Letter

Concave reagents part 33: transition metal complexes of 1,10-phenanthroline bridged calix[6]arenes†

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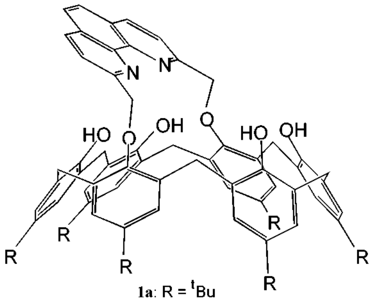
1,10-Phenanthroline bridged calix[6]arenes 1a and 1b have been synthesized and metal salt complexes with Cu^{+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Eu^{3+} have been isolated. In contrast to the concave 1,10-phenanthrolines 2, which only form 1 : 1 complexes with metal salts, 1 also forms 2 : 1 complexes with Cu^{2+}, Co^{2+} and Ni^{2+}. Only Cu^{+} forms 1 : 1 complexes exclusively.

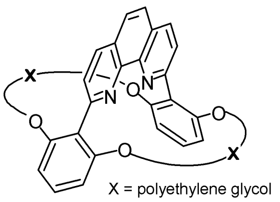
For some time now, calixarenes have widely been used as hosts for complexing transition metal ions.[1] Besides unfunctionalized calixarenes,[1] functionalized ones[1,2] have also been employed. For the complexation of transition metals such as Co, Ni and Cu, calixarenes with nitrogen atom containing groups like picolyl or bipyridyl units as metal binding sites at the narrow rim have often been used.[2a,c] However, most of the hosts were based on calix[4]arene.[2a] In contrast, only a small number of complexes of calix[6]arenes are known.[1,2b]

Inoue *et al.*[3] used calix[6]arenes functionalized at the narrow rim with four bipyridyl units to complex Ru^{2+} ions; these complexes exhibit interesting photochemical properties. To mimic metalloenzymes Reinaud *et al.*[4a,b] complexed Cu^{+} or Zn^{2+} with calix[6]arenes bearing three picolyl groups or three imidazol units,[4c] respectively.

In this communication we present transition metal ion complexes of 1,10-phenanthroline bridged calix[6]arenes, **1**, which have been successfully used in the catalysis of the cyclopropanation of alkenes by diazoacetates.[5] The synthesis of the 1,10-phenanthroline bridged calix[6]arene **1a** has already been published.[6] Now **1b** has been synthesized analogously.



1a: R = ^{t}Bu
1b: R = H



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1,10-Phenanthrolines have been widely used as ligands for the complexation of transition metal ions. So have the bimacrocyclic concave 1,10-phenanthrolines **2**.[7] Remarkably, the latter only form 1 : 1 complexes with transition metal salts, leaving one side of these complexes open for the coordination and/or for catalysis of additional ligands. Therefore, the complexing behavior of the bridged calixarene ligands **1** has now been investigated. Several metal salts have been used with varying counter ions. In general, non-coordinating anions have been used for the titrations (nonafluorobutanesulfonates or hexafluorophosphates) while crystallizations were easier with halides because nonafluorobutanesulfonates are more hygroscopic.

The complexation of the diamagnetic Cu^{+} ion by **1** can be followed by the low-field shift of the NMR resonances of the 1,10-phenanthroline unit (up to −0.66 ppm). Thus for instance, the doublet of the hydrogen atoms in the 4- and 7-positions of the 1,10-phenanthroline bridge of **1a** shifts downfield by 0.33 ppm when CuPF$_6$ is added. The calix[6]arene cone conformation (all-*up* conformation) is not changed by Cu^{+} complexation, as is proven by the coupling pattern of the methylene hydrogen atoms between 3.5 to 4.5 ppm for **1a** and 3.3 to 4.3 ppm for **1b**.[8]

The 1 : 1 stoichiometry of the complexes between Cu^{+} and **1a** and **1b** was proven by "Job plots", by elemental analyses of the isolated complexes, and by titrations.[9] Fig. 1 shows the Job plot obtained from UV measurements at 330 nm for mixtures of **1a** and a Cu^{+} salt at constant total concentrations, [**1a**] + [Cu^{+}], but different [**1a**] : [Cu^{+}] ratios. The maximum at the molar fraction $\chi = 0.5$ proves the 1 : 1 stoichiometry.

The complex association constants between various transition metals and **1a** or **1b** were determined by UV titrations.

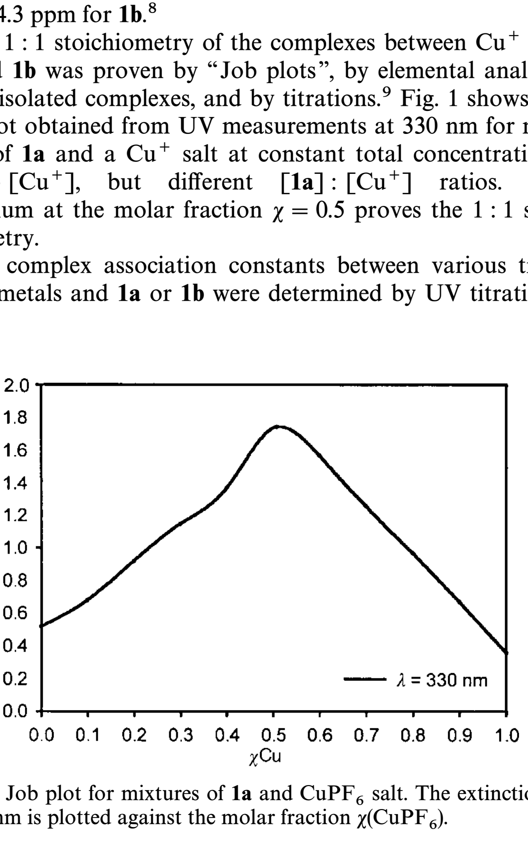

Fig. 1 Job plot for mixtures of **1a** and CuPF$_6$ salt. The extinction E at 330 nm is plotted against the molar fraction χ(CuPF$_6$).

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† For part 32, see ref. 5.

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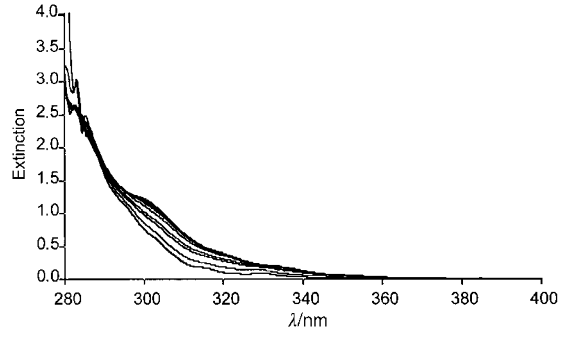

Fig. 2 UV titration of **1a** with a $CuPF_6$ salt: [**1a**] = 140 μM; addition of the Cu^+ salt in aliquots of 0.1 equiv. The lowest curve at long wavelengths is the free ligand.

From the change in absorption of a shoulder at 330 nm, complex formation constants K_{ass} have been calculated. As an example, the titration of **1a** with a Cu^+ salt is shown in Fig. 2. The lowest curve in the region between 290 and 340 nm results from the uncomplexed ligand **1a**. For complex formation with **1a**, a log K_{ass} of 5.5 was found, while with **1b** it is >5.9.[10] In the titrations of **1a** and **1b** with Cu^+, isosbestic points at 292 and 295 nm, respectively, have been observed as expected for a simple equilibrium of the form:

$$M^+ + L \rightleftharpoons [ML]^+$$

But when Co^{2+}, Ni^{2+} or Cu^{2+} salts were titrated with the ligands **1**, isosbestic points could not be observed, a fact that indicates the existence of more than one equilibrium during the titrations. In Fig. 3, the change of extinction ΔE (difference between the extinction of the complexes and the free ligand) at $\lambda = 330$ nm is plotted against the addition of metal salt, Co^{2+} in this example. The dashed line in Fig. 3 shows the theoretical titration curve for a 1 : 1 complex with an infinite complex formation constant. The measured curves for Co^{2+}, Ni^{2+} and Cu^{2+} salts differ remarkably: (i) the maximum extinction is reached before even 1 equiv. of the metal ion has been added and (ii) the titration curves show a higher extinction during the titration than at a high metal salt concentration. The metal ion-to-ligand ratio of *ca.* 0.5 at the maximum extinction suggests that 2 : 1 complexes (ligand-to-metal) are formed at low metal ion concentrations, from which 1 : 1 complexes are then formed with increasing metal salt concentration.

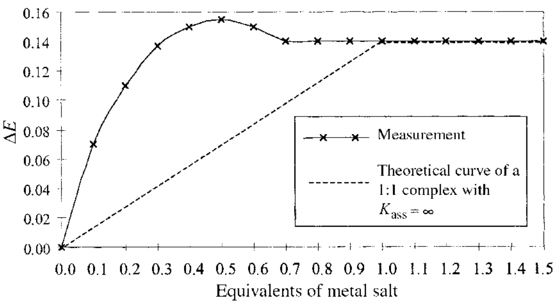

Fig. 3 Titration of **1a** with $CoNf_2$. ΔE at $\lambda = 330$ nm is plotted against the addition of metal salt: [**1a**] = 140 μM.

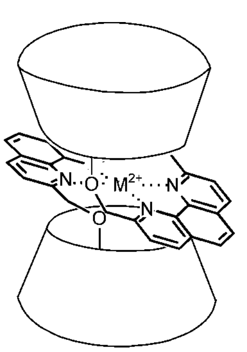

Fig. 4 Schematic drawing of a potential 2 : 1 complex between **1** and a metal ion.

The differences between the titration curves observed for Cu^+ on the one hand and Co^{2+}, Ni^{2+} or Cu^{2+} on the other may be explained by the different coordination number and geometry (tetrahedral *vs.* octahedral coordination). Due to the oxygen–methylene links between the calixarene and the 1,10-phenanthroline unit, the ligands **1** may twist whereas the more rigid concave 1,10-phenanthrolines **2** may not. Bent geometries have been investigated for related bridged calix[6]arenes.[11] Low-temperature NMR studies of the **1a** · $CuPF_6$ complex argue for such a bent conformation in the complexes, too. The number of signals for the hydrogen atoms of the ligand increases according to the lower symmetry of the bent conformation. The *tert*-butyl signals even split into four signals with intensities of 18 : 18 : 9 : 9, indicating an even lower symmetry that could speculatively be interpreted as arising from the coordination of one of the phenol oxygen atoms to the copper ion, making the *tert*-butyl groups of two adjacent aryl rings inequivalent. Starting from such a bent geometry, 2 : 1 complexes should be possible when the metal ions prefer an octahedral or square planar coordination (as shown in Fig. 4), while steric hindrance prohibits the formation of 2 : 1 complexes with a tetrahedral coordination. In contrast to the concave ligands **2**, the formation of 2 : 1 complexes between the bridged calixarenes **1** and a metal ion is not strictly excluded for steric reasons, as Fig. 4 shows. At high metal salt concentrations however, 1 : 1 complexes are finally formed with the octahedrally coordinating metal ions as well, as the constant extinctions for high metal salt concentrations prove. The isolated complexes show 1 : 1 (Cu^+, Cu^{2+}, Co^{2+}, Eu^{3+}) and 2 : 1 (Ni^{2+}) stoichiometries.

Experimental

Preparation of 1b

Hexahydroxycalix[6]arene (636 mg, 1.00 mmol) in THF is reacted under nitrogen with Bu^tOK (690 mg, 6.15 mmol) and 2,9-bis(bromomethyl)-1,10-phenanthroline (450 mg, 1.23 mmol). After stirring for 24 h at room temperature, the mixture is treated with 20 ml of 0.1 N HCl. The crude product is purified by chromatography on silica eluting with dichloromethane ($R_f = 0.32$), followed by recrystallization from dichloromethane–methanol to yield **1b** as a colorless solid. Yield: 310 mg (64%), mp 222–226 °C. MS (EI, 70 eV) *m*/*z* (%): 841 (100) $[M]^+$, 636 (29) $[M - Phen]^+$, 208 (81). IR (KBr): $\tilde{\nu} = 3453$ (OH), 3326, 3038 (CH arom.), 2913 (CH aliph.), 1620, 1590 (arom.), 1500, 1453, 1371, 1261, 1192, 1081, 1029, 873, 778, 753 (out-of-plane), 637 cm^{-1}. UV/Vis ($CHCl_3$) λ_{max} (ε): 330 (571), 305 (5071), 280 (18 571 M^{-1} cm^{-1}) nm. ^1H-NMR (200 MHz, $CDCl_3$, D_2O exchange): δ 8.31 (d, $J = 8.3$, 2 H, 4-H, 7-H), 7.83 (d, $J = 8.3$, 2 H, 3-H, 8-H), 7.80 (s, 2 H, 5-H, 6-H), 7.03 (dd, $J_1 = 7.3$, $J_2 = 1.8$, 4 H, Ar–H), 6.99 (dd, $J_1 = 7.5$, $J_2 = 1.8$, 4 H, Ar–H), 6.92 (s, 6 H, Ar–H), 6.65 (t, $J = 7.5$, 4 H, Ar–H), 5.70 (s, 4 H, OCH_2), 5.30 (s, 4H, CH_2Cl_2), 4.52 (d, $J = 15.4$, 4 H, Ar–CH_2–Ar), 4.08 (d, $J = 14.9$, 2 H, Ar–CH_2–Ar), 3.57 (d, $J = 15.8$, 4 H, Ar–CH_2–Ar), 3.38 (d, $J = 14.9$ Hz, 2 H, Ar–CH_2–Ar). Prior to the D_2O exchange the OH signal appeared as a br s between *ca.* 7.0 and 7.9 ppm, overlapping the signals of the 1,10-phenanthroline bridge. Elem. anal. for $C_{56}H_{44}N_2O_6 \cdot 2CH_2Cl_2 \cdot H_2O$: calc. C 67.51, H 4.93, N 2.76; found C 67.71, H 4.90, N 2.68%.

Determination of association constants K_{ass} for complexes $1\cdot M^{n+}$[9]

To 2 ml of a 140 μM solution of a 1,10-phenanthroline bridged calix[6]arene **1** in dry chloroform, a 2 mM solution of the transition metal salt in dry acetonitrile was added in 9 μl aliquots. In order to use non-nucleophilic anions, Co^{2+}, Ni^{2+} and Cu^{2+} ions were added as nonafluorobutanesulfonates (Nf);[7] Cu^+ was not available as the nonafluorobutanesulfonate and therefore was added as tetrakis(acetonitrile)copper(I) hexafluorophosphate. The titration was followed by UV, and from a shoulder at 330 nm the association constants were calculated. In the case of Cu^+, isosbestic points were observed at 292 nm for **1a** and at 295 nm for **1b**.

Determination of the $1a\cdot Cu^+$ complex stoichiometry by the method of continuous variations ("Job plot")[9]

Mixtures of $[(CH_3CN)_4Cu]PF_6$ and ligand **1a** with ratios varying from 10 : 0 to 0 : 10 but at a constant total concentration ($[\{(CH_3CN)_4Cu\}PF_6] + [L]$) were made from 1 mM solutions of **1a** and $\{(CH_3CN)_4Cu\}PF_6$ in dry chloroform–acetonitrile (1 : 1). The UV extinction at $\lambda = 330$ nm was plotted against the molar fraction (see Fig. 1).

General procedure for the synthesis of transition metal complexes of 1a

To 50 μmol of **1a** in 5–20 ml of dry dichloromethane, a solution of 50 μmol of a transition metal salt in 2 ml of dry methanol was slowly added. After 2 h of stirring at room temperature, the solvents were removed *in vacuo*. The residue was recrystallized from benzene–dichloromethane or benzene–chloroform (see Table 1 for yields, melting points and elemental analyses).

IR (KBr) spectra of $1\cdot M^{n+}$ complexes. **1a** · $CoCl_2$: $\tilde{\nu} = 3421$ (OH), 2959 (CH aliph.), 1654 (arom.), 1482, 1363, 1292, 1199, 1196, 1118, 873 (out-of-plane) cm^{-1}. **1a** · NiI_2: $\tilde{\nu} = 3422$ (OH), 2960 (CH aliph.), 1624 (arom.), 1482, 1362, 1292, 1198, 1119, 1029, 873 (out-of-plane) cm^{-1}. **1a** · $CuBr_2$: $\tilde{\nu} = 3385$ (OH), 2960, 2867 (CH aliph.), 1654 (arom.), 1481, 1392, 1362, 1201, 1120, 981, 872 (out-of-plane) cm^{-1}. **1a** · CuBr: $\tilde{\nu} = 3414$ (OH), 2959, 2867 (CH aliph.), 1654 (arom.), 1482, 1362, 1291, 1201, 981, 871, 818 (out-of-plane) cm^{-1}. **1a** · $EuCl_3$: $\tilde{\nu} = 3418$ (OH), 2958 (CH aliph.), 1624 (arom.), 1482, 1363, 1292, 1200, 1119, 873 (out-of-plane) cm^{-1}.

UV/Vis ($CHCl_3$) spectra of $1\cdot M^{n+}$ complexes. **1a** · $CoNf_2$ 1 : 1 complex λ_{max} (ε): 330 (2500), 300 (10 523), 280 (20 877 M^{-1} cm^{-1}) nm; 2 : 1 complex λ_{max} (ε): 330 (2387), 300 (12 444), 280 (21 714 M^{-1} cm^{-1}) nm. **1a** · $NiNf_2$ 1 : 1 complex λ_{max} (ε): 330 (2565), 300 (11 116), 280 (25 000 M^{-1} cm^{-1}) nm; 2 : 1 complex λ_{max} (ε): 330 (2006), 300 (12 510), 280 (24 643 M^{-1} cm^{-1}) nm. **1a** · $CuNf_2$ 1 : 1 complex λ_{max} (ε): 330 (5013), 300 (13 920), 280 (25 000 M^{-1} cm^{-1}) nm; 2 : 1 complex λ_{max} (ε): 330 (4411), 300 (11 818), 280 (23 571 M^{-1} cm^{-1}) nm. **1a** · $[(CH_3CN)_4Cu]PF_6$ λ_{max} (ε): 330 (1571), 300 (9643), 292 (11 143), 280 (19 143 M^{-1} cm^{-1}) nm. **1b** · $CoNf_2$ 1 : 1 complex λ_{max} (ε): 330 (1786), 305 (8857), 280 (19 429 M^{-1} cm^{-1}) nm. 2 : 1 complex λ_{max} (ε): 330 (1500), 305 (6929), 280 (19 286) nm. **1b** · $NiNf_2$ 1 : 1 complex λ_{max} (ε): 330 (1571), 305 (8714), 280 (19 571 M^{-1} cm^{-1}) nm. 2 : 1 complex λ_{max} (ε): 330 (1357), 305 (7214), 280 (19 571 M^{-1} cm^{-1}) nm. **1b** · $CuNf_2$ 1 : 1 complex λ_{max} (ε): 330 (2429), 305 (8286), 280 (18 643 M^{-1} cm^{-1}) nm; 2 : 1 complex λ_{max} (ε): 330 (2071), 305 (6357), 280 (18 286 M^{-1} cm^{-1}) nm. **1b** · $[(CH_3CN)_4Cu]PF_6$ 1 : 1 complex λ_{max} (ε): 330 (2143), 305 (8286), 295 (13 571), 280 (18 143 M^{-1} cm^{-1}) nm.

Table 1 Elemental analyses for **1a** · MX_n

MX_n	Formula Elem. anal. calc. (%) Elem. anal. found (%)	Yield (%)	Mp/°C
CuBr	$[C_{80}H_{92}N_2O_6\cdot CuBr]\cdot CHCl_3$ C 70.93, H 6.98, N 2.04 C 70.71, H 6.76, N 2.12	81	>250
$CuBr_2$	$[C_{80}H_{92}N_2O_6\cdot CuBr_2]$ C 68.59, H 6.62, N 2.00 C 68.40, H 6.62, N 1.90	72	>250
$CoCl_2$	$[C_{80}H_{92}N_2O_6\cdot CoCl_2]\cdot CH_2Cl_2$ C 69.87, H 6.80, N 2.01 C 69.72, H 6.81, N 1.95	65	>250
NiI_2	$[(C_{80}H_{92}N_2O_6)_2\cdot NiI_2]$ C 72.03, H 6.95, N 2.10 C 72.11, H 7.10, N 1.94	75	245
$EuCl_3$	$[C_{80}H_{92}N_2O_6\cdot EuCl_3]\cdot C_6H_6$ C 68.22, H 6.52, N 1.85 C 68.11, H 6.79, N 1.85	86	>250

^{1}H-NMR spectra of $1\cdot CuPF_6$ complexes. 1a. ^{1}H-NMR (200 MHz, $CDCl_3$, D_2O exchange): δ 8.25 (d, $J = 8.3$, 2 H, 4-H, 7-H), 7.82 (d, $J = 8.3$, 2 H, 3-H, 8-H), 7.74 (s, 2 H, 5-H, 6-H), 6.97 (d, $J = 2.5$, 4 H, Ar–H), 6.96 (s, 4 H, Ar–H), 6.88 (d, $J = 2.3$, 4 H, Ar–H), 5.53 (s, 4 H, OCH_2), 4.48 (d, $J = 15.3$, 4 H, Ar–CH_2–Ar), 3.84 (d, $J = 14.8$, 2 H, Ar–CH_2–Ar), 3.58 (d, $J = 14.8$, 2 H, Ar–CH_2–Ar), 3.55 (d, $J = 15.4$ Hz, 4 H, Ar–CH_2–Ar), 1.15 (s, 18 H, CH_3), 1.10 (s, 36 H, CH_3). Prior to the D_2O exchange the OH signal appeared as a broad singlet between *ca.* 7.3 and 8.0 ppm, overlapping the signals of the 1,10-phenanthroline bridge. **1a** · $CuPF_6$ ^{1}H-NMR {300 MHz, $CDCl_3$, *ca.* 1.3 equiv. of $[(CH_3CN)_4Cu]PF_6$}: δ 8.58 (d, $J = 8.2$, 2 H, 4-H, 7-H), 7.99 (s, 2 H, 5-H, 6-H), 7.95 (d, $J = 8.3$, 2 H, 3-H, 8-H), 7.64 (br s, 4 H, OH), 6.96 (br s, 8 H, Ar–H), 6.86 (s, 4 H, Ar–H), 5.60 (s, 4 H, OCH_2), 4.50 (d, $J = 15.0$, 4 H, Ar–CH_2–Ar), 3.82 (d, $J = 14.0$, 2 H, Ar–CH_2–Ar), 3.58 (d, $J = 14.1$, 2 H, Ar–CH_2–Ar), 3.55 (d, $J = 15.4$ Hz, 4 H, Ar–CH_2–Ar), 1.15 (s, 18 H, CH_3), 1.10 (s, 36 H, CH_3). ^{1}H-NMR {500 MHz, CD_2Cl_2–CD_3CN (10 : 1), *ca.* 1.5 equiv. of $[(CH_3CN)_4Cu]PF_6$, $T = 233$ K}: δ 8.73, 8.60, 8.32 (br d, $J \approx 10$, br s, br s, 4 H), 8.15, 7.75 (s, br d, $J \approx 10$, 4 H), 7.48, 7.40, 7.32, 7.22 (br s, br s, br s, br d, $J \approx 8$, 7 H), 6.98, 6.91 (br s, br s, 4 H), 6.55, 6.50 (br s, br s, 2 H), 6.24, 6.14 (br s, br s, 4 H), 4.25, 4.20 (br d, $J \approx 15$, br d, $J \approx 15$, 2 H), 4.05, 3.95, 3.80 (br d, $J \approx 16$, br d, $J \approx 15$, br d, $J \approx 16$, 6 H), 3.55, 3.47, 3.38 (br s, br d, $J \approx 14$, br d, $J \approx 14$, 3 H), 3.21, 2.95 (br d, $J \approx 14$, br d, $J \approx 14$ Hz, 2 H), 1.25, 1.18 (br s, br s, 36 H), 0.78, 0.66 (br s, br s, 18 H). **1b** · $CuPF_6$ ^{1}H-NMR {300 MHz, $CDCl_3$, *ca.* 1.3 equiv. $[(CH_3CN)_4Cu]PF_6$}: δ 8.55 (d, $J = 8.2$, 2 H, 4-H, 7-H), 8.46 (s, 2 H, 5-H, 6-H), 7.92 (d, $J = 8.2$, 2 H, 3-H, 8-H), 7.20 (m, 6, H Ar–H), 6.99 (d, $J = 7.7$, 4 H, Ar–H), 6.86 (d, $J = 7.7$, 4 H, Ar–H), 6.65 (t, $J = 7.5$, 4 H, Ar–H), 5.70 (s, 4 H, OCH_2), 4.33 (br d, $J = 15.2$, 4 H, Ar–CH_2–Ar), 3.68 (br d, $J = 15.1$, 2 H, Ar–CH_2–Ar), 3.50 (d, $J = 15.3$, 4 H, Ar–CH_2–Ar), 3.41 (d, $J = 15.4$ Hz, 2 H, Ar–CH_2–Ar).

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