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# Stereoselective preparation of spirane bridged, sandwiched bisarenes

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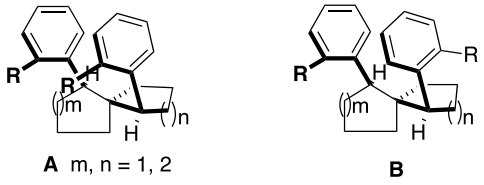
**Abstract**—Preparation of α-oxo derivatives of spiro[4.4]nonane, spiro[4.5]decane and spiro[5.5]undecane derivatives is described. An efficient method for spiroannulation by Rh(I)-catalysed intramolecular hydroacylation provides α,α′-difunctionalised spiro[4.5]decanes. The α,α′-dioxo groups have been converted into vinyl triflates for arylation by Pd-catalysed cross-coupling reactions under Stille, Negishi or Suzuki conditions depending on relative reactivities. Stereoselective saturation of the conjugated aryl olefinic bonds by catalytic hydrogenation over Pd–carbon provides methodology for stereoselective preparation of α-aryl- and α,α′-*cis*,*cis*-diaryl spiranes, the latter with a sandwich like structure. Single crystal X-ray analyses have been used in the structural assignments.


## 1. Introduction

The rigid framework in small-ring spiranes constitutes a potentially useful scaffold for attachment of configurationally highly oriented coordinating functions as ligands for metal complexation, or for stereochemically controlled attachment of pharmacophoric groups useful in medicinal chemistry. A spirane bridged sandwich like the bisarene **A** and its conformer **B** in Scheme 1 are reminiscent of certain ligands for metallocenes. In these spiranes the functional substituents R are situated in the α,α′-positions to be close to the spirocenter. Alternative sites are the β- or γ-positions or combinations thereof.




**Scheme 1.**

The two rings in the spirane are interconnected through a common ring atom. The two rings have an orthogonal relationship. Conformational freedom is highly restricted, and this restriction is transferred to the substituents. The rigidity in the spirane is controlled by the size of the two rings forming the spirane. Small-ring spiranes are very stiff. The larger ring systems are more flexible.

We have initiated studies with the ultimate aim of constructing spirobridges between functional units. Essential intermediates are oxospiranes. A rhodium(II)-carbenoid C–H insertion reaction has been used for spiroannulation to provide β,β′- and α,α′-dioxospiranes. The ring size of the carbocyclic substrate could be varied, but spiroannulation was limited to the addition of five-membered carbocycles.[1] In a method with a potentially wider application, functionalised spiranes were constructed using ruthenium(II)-catalysed ring-closing metathesis. The products were α,α′-dioxospiranes or derivatives thereof. The substrates were appropriately substituted five-, six- and seven-membered cycloalkanes which were spiroannulated by five-, six and seven-membered rings, respectively.[2]

Nucleophilic substitutions in spiranes in the most desirable α-position are complicated by the *neo*-effect from the spirocenter, and reactions involving carbonium intermediates at the α-carbon are likely to result in skeletal rearrangements. Addition of metal hydrides or organometallics to an α,α′-dioxospirane gives diols which are sensitive to ring-opening reactions, especially when the carbon substituent is an arene.[3,4]

A method for carbylation in the α-oxo position has been found by initial formation of enol triflate and a subsequent

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Pd-mediated cross-coupling reaction.[5] Full stereoselectivity in the generation of *cis*,*cis*-α,α′-diarylspiranes has been achieved by way of catalytic hydrogenation of the corresponding α,α′-dienospiranes as shown in Schemes 7 and 8.

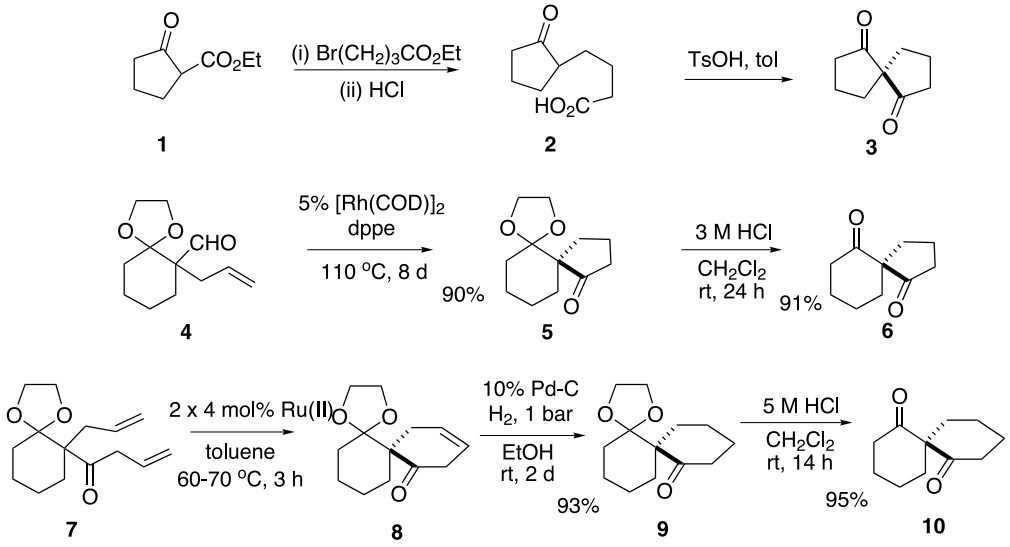
## 2. Results and discussion

Scheme 2 outlines the preparation of α,α′-dioxospirane intermediates. The smallest member of the dioxospirane family in this work was spiro[4.4]nonane-1,6-dione (**3**), which was available by a simple alkylation of ethyl 2-oxocyclopentanecarboxylate, and provided a subsequent acid hydrolysis product **2** which was cyclised under acid catalysis (Scheme 1).[6] For the higher homologue **6**, a new synthetic route was developed. From the literature, it is known that rhodium-catalysed intramolecular hydroacylation of 4-alkenyls constitutes a useful method for the preparation of cyclopentanones.[7] The main steps in the catalytic hydroacylation reaction are thought to be oxidative insertion into the aldehyde C–H bond, a subsequent olefin insertion to furnish a rhodacycle intermediate which on reductive elimination regenerates the catalyst and produces a cyclopentanone.[8] The synthesis of ketones from aldehydes, however, is complicated by decarbonylation in the acylmetal intermediate by a rearrangement whereby the carbonyl group becomes coordinated to the metal as carbon monoxide leading to a less reactive catalyst complex as well as to decarbonylation.[9] In the synthesis of spiro[4.5]decane-1,6-dione derivatives by hydroacylation of 4-pentenals, product analysis showed extensive decarbonylation. The reactions were run in benzonitrile.[10] In our initial work we also used benzonitrile as solvent at 110 °C with an acetal of 2-allylcyclohexanone-2-carbaldehyde **4** (Scheme 2) as substrate. A satisfactory catalyst system was 10% Rh(COD)(dppe)Cl. Decarbonylation, however, was significant. The desired product was obtained together with 25% of decarbonylated material. With nitromethane as an alternative solvent, there was an increase in the decarbonylation, up to 33%. We then discovered that the decarbonylation could largely be avoided when the hydroacylations were run in the absence of a solvent. In this procedure, the aldehyde and 5% $[Rh(COD)Cl]_2$ were heated together with dppe at 110 °C for 8 d. The yield of decarbonylated material was reduced to barely 2% whereas the spiroannulated cyclopentanone **5** was obtained in a very high yield, 90%. The spiranedione **6** was readily available by acid hydrolysis of the acetal **5**. The spirane **6** could also be prepared from 2-allyl-2-formylcyclohexanone by the rhodium(I)-catalysed hydridoacylation. The relatively high volatility of the aldehyde substrate, however, made this reaction less attractive.

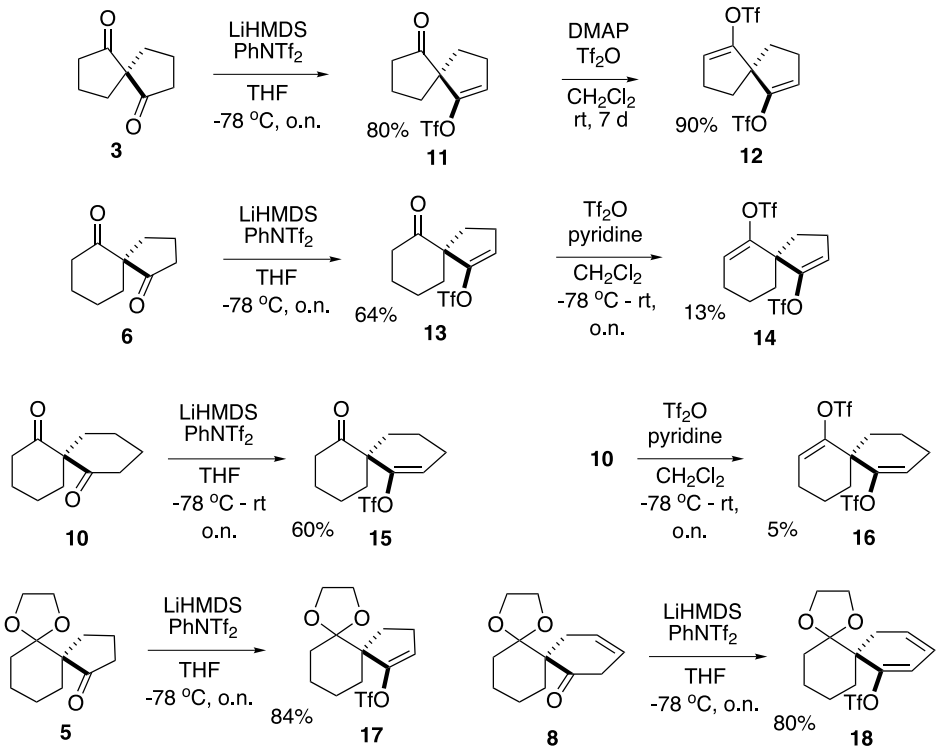
The spiro[5.5]undecan-1,7-dione series was available by an initial Ru(II)-catalysed RCM reaction of the diene **7**.[2] The product was the unsaturated spiranone **8**. Saturation of the carbon–carbon double bond over 10% Pd–C, and a subsequent acid catalysed hydrolysis of the acetal function, furnished the 1,7-dioxospirane **10**.

Scheme 3 shows the preparation of triflate reactants for the cross-coupling carbylation reactions. For triflation at the α-carbon, either $PhNTf_2$ or $Tf_2O$ was used. The milder reagent $PhNTf_2$ was generally the better.

With LiHMDS as base and $PhNTf_2$ for triflation, the monotriflate **11** was isolated in 80% yield, and the ditriflate **12** in 5% yield. A second triflation to form the corresponding α,α′-ditriflate in the spirane series in general has been difficult to effect. In the case of the spiro[4.4]nonane series, however, the ditriflate **12** was finally obtained in excellent yield (90%) when the triflation was run with $Tf_2O$ in DMAP using the monotriflate **11** as substrate. The reaction was slow. Monotriflation in the spiro[4.5]decane-1,6-dione series proceeded well with LiHMDS as base. Only one monotriflated product was seen. The product was the five-membered ring triflate **13**, yield 64%. The α-protons in the five-membered ring ketone are more acidic than in the six-membered ring ketone. Direct ditriflation from the α,α′-diketone **6**, however, gave only the ditriflate **14** in a very low yield. As experienced in the spiro[4.4]nonane series, ditriflation could be effected in a two-step operation albeit




**Scheme 2.**

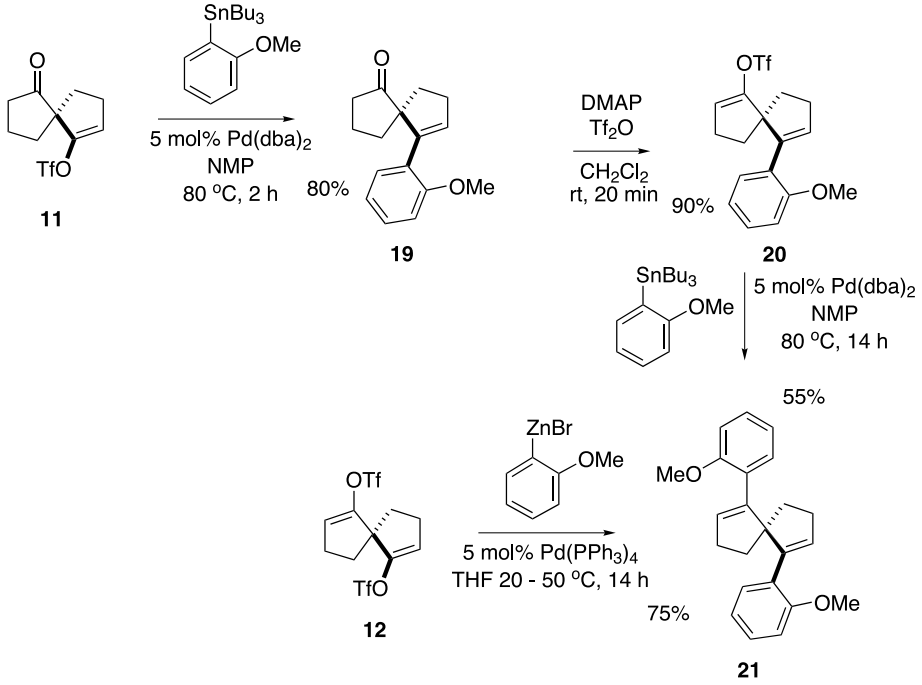



**Scheme 3.**

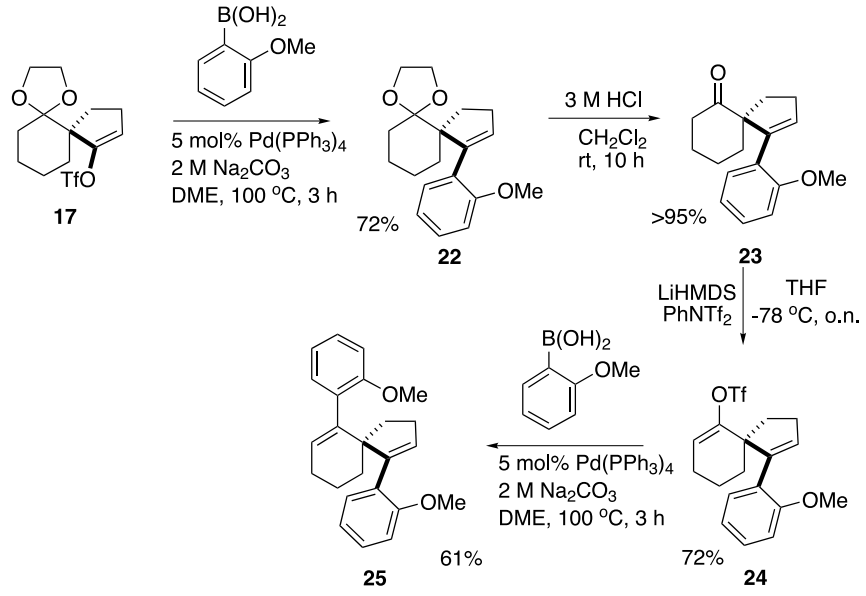
in a low 13% yield of the ditriflate **14** using triflic anhydride in pyridine. Apparently, a H-3 proton in the five-membered ring is abstracted preferentially rather than an α-oxo proton in the six-membered ring.

In the spiro[5.5]undecan-1,7-dione series, the monotriflated product **15** was isolated. Further triflation was difficult to effect. Monotriflation of the acetals **5** and **8** proceeded readily to provide the triflates **17** and **18** in ca. 80% yield.

Carbon–carbon bond forming reactions by Pd-catalysis are shown in Scheme 4. A preliminary study of *ortho*-substituted organometallic reactants showed that the cross-coupling into the shielded α-position in spiranes was sensitive to steric interactions from the *o*-substituent. A




**Scheme 4.**

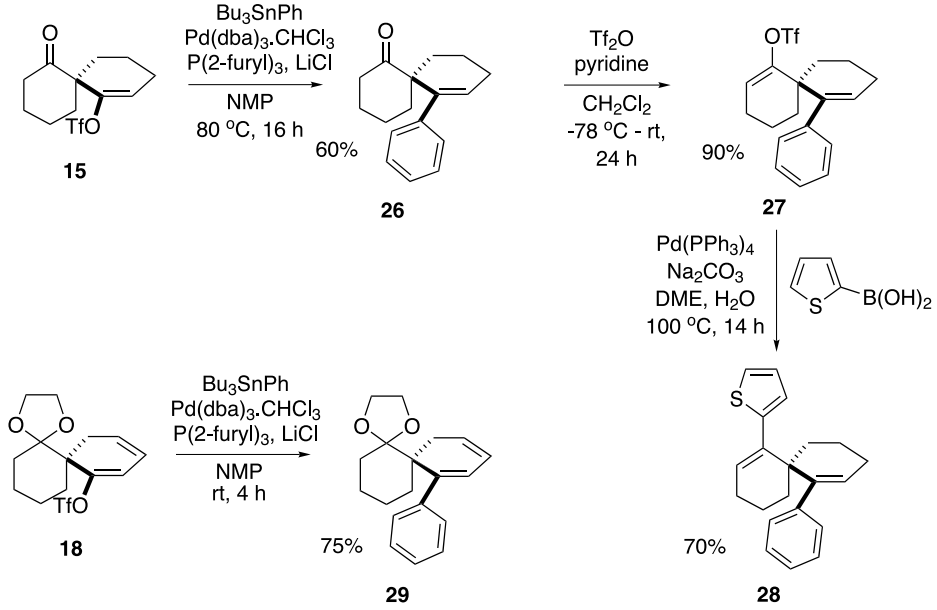



**Scheme 5.**

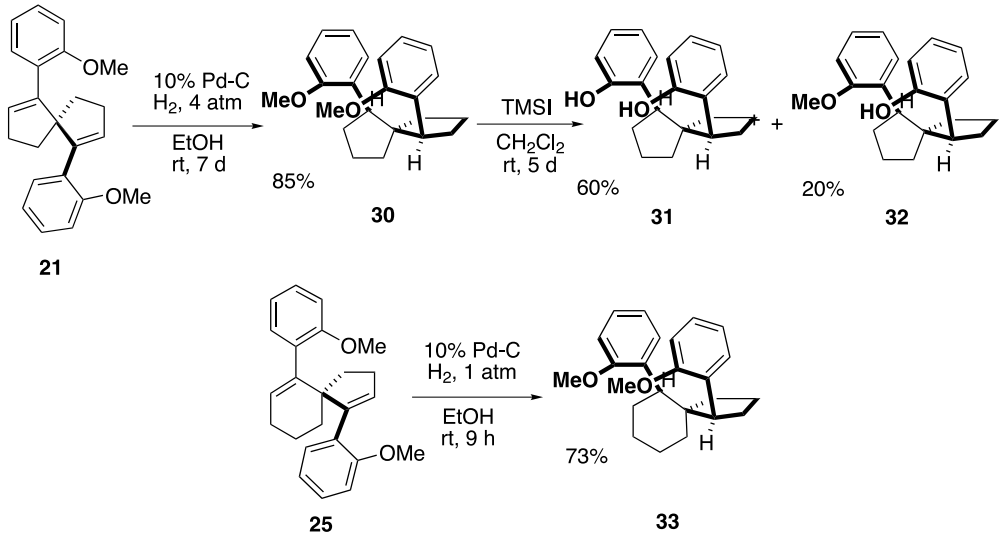
2-methoxy group in the organometallic reactant provided a reasonably good yield in the cross-coupling reaction. Hence organometallic anisole derivatives were used for the subsequent cross-coupling reactions. Thus, the Stille coupling between 2-(tri-*n*-butylstannyl)anisole and the monotriflate **11** proceeded readily to furnish the mono-arylated product **19** in high yield. For a further carbylation reaction, product **19** was triflated using $Tf_2O$ in DMAP. Stille reaction conditions provided the product **21**. This approach allows for differential carbylation in the two α,α′-positions in spiranes. In this case the same stannyl coupling reagent was used, thereby providing the $C_2$-symmetric diarylated product **21**. The successful preparation of the bistriflate **12**, allowed direct Pd-catalysed dicoupling. In this case, however, Negishi coupling conditions with an organozinc reactant gave a better yield, 75% (Scheme 5).

The cross-coupling under Stille conditions of the acetalised triflate of spiro[4.5]undecane **17** was not satisfactory. We therefore effected the coupling with the appropriate benzeneboronic acid under Suzuki conditions with sodium carbonate as base in aqueous DME. The cross-coupled product **22** was isolated in high yield and was subsequently hydrolysed to ketone **23** under acidic conditions. Triflation of the ketone **23** was effected with lithiation at low temperature and treatment with $PhNTf_2$ to furnish the triflate **24**. Suzuki coupling conditions as above provided the diarylated spirane **25**. Dicoupling with the ditriflate **14** (Scheme 3) as substrate had previously failed to provide the dianisole product **25**.

In the spiro[5,5]undecane series, a two-step process was used for introduction of the two arene groups (Scheme 6).




**Scheme 6.**

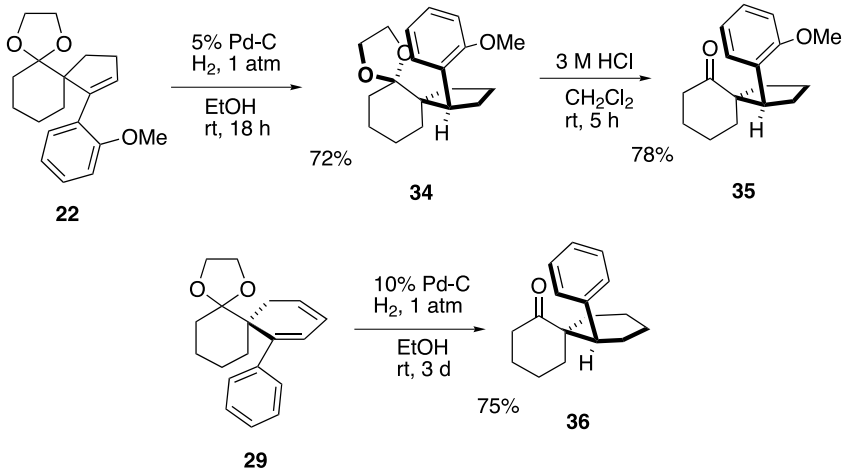



**Scheme 7.**

With the phospine P(2-furyl)$_3$ for ligation of palladium, the Stille conditions in NMP as solvent provided the arylated spirane **26** from the keto triflate **15**. Triflation in the monoaryl spirane **26** was effected with triflic anhydride in pyridine and furnished the triflate **27** in high yield. As stated above, this two-step process allows for differential carbylation in the two spirane rings. In this case, a 2-thienyl group was introduced under Suzuki conditions to provide the mixed diarylated product **28** in good yield. The coupling of the diene acetal **18** under Stille conditions proceeded more readily than for the ene triflate **15**.

In the target spirane structure **A** in Scheme 1, the functionalized aryl rings have a *cis*,*cis*-relationship. In the substrates from the cross-coupling reactions, the aryl groups are hinged to an sp$^2$-hybridised carbon and are thus coplanar with the orthogonal spirane rings, respectively. In a saturated spirane, the $\alpha,\alpha'$-substituents at sp$^3$-hybridised carbons can have a *cis*,*cis*-, a *cis*,*trans*-, or *trans*,*trans*-relationship. A stereoselective reduction of the double bonds for formation of the *cis*- or the *cis*,*cis*-isomer is required. The *cis*,*cis*-configuration, however, leads to a significant repulsive interaction, and is thermodynamically the least favourable structure of the three geometrical isomers. For steric reasons, on heterogenous hydrogenation the less sterically shielded face of a spirane ring becomes associated with the metal catalyst. A subsequent transfer of hydrogen from the metal to the double bond forces the substituent into a *cis*-position. Thus both the styrene double bonds in structures **21** and **25** were saturated over 10% Pd–charcoal (Scheme 7). The long reaction times may reflect steric crowding, but the reaction was fully stereoselective in that only one product was seen, viz. the *cis*,*cis*-isomers **30** and **33**. The relative configuration assigned for the latter has been ascertained by a single crystal X-ray analysis (vide infra). The assignment of the relative configuration of the former is based on the established configuration of its lower phenyl analogue.[5]

The monoarylated substrates **22** and **29** in Scheme 8 reacted under similar conditions to provide a single reduction product. The spiro[5.5]undecane substrate **29** is a 1,3-diene. Stereoselectivity in the reduction furnished a single product which was found by a single crystal X-ray analysis to be the *cis*-isomer **36**. The double bond in the spiro[4.5]decane substrate **22** was saturated under similar conditions. The




**Scheme 8.**

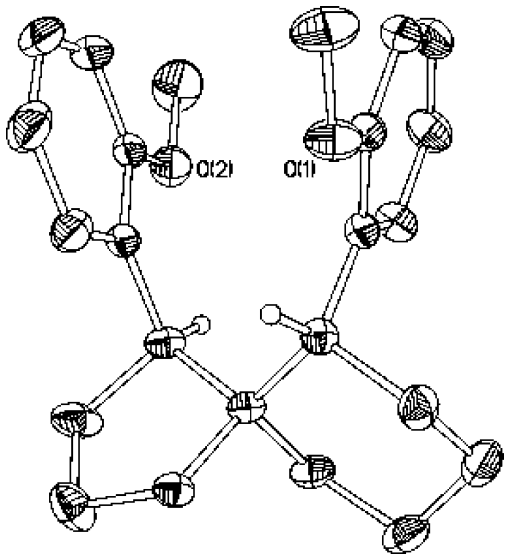



**Figure 1.** The ORTEP plot of compound **33**. Ellipsoids are shown at 50% probability. For clarity only the hydrogen at stereogenic centers and at double bonds are shown.

product has tentatively been assigned the *cis*-structure **34** by analogy to the formation of the *cis*-isomer **36** and the *cis*,*cis*-isomers **30** and **33**. The ketone **35** was available after acid hydrolysis of the acetal **34**.

In spiro-bridged sandwich-like bisarene structures with ligand properties towards a metal in the center, the aryl group would carry substituents with coordinating properties. The model substituent in the present work was the *o*-methoxy group (Scheme 7). The methoxy group can also be regarded as a methyl *O*-protected phenolic group. Trimethylsilyl iodide was used to cleave the methyl aryl ether **30** to furnish the diphenol sandwich structure **31** (Scheme 7). Slow cleavage required the use of a large excess of the silyl iodide reagent. The diol **31** and the semihydrolysed product **32** were isolated in 76 and 20% respectively, after 5 d at ambient temperature.

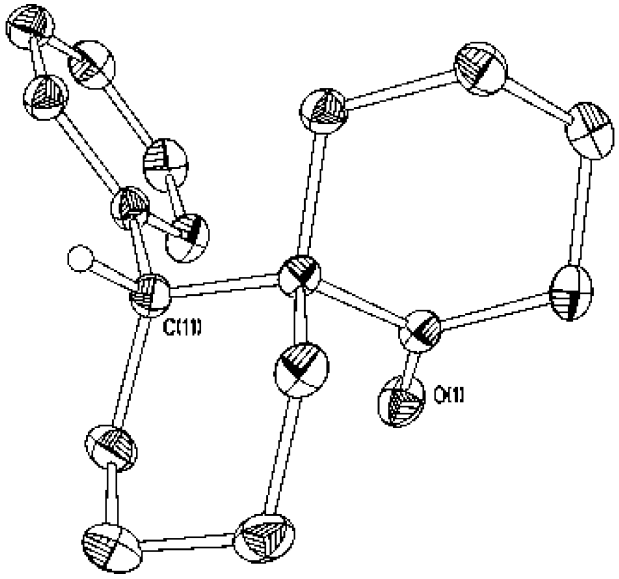



**Figure 2.** The ORTEP plot of compound **36**. Ellipsoids are shown at 50% probability. For clarity only the hydrogen at stereogenic centers and at double bonds are shown.

The relative stereochemistry of compounds **33** and **36** was determined by single crystal X-ray analyses. The ORTEP plots of the crystal structures are shown in Figures 1 and 2. In the crystal structure the anisole units in structure **33** have an antiparallel arrangement corresponding to conformer **B** in Scheme 1.

## 3. Conclusion

In conclusion, we have described a method for the preparation of spiro[4.4]nonane, spiro[4.5]decane and spiro[5.5]undecane α-oxo derivatives. In particular, an efficient method for Rh-catalysed intramolecular hydroacylation was developed for the preparation of α,α-difunctionalised spiro[4.5]decanes. Substitutions in the α-positions in the spiranes has been effected from the corresponding ketones by way of vinyl triflates and palladium catalysed cross-coupling reactions. In most cases, ditriflation was best effected in a step-wise manner. To cope with different reactivities of the vinyl triflate substituents in the spiranes, Stille, Negishi and Suzuki conditions were all employed. Catalytic hydrogenation over Pd–carbon provides methodology for stereoselective preparation of α-*cis*-aryl- and α,α′-*cis*,*cis*-diaryl spiranes, the latter with a sandwich like structure.

## 4. Experimental

The $^{1}$H NMR spectra were recorded at 300 or 500 MHz and the $^{13}$C NMR spectra at 75 or 125 MHz. Chemical shifts are given in ppm relative to the solvent $CDCl_3$. Coupling constants *J* are given in Hz. Interpretation of the NMR spectra was helped by COSY, DEPT HETCOR and COLOC techniques. The mass spectra were recorded at 70 eV under electron impact conditions (EI) and are presented as *m*/*z* (rel. int.). IR spectra were measured on a Nicolet Magna 550 spectrometer using ATR (attenuated total reflectance).

THF, toluene and diethyl ether were dried over sodium. Dichloromethane was distilled over calcium hydride. Solvents were degassed by bubbling argon through. Reactions under dry conditions were run under an argon atmosphere.

### 4.1. X-ray crystallographic analysis for compounds 33 and 36

X-ray data were collected on a Siemens SMART CCD diffractometer[11] using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection method: ω-scan, range 0.6°, crystal to detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP programs.[11] Absorption corrections were applied by the use of the SADABS program.[12] The structures were determined and refined using the SHELXTL program package.[13] The non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were

located from difference Fourier maps and refined with isotropic thermal parameters.

Structural data have been deposited at the Cambridge Crystallographic Data Centre deposition number CCDC 250768 for compound **33**, and CCDC 250769 for compound **36**.

**4.1.1. Crystal data for $C_{24}H_{30}O_2$ (33).** $M=350.48$, monoclinic, $P2_1/n$, $a=8.133(1)$ Å, $b=25.511(1)$ Å, $c=9.848(1)$ Å, $\beta=107.84(1)°$, $V=1925.3(1)$ Å$^3$, $Z=4$, $D_x=1.209$ Mg m$^{-3}$, $\mu=0.075$ mm$^{-1}$, $T=105(2)$ K, measured 27,375 reflections in $2\theta$ range 5.4–61.0°, $R_{int}=0.032$. 355 parameters refined against 5859 $F^2$, $R=0.050$ for $I_o>2\sigma(I_o)$ and 0.063 for all data.

**4.1.2. Crystal data for $C_{17}H_{22}O$ (36).** $M=242.35$, monoclinic, $Pca2_1$, $a=14.367(1)$ Å, $b=12.610(1)$ Å, $c=7.490(1)$ Å, $V=1356.9(1)$ Å$^3$, $Z=4$, $D_x=1.186$ Mg m$^{-3}$, $\mu=0.071$ mm$^{-1}$, $T=105(2)$ K, measured 28,782 reflections in $2\theta$ range 3.2–72.8°, $R_{int}=0.026$. 251 parameters refined against 6380 $F^2$, $R=0.033$ for $I_o>2\theta(I_o)$ and 0.039 for all data.

**4.1.3. 1,4-Dioxadispiro[4.0.4.4]tetradecan-7-one (5).** 6-Allyl-1,4-dioxaspiro[4.5]decane-6-carbaldehyde[2] (**4**) (4.929 g, 23.5 mmol), $(Rh(COD)Cl)_2$ (0.261 g, 0.59 mmol) and dppe (0.468 g, 1.18 mmol) were heated together at 110 °C for 8 d when GLC showed the reaction to be complete. Excess hexane was added to the reaction mixture to precipitate the catalyst which was removed by filtration and the filtrate evaporated. The residual material was subjected to flash chromatography using 30% diethyl ether in hexane. The product was a yellow oil; yield 3.641 g (64%). (Found: C 68.51, H 8.67. Calcd for $C_{12}H_{18}O_3$: C 68.54, H 8.63%); HRMS(EI): *M* 210.1260. Calcd for $C_{12}H_{18}O_3$: 210.1256. IR (film) $\nu$ cm$^{-1}$ 2935 (m), 2884 (m), 1732 (s); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.26–1.95 (11H, m, $CH_2$), 2.14–2.24 (3H, m, $CH_2$), 3.79–3.89 (4H, m, H2 and H3); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 18.4 ($CH_2$), 20.3 ($CH_2$), 23.0 ($CH_2$), 31.1 ($CH_2$), 32.1 ($CH_2$), 32.5 ($CH_2$), 39.7 (C8), 55.2 (C5), 64.3 (C2 or C3), 65.0 (C3 or C2), 110.7 (C5), 218.9 (C7); *m/z* (EI): 210 (M, 32%), 165 (22), 99 (100), 86 (45).

**4.1.4. Spiro[4,5]decane-1,6 dione (6).**[14] 1,4-Dioxadispiro-[4.0.4.4]tetradecan-7-one (**5**) (1.242 g, 5.91 was added to 3 M HCl (10 mL) in $CH_2Cl_2$ (15 mL)and conc. HCl (3 mL) added. The mixture was stirred at room temperature overnight before addition of aqueous saturated $NaHCO_3$ (20 mL). Dichloromethane (5×20 mL) extraction furnished the diketone; yield 1.130 g (91%).

**4.1.5. 1,4-Dioxadispiro[4.0.5.4]pentadecan-7-one (9).** 1,4-Dioxadispiro[4.0.5.4]pentadec-9 en-7-one (**8**)[2] (500 mg, 2.25 mmol) in ethanol (30 mL) was hydrogenated over 10% palladium on charcoal (500 mg) at 1 atm and ambient temperature for 2 d. The catalyst was filtered off and the solvent evaporated. The crude product was purified by flash chromatography using hexane/EtOAc 20:1.The product appeared as a yellow oil; yield 0.47 g, (93%). HRMS. Found *M* 224.1409. Calcd for $C_{13}H_{20}O_3$: 224.1412. IR (film) $\nu$ cm$^{-1}$ 2938 (C–H), 1702 (C=O); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.20–1.74 (12H, m, $CH_2$), 2.15–2.47 (4H, m, $CH_2$), 3.79–3.96 (4H, m, H2, H3); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 20.6 ($CH_2$) 21.1 ($CH_2$), 23.2 ($CH_2$), 27.2 ($CH_2$), 31.8 ($CH_2$), 32.7 ($CH_2$), 33.3 ($CH_2$), 40.4 ($CH_2$), 56.0 (C6), 64.1 (C2) 64.0 (C3), 110.9 (C5), 213.2 (C7); MS(EI): 224 (M, 26%), 179 (52), 99 (100), 86 (38).

**4.1.6. Spiro[5.5]undecane-1,7-dione (10).** A solution of the 1,4-dioxadispiro[4.0.5.4]pentadecan-7-one (**9**) (500 mg, 2.2 mmol) in $CH_2Cl_2$ (10 mL) and 5 M HCl (8 mL) was stirred overnight at ambient temperature. The mixture was extracted with diethyl ether (2×15 mL), washed with water, with saturated $NaHCO_3$ solution and brine. The solvent was evaporated and the crude product purified by flash chromatography using hexane/EtOAc 6:1; yield 0.38 g (95%) of a white crystalline solid, mp 49–50 °C. (Found: C, 73.30; H 8.95. Calcd for $C_{11}H_{16}O_2$: C, 73.09; H, 9.04%). HRMS: *M* 180.1146. Calcd for $C_{11}H_{16}O_2$: 180.1150. IR (film) $\nu$ cm$^{-1}$ 2900 (C–H), 1686 (C=O); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.21–1.75 (3H, m, $CH_2$), 2.45–3.38 (1H, m, H2, H8); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 21.2 ($CH_2$), 21.6 ($CH_2$), 27.7 ($CH_2$), 36.2 ($CH_2$), 40.8 (C2, C8), 64.5 (C6), 210.9 (C1, C7). MS (EI): 180 (M, 41%), 152 (57), 124 (70), 111 (61), 67 (63), 55 (95), 41 (100).

**4.1.7. Trifluoromethanesulfonic acid 6-trifluoromethanesulfonyloxyspiro[4.4]nona-1,6-diene-1-yl ester (12).**[5] A solution of trifluoromethanesulfonic acid 6-oxospiro[4.4]non-1-en-1-yl ester (**11**) (1.5 g, 5.2 mmol) and DMAP (708 mg, 5.8 mmol) in dry dichloromethane (100 mL) was stirred at room temperature for 24 h before triflic anhydride (1.12 mL, 6.76 mmol) was added and the mixture stirred at room temperature for 6 d to complete the reaction (TLC). The solvent was evaporated and the product purified by flash chromatography using hexane/EtOAc 5:1; yield 90% of a colourless oil.[5]

**4.1.8. Trifluoromethanesulfonic acid 6-oxospiro[4.5]dec-1-en-1-yl ester (13).** A solution of HMDS (0.778 g, 4.82 mmol) and *n*BuLi (1.85 mL, 2.77 mmol) in THF (5 mL) was added dropwise over 20 min to a solution of spiro[4.5]decane-1,6-dione (**6**) (0.401 g, 2.40 mmol) and $PhNTf_2$ (0.987 g, 2.77 mmol) in THF (15 mL). at −78 °C. The mixture was allowed to reach room temperature overnight. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (20 mL) and the mixture extracted with diethyl ether (3×20 mL). The ether extracts were dried ($MgSO_4$), evaporated and the residual material subjected to flash chromatography on slica gel using 20% EtOAc in hexane. The product was a yellow oil; yield 0.460 g (64%). (Found: C, 44.14; H, 4.74. Calcd for $C_{11}H_{12}O_4F_3S_1$: C, 44.29; H, 4.39%). HRMS: *M* 299.0570. Calcd for $C_{11}H_{12}O_4F_3S_1$: 299.0565. IR (film) $\nu$ cm$^{-1}$ 2944 (m), 2867 (w), 1710 (s), 1425 (s), 1209 (s), 1148 (s), 1017 (m); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.66–1.74 (2H, m, $CH_2$), 1.83–1.88 (2H, m, $CH_2$), 1.95–2.07 (3H, m, $CH_2$), 2.13–2.18 (1H, m, H4), 2.32–2.38 (2H, m, H7) 2.39–2.45 (2H, m, H3), 5.78 (1H, t, $J=2.1$ Hz, H2); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 20.5 (C4), 24.7 (C3), 25.2 (C10), 32.2 (C11), 34.4 (C12), 38.2 (C7), 60.2 (C5), 115.9 (C2), 117.4 (q, $J=319$ Hz, $CF_3$), 148.1 (C1), 209.2 (C6); *m/z* (CI): *M* 299 (100%), 281 (85), 254 (62), 165 (89), 149 (73), 121 (46).

**4.1.9. Trifluoromethylsulfonic acid 6-trifluoromethylsulfonyloxyspiro[4.5]deca-1,6-dien-1-yl ester (14).** Triflic acid anhydride (0.083 mL, 0.50 mmol) was added dropwise over 5 min to a solution of trifluoromethanesulfonic acid 6-oxospiro[4.5]dec-1-en-1-yl ester (**13**) (0.100 g, 0.34 mmol) and pyridine (0.040 g, 0.50 mmol) in dichloromethane (8 mL) at −78 °C. The temperature was allowed to reach room temperature overnight. The reaction mixture was stirred for 3 d at room temperature before the solvents were distilled off and the residual material subjected to flash chromatography on silica gel using 10% EtOAc in hexane. The product was an oily material; yield 0.019 g, 13%. HRMS: *M* 297.0413. Calcd for $C_{11}H_{12}O_4F_3S_1$: 297.0408; IR (film) $\nu$ $cm^{-1}$ 2927 (s), 2861 (m), 2358 (w), 1419 (m), 1207 (s), 1140 (m); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.56–1.63 (1H, m, H9), 1.75–1.80 (1H, m, H10), 1.80–1.84 (1H, m, H9), 1.91–1.94 (1H, m, H10), 1.95–1.99 (1H, m, H4), 2.20–2.25 (2H, m, H8), 2.25–2.31 (1H, m, H4), 2.35–2.41 (1H, m, H3), 2.44–2.51 (1H, m, H3), 5.81 (1H, dd, $J$=2.6, 2.5 Hz, H2), 5.91 (1H, dd, $J$=4.3, 4.0 Hz, H7); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 18.7 (C9), 24.2 (C8), 25.7 (C3), 33.4 (C4), 34.0 (C10), 51.0 (C5), 117.2 (C2), 118.7 (q, $J$=319 Hz, $CF_3$), 118.8 (q, $J$=319 Hz, $CF_3$), 120.1 (C7), 148.5 (C1), 148.5 (C6); *m/z* (CI, $NH_3$): 448 ($M+NH_4^+$, 100%), 391 (9), 281 (12), 213 (16), 147 (38).

**4.1.10. Trifluoromethanesulfonic acid 7-oxospiro[5.5]-undec-1-en-1-yl ester (15).** LiHMDS (2.4 mmol) in THF (10 mL) was added dropwise to a solution of spiro[5.5]-undecane-1,7-dione (**10**) (370 mg, 2.05 mmol) and $PhNTf_2$ (900 mg, 2.46 mmol) in THF (15 mL) under argon at −78 °C. The mixture was allowed to reach ambient temperature overnight. When GLC showed the reaction to be complete, diethyl ether and water were added to the cold reaction mixture, the layers separated and the aqueous layer extracted with diethyl ether (2×). The combined ether extract was shaken with aqueous $Na_2CO_3$, dried ($MgSO_4$), and the solution evaporated to dryness. The product was isolated from the residual material after flash chromatography using hexane/EtOAc 10:1.The product was a yellow oil; yield 222 mg (60%). HRMS: *M* 313.0713. Calcd for $C_{12}H_{15}O_4SF_3$: 313.0721; IR (film) $\nu$ $cm^{-1}$ 2926, 2855 (C–H), 1710 (C=O); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.36–2.31 (12H, $CH_2$), 2.30–2.60 (2H, m, H8), 5.90 (1H, t, $J$=4.2 Hz, H2); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 18.1 ($CH_2$), 20.6 ($CH_2$), 24.4 ($CH_2$), 26.5 ($CH_2$), 33.4 ($CH_2$), 34.8 ($CH_2$), 38.5 (C8), 54.5 (C6), 86.7 ($CF_3$), 120.7 (C2), 149.8 (C1), 209.6 (C7); MS (EI): 313 (M, 55%), 268 (31), 179 (138), 163 (100), 135 (62), 179 (38).

**4.1.11. Trifluoromethanesulfonic acid 7-trifluoromethanesulfonyloxyspiro[5.5]undeca-1,7-dien-1-yl (16).** Neat triflic anhydride (0.9 mL, 5.6 mmol) was added with a syringe to a solution of spiro[5.5]undecane-1,7-dione (**10**) (0.5 mg, 2.8 mmol) and pyridine (442 mg, 5.6 mmol) in dry dichloromethane (40 mL) at −78 °C under argon. The reaction mixture was allowed to reach room temperature and stirred at room temperature for 7 d. The solvent was evaporated and the crude product was purified by flash chromatography on silica gel using hexane/EtOAc 5:1; yield 0.025 mg, 5%) of a colourless oil. IR (film) $\nu$ $cm^{-1}$ 1634 (C=C), 2880 (C–H). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.56–1.91 (4H, m, $CH_2$), 2.17–2.22 (2H, m, H3, H9), 5.95–5.97 (1H, t, $J$=3.0 Hz, H2, H8); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 17.7 ($CH_2$), 24.0 ($CH_2$), 31.7 ($CH_2$), 43.6 (C6), 116.2 (q, $CF_3$), 120.3 (C2, C8), 148.6 (C1, C7); MS (CI): 444 (M, 100%), 445 (24), 446 (16), 311 (9), 143 (20).

**4.1.12. Trifluoromethanesulfonic acid 1,4-dioxadispiro[4.0.4.4]tetradec-7-en-7-yl ester (17).** A solution of HMDS (5.129 g, 31.8 mmol) and *n*BuLi (12.5 mL, 19.1 mmol) in THF (20 mL) was added dropwise over 20 min to a solution of 1,4-dioxadispiro[4.0.4.4]tetradecan-7-one (**5**) (3.337 g, 15.9 mmol) and $PhNTf_2$ (6.812 g, 19.1 mmol) in THF (50 mL) at −78 °C. The temperature was allowed to reach room temperature overnight and saturated aqueous sodium hydrogen carbonate (70 mL) added. The mixture was extracted with diethyl ether (3× 70 mL), the solution dried ($MgSO_4$), filtered, the filtrate evaporated and the residual material subjected to flash chromatograpy on silica gel using 20% $Et_2O$ in hexane. The product was a yellow oil; yield 4.673 g (84%). HRMS (EI): *M* 342.0742. Calcd for $C_{13}H_{17}O_5F_3S_1$: 342.0749. IR (film) $\nu$ $cm^{-1}$ 2939 (s), 2895 (s), 2865 (s), 1655 (m), 1421 (s), 1250 (s), 1211 (s); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.23–1.32 (1H, m, $CH_2$), 1.45–1.49 (1H, m, $CH_2$), 1.52–1.66 (5H, m, $CH_2$), 1.74–1.77 (1H, m, H10), 1.99 (1H, dt, $J$=13.3, 3.7 Hz, $CH_2$) 2.19–2.24 (2H, m, H9, H10) 2.42–2.45 (1H, m, H9), 3.82–3.87 (2H, m, H2, H3), 3.90–3.94 (1H, m, H2 or H3), 3.96–3.98 (1H, m, H3 or H2), 5.70 (1H, t, $J$=2.6 Hz, H8); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 21.2 ($CH_2$), 23.2 ($CH_2$), 26.1 (C9), 32.3 ($CH_2$), 32, 5 (C10), 33.6 ($CH_2$), 54.5 (C6), 64.4 (C3 or C2), 65.1 (C2 or C3), 112.0 (C8), 118.1 (C5), 118.4 (q, $J$=318 Hz, $CF_3$), 150.9 (C7); *m/z* (EI): 342 (M, 1.0%), 279 (16), 209 (41), 167 (33), 149 (100), 99 (43).

**4.1.13. Trifluoromethanesulfonic acid 1,4-dioxadispiro-[4.0.5.4]pentadeca-7,9-dien-7-yl ester (18).** 1 M LiHMDS (600 mg, 3.76 mmol) in THF (15 mL) was added dropwise to a solution of 1,4-dioxadispiro[4.0.5.4]pentadec-9-en-7-one (**8**) and $PhNTf_2$ (1.36 g, 3.8 mmol) in THF (10 mL) under argon at −78 °C. The mixture was allowed to reach ambient temperature overnight when GLC showed the reaction to be complete. Diethyl ether and water were added to the cold reaction mixture, the layers separated, the aqueous layer extracted with diethyl ether (2×), the combined ether solutions shaken with aqueous $Na_2CO_3$, dried over $MgSO_4$ and the solution evaporated to dryness. The product was isolated from the residual material after flash chromatography using hexane/EtOAc 10:1. The product was a yellow oil; yield 1.10 g (80%). HRMS: *M* 354.0731. Calcd for $C_{14}H_{17}O_5F_3S$: 354.0749; IR (film) $\nu$ $cm^{-1}$ 2950 (C–H), 1664 (C=C); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.51–1.71 (6H, m, $CH_2$), 2.15 (2H, m, H15), 2.36 (2H, m, H11), 3.79–4.04 (4H, m, H2, H3), 5.7 (1H, t, $J$=3.0 Hz, H9) 5.77 (1H, q, $J$=3.0 Hz, H10), 5.95 (1H, d, $J$=6.0 Hz, H8); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 20.1 ($CH_2$), 23.5 ($CH_2$), 30.5 ($CH_2$), 34.0 ($CH_2$), 35.2 ($CH_2$), 45.0 (C6), 64.7 (C2 or C3), 65.9 (C3 or C2), 117.0 (q, $CF_3$), 118.5 (C5), 120.5 (C8), 127.8 (C9), 130.2 (C10), 151.7 (C7). MS (EI): 354 (M, 32), 353 (100), 220 (28), 99 (46).

**4.1.14. 6-(2-Methoxyphenyl)spiro[4.4]non-6-en-1-one (19).** Trifluoromethanesulfonic acid 6-oxospiro[4.4]non-1-en-1-yl) (**11**) (284 mg, 1 mmol) and $Pd(dba)_2$ (28.8 mg, 0.05 mmol) were dissolved in dry NMP (10 mL) and

2-methoxyphenyltributyltin (436 mg, 1.1 mmol) added with a syringe after 10 min. The solution was stirred at 80 °C until the reaction was completed after 2 h (GLC). 1 M aqueous KF solution (1 mL) was added and the mixture stirred for 30 min, diluted with ethyl acetate and filtered. The filtrate was washed with water (3×), dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography using hexane/EtOAc 4:1; yield 194 mg (80%) of a pale yellow oil. (Found: C, 79.55; H, 7.62. Calcd for $C_{16}H_{18}O_2$: C, 79.33; H, 7.43%). HRMS: *M* 242.1306. Calcd for $C_{16}H_{18}O_2$: 242.1306. IR (film) $\nu$ $cm^{-1}$ 2910, 2220, 1710, 1450, 1250, 820, 720; $^1H$ NMR (300 MHz): $\delta$ 1.8 (4H, m, $CH_2$), 2.0–2.2 (1H, m, $CH_2$), 2.2–2.5 (4H, m, $CH_2$), 2.5–2.8 (1H, m, $CH_2$), 3.75 (3H, s, $CH_3$), 6.13 (1H, t, $J$=2.5 Hz, H7), 6.8–6.95 (2H, m, H-Ar), 7.15–7.35 (2H, m, Ph); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 19.8 ($CH_2$), 30.0 ($CH_2$), 34.5 ($CH_2$), 35.6 ($CH_2$), 37.7 ($CH_2$), 54.0 ($CH_3$), 63.7 (C5), 110, 120 (C7), 126, 128, 130, 133, 143, 156, 219 (C1); MS(EI) *m/z* 242 (M, 100), 224 (33), 186 (99), 185 (34), 171 (50), 158 (15), 128 (14), 115 (13).

**4.1.15. Trifluoromethanesulfonic acid 6-(2-methoxyphenyl)spiro[4.4]nona-1,6-dien-1-yl ester (20).** DMAP (346 mg, 2.48 mmol) was added to a solution of 6-(2-methoxyphenyl)spiro[4.4]non-6-en-1-one (**19**) (345 mg, 1.42 mmol) in dry $CH_2Cl_2$ (15 mL) at room temperature and the mixture stirred for 20 min. A solution of triflic anhydride (600 mg, 2.13 mmol) in $CH_2Cl_2$ (1 mL) was added dropwise and the mixture stirred at ambient temperature for another 20 min to complete the reaction (TLC). The solvent was evaporated and the product isolated after flash chromatography of the residual material using 10% EtOAc in hexane; yield 480 mg (90%) of a pale yellow oil. (Found: C, 54.73; H, 4.80. Calcd for $C_{17}F_3H_{17}O_4S$: C, 54.54; H, 4.54%). HRMS: *M* 374.0786. Calcd for $C_{17}F_3H_{17}O_4S$: 374.0799. IR (film) $\nu$ $cm^{-1}$ 3000, 2949, 2860, 1600, 1425, 1213; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.9–2.6 (8H, m, $CH_2$), 3.8 (3H, s, $CH_3$), 5.5 (1H, t, $J$=2.1 Hz, H2), 5.95 (1H, t, $J$=2.4 Hz, H7), 6.9–7.25 (4H, m, H-Ar), 7.25 (1H, d, H-Ar); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 21.0 ($CH_2$), 29.6 ($CH_2$), 33.9 ($CH_2$), 37.0 ($CH_2$), 55.0 ($CH_3$), 63.0 (C5), 112 (C2), 114 (C7), 120, 126, 128, 130, 133, 142, 154, 158; MS (EI): *m/z* 374 (M, 100%), 241 (34), 213 (46), 171 (41), 133 (46), 131 (45), 121 (72), 115 (50), 69 (94), 55 (80).

**4.1.16. 1,6-Bis(2-methoxyphenyl)spiro[4.4]nona-1,6-diene (21).**

**4.1.16.1. Procedure (i).** Trifluoromethanesulfonic acid 6-(2-methoxyphenyl)spiro[4.4]nona-1,6-dien-1-yl ester (**20**) (374 mg, 1 mmol) and $Pd(dba)_2$ (28.8 mg, 0.05 mmol) were dissolved in dry NMP (15 mL). 2-Methoxyphenyltributyltin (436 mg, 1.1 mmol) was added with a syringe after 10 min. The solution was stirred at 80 °C overnight. A solution of aqueous KF (1 M, 1.5 mL) was added and the mixture stirred for 30 min. Dilution with ethyl acetate, filtration, shaking the filtrate with water (3×), drying ($MgSO_4$) and distilling off the solvents left an oily residue. Pure product was isolated after flash chromatography on silica gel using hexane/EtOAc 10:1; yield 55% of a pale yellow oil. (Found: C, 83.32; H, 7.20. Calcd for $C_{23}H_{24}O_2$: C, 83.13; H, 7.22%). HRMS: *M* 332.1766. Calcd for $C_{23}H_{24}O_2$: 332.1776. IR (film) $\nu$ $cm^{-1}$ 3050, 3030, 2950, 2843, 2450, 1600; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.9–2.4 (4H, m, $CH_2$), 3.8 (3H, s, $CH_3$), 6.15 (1H, t, $J$=2.6 Hz, H2, H7), 6.7–7.4 (4H, m, H-Ar); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 31.1 ($CH_2$), 36.7 ($CH_2$), 60.0 ($CH_3$), 63.0 (C5), 111, 120 (C2, C7), 126, 127, 129, 132, 143 (C1, C6), 158 (Ph); MS(EI): *m/z* 332 (M, 100%), 211 (34), 185 (15), 149 (7), 147 (11), 121 (9), 91 (28), 84 (14).

**4.1.16.2. Procedure (ii).** *n*BuLi (1.6 M in 3.75 mL of THF) was added dropwise to a solution of 2-bromoanisole (1 mL, 5.7 mmol) in dry THF (40 mL) under argon at −78 °C, and the mixture was stirred at room temperature for 2 h. A solution of dried $ZnBr_2$ (1.35 g, 6 mmol) in dry THF (5 mL) was added. The mixture was stirred at −78 °C for 1 h, and the temperature allowed slowly to reach room temperature. Another solution of 1,6-bis(trifluoromethanesulfonyloxy)spiro[4.4]nona-1,6-diene (1.0 g, 2.4 mmol) (**12**) in dry THF (10 mL) and $Pd(PPh_3)_4$ (138.6 mg, 0.12 mmol, 5 mol%) was prepared and stirred at room temperature for 10 min before the solution was added to the solution containing the organozinc reagent. The resultant mixture was stirred at room temperature for 30 min, and at 50 °C for 90 min when GLC showed the reaction to be complete. The reaction mixture was worked up as above; yield 75%.

**4.1.17. 7-(2-Methoxyphenyl)-1,4-dioxadispiro[4.0.4.4]-tetradec-7-ene (22).** $Pd(PPh_3)_4$ (0.243 g, 2.15 mmol) was added to a mixture of trifluoromethanesulfonic acid 1,4-dioxadispiro[4.0.4.4]tetradec-7-en-7-yl ester (**17**) (1.469 g, 4.30 mmol), 2-anisoleboronic acid (0.950 g, 6.45 mmol), aqueous 2 M $Na_2CO_3$ (10 mL) and DME (30 mL), and the mixture heated at 100 °C for 3 h. Saturated sodium hydrogen carbonate (30 mL) was added to the cold reaction mixture, the mixture extracted with hexane (3×30 mL), and the dried ($MgSO_4$) hexane solution evaporated. The residual material was subjected to flash chromatography on silica gel using hexane; yield 0.928 g (72%) of a white crystalline material; mp 65–66 °C. (Found C, 75.47; H, 7.85. Calcd for $C_{19}H_{24}O_3$: C, 75.97H, 8.00%). IR (film) $\nu$ $cm^{-1}$ 3036 (w), 2928 (s), 2966 (w), 1495 (w); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.35–1.54 (6H, m, $CH_2$), 1.66–1.75 (1H, m, $CH_2$), 1.85–1.94 (1H, m, H10), 2.01–2.10 (1H, m, $CH_2$), 2.23–2.51 (3H, m, H9 and H10), 3.41 (1H, m, H2 or H3), 3.68 (1H, q, $J$= 7.3 Hz, H2 or H3), 3.92 (2H, m, H3 or H2), 3.74 (3H, s, $CH_3$), 5.68 (1H, t, $J$=2.4 Hz, H8), 6.84 (2H, m, H-Ar), 7.04 (1H, dd, $J$=7.3, 1.6 Hz, H-Ar), 7.16 (1H, m, H-Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 22.4 ($CH_2$), 23.4 ($CH_2$), 30.5 (C9), 31.48 ($CH_2$), 34.3 (C10), 35.5 ($CH_2$), 55.2 ($CH_3$), 59.9 (C6), 63.5 (C2 or C3), 64.1 (C3 or C2), 110.4 (C-Ar), 113.2 (C5), 119.3 (C-Ar), 127.3 (C-Ar), 130.3 (C-Ar), 131.4 (C-Ar), 133.22 (C8), 144.4 (C7), 156.9 (C-Ar); *m/z* (EI): 300 (M, 100%), 238 (29), 212 (95), 185 (42), 99 (37).

**4.1.18. 1-(2-Methoxyphenyl)spiro[4.5]dec-1-en-6-one (23).** A solution of 7-(2-methoxyphenyl)-1,4-dioxadispiro-[4.0.4.4]tetradec-7-ene (**22**) (0.687 g, 2.29 mmol, 1 equiv), 3 M HCl (6 mL) in $CH_2Cl_2$ (7 mL) was stirred at room temperature for 4 h. Saturated aqueous sodium bicarbonate (10 mL) was added and the mixture extracted with dichloromethane (4×10 mL). Evaporation of the dried ($MgSO_4$) extracts provided a white crystalline material; yield 0.551 g (94%), mp 60–62 °C. HRMS(EI): *M* 256.1462. Calcd for $C_{17}H_{20}O_2$: 256.1463; IR (film) $\nu$ $cm^{-1}$ 2937 (s),

2862 (s), 1741 (s), 1698 (s); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.47–1.67 (4H, m, $CH_2$), 1.81–1.95 (3H, m, $CH_2$), 2.18–2.23 (1H, m, $CH_2$), 2.31–2.37 (2H, m, H3), 2.39–2.46 (2H, m, $CH_2$), 3.62 (3H, s, $CH_3$), 6.10 (1H, dd, $J$=2.8, 2.3 Hz, H2), 6.75–6.84 (2H, m, H-Ar), 7.10–7.23 (2H, m, H-Ar); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 22.0 ($CH_2$), 25.2 ($CH_2$), 30.2 (C3), 36.7 ($CH_2$), 39.0 ($CH_2$), 39.2 ($CH_2$), 54.8 ($CH_3$), 64.3 (C-Ar), 111.0 (C-Ar), 120.5 (C-Ar), 125.8 (C-Ar), 128.3 (C-Ar), 130.7 C-Ar), 133.1 (C2), 143.7 (C1), 156.3 (C-Ar), 211.0 (C6); *m/z* (EI): 256 (M, 100%), 238 (48), 228 (77), 199 (86), 186 (58), 185 (95).

**4.1.19. Trifluoromethanesulfonic acid 1-(2-methoxyphenyl)spiro[4.5]deca-1,6-dien-6-yl ester (24).** A solution of HMDS (1.009 g, 6.25 mmol) and *n*BuLi (1.45 mL, 2.03 mmol) in THF (2.0 mL) was added dropwise over 5 min to a solution of 1-(2-methoxyphenyl)spiro[4.5]dec-1-en-6-one (**23**) (0.400 g, 1.56 mmol) and $PhNTf_2$ (0.726 g, 2.03 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to reach room temperature overnight. Saturated aqueous $NaHCO_3$ solution (30 mL) was added and the mixture extracted with diethyl ether (3×30 mL). The dried extracts were evaporated and the residual material subjected to flash chromatography on silica gel using 10% EtOAc in hexane. The product was a colourless oil; yield 0.438 g (72%). HRMS (EI): *M* 388.0948. Calcd for $C_{18}H_{19}F_3O_4S_1$: 388.0947; IR (film) $\nu$ cm$^{-1}$ 2936 (m), 2867 (w), 1402 (m), 1248 (m), 1209 (s), 1140 (m), 1032 (m); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.40–1.53 (2H, m, H9), 1.67–1.71 (1H, m, H10), 1.88–1.93 (1H, m, H10), 1.96–2.06 (2H, m, H4 and H8), 2.10–2.17 (1H, m, H8), 2.33–2.38 (1H, m, H4), 2.41–2.47 (1H, m, H3), 2.53–2.60 (1H, m, H3), 3.74 (3H, s, $CH_3$), 5.71 (1H, dd, $J$=4.9, 3.5 Hz, H7), 6.00 (1H, dd, $J$=2.5, 2.4 Hz, H2), 6.87 (2H, m, H-Ar), 7.13 (1H, dd, $J$=7.5, 1.6 Hz, H-Ar), 7.21 (1H, m, H-Ar); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 19.3 ($CH_2$), 24.5 ($CH_2$), 30.8 (C3), 35.9 (C8), 37.6 (C4), 55.1 ($CH_3$), 55.3 (C5), 110.8 (C-Ar), 115.4 (C7), 118.7 (q, $J$=318 Hz, $CF_3$), 119.9 (C-Ar), 126.0 (C-Ar), 128.3 (C-Ar), 123.0 (C-Ar), 134.4 (C2), 140.8 (C1), 153.7 (C6), 157.5 (C-Ar); *m/z* (EI): 388 (M, 100%), 238 (25), 207 (100), 111 (16), 121 (41).

**4.1.20. 1,6-Bis-(2-methoxyphenyl)spiro[4.5]deca-1,6-diene (25).** $Pd(PPh_3)_4$ (0.072 g, 2.15 mmol) was added to a solution of trifluoromethanesulfonic acid 1-(2-methoxyphenyl)spiro[4.5]deca-1,6-dien-6-yl ester (**24**) (0.372 g, 0.95 mmol), 2-anisoleboronic acid (0.216 g, 1.43 mmol) and 2 M $Na_2CO_3$ (3 mL) in DME (9 mL) and the reaction mixture heated at 100 °C for 4 h. Saturated aqueous $NaHCO_3$ (15 mL) was added to the cold reaction mixture which was extracted with hexane (3×15 mL). The dried ($MgSO_4$) hexane extracts were evaporated and the residual material subjected to flash chromatography on silica gel using 30% $CH_2Cl_2$ in hexane. The product was a white crystalline material; yield 0.201 g (61%), mp 86–89 °C. HRMS (EI): *M* 346.1929. Calcd for $C_{24}H_{26}O_2$ 346.1933; IR (film) $\nu$ cm$^{-1}$ 2994 (w), 2930 (s), 2832 (s), 1595 (m), 1490 (s), 1462 (s), 1433 (s), 1244 (s), 1028 (m); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.45–1.51 (1H, m, $CH_2$), 1.53–1.64 (3H, m, $CH_2$), 1.73–1.79 (1H, m, $CH_2$), 2.06–2.20 (4H, m, $CH_2$), 2.30–2.35 (1H, m, $CH_2$), 3.69 (3H, s, $CH_3$), 3.76 (3H, s, $CH_3$), 5.58 (1H, dd, $J$=3.1, 3.0 Hz, H7), 6.11 (1H, dd, $J$=2.6, 2.5 Hz, H2), 6.7 (1H, dd, $J$=7.6, 7.1 Hz, H-Ar), 6.81 (1H, d, $J$=8.1 Hz, H-Ar), 6.89–6.93 (2H, m, H-Ar), 7.06 (1H, dd, $J$=7.6, 1.5 Hz, H-Ar), 7.05–7.15 (1H, m, H-Ar), 7.14–7.22 (1H, m, H-Ar), 7.71 (1H, dd, $J$=7.7, 1.6 Hz, H-Ar); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 20.2 ($CH_2$), 25.8 (C7), 31.3 (C2), 36.6 ($CH_2$), 39.8 ($CH_2$), 55.3 ($CH_3$), 55.4 (C5 and $CH_3$), 110.6 (C-Ar), 111.1 (CH), 119.2 (C-Ar), 119.9 (CH), 127.1 (CH), 127.3 (C1 or C6), 127.3 (CH), 127.7 (CH), 129.8 (C-Ar), 130.8 (C-Ar), 131.9 (C6 or C1), 134.0 (C-Ar), 139.4 (C-Ar), 142.3 (C-Ar), 157.5 (C-Ar), 157.8 (C-Ar); *m/z* (EI): 346 (M, 100%), 318 (12), 225 (18), 199 (34), 160 (14), 91 (9).

**4.1.21. 7-Phenylspiro[5,5]undec-7-en-1-one (26).** $Pd(dba)_3\cdot CHCl_3$ (13 mg, 0.03 mmol) was added to a solution of trifluoromethanesulfonic acid 7-oxospiro[5.5]-undec-1-yl ester (**15**) (130 mg, 0.42 mmol), tri(2-furyl)phosphine (12 mg, 0.05 mmol) and LiCl (35.2 mg, 0.83 mmol) in dry NMP (7 mL). The mixture was stirred for 10 min at room temperature before phenyltributylstannane (1.6 mL, 0.5 mmol) was added with a syringe. The solution was stirred at 80 °C for 16 h. 1 M aqueous KF (7 mL) was added over 30 min to the cold reaction mixture which was diluted with ethyl acetate and filtered. The filtrate was washed with water (10 mL), dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography on silica gel using hexane/EtOAc 10:1. The product was a colorless oil; yield 0.08 g (60%). HRMS: *M* 240.1510. Calcd for $C_{17}H_{20}O$: 240.1514; IR (film) $\nu$ cm$^{-1}$ 2938, 2862 (C–H), 3028 (C–H, Ar), 1700 (C=O), 1600 (C=C); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.23–1.66 (10H, m, $CH_2$), 1.80–1.87 (2H, m, $CH_2$), 2.20–2.61 (2H, m, $CH_2$), 5.94 (1H, t, $J$=6.0 Hz, H8), 7.08–7.22 (5H, m, H-Ar); $^{13}$CNMR (75 MHz, $CDCl_3$) $\delta$ 18.1 ($CH_2$), 20.5 ($CH_2$). 25.6 ($CH_2$), 26.1 ($CH_2$), 34.4 ($CH_2$), 37.6 ($CH_2$), 38.5 (C7), 54.1 (C6), 126.2, 127.8, 128.5, 130.5, 141.1, 142.7, 208.7 (C1); MS (EI): 240 (M, 100%), 211 (77), 169 (31), 155 (31), 141 (38), 91 (27), 77 (15).

**4.1.22. Trifluoromethanesulfonic acid 7-phenylspiro-[5.5]undeca-1,7-dien-1-yl ester (27).** Neat triflic anhydride (110 mg, 0.39 mmol) was added with a syringe to a solution of 7-phenylspiro[5,5]undec-7-en-1-one (**26**) (63 mg, 0.262 mmol) and pyridine (30.8 mg, 0.39 mmol) in dry $CH_2Cl_2$ (6 mL) at −78 °C under argon. The reaction mixture was allowed to reach ambient temperature over 24 h. The product was purified by flash chromatography on silica gel using hexane/EtOAc 10:1. The product was a yellow oil; yield 131 mg (90%). (Found: C 57.74; H, 5.65. Calcd for $C_{18}H_{19}O_3F_3S$: C, 57.36; H, 5.87%). IR (film) $\nu$ cm$^{-1}$ 2910 (C–H), 3020 (C–H Ar), 1672 (C=C); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.3–2.2 (12H, m, $CH_2$), 5.80 (1H, dd, $J$=3.0, 2.7 Hz, H8), 7.0–7.3 (H-Ar); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 16.9 ($CH_2$), 17.3 ($CH_2$), 23.4 ($CH_2$), 24.4 ($CH_2$), 31.5 ($CH_2$), 32.8 ($CH_2$), 42.0 (C6), 117.1 (H2), 116.9 (q, $CF_3$), 125.7, 126.7, 128.1, 139.7, 130.7, 140.9 (C7), 151.9 (C1); MS (EI): 372 (M, 27%), 222 (29), 130 (100), 117 (39), 91 (9).

**4.1.23. 2-(7-Phenylspiro[5.5]undeca-1,7-dien-1-yl)thiophene (28).** $Pd(PPh_3)_4$ (94 mg, 0.089 mmol) was added to a solution of trifluoromethanesulfonic acid 7-phenylspiro[5.5]undeca-1,7-dien-1-yl ester (**27**) (300 mg, 0.81 mmol), and 2-thiopheneboronic acid (207 mg,

1.61 mmol) in 1:3 2 M $Na_2CO_3$/DME (10 mL). The reaction mixture was heated at 100 °C overnight. Ethyl acetate and water were added. The aqueous phase was collected, extracted with EtOAc, the combined organic extracts washed with dilute aqueous sodium bicarbonate, brine, and dried ($MgSO_4$) before the solvent was distilled off. Flash chromatography of the residual material using hexane/EtOAc 20:1 gave the product as a colourless oil; yield 174 mg (70%). HRMS: *M* 306.1430. Calcd for $C_{21}H_{22}S$: 306.1442; IR (film) $\nu$ $cm^{-1}$ 1618 (C=C), 2824–2966 (C–H), 3072 (C–H Ar); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.27–1.74 (8H, m, $CH_2$), 2.03–2.3 (4H, m, $CH_2$), 6.01 (1H, t, $J=4.0$ Hz, H8), 6.28 (1H, t, $J=3.0$ Hz, H2), 6.87–6.90 (1H, m, H-Ar), 7.03 (1H, t, $J=3.0$ Hz, H-Ar), 7.16–7.33 (6H, m, CH-Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 14.2 ($CH_2$), 18.2 ($CH_2$), 26.1 ($CH_2$), 26.2 ($CH_2$), 34.7 ($CH_2$), 34.9 ($CH_2$), 42.7 ($CH_2$), 123.0, 124.2, 126.3, 126.9, 127.6, 128.8, 129.3, 130.6, 138.3, 143.1, 144.8, 146.3. MS (EI): 306 (M, 24%), 302 (16), 208 (100), 212 (29), 176 (12), 91 (38).

**4.1.24. 7-Phenyl-1,4-dioxadispiro[4.0.5.4]pentadeca-7,9-diene (29).** $Pd(dba)_2$ (130 mg, 0.12 mmol) was added to a solution of trifluoromethanesulfonic acid 1,4-dioxadispiro-[4.0.5.4]pentadeca-7,9-dien-7-yl ester (**18**) (860 mg, 2.43 mmol) in dry *N*-methylpyrrolidin-2-one (NMP, 20 mL) and the mixture stirred at room temperature for 4 h. 1 M aqueous KF solution (9 mL) was added dropwise over 30 min, the mixture diluted with ethyl acetate and filtered. The filtrate was washed with water (2×), dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography on silica gel using hexane/EtOAc 10:1; yield 0.64 g (75%) of a colorless oil. HRMS: *M* 282.1623. Calcd for $C_{19}H_{22}O_2$: 282.1620. IR (film) $\nu$ $cm^{-1}$ 1653 (C=C), 2950 (C–H), 3451 (C–H, Ar); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.19–1.68 (8H, m, $CH_2$), 2.72–2.73 (2H, m, H12), 3.22–3.83 (4H, m, H2, H3), 5.71–5.78 (2H, m, H9, H10), 5.89–5.92 (1H, m, H8), 7.11–7.25 (5H, m, H-Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 19.7 ($CH_2$), 22.3 ($CH_2$), 29.6 ($CH_2$), 31.1 ($CH_2$), 33.1 (C11), 44.1 (C6), 62.3 (C2), 63.8 (C3), 112.6 (C5), 123.2 (C8), 124.2, 124.7, 125.5, 126.4, 128.6, 143.1, 143.8 (C7); MS (EI): 282 (M, 45%), 281 (44), 220 (83), 167 (79),165 (55), 128 (37), 99 (56), 73 (100).

**4.1.25. *cis*,*cis*-1,6-Bis(2-methoxyphenyl)spiro[4.4]nonane (30).** A solution of 1,6-bis-(2-methoxyphenyl)-spiro[4.4]-nona-1,6-diene (**21**) (332 mg, 1 mmol) in ethanol (20 mL) was hydrogenated over 10% palladium on charcoal (100 mg, 0.1 mmol) at 4 atm in a Parr apparatus at room temperature for 3 d. The catalyst was removed by filtration through Celite. The filtrate was evaporated and the residual product purified by flash chromatography on silica gel using hexane/EtOAc, 12:1. Recrystallisation of the product from diethyl ether and ethanol yielded 302 mg (90%) of a white crystalline material, mp 131 °C. (Found: C, 82.66; H, 8.54. Calcd for $C_{23}H_{28}O_2$: C, 82.40; H, 8.33%). HRMS: *M* 336.2083. Calcd for $C_{23}H_{28}O_2$: 336.2089. IR (film) $\nu$ $cm^{-1}$ 3000, 2950, 2450, 1600, 1500, 1250; $^1H$ NMR (200 MHz) $\delta$ 1.7–2.2 (6H×2, m, $CH_2$), 3.40 (3H×2, s, $CH_3$), 3.55 (1H×2, d, $J=7.2$ Hz, H1, H6), 6.2–7.1 (4H×2, m, H-Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 22.4 ($CH_2$), 34.8 ($CH_2$), 41.6 ($CH_2$), 43.8 ($CH_2$), 54.9 ($CH_3$), 60.7 (C-5), 109 (C-Ar), 119 (C-Ar), 125 (C-Ar), 128 (C-Ar), 136 (C-Ar), 156 (C-Ar); MS(EI): *m*/*z* 336 (M, 100%), 202 (7), 187 (25), 174 (36), 173 (24), 134 (15), 121 (24), 91 (25), 77 (6).

**4.1.26. *cis*,*cis*-1,6-Bis(2-hydroxyphenyl)spiro[4.4]nonane (31).** A flask containing a solution of *cis*,*cis*-1,6-bis(2-methoxyphenyl)spiro[4.4]nonane (**30**) (336 mg, 1 mmol) in dry dichloromethane (10 mL) under argon was protected from light by covering with aluminium foil. TMSI (2 equiv×5) was added at intervals and the mixture stirred at room temperature. TLC monitoring showed that the starting material was consumed after 5 d when the reaction was stopped. Two new major products had been formed after 5 d. The reaction mixture was evaporated to dryness and the residual material subjected to flash chromatography on silica gel using hexane/EtOAc, 12:1. The major product was the diol **31**; yield 60%. The minor product was the monomethoxy intermediate *cis*/*cis*-1-(2-methoxyphenyl)-6-(2-hydroxyphenyl)spiro[4.4]nonane (**32**); yield: 20%.

Product **31** was a white crystalline material, mp 178–180 °C ($CHCl_3$). HRMS: *M* 308.1768. Calcd for $C_{21}H_{24}O_2$: 308.1776. IR (film) $\nu$ $cm^{-1}$ 3480 (br.), 2958, 1470. $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 1.70 (1H, m, $CH_2$), 2.03 (4H, m, $CH_2$), 2.15 (1H, m, $CH_2$), 3.11 (1H, d, $J=8$ Hz, H1, H6), 3.28 (1H, s, OH), 6.4–7.2 (4H, m, H-Ar);. $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 22.3 ($CH_2$), 34.2 ($CH_2$), 40.4 ($CH_2$), 43.8 (C1, C6), 61.8 (C5), 117 (C-Ar), 122 (C-Ar), 127 (C-Ar), 128 (C-Ar), 135 (C-Ar), 153 (C-Ar); MS(EI): *m*/*z* 308 (M,100%), 173 (37), 160 (43), 159 (44), 149 (24), 145 (25), 133 (25), 120 (25), 107 (57), 91 (29).

The second product was *cis*,*cis*-1-(2-methoxyphenyl)-6-(2-hydroxyphenyl)spiro[4.4]nonane (**32**).

**4.1.27. *cis*,*cis*-1-(2-methoxyphenyl)-6-(2-hydroxyphenyl)spiro[4.4]nonane (32).** The title compound was obtained as a pale yellow crystalline material, mp 154 °C ($CHCl_3$). (Found: C, 82.20; H, 8.15. Calcd for $C_{22}H_{26}O_2$: C, 81.98; H, 8.07%). HRMS: *M* 322.1941. Calcd for $C_{22}H_{26}O_2$: 322.1932. IR (film) $\nu$ $cm^{-1}$ 3480 (br.), 3050, 2945, 2840, 1470. $^1H$ NMR (300 MHz) $\delta$ 1.5–1.7 (2H, m, $CH_2$), 1.8–2.1 (8H, m, $CH_2$), 2.1–2.2 (2H, m, $CH_2$), 3.1–3.3 (1H, m, H1), 3.30 (3H, s, $CH_3$), 3.40 (1H, s, OH), 3.54 (1H, d, $J=7.5$ Hz, H6), 6.3–7.2 (8H, m, H-Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 22.0 ($CH_2$), 34.0 ($CH_2$), 40.4 ($CH_2$), 40.7 ($CH_2$), 43.4 (C1), 44.0 (C6), 54.6 ($CH_3$), 61.1 (C5), 110 (C-Ar), 116 (C-Ar), 120 (C-Ar), 121 (C-Ar), 126.1 (C-Ar), 126.5 (C-Ar), 127.5 (C-Ar), 128.0 (C-Ar), 134.5 (C-Ar), 136.0 (C-Ar), 152.5 (C-Ar), 156.5 (C-Ar); MS(EI): *m*/*z* 322 (M, 100%), 187 (17), 174 (28), 173 (34), 159 (26), 145 (17), 134 (29), 121 (43), 107 (62), 91 (70).

**4.1.28. *cis*,*cis*-1,6-Bis(2-methoxyphenyl)spiro[4.5]decane (33).** 10% Pd–C (0.204 g) was added to a solution of 1,6-bis(2-methoxyphenyl)spiro[4.5]deca-1,6-diene (**25**) (0.139 g, 0.40 mmol) in ethanol (25 mL) and the mixture stirred under hydrogen (1 atm) for 9 h. The catalyst was filtered off and the product isolated after flash chromatography on silica gel using 3% $Et_2O$ in hexane. The product was a white crystalline material; yield 0.100 g (73%), mp 97–100 °C (MeOH). HRMS: *M* 350.2253. Calcd for $C_{24}H_{30}O_2$: 350.2246. IR (film) $\nu$ $cm^{-1}$ 3060 (w), 2928

(s), 2859 (s), 2836 (m); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.32–1.36 (1H, m, $CH_2$), 1.41–1.48 (2H, m, $CH_2$), 1.53–1.56 (1H, m, $CH_2$), 1.63–1.71 (3H, m, $CH_2$), 1.74–1.77 (1H, m, $CH_2$), 1.84–1.89 (2H, m, $CH_2$), 1.94–1.97 (1H, m, $CH_2$), 2.01–2.09 (1H, m, $CH_2$), 2.22–2.29 (2H, m, $CH_2$), 3.30 (1H, dd, $J$= 4.3, 4.0 Hz, H6 or H1), 3.36 (3H, s, C17 $CH_3$), 3.38 (3H, s, $CH_3$), 3.56 (1H, s, H1 or H6), 6.29 (1H, d, $J$=8.1 Hz, CH), 6.37 (1H, d, $J$=8.11 Hz, CH), 6.62–6.66 (2H, m, CH), 6.85–6.92 (2H, m, CH), 6.99 (1H, s, CH), 7.35 (1H, s, CH); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 21.0 ($CH_2$), 22.7 ($CH_2$), 22.9 ($CH_2$), 29.8 ($CH_2$), 33.4 ($CH_2$), 35.4 ($CH_2$), 38.5 ($CH_2$), 38.6 (C6 or C1), 51.4 (C5), 54.6, 55.0, 108.8 (CH), 109.0 (CH), 118.6 (CH), 119.5 (CH), 125.1 (CH), 125.4 (CH), 128.8 (CH), 123.0 (CH), 134.0 (C), 134.6 (C), 156.0 (C), 156.5 (C); *m/z* (EI): 350 (M, 87%), 188 (28), 147 (40), 121 (100), 91 (67).

**4.1.29. 7-(2-Methoxyphenyl)-1,4-dioxadispiro[4.0.4.4]-tetradecane (34).** 5% Pd–C (0.212 g) was added to a solution of 7-(2-methoxyphenyl)-1,4-dioxadispiro[4.0.4.4]-tetradec-7-ene (**22**) (0.104 g, 0.35 mmol) in EtOH (20 mL) and the mixture stirred under hydrogen (1 atm) at room temperature for 18 h. The catalyst was filtered off through Celite, the filtrate evaporated and the residual product purified by flash chromatography on silica gel using 5% EtOAc in hexane. The product was a white solid; yield 0.074 g (72%), mp 93–95 °C (MeOH). (Found: C, 75.25; H, 8.95. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H 8.67%). HRMS (EI): $M$ 302.1881. Calcd for $C_{19}H_{26}O_3$: 302.1882. IR (film) $\nu$ $cm^{-1}$ 2941 (s), 2884 (s), 1603 (w), 1492 (m); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.21–1.62 (8H, m, $CH_2$), 1.79–1.90 (3H, m, $CH_2$), 1.95–2.12 (3H, m, $CH_2$), 2.61 (1H, q, $J$= 7.2 Hz, H2 or H3), 3.03–3.31 (2H, m, H7 and H2 or H3), 3.46 (1H, dq, $J$=6.9, 1.3 Hz, H2 or H3), 3.62 (1H, dq, $J$= 7.3, 1.2 Hz, H3 or H2), 3.81 (3H, s, $CH_3$), 6.80–6.84 (2H, m, H-Ar), 7.02-7.06 (1H, m, H-Ar), 7.31 (1H, dd, $J$=7.6, 1.7 Hz, H-Ar); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 22.5 ($CH_2$), 22.9 ($CH_2$), 24.0 ($CH_2$), 31.2 ($CH_2$), 33.9 ($CH_2$), 34.2 ($CH_2$), 37.4 ($CH_2$), 47.1 (C7), 53.8 (C6), 55.6 ($CH_3$), 62.7 (C2 or C3), 63.1 (C3 or C2), 110.1 (C-Ar), 113.5 (C5), 119.3 (C-Ar), 125.6 (C-Ar), 130.2 (C-Ar), 134.1 (C-Ar), 157.7 (C-Ar); *m/z* (EI): 302 (M, 40%), 240 (48), 174 (73), 99 (100).

**4.1.30. 1-(2-Methoxyphenyl)spiro[4.5]decan-6-one (35).** A solution of 7-(2-methoxyphenyl)-1,4-dioxadispiro-[4.0.4.4]tetradecane (**34**). (0.069 g, 0.23 mmol) in 3 M HCl (3 mL) and $CH_2Cl_2$ (4 mL) was stirred at room temperature for. 5 h. Additional dichloromethane was added, the two phases separated, the organic solution dried ($MgSO_4$) and evaporated. The residual material was subjected to flash chromatography on silica gel using 10% EtOAc in hexane. The product was a yellowish oil; yield 0.049 g (82%). (Found: C, 78.78; H 8.61. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H 8.58%). HRMS(EI): $M$ 258.1623. Calcd for $C_{17}H_{22}O_2$: 258.1620. IR (film) $\nu$ $cm^{-1}$: 2938 (s), 2866 (m), 1699 (s), 1492 (m); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.34–1.70 (6H, m, $CH_2$), 1.72–1.99 (5H, m, $CH_2$), 2.08–2.17 (2H, m, $CH_2$), 2.58–2.68 (1H, m, $CH_2$), 3.79 (1H, dd, $J$=7.9, 6.9 Hz, H1), 3.81 (3H, s, $CH_3$), 6.81–6.85 (2H, m, H-Ar), 7.01 (1H, dd, $J$=7.7, 1.7 Hz, H-Ar), 7.10-7.15 (1H, m, H-Ar); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 21.9 ($CH_2$), 23.4 ($CH_2$), 27.3 ($CH_2$), 35.2 ($CH_2$), 36.4 ($CH_2$), 41.2 ($CH_2$), 41.5 ($CH_2$), 45.2 (C1), 55.3 ($CH_3$), 62.1 (C5), 110.3 (C-Ar), 120.8 (C-Ar), 127.2 (C-Ar), 129.3 (C-Ar), 132.1 (C-Ar), 156.5 (C-Ar), 214.5 (C6); *m/z* (EI): 258 (M, 40%), 240 (22), 148 (100), 111 (48), 91 (16).

**4.1.31. *cis*-7-Phenylspiro[5,5]undecan-1-one (36).** A solution of 7-phenyl-1,4-dioxadispiro[4.0.5.4]pentadeca-7,9-diene (**29**) (220 mg, 0.78 mmol) in ethanol (30 mL) was hydrogenated over 10% palladium on charcoal (440 mg) at 1 atm and ambient temperature for 3 d. The catalyst was filtered off through Celite and the solvent evaporated. The crude product was purified by flash chromatography using hexane/EtOAc 20:1. The product was a white solid with mp 88 °C; yield 160 mg, (75%). HRMS: $M$ 242.1664. Calcd for $C_{17}H_{22}O$: 242.1670. IR (film) $\nu$ $cm^{-1}$: 1702 (C=O), 2900 (C–H), 3030 (C–H Ar); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.31–1.80 (12H, m, $CH_2$), 2.00–2.40 (4H, m, $CH_2$), 2.60–2.70 (1H, m, H7), 7.1–7.3 (5H, m, H-Ar); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 20.0 ($CH_2$), 21.1 ($CH_2$), 25.9 ($CH_2$), 26.4 ($CH_2$), 29.6 ($CH_2$), 36.8 ($CH_2$), 38.8 ($CH_2$), 40.1 ($CH_2$), 52.4 (C6), 53.9 (C7), 127.6 (C-Ar), 130.4 (C-Ar), 143.6 (C-Ar), 162.3 (C-Ar), 214.5 (c1); MS (EI): 242 (M, 100%), 129 (51), 111 (65), 98 (50), 91 (60).

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