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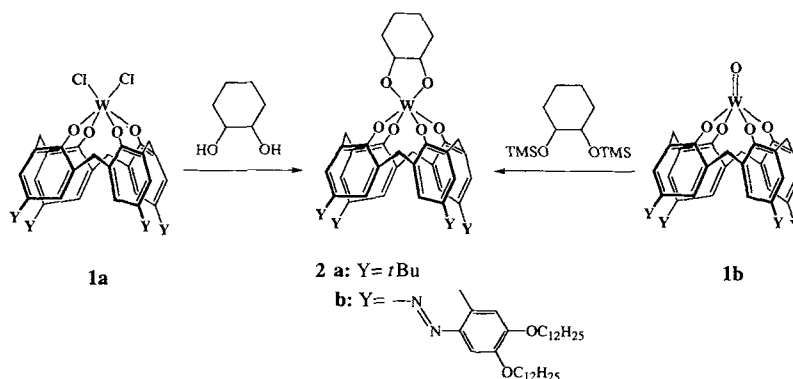
Chiral Metallocalix[4]arenes: Resolution by Diastereomeric Tungsten(vi) Alkoxides**

Bing Xu, Partrick J. Carroll, and Timothy M. Swager*

Efficient preparations of chiral supramolecular systems are critical to the design of new materials and catalysts. Calixarenes^[1] present one of the most versatile platforms for the construction of supramolecular receptor assemblies with well-defined structures and specific functions.^[2] Recent applications include the use of calixarenes as highly specific ligands,^[3] sensors,^[4] nonlinear optical chromophores,^[5] porous monolayers,^[6] and bowl-like liquid crystals.^[7] Chiral calix[4]arenes have been produced by unsymmetric substitution of the lower rim,^[8] by the addition of chiral appendages,^[9] and by the incorporation of unsymmetric substitution patterns on the phenyl rings.^[10] *meta*-Substituted systems with C₄ symmetry of the latter type have been prepared as racemates,^[10b] and a route to analogs with a variety of functional groups has recently been reported.^[11] In spite of the interest in chiral calix[4]arenes, few resolutions have been developed. We have been investigating

transition metal containing calix[4]arenes^[12] with rigid well-defined receptor cavities for the development of supramolecular materials and catalysts. We report herein the first resolution of chiral metallocalix[4]arenes. This method makes use of tungsten alkoxides,^[13] which may be efficiently transformed into Lewis acidic oxotungsten(vi) calix[4]arene complexes or dichlorotungsten(vi) calix[4]arenes.^[7a, 12a]

Among many resolution methods, we have concentrated on the use of diastereomeric intermediates to resolve the chiral metallocalix[4]arenes. Since the racemic R₄W=O complex can be considered as a conceptual analog of a R₂C=O, the complex R₂W(OR*)₂ was chosen to provide separable diastereomers similar to classical resolutions of chiral ketones via diastereomeric ketals. After separation, removal of the alkoxy groups produces resolved enantiomers. To test the accessibility and stability of cyclic tungsten(vi) calix[4]arene alkoxides,^[14] we synthesized *trans*-1,2-cyclohexanediol-based chelates to produce complexes **2a** and **2b**. Two synthetic procedures were developed (Scheme 1). In one route, dichlorotungsten(vi) *p*-*t*Bu-calix[4]-arene (**1a**) was heated to reflux with doubly deprotonated cyclohexanediol in toluene for four hours to give **2a** in 96% yield. Alternatively, oxotungsten(vi) calix[4]arene (**1b**) is transformed to **2b** in 10% yield when treated with silylated cyclohexanediol in refluxing toluene for two days. The



Scheme 1. Synthesis of **2**.

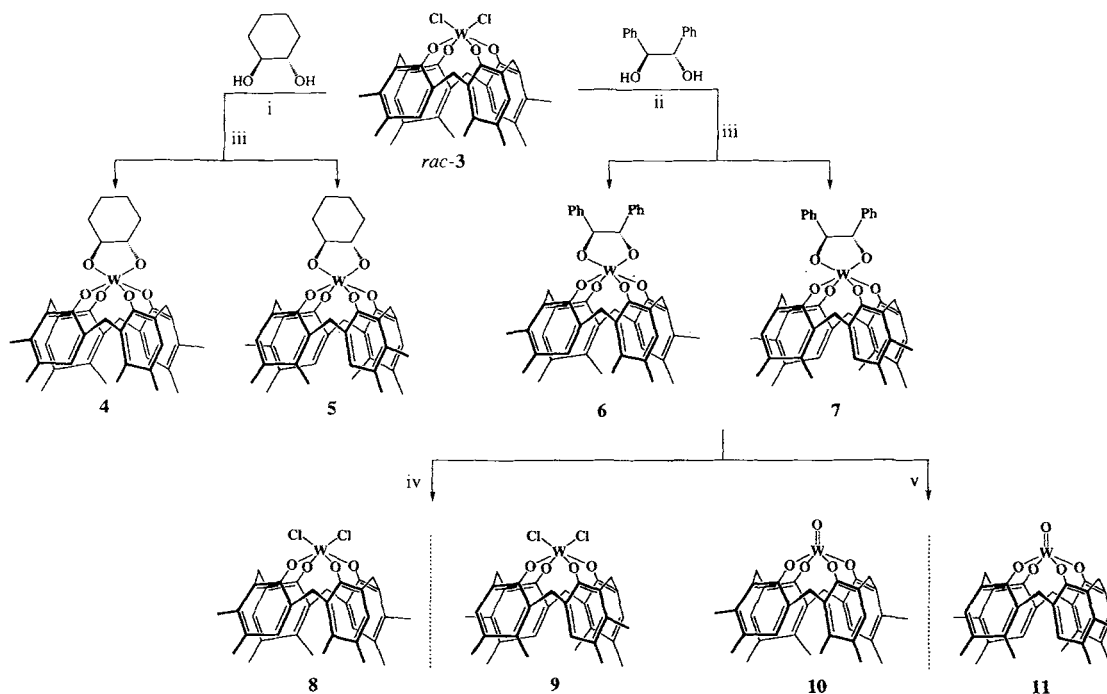
¹H NMR spectra displayed by these calix[4]arenes are diagnostic for the formation of **2**. Due to lower symmetry of **2**, the methylene groups of the calix[4]arene core are inequivalent and produce two sets of coupled geminal protons for a total of four doublets. Both **2a** and **2b** can be purified by chromatography on a silica gel column without any decomposition.

With methods to prepare tungsten(vi) dialkoxy calix[4]arenes in hand, we endeavored to synthesize diastereomeric complexes in which both the calix[4]arene and dialkoxy ligands are chiral (Scheme 2). We employed 3,4-dimethylcalix[4]arene, which had been previously reported by Böhmer et al., since it has an interesting inherently chiral structure with C₄ symmetry.^[10b] Reaction of 3,4-dimethylcalix[4]arene with WCl₆ in benzene produced the dichlorotungsten(vi) complex **3** in 81% yield. The ¹H NMR spectrum contained four doublets for the calix[4]arene methylene protons, which is consistent with **3** having an elliptical cone conformation with C₂ symmetry.^[12a] Racemic **3** reacts with (1*S*,2*S*)-*trans*-1,2-cyclohexanediol under the same conditions used to prepare **2a** to give a mixture of the diastereomers **4** and **5**. The diastereomeric relationship is apparent from the ¹H NMR resonances for the methylene protons (eight doublets, Fig. 1). The two diastereomers **4** and **5** can be separated by

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Scheme 2. Conditions: i) *n*BuLi, toluene, 4 h, 96%; ii) *n*BuLi, toluene, 4 h, 75%; iii) HPLC; iv) AlCl₃, CHCl₃, reflux, 3 min, 98%; v) trimethylsilyl triflate (TMSOTf), toluene, reflux overnight, 76%.

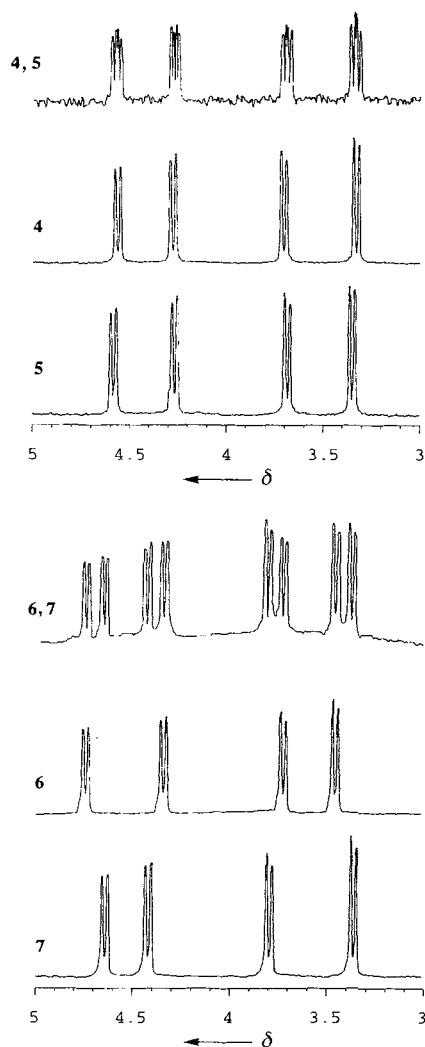


Fig. 1. ¹H NMR spectra of the characteristic calix[4]arene methylene protons of the diastereomeric mixtures (4, 5 and 6, 7), the first components from HPLC (4 and 6), and the second components from HPLC (5 and 7).

chromatography on silica gel (HPLC; eluent, *n*-hexane:CH₂Cl₂ 3:1), and each compound has the expected four methylene doublets (Fig. 1).

After separation of 4 and 5, we tried to complete the resolution and produce pure enantiomers 8 and 9 or oxo analogs 10 and 11. However, a variety of deprotection protocols (H₂O, HCl, AlCl₃, BBr₃) proved ineffective. This difficulty is likely due to the inert nature of the W–O bond, which is considered to be very strong.^[14c] We considered that a more productive approach would use dialkoxy groups in which the C–O bond may be cleaved. We prepared a (*S,S*)-(–)-hydrobenzoin-based diastereomeric mixture, 6 and 7, in 75% yield (Scheme 2). Similar to 4 and 5, the diagnostic calix[4]arene methylene protons of the diastereomeric mixture display eight pairs of doublets in the ¹H NMR spectrum. However, in this case we observe a greater dispersion in chemical shift (Fig. 1), which suggests that 6 and 7 have larger variations in their properties. Indeed their chromatography properties reflect this; 6 and 7 are more easily separated (silica: flash or HPLC) than 4 and 5.

In order to assign the absolute configuration of the chiral tungsten(VI) calixarenes, we performed a crystal structure determination^[15a] of compound 7 (the second component from the HPLC separation). In the crystal structure (Fig. 2), the tungsten(VI) center is approximately octahedral,^[15b] and the calix[4]arene phenyl rings define an elliptical cone similar to that reported for dichlorotungsten(VI) *p*-*t*Bu-calix[4]arene.^[12a] Crystals of 7 exhibit a noncentrosymmetric highly polar structure (Fig. 3).

The higher reactivity of the C–O bonds facilitates the transformation of 6 and 7 to enantiomeric metalocalix[4]arenes. Indeed, 6 and 7 are converted to the respective dichlorotungsten(VI) complexes 8 and 9 in near quantitative yield when treated with excess AlCl₃ (in refluxing CHCl₃, 3 min). The short reaction time was necessary since 8 and 9 were observed to decompose with longer reaction times. The CD spectra of compounds 8 and 9 are mirror images (Fig. 4), thereby confirming that they are indeed optical isomers. The strong Cotton effects observed

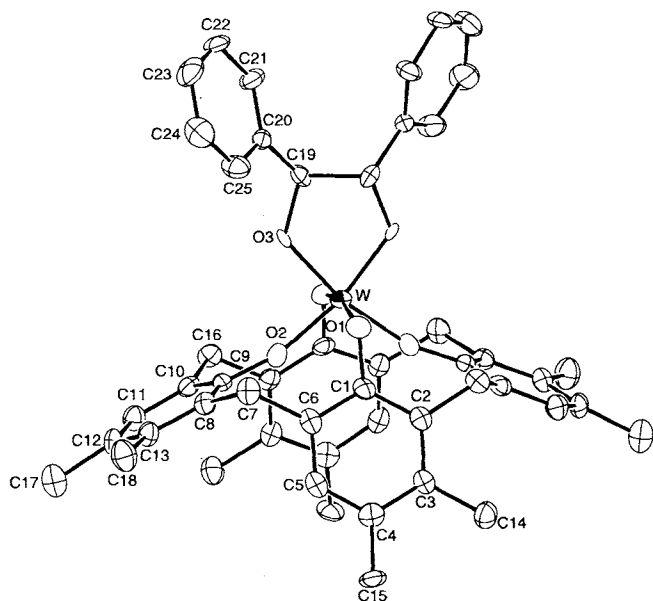


Fig. 2. X-ray structure of compound 7 [15b].

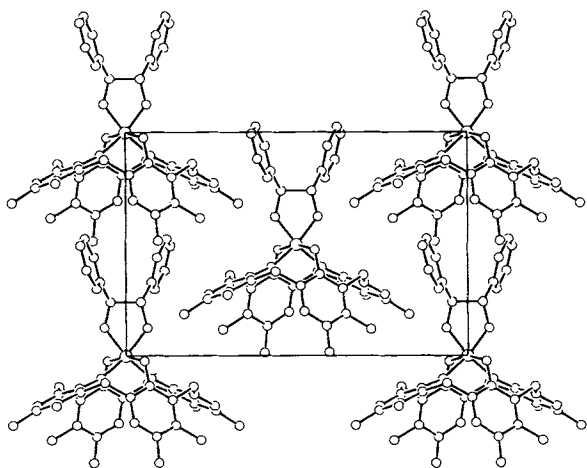
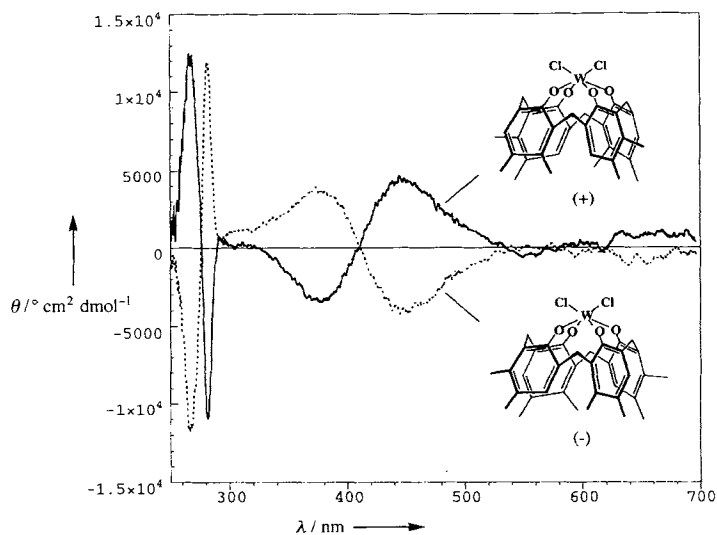
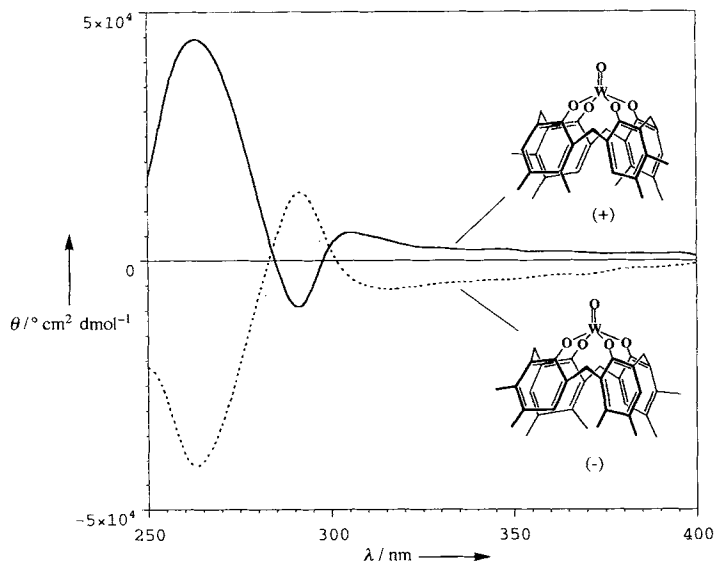


Fig. 3. Crystal packing of 7.

Fig. 4. CD spectra of resolved **8** and **9**.

at 250–300 nm are similar to what has been observed in other optically pure chiral calix[4]arenes^[17] and likely result from exciton coupling of the aromatic chromophores.^[16] The Cotton effects at 375–450 nm are most probably ligand–metal charge transfer in character. At λ_{\max} (280 nm), θ is quite large (+12540), indicating that these chiral metalcalix[4]arenes have very strong rotary power. On the basis of the X-ray structure of **7**, we can assign the absolute configurations of **8** and **9** (Fig. 4).

To prepare Lewis acidic chiral oxotungsten(vi) calix[4]arenes with C_4 symmetry, we first investigated the method applied by Floriani et al.^[12a] for the transformation of the dichlorotungsten(vi) group of **3** to an oxotungsten group. However, in contrast to other dichlorotungsten calix[4]arenes such as **1a**, which is hydrolytically sensitive, **3** has remarkably high stability and is even stable to chromatography on silica. To prepare oxotungsten calix[4]arenes **10** and **11**, we treated **6** and **7** with trimethylsilyl triflate followed by an aqueous workup (Scheme 2). Presumably, the initial product is a ditriflate, which is hydrolyzed to give the oxo compound. The calix[4]arene methylene protons in the ¹H NMR spectrum collapse to a pair of doublets at $\delta = 4.55$ and 3.59, indicating the C_4 symmetry of compounds **10** and **11**. The CD spectra of **10** and **11** again indicate that these complexes are optical isomers (Fig. 5). It is also interesting to note that **10** and **11** have yet stronger rotary power than **8** and **9** ($\theta = +45100$ at 265 nm (λ_{\max})). The absolute configurations of **10** and **11** are shown in Figure 5.

Fig. 5. CD spectra of optical isomers of **10** and **11**.

In summary, we have demonstrated the first resolution of metalcalix[4]arenes. The Lewis acidity and rigid chiral cavity of the oxotungsten(vi) calix[4]arenes present opportunities for the development of catalytic and liquid crystalline systems. Such applications are the subject of ongoing investigations in our laboratory.

Experimental Procedure

2a: *trans*-1,2-Cyclohexanediol (0.064 g, 0.56 mmol) in dry toluene (20 mL) was treated with *n*BuLi (1.1 mL, 1.6 M) at room temperature under an argon atmosphere. After the solution had been stirred for 1 h, it was transferred to a suspension of dichlorotungsten(vi) *p*-*t*Bu-calix[4]arene (0.56 g, 0.56 mmol) in toluene [12a]. The resulting dark purple suspension was heated to reflux for 4 h to give a clear orange-red solution. After the toluene had been evaporated, the residue was

purified by flash chromatography (*n*-hexane:dichloromethane 3:1) to give an orange solid (0.51 g, 96%). positive-ion FABMS: m/z : 943 [$M+1$]; $^1\text{H NMR}$ (CDCl_3 , 200 MHz): δ = 1.18 (s, 18H, *t*Bu), 1.29 (s, 18H, *t*Bu), 1.30 (m, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 2.16 (m, 2H, CH_2), 3.30 (dd, $^2J = 14.02$, $^3J = 4.02$ Hz, 4H, ArCH_2Ar), 4.62 (dd, $^2J = 13.38$, $^3J = 5.08$ Hz, 4H, ArCH_2Ar), 5.17 (m, 2H, OCH), 7.01 (s, 4H, ArH), 7.18 (s, 4H, ArH).

2b: *trans*-1,2-Cyclohexanediol (0.022 g, 0.19 mmol) was dissolved in THF (5 mL) under an argon atmosphere, excess TMSCl (0.2 mL) and Et_3N (0.2 mL) were added at room temperature. The reaction mixture was allowed to stir until TLC showed the disappearance of cyclohexanediol, then THF, excess TMSCl, and Et_3N were removed under reduced pressure. Then **1b** (0.40 g, 0.171 mmol) [**7a**] in dry toluene (20 mL) was added to the residue, and the reaction mixture was heated to reflux for two days. Purification by flash chromatography (*n*-hexane:dichloromethane 3:1) gave an orange-red solid 50 mg (10%). Positive-ion FABMS: m/z : 2666 [$M+1$], $^1\text{H NMR}$ (CDCl_3 , 250 MHz): δ = 0.85 (t, 24H, CH_3), 1.10–2.00 (m, 166H, alkyl and CH_2), 2.20–2.30 (m, 2H, CH_2), 2.56 (s, 6H, ArCH_3), 2.74 (s, 6H, ArCH_3), 3.63 (dd, $^2J = 13.52$, $^3J = 4.52$ Hz, 4H, ArCH_2Ar), 3.89 (t, 4H, OCH₂), 3.97 (t, 4H, OCH₂), 4.00–4.10 (m, 8H, OCH₂), 4.71 (dd, $^2J = 13.62$, $^3J = 6.42$ Hz, 4H, ArCH_2Ar), 5.35–5.45 (m, 2H, OCH), 6.65 (s, 2H, ArH), 6.79 (s, 2H, ArH), 7.11 (s, 2H, ArH), 7.36 (s, 2H, ArH), 7.67 (s, 4H, ArH), 7.88 (s, 4H, ArH).

3: 3,4-Dimethylcalix[4]arene (0.501 g, 0.93 mmol) [**10b**] and WCl_6 (0.40 g, 1.0 mmol) were stirred in dry benzene (10 mL) overnight. After the solvent had been removed, the residue was purified by flash chromatography (*n*-hexane:dichloromethane 3:1) to give **3** as dark purple product (0.59 g, 81%). positive-ion FABMS: m/z : 787 [$M+1$], $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 2.06 (s, 6H, CH_3), 2.37 (s, 6H, CH_3), 2.39 (s, 6H, CH_3), 2.58 (s, 6H, CH_3), 3.52 (d, $^2J = 14.19$ Hz, 2H, ArCH_2Ar), 3.91 (d, $^2J = 14.19$ Hz, 2H, ArCH_2Ar), 4.43 (d, $^2J = 14.16$ Hz, 2H, ArCH_2Ar), 4.70 (d, $^2J = 14.17$ Hz, 2H, ArCH_2Ar), 6.83 (s, 2H, ArH), 7.13 (s, 2H, ArH).

4 and 5: These compounds were prepared in 92% yield by using the same procedure as for **2a**. Positive-ion FABMS: m/z : 831 [$M+1$]. The mixture was separated by HPLC to give **4** and **5**. (Rainin preparative silica column, *n*-hexane:dichloromethane 3:1, flow rate 20 mL min⁻¹). First component: $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 1.36 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 1.84 (m, 2H, CH_2), 2.06 (s, 6H, CH_3), 2.15 (m, 2H, CH_2), 2.17 (s, 6H, CH_3), 2.353 (s, 6H, CH_3), 2.347 (s, 6H, CH_3), 3.33 (d, $^2J = 13.79$ Hz, 2H, ArCH_2Ar), 3.71 (d, $^2J = 13.84$ Hz, 2H, ArCH_2Ar), 4.28 (d, $^2J = 13.83$ Hz, 2H, ArCH_2Ar), 4.57 (d, $^2J = 13.68$ Hz, 2H, ArCH_2Ar), 5.17 (m, 2H, OCH), 6.76 (s, 2H, ArH), 7.01 (s, 2H, ArH), 7.17 (m, 2H, ArH); second component: $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 1.36 (m, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 2.07 (s, 6H, CH_3), 2.15 (m, 2H, CH_2), 2.17 (s, 6H, CH_3), 2.354 (s, 6H, CH_3), 2.344 (s, 6H, CH_3), 3.35 (d, $^2J = 13.80$ Hz, 2H, ArCH_2Ar), 3.69 (d, $^2J = 13.80$ Hz, 2H, ArCH_2Ar), 4.27 (d, $^2J = 13.77$ Hz, 2H, ArCH_2Ar), 4.59 (d, $^2J = 13.78$ Hz, 2H, ArCH_2Ar), 5.16 (m, 2H, OCH), 6.75 (s, 2H, ArH), 7.01 (s, 2H, ArH).

6 and 7: These compounds were also prepared by the same procedure as for **2a** (75% yield). positive-ion FABMS: m/z : 929 [$M+1$]. Again separation by HPLC (*n*-hexane:dichloromethane 3:1) afforded **6** and **7**. First component: $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 2.09 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.325 (s, 6H, CH_3), 2.344 (s, 6H, CH_3), 3.45 (d, $^2J = 13.91$ Hz, 2H, ArCH_2Ar), 3.72 (d, $^2J = 13.81$ Hz, 2H, ArCH_2Ar), 4.34 (d, $^2J = 13.83$ Hz, 2H, ArCH_2Ar), 4.74 (d, $^2J = 13.79$ Hz, 2H, ArCH_2Ar), 6.52 (s, 2H, ArH), 6.80 (s, 2H, ArH), 7.02 (s, 2H, ArH), 7.29–7.38 (m, 10H, ArH); second component: $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 2.08 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.334 (s, 6H, CH_3), 2.345 (s, 6H, CH_3), 3.36 (d, $^2J = 13.84$ Hz, 2H, ArCH_2Ar), 3.79 (d, $^2J = 13.86$ Hz, 2H, ArCH_2Ar), 4.42 (d, $^2J = 13.94$ Hz, 2H, ArCH_2Ar), 4.64 (d, $^2J = 13.72$ Hz, 2H, ArCH_2Ar), 6.51 (s, 2H, ArH), 6.81 (s, 2H, ArH), 6.99 (s, 2H, ArH), 7.29–7.38 (m, 10H, ArH).

8 and 9: Compound **6** (or **7**) (1.2 mg) was dissolved in CHCl_3 (2 mL), then AlCl_3 (10 mg) was quickly added to the solution, and the solution was heated to reflux for about 3 min, upon which the color of the solution changed from orange to dark purple. The reaction was quenched with water (0.5 mL) and dried under reduced pressure. The residue was purified by HPLC (*n*-hexane:dichloromethane 3:1) to give the dichlorotungsten(vi) calix[4]arene (1 mg) **8** (or **9**), as a dark purple solid (98%). Positive-ion FABMS: m/z : 787 [$M+1$], $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 2.06 (s, 6H, CH_3), 2.36 (s, 6H, CH_3), 2.39 (s, 6H, CH_3), 2.58 (s, 6H, CH_3), 3.52 (d, $^2J = 14.20$ Hz, 2H, ArCH_2Ar), 3.91 (d, $^2J = 14.19$ Hz, 2H, ArCH_2Ar), 4.43 (d, $^2J = 14.11$ Hz, 2H, ArCH_2Ar), 4.70 (d, $^2J = 14.17$ Hz, 2H, ArCH_2Ar), 6.83 (s, 2H, ArH), 7.13 (s, 2H, ArH).

10 and 11: Excess trimethylsilyl triflate was added to a solution containing compound **6** (or **7**) (2 mg) in toluene (10 mL). The solution changed from orange to red-orange under heating to reflux overnight under argon. The reaction was quenched with water (1 mL) and neutralized by the addition of triethylamine. The solvent was removed and the residue was purified by flash chromatography ($\text{AcOH}:\text{CH}_2\text{Cl}_2$ 5:95) to give the oxotungsten(vi) calix[4]arene **10** (or **11**) (1 mg) as a yellow solid (76%). Positive-ion FABMS: m/z : 733 [$M+1$], $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 2.14 (s, 12H, CH_3), 2.31 (s, 12H, CH_3), 3.59 (d, $^2J = 13.46$ Hz, 4H, ArCH_2Ar), 4.55 (d, $^2J = 13.40$ Hz, 4H, ArCH_2Ar), 7.04 (s, 4H, ArH).

Keywords: calixarenes • enantiomeric resolution • NMR spectroscopy • tungsten compounds

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