

Electronic Supplementary Information

Hybridization of helical poly(phenylacetylene)s bearing L-proline tripeptide pendants into silica porous microspheres as a solvent tolerability CSP for liquid chromatography

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1. Characterization of intermediate products

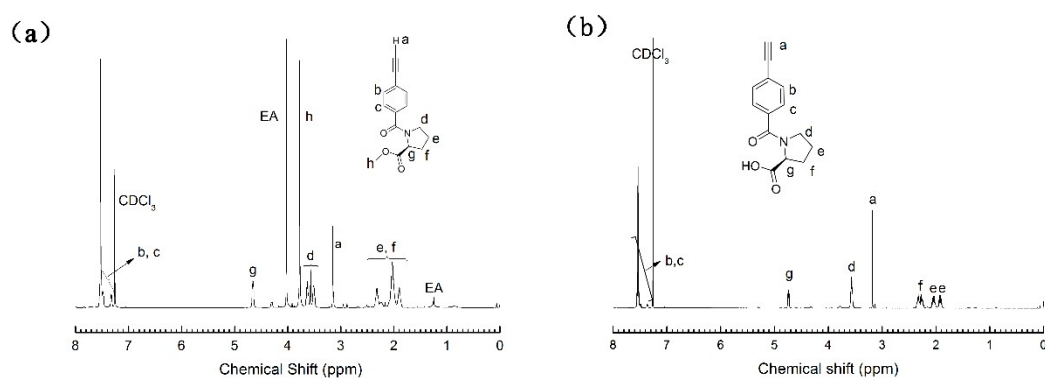


Fig. S1† ¹H-NMR spectra of (a) intermediate product **a** and (b) intermediate product

b.

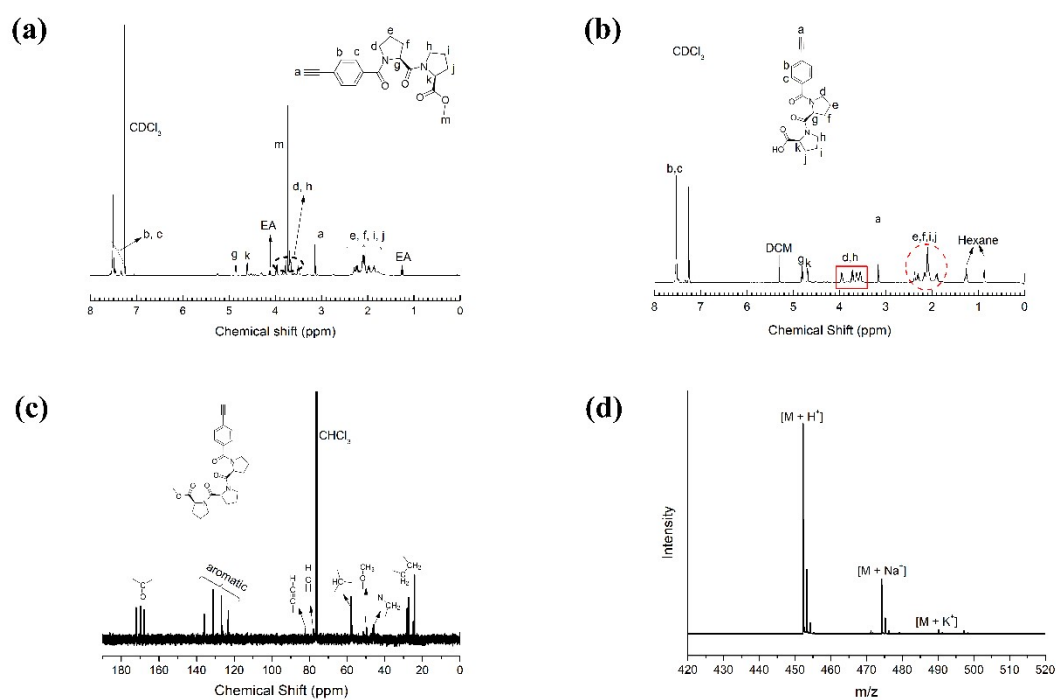


Fig. S2† $^1\text{H-NMR}$ spectra of (a) intermediate product **c** and (b) intermediate products **d**; (c) $^{13}\text{C-NMR}$ spectrum of PA-P₃-ee; (d) ESI-MS spectrum of PA-P₃-ee 4-Ethynylbenzoic acid (Fig. S3† (a)): $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS, 20 °C, ppm): $\delta = 8.06$ (Ar-**H**, 2H), 7.55 (Ar-**H**, 2H), 3.26 ($\equiv\text{CH}$, 1H).

PA-APTES (Fig. S3† (b)): $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS, 20 °C, ppm): $\delta = 7.99$ -7.97 (Ar-**H**, 2H), 7.53-7.51 (Ar-**H**, 2H), 4.40-4.36 (-O-**CH**₂-CH₃, 2H), 1.41-1.37 (-CH₂-**CH**₃, 3H), 0.25 (-Si-(**CH**₃)₃, 9H).

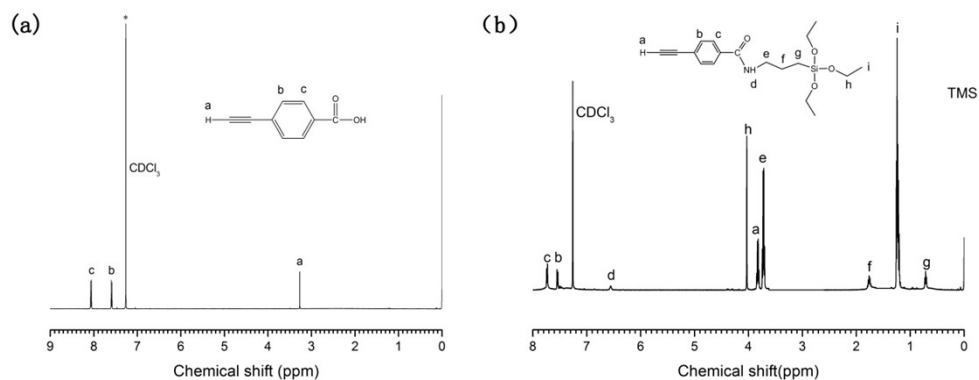


Fig. S3† $^1\text{H-NMR}$ spectra of (a) 4-ethynylbenzoic acid and (b) PA-APTES

2 Preparation of homopolymer PPA

The typical procedure for preparing CPA is depicted as follows. PA-P₃-ee (0.20

g, 0.44 mmol), PA-APTES (3.2 mg, 0.0092 mmol), Rh(nbd)BPh₄ (4.56 mg, 0.0087 mmol) and CHCl₃ (15 mL) were added into a flask (50 mL) under a N₂ atmosphere, stirring at 28 °C for 24 h, PPh₃ (5.2 mg, 0.020 mmol) was added into the solutions. The mixture was concentrated, and then dropped it into a lot of n-hexane, a yellow solid CPA was obtained by filtrated. ¹H-NMR (500 MHz, DMSO-*d*₆, TMS, 80 °C, ppm) (Fig. S4†) δ = 7.69-6.71 (aromatic, 4H), 5.92 (main chain, 1H), 4.96-4.11 (-N-CHCOO-, 3H), 3.72-3.43 (-O-CH₃, 3H), 3.39-3.06 (-N-CH₂-, 6H), 2.33-1.36 (-CH₂-CH₂-, 12H).

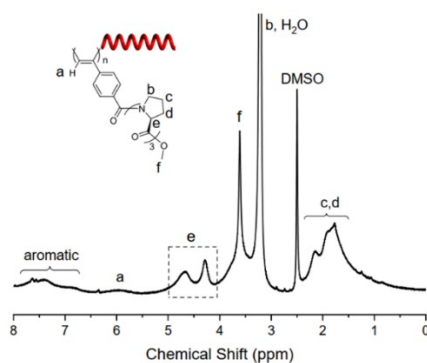


Fig. S4† ¹H-NMR spectrum of PPA

3 Preparation of SiO₂ porous microspheres (SiO₂ PMS)

A typical procedure for preparing SiO₂ PMS is described as follows. The aqueous solution of tetraethyl orthosilicate (TEOS) was added in a mixture solution (120 mL) of H₂O, ethanol and NH₃·H₂O. The solution was stirred at 25 °C for 6 h to obtain SiO₂ seeds solution. CTAB (6.5 g, 17.84 mmol), H₂O, NH₃·H₂O and SiO₂ seeds solution were mixture at 25 °C. After that, the aqueous solution of TEOS (300 mL) was added into the reaction system stirred at 25 °C for 6 h, the SiO₂ PMS was obtained by centrifuged and vacuum dried at 30 °C for 12 h.

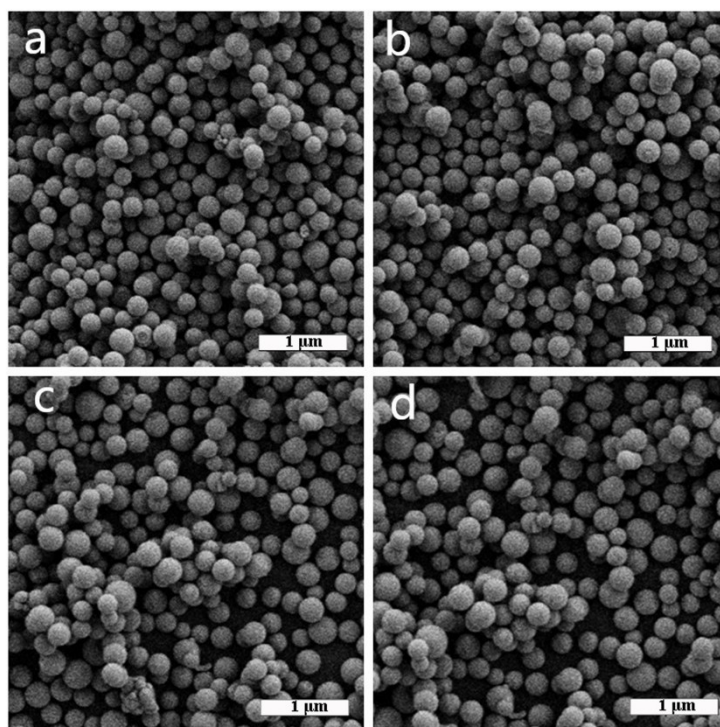


Fig. S5† SEM images of SiO₂ seeds prepared in different [TEOS] ([NH₃·H₂O] = 0.8 mol/L, [H₂O] = 3.0 mol/L, T=25 °C): (a): [TEOS]=0.3 mol/L; (b): [TEOS]=0.4 mol/L; (c): [TEOS]=0.5 mol/L; (d): [TEOS]=0.6 mol/L

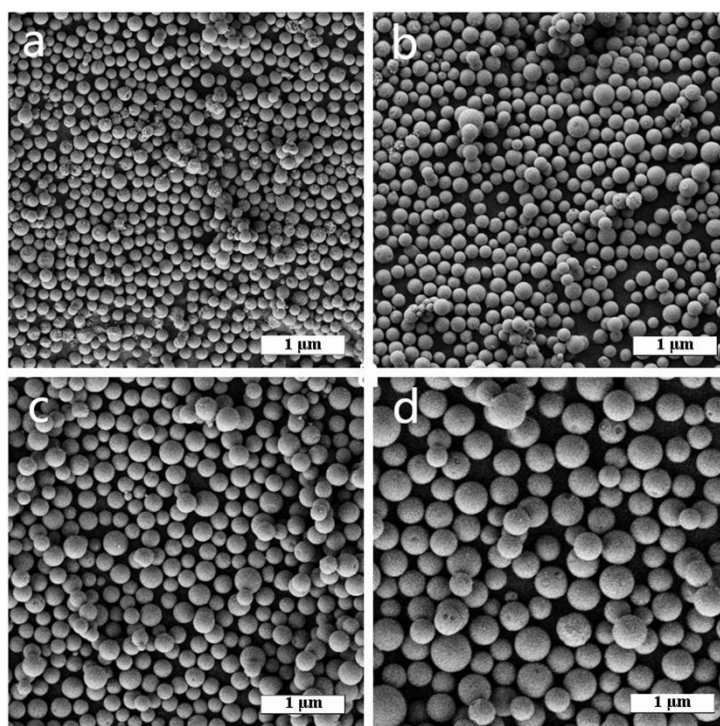


Fig. S6† SEM images of SiO₂ seeds prepared in different [NH₃·H₂O] ([TEOS] = 0.3 mol/L, [H₂O] = 3.0 mol/L, T=25 °C): (a): [NH₃·H₂O] =0.4 mol/L; (b): [NH₃·H₂O] =0.6 mol/L; (c): [NH₃·H₂O] =0.8 mol/L; (d): [NH₃·H₂O] =1.0 mol/L

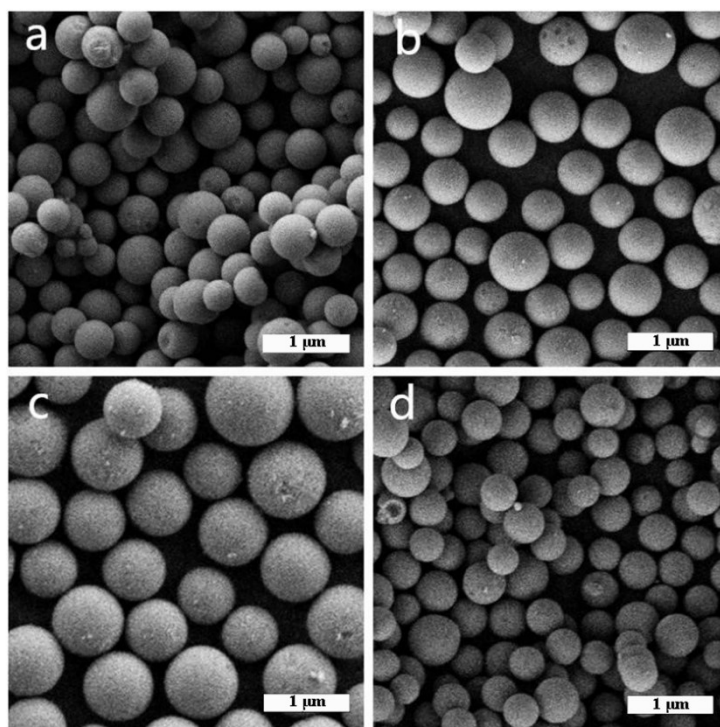


Fig. S7† SEM images of SiO₂ seeds prepared in different [H₂O] ([NH₃·H₂O] = 1 mol/L, [TEOS] = 0.3 mol/L, T=25 °C): (a): [H₂O] =4 mol/L; (b): [H₂O] =6 mol/L; (c): [H₂O] =8 mol/L; (d): [H₂O] =10.0 mol/L

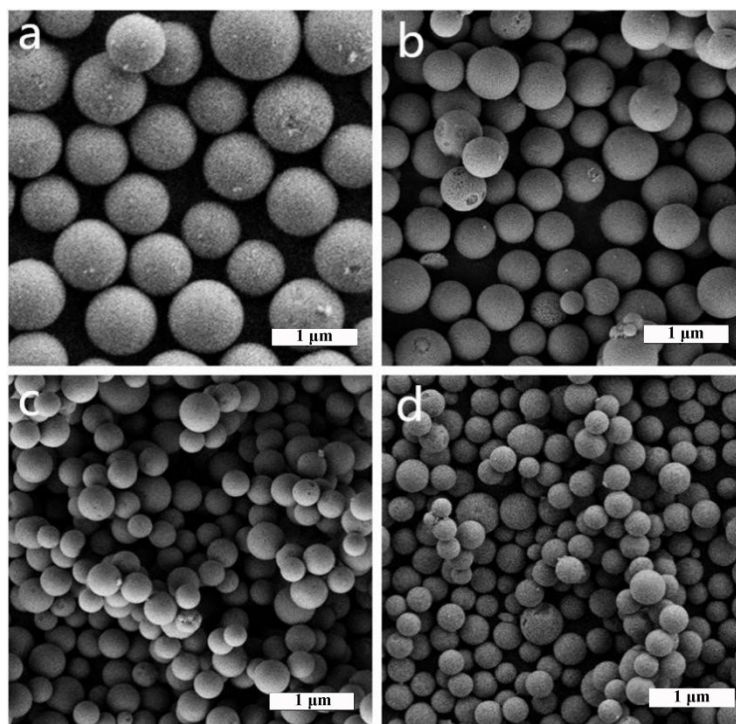


Fig. S8† SEM images of SiO₂ seeds prepared in different temperature ([NH₃·H₂O] = 1 mol/L, [H₂O] = 8 mol/L, [TEOS]=0.3 mol/L): (a): T = 25 °C; (b): T =30 °C; (c): T =35 °C; (d): T =40 °C

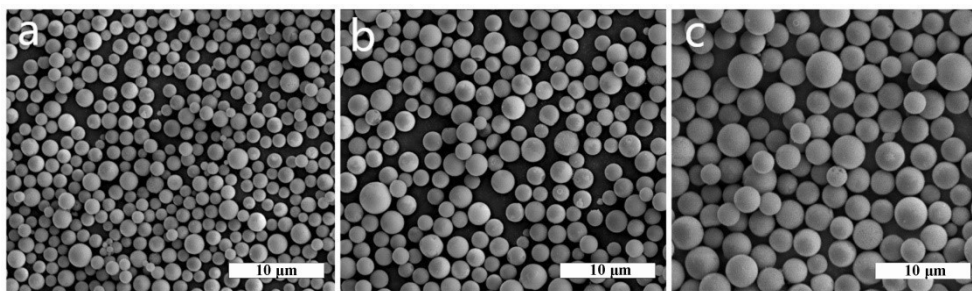


Fig. S9† SEM images of SiO₂ PMS prepared in different [TEOS] ([NH₃·H₂O] = 1 mol/L, T=25 °C): (a): [TEOS] = 0.3 mol/L; (b): [TEOS] = 0.4 mol/L; (c): [TEOS] = 0.5 mol/L.

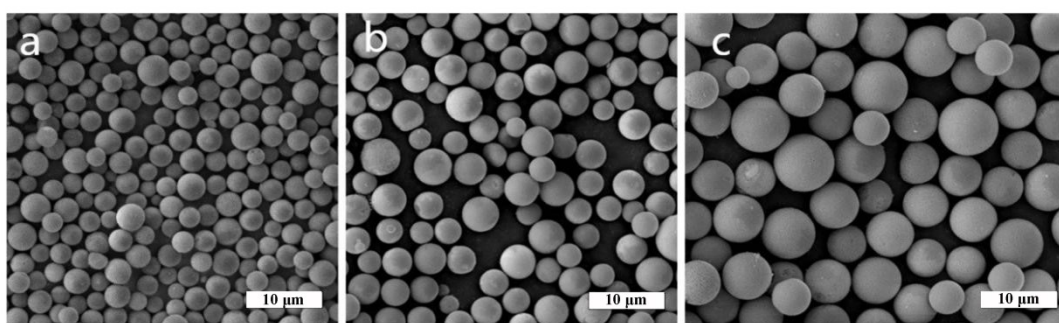


Fig. S10† SEM images of SiO₂ PMS prepared in different [NH₃·H₂O] ([TEOS] = 0.4 mol/L, T=25 °C): (a): [NH₃·H₂O] = 1 mol/L; (b): [NH₃·H₂O] = 1.5 mol/L; (c): [NH₃·H₂O] = 2.0 mol/L.

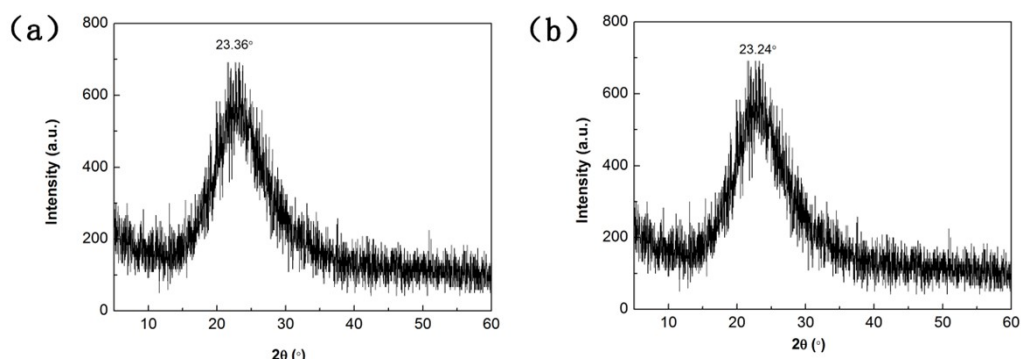


Fig. S11† XRD patterns of (a) SiO₂ seeds and (b) SiO₂ PMS

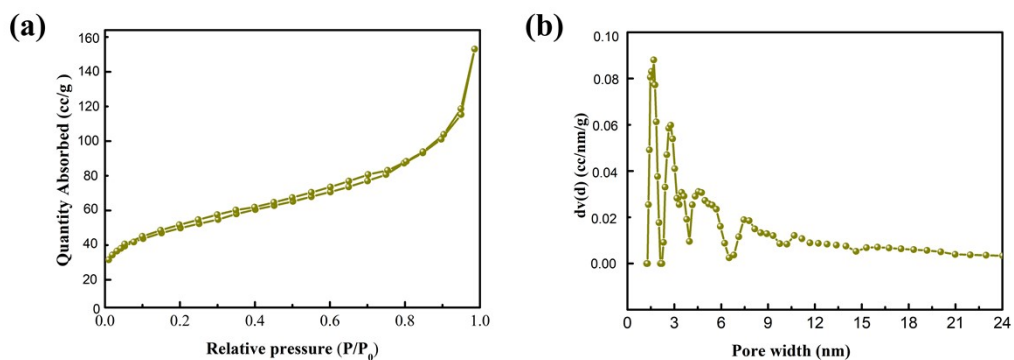


Fig. S12† The (a) N₂ adsorption–desorption isotherms and (b) pore size distribution of SiO₂ PMS

4. Hybridization of CPA into SiO₂ PMS during the growth process of microspheres

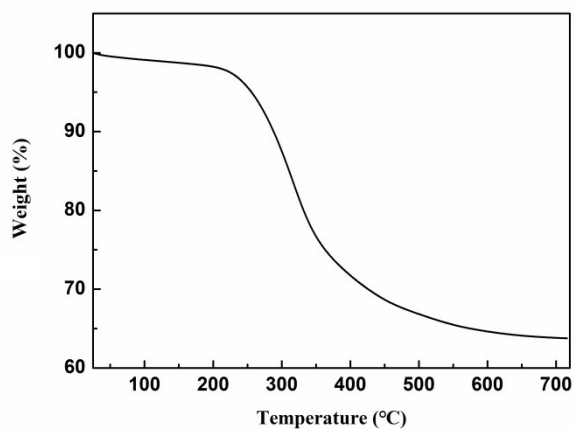


Fig. S13† TGA curve of HCSP

5. Evaluation of chiral recognition ability of the HCSP

Table S1† Solubility of PPA-CSP and HCSP ^a

Solvent	MeOH	CHCl ₃	THF	DMF	DMAc	DMSO	H ₂ O	n-hexane
PPA-CSP	++	++	++	++	++	++	++	-
HCSP	-	-	-	-	-	-	-	-

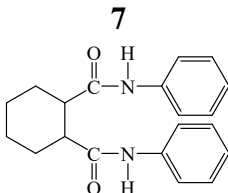
^a ++: Soluble; -: insoluble;

Table S2† Resolution of the racemates 1-8 on the HCSP after introducing THF ^a

Racemates	HCSP (H/I/T=94/5/1)			HCSP (H/I/T=94/1/5)		
	k_I'	α	R_s	k_I'	α	R_s
1	0.54(-)	~1	-	0.43(-)	~1	-
2	0.58(+)	1.28	1.33	0.31(+)	1.21	1.28
3	12.69(+)	1.21	1.29	9.05(+)	1.20	1.25
4	1.95	1.00	-	0.97	1.00	-
5	3.31(+)	~1	-	2.41(+)	~1	-
6	3.41	1.00	-	2.59	1.00	-
7	12.36(-)	1.20	1.52	9.75(-)	1.15	1.27
8	12.98(-)	~1	-	10.25(-)	~1	-

^a Column: 0.2 × 25 cm (ID). Flow rate: 0.1 mL/min. The signs in parentheses stand for the optical rotation of the first-eluted enantiomer. Eluent: H, n-hexane; I, isopropanol; T, THF.

Table S3† Comparison of the separation factors (α) for racemate **7** on the commercial columns and HCSP

Racemate	Daicel Chiralpak or Chiralcel			HCSP ^b
	AD ^a	AS ^a	OD ^a	
<p>7</p> 	1.02 (-)	1.25 (-)	2.07 (-)	3.43 (-)

^a Column: 25 cm × 0.46 cm (ID). Flow rate: 0.1 mL/min. Eluent: hexane/isopropanol (90/10, v/v)

^b Column: 25 cm × 0.2 cm (ID). Flow rate: 0.1 mL/min. Eluent: hexane/isopropanol/CHCl₃ (H/I/C=94/1/5, v/v/v)

