

## Supporting Information

# Enantioselective Diels–Alder reaction in confined space of homochiral metal–organic frameworks

K. Tanaka,\* S. Nagase, T. Anami, M. Wierzbicki, Z. Urbanczyk-Lipkowska

<sup>a</sup>Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan.

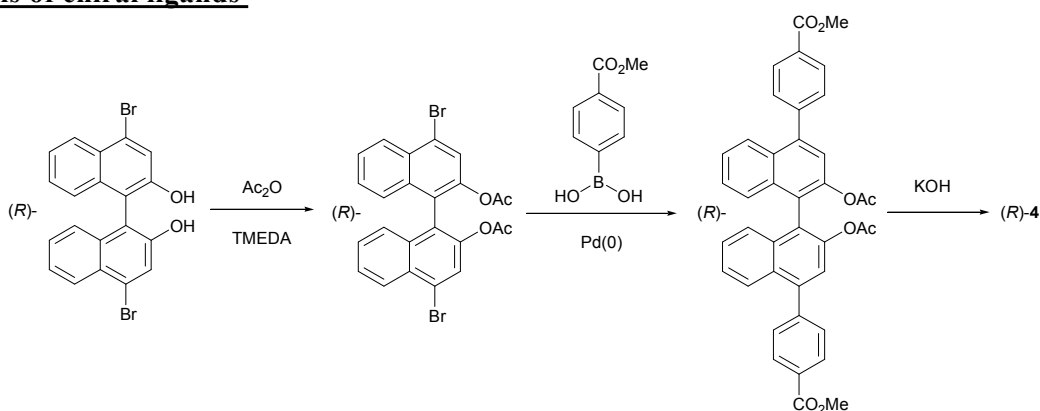
<sup>b</sup>Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland.

E-mail: [ktanaka@kansai-u.ac.jp](mailto:ktanaka@kansai-u.ac.jp)

### General procedures

<sup>1</sup>H-NMR spectra were recorded on JEOL JNM-GSX 400 spectrometer, with tetramethylsilane (TMS) as the internal standard. IR spectra were recorded with a JASCO FT-IR 4100 spectrometer. Thermogravimetric analyses (TG) were performed on a Rigaku TG-8120 instrument.

### Synthesis of chiral ligands



### (R)-4,4'-dibromo-2,2'-diacetyl-1,1'-binaphthyl

A mixture of 4,4'-dibromo-2,2'-binaphthol<sup>1</sup> (1.00 g, 2.3 mmol), *N,N,N',N'*-tetramethylethylene diamine (0.5 mL) and acetic anhydride (0.97 g, 5.2 mmol) was stirred at room temperature for 1 h. The resultant mixture was extracted with ethyl acetate and dried over anhydrous MgSO<sub>4</sub>. After evaporation of the solvent, (R)-4,4'-dibromo-2,2'-diacetyl-1,1'-binaphthyl was obtained as a white solid (0.90 g) in 76% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.33 (d, *J* = 8.8 Hz, 2H), 7.78 (s, 2H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 1.89 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 169.0, 146.1, 133.6, 130.1, 127.7, 127.3, 127.2, 126.5, 126.0, 123.6, 122.8, 20.5; IR (KCl, cm<sup>-1</sup>) 1766, 1569, 1501, 1455, 1411, 1367, 1345, 1315, 1255, 1205, 1134, 1090, 1044, 1012, 969, 947, 908, 877, 847, 757, 712, 670, 625, 587, 548, 518.

### (R)-2,2'-diacetyl-4,4'-di(4-methoxycarbonylphenyl)-1,1'-binaphthyl

To a mixture of (R)-4,4'-dibromo-2,2'-diacetyl-1,1'-binaphthyl (633 mg, 1.20 mmol), 4-methoxycarbonyl phenyl boronic acid (860 mg, 4.79 mmol), and CsF<sub>2</sub> (794 mg, 5.23 mmol) in dimethoxyethane (45 mL) and H<sub>2</sub>O (0.7 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (121 mg, 0.1 mmol). The resulting mixture was heated at 100°C for 48 h under Ar atmosphere. After removal of the solvent, the residue was diluted with CHCl<sub>3</sub> and water. The organic phase was separated, and the aqueous phase was extracted with CHCl<sub>3</sub>. The combined organic phase was washed with brine and dried over anhydrous MgSO<sub>4</sub>. After evaporation of the solvent, the

residue was purified by flash column chromatography (*n*-hexane–ethyl acetate) to give the desired compound as a white solid (539 mg) in 71% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.22 (d, *J* = 8.0 Hz, 4H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 4H), 7.45–7.34 (m, 8H), 4.00 (s, 6H), 1.93 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 169.3, 166.9, 144.3, 140.8, 135.5, 133.8, 130.2, 129.6, 129.4, 128.9, 128.7, 126.7, 126.1, 125.9, 123.2, 122.9, 52.2, 30.9, 20.6; IR (KCl, cm<sup>-1</sup>) 1762, 1722, 1609, 1435, 1365, 1341, 1278, 1213, 1103, 1017, 867, 769, 710, 596.

### **(R)-2,2'-dihydroxy-1,1'-binaphthyl-4,4'-dibenzoic acid (4)**

To a solution of 2,2'-diacetyl-4,4'-di(4-methoxycarbonylphenyl)-1,1'-binaphthyl (301 mg, 0.47 mmol) in MeOH (10 mL), H<sub>2</sub>O (5 mL) and THF (20 mL) was added KOH (800 mg, 13.3 mmol). The mixture was stirred at room temperature for 18 h. After being dried under vacuum, dil. HCl aqueous solution (5 mL) was added to the reaction mixture. Then the reaction mixture was extracted with EtOAc. The combined organic phase was washed with brine and dried over anhydrous MgSO<sub>4</sub>. After evaporation of the solvent, (*R*)-**4** was obtained as a white solid (240 mg) in 94% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ (ppm): 13.07 (brs, 2H), 9.39 (s, 2H), 8.50 (s, 2H), 8.15 (d, *J* = 8.4 Hz, 4H), 7.72 (d, *J* = 8.0 Hz, 6H), 7.27–7.25 (m, 6H), 7.14–7.11 (m, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ (ppm): 167.0, 152.3, 144.5, 139.3, 134.5, 129.8, 129.7, 129.4, 125.9, 125.7, 125.2, 124.9, 122.8, 119.3, 115.6; IR (KCl, cm<sup>-1</sup>) 3388, 1686, 1607, 1507, 1417, 1374, 1316, 1278, 1181, 1143, 1043, 1019, 943, 862, 763, 713, 665, 601, 545.

### **Synthesis and characterization of (R)-MOF-4.**

A mixture of (*R*)-**4** (5 mg, 0.01 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (5 mg, 0.02 mmol) was dissolved into a mixed solvent (DMF–H<sub>2</sub>O, 1.5/3.0 mL) in a screw-capped vial (20 mL). The vial was capped and heated at 55°C for 4 days. (*R*)-MOF-4 was obtained as green prisms (5 mg). IR (KCl, cm<sup>-1</sup>) 2927, 1659, 1608, 1589, 1403, 1178, 1100, 943, 864, 792, 766, 718, 666, 488, 423, 405; TGA data for loss of guest solvent: 28%.

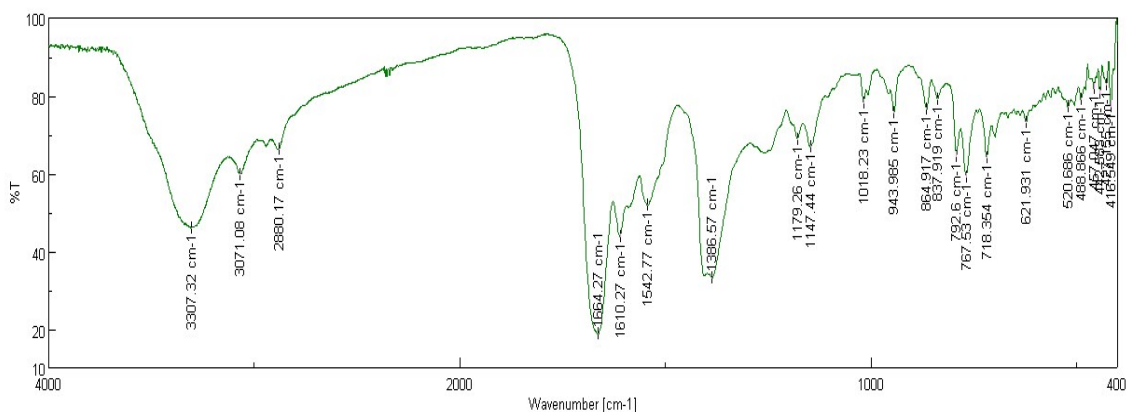


Fig. S1 IR spectrum of (*R*)-MOF-4

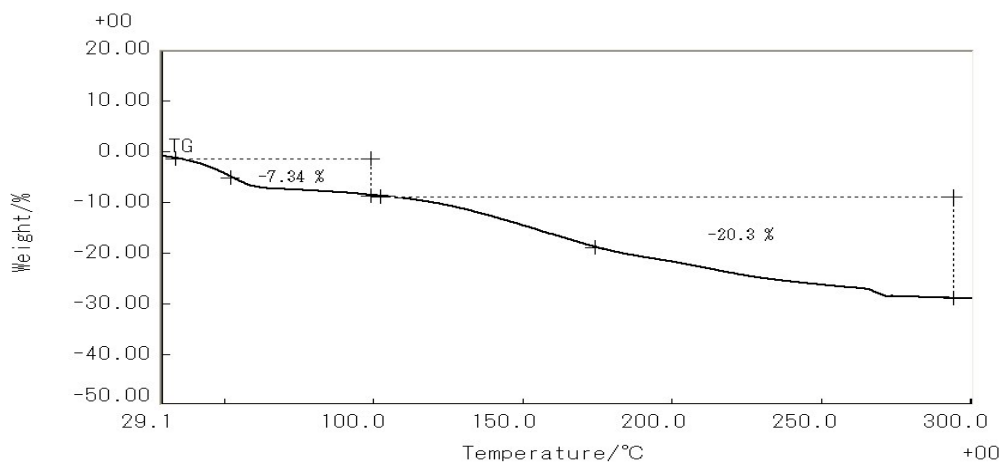


Fig. S2 TG trace of (*R*)-MOF-4

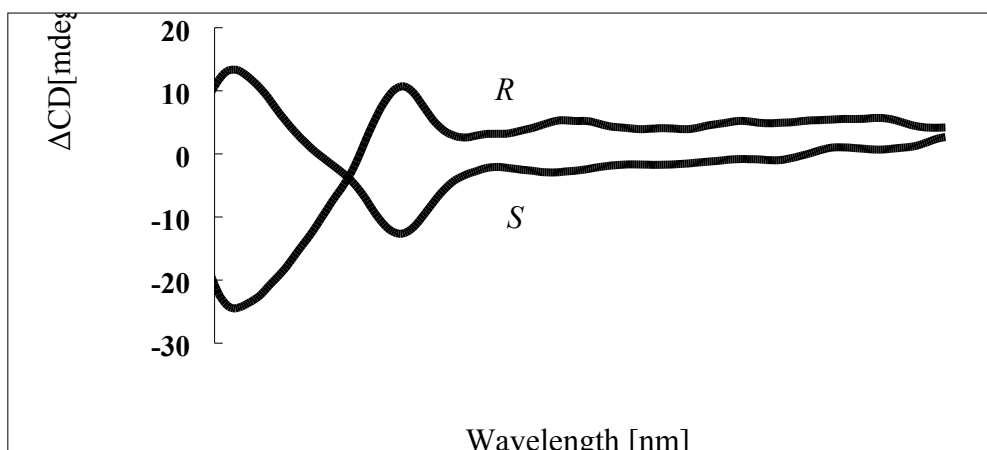


Fig. S3 Solid CD spectra of (*R*)- and (*S*)-MOF-4 in KBr pellet.

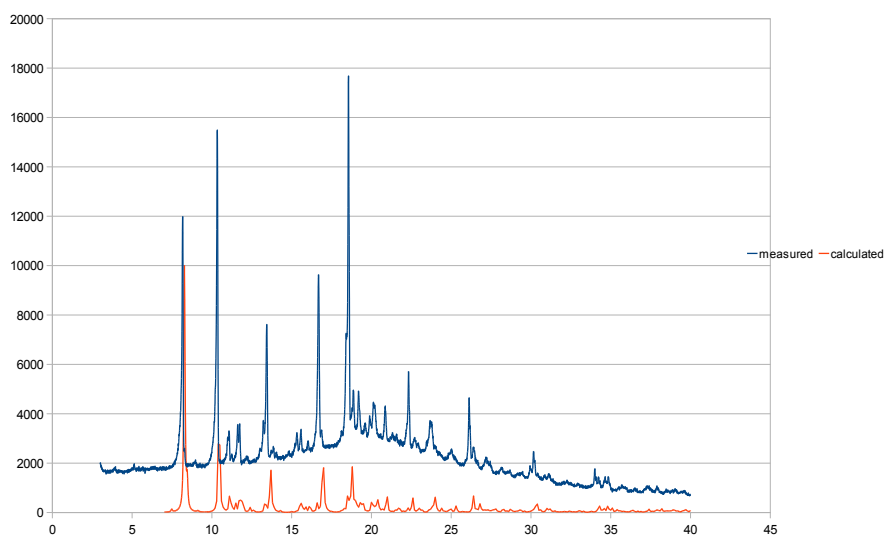


Fig. S4 Powder XRD patterns of (*R*)-MOF-4.

### X-ray data collection and structure determinations

Single crystals from bulk sample were isolated and mounted immediately into a loop. X-ray measurements were carried out at the PETRA III synchrotron beamline P13 (Hamburg, Germany) at  $\lambda = 0.6888$ .

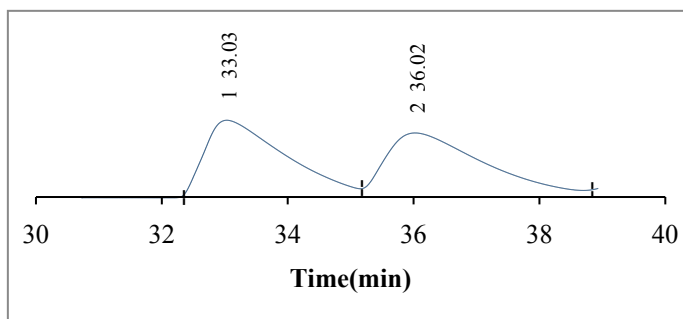
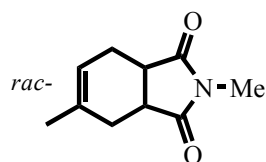
Integration, space group assignment and corrections were done using the XDS software.<sup>2</sup> Structures were solved *via* direct methods SHELXS-2014.<sup>3</sup> Structures were refined using SHELXL-2014 in the WinGX64<sup>4</sup> software suite. In each structure, all non-hydrogen atoms were located *via* difference Fourier maps and refined anisotropically. Aromatic, methyl and methine group hydrogen atoms were placed at their idealized positions and allowed to ride on the coordinates of the parent atom with isotropic thermal parameters (Uiso) fixed at 1.2 Ueq of the carbon atom to which they are attached. Disordered dimethylformamide (DMF) and *N*-methylformamide (NMF) molecules were refined with restraints of molecular geometry.

Crystal data for (*R*)-**MOF-4**:  $C_{78}H_{64}Cu_2N_3O_{16}$ , MW = 1426.40,  $a = b = 33.835(5)$ ,  $c = 39.859(8)$  Å,  $\beta = 120.0^\circ$ ,  $V = 39517(14)$  Å<sup>3</sup>,  $F(000) = 13302$ ,  $d_{\text{exp}} = 1.328(4)$  and  $d_{\text{calc}} = 1.079$  Mg m<sup>-3</sup>, trigonal; space group  $R\bar{3}2$  (No. 155),  $Z = 18$ ,  $\mu(\text{MoK}\alpha) = 0.541$  cm<sup>-1</sup>,  $\lambda = 0.6888$  Å,  $T = 100(2)$  K, 137923 reflections measured, 17540 unique ( $R_{\text{int}} = 0.0292$ ), final  $R_1 = 0.0732$ ,  $wR_2 = 0.2230$ , for 16757 observed reflections with  $I > 2\sigma(I)$ ; GOF = 1.041.

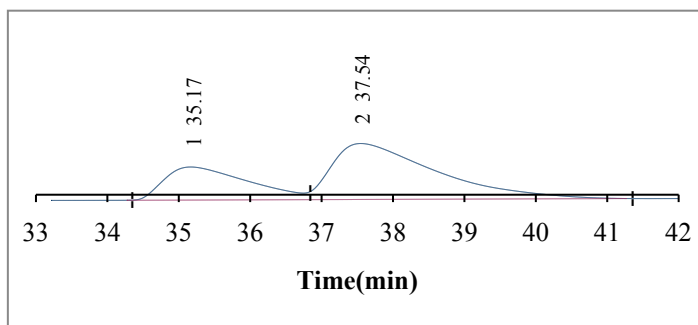
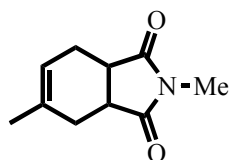
Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC); the deposition numbers are CCDC 1483410.

## General Procedure for the Asymmetric Diels-Alder reaction of isoprene with *N*-ethyl maleimide in the presence of chiral MOF

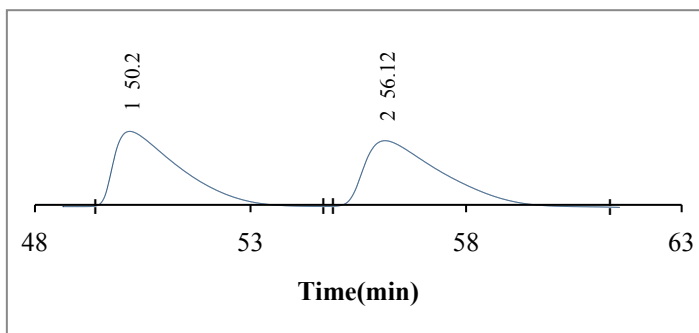
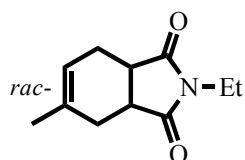
A mixture of isoprene (0.5 mmol) and *N*-ethyl maleimide (0.25 mmol) and (*R*)-MOF-4 (5 mg, 3.4 mol %) in AcOEt (2 mL) was stirred at 0°C for 48h. The resultant mixture was filtered and evaporated the solvent under reduced pressure. The yield of the product was determined by <sup>1</sup>H-NMR spectra using dimethyl tere-phtharate as internal standard. The optical purity was determined by HPLC (Chiralcel OB-H, hexane/IPA=95/5).



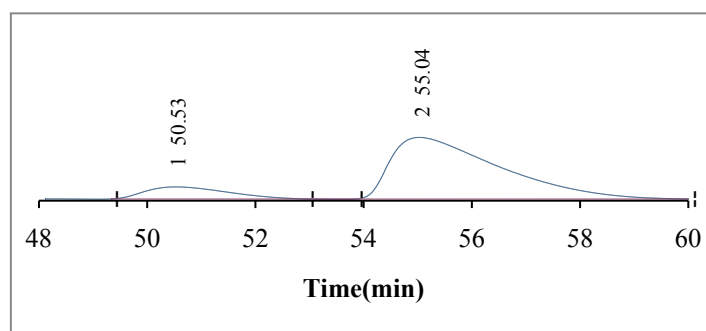
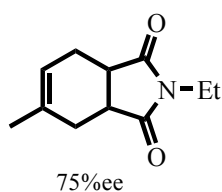
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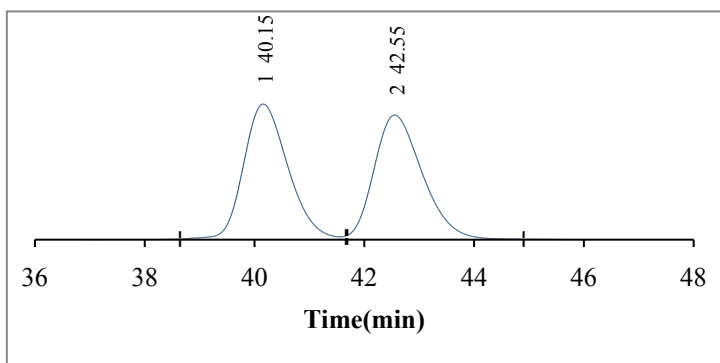
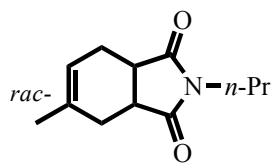
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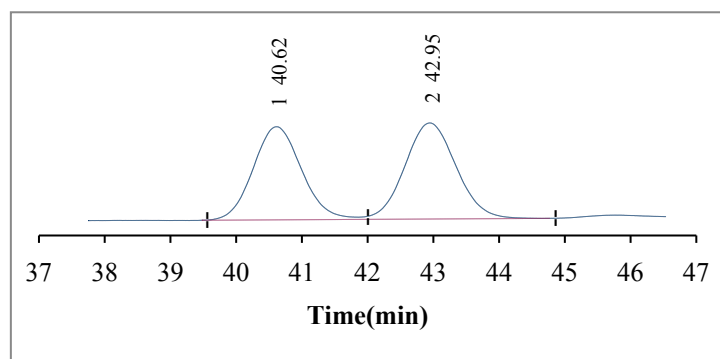
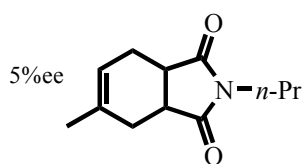
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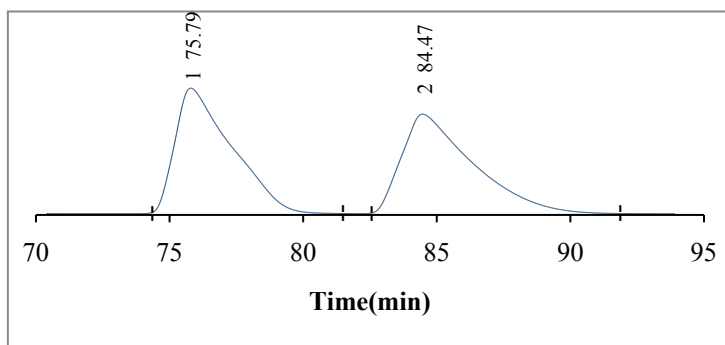
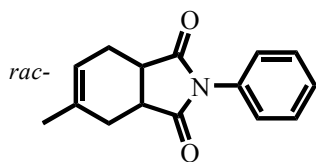
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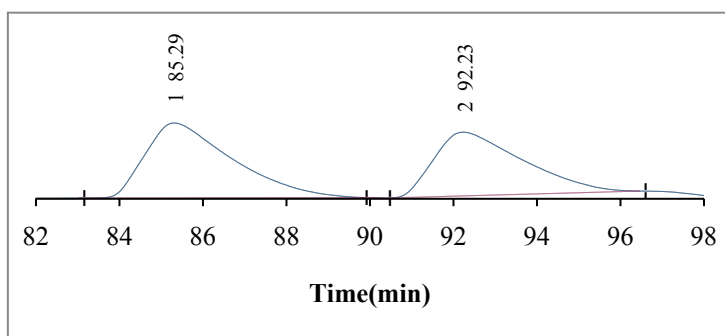
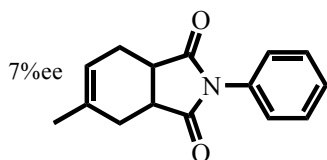
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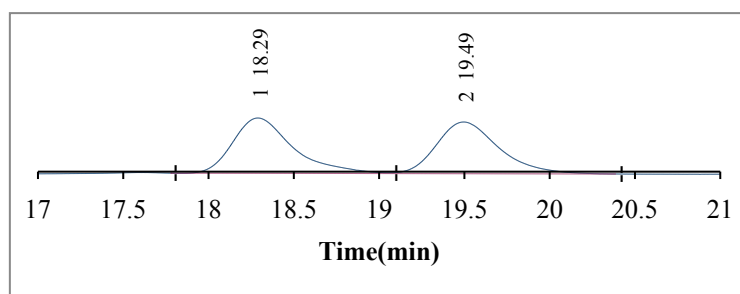
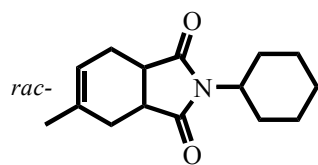
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Column : Chiralpak IA, hexane/IPA=98/2, Flow rate : 0.5 ml/min, Detection : UV 220 nm



Column : Chiralpak IA, hexane/IPA=98/2, Flow rate : 0.5 ml/min, Detection : UV 220 nm



Column : Chiralpak AD-H, hexane/IPA=95/5, Flow rate : 0.5 ml/min, Detection : UV 220 nm

### **References**

- 1) M.W.A. MacLean, T.K. Wood, G. Wu, R. P. Lemieux, C. M. Crudden, *Chem. Mater.*, **2014**, 26, 5852–5859.
  - 2) W. Kabsch, *Acta Cryst. D***66**, 125-132 (2010).
  - 3) G. M. Sheldrick, *Acta Cryst. A***64**, 112–122 (2008).
  - 4) G. M. Sheldrick, *Acta Cryst. C***71**, 3–8 (2015).
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