

Calix[n]arene sulfonic acids bearing pendant aliphatic chains as recyclable surfactant-type Brønsted acid catalysts for allylic alkylation with allyl alcohols in water

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Supplemental Information

Experimental

General

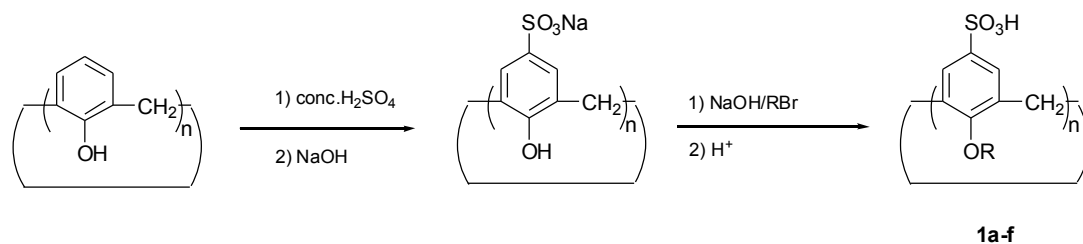
IR spectra were recorded with a Perkin–Elmer 782 IR spectrometer. ¹H NMR and ¹³C NMR spectra were obtained in CDCl₃ at room temperature with a Bruker DMX-300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). Mass spectra were measured on Bruker APEX-2 FT-ICRMS spectrometer.

The values of critical micelle concentration (cmc) were measured by isothermal titration microcalorimetry. The TAM 2277-201 isothermal titration microcalorimeter (Thermometric AB, Järfälla, Sweden) was used to obtain the cmc. The pH values were determined by Acidity Meter pHs-2C.

Materials

Starting from *p*-H-calix[n]arene, calyx[n]arene sulfonic acids (**1a-f**) were prepared through sulfonation by conc. H₂SO₄ or chlorosulfonic acid and condensation with alkyl bromids. *p*-Alkoxybenzenesulfonic acids (**5c-d**) were prepared by means of the sulfonation reaction of alkyl phenyl ether. *p*-Toluenesulfonic acid (**5a**, TsOH), *p*-dodecylsulfonic acid (DBSA, **5b**) and PS-SO₃H (**6**, amberlyst-15) were available commercially. Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification.

Typical procedure for synthesis of calyx[n]arene-SO₃H catalyst



The hexasodium salt of calix[6]arene-*p*-hexasulfonate (3.00 g, 1.92 mmol)¹ was mixed with NaOH (2.35 g, 58.8 mmol) in water (15 mL) and octyl bromide (8.40 g, 59.2 mmol) in dimethyl sulfoxide (60 mL), and the reaction mixture was stirred at 80 °C for 72 h. After cooling, the solution was diluted with methanol to give a solid, which was filtered and dissolved in water (10 mL). After an insoluble material was removed by filtration, the solid was precipitated again by adding ethanol. After dried under vacuum at 40 °C, a white powder (3.0 g, 81%) was obtained. The powder (0.8 g, 0.27 mmol) was dissolved in water (10 mL), then the solution passed through ion-exchange column, the water was evaporated and dried under vacuum at 40 °C for 1 day, giving a pale yellow solid **1d** (0.39 g, overall yield 80%).

Hexasulfonato-hexakis(octyloxy)calix[6]arene (**1d**)¹

$\nu_{\max}/\text{cm}^{-1}$ 3422, 2926, 2858, 1721, 1641, 1459, 1384, 1219, 1177, 1117, 1047, 670, 629; δ_{H} (300 MHz, D₂O; Me₄Si) 0.52 (18H, s), 0.94-1.11 (60H, m), 1.39 (12H, s), 3.25 (18H, br), 4.11 (6H, s), 7.05 (12H, s); δ_{C} (75 MHz, D₂O; Me₄Si) 13.8, 22.8, 26.6, 30.1, 30.3, 32.3, 73.7, 126.5, 133.5, 138.1, 136.4; m/z (TOF) 1812.3 (M+Na⁺ requires 1811.7).

Hexasulfonato-hexakis(butyloxy)calix[6]arene (**1c**)

$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3357, 2958, 2873, 1721, 1457, 1221, 1166, 1116, 1042, 889, 664, 623; δ_{H} (300 MHz, CDCl₃; Me₄Si) 0.28 (18H, br), 0.62-1.04 (24H, br), 3.09 (18H, br), 3.94 (6H, br), 7.04 (12H, s, br); δ_{C} (75 MHz, CDCl₃; Me₄Si) 13.5, 18.8, 28.6, 30.5, 31.9, 48.8, 60.7, 73.1, 126.2, 127.8, 133.5, 137.4, 153.0; m/z (TOF) 1475.1 (M+Na⁺ requires 1475.4).

Tetrasulfonato-tetrakis(octyloxy)calix[4]arene (**1e**)

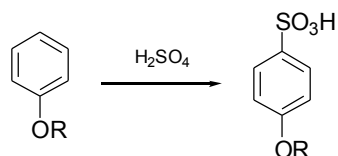
$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3392, 2925, 2858, 1710, 1462, 1384, 1220, 1120, 1042, 890, 663, 623, 557; δ_{H} (300 MHz, CDCl₃; Me₄Si) 0.68 (12H, br), 1.09 (40 H, br), 1.77 (8H, br), 3.15 (8H, br), 3.64 (4H, br), 4.16 (4H, br), 7.08 (8H, br); δ_{C} (75 MHz, CDCl₃; Me₄Si) 13.7, 22.6, 26.3, 28.1, 29.7, 30.1, 30.3, 32.0, 75.6, 134.4, 137.1, 158.0, 165.5; m/z (TOF) 1215.3 (M+Na⁺ requires 1215.5).

Octasulfonato-octakis(octyloxy)carlix[8]arene (**1f**)¹

ν_{max} (film)/ cm^{-1} 3439, 2926, 2858, 1705, 1646, 1460, 1218, 1177, 1045, 668, 627, 560; δ_{H} (300 MHz, CDCl_3 ; Me_4Si) 0.50 (24H, br), 0.92-0.98 (96H, m), 1.39 (16H, br), 3.35 (24H, br), 4.10 (8H, br), 7.09 (16H, br); δ_{C} (75 MHz, CDCl_3 ; Me_4Si) 13.8, 22.8, 26.8, 30.1, 30.3, 32.3, 33.5, 73.5, 133.5, 138.5, 156.7, 165.5; m/z (TOF) 2408.1 ($\text{M}+\text{Na}^+$ requires 2408.0).

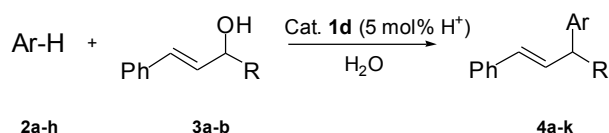
According to the same procedure, **Hexasulfonato-hexakis(dodecyloxy)calix[6]arene (**1e**)¹** was synthesized.

Typical procedure for synthesis of mono-alkylbenzenesulfonic acid (**5c-d**):



Concentrate sulfuric acid (5.0 ml) was added to octyl phenyl ether (5.0 g), and the mixture was stirred for 30 min at room temperature. The mixture was poured into a saturated aqueous solution of sodium chloride, and the precipitates were collected by suction, which was dissolved in water, following by passing through an ion-exchange resin column. After the solvent was evaporated, the residue was dried under vacuum at 40 °C for 1 day to give a yellow oil **5c**² (4.35 g, 63%). In terms of the same procedure **5d**² was synthesized.

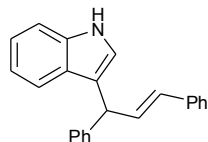
Typical procedure for allylic alkylation



A mixture of indole **2a** (58.6 mg, 0.5mmol), (*E*)-1,3-diphenylprop-2-en-1-ol **3a** (105.1 mg, 0.5 mmol) and **1d** (1.5 mg, 5 mol% H⁺) in water (2 mL) was stirred vigorously at room temperature for 18 h. The reaction mixture was extracted by ether (2 mL×3), and the organic phase was collected, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure to give crude

product, which was purified by flash chromatograph on silica gel (eluent: petroleum ether : ethyl acetate = 12 : 1) to give yellow solid **4a** (128.2 mg, 83%).

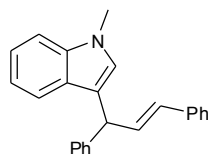
3-((E)-1,3-diphenylallyl)-1H-indole (**4a**)³



White solid

$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3058, 3030, 2925, 1697, 1615, 1491, 1453, 1334, 1264, 1219, 1100, 1026, 969, 742, 699; δ_{H} (300 MHz, CDCl_3 ; Me_4Si) 5.01 (1H, d, $J = 7.2\text{Hz}$), 6.33 (1H, d, $J = 15.8\text{Hz}$), 6.62 (1H, dd, $J = 15.8, 7.2\text{Hz}$), 6.72 (1H, s); δ_{C} (75 MHz, CDCl_3 ; Me_4Si) 46.4, 111.4, 118.7, 119.6, 120.0, 122.3, 122.8, 126.5, 126.6, 127.0, 127.4, 128.7, 130.7, 132.8, 136.8, 137.7, 143.6

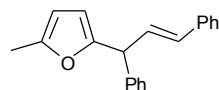
1-methyl-3-((E)-1,3-diphenylallyl)-1H-indole (**4b**)⁴



A white solid

$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3053, 3026, 1600, 1476, 1371, 1329, 1078, 962, 741, 699, 624, 493; δ_{H} (300 MHz, CDCl_3 ; Me_4Si) 3.72 (3H, s), 5.12 (1H, d, $J = 7.3\text{Hz}$), 6.43 (1H, d, $J = 15.8\text{Hz}$), 6.71 (1H, dd, $J = 15.8, 7.3\text{Hz}$), 6.74 (1H, s), 6.98-7.43 (14H, m); δ_{C} (75 MHz, CDCl_3 ; Me_4Si) 32.8, 46.5, 109.5, 117.3, 119.2, 120.2, 121.9, 126.6, 127.4, 127.5, 127.6, 128.8, 130.7

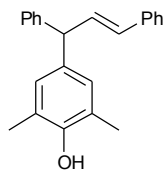
2-methyl-5-((E)-1,3-diphenylallyl)furan (**4e**)



Yellow oil

$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3059, 3027, 1599, 1218, 965, 745, 697; δ_{H} (300 MHz, CDCl_3 ; Me_4Si) 2.34 (3H, s), 4.93 (1H, d, $J = 7.3\text{Hz}$), 5.98 (1H, d, $J = 2.0\text{Hz}$), 6.05 (1H, d, $J = 2.0\text{Hz}$), 6.48 (1H, d, $J = 15.9\text{Hz}$), 6.65 (1H, dd, $J = 15.9\text{Hz}$), 7.28-7.46 (10H, m); δ_{C} (75 MHz, CDCl_3 ; Me_4Si) 13.7, 48.5, 106.1, 107.6, 126.5, 126.9, 127.5, 128.4, 128.5, 128.6, 130.2, 131.5, 137.2, 141.5, 151.5, 154.3; m/z (EI) 274.1355 (M^+ $\text{C}_{20}\text{H}_{18}\text{O}$ requires 274.1358).

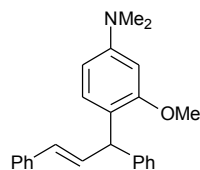
2,6-dimethyl-4-((E)-1,3-diphenylallyl)phenol (4f)



Yellow oil

$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3444, 3058, 2921, 2860, 1696, 1644, 1595, 1487, 1449, 1321, 1205, 1136, 1070, 741, 703; δ_{H} (300 MHz, CDCl_3 ; Me_4Si) 2.16 (6H, s), 4.54 (1H, dd, $J = 4.5, 3.0\text{Hz}$), 4.74 (1H, d, $J = 3.9\text{Hz}$), 6.31 (1H, d, $J = 7.2\text{Hz}$), 6.48 (1H, m), 6.82 (2H, s), 7.14-7.22 (10H, m); δ_{C} (75 MHz, CDCl_3 ; Me_4Si) 16.2, 53.7, 123.2, 123.2, 126.5, 127.4, 128.6, 128.7, 128.8, 128.9, 131.1, 133.3, 135.3, 137.6, 144.2, 150.9; m/z (EI) 314.1674 (M^+ $\text{C}_{23}\text{H}_{22}\text{O}$ requires 314.1671).

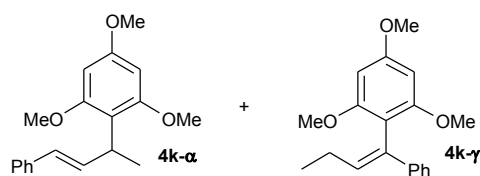
3-methoxy-N,N-dimethyl-4-((E)-1,3-diphenylallyl)benzenamine (4g)



White solid, m.p. 89-91°C

$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3024, 2932, 2836, 1795, 1611, 1571, 1513, 1447, 1352, 1239, 1114, 972, 812, 744, 697, 542, 470; δ_{H} (300 MHz, CDCl_3 ; Me_4Si) 2.86 (6H, s), 3.70 (3H, s), 5.21 (1H, d, $J = 7.0\text{Hz}$), 6.27 (3H, m), 6.67 (1H, dd, $J = 15.9, 7.0\text{Hz}$), 7.00-7.33 (11H, m); δ_{C} (75 MHz, CDCl_3 ; Me_4Si) 40.9, 46.6, 55.7, 96.8, 105.0, 120.5, 126.1, 126.4, 127.1, 128.3, 128.6, 128.8, 130.0, 130.7, 133.5, 138.0, 144.5, 150.9, 158.0; m/z (EI) 343.1939 (M^+ $\text{C}_{24}\text{H}_{25}\text{NO}$ requires 343.1936).

1-[(E)-3-(2,4,6-trimethoxyphenyl)but-1-enyl]benzene and 1-[(E)-1-(2,4,6-trimethoxyphenyl)-but-2-enyl]benzene (4K- α and 4k- γ)

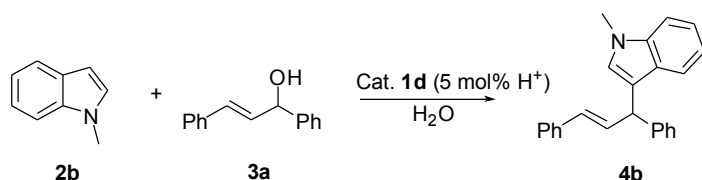


$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3078, 3021, 2997, 2957, 2938, 2836, 1600, 1491, 1459, 1418, 1327, 1289, 1204, 1151, 1124, 1063, 969, 813, 741, 696; δ_{H} (300 MHz, CDCl_3 ; Me_4Si): for **4k- α** : 1.34 (3H, d, $J =$

7.1 Hz), 3.68 (3H, s), 3.71 (3H, s), 3.72 (3H, s), 4.14 (1H, m), 6.06 (2H, br), 6.27 (1H, d, $J = 15.9\text{Hz}$), 6.59 (1H, dd, $J = 15.9, 7.3\text{Hz}$), 7.03-7.26 (5H, m); for **4k- γ** : 1.64 (2.1H, d, $J = 6.4\text{Hz}$), 3.68 (2.1H, s), 3.71 (2.1H, s), 3.72 (2.1H, s), 5.15 (0.7H, d, $J = 8.1\text{Hz}$), 5.52 (0.7H, m), 5.52 (0.7H, m), 6.06 (1.4H, br), 6.10 (0.7H, m), 7.03-7.26 (3.5H, m), **4k- α** /**4k- γ** = 1.4 : 1; δ_{C} (75 MHz, CDCl_3 , Me_4Si) 18.1(γ), 19.4(α), 32.6(α), 43.0(γ), 55.3(α, γ), 55.9(α, γ), 91.5(α), 91.7(γ), 93.0(α, γ), 114.7(α), 125.1(γ), 126.1(α, γ), 126.5(α, γ), 127.4(γ), 127.6(α), 127.7(γ), 128.4(α), 132.4(γ), 135.8(α), 138.6(α), 145.4(γ), 158.9(α, γ), 159.5(α, γ), 161.7(α, γ); m/z (EI) 298.1571 (M^+ $\text{C}_{19}\text{H}_{22}\text{O}_3$ requires 298.1569).

According to the same procedure, 2-methyl-3-[(*E*)-1,3-diphenylallyl]-1H-indole (**4c**)⁵, 5-bromo-3-[(*E*)-1,3-diphenylallyl]-1H-indole (**4d**)⁵, 1,3,5-trimethoxy-2-[(*E*)-1,3-diphenylallyl]benzene (**4h**)⁶, 3-[(*E*)-4-phenylbut-3-en-2-yl]-1H-indole (**4i- α**) and 3-[(*E*)-1-phenylbut-2-enyl]-1H-indole (**4i- γ**)⁷, 1-methyl-3-[(*E*)-1-phenylbut-2-enyl]-1H-indole (**4j- α**) and 1-methyl-3-[(*E*)-4-phenylbut-3-en-2-yl]-1H-indole (**4j- γ**)⁷ were synthesized.

Typical procedure for recycling experiment

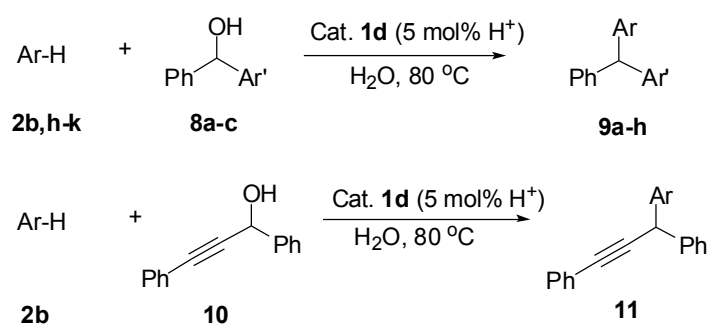


A mixture of *N*-methyl indole **2b** (63.9 μL , 0.5 mmol), **3a** (105 mg, 0.5 mmol) and **1d** (7.5 mg, 5 mol% H^+) in water (2 mL) was stirred vigorously at room temperature for 6 h. When the reaction finished by TLC detection, the reaction mixture was extracted by ethyl acetate (2 mL \times 3), then two-phase was separated further by centrifugation. The organic phase was collected using syringe, dried over anhydrous Na_2SO_4 , and evaporated under reduced pressure to give a crude product, which was purified by flash chromatograph on silica gel (eluent: petroleum ether/ethyl acetate = 12 : 1) to give a white solid **4b** (152 mg, 94% yield). The aqueous phase containing the catalyst was reused in the next cycle of aqueous reaction directly.

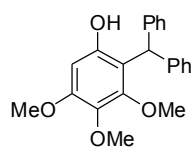
Typical procedure for Friedel-Crafts alkylation

A mixture of *N*-methyl indole **2b** (65.6 mg, 0.5 mmol), diphenylmethanol **8a** (92.1 mg, 0.5 mmol)

and **1d** (1.5 mg, 5 mol% H⁺) in water (2 mL) was stirred vigorously at 80 °C for 24h. When the reaction was finished by TLC detection, the reaction mixture was extracted by ethyl acetate (2mL×3). The organic phase was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to give crude product, which was purified by flash chromatograph on silica gel (eluent: petroleum ether/ethyl acetate = 50 : 1) to give a white solid, 3-benzhydryl-1-methyl-1*H*-indole (**9a**)⁸ (140.9 mg, yield 95%).



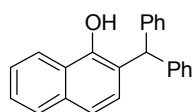
2-benzhydryl-3,4,5-trimethoxyphenol (**9d**)



White solid, m.p. 128-129 °C

ν_{max} (film)/cm⁻¹ 3429, 3059, 3024, 2938, 2840, 1604, 1460, 1413, 1357, 1229, 1196, 1124, 1078, 1034, 992, 733, 699; δ_{H} (300 MHz, CDCl₃; Me₄Si) 3.56 (3H, s), 3.75 (3H, s), 3.81 (3H, s), 4.92 (1H, s), 6.05 (1H, s), 6.20 (1H, s), 7.20-7.32 (10H, m); δ_{C} (75 MHz, CDCl₃; Me₄Si) 46.2, 55.8, 61.0, 61.0, 97.3, 116.0, 126.8, 128.8, 129.0, 136.3, 142.4, 151.0, 152.3, 153.0; m/z (EI) 350.1516 (M⁺ C₂₂H₂₂O₄ requires 350.1518).

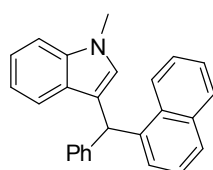
2-benzhydrylnaphthalen-1-ol (**9f**)



White or pale yellow solid, m.p.176-178°C

$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3502, 3075, 3053, 3024, 2866, 1955, 1840, 1626, 1589, 1515, 1492, 1447, 1376, 1350, 1320, 1278, 1256, 1206, 1139, 1077, 1050, 1030, 1004, 756, 735, 701, 597; δ_{H} (300 MHz, CDCl_3 ; Me_4Si) 5.16 (1H, s), 6.16 (1H, s), 6.58 (1H, d, $J = 7.8\text{Hz}$), 6.71 (1H, d, $J = 7.8\text{Hz}$), 7.08-7.47 (11H, m), 7.91 (1H, d, $J = 7.8\text{Hz}$), 8.10 (1H, d, $J = 7.8\text{Hz}$); δ_{C} (75 MHz, CDCl_3 ; Me_4Si) 52.8, 107.8, 122.3, 124.4, 124.8, 125.0, 126.4, 126.8, 127.6, 128.4, 129.7, 132.6, 133.0, 144.1, 150.4; m/z (EI) 310.1356 (M^+ $\text{C}_{23}\text{H}_{18}\text{O}$ requires 310.1358).

1-methyl-3-(naphthalen-1-yl(phenyl)methyl)-1H-indole (9h)



White solid

$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3053, 2933, 1598, 1471, 1371, 1329, 794, 740, 703; δ_{H} (300 MHz, CDCl_3 ; Me_4Si) 3.63 (3H, s), 6.30 (1H, s), 6.42 (1H, s), 6.96 (1H, t, $J = 7.5\text{Hz}$), 7.12 (1H, d, $J = 7.6\text{Hz}$), 7.19-7.46 (11H, m), 7.73 (1H, d, $J = 8.2\text{Hz}$), 7.86 (1H, d, $J = 7.6\text{Hz}$), 8.10 (1H, d, $J = 8.2\text{Hz}$); δ_{C} (75 MHz, CDCl_3 ; Me_4Si) 32.7, 44.7, 118.1, 118.9, 119.9, 121.7, 124.4, 125.3, 125.4, 126.0, 126.3, 126.9, 127.1, 128.4, 128.7, 129.2, 129.4, 132.1, 134.0, 139.8, 143.9; m/z (EI) 347.1678 (M^+ $\text{C}_{23}\text{H}_{18}\text{O}$ requires 347.1674).

According to the same procedure, the following compounds were synthesized: 3-benzhydryl-2-methyl-1H-indole (**9b**),⁹ 2-benzhydryl-1,3,5-trimethoxybenzene (**9c**),¹⁰ 1-benzhydrylnaphthalen-2-ol (**9e**),¹¹ 1-methyl-3-trityl-1H-indole (**9g**)¹² and 3-(1,3-diphenylprop-2-ynyl)-1-methyl-1H-indole (**11**)¹³.

References

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