

**Supplementary information**

**CaPd(II)-catalyzed atroposelective and  
enantioselective C–H olefination of  
[*n*]metacyclophanes**

Xin-En Yan, Jia Li, Ziyang Dong, Hongxuan Zhai, Quan Tang, Changgui Zhao

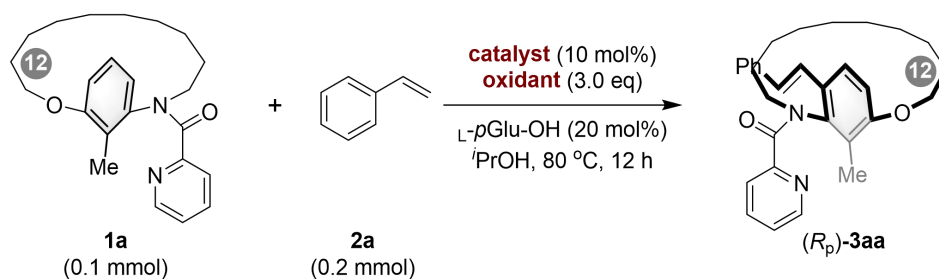
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## 1. General Information

Unless otherwise noted, all materials were purchased from commercial suppliers. Column chromatography was performed using silica gel (normal phase, 200 – 300 mesh) from Yantai Xinnuo Chemical Co., Ltd., usually with petroleum ether (PE, bp 60 – 90 °C) and ethyl acetate (EtOAc) as eluent. Reactions were monitored by thin-layer chromatography (TLC) on G254 silica gel plates (0.2 mm) from Yantai Xinnuo Chemical Co., Ltd. The plates were visualized by UV light and other TLC stains (1% potassium permanganate in water; 10 g of phosphomolybdic acid in 100 mL ethanol). <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>31</sup>P NMR spectra were recorded on JEOL Delta (400 MHz or 600 MHz) spectrometers with CDCl<sub>3</sub> as solvent and deuterated solvent residual peak or tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) are reported in Hertz (Hz), and the chemical shifts (*δ*) were reported in parts per million (ppm). Multiplicities are indicated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), doublet of doublets (dd), triplet of doublets (td), doublet of triplets (dt), triplet of triplets (tt), doublet of doublet of doublets (ddd) and multiplet (m). HPLC analysis was conducted on SHIMADZU LC-20ADXR instrument with chiral columns (Chiralpak IE, IB N-5, IC, AD-H, AS-H, and IF, column 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)). High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier XE mass spectrometer with TOF. Crystallographic data were collected using a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer equipped with a HyPix-6000E area detector at 100 K using Cu K α ( $\lambda = 1.54184 \text{ \AA}$ ) from a PhotonJet micro-focus X-ray source.

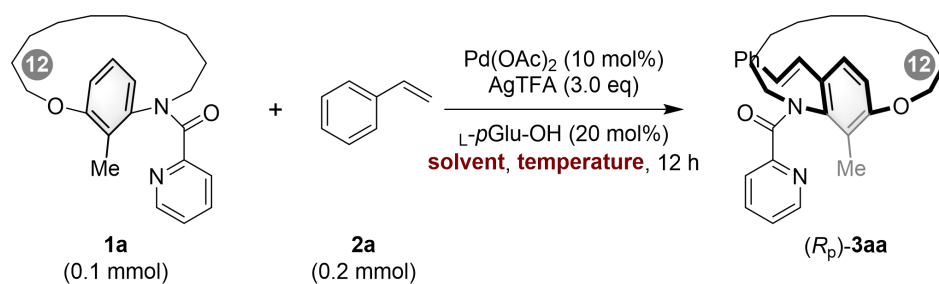
## 2.Optimization Studies



**Table S1.** Optimization of catalysts and oxidants.<sup>a</sup>

entry	catalyst	oxidant	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	PdCl <sub>2</sub>	AgTFA	72	69
2	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	AgTFA	99	71
3	Pd(COD)Cl <sub>2</sub>	AgTFA	99	69
4	PdBr <sub>2</sub>	AgTFA	84	69
5	Pd(MeCN) <sub>2</sub> Cl <sub>2</sub>	AgTFA	99	70
6	Pd(OAc) <sub>2</sub>	AgTFA	99	88
7	Pd(OAc) <sub>2</sub>	Ag <sub>2</sub> O	70	69
8	Pd(OAc) <sub>2</sub>	AgOAc	85	72
9	Pd(OAc) <sub>2</sub>	Ag <sub>2</sub> SO <sub>4</sub>	68	72
10	Pd(OAc) <sub>2</sub>	AgNO <sub>3</sub>	99	84
11	Pd(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	75	73

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), catalyst (0.01 mmol, 0.1 equiv.), *L*-pGlu-OH (0.02 mmol, 0.2 equiv.) and oxidant (0.3 mmol, 3.0 equiv.) were used at 80 °C for 12 h in *i*PrOH (2 mL) under air. <sup>b</sup>The yields were determined by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene (1/3 equiv.) as an internal standard. <sup>c</sup>The ee values were determined by chiral HPLC.



**Table S2.** Optimization of solvents and temperature. <sup>a</sup>

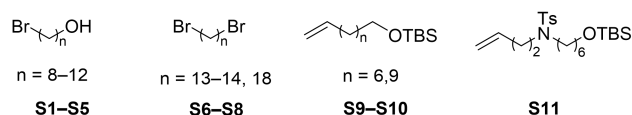
entry	solvent	temperature (°C)	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<i>t</i> -AmylOH	80	99	82
2	EtOH	80	99	84
3	TFE	80	70	60
4	MeCN	80	64	83
5	toluene	80	64	53
6	1,4-dioxane	80	99	70
7	PhCl	80	99	27
8	DME	80	99	56
9	<i>i</i> PrOH	70	96	90
10	<i>i</i> PrOH	60	<b>90(80<sup>e</sup>)</b>	<b>95</b>

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), Pd(OAc)<sub>2</sub> (0.01 mmol, 10 mol%), *L*-*p*Glu-OH (0.02 mmol, 0.2 equiv.) and AgTFA (0.3 mmol, 3.0 equiv.) were used at different temperature for 12 h in solvent (2.0 mL) under air. <sup>b</sup> The yields were determined by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene (1/3 equiv.) as an internal standard. <sup>c</sup> The ee values were determined by chiral HPLC. The ratio of *cis/trans* rotamer was determined by <sup>1</sup>H NMR.

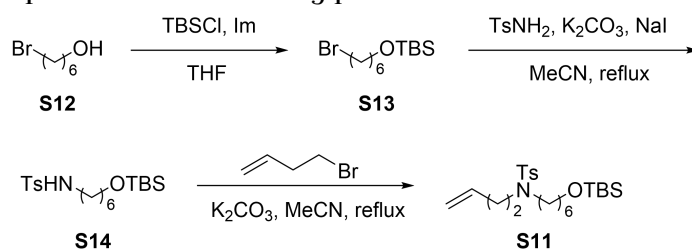
### 3. Methods and Procedures for the Synthesis of Substrates

#### 3.1 Procedure for the Synthesis of ansa Chain

The ansa chain **S1–S8** were purchased from commercial suppliers and used without further purification. **S9–S10**<sup>[1]</sup> were prepared according to literature procedure from commercially available materials. The spectra are in accordance with literature.



**S11** was prepared as the following procedure.



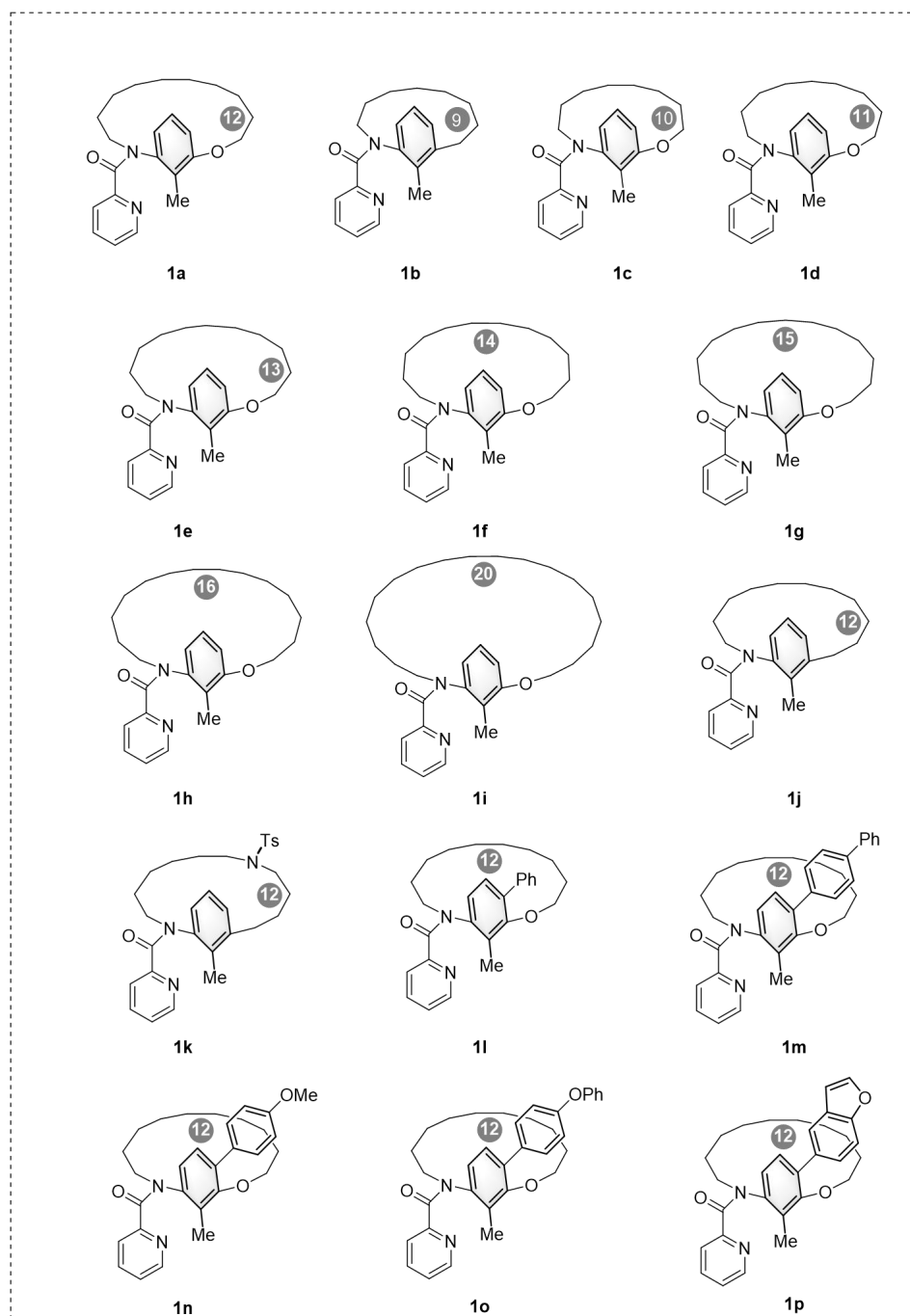
**S12** were obtained from commercial sources and used without further purification. To a solution of **S12** (3.62 g, 20 mmol, 1.0 equiv.) in dry THF (150 mL) was added imidazole (1.64 g, 24.0 mmol, 1.2 equiv.) and TBSCl (3.62 g, 24.0 mmol, 1.2 equiv.). The reaction mixture was stirred for 6 h. Then saturated NH<sub>4</sub>Cl (150 mL) was added and the organic phase was separated. The aqueous phase was extracted with EtOAc (150 mL×3), the combined organic phases were washed by brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 100:1, v/v) to afford the crude product **S13**.

To a solution of **S13** (4.43 g, 15.0 mmol, 1.0 equiv.) in MeCN (60 mL) was added K<sub>2</sub>CO<sub>3</sub> (8.29 g, 60.0 mmol, 2.0 equiv.), NaI (0.22 g, 1.5 mmol, 0.1 equiv.) and TsNH<sub>2</sub> (5.14 g, 30.0 mmol, 2.0 equiv.). The reaction mixture was heated to reflux in a heating mantle for overnight. The reaction mixture was cooled to room temperature and filtered, the solid was washed by EtOAc. Then, the solvent was removed *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 3:1, v/v) to afford the crude product **S14**.

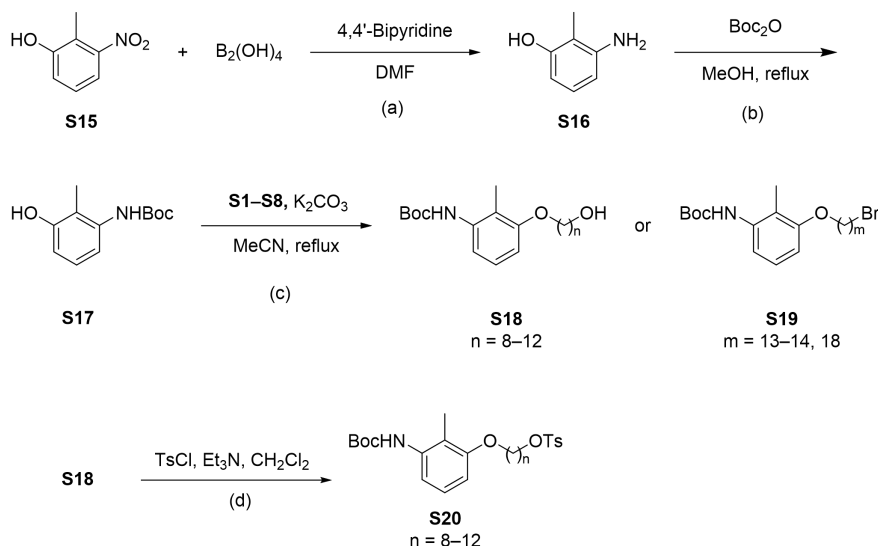
To a stirred suspension of **S14** (15.0 mmol, 1.0 equiv.) in MeCN (100 mL) was added K<sub>2</sub>CO<sub>3</sub> (8.29 g, 60.0 mmol, 4.0 equiv.). The reaction mixture was heated to reflux. And then, the stirring and refluxing suspension was added a solution of 4-bromo-1-butene (7.34 g, 45.0 mmol, 3.0 equiv.). The reaction mixture was stirred for overnight. After cooling to room temperature, the mixture was quenched and diluted by water (150 mL). Then the solution was extracted with EtOAc (150 mL×3) and the combined organic layers were dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then, the solvent was removed *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 20:1, v/v) to afford the crude product **S11**.

### 3.2 Experimental Procedures for Synthesis of Cyclophanes 1

The Cyclophanes **1** used in this study were synthesized through the procedure.



**Figure S1.** The structure of cyclophanes **1** used in this article.



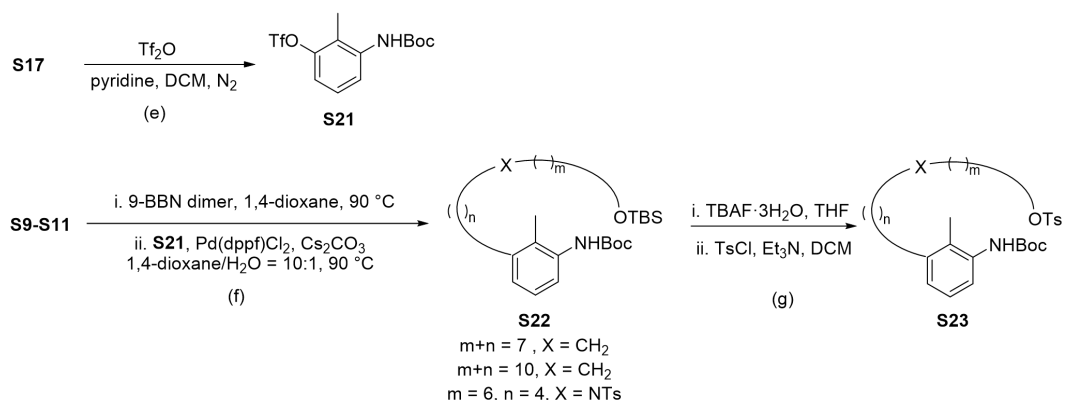
(a) To a solution of **S15** (7.66 g, 50 mmol, 1.0 equiv.) in dry DMF (30 mL) was added 4,4-Bipyridine (391 mg, 2.5 mmol, 0.05 equiv.). Then the  $\text{B}_2(\text{OH})_4$  (17.93 g, 200 mmol, 4.0 equiv.) was added to the reaction at 0 °C. After addition, the reaction mixture was warmed to room temperature and stirred for 2 h. Then the reaction mixtures were diluted with water (150 mL) and extracted with EtOAc (50 mL  $\times$  3). The combined organic phases were washed by brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and removing the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 2:1, v/v) to afford the crude product **S16** in 90% yield.

(b) To a 250 mL round-bottom flask equipped with a stirrer bar,  $\text{Boc}_2\text{O}$  (13.1 g, 60 mmol, 1.2 equiv.) was added to a solution of **S16** (50 mmol, 1.0 equiv.) in MeOH (150 mL). The mixture was refluxed (oil bath) until the **S16** was consumed completely (monitored by TLC). Then, after cooling to room temperature and removing the volatiles *in vacuo*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 3:1, v/v) to afford the crude product **S17** in 95% yield.

(c) The crude product **S17** (10 mmol, 1.0 equiv.), **S1-S8** (12 mmol, 1.2 equiv.) and  $\text{K}_2\text{CO}_3$  (5.53 g, 40 mmol, 4.0 equiv.) were charged into a 250 mL round-bottom flask and dissolved in MeCN (150 mL), and then refluxed (oil bath) until the **S14** was consumed completely (monitored by TLC). After cooling to room temperature, the mixture was diluted by water (300 mL) and extracted with EtOAc (150 mL  $\times$  3). The combined organic layers were dried over by anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel afforded the crude products **S18** or **S19** in 60% – 75% yields.

(d) To a solution of crude product **S18** (7 mmol, 1.0 equiv.) in a mixture of  $\text{Et}_3\text{N}$  and  $\text{CH}_2\text{Cl}_2$  (1:2 v/v, 90 mL) was added TsCl (1.60 g, 8.4 mmol, 1.2 equiv.), and then stirred at room temperature for overnight. The mixture was diluted by water (100 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (100 mL  $\times$  3), the combined organic phases were

washed by brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 10:1, v/v) to afford the products S20 in 80% yield.



(e) S17 (4.47g 20 mmol, 1.0 equiv.) were charged into a 250 mL round-bottom flask and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (150 mL), followed by the addition of pyridine (4.75 g, 60 mmol, 3.0 equiv.) and triflic anhydride (Tf<sub>2</sub>O, 6.77 g, 24 mmol, 1.2 equiv.) to the mixture at 0 °C (ice bath) under N<sub>2</sub> atmosphere. The reaction mixture was warmed to room temperature and stirred for overnight. The mixture was washed with a saturated aqueous solution of NaHCO<sub>3</sub> (100 mL), and the aqueous phase was further extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic phases were washed by brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 5:1, v/v) to afford the product S21.

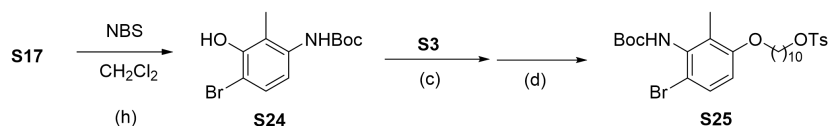
(f) To a solution of S9–S11 (10.0 mmol, 1.0 equiv.) in dry 1,4-dioxane (20.0 mL) was added 9-BBN dimer (1.82 g, 15.0 mmol, 1.5 equiv.) under N<sub>2</sub> atmosphere. The reaction mixture was stirred at 90 °C for 4 h and used directly for next step.

In another flask, S21 (2.66 g, 12.0 mmol, 1.2 equiv.), Pd(dppf)Cl<sub>2</sub> (0.37 g, 0.5 mmol, 0.05 equiv.), and Cs<sub>2</sub>CO<sub>3</sub> (9.75 g, 30.0 mmol, 3.0 equiv.) were added under N<sub>2</sub> atmosphere. The degassed 1,4-dioxane:H<sub>2</sub>O (30.0 mL, 10:1, v/v) was added to the reaction. Then, the above solution was added through a syringe. The reaction mixture was stirred at 90 °C for 8 h. Then saturated NH<sub>4</sub>Cl (20 mL) was added and the organic phase was separated. The aqueous phase was extracted with EtOAc (50 mL × 3), the combined organic phases were washed by brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 20:1, v/v) to afford the crude products S22.

(g) To a solution of the crude product S22 (8 mmol, 1.0 equiv.) in THF (50 mL) was added TBAF·3H<sub>2</sub>O (2.68 g, 9.6 mmol, 1.2 equiv.). The reaction was stirred at room temperature for 6 h. Then the aqueous phase was extracted with EtOAc (20 mL×3), the combined organic phases were washed by brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc =

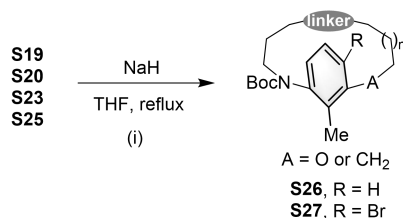
3:1, v/v) the crude product is obtained in quantitative yield and the crude product was used directly for next step.

To a solution of crude products in a mixture of Et<sub>3</sub>N and CH<sub>2</sub>Cl<sub>2</sub> (1:2 v/v, 60 mL) was added TsCl (1.83 g, 9.6 mmol, 1.2 equiv.), and then stirred at room temperature for overnight. The mixture was diluted by water (30 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL × 3), the combined organic phases were washed by brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 10:1, v/v) to afford the products S23.



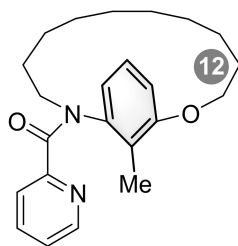
(h) S17 (4.47g 20 mmol, 1.0 equiv.) were charged into a 250 mL round-bottom flask and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (150 mL), *N*-Bromosuccinimide (NBS, 3.92g, 22 mmol, 1.1 equiv.) was added slowly to the mixture. The mixture was refluxed (oil bath) until the S14 was consumed completely (monitored by TLC). The mixture was diluted by water (30 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL × 3), the combined organic phases were washed by brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 10:1, v/v) to afford the product S24.

S24 and S3 undergo the similar reaction process of (c) and (d) to obtain S25.



(i) NaH (60% in mineral oil, 0.2 g, 20 mmol, 4.0 equiv.) and dry THF (150 mL) were successively charged into an oven-dried 250 mL round-bottom flask. The reaction mixture was heated to reflux. And then, the stirring and refluxing suspension was added a solution of S19, S20, S23 or S25 (5 mmol, 1.0 equiv.) in THF (50 mL) dropwise over 18 h. Upon addition, the reaction mixture was stirred for another 2 h. After cooling to room temperature, the mixture was quenched and diluted by water (300 mL). Then the solution was extracted with EtOAc (150 mL × 3) and the combined organic layers were dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removing the solvent *in vacuum*, the residue was purified by column chromatography (PE:EtOAc = 50:1, v/v) to get the crude product S26 or S27 in 65% – 85% yields.



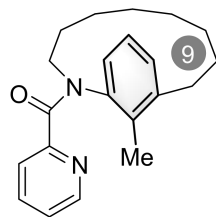


**1a**, white solid, *cis:trans* = 8:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.35 (d, *J* = 4.8 Hz, 1H), 7.51 (td, *J* = 7.8, 1.8 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.08 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 4.36 (ddd, *J* = 12.0, 5.5, 3.4 Hz, 1H), 4.15 (ddd, *J* = 12.2, 9.3, 3.0 Hz, 1H), 3.96 (dt, *J* = 13.4, 7.4 Hz, 1H), 3.80 (ddd, *J* = 13.8, 8.3, 5.8 Hz, 1H), 2.14 (s, 3H), 1.80 – 1.61 (m, 3.3H), 1.48 – 1.39 (m, 2.2H), 1.27 – 1.19 (m, 3.3H), 1.17 – 1.09 (m, 3.5H), 1.04 – 0.97 (m, 3.9H), 0.97 – 0.90 (m, 2.6H), 0.86 – 0.80 (m, 1.2H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.6, 157.1, 154.6, 148.7, 142.5, 136.0, 126.5, 126.1, 124.0, 123.2, 122.6, 113.5, 69.5, 47.8, 27.6, 27.5, 27.3, 26.9, 26.4, 25.4, 25.1, 24.8, 12.6.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>23</sub>H<sub>31</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 367.2381, found 367.2388.

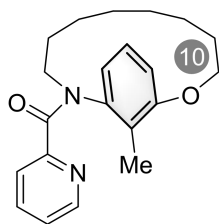


**1b**, white solid, *cis:trans* = 7:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.37 (d, *J* = 4.2 Hz, 1H), 7.56 (td, *J* = 7.7, 1.9 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.94 – 6.84 (m, 2H), 6.69 (d, *J* = 7.6 Hz, 1H), 4.42 (ddd, *J* = 14.3, 7.8, 3.7 Hz, 1H), 3.65 – 3.58 (m, 1H), 2.99 (dt, *J* = 13.3, 5.4 Hz, 1H), 2.48 – 2.46 (m, 1H), 2.45 (s, 3H), 1.88 – 1.70 (m, 1.9H), 1.57 – 1.45 (m, 2.7H), 1.36 – 1.27 (m, 1.2H), 1.24 – 1.16 (m, 1.3H), 1.14 – 0.99 (m, 2.6H), 0.94 – 0.80 (m, 4.0H), 0.38 – 0.31 (m, 1.1H), 0.24 – 0.16 (m, 1.1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.7, 154.9, 148.7, 143.3, 141.4, 136.1, 133.8, 129.6, 128.6, 125.7, 124.0, 123.2, 43.2, 33.8, 25.8, 25.1, 24.9, 24.2, 24.11, 24.07, 16.5.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>27</sub>N<sub>2</sub>O<sup>+</sup> 323.2118, found 323.2120.

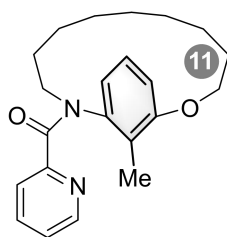


**1c**, white solid, *cis:trans* = 6:1.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.34 (d, *J* = 4.3 Hz, 1H), 7.54 (td, *J* = 7.8, 1.8 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.10 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 16.3 Hz, 1H), 6.80 (d, *J* = 16.3 Hz, 1H), 4.33 – 4.24 (m, 1H), 4.22 – 4.16 (m, 1H), 3.86 (ddd, *J* = 14.1, 7.7, 2.3 Hz, 1H), 2.15 (s, 3H), 1.66 – 1.48 (m, 3H), 1.44 – 1.34 (m, 2.4H), 1.13 – 1.00 (m, 3.3H), 0.92 – 0.85 (m, 2.4H), 0.81 – 0.63 (m, 2.3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.6, 157.2, 154.7, 148.6, 142.1, 136.1, 129.4, 126.2, 124.0, 123.4, 117.8, 71.5, 47.0, 28.0, 26.8, 26.7, 26.1, 25.3, 22.9, 13.3.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 339.2068, found 339.2062.

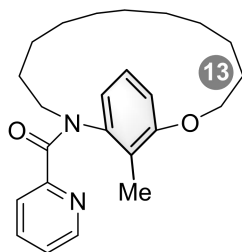


**1d**, white solid, *cis:trans* = 7:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.36 (d, *J* = 4.2 Hz, 1H), 7.51 (td, *J* = 7.7, 1.7 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.09 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 5H), 6.95 (t, *J* = 8.0 Hz, 5H), 6.74 (d, *J* = 8.2 Hz, 5H), 6.68 – 6.60 (m, 5H), 4.35 (ddd, *J* = 11.8, 6.0, 3.6 Hz, 5H), 4.17 (ddd, *J* = 12.1, 8.8, 3.5 Hz, 1H), 4.03 (ddd, *J* = 13.9, 7.5, 4.4 Hz, 1H), 3.96 (ddd, *J* = 13.9, 7.0, 4.5 Hz, 1H), 2.19 (s, 3H), 1.66 – 1.53 (m, 3.7H), 1.51 – 1.42 (m, 1.8H), 1.31 – 1.22 (m, 7.6H), 1.17 – 1.06 (m, 3.8H), 0.81 – 0.71 (m, 1.3H), 0.80 – 0.70 (m, 1.3H), 0.66 – 0.58 (m, 1.3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.7, 157.4, 154.7, 148.7, 143.1, 136.0, 126.7, 126.1, 124.0, 123.3, 122.8, 114.8, 69.4, 46.0, 27.59, 27.57, 26.5, 26.4, 26.0, 25.9, 22.4, 12.7.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>29</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 353.2224, found 353.2227.

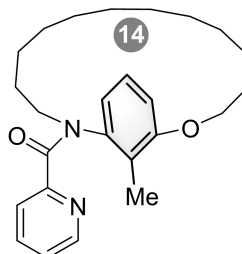


**1e**, white solid, *cis:trans* = 8:1.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.36 (d, *J* = 5.0 Hz, 1H), 7.49 (td, *J* = 7.7, 1.7 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.08 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 6.95 (t, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 4.23 (ddd, *J* = 10.6, 6.6, 3.6 Hz, 1H), 4.13 (ddd, *J* = 11.2, 7.1, 3.8 Hz, 1H), 4.00 (ddd, *J* = 13.5, 8.5, 6.7 Hz, 1H), 3.86 (ddd, *J* = 13.7, 8.7, 5.5 Hz, 1H), 2.11 (s, 3H), 1.68 – 1.53 (m, 3.5H), 1.51 – 1.34 (m, 2.2H), 1.27 – 1.10 (m, 9.5H), 1.08 – 0.94 (m, 4.2H), 0.89 – 0.78 (m, 1.2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 157.3, 154.7, 148.7, 142.1, 135.9, 126.1, 125.4, 123.9, 123.1, 121.9, 111.5, 68.0, 47.4, 28.1, 27.7, 27.6, 27.2, 26.9, 26.7, 25.5, 25.1, 24.4, 12.4.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>24</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 381.2537, found 381.2539.

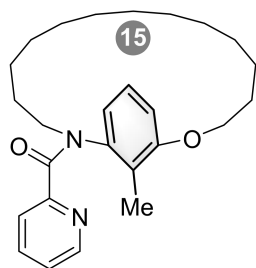


**1f**, white solid, *cis:trans* = 8:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.34 (d, *J* = 5.0 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.09 – 7.05 (m, 1H), 7.01 (t, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 4.12 – 4.01 (m, 3H), 3.74 – 3.66 (m, 1H), 2.05 (s, 3H), 1.75 – 1.61 (m, 5.1H), 1.59 – 1.47 (m, 2.4H), 1.37 – 1.30 (m, 1.6H), 1.25 – 1.17 (m, 5.5H), 1.16 – 0.93 (m, 12.5H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.6, 157.2, 154.7, 148.6, 142.7, 135.9, 126.3, 125.5, 123.9, 123.1, 121.4, 111.0, 67.7, 49.6, 28.3, 28.1, 27.9, 27.6, 27.5, 27.4, 27.1, 26.1, 25.7, 25.1, 12.3.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>25</sub>H<sub>35</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 395.2694, found 395.2699.

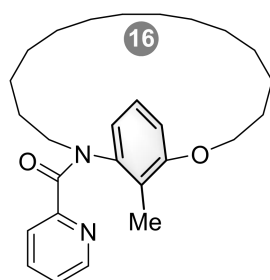


**1g**, white solid, *cis:trans* = 8:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.33 (d, *J* = 4.0 Hz, 1H), 7.48 (td, *J* = 7.7, 1.7 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.97 (t, *J* = 8.1 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 1H), 4.06 (dt, *J* = 9.9, 4.2 Hz, 1H), 3.99 – 3.93 (m, 2H), 3.82 (ddd, *J* = 13.2, 9.9, 5.6 Hz, 1H), 2.07 (s, 3H), 1.87 – 1.79 (m, 1.7H), 1.64 – 1.53 (m, 3.3H), 1.51 – 1.43 (m, 1.2H), 1.41 – 1.33 (m, 1.3H), 1.32 – 1.26 (m, 2.4H), 1.25 – 1.17 (m, 7.2H), 1.15 – 1.01 (m, 7.8H), 1.00 – 0.92 (m, 1.3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 157.8, 154.8, 148.7, 141.9, 135.8, 126.2, 125.0, 123.8, 123.0, 121.5, 110.1, 67.1, 48.6, 28.5, 28.32, 28.29, 28.2, 27.6, 27.3, 27.0, 26.8, 25.4, 25.1, 24.6, 12.2.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>38</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 409.2850, found 409.2855.

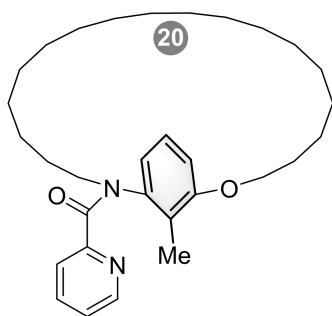


**1h**, yellow oil, *cis:trans* = 15:1.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.33 – 8.31 (m, 1H), 7.47 (td, *J* = 7.7, 2.0 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.09 – 6.96 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 4.19 – 4.09 (m, 1H), 4.04 – 3.98 (m, 1H), 3.90 – 3.83 (m, 1H), 3.63 – 3.54 (m, 1H), 2.01 (s, 3H), 1.86 – 1.70 (m, 3.9H), 1.62 – 1.52 (m, 3.5H), 1.37 – 1.19 (m, 13.1H), 1.18 – 1.12 (m, 7.0H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.7, 157.7, 154.7, 150.0, 148.6, 142.3, 137.1, 135.8, 127.0, 126.3, 125.3, 125.2, 123.8, 123.0, 121.2, 110.0, 67.5, 50.2, 29.7, 29.0, 28.8, 28.5, 28.3, 28.1, 28.0, 27.5, 27.3, 26.2, 26.1, 25.9, 12.2.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>26</sub>H<sub>37</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 423.3007, found 423.3011.

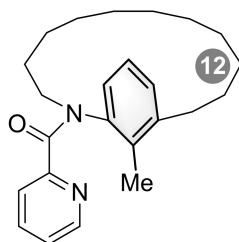


**1i**, light yellow oil, *cis:trans* = 16:1.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.37 – 8.31 (m, 1H), 7.55 – 7.46 (m, 2H), 7.12 – 6.97 (m, 2H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 4.14 – 4.06 (m, 1H), 3.99 – 3.93 (m, 1H), 3.89 – 3.83 (m, 1H), 3.65 – 3.55 (m, 1H), 2.02 (s, 3H), 1.59 (m, 16.0H), 1.37 – 1.16 (m, 20.5H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.7, 157.9, 154.8, 148.6, 142.5, 135.8, 126.3, 125.3, 123.8, 122.9, 121.2, 109.8, 68.0, 50.7, 29.8, 29.1, 29.00, 28.97, 28.9, 28.7, 28.64, 28.61, 28.4, 28.3, 28.2, 26.9, 25.9, 12.0.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>47</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 479.3633, found 479.3637.

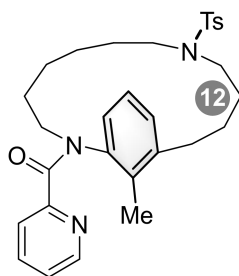


**1j**, colorless oil, *cis:trans* = 5:1.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.34 (d, *J* = 4.8 Hz, 1H), 7.50 (td, *J* = 7.7, 1.8 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.06 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 6.96 – 6.87 (m, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 4.08 (ddd, *J* = 13.4, 9.6, 6.1 Hz, 1H), 3.65 (ddd, *J* = 13.4, 9.7, 5.5 Hz, 1H), 2.82 (ddd, *J* = 13.0, 8.9, 3.5 Hz, 1H), 2.49 (ddd, *J* = 13.0, 8.2, 3.7 Hz, 1H), 2.28 (s, 3H), 1.80 – 1.68 (m, 3.0H), 1.60 – 1.37 (m, 4.1H), 1.28 – 1.16 (m, 4.0H), 1.17 – 1.06 (m, 8.2H), 1.05 – 0.87 (m, 6.7H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.7, 154.9, 148.8, 142.7, 141.3, 135.9, 133.9, 129.3, 127.9, 125.6, 123.8, 122.9, 47.9, 33.0, 29.0, 27.6, 27.0, 26.6, 26.5, 26.1, 26.0, 25.2, 24.9.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>24</sub>H<sub>33</sub>N<sub>2</sub>O<sup>+</sup> 365.2588, found 365.2589.

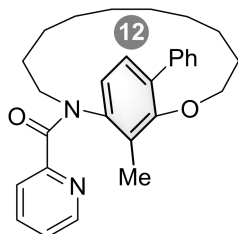


**1k**, colorless oil, *cis:trans* = 9:1.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.38 – 8.33 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 3H), 7.54 – 7.51 (m, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.12 – 7.06 (m, 1H), 6.90 – 6.87 (m, 2H), 6.74 – 6.70 (m, 1H), 4.15 (ddd, *J* = 14.6, 9.2, 6.1 Hz, 1H), 3.57 (ddd, *J* = 14.2, 9.3, 5.9 Hz, 1H), 3.25 (dt, *J* = 14.6, 7.9 Hz, 1H), 3.06 (dt, *J* = 14.7, 7.9 Hz, 1H), 2.88 (ddd, *J* = 12.9, 8.5, 3.7 Hz, 1H), 2.59 – 2.43 (m, 3H), 2.40 (s, 3H), 2.32 (s, 3H), 1.97 – 1.79 (m, 1.3H), 1.71 – 1.55 (m, 5.7H), 1.45 – 1.35 (m, 2.2H), 1.33 – 1.13 (m, 7.2H), 1.09 – 1.01 (m, 1.4H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.6, 148.7, 143.2, 136.2, 133.8, 129.7, 129.0, 128.3, 127.2, 125.9, 124.0, 123.1, 50.8, 50.6, 47.1, 32.2, 28.8, 27.9, 27.4, 25.3, 25.2, 25.0, 21.6, 15.6.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>38</sub>N<sub>3</sub>O<sub>3</sub>S<sup>+</sup> 520.2629, found 520.2625.

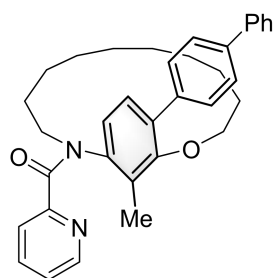


**1l**, white solid, *cis:trans* = 10:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.40 – 8.31 (m, 1H), 7.54 – 7.50 (m, 1H), 7.50 – 7.47 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 4.24 (ddd, *J* = 13.2, 10.4, 6.0 Hz, 1H), 3.81 (ddd, *J* = 10.9, 6.3, 4.1 Hz, 1H), 3.48 (ddd, *J* = 14.6, 10.8, 4.6 Hz, 1H), 3.42 (ddd, *J* = 11.9, 8.0, 3.6 Hz, 1H), 2.37 (s, 3H), 1.80 – 1.74 (m, 1.1H), 1.56 – 1.50 (m, 1.3H), 1.44 – 1.36 (m, 3.5H), 1.32 – 1.22 (m, 3.3H), 1.20 – 1.08 (m, 5.9H), 1.05 – 1.00 (m, 1.8H), 0.98 – 0.94 (m, 1.6H), 0.92 – 0.86 (m, 2.6H), 0.81 – 0.75 (m, 1.2H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.7, 155.8, 154.5, 148.8, 141.4, 139.2, 136.1, 132.8, 129.8, 128.9, 128.6, 128.3, 127.3, 125.3, 124.0, 122.9, 72.5, 47.1, 30.6, 27.1, 27.0, 25.5, 25.4, 24.9, 24.8, 23.8, 13.4.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>35</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 443.2694, found 443.2696.

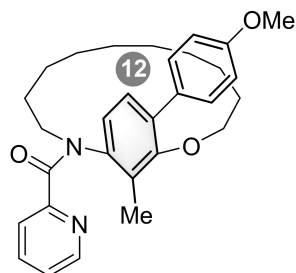


**1m**, white solid, *cis:trans* = 14:1.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.35 (d, *J* = 6.0 Hz, 1H), 7.69 – 7.55 (m, 7H), 7.48 – 7.40 (m, 2H), 7.38 – 7.30 (m, 3H), 7.10 – 7.06 (m, 1H), 6.96 – 6.90 (m, 1H), 6.70 – 6.64 (m, 1H), 4.29 – 4.18 (m, 1H), 3.90 – 3.80 (m, 1H), 3.57 – 3.39 (m, 2H), 2.38 (s, 3H), 1.84 – 1.70 (m, 2.1H), 1.57 – 1.21 (m, 6.7H), 1.19 – 0.79 (m, 11.4H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.7, 155.9, 154.5, 148.8, 141.4, 140.7, 140.0, 138.1, 136.1, 132.3, 129.9, 129.2, 128.9, 128.2, 127.5, 127.2, 127.1, 125.4, 124.0, 122.9, 72.6, 47.0, 30.6, 27.1, 27.0, 25.43, 25.41, 24.9, 24.7, 23.8, 13.4.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 519.3007, found 519.3013.

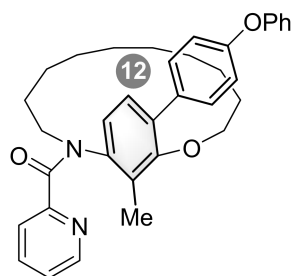


**1n**, white solid, *cis:trans* = 10:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.36 (d, *J* = 4.8 Hz, 1H), 7.53 – 7.30 (m, 4H), 7.34 – 7.29 (m, 1H), 7.13 – 7.05 (m, 1H), 6.98 – 6.85 (m, 4H), 6.65 – 6.60 (m, 1H), 4.27 – 4.18 (m, 1H), 3.88 – 3.80 (m, 5H), 3.55 – 3.37 (m, 2H), 2.36 (d, *J* = 5.1 Hz, 3H), 1.82 – 1.67 (m, 1.8H), 1.57 – 1.48 (m, 2.2H), 1.45 – 1.32 (m, 4.0H), 1.30 – 1.22 (m, 4.1H), 1.18 – 1.06 (m, 5.3H), 0.98 – 0.84 (m, 3.2H), 0.81 – 0.76 (m, 1.5H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 159.0, 155.7, 154.6, 148.8, 140.9, 136.1, 132.5, 131.5, 130.0, 129.8, 128.1, 125.3, 123.9, 122.9, 114.0, 72.2, 55.4, 47.1, 30.5, 27.1, 27.0, 25.5, 25.4, 24.9, 24.7, 23.8, 13.4.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>37</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> 473.2799, found 473.2790.

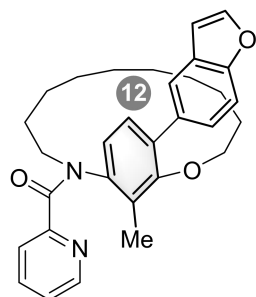


**10**, light yellow solid, *cis:trans* = 11:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.35 (d, *J* = 4.8 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.47 – 7.44 (m, 2H), 7.37 – 7.31 (m, 3H), 7.13 – 7.10 (m, 1H), 7.09 – 7.05 (m, 1H), 7.04 – 6.99 (m, 4H), 6.90 – 6.86 (d, *J* = 5.8 Hz, 1H), 6.64 (d, *J* = 5.7 Hz, 1H), 4.27 – 4.20 (m, 1H), 3.88 – 3.82 (m, 1H), 3.52 – 3.43 (m, 2H), 2.37 (s, 3H), 1.80 – 1.48 (m, 4.3H), 1.46 – 1.22 (m, 7.2H), 1.20 – 1.01 (m, 4.2H), 0.98 – 0.75 (m, 5.1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.7, 157.2, 156.7, 155.7, 154.6, 148.8, 141.3, 136.1, 134.1, 132.2, 130.5, 130.3, 129.93, 129.88, 128.1, 125.4, 124.0, 123.6, 122.9, 119.1, 118.8, 72.4, 47.1, 30.5, 27.1, 27.0, 25.5, 25.4, 24.9, 24.7, 23.9, 13.4.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>39</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> 535.2956, found 535.2957.



**1p**, white solid, *cis:trans* = 7:1.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.36 (d, *J* = 4.8 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.64 – 7.62 (m, 1H), 7.53 – 7.48 (m, 2H), 7.42 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.35 – 7.33 (m, 1H), 7.09 – 7.02 (m, 1H), 6.94 – 6.91 (m, 1H), 6.77 – 6.75 (m, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 4.24 (ddd, *J* = 13.1, 10.6, 6.1 Hz, 1H), 3.81 – 3.75 (m, 1H), 3.49 (ddd, *J* = 13.1, 10.9, 4.5 Hz, 1H), 3.38 (ddd, *J* = 11.8, 7.9, 3.5 Hz, 1H), 2.38 (s, 3H), 1.82 – 1.51 (m, 5.4H), 1.44 – 1.36 (m, 3.6H), 1.29 – 1.21 (m, 3.0H), 1.18 – 1.07 (m, 5.0H), 1.05 – 0.87 (m, 5.4H), 0.82 – 0.76 (m, 1.1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 155.7, 154.6, 154.4, 148.8, 145.6, 141.2, 136.1, 134.0, 133.1, 129.8, 128.6, 127.7, 125.5, 125.3, 124.0, 122.9, 121.5, 111.4, 106.8, 72.3, 47.1, 30.5, 27.1, 27.0, 25.5, 25.4, 24.9, 24.8, 23.8, 13.5.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>35</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> 483.2643, found 483.2646.

### 3.2 Procedure for the Synthesis of Alkenes 2a–2t

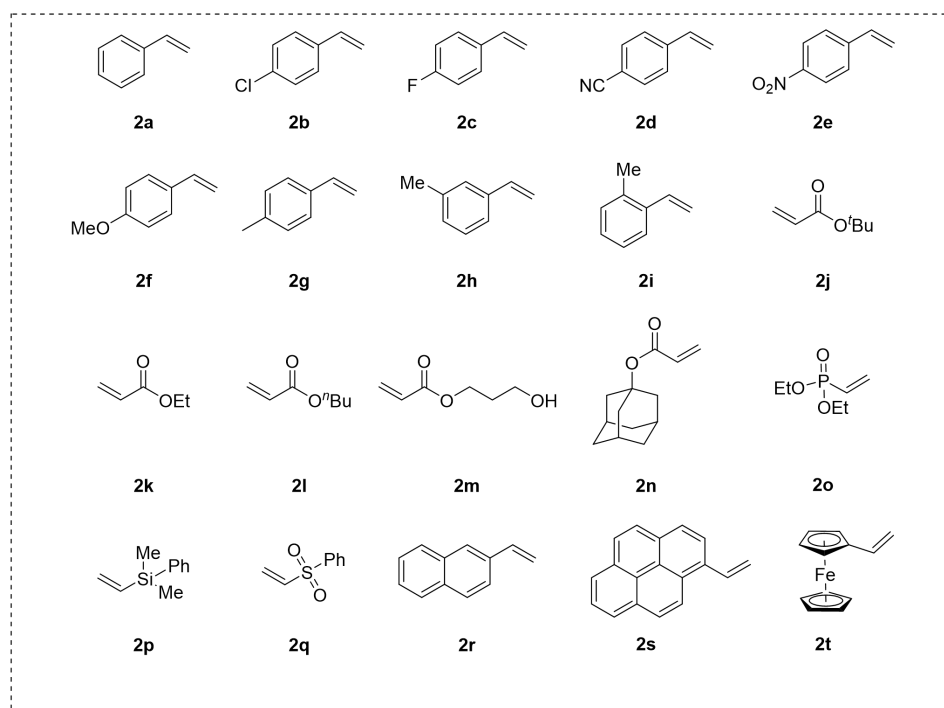
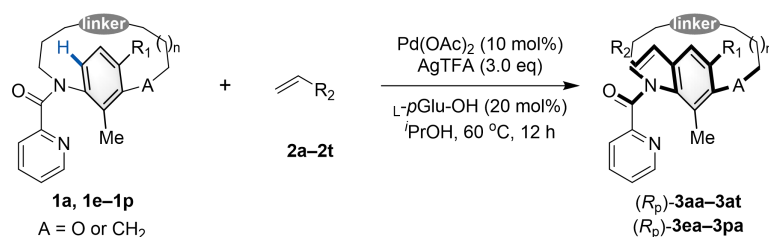


Figure S2. The structure of alkenes 2 used in this article.

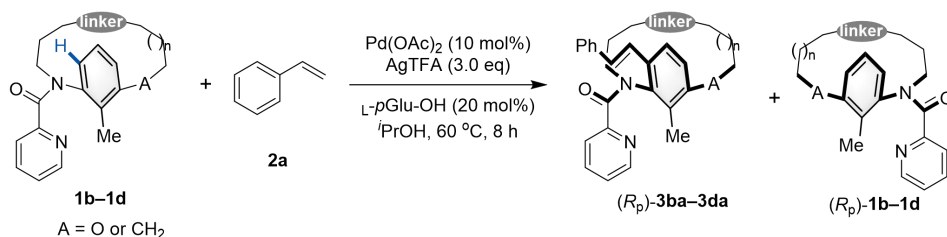
Alkenes 2a–2r and 2t were purchased from commercial suppliers and used without further purification. Known olefins 2s<sup>[1]</sup> were prepared according to literature procedure from commercially available materials. The spectra are in accordance with the literature.

## 4. Procedures for the Reaction of Cyclophanes **1** and Alkenes **2**

### 4.1 General Procedure



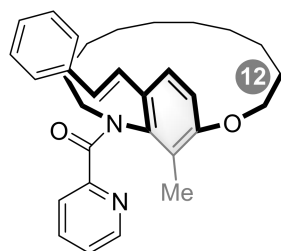
A 10 mL-reaction tube equipped with a magnetic stirring bar was charged with cyclophanes **1a, 1e-1p** (0.1 mmol, 1.0 equiv.), alkene **2a-2t** (0.2 mmol, 2.0 equiv.), Pd(OAc)<sub>2</sub> (2.2 mg, 0.01 mmol, 0.1 equiv.), L-pGlu-OH (2.6 mg, 0.02 mmol, 0.2 equiv.) and AgTFA (66.3 mg, 0.3 mmol, 3.0 equiv.). The tube was sealed and iPrOH (2.0 mL) was injected to the tube *via* a syringe. The reaction mixture was allowed to stir at 60 °C (pre-heated metal module) under air for 12 h. And then the reaction mixture was immediately cooled to room temperature. The solvent was evaporated and the residue was purified by alkaline alumina column chromatography (PE/EtOAc = 2:1, v/v) affording the cyclophanes **3aa-3at, 3ea-3pa**.



A 10 mL-reaction tube equipped with a magnetic stirring bar was charged with cyclophanes **1b-1d** (0.1 mmol, 1.0 equiv.), alkene **2a** (0.05 mmol, 0.5 equiv.), Pd(OAc)<sub>2</sub> (2.2 mg, 0.01 mmol, 0.1 equiv.), L-pGlu-OH (2.6 mg, 0.02 mmol, 0.2 equiv.) and AgTFA (66.3 mg, 0.3 mmol, 3.0 equiv.). The tube was sealed and iPrOH (2.0 mL) was injected to the tube *via* a syringe. The reaction mixture was allowed to stir at 60 °C (pre-heated metal module) under air stirred for 8 h. And then the reaction mixture was immediately cooled to room temperature. The solvent was evaporated and the residue was purified by alkaline alumina column chromatography (PE/EtOAc = 2:1, v/v) affording the cyclophanes **3ba-3da**.

**Note:** Racemic samples for the standard of chiral HPLC spectra were prepared using DL-pGlu-OH as catalyst.

## 4.2 Analytic Data of Products for Scope of Alkenes



(*R<sub>p</sub>*)-**3aa**, colorless oil, 37.4 mg, 80% yield, *cis:trans* = 8:1, 95% ee.

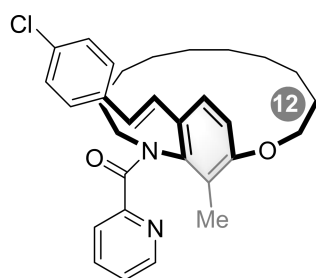
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.27 (d, *J* = 4.8 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.48 – 7.43 (m, 2H), 7.40 (d, *J* = 16.2 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.23 (d, *J* = 6.5 Hz, 1H), 7.05 (ddd, *J* = 7.1, 4.9, 2.3 Hz, 1H), 6.90 (d, *J* = 16.3 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 4.38 (ddd, *J* = 11.9, 5.4, 3.5 Hz, 1H), 4.21 – 4.07 (m, 2H), 3.71 – 3.58 (m, 1H), 2.12 (s, 3H), 1.74 – 1.58 (m, 2.2H), 1.53 – 1.41 (m, 2.5H), 1.34 – 1.22 (m, 3.9H), 1.17 – 1.10 (m, 3.2H), 1.08 – 0.99 (m, 4.4H), 0.98 – 0.87 (m, 2.3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.9, 156.3, 154.4, 148.3, 140.7, 137.7, 135.8, 129.0, 128.9, 128.5, 127.7, 127.2, 126.6, 125.1, 124.1, 123.5, 123.0, 113.8, 69.3, 48.6, 27.4, 27.3, 26.9, 26.4, 25.6, 24.9, 24.8, 13.1.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>37</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 469.2850, found 469.2859.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t<sub>R</sub>* = 8.96 min (minor), 12.02 min (major).

**[ $\alpha$ ]<sub>D</sub><sup>25</sup>** = -320.0 (c = 0.22, CH<sub>2</sub>Cl<sub>2</sub>).



(*R<sub>p</sub>*)-**3ab**, colorless oil, 33.1 mg, 66% yield, *cis:trans* = 8:1, 92% ee.

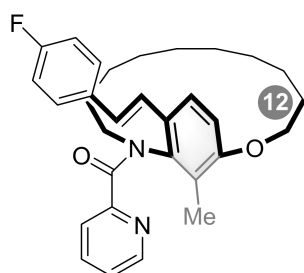
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.24 (d, *J* = 4.8 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.43 – 7.37 (m, 3H), 7.33 – 7.30 (m, 2H), 7.19 (d, *J* = 16.2 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.85 – 6.79 (m, 2H), 4.38 (ddd, *J* = 11.6, 5.5, 3.3 Hz, 1H), 4.15 (ddd, *J* = 12.0, 9.4, 2.9 Hz, 1H), 4.09 (dt, *J* = 13.9, 7.1 Hz, 1H), 3.62 (dt, *J* = 14.1, 7.3 Hz, 1H), 2.11 (s, 3H), 1.73 – 1.65 (m, 1.4H), 1.63 – 1.57 (m, 1.2H), 1.50 – 1.41 (m, 2.5H), 1.31 – 1.21 (m, 4.3H), 1.16 – 1.10 (m, 2.4H), 1.08 – 0.99 (m, 4.8H), 0.96 – 0.88 (m, 2.9H)

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 156.5, 154.3, 148.3, 140.8, 136.2, 135.8, 133.2, 129.0, 128.9, 128.2, 127.8, 127.7, 127.6, 127.5, 127.1, 125.8, 124.2, 123.6, 123.0, 113.8, 69.3, 48.6, 27.4, 27.34, 27.32, 26.9, 26.4, 25.6, 24.9, 24.8, 13.1.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{31}\text{H}_{36}\text{ClN}_2\text{O}_2^+$  503.2460, found 503.2454.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 8.72 min (minor), 15.68 min (major).

$[\alpha]_{\text{D}}^{25} = -298.9$  ( $c = 0.18$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-3ac, colorless oil, 36.0 mg, 74% yield, *cis:trans* = 6:1, 91% ee.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 – 8.22 (m, 1H), 7.49 – 7.43 (m, 4H), 7.39 (d,  $J = 8.6$  Hz, 1H), 7.13 (d,  $J = 16.3$  Hz, 1H), 7.04 (dd,  $J = 9.7, 7.5$  Hz, 3H), 6.87 – 6.80 (m, 2H), 4.40 – 4.34 (m, 1H), 4.21 – 4.06 (m, 2H), 3.66 – 3.58 (m, 1H), 2.11 (s, 3H), 1.75 – 1.56 (m, 3.1H), 1.52 – 1.40 (m, 2.6H), 1.34 – 1.22 (m, 4.1H), 1.16 – 1.08 (m, 2.8H), 1.06 – 0.98 (m, 3.5H), 0.97 – 0.88 (m, 2.6H).

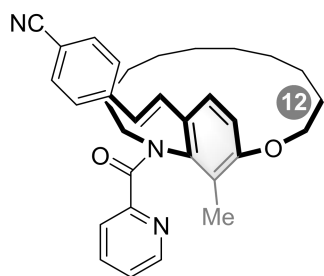
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 162.4 (d,  $J = 247.2$  Hz), 156.3, 154.3, 148.4, 140.6, 137.1, 135.8, 133.9 (d,  $J = 3.1$  Hz), 128.4, 128.1 (d,  $J = 8.0$  Hz), 127.8, 127.1, 125.0, 124.9, 124.2, 123.5, 122.9, 115.8 (d,  $J = 21.6$  Hz), 113.8, 69.3, 48.6, 27.33, 27.30, 26.9, 26.4, 25.6, 24.9, 24.8, 13.1.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.12, -114.65.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{31}\text{H}_{37}\text{FN}_2\text{O}_2^+$  487.2756, found 487.2750.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 8.52 min (minor), 14.82 min (major).

$[\alpha]_{\text{D}}^{25} = -391.7$  ( $c = 0.15$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**3ad**, colorless oil, 44.4 mg, 90% yield, *cis:trans* = 6:1, 92% ee.

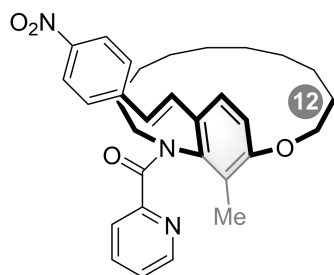
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.21 (d, *J* = 4.0 Hz, 1H), 7.62 – 7.58 (m, 3H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.35 (d, *J* = 16.3 Hz, 1H), 7.06 (ddd, *J* = 6.7, 4.8, 1.7 Hz, 1H), 6.89 – 6.82 (m, 2H), 4.42 – 4.32 (m, 1H), 4.15 (ddd, *J* = 12.2, 9.5, 2.9 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.59 (dt, *J* = 13.9, 7.1 Hz, 1H), 2.09 (s, 3H), 1.71 – 1.66 (m, 1.6H), 1.59 (dt, *J* = 13.9, 7.0 Hz, 1.1H), 1.50 – 1.31 (m, 2.4H), 1.30 – 1.20 (m, 4.0H), 1.14 – 1.08 (m, 2.6H), 1.05 – 0.98 (m, 5.5H), 0.95 – 0.85 (m, 2.3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 157.1, 154.1, 148.7, 148.2, 142.3, 141.3, 135.9, 132.6, 132.5, 129.1, 127.6, 127.1, 127.0, 126.9, 126.7, 124.31, 124.28, 123.9, 123.0, 119.2, 113.6, 110.5, 69.2, 48.7, 27.31, 27.28, 27.2, 26.9, 26.4, 25.6, 24.9, 24.8, 13.0.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>32</sub>H<sub>36</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> 494.2803, found 494.2809.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t*<sub>R</sub> = 11.12 min (minor), 20.62 min (major).

**[ $\alpha$ ]<sub>D</sub><sup>25</sup>** = -299.5 (c = 0.20, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3ae**, yellow oil, 27.7mg, 54% yield, *cis:trans* =5:1, 86% ee.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.21 – 8.19 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.42 (d, *J* = 16.2 Hz, 1H), 7.12 – 7.05 (m, 1H), 6.95 – 6.90 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 1H), 4.45 – 4.38 (m, 1H), 4.20 – 4.15 (m, 1H), 4.12 (dt, *J* = 13.9, 6.7 Hz, 1H), 3.60 (dt, *J* = 14.0, 7.1 Hz, 1H), 2.09 (s, 3H), 1.73 – 1.66 (m, 2.2H), 1.52 – 1.42 (m, 3.6H), 1.34 – 1.19 (m, 6.7H), 1.16 – 1.09 (m, 2.9H), 1.08 – 0.98 (m, 7.5H), 0.96 – 0.84 (m, 3.7H).

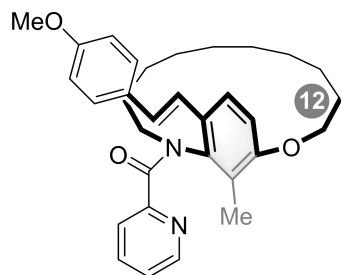
**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 157.3, 154.1, 148.3, 144.3, 141.5, 136.0, 130.1,

129.4, 127.0, 126.3, 124.38, 124.36, 124.0, 123.4, 123.1, 113.6, 69.3, 48.9, 27.4, 27.32, 27.26, 26.9, 26.5, 25.6, 25.0, 24.8, 13.1.

**HPLC:** Chiralpak IB N-5 column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 6.75 min (minor), 7.57 min (major).

**HRMS (ESI):**  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>36</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup> 514.2701, found 514.2708.

$[\alpha]_D^{25}$  = -358.7 (c = 0.24, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3af**, colorless oil, 32.9 mg, 66% yield, *cis:trans* = 7:1, 92% ee.

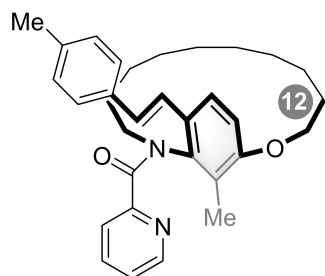
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.27 (d,  $J$  = 4.2 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.39 (d,  $J$  = 8.6 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.89 (d,  $J$  = 8.8 Hz, 2H), 6.84 (d,  $J$  = 12.0 Hz, 1H), 6.81 (d,  $J$  = 4.4 Hz, 1H), 4.37 (ddd,  $J$  = 11.9, 5.4, 3.5 Hz, 1H), 4.16 – 4.03 (m, 2H), 3.82 (s, 3H), 3.63 (ddd,  $J$  = 13.9, 8.0, 6.5 Hz, 1H), 2.11 (s, 3H), 1.71 – 1.57 (m, 2.1H), 1.51 – 1.41 (m, 2.6H), 1.33 – 1.21 (m, 3.8H), 1.18 – 1.08 (m, 3.1H), 1.06 – 0.96 m, 4.9H), 0.95 – 0.87 (m, 2.7H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.9, 159.4, 156.0, 154.4, 148.4, 140.3, 135.7, 130.5, 128.8, 128.6, 127.8, 127.1, 124.1, 123.3, 122.94, 122.90, 114.3, 114.2, 113.9, 69.3, 55.5, 48.5, 27.4, 27.34, 27.31, 26.9, 26.4, 25.6, 24.9, 24.8, 13.1.

**HRMS (ESI):**  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>32</sub>H<sub>39</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> 499.2956, found 499.2959.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 9.26 min (minor), 16.94 min (major).

$[\alpha]_D^{25}$  = -305.8 (c = 0.24, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3ag**, colorless oil, 37.6 mg, 78% yield, *cis:trans* = 6:1, 90% ee.

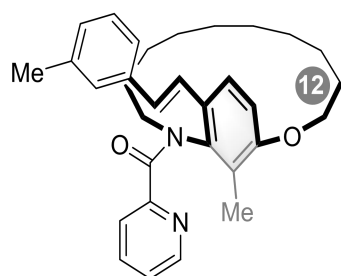
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.27 (d, *J* = 4.8 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.41 – 7.39 (m, 3H), 7.21 – 7.13 (m, 3H), 7.06 (ddd, *J* = 6.8, 4.8, 1.7 Hz, 1H), 6.86 (d, *J* = 16.5 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 4.38 (ddd, *J* = 11.9, 5.4, 3.5 Hz, 1H), 4.22 – 4.04 (m, 2H), 3.63 (dt, *J* = 13.9, 7.1 Hz, 1H), 2.36 (s, 3H), 2.12 (s, 3H), 1.75 – 1.57 (m, 3.4H), 1.53 – 1.42 (m, 2.7H), 1.35 – 1.22 (m, 5.3H), 1.14 – 1.07 (m, 3.1H), 1.06 – 0.99 (m, 4.1H), 0.98 – 0.85 (m, 2.4H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 169.0, 156.2, 154.4, 148.4, 140.5, 137.7, 135.8, 134.9, 129.6, 129.0, 128.7, 127.2, 126.5, 124.06, 124.13, 123.4, 122.9, 113.9, 69.3, 48.6, 27.41, 27.37, 27.3, 26.9, 26.4, 25.6, 24.9, 24.8, 21.4, 13.1.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>32</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 483.3007, found 483.3010.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, *t<sub>R</sub>* = 7.59 min (minor), 12.14 min (major).

[α]<sub>D</sub><sup>25</sup> = -314.2 (c = 0.19, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3ah**, colorless oil, 39.5 mg, 82% yield, *cis:trans* = 6:1, >99% ee.

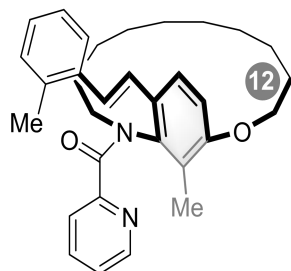
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.28 (d, *J* = 3.9 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.27 (d, *J* = 3.9 Hz, 1H), 7.25 (d, *J* = 3.8 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.89 (d, *J* = 16.3 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 4.44 – 4.35 (m, 1H), 4.22 – 4.11 (m, 2H), 3.60 (dt, *J* = 13.9, 7.1 Hz, 1H), 2.39 (s, 3H), 2.11 (s, 3H), 1.72 – 1.58 (m, 1.9H), 1.54 – 1.42 (m, 2.5H), 1.34 – 1.21 (m, 4.1H), 1.18 – 1.10 (m, 2.8H), 1.08 – 0.99 (m, 4.9H), 0.98 – 0.91 (m, 2.7H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 168.9, 156.2, 154.4, 148.4, 140.6, 138.4, 137.6, 135.8, 129.2, 128.8, 128.6, 127.21, 127.15, 124.9, 124.1, 123.9, 123.6, 123.0, 113.8, 69.2, 48.6, 27.4, 27.3, 26.9, 26.5, 25.7, 25.0, 24.8, 21.6, 13.1.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>32</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 483.3007, found 483.3011.

**HPLC:** Chiralpak AD-H column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, *t<sub>R</sub>* = 13.89 min (major), 15.58 min (minor).

$[\alpha]_{\text{D}}^{25} = -262.7$  ( $c = 0.38$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**3ai**, colorless oil, 33.3 mg, 69% yield, *cis:trans* = 6:1, 90% ee.

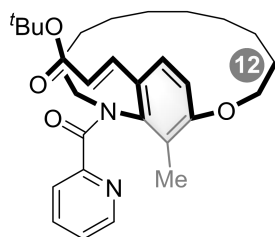
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.35 (d,  $J = 5.0$  Hz, 1H), 7.70 (d,  $J = 7.4$  Hz, 1H), 7.59 – 7.54 (m, 2H), 7.51 (d,  $J = 8.6$  Hz, 1H), 7.33 (d,  $J = 14.0$  Hz, 2H), 7.28 – 7.19 (m, 3H), 7.17 – 7.12 (m, 1H), 6.92 (d,  $J = 8.7$  Hz, 1H), 4.56 – 4.43 (m, 1H), 4.31 – 4.15 (m, 3H), 3.73 (dt,  $J = 13.8, 7.2$  Hz, 1H), 2.49 (s, 3H), 2.21 (s, 3H), 1.86 – 1.68 (m, 1.9H), 1.64 – 1.52 (m, 2.6H), 1.46 – 1.32 (m, 4.3H), 1.30 – 1.18 (m, 3.1H), 1.22 – 1.12 (m, 4.3H), 1.09 – 0.97 (m, 2.6H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 156.3, 154.4, 148.3, 140.6, 136.6, 135.8, 135.6, 130.5, 128.9, 127.6, 127.2, 126.8, 126.5, 125.6, 124.1, 123.8, 122.9, 113.8, 69.3, 48.5, 27.3, 26.9, 26.4, 25.6, 25.0, 24.8, 20.1, 13.1.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{32}\text{H}_{39}\text{N}_2\text{O}_2^+$  483.3007, found 483.3010.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R = 8.02$  min (minor), 9.65 min (major).

$[\alpha]_{\text{D}}^{25} = -295.6$  ( $c = 0.28$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**3aj**, colorless oil, 33.9 mg, 69% yield, *cis:trans* = 9:1, 93% ee.

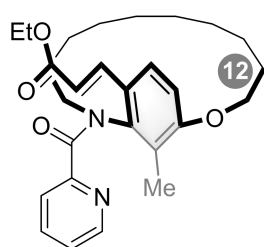
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.66 (s, 1H), 7.72 – 7.61 (m, 1H), 7.55 (d,  $J = 8.1$  Hz, 1H), 7.51 – 7.46 (m, 1H), 7.38 – 7.31 (m, 1H), 7.14 – 7.10 (m, 1H), 6.91 – 6.87 (m, 1H), 6.29 – 6.20 (m, 1H), 4.44 – 4.36 (m, 1H), 4.30 – 4.22 (m, 1H), 4.22 – 4.14 (m, 1H), 3.56 – 3.45 (m, 1H), 2.04 (s, 3H), 1.54 – 1.47 (m, 9H), 1.34 – 1.17 (m, 8.8H), 1.13 – 1.06 (m, 2.4H), 1.06 – 0.97 (m, 4.1H), 0.93 – 0.86 (m, 4.9H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 166.3, 158.8, 151.4, 141.3, 138.5, 138.5, 137.6, 127.1, 126.2, 126.1, 124.7, 124.1, 121.2, 121.1, 113.9, 69.3, 50.3, 28.33, 28.30, 27.42, 27.39, 27.31, 27.28, 27.0, 26.8, 26.71, 26.68, 25.74, 25.71, 24.9, 13.0.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{30}\text{H}_{41}\text{N}_2\text{O}_4^+$  493.3061, found 493.3067.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 8.17 min (minor), 8.62 min (major).

$[\alpha]_{\text{D}}^{25} = -175.8$  (c = 0.27,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**3ak**, colorless oil, 31.7 mg, 68% yield, *cis:trans* = 7:1, 89% ee.

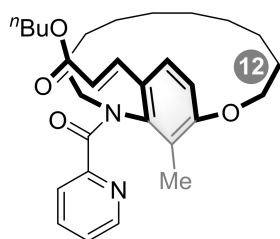
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J$  = 1.5 Hz, 1H), 7.81 (d,  $J$  = 16.0 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.39 (d,  $J$  = 8.7 Hz, 1H), 7.06 (ddd,  $J$  = 6.8, 4.8, 1.8 Hz, 1H), 6.80 (d,  $J$  = 8.7 Hz, 1H), 6.25 (d,  $J$  = 15.9 Hz, 1H), 4.39 (ddd,  $J$  = 11.9, 5.2, 3.4 Hz, 1H), 4.21 – 4.06 (m, 2H), 3.45 (dt,  $J$  = 13.8, 7.0 Hz, 1H), 2.02 (s, 3H), 1.73 – 1.63 (m, 1.2H), 1.60 – 1.51 (m, 1.2H), 1.50 – 1.39 (m, 2.8H), 1.33 – 1.27 (m, 4.7H), 1.28 – 1.23 (m, 3.1H), 1.14 – 1.07 (m, 2.2H), 1.04 – 0.96 (m, 4.9H), 0.93 – 0.78 (m, 3.9H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 167.1, 158.3, 154.0, 148.1, 142.6, 141.2, 136.0, 127.5, 125.5, 125.2, 124.3, 123.5, 118.2, 113.2, 69.2, 60.5, 49.2, 27.4, 27.3, 27.0, 26.6, 25.7, 25.1, 24.8, 14.5, 13.0.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{28}\text{H}_{37}\text{N}_2\text{O}_4^+$  465.2748, found 465.2741.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 17.98 min (minor), 28.30 min (major).

$[\alpha]_{\text{D}}^{25} = -220.0$  (c = 0.23,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**3al**, colorless oil, 29.5 mg, 60% yield, *cis:trans* = 8:1, 90% ee.

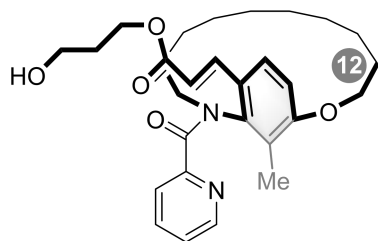
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.22 (d,  $J$  = 4.9 Hz, 1H), 7.81 (d,  $J$  = 16.0 Hz, 1H), 7.56 (d,  $J$  = 4.6 Hz, 2H), 7.40 (d,  $J$  = 8.7 Hz, 1H), 7.10 (p,  $J$  = 4.5 Hz, 1H), 6.81 (d,  $J$  = 8.5 Hz, 1H), 6.26 (d,  $J$  = 15.9 Hz, 1H), 4.39 (dt,  $J$  = 11.6, 4.2 Hz, 1H), 4.26 – 4.16 (m, 4H), 3.48 (dt,  $J$  = 13.5, 6.8 Hz, 1H), 2.05 (s, 3H), 1.72 – 1.66 (m, 4.1H), 1.60 – 1.56 (m, 1.1H), 1.48 – 1.40 (m, 5.5H), 1.34 – 1.20 (m, 1.3H), 1.15 – 1.07 (m, 1.1H), 1.06 – 0.99 (m, 5.7H), 0.98 – 0.92 (m, 3.2H), 0.93 – 0.88 (m, 2.8H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 167.2, 152.0, 151.0, 141.1, 139.2, 137.9, 127.2, 126.6, 126.2, 124.5, 124.2, 119.4, 114.2, 69.5, 65.1, 50.4, 30.8, 27.4, 27.3, 26.94, 26.88, 26.7, 25.6, 24.9, 24.8, 19.3, 13.8, 13.0.

**HRMS (ESI):**  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>41</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> 493.3061, found 493.3066.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 13.64 min (minor), 22.51 min (major).

$[\alpha]_D^{25}$  = -207.9 (c = 0.17, CH<sub>2</sub>Cl<sub>2</sub>).



(*R<sub>p</sub>*)-**3am**, slight yellow oil, 34.6 mg, 70% yield, *cis:trans* = 3:1, 94% ee.

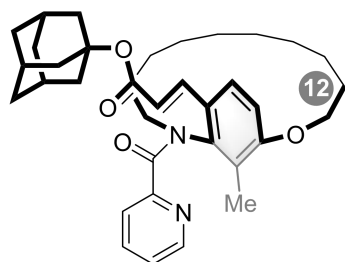
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.24 (d,  $J$  = 4.7 Hz, 1H), 7.84 (d,  $J$  = 15.8 Hz, 1H), 7.53 (td,  $J$  = 7.7, 1.7 Hz, 1H), 7.46 (d,  $J$  = 7.8 Hz, 1H), 7.37 (d,  $J$  = 8.7 Hz, 1H), 7.10 (ddd,  $J$  = 7.5, 4.7, 1.3 Hz, 1H), 6.83 (d,  $J$  = 8.7 Hz, 1H), 6.20 (d,  $J$  = 15.9 Hz, 1H), 4.41 (ddd,  $J$  = 12.0, 5.9, 3.3 Hz, 2H), 4.31 – 4.23 (m, 1H), 4.20 – 4.11 (m, 1H), 3.99 (ddd,  $J$  = 14.2, 8.3, 6.3 Hz, 1H), 3.92 – 3.85 (m, 2H), 3.73 – 3.64 (m, 1H), 2.46 (s, 3H), 2.11 (s, 3H), 1.70 – 1.60 (m, 1.7H), 1.53 – 1.44 (m, 1.4H), 1.42 – 1.34 (m, 1.8H), 1.30 – 1.21 (m, 3.0H), 1.14 – 1.06 (m, 3.1H), 1.04 – 0.98 (m, 4.3H), 0.97 – 0.92 (m, 2.2H), 0.90 – 0.86 (m, 1.9H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.5, 167.2, 158.7, 153.5, 148.3, 142.5, 141.8, 136.2, 127.3, 125.4, 125.2, 124.5, 123.3, 117.4, 113.5, 69.3, 66.4, 61.4, 48.8, 27.3, 27.2, 26.9, 26.4, 25.5, 24.8, 24.6, 13.0

**HRMS (ESI):**  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>39</sub>N<sub>2</sub>O<sub>5</sub><sup>+</sup> 495.2854, found 495.2850.

**HPLC:** Chiralpak IF column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 14.65 min (major), 23.76 min (minor).

$[\alpha]_D^{25}$  = -158.6 (c = 0.15, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3an**, colorless oil, 41.0 mg, 72% yield, *cis:trans* = 6:1, 94% ee.

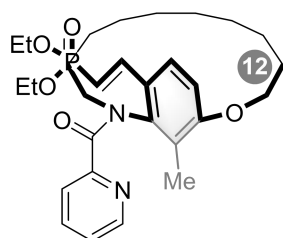
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.20 (d, *J* = 4.8, 1H), 7.69 (d, *J* = 15.9 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.06 (ddd, *J* = 6.2, 4.7, 2.7 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 6.14 (d, *J* = 15.9 Hz, 1H), 4.38 (ddd, *J* = 12.0, 5.2, 3.5 Hz, 1H), 4.21 – 4.06 (m, 2H), 3.52 (dt, *J* = 13.9, 7.0 Hz, 1H), 2.17 (d, *J* = 7.5 Hz, 12H), 2.05 (s, 3H), 1.73 – 1.55 (m, 10.7H), 1.50 – 1.40 (m, 2.7H), 1.31 – 1.19 (m, 3.7H), 1.14 – 1.05 (m, 2.9H), 1.05 – 0.94 (m, 5.9H), 0.93 – 0.82 (m, 3.2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.5, 166.1, 158.1, 154.0, 148.1, 142.4, 140.1, 135.9, 127.4, 125.7, 125.0, 124.2, 123.4, 120.2, 113.3, 80.6, 69.2, 49.0, 41.6, 36.3, 30.9, 27.32, 27.27, 27.1, 26.9, 26.5, 25.6, 24.9, 24.8, 13.0.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>47</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> 571.3531, found 571.3537.

**HPLC:** Chiralpak IC column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t<sub>R</sub>* = 18.28 min (minor), 23.13 min (major).

**[ $\alpha$ ]<sub>D</sub><sup>25</sup>** = -181.5 (c = 0.20, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3ao**, light yellow oil, 30.6 mg, 58% yield, *cis:trans* = 7:1, 94% ee.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.38 – 8.24 (m, 1H), 7.60 – 7.50 (m, 2H), 7.48 – 7.44 (m, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.18 – 6.04 (m, 1H), 4.43 – 4.35 (m, 1H), 4.20 – 4.05 (m, 8H), 3.55 – 3.42 (m, 1H), 2.04 (s, 3H), 1.40 – 1.30 (m, 9.1H), 1.29 – 1.19 (m, 6.8H), 1.08 – 0.89 (m, 8.1H).

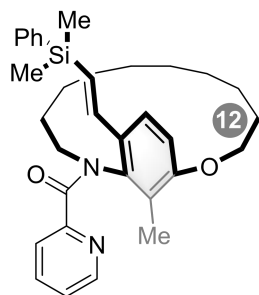
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.6, 158.4, 153.3, 148.9, 144.3, 144.2, 141.9, 136.4, 127.2, 125.2, 124.8, 123.5, 115.1, 113.4, 113.2, 69.3, 62.22, 62.16, 49.3, 27.4, 27.3, 27.03, 26.95, 26.5, 25.7, 25.0, 24.9, 16.6, 16.5, 13.0.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.34, 20.02.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{29}\text{H}_{42}\text{N}_2\text{O}_5\text{P}^+$  529.2826, found 529.2820.

HPLC: Chiralpak IF column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 10.98 min (minor), 11.79 min (major).

$[\alpha]_{\text{D}}^{25}$  = -80.0 ( $c$  = 0.12,  $\text{CH}_2\text{Cl}_2$ ).



(Rp)-3ap<sub>2</sub>, slight yellow oil, 22.7 mg, 43% yield, *cis:trans* = 6:1, 93% ee.

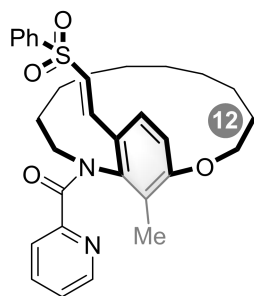
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (ddd,  $J$  = 4.9, 1.7, 1.0 Hz, 1H), 7.69 (d,  $J$  = 15.6 Hz, 1H), 7.52 (td,  $J$  = 7.7, 1.7 Hz, 1H), 7.39 (dt,  $J$  = 7.9, 1.1 Hz, 1H), 7.08 (ddd,  $J$  = 7.6, 4.8, 1.2 Hz, 1H), 6.95 (dd,  $J$  = 15.5, 1.7 Hz, 1H), 6.88 (s, 1H), 6.73 (s, 1H), 4.40 – 4.21 (m, 2H), 4.16 – 4.11 (m, 1H), 3.31 – 3.26 (m, 1H), 3.15 (s, 3H), 3.08 (s, 3H), 2.06 (s, 3H), 1.74 – 1.59 (m, 4.1H), 1.46 – 0.75 (m, 20.3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 166.9, 155.2, 154.6, 148.6, 138.4, 136.1, 134.1, 133.3, 130.5, 129.6, 123.9, 123.1, 120.1, 111.9, 67.4, 48.3, 37.7, 36.0, 28.4, 28.1, 27.7, 27.6, 27.1, 26.7, 26.5, 25.23, 25.19, 23.6, 16.1.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{33}\text{H}_{43}\text{N}_2\text{O}_2\text{Si}^+$  527.3089, found 527.3094

HPLC: Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 5.72 min (major), 7.77 min (minor).

$[\alpha]_{\text{D}}^{25}$  = -78.8 ( $c$  = 0.09,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**3aq**, whites solid, 31.9 mg, 60% yield, *cis:trans* = 6:1, 82% ee.

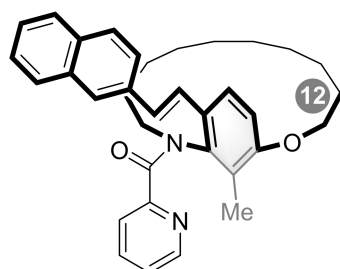
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.04 – 8.00 (m, 1H), 7.96 – 7.91 (m, 2H), 7.76 (d, *J* = 15.5 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.54 – 7.52 (m, 1H), 7.51 – 7.47 (m, 2H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.04 – 7.01 (m, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 6.68 (d, *J* = 15.4 Hz, 1H), 4.38 (ddd, *J* = 12.0, 5.2, 3.4 Hz, 1H), 4.14 (ddd, *J* = 12.3, 9.6, 3.0 Hz, 1H), 4.04 (ddd, *J* = 13.9, 7.8, 6.3 Hz, 1H), 3.54 – 3.45 (m, 1H), 2.03 (s, 3H), 1.67 – 1.59 (m, 1.5H), 1.57 – 1.49 (m, 1.2H), 1.47 – 1.41 (m, 1.4H), 1.41 – 1.29 (m, 2.2H), 1.28 – 1.16 (m, 4.4H), 1.13 – 1.02 (m, 3.1H), 1.03 – 0.93 (m, 6.9H), 0.93 – 0.82 (m, 3.5H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 168.5, 159.1, 153.7, 147.8, 143.1, 141.2, 140.1, 136.2, 133.3, 129.3, 127.84, 127.80, 127.76, 126.8, 126.0, 124.4, 123.8, 123.5, 113.1, 69.3, 49.0, 27.34, 27.28, 27.0, 26.9, 26.5, 25.6, 24.9, 24.8, 12.9.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>37</sub>N<sub>2</sub>O<sub>4</sub>S<sup>+</sup> 533.2469, found 533.2463.

**HPLC:** Chiralpak AS-H column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> = 8.45 min (minor), 11.18 min (major).

[α]<sub>D</sub><sup>25</sup> = -133.7 (c = 0.18, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3ar**, yellow oil, 20.7 mg, 40% yield, *cis:trans* = 8:1, 96% ee.

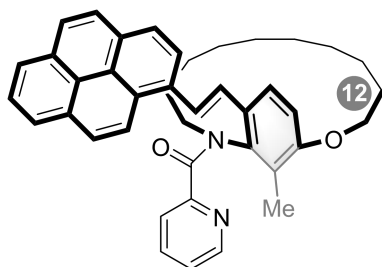
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.28 (d, *J* = 5.1 Hz, 1H), 7.84 – 7.80 (m, 4H), 7.76 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.49 – 7.46 (m, 4H), 7.45 – 7.44 (m, 1H), 7.36 (d, *J* = 16.2 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 1H), 4.39 (ddd, *J* = 12.0, 5.4, 3.5 Hz, 1H), 4.20 – 4.11 (m, 2H), 3.71 – 3.64 (m, 1H), 2.13 (s, 3H), 1.73 – 1.60 (m, 2.2H), 1.55 – 1.42 (m, 2.4H), 1.36 – 1.27 (m, 2.4H), 1.25 – 1.22 (m, 1.2H), 1.19 – 1.11 (m, 2.4H), 1.10 – 1.06 (m, 1.5H), 1.05 – 1.00 (m, 3.6H), 0.99 – 0.88 (m, 2.8H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 169.0, 154.3, 148.4, 140.7, 135.8, 133.8, 129.1, 128.6, 128.1, 127.9, 127.2, 126.6, 126.5, 126.0, 125.4, 124.2, 123.6, 123.0, 113.9, 69.3, 48.7, 27.4, 27.3, 26.9, 26.4, 25.6, 24.9, 24.8, 13.1.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 519.3007, found 519.3016.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> = 10.97 min (minor), 17.66 min (major).

$[\alpha]_{\text{D}}^{25} = -326.0$  (c = 0.3, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-3as, yellow solid, 26.6 mg, 45% yield, *cis:trans* = 7:1, 94% ee.

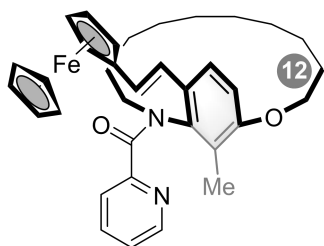
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.44 (d, *J* = 9.3 Hz, 1H), 8.36 (d, *J* = 8.1 Hz, 1H), 8.31 (d, *J* = 3.3 Hz, 1H), 8.24 – 8.16 (m, 4H), 8.11 (d, *J* = 9.2 Hz, 1H), 8.06 (d, *J* = 1.7 Hz, 2H), 8.00 – 7.95 (m, 2H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.10 – 7.05 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 4.50 – 4.38 (m, 1H), 4.24 – 4.11 (m, 2H), 3.86 – 3.74 (m, 1H), 2.18 (s, 3H), 1.80 – 1.64 (m, 3.1H), 1.61 – 1.46 (m, 2.4H), 1.38 – 1.26 (m, 3.4H), 1.20 – 1.12 (m, 2.7H), 1.10 – 1.04 (m, 4.9H), 1.02 – 0.94 (m, 2.4H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  169.0, 156.5, 154.4, 148.4, 140.9, 135.9, 132.2, 131.7, 131.1, 131.0, 129.1, 128.4, 128.2, 127.7, 127.6, 127.34, 127.32, 126.1, 125.9, 125.5, 125.4, 125.2, 125.13, 125.07, 124.2, 123.9, 123.8, 123.1, 113.9, 69.4, 48.6, 27.43, 27.39, 27.36, 27.0, 26.5, 25.7, 25.0, 24.9, 13.2.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>41</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 593.3163, found 593.3169.

**HPLC:** Chiralpak IB N-5 column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t*<sub>R</sub> = 15.68 min (minor), 20.52 min (major).

$[\alpha]_{\text{D}}^{25} = -462.4$  (c = 0.21, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-3at, brownish red oil, 41.0 mg, 70% yield, *cis:trans* = 7:1, 86% ee.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.31 (d, *J* = 5.0 Hz, 1H), 7.50 (ddd, *J* = 7.5, 5.7, 1.6 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.07 (ddt, *J* = 7.3, 4.8, 1.2 Hz, 1H), 6.83 – 6.79 (m, 2H), 6.69 (d, *J* = 16.1 Hz, 1H), 4.50 (dd, *J* = 2.5, 1.3 Hz, 1H), 4.46 (dt, *J* = 2.5, 1.3 Hz, 1H), 4.36 (ddd, *J* = 11.9, 5.5, 3.5 Hz, 1H), 4.28 (ddt, *J* = 3.8, 2.5, 1.4 Hz, 2H), 4.17 – 4.13 (m, 2H), 4.12 – 4.10 (m, 6H), 3.63 (ddd, *J* = 13.9, 7.9, 6.3 Hz, 1H), 2.10 (s, 3H), 1.74 – 1.66 (m, 1.9H), 1.64 – 1.58 (m, 1.4H), 1.54 – 1.43 (m, 3.1H), 1.32 – 1.22 (m, 4.4H), 1.18 – 1.12 (m, 2.0H), 1.08 – 0.98 (m, 4.1H), 0.97 – 0.88 (m, 2.5H).

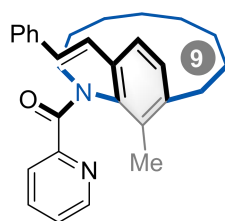
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 155.7, 154.4, 148.5, 139.6, 135.8, 129.1, 127.4, 127.3, 124.1, 123.0, 122.8, 122.4, 114.1, 83.7, 69.3, 67.3, 66.9, 48.4, 27.4, 27.3, 26.9, 26.4, 25.7, 24.9, 24.8, 13.0.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{35}\text{H}_{51}\text{FeN}_2\text{O}_2^+$  587.3295, found 587.3299.

**HPLC:** Chiralpak IB N-5 column, 85:15 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 6.75 min (minor), 7.57 min (major).

$[\alpha]_{\text{D}}^{25}$  = -261.2 ( $c$  = 0.17,  $\text{CH}_2\text{Cl}_2$ ).

### 4.3. Analytic Data of Products of ansa Chain and Cyclophanes



(*R*<sub>p</sub>)-3ba, colorless oil, 18.3 mg, 43% yield, *cis:trans* = 6:1, 86% ee.

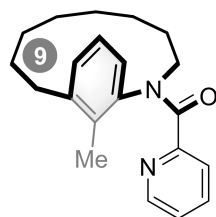
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J$  = 4.8 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.51 – 7.47 (m, 4H), 7.38 – 7.32 (m, 3H), 7.30 – 7.27 (m, 1H), 7.18 (d,  $J$  = 16.3 Hz, 1H), 7.09 – 7.05 (m, 1H), 7.02 (d,  $J$  = 8.0 Hz, 1H), 6.90 (d,  $J$  = 16.3 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.97 (ddd,  $J$  = 13.6, 9.1, 2.9 Hz, 1H), 2.92 (ddd,  $J$  = 13.3, 8.3, 4.8 Hz, 1H), 2.63 – 2.45 (m, 1H), 2.37 (s, 3H), 1.88 – 1.69 (m, 2.9H), 1.58 – 1.33 (m, 2.3H), 1.23 – 1.01 (m, 4.5H), 0.97 – 0.81 (m, 4.1H), 0.69 – 0.57 (m, 1.1H), 0.24 – 0.12 (m, 1.1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 154.7, 148.2, 142.3, 138.7, 137.4, 135.9, 134.3, 130.2, 130.0, 128.9, 127.9, 126.7, 125.1, 124.1, 123.2, 122.9, 45.3, 33.3, 26.6, 25.8, 25.3, 24.8, 24.5, 24.3, 17.0.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_2^+$  425.2588, found 425.2582.

**HPLC:** Chiralpak IC column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 10.37 min (minor), 14.47 min (major).

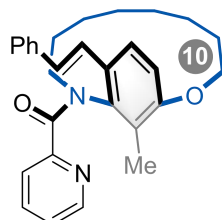
$[\alpha]_{\text{D}}^{25}$  = -117.1 ( $c$  = 0.07,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**1b**, white solid, 10.6 mg, 32% yield, >99% ee.

**HPLC:** Chiralpak AS-H column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 19.79 min (major), 34.79 min (minor).

$[\alpha]_D^{25} = -220.0$  (c = 0.24, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3ca**, colorless oil, 17.8 mg, 40% yield, *cis:trans* = 7:1, 87% ee.

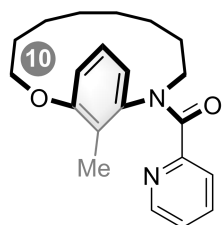
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.28 (d, *J* = 4.8 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.46 (d, *J* = 8.7 Hz, 0H), 7.39 – 7.32 (m, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 4.41 – 4.29 (m, 2H), 4.19 – 4.09 (m, 1H), 3.70 – 3.60 (m, 1H), 2.11 (s, 3H), 1.68 – 1.50 (m, 2.4H), 1.39 – 1.28 (m, 1.4H), 1.24 – 0.98 (m, 6.1H), 0.96 – 0.84 (m, 2.6H), 0.80 – 0.70 (m, 1.1H), 0.69 – 0.69 (m, 1.3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.9, 155.9, 154.5, 148.3, 139.7, 137.5, 135.9, 130.3, 129.8, 129.7, 128.9, 127.8, 126.7, 125.0, 124.2, 123.2, 123.0, 117.9, 70.6, 47.6, 27.2, 26.6, 26.4, 26.1, 25.4, 22.1, 13.5.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 441.2537, found 441.2539.

**HPLC:** Chiralpak IE column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 12.72min (minor), 15.11 min (major).

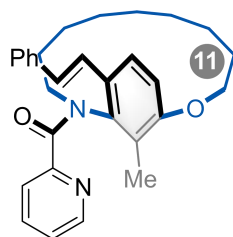
$[\alpha]_D^{25} = -312.3$  (c = 0.30, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**1c**, white solid, 11.2 mg, 33% yield, >99% ee.

**HPLC:** Chiralpak AD-H column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 15.25 min (minor), 21.44 min (major).

$[\alpha]_D^{25} = -166.2$  (c = 0.07, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**3da**, colorless oil, 16.8 mg, 37% yield, *cis:trans* = 6:1, 84% ee.

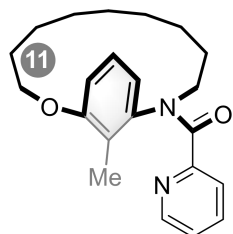
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.26 (s, 1H), 7.52 – 7.46 (m, 4H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.28 (d, *J* = 16.5 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.08 – 7.03 (m, 1H), 6.90 (d, *J* = 16.3 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 4.36 – 7.28 (m, 2H), 4.22 – 4.16 (m, 1H), 3.70 – 3.66 (m, 1H), 2.15 (s, 3H), 1.73 – 1.49 (m, 5.6H), 1.43 – 1.25 (m, 1.4H), 1.20 – 1.00 (m, 7.6H), 0.99 – 0.78 (m, 3.9H), 0.70 – 0.55 (m, 1.1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.9, 156.9, 148.3, 141.1, 137.6, 135.8, 129.1, 128.8, 127.7, 126.6, 125.1, 123.7, 115.3, 69.5, 47.1, 28.0, 27.4, 26.5, 26.4, 26.2, 26.1, 22.5, 13.0.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>35</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 455.2694, found 455.2690.

**HPLC:** Chiralpak IE N-5 column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t*<sub>R</sub> = 11.48 min (major), 14.32 min (minor).

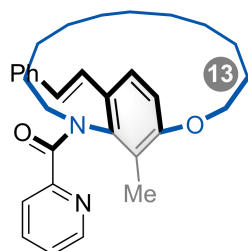
[ $\alpha$ ]<sub>D</sub><sup>25</sup> = -229.3 (c = 0.23, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-**1d**, white solid, 12.3 mg, 35% yield, >99% ee.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t*<sub>R</sub> = 8.45 min (minor), 11.17 min (major).

[ $\alpha$ ]<sub>D</sub><sup>25</sup> = -140.0 (c = 0.15, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-3ea, colorless oil, 43.4 mg, 90% yield, *cis:trans* = 10:1, 95% ee.

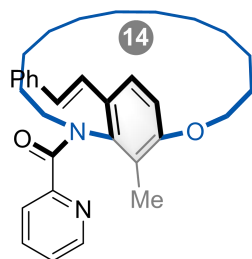
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.27 (d, *J* = 4.4 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.46 (td, *J* = 7.7, 1.7 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.24– 7.20(m, 1H), 7.05 (ddd, *J* = 7.4, 4.8, 1.3 Hz, 1H), 6.87 (d, *J* = 16.3 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 4.25 (ddd, *J* = 10.7, 6.6, 3.8 Hz, 1H), 4.16 (ddd, *J* = 11.1, 6.6, 4.2 Hz, 1H), 4.09 (ddd, *J* = 14.1, 9.2, 5.5 Hz, 1H), 3.72 (ddd, *J* = 13.5, 9.0, 6.5 Hz, 1H), 2.10 (s, 3H), 1.71 – 1.62 (m, 2.3H), 1.57 – 1.52 (m, 1.1H), 1.46 – 1.37 (m, 2.1H), 1.31 – 1.13 (m, 8.9H), 1.13 – 0.98 (m, 5.1H), 0.95 – 0.86 (m, 1.3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 169.1, 156.7, 154.4, 148.4, 140.3, 137.7, 135.7, 128.9, 128.8, 128.7, 128.1, 127.7, 126.64, 126.60, 126.3, 125.1, 124.1, 123.63, 123.60, 122.9, 112.3, 77.4, 68.2, 48.3, 28.12, 28.06, 27.4, 27.2, 26.9, 26.7, 25.7, 24.9, 24.6, 12.8.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>32</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 483.3007, found 483.3014.

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> = 8.91 min (minor), 10.27 min (major).

[α]<sub>D</sub><sup>25</sup> = -288.3 (c = 0.44, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-3fa, white solid, 46.6 mg, 94% yield, *cis:trans* = 10:1, 94% ee.

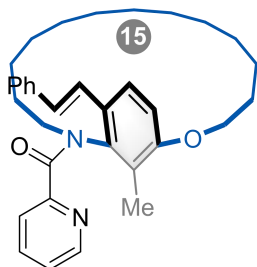
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.28 (d, *J* = 4.8 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.46 (dd, *J* = 5.6, 2.0 Hz, 2H), 7.42 (d, *J* = 9.4 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.29 (d, *J* = 9.9 Hz, 1H), 7.05 (ddd, *J* = 7.5, 4.8, 1.4 Hz, 1H), 6.94 (d, *J* = 16.2 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 4.31 (ddd, *J* = 13.3, 8.9, 6.1 Hz, 1H), 4.11 – 4.08 (m, 2H), 3.33 (ddd, *J* = 13.3, 8.9, 6.1 Hz, 1H), 2.05 (s, 3H), 1.74 – 1.51 (m, 6.1H), 1.39 – 1.30 (m, 1.6H), 1.28 – 1.13 (m, 11.2H), 1.10 – 1.02 (m, 4.1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 168.9, 156.7, 154.3, 148.4, 140.8, 137.7, 135.7, 128.9, 128.7, 127.8, 127.7, 126.6, 126.2, 125.1, 124.1, 123.8, 122.8, 111.7, 67.7, 50.2, 28.4, 28.2, 27.7, 27.5, 27.4, 27.0, 25.8, 25.7, 25.4, 12.8.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>33</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 497.3163, found 497.3166

**HPLC:** Chiralpak AD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> = 7.67 min (minor), 9.27 min (major).

$[\alpha]_{\text{D}}^{25} = -371.6$  ( $c = 0.16$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**3ga**, white solid, 35.7 mg, 70% yield, *cis:trans* = 9:1, 96% ee.

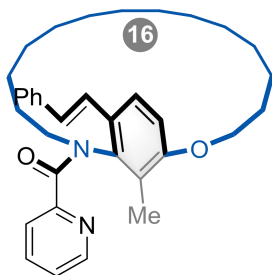
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.27 (d,  $J = 4.8$  Hz, 1H), 7.52 (d,  $J = 7.6$  Hz, 2H), 7.46 (td,  $J = 7.7, 1.7$  Hz, 1H), 7.42 (d,  $J = 8.6$  Hz, 1H), 7.38 – 7.36 (m, 1H), 7.36 (d,  $J = 7.7$  Hz, 2H), 7.27 (d,  $J = 6.4$  Hz, 1H), 7.05 (dd,  $J = 7.6, 4.9$  Hz, 1H), 6.90 (d,  $J = 16.2$  Hz, 1H), 6.74 (d,  $J = 8.6$  Hz, 1H), 4.21 (ddd,  $J = 13.3, 10.8, 5.4$  Hz, 1H), 4.10 (dt,  $J = 9.1, 4.1$  Hz, 1H), 3.99 (td,  $J = 9.9, 2.6$  Hz, 1H), 3.48 (ddd,  $J = 13.3, 10.7, 5.3$  Hz, 1H), 2.08 (s, 3H), 1.88 – 1.81 (m, 1.1H), 1.77 – 1.69 (m, 1.4H), 1.66 – 1.46 (m, 4.8H), 1.41 – 1.31 (m, 2.4H), 1.28 – 1.18 (m, 9.2H), 1.17 – 1.09 (m, 7.4H), 1.05 – 0.97 (m, 2.6H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  169.1, 157.3, 154.4, 148.4, 140.1, 137.7, 135.7, 128.9, 128.8, 127.9, 127.7, 126.6, 125.9, 125.1, 124.0, 123.8, 122.7, 111.0, 67.3, 49.4, 28.48, 28.46, 28.35, 28.25, 27.6, 27.5, 27.2, 26.8, 25.6, 25.1, 24.8, 12.8.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{34}\text{H}_{43}\text{N}_2\text{O}_2^+$  511.3320, found 511.3315.

**HPLC:** Chiralpak IF column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R = 12.18$  min (minor), 13.43 min (major).

$[\alpha]_{\text{D}}^{25} = -277.3$  ( $c = 0.26$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R*<sub>p</sub>)-**3ha**, light yellow oil, 34.1 mg, 65% yield, *cis:trans* = 10:1, 94% ee.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.29 (d,  $J = 5.2$  Hz, 1H), 7.53 (d,  $J = 7.5$  Hz, 2H), 7.48 – 7.43 (m, 3H), 7.38 – 7.34 (m, 3H), 7.28 (d,  $J = 10.9$  Hz, 1H), 7.25 – 7.24 (m, 1H), 7.06 (ddd,  $J = 7.6, 4.8, 1.2$  Hz, 1H), 6.94 (d,  $J = 16.3$  Hz, 1H), 6.74 (d,  $J = 8.6$  Hz, 1H), 4.36 (ddd,  $J = 13.3, 10.0, 6.0$  Hz, 1H), 4.07 (dt,  $J = 9.0, 4.2$  Hz, 1H), 3.91 (td,  $J = 9.8, 2.8$  Hz, 1H), 3.26 (ddd,  $J = 13.2, 10.1, 5.1$  Hz, 1H), 2.04 (s, 3H), 1.88 – 1.81 (ddt,  $J = 15.0, 9.7,$

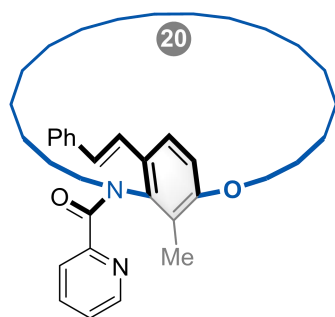
4.8 Hz, 1.1H), 1.72 – 1.65 (m, 4.4H), 1.62 – 1.56 (m, 1.1H), 1.52 – 1.48 (m, 1.1H), 1.38 – 1.31 (m, 2.2H), 1.31 – 1.24 (m, 8.3H), 1.23 – 1.14 (m, 8.4H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  169.0, 157.2, 154.4, 148.5, 140.6, 137.7, 135.7, 128.93, 128.89, 127.9, 127.7, 126.6, 125.9, 125.1, 124.0, 123.9, 122.6, 110.9, 67.6, 50.7, 29.2, 28.9, 28.4, 28.3, 28.1, 27.9, 27.4, 27.3, 26.13, 26.10, 26.0, 12.8.

**HRMS (ESI):**  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>45</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 525.3476, found 525.3470.

**HPLC:** Chiralpak IE column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 18.90 min (major), 25.99 min (minor).

$[\alpha]_D^{25}$  = -241.7 (c = 0.12, CH<sub>2</sub>Cl<sub>2</sub>).



(*R<sub>p</sub>*)-3ia, light yellow oil, 33.6 mg, 58% yield, *cis:trans* = 10:1, 96% ee.

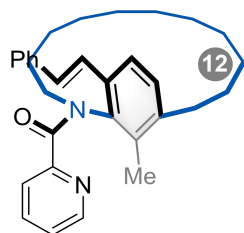
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.30 (d,  $J$  = 4.0 Hz, 1H), 7.52 (d,  $J$  = 7.5 Hz, 2H), 7.47 (td,  $J$  = 7.8, 1.8 Hz, 1H), 7.44 (d,  $J$  = 8.6 Hz, 1H), 7.38 – 7.33 (m, 4H), 7.28 (d,  $J$  = 7.8 Hz, 1H), 7.07 (dd,  $J$  = 7.6, 4.8 Hz, 1H), 6.93 (d,  $J$  = 16.2 Hz, 1H), 6.73 (d,  $J$  = 8.6 Hz, 1H), 4.30 (ddd,  $J$  = 13.1, 10.8, 5.6 Hz, 1H), 3.99 (dt,  $J$  = 9.3, 4.7 Hz, 1H), 3.88 (td,  $J$  = 9.2, 3.5 Hz, 1H), 3.30 (ddd,  $J$  = 13.0, 10.9, 4.8 Hz, 1H), 2.05 (s, 3H), 1.82– 1.74 (m, 2.5H), 1.71 – 1.65 (m, 1.3H), 1.58 – 1.39 (m, 5.5H), 1.37 – 1.33 (m, 3.9H), 1.32 – 1.19 (m, 23.1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.8, 157.4, 154.2, 148.3, 140.7, 137.7, 135.9, 129.0, 128.9, 128.7, 127.8, 127.7, 126.6, 125.9, 125.0, 124.1, 123.8, 122.6, 110.6, 68.2, 51.1, 29.2, 29.1, 29.0, 28.9, 28.82, 28.78, 28.7, 28.5, 28.4, 28.3, 28.2, 28.1, 27.1, 26.9, 26.0, 12.6.

**HRMS (ESI):**  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>39</sub>H<sub>53</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 581.4102, found 581.4107.

**HPLC:** Chiralpak IC column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 9.54 min (minor), 16.84 min (major).

$[\alpha]_D^{25}$  = -238.2 (c = 0.17, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-3ja, colorless oil, 40.5 mg, 87% yield, *cis:trans* = 5:1, 96% ee.

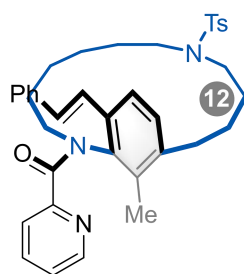
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.25 (d, *J* = 3.3 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.45 (td, *J* = 7.7, 1.7 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 16.4 Hz, 1H), 7.04 (ddd, *J* = 7.4, 4.8, 1.3 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 16.2 Hz, 1H), 3.97 (ddd, *J* = 13.4, 9.6, 6.3 Hz, 1H), 3.80 (ddd, *J* = 13.4, 9.5, 6.5 Hz, 1H), 2.80 (ddd, *J* = 13.1, 8.8, 3.6 Hz, 1H), 2.50 (ddd, *J* = 13.0, 8.2, 3.8 Hz, 1H), 2.26 (s, 3H), 1.78 – 1.74 (m, 1.2H), 1.50 – 1.39 (m, 3.3H), 1.31 – 1.24 (m, 1.4H), 1.23 – 1.17 (m, 5.2H), 1.15 – 1.10 (m, 3.4H), 1.08 – 1.04 (m, 2.6H), 1.03 – 0.96 (m, 3H), 0.95 – 0.88 (m, 1.1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  169.0, 154.6, 148.3, 141.8, 139.3, 137.5, 135.8, 135.2, 133.2, 130.0, 129.7, 128.9, 128.8, 127.9, 126.8, 126.7, 125.2, 124.0, 122.84, 122.81, 48.8, 32.9, 29.3, 27.4, 26.9, 26.6, 25.9, 25.6, 25.2, 24.4, 15.8.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>39</sub>N<sub>2</sub>O<sup>+</sup> 467.3057, found 467.3059.

**HPLC:** Chiralpak IC column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t<sub>R</sub>* = 13.41 min (minor), 19.44 min (major).

**[ $\alpha$ ]<sub>D</sub><sup>25</sup>** = -280.0 (c = 0.19, CH<sub>2</sub>Cl<sub>2</sub>).



(*R*<sub>p</sub>)-3ka, light yellow oil, 21.7 mg, 35% yield, *cis:trans* = 4:1, 96% ee.

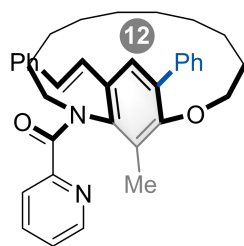
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.22 (d, *J* = 4.8 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 3H), 7.50 – 7.44 (t, *J* = 5.2 Hz, 4H), 7.40 – 7.30 (m, 4H), 7.28 (d, *J* = 2.8 Hz, 2H), 7.19 (d, *J* = 16.3 Hz, 1H), 7.07 – 7.02 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 16.2 Hz, 1H), 3.96 – 3.88 (m, 1H), 3.85 – 3.75 (m, 1H), 3.32 – 3.22 (m, 1H), 3.09 – 3.00 (m, 1H), 2.60 – 2.44 (m, 4H), 2.40 (s, 3H), 2.27 (s, 3H), 1.66 – 1.57 (m, 1.6H), 1.56 – 1.36 (m, 4.5H), 1.36 – 1.18 (m, 8.3H), 1.15 – 1.05 (m, 2.6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 154.3, 148.2, 143.2, 141.2, 139.5, 137.4, 136.2, 135.1, 133.5, 130.3, 129.7, 129.4, 128.9, 128.8, 128.0, 127.2, 126.9, 126.7, 125.0, 124.2, 123.1, 50.5, 49.9, 48.1, 32.1, 28.4, 27.8, 25.0, 24.9, 24.5, 21.6, 16.2.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{38}\text{H}_{44}\text{N}_3\text{O}_3\text{S}^+$  622.3098, found 622.3090.

**HPLC:** Chiralpak IF column, 50:50 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 24.77 min (minor), 28.57 min (major).

$[\alpha]_{\text{D}}^{25} = -83.2$  ( $c = 0.25$ ,  $\text{CH}_2\text{Cl}_2$ ).



( $R_p$ )-3la, white solid, 47.3 mg, 87% yield, *cis:trans* = 5:1, 95% ee.

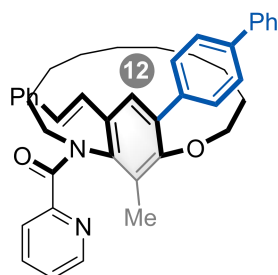
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (d,  $J = 4.8$  Hz, 1H), 7.57 (d,  $J = 7.6$  Hz, 2H), 7.49 – 7.42 (m, 6H), 7.35 (d,  $J = 8.0$  Hz, 4H), 7.18 (d,  $J = 16.2$  Hz, 1H), 7.04 (d,  $J = 4.5$  Hz, 1H), 6.80 (d,  $J = 16.2$  Hz, 1H), 4.07 (ddd,  $J = 13.3, 10.9, 5.7$  Hz, 1H), 3.89 – 3.70 (m, 2H), 3.43 (ddd,  $J = 12.0, 7.5, 4.5$  Hz, 1H), 2.37 (s, 3H), 1.75 – 1.65 (m, 1.2H), 1.61 – 1.52 (m, 1.2H), 1.45 – 1.37 (m, 2.1H), 1.35 – 1.23 (m, 5.1H), 1.21 – 1.08 (m, 6.1H), 1.00 (q,  $J = 7.9, 6.6$  Hz, 3.0H), 0.94 – 0.83 (m,  $J = 6.1, 5.4$  Hz, 1.2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 155.0, 154.2, 148.2, 139.6, 139.3, 137.5, 135.8, 133.3, 130.9, 130.7, 129.8, 129.2, 129.0, 128.9, 128.7, 128.59, 128.56, 127.8, 127.4, 126.8, 126.6, 125.6, 124.6, 124.2, 123.1, 72.7, 48.1, 30.1, 27.1, 26.8, 25.6, 25.3, 24.9, 24.7, 23.7, 14.0.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{37}\text{H}_{41}\text{N}_2\text{O}_2^+$  545.3163, found 545.3169.

**HPLC:** Chiralpak IE column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 15.81 min (minor), 22.96 min (major).

$[\alpha]_{\text{D}}^{25} = -199.2$  ( $c = 0.13$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R<sub>p</sub>*)-3ma, white solid, 42.2 mg, 68% yield, *cis:trans* = 6:1, 94% ee.

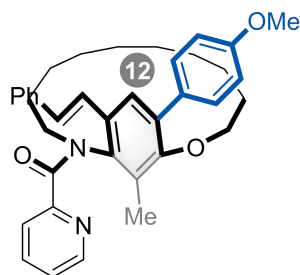
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.25 (d, *J* = 4.8 Hz, 1H), 7.68 – 7.66 (m, 5H), 7.51 – 7.43 (m, 7H), 7.41 – 7.34 (m, 4H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 16.3 Hz, 1H), 7.07 – 7.02 (m, *J* = 4.5 Hz, 1H), 6.82 (d, *J* = 16.2 Hz, 1H), 4.09 (ddd, *J* = 13.3, 11.0, 5.7 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.80 – 3.70 (m, 1H), 3.52 (ddd, *J* = 12.0, 7.5, 4.5 Hz, 1H), 2.40 (s, 3H), 1.81 – 1.65 (m, 1.9H), 1.65 – 1.50 (m, 1.5H), 1.50 – 1.40 (m, 2.3H), 1.39 – 1.25 (m, 4.4H), 1.24 – 1.09 (m, 7.8H), 1.07 – 0.83 (m, 5.4H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  169.0, 155.2, 154.2, 148.2, 140.7, 140.2, 139.6, 138.2, 137.5, 135.8, 132.8, 131.0, 130.8, 129.8, 129.3, 129.0, 128.9, 127.9, 127.5, 127.23, 127.16, 127.1, 126.6, 125.5, 124.6, 124.2, 123.1, 72.9, 48.1, 30.1, 27.1, 26.8, 25.6, 25.3, 24.9, 24.7, 23.7, 14.0.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>43</sub>H<sub>45</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 621.3476, found 621.3470.

**HPLC:** Chiralpak IE column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t<sub>R</sub>* = 22.38 min (minor), 25.21 min (major).

**[ $\alpha$ ]<sub>D</sub><sup>25</sup>** = -141.6 (c = 0.38, CH<sub>2</sub>Cl<sub>2</sub>).



(*R<sub>p</sub>*)-3na, colorless oil, 40.2 mg, 70% yield, *cis:trans* = 6:1, 92% ee.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.23 (d, *J* = 4.7 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.42 (m, 2H), 7.38 – 7.30 (m, 3H), 7.17 (d, *J* = 16.2 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 16.2 Hz, 1H), 4.05 (td, *J* = 12.2, 5.5 Hz, 1H), 3.86 (s, 3H), 3.84 – 3.81 (m, 1H), 3.75 (td, *J* = 12.4, 4.7 Hz, 1H), 3.48 – 3.42 (m, 1H), 2.35 (s, 3H), 1.73 – 1.66 m, 1.0H), 1.60 – 1.50 (m, 1.7H), 1.46 – 1.36 (m, 2.1H), 1.35 – 1.25 (m, 3.4H), 1.20 – 1.06 m, 5.5H), 1.06 – 0.93 (m, 3.8H), 0.95 – 0.86 (m, 1.0H).

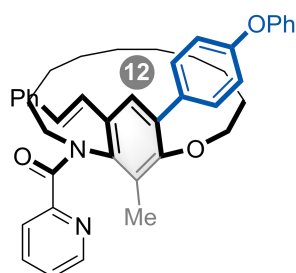
**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  169.1, 159.1, 155.0, 154.3, 148.2, 139.2, 137.6, 135.8, 133.0, 131.6, 130.9, 130.7, 130.3, 130.1, 129.7, 128.9, 128.7, 127.8, 126.8, 126.6, 125.4, 124.7, 124.1, 123.0, 114.0, 72.5, 55.4, 48.2, 30.0, 27.1, 26.8, 25.6, 25.3, 24.9, 24.8, 23.8, 14.0.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>38</sub>H<sub>43</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> 575.3269, found 575.3272.

**HPLC:** Chiralpak IE column, 50:50 hexanes/isopropanol, flow rate = 1.0 mL/min,

$\lambda = 254 \text{ nm}$ ,  $t_R = 10.72 \text{ min}$  (major),  $14.61 \text{ min}$  (minor).

$[\alpha]_D^{25} = -200.9$  ( $c = 0.12$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R\_p*)-**30a**, white solid, 59.1 mg, 93% yield, *cis:trans* = 6:1, 94% ee.

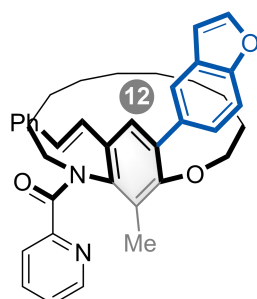
**$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.22 (dt,  $J = 4.9, 1.4 \text{ Hz}$ , 1H), 7.56 – 7.51 (m, 2H), 7.48 – 7.42 (m, 4H), 7.38 – 7.31 (m, 6H), 7.16 (d,  $J = 16.2 \text{ Hz}$ , 1H), 7.12 (dt,  $J = 6.3, 1.1 \text{ Hz}$ , 1H), 7.10 – 7.07 (m, 1H), 7.06 – 7.04 (m, 4H), 6.79 (d,  $J = 16.2 \text{ Hz}$ , 1H), 4.05 (ddd,  $J = 13.4, 11.0, 5.7 \text{ Hz}$ , 1H), 3.86 (ddd,  $J = 11.6, 6.5, 4.9 \text{ Hz}$ , 1H), 3.74 (ddd,  $J = 13.3, 11.2, 4.8 \text{ Hz}$ , 1H), 3.48 (ddd,  $J = 12.0, 7.4, 4.5 \text{ Hz}$ , 1H), 2.35 (s, 3H), 1.71 – 1.65 (m, 1.0H), 1.57 – 1.50 (m, 1.1H), 1.48 – 1.37 (m, 2.1H), 1.35 – 1.24 (m, 3.1H), 1.21 – 1.07 (m, 5.7H), 1.05 – 0.86 (m, 4.7H).

**$^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )**  $\delta$  169.0, 157.2, 156.8, 155.0, 154.2, 148.2, 139.5, 137.5, 135.8, 134.2, 132.7, 131.0, 130.8, 130.5, 130.4, 130.0, 129.8, 128.9, 128.8, 127.9, 126.8, 126.6, 125.4, 124.6, 124.2, 123.6, 123.1, 119.2, 119.1, 118.8, 72.7, 48.2, 30.1, 27.1, 26.8, 25.6, 25.3, 24.9, 24.7, 23.8, 14.0.

**HRMS (ESI):**  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{43}\text{H}_{45}\text{N}_2\text{O}_3^+$  637.3425, found 637.3429.

**HPLC:** Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda = 254 \text{ nm}$ ,  $t_R = 9.54 \text{ min}$  (minor),  $16.84 \text{ min}$  (major).

$[\alpha]_D^{25} = -171.3$  ( $c = 0.12$ ,  $\text{CH}_2\text{Cl}_2$ ).



(*R\_p*)-**3pa**, white solid, 28.0 mg, 48% yield, *cis:trans* = 4:1, 94% ee.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.24 (dt,  $J$  = 4.8, 1.4 Hz, 1H), 7.79 (d,  $J$  = 1.7 Hz, 1H), 7.66 (d,  $J$  = 2.2 Hz, 1H), 7.58 (d,  $J$  = 9.4 Hz, 10H), 7.54 – 7.48 (m, 3H), 7.47 – 7.43 (m, 3H), 7.39 – 7.32 (m, 3H), 7.19 (d,  $J$  = 16.2 Hz, 1H), 7.04 (q,  $J$  = 4.5 Hz, 1H), 6.85 – 6.77 (m, 2H), 4.07 (ddd,  $J$  = 13.2, 10.9, 5.7 Hz, 1H), 3.81 – 3.69 (m, 2H), 3.39 (ddd,  $J$  = 12.0, 7.5, 4.5 Hz, 1H), 2.38 (s, 3H), 1.80 – 1.65 (m, 1.8H), 1.63 – 1.50 (m, 1.4H), 1.47 – 1.35 (m, 2.8H), 1.35 – 1.23 (m, 3.4H), 1.22 – 1.07 (m, 5.9H), 1.06 – 0.87 (m, 4.1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  169.1, 155.0, 154.4, 154.3, 148.2, 145.6, 139.4, 137.5, 135.8, 134.1, 133.6, 130.9, 130.7, 129.7, 128.9, 127.84, 127.78, 126.8, 126.6, 126.0, 125.6, 124.7, 124.2, 123.1, 121.5, 111.4, 106.9, 72.6, 48.2, 30.1, 27.1, 26.8, 25.6, 25.3, 24.9, 24.7, 23.7, 14.0.

**HRMS (ESI):**  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>39</sub>H<sub>41</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> 585.3112, found 585.3118.

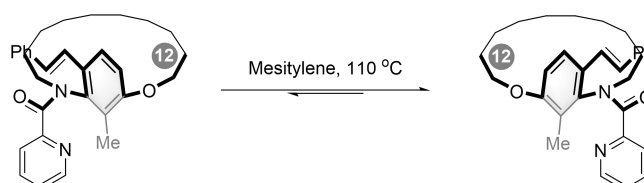
**HPLC:** Chiralpak IE column, 50:50 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 10.27 min (minor), 15.86 min (major).

$[\alpha]_D^{25}$  = -256.1 (c = 0.16, CH<sub>2</sub>Cl<sub>2</sub>).

## 5. Conformational Stability Studies

### 5.1. Racemization Tests

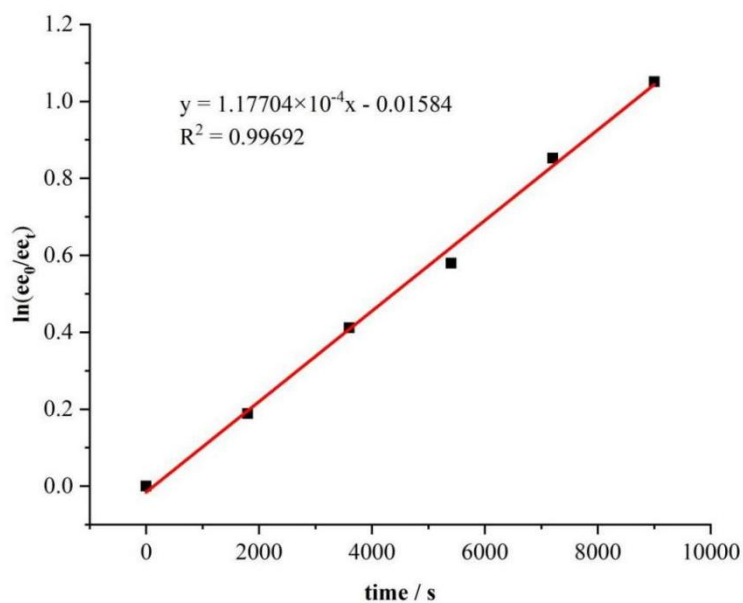
The racemization experiment of (*R<sub>p</sub>*)-3aa at 110 °C



Compound 3aa (10 mg, 0.021 mmol, 74.056% ee) was dissolved in mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 110 °C (pre-heated metal module) under air. Within the same time interval, small sample (30  $\mu$ L) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess.

Table S3. The racemization experiment of (*R<sub>p</sub>*)-3aa at 110 °C

time (s)	ee <sub>t</sub> (%)	ln(ee <sub>0</sub> /ee <sub>t</sub> )
0	74.056 (ee <sub>0</sub> )	0
1800	61.324	0.18865028
3600	49.084	0.411288448
5400	41.490	0.579369129
7200	31.572	0.852550912
9000	25.886	1.051119282



**Figure S3.** The racemization curves of (*R<sub>p</sub>*)-**3aa** at 110 °C

$$T_1 = 110\text{ °C} = 383.15\text{ K}, T_2 = 60\text{ °C} = 333.15\text{ K}, T_3 = 25\text{ °C} = 298.15\text{ K}$$

$$k_{\text{rac}}(110\text{ °C}) = 1.77 \times 10^{-4}\text{ s}^{-1}$$

$$\tau_{1/2}(110\text{ °C}) = \ln 2 / k_{\text{rac}}(110\text{ °C}) = 3913.7\text{ s} = 65.2\text{ min}$$

$$k_{\text{ent}}(110\text{ °C}) = k_{\text{rac}}(110\text{ °C}) / 2 = 8.85 \times 10^{-5}\text{ s}^{-1}$$

$$\Delta G^{\ddagger}_{\text{ent}} = RT_1 \cdot \ln((k_B T_1) / (h k_{\text{ent}})) = 124.37\text{ kJ} \cdot \text{mol}^{-1} = 29.73\text{ kcal} \cdot \text{mol}^{-1}$$

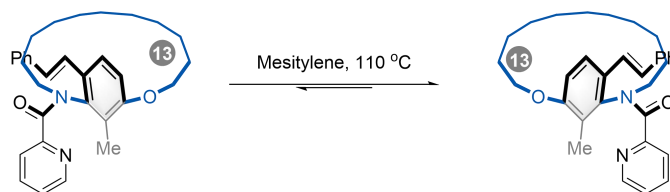
$$k_{\text{rac}}(T_2) = 2 \cdot k_B T_2 \cdot h^{-1} \cdot e^{-(\Delta G^{\ddagger}_{\text{ent}} / (RT_2))}$$

$$k_{\text{rac}}(60\text{ °C}) = 4.39 \times 10^{-7}\text{ s}^{-1}$$

$$\tau_{1/2}(60\text{ °C}) = \ln 2 / k_{\text{rac}}(60\text{ °C}) = 1.58 \times 10^6\text{ s} = 438.9\text{ days} = 1.2\text{ years}$$

$$k_{\text{rac}}(25\text{ °C}) = 2.02 \times 10^{-9}\text{ s}^{-1}$$

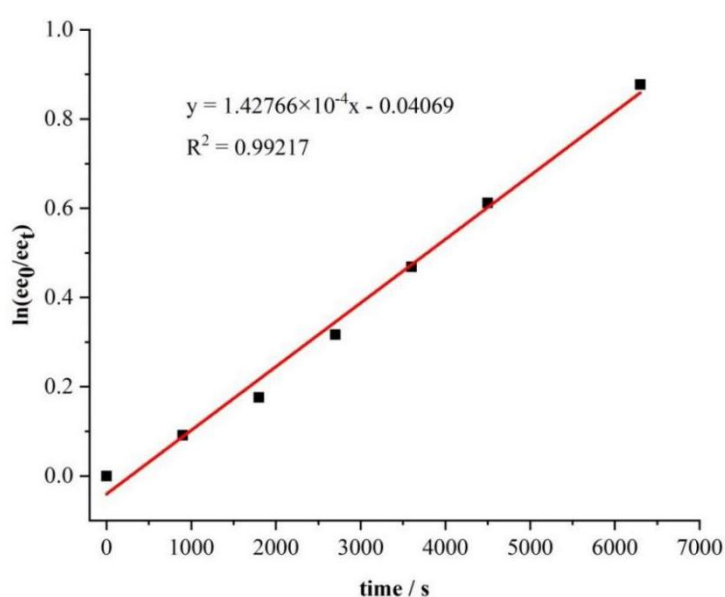
$$\tau_{1/2}(25\text{ °C}) = \ln 2 / k_{\text{rac}}(25\text{ °C}) = 3.43 \times 10^8\text{ s} = 9.53 \times 10^4\text{ h} = 3970.8\text{ days} = 10.9\text{ years}$$



Compound **3ea** (10 mg, 0.020 mmol, 95.394% ee) was dissolved in mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 110 °C (pre-heated metal module) under air. Within the same time interval, small sample (30  $\mu$ L) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess.

**Table S4.** The racemization experiment of (*R<sub>p</sub>*)-**3ea** at 110 °C

time (s)	ee <sub>t</sub> (%)	ln(ee <sub>0</sub> /ee <sub>t</sub> )
0	95.394 (ee <sub>0</sub> )	0
900	87.056	0.091464094
1800	80.010	0.175864057
2700	69.478	0.317005528
3600	59.716	0.468415692
4500	51.718	0.6122098
6300	39.688	0.876966808



**Figure S4.** The racemization curves of (*R<sub>p</sub>*)-**3ea** at 110 °C

$$T_1 = 110 \text{ }^\circ\text{C} = 383.15 \text{ K}, T_2 = 60 \text{ }^\circ\text{C} = 333.15 \text{ K}, T_3 = 25 \text{ }^\circ\text{C} = 298.15 \text{ K}$$

$$k_{\text{rac}}(110 \text{ }^\circ\text{C}) = 1.43 \times 10^{-4} \text{ s}^{-1}$$

$$\tau_{1/2}(110 \text{ }^\circ\text{C}) = \ln 2 / k_{\text{rac}}(110 \text{ }^\circ\text{C}) = 4855.1 \text{ s} = 80.9 \text{ min}$$

$$k_{\text{ent}}(110 \text{ }^\circ\text{C}) = k_{\text{rac}}(110 \text{ }^\circ\text{C}) / 2 = 7.14 \times 10^{-5} \text{ s}^{-1}$$

$$\Delta G^\ddagger_{\text{ent}} = RT_1 \cdot \ln((k_B T_1) / (h k_{\text{ent}})) = 125.06 \text{ kJ} \cdot \text{mol}^{-1} = 28.89 \text{ kcal} \cdot \text{mol}^{-1}$$

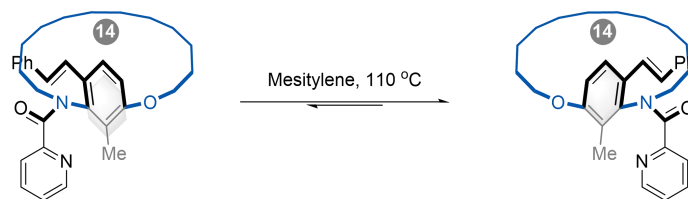
$$k_{\text{rac}}(T_2) = 2 \cdot k_B T_2 \cdot h^{-1} \cdot e^{(-\Delta G^\ddagger_{\text{ent}} / (RT_2))}$$

$$k_{\text{rac}}(60 \text{ }^\circ\text{C}) = 3.42 \times 10^{-7} \text{ s}^{-1}$$

$$\tau_{1/2}(60 \text{ }^\circ\text{C}) = \ln 2 / k_{\text{rac}}(60 \text{ }^\circ\text{C}) = 2.02 \times 10^6 \text{ s} = 561.1 \text{ h} = 23.4 \text{ days}$$

$$k_{\text{rac}}(25 \text{ }^\circ\text{C}) = 1.53 \times 10^{-9} \text{ s}^{-1}$$

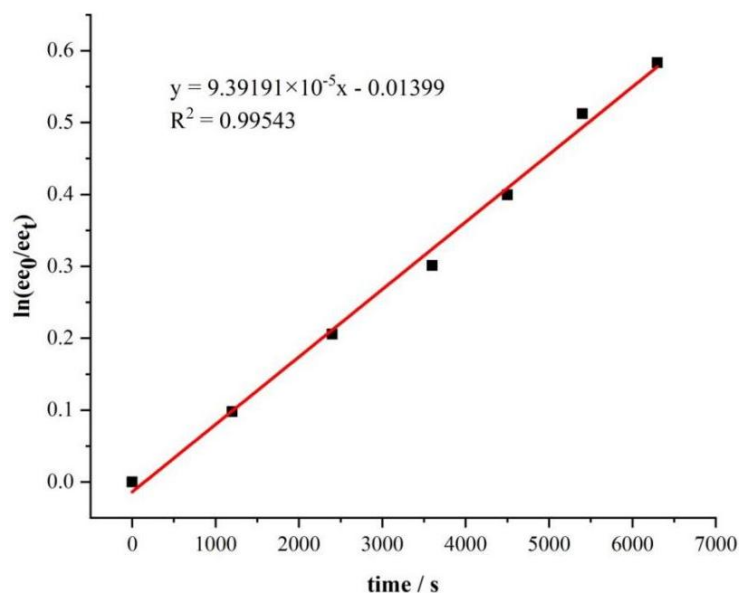
$$\tau_{1/2}(25 \text{ }^\circ\text{C}) = \ln 2 / k_{\text{rac}}(25 \text{ }^\circ\text{C}) = 4.52 \times 10^8 \text{ s} = 1.26 \times 10^5 \text{ h} = 5231.5 \text{ days} = 14.3 \text{ years}$$



Compound **3fa** (10 mg, 0.020 mmol, 94.280% ee) was dissolved in mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 110 °C (pre-heated metal module) under air. Within the same time interval, small sample (30  $\mu$ L) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess.

**Table S5.** The racemization experiment of (*R<sub>p</sub>*)-**3fa** at 110 °C

time (s)	ee <sub>t</sub> (%)	ln(ee <sub>0</sub> /ee <sub>t</sub> )
0	94.280 (ee <sub>0</sub> )	0
1200	85.494	0.097823
2400	76.740	0.205846
3600	69.774	0.301008
4500	63.244	0.399269
5400	56.470	0.51256
6300	52.614	0.583287



**Figure S5.** The racemization curves of (*R<sub>p</sub>*)-**3fa** at 110 °C

$T_1 = 110\text{ °C} = 383.15\text{ K}$ ,  $T_2 = 60\text{ °C} = 333.15\text{ K}$ ,  $T_3 = 25\text{ °C} = 298.15\text{ K}$

$$k_{\text{rac}}(110\text{ }^{\circ}\text{C}) = 9.39 \times 10^{-5} \text{ s}^{-1}$$

$$\tau_{1/2}(110\text{ }^{\circ}\text{C}) = \ln 2 / k_{\text{rac}}(110\text{ }^{\circ}\text{C}) = 7380.3 \text{ s} = 123.0 \text{ min}$$

$$k_{\text{ent}}(110\text{ }^{\circ}\text{C}) = k_{\text{rac}}(110\text{ }^{\circ}\text{C}) / 2 = 4.70 \times 10^{-5} \text{ s}^{-1}$$

$$\Delta G^{\ddagger}_{\text{ent}} = RT_1 \cdot \ln((k_B T_1) / (h k_{\text{ent}})) = 126.39 \text{ kJ} \cdot \text{mol}^{-1} = 30.21 \text{ kcal} \cdot \text{mol}^{-1}$$

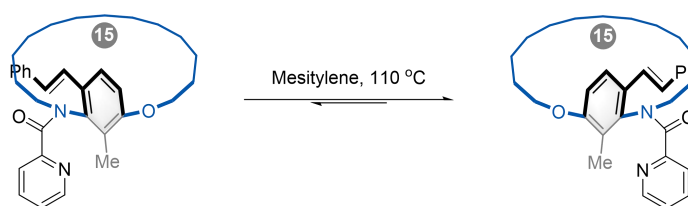
$$k_{\text{rac}}(T_2) = 2 \cdot k_B T_2 \cdot h^{-1} \cdot e^{(-\Delta G^{\ddagger}_{\text{ent}} / (RT_2))}$$

$$k_{\text{rac}}(60\text{ }^{\circ}\text{C}) = 2.12 \times 10^{-7} \text{ s}^{-1}$$

$$\tau_{1/2}(60\text{ }^{\circ}\text{C}) = \ln 2 / k_{\text{rac}}(60\text{ }^{\circ}\text{C}) = 3.27 \times 10^6 \text{ s} = 908.3 \text{ h} = 37.8 \text{ days}$$

$$k_{\text{rac}}(25\text{ }^{\circ}\text{C}) = 8.94 \times 10^{-10} \text{ s}^{-1}$$

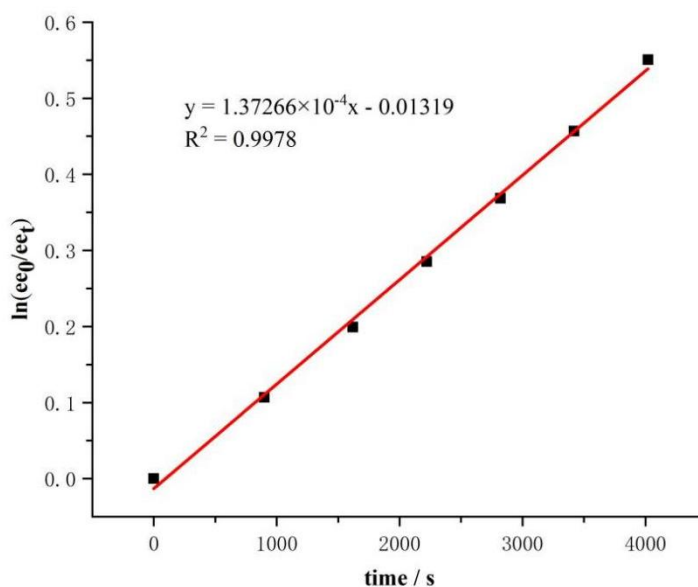
$$\tau_{1/2}(25\text{ }^{\circ}\text{C}) = \ln 2 / k_{\text{rac}}(25\text{ }^{\circ}\text{C}) = 7.75 \times 10^8 \text{ s} = 2.15 \times 10^5 \text{ h} = 8969.1 \text{ days} = 24.6 \text{ years}$$



Compound **3ga** (10 mg, 0.019 mmol, 95.852% ee) was dissolved in mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 110 °C (pre-heated metal module) under air. Within the same time interval, small sample (30  $\mu$  L) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess.

**Table S6.** The racemization experiment of (*R*<sub>p</sub>)-**3ga** at 110 °C

time (s)	ee <sub>t</sub> (%)	ln(ee <sub>0</sub> /ee <sub>t</sub> )
0	95.852 (ee <sub>0</sub> )	0
900	86.144	0.106785
1620	78.546	0.199121
2220	72.068	0.285195
2820	66.31	0.368465
3420	60.716	0.456598
4020	55.274	0.550503



**Figure S6.** The racemization curves of (*R<sub>p</sub>*)-**3ga** at 110 °C

$$T_1 = 110\text{ °C} = 383.15\text{ K}, T_2 = 60\text{ °C} = 333.15\text{ K}, T_3 = 25\text{ °C} = 298.15\text{ K}$$

$$k_{\text{rac}}(110\text{ °C}) = 1.37 \times 10^{-4}\text{ s}^{-1}$$

$$\tau_{1/2}(110\text{ °C}) = \ln 2 / k_{\text{rac}}(110\text{ °C}) = 5049.7\text{ s} = 84.2\text{ min}$$

$$k_{\text{ent}}(110\text{ °C}) = k_{\text{rac}}(110\text{ °C}) / 2 = 6.86 \times 10^{-5}\text{ s}^{-1}$$

$$\Delta G^{\ddagger}_{\text{ent}} = RT_1 \cdot \ln((k_B T_1) / (h k_{\text{ent}})) = 125.18\text{ kJ} \cdot \text{mol}^{-1} = 29.92\text{ kcal} \cdot \text{mol}^{-1}$$

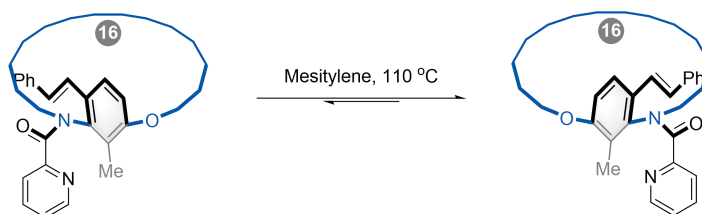
$$k_{\text{rac}}(T_2) = 2 \cdot k_B T_2 \cdot h^{-1} \cdot e^{-(\Delta G^{\ddagger}_{\text{ent}} / (RT_2))}$$

$$k_{\text{rac}}(60\text{ °C}) = 3.28 \times 10^{-7}\text{ s}^{-1}$$

$$\tau_{1/2}(60\text{ °C}) = \ln 2 / k_{\text{rac}}(60\text{ °C}) = 2.11 \times 10^6\text{ s} = 587.4\text{ h} = 24.5\text{ days}$$

$$k_{\text{rac}}(25\text{ °C}) = 1.46 \times 10^{-9}\text{ s}^{-1}$$

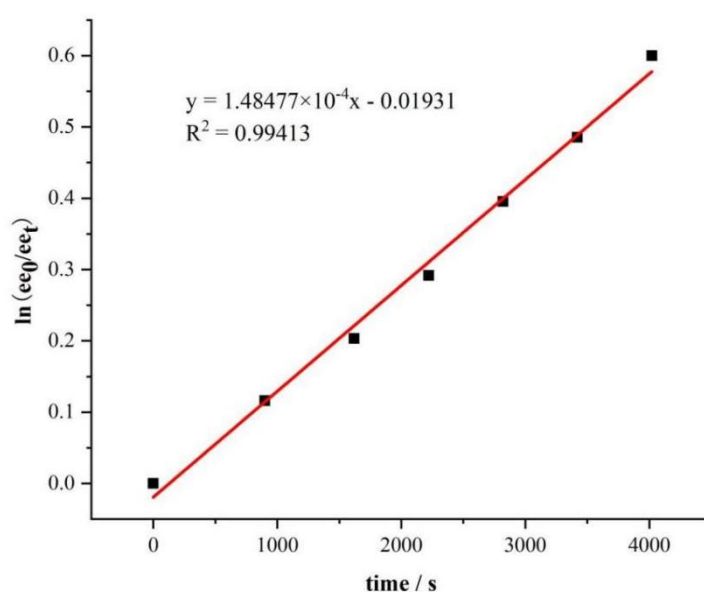
$$\tau_{1/2}(25\text{ °C}) = \ln 2 / k_{\text{rac}}(25\text{ °C}) = 4.76 \times 10^8\text{ s} = 1.32 \times 10^5\text{ h} = 5507.5\text{ days} = 15.1\text{ years}$$



Compound **3ha** (10 mg, 0.019 mmol, 93.698% ee) was dissolved in mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 110 °C (pre-heated metal module) under air. Within the same time interval, small sample (30  $\mu$ L) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess.

**Table S7.** The racemization experiment of (*R<sub>p</sub>*)-**3ha** at 110 °C

time (s)	ee <sub>t</sub> (%)	ln(ee <sub>0</sub> /ee <sub>t</sub> )
0	93.698 (ee <sub>0</sub> )	0
900	83.432	0.116045
1620	76.466	0.203231
2220	69.992	0.291696
2820	63.090	0.395515
3420	57.654	0.485617
4020	51.430	0.599855



**Figure S7.** The racemization curves of (*R<sub>p</sub>*)-**3ha** at 110 °C

$$T_1 = 110 \text{ °C} = 383.15 \text{ K}, T_2 = 60 \text{ °C} = 333.15 \text{ K}, T_3 = 25 \text{ °C} = 298.15 \text{ K}$$

$$k_{\text{rac}}(110 \text{ °C}) = 1.48 \times 10^{-4} \text{ s}^{-1}$$

$$\tau_{1/2}(110 \text{ °C}) = \ln 2 / k_{\text{rac}}(110 \text{ °C}) = 4668.4 \text{ s} = 77.8 \text{ min}$$

$$k_{\text{ent}}(110 \text{ °C}) = k_{\text{rac}}(110 \text{ °C}) / 2 = 7.42 \times 10^{-5} \text{ s}^{-1}$$

$$\Delta G^{\ddagger}_{\text{ent}} = RT_1 \cdot \ln((k_B T_1) / (h k_{\text{ent}})) = 124.9 \text{ kJ} \cdot \text{mol}^{-1} = 29.86 \text{ kcal} \cdot \text{mol}^{-1}$$

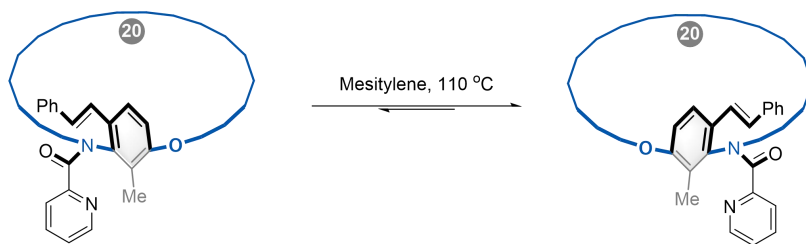
$$k_{\text{rac}}(T_2) = 2 \cdot k_B T_2 \cdot h^{-1} \cdot e^{(-\Delta G^{\ddagger}_{\text{ent}} / (RT_2))}$$

$$k_{\text{rac}}(60 \text{ °C}) = 3.59 \times 10^{-7} \text{ s}^{-1}$$

$$\tau_{1/2}(60 \text{ °C}) = \ln 2 / k_{\text{rac}}(60 \text{ °C}) = 1.93 \times 10^6 \text{ s} = 536.7 \text{ h} = 22.4 \text{ days}$$

$$k_{\text{rac}}(25 \text{ °C}) = 1.61 \times 10^{-9} \text{ s}^{-1}$$

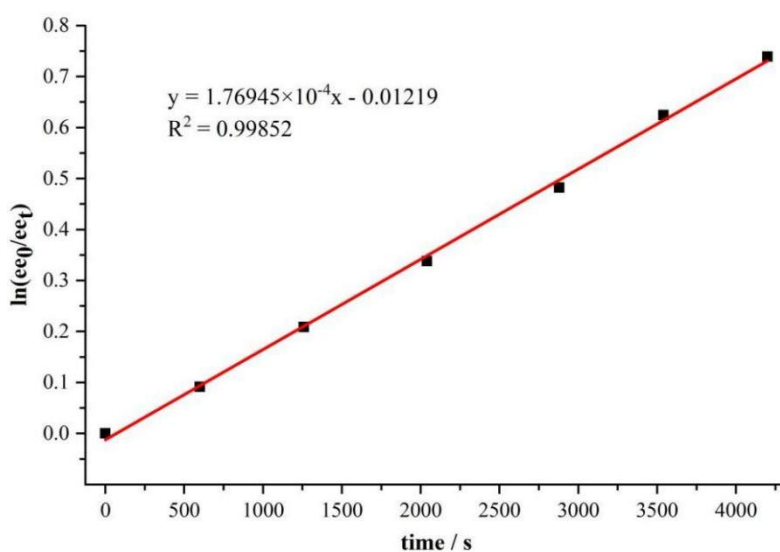
$$\tau_{1/2}(25 \text{ °C}) = \ln 2 / k_{\text{rac}}(25 \text{ °C}) = 4.30 \times 10^8 \text{ s} = 1.19 \times 10^5 \text{ h} = 4978.9 \text{ days} = 13.6 \text{ years}$$



Compound **3ia** (10 mg, 0.017 mmol, 95.620% ee) was dissolved in Mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 110 °C (pre-heated metal module) under air. Within the same time interval, small sample (30  $\mu$ L) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess.

**Table S8.** The racemization experiment of (*R<sub>p</sub>*)-**3ia** at 110 °C

time (s)	ee <sub>t</sub> (%)	ln(ee <sub>0</sub> /ee <sub>t</sub> )
0	95.620 (ee <sub>0</sub> )	0
600	87.574	0.087898
1260	77.874	0.20529
2040	68.432	0.334541
2880	59.250	0.478616
3540	51.412	0.62051
4200	45.822	0.735618



**Figure S8.** The racemization curves of (*R<sub>p</sub>*)-**3ia** at 110 °C

$$T_1 = 110 \text{ } ^\circ\text{C} = 383.15 \text{ K}, T_2 = 60 \text{ } ^\circ\text{C} = 333.15 \text{ K}, T_3 = 25 \text{ } ^\circ\text{C} = 298.15 \text{ K}$$

$$k_{\text{rac}}(110\text{ }^{\circ}\text{C}) = 1.77 \times 10^{-4} \text{ s}^{-1}$$

$$\tau_{1/2}(110\text{ }^{\circ}\text{C}) = \ln 2 / k_{\text{rac}}(110\text{ }^{\circ}\text{C}) = 3917.3 \text{ s} = 65.3 \text{ min}$$

$$k_{\text{ent}}(110\text{ }^{\circ}\text{C}) = k_{\text{rac}}(110\text{ }^{\circ}\text{C}) / 2 = 8.85 \times 10^{-5} \text{ s}^{-1}$$

$$\Delta G^{\ddagger}_{\text{ent}} = RT_1 \cdot \ln((k_B T_1) / (h k_{\text{ent}})) = 124.37 \text{ kJ} \cdot \text{mol}^{-1} = 29.73 \text{ kcal} \cdot \text{mol}^{-1}$$

$$k_{\text{rac}}(T_2) = 2 \cdot k_B T_2 \cdot h^{-1} \cdot e^{(-\Delta G^{\ddagger}_{\text{ent}} / (RT_2))}$$

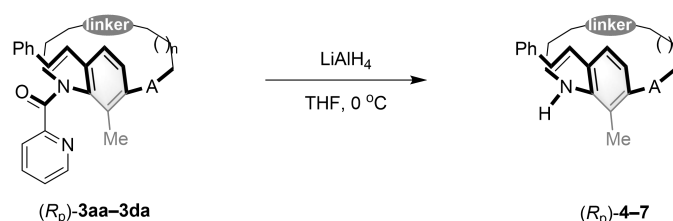
$$k_{\text{rac}}(60\text{ }^{\circ}\text{C}) = 4.39 \times 10^{-7} \text{ s}^{-1}$$

$$\tau_{1/2}(60\text{ }^{\circ}\text{C}) = \ln 2 / k_{\text{rac}}(60\text{ }^{\circ}\text{C}) = 1.58 \times 10^6 \text{ s} = 438.9 \text{ h} = 18.3 \text{ days}$$

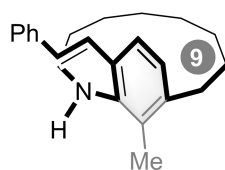
$$k_{\text{rac}}(25\text{ }^{\circ}\text{C}) = 2.02 \times 10^{-9} \text{ s}^{-1}$$

$$\tau_{1/2}(25\text{ }^{\circ}\text{C}) = \ln 2 / k_{\text{rac}}(25\text{ }^{\circ}\text{C}) = 3.43 \times 10^8 \text{ s} = 9.5 \times 10^4 \text{ h} = 3974.1 \text{ days} = 10.9 \text{ years}$$

## 5.2 Procedures for Reduction of Cyclophanes 3aa–3da



To a solution of **3aa–3da** (0.1 mmol, 1.0 equiv.) in dry THF (2.0 mL) was added  $\text{LiAlH}_4$  (7.6 mg, 0.2 mmol, 2.0 equiv.) at 0 °C. The reaction was warmed to room temperature and reacted for 6 h. The mixture was diluted by water (5 mL) and extracted with EtOAc (5 mL  $\times$  3). The combined organic layers were dried over by anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel (PE/EtOAc = 20:1, v/v) afforded the product **4–7**.



(*R\_p*)-**4**, colorless oil, 16.6 mg, 52% yield, 85% ee.

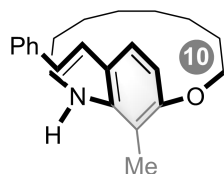
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.54 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.25 – 7.23 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 16.2 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.28 – 3.20 (m, 1H), 3.17 – 3.06 (m, 1H), 3.00 – 2.92 (m, 1H), 2.60 – 2.52 (m, 1H), 2.41 (s, 1H), 1.92 – 1.83 (m, 1H), 1.45 – 1.25 (m, 2H), 1.21 – 0.99 (m, 6H), 0.97 – 0.79 (m, 5H), 0.78 – 0.66 (m, 1H), 0.15 – 0.04 (m, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  142.0, 138.2, 128.8, 128.5, 127.6, 127.35, 127.28, 126.5, 124.0, 123.9, 46.6, 33.5, 28.5, 27.2, 26.7, 25.9, 24.9, 23.2, 15.9.

**HRMS (ESI):**  $m/z$   $[M + H]^+$  calculated for  $C_{23}H_{30}O^+$  320.2373, found 320.2376.

**HPLC:** Chiralpak IF column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 4.56 min (minor), 6.26 min (major).

$[\alpha]_D^{25} = +5.2$  (c = 0.25,  $CH_2Cl_2$ ).



(*R*<sub>p</sub>)-5, colorless oil, 18.5 mg, 55% yield, 82% ee.

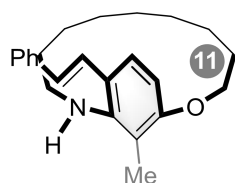
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  7.54 (d,  $J$  = 7.8 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.25 – 7.22 (m, 1H), 6.94 (d,  $J$  = 16.2 Hz, 1H), 6.71 (d,  $J$  = 8.4 Hz, 1H), 4.29 – 4.24 (m, 2H), 3.26 – 3.13 (m, 2H), 2.30 (s, 3H), 1.62 – 1.52 (m, 2H), 1.48 – 1.40 (m, 1H), 1.31 – 1.17 (m, 1H), 1.17 – 1.03 (m, 3H), 1.00 – 0.88 (m, 3H), 0.87 – 0.74 (m, 4H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  156.9, 138.5, 128.8, 127.22, 127.17, 126.7, 126.4, 124.7, 124.0, 121.9, 113.5, 72.0, 48.1, 31.3, 28.9, 26.83, 26.79, 23.9, 23.3, 11.8.

**HRMS (ESI):**  $m/z$   $[M + H]^+$  calculated for  $C_{23}H_{30}NO^+$  336.2322, found 336.2320.

**HPLC:** Chiralpak IF column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 5.99 min (minor), 7.04 min (major).

$[\alpha]_D^{25} = +12.0$  (c = 0.38,  $CH_2Cl_2$ ).



(*R*<sub>p</sub>)-6, colorless oil, 19.6 mg, 56% yield, 80% ee.

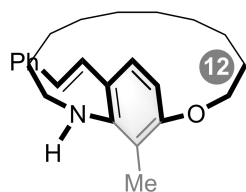
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  7.60 – 7.49 (m, 2H), 7.39 – 7.28 (m, 4H), 7.24 – 7.18 (m, 1H), 6.91 (d,  $J$  = 16.2 Hz, 1H), 6.63 (d,  $J$  = 8.5 Hz, 1H), 4.43 – 4.30 (m, 1H), 4.25 (ddd,  $J$  = 11.6, 7.5, 3.5 Hz, 1H), 3.31 (ddd,  $J$  = 14.8, 7.0, 3.0 Hz, 1H), 3.15 (ddd,  $J$  = 14.6, 8.4, 2.9 Hz, 1H), 2.27 (s, 3H), 1.70 – 1.54 (m, 3H), 1.52 – 1.44 (m, 1H), 1.35 – 1.22 (m, 3H), 1.21 – 0.93 (m, 6H), 0.93 – 0.82 (m, 4H), 0.82 – 0.72 (m, 1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  157.5, 138.5, 129.0, 128.8, 128.2, 127.2, 127.1, 126.8, 126.3, 125.1, 122.7, 119.4, 110.5, 70.1, 33.3, 28.9, 27.1, 26.8, 26.7, 25.4, 23.3, 11.6.

**HRMS (ESI):**  $m/z$   $[M + H]^+$  calculated for  $C_{24}H_{32}NO^+$  350.2479, found 350.2475.

**HPLC:** Chiralpak IF column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 5.80 min (minor), 8.30 min (major).

$[\alpha]_D^{25} = +34.5$  ( $c = 0.54$ ,  $CH_2Cl_2$ ).



( $R_p$ )-7, colorless oil, 24.7 mg, 68% yield, 5% ee.

**$^1H$  NMR (600 MHz,  $CDCl_3$ )**  $\delta$  7.52 (d,  $J = 7.7$  Hz, 2H), 7.36 – 7.31 (m, 2H), 7.28 (d,  $J = 16.0$  Hz, 1H), 7.24 – 7.20 (m, 1H), 6.89 (d,  $J = 16.2$  Hz, 1H), 6.59 (d,  $J = 8.5$  Hz, 1H), 4.39 – 4.33 (m, 1H), 4.18 (ddd,  $J = 12.0, 8.7, 3.4$  Hz, 1H), 3.24 – 3.18 (m, 2H), 2.22 (s, 3H), 1.74 – 1.66 (m, 1H), 1.62 – 1.52 (m, 2H), 1.46 – 1.39 (m, 1H), 1.37 – 1.24 (m, 5H), 1.22 – 1.14 (m, 1H), 1.11 – 0.96 (m, 9H), 0.92 – 0.84 (m, 1H).

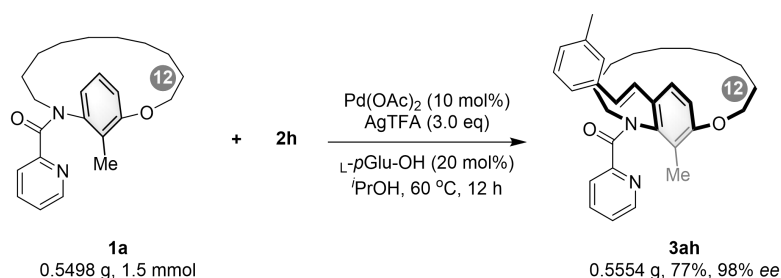
**$^{13}C$  NMR (151 MHz,  $CDCl_3$ )**  $\delta$  156.5, 138.6, 129.0, 128.8, 128.2, 127.4, 127.0, 126.4, 126.3, 125.0, 122.4, 118.1, 108.4, 69.2, 49.0, 30.8, 27.6, 27.5, 27.4, 27.3, 27.2, 25.4, 25.0, 10.9.

**HRMS (ESI):**  $m/z$   $[M + H]^+$  calculated for  $C_{25}H_{34}NO^+$  364.2635, found 364.2639.

**HPLC:** Chiralpak IC column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 5.15 min (minor), 5.82 min (major).

## 6. Gram-Scale Synthesis and Derivatizations

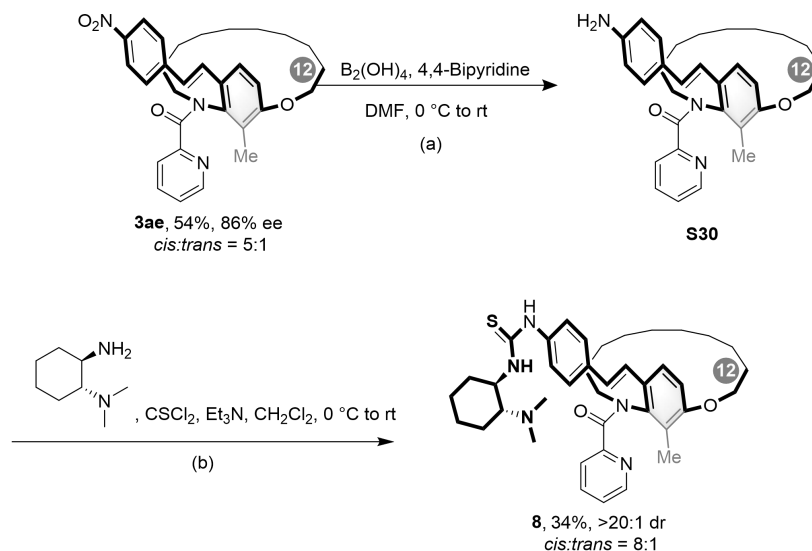
### 6.1. Gram-Scale Synthesis



A 100 mL round-bottom flask equipped with a magnetic stirring bar was charged with cyclophane **1a** (0.5498 mg, 1.5 mmol, 1.0 equiv.), **2h** (0.3545 g, 0.40 mL, 2 mmol, 2.0 equiv.),  $Pd(OAc)_2$  (33.7 mg, 0.15 mmol, 10 mmol%),  $L$ - $p$ Glu-OH (38.7 mg, 0.30 mmol, 20 mmol%), AgTFA (0.9940 g, 4.5 mmol, 3.0 equiv.), and  $i$ PrOH (20 mL). Then the reaction mixture was stirred at 60 °C under air. After 12 h, the reaction mixture was immediately cooled to room temperature. The resulting

mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel to afford the corresponding product **3ah** (0.5554 g, 1.15 mmol, 77% yield, 98% ee).

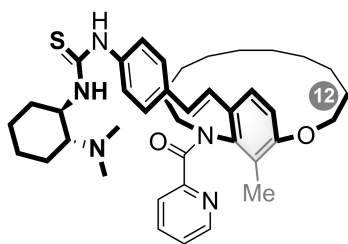
## 6.2. Derivatizations of **3ae**



(a) To a solution of **3ae** (51.3 mg, 0.1 mmol, 1.0 equiv.) in dry DMF (1 mL) was added 4,4-Bipyridine (0.8 mg, 0.005 mmol, 0.05 equiv.) at 0 °C. Then the  $B_2(OH)_4$  (35.9 mg, 0.4 mmol, 4.0 equiv.) was added to the reaction at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. Then the reaction mixtures were diluted with water (2 mL) and extracted with EtOAc (5 mL  $\times$  3). The combined organic phases were washed by brine and dried over anhydrous  $Na_2SO_4$ . After filtration and removing the solvent *in vacuum*, the crude product is obtained. The crude product **S30** was used directly for next step.

(b) Thiophosgene (0.01 mL, 0.13 mmol, 1.3 equiv.) was added dropwise to a solution of (1*R*,2*R*)-*N,N*-dimethylcyclohexane-1,2-diamine (0.02 mL, 0.12 mmol, 1.2 equiv) and  $Et_3N$  (0.4 mL, 3 mmol, 30.0 equiv.) in  $CH_2Cl_2$  (1.0 mL). The mixture was stirred for 30 min at 0 °C. Then, the cold bath was removed, and stirring was continued for an additional 3 h. The mixture was extracted with  $CH_2Cl_2$  (5 mL  $\times$  3). The combined organic phases were washed with brine and dried over anhydrous  $Na_2SO_4$ . After filtration and removal of the solvent *in vacuum*, the crude product was obtained as a brown oil<sup>[2]</sup>.

Under an  $N_2$  atmosphere, the aforementioned crude brown oil was added to a solution of **S30** (0.1 mmol, 1.0 equiv.) in dry  $CH_2Cl_2$ . The reaction mixture was stirred for 24 h at room temperature, and the reaction progress was monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel ( $CH_2Cl_2/MeOH$  = 20:1, v/v) to afford the desired product **8** (34%, >20:1 dr, *cis:trans* = 8:1).

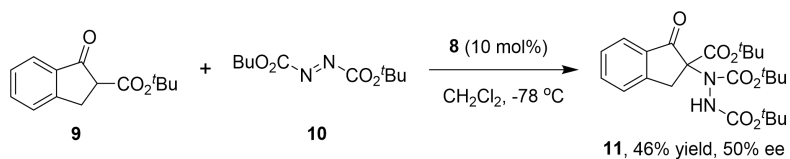


**8**, yellow solid, 22.7 mg, 34% yield, >20:1 *dr*.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.26 (d, *J* = 4.8 Hz, 1H), 7.52 – 7.48 (m, 4H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 16.2 Hz, 1H), 7.07 (dd, *J* = 7.8, 4.9 Hz, 1H), 6.86 (d, *J* = 16.6 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 4.40– 4.36 (m, 1H), 4.18 – 4.13 (m, 1H), 4.13 – 4.07 (m, 1H), 3.63 – 3.58 (m, 1H), 2.27 (s, 6H), 2.10 (s, 3H), 1.88 – 1.78 (m, 2.6H), 1.72 – 1.60 (m, 8.1H), 1.50 – 1.42 (m, 2.6H), 1.34 – 1.22 (m, 6.1H), 1.16 – 0.97 (m, 9.3H), 0.96 – 0.86 (m, 2.5H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  168.9, 156.4, 154.3, 148.4, 140.7, 135.9, 129.9, 128.4, 127.9, 127.6, 127.1, 123.6, 123.0, 113.8, 113.4, 69.3, 67.3, 56.4, 48.6, 40.1, 32.9, 29.8, 26.9, 26.4, 25.6, 25.1, 24.9, 24.8, 24.7, 22.0, 13.1.

**HRMS (ESI):** *m/z* [M + H]<sup>+</sup> calculated for C<sub>40</sub>H<sub>54</sub>N<sub>5</sub>O<sub>2</sub>S<sup>+</sup> 668.3993, found 668.3999.

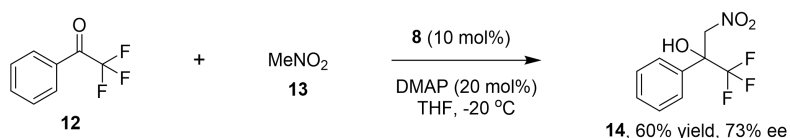


Compound **11** was prepared in 46% yield, 50% ee according to the known procedure with compound **8** (>20:1 *dr*) as catalyst.<sup>[3]</sup> This compound is known and the spectroscopic data match those reported<sup>[3]</sup>.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  7.79 – 7.68 (m, 1H), 7.65 – 7.57 (m, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 4.16 – 3.71 (m, 5H), 1.50 – 1.25 (m, 18H).

**HPLC:** Chiralpak IE column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, *t<sub>R</sub>* = 16.24 min (major), 18.64 min (minor).

**[ $\alpha$ ]<sub>D</sub><sup>25</sup>** = +7.1 (*c* = 0.21, CH<sub>2</sub>Cl<sub>2</sub>).



Compound **14** was prepared in 60% yield, 73% ee according to the known procedure with compound **8** (>20:1 *dr*) as catalyst.<sup>[4]</sup> This compound is known and the spectroscopic data match those reported<sup>[4]</sup>.

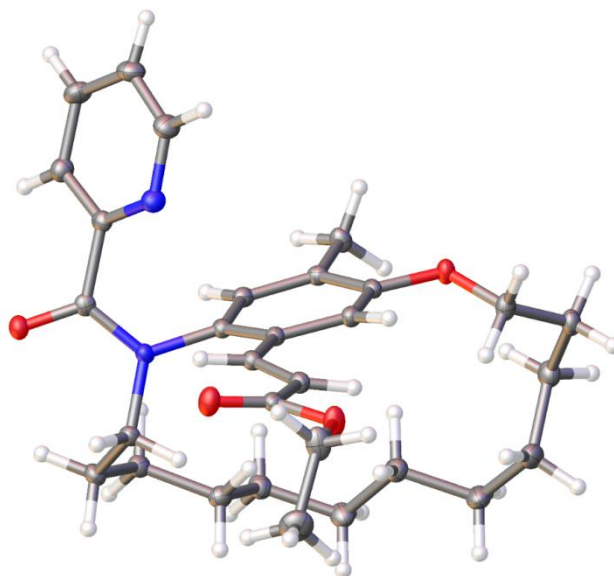
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** 7.62 – 7.59 (m, 2H), 7.48 – 7.44 (m, 3H), 5.03 (m, 2H), 4.63

(s, 1H) .

**HPLC:** Chiralpak IB N-5 column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  = 15.87 min (minor), 19.98 min (major).

$[\alpha]_D^{25} = +134.0$  (c = 0.21, CH<sub>2</sub>Cl<sub>2</sub>).

## 7.X-Ray Report



**Figure S9.** Thermal ellipsoid plot for the crystal structure of **3ga** (at 50% probability level, CCDC 2519473<sup>[5]</sup>).

### Experimental

Single crystals of  $C_{34}H_{42}N_2O_4$  (**3ga**) were recrystallized from  $CH_2Cl_2$  and PE. A suitable crystal was selected and mounted in inert oil and transferred to the cold gas stream of the diffractometer. The crystal was kept at 100.00(10) K during data collection.

### Crystal structure determination of 3ga

**Crystal Data** for  $C_{34}H_{42}N_2O_4$  ( $M = 510.69$  g/mol): monoclinic, space group C2 (no. 5),  $a = 21.4203(5)$  Å,  $b = 8.68280(10)$  Å,  $c = 16.9906(4)$  Å,  $\beta = 112.528(3)^\circ$ ,  $V = 2918.91(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 100.01(10)$  K,  $\mu$  (Cu K $\alpha$ ) = 0.553 mm<sup>-1</sup>,  $D_{calc} = 1.162$  g/cm<sup>3</sup>, 20705 reflections measured ( $8.55^\circ \leq 2\theta \leq 150.98^\circ$ ), 4870 unique ( $R_{int} = 0.0433$ ,  $R_{sigma} = 0.0363$ ) which were used in all calculations. The final  $R_1$  was 0.0396 ( $I > 2 \sigma(I)$ ) and  $wR_2$  was 0.1044 (all data).

Table S9 Crystal data and structure refinement for 3ga.

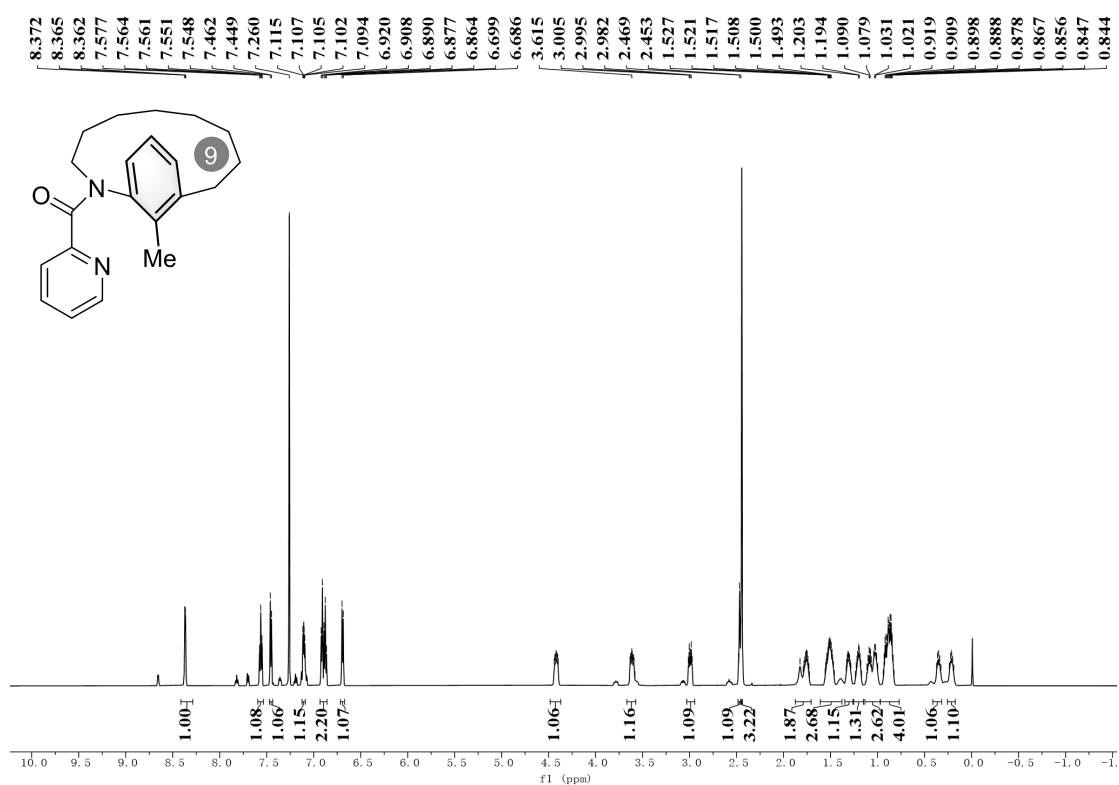
Empirical formula	C <sub>34</sub> H <sub>42</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	510.69
Temperature [K]	100.01(10)
Crystal system	monoclinic
Space group (number)	<i>C</i> 2 (5)
<i>a</i> [Å]	21.4203(5)
<i>b</i> [Å]	8.68280(10)
<i>c</i> [Å]	16.9906(4)
$\alpha$ [°]	90
$\beta$ [°]	112.528(3)
$\gamma$ [°]	90
Volume [Å <sup>3</sup> ]	2918.91(12)
<i>Z</i>	4
$\rho_{\text{calc}}$ [gcm <sup>-3</sup> ]	1.162
$\mu$ [mm <sup>-1</sup> ]	0.553
<i>F</i> (000)	1104
Crystal size [mm <sup>3</sup> ]	0.2×0.15×0.05
Radiation	Cu <i>K</i> <sub>α</sub> ( $\lambda$ = 1.54184 Å)
2 $\theta$ range [°]	8.55 to 150.98 (0.80 Å)
Index ranges	-26 ≤ <i>h</i> ≤ 25 -10 ≤ <i>k</i> ≤ 9 -21 ≤ <i>l</i> ≤ 20
Reflections collected	20705
Independent reflections	4870 [ <i>R</i> <sub>int</sub> = 0.0433], [ <i>R</i> <sub>sigma</sub> = 0.0363]
Data / Restraints / Parameters	4870/188/426
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.053
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0396 <i>wR</i> <sub>2</sub> = 0.0953
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0483 <i>wR</i> <sub>2</sub> = 0.1044
Largest peak/hole [eÅ <sup>-3</sup> ]	0.29/-0.25
Flack <i>X</i> parameter	-0.11(15)

## 8. References

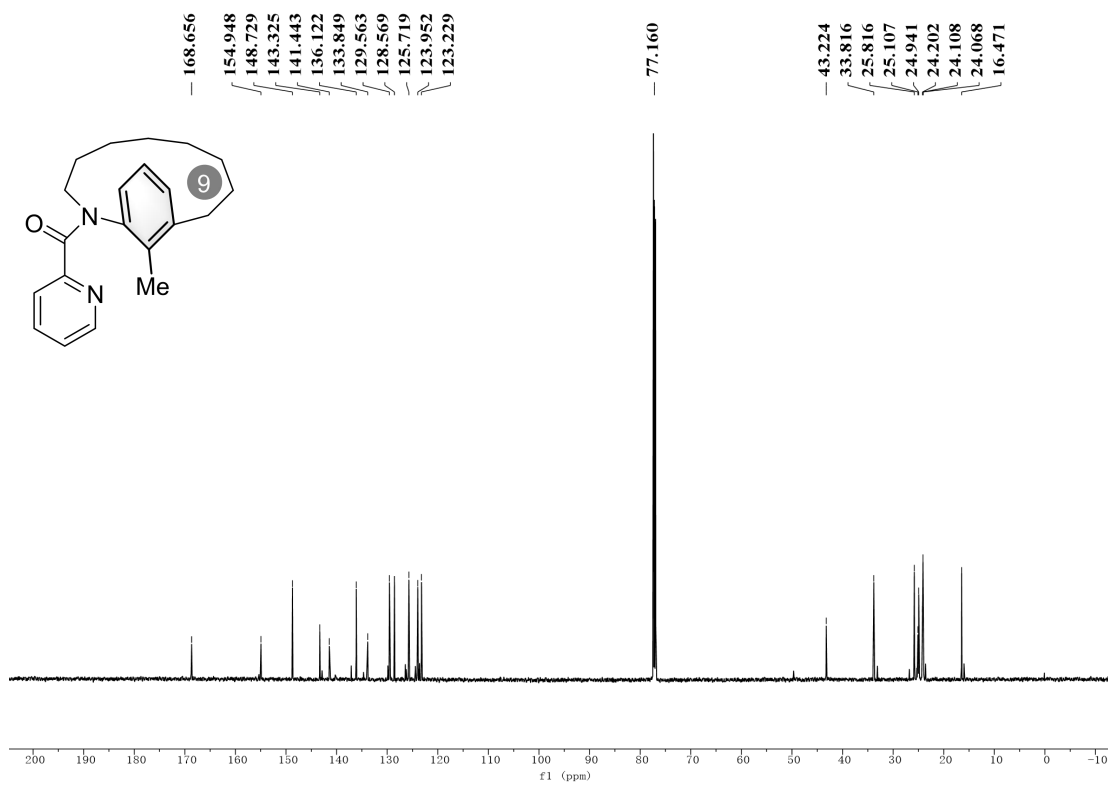
1. Unny D, Kandregula GR, Sivanadanam J, Ramanujam K. Molecular engineering of pyrene carbazole dyes with a single bond and double bond as the mode of linkage. *New J Chem*. 2020;44(38):16511-16525. [DOI:10.1039/d0nj03228j]
2. Feng X, Geng X, Zhang C, Zhang X. Chain shuttle between dual sites of a monomolecular organocatalyst enables controlled ring-opening copolymerization. *Macromolecules*. 2024;57(17):8401-8408. [DOI:10.1021/acs.macromol.4c01561]
3. Mang JY, Kwon DG, Kim DY. Catalytic asymmetric electrophilic  $\alpha$ -amination of  $\beta$ -ketoesters in the presence of chiral nickel complexes. *Bull Korean Chem Soc*. 2009;30(1):249-252. [DOI:10.1055/s-2008-1078564]
4. Otevrel J, Svestka D, Bobal P. Bianthryl-based organocatalysts for the asymmetric Henry reaction of fluoroketones. *Org Biomol Chem*. 2019;17(21):5244-5248. [DOI:10.1039/c9ob00884e]
5. CCDC 2519473: Experimental crystal structure determination. 2026. [DOI:10.5517/ccdc.csd.cc2qkqbc]



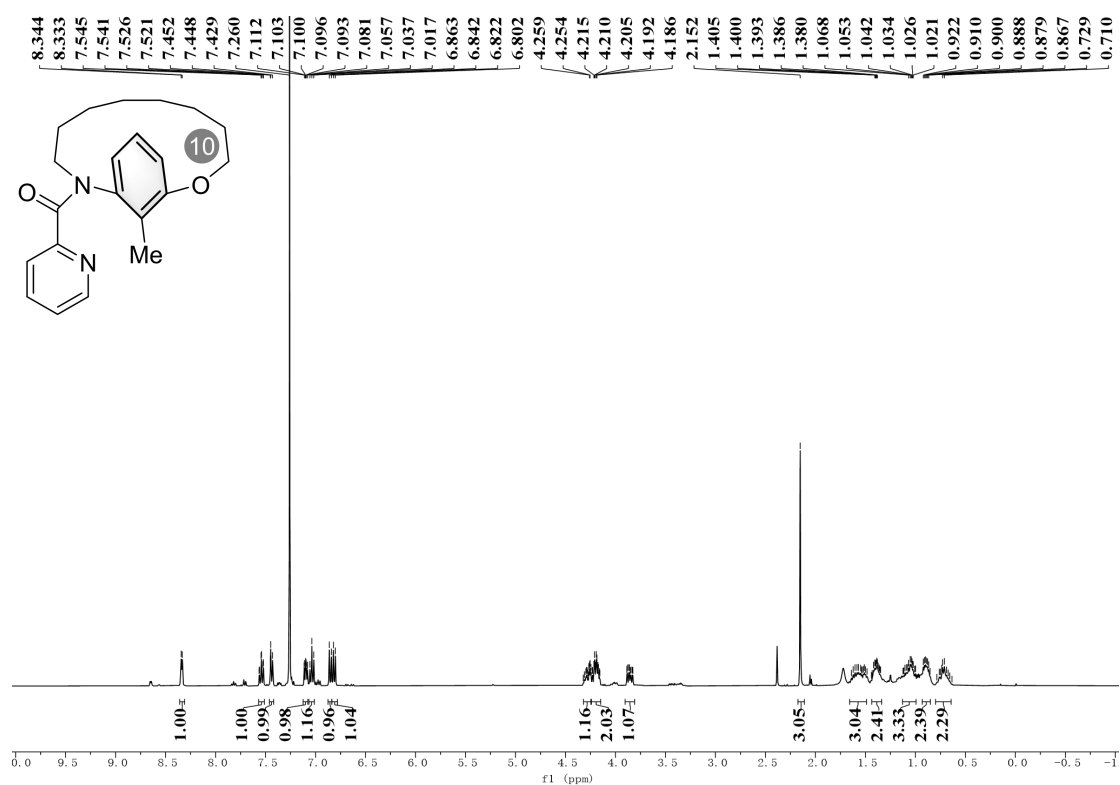
**1b**, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



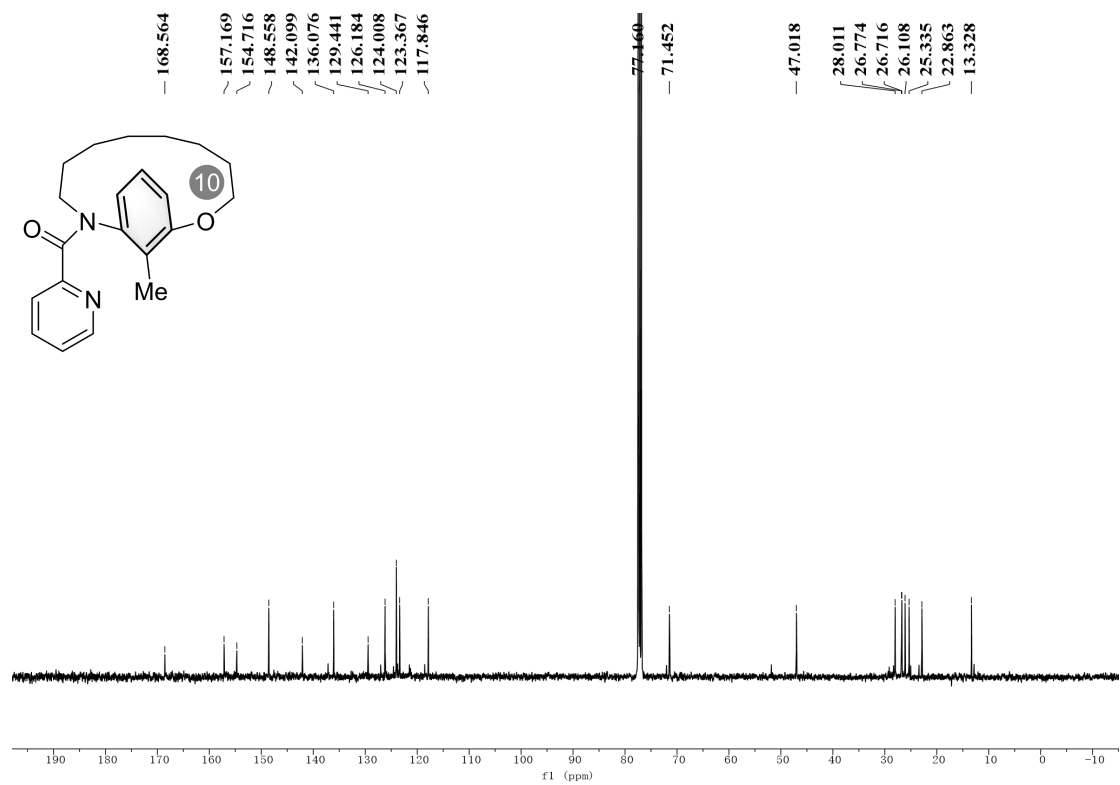
**1b**, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



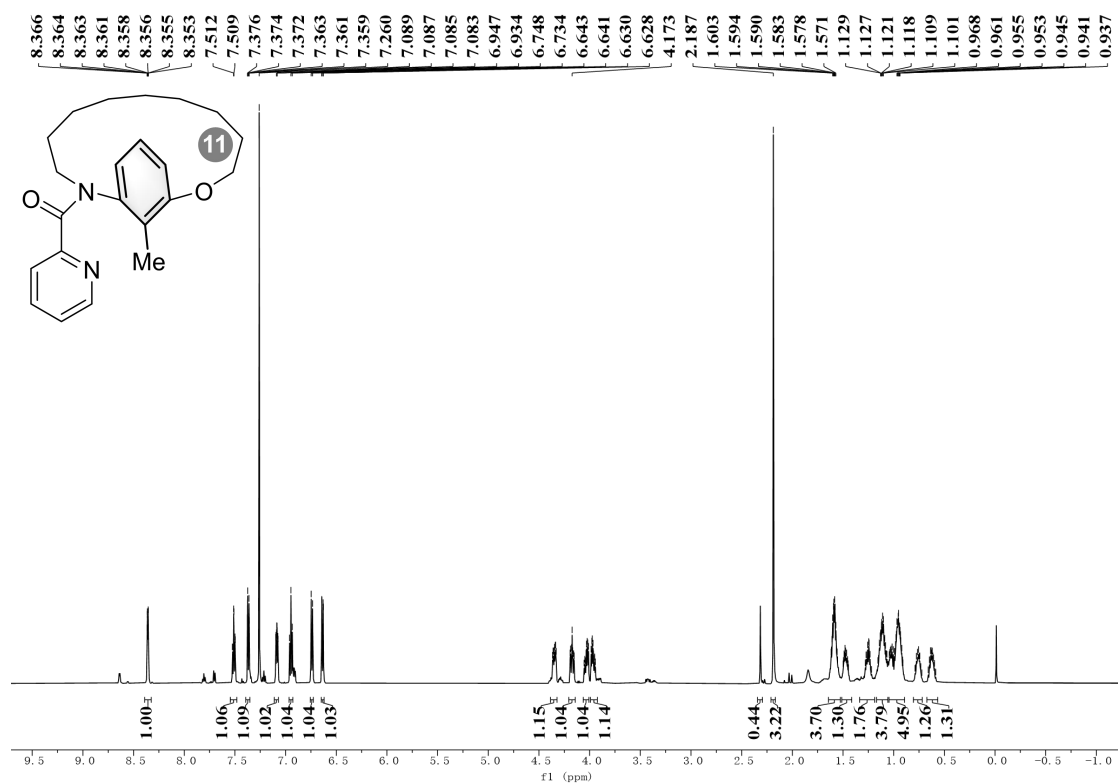
**1c**,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



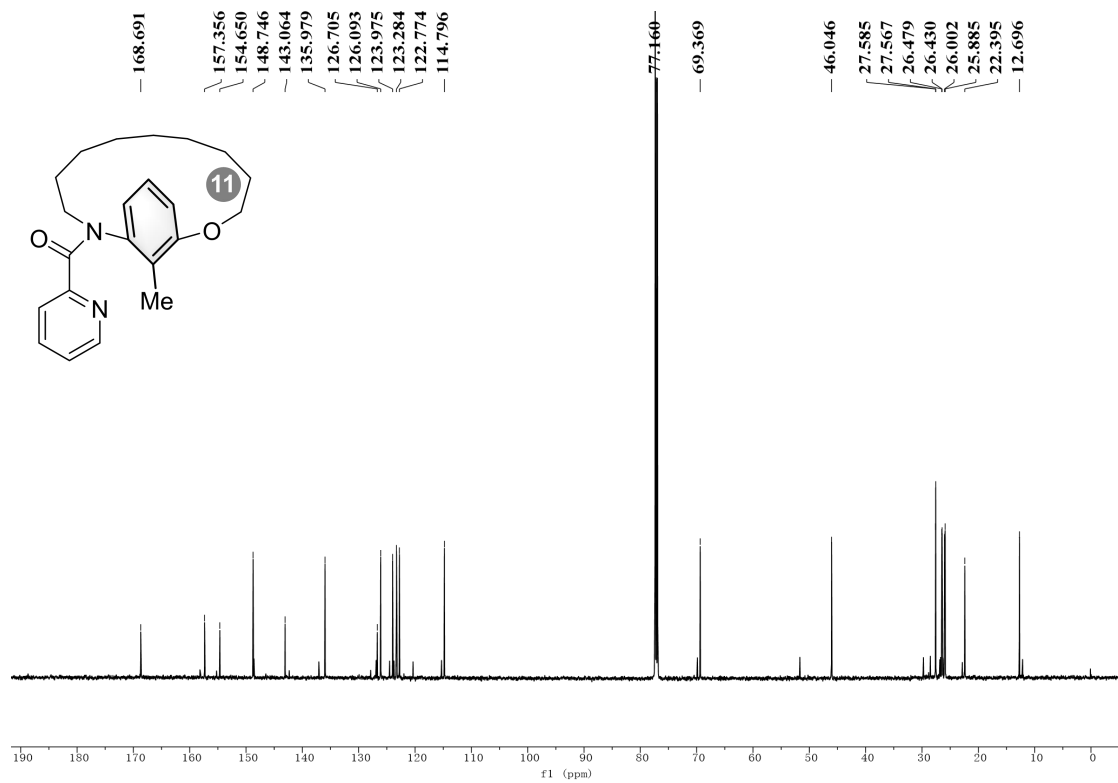
**1c**,  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



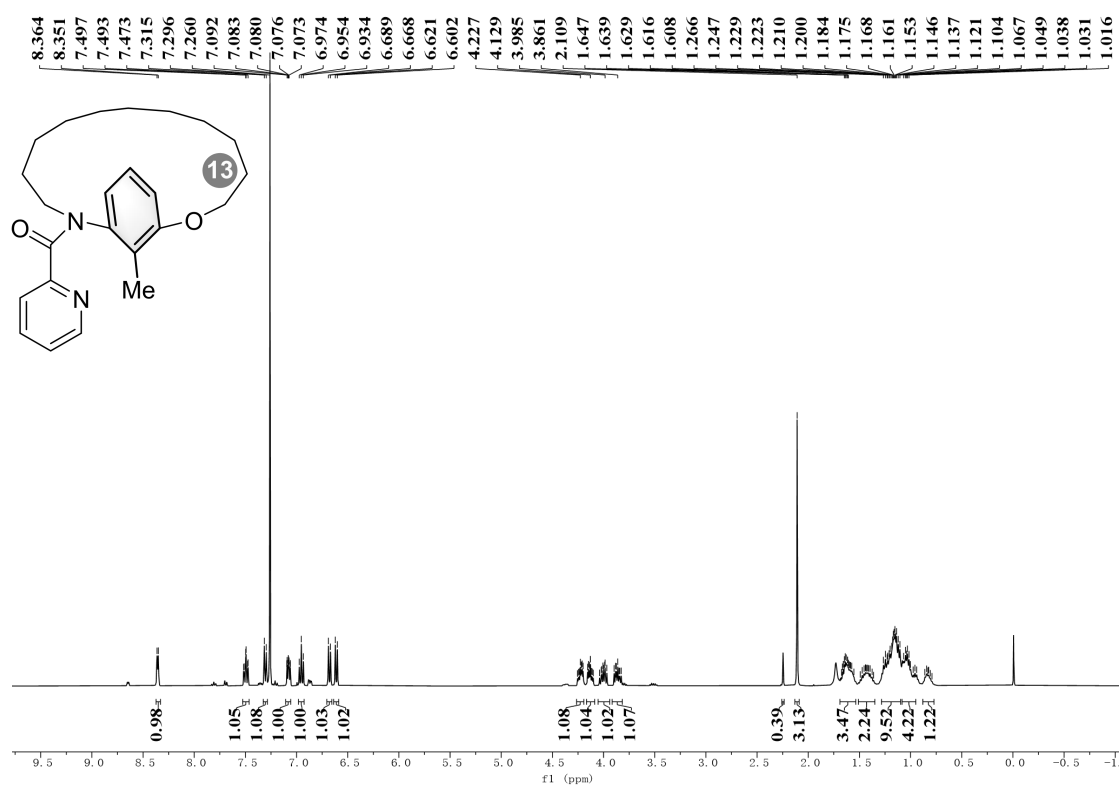
**1d**,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



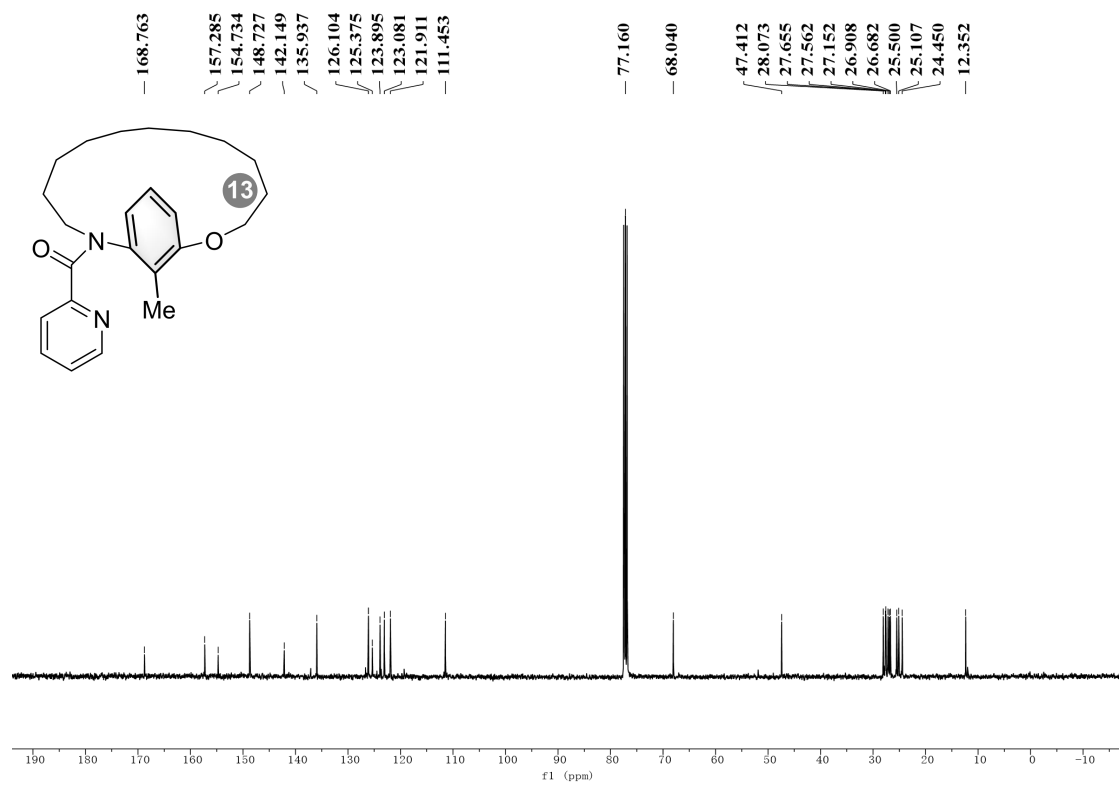
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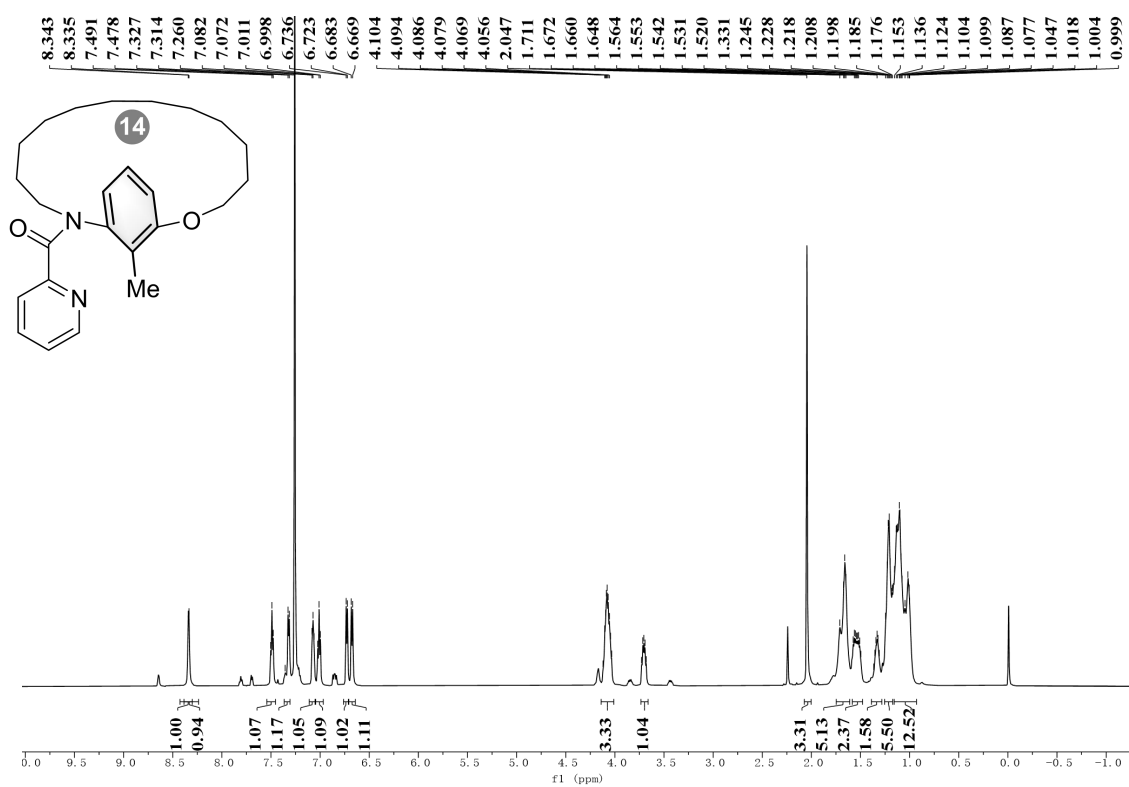
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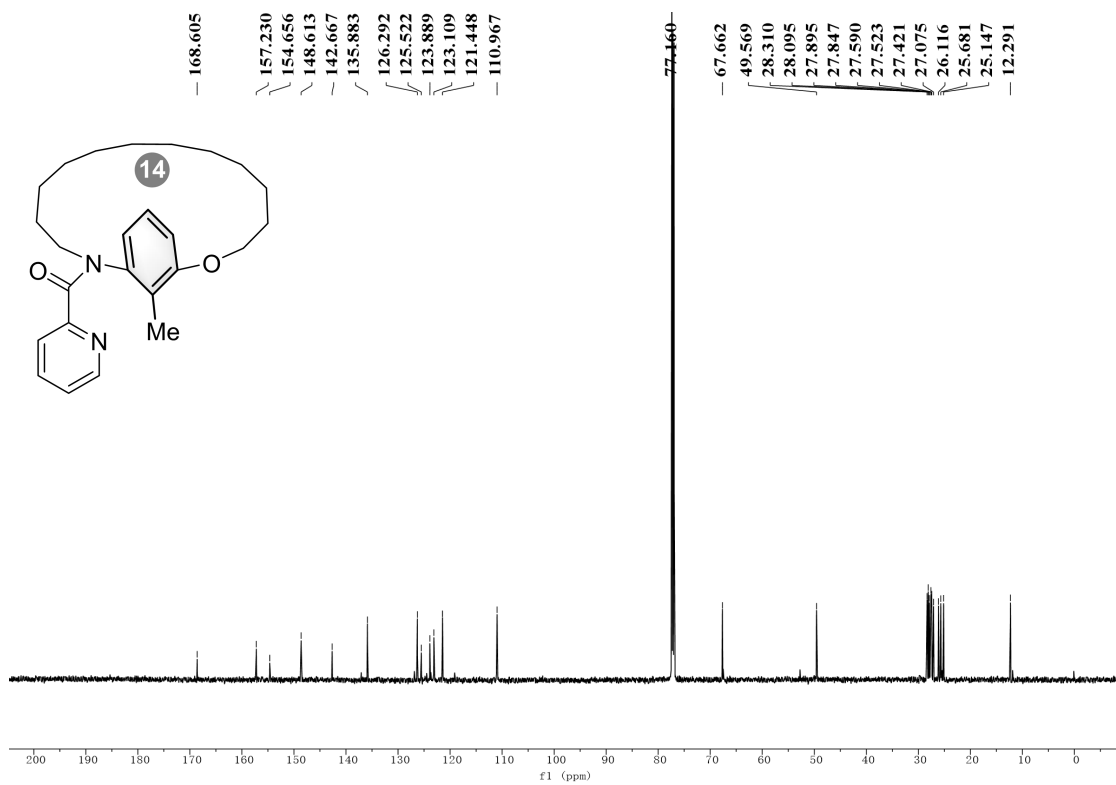
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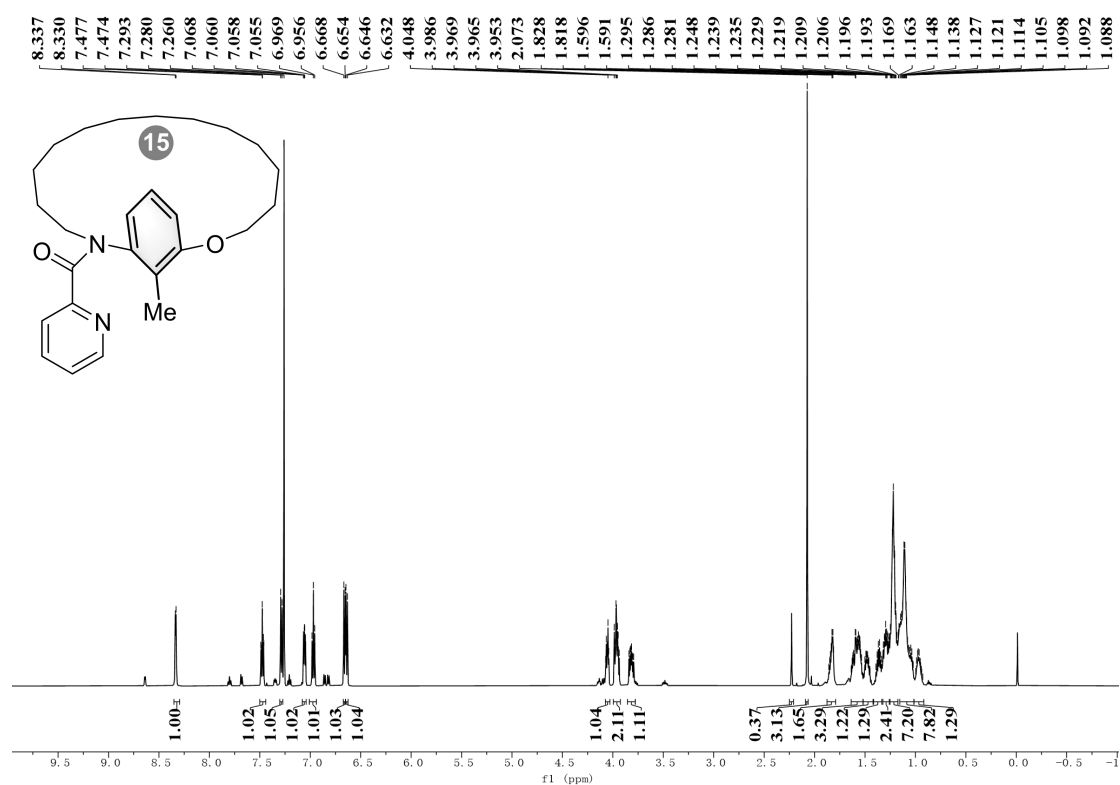
**1f**,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



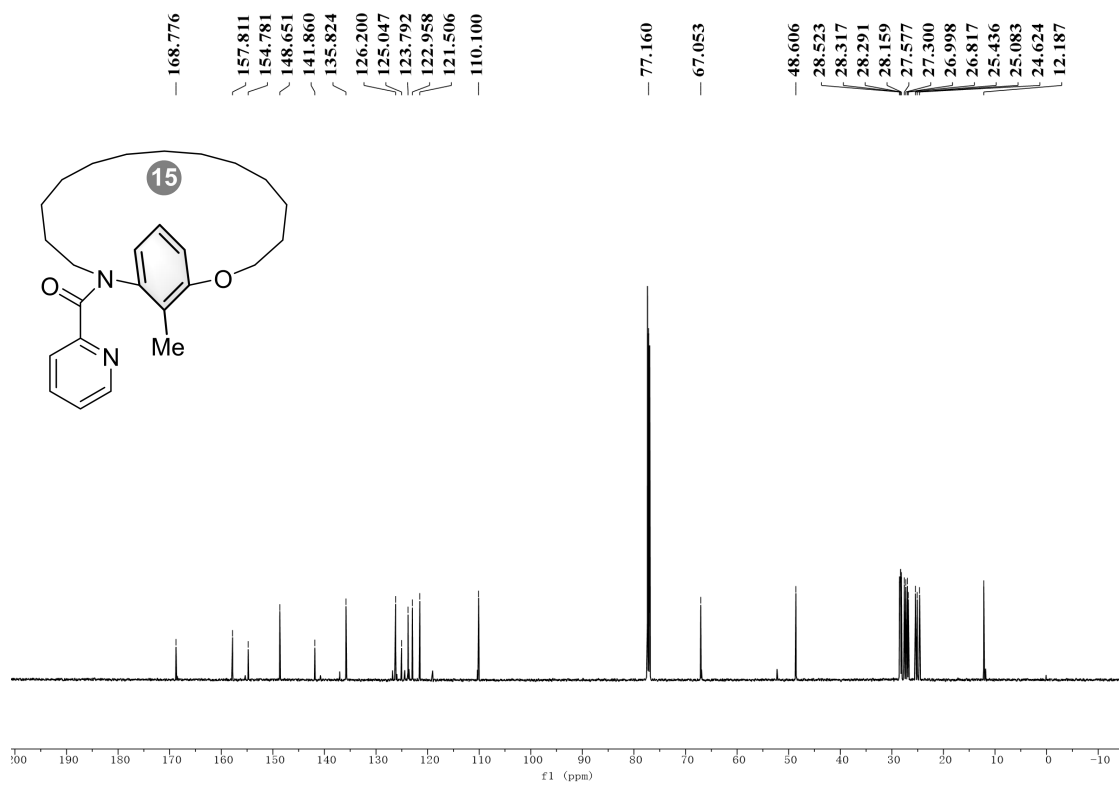
**1f**,  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )



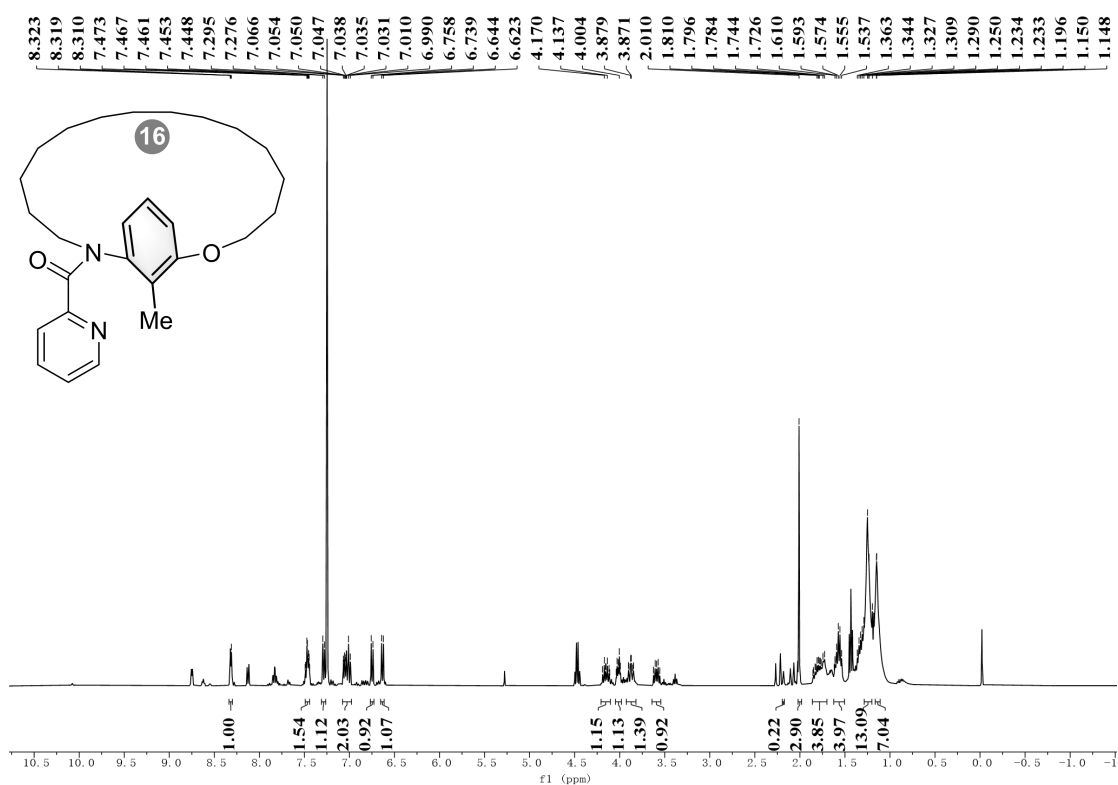
**1g, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**



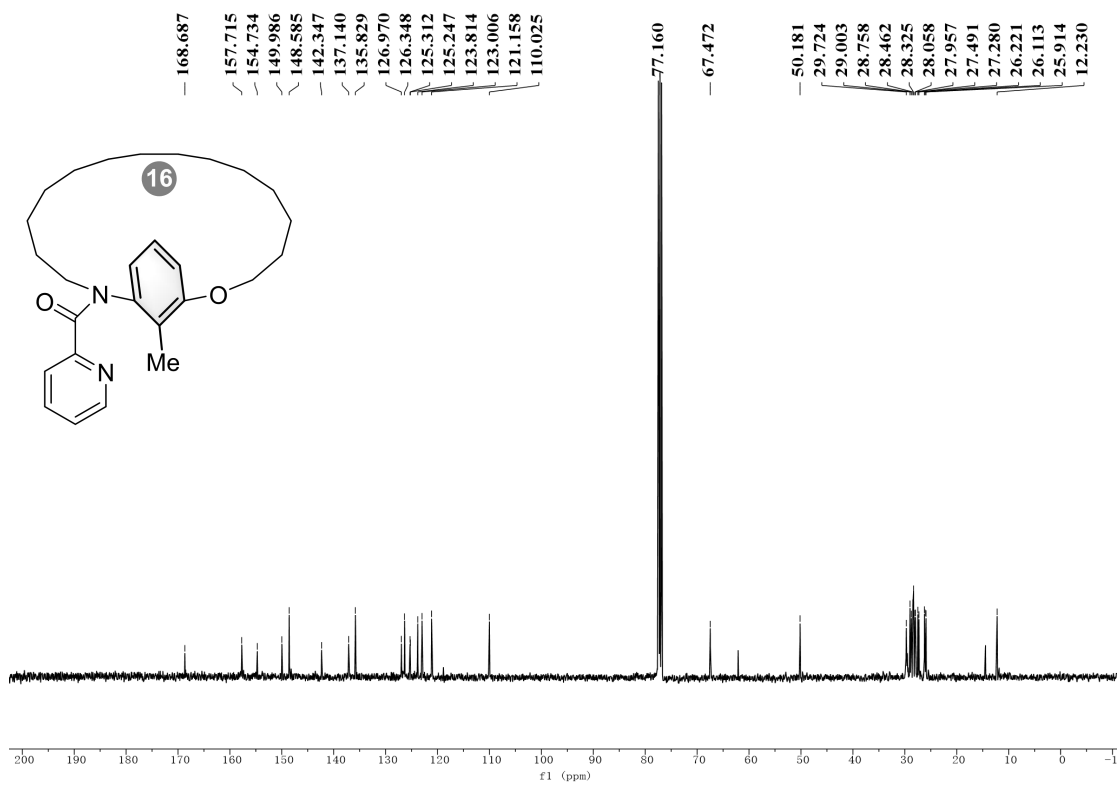
**1g, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**



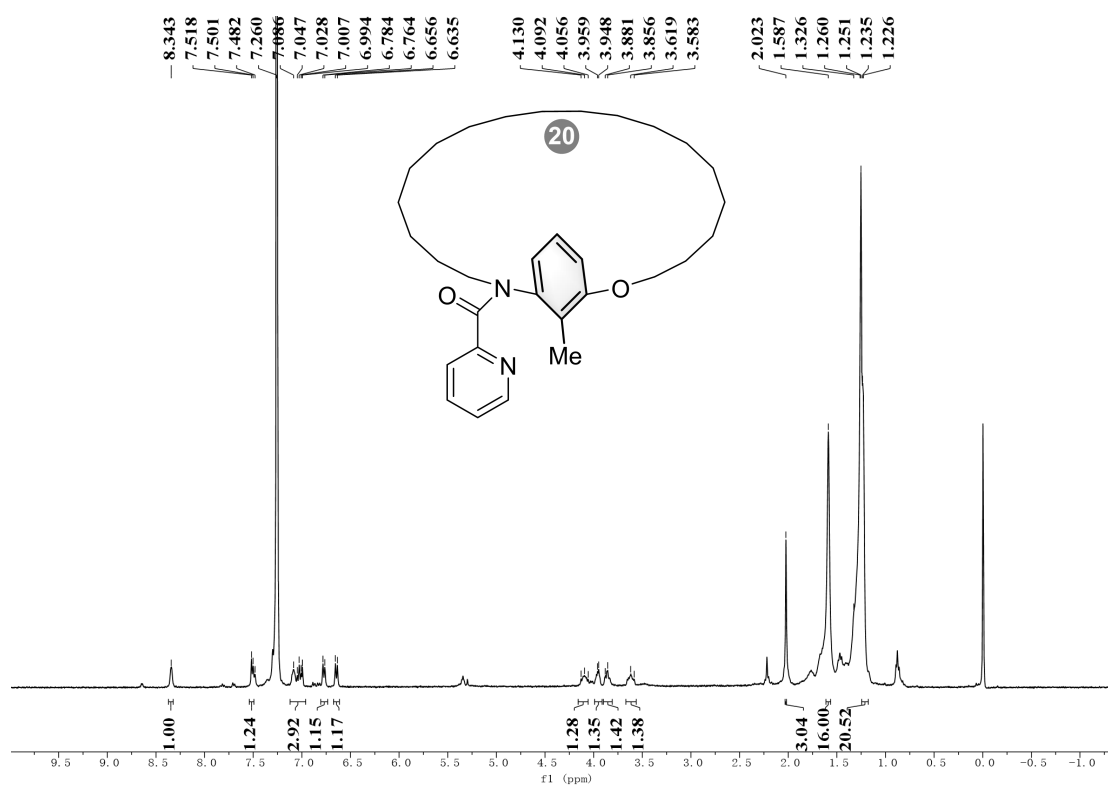
1h, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



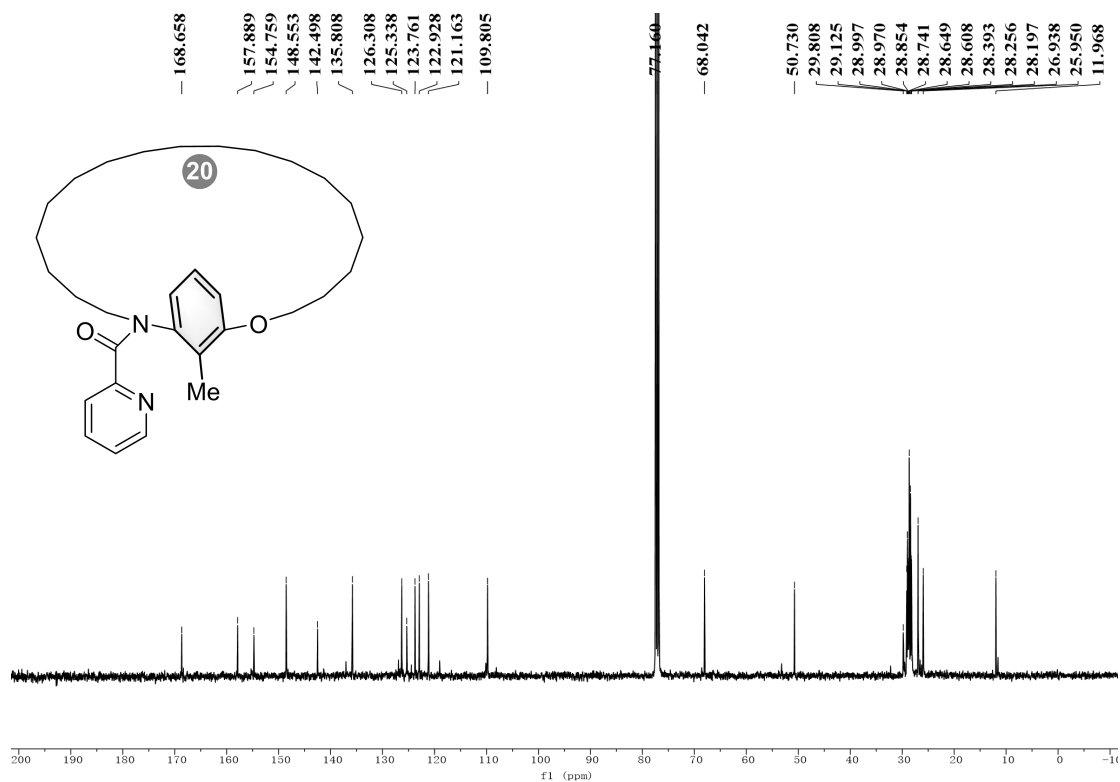
1h, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



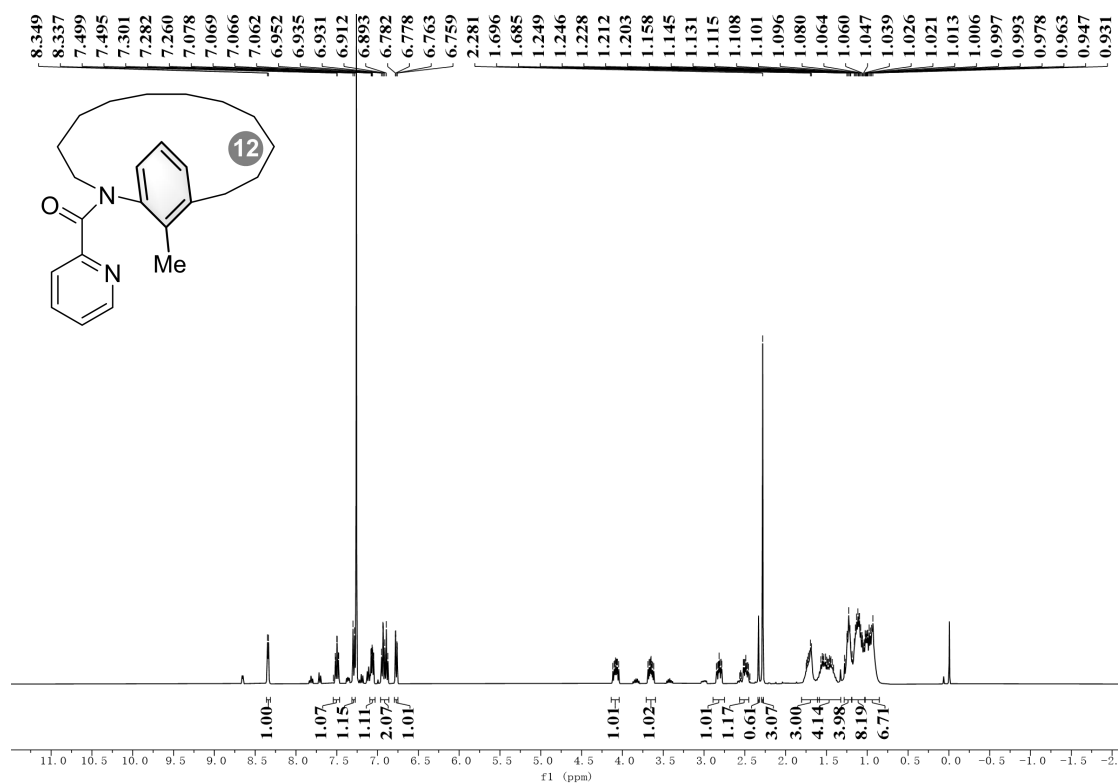
**1i**,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



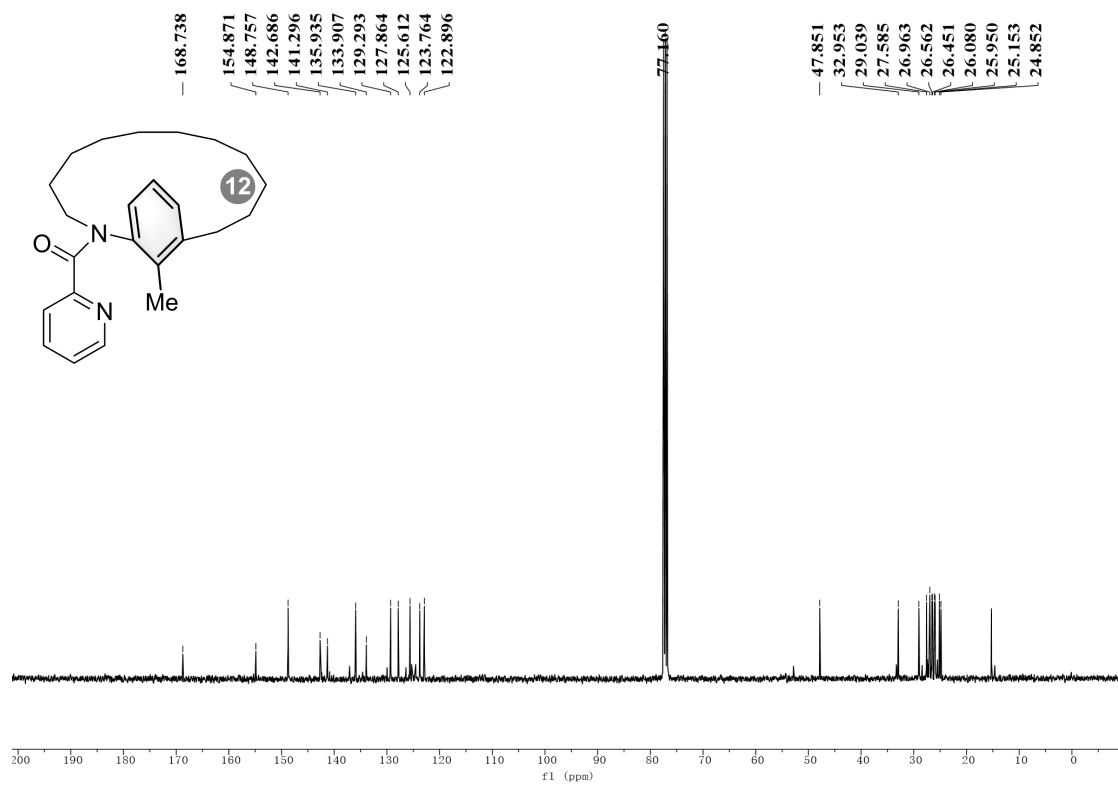
**1i**,  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



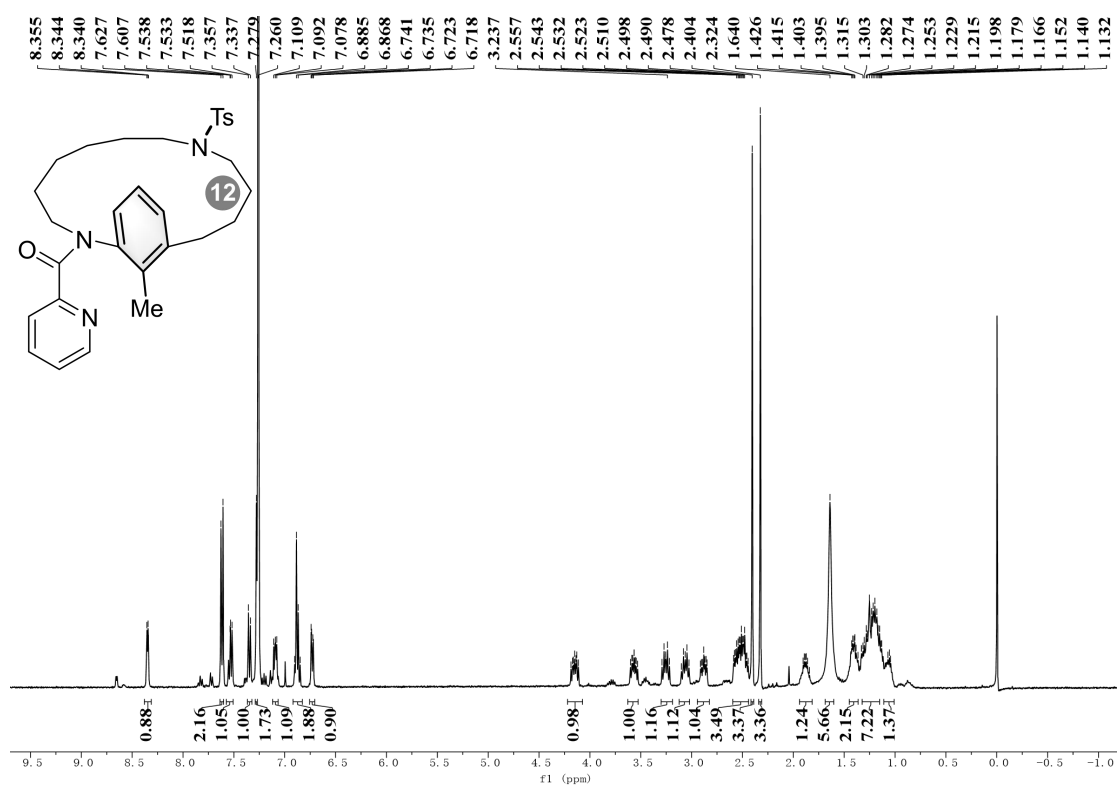
**1j**, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



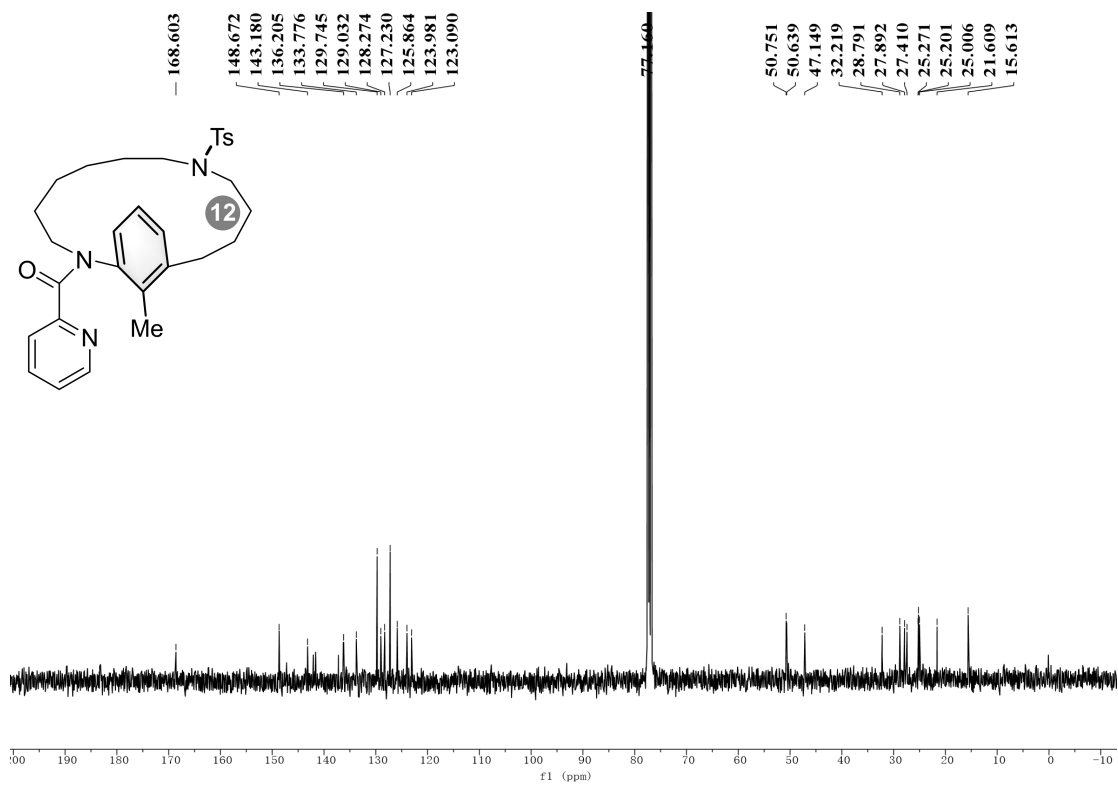
**1j**, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



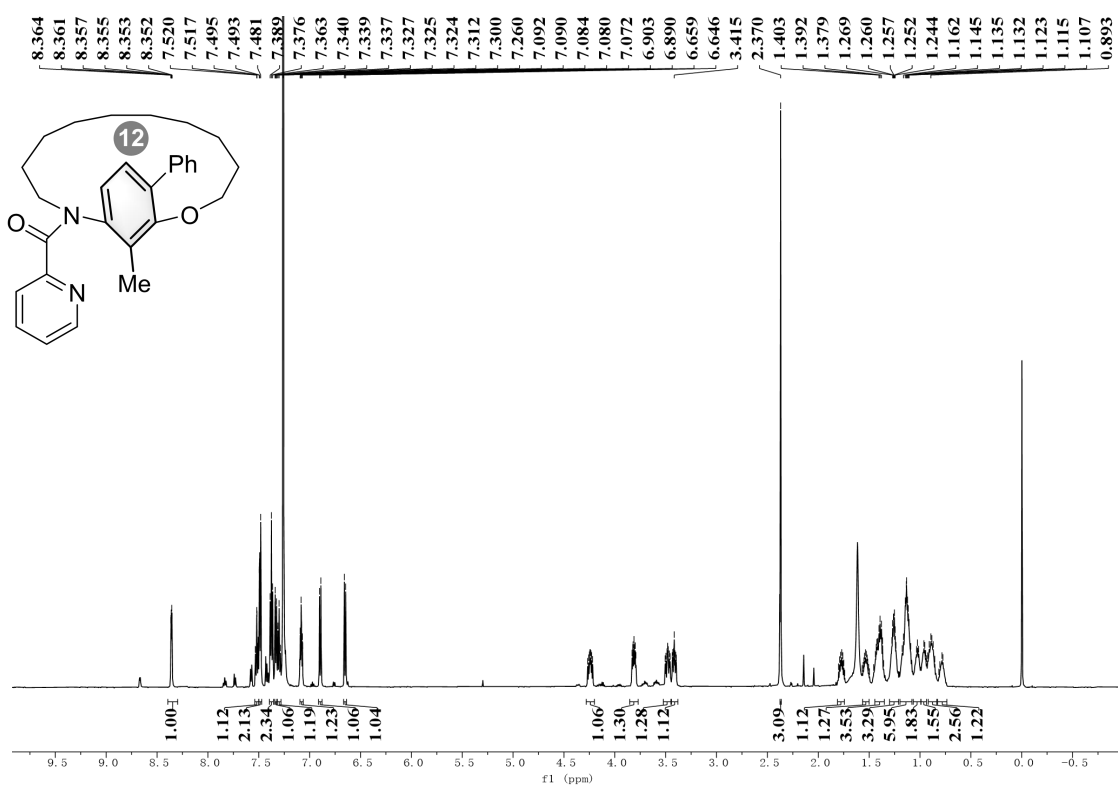
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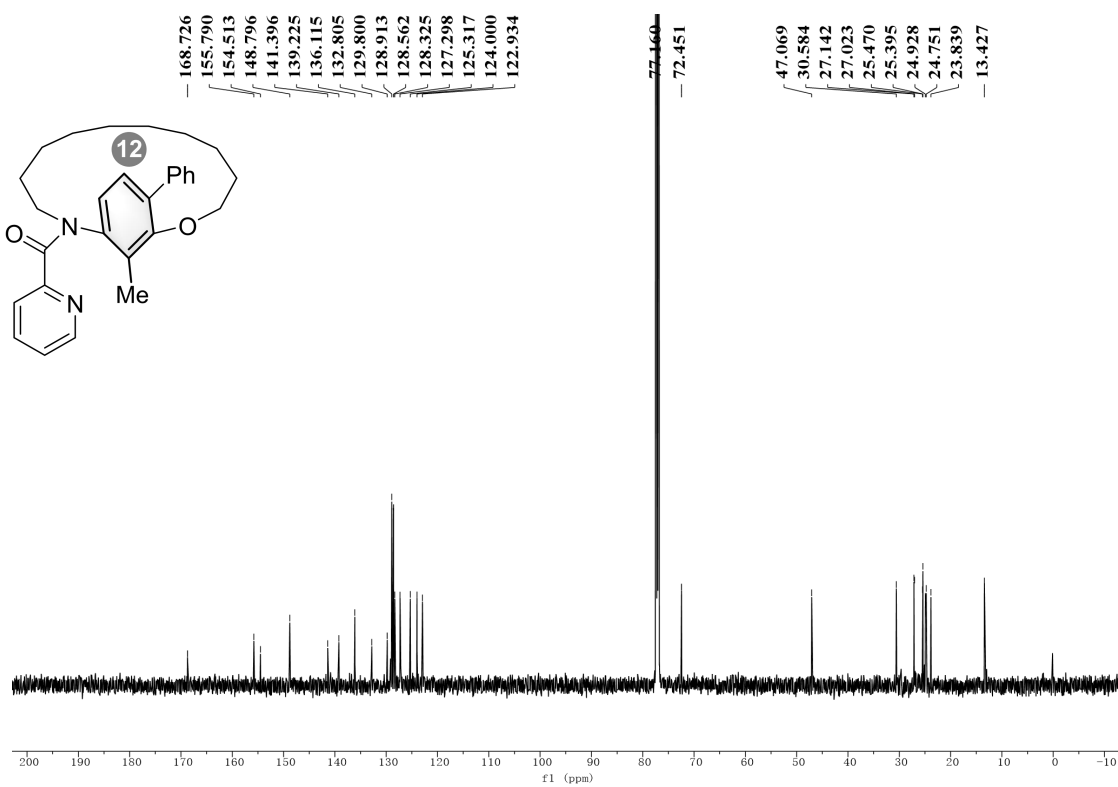
**1k**,  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



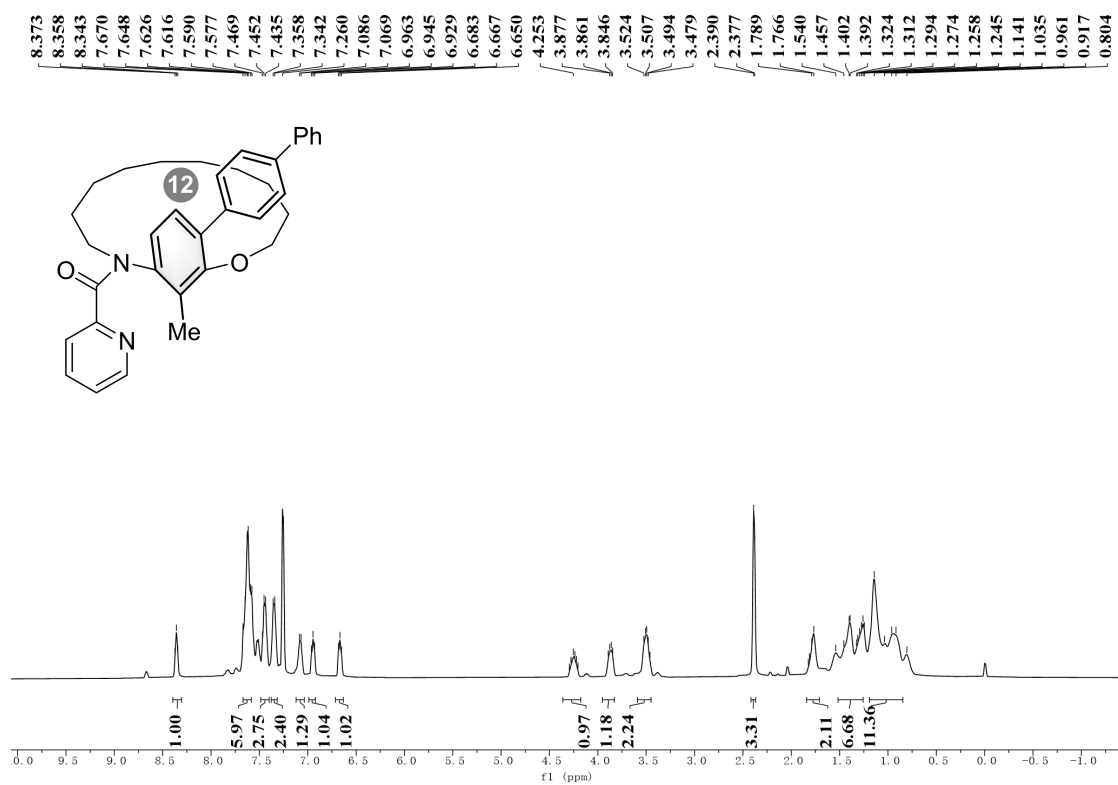
11, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



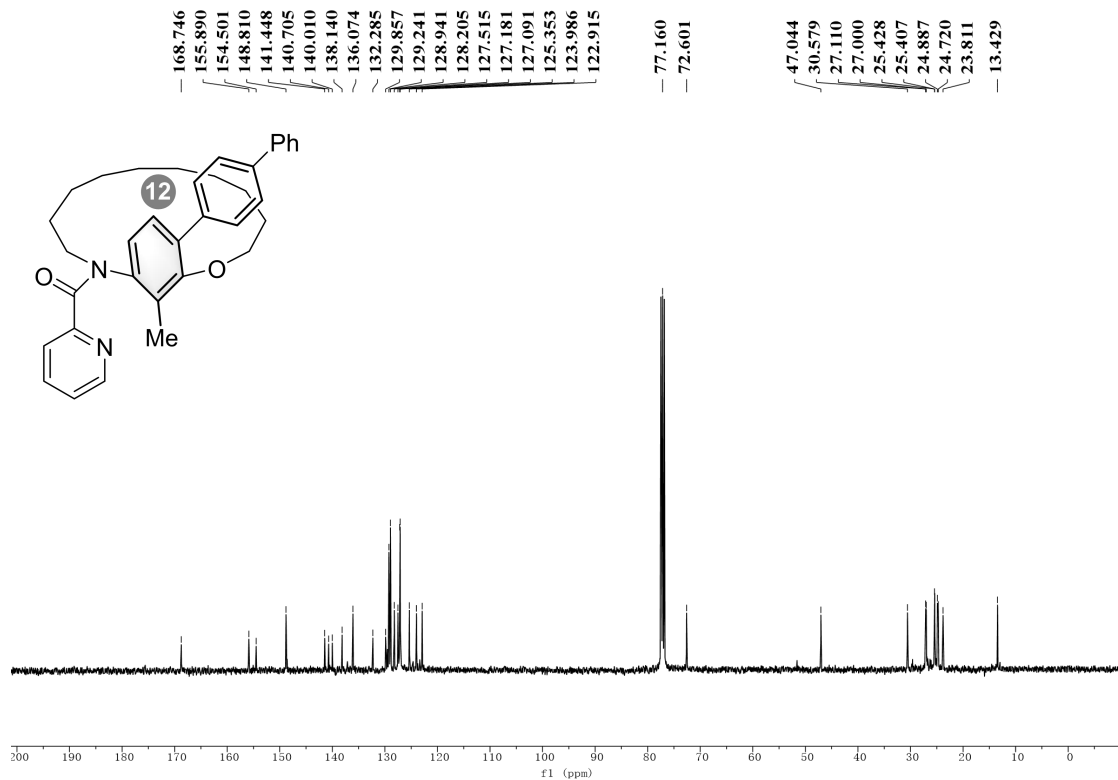
11, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



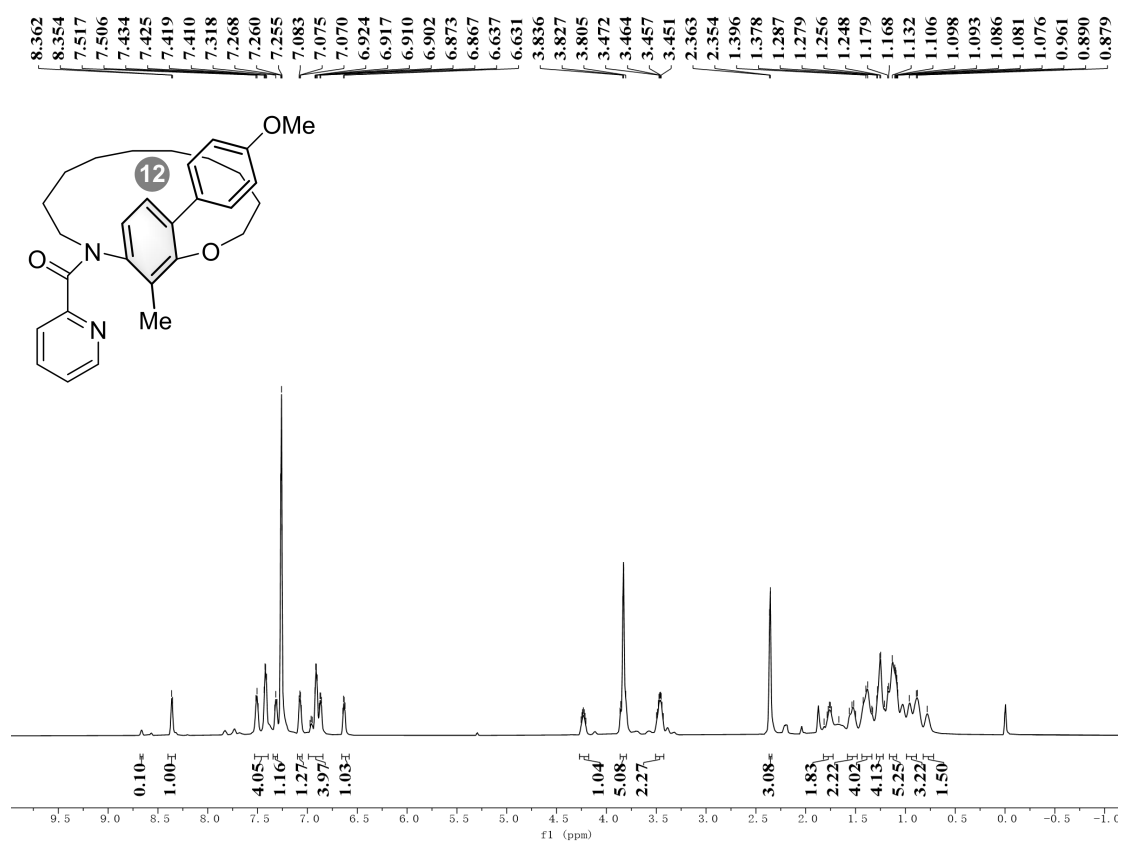
1m, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



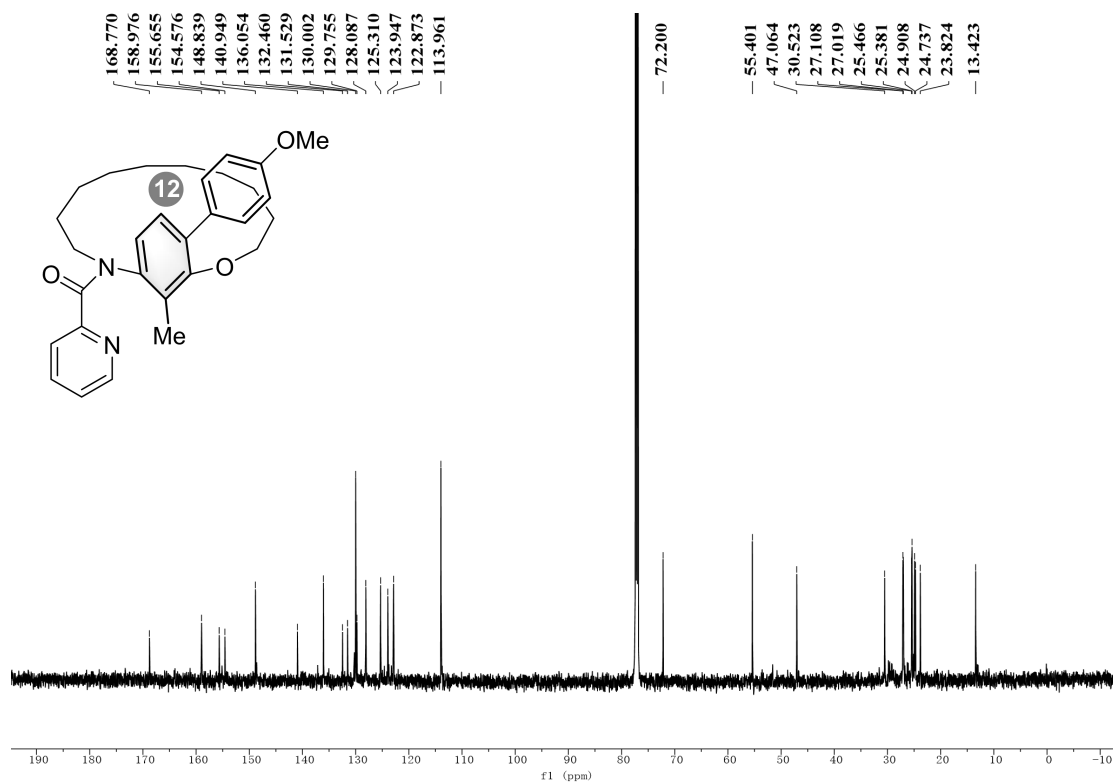
1m, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



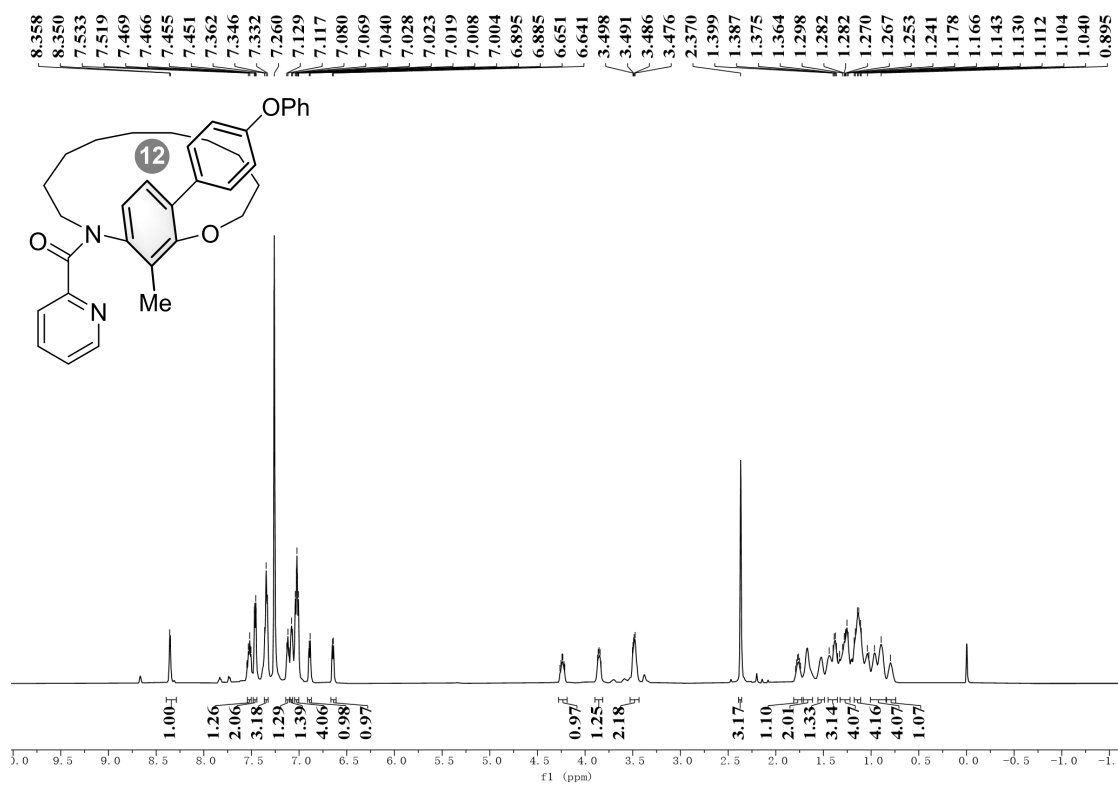
**1n**,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



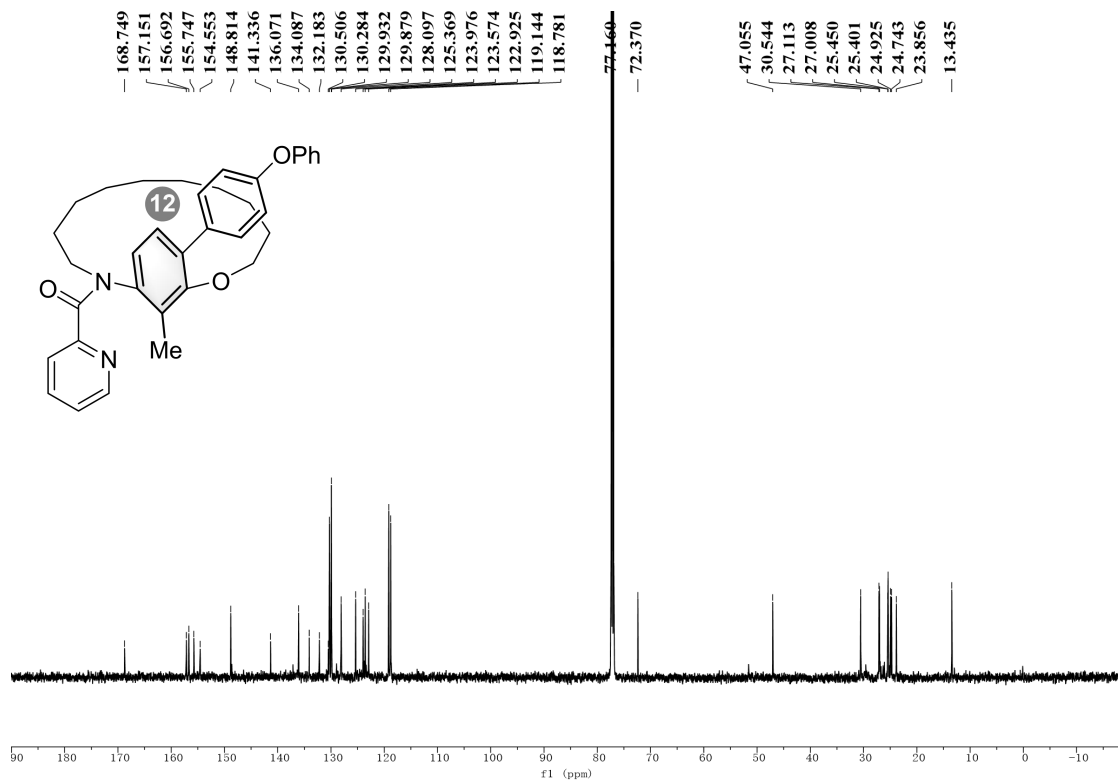
**1n**,  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )



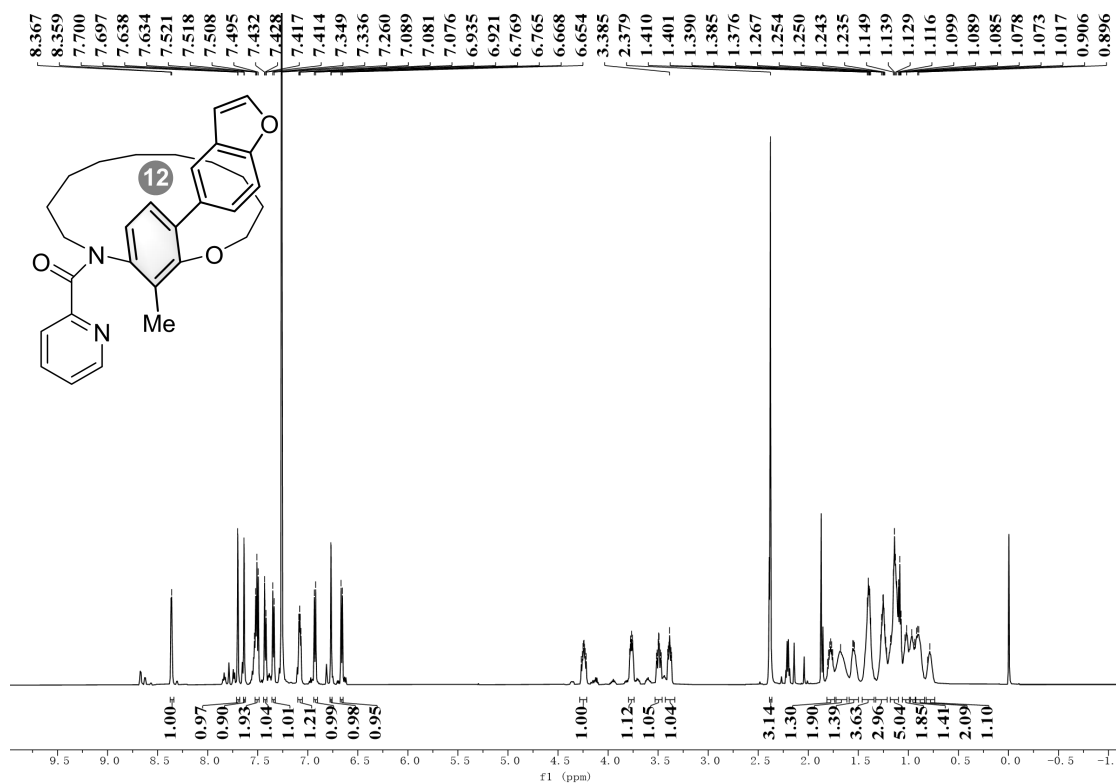
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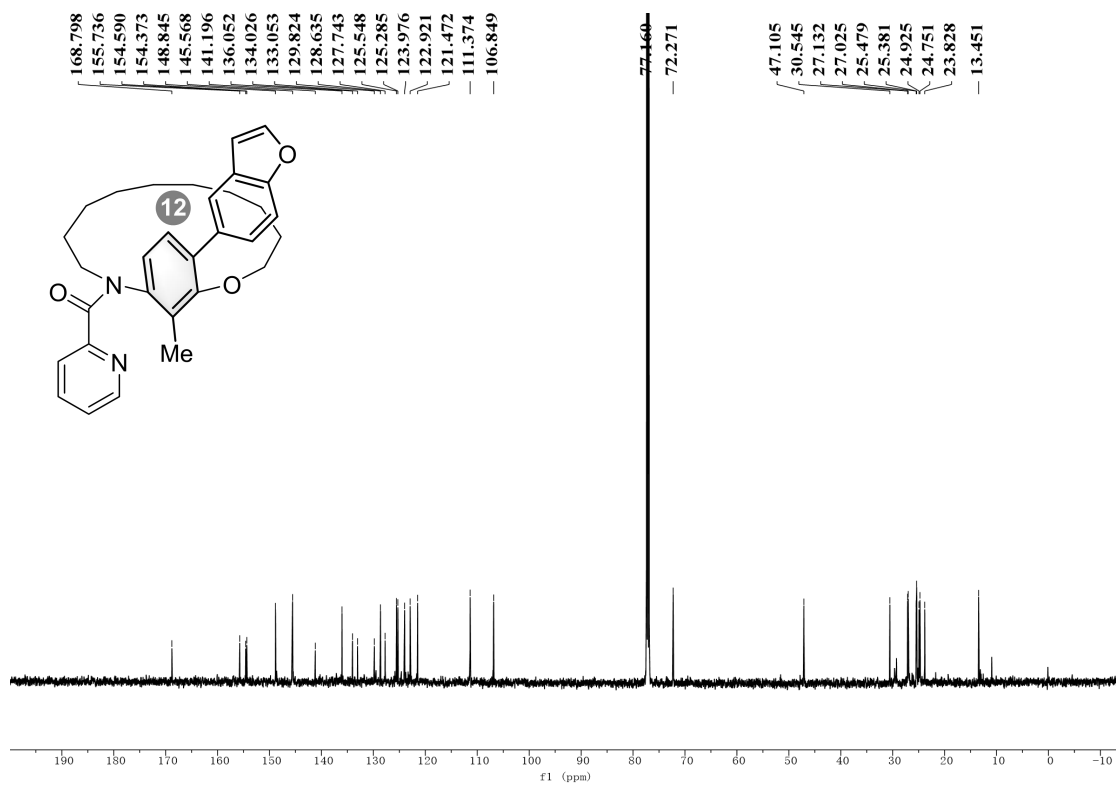
**10**,  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )



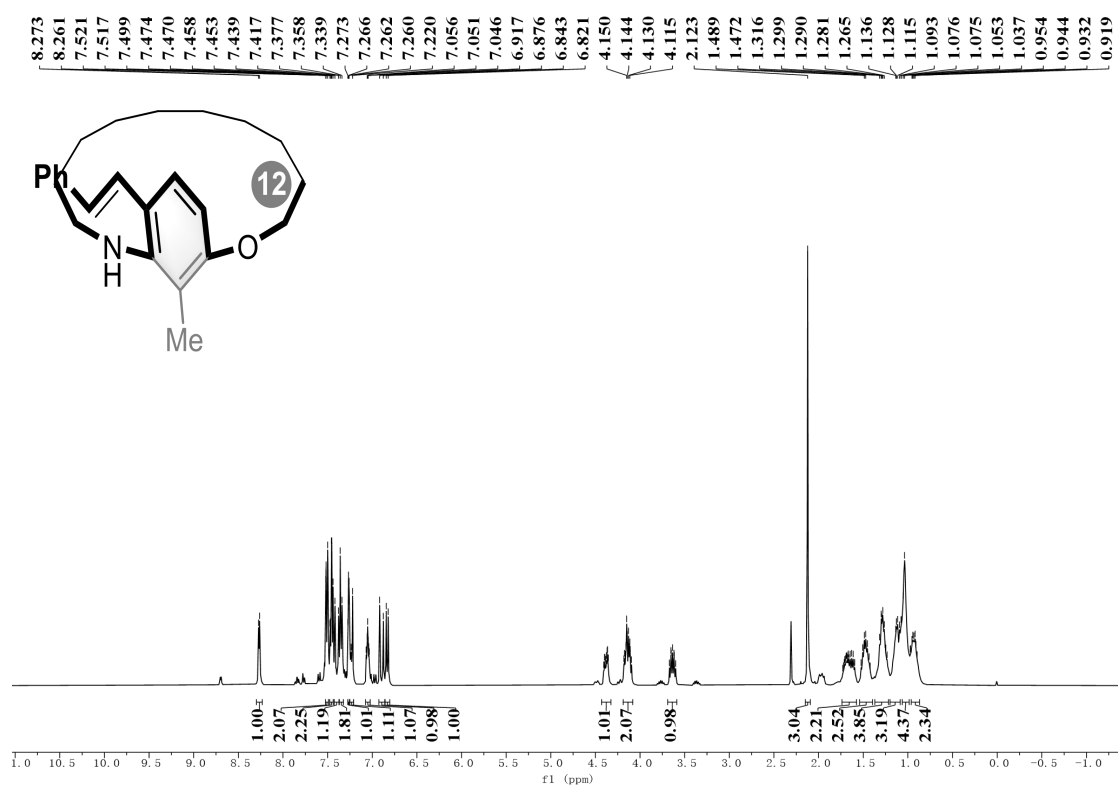
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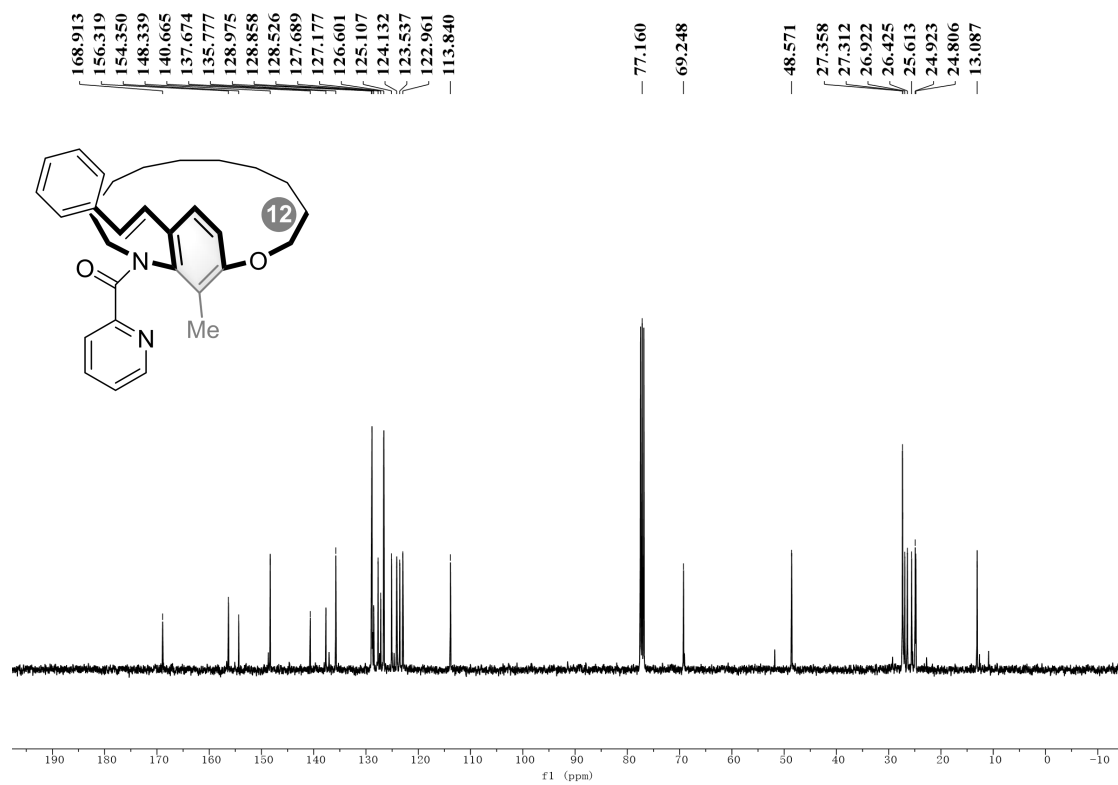
**1p**,  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )



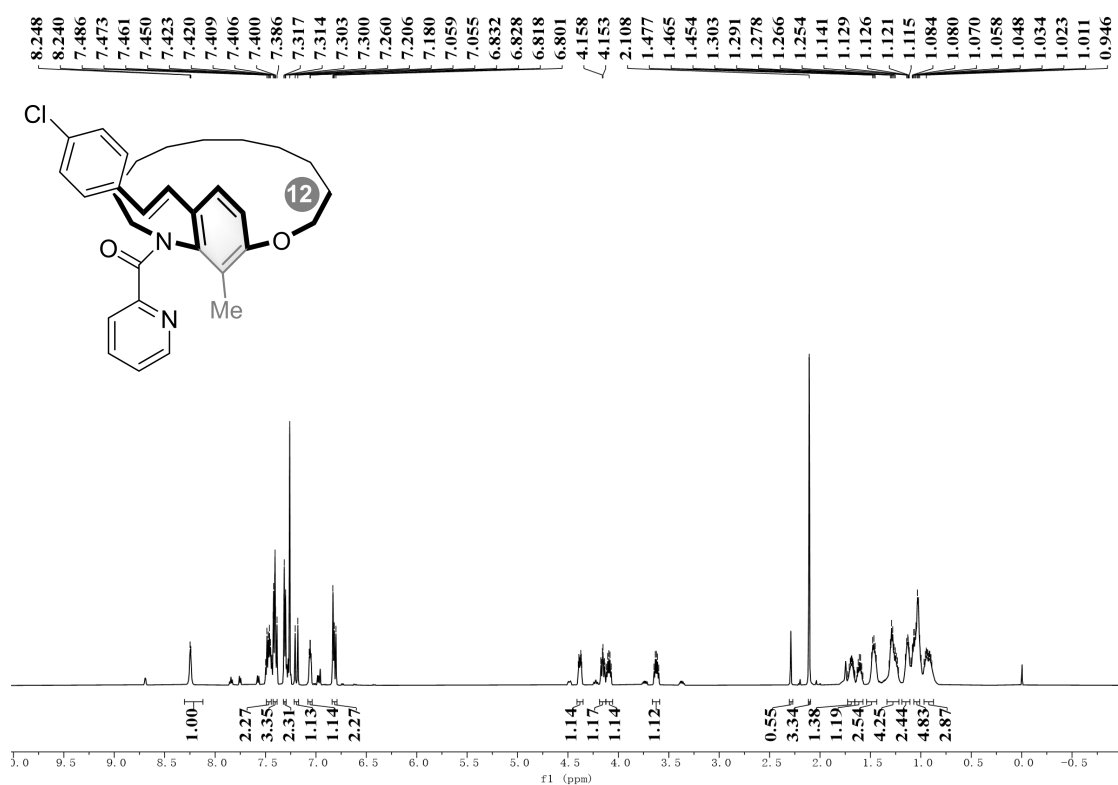
(*R*<sub>p</sub>)-3aa, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



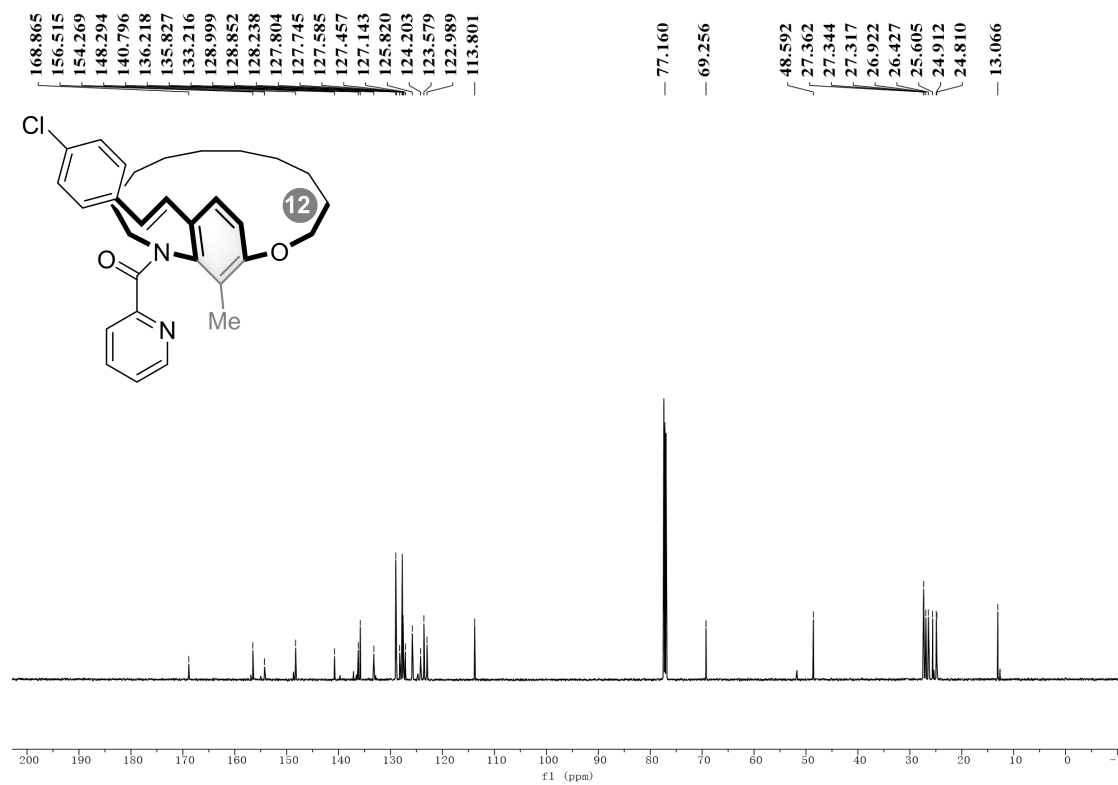
(*R*<sub>p</sub>)-3aa, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



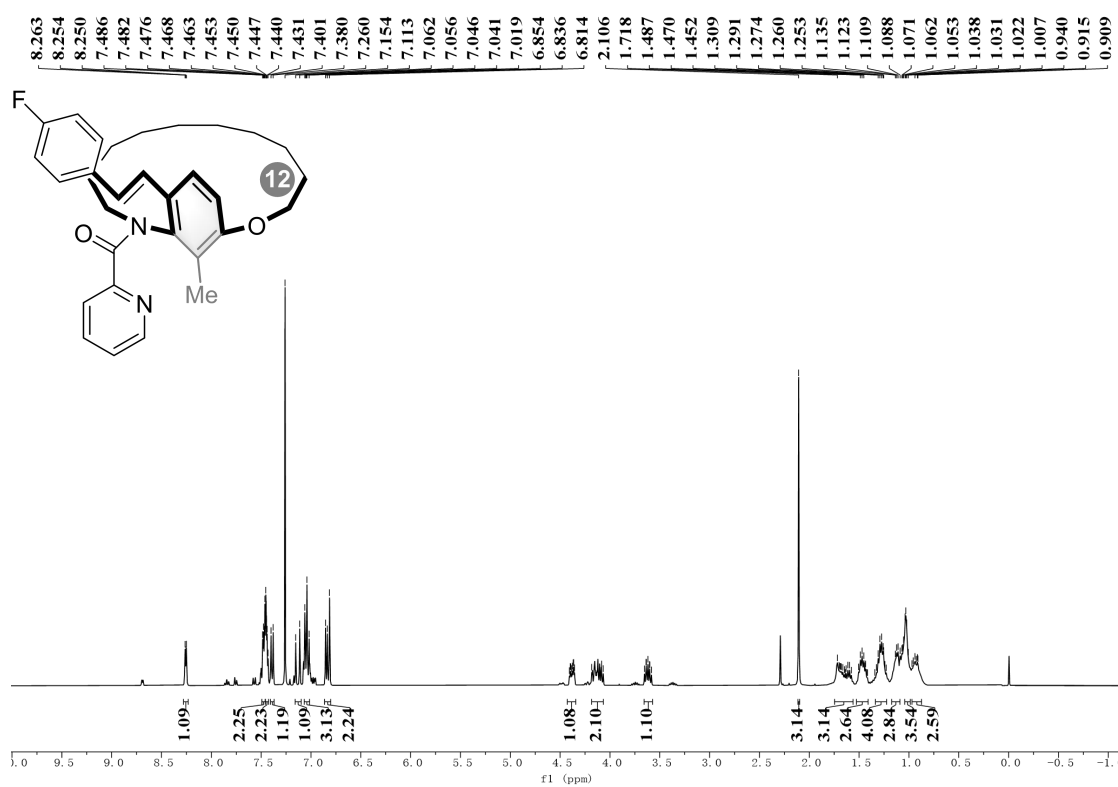
(*R*<sub>p</sub>)-3ab, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



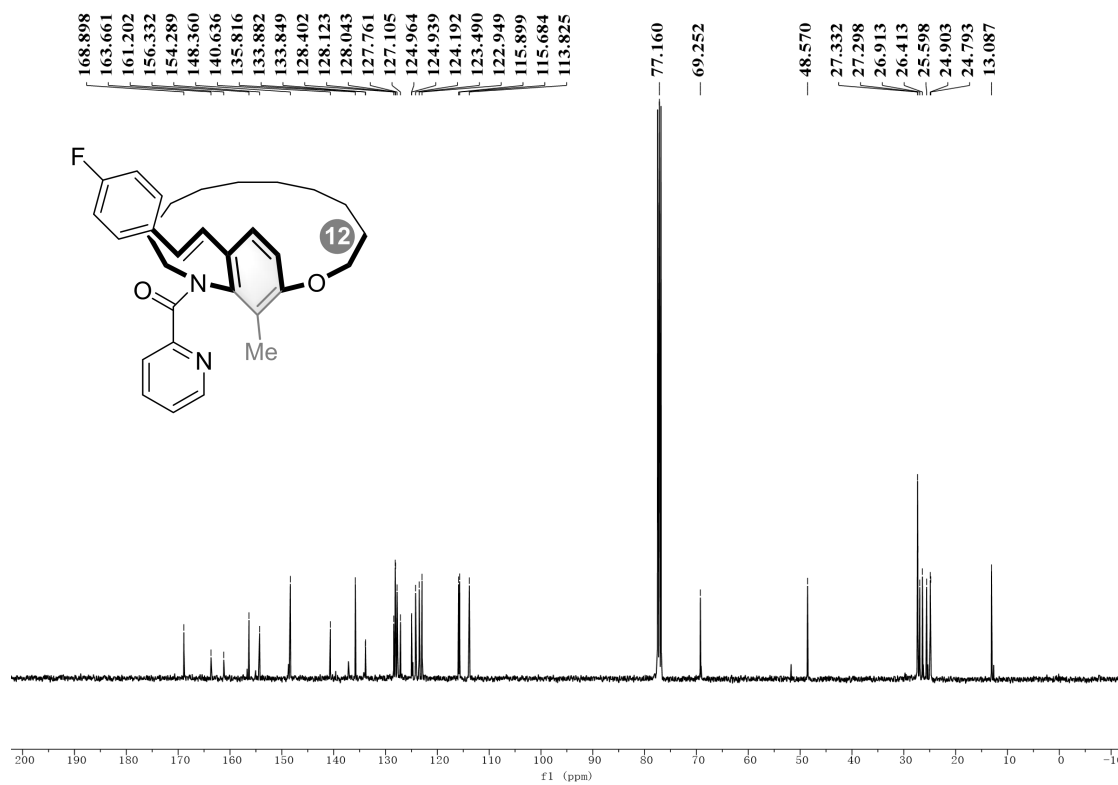
(*R*<sub>p</sub>)-3ab, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



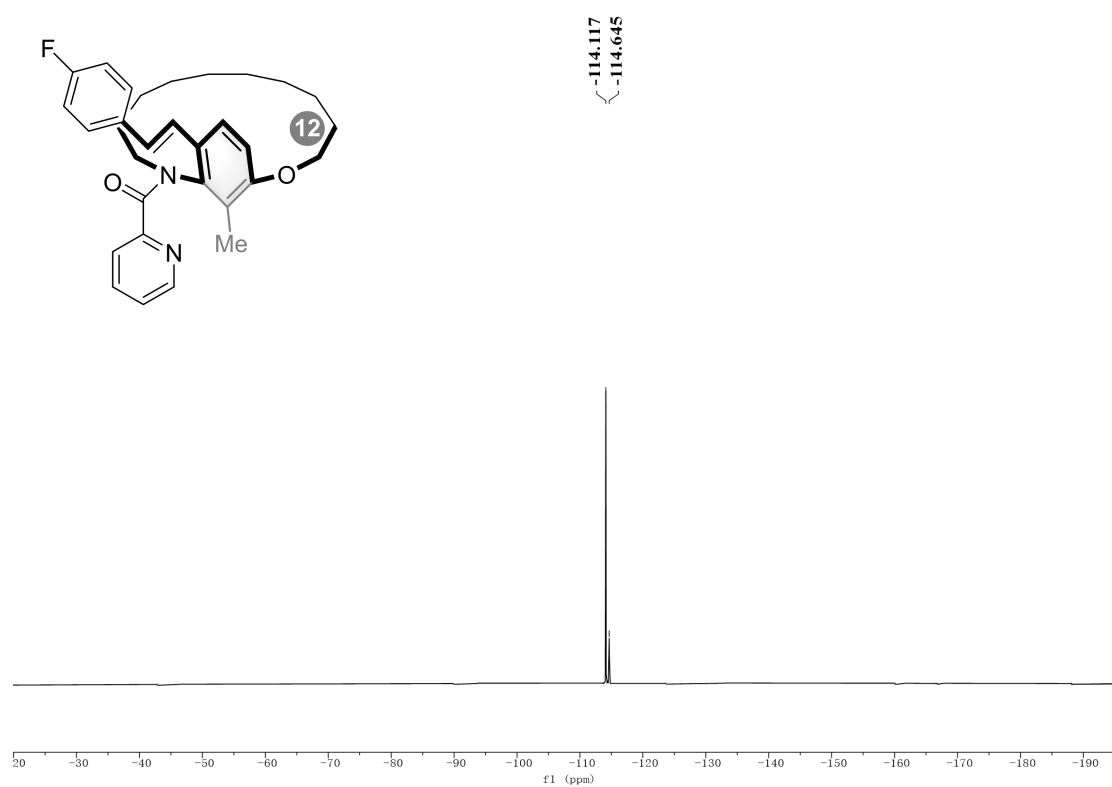
(*R*<sub>p</sub>)-3ac, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



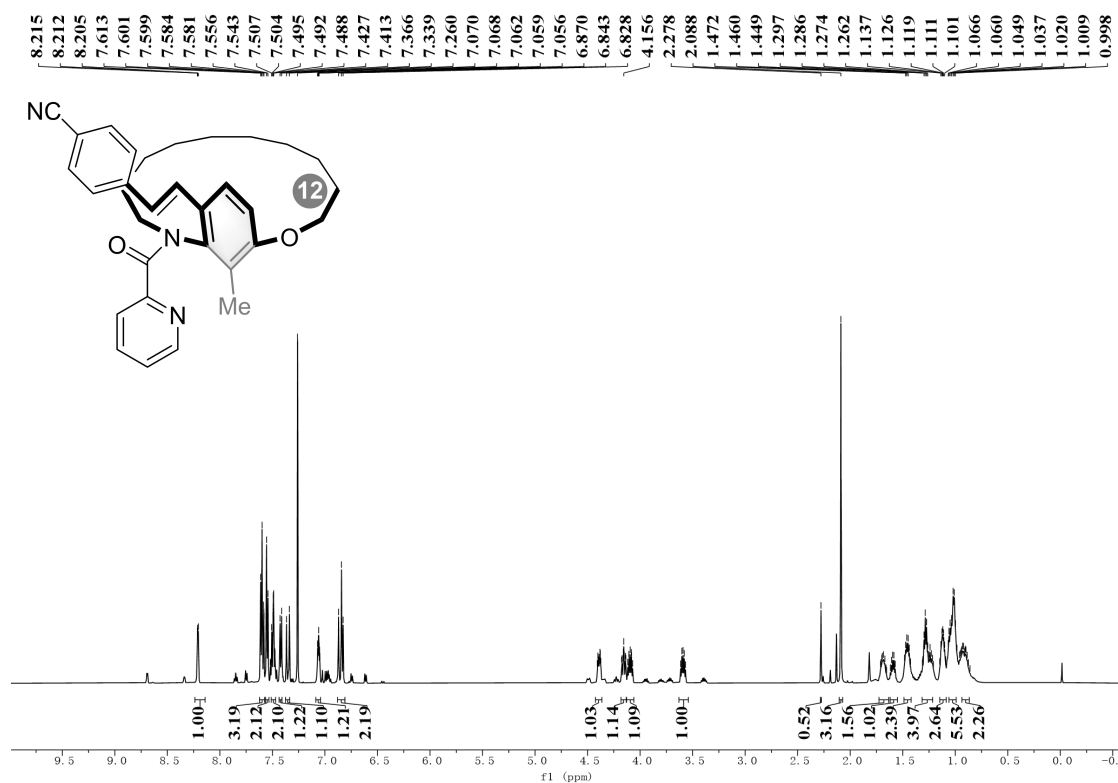
(*R*<sub>p</sub>)-3ac, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



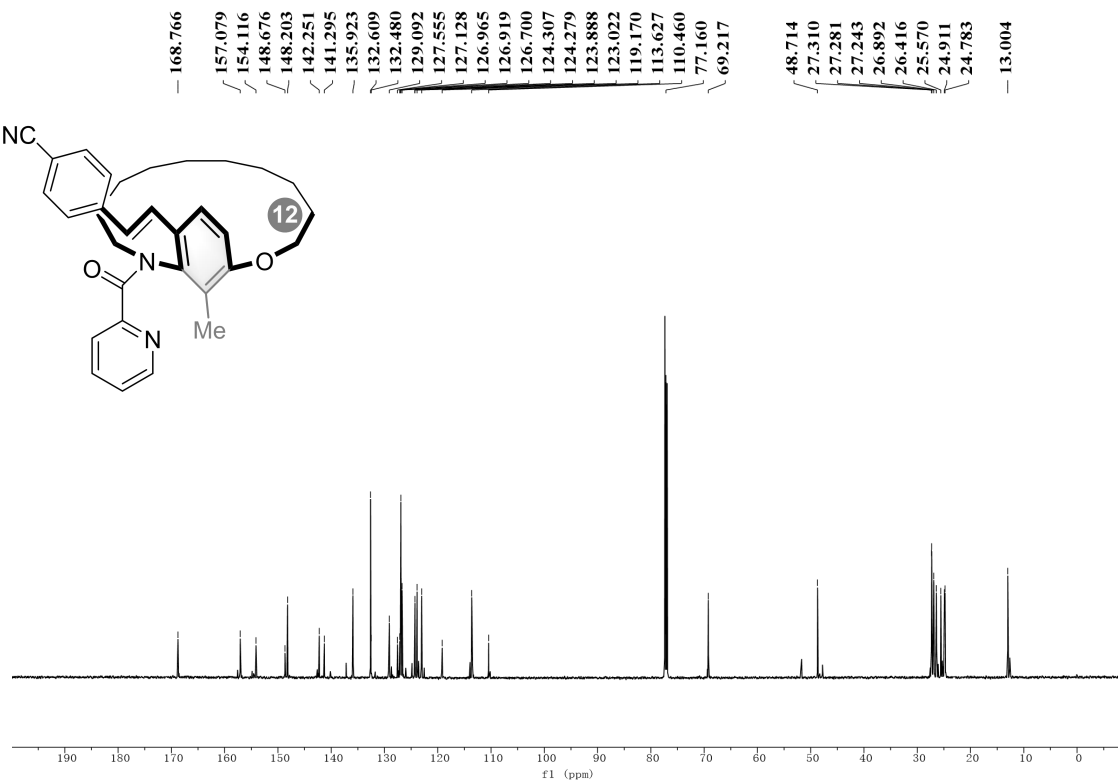
(*R<sub>p</sub>*)-3ac, <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



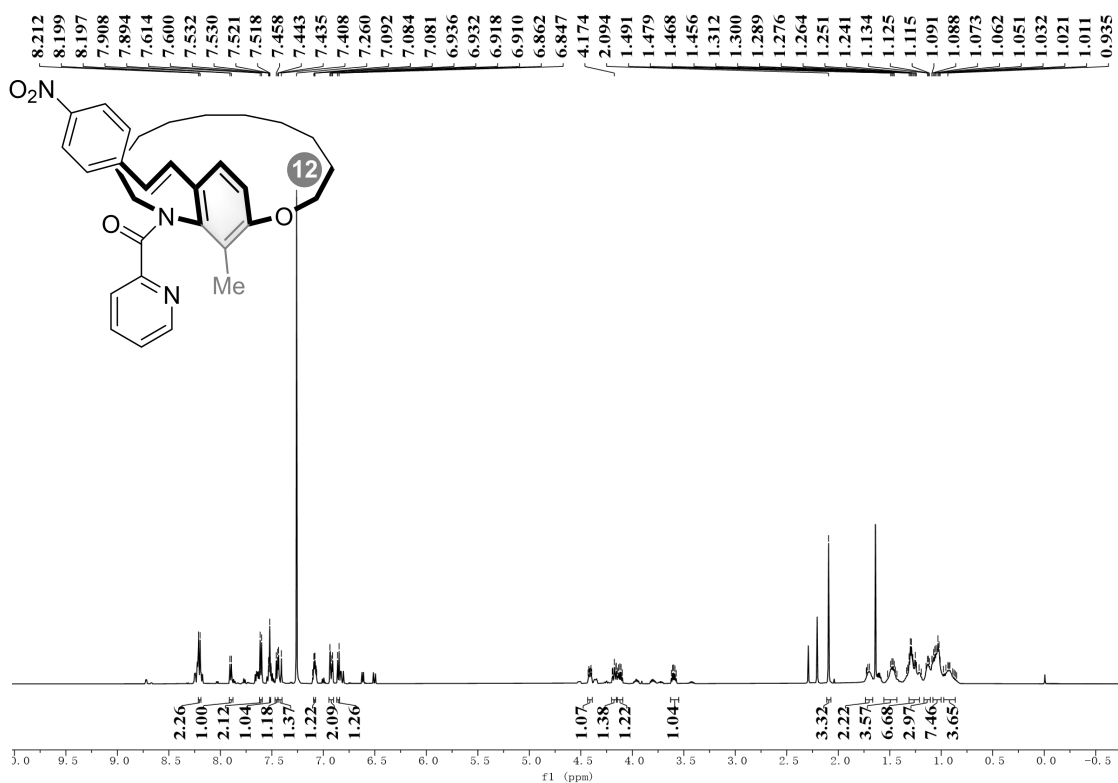
(*R*<sub>p</sub>)-3ad, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



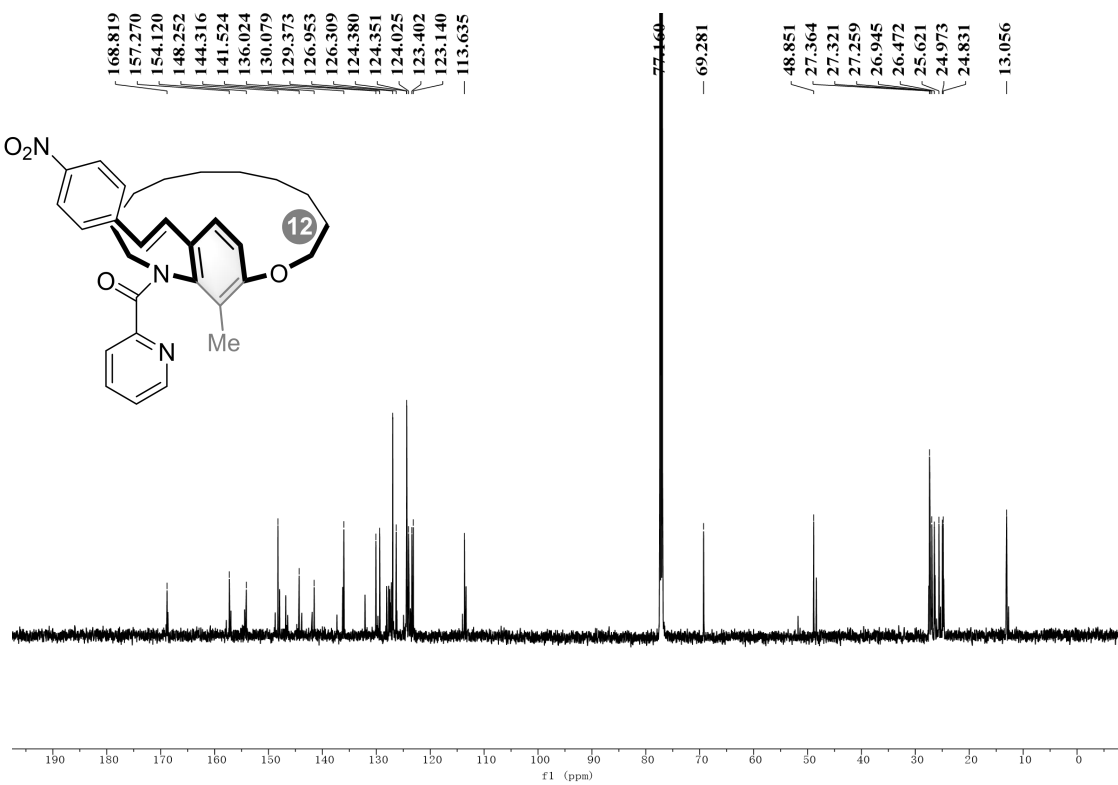
(*R*<sub>p</sub>)-3ad, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



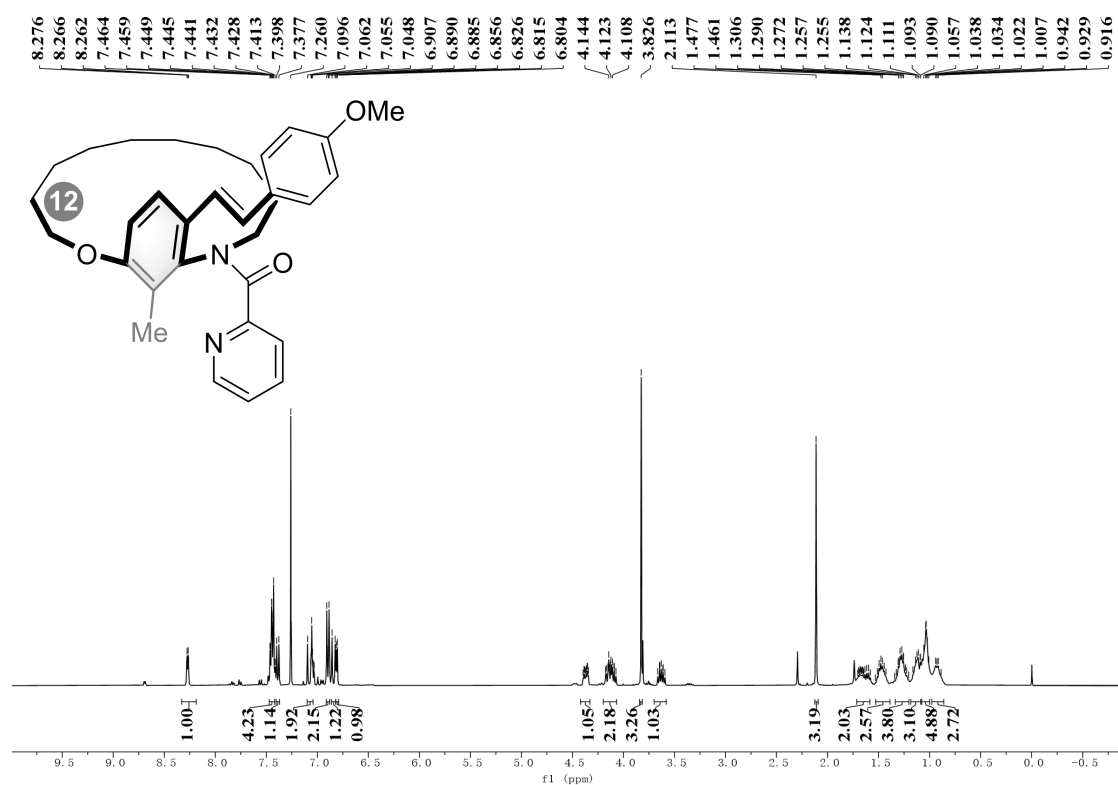
(*R*<sub>p</sub>)-3ae, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



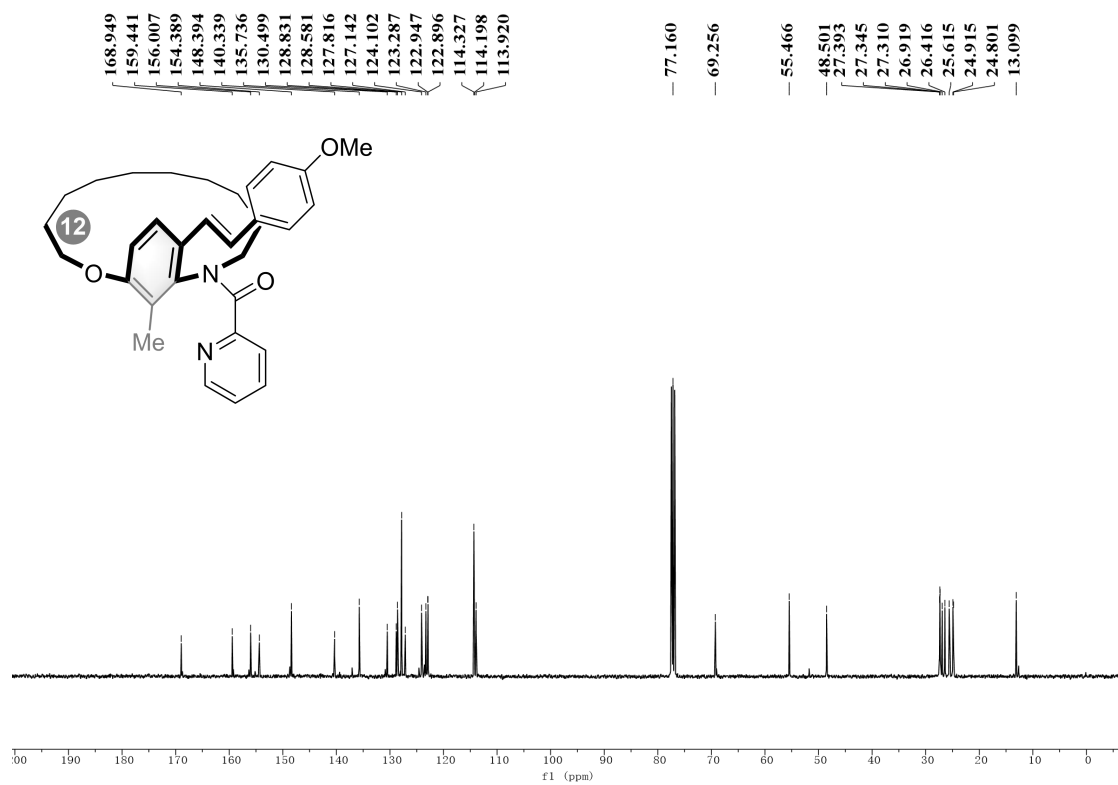
(*R*<sub>p</sub>)-3ae, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



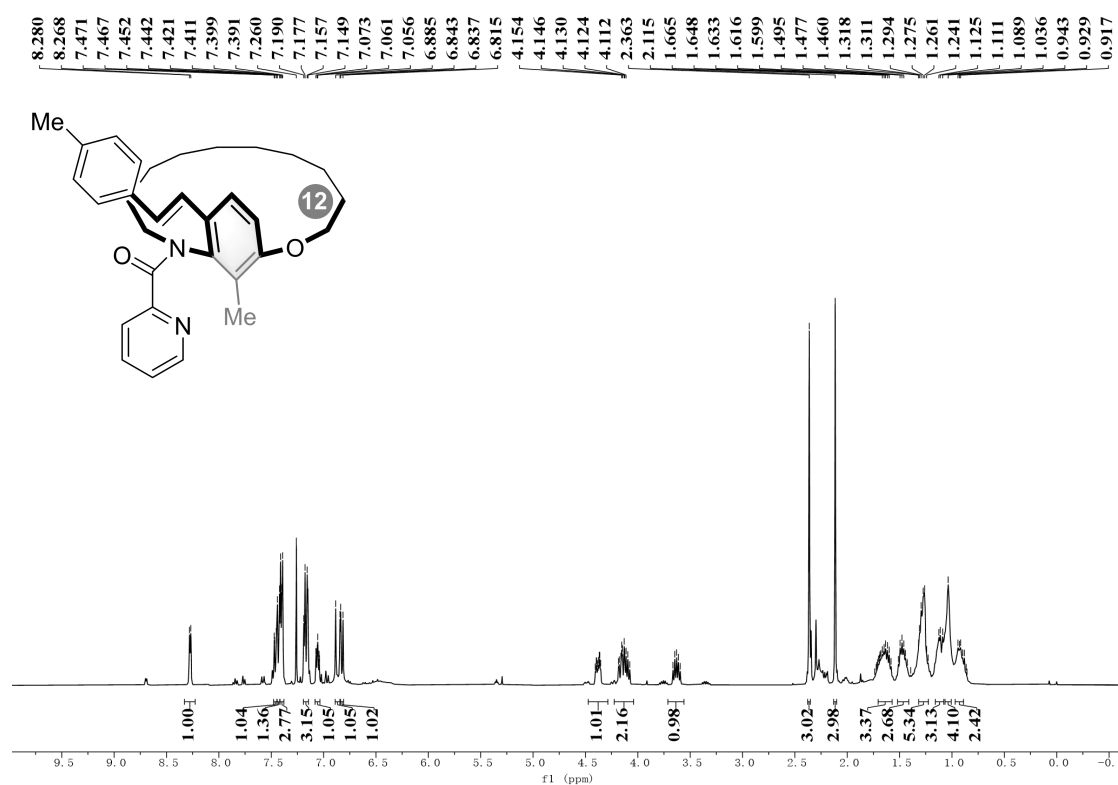
(*R*<sub>p</sub>)-3af, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



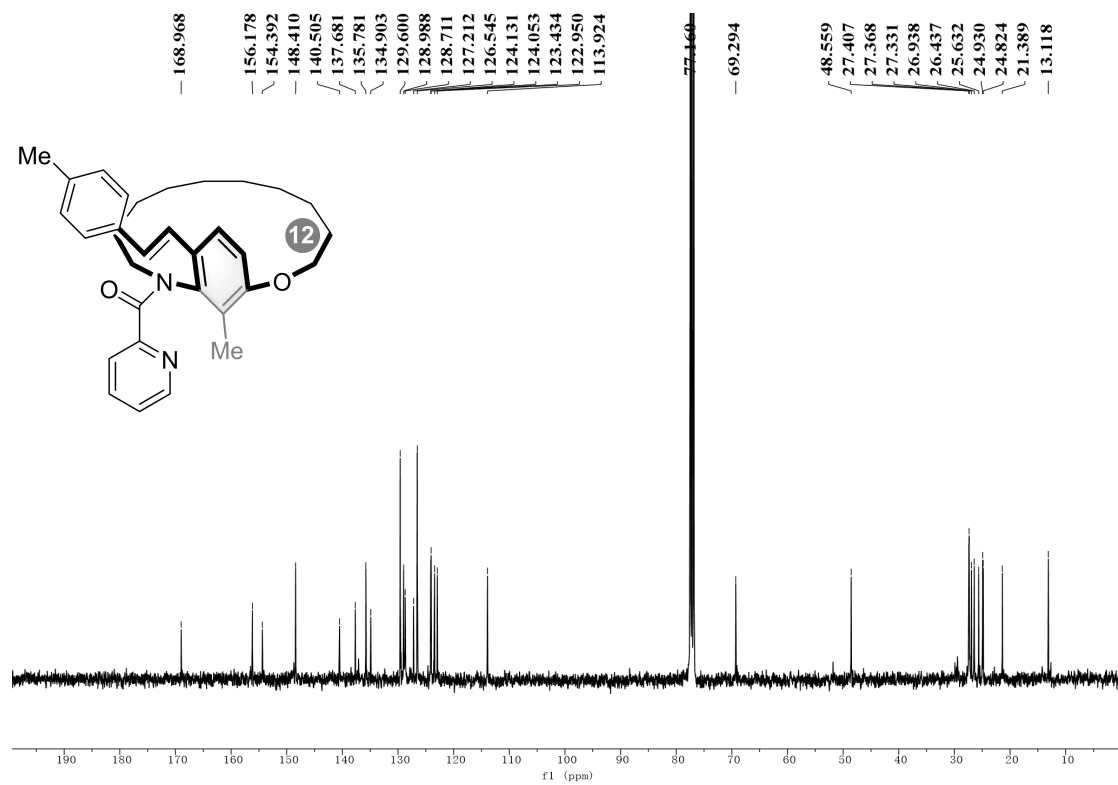
(*R*<sub>p</sub>)-3af, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



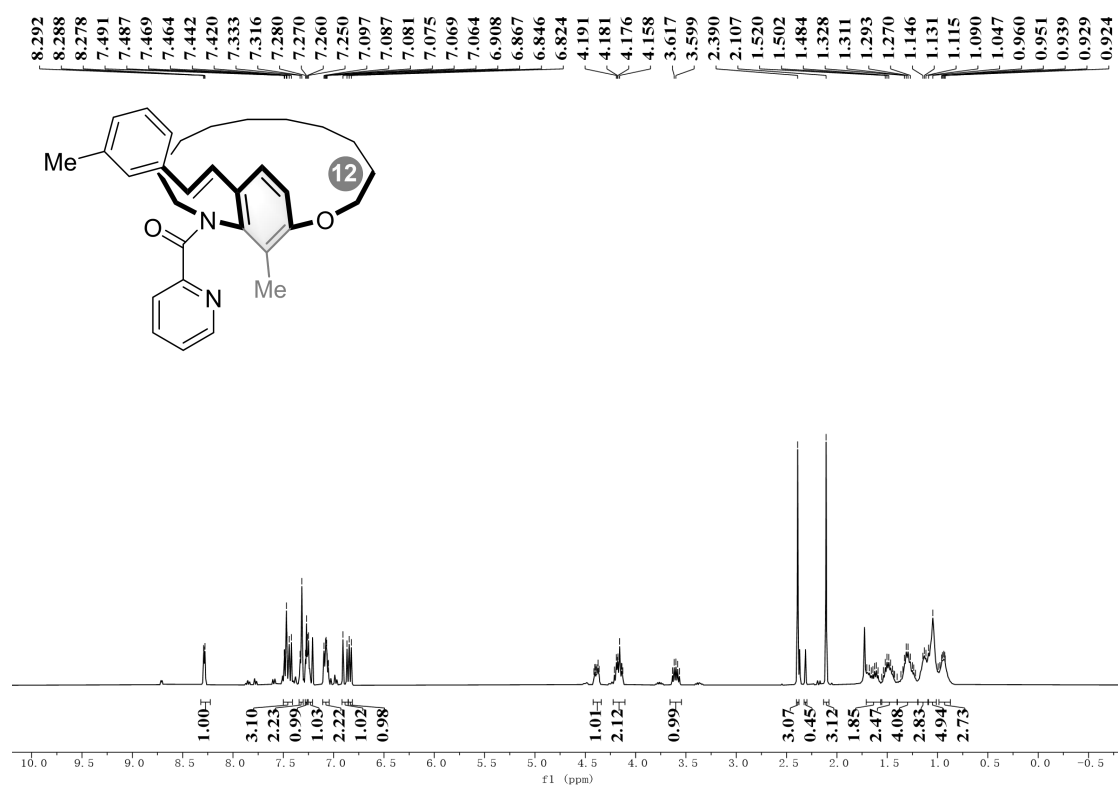
(*R*<sub>p</sub>)-3ag, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



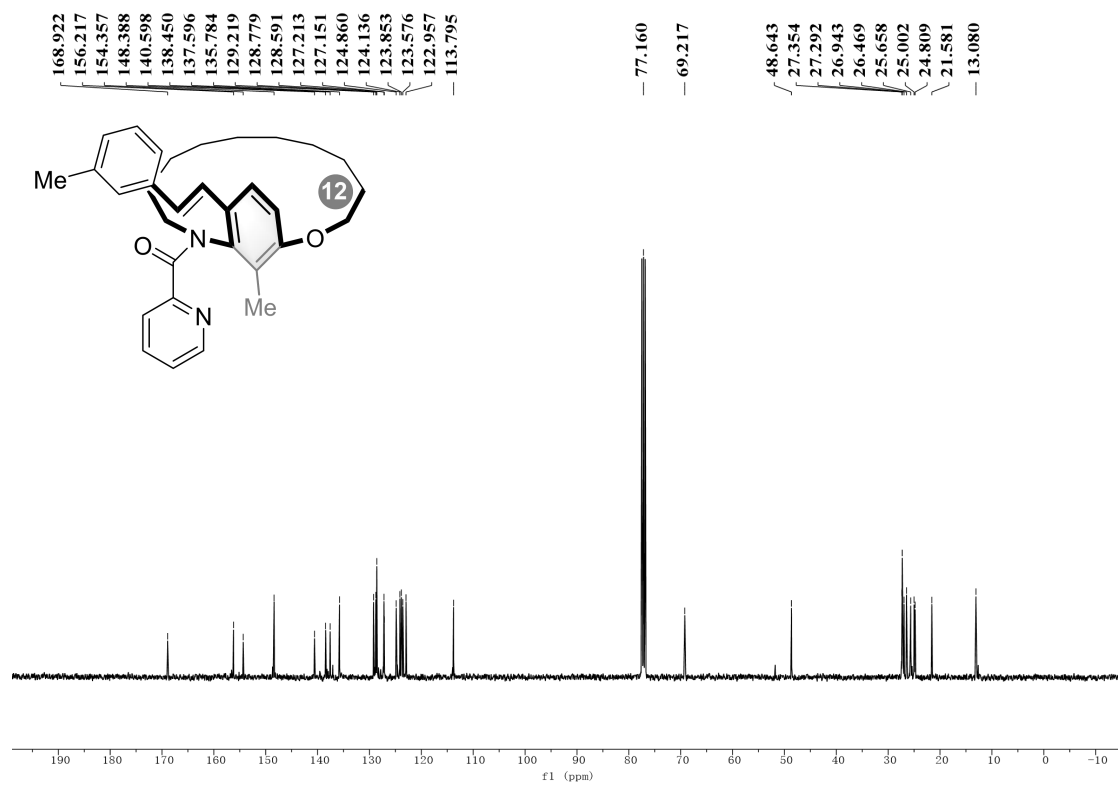
(*R*<sub>p</sub>)-3ag, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



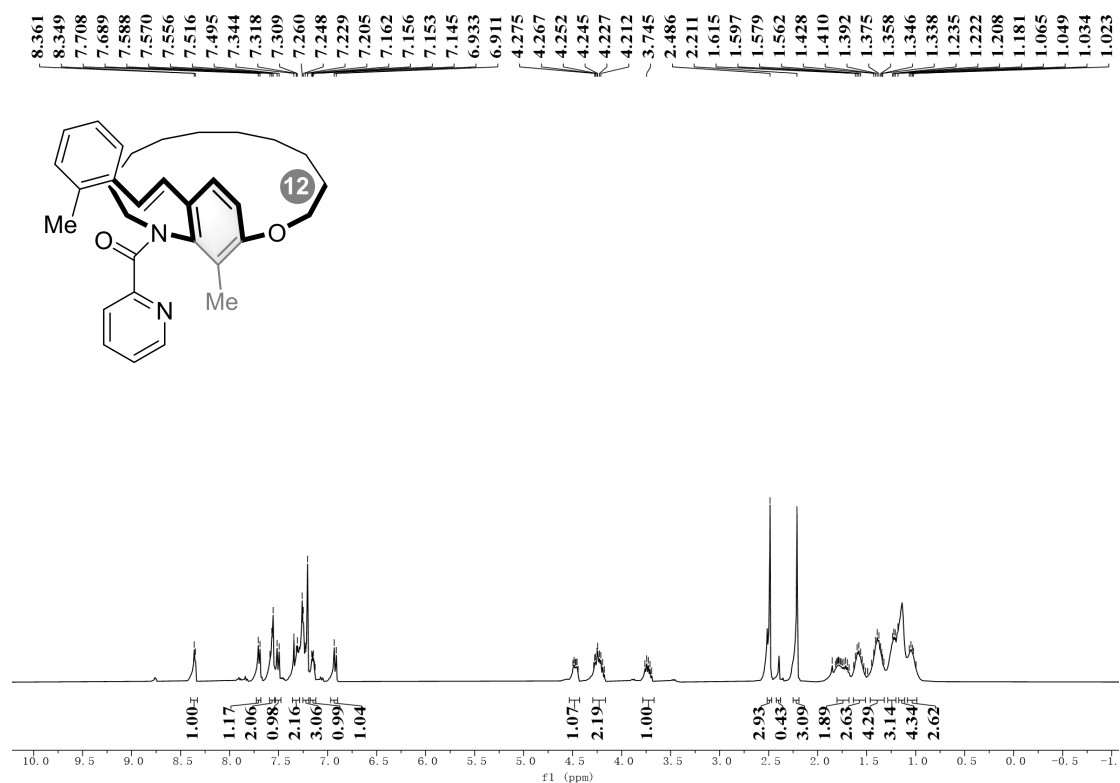
(*R*<sub>p</sub>)-3ah, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



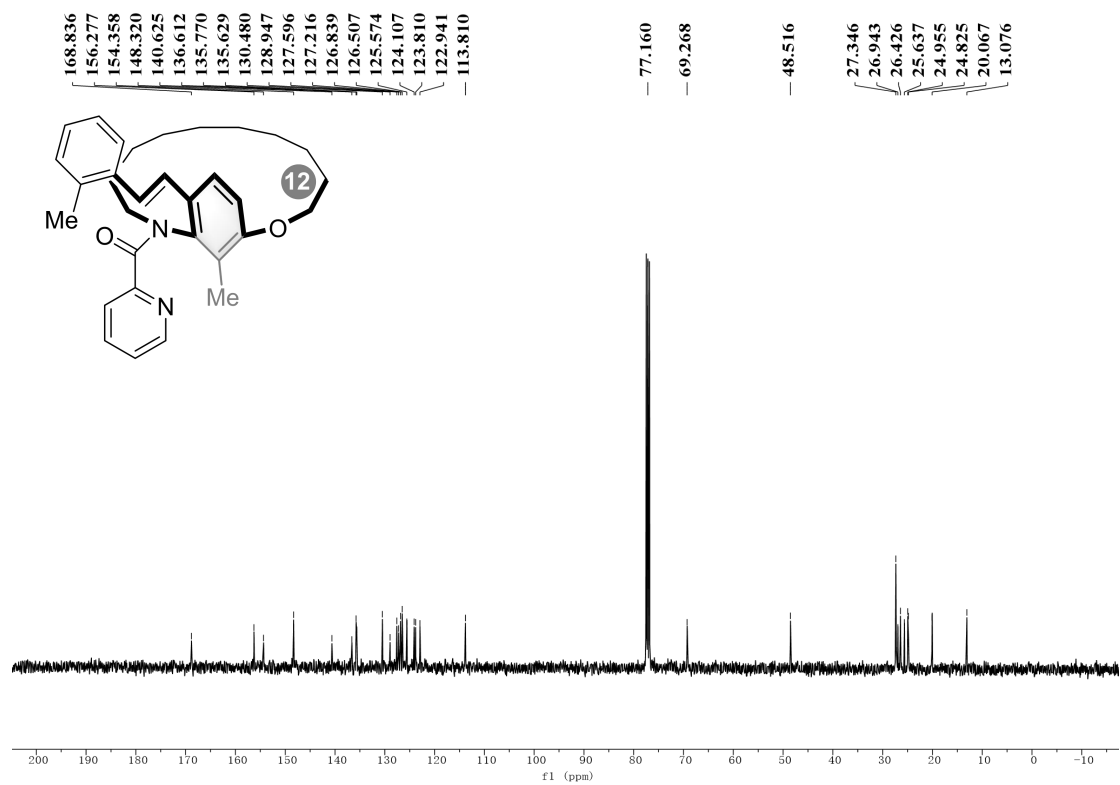
(*R*<sub>p</sub>)-3ah, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



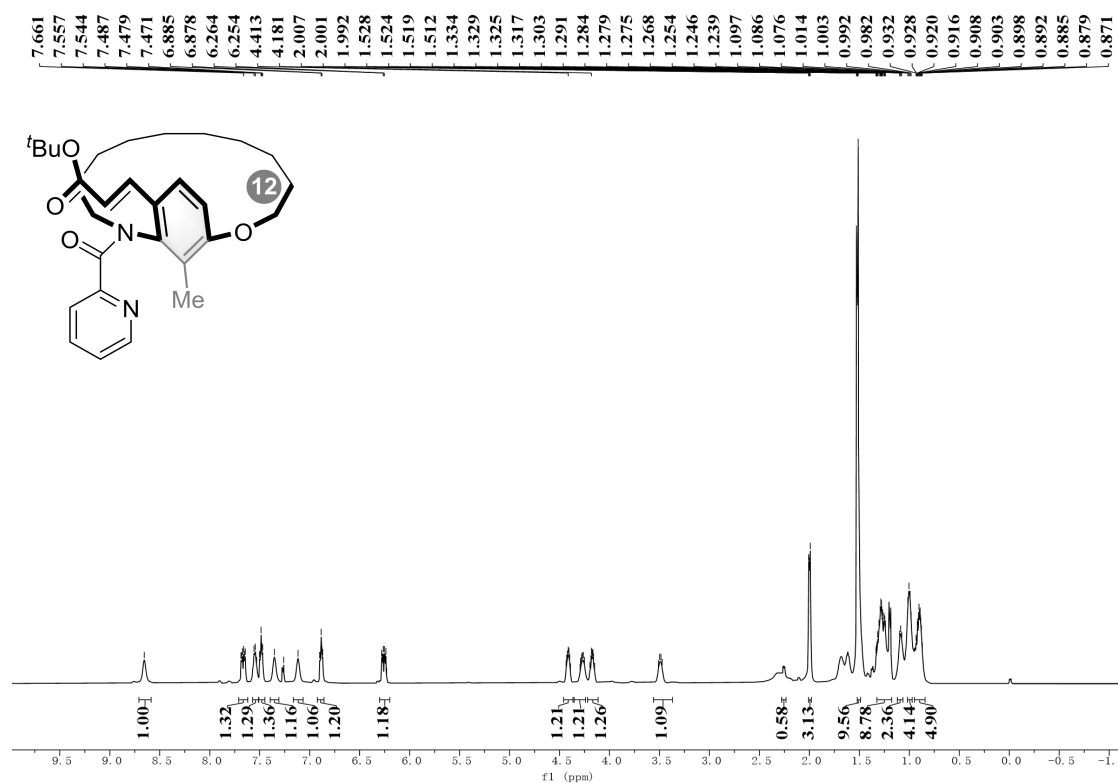
(*R<sub>p</sub>*)-3ai, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



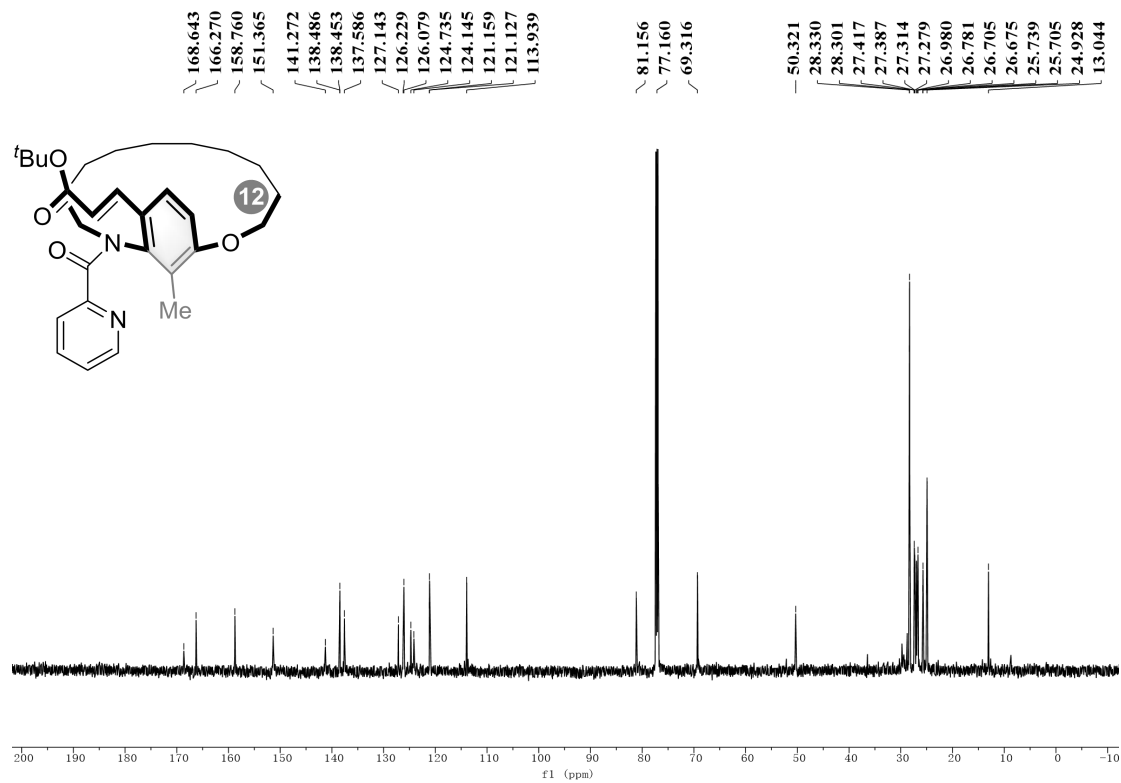
(*R<sub>p</sub>*)-3ai, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



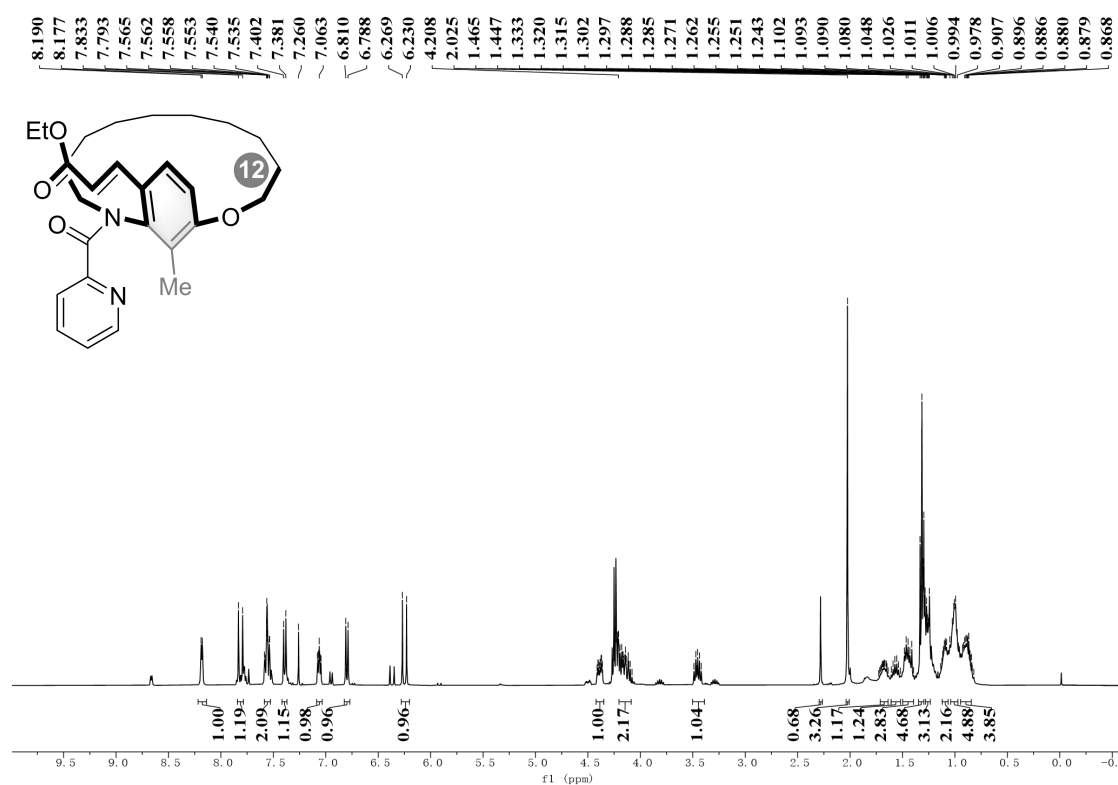
(*R*<sub>p</sub>)-3aj, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



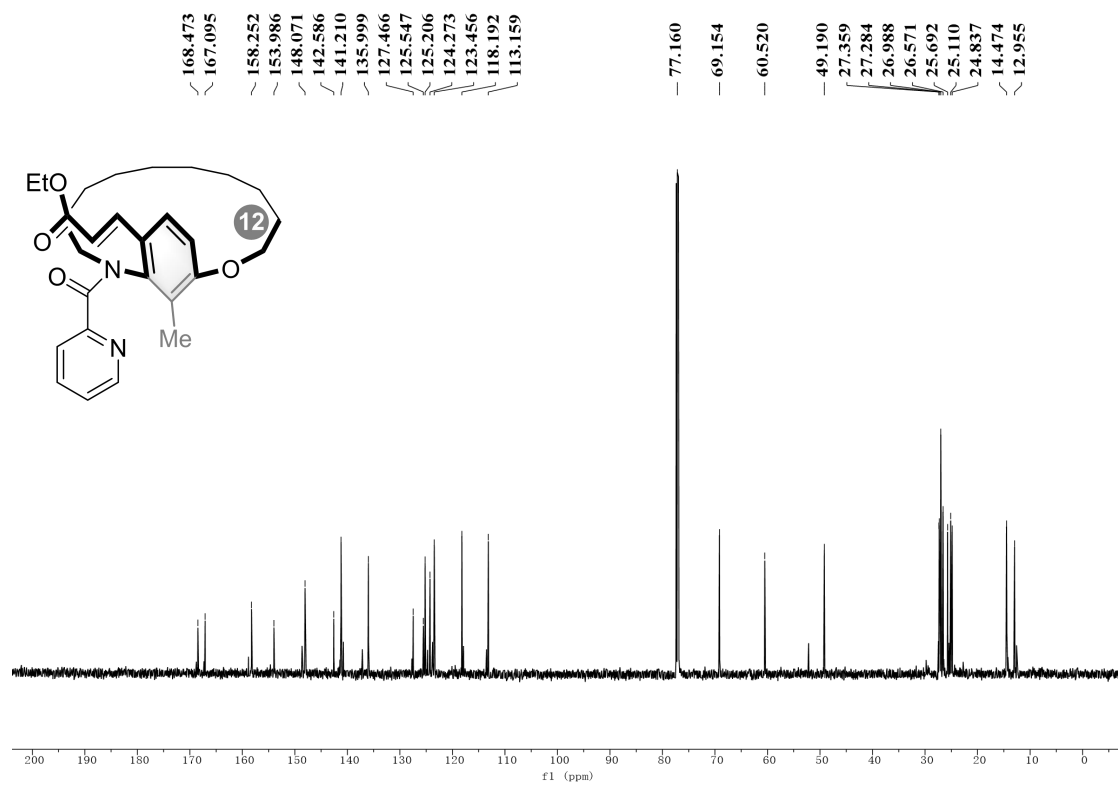
(*R*<sub>p</sub>)-3aj, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



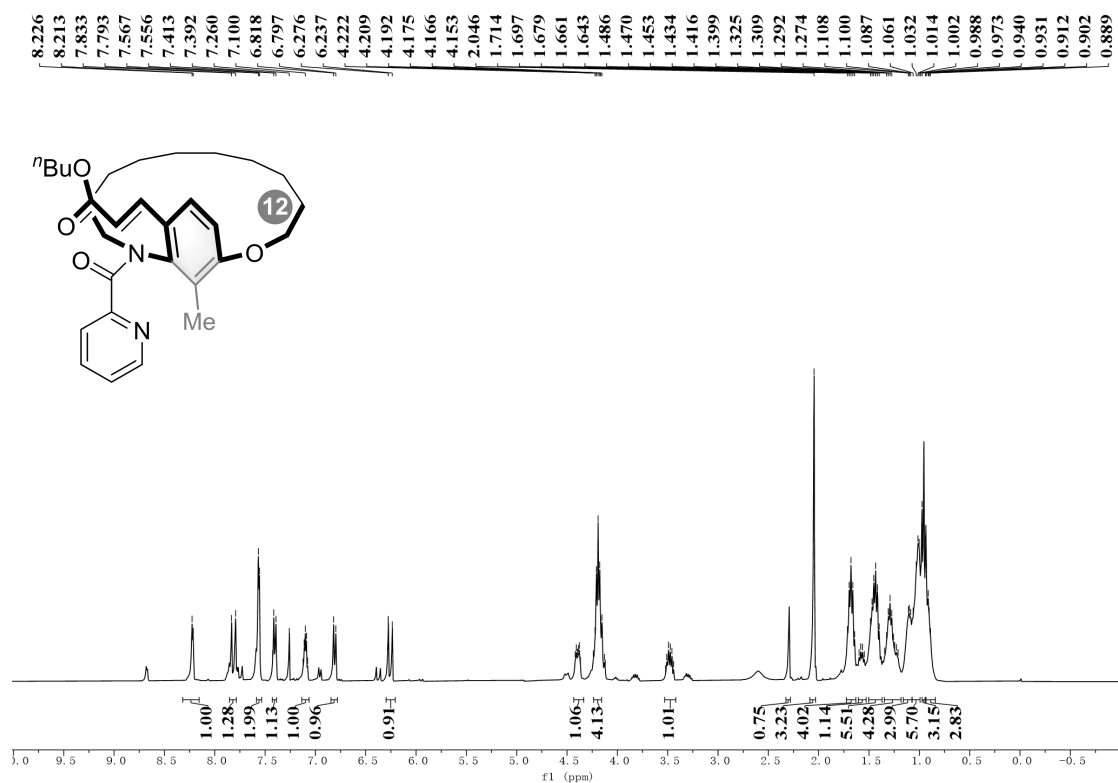
(*R*<sub>p</sub>)-3ak, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



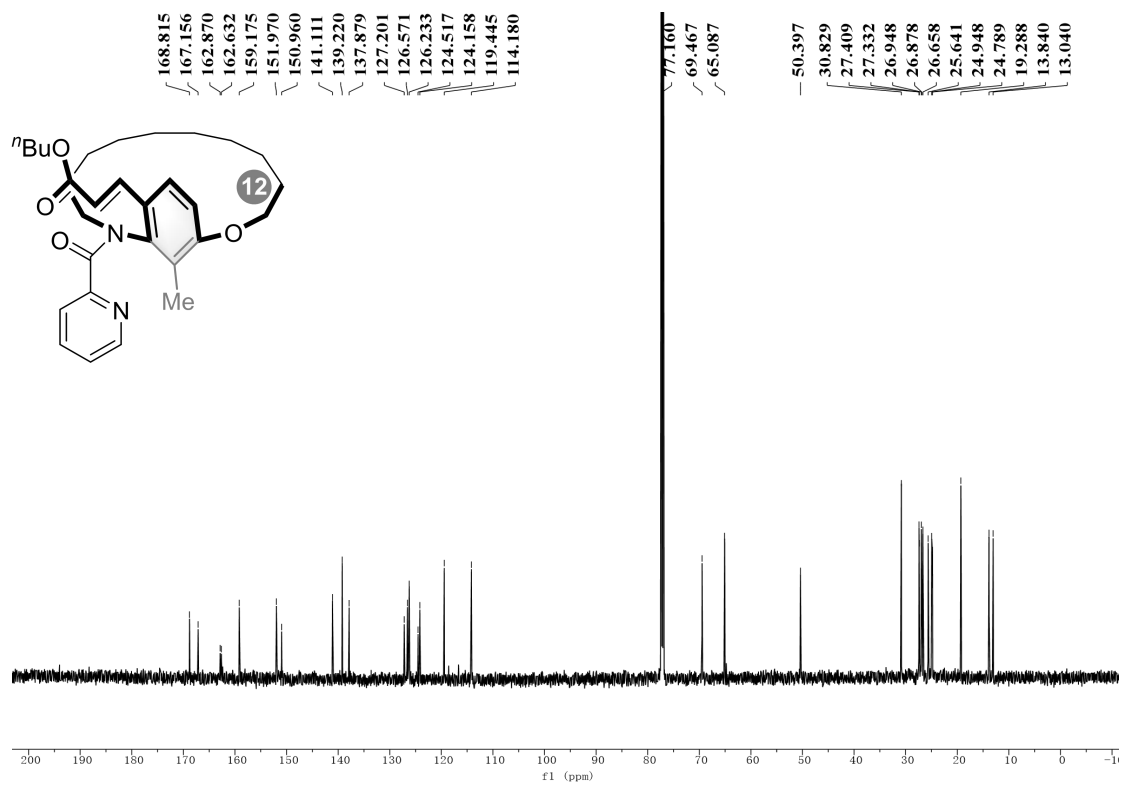
(*R*<sub>p</sub>)-3ak, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



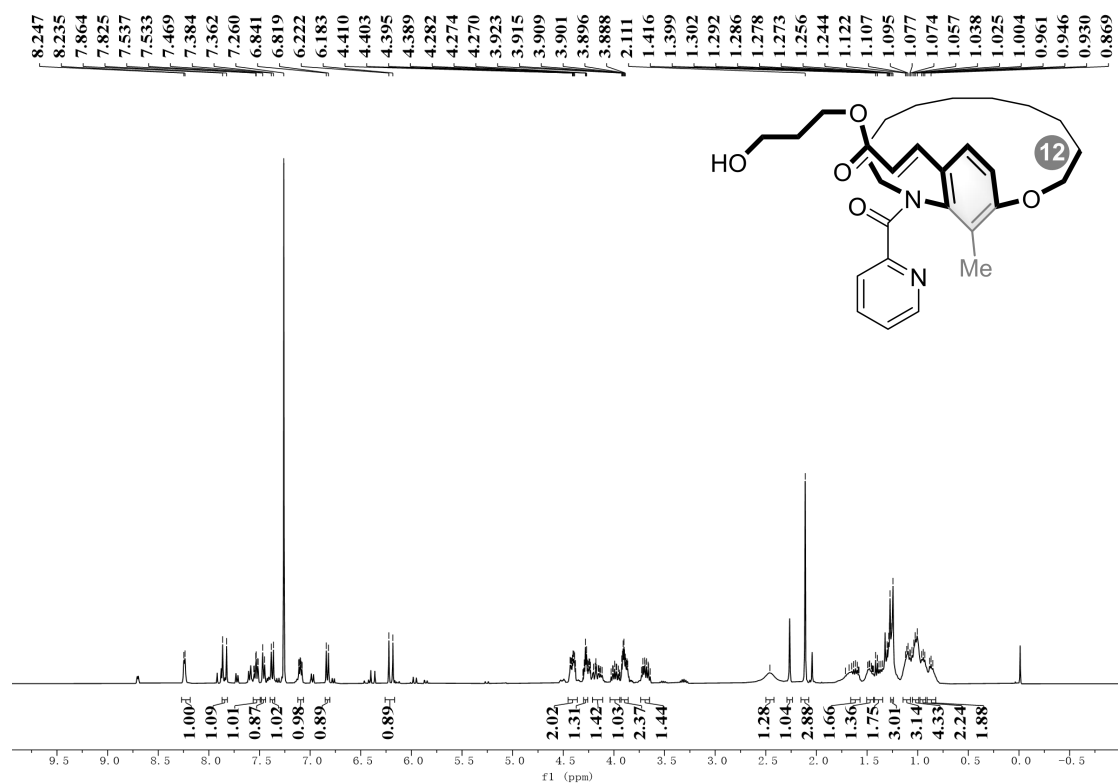
(*R<sub>p</sub>*)-3aI, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



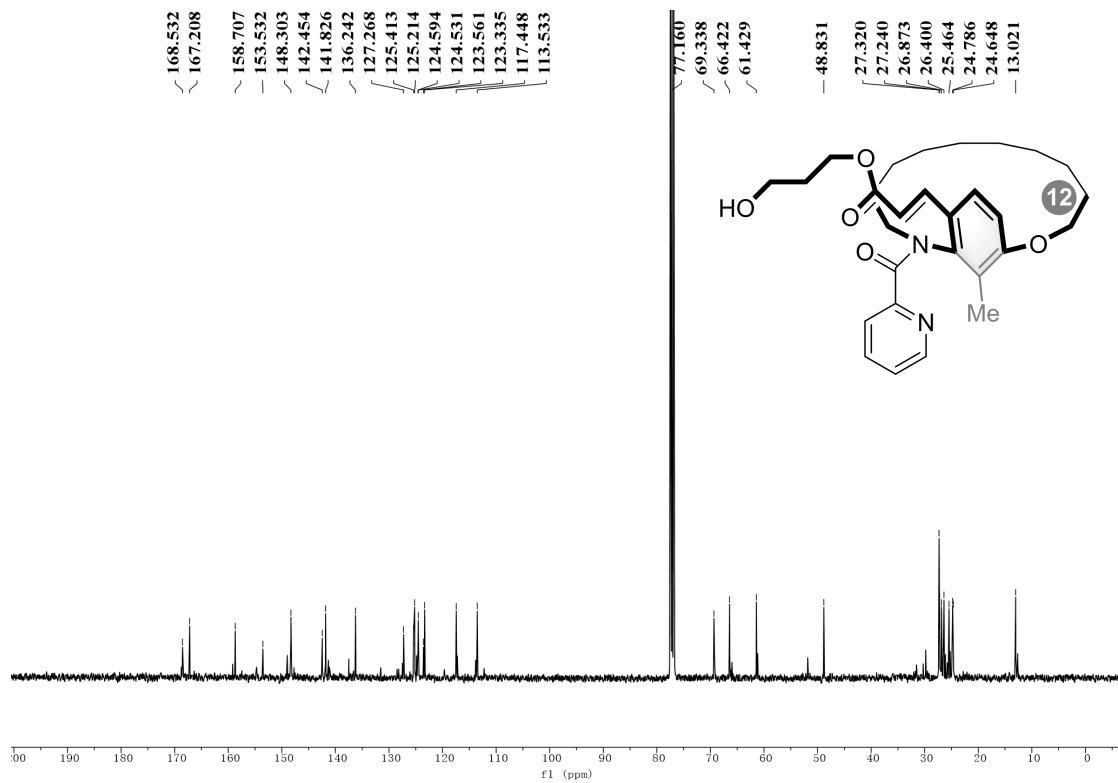
(*R<sub>p</sub>*)-3aI, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



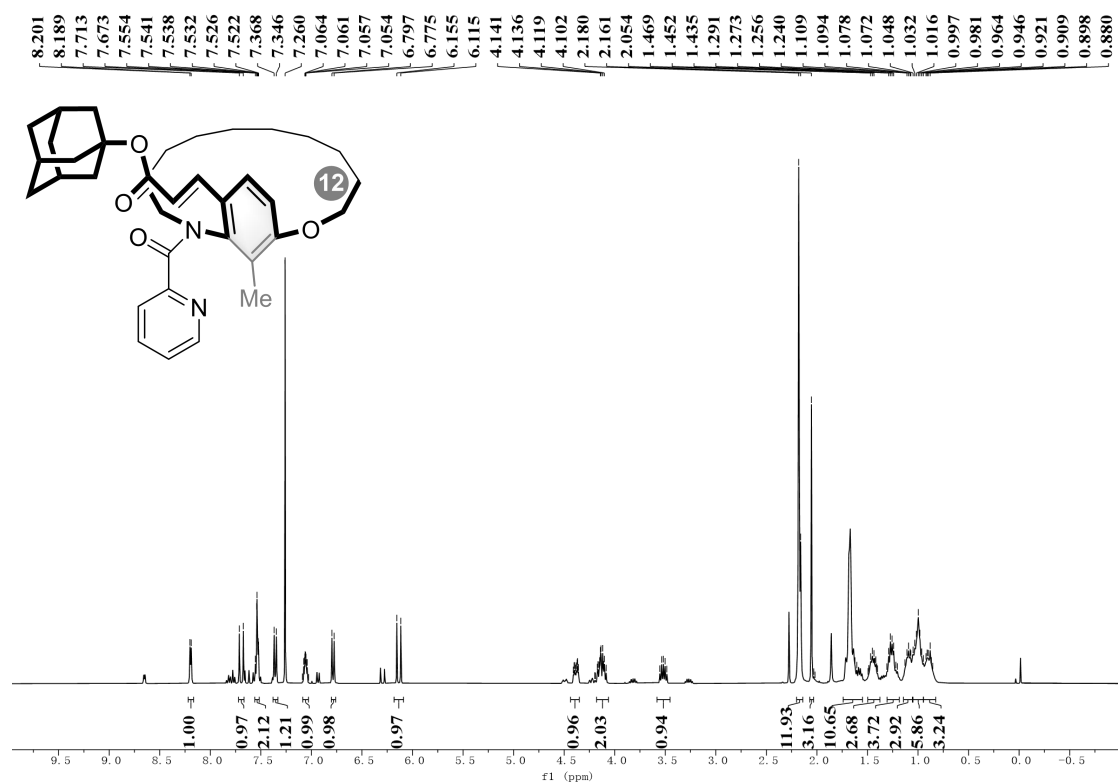
(*R<sub>p</sub>*)-3am, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



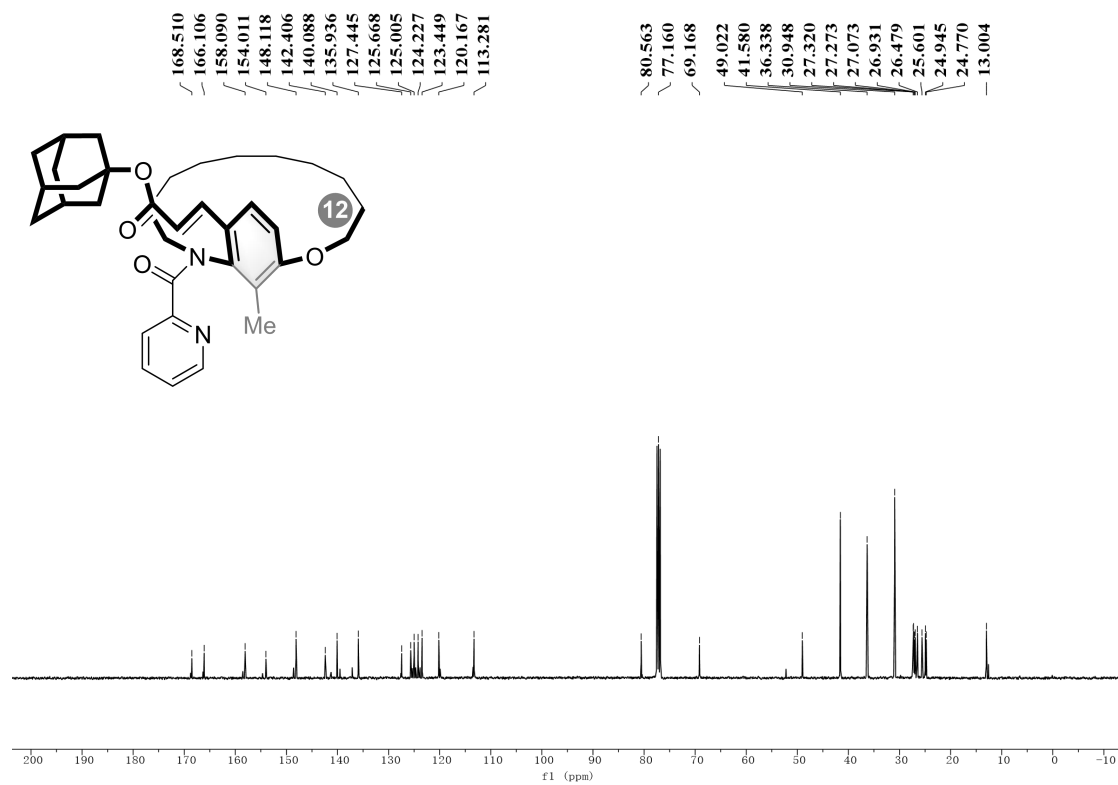
(*R<sub>p</sub>*)-3am, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



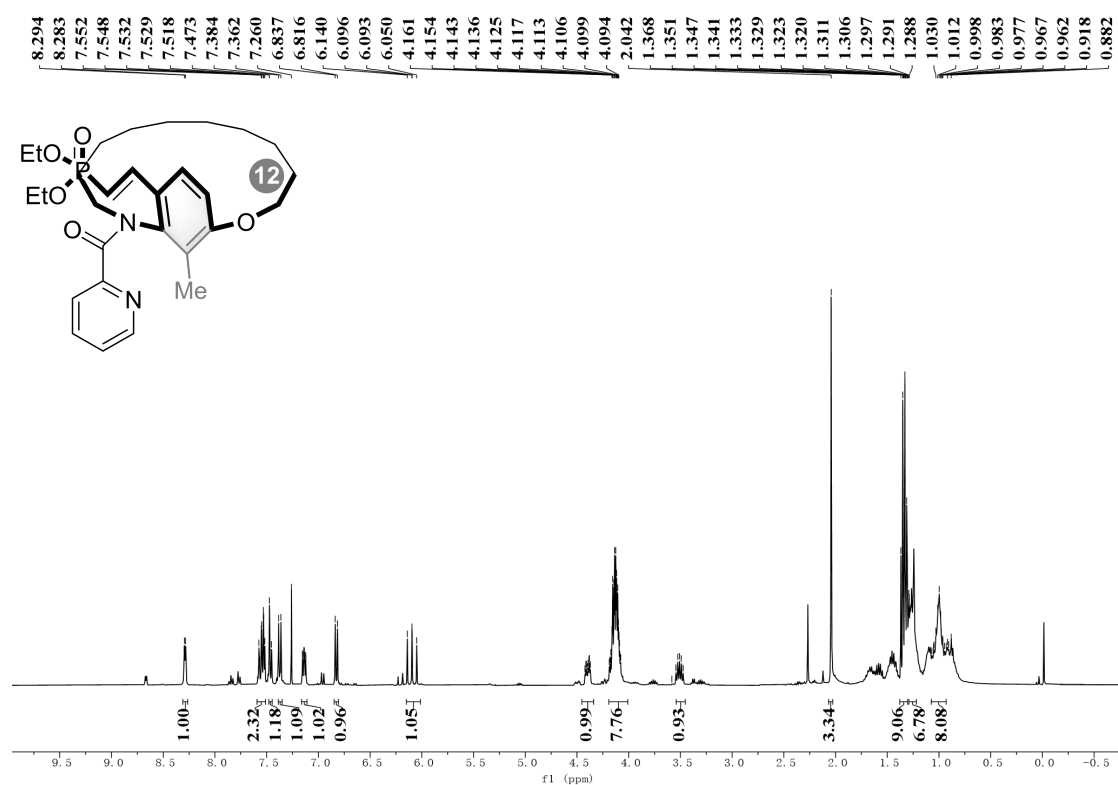
(*R<sub>p</sub>*)-3an, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



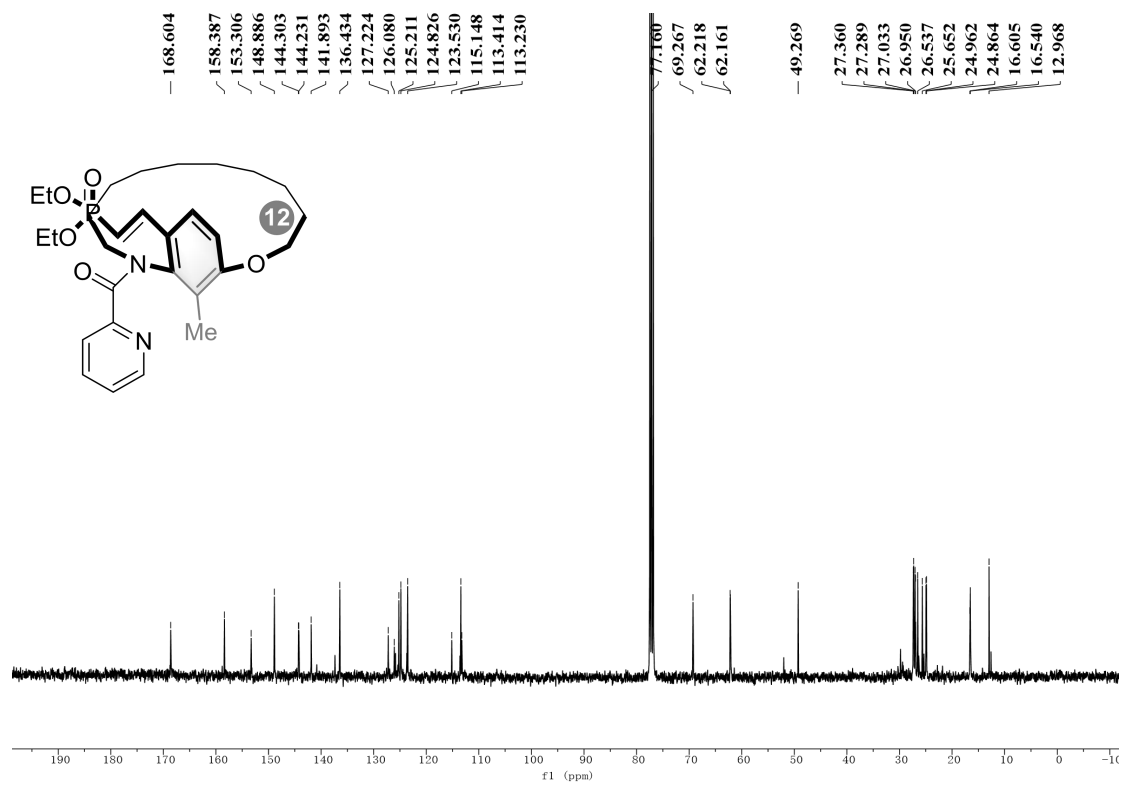
(*R<sub>p</sub>*)-3an, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



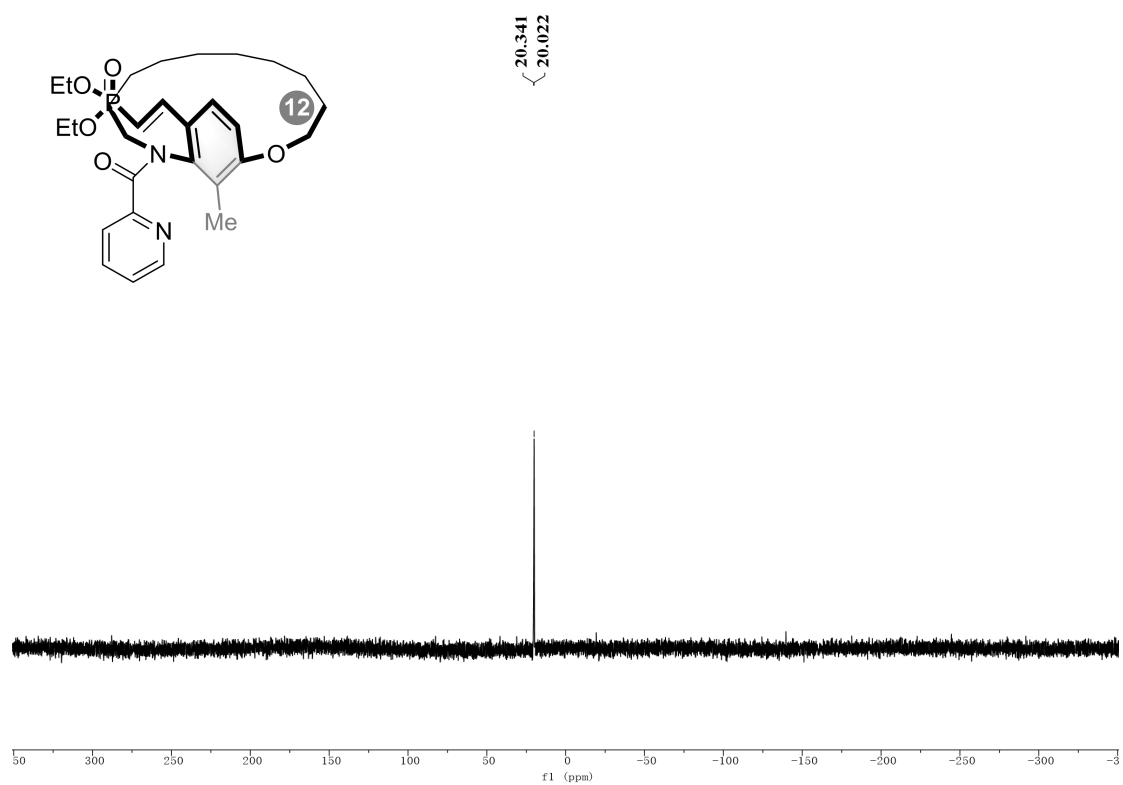
(*R*<sub>p</sub>)-3ao, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



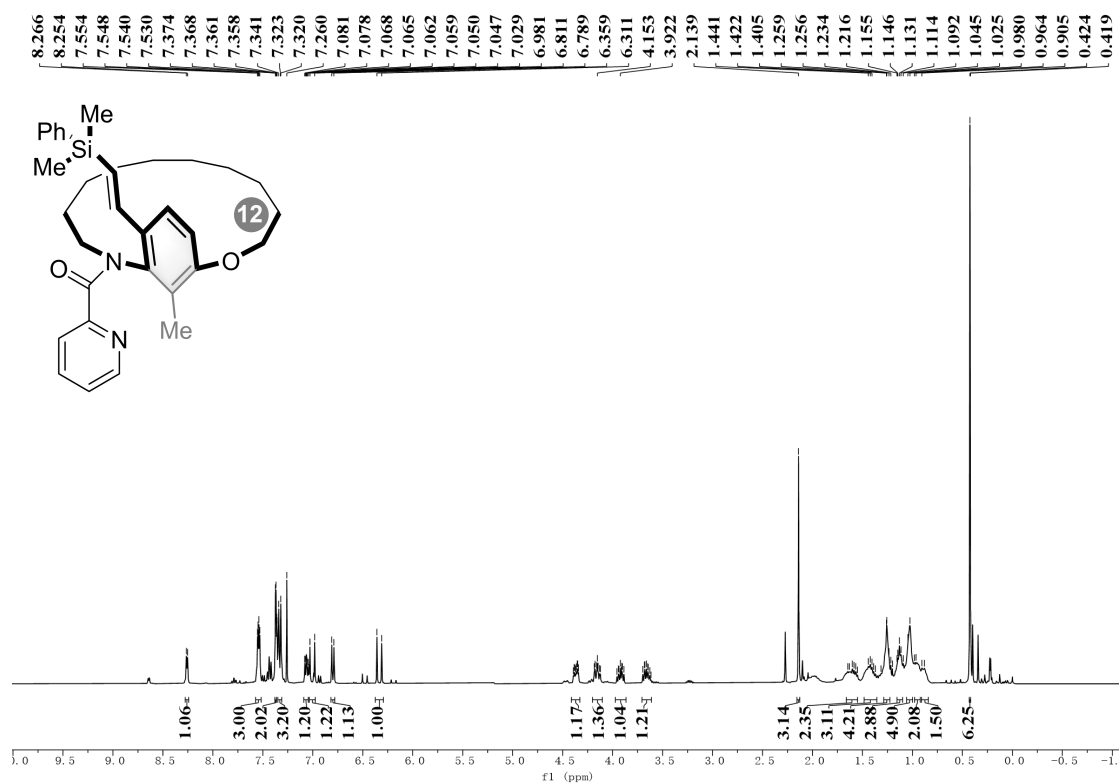
(*R*<sub>p</sub>)-3ao, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



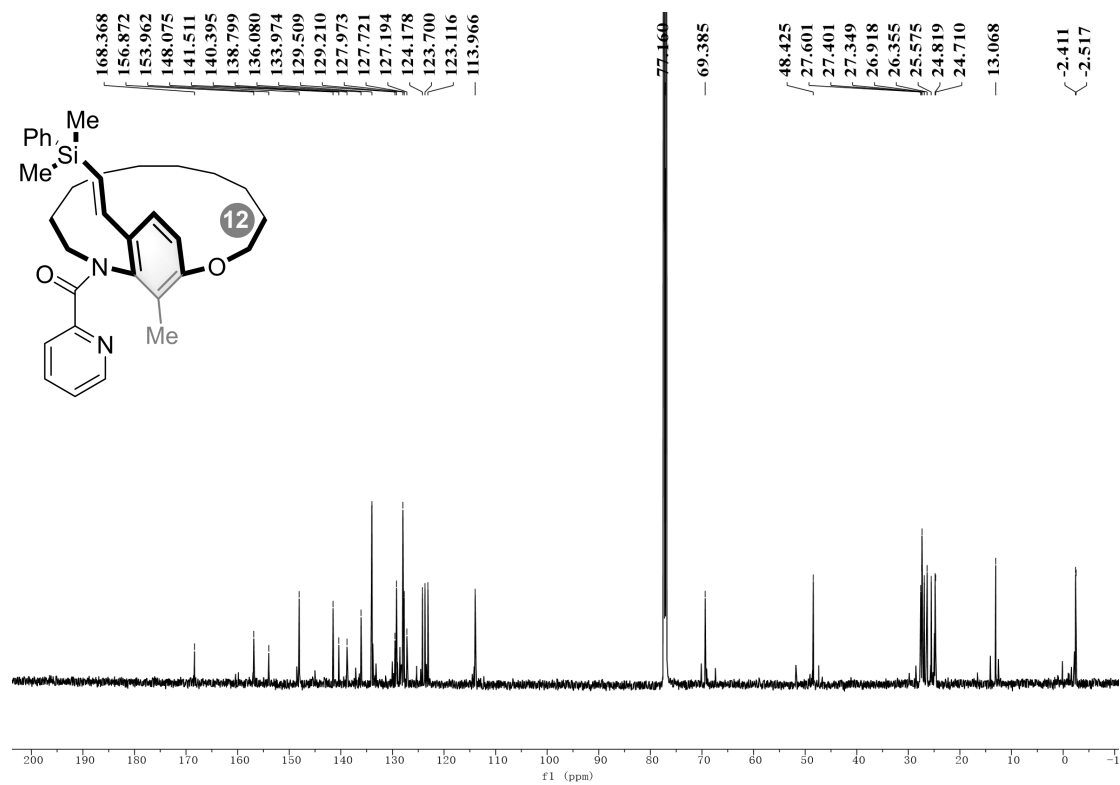
(*R*<sub>p</sub>)-3ao <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)



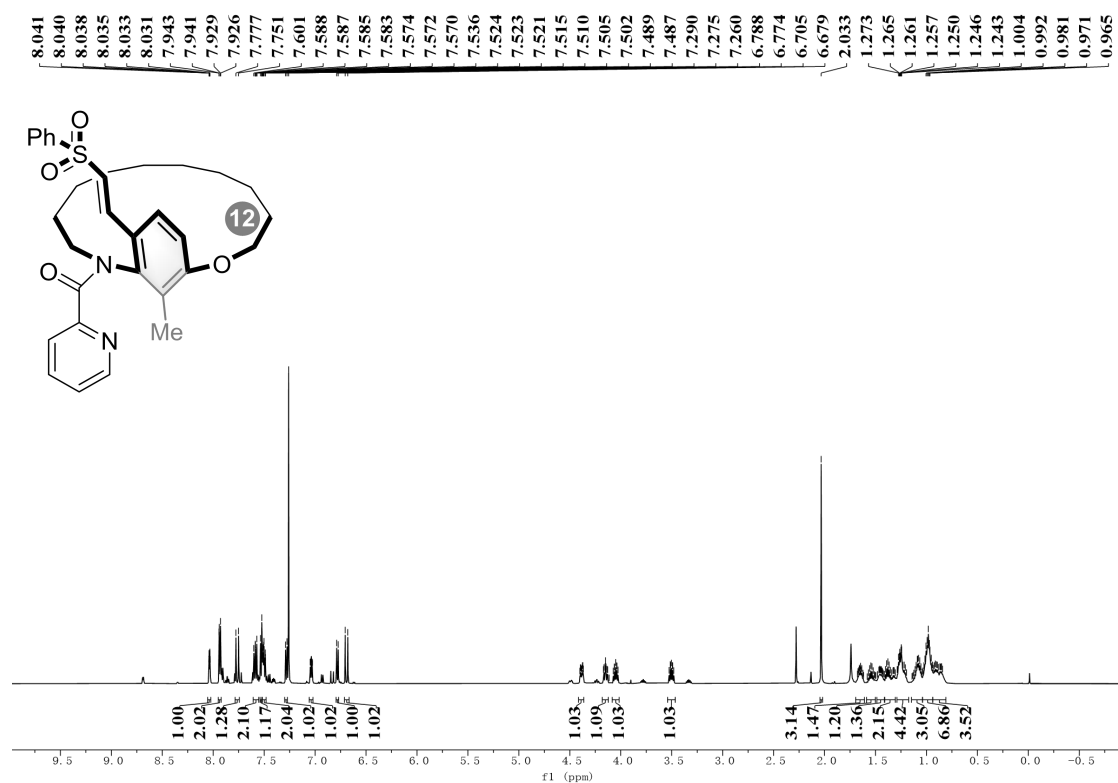
(*R*<sub>p</sub>)-3ap, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



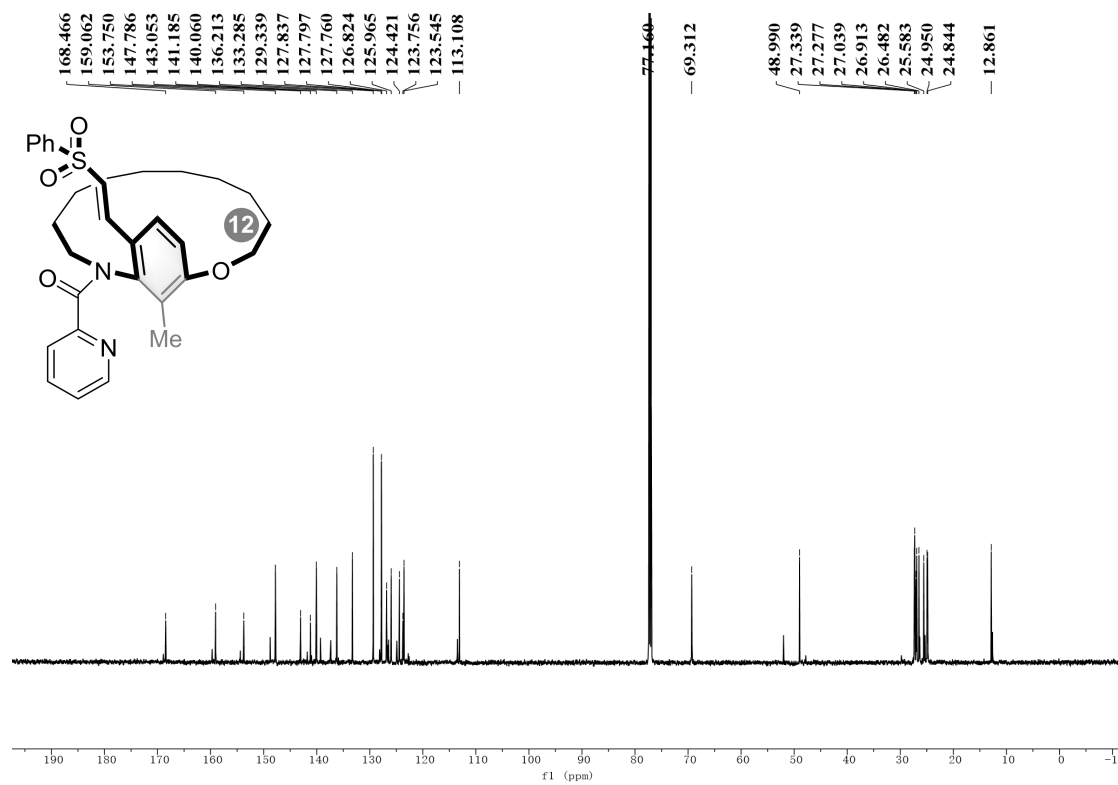
(*R*<sub>p</sub>)-3ap, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



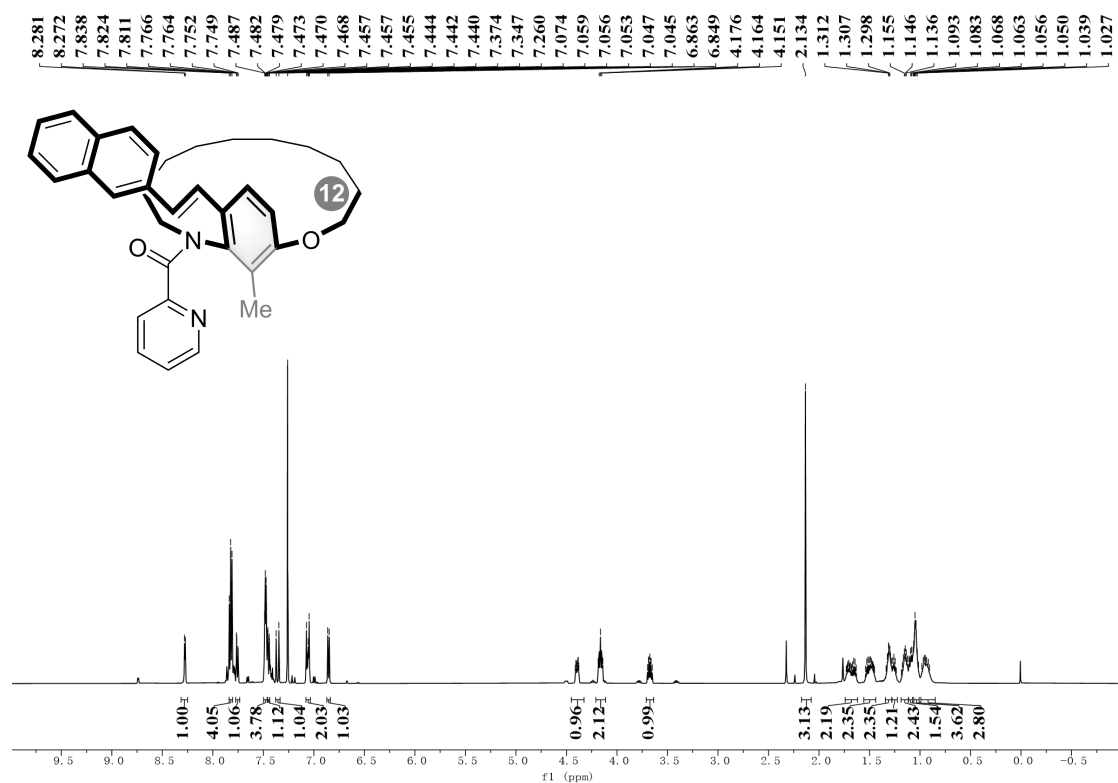
(*R<sub>p</sub>*)-3aq, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



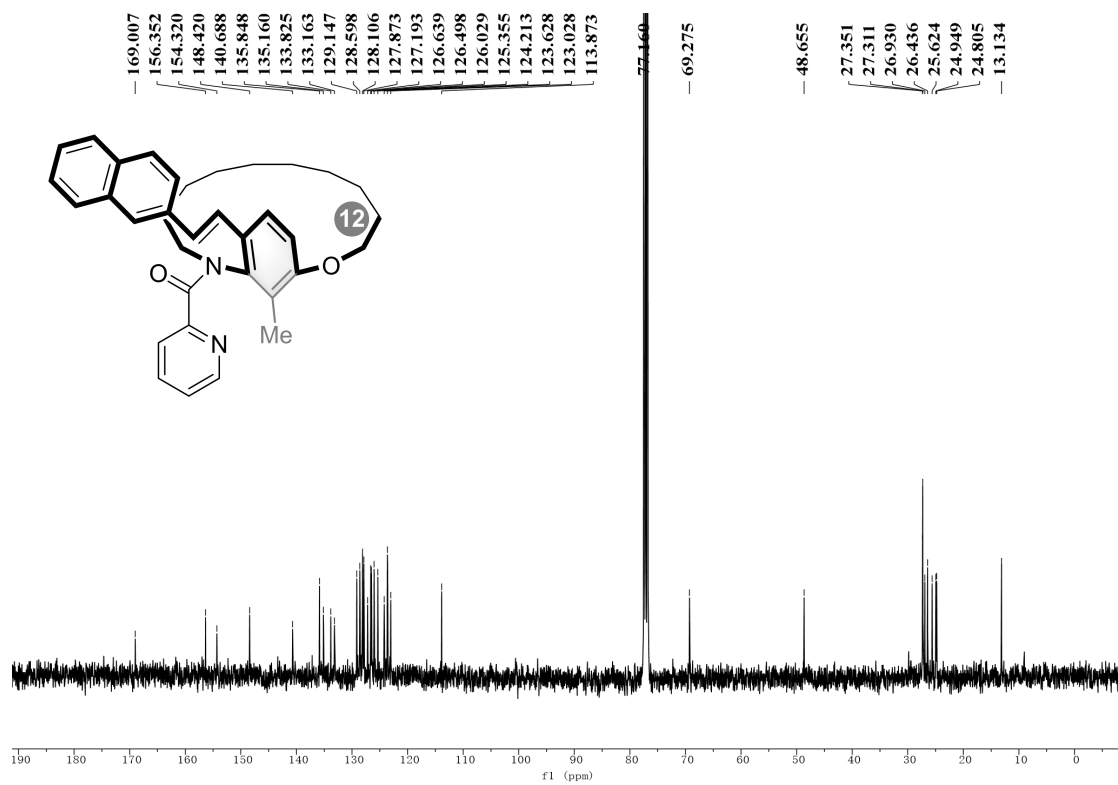
(*R<sub>p</sub>*)-3aq, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



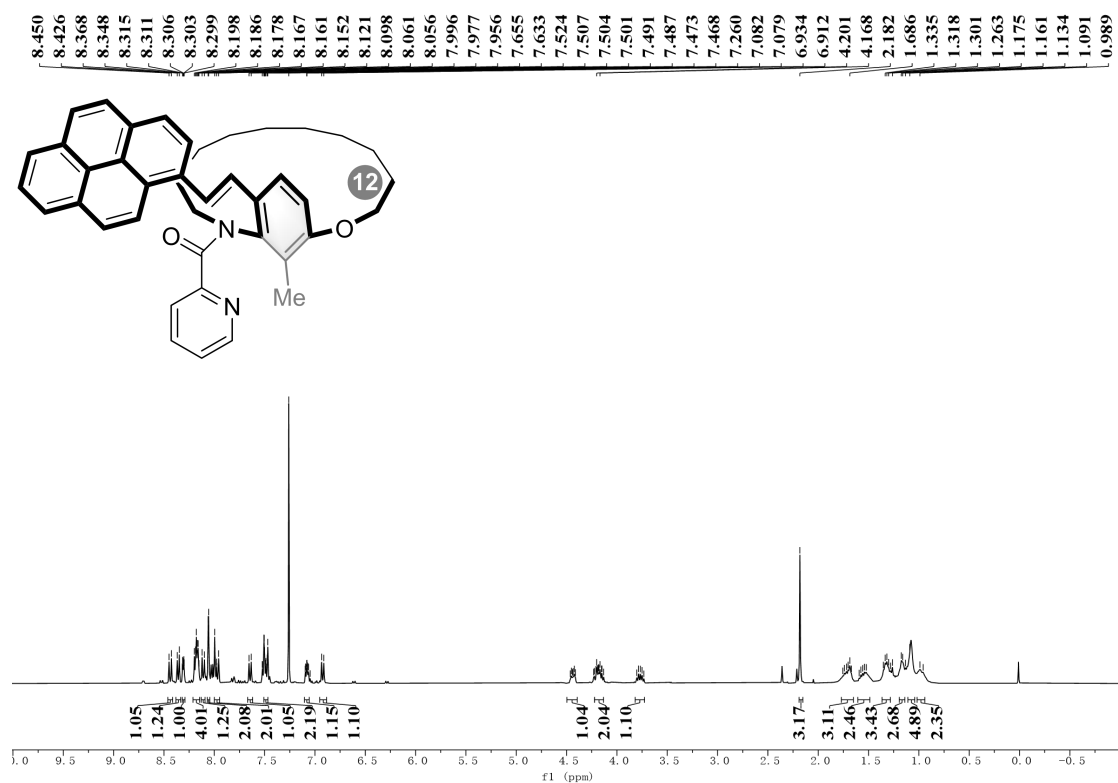
(*R*<sub>p</sub>)-3ar, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



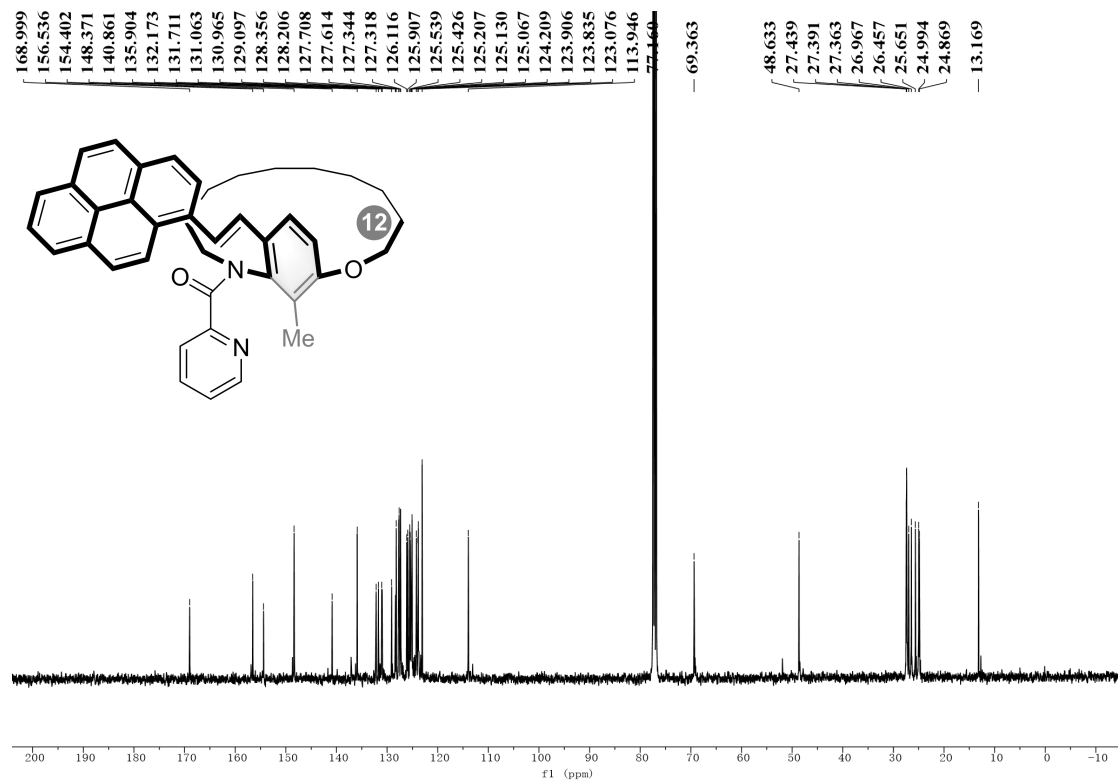
(*R*<sub>p</sub>)-3ar, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



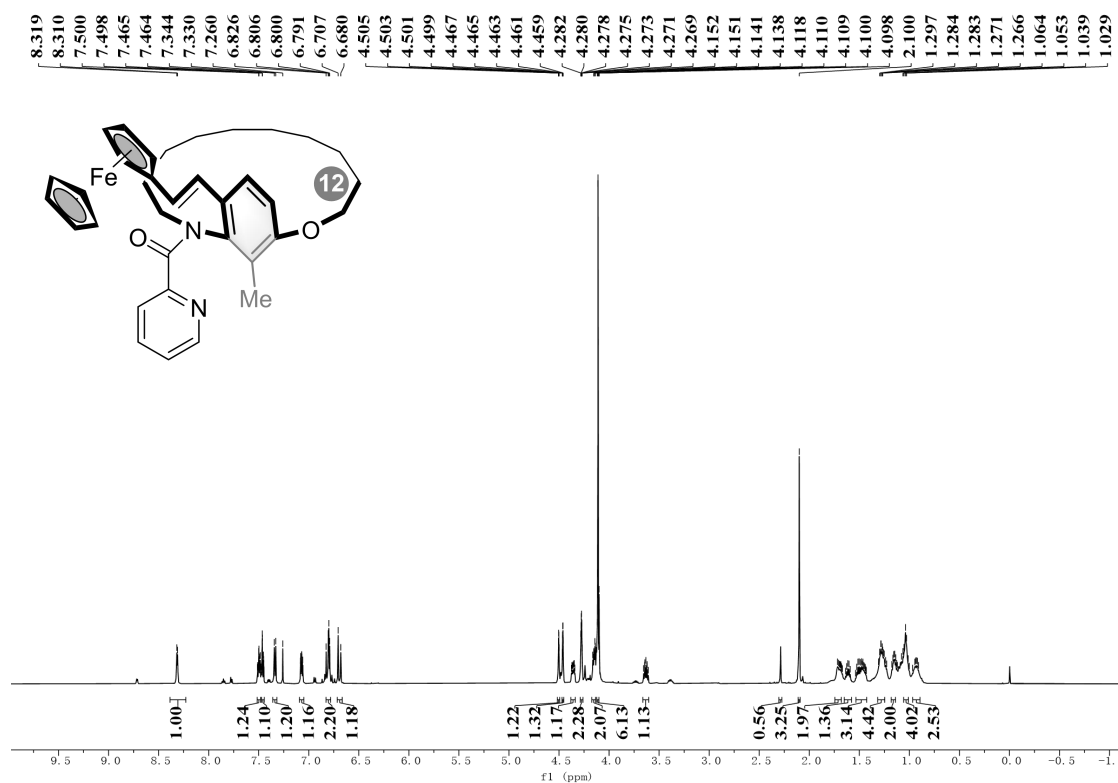
(*R*<sub>p</sub>)-3as, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



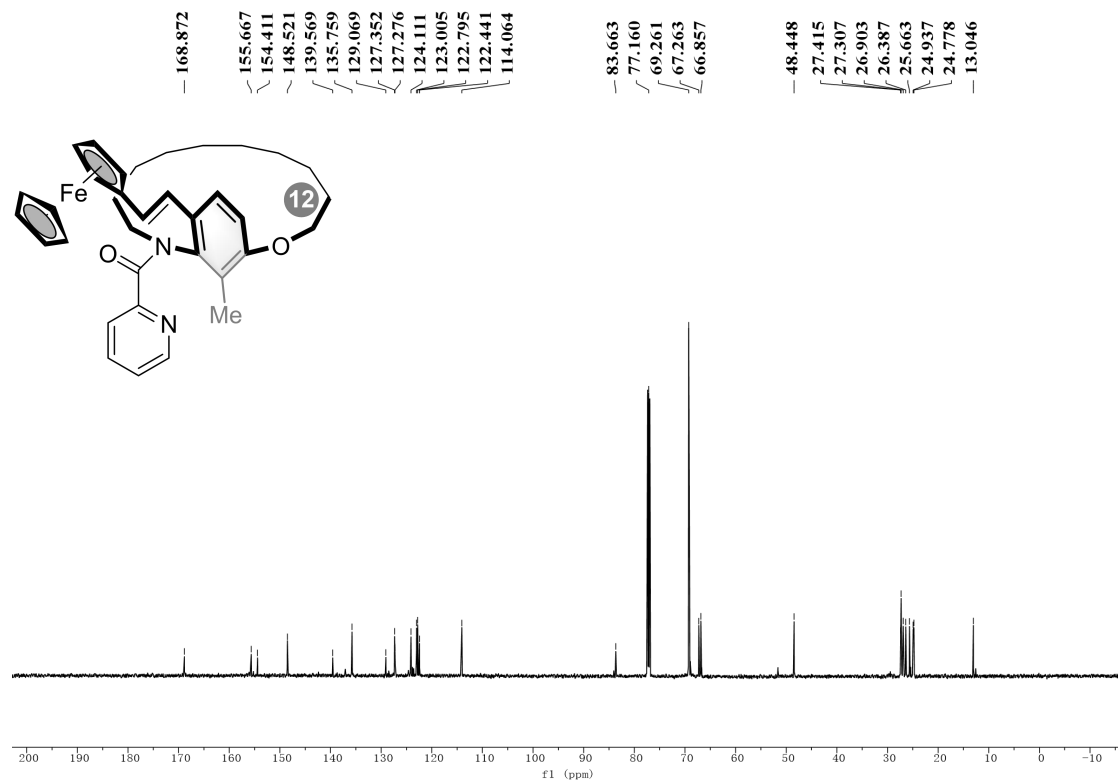
(*R*<sub>p</sub>)-3as, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



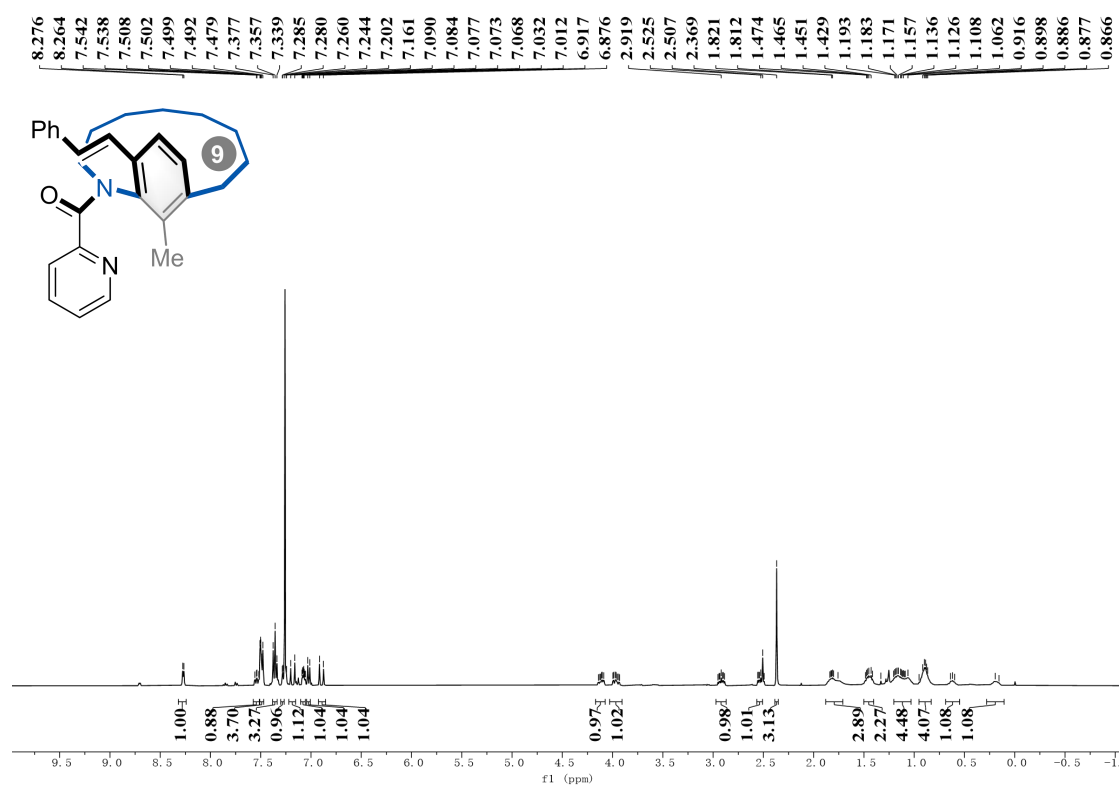
(*R<sub>p</sub>*)-3at, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



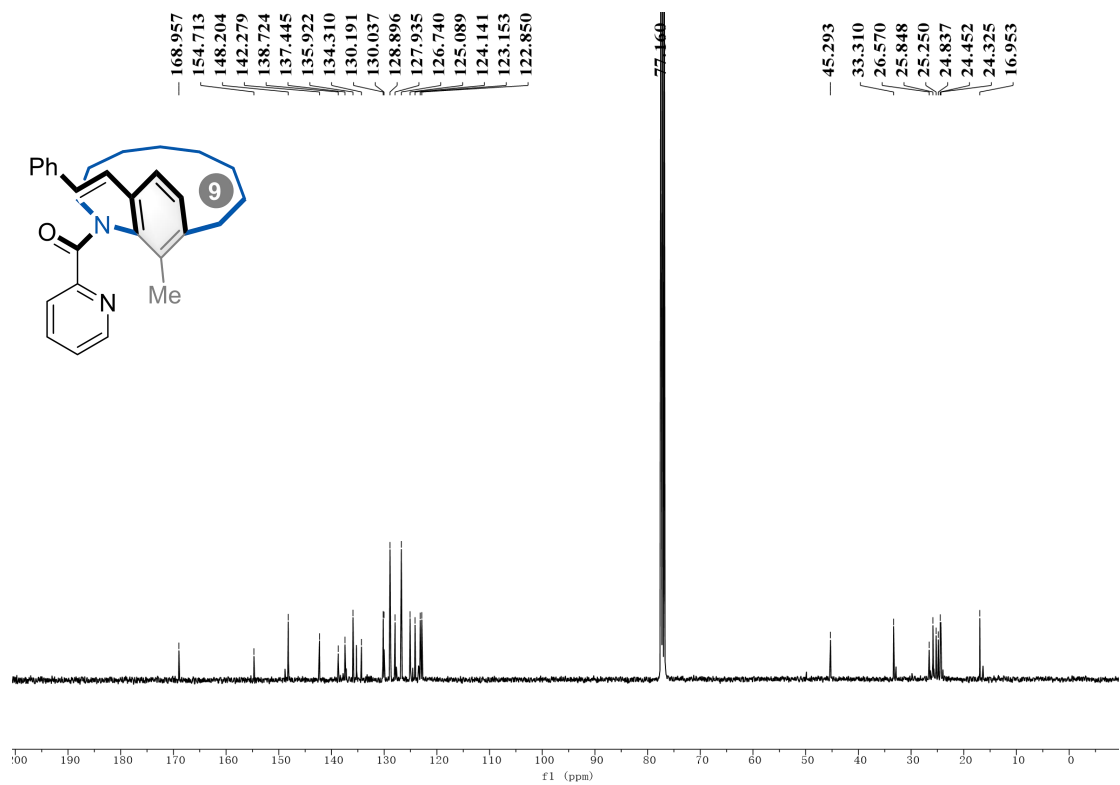
(*R<sub>p</sub>*)-3at, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



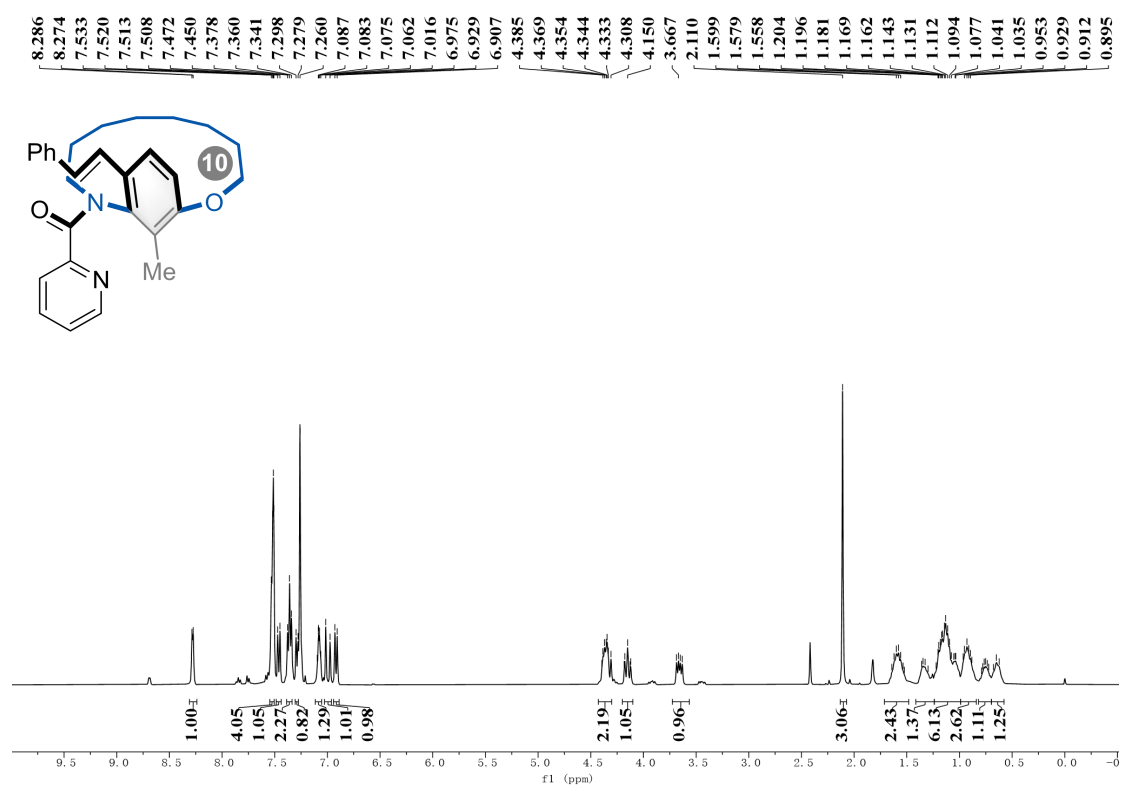
(*R*<sub>p</sub>)-3ba, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



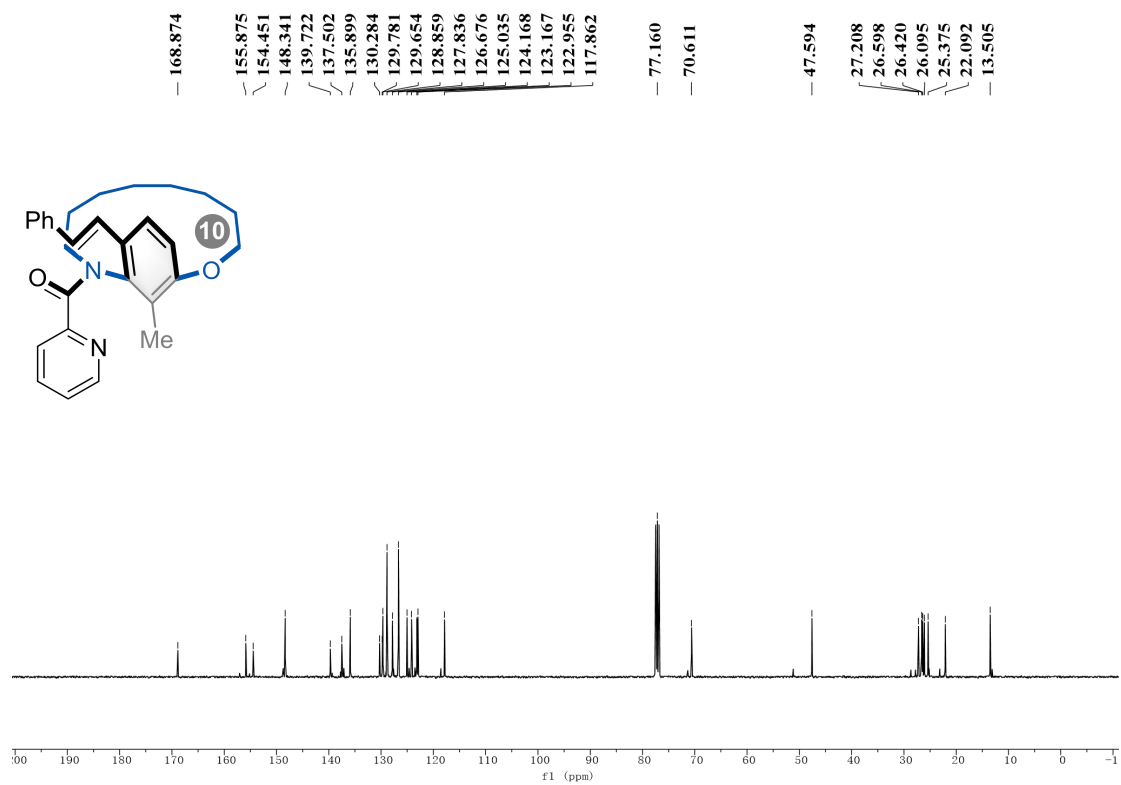
(*R*<sub>p</sub>)-3ba, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



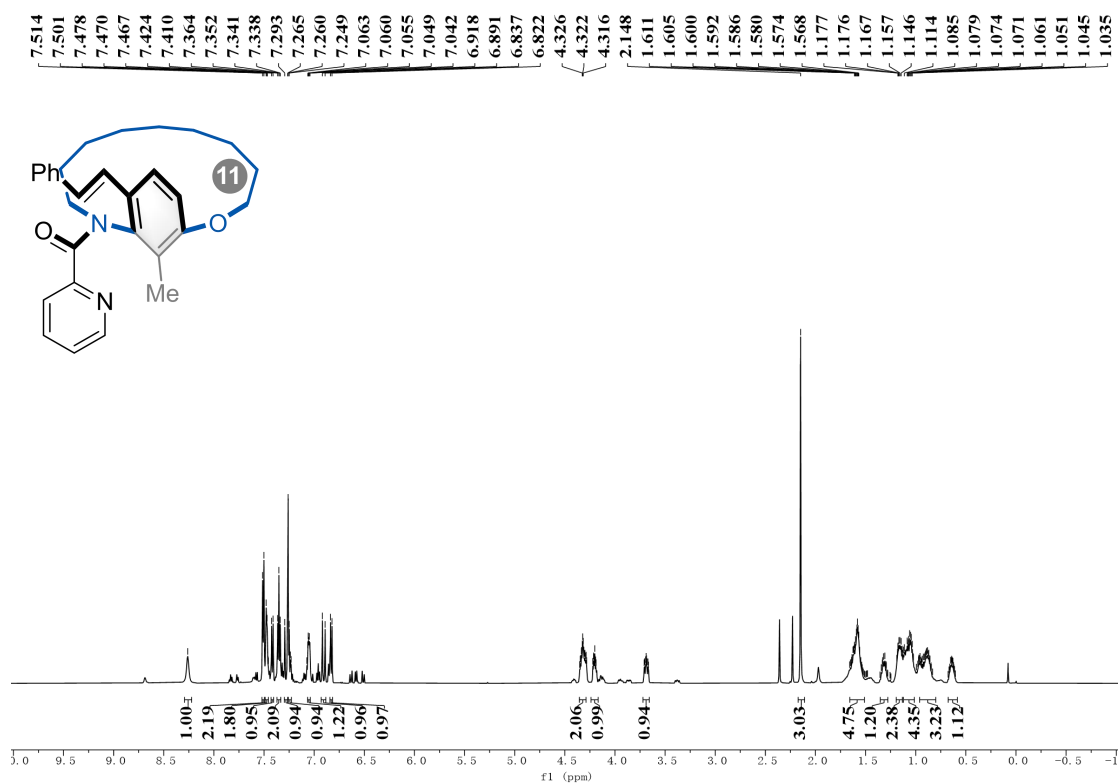
(*R*<sub>p</sub>)-3ca, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



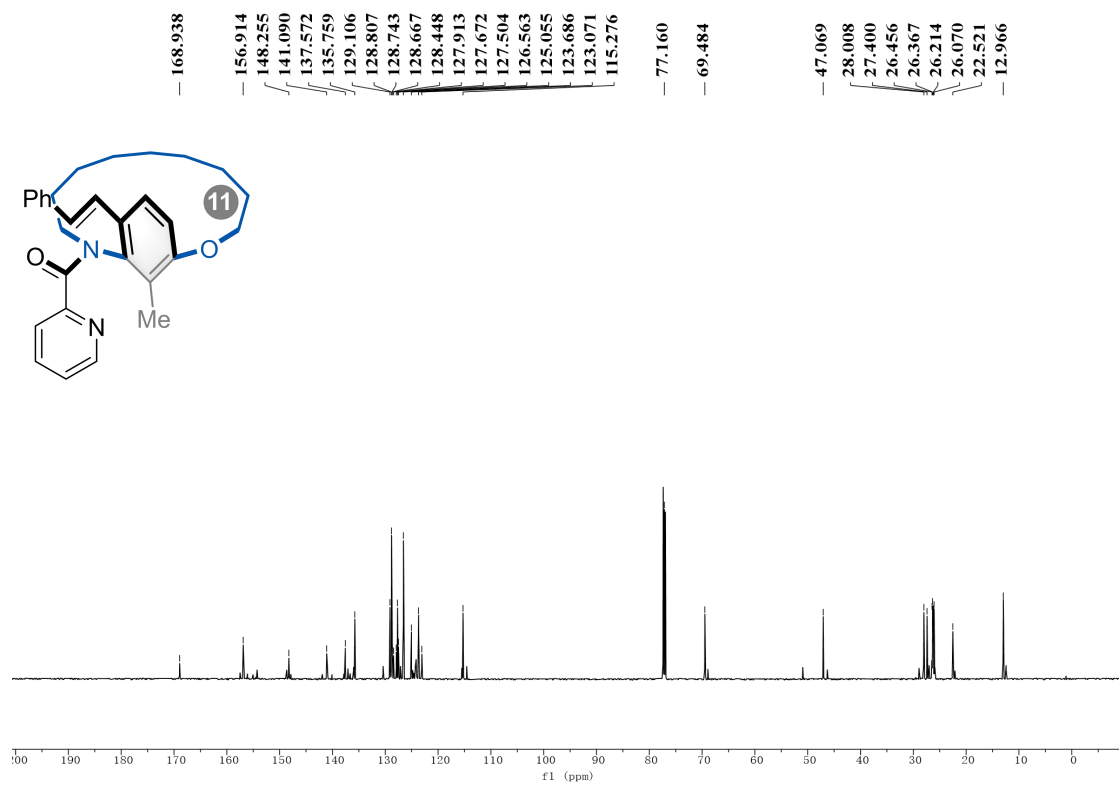
(*R*<sub>p</sub>)-3ca, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



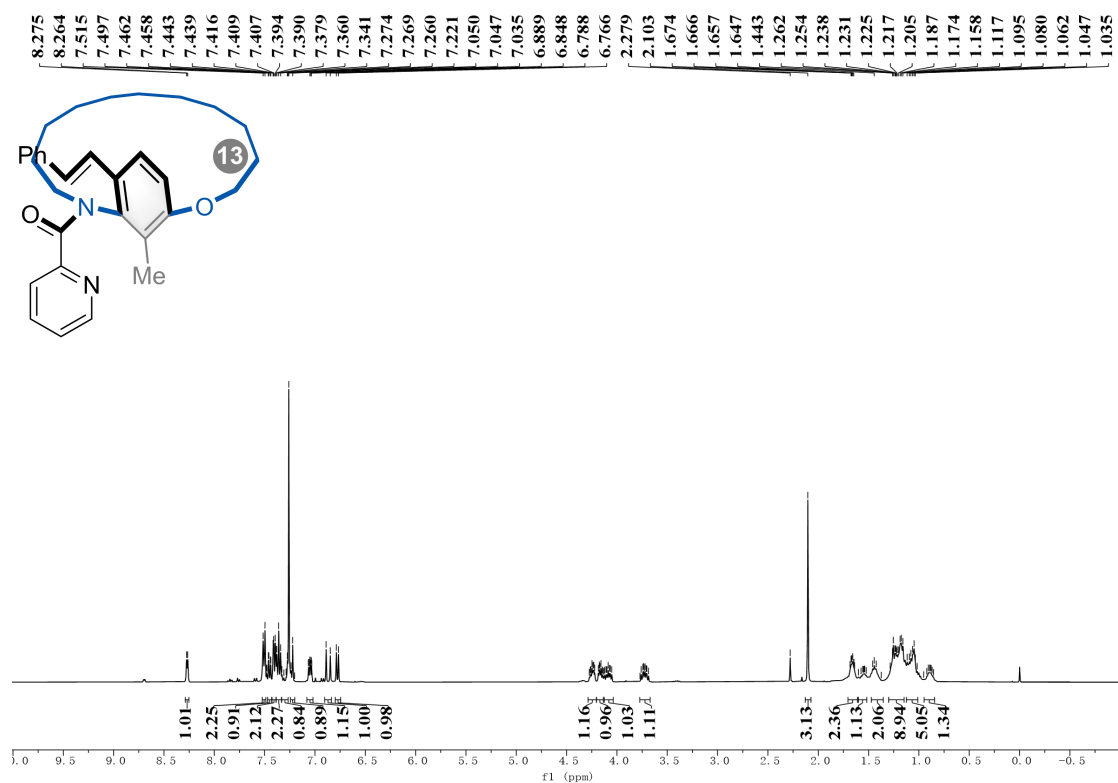
(*R*<sub>p</sub>)-3da, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



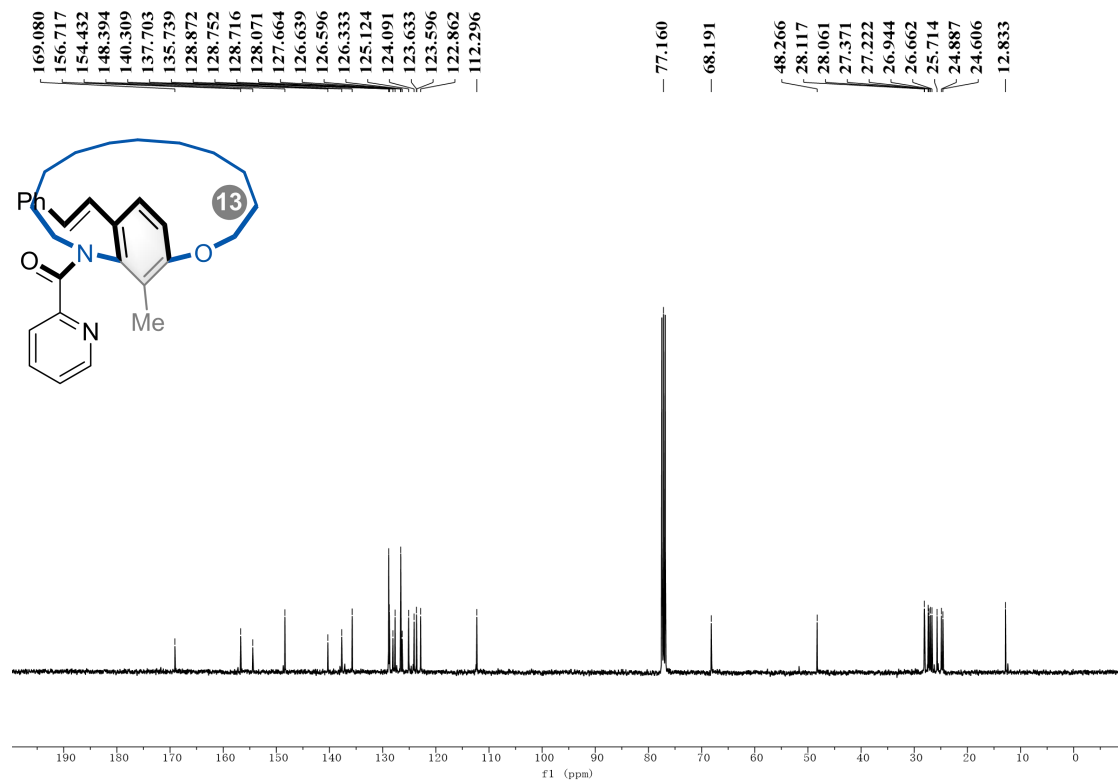
(*R*<sub>p</sub>)-3da, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



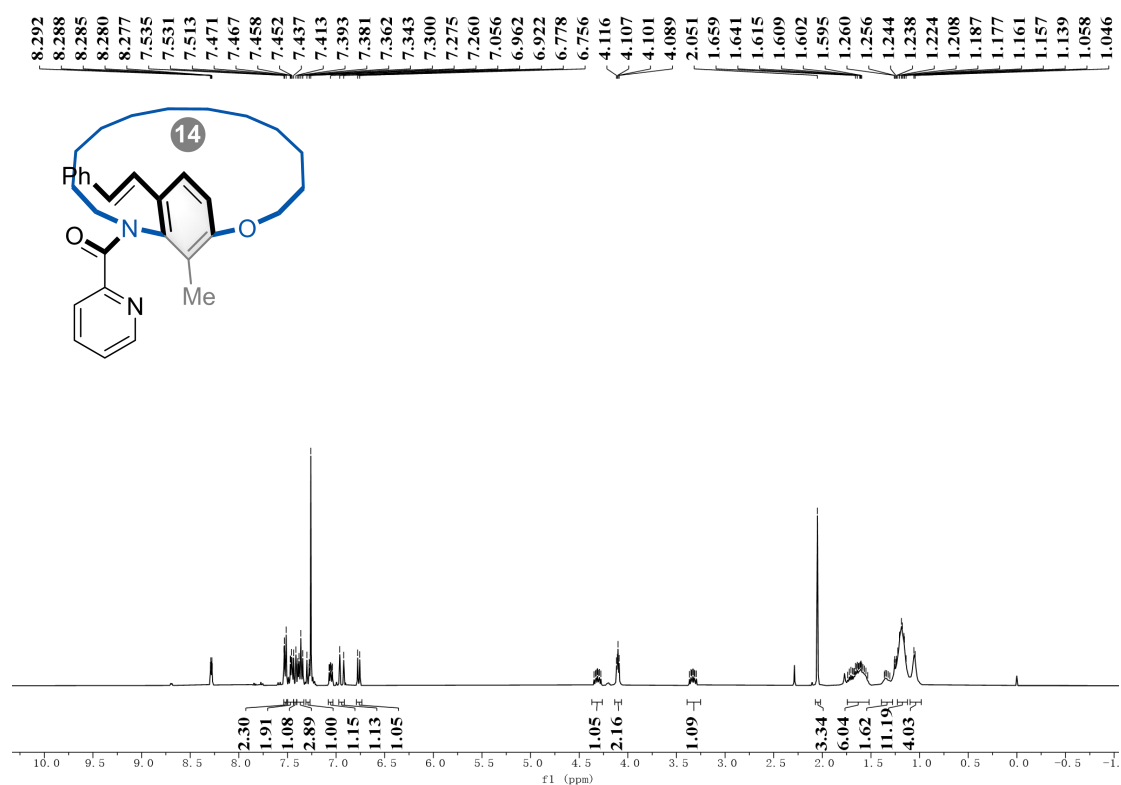
(*R<sub>p</sub>*)-3ea, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



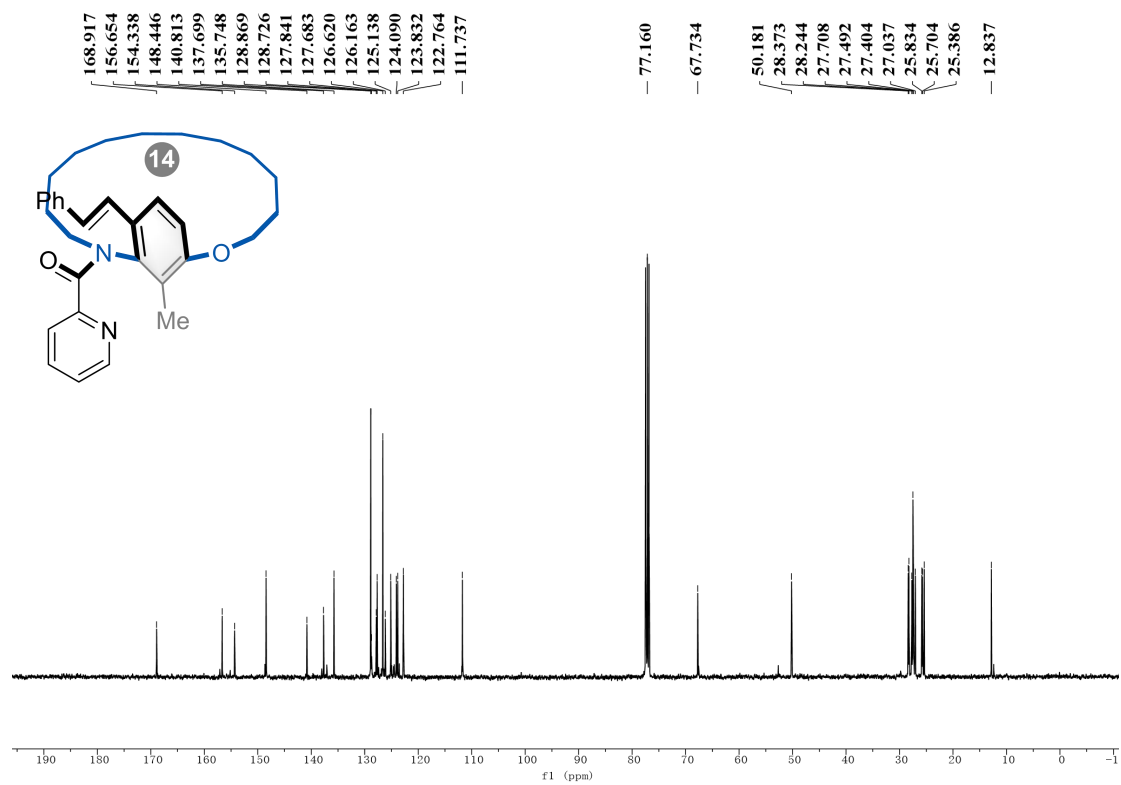
(*R<sub>p</sub>*)-3ea, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



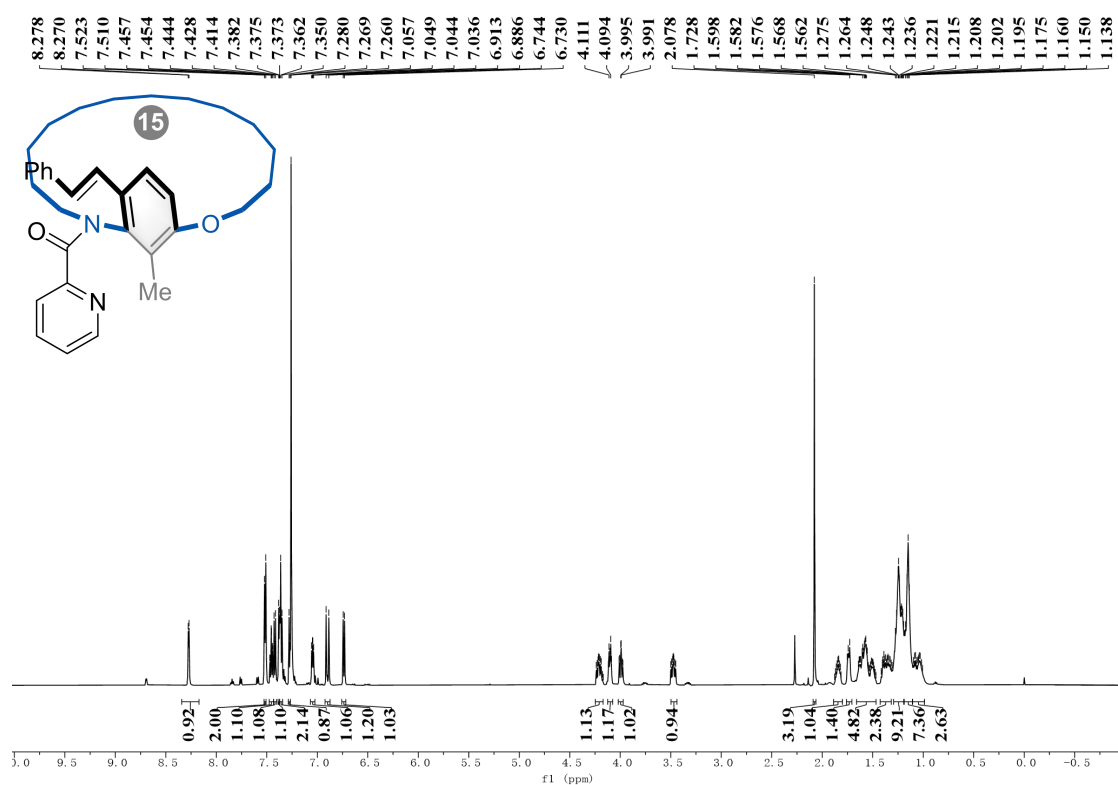
(*R*<sub>p</sub>)-3fa, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



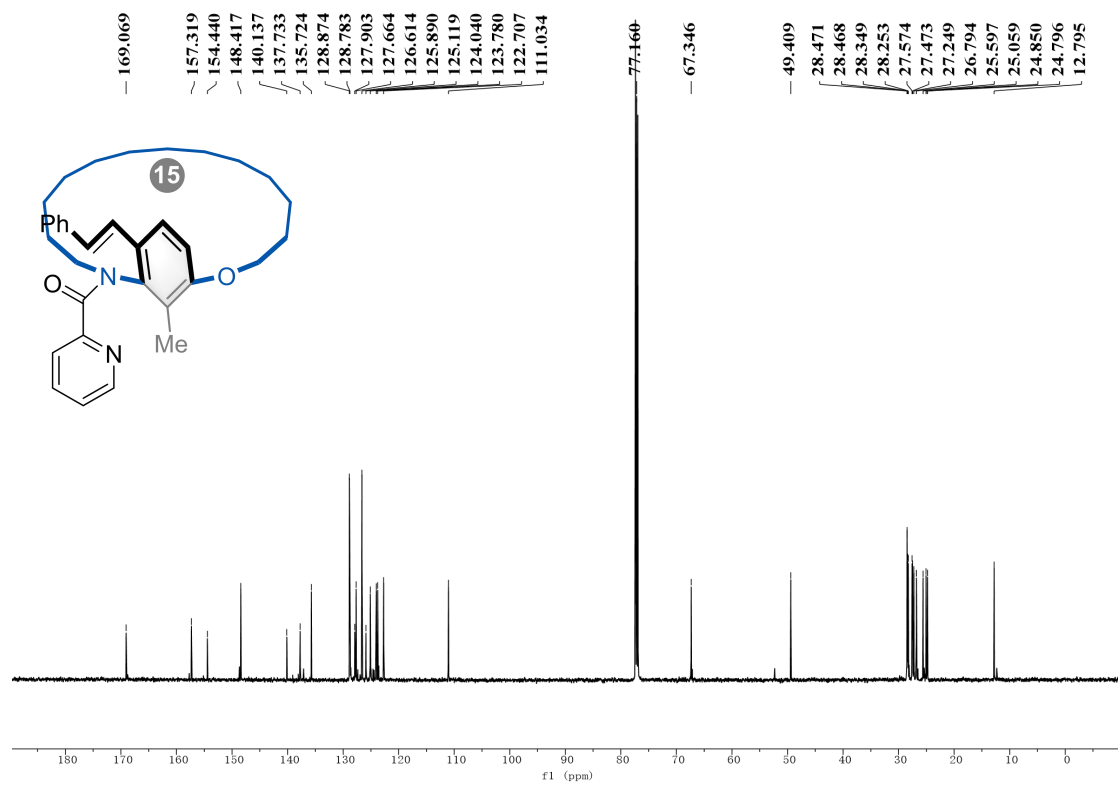
(*R*<sub>p</sub>)-3fa, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



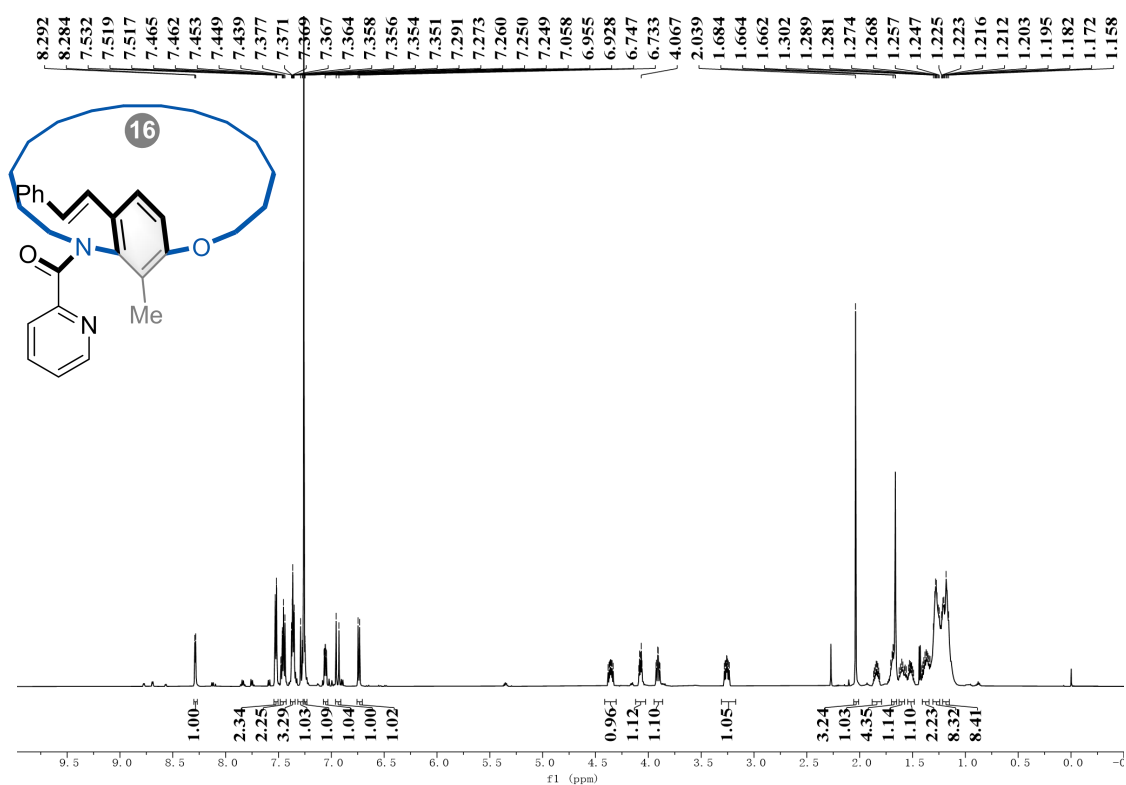
(*R*<sub>p</sub>)-3ga, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



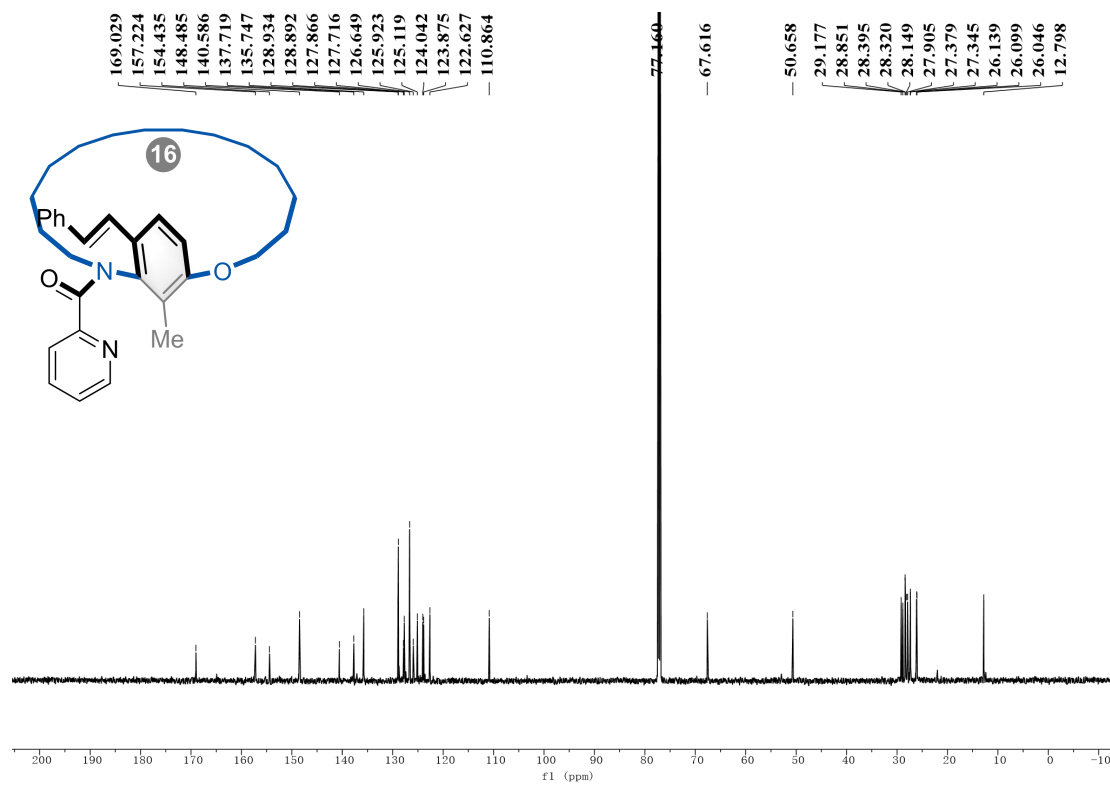
(*R*<sub>p</sub>)-3ga, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



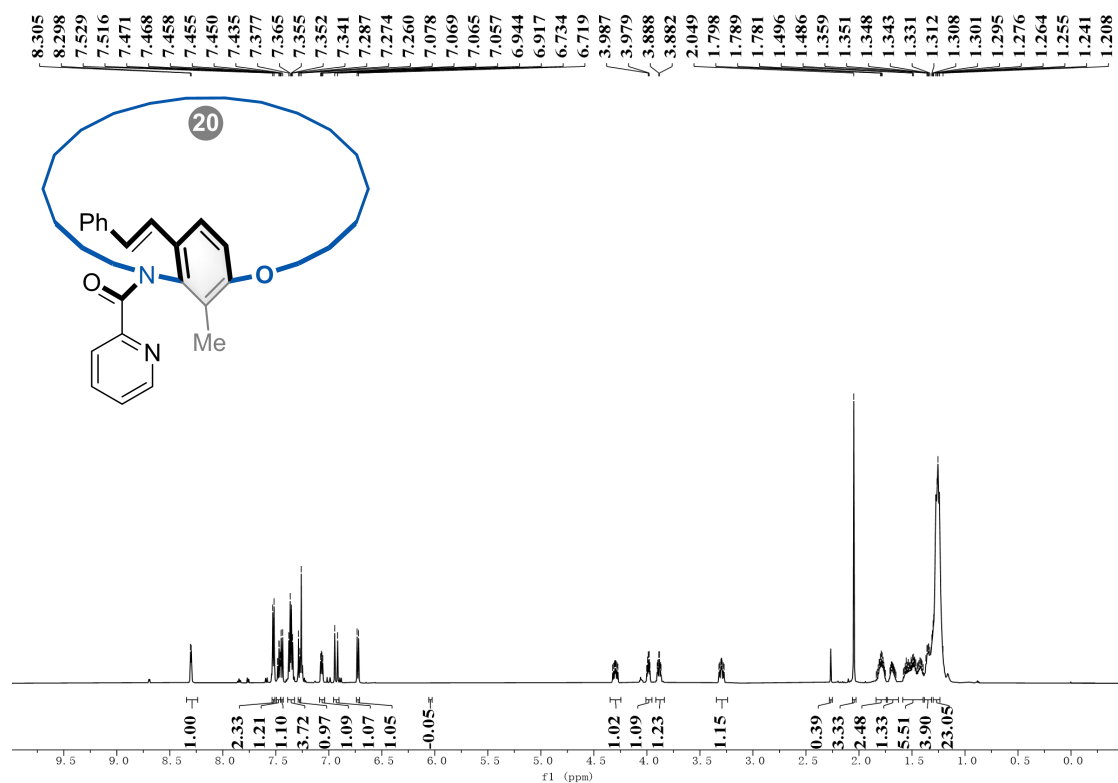
(*R*<sub>p</sub>)-3ha, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



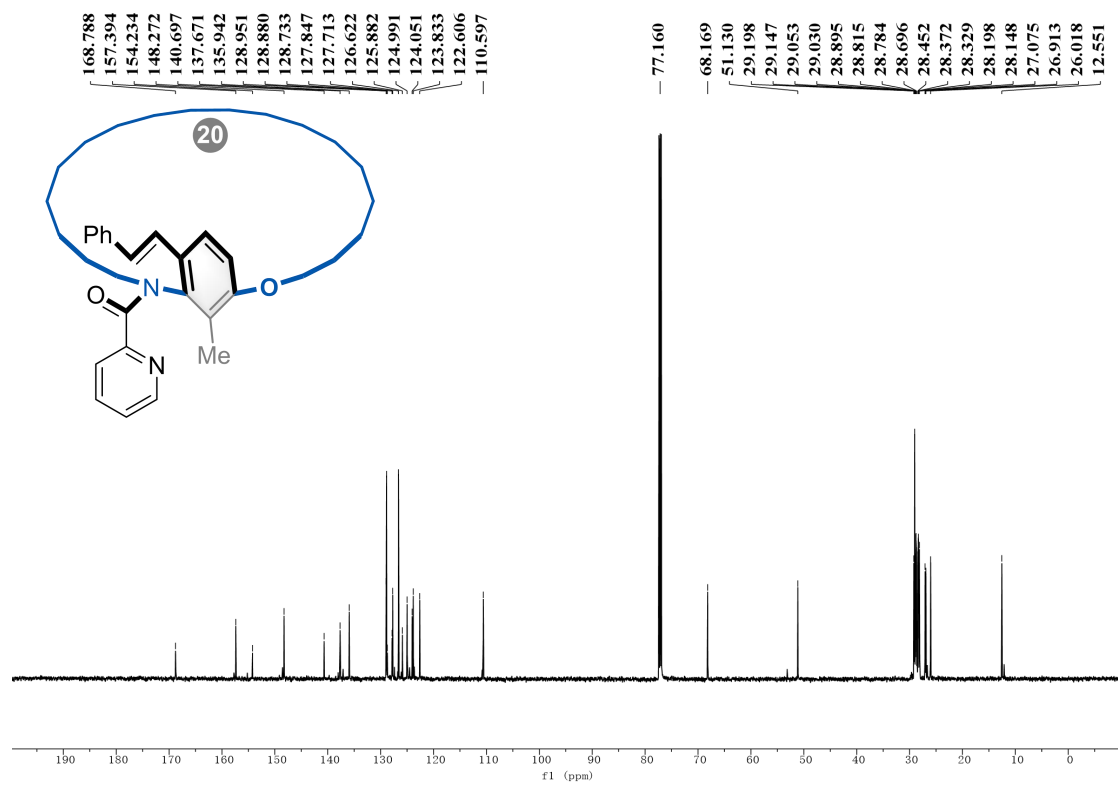
(*R*<sub>p</sub>)-3ha, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



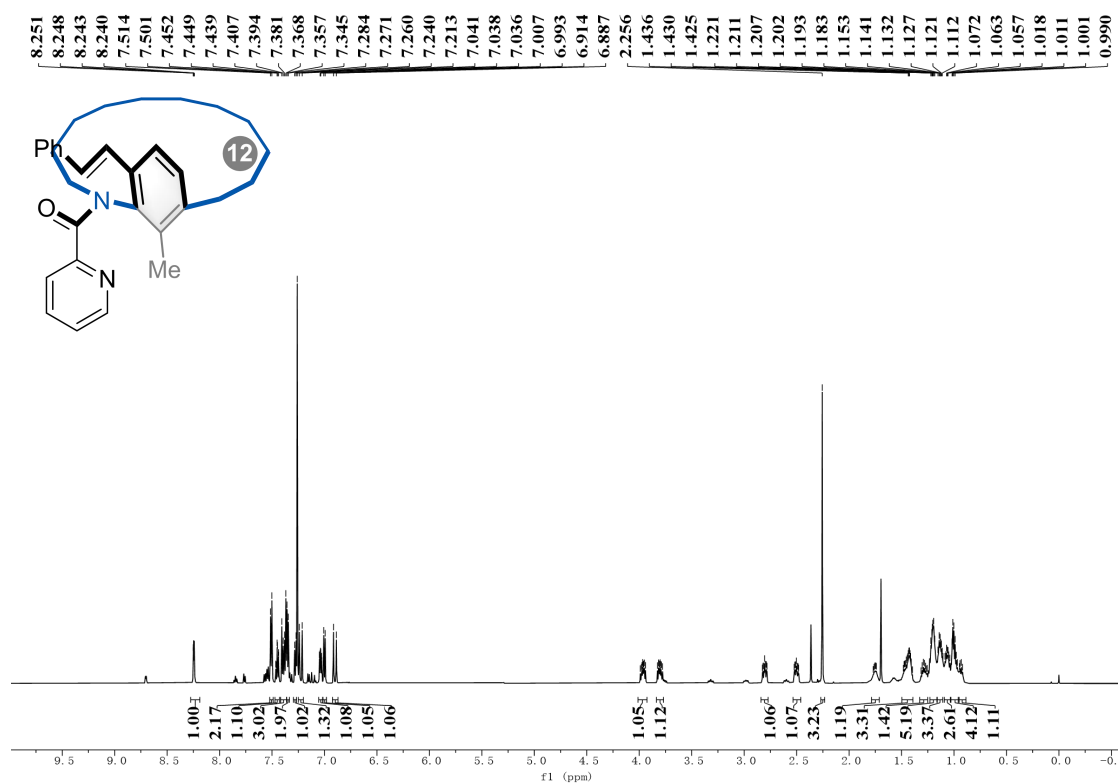
(*R<sub>p</sub>*)-3ia, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



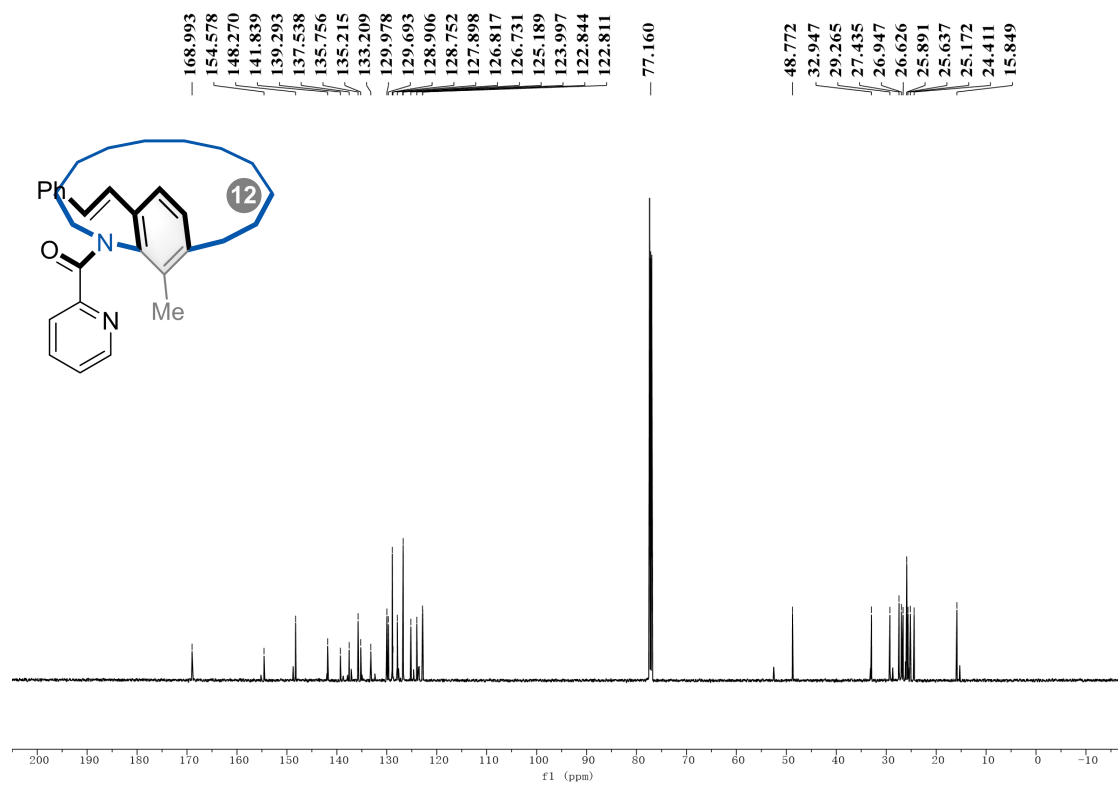
(*R<sub>p</sub>*)-3ia, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



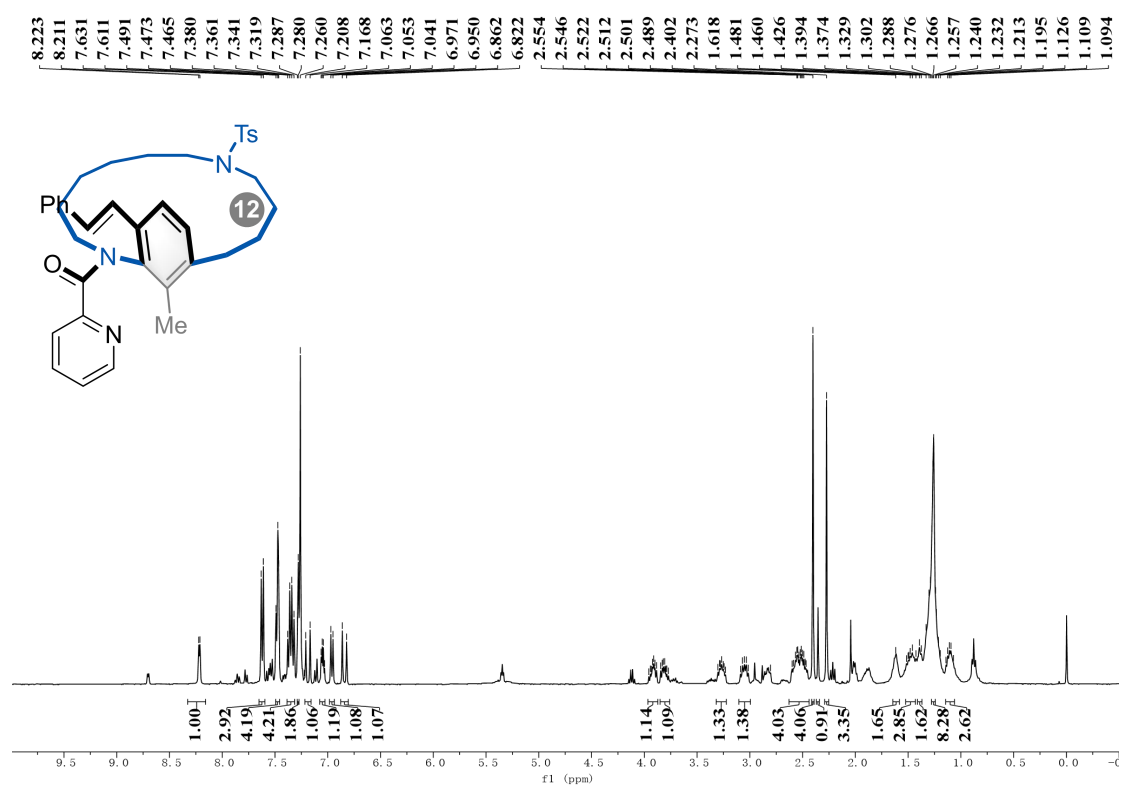
(*R*<sub>p</sub>)-3ja, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



(*R*<sub>p</sub>)-3ja, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



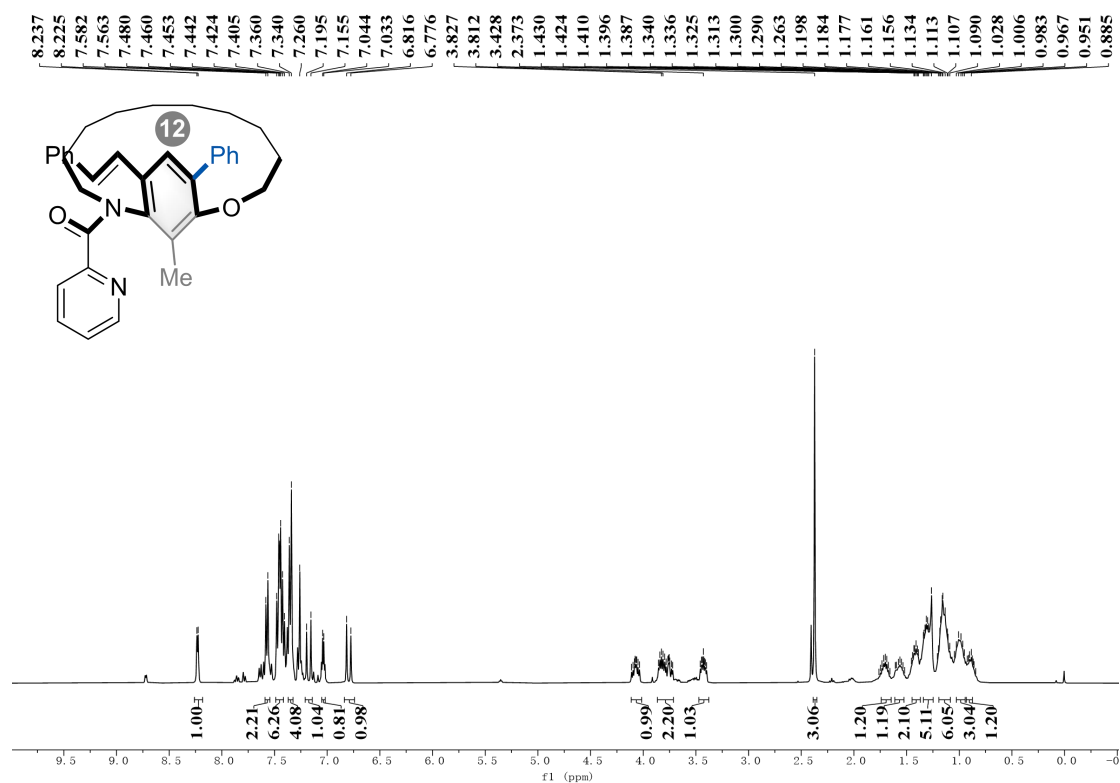
(*R*<sub>p</sub>)-3ka, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



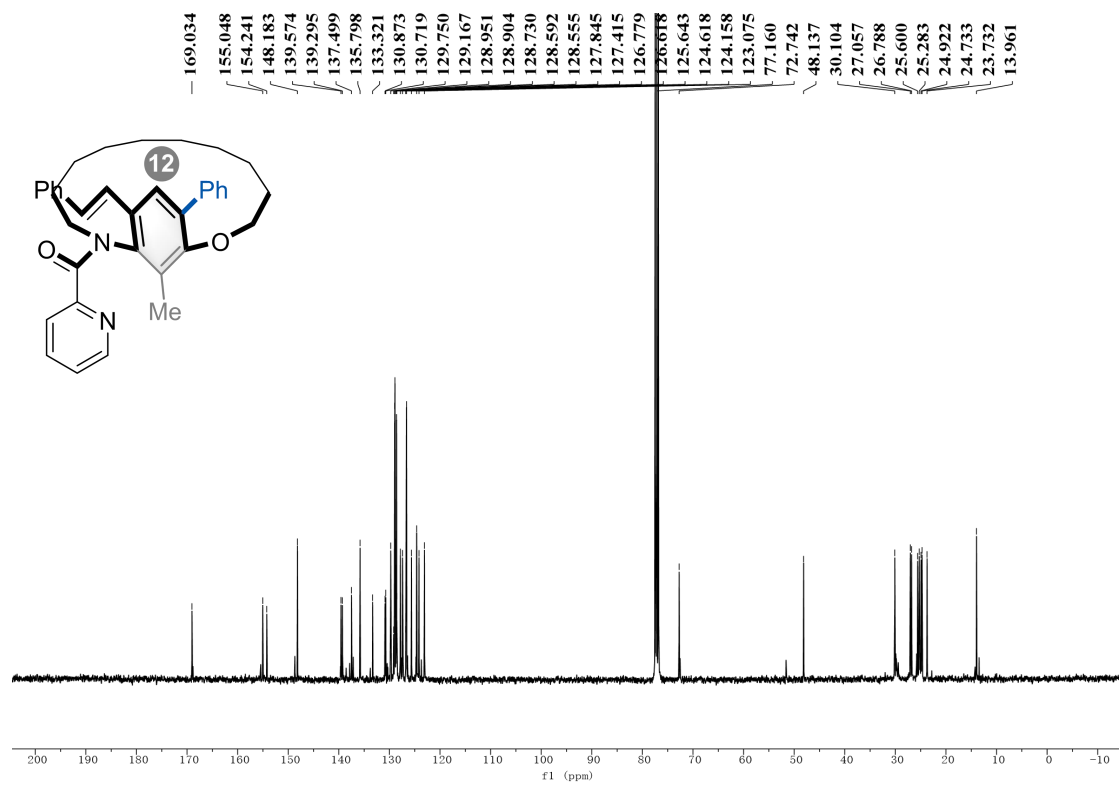
(*R*<sub>p</sub>)-3ka, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



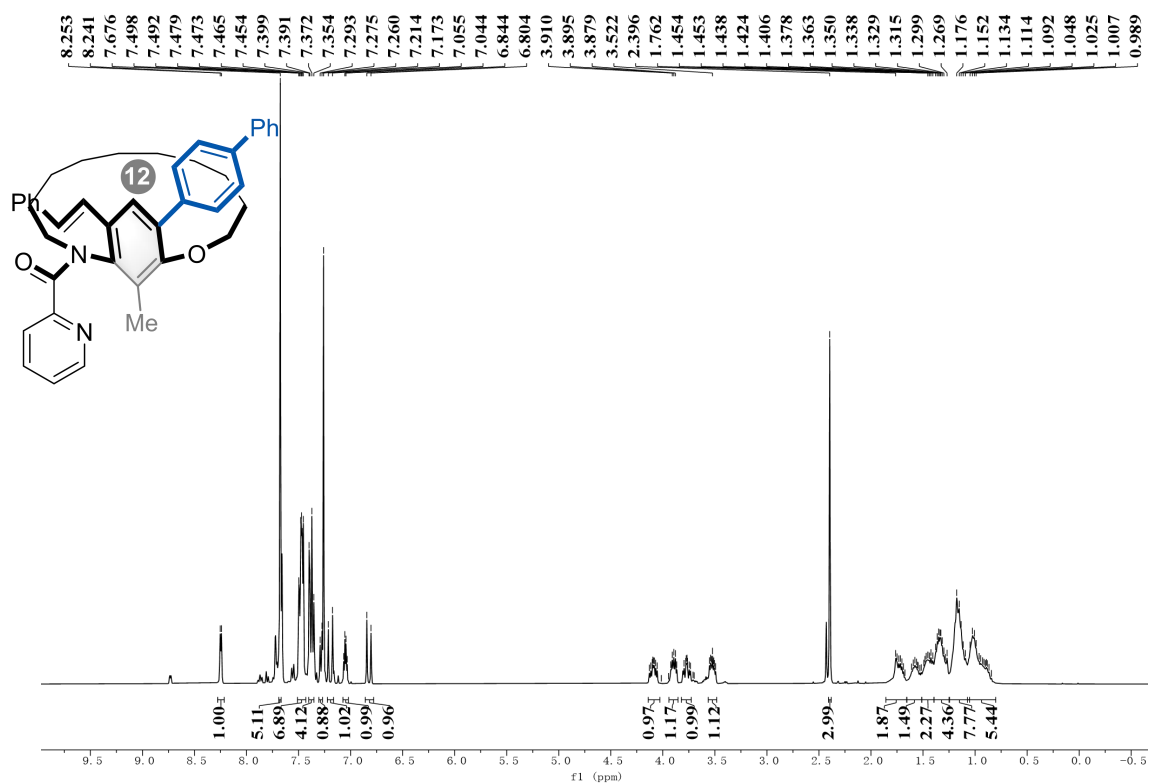
(*R<sub>p</sub>*)-31a, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



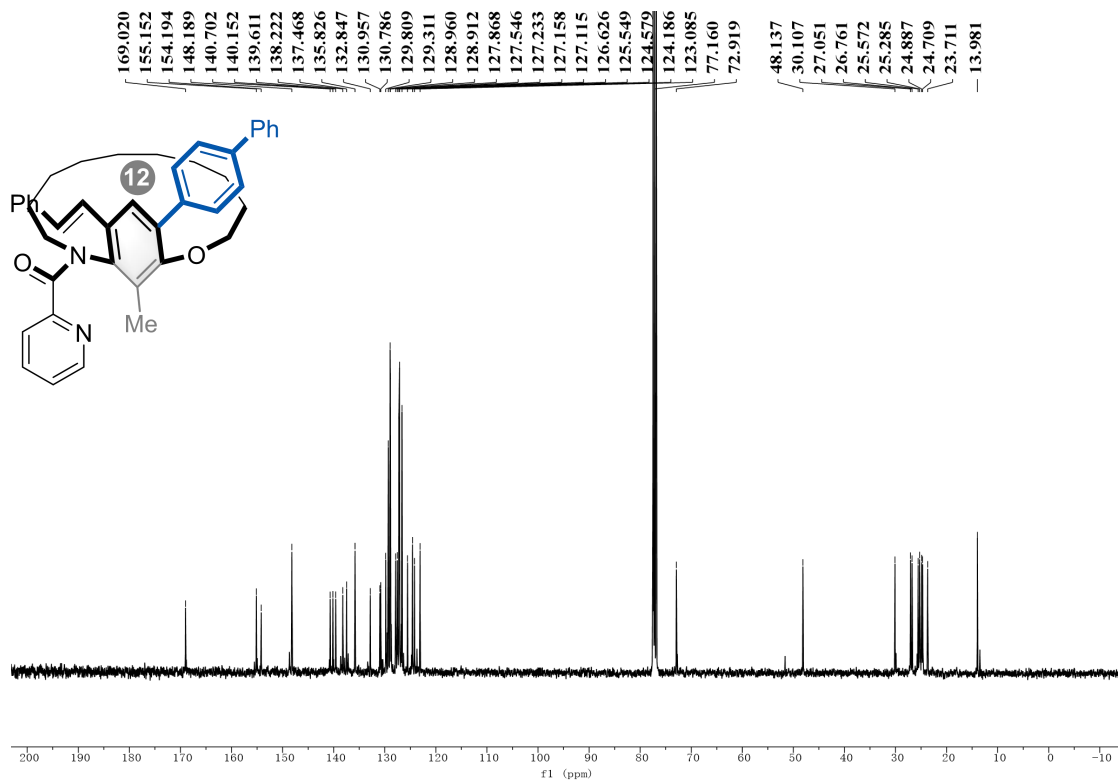
(*R<sub>p</sub>*)-31a, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



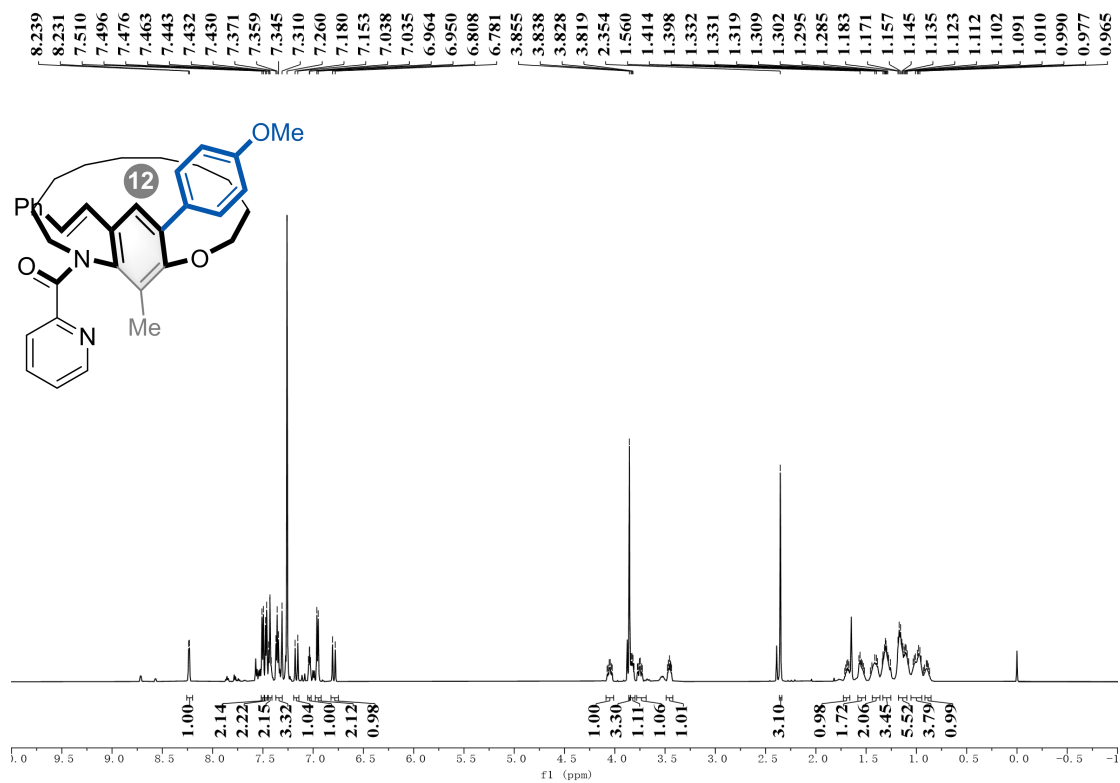
(R<sub>p</sub>)-3ma, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



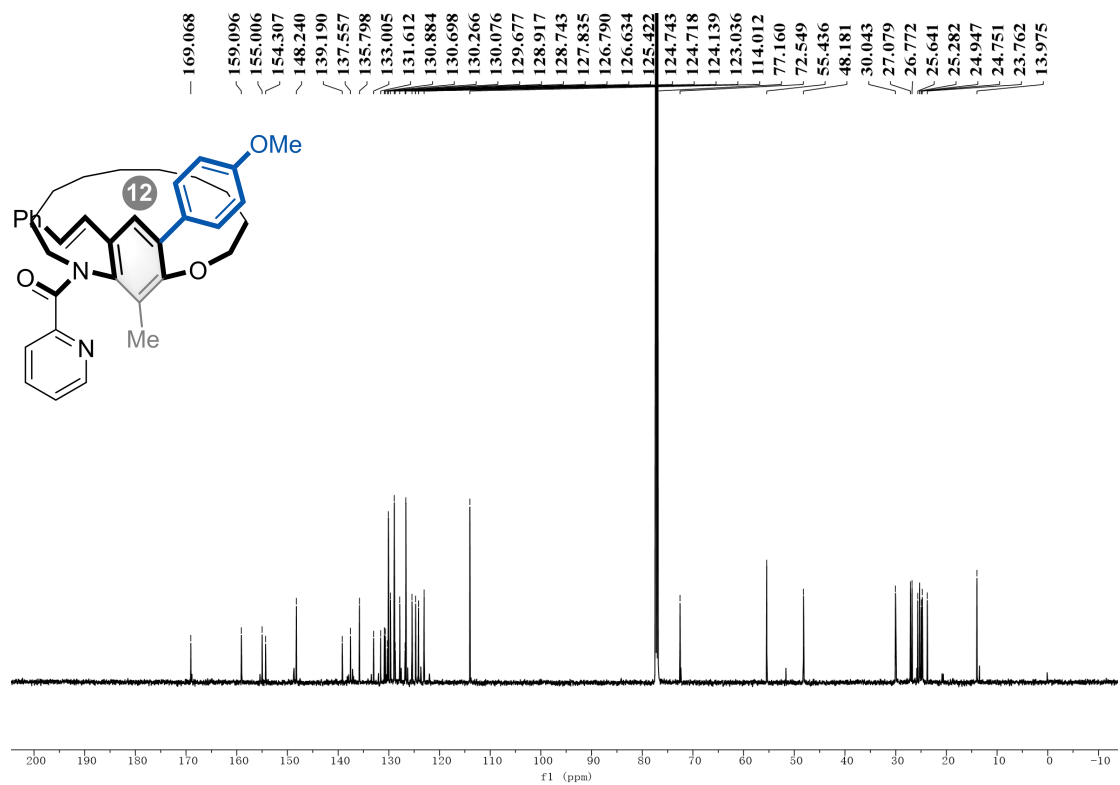
(R<sub>p</sub>)-3ma, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



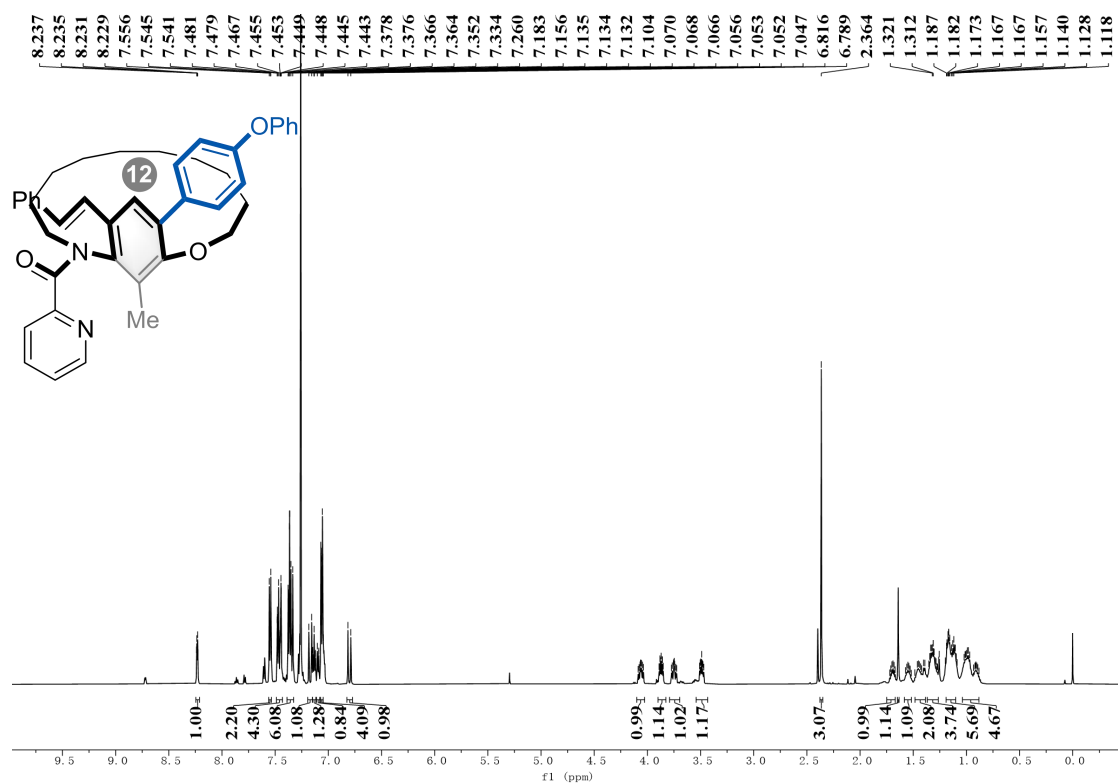
(*R<sub>p</sub>*)-3na, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



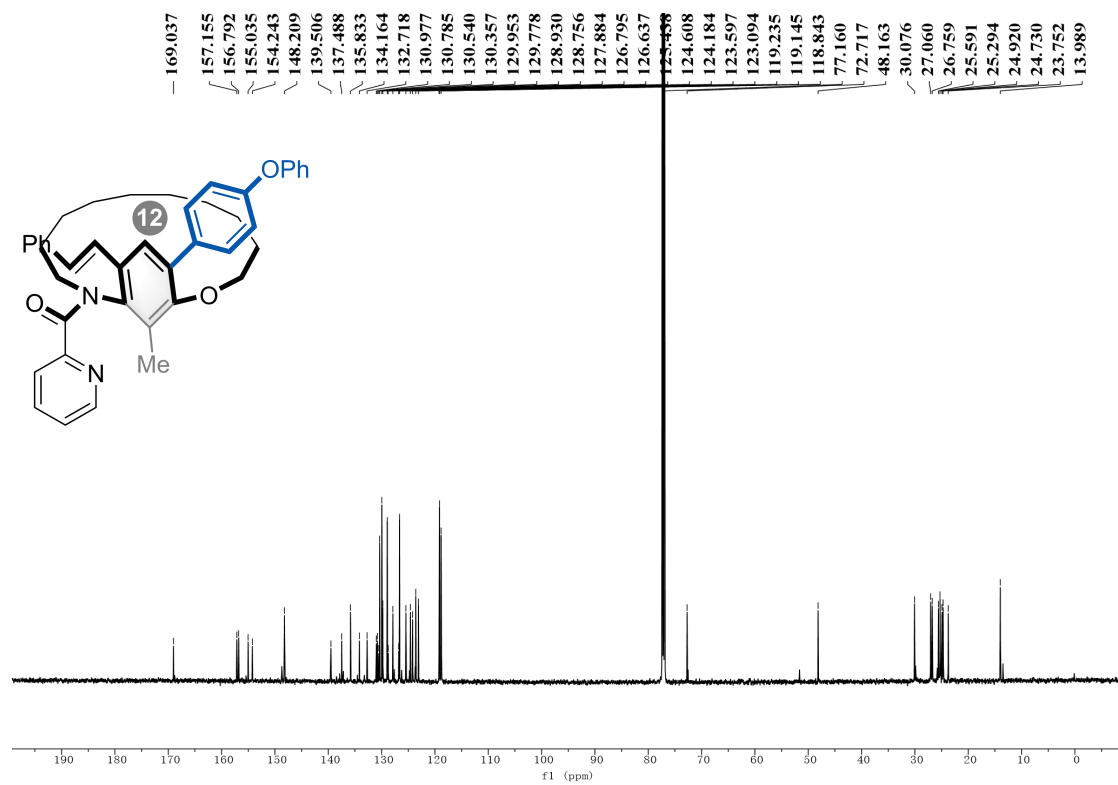
(*R<sub>p</sub>*)-3na, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



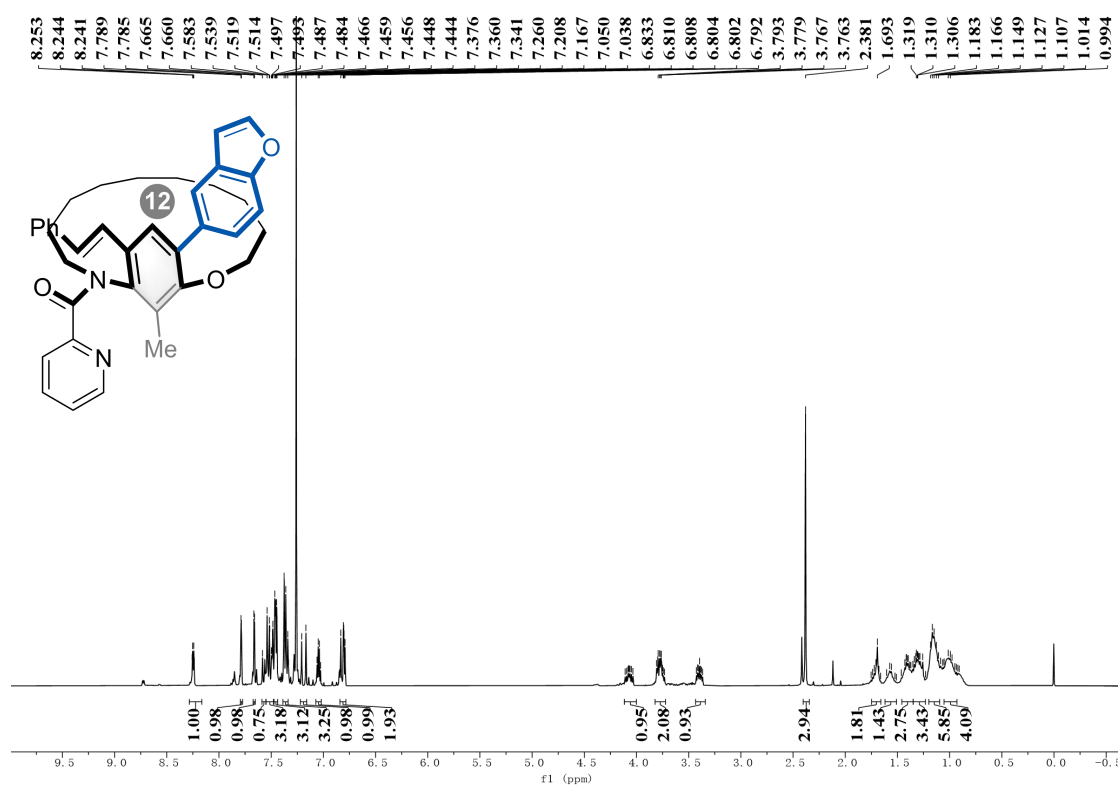
(*R*<sub>p</sub>)-30a, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



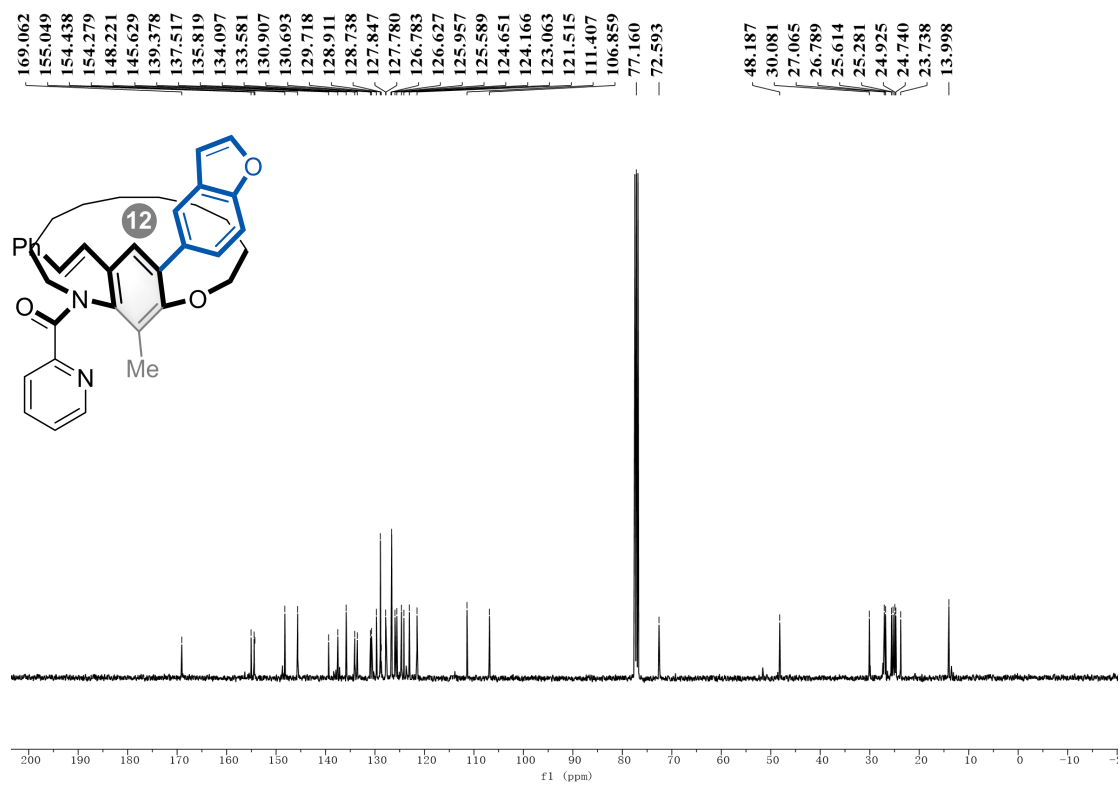
(*R*<sub>p</sub>)-30a, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



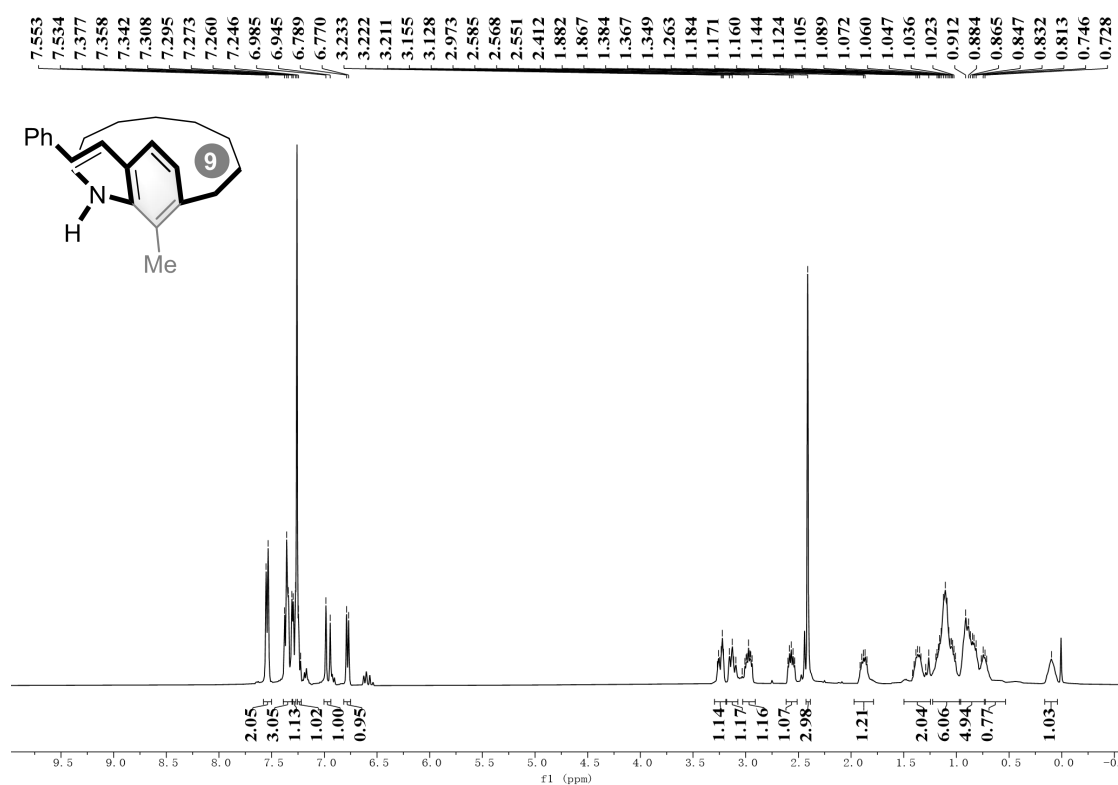
(*R*<sub>p</sub>)-3pa, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



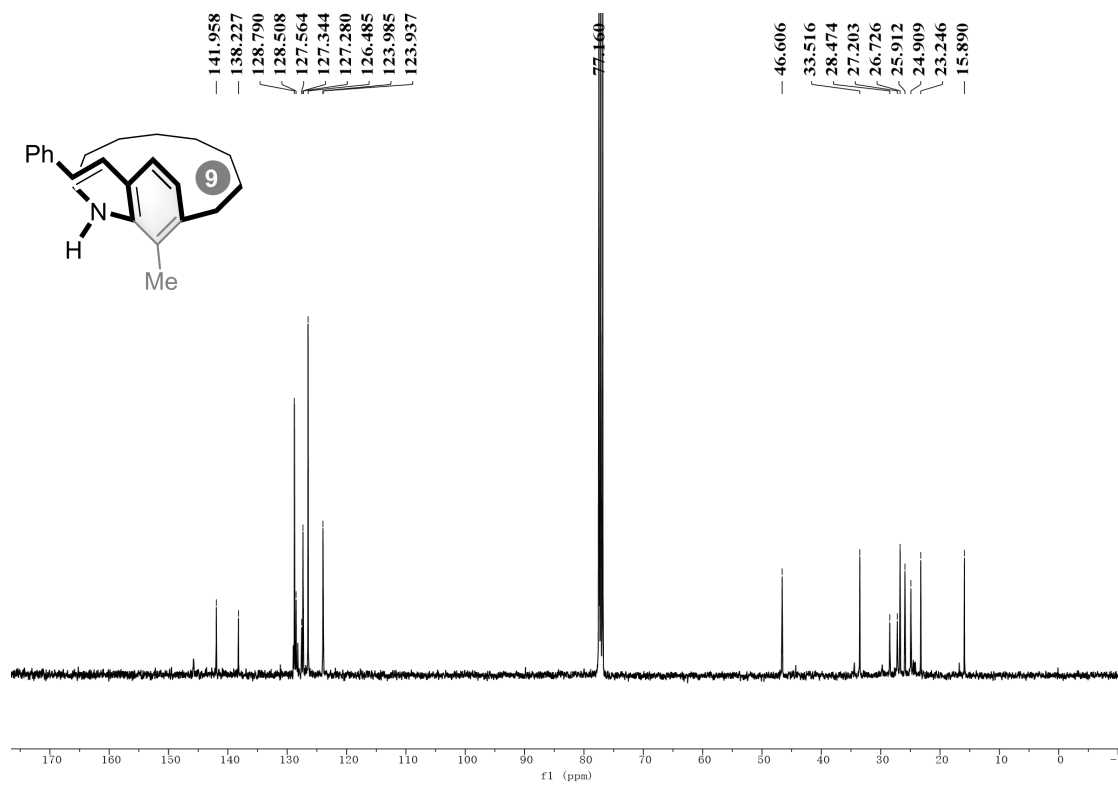
(*R*<sub>p</sub>)-3pa, <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



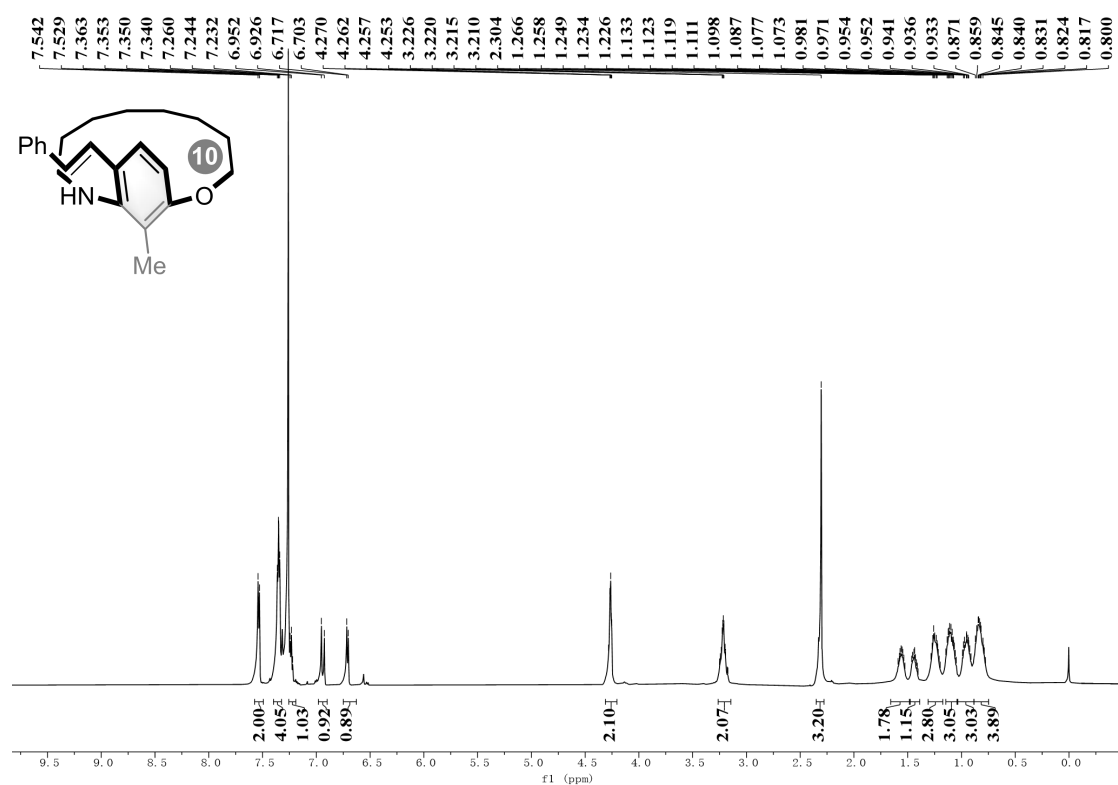
(*R*<sub>p</sub>)-4, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



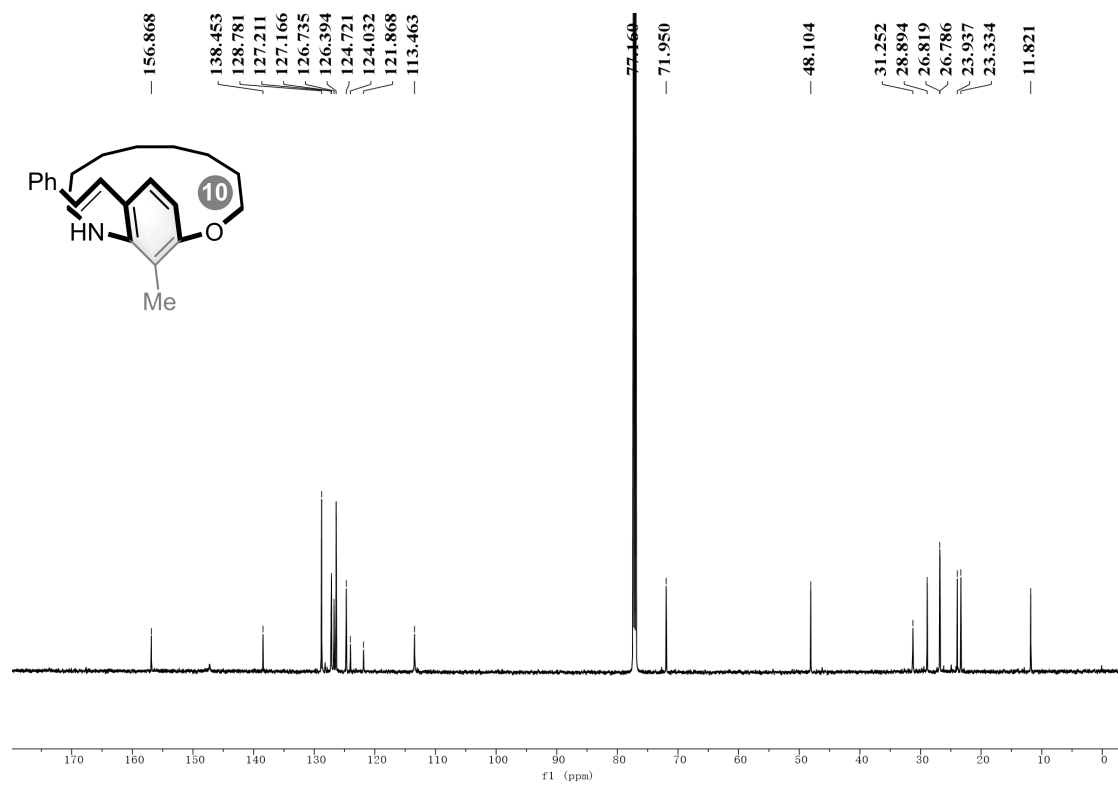
(*R*<sub>p</sub>)-4, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



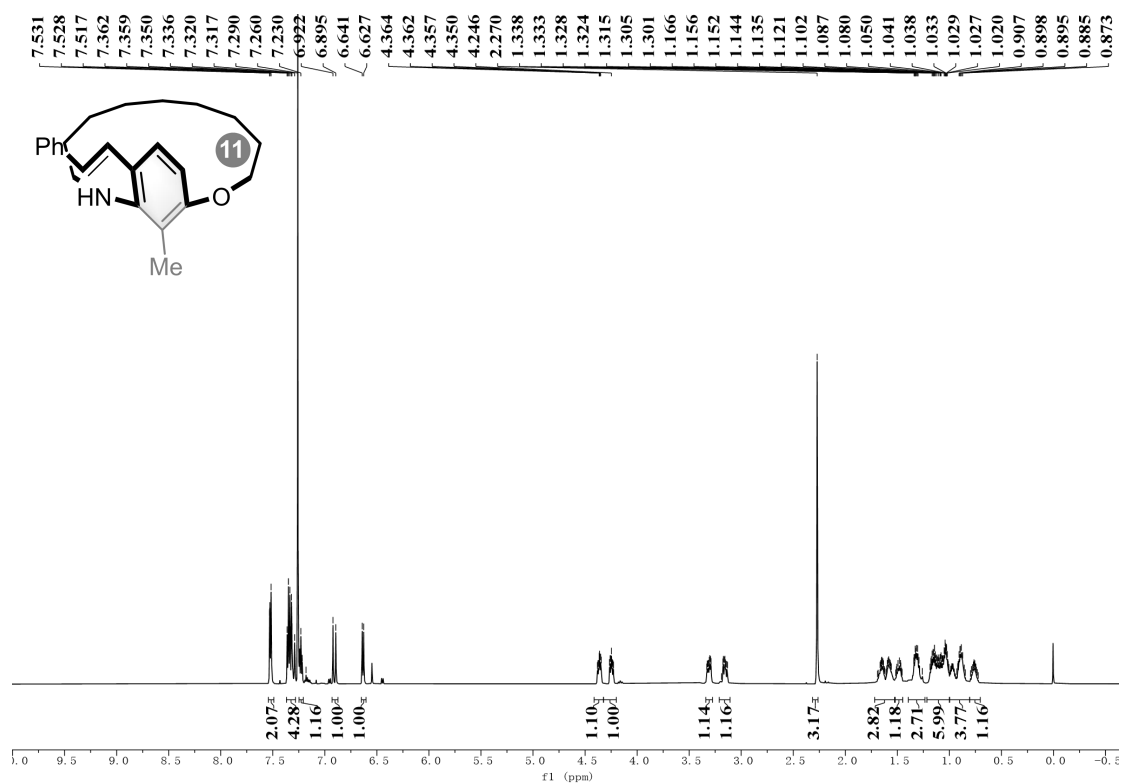
(R<sub>p</sub>)-5, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



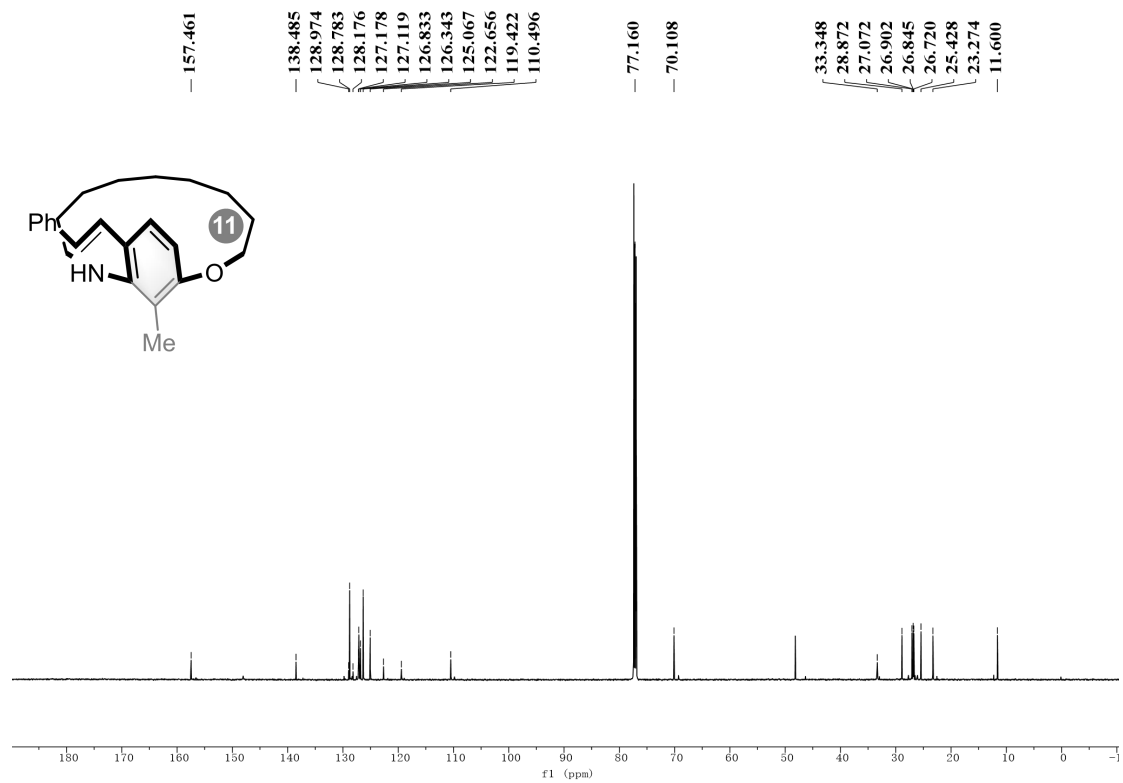
(R<sub>p</sub>)-5, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



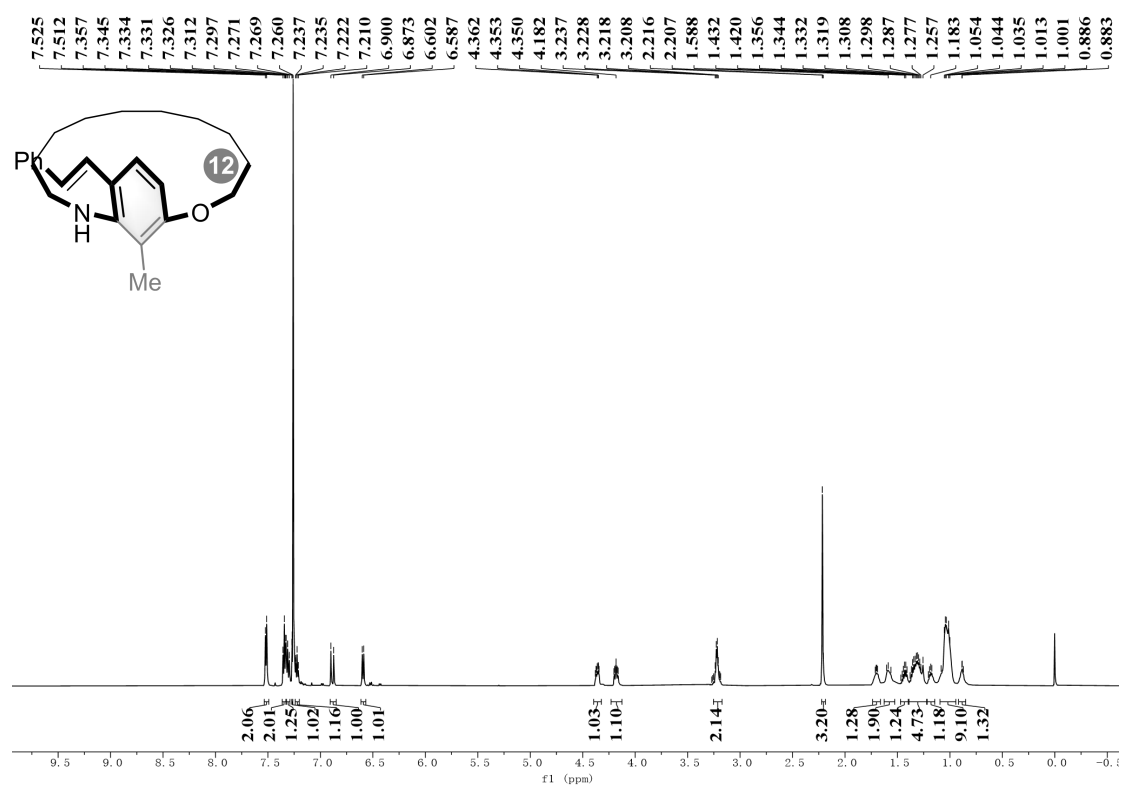
(R<sub>p</sub>)-6, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



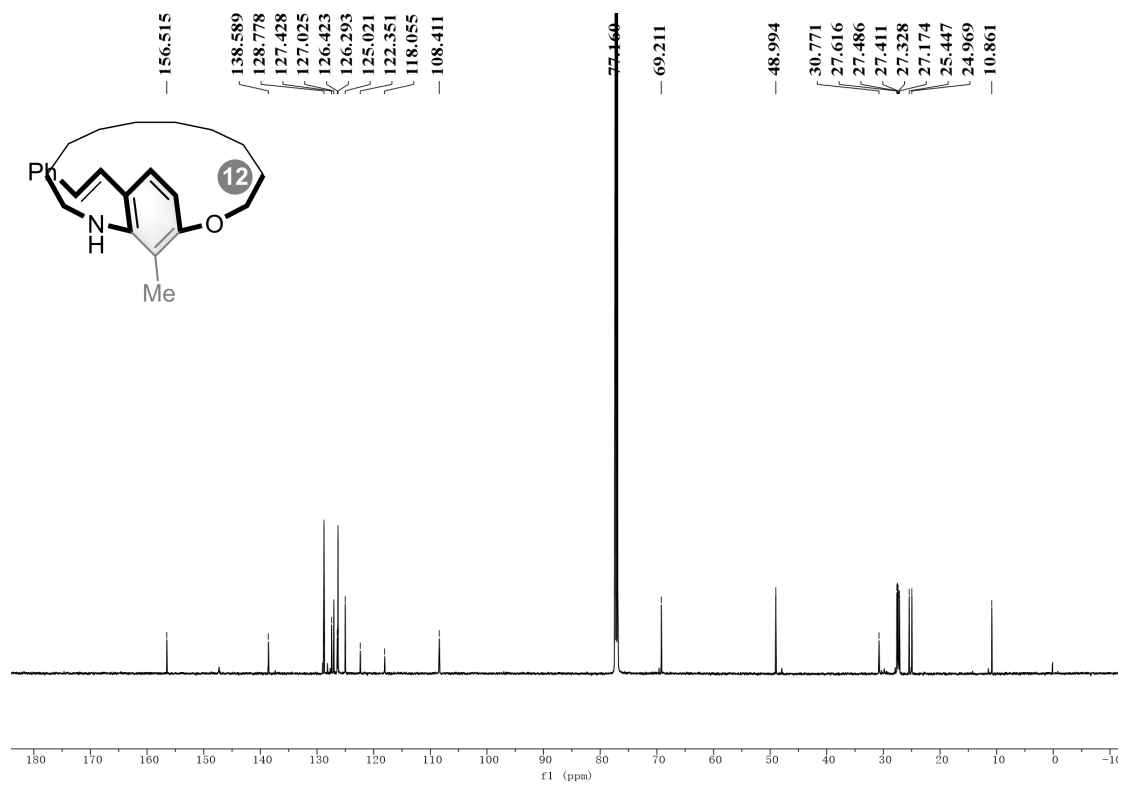
(R<sub>p</sub>)-6, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



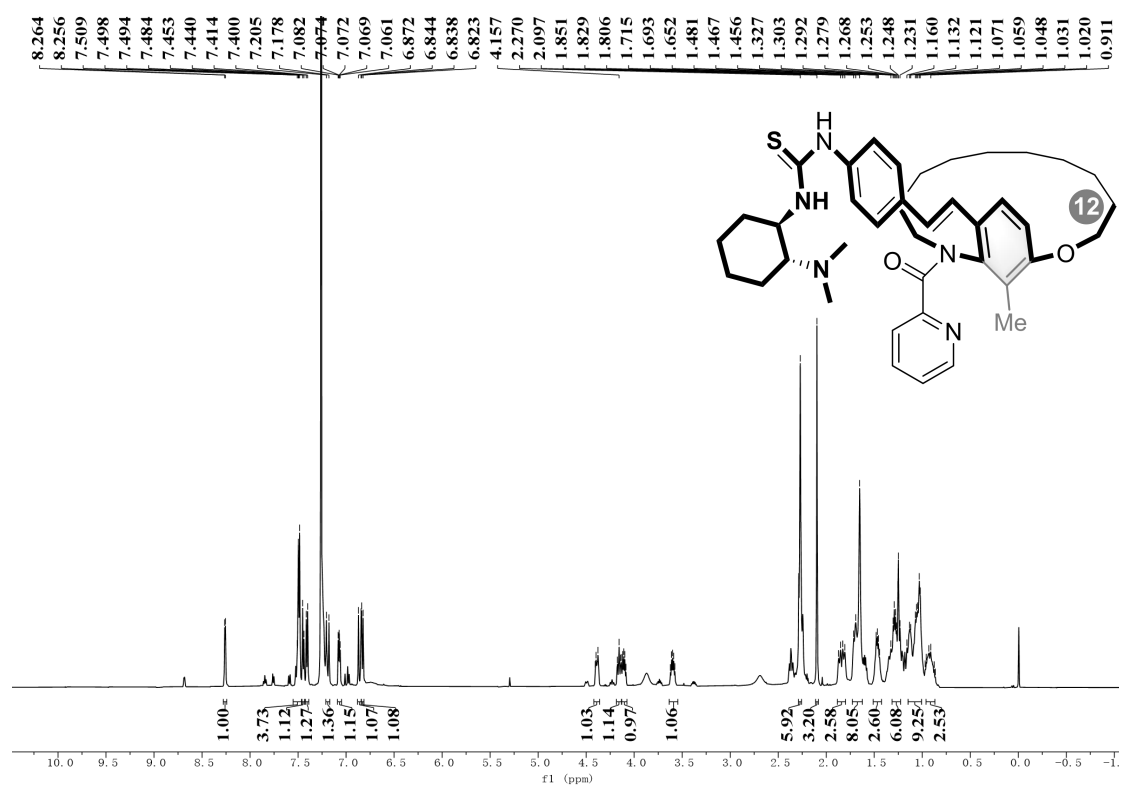
(R<sub>p</sub>)-7, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



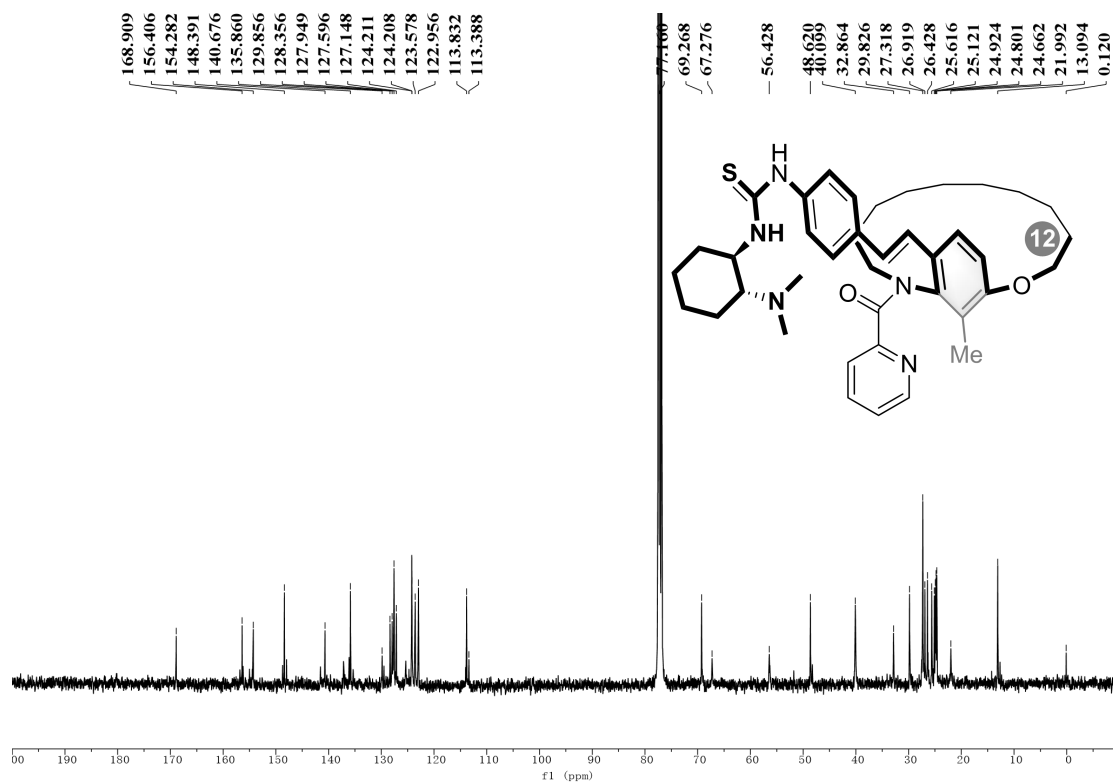
(R<sub>p</sub>)-7, <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)



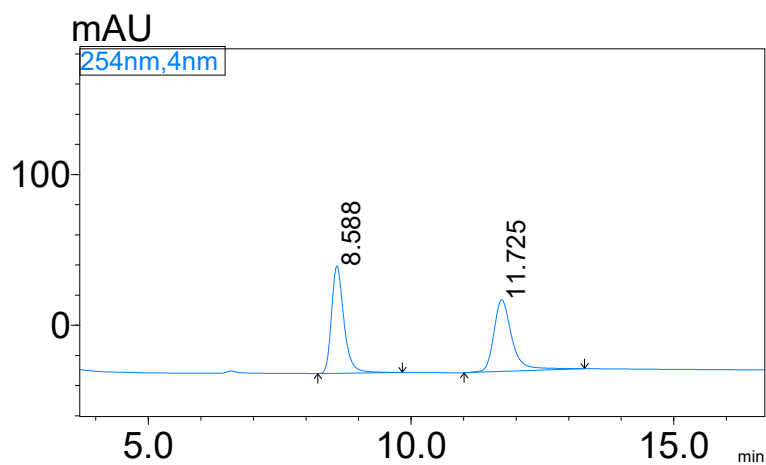
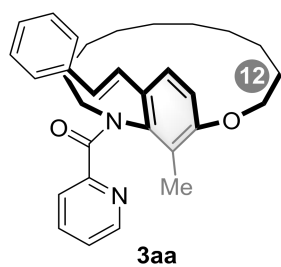
(R<sub>p</sub>)-8, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



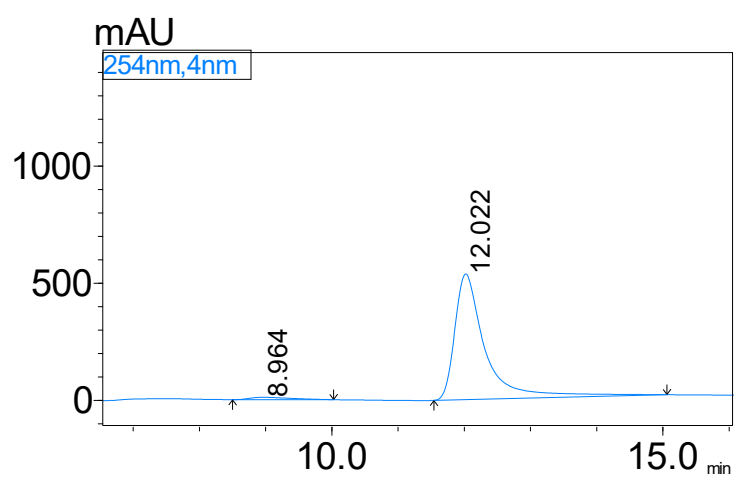
8, <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>)



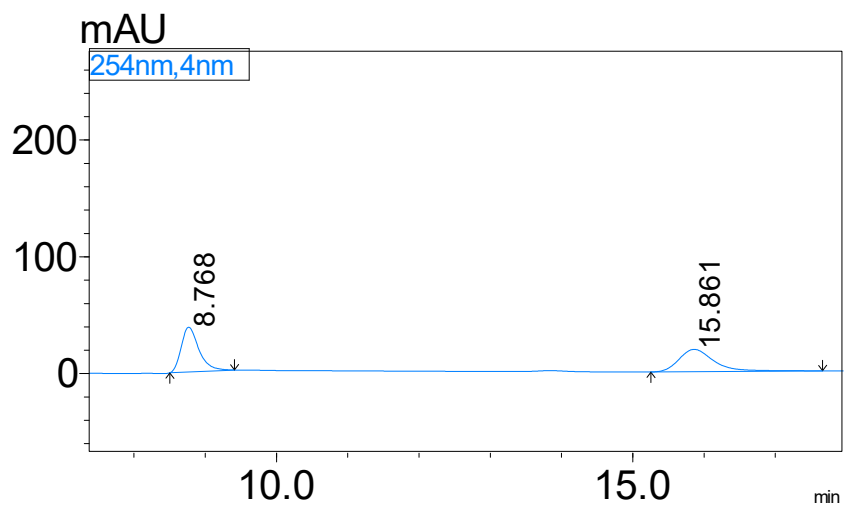
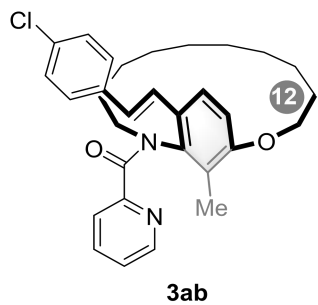
## 10.Copies of HPLC Spectra



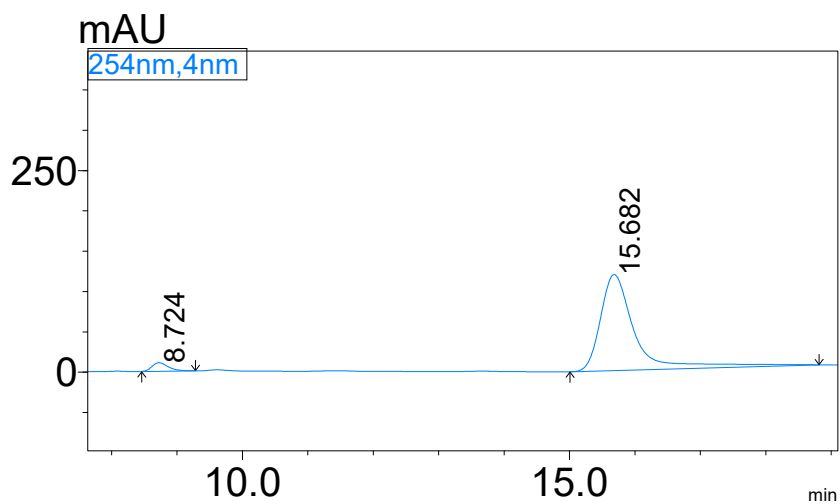
Peak	Time	Area	Height	Area%
1	8.588	1173745	71250	50.472
2	11.725	1151782	47600	49.528



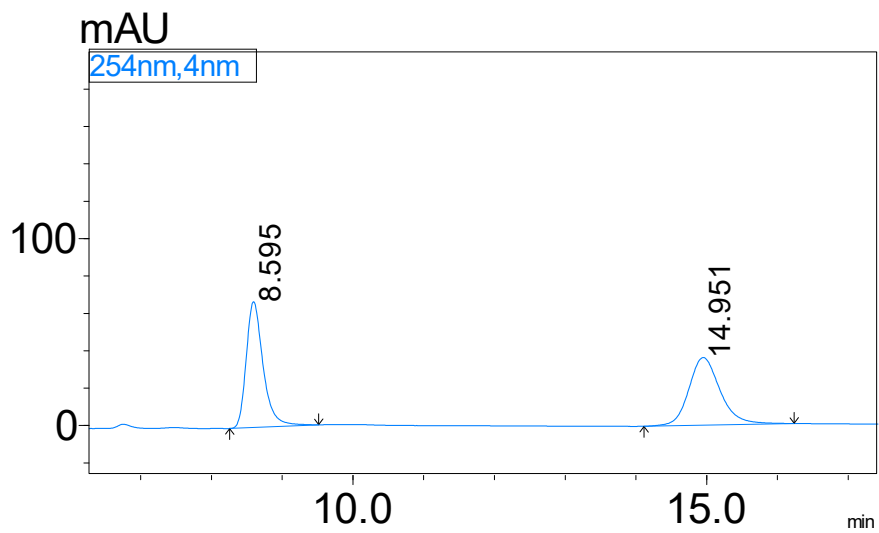
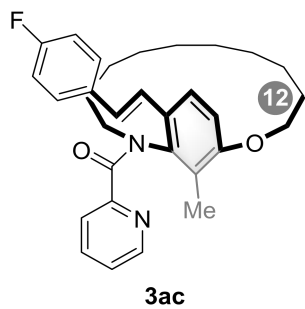
Peak	Time	Area	Height	Area%
1	8.964	430353	9906	2.435
2	12.022	17242557	536445	97.565



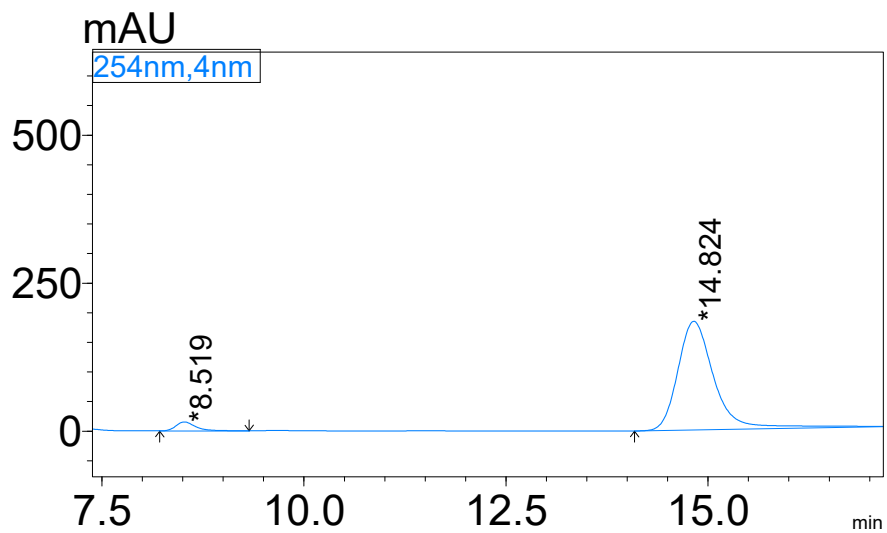
Peak	Time	Area	Height	Area%
1	8.768	665031	38350	50.221
2	15.861	659177	19155	49.779



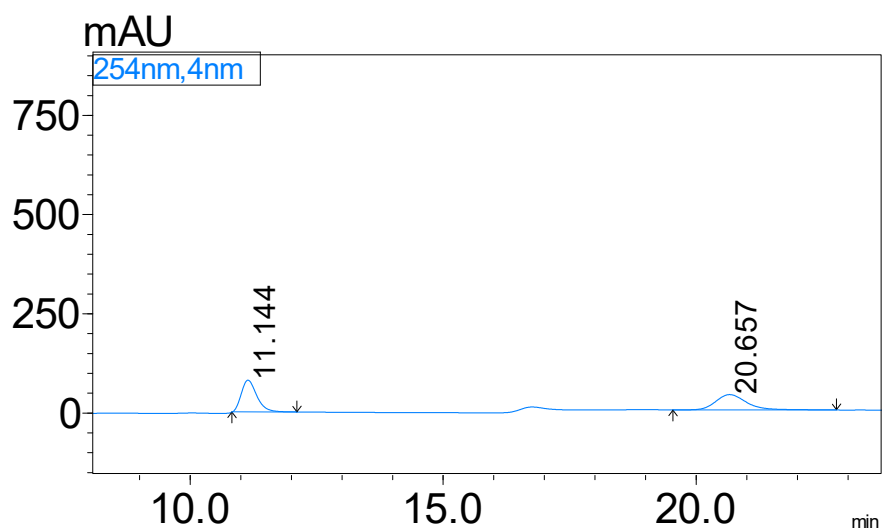
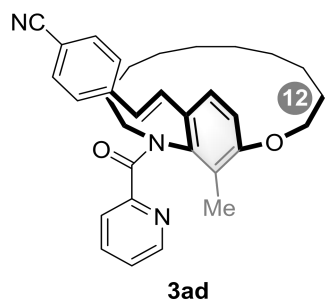
Peak	Time	Area	Height	Area%
1	8.724	185186	10679	4.091
2	15.682	4341010	119008	95.909



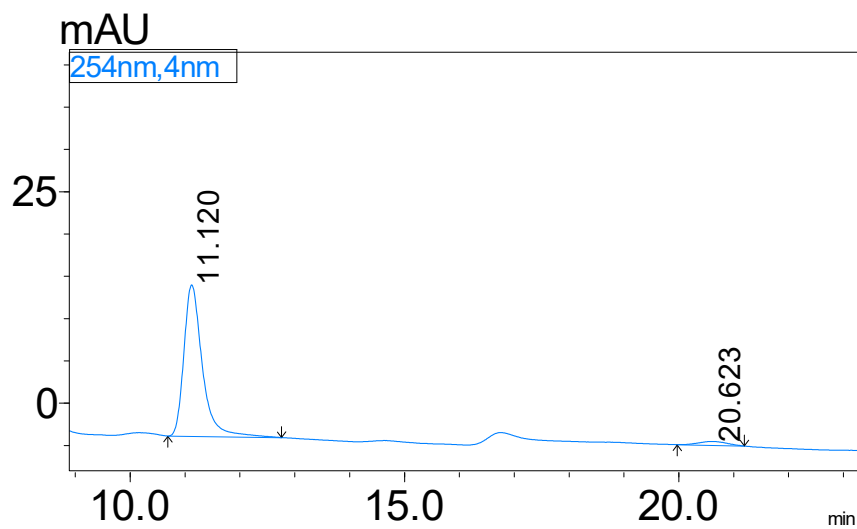
Peak	Time	Area	Height	Area%
1	8.595	1121232	67341	50.074
2	14.951	1117938	36205	49.926



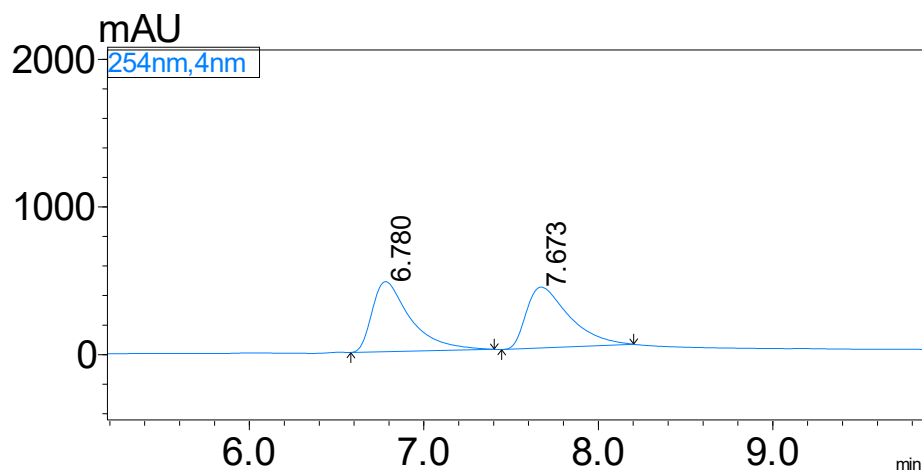
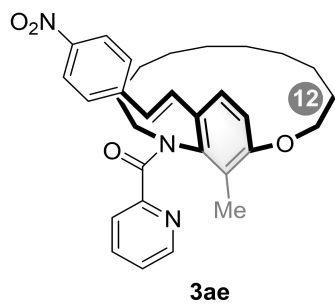
Peak	Time	Area	Height	Area%
1	8.519	280503	15455	4.588
2	14.824	5832850	183665	95.412



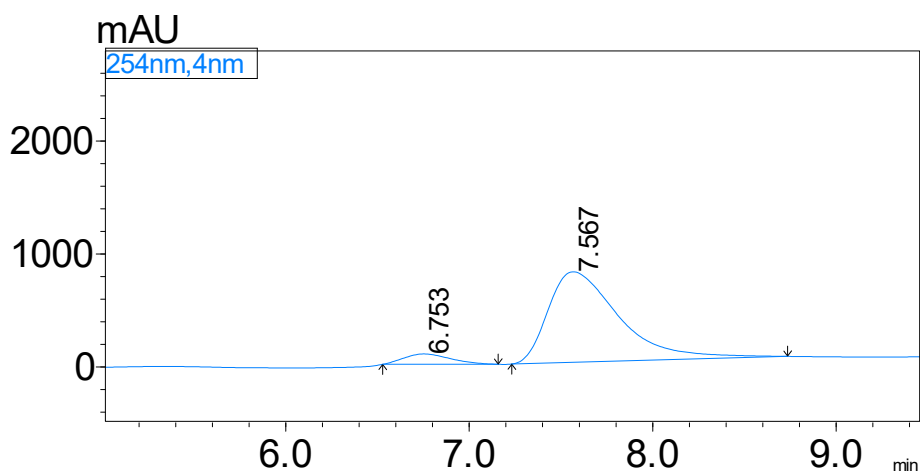
Peak	Time	Area	Height	Area%
1	11.144	1656966	79491	50.548
2	20.657	1621039	38487	49.452



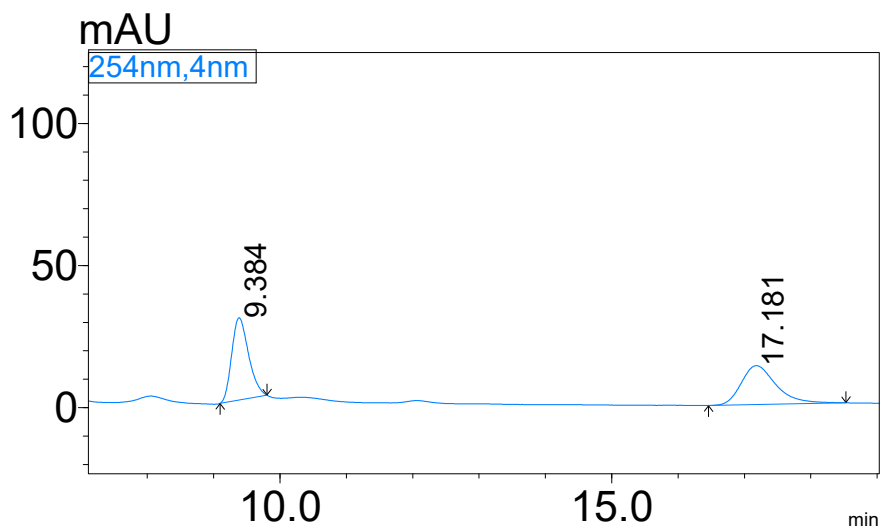
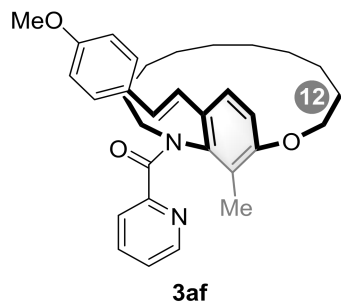
Peak	Time	Area	Height	Area%
1	11.120	421113	17901	96.195
2	20.623	16656	471	3.805



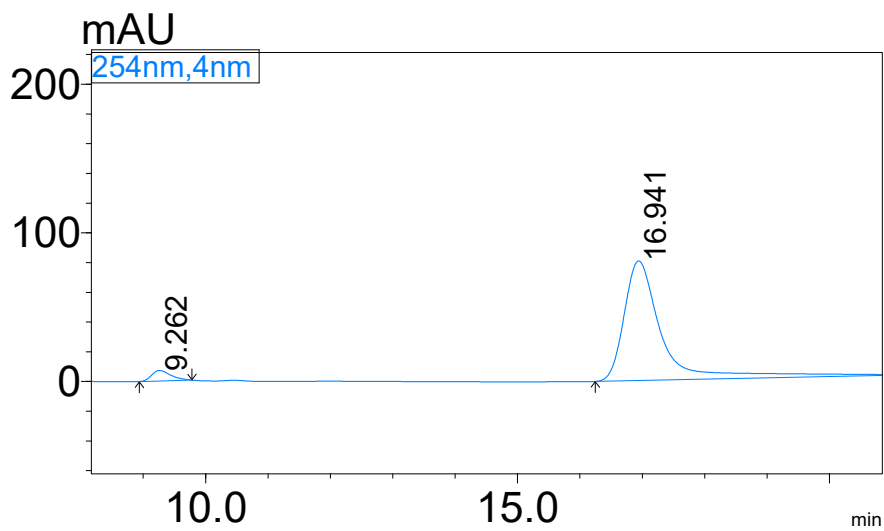
Peak	Time	Area	Height	Area%
1	6.780	7263015	474691	50.619
2	7.673	7085470	412833	49.381



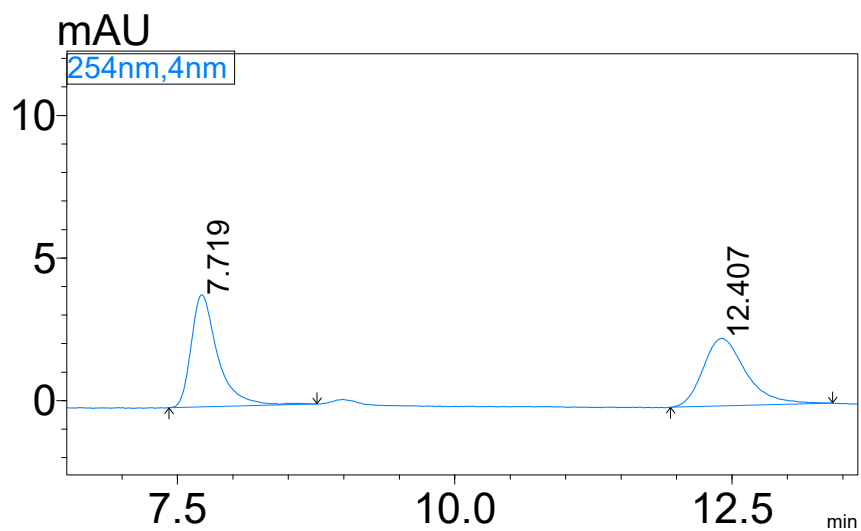
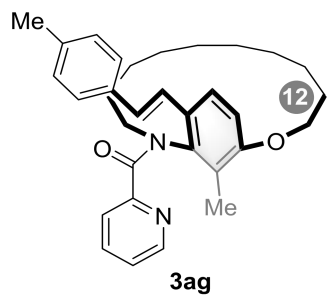
Peak	Time	Area	Height	Area%
1	6.753	1624015	91964	6.990
2	7.567	21609579	801620	93.010



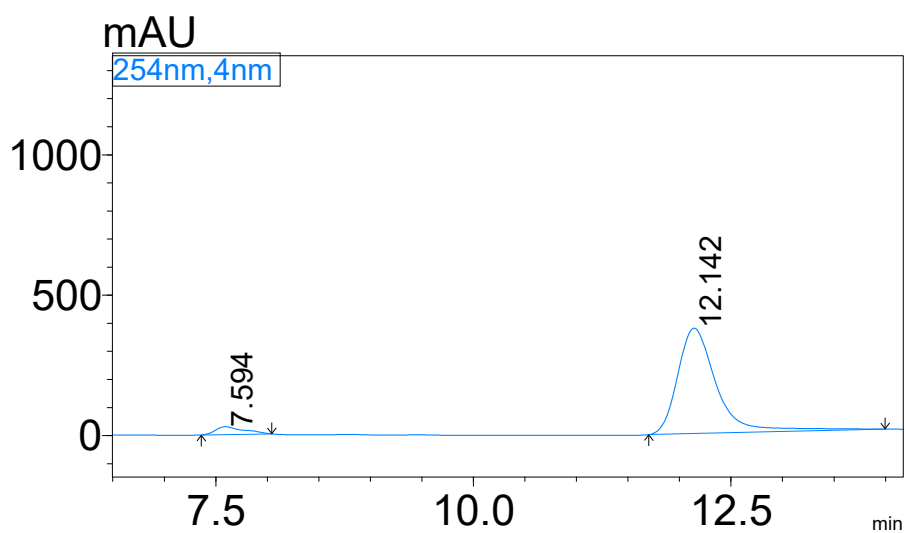
Peak	Time	Area	Height	Area%
1	9.384	511860	28967	50.541
2	17.181	500895	13685	49.459



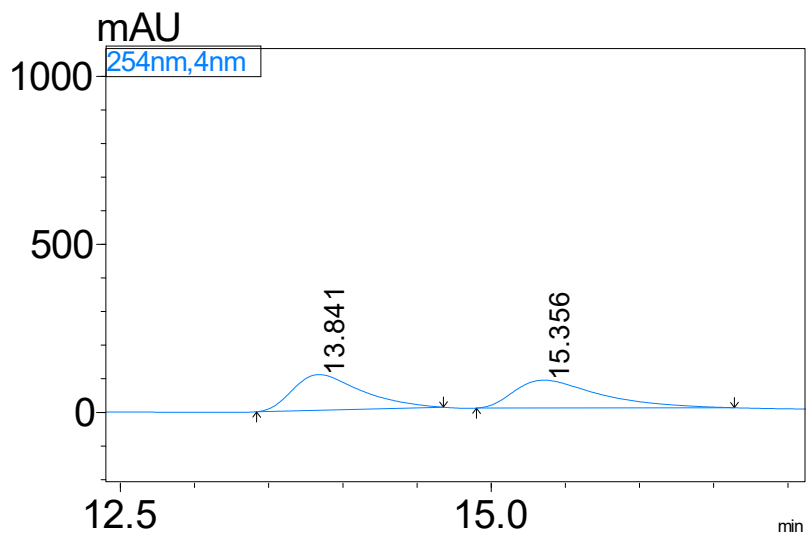
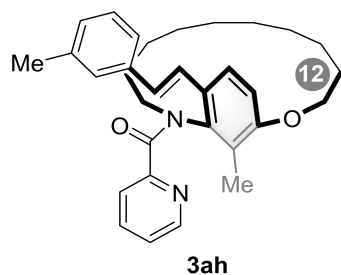
Peak	Time	Area	Height	Area%
1	9.262	152323	7101	4.219
2	16.941	3458012	80485	95.781



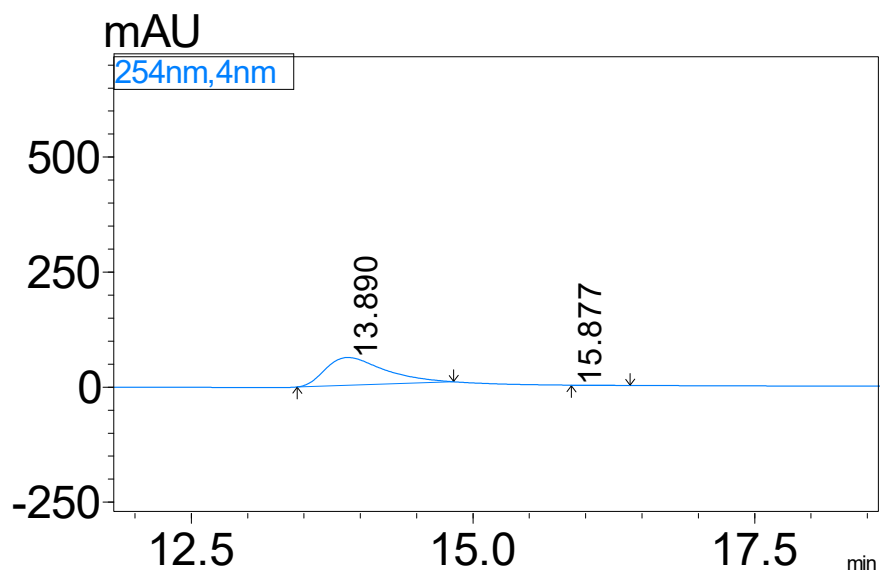
Peak	Time	Area	Height	Area%
1	7.719	65593	3932	50.733
2	12.407	63697	2371	49.267



Peak	Time	Area	Height	Area%
1	7.594	539637	28033	5.188
2	12.142	9861722	375228	94.812

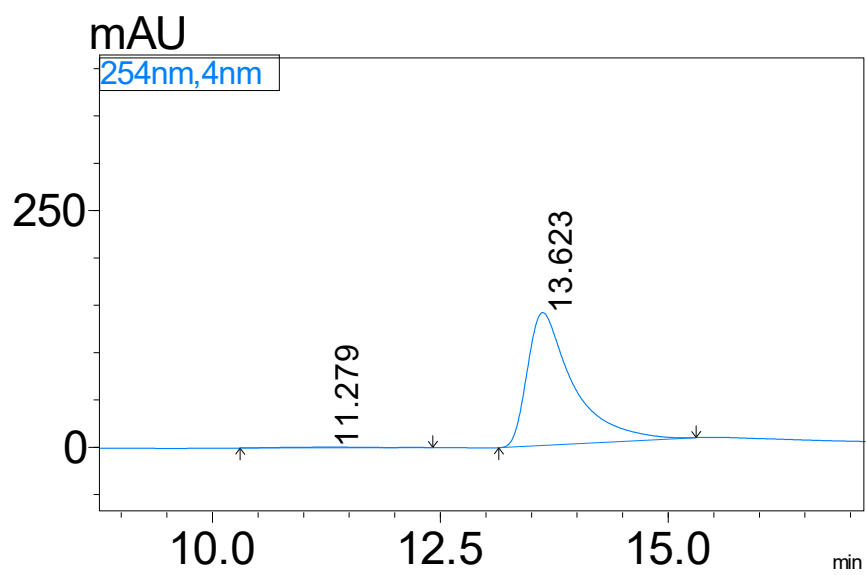


Peak	Time	Area	Height	Area%
1	13.841	3432259	106110	50.782
2	15.356	3326542	83028	49.218



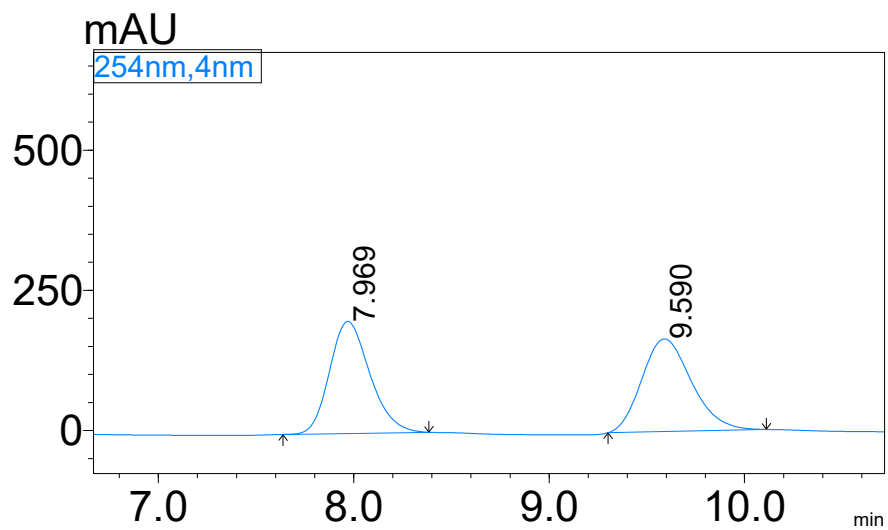
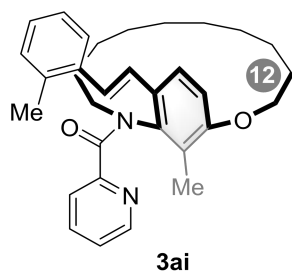
Note: 1a was 0.1 mmol.

Peak	Time	Area	Height	Area%
1	13.890	2204037	60351	99.566
2	15.877	9600	492	0.434

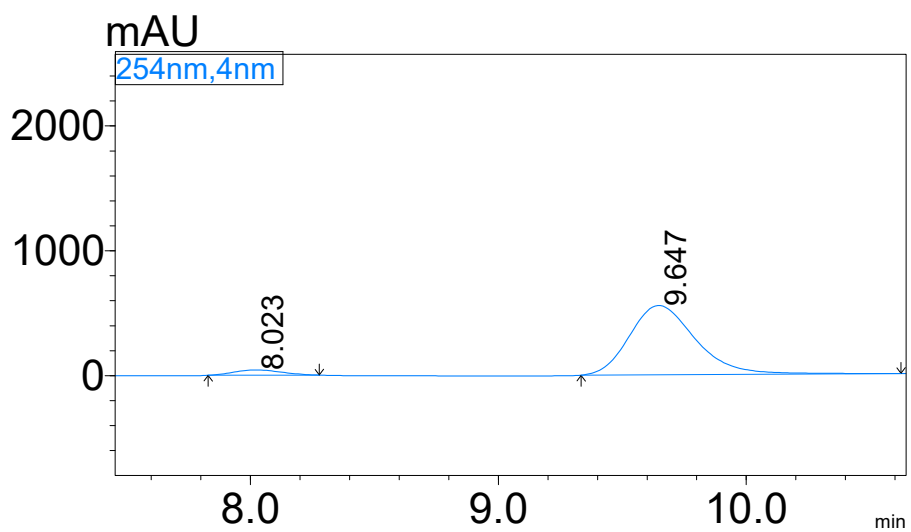


Note: **1a** was 1.5 mmol (Gram-up).

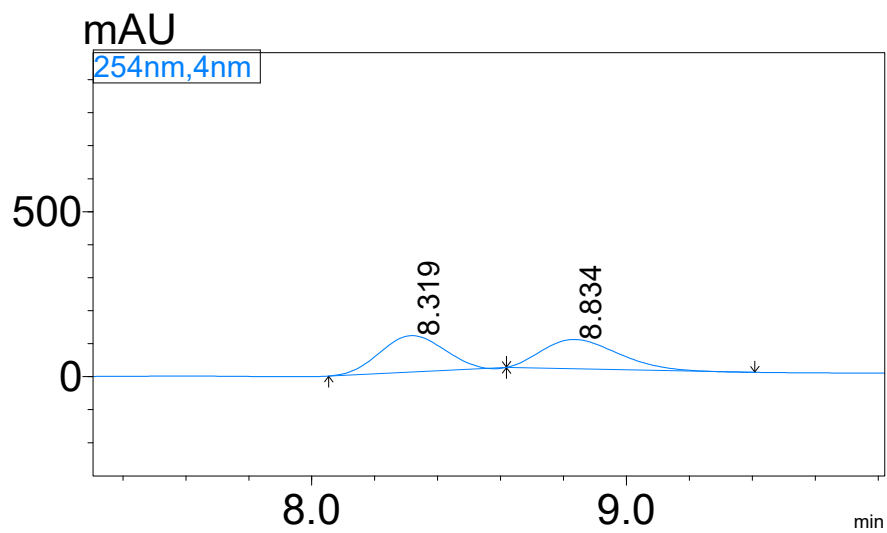
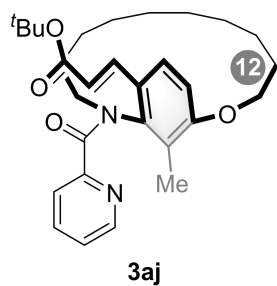
Peak	Time	Area	Height	Area%
1	11.279	51002	817	1.025
2	13.623	4925651	140337	98.975



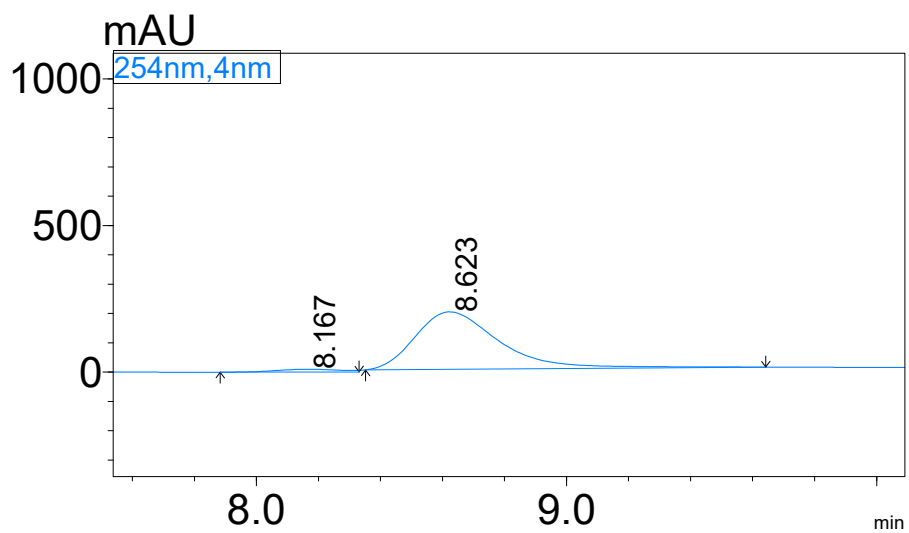
Peak	Time	Area	Height	Area%
1	7.969	2864843	200024	49.474
2	9.590	2925725	165402	50.526



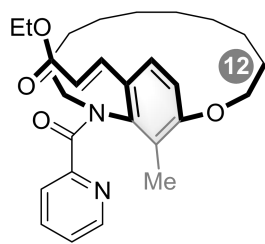
Peak	Time	Area	Height	Area%
1	8.023	560627	42183	5.165
2	9.647	10293066	554549	94.835



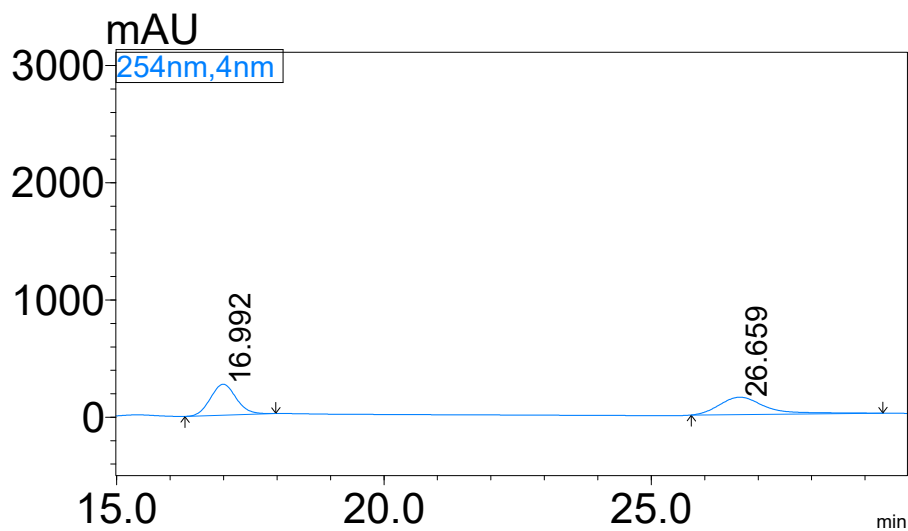
Peak	Time	Area	Height	Area%
1	8.319	1556238	110325	50.995
2	8.834	1495507	88883	49.005



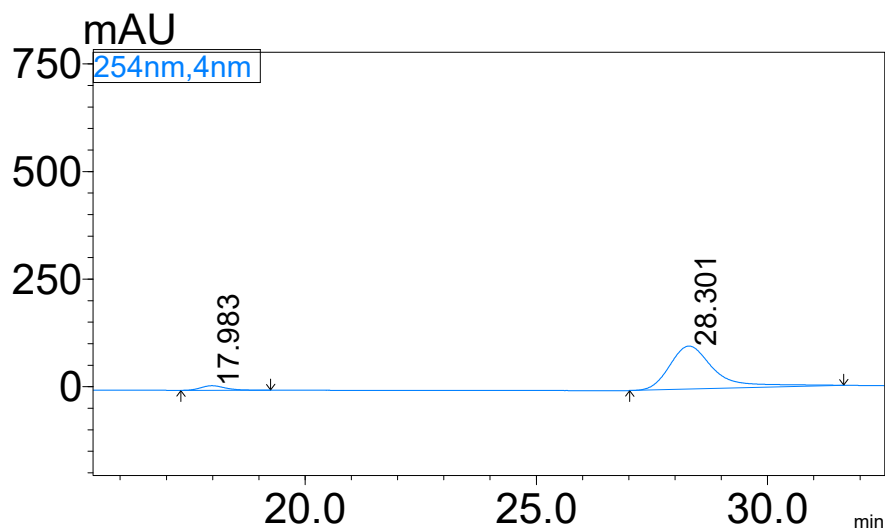
Peak	Time	Area	Height	Area%
1	8.167	144929	10027	3.777
2	8.623	3692568	195679	96.223



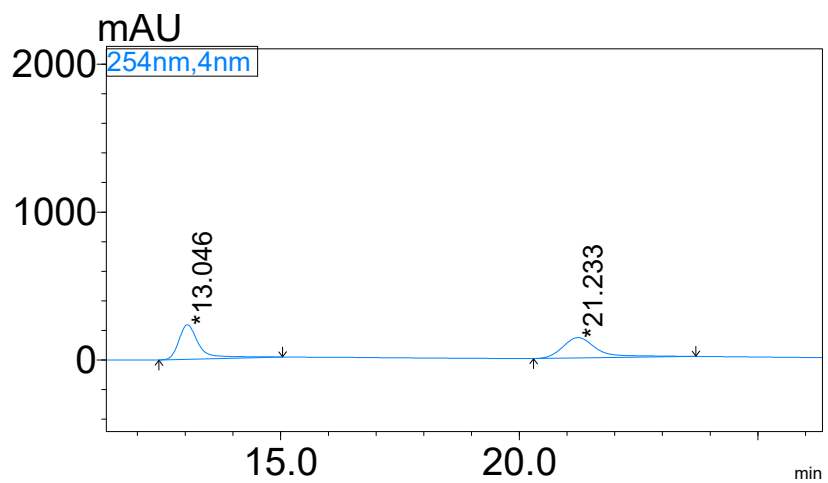
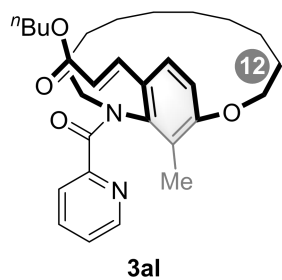
3ak



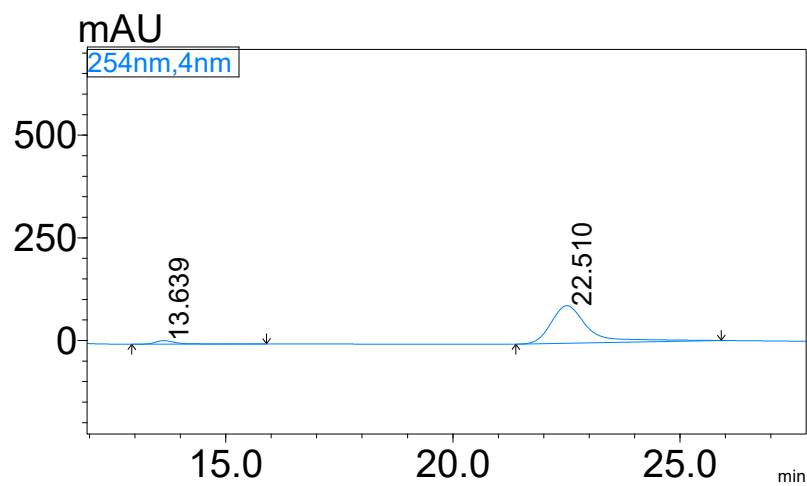
Peak	Time	Area	Height	Area%
1	16.992	8915061	264273	50.008
2	26.659	8912035	148071	49.992



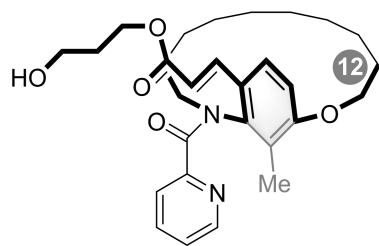
Peak	Time	Area	Height	Area%
1	17.983	393255	10651	5.477
2	28.301	6786386	100080	94.523



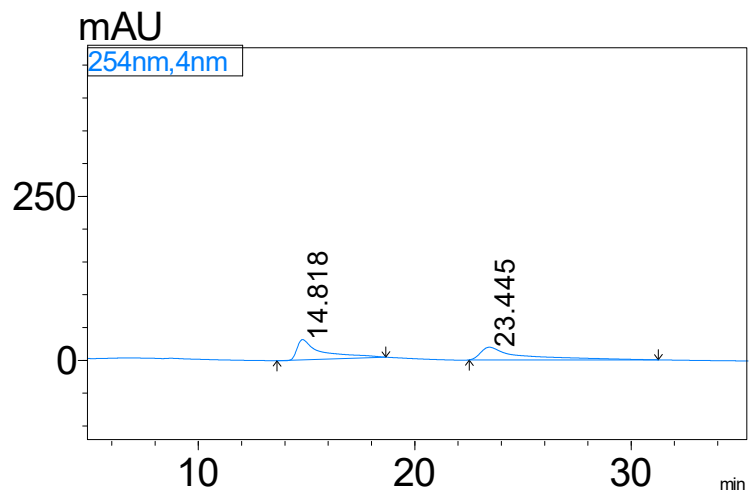
Peak	Time	Area	Height	Area%
1	13.046	6958061	233288	49.842
2	21.233	7002121	137923	50.158



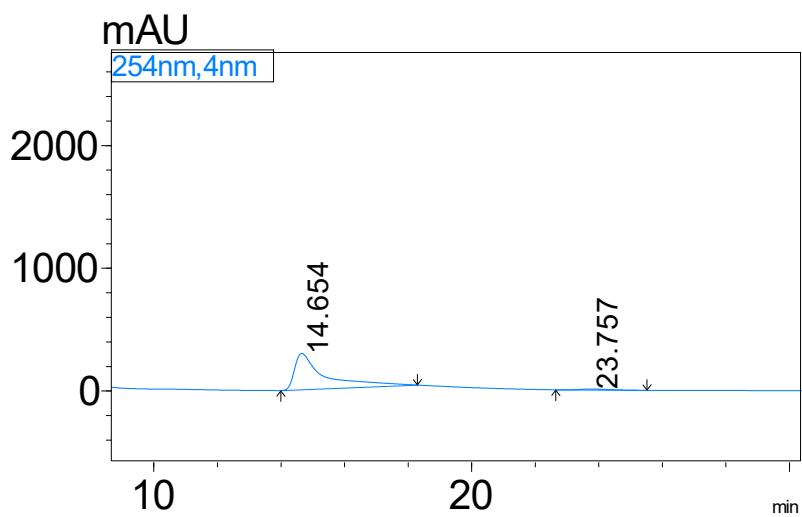
Peak	Time	Area	Height	Area%
1	13.639	272232	8363	4.946
2	22.510	5231807	91407	95.054



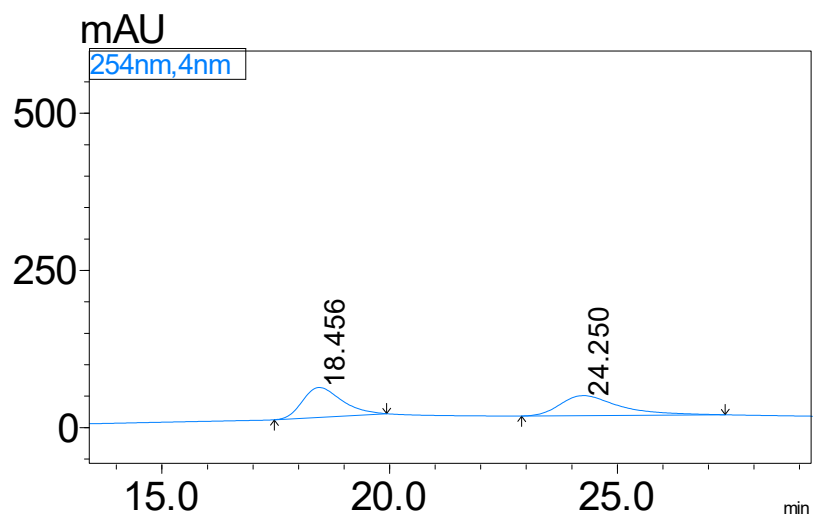
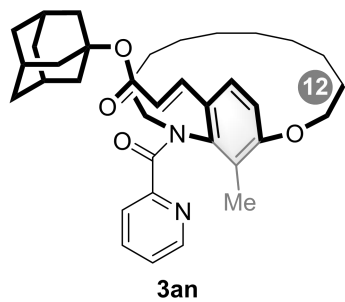
3am



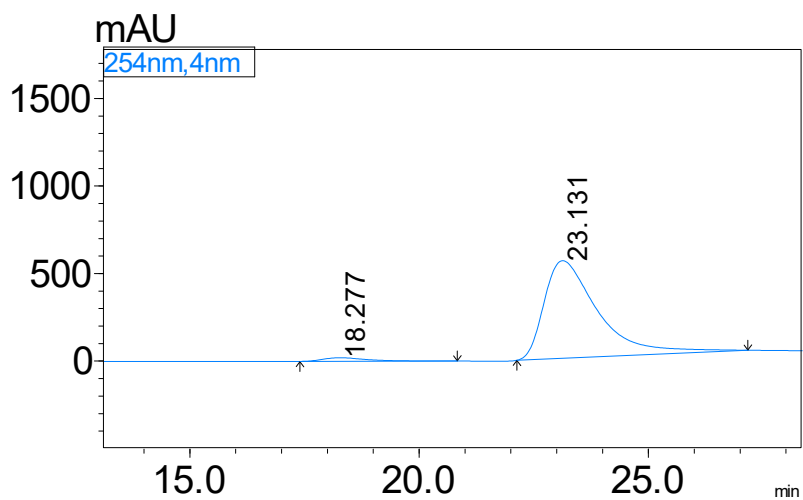
Peak	Time	Area	Height	Area%
1	14.818	2451930	30900	49.651
2	23.445	2486386	19288	50.349



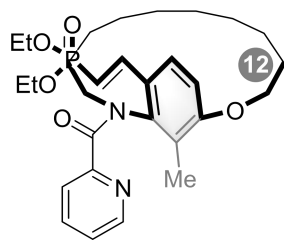
Peak	Time	Area	Height	Area%
1	14.654	19618623	295525	97.415
2	23.757	520650	7668	2.585



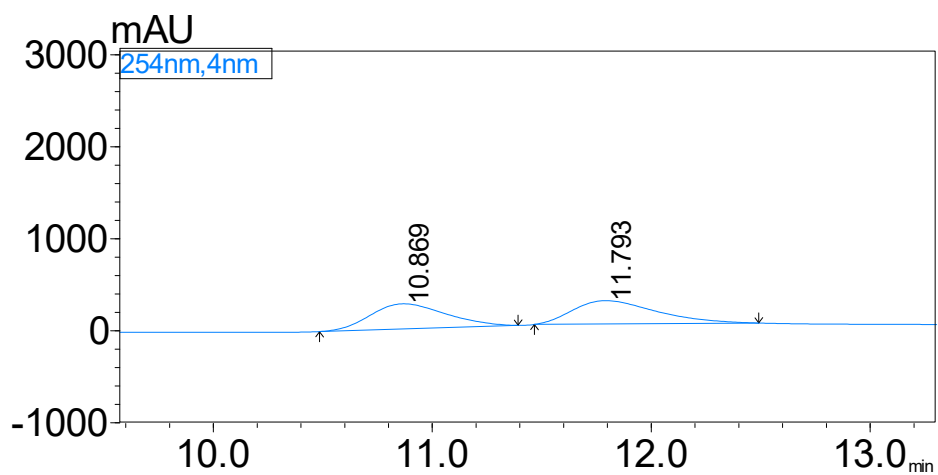
Peak	Time	Area	Height	Area%
1	18.456	2870815	47429	49.919
2	24.250	2880106	31802	50.081



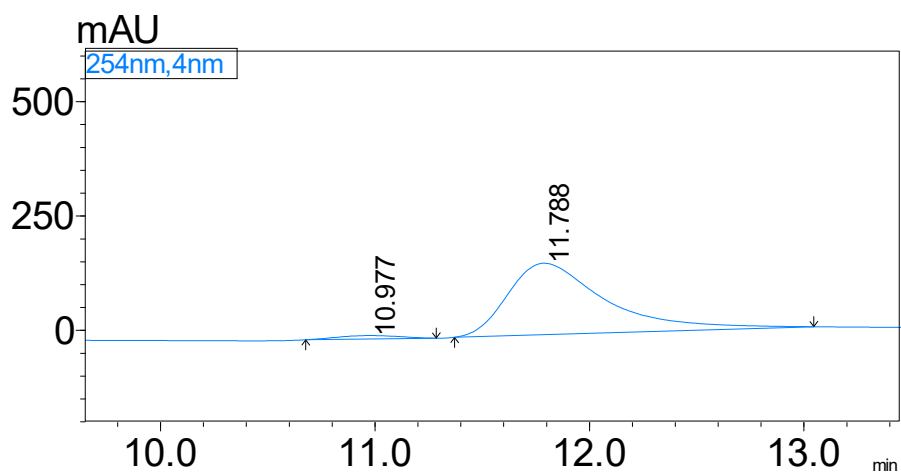
Peak	Time	Area	Height	Area%
1	18.277	1374528	20651	2.928
2	23.131	45576529	557523	97.072



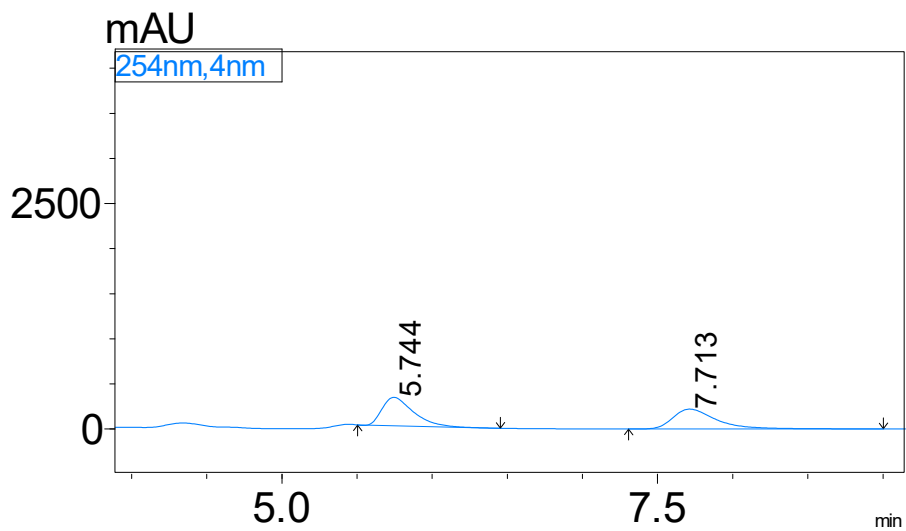
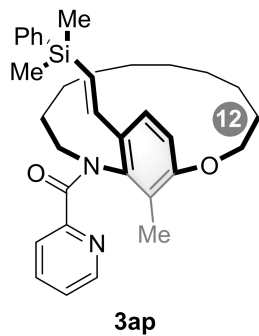
3ao



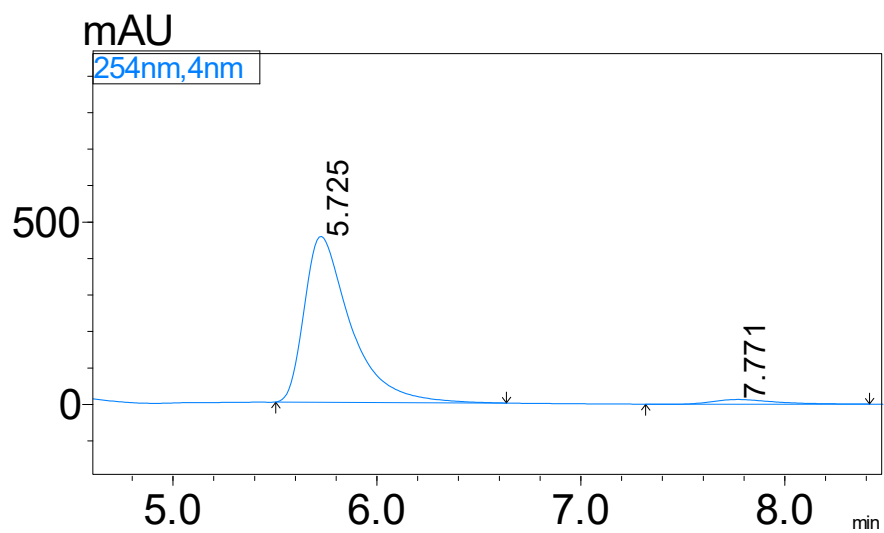
Peak	Time	Area	Height	Area%
1	15.931	1298959	33796	50.551
2	18.528	1270660	28270	49.449



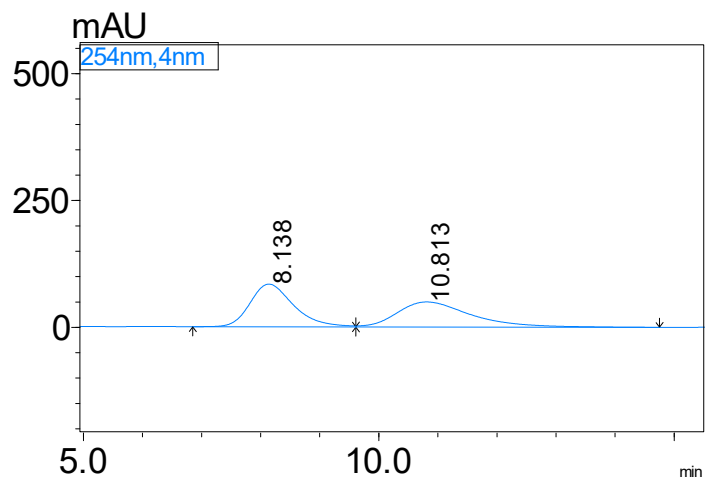
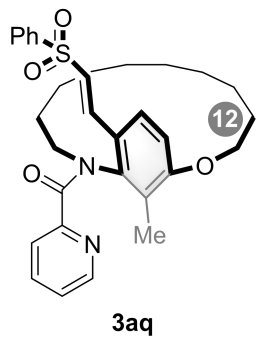
Peak	Time	Area	Height	Area%
1	10.977	152452	7468	2.977
2	11.788	4968713	156282	97.023



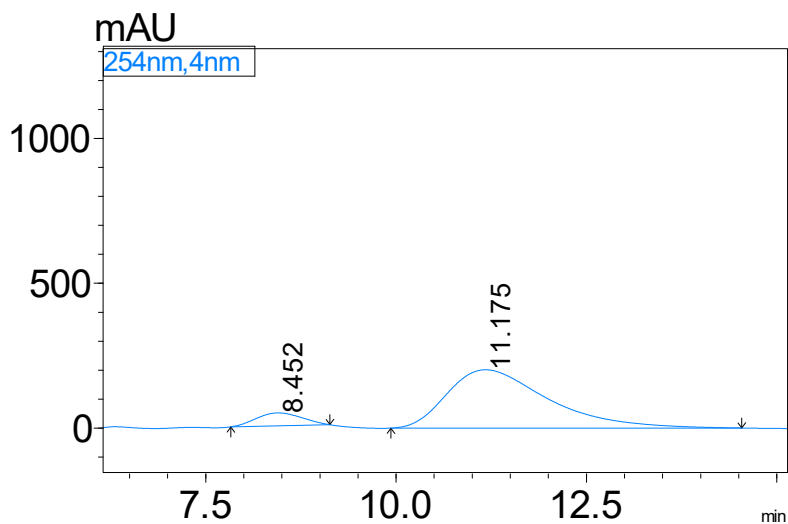
Peak	Time	Area	Height	Area%
1	5.744	4553245	315350	50.629
2	7.713	4440047	220808	49.371



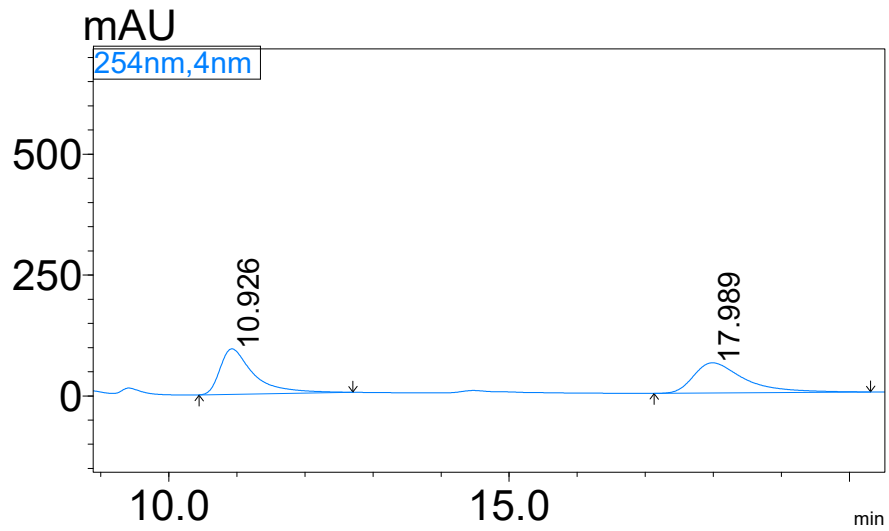
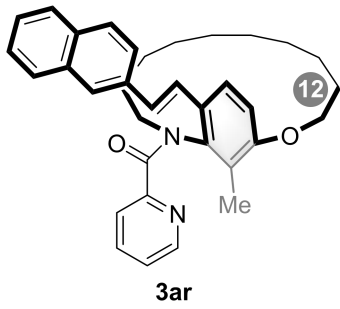
Peak	Time	Area	Height	Area%
1	5.725	7180535	454241	96.448
2	7.771	264417	12753	3.552



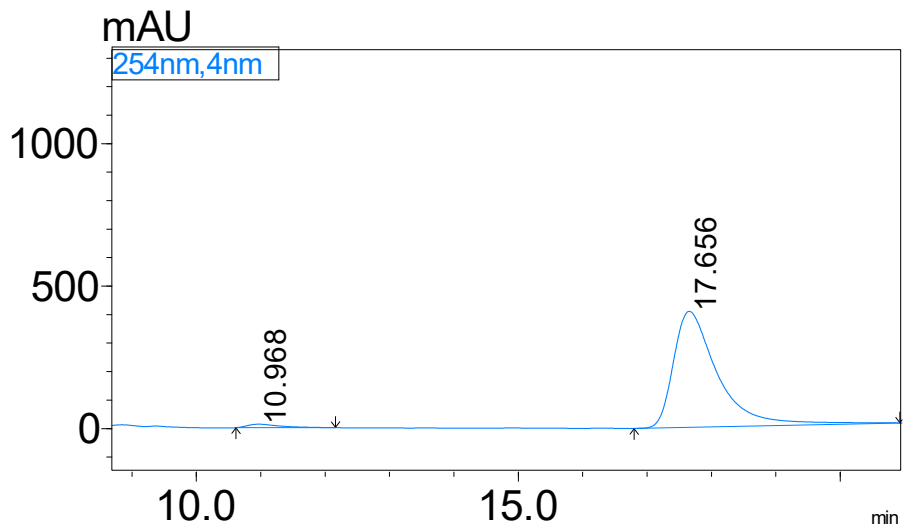
Peak	Time	Area	Height	Area%
1	8.138	4323404	84190	50.123
2	10.813	4302108	49443	49.877



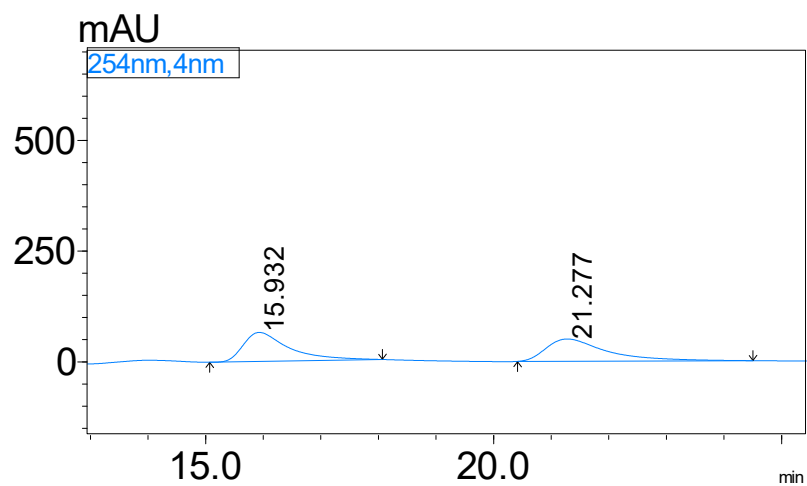
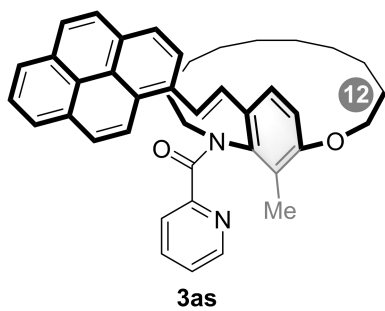
Peak	Time	Area	Height	Area%
1	8.452	1853375	44598	9.073
2	11.175	18573229	201330	90.927



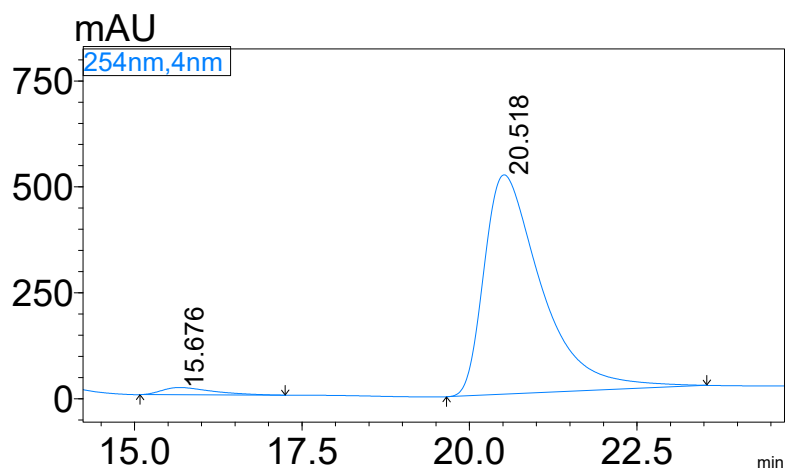
Peak	Time	Area	Height	Area%
1	10.926	3259968	94096	50.019
2	17.989	3257457	62509	49.981



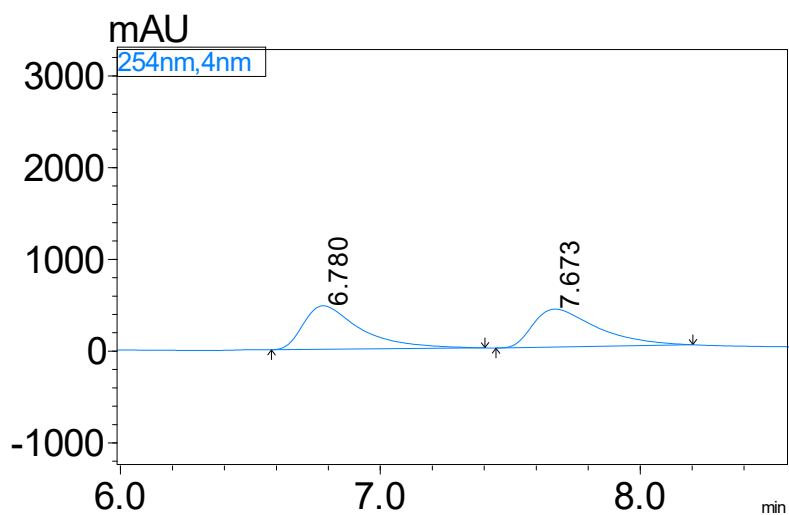
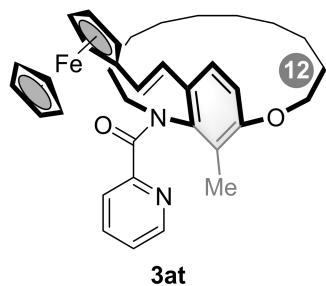
Peak	Time	Area	Height	Area%
1	10.968	434556	12303	2.188
2	17.656	19422725	406648	97.812



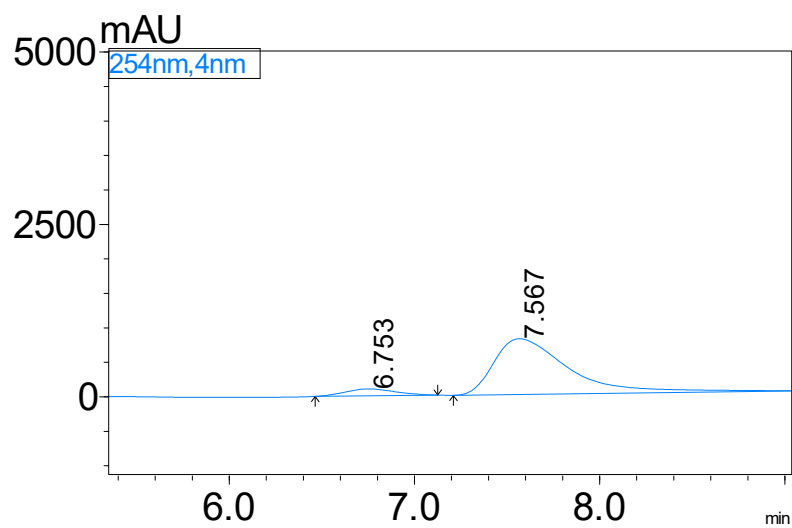
Peak	Time	Area	Height	Area%
1	15.932	3629174	65688	49.697
2	21.277	3673407	50256	50.303



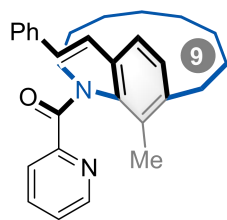
Peak	Time	Area	Height	Area%
1	15.676	899201	17186	2.820
2	20.518	30988103	517711	97.180



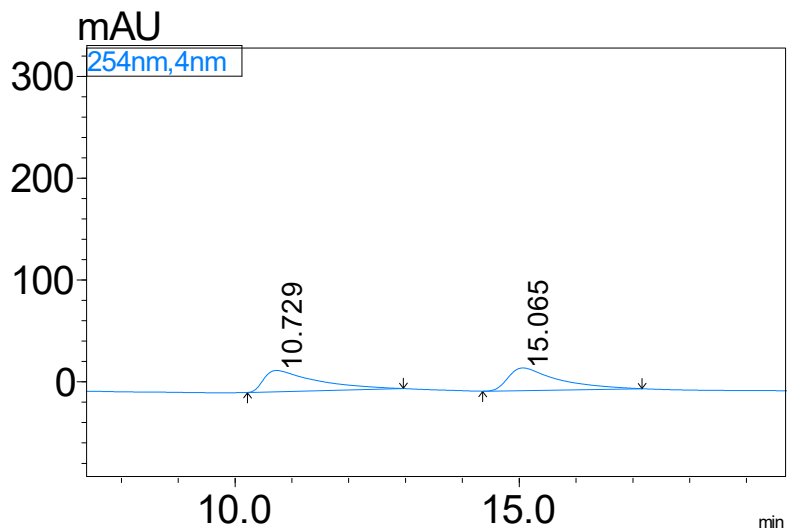
Peak	Time	Area	Height	Area%
1	6.780	7263015	474691	50.619
2	7.673	7085470	412833	49.381



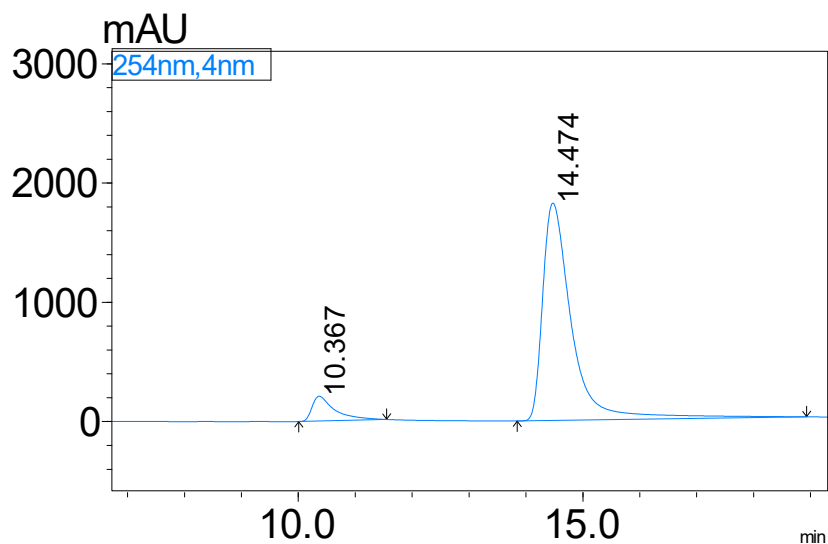
Peak	Time	Area	Height	Area%
1	6.753	1624015	91964	6.990
2	7.567	21609679	801620	93.010



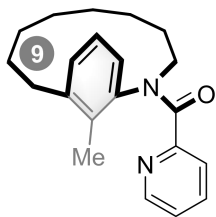
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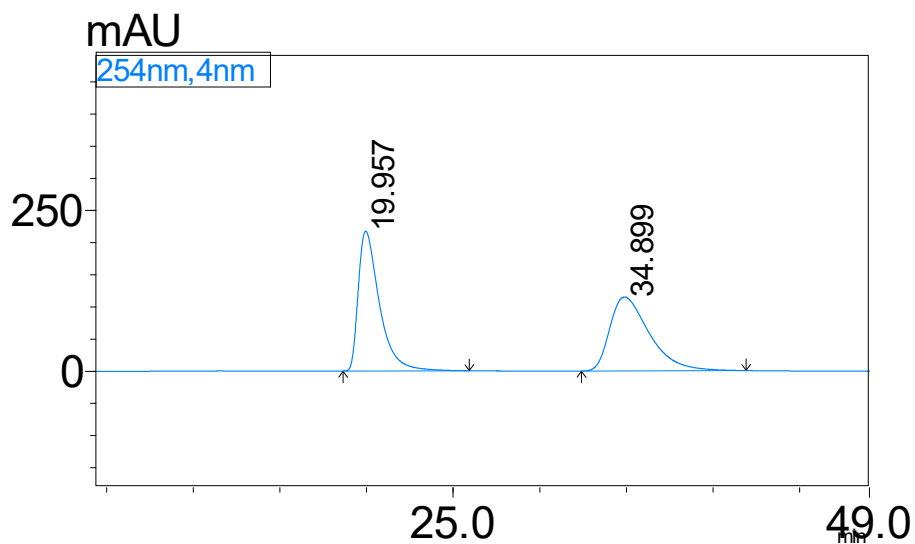
Peak	Time	Area	Height	Area%
1	10.729	1339087	20881	49.737
2	15.065	1353262	22259	50.263



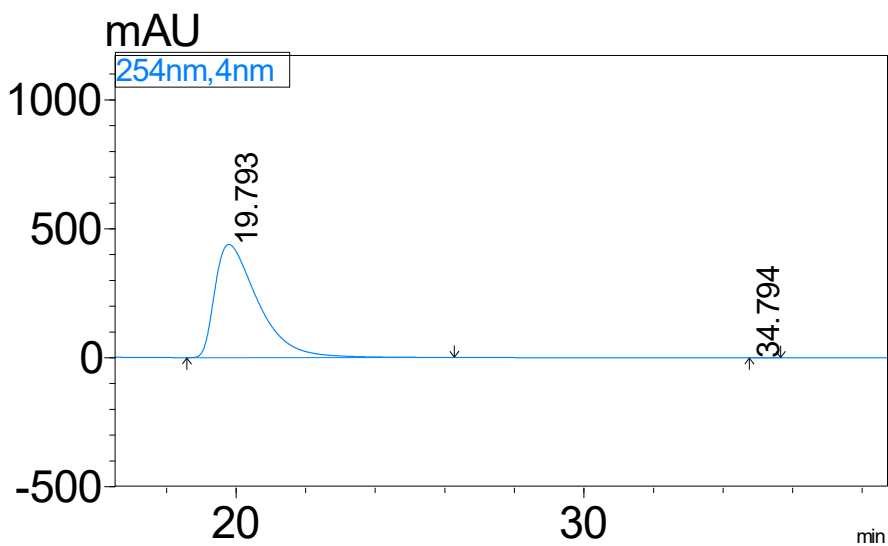
Peak	Time	Area	Height	Area%
1	10.367	5799298	208035	8.184
2	14.474	65061966	1822968	91.816



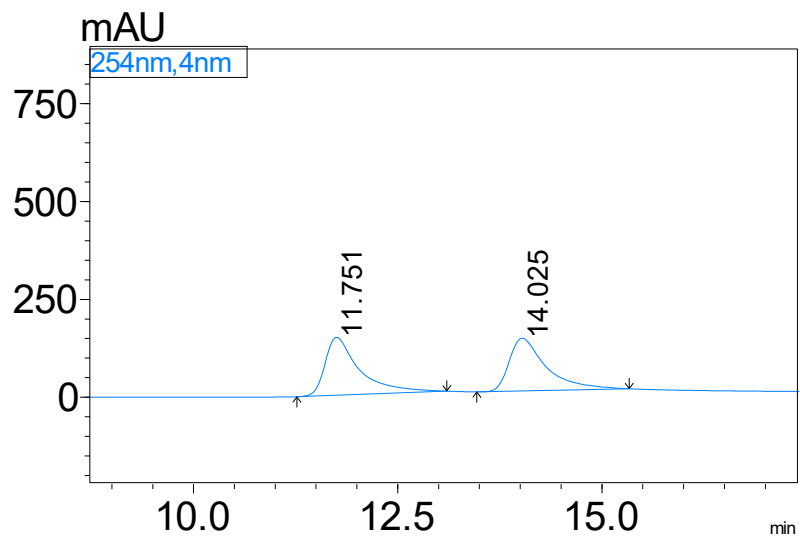
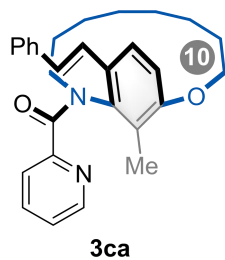
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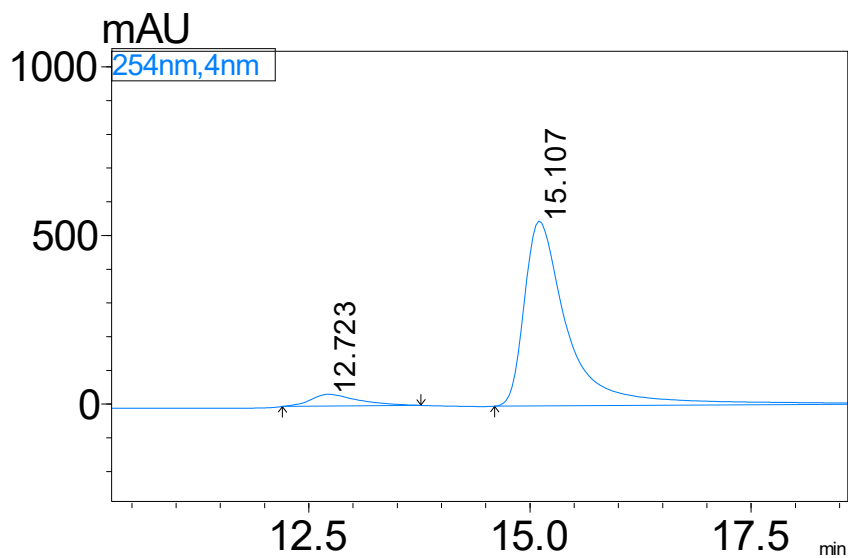
Peak	Time	Area	Height	Area%
1	19.957	18499742	217637	50.315
2	34.899	18268246	115015	49.685



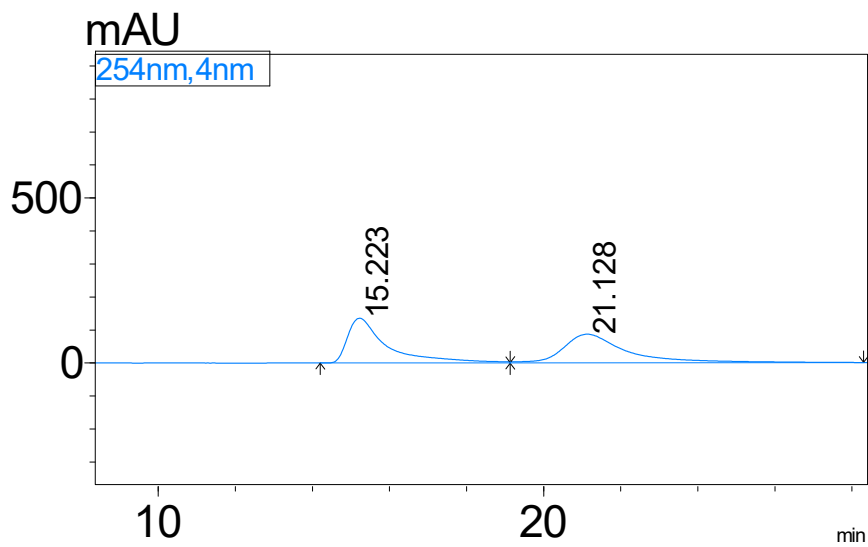
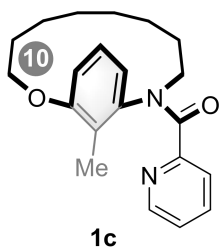
Peak	Time	Area	Height	Area%
1	19.793	37860326	439051	99.997
2	34.794	1008	24	0.003



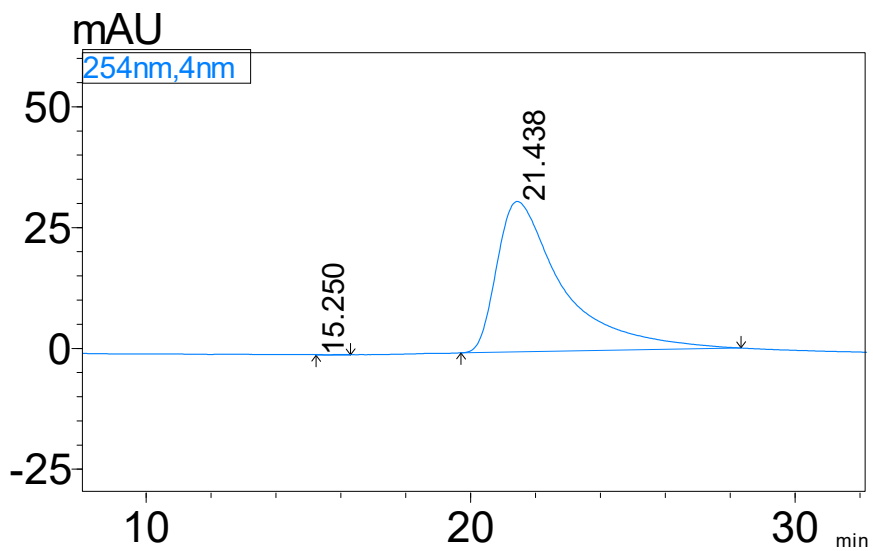
Peak	Time	Area	Height	Area%
1	11.751	4370024	147888	50.726
2	14.025	4244936	134518	49.274



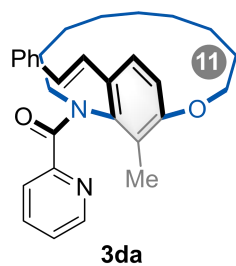
Peak	Time	Area	Height	Area%
1	12.723	1323957	35297	6.438
2	15.107	19241224	548478	93.562



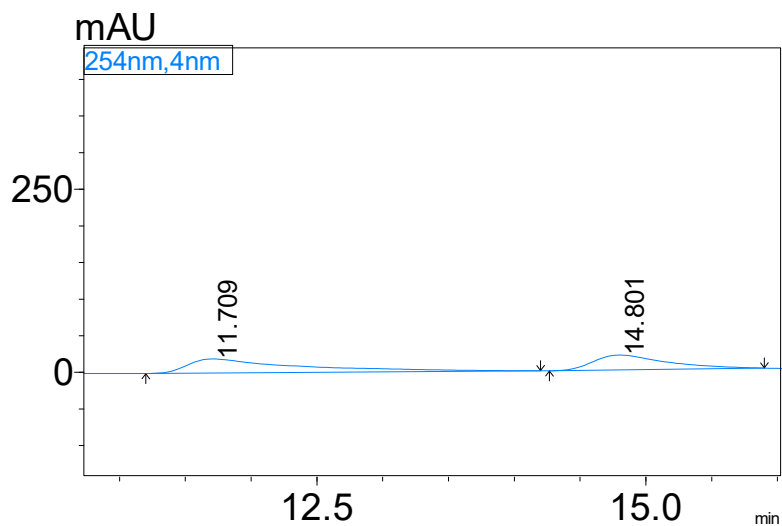
Peak	Time	Area	Height	Area%
1	15.223	9721380	135449	49.605
2	21.128	9876220	86608	50.395



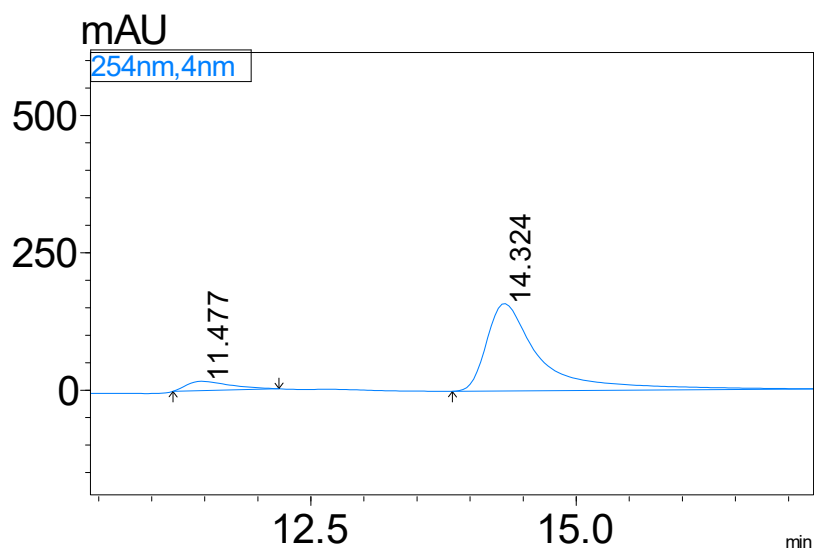
Peak	Time	Area	Height	Area%
1	15.250	4099	91	0.093
2	21.438	4384105	31140	99.907



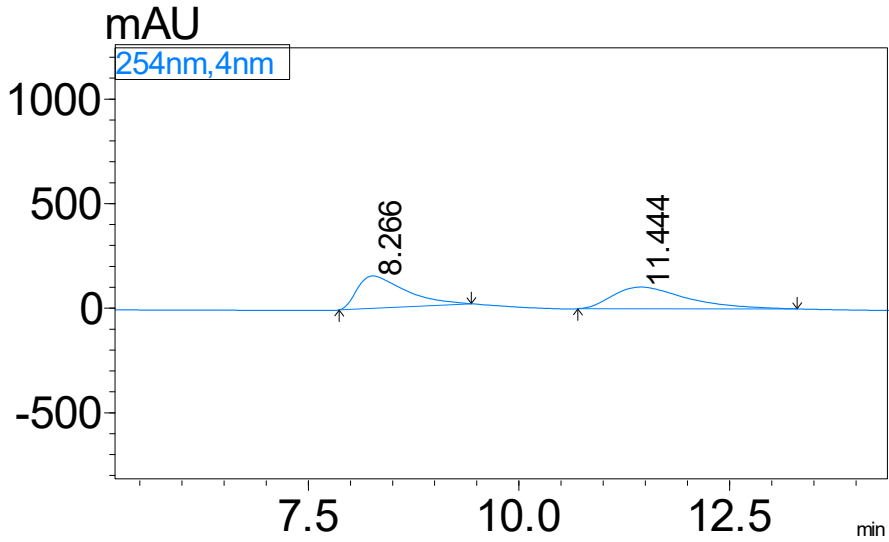
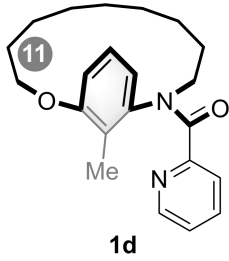
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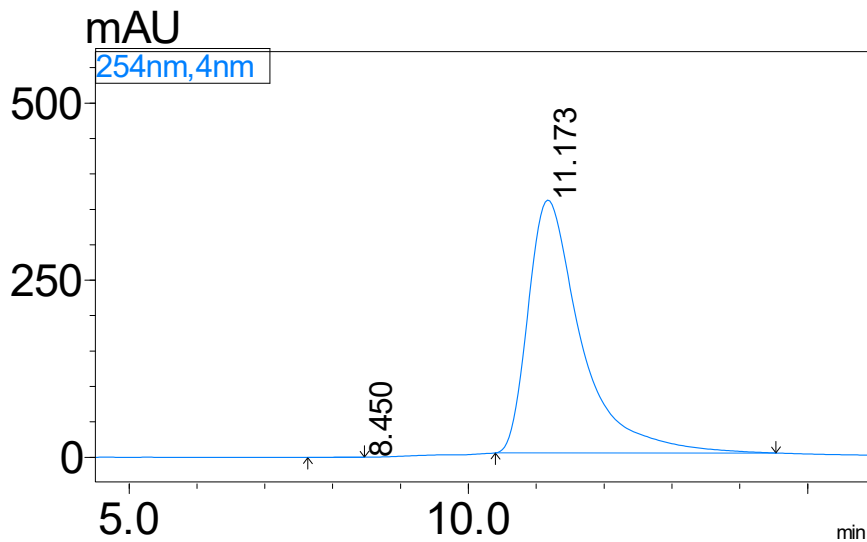
Peak	Time	Area	Height	Area%
1	11.709	1140575	19221	59.047
2	14.801	791057	20442	40.953



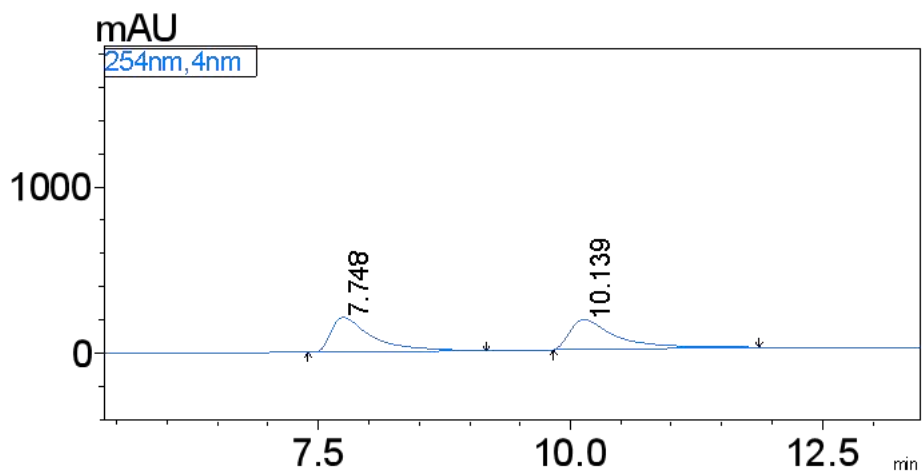
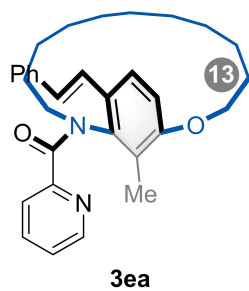
Peak	Time	Area	Height	Area%
1	11.477	492442	16990	8.010
2	14.324	5655677	159040	91.990



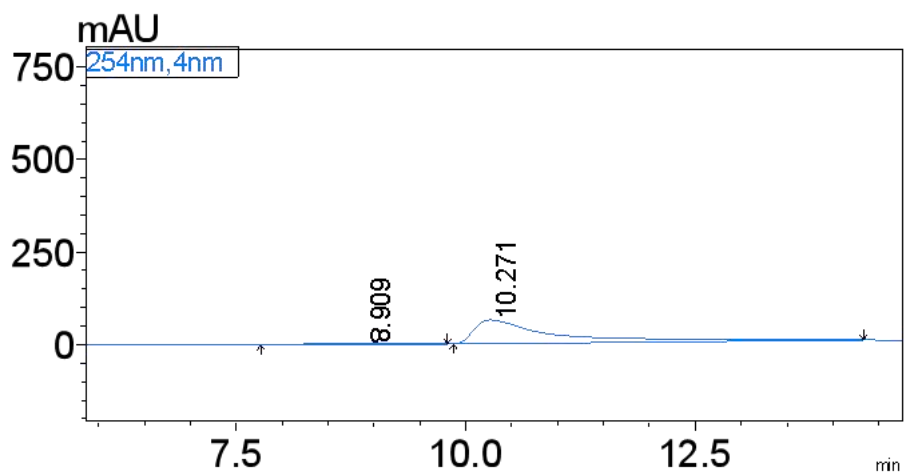
Peak	Time	Area	Height	Area%
1	8.588	1173745	71250	50.472
2	11.725	1151782	47600	49.528



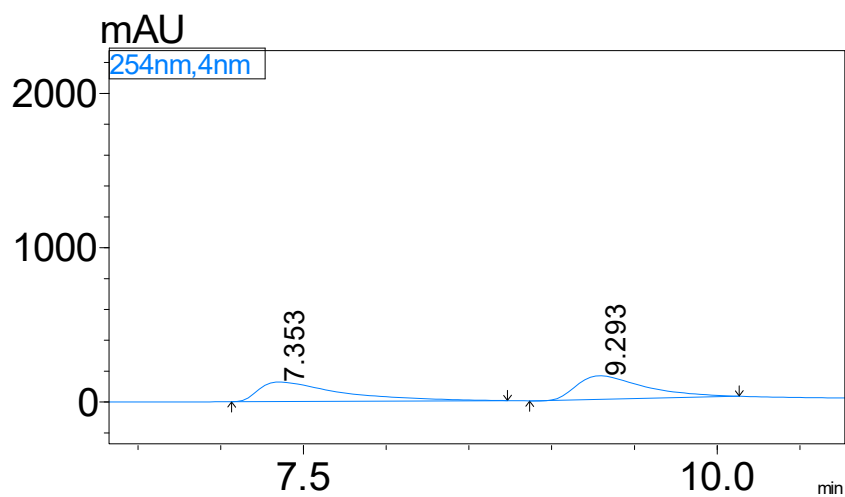
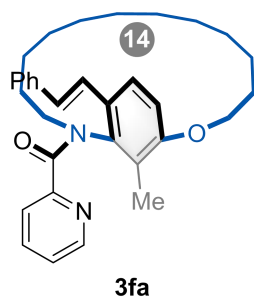
Peak	Time	Area	Height	Area%
1	8.450	13970	425	0.072
2	11.173	19447636	357039	99.928



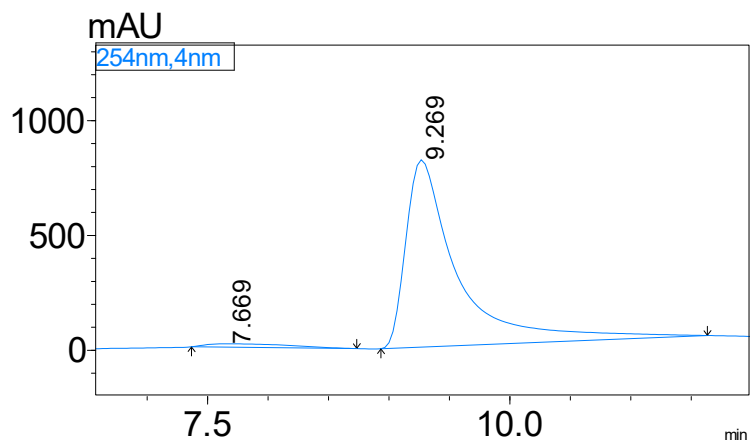
Peak	Time	Area	Height	Area%
1	7.748	5941071	207335	50.294
2	10.139	5871730	180555	49.706



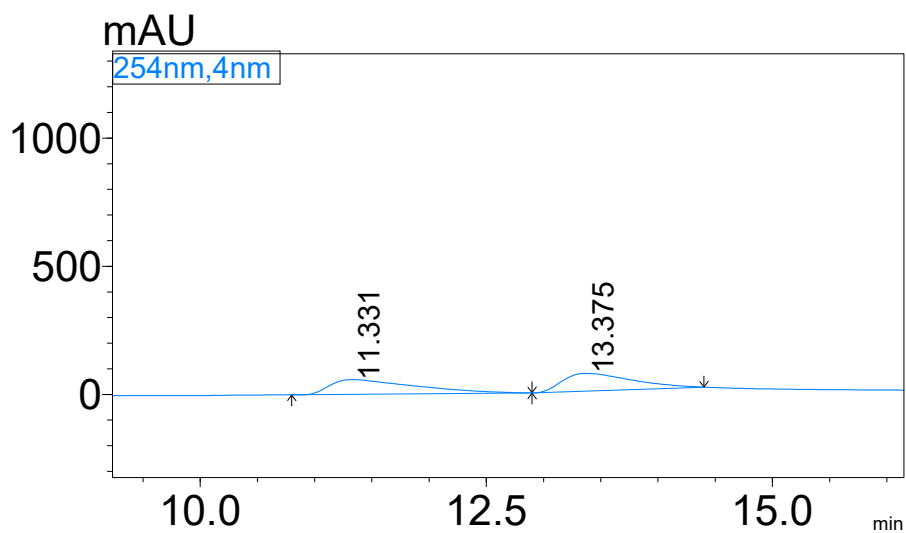
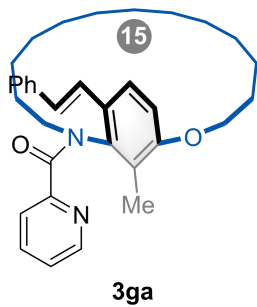
Peak	Time	Area	Height	Area%
1	8.909	94980	1337	2.303
2	10.271	4029120	63952	97.697



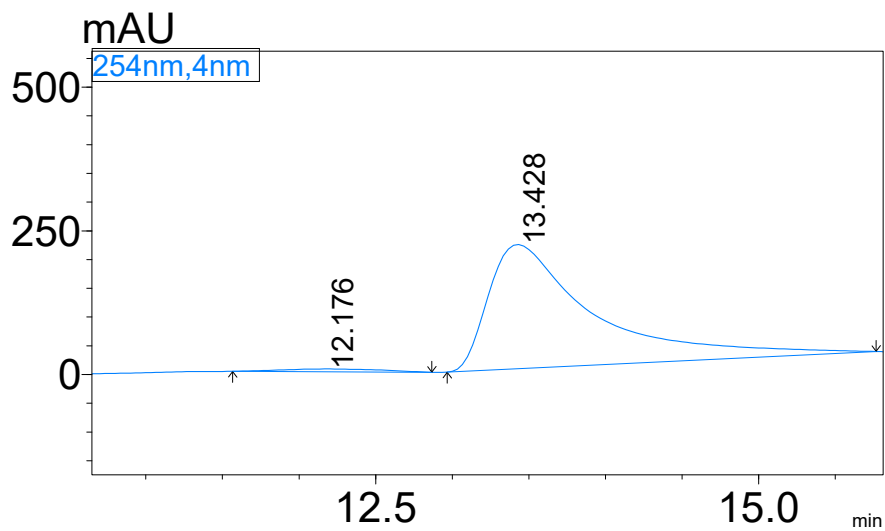
Peak	Time	Area	Height	Area%
1	9.412	3377593	115003	50.541
2	12.751	3305314	92342	49.459



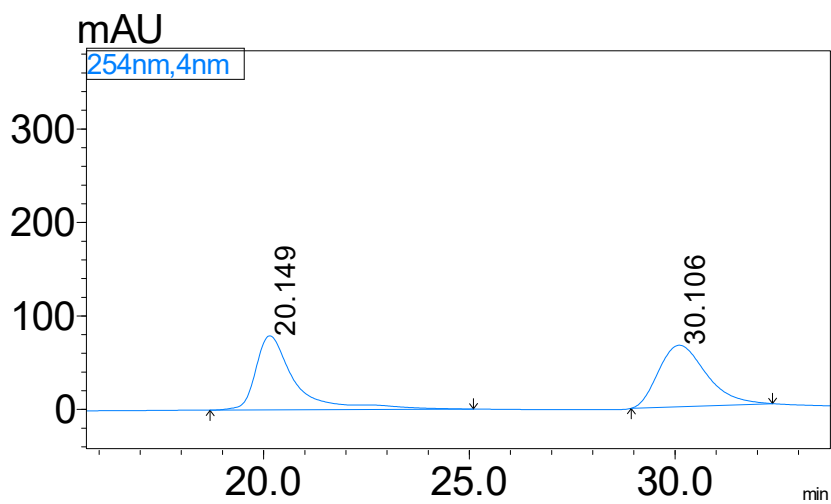
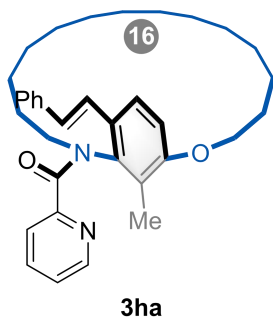
Peak	Time	Area	Height	Area%
1	7.669	723246	14538	2.860
2	9.269	24562618	815770	97.140



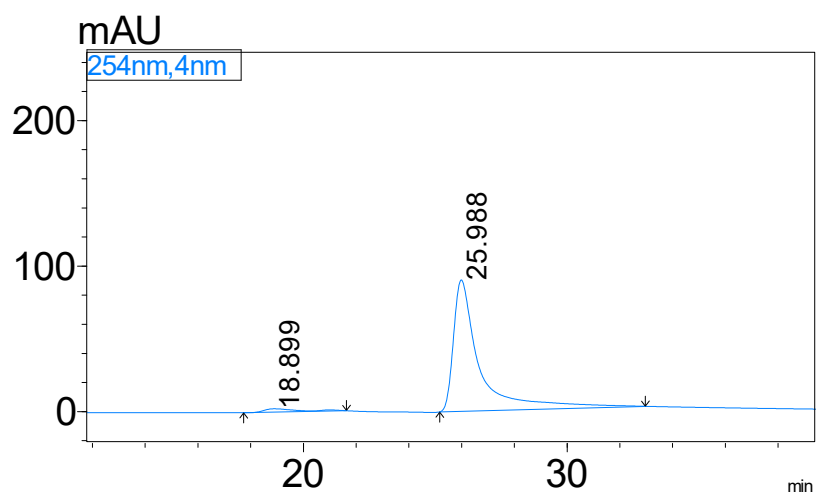
Peak	Time	Area	Height	Area%
1	11.331	3008270	57917	50.708
2	13.375	2924299	69512	49.292



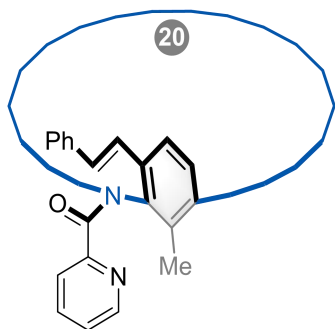
Peak	Time	Area	Height	Area%
1	12.176	219956	4842	2.074
2	13.428	10384223	216317	97.926



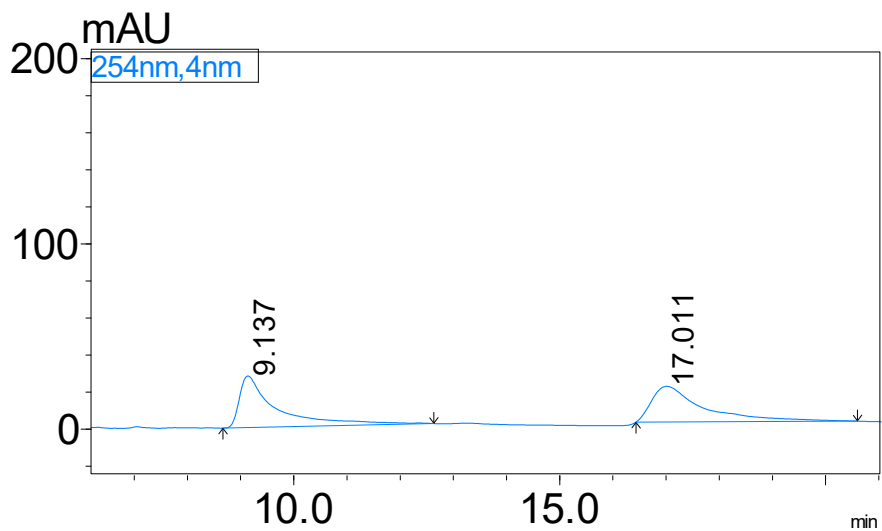
Peak	Time	Area	Height	Area%
1	20.149	5274829	79240	49.781
2	30.106	5321254	65851	50.219



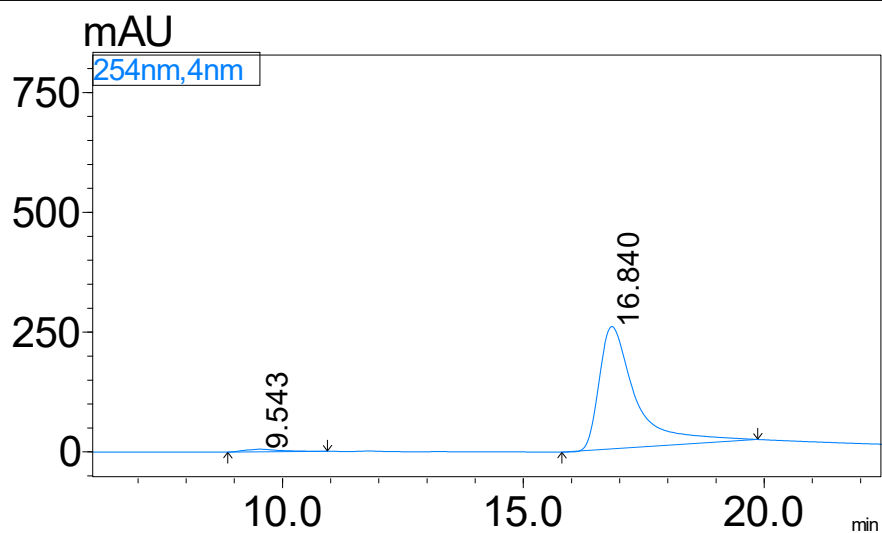
Peak	Time	Area	Height	Area%
1	18.899	205856	2321	3.176
2	25.988	6275405	90279	96.824



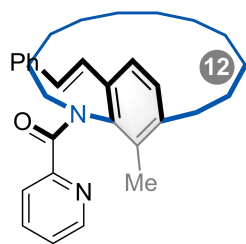
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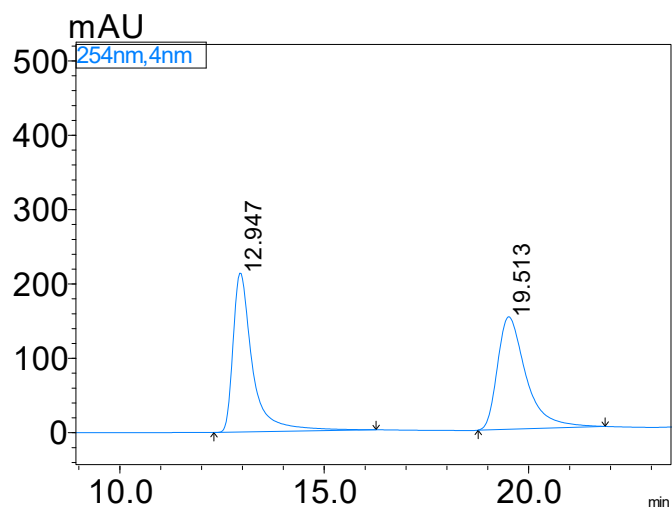
Peak	Time	Area	Height	Area%
1	9.137	1371856	28000	50.959
2	17.011	1320233	19335	49.041



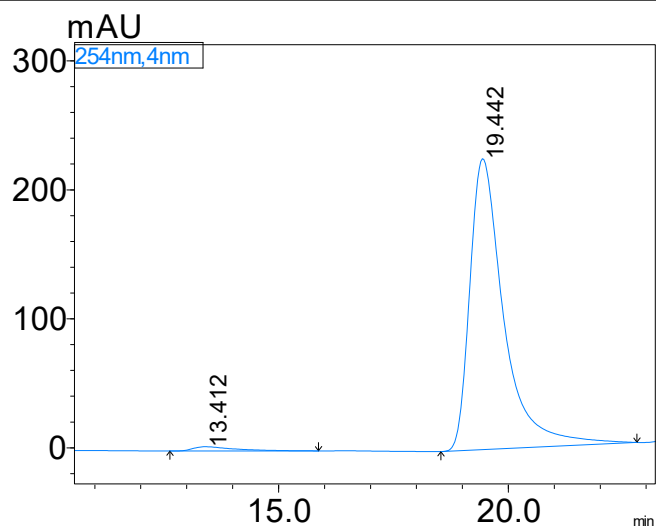
Peak	Time	Area	Height	Area%
1	9.543	279747	5455	2.019
2	16.840	13579077	255180	97.981



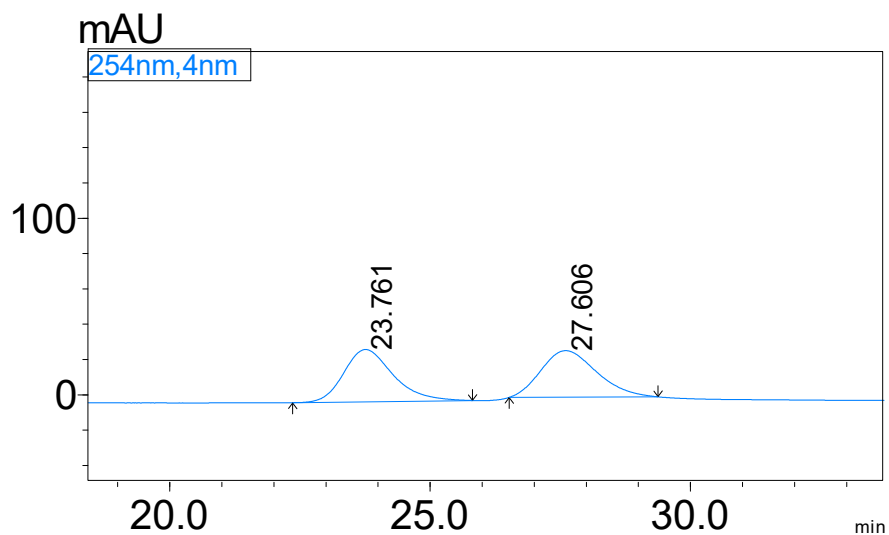
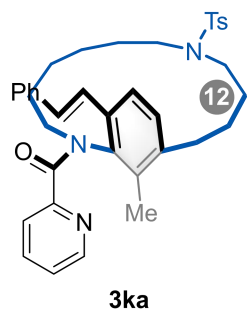
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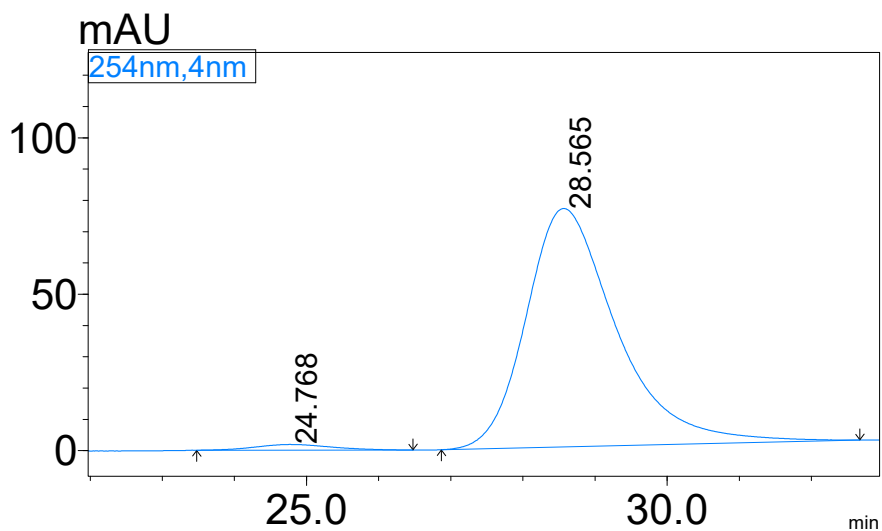
Peak	Time	Area	Height	Area%
1	12.947	7101130	213845	49.157
2	19.513	7344763	151135	50.843



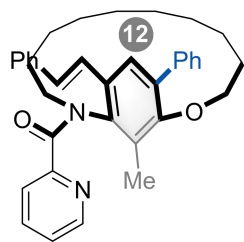
Peak	Time	Area	Height	Area%
1	13.412	211309	3327	1.780
2	19.442	11657870	225575	98.220



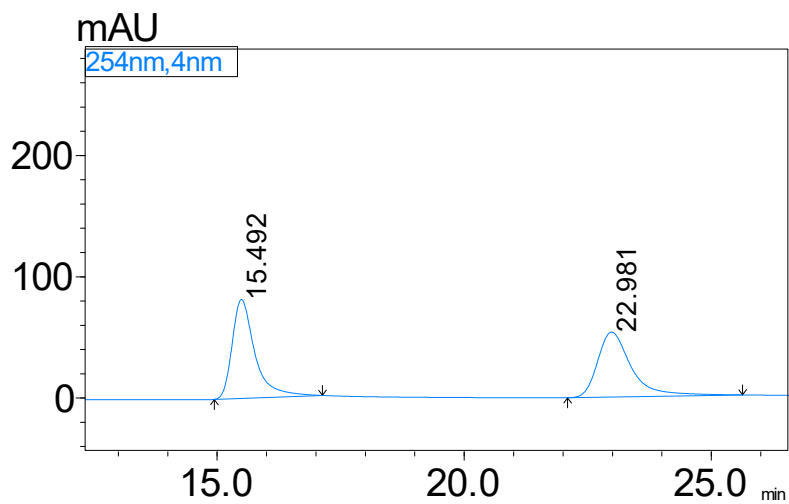
Peak	Time	Area	Height	Area%
1	23.761	1956787	29602	49.969
2	27.606	1959214	26350	50.031



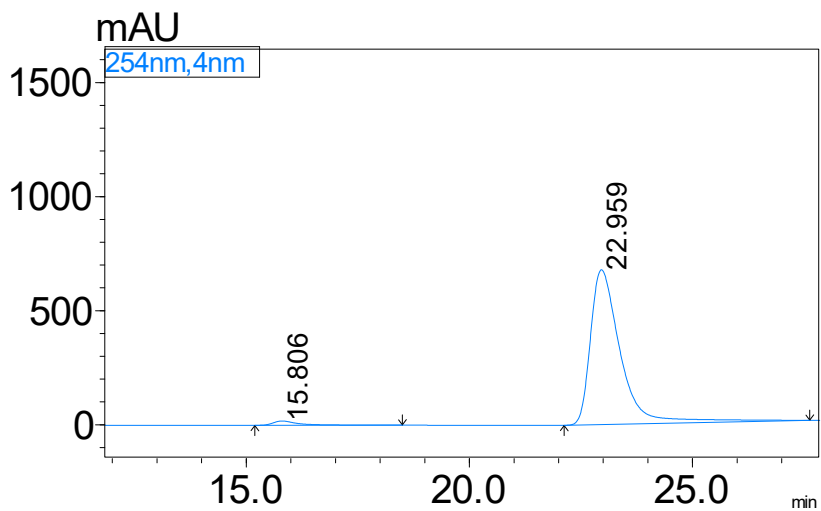
Peak	Time	Area	Height	Area%
1	24.768	134957	1827	1.977
2	28.565	6692509	76216	98.023



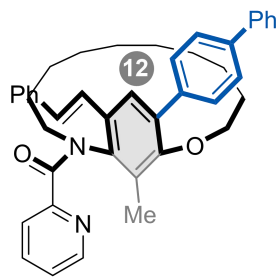
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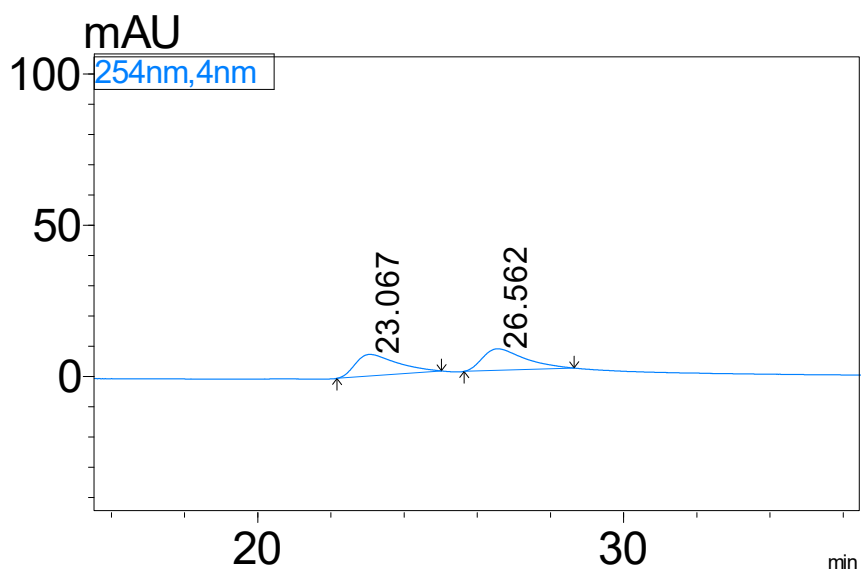
Peak	Time	Area	Height	Area%
1	15.492	2626271	81602	50.732
2	22.981	2550461	53594	49.268



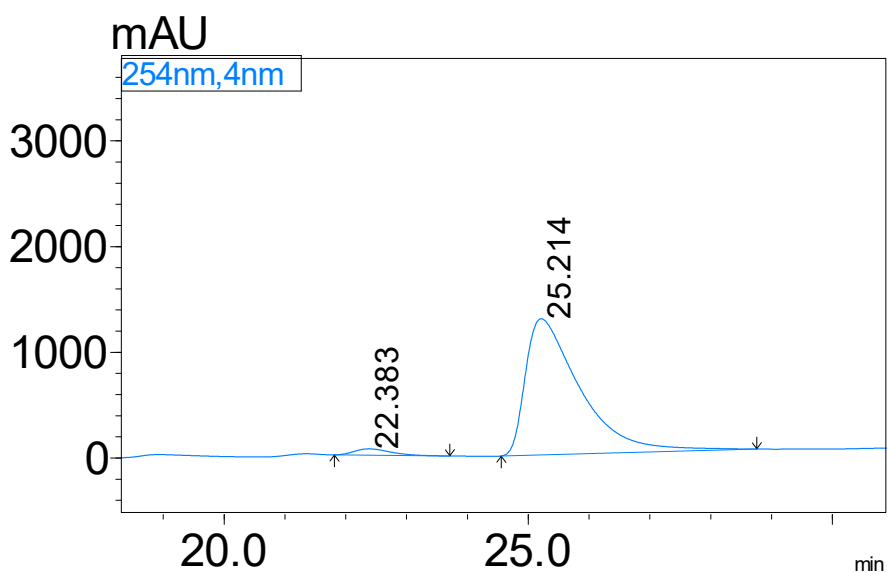
Peak	Time	Area	Height	Area%
1	15.806	760397	18782	2.333
2	22.959	31828735	678314	97.667



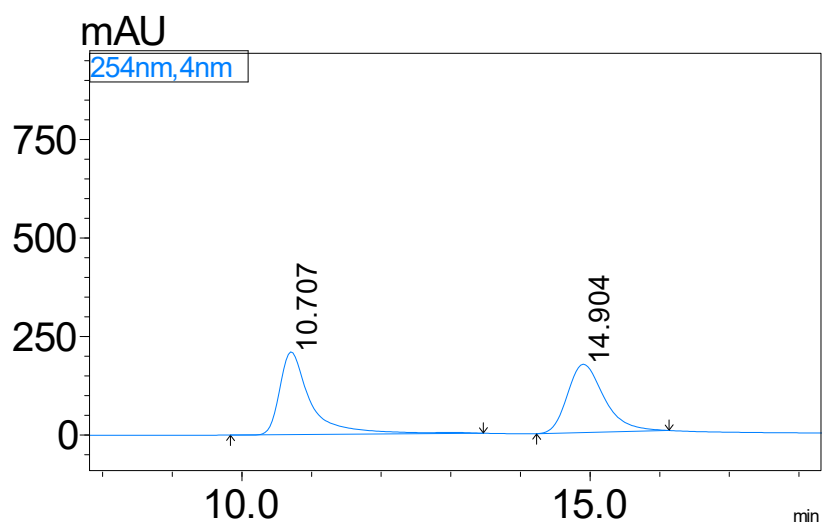
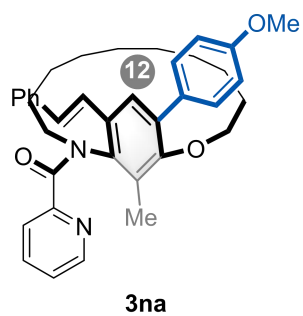
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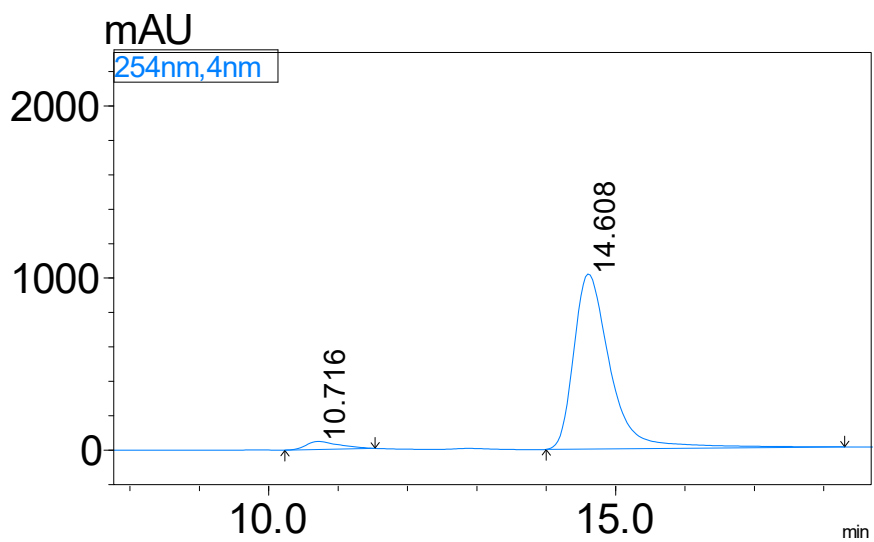
Peak	Time	Area	Height	Area%
1	23.067	563336	7130	49.642
2	26.562	571461	7106	50.358



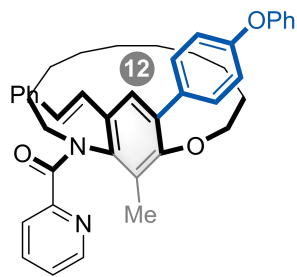
Peak	Time	Area	Height	Area%
1	22.383	2508504	60403	3.026
2	25.214	80398706	1287719	96.974



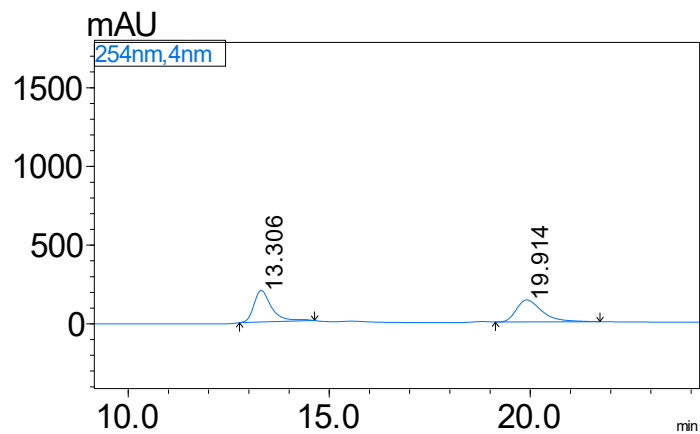
Peak	Time	Area	Height	Area%
1	10.707	6538740	209579	50.711
2	14.904	6355427	173173	49.289



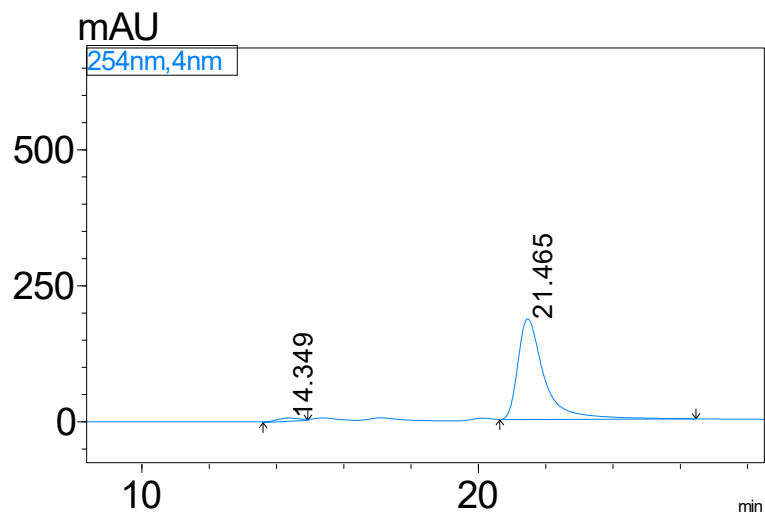
Peak	Time	Area	Height	Area%
1	10.716	1546379	46672	3.987
2	14.608	37235074	1016834	96.013



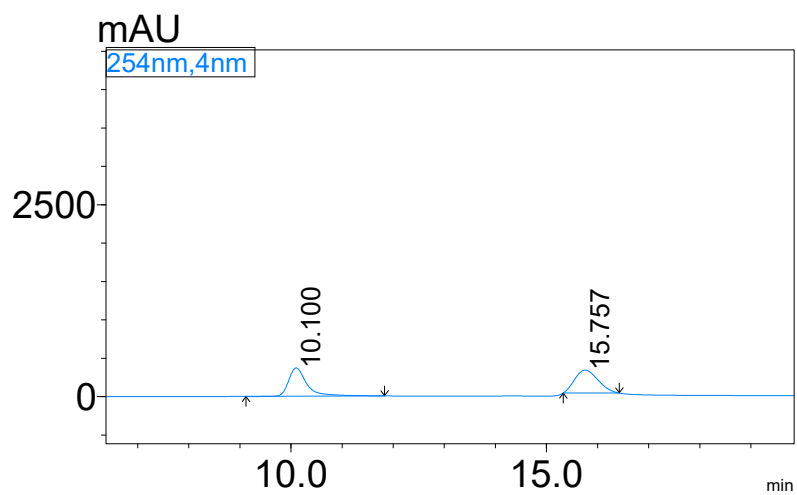
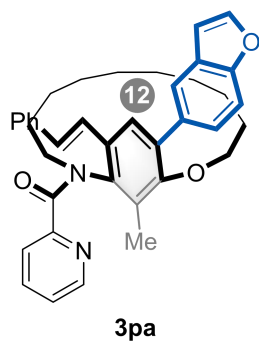
**3oa**



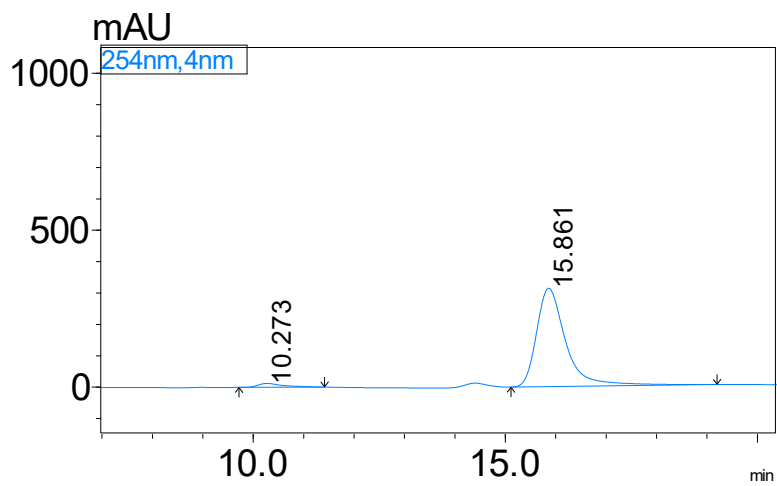
Peak	Time	Area	Height	Area%
1	13.306	6205248	201279	50.016
2	19.914	6201355	139973	49.984



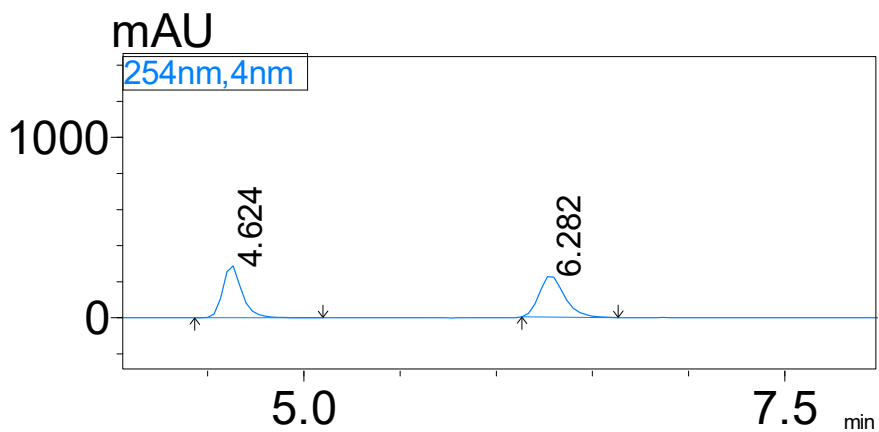
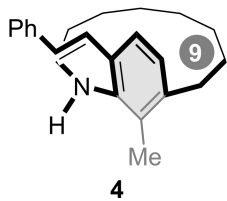
Peak	Time	Area	Height	Area%
1	14.349	308325	6100	2.966
2	21.465	10086469	185213	97.034



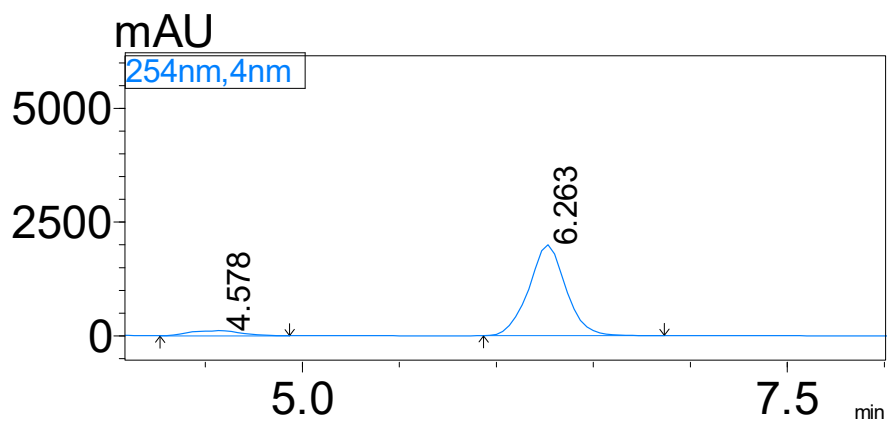
Peak	Time	Area	Height	Area%
1	10.100	9251783	369481	49.264
2	15.757	9528043	299325	50.736



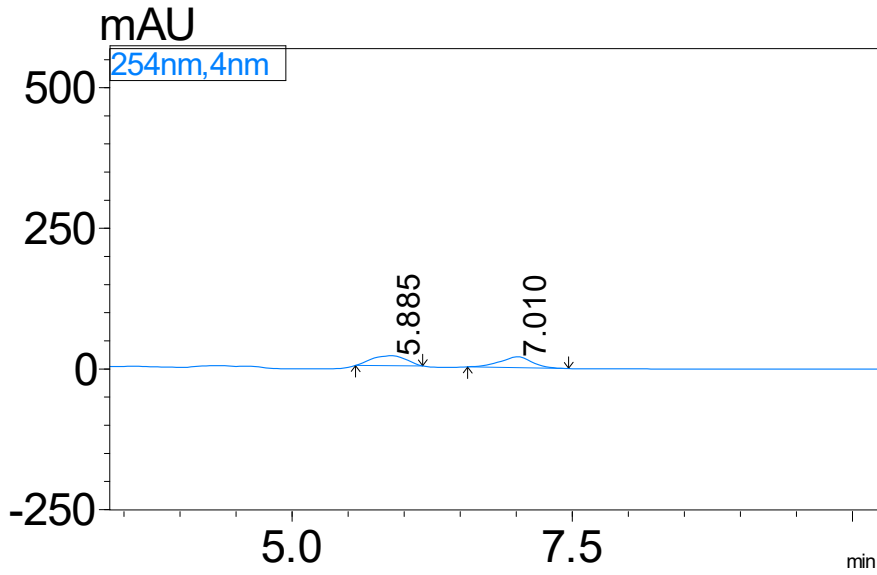
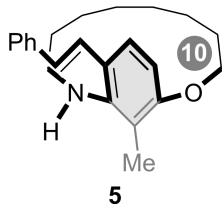
Peak	Time	Area	Height	Area%
1	10.273	428040	12202	3.270
2	15.861	12662957	313780	96.730



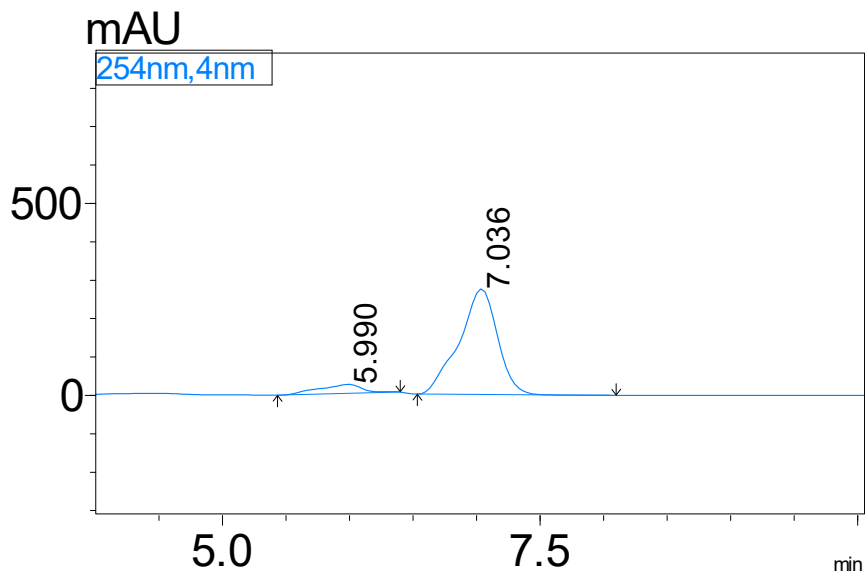
Peak	Time	Area	Height	Area%
1	4.624	2024483	288167	49.084
2	6.282	2100081	224840	50.916



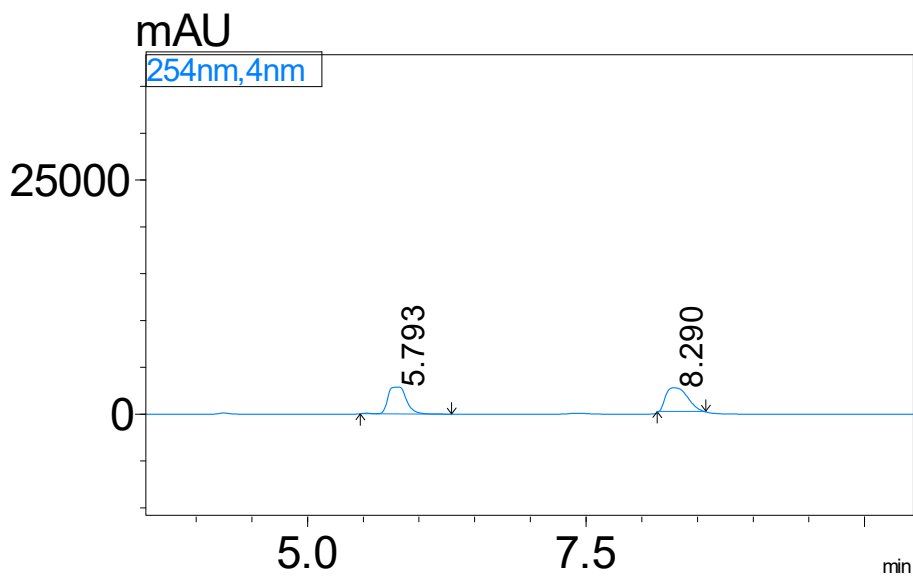
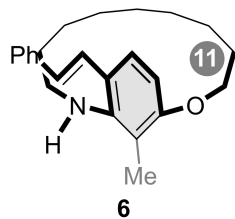
Peak	Time	Area	Height	Area%
1	4.578	2084108	113094	7.266
2	6.263	26598221	2000908	92.734



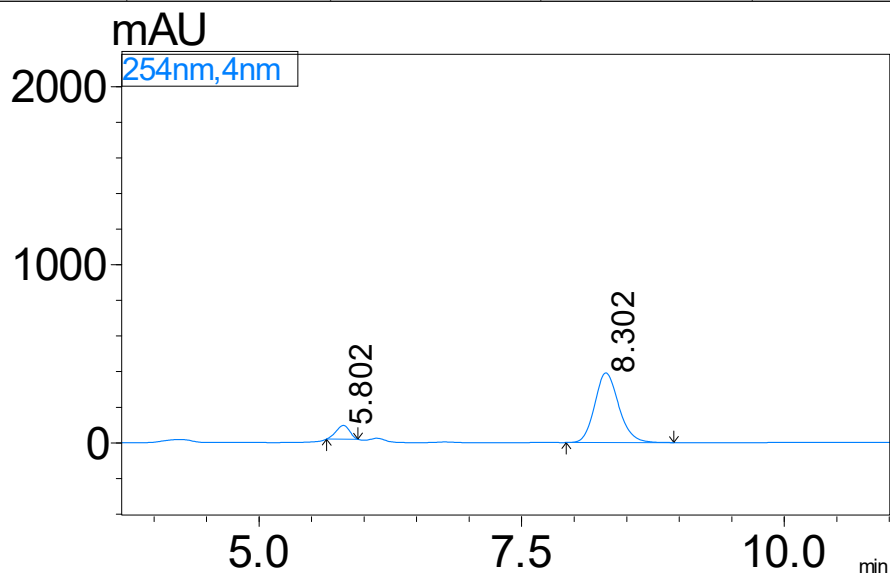
Peak	Time	Area	Height	Area%
1	5.885	379071	17864	49.656
2	7.010	384327	19490	50.344



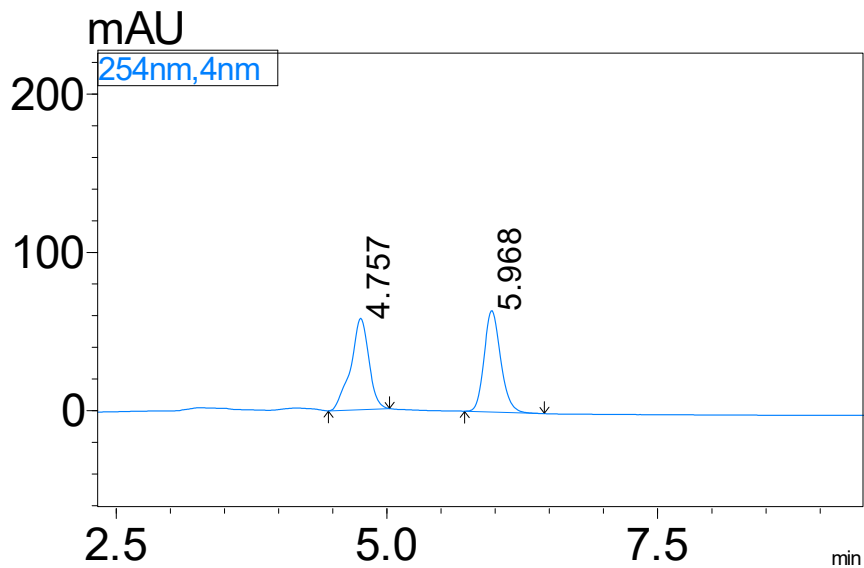
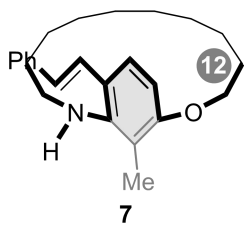
Peak	Time	Area	Height	Area%
1	5.990	573179	23778	9.052
2	7.036	5759111	274998	90.948



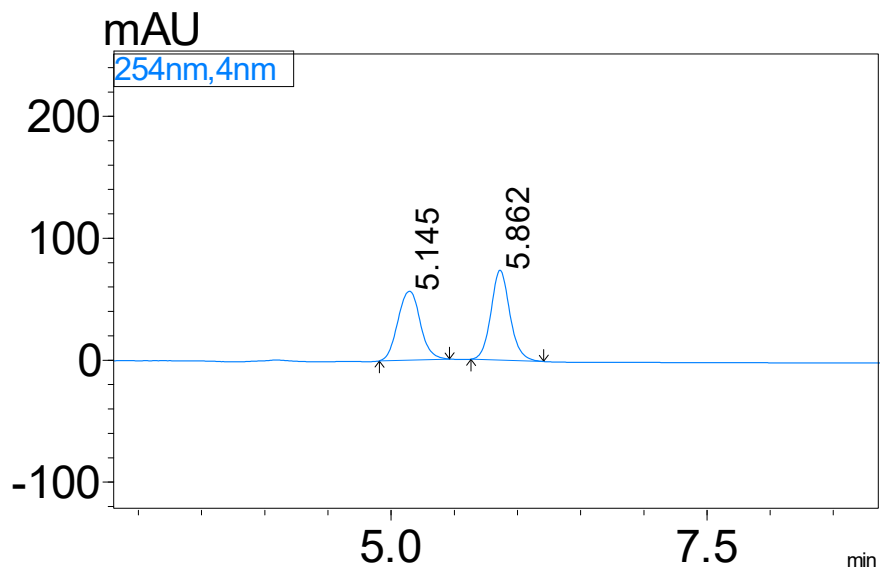
Peak	Time	Area	Height	Area%
1	5.793	32764771	2851676	49.082
2	8.290	33990436	2516927	50.918



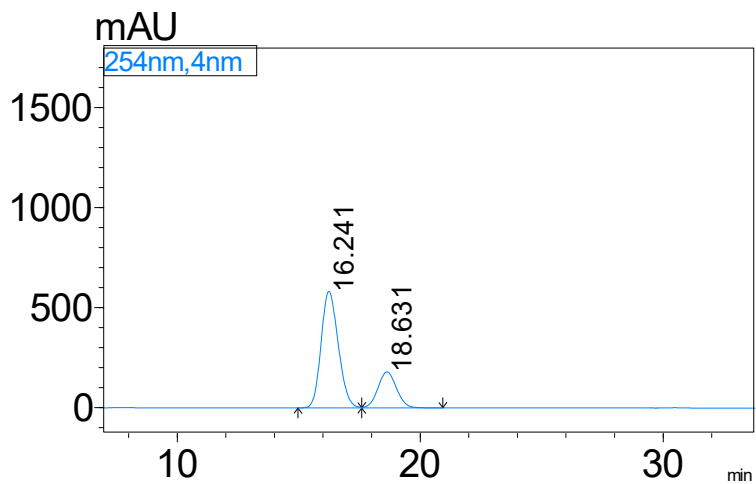
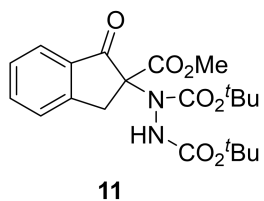
Peak	Time	Area	Height	Area%
1	5.802	693313	77824	9.992
2	8.302	6245171	391225	90.008



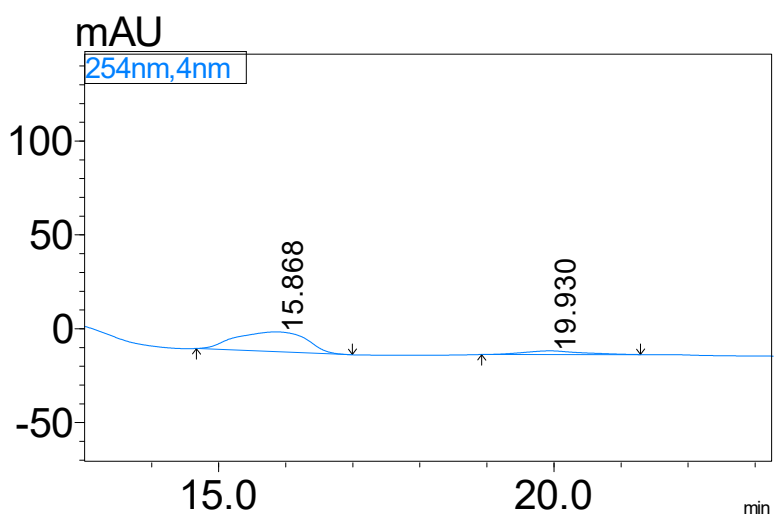
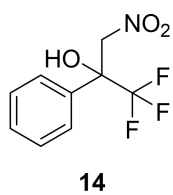
Peak	Time	Area	Height	Area%
1	4.757	671879	57668	49.601
2	5.968	682683	63868	50.399



Peak	Time	Area	Height	Area%
1	5.145	695916	56397	47.506
2	5.862	768977	73637	52.494



Peak	Time	Area	Height	Area%
1	15.868	764676	10584	86.615
2	19.930	118168	1981	13.385



Peak	Time	Area	Height	Area%
1	15.868	764676	10584	86.615
2	19.930	118168	1981	13.385