

## Kinetic resolution of 1,1'-binaphthyl-2,2'-diamine derivatives by chiral calcium phosphate catalyzed acylation

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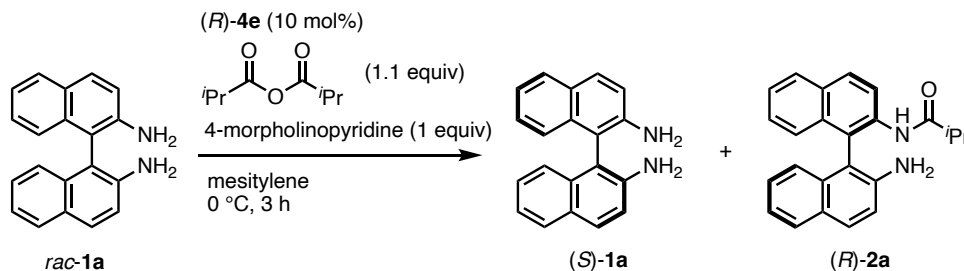
## 1. General Methods

All operations were performed under nitrogen unless otherwise noted. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F254, Art 5715, 0.25 mm) were used. Column chromatography and preparative TLC (PTLC) were performed on PSQ 60B, Fuji Silysia Chemical Ltd. and Wakogel B-5F, Wako pure Chemical Industries, respectively. NMR spectra for products data ( $^1\text{H}$  and  $^{13}\text{C}$ ) were recorded on a Bruker AVANCE-III (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ , 376 MHz for  $^{19}\text{F}$ ) and JEOL ECZ-400 (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ , 376 MHz for  $^{19}\text{F}$ ) spectrometer using  $\text{CDCl}_3$  [tetramethylsilane (0 ppm) served as an internal standard in  $^1\text{H}$  NMR and  $\text{CDCl}_3$  (77.0 ppm) in  $^{13}\text{C}$  NMR]. Chemical shifts are expressed in parts per million (ppm). ESI mass analyses were performed on Bruker micrOTOF mass spectrometer. IR spectra were recorded on a FT/IR-4200 (JASCO Co., Ltd.). High performance liquid chromatography (HPLC) was performed on a Chromaster (Hitachi High-Tech Co., Ltd.) with Daicel CHIRALCEL® (Daicel Co., Ltd.).

Solvents were distilled according to the usual procedures and stored over molecular sieves unless otherwise noted. All of the substrates were purified by distillation (for liquid) or recrystallization (for solid). Other chemicals were purchased and used as received.

## 2. Experimental section

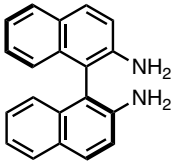
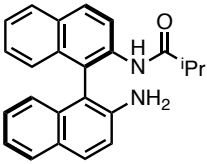
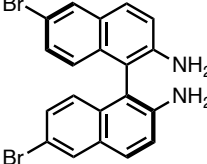
### 2-1. General procedure of kinetic resolution of BINAM derivatives (Procedure I)



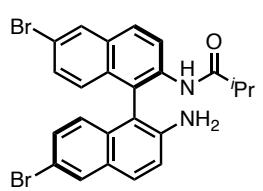
In a dried test tube, **1a** (14.2 mg, 0.05 mmol), 4-morpholinopyridine (4.2 mg, 0.025 mmol), chiral phosphate *(R)*-**4e** (10.1 mg, 0.005 mmol) were mixed in mesitylene (1 mL). The mixture was cooled to 0 °C, and isobutyric anhydride (8.3  $\mu$ L, 0.05 mmol) in mesitylene (1 mL) was added by dropwise to the mixture for 2 minutes at 0 °C. After stirred for 3 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub> aq. and extracted with EtOAc 3 times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated *in vacuo* by rotary evaporator and resulting mesitylene was removed by smart evaporator C1 (BioChromato Co., Ltd.). The crude mixture was purified by preparative TLC on SiO<sub>2</sub> (toluene: ethyl acetate = 10 : 1) to give *(S)*-**1a** and *(R)*-**2a**. The ee of the products were determined by HPLC analysis.

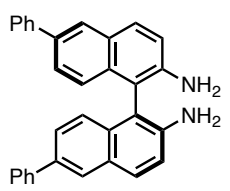
The reactions in Figure 3 were performed based on the Procedure I.

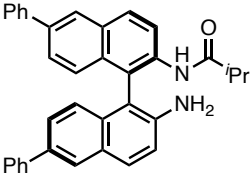
## Data of products

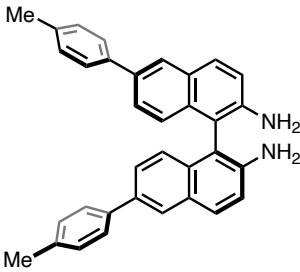
<p><b>(S)-1a</b></p>	<p>White solid.</p>
	<p><math>^1\text{H NMR}</math> (400 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 7.87 – 7.75 (m, 4H), 7.28 – 7.16 (m, 4H), 7.13 (d, <math>J</math> = 8.7 Hz, 2H), 7.11 – 7.05 (m, 2H), 3.63 (brs, 4H).</p>
	<p><math>^{13}\text{C NMR}</math> (101 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 142.7, 133.7, 129.5, 128.4, 128.1, 126.8, 123.9, 122.4, 118.3, 112.5.</p>
	<p><math>[\alpha]_{\text{D}}^{24}</math> –116.3 (c 0.35, <math>\text{CHCl}_3</math>).</p>
<p><b>(R)-2a</b></p>	<p>White solid.</p>
	<p><math>^1\text{H NMR}</math> (400 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.64 (d, <math>J</math> = 9.0 Hz, 1H), 8.00 (d, <math>J</math> = 9.1 Hz, 1H), 7.92 (dt, <math>J</math> = 8.4, 1.0 Hz, 1H), 7.86 (dd, <math>J</math> = 8.9, 0.8 Hz, 1H), 7.81 (dd, <math>J</math> = 7.6, 1.5 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.32 – 7.17 (m, 4H), 7.15 (d, <math>J</math> = 8.8 Hz, 1H), 7.08 (brs, 1H), 6.96 – 6.91 (m, 1H), 3.67 (brs, 2H), 2.13 (sept, <math>J</math> = 7.0 Hz, 1H), 0.87 (d, <math>J</math> = 7.0 Hz, 3H), 0.81 (d, <math>J</math> = 7.0 Hz, 3H).</p>
	<p><math>^{13}\text{C NMR}</math> (101 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 175.3, 142.7, 135.1, 133.5, 132.3, 131.2, 130.3, 129.2, 128.3, 128.2, 128.1, 127.3, 126.8, 125.3, 125.0, 123.6, 122.7, 120.9, 120.5, 118.0, 110.3, 36.4, 19.1, 19.0.</p>
	<p>LRMS (ESI): <math>m/z</math> = 377 [M+Na].</p>
	<p>HRMS (ESI): Calcd for <math>\text{C}_{24}\text{H}_{22}\text{NaN}_2\text{O}</math>: 377.1630. Found 377.1633.</p>
	<p><math>[\alpha]_{\text{D}}^{24}</math> +52.9 (c 0.41, <math>\text{CHCl}_3</math>).</p>
	<p>IR (neat, <math>\text{cm}^{-1}</math>): 3355, 1685, 1619, 1595, 1497, 1277, 817, 748.</p>
<p><b>(S)-1b</b></p>	<p>Ocher solid.</p>
	<p><math>^1\text{H NMR}</math> (400 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 7.93 (d, <math>J</math> = 2.1 Hz, 2H), 7.71 (dd, <math>J</math> = 8.9, 0.8 Hz, 2H), 7.26 (dd, <math>J</math> = 9.0, 2.1 Hz, 2H), 7.15 (d, <math>J</math> = 8.8 Hz, 2H), 6.89 (d, <math>J</math> = 9.0 Hz, 2H), 3.73 (brs, 4H).</p>
	<p><math>^{13}\text{C NMR}</math> (101 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 143.0, 132.1, 130.1, 130.1, 129.5, 128.8, 125.6, 119.2, 116.0, 111.8.</p>
	<p>LRMS (ESI): <math>m/z</math> = 463, 465, 467 [M+Na].</p>

	HRMS (ESI): Calcd for C <sub>20</sub> H <sub>14</sub> <sup>79</sup> Br <sup>81</sup> BrN <sub>2</sub> Na: 464.9421. Found 464.9423.
	[α] <sub>D</sub> <sup>24</sup> –13.0 (c 0.47, CHCl <sub>3</sub> ).
	IR (neat, cm <sup>-1</sup> ): 3370, 1616, 1495, 1384, 1351, 812.

<b>(R)-2b</b>	Ocher solid.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 8.66 (d, <i>J</i> = 9.1 Hz, 1H), 8.07 (d, <i>J</i> = 2.0 Hz, 1H), 7.96 (d, <i>J</i> = 2.1 Hz, 1H), 7.91 (d, <i>J</i> = 9.0 Hz, 1H), 7.77 (d, <i>J</i> = 8.8 Hz, 1H), 7.34 (dd, <i>J</i> = 9.0, 2.0 Hz, 1H), 7.26 (dd, <i>J</i> = 9.0, 2.1 Hz, 1H), 7.16 (d, <i>J</i> = 8.8 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.74 (d, <i>J</i> = 8.9 Hz, 1H), 3.71 (brs, 2H), 2.16 (sept, <i>J</i> = 6.9 Hz, 1H), 0.90 (d, <i>J</i> = 7.0 Hz, 3H), 0.86 (d, <i>J</i> = 6.9 Hz, 3H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 175.4, 143.1, 135.5, 132.2, 132.0, 130.8, 130.6, 130.28 (2C), 130.25, 129.6, 129.2, 128.5, 127.0, 125.2, 122.1, 120.1, 119.2, 118.9, 116.4, 109.6, 36.4, 19.1, 19.0.
	LRMS (ESI): <i>m/z</i> = 533, 535, 537 [M+Na].
	HRMS (ESI): Calcd for C <sub>24</sub> H <sub>20</sub> <sup>79</sup> Br <sub>2</sub> N <sub>2</sub> NaO: 532.9840. Found 532.9836.
	[α] <sub>D</sub> <sup>24</sup> –40.5 (c 0.6, CHCl <sub>3</sub> ).
	IR (neat, cm <sup>-1</sup> ): 3356, 1684, 1619, 1588, 1488, 1388, 813, 755.

<b>(S)-1c</b>	White solid.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 8.02 (d, <i>J</i> = 1.6 Hz, 2H), 7.88 (d, <i>J</i> = 8.8 Hz, 2H), 7.66 (d, <i>J</i> = 9.3 Hz, 2H), 7.50 (dd, <i>J</i> = 8.7, 1.9 Hz, 2H), 7.44 (t, <i>J</i> = 7.7 Hz, 4H), 7.32 (t, <i>J</i> = 7.4 Hz, 2H), 7.22 – 7.15 (m, 4H), 3.77 (brs, 4H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 142.9, 141.2, 135.2, 132.9, 129.9, 128.74, 128.68, 127.1, 126.8, 126.5, 126.2, 124.5, 118.8, 112.3.
	LRMS (ESI): <i>m/z</i> = 459 [M+Na].
	HRMS (ESI): Calcd for C <sub>32</sub> H <sub>24</sub> N <sub>2</sub> Na: 459.1837. Found 459.1839.
	[α] <sub>D</sub> <sup>24</sup> +50.8 (c 0.53, CHCl <sub>3</sub> ).
	IR (neat, cm <sup>-1</sup> ): 3377, 1619, 1492, 1385, 759.

<b>(R)-2c</b>	White solid.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 8.69 (d, $J$ = 9.0 Hz, 1H), 8.13 (d, $J$ = 1.9 Hz, 1H), 8.07 (d, $J$ = 9.0 Hz, 1H), 8.04 (d, $J$ = 1.9 Hz, 1H), 7.93 (d, $J$ = 8.7 Hz, 1H), 7.71 – 7.63 (m, 4H), 7.57 (dd, $J$ = 8.8, 1.9 Hz, 1H), 7.52 – 7.42 (m, 5H), 7.39 – 7.30 (m, 3H), 7.19 (d, $J$ = 8.8 Hz, 1H), 7.15 (brs, 1H), 7.05 (d, $J$ = 8.8 Hz, 1H), 3.73 (brs, 2H), 2.17 (sept, $J$ = 6.9 Hz, 1H), 0.91 (d, $J$ = 7.0 Hz, 3H), 0.86 (d, $J$ = 6.9 Hz, 3H).
	$^{13}\text{C NMR}$ (101 MHz, $\text{CDCl}_3$ ) $\delta$ 175.4, 142.9, 140.9, 140.8, 137.8, 135.4, 135.2, 132.8, 131.5, 131.5, 130.7, 129.6, 128.84, 128.81, 128.4, 127.31, 127.25, 127.0, 126.9, 126.5, 126.2, 125.9, 124.2, 121.4, 120.3, 118.4, 110.1, 36.5, 19.1, 19.0.
	LRMS (ESI): $m/z$ = 529 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{36}\text{H}_{30}\text{N}_2\text{NaO}$ : 529.2256. Found 529.2253.
	$[\alpha]_{\text{D}}^{24}$ –98.3 (c 0.6, $\text{CHCl}_3$ ).
IR (neat, $\text{cm}^{-1}$ ): 1684, 1599, 1489, 757, 697.	

<b>(S)-1d</b>	White solid.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 7.99 (d, $J$ = 1.9 Hz, 2H), 7.87 (d, $J$ = 8.7 Hz, 2H), 7.56 (d, $J$ = 8.2 Hz, 4H), 7.48 (dd, $J$ = 8.8, 1.9 Hz, 2H), 7.29 – 7.22 (m, 4H), 7.18 (d, $J$ = 8.8 Hz, 4H), 3.76 (brs, 4H), 2.39 (s, 6H).
	$^{13}\text{C NMR}$ (101 MHz, $\text{CDCl}_3$ ) $\delta$ 142.7, 138.4, 136.6, 135.1, 132.8, 129.8, 129.5, 128.7, 126.9, 126.4, 125.8, 124.4, 118.7, 112.4, 21.1.
	LRMS (ESI): $m/z$ = 487 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{Na}$ : 487.2150. Found 487.2148.
	$[\alpha]_{\text{D}}^{24}$ +116.8 (c 0.53, $\text{CHCl}_3$ ).
IR (neat, $\text{cm}^{-1}$ ): 3374, 1620, 1496, 1385, 1360, 814, 755.	

<b>(R)-2d</b>	White solid.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 8.67 (d, $J$ = 9.0 Hz, 1H), 8.10 (d, $J$ = 1.9 Hz, 1H), 8.05 (d, $J$ = 9.0 Hz, 1H), 8.01 (d, $J$ = 1.9 Hz, 1H), 7.95 – 7.87 (m, 1H), 7.63 – 7.52 (m,

	<p><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 5H), 7.48 (dd, <math>J = 8.8, 1.9</math> Hz, 1H), 7.33 (d, <math>J = 8.8</math> Hz, 1H), 7.29 – 7.23 (m, 4H), 7.17 (d, <math>J = 8.8</math> Hz, 1H), 7.14 (brs, 1H), 7.03 (d, <math>J = 8.7</math> Hz, 1H), 3.73 (brs, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 2.16 (sept, <math>J = 6.9</math> Hz, 1H), 0.90 (d, <math>J = 6.9</math> Hz, 3H), 0.85 (d, <math>J = 6.9</math> Hz, 3H).</p>
	<p><math>^{13}\text{C}</math> NMR (101 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 175.4, 142.7, 138.0, 137.9, 137.7, 137.1, 136.8, 135.4, 135.0, 132.6, 131.5, 131.4, 130.6, 129.6, 129.54, 129.47, 128.4, 127.1, 126.8, 126.5, 125.9, 125.8, 124.1, 121.3, 120.4, 118.4, 110.2, 36.5, 21.11, 21.09, 19.1, 19.0.</p>
	<p>LRMS (ESI): <math>m/z = 557</math> [<math>\text{M} + \text{Na}</math>].</p>
	<p>HRMS (ESI): Calcd for <math>\text{C}_{38}\text{H}_{34}\text{N}_2\text{NaO}</math>: 557.2569. Found 557.2566.</p>
	<p><math>[\alpha]_{\text{D}}^{24} -191.8</math> (c 0.63, <math>\text{CHCl}_3</math>).</p>
	<p>IR (neat, <math>\text{cm}^{-1}</math>): 3387, 1684, 1598, 1488, 814, 756.</p>

<p><b>(S)-1e</b></p>	<p>Ocher solid.</p>
	<p><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 7.96 (d, <math>J = 2.0</math> Hz, 2H), 7.90 – 7.85 (m, 2H), 7.64 – 7.58 (m, 4H), 7.43 (dd, <math>J = 8.7, 2.0</math> Hz, 2H), 7.19 (t, <math>J = 8.4</math> Hz, 4H), 7.12 (t, <math>J = 8.7</math> Hz, 4H), 3.78 (brs, 4H).</p>
	<p><math>^{13}\text{C}</math> NMR (101 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 162.2 (d, <math>J = 245.8</math> Hz), 142.9, 137.3 (d, <math>J = 3.3</math> Hz), 134.2, 132.8, 129.9, 128.6, 128.5 (d, <math>J = 8.0</math> Hz), 126.2 (d, <math>J = 27.6</math> Hz), 124.5, 118.9, 115.7, 115.5, 112.2.</p>
	<p>LRMS (ESI): <math>m/z = 495</math> [<math>\text{M} + \text{Na}</math>].</p>
	<p>HRMS (ESI): Calcd for <math>\text{C}_{32}\text{H}_{22}\text{F}_2\text{N}_2\text{Na}</math>: 495.1649. Found 495.1651.</p>
	<p><math>[\alpha]_{\text{D}}^{24} +54.8</math> (c 0.46, <math>\text{CHCl}_3</math>).</p>
	<p>IR (neat, <math>\text{cm}^{-1}</math>): 3370, 1620, 1497, 1386, 1223, 1157, 822, 754.</p>

<p><b>(R)-2e</b></p>	<p>Ocher solid.</p>
	<p><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.69 (d, <math>J = 9.0</math> Hz, 1H), 8.09 – 8.04 (m, 2H), 7.98 (d, <math>J = 2.0</math> Hz, 1H), 7.92 (dd, <math>J = 8.9, 0.7</math> Hz, 1H), 7.68 – 7.57 (m, 4H), 7.50 (dd, <math>J = 8.8, 1.9</math> Hz, 1H), 7.43 (dd, <math>J = 8.7, 2.0</math> Hz, 1H), 7.32 (d, <math>J = 8.7</math> Hz, 1H), 7.20 (d, <math>J = 8.7</math> Hz, 1H), 7.18 – 7.10 (m, 5H), 7.03 (d, <math>J = 8.7</math> Hz, 1H), 3.74 (brs, 2H), 2.17 (sept, <math>J</math></p>

	= 6.9 Hz, 1H), 0.91 (d, $J = 7.0$ Hz, 3H), 0.86 (d, $J = 6.9$ Hz, 3H).
	$^{13}\text{C}$ NMR (101 MHz, $\text{CDCl}_3$ ) $\delta$ 175.4, 162.5 (d, $J = 246.6$ Hz), 162.3 (d, $J = 246.2$ Hz), 142.9, 137.0 (d, $J = 3.2$ Hz), 136.9 (d, $J = 3.3$ Hz), 136.8, 135.3, 134.5, 132.7, 131.48, 131.45, 130.7, 129.5, 128.8 (d, $J = 8.1$ Hz), 128.5 (d, $J = 8.0$ Hz), 128.4, 126.8, 126.4, 126.0, 124.3, 121.5, 120.3, 118.5, 115.8 (d, $J = 21.4$ Hz), 115.7 (d, $J = 21.4$ Hz), 110.1, 36.5, 19.2, 19.0.
	LRMS (ESI): $m/z = 565$ [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{36}\text{H}_{28}\text{F}_2\text{N}_2\text{NaO}$ : 565.2067. Found 565.2071.
	$[\alpha]_{\text{D}}^{24} -101.5$ (c 0.45, $\text{CHCl}_3$ ).
IR (neat, $\text{cm}^{-1}$ ): 3392, 1683, 1604, 1518, 1289, 1226, 822.	

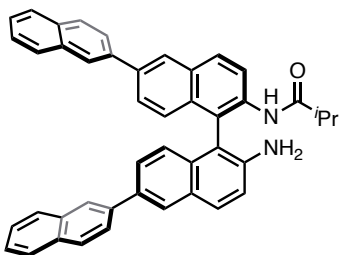
<b>(S)-1f</b>	Ocher solid.
	$^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ) $\delta$ 7.96 (d, $J = 2.0$ Hz, 2H), 7.89 – 7.83 (m, 2H), 7.59 (d, $J = 8.8$ Hz, 4H), 7.46 (dd, $J = 8.7, 2.0$ Hz, 2H), 7.22 – 7.15 (m, 4H), 6.99 (d, $J = 8.8$ Hz, 4H), 3.85 (s, 6H), 3.75 (brs, 4H).
	$^{13}\text{C}$ NMR (101 MHz, $\text{CDCl}_3$ ) $\delta$ 158.8, 142.6, 134.8, 133.8, 132.6, 129.7, 128.8, 128.1, 126.3, 125.5, 124.5, 118.7, 114.2, 112.4, 55.3.
	LRMS (ESI): $m/z = 519$ [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{NaO}$ : 519.2048. Found 519.2046.
	$[\alpha]_{\text{D}}^{24} -44.1$ (c 0.32, $\text{CHCl}_3$ ).
IR (neat, $\text{cm}^{-1}$ ): 1608, 1519, 1245, 1180, 1040, 821.	

<b>(R)-2f</b>	Ocher solid.
	$^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ) $\delta$ 8.67 (d, $J = 9.0$ Hz, 1H), 8.07 (d, $J = 1.9$ Hz, 1H), 8.05 (d, $J = 9.1$ Hz, 1H), 7.98 (d, $J = 1.9$ Hz, 1H), 7.91 (d, $J = 8.8$ Hz, 1H), 7.65 – 7.57 (m, 4H), 7.53 (dd, $J = 8.8, 1.9$ Hz, 1H), 7.46 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.32 (d, $J = 8.7$ Hz, 1H), 7.18 (d, $J = 8.8$ Hz, 1H), 7.14 (s, 1H), 7.05 – 6.96 (m, 5H), 3.86 (s, 3H), 3.85 (s, 3H), 3.72 (brs, 2H), 2.17 (sept, $J = 6.9$ Hz, 1H), 0.91 (d, $J = 6.9$ Hz, 3H), 0.86 (d, $J = 6.9$ Hz, 3H).

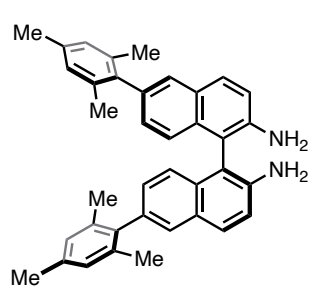


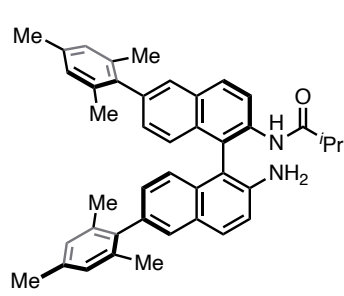
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 175.4, 159.2, 159.0, 142.7, 137.4, 135.1, 134.9, 133.5, 133.4, 132.5, 131.6, 131.2, 130.6, 129.4, 128.5, 128.3, 128.1, 126.8, 126.4, 125.9, 125.5, 125.4, 124.2, 121.4, 120.4, 118.4, 114.35, 114.31, 110.3, 55.4 (2C), 36.5, 19.2, 19.0.
	LRMS (ESI): <i>m/z</i> = 589 [M+Na].
	HRMS (ESI): Calcd for C <sub>38</sub> H <sub>34</sub> N <sub>2</sub> NaO <sub>3</sub> : 589.2467. Found 589.2471.
	[α] <sub>D</sub> <sup>24</sup> -106.3 (c 0.27, CHCl <sub>3</sub> ).
	IR (neat, cm <sup>-1</sup> ): 1684, 1608, 1519, 1488, 1283, 1247, 821.

<b>(S)-1g</b>	White solid.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 8.16 (d, <i>J</i> = 1.9 Hz, 2H), 8.10 (d, <i>J</i> = 1.8 Hz, 2H), 7.95 – 7.81 (m, 10H), 7.64 (dd, <i>J</i> = 8.7, 2.0 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.26 (d, <i>J</i> = 8.9 Hz, 2H), 7.21 (d, <i>J</i> = 8.8 Hz, 2H), 3.80 (s, 4H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 143.0, 138.5, 135.0, 133.8, 133.0, 132.4, 130.0, 128.8, 128.4, 128.1, 127.6, 126.6, 126.5, 126.2, 125.7, 125.6, 125.5, 124.6, 118.8, 112.3.
	LRMS (ESI): <i>m/z</i> = 559 [M+Na].
	HRMS (ESI): Calcd for C <sub>40</sub> H <sub>28</sub> N <sub>2</sub> Na: 559.2150. Found 559.2147.
	[α] <sub>D</sub> <sup>24</sup> +209.7 (c 0.56, CHCl <sub>3</sub> ).
	IR (neat, cm <sup>-1</sup> ): 3376, 1618, 1483, 1385, 817, 748.

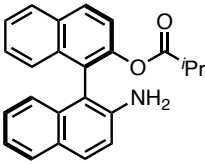
<b>(S)-2g</b>	White solid.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 8.73 (d, <i>J</i> = 9.0 Hz, 1H), 8.27 (d, <i>J</i> = 1.9 Hz, 1H), 8.18 (d, <i>J</i> = 1.9 Hz, 1H), 8.15 – 8.09 (m, 3H), 8.01 – 7.81 (m, 9H), 7.71 (dd, <i>J</i> = 8.8, 1.9 Hz, 1H), 7.64 (dd, <i>J</i> = 8.8, 2.0 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.40 (d, <i>J</i> = 8.7 Hz, 1H), 7.22 (d, <i>J</i> = 8.8 Hz, 1H), 7.19 (s, 1H), 7.11 (d, <i>J</i> = 8.7 Hz, 1H), 3.79 (s, 2H), 2.19 (sept, <i>J</i> = 6.9 Hz, 1H), 0.93 (d, <i>J</i> = 6.9 Hz, 3H), 0.89 (d, <i>J</i> = 6.9 Hz, 3H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 175.4, 143.0, 138.2, 138.1, 137.7, 135.3, 133.74,

	133.70, 132.9, 132.6, 132.5, 131.63, 131.55, 130.8, 129.6, 128.54, 128.47, 128.2, 128.1, 127.7, 127.6, 127.1, 126.7, 126.5, 126.34, 126.30, 126.1, 125.99, 125.96, 125.8, 125.6, 125.54, 125.47, 124.3, 121.5, 120.4, 118.5, 110.2, 36.5, 19.2, 19.0.
	LRMS (ESI): $m/z = 629$ [M+Na].
	HRMS (ESI): Calcd for C <sub>44</sub> H <sub>34</sub> N <sub>2</sub> NaO: 629.2569. Found 629.2571.
	$[\alpha]_D^{24} -207.9$ (c 0.57, CHCl <sub>3</sub> ).
	IR (neat, cm <sup>-1</sup> ): 1685, 1619, 1594, 1507, 1486, 818, 747.

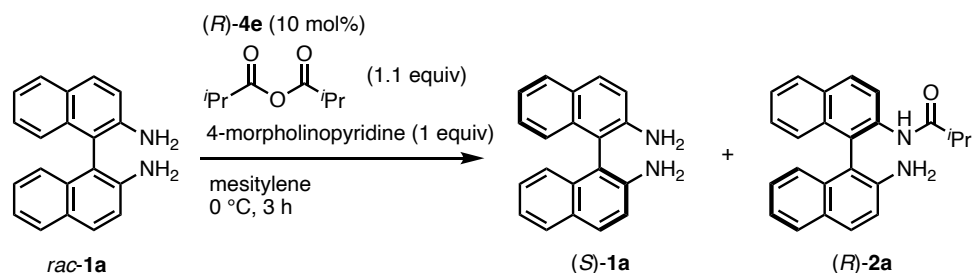
<b>(S)-1h</b>	White solid.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 7.79 (d, $J = 8.8$ Hz, 2H), 7.55 (d, $J = 1.7$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.7$ Hz, 2H), 7.06 (dd, $J = 8.5, 1.7$ Hz, 2H), 6.95 (s, 4H), 3.77 (s, 4H), 2.34 (s, 6H), 2.05 (s, 12H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) <sup>13</sup> C NMR (101 MHz, Chloroform- <i>d</i> ) δ 142.5, 139.0, 136.5, 136.42, 136.37, 135.0, 132.4, 129.4, 128.9, 128.6, 128.2, 128.04, 128.00, 123.9, 118.4, 112.8, 21.01, 20.99, 20.96.
	LRMS (ESI): $m/z = 543$ [M+Na].
	HRMS (ESI): Calcd for C <sub>38</sub> H <sub>36</sub> N <sub>2</sub> Na: 543.2776. Found 543.2775.
	$[\alpha]_D^{24} -37.4$ (c 0.6, CHCl <sub>3</sub> ).
	IR (neat, cm <sup>-1</sup> ): 3376, 1611, 1488, 1381, 754.

<b>(R)-2h</b>	White solid.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 8.67 (d, $J = 9.0$ Hz, 1H), 7.98 (d, $J = 9.0$ Hz, 1H), 7.84 (d, $J = 8.8$ Hz, 1H), 7.68 (d, $J = 1.7$ Hz, 1H), 7.58 (d, $J = 1.6$ Hz, 1H), 7.45 (d, $J = 8.6$ Hz, 1H), 7.22 – 7.03 (m, 5H), 6.97 (s, 2H), 6.96 (s, 2H), 3.73 (s, 2H), 2.34 (s, 3H), 2.34 (s, 3H), 2.15 (sept, $J = 6.9$ Hz, 1H), 2.05 (s, 6H), 2.04 (s, 3H), 1.98 (s, 3H), 0.87 (d, $J = 6.9$ Hz, 3H), 0.76 (d, $J = 7.0$ Hz, 3H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 175.1, 142.7, 138.8, 138.6, 137.8, 136.7, 136.6, 136.32, 136.27, 136.14, 136.13, 135.4, 134.9, 132.1, 131.3, 130.9, 130.3, 129.4, 129.1,

	129.0, 128.34, 128.30, 128.13, 128.11, 128.08, 128.0, 125.3, 123.6, 121.0, 120.5, 118.2, 110.5, 36.5, 21.0 (2C), 20.94 (2C), 20.92, 20.7, 19.2, 18.8.
	LRMS (ESI): $m/z = 613$ [M+Na].
	HRMS (ESI): Calcd for $C_{42}H_{42}N_2NaO$ : 613.3195. Found 613.3193.
	$[\alpha]_D^{24} -17.3$ (c 0.59, $CHCl_3$ ).
	IR (neat, $cm^{-1}$ ): 3392, 1685, 1596, 1487, 1280, 755.

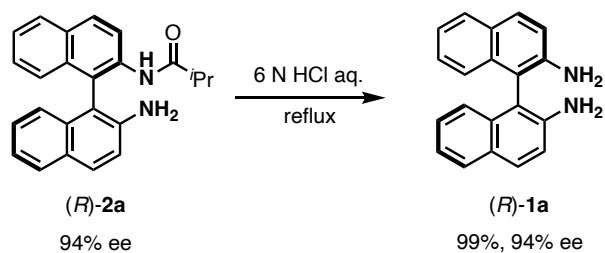
( <i>R</i> )- <b>2i</b>	White solid.
	$^1H$ NMR (400 MHz, $CDCl_3$ ) $\delta$ 8.02 (d, $J = 8.9$ Hz, 1H), 7.96 (d, $J = 8.2$ Hz, 1H), 7.80 – 7.72 (m, 2H), 7.49 (ddd, $J = 8.2, 6.5, 1.5$ Hz, 1H), 7.42 – 7.33 (m, 3H), 7.24 – 7.16 (m, 3H), 7.07 (d, $J = 8.8$ Hz, 1H), 7.02 – 6.96 (m, 1H), 3.62 (brs, 2H), 2.35 (sept, $J = 6.9$ Hz, 1H), 0.72 (d, $J = 7.0$ Hz, 3H), 0.61 (d, $J = 7.0$ Hz, 3H).
	$^{13}C$ NMR (101 MHz, $CDCl_3$ ) $\delta$ 175.8, 147.4, 142.6, 133.9, 133.1, 132.2, 129.7, 129.4, 128.3, 127.9, 127.8, 127.0, 126.5, 125.92, 125.88, 125.5, 124.0, 122.2, 122.1, 118.2, 111.9, 33.8, 18.3, 18.1.
	LRMS (ESI): $m/z = 378$ [M+Na].
	HRMS (ESI): Calcd for $C_{24}H_{21}NNaO_2$ : 378.1470. Found 378.1472.
	IR (neat, $cm^{-1}$ ): 1749, 1623, 1507, 1215, 1137, 810, 749.

## 2-2. 1 mmol scale experiment



In a dried test tube, **1a** (284.4 mg, 1 mmol), 4-morpholinopyridine (85.1 mg, 1 mmol), chiral phosphate *(R)*-**4e** (202.4 mg, 0.1 mmol) were mixed in mesitylene (20 mL). The mixture was cooled to 0 °C, and isobutyric anhydride (166  $\mu$ L, 1.1 mmol) in mesitylene (20 mL) was added to the mixture by dropwise for 2 minutes at 0 °C. After stirred for 3 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub> aq. and extracted with EtOAc 3 times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated *in vacuo* by rotary evaporator and resulting mesitylene was removed by smart evaporator C1 (BioChromato Co., Ltd.). The crude mixture was purified by preparative TLC on SiO<sub>2</sub> (toluene: ethyl acetate = 10 : 1) to give *(S)*-**1a** and *(R)*-**2a**. The ee of the products were determined by HPLC analysis.

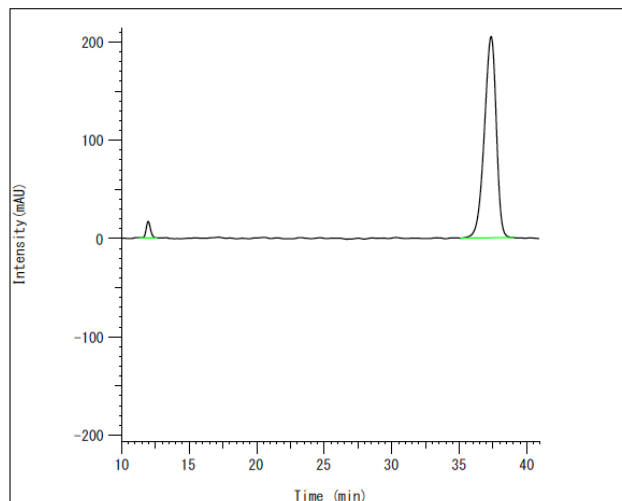
### 2-3. Hydrolysis of (*R*)-2a



In a test tube, (*R*)-2a (17.7 mg, 0.05 mmol) was treated with 6 M HCl aq. (2 mL). After the mixture was refluxed stirred for 30 min, NaOH aq. was added and the alkaline solution was extracted with ethyl acetate for 3 times. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by preparative TLC on SiO<sub>2</sub> (toluene: ethyl acetate = 10 : 1) to give the deprotected product (*R*)-1a (14.1 mg, 0.0495 mmol) in 99% with 94% ee.

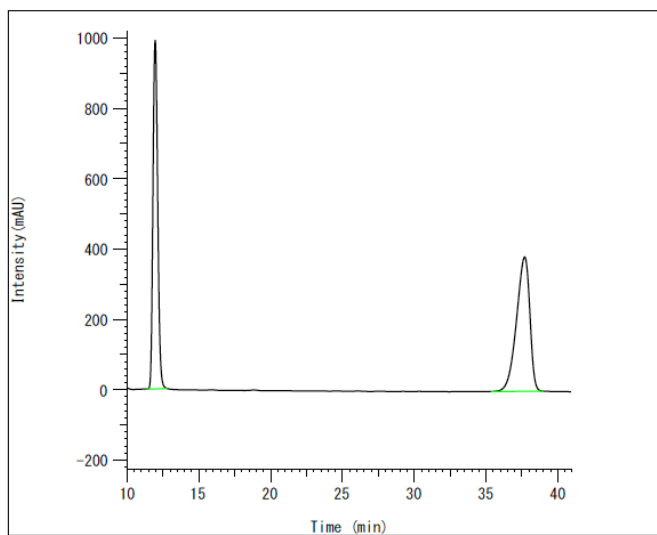
### 3. HPLC data

#### 1a



No. Compounds	RT	Area	Area%
1 Peak 1	11.967	376775	2.903
2 Peak 2	37.353	12600372	97.097
		12977147	100.000

#### Racemate

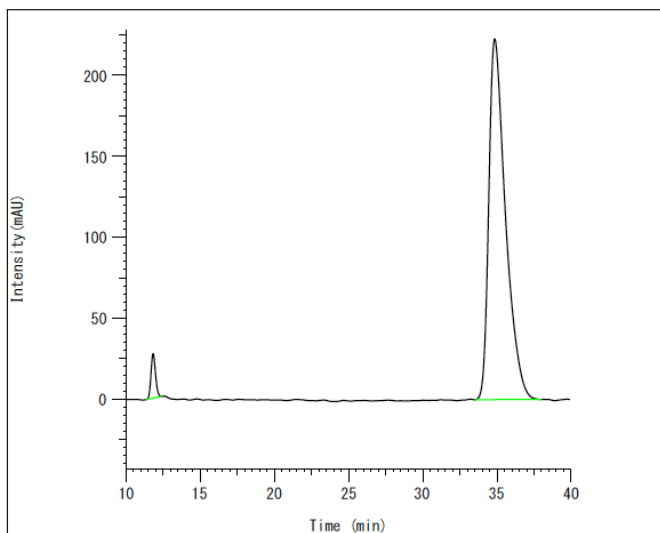


No. Compounds	RT	Area	Area%
1 Peak 1	11.960	22742101	48.001
2 Peak 2	37.687	24636372	51.999
		47378473	100.000

HPLC: CHIRALPAK® AD-H (4.6 x 250 mm), hexane/2-propanol = 4/1, 0.5 mL/min, 254 nm.

Retention time:  $t_{\text{minor}} = 12.0 \text{ min.}$ ,  $t_{\text{major}} = 37.4 \text{ min.}$

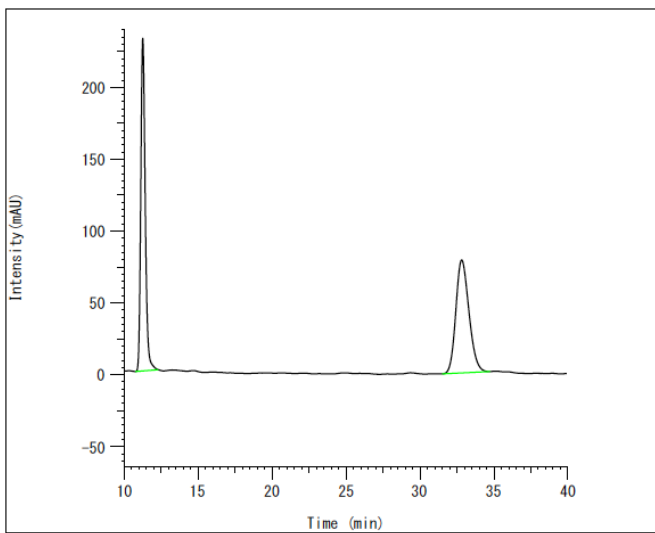
2a



5430 Diode Array Detector SampleID:2 yk\_536\_mono (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	11.827	578563	3.212
2 Peak 2	34.847	17433723	96.788
		18012287	100.000

Racemate



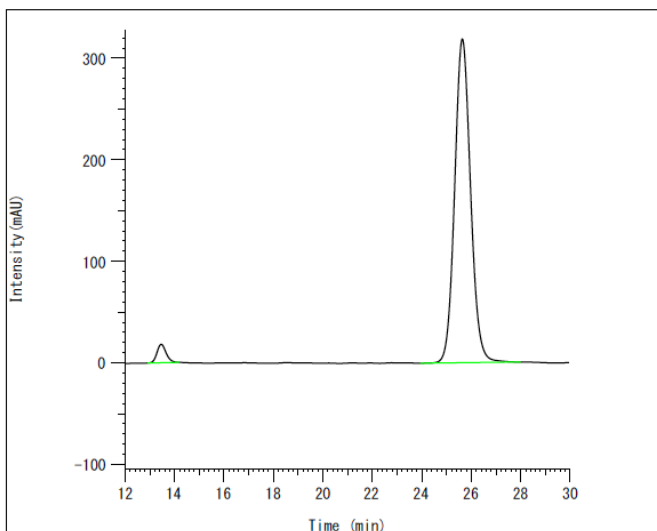
5430 Diode Array Detector SampleID:2 yk\_521\_mono (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	11.253	4838654	50.009
2 Peak 2	32.820	4837001	49.991
		9675655	100.000

HPLC: CHIRALPAK® AD-H (4.6 x 250 mm), hexane/2-propanol = 4/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{minor}} = 11.8 \text{ min.}$ ,  $t_{\text{major}} = 34.8 \text{ min.}$

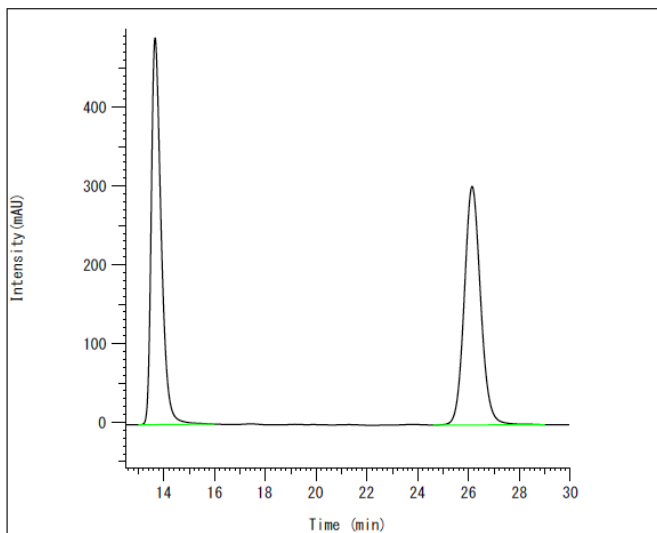
1b



5430 Diode Array Detector SampleID:1 yk\_539\_binam (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	13.460	467005	3.174
2 Peak 2	25.640	14248681	96.826
		14715686	100.000

Racemate



5430 Diode Array Detector SampleID:1 yk\_528\_binam (Extract, 254nm) Repeat:1

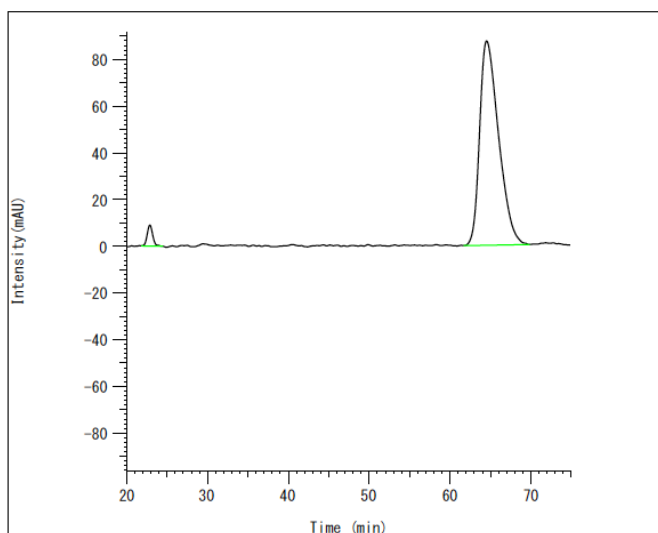
No. Compounds	RT	Area	Area%
1 Peak 1	13.660	13271758	49.478
2 Peak 2	26.133	13552022	50.522
		26823780	100.000

HPLC: CHIRALPAK® AD-H (4.6 x 250 mm), hexane/2-propanol = 4/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{minor}} = 13.5 \text{ min.}$ ,  $t_{\text{major}} = 25.6 \text{ min.}$



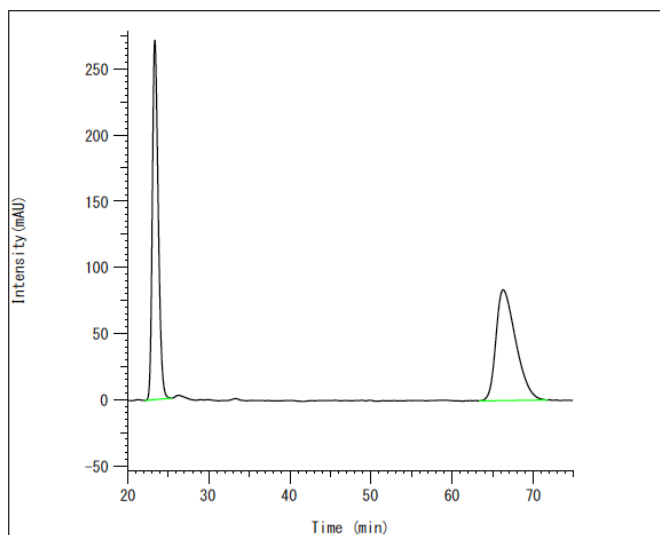
2b



5430 Diode Array Detector SampleID:2 yk\_539\_mono (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	22.867	424308	2.889
2 Peak 2	64.507	14263139	97.111
		14687447	100.000

Racemate



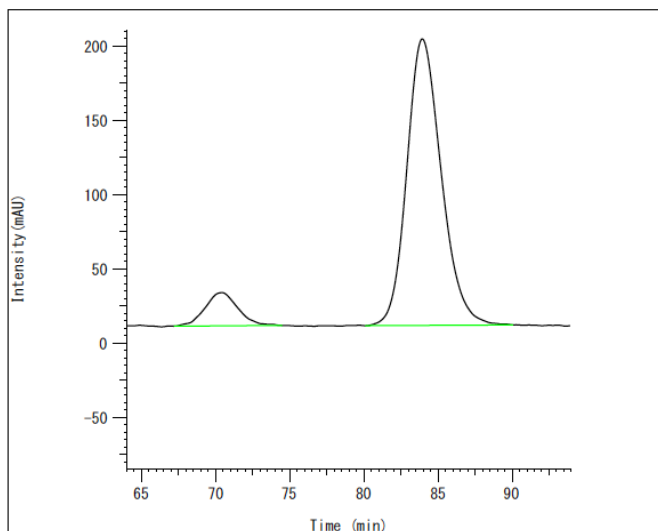
5430 Diode Array Detector SampleID:1 yk\_528\_mono (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	23.347	13716825	49.121
2 Peak 2	66.300	14207466	50.879
		27924290	100.000

HPLC: CHIRALPAK® AD-H (4.6 x 250 mm), hexane/2-propanol = 4/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{minor}} = 22.3 \text{ min.}$ ,  $t_{\text{major}} = 64.5 \text{ min.}$

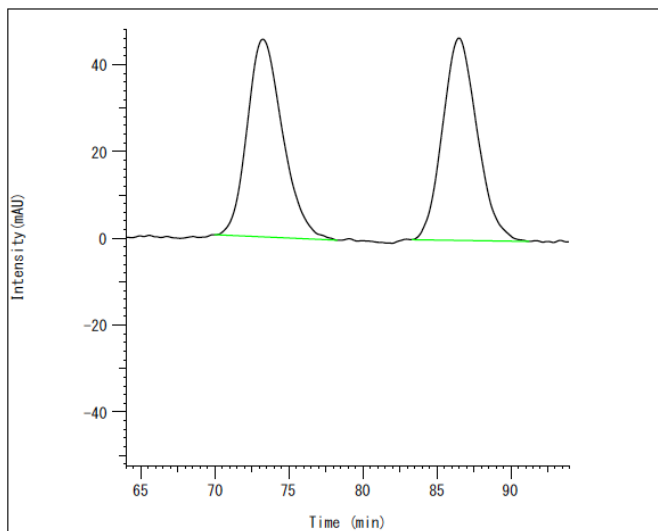
1c



5430 Diode Array Detector SampleID:1 yk\_573\_binam (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	70.427	3452421	9.953
2 Peak 2	83.940	31234445	90.047
		34686867	100.000

Racemate



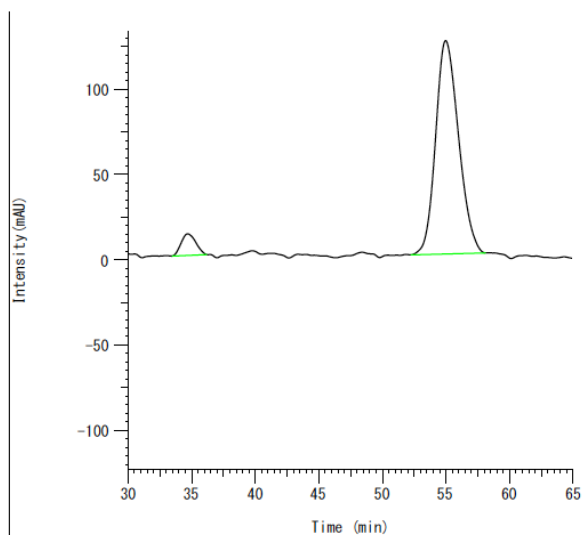
5430 Diode Array Detector SampleID:3 yk\_538\_binam (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	73.240	7606351	49.987
2 Peak 2	86.493	7610443	50.013
		15216793	100.000

HPLC: CHIRALPAK® AD-H (4.6 x 250 mm), hexane/2-propanol = 4/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{minor}} = 70.4 \text{ min.}$ ,  $t_{\text{major}} = 83.9 \text{ min.}$

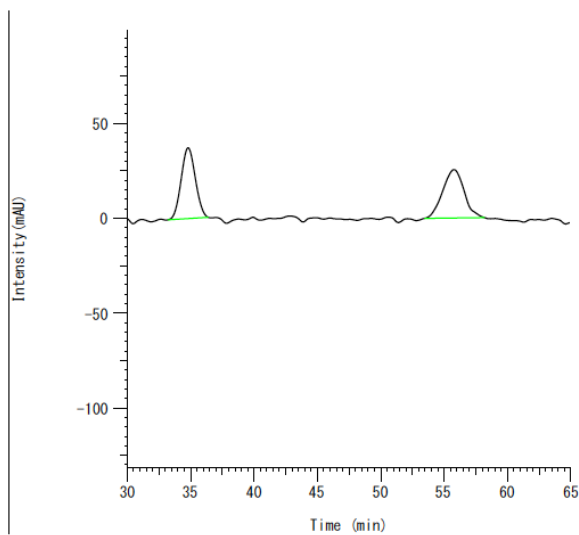
2c



5430 Diode Array Detector SampleID:4 yk\_573\_mono (Extract, 230nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	34.673	1014020	6.065
2 Peak 2	54.980	15705235	93.935
		16719255	100.000

Racemate



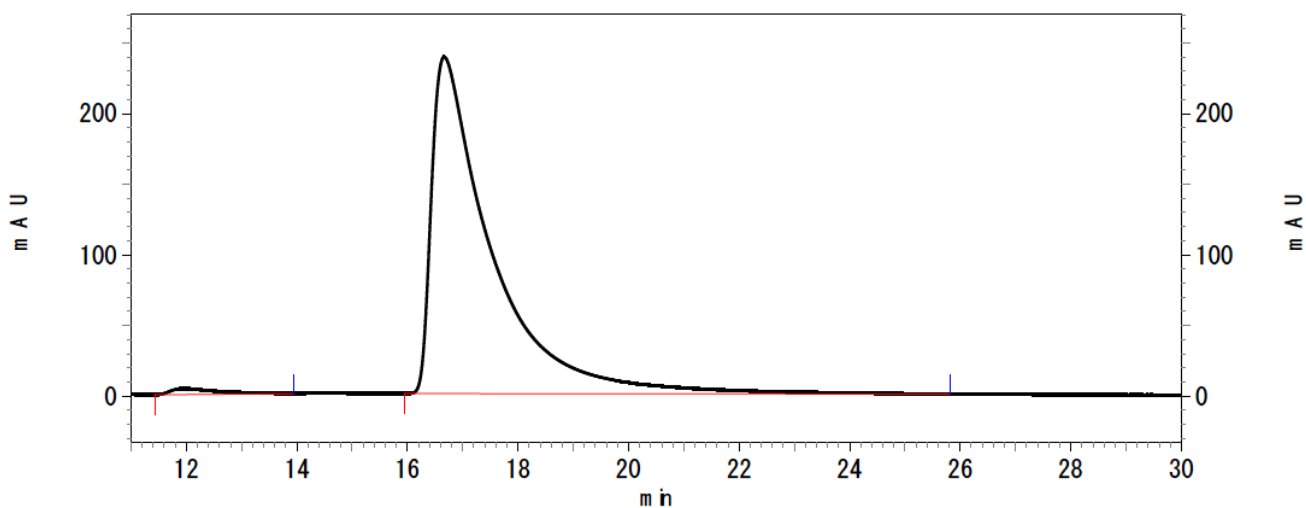
5430 Diode Array Detector SampleID:3 yk\_538\_mono (Extract, 230nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	34.800	2901866	49.309
2 Peak 2	55.787	2983214	50.691
		5885080	100.000

HPLC: CHIRALPAK® AD-H (4.6 x 250 mm), hexane/2-propanol = 4/1, 1.0 mL/min, 230 nm.

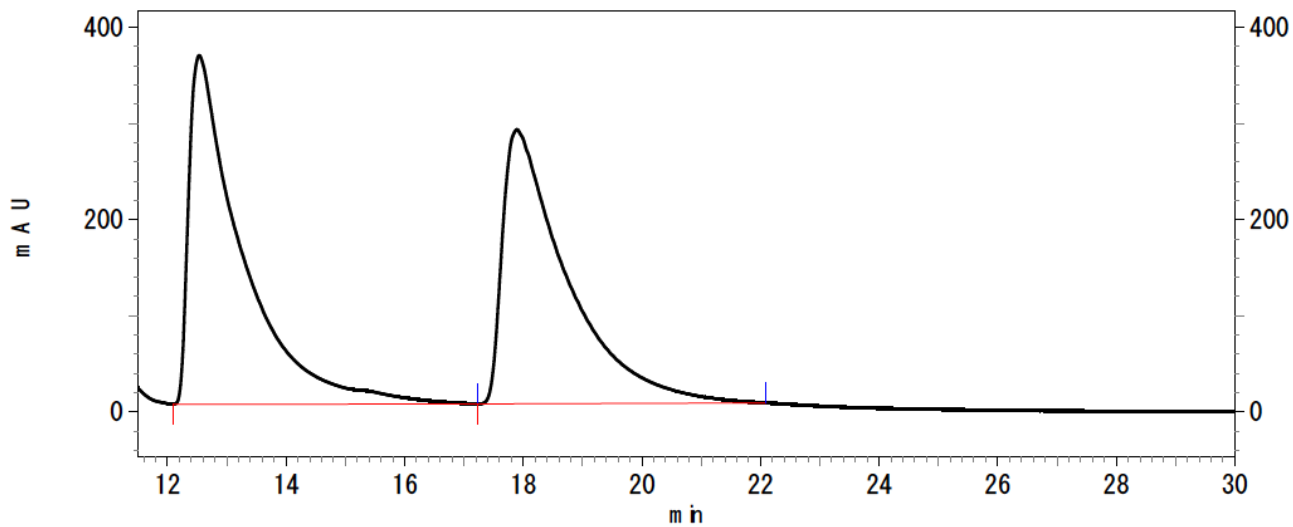
Retention time:  $t_{\text{minor}} = 34.7$  min.,  $t_{\text{major}} = 55.0$  min.

1d



Pk #	Retention time	Area	Area%	Baseline code
1	11.960	1024154	1.404	BB
2	16.667	71935349	98.596	BB

Racemate

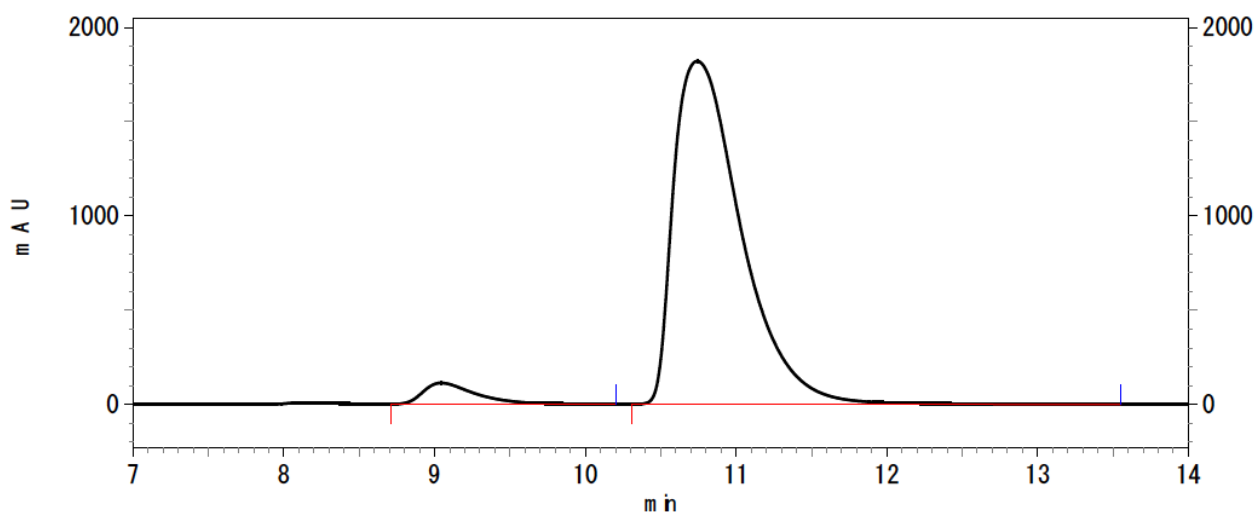


Pk #	Retention time	Area	Area%	Baseline code
1	12.533	90080115	51.232	BB
2	17.893	85747059	48.768	BB

HPLC: CHIRALPAK® IA-3 (4.6 x 250 mm), hexane/2-propanol = 100/1, 0.5 mL/min, 254 nm.

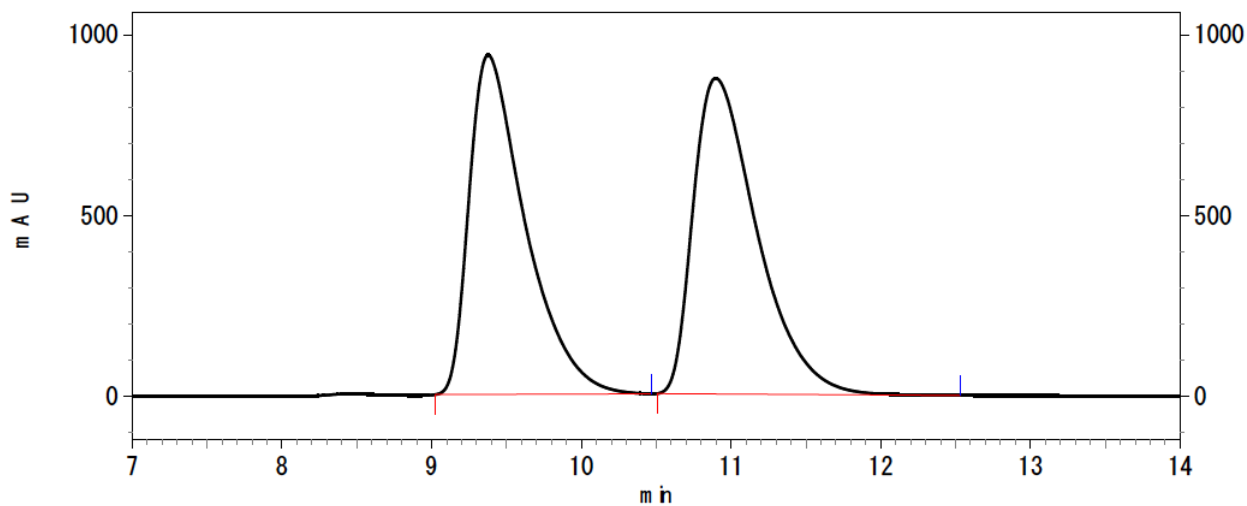
Retention time:  $t_{\text{minor}} = 12.0$  min.,  $t_{\text{major}} = 16.7$  min.

2d



Pk #	Retention time	Area	Area%	Baseline code
1	9.047	11004076	4.639	BB
2	10.747	226204614	95.361	BB

Racemate

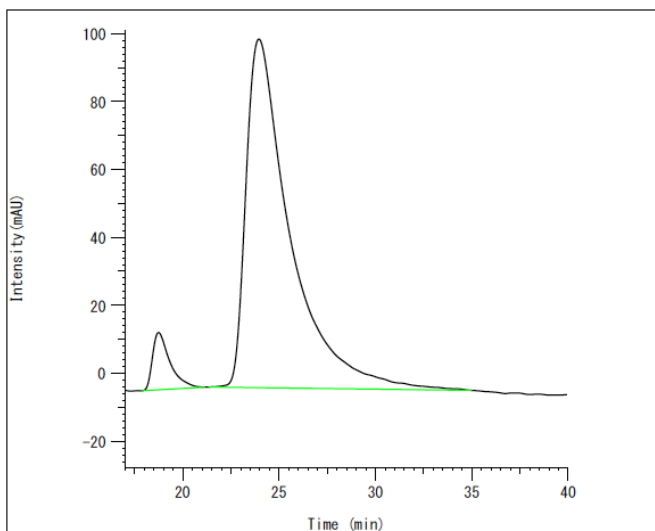


Pk #	Retention time	Area	Area%	Baseline code
1	9.380	97824521	48.557	BB
2	10.900	103639974	51.443	BB

HPLC: CHIRALPAK® IA-3 (4.6 x 250 mm), hexane/2-propanol = 100/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{minor}} = 9.0$  min.,  $t_{\text{major}} = 10.7$  min.

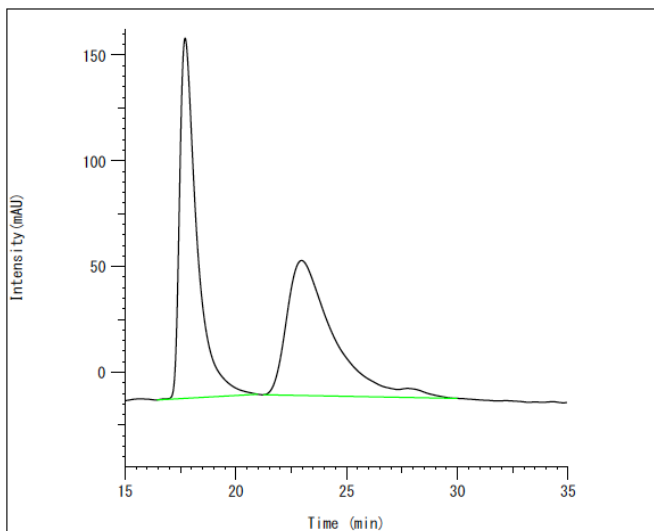
1e



5430 Diode Array Detector SampleID:1 yk\_558\_binam (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	18.747	1057976	6.086
2 Peak 2	23.940	16325746	93.914
		17383722	100.000

Racemate



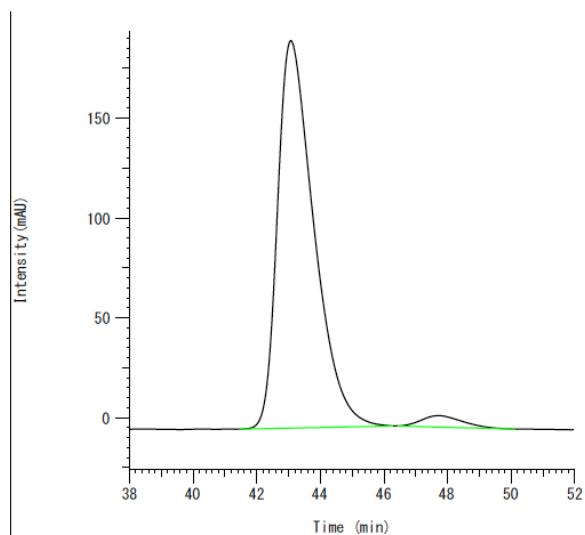
5430 Diode Array Detector SampleID:1 yk\_556\_binam (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	17.713	9239359	49.735
2 Peak 2	22.967	9337888	50.265
		18577246	100.000

HPLC: CHIRALPAK® IF-3 (4.6 x 250 mm), hexane/2-propanol = 9/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{minor}} = 18.7 \text{ min.}$ ,  $t_{\text{major}} = 23.9 \text{ min.}$

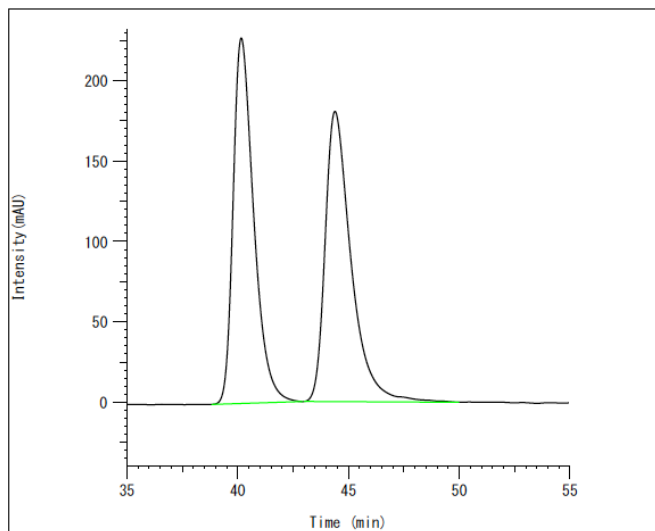
2e



5430 Diode Array Detector SampleID:1 yk\_558\_mono (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	43.073	15404773	96.776
2 Peak 2	47.733	513119	3.224
		15917892	100.000

**Racemate**



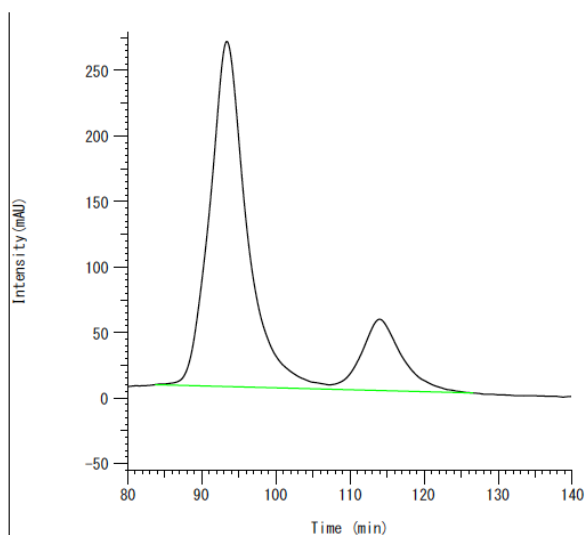
5430 Diode Array Detector SampleID:2 yk\_556\_mono (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	40.160	14654603	49.901
2 Peak 2	44.393	14712647	50.099
		29367249	100.000

HPLC: CHIRALPAK® IF-3 (4.6 x 250 mm), hexane/2-propanol = 9/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{major}} = 43.1$  min.,  $t_{\text{minor}} = 47.7$  min.

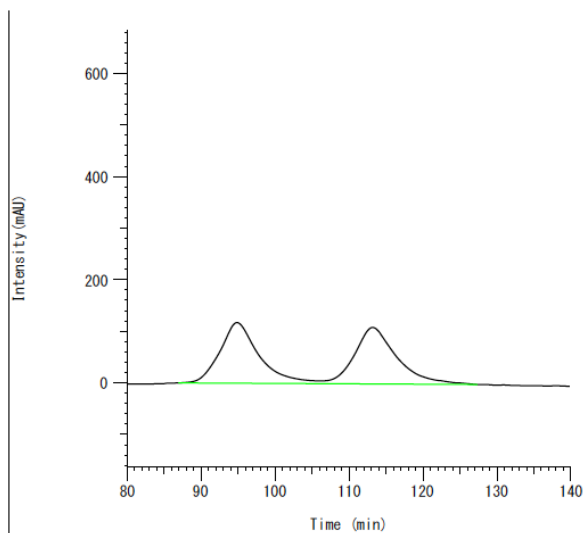
1f



5430 Diode Array Detector SampleID:2 yk\_66-OMePh\_binam\_2 (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	93.367	92245129	81.575
2 Peak 2	113.973	20834746	18.425
		113079876	100.000

Racemate



5430 Diode Array Detector SampleID:2 yk\_66-OMePh\_binam\_2 (Extract, 254nm) Repeat:1

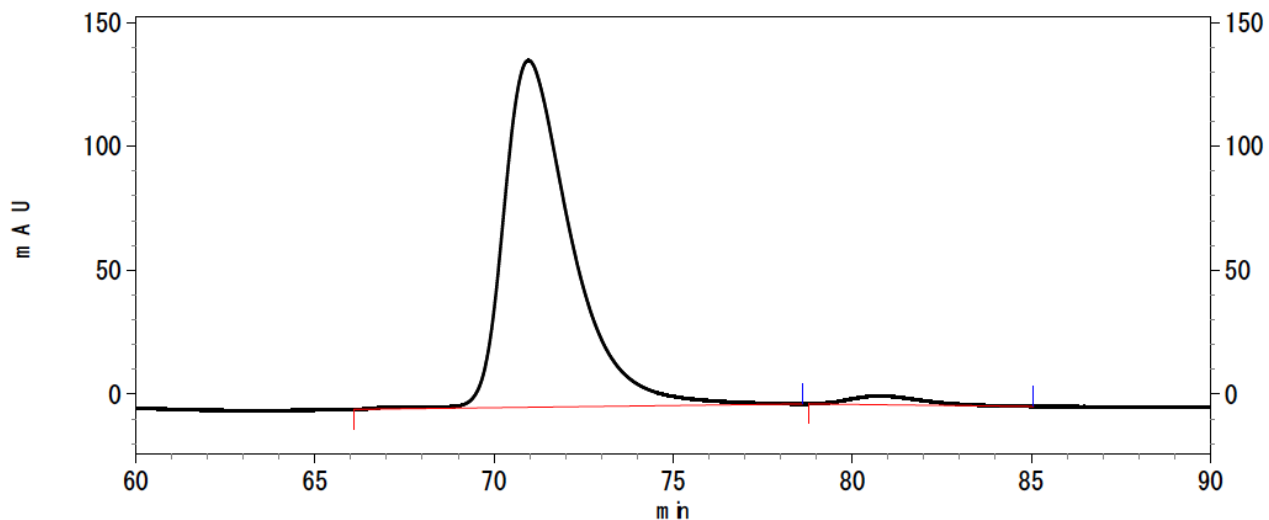
No. Compounds	RT	Area	Area%
1 Peak 1	94.847	43416477	49.937
2 Peak 2	113.193	43525352	50.063
		86941829	100.000

HPLC: CHIRALCEL® OD-H (4.6 x 250 mm), hexane/2-propanol = 4/1, 0.5 mL/min, 300 nm.

Retention time:  $t_{\text{major}} = 93.4 \text{ min.}$ ,  $t_{\text{minor}} = 114.0 \text{ min.}$

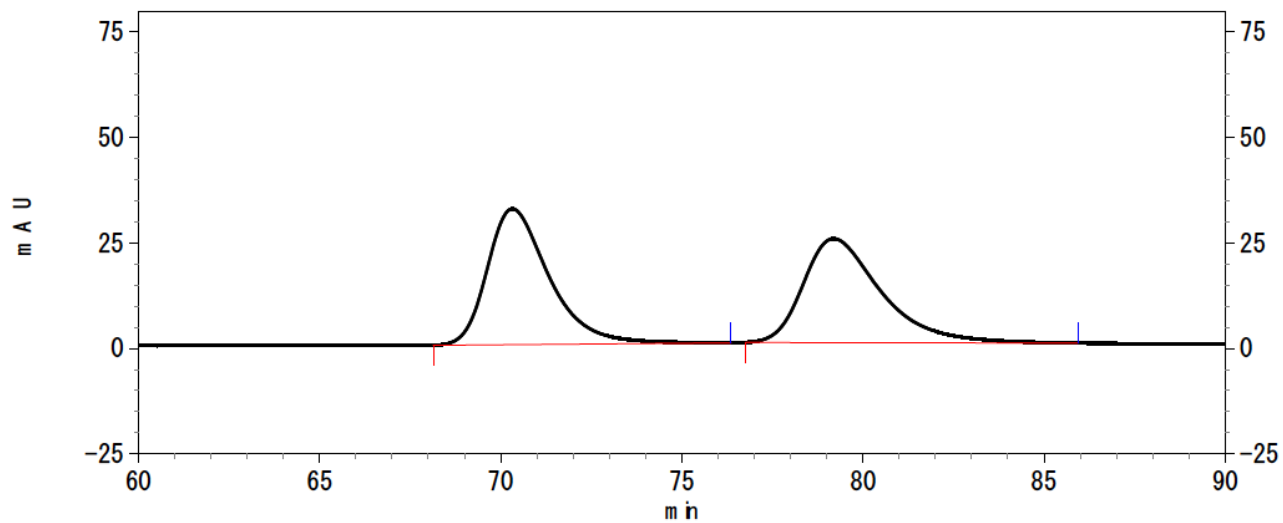


2f



Pk #	Retention time	Area	Area%	Baseline code
1	70.967	73298413	97.376	BB
2	80.800	1975175	2.624	BB

Racemate

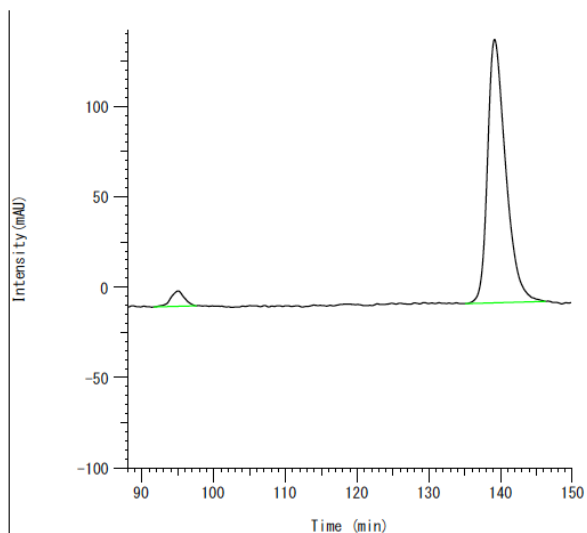


Pk #	Retention time	Area	Area%	Baseline code
1	70.327	15321798	51.054	BB
2	79.193	14689238	48.946	BB

HPLC: CHIRALPAK® IF-3 (4.6 x 250 mm), hexane/2-propanol = 9/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{major}} = 70.1 \text{ min.}$ ,  $t_{\text{minor}} = 80.8 \text{ min.}$

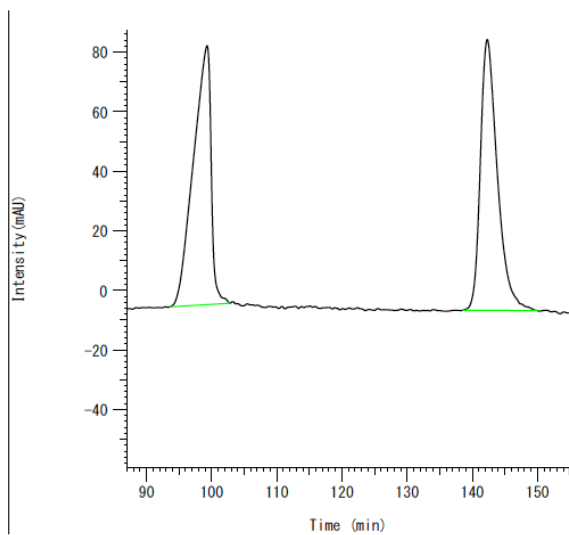
1g



5430 Diode Array Detector SampleID:1 yk\_570\_binam (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	95.027	1126246	4.207
2 Peak 2	139.160	25646940	95.793
		26773185	100.000

Racemate



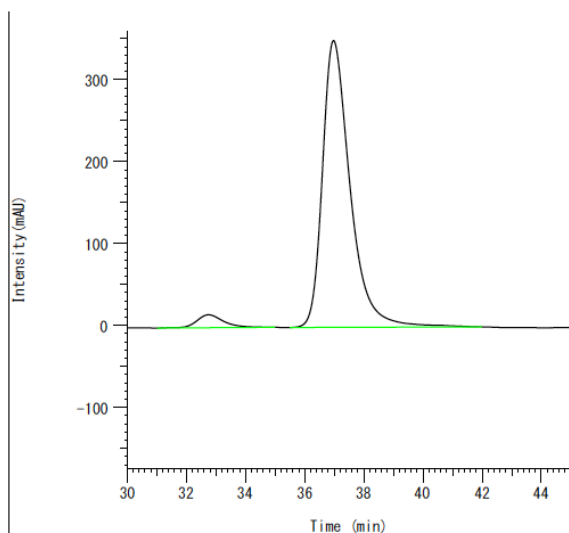
5430 Diode Array Detector SampleID:1 yk\_560\_binam (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	99.293	16439021	49.915
2 Peak 2	142.300	16495023	50.085
		32934044	100.000

HPLC: CHIRALPAK® IA-3 (4.6 x 250 mm), hexane/2-propanol = 4/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{minor}} = 95.0 \text{ min.}$ ,  $t_{\text{major}} = 139.2 \text{ min.}$

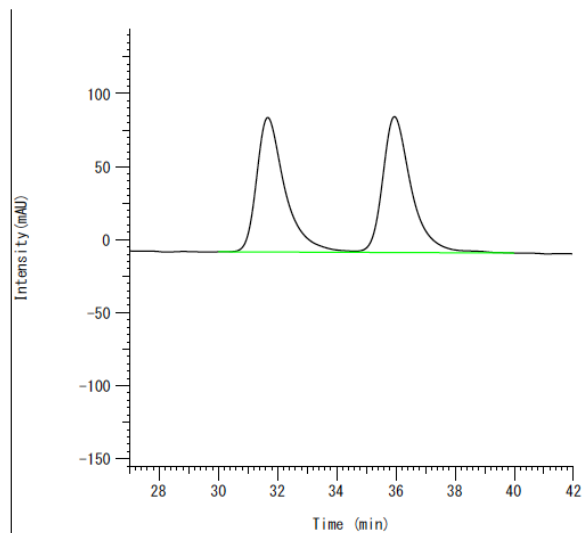
2g



5430 Diode Array Detector SampleID:3 yk\_570\_mono (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	32.753	998226	4.201
2 Peak 2	36.973	22762750	95.799
		23760977	100.000

Racemate



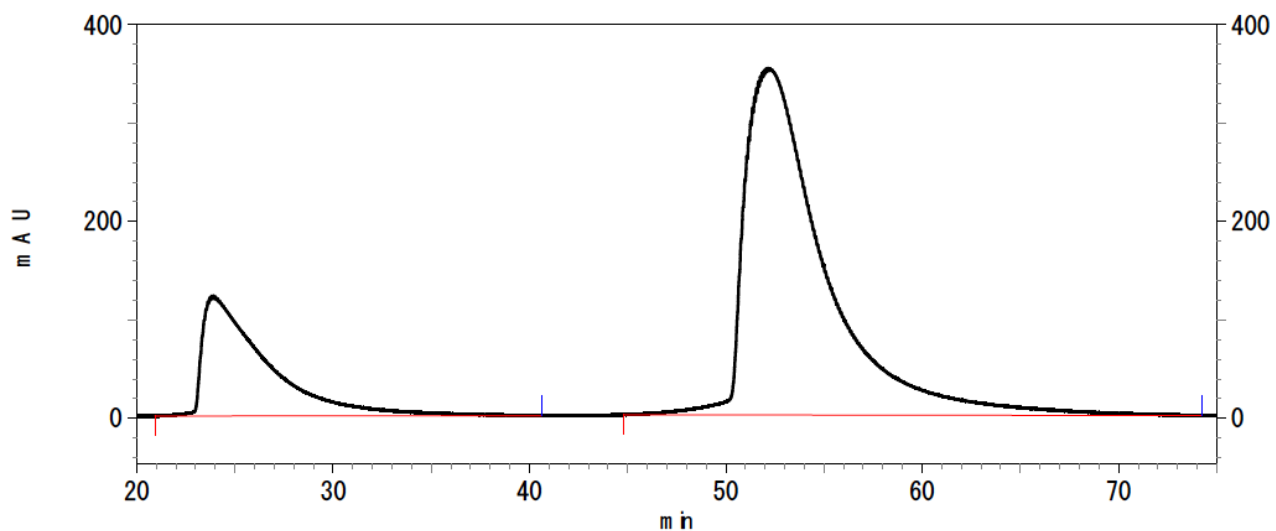
5430 Diode Array Detector SampleID:5 yk\_560\_mono\_3 (Extract, 254nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	31.667	6129162	49.517
2 Peak 2	35.953	6248847	50.483
		12378009	100.000

HPLC: CHIRALPAK® IF-3 (4.6 x 250 mm), hexane/2-propanol = 4/1, 1.0 mL/min, 254 nm.

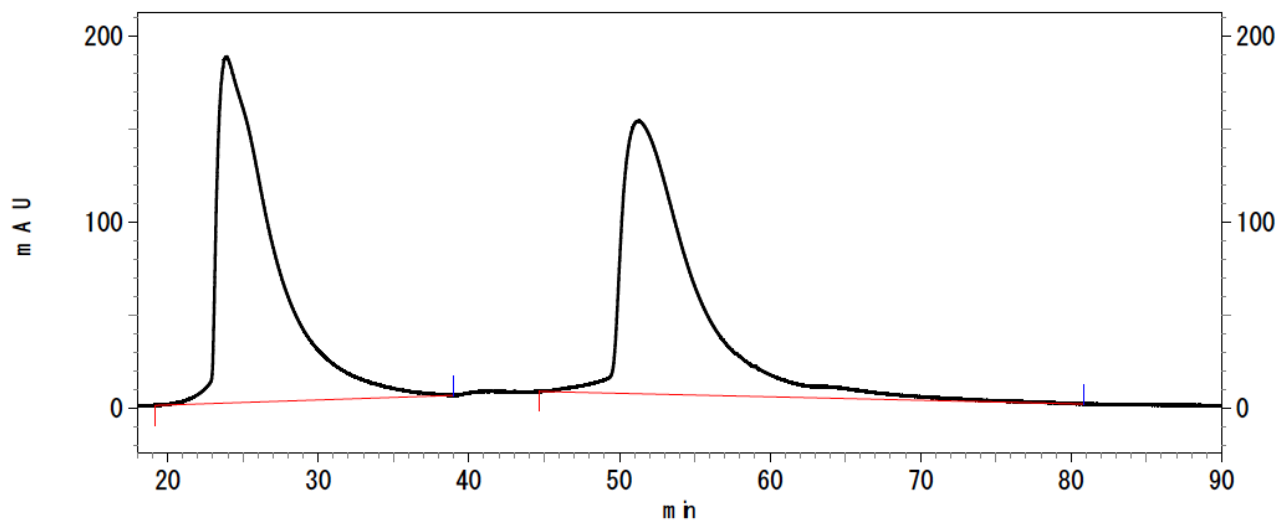
Retention time:  $t_{\text{minor}} = 32.8 \text{ min.}$ ,  $t_{\text{major}} = 37.0 \text{ min.}$

1h



Pk #	Retention time	Area	Area%	Baseline code
1	23.913	110150420	21.668	BB
2	52.153	398213075	78.332	BB

Racemate

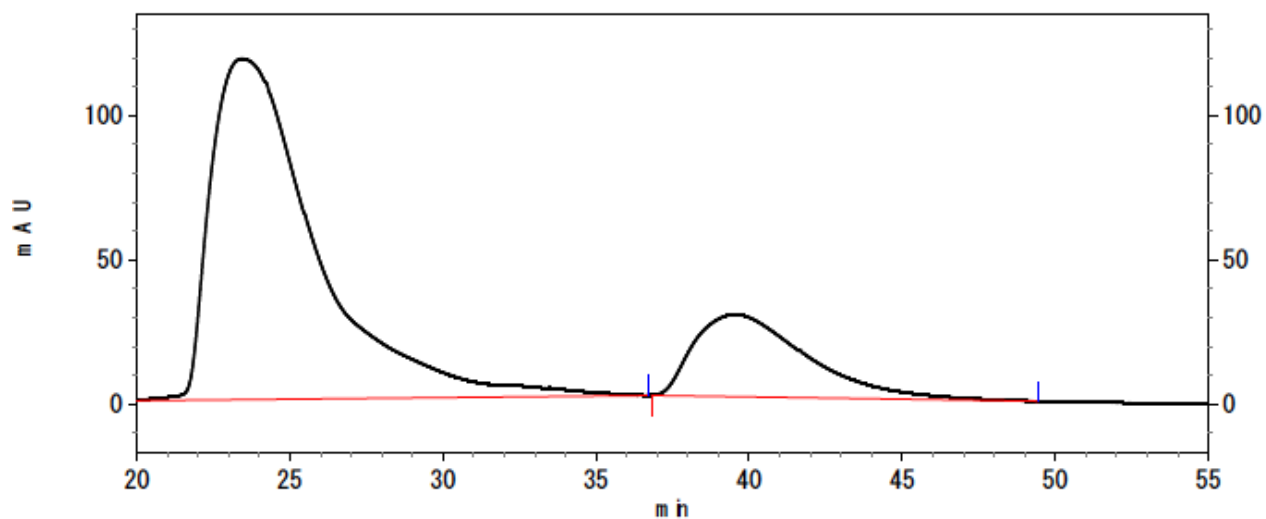


Pk #	Retention time	Area	Area%	Baseline code
1	23.940	189842323	49.863	BB
2	51.267	190884981	50.137	BB

HPLC: CHIRALPAK®IA-3 (4.6 x 250 mm), hexane/2-propanol = 100/1, 1.0 mL/min, 254 nm.

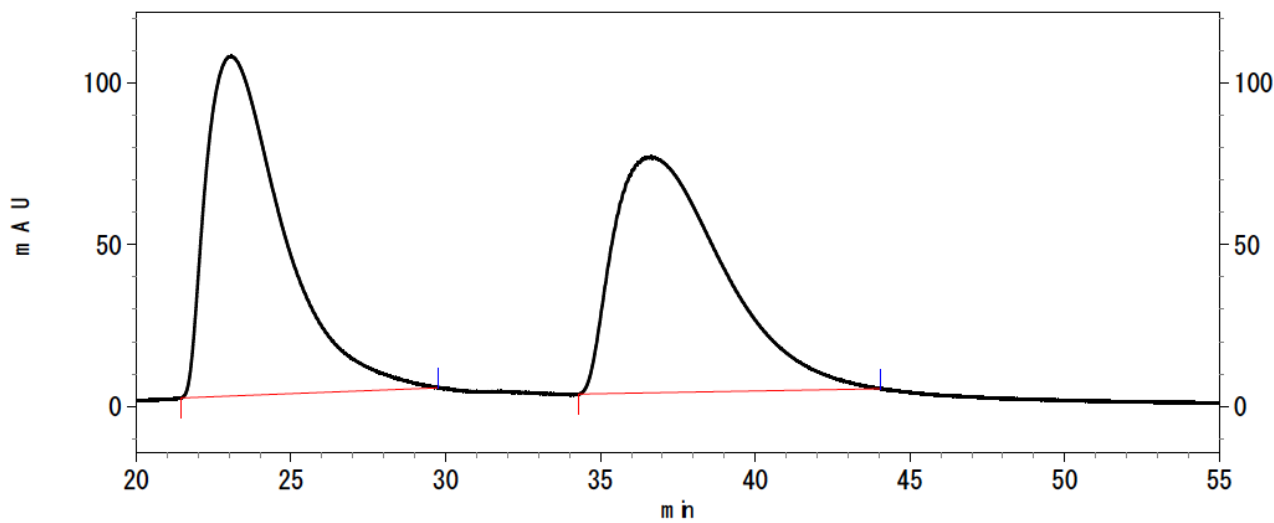
Retention time:  $t_{\text{minor}} = 23.9 \text{ min.}$ ,  $t_{\text{major}} = 52.2 \text{ min.}$

2h



Pk #	Retention time	Area	Area%	Baseline code
1	23.473	113429511	79.556	BB
2	39.540	29149314	20.444	BB

Racemate

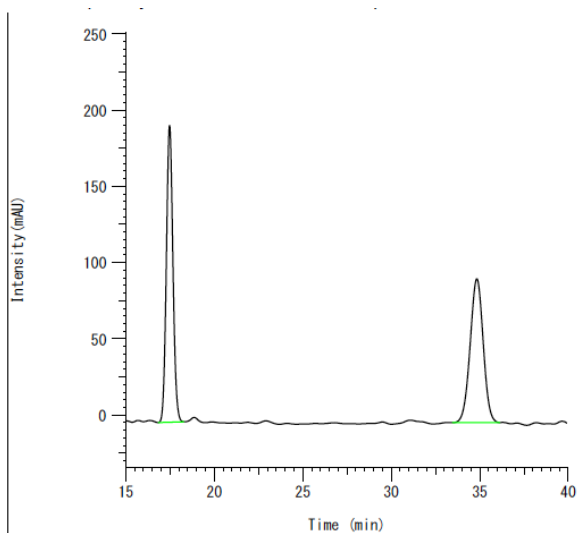


Pk #	Retention time	Area	Area%	Baseline code
1	23.080	72398537	50.191	BB
2	36.633	71847965	49.809	BB

HPLC: CHIRALPAK® IA-3 (4.6 x 250 mm), hexane/2-propanol = 100/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{major}} = 23.5 \text{ min.}$ ,  $t_{\text{minor}} = 39.5 \text{ min.}$

1i



5430 Diode Array Detector SampleID:1 yk\_596\_binam (Extract, 254nm) Repeat:1

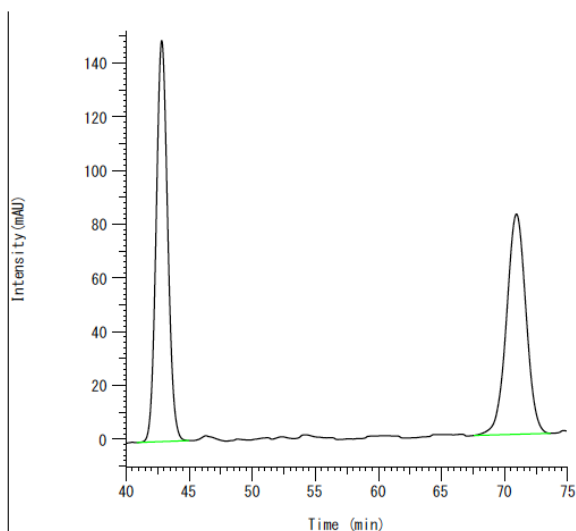
No. Compounds	RT	Area	Area%
1 Peak 1	17.473	5003974	50.855
2 Peak 2	34.840	4835631	49.145
		9839605	100.000

### Racemate

HPLC: CHIRALCEL® AD-H (4.6 x 250 mm), hexane/2-propanol = 9/1, 1.0 mL/min, 254 nm.

Retention time:  $t_{\text{major}} = 17.5 \text{ min.}$ ,  $t_{\text{minor}} = 34.8 \text{ min.}$

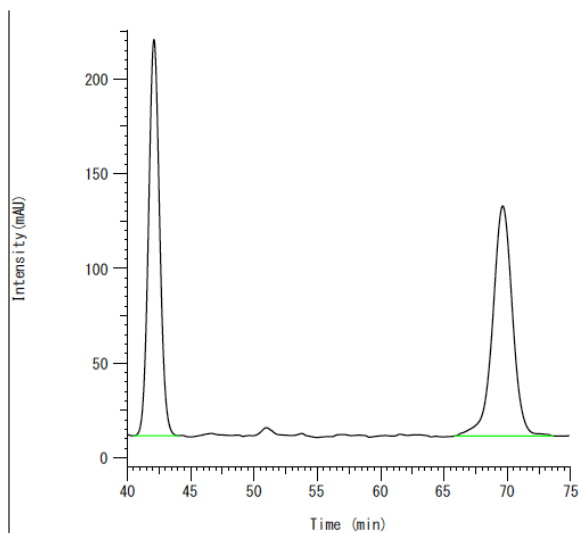
2i



5430 Diode Array Detector SampleID:2 yk\_596\_mono (Extract, 220nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	42.827	9458797	51.765
2 Peak 2	70.933	8813604	48.235
		18272401	100.000

### Racemate



5430 Diode Array Detector SampleID:3 yk\_697\_mono (Extract, 220nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	42.107	12678908	48.906
2 Peak 2	69.633	13246151	51.094
		25925059	100.000

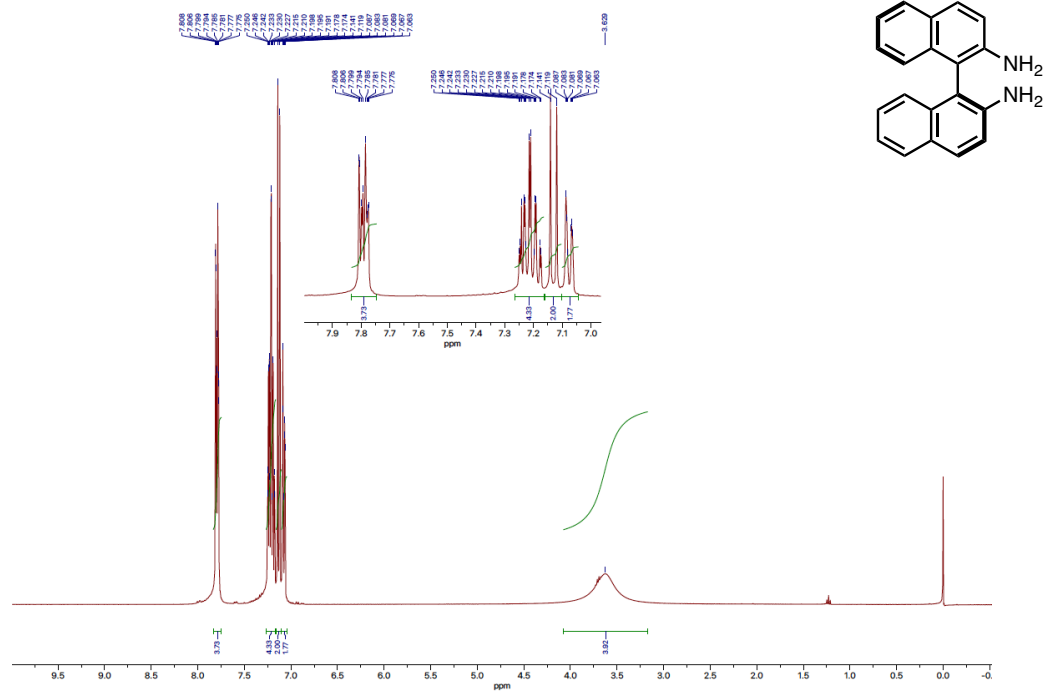
HPLC: CHIRALCEL® AD-H (4.6 x 250 mm), hexane/2-propanol = 99/1, 1.0 mL/min, 220 nm.

Retention time:  $t_{\text{major}} = 42.8 \text{ min.}$ ,  $t_{\text{minor}} = 70.9 \text{ min.}$

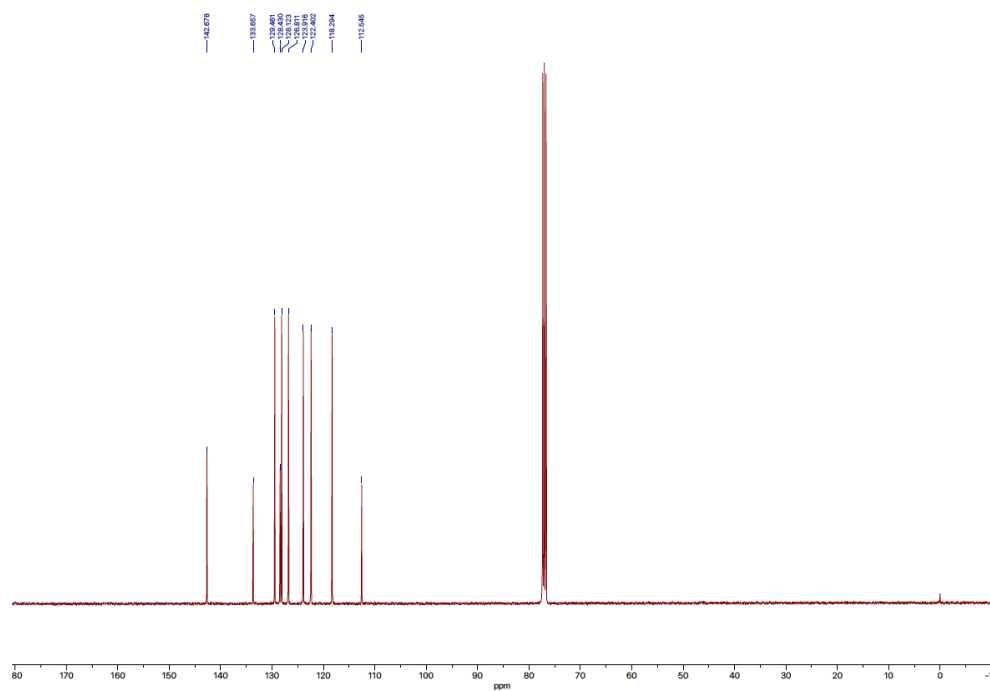
## 4. NMR spectra

(S)-1a

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



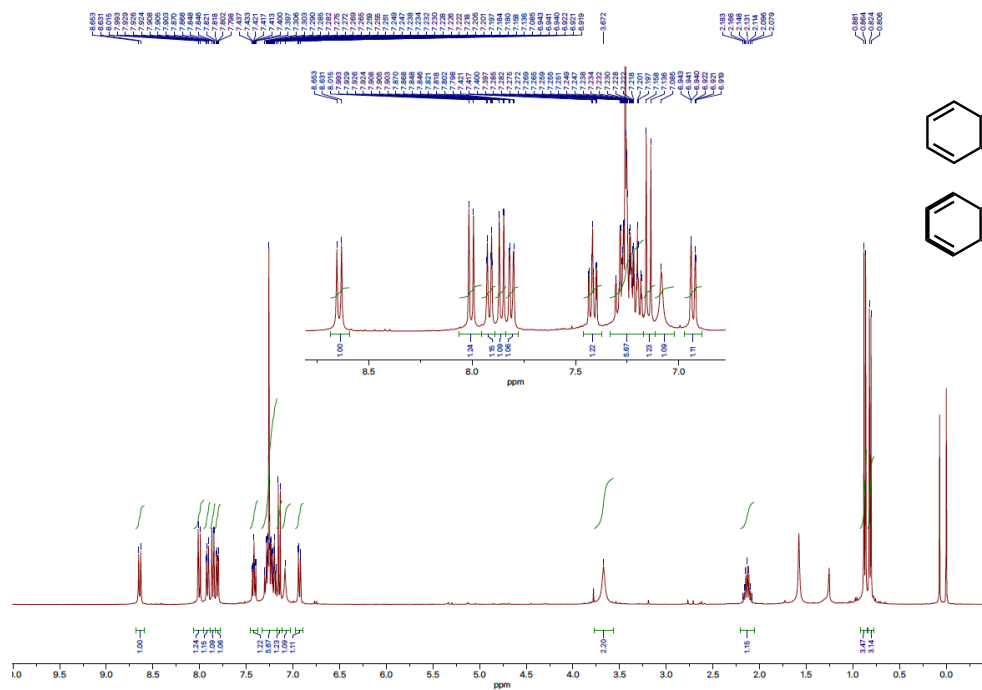
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



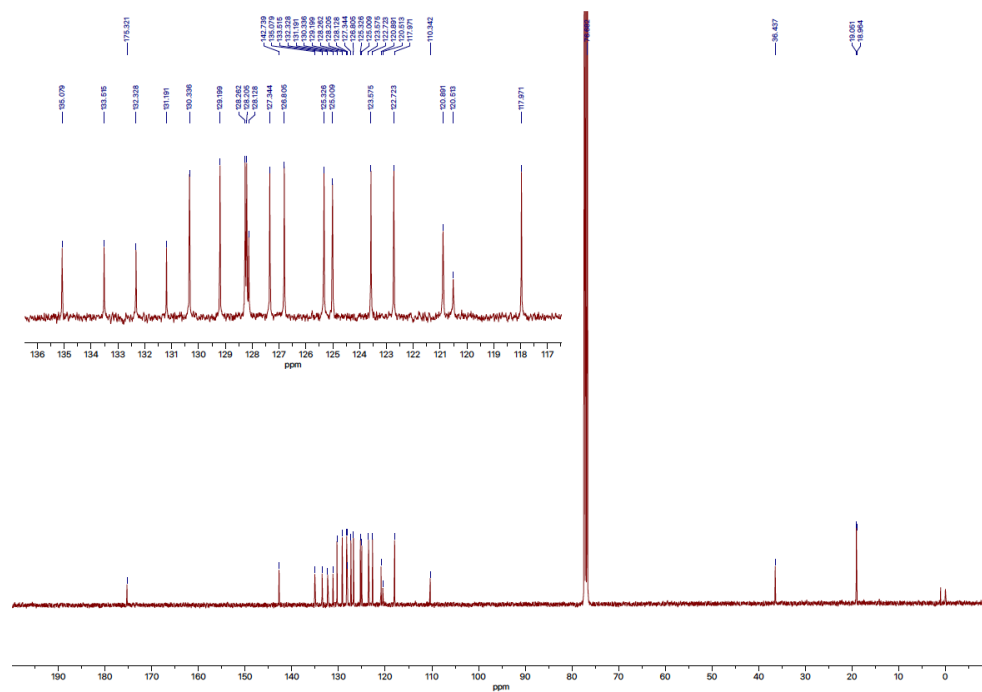


**(R)-2a**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

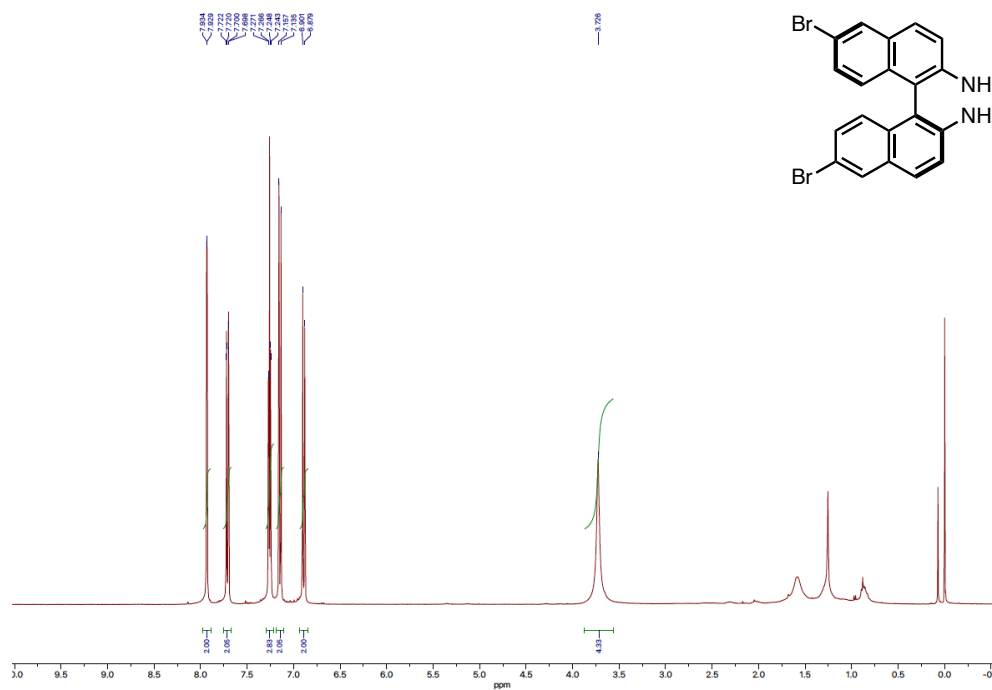


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**

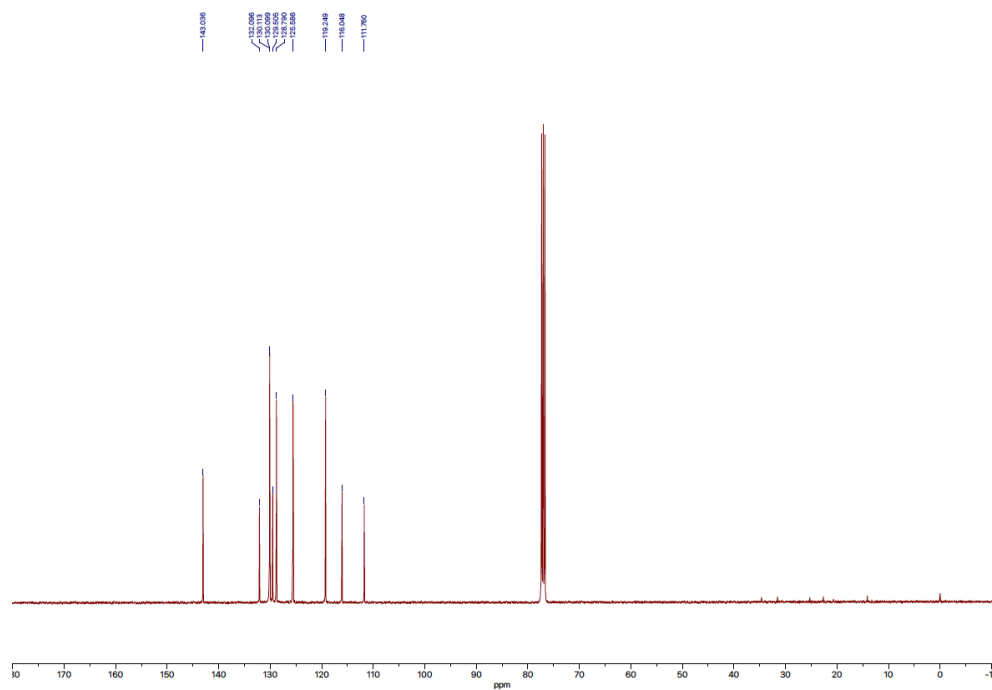


**(S)-1b**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

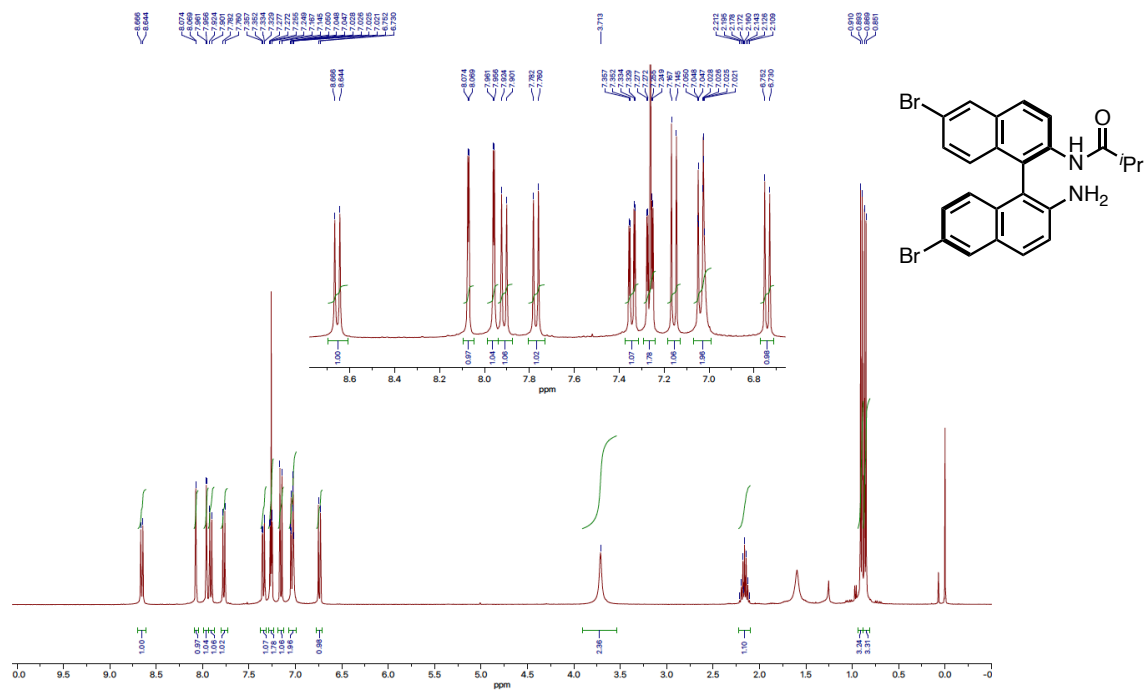


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**

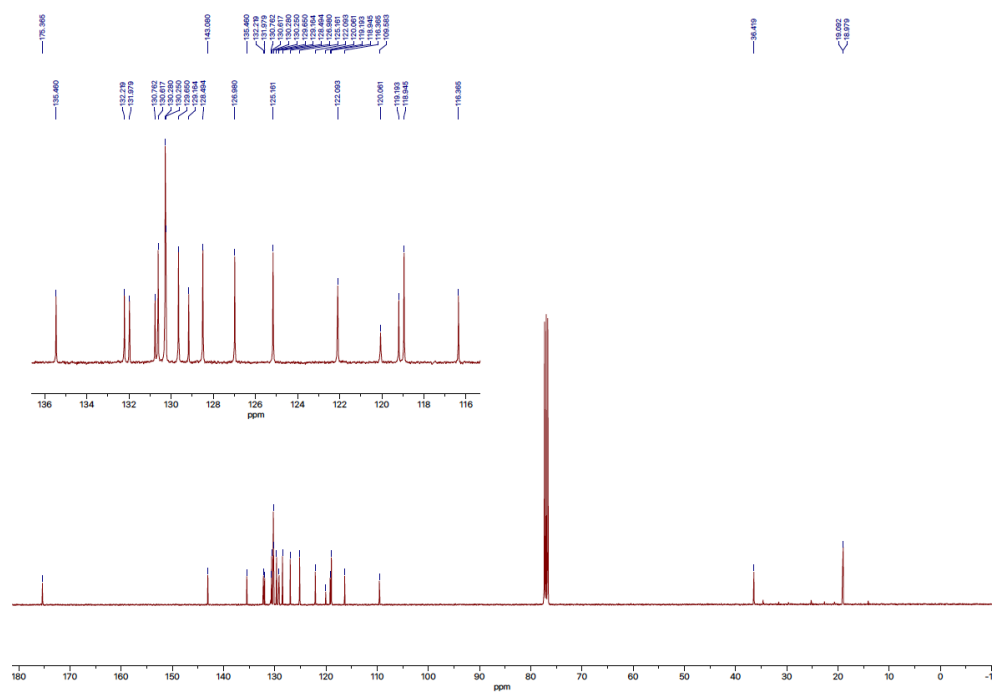


(R)-2b

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

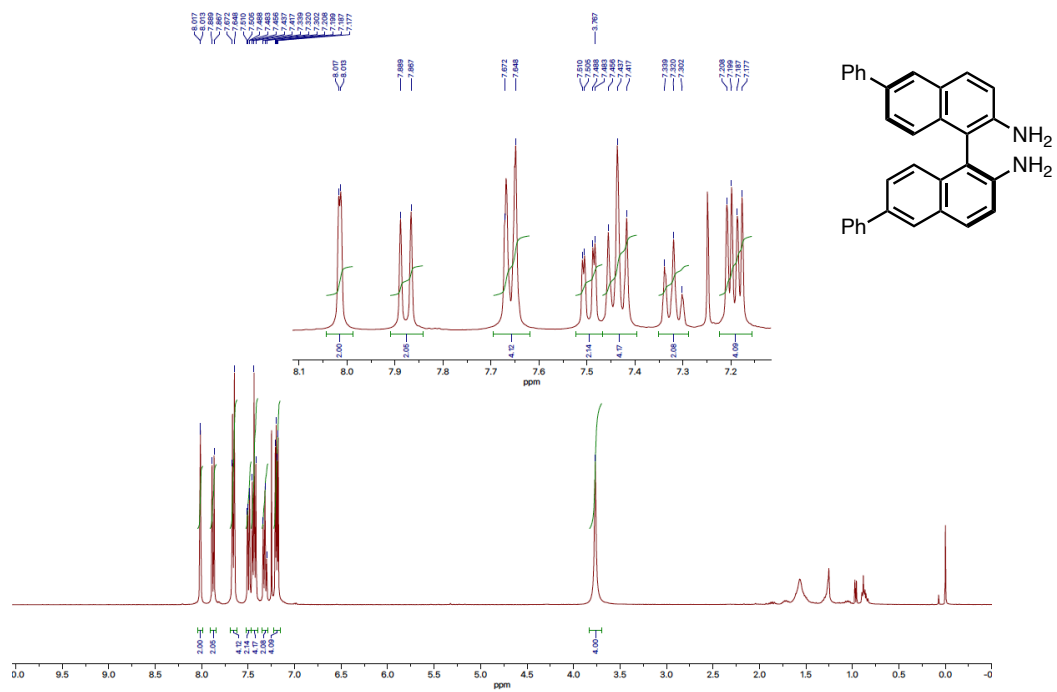


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

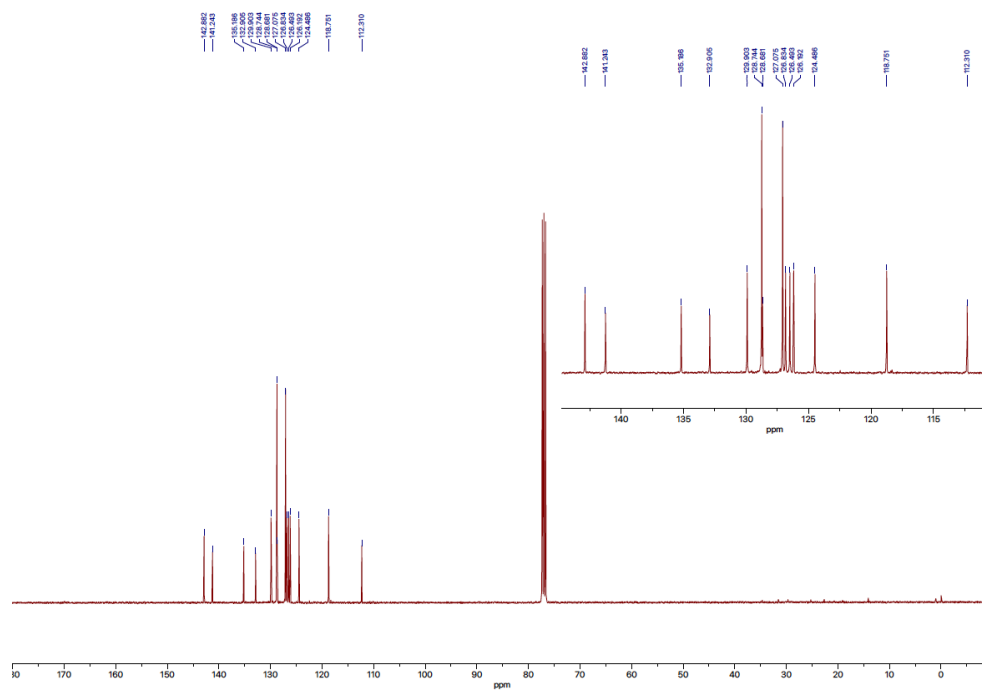


(S)-1c

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

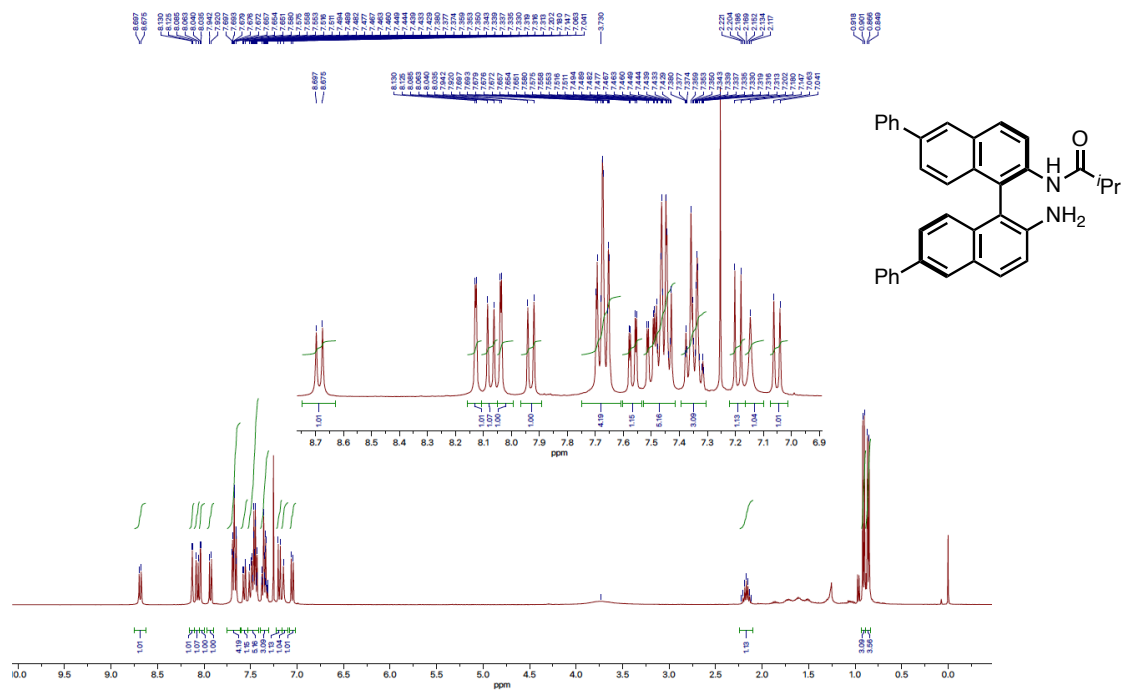


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

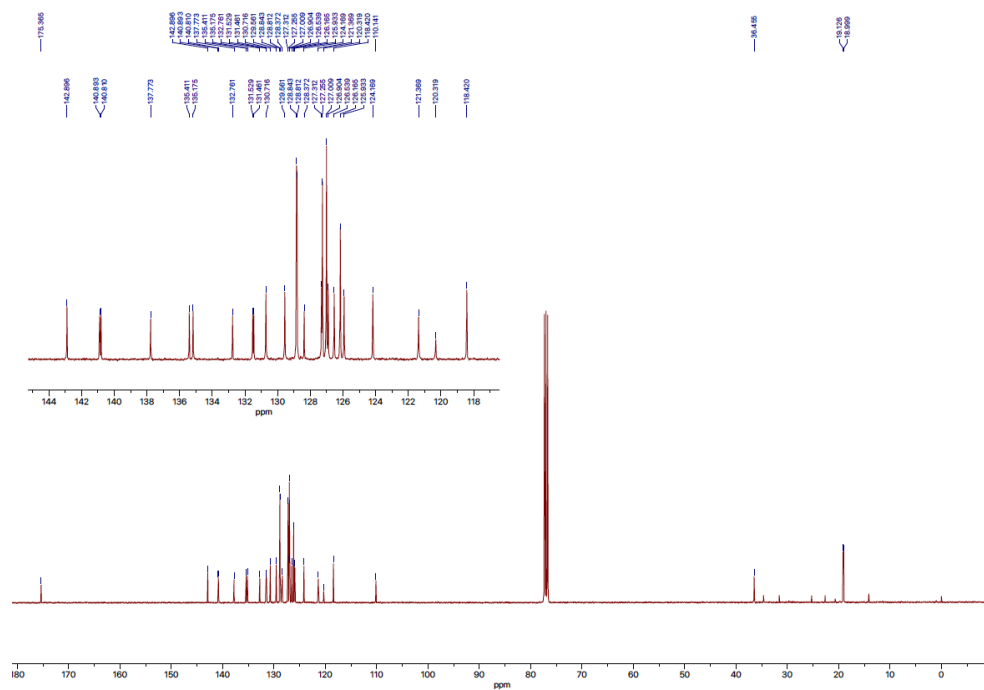


(R)-2c

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



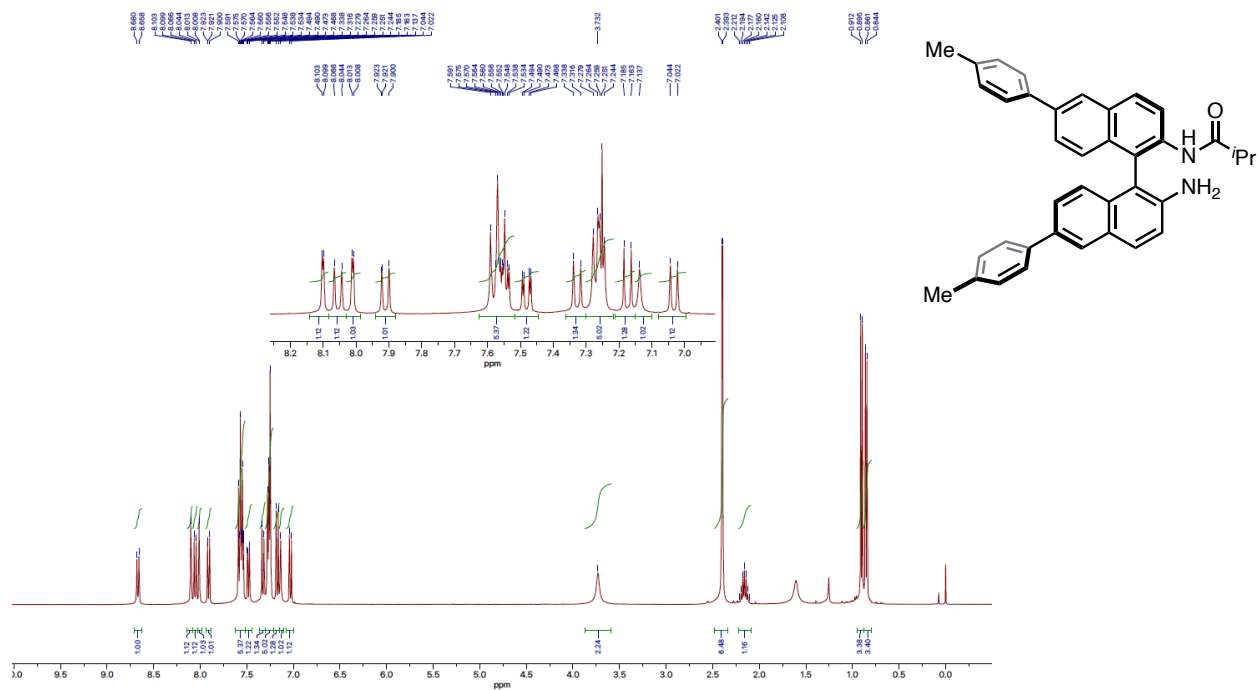
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



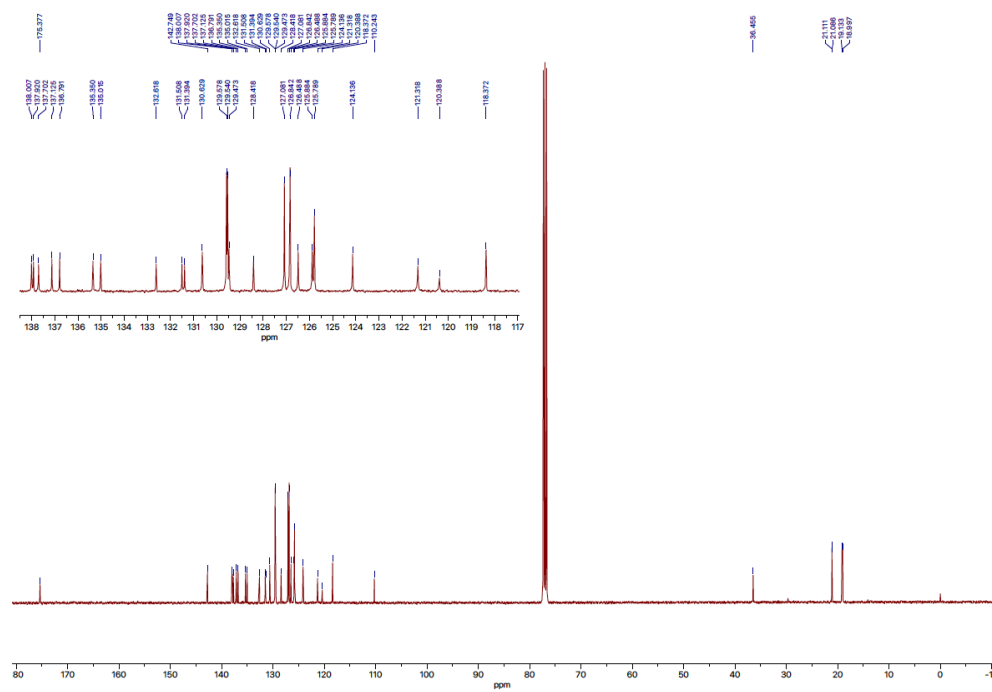


**(R)-2d**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**

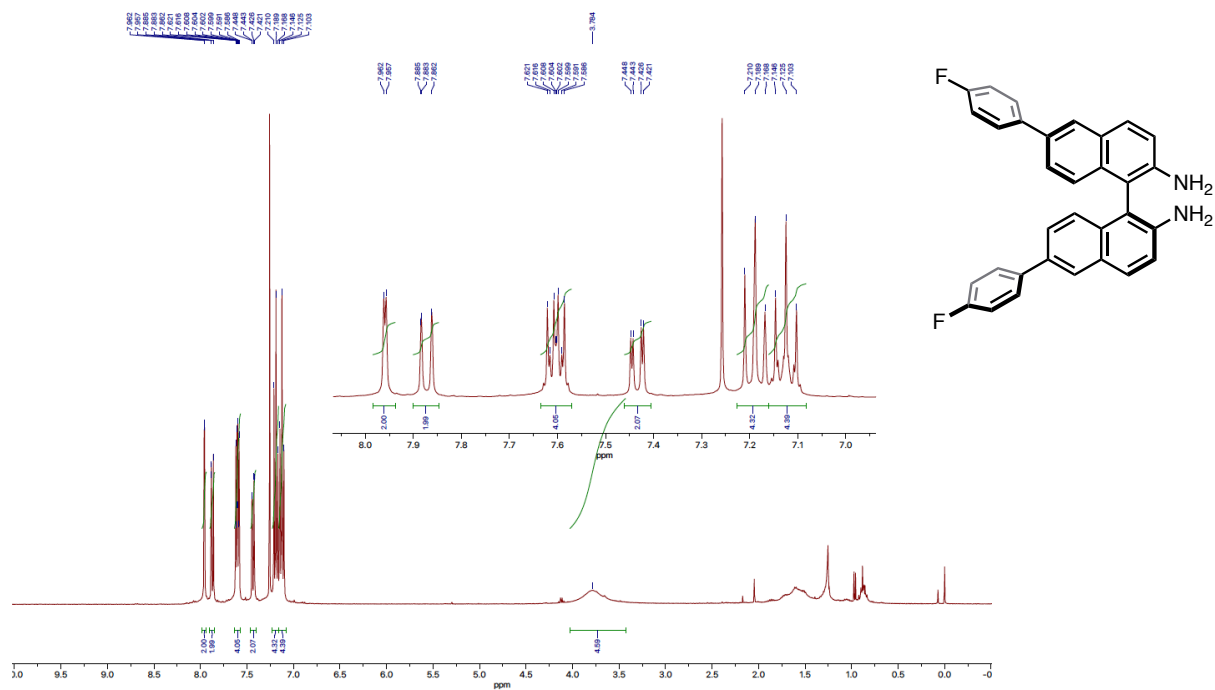


**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**

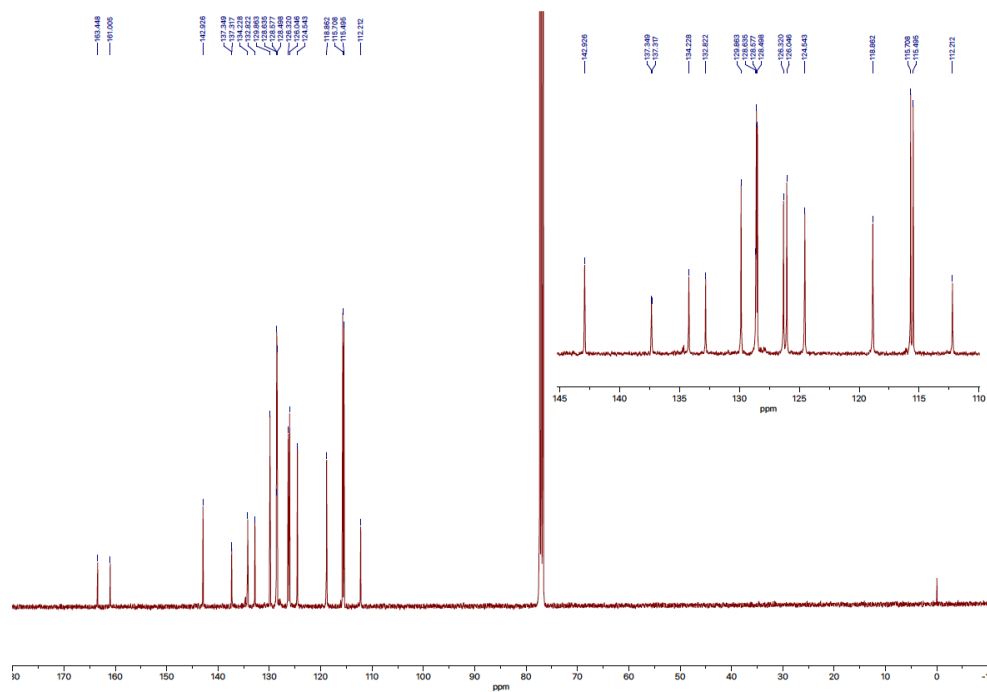


(S)-1e

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



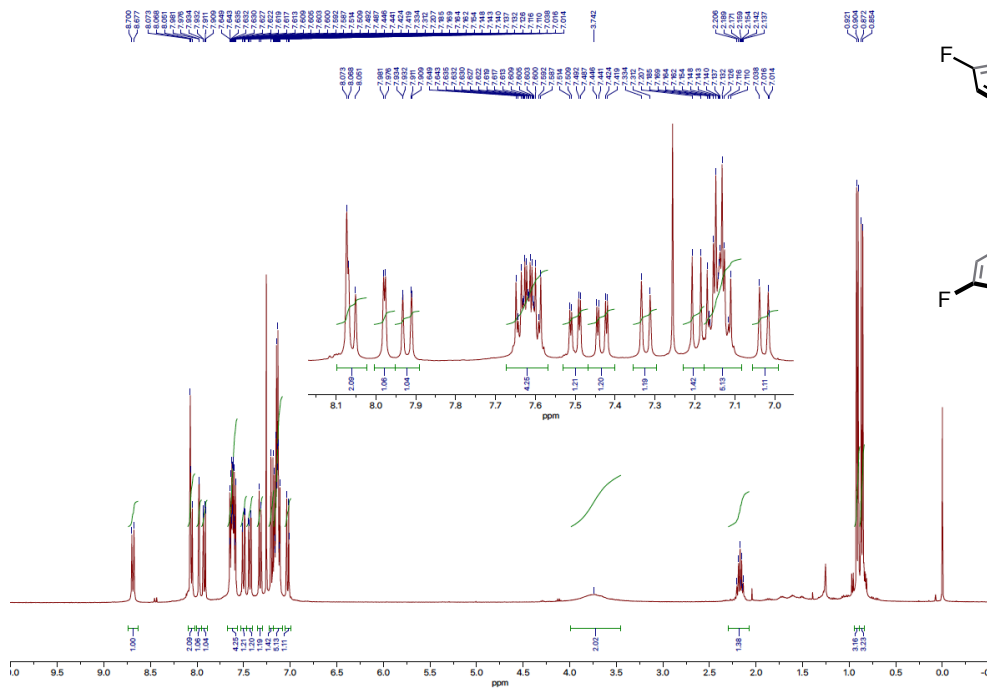
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



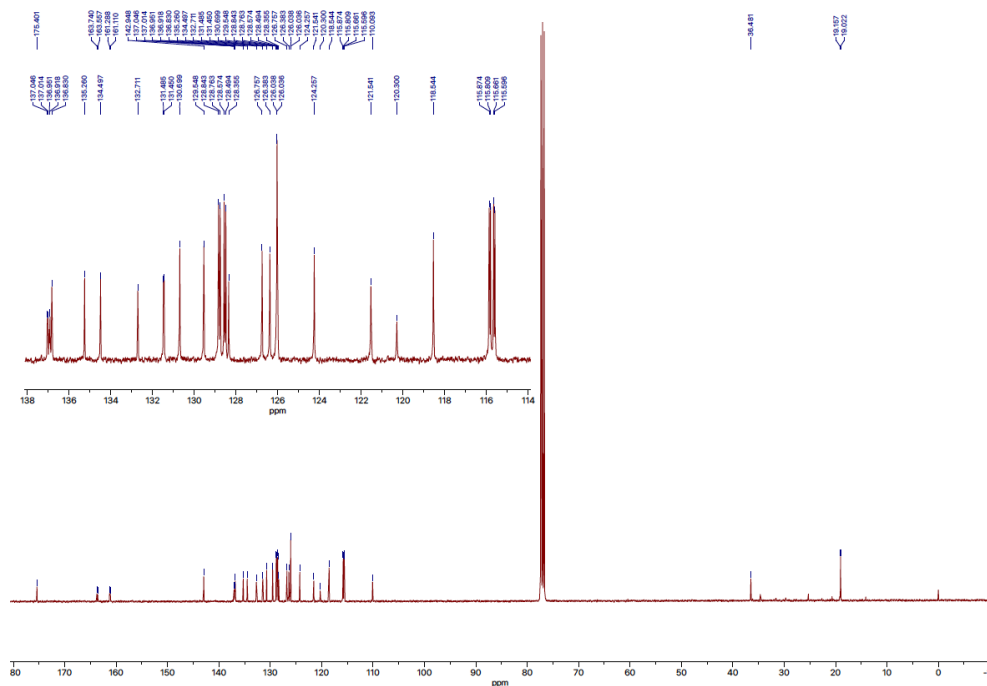


(R)-2e

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

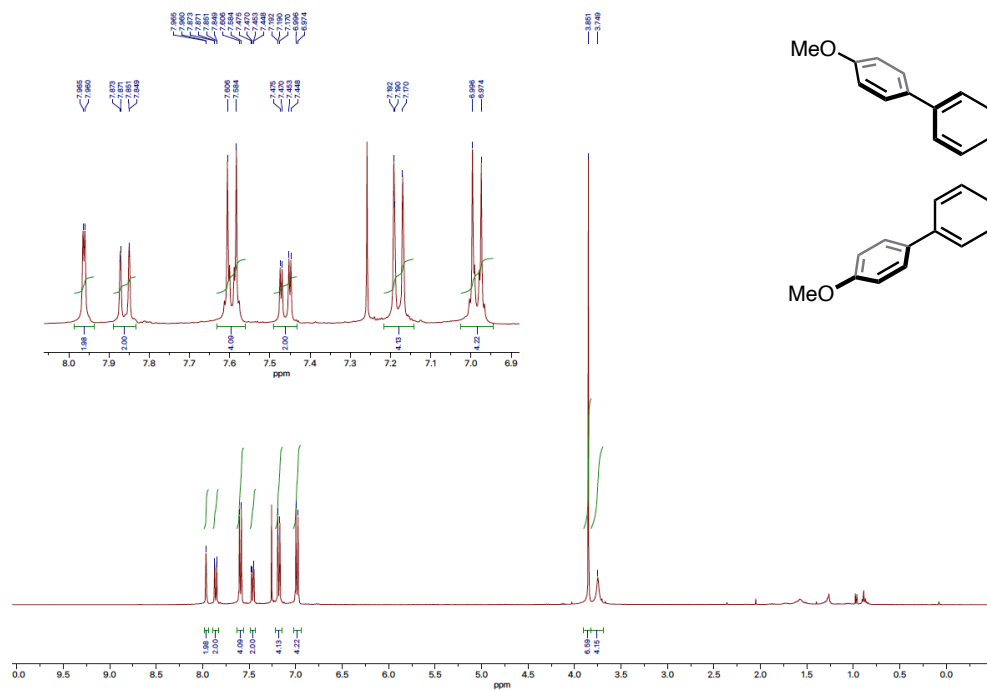


$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )

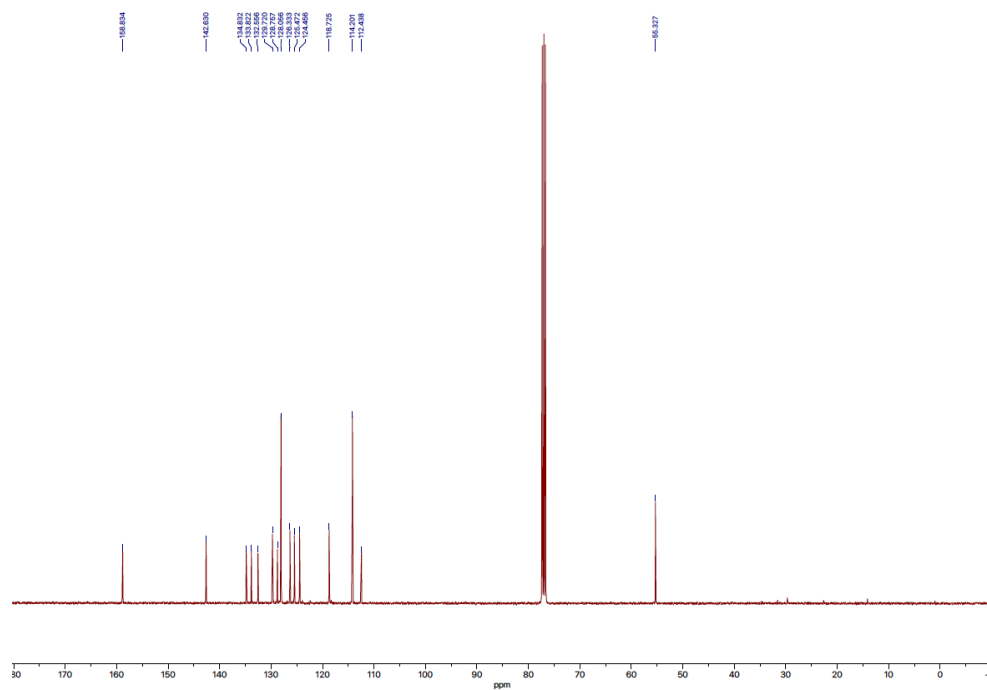


(S)-1f

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

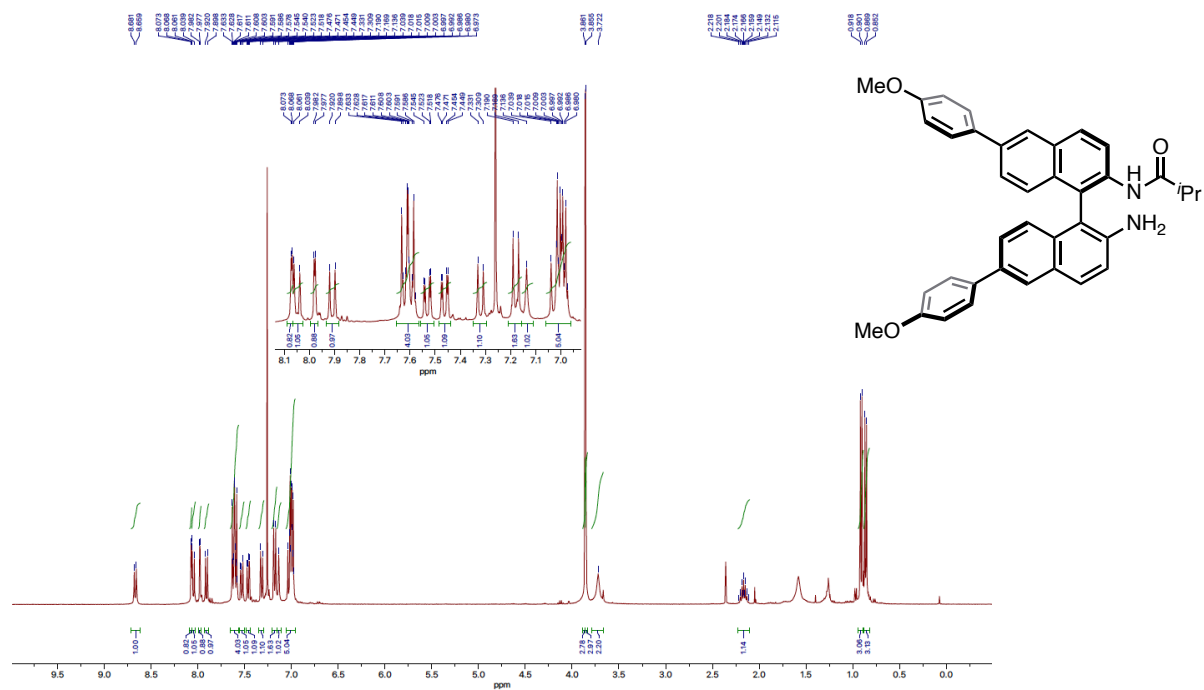


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

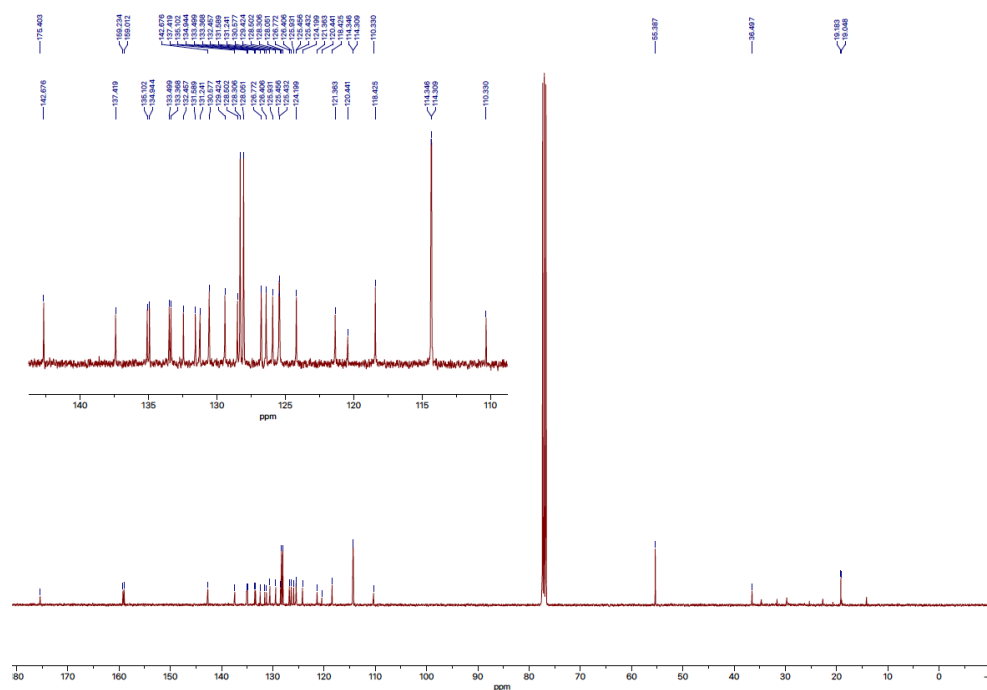


(R)-2f

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

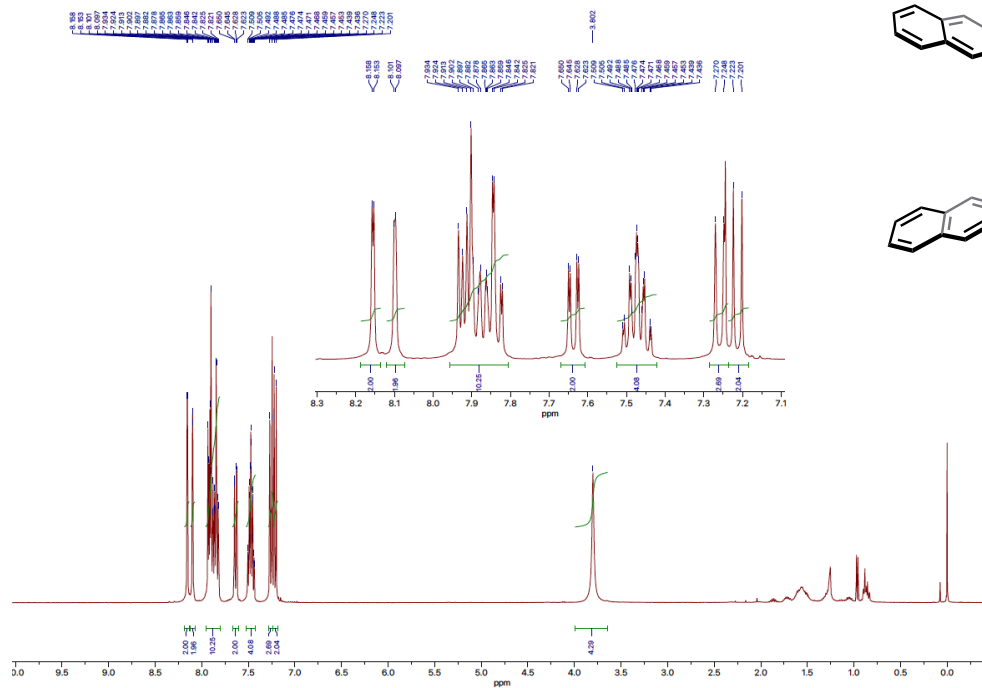


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

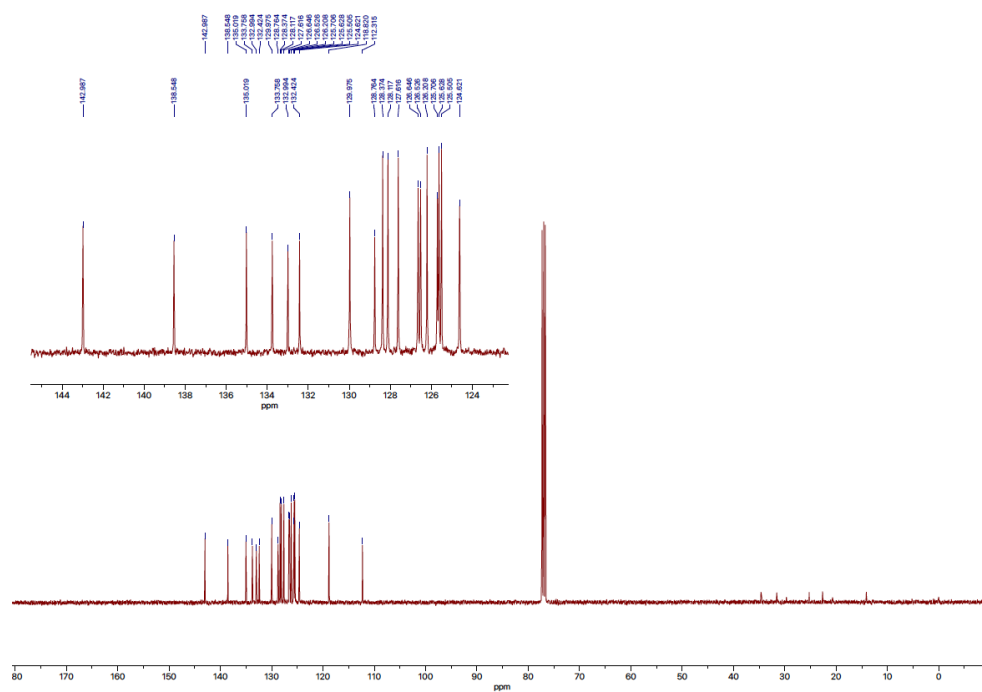


**(S)-1g**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

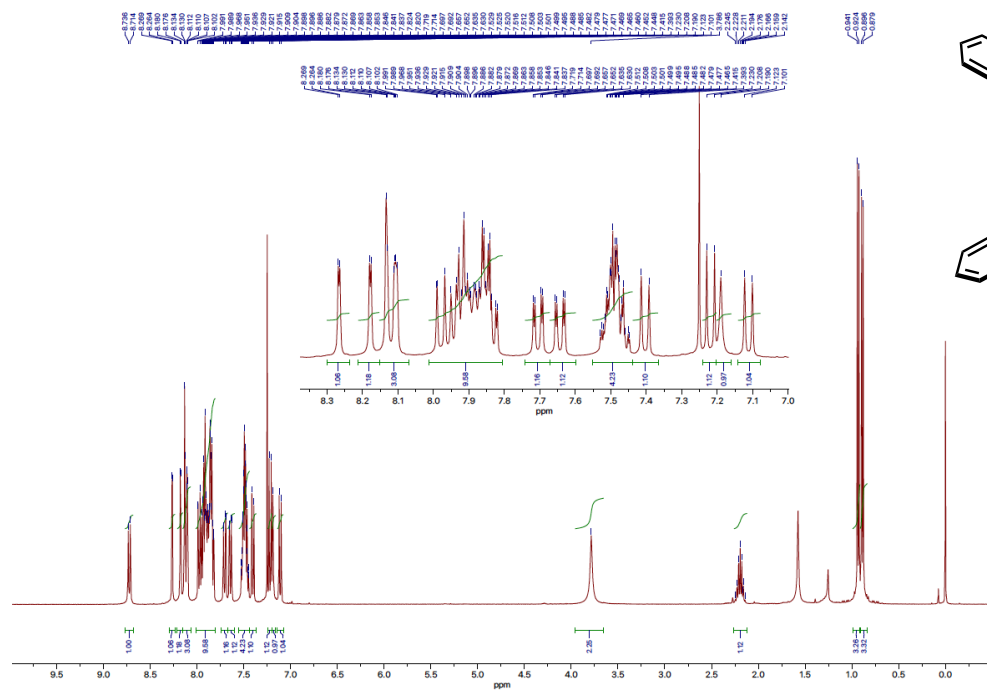


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**

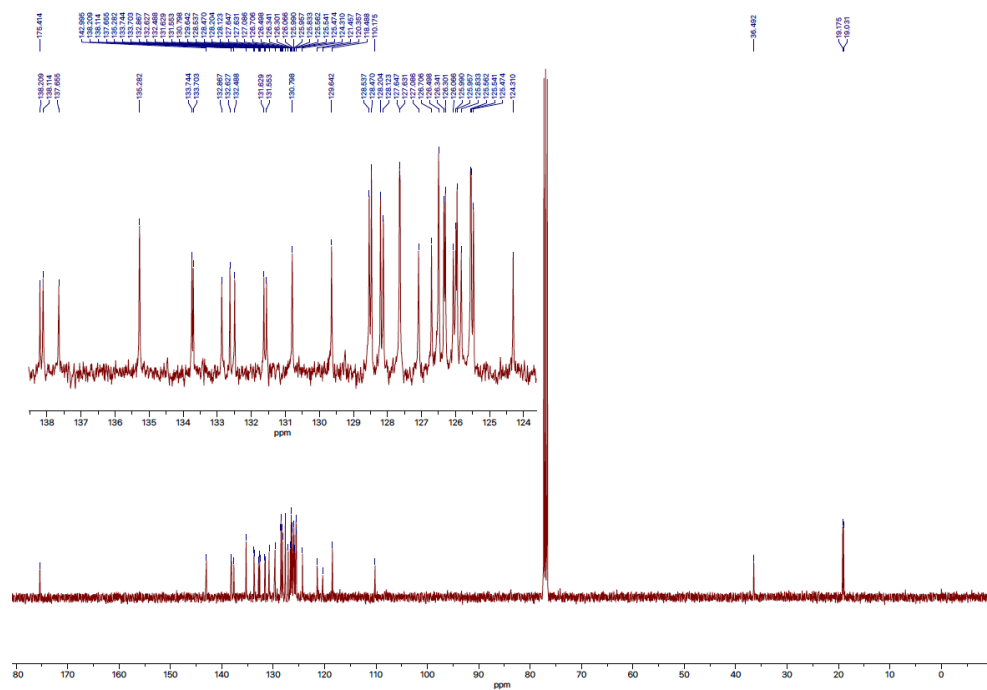


(R)-2g

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

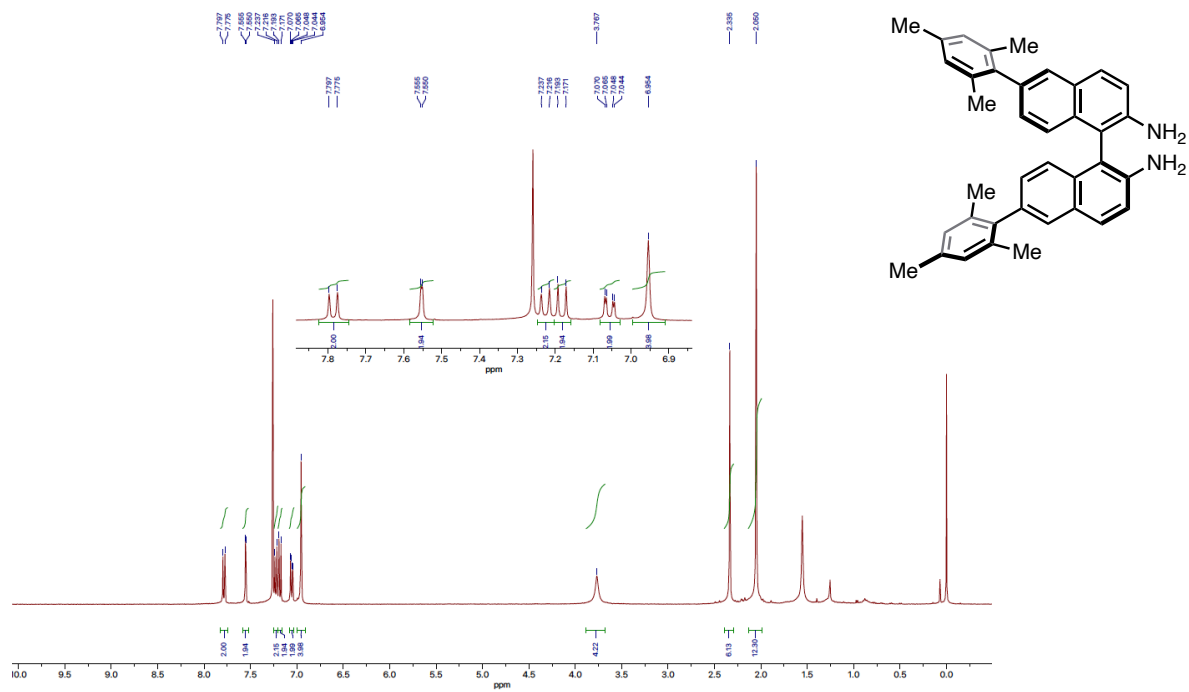


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

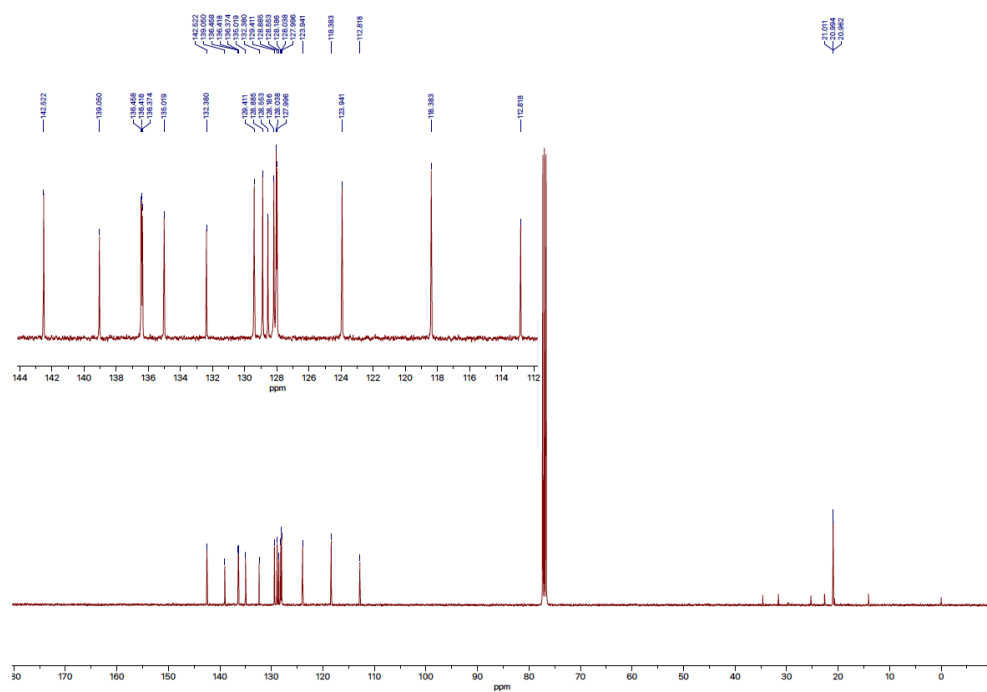


**(S)-1h**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

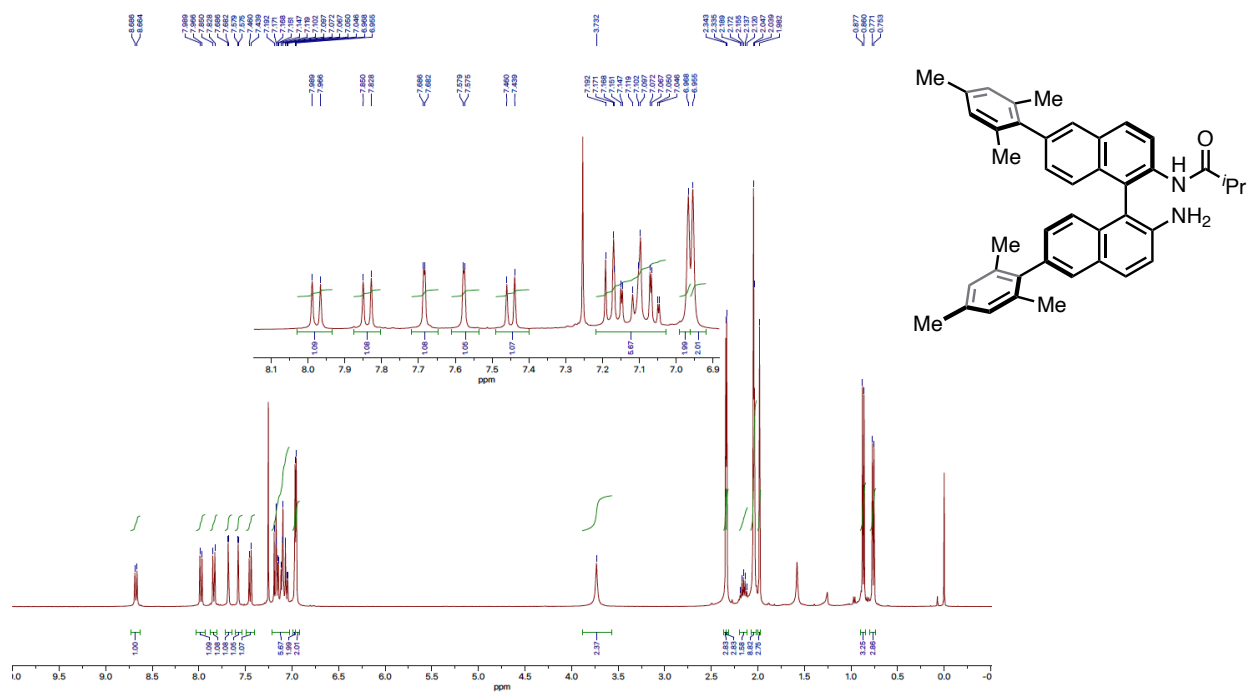


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**

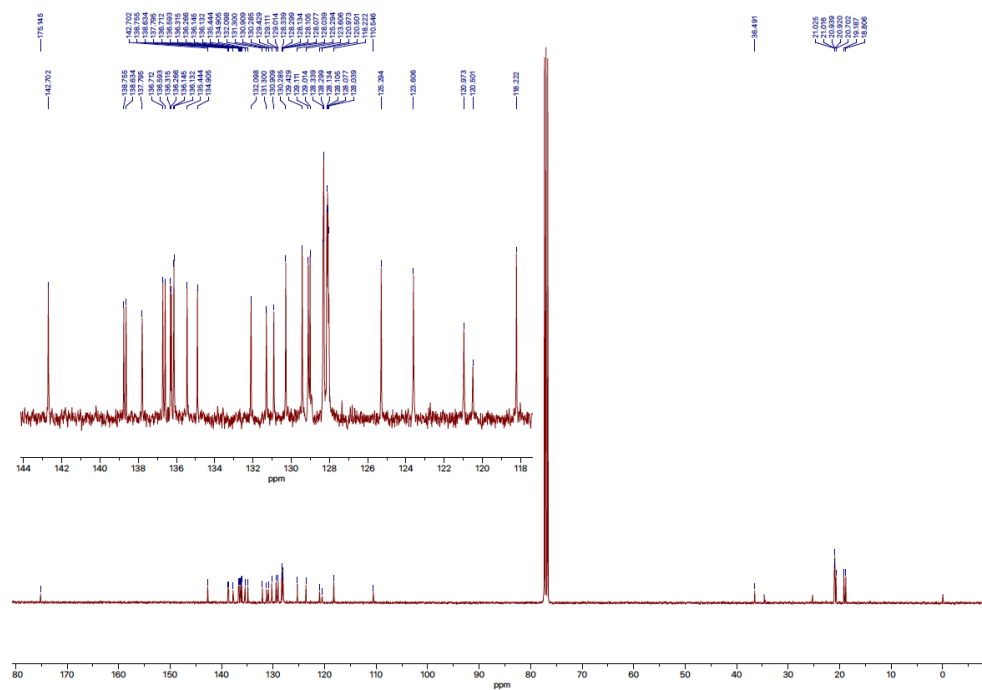


(R)-2h

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

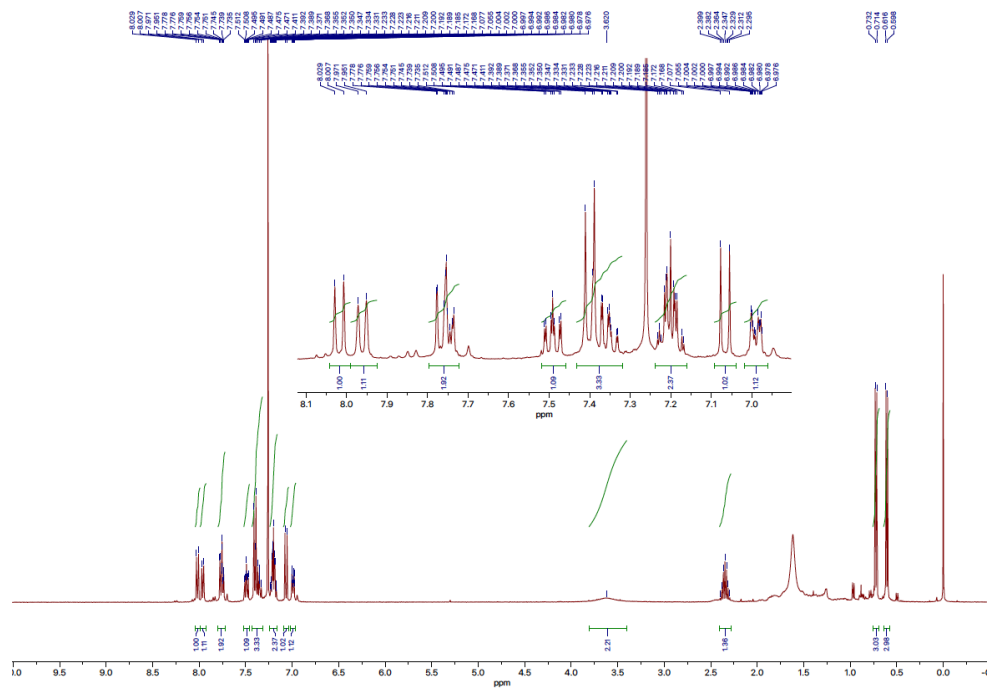


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



(R)-2i

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

