

## Supplementary Information

# Improved design of inherently chiral calix[4]arenes as organocatalysts

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### 3-(Phenylthio)cyclohexanone (4a)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.43 (m, 2H), 7.25–7.33 (m, 3H), 3.39–3.45 (m, 1H), 2.65–2.70 (m, 1H), 2.28–2.40 (m, 3H), 2.10–2.16 (m, 2H), 1.66–1.78 (m, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  208.71, 133.15, 132.96, 129.03, 127.74, 47.69, 46.04, 40.83, 31.15, 23.97 ppm; IR 2946, 1715, 1222, 745, 694  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  206 ( $\text{M}^+$ ), 110, 97. HPLC analysis: CHIRALPAC IA, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min, retention time; 6.6 min (*S*) and 8.3 min (*R*).

### 3-(4-*tert*-Butylphenylthio)cyclohexanone (4b)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.37 (m, 4H), 3.33–3.39 (m, 1H), 2.64–2.69 (m, 1H), 2.25–2.39 (m, 3H), 2.09–2.19 (m, 2H), 1.66–1.77 (m, 2H), 1.30 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  208.85, 151.13, 133.42, 129.26, 126.07, 47.83, 46.29, 40.84, 34.55, 31.22, 24.05 ppm; IR 2963, 1716, 734  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  262 ( $\text{M}^+$ ), 166, 97. HPLC analysis: CHIRALPAC IA, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min, retention time; 4.9 min (*S*) and 5.4 min (*R*).

### 3-(2-Naphthylthio)cyclohexanone (4c)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74–7.89 (m, 4H), 7.43–7.49 (m, 3H), 3.48–3.55 (m, 1H), 2.68–2.75 (m, 1H), 2.26–2.43 (m, 3H), 2.07–2.16 (m, 2H), 1.62–1.75 (m, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  208.54, 133.41, 132.34, 131.91, 130.24, 130.02, 128.50, 127.54, 127.31, 126.48, 126.29, 47.55, 45.86, 40.70, 31.04, 23.82 ppm; IR 2933, 2858, 1713, 820, 746  $\text{cm}^{-1}$ . HPLC analysis: CHIRALPAC IA, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min, retention time; 9.2 min (*S*) and 10.5 min (*R*).

### 3-(Phenylthio)cycloheptanone (4d)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.42 (m, 2H), 7.23–7.33 (m, 3H), 3.38–3.44 (m, 1H), 2.68–2.82 (m, 2H), 2.44–2.60 (m, 2H), 2.12–2.17 (m, 1H), 1.94–2.00 (m, 1H), 1.81–1.88 (m, 1H), 1.62–1.78 (m, 2H), 1.46–1.57 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.47, 133.96, 132.34, 129.01, 127.40, 49.41, 44.10, 43.94, 36.79, 28.05, 23.82 ppm; IR 3057, 2929, 2856, 1670, 1478, 1440, 741, 692  $\text{cm}^{-1}$ . HPLC analysis: CHIRALPAC AS, hexane/*i*-PrOH = 50/50, flow rate = 1.0 ml/min, retention time; 7.8 min (*R*) and 12.0 min (*S*).

### 1,3-Diphenyl-3-(phenylthio)propan-1-one (4e)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J$  = 7.4 Hz, 2H), 7.54 (t,  $J$  = 7.4 Hz, 1H), 7.43 (t,  $J$  = 7.7 Hz, 2H), 7.31–7.34 (m, 4H), 7.17–7.27 (m, 6H), 4.95 (dd,  $J$  = 6.0, 8.1 Hz, 1H), 3.67 (dd,  $J$  = 8.2, 17.2 Hz, 1H), 3.57 (dd,  $J$  = 5.9, 17.2 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.88, 141.07, 136.56, 134.13, 133.17, 132.61, 128.76, 128.51, 128.36, 127.95, 127.70, 127.42, 127.27, 48.07, 44.56 ppm;

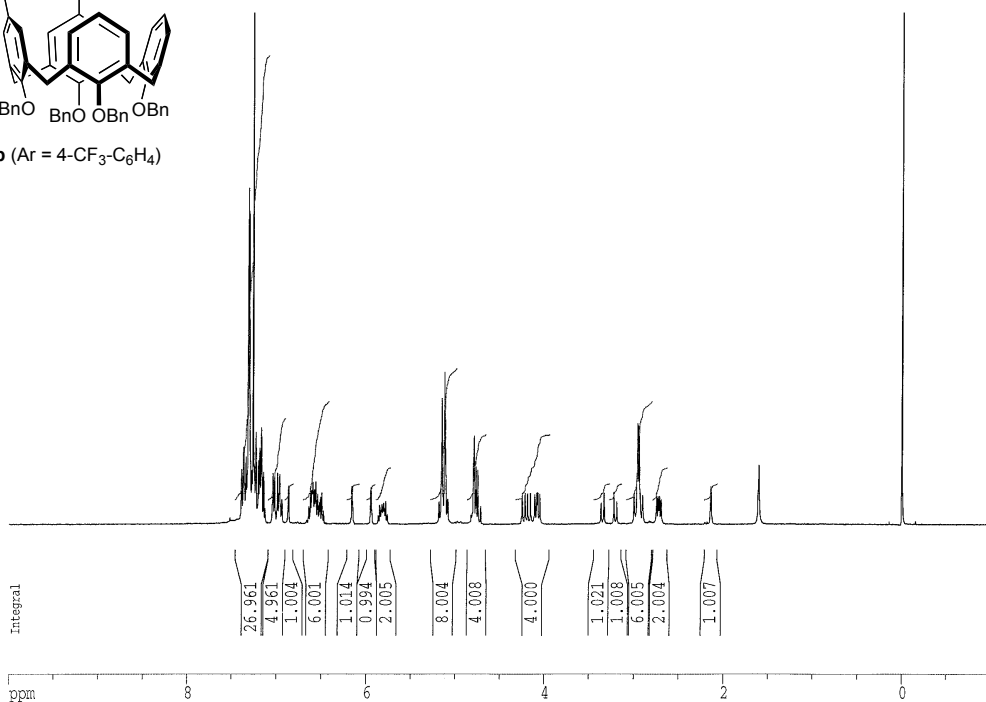
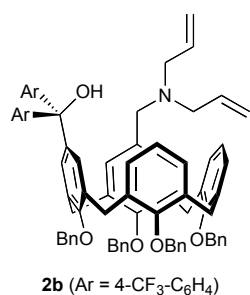
IR 3060, 2902, 1679, 1451, 1230, 739, 696, 684  $\text{cm}^{-1}$ . HPLC analysis: CHIRALCEL OD, hexane/*i*-PrOH = 99/1, flow rate = 1.0 ml/min, retention time; 15.0 min (*S*) and 18.1 min (*R*).

***tert*-Butyl 2-(diphenylmethyleamino)-3-phenylpropanoate (5a)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56–7.58 (m, 2H), 7.24–7.38 (m, 6H), 7.15–7.21 (m, 3H), 7.04–7.06 (m, 2H), 6.59 (br d,  $J = 5.8$  Hz, 2H), 4.11 (dd,  $J = 4.3, 9.2$  Hz, 1H), 3.23 (dd,  $J = 4.3, 13.3$  Hz, 1H), 3.16 (dd,  $J = 9.2, 13.3$  Hz, 1H), 1.44 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.81, 170.29, 139.51, 138.30, 136.32, 130.05, 129.84, 128.68, 128.15, 128.04, 128.01, 127.90, 127.61, 126.12, 81.10, 67.89, 39.54, 28.00 ppm; IR 3060, 3028, 2977, 2928, 1735, 1150, 1081, 698  $\text{cm}^{-1}$ . HPLC analysis: CHIRALCEL OD, hexane/*i*-PrOH = 99/1, flow rate = 1.0 ml/min, retention time; 6.7 min (*R*) and 10.3 min (*S*).

***tert*-Butyl 2-(diphenylmethyleamino)pent-4-enoate (5b)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63–7.65 (m, 2H), 7.30–7.47 (m, 6H), 7.16–7.19 (m, 2H), 5.67–5.77 (m, 1H), 5.00–5.09 (m, 2H), 4.01 (dd,  $J = 5.3, 7.6$  Hz, 1H), 2.57–2.70 (m, 2H), 1.44 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.87, 170.11, 139.67, 136.62, 134.68, 130.15, 128.77, 128.48, 128.36, 127.95, 127.90, 117.27, 81.02, 65.78, 38.12, 28.04 ppm; IR 3061, 2978, 2925, 1734, 1624, 1153, 698  $\text{cm}^{-1}$ . HPLC analysis: CHIRALPAC IC, hexane/*i*-PrOH = 99/1, flow rate = 1.0 ml/min, retention time; 6.8 min (*R*) and 8.1 min (*S*).



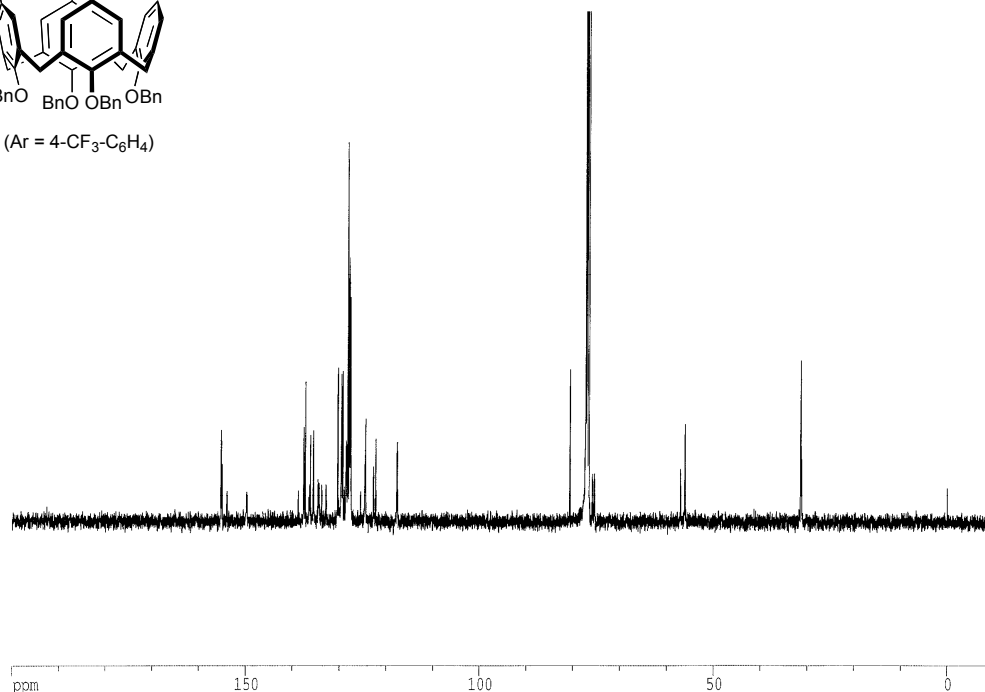
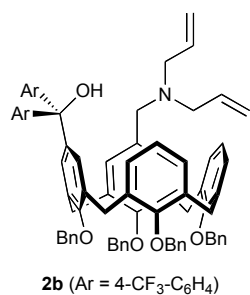
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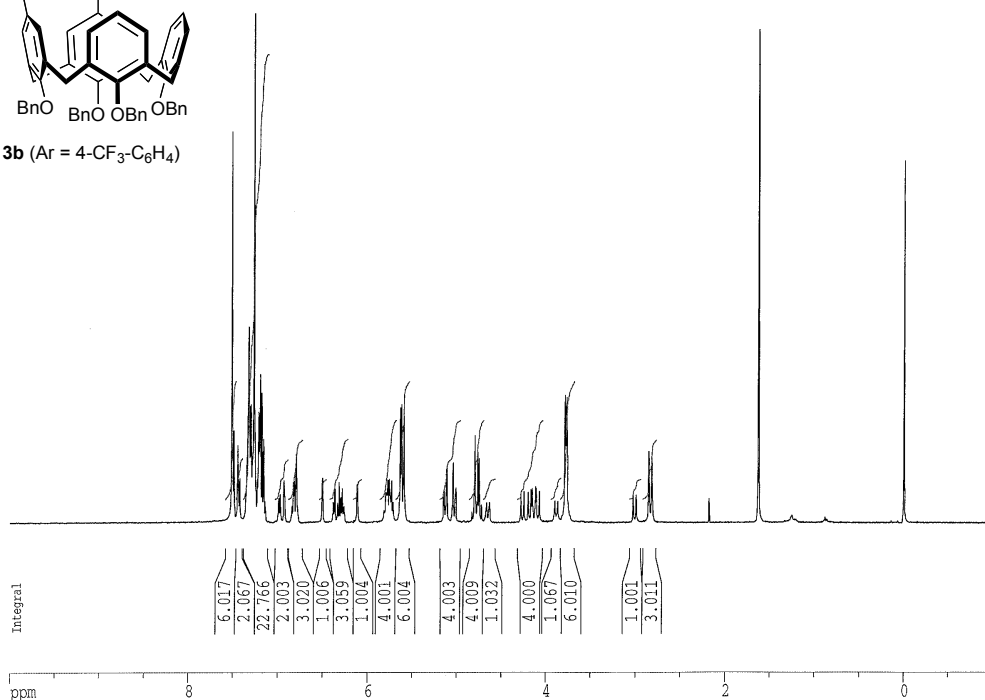
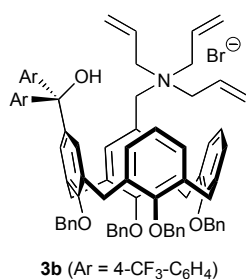
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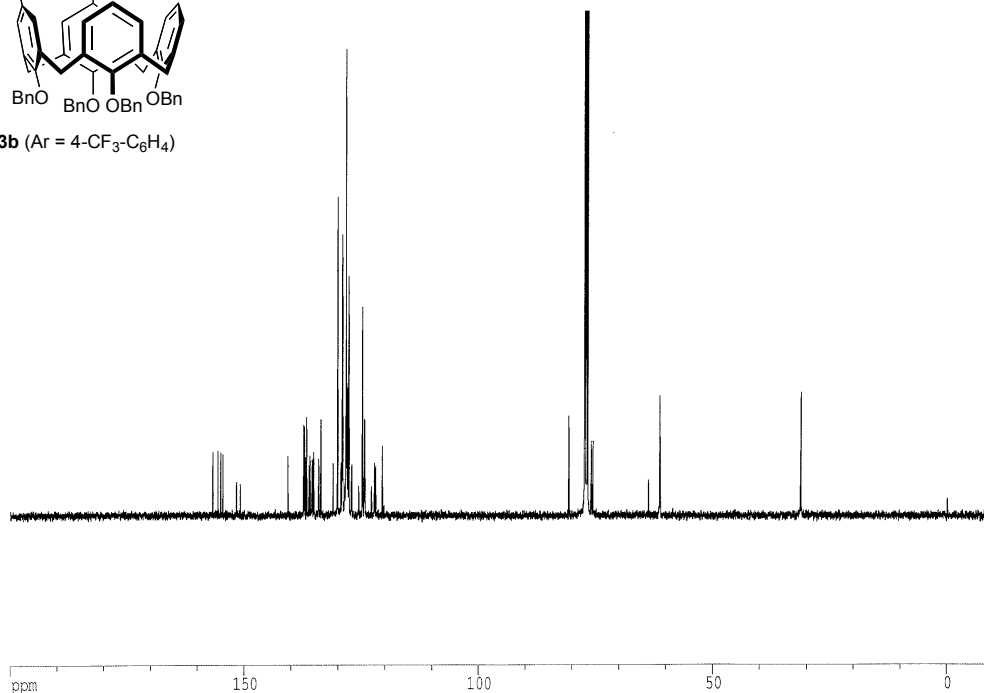
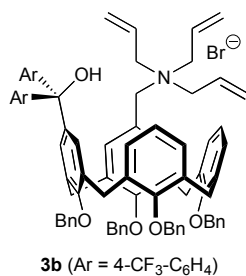
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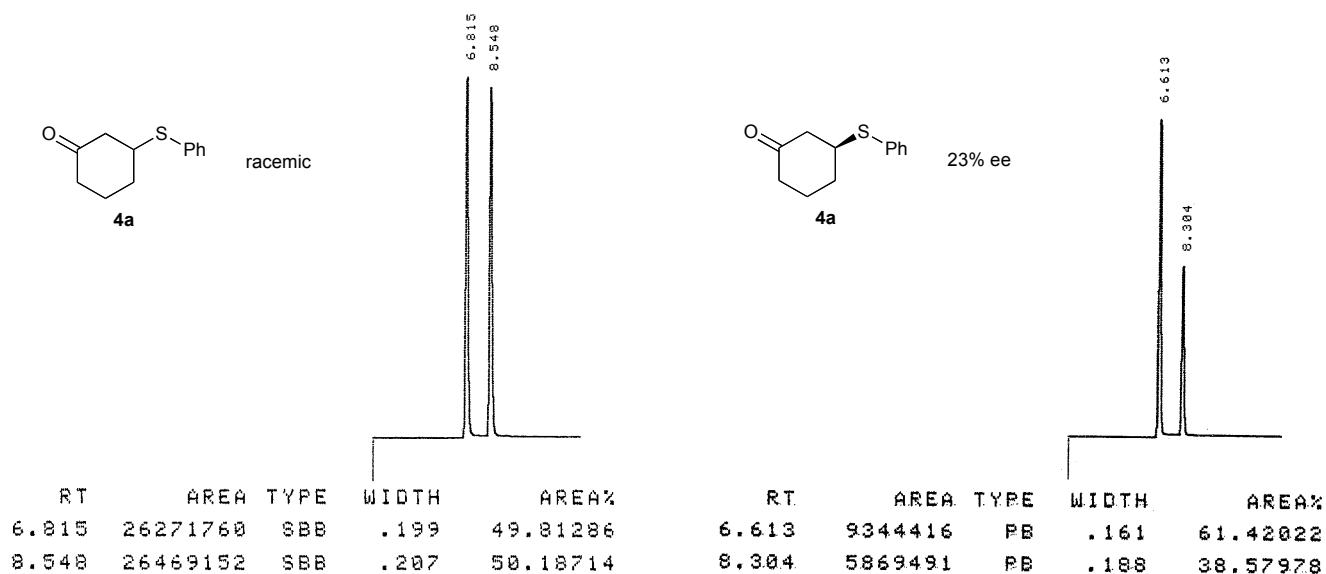
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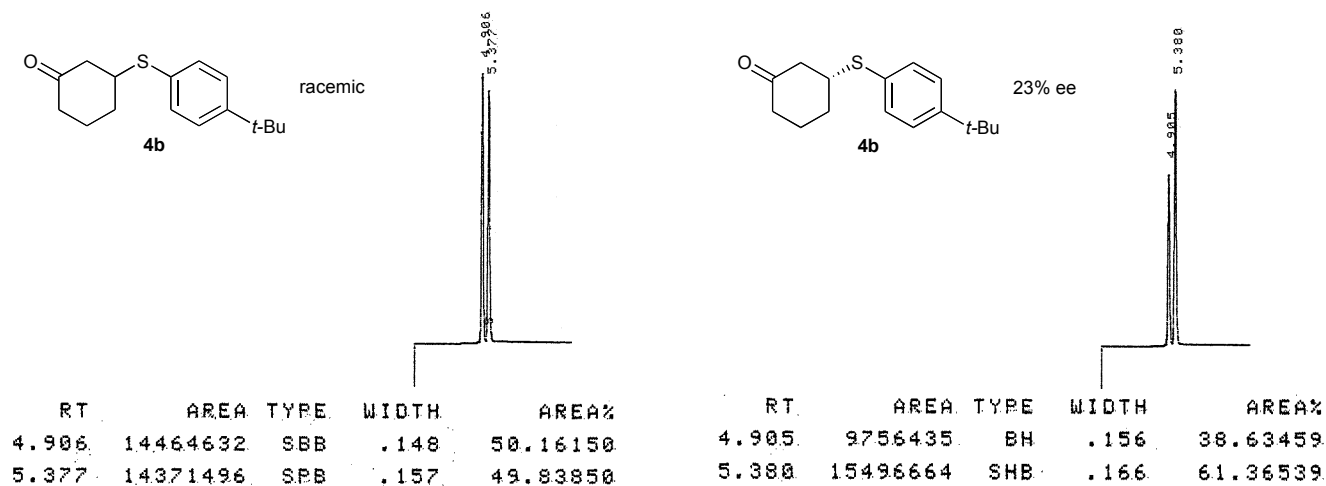
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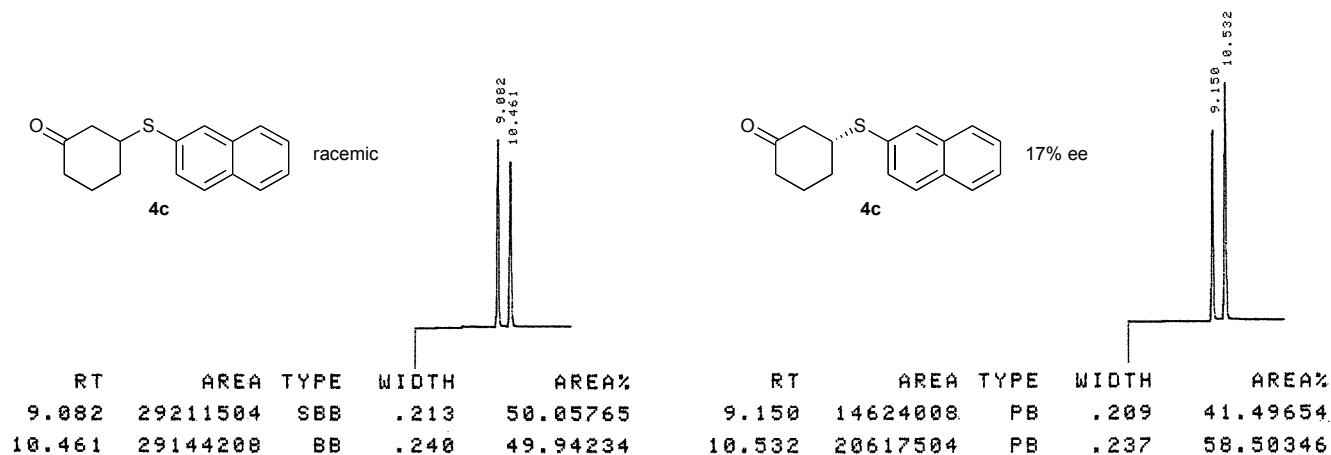
**4a:** CHIRALPAC IA, hexane/*i*-PrOH = 90/10, 1.0 ml/min



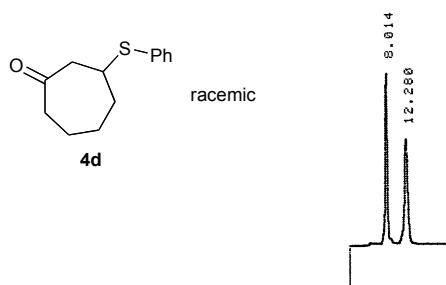
**4b:** CHIRALPAC IA, hexane/EtOH = 90/10, 1.0 ml/min



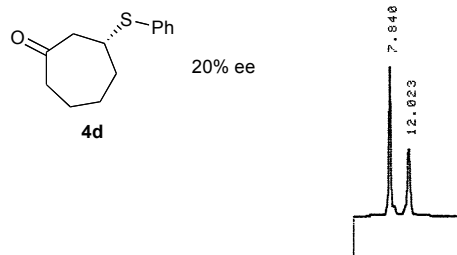
**4c:** CHIRALPAC IA, hexane/*i*-PrOH = 90/10, 1.0 ml/min



**4d:** CHIRALPAC AS, hexane/ *i*-PrOH = 50/50, 1.0 ml/min

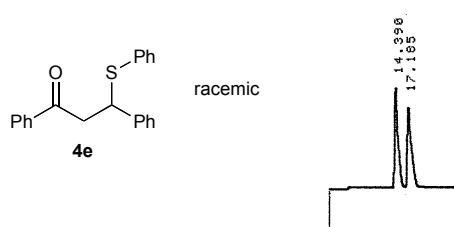


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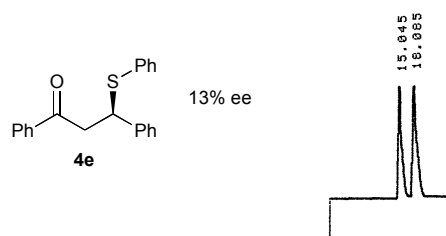


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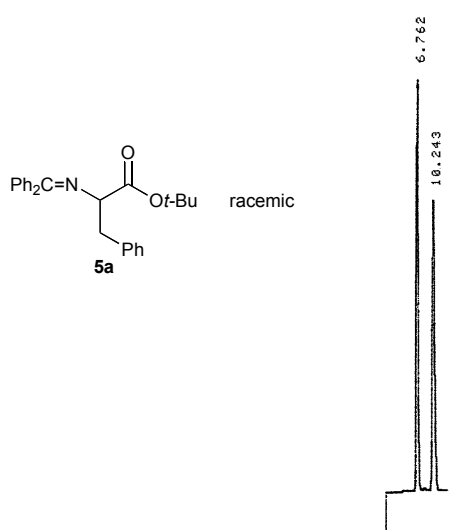


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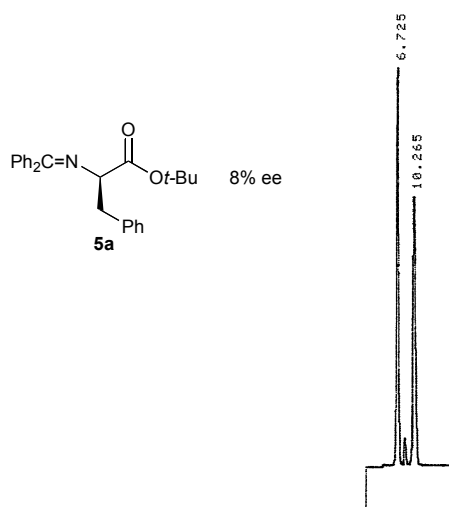


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**5a:** CHIRALCEL OD, hexane/ *i*-PrOH = 99/1, 1.0 ml/min



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**5b**: CHIRALPAC IC, hexane/*i*-PrOH = 99/1, 1.0 ml/min

