

# Bromosubstituted norbornadienes and their reversible photolytic transformation to quadricyclanes

Peter Hammershøj<sup>1</sup>, Thomas Just Sørensen<sup>1</sup>, Anders Ø. Madsen<sup>1</sup>, Martin M. Nielsen<sup>2</sup>, and Klaus Bechgaard<sup>1\*</sup>

<sup>1</sup>Nano-Science Center & Department of Chemistry, University of Copenhagen, København Ø, Denmark

<sup>2</sup>Department of Physics, Technical University of Denmark, Fysikvej 307, 2800 Kgs. Lyngby

\*Corresponding author's e-mail address: klbe@kiku.dk

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## ABSTRACT

Two new model systems for use within the rapidly developing ultrafast time resolved x-ray scattering techniques have been prepared. Their photoisomerisation from norbornadiene to quadricyclane was found to be a suitable reaction to follow. Simulations of scattering patterns (not included in this report) showed that if heavy atoms are included in these molecular structures, then the transformation can be followed by transient X-ray scattering techniques. Two new bromosubstituted norbornadienes were synthesised and characterised. Absorption spectroscopy showed that the norbornadienes are converted quantitatively to quadricyclanes under ultraviolet irradiation. Nuclear magnetic resonance (NMR) studies showed that the process was fully reversible and that the norbornadienes could be completely recovered even without addition of catalysts. Furthermore, it was shown that the formation of quadricyclane from norbornadiene was unaffected by triplet sensitisers. The two new model systems synthesised thus are strong candidates for use in time-resolved X-ray scattering studies in both gas and condensed phases.

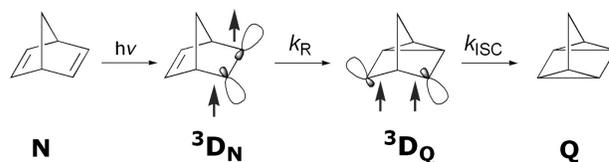
## INTRODUCTION

Recent development of time-resolved X-ray scattering techniques have allowed for detection of the structure of several transient species employing a laser-pump and an X-ray scattering-probe [1–6]. Tracking nuclear motion in a solvent system enables the structural description of transients during the progression of a chemical reaction. The requirements for the systems that are to be investigated are strict. The lifetime of the transient species must be known, a large concentration of the species must be generated and the species must scatter X-rays significantly different from the species present at equilibrium. In this article, potential candidates for the study of transients in a 2 + 2 cycloaddition reaction with time-resolved

X-ray scattering studies in solution and the gas phase are presented.

The norbornadiene-quadricyclane system has been investigated as a potential system for solar energy storage [7–12]. The system has been a topic of intense interest [13–19], and a mechanism for the conversion from norbornadiene to quadricyclane has been proposed [7, 15, 20–29]. The mechanism is shown in Figure 1 and involves two transient species with different structures. If the mechanism is correct, the system will display a disappearance of **N**, the grow-in and disappearance of <sup>3</sup>**D<sub>N</sub>** and <sup>3</sup>**D<sub>Q</sub>**, and the finally grow-in of **Q** if investigated using a pump-probe technique capable of determining structural change.

Simulations employing structure minimisation and calculation of scattering patterns show that the structure of the different species can indeed be resolved by X-ray scattering if heavy atoms are substituted onto the system (assuming an overall quantum yield of 10% for the process). Furthermore, we speculated that if the heavy atoms were introduced in a conjugated system they would bring the systems absorption energy out of the ultraviolet (UV) region, minimising the chance of photoinduced carbon-bromine homolytic bond dissociation.



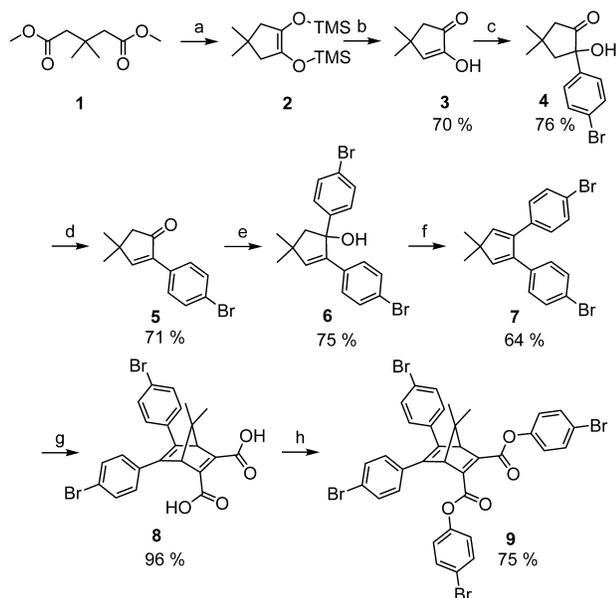
**Figure 1.** The mechanism of valence isomerisation from norbornadiene to quadricyclane. The different species are norbornadiene (**N**), norbornadiene diradical (<sup>3</sup>**D<sub>N</sub>**), quadricyclane diradical (<sup>3</sup>**D<sub>Q</sub>**), quadricyclane (**Q**).

Two new norbornadienes were prepared with two and four bromine substituents, respectively. By absorption and NMR spectroscopy, both systems were shown to reversibly form the corresponding quadricyclanes.

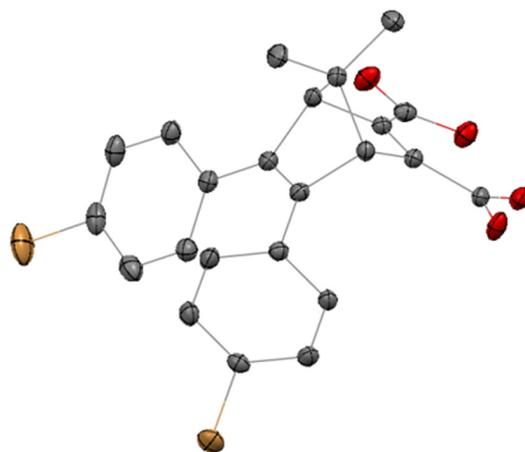
## RESULTS AND DISCUSSION

The synthetic route to 5,6-bis(4-bromophenyl)-7,7-dimethylnorbornadiene-2,3-dicarboxylic acid (**8**) and the corresponding bis(4-bromophenyl) ester (**9**) is shown in Scheme 1. The starting material **1** [30] was converted to the key intermediate: 2-hydroxy-4,4-dimethylcyclopent-2-enone (**3**), by an acyloin condensation [31–32]. The sodium/potassium alloy used in this step is highly flammable and limits the reaction scale to 10 g. Two sequential reactions with 4-bromophenyllithium followed by dehydration with 4-toluenesulfonic acid give 2,3-bis(4-bromophenyl)-5,5-dimethyl cyclopentadiene (**7**) in an overall yield of 26%. Acetylenedicarboxylic and **7** underwent a Diels-Alder condensation in excellent yields to form the norbornadiene acid **8**, which was made into the norbornadiene ester **9** *via* the acid chloride and 4-bromophenol. The multi-step synthesis gave **8** and **9** in acceptable overall yields of 17% and 13%, respectively.

The molecular structure of the sodium salt of **8** as crystallised from acetone was confirmed by single-crystal X-ray diffraction (CCDC 817053) and is shown in Figure 2. The structure clearly reveals the locked stilbene system that the bromine atoms are placed in. The aromatic rings may rotate, but the positions of the bromine atoms are fixed. In **9**, the bromine



**Scheme 1** (a). Na/K alloy, TMSCl, benzene; (b) Br<sub>2</sub>; (c) *n*-BuLi, *p*-dibromobenzene, –78°C; (d) *p*-TsOH, Toluene, reflux; (e) *n*-BuLi, *p*-dibromobenzene, –78°C; (f) *p*-TsOH, toluene, reflux; (g) Butynedioic acid, toluene, reflux; (h) 1. Oxalylchloride, DMF, Et<sub>3</sub>N. 2. DMAP, *p*-bromophenol.

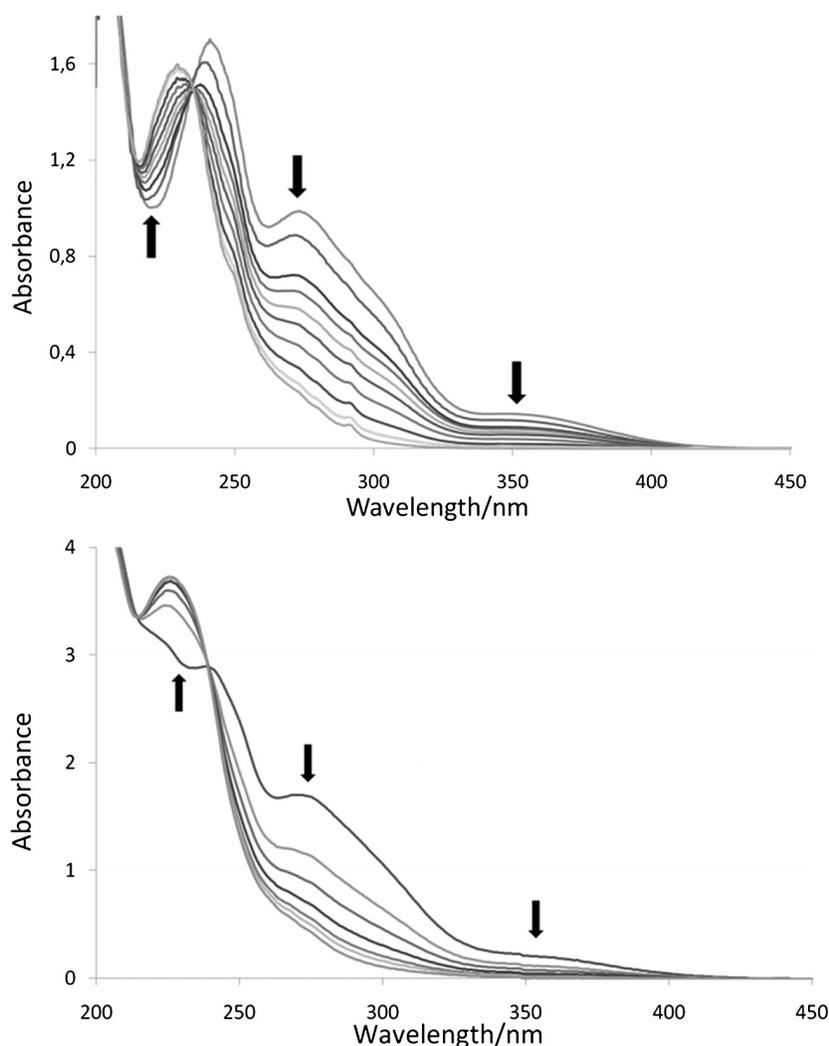


**Figure 2.** Single crystal structure of 5,6-bis(4-bromophenyl)-7,7-dimethylnorbornadiene-2,3-dicarboxylic acid (**8**) as its sodium salt. Hydrogen atoms, sodium ions and solvent molecules are omitted for clarity. The structure is shown with 50% probability ellipsoids.

atoms in the ester groups have a higher degree of freedom and more conformers are possible. Even so, the structural changes when norbornadiene becomes quadricyclane will result in systematic changes in the interatomic distances, in particular for the bromine atoms in **8** and **9**. The bromine atoms contribute very significantly to the X-ray scattering signature of the systems by introducing a strong modulation in the electron density distribution. Hence, these changes can be monitored using time-resolved X-ray scattering techniques. The bromine atoms account for more than 25% of the total electrons of the system.

If the norbornadienes **8** and **9** are to be studied using ultrafast X-ray scattering techniques, it must first be shown that the norbornadienes **8** and **9** can undergo photolytic isomerisation to the corresponding quadricyclanes **8q** and **9q**. As triplet states are involved in the transformation [7–12], the bromine atoms might make the process slow or prevent it from happening. Two photolysis experiments are shown in Figure 3. It clearly shows a reaction happening. A NMR investigation of the photolysis product confirms that the quadricyclane is the only product formed. The photolysis was carried out for **8** and **9** using 290 nm and 350 nm light in several solvents (Benzene, CHCl<sub>3</sub>, CH<sub>3</sub>CN, CH<sub>3</sub>OH). Although, the absorption is strongest at 290 nm, the produced quadricyclanes also absorb light at this wavelength. Hence, 350 nm light was used in the experiments shown here.

The effect of triplet sensitizers was tested using identical conditions as those used to generate the data in Figure 3. No effect of the sensitizers was found. The data are in all cases identical to those shown in Figure 3 when the sensitizer absorbance has been subtracted. The bromine atoms seem to act as internal triplet sensitizers and as such allow for an efficient conversion from norbornadiene to quadricyclane.



**Figure 3.** Photolysis of the norbornadiene acid **8** (top) and **9** (bottom) to the corresponding quadricyclane in methanol with 350 nm irradiation. The data points are at 2, 4, 6, 8, 10, 14, 20, 30, and 60 minutes.

The photolysis was also carried out in deuterated solvents in order to perform NMR experiments. Using NMR, it was determined that the photostationary state at 350 nm gave a ratio of  $[Q]/[N] = 92:8$  in chloroform and  $90:10$  in benzene.

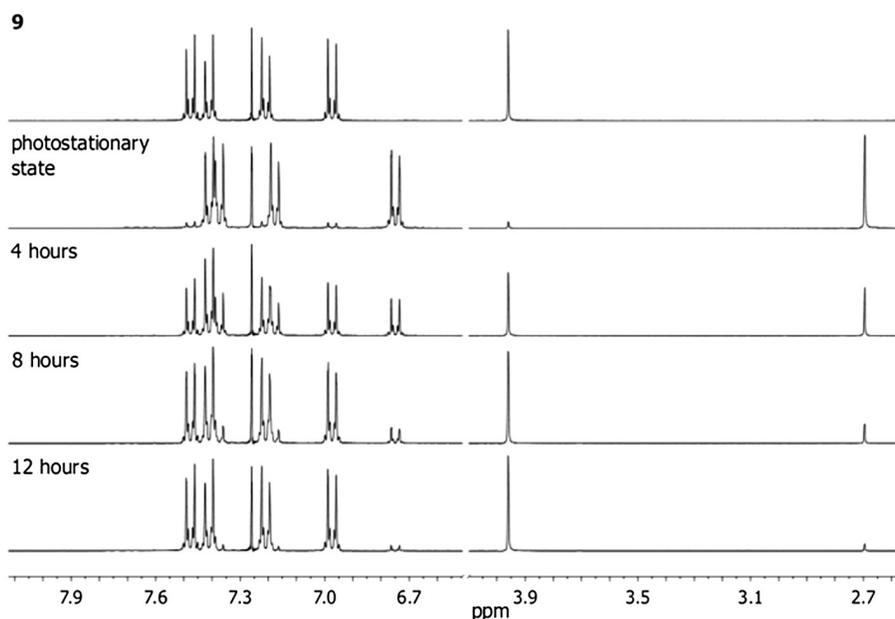
In most cases, the reverse process, from quadricyclane to norbornadiene, has to be catalysed [26, 33]. Furthermore, the quadricyclane formation is not fully reversible in the known systems [34]. In both **8/8q** and **9/9q**, the photolysis is fully thermally reversible. Figure 4 shows a time-lapse NMR experiment in deuterio-chloroform. It shows the thermal regeneration of norbornadiene over 12 hours at room temperature. The sample is kept in the dark.

Figure 5 shows the kinetic traces generated from the NMR experiments in deuterio-chloroform and deuterio-benzene. The  $t_{1/2} = 3$  hours and the half-life is the same for all investigated solvents and the same for both systems **8/8q** and **9/9q**. After

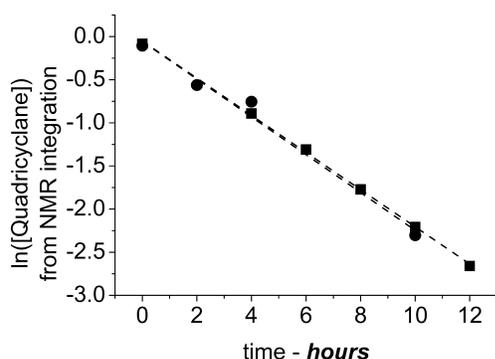
24 hours, no traces of quadricyclane or other impurities remain. Thus, the system can be cycled repeatedly between norbornadiene and quadricyclane without loss of material.

### CONCLUSIONS

Two new norbornadienes with bromine substituents have been synthesised and characterised. They are both capable of photolytic valence isomerisation to quadricyclane and can thermally be converted back to norbornadiene. The full recovery of the norbornadiene, combined with the unsensitised photoactivated isomerisation, make these systems good candidates for time-resolved X-ray studies using pump-probe techniques. The structural changes when going from norbornadiene over the relevant intermediates to quadricyclane are accompanied by the significant changes in electron density distribution due to the bromine atoms and can therefore be probed directly by X-ray scattering.



**Figure 4.**  $^1\text{H}$  NMR spectra of quadricyclane to **9** dark at RT in  $\text{CDCl}_3$  after illumination at 350 nm. The singlet at 3.9 ppm is from **9** and the singlet at 2.7 ppm is from the corresponding quadricyclane.



**Figure 5.** Kinetic traces of the formation of norbornadiene **9** in chloroform (squares) and benzene (circles) from time lapse  $^1\text{H}$  NMR spectra. The linear fit to the data points are shown as dashed lines.

## EXPERIMENTAL SECTION

Unless otherwise stated, all starting materials were obtained from commercial suppliers and used as received. Solvents were of HPLC grade and were used as received. Ground-state absorption spectroscopy was routinely recorded with a Cary 100 Bio spectrophotometer as solutions in the stated solvents.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a 400 MHz (Varian) instrument (400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR) or on a 500 MHz (Varian) instrument (500 MHz for  $^1\text{H}$  NMR and 125 MHz for  $^{13}\text{C}$  NMR). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) and carbon chemical shifts in ppm downfield of TMS, using the resonance of the solvent as internal standard.

Melting points were measured on a Gallenkamp apparatus and are uncorrected. High resolution mass spectrometry (HRMS) were recorded on a Micromass Q-TOF apparatus using electrospray ionisation (ESI) technique. Matrix assisted laser desorption ionisation time of flight (MALDI-TOF) mass spectra were recorded on a VG ToFSpec spectrometer. Electrospray ionisation (ESI) was recorded on a ThermoQuest Finnigan LCQ DECA instrument. Dry column vacuum chromatography was performed on Merck Kieselgel 60 (0.015–0.040 mm) and gravity feed column chromatography was performed on Merck Kieselgel 60 (0.040–0.063 mm). Thin layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554).

*4,4-Dimethyl-1,2-cyclopentadione/2-hydroxy-4,4-dimethylcyclopent-2-enone (3)*. A flame-dried 2-L tree-necked round-bottom flask equipped with a reflux condenser, addition funnel and a mechanical stirrer was maintained under an oxygen-free, nitrogen atmosphere. The flask is charged with freshly cut sodium (60 g) and freshly cut potassium (12 g), and the flask is heated with a heat gun, forming the low-melting alloy. Dry benzene (1200 mL) is added, and the stirrer is operated at high speed until the alloy is dispersed and then at a slower speed for the remaining reaction time. The dispersion was kept at 25°C and diester **1** (21.4 g, 0.11 mol), and  $\text{Me}_3\text{SiCl}$  (87.6 g, 0.8 mol) was dissolved in dry benzene (100 mL) and added carefully through the addition funnel. After 20 hours with rapid stirring, the mixture was filtered through a plug of celite under an argon atmosphere and concentrated *in vacuo* to give a colourless oil of compound **2**. TLC (50%  $\text{CH}_2\text{Cl}_2$ /Hexane)  $R_f = 0.8$ ; Gas chromatography mass spectrometry (GCMS) ( $m/z$  (intensities)): 272 (100), 147 (44), 73 (85). The

oil was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (500 mL) at  $-78^\circ\text{C}$  under an  $\text{N}_2$  atmosphere, and  $\text{Br}_2$  (17.8 g, 1.1 mol) was added dropwise over a 5-minute period, and the reaction was allowed to warm to  $25^\circ\text{C}$ . The mixture was concentrated *in vacuo*. The product was purified by dry column vacuum chromatography (from heptane to EtOAc-heptane with 10% increments). Yield: 10.1 g, 72%; TLC (50%  $\text{CH}_2\text{Cl}_2$ /Hexane)  $R_f = 0.8$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$ 6.41 (s, 1H), 6.23 (s, 1H), 2.30 (s, 2H), 1.25 (s, 6H); GCMS (m/z (intensities)): 126 (35), 111 (100), 83 (45), 55 (45), 43 (50).

#### 2-(4-Bromophenyl)-2-hydroxy-4,4-dimethylcyclopentanone (4).

A flame-dried 50-mL round-bottom flask equipped with a rubber septum was added *p*-Dibromobenzene (3.54 g, 15 mmol) dissolved in a mixture of THF (30 mL) and diethyl ether (30 mL). *n*-Butyllithium (2.5 M in hexane, 6 mL, 15 mmol) was added dropwise using a syringe at  $-78^\circ\text{C}$  under a nitrogen atmosphere. After stirring under argon at  $-78^\circ\text{C}$  for an additional half an hour, 2-hydroxy ketone **3** (500 mg, 3.96 mmol) dissolved in dry diethyl ether (15 mL) was added dropwise using a syringe, then the mixture was allowed to reach room temperature over a period of 16 hours. The reaction mixture was quenched in ice water and extracted with ether ( $2 \times 50$  mL). The extracts were washed with brine (50 mL), dried with  $\text{MgSO}_4$  and evaporated to dryness *in vacuo*. Purification by dry column vacuum chromatography (from heptane to EtOAc-heptane with 5% increments, starting by washing with heptane) yielded: 860 mg, 76%; m.p. =  $94\text{--}95^\circ\text{C}$ ; TLC (50% EtOAc/Hexane)  $R_f = 0.9$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 400 MHz):  $\delta$ 7.51 (d, 2H,  $J = 8.8$  Hz), 7.30 (d, 2H,  $J = 8.8$  Hz), 3.89 (s, 1H), 2.40 (q, 2H,  $J = 16.8$  Hz), 2.17 (m, 2H), 1.23 (s, 3H), 1.16 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$ 217.2, 143.5, 131.4, 127.9, 120.9, 81.2, 53.5, 52.8, 33.1, 29.6, 28.9; GCMS (m/z (intensities)): 200 (97), 198 (100), 185 (52), 183 (55); Anal. Calcd. For  $\text{C}_{13}\text{H}_{15}\text{BrO}_2$ : C, 55.14; H, 5.35; Found: C, 54.16; H, 5.35.

#### 2-(4-Bromophenyl)-4,4-dimethylcyclopent-2-enone (5).

In a 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, a reflux condenser was added a solution of hydroxy-cyclopentanone **4** (3.0 g, 10.6 mmol) dissolved in toluene (120 mL) and  $\text{TsOH}\cdot\text{H}_2\text{O}$  (2.0 g, 10.8 mmol) was added. The mixture was heated to reflux for 40 minutes. The reaction mixture was allowed to cool to room temperature and then poured into 10% NaOH solution (100 mL) and extracted with diethyl ether ( $2 \times 50$  mL). The extracts were washed with brine (100 mL), dried with  $\text{MgSO}_4$  and evaporated to dryness *in vacuo*. Purification by dry column vacuum chromatography (from heptane to EtOAc-heptane with 10% increments) yielded: 2.0 g, 71%; m.p. =  $65\text{--}67^\circ\text{C}$ ; TLC (20% EtOAc/Hexane)  $R_f = 0.5$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$ 7.60 (d, 2H,  $J = 8.5$  Hz), 7.58 (s, 1H), 7.59 (d, 2H,  $J = 8.5$  Hz), 2.47 (s, 2H), 1.30 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  207.08, 168.25, 139.33, 131.76, 130.43, 128.97, 122.74, 51.62, 38.55, 28.43; GCMS (m/z (intensities)): 266 (53), 264 (55), 251 (42), 249 (44), 157 (40), 142 (100); Anal. Calcd. For  $\text{C}_{13}\text{H}_{13}\text{BrO}$ : C, 58.89; H, 4.94; Found: C, 58.65; H, 5.02.

#### 1,2-Bis(4-bromophenyl)-4,4-dimethylcyclopent-2-en-1-ol (6).

A flame-dried 50-mL round-bottom flask equipped with a rubber septum was added *p*-dibromobenzene (3.54 g, 15 mmol) dissolved in a mixture of dry THF (30 mL) and dry diethyl ether (30 mL). *n*-Butyllithium (2.5 M in hexanes, 5 mL, 1.3 mmol) was added dropwise using a syringe at  $-78^\circ\text{C}$  under a nitrogen atmosphere. After stirring under argon at  $-78^\circ\text{C}$  for an additional half hour, cyclopentenone **5** (1.00 g, 3.77 mmol) dissolved in dry diethyl ether (15 mL) was added dropwise using a syringe and then the mixture was allowed to reach room temperature over a period of 16 hours. The reaction mixture was quenched in a ice water (200 mL) and extracted with ether ( $2 \times 100$  mL). The extracts were washed with brine, dried with  $\text{MgSO}_4$  and evaporated to dryness *in vacuo*. Purification by dry column vacuum chromatography (from heptane to EtOAc-heptane with 50% increments, starting by washing with heptane) yielded: 1.2 g, 75%; m.p. =  $103\text{--}106^\circ\text{C}$ ; TLC (20% EtOAc/Hexane)  $R_f = 0.7$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 400 MHz):  $\delta$ 7.31 (d, 2H,  $J = 8.8$  Hz), 7.21 (m, 4H), 7.13 (d, 2H,  $J = 8.8$  Hz), 6.22, (s, 1H), 2.16 (d, 2H,  $J = 4.2$  Hz), 1.22 (s, 3H), 1.09 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$ 146.04, 143.41, 141.87, 132.96, 131.56, 131.51, 128.96, 127.37, 121.49, 120.71, 88.35, 77.58, 77.26, 76.94, 60.64, 42.90, 30.81, 29.11; GCMS (m/z(intensities)): 422 (45), 225 (54), 223 (58), 185 (98), 183 (100), 128 (64); Anal. Calcd. For  $\text{C}_{19}\text{H}_{18}\text{Br}_2\text{O}$ : C, 50.06; H, 4.30; Found: C, 50.09; H, 4.38.

#### 2,3-bis(*p*-bromophenyl)-5,5-dimethyl cyclopentadiene (7).

In a 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, a reflux condenser was added a solution of hydroxyl-cyclopentenone **6** (1.2 g, 2.4 mmol) dissolved in toluene (50 mL) and  $\text{TsOH}\cdot\text{H}_2\text{O}$  (480 mg, 2.5 mmol) was added. The mixture was heated to reflux for 40 minutes. The mixture were poured into 10% NaOH solution and extracted with diethyl ether ( $3 \times 50$  mL). The extracts were washed with brine (100 mL), dried with  $\text{MgSO}_4$  and evaporated to dryness *in vacuo*. Purification by dry column vacuum chromatography (heptane) yielded: 740 mg, 64%; m.p. =  $158\text{--}159^\circ\text{C}$ ; TLC (20% toluene/Hexane)  $R_f = 0.7$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$ 7.36 (d, 4H,  $J = 8.6$  Hz), 6.98 (d, 4H,  $J = 8.6$  Hz), 6.34 (s, 2H), 1.31 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$ 145.4, 140.4, 134.6, 130.6, 129.2, 120.4, 50.5, 21.9; GCMS (m/z(intensities)): 404 (100), 229 (58), 228 (52); Anal. Calcd. For  $\text{C}_{19}\text{H}_{16}\text{Br}_2$ : C, 56.47; H, 3.99; Found: C, 56.36; H, 4.03.

#### 5,6-bis(4-bromophenyl)-7,7-dimethylnorbornadiene-2,3-dicarboxylic acid (8).

Acetylenedicarboxylic acid (23 mg, 0.2 mmol) was added to a stirring solution of cyclopentadiene **7** (50 mg, 0.124 mmol) dissolved in toluene (20 mL). After stirring for 8 hours at reflux under an  $\text{N}_2$  atmosphere, the resulting colourless solution was concentrated *in vacuo*. The residue was subjected to dry column vacuum chromatography (from heptane to EtOAc-heptane with 10% increments) yielded light yellow crystals. Yield: 62 mg, 96%; m.p. =  $\sim 160^\circ\text{C}$  (decomp.); TLC (EtOAc)  $R_f = 0.1$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.22 (d,  $J =$

8.3, 2H), 7.03 (d,  $J = 8.3$ , 2H), 3.76 (s, 1H), 1.17 (d,  $J = 12.6$ , 2H), 1.04 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 101 MHz)  $\delta$  146.34, 135.93, 131.57, 129.10, 121.08, 80.32, 69.68, 21.73, 21.61, 6.42; Anal. Calcd. For  $\text{C}_{23}\text{H}_{18}\text{Br}_2\text{O}_4 + \frac{1}{2}\text{H}_2\text{O}$ : C, 52.40; H, 3.63; Found: C, 52.48; H, 3.59.

*Bis(4-bromophenyl)5,6-bis(4-bromophenyl)-7,7-dimethylnorbornadiene-2,3-dicarboxylate (9)*. A flame-dried 500 mL three-necked round-bottom flask equipped with a rubber septum and a reflux condenser was added bis(carboxylic acid) **8** (200 mg, 0.386 mmol) dissolved in dry  $\text{CH}_2\text{Cl}_2$  (40 mL). Oxalyl chloride (1.0 mL, 1.1 mmol) was added dropwise using a syringe followed by addition of DMF (cat. Amount 2 drops) at  $0^\circ\text{C}$  under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature over a period of 1 hour. The reaction mixture was transferred to a 50 mL round-bottom flask and evaporated to dryness *in vacuo* affording the desired crude acid chloride as a light yellow solid. The acid chloride was used immediately in the next step. To the crude acid chloride was added dry  $\text{CH}_2\text{Cl}_2$  (20 mL),  $\text{Et}_3\text{N}$  (2 mL) and 4-bromophenol (260 mg, 1.5 mmol), followed by addition of 4-dimethylamino-pyridine (DMAP, cat. Amount 2–4 mg). The mixture was stirred at room temperature for 1 hour and concentrated *in vacuo*. Purification by dry vacuum chromatography (from heptane to EtOAc with 1% increments) yielded a yellow powder. Yield: 240 mg, 74%. m.p. =  $296\text{--}298^\circ\text{C}$ ; TLC (20% EtOAc/Hexane)  $R_f = 0.8$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.40 (d, 4H,  $J = 8.6$  Hz), 7.33 (d, 4H,  $J = 8.6$  Hz), 7.12 (d, 4H,  $J = 8.5$  Hz), 6.90 (d, 4H,  $J = 8.5$  Hz), 3.89 (s, 2H), 1.37 (s, 3 H), 1.35 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  162.8, 150.8, 149.0, 145.7, 134.9, 132.5, 131.8, 128.8, 123.1, 121.7, 119.3, 81.9, 69.2, 29.6, 22.6; Anal. Calcd. For  $\text{C}_{35}\text{H}_{24}\text{Br}_4\text{O}_4$ : C, 50.76; H, 2.92; Found: C, 50.52; H, 3.03; MS (MALDI(TOF))  $m/z$ : calculated for  $\text{C}_{35}\text{H}_{24}\text{Br}_4\text{O}_4 + \text{H}_3\text{O}^+$ : 847.2, found: 847.7.

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### Competing Interests

We declare that we have no conflicts of interest with the industry.

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