



# Li-selective calix[4]arene with trialkyl-monoacetic acid groups: effect of three alkyl branches and *t*-octyl groups at *p*-position on selectivity for Li extraction

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## Abstract

Trialkyl-monoacetic acid derivatives of *p*-*t*-octylcalix[4]arene and calix[4]arene were prepared to investigate the effect of the alkyl branches attached to the phenoxy oxygen atoms and the *p*-position on the selective extraction of Li<sup>+</sup> over Na<sup>+</sup>. Alkyl branches on the phenoxy oxygen atoms remarkably affected the Li<sup>+</sup> selectivity, whereas those at the *p*-position had less effect. The former can contribute to excluding Na<sup>+</sup> extraction while enabling Li<sup>+</sup> extraction. Optimal selection of the alkyl branch improves the Li<sup>+</sup> selectivity of calix[4]arene. However, sterically-hindered *p*-*t*-octylcalix[4]arene with three 2-ethylbutyl branches exhibited opposite selectivity.

**Keywords** Calix[4]arene · Lithium selectivity · Ion discrimination · Extraction · Separation · Alkyl branches

## Introduction

Li is employed in lithium ion batteries for electric vehicles [1], ceramics and glass, greases, pharmaceuticals, and polymers [2]. From comprehensive analysis of global lithium resources and projection of the global lithium demand spanning the years 2010–2100, a sudden surge in the demand is anticipated due to electric vehicles [1, 3]. The demand for LIBs is estimated to reach 2.2 million tonnes by 2030 [4]. The recycling rate of Li is currently less than 1% [5]; however, the price of lithium has continued to appreciate strongly each year; thus, methods of increasing the Li recycling rate have been reviewed [6].

Various  $\beta$ -diketone reagents for the selective recovery of Li were also reported in a review article [7]. The lithium ion is monovalent, small, and highly hydrated. Thus, size-discrimination using macrocyclic compounds with small coordination sites has been employed for Li recovery. Since the discovery of crown ethers by Pedersen [8] and the correlation between the cavity size of these molecules and the ionic diameters by Frensdorff [9], various derivatives have

been synthesized and their potential as representative macrocyclic host compounds for molecules and ions has been investigated. A number of books and review articles has correspondingly been published [10–12]. Katsuta et al. prepared arene trinuclear ruthenium complexes bridged by 2,3-pyridinediolate as a macrocyclic host compound for Li<sup>+</sup> [13, 14], which exhibited high selectivity for Li<sup>+</sup> over Na<sup>+</sup>.

Calixarenes are macrocyclic compounds prepared in a single step by the condensation reaction of the corresponding phenols and formaldehyde [15]. Various derivatives have been prepared and their ion-discrimination ability has been investigated; related books and review articles have been also published [16–20]. Various calixarene derivatives exhibit specific structural effects for metal extraction, as demonstrated in our studies [21–23]. Among calixarene derivatives, calix[4]arene derivatives have been the main focus of our research as they provide a narrow coordination site and rigid structure. Calix[4]arene was originally prepared by using Na<sup>+</sup> as a templating ion. Most calix[4]arene derivatives exhibit selectivity for Na<sup>+</sup> over other alkali metal ions owing to the size-discriminating effect. However, gradual substitution of the carboxyl groups of calix[4]arene tetraacetic acid with coordinative-inert propyl group(s) changes the selectivity for alkali metal ions from larger to smaller ions, demonstrating an allosteric effect involving co-extraction of the second ion with the first (Na<sup>+</sup>). The tripropyl-monoacetic acid derivative exhibits Li<sup>+</sup> selectivity [24,

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[25]. It was found that slight change of substituents resulted in drastic change of metal selectivity; however, the effects of alkyl groups attached on phenoxy oxygen atoms and at the *p*-position of calix[4]arene have not yet been investigated.

Herein, we report the synthesis of trialkyl-monoacetic acid derivatives of calix[4]arene and investigate the effects of alkyl groups attached to the phenoxy oxygen atoms and at the *p*-position of calix[4]arene on the extraction of alkali metal ions.

## Experimental

### Reagents

All reagents were of analytical grade and were supplied by Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used without further purification. 25,26,27-Tripropoxy-28-carboxymethoxy-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene **4Pr** was obtained in a manner similar to that reported in a previous paper [25]. The extraction reagents, (trialkyl-monoacetic acid derivatives of *p*-*t*-octylcalix[4]arene and calix[4]arene with other alkyl branches) were synthesized by modifying this method, aiming to confirm the effects of the three alkyl branches at the lower rim and of the *t*-octyl groups at the upper rim of the calixarene on selective Li extraction.

The chemical structures of the extraction reagents synthesized herein are shown in Fig. 1. The schemes for synthesizing the extraction reagents are shown in Figs. 2 and 3. 5,11,17,23-Tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene-25,26,27,28-tetrol (**1**) [26] and calix[4]arene-25,26,27,28-tetrol (**4**) [27] were synthesized by modified literature methods.

### Synthesis of trialkyl-monohydroxyl derivatives of *t*-octylcalix[4]arene (**2**)

Under a nitrogen stream, **1** and alkali earth hydroxide octahydrate were added to dry dimethylformamide (DMF) and the mixture was stirred. Thereafter, an alkyl halogenide was added to the mixture and stirred at 30 °C for the desired period. After filtration and removal of the solvent in vacuo, the desired compound was extracted from the residue using chloroform. The solution was washed 3 times with 1 M ( $M = \text{mol dm}^{-3}$ ) hydrochloric acid and thrice with distilled water. After drying over anhydrous magnesium sulfate, the solution was filtered, and the solvent then removed in vacuo; the desired compound was recrystallized from acetonitrile to yield a white powder. The detailed conditions of the synthesis are listed in Table 1. The  $^1\text{H-NMR}$  and FT-IR spectra of **2Oct**, **2Bz**, and **2<sup>2</sup>EtBu** are shown in Fig. S1a–c, respectively. Based on the  $^1\text{H-NMR}$  spectra, all derivatives adopted the cone conformation, in which three *O*-alkyl and a carboxy groups were oriented in the same direction.

### 25,26,27-Trioctoxy-28-hydroxy-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (**2Oct**)

TLC ( $\text{SiO}_2$ , chloroform,  $R_f = 0.91$ ),  $^1\text{H-NMR}$  (300 MHz,  $\delta$ ,  $\text{CDCl}_3$ , TMS, 25 °C), 0.51 (18H, s,  $2\text{C}(\text{CH}_3)_3$ ), 0.76 (18H, s,  $2\text{C}(\text{CH}_3)_3$ ), 0.88 (12H, s,  $2\text{C}(\text{CH}_3)_2$ ), 0.90 (9H, t,  $3\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ), 1.2–1.4 (30H, t,  $3\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ), 1.35 (12H, s,  $\text{C}(\text{CH}_3)_2$ ), 1.36 (4H, s,  $2\text{CCH}_2\text{C}$ ), 1.74 (4H, s,  $2\text{CCH}_2\text{C}$ ), 1.89 (4H, quint,  $2\text{CH}_2\text{CH}_2(\text{CH}_2)_5$ ), 2.27 (2H, quint,  $2\text{CH}_2\text{CH}_2(\text{CH}_2)_5$ ), 3.15 (2H, d,  $2\text{exo-CH}_2$ ), 3.21 (2H, d,  $2\text{exo-CH}_2$ ), 3.75 (4H, t,  $2\text{CH}_2\text{CH}_2(\text{CH}_2)_5$ ), 3.91 (2H, t,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_5$ ), 4.34 (2H, d,  $2\text{endo-CH}_2$ ), 4.39 (2H, d,  $2\text{endo-CH}_2$ ), 5.74 (1H, s, OH), 6.56 (4H, s, 4ArH), 7.00

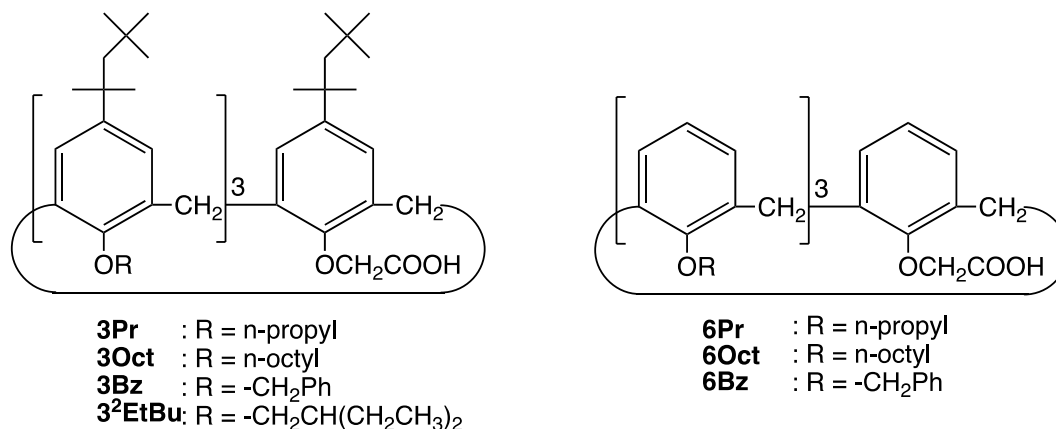
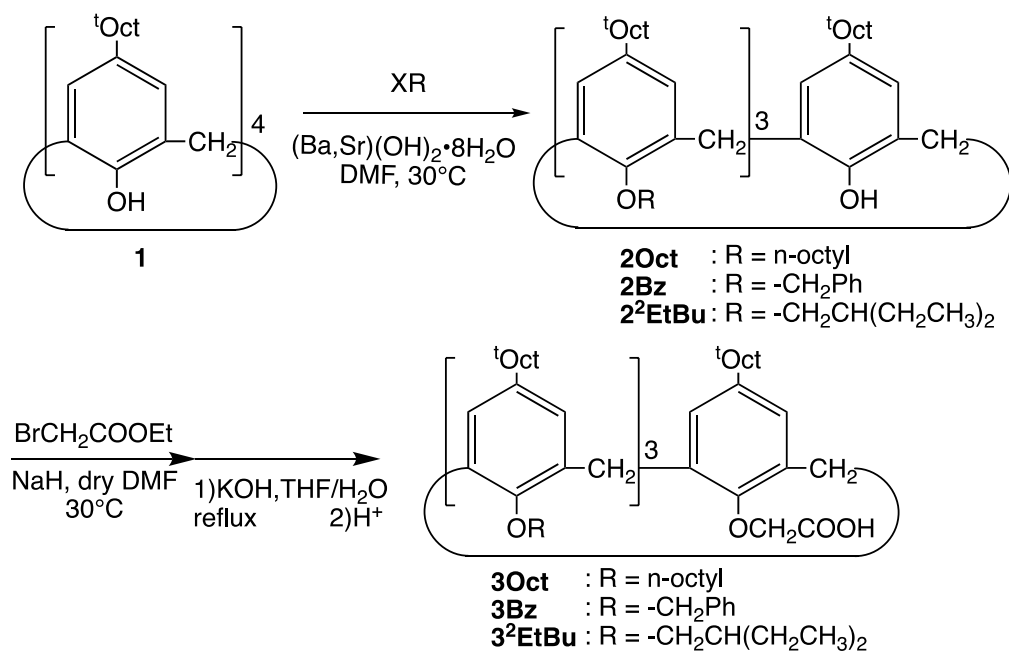
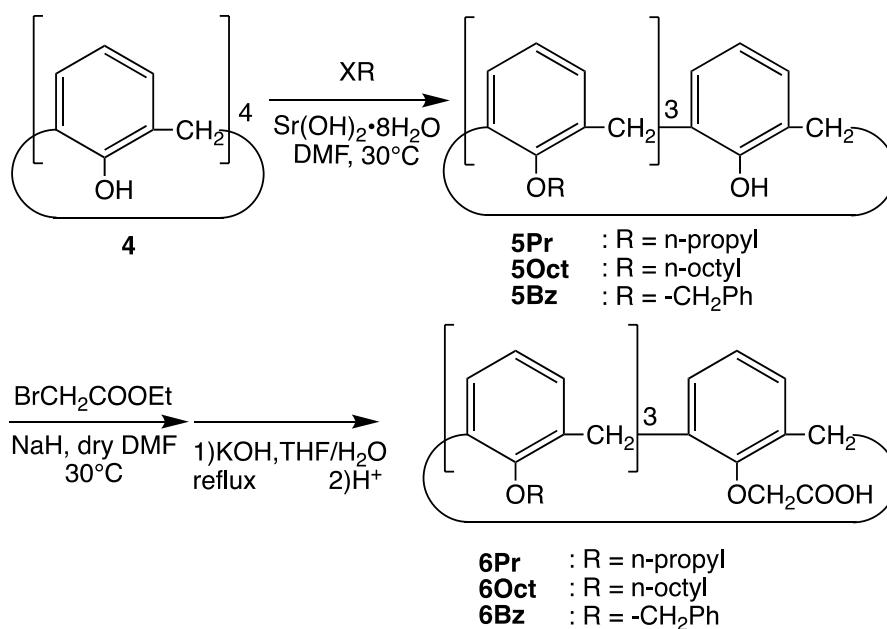


Fig. 1 Chemical structures of the extraction reagents



**Fig. 2** Schematic of synthesis of trialkyl-monoacetic acid derivatives of *p*-*t*-octylcalix[4]arene

**Fig. 3** Schematic of synthesis of trialkyl-monoacetic acid derivatives of calix[4]arene



**Table 1** Conditions for synthesis of trialkyl-monoacetic acid derivatives of *p*-*t*-octylcalix[4]arene

1/g (mmol)	Base/g (mmol)	Reactant/g (mmol)	DMF/cm <sup>3</sup>	Temp/°C	Time/h	Product/Yield g (%)
5.00 (5.73)	Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O 5.73 (18.2)	BrOct 6.43 (30.3)	150	30	24	<b>2Oct</b> /5.58 (80.6)
5.01 (5.74)	Sr(OH) <sub>2</sub> ·8H <sub>2</sub> O 6.17 (19.6)	BrBzl 3.98 (23.3)	100	30	1	<b>2Bz</b> /6.04 (92.1)
5.01 (5.74)	Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O 6.61 (21.0)	Br <sup>2</sup> EtBu 19.62 (119)	100	60	96	<b>2<sup>2</sup>EtBu</b> /5.50 (85.2)

(2H, s, 2ArH), 7.06 (2H, s, 2ArH). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3543 (sharp peak;  $\nu_{\text{FreeO-H}}$ ), 3570–3260 (low-intensity peak;  $\nu_{\text{O-H}}$ ), 2955 ( $\nu_{\text{C-H}}$ ), 1470 ( $\nu_{\text{C=C}}$ ), 1207 ( $\nu_{\text{C-O}}$ ).

### 25,26,27-Tribenzoyloxy-28-hydroxy-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl) calix[4]arene (2Bz)

TLC ( $\text{SiO}_2$ , chloroform,  $R_f=0.91$ ),  $^1\text{H-NMR}$  (300 MHz,  $\delta$ ,  $\text{CDCl}_3$ , TMS, 25 °C), 0.39 (18H, s,  $2\text{C}(\text{CH}_3)_3$ ), 0.75 (18H, s,  $2\text{C}(\text{CH}_3)_3$ ), 0.96 (12H, s,  $2\text{C}(\text{CH}_3)_2$ ), 1.31 (12H, s,  $2\text{C}(\text{CH}_3)_2$ ), 1.36 (4H, s,  $2\text{CCH}_2\text{C}$ ), 1.68 (4H, s,  $2\text{CCH}_2\text{C}$ ), 2.89 (2H, d,  $2\text{exo-CH}_2$ ), 3.01 (2H, d,  $2\text{exo-CH}_2$ ), 4.06 (2H, d,  $2\text{endo-CH}_2$ ), 4.17 (2H, d,  $2\text{endo-CH}_2$ ), 4.64 (4H, s,  $2\text{CH}_2\text{Ph}$ ), 4.93 (2H, s,  $\text{CH}_2\text{Ph}$ ), 6.60 (2H, s, 2ArH), 6.66 (2H, s, 2ArH), 6.74 (1H, s, OH), 6.94 (2H, s, 2ArH), 7.01 (2H, s, 2ArH), 7.24 (15H, m, 3Bz-ArH). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3404 (broad peak;  $\nu_{\text{FreeO-H}}$ ), 3570–3260 (low-intensity peak;  $\nu_{\text{O-H}}$ ), 2955 ( $\nu_{\text{C-H}}$ ), 1476 ( $\nu_{\text{C=C}}$ ), 1209 ( $\nu_{\text{C-O}}$ ).

### 25,26,27-Tris(2-ethylbutyloxy)-28-hydroxy-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl) calix[4]arene (2<sup>2</sup>EtBu)

TLC ( $\text{SiO}_2$ , chloroform,  $R_f=0.91$ ),  $^1\text{H-NMR}$  (300 MHz,  $\delta$ ,  $\text{CDCl}_3$ , TMS, 25 °C), 0.50 (18H, s,  $2\text{C}(\text{CH}_3)_3$ ), 0.73 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 0.79 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 0.89 (12H, s,  $\text{C}(\text{CH}_3)_2$ ), 0.91 (18H, t,  $6\text{CH}_2\text{CH}_3$ ), 1.35 (12H + 4H, s + s,  $2\text{C}(\text{CH}_3)_2 + 2\text{CCH}_2\text{C}$ ), 1.46 (8H, quint,  $4\text{CH}_2\text{CH}_3$ ), 1.63 (4H, quint,  $2\text{CH}_2\text{CH}_3$ ), 1.70 (2H, s,  $\text{CCH}_2\text{C}$ ), 1.74 (2H, s,  $\text{CCH}_2\text{C}$ ), 1.79 (2H, sep,  $2\text{CH}_2\text{CH}(\text{Et})\text{CH}_2$ ), 2.10 (1H, sep,  $\text{CH}_2\text{CH}(\text{Et})\text{CH}_2$ ), 3.21 (4H, d,  $4\text{exo-CH}_2$ ), 3.54 (2H, d,  $\text{OCH}_2\text{CH}$ ), 3.72 (2H, d,  $\text{OCH}_2\text{CH}$ ), 4.01 (2H, d,  $\text{OCH}_2\text{CH}$ ), 4.34 (2H, d,  $2\text{endo-CH}_2$ ), 4.47 (2H, d,  $2\text{endo-CH}_2$ ), 5.87 (1H, s, OH), 6.52 (2H, s, 2ArH), 6.62 (2H, s, 2ArH), 7.01

(2H, s, 2ArH), 7.06 (2H, s, 2ArH). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3543 (sharp peak;  $\nu_{\text{FreeO-H}}$ ), 3570–3260 (low-intensity peak;  $\nu_{\text{O-H}}$ ), 2955 ( $\nu_{\text{C-H}}$ ), 1475 ( $\nu_{\text{C=C}}$ ), 1205 ( $\nu_{\text{C-O}}$ ).

### Synthesis of trialkyl-monoacetic acid derivatives of t-octylcalix[4]arene (3)

Under a nitrogen stream, trialkyl-monohydroxy derivatives of *p*-t-octylcalix[4]arene (2) were dissolved by immersion in THF for 15 min, after which sodium hydride was added to the mixture and stirred for 15 min. Ethyl bromoacetate was added and the mixture was stirred at room temperature for 24 h. After monitoring by TLC, the excess sodium hydride was deactivated with ethanol in an ice-bath; the ethanol was then removed in vacuo. The desired compound was extracted with chloroform. The organic layer was washed 3 times with 1 M hydrochloric acid and thrice with distilled water. After drying over anhydrous magnesium sulfate, the solution was filtered, and the solvent was removed in vacuo. Intermittently, sodium hydroxide, THF, and distilled water were added to the residue and the mixture was stirred at the desired temperature for a certain period. After monitoring by TLC, the solvent was removed in vacuo and chloroform was added to extract the desired compound from the residue. The solution was washed once with 6 M, twice with 1 M hydrochloric acid, and 3 times with distilled water. After drying over anhydrous magnesium sulfate, the solution was filtered, and the solvent was removed in vacuo. The desired compound was recrystallized from acetonitrile to yield a white powder. The detailed conditions of the synthesis are listed in Tables 2 and 3. The  $^1\text{H-NMR}$  and FT-IR spectra of **3Oct**, **3Bz**, and **3<sup>2</sup>EtBu** are shown in Fig. S2a–c, respectively. All derivatives adopted the cone conformation, as indicated by the  $^1\text{H-NMR}$  spectra.

**Table 2** Conditions for synthesis of trialkyl-monoacetic acid derivatives of *p*-t-octylcalix[4]arene. (up to trialkyl-monoester derivatives)

Calixarene 2/g(mmol)	NaH/g (mmol)	BrCH <sub>2</sub> COOEt/g (mmol)	THF/cm <sup>3</sup>	temperature/°C	time /h
<b>2Oct</b> 8.97 (4.13)	4.93 (123)	20.0 (120)	300	25	24
<b>2Bz</b> 4.00 (5.76)	3.05 (76.3)	11.7 (70.1)	120	25	24
<b>2<sup>2</sup>EtBu</b> 3.00 (2.66)	0.95 (23.8)	3.83 (22.9)	60	25	24

**Table 3** Conditions for synthesis of trialkyl-monoacetic acid derivatives

Calixarene 2	NaOH/g(mmol)	H <sub>2</sub> O/g(mmol)	THF/cm <sup>3</sup>	Temp/°C	Time/h	Product/Yield g (%)
<b>2Oct</b>	9.48 (237)	100 (5.56)	300	25	24	<b>3Oct</b> /10.8 (111*)
<b>2Bz</b>	4.62 (116)	50.0 (2.78)	150	25	24	<b>3Bz</b> /4.62 (106*)
<b>2<sup>2</sup>EtBu</b>	10.7 (267)	100 (5.56)	100	60	120	<b>3<sup>2</sup>EtBu</b> /3.10 (98.3)

Contained mineral oil in NaH

### 25,26,27-Trioctoxyoxy-28-carboxymethoxy-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl) calix[4]arene (3Oct)

TLC (SiO<sub>2</sub>, chloroform:methanol = 10:1,  $R_f$  = 0.77), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 0.43 (18H, s, 2C(CH<sub>3</sub>)<sub>3</sub>), 0.76 (18H, s, 2C(CH<sub>3</sub>)<sub>3</sub>), 0.86 (9H, t, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 0.93 (12H, s, 2C(CH<sub>3</sub>)<sub>2</sub>), 1.28 (30H, m, 3(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.33 (4H, s, 2CCH<sub>2</sub>C), 1.37 (12H, s, 2C(CH<sub>3</sub>)<sub>2</sub>), 1.70 (4H, s, 2CCH<sub>2</sub>C), 1.83 (6H, quint, 3CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 3.16 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.21 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.75 (4H, t, OCH<sub>2</sub>CH<sub>2</sub>), 4.11 (2H, t, OCH<sub>2</sub>CH<sub>2</sub>), 4.22 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.47 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.64 (2H, s, CH<sub>2</sub>-COOH), 6.55 (2H, s, 2ArH), 6.66 (2H, s, 2ArH), 7.08 (2H, s, 2ArH), 7.10 (2H, s, 2ArH), 11.35 (1H, s, COOH). FT-IR (KBr, cm<sup>-1</sup>): peaks at 3543 ( $\nu_{\text{FreeO-H}}$ ) and 3570–3260 ( $\nu_{\text{O-H}}$ ) disappeared, 3181 (low-intensity, broad peak;  $\nu_{\text{FreeCOO-H}}$ ), 2955 ( $\nu_{\text{C-H}}$ ), 1759 ( $\nu_{\text{C=O}}$ ), (1477 ( $\nu_{\text{C=C}}$ ), 1204 ( $\nu_{\text{C-O}}$ ).

### 25,26,27-Tribenzyloxy-28-carboxymethoxy-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl) calix[4]arene (3Bz)

TLC (SiO<sub>2</sub>, chloroform:methanol = 10:1,  $R_f$  = 0.63), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 0.41 (18H, s, 2C(CH<sub>3</sub>)<sub>3</sub>), 0.72 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.81 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.90 (12H, s, 2C(CH<sub>3</sub>)<sub>2</sub>), 1.26 (12H, s, 2C(CH<sub>3</sub>)<sub>2</sub>), 1.33 (4H, s, 2CCH<sub>2</sub>C), 1.62 (2H, s, CCH<sub>2</sub>C), 1.73 (2H, s, CCH<sub>2</sub>C), 2.62 (2H, d, 2 $exo$ -CH<sub>2</sub>), 2.78 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.68 (2H, d, 2 $endo$ -CH<sub>2</sub>), 3.90 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.43 (2H, s, CH<sub>2</sub>-COOH), 4.53 (2H, s, CH<sub>2</sub>Ph), 5.04 (2H, s, CH<sub>2</sub>Ph), 5.07 (2H, s, CH<sub>2</sub>Ph), 6.47 (2H, s, 2ArH), 6.67 (2H, s, 2ArH), 6.92 (2H, s, 2ArH), 7.03 (2H, s, 2ArH), 7.1–7.4 (15H, m, CH<sub>2</sub>Ph), 11.65 (1H, s, COOH). FT-IR (KBr, cm<sup>-1</sup>): peaks at 3543 ( $\nu_{\text{FreeO-H}}$ ) and 3570–3260 ( $\nu_{\text{O-H}}$ ) disappeared, 3379 (low-intensity, broad peak;  $\nu_{\text{FreeCOO-H}}$ ), 2955 ( $\nu_{\text{C-H}}$ ), 1759 ( $\nu_{\text{C=O}}$ ), 1477 ( $\nu_{\text{C=C}}$ ), 1204 ( $\nu_{\text{C-O}}$ ).

### 25,26,27-Tris(2-ethylbutyloxy)-28-carboxymethoxy-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl) calix[4]arene (3<sup>2</sup>EtBu)

TLC (SiO<sub>2</sub>, chloroform:methanol = 10:1,  $R_f$  = 0.77), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 0.52 (18H, s, 2C(CH<sub>3</sub>)<sub>3</sub>), 0.73 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.80 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.86 (12H, s, 2C(CH<sub>3</sub>)<sub>2</sub>), 0.91 (18H, t, 3CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.33 (4H, s, 2CCH<sub>2</sub>C), 1.38 (12H, s, 2C(CH<sub>3</sub>)<sub>2</sub>), 1.3–1.6 (12H, m, 3CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.72 (3H, sept, 3 CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.74 (4H, s, CCH<sub>2</sub>C), 3.21 (4H, d, 2 $exo$ -CH<sub>2</sub>), 3.52 (2H, d, CH<sub>2</sub>CH), 3.71 (2H, d, CH<sub>2</sub>CH), 4.01 (2H, d, CH<sub>2</sub>CH), 4.25 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.44 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.46 (2H, s, CH<sub>2</sub>-COOH), 6.47 (2H, s, 2ArH), 6.63 (2H, s, 2ArH), 7.08 (2H, s, 2ArH), 7.11 (2H, s, 2ArH), 10.82 (1H, s, COOH). FT-IR (KBr, cm<sup>-1</sup>): peaks at 3543 ( $\nu_{\text{FreeO-H}}$ ) and 3570–3260 ( $\nu_{\text{O-H}}$ ) disappeared, 3426 ( $\nu_{\text{COO-H}}$ ), 3424 (low-intensity, broad peak;  $\nu_{\text{FreeCOO-H}}$ ), 2955 ( $\nu_{\text{C-H}}$ ), 1764 ( $\nu_{\text{C=O}}$ ), 1477 ( $\nu_{\text{C=C}}$ ), 1204 ( $\nu_{\text{C-O}}$ ).

### Synthesis of trialkyl-monohydroxy derivatives of calix[4]arene (5)

Only propyl, octyl, and benzyl groups were selected as the introduced alkyl branches, because 2-ethylbutyl-branched *p*-t-octylcalixarene exhibited selectivity for sodium ion over the lithium ion.

Under a nitrogen stream, **4** and strontium hydroxide octahydrate were added to dry DMF, and the mixture was stirred. Thereafter, alkyl halogenide was added to the mixture and stirred at 30 °C for the desired period. The remaining procedures were the same as those for **2**. The detailed synthesis conditions are listed in Table 4. The <sup>1</sup>H-NMR and FT-IR spectra of **5Oct**, **5Bz**, and **5<sup>2</sup>EtBu** are shown in Fig. S3a–c, respectively. All derivatives adopted the cone conformation, as confirmed by the <sup>1</sup>H-NMR spectra.

**Table 4** Conditions for synthesis of trialkyl-monohydroxy derivatives of calix[4]arene

Calixarene <b>4</b> /g (mmol)	Base/g (mmol)	Reactant/g (mmol)	DMF/cm <sup>3</sup>	Temp/°C	Time/h	Product/yield g (%)
<b>4</b> 2.16 (5.09)	Sr(OH) <sub>2</sub> ·8H <sub>2</sub> O 3.94 (15.1)	InPr 25.4 (149)	180	30	21	<b>5Pr</b> /1.81 (64.6)
<b>4</b> 5.01 (11.8)	Sr(OH) <sub>2</sub> ·8H <sub>2</sub> O 9.44 (35.5)	BrOct 36.8 (190)	150	25–35	24	<b>5Oct</b> /9.40 (105*)
<b>4</b> 0.30 (0.707)	Sr(OH) <sub>2</sub> ·8H <sub>2</sub> O 0.567 (2.13)	BrBzl 0.491 (2.87)	10	30	24	<b>5Bz</b> /0.24 (48.9)

\*Contained minerals

**25,26,27-Tripropoxy-28-hydroxy-calix[4]arene (5Pr)**

TLC (SiO<sub>2</sub>, chloroform,  $R_f$  = 0.90), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 0.92 (3H, t, CH<sub>2</sub>CH<sub>3</sub>), 1.11 (6H, t, 2CH<sub>2</sub>CH<sub>3</sub>), 1.89 (4H, sext, 2CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.27 (2H, sext, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.21 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.29 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.74 (4H, t, 2CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.84 (2H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.38 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.42 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.68 (1H, s, OH), 6.37 (6H, m, 6ArH), 6.77 (1H, t, ArH), 6.97 (1H, t, ArH), 7.09 (2H, d, ArH), 7.17 (2H, d, ArH). FT-IR (KBr, cm<sup>-1</sup>): 3545 (sharp peak;  $\nu_{FreeO-H}$ ), 3655–2955 (low-intensity peak;  $\nu_{O-H}$ ), 2963 ( $\nu_{C-H}$ ), 1459 ( $\nu_{C=C}$ ), 1200 ( $\nu_{C-O}$ ), 762 ( $\sigma_{\angle HCC(Ar)}$ ).

**25,26,27-Trioctoxy-28-hydroxy-calix[4]arene (5Oct)**

TLC (SiO<sub>2</sub>, chloroform,  $R_f$  = 0.90), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 0.88 (9H, t, 3CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.50 (30H, m, 3CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.89 (4H, quint, 2CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>), 2.20 (2H, quint, 2CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>), 3.20 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.28 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.78 (4H, t, 2OCH<sub>2</sub>), 3.90 (2H, t, OCH<sub>2</sub>), 4.37 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.41 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.72 (1H, s, OH), 6.37 (6H, m, 6ArH), 6.77 (1H, t, ArH), 6.96 (1H, t, ArH), 7.09 (2H, d, ArH), 7.16 (2H, d, ArH). FT-IR (KBr, cm<sup>-1</sup>): 3545 (sharp peak;  $\nu_{FreeO-H}$ ), 3655–2955 (low-intensity peak;  $\nu_{O-H}$ ), 2926 ( $\nu_{C-H}$ ), 1458 ( $\nu_{C=C}$ ), 1199 ( $\nu_{C-O}$ ), 761 ( $\sigma_{\angle HCC(Ar)}$ ).

**25,26,27-Tribenzyloxy-28-hydroxy-calix[4]arene (5Bz)**

TLC (SiO<sub>2</sub>, chloroform,  $R_f$  = 0.88), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 2.96 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.14 (2H, d, 2 $exo$ -CH<sub>2</sub>), 4.12 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.34 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.73 (4H, s + s, 2CH<sub>2</sub>Ph), 5.05 (2H, s, CH<sub>2</sub>Ph), 5.29

(1H, s, OH), 6.41 (6H, m, 6ArH), 6.75 (1H, t, 1ArH), 6.89 (1H, t, ArH), 7.05 (2H, d, 2ArH), 7.11 (2H, d, 2ArH), 7.2–7.4 (15H, m, 3Bz-ArH). FT-IR (KBr, cm<sup>-1</sup>): 3545 (broad peak;  $\nu_{O-H}$ ), 2963 ( $\nu_{C-H}$ ), 1459 ( $\nu_{C=C}$ ), 1200 ( $\nu_{C-O}$ ), 762 ( $\sigma_{\angle HCC(Ar)}$ ).

**Synthesis of trialkyl-monoacetic acid derivatives of calix[4]arene (6)**

Under a nitrogen stream, trialkyl-monoalcohol derivatives of calix[4]arene (**5**) were dissolved by immersion in THF for 15 min, after which sodium hydride was added to the mixture and stirred for 15 min. Ethyl bromoacetate was added and the mixture was stirred at room temperature for 24 h. The rest procedures were same with those for **3**. The detailed synthetic condition is listed in Tables 5 and 6. The <sup>1</sup>H-NMR and FT-IR spectra of **6Oct**, **6Bz**, and **6<sup>2</sup>EtBu** are shown in Fig. S4a–c, respectively. All derivatives were confirmed to take cone conformation by <sup>1</sup>H-NMR spectra.

**25,26,27-Tripropoxy-28-carboxymethoxy-calix[4]arene (6Pr)**

TLC (SiO<sub>2</sub>, chloroform:methanol = 10:1,  $R_f$  = 0.57), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 0.86 (3H, t, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.02 (6H, t, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.90 (6H, sext, 3CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.19 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.30 (2H, d, 2 $exo$ -CH<sub>2</sub>), 3.77 (4H, t, 2OCH<sub>2</sub>), 3.98 (2H, t, 2OCH<sub>2</sub>), 4.33 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.46 (2H, d, 2 $endo$ -CH<sub>2</sub>), 4.88 (2H, s, CH<sub>2</sub>-COOH), 6.2–6.4 (6H, m, 6ArH), 6.96 (1H, t, ArH), 6.99 (1H, t, ArH), 7.15 (4H, d, 2ArH), 11.35 (1H, s, COOH). FT-IR (KBr, cm<sup>-1</sup>): peak at 3543 ( $\nu_{FreeO-H}$ )

**Table 5** Conditions for synthesis of trialkyl-monoalcohol derivatives of calix[4]arene. (up to trialkyl-monoester derivatives for **6Oct** and **6Bz**)

Calixarene <b>5</b> /g (mmol)	NaH/g (mmol)	BrCH <sub>2</sub> COOEt/g (mmol)	THF/cm <sup>3</sup>	Temperature/°C	Time/h
<b>5Pr</b> 0.31 (0.56)	0.28 (12.0)	0.80 (4.80)	30	25	13
<b>5Oct</b> 8.97 (11.8)	4.93 (123)	20.0 (120)	300	25	24
<b>5Bz</b> 4.00 (5.76)	3.05 (76.3)	11.71 (70.1)	120	25	24

**Table 6** Conditions for synthesis of trialkyl-monoalcohol derivatives

Calixarene <b>5</b>	NaOH/g (mmol)	H <sub>2</sub> O/g (mmol)	THF/cm <sup>3</sup>	Temp/°C	Time/h	Product/yield g (%)
<b>5Pr</b>	–	–	–	–	–	<b>6Pr</b> /0.13 (38.0)
<b>5Oct</b>	9.48 (237)	100 (5.56)	300	25	24	<b>6Oct</b> /10.8 (111*)
<b>5Bz</b>	4.62 (116)	50.0 (2.78)	150	25	24	<b>6Bz</b> /4.62 (106**)

\***5Pr** was obtained without hydrolysis

\*\*Contained mineral oil in NaH

disappeared, 3197 (broad peak;  $\nu_{\text{FreeCOO-H}}$ ), 2961 ( $\nu_{\text{C-H}}$ ), 1763 ( $\nu_{\text{C=O}}$ ), 1460 ( $\nu_{\text{C=C}}$ ), 1200 ( $\nu_{\text{C-O}}$ ), 762 ( $\sigma_{\text{HCC(Ar)}}$ ).

### 25,26,27-Trioctoxy-28-carboxymethoxy-calix[4]arene (6Oct)

TLC (SiO<sub>2</sub>, chloroform:methanol = 10:1,  $R_f$  = 0.92), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 0.86 (9H, t, 3(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.29 (30H, m, 3(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.87 (6H, quint, 3CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 3.18 (2H, d, 2<sub>exo</sub>-CH<sub>2</sub>), 3.30 (2H, d, 2<sub>exo</sub>-CH<sub>2</sub>), 3.79 (4H, t, OCH<sub>2</sub>), 4.01 (2H, t, OCH<sub>2</sub>), 4.32 (2H, d, 2<sub>endo</sub>-CH<sub>2</sub>), 4.44 (2H, d, 2<sub>endo</sub>-CH<sub>2</sub>), 4.88 (2H, s, CH<sub>2</sub>-COOH), 6.20 (2H, t, 2ArH), 6.28 (4H, d, 4ArH), 6.97 (2H, t, 2ArH), 7.15 (4H, d, 4ArH), 11.63 (1H, s, COOH). FT-IR (KBr, cm<sup>-1</sup>): peak at 3543 ( $\nu_{\text{FreeO-H}}$ ) disappeared, 3237 ( $\nu_{\text{FreeCOO-H}}$ ), 2961 ( $\nu_{\text{C-H}}$ ), 1762 ( $\nu_{\text{C=O}}$ ), 1459 ( $\nu_{\text{C=C}}$ ), 1198 ( $\nu_{\text{C-O}}$ ), 760 ( $\sigma_{\text{HCC(Ar)}}$ ).

### 25,26,27-Tribenzyloxy-28-carboxymethoxy-calix[4]arene (6Bz)

TLC (SiO<sub>2</sub>, chloroform:methanol = 10:1,  $R_f$  = 0.75), <sup>1</sup>H-NMR (300 MHz,  $\delta$ , CDCl<sub>3</sub>, TMS, 25 °C), 2.82 (2H, d, 2<sub>exo</sub>-CH<sub>2</sub>), 2.83 (2H, d, 2<sub>exo</sub>-CH<sub>2</sub>), 3.93 (2H, d, 2<sub>endo</sub>-CH<sub>2</sub>), 3.97 (2H, d, 2<sub>endo</sub>-CH<sub>2</sub>), 4.65 (2H, s, CH<sub>2</sub>Ph), 4.67 (2H, s, CH<sub>2</sub>-COOH), 4.96 (2H, s, CH<sub>2</sub>Ph), 5.01 (2H, s, CH<sub>2</sub>Ph), 6.26 (2H, t, 2ArH), 6.36 (4H, d, 4ArH), 6.90 (2H, t, 2ArH), 7.01 (4H, d, 4ArH), 7.1–7.4 (15H, m, 3CH<sub>2</sub>Ph), 11.80 (1H, s, COOH). FT-IR (KBr, cm<sup>-1</sup>): peak at 3543 ( $\nu_{\text{FreeO-H}}$ ) disappeared, 3160 (broad peak;  $\nu_{\text{FreeCOO-H}}$ ), 2961 ( $\nu_{\text{C-H}}$ ), 1755 ( $\nu_{\text{C=O}}$ ), 1460 ( $\nu_{\text{C=C}}$ ), 1192 ( $\nu_{\text{C-O}}$ ), 754 ( $\sigma_{\text{HCC(Ar)}}$ ).

### Distribution study

The extraction study was performed using a previously described procedure [28]. The organic solution was prepared by dissolving each trialkyl-monoacetic acid reagent, **4**, in chloroform to a concentration of 5 mM. The aqueous solution was prepared by dissolving each alkali metal chloride in 0.1 M HEPES buffer solution (*N*-(2-hydroxyethyl)piperazin-*N'*-(2-ethanesulfonic acid)). The pH of this solution was adjusted by adding 1 M ammonia solution. Equal volumes (5 cm<sup>3</sup>) of both the organic and aqueous phases, were mixed and shaken (150 rpm) for an adequate time at 30 °C. After phase separation, the pH after reaching equilibrium and the

metal concentrations before and after reaching equilibrium were measured using a pH meter (HM-30R, TOA-DKK, Tokyo) and atomic absorption spectrophotometer (abbreviated as AAS, Shimadzu Instruments AA-6800). The pH meter was pre-calibrated by using pH 4.01, 6.86, and 9.18 standard solutions.

The extraction percentage (%*E*) and distribution ratio (*D*) were respectively calculated using Eqs. (1 and 2).

$$\%E = \frac{C_i - C_e}{C_i} \times 100, \quad (1)$$

$$D = \frac{C_i - C_e}{C_e}, \quad (2)$$

where  $C_i$  and  $C_e$  represent the initial and equilibrium metal concentrations in the aqueous phase, respectively.

## Results and discussion

### Synthesis of trialkyl-monoacetic acid derivatives

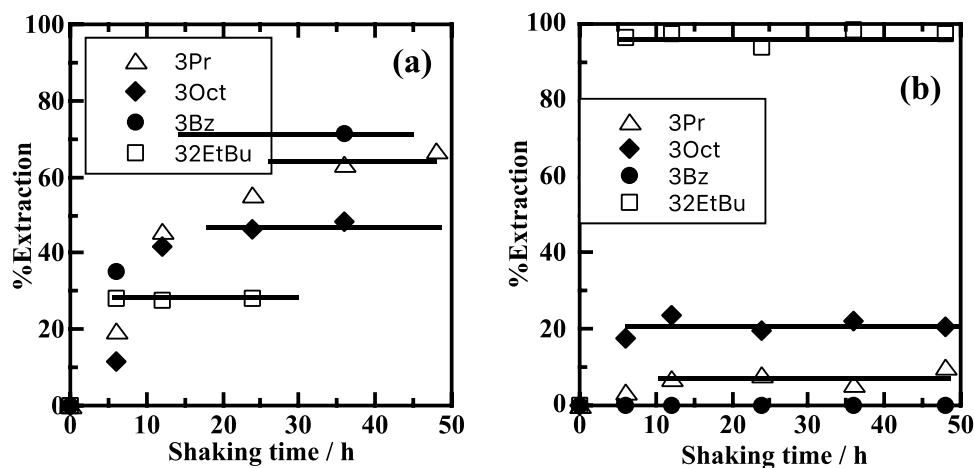
Tri-substitution of the alkyl branches on the phenol groups was successfully carried out, and was facilitated by using strontium salts instead of barium salts as the templating ion. All spectral data support the successful preparation of the desired compounds, including the intermediate compounds. The hydroxy peaks in the <sup>1</sup>H-NMR spectra of the trialkyl-monoacetic acid derivatives appeared at 4.68–6.74 ppm, where the chemical shifts are much lower than those of the tetrahydroxy derivative (9.95 ppm for **1** [26], 10.20 ppm for **4** [29]). This means that the strong hydrogen bonds were broken by the introduction of the three alkyl groups. This was supported by the decreased intensity of the broad  $\nu_{\text{O-H}}$  peaks in the IR spectra. The carboxy peaks in the <sup>1</sup>H-NMR spectra of the trialkyl-monoacetic acid derivatives appeared at 11.35–11.80 ppm, corresponding to a higher magnetic field compared with that of normal carboxylic acid derivatives, consistent with the appearance of the IR peaks of the carboxylic acid at a higher (more than 3100 cm<sup>-1</sup>) wavenumber. These data also indicate that the strong hydrogen bonds were broken by introducing the three alkyl groups.

The peak position of the aryl protons in the <sup>1</sup>H-NMR spectra of **3** and **6** can provide an indicator of the coordination site, because these protons are far from the coordination site for alkali metal ions and are thus not electrostatically

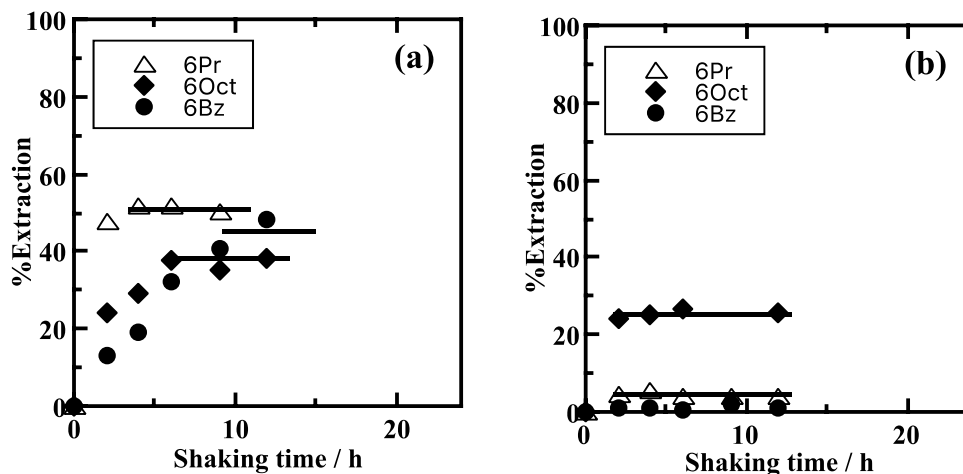
affected by the alkyl branches introduced on the phenoxy oxygen atoms. The appearance of the aryl proton peaks at relatively higher magnetic field indicates that the four benzene rings are positioned upright, whereas their appearance at lower magnetic field indicates that the calixarene changed to a flattened orientation. The former structure would provide a broader coordination site, whereas the latter structure would provide a narrower site, which would consequently contribute to efficient separation among the alkali metal ions with different ionic sizes. However, the difference in the positions were insignificant and the introduced alkyl branches may not have a significant impact on the extraction behavior.

### Extraction time to reach equilibrium

The extraction time required to reach equilibration was first investigated. The effect of the shaking time on the percentage extraction of lithium and sodium ions with **3** and **6** is shown in Figs. 4a and b, and 5 a and b, respectively. The extraction times to reach equilibration for  $\text{Li}^+$  and  $\text{Na}^+$  with **3** were 6–24 h, and 6–12 h, respectively. The extraction times to reach equilibration for  $\text{Li}^+$  and  $\text{Na}^+$  with **6** were 4 h to longer than 12 h, and 3 h, respectively.  $\text{Li}^+$  extraction with **3** and **6** required a longer time than  $\text{Na}^+$  extraction. Thus, the shaking times were set for longer than the obtained periods.



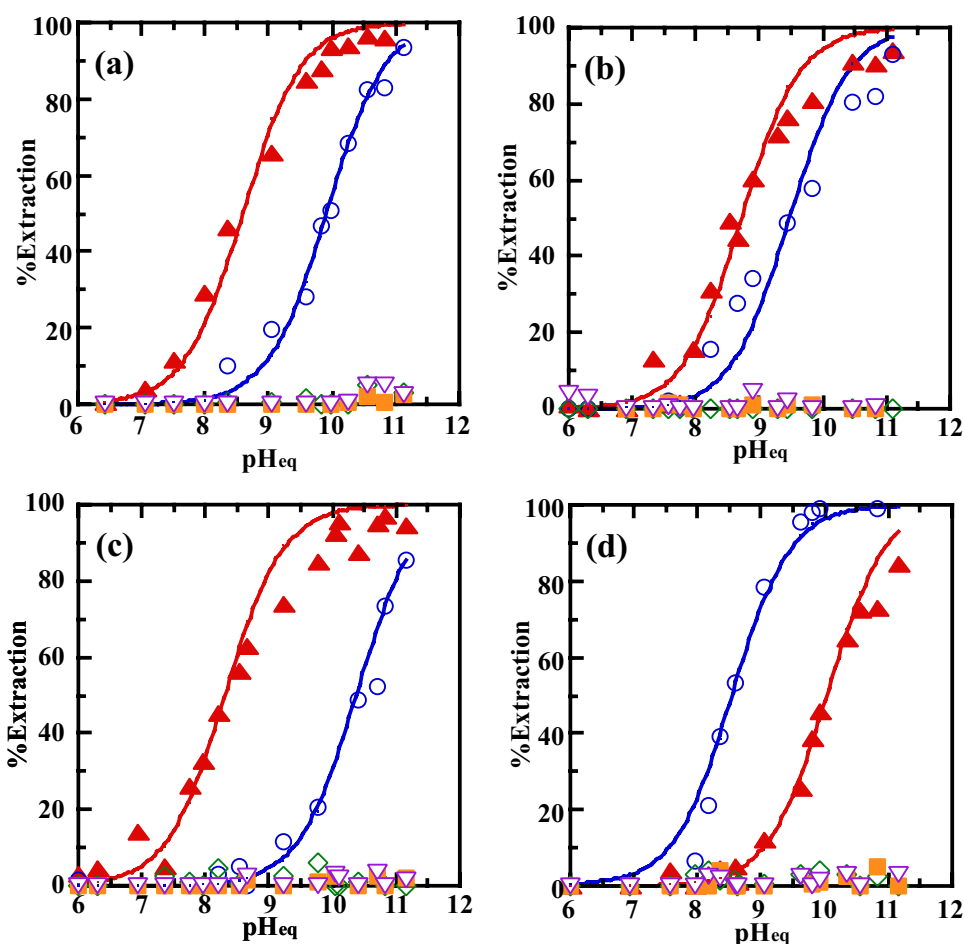
**Fig. 4** Effect of shaking time on the percentage extraction of **a**  $\text{Li}^+$  and **b**  $\text{Na}^+$  with **3Pr** (open triangle), **3Oct** (closed diamond), **3Bz** (closed circle), and **3<sup>2</sup>EtBu** (open square) in competitive system.  $[\text{M}^+]_i = 0.1 \text{ mM}$ ,  $[\text{Extractant}] = 5.0 \text{ mM}$ ,  $[\text{HEPES}] = 0.1 \text{ M}$  +  $[\text{NH}_3] = 1.0 \text{ M}$



**Fig. 5** Effect of shaking time on the percentage extraction of **a**  $\text{Li}^+$  and **b**  $\text{Na}^+$  with **6Pr** (open triangle), **6Oct** (closed diamond), and **6Bz** (closed circle) in competitive system.  $[\text{M}^+]_i = 0.1 \text{ mM}$ ,  $[\text{Extractant}] = 5.0 \text{ mM}$ ,  $[\text{HEPES}] = 0.1 \text{ M}$  +  $[\text{NH}_3] = 1.0 \text{ M}$



**Fig. 6** Effect of equilibrium pH on percentage extraction of alkali metal ions with **a** **3Pr**, **b** **3Oct**, **c** **3Bz**, and **d** **3<sup>2</sup>EtBu** in competitive system. Li<sup>+</sup> (closed triangle), Na<sup>+</sup> (open circle), K<sup>+</sup> (open diamond), Rb<sup>+</sup> (closed square), and Cs<sup>+</sup> (open up triangle), [M(I)]<sub>i</sub> = 0.1 mM, [Extractant] = 5.0 mM



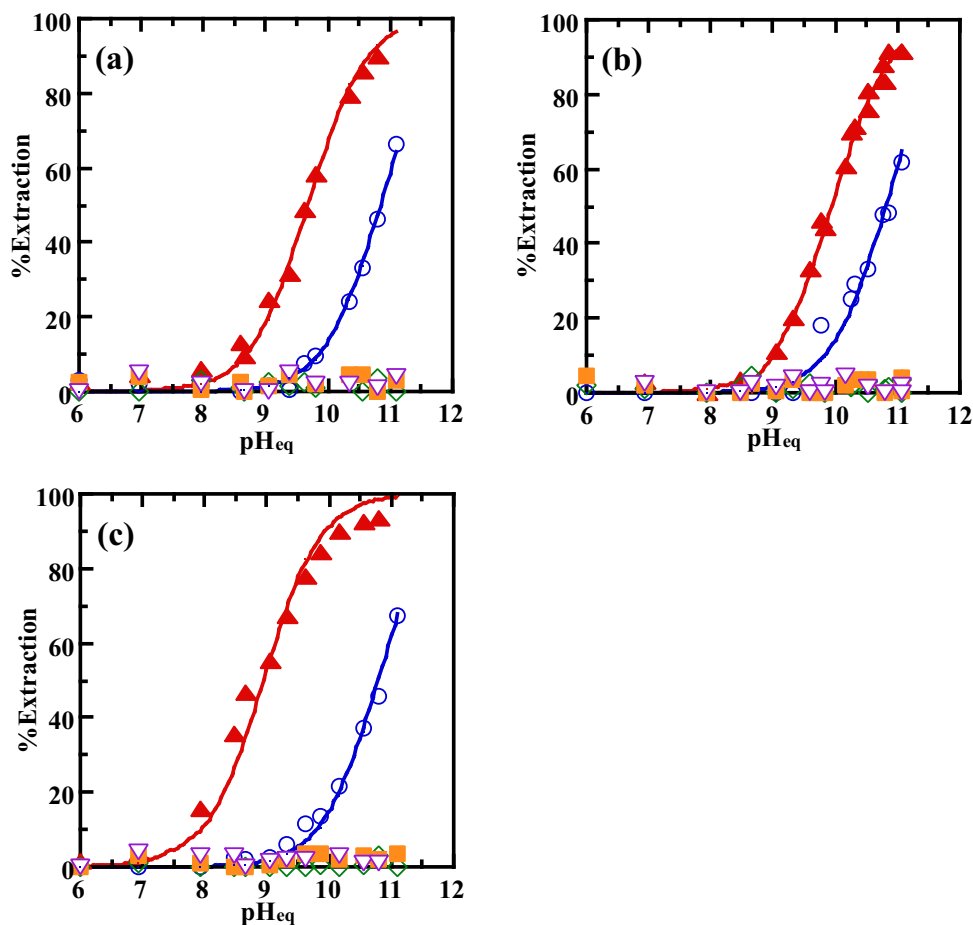
### Extraction of various alkali metal ions in competitive systems

In the previous paper [25], the extraction of Li<sup>+</sup> with **3Pr** was expressed as the loading percentage, which is the extent to which certain amounts of alkali metal ions in high concentrations (0.10 M) are loaded on a lower concentration of **3Pr** (5 mM). In this study, the data were reconstructed by changing the metal concentration for comparison with the data for **3** with other alkyl branches.

The effects of the equilibrium pH on the percentage extractions (%Extraction) of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> using **3Pr**, **3Oct**, **3Bz**, and **3<sup>2</sup>EtBu**, in a competitive system are shown in Fig. 6a–d, respectively. As reported in the previous paper using **3Pr** in the individual system [25], trialkylmonoacetic acid derivatives were ineffective for extracting larger K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, but extracted smaller Li<sup>+</sup> and Na<sup>+</sup>. In the previous section, it was expected that little difference in the extraction behavior would be observed by using **3**

with different alkyl branches; the slight difference in the peak position of the aryl protons was expected to have a minimal effect on the extraction behavior. However, the alkyl branches obviously affected the extraction behavior. In particular, the separation efficiency was higher for Li<sup>+</sup> than for Na<sup>+</sup>, with an obvious difference in the pH of the extraction region. Careful observation shows that sodium extraction was affected with **3Pr**, **3Oct**, and **3Bz**. Because the original calix[4]arene was synthesized by using sodium base as the templating ion, most of the calix[4]arene derivatives exhibited selectivity for Na<sup>+</sup> over the other alkali metal ions. Nevertheless, **3Pr**, **3Oct**, and **3Bz** providing metal coordination sites closely similar to the size of Li<sup>+</sup> and thus exhibited selectivity for Li<sup>+</sup> extraction over Na<sup>+</sup> extraction, consequently affecting the separation efficiency. Therefore, the introduced alkyl branches effectively exclude the sodium ion by lipophilic-hydrophobic repulsion and steric hindrance. A significant effect was also observed for more sterically-hindered **3<sup>2</sup>EtBu**. In contrast, selectivity for Na<sup>+</sup> over Li<sup>+</sup>

**Fig. 7** Effect of equilibrium pH on percentage extraction of alkali metal ions with **a** **6Pr**, **b** **6Oct**, and **c** **6Bz** in competitive system.  $\text{Li}^+$  (closed triangle),  $\text{Na}^+$  (open circle),  $\text{K}^+$  (open diamond),  $\text{Rb}^+$  (closed square), and  $\text{Cs}^+$  (open up triangle),  $[\text{M}(\text{I})]_i = 0.1 \text{ mM}$ ,  $[\text{Extractant}] = 5.0 \text{ mM}$



was observed with **3<sup>2</sup>EtBu**, which suppressed  $\text{Li}^+$  extraction, although a definite reason was not clarified.

The effect of the alkyl branches at the *p*-position on the extraction was also investigated. The effects of the equilibrium pH on the percentage extractions (%Extraction) of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  using **6Pr**, **6Oct**, and **6Bz**, in a competitive system are shown in Fig. 7a–d, respectively. **6<sup>2</sup>EtBu** was not prepared because **3<sup>2</sup>EtBu** exhibited  $\text{Na}^+$  selectivity. Dealkylated reagents, **6**, exhibited less extraction ability compared with **3**, plausibly because the extraction shifted with the pH region. This is plausible attributed to the lower lipophilicity in the absence of alkyl branches at the *p*-position. The separation efficiency of **6** was similar to that of **3**, which means that the alkyl branches at the *p*-position have less effect on the separation efficiency.

### Extraction reactions, and extraction equilibrium constants and separation factors

The extraction of monovalent alkali metal ions using trialkyl-monoacetic acid derivatives **3** and **6** was investigated because trialkyl-monoacetic acid derivatives are

mono-ionizable and release a single proton during the extraction. The reaction proposed in the previous paper [25] is represented by Eq. (3):



where RH and M represent **3** or **6**, and the alkali metal ion, respectively. The extraction equilibrium constant was obtained using Eq. (4),

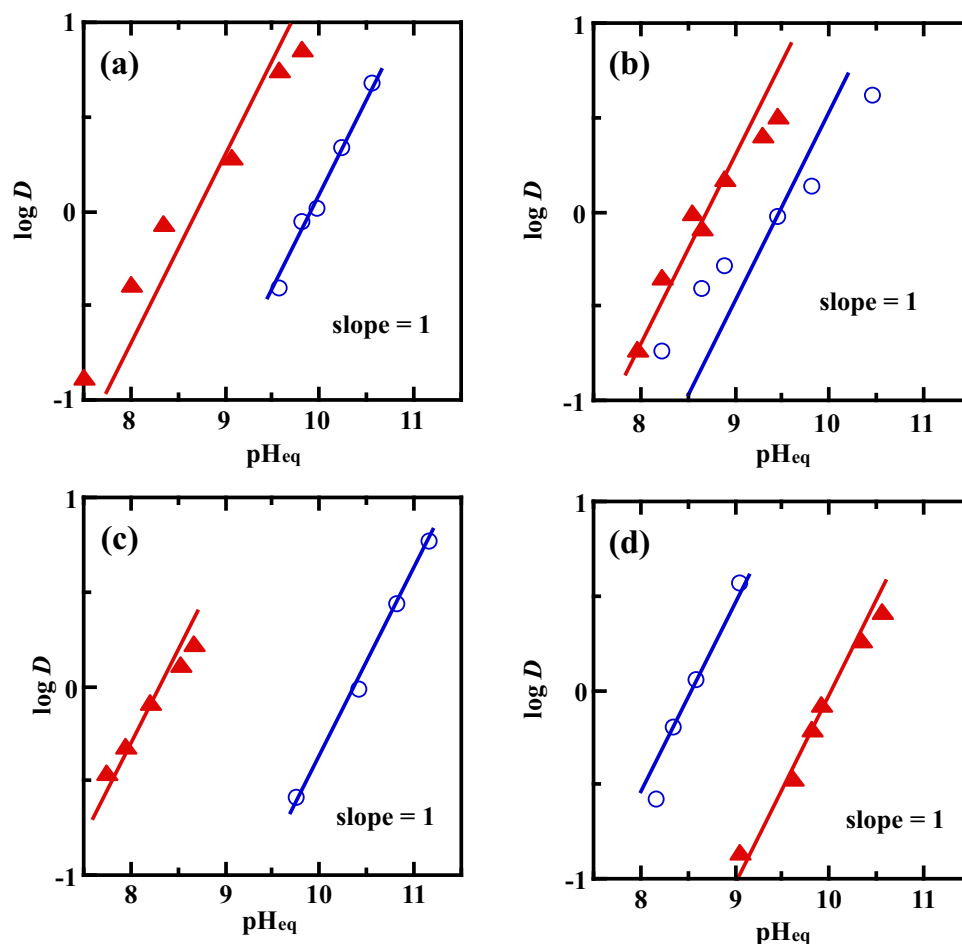
$$K_{\text{ex}} = \frac{[\text{RM}][\text{H}^+]}{[\text{RH}][\text{M}^+]} = D \frac{[\text{H}^+]}{[\text{RH}]}, \quad (4)$$

where the distribution ratio, *D*, is the ratio of the metal concentrations in the organic and aqueous phases, and defined in Eq. (2). After taking logarithms, Eq. (5) was obtained.

$$\log D = \text{pH} + \log[\text{RH}] + \log K_{\text{ex}}. \quad (5)$$

The effects of the equilibrium pH on the distribution ratio of  $\text{Li}^+$  and  $\text{Na}^+$  with **3Pr**, **3Oct**, **3Bz**, and **3<sup>2</sup>EtBu** are shown in Fig. 8a–d, respectively. The effects of the equilibrium pH on the distribution ratio of  $\text{Li}^+$  and  $\text{Na}^+$  with **6Pr**, **6Oct**, and **6Bz** are shown in Fig. 9a–c, respectively. All plots lie

**Fig. 8** Effect of equilibrium pH on distribution ratio of  $\text{Li}^+$  (closed triangle) and  $\text{Na}^+$  (open circle) with **a** 3Pr, **b** 3Oct, **c** 3Bz, and **d** 3<sup>2</sup>EtBu in competitive system.  $[\text{M(I)}]_i = 0.1 \text{ mM}$ ,  $[\text{Extractant}] = 5.0 \text{ mM}$



on straight lines, each with a slope of unity. The slope corresponds to the monovalent charge of both metal ions. The data confirm that the extraction takes place by a simple ion-exchange mechanism. The concentration of the extraction reagent was sufficiently higher than the total concentration of the metal ions. The extraction equilibrium constants for both ions with all reagents were obtained from the intercepts of  $\log D$  vs.  $\text{pH}$ . The extraction equilibrium constants,  $K_{\text{ex}}$ , of  $\text{Li}^+$  and  $\text{Na}^+$  with **3** and **6**, as well as the separation factors,  $\beta$ , for  $\text{Li}^+$  and  $\text{Na}^+$  are listed in Table 7. The separation factors,  $\beta$ , is defined by Eq. (6).

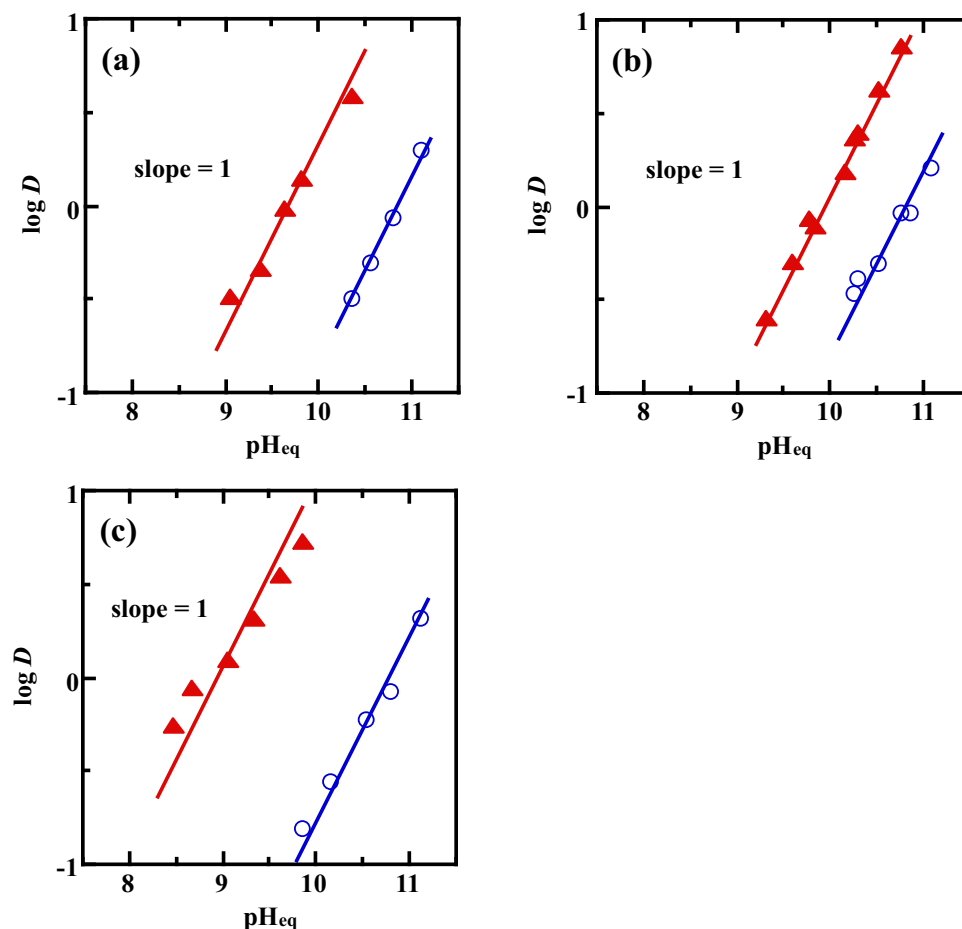
$$\beta_{\text{Li}/\text{Na}} = \frac{K_{\text{ex,Li}}}{K_{\text{ex,Na}}} \quad (6)$$

The theoretical curve and straight lines drawn in Figs. 6a–d, 7a–c, 8a–d, and 9a–c were obtained by using the extraction equilibrium constants.

## Conclusions

Four and three trialkyl-monoacetic acid derivatives of *p*-*t*-octylcalix[4]arene and calix[4]arene were respectively prepared to investigate the effect of the alkyl branches attached to the phenoxy oxygen atoms and to the *p*-position on the selective extraction of  $\text{Li}^+$  over  $\text{Na}^+$ . Alkyl branches on the phenoxy oxygen atoms remarkably affected the selectivity for  $\text{Li}^+$  over  $\text{Na}^+$  by excluding  $\text{Na}^+$  extraction while maintaining  $\text{Li}^+$  extraction. However, the introduction of a more-hindered alkyl branch depressed the  $\text{Li}^+$  extraction. The data can contribute to elucidating the origin of the high  $\text{Li}^+$  selectivity and the  $\text{Li}^+$  extraction mechanism. Optimization of the alkyl branch improves the  $\text{Li}^+$  selectivity.

**Fig. 9** Effect of equilibrium pH on distribution ratio of  $\text{Li}^+$  (close triangle) and  $\text{Na}^+$  (open circle) with **a** 6Pr, **b** 6Oct, and **c** 6Bz in competitive system.  $[\text{M}(\text{I})]_i = 0.1 \text{ mM}$ ,  $[\text{Extractant}] = 5.0 \text{ mM}$



**Table 7** Extraction equilibrium constants for  $\text{Li}^+$  and  $\text{Na}^+$  with **3** and **6**, and separation factors between both ions

Extraction reagent	$K_{\text{ex,Li}}$	$K_{\text{ex,Na}}$	$\beta_{\text{Li/Na}} (\beta_{\text{Na/Li}})$
3Pr	$5.2 \times 10^{-7}$	$2.5 \times 10^{-8}$	21
3Oct	$3.9 \times 10^{-7}$	$6.8 \times 10^{-8}$	5.7
3Bz	$1.0 \times 10^{-6}$	$8.6 \times 10^{-9}$	120
3 <sup>2</sup> EtBu	$1.9 \times 10^{-8}$	$5.8 \times 10^{-7}$	0.033 (30)
6Pr	$4.3 \times 10^{-8}$	$2.9 \times 10^{-9}$	15
6Oct	$2.3 \times 10^{-8}$	$3.1 \times 10^{-9}$	7.4
6Bz	$2.3 \times 10^{-7}$	$3.3 \times 10^{-9}$	70

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**Author contributions** KO planned this research work, elucidated the extraction mechanism, and wrote the paper. HS prepared most of the reagents, measured spectra data, and carried out extraction. TH prepared one of the reagents, measured spectra data, and carried out extraction. SM discussed with spectra data of the reagents. HK supported for the extraction reaction and for drawing the theoretical lines to estimate the extraction constants and separation factors.

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**Data availability** No datasets were generated or analysed during the current study.

## Declarations

**Conflict of interest** There are no conflict to declare.

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