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Ortho-spirocarbonates and ortho-spirothiocarbonates: synthesis, functionalization and coupling

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ABSTRACT

This paper describes a new efficient synthesis of 2,2′-spirobi-(1,3-benzoxathiole) (**1**), 2,2′-spirobi-(1,3-benzodithiole) (**2**) and 2,2′-spirobi-(1,3-benzodioxole) (**3**). Compound **3** has been functionalized by means of metallation reaction followed by electrophilic quenching to give carboxylic acids, aldehydes and alcohols. Furthermore compound **3** was subjected to homo-coupling and its dimeric structure was determined by XRD analysis.

1. Introduction

The efficiency of the catalyst in asymmetric synthetic processes with transition metals is greatly affected by the structure of the ligand. In this field biaryl ligands play a pre-eminent role due to their intrinsic chirality: this structural property make such ligands the first choice in asymmetric oxidations, reductions and C–C bond forming reactions.[1] Recent studies have reported the application of benzodioxolic systems bearing suitable substituents as chiral catalysts.[2–4]

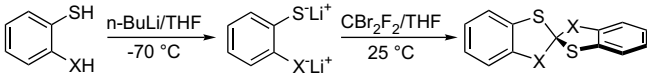
In this work we report a study on the synthesis and functionalization of *ortho*-spirocarbonates and *ortho*-thiospirocarbonates by means of organolithium compounds: these molecules, after convenient functionalization, could give rise to intrinsically chiral moieties analogous to biaryls through a cross-coupling reaction.

The spiro compounds bearing heteroatoms in the spiranic bonds have received little attention. In fact, the 2,2′-spirobi-(1,3-benzoxathiole) (**1**) has never been prepared before and the 2,2′-spirobi-(1,3-benzodithiole) (**2**) has been obtained in low yield as by-product,[5–7] or with tedious multi-step procedures.[8] The 2,2′-spirobi-(1,3-benzodioxole) (**3**) has been synthesized before in good yields, but all procedures required high temperatures (120 °C) and did not use commercial reagents,[9] or long sequences of steps with lowering of the global yield[10] or high costing reagents.[11] As regards the functionalization of the spiro system **3**, only some *tert*-butyl derivatives have been prepared.[12–14] In connection with our previous studies on the synthesis and functionalization of heterocyclic compounds by metallation reactions,[15–18] and considering the few data reported in the literature on spiro compounds, we decided to study new synthetic procedures to prepare compounds **1**–**3** and their functionalization by means of organolithium reagents. In addition, we examined the homo-coupling reaction of compound **3**: to our knowledge there are no examples of coupling of spiro compounds in the literature. The derived dimeric compound, when functionalized with proper groups, could be characterized, as biaryls,[1–4] by an hindered rotation around the new C–C bond resulting in an intrinsic chirality. The further development of this study will be to test all prepared spiro compounds as metal ligands and chiral catalysts.

2. Results and discussion

Compounds **1** and **2** were synthesized starting from 2-hydroxybenzenethiole and 1,2-benzene dithiole[7] by reaction with *n*-BuLi (*n*-butyllithium) in THF and following nucleophilic attack of the lithium salt on dibromodifluoromethane in THF. The optimized temperature values were found to be −70 °C for the first step and 25 °C for the second one (Method A) (Scheme 1).

Compound **1** was obtained in a global yield of 40% while the yield for **2** was considerably higher (80%).



2-hydroxybenzenethiole X = O
1,2-benzenedithiole X = S

1: X = O
2: X = S

Scheme 1.

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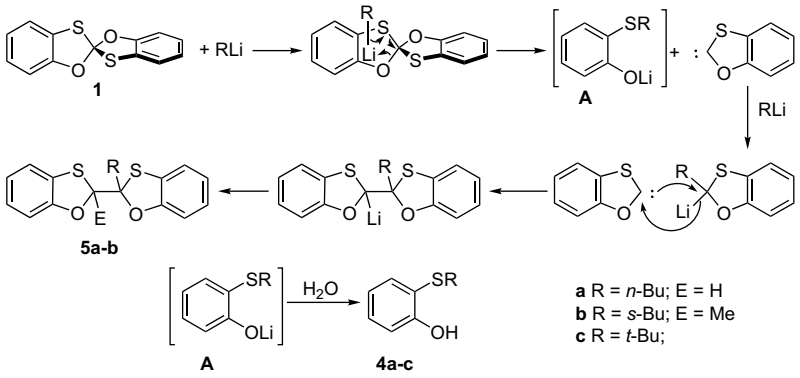
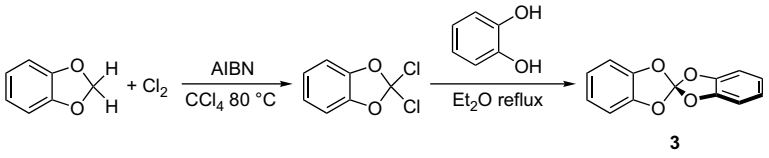
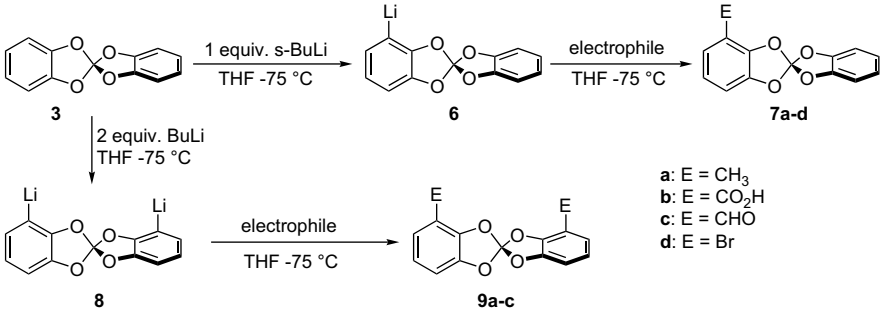


Scheme 2.



Scheme 3.



Scheme 4.

The use of a weaker base e.g., sodium methoxide in methanol did not give product **1** not even in traces. The total lack of reactivity of the system MeONa/MeOH is certainly attributable to the great stabilization of the sodium salt of the 2-hydroxythiophenol by methanol: on the other hand, it resulted impossible to rise the temperature of the second reaction step because of the low boiling point of dibromodifluoromethane. All attempts to functionalize compound **1** in the *ortho* positions through metallation reactions failed: in fact *n*-BuLi, *s*-BuLi or *t*-BuLi did not extract the *ortho* protons but attacked the carbon–sulfur bond in an Umpolung scheme leading up to the opening of the oxathiolic ring with formation of products **4a**–**c** (Scheme 2).

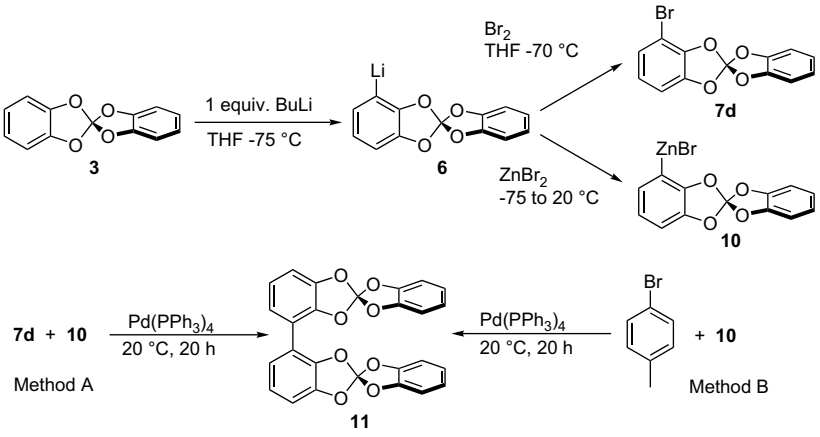
This peculiar behaviour can be rationalized considering the small difference in the charge on the carbon and sulfur atom in **1** (0.40 and 0.39, respectively, as determined by NBO analysis).[18,19] The base attacked the sulfur atom instead of the spiranic carbon, in spite of its higher positive charge, probably because of the greater steric hindrance around the carbon. This attack led to the formation of a carbene species, which reacted with one organolithium molecule giving the lithium intermediate **A**, which in turn can attack another carbene unit to give products **4a**–**c**[20] and **5a**,**b** whose formation can be justified only through a carbene mediated mechanism. Compound **2** showed an analogous behaviour leading to the opening of the spiro-ring upon treatment with *n*-BuLi.

The synthesis of 2,2′-benzobi-(1,3-benzodioxole) (**3**) starting from 1,2-dihydroxybenzene with the same procedure employed for **1** and **2**, did not give the expected results. We were prompted to adapt an old literature procedure[10,21] performing a one pot reaction which led to higher yield. This process started from 1,3-benzodioxole and consisted in a radical chlorination in the presence of AIBN (2,2′-azobisisobutyronitrile): the formed 2,2-dichloro-

Table 1
Synthesis of spiro compounds **7a**–**d** and **9a**–**c**

Compound	Electrophile	E	Yield[a] %
7a	$(CH_3)_2SO_4$	CH_3	70
7b	DMF	CHO	41
7c	CO_2	COOH	50
7d	Br_2	Br	80
9a	$(CH_3)_2SO_4$	CH_3	70
9b	DMF	CHO	50
9c	CO_2	COOH	50

[a] Yields of pure chromatographed products.



Scheme 5.

1,3-benzodioxole was reacted with 1,2-dihydroxybenzene affording **3** in 80% yield (Method B) (Scheme 3).

Compound **3**, unlike sulfur-compounds **1** and **2**, can be functionalized by means of metallation reactions only with *s*-BuLi at −75 °C and subsequent electrophilic quenching. The reaction of **3** with one molar equivalent of *s*-BuLi led to the monolithiated intermediate **6** (along with a 3% of the dilithiated **8**), which gave products **7a–d** after quenching with various electrophiles (Scheme 4, Table 1). Using two molar equivalents of the same reagent the spiro compound **3** was lithiated in both aromatic rings giving rise to the dilithiated compound **8** and then to products **9a–c** (Scheme 4, Table 1).

The reaction yields varied according to the electrophile used, being at a maximum for Br_2 (Table 1).

It is noteworthy that **3** could not be metallated by *n*-BuLi at −75 °C: performing the reaction at 0 °C only the starting material was recovered from the reaction mixture, while at room temperature only decomposition products were found. Compound **3** could be lithiated in the reaction conditions reported by Schlosser for 2,2-difluoro-1,3-benzodioxole:[22] probably the oxygen atoms in **3** exert an electron attractive effect like the fluorine atoms in 2,2-difluoro-1,3-benzodioxole, causing a decrease in the coordinating power towards the lithium cation and an increase in the acidity of the *ortho* protons; on the other hand, in THF *s*-BuLi is dimeric while *n*-BuLi is tetrameric.[23] As model compounds, the 2,2-dimethyl benzodioxole and 2,2-diphenyl benzodioxole can be lithiated with the less basic, but more coordinated *n*-BuLi at 0 °C to room temperature.[24,25]

2.1. Homo-coupling of 2,2′-benzobi-(1,3-benzodioxole) 3

The first attempt to perform the coupling of compound **3** followed the Suzuki protocol[26] but the boron derivative of our spiro compound could not be obtained. In fact the lithium derivative **6** decomposed when treated with $B(OCH_3)_3$, while with $ZnBr_2$ formed the zinc derivative. On the other side **3** did not decompose when treated with $B(OCH_3)_3$ or with $AlBr_3$ at 80 °C for 1 h. Then we tried to follow the Negishi procedure,[27–29] using two different approaches. In the first procedure (Method C), the bromo-derivative **7d** has been reacted with the zinc derivative **10**[30] using $Pd(PPh_3)_4$ as catalyst: both compounds **7d** and **10** have been obtained from the lithium derivative **6** with bromine and zinc bromide, respectively. The coupling product **11** has been obtained in 43% yield. The second procedure (Method D) consisted of a 'one pot' procedure in which the zinc derivative **10** was reacted with 4-bromotoluene giving a 63% yield. Considering the higher yield and the more direct approach (one step less), the Method D resulted the more convenient (Scheme 5).

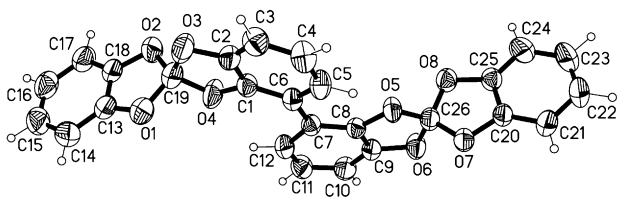


Figure 1.

The reaction path of Method D can be described as a first transmetallation reaction between **10** and 4-bromotoluene leading to compound **7d**, which in turn can react with **10** to give **11**. The absence of the hetero-coupling product between the spiro compound **3** and the 4-bromotoluene clearly showed the transmetallation reaction being much faster than the hetero-coupling one, but slower than the homo-coupling: in this reaction conditions the just formed **7d** reacted with **10** to give **11**. The use of dibenzylidenacetone (dba)[30] as catalyst gave a lower yield for both methods.

2.2. XRD structure

The XRD analysis showed the dimer **11** assuming in the solid state a *transoid* conformation around the C–C biphenyl bond (Fig. 1), with the dihedral C1–C6–C7–C8 measuring 162.90°. The rotation around the C6–C7 biphenyl bond is free: in fact the distances H5···O5 (2.20 Å) and H12···O4 (2.32 Å) are too long to block this rotation, considering that the distance H5···O5, when calculated for a dihedral C1–C6–C7–C8 of 180°, resulted 1.87 Å.

3. Conclusion

The data reported clearly demonstrated that the synthetic approach to compounds **1**–**3** strongly depends upon the sulfur atom presence. In fact, the Method A allowed us to prepare only **1** and **2** (**2** with a better yield than **1**) but not **3**. Therefore, the Method A can work only with strong thiolate nucleophiles; in fact the reaction cannot be performed at higher temperatures due to the low boiling point of CBr_2F_2.

Moreover the spiro compounds **1** and **2** were decomposed by organolithiums through a nucleophilic attack on the sulfur atom while **3** underwent a smooth deprotonation by *s*-BuLi in the positions *ortho* to the oxygen atoms.

It is noteworthy the behaviour of **3** towards Lewis acids. Upon treating **3** with $AlBr_3$ at high temperatures (80 °C) no decomposition product can be isolated. The lithium derivative **6** underwent a lithium–zinc exchange with $ZnBr_2$ to give intermediate **10**, while it was decomposed by $B(OCH_3)_3$, even at low temperatures, leading to products (as the 1,3-benzodioxole-2-one[31]) derived from the opening of the spiranic system. This peculiar reactivity can be ascribed to the increased electronic density on the oxygen atom, caused by the negative charge in the adjacent *ortho* position, with consequent attack of $B(OCH_3)_3$ on this atom The preferential attack of $ZnBr_2$ on the carbanionic site and of $B(OCH_3)_3$ on the oxygen atom, can be rationalized through the HSAB theory (Hard and Soft Acids and Bases).[32,33]

4. Experimental

4.1. General

Commercially available reagent-grade starting materials and solvents were used. Solutions of buthyllithium in hexane were obtained from Aldrich Chemical Company and were analyzed before use.[34] NMR spectra were recorded on a Varian VXR-300 spectrometer with tetramethylsilane as internal reference. IR spectra were recorded on a FT-IR Bruker Equinox 55 spectrophotometer. The GC–MS analyses were performed with a Hewlett-Packard 5989A MS spectrometer using the direct insertion probe (DIP) method. All chromatographies were performed on silica gel 60, 0.04–0.063 (Fluka). Microanalyses were carried out with a Carlo Erba EA1108 CHNS analyser. Melting points were obtained on a Kofler hot stage microscope and are uncorrected.

4.2. 2,2′-Spirobi-(1,3-benzoxathiole) (1)

A 1.6 M solution of *n*-BuLi in hexane (20 mL, 32 mmol) was added dropwise to a vigorously stirred solution of 2-hydroxybenzenethiole (2.0 g, 15.8 mmol), in dry THF (25 mL) at −70 °C under argon. After 15 min, the mixture was warmed up to 25 °C and a solution of CBr_2F_2 (22 mmol) in dry THF (35 mL) was added dropwise. The reaction was completed by vigorously stirring for 3 h at the same temperature and then hydrolyzed with aqueous HCl (10%). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL); the organic phases were combined, dried (Na_2SO_4) and concentrated. The crude product was purified by chromatography (PE) to give **1** (2.9 g, 40% yield) as colourless needles, mp 107 °C, R_f=0.56 (PE). IR (KBr): ν=3065, 3017, 1582, 1471, 1455, 1325, 1184, 1067, 1028, 823, 750, 671 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ=7.00 (s, 8H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ=144.1, 122.7, 121.7, 108.8 ppm. MS (EI): *m*/*z* (%)=228 (100, M^+), 136 (4), 120 (21), 92 (34), 80 (3), 64 (37), 63 (41), 52 (9), 50 (9). Anal. Calcd for $C_{13}H_8O_2S_2$: C, 59.98; H, 3.10; S, 24.63. Found: C, 59.92; H, 3.12; S, 24.56.

4.3. 2,2′-Spirobi-(1,3-benzodithiole) (2)

Compound **2** was prepared following the same procedure as **1**. The product was identified by comparison of its spectral data with those reported in the literature.[8]

4.4. 2,2′-Spirobi-(1,3-benzodioxole) (3)

A solution of 1,3-benzodioxole (3.66 g, 30 mmol) and AIBN (0.08 g, 0.045 mmol) in CCl_4 (35 mL) at 80 °C was flushed with anhydrous Cl_2 for 3.5 h. The solvent was evaporated nearly to dryness and the residue was cooled to room temperature. This mixture was treated with a solution of 1,2-dihydroxybenzene (3.30 g, 30 mmol) in dry Et_2O (25 mL) and then warmed to reflux until the HCl evolution ceased. The solvent was evaporated and the obtained solid washed with aqueous K_2CO_3 (10%) to remove the unreacted starting material. The crude product was purified by chromatography (PE) to give **3** (5.4 g, 80% yield) as white leafs, mp 107 °C, R_f=0.58 (PE). IR (KBr): ν=3070, 3043, 1637, 1479, 1328, 1223, 1175, 993, 753, 732 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ=7.00 (s, 8H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ=144.1, 122.7, 121.7, 108.8 ppm. MS (EI): *m*/*z* (%)=228 (100, M^+), 136 (4), 120 (21), 92 (34), 80 (3), 64 (37), 63 (41), 52 (9), 50 (9). Anal. Calcd for $C_{13}H_8O_4$: C, 68.42; H, 3.53. Found: C, 68.32; H, 3.71.

4.5. 1′,3′-Benzodioxol-2′-spiro-(4-methyl-1, 3-benzodioxole) (7a)

A 1.4 M solution of *s*-BuLi in cyclohexane (18 mL, 25.2 mmol) was added dropwise (very slowly) to a vigorously stirred solution of **3** (0.5 g, 2.2 mmol) in dry THF (10 mL) at −75 °C under argon: in 30 min the lithium carbanion **6** was formed. A solution of $(CH_3)_2SO_4$ (6.6 mmol) in dry THF (5 mL) was added dropwise and the reaction was completed by vigorously stirring for 1 h at the same temperature. The cooling bath was removed and the reaction mixture was hydrolyzed with aqueous HCl (10%). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL); the organic phases were combined, dried (Na_2SO_4) and concentrated. The crude product was purified by chromatography (PE) to give **7a** (378 mg, 70% yield) as amorphous white solid, mp 90–93 °C, R_f=0.53 (PE). IR (KBr): ν=2928, 1651, 1602, 1495, 1472, 1263, 1257, 1224, 1181, 1152, 1076, 1072, 982, 947, 859, 774, 753, 726, 682 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ=7.00 (s, 4H, ArH), 6.87 (m, 3H, ArH), 2.30 (s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ=144.1, 143.7, 142.7, 124.5, 122.6, 122.3, 119.3, 108.7, 106.1, 14.5 ppm. MS (EI): *m*/*z* (%)=242 (100, M^+), 150 (4.2), 136 (20), 120 (5), 106 (42), 105 (50), 92 (30), 78 (89), 77 (36), 64 (58), 63 (75), 52 (44), 51 (42), 50 (28). Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.31; H, 4.05.

4.6. 2,2′-Spirobi-(1,3-benzodioxol)-4-carbaldehyde (7b)

A solution of DMF (0.34 mL, 4.4 mmol) was added dropwise to the solution of **6** in THF prepared as described above and the reaction was completed by vigorously stirring for 1 h at the same temperature. The cooling bath was removed and the reaction mixture was worked up as described above. The crude product was purified by chromatography (Et_2O/PE, 3:1) to give **7b** (230 mg, 41% yield) as amorphous white solid, mp 135–136 °C, R_f=0.60 (Et_2O/PE, 1:10). IR (KBr): ν=3123, 3069, 2923, 2844, 2755, 1695, 1643, 1606, 1471, 1399, 1270, 1241, 1174, 950, 786, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ=10.09 (s, 1H, CHO), 7.41 (d, *J*=7.8 Hz, 1H, ArH), 7.05 (t, *J*=8 Hz, 1H, ArH), 6.96 (s, 4H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ=186.8, 145.1, 144.0, 123.1, 122.8, 122.1, 119.1, 113.8, 109.0 ppm. MS (EI): *m*/*z* (%)=256 (27, M^+), 228 (11), 163 (5), 137 (5), 136 (26), 120 (24), 119 (4), 92 (72), 91 (15), 64 (61), 63 (100), 62 (26), 53 (13), 52 (17), 51 (20), 50 (23), 38 (3). Anal. Calcd for $C_{14}H_8O_5$: C, 65.63; H, 3.15. Found: C, 65.71; H, 3.20.

4.7. 2,2′-Spirobi-(1,3-benzodioxol)-4-carboxylic acid (7c)

A solution of **6** in THF, prepared as described above, was injected by a syringe in a flask containing crushed solid CO_2 (ca. 100 g). The reaction was completed in 15 h and the reaction mixture was worked up as described above. The crude product was purified by crystallization (EtOH/H_2O) to give **7c** (299 mg, 50% yield) as amorphous white solid, mp 212–216 °C. IR (KBr): ν=2967 (br), 2695, 2583, 1693, 1485, 1461, 1422, 1311, 1178, 1033, 1002, 954, 782, 747 cm^{-1}. ^1H NMR (DMSO, 300 MHz): δ=7.65 (d, *J*=8.1 Hz, 1H, ArH), 7.23–7.06 (m, 2H, ArH), 7.01 (s, 4H, ArH) ppm. ^{13}C NMR (DMSO,

75.4 MHz): δ=164.2, 144.2, 143.2, 124.5, 123.8, 123.3, 114.1, 113.3, 109.4 ppm. MS (EI): *m*/*z* (%)=272 (36, M^+), 255 (5), 228 (22), 136 (14), 119 (14), 92 (100), 64 (48), 63 (45), 52 (11). Anal. Calcd for $C_{14}H_8O_6$: C, 61.77; H, 2.96. Found: C, 61.65; H, 2.91.

4.8. 1′,3′-Benzodioxol-2′-spiro-(4-bromo-1, 3-benzodioxole) (7d)

A solution of Br_2 (0.34 mL, 4.4 mmol) in dry THF (10 mL) was added dropwise to a solution of **6** in THF, prepared as described above, and the reaction was completed by vigorously stirring for 1 h at the same temperature. The cooling bath was removed and the reaction mixture was worked up as described above. The crude product was purified by chromatography (PE) to give **7d** (0.4 g, 80% yield) as amorphous white solid, mp 56.5–58.5 °C, R_f=0.54 (PE). IR (KBr): ν=2923, 2853, 1622, 1472, 1455, 1242, 1183, 996, 763, 743 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ=7.16 (dd, *J*=8.0, 1.2 Hz, 1H, ArH), 6.95 (m, 4H, ArH), 6.86 (m, 2H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ=144.3, 143.9, 142.5, 126.0, 123.6, 122.7, 108.7, 107.7, 100.7 ppm. MS (EI): *m*/*z* (%)=308 (98, M^++2), 306 (100, M^+), 200 (7), 198 (7), 172 (17), 170 (17), 155 (6), 136 (8), 120 (25), 107 (5), 92 (40), 64 (40), 63 (60), 52 (12), 51 (10). Anal. Calcd for $C_{13}H_7BrO_4$: C, 50.84; H, 2.30. Found: C, 50.79; H, 2.26.

4.9. 2,2′-Spirobi-(4-methyl-1,3-benzodioxole) (9a)

A 1.4 M solution of *s*-BuLi (3.3 mL, 4.62 mol) in cyclohexane was added dropwise (very slowly) to a vigorously stirred solution of **3** (0.5 g, 2.2 mmol) in dry THF (10 mL) at −75 °C under argon: after 30 min, the dilithium carbanion **8** was formed. A solution of $(CH_3)_2SO_4$ (6.6 mmol) in dry THF (5 mL) was added dropwise and the reaction was completed by vigorously stirring for 1 h at the same temperature. The cooling bath was removed and the reaction mixture was worked up as described above. The crude product was purified by chromatography (PE) to give **9a** (406 mg, 72% yield) as white needles, mp 80–81 °C, R_f=0.51 (PE). IR (KBr): ν=2924, 1655, 1609, 1489, 1464, 1267, 1251, 1227, 1186, 1159, 1085, 1063, 986, 941, 853, 779, 759, 719, 785 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ=6.85 (m, 6H, ArH), 2.27 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ=143.6, 142.6, 124.4, 122.8, 122.3, 119.3, 106.0, 14.4 ppm. MS (EI): *m*/*z* (%)=256 (40, M^+), 175 (16), 134 (3.4), 106 (31), 105 (77), 89 (8), 78 (100), 77 (54). Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72. Found: C, 70.19; H, 4.78.

4.10. 2,2′-Spirobi-(1,3-benzodioxol-4-carbaldehyde) (9b)

A solution of DMF (0.34 mL, 4.4 mmol) was added dropwise to a solution of **8** in THF, prepared as described above, and the reaction was completed by vigorously stirring for 1 h at the same temperature. The cooling bath was removed and the reaction mixture was worked up as described above. The crude product was purified by crystallization (EtOH/H_2O) to give **9b** (310 mg, 50% yield) as white needles, mp 167–168 °C. IR (KBr): ν=3069, 3035, 2833, 2748, 1694, 1638, 1460, 1367, 1249, 1193, 1166, 967, 784, 706 cm^{-1}. ^1H NMR (DMSO, 300 MHz): δ=10.20 (s, 2H, ArH), 7.77 (d, *J*=8.1 Hz, 2H, ArH), 7.76 (d, *J*=7.8 Hz, 2H, ArH), 7.48 (m, 2H, ArH) ppm. ^{13}C NMR (DMSO, 75.4 MHz): δ=188.5, 144.2, 142.7, 124.6, 124.2, 119.6, 114.8 ppm. MS (EI): *m*/*z* (%)=284 (40, M^+), 256 (10), 165 (9), 163 (16), 149 (12), 120 (38), 119 (79), 92 (66), 91 (43), 74 (25), 64 (39), 63 (100), 62 (31), 53 (16), 50 (25), 38 (16). Anal. Calcd for $C_{15}H_8O_6$: C, 63.39; H, 2.84. Found: C, 63.22; H, 2.80.

4.11. 2,2′-Spirobi-(1,3-benzodioxol-4-carboxylic) acid (9c)

A solution of **8** in THF, prepared as described above, was injected by a syringe in a flask containing crushed solid CO_2 (ca. 100 g). The reaction was completed in 15 h and the reaction mixture was worked up as described above. The crude product was purified by crystallization (EtOH/H_2O) to give **9c** (695 mg, 50% yield) as amorphous white solid, mp 299–300 °C (with decomposition). IR (KBr): ν=2966 (br), 2689, 2576, 1695, 1487, 1461, 1422, 1307, 1190, 1037, 948, 783, 743 cm^{-1}. ^1H NMR (DMSO, 300 MHz): δ=7.75 (d, *J*=1.9 Hz, 2H, ArH), 7.66 (d, *J*=1.8 Hz, 2H, ArH), 7.36 (t, *J*=1.9 Hz, 2H, ArH) ppm. ^{13}C NMR (DMSO, 75.4 MHz): δ=164.1, 144.1, 143.1, 124.7, 123.5, 114.2, 113.4 ppm. MS (EI): *m*/*z* (%)=316 (37, M^+), 299 (5), 272 (15), 181 (7), 180 (3), 163 (6), 136 (28), 119 (41), 108 (7), 107 (4), 92 (100), 91 (91), 79 (10), 64 (20), 63 (40), 52 (14), 51 (14), 44 (16). Anal. Calcd for $C_{15}H_8O_8$: C, 56.97; H, 2.55. Found: C, 56.82; H, 2.59.

4.12. 4,4′-Bi-[2,2′-spirobi-(1,3-benzodioxole)] (11)

Method C. A solution of $ZnBr_2$ (1.8 g, 2.8 mmol) in THF (8 mL) was added dropwise to the solution of **6** (2.28 mmol) in THF (10 mL) prepared as described above and the reaction mixture was maintained by vigorously stirring for 30 min at the same temperature. The cooling bath was removed and the temperature increased to 23 °C: after 1 h **10** was formed, then compound **7d** (0.859 g, 2.8 mmol) in THF (3 mL) was added and after 5 min $Pd(Ph_3)_4$ (0.016 g, 0.014 mmol) in THF (3 mL) was added; the reaction was completed in 20 h. The reaction mixture was hydrolyzed with aqueous NH_4Cl (10%). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL); the organic phases were combined, dried (Na_2SO_4) and concentrated.

Method D. A solution of 4-bromotoluene (0.35 mL, 2.8 mmol) in THF (3 mL) was added dropwise to the solution of **10** prepared as described above, after 5 min $Pd(Ph_3)_4$ (0.016 g, 0.014 mmol) in THF (3 mL) was added and the reaction was maintained by stirring for 20 h at the same temperature. The reaction mixture was hydrolyzed with aqueous NH_4Cl (10%). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL); the organic phases were combined, dried (Na_2SO_4) and concentrated. Purified by chromatography (Et_2O/PE, 1:4); white crystals (EtOH/hexane), 0.31 g, yield 62%, mp 206–208 °C, R_f=0.68 (Et_2O/PE, 1:4). IR (KBr) ν=3082, 2924, 1642, 1590, 1484, 1431, 1239, 1171 (br), 993, 775, 755. ^1H NMR (300 MHz, $CDCl_3$): δ=7.47 (dd, *J*=8.1, 1.3 Hz, 2H, ArH), 7.08 (t, *J*=8.1 Hz, 2H, ArH), 7.02–6.98 (m, 10H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=144.6, 144.2, 141.4, 123.5, 122.8, 122.8, 117.3, 108.9, 108.4 ppm. MS (EI): *m*/*z* (%)=454 (100, M^+), 318 (24), 290 (6), 262 (5), 261 (4), 182 (10), 154 (19), 126 (30), 92 (6), 64 (16), 63 (14). Anal. Calcd for $C_{26}H_{14}O_8$: C, 68.73; H, 3.11. Found: C, 68.70; H, 3.13.

4.13. Experimental data for the crystal structure of 11[35]

Formula $C_{26}H_{14}O_8$, *M*=454.37, white crystals 0.42×0.35×0.30 mm^3, *a*=8.4831(1) Å, *b*=22.4949(3) Å, *c*=10.8643(1) Å, α=90°, β=99.420(1)°, γ=90°, *V*=2045.24(4) $Å^3$, ρ_{calcd}=1.476 g/cm^3, μ=0.111 mm^{-1}, *Z*=4, monoclinic, space group *P*2(1)/*n*, λ=0.71073 Å, *T*=296(2) K, 48,703 reflections collected.

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