Synthesis of Tetra(BINOL) Substituted Spirobifluorenes

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Abstract: A series of tetra(BINOL) substituted spirobifluorenes (**1**, **12**–**15**) has been prepared via fourfold Sonogashira cross-coupling reaction from 2,2′,7,7′-tetraiodospirobifluorene (**3**) and 2,2′-bis(methoxymethoxy)-3-ethynyl-1,1′-binaphthyl (**10**) or 2,2′-bis(methoxymethoxy)-3-ethynyl-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthyl (**11**), respectively. Whereas the deprotection of the readily available fully methoxymethyl ether protected precursors **12** and **13** proved to be difficult in the case of the sterically shielded spirobifluorenes **14**, **15**, not further substituted tetra(BINOL) **1** could be obtained in good yield after acidic hydrolysis. This chiral spirobifluorene closely reassembles the structure of copper(I) or silver(I) complexes of a bis(BINOL) substituted 2,2-bipyridine (**2**) and can also form two clefts with the BINOL groups orientated in a fashion potentially useful for the co-operative molecular recognition of chiral substrates.

Key words: cross-coupling reactions, palladium, BINOL, spiro compounds, supramolecular chemistry

2,2′-Dihydroxy-1,1′-binaphthyl (BINOL) and its derivatives have been demonstrated to be very important components of catalysts that are routinely used in asymmetric synthesis[1] but they have also been shown to be very effective for the recognition of chiral substrates both in solid and solution phase supramolecular chemistry.[2,3] Within the course of these studies it turned out that the efficiency of catalysts for asymmetric synthesis as well as of receptors could often be increased through the use of compounds containing multiple BINOL units.[4] This is particularly true for receptors that are thought to be used in the recognition of carbohydrates which has attracted a lot of interest in supramolecular chemistry[2c,5] because of the dominant role of these compounds in intercellular recognition events.[6]

However, the synthesis of many efficient receptors proved to be quite tedious because divergent strategies had to be used. Therefore, our approach aims at the development of chiral receptors that are either formed in self-assembly processes[7] or covalent analogues of these, which we design by using molecular modelling methods following the basic idea to employ a convergent modular approach, where elaborated building blocks can be combined in a rather fast and flexible manner.

Here, we would like to report on our design and synthesis concept based on a tetrafunctionalised spirobifluorene[8] (**1**) as a rigid structure determining element that closely reassembles the copper(I) or silver(I) complex of a bis(BINOL) substituted 2,2′-bipyridine (**2**) which we were able to synthesise recently.[7b] Figure 1 shows the force field minimised structures of compound (*all-S*$_a$)-**1** and its analogous [Cu(*all-S*$_a$)-**2**$_2$]$^+$-complex.[9]

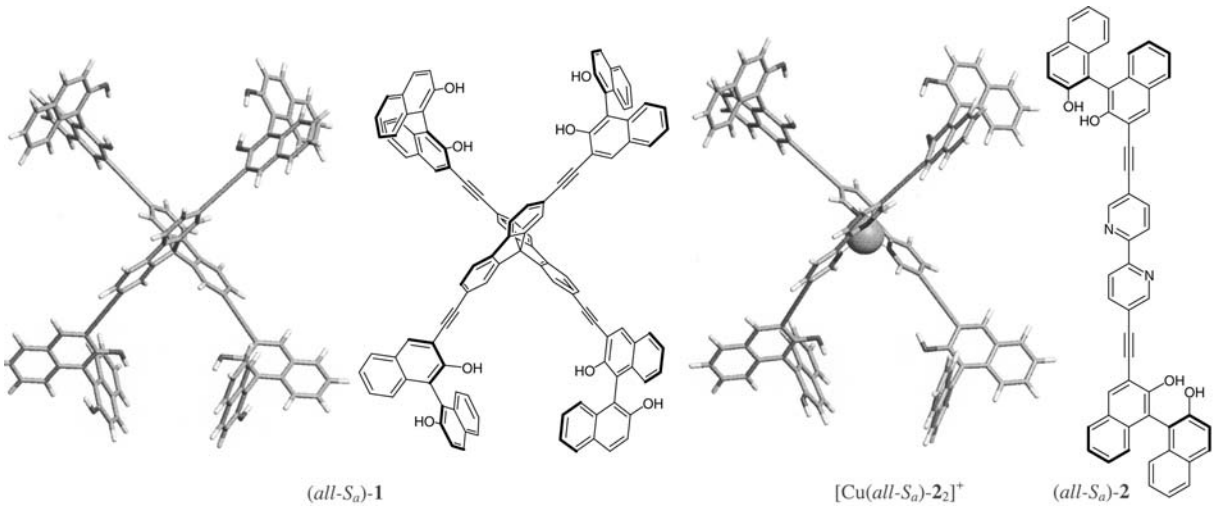

Figure 1 MM2-minimised structure of tetra(BINOL) substituted spirobifluorene (*all-S*$_a$)-**1** (left) and MMFF-minimised structure of its analogous [Cu(*all-S*$_a$)-**2**$_2$]$^+$-complex (right)

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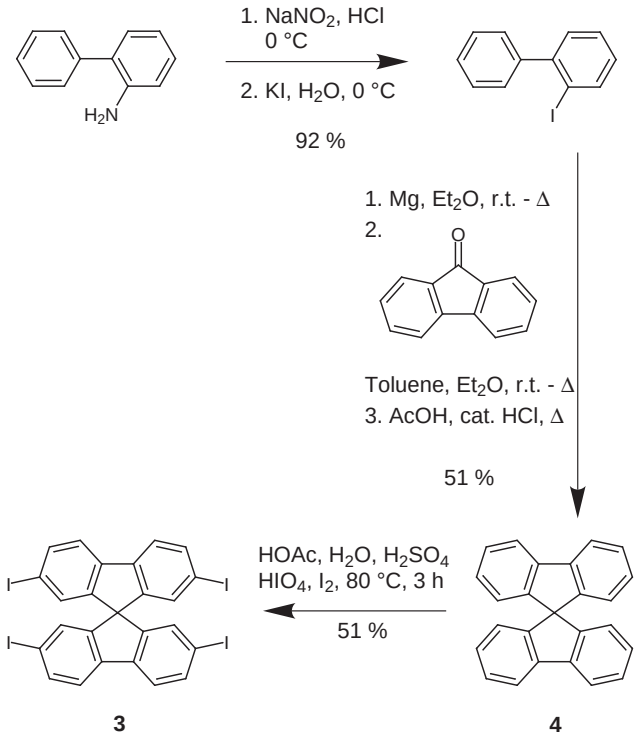
The central 2,2′,7,7′-tetraiodo-9,9′-spirobifluorene **3** is readily prepared in four steps starting from commercially available 2-aminobiphenyl (Scheme 1). Initial Sandmeyer reaction was followed by a Grignard reaction with 9-fluorenone, and subsequent condensation under acidic conditions to give 9,9′-spirobifluorene (**4**)[10] in an overall yield of 47%. Finally, the four-fold iodination was achieved in 51% yield using a procedure reported by Tour et al. which we slightly modified.[11]

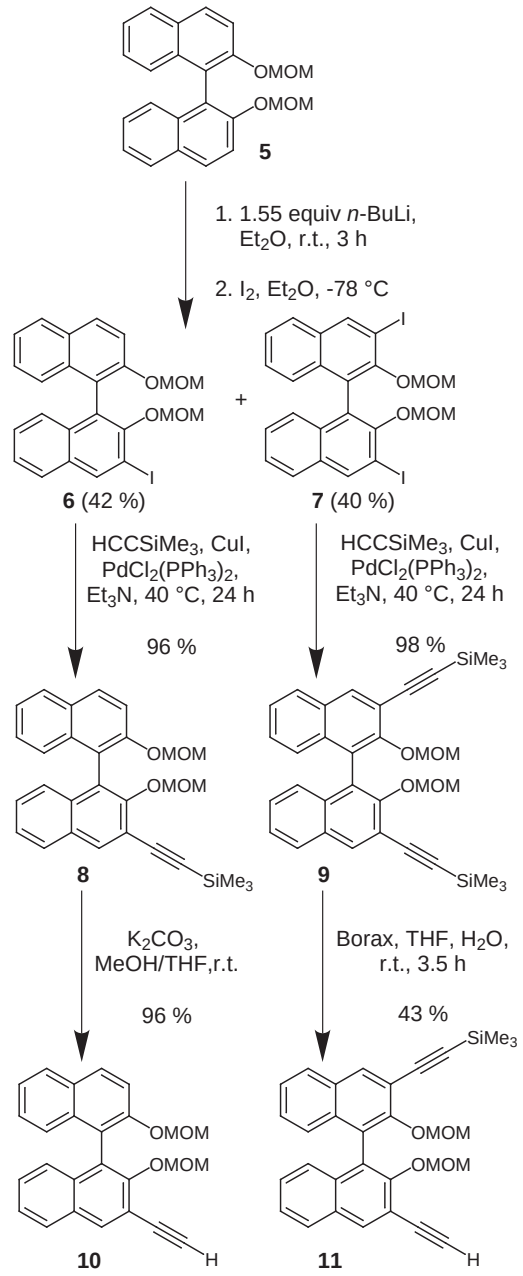


Scheme 1

Racemic 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) was prepared from β-naphthol by oxidative coupling.[12] Subsequent resolution was performed through clathrate formation with *N*-benzylcinchonidinium chloride[13] to afford enantiomerically pure (S_a)- and (R_a)-BINOL in 68 and 64% yield, respectively. Standard methoxymethyl ether protection of the hydroxyl functions gave the 2,2′-bis-MOM protected intermediate **5** in 80% yield.[14]

ortho-Lithiation facilitated by the protecting groups followed by quenching with iodine furnished the desired mono- and diiodinated BINOL-derivatives **6**[7b,15] and **7**[16] in almost equal yield which could easily be separated by column chromatography on silica. One- or two-fold coupling with TMS-acetylene under standard Sonogashira conditions gave compounds **8** and **9**[16] in excellent yields. The synthesis of the BINOL building blocks **10** and **11**,[16] was completed by deprotection and selective mono-deprotection of acetylenic groups under basic conditions, as depicted in Scheme 2.

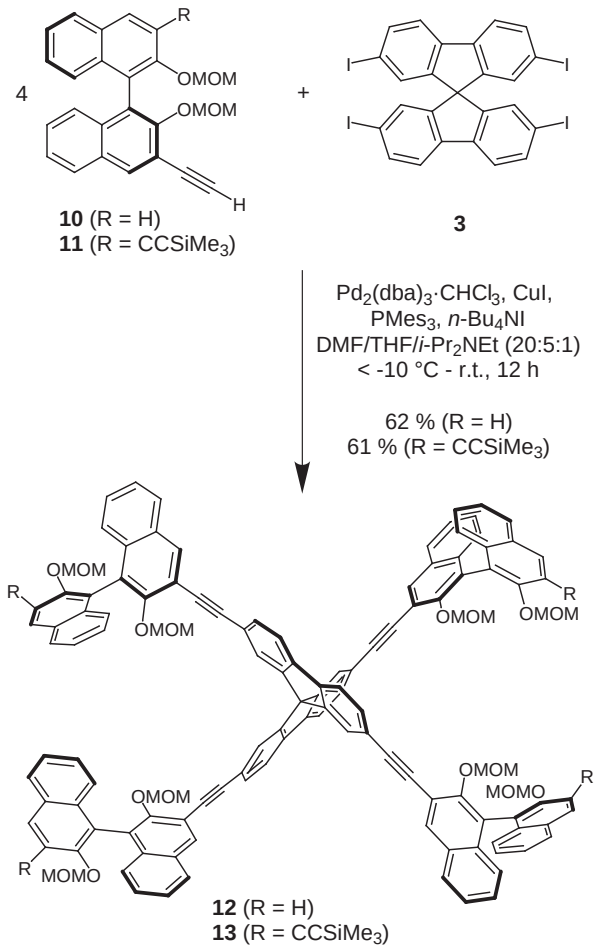
With the BINOL building blocks in both enantiomerically pure forms in hand, the next task was to react **10** and **11**



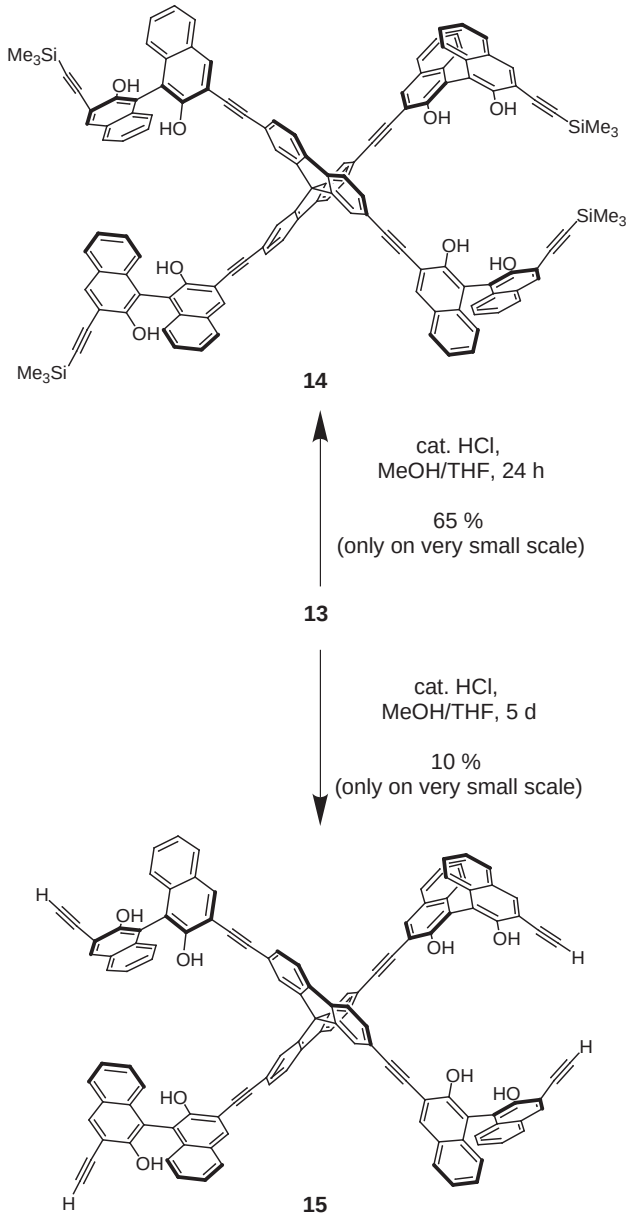
Scheme 2

with spirobifluorene **3**. Initially applied standard Sonogashira coupling conditions, $PdCl_2(PPh_3)_2$, CuI, and triethylamine, gave only unsatisfactory yields due to severe problems to separate the product from triphenylphosphine and triphenylphosphine oxide. However, we were able to overcome this problem by variation of the catalytic system according to a procedure published by Yamaguchi et al.[17] as shown in Scheme 3. In this way we were able to isolate totally MOM protected tetrasubstituted spirobifluorenes **12** and **13** in satisfying yields.

Sterically shielded clefts **14** and **15** were available through acidic hydrolysis (Scheme 4). However, even if hydrolysis of the TMS-protecting groups proved to need longer reaction times, we ran into problems when we tried to



Scheme 3



Scheme 4

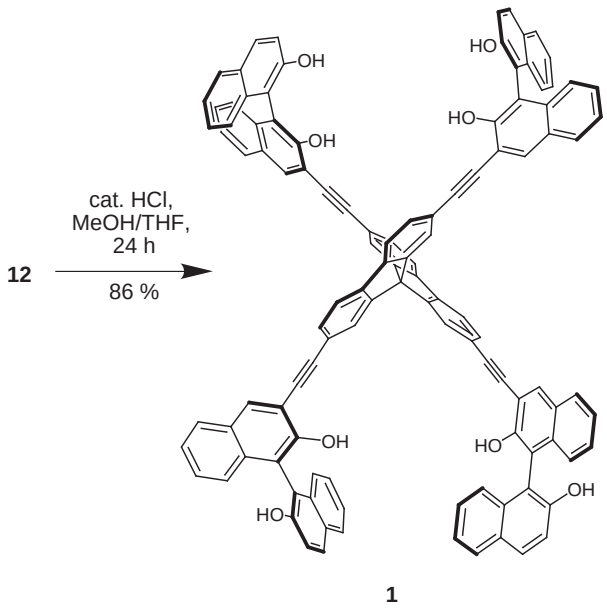
deprotect all eight hydroxy groups selectively. Thus, we were only able to obtain octol **14** in satisfactory yield after treatment of **13** with catalytical amounts of hydrochloric acid for only one day when we worked on a very small scale but upscaling of the reaction gave an undesirable mixture of partly deprotected hydroxy compounds lacking one or some of the TMS-groups which could not be separated by column chromatography.

Prolonged reaction time of 5 days lead to fully deprotected compound **15**. However, the yield of 10% was not very satisfying. Unfortunately, alternative stepwise deprotection strategies involving the use of potassium carbonate, sodium fluoride, or tetrabutylammonium fluoride to remove the silyl groups and subsequent acidic hydrolysis of the MOM-protecting groups did not result in better yields but even increased the problems with the isolation.

However, acidic hydrolysis of the MOM protecting groups of **12** easily afforded compound **1** in 86% yield (Scheme 5).

In conclusion, although this approach has its obvious limitations in the case of further functionalised, sterically more demanding tetra(BINOL) substituted spirobifluorenes **14** and **15**, a practical synthesis of tetrafunctionalised chiral spirobifluorene **1** from versatile spirobifluorene **3** and BINOL building block **10** has been accomplished in both enantiomerically pure forms, respectively. The crucial four-fold Sonogashira-coupling could be achieved in good yields by applying Yamaguchi's conditions. With reasonable amounts of **1** in hands, we are now studying the recognition behaviour of **1** and its analogous metal coordination complexes towards chiral substrates like monosaccharides in order to learn more about the influence of the metal ion on the binding process.

2-Aminobiphenyl was purchased from Sigma-Aldrich Chemie GmbH and used as received. Trimethylsilylacetylene was a generous gift from Wacker-Chemie GmbH. 9,9′-Spirobifluorene (**4**),[10] (S_a)- and (R_a)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl [(S_a)-**5**



Scheme 5

and (R_a)-**5**],[14] (S_a)- and (R_a)-2,2′-bis(methoxymethoxy)-3,3′-bis[(trimethylsilyl)ethynyl]-1,1′-binaphthyl [(S_a)-**9** and (R_a)-**9**],[16] and (S_a)- and (R_a)-2,2′-bis(methoxymethoxy)-3-ethynyl-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthyl [(S_a)-**11** and (R_a)-**11**][16] were prepared after published procedures. THF and Et_2O were dried over and distilled from sodium benzophenone ketyl. Bis(triphenylphosphino)palladium dichloride [$PdCl_2(PPh_3)_2$],[18] tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3·$CHCl_3$),[19] and trimesitylphosphine[20] were prepared after published procedures. BuLi solutions were purchased from Merck and were titrated prior to use against *N*-pivaloyl-*o*-toluidine.[21] Petroleum ether used has a bp of 40–60 °C. Most reactions were performed under an argon atmosphere in oven-dried glassware using standard Schlenk techniques.

TLC was performed on aluminium TLC plates silica gel 60 F_{254} from Merck. Detection was done by UV-light (254 and 366 nm). Products were purified by column chromatography on silica gel 60 (70–230 mesh) from Merck. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer at 500.1 and 125.8 MHz, respectively. ^1H NMR chemical shifts are reported on the δ-scale (ppm) relative to residual non-deuterated solvent as internal standard. ^{13}C NMR chemical shifts are reported on the δ-scale relative to deuterated solvent as internal standard. Signals were assigned on the basis of ^1H, ^{13}C, H,H-COSY, HMQC, and (in some cases) HMBC NMR experiments. Mass spectra were taken on a Finnigan MAT 212 with data system MMS–ICIS (EI, CI, *iso*-butane, NH_3), a Finnigan MAT 95 with data system DEC-Station 5000 (CI, *iso*-butane or NH_3; HiRes-CI, *iso*-butane or NH_3; FD), a Thermoquest Finnigan LCQ with software-packet Xcalibur (ESI), or a Reflex III from Bruker [MALDI-TOF, 2-(4′-hydroxy-phenylazo)benzoic acid (HABA) was used as matrix]. Mps were measured with a hot-stage microscope SM-Lux from Leitz and are not corrected. Specific optical rotations were measured on a Perkin Elmer Polarimeter 343 in a 10 cm cuvette. Elemental analyses were carried out with a Fisons Instrument EA1108.

2,2′,7,7′-Tetraiodo-9,9′-spirobifluorene (3)[11]

Concd sulphuric acid (0.1 mL), periodic acid (0.57 g, 2.5 mmol), and iodine (1.26 g, 4.97 mmol) were added to a suspension of 9,9′-spirobifluorene (**4**) (0.50 g, 1.57 mmol) in H_2O (0.3 mL) and glacial HOAc (8 mL). The resulting mixture was stirred at 80 °C for 3 h. Upon cooling to r.t. the precipitated product was collected through filtration and washed with toluene–EtOH (3:1). After dissolving the solid in a mixture of THF–CH_2Cl_2, the solution was washed with sat. aq $NaHCO_3$ until no further gas evolution was observed. The organic layer was then washed with 10% aq sodium thiosulfate, H_2O, brine and dried (Na_2SO_4). After concentration in vacuo the crude product was treated with a small amount of $CHCl_3$ to give the pure product after filtration.

Yield: 0.66 g (51%); white solid; mp > 300 °C.

The spectroscopic data were in agreement with the ones published by Wu et al.[11]

2,2′-Bis(methoxymethoxy)-3-iodo-1,1′-binaphthyl (6)[7b,15] **and 2,2′-Bis(methoxymethoxy)-3,3′-diiodo-1,1′-binaphthyl (7)**[16]

Under argon atmosphere BuLi (1.6 M in hexane, 1.16 mL, 1.85 mmol) was added to a solution of (R_a)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl [(R_a)-**5**] (0.45 g, 1.2 mmol) in abs. Et_2O (20 mL). After stirring for 3 h at r.t. the solution was cooled to –78 °C and a solution of iodine (0.61 g, 2.4 mmol) in abs. Et_2O (20 mL) was slowly added dropwise. After the solution was stirred for another 2 h at –78 °C, it was allowed to warm to r.t. and subsequently quenched with 10% aq sodium disulfite solution (10 mL). The layers were separated and the aq phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. Column chromatography of the residue [silica gel; petroleum ether–EtOAc, 9:1, containing Et_3N (0.5%)] gave the desired products.

Compound 6

Yield: 252 mg (42%); white solid; R_f 0.36 [petroleum ether–EtOAc, 9:1, containing Et_3N (0.5%)]; mp 114 °C; (R_a)-**6** $[\alpha]_D^{20}$ +99.5 (*c* 0.99, THF); (S_a)-**6** $[\alpha]_D^{20}$ –100.1 (*c* 0.99, THF).

^1H NMR ($CDCl_3$): δ = 8.52 (s, 1 H), 7.96 (d, 1 H, *J* = 9.3 Hz), 7.89 (d, 1 H, *J* = 7.7 Hz), 7.77 (d, 1 H, *J* = 8.2 Hz), 7.58 (d, 1 H, *J* = 9.3 Hz), 7.40–7.34 (m, 2 H), 7.29–7.22 (m, 2 H), 7.19–7.14 (m, 2 H), 5.40 (d, 1 H, *J* = 7.1 Hz), 5.13 (d, 1 H, *J* = 7.1 Hz), 4.73 (d, 1 H, *J* = 5.5 Hz), 4.69 (d, *J* = 5.5 Hz), 3.19 (s, 3 H), 2.72 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 152.9, 151.6, 139.3, 133.8, 132.4, 130.1, 129.5, 127.8, 126.8, 126.7, 126.1, 125.6, 125.4, 124.4, 124.1, 120.1, 116.2, 99.1, 94.8, 92.9, 56.7, 56.0.

MS (CI, NH_3): *m*/*z* (%) = 518.0 (M + NH_4^+, 100).

HRMS (CI, NH_3): *m*/*z* calcd for $C_{24}H_{25}INO_4$: 518.0828; found: 518.0888.

Anal. Calcd for $C_{24}H_{21}IO_4$: C, 57.61; H, 4.23. Found: C, 57.72; H, 4.37.

Compound 7

Yield: 300 mg (40%).

The analytical data of (R_a)-**7** and (S_a)-**7** were in agreement with the ones published by Diederich et al.[16]

2,2′-Bis(methoxymethoxy)-3-[(trimethylsilyl)ethynyl]-1,1′-binaphthyl (8)

To a degassed solution of (R_a)-**6** (700 mg, 1.4 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 5 mol%), and CuI (13.5 mg, 5 mol%) in Et_3N (35 mL) was added trimethylsilylacetylene (0.50 mL, 2.2 mmol) under an argon atmosphere. The resulting mixture was stirred for 24 h at 40 °C. After complete consumption of the starting material the reaction mixture was quenched with brine (15 mL), filtered through Celite, and extracted with CH_2Cl_2 (3×). The combined organic layers were washed with sat. aq $NaHCO_3$, H_2O, and brine, dried (Na_2SO_4), and concentrated in vacuo. The title compound was obtained after column chromatography [silica gel; petroleum ether–EtOAc, 5:1 containing Et_3N (0.5%)].

Yield: 630 mg (96%); white solid; R_f 0.65 [petroleum ether–EtOAc, 5:1, containing Et_3N (0.5%)]; mp 121 °C (hexane); (R_a)-**8** $[\alpha]_D^{20}$ +128.8 (*c* 1.01, THF); (S_a)-**8** $[\alpha]_D^{20}$ –127.9 (*c* 1.00, THF).

^{1}H NMR ($CDCl_3$): δ = 8.15 (s, 1 H), 7.94 (d, 1 H, *J* = 8.8 Hz), 7.85–7.80 (m, 2 H), 7.55 (d, 1 H, *J* = 8.8 Hz), 7.39–7.33 (m, 2 H), 7.27–7.21 (m, 2 H), 7.16–7.14 (m, 2 H), 5.13 (d, 1 H, *J* = 6.6 Hz), 5.00 (d, 1 H, *J* = 6.0 Hz), 4.96 (d, 1 H, *J* = 6.6 Hz), 4.87 (d, 1 H, *J* = 6.0 Hz), 3.13 (s, 3 H), 2.60 (s, 3 H), 0.26 (s, 9 H).

^{13}C NMR ($CDCl_3$) δ = 153.0, 152.9, 134.6, 134.0, 133.9, 130.0, 129.7, 129.6, 127.7, 127.1, 126.5, 126.1, 126.0, 125.7, 125.1, 124.1, 120.6, 117.3, 116.7, 102.9, 98.6, 95.1, 56.1, 55.8, –0.2.

MS (CI, NH_3): *m*/*z* (%) = 488.2 (M + NH_4^+, 100).

HRMS (CI, NH_3): *m*/*z* calcd for $C_{29}H_{34}NO_4Si$: 488.2257; found: 488.2249.

2,2′-Bis(methoxymethoxy)-3-ethynyl-1,1′-binaphthyl (10)

A solution of (R_a)-**8** (600 mg, 1.27 mmol) and K_2CO_3 (1.242 g, 8.9 mmol) in THF–MeOH (1:1; 130 mL) was stirred at r.t. for 3 h. After that time CH_2Cl_2 (500 mL) was added and the resulting mixture was washed with H_2O. After drying of the organic layer (Na_2SO_4), the solvents were evaporated in vacuo and the residue subjected to column chromatography [silica gel; petroleum ether–EtOAc, 5:1, containing Et_3N (0.5%)] to give the title compound.

Yield: 490 mg (96%); off-white oil;. R_f 0.45 [petroleum ether–EtOAc, 5:1, containing Et_3N (0.5%)]; (R_a)-**10** $[\alpha]_D^{20}$ +113.9 (*c* 0.84, THF); (S_a)-**10** $[\alpha]_D^{20}$ –114.8 (*c* 0.86, THF).

^{1}H NMR ($CDCl_3$): δ = 8.24 (s, 1 H), 8.00 (d, 1 H, *J* = 9.2 Hz), 7.91–7.88 (m, 2 H), 7.63 (d, 1 H, *J* = 9.2 Hz), 7.45 (ddd, 1 H, *J* = 1.1, 7.5, 7.5 Hz), 7.40 (ddd, 1 H, *J* = 1.1, 7.5, 7.5 Hz), 7.33–7.29 (m, 2 H), 7.24–7.21 (m, 2 H), 5.19 (d, 1 H, *J* = 7.0 Hz), 5.06 (d, 1 H, *J* = 7.0 Hz), 4.99 (d, 1 H, *J* = 5.9 Hz), 4.89 (d, 1 H, *J* = 5.9 Hz), 3.37 (s, 3 H), 3.23 (s, 3 H), 2.70 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 152.9, 134.9, 134.0, 133.9, 130.3, 129.8, 129.6, 127.7, 127.7, 127.3, 126.6, 126.3, 126.0, 125.6, 125.4, 124.1, 120.1, 116.5, 116.5, 98.8, 95.0, 81.2, 80.9, 56.3, 55.9.

MS (CI, NH_3): *m*/*z* (%) = 415.9 (M + NH_4^+, 100).

HRMS (CI, NH_3): *m*/*z* calcd for $C_{26}H_{26}NO_4$: 416.1862; found: 416.1861.

Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.77; H, 5.68.

Totally MOM-Protected Tetrasubstituted Spirobifluorene 12

Compound **3** (180 mg, 0.22 mmol) was mixed with CuI (33.6 mg, 80 mol%), $PMes_3$ (68.5 mg, 80 mol%), *n*-Bu_4NI (651 mg, 800 mol%), and $Pd_2(dba)_3{\cdot}CHCl_3$ (22.8 mg, 10 mol%) and repeatedly evacuated and flushed with argon. The solids were then dissolved in DMF–THF–*i*-Pr_2NEt (10:5:1; 16 mL) at r.t. under an argon atmosphere. After cooling to –10 °C, (S_a)-**10** (360 mg, 0.904 mmol) dissolved in DMF (10 mL) was added via syringe. After 30 min the reaction mixture was allowed to warm up to r.t. and stirred overnight. After TLC monitoring revealed complete consumption of the starting material the reaction was quenched with sat. aq NH_4Cl and filtered through Celite. After separation of the phases the aq phase was repeatedly extracted with CH_2Cl_2. Combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was subjected to column chromatography [silica gel; hexane–EtOAc, 3:2 containing Et_3N (0.5%)] to give the desired product.

Yield: 260 mg (62%); yellow solid; R_f 0.26 [hexane–EtOAc, 3:2, containing Et_3N (0.5%)]; (S_a)-**12** $[\alpha]_D^{20}$ –170.7 (*c* 1.12, THF); (R_a)-**12** $[\alpha]_D^{20}$ +168.9 (*c* 0.48, THF).

^{1}H NMR ($CDCl_3$): δ = 8.14 (s, 4 H), 8.00 (d, 4 H, *J* = 9.1 Hz), 7.89–7.86 (m, 8 H), 7.82 (d, 4 H, *J* = 8.1 Hz), 7.65 (dd, 4 H, *J* = 8.1, 1.1 Hz), 7.58 (d, 4 H, *J* = 9.1 Hz), 7.41–7.35 (m, 8 H), 7.28–7.23 (m, 8 H), 7.19–7.17 (m, 8 H), 7.03 (d, 4 H, *J* = 1.1 Hz), 5.15 (d, 4 H, *J* = 7.0 Hz), 4.99 (d, 4 H, *J* = 7.0 Hz), 4.96 (d, 4 H, *J* = 5.9 Hz), 4.59 (d, 4 H, *J* = 5.9 Hz), 3.14 (s, 12 H), 2.60 (s, 12 H).

^{13}C NMR ($CDCl_3$): δ = 152.9, 152.6, 148.2, 141.2, 133.9, 133.7, 132.1, 132.0, 131.9, 130.4, 129.7, 129.6, 127.7, 127.3, 127.0, 126.5, 126.0, 125.7, 125.3, 124.1, 120.5, 117.3, 116.7, 98.8, 95.1, 93.5, 87.8, 65.2, 56.1, 55.8.

MS (FD): *m*/*z* (%) = 1901.5 (M^+, 100).

MS (ESI, positive mode, NH_4OAc): *m*/*z* (%) = 1919.3 (M + NH_4^+, 100).

HRMS (CI, NH_3) could not be performed.

Anal. Calcd for $C_{129}H_{96}O_{16}{\cdot}4\ H_2O$: C, 78.48; H, 5.31. Found: C, 78.74; H, 5.65.

Totally MOM-Protected Tetrasubstituted Spirobifluorene 13

Compound **3** (137 mg, 0.168 mmol) was mixed with CuI (25.5 mg, 80 mol%), $PMes_3$ (52.1 mg, 80 mol%), *n*-Bu_4NI (495 mg, 800 mol%), and $Pd_2(dba)_3{\cdot}CHCl_3$ (17.4 mg, 10 mol%) and repeatedly evacuated and flushed with argon. The solids were then dissolved in DMF–THF–*i*-Pr_2NEt (10:5:1; 12 mL) at r.t. under argon atmosphere. After cooling to –10 °C (S_a)-**11** (340 mg, 0.687 mmol) dissolved in DMF (8 mL) was added via syringe. After 30 min the reaction mixture was allowed to warm up to r.t. and stirred overnight. After TLC monitoring revealed complete consumption of the starting material, the reaction was quenched with sat. aq NH_4Cl and filtered through Celite. After separation of the phases the aq phase was repeatedly extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was subjected to column chromatography [silica gel; hexane–EtOAc, 4:1, containing Et_3N (0.5%) and then toluene–MeOH, 2:1] to give a crude mixture of the title compound together with some *n*-Bu_4NI which was again submitted to column chromatography (silica gel; CH_2Cl_2) to give the title compound.

Yield: 190 mg (61%); yellow solid; R_f 0.21 [hexane–EtOAc, 4:1, containing Et_3N (0.5%)]; (S_a)-**13** $[\alpha]_D^{20}$ +57.4° (*c* 0.24, THF); (R_a)-**13** $[\alpha]_D^{20}$–57.8 (*c* 0.32, THF).

^{1}H NMR ($CDCl_3$): δ = 8.06 (s, 4 H), 8.03 (s, 4 H), 7.79 (d, 4 H, *J* = 8.2 Hz), 7.71–7.67 (m, 8 H), 7.55–7.53 (m, 4 H), 7.30–7.27 (m, 8 H), 7.17–7.14 (m, 8 H), 7.08–7.05 (m, 8 H), 6.93 (m, 4 H), 5.05 (d, 4 H, *J* = 6.0 Hz), 4.99 (d, 4 H, *J* = 6.0 Hz), 4.75 (d, 4 H, *J* = 6.0 Hz), 4.75 (d, 4 H, *J* = 6.0 Hz), 2.34 (s, 12 H), 2.31 (s, 12 H), 0.16 (s, 36 H).

^{13}C NMR ($CDCl_3$): δ = 153.4, 152.9, 148.3, 141.3, 134.9, 134.2, 133.8, 133.8, 131.8, 130.2, 130.1, 127.5, 127.4, 127.2, 127.1, 126.5, 126.5, 125.7, 125.7, 125.4, 123.1, 120.6, 117.1, 117.0, 101.9, 99.0, 98.9, 98.6, 93.9, 87.4, 65.2, 56.0, 55.9, –0.1.

MS [MALDI, 2′-(4-hydroxyphenylazo)benzoic acid (HABA)]: *m*/*z* = 2310 (M + Na^+), 2326 (M + K^+).

HRMS (CI, NH_3) could not be performed.

Tetra(BINOL)-Substituted Spirobifluorene (*all*-R_a)-14

A solution of (*all*-R_a)-**13** (20 mg, 8.7 μmol) in MeOH–THF (1:1) (60 mL) was treated with one drop of concd hydrochloric acid. After stirring for 24 h the mixture was diluted with CH_2Cl_2 and neutralised through washing with sat. aq $NaHCO_3$. The organic layer was further washed with H_2O and brine and dried (Na_2SO_4). After evaporation of the solvents, the product was obtained after repeated preparative TLC [CH_2Cl_2–hexane, 5:1 containing Et_3N (0.5%)].

Yield: 11 mg (65%); R_f 0.9 [CH_2Cl_2–hexane, 5:1, containing Et_3N (0.5%)]; $[\alpha]_D^{20}$ –23.3 (*c* 1.1, THF).

^{1}H NMR ($CDCl_3$): δ = 8.07 (s, 4 H), 8.05 (s, 4 H), 7.79 (d, 4 H, *J* = 8.2 Hz), 7.78–7.75 (m, 8 H), 7.59 (m, 4 H, *J* = 8.2 Hz), 7.30–

7.29 (m, 8 H), 7.24–7.21 (m, 8 H), 7.10 (m, 8 H), 6.95 (m, 4 H), 5.87 (br s, 4 H), 5.62 (br s, 4 H), 0.25 (s, 36 H).

The small amount of material did not allow the recording of a satisfactory ^{13}C NMR.

Despite numerous attempts we were not able to detect an intact molecule ion in the MS by any of the following ionisation techniques: CI (*iso*-butane, NH_3), EI, FD, FAB, MALDI (HABA-matrix), or ESI (positive and negative mode, also when tried to label with additional ions, like ammonium or alkali metal ions).

Tetra(BINOL)-Substituted Spirobifluorene (*all*-R_a)-15

A solution of (*all*-R_a)-**13** (14 mg, 6.1 μmol) in MeOH–THF (1:1, 8 mL) was treated with two drops of concentrated hydrochloric acid. After stirring for 5 d the mixture was diluted with CH_2Cl_2 and neutralised through washing with sat. aq $NaHCO_3$. The organic layer was further washed with H_2O and brine and dried (Na_2SO_4). After evaporation of the solvents, the product was obtained after repeated preparative TLC [hexane–EtOAc, 4:1, containing Et_3N (0.5%)].

Yield: 1 mg (10%); R_f 0.26 [hexane–EtOAc, 4:1, containing Et_3N (0.5%)].

^1H NMR ($CDCl_3$): δ = 7.99 (s, 4 H), 7.97 (s, 4 H), 7.90–7.88 (m, 8 H), 7.71–7.69 (m, 4 H), 7.53–7.51 (m, 4 H), 7.39 (m, 4 H), 7.38–7.36 (m, 8 H), 7.32–7.29 (m, 8 H), 7.16–7.14 (m, 8 H), 5.34 (br s, 4 H), 5.05 (br s, 4 H), 3.66 (s, 4 H).

The small amount of material did not allow the recording of a satisfying ^{13}C NMR spectrum nor the determination of an accurate specific rotation.

MS (ESI, negative mode, pyridine): *m*/*z* (%) = 1644.8 (M – H^+, 100).

HRMS (CI, NH_3) could not be performed.

(*all*-R_a)-2,2′,7,7′-Tetra[2,2′-bis(methoxymethoxy)-3-ethyndiyl-3′-ethynyl-1,1′-binaphthyl]-9,9′-spirobifluorene [(*all*-R_a)-16]

Compound (*all*-R_a)-**13** (17.1 mg, 7.5 μmol) was dissolved in MeOH–THF (1:1; 30 mL) and treated with K_2CO_3 (28.9 mg, 0.21 mmol). After stirring for 4 d at r.t. the reaction mixture was diluted with CH_2Cl_2, washed with H_2O and brine, and finally dried (Na_2SO_4). After evaporation of the solvents the product was obtained after repeated preparative TLC [hexane–EtOAc, 2:1, containing Et_3N (0.5%)].

Yield: 7 mg (47%).

Compound (*all*-R_a)-**16** could also be obtained through fluoride mediated cleavage of the silyl groups. Thus, (*all*-R_a)-**13** (13 mg, 5.7 mol) dissolved in THF (20 mL) and H_2O (8 mL) was treated with TBAF (448 mg, 1.42 mmol) for 16 h at r.t.. After that time the mixture was diluted with CH_2Cl_2, washed several times with H_2O and brine, and dried (Na_2SO_4). After evaporation of the solvents the product was obtained after repeated preparative TLC.

Yield: 4 mg (36%); R_f 0.28 [hexane–EtOAc, 2:1, containing Et_3N (0.5%)]; $[\alpha]_D^{20}$ –65.8 (*c* 0.7, THF).

^1H NMR ($CDCl_3$): δ = 8.15 (s, 4 H), 8.09 (s, 4 H), 7.85 (d, 4 H, *J* = 8.2 Hz), 7.83–7.75 (m, 8 H), 7.61–7.59 (m, 4 H), 7.40–7.34 (m, 8 H), 7.27–7.23 (m, 8 H), 7.17–7.13 (m, 8 H), 6.99 (m, 4 H), 5.05 (d, 4 H, *J* = 6.0 Hz), 5.02 (d, 4 H, *J* = 6.0 Hz), 4.85 (d, 4 H, *J* = 6.0 Hz), 4.81 (d, 4 H, *J* = 6.0 Hz), 3.29 (s, 4 H), 2.44 (s, 12 H), 2.43 (s, 12 H).

The small amount of material did not allow the recording of a satisfactory ^{13}C NMR.

MS (MALDI, HABA): *m*/*z* = 2006 (M + Li^+), 2132 (M + Cs^+).

MS (ESI, negative mode, pyridine): *m*/*z* (%) = 1953 (M – MOM – H^+,100).

HRMS (CI, NH_3) could not be performed.

Tetra(BINOL)-Substituted Spirobifluorene 1

Compound (*S*$_a$)-**12** (200 mg, 0.105 mmol) was dissolved in MeOH–THF (1:1; 500 mL) and treated with concd hydrochloric acid (0.5 mL). After 12 h another portion of concd hydrochloric acid (0.5 mL) was added. After complete consumption of the starting material the solution was diluted with CH_2Cl_2 (500 mL), washed with sat. aq $NaHCO_3$, and dried (Na_2SO_4). After evaporation of the solvents the residue was subjected to column chromatography (silica gel; hexane–EtOAc, 4:3). The resulting crude product was dissolved in CH_2Cl_2 (10 mL) and triturated with hexane (50 mL). The precipitate was filtered off through Celite, washed with hexane (500 mL), and eluted with CH_2Cl_2 (500 mL). Evaporation of the solvent gave the desired product.

Yield: 140 mg (86%); yellow solid; R_f 0.21 (hexane–EtOAc, 4:3); (*S*$_a$)-**1** $[\alpha]_D^{20}$ –297.9 (*c* 1.18, THF); (*R*$_a$)-**1** $[\alpha]_D^{20}$ +296.2 (*c* 0.39, THF).

^1H NMR ($CDCl_3$): δ = 8.09 (s, 4 H), 7.91 (d, 4 H, *J* = 8.9 Hz), 7.84 (d, 4 H, *J* = 8.0 Hz), 7.83 (d, 4 H, *J* = 8.2 Hz), 7.78 (d, 4 H, *J* = 8.0 Hz), 7.60 (dd, 4 H, *J* = 1.1, 8.2 Hz), 7.33 (m, 4 H), 7.32 (m, 4 H), 7.31 (m, 4 H, *J* = 8.0 Hz), 7.26 (m, 4 H), 7.22 (m, 4 H), 7.10 (d, 4 H, *J* = 8.2 Hz), 7.05 (d, 4 H, *J* = 8.2 Hz), 6.96 (d, 4 H, *J* = 1.1 Hz), 5.63 (br s, 4 H), 4.90 (br s, 4 H).

^{13}C NMR ($CDCl_3$): δ = 152.0, 151.5, 148.1, 141.5, 133.9, 133.7, 133.2, 132.0, 130.9, 129.3, 128.8, 128.3, 128.2, 127.5, 127.1, 124.6, 124.5, 124.3, 123.7, 122.4, 120.8, 117.6, 112.2, 112.0, 111.8, 96.1, 85.0, 65.1.

MS (ESI, negative mode, pyridine): *m*/*z* (%) = 1548.5 (M – H^+,100).

MS (ESI, positive mode, NH_4OAc): *m*/*z* (%) = 1567.1 (M + NH_4^+,100), 1550.4 (M + H^+, 45).

HRMS (CI, NH_3) could not be performed.

Anal. Calcd for $C_{113}H_{64}O_8 \cdot 3H_2O$: C, 84.63; H, 4.40. Found: C, 84.51; H, 4.44.

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