Supporting Information

Pd(II)-Catalyzed Atroposelective C−H Olefination to Access [n]Naphthalenophanes

Xiaoyu Wang,[a] Jia Li,[a] Quan Tang,[a,*] and Changgui Zhao[a,*]

[a]Key Laboratory of Radiopharmaceuticals, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China.

Email: tangquan@bnu.edu.cn for Quan Tang; cgzhao@bnu.edu.cn for Changgui Zhao

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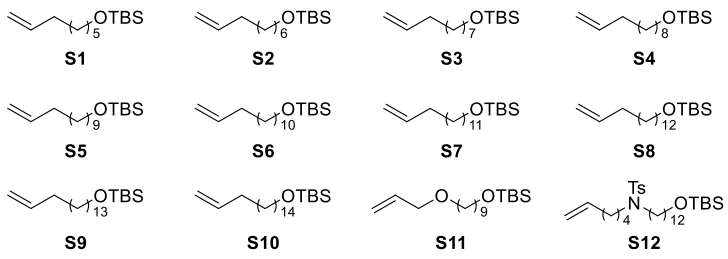
1. General Information

Unless otherwise noted, all chemicals were purchased from commercial sources including dichloromethane (CH_2Cl_2), *n*-hexane, ethyl acetate (EA), methanol (MeOH), tetrahydrofuran (THF), acetone and petroleum ether (PE) were purchased from Beijing Chemical Factory (Beijing, China) and Beijing Tong Guang Fine Chemicals Company (Beijing, China). Column chromatography was performed using silica gal (normal phase, 200 – 300 mesh) from Yantai Xinnuo Chemical Co., Ltd., usually with petroleum ether (PE, bp 60 – 90 °C) and ethyl acetate (EA) as eluent. Reactions were monitored by thin-layer chromatography (TLC) on G254 silica gal 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). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL Delta (400 MHz or 600 MHz) spectrometer with $CDCl_3$ or $(CD_3)_2CO$-d_6 as solvents 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), 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, IA, ID, AD-H, AS-H, OD-H, OJ-H, and IF, column 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)). UV spectra were measured on UV-2600 and Fluorescence spectra were measured on FluoroLog-3. PLQY was determined on Hamamatsu C11347-11. The circularly polarized luminescence (CPL) spectra were recorded with a JASCO CPL-300 spectrometer at room temperature. Circular dichroism spectra (CD) were recorded on JASCO J-1700. Circular Dichroism Spectrometer from Applied Photophysics. High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier XE mass spectrometer with TOF. The $[\alpha]_D$ were recorded on RUDOLPH Autopol III. Crystallographic data were collected using a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer equipped with a HyPix-6000E area detector at 100 K using Cu Kα (λ = 1.54184 Å) from a PhotonJet micro-focus X-ray source.

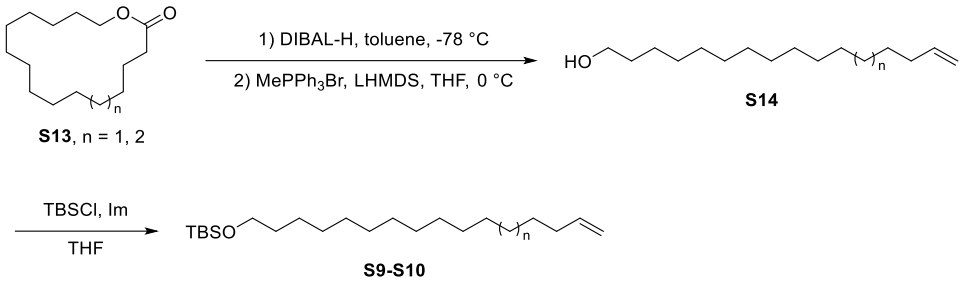
2. Methods and Procedures for the Synthesis of Substrates

a) Procedure for the Synthesis of *Ansa* Chain S1–S12

The *ansa* chain **S1-S8** and **S11**[1] were prepared according to literature procedure from commercially available materials. The spectra are in accordance with literature.



S9–S10 was prepared as the following procedure.

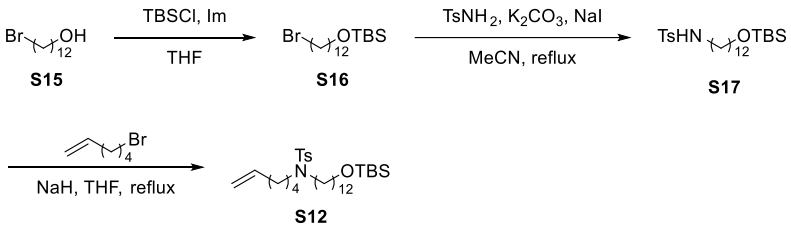


To a stirred suspension of methyltriphenylphosphonium bromide (8.57 g, 24.0 mmol, 2.0 equiv.) in dry THF (40 mL) was added a solution of lithium bis(trimethylsilyl)amide (LHMDS, 1.0 M in THF, 24.0 mL, 24.0 mmol, 2.0 equiv.) at 0 °C. The mixture was stirred for 2 h at 0 °C to prepare a solution of methylenetriphenylphosphorane. To a stirred solution of commercial macrolides **S13** (12.0 mmol, 1.0 equiv.) in dry toluene (60 mL) at -78 °C, a solution of diisobutylaluminum hydride (DIBAL-H, 1.0 M in toluene, 13.2 mL, 13.2 mmol, 1.1 equiv.) was slowly added over 30 min. After stirring at -78 °C for 30 min, the yellow solution of the phosphorous ylide just prepared was slowly added over 10 min. The formed mixture was gradually warmed to room temperature while stirring overnight. The reaction was then quenched with 1 M hydrochloric acid. After stirring for 30 min, the mixture was extracted with EA (40 mL×3), and the combined organic phase was washed with water, saturated aqueous $NaHCO_3$ solution and brine, and then dried with Na_2SO_4. After filtration, the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EA = 10:1, *v*/*v*) to obtain the crude products **S14**.

To a solution of **S14** (10.0 mmol, 1.0 equiv.) in dry THF (50 mL) was added imidazole (0.82 g, 12.0 mmol, 1.2 equiv.) and TBSCl (1.81 g, 12.0 mmol, 1.2 equiv.). The reaction mixture was stirred for 8 h. Then saturated NH_4Cl (50 mL) was added and the organic phase was separated. The aqueous phase was extracted with EA (20 mL×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 residue was purified by flash column chromatography on silica gel (PE/EA = 200:1, *v*/*v*) to afford the products **S9–S10**.

S12 was prepared as the following procedure.

The 12-bromo-1-dodecanol **S15** were obtained from commercial sources and used without further purification.

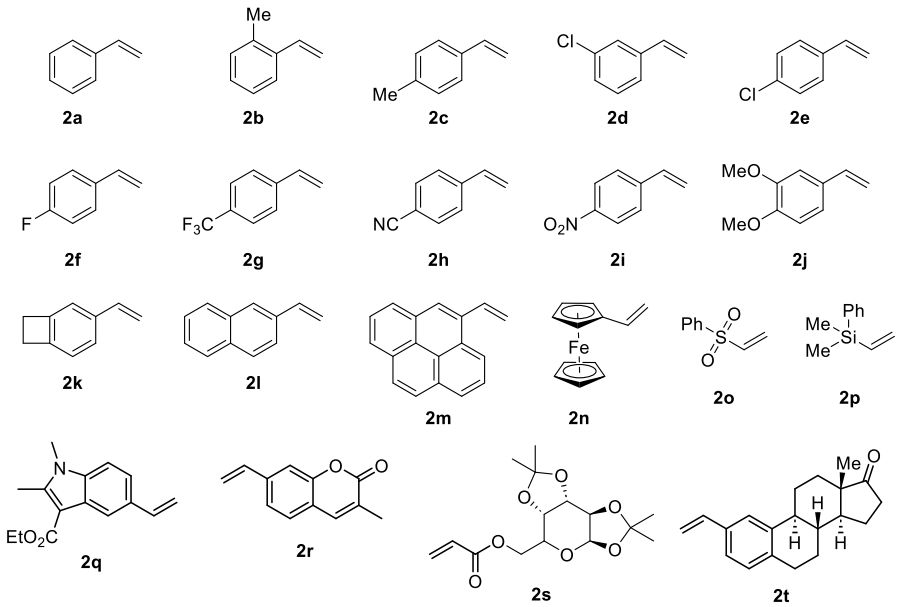


To a solution of **S15** (5.30 g, 20.0 mmol, 1.0 equiv.) in dry THF (150 mL) was added imidazole (1.63 g, 24.0 mmol, 1.2 equiv.) and TBSCl (3.62 g, 24.0 mmol, 1.2 equiv.). The reaction mixture was stirred for 4 h. Then saturated NH_4Cl (150 mL) was added and the organic phase was separated. The aqueous phase was extracted with EA (40 mL×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 residue was purified by flash column chromatography on silica gel (PE/EA = 200:1, *v*/*v*) to afford the crude products **S16**.

To a solution of **S16** (5.69 g, 15.0 mmol, 1.0 equiv.) in MeCN (60 mL) was added K_2CO_3 (4.15 g, 30.0 mmol, 2.0 equiv.), NaI (0.28 g, 1.5 mmol, 0.1 equiv.) and $TsNH_2$ (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 PE. Then, the solvent was removed *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EA = 3:1, *v/v*) to afford the crude products **S17**.

To a stirred suspension of **S17** (15.0 mmol, 1.0 equiv.) in dry THF (100 mL) was added NaH (60% in mineral oil, 1.08 g, 45.0 mmol, 3.0 equiv.). The, reaction mixture was heated to reflux. And then, the stirring and refluxing suspension was added a solution of 6-bromo-1-hexene (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 EA (150 mL×3) and the combined organic layers were dried over by anhydrous Na_2SO_4. Then, the solvent was removed *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EA = 20:1, *v/v*) to afford the crude products **S12**.

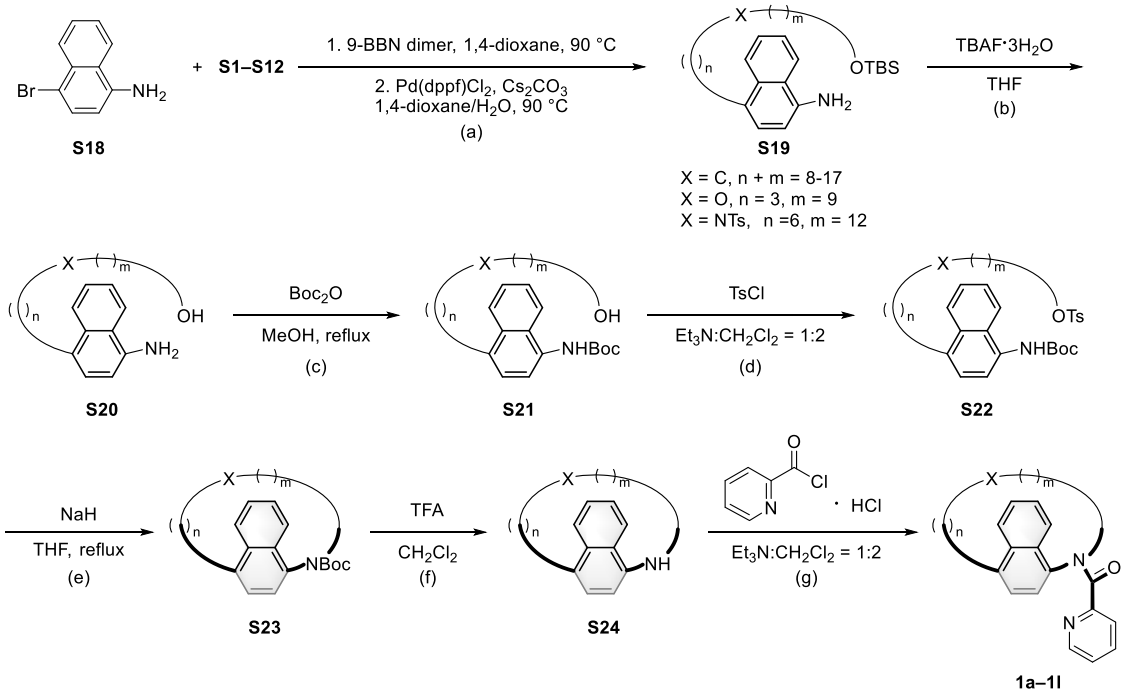
b) Procedure for the Synthesis of Alkenes 2a–2t



Alkenes **2a–2l** and **2n–2p** were purchased from commercial suppliers and used without further purification. Known olefins **2m**,[2] **2q**[3], **2r**[4], **2s**[5], **2t**[4] were prepared according to literature procedure from commercially available materials. The spectra are in accordance with the literature.

c) General Procedure for the Synthesis of Naphthalenophanes 1a–1l and 4

The naphthalenophanes **1a–1l** used in this study were synthesized through the procedure described below.



(a) To a solution of **S1-S12** (10.0 mmol, 1.0 equiv.) in dry 1,4-dioxane (20.0 mL) was added 9-BBN dimer (3.63 g, 15.0 mmol, 1.5 equiv.) under N_2 atmosphere. The reaction mixture was stirred at 90 ℃ for 4 h and used directly for next step.

In another flask, 4-bromo-1-naphthylamine **S18** (2.66 g, 12.0 mmol, 1.2 equiv.), $Pd(dppf)Cl_2$ (0.37 g, 0.5 mmol, 0.05 equiv.) and Cs_2CO_3 (9.75 g, 30.0 mmol, 3.0 equiv.) were added under N_2 atmosphere. The degassed 1,4-dioxane:H_2O (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 ºC for 8 h. Then saturated NH_4Cl (20 mL) was added and the organic phase was separated. The aqueous phase was extracted with EA (30 mL × 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 residue was purified by flash column chromatography on silica gel (PE/EA = 20:1, *v*/*v*) to afford the crude products **S19**.

(b) To a solution of the crude products **S19** in THF (30 mL) was added TBAF·$3H_2O$ (3.03 g, 9.6 mmol, 1.2 equiv.). The reaction was stirred at room temperature for 6 h. Then the aqueous phase was extracted with EA (15 mL×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 residue was purified by flash column chromatography on silica gel (PE/EA = 2:1, *v*/*v*) to afford the crude products **S20**.

(c) To a solution of crude products **S20** in MeOH (50 mL) was added Boc_2O (2.2 mL, 9.6 mmol, 1.2 equiv.). The mixture was refluxed until **S20** was consumed completely (monitored by TLC). Then, after cooling to room temperature and removing the volatiles *in vacuum*, the crude products **S21** was obtained in quantitative yield.

(d) To a solution of crude products **S21** in a mixture of Et_3N:CH_2Cl_2 (10 mL, 1:2 *v*/*v*) was added TsCl (1.68 g, 8.8 mmol, 1.1 equiv.), and then stirred at room temperature for overnight. The mixture was diluted by water (30 mL) and extracted with CH_2Cl_2 (15 mL × 3), the combined organic phases were washed by brine and dried over anhydrous Na_2SO_4. After filtration and

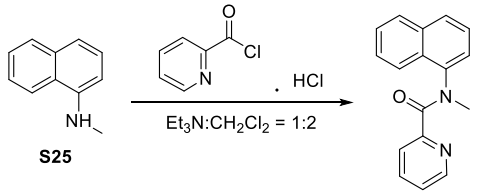
removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EA = 8:1, *v*/*v*) to afford the crude products **S22**.

(e) NaH (60% in mineral oil, 0.48 g, 20.0 mmol, 4.0 equiv.) and dry THF (50 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 crude products **S22** in THF (50 mL) dropwise over 12 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 (20 mL). Then the solution was extracted with EA (50 mL × 3) and the combined organic phases were washed by brine and dried over anhydrous Na_2SO_4. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EA = 50:1, *v*/*v*) to afford the crude products **S23**.

(f) To a solution of crude products **S23** in dry CH_2Cl_2 (10 mL) was added dropwise trifluoroacetic acid (TFA, 3.0 mL, 1 mL/mmol), and the resulting mixture was stirred at room temperature for 2 h. The reaction was quenched by saturated $NaHCO_3$ aqueous solution dropwise until no bubbles were released. And then the mixture was extracted with CH_2Cl_2 (10 mL × 3) and the combined organic phases were washed by brine and dried over anhydrous Na_2SO_4. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EA = 20:1, *v*/*v*) to afford the crude products **S24**.

(g) To a solution of crude products **S24** in a mixture of dry Et_3N:CH_2Cl_2 (10 mL, 1:2 *v*/*v*), cooled to 0 °C in an ice bath, was added picolinoyl chloride hydrochloride (0.53 g, 3.0 mmol, 1.5 equiv.) portion wise. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was quenched and diluted by water (10 mL) and extracted with CH_2Cl_2 (10 mL × 3) and the combined organic phases were washed by brine and dried over anhydrous Na_2SO_4. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EA = 2:1, *v*/*v*) to afford the products **1a–1l**.

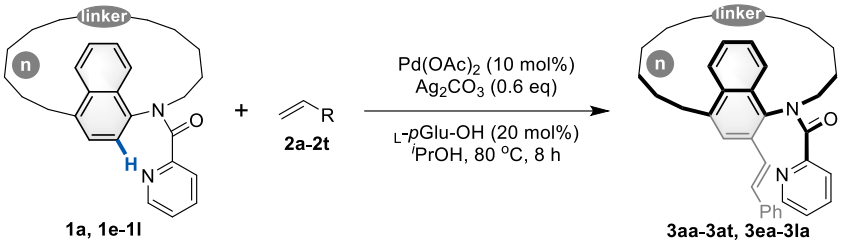
The **4** used in this study were synthesized through the procedure described below.



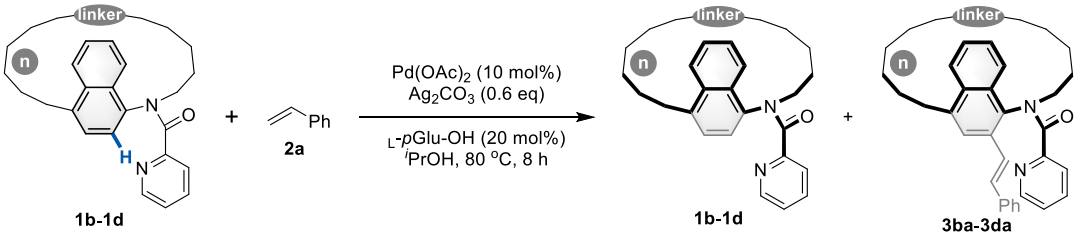
S25 **4**

To a solution of crude products **S25** (0.16 g, 1.0 mmol, 1.0 equiv.) in a mixture of dry Et_3N:CH_2Cl_2 (6 mL, 1:2 *v*/*v*), cooled to 0 °C in an ice bath, was added picolinoyl chloride hydrochloride (0.27 g, 1.5 mmol, 1.5 equiv.) portion wise. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was quenched and diluted by water (5 mL) and extracted with CH_2Cl_2 (5 mL × 3) and the combined organic phases were washed by brine and dried over anhydrous Na_2SO_4. After filtration and removing the solvent *in vacuum*, the residue was purified by flash column chromatography on silica gel (PE/EA = 2:1, *v*/*v*) to afford the products **4**.

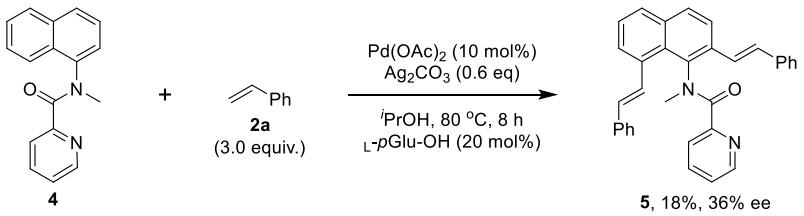
d) Procedures for the Reaction of Naphthalenophanes 1a–1l, 4 and Alkenes 2a–2t, 5



A 10 mL-reaction tube equipped with a magnetic stirring bar was charged with naphthalenophanes **1a**, **1e–1l** (0.1 mmol, 1.0 equiv.), alkene **2a–2t** (0.3 mmol, 3.0 equiv.), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 10 mol%), L-*p*Glu-OH (2.6 mg, 0.02 mmol, 20 mol%) and Ag_2CO_3 (16.5 mg, 0.06 mmol, 0.6 equiv.). The tube was sealed and ^{i}PrOH (2.0 mL) was injected to the tube *via* a syringe. The reaction mixture was allowed to stir at 80 °C (pre-heated metal module) under air for 8 h. And then the reaction mixture was immediately cooled to room temperature. The solvent was evaporated and the residue was purified by silica gel column chromatography (PE/EA = 3:1, *v*/*v*) affording the planar-chiral naphthalenophanes **3aa–3at, 3ea–3la**.



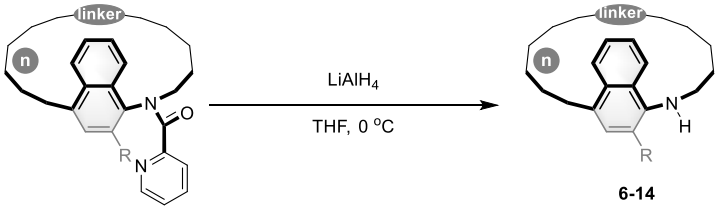
A 10 mL-reaction tube equipped with a magnetic stirring bar was charged with naphthalenophanes **1b–1d** (0.1 mmol, 1.0 equiv.), Styrene **2a** (0.3 mmol, 3.0 equiv.), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 10 mol%), L-*p*Glu-OH (2.6 mg, 0.02 mmol, 20 mol%) and Ag_2CO_3 (16.5 mg, 0.06 mmol, 0.6 equiv.). The tube was sealed and ^{i}PrOH (2.0 mL) was injected to the tube *via* a syringe. The reaction mixture was allowed to stir at 80 °C (pre-heated metal module) under air for 8 h. And then the reaction mixture was immediately cooled to room temperature. The solvent was evaporated and the residue was purified by silica gel column chromatography (PE/EA = 3:1, *v*/*v*) affording the planar-chiral naphthalenophanes **1b**–**1d** and **3ba–3da**.



A 10 mL-reaction tube equipped with a magnetic stirring bar was charged with **4** (0.1 mmol, 1.0 equiv.), alkene **2a** (0.3 mmol, 3.0 equiv.), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 10 mol%), L-*p*Glu-OH (2.6 mg, 0.02 mmol, 20 mol%) and Ag_2CO_3 (16.5 mg, 0.06 mmol, 0.6 equiv.). The tube was sealed and ^{i}PrOH (2.0 mL) was injected to the tube *via* a syringe. The reaction mixture was allowed to stir at 80 °C (pre-heated metal module) for 8 h. And then the reaction mixture was immediately cooled to room temperature. The solvent was evaporated and the residue was purified by silica gel column chromatography (PE/EA = 8:1, *v*/*v*) affording **5**.

Note: Racemic samples for the standard of chiral HPLC spectra were prepared using $_{DL}$-*p*Glu-OH as catalyst.

e) Procedures for Reduction of Naphthalenophanes 6–14



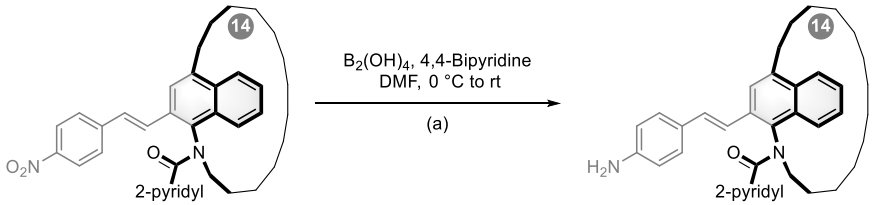
R = H or phenylethene

1c, 1d, 3aa, 3ca-3da, 3ha-3ka

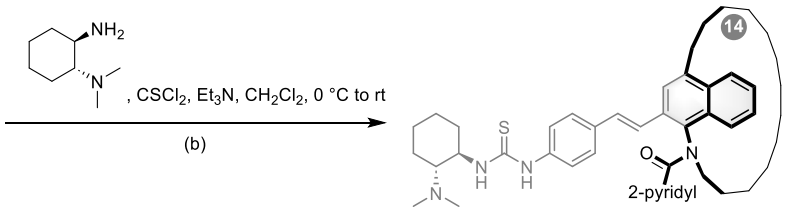
To a solution of **1c, 1d, 3aa, 3ca–3da, 3ha–3ka** (0.1 mmol, 1.0 equiv.) in THF (2.0 mL) was added $LiAlH_4$ (7.6 mg, 0.2 mmol, 2.0 equiv.) at 0 °C. The reaction was warmed to room temperature and reacted for 6 h. The mixture was added dropwise with saturated $NaHCO_3$ solution until the system no longer produced bubbles. The mixture was diluted by water (5 mL) and extracted with EA (5 mL × 3). The combined organic layers were dried over by anhydrous Na_2SO_4. After filtration and removing the solvent *in vacuum*, the residue was purified by column chromatography on silica gel (PE/EA = 20:1, *v*/*v*) afforded the product **6–14**.

3. Derivatization and Conformational Stability Studies

a) Derivatization of the Planar-Chiral Naphthalenophanes



3ai **S26**



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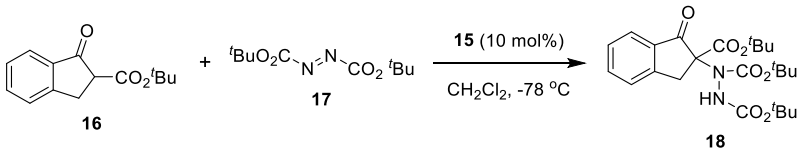
(a) To a solution of **3ai** (53.0 mg, 0.1 mmol, 1.0 equiv.) in dry DMF (1 mL) was added 4,4-Bipyridine (0.8 mg, 0.005 mmol, 0.05 equiv.) at 0 °C. Then the $B_2(OH)_4$ (35.9 mg, 0.4 mmol, 4.0 equiv.) was added to the reaction at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. Then the reaction mixtures were diluted with water (2 mL) and extracted with EA (5 mL × 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 **S26** was used directly for next step.

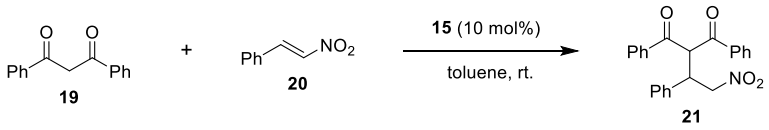
(b) Thiophosgene (0.01 mL, 0.13 mmol, 1.3 equiv.) was added dropwise to a solution of (*1R*,*2R*)-*N*,*N*-dimethylcyclohexane-1,2-diamine (0.02 mL, 0.12 mmol, 1.2 equiv.) and Et_3N (0.4 mL, 3 mmol, 30.0 equiv.) in CH_2Cl_2 (1.0 mL). The mixture was stirred for 30 min at 0 °C. Then,

the cold bath was removed, and stirring was continued for an additional 3 h. The mixture was extracted with CH_2Cl_2 (5 mL × 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.[6]

Under an N_2 atmosphere, the aforementioned crude brown oil was added to a solution of **S26** (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 **15**.

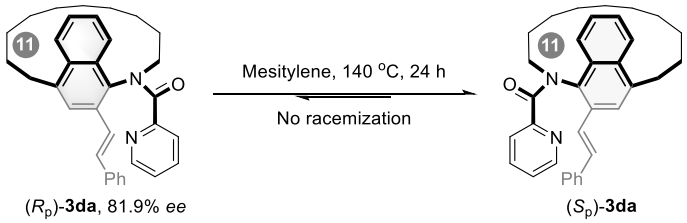


Compound **18** was prepared in 63% yield, 74% *ee* (29.1 mg, 0.10 mmol scale) according to the known procedure with compound **15** (>20:1 *dr*) as catalyst.[7] This compound is known and the spectroscopic data match those reported. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.80 – 7.68 (m, 1H), 7.64 – 7.57 (m 1H), 7.49 – 7.43 (m, 1H), 7.38 – 7.31 (m, 1H), 6.73 (s, 1H), 4.26 – 3.50 (m, 2H), 1.66 – 1.32 (m, 27H). **$[\alpha]_D^{25}$** = +116.2 (c = 1.47, CH_2Cl_2). **HPLC**: Chiralpak IE column, 95:5 hexanes/isopropanol, flow rate = 1.5 mL/min, λ = 254 nm, t_R = 29.00 min (minor), 31.29 min (major).



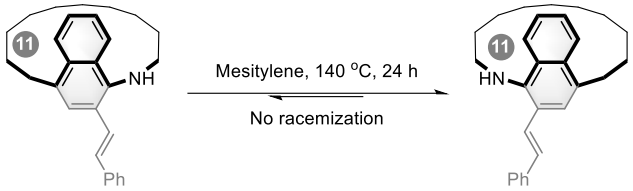
Compound **21** was prepared in 80% yield, 61% *ee* (29.7 mg, 0.10 mmol scale) according to the known procedure with compound **15** (>20:1 *dr*) as catalyst. This compound is known and the spectroscopic data match those reported.[8] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.42 – 7.31 (m, 4H), 7.24 – 7.13 (m, 5H), 5.85 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.00 (d, *J* = 6.9 Hz, 2H), 4.67 – 4.57 (m 1H). **$[\alpha]_D^{25}$** = -24.7 (c = 0.42, CH_2Cl_2). **HPLC**: Chiralpak AS-H column, 85:15 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 17.76 min (minor), 24.11 min (major).

b) Racemization Experiment of 3da, 9, 1d and 8



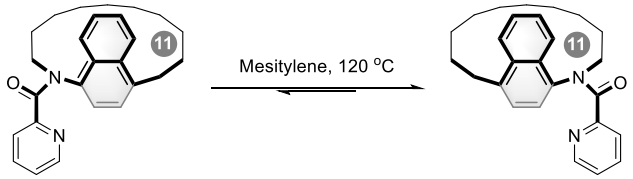
(R_p)-**3da**, 81.9% *ee* (S_p)-**3da**

Compound (R_p)-**3da** (10 mg, 0.02 mmol, 81.9% *ee*) was dissolved in mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 140 °C (pre-heated metal module) under air. Within the same time interval, small sample (30 μL) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess. After 24 h, no epimerization was detected; instead, decomposition of (R_p)-**3da** occurred.



(R_p)-**9**, 73.3% *ee* (S_p)-**9**

Compound (R_p)-**9** (10 mg, 0.026 mmol, 73.3% *ee*) was dissolved in mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 140 °C (pre-heated metal module) under air. Within the same time interval, small sample (30 μL) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess. After 24 h, no epimerization was detected; instead, decomposition of (R_p)-**9** occurred.



(R_p)-**1d**, 81.7% *ee* (S_p)-**1d**

Compound (R_p)-**1d** (10 mg, 0.026 mmol, 81.7% *ee*) was dissolved in mesitylene (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 120 °C (pre-heated metal module) under air. Within the same time interval, small sample (30 μL) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess.

Table S1. The racemization experiment of (R_p)-**1d** at 120 °C

time (s)	ee_t (%)	ee_t/ee_0	$\ln(ee_0/ee_t)$
0	81.70	1.0000	0.0000
900	80.37	0.9837	0.0164
1800	75.77	0.9274	0.0754
2700	73.72	0.9023	0.1028
3600	71.19	0.8714	0.1377
4800	67.30	0.8237	0.1939
6000	63.37	0.7756	0.2541

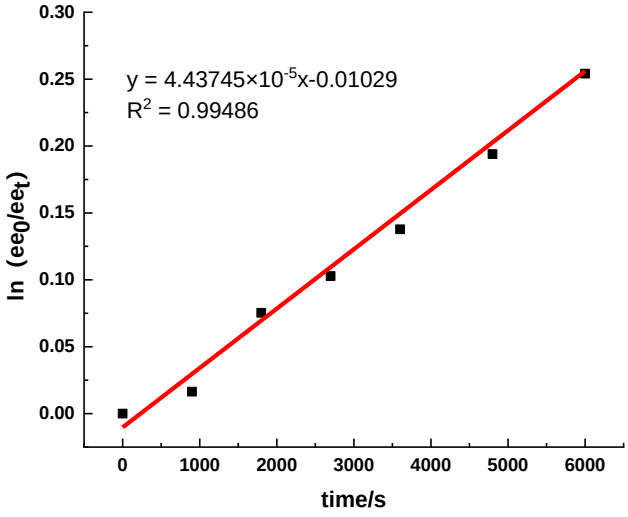


Figure S1. The racemization curves of (R_p)-**1d** at 120 °C

T_1 = 120 °C = 393.15 K, T_2 = 25 °C = 298.15 K

k_{rac}(120 °C) = 4.44 × 10^{-5} s^{-1}

$\tau_{1/2}$(120 °C) = ln2 / k_{rac}(120 °C) = 15620.39 s = 260.34 min

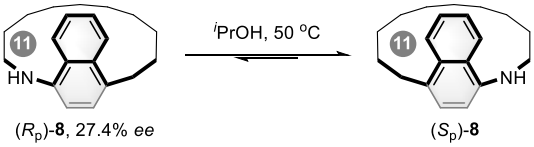
k_{ent}(120 °C) = k_{rac}(120 °C) / 2 = 2.22 × 10^{-5} s^{-1}

$\Delta G^{\neq}_{ent} = RT_1 \cdot \ln((k_B T_1)/(hk_{ent})) = 132.23$ kJ·mol^{-1} = 31.60 kcal·mol^{-1}

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

k_{rac}(25 °C) = 8.50 × 10^{-11} s^{-1}

$\tau_{1/2}$(25 °C) = ln2 / k_{rac}(25 °C) = 8.15 × 10^9 s = 2.26 × 10^6 h = 9.42 × 10^4 days = 258 years



(R_p)-**8**, 27.4% *ee* (S_p)-**8**

Compound (R_p)-**8** (10 mg, 0.036 mmol, 29.1% *ee*) was dissolved in ^{i}PrOH (2.0 mL) in a sealed tube. The reaction mixture was allowed to stir at 120 °C (pre-heated metal module) under air. Within the same time interval, small sample (30 μL) was removed *via* a syringe and diluted by isopropanol, then sample was injected into the HPLC to measure the enantiomeric excess.

Table S2. The racemization experiment of (R_p)-**8** at 50 °C

time (s)	ee_t (%)	ee_t/ee_0	$\ln(ee_0/ee_t)$
0	27.40	1.0000	0.0000
300	26.86	0.9804	0.0198
600	26.36	0.9621	0.0386

900	26.00	0.9490	0.0523
1200	25.37	0.9261	0.0768
1500	25.14	0.9177	0.0859
1800	24.61	0.8985	0.1071

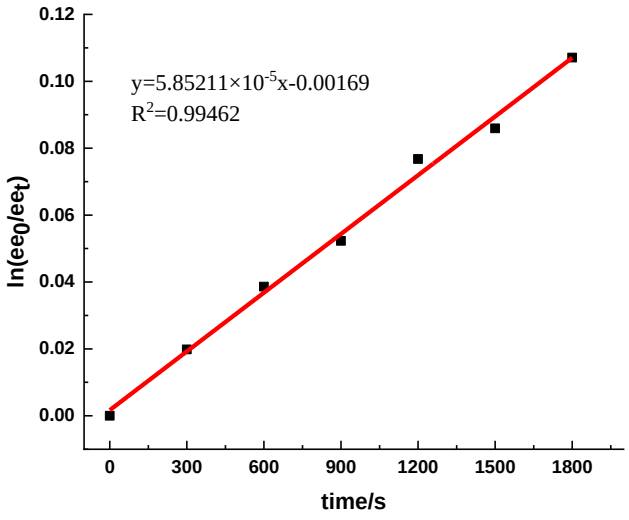


Figure S2. The racemization curves of (R_p)-**8** at 50 °C

T_1 = 50 °C = 323.15 K, T_2 = 25 °C = 298.15 K

k_{rac}(50 °C) = 5.85×10^{-5} s^{-1}

$\tau_{1/2}$(50 °C) = ln2 / k_{rac}(50 °C) = 11844.40 s = 197.41 min = 3.3 h

k_{ent}(50 °C) = k_{rac}(50 °C) / 2 = 2.93×10^{-5} s^{-1}

$\Delta G^{\neq}_{ent} = RT_1 \cdot \ln((k_B T_1)/(hk_{ent})) = 107.41$ kJ·mol^{-1} = 25.67 kcal·mol^{-1}

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

k_{rac}(25 °C) = 1.89×10^{-6} s^{-1}

$\tau_{1/2}$(25 °C) = ln2 / k_{rac}(25 °C) = 3.67×10^5 s = 101.86 h = 4.24 days

4. Optical Properties of R_p/S_p-10

a) UV-Vis Absorption Spectroscopic Study for (R_p)-10

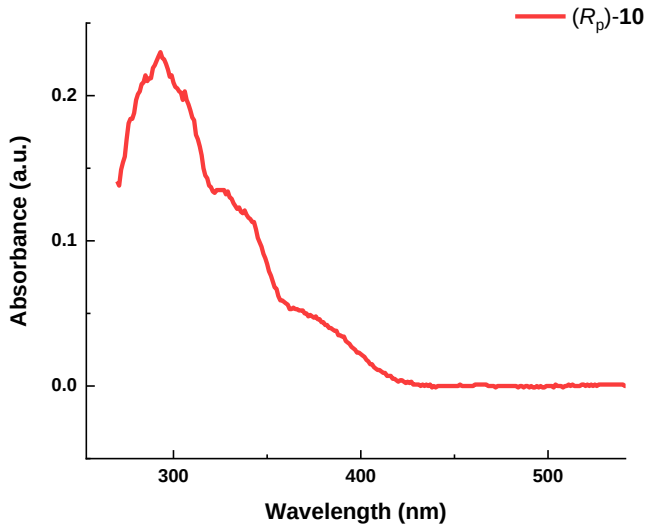


Figure S3. UV/Vis absorption spectra of (R_p)-**10** measured in CH_2Cl_2 (c = 1.0 × 10^{-5} M).

b) Fluorescence Spectroscopic Study for (R_p)-10

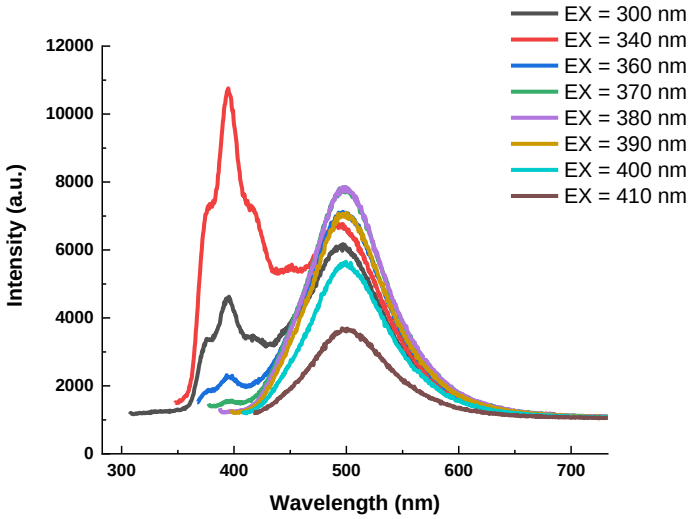


Figure S4. Fluorescence emission spectra of (R_p)-**10** measured in CH_2Cl_2 (c = 1.0 × 10^{-5} M).

c) Circular Dichroism (CD) Spectroscopic Study for R_p/S_p-10

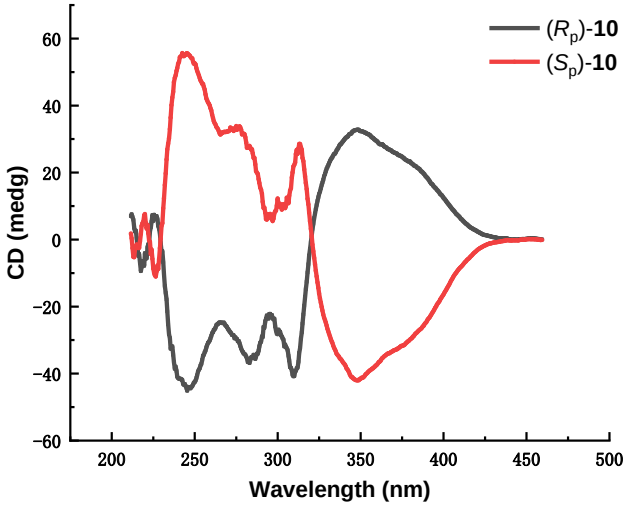


Figure S5. Circular Dichroism (CD) Spectroscopic spectra of R_p/S_p-**10** (c = 0.5 mg/mL).

d) Circularly Polarized Luminescence (CPL) Spectroscopic Study for R_p/S_p-10

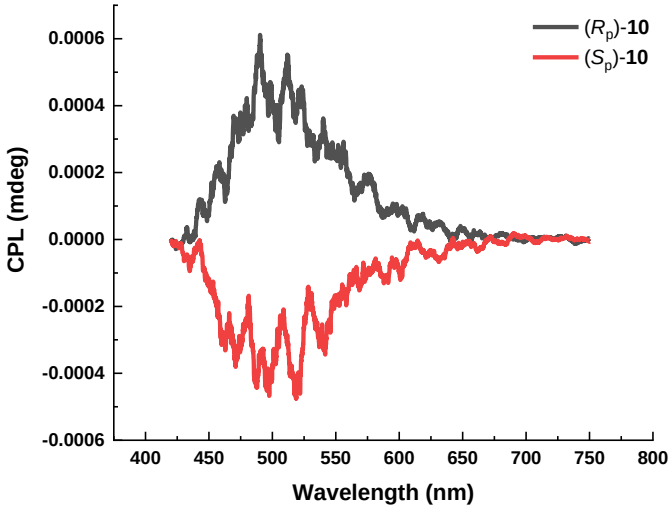
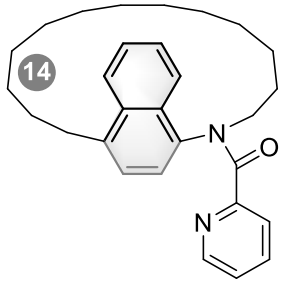


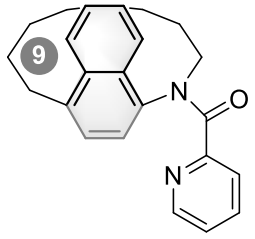
Figure S6. Circularly polarized luminescence (CPL) spectra of R_p/S_p-**10** (c = 1 mg/mL).

5. Characterization Data

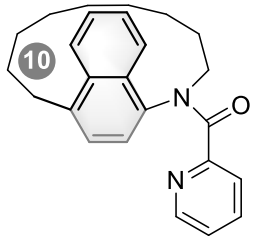
a) Characterization Data of Substrates 1a–1g and 4



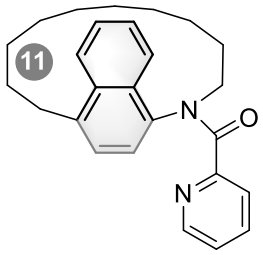
1a, white solid. 1.14 g, 27% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* = 13:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 4.9 Hz, 1H), 8.08 – 8.00 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 (ddd, *J* = 8.2, 6.7, 1.4 Hz, 1H), 7.30 (td, *J* = 7.7, 1.7 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.95 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.49 (ddd, *J* = 13.1, 9.5, 6.2 Hz, 1H), 3.53 – 3.40 (m, 2H), 2.63 (ddd, *J* = 14.2, 9.2, 5.4 Hz, 1H), 1.75 – 1.66 (m, 2.3H), 1.64 – 1.49 (m, 2.1H), 1.46 – 1.38 (m, 1.1H), 1.30 – 1.23 (m, 2.4H), 1.15 – 1.03 (m, 6.1H), 1.00 – 0.92 (m, 4.1H), 0.91 – 0.86 (m, 3.1H), 0.83 – 0.77 (m, 2.1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.5, 154.9, 148.8, 138.5, 136.5, 135.8, 132.9, 130.7, 127.4, 126.5, 126.3, 126.0, 125.0, 124.0, 123.7, 122.1, 48.7, 32.3, 29.0, 28.4, 28.2, 27.71, 27.66, 27.3, 26.7, 26.6, 26.2, 25.4, 25.2. **HRMS** (ESI): *m/z* calculated for $C_{29}H_{37}N_2O^+$ $[M + H]^+$ 429.2901, found 429.2904.



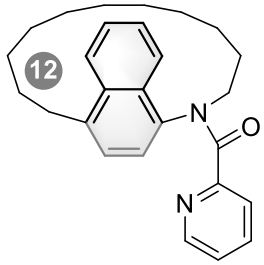
1b, white solid. 0.18 g, 5% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* = 9:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.32 (dt, *J* = 4.7, 1.4 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.59 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.54 – 7.51 (m, 1H), 7.51 – 7.48 (m, 1H), 7.20 (q, *J* = 7.5 Hz, 2H), 7.06 (ddd, *J* = 7.8, 3.6, 2.4 Hz, 1H), 4.07 (t, *J* = 11.1 Hz, 1H), 3.83 – 3.76 (m, 1H), 3.52 – 3.45 (m, 1H), 2.63 (ddd, *J* = 13.8, 9.5, 4.8 Hz, 1H), 1.66 – 1.55 (m, 1.1H), 1.44 – 1.35 (m, 1.1H), 1.27 – 1.19 (m, 1.0H), 1.17 – 1.08 (m, 1.1H), 0.93 – 0.84 (m, 1.1H), 0.82 – 0.76 (m, 1.0H), 0.48 – 0.40 (m, 2.3H), 0.35 – 0.26 (m, 1.1H), 0.22 – 0.13 (m, 1.1H), 0.06 – 0.00 (m, 1.0H), -0.17 – -0.29 (m, 1.0H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.9, 154.8, 148.8, 139.3, 136.25, 136.17, 133.9, 132.0, 128.5, 127.2, 126.6, 126.2, 124.8, 124.4, 124.1, 122.9, 47.9, 32.4, 28.2, 27.6, 26.1, 26.0, 25.7, 23.6. **HRMS (ESI)**: *m/z* calculated for $C_{24}H_{27}N_2O^+$ $[M + H]^+$ 359.2118, found 359.2112.



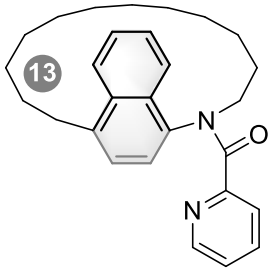
1c, white solid, 0.52 g, 14% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* = 17:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.31 (dt, *J* = 4.9, 1.3 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.60 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.54 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.39 (td, *J* = 7.6, 1.7 Hz, 1H), 7.36 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.01 (ddd, *J* = 7.4, 4.9, 1.4 Hz, 1H), 4.71 (ddd, *J* = 14.0, 8.2, 2.7 Hz, 1H), 3.54 (dt, *J* = 13.6, 4.5 Hz, 1H), 3.40 (ddd, *J* = 14.1, 7.9, 2.8 Hz, 1H), 2.59 (ddd, *J* = 13.4, 11.4, 5.1 Hz, 1H), 1.86 – 1.79 (m, 1.1H), 1.56 – 1.46 (m, 2.2H), 1.40 (d, *J* = 12.6 Hz, 1.3H), 1.23 – 1.13 (m, 1.1H), 0.92 – 0.84 (m, 1.0H), 0.75 – 0.66 (m, 1.9H), 0.66 – 0.60 (m, 1.2H), 0.59 – 0.52 (m, 1.2H), 0.51 – 0.40 (m, 2.3H), 0.12 – 0.01 (m, 1.1H), -0.40 – -0.54 (m, 1.0H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 154.9, 148.8, 138.6, 136.0, 133.2, 130.9, 128.7, 126.764, 126.758, 126.2, 125.0, 124.0, 123.9, 122.4, 47.0, 33.4, 28.2, 27.5, 26.8, 26.6, 26.39, 26.37, 25.5. **HRMS (ESI)**: *m/z* calculated for $C_{25}H_{29}N_2O^+$ $[M + H]^+$ 373.2275, found 373.2278.



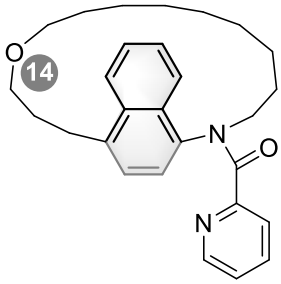
1d, white solid, 0.74 g, 19% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* > 20:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.33 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.63 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 1H), 7.57 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1H), 7.34 (td, *J* = 7.7, 1.7 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.04 – 6.98 (m, 3H), 4.60 (ddd, *J* = 13.7, 6.2, 4.3 Hz, 1H), 3.54 (dt, *J* = 13.6, 4.1 Hz, 1H), 3.43 (ddd, *J* = 13.4, 9.0, 4.1 Hz, 1H), 2.50 (td, *J* = 12.9, 3.9 Hz, 1H), 2.09 – 1.97 (m, 1.0H), 1.94 – 1.82 (m, 1.1H), 1.69 – 1.59 (m, 1.1H), 1.55 – 1.46 (m, 1.1H), 1.41 – 1.31 (m, 1.2H), 1.22 – 1.11 (m, 1.1H), 1.07 – 0.97 (m, 1.0H), 0.93 – 0.80 (m, 1.1H), 0.76 – 0.66 (m, 3.1H), 0.64 – 0.48 (m, 3.1H), 0.37 – 0.23 (m, 1.3H), 0.07 – 0.00 (m, 1.1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.4, 154.7, 149.1, 138.6, 138.2, 135.9, 132.9, 129.9, 127.7, 126.7, 126.4, 126.2, 125.2, 124.1, 123.8, 122.1, 46.9, 34.0, 27.8, 27.6, 27.5, 27.2, 26.7, 26.6, 25.44, 25.40. **HRMS (ESI)**: *m/z* calculated for $C_{26}H_{31}N_2O^+$ $[M + H]^+$ 387.2431, found 387.2437.



1e, white solid, 0.96 g, 24% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* = 10:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, J = 4.7 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.39 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.03 (s, 2H), 6.78 (ddd, J = 6.9, 4.9, 1.7 Hz, 1H), 4.32 (dt, J = 13.8, 7.0 Hz, 1H), 3.56 (dt, J = 13.7, 6.9 Hz, 1H), 3.35 (ddd, J = 13.8, 6.3, 3.6 Hz, 1H), 2.51 (ddd, J = 14.1, 10.4, 3.9 Hz, 1H), 1.71 – 1.64 (m, 1.0H), 1.62 – 1.57 (m, 1.1H), 1.57 – 1.49 (m, 2.1H), 1.08 – 1.01 (m, 1.0H), 0.99 – 0.91 (m, 3.0H), 0.87 – 0.82 (m, 1.2H), 0.78 – 0.67 (m, 5.1H), 0.61 – 0.52 (m, 2.0H), 0.52 – 0.46 (m, 1.1H), 0.45 – 0.37 (m, 1.1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.6, 154.1, 148.0, 138.4, 136.8, 136.8, 135.2, 132.4, 129.9, 126.6, 125.9, 125.5, 124.4, 123.4, 123.2, 121.8, 47.9, 32.2, 28.1, 27.2, 26.7, 26.6, 26.3, 26.1, 26.0, 25.1, 24.9. **HRMS (ESI)**: *m/z* calculated for $C_{27}H_{33}N_2O^+$ $[M + H]^+$ 401.2588, found 401.2589.

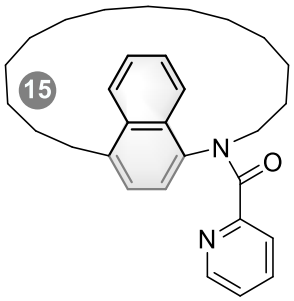


1f, white solid, 1.06 g, 25% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* = 17:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (dt, J = 8.5, 4.0 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.51 (q, J = 6.6 Hz, 1H), 7.44 (t, J = 7.0 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.13 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 3.6 Hz, 2H), 6.88 – 6.77 (m, 1H), 4.51 (dt, J = 14.0, 7.2 Hz, 1H), 3.38 (ddd, J = 13.8, 6.4, 3.3 Hz, 1H), 3.35 – 3.26 (m, 1H), 2.51 – 2.45 (m, 1H), 1.82 – 1.68 (m, 2.2H), 1.63 – 1.50 (m, 2.2H), 1.22 – 1.11 (m, 1.3H), 1.06 – 0.98 (m, 4.0H), 0.97 – 0.90 (m, 3.3H), 0.88 – 0.79 (m, 4.0H), 0.79 – 0.67 (m, 3.0H), 0.65 – 0.57 (m, 1.0H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.2, 154.4, 148.6, 138.6, 137.0, 135.8, 132.7, 130.2, 126.5, 126.3, 125.9, 125.9, 124.9, 123.8, 123.6, 121.9, 48.7, 32.7, 28.6, 27.9, 27.3, 27.2, 26.94, 26.90, 26.8, 26.35, 26.31, 25.6. **HRMS (ESI)**: *m/z* calculated for $C_{28}H_{35}N_2O^+$ $[M + H]^+$ 415.2744, found 415.2749.

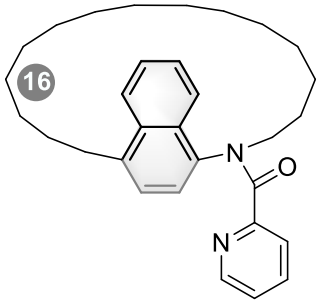


1g, white solid, 0.93 g, 22% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* = 13:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, J = 4.5 Hz, 1H), 8.04 (dd, J = 8.4, 1.4 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.61 – 7.48 (m, 2H), 7.31 (td, J = 7.7, 1.7 Hz, 1H), 7.22 – 7.09 (m, 3H), 6.96 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 4.56 – 4.46 (m, 1H), 3.54 – 3.37 (m, 2.1H), 3.31 – 3.19 (m, 2.3H), 3.17 – 3.06 (m, 2.1H), 2.79 (ddd, J = 14.3, 9.7, 4.5 Hz, 1H), 2.11 – 1.97 (m, 2.2H), 1.72 – 1.60 (m, 2.3H), 1.49 – 1.38 (m, 1.1H), 1.30 – 1.25 (m, 1.2H), 1.22 – 1.15 (m, 2.2H), 1.13 – 1.01 (m, 4.3H), 0.97 – 0.87 (m, 4.3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.5, 154.8, 148.7, 137.8, 137.0, 135.9, 132.9, 130.6, 127.4, 126.6, 126.4, 126.1, 124.9, 124.0, 123.7, 122.1, 70.3, 68.3, 48.8, 29.4, 28.9, 28.00, 27.97, 27.0, 25.8, 25.2, 25.0. **HRMS (ESI)**: *m/z* calculated for $C_{28}H_{35}N_2O_2^+$ $[M + H]^+$

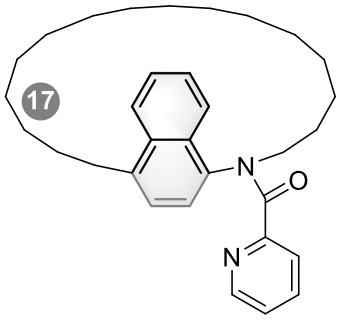
431.2694, found 431.2690.



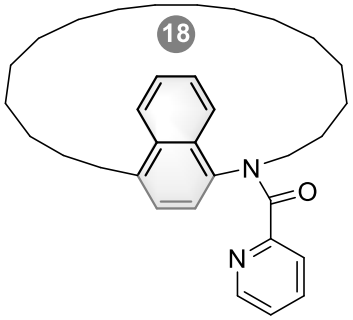
1h, yellow oil. 0.87 g, 20% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* > 20:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 4.9 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.08 – 6.98 (m, 2H), 6.88 (t, *J* = 6.3 Hz, 1H), 4.57 (dt, *J* = 14.1, 7.4 Hz, 1H), 3.44 – 3.23 (m, 2H), 2.63 – 2.52 (m, 1H), 1.72 – 1.53 (m, 4.2H), 1.37 – 1.31 (m, 1.1H), 1.20 – 1.17 (m, 2.3H), 1.15 – 1.08 (m, 5.2H), 1.06 – 0.91 (m, 12.3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.3, 154.6, 148.5, 138.3, 136.7, 135.7, 132.7, 130.4, 127.2, 126.4, 126.0, 125.9, 124.9, 123.8, 123.5, 121.8, 49.3, 32.3, 29.1, 28.8, 28.4, 27.95, 27.92, 27.6, 27.5, 27.24, 27.18, 27.1, 26.8, 25.5. **HRMS (ESI)**: *m/z* calculated for $C_{30}H_{39}N_2O^+$ $[M + H]^+$ 443.3057, found 443.3064.



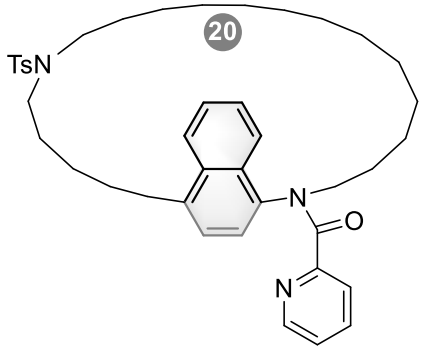
1i, yellow oil. 0.94 g, 21% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* = 16:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.12 – 6.98 (m, 2H), 6.87 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.54 (ddd, *J* = 13.0, 9.6, 6.0 Hz, 1H), 3.38 (ddt, *J* = 15.2, 11.0, 5.4 Hz, 2H), 2.60 (ddd, *J* = 14.4, 9.8, 4.8 Hz, 1H), 1.78 – 1.59 (m, 3.4H), 1.59 – 1.47 (m, 1.2H), 1.44 – 1.36 (m, 1.3H), 1.18 – 1.09 (m, 9.0H), 1.09 – 0.97 (m, 12.1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.3, 154.6, 148.5, 138.6, 136.5, 135.7, 132.7, 130.6, 127.3, 126.4, 125.9, 125.8, 124.8, 123.8, 123.5, 121.9, 49.0, 32.3, 29.5, 28.3, 28.2, 28.0, 27.9, 27.7, 27.65, 27.62, 27.5, 27.2, 26.8, 25.7. **HRMS (ESI)**: *m/z* calculated for $C_{31}H_{41}N_2O^+$ $[M + H]^+$ 457.3214, found 457.3217.



1j, yellow oil. 0.83 g, 18% yield , over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* > 20:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 4.8 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.03 (q, *J* = 7.4 Hz, 2H), 6.86 (t, *J* = 6.2 Hz, 1H), 4.62 (dt, *J* = 14.6, 6.4 Hz, 1H), 3.37 – 3.32 (m, 1H), 3.31 – 3.26 (m, 1H), 2.59 (ddd, *J* = 14.7, 10.2, 4.5 Hz, 1H), 1.78 – 1.68 (m, 2.1H), 1.68 – 1.59 (m, 1.1H), 1.59 – 1.49 (m, 1.1H), 1.47 – 1.39 (m, 1.0H), 1.38 – 1.29 (m, 1.0H), 1.21 – 1.15 (m, 10.0H), 1.14 – 1.06 (m, 12.0H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.3, 154.6, 148.5, 138.5, 136.4, 135.6, 132.7, 130.4, 127.4, 126.4, 125.9, 125.7, 124.7, 123.7, 123.4, 121.7, 49.1, 32.4, 29.4, 28.8, 28.6, 28.5, 28.32, 28.26, 28.2, 27.8, 27.6, 27.3, 27.2, 27.1, 27.0, 26.1. **HRMS (ESI)**: *m/z* calculated for $C_{32}H_{43}N_2O^+$ $[M + H]^+$ 471.3370, found 471.3377.

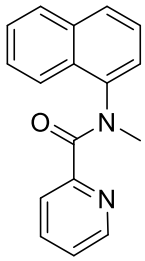


1k, yellow oil. 1.21 g, 25% yield, over 7 steps, eluent (silica gel, PE/EA = 3:1, *v/v*), *cis:trans* > 20:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 4.9 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.09 – 7.00 (m, 2H), 6.89 (t, *J* = 6.3 Hz, 1H), 4.55 (ddd, *J* = 14.3, 9.5, 6.1 Hz, 1H), 3.41 – 3.23 (m, 2H), 2.62 (dt, *J* = 14.5, 7.4 Hz, 1H), 1.77 – 1.66 (m, 2.1H), 1.65 – 1.57 (m, 1.0H), 1.53 – 1.45 (m, 1.1H), 1.42 – 1.34 (m, 1.1H), 1.20 – 1.04 (m, 25.4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.5, 154.7, 148.6, 138.9, 136.5, 135.7, 132.7, 130.6, 127.5, 126.5, 126.0, 125.7, 124.8, 123.8, 123.5, 121.9, 49.2, 32.6, 29.8, 28.8, 28.6, 28.5, 28.41, 28.37, 28.3, 28.20, 28.18, 28.1, 28.0, 27.8, 27.2, 26.1. **HRMS (ESI)**: *m/z* calculated for $C_{33}H_{45}N_2O^+$ $[M + H]^+$ 485.3527, found 485.3529.



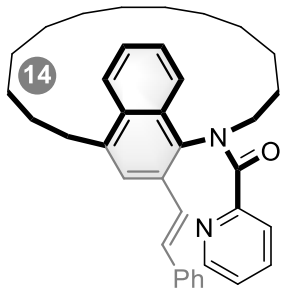
1l, yellow oil. 1.90 g, 28% yield, over 7 steps eluent (silica gel, PE/EA = 2:1, *v/v*), *cis:trans* = 17:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 4.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.58 (td, *J* = 7.0, 3.6 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.32 – 7.27 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.93 (m, 1H), 4.55 (ddd, *J* = 13.2, 9.3, 6.2 Hz, 1H), 3.44 – 3.36 (m, 1H), 3.27 (dt, *J* = 13.7, 6.5 Hz, 1H), 3.01 (ddd, *J* = 27.1, 14.6, 7.1 Hz, 2H), 2.96 – 2.87 (m, 2H), 2.68 (dt, *J* = 14.8, 7.7 Hz, 1H), 2.40 (s, 3H), 1.80 – 1.70 (m, 2.4H), 1.67 – 1.56 (m, 2.4H), 1.53 – 1.46 (m, 2.1H), 1.40 – 1.31 (m, 3.1H),

1.30 – 1.24 (m, 3.3H), 1.22 – 1.15 (m, 7.4H), 1.13 – 1.05 (m, 9.3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.5, 154.7, 148.7, 143.1, 138.8, 136.9, 136.6, 135.9, 132.8, 130.7, 129.7, 127.6, 127.3, 126.6, 126.1, 125.5, 124.7, 124.0, 123.7, 122.0, 49.6, 49.5, 49.4, 32.9, 30.1, 29.4, 29.22, 29.18, 28.93, 28.89, 28.8, 28.5, 28.4, 28.2, 27.3, 27.0, 26.6, 26.1, 21.6. **HRMS (ESI)**: *m/z* calculated for $C_{41}H_{54}N_3O_3S^+$ $[M + H]^+$ 668.3881, found 668.3889.

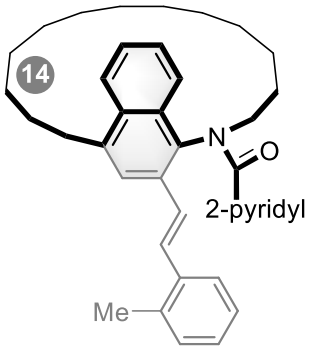


4, brown solid. 0.25 g, 95% yield, (silica gel, PE/EA = 2:1, *v/v*), *cis:trans* = 17:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 4.8 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 6.90 (ddd, *J* = 6.9, 4.8, 1.7 Hz, 1H), 3.54 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.5, 153.8, 148.2, 140.3, 135.6, 134.1, 129.8, 128.3, 127.9, 126.9, 126.2, 126.0, 125.1, 123.6, 122.7, 122.2, 37.9.

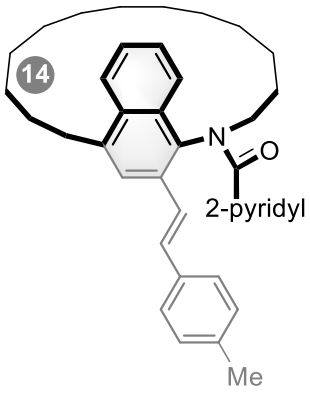
b) Characterization Data of Naphthalenophanes 3aa–3at



(R_p)-**3aa**, *cis:trans* = 13:1, colorless oil, 44.1 mg, 83% yield, 98% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 4.6 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 5.6 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.93 – 6.84 (m, 1H), 4.27 (ddd, *J* = 13.2, 10.8, 5.6 Hz, 1H), 3.80 (ddd, *J* = 13.4, 10.9, 5.5 Hz, 1H), 3.49 (dt, *J* = 13.9, 4.9 Hz, 1H), 2.71 (dt, *J* = 14.2, 7.3 Hz, 1H), 1.81 – 1.72 (m, 2.2H), 1.60 – 1.45 (m, 2.4H), 1.33 – 1.27 (m, 2.3H), 1.14 – 1.01 (m, 8.2H), 0.96 – 0.87 (m, 4.5H), 0.83 – 0.72 (m, 4.0H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 154.2, 148.4, 138.4, 137.3, 135.5, 134.2, 132.3, 131.9, 131.7, 131.1, 129.0, 128.2, 126.9, 126.8, 125.8, 124.9, 124.75, 124.70, 123.9, 123.8, 122.2, 49.6, 32.7, 28.9, 28.2, 28.0, 27.7, 27.6, 26.9, 26.6, 26.2, 25.3, 24.6. **HRMS (ESI)**: *m/z* calculated for $C_{37}H_{43}N_2O^+$ $[M + H]^+$ 531.3370, found 531.3374. **$[\alpha]_D^{25}$** = -235.9 (c = 0.74, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 19.87 min (minor), 29.38 min (major).

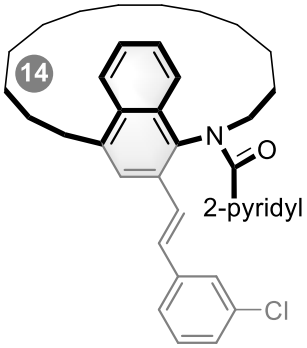


(R_p)-**3ab**, *cis:trans* = 8:1, colorless oil, 36.6 mg, 67% yield, 92% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 4.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.39 (d, *J* = 16.2 Hz, 1H), 7.30 – 7.28 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 5.9 Hz, 2H), 6.91 (td, *J* = 5.1, 3.0 Hz, 1H), 4.24 (ddd, *J* = 13.1, 10.9, 5.5 Hz, 1H), 3.81 (ddd, *J* = 13.2, 10.8, 5.6 Hz, 1H), 3.50 (dt, *J* = 14.0, 4.9 Hz, 1H), 2.72 (dt, *J* = 14.4, 7.4 Hz, 1H), 2.44 (s, 3H), 1.80 – 1.74 (m, 2.2H), 1.57 – 1.43 (m, 2.3H), 1.35 – 1.28 (m, 2.3H), 1.12 – 1.03 (m, 9.3H), 0.99 – 0.94 (m, 2.2H), 0.92 – 0.87 (m, 2.5H), 0.85 – 0.76 (m, 4.2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.7, 154.3, 148.4, 138.5, 136.4, 135.9, 135.6, 134.2, 132.4, 132.3, 131.8, 130.5, 129.1, 128.1, 126.8, 126.7, 126.5, 126.0, 125.8, 124.8, 124.7, 124.2, 123.9, 122.3, 49.6, 32.7, 28.9, 28.3, 28.0, 27.7, 27.0, 26.6, 26.31, 26.27, 25.4, 24.7, 20.0. **HRMS (ESI)**: *m/z* calculated for $C_{38}H_{45}N_2O^+$ $[M + H]^+$ 545.3527, found 545.3532. **$[\alpha]_D^{25}$** = -122.9 (c = 1.06, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 15.79 min (minor), 24.29 min (major).

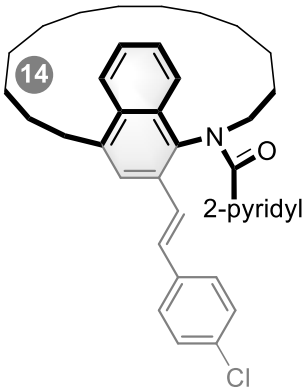


(R_p)-**3ac**, *cis:trans* = 8:1, pale yellow oil, 38.1 mg, 70% yield, 91% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 4.7 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.47 – 7.41 (m, 3H), 7.39 (s, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 16.5 Hz, 1H), 6.93 – 6.87 (m, 1H), 4.26 – 4.14 (m, 1H), 3.90 – 3.81 (m, 1H), 3.49 (dt, *J* = 14.0, 4.9 Hz, 1H), 2.70 (dt, *J* = 14.2, 7.4 Hz, 1H), 2.42 (s, 3H), 1.82 – 1.70 (m, 2.2H), 1.56 – 1.42 (m, 2.4H), 1.34 – 1.28 (m, 2.4H), 1.12 – 1.00 (m, 7.4H), 0.96 – 0.85 (m, 5.3H), 0.84 – 0.71 (m, 4.1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 154.4, 148.4, 138.6, 138.4, 137.4, 135.5, 134.2, 132.2, 132.0, 131.9, 131.4, 129.1, 128.9, 127.8, 126.7, 125.8, 124.8, 124.7, 124.1, 123.91, 123.88, 122.3, 49.6, 32.8, 29.0, 28.3, 28.0, 27.7, 27.6, 27.0, 26.6, 26.2, 25.4, 24.7, 21.6. **HRMS (ESI)**: *m/z* calculated for $C_{38}H_{45}N_2O^+$ $[M + H]^+$ 545.3527, found 545.3522. **$[\alpha]_D^{25}$** = -171.3 (c = 2.11, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 16.19 min (minor), 23.99 min

(major).

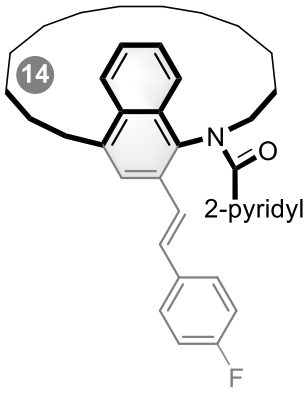


(R_p)-**3ad**, *cis:trans* = 8:1, pale yellow oil, 55.2 mg, 98% yield, 96% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.08 (d, J = 4.2 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.50 – 7.44 (m, 4H), 7.34 (t, J = 7.8 Hz, 1H), 7.31 – 7.27 (m, 3H), 6.97 (d, J = 16.3 Hz, 1H), 6.90 (td, J = 5.1, 3.1 Hz, 1H), 4.23 (ddd, J = 13.0, 10.9, 5.4 Hz, 1H), 3.81 (ddd, J = 13.2, 10.9, 5.4 Hz, 1H), 3.49 (dt, J = 13.9, 5.0 Hz, 1H), 2.70 (dt, J = 14.3, 7.4 Hz, 1H), 1.80 – 1.74 (m, 2.5H), 1.56 – 1.51 (m, 1.2H), 1.50 – 1.45 (m, 1.5H), 1.34 – 1.28 (m, 2.4H), 1.23 – 1.17 (m, 1.2H), 1.13 – 1.01 (m, 8.3H), 0.97 – 0.92 (m, 2.1H), 0.90 – 0.86 (m, 2.4H), 0.83 – 0.73 (m, 4.2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.7, 154.2, 148.3, 139.3, 138.6, 135.6, 134.9, 134.7, 132.5, 131.7, 131.5, 130.2, 129.7, 128.0, 127.3, 126.8, 126.7, 126.1, 124.78, 124.76, 124.6, 124.0, 123.8, 122.3, 49.7, 32.7, 28.9, 28.3, 28.0, 27.7, 27.6, 27.0, 26.7, 26.3, 25.4, 24.7. **HRMS (ESI)**: *m/z* calculated for $C_{37}H_{42}ClN_2O^+$ $[M + H]^+$ 565.2981, found 565.2984. **$[\alpha]_D^{25}$** = -152.9 (c = 1.36, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 13.19 min (minor), 20.73 min (major).

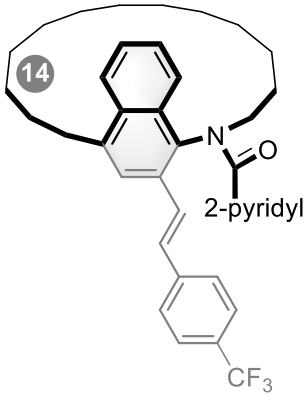


(R_p)-**3ae**, *cis:trans* = 11:1, pale yellow oil, 55.1 mg, 97% yield, 97% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.09 (d, J = 4.8 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.57 – 7.50 (m, 4H), 7.48 – 7.44 (m, 3H), 7.37 (d, J = 8.4 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.23 (d, J = 7.9 Hz, 1H), 6.97 (d, J = 16.3 Hz, 1H), 6.93 – 6.87 (m, 1H), 4.27 (ddd, J = 13.1, 10.9, 5.4 Hz, 1H), 3.75 (ddd, J = 13.1, 11.0, 5.3 Hz, 1H), 3.49 (dt, J = 13.9, 4.9 Hz, 1H), 2.70 (dt, J = 14.3, 7.4 Hz, 1H), 1.79 – 1.73 (m, 2.5H), 1.57 – 1.49 (m, 1.3H), 1.49 – 1.41 (m, 1.4H), 1.34 – 1.27 (m, 2.2H), 1.13 – 1.07 (m, 3.3H), 1.07 – 1.00 (m, 4.4H), 0.97 – 0.91 (m, 2.1H), 0.91 – 0.83 (m, 3.1H), 0.83 – 0.73 (m, 4.3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.7, 154.2, 148.4, 138.6, 135.9, 135.6, 134.4, 133.8, 132.4, 131.70, 131.68, 129.8, 129.2, 128.1, 126.9, 126.0, 125.7, 124.8, 124.7, 124.0, 123.7, 122.2, 49.7, 32.7, 28.9, 28.3, 28.0, 27.7, 27.6, 27.0, 26.7, 26.27, 26.25, 25.4, 24.7. **HRMS (ESI)**: *m/z* calculated for $C_{37}H_{42}ClN_2O^+$ $[M + H]^+$ 565.2981, found 565.2983. **$[\alpha]_D^{25}$** = -206.7 (c = 1.33,

CH_2Cl_2). **HPLC**: Chiralpak IE column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 21.48 min (minor), 29.60 min (major).

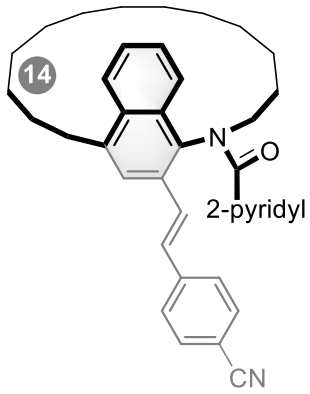


(R_p)-**3af**, *cis:trans* = 11:1, pale yellow oil, 53.7 mg, 98% yield, 88% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 5.0 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.54 (m, 4H), 7.50 (d, *J* = 6.0 Hz, 2H), 7.43 (d, *J* = 16.4 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.14 (t, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 16.2 Hz, 1H), 6.98 – 6.90 (m, 1H), 4.31 (td, *J* = 12.1, 5.5 Hz, 1H), 3.80 (td, *J* = 12.0, 5.4 Hz, 1H), 3.53 (dt, *J* = 13.9, 5.0 Hz, 1H), 2.74 (dt, *J* = 14.2, 7.4 Hz, 1H), 1.84 – 1.74 (m, 2.2H), 1.62 – 1.49 (m, 2.2H), 1.37 – 1.28 (m, 2.5H), 1.17 – 1.05 (m, 7.4H), 1.02 – 0.90 (m, 5.5H), 0.88 – 0.76 (m, 4.3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 162.7 (d, $J_{C\text{-}F}$ = 247.9 Hz), 161.5, 154.3, 148.4, 138.5, 135.5, 134.2, 133.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 132.3, 131.8, 131.7, 129.9, 128.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 126.8, 125.9, 125.0, 124.9, 124.7 (d, $J_{C\text{-}F}$ = 7.3 Hz), 123.8 (d, $J_{C\text{-}F}$ = 20.5 Hz), 122.1, 115.9 (d, $J_{C\text{-}F}$ = 21.7 Hz), 49.6, 32.7, 28.9, 28.3, 28.0, 27.7, 27.6, 27.0, 26.6, 26.2, 25.4, 24.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.30, -113.83. **HRMS (ESI)**: *m/z* calculated for $C_{37}H_{42}FN_2O^+$ [M + H]$^+$ 549.3276, found 549.3272. **$[\alpha]_D^{25}$** = -173.0 (c = 1.64, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 14.91 min (minor), 20.45 min (major).

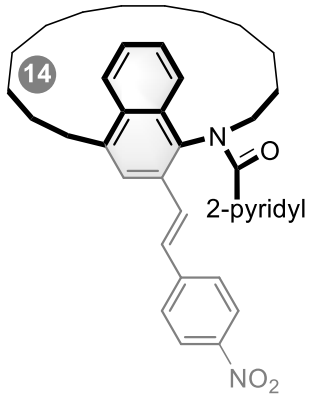


(R_p)-**3ag**, *cis:trans* = 9:1, pale yellow oil, 48.6 mg, 81% yield, 96% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 3.9 Hz, 1H), 8.01 (t, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.60 (m, 3H), 7.59 – 7.57 (m, 1H), 7.57 – 7.53 (m, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.30 – 7.26 (m, 2H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.90 (ddd, *J* = 7.8, 4.8, 2.8 Hz, 1H), 4.29 (ddd, *J* = 13.2, 10.8, 5.5 Hz, 1H), 3.75 (ddd, *J* = 13.2, 10.9, 5.5 Hz, 1H), 3.50 (dt, *J* = 13.9, 4.9 Hz, 1H), 2.71 (dt, *J* = 14.3, 7.3 Hz, 1H), 1.81 – 1.74 (m, 2.1H), 1.59 – 1.44 (m, 2.4H), 1.35 – 1.25 (m, 2.4H), 1.12 – 1.03 (m, 8.2H), 0.96 – 0.85 (m, 5.1H), 0.83 – 0.72 (m, 4.5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.7, 154.2, 148.4, 140.8, 138.7, 135.6, 134.9, 132.6, 131.7, 131.4, 129.7 (q, $J_{C\text{-}F}$ =

32.6 Hz), 129.2, 127.7, 127.0, 126.9, 126.2, 125.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.83, 124.75, 124.3 (q, $J_{C\text{-}F}$ = 271.8 Hz), 124.0, 123.6, 122.2, 49.7, 32.7, 28.9, 28.2, 28.0, 27.7, 27.6, 27.0, 26.7, 26.3, 26.2, 25.3, 24.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -162.32. **HRMS (ESI)**: *m/z* calculated for $C_{38}H_{42}F_3N_2O^+$ $[M + H]^+$ 599.3244, found 599.3248. **$[\alpha]_D^{25}$** = -192.2 (c = 2.26, CH_2Cl_2). **HPLC**: Chiralpak IF column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 6.67 min (minor), 8.02 min (major).

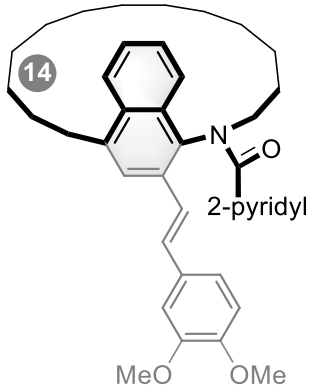


(R_p)-**3ah**, *cis:trans* = 8:1, pale yellow oil, 48.2 mg, 87% yield, 98% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 (dt, *J* = 4.8, 1.3 Hz, 1H), 8.02 (d, *J* = 3.7 Hz, 1H), 8.00 (d, *J* = 3.5 Hz, 1H), 7.68 (s, 4H), 7.65 (d, *J* = 6.6 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.50 (m, 1H), 7.46 (s, 1H), 7.31 – 7.27 (m, 1H), 7.01 (d, *J* = 16.3 Hz, 1H), 6.91 (ddd, *J* = 6.7, 4.8, 1.6 Hz, 1H), 4.29 (ddd, *J* = 13.1, 10.8, 5.5 Hz, 1H), 3.73 (ddd, *J* = 13.1, 10.9, 5.4 Hz, 1H), 3.50 (dt, *J* = 13.8, 4.9 Hz, 1H), 2.71 (dt, *J* = 14.3, 7.3 Hz, 1H), 1.81 – 1.73 (m, 2.2H), 1.58 – 1.40 (m, 3.0H), 1.34 – 1.26 (m, 3.1H), 1.11 – 1.02 (m, 7.2H), 0.94 – 0.87 (m, 4.3H), 0.82 – 0.73 (m, 4.4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.6, 154.1, 148.4, 141.9, 138.8, 135.7, 135.2, 132.8, 132.6, 131.6, 131.1, 129.0, 128.9, 127.3, 127.1, 126.4, 124.9, 124.7, 124.1, 123.5, 122.2, 119.1, 111.1, 49.8, 32.7, 28.9, 28.2, 28.0, 27.7, 27.6, 27.0, 26.7, 26.3, 26.2, 25.3, 24.8. **HRMS (ESI)**: *m/z* calculated for $C_{38}H_{42}N_3O^+$ $[M + H]^+$ 556.3323, found 556.3318. **$[\alpha]_D^{25}$** = -262.5 (c = 1.04, CH_2Cl_2). **HPLC**: Chiralpak IC column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 138.56 min (major), 191.91 min (minor).

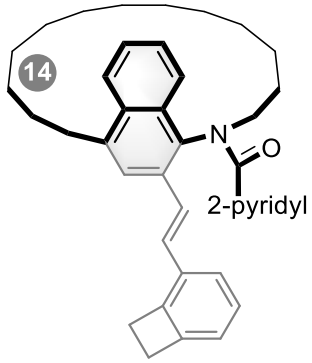


(R_p)-**3ai**, *cis:trans* = 7:1, pale yellow oil, 31.1 mg, 54% yield, 98% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.25 (d, *J* = 8.3 Hz, 2H), 8.07 (d, *J* = 5.0 Hz, 1H), 8.01 (t, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 3H), 7.68 (d, *J* = 16.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.48 (s, 1H), 7.31 – 7.27 (m, 2H), 7.07 (d, *J* = 16.3 Hz, 1H), 6.92 – 6.89 (m, 1H), 4.30 (ddd, *J* = 13.0, 10.9, 5.3 Hz, 1H), 3.77 – 3.70 (m, 1H), 3.50 (dt, *J* = 13.9, 5.0 Hz, 1H), 2.71 (dt, *J* = 14.3, 7.4 Hz, 1H),

1.80 – 1.73 (m, 2.0H), 1.57 – 1.50 (m, 1.5H), 1.49 – 1.42 (m, 1.0H), 1.33 – 1.27 (m, 2.3H), 1.21 – 1.16 (m, 1.2H), 1.15 – 1.07 (m, 4.2H), 1.06 – 0.99 (m, 4.3H), 0.96 – 0.91 (m, 2.2H), 0.90 – 0.84 (m, 3.1H), 0.82 – 0.78 (m, 2.2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.6, 154.1, 148.3, 147.1, 143.9, 138.8, 135.7, 135.4, 132.8, 131.5, 131.0, 129.9, 128.4, 127.3, 127.1, 126.5, 124.9, 124.7, 124.3, 124.0, 123.5, 122.2, 49.8, 32.7, 28.8, 28.2, 28.0, 27.64, 27.55, 26.9, 26.6, 26.22, 26.19, 25.3, 24.8. **HRMS (ESI)**: *m/z* calculated for $C_{37}H_{42}N_3O_3^+$ $[M + H]^+$ 576.3221, found 576.3229. **$[\alpha]_D^{25}$** = -86.5 (c = 0.31, CH_2Cl_2). **HPLC**: Chiralpak AD-H column, 90:10 hexanes/isopropanol, flow rate = 1.5 mL/min, λ = 254 nm, t_R = 42.52 min (minor), 51.80 min (major).

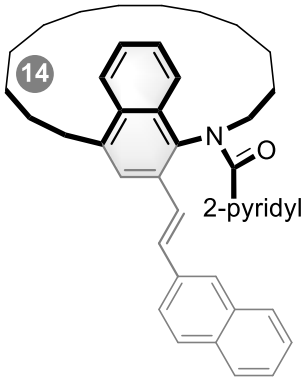


(R_p)-**3aj**, *cis:trans* = 7:1, pale yellow oil, 52.2 mg, 88% yield, 99% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 4.7 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.34 (d, *J* = 16.1 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.20 – 7.15 (m, 2H), 7.00 (d, *J* = 16.1 Hz, 1H), 6.93 – 6.88 (m, 2H), 4.29 – 4.22 (m, 1H), 3.99 (s, 3H), 3.93 (s, 3H), 3.80 – 3.74 (m, 1H), 3.48 (dt, *J* = 13.6, 4.8 Hz, 1H), 2.69 (dt, *J* = 14.3, 7.4 Hz, 1H), 1.79 – 1.72 (m, 2.1H), 1.58 – 1.45 (m, 2.4H), 1.32 – 1.29 (m, 2.1H), 1.11 – 1.03 (m, 8.5H), 0.97 – 0.92 (m, 2.1H), 0.90 – 0.84 (m, 3.3H), 0.82 – 0.73 (m, 4.4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.9, 154.3, 149.4, 149.3, 148.5, 138.4, 135.5, 133.8, 132.15, 132.12, 131.8, 130.9, 130.6, 126.7, 125.7, 124.71, 124.69, 123.9, 123.8, 123.3, 122.1, 120.0, 111.5, 109.6, 56.1, 49.6, 32.7, 28.9, 28.3, 28.0, 27.7, 27.6, 27.0, 26.7, 26.27, 26.25, 25.4, 24.7. **HRMS (ESI)**: *m/z* calculated for $C_{39}H_{47}N_2O_3^+$ $[M + H]^+$ 591.3582, found 591.3586. **$[\alpha]_D^{25}$** = -149.1 (c = 1.21, CH_2Cl_2). **HPLC**: Chiralpak IF column, 50:50 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 10.80 min (minor), 14.01 min (major).

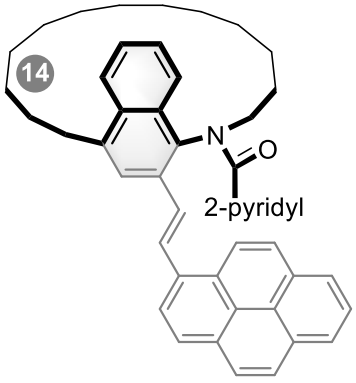


(R_p)-**3ak**, *cis:trans* = 14:1, pale yellow oil, 30.6 mg, 55% yield, 98% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 4.7 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.48 (s, 1H), 7.47 – 7.43 (m, 1H), 7.41 (d, *J* = 16.2 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.26 – 7.22 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.89 (ddd, *J* = 6.8, 4.8, 2.0 Hz,

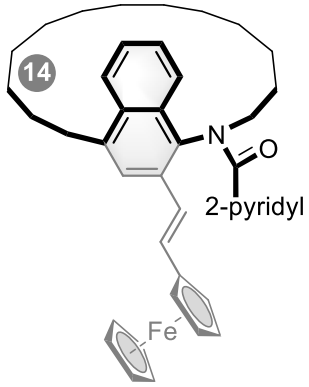
1H), 4.29 – 4.21 (m, 1H), 3.83 – 3.75 (m, 1H), 3.48 (dt, *J* = 13.9, 4.9 Hz, 1H), 3.24 – 3.23 (m, 2H), 3.22 – 3.20 (m, 2H), 2.70 (dt, *J* = 14.3, 7.4 Hz, 1H), 1.79 – 1.73 (m, 3.0H), 1.58 – 1.44 (m, 2.5H), 1.33 – 1.27 (m, 2.4H), 1.22 – 1.17 (m, 1.2H), 1.12 – 1.07 (m, 3.2H), 1.07 – 1.03 (m, 4.3H), 0.98 – 0.92 (m, 2.2H), 0.90 – 0.85 (m, 2.4H), 0.82 – 0.80 (m, 1.4H), 0.79 – 0.72 (m, 2.3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 154.3, 148.4, 146.6, 146.4, 138.4, 136.3, 135.5, 133.9, 132.3, 132.2, 131.8, 126.7, 125.7, 124.8, 124.7, 123.9, 123.8, 123.6, 123.0, 122.1, 120.3, 49.6, 32.7, 29.7, 29.6, 28.9, 28.3, 28.0, 27.7, 27.6, 27.0, 26.6, 26.2, 25.4, 24.6. **HRMS (ESI)**: *m/z* calculated for $C_{39}H_{45}N_2O^+$ $[M + H]^+$ 557.3527, found 557.3539. **$[\alpha]_D^{25}$** = -211.3 (c = 1.34, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 14.26 min (minor), 22.47 min (major).



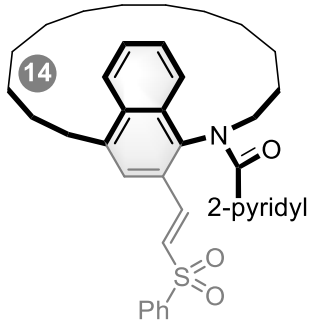
(R_p)-**3al**, *cis:trans* = 14:1, yellow oil, 52.9 mg, 91% yield, 97% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 5.0 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.93 – 7.84 (m, 6H), 7.62 (d, *J* = 16.2 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.48 (q, *J* = 7.6, 7.1 Hz, 3H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 16.2 Hz, 1H), 6.89 (dd, *J* = 7.4, 4.9 Hz, 1H), 4.30 (ddd, *J* = 13.0, 11.0, 5.4 Hz, 1H), 3.83 (ddd, *J* = 13.0, 10.9, 5.3 Hz, 1H), 3.51 (dt, *J* = 14.0, 5.0 Hz, 1H), 2.73 (dt, *J* = 14.3, 7.3 Hz, 1H), 1.82 – 1.75 (m, 2.4H), 1.64 – 1.47 (m, 2.4H), 1.36 – 1.28 (m, 2.3H), 1.14 – 1.10 (m, 2.4H), 1.10 – 1.03 (m, 5.1H), 0.98 – 0.92 (m, 2.2H), 0.92 – 0.86 (m, 3.0H), 0.85 – 0.81 (m, 2.0H), 0.81 – 0.73 (m, 2.4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.8, 154.3, 148.4, 138.5, 135.6, 134.9, 134.3, 133.8, 133.4, 132.3, 132.0, 131.8, 131.3, 128.8, 128.2, 127.9, 127.3, 126.8, 126.6, 126.3, 125.9, 125.3, 124.8, 124.7, 123.9, 123.8, 123.7, 122.3, 49.7, 32.8, 28.9, 28.3, 28.0, 27.7, 27.6, 27.0, 26.7, 26.3, 26.2, 25.4, 24.7. **HRMS (ESI)**: *m/z* calculated for $C_{41}H_{45}N_2O^+$ $[M + H]^+$ 581.3527, found 581.3520. **$[\alpha]_D^{25}$** = -204.3 (c = 1.83, CH_2Cl_2). **HPLC**: Chiralpak IF column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 10.59 min (minor), 12.46 min (major).



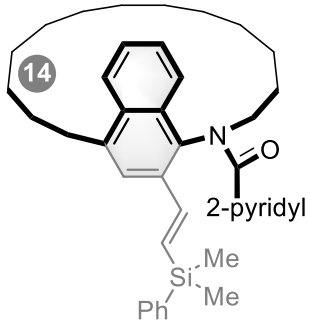
(R_p)-**3am**, *cis:trans* = 11:1, yellow solid, 63.3 mg, 97% yield, 95% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, *J* = 7.1 Hz, 1H), 8.45 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 7.4 Hz, 2H), 8.17 – 8.13 (m, 3H), 8.13 – 8.08 (m, 4H), 8.07 – 8.02 (m, 2H), 7.77 (d, *J* = 16.1 Hz, 1H), 7.73 (s, 1H), 7.63 – 7.57 (m, 1H), 7.55 – 7.49 (m, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 6.94 – 6.89 (m, 1H), 4.39 (td, *J* = 11.8, 5.0 Hz, 1H), 3.85 (td, *J* = 12.0, 5.0 Hz, 1H), 3.57 (dt, *J* = 14.3, 4.5 Hz, 1H), 2.83 (dt, *J* = 14.9, 7.5 Hz, 1H), 1.68 – 1.55 (m, 2.4H), 1.43 – 1.32 (m, 2.4H), 1.26 – 1.13 (m, 7.4H), 1.11 – 1.07 (m, 2.3H), 1.04 – 0.98 (m, 3.0H), 0.96 – 0.89 (m, 4.3H), 0.86 – 0.79 (m, 2.5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 154.4, 148.4, 138.6, 135.6, 134.5, 132.5, 132.4, 131.8, 131.6, 131.3, 131.0, 128.5, 128.2, 128.2, 127.73, 127.69, 127.5, 126.9, 126.1, 125.9, 125.7, 125.5, 125.2, 125.1, 125.0, 124.8, 124.2, 124.1, 123.9, 122.9, 122.3, 49.7, 32.7, 29.0, 28.3, 28.1, 27.8, 27.7, 27.0, 26.7, 26.4, 26.3, 25.4, 24.8. **HRMS (ESI)**: *m/z* calculated for $C_{47}H_{47}N_2O^+$ $[M + H]^+$ 655.3683, found 655.3694. **$[\alpha]_D^{25}$** = -152.1 (c = 2.57, CH_2Cl_2). **HPLC**: Chiralpak AS-H column, 60:40 hexanes/isopropanol, flow rate = 0.1 mL/min, λ = 254 nm, t_R = 56.59 min (minor), 67.78 min (major).



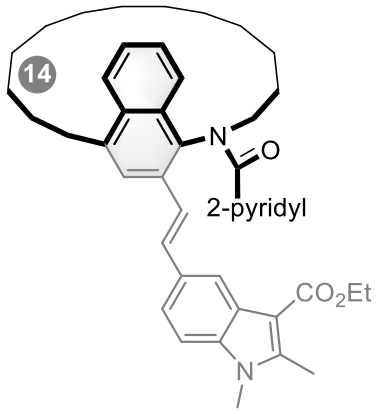
(R_p)-**3an**, *cis:trans* = 10:1, orangered solid, 61.4 mg, 95% yield, 99% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (t, *J* = 4.7 Hz, 1H), 7.99 (dd, *J* = 8.7, 4.3 Hz, 1H), 7.94 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.35 – 7.28 (m, 2H), 7.13 – 7.04 (m, 1H), 6.97 – 6.86 (m, 2H), 4.59 (s, 2H), 4.35 (s, 2H), 4.21 (tt, *J* = 11.3, 5.4 Hz, 1H), 4.14 (s, 3H), 4.13 (s, 2H), 3.81 (tt, *J* = 9.8, 4.6 Hz, 1H), 3.49 (dt, *J* = 14.7, 5.2 Hz, 1H), 2.69 (ddt, *J* = 14.3, 10.2, 4.8 Hz, 1H), 1.81 – 1.71 (m, 2.1H), 1.59 – 1.46 (m, 2.3H), 1.37 – 1.29 (m, 2.3H), 1.13 – 1.04 (m, 8.3H), 0.98 – 0.87 (m, 5.2H), 0.83 – 0.78 (m, 4.0H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.7, 154.3, 148.5, 138.3, 135.5, 132.7, 132.1, 132.0, 131.8, 129.5, 126.7, 125.4, 124.6, 123.8, 123.3, 122.1, 122.0, 83.1, 69.60, 69.58, 69.4, 67.5, 67.4, 49.5, 32.8, 29.0, 28.2, 27.9, 27.7, 27.6, 27.0, 26.5, 26.2, 25.4, 24.5. **HRMS (ESI)**: *m/z* calculated for $C_{41}H_{47}FeN_2O^+$ $[M + H]^+$ 639.3027, found 639.3028. **$[\alpha]_D^{25}$** = -119.0 (c = 1.64, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 20.25 min (minor), 23.75 min (major).



(R_p)-**3ao**, *cis:trans* = 6:1, pale yellow oil, 46.2 mg, 78% yield, 95% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 15.4 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 2H), 7.98 – 7.92 (m, 2H), 7.81 (d, *J* = 4.8 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.59 – 7.49 (m, 6H), 7.36 (t, *J* = 7.8 Hz, 1H), 6.92 – 6.83 (m, 2H), 4.19 (td, *J* = 11.8, 5.2 Hz, 1H), 3.66 (td, *J* = 12.9, 4.8 Hz, 1H), 3.44 (dt, *J* = 13.9, 5.0 Hz, 1H), 2.63 (dt, *J* = 14.0, 6.8 Hz, 1H), 1.75 – 1.67 (m, 2.3H), 1.48 – 1.39 (m, 1.3H), 1.34 – 1.22 (m, 3.2H), 1.11 – 0.96 (m, 8.3H), 0.90 – 0.79 (m, 5.4H), 0.76 – 0.60 (m, 5.0H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.2, 153.7, 147.7, 140.8, 140.0, 139.1, 138.2, 136.1, 133.9, 133.5, 131.6, 129.4, 129.3, 128.1, 128.0, 127.7, 127.4, 127.3, 125.2, 124.9, 124.2, 123.7, 123.3, 50.2, 32.6, 28.8, 28.2, 28.0, 27.62, 27.55, 26.8, 26.6, 26.22, 26.15, 25.2, 24.7. **HRMS (ESI)**: *m/z* calculated for $C_{37}H_{43}N_2O_3S^+$ $[M + H]^+$ 595.2989, found 595.2982. **$[\alpha]_D^{25}$** = -99.0 (c = 0.31, CH_2Cl_2). **HPLC**: Chiralpak OD-H column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 38.15 min (minor), 66.23 min (major).

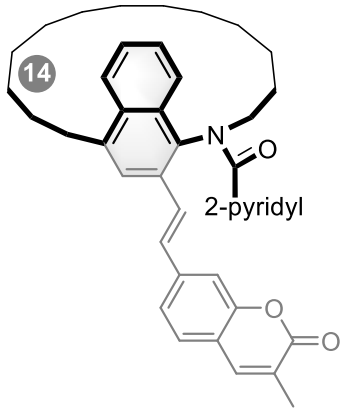


(R_p)-**3ap**, *cis:trans* = 13:1, pale yellow oil, 38.7 mg, 66% yield, 97% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 1.7 Hz, 1H), 8.03 (d, *J* = 5.8 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.42 – 7.38 (m, 4H), 7.37 – 7.32 (m, 1H), 7.28 (d, *J* = 9.4 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 6.90 (ddd, *J* = 7.4, 4.8, 1.4 Hz, 1H), 6.55 (d, *J* = 19.1 Hz, 1H), 4.29 (ddd, *J* = 13.1, 10.4, 5.7 Hz, 1H), 3.58 (ddd, *J* = 13.1, 10.4, 5.6 Hz, 1H), 3.45 (dt, *J* = 13.8, 4.8 Hz, 1H), 2.67 (dt, *J* = 14.3, 7.3 Hz, 1H), 1.78 – 1.70 (m, 3H), 1.53 – 1.40 (m, 2.1H), 1.12 – 1.05 (m, 5.2H), 1.04 – 0.96 (m, 4.1H), 0.95 – 0.86 (m, 4.0H), 0.85 – 0.77 (m, 4.4H), 0.49 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.4, 154.2, 148.3, 141.7, 138.3, 135.5, 134.4, 134.2, 134.0, 132.7, 132.3, 131.6, 130.5, 129.3, 128.0, 126.7, 126.0, 125.1, 124.7, 123.9, 123.8, 122.4, 49.8, 32.5, 28.8, 28.3, 28.2, 27.8, 27.7, 27.1, 26.7, 26.3, 25.4, 24.8, -2.48, -2.54. **HRMS (ESI)**: *m/z* calculated for $C_{39}H_{49}N_2OSi^+$ $[M + H]^+$ 589.3609, found 589.3614. **$[\alpha]_D^{25}$** = -114.3 (c = 0.96, CH_2Cl_2). **HPLC**: Chiralpak IE column, 73:27 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 10.64 min (minor), 15.20 min (major).

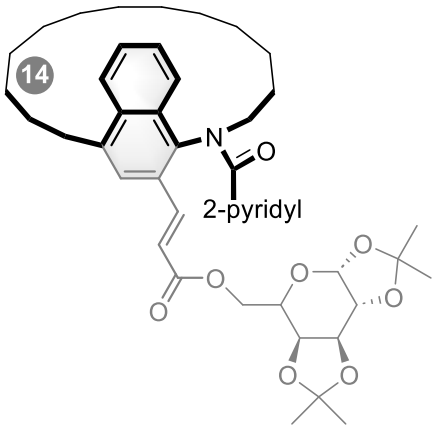


(R_p)-**3aq**, *cis:trans* = 10:1, white solid, 56.6 mg, 84% yield, 99% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)**

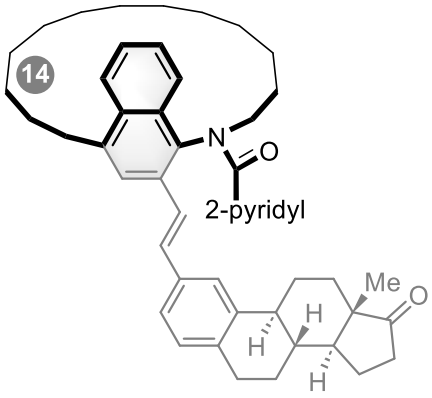
δ 8.24 (s, 1H), 8.08 (d, J = 4.9 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.63 (dd, J = 8.5, 1.7 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.47 (d, J = 16.2 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.24 – 7.19 (m, 2H), 6.85 (dd, J = 7.4, 5.0 Hz, 1H), 4.44 (q, J = 7.2 Hz, 2H), 4.23 (ddd, J = 13.2, 10.5, 5.8 Hz, 1H), 3.85 (ddd, J = 13.3, 10.5, 5.9 Hz, 1H), 3.69 (s, 3H), 3.48 (dt, J = 14.0, 5.0 Hz, 1H), 2.76 (s, 3H), 2.70 (dd, J = 14.2, 7.2 Hz, 1H), 1.79 – 1.73 (m, 2H), 1.56 – 1.50 (m, 2H), 1.48 (t, J = 7.1 Hz, 3H), 1.31 – 1.26 (m, 2.1H), 1.22 – 1.17 (m, 1.1H), 1.12 – 1.08 (m, 2.9H), 1.07 – 1.01 (m, 4.4H), 0.96 – 0.90 (m, 2.1H), 0.89 – 0.85 (m, 2.2H), 0.82 – 0.79 (m, 2H), 0.78 – 0.72 (m, 2.2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.9, 166.1, 154.4, 148.3, 145.9, 138.3, 136.6, 135.4, 133.6, 132.8, 132.5, 132.0, 131.8, 131.2, 127.0, 126.6, 125.5, 124.7, 124.6, 124.0, 123.8, 122.8, 122.2, 121.3, 120.3, 109.8, 104.4, 59.6, 49.5, 32.7, 29.9, 28.9, 28.2, 28.0, 27.7, 27.6, 27.0, 26.6, 26.2, 25.4, 24.7, 14.8, 12.1. **HRMS (ESI)**: *m/z* calculated for $C_{44}H_{52}N_3O_3^+$ $[M + H]^+$ 670.4004, found 670.4012. **$[\alpha]_D^{25}$** = -253.2 (c = 2.56, CH_2Cl_2). **HPLC**: Chiralpak AS–H column, 90:10 hexanes/isopropanol, flow rate = 0.3 mL/min, λ = 254 nm, t_R = 95.62 min (minor), 121.32 min (major).



(R_p)-**3ar**, *cis:trans* = 5:1, white solid, 56.8 mg, 93% yield, 96% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 8.08 (d, J = 4.9 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.63 (dd, J = 8.5, 1.7 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.47 (d, J = 16.2 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.24 – 7.19 (m, 2H), 6.85 (dd, J = 7.4, 5.0 Hz, 1H), 4.44 (q, J = 7.2 Hz, 2H), 4.23 (ddd, J = 13.2, 10.5, 5.8 Hz, 1H), 3.85 (ddd, J = 13.3, 10.5, 5.9 Hz, 1H), 3.69 (s, 3H), 3.48 (dt, J = 14.0, 5.0 Hz, 1H), 2.76 (s, 3H), 2.70 (dd, J = 14.2, 7.2 Hz, 1H), 1.79 – 1.73 (m, 2.0H), 1.56 – 1.50 (m, 2.0H), 1.48 (t, J = 7.1 Hz, 3H), 1.31 – 1.26 (m, 2.1H), 1.22 – 1.17 (m, 1.1H), 1.12 – 1.08 (m, 2.9H), 1.07 – 1.01 (m, 4.4H), 0.96 – 0.90 (m, 2.1H), 0.89 – 0.85 (m, 2.2H), 0.82 – 0.79 (m, 2H), 0.78 – 0.72 (m, 2.2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.9, 166.1, 154.4, 148.3, 145.9, 138.3, 136.6, 135.4, 133.6, 132.8, 132.5, 132.0, 131.8, 131.2, 127.0, 126.6, 125.5, 124.7, 124.6, 124.0, 123.8, 122.8, 122.2, 121.3, 120.3, 109.8, 104.4, 59.6, 49.5, 32.7, 29.9, 28.9, 28.2, 28.0, 27.7, 27.6, 27.0, 26.6, 26.2, 25.4, 24.7, 14.8, 12.1. **HRMS (ESI)**: *m/z* calculated for $C_{41}H_{45}N_2O_3^+$ $[M + H]^+$ 613.3425, found 613.3429. **$[\alpha]_D^{25}$** = -117.4 (c = 0.74, CH_2Cl_2). **HPLC**: Chiralpak AS–H column, 50:50 hexanes/isopropanol, flow rate = 0.1 mL/min, λ = 254 nm, t_R = 110.24 min (major), 137.33 min (minor).



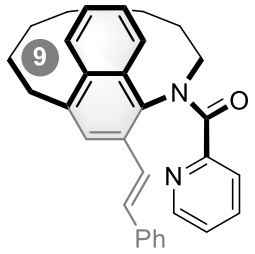
3as, *cis:trans* = 5:1, white solid, 72.6 mg, 98% yield, >20:1 *dr*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 16.1 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 4.7 Hz, 1H), 7.52 (dd, *J* = 5.5, 1.2 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.40 (td, *J* = 7.9, 1.8 Hz, 1H), 7.38 (s, 1H), 6.88 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.58 (d, *J* = 5.0 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.44 – 4.38 (m, 2H), 4.37 – 4.33 (m, 2H), 4.16 – 4.10 (m, 2H), 3.84 – 3.77 (m, 1H), 3.47 (dt, *J* = 13.8, 4.9 Hz, 1H), 2.65 (ddd, *J* = 14.3, 9.4, 5.3 Hz, 1H), 1.76 – 1.67 (m, 2H), 1.54 (s, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.33 – 1.32 (m, 5.2H), 1.30 – 1.25 (m, 2.4H), 1.21 – 1.14 (m, 1.3H), 1.10 – 1.04 (m, 5.1H), 1.02 – 0.98 (m, 2.5H), 0.97 – 0.91 (m, 3.0H), 0.89 – 0.81 (m, 3.1H), 0.77 – 0.69 (m, 4.5H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.2, 166.6, 153.9, 147.8, 141.4, 138.7, 137.5, 135.8, 133.5, 131.6, 129.1, 126.95, 126.87, 125.4, 124.7, 123.9, 123.7, 123.3, 119.9, 109.8, 108.9, 96.5, 71.2, 70.8, 70.6, 66.1, 63.6, 50.2, 32.7, 28.9, 28.2, 28.0, 27.7, 27.5, 26.9, 26.6, 26.19, 26.16, 26.1, 25.2, 25.1, 24.62, 24.60. **HRMS (ESI)**: *m/z* calculated for $C_{44}H_{56}N_2O_8^+$ $[M + H]^+$ 741.4110, found 741.4100. **$[\alpha]_D^{25}$** = -185.3 (c = 3.54, CH_2Cl_2).



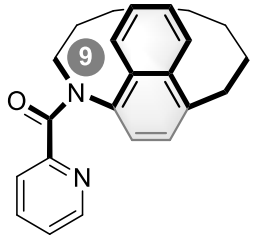
3at, *cis:trans* = 11:1, white oil, 68.5 mg, 97% yield, >20:1 *dr*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 4.6 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 13.2 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.35 (d, *J* = 10.3 Hz, 2H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.05 (d, *J* = 16.2 Hz, 1H), 6.87 (ddd, *J* = 6.9, 4.8, 2.2 Hz, 1H), 4.18 (ddd, *J* = 13.2, 10.1, 6.2 Hz, 1H), 3.86 (ddd, *J* = 13.3, 10.1, 6.3 Hz, 1H), 3.48 (dt, *J* = 13.9, 5.0 Hz, 1H), 3.00 (dt, *J* = 8.4, 4.5 Hz, 2H), 2.69 (dt, *J* = 14.3, 7.3 Hz, 1H), 2.52 (dd, *J* = 18.9, 8.7 Hz, 1H), 2.49 – 2.44 (m, 1.1H), 2.35 (td, *J* = 11.1, 4.1 Hz, 1.2H), 2.20 – 2.14 (m, 1.1H), 2.10 – 2.05 (m, 2.3H), 2.00 (dt, *J* = 12.6, 2.9 Hz, 1.3H), 1.78 – 1.72 (m, 2.1H), 1.69 – 1.63 (m, 2.4H), 1.58 – 1.54 (m, 2.4H), 1.53 – 1.46 (m, 4.4H), 1.28 (ddd, *J* = 17.0, 11.1, 6.1 Hz, 3.2H), 1.22 – 1.16 (m, 1.3H), 1.11 – 1.07 (m, 3.1H), 1.06 – 1.02 (m, 4.3H), 0.93 (s, 3H), 0.90 – 0.84 (m, 3.1H), 0.83 – 0.78 (m, 2.0H), 0.77 – 0.71 (m, 2.2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 220.9, 169.8, 154.3, 148.3, 140.1, 138.4, 137.0, 135.5, 135.0, 134.0, 132.1, 132.0, 131.8, 130.9, 127.4, 126.7, 126.0, 125.7, 124.7, 124.6, 124.5, 124.3, 123.8, 122.2, 50.6, 49.5, 48.1, 44.7, 38.2, 35.9, 32.7, 31.7, 29.6, 28.9, 28.2, 27.9, 27.58, 27.55, 26.9, 26.6, 26.5, 26.2, 25.8, 25.3, 24.6, 21.7, 13.9. **HRMS (ESI)**: *m/z* calculated for $C_{49}H_{59}N_2O_2^+$ $[M + H]^+$ 707.4572, found 707.4584. **$[\alpha]_D^{25}$** = -122.7 (c = 3.25, CH_2Cl_2).

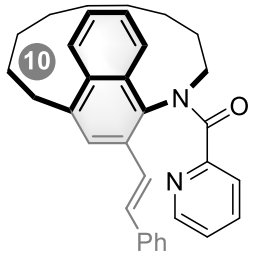
c) Characterization Data of Naphthalenophanes 3ba–3la and 5



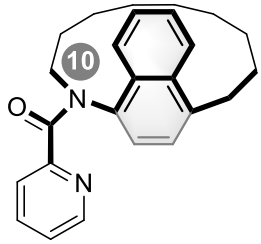
(R_p)-**3ba**, *cis:trans* = 8:1, colorless oil, 19.9 mg, 43% yield, 84% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 4.7 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 3H), 7.59 (s, 1H), 7.53 (d, *J* = 16.3 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.42 (q, *J* = 7.3 Hz, 3H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 16.3 Hz, 1H), 6.99 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 4.45 – 4.37 (m, 1H), 3.65 – 3.56 (m, 2H), 2.64 (ddd, *J* = 13.0, 11.0, 4.9 Hz, 1H), 1.77 (tt, *J* = 8.8, 4.2 Hz, 1.2H), 1.72 – 1.59 (m, 1.2H), 1.32 – 1.29 (m, 1.2H), 1.17 – 1.09 (m, 1.0H), 0.87 (dt, *J* = 14.5, 7.3 Hz, 1.0H), 0.81 – 0.75 (m, 1.0H), 0.48 (ddd, *J* = 21.7, 12.9, 6.5 Hz, 2.1H), 0.35 (tq, *J* = 13.2, 7.2 Hz, 1.2H), 0.27 – 0.20 (m, 1.2H), 0.14 (dq, *J* = 13.9, 6.7 Hz, 1.2H), -0.31 (dt, *J* = 14.2, 6.9 Hz, 1.0H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 154.4, 148.5, 138.8, 137.3, 136.0, 133.6, 133.3, 133.0, 132.9, 131.5, 129.0, 128.3, 127.1, 126.7, 126.0, 125.3, 124.7, 124.6, 124.4, 124.2, 122.8, 47.5, 33.2, 27.6, 27.1, 26.1, 25.8, 24.7, 23.9. **HRMS (ESI)**: *m/z* calculated for $C_{32}H_{33}N_2O^+$ $[M + H]^+$ 461.2588, found 461.2582. **$[\alpha]_D^{25}$** = 222.5 (c = 0.32, CH_2Cl_2). **HPLC**: Chiralpak AS–H column, 80:20 hexanes/isopropanol, flow rate = 0.3 mL/min, λ = 254 nm, t_R = 21.39 min (minor), 39.11 min (major).



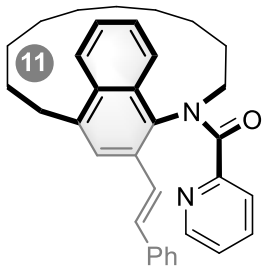
(R_p)-**1b**, white solid, 10.3 mg, 29% yield, 99% *ee*. **$[\alpha]_D^{25}$** = -141.1 (c = 0.27, CH_2Cl_2). **HPLC**: Chiralpak ID column, 90:10 hexanes/isopropanol, flow rate = 1.5 mL/min, λ = 254 nm, t_R = 25.99 min (minor), 29.84 min (major).



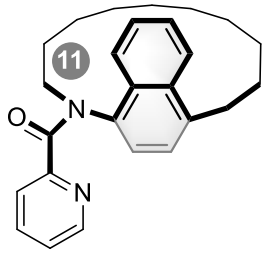
(R_p)-**3ca**, *cis:trans* = 13:1, colorless oil, 29.8 mg, 63% yield, 83% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.51 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 16.3 Hz, 1H), 6.95 – 6.90 (m, 1H), 4.55 (ddd, *J* = 14.3, 7.8, 2.8 Hz, 1H), 3.75 (ddd, *J* = 14.3, 8.1, 2.9 Hz, 1H), 3.59 (dt, *J* = 13.6, 4.4 Hz, 1H), 2.67 (td, *J* = 12.7, 4.9 Hz, 1H), 1.92 – 1.86 (m, 1.1H), 1.75 – 1.62 (m, 1.4H), 1.58 – 1.49 (m, 1.3H), 1.45 – 1.36 (m, 2.5H), 0.99 – 0.91 (m, 1.3H), 0.74 – 0.63 (m, 2.1H), 0.60 – 0.49 (m, 3.3H), 0.47 – 0.39 (m, 1.1H), 0.21 – 0.10 (m, 1.1H), -0.27 – -0.38 (m, 1.0H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.9, 154.5, 148.4, 138.7, 137.3, 135.7, 133.4, 133.1, 132.7, 132.3, 131.2, 129.0, 128.3, 127.1, 127.0, 126.0, 125.1, 124.8, 124.1, 124.0, 122.4, 48.0, 33.9, 28.2, 27.1, 26.7, 26.51, 26.46, 26.1, 25.1. **HRMS (ESI)**: *m/z* calculated for $C_{33}H_{35}N_2O^+$ $[M + H]^+$ 475.2744, found 475.2749. **$[\alpha]_D^{25}$** = -52.7 (c = 0.15, CH_2Cl_2). **HPLC**: Chiralpak AS – H column, 80:20 hexanes/isopropanol, flow rate = 0.3 mL/min, λ = 254 nm, t_R = 23.17 min (minor), 51.76 min (major).



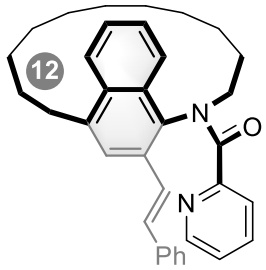
(R_p)-**1c**, white solid, 11.9 mg, 32% yield, 93% *ee*. **$[\alpha]_D^{25}$** = -404.3 (c = 1.57, CH_2Cl_2). **HPLC**: Chiralpak ID column, 80:20 hexanes/isopropanol, flow rate = 0.7 mL/min, λ = 254 nm, t_R = 29.35 min (minor), 32.61 min (major).



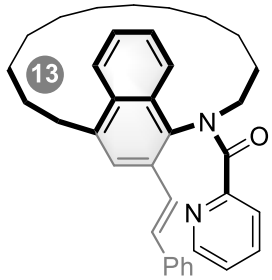
(R_p)-**3da**, *cis:trans* = 11:1, colorless oil, 25.4 mg, 52% yield, 82% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 4.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.48 (s, 1H), 7.43 (d, *J* = 11.6 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.32 (t, *J* = 6.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 16.3 Hz, 1H), 6.92 (dd, *J* = 7.5, 4.8 Hz, 1H), 4.56 (ddd, *J* = 13.9, 7.1, 4.3 Hz, 1H), 3.65 (ddd, *J* = 13.4, 8.1, 4.2 Hz, 1H), 3.57 (dt, *J* = 13.7, 4.3 Hz, 1H), 2.61 (td, *J* = 13.4, 12.8, 3.8 Hz, 1H), 1.95 – 1.81 (m, 2.3H), 1.68 – 1.55 (m, 2.2H), 1.45 – 1.36 (m, 1.3H), 1.16 – 1.07 (m, 1.2H), 1.13 – 1.09 (m, 1.0H), 0.82 – 0.75 (m, 1.1H), 0.74 – 0.65 (m, 4.0H), 0.63 – 0.53 (m, 2.3H), 0.49 – 0.41 (m, 1.2H), 0.24 – 0.19 (m, 1.0H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.8, 154.1, 148.3, 138.9, 137.3, 135.7, 135.3, 132.6, 131.9, 131.3, 131.1, 129.0, 128.8, 128.2, 127.1, 127.0, 126.1, 125.0, 124.9, 124.7, 124.2, 124.1, 123.8, 122.6, 47.6, 34.2, 27.9, 27.4, 27.3, 27.1, 26.8, 26.5, 25.6, 25.4. **HRMS (ESI)**: *m/z* calculated for $C_{34}H_{37}N_2O^+$ $[M + H]^+$ 489.2901, found 489.2907. **$[\alpha]_D^{25}$** = -85.8 (c = 1.90, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 16.74 min (minor), 23.69 min (major).



(R_p)-**1d**, white solid, 16.6 mg, 43% yield, 99% *ee*. **[α]$_D^{25}$** = -306.7 (c = 2.18, CH_2Cl_2). **HPLC**: Chiralpak OD–H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 10.56 min (minor), 12.13 min (major).

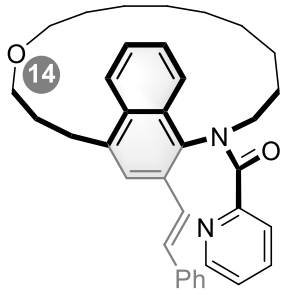


(R_p)-**3ea**, *cis:trans* = 9:1, colorless oil, 47.5 mg, 94% yield, 98% *ee*. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 4.3 Hz, 1H) , 8.02 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.55 (s, 1H), 7.54 – 7.50 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 8.1 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.09 (d, *J* = 16.3 Hz, 1H), 6.91 – 6.87 (m, 1H), 4.12 (ddd, *J* = 14.2, 8.2, 6.3 Hz, 1H), 4.01 (ddd, *J* = 13.9, 8.3, 6.3 Hz, 1H), 3.52 (ddd, *J* = 13.8, 6.3, 3.6 Hz, 1H), 2.68 (ddd, *J* = 14.2, 10.9, 3.8 Hz, 1H), 1.85 – 1.77 (m, 1.1H), 1.74 – 1.65 (m, 1.1H), 1.57 – 1.43 (m, 2.1H), 1.21 – 1.12 (m, 1.2H), 1.10 – 1.04 (m, 1.1H), 1.03 – 0.96 (m, 2.1H), 0.94 – 0.81 (m, 6.1H), 0.75 – 0.68 (m, 2.2H), 0.67 – 0.61 (m, 1.2H), 0.60 – 0.53 (m, 1.1H), 0.53 – 0.44 (m, 1.1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 169.7, 154.2, 148.4, 139.0, 137.3, 135.6, 134.6, 132.3, 131.7, 131.1, 128.9, 128.2, 127.0, 126.7, 125.8, 124.9, 124.8, 124.7, 123.9, 122.4, 48.9, 33.1, 28.5, 27.8, 27.1, 26.9, 26.8, 26.3, 26.2, 25.3, 24.7. **HRMS (ESI)**: *m/z* calculated for $C_{35}H_{39}N_2O^+$ $[M + H]^+$ 503.3057, found 503.3051. **[α]$_D^{25}$** = -167.2 (c = 2.73, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 15.38 min (minor), 22.15 min (major).

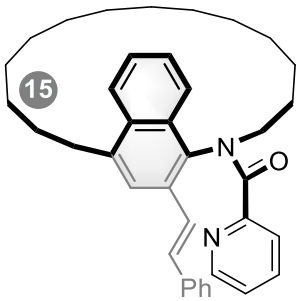


(R_p)-**3fa**, *cis:trans* = 11:1, colorless oil, 46.2 mg, 89% yield, 98% *ee*. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 4.7 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.92 – 6.87 (m, 1H), 4.39 (ddd, *J* = 13.1, 8.7, 6.3 Hz, 1H), 3.64 (ddd, *J* = 14.1, 9.0, 5.6 Hz, 1H), 3.51 (ddd, *J* = 13.9, 6.4, 3.3 Hz, 1H), 2.65 (ddd, *J* = 14.1, 11.2, 3.3 Hz, 1H), 1.86 – 1.79 (m, 1.3H), 1.78 – 1.72 (m, 1.2H), 1.71 – 1.57 (m, 2.5H), 1.17 – 1.09 (m, 3.4H),

1.02 – 0.94 (m, 3.0H), 0.94 – 0.82 (m, 6.0H), 0.80 – 0.73 (m, 3.4H), 0.71 – 0.61 (m, 1.2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.7, 154.1, 148.4, 138.7, 137.3, 135.6, 134.9, 132.4, 131.7, 131.4, 131.1, 128.9, 128.2, 126.9, 126.8, 125.9, 124.9, 124.84, 124.76, 123.93, 123.87, 122.3, 49.8, 33.1, 28.6, 27.8, 27.6, 27.5, 27.2, 27.1, 26.7, 26.6, 25.7, 25.6. **HRMS (ESI)**: *m/z* calculated for $C_{36}H_{41}N_2O^+$ $[M + H]^+$ 517.3214, found 517.3219. **$[\alpha]_D^{25}$** = -207.5 (c = 0.52, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 14.62 min (minor), 21.18 min (major).

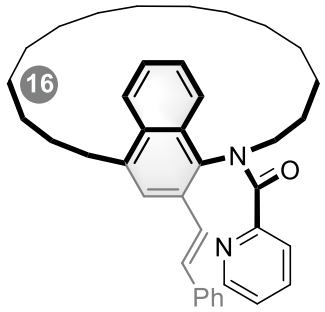


(R_p)-**3ga**, *cis:trans* = 14:1, colorless oil, 51.6 mg, 97% yield, 98% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 4.7 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 1.5 Hz, 1H), 7.59 (d, *J* = 4.6 Hz, 2H), 7.54 (td, *J* = 7.0, 6.5, 1.2 Hz, 2H), 7.49 (d, *J* = 3.3 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.30 (m, 1H), 7.29 – 7.26 (m, 1H), 7.09 (d, *J* = 16.3 Hz, 1H), 6.88 (ddd, *J* = 6.5, 4.8, 2.5 Hz, 1H), 4.24 (dt, *J* = 13.2, 7.7 Hz, 1H), 3.81 (dt, *J* = 13.1, 7.4 Hz, 1H), 3.47 (dt, *J* = 14.4, 5.1 Hz, 1H), 3.34 – 3.13 (m, 4.1H), 2.86 (ddd, *J* = 14.3, 8.4, 5.7 Hz, 1H), 2.15 – 2.07 (m, 2H), 1.32 – 1.24 (m, 2.0H), 1.24 – 1.18 (m, 1.2H), 1.15 (t, *J* = 7.0 Hz, 2H), 1.08 (td, *J* = 7.5, 2.8 Hz, 1.2H), 1.03 (t, *J* = 6.8 Hz, 2.1H), 1.00 – 0.95 (m, 1.0H), 0.94 – 0.87 (m, 3.1H), 0.83 – 0.69 (m, 2.0H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 154.2, 148.4, 137.7, 137.3, 135.6, 134.7, 132.3, 131.72, 131.65, 131.1, 129.0, 128.2, 126.9, 126.8, 126.0, 124.9, 124.8, 124.5, 123.9, 123.7, 122.2, 70.2, 68.5, 49.7, 29.7, 28.8, 27.8, 27.7, 26.6, 26.4, 25.2, 24.9, 24.8. **HRMS (ESI)**: *m/z* calculated for $C_{36}H_{41}N_2O_2^+$ $[M + H]^+$ 533.3163, found 533.3166. **$[\alpha]_D^{25}$** = -225.0 (c = 1.93, CH_2Cl_2). **HPLC**: Chiralpak AS – H column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 11.11 min (minor), 18.68 min (major).

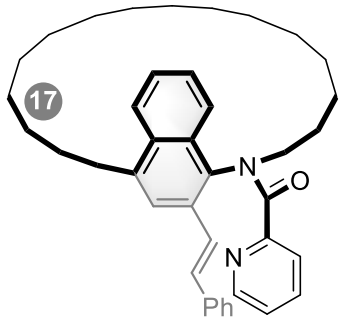


(R_p)-**3ha**, *cis:trans* = 13:1, colorless oil, 41.7 mg, 77% yield, 95% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 4.8 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 16.2 Hz, 1H), 6.92 (t, *J* = 6.1 Hz, 1H), 4.42 (ddd, *J* = 13.2, 9.8, 5.7 Hz, 1H), 3.59 (ddd, *J* = 13.3, 9.8, 5.4 Hz, 1H), 3.48 (ddd, *J* = 13.9, 6.0, 4.0 Hz, 1H), 2.70 (ddd, *J* = 14.3, 10.4, 4.3 Hz, 1H), 1.78 – 1.73 (m, 1.2H), 1.72 – 1.67 (m, 1.2H), 1.65 – 1.57 (m, 1.2H), 1.33 – 1.30 (m, 1.1H), 1.24 – 1.21 (m, 1.1H), 1.19 – 1.16

(m, 3.0H), 1.14 – 1.11 (m, 5.0H), 1.04 – 1.01 (m, 4.3H), 0.99 – 0.94 (m, 3.0H), 0.91 – 0.88 (m,, 4.2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 154.0, 148.2, 138.5, 137.3, 135.9, 134.7, 132.4, 131.9, 131.6, 131.3, 129.0, 128.8, 128.2, 126.94, 126.91, 125.9, 125.0, 124.81, 124.77, 124.0, 123.7, 122.3, 50.7, 32.8, 29.2, 28.8, 28.4, 28.1, 27.74, 27.65, 27.3, 27.0, 26.3, 25.8. **HRMS (ESI)**: *m/z* calculated for $C_{38}H_{45}N_2O^+$ $[M + H]^+$ 545.3527, found 545.3529. **$[\alpha]_D^{25}$** = -101.1 (c = 1.72, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 13.02 min (minor), 17.10 min (major).

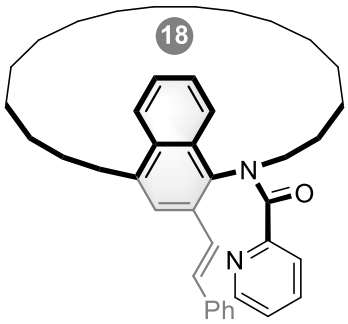


(R_p)-**3ia**, *cis:trans* = 14:1, colorless oil, 53.2 mg, 95% yield, 98% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.54 (d, *J* = 5.6 Hz, 1H), 7.50 (s, 2H), 7.47 (d, *J* = 7.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.06 (d, *J* = 16.3 Hz, 1H), 6.92 (t, *J* = 6.0 Hz, 1H), 4.31 (ddd, *J* = 13.1, 10.9, 5.5 Hz, 1H), 3.72 (ddd, *J* = 13.0, 10.8, 5.3 Hz, 1H), 3.44 (dt, *J* = 13.9, 5.4 Hz, 1H), 2.72 (ddd, *J* = 14.3, 9.5, 5.1 Hz, 1H), 1.82 – 1.72 (m, 2.2H), 1.67 – 1.61 (m, 1.0H), 1.56 – 1.50 (m, 1.0H), 1.38 – 1.33 (m, 1.2H), 1.30 – 1.24 (m, 2.1H), 1.21 – 1.14 (m, 6.4H), 1.11 – 1.04 (m, 6.0H), 1.03 – 0.95 (m, 7.1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.4, 153.9, 148.1, 138.7, 137.3, 136.0, 134.4, 132.3, 132.0, 131.7, 131.3, 129.0, 128.2, 127.0, 126.9, 125.9, 125.0, 124.8, 124.7, 124.0, 123.5, 122.3, 50.3, 32.8, 29.6, 28.5, 28.2, 28.1, 28.0, 27.8, 27.7, 27.6, 27.5, 27.4, 26.2, 26.1. **HRMS (ESI)**: *m/z* calculated for $C_{39}H_{47}N_2O^+$ $[M + H]^+$ 559.3683, found 559.3680. **$[\alpha]_D^{25}$** = -174.2 (c = 0.33, CH_2Cl_2). **HPLC**: Chiralpak IE column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 19.37 min (minor), 25.00 min (major).

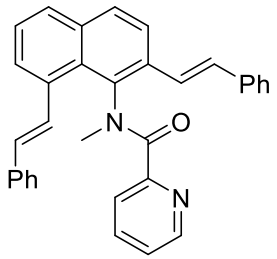


(R_p)-**3ja**, *cis:trans* = 20:1, colorless oil, 41.1 mg, 72% yield, 91% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 4.8 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 3H), 7.52 – 7.48 (m, 2H), 7.47 (s, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.0 Hz, 2H), 7.01 (d, *J* = 16.3 Hz, 1H), 6.90 (t, *J* = 6.1 Hz, 1H), 4.48 (ddd, *J* = 12.8, 10.3, 5.6 Hz, 1H), 3.53 (ddd, *J* = 13.1, 10.6, 5.3 Hz, 1H), 3.41 (dt, *J* = 13.7, 5.4 Hz, 1H), 2.72 (ddd, *J* = 14.5, 10.0, 4.9 Hz, 1H), 1.84 – 1.71 (m, 4.4H), 1.61 – 1.53 (m, 1.3H), 1.43 – 1.40 (m, 1.0H), 1.36 – 1.32 (m, 1.1H), 1.24 – 1.19 (m, 6.1H), 1.14 – 1.09 (m, 7.0H), 1.00 – 0.95 (m, 8.2H). **^{13}C NMR (151**

MHz, $CDCl_3$) δ 169.8, 154.3, 148.4, 138.5, 137.3, 135.5, 134.7, 132.4, 132.1, 131.6, 131.1, 128.9, 128.2, 126.95, 126.87, 125.9, 125.1, 124.8, 124.7, 123.9, 123.3, 122.1, 50.7, 32.7, 29.5, 28.8, 28.7, 28.45, 28.42, 28.3, 28.2, 27.9, 27.7, 27.4, 27.3, 26.6, 26.4. **HRMS (ESI)**: *m/z* calculated for $C_{40}H_{49}N_2O^+$ $[M + H]^+$ 573.3840, found 573.3835. $[\alpha]_D^{25}$ = -94.8 (c = 1.78, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 13.63 min (minor), 15.08 min (major).

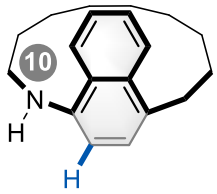


(R_p)-**3ka**, *cis:trans* = 8:1, colorless oil, 51.8 mg, 88% yield, 96% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 4.6 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 3H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 9.8 Hz, 1H), 7.48 (s, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.03 (d, *J* = 16.4 Hz, 1H), 6.87 (q, *J* = 4.6 Hz, 1H), 4.35 (ddd, *J* = 13.1, 11.1, 5.3 Hz, 1H), 3.66 (ddd, *J* = 13.1, 11.1, 5.2 Hz, 1H), 3.38 (dt, *J* = 13.3, 6.2 Hz, 1H), 2.71 (ddd, *J* = 14.6, 9.0, 6.3 Hz, 1H), 1.85 – 1.65 (m, 4.3H), 1.58 – 1.49 (m, 1.5H), 1.27 – 1.24 (m, 2.2H), 1.21 – 1.13 (m, 9.4H), 1.10 – 1.06 (m, 6.2H), 1.01 – 0.95 (m, 8.0H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 154.3, 148.3, 138.8, 137.3, 135.5, 134.6, 132.3, 132.1, 131.7, 131.0, 128.9, 128.2, 126.9, 126.8, 125.9, 125.0, 124.8, 124.6, 123.8, 123.1, 122.1, 50.6, 33.0, 29.9, 29.0, 28.5, 28.5, 28.41, 28.35, 28.3, 28.21, 28.16, 28.1, 28.0, 27.9, 26.7, 26.5. **HRMS (ESI)**: *m/z* calculated for $C_{41}H_{51}N_2O^+$ $[M + H]^+$ 587.3996, found 587.3991. $[\alpha]_D^{25}$ = -138.6 (c = 0.72, CH_2Cl_2). **HPLC**: Chiralpak IC column, 50:50 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 8.71 min (major), 18.22 min (minor).

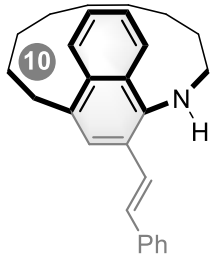


5, *cis:trans* = 13:1, white solid, 8.4 mg, 18% yield, 36% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (d, *J* = 16.0 Hz, 1H), 7.97 (d, *J* = 5.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.64 (dd, *J* = 7.6, 3.6 Hz, 2H), 7.57 (dd, *J* = 8.6, 3.4 Hz, 3H), 7.54 – 7.45 (m, 5H), 7.38 (dt, *J* = 15.6, 7.5 Hz, 5H), 7.18 (d, *J* = 16.2 Hz, 1H), 6.99 (dd, *J* = 6.6, 1.9 Hz, 1H), 6.90 (t, *J* = 16.4 Hz, 2H), 3.31 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 170.1, 154.2, 147.7, 138.5, 138.0, 137.2, 136.1, 134.8, 133.2, 132.4, 131.8, 130.9, 129.9, 129.12, 129.05, 129.0, 128.9, 128.5, 128.4, 127.6, 126.84, 126.81, 126.2, 124.1, 123.8, 123.7, 123.1, 38.5. **HRMS (ESI)**: *m/z* calculated for $C_{33}H_{27}N_2O^+$ $[M + H]^+$ 467.2118, found 467.2123. $[\alpha]_D^{25}$ = -42.7 (c = 0.30, CH_2Cl_2). **HPLC**: Chiralpak AD–H column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 7.18 min (minor), 11.58 min (major).

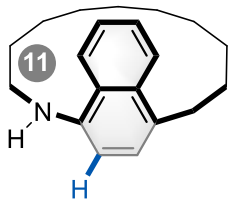
d) Characterization Data of Naphthalenophanes 6–15



(R_p)-**6**, pale yellow oil, 24.9 mg, 93% yield, 99% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, J = 7.1 Hz, 1H), 7.85 (d, J = 7.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.17 (d, J = 7.5 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 3.71 (dt, J = 14.6, 4.1 Hz, 1H), 3.62 (dt, J = 13.4, 3.8 Hz, 1H), 3.27 (ddd, J = 14.9, 11.1, 4.2 Hz, 1H), 2.49 (td, J = 13.1, 4.9 Hz, 1H), 2.12 (ddt, J = 18.5, 15.2, 7.8 Hz, 1H), 1.88 – 1.75 (m, 1H), 1.37 – 1.28 (m, 3H), 1.08 – 0.94 (m, 2H), 0.82 – 0.72 (m, 4H), 0.45 – 0.31 (m, 1H), -0.01 – -0.17 (m, 1H), -1.09 – -1.24 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 142.2, 132.8, 128.2, 126.5, 126.3, 125.3, 125.1, 124.7, 120.5, 111.7, 45.1, 34.1, 28.4, 27.4, 26.71, 26.67, 26.1, 23.5, 21.1. **HRMS (ESI)**: *m/z* calculated for $C_{19}H_{26}N^+$ $[M + H]^+$ 268.2060, found 268.2064. **$[\alpha]_D^{25}$** = +158.8 (c = 0.20, CH_2Cl_2). **HPLC**: Chiralpak OD-H column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 8.424 min (major), 9.346 min (minor).

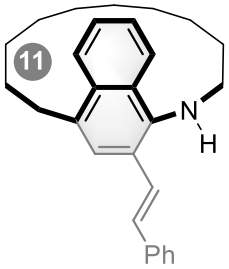


(R_p)-**7**, pale yellow oil, 27.3 mg, 74% yield, 85% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 – 7.96 (m, 2H), 7.62 (d, J = 7.4 Hz, 2H), 7.56 – 7.47 (m, 4H), 7.40 (t, J = 7.4 Hz, 2H), 7.29 (d, J = 7.4 Hz, 1H), 7.14 (d, J = 16.3 Hz, 1H), 3.63 (dt, J = 13.5, 4.2 Hz, 1H), 3.53 (ddd, J = 14.2, 6.9, 3.3 Hz, 1H), 3.34 (ddd, J = 14.2, 8.7, 3.4 Hz, 1H), 2.62 (td, J = 12.8, 4.9 Hz, 1H), 1.91 – 1.82 (m, 1H), 1.53 – 1.40 (m, 2H), 1.35 – 1.31 (m, 1H), 1.19 – 1.07 (m, 1H), 1.02 – 0.90 (m, 1H), 0.79 – 0.69 (m, 2H), 0.68 – 0.54 (m, 3H), 0.47 – 0.36 (m, 1H), 0.35 – 0.24 (m, 1H), -0.32 – -0.46 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.5, 138.3, 132.6, 130.9, 129.0, 128.8, 128.1, 127.4, 126.5, 125.4, 125.3, 125.1, 125.0, 122.9, 121.8, 48.6, 33.7, 28.2, 27.7, 27.1, 26.9, 26.7, 24.8. **HRMS (ESI)**: *m/z* calculated for $C_{27}H_{32}N^+$ $[M + H]^+$ 370.2530, found 370.2537. **$[\alpha]_D^{25}$** = +209.9 (c = 0.77, CH_2Cl_2). **HPLC**: Chiralpak IE column, 70:30 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 5.23 min (major), 7.69 min (minor).

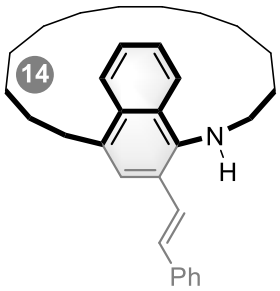


(R_p)-**8**, pale yellow oil, 13.3 mg, 47% yield, 64% *ee*. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (ddd, J = 9.9, 6.4, 3.3 Hz, 2H), 7.50 (td, J = 6.0, 5.5, 3.1 Hz, 2H), 7.19 (d, J = 7.5 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 3.64 (ddd, J = 14.3, 7.3, 3.8 Hz, 1H), 3.55 (dt, J = 13.7, 4.3 Hz, 1H), 3.37 (ddd, J = 14.3, 7.8, 3.9 Hz, 1H), 2.56 (ddd, J = 13.6, 11.7, 4.0 Hz, 1H), 1.82 (dddp, J = 14.9, 11.7, 7.7, 4.1 Hz, 2H), 1.58 – 1.44 (m, 2H), 1.35 – 1.26 (m, 2H), 1.17 – 1.04 (m, 2H), 0.87 – 0.67 (m, 2H), 0.64 –

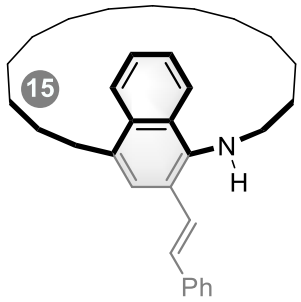
0.52 (m, 4H), 0.50 – 0.41 (m, 1H), 0.16 – 0.06 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.1, 127.0, 126.3, 125.7, 125.2, 125.0, 122.3, 46.7, 33.6, 28.4, 27.9, 27.6, 27.0, 26.91, 26.88, 26.1. **HRMS (ESI)**: *m/z* calculated for $C_{20}H_{28}N^+$ $[M + H]^+$ 282.2217, found 282.2214. **$[\alpha]_D^{25}$** = +33.7 (c = 0.22, CH_2Cl_2). **HPLC**: Chiralpak IF column, 50:50 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 5.78 min (major), 9.89 min (minor).



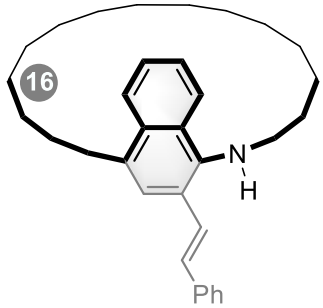
(R_p)-**9**, pale yellow oil, 19.2 mg, 50% yield, 73% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 – 8.11 (m, 1H), 8.00 (dd, *J* = 6.8, 3.0 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 16.0 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 16.1 Hz, 1H), 3.57 (dt, *J* = 13.9, 4.5 Hz, 1H), 3.44 (t, *J* = 5.5 Hz, 2H), 2.63 (ddd, *J* = 15.0, 12.7, 4.0 Hz, 2H), 1.92 – 1.85 (m, 1H), 1.68 – 1.58 (m, 2H), 1.51 – 1.44 (m, 1H), 1.42 – 1.36 (m, 1H), 1.18 – 1.12 (m, 1H), 1.03 – 0.94 (m, 1H), 0.86 – 0.74 (m, 2H), 0.72 – 0.53 (m, 5H), 0.51 – 0.41 (m, 1H), 0.26 – 0.17 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 142.9, 138.2, 133.0, 131.8, 129.5, 128.9, 128.6, 127.6, 126.6, 125.6, 125.6, 125.4, 125.0, 124.9, 124.2, 123.5, 48.4, 33.8, 33.1, 28.5, 28.1, 27.5, 27.4, 26.8, 26.1, 25.5. **HRMS (ESI)**: *m/z* calculated for $C_{28}H_{34}N^+$ $[M + H]^+$ 384.2686, found 384.2682. **$[\alpha]_D^{25}$** = +180.4 (c = 0.39, CH_2Cl_2). **HPLC**: Chiralpak OD-H column, 90:10 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 7.51 min (minor), 8.50 min (major).



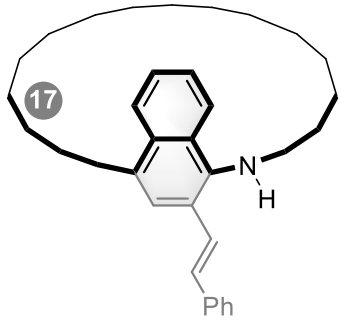
10, pale yellow oil, 36.6 mg, 86% yield, 97% *ee*. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 8.35 – 8.28 (m, 1H), 8.08 – 8.01 (m, 1H), 7.74 (d, *J* = 16.4 Hz, 1H), 7.67 – 7.62 (m, 3H), 7.49 – 7.45 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 16.4 Hz, 1H), 3.52 (ddd, *J* = 14.0, 5.8, 3.8 Hz, 1H), 3.47 – 3.33 (m, 2H), 2.75 (ddd, *J* = 14.3, 10.7, 4.1 Hz, 1H), 1.91 – 1.69 (m, 2H), 1.44 – 1.27 (m, 4H), 1.21 – 1.09 (m, 7H), 1.07 – 0.97 (m, 3H), 0.93 – 0.85 (m, 4H), 0.80 (q, *J* = 7.0 Hz, 2H). **^{13}C NMR (101 MHz, Acetone-d_6)** δ 142.9, 139.3, 133.3, 131.5, 130.3, 129.6, 128.4, 128.0, 127.7, 127.2, 126.4, 126.2, 125.6, 125.5, 124.5, 124.4, 50.5, 32.7, 29.5, 29.2, 28.7, 28.5, 28.2, 28.0, 27.9, 27.2, 27.0, 26.6, 25.9. **HRMS (ESI)**: *m/z* calculated for $C_{31}H_{40}N^+$ $[M + H]^+$ 426.3156, found 426.3159. (R_p)-**10** **$[\alpha]_D^{25}$** = +128.4 (c = 0.27, CH_2Cl_2). **HPLC**: Chiralpak IC column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 4.34 min (major), 6.45 min (minor). (S_p)-**10** **$[\alpha]_D^{25}$** = -116.85 (c = 0.45, CH_2Cl_2). **HPLC**: Chiralpak IC column, 80:20 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 4.34 min (major), 6.46 min (minor).



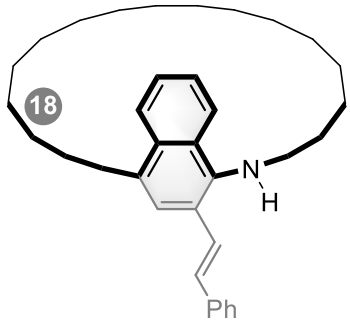
(R_p)-**11**, pale yellow oil, 39.4 mg, 90% yield, 94% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 – 8.10 (m, 1H), 8.06 – 8.01 (m, 1H), 7.63 – 7.57 (m, 3H), 7.52 – 7.46 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 16.2 Hz, 1H), 3.50 (dt, *J* = 14.0, 5.0 Hz, 1H), 3.46 – 3.33 (m, 2H), 2.73 (dt, *J* = 14.4, 7.1 Hz, 1H), 1.83 – 1.77 (m, 2H), 1.49 – 1.42 (m, 2H), 1.38 – 1.33 (m, 1H), 1.24 – 1.18 (m, 4H), 1.16 – 0.99 (m, 11H), 0.98 – 0.88 (m, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.7, 138.3, 132.7, 131.8, 129.0, 128.9, 127.4, 126.50, 126.48, 125.6, 125.4, 125.02, 124.99, 124.2, 123.6, 50.9, 32.6, 31.4, 29.4, 28.8, 28.4, 28.1, 27.9, 27.5, 27.4, 27.3, 27.2, 26.0. **HRMS (ESI)**: *m/z* calculated for $C_{32}H_{42}N^+$ $[M + H]^+$ 440.3312, found 440.3319. **$[\alpha]_D^{25}$** = +62.7 (c = 0.92, CH_2Cl_2). **HPLC**: Chiralpak IB N-5 column, 60:40 hexanes/isopropanol, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 7.20 min (minor), 7.85 min (major).



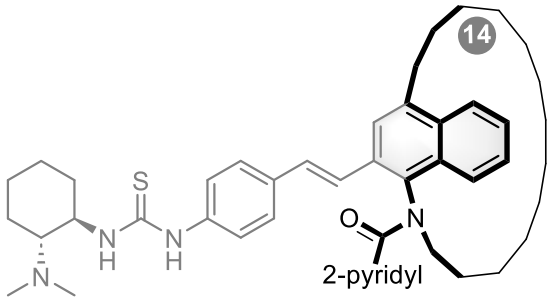
(R_p)-**12**, pale yellow oil, 43.0 mg, 95% yield, 89% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 – 8.08 (m, 1H), 8.05 – 8.00 (m, 1H), 7.62 – 7.57 (m, 3H), 7.53 – 7.46 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 16.2 Hz, 1H), 3.47 (dt, *J* = 14.0, 5.3 Hz, 1H), 3.37 (ddd, *J* = 14.3, 8.6, 6.0 Hz, 1H), 3.29 (ddd, *J* = 14.1, 8.7, 6.2 Hz, 1H), 2.75 (dt, *J* = 14.5, 7.9 Hz, 1H), 1.80 – 1.75 (m, 2H), 1.47 – 1.42 (m, 1H), 1.42 – 1.34 (m, 2H), 1.32 – 1.26 (m, 1H), 1.23 – 1.13 (m, 8H), 1.10 – 1.00 (m, 10H), 0.99 – 0.94 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.5, 138.3, 132.6, 132.1, 129.2, 128.9, 128.8, 127.4, 126.5, 125.43, 125.41, 125.1, 125.0, 124.5, 123.3, 50.9, 32.5, 30.1, 29.5, 28.3, 28.23, 28.18, 27.75, 27.74, 27.6, 27.52, 27.51, 27.3, 26.0. **HRMS (ESI)**: *m/z* calculated for $C_{33}H_{44}N^+$ $[M + H]^+$ 454.3469, found 454.3474. **$[\alpha]_D^{25}$** = +74.0 (c = 0.55, CH_2Cl_2). **HPLC**: Chiralpak IB N-5 column, 70:30 hexanes/isopropanol, flow rate = 0.3 mL/min, λ = 254 nm, t_R = 20.97 min (major), 22.12 min (minor).



(R_p)-**13**, pale yellow oil, 43.0 mg, 90% yield, 95% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 (d, J = 7.7 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 16.1 Hz, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.52 (s, 1H), 7.50 – 7.47 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 16.1 Hz, 1H), 3.44 (dt, J = 14.1, 5.5 Hz, 1H), 3.37 (dt, J = 14.2, 7.2 Hz, 1H), 3.30 (dt, J = 13.8, 7.2 Hz, 1H), 2.75 (ddd, J = 14.6, 9.6, 5.5 Hz, 1H), 1.83 – 1.75 (m, 2H), 1.54 – 1.48 (m, 2H), 1.41 – 1.37 (m, 1H), 1.24 – 1.17 (m, 7H), 1.14 – 1.08 (m, 7H), 1.06 – 0.96 (m, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.2, 132.7, 129.33, 129.26, 129.0, 128.8, 127.5, 126.6, 126.1, 125.5, 125.24, 125.18, 124.9, 123.7, 51.4, 32.6, 29.6, 28.83, 28.82, 28.7, 28.6, 28.43, 28.37, 27.9, 27.8, 27.6, 27.5, 26.3. **HRMS (ESI)**: *m/z* calculated for $C_{34}H_{46}N^+$ $[M + H]^+$ 468.3625, found 468.3621. **$[\alpha]_D^{25}$** = +157.2 (c = 0.44, CH_2Cl_2). **HPLC**: Chiralpak IC column, 80:20 hexanes/isopropanol, flow rate = 0.3 mL/min, λ = 254 nm, t_R = 15.22 min (major), 19.49 min (minor).



(R_p)-**14**, pale yellow oil, 36.8 mg, 76% yield, 4% *ee*. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 – 8.10 (m, 1H), 8.05 – 8.02 (m, 1H), 7.66 – 7.59 (m, 3H), 7.54 (s, 1H), 7.51 – 7.47 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 16.2 Hz, 1H), 3.43 (dt, J = 13.9, 5.7 Hz, 1H), 3.32 (ddd, J = 14.6, 8.7, 6.1 Hz, 1H), 3.26 (ddd, J = 13.2, 8.9, 6.1 Hz, 1H), 2.77 (ddd, J = 14.7, 9.4, 6.1 Hz, 1H), 1.84 – 1.71 (m, 2H), 1.57 – 1.48 (m, 2H), 1.42 – 1.34 (m, 1H), 1.32 – 1.29 (m, 1H), 1.28 – 1.25 (m, 2H), 1.25 – 1.20 (m, 4H), 1.19 – 1.15 (m, 5H), 1.13 – 1.09 (m, 6H), 1.08 – 1.02 (m, 7H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.2, 132.6, 129.3, 129.1, 129.0, 128.8, 127.5, 126.6, 126.1, 125.5, 125.3, 125.1, 124.9, 123.4, 51.2, 32.7, 29.7, 28.72, 28.68, 28.63, 28.5, 28.4, 28.3, 28.14, 28.11, 28.05, 28.00, 27.95, 27.88, 26.2. **HRMS (ESI)**: *m/z* calculated for $C_{35}H_{48}N^+$ $[M + H]^+$ 482.3782, found 482.3787. **HPLC**: Chiralpak IC column, 99:1 hexanes/isopropanol, flow rate = 1.1 mL/min, λ = 254 nm, t_R = 10.93 min (major), 16.48 min (minor).



15, *cis:trans* = 14:1, yellow solid, 30.7 mg, 42% yield, *dr* > 20:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 4.8 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.98 (dd, *J* = 14.0, 8.5 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.45 (d, *J* = 9.4 Hz, 2H), 7.36 (d, *J* = 16.1 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 16.1 Hz, 1H), 6.93 – 6.88 (m, 1H), 4.79 (d, *J* = 10.3 Hz, 1H), 4.23 (td, *J* = 12.1, 5.3 Hz, 1H), 3.77 (td, *J* = 12.8, 12.3, 5.6 Hz, 1H), 3.47 (dd, *J* = 12.0, 7.0 Hz, 1H), 3.40 (t, *J* = 12.6 Hz, 1H), 2.81 (s, 6H), 2.69 (dt, *J* = 14.3, 7.3 Hz, 1H), 2.29 (s, 1H), 2.03 (d, *J* = 9.6 Hz, 2.2H), 1.92 (d, *J* = 12.5 Hz, 1.2H), 1.81 – 1.73 (m, 3.1H), 1.42 – 1.40 (m, 3.1H), 1.25 (s, 10.2H), 1.08 – 1.04 (m, 5.4H), 0.87 – 0.85 (m, 3.2H), 0.77 – 0.75 (m, 2.2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 181.3, 169.8, 154.1, 148.5, 138.6, 135.7, 133.9, 132.3, 132.1, 131.7, 130.9, 127.1, 126.8, 125.8, 124.8, 124.7, 124.3, 124.1, 123.9, 122.8, 122.2, 77.2, 67.5, 53.5, 49.7, 32.7, 32.0, 29.8, 29.5, 29.0, 28.3, 28.0, 27.7, 27.6, 27.0, 26.7, 26.3, 25.4, 24.7, 24.4, 22.8, 14.2. **HRMS (ESI)**: *m/z* calculated for $C_{46}H_{60}N_5OS^+$ $[M + H]^+$ 730.4514, found 730.4527. **$[\alpha]_D^{25}$** = -160.0 (c = 0.13, CH_2Cl_2).

6. References

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7. X-Ray Report

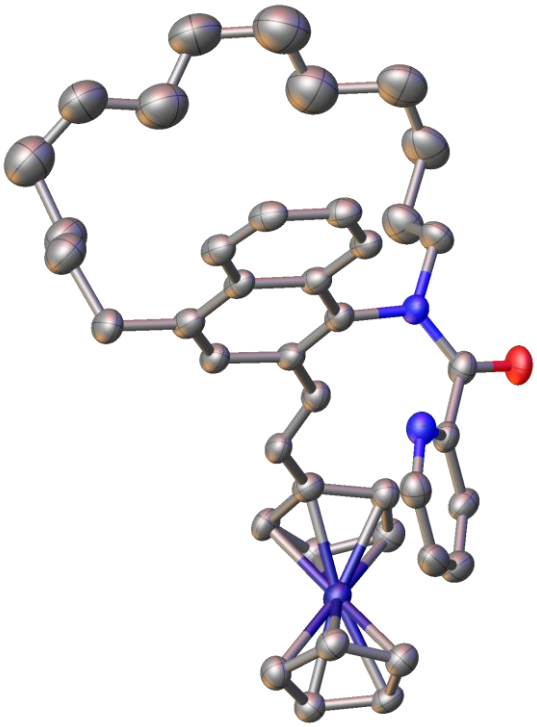


Figure S6. Thermal ellipsoid plot for the crystal structure of 3an (at 50% probability level, CCDC No. 2444735)

Experimental

Single crystals of $C_{41}H_{46}FeN_2O$ (**3an**) were recrystallised from *n*-hexane and acetone 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.

Table S3 Crystal data and structure refinement for 3an.

Identification code	**3an**
Empirical formula	$C_{41}H_{46}FeN_2O$
Formula weight	638.65
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.9600(3)
b/Å	10.2250(3)
c/Å	32.0026(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3259.18(16)
Z	4
ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	3.972
F(000)	1360
Crystal size/mm^3	0.1 × 0.05 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.08 to 152.556
Index ranges	$-12 \le h \le 12$, $-11 \le k \le 12$, $-39 \le l \le 40$
Reflections collected	19690
Independent reflections	6547 [R_{int} = 0.0680, R_{sigma} = 0.0714]
Data/restraints/parameters	6547/997/406
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0726, wR_2 = 0.1935
Final R indexes [all data]	R_1 = 0.0873, wR_2 = 0.2055
Largest diff. peak/hole / e Å^{-3}	1.12/-0.54
Flack parameter	0.006(4)

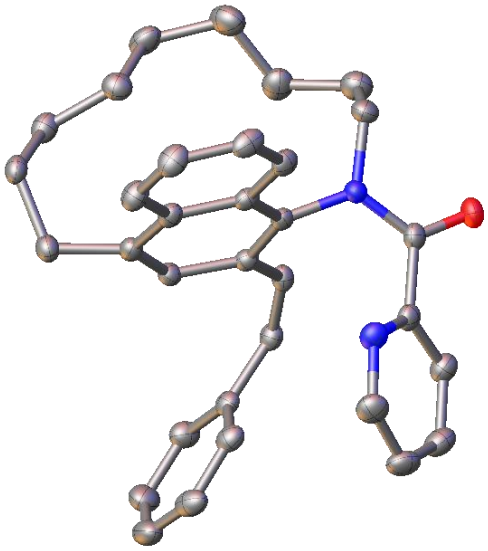


Figure S7. Thermal ellipsoid plot for the crystal structure of (*Z*)-3ca (at 50% probability level, CCDC No. 2489987

Experimental

Single crystals of $C_{33}H_{34}N_2O$ (**(*Z*)-3ca**) were recrystallised from *n*-hexane and ethyl acetate (EA) 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.

Table S4 Crystal data and structure refinement for (*Z*)-3ca.

Identification code	**(*Z*)-3ca**
Empirical formula	$C_{33}H_{34}N_2O$
Formula weight	474.62
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	19.8085(3)
b/Å	8.55460(10)
c/Å	30.3075(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5135.72(13)
Z	8
ρ_{calc}g/cm^3	1.228
μ/mm^{-1}	0.567
F(000)	2032
Crystal size/mm^3	0.02 × 0.02 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.344 to 152.79
Index ranges	-24 ≤ h ≤ 23, -10 ≤ k ≤ 10, -35 ≤ l ≤ 38
Reflections collected	29355
Independent reflections	5239 [R_{int} = 0.0564, R_{sigma} = 0.0332]
Data/restraints/parameters	5239/0/325
Goodness-of-fit on F^2	0.922
Final R indexes [I>=2σ (I)]	R_1 = 0.0641, wR_2 = 0.1540
Final R indexes [all data]	R_1 = 0.0678, wR_2 = 0.1564
Largest diff. peak/hole / e Å^{-3}	0.66/-0.32
Flack parameter	N

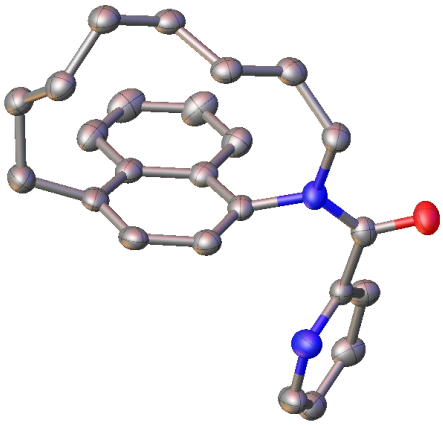


Figure S8. Thermal ellipsoid plot for the crystal structure of 1b (at 50% probability level, CCDC No. 2489984)

Experimental

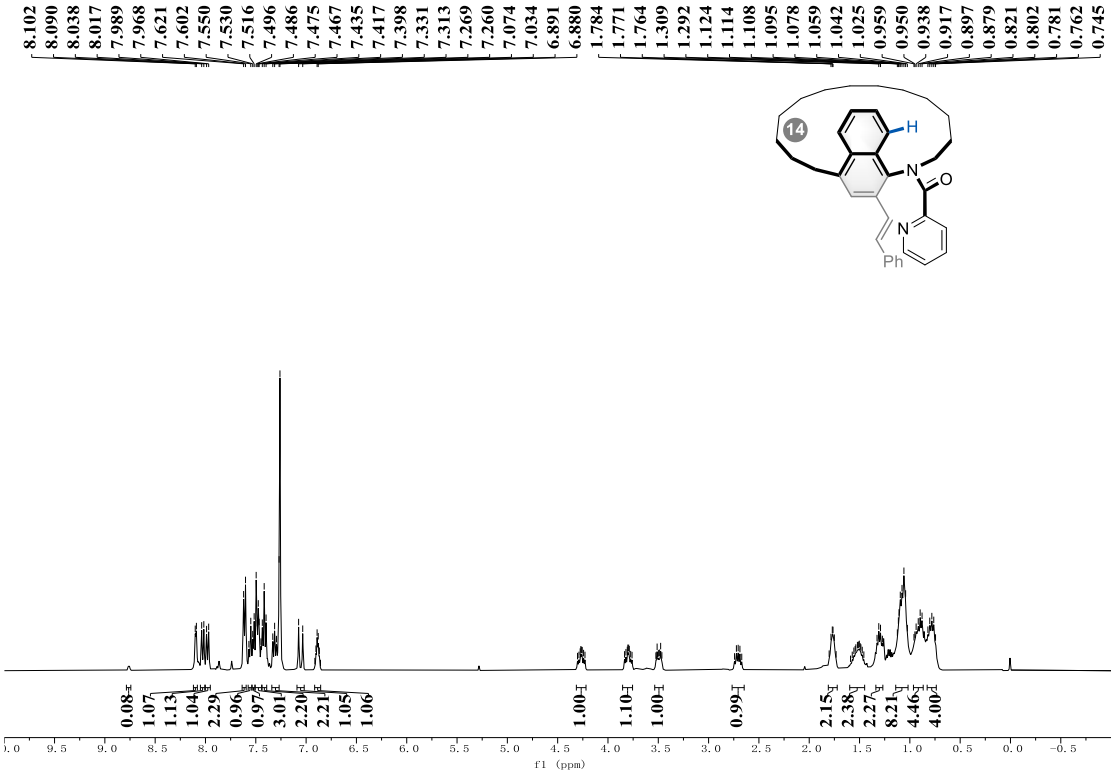
Single crystals of $C_{24}H_{26}N_2O$ (**1b**) were recrystallised from *n*-hexane and ethyl acetate (EA) mounted in inert oil and transferred to the cold gas stream of the diffractometer. The crystal was kept at 100.00(10) K during data collection.

Table S5 Crystal data and structure refinement for 1b.

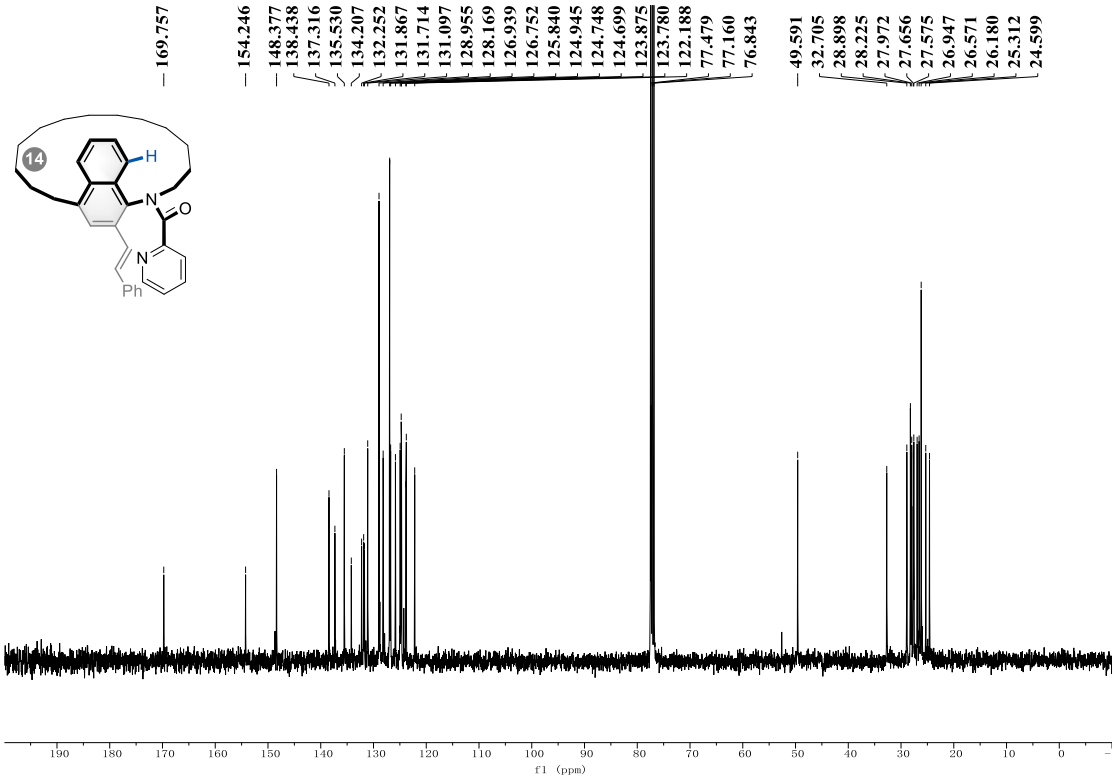
Identification code	**1b**
Empirical formula	$C_{24}H_{26}N_2O$
Formula weight	358.47
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	7.8587(5)
b/Å	8.7955(8)
c/Å	14.6593(10)
α/°	93.462(7)
β/°	93.465(6)
γ/°	109.408(7)
Volume/Å^3	950.45(13)
Z	2
ρ_{calc}g/cm^3	1.253
μ/mm^{-1}	0.594
F(000)	384
Crystal size/mm^3	0.02 × 0.02 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.704 to 154.248
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 10$, $-18 \le l \le 18$
Reflections collected	10137
Independent reflections	3759 [R_{int} = 0.0774, R_{sigma} = 0.0895]
Data/restraints/parameters	3759/0/244
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1400
Final R indexes [all data]	R_1 = 0.1039, wR_2 = 0.1605
Largest diff. peak/hole / e Å^{-3}	0.24/-0.27
Flack parameter	N

8. Copies of NMR Spectra

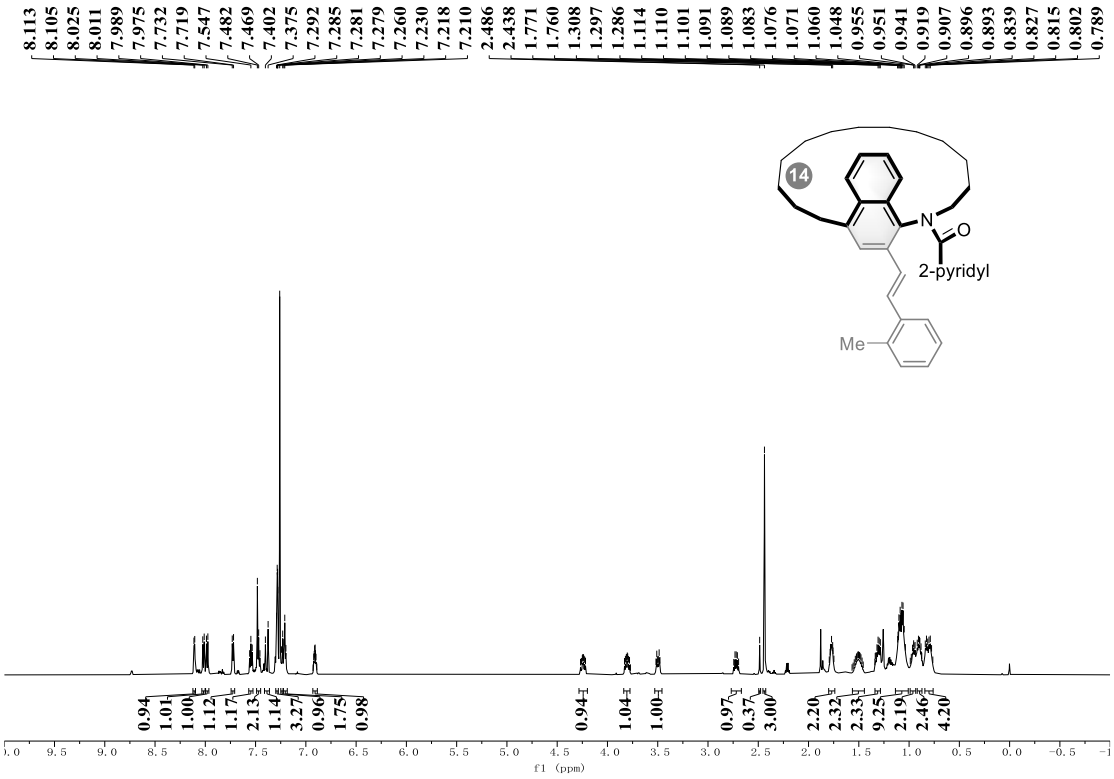
(R_p)-**3aa**, ^{13}C NMR (400 MHz, $CDCl_3$)



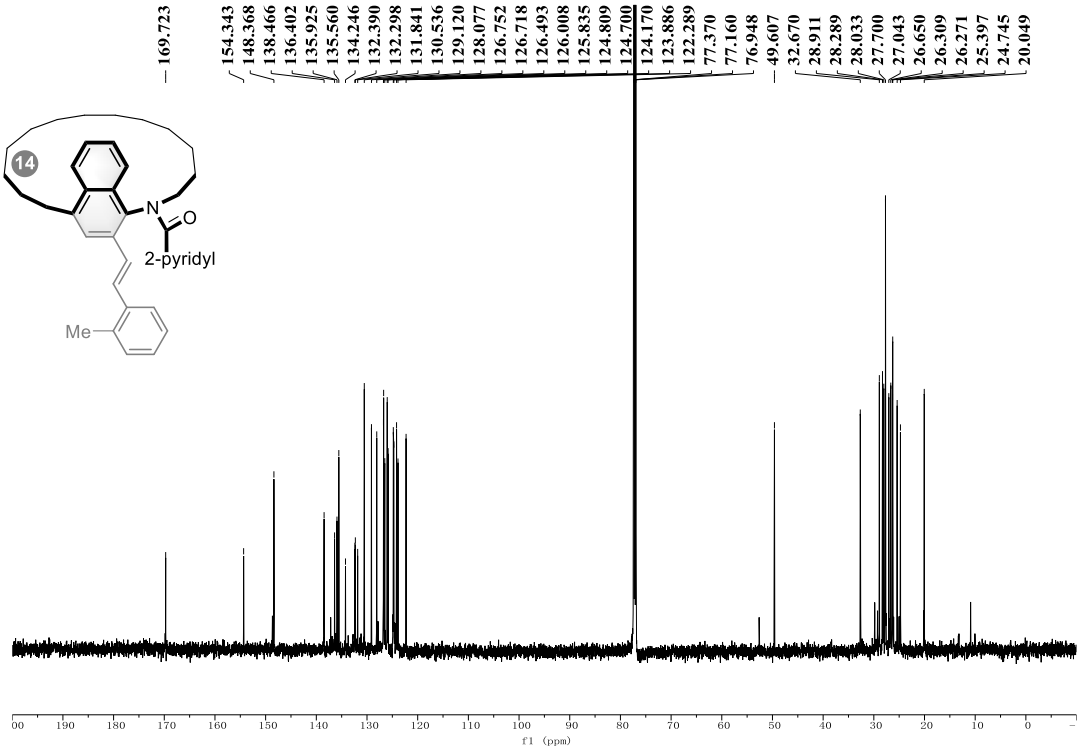
(R_p)-**3aa**, ^{13}C NMR (101 MHz, $CDCl_3$)



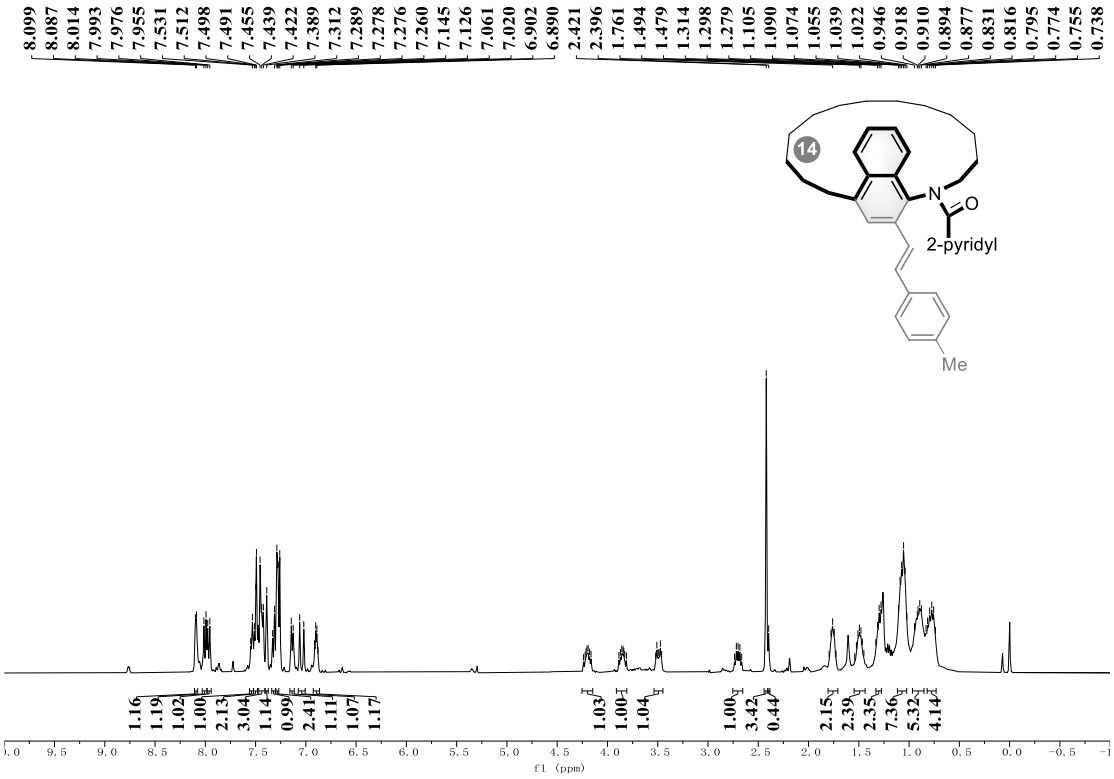
(R_p)-**3ab**, ^{1}H NMR (600 MHz, $CDCl_3$)



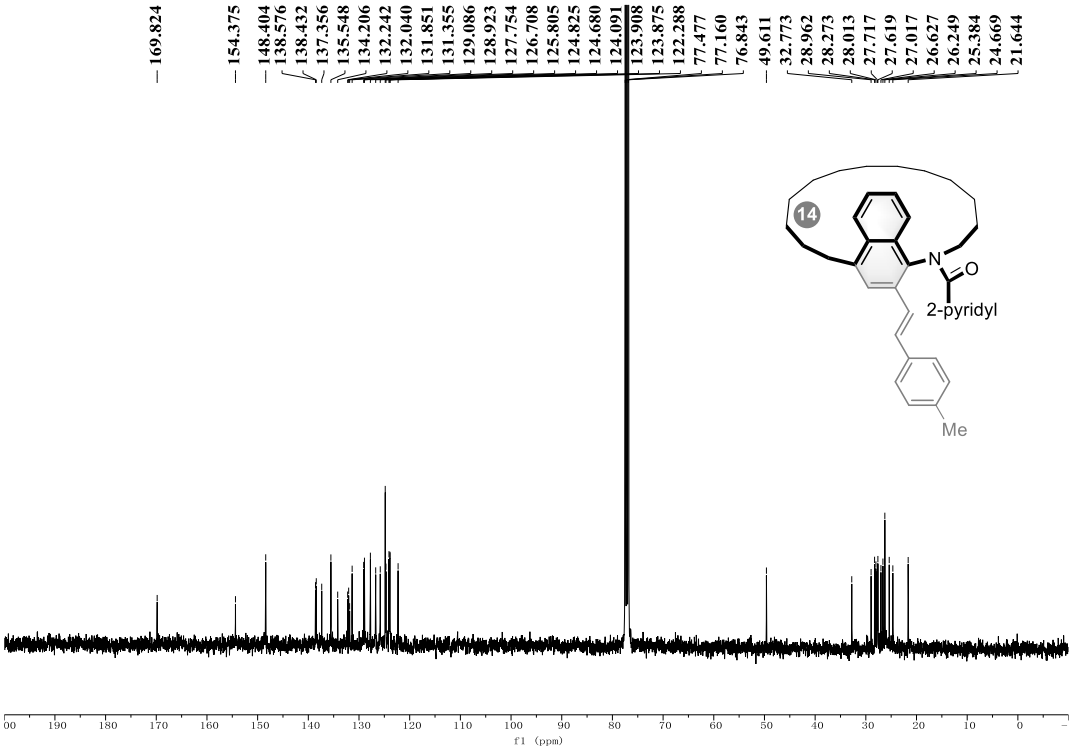
(R_p)-**3ab**, ^{13}C NMR (151 MHz, $CDCl_3$)



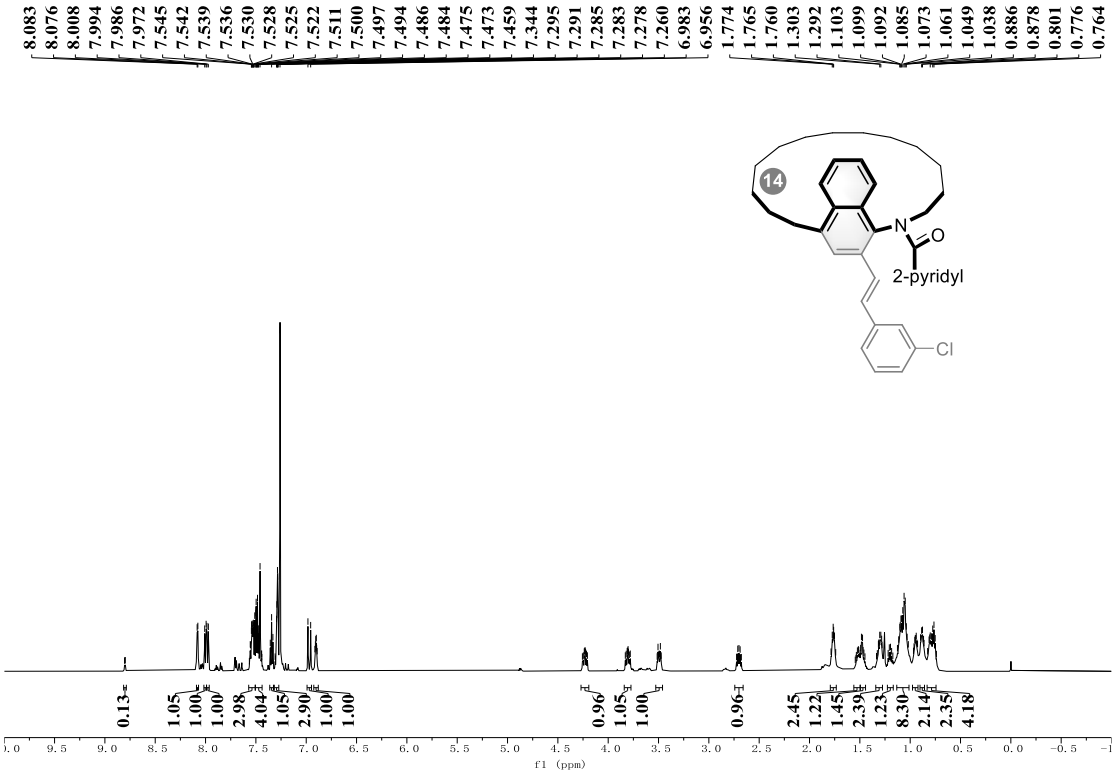
(R_p)-**3ac**, ^{1}H NMR (400 MHz, $CDCl_3$)



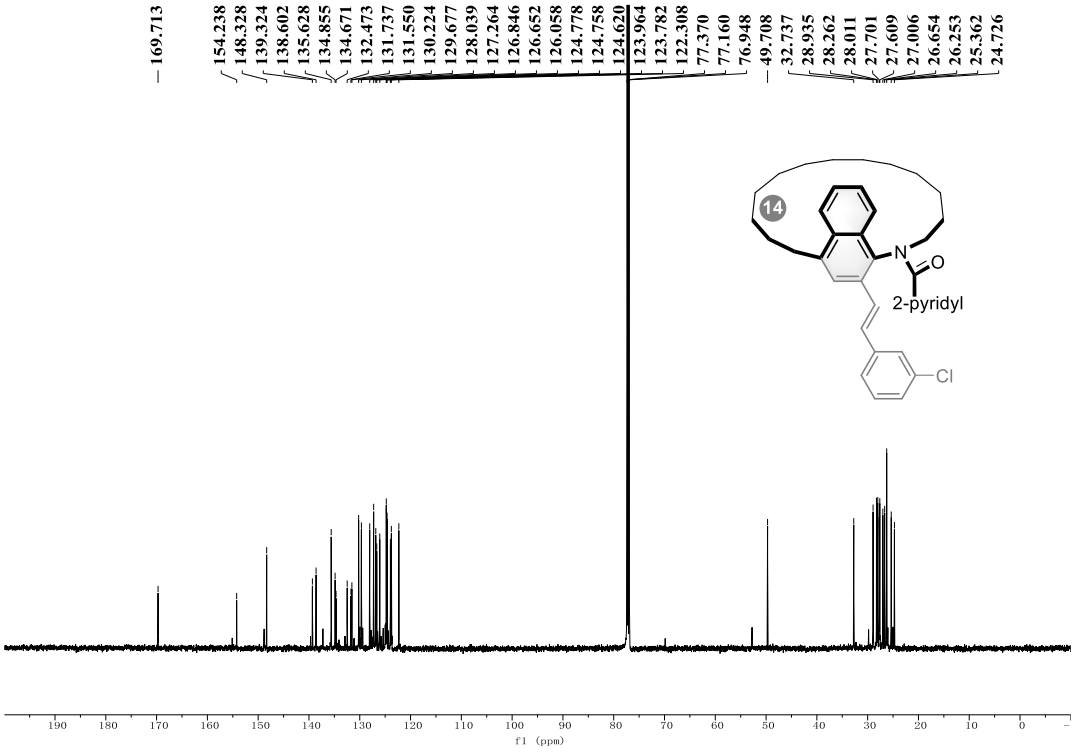
(R_p)-**3ac**, ^{13}C NMR (101 MHz, $CDCl_3$)



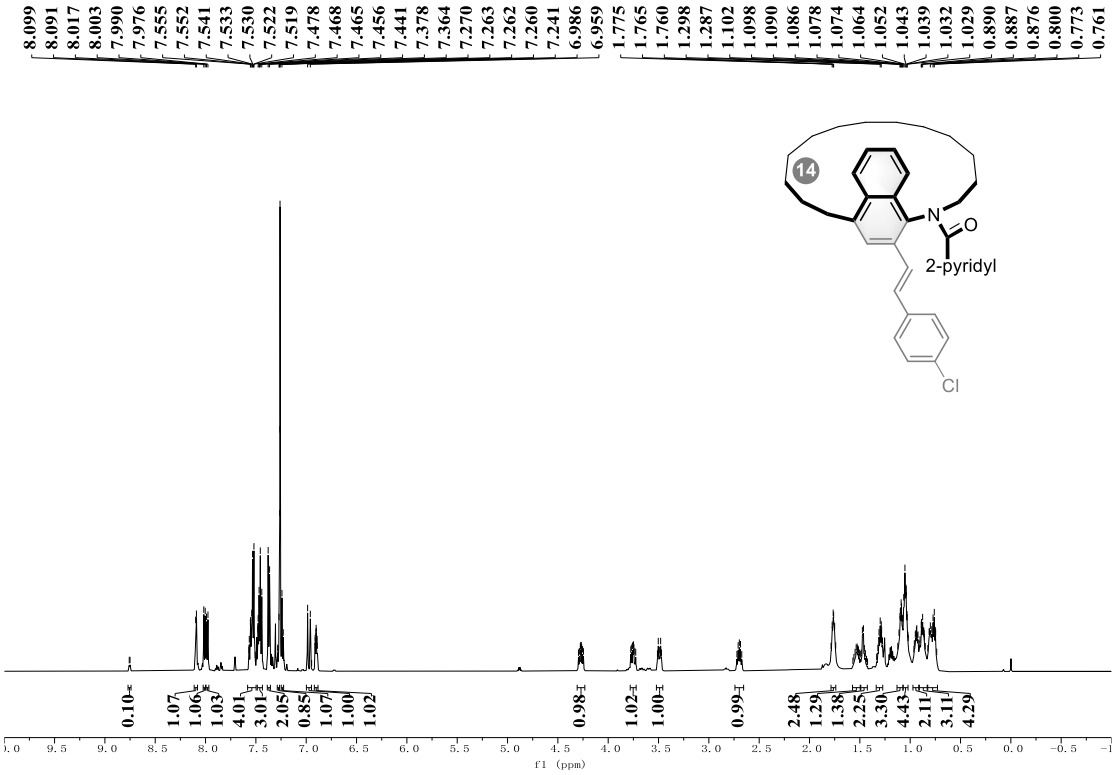
(R_p)-**3ad**, ^{1}H NMR (600 MHz, $CDCl_3$)



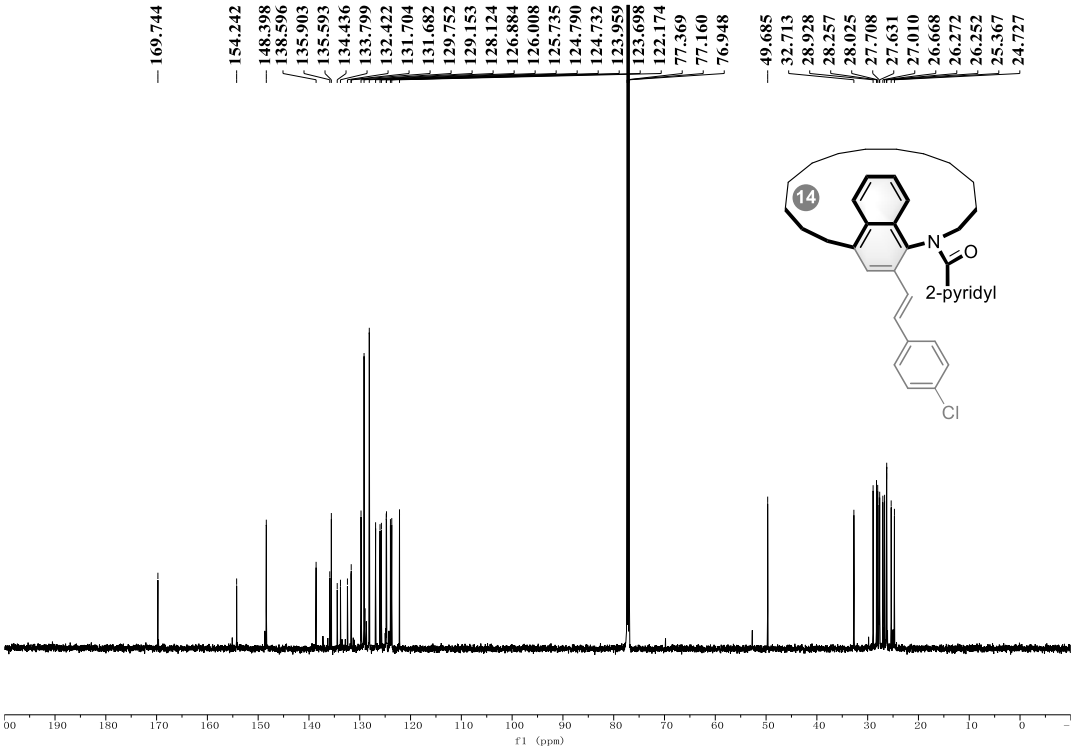
(R_p)-**3ad**, ^{13}C NMR (151 MHz, $CDCl_3$)



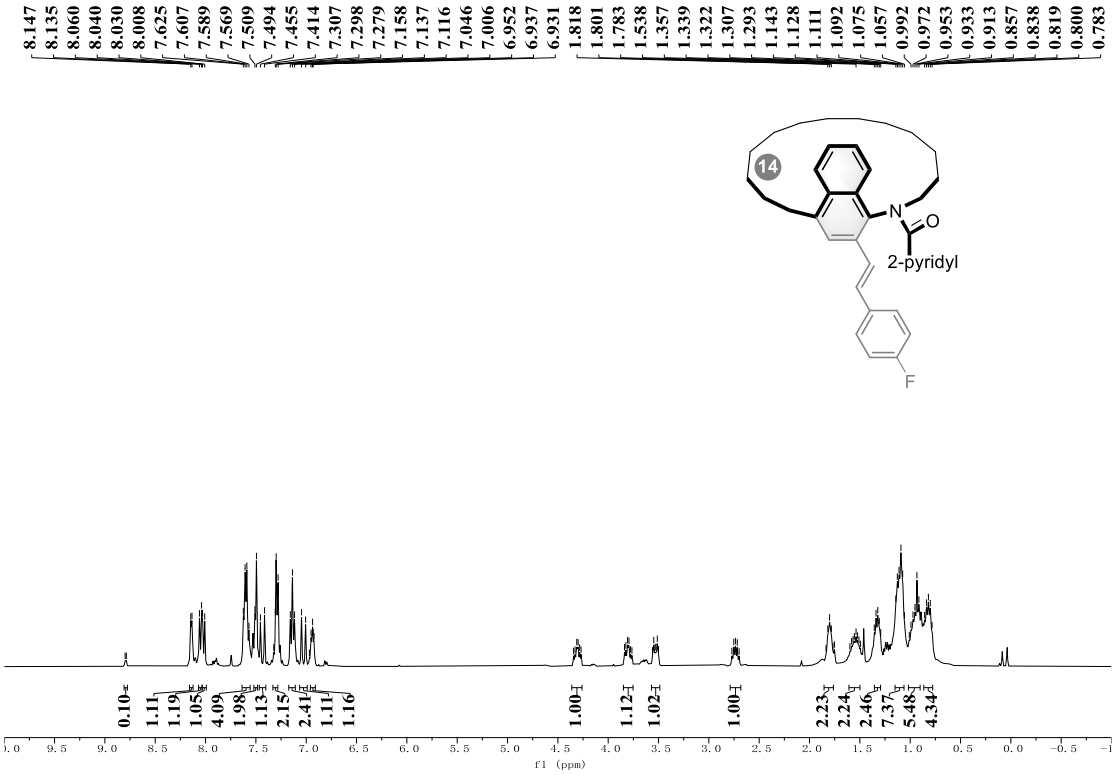
(R_p)-**3ae**, ^{1}H NMR (600 MHz, $CDCl_3$)



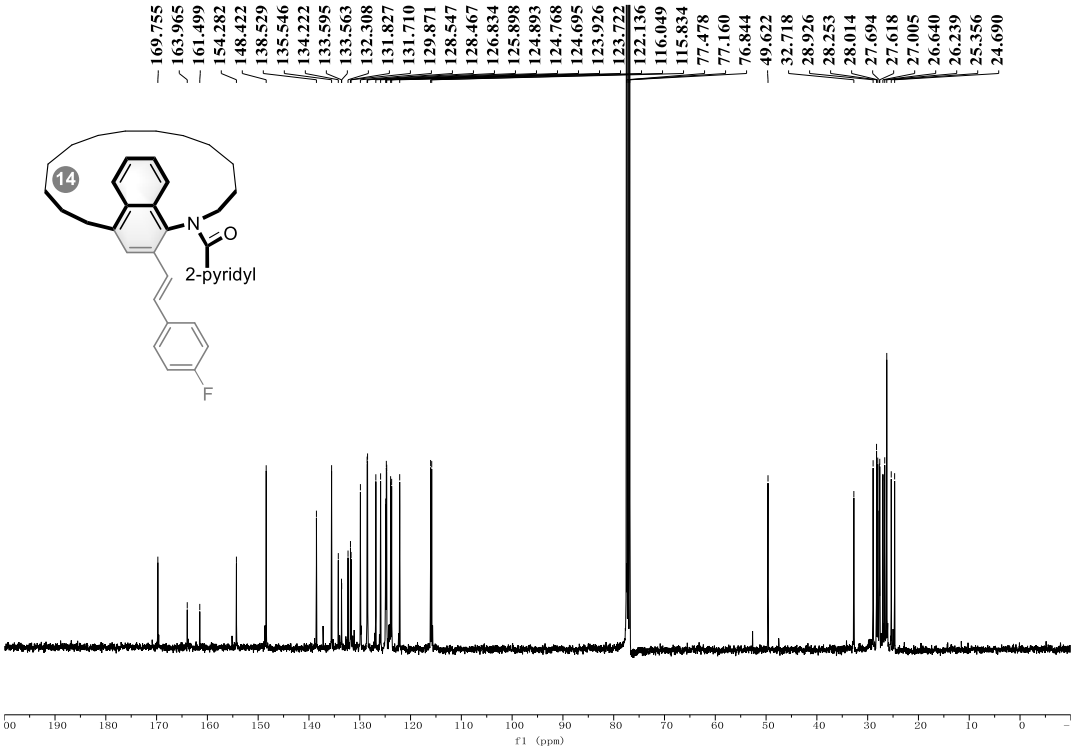
(R_p)-**3ae**, ^{13}C NMR (151 MHz, $CDCl_3$)



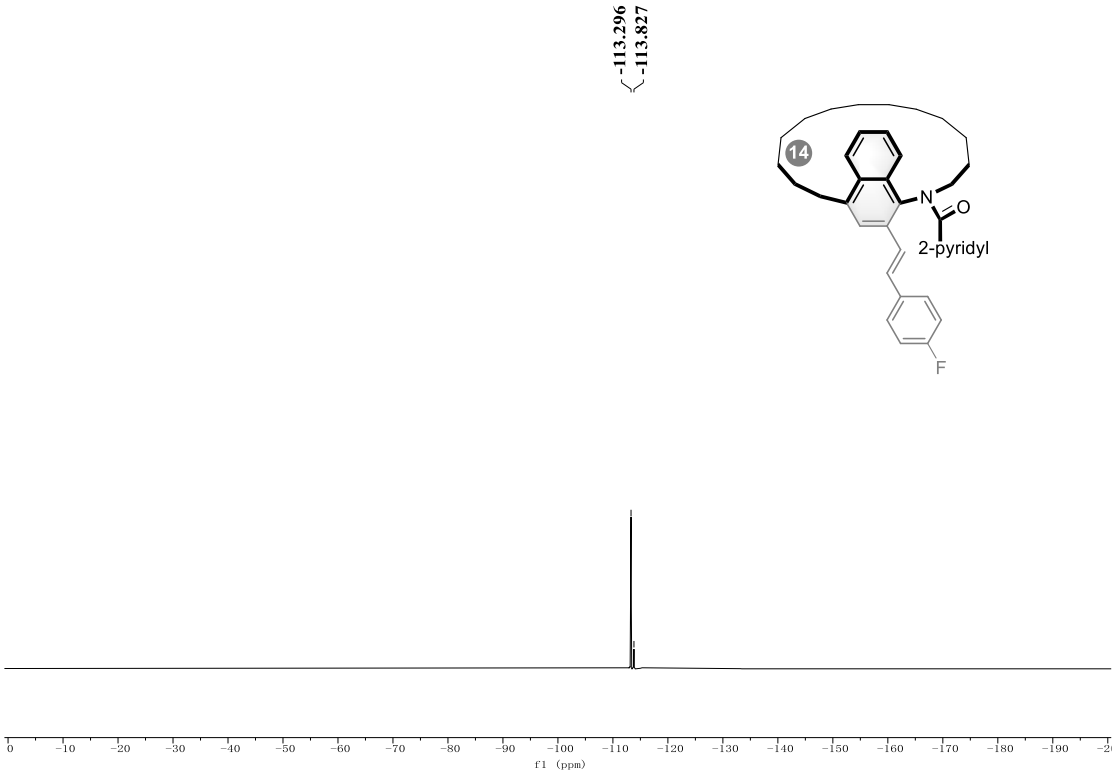
(R_p)-**3af**, ^{1}H NMR (400 MHz, $CDCl_3$)



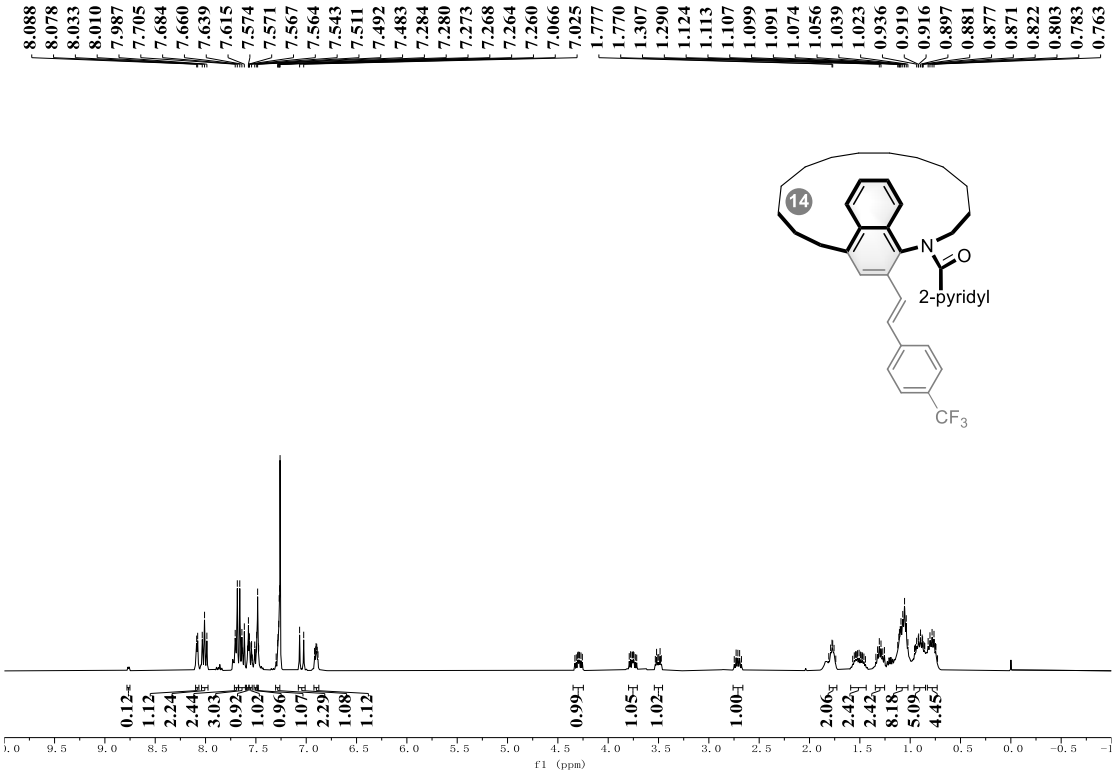
(R_p)-**3af**, ^{13}C NMR (101 MHz, $CDCl_3$)



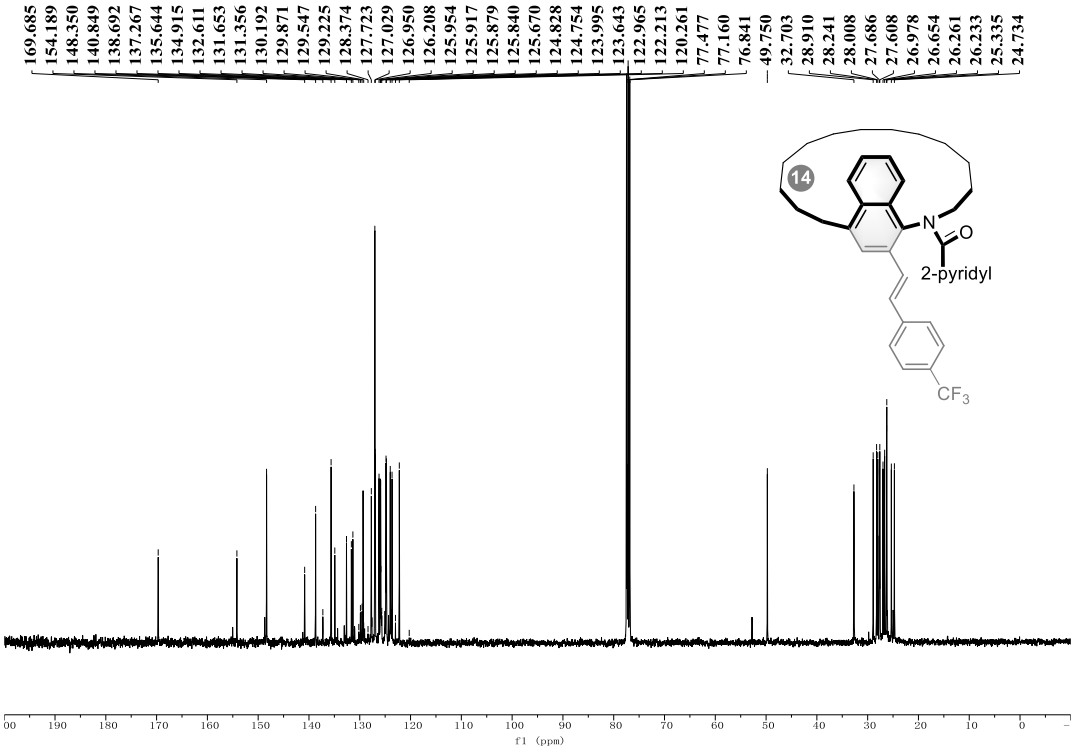
(R_p)-**3af**, ^{19}F NMR (376 MHz, $CDCl_3$)



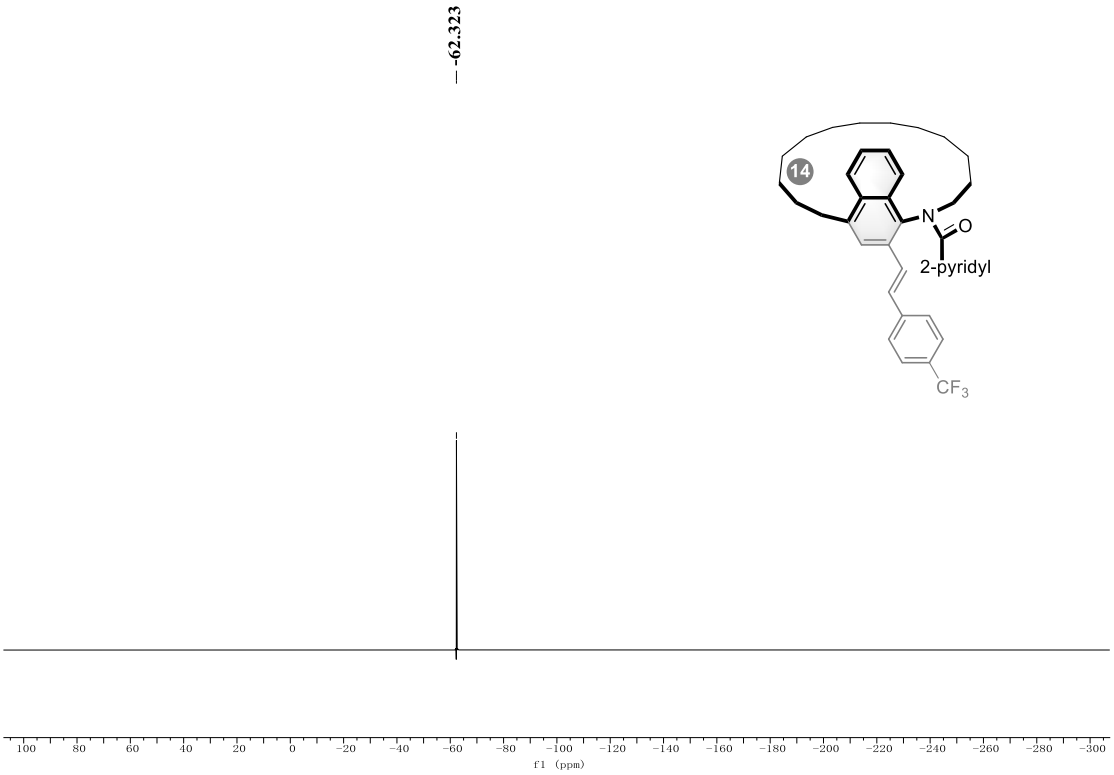
(R_p)-**3ag**, ^{1}H NMR (400 MHz, $CDCl_3$)



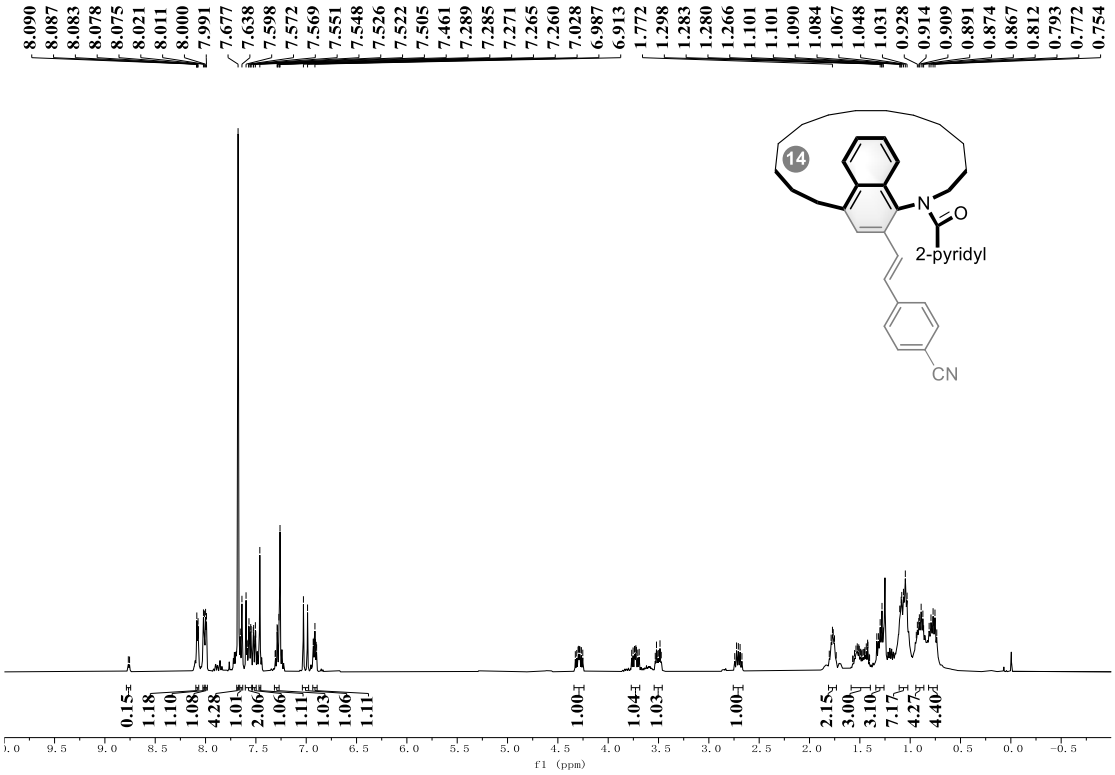
(R_p)-**3ag**, ^{13}C NMR (101 MHz, $CDCl_3$)



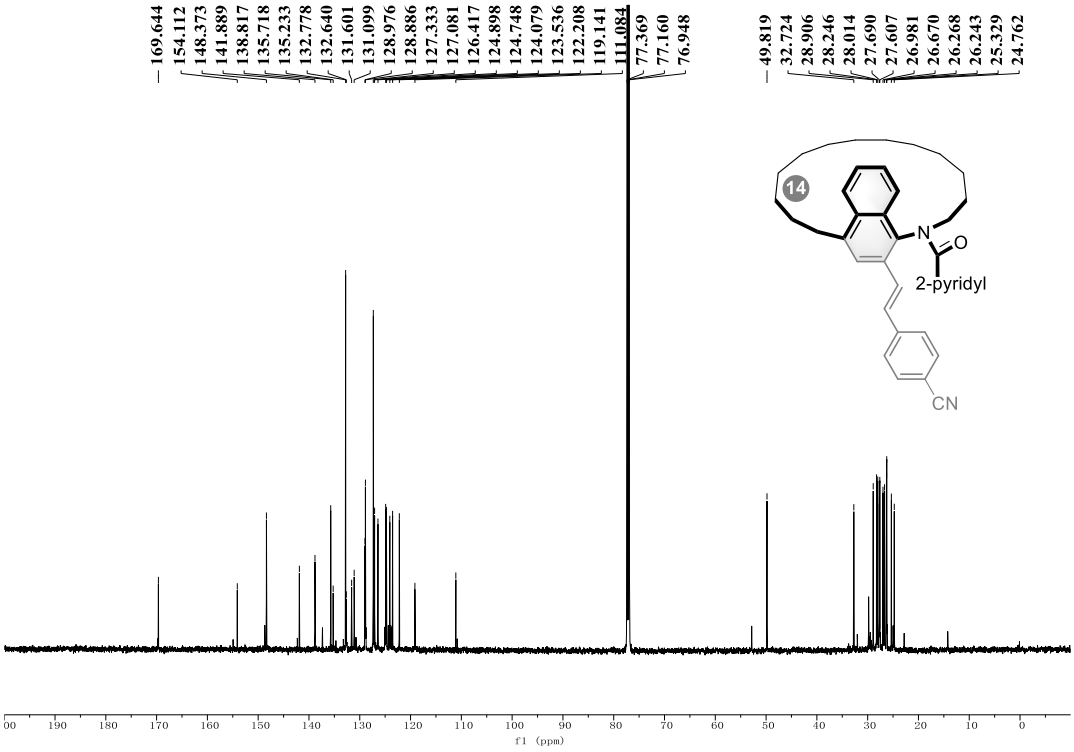
(R_p)-**3ag**, ^{19}F NMR (376 MHz, $CDCl_3$)



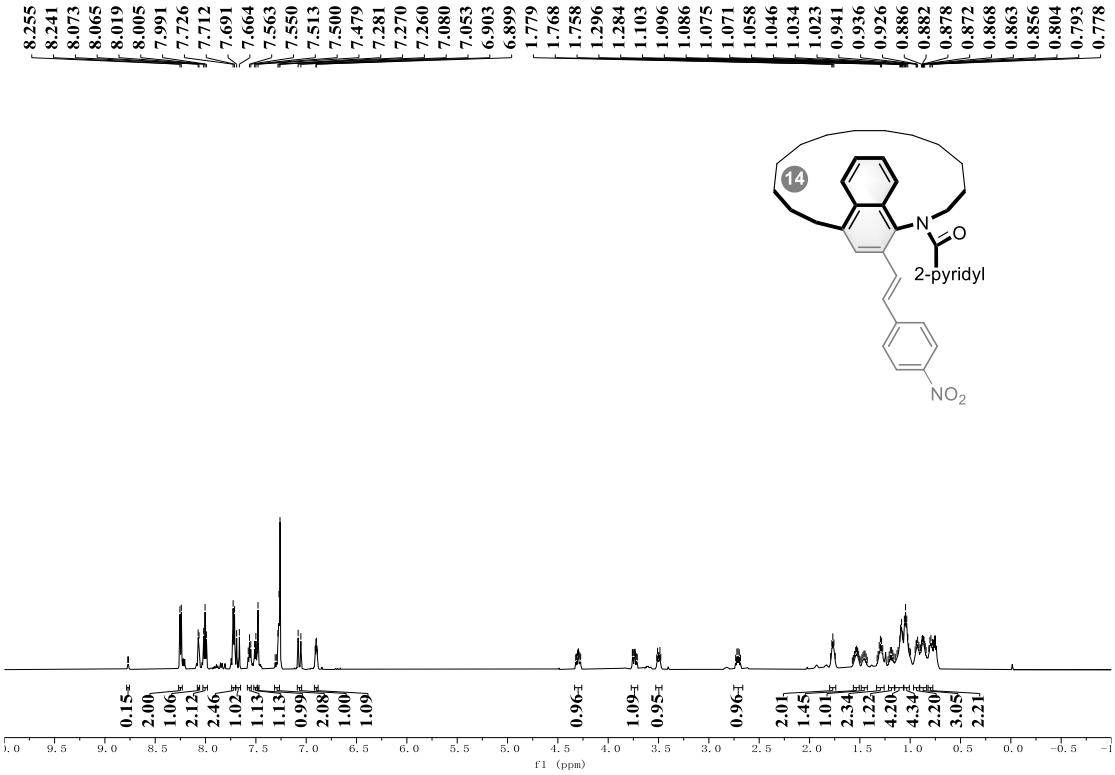
(R_p)-**3ah**, ^{1}H NMR (400 MHz, $CDCl_3$)



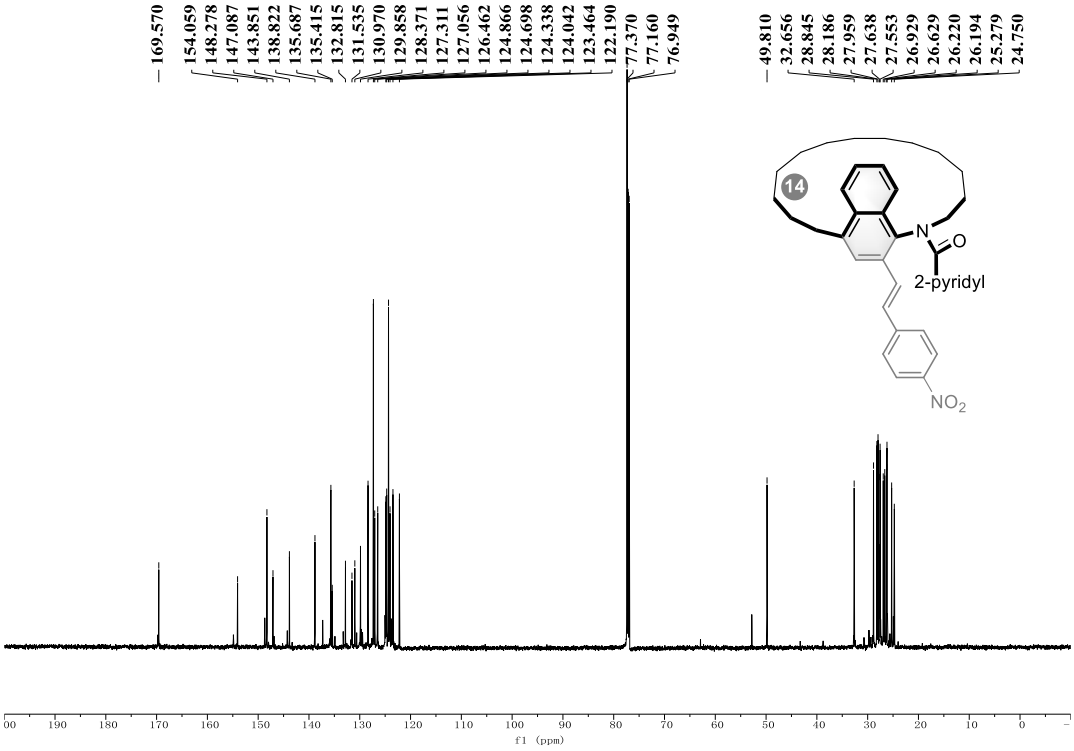
(R_p)-**3ah**, ^{13}C NMR (151 MHz, $CDCl_3$)



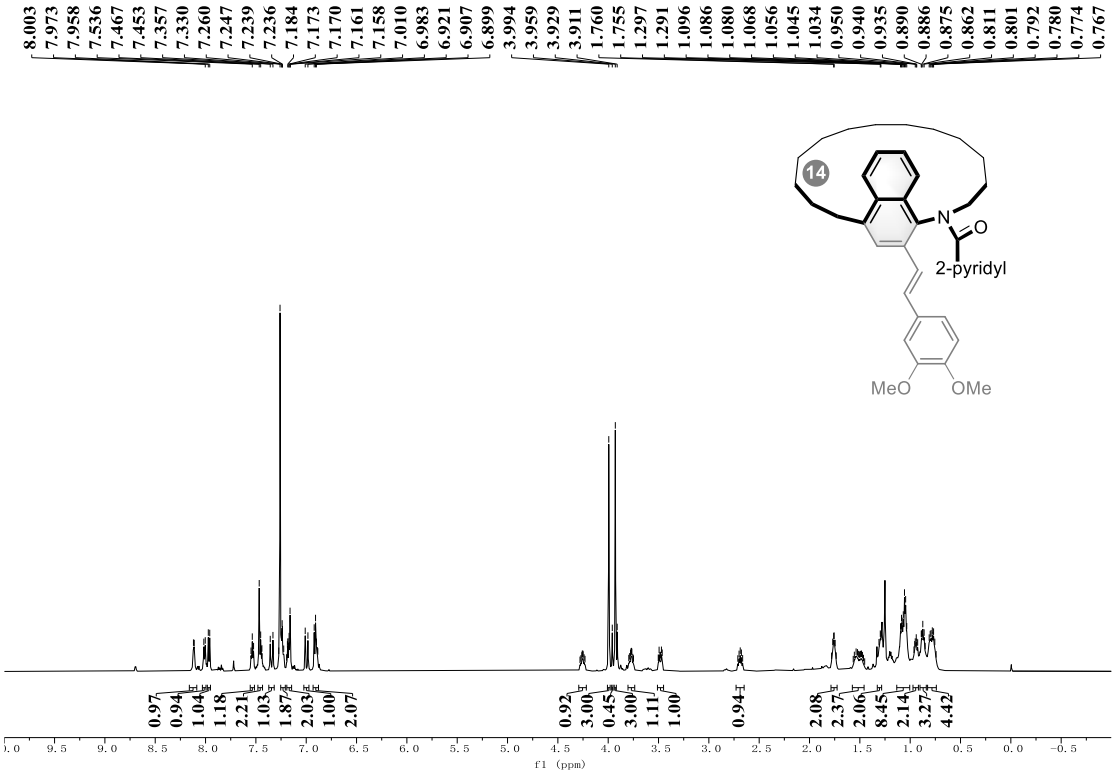
(R_p)-**3ai**, ^{1}H NMR (600 MHz, $CDCl_3$)



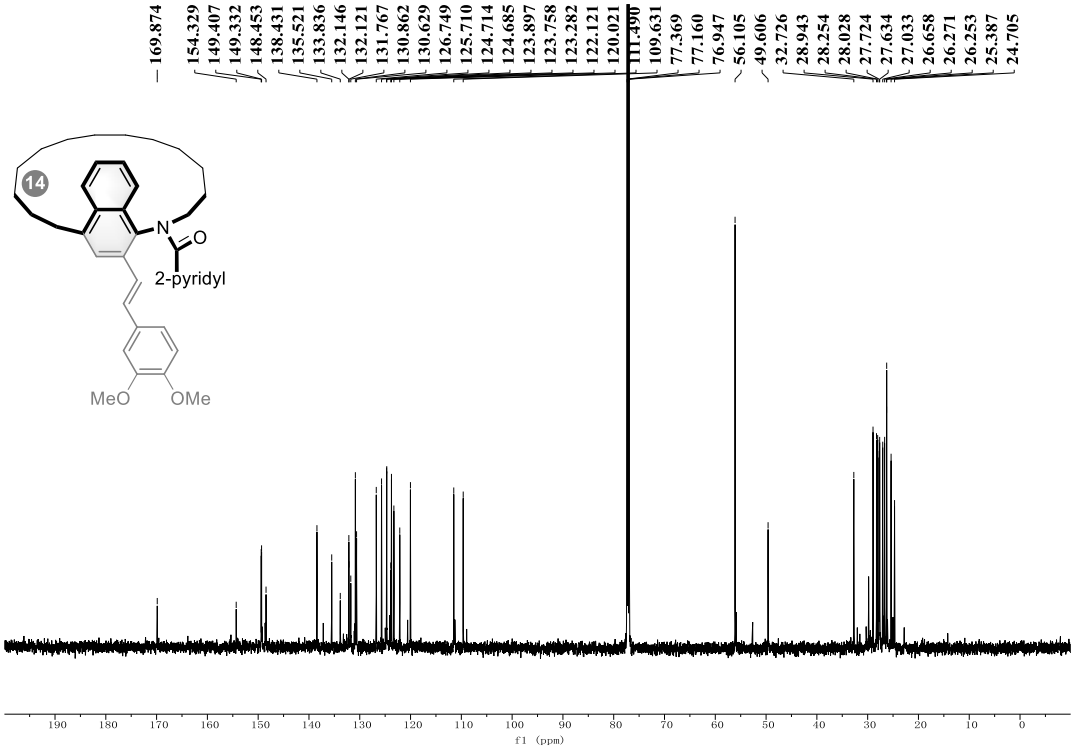
(R_p)-**3ai**, ^{13}C NMR (151 MHz, $CDCl_3$)



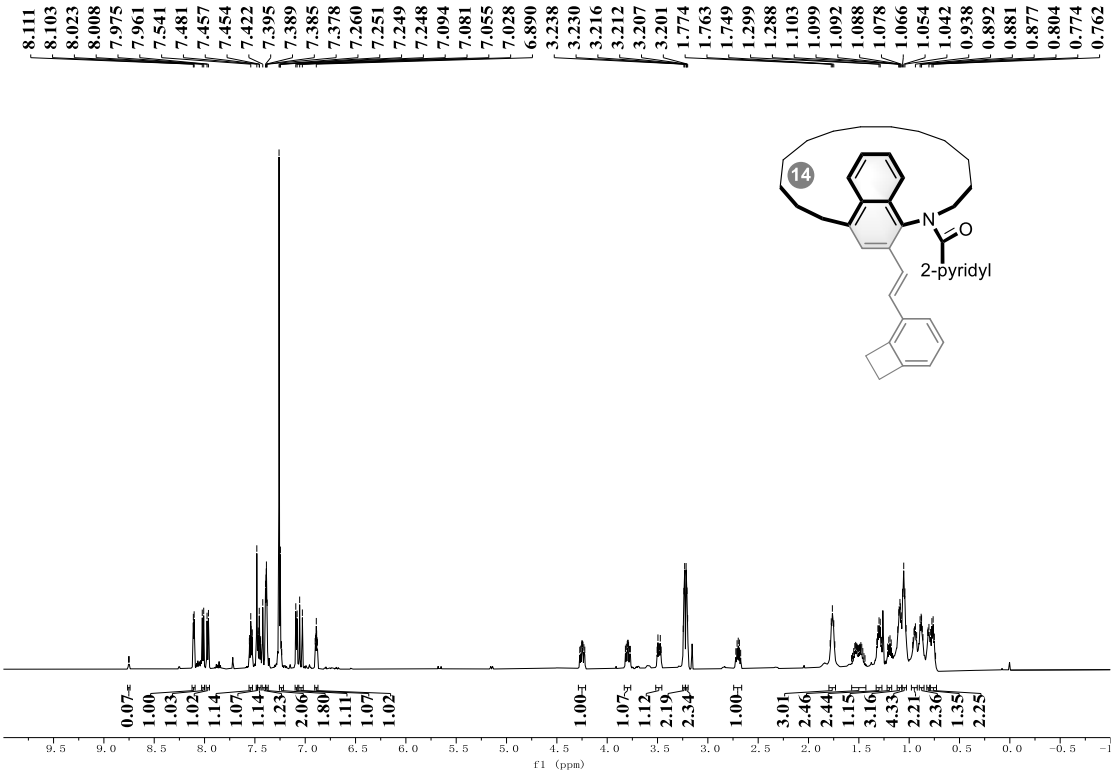
(R_p)-**3aj**, ^{1}H NMR (600 MHz, $CDCl_3$)



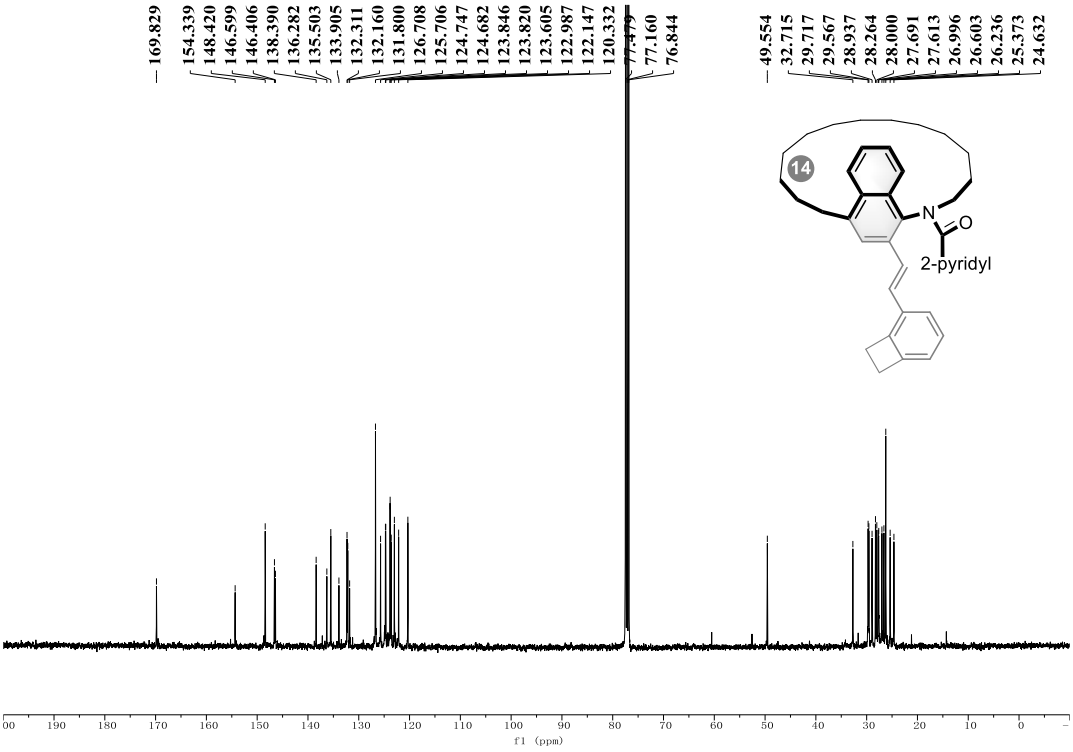
(R_p)-**3aj**, ^{13}C NMR (151 MHz, $CDCl_3$)



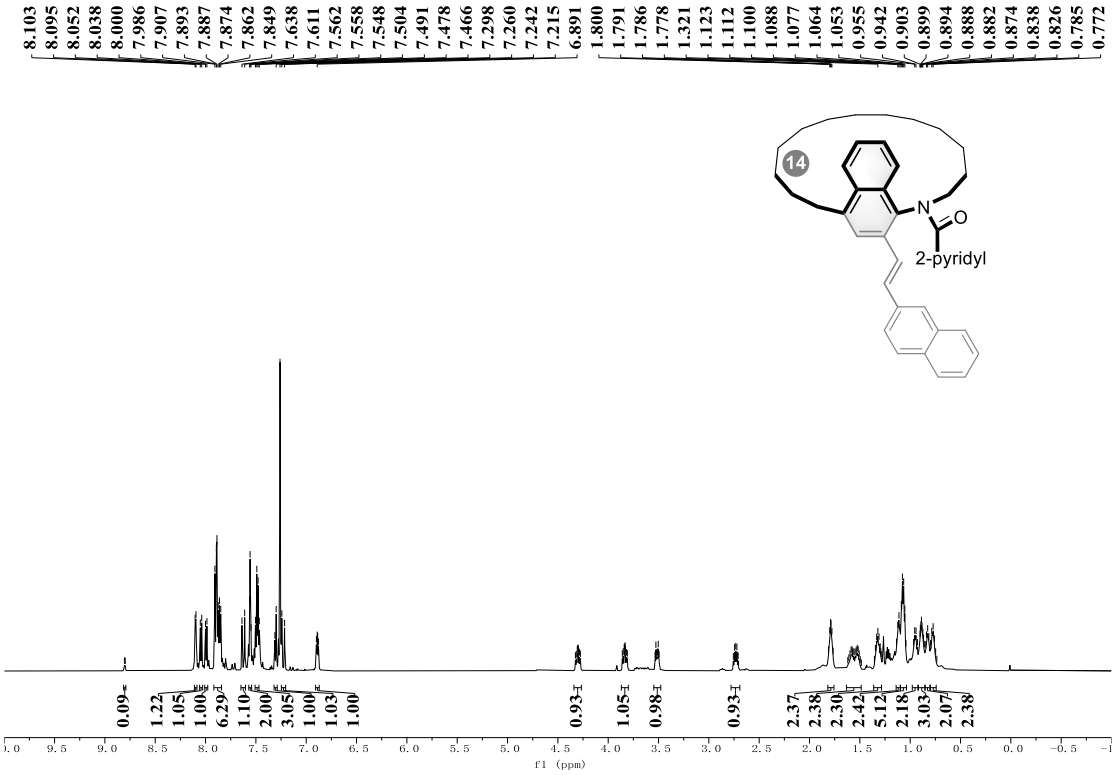
(R_p)-**3ak**, ^{1}H NMR (600 MHz, $CDCl_3$)



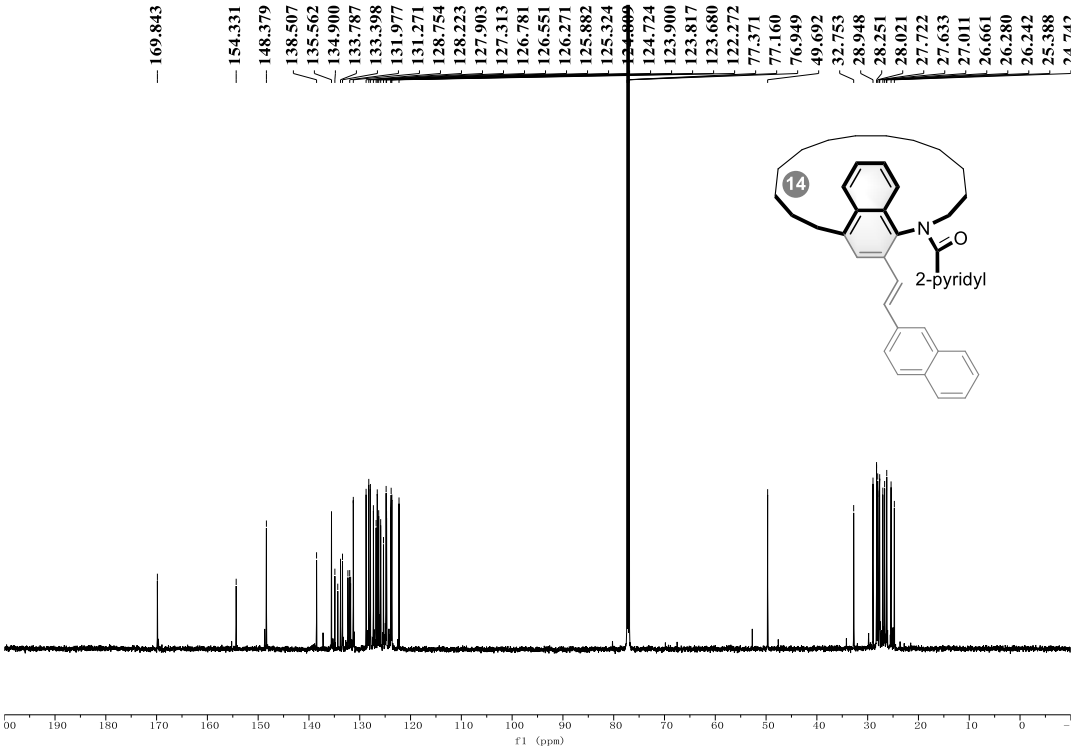
(R_p)-**3ak**, ^{13}C NMR (101 MHz, $CDCl_3$)



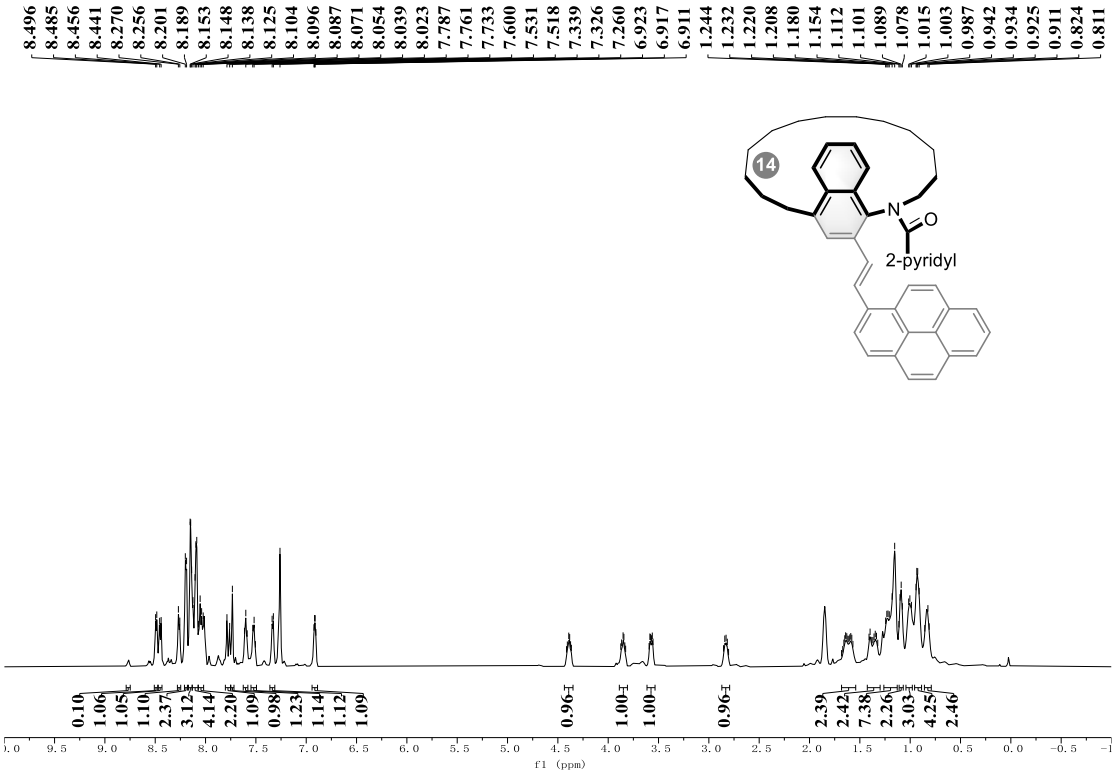
(R_p)-**3al**, ^{1}H NMR (600 MHz, $CDCl_3$)



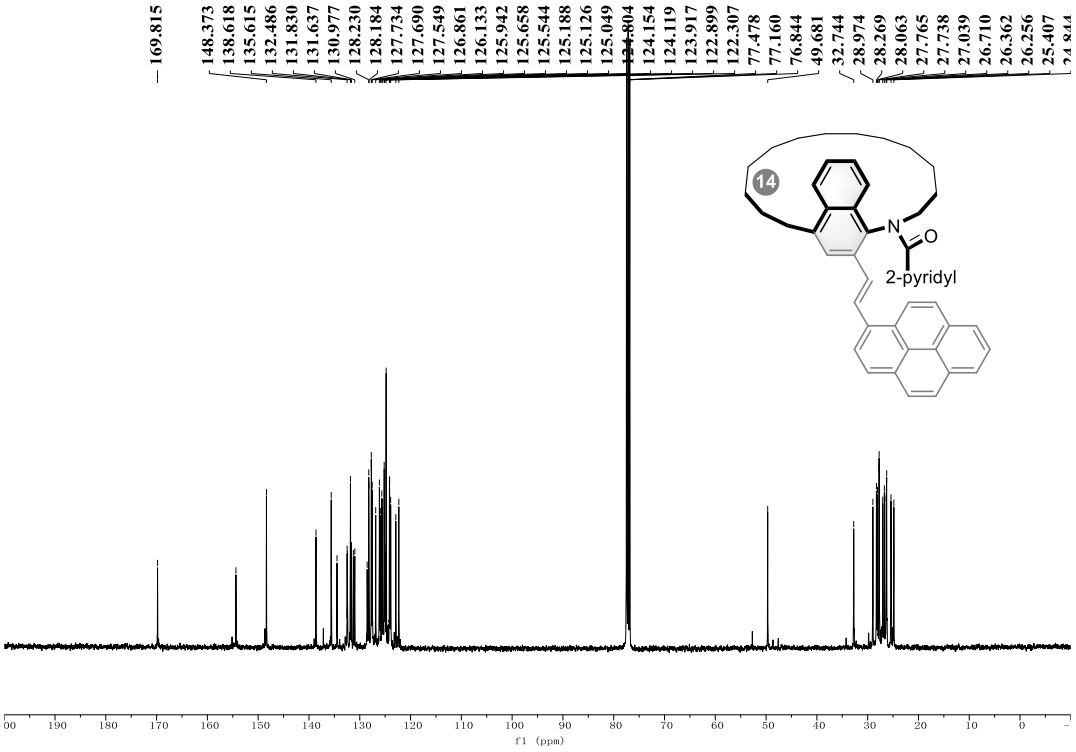
(R_p)-**3al**, ^{13}C NMR (151 MHz, $CDCl_3$)



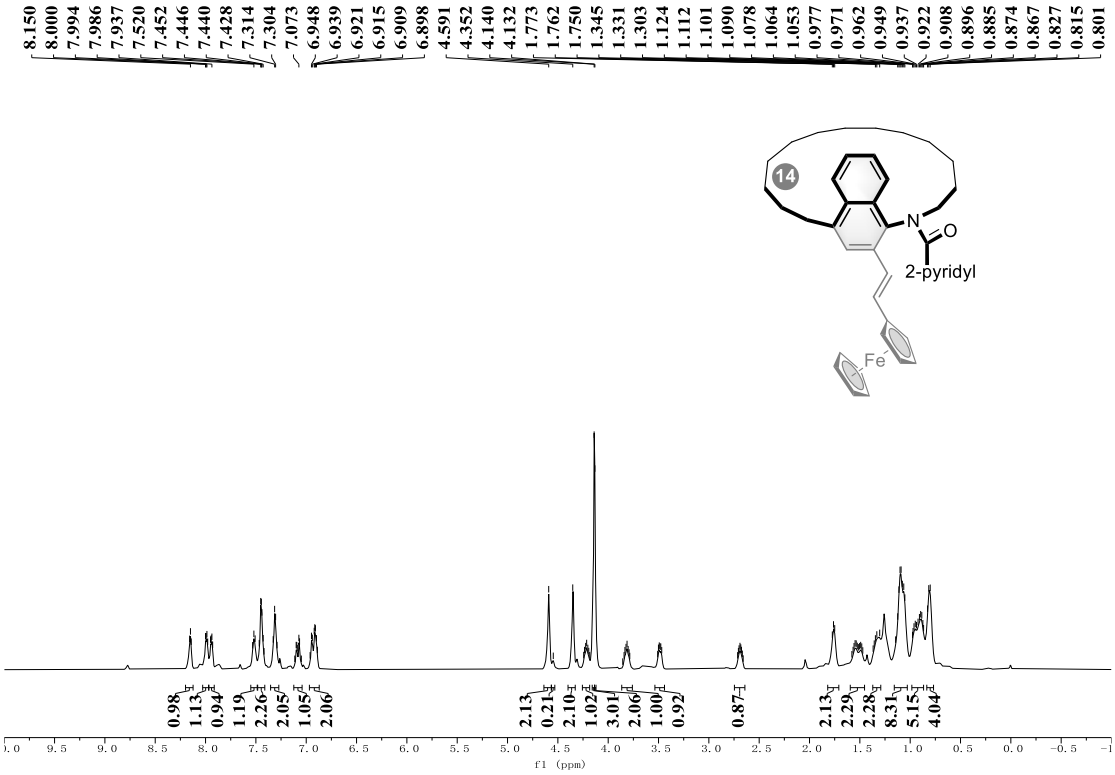
(R_p)-**3am**, ^{1}H NMR (600 MHz, $CDCl_3$)



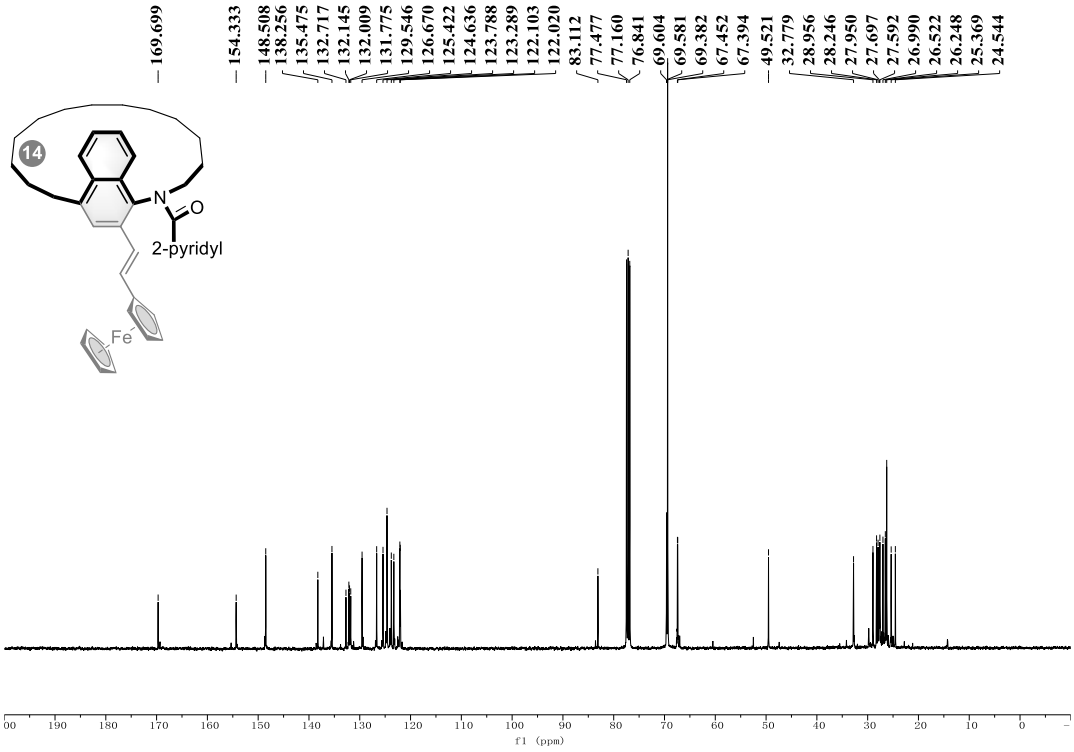
(R_p)-**3am**, ^{13}C NMR (101 MHz, $CDCl_3$)



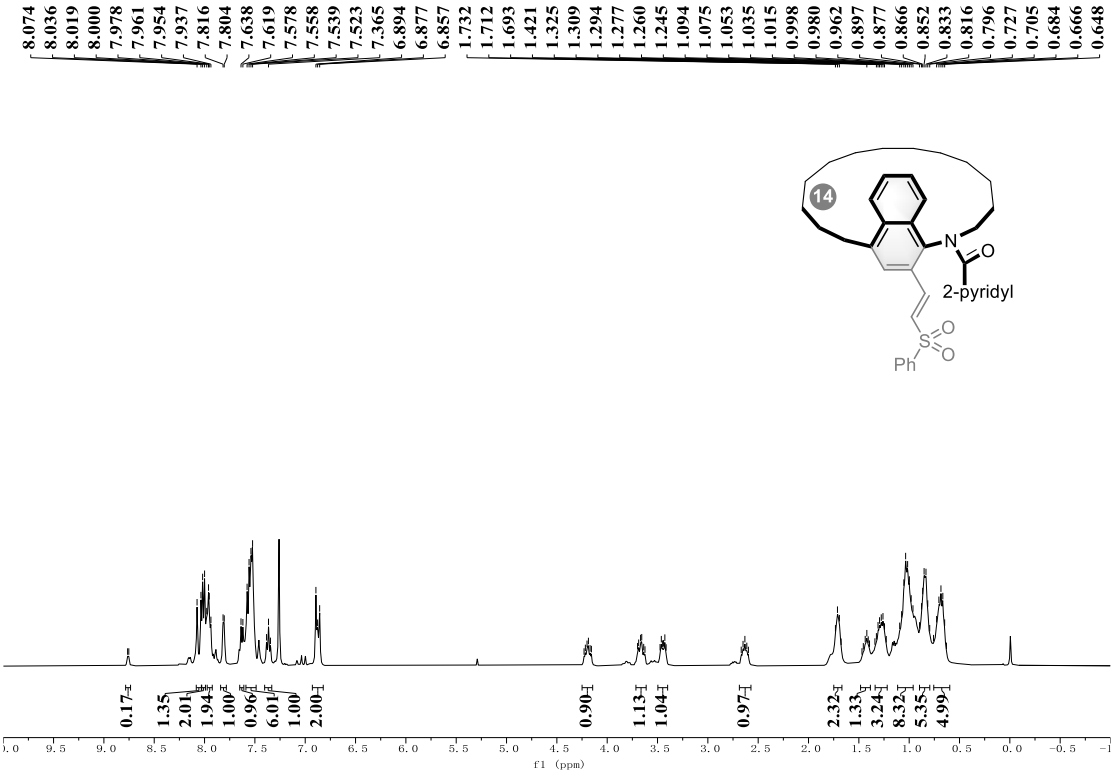
(R_p)-**3an**, ^{1}H NMR (600 MHz, $CDCl_3$)



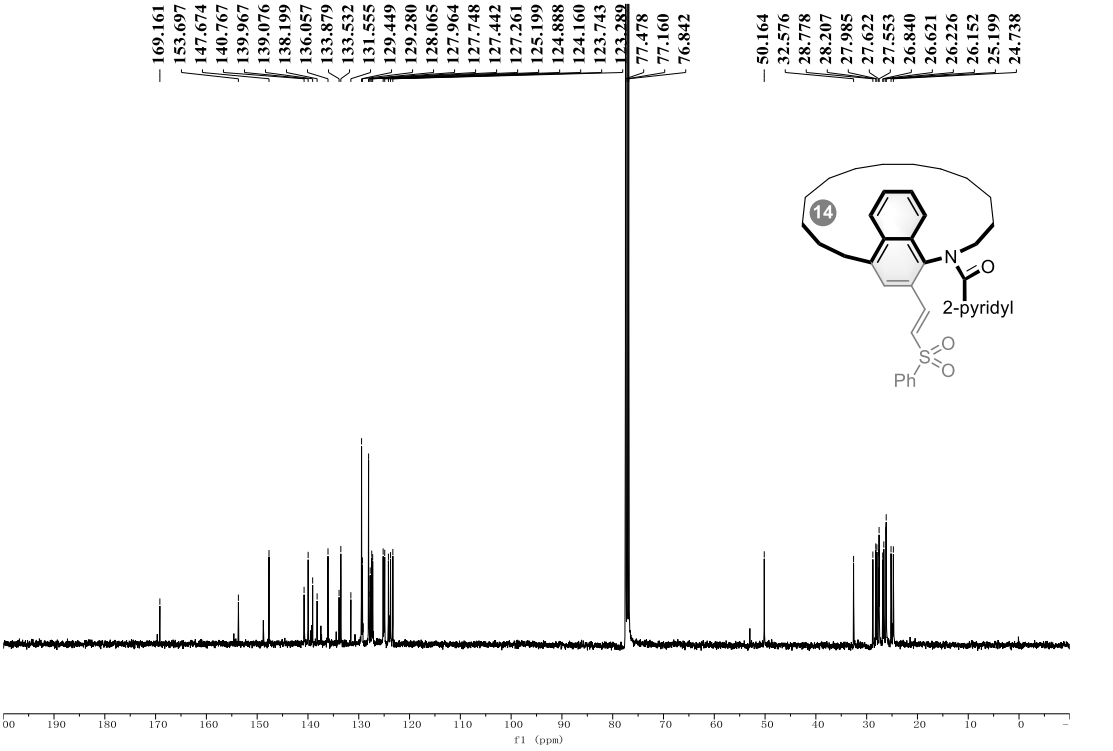
(R_p)-**3an**, ^{13}C NMR (101 MHz, $CDCl_3$)



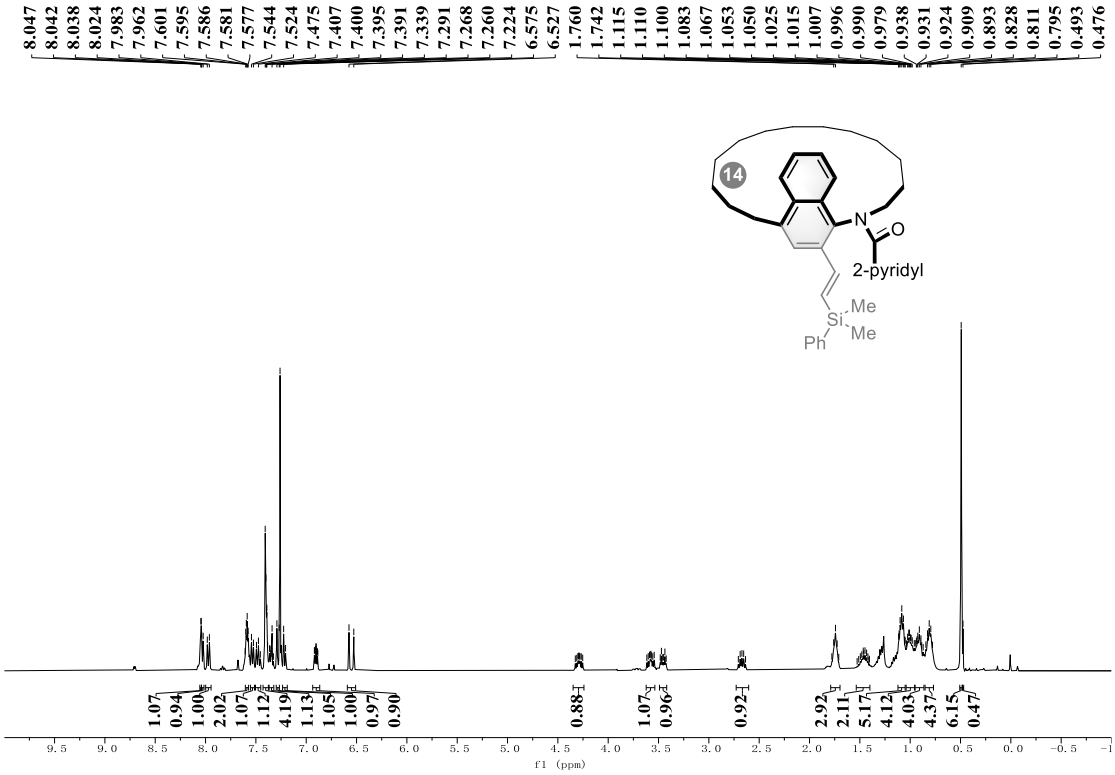
(R_p)-**3ao**, ^{1}H NMR (400 MHz, $CDCl_3$)



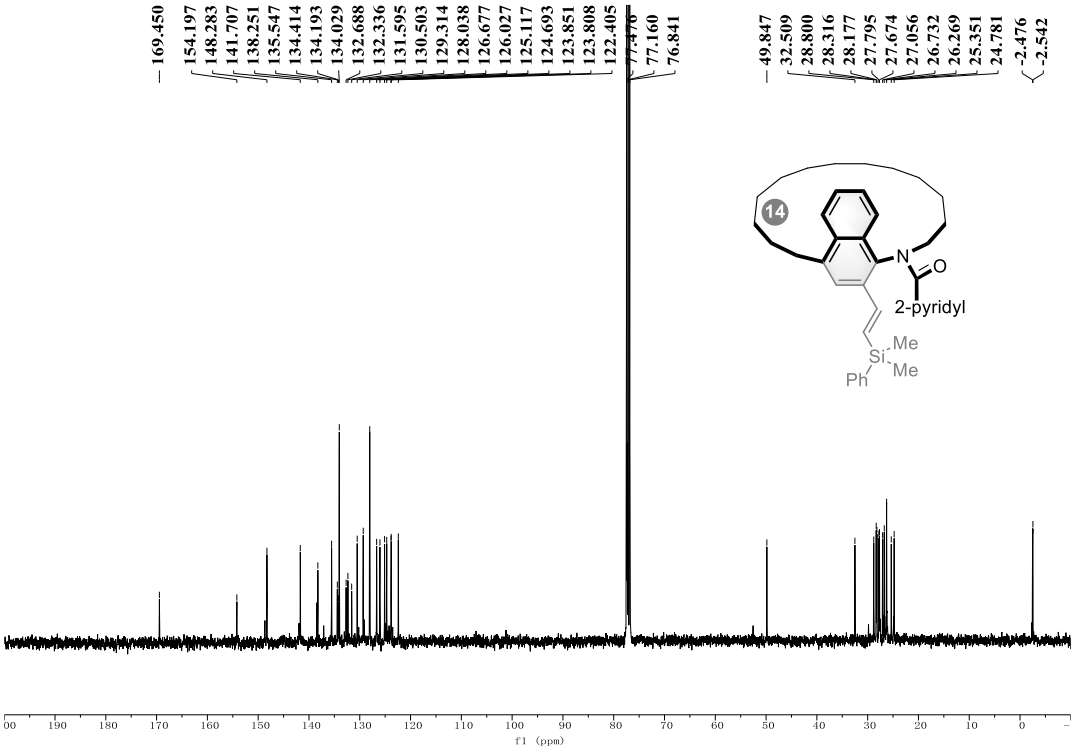
(R_p)-**3ao**, ^{13}C NMR (101 MHz, $CDCl_3$)



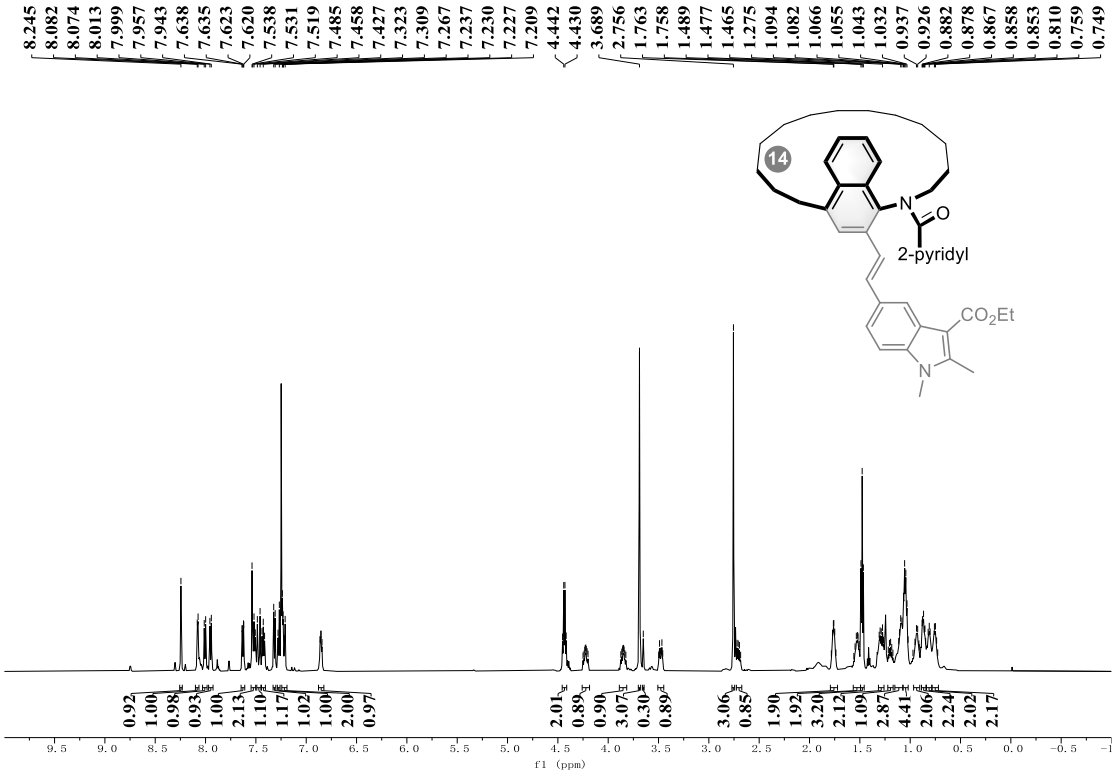
(R_p)-**3ap**, ^{1}H NMR (400 MHz, $CDCl_3$)



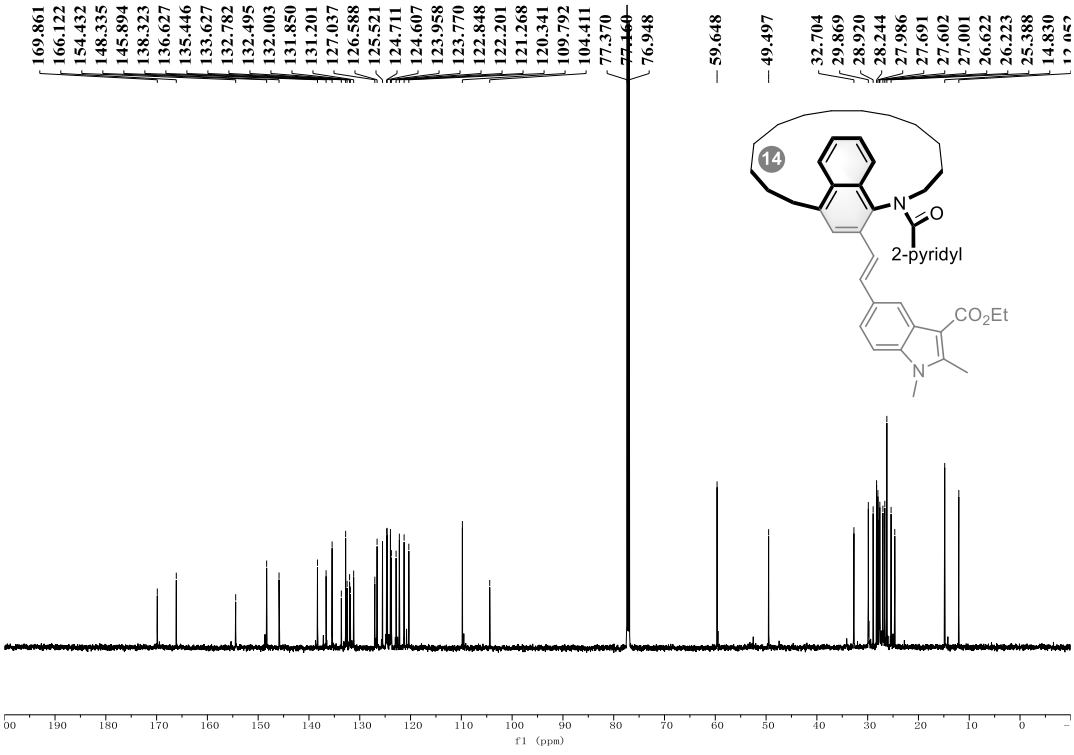
(R_p)-**3ap**, ^{13}C NMR (101 MHz, $CDCl_3$)



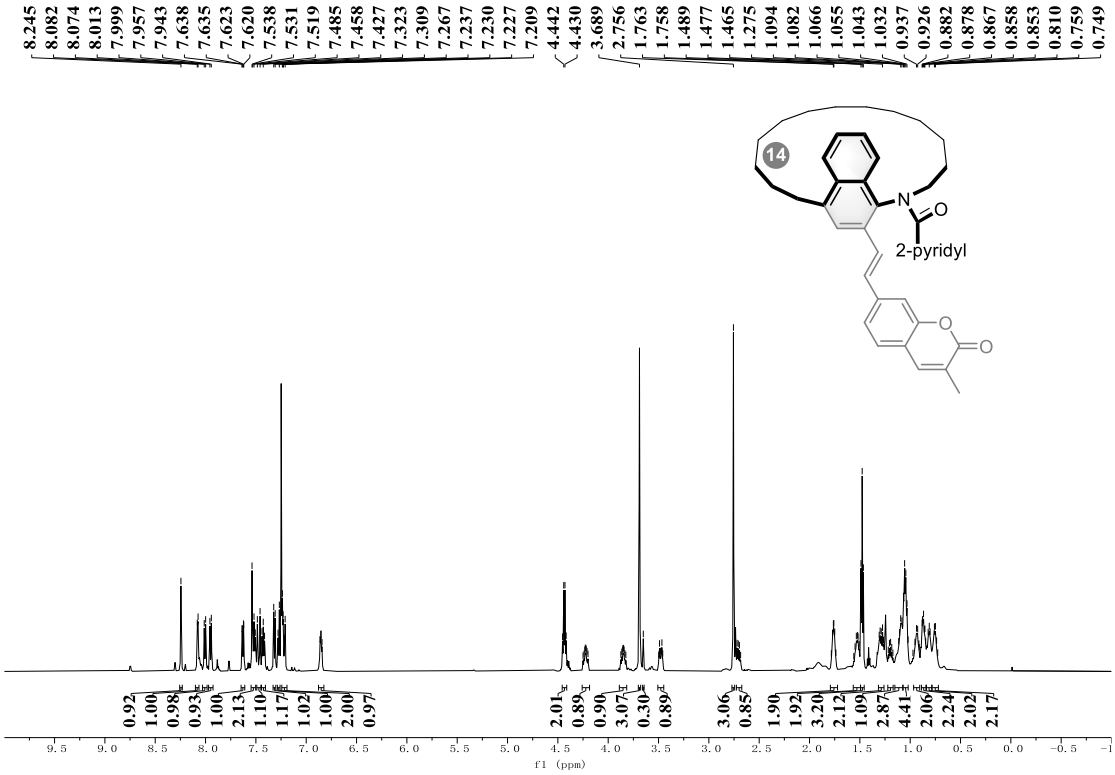
(R_p)-**3aq**, ^{1}H NMR (600 MHz, $CDCl_3$)



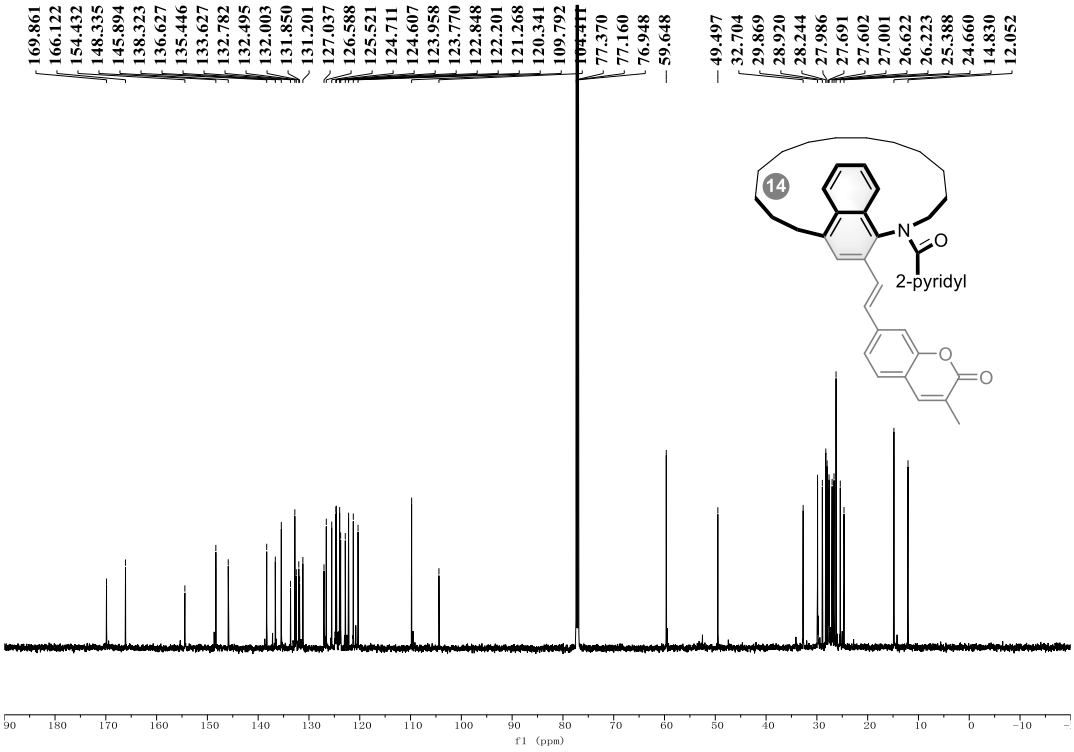
(R_p)-**3aq**, ^{13}C NMR (151 MHz, $CDCl_3$)



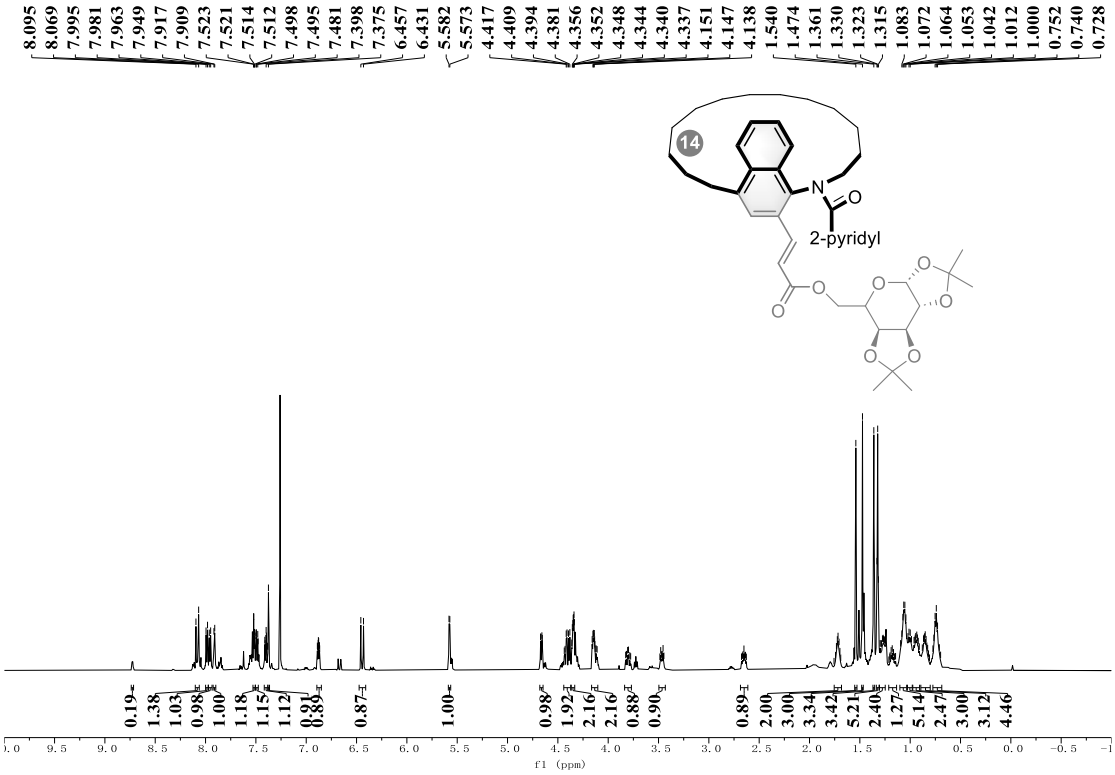
(R_p)-**3ar**, ^{1}H NMR (600 MHz, $CDCl_3$)



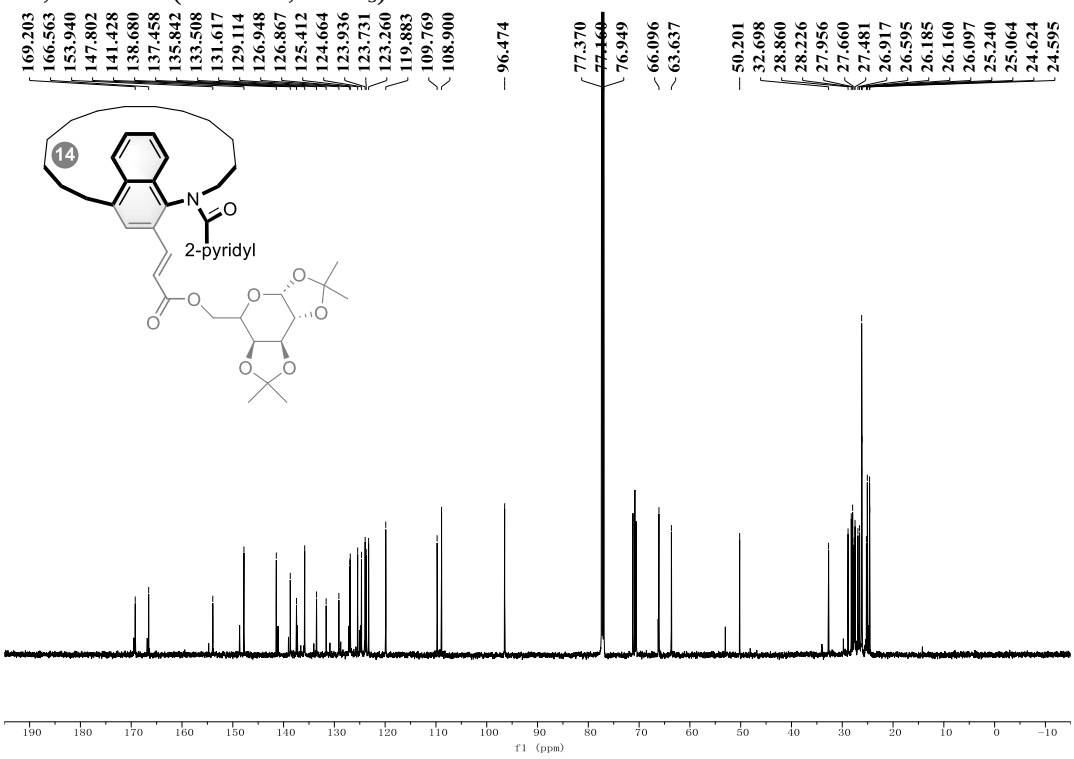
(R_p)-**3ar**, ^{13}C NMR (151 MHz, $CDCl_3$)



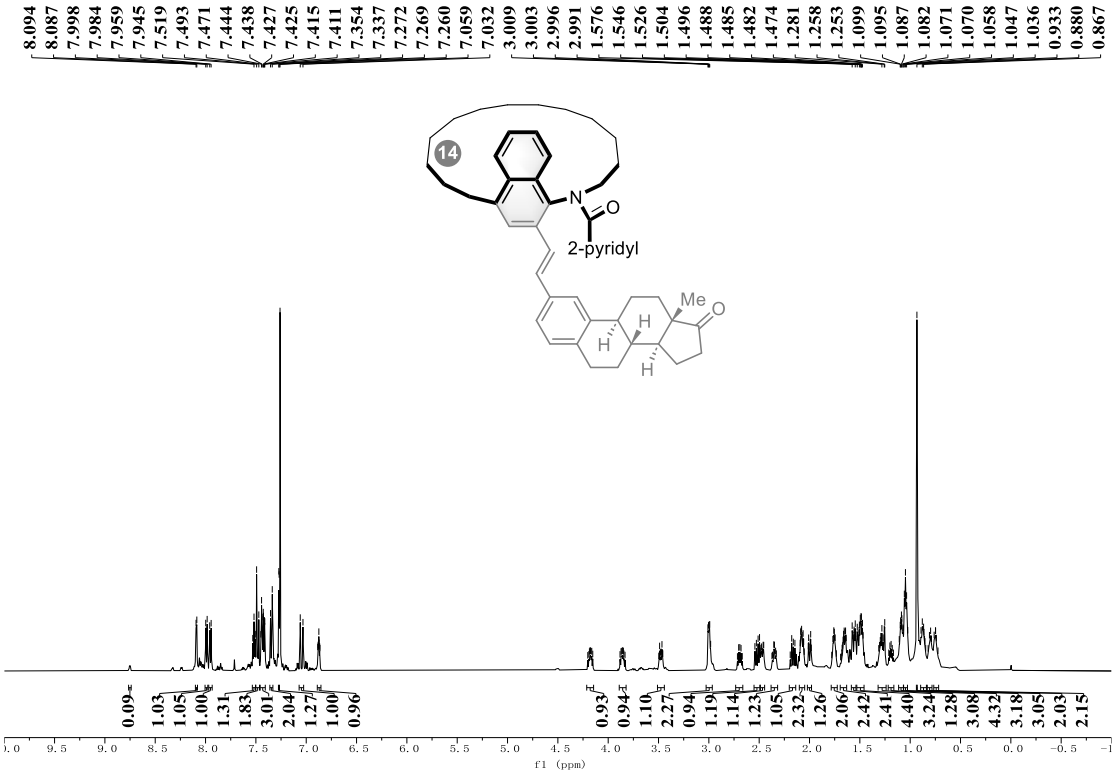
3as, ^{1}H NMR (600 MHz, $CDCl_3$)



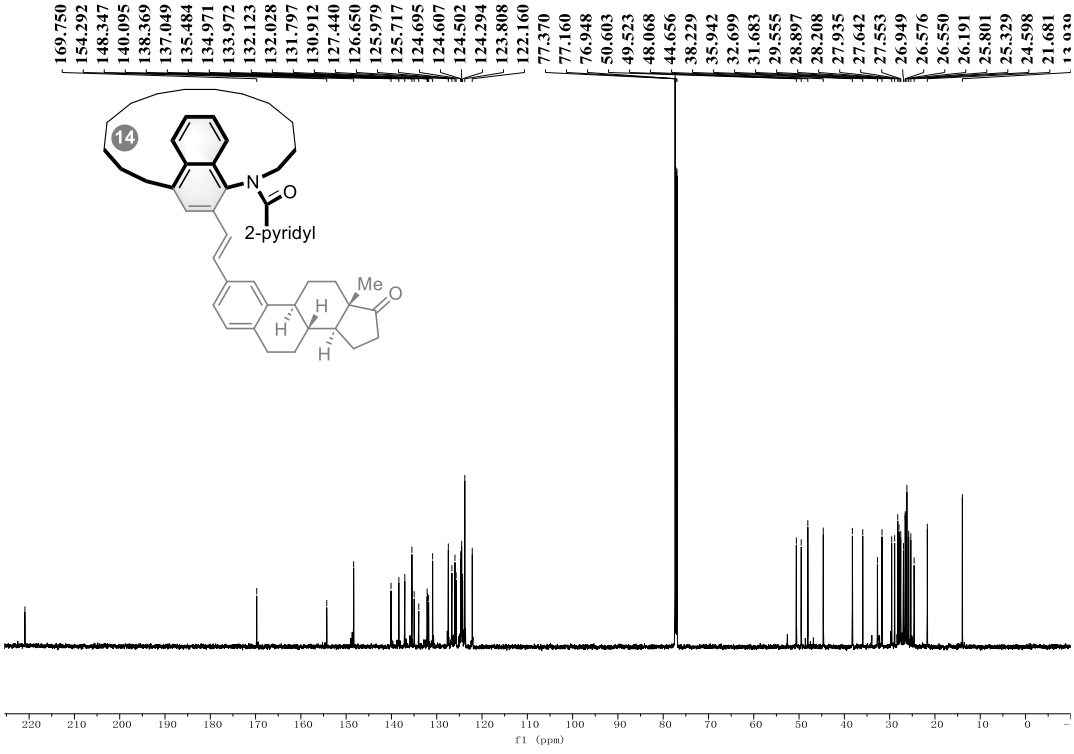
3as, ^{13}C NMR (151 MHz, $CDCl_3$)



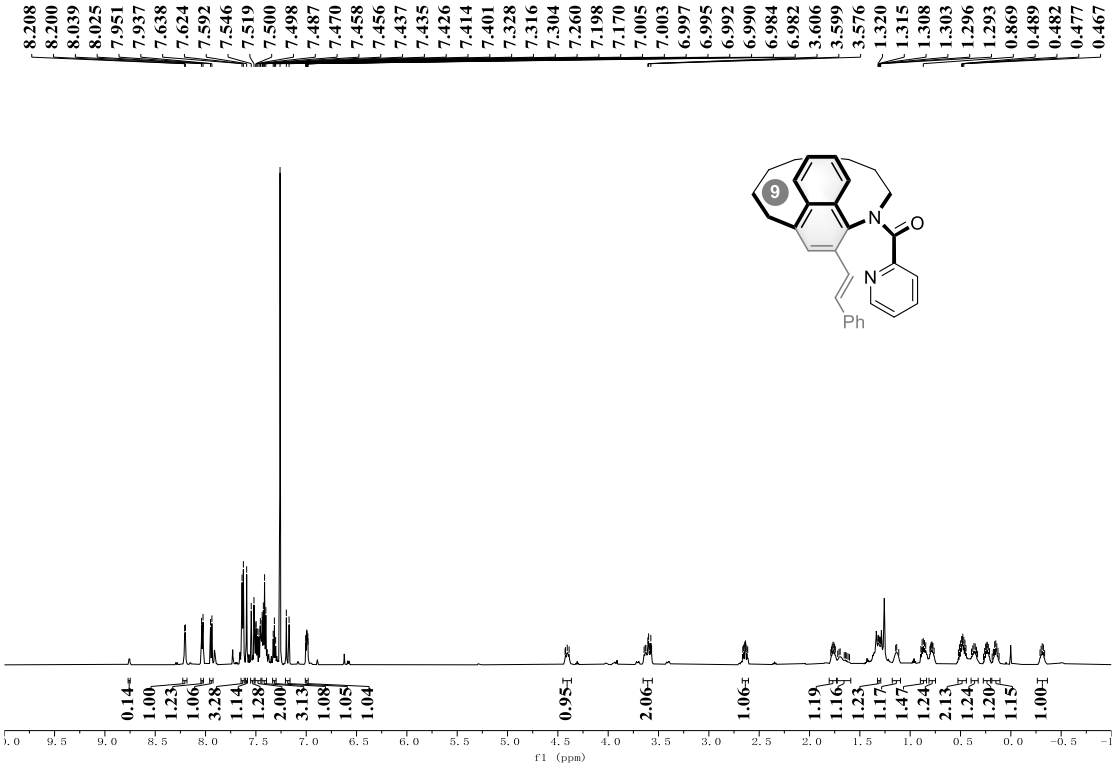
3at, ^{1}H NMR (600 MHz, $CDCl_3$)



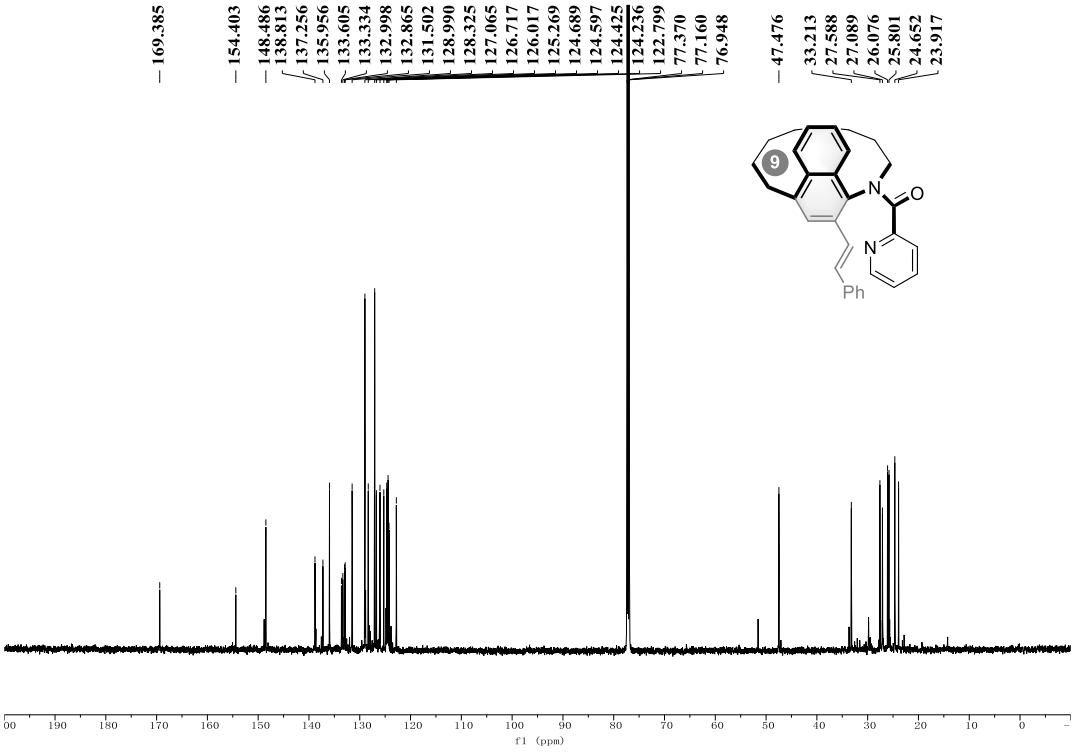
3at, ^{13}C NMR (151 MHz, $CDCl_3$)



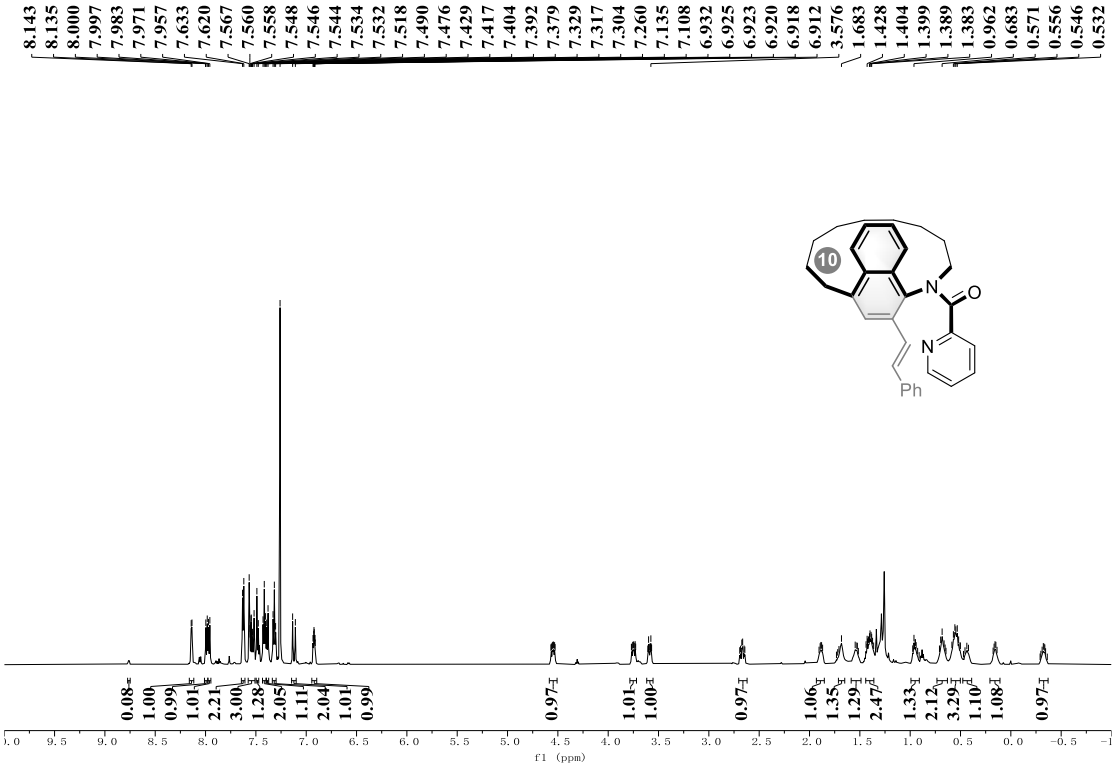
(R_p)-**3ba**, ^{1}H NMR (600 MHz, $CDCl_3$)



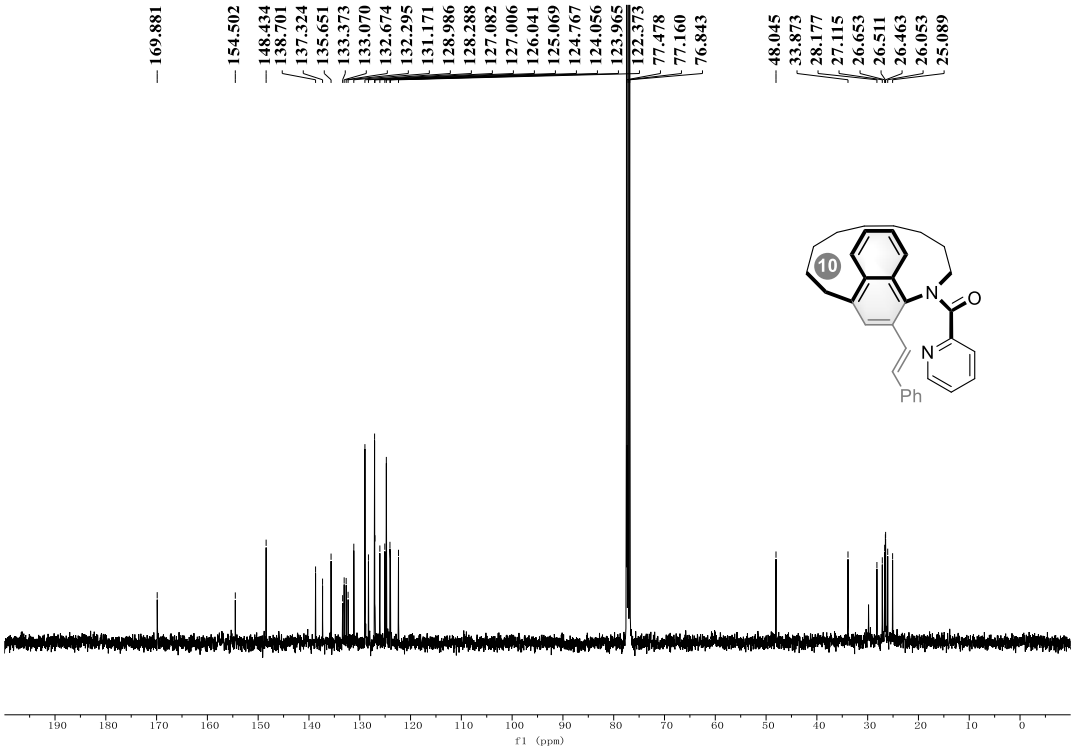
(R_p)-**3ba**, ^{13}C NMR (151 MHz, $CDCl_3$)



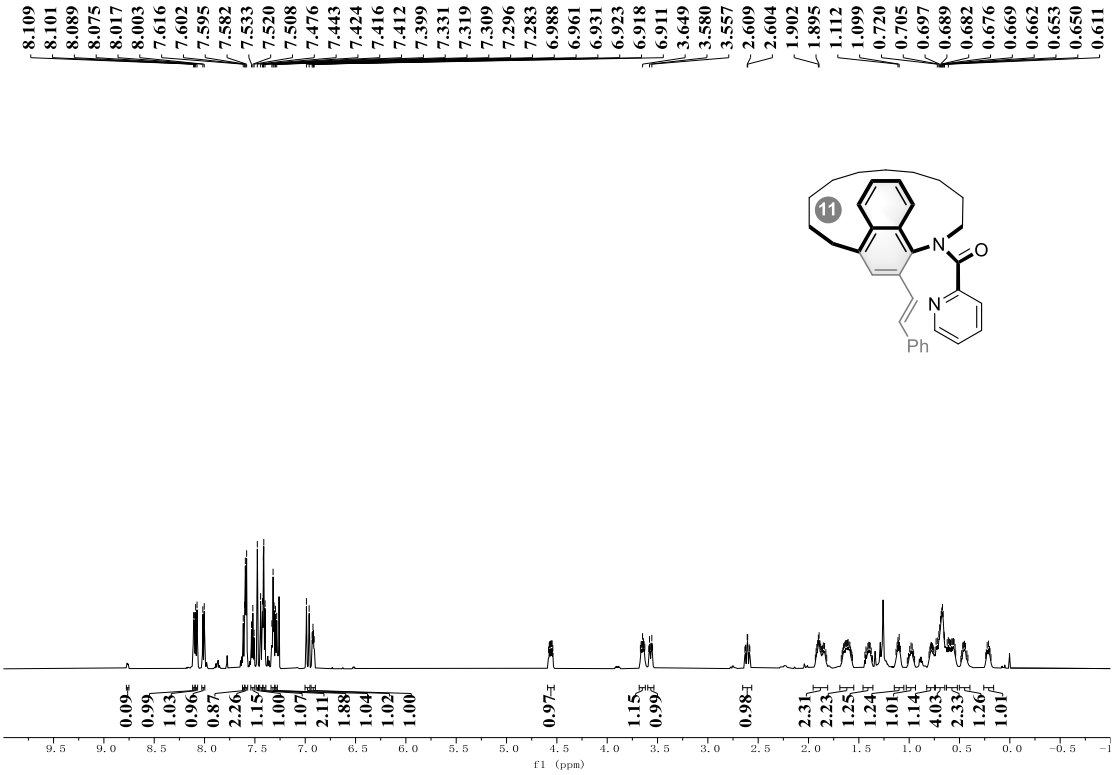
(R_p)-**3ca**, ^{1}H NMR (400 MHz, $CDCl_3$)



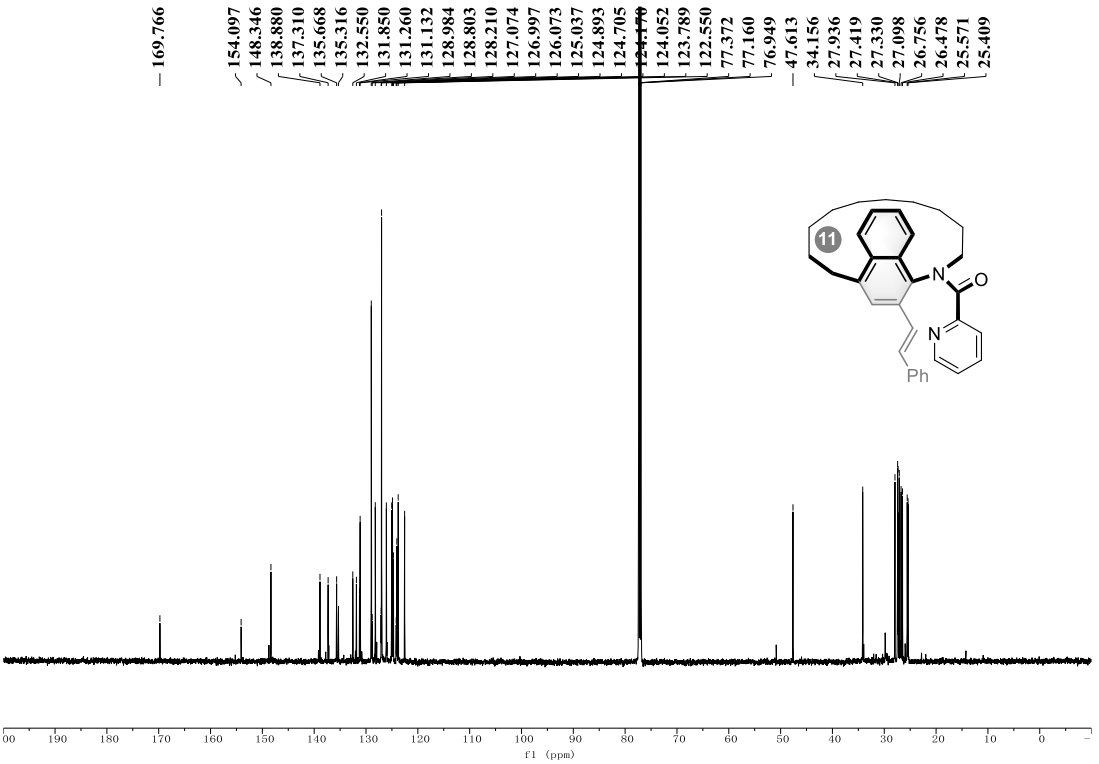
(R_p)-**3ca**, ^{13}C NMR (101 MHz, $CDCl_3$)



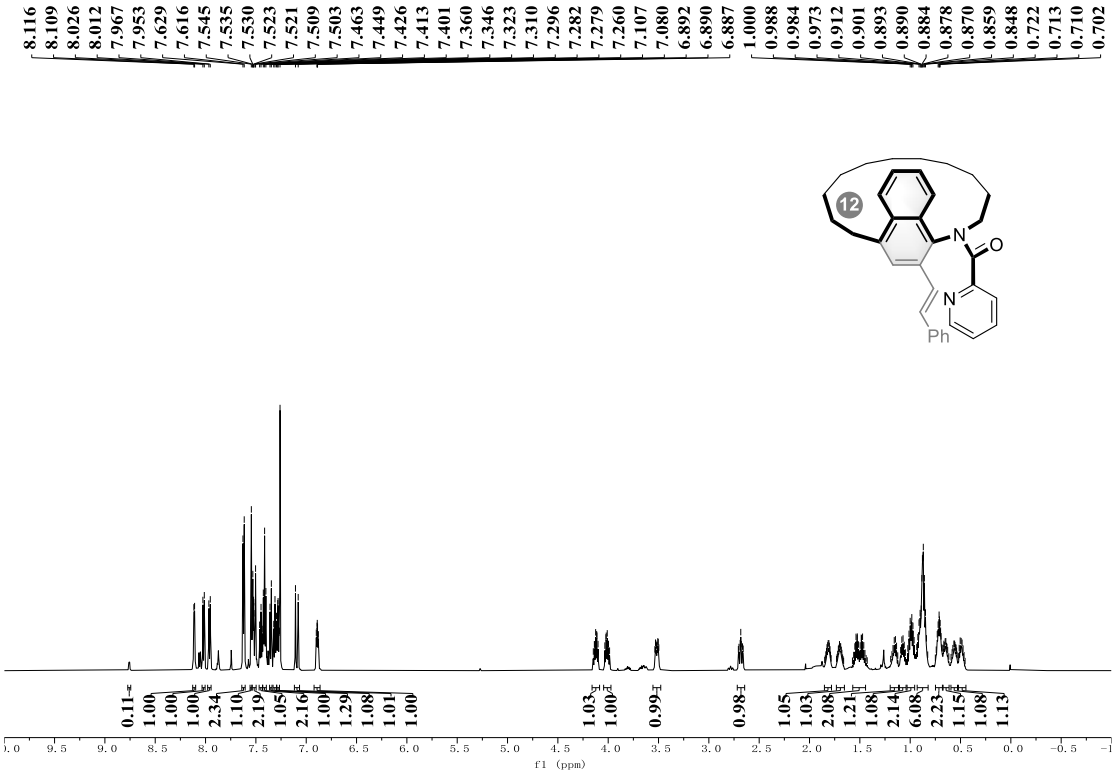
(R_p)-**3da**, ^{1}H NMR (600 MHz, $CDCl_3$)



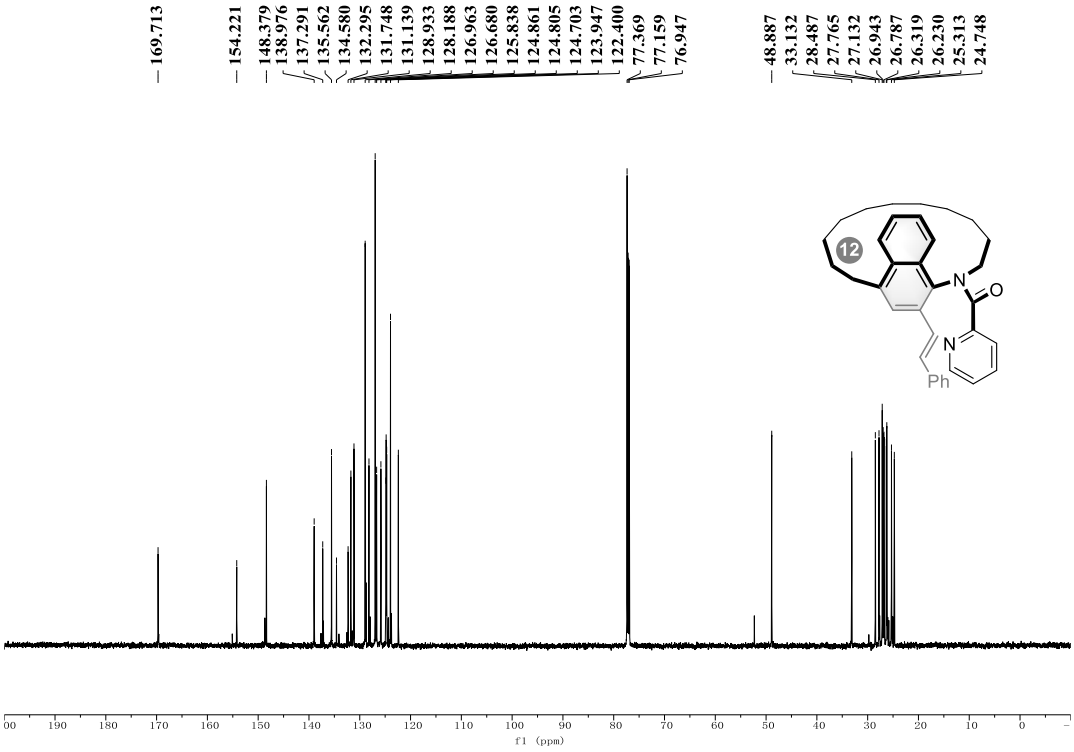
(R_p)-**3da**, ^{13}C NMR (151 MHz, $CDCl_3$)



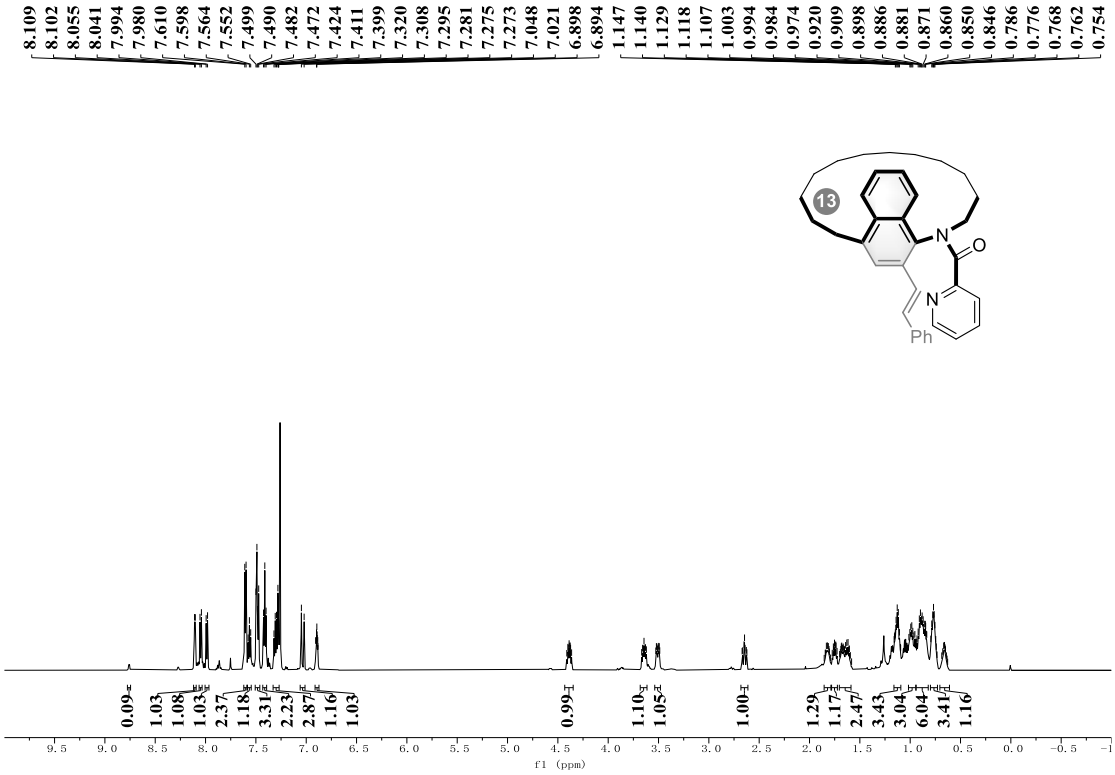
(R_p)-**3ea**, ^{1}H NMR (600 MHz, $CDCl_3$)



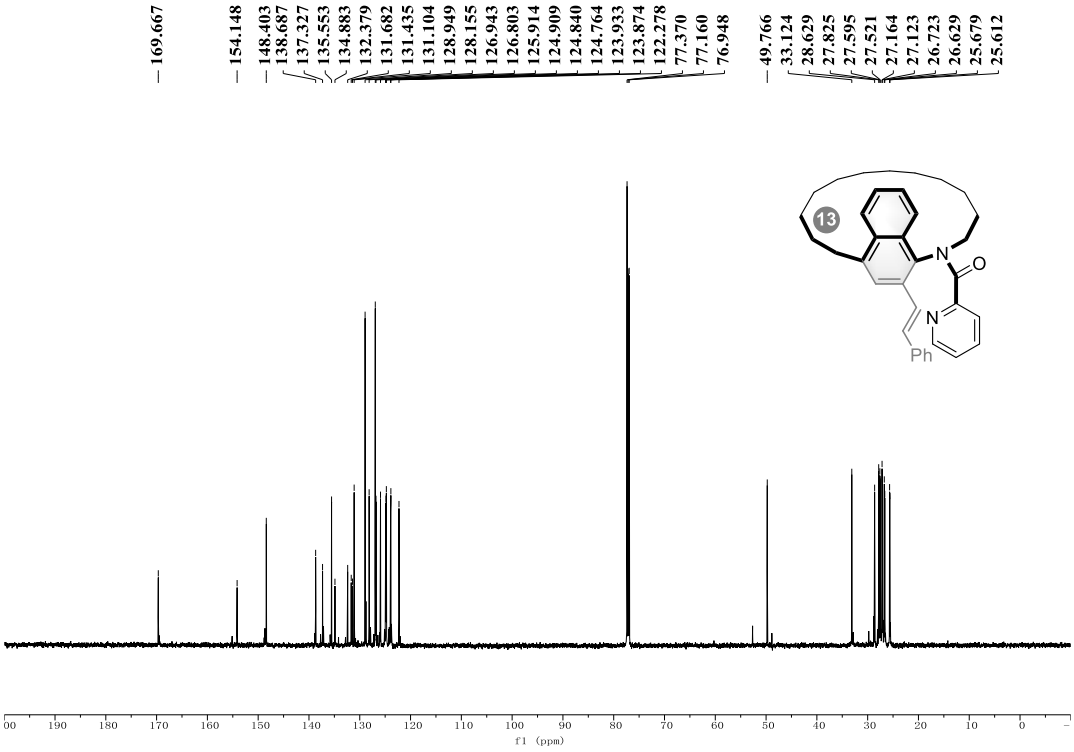
(R_p)-**3ea**, ^{13}C NMR (151 MHz, $CDCl_3$)



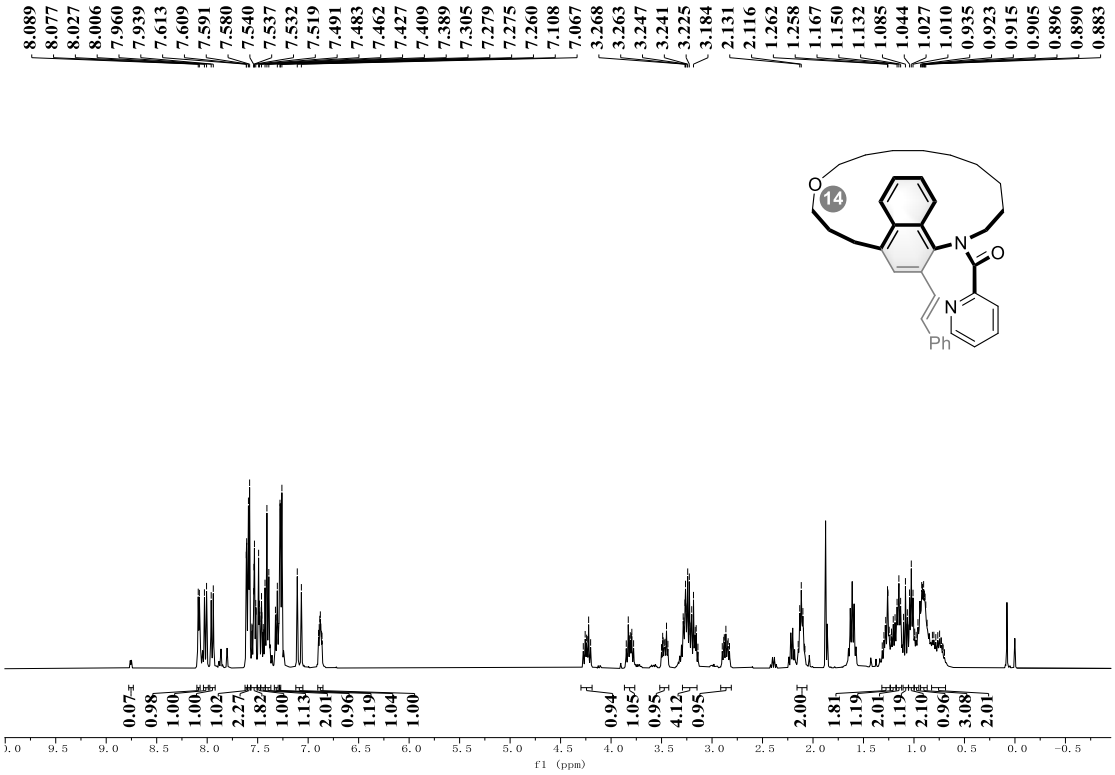
(R_p)-**3fa**, ^{1}H NMR (600 MHz, $CDCl_3$)



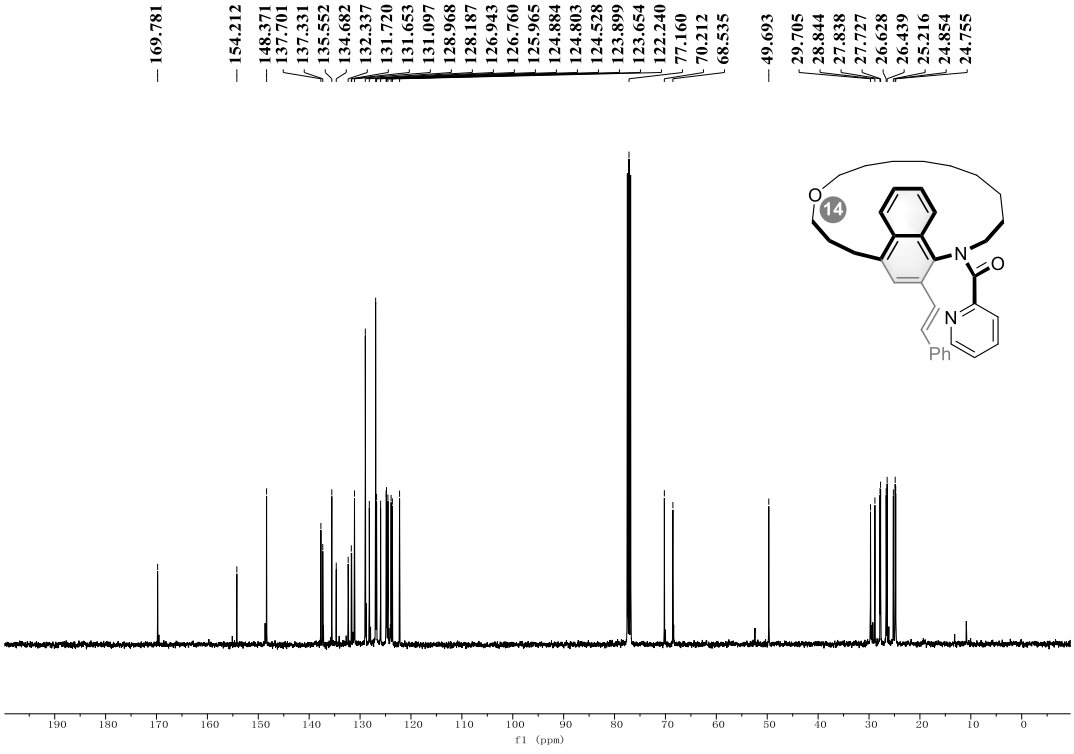
(R_p)-**3fa**, ^{13}C NMR (151 MHz, $CDCl_3$)



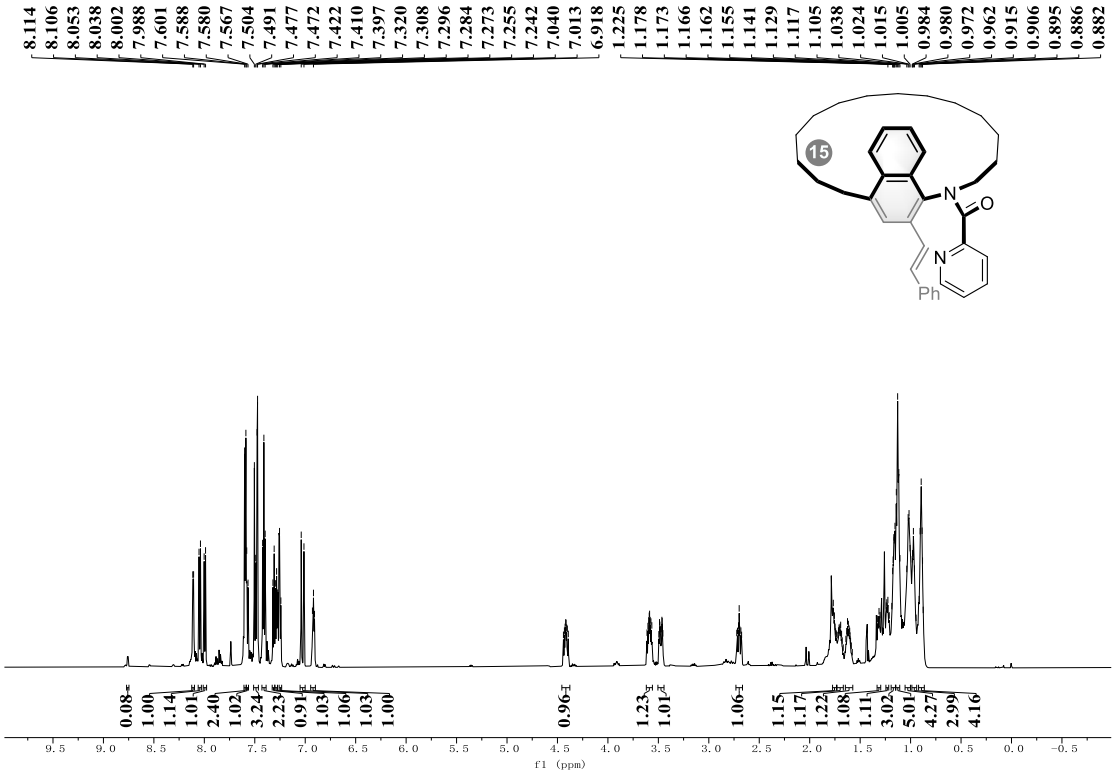
(R_p)-**3ga**, ^{1}H NMR (400 MHz, $CDCl_3$)



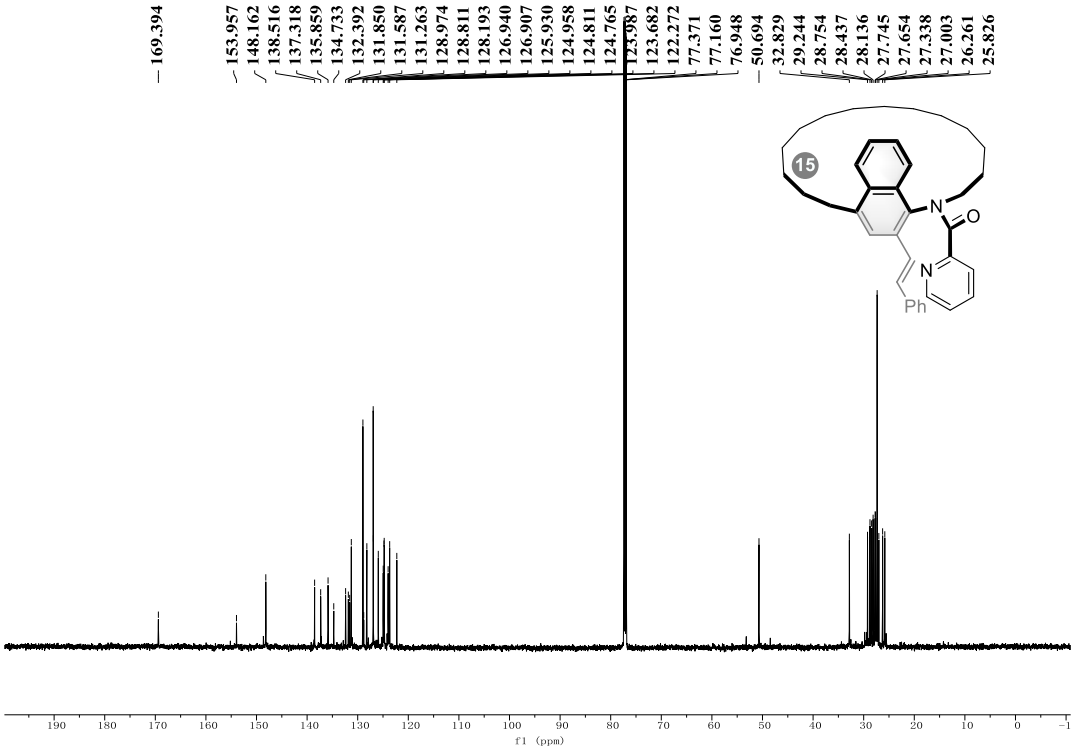
(R_p)-**3ga**, ^{13}C NMR (101 MHz, $CDCl_3$)



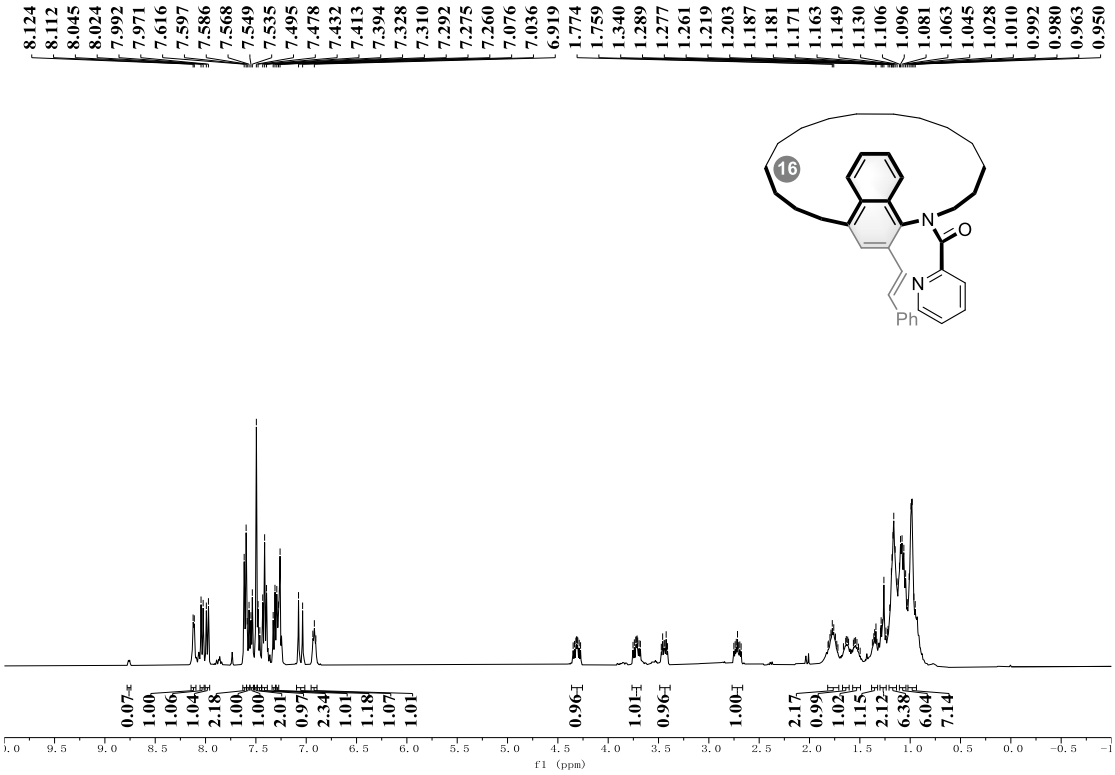
(R_p)-**3ha**, ^{1}H NMR (600 MHz, $CDCl_3$)



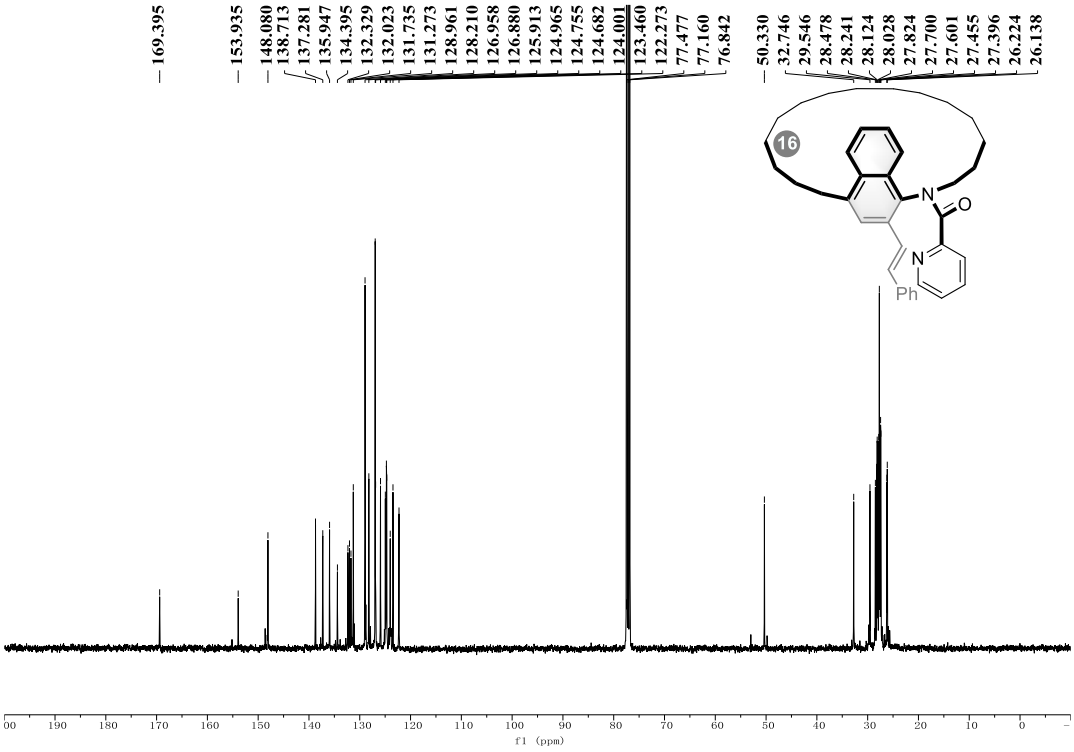
(R_p)-**3ha**, ^{13}C NMR (151 MHz, $CDCl_3$)



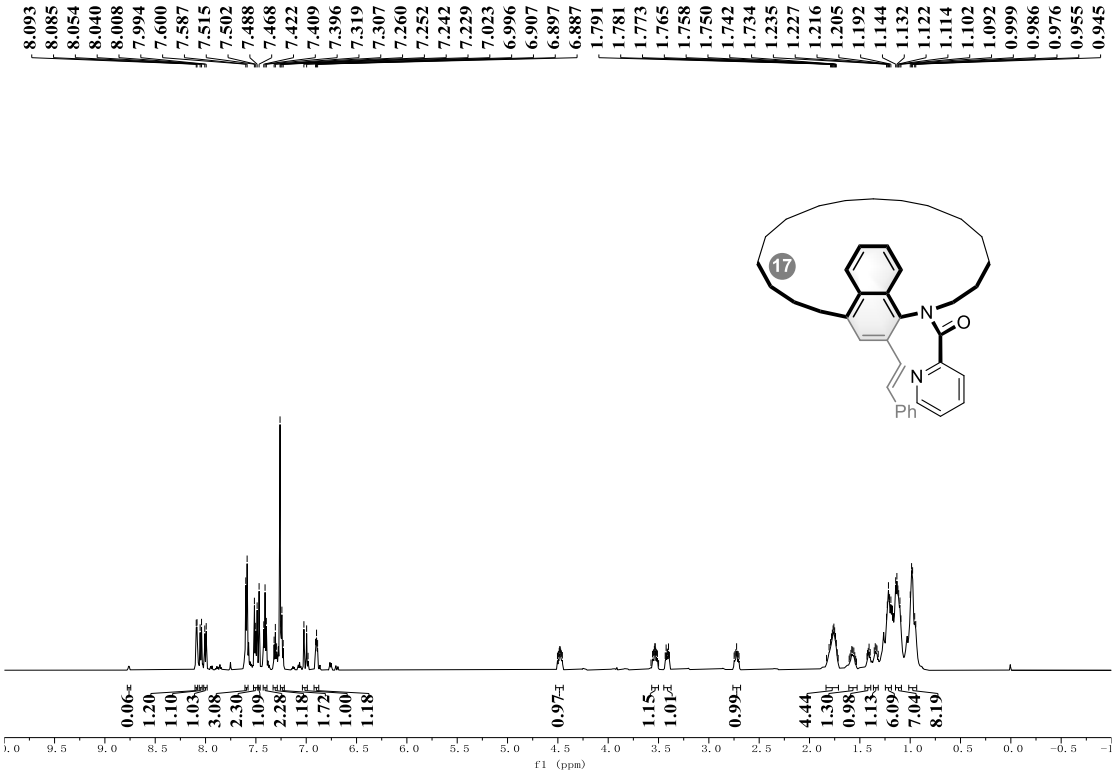
(R_p)-**3ia**, ^{1}H NMR (400 MHz, $CDCl_3$)



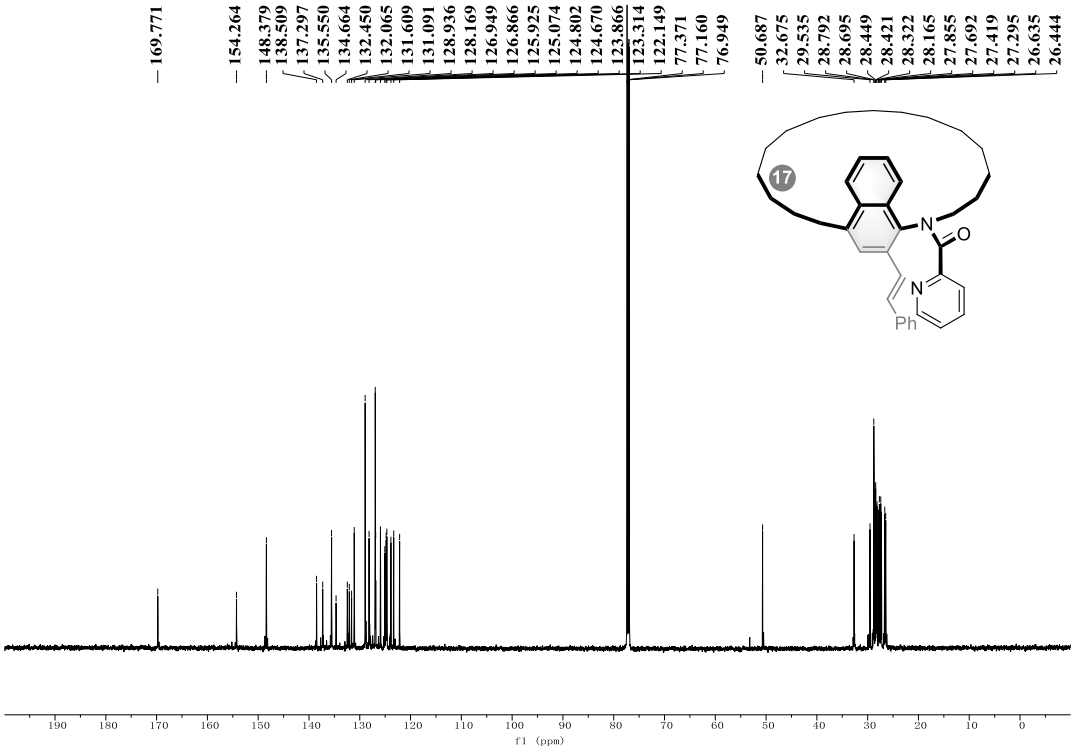
(R_p)-**3ia**, ^{13}C NMR (101 MHz, $CDCl_3$)



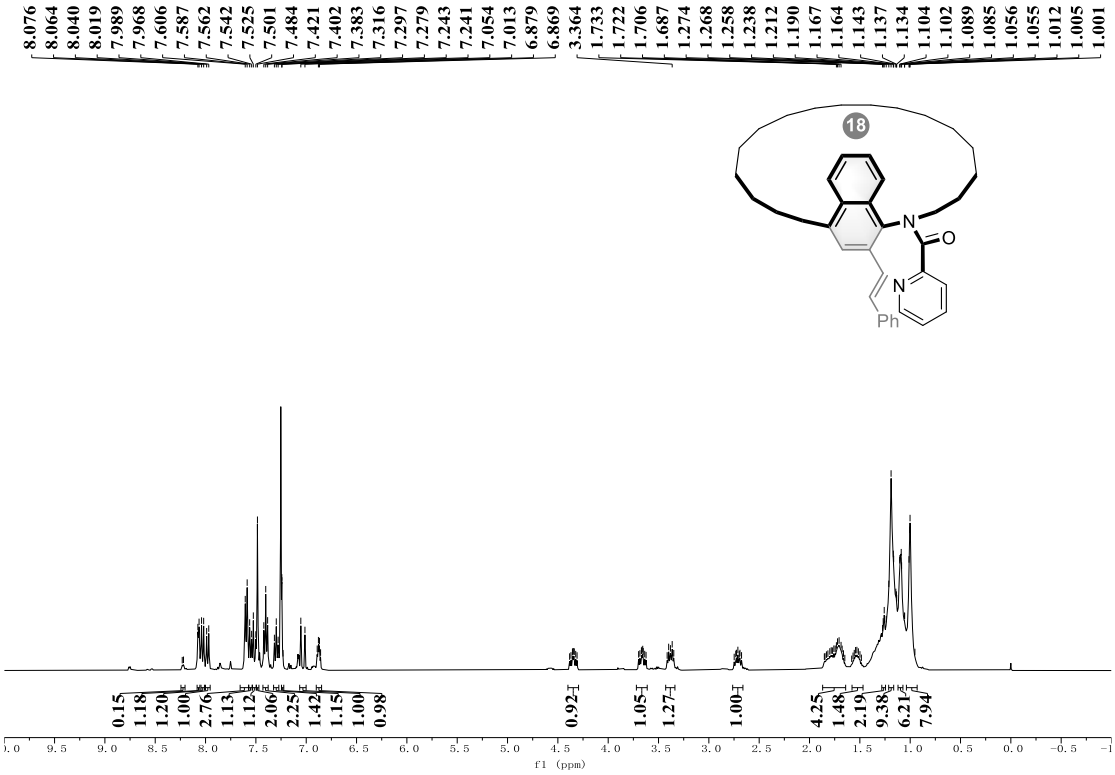
(R_p)-**3ja**, ^{1}H NMR (600 MHz, $CDCl_3$)



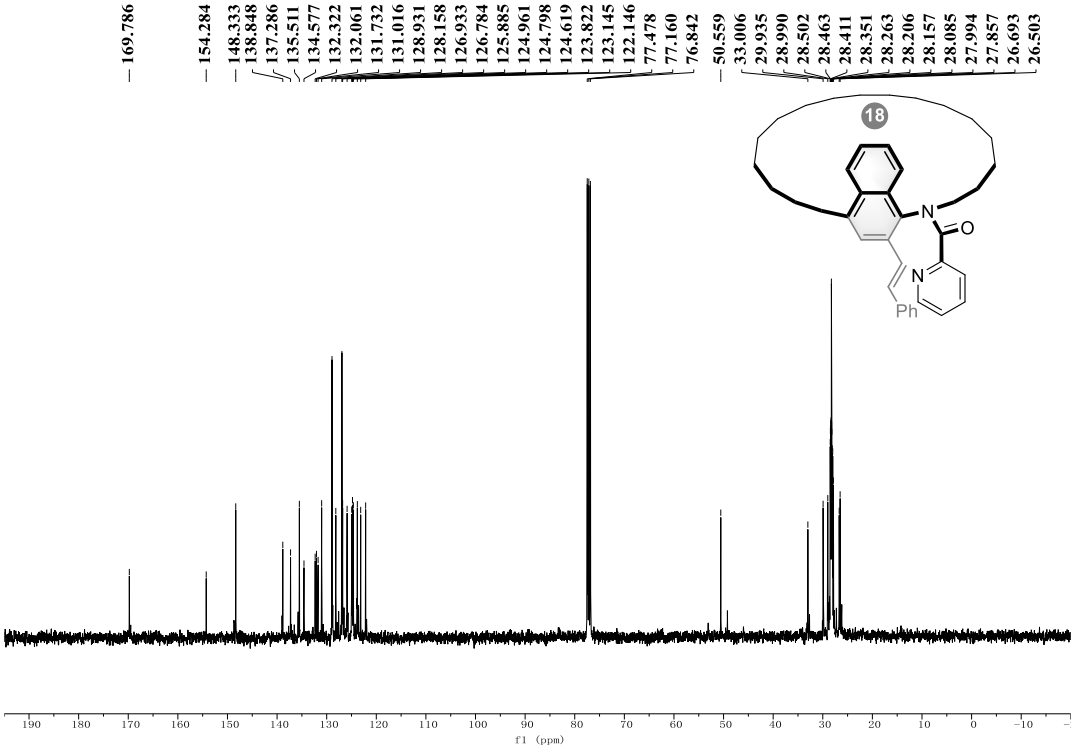
(R_p)-**3ja**, ^{13}C NMR (151 MHz, $CDCl_3$)



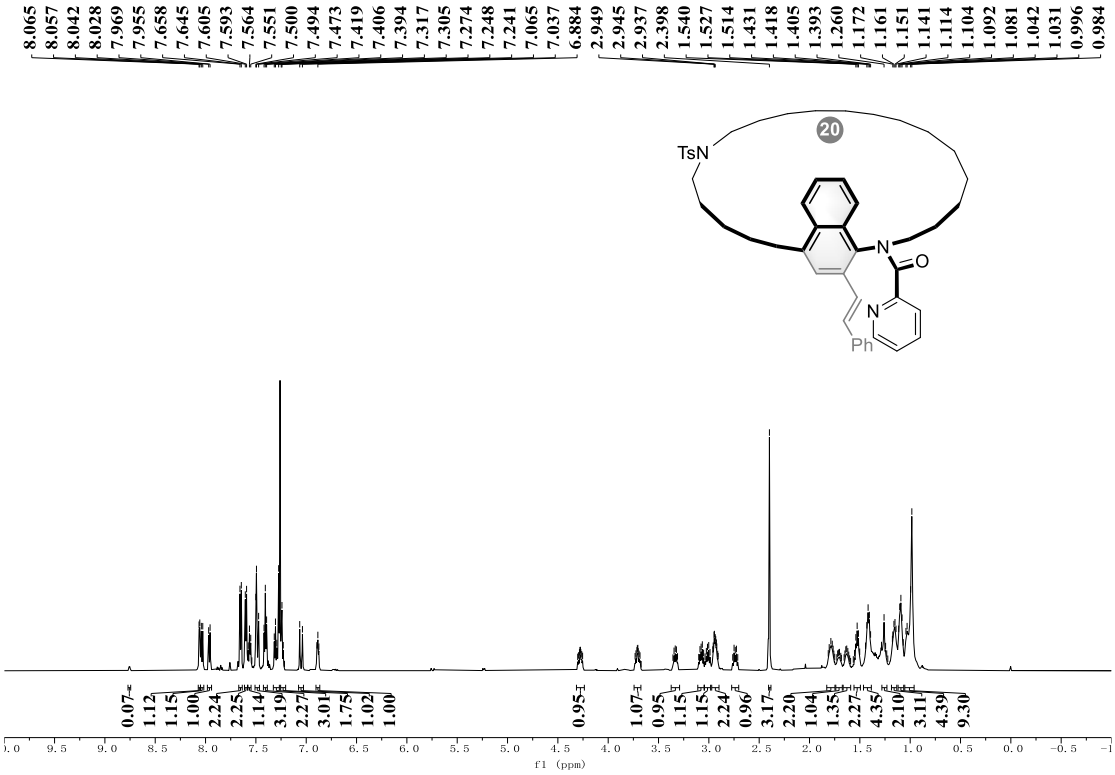
(R_p)-**3ka**, ^{1}H NMR (400 MHz, $CDCl_3$)



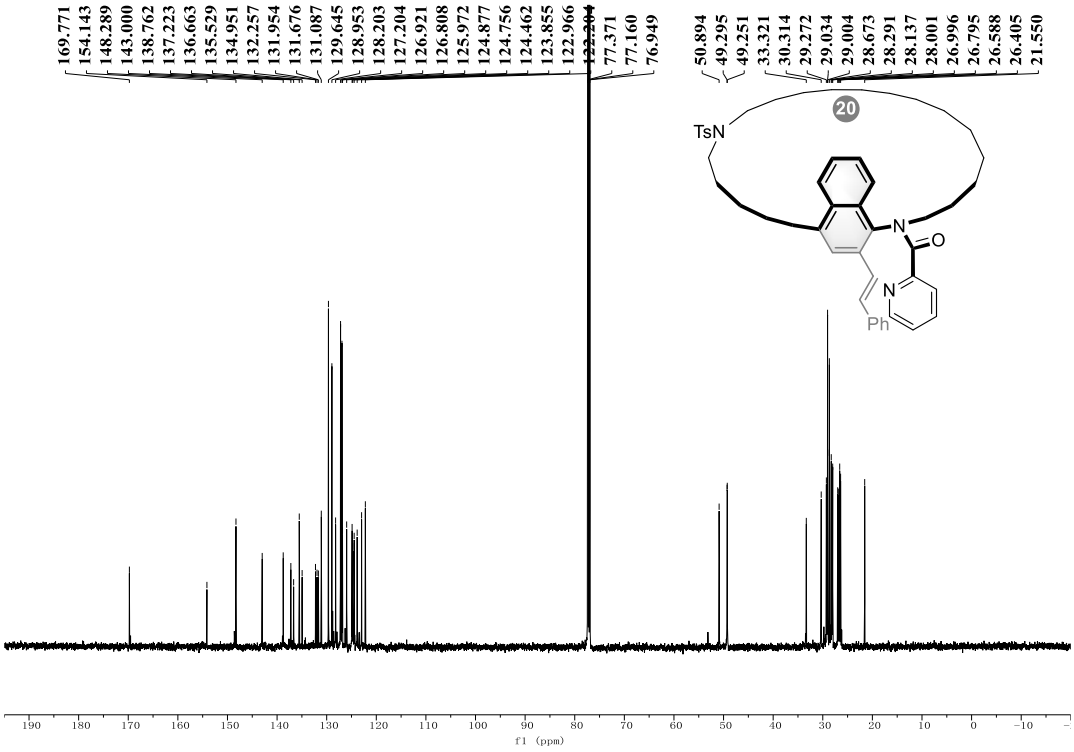
(R_p)-**3ka**, ^{13}C NMR (101 MHz, $CDCl_3$)



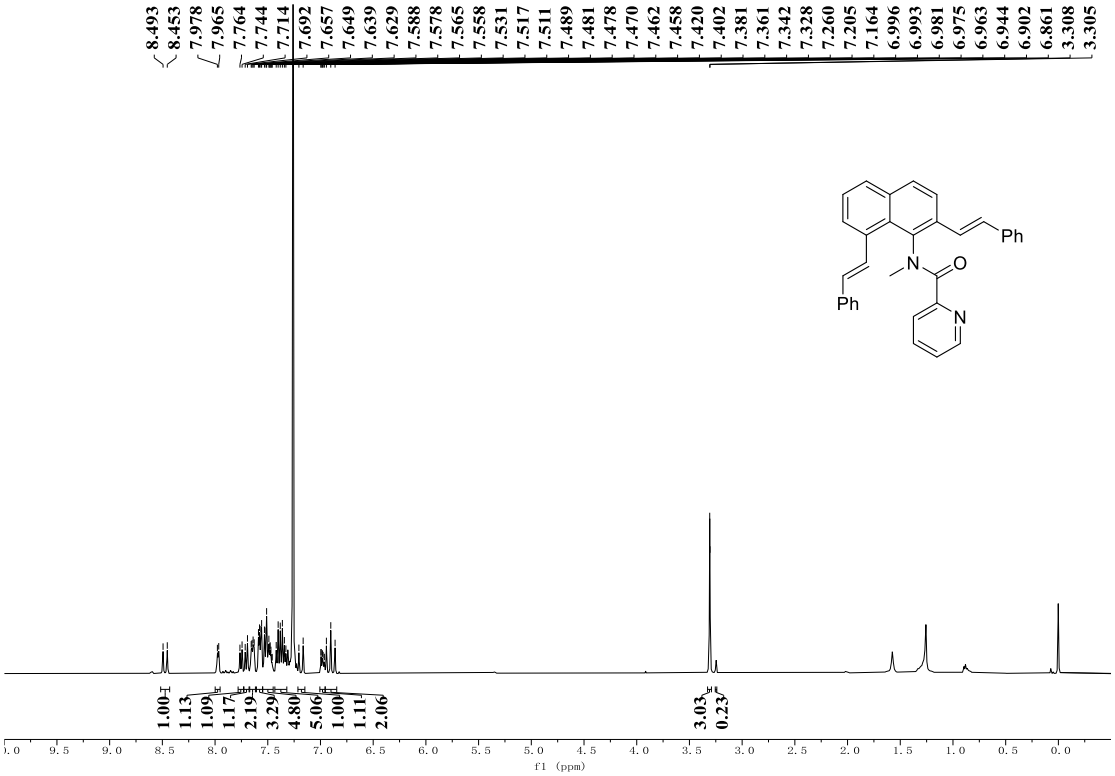
(R_p)-**3la**, ^{1}H NMR (600 MHz, $CDCl_3$)



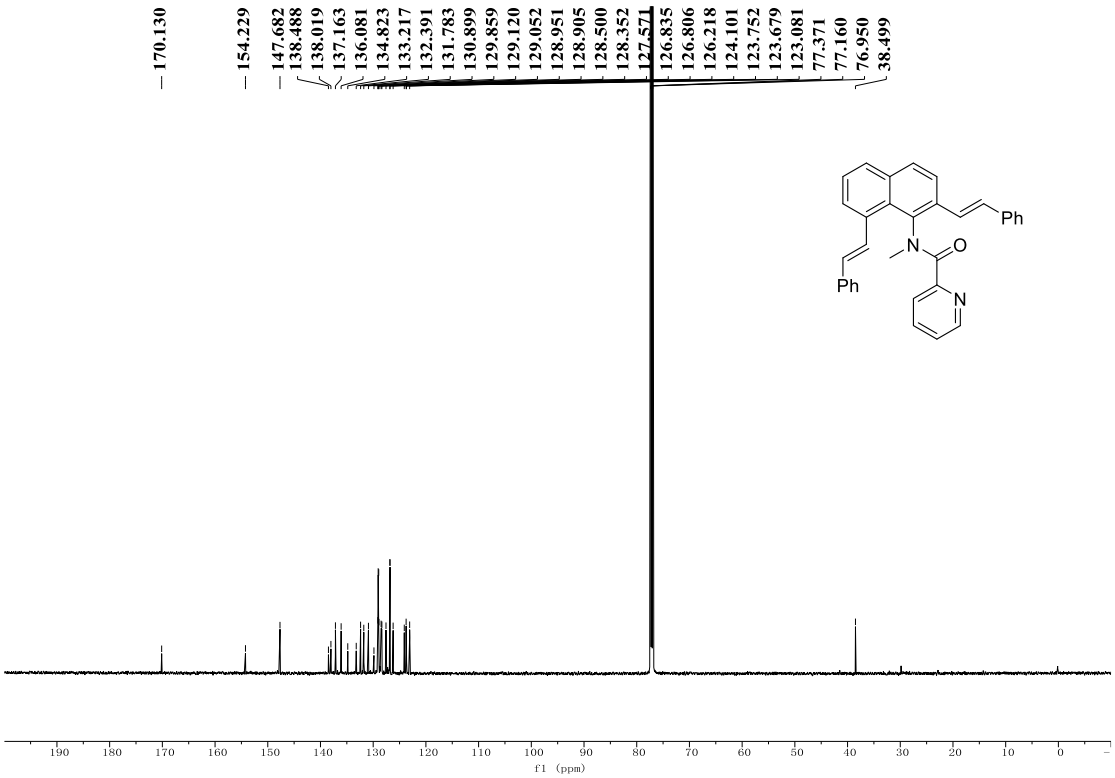
(R_p)-**3la**, ^{13}C NMR (151 MHz, $CDCl_3$)



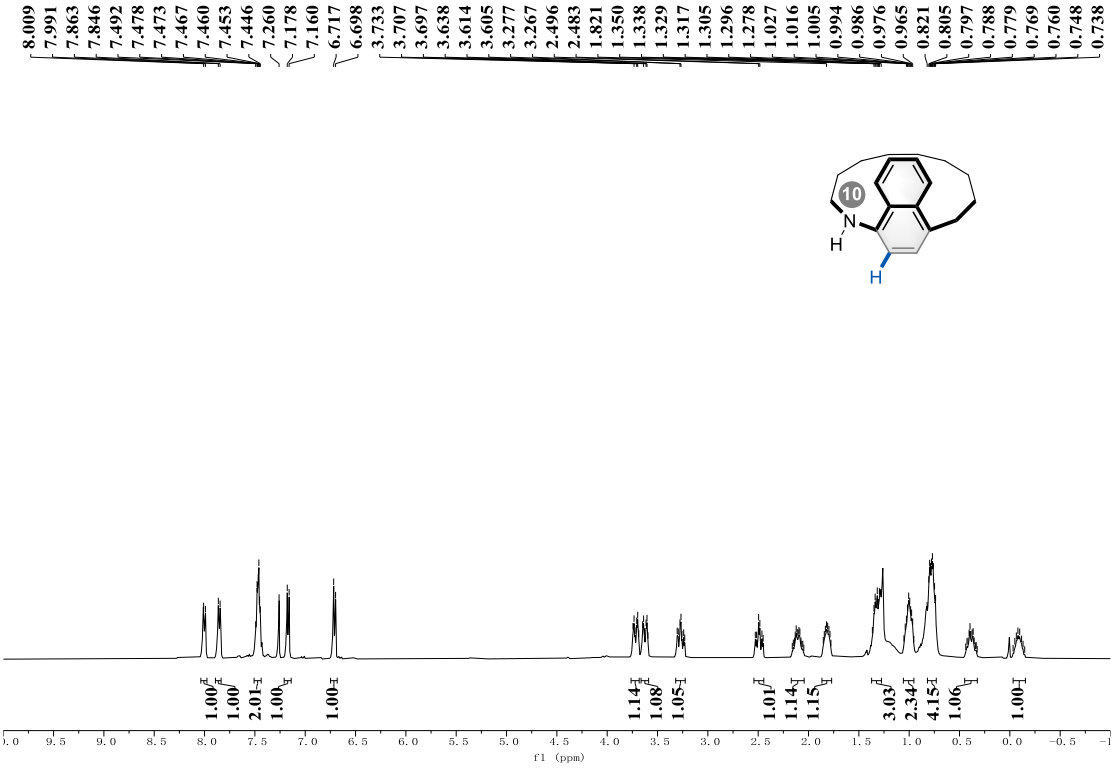
5, ^{1}H NMR (400 MHz, $CDCl_3$)



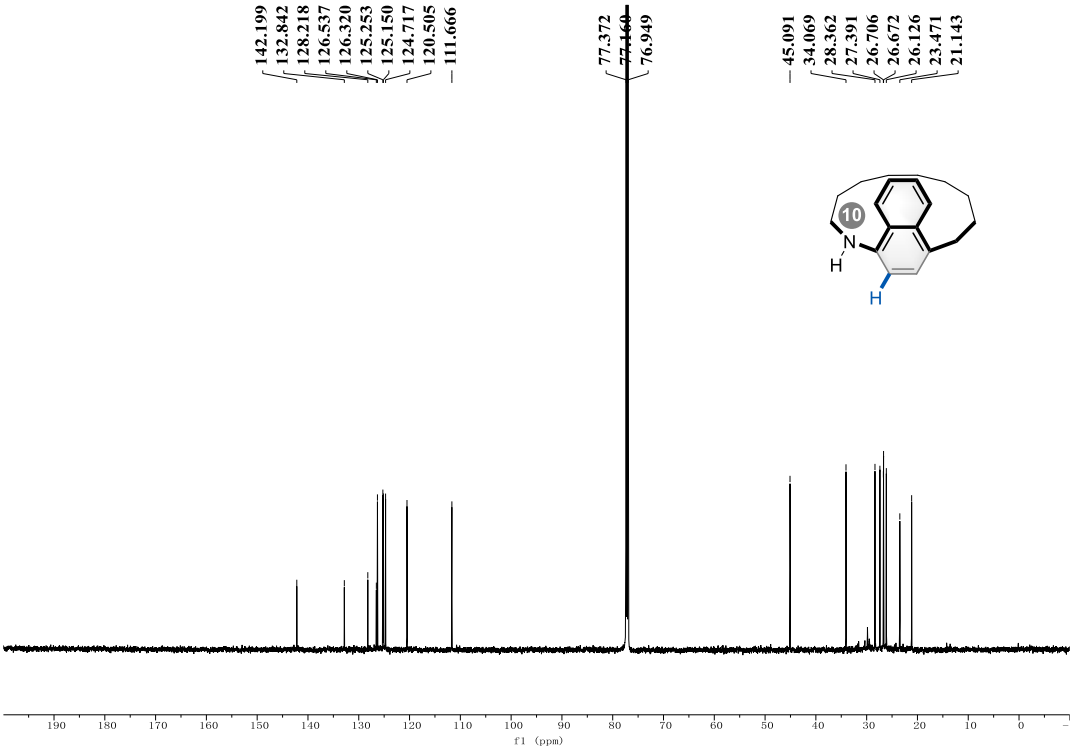
5, ^{13}C NMR (151 MHz, $CDCl_3$)



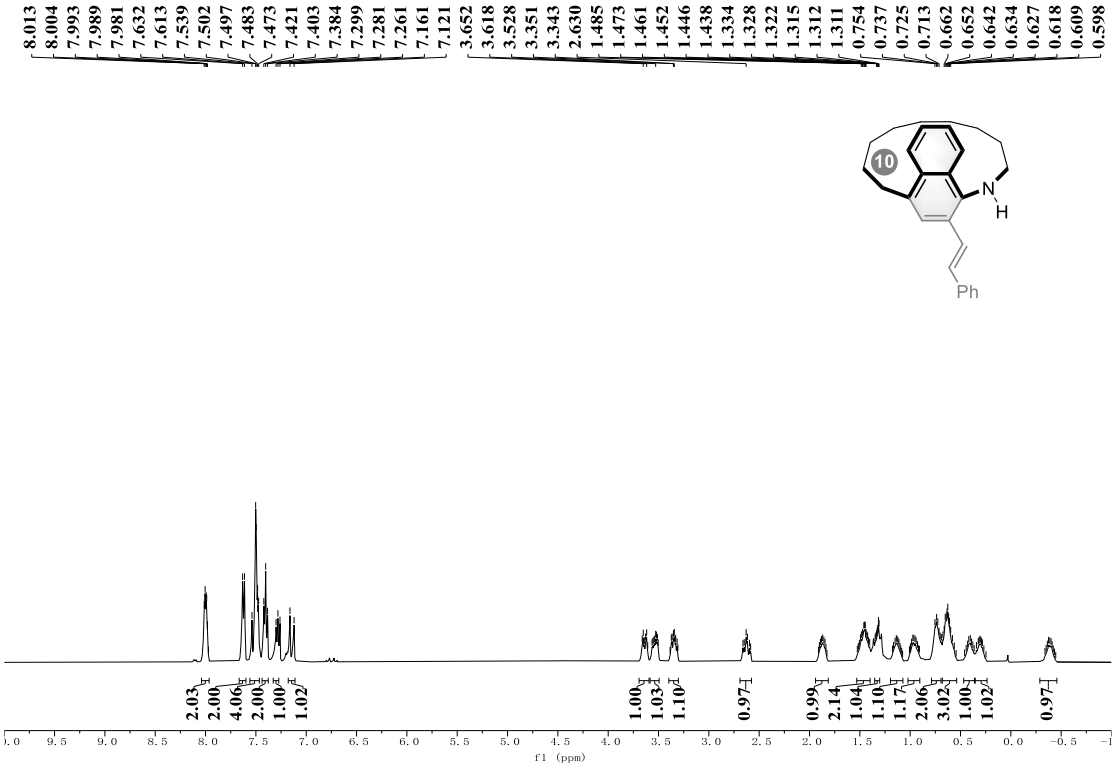
(R_p)-**6**, ^{1}H NMR (400 MHz, $CDCl_3$)



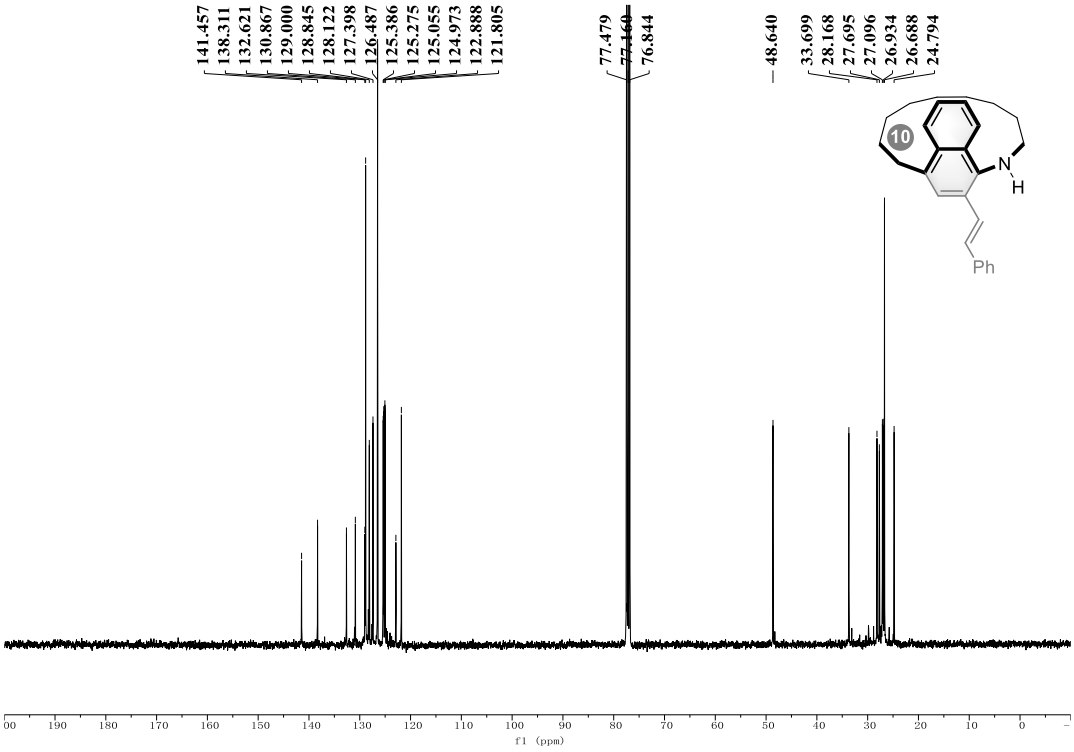
(R_p)-**6**, ^{13}C NMR (151 MHz, $CDCl_3$)



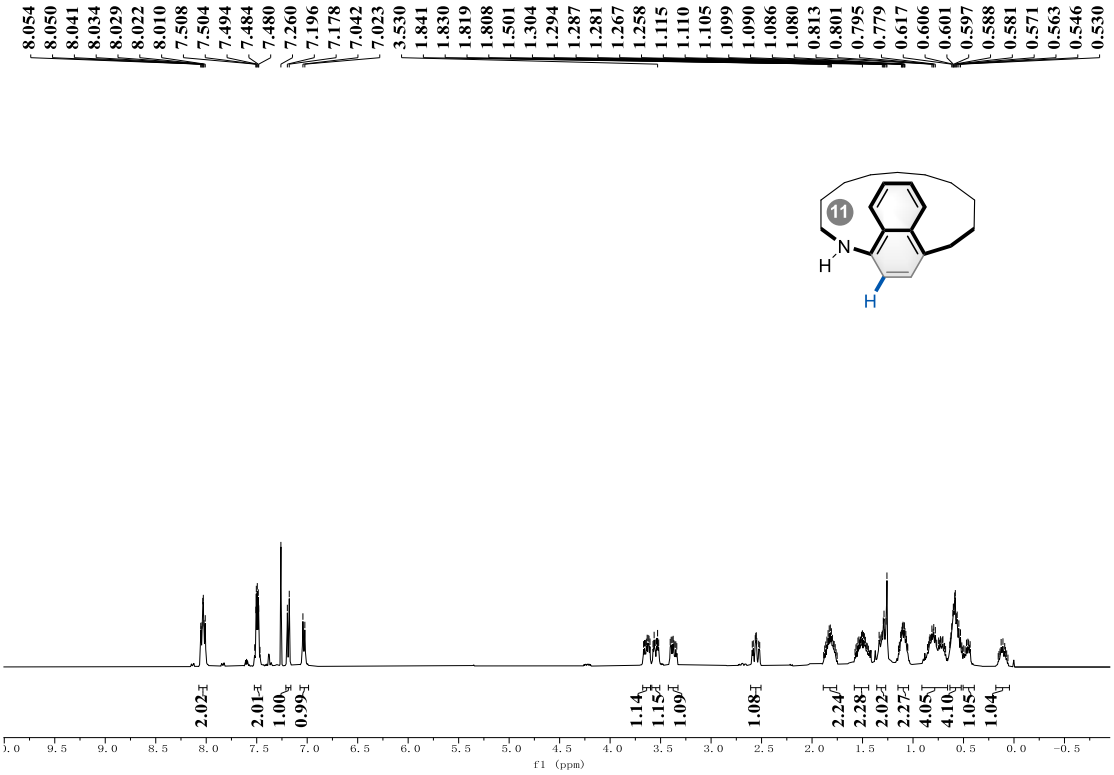
(R_p)-**7**, ^{1}H NMR (400 MHz, $CDCl_3$)



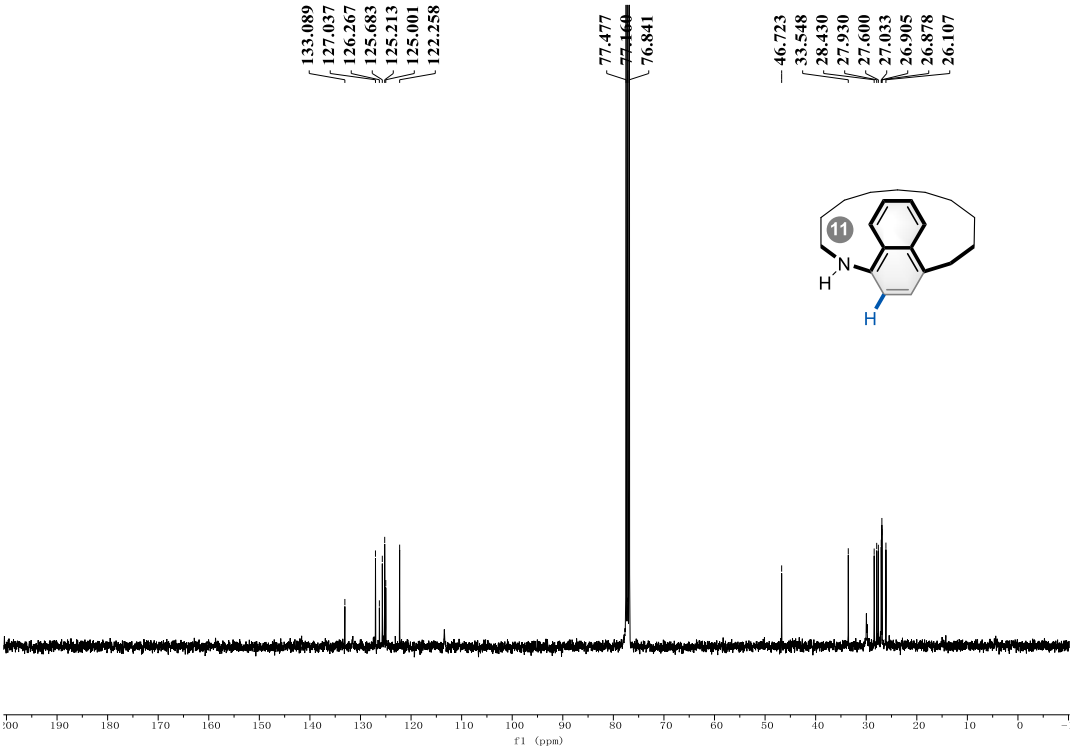
(R_p)-**7**, ^{13}C NMR (101 MHz, $CDCl_3$)



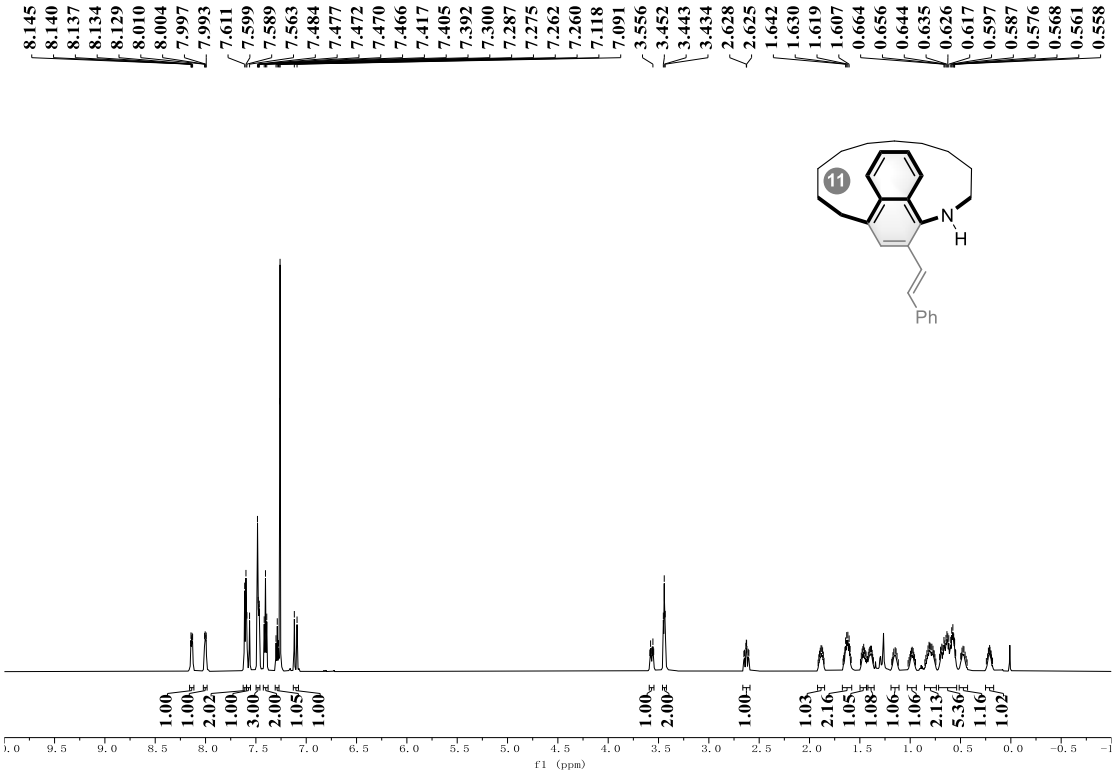
(R_p)-**8**, ^{1}H NMR (400 MHz, $CDCl_3$)



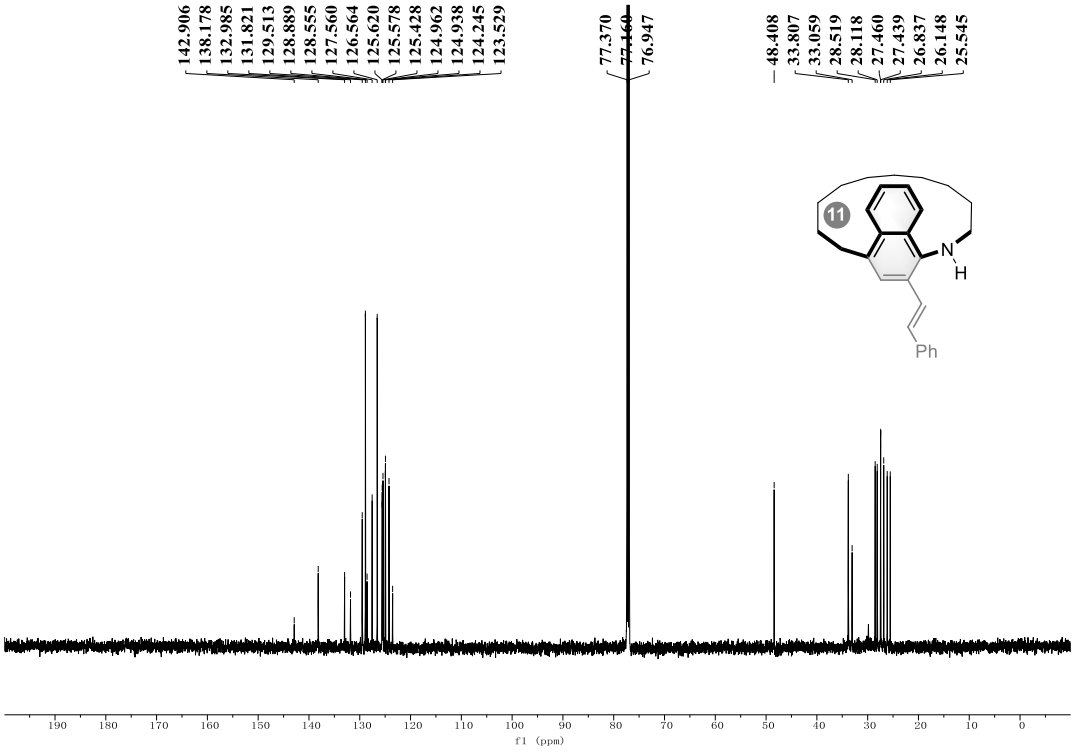
(R_p)-**8**, ^{13}C NMR (101 MHz, $CDCl_3$)



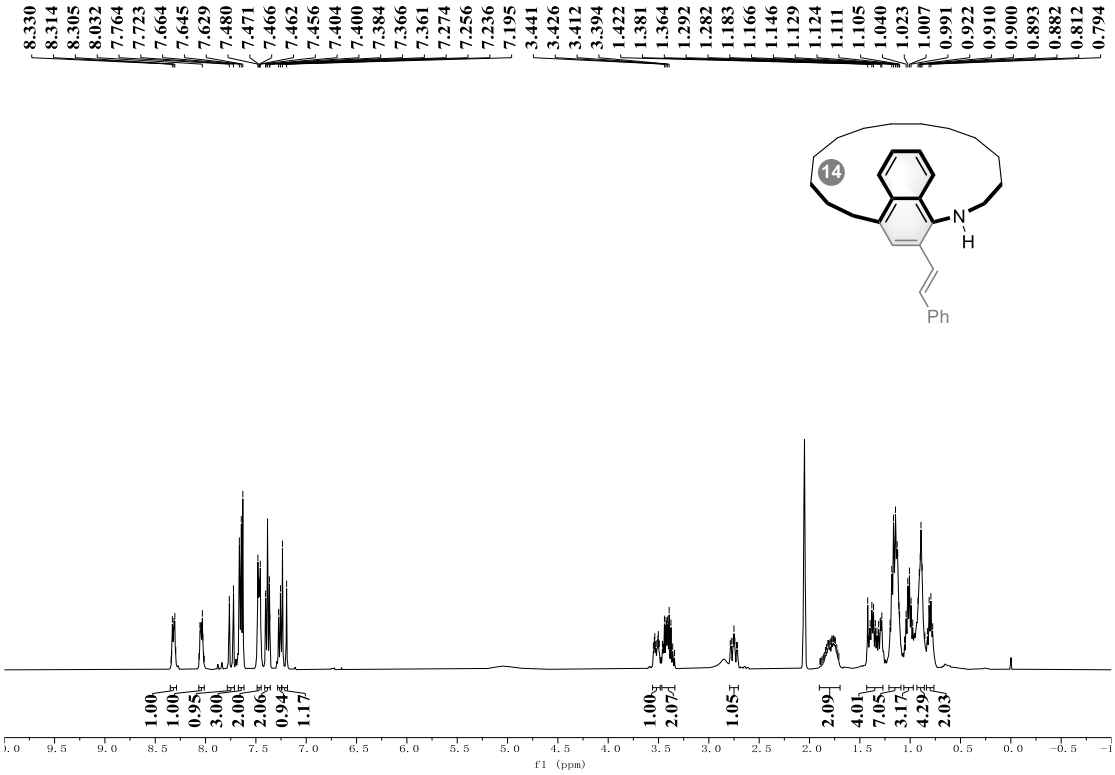
(R_p)-**9**, ^{1}H NMR (600 MHz, $CDCl_3$)



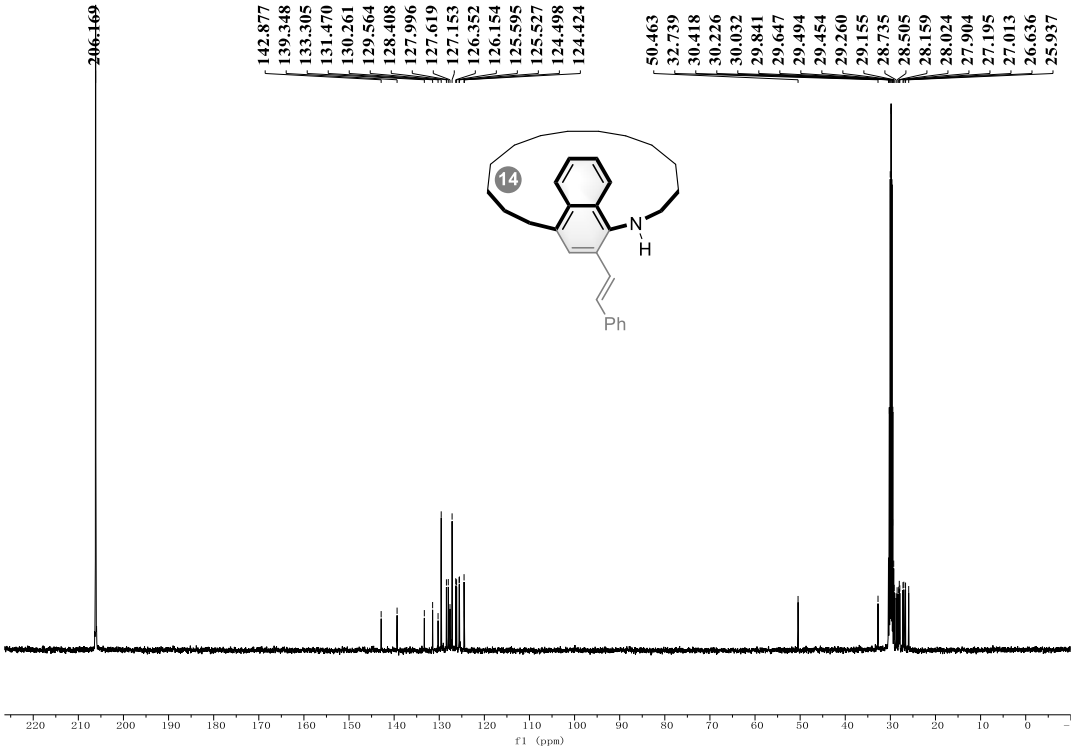
(R_p)-**9**, ^{13}C NMR (151 MHz, $CDCl_3$)



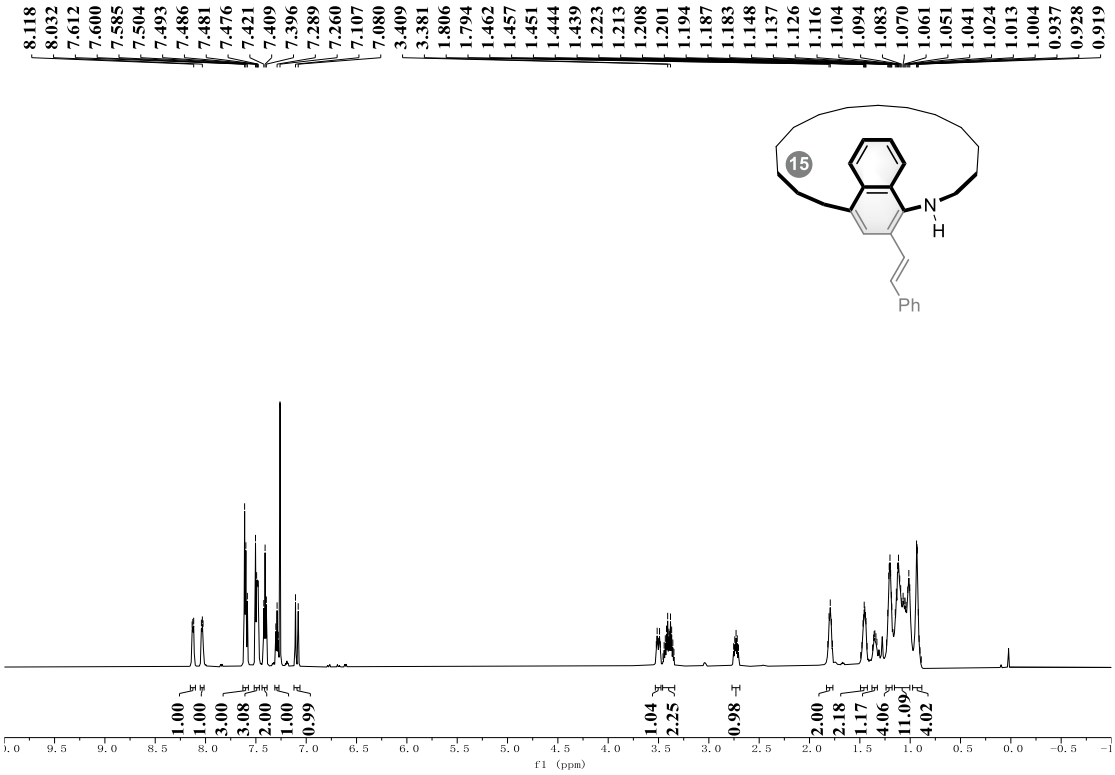
(R_p)-**10**, ^{1}H NMR (400 MHz, Acetone-d_6)



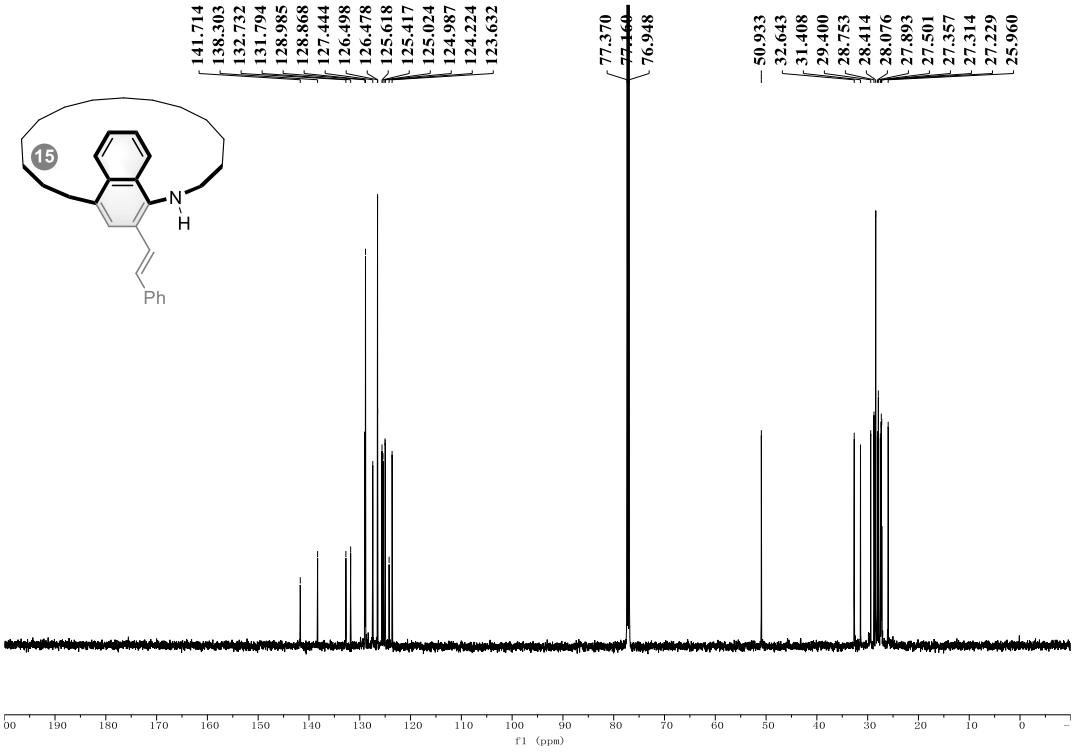
(R_p)-**10**, ^{13}C NMR (101 MHz, Acetone-d_6)



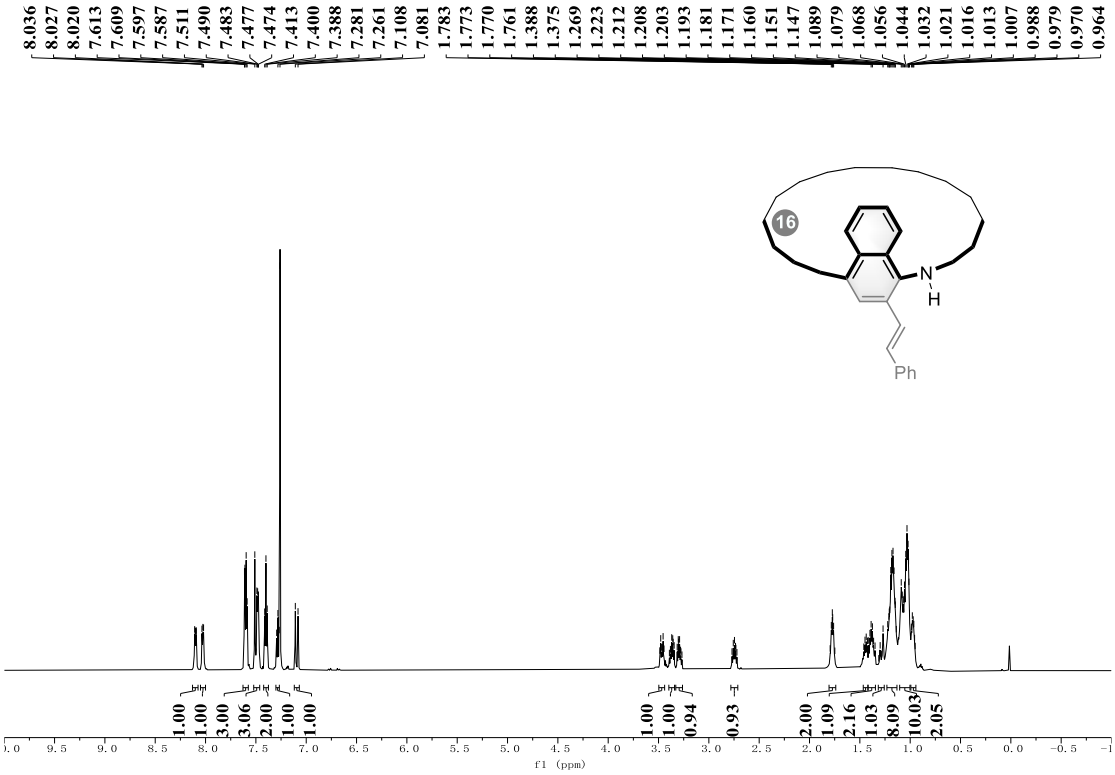
(R_p)-**11**, ^{1}H NMR (600 MHz, $CDCl_3$)



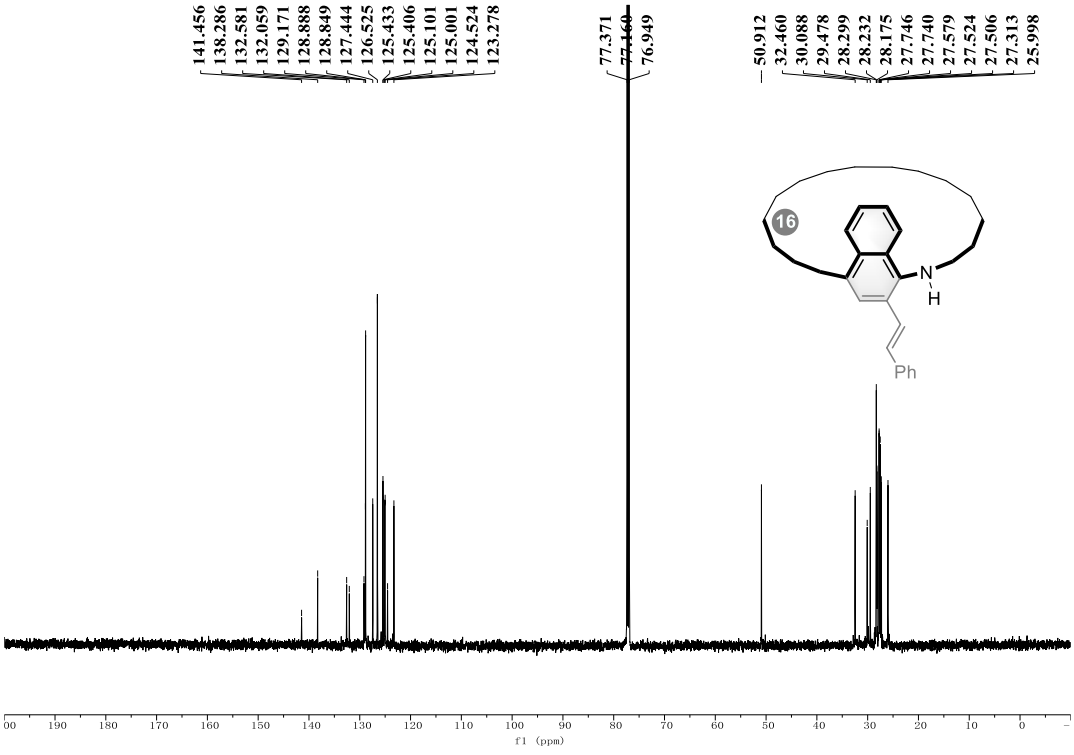
(R_p)-**11**, ^{13}C NMR (151 MHz, $CDCl_3$)



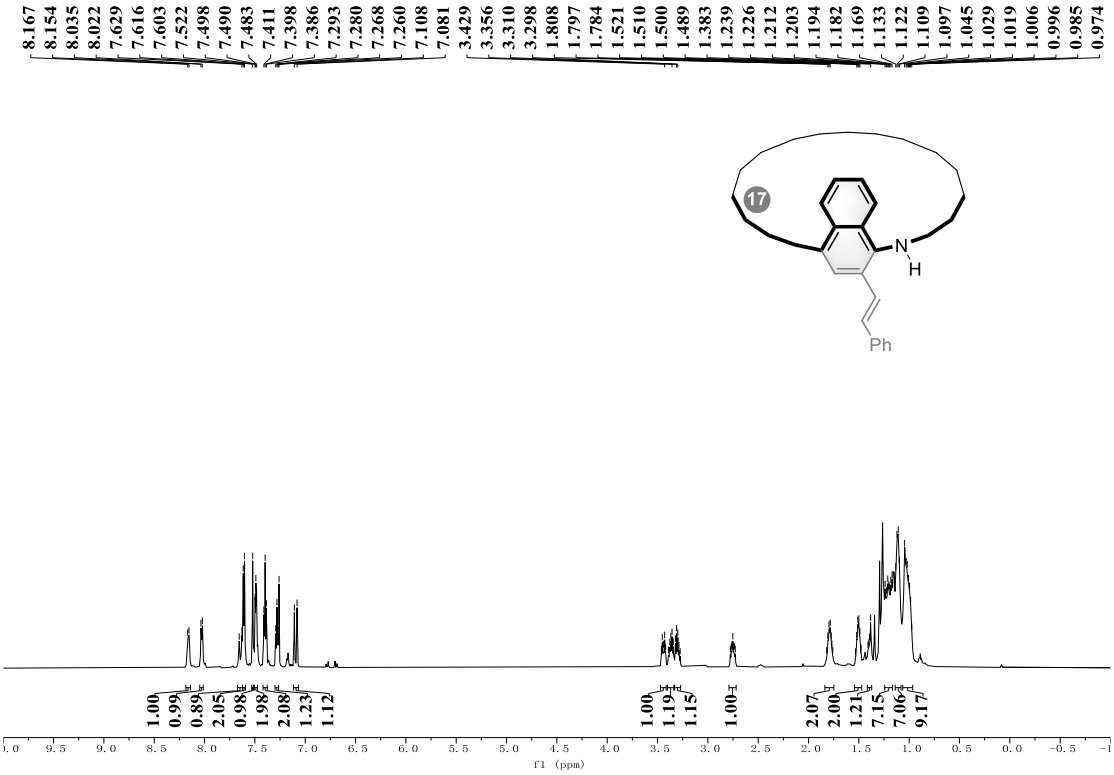
(R_p)-**12**, ^{1}H NMR (600 MHz, $CDCl_3$)



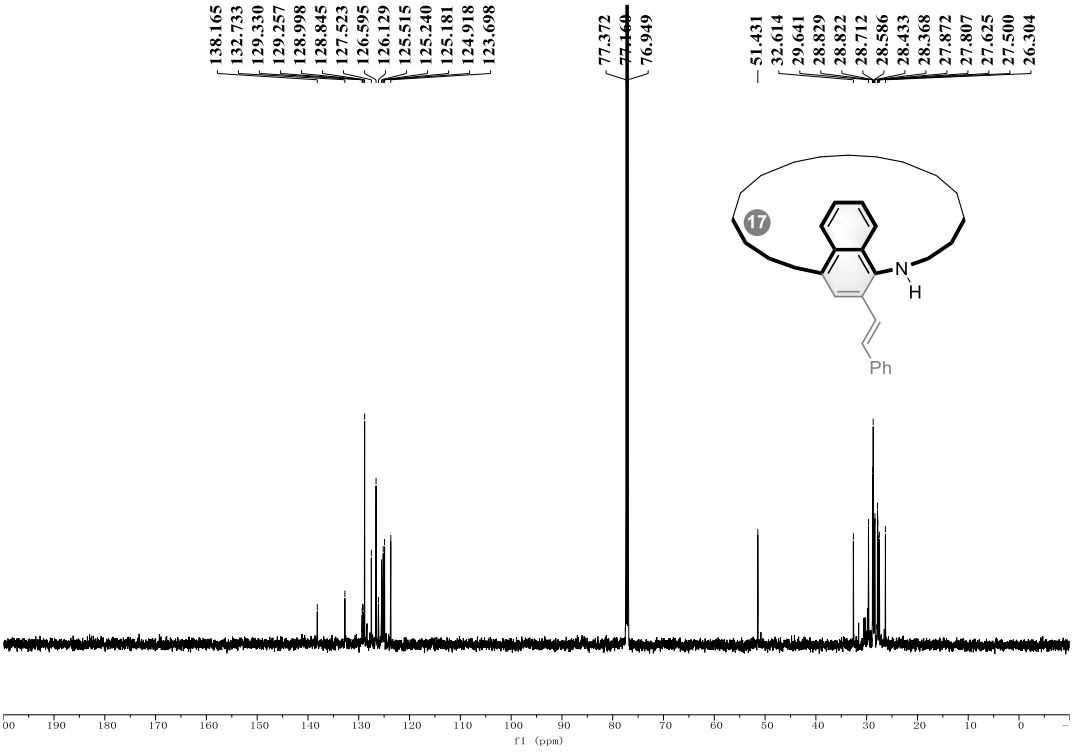
(R_p)-**12**, ^{13}C NMR (151 MHz, $CDCl_3$)



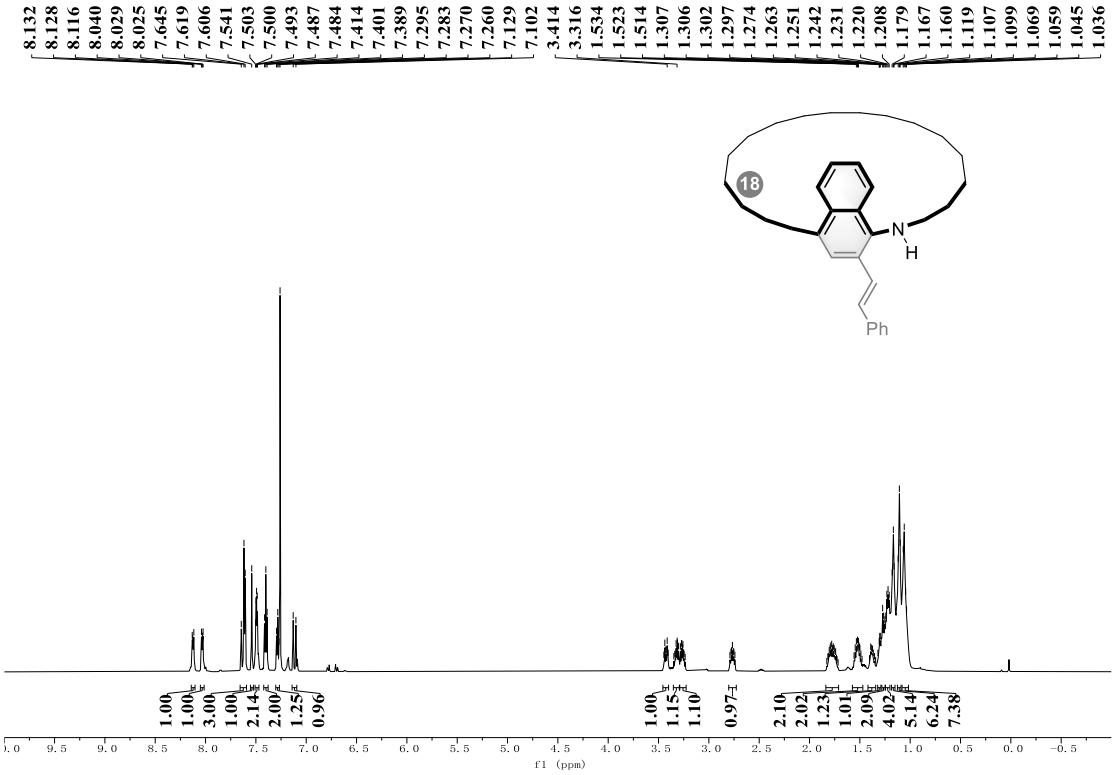
(R_p)-**13**, ^{1}H NMR (600 MHz, $CDCl_3$)



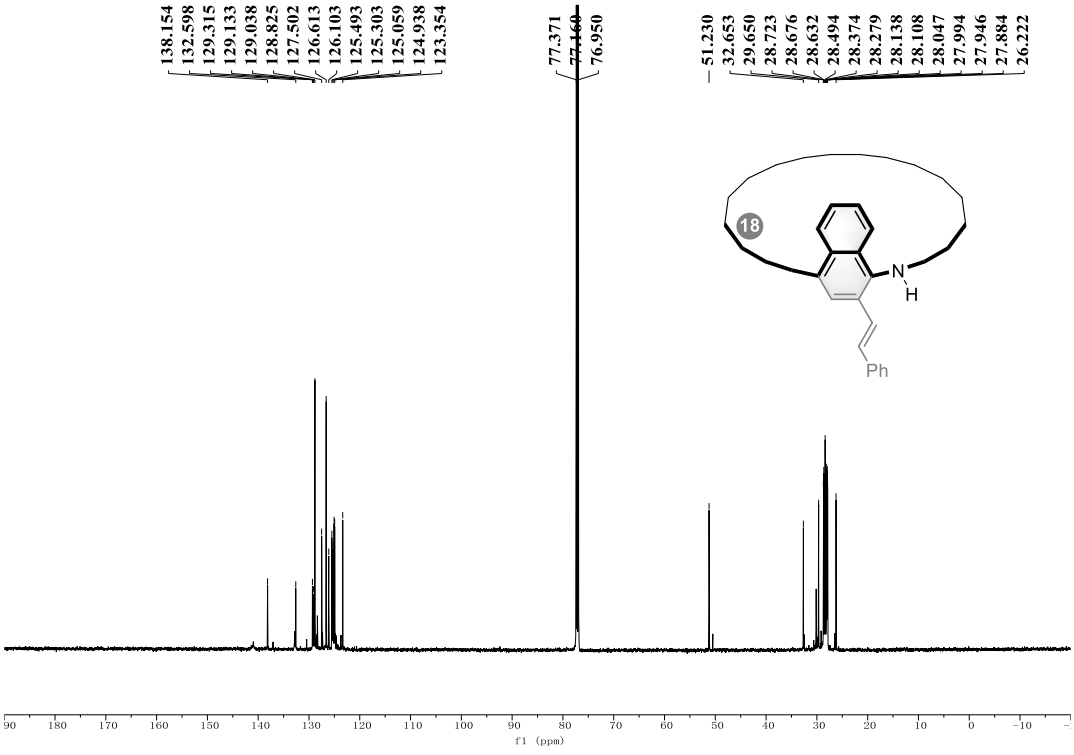
(R_p)-**13**, ^{13}C NMR (151 MHz, $CDCl_3$)



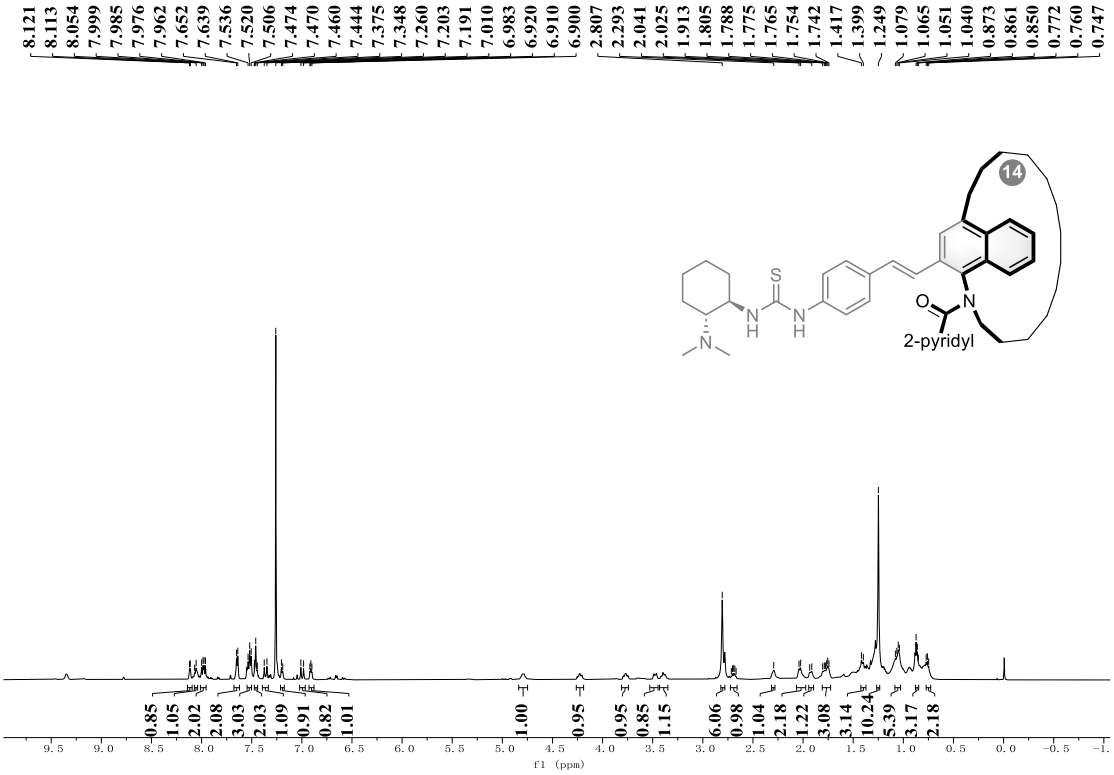
(R_p)-**14**, ^{1}H NMR (600 MHz, $CDCl_3$)



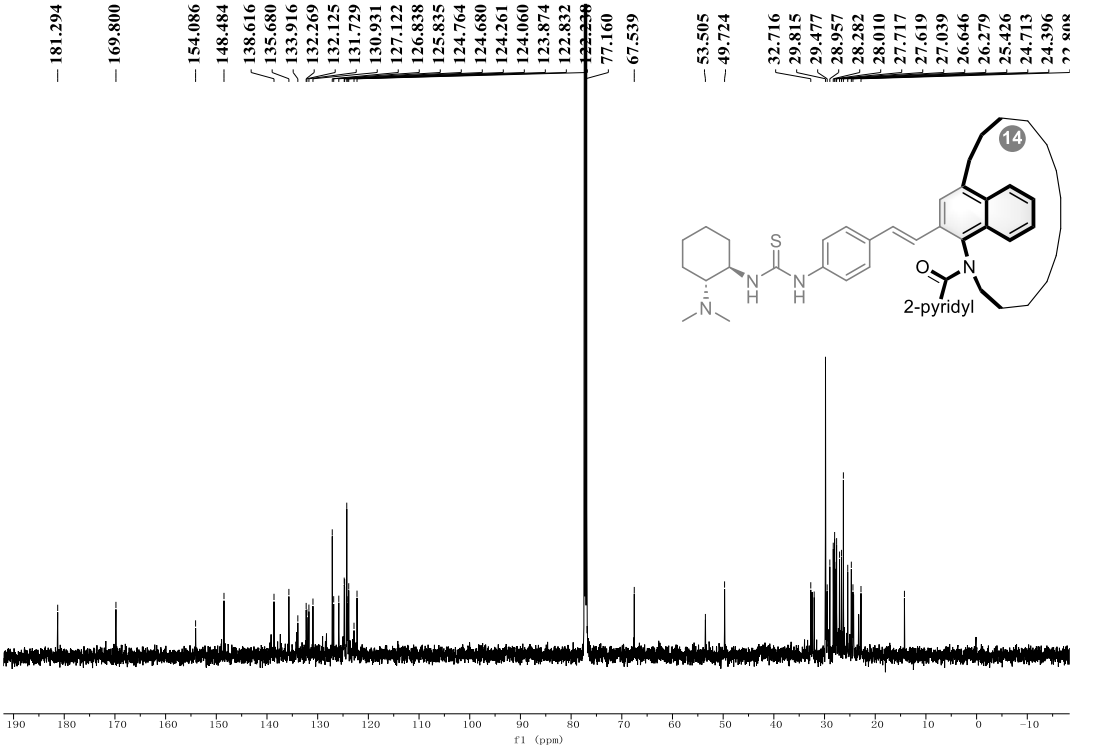
(R_p)-**14**, ^{13}C NMR (151 MHz, $CDCl_3$)



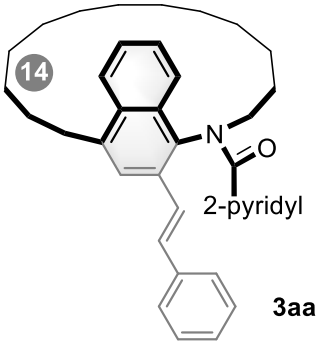
15, ^{1}H NMR (600 MHz, $CDCl_3$)



15, ^{13}C NMR (151 MHz, $CDCl_3$)



9. Copies of HPLC Spectra



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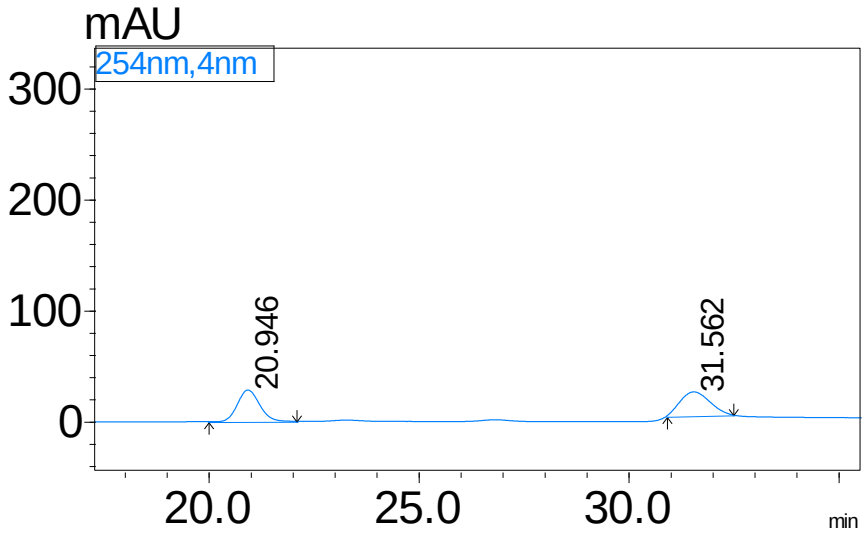
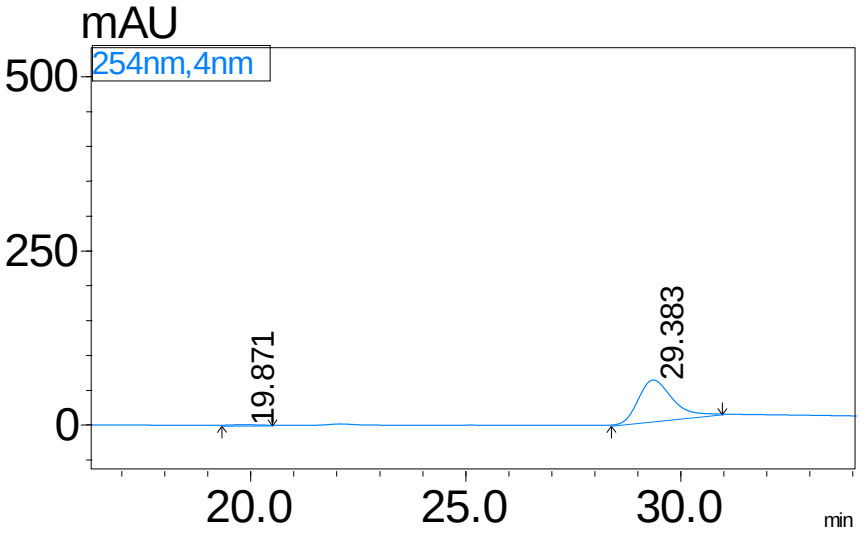
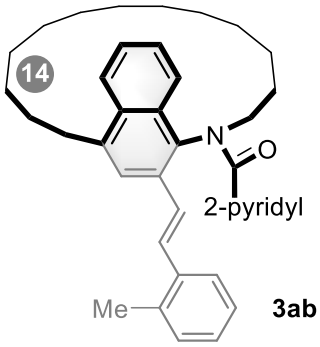


Peak	Time	Area	Height	Area%
1	20.946	1024614	28331	49.407
2	31.562	1049206	21464	50.593



Peak	Time	Area	Height	Area%
1	19.871	27265	850	0.851
2	29.383	3178486	58567	99.149



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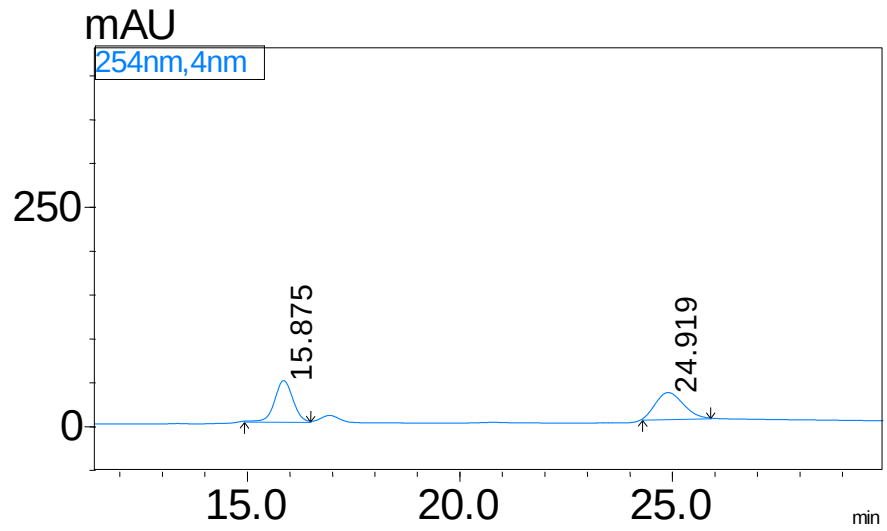
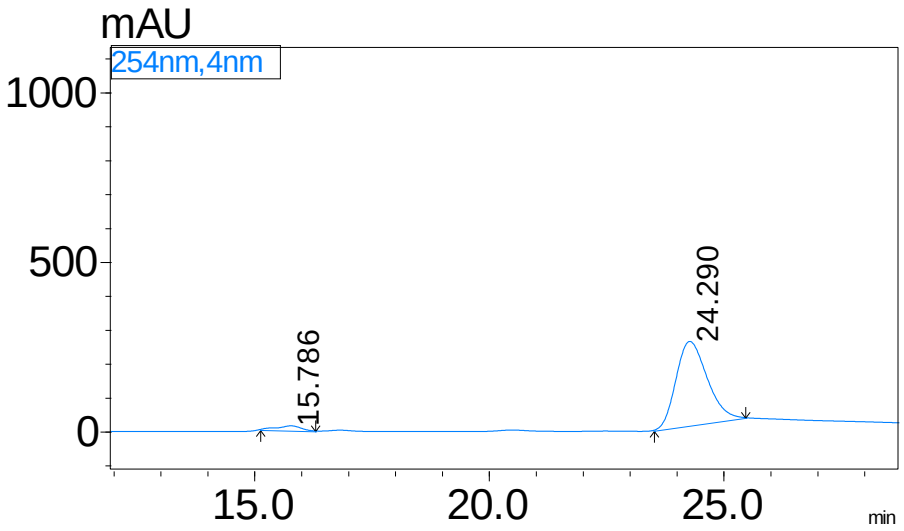
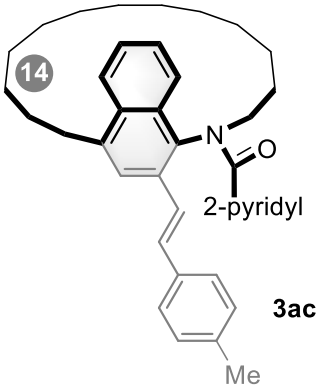


Peak	Time	Area	Height	Area%
1	15.875	1333304	46300	49.833
2	24.919	1342245	29957	50.167



Peak	Time	Area	Height	Area%
1	15.786	457801	13483	3.864
2	24.290	11390213	247378	96.136



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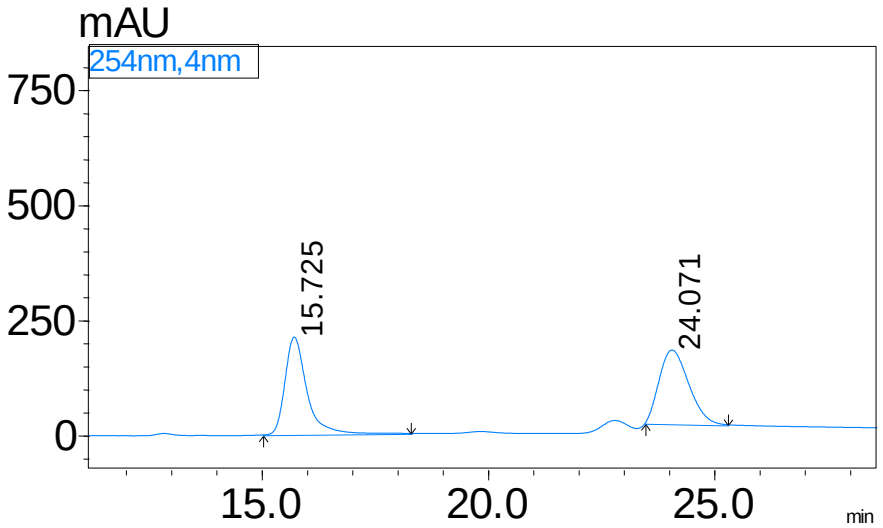
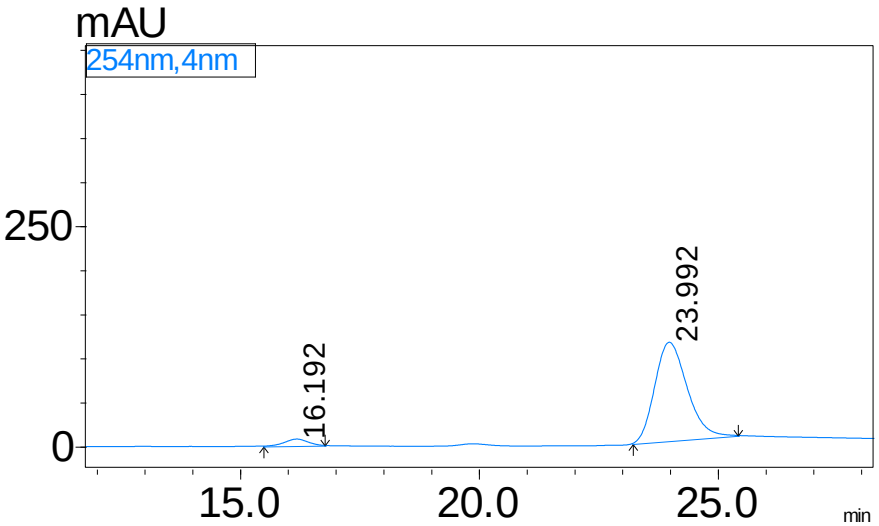
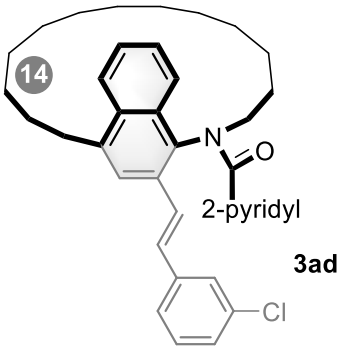


Peak	Time	Area	Height	Area%
1	15.725	7089181	212011	49.517
2	24.071	7227357	160325	50.483



Peak	Time	Area	Height	Area%
1	16.192	244693	7481	4.464
2	23.992	5237117	111621	95.536



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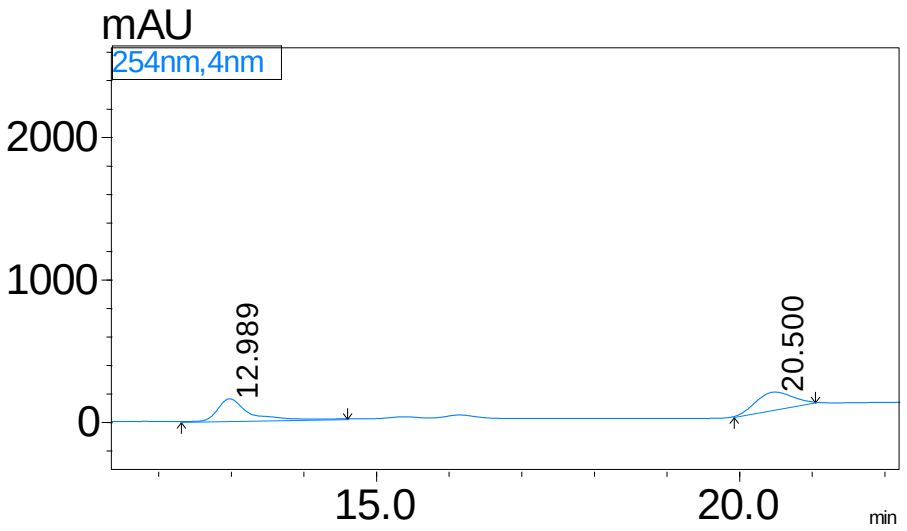
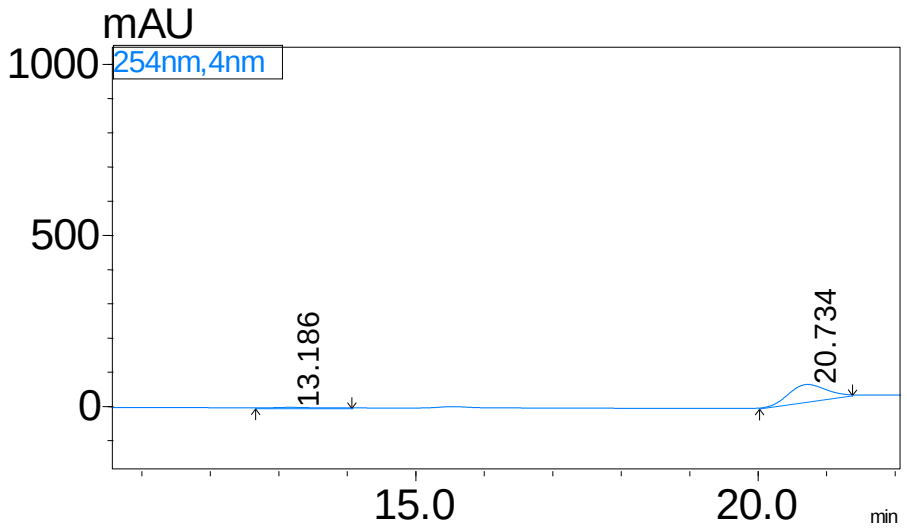
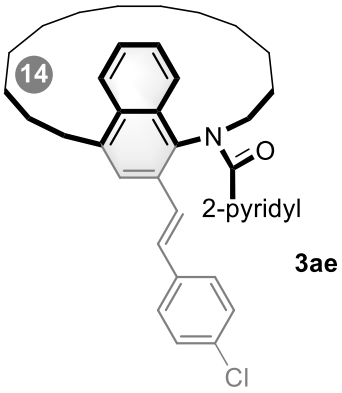


Peak	Time	Area	Height	Area%
1	12.989	4241763	153237	50.267
2	20.500	4196686	120274	49.733



Peak	Time	Area	Height	Area%
1	13.186	39558	1385	2.156
2	20.734	1795538	48671	97.844



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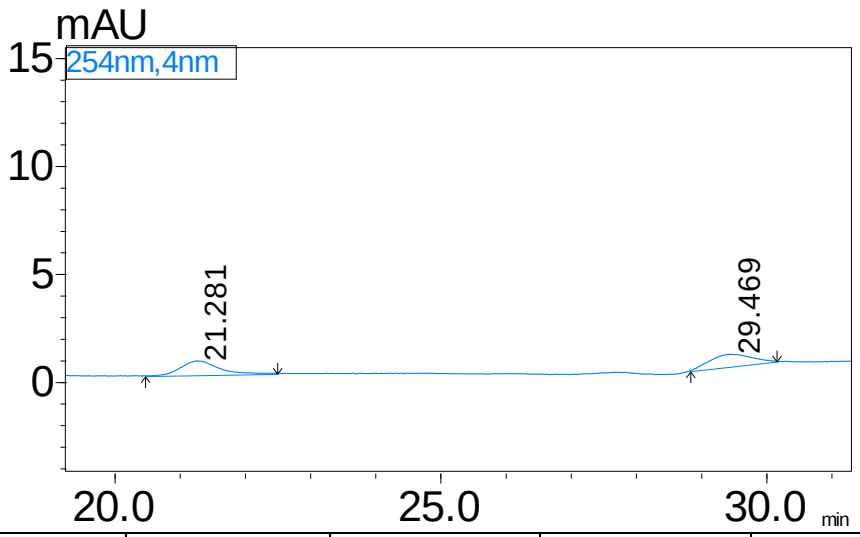
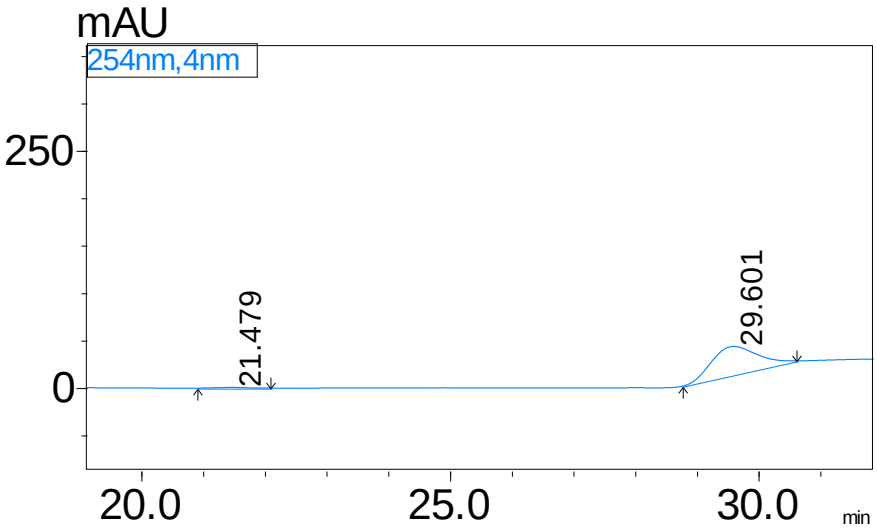
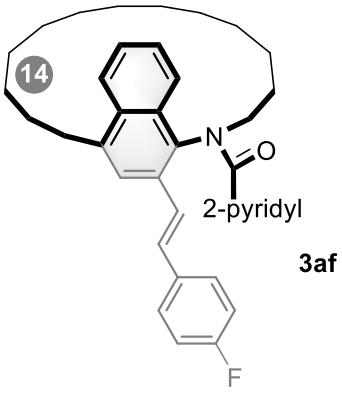


Peak	Time	Area	Height	Area%
1	21.281	24981	645	50.365
2	29.469	24618	557	49.635



Peak	Time	Area	Height	Area%
1	21.479	22430	671	1.423
2	29.601	1553547	29976	98.577



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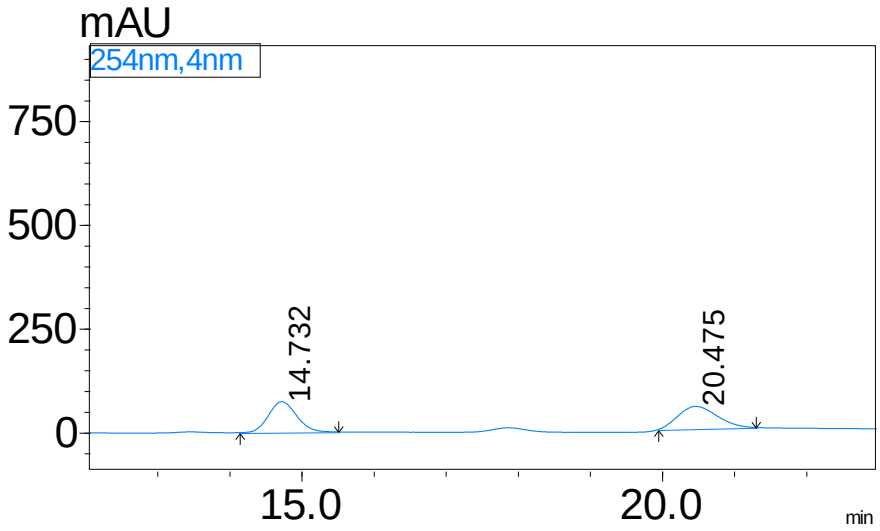
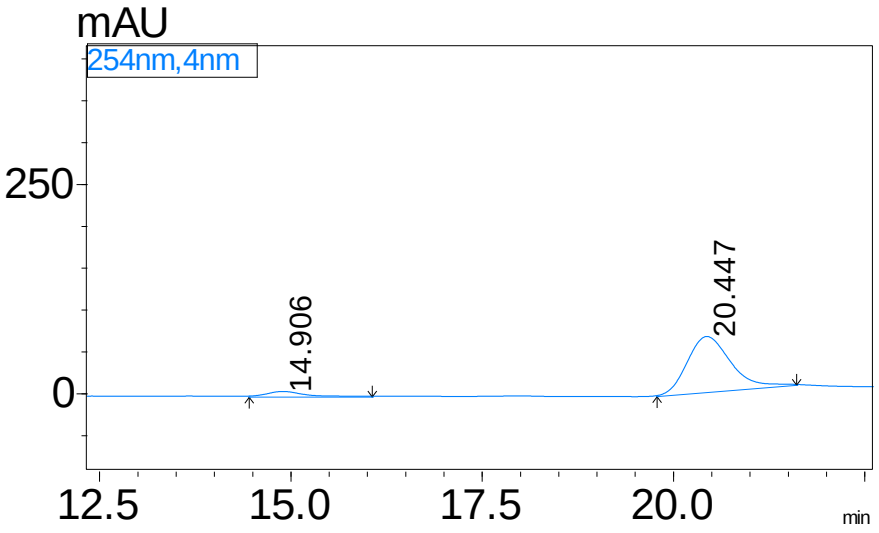
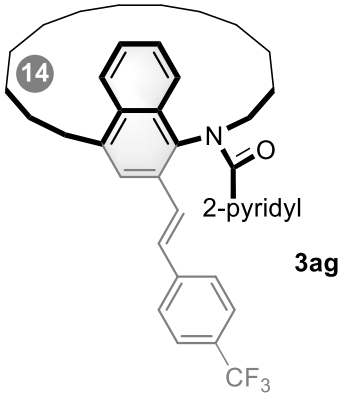


Peak	Time	Area	Height	Area%
1	14.732	1997191	73806	49.577
2	20.475	2031262	53955	50.423



Peak	Time	Area	Height	Area%
1	14.906	163202	5637	6.016
2	20.447	2549743	65853	93.984



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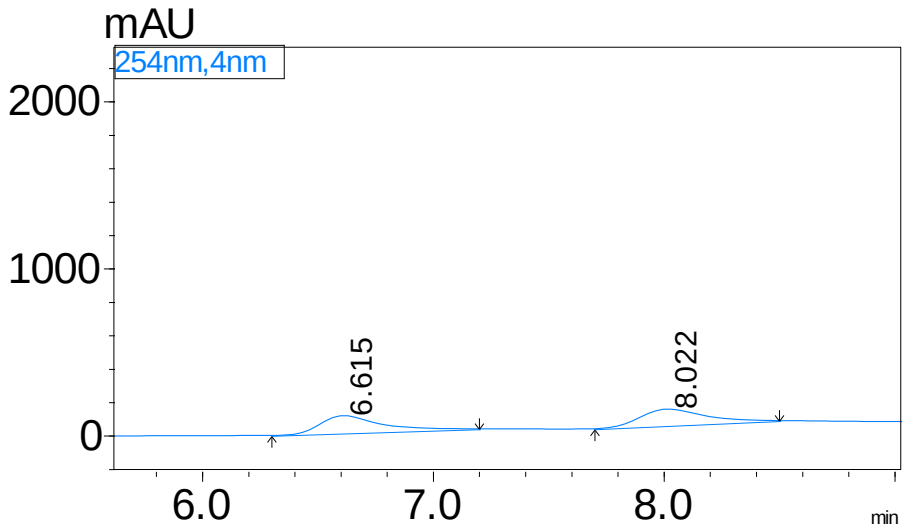
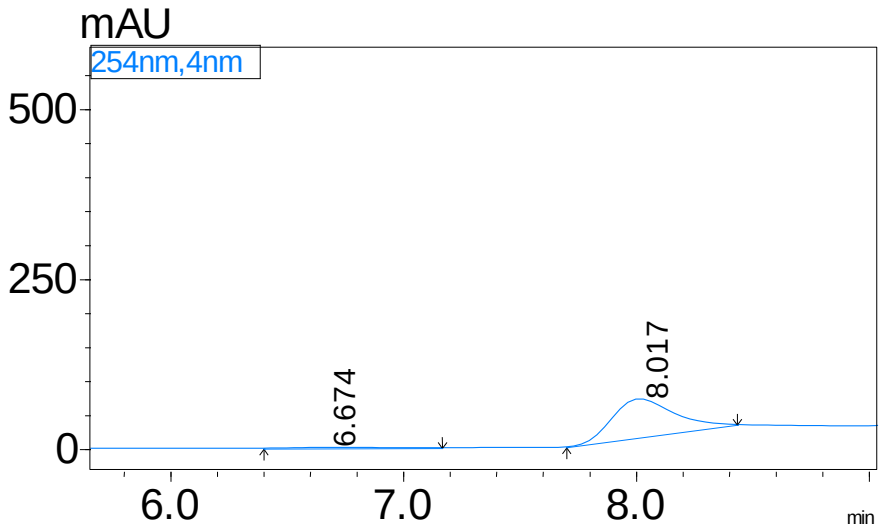
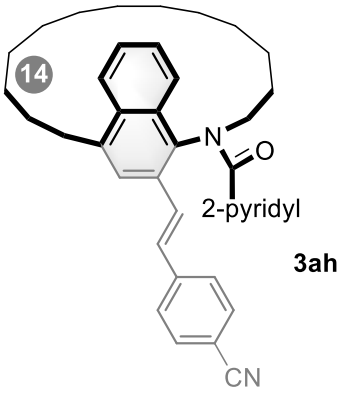


Peak	Time	Area	Height	Area%
1	6.615	1916634	103914	49.692
2	8.022	1940414	97546	50.308



Peak	Time	Area	Height	Area%
1	6.674	19985	978	1.838
2	8.017	1067309	56251	98.162



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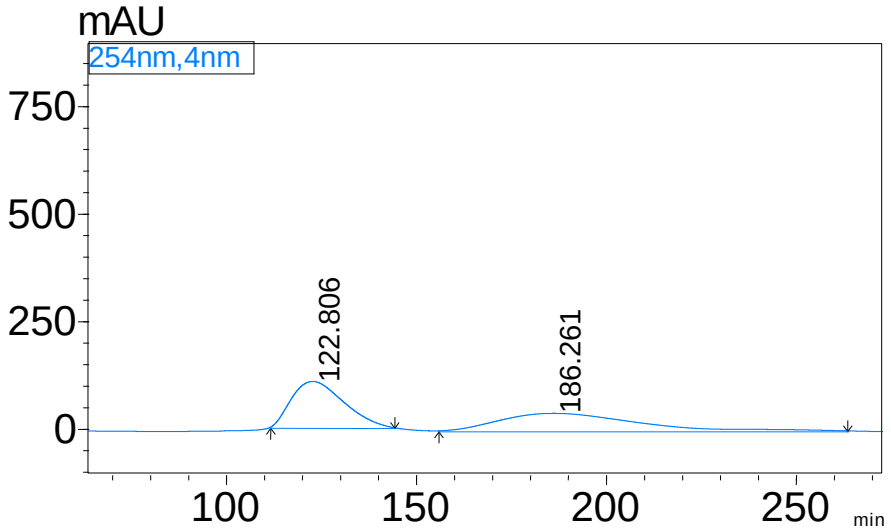
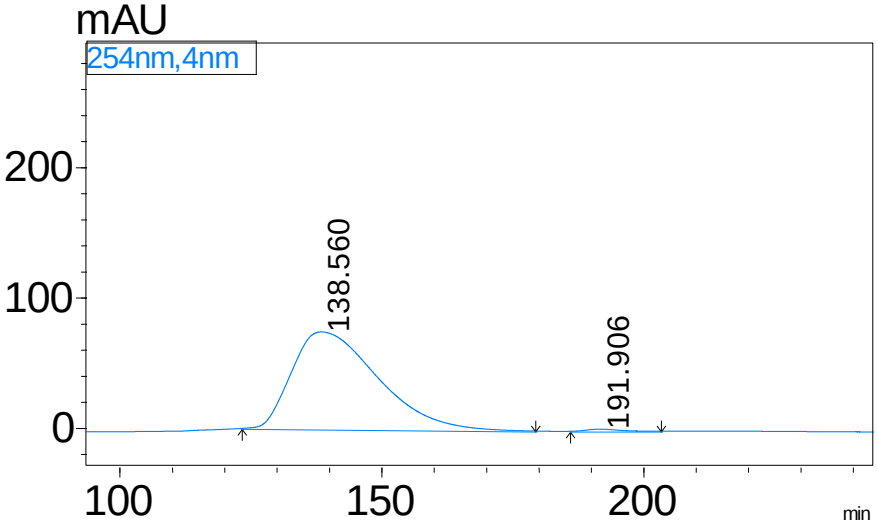
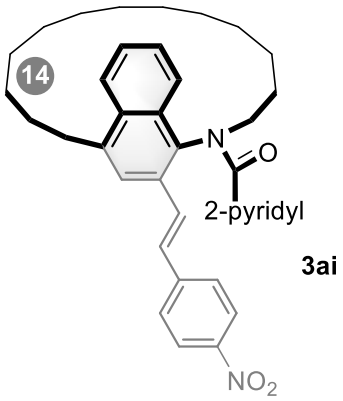


Peak	Time	Area	Height	Area%
1	122.806	102196939	107143	50.712
2	186.261	99326460	40673	49.288



Peak	Time	Area	Height	Area%
1	138.560	84996948	74622	99.234
2	191.906	656092	1635	0.766



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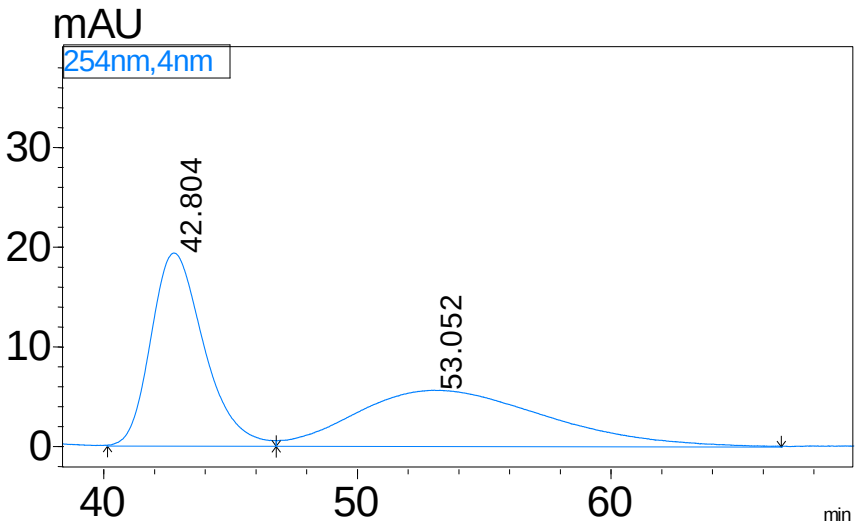
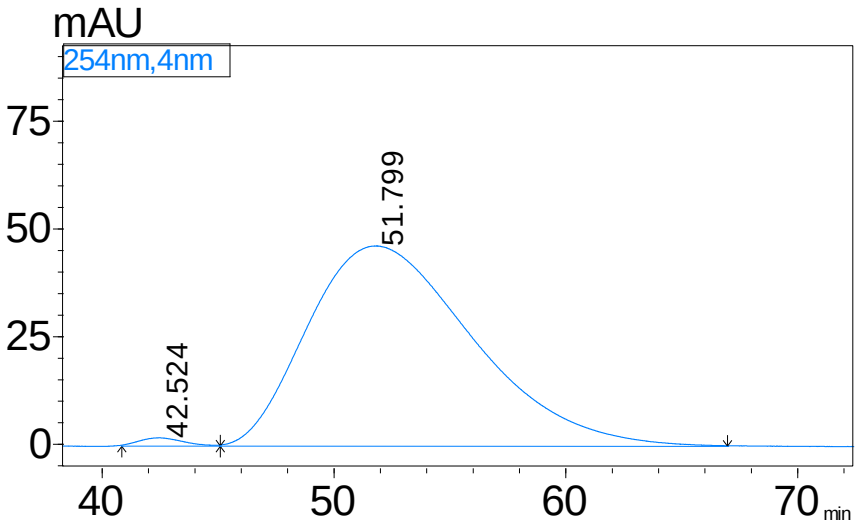
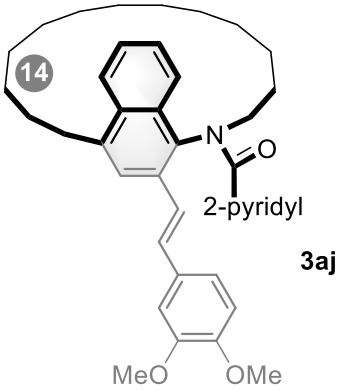


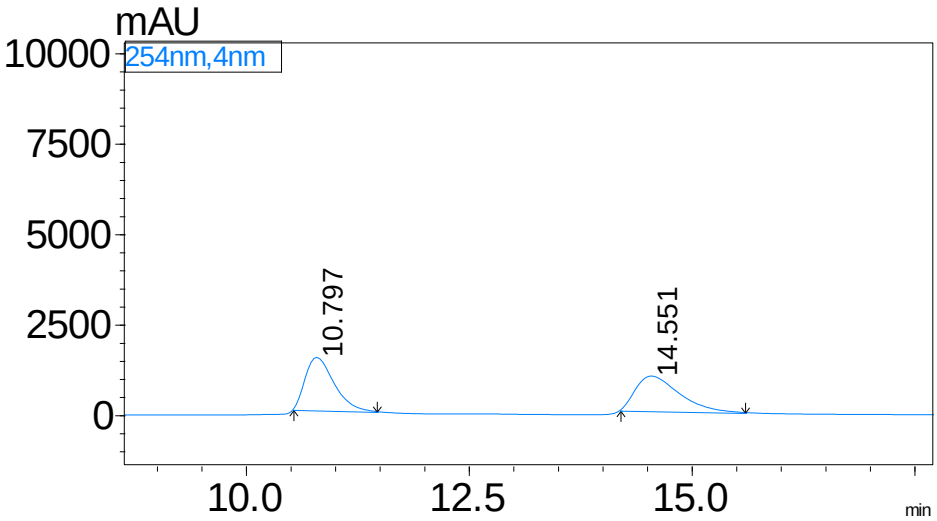
Peak	Time	Area	Height	Area%
1	42.804	2791739	19298	49.427
2	53.052	2856466	5571	50.573



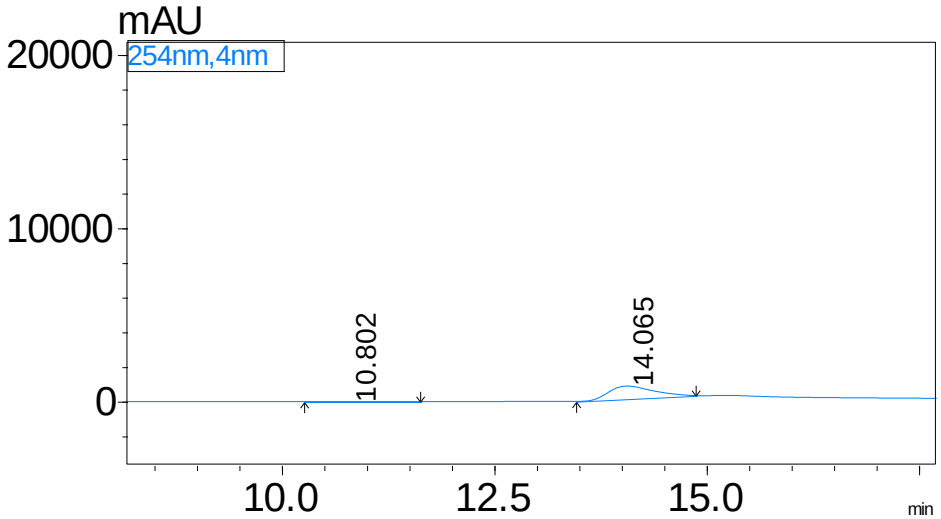
Peak	Time	Area	Height	Area%
1	42.524	210107	1743	0.910
2	51.799	22880402	46307	99.090



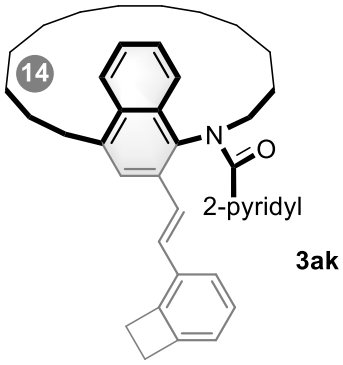
3aj



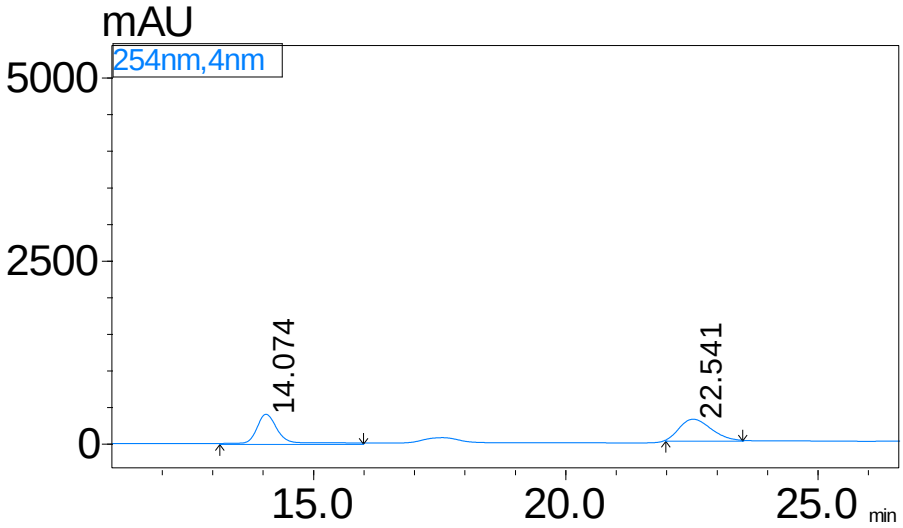
Peak	Time	Area	Height	Area%
1	10.797	32588490	1463058	50.068
2	14.551	32500428	962469	49.932



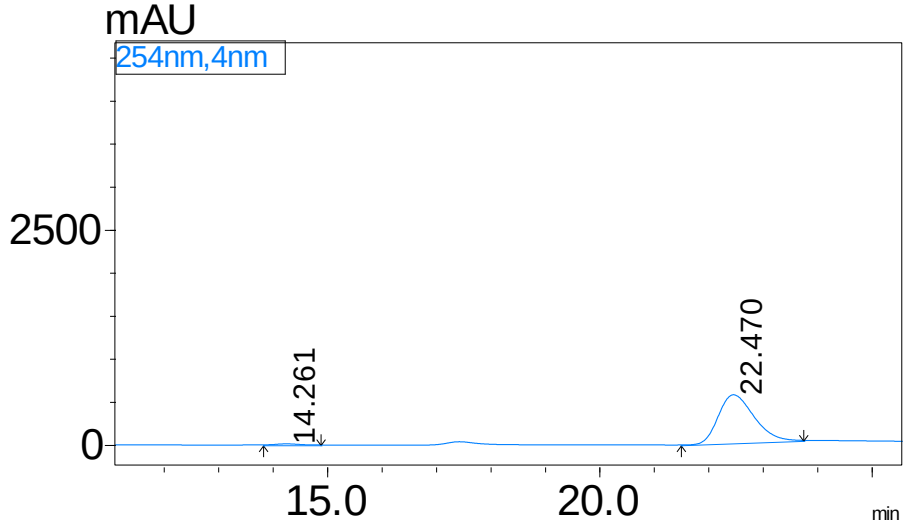
Peak	Time	Area	Height	Area%
1	10.802	93085	2204	0.346
2	14.065	26787198	745484	99.654



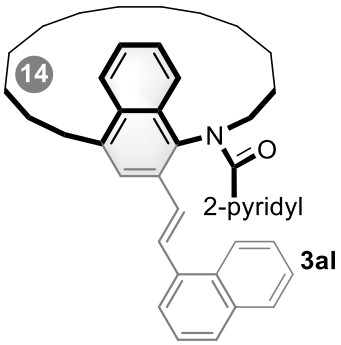
3ak



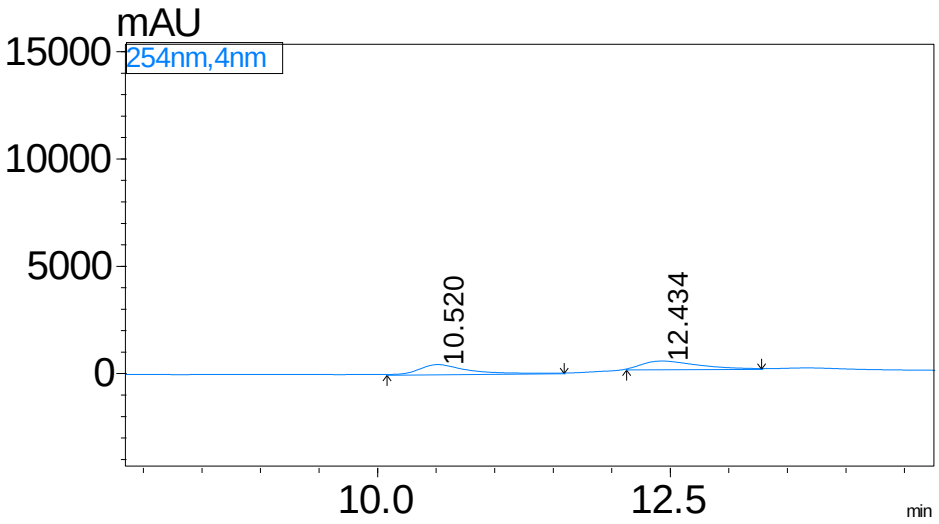
Peak	Time	Area	Height	Area%
1	14.074	11338089	398031	48.198
2	22.541	12185784	287623	51.802



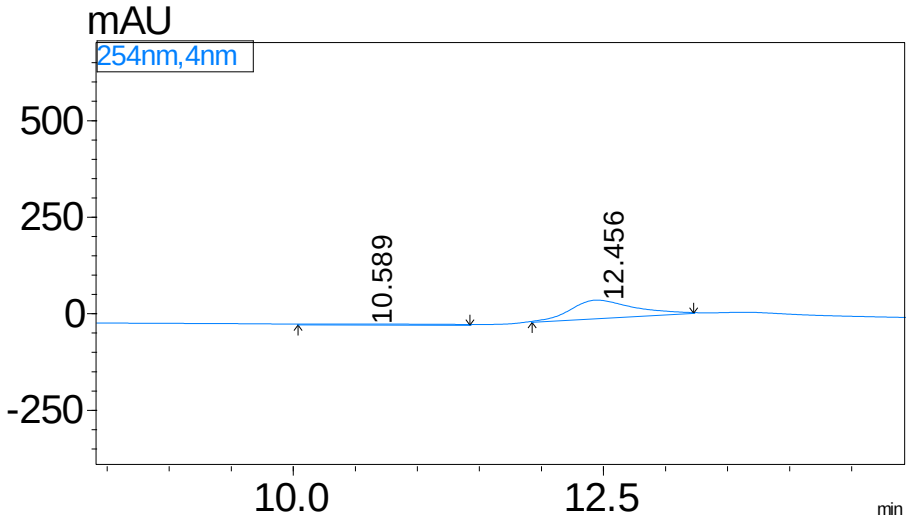
Peak	Time	Area	Height	Area%
1	14.261	318668	12405	1.244
2	22.470	25292574	560568	98.756



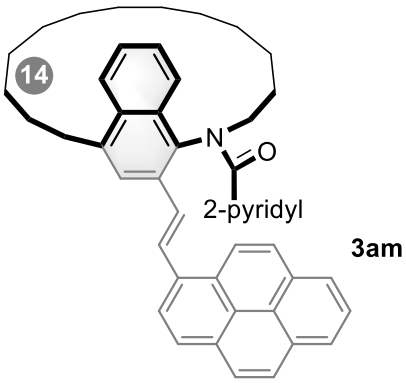
3al



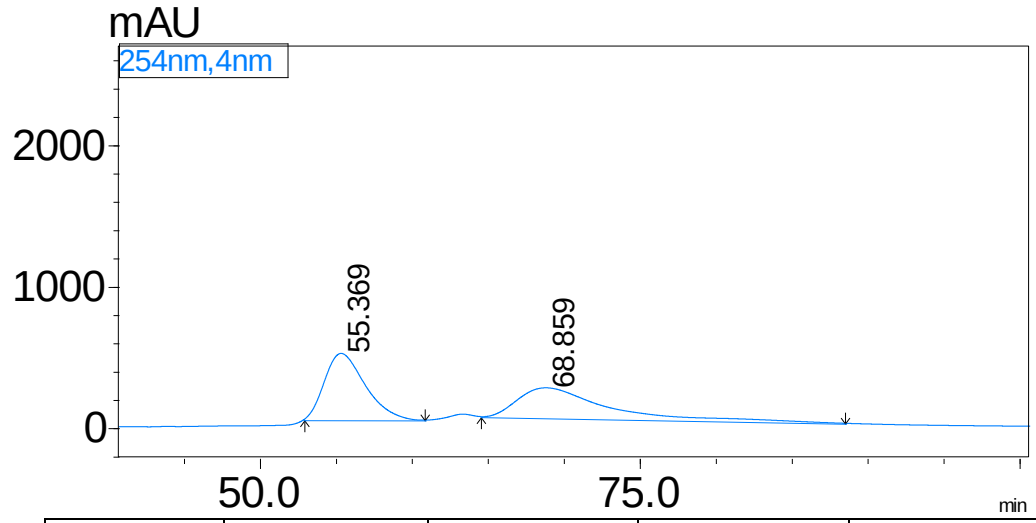
Peak	Time	Area	Height	Area%
1	10.520	11144158	437317	49.475
2	12.434	11380827	368925	50.525



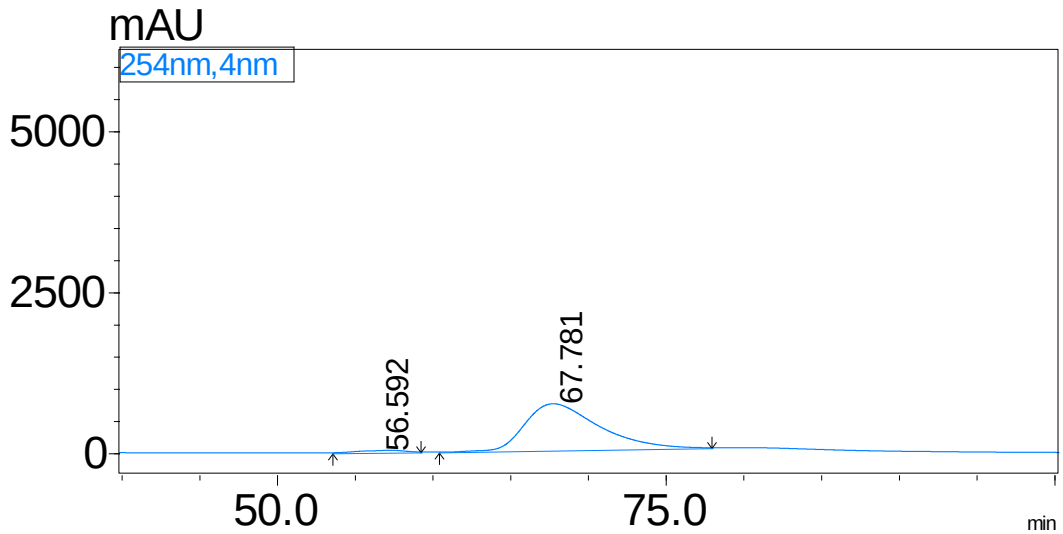
Peak	Time	Area	Height	Area%
1	10.589	21028	626	1.338
2	12.456	1550539	45800	98.662



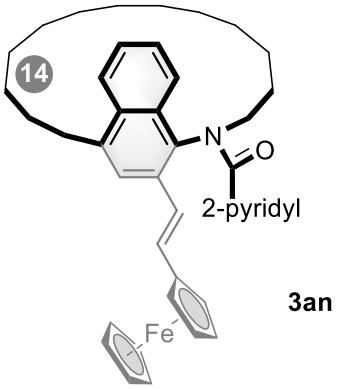
3am



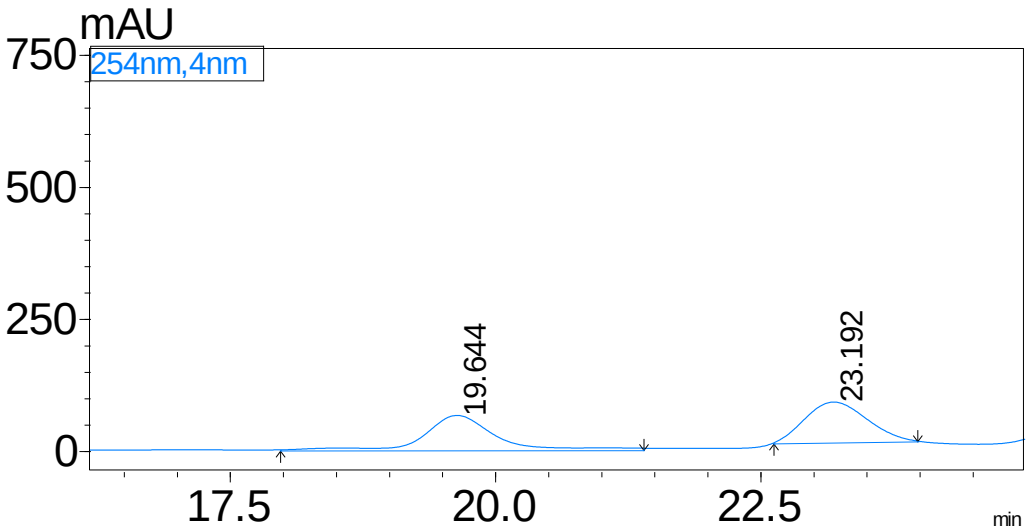
Peak	Time	Area	Height	Area%
1	55.369	86976387	469166	50.530
2	68.859	85152145	212214	49.470



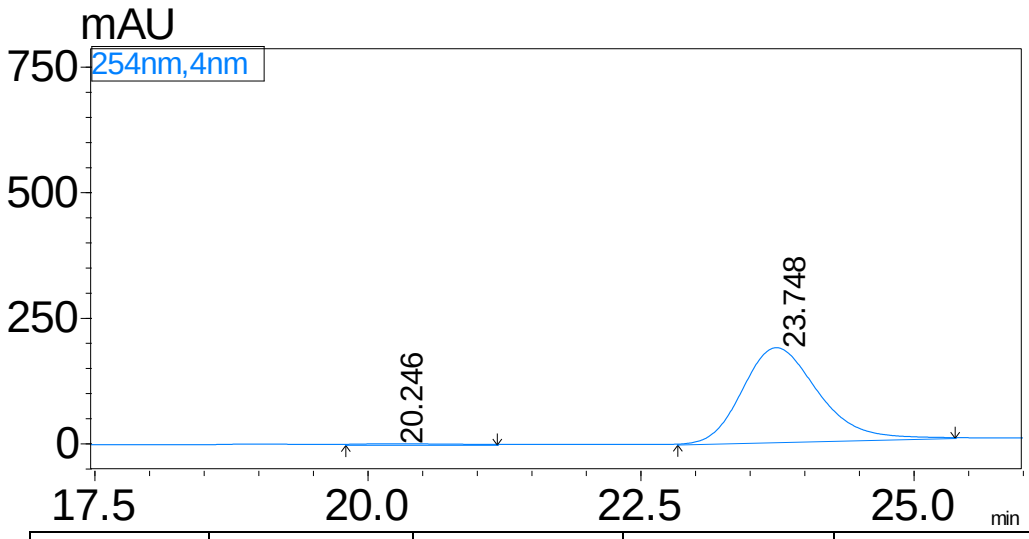
Peak	Time	Area	Height	Area%
1	56.592	5673095	26849	2.347
2	67.781	236061573	721786	97.653



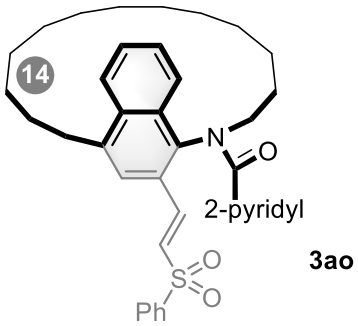
3an



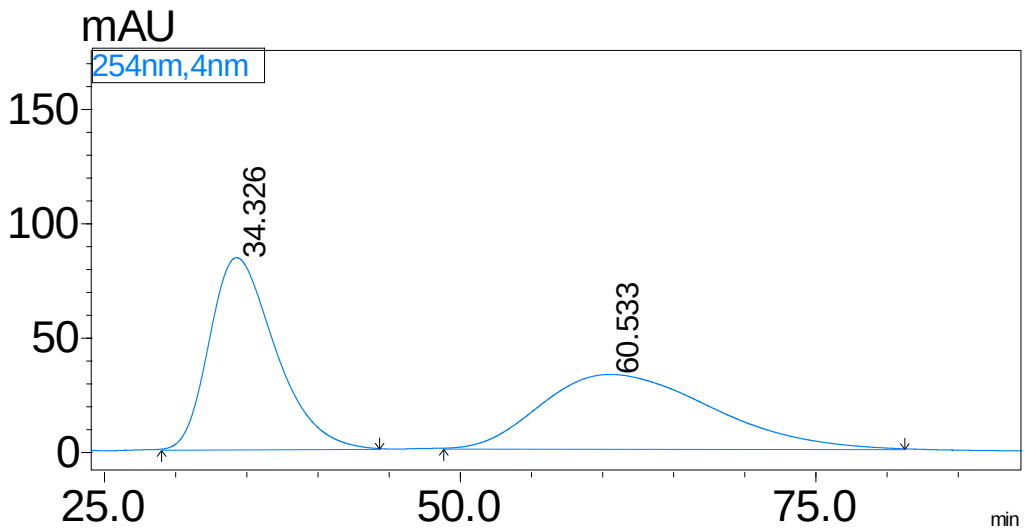
Peak	Time	Area	Height	Area%
1	19.644	2952129	65269	49.083
2	23.192	3062451	76005	50.917



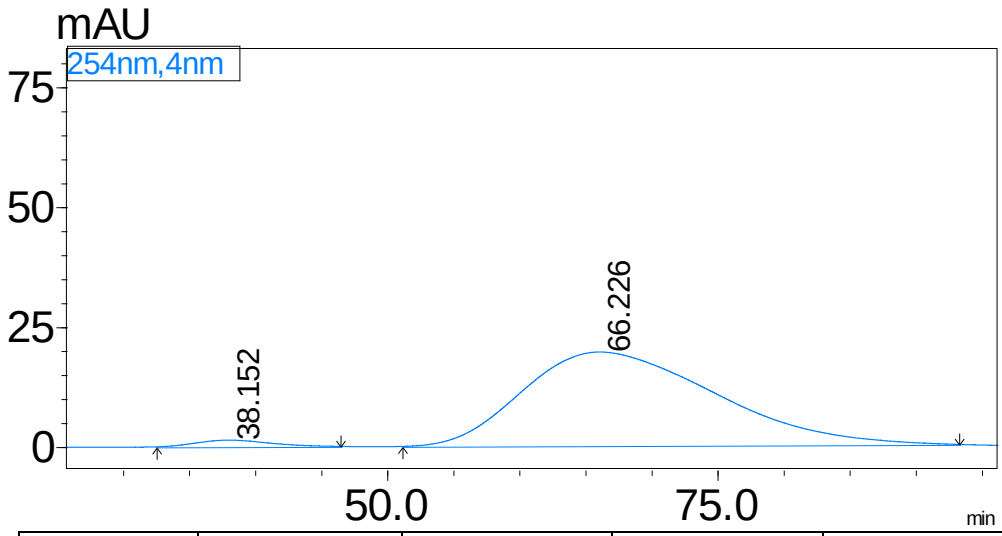
Peak	Time	Area	Height	Area%
1	20.246	50718	1271	0.561
2	23.748	8994608	187502	99.439



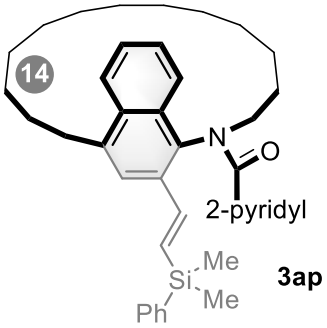
3ao



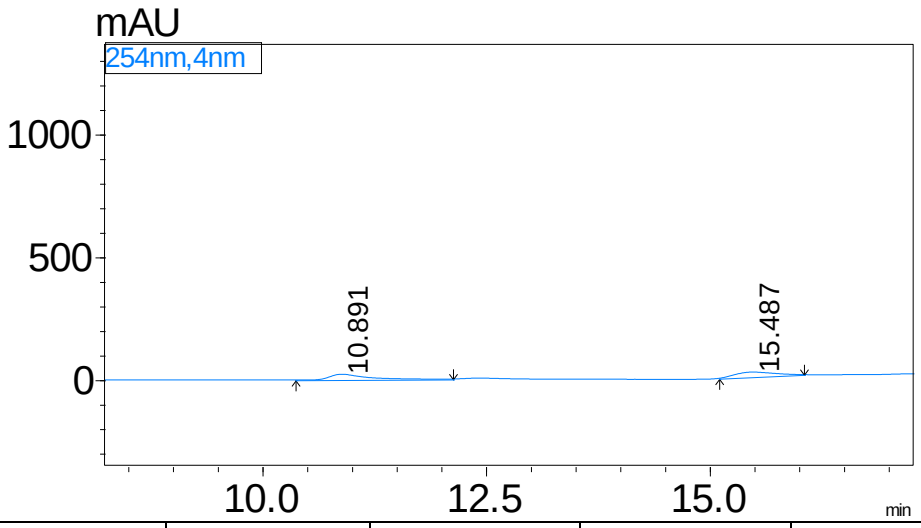
Peak	Time	Area	Height	Area%
1	34.326	26908371	83693	50.140
2	60.533	26758134	32366	49.860



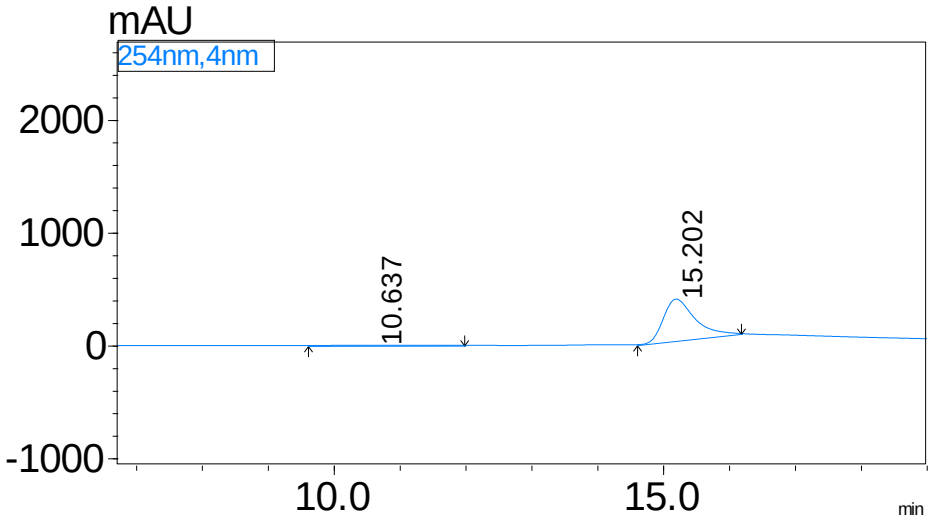
Peak	Time	Area	Height	Area%
1	38.152	521665	1371	2.571
2	66.226	19767364	19546	97.429



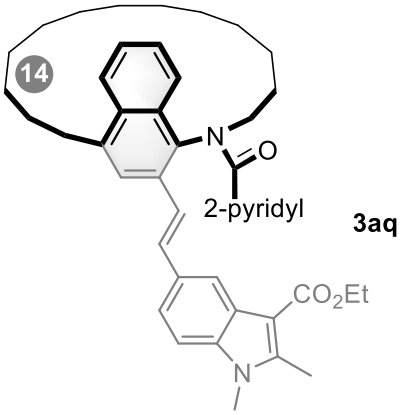
3ap



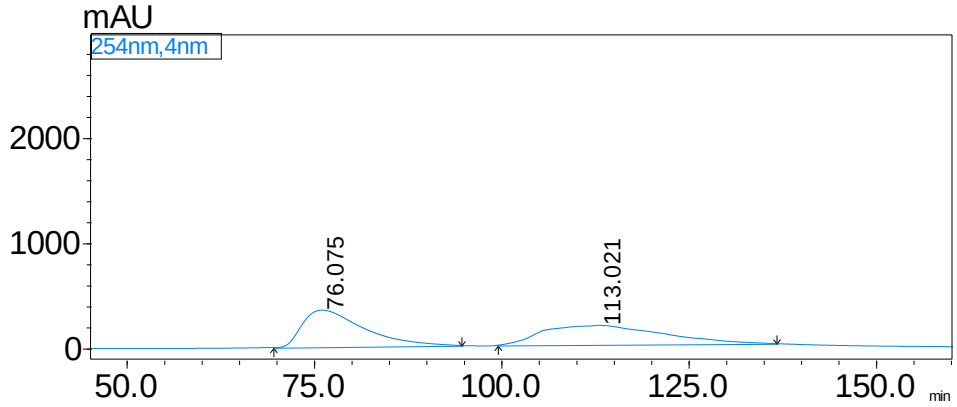
Peak	Time	Area	Height	Area%
1	10.891	592175	22233	50.419
2	15.487	582344	19341	49.581



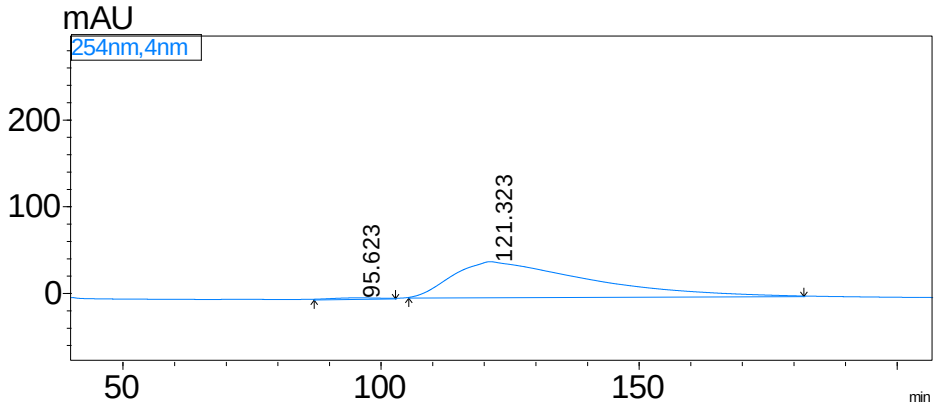
Peak	Time	Area	Height	Area%
1	10.637	143585	1912	1.177
2	15.202	12053893	367173	98.823



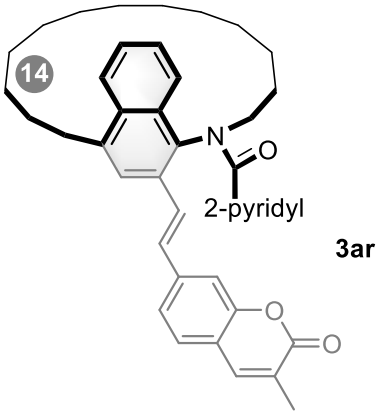
3aq



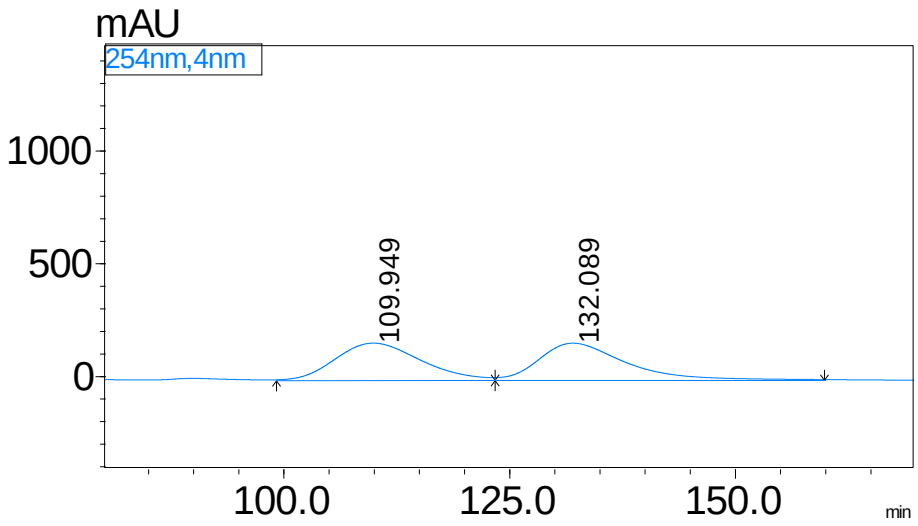
Peak	Time	Area	Height	Area%
1	76.075	198729016	351484	49.440
2	113.021	203230416	183028	50.560



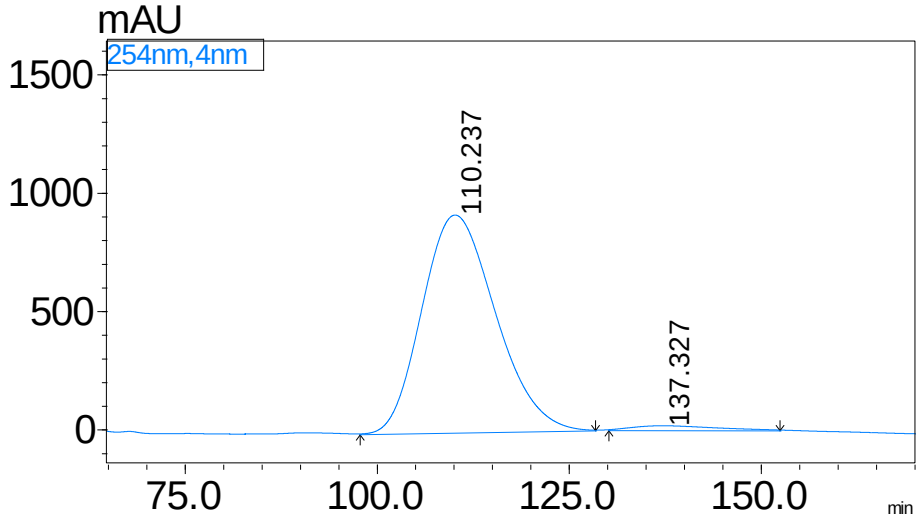
Peak	Time	Area	Height	Area%
1	95.623	530566	983	0.721
2	121.323	73052314	40908	99.279



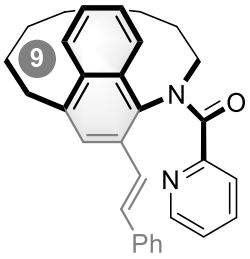
3ar



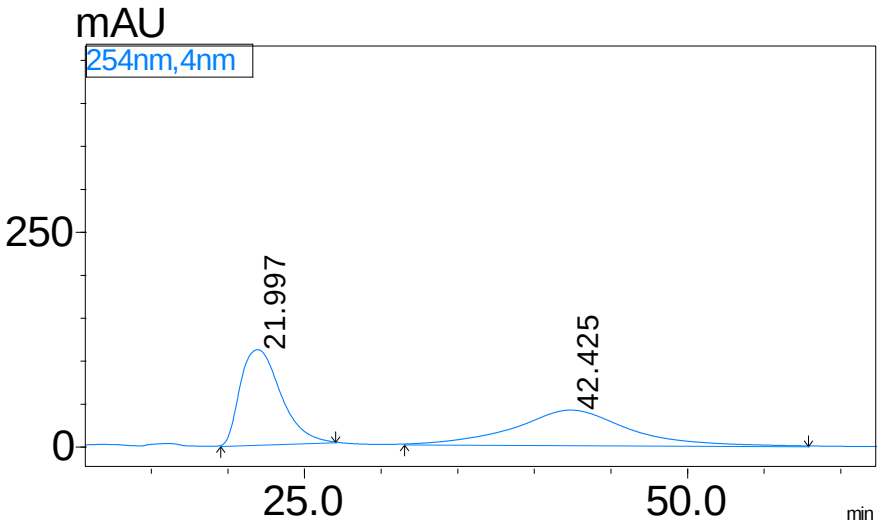
Peak	Time	Area	Height	Area%
1	109.949	104955762	162570	49.915
2	132.089	105313424	161984	50.085



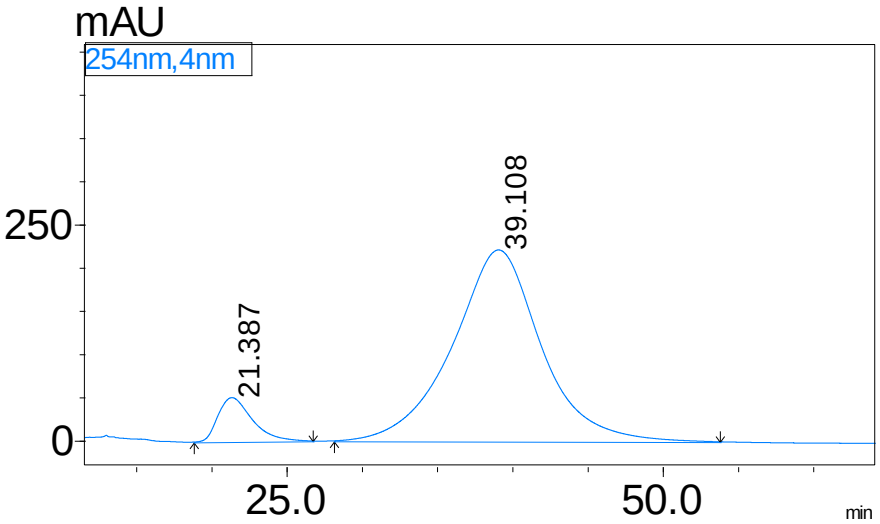
Peak	Time	Area	Height	Area%
1	110.237	609487412	918016	98.050
2	137.327	12121217	17365	1.950



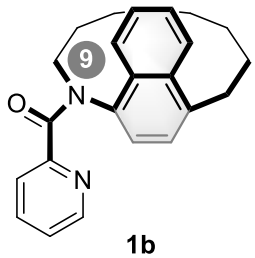
3ba



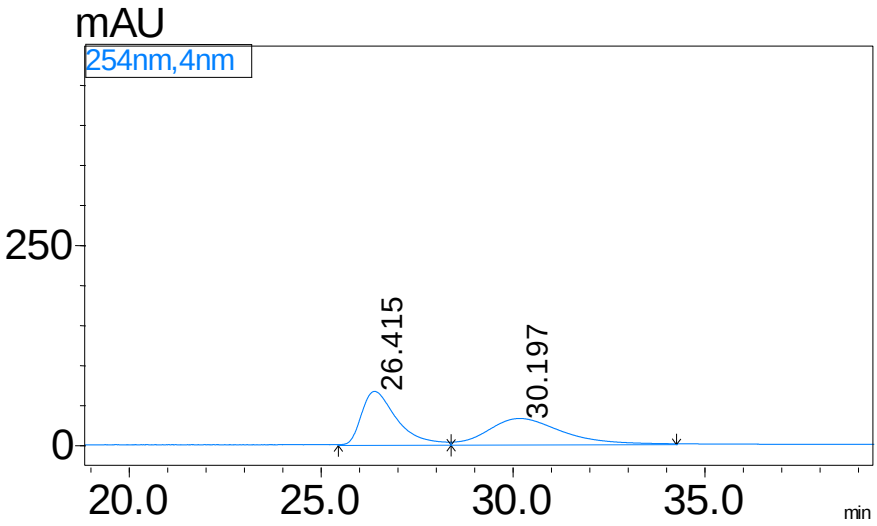
Peak	Time	Area	Height	Area%
1	21.997	20264246	110410	50.037
2	42.425	20234133	40387	49.963



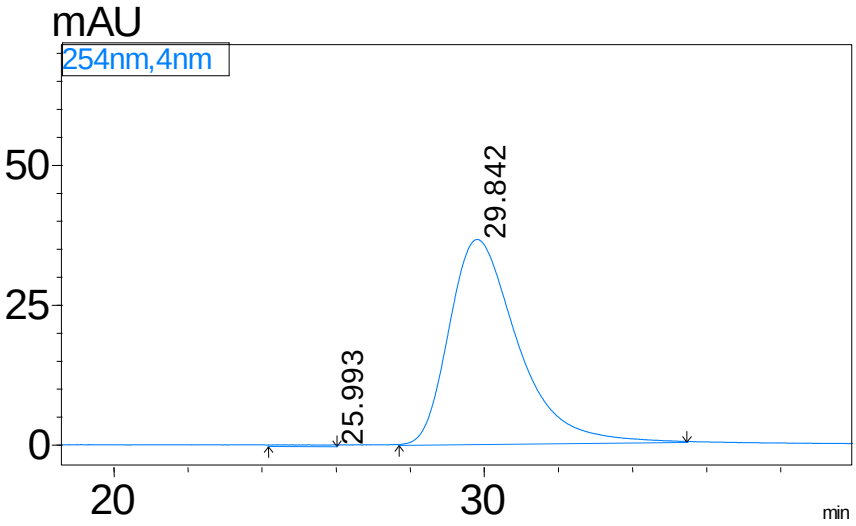
Peak	Time	Area	Height	Area%
1	21.387	8033867	50989	8.139
2	39.108	90672611	221245	91.861



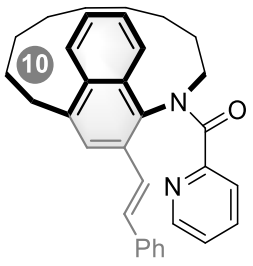
1b



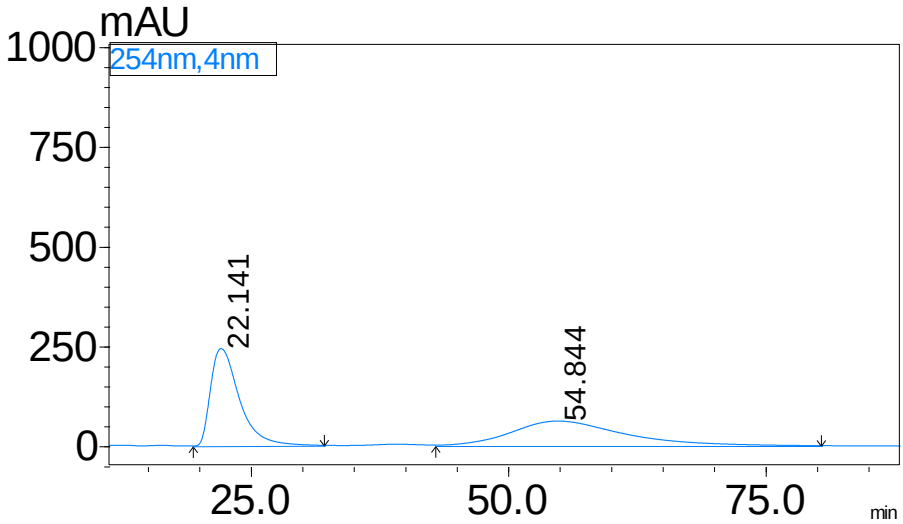
Peak	Time	Area	Height	Area%
1	26.415	4195562	66471	50.089
2	30.197	4180602	32129	49.911



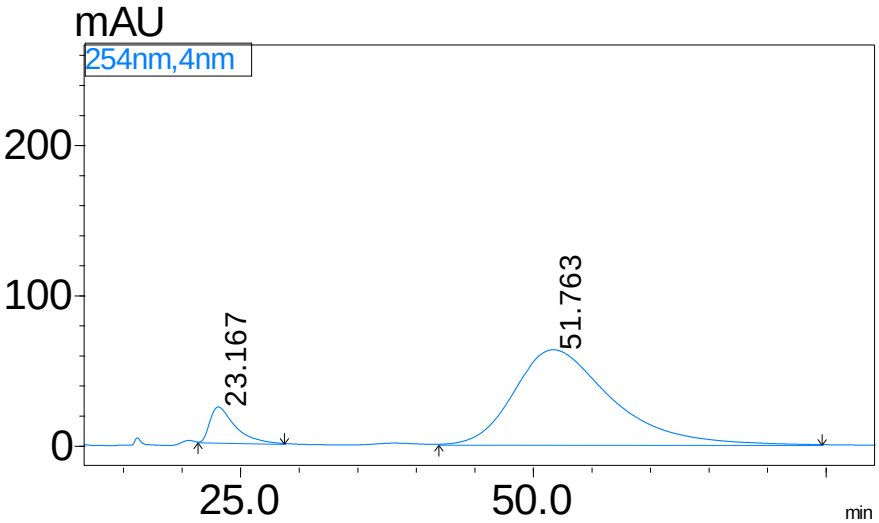
Peak	Time	Area	Height	Area%
1	25.993	15459	194	0.331
2	29.842	4660591	36486	99.669



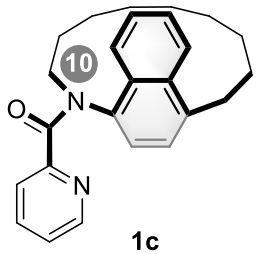
3ca



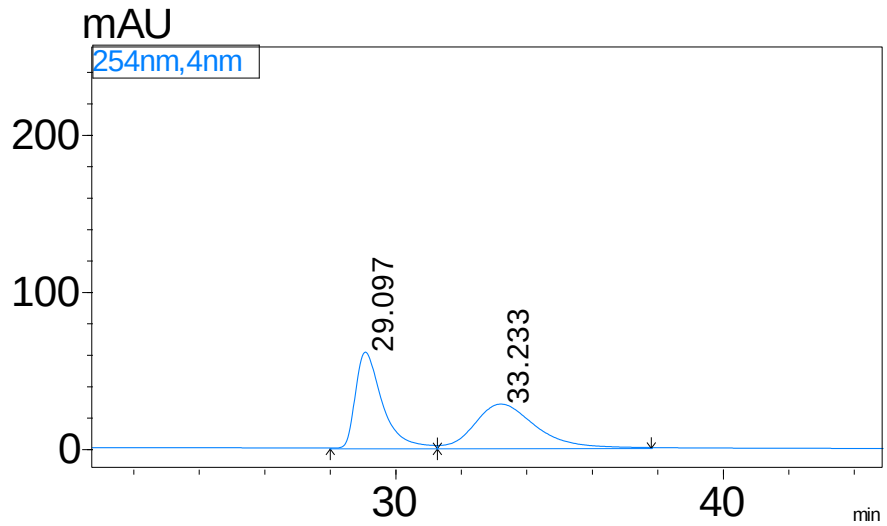
Peak	Time	Area	Height	Area%
1	22.141	47213087	243497	50.606
2	54.844	46081953	61481	49.394



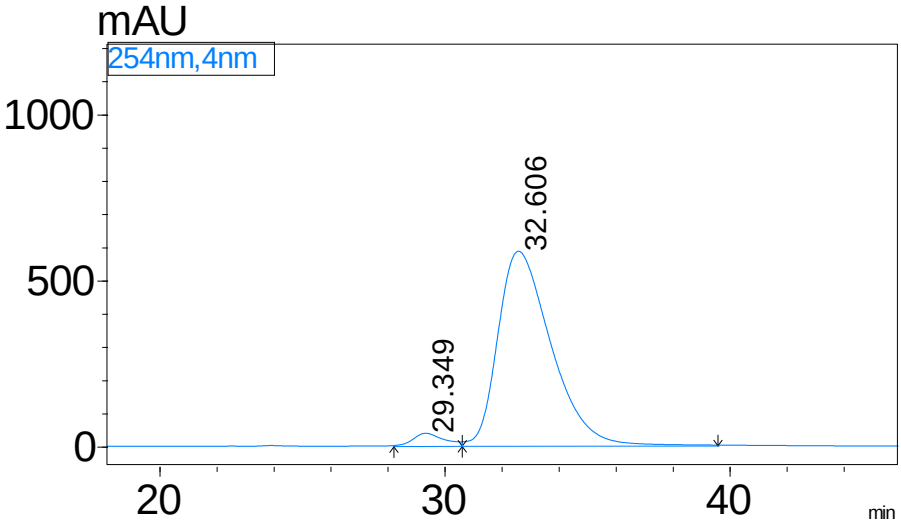
Peak	Time	Area	Height	Area%
1	23.167	3452236	23581	8.717
2	51.763	36150470	62994	91.283



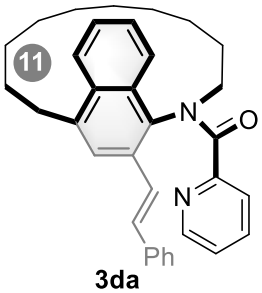
1c



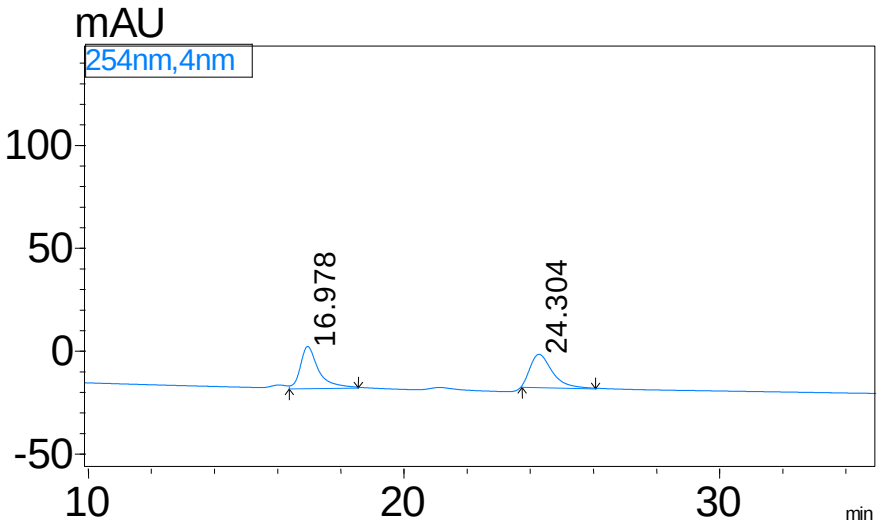
Peak	Time	Area	Height	Area%
1	29.097	3447083	60958	49.420
2	33.233	3528048	27819	50.580



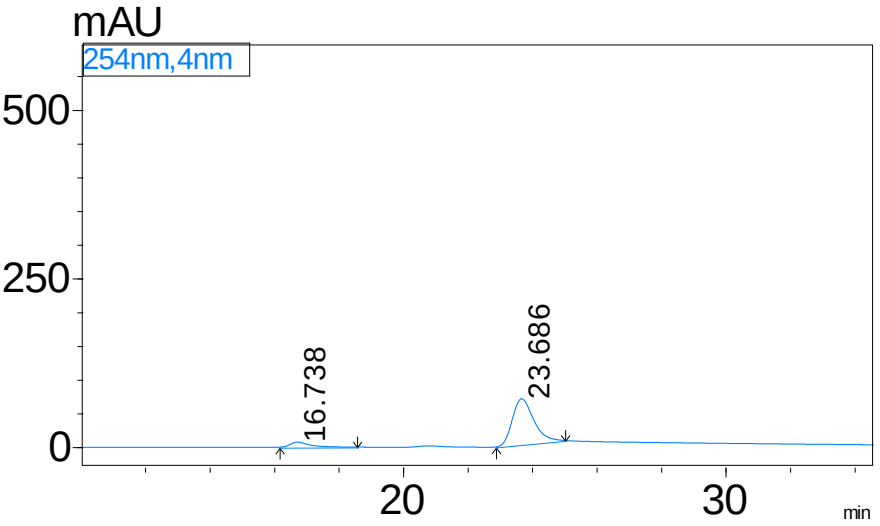
Peak	Time	Area	Height	Area%
1	29.349	2677835	37068	3.433
2	32.606	75322355	584800	96.567



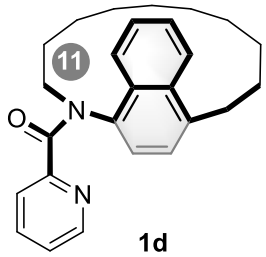
3da



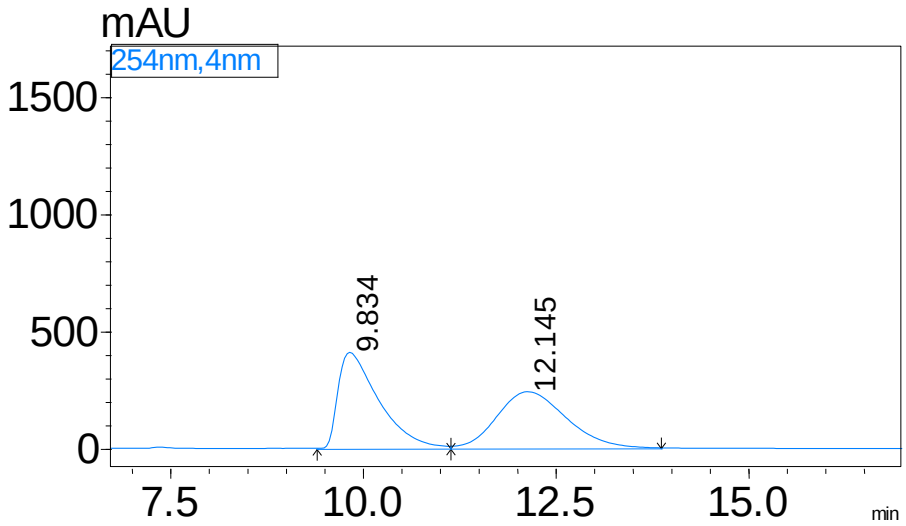
Peak	Time	Area	Height	Area%
1	16.978	773278	20068	50.811
2	24.304	748597	15849	49.189



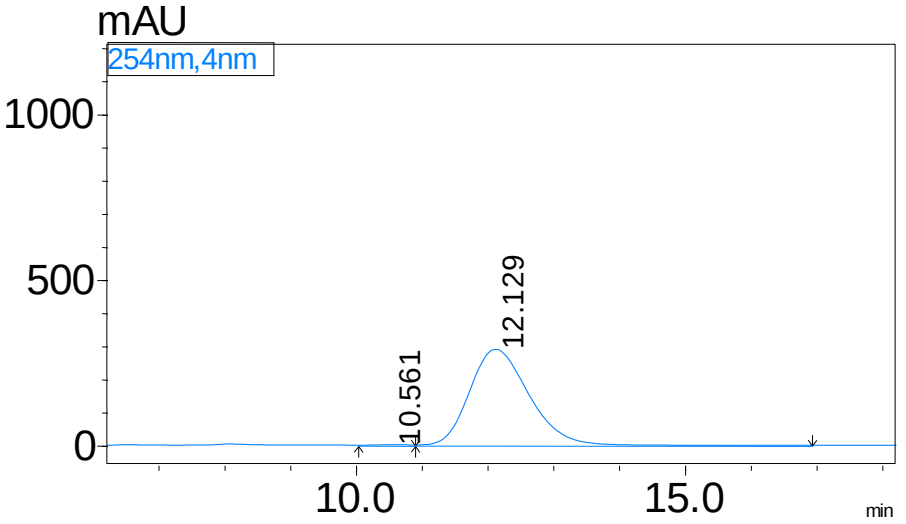
Peak	Time	Area	Height	Area%
1	16.738	311295	7510	9.062
2	23.686	3123910	67787	90.938



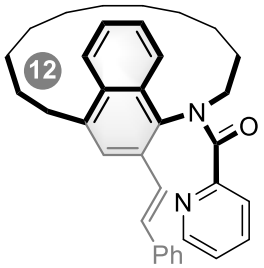
1d



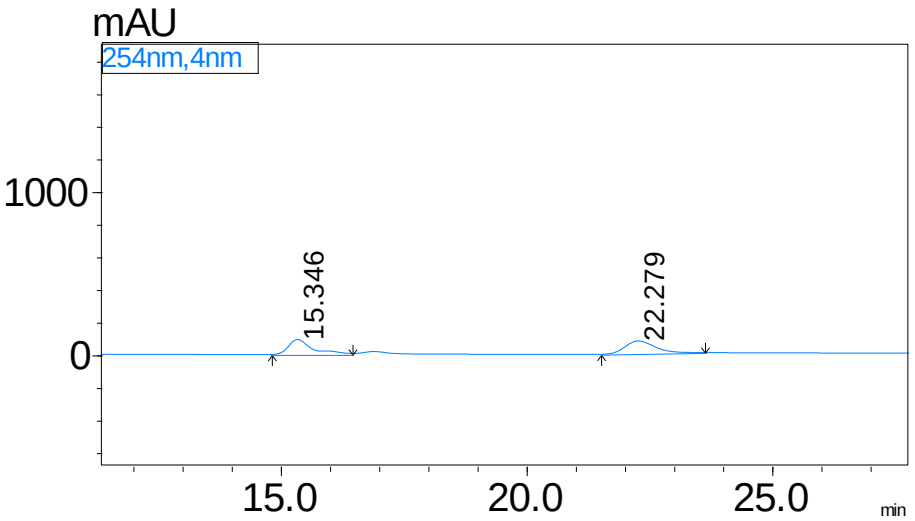
Peak	Time	Area	Height	Area%
1	9.834	15011372	409704	50.131
2	12.145	14932928	240451	49.869



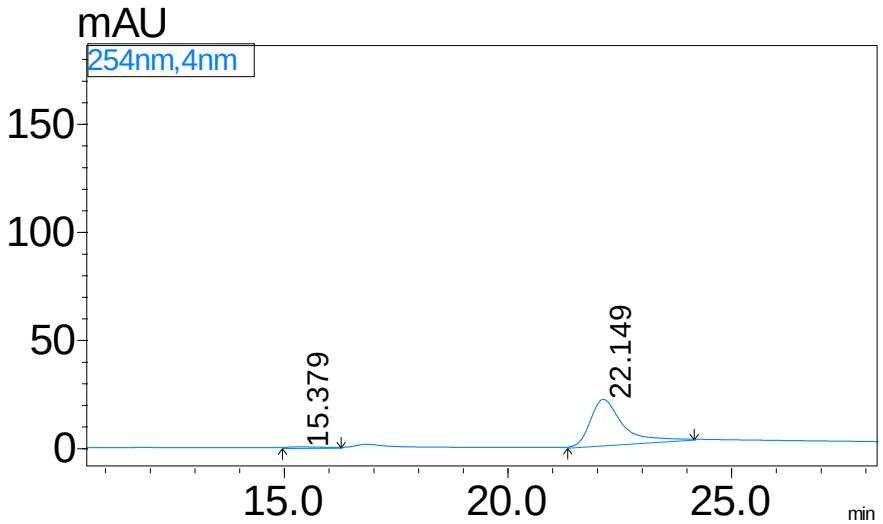
Peak	Time	Area	Height	Area%
1	10.561	75299	2118	0.413
2	12.129	18169201	290144	99.587



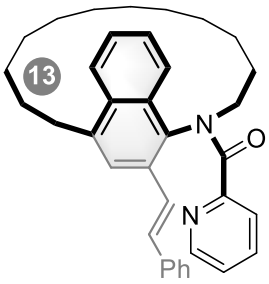
3ea



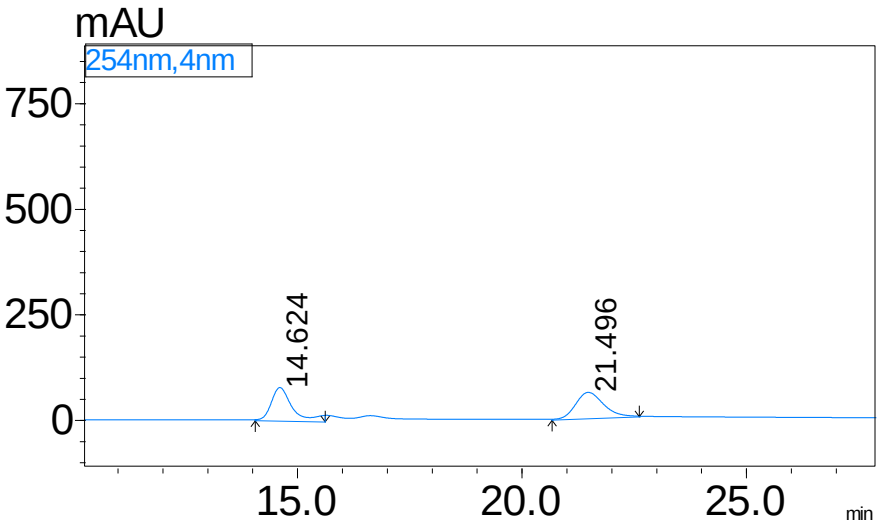
Peak	Time	Area	Height	Area%
1	15.346	3222731	91843	49.321
2	22.279	3311511	77849	50.679



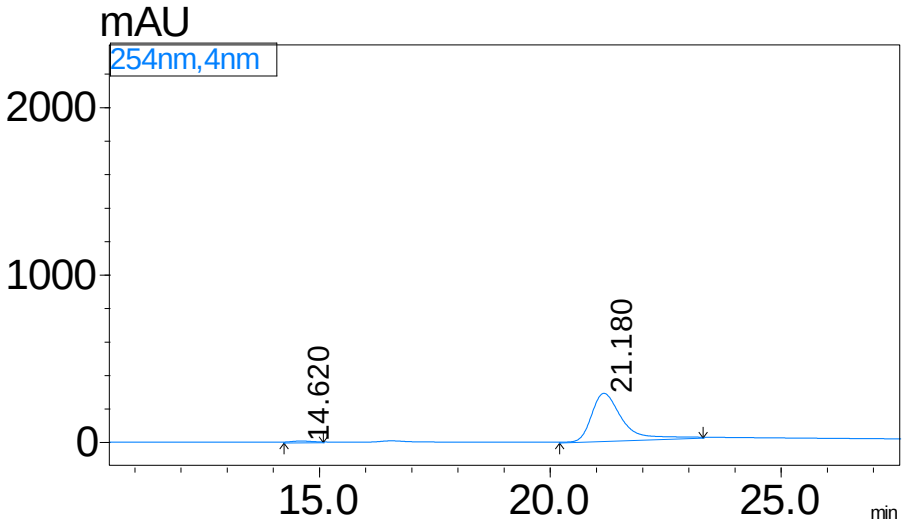
Peak	Time	Area	Height	Area%
1	15.379	10986	319	1.050
2	22.149	1035584	21071	98.950



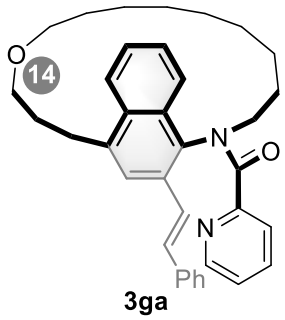
3fa



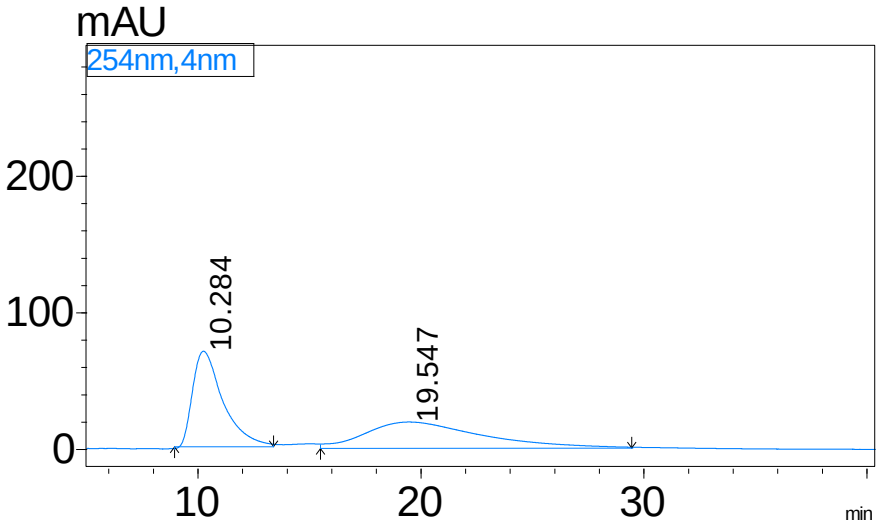
Peak	Time	Area	Height	Area%
1	14.624	2470825	77389	49.052
2	21.496	2566282	60634	50.948



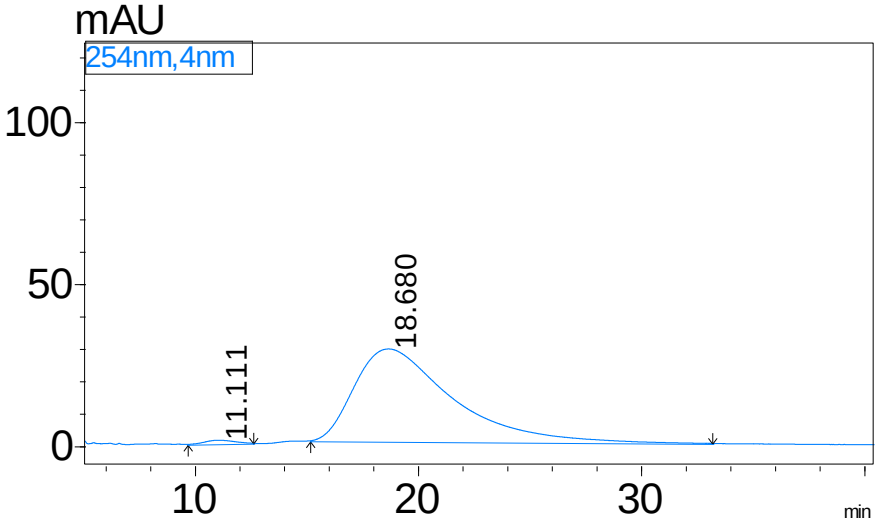
Peak	Time	Area	Height	Area%
1	14.620	154114	5946	1.219
2	21.180	12490074	281991	98.781



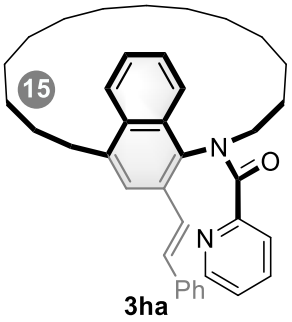
3ga



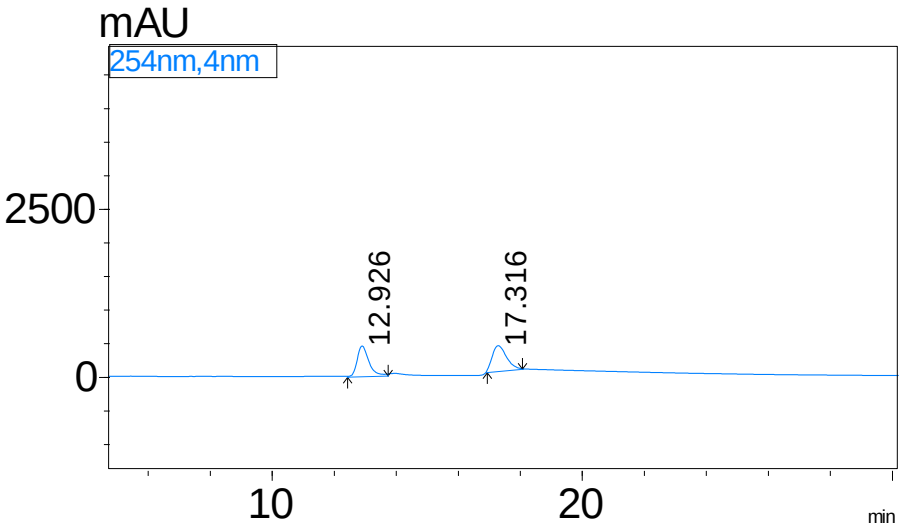
Peak	Time	Area	Height	Area%
1	10.284	6476815	69405	49.928
2	19.547	6495415	18630	50.072



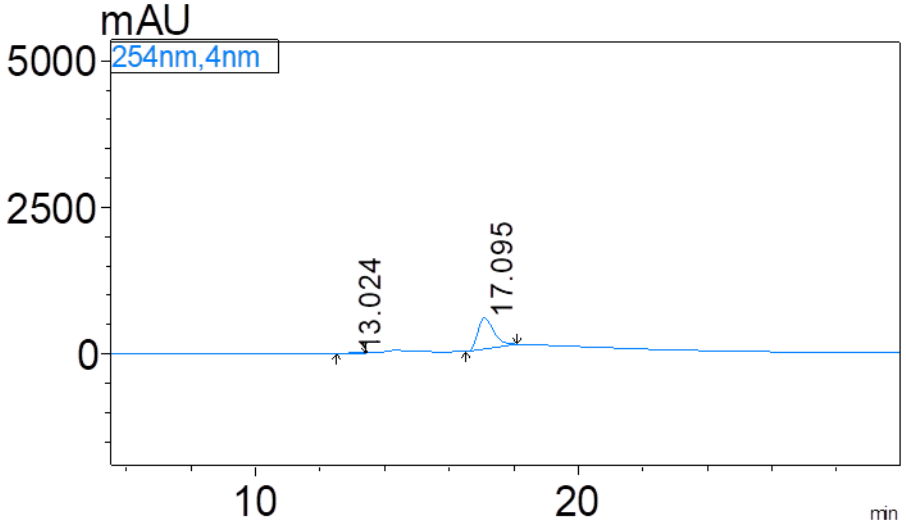
Peak	Time	Area	Height	Area%
1	11.111	97928	1111	1.121
2	18.680	8636525	28530	98.879



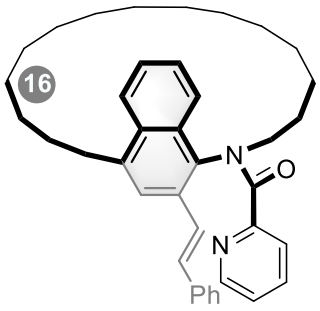
3ha



Peak	Time	Area	Height	Area%
1	12.926	11317790	447552	49.422
2	17.316	11582324	371561	50.578



Peak	Time	Area	Height	Area%
1	13.024	444620	13043	2.374
2	17.095	18284991	529305	97.626



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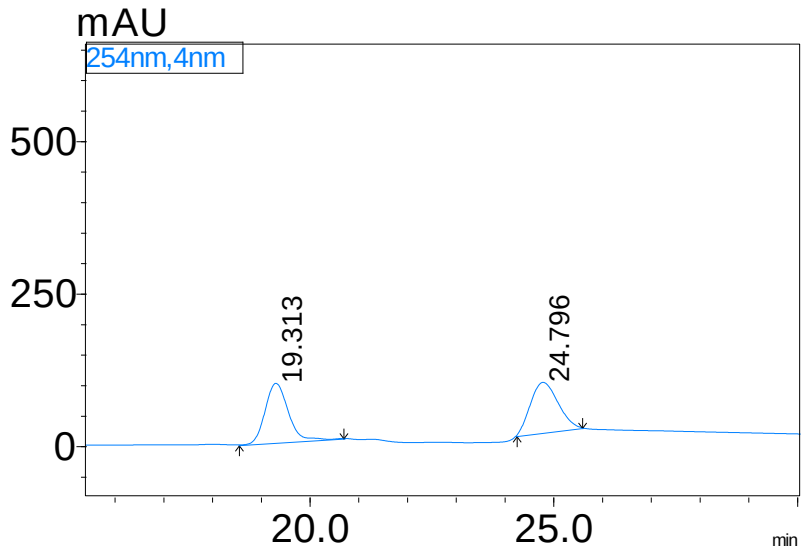
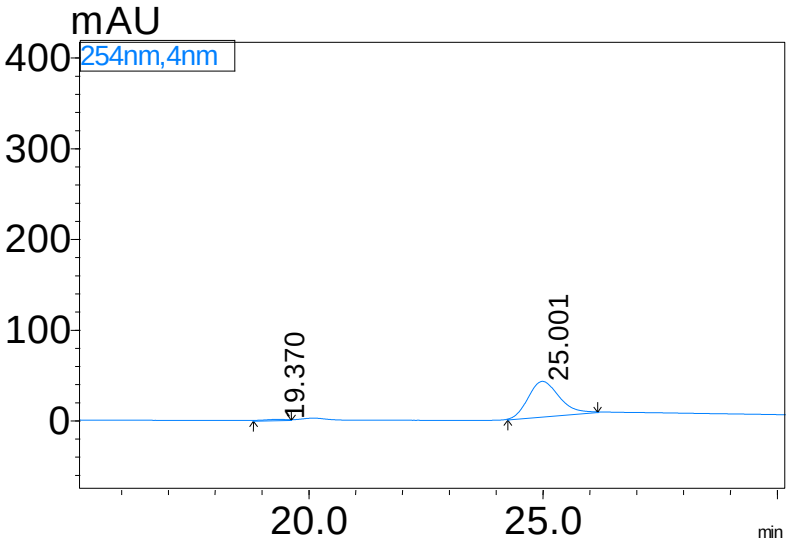
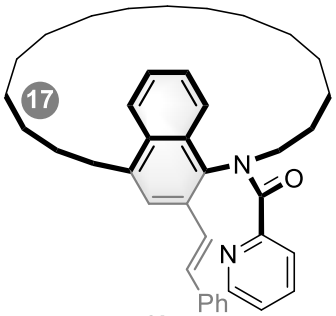


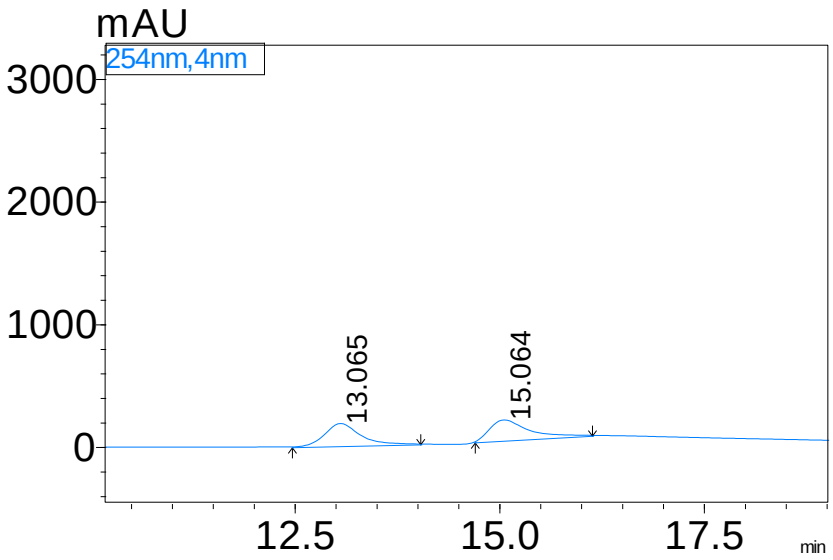
Peak	Time	Area	Height	Area%
1	19.313	3140849	97183	49.391
2	24.796	3218295	82104	50.609



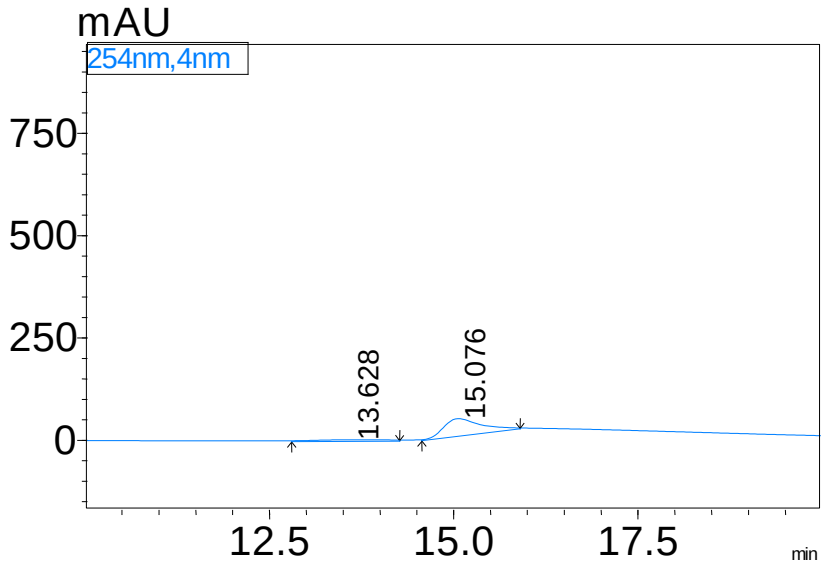
Peak	Time	Area	Height	Area%
1	19.370	13264	524	0.751
2	25.001	1752198	38573	99.249



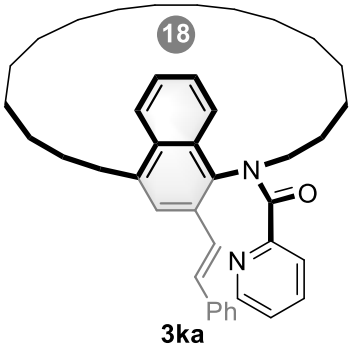
3ja



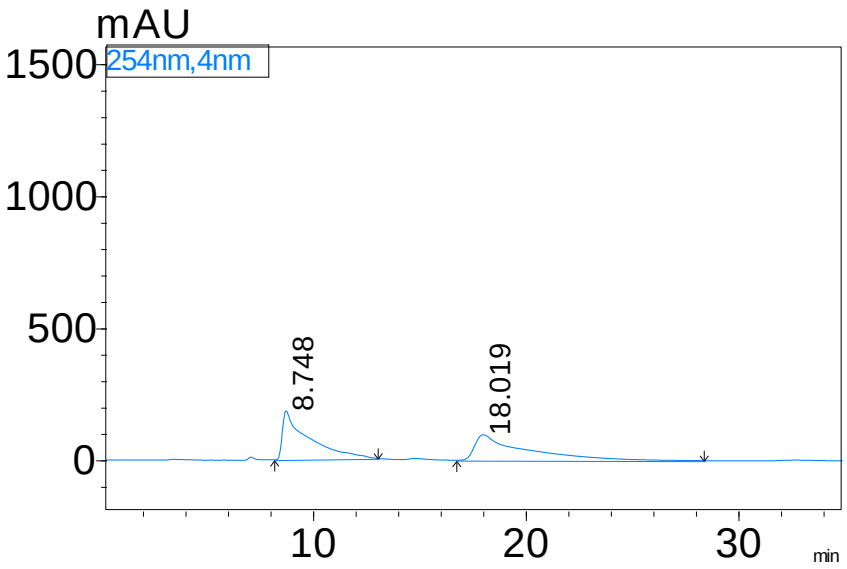
Peak	Time	Area	Height	Area%
1	13.065	5387210	182145	49.819
2	15.064	5426365	166559	50.181



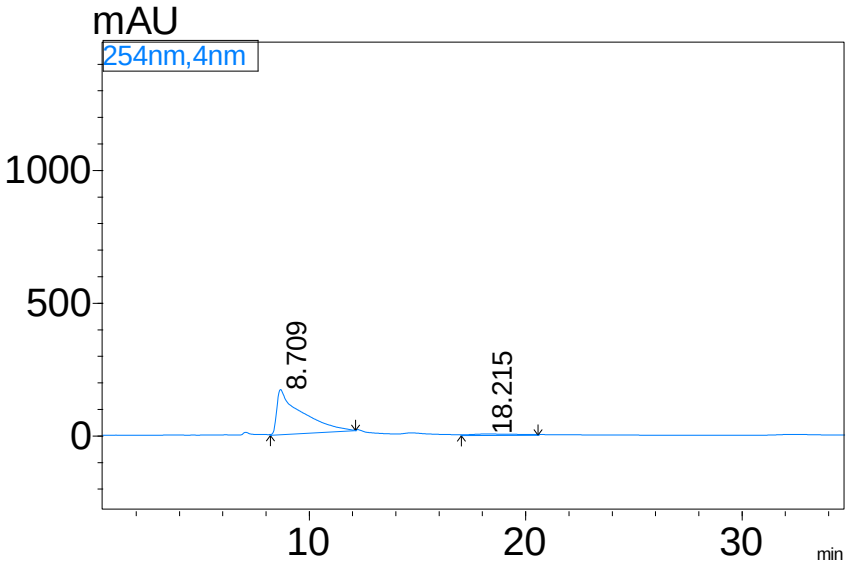
Peak	Time	Area	Height	Area%
1	13.628	64940	1215	4.471
2	15.076	1387443	40679	95.529



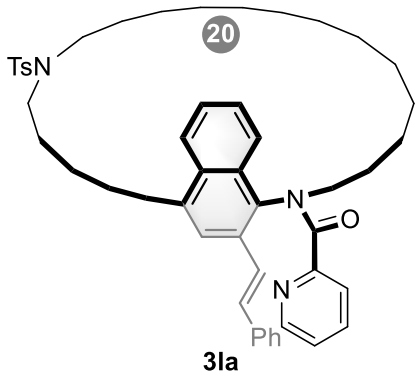
3ka



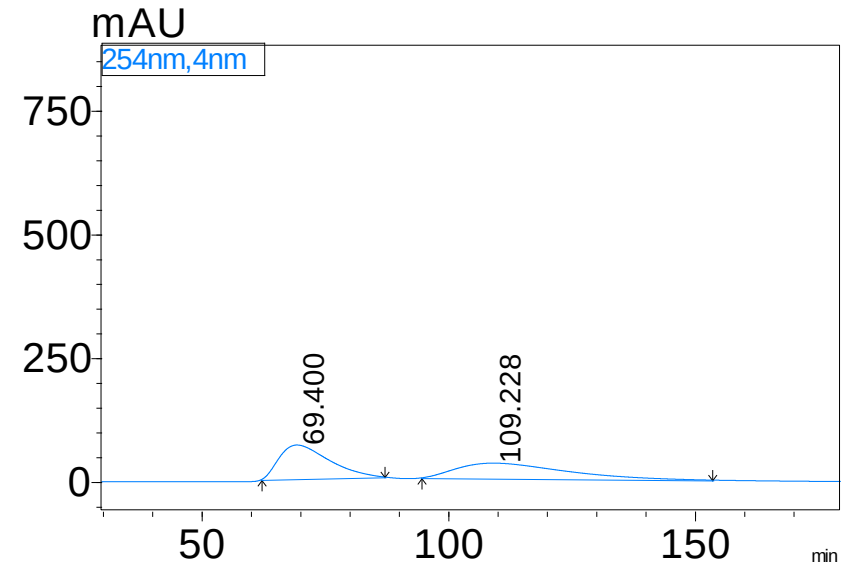
Peak	Time	Area	Height	Area%
1	8.748	15600907	184101	50.003
2	18.019	15599213	96855	49.997



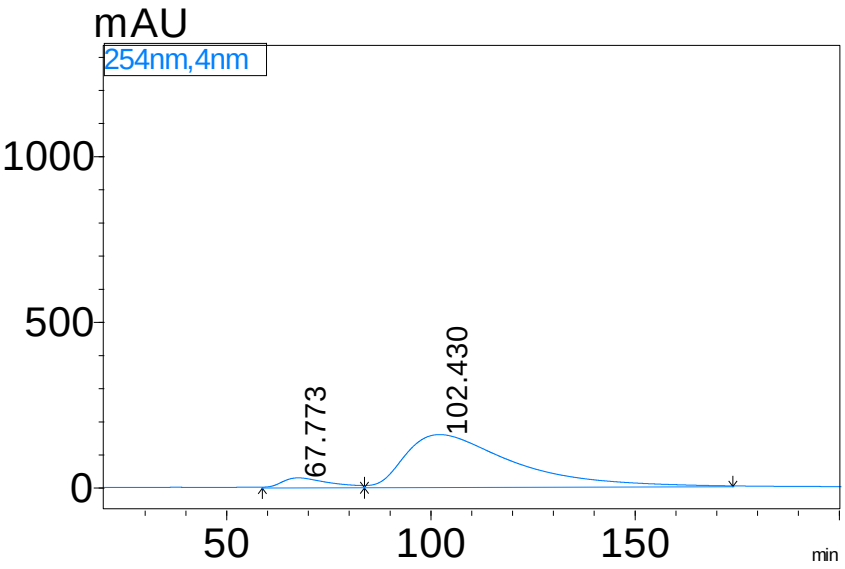
Peak	Time	Area	Height	Area%
1	8.709	12843848	167457	98.036
2	18.215	257317	2526	1.964



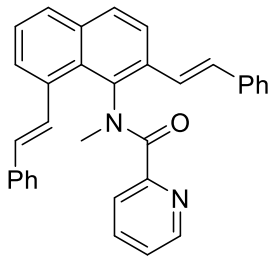
3la



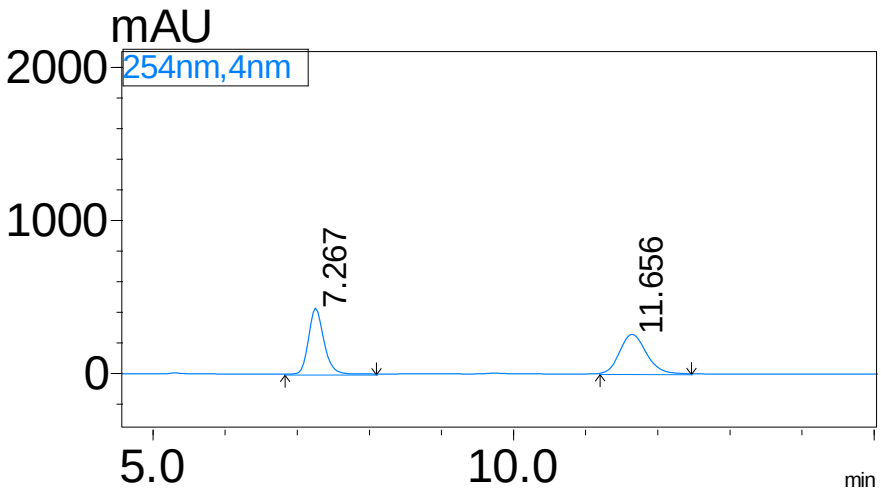
Peak	Time	Area	Height	Area%
1	69.400	47944688	68484	50.805
2	109.228	46426157	30900	49.195



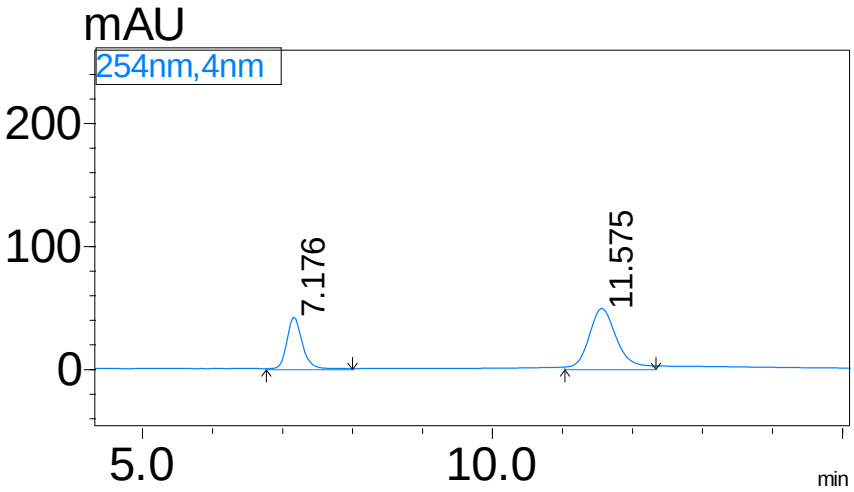
Peak	Time	Area	Height	Area%
1	67.773	20596345	27882	6.771
2	102.430	283593020	157308	93.229



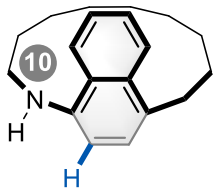
5



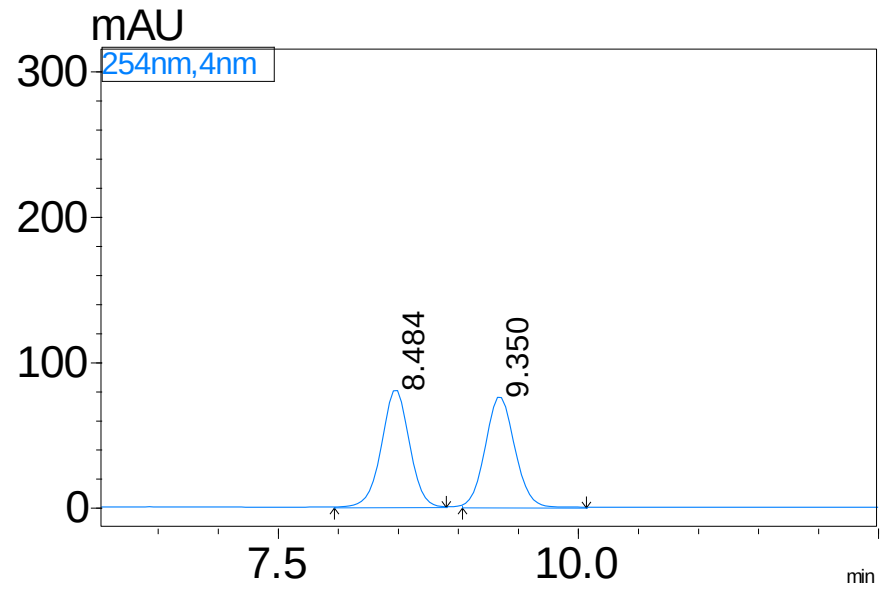
Peak	Time	Area	Height	Area%
1	7.267	6298379	431415	49.300
2	11.656	6477322	255993	50.700



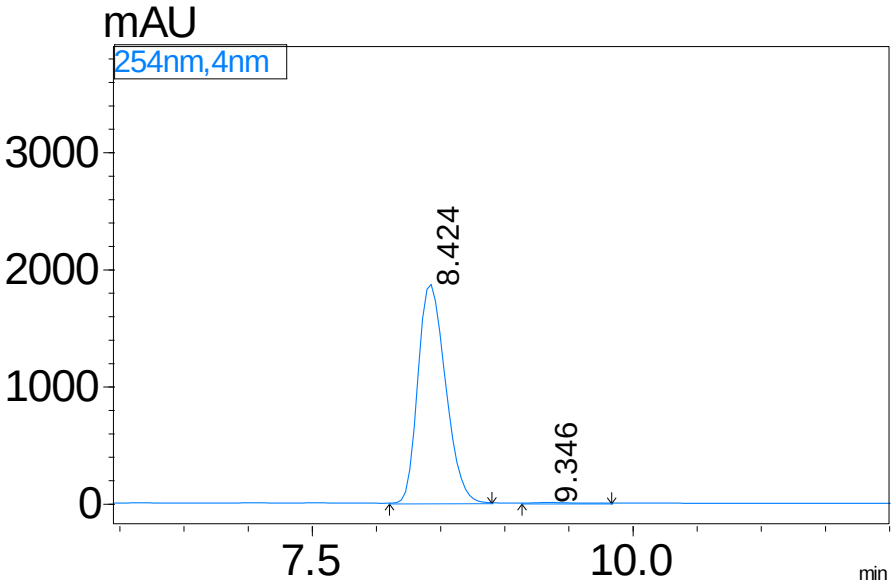
Peak	Time	Area	Height	Area%
1	7.176	627113	41800	31.753
2	11.575	1347888	48970	68.247



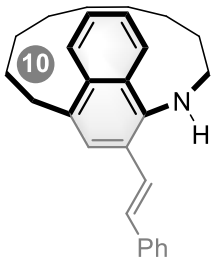
6



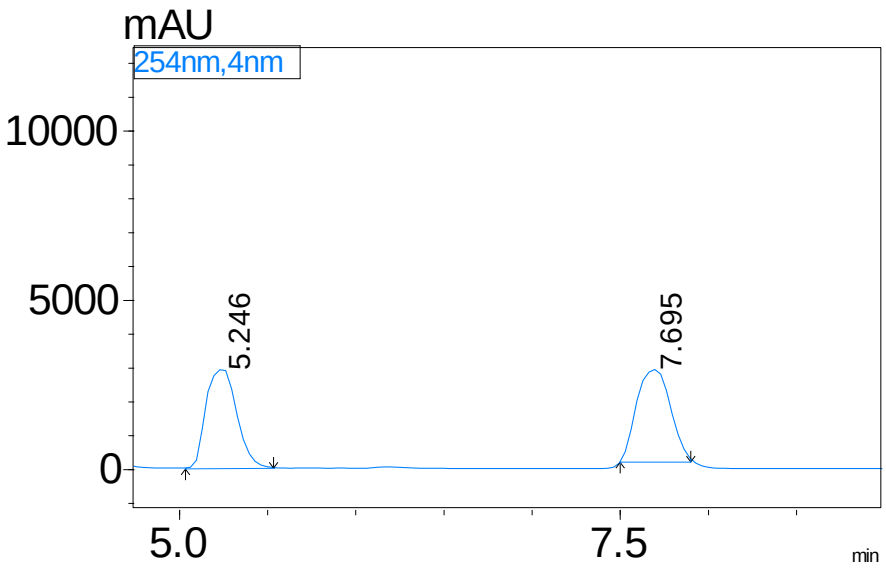
Peak	Time	Area	Height	Area%
1	8.484	1297929	79861	50.152
2	9.350	1290037	75405	49.848



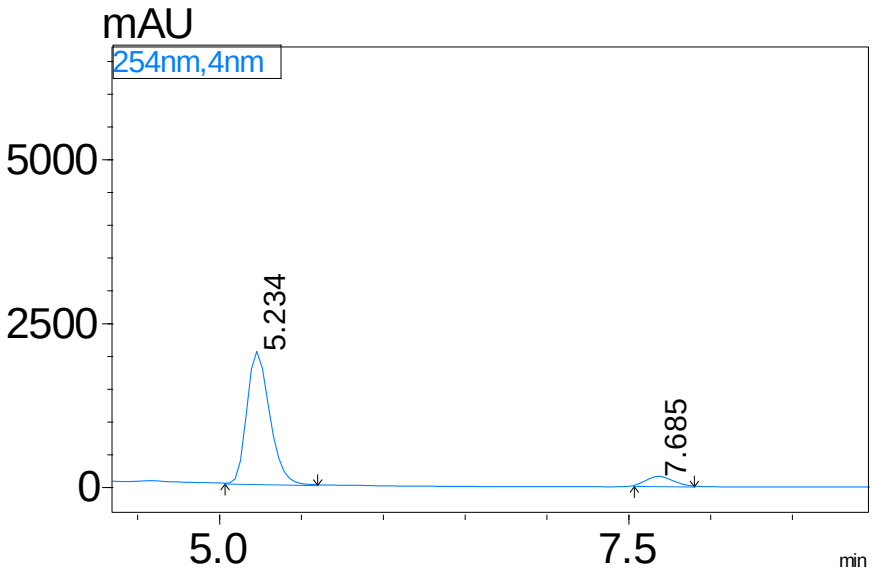
Peak	Time	Area	Height	Area%
1	8.424	27889098	1866138	99.759
2	9.346	67411	4574	0.241



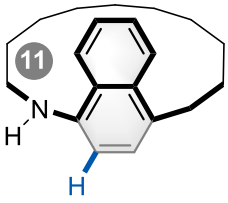
7



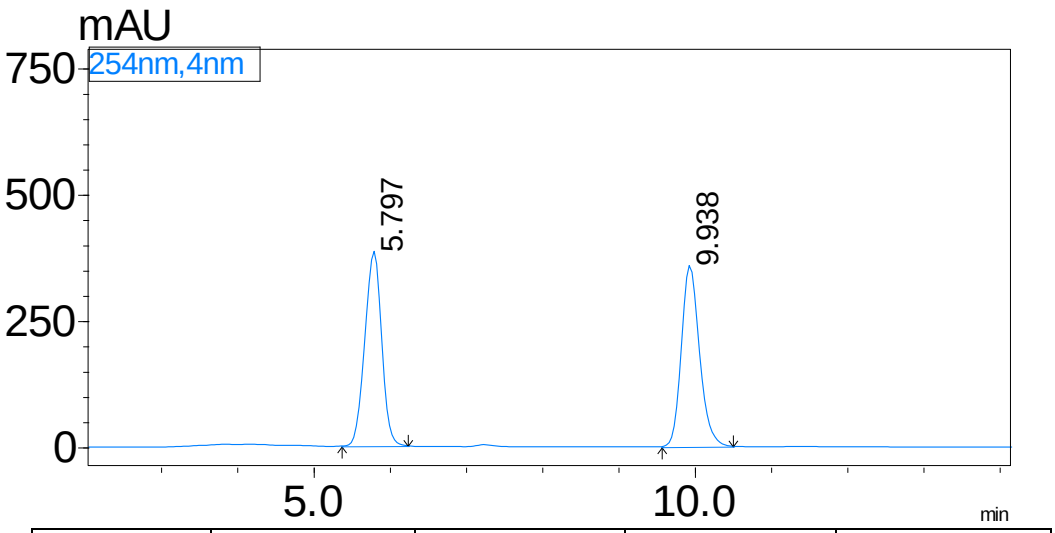
Peak	Time	Area	Height	Area%
1	5.246	34913372	2894743	49.250
2	7.695	35977155	2702655	50.750



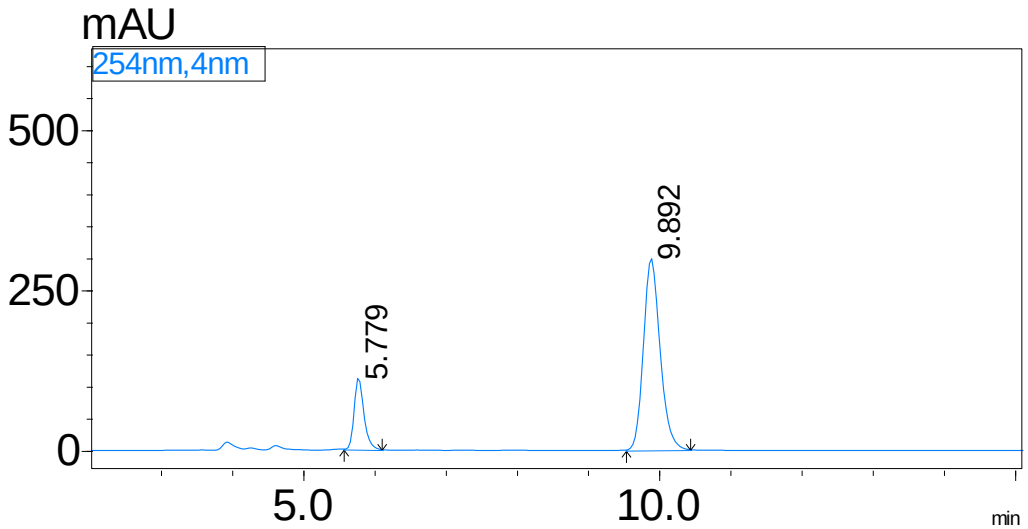
Peak	Time	Area	Height	Area%
1	5.234	19312596	2020698	92.492
2	7.685	1567662	142201	7.508



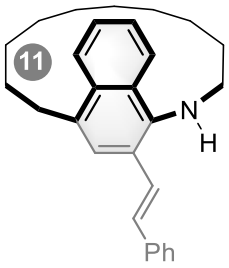
8



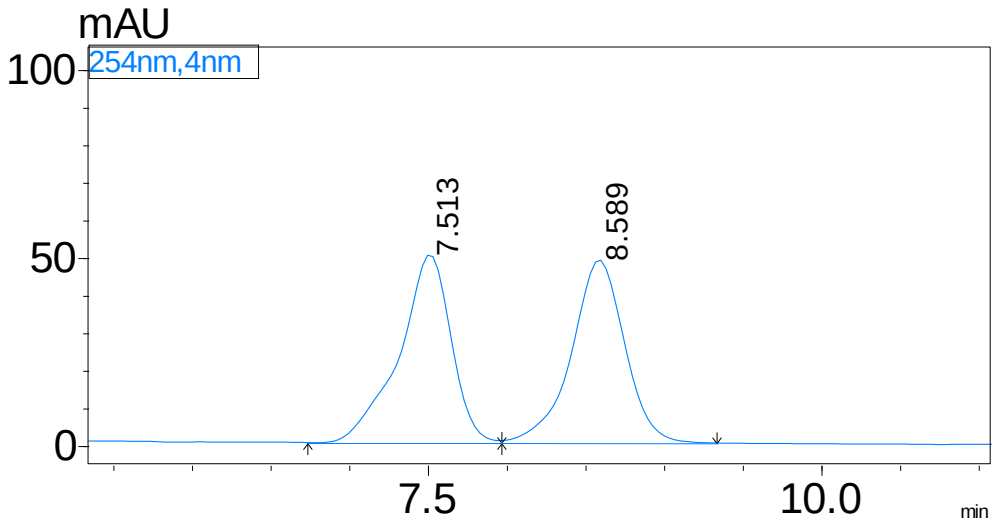
Peak	Time	Area	Height	Area%
1	5.797	5894286	385096	49.944
2	9.938	5907546	358247	50.056



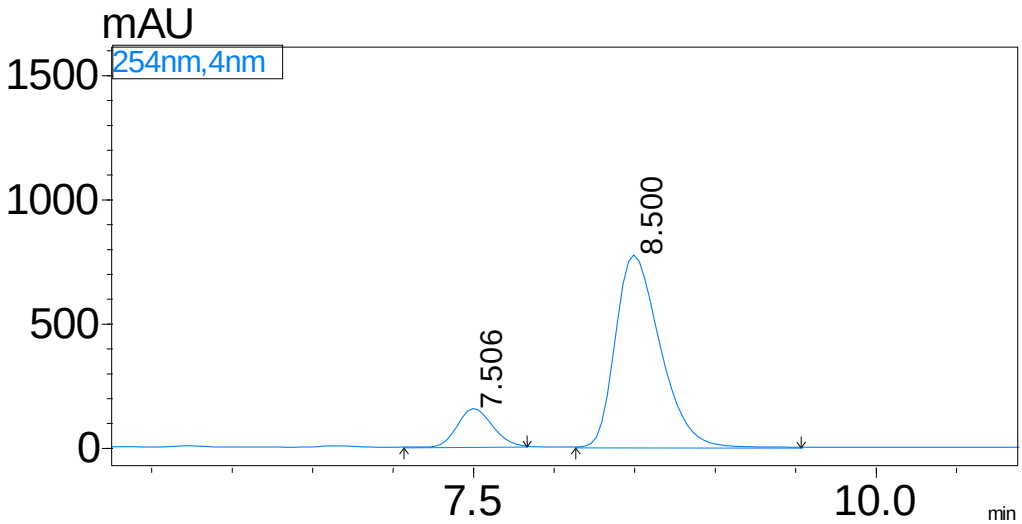
Peak	Time	Area	Height	Area%
1	5.779	1049594	110324	17.787
2	9.892	4851242	298231	82.213



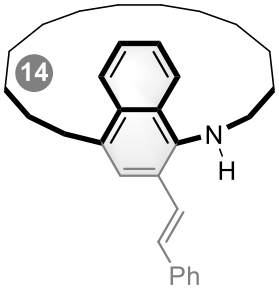
9



Peak	Time	Area	Height	Area%
1	7.513	1149286	49872	50.119
2	8.589	1143841	48585	49.881



Peak	Time	Area	Height	Area%
1	7.506	2277030	153186	13.288
2	8.500	14858780	773040	86.712



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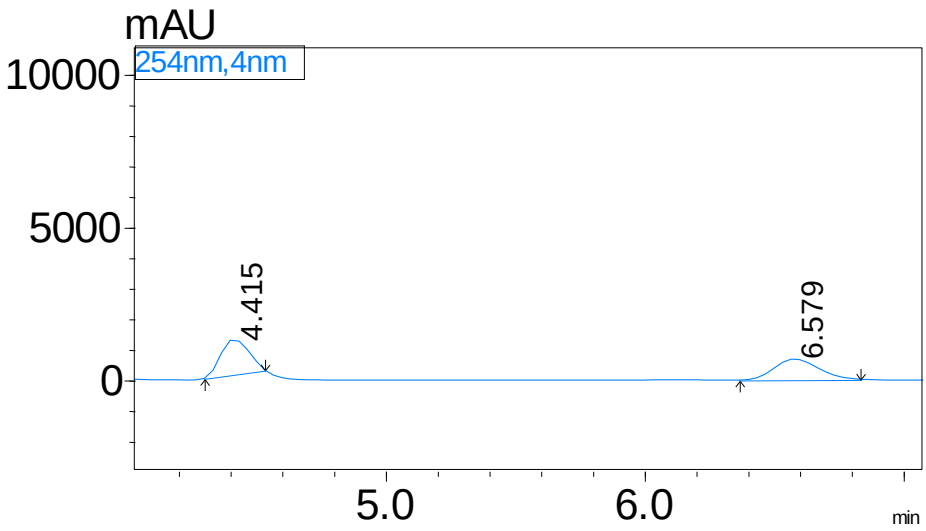
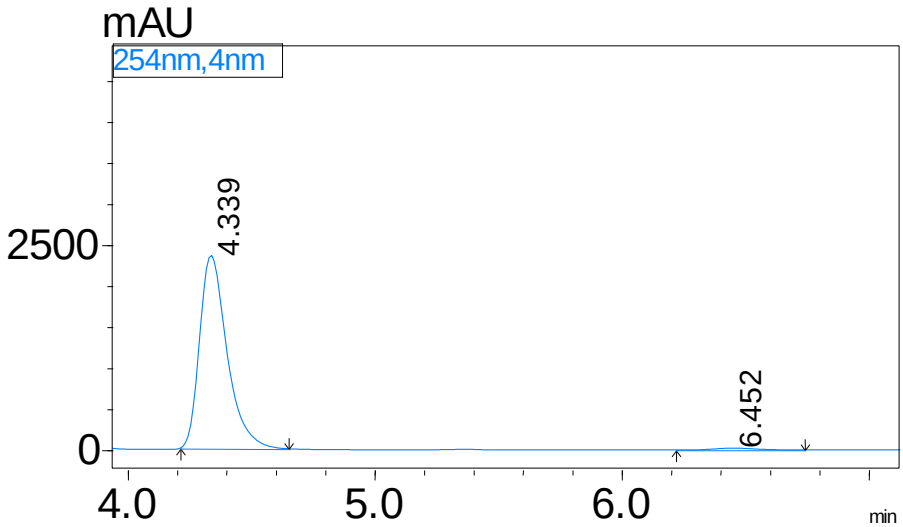
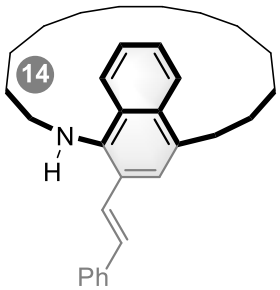


Peak	Time	Area	Height	Area%
1	4.415	8814550	1113061	52.618
2	6.579	7937563	670141	47.382



Peak	Time	Area	Height	Area%
1	4.339	18155921	2352865	98.697
2	6.452	239729	21545	1.303



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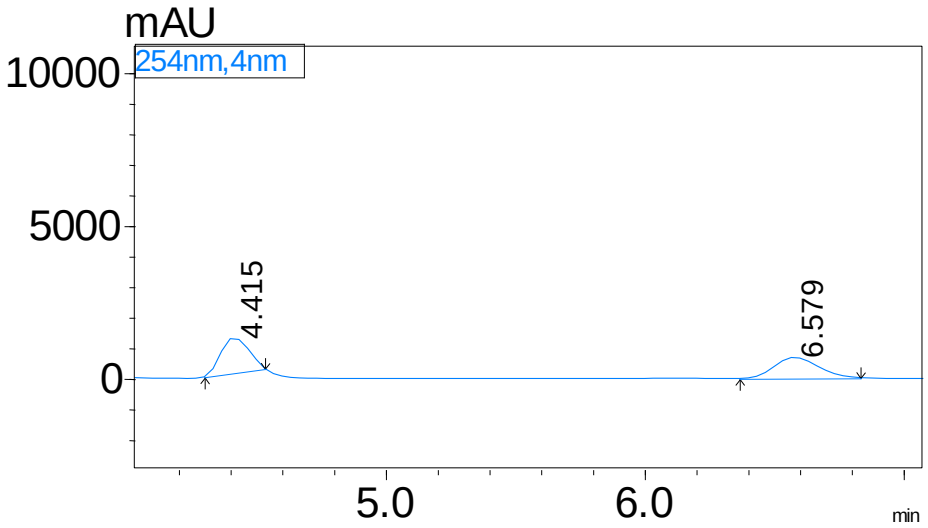
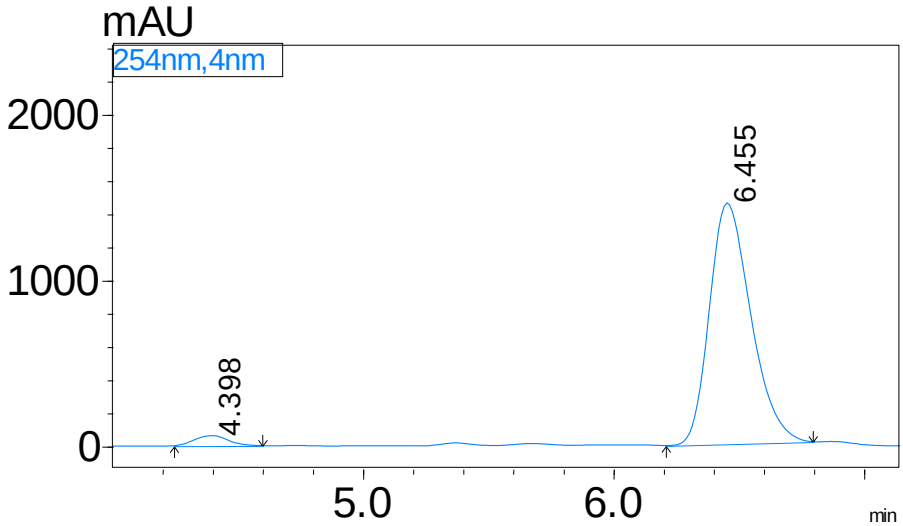
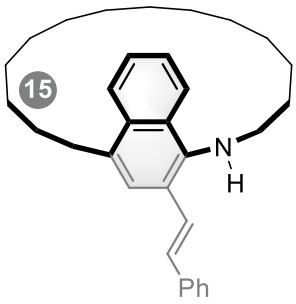


Peak	Time	Area	Height	Area%
1	4.415	8814550	1113061	52.618
2	6.579	7937563	670141	47.382



Peak	Time	Area	Height	Area%
1	4.398	557682	60741	3.236
2	6.455	16676391	1452048	96.764



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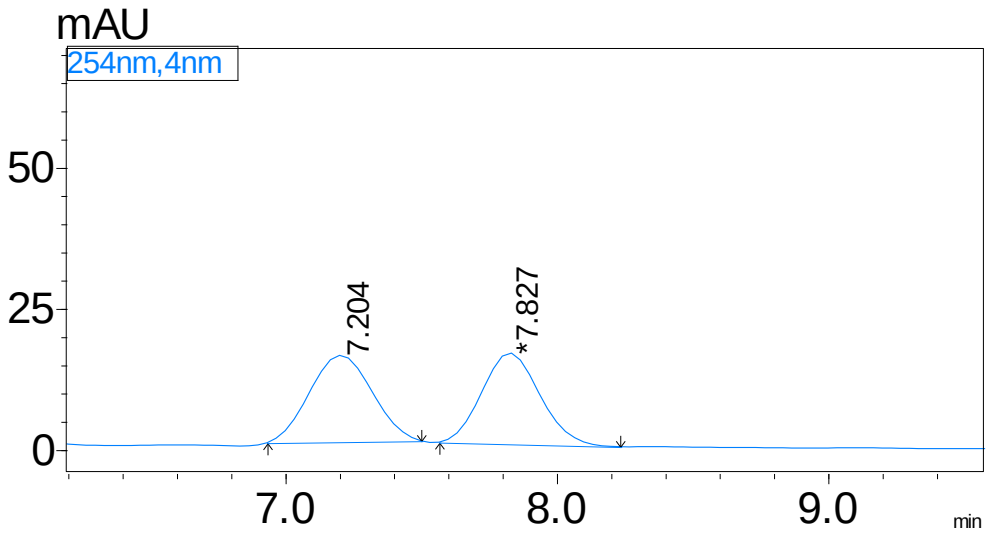
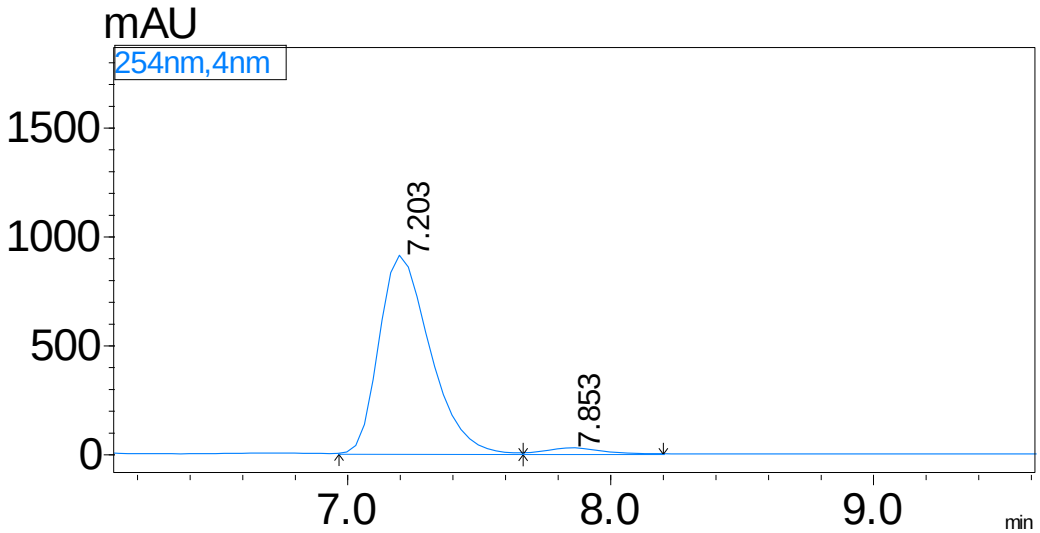
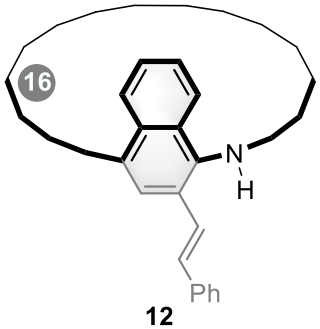


Peak	Time	Area	Height	Area%
1	7.204	244918	15334	50.666
2	7.827	238477	16099	49.334



Peak	Time	Area	Height	Area%
1	7.203	12212243	909591	97.129
2	7.853	360987	26761	2.871



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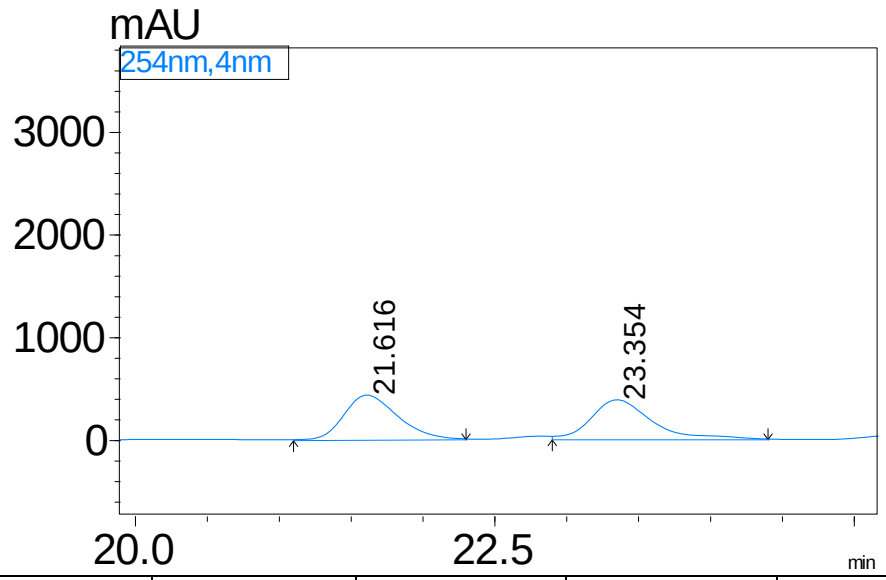
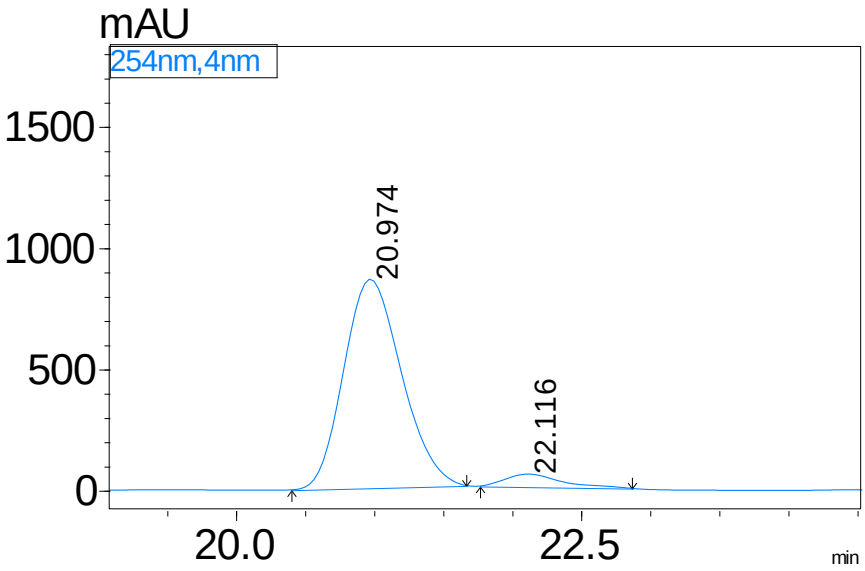
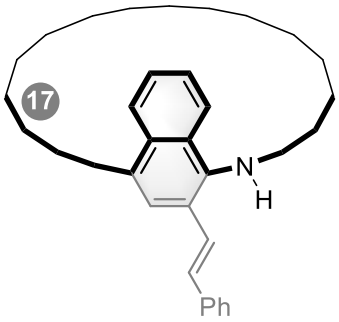


Peak	Time	Area	Height	Area%
1	21.616	10977204	429486	49.988
2	23.354	10982621	380653	50.012



Peak	Time	Area	Height	Area%
1	20.974	25050484	860259	94.548
2	22.116	1444441	51933	5.452



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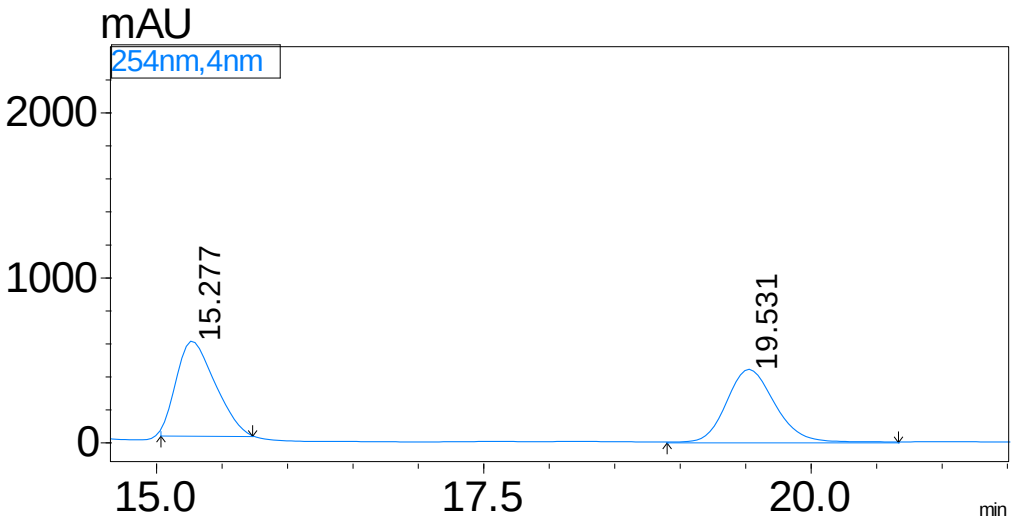
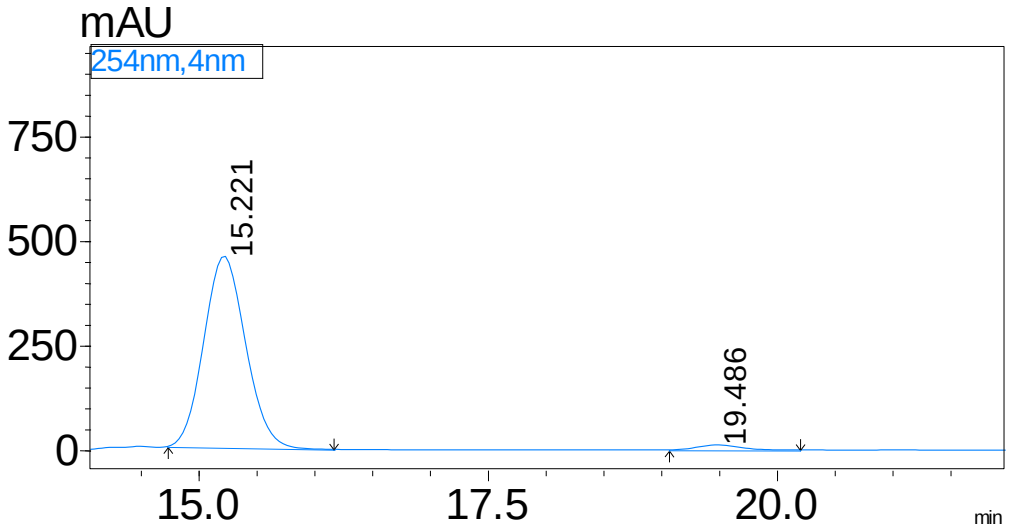
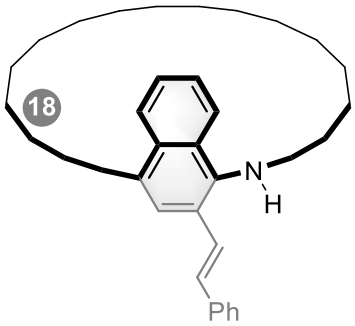


Peak	Time	Area	Height	Area%
1	15.277	11659217	569944	50.980
2	19.531	11210869	441037	49.020



Peak	Time	Area	Height	Area%
1	15.221	11475507	456785	97.508
2	19.486	293251	11881	2.492



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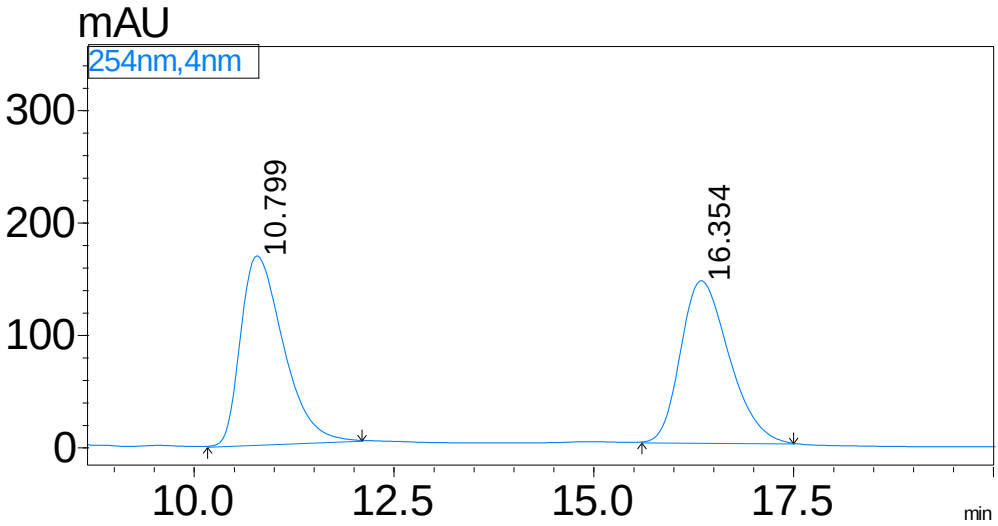
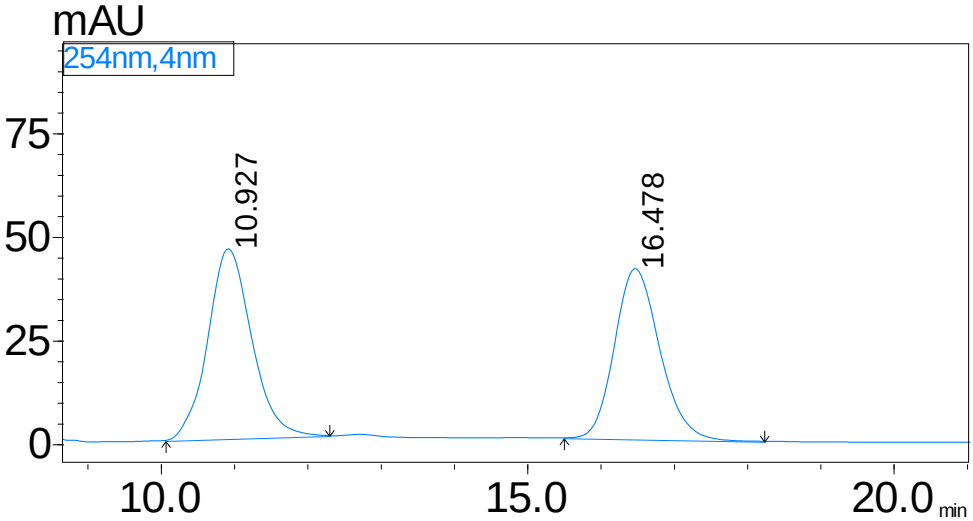
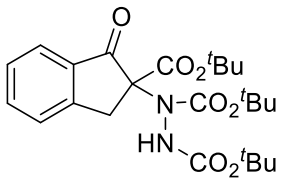


Peak	Time	Area	Height	Area%
1	10.799	6220882	167877	50.673
2	16.354	6055691	143915	49.327



Peak	Time	Area	Height	Area%
1	10.927	1908950	45824	52.080
2	16.478	1756459	41107	47.920



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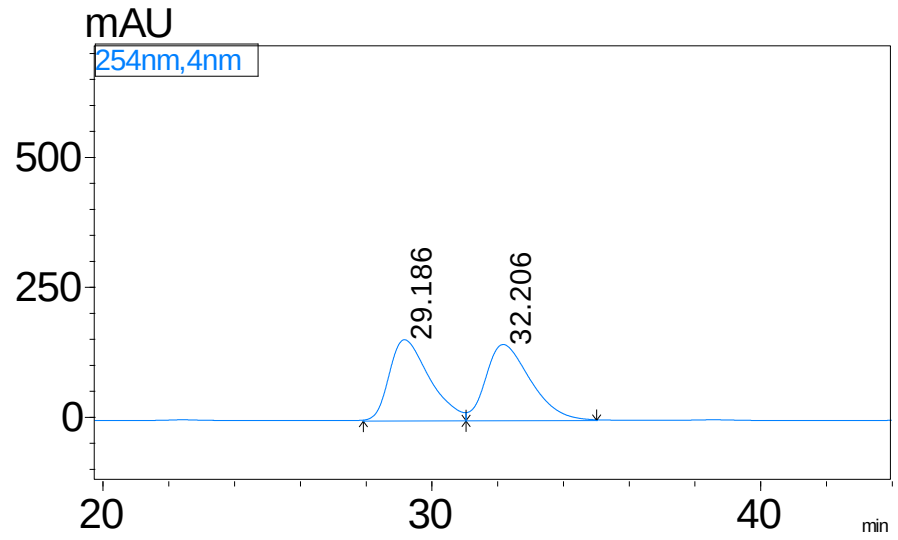
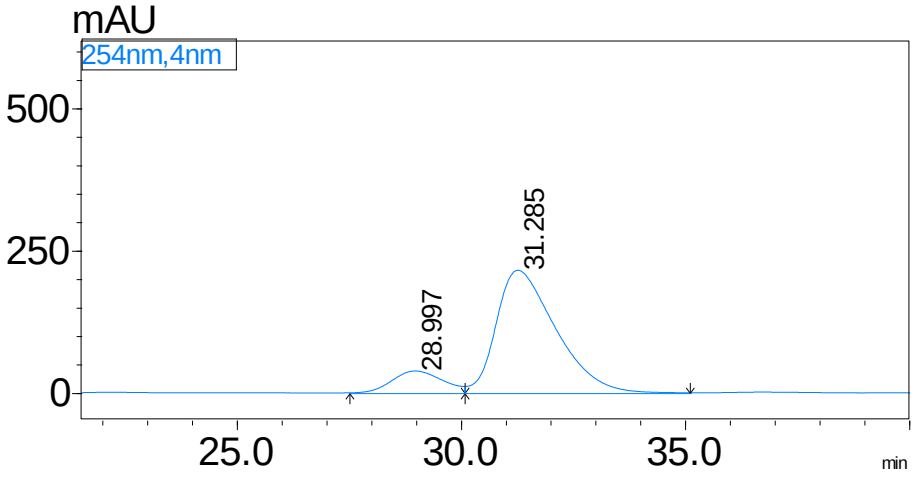
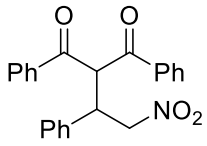


Peak	Time	Area	Height	Area%
1	29.186	13039276	154564	49.051
2	32.206	13544013	145016	50.949



Peak	Time	Area	Height	Area%
1	28.997	2970267	38352	13.041
2	31.285	19806168	215308	86.959



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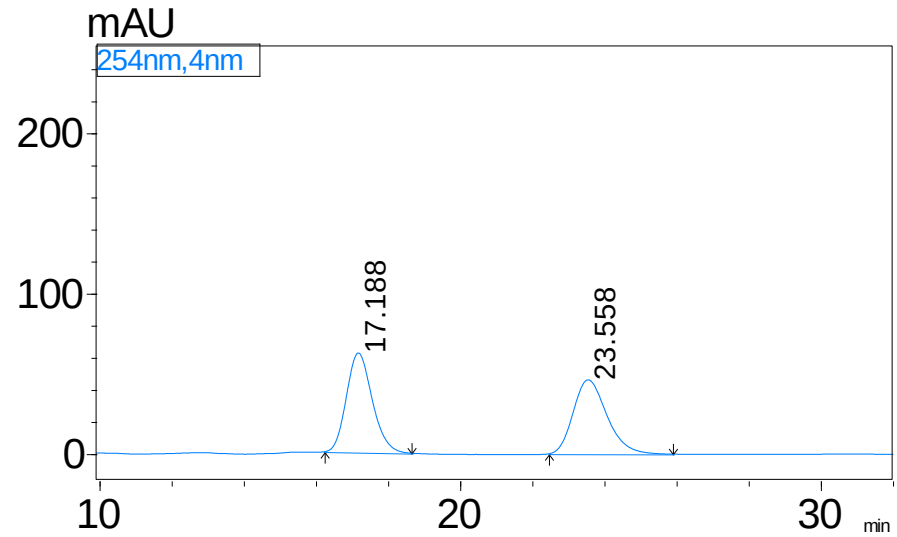
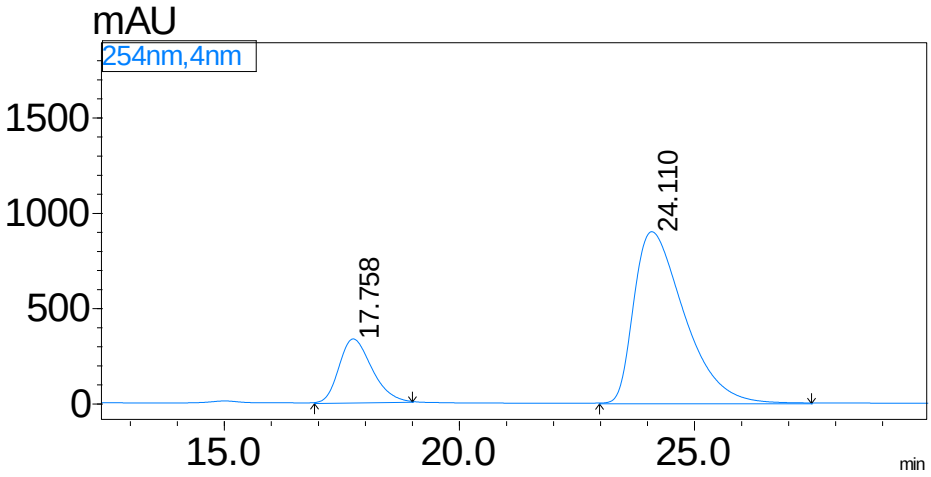


Peak	Time	Area	Height	Area%
1	17.188	3076733	61944	50.684
2	23.558	2993632	46236	49.316



Peak	Time	Area	Height	Area%
1	17.758	16272798	333918	19.555
2	24.110	66942408	898967	80.445