium 2,6-di-*tert*-butyl-4-lithioethynylphenoxide (**4**) as an effective synthon, and have been able to establish the structural and some of the electronic properties of these interesting π systems. The extension of conjugation causes bathochromic shifts in absorption spectra and increases the dipolar character of molecules. The rotational barriers of the diarylmethylidene bond of **2b** indicate that the order of the dipolar character are dicyanoquinodimethanes > **2** > quinone methides. From cyclic voltammetric analyses of **2**, both the electron-releasing and -accepting properties are enhanced; the amphoteric character of **2a** is almost similar to that of **8**. However, the corresponding radical anions and cations of **2** are highly reactive. The crystallographic analyses reveal that the dihedral angles between the two aromatic rings (47° for **2a** and 52° for **2e**) are significantly smaller than those of the known *p*-quinone methides. The structural properties account for the high reactivity of radical anions **2^{•-}**. The molecular structures are also characterized by the short central double bond and the long side double bonds, probably indicating large resonance contributions of the dipolar structures possessing an acetylenic bond. Thus, the extension to conjugation by insertion of two sp carbon atoms has been shown to be an effective way to construct highly colored organic compounds. Work along these lines is under way and the results will be communicated in due course.

Experimental Section

General Remarks: Melting points were recorded with a Yanaco MP 500D apparatus and are uncorrected. FAB and EI mass spectra were measured with a JEOL JMS-SX 102 instrument. ¹H NMR spectra (tetramethylsilane; δ = 0 ppm as an internal standard) and ¹³C NMR spectra (CDCl₃; 77.0 ppm as an internal standard) were

recorded with JEOL EX-270 and JEOL GSX-400 instruments. The chemical shifts are given in ppm. IR spectra were obtained with a Perkin–Elmer 1650 spectrometer. The microanalyses were performed at the Elemental Analysis Center, Faculty of Science, Osaka University. Electronic spectra (UV/Vis) were obtained with a Jasco V-570 spectrophotometer. Column chromatography was performed with Merck Kieselgel 60. Cyclic voltammograms were recorded with a BAS Voltammetric Analyzer BAS100B/W(CV-50 W). All electrochemical measurements were carried out in DMF solutions containing 0.1 mol·dm⁻³ tetra(*n*-butyl)ammonium perchlorate (Nakarai Tesque) at 25 °C under argon. All reagents were of commercial quality and were used as supplied unless otherwise stated; tetrahydrofuran was dried by standard procedures where necessary. Compounds **1** were prepared as described previously.

2,6-Di-*tert*-butyl-4-ethynylphenol (5): (Dichloro)bis(triphenylphosphane)palladium (240 mg, 0.4 mmol) and CuI (40 mg, 0.2 mmol) were added to a solution of 4-bromo-2,6-di-*tert*-butyl(trimethylsiloxy)benzene (7.15 g, 0.02 mol) and (trimethylsilyl)acetylene (5.6 mL, 0.02 mol) in anhydrous triethylamine (90 mL). The reaction mixture was stirred at reflux under N₂. After 4 h, the mixture was cooled to 0 °C, diluted with hydrochloric acid (2 M, 100 mL), and extracted with hexane (100 mL × 2). The extracts were combined, washed with brine (100 mL), dried with anhydrous MgSO₄, concentrated, and chromatographed on silica gel with hexane elution to give 4-(2-trimethylsilylethynyl)-2,6-di-*tert*-butyl(trimethylsiloxy)benzene as a colorless oil (6.14 g). The oil was diluted with THF (80 mL) under N₂. *n*Bu₄NF (1 M solution in THF, 60 mL, 60 mmol) was added to the degassed solution, and the mixture was stirred at 0 °C under N₂. After 2 h, the mixture was diluted with aqueous NH₄Cl (100 mL) and extracted with hexane (2 × 100 mL). The extracts were combined, washed with brine (100 mL), dried with anhydrous MgSO₄, concentrated, and chromatographed on silica gel with hexane elution to give 3.91 g (85%, two steps) of colorless prisms. M.p. 107–108 °C (ref. 106–107 °C).^[15]

General Procedure for the Preparation of Compounds 2a–d, and 6e–f: *n*BuLi (1.3 M solution in hexane, 1.3 mL, 2.1 mmol) was added at –78 °C under N₂ to a solution of **5** (230 mg, 1 mmol) in dry THF (20 mL), and the mixture was stirred at –78 °C for 1 h to generate anion **4**. A solution of the appropriate diaryl ketone (1 mmol) in THF (10 mL) was added dropwise by syringe at –78 °C to the reaction mixture. The mixture was warmed to room temp., stirred for 1 h, diluted with aqueous NH₄Cl (100 mL), and extracted with benzene (2 × 100 mL). The extracts were combined, washed with brine (100 mL), dried with anhydrous MgSO₄, and concentrated. Silica gel column chromatography of the residue as indicated afforded the relevant product **6** and/or **2**.

Quinopropadiene 2a: This compound was prepared from **5** (1 mmol) and Michler's ketone (268 mg, 1 mmol); elution at 0 °C with benzene/hexane (1:1, v/v) afforded the product **2a** (158 mg, 32%) as green prisms; m.p. 195–197 °C. IR (KBr): $\tilde{\nu}$ = 2949 (m), 2043 (s, C=C=C=C), 1594 (s), 1551 (s, C=O), 1481 (m), 1446 (m), 1371 (m), 1320 (m), 1228 (m), 1164 (s), 1097 (m), 947 (w), 910 (w), 820 (w), 572 (w), 478 (w) cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 1.35 (s, 18 H), 3.09 (s, 12 H), 6.75 (d, *J* = 9.1 Hz, 4 H), 7.14 (s, 2 H), 7.61 (d, *J* = 9.1 Hz, 4 H). ¹³C NMR (67.8 MHz, CDCl₃): δ = 29.7 [–C(CH₃)₃], 35.3 [–C(CH₃)₃], 40.2 [–N(CH₃)₂], 109.1 (C-4), 111.7 (C'-3), 126.5 (C'-1), 130.4 (C-9), 131.4 (C-3), 132.1 (C'-2), 137.3 (C-8), 146.3 (C-2), 151.6 (C'-4), 153.7 (C-7), 184.7 (C-1) ppm. UV/Vis (cyclohexane): λ_{max} (log ϵ) = 283 (4.12), 332 (4.25), 424 (3.59), 505 (4.49), 641 nm (4.65). MS (EI): *m/z* (%) = 481 (39) [M⁺ + H], 480 (100) [M⁺], 465 (76) [M⁺ – Me], 396 (76) [M⁺ – *t*Bu].

C₃₃H₄N₂O (444.4): calcd. C 82.45, H 8.39, N 5.83, found C 82.46, H 8.39, N 5.78.

Quinopropadiene 2b: This compound was prepared from **5** (1 mmol) and 4-(dimethylamino)benzophenone (149 mg, 0.66 mmol); elution with benzene/hexane (1:1, v/v) at 0 °C afforded the product **2b** (102 mg, 35%) as green prisms; m.p. 147–149 °C. IR (KBr): $\tilde{\nu}$ = 2952 (m), 2037 (s, C=C=C=C), 1598 (s), 1571 (s, C=O), 1482 (w), 1442 (w), 1371 (m), 1298 (m), 1166 (s), 1099 (w), 906 (w), 817 (w), 691 (w), 524 (w) cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 1.33 (s, 9 H), 1.36 (s, 9 H), 3.09 (s, 6 H), 6.73 (d, *J* = 9.2 Hz, 2 H), 7.07 (d, *J* = 2.3 Hz, 1 H), 7.14 (d, *J* = 2.3 Hz, 1 H), 7.44–7.46 (m, 3 H), 7.59 (d, *J* = 9.2 Hz, 2 H), 7.62–7.65 (m, 2 H) ppm. ¹³C NMR (67.8 MHz, CDCl₃): δ = 29.7 [–C(CH₃)₃], 35.4 [–C(CH₃)₃], 40.2 [–N(CH₃)₂], 111.9 (C'-3), 112.0 (C-4), 126.4 (C'-1), 128.4 (C''-1), 128.6 (C''-3), 129.5 (C-3 or 5), 130.2 (C''-2), 131.1 (C-5 or 3), 131.2 (C-9), 131.8 (C'-2), 135.2 (C''-1), 138.7 (C-8), 147.3 (C-2 or 5), 147.4 (C-5 or 2), 151.6 (C'-4), 155.7 (C-7), 185.2 (C-1) ppm. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 284 (4.19), 332 (4.13), 362 (4.06), 455 (4.01), 595 nm (4.65). MS (EI): *m/z* (%) = 438 (34) [M⁺ + H], 437 (95) [M⁺], 422 (96) [M⁺ – Me], 380 (100) [M⁺ – *t*Bu]. C₃₁H₃₅NO (437.6): calcd. C 85.08, H 8.06, N 3.20; found C 84.86, H 7.94, N 3.01.

Quinopropadiene 2c: This compound was prepared from **5** (2 mmol) and 4,4'-dimethoxybenzophenone (484 mg, 2 mmol); the residue was loaded onto chromatography silica gel at room temp. for 3 h, and then eluted with benzene/hexane (1:2, v/v) to afford the product **2c** (609 mg, 67%) as reddish purple needles; m.p. 175–176 °C. IR (KBr): $\tilde{\nu}$ = 2955 (m), 2040 (m, C=C=C=C), 1595 (m), 1579 (s, C=O), 1507 (m), 1458 (w), 1387 (w), 1361 (m), 1302 (m), 1259 (s), 1202 (w), 1171 (s), 1098 (w), 1036 (m), 913 (w), 834 (m), 579 (w), 508 (w) cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 1.34 (s, 18 H), 3.89 (s, 6 H), 6.98 (d, *J* = 8.9 Hz, 4 H), 7.09 (s, 2 H), 7.60 (d, *J* = 8.9 Hz, 4 H) ppm. ¹³C NMR (67.8 MHz, CDCl₃): δ = 29.7 [–C(CH₃)₃], 35.4 [–C(CH₃)₃], 55.5 (–OCH₃), 113.0 (C-4), 114.3 (C'-3), 131.0 (C'-1), 131.6 (C'-2), 133.4 (C-9), 137.4 (C-8), 147.8 (C-2), 156.7 (C-7), 161.3 (C'-4), 185.4 (C-1) ppm. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 290 (4.17), 378 (3.99), 399 (3.98), 520 nm (4.64). MS (EI): *m/z* (%) = 455 (17) [M⁺ + H], 454 (61) [M⁺], 439 (60) [M⁺ – Me], 397 (100) [M⁺ – *t*Bu]. C₃₁H₃₄O₃ (454.6): calcd. C 81.90, H 7.54; found C 81.81, H 7.52.

Quinopropadiene 2d: This compound was prepared from **5** (2 mmol) and 4,4'-dimethylbenzophenone (452 mg, 2 mmol); the residue was loaded onto chromatography silica gel at room temp. for 12 h, and then eluted with benzene/hexane (1:2, v/v) to afford the product **2d** (570 mg, 67%) as reddish purple plates; m.p. 201–203 °C. IR (KBr): $\tilde{\nu}$ = 2954 (m), 2033 (m, C=C=C=C), 1585 (s, C=O), 1458 (w), 1359 (w), 1312 (w), 1294 (m), 1252 (w), 1202 (w), 1180 (m), 1096 (w), 908 (w), 823 (w), 613 (w), 576 (w) cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 1.33 (s, 18 H), 2.42 (s, 6 H), 7.08 (s, 2 H), 7.26 (d, *J* = 8.2 Hz, 4 H), 7.54 (d, *J* = 8.2 Hz, 4 H) ppm. ¹³C NMR (67.8 MHz, CDCl₃): δ = 21.5 (–CH₃), 29.6 [–C(CH₃)₃], 35.4 [–C(CH₃)₃], 114.4 (C-4), 129.5 (C-2), 129.9 (C-3), 131.0 (C-3), 133.6 (C'-1), 135.7 (C-9), 139.8 (C-8), 140.3 (C'-4), 148.1 (C-2), 157.8 (C-7), 185.5 (C-1) ppm. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 282 (4.23), 350 (3.83), 491 nm (4.67). MS (EI): *m/z* (%) = 423 (7) [M⁺ + H], 422 (23) [M⁺], 407 (33) [M⁺ – Me], 365 (100) [M⁺ – *t*Bu]. C₃₁H₃₄O (422.6): calcd. C 88.11, H 8.11; found C 88.11, H 8.14.

Alcohol 6e: This compound was prepared from **5** (1 mmol) and benzophenone (180 mg, 1 mmol); elution with benzene/hexane (1:1, v/v) afforded the alcohol **6e** (370 mg, 90%) as a colorless powder;

m.p. 148–149 °C. IR (KBr): $\tilde{\nu}$ = 3588 (m, OH), 3367 (br. s, OH), 2962 (s), 2225 (w, C $\equiv$ C), 1490 (m), 1448 (s), 1432 (s), 1390 (m), 1361 (m), 1201 (m), 1225 (m), 1181 (m), 1155 (m), 1056 (m), 767 (s), 697 (s) cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 1.43 (s, 18 H), 2.81 (s, 1 H), 5.37 (s, 1 H), 7.40–7.53 (m, 6 H), 7.65–7.75 (m, 4 H) ppm. ¹³C NMR (67.8 MHz, CDCl₃): δ = 30.3, 34.4, 74.9, 88.4, 89.3, 113.2, 126.0, 127.5, 128.2, 128.7, 136.0, 145.3, 154.5 ppm. MS (EI): m/z = 412 (30) [M⁺], 397 (4) [M⁺ – Me], 354 (28) [M⁺ – *t*BuH], 279 (22), 149 (50), 87 (100). HRMS calcd. 412.2404; found 412.2465.

Alcohol 6f: This compound was prepared from **5** (2 mmol) and 4,4'-dichlorobenzophenone (502 mg, 2 mmol); elution with benzene/hexane (1:1, v/v) afforded the alcohol **6f** (590 mg, 61%) as a colorless powder; m.p. 137–138 °C. IR (KBr): $\tilde{\nu}$ = 3632 (s, OH), 3406 (br. s, OH), 2959 (s), 2872 (m), 2215 (w, C $\equiv$ C), 1490 (s), 1434 (s), 1362 (m), 1236 (m), 1070 (m), 1093 (s), 1016 (m), 901 (m), 830 (s) cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 1.43 (s, 18 H), 2.83 (s, 1 H), 5.42 (s, 1 H), 7.31 (m, J = 8.6 Hz, 4 H), 7.58 (m, J = 8.6 Hz, 4 H) ppm. ¹³C NMR (67.8 MHz, CDCl₃): δ = 30.2, 43.4, 74.1, 88.3, 89.1, 112.6, 127.4, 128.4, 128.7, 133.6, 136.2, 143.5, 154.8 ppm. MS (EI): m/z (%) = 482 (18) [M⁺, 2 $\times$ ³⁷Cl], 481 (11) [M⁺, ³⁷Cl + ³⁵Cl], 480 (29) [M⁺, 2 $\times$ ³⁵Cl], 465 (7) [M⁺ – Me]. HRMS calcd. 480.1625; found 480.1598.

Preparation of Compounds 2e–f: Degassed suspensions of the precursors **6** (0.5 mmol), anhydrous CuSO₄ (400 mg, 2.5 mmol), and anhydrous ZnCl₂ (340 mg, 2.5 mmol) in THF (20 mL) were heated at reflux with stirring for 2 h. After cooling, the mixtures were filtered through celite columns and eluted with benzene/hexane (1:1, v/v). The eluents were concentrated and chromatographed on silica gel with benzene/hexane (1:2, v/v) elution to give 138 mg of **2e** (70%) and 165 mg of **2f** (71%), respectively:

Compound 2e: Reddish orange prisms; m.p. 185–187 °C. IR (KBr): $\tilde{\nu}$ = 2956 (m), 2027 (m, C=C=C=C), 1588 (s, C=O), 1481 (w), 1455 (m), 1381 (w), 1360 (m), 1250 (w), 1198 (w), 1181 (m), 1099 (w), 906 (m), 883 (w), 817 (w), 776 (m), 691 (m), 626 (w), 519 (w) cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 1.34 (s, 18 H), 7.08 (s, 2 H), 7.43–7.48 (m, 6 H), 7.62–7.66 (m, 4 H). ¹³C NMR (67.8 MHz, CDCl₃): δ = 29.6 [–C(CH₃)₃], 35.5 [–C(CH₃)₃], 115.5 (C-4), 128.7 (C'-2), 129.7 (C'-4), 129.8 (C'-3), 130.8 (C-3), 132.9 (C'-1), 138.3 (C-9), 141.6 (C-8), 148.6 (C-2), 158.3 (C-7), 185.6 (C-1) ppm. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 276 (4.19), 349 (3.56), 472 nm (4.67). MS (EI): m/z (%) = 395 (8) [M⁺ + H], 394 (37) [M⁺], 379 (41) [M⁺ – Me], 337 (100) [M⁺ – *t*Bu]. C₂₉H₃₀O (394.6): calcd. C 88.28, H 7.66; found C 88.25, H 7.66.

Compound 2f: Reddish orange prisms; m.p. 188–190 °C. IR (KBr): $\tilde{\nu}$ = 2959 (m), 2027 (m, C=C=C=C), 1590 (s, C=O), 1585 (s), 1487 (m), 1397 (m), 1361 (m), 1198 (w), 1177 (w), 1099 (s), 1012 (m), 904 (m), 834 (m), 816 (w), 724 (w), 612 (w), 531 (w), 472 (w) cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 1.33 (s, 18 H), 7.04 (s, 2 H), 7.43 (d, J = 8.6 Hz, 4 H), 7.52 (d, J = 8.6 Hz, 4 H) ppm. ¹³C NMR (67.8 MHz, CDCl₃): δ = 29.6 [–C(CH₃)₃], 35.5 [–C(CH₃)₃], 116.4 (C-4), 129.1 (C'-2), 129.4 (C'-4), 130.6 (C-3), 130.8 (C'-3), 136.0 (C'-1 or C9), 136.4 (C-9 or C'-1), 141.6 (C-8), 149.0 (C-2), 157.1 (C-7), 185.6 (C-1) ppm. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 286 (4.27), 300 (4.29), 349 (3.76), 473 nm (4.73). MS (EI): m/z (%) = 466 (9) [M⁺, 2 $\times$ ³⁷Cl], 464 (17) [M⁺, ³⁷Cl + ³⁵Cl], 462 (2) [M⁺, 2 $\times$ ³⁵Cl], 447 (32) [M⁺, – Me], 405 (76) [M⁺ – *t*Bu]. C₂₉H₂₈Cl₂O (463.4): calcd. C 75.16, H 6.09; found C 75.29, H 6.07.

X-ray Crystallography: The diffraction data were collected with a Rigaku AFC7R diffractometer with the use of Mo- K_{α} radiation (λ = 0.71069 Å). The structures were solved by direct methods and

refined by full-matrix, least-squares against F^2 of all data, by use of SHELXS-86. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined by use of a rigid model.

Crystal Data for 2a: C₃₃H₄₀N₂O, M = 480.69, triclinic, space group $P\bar{1}$ (#2), a = 12.924(3) Å, b = 13.377(2) Å, c = 8.735(1) Å, α = 100.76(1)°, β = 102.49(1)°, γ = 81.99(2)°, V = 1440.8(5) Å³, Z = 2, $D_{\text{calcd.}}$ = 1.108 g·cm⁻³, μ = 0.66 cm⁻¹, $R(R_w)$ = 0.158 (0.159), $R1$ = 0.052 for 1573 reflections [$I > 2\sigma(I)$]. CCDC-207099.

Crystal Data for 2e: C₂₉H₃₀O, M = 394.56, monoclinic, space group $P2_1/a$ (#14), a = 8.351(7) Å, b = 23.185(5) Å, c = 12.557(4) Å, β = 99.98(4)°, V = 2394(2) Å³, Z = 4, $D_{\text{calcd.}}$ = 1.094 g cm⁻³, μ = 0.64 cm⁻¹, $R(R_w)$ = 0.111 (0.121), $R1$ = 0.054 for 1439 reflections [$I > 2\sigma(I)$]. CCDC-207100.

CCDC-207099 (for **2a**) and -207100 (for **2e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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