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First synthesis of nitro-substituted 2,2-diphenyl-2*H*-1-benzopyrans via the *ipso*-nitration reaction

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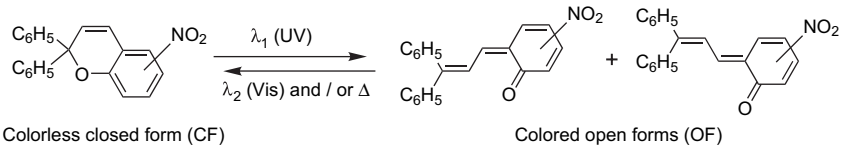
Abstract—The first synthesis of a series of nitro-substituted 2,2-diphenyl-2*H*-1-benzopyrans is reported. Our synthetic approach is based on a linear synthesis in two steps from appropriate brominated 2,2-diphenyl-2*H*-1-benzopyrans **12**–**17**, which requires the preliminary preparation of bromophenols **7**–**11**. These latter were easily obtained by the reaction of phenols **1**–**5** with a mild and selective brominating agent tetrabutylammonium tribromide (TBA·Br_3). The key intermediates **12**–**17** were efficiently elaborated through an univocal classic chromenization between the commercially available 1,1-diphenyl-2-yn-1-ol and the brominated phenols **6**–**11**. The compounds **12**–**17** so obtained were converted into arylboronic acids **18**–**23** by a metalation/boronylation sequence, followed by acid hydrolysis. From advanced building blocks **18**–**23**, the introduction of nitro group, which constitutes the ultimate step of our strategy, was achieved by an *ipso*-nitration reaction using the Crivello's reagent. This highly selective method provides only the *ipso*-nitrated products **24**–**29** in moderate to high yield.

1. Introduction

In the last decades, a renewal of interest in the design and the synthesis of 2*H*-1-benzopyrans (chromenes) has been observed due to their industrial applications for variable optical transmission materials (ophthalmic glasses and lenses)[1] and their novel applications in emerging optoelectronic and photonic technologies.[2] The photochromic properties of the 2*H*-chromene structure arise from an equilibrium between a closed form and a set of open forms (photomerocyanines).[3] The initial closed form (CF) absorbs in the UV region and, through excited intermediates, gives cleavage of the Csp^3–O bond and isomerization. It leads to different stereoisomers of quasi-planar opened form (OF) absorbing in the visible range. Both opened isomers are thermally instable and the visible light stimulates photobleaching, leading to the initial closed form[4] as depicted in Scheme 1.

The spirocarbon atom can change reversibly its hybridization from sp^3 to sp^2, allowing or stopping the electron flow between different parts of the molecular system. This concomitant electronic change, transforming an unconjugated off-state to a conjugated on-state, can be used to control and modulate the physical properties of organic molecular material, which depend on the conjugation state. Thus, the photochromic system working through an external light stimulus can be the basic unit for a molecular switch.[5] Each individual chromene constitutes attractive building blocks for the design and the synthesis of molecular switches at a meso or macroscopic scale. The incorporation of photochromic units into such macromolecular architectures requires the preliminary preparation of functionalized individual photochromic sections. Organic chemist must have outstanding synthetic tools at its disposal to introduce various functionalizations into photochromic skeleton. In this context, we have previously



Scheme 1. Photochromic equilibrium for 2*H*-1-benzopyrans.

Keywords: Heterocycles; Synthesis design; *ipso*-Nitration; Photochromism.
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demonstrated that the palladium-catalyzed cross-coupling reactions could be successfully applied to [2*H*]-chromenes.[6] Surprisingly, to the best of our knowledge, the introduction of a nitro group into the benzopyran or naphthopyran part has never been investigated. This unsolved synthetic problem is undoubtedly attributable to the lack of regioselectivity, harshness of nitration reaction conditions. The classical nitration methods are not suitable.[7] They led very often to the formation of various tarry by-products.

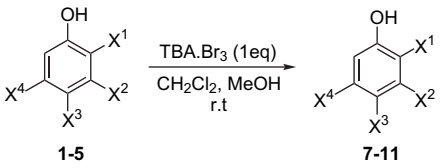
Herein, we report the first synthesis of a series of nitro-substituted 2,2-diphenyl-2*H*-1-benzopyrans. The introduction of a nitro group into different positions of the benzopyranic part has been achieved. The resolution of this challenging synthetic problem opens new perspectives towards improvements in photochromic properties of benzopyrans.

2. Results and discussion

Commonly, two synthetic methods are used for the building of the 2,2-diphenyl-2*H*-1-benzopyrans. The usual approach is based on a 'one-pot reaction' between an appropriate phenol and the commercially available 1,1-diphenyl-2-yn-1-ol.[8] This condensation takes place in an apolar solvent (CH_2Cl_2, toluene) under acid catalysis (PTSA,[9] PPTS[6c,10]). The reaction proceeds via a Claisen-like [3,3]-sigmatropic rearrangement of alkynyl aryl ether, resulting from phenol 'O-alkylation', which is followed by enolization and a [1,5]-sigmatropic H-shift. An electrocyclization completes the process. The second method involves the reaction of the α,β-unsaturated aldehyde with titanium(IV) salts of phenols[11] leading to the C-alkylation in a *ortho*-position; subsequent electrocyclization yields the 2*H*-1-benzopyran moiety. In the beginning of our investigations relating to the preparation of the 2,2-diphenyl-6-nitro-2*H*-1-benzopyran, these two synthetic methods have been tested: the 4-nitrophenol was reacted with the commercially available 1,1-diphenyl-2-yn-1-ol and the β-phenylcinnamaldehyde, respectively (Scheme 2).

In both cases, no positive result was obtained even with extended reaction time. Only unchanged starting materials were recovered. The strong electron-withdrawing property of the nitro group deactivates the phenol. Its nucleophilic character is totally inhibited. In view of these disappointing results, it became apparent that introduction of the nitro group must occur after formation of the chromenic structure. Thus, we designed the retrosynthetic analysis depicted in Scheme 3.

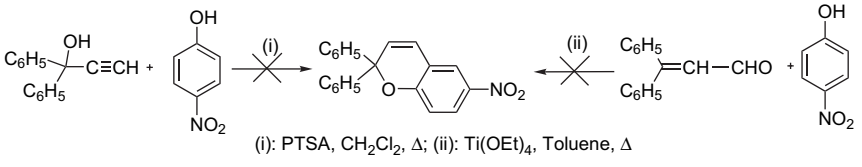
The adopted synthetic strategy began with the synthesis of the brominated chromenes **12–17**, which were submitted to a metalation/boronylation sequence, followed by acidic hydrolysis to furnish the advanced boronic acids **18–23**. Finally, the introduction of the nitro group should be realized by an *ipso*-nitration reaction, which completes the retrosynthetic approach. The overall synthetic procedure from **12–17** to **24–29** exhibits three different reaction types. Synthesis of the brominated chromenes **12–17** requires the preliminary preparation of the suitable brominated phenols **7–11**. Conversion of phenols **1–5** into their brominated homologues **7–11** was achieved using a mild and selective brominating agent: tetrabutylammonium tribromide ($TBA\cdot Br_3$)[12] (Scheme 4).



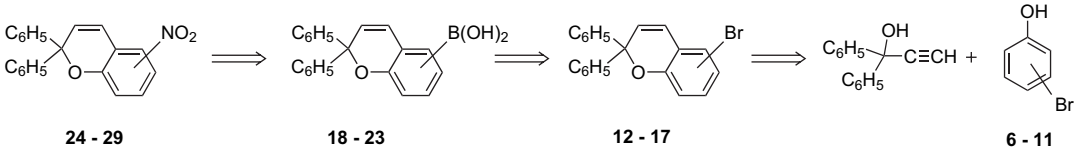
Scheme 4.

The reaction of commercial phenols **1–5** with a molar quantity of $TBA\cdot Br_3$, in dichloromethane–methanol solution, for 1 h, at room temperature, gave selectively the expected monobromophenols **7–11**.[13] This very simple procedure for bromination of phenols proceeded rapidly and smoothly. The active species, which generates Br^+ is presumably methyl hypobromite produced from the reaction of $TBA\cdot Br_3$ with methanol.[13b,14] The isolated yields are good to excellent ranging from 88 to 98%, after recrystallization from methanol–water. The results are summarized in Table 1.

The commercially available 4-bromophenol **6** and the previous monobrominated phenols **7–11** were subsequently involved in the standard chromenization procedure as outlined in Scheme 5.



Scheme 2. Two classic procedures for the synthesis of benzopyranic structures.

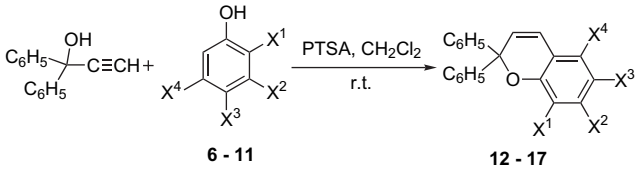


Scheme 3. Retrosynthetic analysis.

Table 1. Preparation of the monobrominated phenols

Entry	X^1	X^2	X^3	X^4	Bromination (yield %)[a]
1	CH_3	H	Br	H	**7** (93)
2	CH_3	CH_3	Br	H	**8** (93)
3	CH_3	H	Br	CH_3	**9** (98)
4	Br	H	CH_3	CH_3	**10** (97)
5	H	CH_3	Br	CH_3	**11** (88)

[a] All the yields are for pure, isolated products.



Scheme 5. Preparation of the chromenic key intermediates **12–17**.

The photochromic compounds **12–17** were obtained in satisfactory yield varying from 54 to 85% (Table 2), from condensation of suitable monobrominated phenols **6–11** with the commercially available 1,1-diphenyl-2-yn-1-ol. The reaction was carried out in dichloromethane, at room temperature in the presence of a catalytic amount of PTSA. The reaction was monitored by TLC and was stopped when the starting brominated phenol was consumed.

Halide-metal exchange of the brominated benzopyrans **12–17** with 2 equiv of *n*-BuLi at −40 °C in dry THF,[15] afforded the corresponding lithium species, which were transmetalated at −90 °C with an excess of tributylborate (Scheme 6).

During acidic workup, the resulting crude boronic esters, not isolated, were hydrolysed to give the corresponding boronic acids[16] **18–23** in 35–89% yield. The results are reported in Table 3.

After the successful synthesis of advanced intermediates **18–23**, our attention turned towards the introduction of the nitro group, which constitutes the ultimate step of our retrosynthetic approach (Scheme 3). The replacement of boronic acid group with nitro group was accomplished by *ipso*-nitration reaction.[17] In this context, two methods were recently reported. The first one was based on the use of Crivello's reagent[18] ($NH_4NO_3/(CF_3CO)_2O$).[19] The second involved the system $AgNO_3/(CH_3)_3SiCl$.[20] We applied the first methodology, for which trifluoroacetylnitrate seems to be the reactive nitrating agent. The typical procedure of nitration began with the preparation of nitrating agent: trifluoroacetic anhydride was slowly and carefully added to a mixture of ammonium nitrate (1.1 equiv) in acetonitrile, with vigorous stirring until all solids had dissolved. The boronic acid (1 equiv) **18–23**, previously dissolved in acetonitrile in the presence of trifluoroacetic anhydride, was reacted with the prepared nitrating agent at −35 °C, to give only one compound: the desired *ipso*-nitrated product **24–29** (Scheme 7). Considering the high oxophilicity of boron, the intermediate active nitrating agent interacted electronically with the boronic acid group, favouring the nitration at the *ipso*-position.

Table 2. Yields in the synthesis of brominated 2,2-diphenyl-2*H*-1-benzopyrans **12–17**

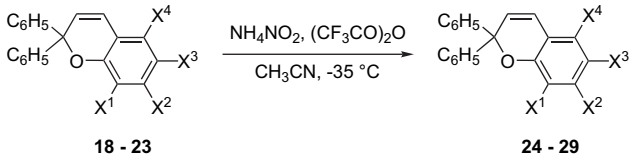
Entry	Starting brominated phenol	Chromenisation (yield %)[a]	X^1	X^2	X^3	X^4
1	**6**	**12** (74)	H	H	Br	H
2	**7**	**13** (69)	CH_3	H	Br	H
3	**8**	**14** (71)	CH_3	CH_3	Br	H
4	**9**	**15** (85)	CH_3	H	Br	CH_3
5	**10**	**16** (54)	Br	H	CH_3	CH_3
6	**11**	**17** (76)	H	CH_3	Br	CH_3

[a] All the yields are for pure, isolated products.

Table 3. Yields in the preparation of boronic acids **18–23**

Entry	Starting brominated phenol	Boronation reaction (yield %)[a]	X^1	X^2	X^3	X^4
1	**12**	**18** (79)	H	H	$B(OH)_2$	H
2	**13**	**19** (89)	CH_3	H	$B(OH)_2$	H
3	**14**	**20** (77)	CH_3	CH_3	$B(OH)_2$	H
4	**15**	**21** (67)	CH_3	H	$B(OH)_2$	CH_3
5	**16**	**22** (65)	$B(OH)_2$	H	CH_3	CH_3
6	**17**	**23** (35)	H	CH_3	$B(OH)_2$	CH_3

[a] All the yields are for pure, isolated products.

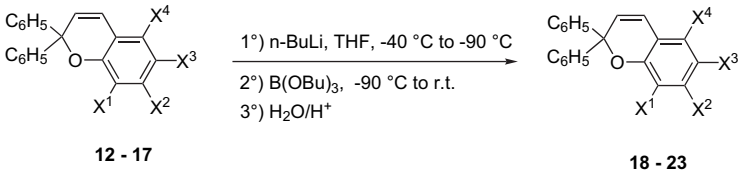


Scheme 7.

After purification by silica gel chromatography, the yields in isolated compounds were moderated to good (32–80%). The results are reported in Table 4. It is noteworthy that in all cases, we observed the complete absence of dinitroproducts.

3. Conclusion

In conclusion, we have described the first efficient and highly selective synthesis of a series of nitro-substituted 2,2-diphenyl-2*H*-1-benzopyrans **24–29** in two steps, starting from their brominated homologues **12–17**, which were



Scheme 6.

Table 4. Yields of *ipso*-nitration: target molecules **24–29**

Entry	Starting boronic acid	*ipso*-Nitrated product (yield %)[a]	X^1	X^2	X^3	X^4
1	**18**	**24** (49)	H	H	NO_2	H
2	**19**	**25** (71)	CH_3	H	NO_2	H
3	**20**	**26** (80)	CH_3	CH_3	NO_2	H
4	**21**	**27** (61)	CH_3	H	NO_2	CH_3
5	**22**	**28** (52)	NO_2	H	CH_3	CH_3
6	**23**	**29** (32)	H	CH_3	NO_2	CH_3

[a] All the yields are for pure, isolated products.

initially obtained by a classical chromenization between the commercially available 1,1-diphenyl-2-yn-1-ol and various brominated phenols **6–11**. These key intermediates were subsequently converted into boronic acids **18–23** by a metalation/boronylation sequence, followed by acidic hydrolysis. We have successfully carried out regioselective electrophilic nitration reaction of these key buildings blocks, using the Crivello's reagent, which constitutes the key step of our strategy. The operative conditions were fully compatible with the benzopyranic structure. The introduction of the nitro group takes place exclusively at the *ipso*-position of the arylboronic acids.

4. Experimental section

4.1. General remarks

Melting points were determined in capillary tubes on a Buchi 510 apparatus and are uncorrected. Glassware used in the reactions described below was dried for a minimum of 12 h in an oven at 120 °C. All the reactions were performed in standard glassware under an inert atmosphere of Ar. Fourier transform IR spectra were recorded on a Matson Polaris spectrophotometer from samples as KBr pellets or as solutions in CCl_4. The frequencies of band positions are given in cm^{-1}. Nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded on either a Bruker AC250 (250 and 62.5 MHz, respectively) or a Bruker Avance-DPX300 (300 and 75 MHz, respectively) spectrometer. Chemicals shifts are reported in parts per million (δ) relative to the nondeuterated solvent peak. Coupling constants (J values) are expressed in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), br s (broad singlet). Elemental analyses were performed on an LECO-932-CNS analyzer. Column chromatography was carried out using silica gel 60 230–400 mesh (Merck & Co.). Silica TLC was conducted on precoated aluminium sheets (60 F_{254}) with a 0.2 mm thickness (Aldrich Chemical Co.).

4.2. Chemicals

THF was distilled prior to use from sodium benzophenone ketyl under argon, while dichloromethane (CH_2Cl_2) was distilled from calcium hydride, and stored over 3 Å molecular sieves. Acetonitrile and methanol were purchased from S.D.S. Chemicals Co. and are used as supplied. Tetrabutylammonium tribromide ($TBA\cdot Br_3$) was commercially available from Aldrich, and was used as received. All starting phenols were obtained from commercial sources, and used without further purification. 2-Methylphenol (**1**) was purchased from Avocado. 2,3-Dimethylphenol (**2**) and 3,5-dimethylphenol (**5**) were purchased from Lancaster and Fluka, respectively. 2,5-Dimethylphenol (**3**), 3,4-dimethylphenol (**4**) and 4-bromophenol (**6**) were purchased from Aldrich Chemical Co. Brominated phenols (**7–11**) have been described before.[13]

4.3. General procedure (1) of 'chromenization' for the synthesis of compounds 12–17

A 50 mL round-bottomed flask was charged with 1,1-diphenylprop-2-yn-1-ol (2.46 g, 11 mmol), the appropriate bromophenol (10 mmol), a catalytic amount of *p*-toluene sulfonic acid (PTSA) and dry dichloromethane (20 mL), purged with argon and stirred at room temperature for 6–10 h. The progress of the reaction was monitored by TLC (pentane/Et_2O, 1:1). After complete disappearance of the bromophenol, the reaction mixture was washed with brine (3×20 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated to dryness under reduced pressure.

The crude material was purified by column chromatography (SiO_2, cyclohexane/dichloromethane gradient 100:0 to 50:50). Data of the individual compounds are given below.

4.3.1. 6-Bromo-2,2-diphenyl-2*H*-1-benzopyran (12). This compound was obtained by general procedure (1), from the commercially available 4-bromophenol **6** (1.73 g, 10 mmol) and 1,1-diphenylprop-2-yn-1-ol (2.46 g, 11 mmol). The product **12** was isolated as a light yellow solid (2.69 g, 7.40 mmol, 74%). Mp 125–126 °C; ^1H NMR (250 MHz, $CDCl_3$): δ=6.13 (d, J=10.0 Hz, 1H), 6.47 (d, J=10.0 Hz, 1H), 6.72 (d, J=7.5 Hz, 1H), 7.04 (d, J=2.5 Hz, 1H), 7.12 (dd, J=2.5, 7.5 Hz, 1H), 7.15–7.35 (m, 10H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=82.9 (OC), 113.2 (C), 118.3 (CH═), 122.4 (CH═), 123.0 (C), 127.0 (4×CH═), 127.7 (2×CH═), 128.2 (4×CH═), 129.0 (CH═), 130.2 (CH═), 132.0 (CH═), 144.4 (2×C), 151.6 (C). Anal. Calcd for $C_{21}H_{15}BrO$: C, 69.43; H, 4.16; Br, 21.99. Found: C, 69.52; H, 4.23; Br, 22.01. FTIR (KBr): ν=3055, 3026, 2968, 2924, 1629, 1597, 1472, 1446, 1416, 1265, 1242, 1212, 1163, 1128, 1053, 993, 945, 915, 876, 816, 767, 752, 701, 558 cm^{-1}.

4.3.2. 6-Bromo-2,2-diphenyl-8-methyl-2*H*-1-benzopyran (13). This compound was obtained by general procedure (1), from 4-bromo-2-methylphenol **7** (1.87 g, 10 mmol) and 1,1-diphenylprop-2-yn-1-ol (2.46 g, 11 mmol). The product **13** was isolated as a white solid (2.60 g, 6.89 mmol, 69%). Mp 73–74 °C; ^1H NMR (250 MHz, $CDCl_3$): δ=2.17 (s, 3H), 6.09 (d, J=10.0 Hz, 1H), 6.46 (d, J=10.0 Hz, 1H), 6.89 (d, J=2.5 Hz, 1H), 7.00 (d, J=2.5 Hz, 1H), 7.12–7.41 (m, 10H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=15.6 (CH_3), 82.7 (OC), 112.6 (C), 122.5 (C), 122.9 (CH═), 126.7 (CH═), 126.8 (4×CH═), 127.6 (2×CH═), 127.8 (C), 128.2 (4×CH═), 129.7 (CH═), 133.2 (CH═), 144.8 (2×C), 149.5 (C). Anal. Calcd for $C_{22}H_{17}BrO$: C, 70.04; H, 4.54; Br, 21.18. Found: C, 69.97; H, 4.48; Br, 21.17. FTIR (KBr): ν=3085, 3054, 3023, 2990, 2963, 2919, 2848, 1636, 1597, 1570, 1491, 1462, 1446, 1381, 1232, 1212, 1170, 1096, 1055, 994, 908, 862, 767, 757, 715, 697, 564 cm^{-1}.

4.3.3. 6-Bromo-7,8-dimethyl-2,2-diphenyl-2*H*-1-benzopyran (14). This compound was obtained by general procedure (1), from 4-bromo-2,3-dimethylphenol **8** (2.01 g, 10 mmol) and 1,1-diphenylprop-2-yn-1-ol (2.46 g, 11 mmol). The product **14** was isolated as a white solid (2.78 g, 7.1 mmol, 71%). Mp 116–117 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.20 (s, 3H), 2.22 (s, 3H), 6.05 (d, J=10.0 Hz, 1H), 6.45 (d, J=10.0 Hz, 1H), 6.99 (s, 1H), 7.12–7.37 (m, 10H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=12.9 (CH_3), 20.0 (CH_3), 82.7 (OC), 116.3 (C), 120.3 (C), 123.0 (CH═), 126.1 (C), 126.8 (4×CH═), 127.0 (CH═), 127.5 (2×CH═), 128.1 (4×CH═), 129.0 (CH═), 137.3 (C), 145.0 (2×C), 149.3 (C). Anal. Calcd for $C_{23}H_{19}BrO$: C, 70.59; H, 4.89; Br, 20.42. Found: C, 70.65; H, 4.93; Br, 20.52. FTIR (KBr): ν=3059, 3026, 2922, 2848, 1639, 1598, 1488, 1446, 1412, 1376, 1231, 1171, 1101, 1050, 971, 941, 906, 881, 766, 755, 714, 696, 506 cm^{-1}.

4.3.4. 6-Bromo-5,8-dimethyl-2,2-diphenyl-2*H*-1-benzopyran (15). This compound was obtained by general procedure (1), from 4-bromo-2,5-dimethylphenol **9** (2.01 g, 10 mmol) and 1,1-diphenylprop-2-yn-1-ol (2.46 g, 11 mmol). The product **15** was isolated as a white solid (3.33 g, 8.51 mmol, 85%). Mp 153–154 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.25 (s, 3H), 2.35 (s, 3H), 6.21 (d, J=10.0 Hz, 1H), 6.84 (d, J=10.0 Hz, 1H), 7.18 (br s, 1H), 7.21–7.46 (m, 10H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=15.5 (CH_3), 18.1 (CH_3), 81.6 (OC), 116.2 (C), 120.9 (C), 121.4 (CH═), 125.2 (C), 126.7 (4×CH═), 127.5 (2×CH═), 128.1 (4×CH═), 129.3 (CH═), 130.8 (C), 133.7 (CH═), 144.9 (2×C), 149.8 (C). FTIR (KBr): ν=3060, 3024, 2952, 2921, 2853, 1625, 1593, 1493, 1450, 1380, 1364, 1236, 1230, 1203, 1168, 1095, 1062, 1031, 970, 907, 864, 770, 754, 700, 573 cm^{-1}. Anal. Calcd for $C_{23}H_{19}BrO$: C, 70.59; H, 4.89; Br, 20.42. Found: C, 70.56; H, 4.79; Br, 20.48.

4.3.5. 8-Bromo-5,6-dimethyl-2,2-diphenyl-2*H*-1-benzopyran (16). This compound was obtained by general procedure (1), from 2-bromo-4,5-dimethylphenol **10** (2.01 g, 10 mmol) and 1,1-diphenylprop-2-yn-1-ol (2.46 g, 11 mmol). Product **16** was isolated as a light yellow solid (2.11 g, 5.4 mmol, 54%). Mp 97–98 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.10 (s, 3H), 2.23 (s, 3H), 6.23 (d, J=10.0 Hz, 1H), 6.74 (d, J=10.0 Hz, 1H), 7.06 (br s, 1H), 7.09–7.28 (m, 6H), 7.38–7.48 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=14.5 (CH_3), 19.6 (CH_3), 82.1 (OC), 107.6 (C), 121.2 (CH═), 121.6 (C), 126.7 (4×CH═), 127.4 (2×CH═), 128.1 (4×CH═), 129.8 (CH═), 130.7 (C), 131.8 (C), 133.2 (CH═), 144.7 (2×C), 147.4 (C). Anal. Calcd for $C_{23}H_{19}BrO$: C, 70.59; H, 4.89; Br, 20.42. Found: C, 70.43; H, 4.75; Br, 20.45. FTIR (KBr): ν=3055, 3024, 2969, 2920, 2857, 1620, 1489, 1448, 1368, 1271, 1231, 1190, 1056, 978, 951, 907, 750, 699, 572 cm^{-1}.

4.3.6. 6-Bromo-5,7-dimethyl-2,2-diphenyl-2*H*-1-benzopyran (17). This compound was obtained by general procedure (1), from 4-bromo-3,5-dimethylphenol **11** (2.01 g, 10 mmol) and 1,1-diphenylprop-2-yn-1-ol (2.46 g, 11 mmol). Product **17** was isolated as a white solid (2.97 g, 7.59 mmol, 76%). Mp 109–110 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.25 (s, 3H), 2.31 (s, 3H), 6.10 (d, J=10.0 Hz, 1H), 6.67 (s, 1H), 6.75 (d, J=10.0 Hz, 1H), 7.13–7.38 (m, 10H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=18.9 (CH_3), 24.4 (CH_3), 81.8 (OC), 116.8 (CH═), 118.9 (C), 121.0 (CH═), 126.6 (C), 127.0 (4×CH═), 127.5 (2×CH═), 128.1 (4×CH═), 128.8 (CH═), 133.8 (C), 139.1 (C), 144.7 (2×C), 151.3 (C). Anal. Calcd for $C_{23}H_{19}BrO$: C, 70.59; H, 4.89; Br, 20.42. Found: C, 70.52; H, 4.79; Br, 20.45. FTIR (KBr): ν=3058, 3024, 2919, 2850, 1626, 1600, 1489, 1446, 1391, 1308, 1227, 1190, 1176, 1153, 1073, 1029, 960, 911, 851, 766, 752, 699, 555 cm^{-1}.

4.4. General procedure (2) for the synthesis of boronic acids 18–23

A stirred solution of the appropriate brominated benzopyran (2.75 mmol) in anhydrous THF (20 mL) under an Ar atmosphere was cooled to −40 °C. A 2.5 M solution of *n*-BuLi in hexane (2.2 mL, 5.5 mmol) was added dropwise over 10 min and stirring was continued for 2 h at −40 °C. The resulting solution was cooled to −90 °C and tributylborate (2.3 mL, 8.26 mmol) was added at once via a syringe. The resulting mixture was maintained at −90 °C for 1 h, then allowed to warm to room temperature. The reaction was quenched by the addition of 1 N aqueous HCl solution (20 mL) and extracted with Et_2O (3×40 mL). The combined organic layers were dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure to give a crude residue, which was subjected to column chromatography (SiO_2; eluent: cyclohexane/ethyl acetate gradient 100:0 to 70:30) to afford the pure desired product. The data for the individual compounds are given below.

Boronic acids in general present a host of difficulties with regard to analysis. The principal difficulty is their spontaneous condensation to boroxines to varying degrees.[21]

The strong O–B signal at 1310–1380 cm^{-1} is usually visible, but not as clearly as for monoboronic acids.[22]

As a consequence of incomplete decoupling of the B–C spin–spin coupling by ^{11}B (or ^{10}B) quadrupolar relaxation,[23] the signal of carbon bonded to the boron atom, which should be very broad, was not observed.

4.4.1. 6-Dihydroxyborane-2,2-diphenyl-2*H*-1-benzopyran (18). This compound was obtained by general procedure (2), starting from **12** (1 g, 2.75 mmol). The product **18** was isolated as a white solid (713 mg, 2.17 mmol, 79%). Mp>260 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.19 (d, J=9.9 Hz, 1H), 6.73 (d, J=9.9 Hz, 1H), 7.00 (d, J=8.1 Hz, 1H), 7.26 (tt, J=1.5, 8.3 Hz, 2H), 7.33 (dd, J=1.5, 7.0 Hz, 4H), 7.44 (dd, J=7.0, 8.3 Hz, 4H), 7.81 (d, J=1.5 Hz, 1H), 7.96 (dd, J=1.5, 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=83.2 (OC), 116.2 (CH═), 120.5 (C), 123.3 (CH═), 127.0 (4×CH═), 127.6 (2×CH═), 128.2 (4×CH═), 128.6 (CH═), 134.3 (CH═), 137.6 (CH═), 144.7 (2×C), 156.5 (C). FTIR (KBr): ν=3054, 1646, 1612, 1577, 1510, 1475, 1445, 1338, 1253, 1124, 1089, 981, 932, 906, 832, 749, 693 cm^{-1}.

4.4.2. 6-Dihydroxyborane-2,2-diphenyl-8-methyl-2*H*-1-benzopyran (19). This compound was obtained by general procedure (2), starting from **13** (1.04 g, 2.75 mmol). The product **19** was isolated as a white solid (838 mg, 2.45 mmol, 89%). Mp>260 °C; ^{1}H NMR (300 MHz,

$CDCl_3$): δ=2.37 (s, 3H), 6.17 (d, J=9.9 Hz, 1H), 6.77 (d, J=9.9 Hz, 1H), 7.15–7.55 (m, 10H), 7.79 (d, J=2.3 Hz, 1H), 7.92 (d, J=2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.8 (CH_3), 83.0 (OC), 120.1 (C), 123.8 (CH═), 125.0 (C), 126.8 (4×CH═), 127.5 (2×CH═), 128.1 (5×CH═), 132.2 (CH═), 138.6 (CH═), 145.2 (2×C), 154.5 (C). FTIR (KBr): ν=3058, 2969, 2920, 1637, 1598, 1489, 1445, 1381, 1338, 1207, 1167, 1102, 1055, 987, 905, 735, 695 cm^{-1}.

4.4.3. 6-Dihydroxyborane-7,8-dimethyl-2,2-diphenyl-2*H*-1-benzopyran (20). This compound was obtained by general procedure (2), starting from **14** (1.07 g, 2.75 mmol). The product **20** was isolated as a white solid (754 mg, 2.12 mmol, 77%). Mp>260 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.29 (s, 3H), 2.63 (s, 3H), 6.11 (d, J=9.6 Hz, 1H), 6.67 (d, J=9.6 Hz, 1H), 7.25 (tt, J=1.5, 8.5 Hz, 2H), 7.31 (dd, J=1.5, 7.0 Hz, 4H), 7.45 (dd, J=7.0, 8.5 Hz, 4H), 7.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.7 (CH_3), 19.0 (CH_3), 83.1 (OC), 117.7 (C), 123.9 (CH═), 124.4 (C), 126.8 (4×CH═), 127.2 (CH═), 127.4 (2×CH═), 128.1 (4×CH═), 133.4 (CH═), 145.4 (2×C), 147.2 (C), 153.5 (C). FTIR (KBr): ν=3059, 3027, 2923, 1632, 1598, 1569, 1445, 1379, 1326, 1217, 1167, 1098, 965, 907, 739, 696, 638 cm^{-1}.

4.4.4. 6-Dihydroxyborane-5,8-dimethyl-2,2-diphenyl-2*H*-*1*-benzopyran (21). This compound was obtained by general procedure (2), starting from **15** (1.07 g, 2.75 mmol). The product **21** was isolated as a white solid (656 mg, 1.84 mmol, 67%). Mp>260 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.31 (s, 3H), 2.69 (s, 3H), 6.19 (d, J=10.1 Hz, 1H), 6.95 (d, J=10.1 Hz, 1H), 7.23 (tt, J=1.5, 8.5 Hz, 2H), 7.31 (dd, J=1.5, 7.0 Hz, 4H), 7.45 (dd, J=7.0, 8.5 Hz, 4H), 7.79 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.9 (CH_3), 17.1 (CH_3), 81.9 (OC), 119.6 (C), 121.1 (CH═), 122.3 (C), 126.8 (4×CH═), 127.4 (2×CH═), 127.9 (CH═), 128.1 (4×CH═), 139.9 (CH═), 140.5 (C), 145.3 (2×C), 154.0 (C). FTIR (KBr): ν=3059, 3026, 2921, 2854, 1632, 1573, 1447, 1390, 1372, 1322, 1219, 1167, 1067, 1022, 969, 906, 739, 695, 638 cm^{-1}.

4.4.5. 8-Dihydroxyborane-5,6-dimethyl-2,2-diphenyl-2*H*-1-benzopyran (22). This compound was obtained by general procedure (2), from **16** (1.07 g, 2.75 mmol). The product **22** was isolated as a white solid (637 mg, 1.79 mmol, 65%). Mp>260 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.18 (s, 3H), 2.22 (s, 3H), 6.12 (d, J=10.1 Hz, 1H), 6.88 (d, J=10.1 Hz, 1H), 7.20–7.40 (m, 10H), 7.45 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.9 (CH_3), 19.7 (CH_3), 83.0 (OC), 118.9 (C), 120.9 (CH═), 127.0 (4×CH═), 127.8 (2×CH═), 128.1 (CH═), 128.4 (4×CH═), 129.6 (C), 136.7 (C), 137.1 (CH═), 144.1 (2×C), 156.0 (C). FTIR (KBr): ν=3500–3100, 3058, 2957, 2922, 2854, 1647, 1595, 1490, 1443, 1391, 1326, 1256, 1219, 1053, 934, 904, 758, 734, 699 cm^{-1}.

4.4.6. 6-Dihydroxyborane-5,7-dimethyl-2,2-diphenyl-2*H*-1-benzopyran (23). This compound was obtained by general procedure (2), starting from **17** (1.07 g, 2.75 mmol). The product **23** was isolated as a white powder (343 mg, 0.962 mmol, 35%). Mp>260 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.26 (s, 3H), 2.29 (s, 3H), 6.12 (d, J=10.0 Hz, 1H), 6.63 (s, 1H), 6.87 (d, J=10.0 Hz, 1H), 7.24 (tt, J=1.7, 8.4 Hz, 2H), 7.30 (dd, J=6.9, 8.4 Hz, 4H), 7.40 (dd, J=1.7, 6.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.2 (CH_3), 21.4 (CH_3), 81.9 (OC), 115.0 (CH═), 117.0 (C), 120.4 (CH═), 127.0 (4×CH═), 127.4 (CH═), 127.5 (2×CH═), 128.1 (4×CH═), 135.5 (C), 141.0 (C), 145.2 (2×C), 152.5 (C). FTIR (KBr): ν=3480–3104, 3085, 3058, 3025, 2956, 2919, 2850, 1632, 1613, 1596, 1562, 1491, 1462, 1446, 1372, 1313, 1224, 1160, 1141, 1092, 1073, 1031, 979, 941, 907, 844, 756, 723, 696 cm^{-1}.

4.5. General procedure (3) for the synthesis of nitrated compounds 24–29

A 50 mL two-necked flask equipped with a magnetic stirrer was charged with boronic acid (1 mmol) and dry acetonitrile (20 mL), purged with argon, and cooled to −35 °C. With rapid stirring, trifluoroacetic anhydride (1 mL) was added dropwise over 10 min with a syringe. Stirring was continued at −35 °C. Under argon atmosphere, in a separate flask, ammonium nitrate (88 mg, 1.1 mmol) and dry acetonitrile (10 mL) were mixed and the resulting mixture was cooled to 0 °C. To this vigorously stirred suspension, trifluoroacetic anhydride (6–8 mL) was carefully and slowly added until all solids had dissolved. The nitrating agent, thus prepared, was transferred by syringe into the reaction flask within 10 min. Stirring was continued for 2 h at −35 °C and the reaction mixture was allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue was diluted with Et_2O (30 mL). The resulting mixture was washed with water (2×20 mL) and brine (3×20 mL), dried with $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The crude material was purified by column chromatography (SiO_2; eluent: cyclohexane/Et_2O gradient 100:0 to 70:30) to yield the *ipso*-nitrated product.

4.5.1. 2,2-Diphenyl-6-nitro-2*H*-1-benzopyran (24). This compound was obtained by general procedure (3), starting from **18** (328 mg, 1 mmol). The product **24** was isolated as a white powder (162 mg, 0.49 mmol, 49%). Mp 134 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.30 (d, J=9.9 Hz, 1H), 6.67 (d, J=9.9 Hz, 1H), 6.97 (d, J=8.8 Hz, 1H), 7.24–7.41 (m, 10H), 7.94 (d, J=2.7 Hz, 1H), 8.04 (dd, J=2.7, 8.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=84.5 (OC), 116.8 (CH═), 120.9 (C), 121.8 (CH═), 122.4 (CH═), 125.6 (CH═), 126.9 (4×CH═), 128.1 (2×CH═), 128.4 (4×CH═), 130.7 (CH═), 142.0 (C), 143.9 (2×C), 158.0 (C). Anal. Calcd for $C_{21}H_{15}NO_3$: C, 76.53; H, 4.59; N, 4.25. Found: C, 76.49; H, 4.71; N, 4.19. FTIR (KBr): ν=3054, 3027, 1647, 1614, 1576, 1509, 1475, 1446, 1335, 1248, 1224, 1124, 1086, 983, 902, 832, 747, 695 cm^{-1}.

4.5.2. 2,2-Diphenyl-8-methyl-6-nitro-2*H*-1-benzopyran (25). This compound was obtained by general procedure (3), starting from **19** (343 mg, 1 mmol). The product **25** was obtained as a dark brown solid (243 mg, 0.71 mmol, 71%). Mp 98 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.33 (s, 3H), 6.26 (d, J=10.1 Hz, 1H), 6.65 (d, J=10.1 Hz, 1H), 7.20–7.50 (m, 10H), 7.79 (d, J=2.3 Hz, 1H), 7.91 (d, J=2.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.9 (CH_3), 84.3 (OC), 120.1 (CH═), 120.3 (C), 122.3 (CH═), 126.3 (CH═), 126.7 (4×CH═ and C), 127.9 (2×CH═), 128.4 (4×CH═), 130.1 (CH═), 141.2 (C), 144.1 (2×C),

155.9 (C). Anal. Calcd for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.99; N, 4.08. Found: C, 76.86; H, 5.11; N, 4.10. FTIR (KBr): ν=3064, 3000, 2900, 2857, 1635, 1600, 1588, 1514, 1447, 1333, 1242, 1165, 1089, 994, 973, 940, 915, 893, 749, 699 cm^{-1}.

4.5.3. 7,8-Dimethyl-2,2-diphenyl-6-nitro-2*H*-1-benzopyran (26). This compound was obtained by general procedure (3), starting from **20** (356 mg, 1 mmol). The product **26** was isolated as a dark yellow solid (286 mg, 0.80 mmol, 80%). Mp 143 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.28 (s, 3H), 2.40 (s, 3H), 6.23 (d, J=9.9 Hz, 1H), 6.61 (d, J=9.9 Hz, 1H), 7.20–7.45 (m, 10H), 7.50 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.2 (CH_3), 16.3 (CH_3), 83.8 (OC), 118.3 (C), 120.6 (CH═), 122.3 (CH═), 126.2 (C), 126.8 (4×CH═), 127.8 (2×CH═), 128.3 (4×CH═), 129.8 (CH═), 133.9 (C), 144.3 (3×C), 153.1 (C). Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.18; H, 5.27; N, 4.03. FTIR (KBr): ν=3059, 3028, 2922, 2852, 1640, 1608, 1557, 1512, 1446, 1379, 1347, 1267, 1243, 1175, 1098, 1026, 966, 932, 912, 880, 763, 696 cm^{-1}.

4.5.4. 5,8-Dimethyl-2,2-diphenyl-6-nitro-2*H*-1-benzopyran (27). This compound was obtained by general procedure (3), starting from **21** (356 mg, 1 mmol). The product **27** was isolated as a light brown solid (218 mg, 0.61 mmol, 61%). Mp 181 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.29 (s, 3H), 2.47 (s, 3H), 6.30 (d, J=10.3 Hz, 1H), 6.89 (d, J=10.3 Hz, 1H), 7.20–7.50 (m, 10H), 7.64 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.7 (CH_3), 15.7 (CH_3), 82.8 (OC), 120.0 (CH═), 120.2 (C), 124.3 (C), 126.7 (4×CH═), 127.1 (CH═), 127.8 (2×CH═), 127.9 (C), 128.3 (4×CH═), 130.0 (CH═), 143.6 (C), 144.2 (2×C), 154.3 (C). Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.25; H, 5.29; N, 4.12. FTIR (KBr): ν=2922, 2853, 1626, 1558, 1511, 1451, 1376, 1320, 1274, 1225, 1068, 1023, 1068, 1023, 965, 758, 699 cm^{-1}.

4.5.5. 5,6-Dimethyl-2,2-diphenyl-8-nitro-2*H*-1-benzopyran (28). This compound was obtained by general procedure (3), starting from **22** (356 mg, 1 mmol). The product **28** was isolated as a light yellow solid (186 mg, 0.52 mmol, 52%). Mp 154–155 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.20 (s, 3H), 2.24 (s, 3H), 6.43 (d, J=10.1 Hz, 1H), 6.89 (d, J=10.1 Hz, 1H), 7.20–7.55 (m, 10H), 7.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.3 (CH_3), 19.7 (CH_3), 83.0 (OC), 120.6 (CH═), 122.2 (C), 125.6 (CH═), 126.6 (4×CH═), 127.7 (2×CH═), 128.3 (4×CH═), 129.4 (C), 130.5 (CH═), 136.1 (C), 139.2 (C), 143.9 (2×C), 144.0 (C). Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 76.98; H, 5.45; N, 3.89. FTIR (KBr): ν=3058, 2900, 2838, 1634, 1576, 1506, 1447, 1333, 1245, 1100, 1058, 997, 966, 744, 699 cm^{-1}.

4.5.6. 5,7-Dimethyl-2,2-diphenyl-6-nitro-2*H*-1-benzopyran (29). This compound was obtained by general procedure (3), starting from **23** (356 mg, 1 mmol). The product **29** was isolated as a light yellow solid (115 mg, 0.32 mmol, 32%). Mp 128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.22 (s, 6H), 6.26 (d, J=10.2 Hz, 1H), 6.69 (s, 1H), 6.76 (d, J=10.2 Hz, 1H), 7.25–7.43 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.5 (CH_3), 17.9 (CH_3), 82.6 (OC), 116.7 (CH═), 118.3 (C), 119.32 (CH═), 126.3 (C), 126.9 (4×CH═), 127.8 (2×CH═), 128.2 (4×CH═), 129.9 (CH═), 131.2 (C), 144.2 (2×C), 146.8 (C), 153.2 (C). Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.34; H, 5.28; N, 3.88. FTIR (KBr): ν=3059, 3031, 2956, 2922, 2852, 1650, 1608, 1583, 1563, 1514, 1462, 1444, 1363, 1315, 1305, 1240, 1212, 1189, 1102, 1090, 1001, 985, 949, 931, 851, 836, 780, 766, 758, 697 cm^{-1}.

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