Supporting Information (SI) for

Successive energy-transfer catalytic dearomative reactions of quinolines with bicyclo[1.1.0]butanes for synthesis of pyridine-fused 3d complicated molecules

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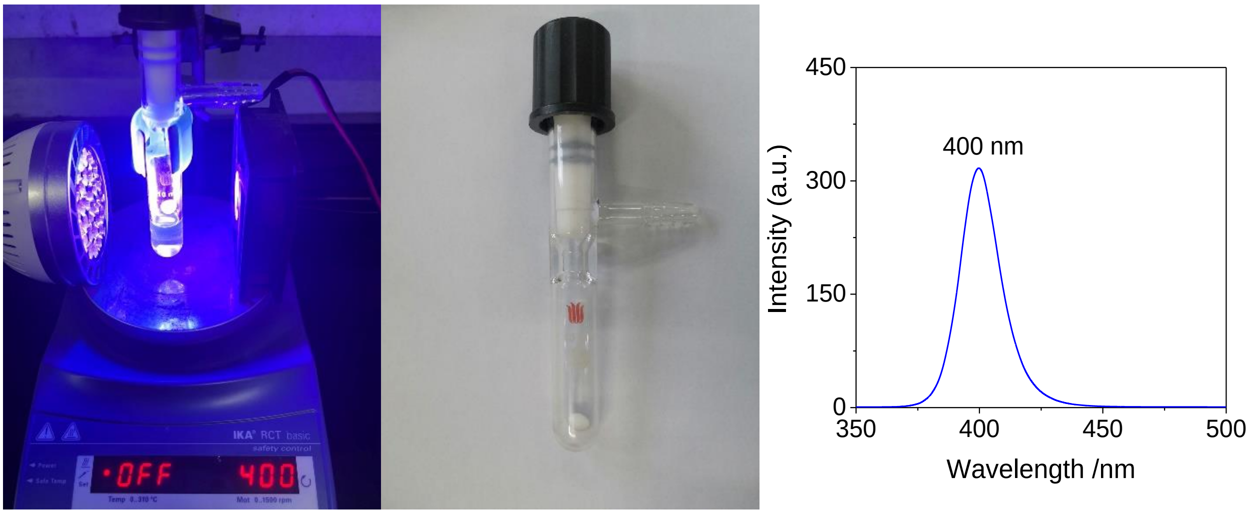
Contents

1. Materials and general methods

Unless otherwise specified, all chemicals and solvents were obtained from commercial suppliers and used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR) or on a Bruker Ascend 500 MHz spectrometer (500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR). The chemical shifts (δ) for ^{1}H and ^{13}C are reported in ppm and are referenced to Me_4Si (TMS) and the residual undeuterated solvent resonances (TMS at 0.00 ppm; $CHCl_3$ at 7.26 ppm ^{1}H NMR and 77.16 ppm ^{13}C NMR respectively). ^{19}F NMR spectra are not calibrated by an internal reference. High resolution mass spectra (HRMS) were acquired using a Q-Exactive plus hybrid quadrupole-orbitrap mass spectrometer (Q-Orbitrap MS) (Thermo Scientific, San Jose, USA) with electrospray ionization (ESI) source. The blue LEDs lamp (inner diameter of 9.5 cm, λ_{max}= 400 nm, 25 W) with fan fort heat dissipation, purchased from Xuzhou Aijia Electronic Technology Company Ltd., was employed as a visible light source without the use of filters.

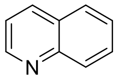


(a) (b) (c)

Figure S1. (a) The photochemical setup with a 10 mL Schlenk tube, a 25 W blue LEDs (left) and a fan (right), (b) a Schlenk reaction tube; (c) the emission spectrum of the LEDs.

2. Experimental procedures and characterization data

2.1 Synthesis of starting materials



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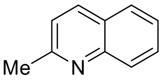

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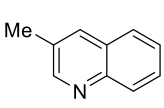

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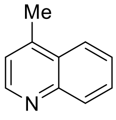

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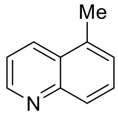

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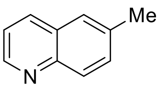

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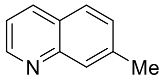

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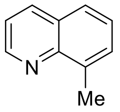

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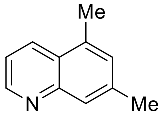

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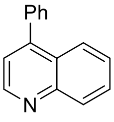

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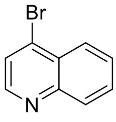

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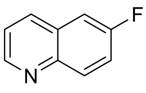

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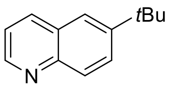

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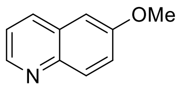

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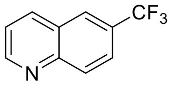

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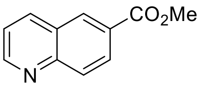

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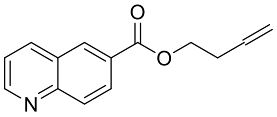

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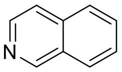

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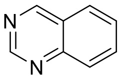

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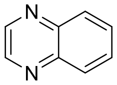
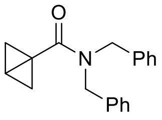


1t

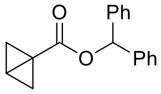
Compounds **1a-1h**, **1k**, **1l**, **1o**, **1p**, **1r-1t** are commercially available and were used as received. The substrate quinolines **1i**, **1m**, **1n** are literature known and were prepared according to known literature procedure[1]. The substrate quinolines **1j**, **1q** were prepared according to known literature procedure[2] and **Step 1** of ***General Procedure 1***, respectively.

Synthesis and characterization of some bicyclo[1.1.0]butanes (BCBs)

The substrate BCBs, **2a-2j**, **2u-2w**, were prepared according to a modified literature procedure by M. Kevin Brown and coworkers.[3]



2a



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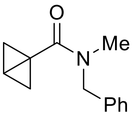

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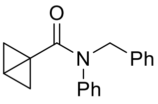

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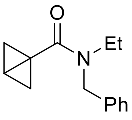
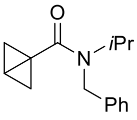


2b



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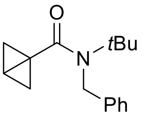

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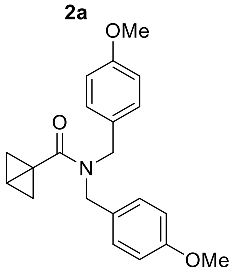

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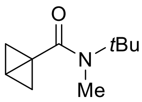

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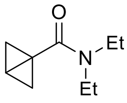

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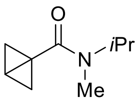

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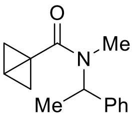

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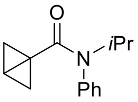
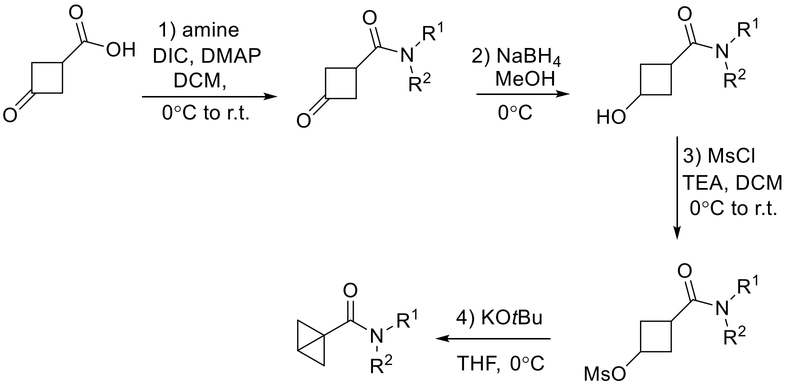


2j

General Procedure 1 for the synthesis of BCBs:

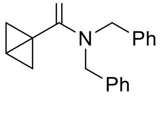


Step 1: The solution of secondary amine (1.0 equiv.), 3-oxocyclobutanecarboxylic acid (1.2 equiv.), DMAP (0.2 equiv.), and DCM (0.14 M) were stirred at 0 °C for 10 mins. After that, DIC (1.2 equiv.) was added dropwise and the solution was warmed to room temperature until the secondary amine was consumed (monitored by TLC). After the reaction was completed, then the precipitate was filtered off and the solution was concentrated under vacuum. Corresponding amide were further purified by column chromatography.

Step 2: The solution of above ketone (1.0 equiv.) and MeOH (1.0 M) were stirred at 0 °C in an ice/water bath for 10 mins. $NaBH_4$ (0.5 equiv. x 4) was added in 4 portions over 10 min (No special caution for avoid O_2 and H_2O in this reaction. Caution needed for gas evolution during addition of $NaBH_4$.). Then the reaction was stirred for 1 h until the ketone was consumed (monitored by TLC). After quenched with H_2O, the solution was concentrated by rotary evaporation to remove most MeOH. The residue was diluted with H_2O and extracted with EtOAc. The combined organic layers were washed with saturated NH_4Cl, dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The crude alcohol was directly used in next reaction without further purification.

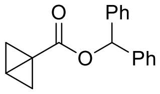
Step 3: The solution of above crude alcohol (1.0 equiv.) and DCM (1.0 M) were stirred at 0 °C in an ice/water bath for 10 mins. MsCl (1.3 equiv.) and Et_3N (1.3 equiv.) were added dropwise in sequence. The reaction was naturally warmed to room temperature and stirred for 12 h. If the alcohol was not consumed completely (monitored by TLC), additional MsCl (1.3 equiv.) and Et_3N (1.3 equiv.) need to be added following the steps above. After quenched with H_2O, the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. Corresponding methylsulfonate were further purified by column chromatography.

Step 4: The solution of methylsulfonate (1.0 equiv.) and THF (0.2 M) were stirred at 0 °C in an ice/water bath for 10 mins. KO*t*Bu (1.0 equiv. x 2) was added slowly in 2 portions over 10 min (monitored by TLC). The solution became viscous after addition of KO*t*Bu. The mixture was vigorously stirred for 15 min at the same temperature and quenched with saturated NH_4Cl solution. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. Corresponding BCBs were further purified by column chromatography.

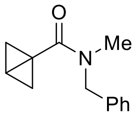


N, N-dibenzylbicyclo[1.1.0]butane-1-carboxamide (2a):[4] The compound **2a** was prepared from dibenzylamine following ***General Procedure 1*** and was obtained as a white solid by column chromatography (petroleum ether/EtOAc= 5/1). Spectroscopic data of **2a** was obtained as a mixture of two rotational isomers. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 6H), 7.21-7.18 (m, 4H), 4.82 (s, 2H), 4.57 (s, 2H), 2.27 (d, J = 3.3Hz, 2H), 2.12-2.09

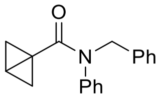
(m, 1H), 1.11 (d, *J* = 2.2Hz, 2H).



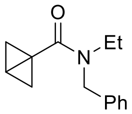
benzhydryl bicyclo[1.1.0]butane-1-carboxylate (2u): The compound **2u** was prepared from diphenylmethanol following ***General Procedure 1*** and was obtained as a white solid by column chromatography (petroleum ether/EtOAc= 10/1). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 8H), 7.29-7.25 (m, 2H), 6.90 (s, 1H), 2.45 (d, *J* =3.4Hz, 2H), 2.10-2.08 (m, 1H), 1.21 (d, *J* =6.6Hz, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 172.2, 140.4, 128.5, 127.9, 127.0, 76.9, 35.9, 16.9, 9.4. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 265.1223. Correlated peaks are not found probably due to the decomposition.



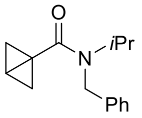
N-benzyl-N-methylbicyclo[1.1.0]butane-1-carboxamide (2v): The compound **2v** was prepared from N-methyl-1-phenylmethanamine following ***General Procedure 1*** and was obtained as a colourless liquid by column chromatography (petroleum ether/EtOAc= 5/1). Spectroscopic data of **2v** was obtained as a mixture of two rotational isomers. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.20 (m, 5H), 4.91-4.61 (m, 2H), 3.15-2.91 (m, 3H), 2.28-2.22 (m, 2H), 2.03 (s, 1H), 1.74-1.72 (m, 1H), 1.19-1.09 (m, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 172.0, 171.7, 153.2, 137.3, 128.9, 128.6, 128.1, 127.5, 127.4, 126.6, 54.2, 53.5, 52.6, 51.0, 37.3, 36.8, 36.0, 33.7, 14.0, 13.0, 8.2. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 202.1226, found: 202.1251.



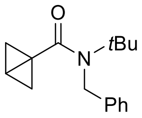
N-benzyl-N-phenylbicyclo[1.1.0]butane-1-carboxamide (2w): The compound **2w** was prepared from N-benzylaniline following ***General Procedure 1*** and was obtained as a white solid by column chromatography (petroleum ether/EtOAc= 5/1). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.19 (m, 8H), 7.14-7.12 (m, 2H), 4.98 (s, 1H), 2.11-2.09 (m, 1H), 4.18 (d, *J* = 3.2Hz, 2H), 0.79 (d, *J* = 2.4Hz, 2H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 171.8, 143.7, 137.7, 129.0, 128.4, 127.8, 127.2, 126.7, 53.6, 37.2, 17.4, 10.2. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 264.1383, found: 264.1411.



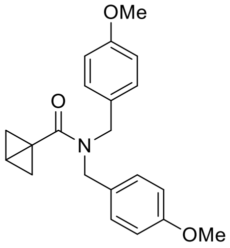
N-benzyl-N-ethylbicyclo[1.1.0]butane-1-carboxamide (2b): The compound **2b** was prepared from N-benzylethanamine following ***General Procedure 1*** and was obtained as a colourless liquid by column chromatography (petroleum ether/EtOAc= 5/1). Spectroscopic data of **2b** was obtained as a mixture of two rotational isomers. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 5H), 4.91-4.63 (m, 2H), 3.63-3.40 (m, 2H), 2.26-2.19 (m, 2H), 2.02 (br, 1H), 1.71-1.70 (m, 1H), 1.14-1.05 (m, 4H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 171.4, 137.7, 128.8, 128.6, 128.0, 127.4, 127.3, 126.5, 51.1, 47.7, 42.1, 40.5, 36.7, 14.1, 12.8, 12.6, 12.3, 8.3. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 216.1383, found: 216.1384.



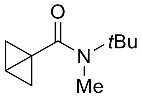
N-benzyl-N-isopropylbicyclo[1.1.0]butane-1-carboxamide (2c): The compound **2c** was prepared from N-benzylpropan-2-amine following ***General Procedure 1*** and was obtained as a colourless liquid by column chromatography (petroleum ether/EtOAc= 5/1). Spectroscopic data of **2c** was obtained as a mixture of two rotational isomers. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.22-7.21 (m, 3H), 5.00-4.55 (m, 3H), 2.27-2.14 (m, 2H), 2.04-2.00 (m, 1H), 1.16 (m, 7H), 0.91 (br, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 139.7, 128.5, 128.4, 126.9, 126.6, 126.4, 49.5, 48.4, 47.5, 44.1, 36.8, 36.5, 21.8, 20.3, 12.6, 9.3, 8.4. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 230.1539, found: 230.1540.



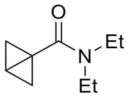
N-benzyl-N-(tert-butyl)bicyclo[1.1.0]butane-1-carboxamide (2d): The compound **2d** was prepared from N-benzyl-2-methylpropan-2-amine following ***General Procedure 1*** and was obtained as a colourless liquid by column chromatography (petroleum ether/EtOAc= 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.27-7.22 (m, 3H), 5.05 (s, 2H), 2.12 (d, *J* = 3.2Hz, 2H), 1.98-1.96 (m, 1H), 1.41 (s, 9H), 0.88 (d, *J* = 2.1Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.9, 140.9, 128.5, 126.8, 126.1, 57.9, 50.4, 36.4, 28.6, 12.6, 10.7. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 244.1696, found: 244.1746.



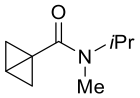
N,N-bis(4-methoxybenzyl)bicyclo[1.1.0]butane-1-carboxamide (2e): The compound **2e** was prepared from bis(4-methoxybenzyl)amine following ***General Procedure 1*** and was obtained as a white solid by column chromatography (petroleum ether/EtOAc= 5/1). Spectroscopic data of **2e** was obtained as a mixture of two rotational isomers. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.08 (m, 4H), 6.90-6.86 (m, 4H), 4.73 (s, 2H), 4.48 (s, 2H), 3.81 (s, 6H), 2.27 (d, *J* = 3.3Hz, 2H), 2.09-2.08 (m, 1H), 1.10 (d, *J* = 2.2Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9, 159.0, 129.8, 129.3, 129.0, 128.0, 114.3, 113.9, 55.3, 49.8, 46.9, 36.9, 13.4, 8.4. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 338.1751, found: 338.1766.



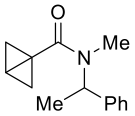
N-(tert-butyl)-N-methylbicyclo[1.1.0]butane-1-carboxamide (2f): The compound **2f** was prepared from N,2-dimethylpropan-2-amine following ***General Procedure 1*** and was obtained as a colourless liquid by column chromatography (petroleum ether/EtOAc= 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.18 (s, 3H), 2.18 (d, *J* = 3.3Hz, 2H), 1.94-1.92 (m, 1H), 1.40 (s, 9H), 1.11-1.10 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.4, 55.3, 35.9, 33.1, 26.7, 14.1, 9.8. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 168.1383, found: 168.1393.



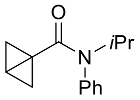
N,N-diethylbicyclo[1.1.0]butane-1-carboxamide (2g): The compound **2g** was prepared from diethylamine following ***General Procedure 1*** and was obtained as a colourless liquid by column chromatography (petroleum ether/EtOAc= 5/1). Spectroscopic data of **2g** was obtained as a mixture of two rotational isomers. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.67 (br, 2H), 3.40 (br, 2H), 2.20 (m, 2H), 1.94-1.93 (m, 1H), 1.20-1.14 (m, 6H), 1.08 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 42.4, 39.9, 36.4, 14.6, 12.8, 11.9, 8.4. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 154.1226, found: 154.1226.



N-isopropyl-N-methylbicyclo[1.1.0]butane-1-carboxamide (2h): The compound **2h** was prepared from N-methylpropan-2-amine following ***General Procedure 1*** and was obtained as a colourless liquid by column chromatography (petroleum ether/EtOAc= 5/1). Spectroscopic data of **2h** was obtained as a mixture of two rotational isomers. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.87-4.80 (m, 1H), 3.07-2.80 (m, 3H), 2.21-2.20 (m, 2H), 1.97-1.92 (m, 1H), 1.77-1.73 (m, 1H), 1.21-1.13 (m, 7H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.9, 48.6, 44.6, 37.0, 36.6, 29.7, 26.4, 20.6, 19.2, 13.5, 12.0, 8.7, 8.1. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 154.1226, found: 154.1226.

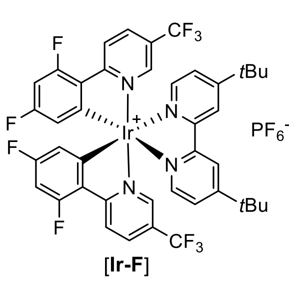


N-methyl-N-(1-phenylethyl)bicyclo[1.1.0]butane-1-carboxamide (2l): The compound **2l** was prepared from N-methyl-1-phenylethan-1-amine following ***General Procedure 1*** and was obtained as a white solid by column chromatography (petroleum ether/EtOAc= 5/1). Spectroscopic data of **2l** was obtained as a mixture of two rotational isomers. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35-7.34 (m, 2H), 7.29 (m, 3H), 5.98 (br, 1H), 2.90-2.69 (m, 3H), 2.27-2.24 (m, 2H), 2.04 (m, 1H), 1.62-1.53 (m, 3H), 1.16-1.12 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.5, 140.6, 128.5, 127.3, 126.6, 55.4, 50.9, 37.2, 36.8, 30.9, 28.3, 17.5, 15.4, 14.0, 12.5, 8.6, 8.2. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 216.1383, found: 216.1381.

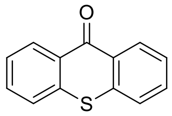


N-isopropyl-N-phenylbicyclo[1.1.0]butane-1-carboxamide (2j): The compound **2j** was prepared from N-isopropylaniline following ***General Procedure 1*** and was obtained as a colourless liquid by column chromatography (petroleum ether/EtOAc= 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 3H), 7.16 (d, *J* =7.4Hz, 2H), 5.05-4.98 (m, 1H), 2.00-1.98 (m, 1H), 1.72 (d, *J* =1.6Hz, 2H), 1.11 (d, *J* =6.8Hz, 6H), 0.64 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.0, 139.8, 130.7, 128.7, 127.5, 47.2, 36.6, 21.0, 15.3, 10.7. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 216.1383, found: 216.1387.

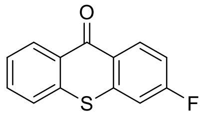
Employed photocatalysts*:* [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) ([Ir-F])and thioxanthone (TX) were obtained from commercial suppliers and used without further purification. 3-FTX, 3-MeOTX, 2-*i*PrTX, 2-MeOTX and 2,2’-MeOTX were prepared according to literature procedure by Kevin Booker-Milburn and coworkers.[5]



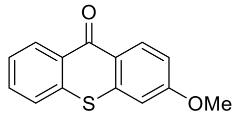
[**Ir-F**]



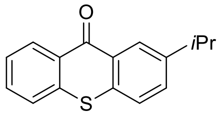
TX



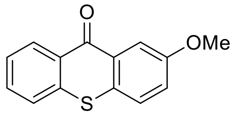
3-F-TX



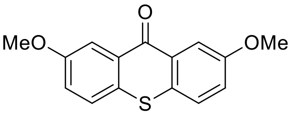
3-MeO-TX



2-*i*PrTX



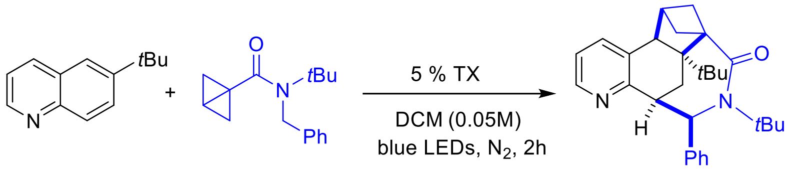
2-MeOTX



2,2'-MeOTX

2.2 Sensitivity Assessment

The sensitivity assessment was performed according to Glorius and co-workers.[6]



1m 1.0 equiv. **2d** 2.0 equiv. **4wd**

Standard condition: $n = 0.1$ mmol, $c = 0.05$ M, $V = 2.0$ mL, inert atmosphere, $T = 25$ °C, $d = 4.0$ cm.

Stock solution: $n = 1.0$ mmol, $c = 0.0556$ M, $V = 18$ mL, **1m**: 185.3 mg, **2d**: 486.7 mg, **TX**: 10.6 mg, DCM: 18 mL.

Stock solution 'big scale': $n = 2.1$ mmol, $c = 0.05$ M, $V = 42$ mL, **1m**: 389.7 mg, **2d**: 1022.1 mg, **TX**: 22.3 mg, DCM: 42 mL.

Table S1. Preparation for condition-based sensitivity screening

Entry	Modification	Preparation
1	Standard	1.8 mL stock sol. + 0.2 mL DCM
2	High c (+10%)	1.8 mL stock sol.
3	Low c (-10%)	1.8 mL stock sol. + 0.4 mL DCM
4	High H_2O (+1%)	1.8 mL stock sol. + 0.2 mL DCM + 20 µL H_2O
5	High O_2 (+ 10 mL air)	1.8 mL stock sol. + 0.2 mL DCM + 10 mL air
6	Low I (1/16)	1.8 mL stock sol. + 0.2 mL DCM, $d = 16$ cm
7	High I (x4)	1.8 mL stock sol. + 0.2 mL DCM, $d = 2$ cm
8	High T (40 °C)	1.8 mL stock sol. + 0.2 mL DCM, T = 40 °C
9	Big scale (20x)	40 mL stock solution'big scale'

***Note*:**

1. High O_2 reaction: 10 mL of air injected in solution achieves higher oxygen concentration.

2. High intensity reaction: a fan close to Schlenk-tube assures that the temperature does not exceed 25 °C.

3. High temperature reaction: standard setup without fans achieves temperature increase to 40 °C.

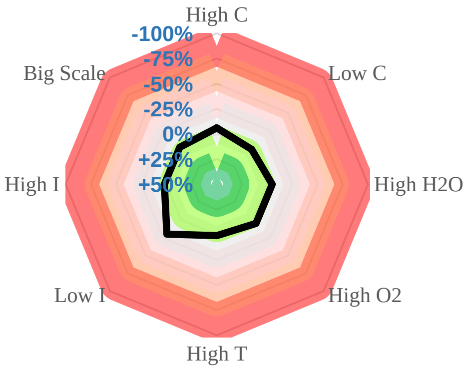
4. Big scale reaction: 2 LEDs are placed around a 50 mL Schlenk-tube. Each LED is fixed at a distance $d = 4.0$ cm

from the reaction.

Table S2. Results for condition-based sensitivity screening

Entry	Modification	yield[a] /%	Deviation /%
1	Standard	60	0
2	High c (+10%)	54	-6
3	Low c (-10%)	61	+1
4	High H_2O (+1%)	55	-5
5	High O_2 (+ 10 mL air)	55	-5
6	Low I (1/16)	40	-20
7	High I (x4)	58	-2
8	High T (40 °C)	59	-1
9	Big scale (20x)	58	-2

[a] Yields of the product are determined by ^{1}H NMR using 1, 3, 5- trimethoxybenzene as an internal standard.



2.3 Stereochemical assignment of *cis*/*trans* products

The *cis*/*trans* stereochemistry could usually be assigned reliably based on the coupling constants in ^{1}H NMR. The *cis*-**4A** displays the C9-H approximate parallel to the adjacent C10-H of BCBs moiety with characteristic larger coupling constants ~10 Hz observed (**Figure S2**), while the C12-H of *trans*-**4A** approximate perpendicular to the C13-H with relatively small coupling constants ~5Hz observed. On the other hand, *cis* and *trans* diastereomers could be also assigned from the ^{1}H NMR by comparison of the shielding/deshielding effects experienced by the unreactived benzylic methylene on the N-atom of BCBs. In *cis*-**4A**, the corresponding C16-methylene was observed in the shielded and deshielded regions of the adjacent C10-phenyl group respectively that results in the chemical shifts of C-H^{16a} relatively downfield at ~5.8 ppm while the C-H^{16b} relatively upfield at ~3.2 ppm. Due to the lack of such shielding effect in the *trans*-**4A**, the unreactived benzylic methylene C21H_2 resonance is found at 4.2-4.8 ppm. Single crystal X-ray experiments for a set of compounds (*cis*-**4f**, *cis*-**4h**, *trans*-**4n**, *cis*-**4wd**) are also consistent with this hypothesis. Additionally, this behaviour is similarly consistent with previous literature.[7]

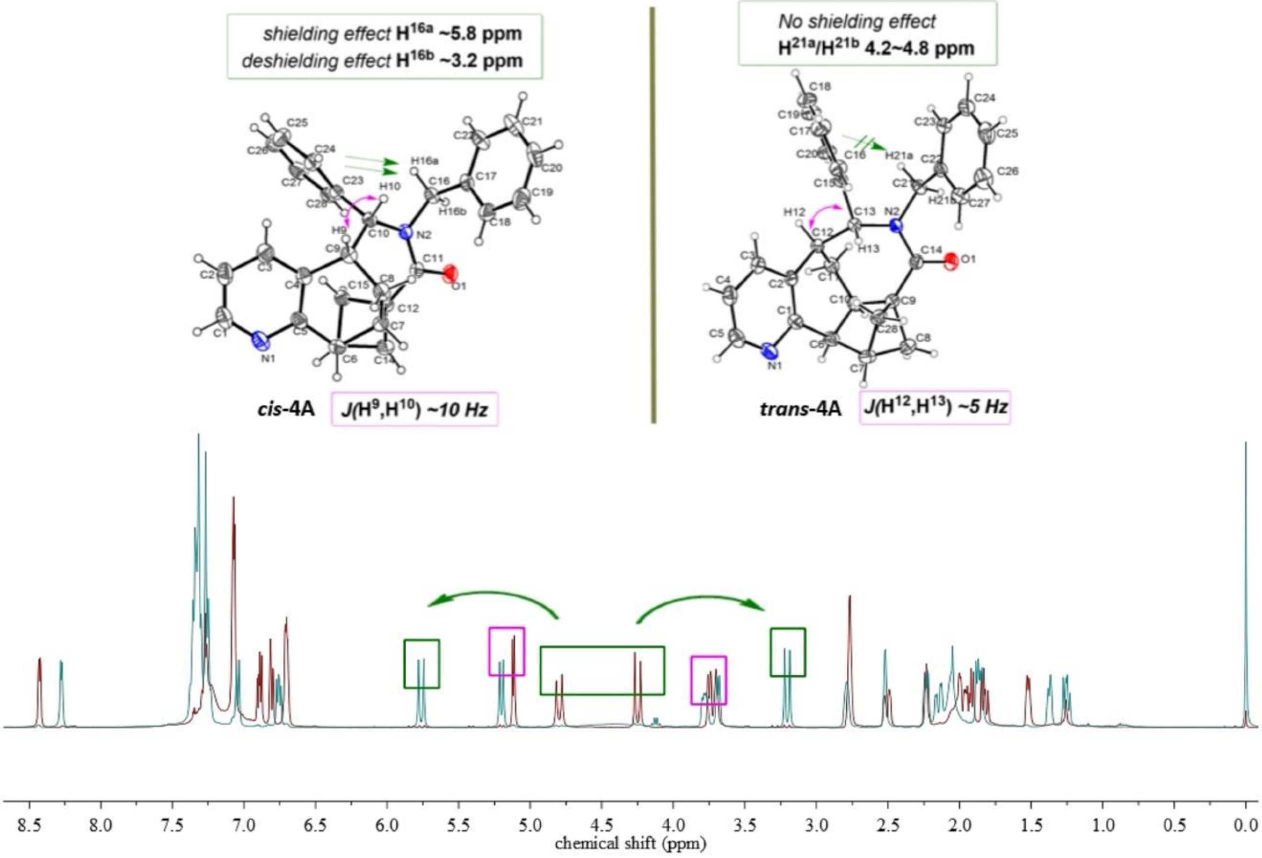
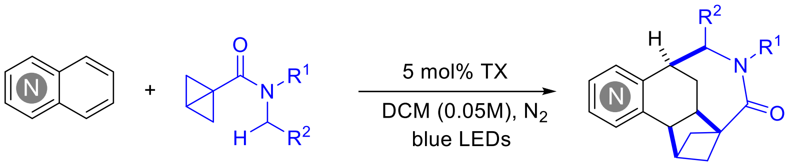


Figure S2. Shielding and deshielding effect observed in the ^{1}H NMR of the unreactived benzylic methylene of *trans*/*cis*-**4A**.

2.4 Synthesis and characterization of photochemical products

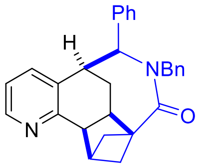
General Procedure 2 for the synthesis of pyridine-fused polycyclic rings



The quinoline substrate (1.0 equiv.), BCBs derivative (2.0 equiv.) and thioxanthone (TX, 5 mol%) were added to a

10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with N_2 three times. Subsequently, anhydrous DCM (0.05M) were added under positive nitrogen pressure. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LEDs (λ_{max}= 400 nm, distance approximately 4.0 cm from the bulb) with a fan at room temperature for the indicated time (monitored by TLC). After the reaction was completed, 1, 3, 5-trimethoxybenzene was added as internal standard to measure the crude ^{1}H NMR which is reported as combined yields of all for diastereo- and regioisomers. Regioisomeric ratio (r.r.) and diastereomeric ratio (d.r.) were determined by ^{1}H NMR analysis of the crude reaction mixture prior to purification. After removal of the solvents under reduced pressure, the desired product was purified by silica gel column chromatography and/or preparative thin-layer chromatography (PTLC). Crude ^{1}H NMR yields are displayed with isolated yields in parentheses.

Note: Only the structure of the major regiomers is shown, using capital letters to show for products from 8-to-7 adduct/cyclization such as **4A**, lowercase letters for 5-to-6 adduct/cyclization such as **4a**. The d.r. values (*cis: trans* ratio) refers to the major regiomers. The distinction of the regio- and diastereomers were determined by one example of each substrate class via single crystal X-ray diffraction and ^{1}H NMR analysis. Based on the high similarity of the spectroscopic data within one class of product motifs, so the corresponding regioselectivity and diastereoselectivity can be determined by analogy.



4A, 92%(68%)
3.5:1 r.r., 1.4:1 d.r.

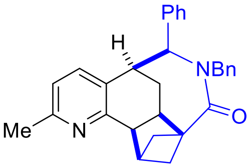
Prepared according to ***General Procedure 2*** using **1a** (26.1 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 2h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4A** (55.2 mg, 68% yield). **HRMS** (ESI, *m/z*) calcd. for [M+ H]$^+$: 407.2118, found: 407.2121.

cis-**4A:** white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.0Hz, 1H), 7.38-7.30 (m, 7H), 7.27-7.23 (m, 3H), 7.04 (d, *J* = 7.6Hz, 1H), 6.76 (dd, *J* = 7.7Hz, 4.9Hz, 1H), 5.76 (d, *J* = 14.6Hz, 1H), 5.20 (d, *J* = 10.2Hz, 1H), 3.78 (dd, *J* = 9.8Hz, 5.4Hz, 1H), 3.69 (d, *J* = 6.9Hz, 1H), 3.20 (d, *J* = 14.7Hz, 1H), 2.79 (s, 1H), 2.52 (d, *J* = 1.8Hz, 1H), 2.23 (d, *J* = 4.7Hz, 1H), 2.15 (dd, *J* = 13.8Hz, 3.6Hz, 1H), 1.78 (dd, *J* = 10.8Hz, 6.2Hz, 2H), 1.38 (d, *J* = 6.7Hz, 1H), 1.26 (dd, *J* = 10.8Hz, 7.8Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 161.3, 147.7, 138.8, 138.2, 137.3, 135.4, 129.0, 128.7, 128.3, 127.8, 127.6, 127.6, 119.8, 68.0, 54.6, 50.1, 46.4, 45.3, 41.0, 40.5, 40.3, 38.7, 26.2.

trans-**4A**: white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.7Hz, 1.6Hz, 1H), 7.36-7.23 (m, 4H), 7.08-7.06 (m, 4H), 6.89 (dd, *J* = 7.7Hz, 4.8Hz, 1H), 6.81 (dd, *J* = 7.7Hz, 1.3Hz, 1H), 6.71-6.69 (m, 2H), 5.12 (d, *J* = 5.4Hz, 1H), 4.80 (d, *J* = 15.7Hz, 1H), 4.25 (d, *J* = 15.7Hz, 1H), 3.75 (d, *J* = 7.0Hz, 1H), 3.70 (br, 1H), 2.77 (m, 2H), 2.50 (ddd, *J* = 13.7Hz, 3.8Hz, 2.4Hz, 1H), 2.24 (dd, *J* = 6.5Hz, 1.5Hz, 1H), 1.98 (ddd, *J* = 13.9Hz, 4.2Hz, 1.4Hz, 1H), 1.93 (dd, *J* = 11.0Hz, 6.5Hz, 1H), 1.83 (dd, *J* = 10.8Hz, 7.2Hz, 1H), 1.53 (dd, *J* = 7.3Hz, 2.2Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 160.5, 148.4, 140.8, 139.1, 137.0, 136.3, 130.6, 128.5, 128.2, 127.8, 127.1, 126.2, 120.9, 66.5, 57.5, 47.7, 46.9, 44.6, 43.6, 41.0, 39.0, 37.7, 25.9.

Analytical data of *cis*-**4a** of minor regioisomer from 1 mmol scale reaction: white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 4.7Hz, 1.6Hz, 1H), 7.52 (m, 2H), 7.36-7.35 (m, 4H), 7.28 (dd, *J* = 7.8Hz, 1.3Hz, 2H), 7.24 (d, *J* = 7.9Hz, 2H), 1.45 (t, *J* = 7.4Hz, 1H), 6.95 (dd, *J* = 7.6Hz, 4.8Hz, 1H), 5.83 (d, *J* = 14.6Hz, 1H), 5.41 (d, *J* = 11.2Hz, 1H), 4.03 (dd, *J* = 11.1Hz, 5.1Hz, 1H), 3.48 (d, *J* = 7.1Hz, 1H), 3.29 (d, *J* = 14.6Hz, 1H), 2.63 (br, 1H), 2.21 (d, *J* = 2.2Hz, 1H), 2.18-2.14 (m, 2H), 1.78 (dd, *J* = 10.7Hz, 6.6Hz, 1H), 1.74 (dd, *J* = 4.9Hz, 1.3Hz, 1H), 1.14 (d, *J* = 6.6Hz, 1H), 0.95 (dd, *J* = 10.7Hz, 8.2Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.9, 159.3, 145.1, 138.3, 137.1, 137.1, 135.4, 129.2, 128.6, 128.4, 127.6, 127.2, 126.7, 122.1, 67.2, 54.4, 50.9, 45.7, 42.9, 42.4, 40.6, 40.1, 37.9, 26.8.

Analytical data of *trans*-**4a** of minor regioisomer from 1 mmol scale reaction: white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 4.7Hz, 1.6Hz, 1H), 7.43 (dd, *J* = 7.7Hz, 1.3Hz, 1H), 7.36-7.29 (m, 1H), 7.25-7.21 (m, 3H), 7.11-7.07 (m, 5H), 6.70-6.69 (m, 2H), 5.21 (d, *J* = 5.0Hz, 1H), 4.82 (d, *J* = 15.7Hz, 1H), 4.19 (d, *J* = 15.7Hz, 1H), 3.91 (m, 1H), 3.65 (d, *J* = 7.0Hz, 1H), 2.70 (m, 1H), 2.56 (ddd, *J* = 14.0Hz, 4.0Hz, 2.3Hz, 1H), 2.51 (d, *J* = 2.4Hz, 1H), 2.22 (dd, *J* = 6.0Hz, 1.4Hz, 1H), 1.99 (ddd, *J* = 13.9Hz, 4.6Hz, 1.8Hz, 1H), 1.90 (dd, *J* = 10.8Hz, 6.3Hz, 1H), 1.81 (dd, *J* = 10.7Hz, 7.3Hz, 1H), 1.50 (dd, *J* = 6.8Hz, 2.0Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 160.9, 146.5, 141.4, 139.2, 136.0, 135.9, 130.5, 128.4, 128.0, 127.8, 127.0, 126.2, 122.5, 66.3, 57.1, 47.9, 46.9, 46.4, 41.7, 41.4, 38.3, 37.7, 26.1.

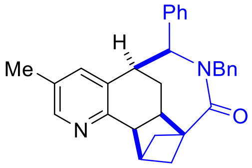


4B, 97%(70%)
2.7:1 r.r., 1.5:1 d.r.

Prepared according to ***General Procedure 2*** using **1b** (27.7 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 12h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded partially separable diastereomers of major regioisomer **4B** (58.9 mg, 70% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 421.2274, found: 421.2276.

cis-**4B** (as a mixture with *trans*-**4B** (*cis*:*trans* 11.6:1)): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) (only *cis* signals reported) δ 7.34-7.30 (m, 7H), 7.27-7.23 (m, 3H), 6.91 (d, *J* = 8.0Hz, 1H), 6.59 (d, *J* = 8.0Hz, 1H), 5.75 (d, *J* = 14.6Hz, 1H), 5.17 (d, *J* = 10.2Hz, 1H), 3.73 (dd, *J* = 9.8Hz, 5.3Hz, 1H), 3.61 (d, *J* = 7.2Hz, 1H), 3.20 (d, *J* = 14.6 Hz, 1H), 2.76 (m, 1H), 2.50-2.48 (m, 1H), 2.37 (s, 3H), 2.20 (dd, *J* = 6.2Hz, 1.8Hz, 1H), 2.12 (dd, *J* = 13.7Hz, 3.8Hz, 1H), 1.85-1.81 (m, 2H), 1.36-1.28 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) (only *cis* signals reported) δ 173.5, 160.5, 156.5, 138.9, 138.2, 137.5, 132.0, 129.0, 128.7, 128.2, 127.8, 127.6, 127.5, 119.4, 68.0, 54.6, 50.1, 46.3, 45.4, 40.7, 40.5, 40.2, 38.7, 26.3, 24.0.

trans-**4B** (completely separated) **:** white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.20 (m, 4H), 7.08-7.06 (m, 4H), 6.74 (d, *J* = 7.8Hz, 1H), 6.70-6.68 (m, 3H), 5.09 (d, *J* = 5.3Hz, 1H), 4.80 (d, *J* = 15.7Hz, 1H), 4.24 (d, *J* = 15.7Hz, 1H), 3.70 (d, *J* = 6.3Hz, 1H), 3.65 (br, 1H), 2.77-2.76 (m, 2H), 2.51-2.48 (m, 4H), 2.22 (d, *J* = 3.8Hz, 1H), 1.96 (ddd, *J* = 13.8Hz, 4.1Hz, 1.4Hz, 1H), 1.91-1.84 (m, 2H), 1.50 (dd, *J* = 5.8Hz, 2.6Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 174.4, 159.5, 157.1, 141.1, 139., 136.5, 133.7, 130.5, 128.4, 128.1, 127.8, 127.1, 126.2, 120.5, 66.6, 57.5, 47.7, 46.8, 44.6 ,43.3, 41.1, 39.1, 37.7, 26.0, 24.3.

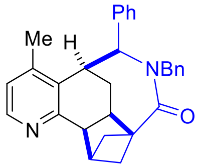


4C, 76%(60%)
3.8:1 r.r., 1.5:1 d.r.

Prepared according to ***General Procedure 2*** using **1c** (29.3 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 12h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4C** (50.5 mg, 60% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 421.2274, found: 421.2271.

cis-**4C**: white solid. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 8.11 (s, 1H), 7.37-7.30 (m, 7H), 7.27-7.25 (m, 3H), 6.86 (s, 1H), 5.75 (d, *J* = 14.7Hz, 1H), 5.19 (d, *J* = 10.1Hz, 1H), 3.73 (dd, *J* = 9.9Hz, 5.5Hz, 1H), 3.66 (d, *J* = 5.1Hz, 1H), 3.22 (d, *J* = 14.7Hz, 1H), 2.77 (m, 1H), 2.51 (d, *J* = 2.2Hz, 1H), 2.22 (dd, *J* = 6.4Hz, 1.8Hz, 1H), 2.14 (dd, *J* = 13.9Hz, 4.2Hz, 1H), 2.03 (s, 3H), 1.86-1.83 (m, 2H), 1.35 (d, *J* = 6.9Hz, 1H), 1.23 (dd, *J* = 10.8Hz, 7.8Hz, 1H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 173.4, 158.0, 147.6, 140.0, 138.2, 137.3, 135.0, 129.3, 129.0, 128.7, 128.2, 127.8, 127.6, 127.6, 68.0, 54.6, 50.1, 46.4, 44.7, 40.9, 40.4, 40.3, 38.6, 26.2, 17.7.

trans-**4C**: white solid. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 8.26 (s, 1H), 7.32-7.26 (m, 5H), 7.08-7.07 (m, 3H), 6.70-6.69 (m, 2H), 6.61 (m, 1H), 5.10 (d, *J* = 5.1Hz, 1H), 4.23 (d, *J* = 15.7Hz, 1H), 3.71 (d, *J* = 6.1Hz, 1H), 3.71 (br, 1H), 2.75 (br, 2H), 2.49 (d, *J* = 13.6Hz, 1H), 2.23 (d, *J* = 4.3Hz, 1H), 2.11 (s, 3H), 1.93-1.82 (m, 4H), 1.51 (d, *J* = 4.3Hz, 1H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 174.5, 157.2, 148.7, 140.9, 139.1, 137.0, 130.4, 129.0, 128.7, 128.5, 128.2, 127.9, 127.0, 126.2, 66.5, 57.4, 47.7, 46.8, 44.1, 43.5, 41.0, 39.0, 37.7, 26.0, 17.9.



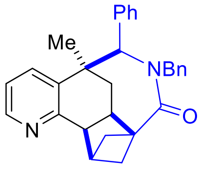
4D, 98%(76%)
3.9:1 r.r., 1.4:1 d.r.

Prepared according to ***General Procedure 2*** using **1d** (29.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 12h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4D** (63.8 mg, 76% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 421.2274, found: 421.2278.

cis-**4D:** white solid. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.47 (d, *J* = Hz, 1H), 7.40-7.35 (m, 6H), 7.32-7.25 (m, 5H), 5.63 (d, *J* = 14.8Hz, 1H), 5.11 (d, *J* = 9.4Hz, 1H), 4.09 (d, *J* = 6.8Hz, 1H), 4.06-4.03 (m, 1H), 3.11 (d, *J* = 14.8Hz, 1H), 2.90-2.87 (m, 2H), 2.33-2.26 (m, 2H), 1.95-1.91 (m, 4H), 1.86 (dd, *J* = 14.0Hz, 4.7Hz, 1H), 1.71 (d, *J* = 7.1Hz, 1H), 1.59 (dd, *J* = 10.2Hz, 8.4Hz, 1H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 171.37, 158.03, 157.99, 139.43, 139.07, 137.70, 137.55, 129.13, 129.04, 128.99, 128.92, 128.89, 127.93, 125.98, 69.17, 54.47, 58.99, 46.56, 42.89, 41.27, 40.89, 38.71, 37.54, 27.07, 22.11.

trans-**4D:** white solid. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 8.27 (d, *J* = 4.9Hz, 1H), 7.52 (d, *J* = 7.4Hz, 1H), 7.42 (t, *J* =

7.0Hz, 1H), 7.25 (t, *J* = 7.5Hz, 1H), 7.08-7.06 (m, 3H), 6.95 (t, *J* = 7.2Hz, 1H), 6.77 (d, *J* = 4.9Hz, 1H), 6.70-6.66 (m, 3H), 5.15 (d, *J* = 5.1Hz, 1H), 4.81 (d, *J* = 15.4Hz, 1H), 4.23 (d, *J* = 15.9Hz, 1H), 3.87 (br, 1H), 3.74 (d, *J* = 7.2Hz, 1H), 2.77 (d, *J* = 2.4Hz, 1H), 2.74 (m, 1H), 2.58 (ddd, *J* = 13.9Hz, 4.0Hz, 2.8Hz, 1H), 2.23 (dd, *J* = 6.2Hz, 1.8Hz, 1H), 2.00 (dd, *J* = 10.9Hz, 7.2Hz, 1H), 1.94 (ddd, *J* = 13.8Hz, 4.3Hz, 1.9Hz, 1H), 1.90 (dd, *J* = 10.8Hz, 6.7Hz, 1H), 1.55 (dd, *J* = 6.1Hz, 1.2Hz, 1H), 1.41 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 174.4, 160.5, 147.4, 146.2, 141.1, 139.3, 136.3, 132.2, 129.6, 128.3, 127.8, 126.8, 126.1, 123.5, 66.3, 57.3, 47.8, 46.4, 45.3, 40.9, 40.9, 38.7, 37.6, 27.1, 20.2.



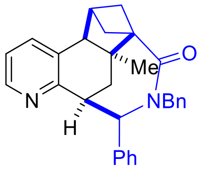
4E, 81%(73%)
13.0:1 r.r., 5.3:1 d.r.

Prepared according to ***General Procedure 2*** using **1e** (29.2 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 8h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded partially separable diastereomers of major regioisomer **4E** with *trans*-diastereomer of minor regioisomer **4e** (61.3 mg, 73% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 421.2274, found: 421.2271.

cis-**4E** (completely separated): white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.26 (d, *J* = 3.6Hz, 1H), 7.39-7.21 (m, 11H), 6.80 (dd, *J* = 8.1Hz, 4.7Hz, 1H), 5.85 (d, *J* = 14.4Hz, 1H), 4.92 (s, 1H), 3.66 (d, *J* = 6.7Hz, 1H), 3.10 (d, *J* = 14.4Hz, 1H), 2.68 (br, 1H), 2.45 (d, *J* = 2.2Hz, 1H), 2.21 (d, *J* = 4.7Hz, 1H), 2.12 (dd, *J* = 14.1Hz, 4.5Hz, 1H), 2.18 (dd, *J* = 10.7Hz, 6.5Hz, 1H), 1.62 (d, *J* = 13.9Hz, 1H), 1.34 (s, 3H), 1.26 (d, *J* = 7.2Hz, 1H), 1.00 (dd, *J* = 10.8Hz, 7.8Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 173.2, 160.8, 147.4, 139.3, 138.4, 137.5, 136.4, 129.3, 128.7, 128.1, 127.8, 127.7, 127.6, 119.8, 74.3, 54.6, 50.6, 46.6, 45.2, 41.9, 40.9, 40.6, 38.6, 37.2, 36.9.

trans-**4E** (as a mixture with *cis*-**4E** (*trans*:*cis* 9:1)): white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) (only *trans* signals reported) δ 8.45-8.44 (m, 1H), 7.32-7.23 (m, 4H), 7.18-7.15 (m, 2H), 7.12-7.09 (m, 3H), 7.00-6.96 (m, 2H), 6.91-6.89 (m, 1H), 5.60 (s, 1H), 4.89 (d, *J* = 16.2Hz, 1H), 4.55 (d, *J* = 16.2Hz, 1H), 3.78 (d, *J* = 7.2Hz, 1H), 2.84 (br, 1H), 2.77 (br, 1H), 2.46 (d, *J* = 14.0Hz, 1H), 2.23 (d, *J* = 6.2Hz, 1H), 1.92 (t, *J* = 8.3Hz, 1H), 1.86 (d, *J* = 14.3Hz, 1H), 1.70-1.67 (m, 1H), 1.65 (br, 1H), 1.10 (d, *J* = 1.6Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) (only *trans* signals reported) δ 174.6, 160.0, 147.7, 142.4, 139.2, 134.8, 134.7, 133.3, 128.5, 128.0, 127.8, 127.1, 126.3, 121.2, 69.3, 58.3, 47.5, 47.4, 47.2, 44.7, 41.8, 39.8, 39.5, 36.1, 30.3.

trans-diastereomer of minor regioisomer **4e**: white solid. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.56 (d, *J* = 3.6Hz, 1H), 7.63 (d, *J* = 7.5Hz, 1H), 7.36-7.24 (m, 7H), 7.09 (d, *J* = 7.0Hz, 2H), 6.99 (d, *J* = 7.1Hz, 2H), 4.65 (d, *J* = 14.6Hz, 1H), 4.29 (d, *J* = 14.6Hz, 1H), 4.16 (s, 2H), 3.65 (d, *J* = 8.5Hz, 1H), 2.64 (s, 1H), 2.35 (d, *J* = 8.6Hz, 1H), 2.05 (s, 1H), 1.96 (s, 1H), 1.55-1.53 (m, 2H), 1.36 (t, *J* = 8.4Hz, 1H), 1.05 (s, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 172.8, 157.1, 147.6, 137.1, 137.1, 136.2, 135.2, 128.9, 128.8, 128.3, 127.6, 127.6, 126.5, 120.9, 57.2, 48.8, 47.3, 46.5, 45.3, 44.2, 43.1, 41.7, 41.5, 37.4, 30.4.

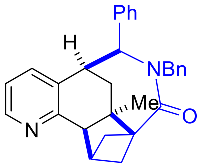


4f, 80%(55%)
2.3:1 r.r., 1.5:1 d.r.

Prepared according to ***General Procedure 2*** using **1f** (29.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 12h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4f** (46.1 mg, 55% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 421.2274, found: 421.2272.

cis-**4f:** white solid. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.28 (dd, *J* = 4.8Hz, 1.4Hz, 1H), 7.35-7.28 (m, 7H), 7.25-7.23 (m, 3H), 6.95 (dd, *J* = 7.9Hz, 1.4Hz, 1H), 6.73 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 5.73 (dd, *J* = 14.7Hz, 4.2Hz, 1H), 5.20 (dd, *J* = 9.7Hz, 4.5Hz, 1H), 3.58 (br, 1H), 3.50 (d, *J* = 9.3Hz, 1H), 3.23 (dd, *J* = 14.6Hz, 5.0Hz, 1H), 2.55 (m, 2H), 2.38 (m, 1H), 2.23 (br, 1H), 1.86-1.83 (m, 2H), 1.37 (br, 1H), 1.28-1.24 (m, 1H), 0.82 (d, *J* = 7.0Hz, 3H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 173.4, 161.4, 147.8, 139.7, 138.1, 137.3, 131.8, 129.0, 128.7, 128.3, 127.9, 127.6, 127.6, 120.0, 68.4, 54.8, 50.0, 48.1, 46.5, 44.8, 42.5, 40.1, 39.8, 29.3, 18.5.

trans-**4f:** white solid. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.43 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.28-7.24 (m, 4H), 7.07-7.05 (m, 4H), 6.90 (dd, *J* = 7.6Hz, 4.8Hz, 1H), 6.78 (dd, *J* = 7.6Hz, 1.6Hz, 1H), 6.67-6.65 (m, 2H), 5.05 (d, *J* = 5.2Hz, 1H), 4.98 (d, *J* = 15.7Hz, 1H), 4.12 (d, *J* = 15.8Hz, 1H), 3.65 (dd, *J* = 6.8Hz, 1.7Hz, 1H), 3.48-3.47 (m, 1H), 2.80-2.79 (m, 1H), 2.75-2.71 (m, 1H), 2.55-2.54 (m, 1H), 2.23 (dd, *J* = 6.1Hz, 1.6Hz, 1H), 1.90 (dd, *J* = 10.7Hz, 6.4Hz, 1H), 1.76 (dd, *J* = 10.8Hz, 7.3Hz, 1H), 1.50 (dd, *J* = 6.9Hz, 2.3Hz, 1H), 0.96 (d, *J* = 7.0Hz, 3H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 174.3, 160.3, 148.3, 141.0, 139.0, 137.4, 134.1, 130.5, 128.5, 128.1, 127.8, 126.9, 126.2, 121.2, 67.0, 57.6, 50.6, 47.8, 47.0, 44.8, 41.8, 40.9, 37.3, 28.7, 17.9.

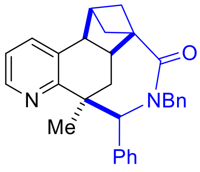


4G, 57%(51%)
10.4:1 r.r., 1.5:1 d.r.

Prepared according to ***General Procedure 2*** using **1g** (29.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 12h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded partially separable diastereomers of major regioisomer **4G** (42.7 mg, 51% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 421.2274, found: 421.2279.

cis-**4G** (as a mixture with *trans*-**4G** (*cis*:*trans* 5.9:1))**:** white solid. ^{1}**H NMR** (500 MHz, CDCl$_3$) (only *cis* signals reported) δ 8.48 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.80 (d, *J* = 6.7Hz, 1H), 7.40-7.26 (m, 10H), 7.08 (d, *J* = 5.7Hz, 1H), 5.77 (d, *J* = 14.7Hz, 1H), 5.31 (d, *J* = 10.1Hz, 1H), 4.02-3.89 (m, 1H), 3.19 (d, *J* = 14.6Hz, 1H), 2.84 (s, 1H), 2.70 (br, 1H), 2.50 (dd, *J* = 11.1Hz, 8.3Hz, 1H), 2.10 (d, *J* = 7.4Hz, 1H), 2.06 (d, *J* = 14.6Hz, 1H), 1.82 (d, *J* = 11.5Hz, 1H), 1.52 (d, *J* = 8.2Hz, 1H), 1.46 (s, 3H), 1.20 (dd, *J* = 10.8Hz, 9.4Hz, 1H). ^{13}**C NMR** (126 MHz, CDCl$_3$) (only *cis* signals reported) δ 171.6, 159.3, 145.1, 140.3, 139.6, 137.7, 135.9, 129.0, 128.9, 128.8, 128.3, 128.0, 126.9, 122.5, 66.9, 58.9, 50.0, 49.1, 43.9, 42.4, 41.6, 40.7, 39.3, 35.5, 27.1.

trans-**4G** (completely separated): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.4Hz, 1.2Hz, 1H), 7.30-7.22 (m, 4H), 7.09-7.08 (m, 4H), 6.92-6.85 (m, 2H), 6.68-6.66 (m, 2H), 5.12 (d, *J* = 4.7Hz, 1H), 4.95 (d, *J* = 15.6Hz, 1H), 4.16 (d, *J* = 15.7Hz, 1H), 3.68 (d, *J* = 1.7Hz, 1H), 3.41 (s, 1H), 2.56 (d, *J* = 1.9Hz, 1H), 2.51-2.44 (m, 2H), 2.11 (dd, *J* = 11.6Hz, 7.4Hz, 1H), 2.02 (d, *J* = 6.5Hz, 1H), 1.96 (dd, *J* = 14.0Hz, 4.8Hz, 1H), 1.81 (br, 1H), 1.53 (d, *J* = 6.4Hz, 1H), 1.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 161.7, 148.0, 142.3, 139.0, 136.9, 136.0, 130.0, 128.5, 128.1, 127.9, 127.0, 126.3, 120.8, 66.9, 61.7, 52.7, 48.0, 45.6, 42.0, 41.5, 39.7, 38.6, 35.9, 28.0.



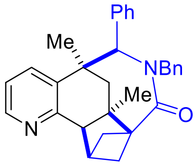
4h, 61%(58%)
2.8:1 r.r., 8.1:1 d.r.

Prepared according to ***General Procedure 2*** using **1h** (29.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 12h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4h** with *cis*-diastereomer of minor regioisomer **4H** (48.8 mg, 58% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 421.2274, found: 421.2271.

cis-**4h:** white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.5Hz, 1H), 7.61 (br, 2H), 7.40-7.31 (m, 5H), 7.25-7.18 (m, 3H),7.12 (t, *J* = 7.3Hz, 1H), 6.94 (dd, *J* = 6.7Hz, 4.6Hz, 1H), 5.97 (d, *J* = 14.3Hz, 1H), 5.08 (s, 1H), 3.48 (d, *J* = 7.1Hz, 1H), 3.21 (d, *J* = 14.2Hz, 1H), 2.53 (br, 1H), 2.17-2.13 (m, 2H), 2.11 (dd, *J* = 6.3Hz, 1.8Hz, 1H), 1.74 (dd, *J* = 10.8Hz, 6.6Hz, 1H), 1.49 (dd, *J* = 14.1Hz, 1.7Hz, 1H), 1.40 (s, 3H), 0.98 (d, *J* = 7.3Hz, 1H), 0.70 (dd, *J* = 10.7Hz, 8.2Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.8, 161.9, 144.8, 138.5, 137.9, 135.3, 129.6, 128.6, 127.8, 127.7, 127.2, 126.7, 121.7, 74.0, 54.6, 51.4, 45.8, 44.2, 42.7, 40.8, 40.7, 38.2, 37.8, 36.4. *One aromaticsignal is missing (probably due to signal overlap).*

trans-**4h:** white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 (m, 1H), 7.38-7.29 (m, 3H), 7.16-7.08 (m, 7H), 6.70-6.68 (m, 2H), 5.04 (s, 1H), 4.70 (d, *J* = 15.7Hz, 1H), 4.28 (d, *J* = 15.6Hz, 1H), 3.79 (br, 1H), 2.91 (br, 1H), 2.49 (d, *J* = 14.1Hz, 1H), 2.45 (br, 1H), 2.26 (d, *J* = 6.2Hz, 1H), 2.07-2.00 (m, 2H), 1.85 (s, 3H), 1.65 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.4, 162.1, 145.6, 139.9, 138.8, 128.7, 128.6, 127.9, 127.1, 126.4, 122.3, 66.5, 57.8, 47.2, 46.1, 43.6, 39.6, 23.7, 21.1. *Three aromatic signals are missing (probably due to signal overlap).*

cis-diastereomer of minor regioisomer **4H**: white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 4.7Hz, 1.6Hz, 1H), 7.37-7.29 (m, 7H), 7.25-7.23 (m, 3H), 6.90 (dd, *J* = 7.9Hz, 1.4Hz, 1H), 6.68 (dd, *J* = 7.8Hz, 4.7Hz, 1H), 5.74 (d, *J* = 14.8Hz, 1H), 5.15 (d, *J* = 10.0Hz, 1H), 3.74 (dd, *J* = 10.0Hz, 5.5Hz, 1H), 3.19 (d, *J* = 14.7Hz, 1H), 2.42 (br, 1H), 2.25 (t, *J* = 2.3Hz, 1H), 2.20 (dd, *J* = 6.6Hz, 2.1Hz, 1H), 2.09 (dd, *J* = 13.4Hz, 3.5Hz, 1H), 1.94 (dd, *J* = 10.8Hz, 6.8Hz, 1H), 1.63 (s, 3H), 1.41 (dd, *J* = 7.4Hz, 2.2Hz, 1H), 1.21 (dd, *J* = 10.9Hz, 7.7Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.2, 164.2, 148.0, 138.2, 138.0, 137.4, 134.5, 129.0, 128.7, 128.4, 128.1, 127.8, 127.6, 119.6, 68.1, 55.0, 50.0, 47.6, 45.9, 45.8, 45.2, 42.3, 41.3, 24.3, 20.6.

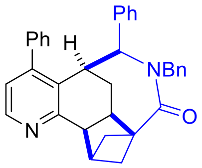


4l,10%(10%)
>19:1 r.r., >19:1 d.r.

Prepared according to ***General Procedure 2*** using **1i** (31.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded a *cis*-diastereomer of major regioisomer **4I** (8.6 mg, 10% yield) with *ortho*-cycloadduct **3I** (29.5 mg, 34% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 435.2431, found: 435.2433.

cis-**4I:** white solid. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 8.24 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.47 (dd, *J* = 8.1Hz, 1.4Hz, 1H), 7.40-7.32 (m, 7H), 7.30-7.27 (m, 2H), 7.22 (t, *J* = 14.3Hz, 1H), 6.85 (dd, *J* = 8.1Hz, 4.8Hz, 1H), 5.90 (d, *J* = 14.3Hz, 1H), 4.97 (s, 1H), 3.30 (s, 1H), 3.09 (d, *J* = 14.3Hz, 1H), 2.38 (dd, *J* = 10.6Hz, 8.1Hz, 1H), 2.26 (d, *J* = 2.3Hz, 1H), 1.98-1.93 (m, 2H), 1.53 (d, *J* =14.2 Hz, 1H), 1.36 (s, 3H), 1.31 (s, 3H), 1.22 (d, *J* = 7.5Hz, 1H), 1.17 (dd, *J* = 11.3Hz, 8.2Hz, 1H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 172.8, 162.1, 146.9, 139.3, 138.6, 137.6, 136.2, 129.4, 128.7, 128.0, 127.8, 127.5, 127.5, 119.8, 74.0, 59.0, 53.2, 50.7, 47.6, 45.0, 43.1, 41.6, 40.0, 38.6, 37.9, 27.6.

3I: yellow oil. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 8.36 (dd, *J* = 4.8Hz, 1.5Hz, 1H), 7.48 (dd, *J* = 7.8Hz, 1.4Hz, 1H), 7.37-7.34 (m, 4H), 7.31-7.29 (m, 2H), 7.24 (d, *J* = 7.2Hz, 2H), 7.14 (d, *J* = 7.4Hz, 2H), 7.08 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 5.58 (s, 1H), 4.87 (d, *J* = 14.6Hz, 1H), 4.56 (d, *J* = 16.7Hz, 1H), 4.33-4.29 (m, 2H), 3.24 (s, 1H), 2.67 (br, 1H), 1.98-1.94 (m, 4H), 1.74-1.72 (m, 1H), 1.86 (dd, *J* = 7.6Hz, 3.1Hz, 1H), 1.66 (dd, *J* = 9.6Hz, 7.6Hz, 1H), 1.41 (s, 3H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 172.4, 157.8, 147.5, 137.7, 136.7, 131.4, 130.3, 129.3, 128.9, 128.6, 128.4, 128.3, 127.5, 127.4, 126.6, 121.5, 61.8, 52.6, 49.8, 47.6, 46.7, 42.9, 40.6, 38.8, 25.7, 19.3. **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 435.2431, found: 435.2431.

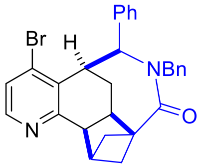


4J, 66%(55%)
7.3:1 r.r., 1.4:1 d.r.

Prepared according to ***General Procedure 2*** using **1j** (41.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 18h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4J** (52.9 mg, 55% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 483.2431, found: 483.2423.

cis-**4J:** white solid. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 8.67 (d, *J* = 5.7Hz, 1H), 7.51-7.48 (m, 1H), 7.46-7.44 (m, 2H), 7.33-7.31 (m, 3H), 7.19-7.13 (m, 4H), 7.02 (t, *J* = 7.7Hz, 2H), 6.95 (d, *J* = 5.7Hz, 2H), 6.48 (d, *J* = 7.5Hz, 2H), 5.55 (d, *J* = 14.9Hz, 1H), 4.93-4.91 (m, 1H), 4.82 (d, *J* = 10.1Hz, 1H), 4.16 (d, *J* = 6.5Hz, 1H), 2.93-2.87 (m, 3H), 2.32-2.30 (m, 2H), 1.98 (d, *J* = 6.3Hz, 1H), 1.96 (d, *J* = 7.1Hz, 1H), 1.62 (d, *J* = 7.1Hz, 1H), 1.45 (dd, *J* = 10.7Hz, 8.2Hz, 1H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 171.9, 159.9, 157.6, 140.8, 138.2, 137.7, 136.9, 136.6, 129.3, 129.2, 128.9, 128.8, 128.7, 128.0, 127.7, 127.5, 126.4, 68.8, 54.6, 49.7, 46.2, 43.4, 41.1, 41.0, 37.2, 34.9, 26.9. *One aromaticsignal is missing (probably due to signal overlap).*

trans-**4J:** white solid. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 8.42 (d, *J* = 4.9Hz, 1H), 7.01-6.91 (m, 6H), 6.80-6.59 (m, 8H), 6.43-6.33 (m, 2H), 5.11 (d, *J* = 5.5Hz, 1H), 4.38 (d, *J* = 15.6Hz, 1H), 4.27 (br, 1H), 4.02 (d, *J* = 15.7Hz, 1H), 3.81 (d, *J* = 6.6Hz, 1H), 2.89 (m, 1H), 2.75 (br, 1H), 2.42 (dd, *J* = 13.5Hz, 2.7Hz, 1H), 2.25(dd, *J* = 5.9Hz, 1.5Hz, 1H), 2.07-2.04 (m, 2H), 1.93 (dd, *J* = 10.5Hz, 6.4Hz, 1H), 1.62 (d, *J* = 4.6Hz, 1H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 174.0, 161.4, 150.6, 147.3, 139.3, 139.2, 138.2, 134.6, 128.7, 128.2, 127.6, 127.5, 127.2, 127.1, 126.0, 123.2, 65.9, 57.7, 47.3, 46.5, 45.6, 41.2, 38.9, 38.4, 36.9, 27.1. *Two aromatic signals are missing (probably due to signal overlap).*

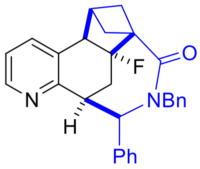


4K, 63% (41%)
2.2:1 r.r., 1:2.1 d.r.

Prepared according to ***General Procedure 2*** using **1k** (42.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4K** (39.7 mg, 41% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 485.1223, found: 485.1226.

cis-**4K:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 5.1Hz, 1H), 7.49-7.48 (m, 1H), 7.46 (d, *J* = 7.4Hz, 2H), 7.40-7.32 (m, 5H), 7.25-7.21 (m, 3H), 5.80 (d, *J* = 14.5Hz, 1H), 5.29 (d, *J* = 10.4Hz, 1H), 4.27 (dd, *J* = 10.5Hz, 2.3Hz, 1H), 3.54 (d, *J* = 7.0Hz, 1H), 3.21 (d, *J* = 14.6Hz, 1H), 2.69 (br, 1H), 2.64 (br, 1H), 2.23 (d, *J* = 14.2Hz, 1H), 2.19 (d, *J* = 6.6Hz, 1H), 1.85-1.81 (m, 1H), 1.73 (dd, *J* = 12.2Hz, 3.1Hz, 1H), 1.28 (d, *J* = 6.7Hz, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.3, 164.6, 148.0, 138.1, 138.0, 129.2, 128.8, 128.8, 128.3, 128.0, 127.8, 127.7, 127.5, 125.9, 67.8, 54.8, 50.8, 46.8, 45.7, 41.4, 40.6, 40.3, 38.4, 28.0.

trans-**4K:** white solid. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 5.2Hz, 1H), 7.49 (d, *J* = 6.6Hz, 1H), 7.38 (t, *J* = 6.3Hz, 1H), 7.22-7.19 (m, 2H), 7.08 (t, *J* = 3.1Hz, 3H), 6.94 (t, *J* = 6.5Hz, 1H), 6.71-6.69 (m, 3H), 5.12 (d, *J* = 4.8Hz, 1H), 4.81 (d, *J* = 15.8Hz, 1H), 4.25 (d, *J* = 15.9Hz, 1H), 4.13-4.09 (m, 1H), 3.75 (dd, *J* = 7.0Hz, 0.6Hz, 1H), 2.77-2.76 (m, 2H), 2.63 (ddd, *J* = 13.9Hz, 4.1Hz, 2.5Hz, 1H), 2.25 (dd, *J* = 6.0Hz, 1.8Hz, 1H), 1.99-1.88 (m, 3H), 1.59 (dd, *J* = 6.8Hz, 2.0Hz, 1H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 174.0, 163.3, 148.2, 141.1, 139.3, 137.8, 135.8, 132.6, 129.9, 128.4, 128.1, 127.8, 126.9, 126.2, 126.2, 66.4, 57.3, 47.9, 46.3, 45.8, 43.8, 41.0, 38.8, 37.5, 27.0.



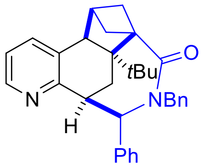
4l, 66%(35%)
1.1:1 r.r., 1.2:1 d.r.

Prepared according to ***General Procedure 2*** using **1l** (29.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded 2 separable diastereomers of major regioisomer **4l** (29.6 mg, 35% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 425.2024, found: 425.2020.

cis-**4l:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 4.6Hz, 1.2Hz, 1H), 7.39-7.32 (m, 5H), 7.29-7.22 (m, 5H), 7.02 (d, *J* = 7.7Hz, 1H), 6.79 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 5.74 (d, *J* = 14.6Hz, 1H), 5.33 (d, *J* = 10.4Hz, 1H), 5.08 (ddd, *J* = 48.5Hz, 5.0Hz, 2.4Hz, 1H), 4.05 (dd, *J* = 12.5Hz, 10.6Hz, 1H), 3.75 (d, *J* = 7.1Hz, 1H), 3.18 (d, *J* = 14.7Hz, 1H), 3.05 (br, 1H), 2.60 (d, *J* = 2.1Hz, 1H), 2.32 (d, *J* = 6.5Hz, 1H), 1.91 (dd, *J* = 10.6Hz, 6.9Hz, 1H), 1.43-1.41 (m, 1H), 1.29 (dd, *J* = 10.5Hz, 8.6Hz, 1H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 172.3, 160.4, 148.2, 139.6, 137.6, 135.8, 129.9, 129.0, 128.9, 128.5, 128.1, 128.0, 127.8, 120.3, 87.7 (d, *J* = 174.5Hz), 65.5 (d, *J* = 10.3Hz), 53.4 (d, *J* = 10.6Hz), 50.0, 46.6, 45.9 (d, *J* = 17.2Hz), 43.3, 42.4 (d, *J* = 20.3Hz), 40.4, 39.8. ^{19}**F NMR** (470 MHz, $CDCl_3$) δ -181.1.

trans-**4l:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.34-7.31 (m, 5H), 7.10-7.08 (m, 3H), 6.95 (dd, *J* = 7.7Hz, 4.9Hz, 1H), 6.83 (dd, *J* = 7.7Hz, 1.1Hz, 1H), 6.68-6.66 (m, 2H), 5.45 (ddd, *J* = 48.6Hz, 4.8Hz, 4.0Hz, 1H), 5.12 (dd, *J* = 5.1Hz, 1.9Hz, 1H), 4.68 (d, *J* = 15.6Hz, 1H), 4.27 (d, *J* = 15.7Hz, 1H), 4.07-4.05

(m, 1H), 3.88 (d, *J* = 6.8Hz, 1H), 3.08 (br, 1H), 2.87 (d, *J* = 2.2Hz, 1H), 2.35 (d, *J* = 6.3Hz, 1H), 2.00 (dd, *J* = 10.5Hz, 6.8Hz, 1H), 1.86 (dd, *J* = 10.7Hz, 7.5Hz, 1H), 1.61-1.60 (m, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 173.2, 159.5, 148.7, 139.4, 138.5, 137.2, 132.1, 128.7, 128.1, 127.0, 126.6, 121.5, 89.4 (d, *J* = 171.1Hz), 65.0 (d, *J* = 9.2Hz), 56.0 (d, *J* = 10.9Hz), 47.9 (d, *J* = 17.7Hz), 47.6, 47.3, 42.8, 42.3 (d, *J* = 19.7Hz), 41.2, 37.7. **^{19}F NMR** (470 MHz, CDCl$_3$) δ -188.3.

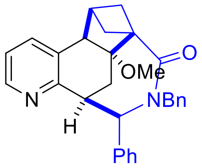


4m, 85%(81%)
>19:1 r.r., 2.9:1 d.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 2h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded partially separable diastereomers of major regioisomer **4m** (74.9 mg, 81% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 463.2744, found: 463.2747.

cis-**4m** (completely separated): white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.22 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.36-7.23 (m, 10H), 6.95 (dd, *J* = 7.9Hz, 1.3Hz, 1H), 6.70 (dd, *J* = 7.9Hz, 4.8Hz, 1H), 5.79 (d, *J* = 14.5Hz, 1H), 5.10 (d, *J* = 10.0Hz, 1H), 3.70 (dd, *J* = 9.9Hz, 1.2Hz, 1H), 3.57 (dd, *J* = 6.9Hz, 1.9Hz, 1H), 3.14 (d, *J* = 14.5Hz, 1H), 2.83-2.81 (m, 1H), 2.54-2.53 (m, 1H), 2.21 (dd, *J* = 6.5Hz, 2.1Hz, 1H), 1.88-1.84 (m, 2H), 1.35 (dd, *J* = 7.5Hz, 2.1Hz, 1H), 1.25 (dd, *J* = 10.7Hz, 8.7Hz, 1H), 0.56 (s, 9H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 173.4, 162.0, 147.5, 138.9, 138.1, 137.0, 133.6, 129.3, 128.6, 128.3, 128.1, 127.7, 127.6, 120.0, 69.3, 55.0, 49.8, 46.4, 44.0, 43.2, 43.0, 40.4, 40.4, 39.9, 33.2, 29.1.

trans-**4m** (as a mixture with *cis*-**4m** (*trans*:*cis* 5:1)): white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) (only *trans* signals reported) δ 8.39 (d, *J* = 4.7Hz, 1H), 7.34-7.27 (m, 5H), 7.09-7.08 (m, 3H), 6.90-6.88 (m, 1H), 6.77 (d, *J* = 7.7Hz, 1H), 6.73-6.72 (m, 2H), 4.95 (d, *J* = 4.2Hz, 1H), 4.69 (d, *J* = 15.1Hz, 1H), 4.32 (d, *J* = 15.7Hz, 1H), 3.69-3.67 (m, 2H), 2.84 (m, 1H), 2.78 (br, 1H), 2.30 (br, 1H), 2.22 (d, *J* = 6.1Hz, 1H), 1.95 (dd, *J* = 10.9Hz, 6.4Hz, 1H), 1.76 (dd, *J* = 10.6Hz, 7.4Hz, 1H), 1.45 (d, *J* = 6.1Hz, 1H), 0.79 (s, 9H). **^{13}C NMR** (126 MHz, CDCl$_3$) (only *trans* signals reported) δ 174.3, 160.9, 148.1, 141.6, 139.0, 136.2, 136.1, 128.3, 128.2, 127.9, 127.3, 126.4, 121.3, 68.0, 58.0, 47.7, 47.0, 46.0, 43.0, 42.6, 41.0, 40.6, 37.2, 33.5, 29.7. *One aromaticsignal is missing (probably due to signal overlap).*

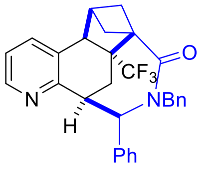


4n, 55%(53%)
>19:1 r.r., 1.0:1 d.r.

Prepared according to ***General Procedure 2*** using **1n** (31.9 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded 2 separable diastereomers of major regioisomer **4n** (46.3 mg, 53% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 437.2224, found: 437.2233.

cis-**4n:** white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.19 (dd, *J* = 4.7Hz, 1.5Hz, 1H), 7.51 (br, 1H), 7.38-7.31 (m, 5H), 7.28-7.25 (m, 3H), 7.16 (t, *J* = 7.3Hz, 1H), 6.94 (dd, *J* = 7.6Hz, 4.8Hz, 1H), 5.90 (d, *J* = 14.5Hz, 1H), 5.45 (d, *J* = 11.3Hz, 1H), 4.15 (ddd, *J* = 11.3Hz, 5.5Hz, 1.8Hz, 1H), 3.34 (s, 3H), 3.26 (d, *J* = 14.5Hz, 1H), 3.22 (br, 1H), 2.58 (dd, *J* = 11.1Hz, 6.3Hz, 1H), 2.52 (dd, *J* = 13.2Hz, 1.8Hz, 1H), 2.12-2.11 (m, 1H), 1.92 (dd, *J* = 13.2Hz, 5.6Hz, 1H), 1.40 (d, *J* = 7.7Hz, 1H), 1.25 (br, 1H), 1.21 (dd, *J* = 11.1Hz, 8.3Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.7, 159.0, 145.4, 138.4, 137.0, 136.7, 135.3, 129.1, 128.7, 128.4, 127.8, 126.9, 121.9, 80.8, 67.0, 59.1, 50.8, 50.7, 50.0, 45.6, 43.7, 40.9, 39.1, 29.2.

trans-**4n:** white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 4.8Hz, 1.5Hz, 1H), 7.42 (d, *J* = 7.6Hz, 1H), 7.26 (m, 4H), 7.10-7.07 (m, 5H), 6.70-6.69 (m, 2H), 5.08 (d, *J* = 4.3Hz, 1H), 4.96 (d, *J* = 15.2Hz, 1H), 4.12 (d, *J* = 15.8Hz, 1H), 4.03-4.00 (m, 1H), 3.41 (br, 1H), 3.38 (s, 3H), 3.07 (dd, *J* = 13.2Hz, 2.2Hz, 1H), 2.74 (dd, *J* = 11.0Hz, 6.6Hz, 1H), 2.37 (d, *J* = 2.2Hz, 1H), 2.22-2.16 (m, 2H), 2.04 (dd, *J* = 11.3Hz, 7.6Hz, 1H), 1.70 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 160.8, 146.9, 142.8, 138.9, 135.9, 135.6, 129.6, 128.6, 128.0, 127.9, 127.1, 126.4, 122.3, 79.7, 67.0, 61.6, 49.8, 49.7, 48.7, 48.3, 42.6, 41.9, 39.7, 28.1.

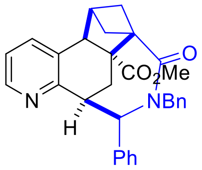


4o, 78%(75%)
>19:1 r.r., 1.2:1 d.r.

Prepared according to ***General Procedure 2*** using **1o** (39.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 20h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded partially separable diastereomers of major regioisomer **4o** (71.2 mg, 75% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 475.1992, found: 475.1992.

cis-**4o** (completely separated): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 4.6Hz, 1.0Hz, 1H), 7.39-7.31 (m, 6H), 7.29-7.28 (m, 2H), 7.26-7.23 (m, 2H), 6.99 (d, *J* = 7.2Hz, 1H), 6.74 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 5.77 (d, *J* = 15.6Hz, 1H), 5.24 (d, *J* = 10.1Hz, 1H), 3.93 (d, *J* = 10.1Hz, 1H), 3.69 (d, *J* = 6.7Hz, 1H), 3.22 (d, *J* = 15.6Hz, 1H), 2.97-2.96 (m, 1H), 2.84 (qd, *J* = 9.6Hz, 3.2Hz, 1H), 2.61 (q, *J* = 2.4Hz, 1H), 2.30 (dd, *J* = 6.6Hz, 1.8Hz, 1H), 1.91 (dd, *J* = 10.7Hz, 6.8Hz, 1H), 1.42 (d, *J* = 7.5Hz, 1H), 1.26 (dd, *J* = 10.8Hz, 8.0Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.1, 160.9, 148.4, 138.9, 137.5, 135.7, 130.2, 129.0, 128.9, 128.5, 128.1, 128.1, 128.0, 126.5 (q, *J* = 279.4Hz), 120.0, 68.0, 54.1, 50.1, 46.6, 43.1, 40.4, 40.2, 40.0, 39.9 (q, *J* = 26.8Hz), 37.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -68.0.

trans-**4o** (as a mixture with *cis*-**4o** (*trans*:*cis* >19:1)): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) (only *trans* signals reported) δ 8.45 (dd, *J* = 3.7Hz, 1.0Hz, 1H), 7.46-7.26 (m, 4H), 7.09-7.06 (m, 4H), 6.93 (dd, *J* = 6.1Hz, 3.8Hz, 1H), 6.80 (dd, *J* = 6.0Hz, 0.8Hz, 1H), 6.66-6.65 (m, 2H), 5.02 (d, *J* = 3.9Hz, 1H), 4.91 (d, *J* = 12.5Hz, 1H), 4.17 (d, *J* = 12.6Hz, 1H), 3.97 (br, 1H), 3.81 (d, *J* = 5.2Hz, 1H), 3.25 (qd, *J* = 7.7Hz, 1.2Hz, 1H), 2.96-2.94 (m, 1H), 2.86 (q, *J* = 1.8Hz, 1H), 2.33 (d, *J* = 4.5Hz, 1H), 1.99 (dd, *J* = 8.6Hz, 5.5Hz, 1H), 1.79 (dd, *J* = 8.6Hz, 6.1Hz, 1H), 1.57 (d, *J* = 4.9Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) (only *trans* signals reported) δ 172.1, 158.8, 147.8, 138.6, 137.4, 135.3, 131.4, 127.9, 127.7, 127.0, 126.1 (q, *J* = 279.2Hz), 125.8, 125.5, 120.3, 65.6, 56.0, 46.7, 46.0, 42.0, 41.3, 40.2, 38.5 (q, *J* = 26.4Hz), 36.8, 36.4. *One aromaticsignal is missing (probably due to signal overlap).* **^{19}F NMR** (470 MHz, $CDCl_3$) (only *trans* signals reported) δ -67.3.

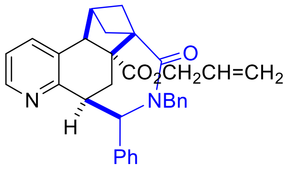


4p, 23%(20%)
>19:1 r.r., 2.3:1 d.r.

Switch of limiting reagent: [Ir-F] (4.4 mg, 2 mol%) as photosensitizer and HFIP (4.0 mL, 0.05M) as solvent. Prepared according to ***General Procedure 2*** using **1p** (38.1 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded 2 separable diastereomers of major regioisomer **4p** (18.6 mg, 20% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 465.2173, found: 465.2166.

cis-**4p**: white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 3.8Hz, 1H), 7.37-7.31 (m, 5H), 7.28-7.26 (m, 5H), 7.01 (d, *J* = 7.8Hz, 1H), 6.74 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 5.72 (d, *J* = 14.7Hz, 1H), 5.29 (d, *J* = 10.0Hz, 1H), 4.25 (d, *J* = 10.2Hz, 1H), 3.73 (d, *J* = 6.4Hz, 1H), 3.52 (s, 3H), 3.22 (d, *J* = 14.7Hz, 1H), 3.19 (m, 1H), 3.07 (d, *J* = 3.6Hz, 1H), 2.53 (d, *J* = 2.1Hz, 1H), 2.28 (dd, *J* = 6.4Hz, 1.7Hz, 1H), 1.92 (dd, *J* = 10.6Hz, 6.7Hz, 1H), 1.40 (d, *J* = 7.1Hz, 1H), 1.25 (dd, *J* = 10.7Hz, 7.9Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 172.5, 160.1, 148.3, 139.2, 137.8, 136.4, 132.6, 128.9, 128.5, 128.0, 127.9, 127.9, 126.9, 120.2, 67.6, 54.2, 52.3, 50.0, 46.4, 44.0, 42.6, 41.3, 40.2, 40.2, 40.1.

trans-**4p**: white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 4.7Hz, 1.6Hz, 1H), 7.50-7.10 (m, 5H), 7.07-7.06 (m, 3H), 6.90 (dd, *J* = 7.7Hz, 4.7Hz, 1H), 6.83 (dd, *J* = 7.7Hz, 1.5Hz, 1H), 6.67-6.66 (m, 2H), 5.08 (d, *J* = 5.2Hz, 1H), 4.89 (d, *J* = 15.6Hz, 1H), 4.23-4.22 (m, 1H), 4.18 (d, *J* = 15.8 Hz, 1H), 3.87 (d, *J* = 6.4Hz, 1H), 3.59 (s, 3H), 3.47 (m, 1H), 3.13 (t, *J* = 3.1Hz, 1H), 2.80 (d, *J* = 2.3Hz, 1H), 2.29 (d, *J* = 4.7Hz, 1H), 1.99 (dd, *J* = 10.6Hz, 6.5Hz, 1H), 1.80 (dd, *J* = 10.7Hz, 7.5Hz, 1H), 1.55 (d, *J* = 4.7Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.6, 173.1, 159.5, 148.9, 140.2, 138.8, 136.8, 134.1, 128.6, 128.5, 127.9, 126.9, 126.4, 121.3, 66.0, 57.0, 52.2, 47.7, 46.8, 45.7, 43.2, 41.1, 41.0, 40.1, 37.7. *One aromaticsignal is missing (probably due to signal overlap).*

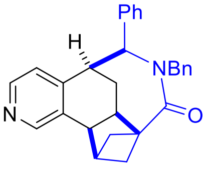


4q, 25%(21%)
>19:1 r.r., 1.5:1 d.r.

Switch of limiting reagent: [Ir-F] (4.4 mg, 2 mol%) as photosensitizer and HFIP (4.0 mL, 0.05M) as solvent. Prepared according to ***General Procedure 2*** using **1q** (45.5 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded 2 separable diastereomers of major regioisomer **4q** (20.6 mg, 21% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 491.2329, found: 491.2327.

cis-**4q:** white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.37-7.33 (m, 3H), 7.30-7.28 (m, 7H), 7.05 (d, *J* = 7.9Hz, 1H), 6.77 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 5.75 (d, *J* = 14.6Hz, 1H), 5.73-5.64 (m, 1H), 5.31 (d, *J* = 10.2Hz, 1H), 5.14 (dd, *J* = 10.5Hz, 1.1Hz, 1H), 5.09 (dd, *J* = 17.1Hz, 1.4Hz, 1H), 4.43 (d, *J* = 5.6Hz, 2H), 4.28 (d, *J* = 10.3Hz, 1H), 3.76 (d, *J* = 7.0Hz, 1H), 3.27-3.23 (m, 2H), 3.12 (d, *J* = 3.8Hz, 1H), 2.55 (d, *J* = 2.3Hz, 1H), 2.31 (dd, *J* = 6.5Hz, 1.9Hz, 1H), 1.95 (dd, *J* = 10.5Hz, 6.7Hz, 1H), 1.42 (d, *J* = 7.5Hz, 1H), 1.28 (dd, *J* = 10.7Hz, 7.9Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.6, 171.6, 160.2, 148.2, 139.3, 137.9, 136.5, 132.7, 131.5, 128.9, 128.9, 128.4, 128.0, 127.9, 127.9, 120.1, 118.4, 67.6, 65.6, 54.2 ,50.0, 46.4, 44.0, 42.7, 41.5, 40.2, 40.2.

trans-**4q:** white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 4.5Hz, 1.2Hz, 1H), 7.31-7.26 (m, 5H), 7.08-7.06 (m, 3H), 6.91 (dd, *J* = 7.7Hz, 4.8Hz, 1H), 6.83 (dd, *J* = 7.6Hz, 0.9Hz, 1H), 6.68-6.66 (m, 2H), 5.77-5.69 (m, 1H), 5.13 (d, *J* = 20.6Hz, 2H), 5.11 (d, *J* = 16.7Hz, 1H), 4.89 (d, *J* = 15.7Hz, 1H), 4.25-4.23 (m, 1H), 4.19 (d, *J* = 15.7Hz, 1H), 3.88 (d, *J* = 6.2 Hz, 1H), 3.49 (br, 1H), 3.16-3.15 (m, 1H), 2.81 (d, *J* = 2.0Hz, 1H), 2.29 (d, *J* = 5.2Hz, 1H), 2.05-1.98 (m, 1H), 1.81 (dd, *J* = 10.6Hz, 7.5Hz, 1H), 1.57 (d, *J* = 5.9Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.6, 172.3, 159.5, 148.9, 140.1, 138.8, 136.8, 134.1, 131.7, 128.9, 128.6, 128.5, 128.0, 126.9, 126.4, 121.3, 118.2, 66.0, 65.4, 57.1, 47.7, 46.8, 45.7, 43.2, 41.3, 40.9, 40.2, 37.7.

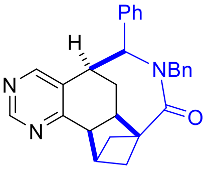


4R, 52%(51%)
>19:1 r.r., 2.1:1 d.r.

Switch of limiting reagent: [Ir-F] (4.4 mg, 2 mol%) as photosensitizer and HFIP (4.0 mL, 0.05M) as solvent. Prepared according to ***General Procedure 2*** using **1r** (26 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded partially separable diastereomers of major regioisomer **4R** (41.3 mg, 51% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 407.2118, found: 407.2108.

cis-**4R** (as a mixture with *trans*-**4R** (*cis*:*trans* 11:1)): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) (only *cis* signals reported) δ 8.19 (d, *J* = 4.0Hz, 1H), 8.06 (s, 1H), 7.36-7.21 (m, 10H), 6.94 (d, *J* = 3.8Hz, 1H), 5.77 (d, *J* = 11.7Hz, 1H), 5.21 (d, *J* = 8.2Hz, 1H), 3.82 (dd, *J* = 7.8Hz, 4.0Hz, 1H), 3.50 (d, *J* = 5.4Hz, 1H), 3.22 (d, *J* = 11.7Hz, 1H), 2.69 (br, 1H), 2.31 (br, 1H), 2.21 (d, *J* = 4.8Hz, 1H), 2.15 (dd, *J* = 10.9Hz, 2.6Hz, 1H), 1.89-1.81 (m, 1H), 1.76 (dd, *J* = 10.4Hz, 3.2Hz, 1H), 1.33 (d, *J* = 5.7Hz, 1H), 1.27-1.24 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) (only *cis* signals reported) δ 173.4, 139.2, 150.8, 148.0, 138.2, 137.1, 135.4, 129.1, 128.7, 128.4, 127.9, 127.7, 127.1, 67.9, 54.3, 50.2, 46.3, 42.6, 40.7, 40.2, 38.3, 37.9, 26.3.

trans-**4R** (completely separated): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 5.0Hz, 1H), 7.76(s, 1H), 7.32-7.23(m, 4H), 7.09-7.07(m, 5H), 6.72-6.69 (m, 2H), 5.10 (d, *J* = 5.4Hz, 1H), 4.79 (d, *J* = 15.6Hz, 1H), 4.27 (d, *J* = 15.6Hz, 1H), 3.72(br, 1H), 3.61 (d, *J* = 5.7Hz, 1H), 2.70(br, 1H), 2.58 (d, *J* = 2.4Hz, 1H), 2.53 (ddd, *J* = 14.0Hz, 4.2Hz, 2.4Hz, 1H), 2.24 (d, *J* = 1.9Hz, 1H), 1.93-1.89(m, 3H), 1.53(m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.1, 149.8, 149.7, 148.9, 140.5, 139.1, 137.0, 130.6, 128.5, 128.3, 127.9, 127.1, 126.3, 123.3, 66.5, 57.2, 47.7, 46.9, 41.2, 40.9, 38.3, 37.8, 26.0.



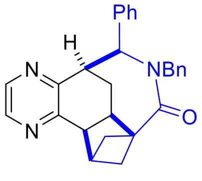
4S, 70%(62%)
7.8:1 r.r., 1.1:1 d.r.

Prepared according to ***General Procedure 2*** using **1s** (26.6 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 18h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded 2 separable diastereomers of major regioisomer **4S** (50.3 mg, 62% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 408.2070, found: 408.2079.

cis-**4S:** white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.14 (s, 1H), 7.37-7.30 (m, 7H), 7.28-7.25 (m, 3H), 5.79 (d, *J* = 14.6Hz, 1H), 5.24 (d, *J* = 9.0Hz, 1H), 3.83 (br, 1H), 3.62 (d, *J* = 5.2Hz, 1H), 3.23 (d, *J* = 14.7Hz, 1H), 2.81 (br, 1H), 2.56 (br, 1H), 2.27 (d, *J* = 5.0Hz, 1H), 2.20 (d, *J* = 11.3Hz, 1H), 1.88 (dd, *J* = 10.6Hz, 6.7Hz, 1H), 1.83 (d, *J* = 12.3Hz, 1H), 1.41 (d, *J* = 6.7Hz, 1H), 1.14 (dd, *J* = 10.5Hz, 8.5Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.8, 170.7, 157.7, 156.5, 137.9, 136.7, 129.1, 128.8, 128.7, 128.0, 127.8, 127.4, 127.3, 67.2, 54.6, 50.2, 46.5, 45.1, 40.4, 40.0, 38.5, 38.3, 25.9

trans-**4S:** white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.87 (s, 1H), 7.31-7.27 (m, 4H), 7.09 (m, 4H), 5.10 (d, *J* = 5.0Hz, 1H), 4.77 (d, *J* = 15.5Hz, 1H), 4.28 (d, *J* = 15.6Hz, 1H), 3.73 (s, 1H), 3.68 (d, *J* = 6.3Hz, 1H), 2.80 (s, 2H), 2.57 (d, *J* = 13.9Hz, 1H), 2.27 (d, *J* = 5.6Hz, 1H), 1.94 (dd, *J* = 11.2Hz, 5.6Hz, 2H), 1.80 (dd, *J* =

10.6Hz, 7.9Hz, 1H), 1.61 (d, *J* = 6.4Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 173.8, 169.5, 157.8, 155.9, 140.0, 138.9, 130.5, 128.7, 128.6, 127.9, 127.1, 126.4, 66.1, 57.5, 47.7, 47.0, 44.3, 41.1, 40.8, 38.6, 37.7, 25.6. *One aromaticsignal is missing (probably due to signal overlap).*

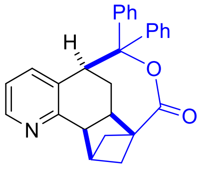


4T, 68%(65%)
1:1.1 d.r.

Prepared according to ***General Procedure 2*** using **1t** (26.3 mg, 0.20 mmol) and **2a** (110.9 mg, 0.40 mmol) for 18h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded **4T** as 2 separable diastereomers (43.3 mg, 65% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 408.2070, found: 408.2073.

cis-**4T:** white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.22 (d, *J* = 2.3Hz, 1H), 8.13 (d, *J* = 2.3Hz, 1H), 7.46 (br, 2H), 7.36-7.31 (m, 5H), 7.27-7.24 (m, 2H), 7.17 (t, *J* = 7Hz, 1H), 5.85 (d, *J* = 14.6Hz, 1H), 5.42 (d, *J* = 11.2Hz, 1H), 4.05 (dd, *J* = 11.0Hz, 5.2Hz, 1H), 3.64 (d, *J* = 6.7Hz, 1H), 3.28 (d, *J* = 14.6Hz, 1H), 2.76 (br, 1H), 2.44 (d, *J* = 2.3Hz, 1H), 2.24-2.18 (m, 2H), 1.86-1.80 (m, 2H), 1.22 (d, *J* = 7.0Hz, 1H), 0.83 (dd, *J* = 10.7Hz, 8.5Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 173.5, 157.5, 155.4, 142.3, 139.8, 138.2, 136.4, 129.2, 128.7, 128.3, 127.7, 127.4, 127.0, 66.7, 54.7, 50.9, 45.9, 44.9, 42.8, 40.3, 39.9, 38.5, 26.3.

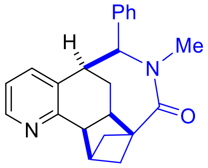
trans-**4T:** white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.36 (d, *J* = 2.4Hz, 1H), 8.17 (d, *J* = 2.4Hz, 1H), 7.38-7.30 (m, 1H), 7.25-7.17 (m, 3H), 7.09-7.08 (m, 4H), 6.70 (m, 2H), 5.22 (d, *J* = 4.9Hz, 1H), 4.81 (d, *J* = 15.7Hz, 1H), 4.22 (d, *J* = 15.8Hz, 1H), 3.94 (br, 1H), 3.79 (d, *J* = 6.9Hz, 1H), 2.81 (br, 1H), 2.73 (d, *J* = 2.2Hz, 1H), 2.61 (ddd, *J* = 14.0Hz, 3.7Hz, 1.8Hz, 1H), 2.26 (d, *J* = 5.0Hz, 1H), 2.04 (dd, *J* = 14.1Hz, 4.6Hz, 1H), 1.94 (dd, *J* = 10.7Hz, 6.6Hz, 1H), 1.67 (dd, *J* = 10.6Hz, 7.8Hz, 1H), 1.57 (d, *J* = 6.0Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 174.1, 157.1, 156.4, 142.9, 141.1, 140.9, 139.0, 130.3, 128.5, 128.2, 127.9, 127.0, 126.3, 66.2, 57.4, 47.9, 46.9, 46.5, 44.4, 41.0, 38.8, 37.5, 25.7.



4U, 43%(43%)
>19:1 r.r.

Prepared according to ***General Procedure 2*** using **1a** (26.1 mg, 0.20 mmol), **2u** (105.7 mg, 0.40 mmol) with 1.25 eq *p*TsOH·H$_2$O (47.5 mg, 0.25 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded major regioisomer **4U** (33.6 mg, 43% yield) as white solid. **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 394.1802, found: 394.1809.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.53 (dd, *J* = 4.5Hz, 1.2Hz, 1H), 7.66 (d, *J* = 7.6Hz, 1H), 7.34-7.30 (m, 5H), 7.29-7.27 (m, 2H), 7.25-7.21 (m, 3H), 6.83 (s, 1H), 3.28 (d, *J* = 8.5Hz, 1H), 3.11 (d, *J* = 5.6Hz, 1H), 2.60 (d, *J* = 1.2Hz, 1H), 2.40 (d, *J* = 8.5Hz, 1H), 2.34 (d, *J* = 5.2Hz, 1H), 1.96 (dd, *J* = 6.4Hz, 2.8Hz, 1H), 1.66 (m, 1H), 1.55 (d, *J* = 6.9Hz, 1H), 0.99 (t, *J* = 8.6Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 171.2, 157.1, 147.9, 140.3, 140.3, 137.0, 132.7, 128.8, 128.5, 128.1, 127.8, 127.3, 126.4, 122.0, 76.7, 56.3, 45.5, 44.5, 44.0, 43.3, 40.9, 36.1, 33.6.

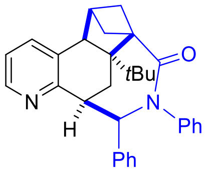


4V, 36 %(30%)
8.0:1 r.r., 1.3:1 d.r.

Prepared according to ***General Procedure 2*** using **1a** (26.1 mg, 0.20 mmol) and **2v** (80.5 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4V** (19.8 mg, 30% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 331.1805, found: 331.1805.

cis-**4V:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 3.7Hz, 1H), 7.33-7.28 (m, 2H), 7.23-7.21 (m, 2H), 7.16 (d, *J* = 7.6Hz, 1H), 6.83 (dd, *J* = 7.7Hz, 5.0Hz, 1H), 5.26 (d, *J* = 10.1Hz, 1H), 4.02 (dd, *J* = 9.8Hz, 5.7Hz, 1H), 3.73 (d, *J* = 6.8Hz, 1H), 2.95 (s, 3H), 2.76 (br, 1H), 2.51 (d, *J* = 2.0Hz, 1H), 2.42 (dd, *J* = 13.8Hz, 3.8Hz, 1H), 2.17 (dd, *J* = 6.2Hz, 1.7Hz, 1H), 2.03 (ddd, *J* = 14.1Hz, 5.7Hz, 1.8Hz, 1H), 1.80 (dd, *J* = 10.6Hz, 7.2Hz, 1H), 1.31 (d, *J* = 7.1Hz, 1H), 1.16 (dd, *J* = 10.8Hz, 7.9Hz, 1H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.0, 161.1, 147.1, 139.5, 137.2, 135.6, 128.3, 127.6, 127.5, 120.1, 72.6, 54.9, 46.4, 44.8, 41.5, 40.5, 40.3, 38.4, 37.0, 26.0.

trans-**4V:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 3.9Hz, 1H), 7.46-7.44 (m, 2H), 7.42-7.39 (m, 1H), 7.36 (d, *J* = 7.0Hz, 2H), 7.08 (dd, *J* = 7.7Hz, 5.0Hz, 1H), 7.04 (dd, *J* = 7.8Hz, 1.6Hz, 1H), 5.13 (d, *J* = 5.6Hz, 1H), 3.82-3.81 (m, 2H), 2.80-2.79 (m, 1H), 2.73 (br, 1H), 2.60 (s, 3H), 2.34 (ddd, *J* = 14.0Hz, 4.2Hz, 2.3Hz, 1H), 2.17 (dd, *J* = 6.1Hz, 1.6Hz, 1H), 2.01 (ddd, *J* = 13.9Hz, 4.3Hz, 2.0Hz, 1H), 1.87 (dd, *J* = 10.8Hz, 6.6Hz, 1H), 1.74 (dd, *J* = 10.9Hz, 7.6Hz, 1H), 1.50 (dd, *J* = 6.8Hz, 1.3Hz, 1H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.4, 159.8, 146.9, 140.5, 138.2, 138.0, 130.2, 129.1, 128.6, 121.7, 65.7, 57.7, 46.8, 43.6, 42.4, 41.2, 39.1, 37.9, 32.1, 25.7.

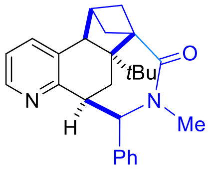


4w, 39%(39%)
>19:1 r.r., 1:2.9 d.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2w** (105.3 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4w** (35 mg, 39% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 449.2587, found: 449.2586.

cis-**4w:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 4.8Hz, 1H), 7.33 (d, *J* = 7.7Hz, 2H), 7.29-7.25 (m, 4H), 7.20-7.18 (m, 2H), 7.08 (d, *J* = 6.3Hz, 2H), 6.99 (d, *J* = 7.9Hz, 1H), 6.77 (dd, *J* = 7.6Hz, 4.8Hz, 1H), 5.53 (d, *J* = 10.0Hz, 1H), 4.01 (d, *J* = 9.8Hz, 1H), 3.70 (d, *J* = 6.7Hz, 1H), 2.96-2.95 (m, 1H), 2.63 (m, 1H), 2.53 (d, *J* = 2.8Hz, 1H), 2.23 (d, *J* = 6.2Hz, 1H), 1.87 (dd, *J* = 10.6Hz, 6.7Hz, 1H), 1.51 (d, *J* = 6.9Hz, 1H), 1.38 (dd, *J* = 10.6Hz, 7.8Hz, 1H), 0.88 (s, 9H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.2, 161.8, 147.0, 145.5, 139.7, 137.2, 134.0, 129.3, 128.4, 128.1, 127.9, 127.6, 127.1, 120.3, 76.6, 55.3, 46.7, 45.0, 43.8, 42.8, 40.6, 40.5, 33.7, 29.7, 29.6.

trans-**4w:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.6Hz, 1H), 7.08 (m, 5H), 7.00 (d, *J* = 7.2Hz, 1H), 6.97-6.94 (m, 3H), 6.87 (d, *J* = 7.5Hz, 1H), 6.78 (m, 2H), 5.30 (d, *J* = 4.5Hz, 1H), 3.75 (br, 1H), 3.72 (d, *J* = 6.3Hz, 1H), 2.93 (t, *J* = 3.0Hz, 1H), 2.81 (br, 1H), 2.69 (br, 1H), 2.19 (d, *J* = 4.1Hz, 1H), 1.90 (t, *J* = 6.0Hz, 2H), 1.53 (d, *J* = 2.8Hz, 1H), 0.92 (s, 9H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.5, 161.0, 148.2, 142.1, 140.9, 136.4, 136.1, 130.6, 130.3, 128.3, 128.3, 127.4, 126.5, 121.4, 69.7, 57.7, 46.8, 46.6, 43.9, 42.7, 41.1, 40.8, 37.5, 33.6, 30.0.

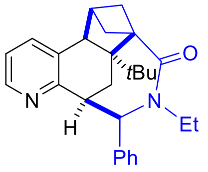


4wa, 74%(71%)
>19:1 r.r., 1:1.4 d.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2v** (161 mg, 0.80 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4wa** (54.8 mg, 71% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 387.2431, found: 387.2431.

cis-**4wa:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 5.8Hz, 1H), 7.31 (t, *J* = 7.5Hz, 2H), 7.25-7.22 (m, 3H), 6.88 (d, *J* = 7.8Hz, 1H), 6.69 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 5.06 (d, *J* = 9.6Hz, 1H), 3.93 (d, *J* = 9.4Hz, 1H), 3.58 (d, *J* = 6.8Hz, 1H), 2.90 (s, 3H), 2.83 (d, *J* = 5.4Hz, 1H), 2.52 (d, *J* = 1.9Hz, 1H), 2.17 (dd, *J* = 7.2Hz, 2.1Hz, 1H), 2.11 (d, *J* = 3.0Hz, 1H), 1.83 (dd, *J* = 10.6Hz, 6.6Hz, 1H), 1.32 (d, *J* = 7.2Hz, 1H), 1.26-1.23 (m, 1H), 0.80 (s, 9H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.1, 162.1, 147.7, 138.6, 137.3, 133.5, 129.3, 128.3, 127.7, 120.0, 75.0, 55.6, 46.6, 44.3, 44.0, 43.2, 40.4, 40.3, 40.3, 36.8, 33.5, 29.4.

trans-**4wa:** white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 4.5Hz, 1H), 7.45-7.38 (m, 3H), 7.31 (m, 2H), 6.93 (dd, *J* = 7.5Hz, 5.1Hz, 1H), 6.85 (d, *J* = 7.4Hz, 1H), 4.94 (d, *J* = 4.4Hz, 1H), 3.76 (br, 1H), 3.64 (d, *J* = 5.3Hz, 1H), 2.75 (m, 2H), 2.60 (s, 3H), 2.15 (d, *J* = 5.0Hz, 1H), 2.04 (d, *J* = 2.5Hz, 1H), 1.88 (dd, *J* = 10.8Hz, 6.4Hz, 1H), 1.71-1.69 (m, 1H), 1.36 (d, *J* = 5.1Hz, 1H), 0.85 (s, 9H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.7, 161.0, 148.1, 142.1, 136.2, 136.1, 129.8, 129.1, 128.4, 121.3, 67.7, 58.2, 46.8, 45.7, 43.4, 42.4, 41.0, 40.9, 37.2, 33.5, 32.6, 29.9.

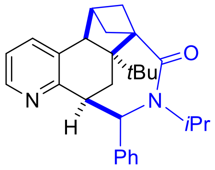


4wb, 66%(51%)
>19:1 r.r., 1.4:1 d.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2b** (86.1 mg, 0.40 mmol) for 16h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded partially separable diastereomers of major regioisomer **4wb** (40.7 mg, 51% yield). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 401.2587, found: 401.2590.

cis-**4wb** (completely separated): white solid. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.29-7.27 (m, 4H), 7.23-7.21 (m, 1H), 7.01 (dd, *J* = 7.8Hz, 1.4Hz, 1H), 6.72 (dd, *J* = 7.8Hz, 1.0Hz, 1H), 5.15 (d, *J* = 9.8Hz, 1H), 4.09-4.01 (m, 1H), 3.98 (dd, *J* = 9.8Hz, 1.6Hz, 1H), 3.57 (dd, *J* = 7.0Hz, 2.1Hz, 1H), 2.81-2.79 (m, 1H), 2.51-2.50 (m, 1H), 2.46-2.37 (m, 1H), 2.15 (dd, *J* = 6.5Hz, 2.0Hz, 1H), 2.08 (d, *J* = 3.2Hz, 1H), 1.81 (dd, *J* = 10.5Hz, 6.6Hz, 1H), 1.29 (dd, *J* = 7.2z, 1.7Hz, 1H), 1.22-1.18 (m, 4H), 0.80 (s, 9H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 172.5, 162.2, 147.7, 138.9, 137.6, 133.5, 128.1, 128.1, 127.5, 120.0, 71.2, 55.2, 46.4, 44.5, 43.4, 43.3, 43.2, 40.3, 40.2, 39.9, 33.4, 29.5, 12.3.

trans-**4wb** (as a mixture with *cis*-**4wb** (*trans*:*cis* 2.5:1)): white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) (only *trans* signals reported) δ 8.42 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.45-7.41 (m, 5H), 6.95 (dd, *J* = 7.6Hz, 4.9Hz, 1H), 6.83 (dd, *J* = 7.6Hz, 1.3Hz, 1H), 4.98 (d, *J* = 4.9Hz, 1H), 3.77 (br, 1H), 3.67 (d, *J* = 6.8Hz, 1H), 3.31-3.25 (m, 1H), 3.10-3.05 (m, 1H), 2.77-2.75 (m, 2H), 2.15-2.14 (m, 1H), 1.87 (dd, *J* = 10.7Hz, 6.5Hz, 1H), 1.68 (dd, *J* = 10.9Hz, 7.6Hz, 1H), 1.37 (d, *J* = 6.5Hz, 1H), 1.26 (m, 1H), 0.85-0.83 (m, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) (only *trans* signals reported) δ 173.0, 160.8, 147.6, 141.5, 136.6, 129.2, 128.5, 128.1, 127.6, 67.2, 58.1, 46.8, 45.4, 43.2, 42.3, 40.9, 40.6, 38.9, 37.3, 33.5, 29.8, 14.2.

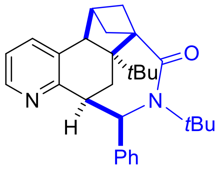


4wc, 65%(52%)
>19:1 r.r., 1.4:1 d.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2c** (91.7 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded 2 separable diastereomers of major regioisomer **4wc** (43.1 mg, 52% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 415.2744, found: 415.2742.

cis-**4wc:** white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.23 (d, *J* = 4.6Hz, 1H), 7.31 (m, 2H), 7.26-7.24 (m, 2H), 7.16 (t, *J* = 7.2Hz, 1H), 7.09 (d, *J* = 7.7Hz, 1H), 6.73 (dd, *J* = 7.7Hz, 4.7Hz, 1H), 5.15 (d, *J* = 10.1Hz, 1H), 4.43 (br, 1H), 3.99 (d, *J* = 10.0Hz, 1H), 3.53 (dd, *J* = 6.7Hz, 1.7Hz, 1H), 2.76-2.75 (m, 1H), 2.49 (d, *J* = 2.1Hz, 1H), 2.14 (d, *J* = 4.8Hz, 1H), 2.03 (d, *J* = 2.9Hz, 1H), 1.80 (dd, *J* = 10.7Hz, 1.5Hz, 1H), 1.29 (d, *J* = 6.7Hz, 3H), 1.26 (br, 1H), 1.17 (dd, *J* = 10.8Hz, 8.0Hz, 1H), 0.95 (d, *J* = 6.8Hz, 3H), 0.78 (s, 9H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 173.3, 162.3, 147.7, 139.3, 139.3, 133.6, 128.4, 127.6, 127.2, 119.9, 68.2, 55.6, 50.1, 46.6, 44.3, 43.7, 43.1, 40.4, 40.2, 39.8, 33.4, 29.5, 20.4, 19.9.

trans-**4wc:** white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.38 (dd, *J* = 4.8Hz, 1.4Hz, 1H), 7.55 (m, 2H), 7.41-7.37 (m, 2H), 7.12 (m, 1H), 6.87 (dd, *J* = 7.6Hz, 4.8Hz, 1H), 6.73 (d, *J* = 7.6Hz, 1H), 5.07 (d, *J* = 5.4Hz, 1H), 3.80 (br, 1H), 3.63 (d, *J* = 6.5Hz, 1H), 3.18-3.13 (m, 1H), 2.73 (m, 2H), 2.18 (d, *J* = 2.8Hz, 1H), 2.10 (d, *J* = 5.0Hz, 1H), 1.84 (dd, *J* = 10.8Hz, 6.3Hz, 1H), 1.65 (dd, *J* = 10.8Hz, 7.4Hz, 1H), 1.41-1.39 (m, 4H), 1.07 (d, *J* = 6.7Hz, 3H), 0.86 (s, 9H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 173.5, 161.1, 148.0, 141.2, 136.2, 136.0, 129.4, 129.0, 128.5, 121.2, 68.0, 59.1, 49.5, 46.7, 44.3, 43.5, 42.5, 40.6, 40.5, 37.7, 33.5, 29.9, 20.1, 20.0.

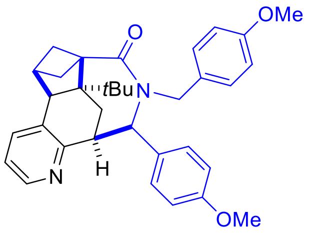


4wd, 60 %(53%)
>19:1 r.r., >19:1 d.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2d** (97.3 mg, 0.40 mmol) for 2h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded a *cis*-diastereomer of major regioisomer **4wd** (45.3 mg, 53% yield) as a white solid. **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 429.2900, found: 429.2896.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.24 (dd, *J* = 4.8Hz, 1.6Hz, 1H), 7.29-7.24 (m, 5H), 7.14 (t, *J* = 7.3Hz, 1H), 6.78 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 5.63 (d, *J* = 10.5Hz, 1H), 4.04 (dd, *J* = 10.4Hz, 1.7Hz, 1H), 3.53 (dd, *J* = 6.9Hz, 2.0Hz, 1H), 2.73-2.71 (m, 1H), 2.44 (d, *J* = 2.4Hz, 1H), 2.09 (d, *J* = 3.6Hz, 1H), 1.78 (dd, *J* = 10.6Hz, 6.5Hz, 1H), 1.42 (s, 9H), 1.20 (dd, *J* = 7.8Hz, 2.4Hz, 1H), 1.01 (dd, *J* = 11.0Hz, 8.0Hz, 1H), 0.78 (s, 9H). **^{13}C NMR** (126 MHz, CDCl$_3$)

δ 174.1, 162.5, 147.6, 140.3, 139.9, 128.3, 127.6, 126.9, 119.8, 67.3, 61.0, 57.0, 46.8, 44.3, 44.0, 43.2, 40.2, 39.8, 39.8, 33.3, 29.5, 29.2.

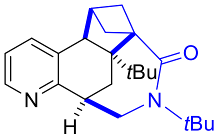


4we, 76%(71%)
>19:1 r.r., 3.8:1 d.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2e** (134.9 mg, 0.40 mmol) for 10h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 2/1) afforded partially separable diastereomers of major regioisomer **4we** (74 mg, 71% yield). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^{+}$: 523.2955, found: 523.2955.

cis-**4we** (completely separated): white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.23 (d, *J* = 3.7Hz, 1H), 7.24 (d, *J* = 8.3Hz, 2H), 7.18 (d, *J* = 7.1Hz, 2H), 6.94 (d, *J* = 7.5Hz, 1H), 6.87 (d, *J* = 8.5Hz, 2H), 6.84 (d, *J* = 8.5Hz, 2H), 6.72 (dd, *J* = 7.5Hz, 4.9Hz, 1H), 5.70 (d, *J* = 14.4Hz, 1H), 5.04 (d, *J* = 9.9Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.65 (d, *J* = 9.1Hz, 1H), 3.55 (d, *J* = 6.2Hz, 1H), 3.09 (d, *J* = 14.4Hz, 1H), 2.80 (d, *J* = 5.6Hz, 1H), 2.52 (br, 1H), 2.20 (d, *J* = 5.0Hz, 1H), 1.85 (dd, *J* = 10.3Hz, 6.7Hz, 1H), 1.79 (br, 1H), 1.31 (d, *J* = 6.7Hz, 1H), 1.25 (dd, *J* = 10.5Hz, 7.6Hz, 1H), 0.56 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 173.3, 162.1, 159.2, 158.8, 147.6, 138.9, 133.7, 130.5, 130.3, 129.2, 128.9, 120.1, 113.9, 113.6, 68.6, 55.4, 55.3, 55.0, 49.1, 46.5, 44.0, 43.2, 40.5, 40.4, 39.9.

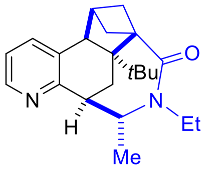
trans-**4we** (as a mixture with *cis*-**4we** (*trans*:*cis* 1:2.8)): white solid. **^{1}H NMR** (500 MHz, CDCl$_3$) (only *trans* signals reported) δ 8.38 (dd, *J* = 4.8Hz, 1.7Hz, 1H), 7.04-6.93 (m, 2H), 6.90-6.86 (m, 1H), 6.80 (dd, *J* = 7.7Hz, 1.6Hz, 1H), 6.74-6.71 (m, 3H), 6.67-6.65 (m, 3H), 4.93 (d, *J* = 4.8Hz, 1H), 4.47 (d, *J* = 15.6Hz, 1H), 4.34 (d, *J* = 15.1Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.66-3.65 (m, 2H), 2.82-2.79 (m, 1H), 2.77 (dd, *J* = 4.9Hz, 2.6Hz, 1H), 2.21 (d, *J* = 3.1Hz, 1H), 1.93 (dd, *J* = 10.6Hz, 6.5Hz, 1H), 1.73 (dd, *J* = 10.8Hz, 7.5Hz, 1H), 1.43-1.41 (m, 1H), 1.27-1.23 (m, 1H), 0.77 (s, 9H). **^{13}C NMR** (126 MHz, CDCl$_3$) (only *trans* signals reported) δ 174.1, 160.9, 159.3, 158.2, 148.0, 136.2, 136.2, 133.4, 131.3, 130.5 (overlapping with *cis*-**4we**), 130.2 (overlapping with *cis*-**4we**), 128.7, 121.2, 113.2, 68.5(overlapping with *cis*-**4we**), 67.2, 58.0, 46.9, 46.7, 45.7, 43.2, 42.9, 42.6, 40.9, 40.7, 37.3, 33.4, 29.7.



4wf, 59%(59%)
>19:1 r.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2f** (134 mg, 0.80 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded major regioisomer **4wf** (41.4 mg, 59% yield) as white solid. **HRMS** (ESI, *m/z*) calcd. for [M+H]$^{+}$: 353.2587, found: 353.2587.

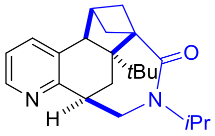
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.43 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.30 (dd, *J* = 7.6Hz, 1.2Hz, 1H), 7.06 (dd, *J* = 7.6Hz, 4.9Hz, 1H), 3.96 (dd, *J* = 16.3Hz, 11.5Hz, 1H), 3.59 (dd, *J* = 6.6Hz, 1.5Hz, 1H), 3.40 (dd, *J* = 16.2Hz, 5.2Hz, 1H), 3.25-3.23 (m, 1H), 2.68-2.67 (m, 1H), 2.65-2.64 (m, 1H), 2.01 (d, *J* = 4.9Hz, 1H), 1.90 (d, *J* = 2.4Hz, 1H), 1.72 (dd, *J* = 10.7Hz, 6.4Hz, 1H), 1.54-1.50 (m, 1H), 1.48 (s, 9H), 1.28-1.26 (m, 1H), 0.78 (s, 9H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 173.6, 161.5, 147.9, 136.7, 136.6, 121.2, 59.3, 58.0, 47.0, 45.9, 42.9, 42.6, 40.7, 40.2, 37.8, 36.3, 32.9, 29.7, 29.5.



4wg, 38%(37%)
>19:1 r.r., <1:19 d.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2g** (122.6 mg, 0.80 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) and subsequent PTLC (petroleum ether/EtOAc= 5/4) afforded a *trans*-diastereomer of major regioisomer **4wg** (25.0 mg, 37% yield) as a white solid. **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 339.2431, found: 339.2431.

^{1}**H NMR** (500 MHz, CDCl$_3$) δ 8.45 (dd, *J* = 4.8Hz, 1.5Hz, 1H), 7.38 (dd, *J* = 7.7Hz, 1.6Hz, 1H), 7.08 (dd, *J* = 7.6Hz, 4.8Hz, 1H), 4.13-4.08 (m, 1H), 3.83-3.79 (m, 1H), 3.58 (dd, *J* = 6.7Hz, 1.6Hz, 1H), 3.38-3.31 (m, 1H), 2.82-2.81 (m, 1H), 2.72 (q, *J* = 2.5Hz, 1H), 2.63-2.62 (m, 1H), 2.06 (dd, *J* = 6.0Hz, 1.2Hz, 1H), 1.81 (dd, *J* = 10.9Hz, 6.4Hz, 1H), 1.75 (d, *J* = 2.6Hz, 1H), 1.58 (d, *J* = 7.0Hz, 3H), 1.28 (d, *J* = 7.0Hz, 1H), 1.18-1.15 (m, 4H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 173.0, 161.4, 148.0, 136.3, 136.2, 121.3, 58.0, 56.3, 46.5, 46.4, 42.8, 42.7, 40.8(2C), 37.6, 36.3, 32.9, 29.7, 21.7, 15.9.



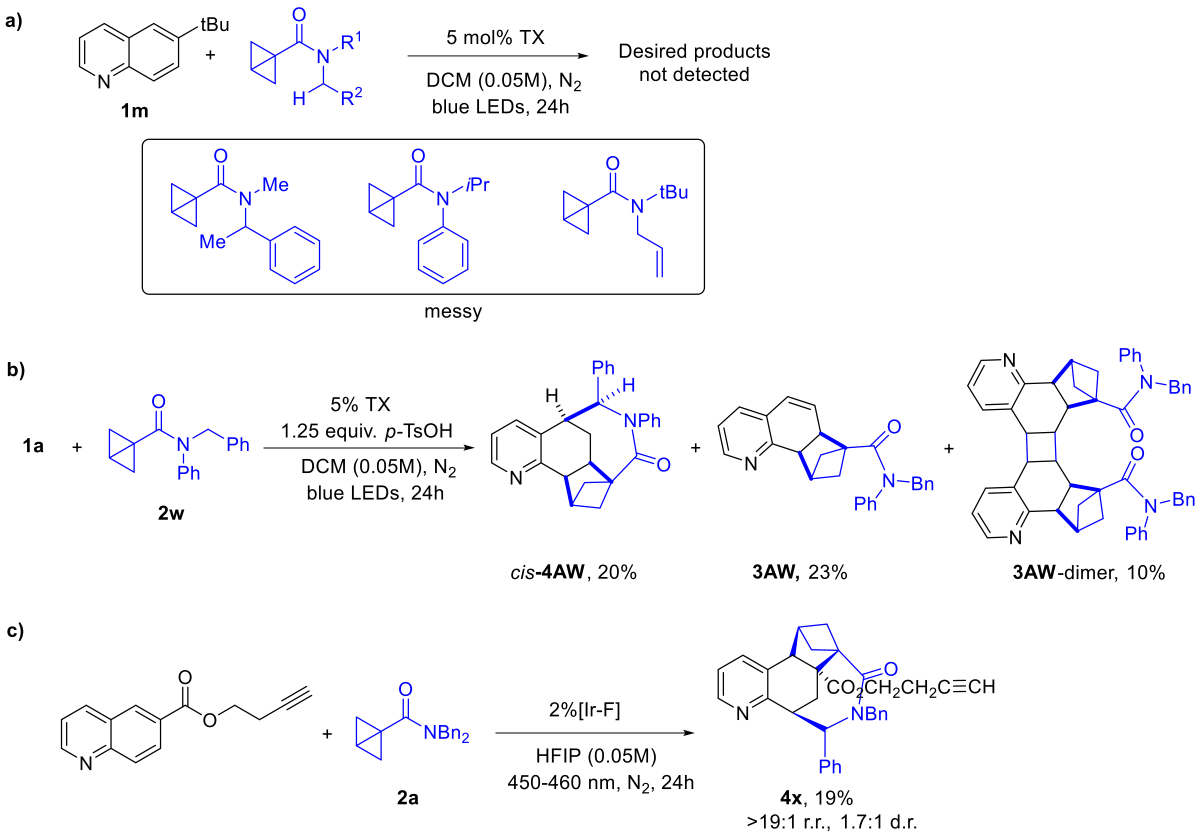
4wh, 25%(25%)
>19:1 r.r.

Prepared according to ***General Procedure 2*** using **1m** (37.1 mg, 0.20 mmol) and **2h** (61.2 mg, 0.40 mmol) for 24h. Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded major regioisomer **4wh** (16.9 mg, 25% yield) as white solid. **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 339.2431, found: 339.2431.

^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.43 (dd, *J* = 4.8Hz, 1.6Hz, 1H), 7.34 (dd, *J* = 7.6Hz, 1.5Hz, 1H), 7.08 (dd, *J* = 7.6Hz, 4.8Hz, 1H), 5.08-4.99 (m, 1H), 3.71 (dd, *J* = 14.4Hz, 10.6Hz, H), 3.60 (dd, *J* = 6.9Hz, 1.8Hz, 1H), 3.37-3.29 (m, 2H), 2.69-2.67 (m, 1H), 2.06 (dd, *J* = 6.4Hz, 1.8Hz, 1H), 1.80-1.76 (m, 2H), 1.51 (dd, *J* = 11.0Hz, 7.5Hz, 1H), 1.19 (dd, *J* = 8.2Hz, 2.2Hz, 1H), 1.16-1.13 (m, 4H), 1.05 (d, *J* = 6.8Hz, 3H), 0.76 (s, 9H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 172.2, 161.2, 147.8, 137.1, 136.7, 121.4, 57.2, 46.1, 45.1, 43.8, 42.6, 42.3, 40.7, 40.5, 36.3, 35.7, 33.1, 29.7, 20.7, 20.2.

2.5 Limitations

Low-selectivity, low-yielding or unsuccessful entries



cis-**4AW**: white solid. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.50 (dd, *J* = 4.5Hz, 1.2Hz, 1H), 7.69 (d, *J* = 6.9Hz, 1H), 7.24-7.20 (m, 5H), 7.10-7.08 (m, 4H), 6.83 (d, *J* = 7.8Hz, 2H), 5.25 (d, *J* = 14.0Hz, 1H), 4.37 (d, *J* = 14.0Hz, 1H), 3.35 (d, *J* = 8.5Hz, 1H), 3.14 (d, *J* = 5.9Hz, 1H), 2.67 (dd,, *J* = 5.4Hz, 1.2Hz, 1H), 2.39 (s, 1H), 2.35 (d, *J* = 8.4Hz, 1H), 1.63 (dd, *J* = 6.8Hz, 2.6Hz, 1H), 1.21 (d, *J* = 7.2Hz, 1H), 0.83 (t, *J* = 8.7Hz, 1H), 0.84 (dd, *J* = 8.8Hz, 7.6Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 171.7, 157.2, 147.7, 141.1, 137.5, 137.1, 133.0, 129.2, 129.1, 128.8, 128.5, 128.3, 127.5, 121.9, 57.9, 53.9, 46.2, 44.7, 43.7, 43.0, 42.4, 36.3, 35.3. **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 393.1961, found: 393.1961.

3AW: white solid. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.44 (d, *J* = 5.4Hz, 1H), 7.84 (d, *J* = 7.7Hz, 1H), 7.56 (dd, *J* = 7.4Hz, 6.1Hz, 1H), 7.33-7.27 (m, 6H), 7.21-7.19 (m, 2H), 6.96 (m, 2H), 6.51 (d, *J* = 10.0Hz, 1H), 6.21 (dd, *J* = 9.9Hz, 4.0Hz, 1H), 5.01 (d, *J* = 14.0Hz, 1H), 4.73 (d, *J* = 14.0Hz, 1H), 3.72 (d, *J* = 9.9Hz, 1H), 3.09 (dd, *J* = 9.8Hz, 3.4Hz, 1H), 3.02 (br, 1H), 2.80 (s, 1H), 1.65-1.64 (m, 1H), 1.44 (t, *J* = 9.1Hz, 1H), 0.41 (dd, *J* = 9.2Hz, 8.2Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 170.2, 153.2, 140.6, 140.2, 138.8, 137.1, 133.7, 132.6, 129.4, 129.1, 129.0, 128.6, 128.5, 127.7, 124.6, 123.5, 60.0, 54.1, 43.9, 43.6, 42.7, 40.0. 39.3, 36.5. **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 393.1961, found: 393.1962.

3AW-dimer: white solid. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.58 (dd, *J* = 4.6Hz, 1.3Hz, 1H), 8.46 (d, *J* = 3.8Hz, 1H), 7.93 (d, *J* = 7.6Hz, 1H), 7.40 (d, *J* = 6.7Hz, 1H), 7.25-7.09 (m, 18H), 7.00-6.76 (m, 3H), 6.51 (m, 1H), 5.13 (d, *J* = 14.0Hz, 1H), 4.88 (d, *J* = 13.9Hz, 1H), 4.68 (d, *J* = 13.9Hz, 1H), 4.49 (d, *J* = 14.0Hz, 1H), 3.38 (d, *J* = 8.4Hz, 1H), 3.21 (d, *J* = 8.2Hz, 1H), 3.11 (d, *J* = 8.1Hz, 1H), 3.08 (d, *J* = 8.5Hz, 1H), 2.65 (dd, *J* = 10.8Hz, 8.3Hz, 1H), 2.47 (dd, *J* = 10.3Hz, 8.4Hz, 1H), 2.43 (d, *J* = 8.8Hz, 1H), 2.39 (br, 1H), 2.21 (d, *J* = 8.4Hz, 1H), 2.07 (br, 1H), 1.69 (ddd, *J* = 10.1Hz, 6.9Hz, 2.7Hz, 1H), 1.18 (d, *J* = 7.2Hz, 1H), 1.12 (d, *J* = 7.0Hz, 1H), 0.90 (dd, *J* = 9.0Hz, 7.2Hz, 1H), 0.80 (t, *J* = 8.7Hz, 1H), 0.70 (dd, *J* = 9.3Hz, 7.1Hz, 1H), 0.61 (t, *J* = 8.7Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.93, 171.58, 157.53, 156.79, 148.27, 147.43, 141.23, 141.06, 137.91, 137.76, 137.43, 136.85, 133.48, 132.84, 129.45, 129.47, 129.43, 129.36, 129.24, 129.09, 128.85, 128.51, 128.31, 128.26, 127.58, 127.32, 121.80, 121.32, 57.91, 57.86, 54.03, 46.54, 43.87, 43.34, 43.07, 42.90, 42.76, 42.31, 41.31, 36.80, 36.16, 35.97, 35.90. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 785.3850, found: 785.3950.

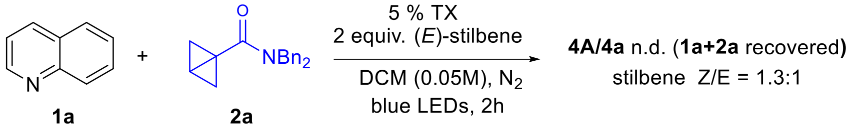
4x: Purification via column chromatography (petroleum ether/EtOAc= 1/1) afforded 2 separable diastereomers of major regioisomer **4x**. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 503.2329, found: 503.2324.

cis-diastereomer of major regioisomer **4x:** white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 4.6Hz, 1.1Hz, 1H), 7.37-7.32 (m, 5H), 7.27-7.25 (m, 5H), 7.03 (dd, *J* = Hz, Hz, 1H), 6.74 (dd, *J* = Hz, Hz, 1H), 5.73 (d, *J* = 14.7Hz, 1H), 5.30 (d, *J* = 10.3Hz, 1H), 4.26 (d, *J* = 10.3Hz, 1H), 4.03 (td, *J* = 6.7Hz, 1.1Hz, 2H), 3.77 (dd, *J* = 6.8Hz, Hz, 1H), 3.25-3.22 (m, 2H), 3.10 (d, *J* = 3.5Hz, 1H), 2.53 (d, *J* = 2.2Hz, 1H), 2.33-2.27 (m, 3H), 1.94-1.91 (m, 2H), 1.41 (d, *J* = 7.0Hz, 1H), 1.26 (dd, *J* = 10.8Hz, 7.9Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.6, 171.7, 160.2, 148.3, 139.3, 137.9, 136.4, 132.5, 128.9, 128.9, 128.4, 127.9, 127.9, 120.1, 79.6, 70.1, 67.6, 62.5, 54.2, 46.4, 44.0, 42.6, 41.4, 40.2, 40.2, 40.1, 18.8. *One aromaticsignal is missing (probably due to signal overlap).*

trans-diastereomer of major regioisomer **4x:** white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.6Hz, 1.4Hz, 1H), 7.31-7.28 (m, 5H), 7.08-7.06 (m, 3H), 6.90 (dd, *J* = 7.7Hz, 4.8Hz, 1H), 6.83 (dd, *J* = 7.7Hz, 1.4Hz, 1H), 6.68-6.66 (m, 2H), 5.09 (d, *J* = 5.3Hz, 1H), 4.89 (d, *J* = 15.7Hz, 1H), 4.25 (t, *J* = 2.6Hz, 1H), 4.18 (d, *J* = 15.7Hz, 1H), 4.10 (t, *J* = 6.6Hz, 2H), 3.90 (d, *J* = 6.0Hz, 1H), 3.50 (dd, *J* = 3.7Hz, 2.0Hz, 1H), 3.15-3.14 (m, 1H), 2.81 (d, *J* = 2.3Hz, 1H), 2.38-2.34 (m, 2H), 2.29 (d, *J* = 2.0Hz, 1H), 2.00 (dd, *J* = 10.6Hz, 6.4Hz, 1H), 1.92 (t, *J* = 2.7Hz, 1H), 1.81 (dd, *J* = 10.7Hz, 7.5Hz, 1H), 1.56 (d, *J* = 5.5Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.6, 172.3, 159.5, 148.9, 148.9, 140.0, 138.7, 136.9, 134.1, 129.0, 128.6, 128.5, 128.0, 126.9, 126.4, 121.3, 79.7, 70.1, 65.9, 62.4, 57.0, 47.7, 46.8, 45.7, 43.2, 41.2, 41.0, 40.1, 37.7, 18.9.

3. Mechanistic studies

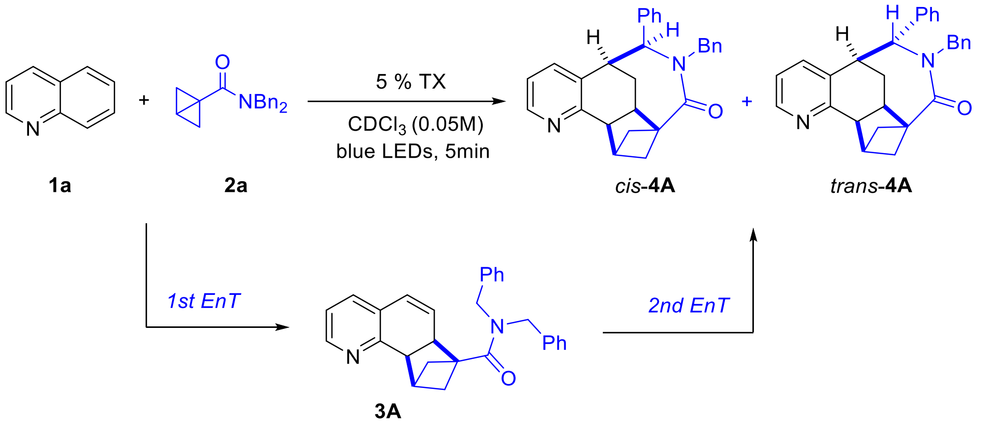
3.1 Reaction inhibition by external triplet quencher



The quinoline substrate **1a** (12.9 mg, 0.1 mmol), BCBs **2a** (55.5 mg, 2.0 equiv.), TX (1.1 mg, 5 mol%) and (*E*)-stilbene (36.0 mg, 2.0 equiv.) were added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with N_2 three times. Subsequently, DCM (2.0 mL, 0.05M) were added under positive nitrogen pressure. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LEDs (λ_{max}= 400 nm, distance approximately 4.0 cm from the bulb) with a fan at room temperature for 2h. 1, 3, 5-trimethoxybenzene was added as internal standard to measure the crude ^{1}H NMR. The reaction was completely inhibited by external triplet quencher. No desired products **4A/4a** were detected and **1a** and **2a** recovered. Meanwhile, the observed *E* to *Z* isomerization of (*E*)-stilbene indicated that this reaction is mediated by triplet EnT.

3.2 Separation of intermediate product

Experimental procedure. The quinoline substrate **1a** (6.5 mg, 0.05mmol), BCBs **2a** (27.8 mg, 2.0 equiv.) and TX (0.6 mg, 5 mol%) were added to a NMR tube. Subsequently, $CDCl_3$ (1.0 mL, 0.05M) were added in the air. Afterwards, the NMR tube was sealed, and the reaction mixture was irradiated with blue LEDs (λ_{max}= 400 nm, distance approximately 4.0 cm from the bulb) with a fan at room temperature. After 5 minutes, the irradiation was interrupted and the NMR tube was directly used to measure the crude ^{1}H NMR without further purification. The intermediate product was detected by NMR and isolated by column chromatography (petroleum ether/EtOAc= 2/1) to afford a [2π+2σ] cycloadduct **3A** containing characteristic olefin protons. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 3.8Hz, 1H), 7.40-7.30 (m, 7H), 7.25 (d, *J* = Hz, 2H), 7.17 (d, *J* = 7.4Hz, 2H), 7.02 (dd, *J* = 7.4Hz, 4.9Hz, 1H), 6.37 (d, *J* = 9.9Hz, 1H), 5.81 (dd, *J* = 9.8Hz, 3.9Hz, 1H), 4.63 (d, *J* = 14.4Hz, 1H), 4.54-4.51 (m, 2H), 4.40 (d, *J* = 16.7Hz, 1H), 3.62 (d, *J* = 10.2Hz, 1H), 3.42 (dd, *J* = 9.9Hz, 3.5Hz, 1H), 2.80 (s, 1H), 1.96 (dd, *J* = 6.8Hz, 2.9Hz, 1H), 1.77 (d, *J* = 7.3Hz, 1H), 1.72-1.67 (m, 1H), 1.59 (dd, *J* = 9.0Hz, 7.0Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.8, 156.9, 148.0, 137.5, 136.5, 133.7, 129.0, 128.7, 128.5, 128.2, 127.9, 127.7, 127.5, 127.3, 126.6, 121.8, 59.8, 49.3, 47.7, 44.7, 44.5, 42.8, 42.6, 36.7. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 407.2118, found: 407.2137.



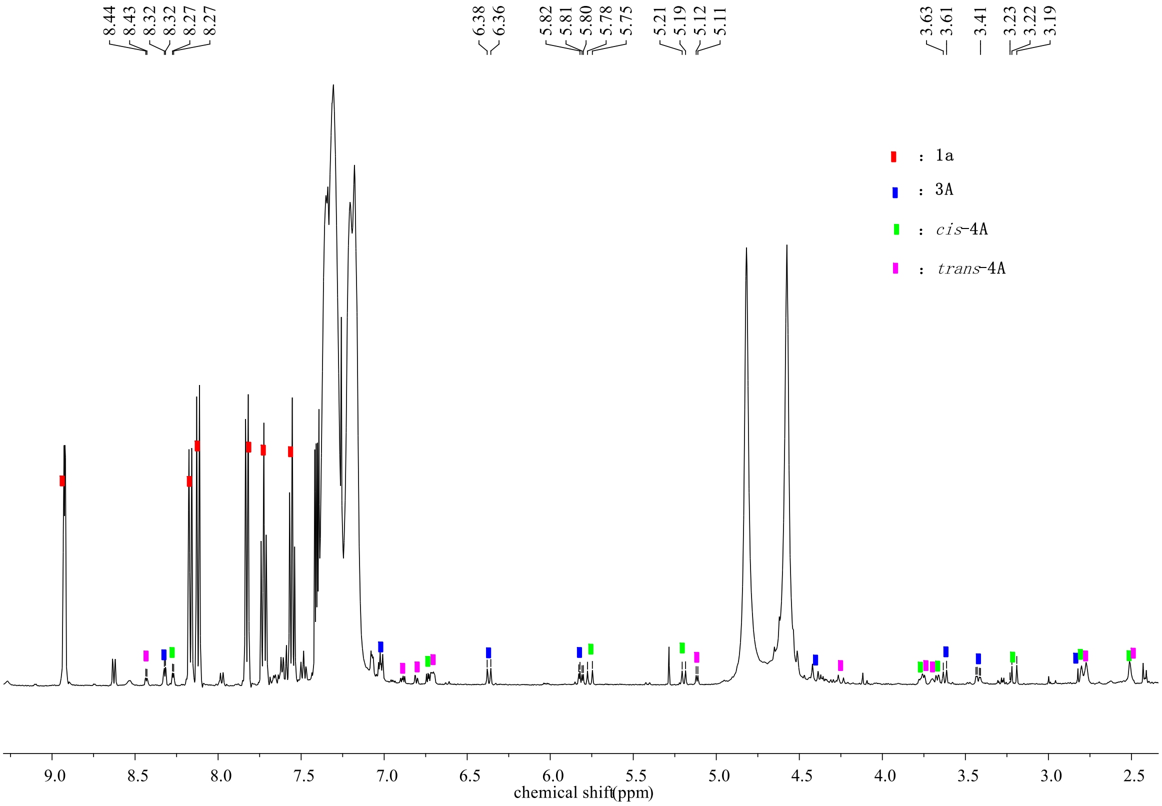


Figure S3. **^{1}H NMR** (500 MHz, $CDCl_3$) spectrum of the reaction of **1a** and **2a** after 5 minutes.

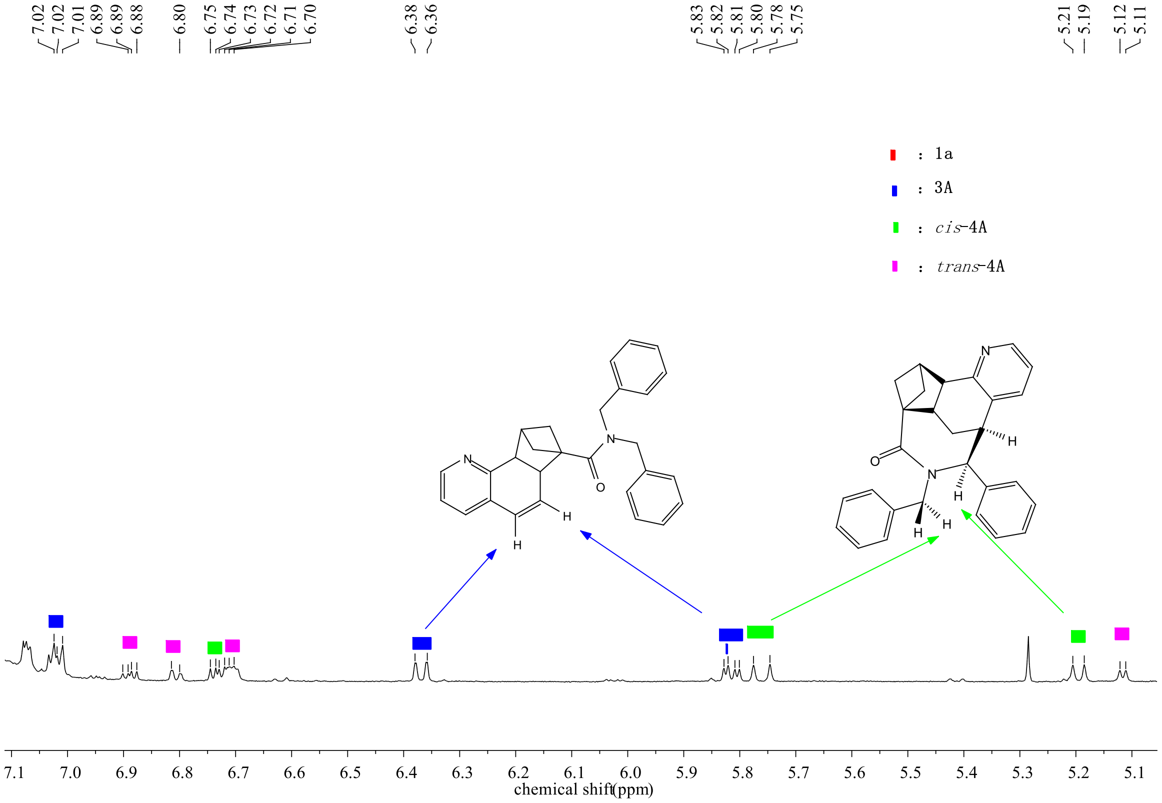


Figure S4. Close-up of the **^{1}H NMR** (500 MHz, $CDCl_3$) spectrum of the reaction of **1a** and **2a** after 5 minutes, with regard of the olefin protons of **3A** and *cis*/*trans*-**4A**.

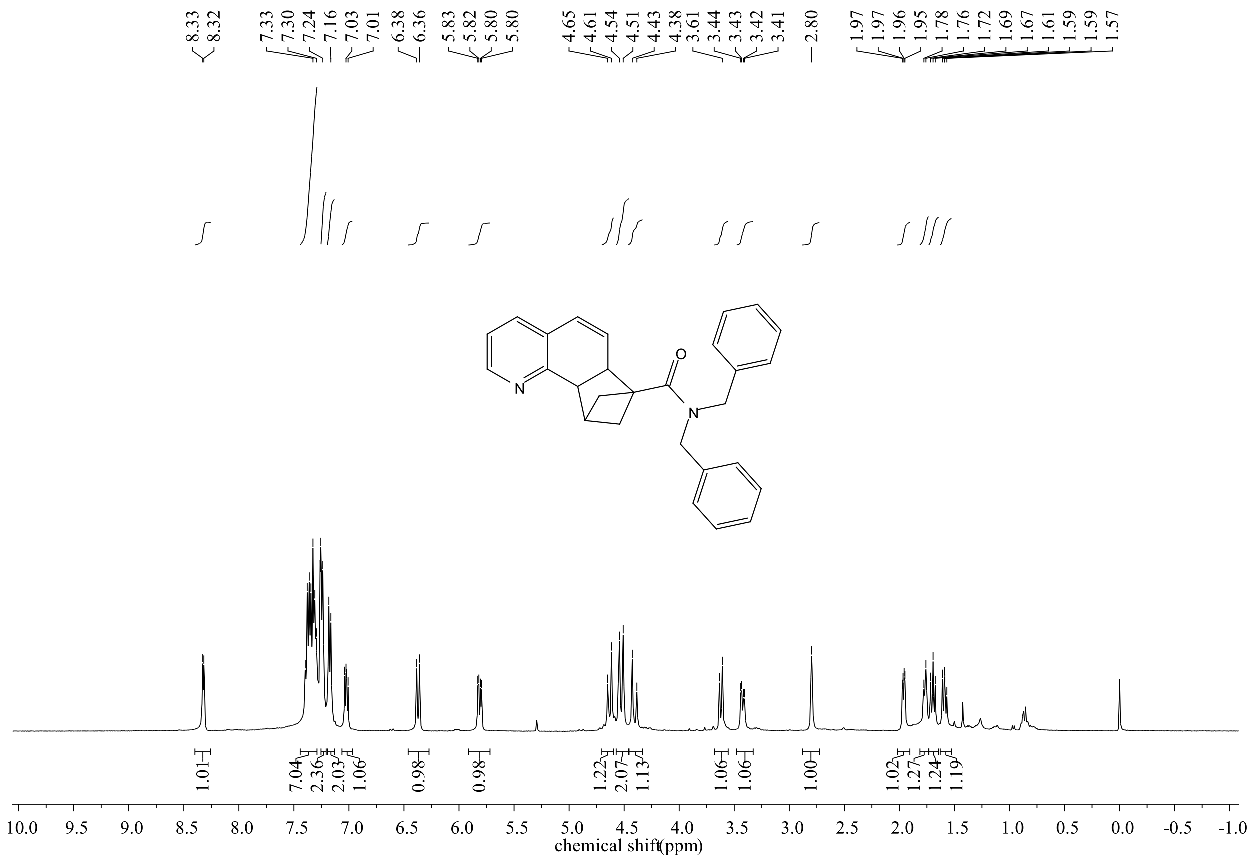


Figure S5. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum of the intermediate product **3A**.

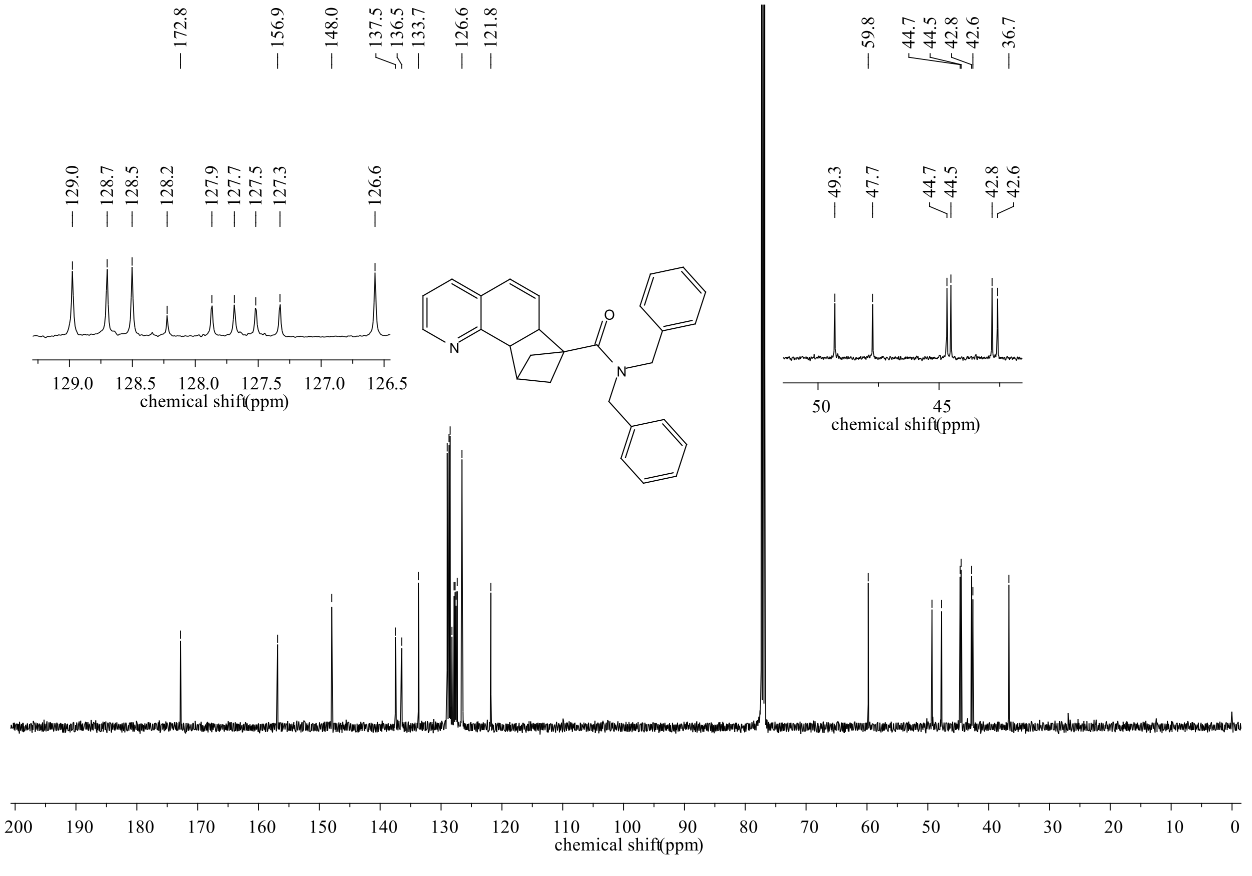
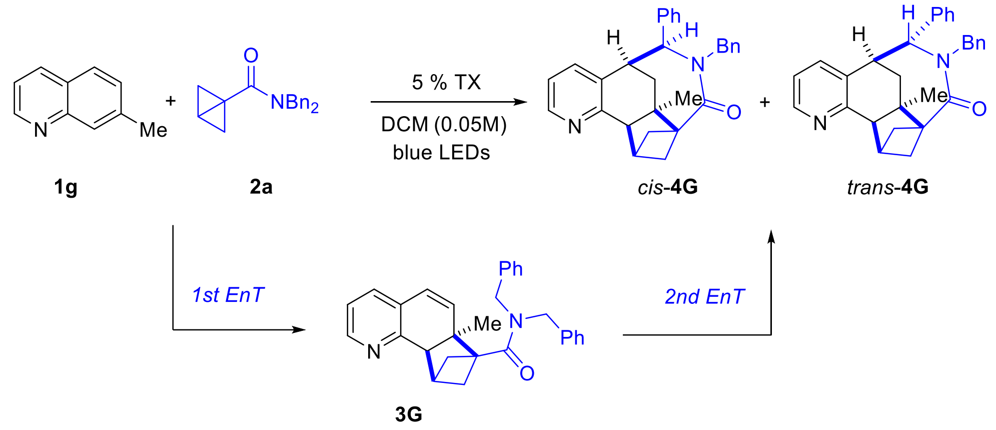


Figure S6. **^{13}C NMR** (126 MHz, $CDCl_3$) spectrum of the intermediate product **3A**.



The intermediate product of the reaction of **1g** and **2a** was detected by NMR and isolated by column chromatography (petroleum ether/EtOAc= 2/1) to afford **3G** containing characteristic olefin protons. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 4.7Hz, 1.5Hz, 1H), 7.35-7.34 (m, 4H), 7.31-7.28 (m, 4H), 7.24 (m, 1H), 7.15 (d, *J* = 7.4Hz, 2H), 7.03 (dd, *J* = 7.5Hz, 4.9Hz, 1H), 6.30 (d, *J* = 9.9Hz, 1H), 5.75 (d, *J* = 9.9Hz, 1H), 4.86 (d, *J* = 14.5Hz, 1H), 4.57 (d, *J* = 16.5Hz, 1H), 4.33 (d, *J* = 16.7Hz, 1H), 4.29 (d, *J* = 14.6Hz, 1H), 3.24 (br, 1H), 2.69 (br, 1H), 1.95 (t, *J* = 8.3Hz, 1H), 1.88 (dd, *J* = 7.5Hz, 3.0Hz, 1H), 1.77-1.72 (m, 2H), 1.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.2, 157.2, 147.9, 137.7, 136.7, 133.9, 133.6, 128.9, 128.7, 128.5, 127.8, 127.6, 127.5, 126.6, 124.4, 121.7, 61.6, 52.7, 49.9, 47.8, 47.7, 42.9, 40.7, 38.8, 25.6. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 421.2274, found: 421.2271.

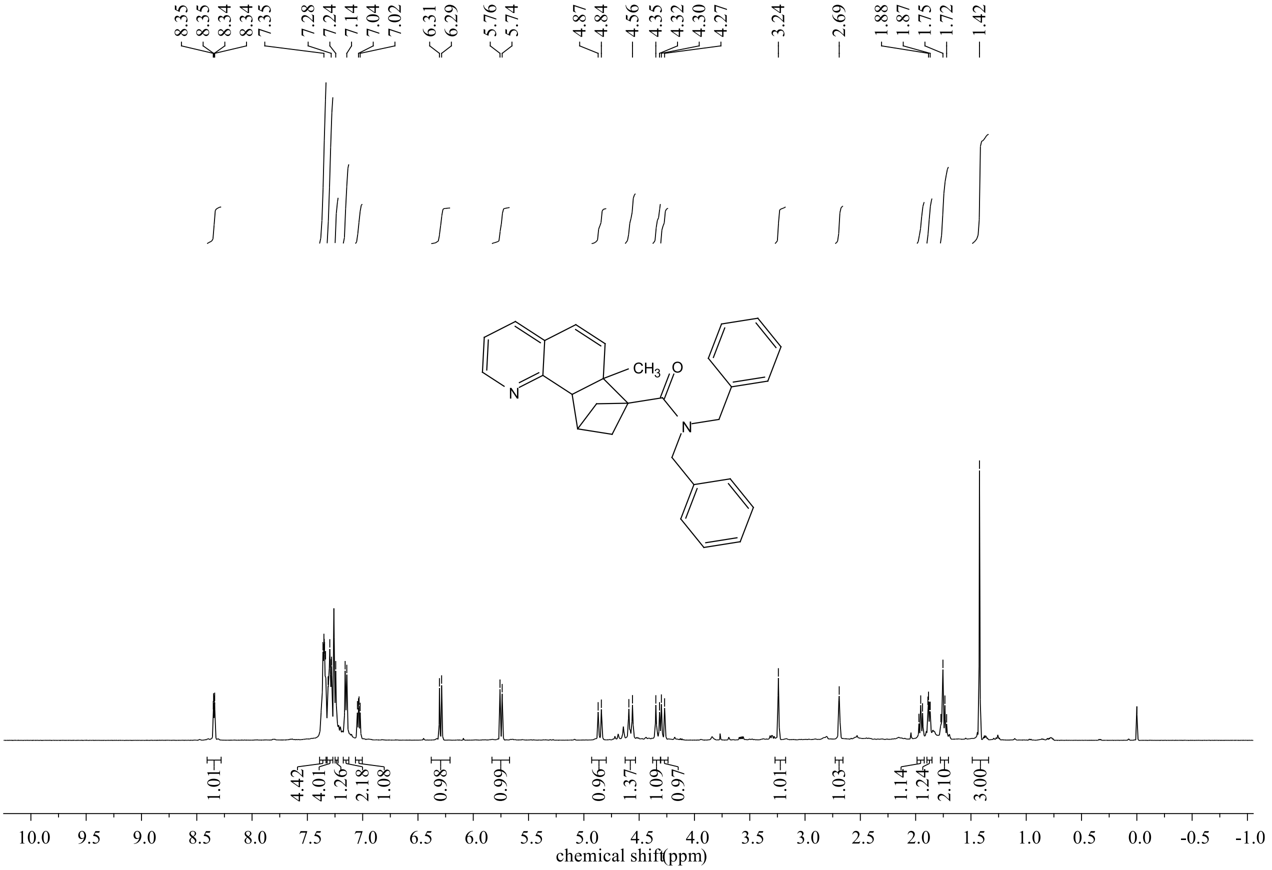


Figure S7. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum of the intermediate product **3G**.

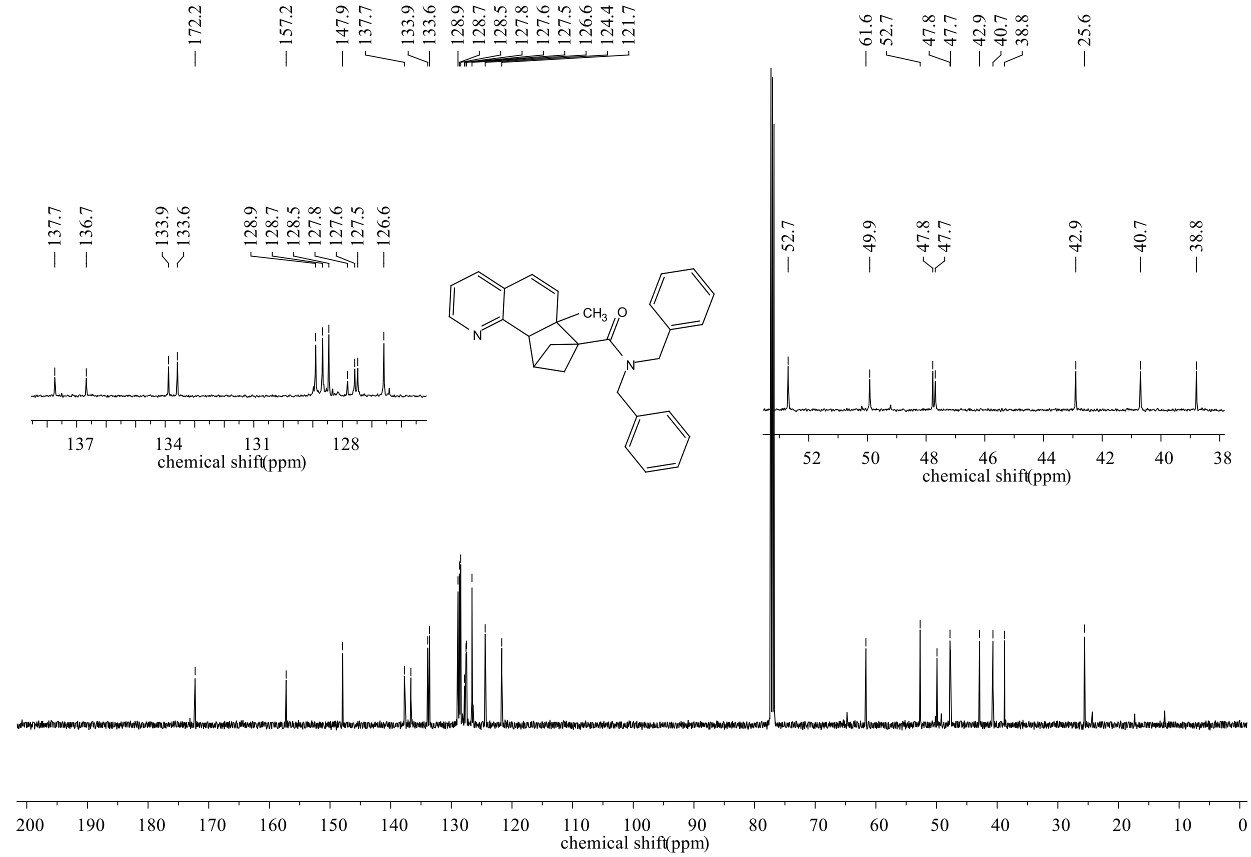
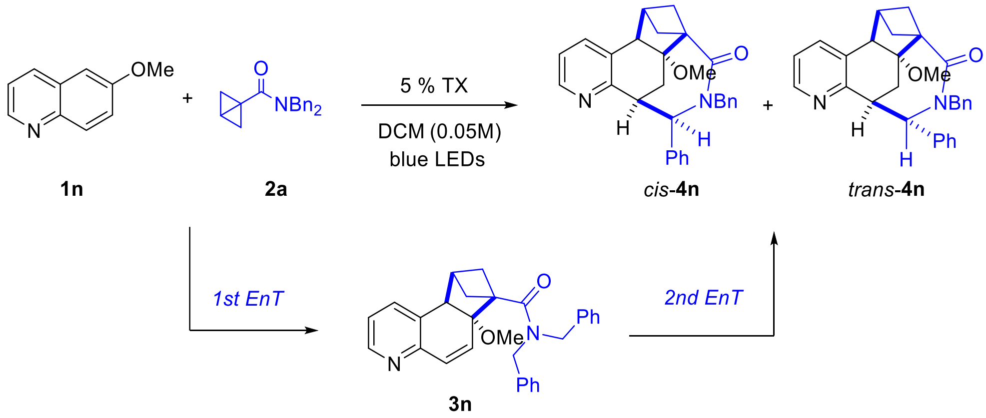


Figure S8. ^{13}**C NMR** (126 MHz, $CDCl_3$) spectrum of the intermediate product **3G**.



1n **2a** *cis*-**4n** *trans*-**4n** **3n**

The intermediate product of the reaction of **1n** and **2a** was detected by NMR and isolated by column chromatography (petroleum ether/EtOAc= 2/1) to afford **3n** containing characteristic olefin protons. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.6Hz, 1H), 7.51 (d, *J* = 7.6Hz, 1H), 7.38-7.26 (m, 7H),7.23-7.19 (m, 3H), 7.11 (dd, *J* = 7.6Hz, 4.8Hz, 1H), 6.99 (d, *J* = 10.2Hz, 1H), 6.12 (d, *J* = 10.2Hz, 1H), 5.07-4.98 (m, 2H), 4.39 (d, *J* = 17.0Hz, 1H), 4.19 (d, *J* = 15.0Hz, 1H), 3.34 (s, 1H), 3.18 (s, 3H), 2.51 (s, 1H), 2.02 (m, 1H), 1.92 (dd, *J* = 6.9Hz, 3.0Hz, 1H), 1.74-1.68 (m, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 171.6, 151.4, 148.0, 137.6, 137.4, 135.5, 133.7, 132.2, 130.8, 128.7, 128.6, 127.8, 127.2, 127.1, 126.8, 122.3, 84.3, 63.0, 52.4, 50.1, 47.9, 47.1, 42.4, 40.5, 38.7. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 437.2224, found: 437.2233.

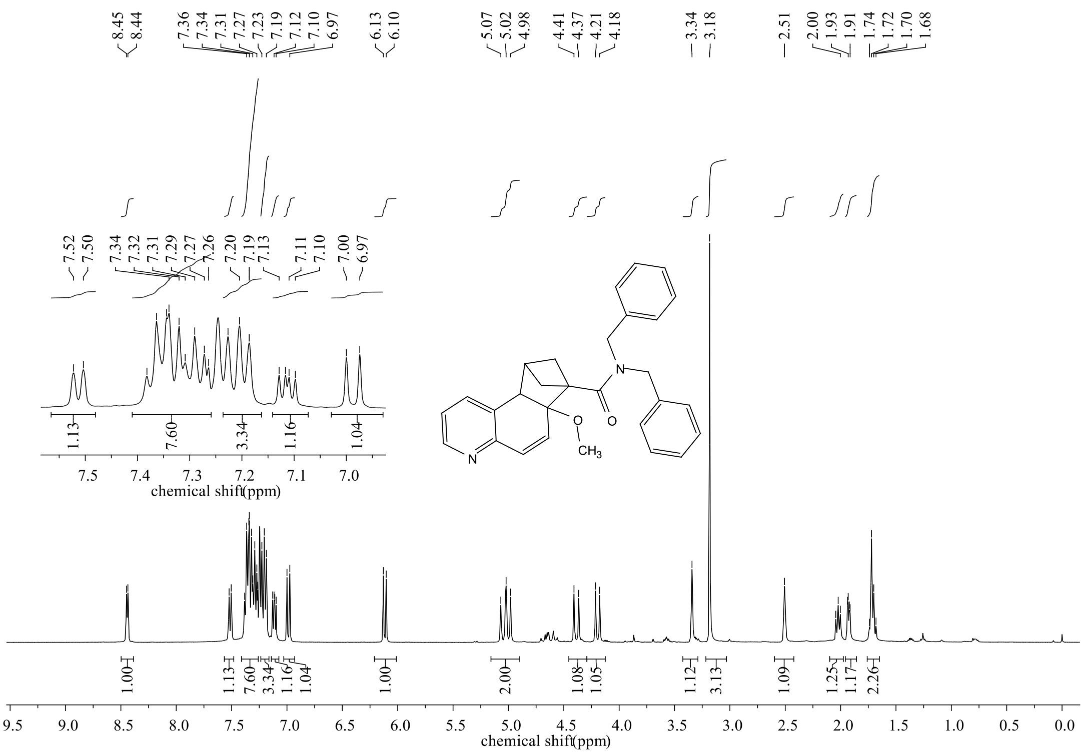


Figure S9. **^{1}H NMR** (400 MHz, CDCl$_3$) spectrum of the intermediate product **3n**.

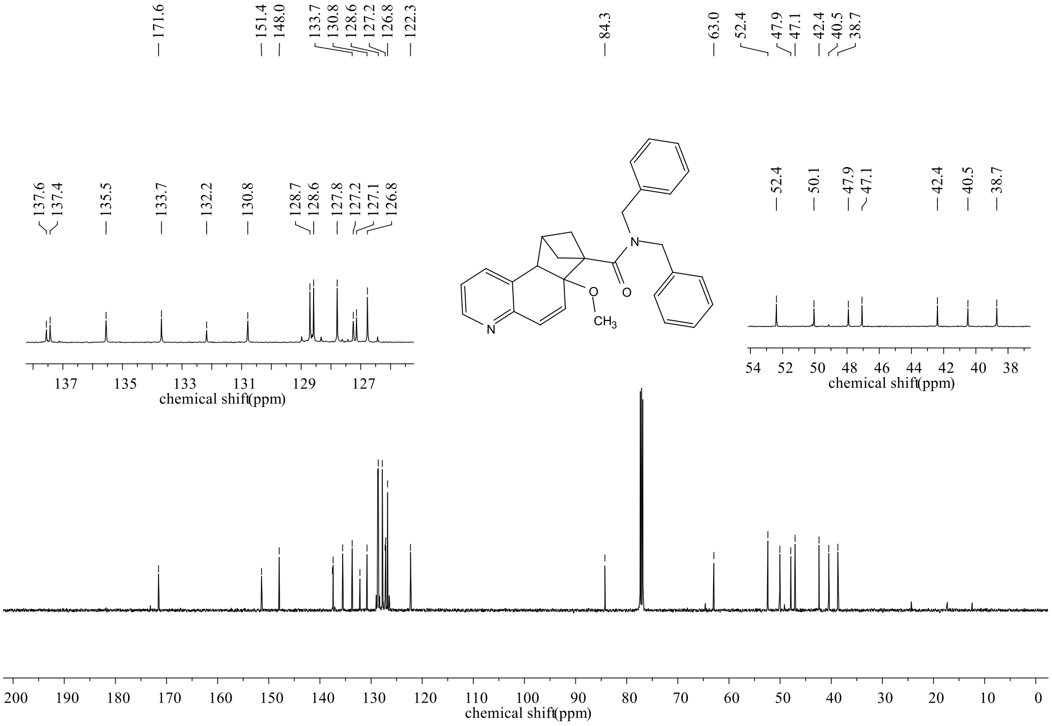


Figure S10. **^{13}C NMR** (126 MHz, CDCl$_3$) spectrum of the intermediate product **3n**.

3.3 Kinetic profile of the photosensitized reaction

The reaction above with 1, 3, 5- trimethoxybenzene as internal standard was irradiated with the custom setup for the indicated amount of time. The yields of **1a**, **4A** and **3A** were monitored by crude ^{1}H NMR analysis over time. In order to accurately scrutinise the ratio of product/**3A**, yields of the product below were reported as the only major regioisomers (*cis/trans*-**4A**).

Table S3. Experimental data for the kinetic measurement using **1a** and **2a** as substrates.

t /min	**1a** (%)	Yield **3A** (%)	Yield **4A** (%)	Ratio **4A/3A**
0.5	98	2	0	0
1	93.5	4	1.5	1: 2.67
1.5	90.5	5.5	3	1: 1.83
2	87	7	5	1: 1.4
2.5	84	7.5	6.5	1: 1.15
3	81	8	8	1: 1
3.5	77.5	9	10	1.11: 1
4	76	9.5	11	1.16: 1
4.5	74	10	12.5	1.25: 1
5	71	9	16	1.78: 1
10	47.5	10.5	28	2.67: 1
15	32	10.5	41	3.90: 1
20	24	8.5	53	6.24: 1
25	15	6	58	9.67: 1
30	9	4	65	16.23: 1
35	5	3	70	23.33: 1
40	2	3	70	23.33: 1

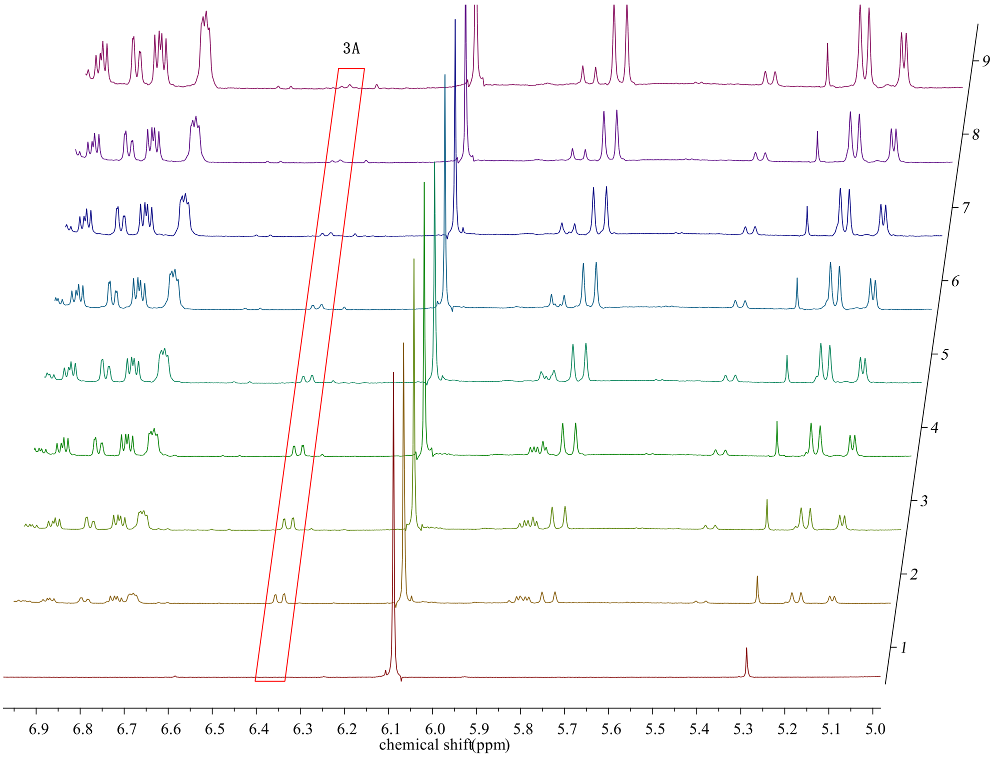
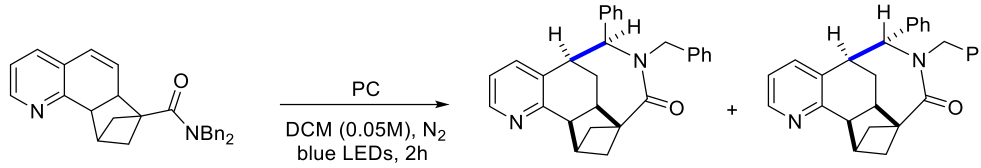


Figure S11. Overlay of ^{1}**H NMR** (500 MHz, $CDCl_3$) spectrum of the crude reactions of **1a** and **2a** within 40 mins, with interval of 5mins.

3.4 Reaction started from 3A



3A *cis*-**4A** *trans*-**4A**

3A (40.7 mg, 0.1 mmol) with or without TX (1.1 mg, 5 mol%) was added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with N_2 three times. Subsequently, DCM (2.0 mL, 0.05M) were added under positive nitrogen pressure. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LEDs (λ_{max}= 400 nm, distance approximately 4.0 cm from the bulb) with a fan at room temperature for 2h. 1, 3, 5- trimethoxybenzene was added as internal standard to measure the crude ^{1}H NMR.

3.5 Stern-Volmer luminescence quenching studies

Stern-Volmer luminescence quenching analysis is carried out using a Hitachi F-4600 spectrofluorometer to identify quenchers of excited photocatalyst. ***Note*****:** For practical reasons, [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) ([Ir-F]) was used as photocatalyst instead of TX.

The following parameters were employed: data interval = 1.0 nm, scan-speed = 240 nm/min, response time = 0.1 s. The samples were measured in fluorescence quartz cuvettes (chamber volume = 3.5 mL, H × W × D = 45 mm × 12.5 mm, 12.5 mm, path length = 10 mm) fitted with a sealed PTFE stopper.

The solution of [Ir-F] ($1\cdot10^{-4}$ M in DCM) was excited at λ_{ex} = 405 nm and the emission was collected at 468 nm. The substrates quinoline (**1a**) and intermediate product **3A** were dissolved in DCM (0.4 M), respectively. For each quenching experiment, 10 µL of the stock solution were titrated to a solution (2 mL) of [Ir-F] in quartz cuvette which refers to an increase of the quencher concentration of 2.0 mM. I_0 is the luminescence intensity without the quencher, I is the intensity in the presence of the quencher. The results are listed below:

Table S4: Results of the luminescence quenching experiments of [Ir-F] with **1a** and **3A** as the quenching species.

Quencher (mM)	0	2	4	6	8	10	12	14
1a	7402	5002	3991	3239	2716	2283	1956	1727
I_0/I	1	1.48	1.855	2.285	2.725	3.242	3.784	4.286
3A	7286	5408	3771	2984	2483	2109	1850	1635
I_0/I	1	1.347	1.932	2.442	2.934	3.455	3.938	4.456

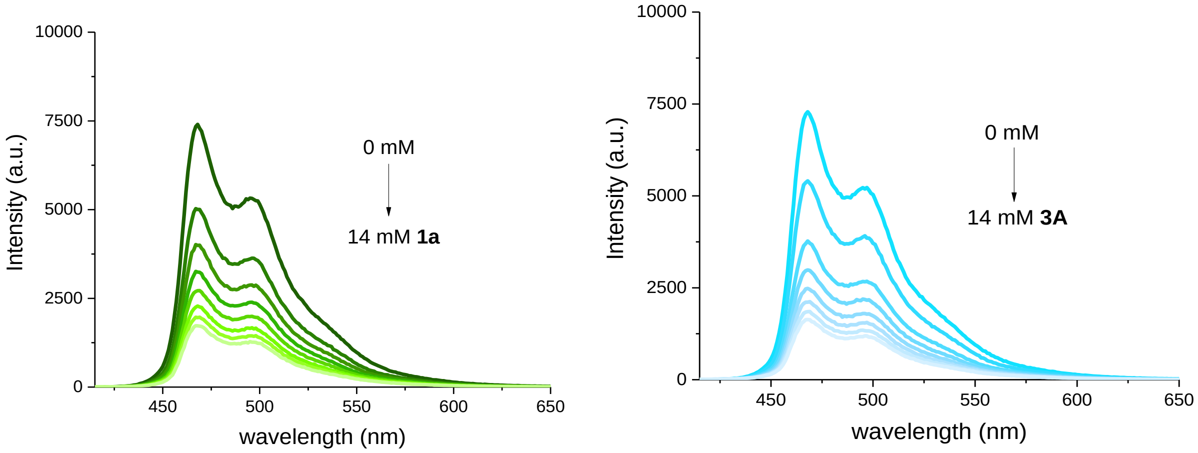
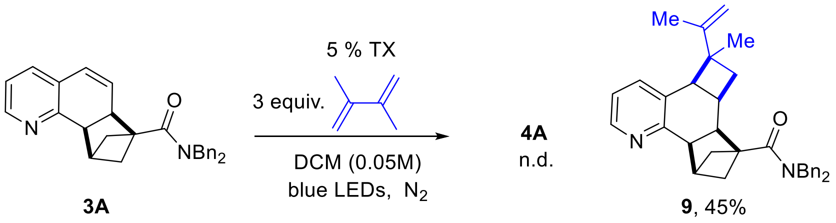


Figure S12. Luminescence spectras of [Ir-F] with quinoline (**1a**) or intermediate product (**3A**) as the quenching species.

3.6 Diradical trapping through intermolecular [2+2] photocycloaddition



3A (40.7 mg, 0.1 mmol), TX (1.1 mg, 5 mol%) and 2,3-dimethylbuta-1,3-diene (33.9 µL, 3.0 equiv.) were added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with N_2 three times. Subsequently, DCM (2.0 mL, 0.05M) were added under positive nitrogen pressure. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LEDs (λ_{max}= 400 nm, distance approximately 4.0 cm from the bulb) with a fan at room temperature for 2h. 1, 3, 5- trimethoxybenzene was added as internal standard to measure the crude ^{1}H NMR. No desired product **4A** was detected. Excited triplet state **3A** could be trapped by adding 2,3-dimethylbuta-1,3-diene to afford the corresponding [2+2] cycloadduct product **9**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 3.9Hz, 1H), 7.40-7.28 (m, 7H), 7.24 (d, *J* = 7.3Hz, 2H), 7.18 (d, *J* = 7.3Hz, 2H), 7.00 (dd, *J* = 7.8Hz, 4.6Hz, 1H), 4.71-4.68 (m, 2H), 4.52-4.41 (m, 4H), 3.57 (d, *J* = 8.6Hz, 1H), 3.30 (dd, *J* = 8.0Hz, 2.6Hz, 1H), 2.94 (q, *J* = 8.9Hz, 1H), 2.58 (d, *J* = 8.7Hz, 1H), 2.52 (s, 1H), 2.12 (dd, *J* = 6.7Hz, 2.9Hz, 1H), 2.07 (t, *J* = 10.6Hz, 1H), 1.69 (dd, *J* = 9.4Hz, 7.0Hz, 1H), 1.59 (d, *J* = 7.9Hz, 1H), 1.54 (s, 3H), 1.36 (s, 3H), 1.31-1.26 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.4, 157.3, 147.8, 147.2, 137.7, 137.5, 136.6, 130.8, 129.0, 128.6, 128.2, 127.7, 127.4, 126.7, 120.6, 112.7, 58.2, 49.4, 48.4, 47.6, 46.4, 46.1, 45.0, 43.5, 42.3, 35.8, 35.5, 27.0, 26.4, 21.8. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 489.2900, found: 489.2922.

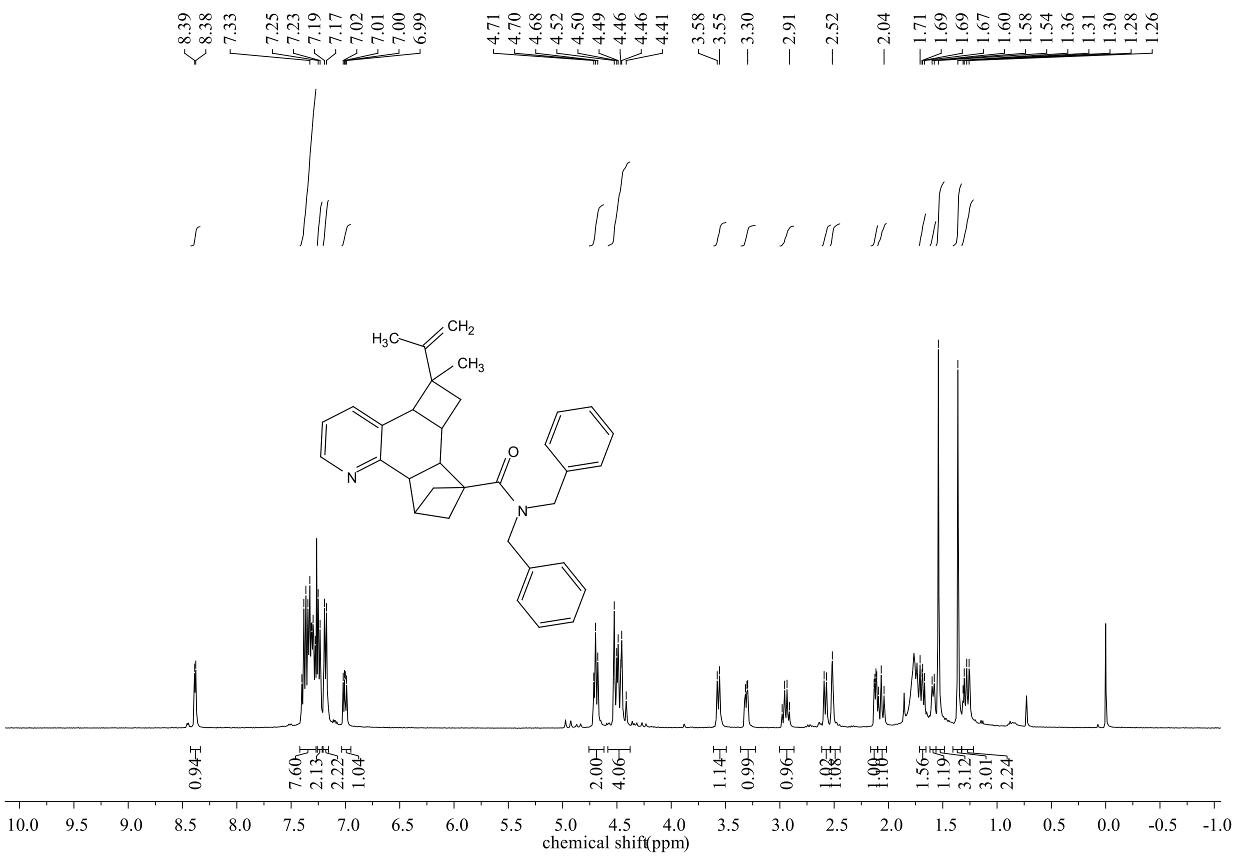


Figure S13. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum of [2+2] cycloadduct product **9**.

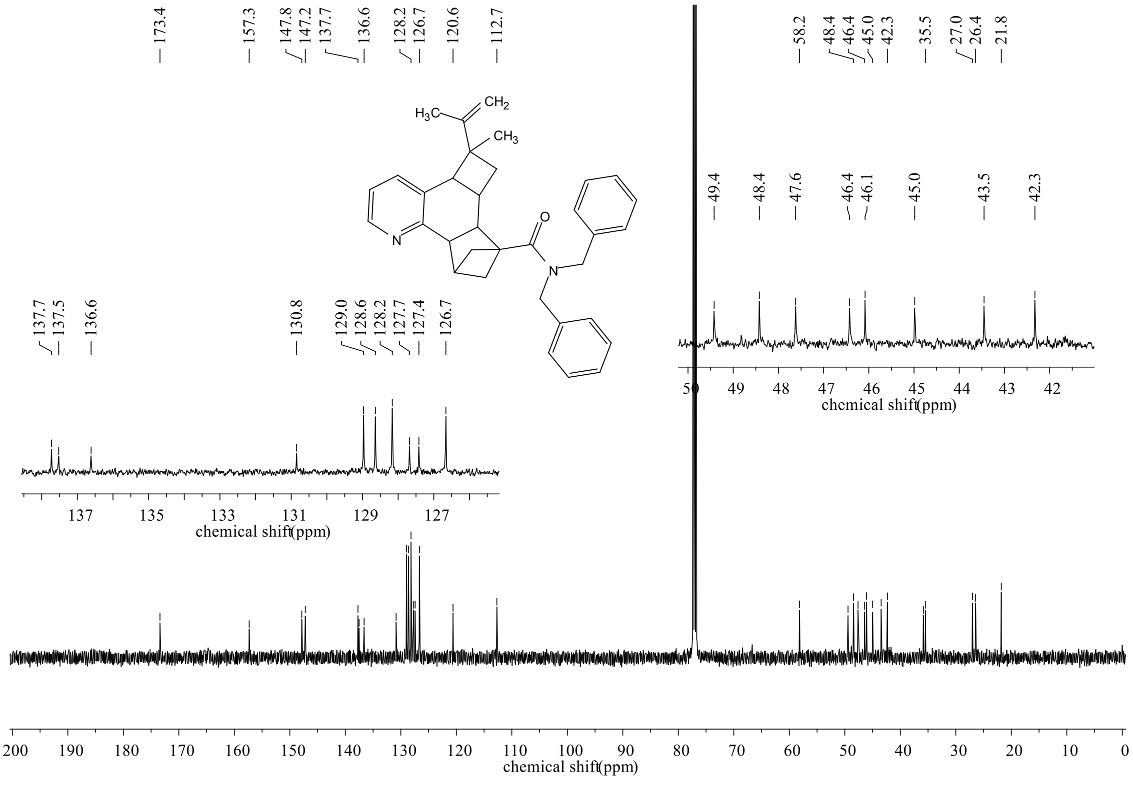
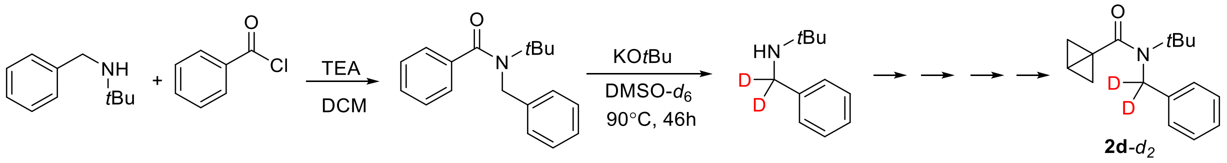


Figure S14. **^{13}C NMR** (126 MHz, $CDCl_3$) spectrum of [2+2] cycloadduct product **9**.

3.7 Deuterium labeling experiment

3.7.1 Procedures for the synthesis of the deuterated compound 2d-d_2 :



N-benzyl-2-methylpropan-2-amine-d_2 was prepared according to a modified literature procedure:[8]

Step1: The solution of N-benzyl-2-methylpropan-2-amine ((5.5 mmol, 1.1 equiv.), TEA (1.25 equiv.) and DCM (0.5 M) were stirred at 0 °C for 10 mins. Then benzoyl chloride (1.0 equiv.) was added dropwise and the solution was warmed to room temperature and stirred for 20 mins. The resulting mixture was extracted with DCM and washed with saturated NH_4Cl. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc= 5/1) on silica gel to give the desired amide.

Step2: A mixture of above amide (5 mmol, 1.0 equiv.) and KO*t*Bu (6.0 equiv.) was stirred in DMSO-d_6 (25 mL) at 90°C under N_2 for 46 h. After completion, the reaction mixture was cooled to room temperature. Water (10 mL) was added and the mixture was extracted with EtOAc. The combined organic phases were extracted with 4N HCl. The aqueous phase was adjusted to pH=10 by the addition of NaOH aqueous solution and then extracted with DCM. The combined organic phase was washed with brine, dried with anhydrous Na_2SO_4, and concentrated under vacuum. **N-benzyl-2-methylpropan-2-amine-d_2** (413 mg, 50%) was directly used in next step without further purification.

2d-d_2 (147 mg, 16%) was prepared according to ***General Procedure 1*** from the above **N-benzyl-2-methylpropan-2-amine-d_2**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H), 7.26-7.23 (m, 3H), 2.12 (d, *J* = 3.2Hz, 2H), 1.98-1.97 (m, 1H), 1.40 (s, 9H), 0.89 (d, *J* = 1.8Hz, 2H). **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 246.1821, found: 246.1434.

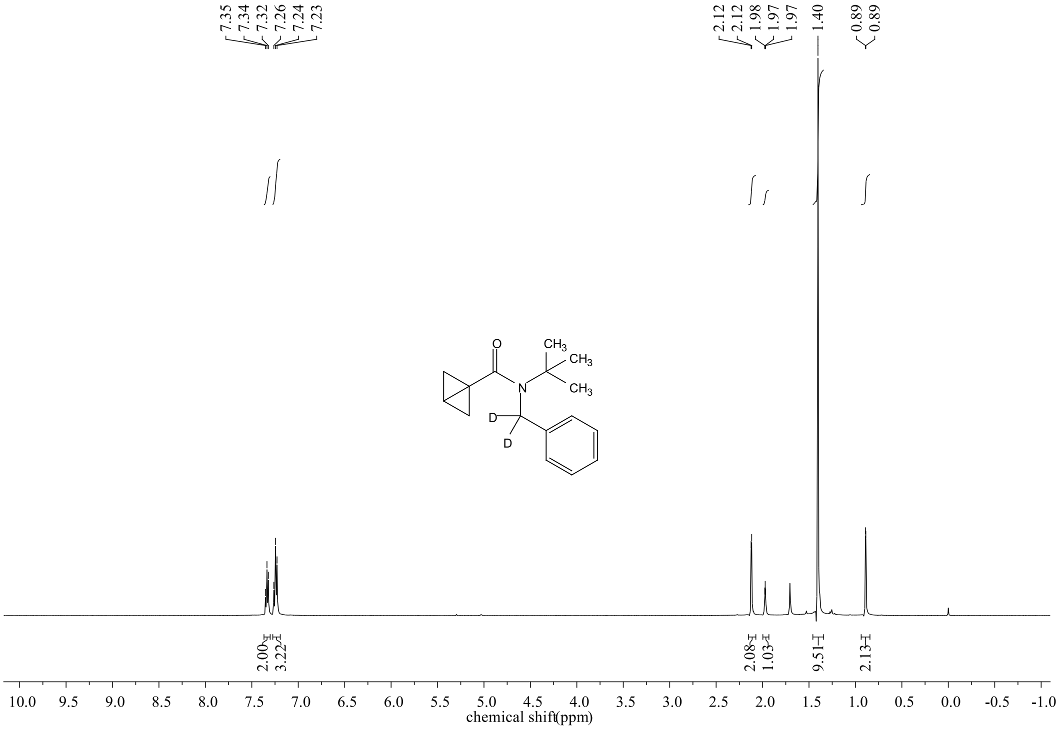
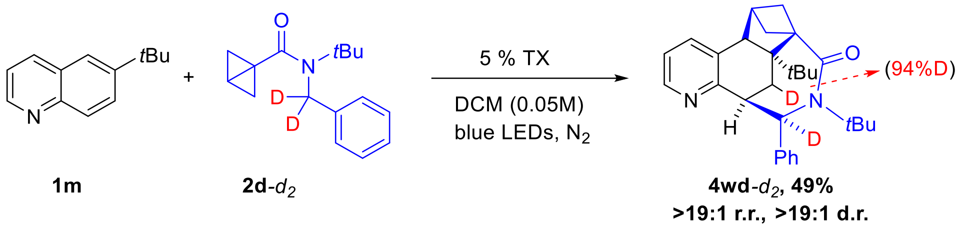
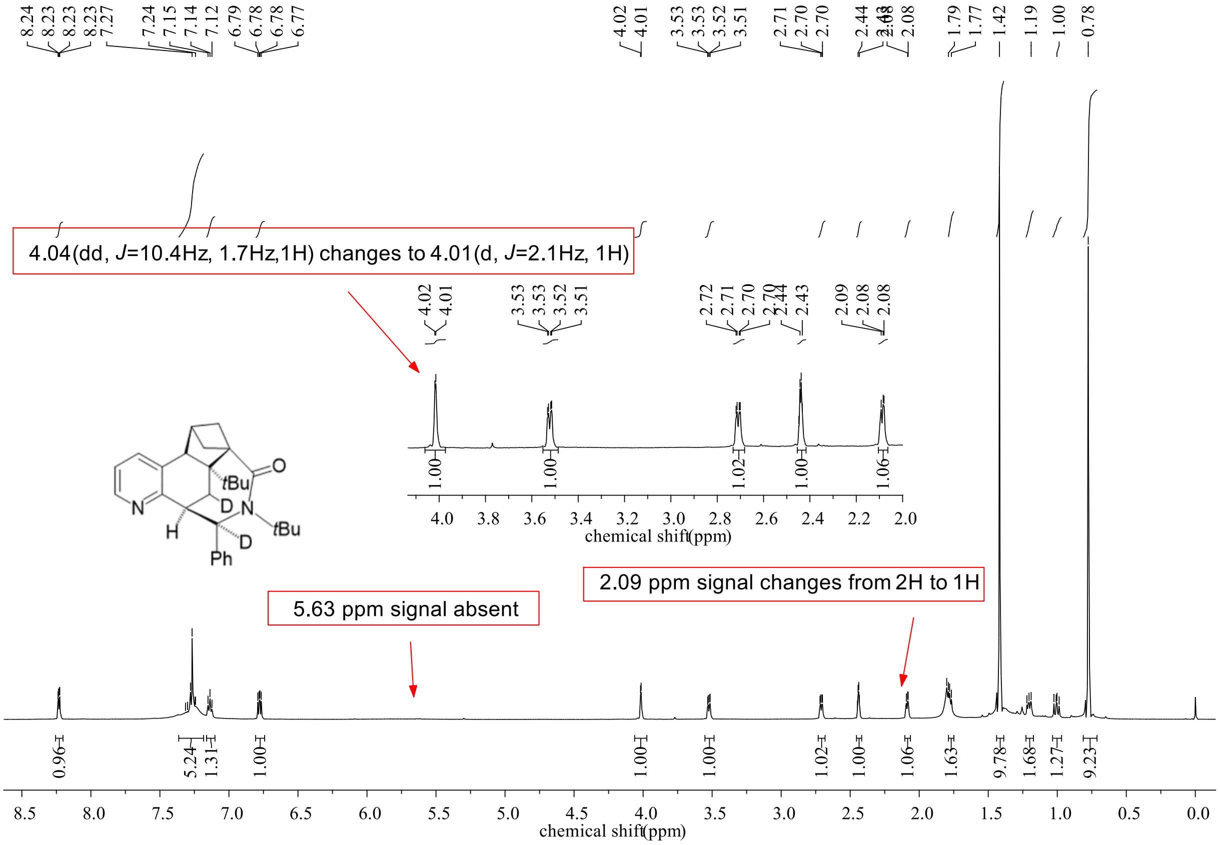


Figure S15. **^{1}H NMR** (400 MHz, CDCl$_3$) spectrum of **2d-*d*$_2$**.

3.7.2 Deuteration experiment with 2d-*d*$_2$



The quinoline substrate **1m** (46 mg, 0.25 mmol), BCBs **2d-*d*$_2$** (123 mg, 2.0 equiv.), TX (2.8 mg, 5 mol%) were added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with N$_2$ three times. Subsequently, DCM (5.0 mL, 0.05M) were added under positive nitrogen pressure. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LEDs (λ_{max}= 400 nm, distance approximately 4.0 cm from the bulb) with a fan at room temperature for 2h. 1, 3, 5- trimethoxybenzene was added as internal standard to measure the crude ^{1}H NMR. The product was purified by column chromatography (petroleum ether/EtOAc= 1/1) to yield the product **4wd-*d*$_2$** (52.7 mg, 49%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.23 (dd, *J* = 4.7Hz, 1.4Hz, 1H), 7.31-7.24 (m, 5H), 7.14 (t, *J* = 7.2Hz, 1H), 6.78 (dd, *J* = 7.8Hz, 4.8Hz, 1H), 4.01 (d, *J* = 2.1Hz, 1H), 3.53 (dd, *J* = 6.9Hz, 2.1Hz, 1H), 2.71 (dd, *J* = 6.8Hz, 2.1Hz, 1H), 2.44 (q, *J* = 2.5Hz, 1H), 2.09 (dd, *J* = 6.2Hz, 1.8Hz, 1H), 1.78 (dd, *J* = 10.7Hz, 6.4Hz, 1H), 1.42 (s, 9H), 1.20 (dd, *J* = 7.6Hz, 2.4Hz, 1H), 1.01 (dd, *J* = 10.9Hz, 8.0Hz, 1H), 0.78 (s, 9H). **HRMS** (ESI, *m/z*) calcd. for [M+H]$^+$: 431.3026, found: 431.3044.



4.04(dd, *J*=10.4Hz, 1.7Hz,1H) changes to 4.01(d, *J*=2.1Hz, 1H)

5.63 ppm signal absent

2.09 ppm signal changes from 2H to 1H

Figure S16. **^{1}H NMR** spectra of **4wd-*d*$_2$**.

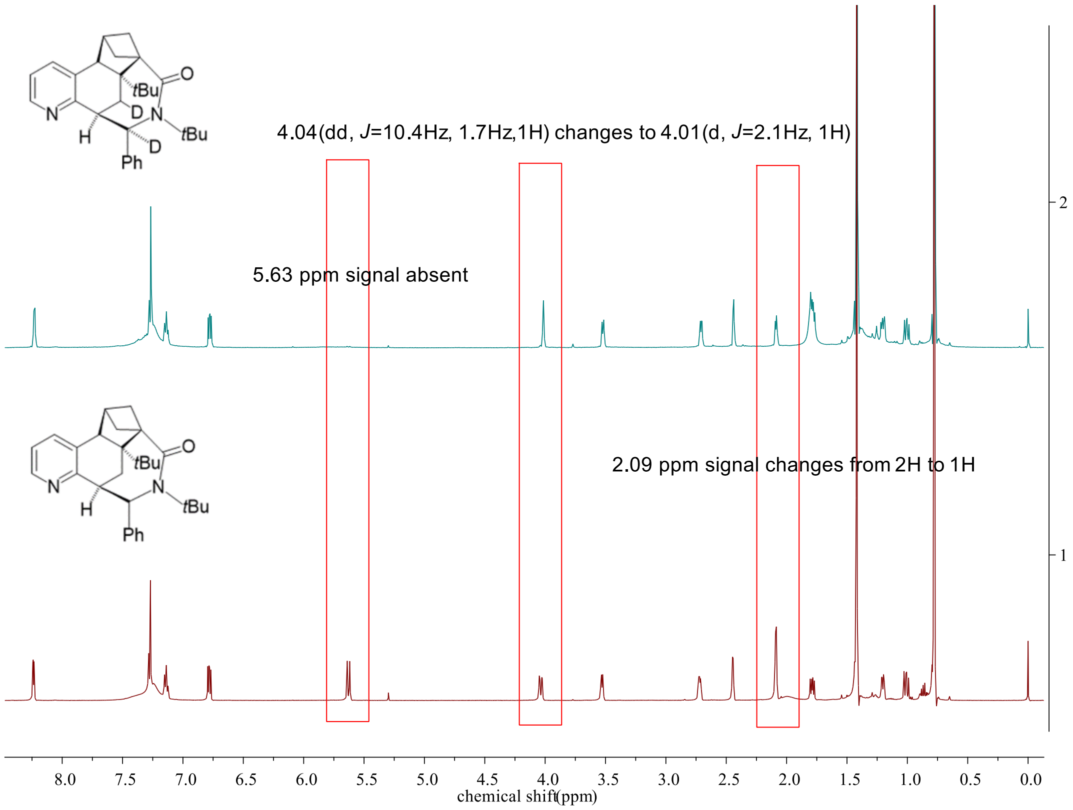


Figure S17. **^{1}H NMR** spectra of **4wd-**d_2 and **4wd**.

3.8 Measurement of quantum yield

The quantum yield of the reaction was measured by chemical actinometry using λ_{max}= 400 nm blue LEDs using potassium ferrioxalate following the procedure of J. N. Demas (*J. Phys. Chem*. **1981**, *85*, 2766), and F. Glorius (*Org. Lett*. **2018**, *20*, 1546).

0.491 g of potassium ferrioxalate trihydrate was dissolved in aq. H_2SO_4 (0.05 M, 10 mL) to afford a 0.006 M ferrioxalate solution and stored in the dark. Then, a buffer solution was prepared by dissolving 2.5 g of sodium acetate and 0.5 mL of H_2SO_4 (98%) in 50 mL of distilled water.

General Protocol to assess the photon flux of the λ_{max}= 400 nm blue LEDs:

To a 10 mL Schlenk flask containing a stirring bar, 1 mL of the actinometer solution was added. Then, the solution was irradiated for 60 s at λ_{max} = 400 nm. Immediately, a 100 µL aliquot was taken and added to a 10 mL volumetric flask containing 15 mg of 1, 10-phenanthroline in 3 mL of the buffer solution. The flask was filled with distilled water was stirred for 1 h to ensure that all Fe(II)-ions were coordinated by 1, 10-phenanthroline. The absorbance of this solution was then measured at 510 nm by UV/vis spectrophotometry. In a similar manner, this procedure is repeated with the actinometer solution stored in the dark. Using then the Beer's Law, the number of moles of Fe^{2+} produced by light irradiation is obtained by:

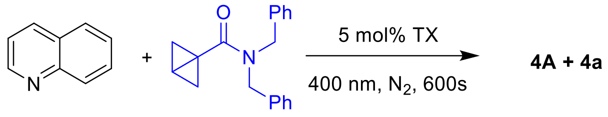
$$mol(Fe^{2+})=\frac{v_1 v_3 \Delta A(510nm)}{10^3 v_2 l \varepsilon(510nm)}=\frac{1mL\times 10mL\times 0.54973}{10^3\times 0.100mL\times 1cm\times 11100L\,mol^{-1}cm^{-1}}=4.953\times 10^{-6}\ \text{mol}$$

Where:
v_1 = Irradiated volume (1 mL).
v_2 = The aliquot of the irradiated solution taken for the estimation of Fe^{2+} ions (0.100 mL).
v_3 = Final volume of the solution after complexation with 1, 10-phenanthroline (10 mL).
ε (510 nm) = Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ complex (11100 L $mol^{-1}cm^{-1}$).
l = Optical path-length of the cuvette (1 cm).
ΔA (510 nm) = Absorbance difference between the irradiated solution and the solution stored in dark (0.54973).
The photon flux (F) is obtained by using the following equation:

$$\Phi\ (\lambda) = \frac{mol(Fe^{2+})}{F(1-10^{-A(\lambda)})t}$$

Where:

$\Phi(\lambda)$ = The quantum yield for Fe^{2+} formation at 406 nm is 1.188. $A(\lambda)$ = ferrioxalate actinometer absorbance at 400 nm, which was measured placing 1 mL of the solution in a cuvette of path length 1 cm by UV/vis spectrophotometry. We obtained an absorbance value of 1.2076. *t* = is the reaction time (60 s). The photon flux (F) is 7.408 x 10^{-8} einsteins/s.



1a **2a**

To obtain the quantum yield (Φ) of this photochemical reaction. The number of moles of the product was determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene as internal standard. As such, a photocatalytic reaction was performed under the set of optimized reaction conditions under visible light irradiation of λ_{max}= 400 nm blue LEDs. After 600 s of light irradiation, 3.0 x 10^{-5} moles of products were obtained. The quantum yield of this reaction was calculated using the following equation:

$$\Phi = \frac{mol\ of\ product}{F(1-10^{-A(400nm)})t} = \frac{3.0\times10^{-5}\ mol}{7.408\ \times10^{-8} einsteins\ s^{-1}\times(1-10^{-0.5933})\times600s}\ = 0.91$$

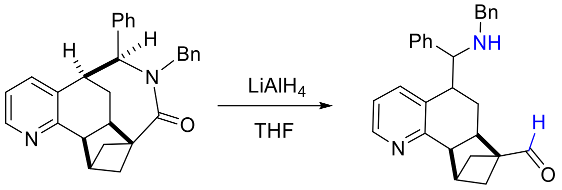
Where:

A(400 nm) = The absorbance at 400 nm of the photocatalytic reaction which was measured placing 1 mL of the solution in a cuvette of path length 1 cm by UV/vis spectrophotometry (0.5933).

t = The reaction time (600 s).

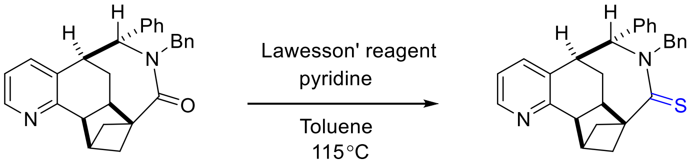
The quantum yield (Φ) of the reaction is 0.91.

4. Synthetic application



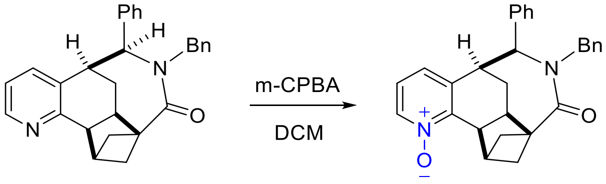
cis-**4A** **5**, 78%

The reduction rea**c**tion was conducted following a modified literature procedure.[9] The solution of *cis*-**4A** (40.6 mg, 0.1 mmol) and THF (1.0 mL, 0.1 M) were stirred at 0 °C in an ice/water bath. $LiAlH_4$ (16 mg, 4.0 equiv.) was added slowly in 2 portions over 10 min. The mixture was stirred for 15 min at 0 °C and stirred at room temperature for 15 min. After quenched with H_2O, the solution was concentrated by rotary evaporation to remove THF. The residue was diluted with H_2O and extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered then concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether/EtOAc= 1/1) to obtain **5** as a white solid in 78% yield (31 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.92 (d, *J* = 4.6Hz, 1H), 7.40 (t, *J* = 7.5Hz, 2H), 7.34-7.27 (m, 7H), 7.26-7.25 (m, 1H), 7.08 (dd, *J* = 7.8Hz, 4.9Hz, 1H), 3.93 (d, *J* = 9.0Hz, 1H), 3.68 (d, *J* = 13.0Hz, 1H), 3.61 (d, *J* = 13.1Hz, 1H), 3.26-3.24 (m, 2H), 2.76-2.71 (m, 2H), 1.98 (dd, *J* = 6.5Hz, 2.0Hz, 1H), 1.66-1.62 (m, 2H), 1.56 (dd, *J* = 9.3Hz, 6.8Hz, 1H), 0.98 (t, *J* = 8.4Hz, 1H), 0.63 (q, *J* = 12.4Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.9, 159.5, 147.2, 141.9, 140.1, 137.6, 132.8, 128.8, 128.5, 128.4, 127.8, 127.6, 127.1, 121.0, 64.4, 62.1, 51.4, 44.1, 44.1, 41.7, 40.8, 40.6, 34.3, 29.9. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 409.2274, found: 409.2270.



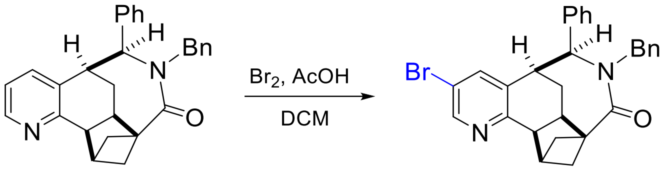
trans-**4A** **6**, 86%

The thionation rea**c**tion was conducted according to a reported procedure.[10] To a solution of *trans*-**4A** (40.6 mg, 0.1 mmol) in toluene (1 mL, 0.1M), Lawesson's reagent (60 mg, 1.5 equiv.) and pyridine (1.6 μL, 0.2 equiv.) were added and the reaction mixture was heated at 115°C. After 1.5h, the crude mixture was allowed to cool the ambient temperature and was subsequently concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (petroleum ether/EtOAc= 1/1) to afford 36 mg (86%) of **6** as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 4.7Hz, 1.6Hz, 1H), 7.46-7.25 (m, 4H), 7.06-7.05 (m, 4H), 6.87 (dd, *J* = 7.7Hz, 4.8Hz, 1H), 6.78-6.73 (m, 3H), 5.53 (d, *J* = 5.7Hz, 1H), 3.79 (d, *J* = 6.8Hz, 1H), 3.77 (m, 1H), 2.77-2.75 (m, 2H), 2.36 (ddd, *J* = 13.8Hz, 4.3Hz, 1H), 2.30 (d, *J* = 4.3Hz, 1H), 2.03-1.99 (m, 2H), 1.92 (dd, *J* = 10.7Hz, 7.1Hz, 1H), 1.74 (br, 2H), 1.55 (d, *J* = 3.9Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.0, 160.6, 148.7, 139.1, 136.7, 136.3, 136.1, 128.7, 128.5, 127.8, 126.7, 126.4, 120.9, 69.9, 65.6, 54.7, 50.7, 45.2, 42.1, 39.8, 38.1, 26.3. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 423.1889, found: 423.1903. *One aromaticsignal is missing (probably due to signal overlap).*



cis-**4A** **7**, 99%

The *N*-oxide was prepared according to a reported procedure.[9] The solution of *cis*-**4A** (40.6 mg, 0.1 mmol) and DCM (2.0 mL, 0.05 M) were stirred at 0 °C in an ice/water bath for 10 mins. *m*-CPBA (purity 85%, 45 mg, 2.2 equiv.) was added portionwise and the solution was warmed to room temperature until full conversion (monitored by TLC).The mixture was quenched by addition of aq. NaOH (1 M) and extracted with DCM. The combined organic layers were dried over $MgSO_4$. Subsequently, the solvent was removed in *vacuo*, and washed with MeOH to give the product **7** (42 mg, 99%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.2Hz, 1H), 7.36-7.25 (m, 10H), 6.75 ((dd, *J* = 7.9Hz, 6.3Hz, 1H), 6.67 (d, *J* = 7.6Hz, 1H), 5.76 (d, *J* = 14.8Hz, 1H), 5.19 (d, *J* = 10.0Hz, 1H), 4.12(d, *J* = 5.5Hz, 1H), 3.81 (dd, *J* = 9.5Hz, 5.5Hz, 1H), 3.20 (d, *J* = 14.7Hz, 1H), 2.88 (d, *J* = 2.1Hz, 1H), 2.84 (br, 1H), 2.25 (d, *J* = 4.2Hz, 1H), 2.13 (dd, *J* = 13.6Hz, 3.9Hz, 1H), 1.88 (dd, *J* = 10.7Hz, 6.6Hz, 1H), 1.48 (d, *J* = 5.2Hz, 1H), 1.25-1.20 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.8, 152.5, 139.4, 138.2, 138.0, 136.9, 129.0, 128.8, 128.7, 128.5, 127.9, 127.8, 127.8, 121.4, 67.6, 54.5, 50.0, 46.1, 41.5, 40.8, 39.7, 38.1, 37.6, 25.7. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 423.2067, found: 423.2070.



cis-**4A** **8**, 68%

The brominated reaction was conducted according to a reported procedure.[11] To a suspension of *cis*-**4A** (40.6 mg, 0.1 mmol) in AcOH (1 mL, 0.1M) was added liquid Br_2 (52µL, 10.0 equiv.) at room temperature. The mixture was stirred for 0.5 h and then DCM (1 mL) was added to the mixture. After stirring overnight at room temperature, the reaction was quenched with saturated $NaHSO_3$ solution and extracted with DCM. The organic layers were washed with brine and then concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether/EtOAc= 1/1) to obtain **8** as a white solid in 68% yield (33.0 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.7Hz, 1H), 7.48 (d, *J* = 8.3Hz, 2H), 7.38-7.32 (m, 3H), 7.29 (d, *J* = 7.2Hz, 1H), 7.25-7.23 (m, 2H), 7.18 (d, *J* = 8.2Hz, 2H), 7.04 (dd, *J* = 7.7Hz, 5.4Hz, 1H), 5.67 (d, *J* = 14.8Hz, 1H), 5.17 (d, *J* = 10.1Hz, 1H), 3.99 (d, *J* = 5.5Hz, 1H), 3.86 (dd, *J* = 9.6Hz, 4.7Hz, 1H), 3.18 (d, *J* = 14.8Hz, 1H), 2.85 (m, 1H), 2.67 (br, 1H), 2.26 (dd, *J* = 6.5Hz, 1.6Hz, 1H), 2.14 (dd, *J* = 14.0Hz, 3.7Hz, 1H), 1.92-1.89 (m, 2H), 1.45 (d, *J* = 7.3Hz, 1H), 1.15 (d, *J* = 6.4Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.7, 142.5, 137.8, 136.9, 136.4, 131.9, 130.8, 129.0, 128.7, 128.2, 127.6, 121.9, 121.5. 121.3, 67.8. 54.4, 49.5, 46.7, 40.9, 40.8, 40.2, 38.2, 25.7, 23.3. **HRMS** (ESI, *m/z*) calcd. for $[M+H]^+$: 485.1223, found: 485.1259.

5. Supplementary references

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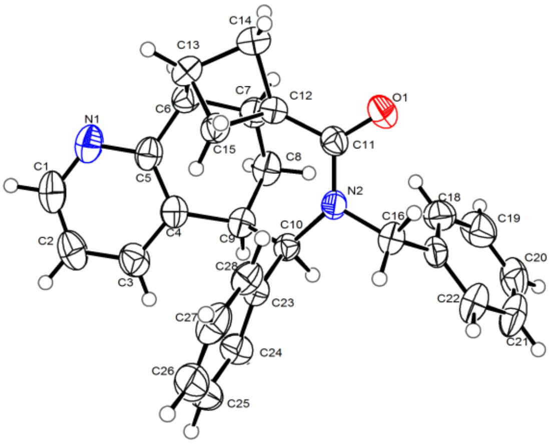
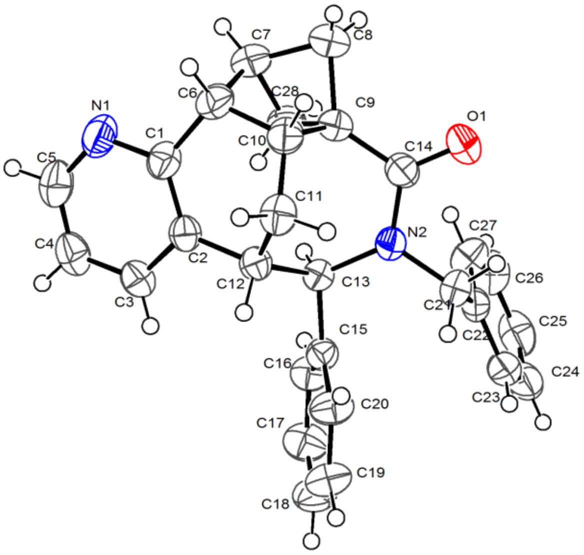
6. X-ray crystal structure data

X-ray crystallographic data of *cis*-4A (CCDC 2382179)



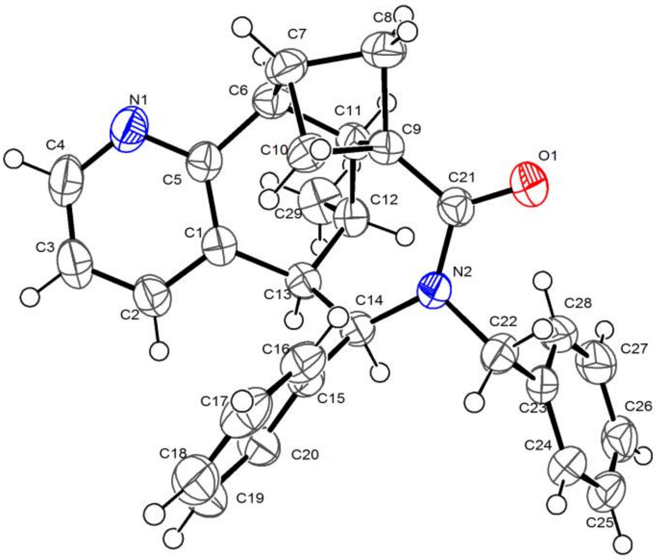
Bond precision:	C-C = 0.0020Å	Wavelength=1.54184	
Cell:	a=10.95607 (12)	b=12.99588 (14)	c=14.67188 (17)
	alpha=90	beta=91.352(1)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2088.46 (4)	2088.45 (4)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	$C_{28}H_{26}N_2O$	$C_{28}H_{26}N_2O$	
Sum formula	$C_{28}H_{26}N_2O$	$C_{28}H_{26}N_2O$	
Mr	406.51	406.51	
Dx,g cm^{-3}	1.293	1.293	
Z	4	4	
Mu (mm^{-1})	0.610	0.610	
F000	864.0	864.0	
F000	866.33		
h, k, lmax	13, 16, 18	13, 15, 17	
Nref	4168	4055	
Tmin, Tmax	0.874, 0.896	0.921, 1.000	
Tmin’	0.874		
Correction method= # Reported T Limits: Tmin=0.921 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.973		Theta(max)= 72.960	
R(reflections)= 0.0406(3598)		wR2(reflections)= 0.1102(4055)	
S = 1.037		Npar= 284	
Displacement ellipsoids are drawn at 50% probability level			

X-ray crystallographic data of *trans*-4A (CCDC 2382180)



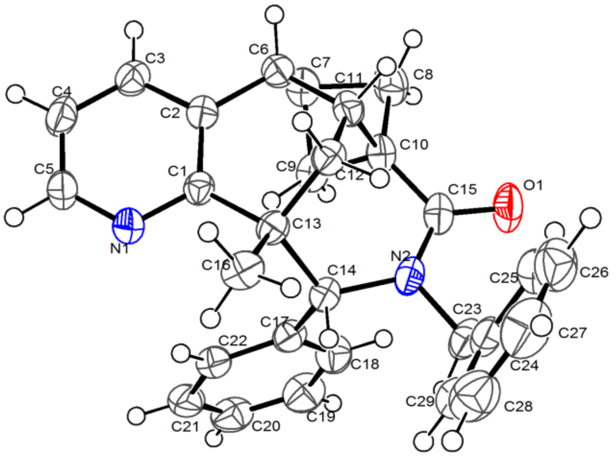
Bond precision:	C-C = 0.0027Å	Wavelength=1.54184	
Cell:	a=11.3527(4)	b=11.9601(4)	c=16.1020(5)
	alpha=90	beta=105.689(4)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2104.87(13)	2104.86(13)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	$C_{28}H_{26}N_2O$	$C_{28}H_{26}N_2O$	
Sum formula	$C_{28}H_{26}N_2O$	$C_{28}H_{26}N_2O$	
Mr	406.51	406.51	
Dx,g cm^{-3}	1.283	1.283	
Z	4	4	
Mu (mm^{-1})	0.605	0.605	
F000	864.0	864.0	
F000	866.33		
h, k, lmax	14, 14, 19	14, 14, 19	
Nref	4193	4079	
Tmin, Tmax	0.877, 0.919	0.777, 1.000	
Tmin’	0.860		
Correction method= # Reported T Limits: Tmin= 0.777 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.973		Theta(max)= 72.867	
R(reflections)= 0.0446(2887)		wR2(reflections)= 0.1198(4079)	
S = 1.020		Npar= 296	
Displacement ellipsoids are drawn at 50% probability level			

X-ray crystallographic data of *cis*-4f (CCDC 2382181)



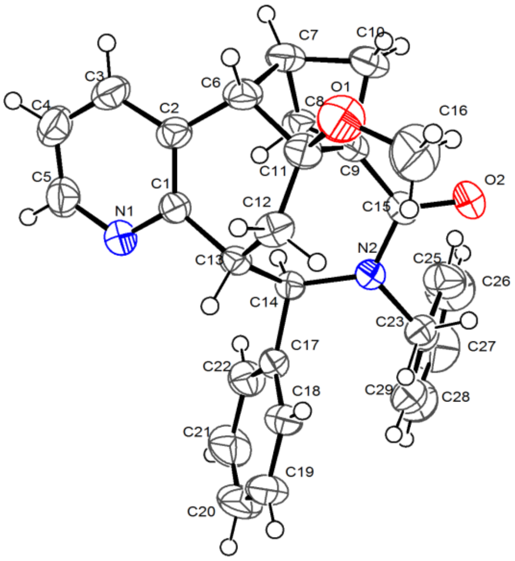
Bond precision:	C-C = 0.0020Å	Wavelength=1.54184	
Cell:	a=10.93903(16)	b=12.54235(16)	c=15.9418(2)
	alpha=90	beta=95.8562(13)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2175.82(5)	2175.81(5)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	$C_{29}H_{28}N_2O$	$C_{29}H_{28}N_2O$	
Sum formula	$C_{29}H_{28}N_2O$	$C_{29}H_{28}N_2O$	
Mr	420.53	420.53	
Dx,g cm^{-3}	1.284	1.284	
Z	4	4	
Mu (mm^{-1})	0.602	0.602	
F000	896.0	896.0	
F000	898.40		
h, k, lmax	13, 15, 19	13, 15, 19	
Nref	4354	4230	
Tmin, Tmax	0.878, 0.919	0.934, 1.000	
Tmin’	0.876		
Correction method= # Reported T Limits: Tmin= 0.934 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.972		Theta(max)= 72.900	
R(reflections)= 0.0405(3692)		wR2(reflections)= 0.1131(4230)	
S = 1.029		Npar= 295	
Displacement ellipsoids are drawn at 50% probability level			

X-ray crystallographic data of *cis*-4h (CCDC 2382182)



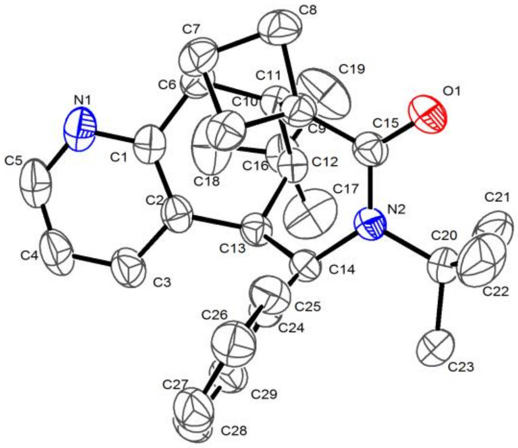
Bond precision:	C-C = 0.0018Å	Wavelength=1.54184	
Cell:	a=9.2984 (2)	b=10.9937(4)	c=11.0879(4)
	alpha=78.304(3)	beta=83.684 (2)	gamma=83.676(2)
Temperature:	293 K		
	Calculated	Reported	
Volume	1098.67(6)	1098.67(6)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	$C_{29}H_{28}N_2O$	$C_{29}H_{28}N_2O$	
Sum formula	$C_{29}H_{28}N_2O$	$C_{29}H_{28}N_2O$	
Mr	420.53	420.53	
Dx,g cm^{-3}	1.271	1.271	
Z	2	2	
Mu (mm^{-1})	0.596	0.596	
F000	448.0	448.0	
F000	449.20		
h, k, lmax	11, 13, 13	11, 13, 13	
Nref	4382	4205	
Tmin, Tmax	0.879, 0.904	0.775, 1.000	
Tmin’	0.877		
Correction method= # Reported T Limits: Tmin= 0.775 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.960		Theta(max)= 72.709	
R(reflections)= 0.0385(3902)		wR2(reflections)= 0.1069(4205)	
S = 1.026		Npar= 291	
Displacement ellipsoids are drawn at 50% probability level			

X-ray crystallographic data of *trans*-4n (CCDC 2382183)



Bond precision:	C-C = 0.0029Å	Wavelength=1.54184	
Cell:	a=10.85402(11)	b=11.58396(11)	c=18.06561(18)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2271.44(4)	2271.43(4)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	$C_{29}H_{28}N_2O_2$	$C_{29}H_{28}N_2O_2$	
Sum formula	$C_{29}H_{28}N_2O_2$	$C_{29}H_{28}N_2O_2$	
Mr	436.53	436.53	
Dx,g cm^{-3}	1.276	1.277	
Z	4	4	
Mu (mm^{-1})	0.630	0.630	
F000	928.0	928.0	
F000	930.60		
h, k, lmax	13, 14, 22	13, 14, 22	
Nref	4538(2579)	4452	
Tmin, Tmax	0.882, 0.898	0.880, 1.000	
Tmin’	0.882		
Correction method= # Reported T Limits: Tmin= 0.880 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 1.73/0.98		Theta(max)= 72.932	
R(reflections)= 0.0307(4240)		wR2(reflections)= 0.0830(4452)	
S = 1.063		Npar= 300	
Displacement ellipsoids are drawn at 50% probability level			

X-ray crystallographic data of *cis*-4wd (CCDC 2382185)



Bond precision:	C-C = 0.0023Å	Wavelength=1.54184	
Cell:	a=15.3885(3)	b=9.63635(13)	c=17.3679(3)
	alpha=90	beta=110.5905(19)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2410.94(8)	2410.94(7)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	$C_{29}H_{36}N_2O$	$C_{29}H_{36}N_2O$	
Sum formula	$C_{29}H_{36}N_2O$	$C_{29}H_{36}N_2O$	
Mr	428.60	428.60	
Dx,g cm^{-3}	1.181	1.181	
Z	4	4	
Mu (mm^{-1})	0.544	0.544	
F000	928.0	928.0	
F000	930.40		
h, k, lmax	19, 11, 21	18, 11, 21	
Nref	4816	4667	
Tmin, Tmax	0.882, 0.897	0.960, 1.000	
Tmin’	0.882		

Correction method= # Reported T Limits: Tmin= 0.960 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.969 Theta(max)= 72.952

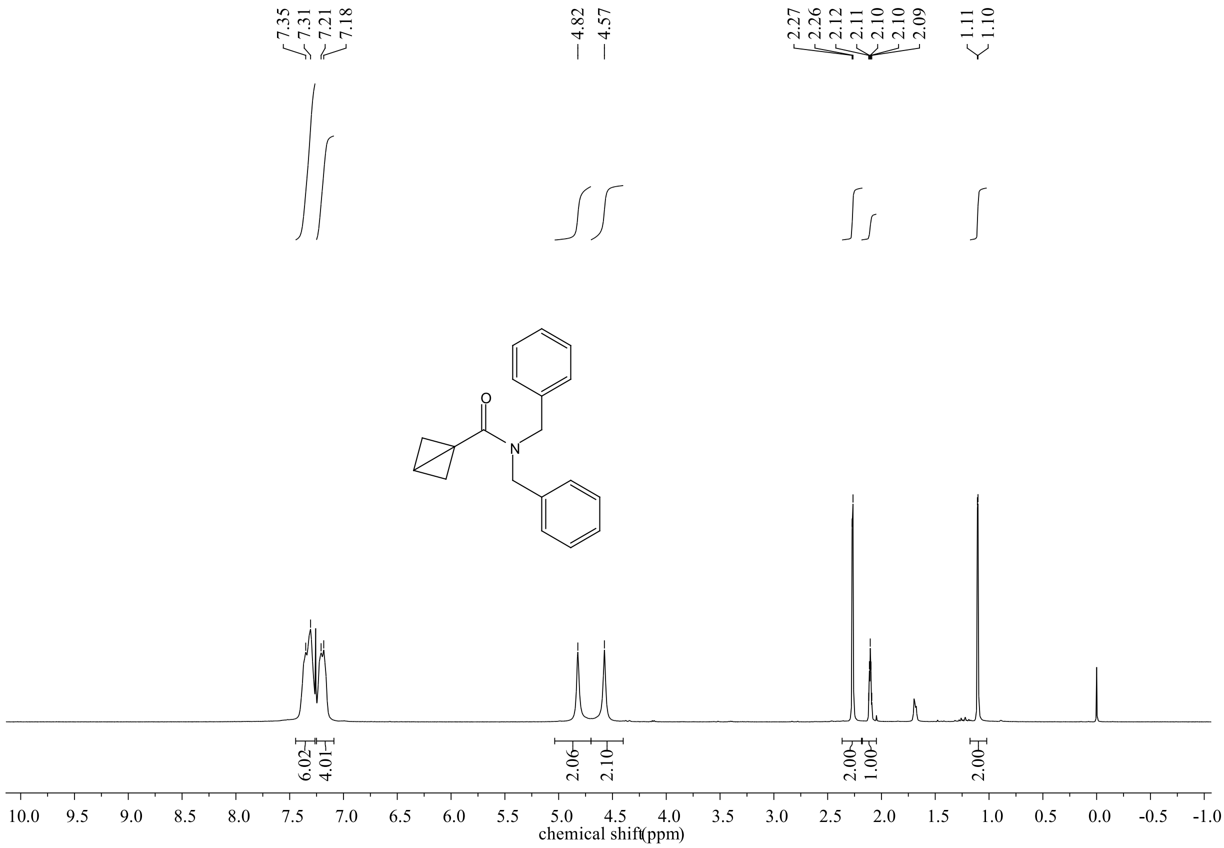
R(reflections)= 0.0450(4010) wR2(reflections)= 0.1299(4667)

S = 1.034 Npar= 299

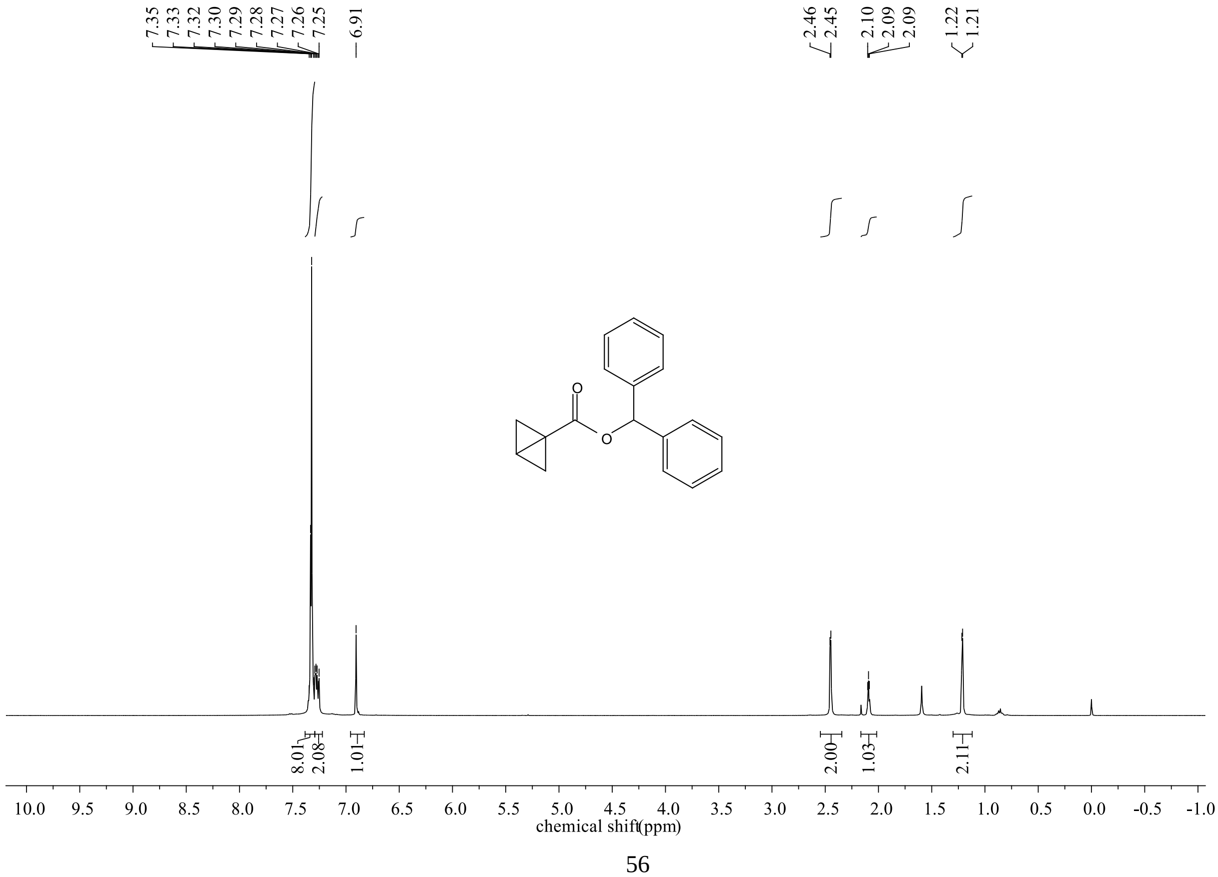
Displacement ellipsoids are drawn at 50% probability level

7. NMR spectra of related compounds

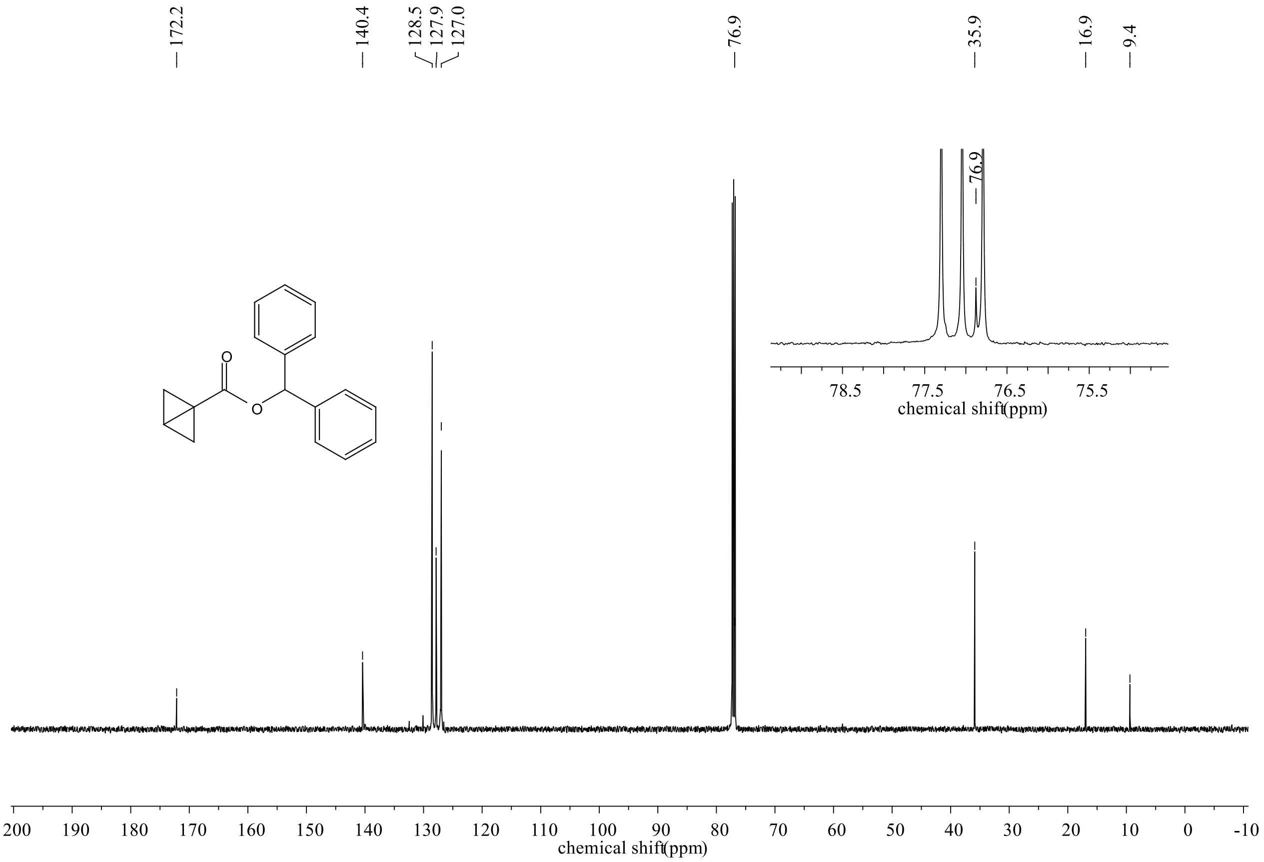
2a ^{1}H NMR (400 MHz, $CDCl_3$)



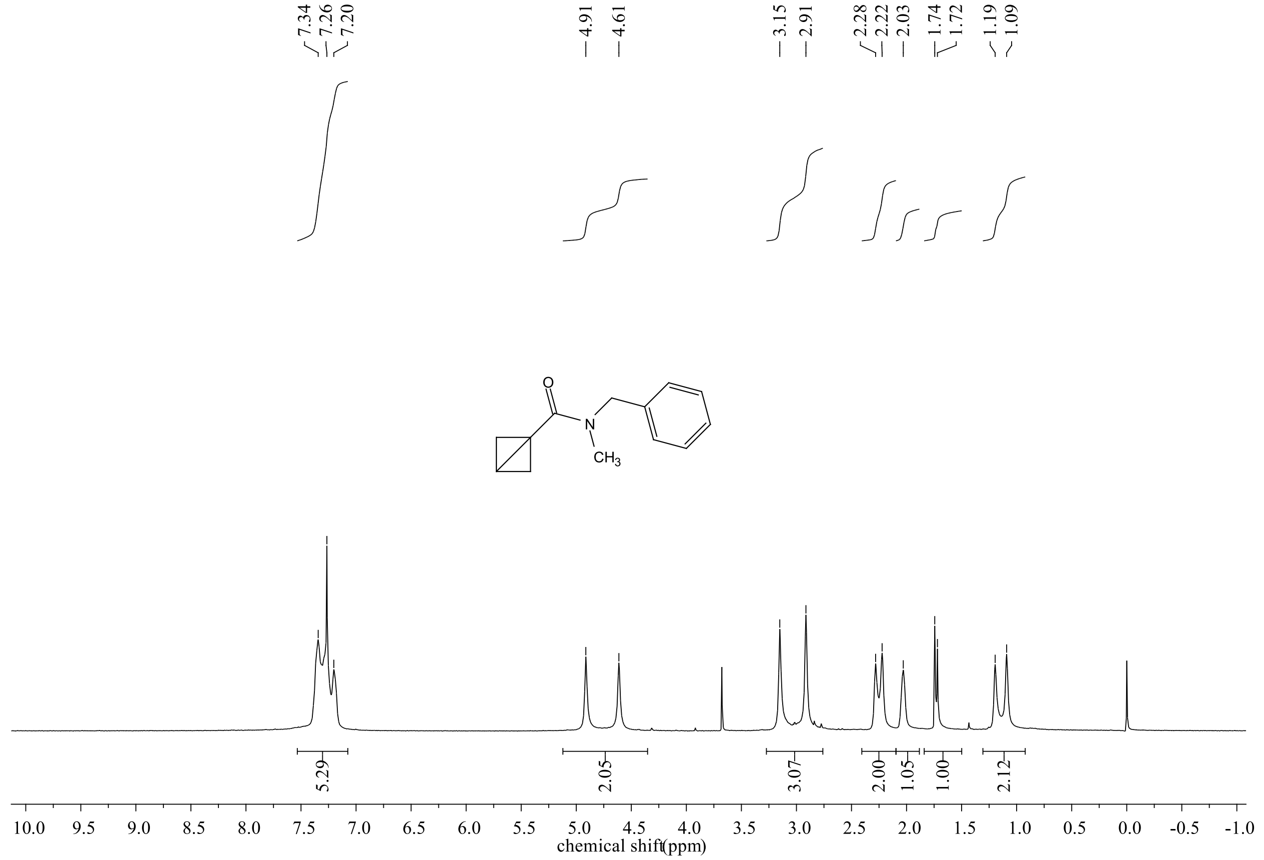
2u ^{1}H NMR (400 MHz, $CDCl_3$)



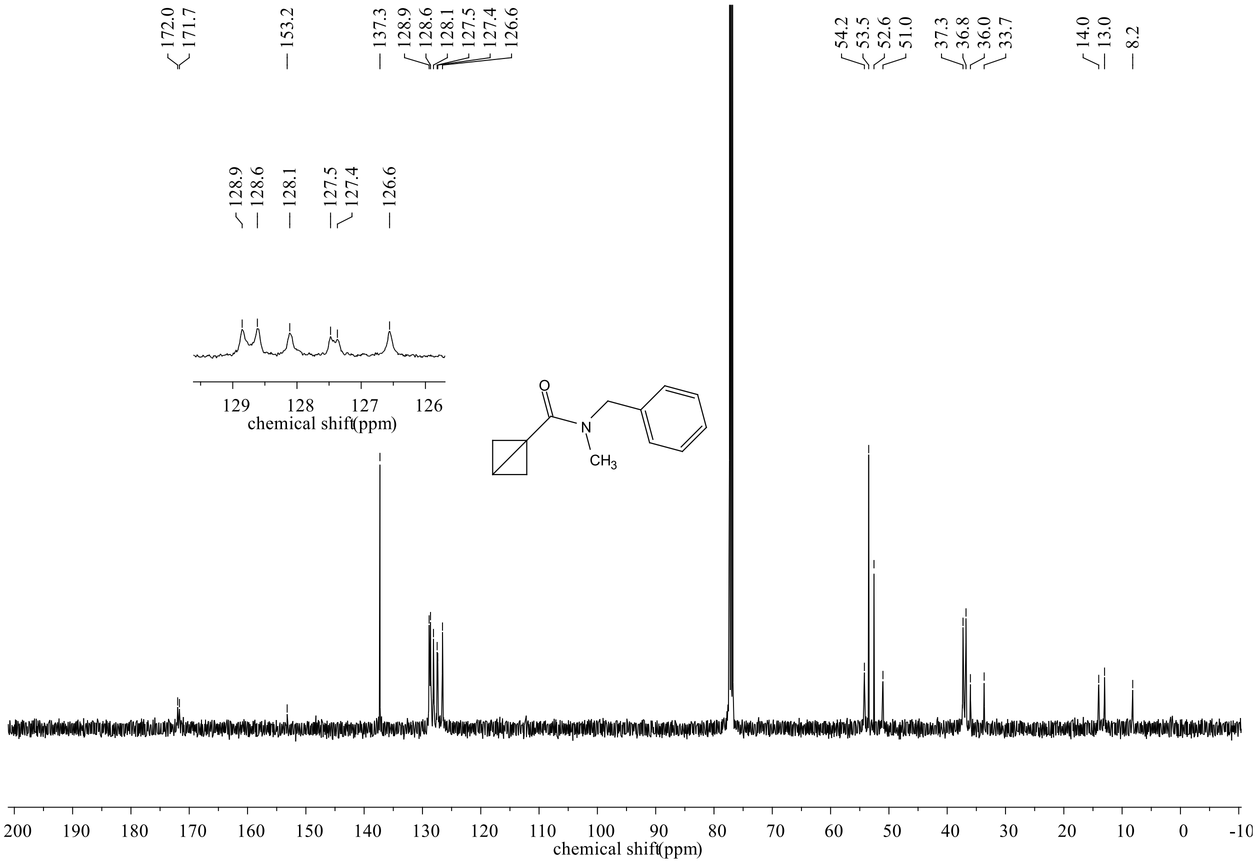
2u ^{13}C NMR (126 MHz, CDCl$_3$)



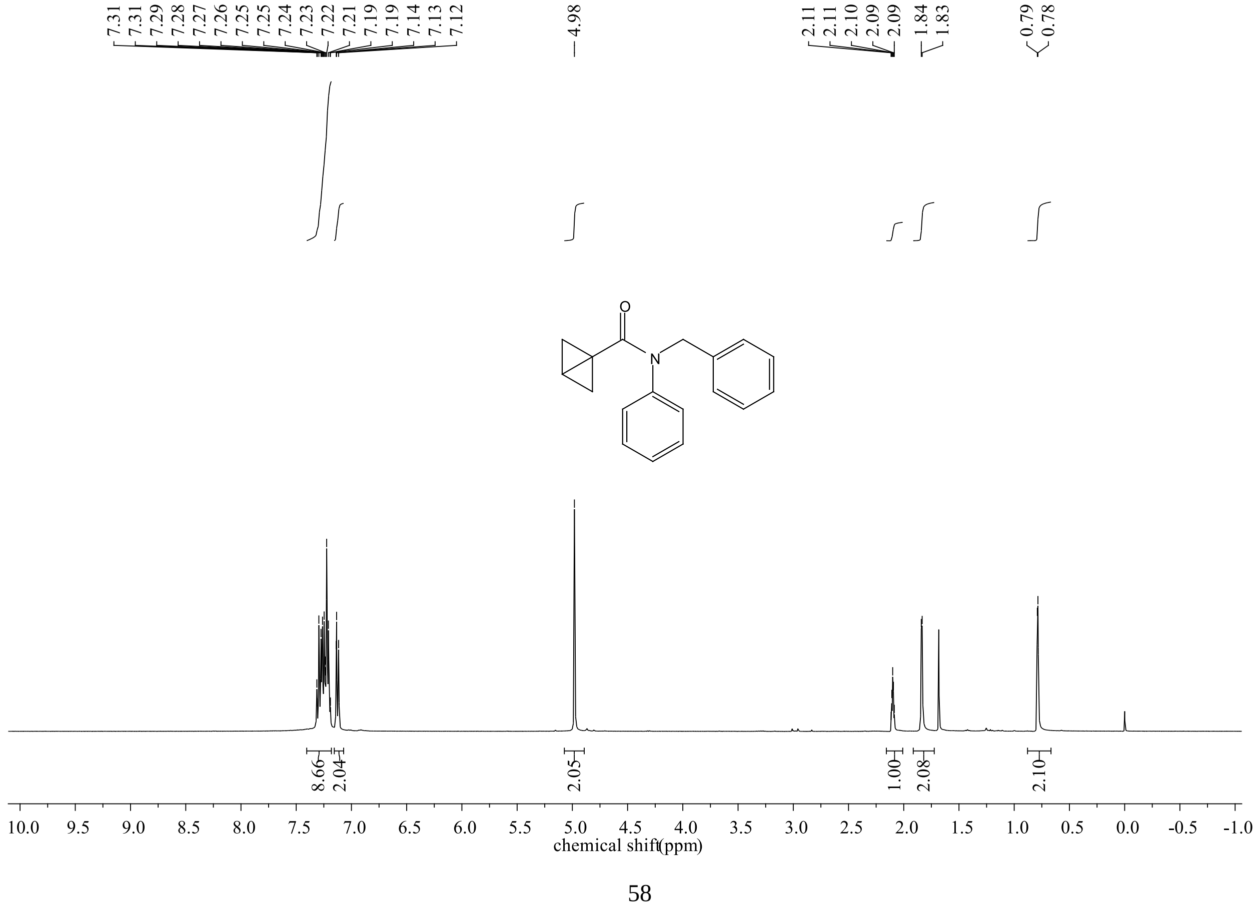
2v ^{1}H NMR (400 MHz, CDCl$_3$)



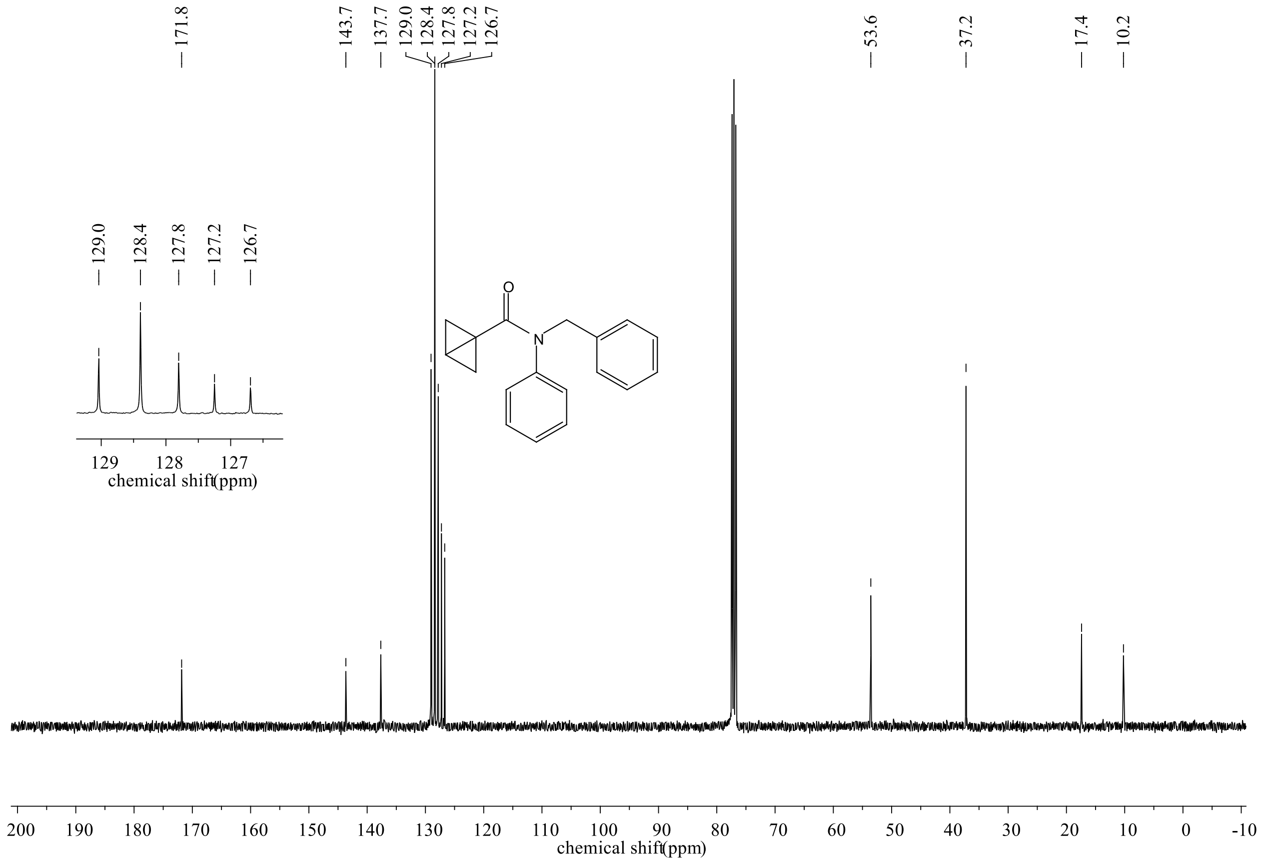
2v ^{13}C NMR (126 MHz, CDCl$_3$)



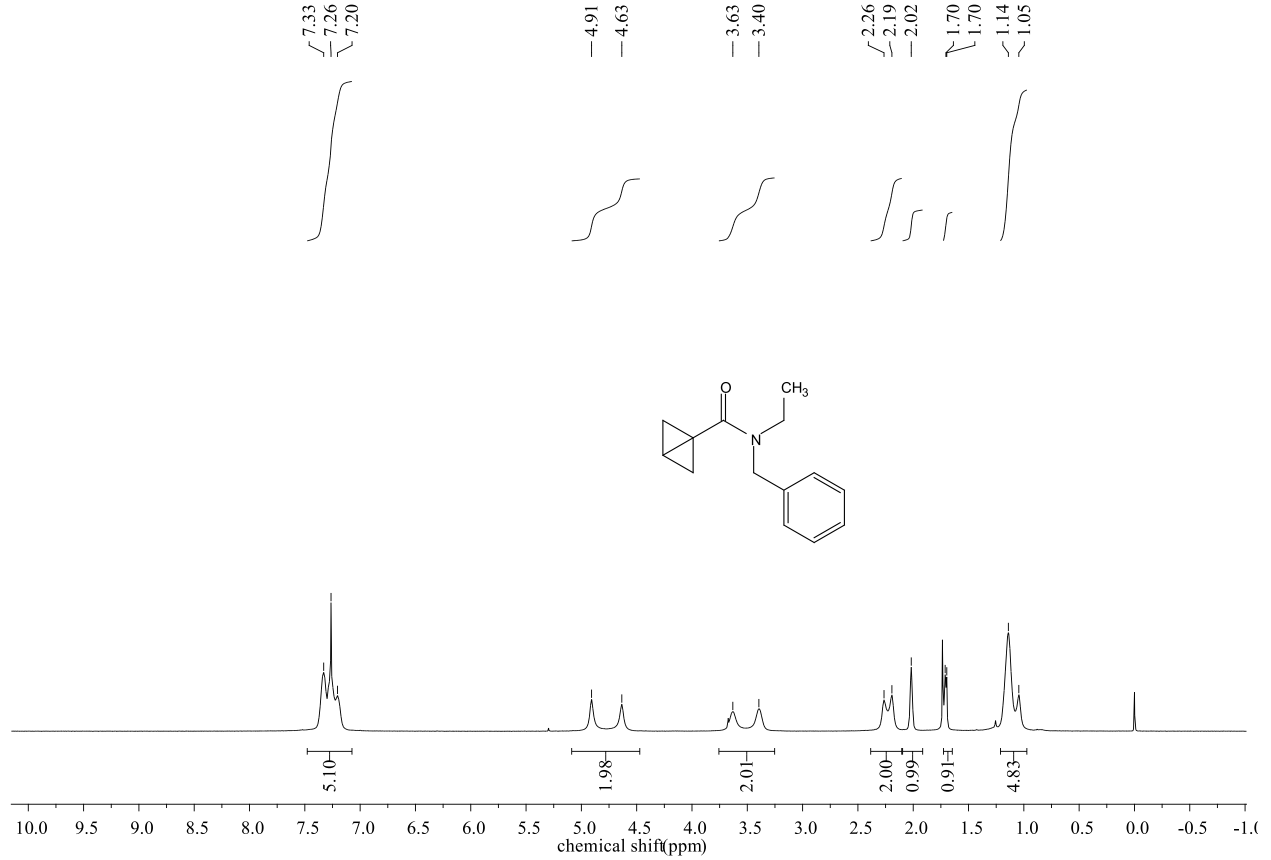
2w ^{1}H NMR (400 MHz, CDCl$_3$)



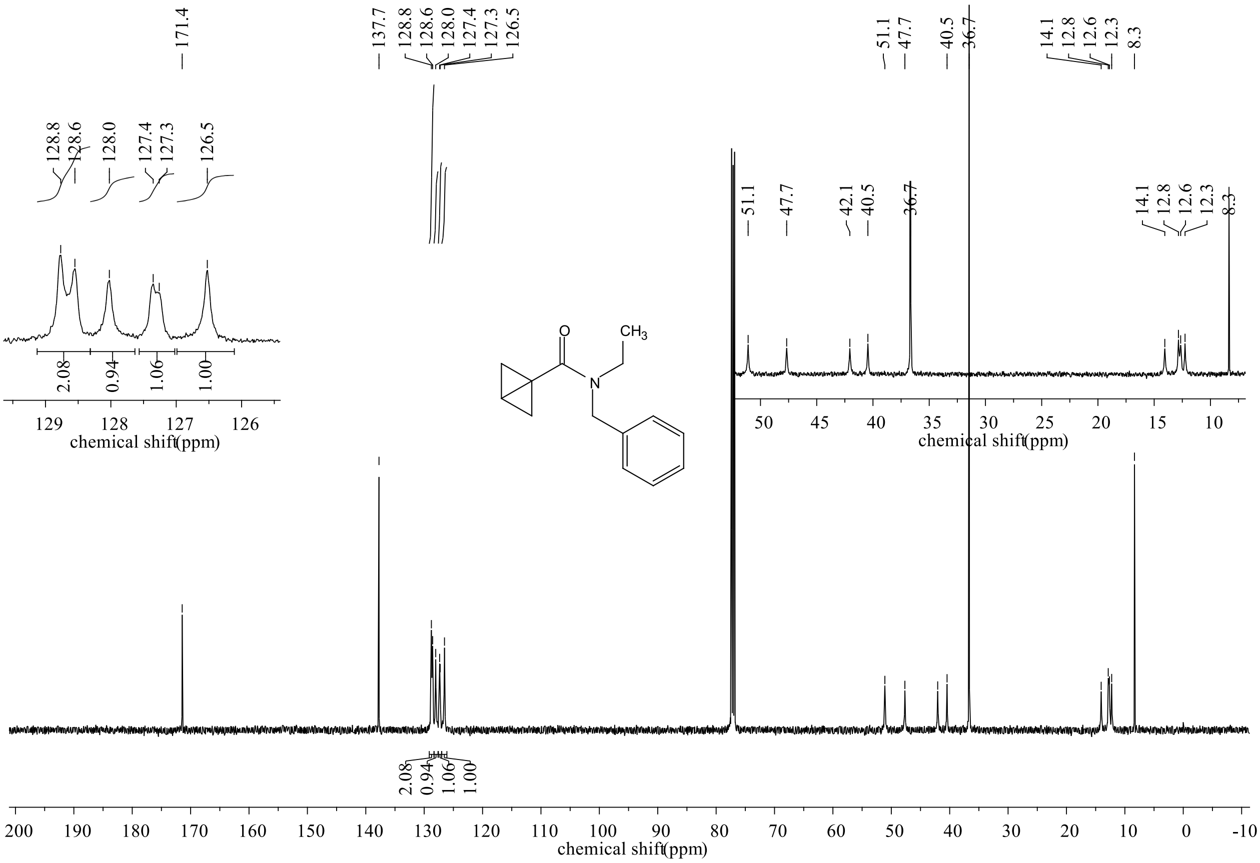
2w ^{13}C NMR (101 MHz, CDCl$_3$)



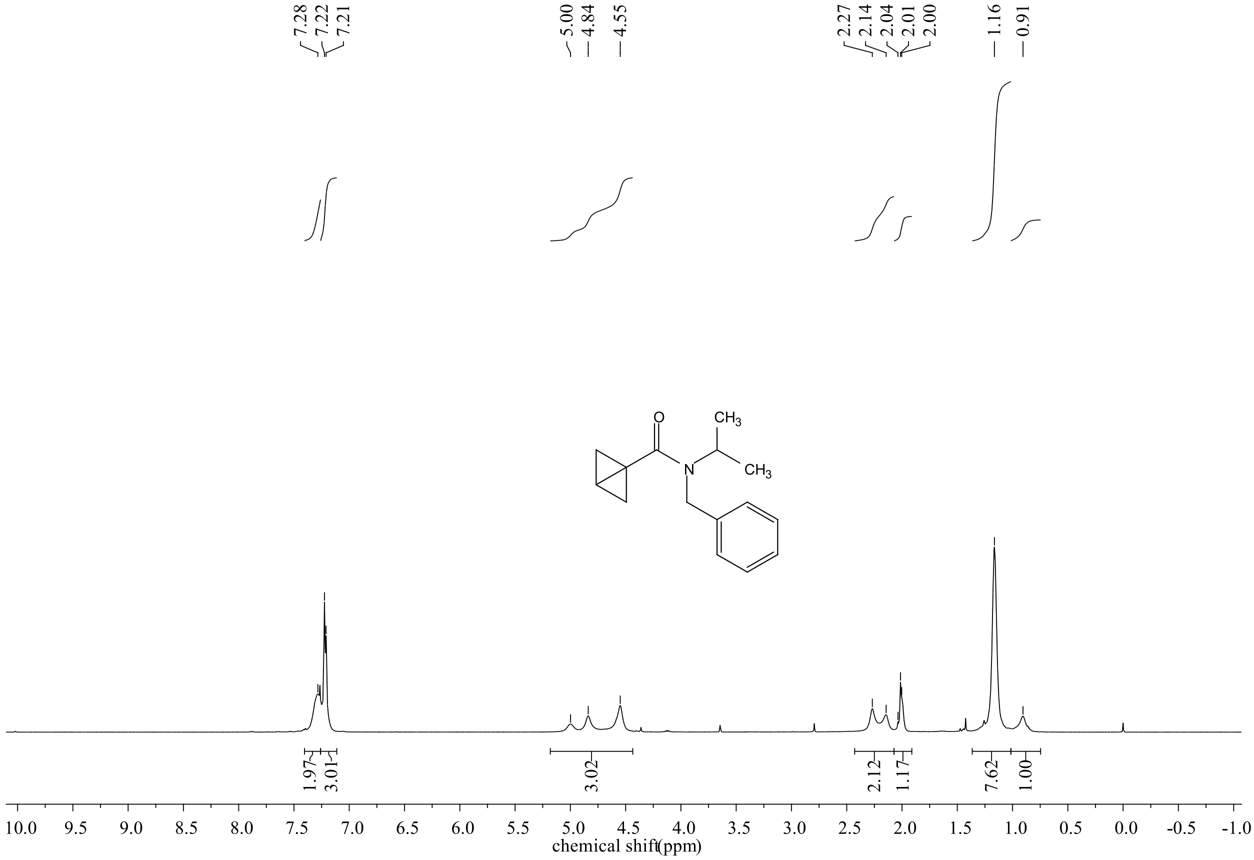
2b ^{1}H NMR (400 MHz, CDCl$_3$)



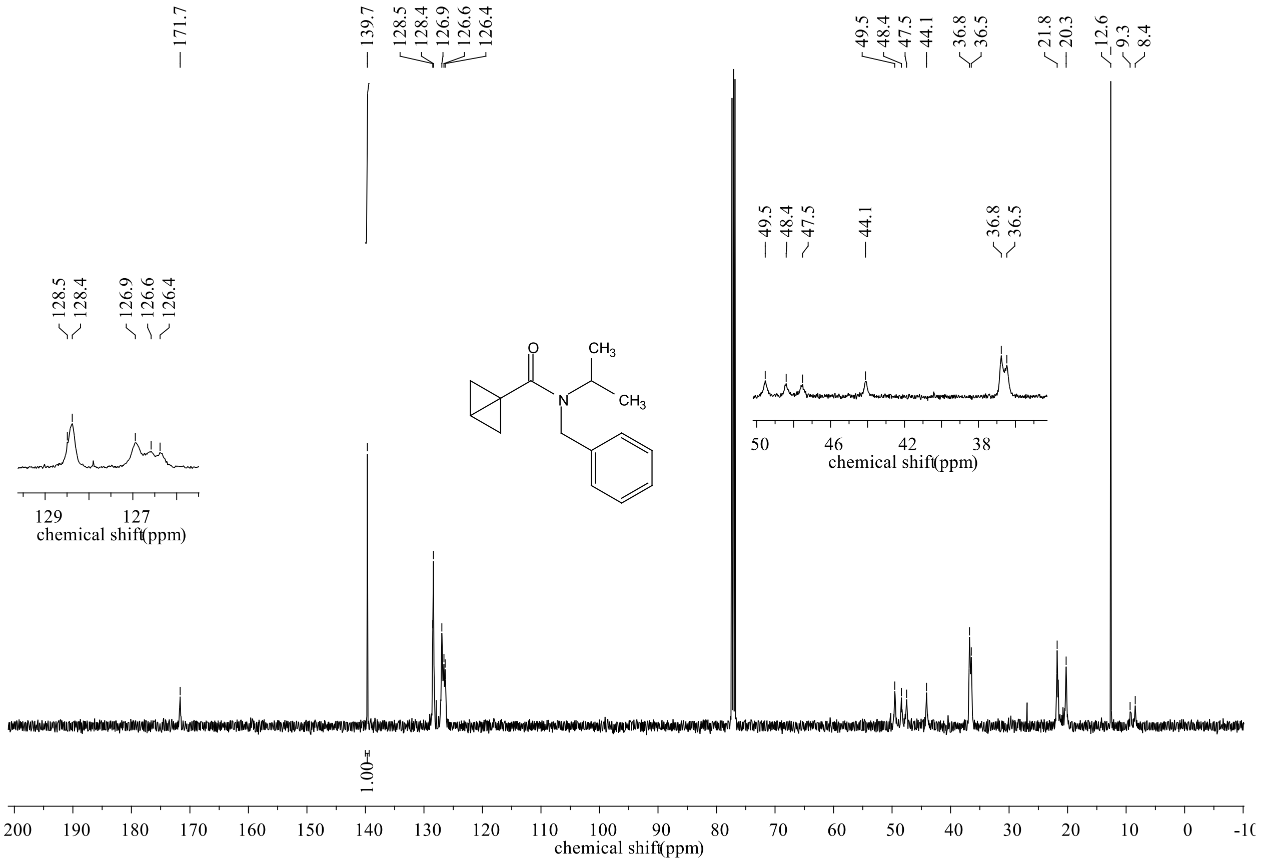
2b ^{13}C NMR (126 MHz, CDCl$_3$)



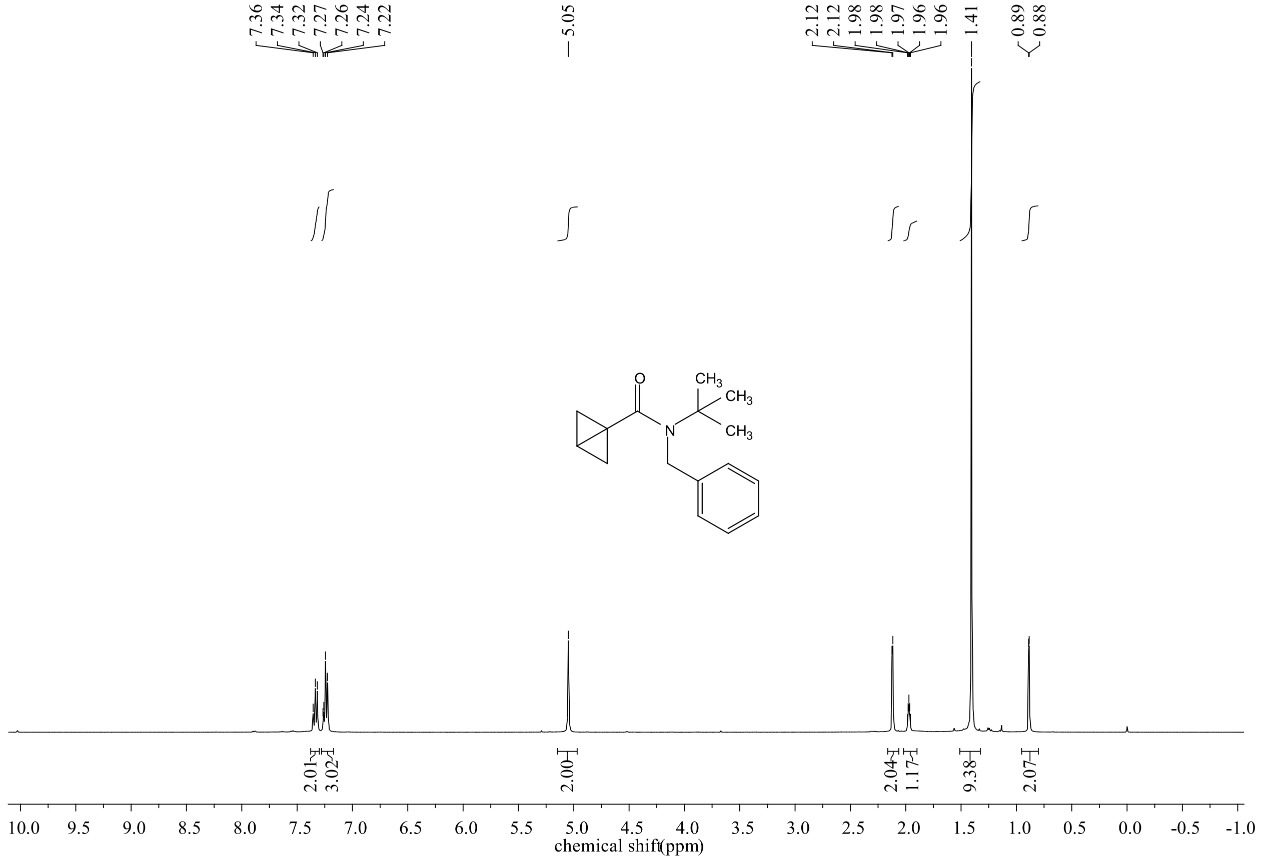
2c ^{1}H NMR (500 MHz, CDCl$_3$)



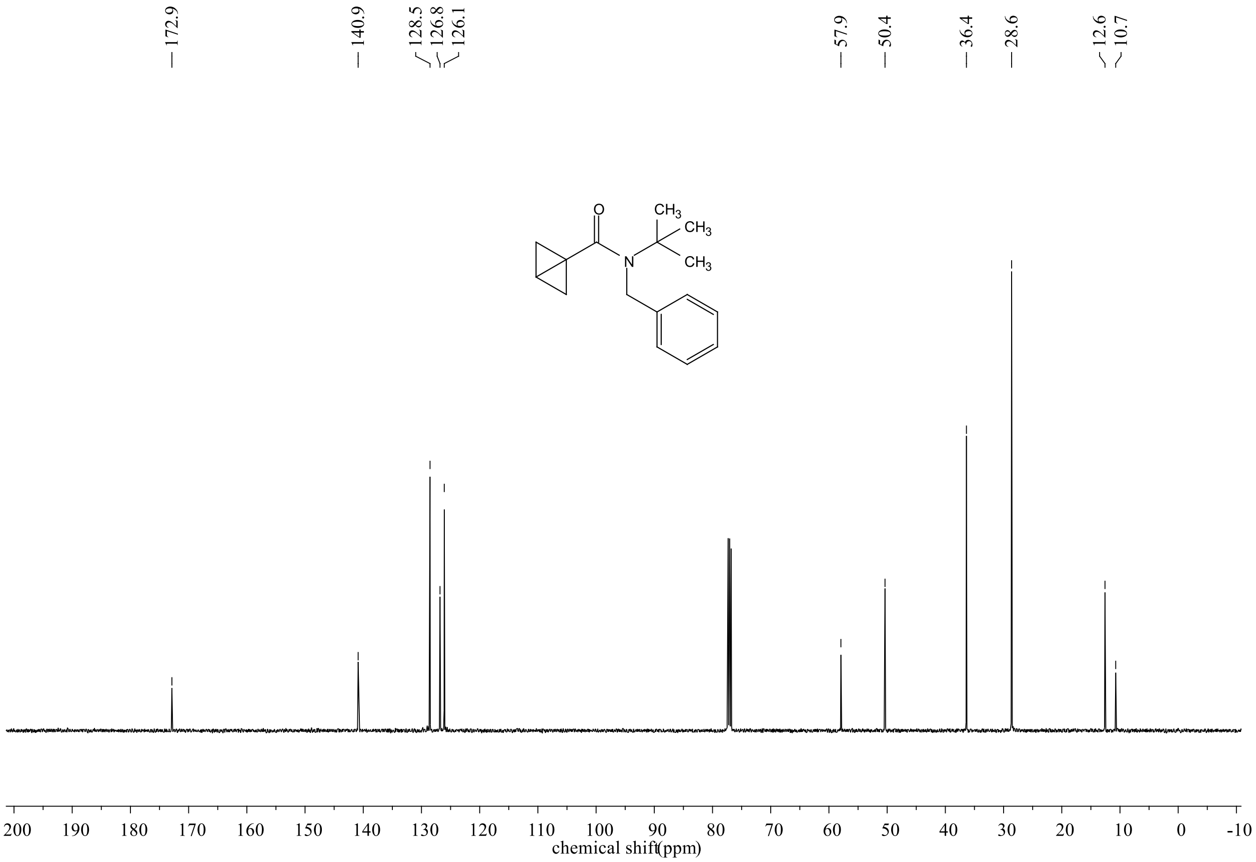
2c ^{13}C NMR (126 MHz, CDCl$_3$)



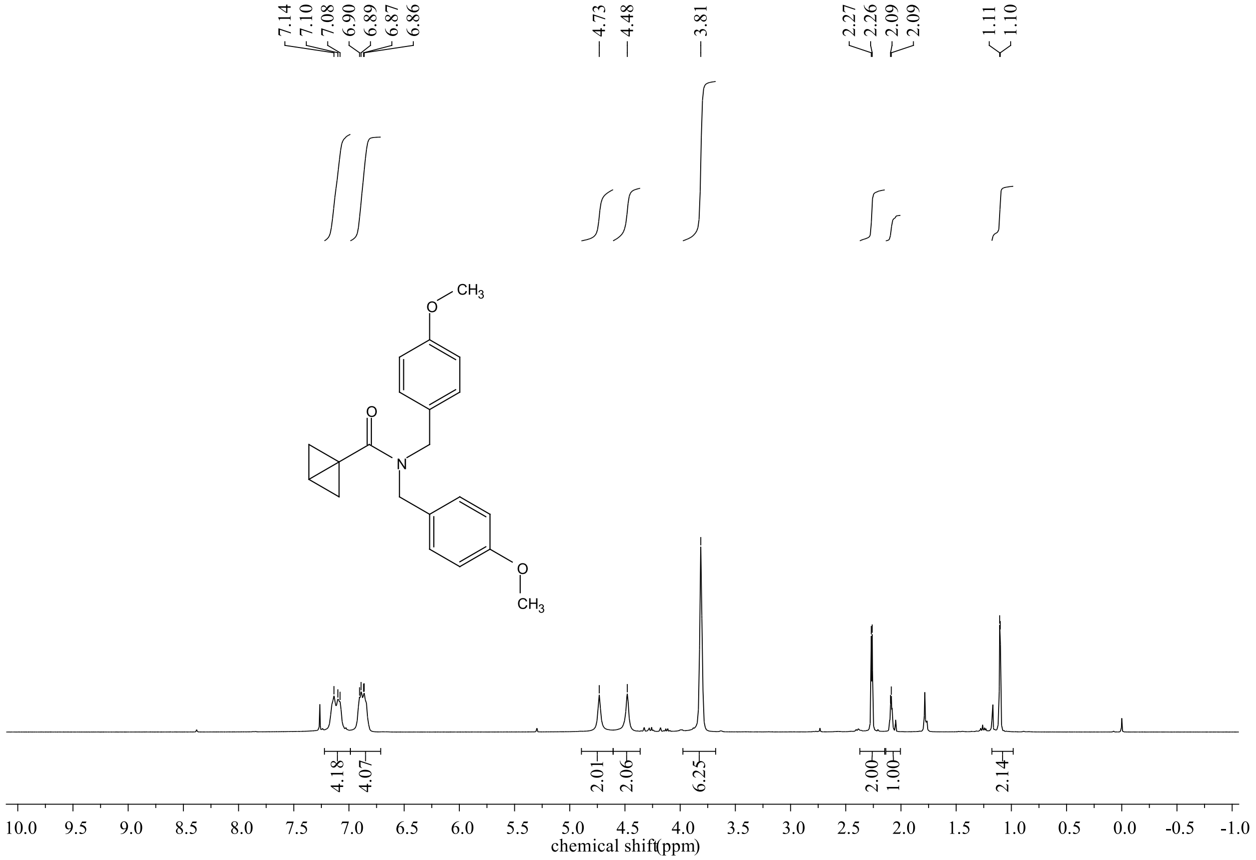
2d ^{1}H NMR (400 MHz, CDCl$_3$)



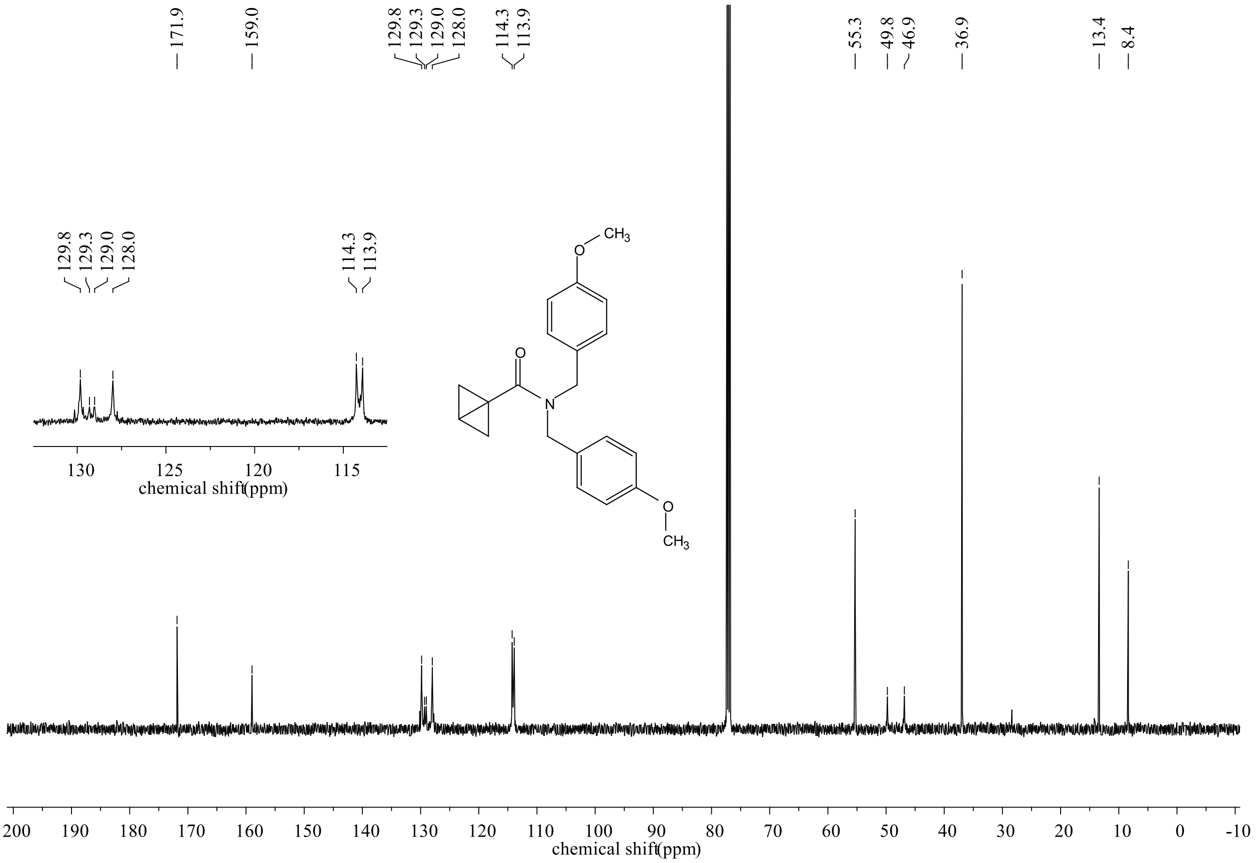
2d ^{13}C NMR (126 MHz, $CDCl_3$).



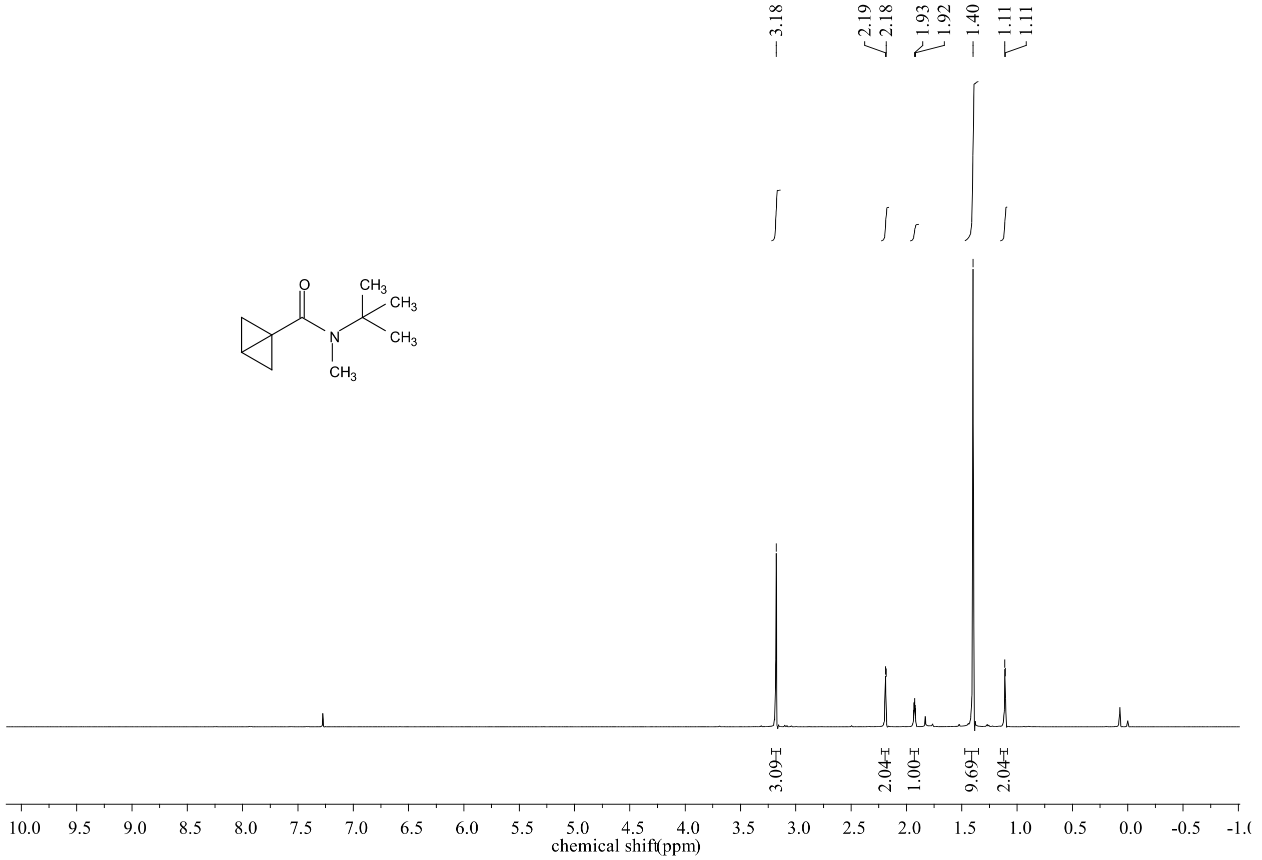
2e ^{1}H NMR (400 MHz, $CDCl_3$)



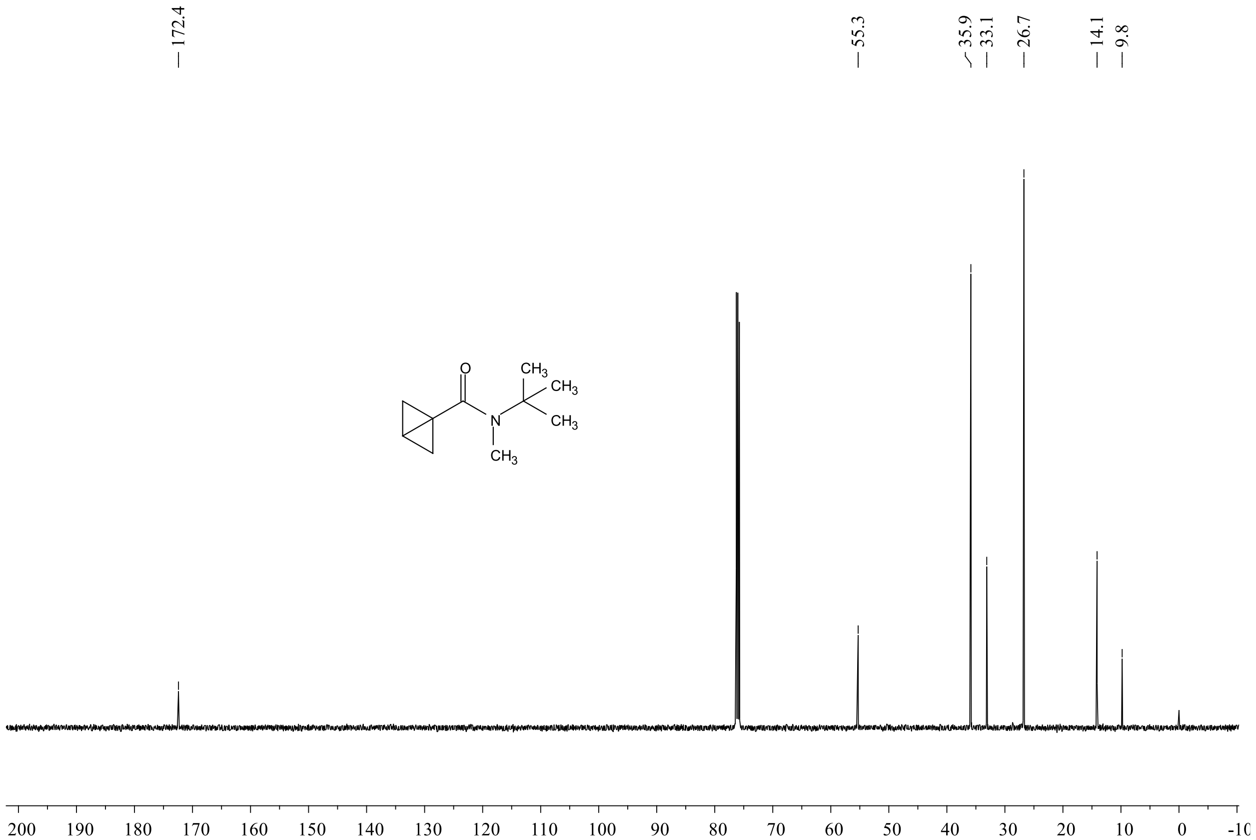
2e ^{13}C NMR (126 MHz, $CDCl_3$)



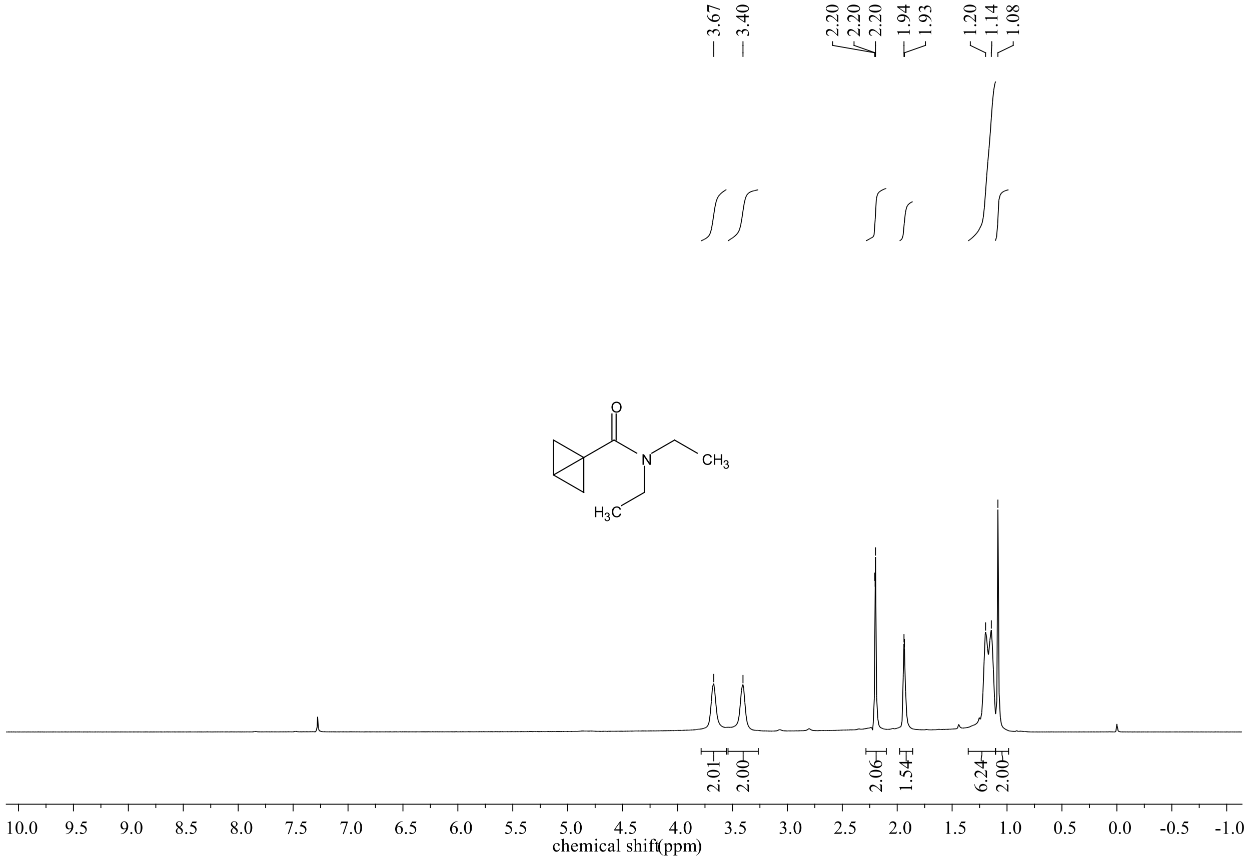
2f ^{1}H NMR (500 MHz, $CDCl_3$)



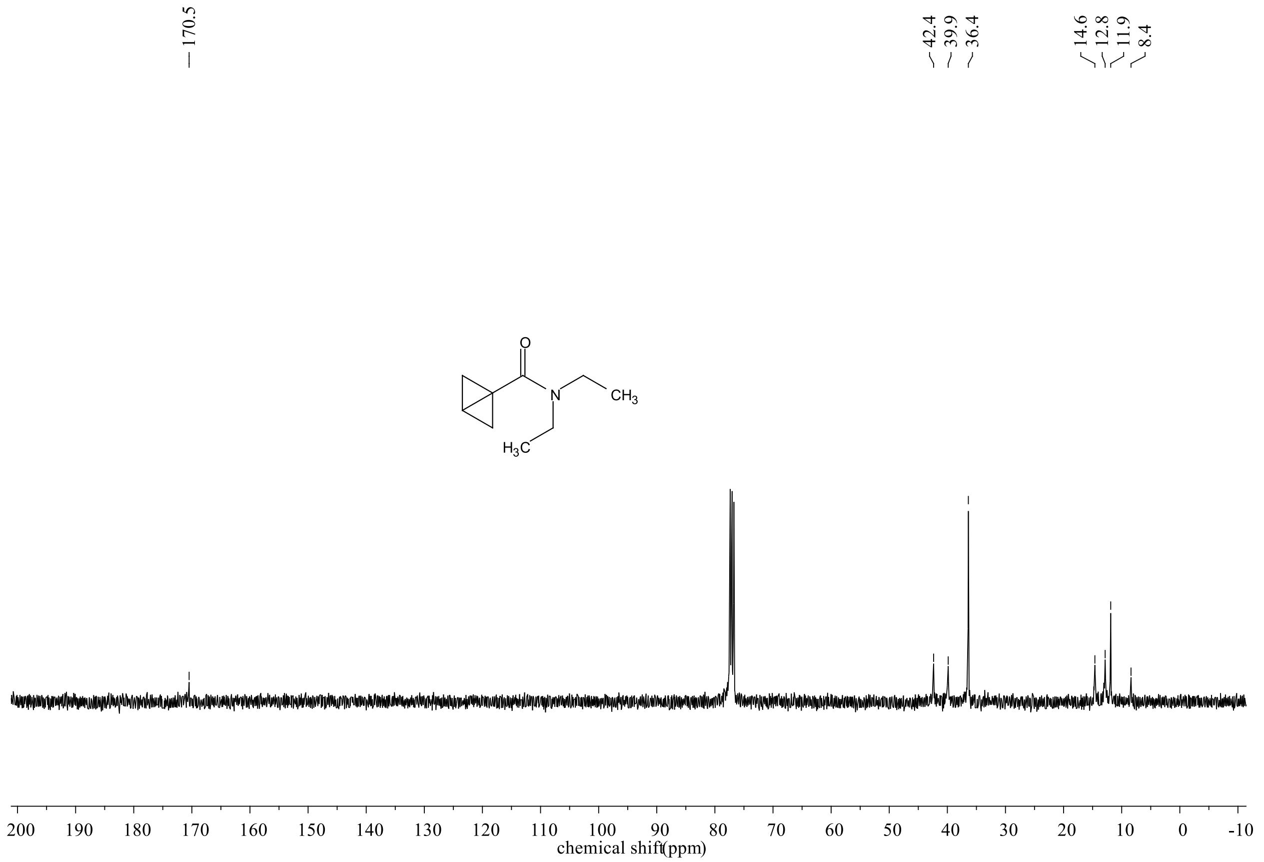
2f ^{13}C NMR (126 MHz, CDCl$_3$).



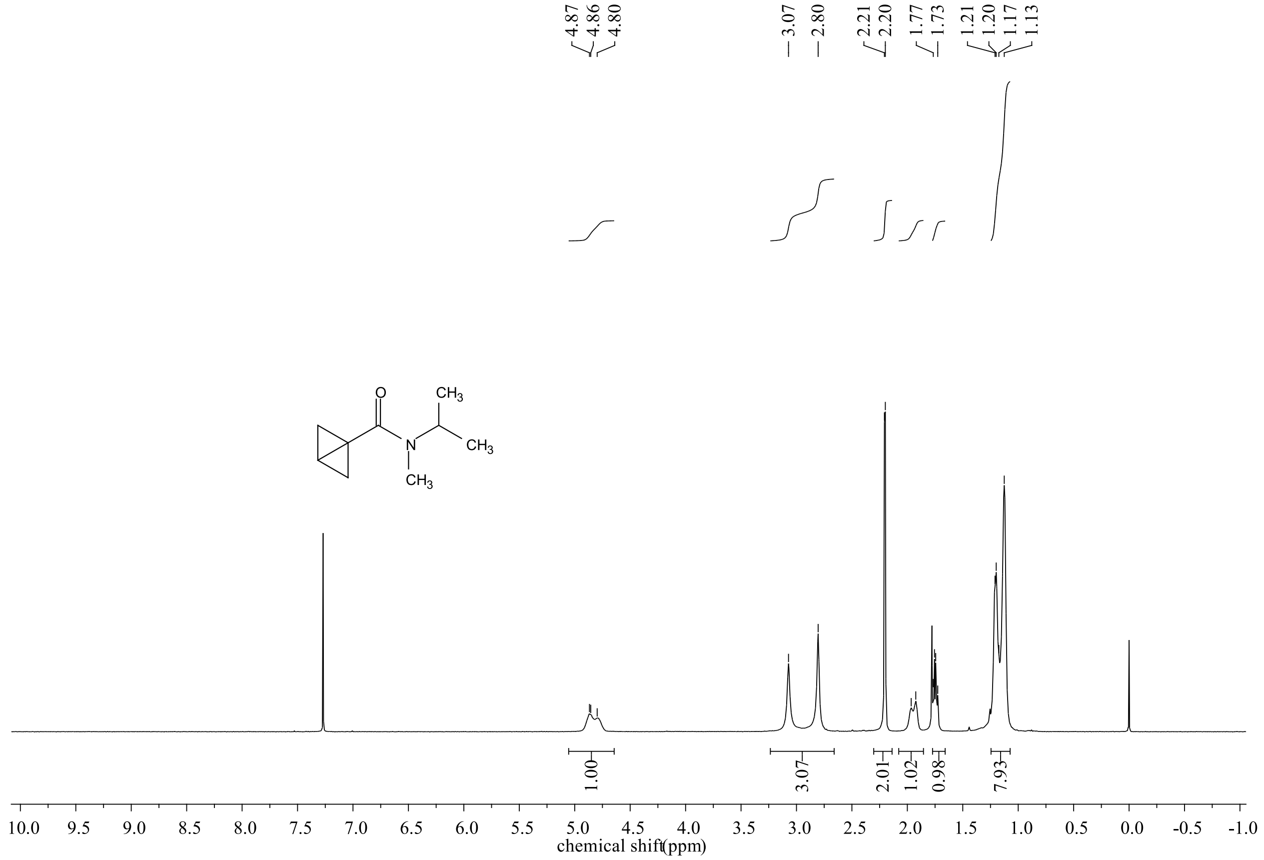
2g ^{1}H NMR (500 MHz, CDCl$_3$)



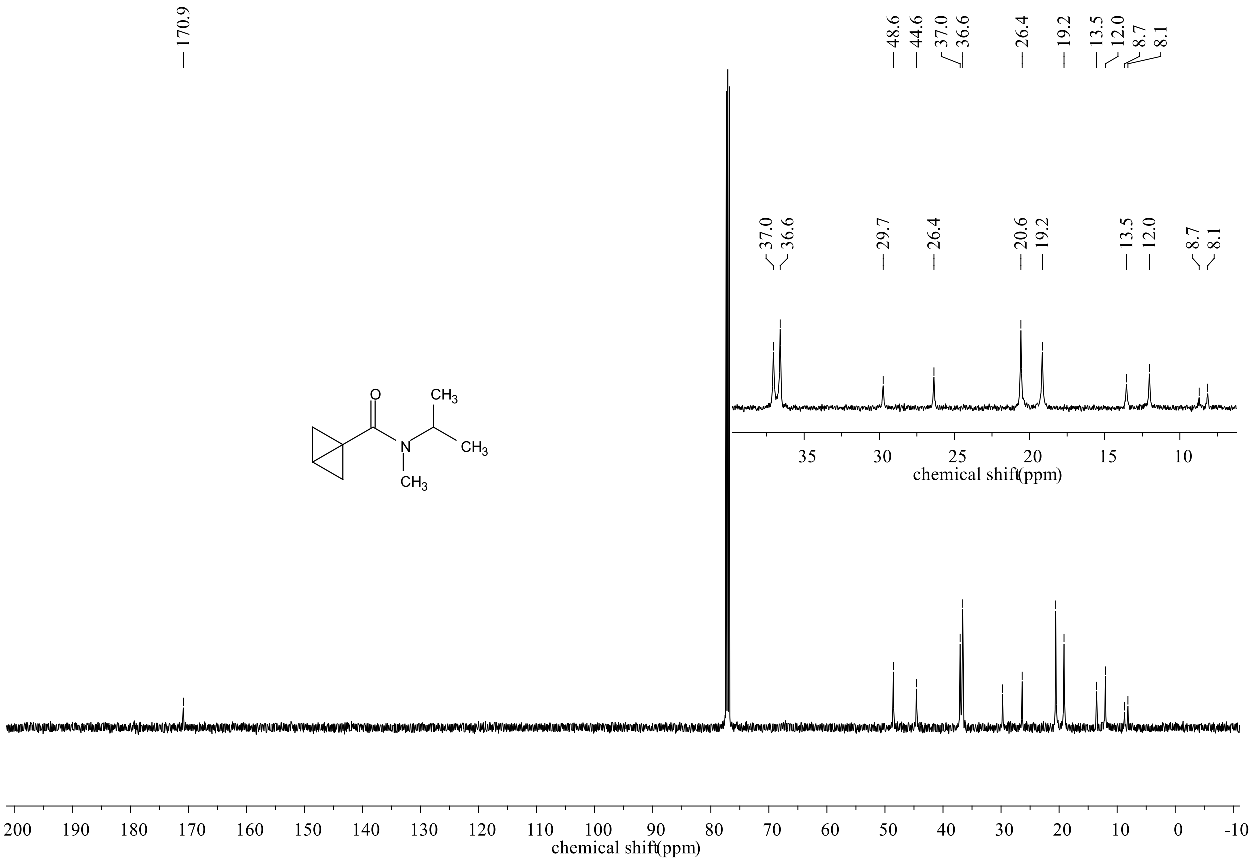
2g ^{13}C NMR (101 MHz, $CDCl_3$)



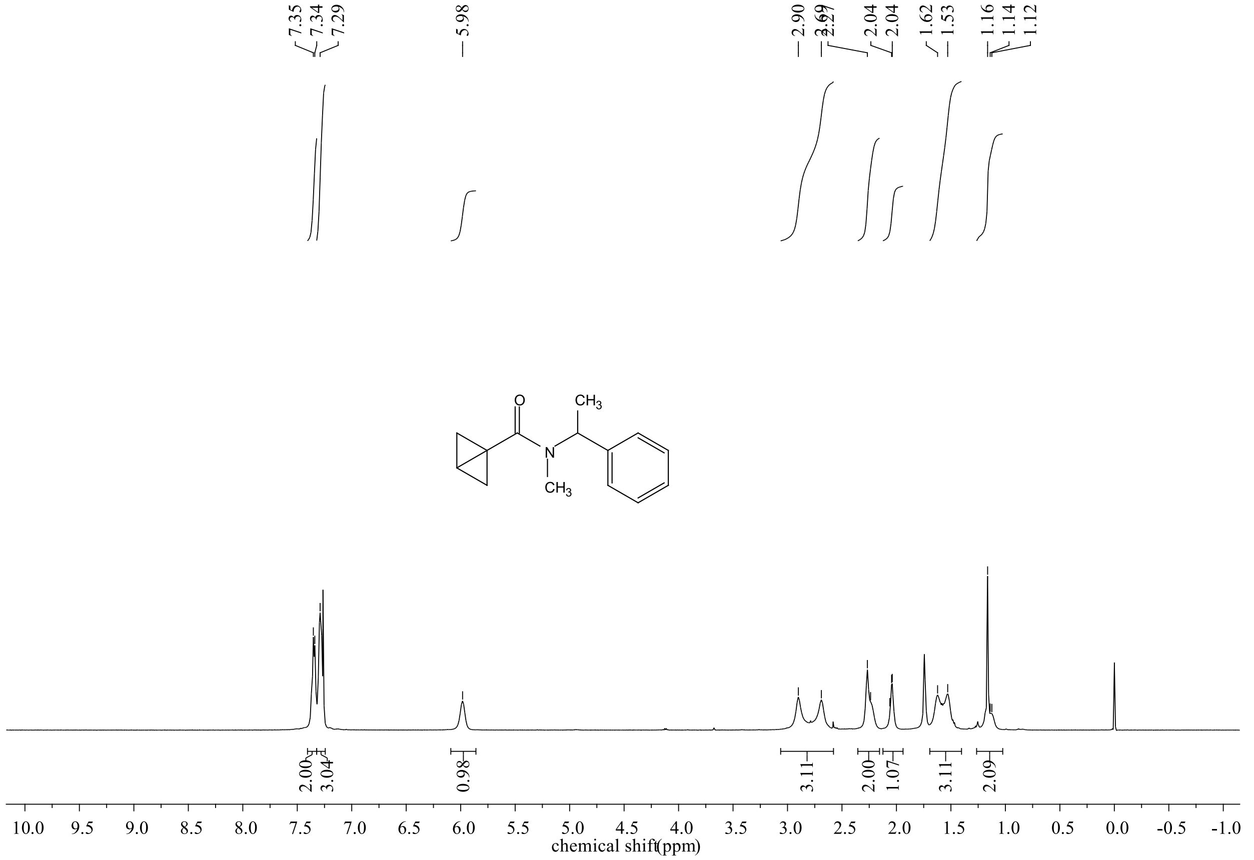
2h ^{1}H NMR (500 MHz, $CDCl_3$)



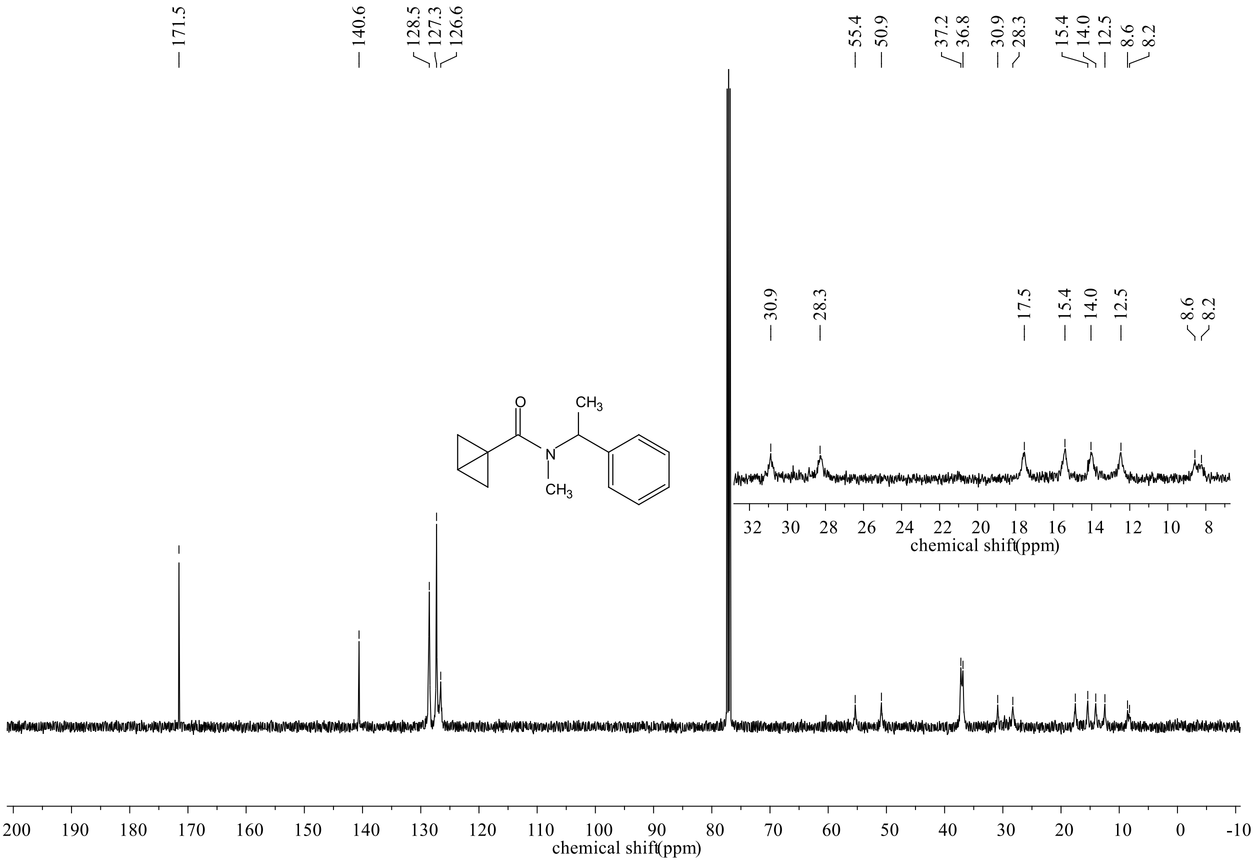
2h ^{13}C NMR (126 MHz, CDCl$_3$)



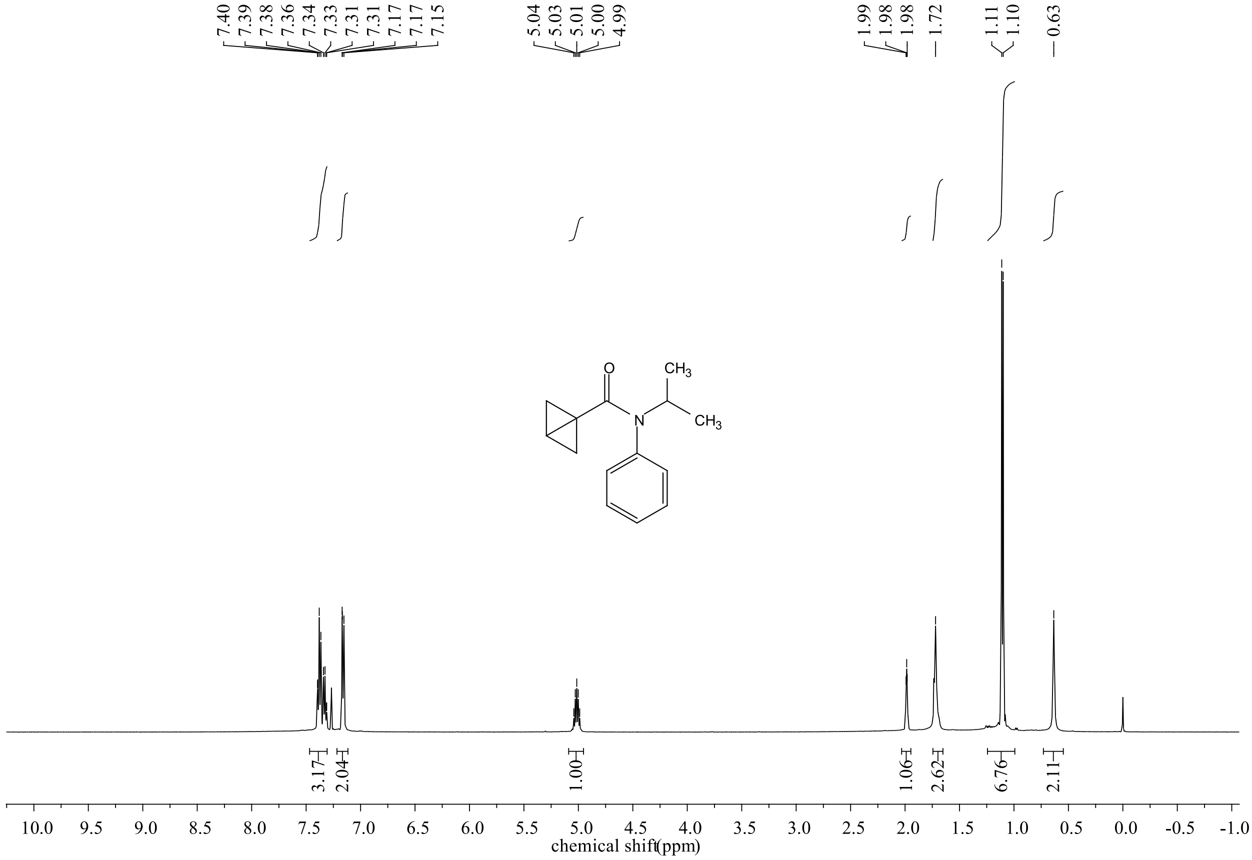
2i ^{1}H NMR (500 MHz, CDCl$_3$)



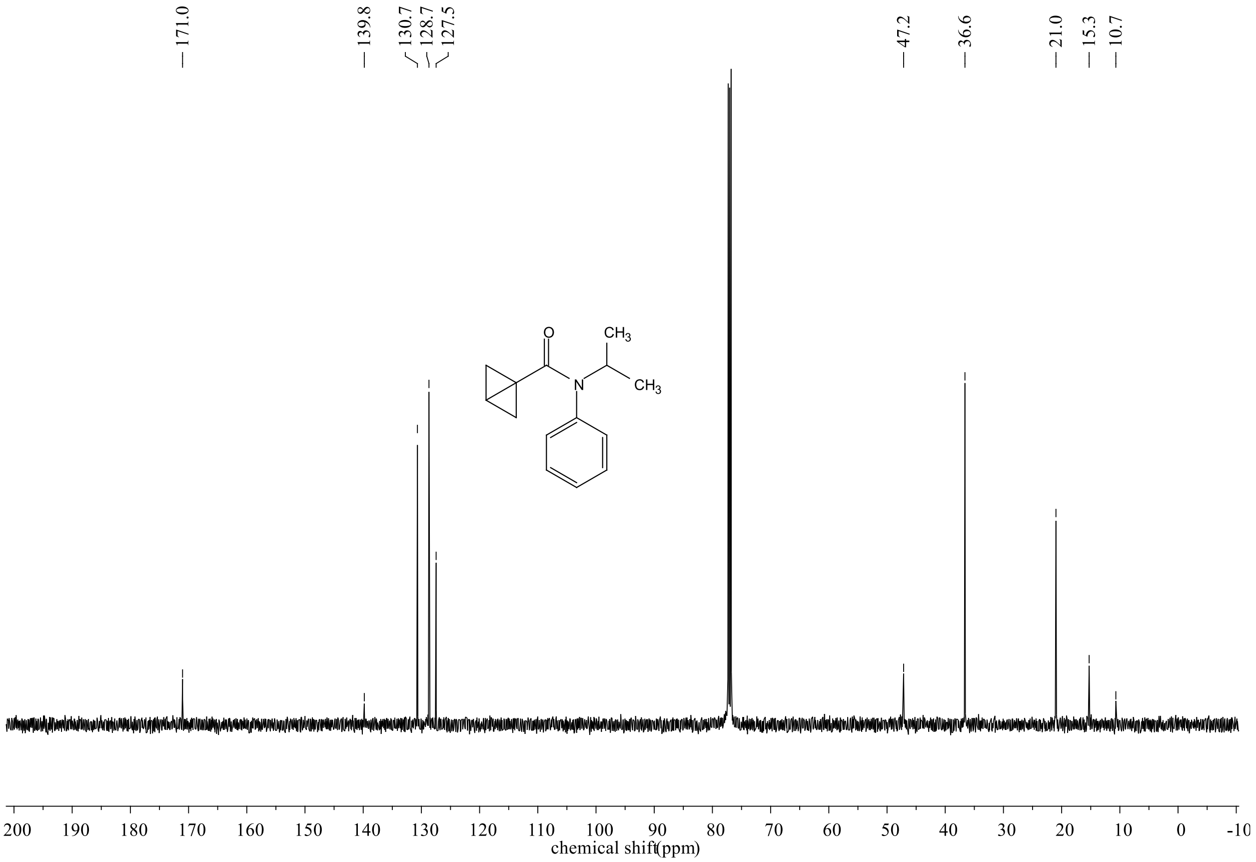
2i ^{13}C NMR (126 MHz, CDCl$_3$)



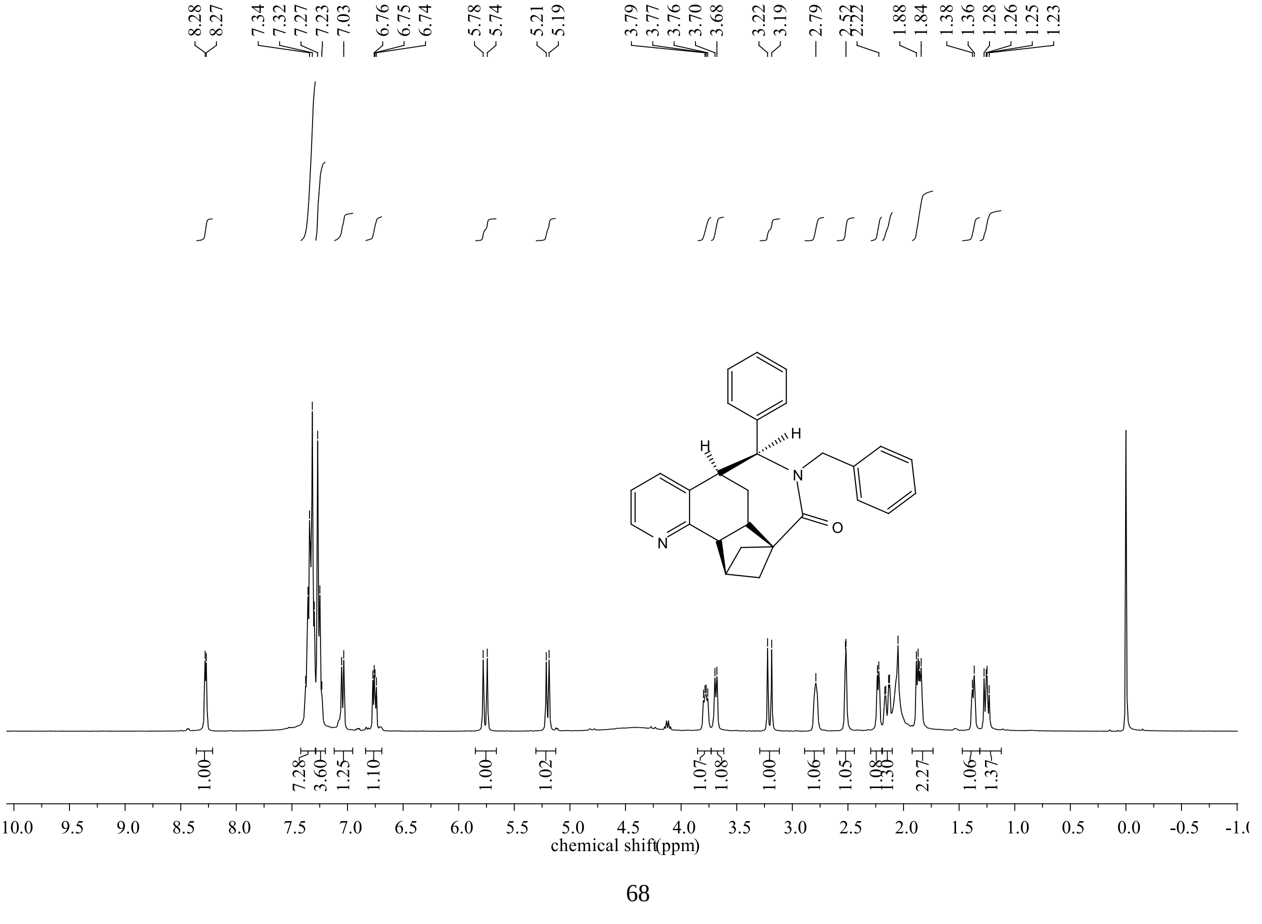
2j ^{1}H NMR (400 MHz, CDCl$_3$)



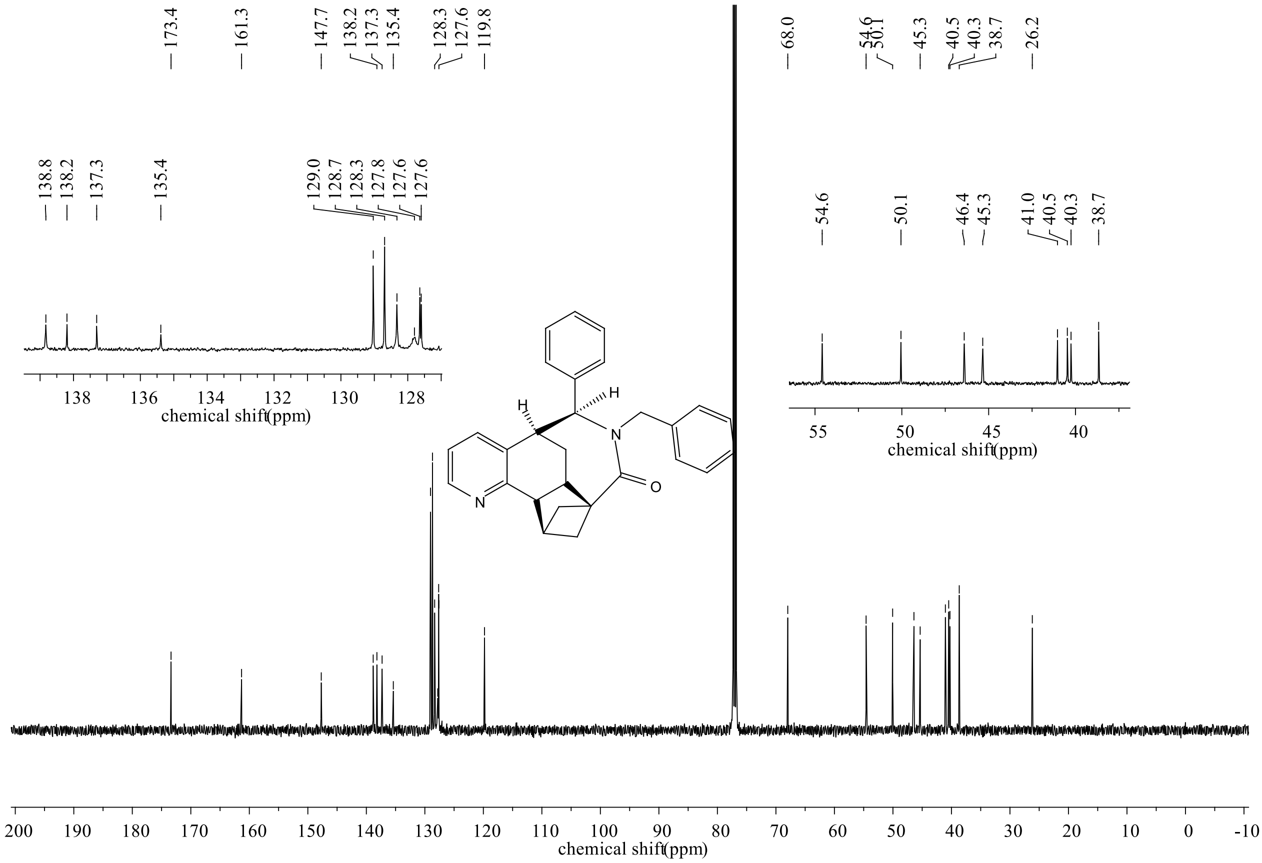
2j ^{13}C NMR (126 MHz, $CDCl_3$)



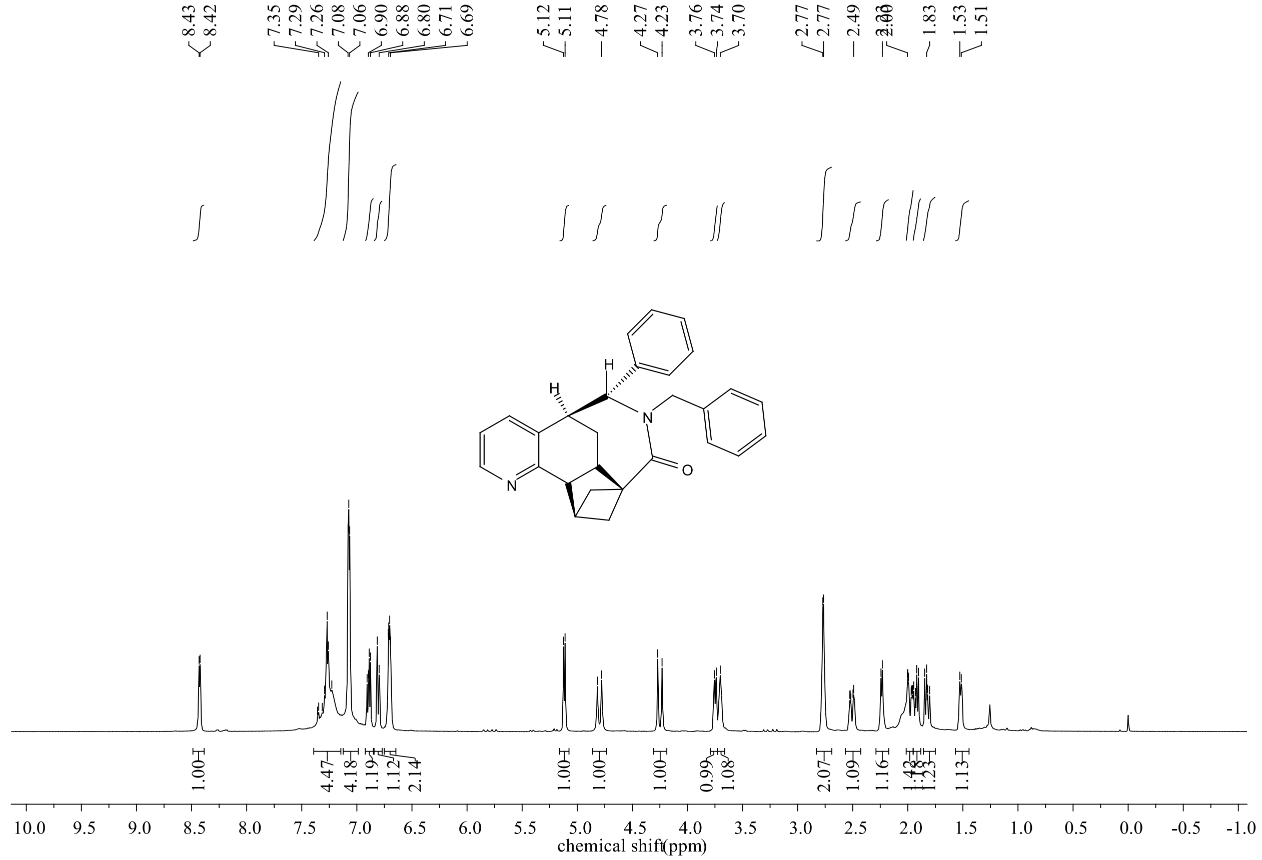
cis-**4A** ^{1}H NMR (400 MHz, $CDCl_3$)



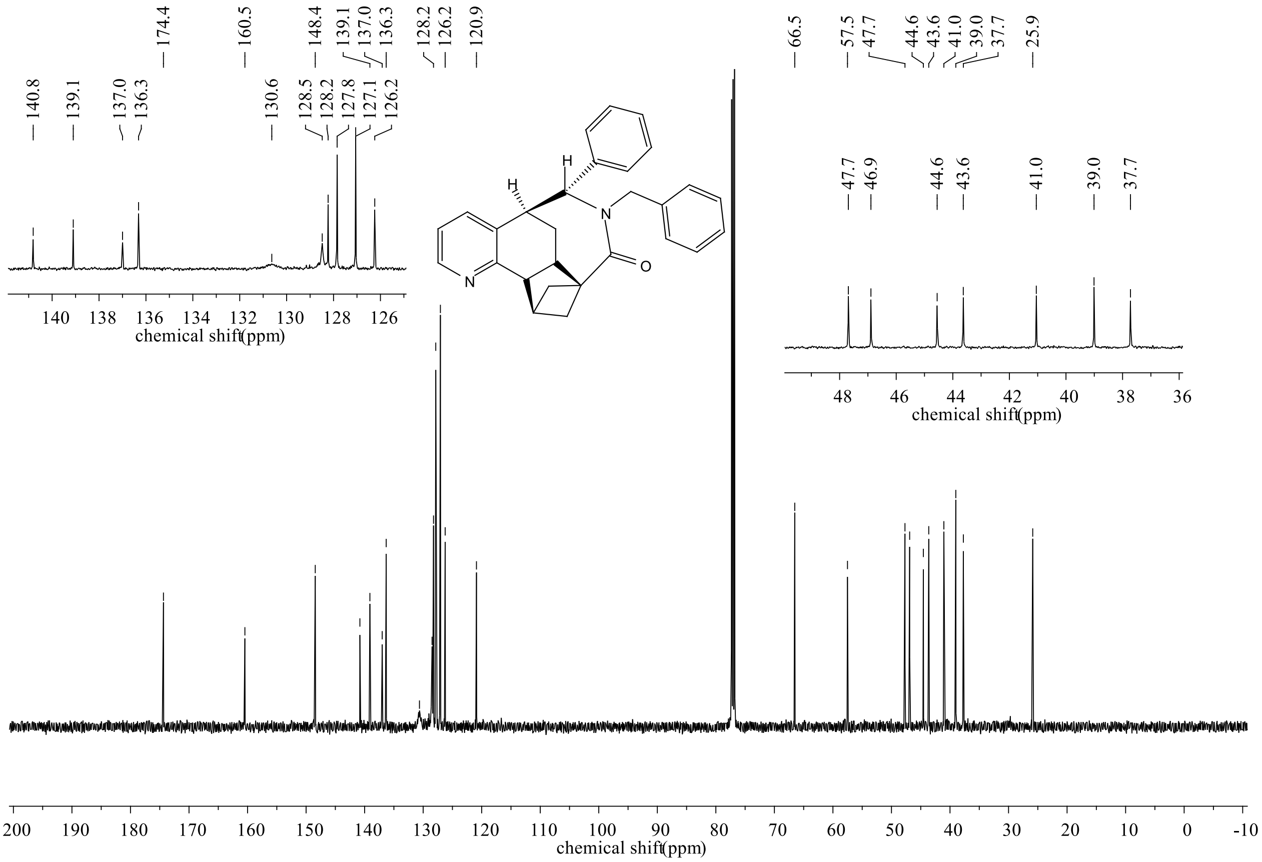
cis-**4A** ^{13}C NMR (101 MHz, CDCl$_3$)



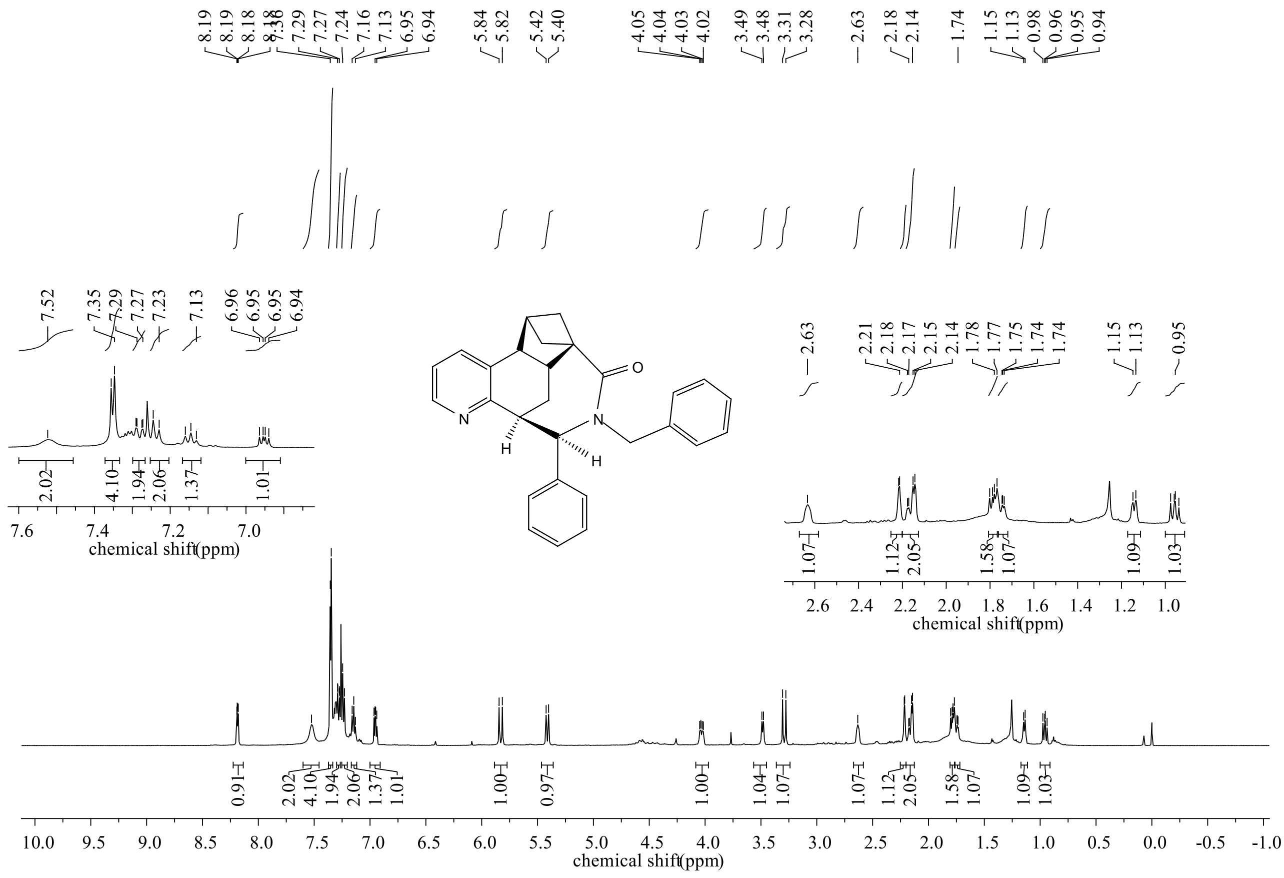
trans-**4A** ^{1}H NMR (400 MHz, CDCl$_3$)



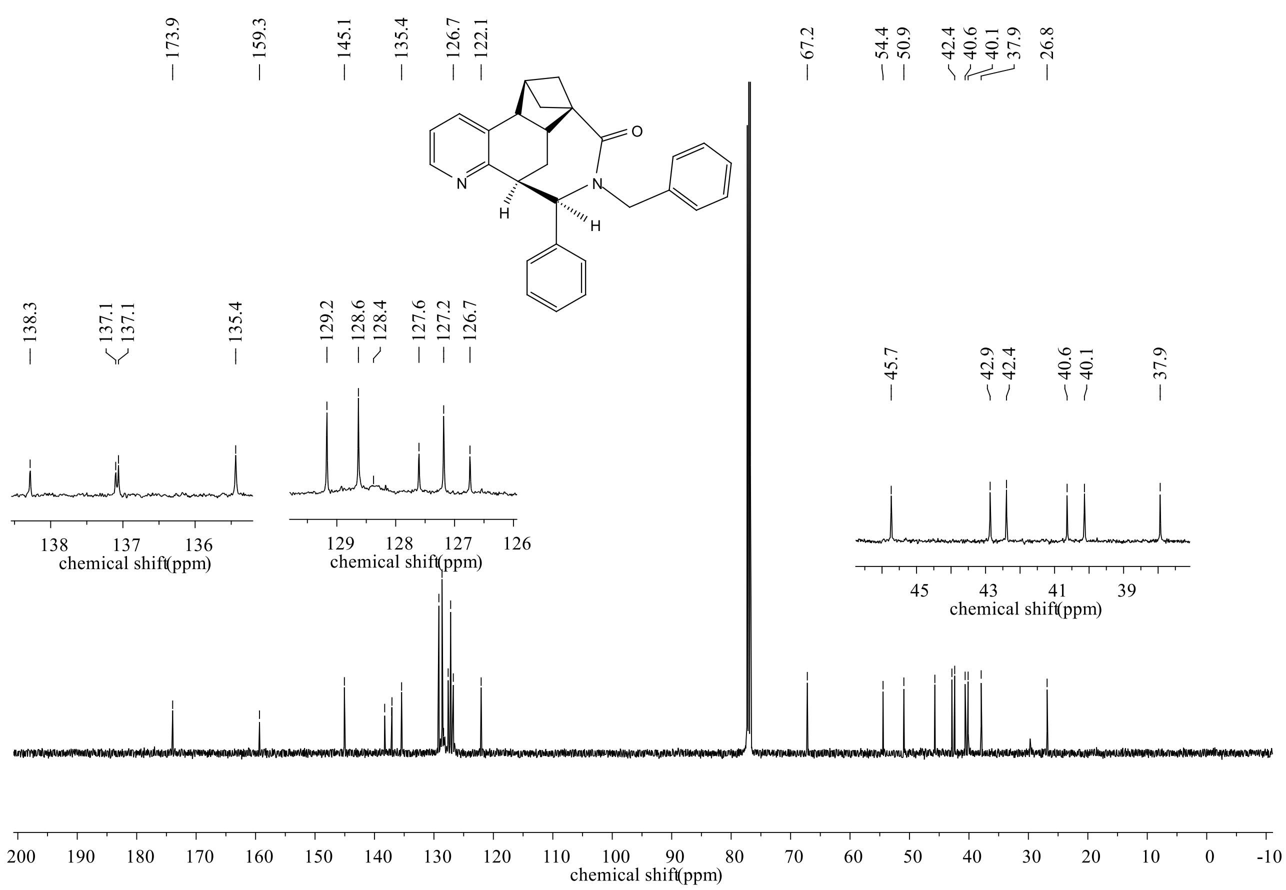
trans-**4A** ^{13}C NMR (126 MHz, CDCl$_3$)



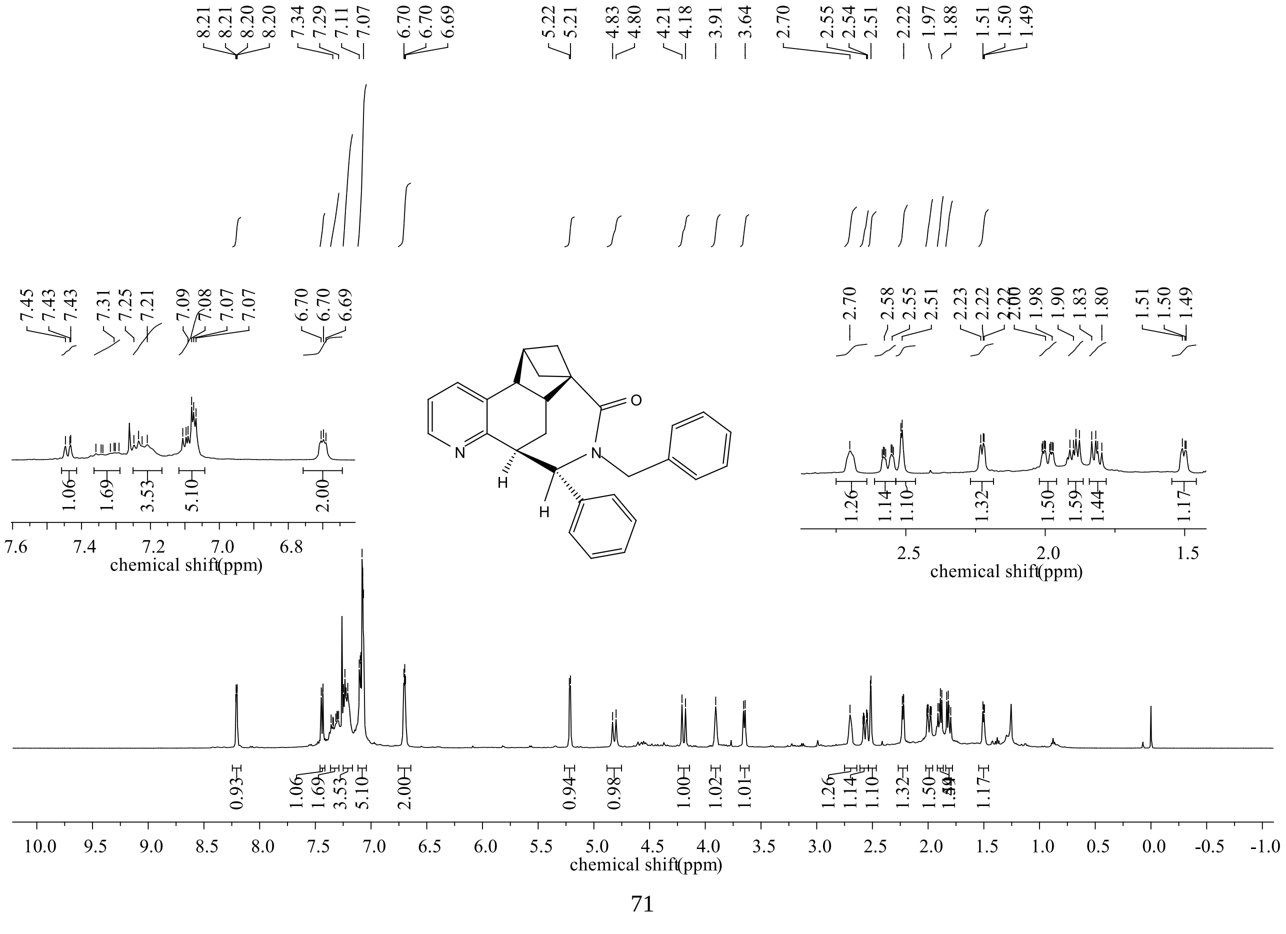
cis-**4a** ^{1}H NMR (500 MHz, CDCl$_3$)



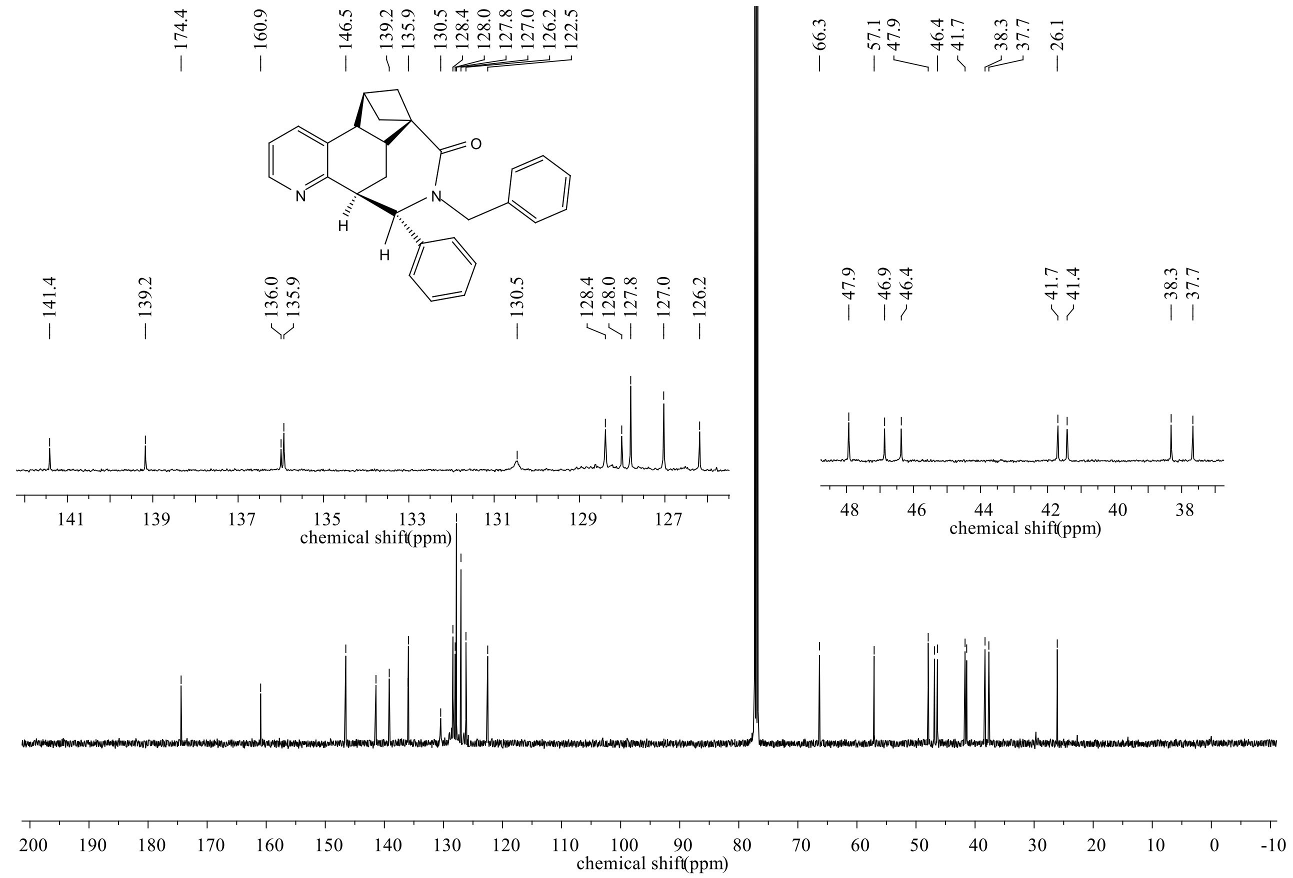
cis-**4a** ^{13}C NMR (126 MHz, $CDCl_3$)



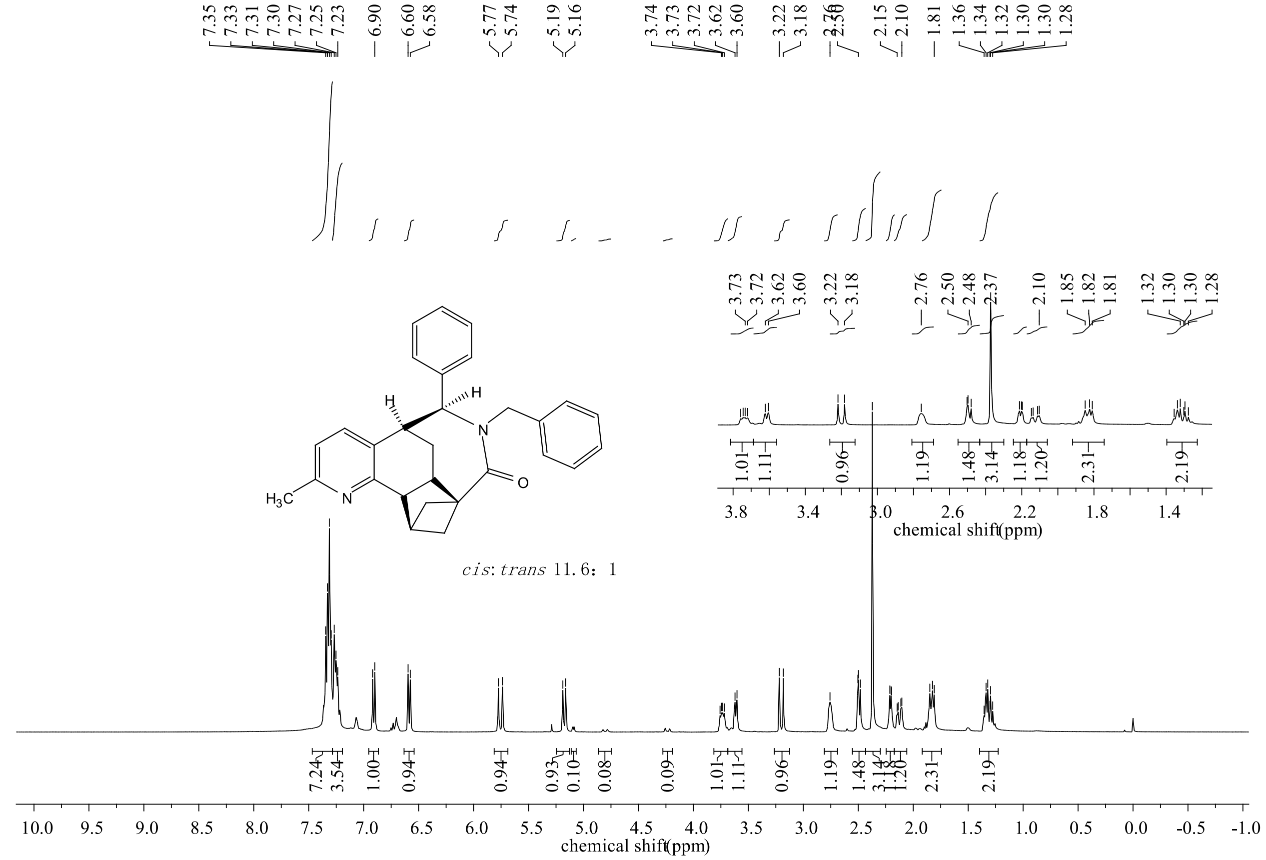
trans-**4a** ^{1}H NMR (500 MHz, $CDCl_3$)



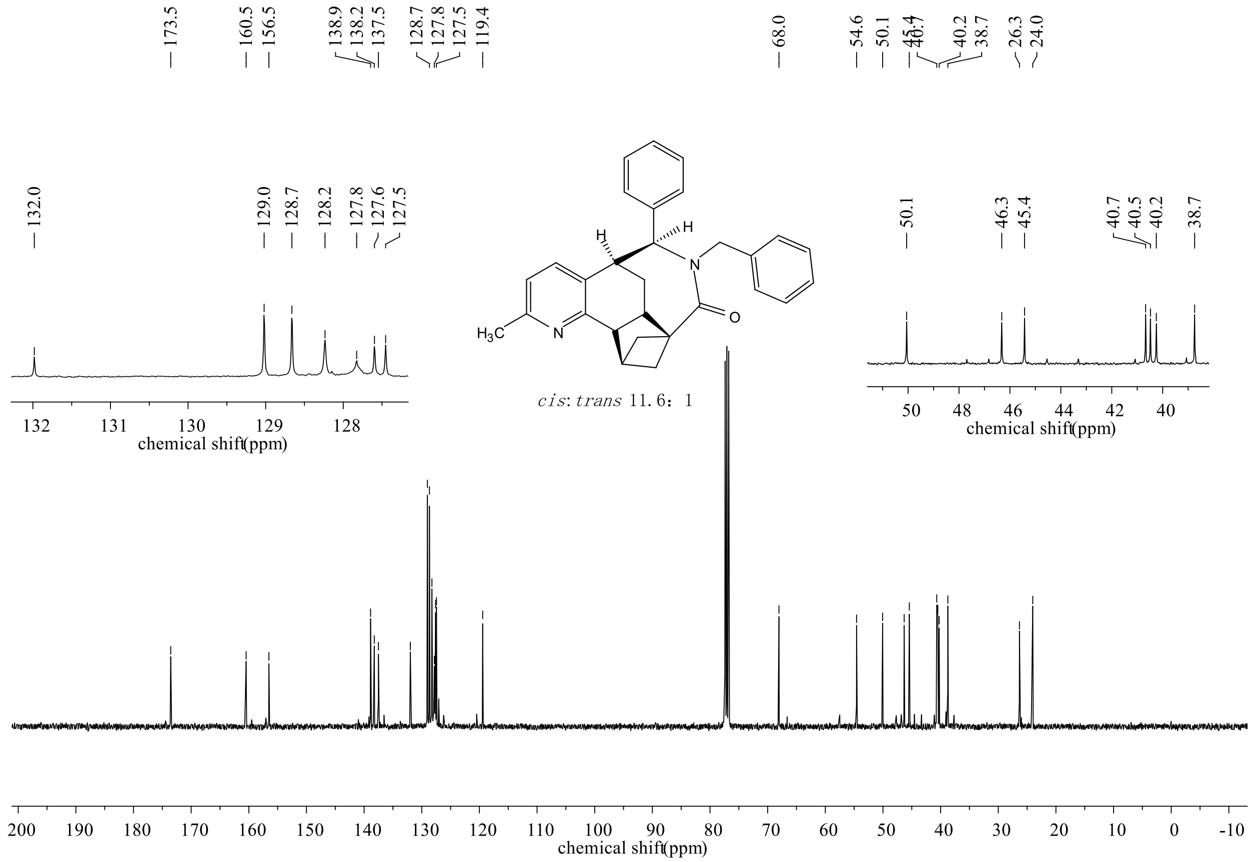
trans-**4a** ^{13}C NMR (126 MHz, CDCl$_3$)



cis-**4B** ^{1}H NMR (400 MHz, CDCl$_3$)

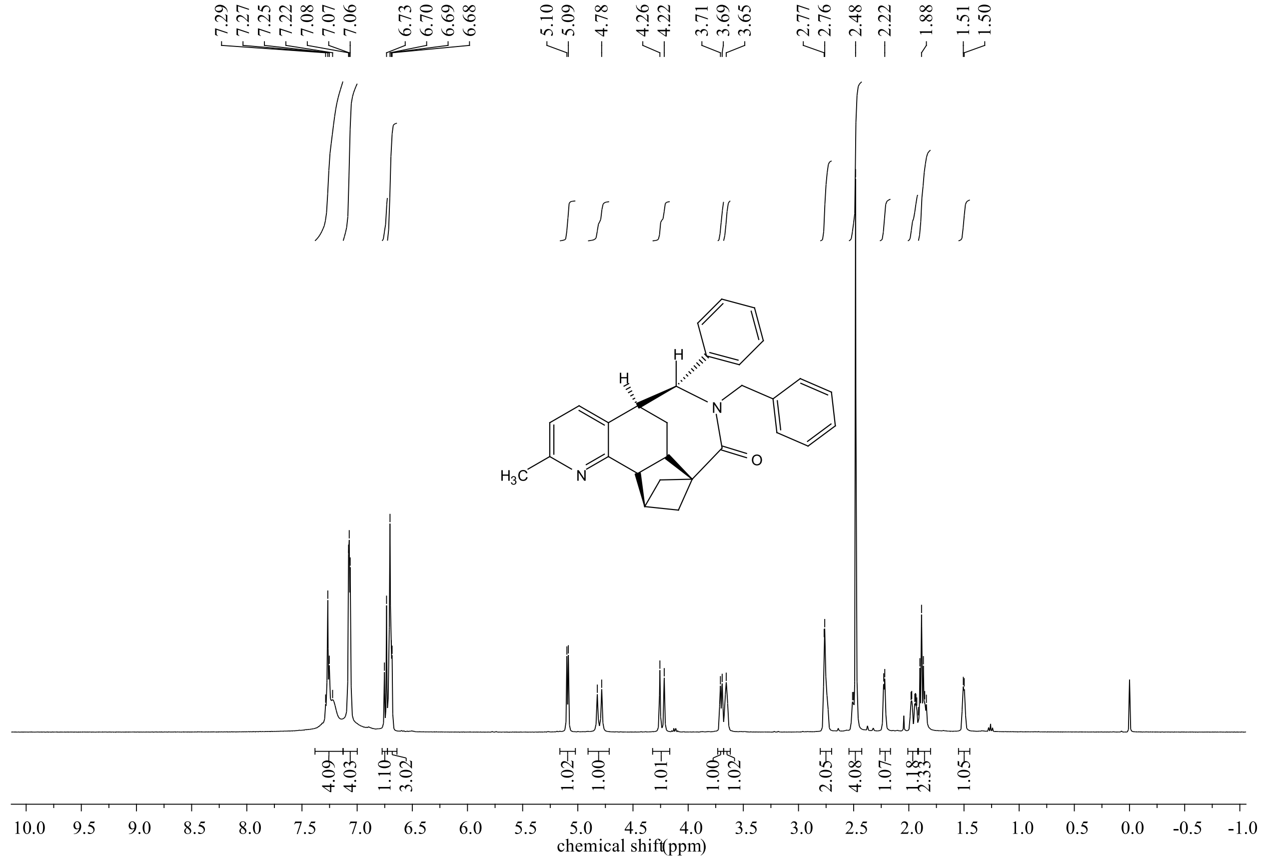


cis-**4B** ^{13}C NMR (101 MHz, CDCl$_3$)

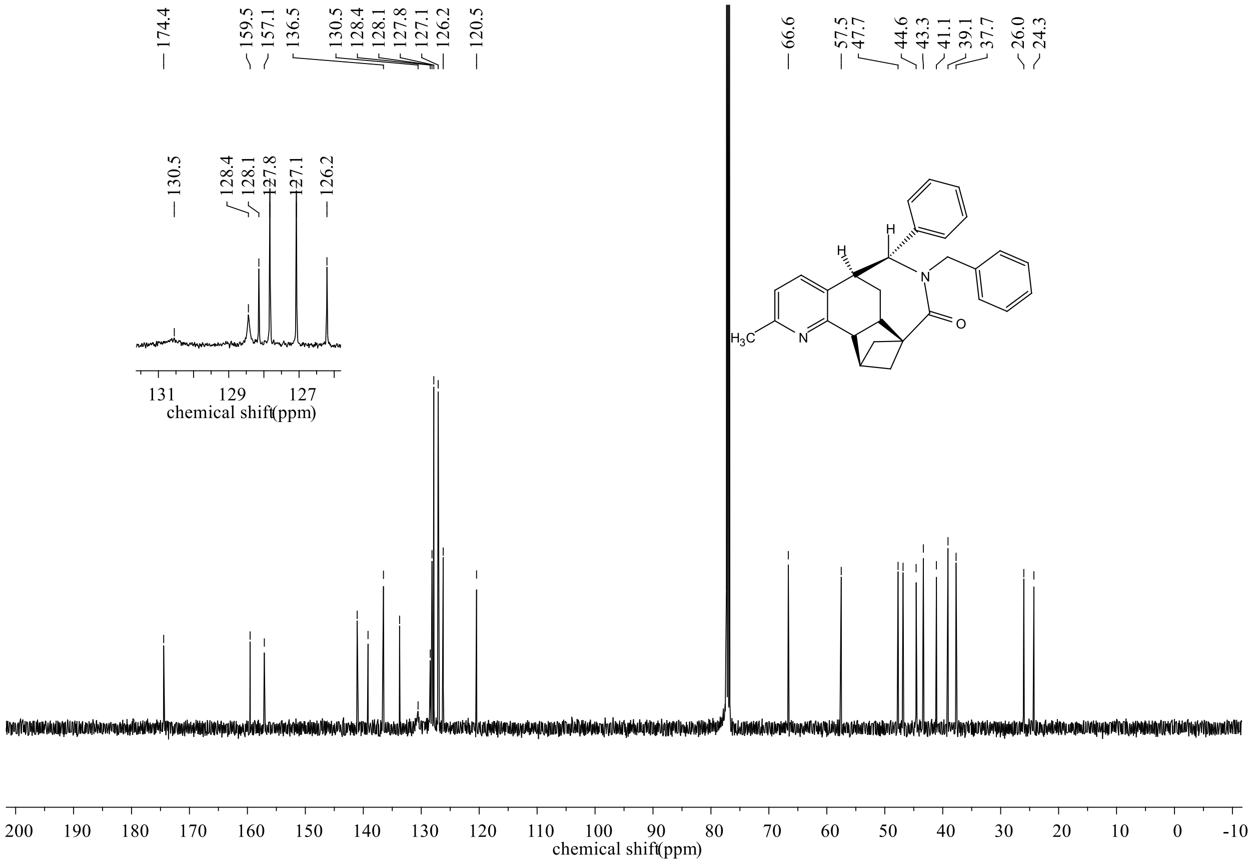


cis: *trans* 11.6：1

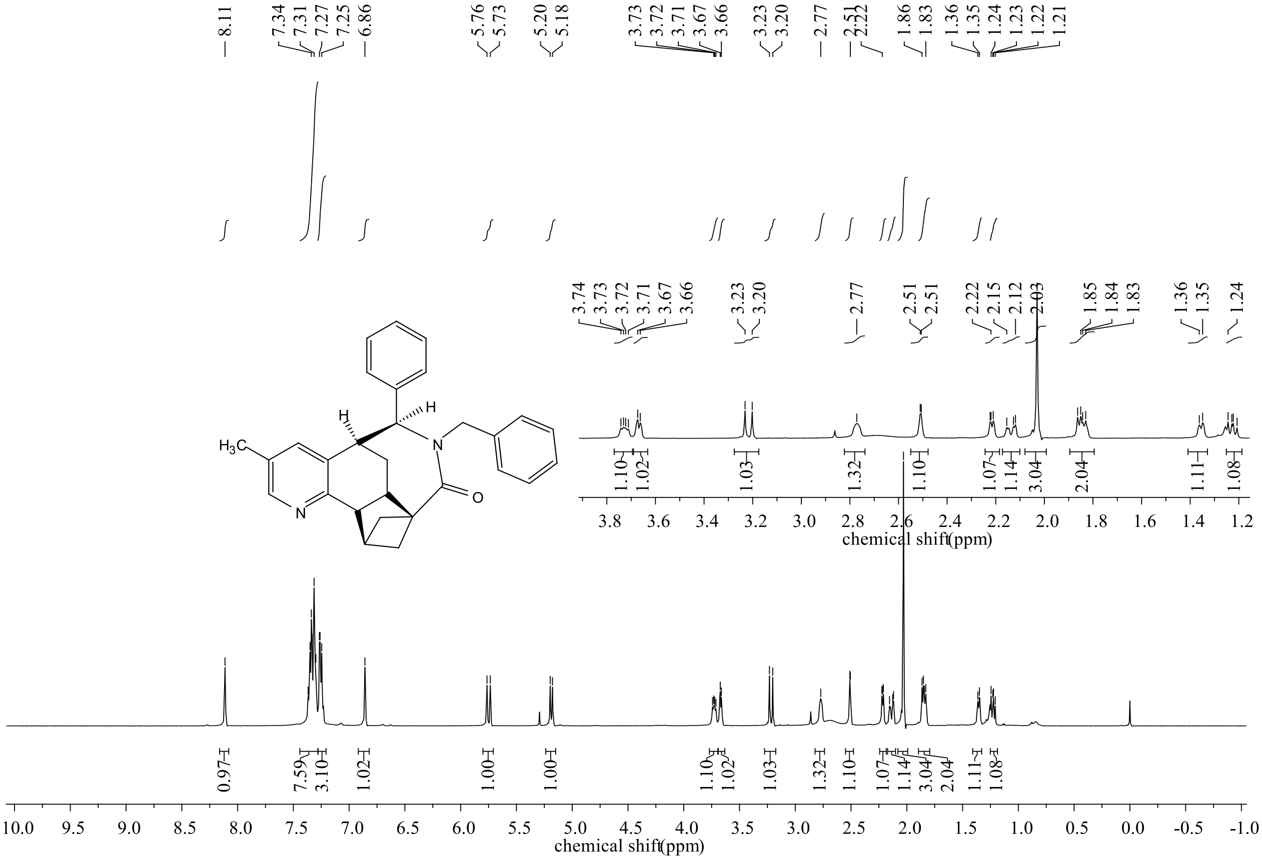
trans-**4B** ^{1}H NMR (400 MHz, CDCl$_3$)



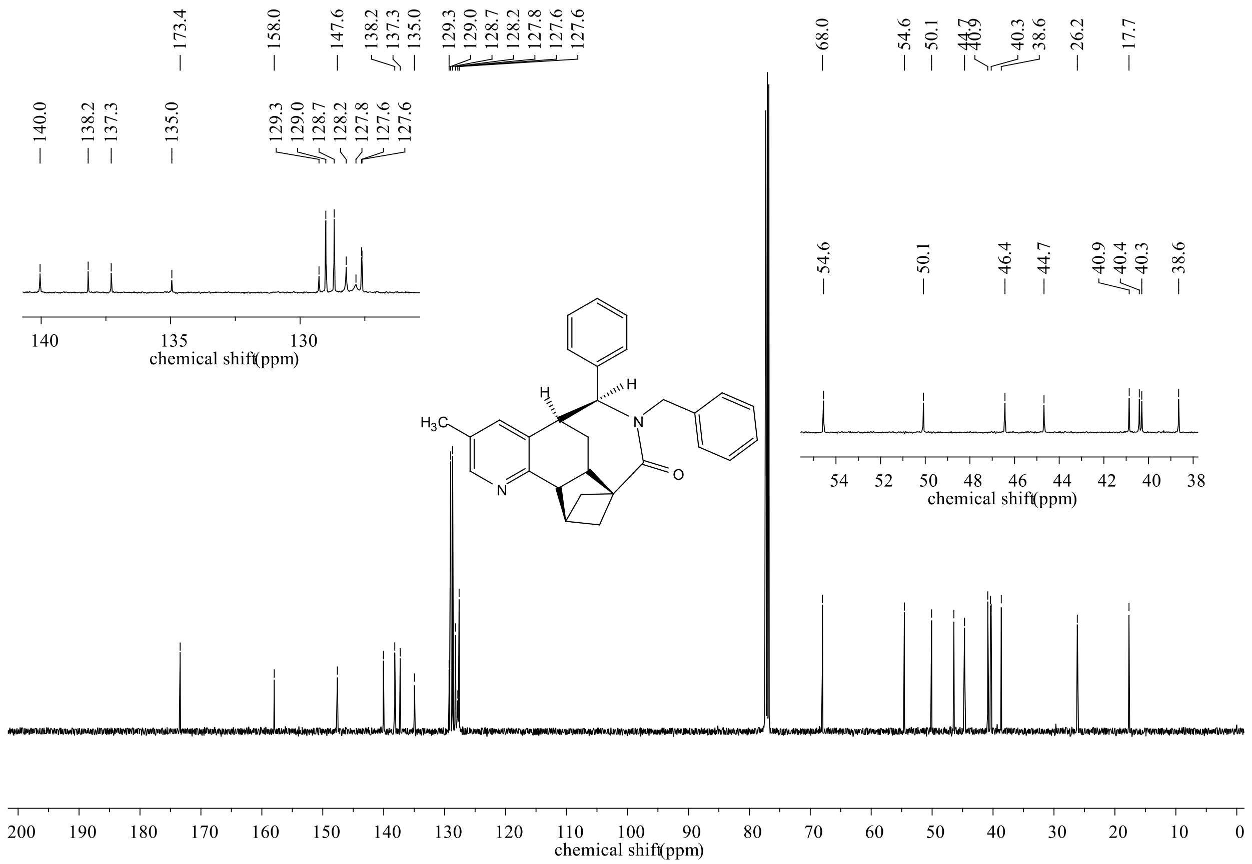
trans-**4B** ^{13}C NMR (126 MHz, CDCl$_3$)



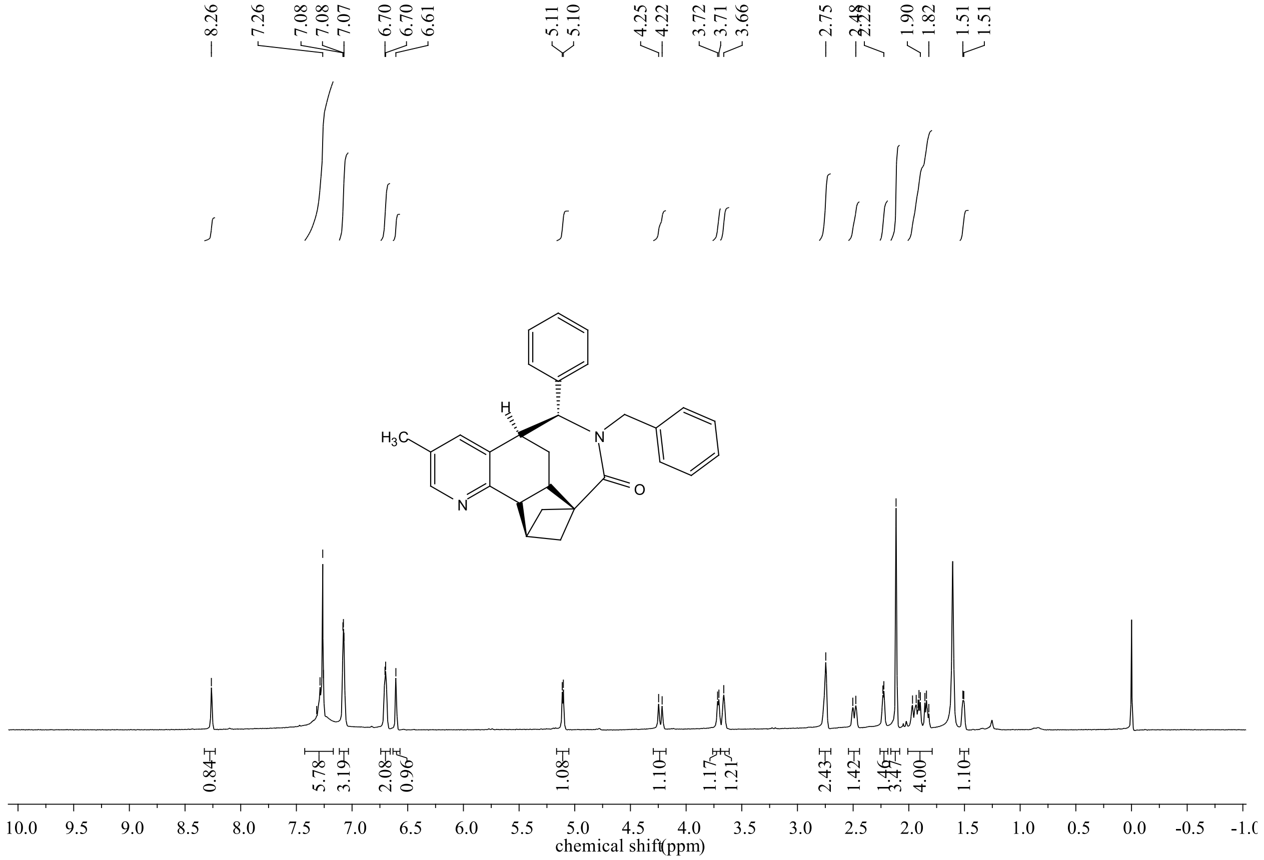
cis-**4C** ^{1}H NMR (500 MHz, CDCl$_3$)



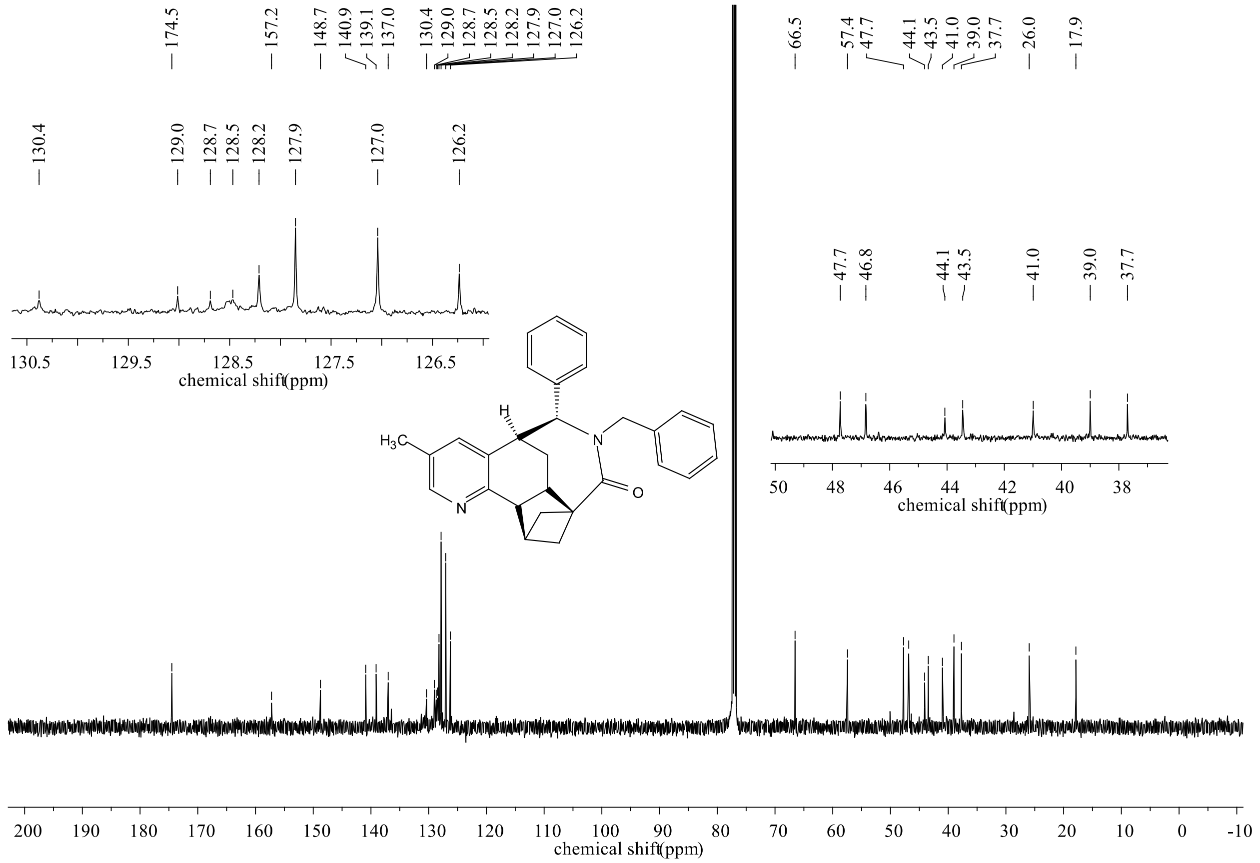
cis-**4C** ^{13}C NMR (126 MHz, CDCl$_3$)



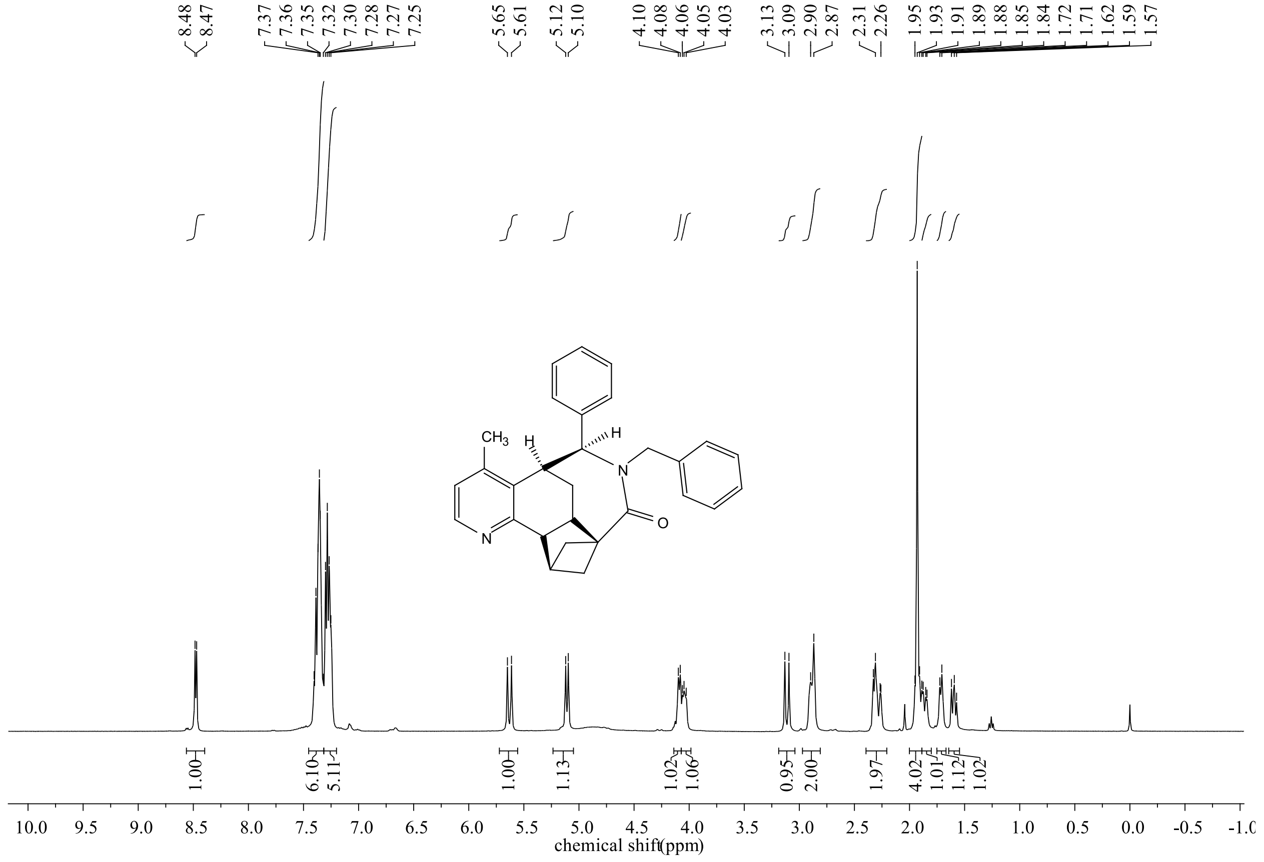
trans-**4C** ^{1}H NMR (500 MHz, CDCl$_3$)



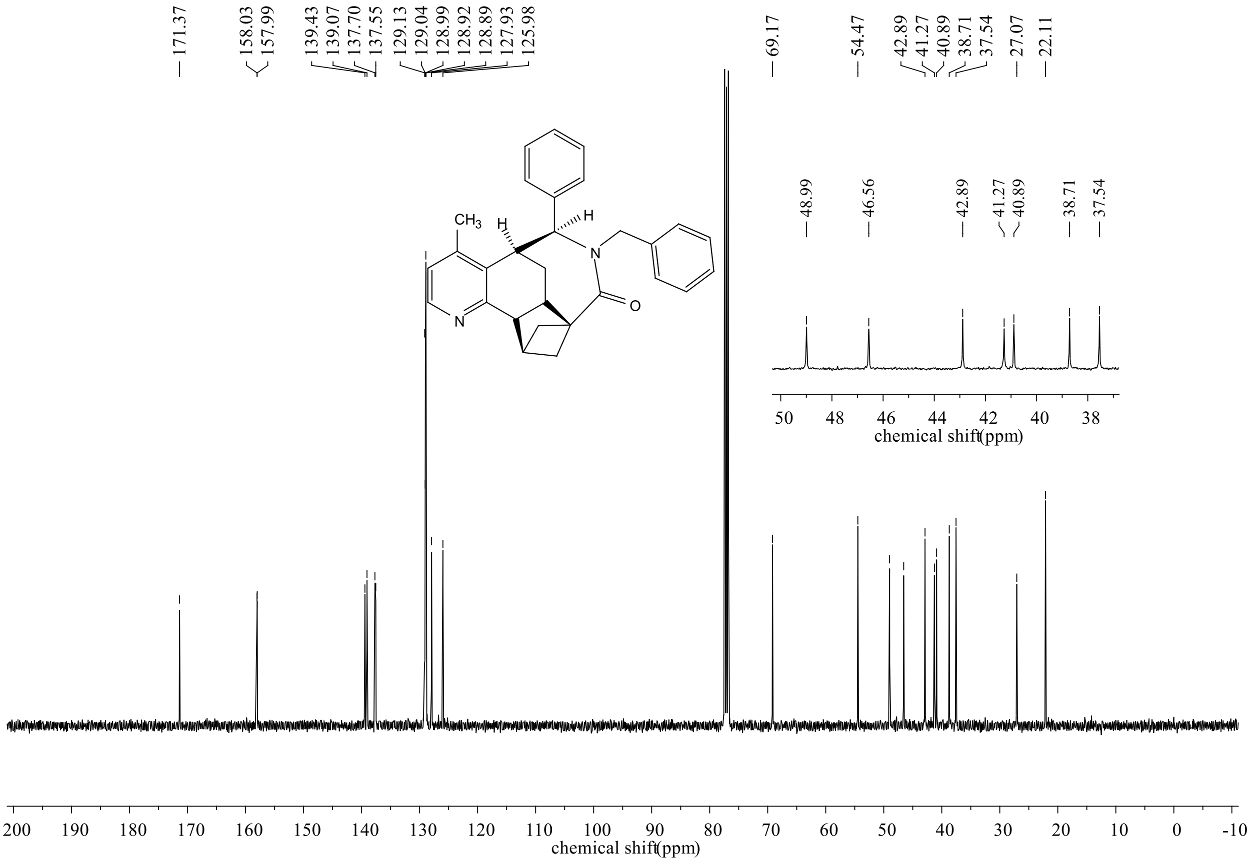
trans-**4C** ^{13}C NMR (126 MHz, CDCl$_3$)



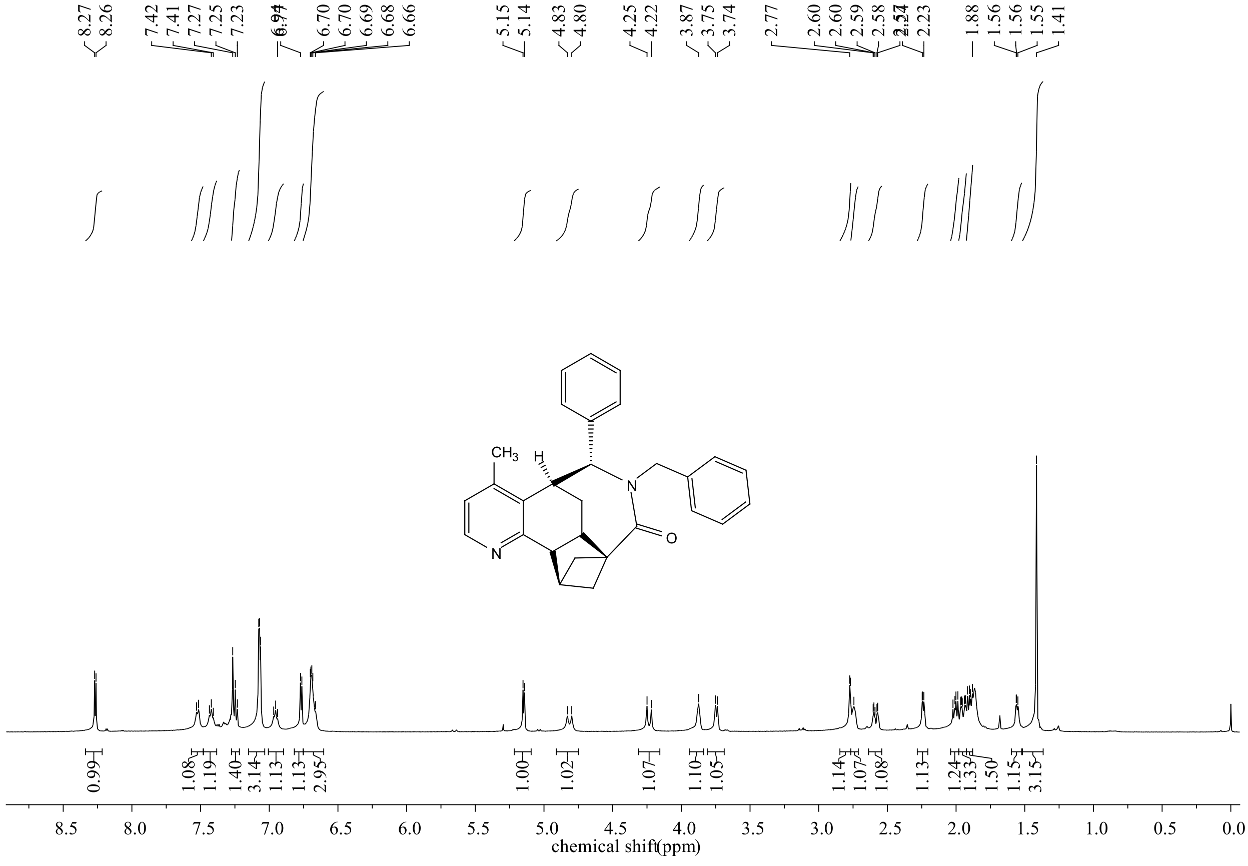
cis-**4D** ^{1}H NMR (400 MHz, CDCl$_3$)



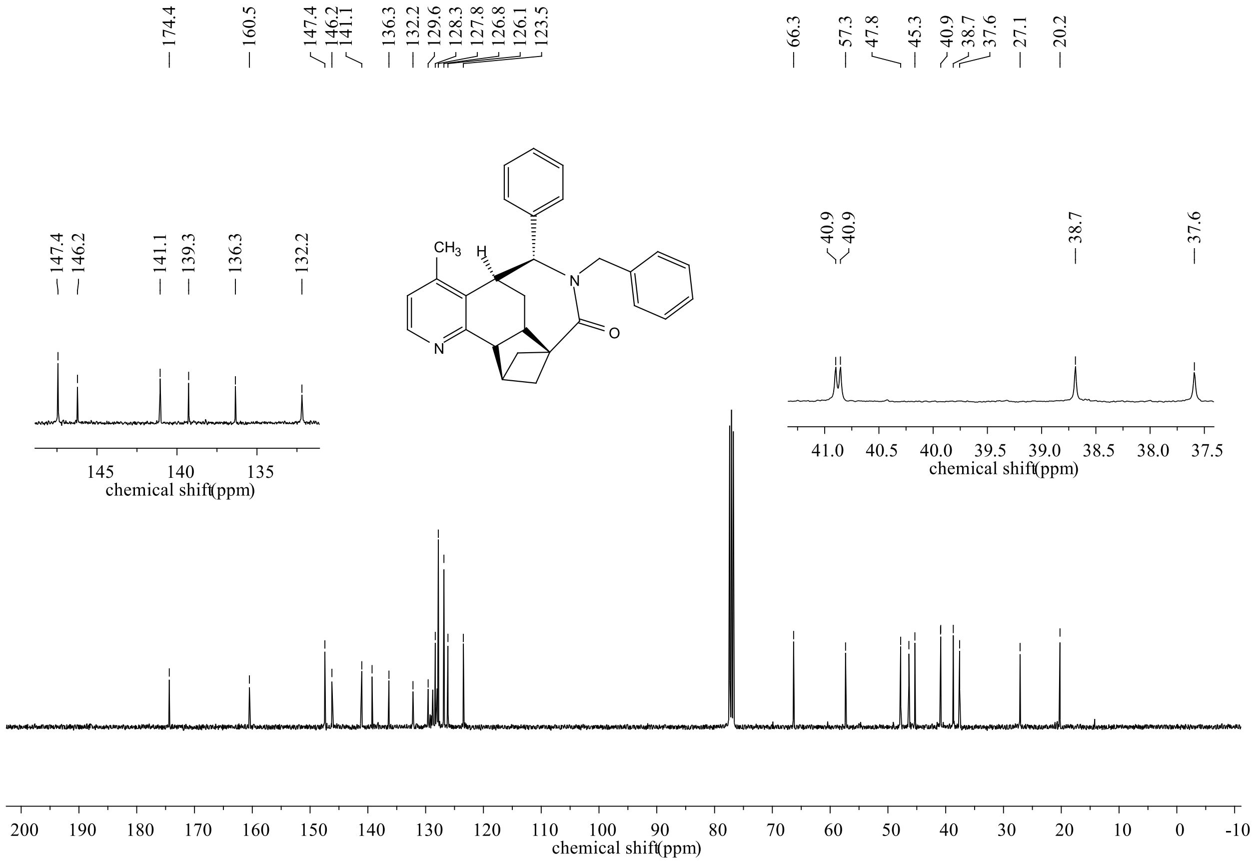
cis-**4D** ^{13}C NMR (101 MHz, $CDCl_3$)



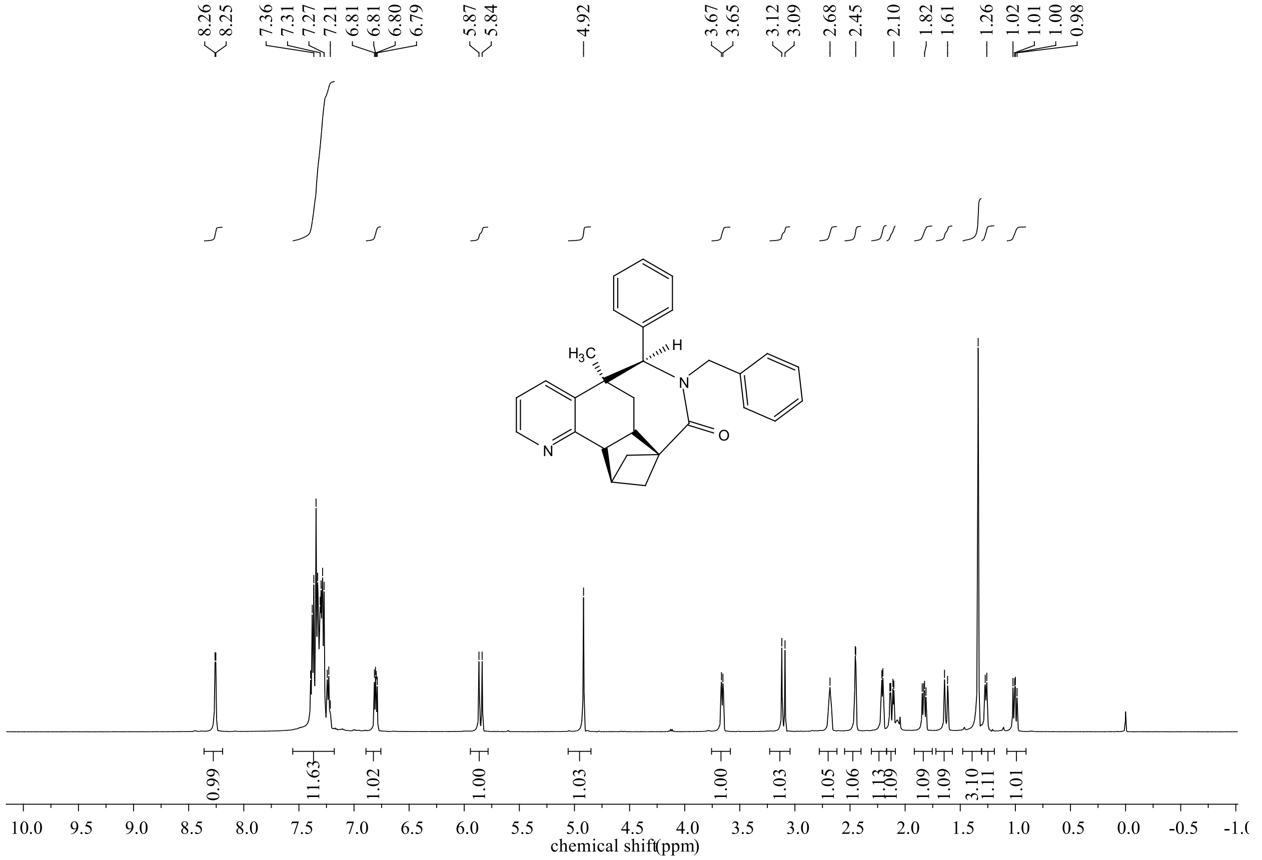
trans-**4D** ^{1}H NMR (500 MHz, $CDCl_3$)



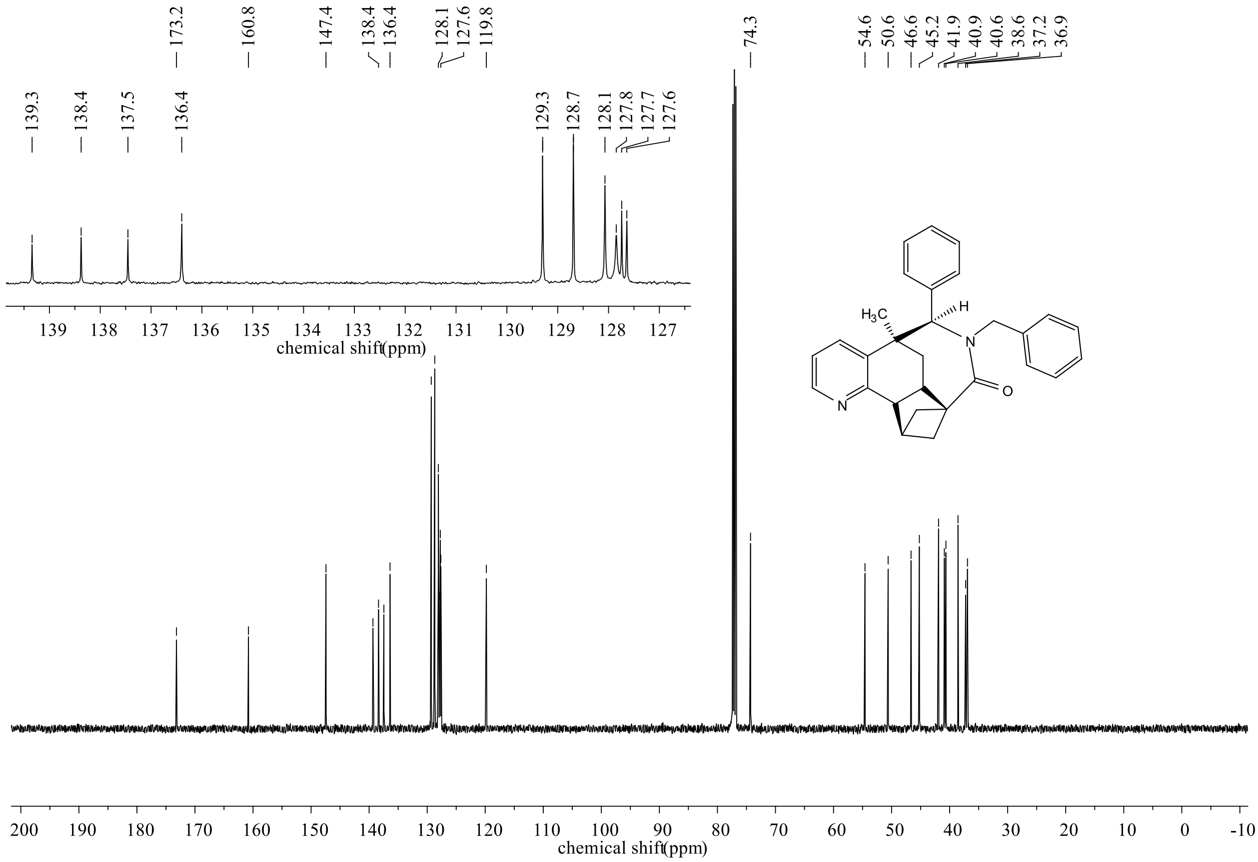
trans-**4D** ^{13}C NMR (101 MHz, $CDCl_3$)



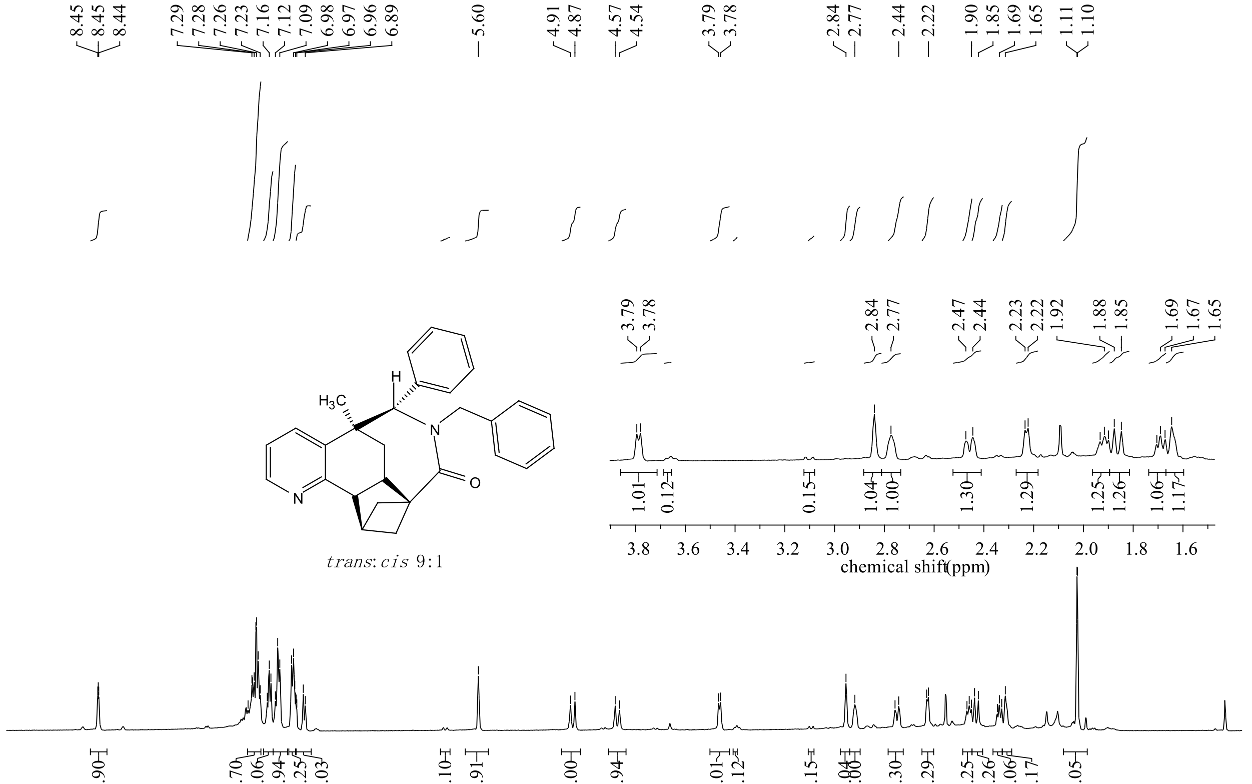
cis-**4E** ^{1}H NMR (500 MHz, $CDCl_3$)



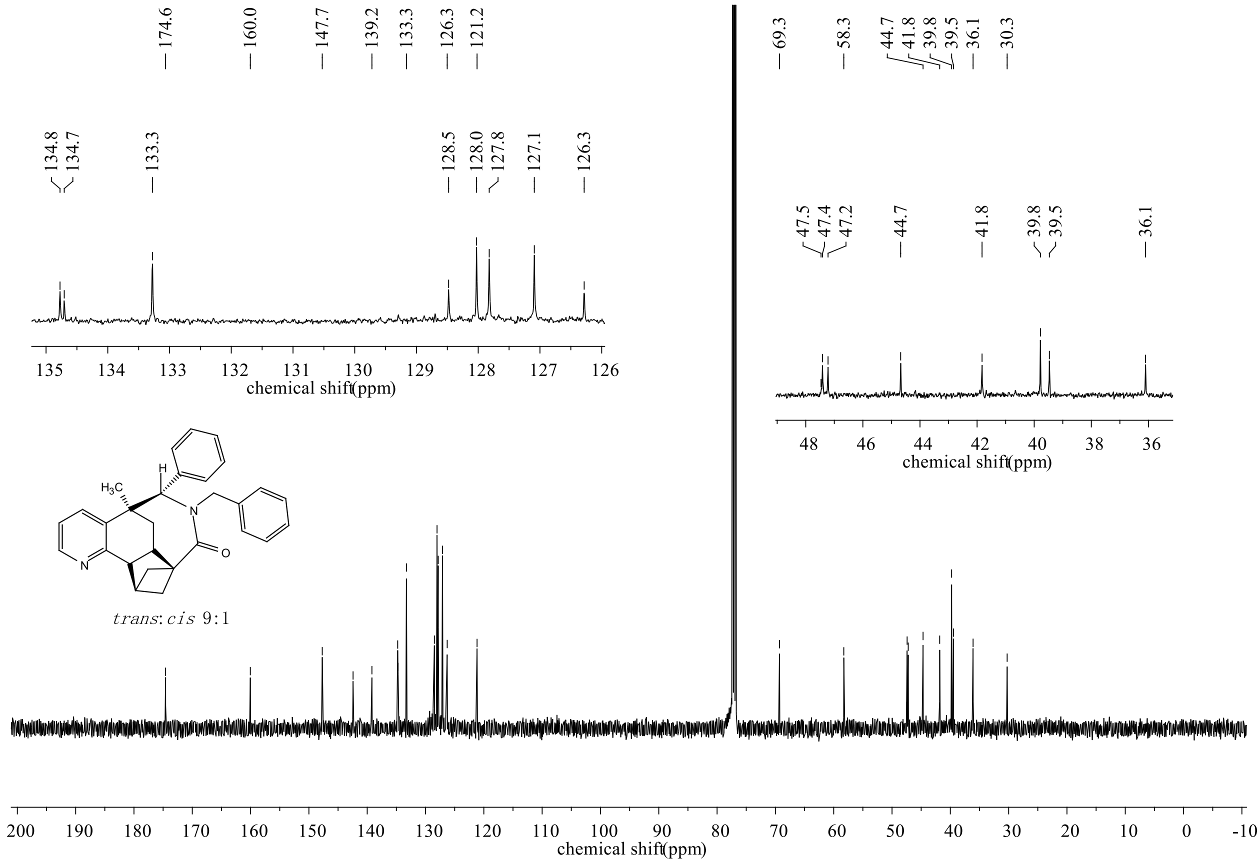
cis-**4E** ^{13}C NMR (126 MHz, $CDCl_3$)



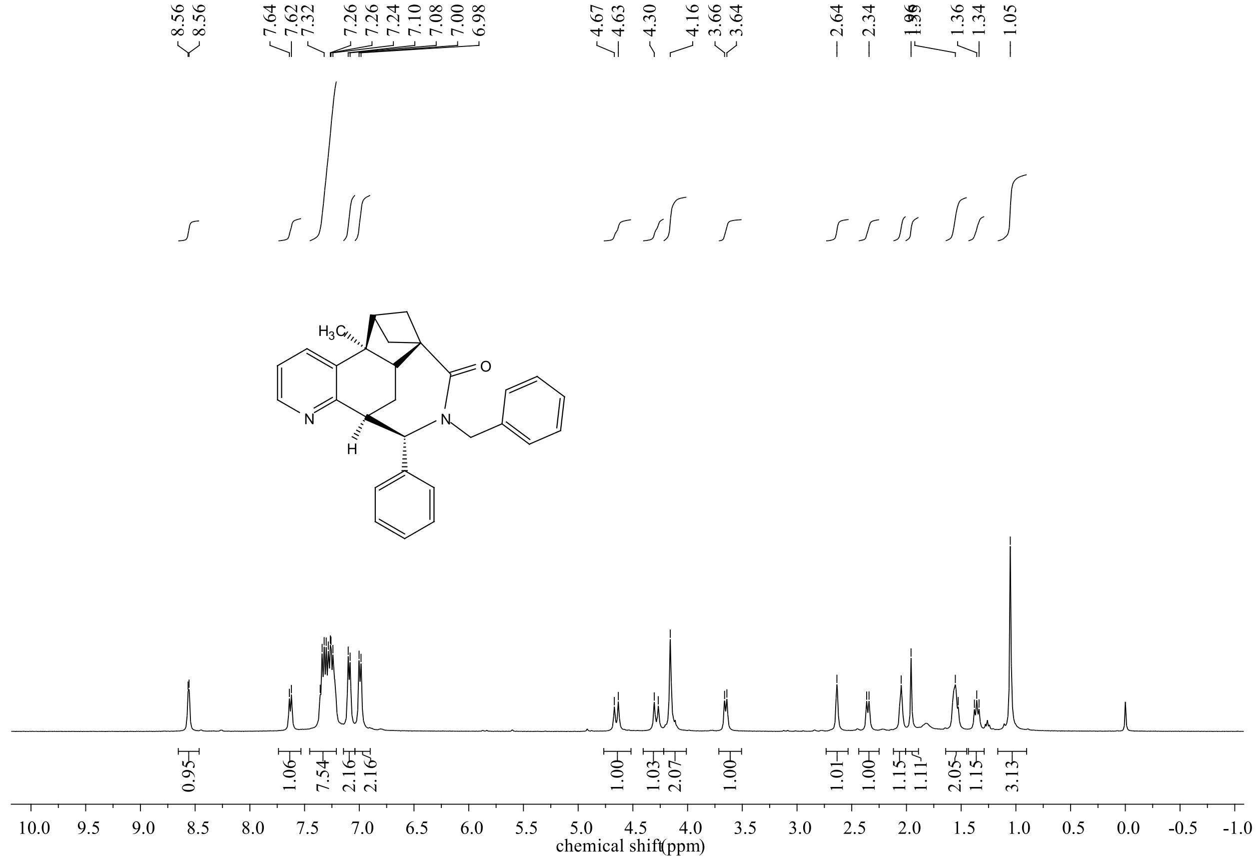
trans-**4E** ^{1}H NMR (500 MHz, $CDCl_3$)



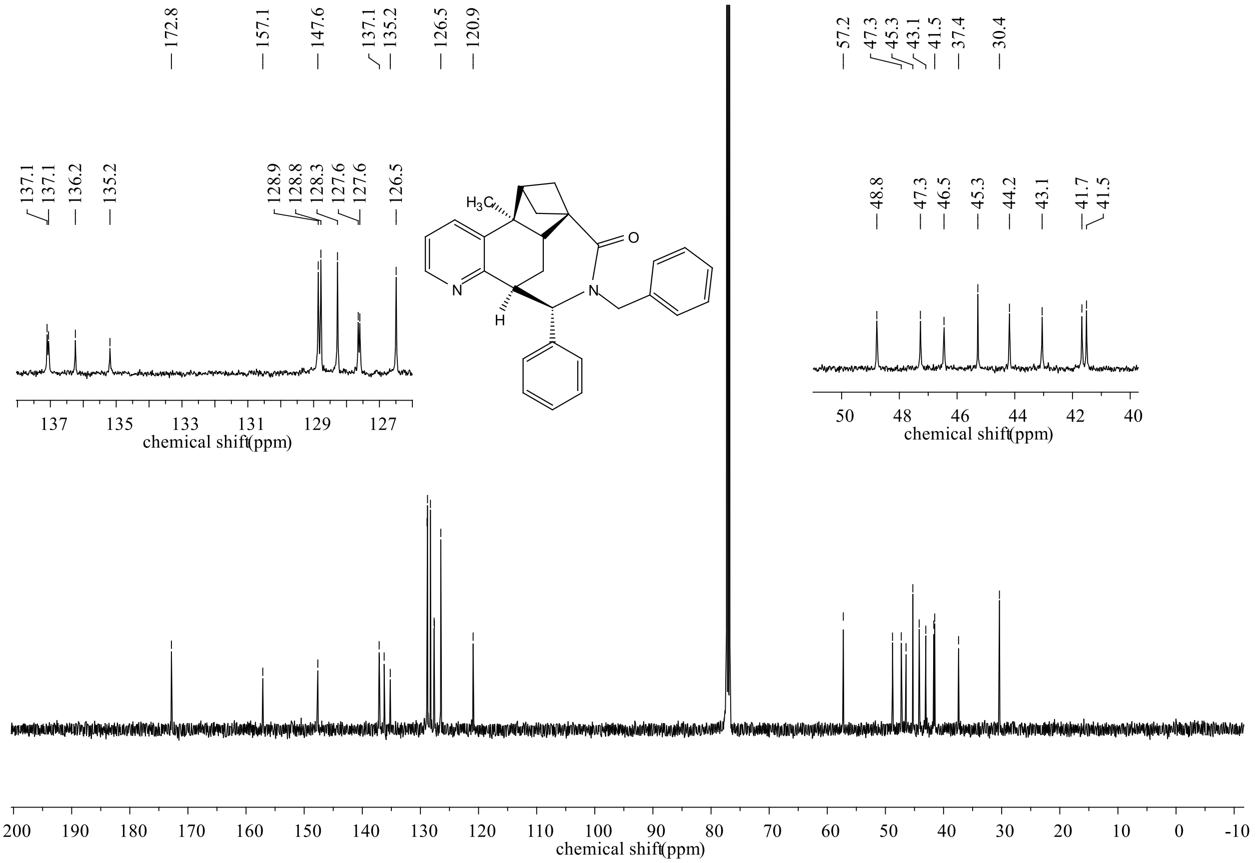
trans-**4E** ^{13}C NMR (126 MHz, $CDCl_3$)



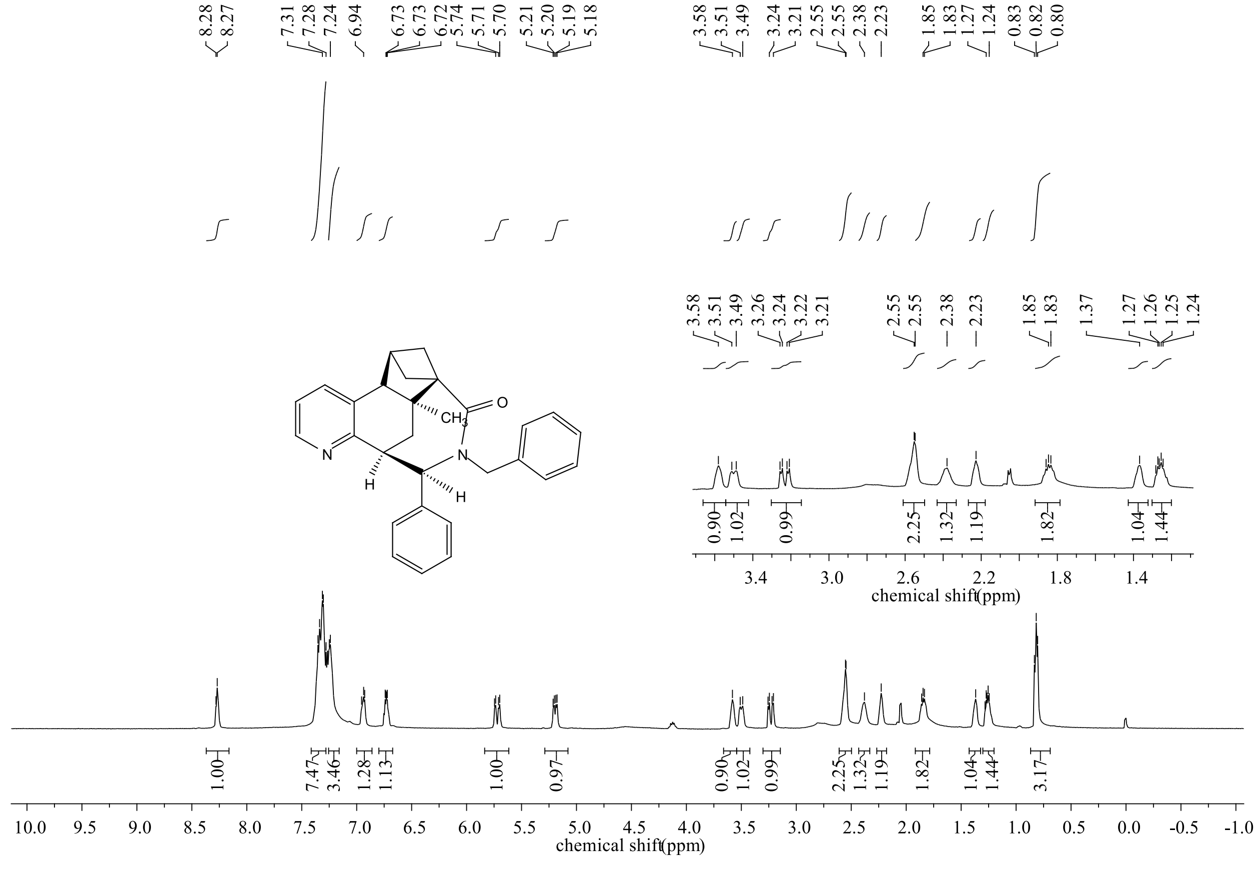
trans-**4e** ^{1}H NMR (400 MHz, $CDCl_3$)



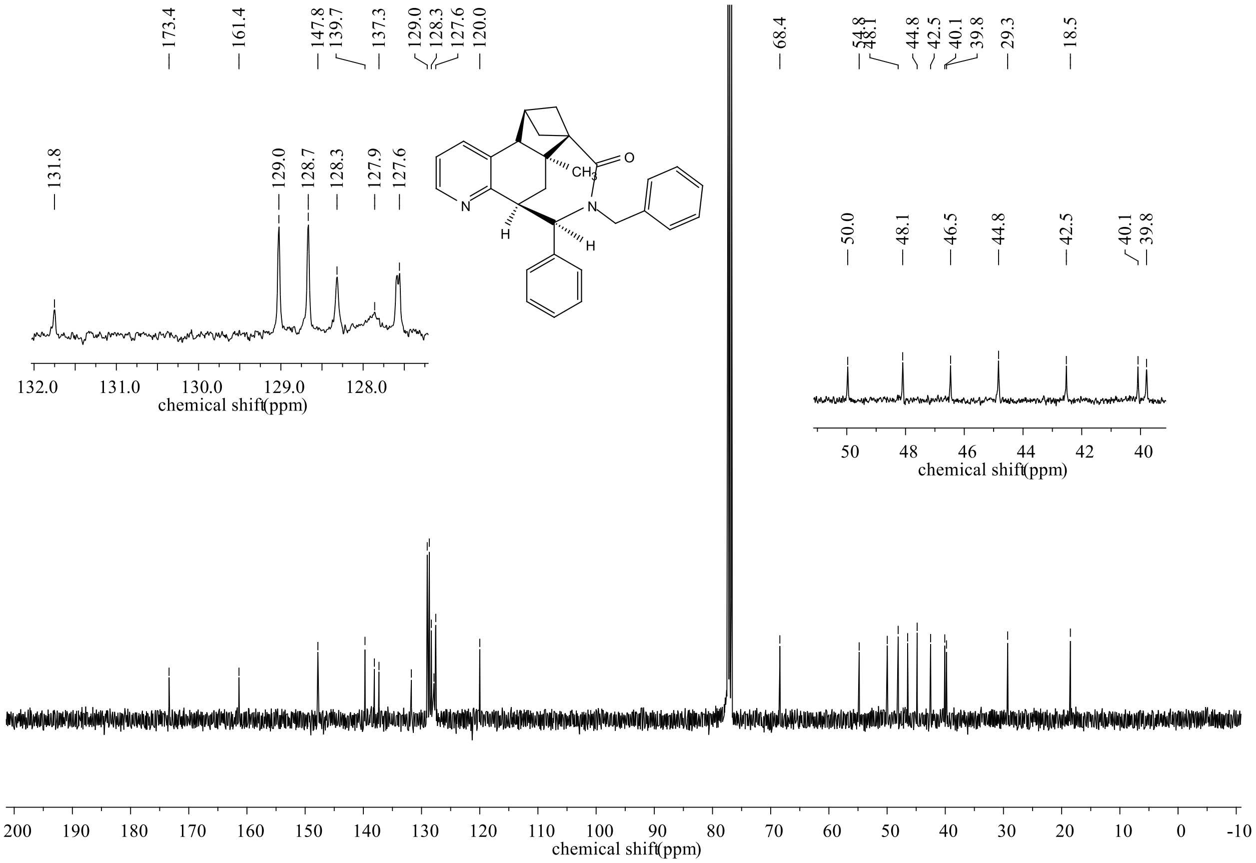
trans-**4e** ^{13}C NMR (126 MHz, CDCl$_3$)



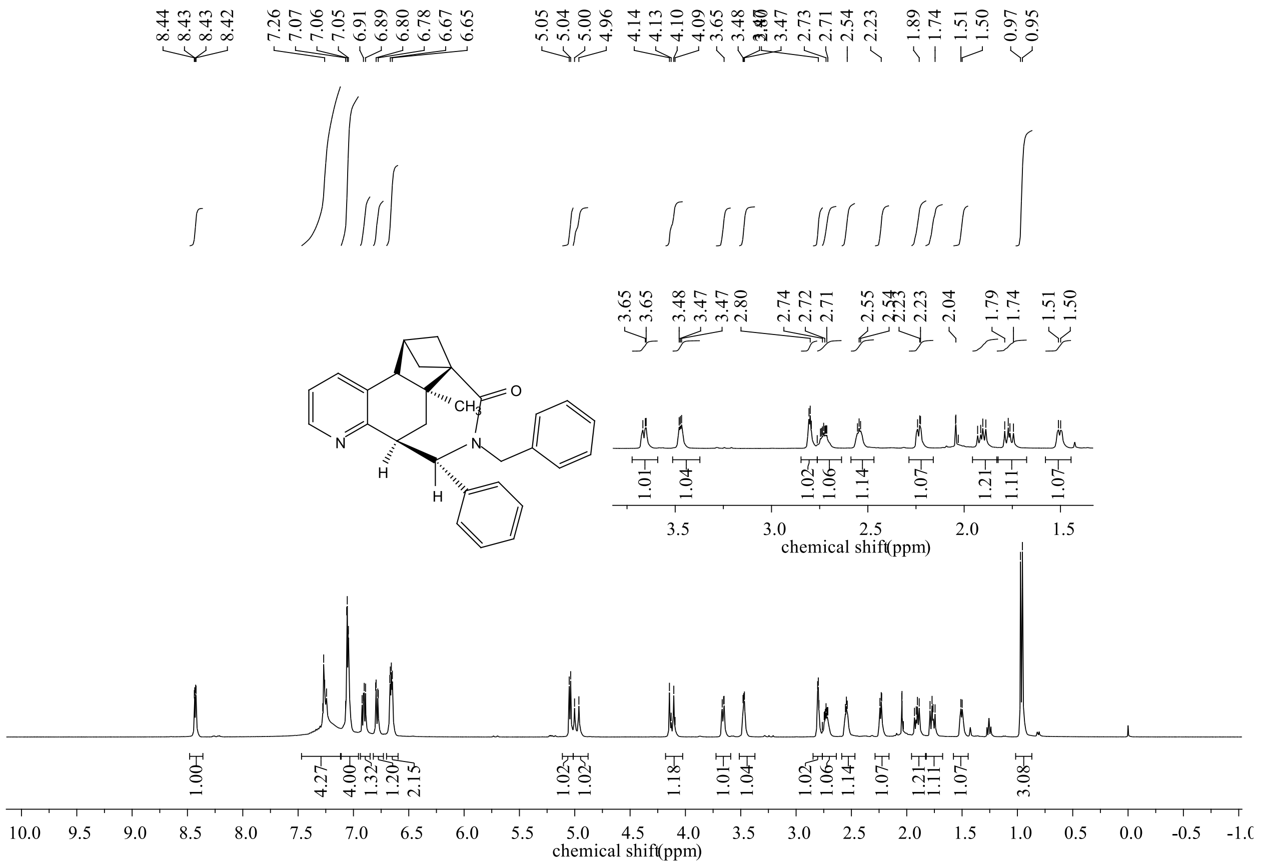
cis-**4f** ^{1}H NMR (400 MHz, CDCl$_3$)



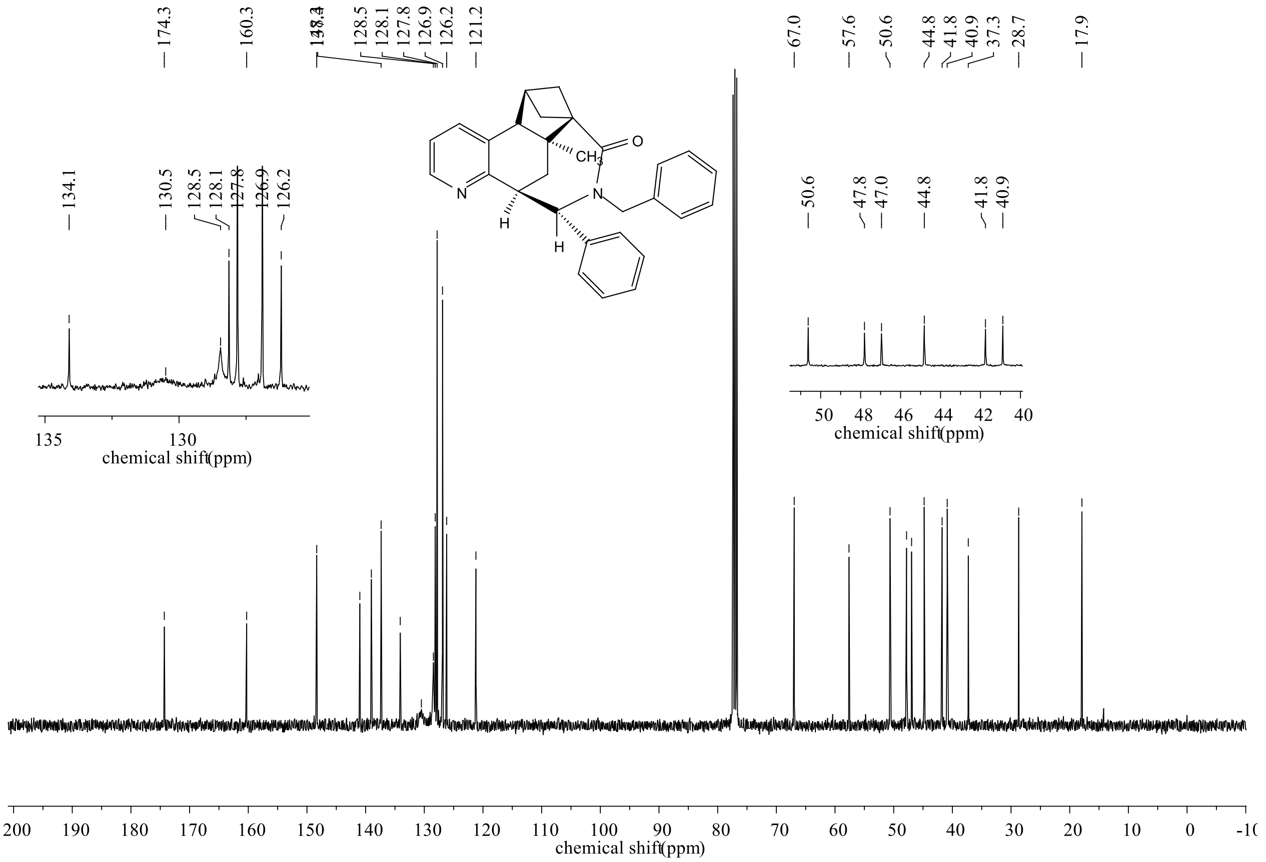
cis-**4f** ^{13}C NMR (101 MHz, $CDCl_3$)



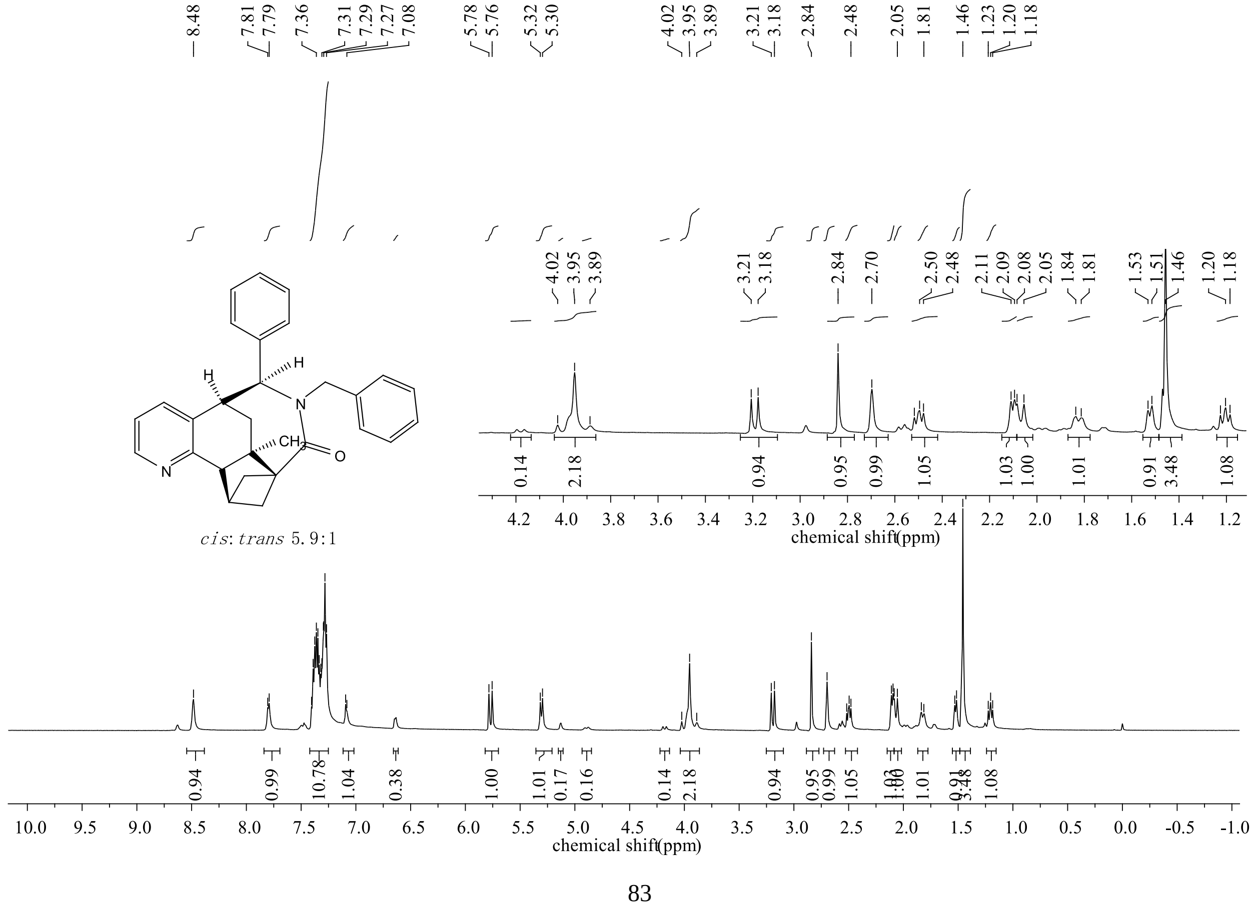
trans-**4f** ^{1}H NMR (400 MHz, $CDCl_3$)



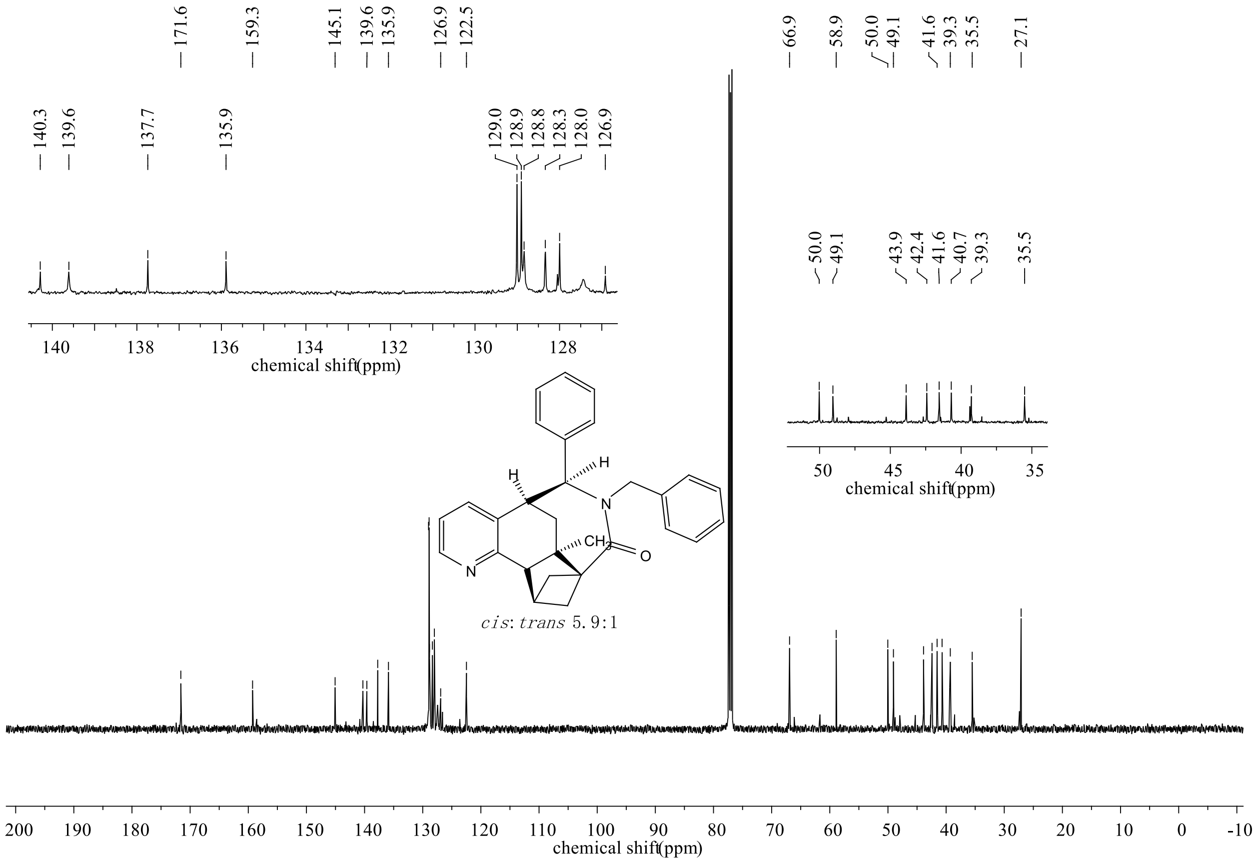
trans-**4f** ^{13}C NMR (101 MHz, CDCl$_3$)



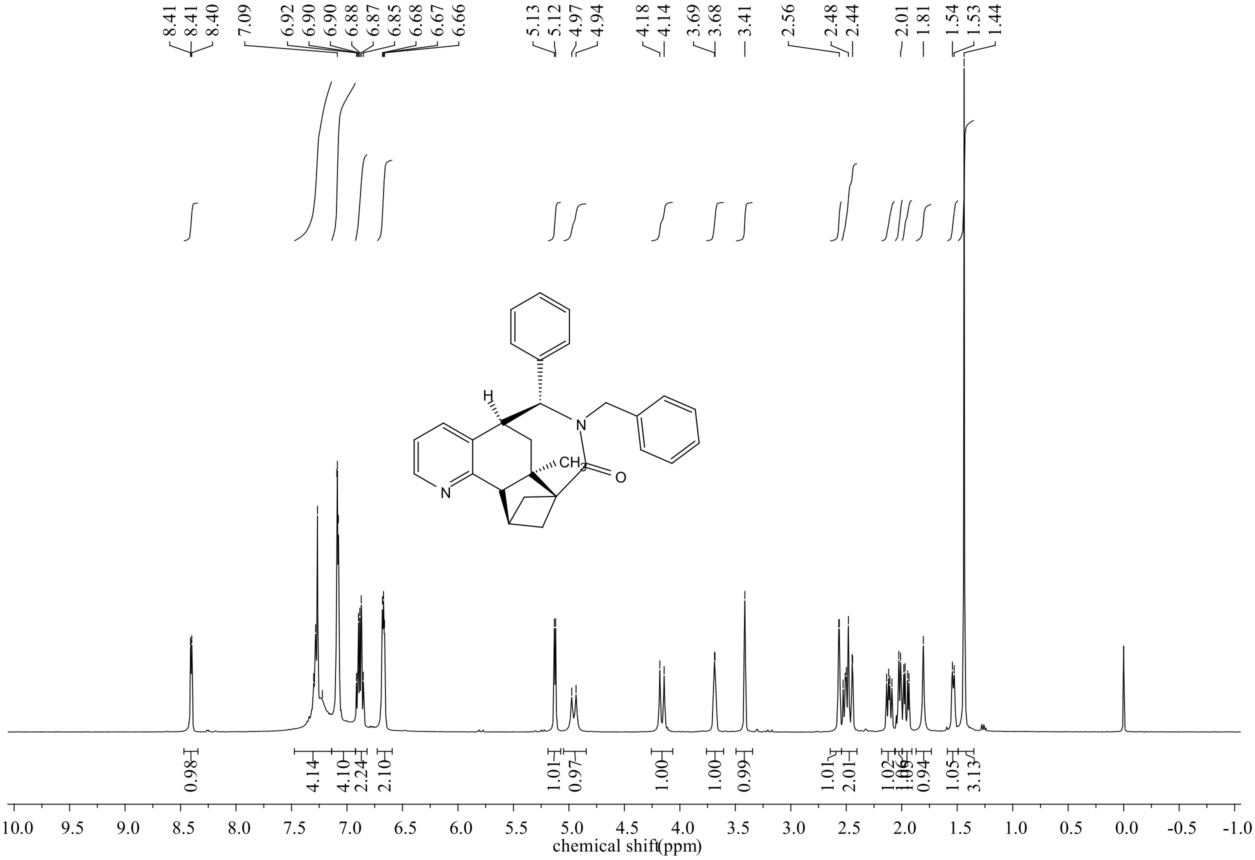
cis-**4G** ^{1}H NMR (500 MHz, CDCl$_3$)



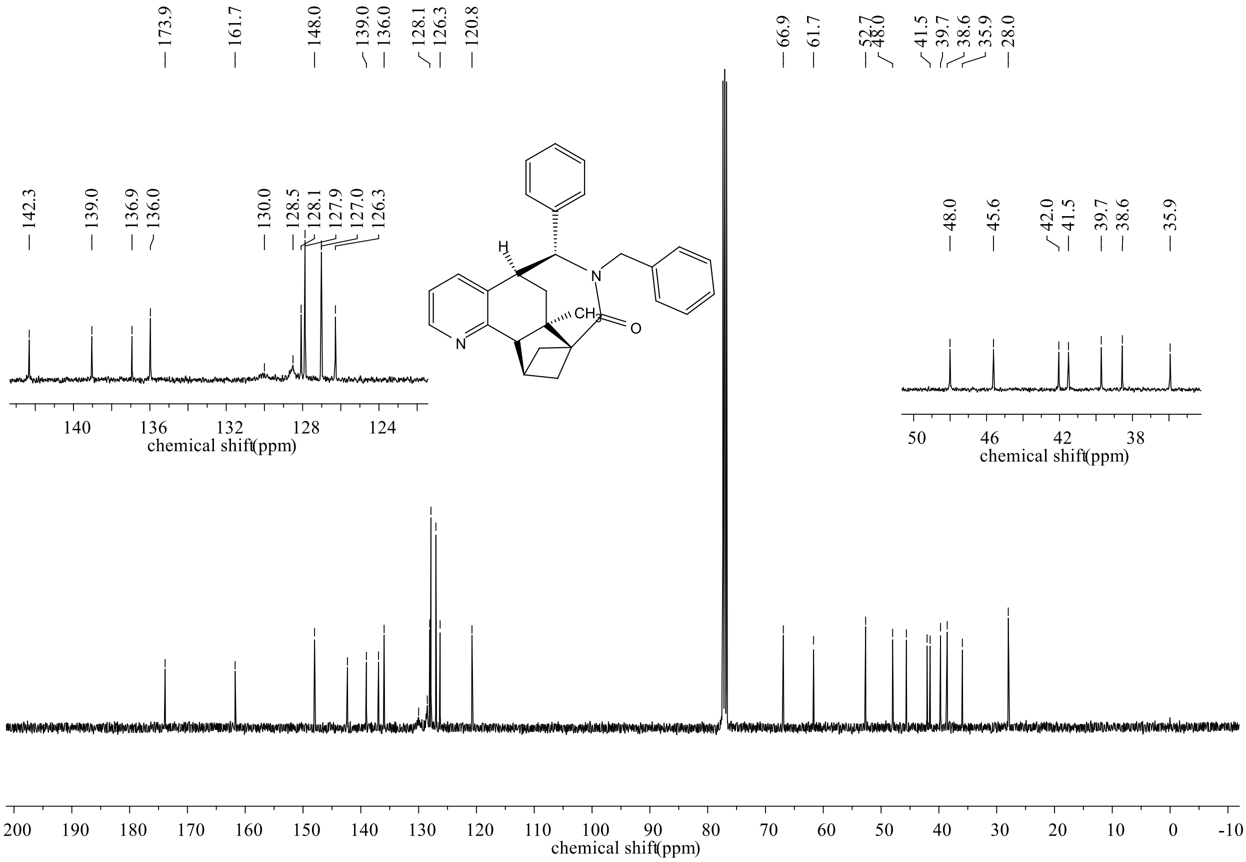
cis-**4G** ^{13}C NMR (126 MHz, CDCl$_3$)



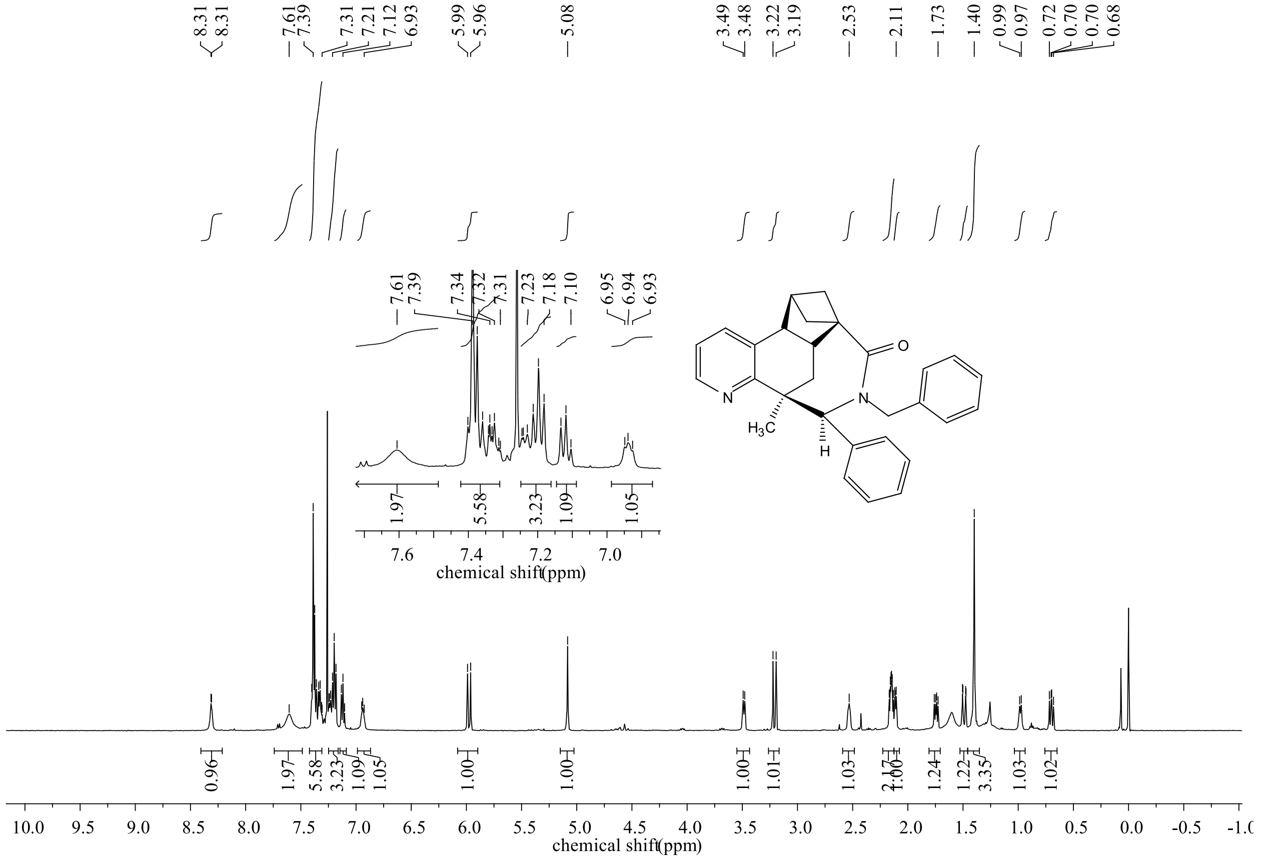
trans-**4G** ^{1}H NMR (400 MHz, CDCl$_3$)



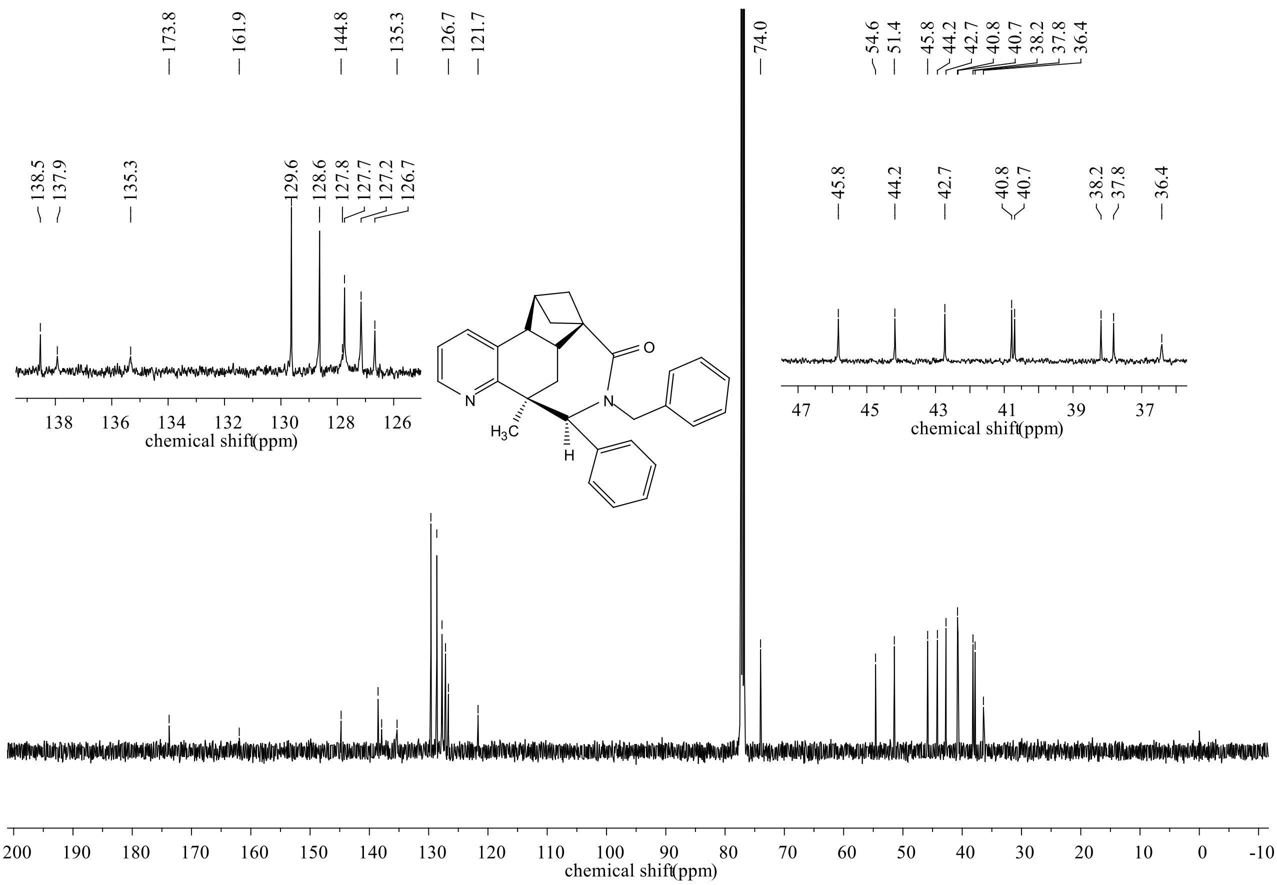
trans-**4G** ^{13}C NMR (101 MHz, CDCl$_3$)



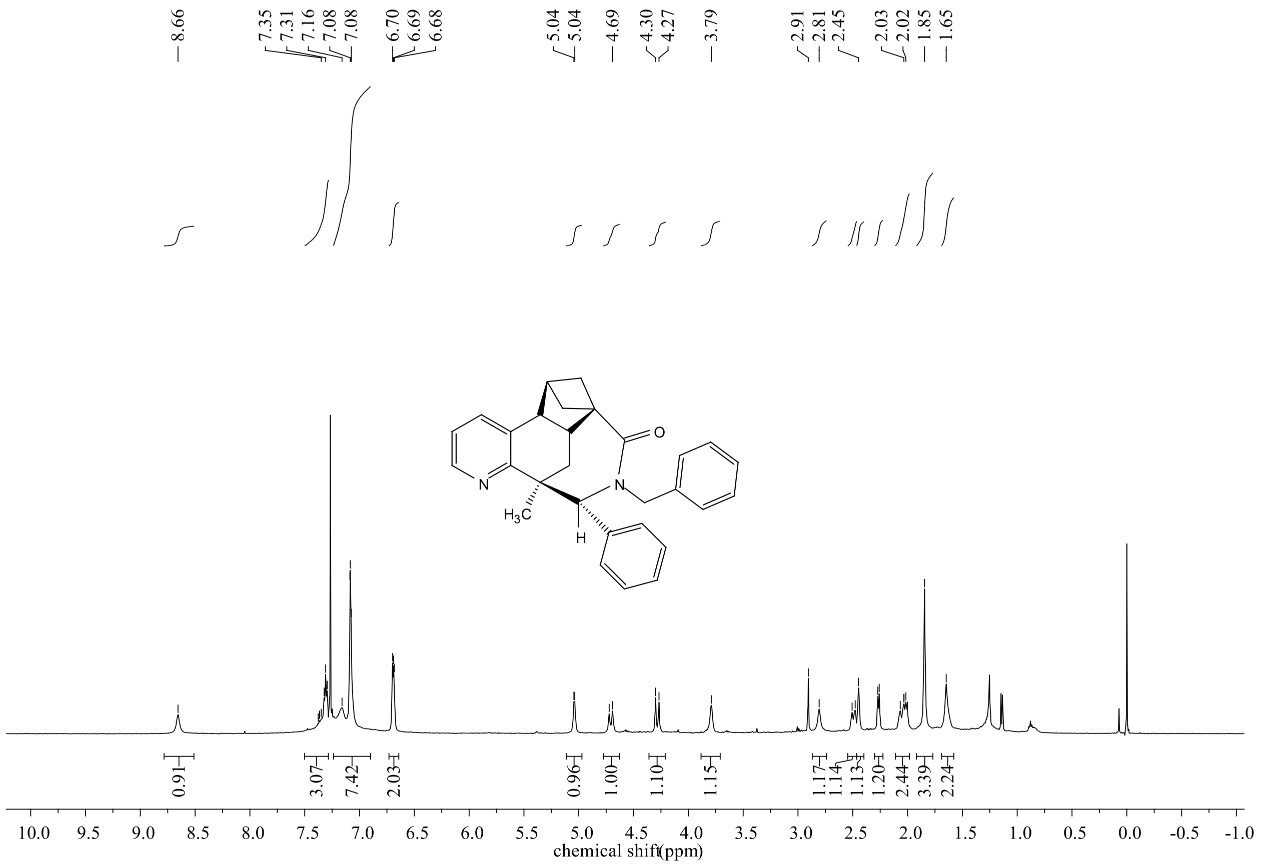
cis-**4h** ^{1}H NMR (500 MHz, CDCl$_3$)



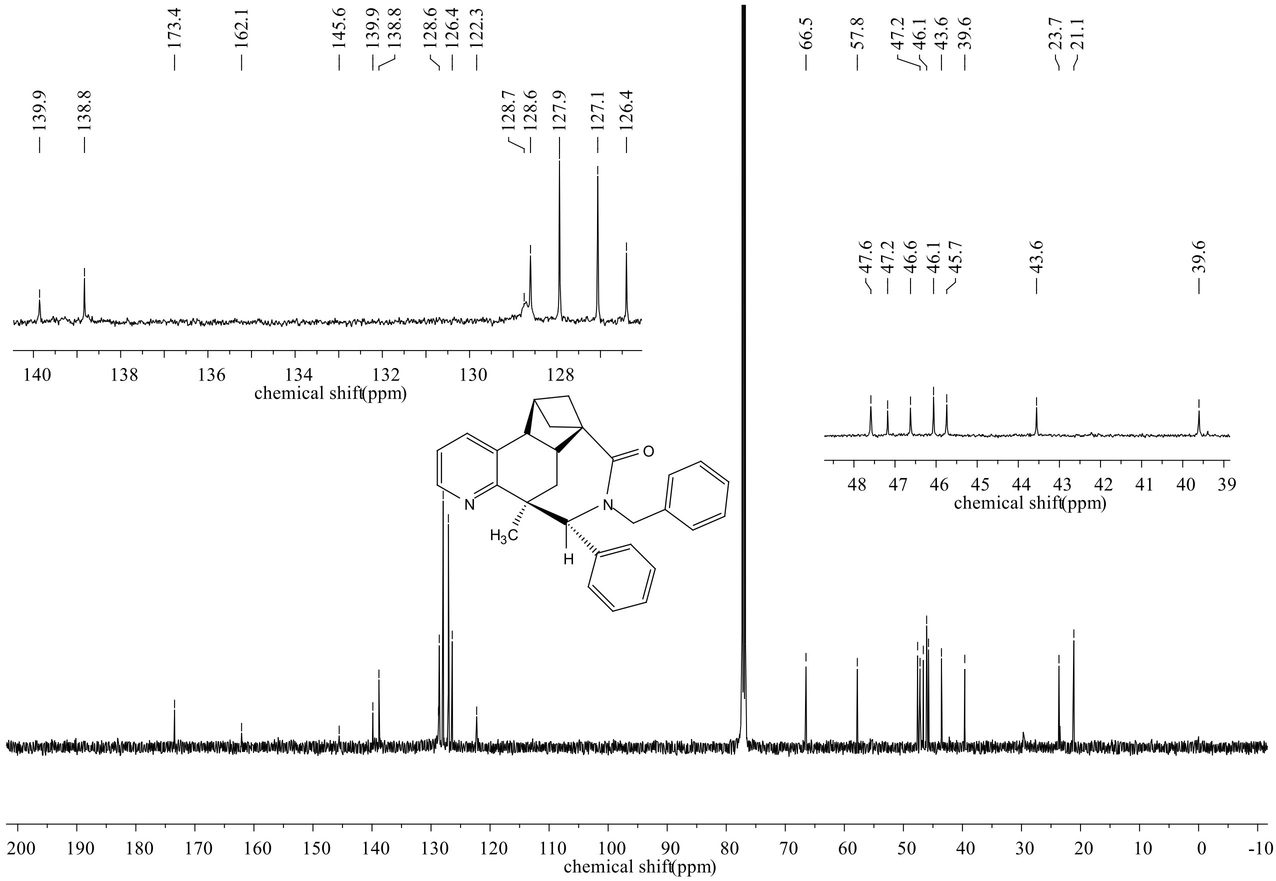
cis-**4h** ^{13}C NMR (126 MHz, CDCl$_3$)



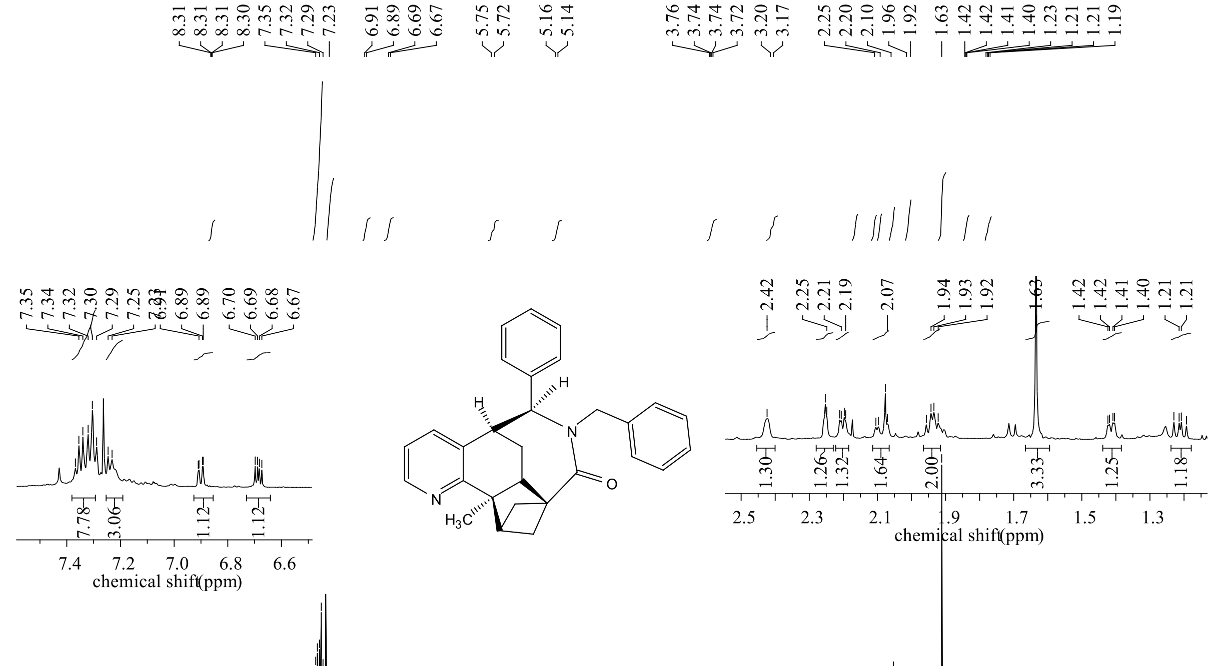
trans-**4h** ^{1}H NMR (500 MHz, CDCl$_3$)



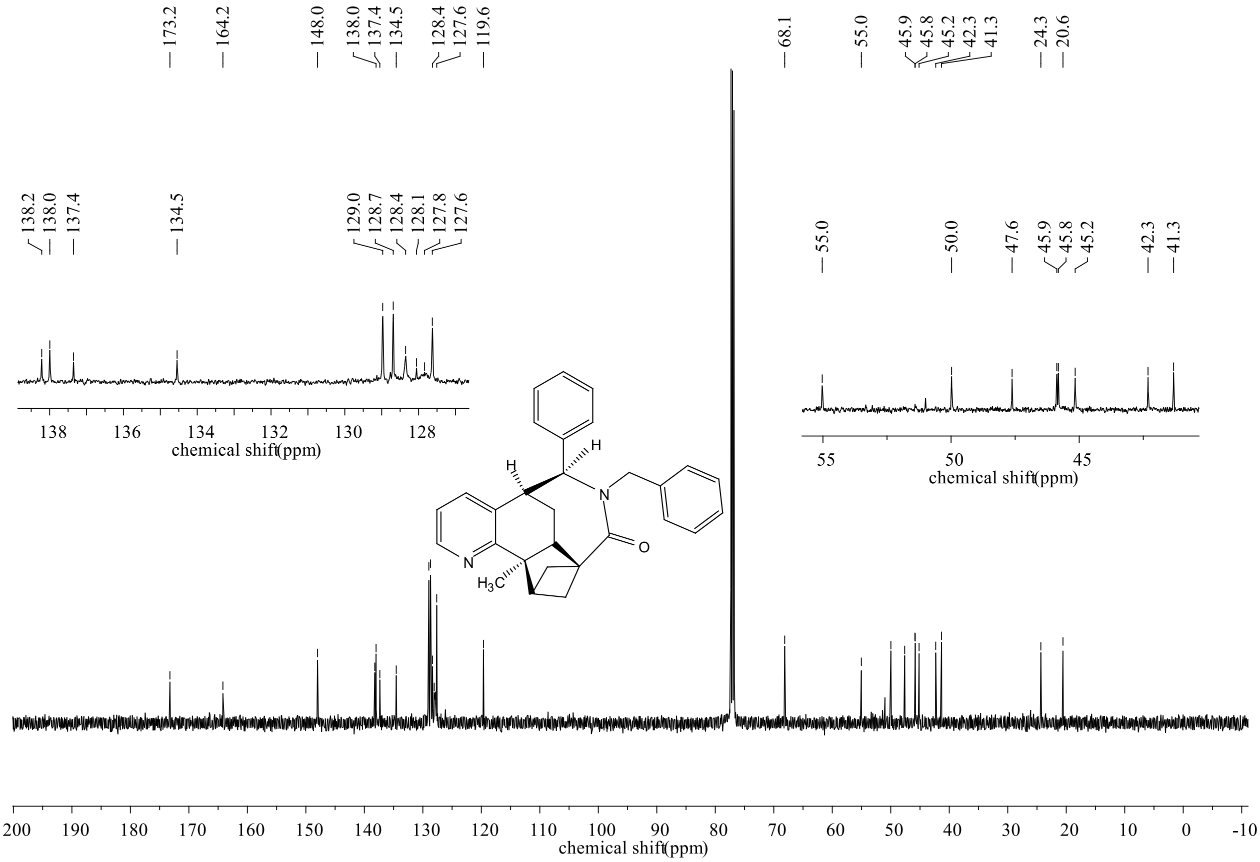
trans-**4h** ^{13}C NMR (126 MHz, CDCl$_3$)



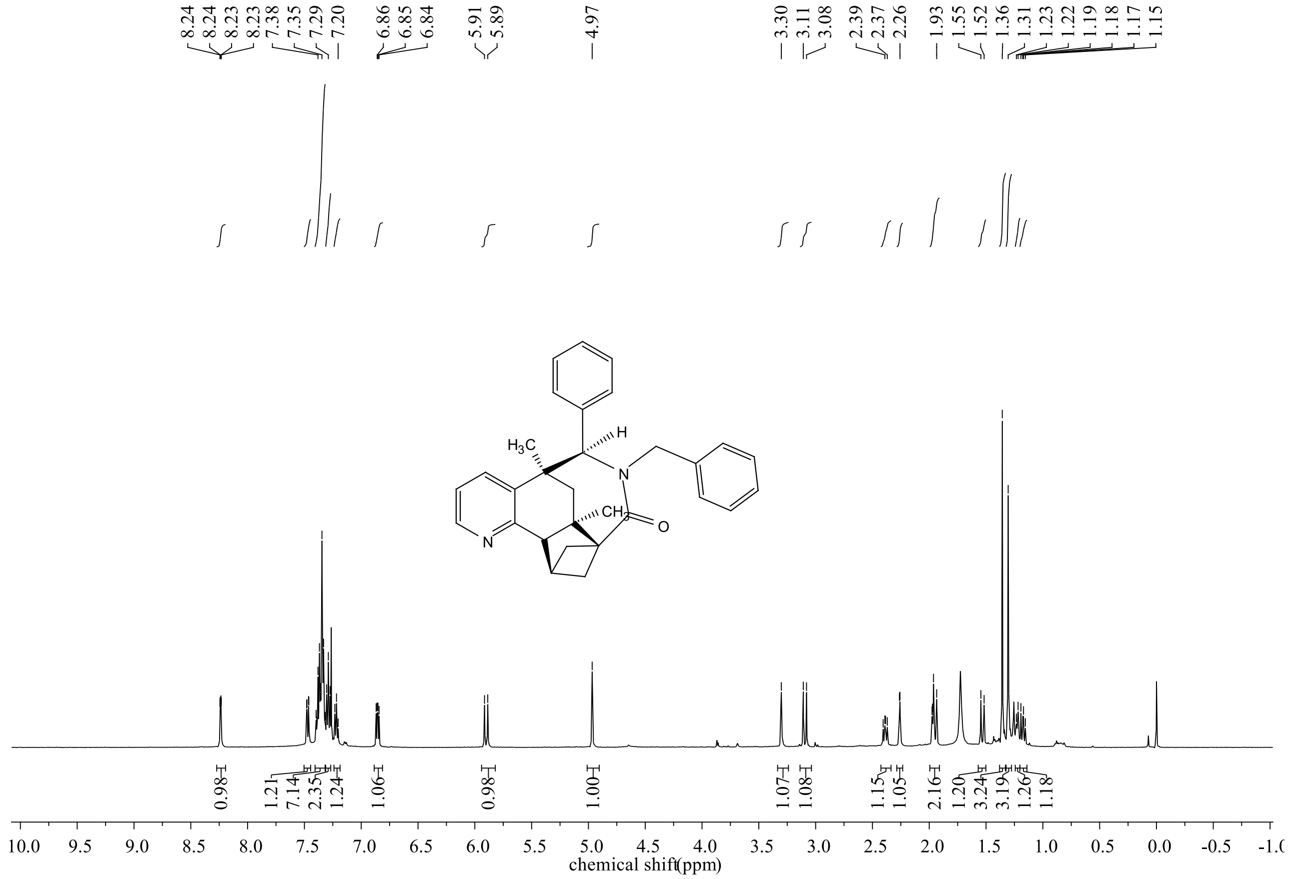
cis-**4H** ^{1}H NMR (500 MHz, CDCl$_3$)



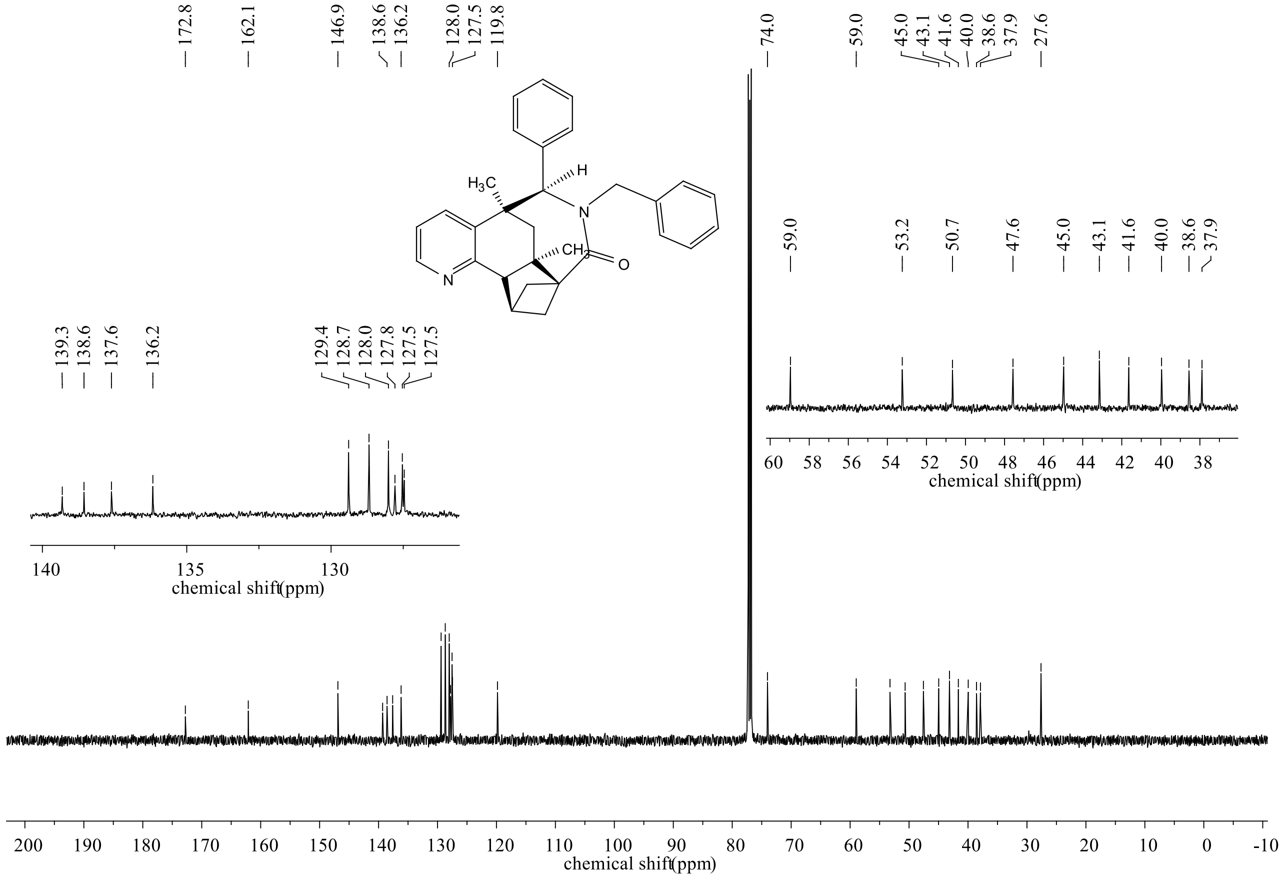
cis-**4H** ^{13}C NMR (126 MHz, $CDCl_3$)



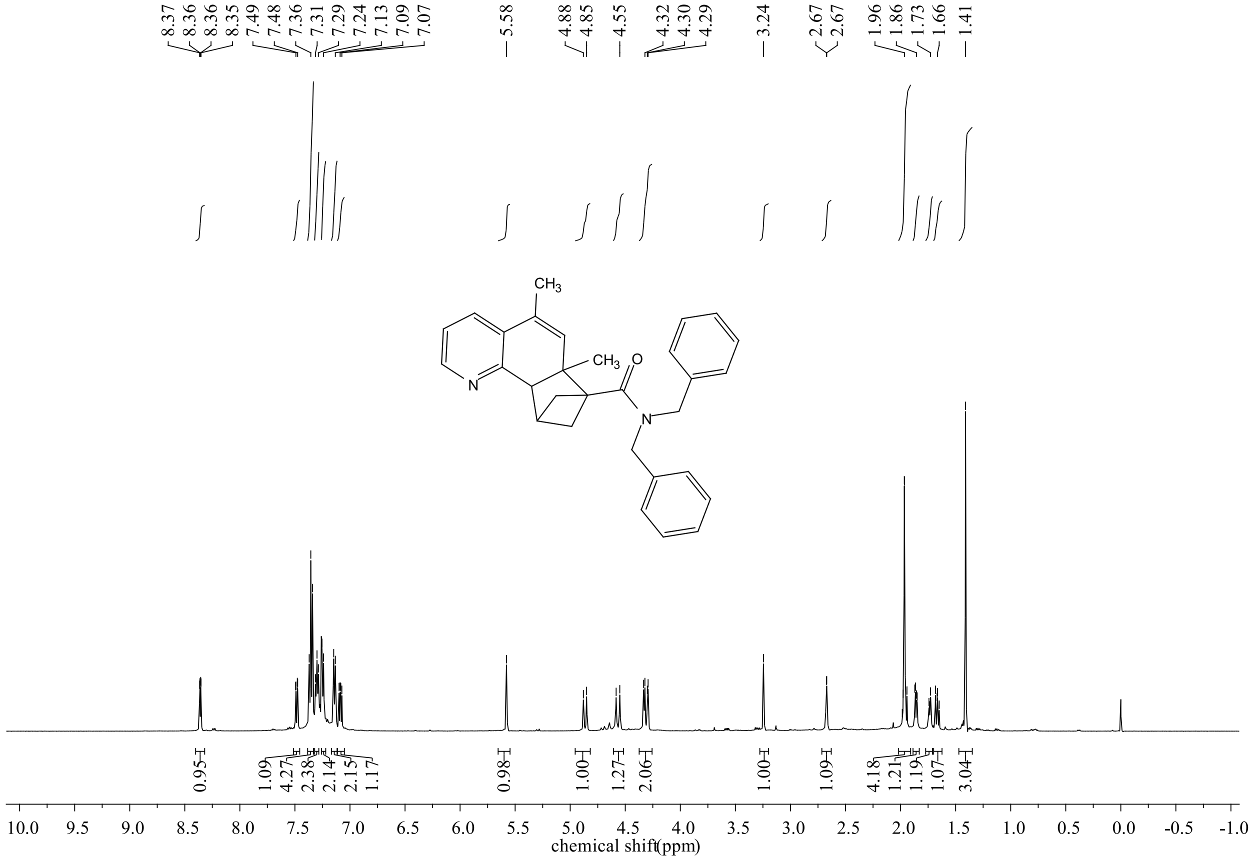
cis-**4I** ^{1}H NMR (500 MHz, $CDCl_3$)



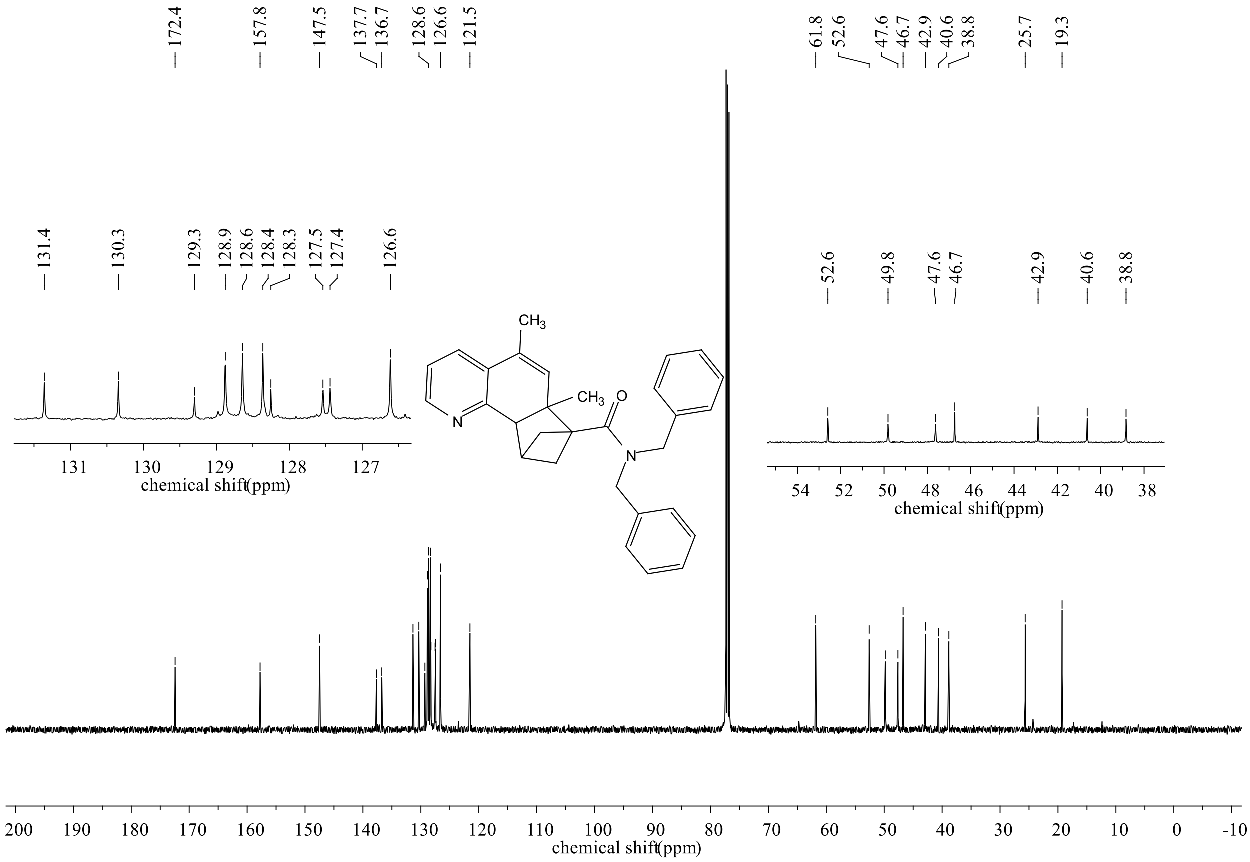
cis-**4l** ^{13}C NMR (126 MHz, $CDCl_3$)



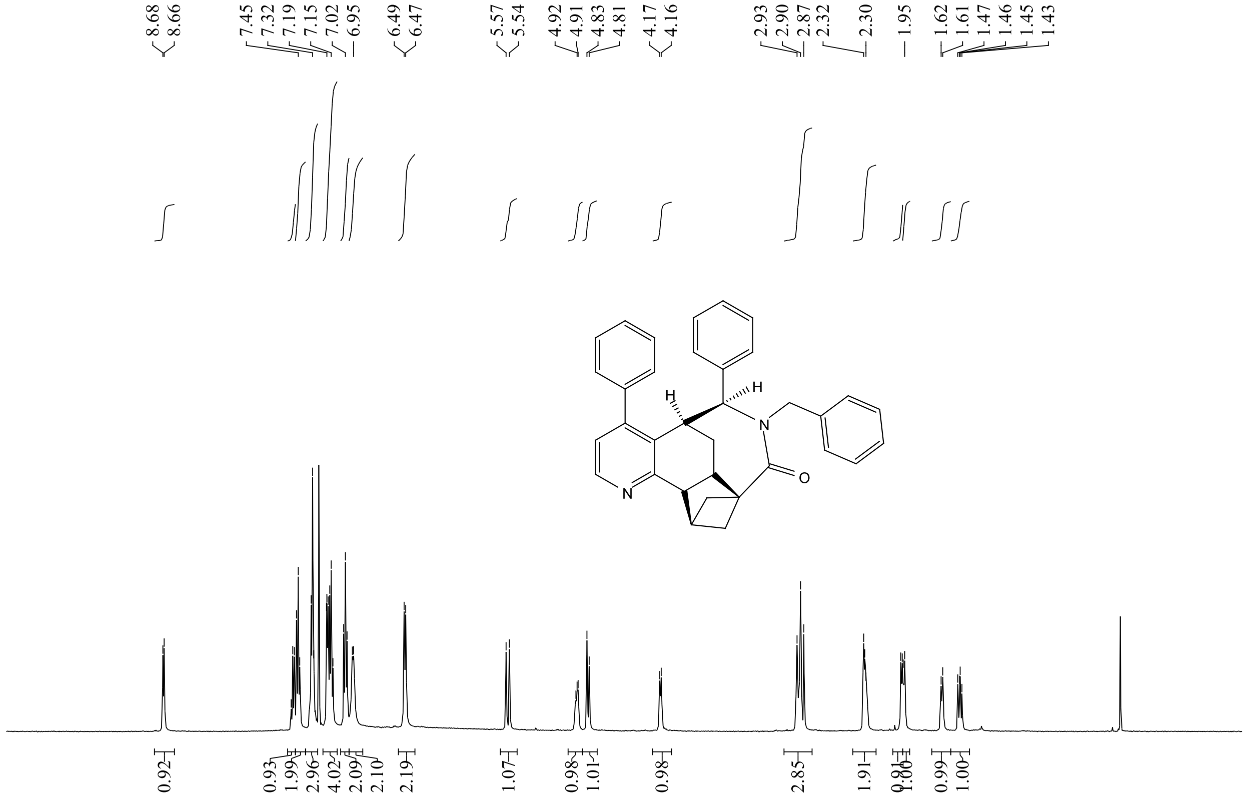
3l ^{1}H NMR (500 MHz, $CDCl_3$).



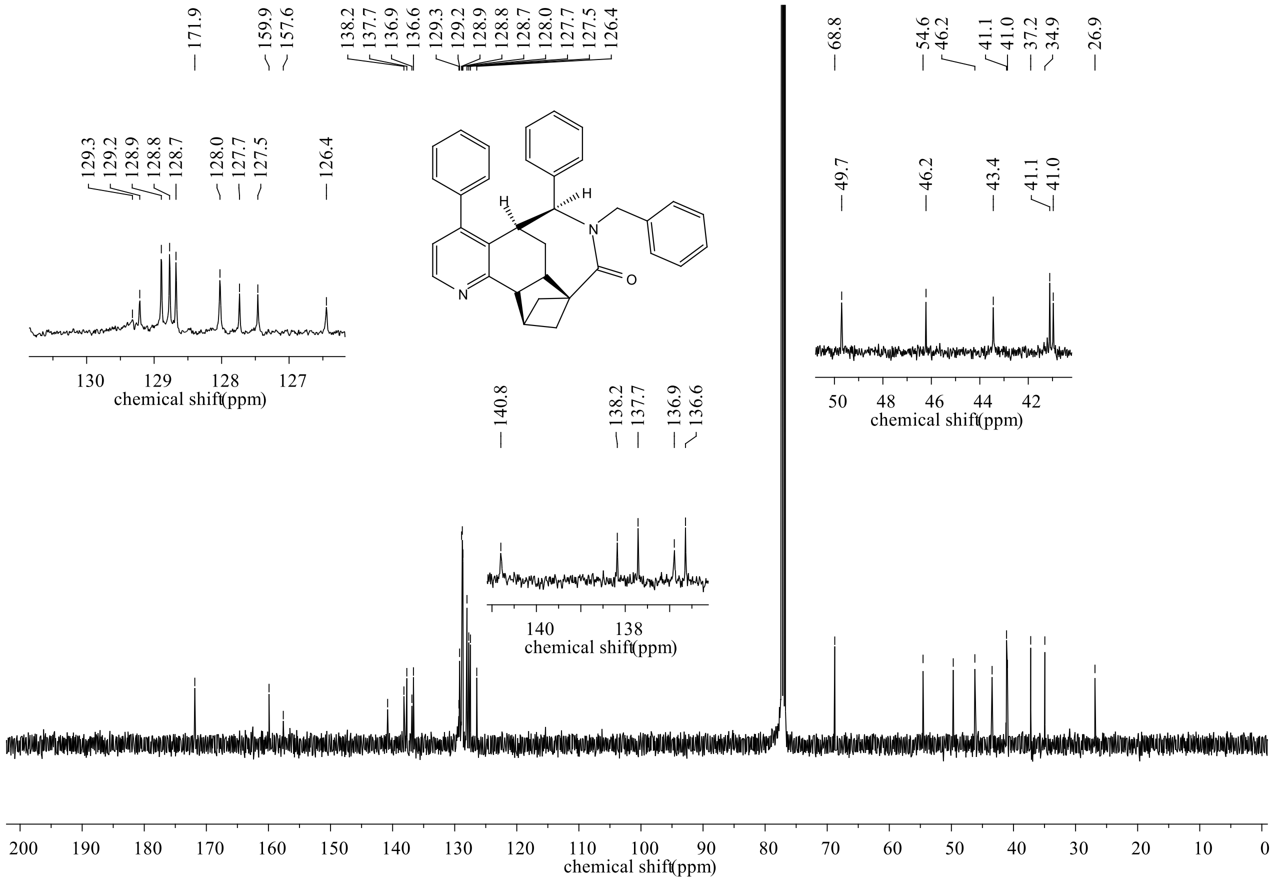
3I ^{13}C NMR (126 MHz, CDCl$_3$)



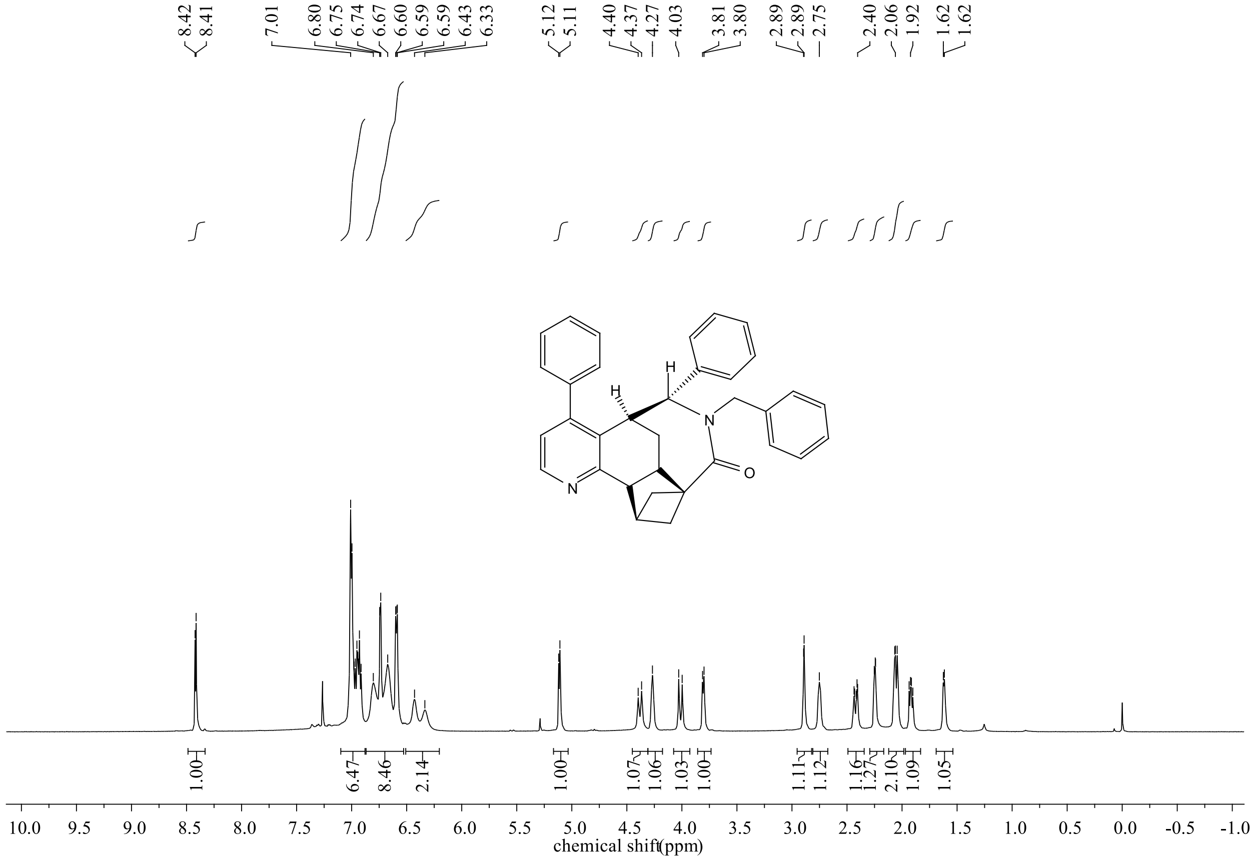
cis-**4J** ^{1}H NMR (500 MHz, CDCl$_3$)



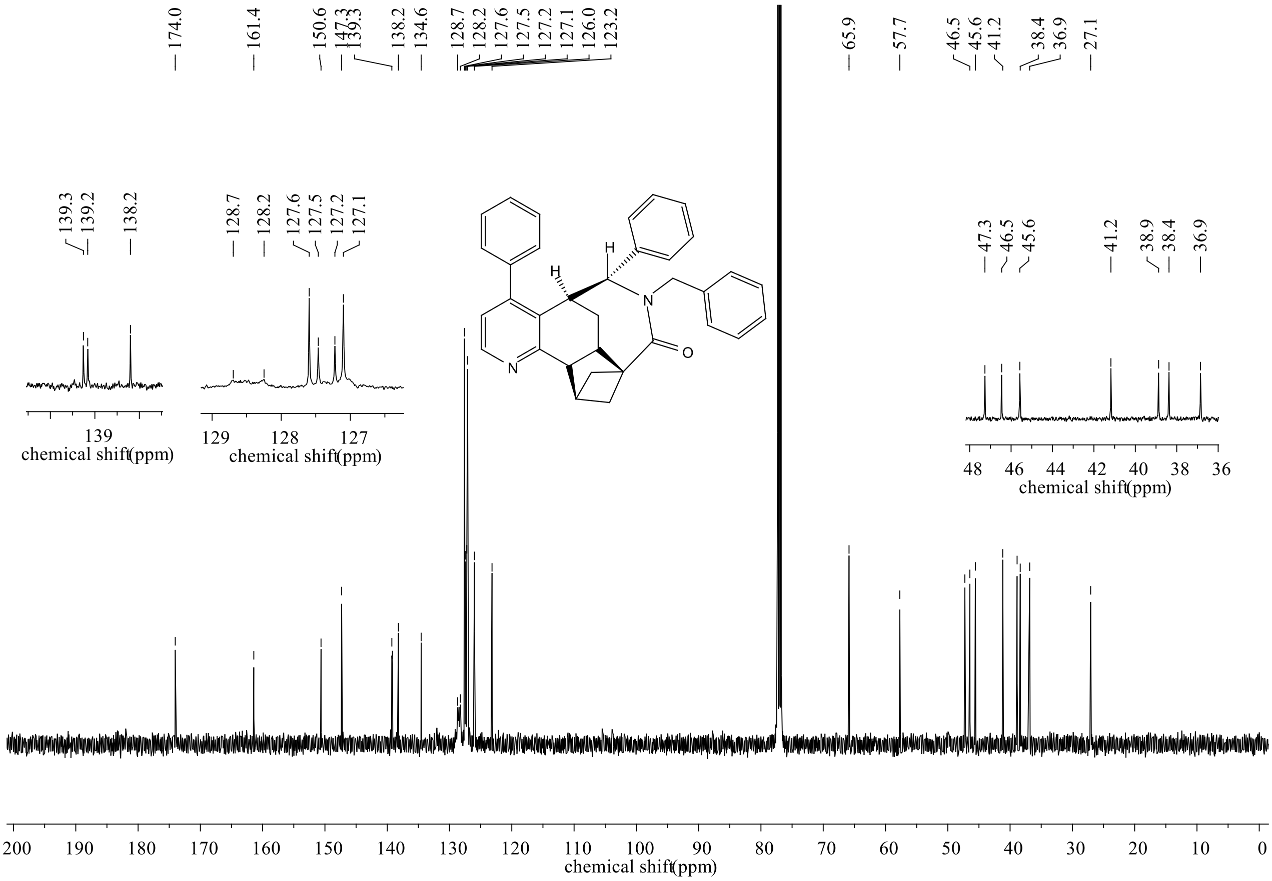
cis-**4J** ^{13}C NMR (126 MHz, $CDCl_3$)



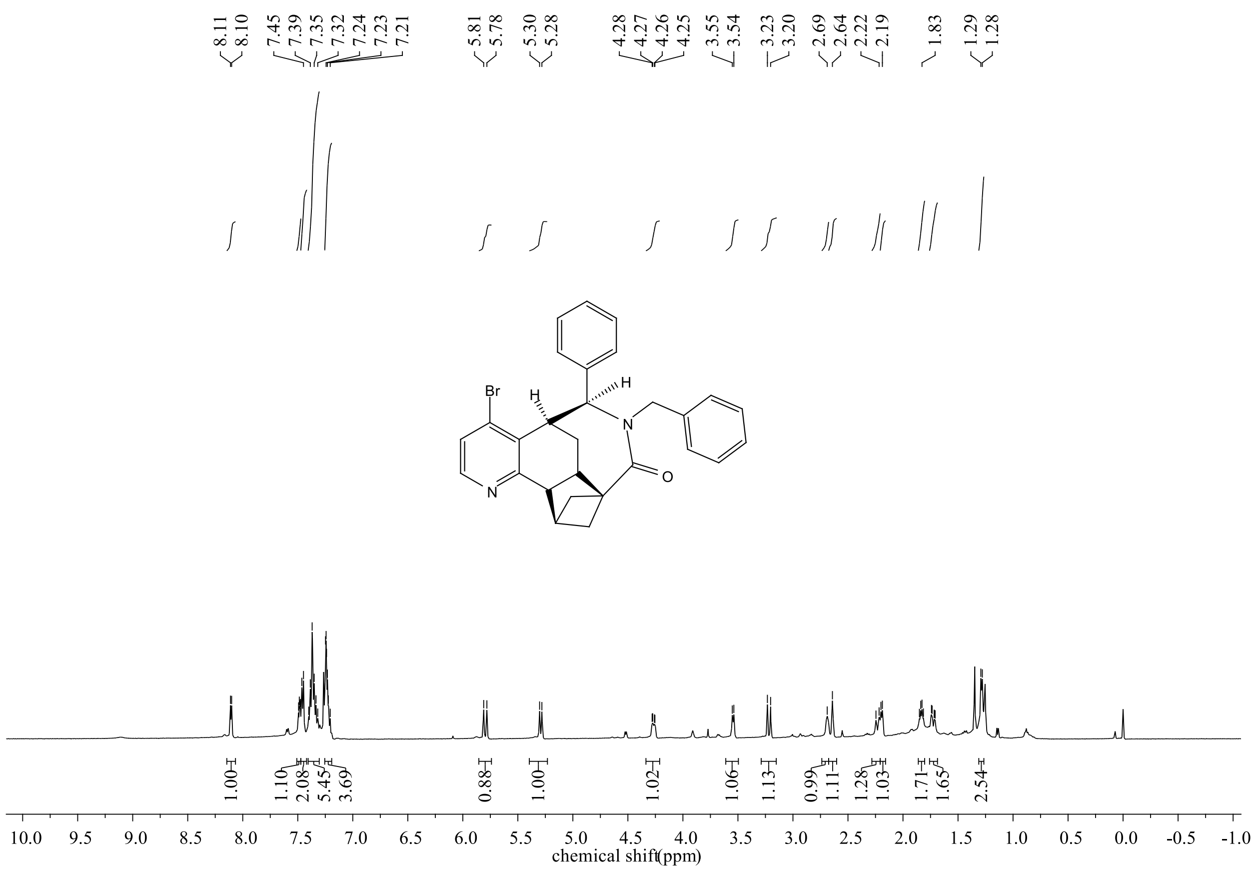
trans-**4J** ^{1}H NMR (500 MHz, $CDCl_3$)



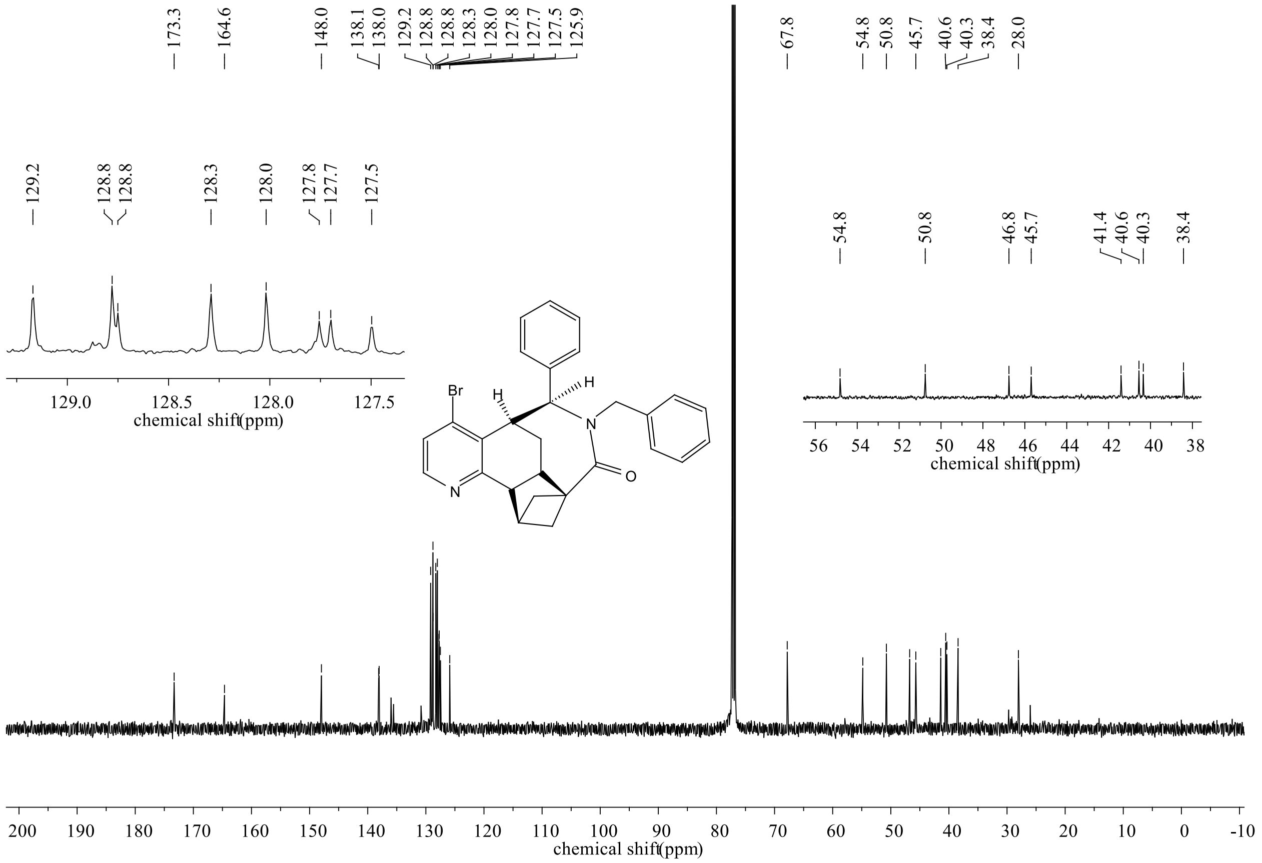
trans-**4J** ^{13}C NMR (126 MHz, CDCl$_3$)



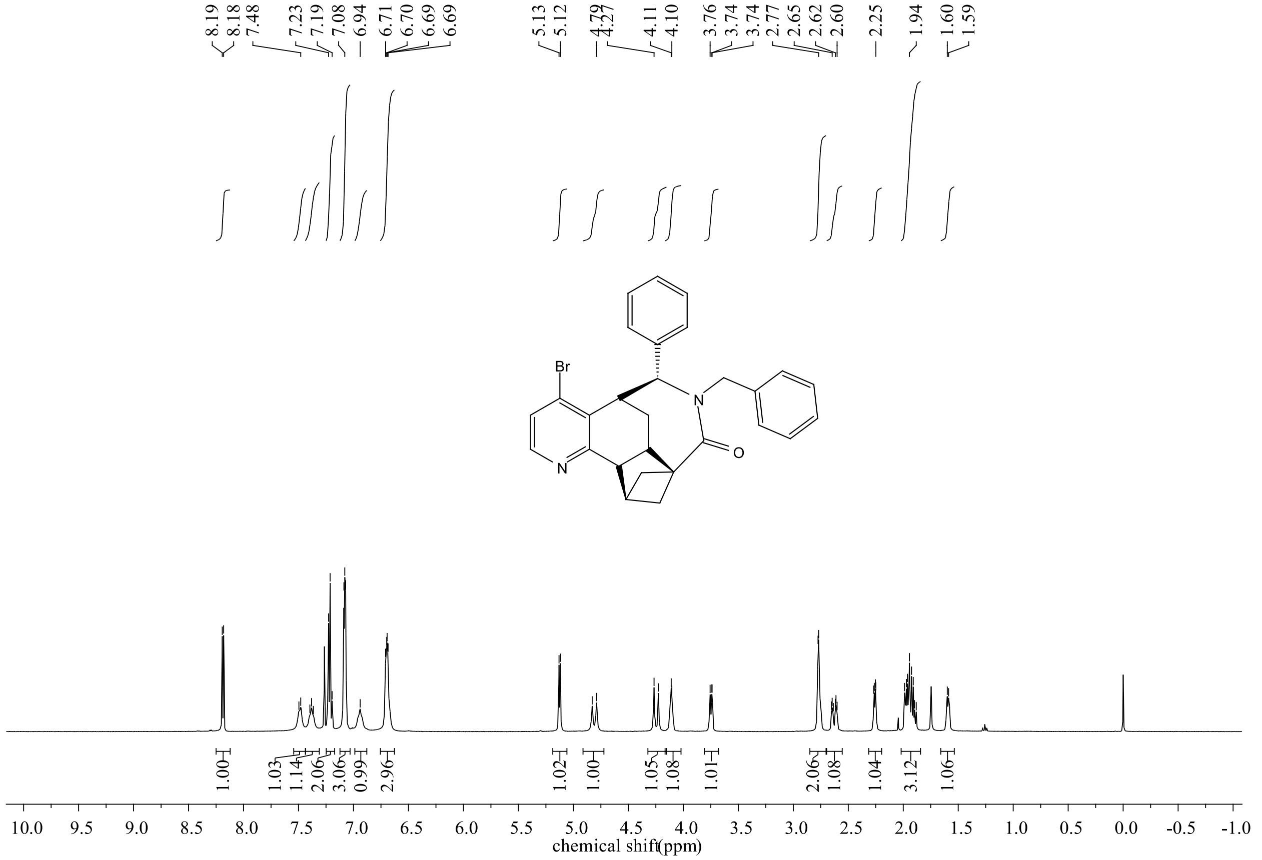
cis-**4K** ^{1}H NMR (500 MHz, CDCl$_3$)



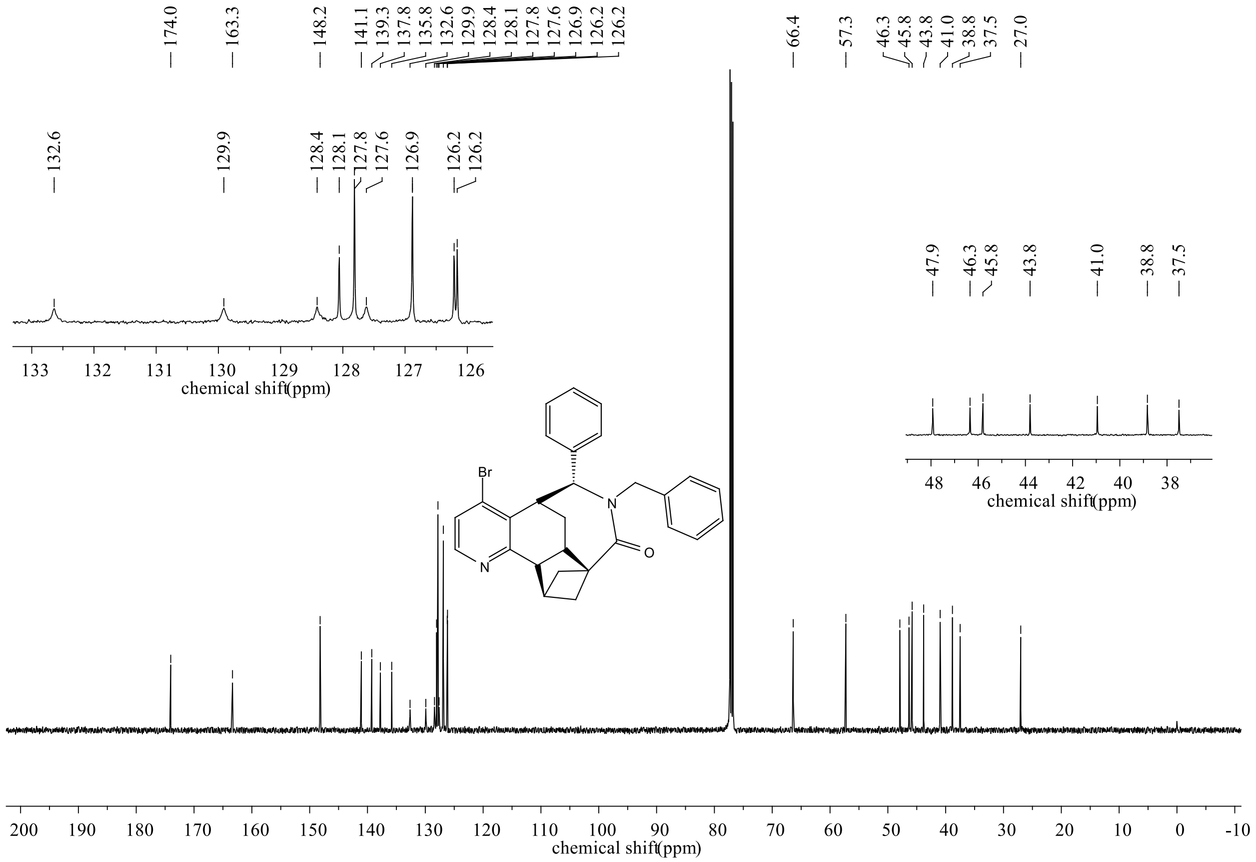
cis-**4K** ^{13}C NMR (126 MHz, $CDCl_3$)



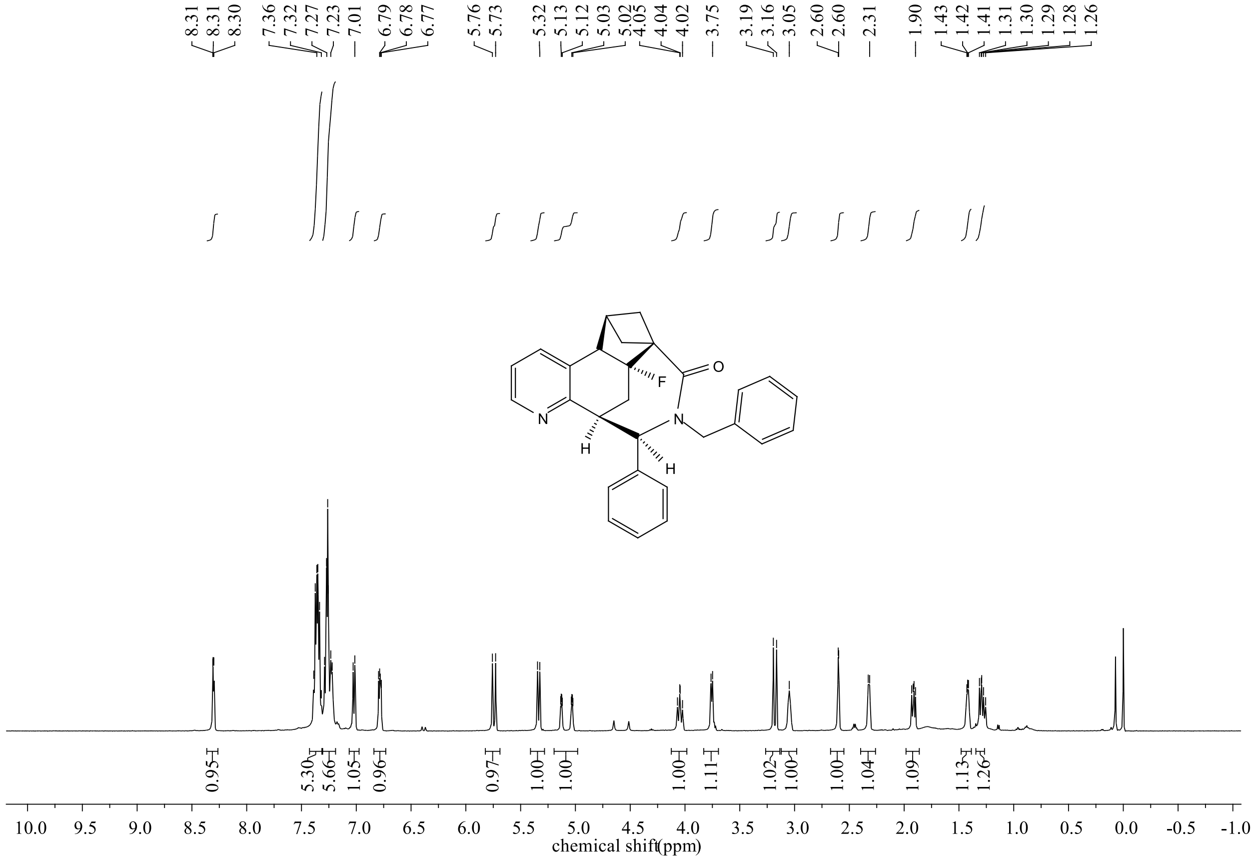
trans-**4K** ^{1}H NMR (400 MHz, $CDCl_3$)



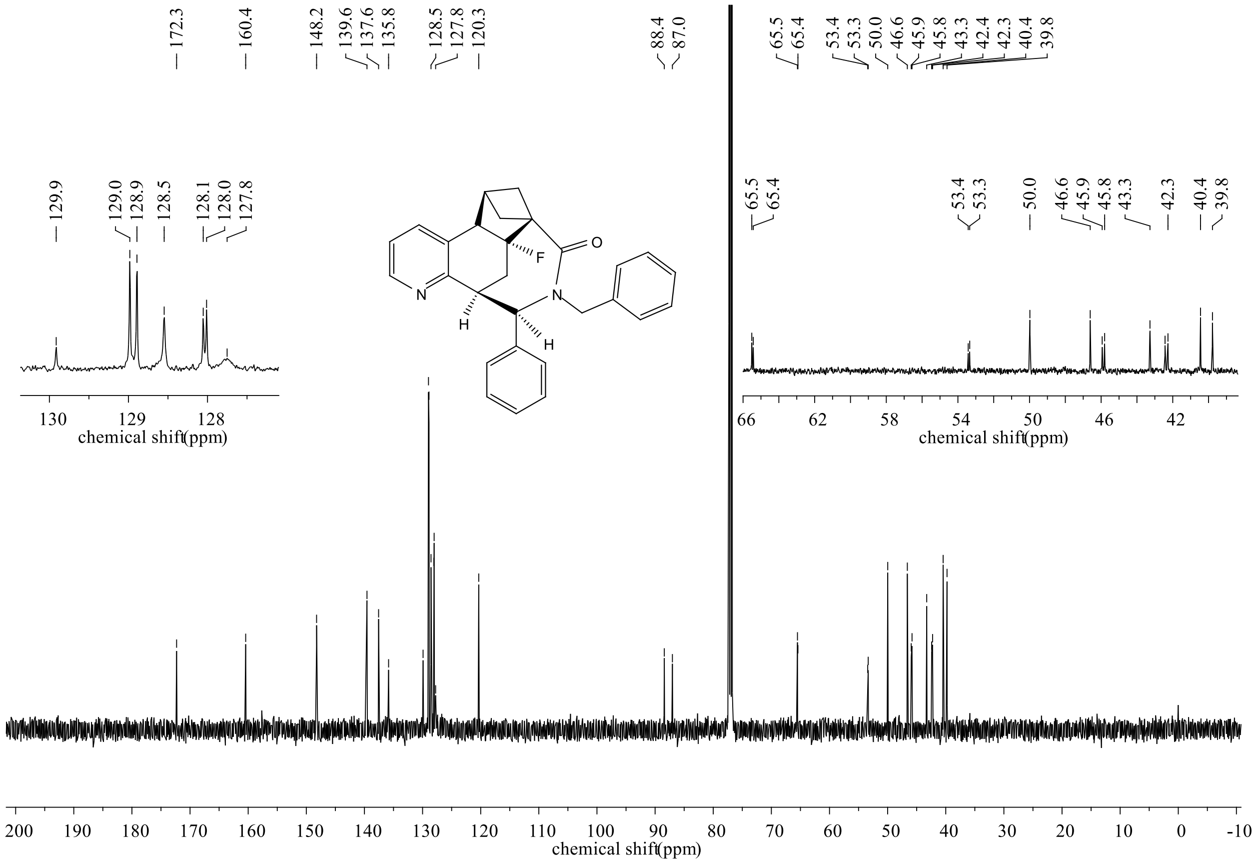
trans-**4K** ^{13}C NMR (126 MHz, CDCl$_3$)



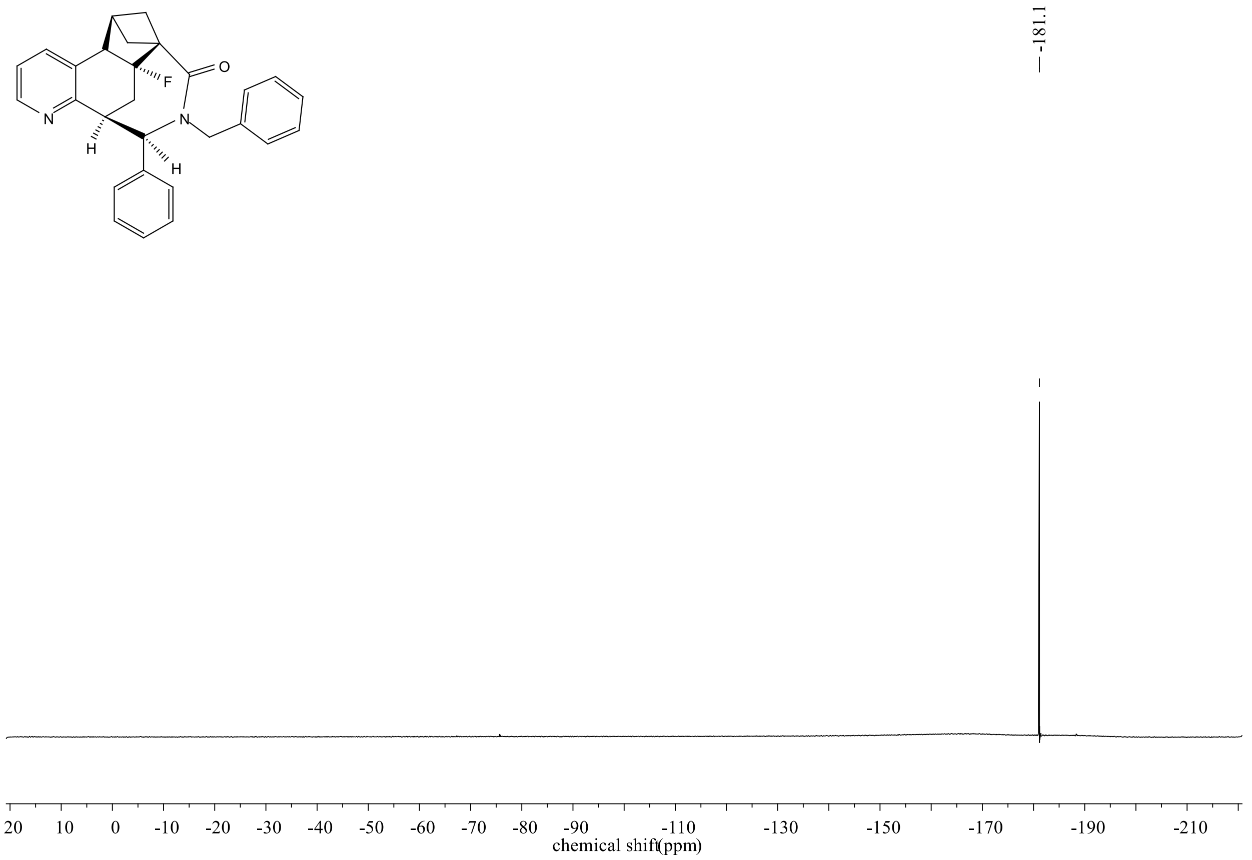
cis-**4l** ^{1}H NMR (500 MHz, CDCl$_3$)



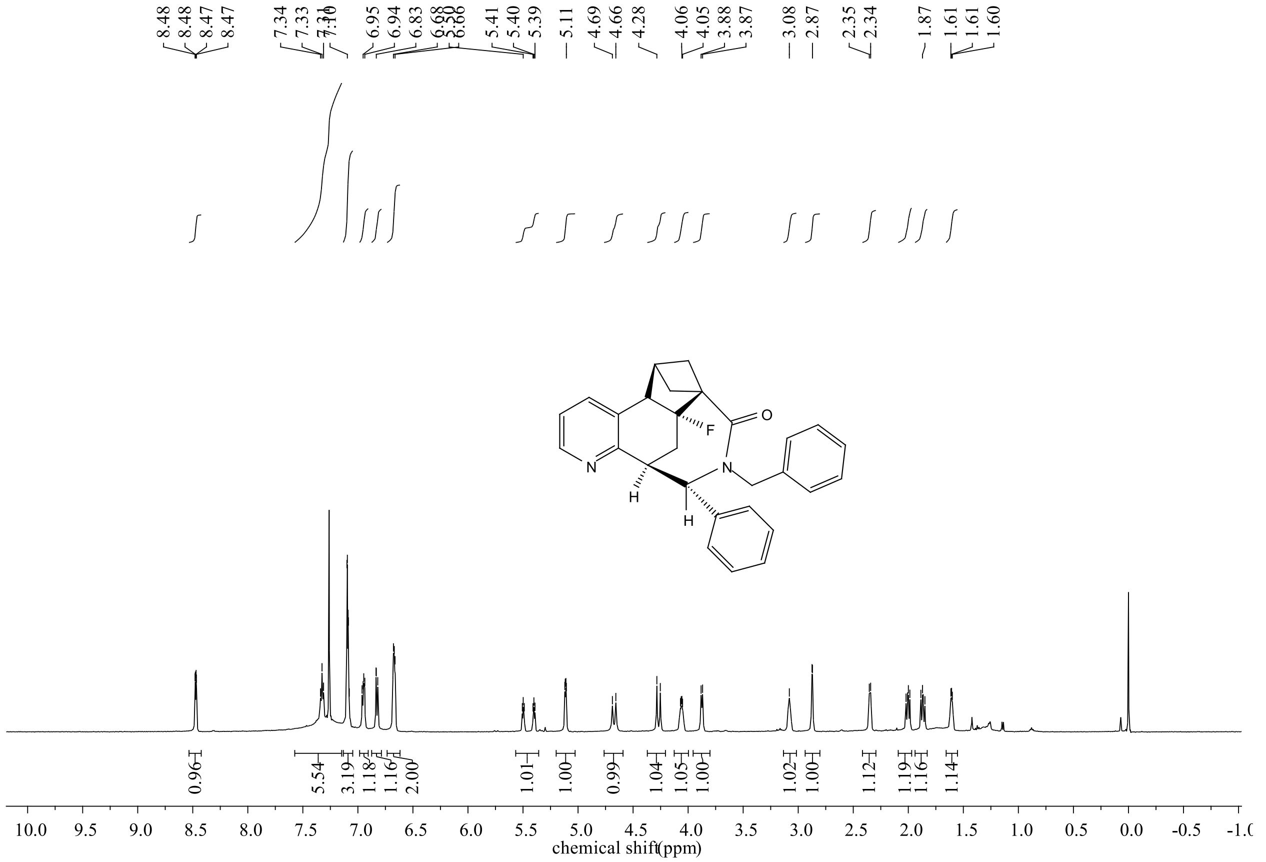
cis-**4l** ^{13}C NMR (126 MHz, CDCl$_3$)



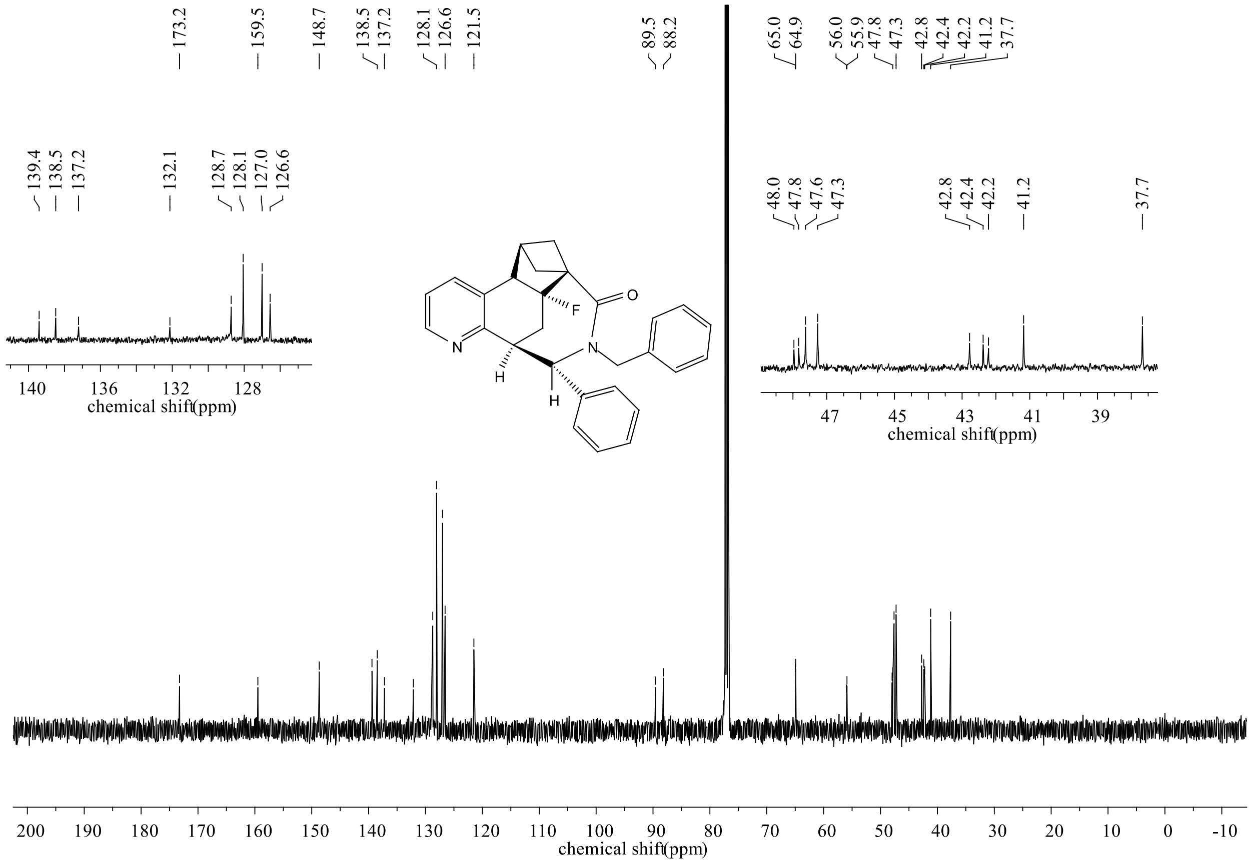
cis-**4l** ^{19}**F NMR** (470 MHz, CDCl$_3$)



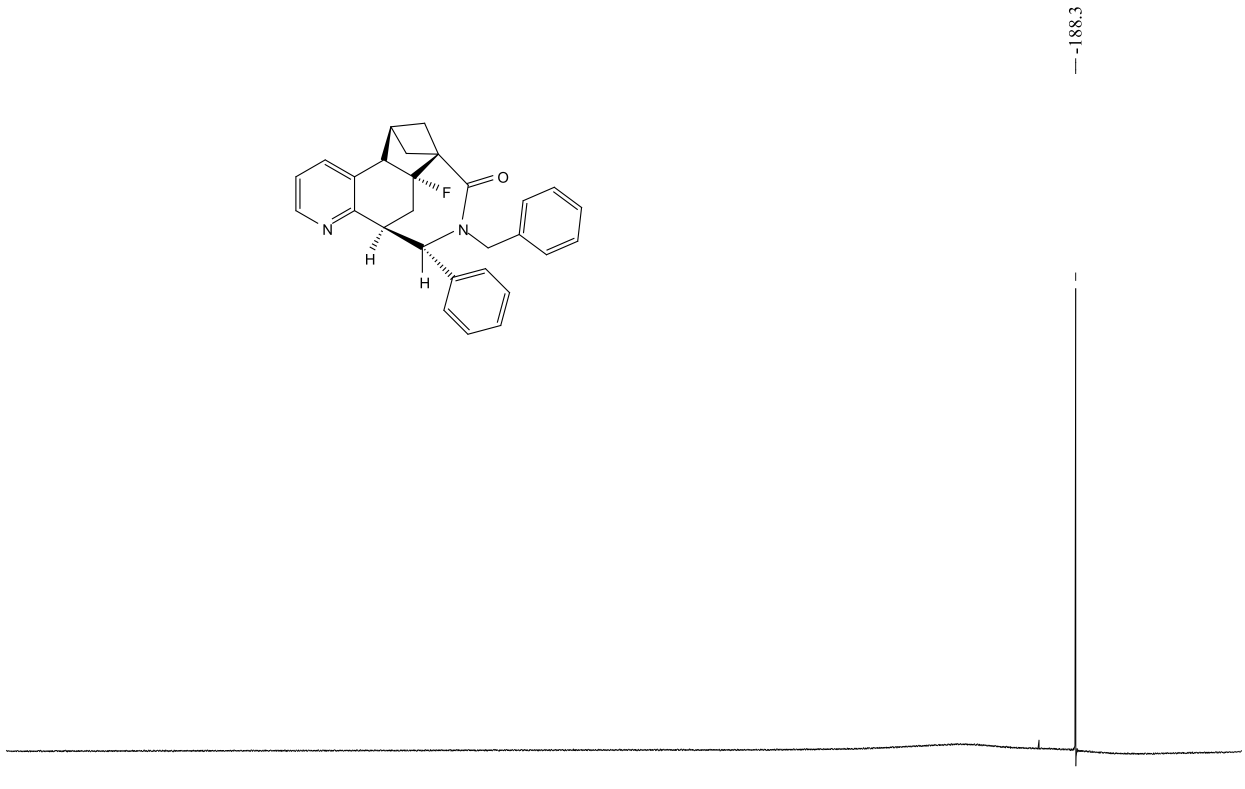
trans-**4l** ^{1}H NMR (500 MHz, $CDCl_3$)



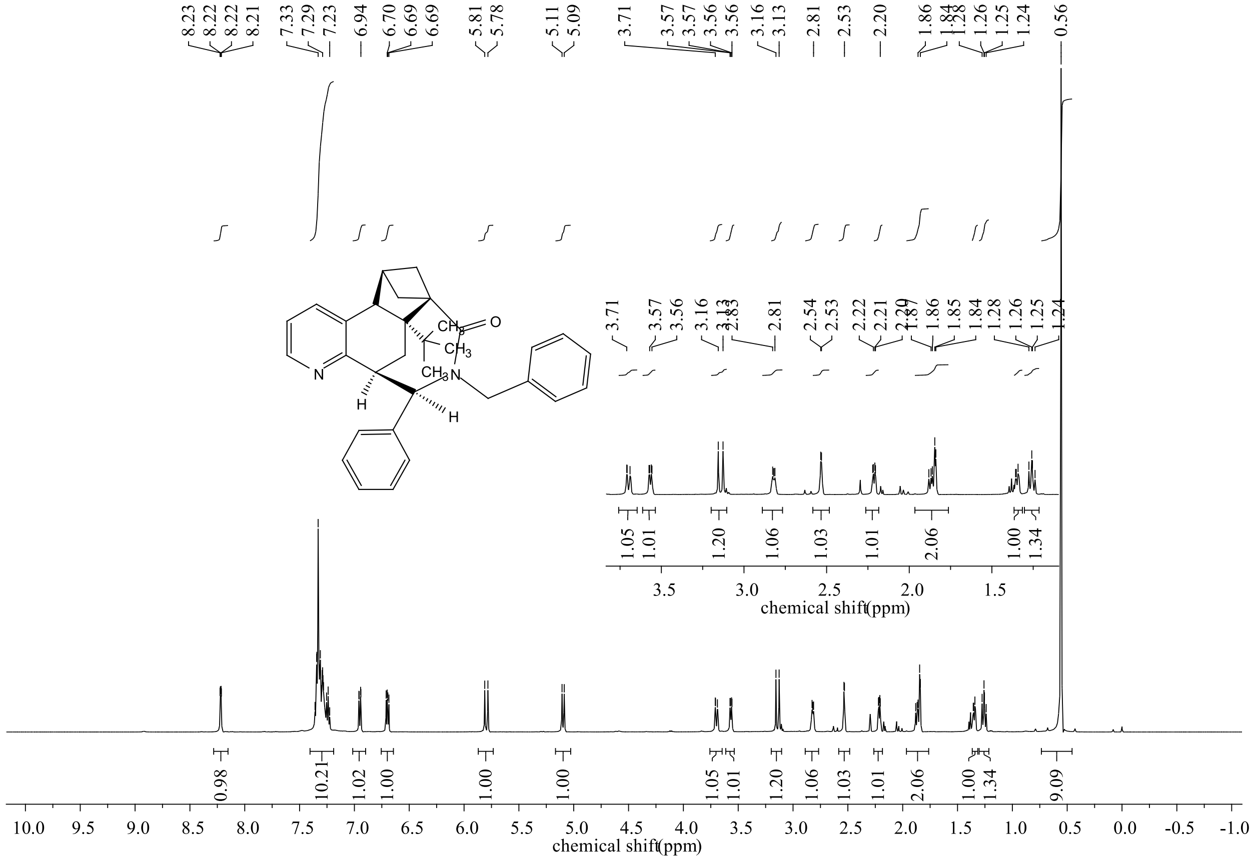
trans-**4l** ^{13}C NMR (126 MHz, $CDCl_3$)



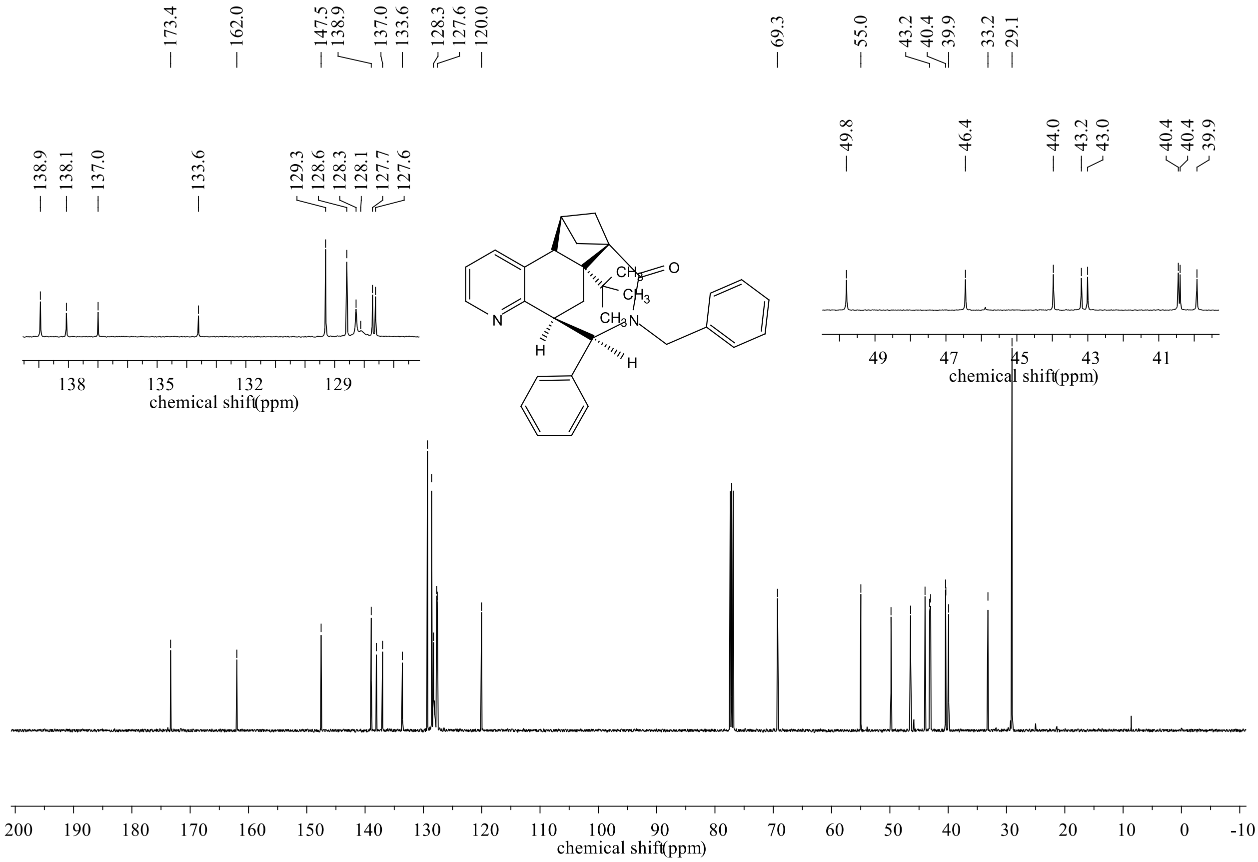
trans-**4l** **^{19}F NMR** (470 MHz, $CDCl_3$)



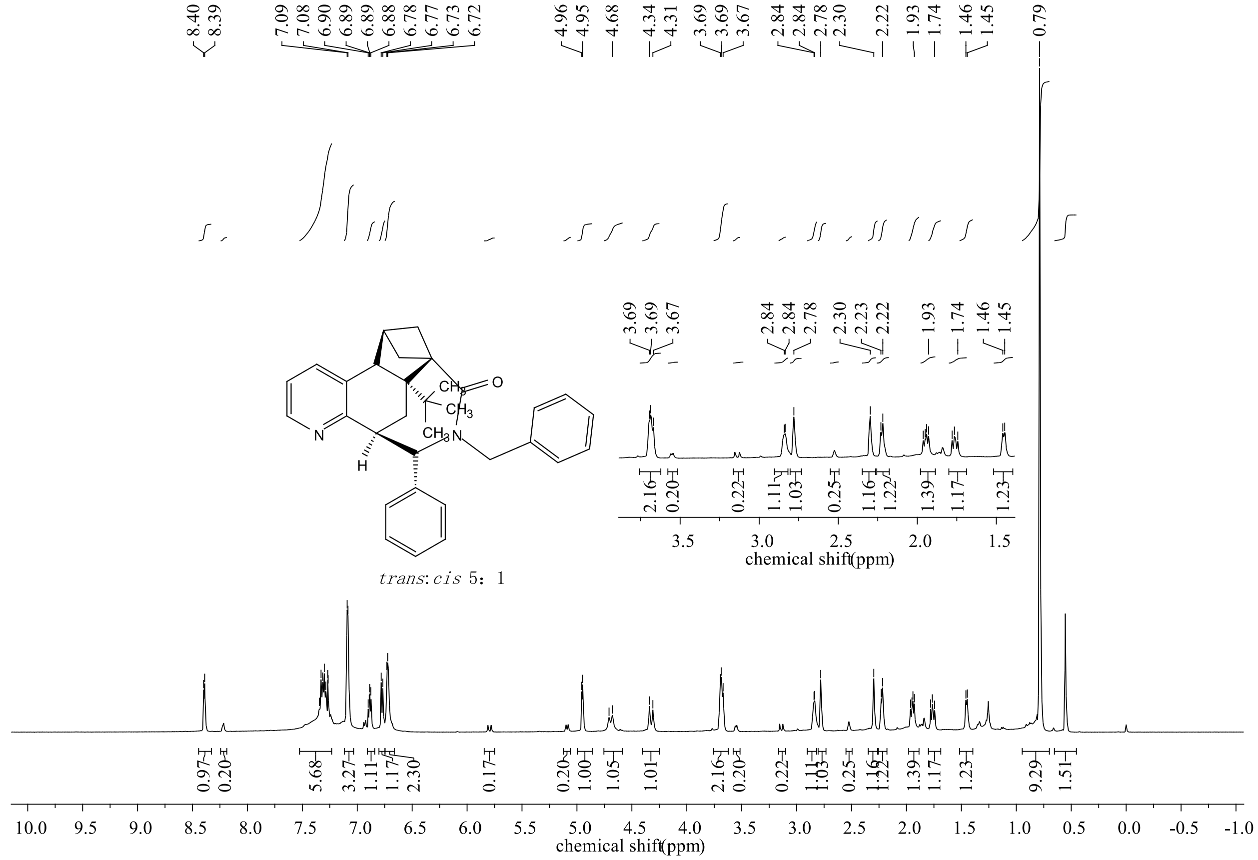
cis-**4m** ^{1}H NMR (500 MHz, $CDCl_3$)



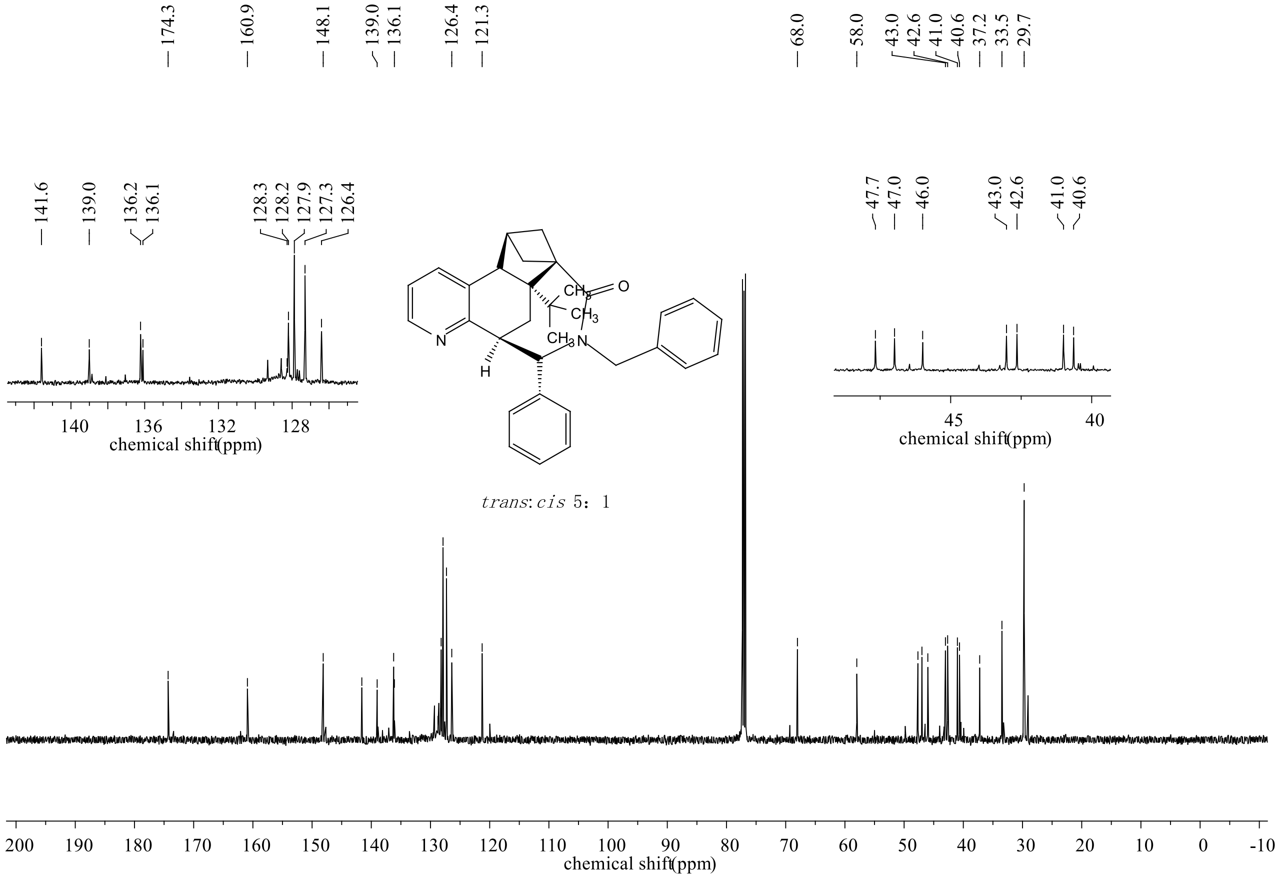
cis-**4m** ^{13}C NMR (126 MHz, $CDCl_3$)



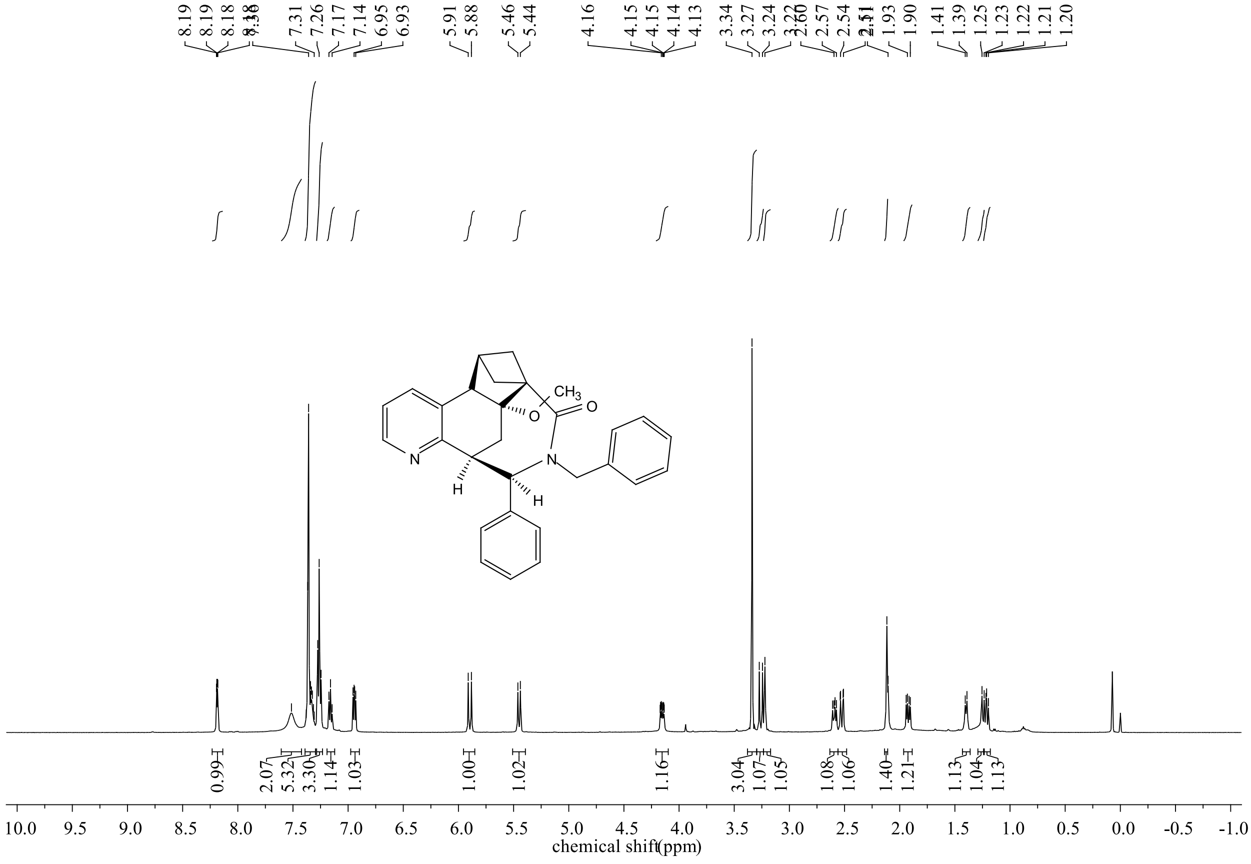
trans-**4m** ^{1}H NMR (500 MHz, $CDCl_3$)



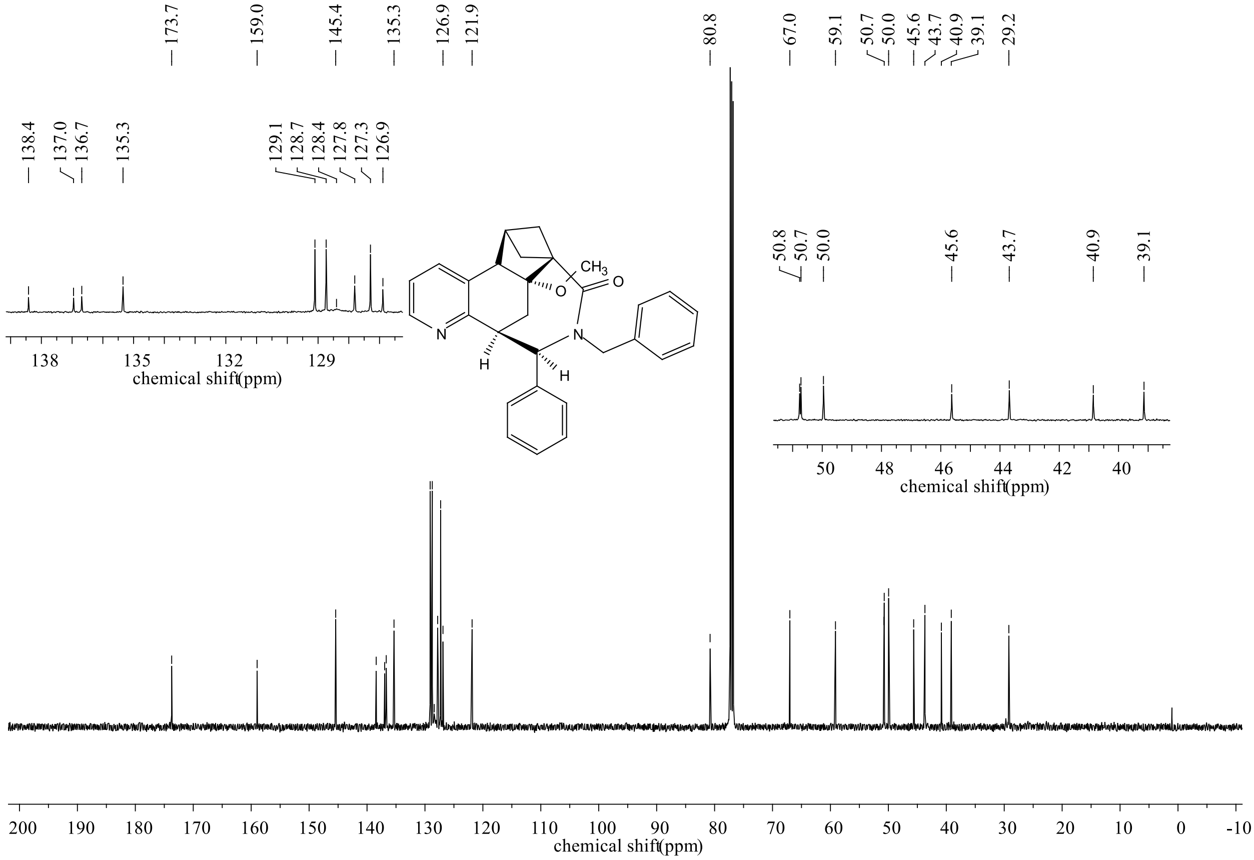
trans-**4m** ^{13}C NMR (126 MHz, CDCl$_3$)



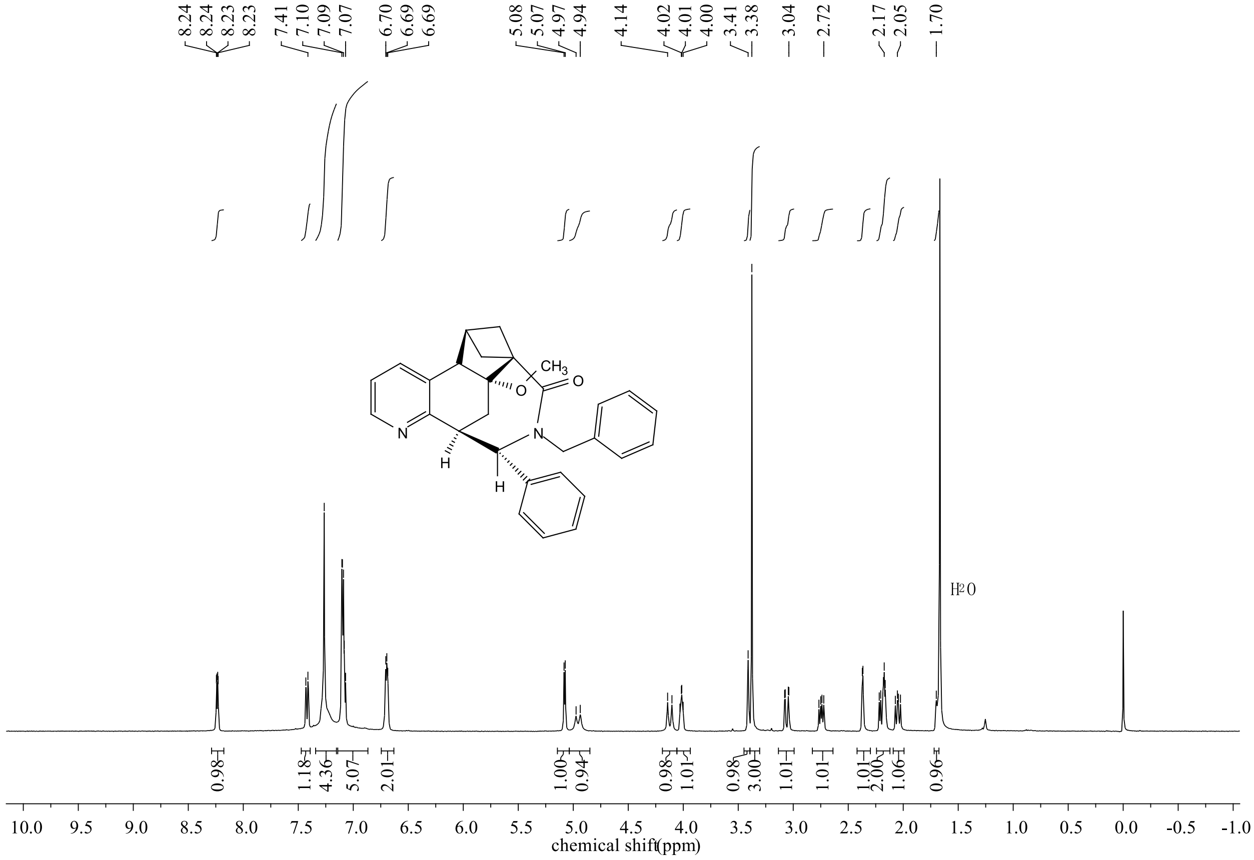
cis-**4n** ^{1}H NMR (500 MHz, CDCl$_3$)



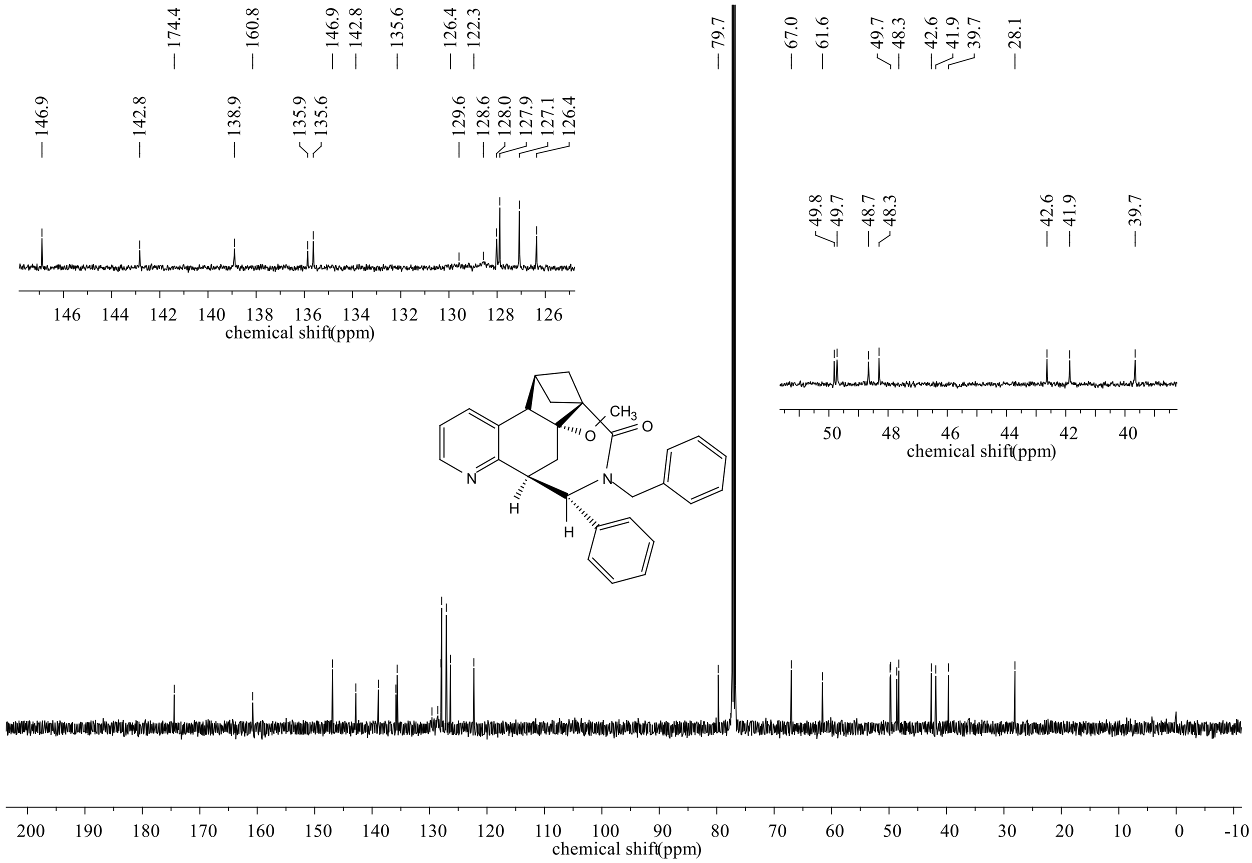
cis-**4n** ^{13}C NMR (126 MHz, $CDCl_3$)



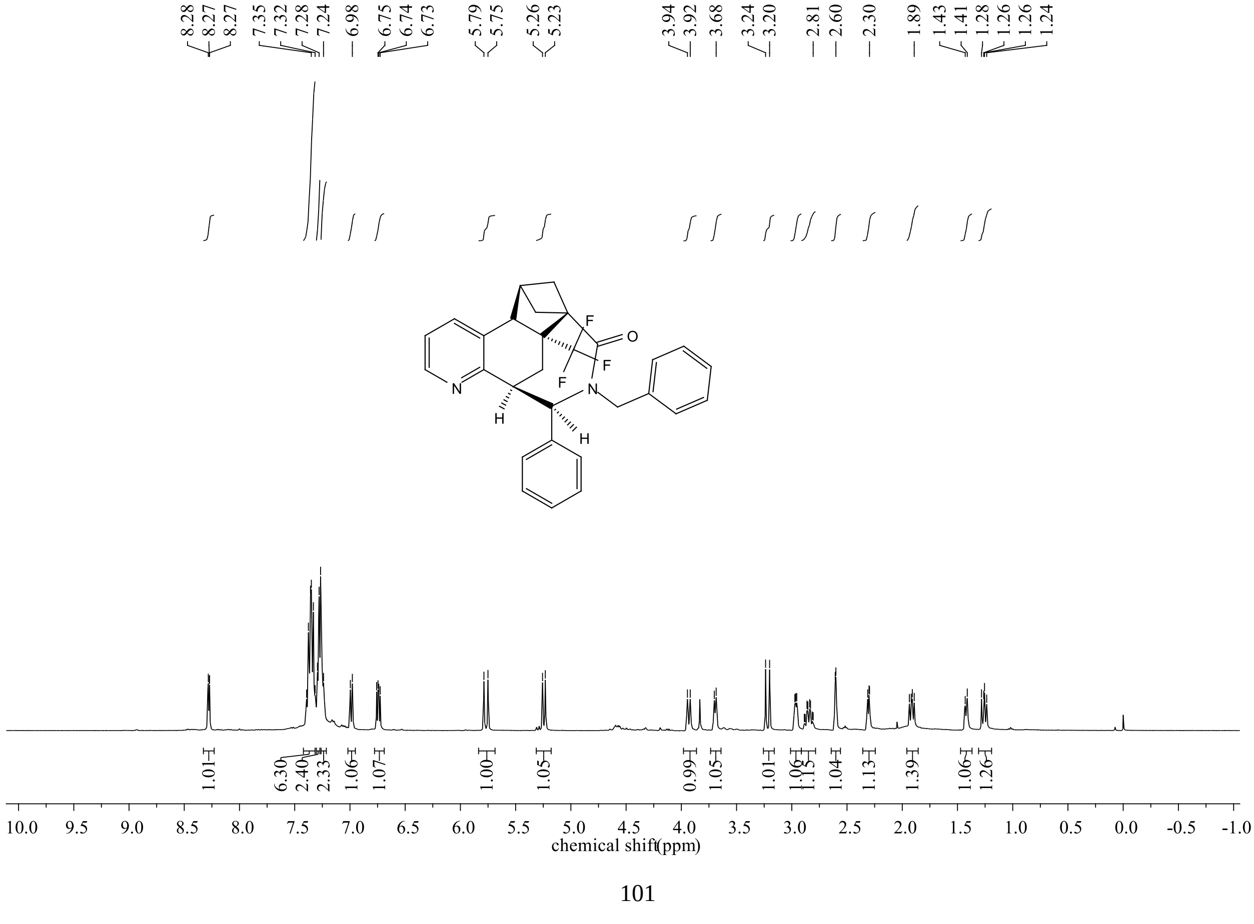
trans-**4n** ^{1}H NMR (400 MHz, $CDCl_3$)



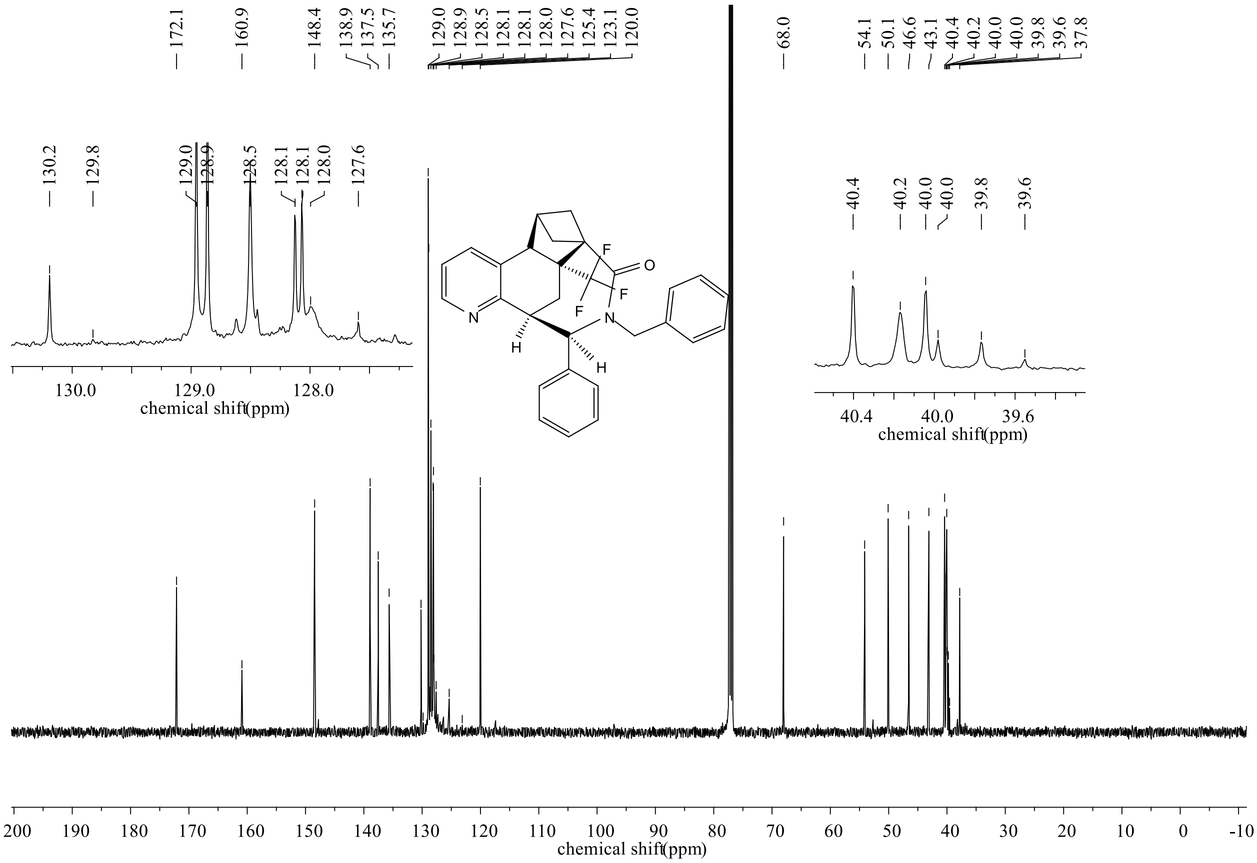
trans-**4n** ^{13}C NMR (126 MHz, $CDCl_3$)



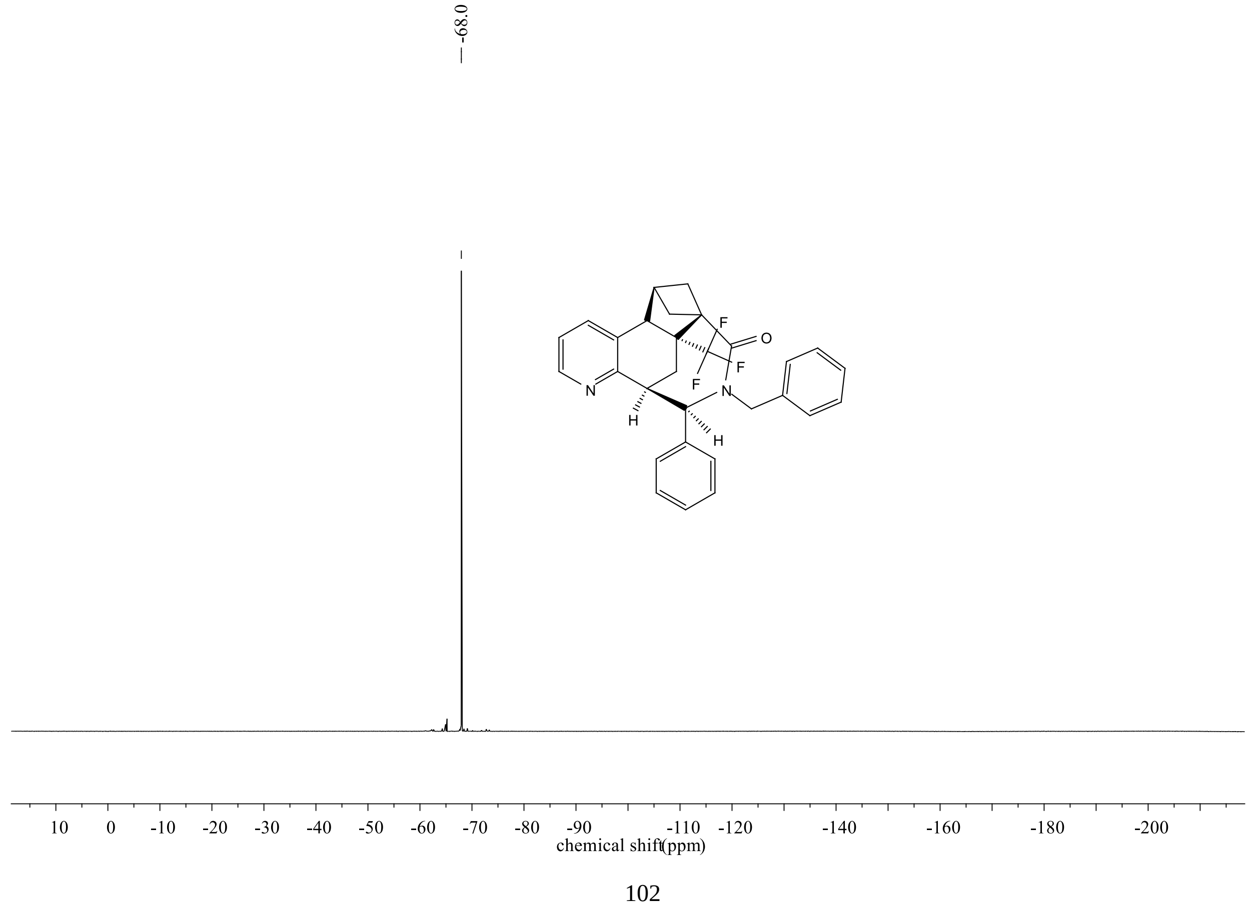
cis-**4o** ^{1}H NMR (400 MHz, $CDCl_3$)



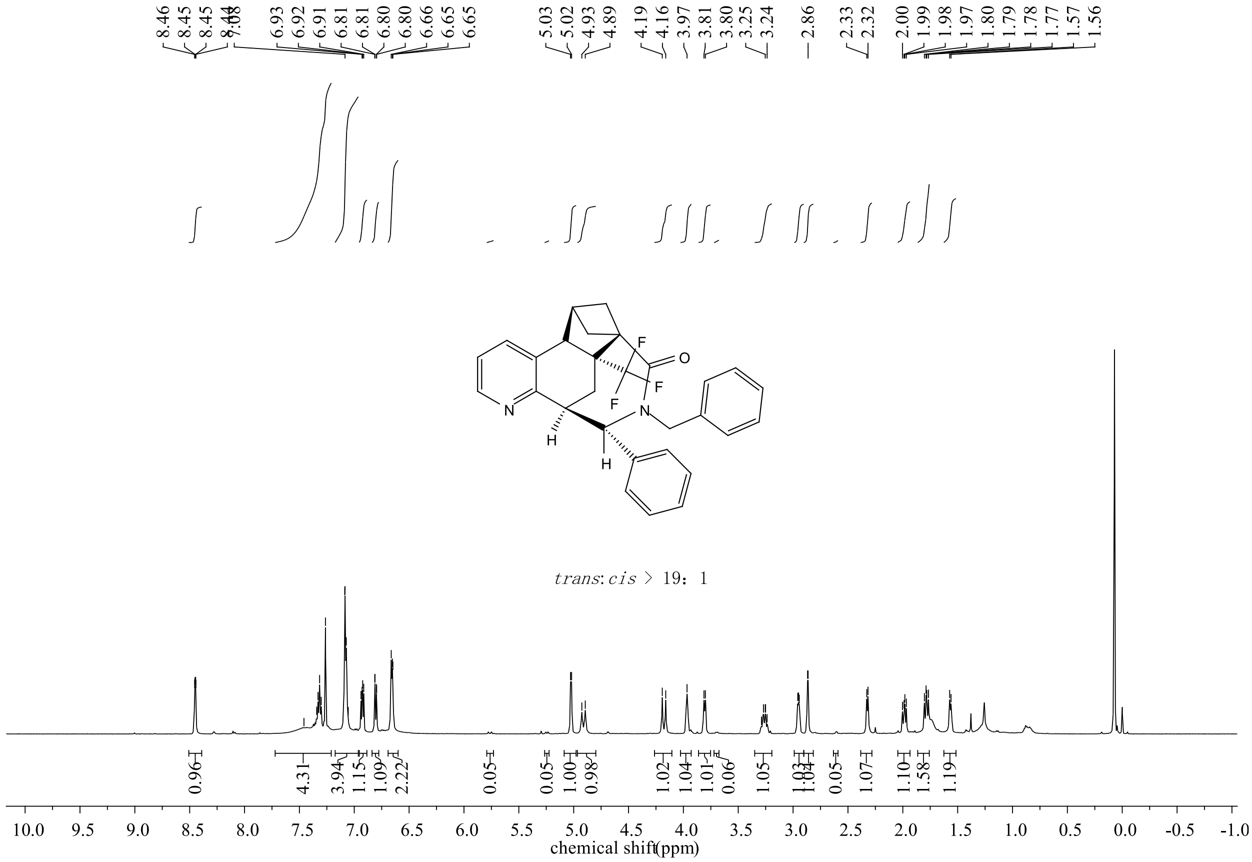
cis-**4o** ^{13}C NMR (126 MHz, CDCl$_3$)



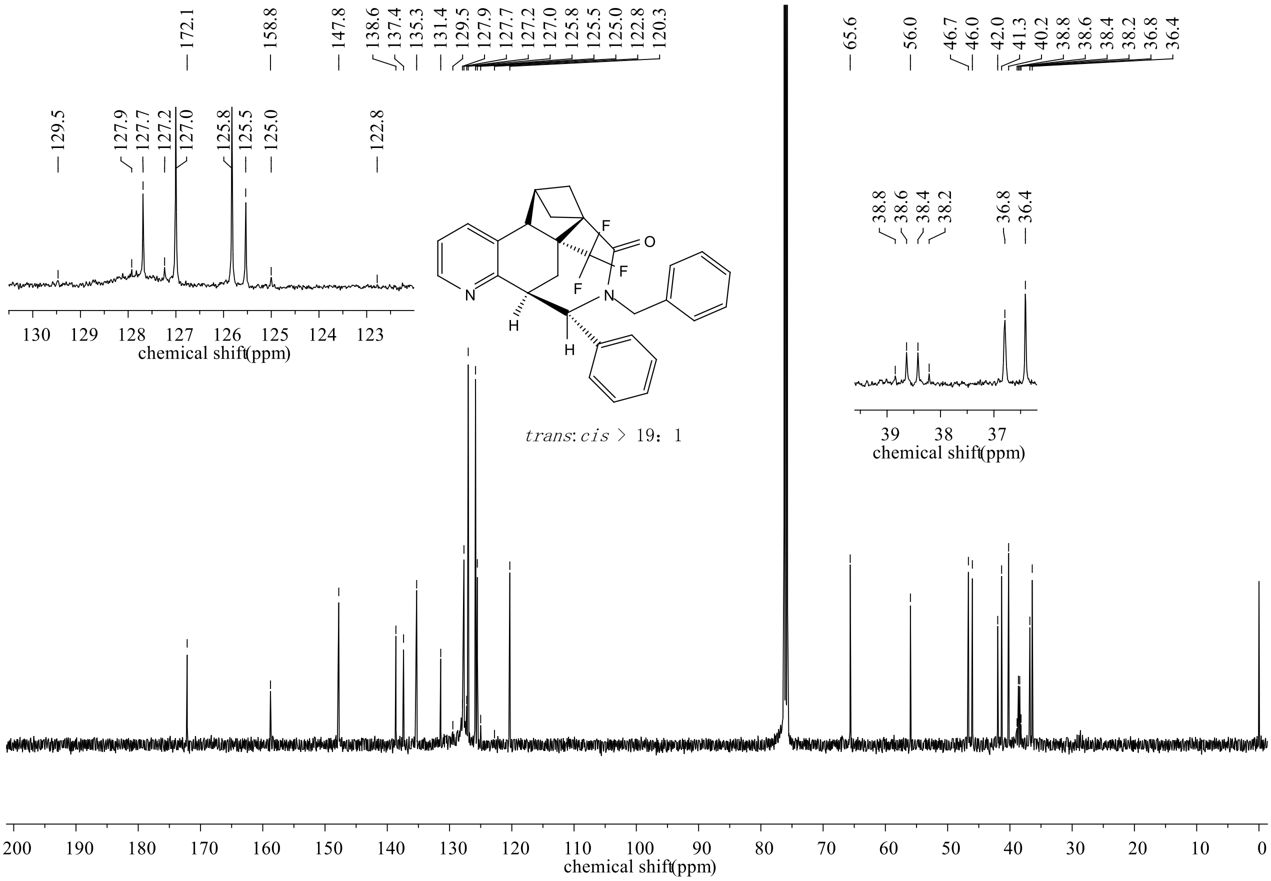
cis-**4o** ^{19}F NMR (377 MHz, CDCl$_3$)



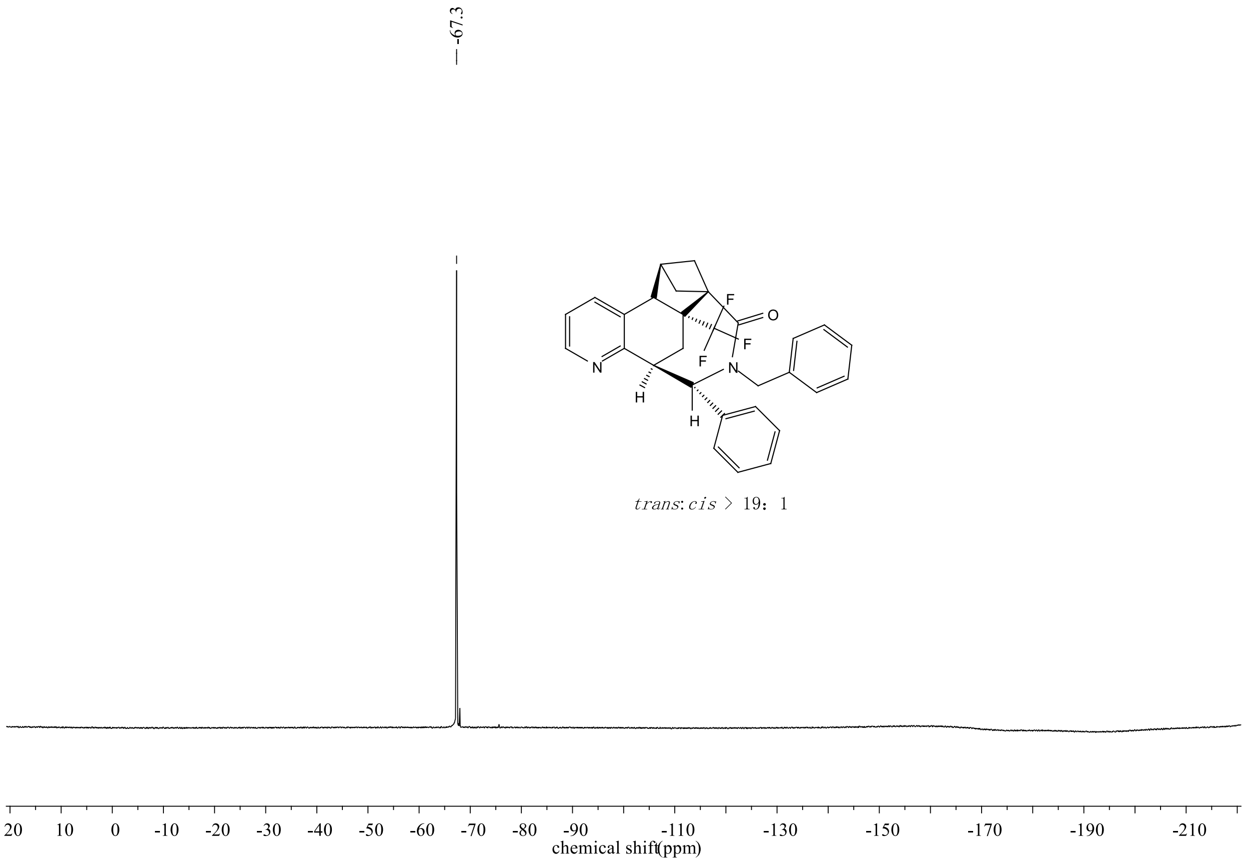
trans-**4o** ^{1}H NMR (400 MHz, CDCl$_3$)



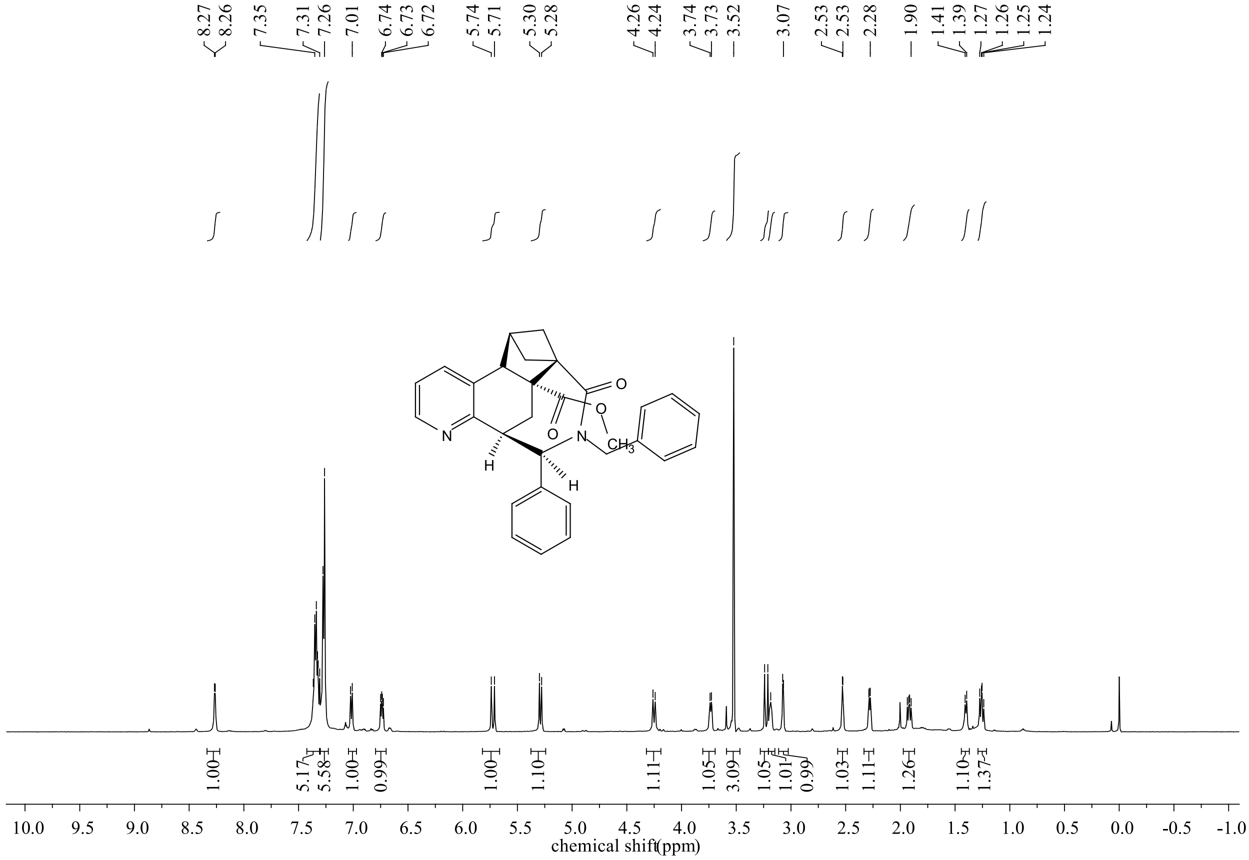
trans-**4o** ^{13}C NMR (126 MHz, CDCl$_3$)



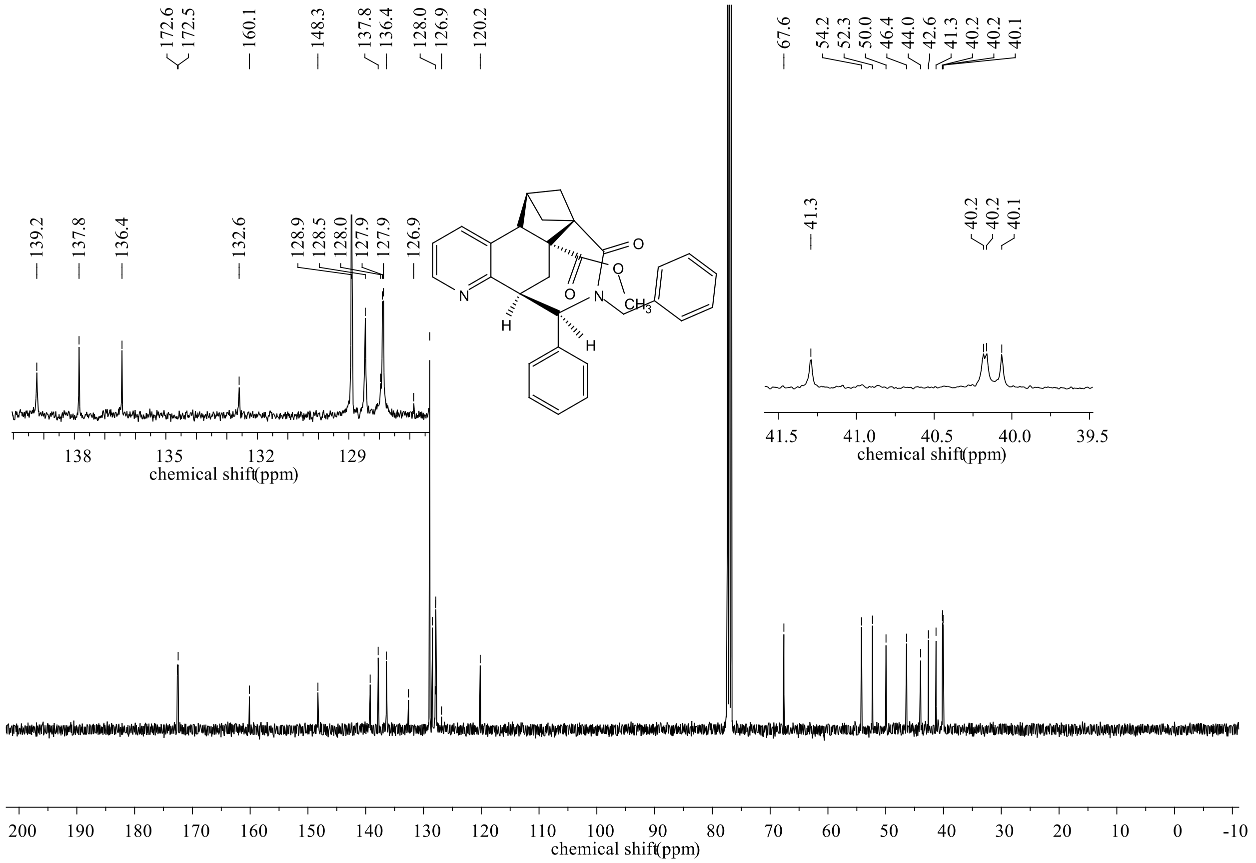
trans-**4o** ^{19}F NMR (470 MHz, $CDCl_3$)



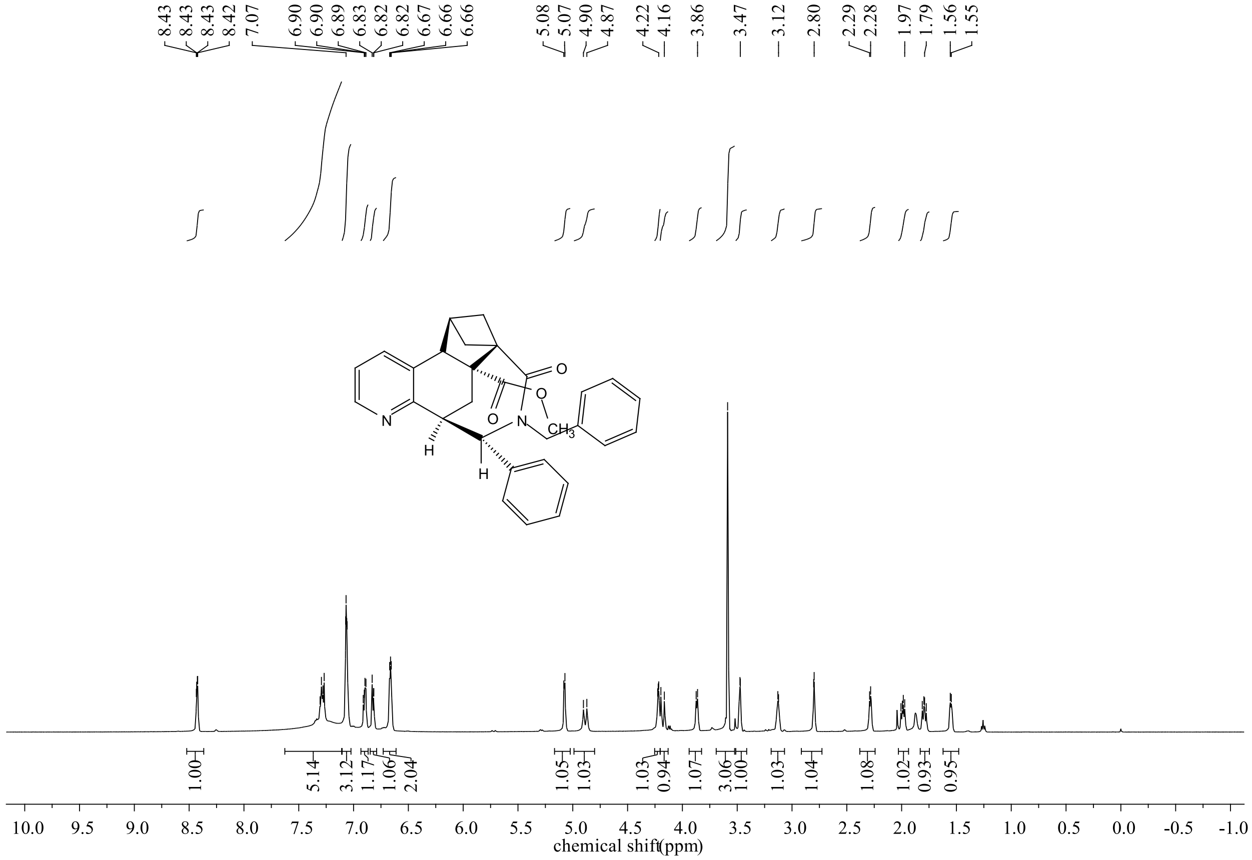
cis-**4p** ^{1}H NMR (500 MHz, $CDCl_3$)



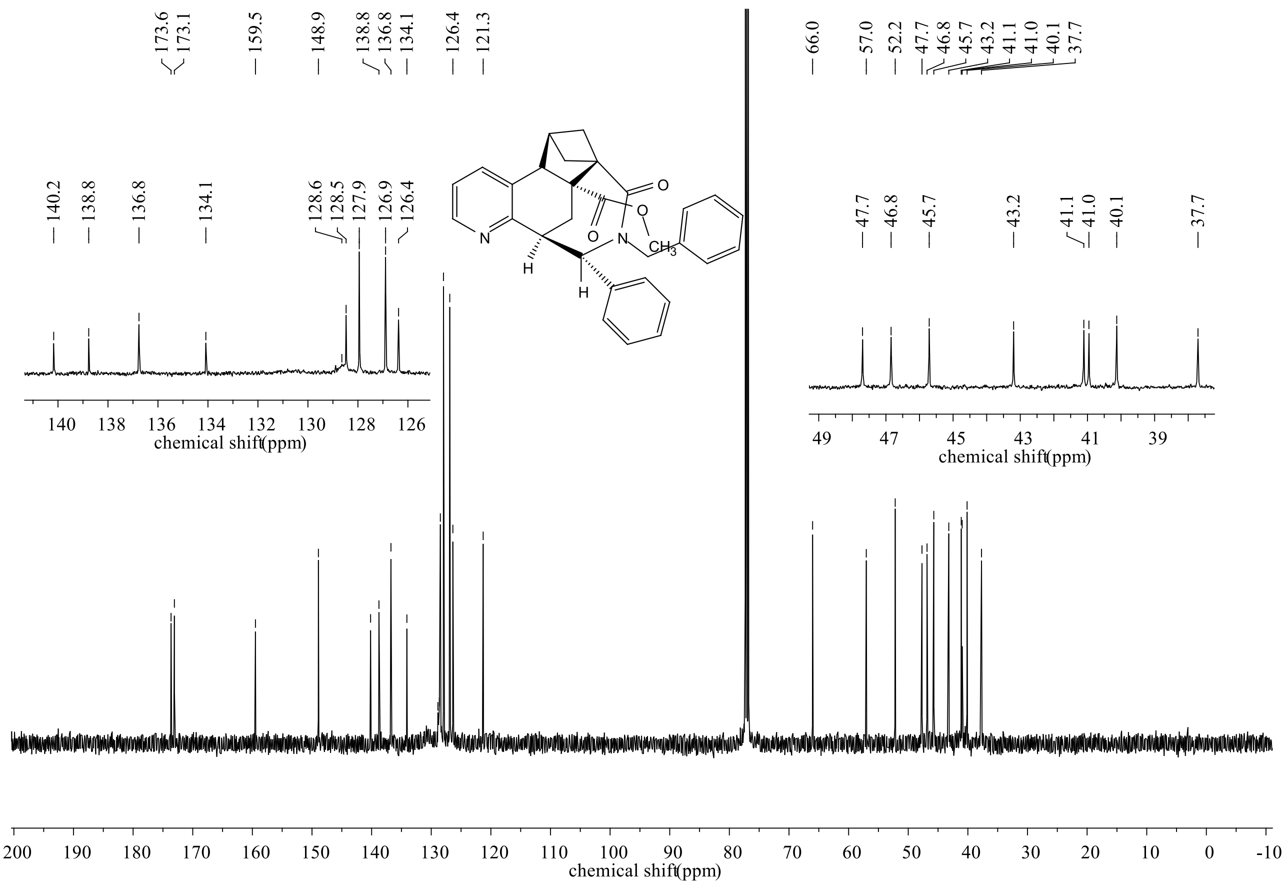
cis-**4p** ^{13}C NMR (101 MHz, CDCl$_3$)



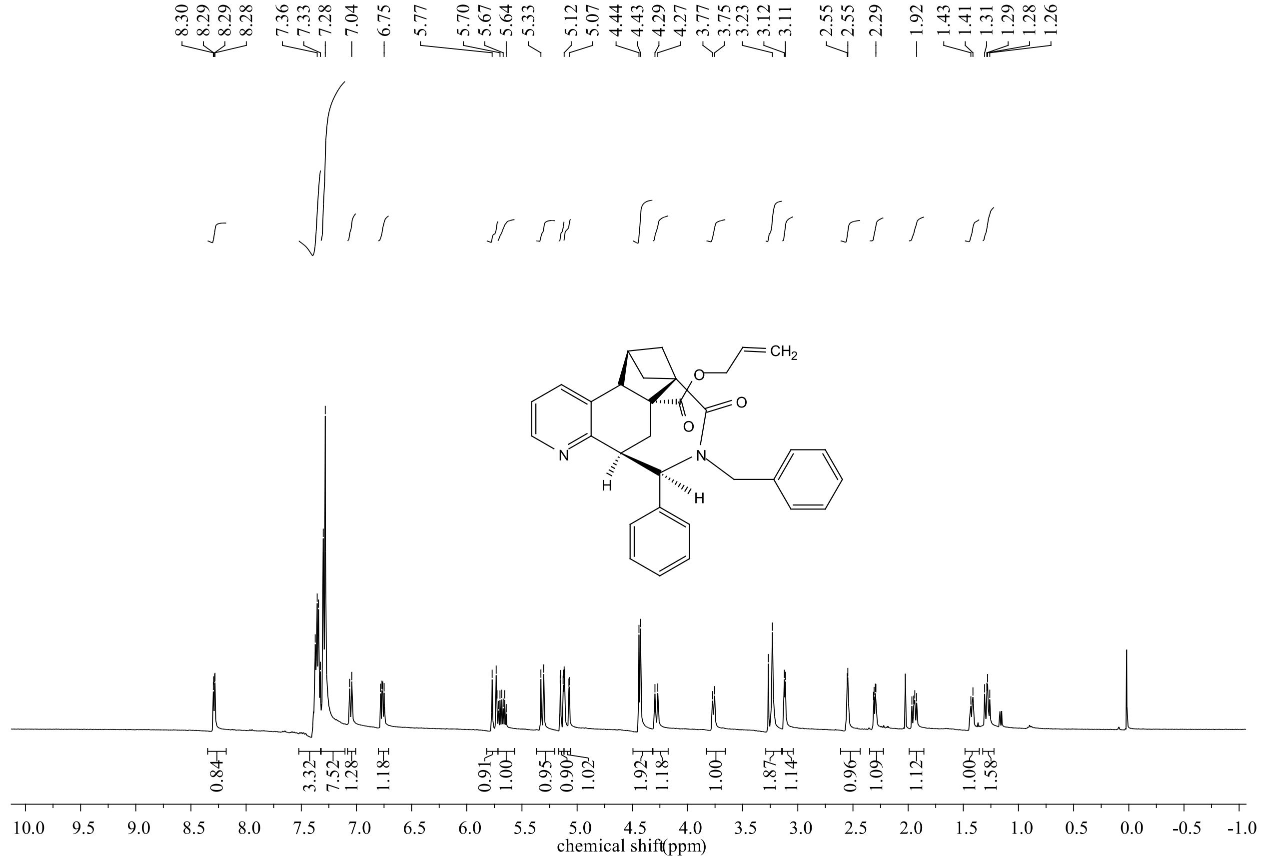
trans-**4p** ^{1}H NMR (500 MHz, CDCl$_3$)



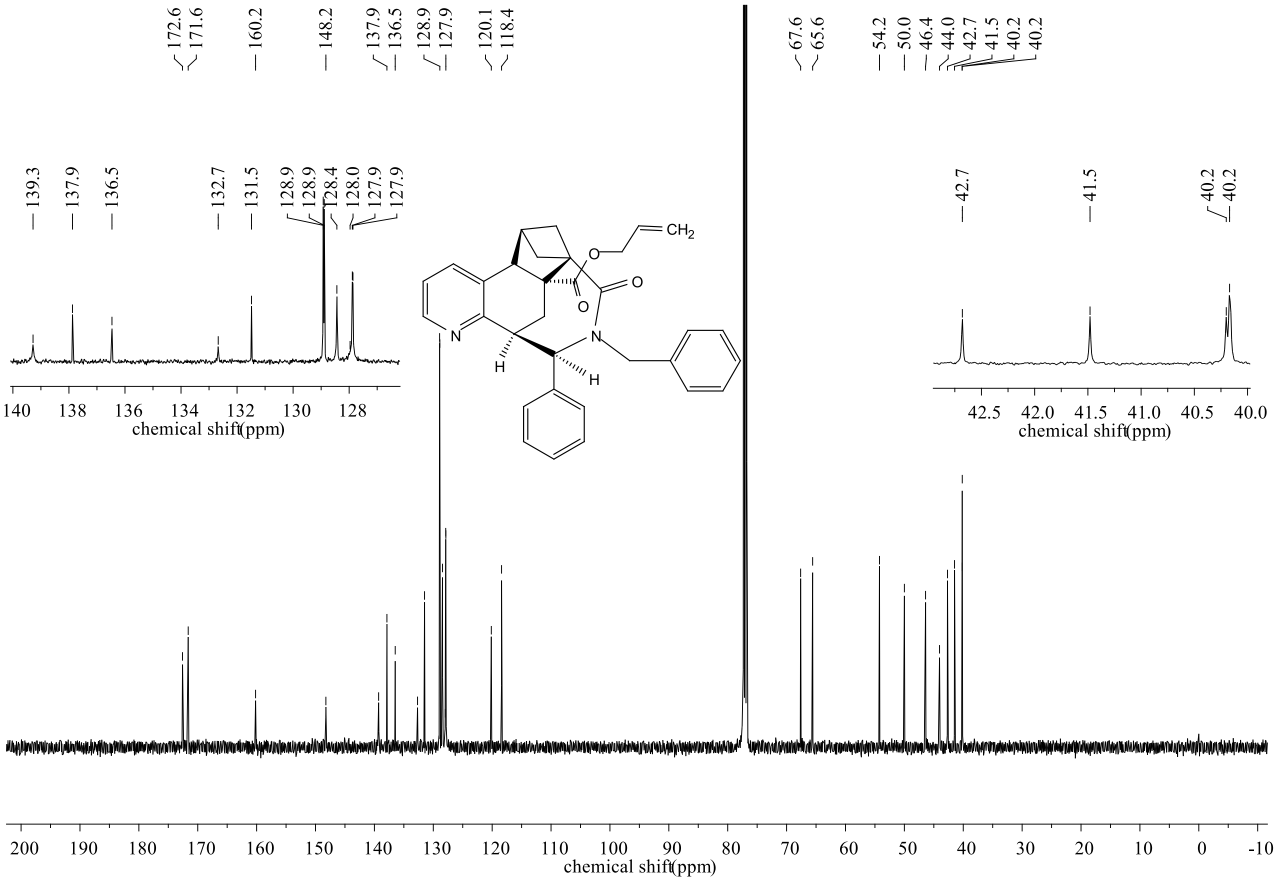
trans-**4p** ^{13}C NMR (126 MHz, CDCl$_3$)



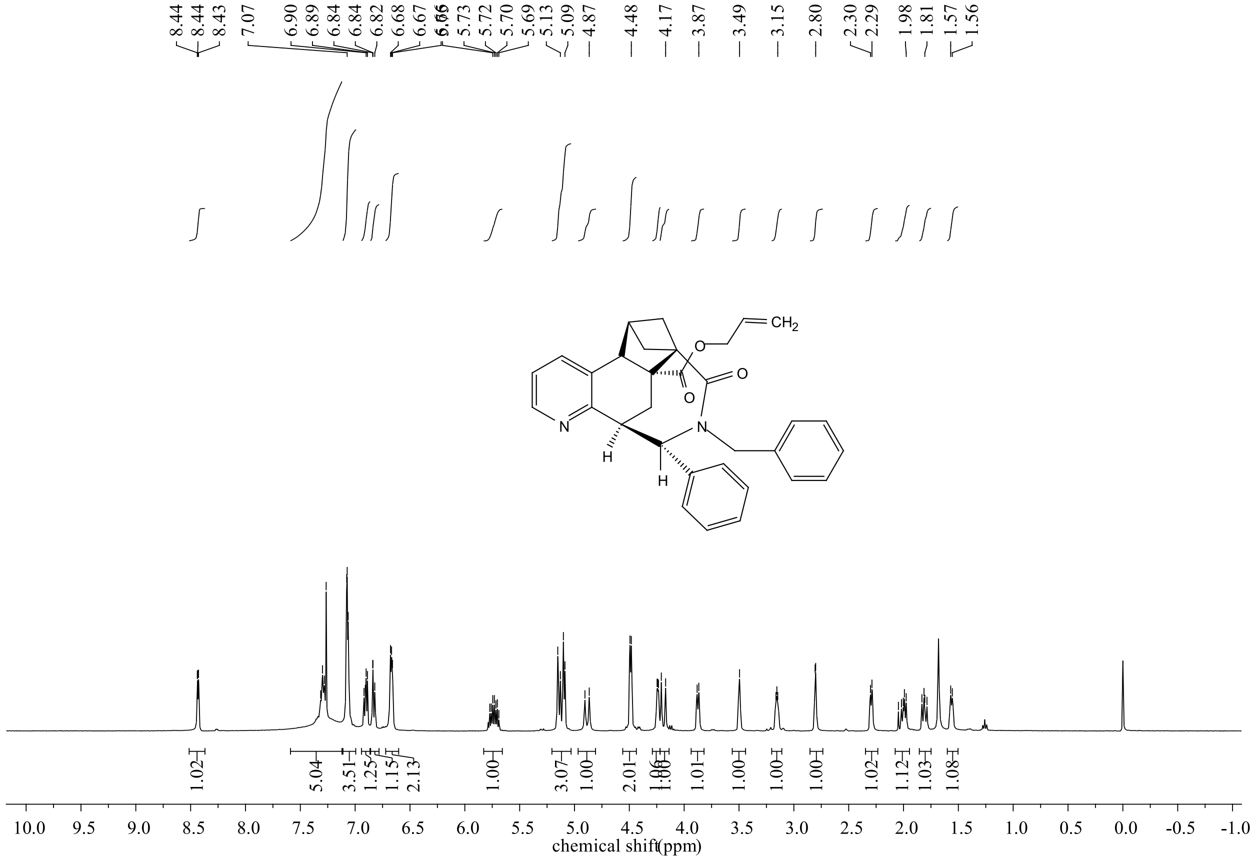
cis-**4q** ^{1}H NMR (400 MHz, CDCl$_3$)



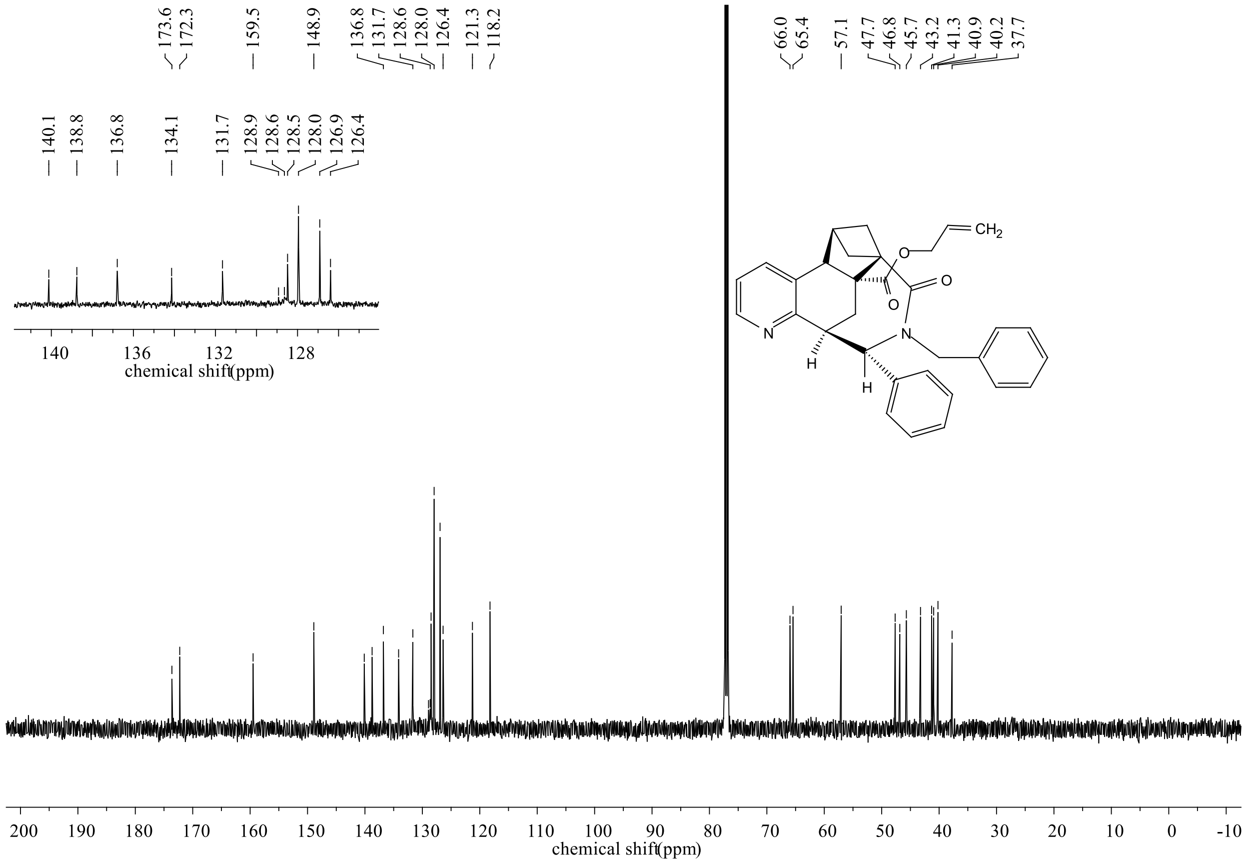
cis-**4q** ^{13}C NMR (126 MHz, $CDCl_3$)



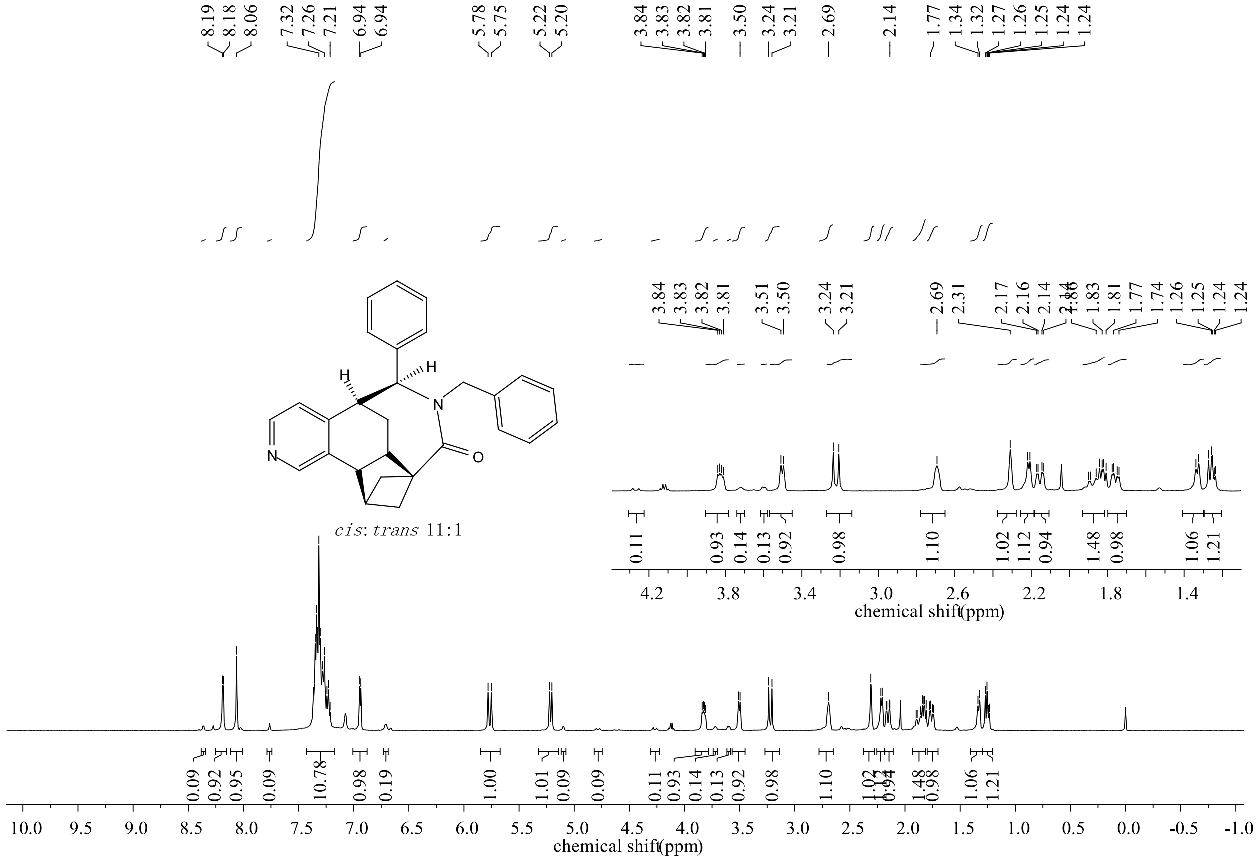
trans-**4q** ^{1}H NMR (400 MHz, $CDCl_3$)



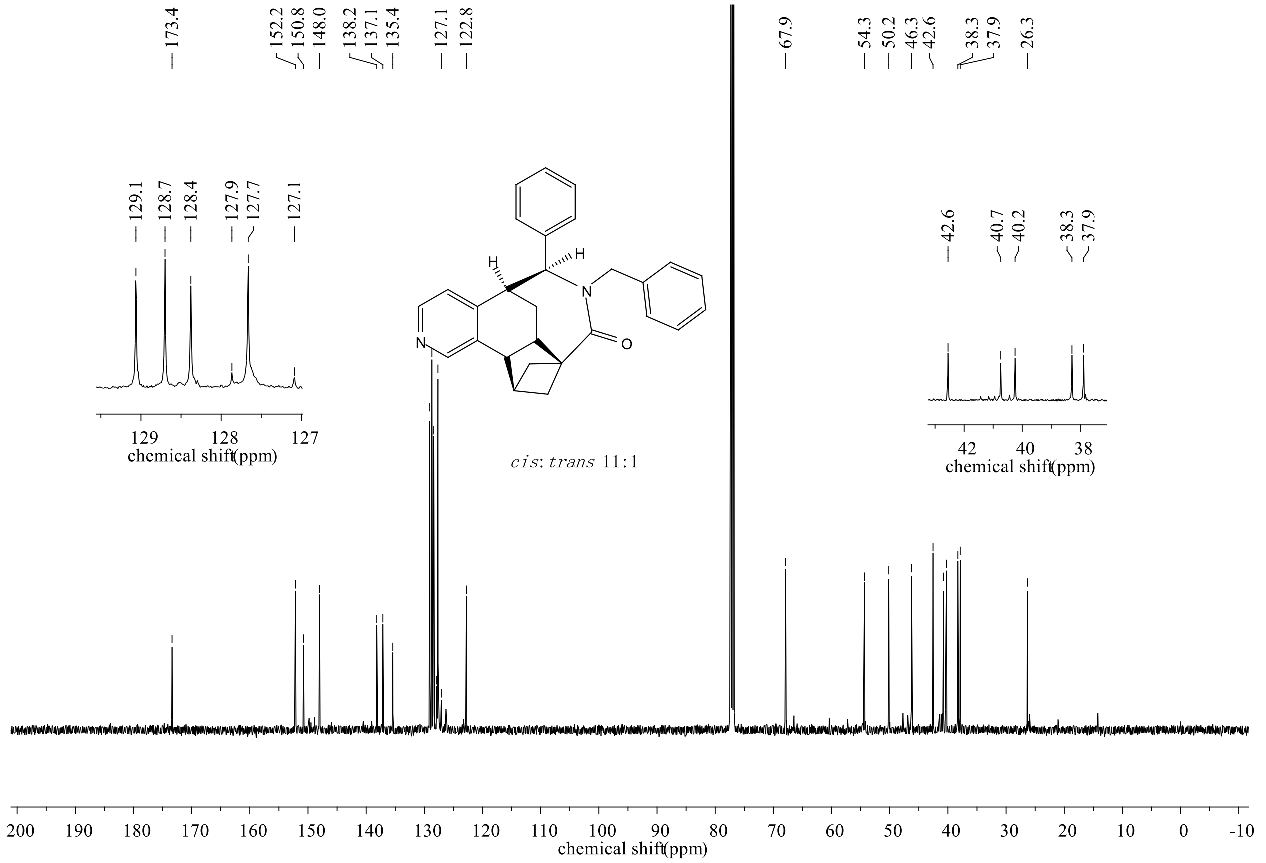
trans-**4q** ^{13}C NMR (126 MHz, CDCl$_3$)



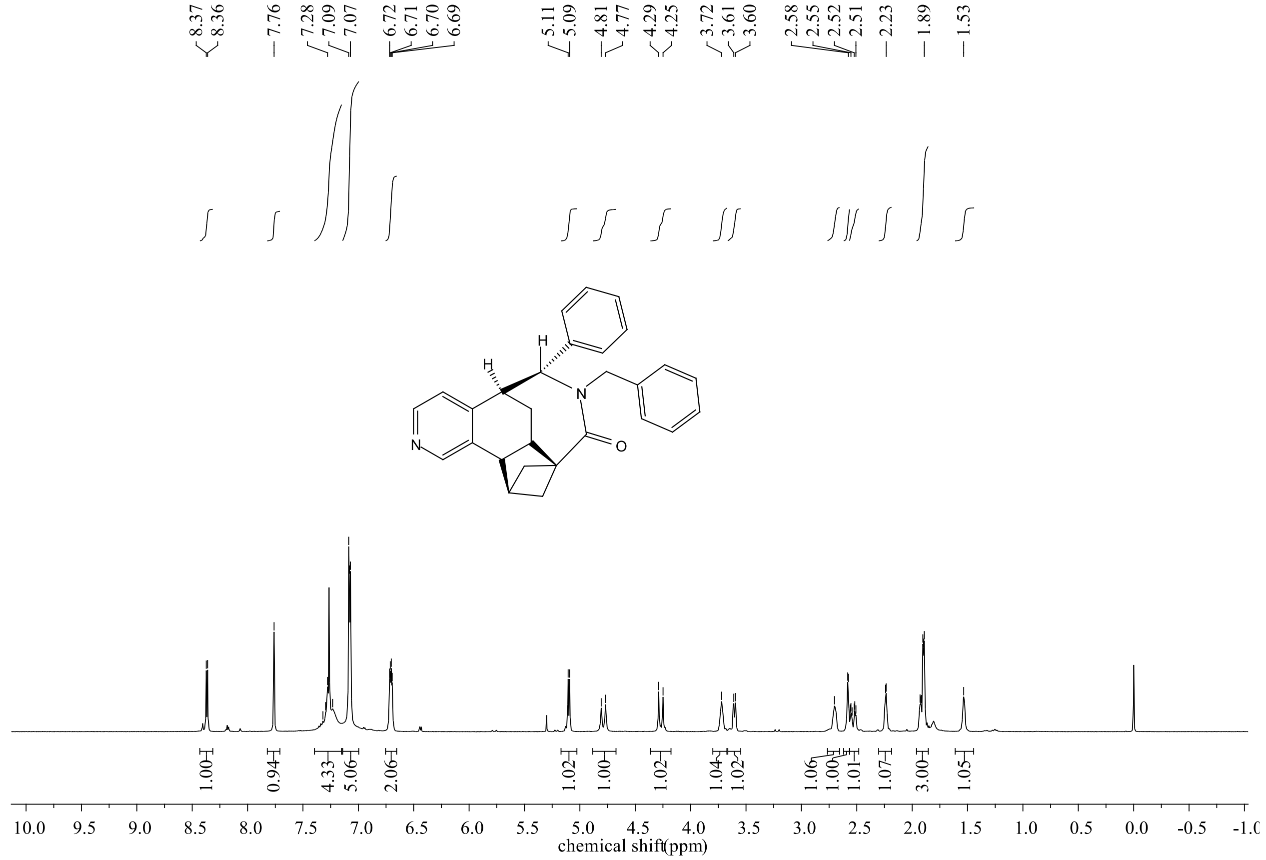
cis-**4R** ^{1}H NMR (400 MHz, CDCl$_3$)



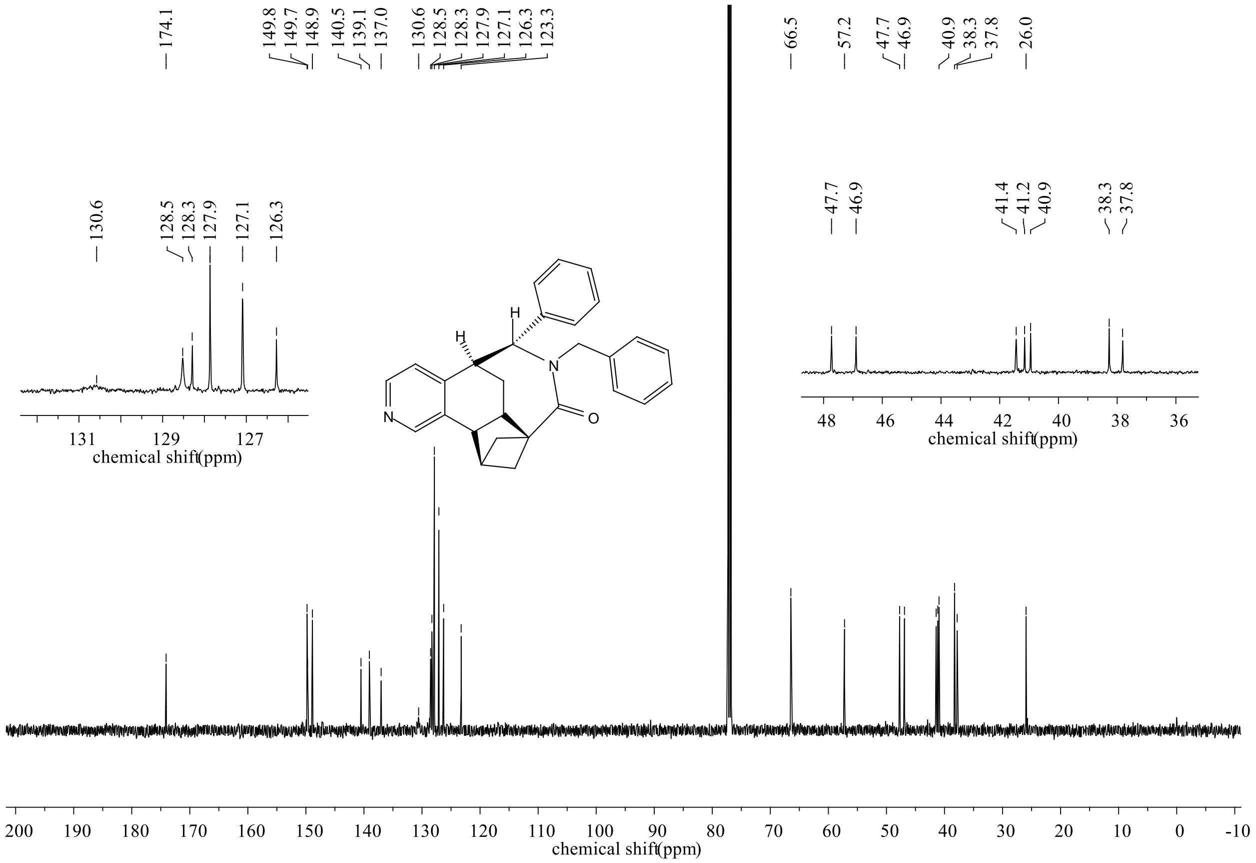
cis-**4R** ^{13}C NMR (126 MHz, $CDCl_3$)



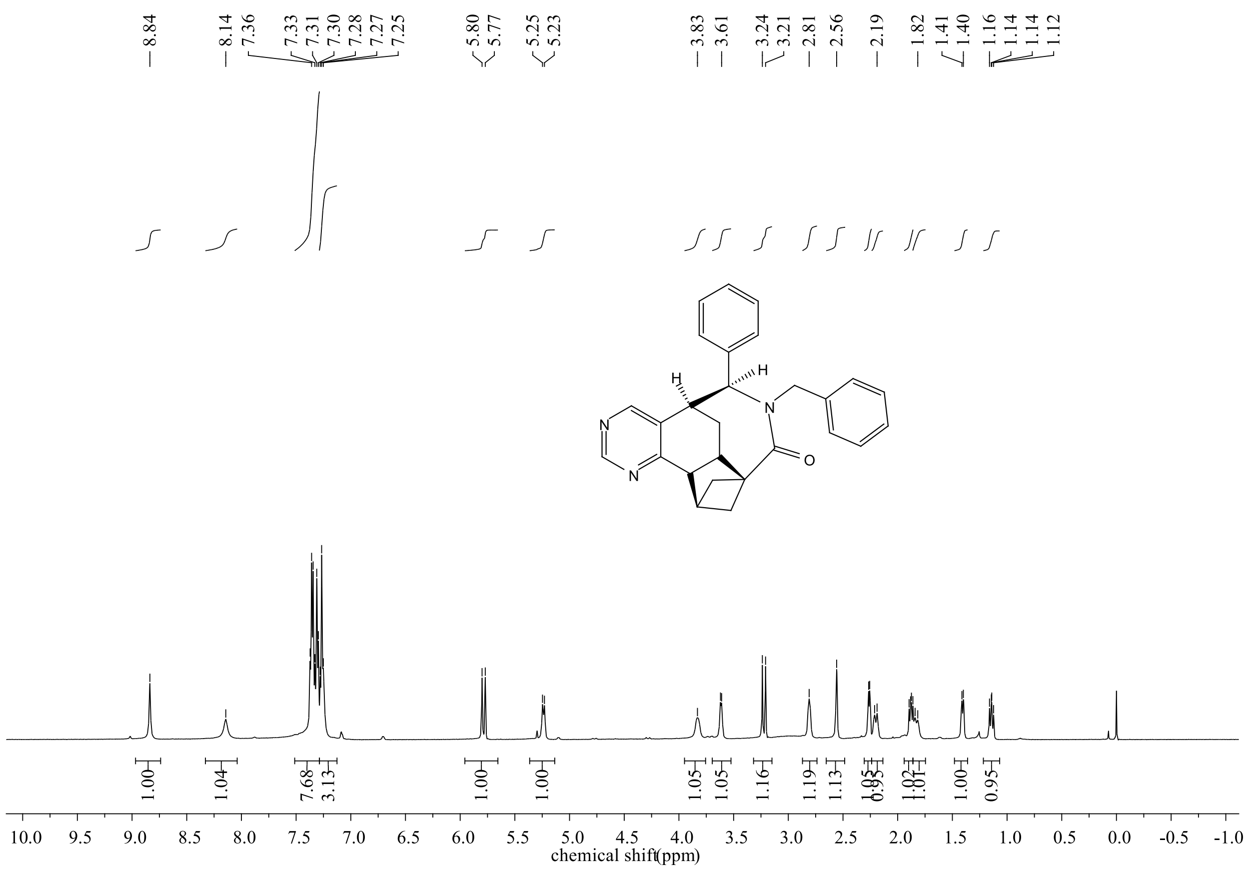
trans-**4R** ^{1}H NMR (400 MHz, $CDCl_3$)



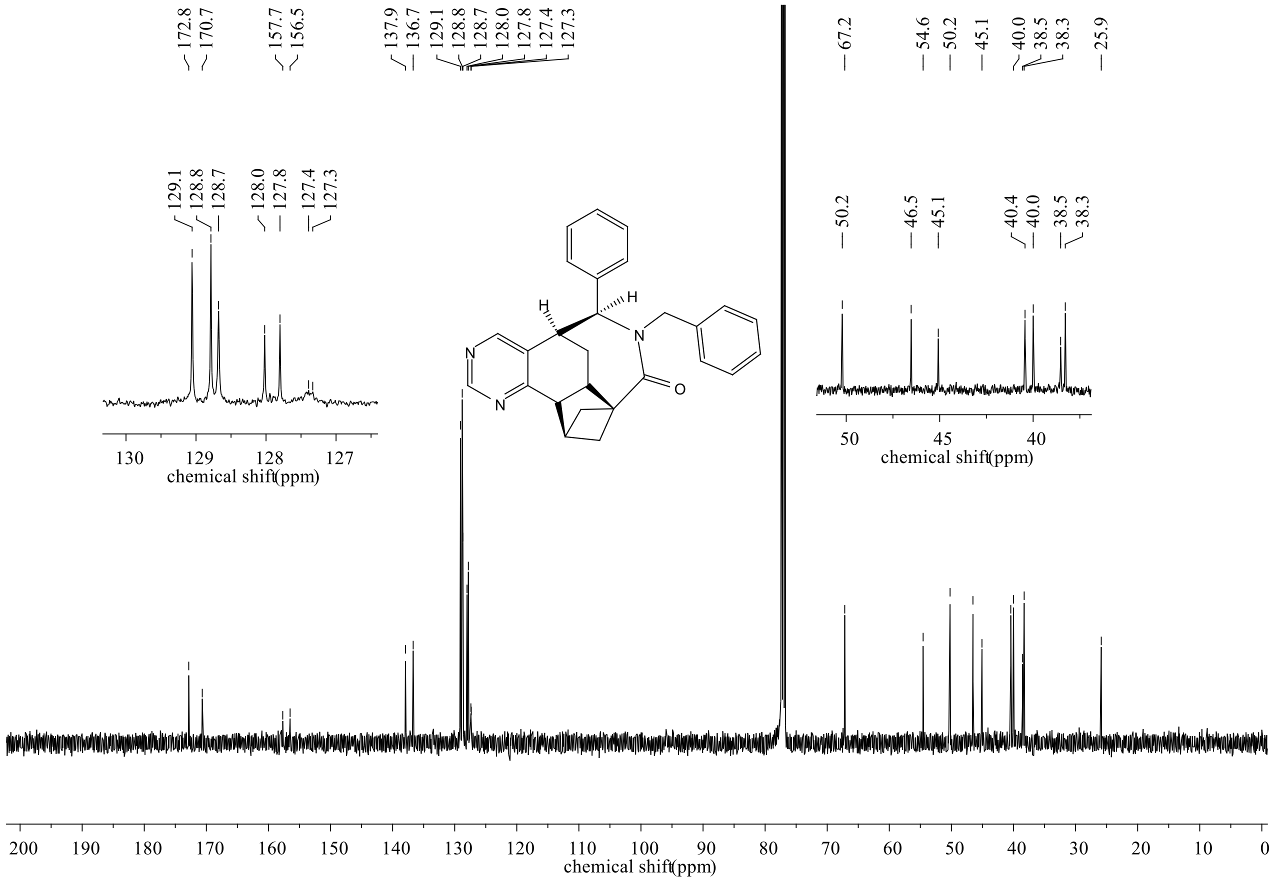
trans-**4R** ^{13}C NMR (126 MHz, CDCl$_3$)



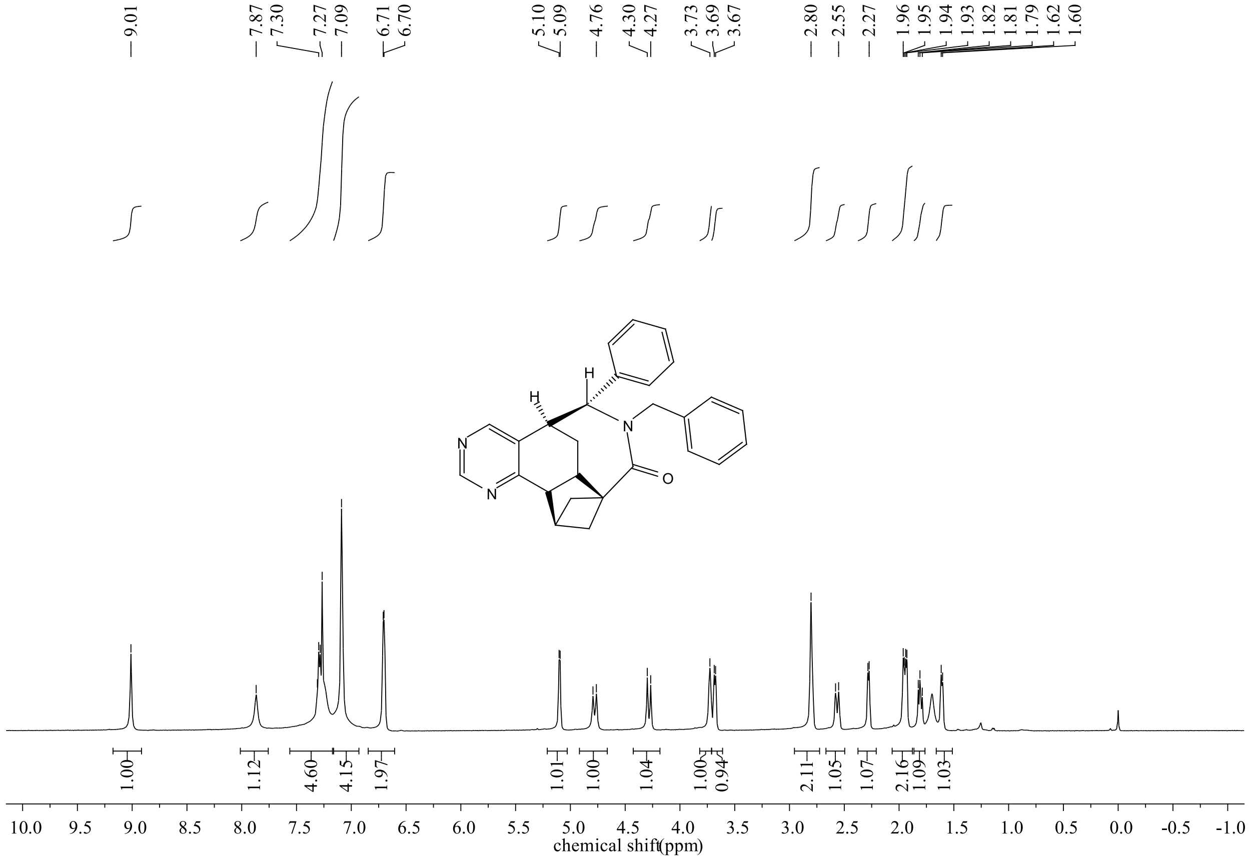
cis-**4S** ^{1}H NMR (500 MHz, CDCl$_3$)



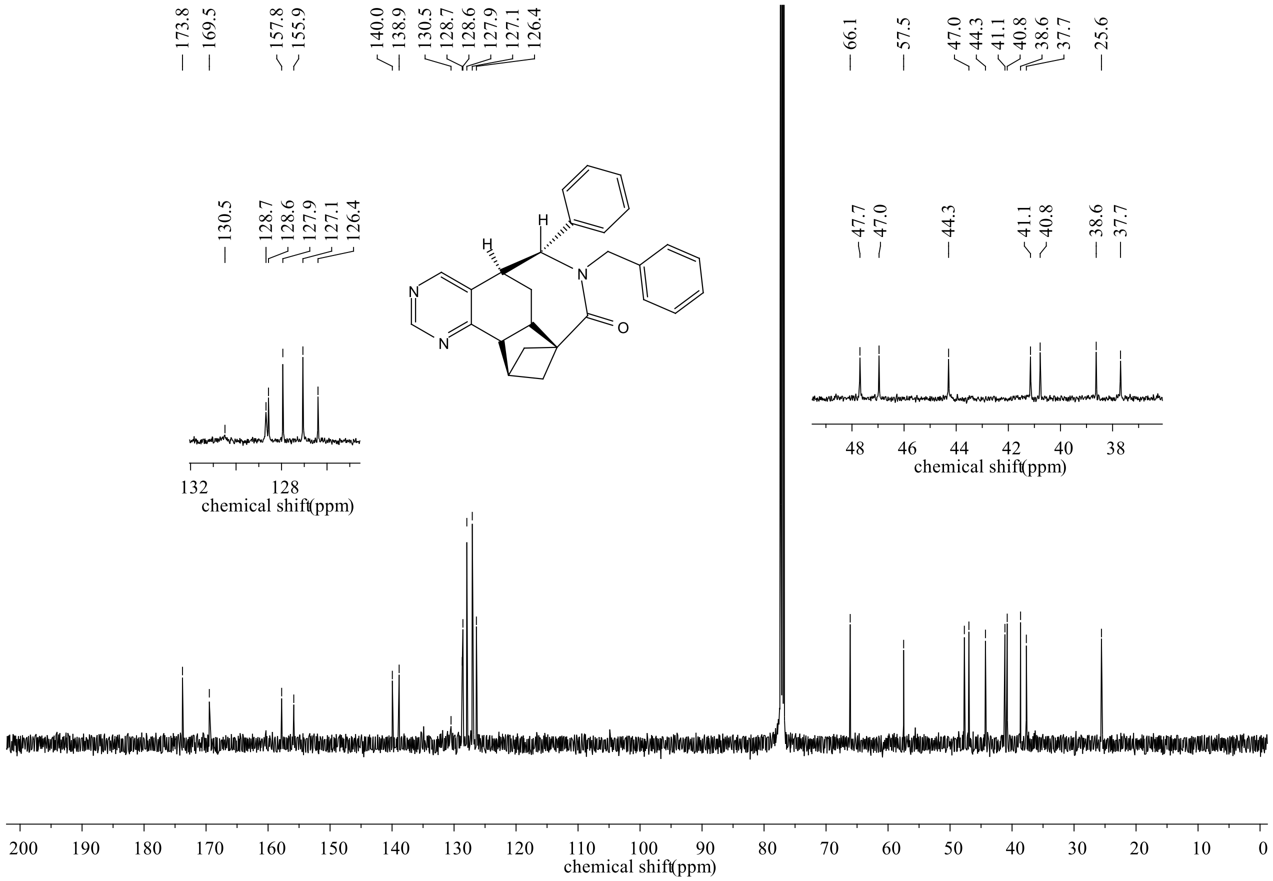
cis-**4S** ^{13}C NMR (126 MHz, $CDCl_3$)



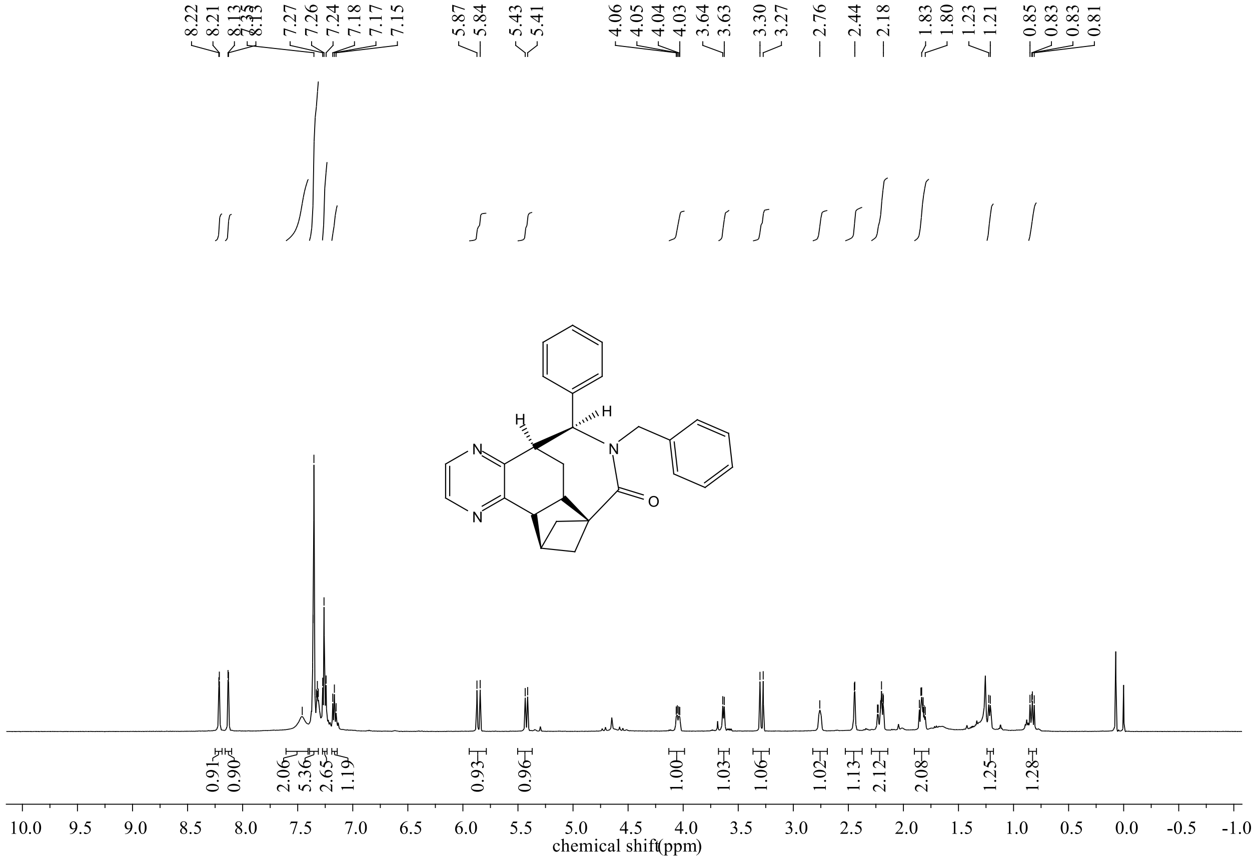
trans-**4S** ^{1}H NMR (500 MHz, $CDCl_3$)



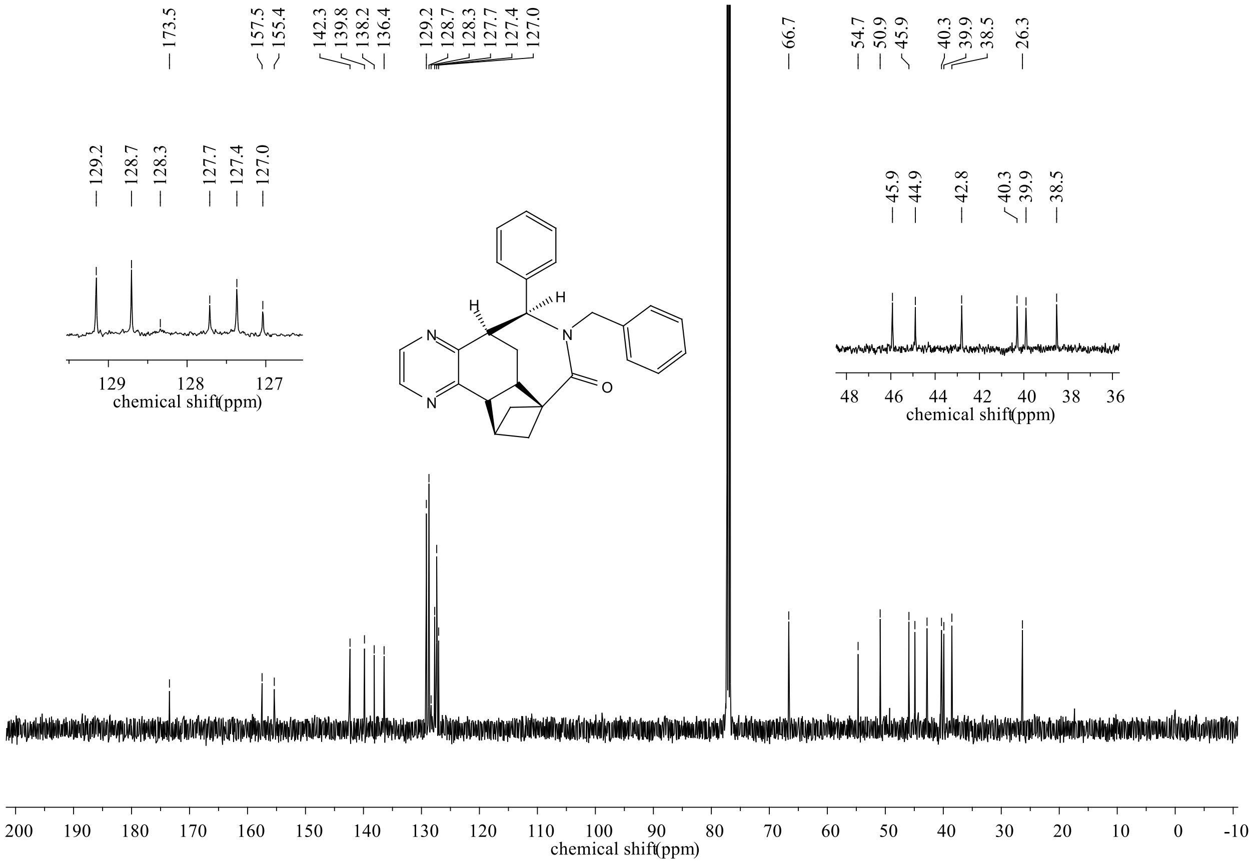
trans-**4S** ^{13}C NMR (126 MHz, $CDCl_3$)



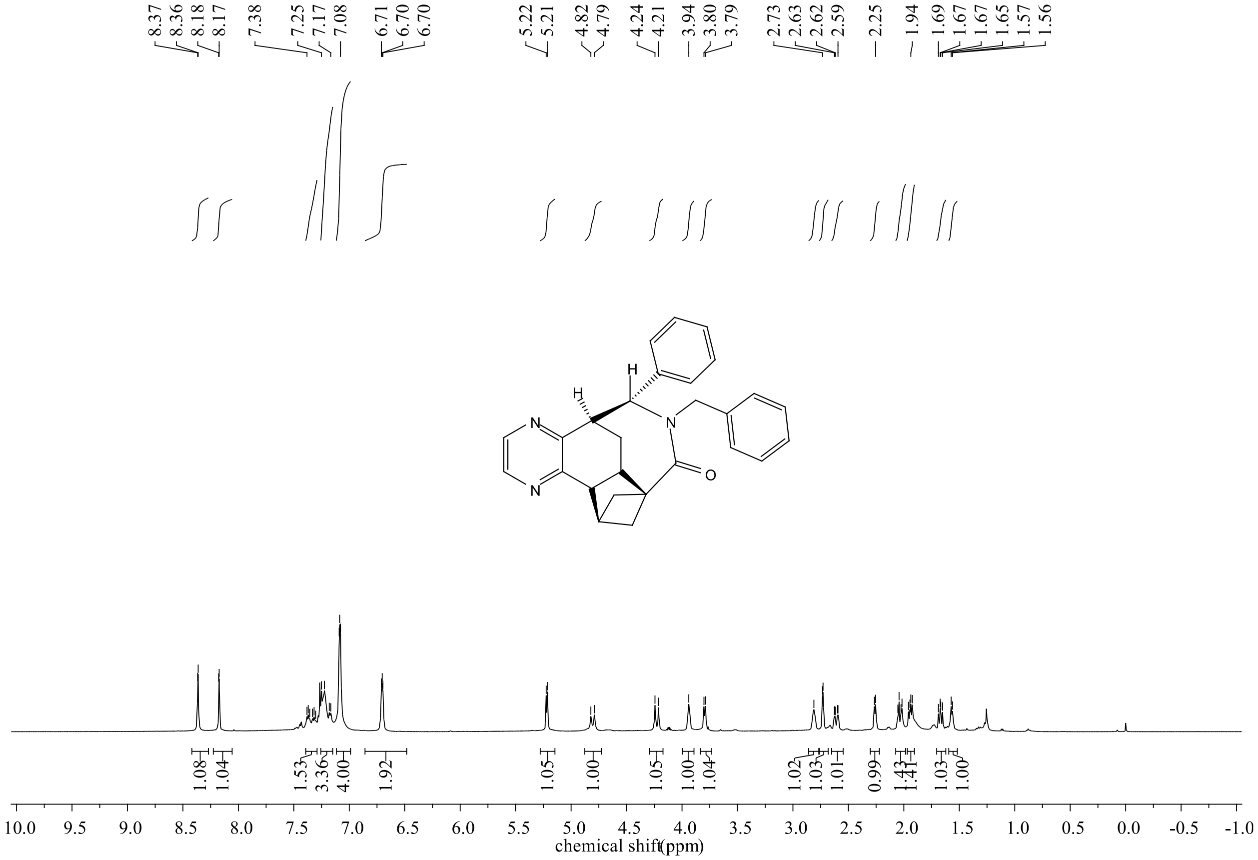
cis-**4T** ^{1}H NMR (500 MHz, $CDCl_3$)



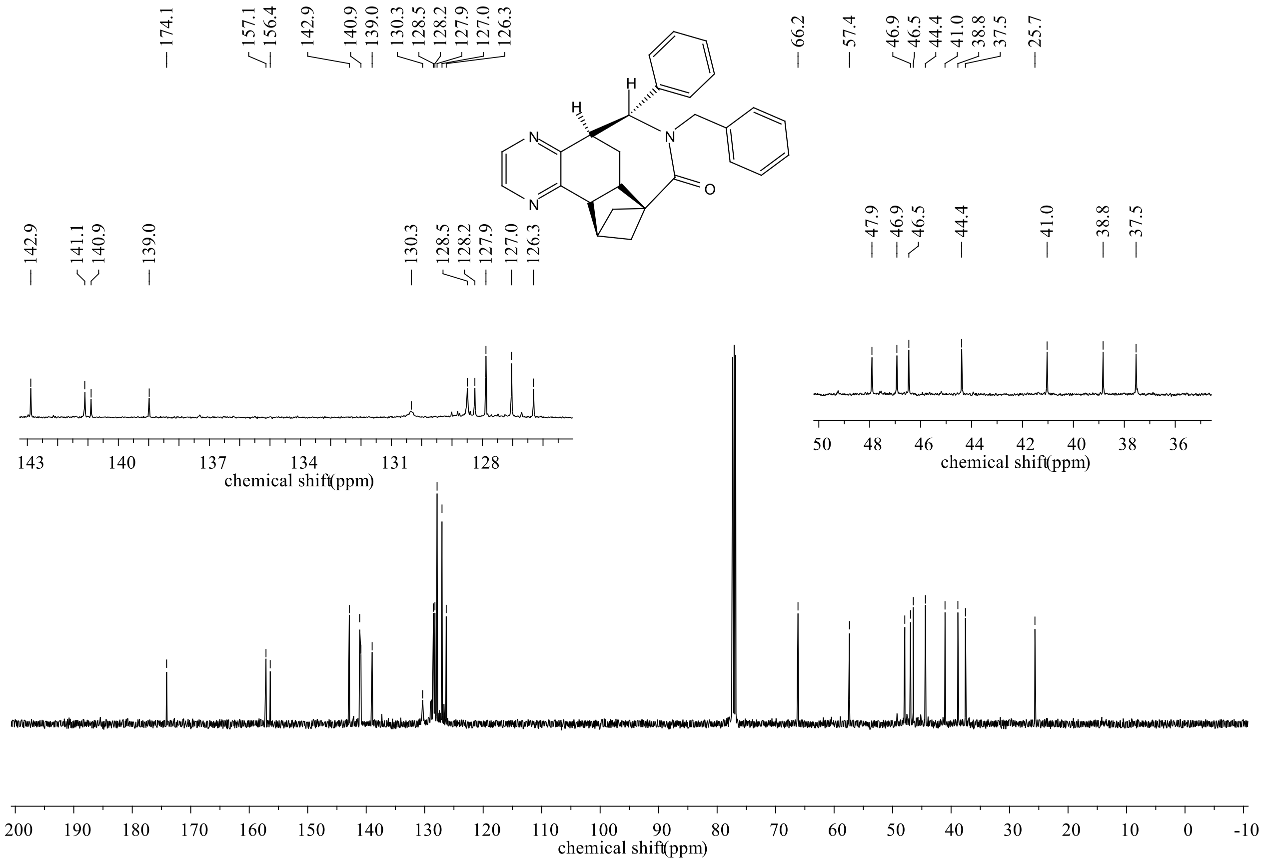
cis-**4T** ^{13}C NMR (126 MHz, CDCl$_3$)



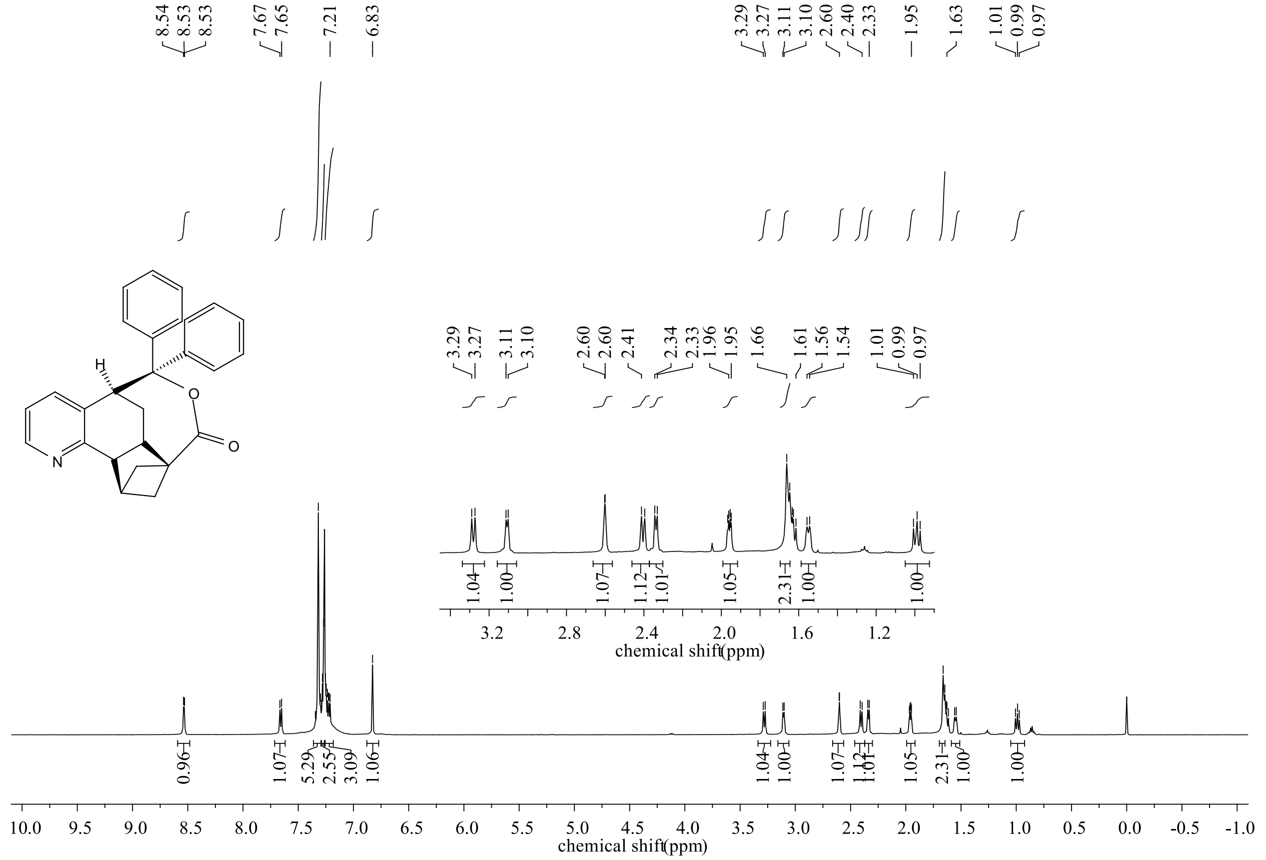
trans-**4T** ^{1}H NMR (500 MHz, CDCl$_3$)



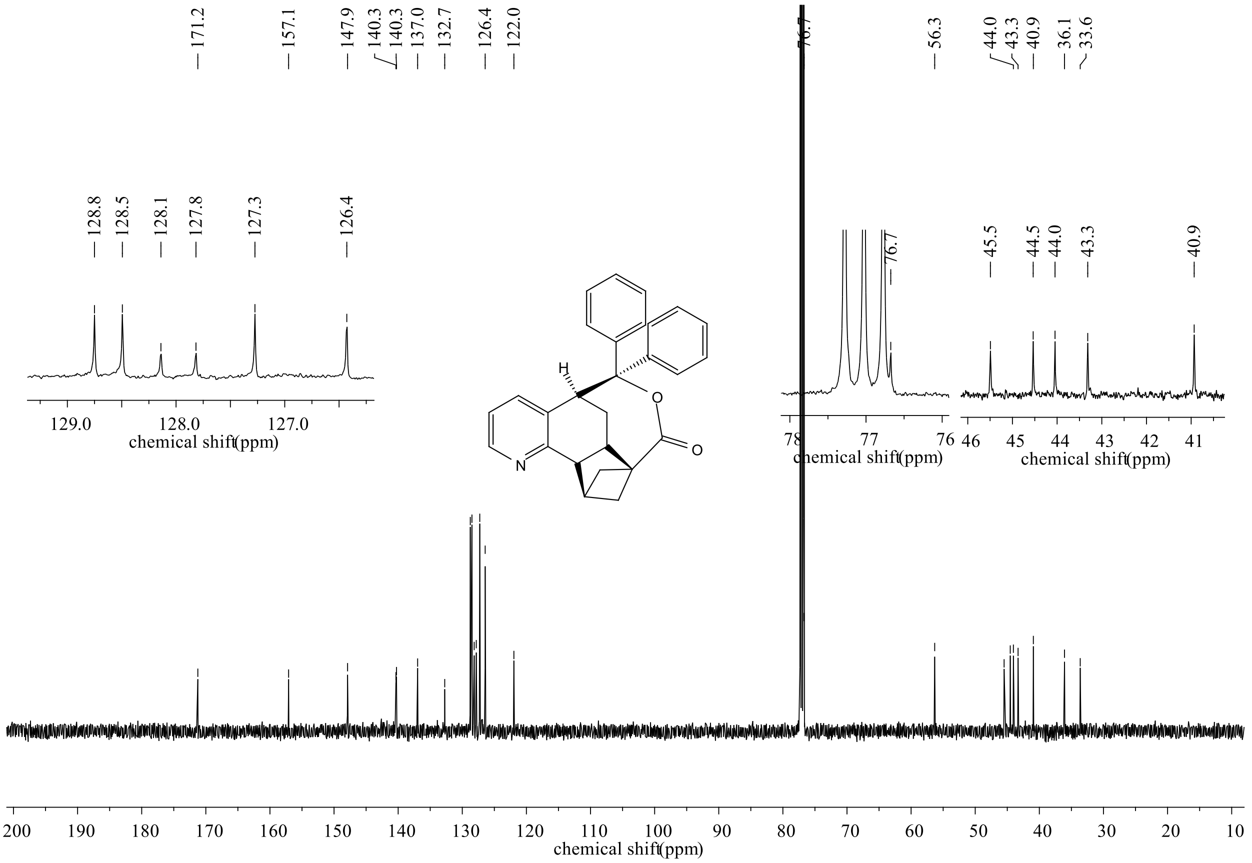
trans-**4T** ^{13}C NMR (126 MHz, CDCl$_3$)



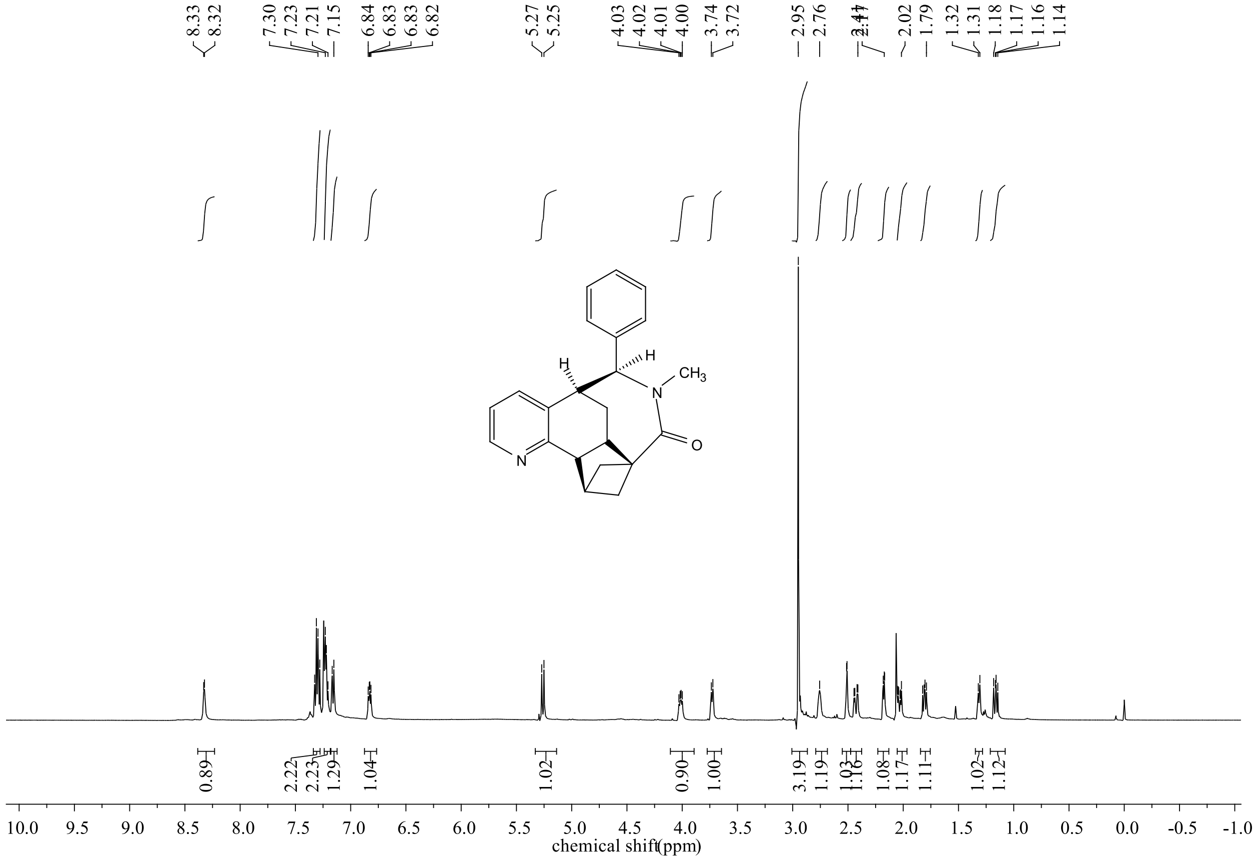
4U ^{1}H NMR (500 MHz, CDCl$_3$)



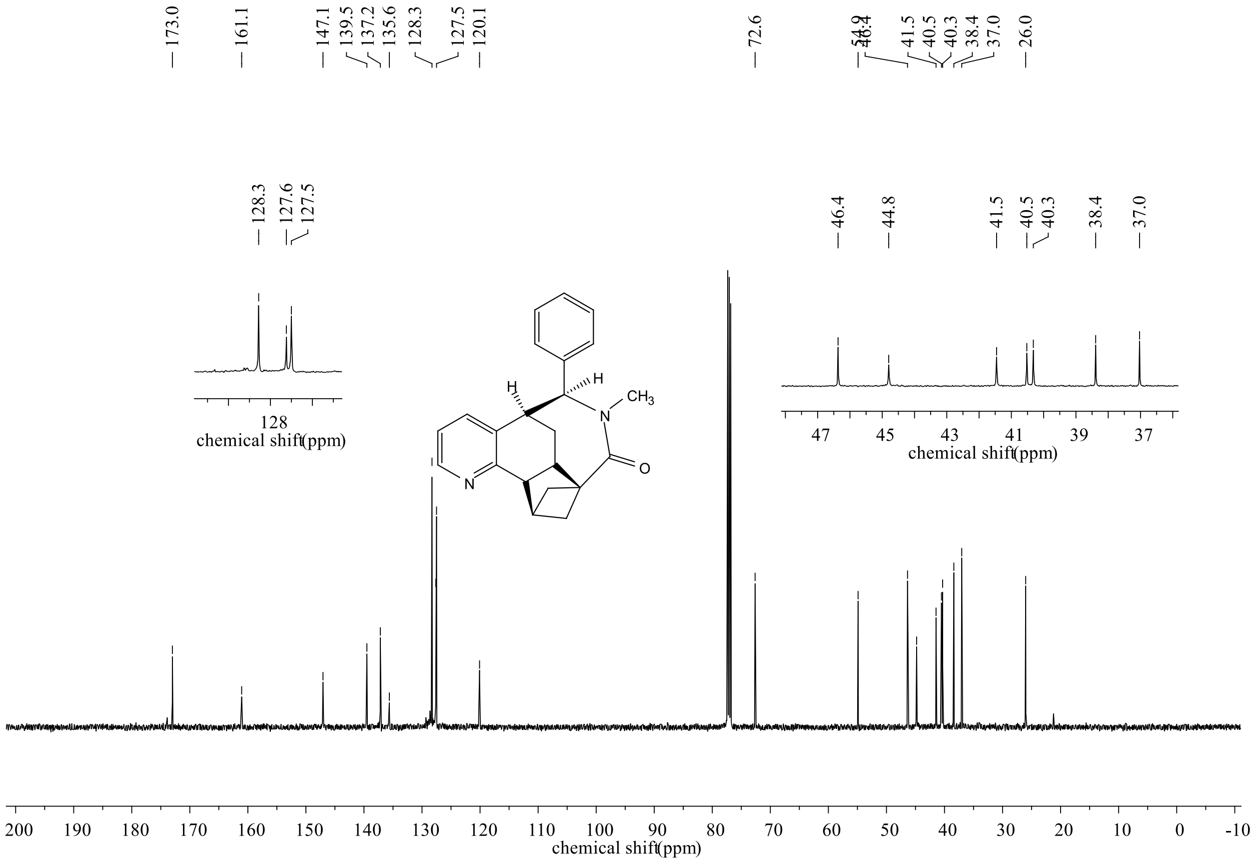
4U ^{13}C NMR (126 MHz, CDCl$_3$)



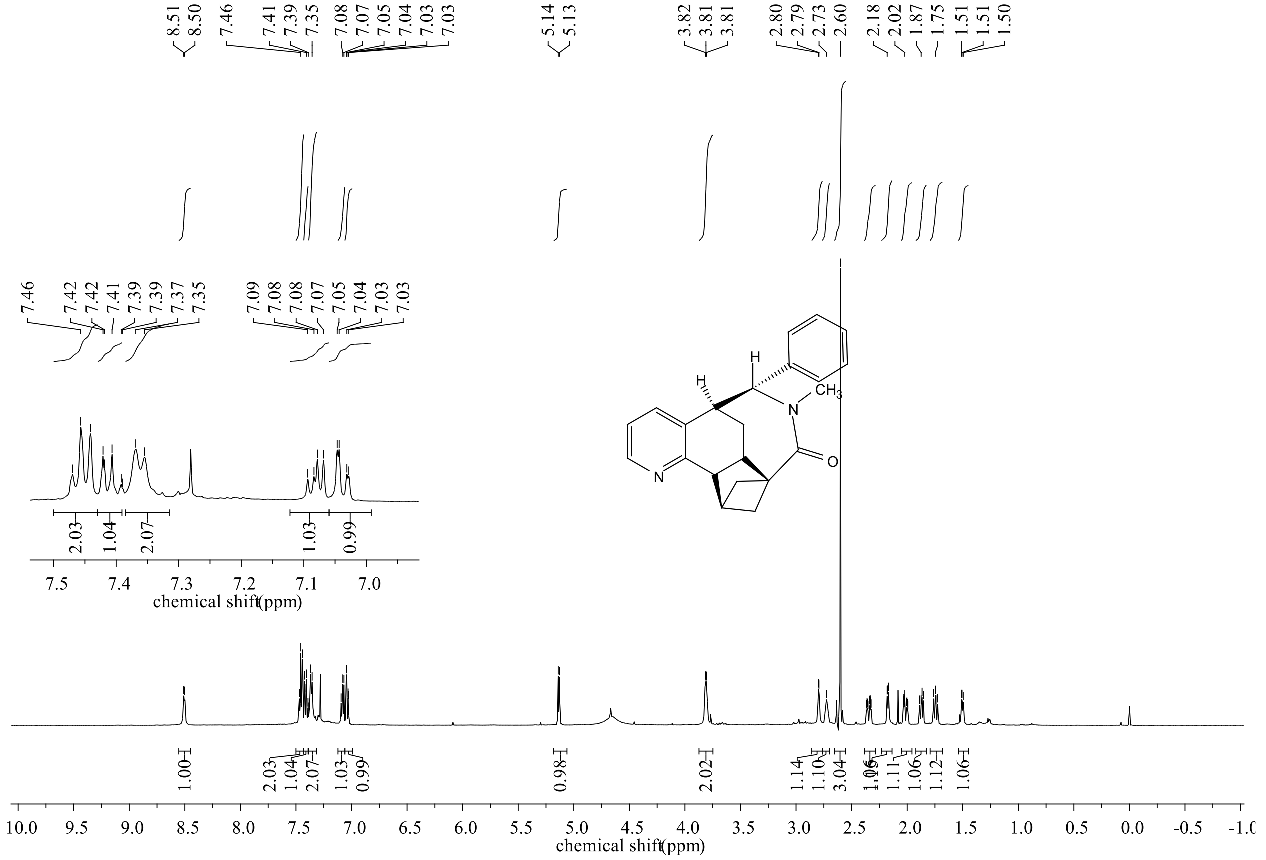
cis-**4V** ^{1}H NMR (500 MHz, CDCl$_3$)



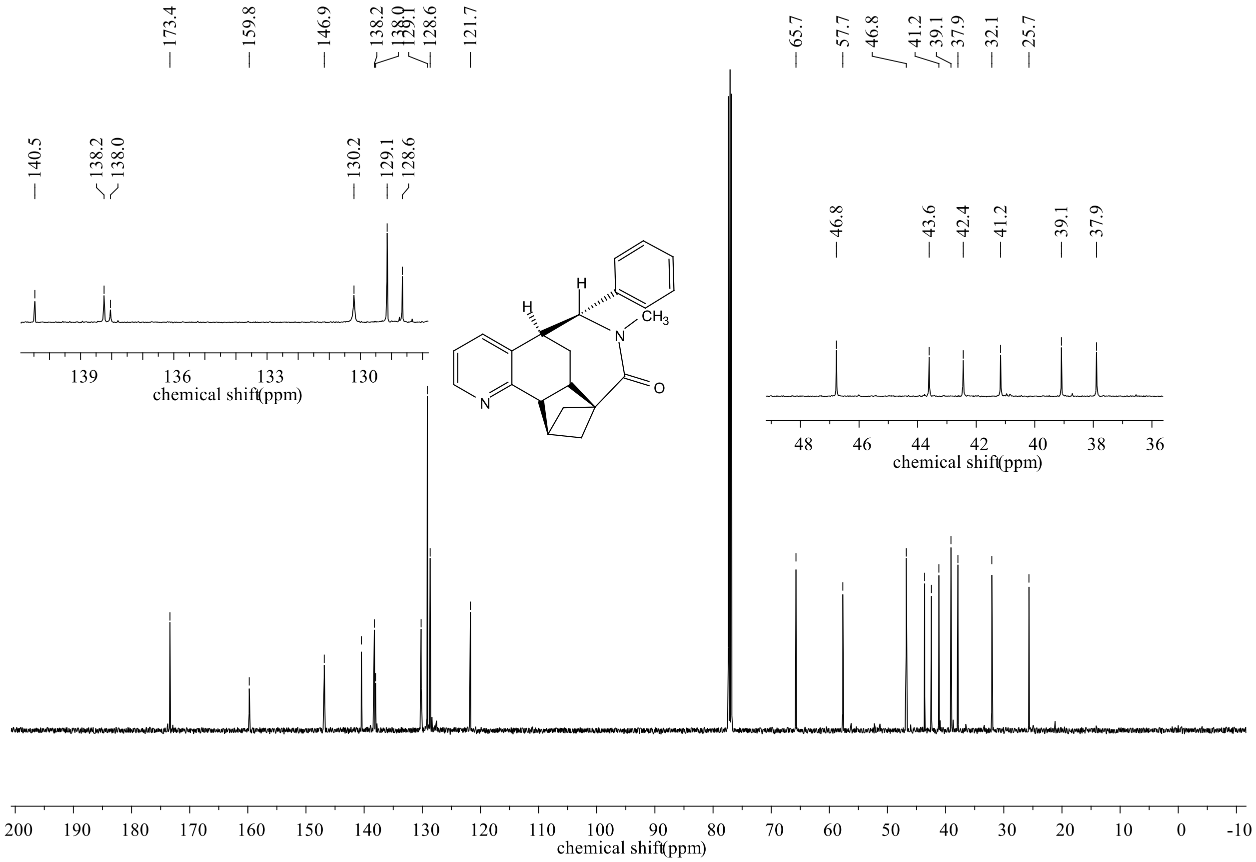
cis-**4V** ^{13}C NMR (126 MHz, CDCl$_3$)



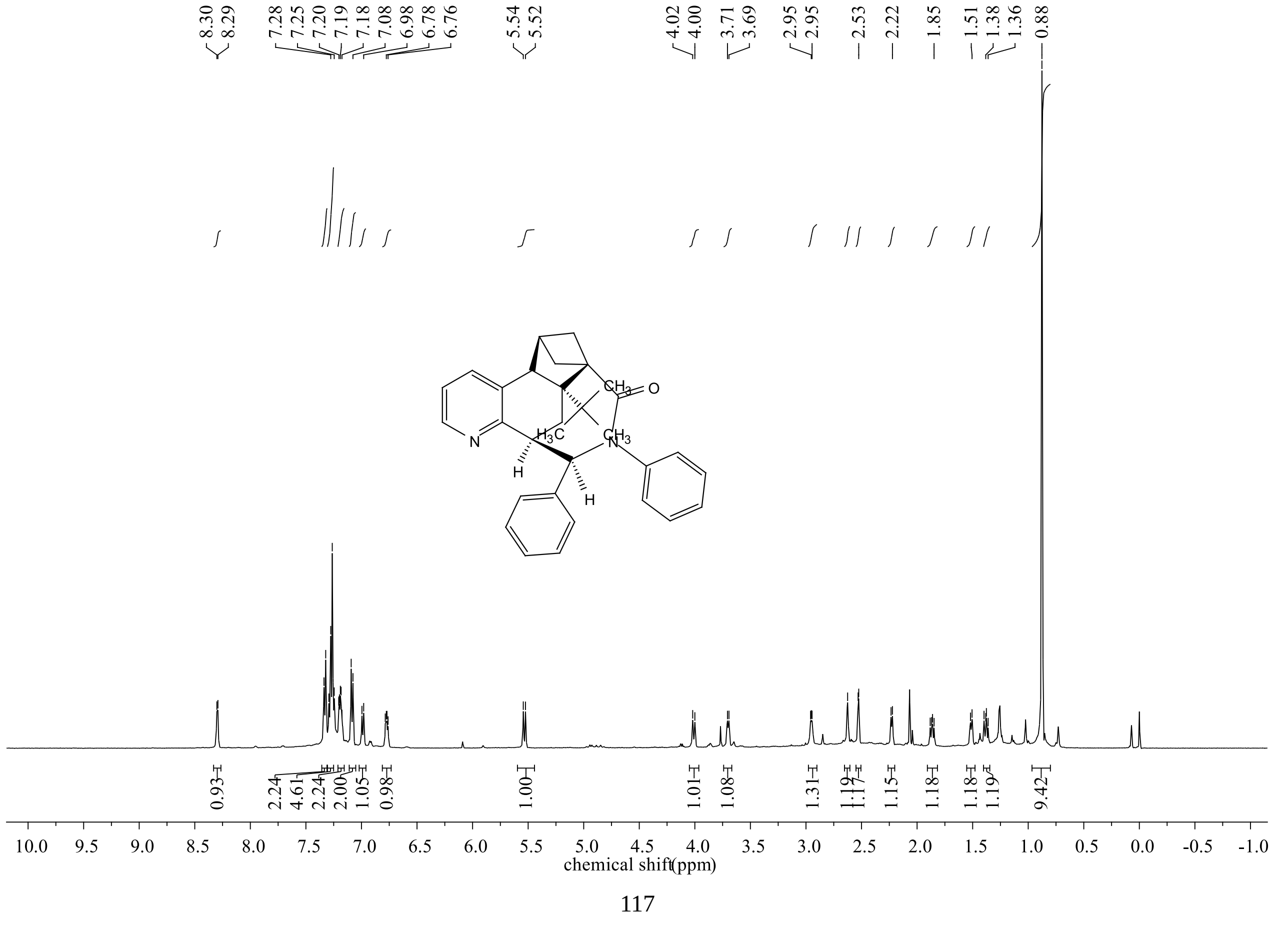
trans-**4V** ^{1}H NMR (500 MHz, CDCl$_3$)



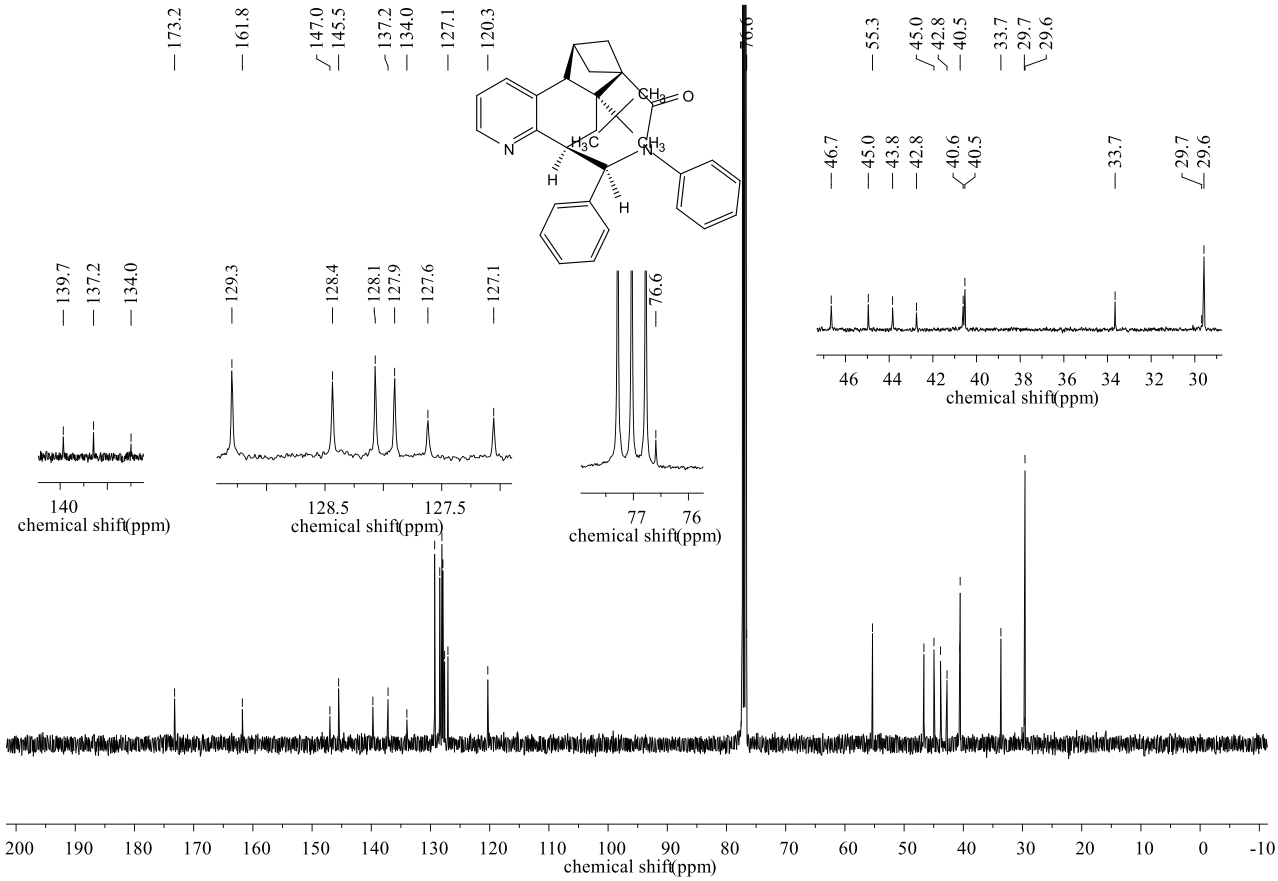
trans-**4V** ^{13}C NMR (126 MHz, $CDCl_3$)



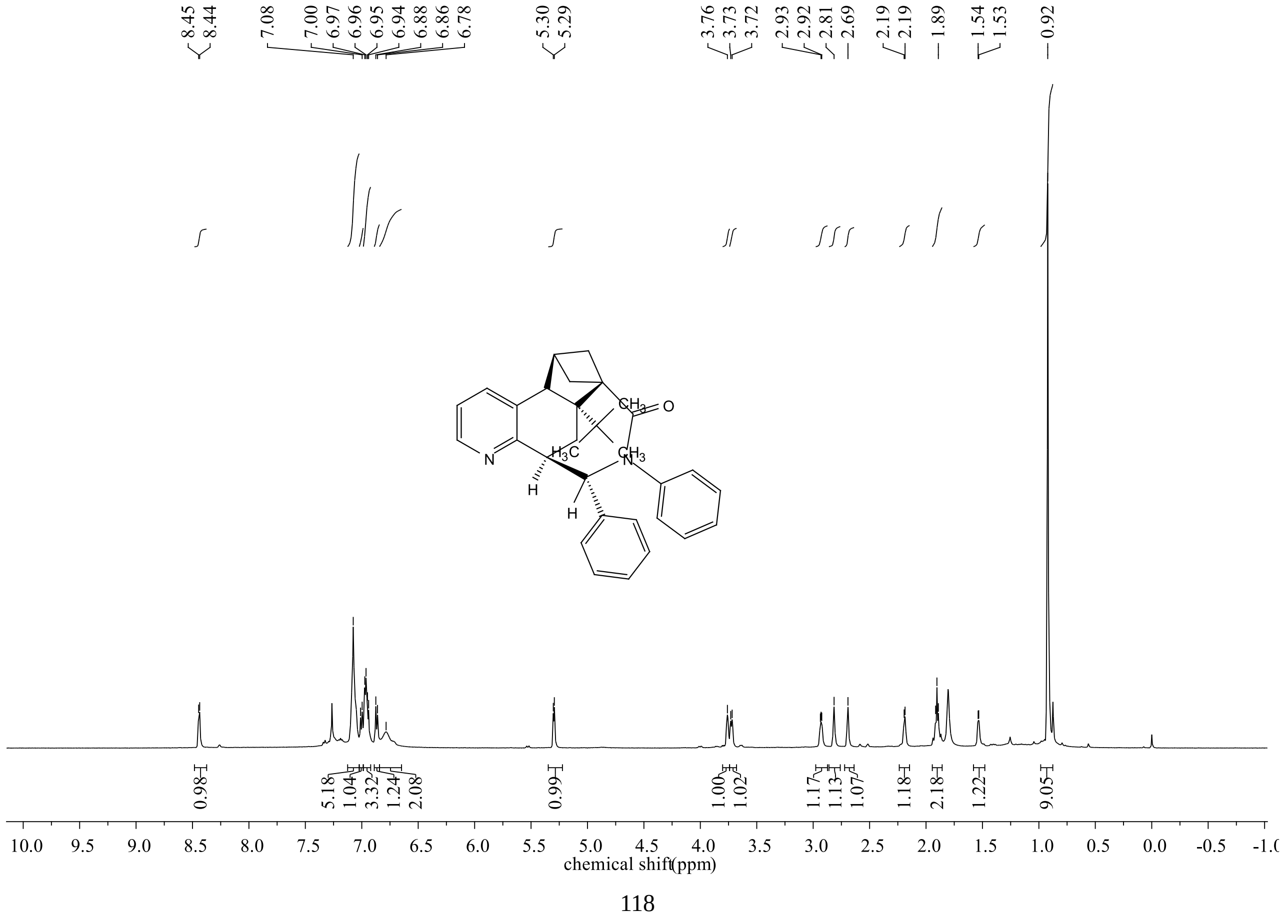
cis-**4w** ^{1}H NMR (500 MHz, $CDCl_3$)



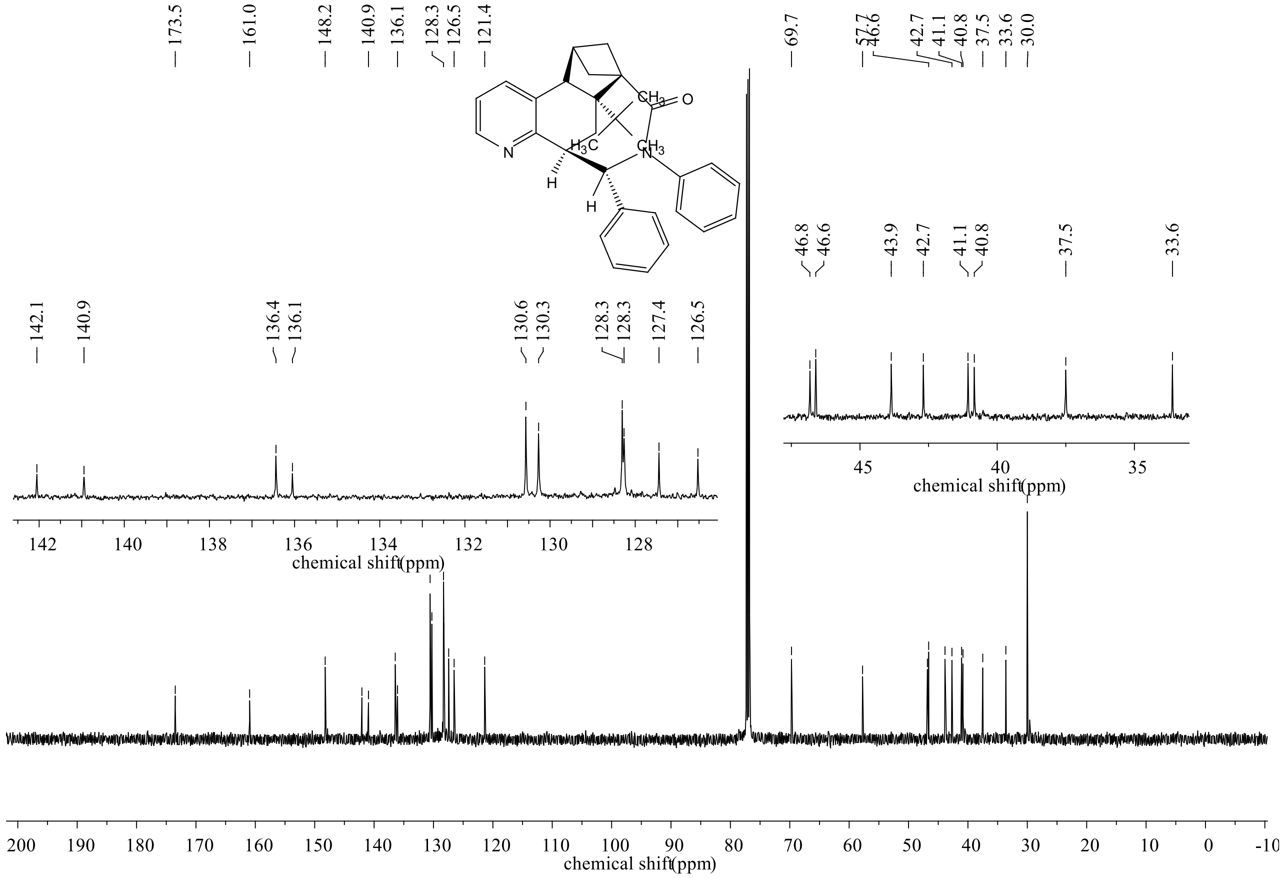
cis-**4w** ^{13}C NMR (126 MHz, CDCl$_3$)



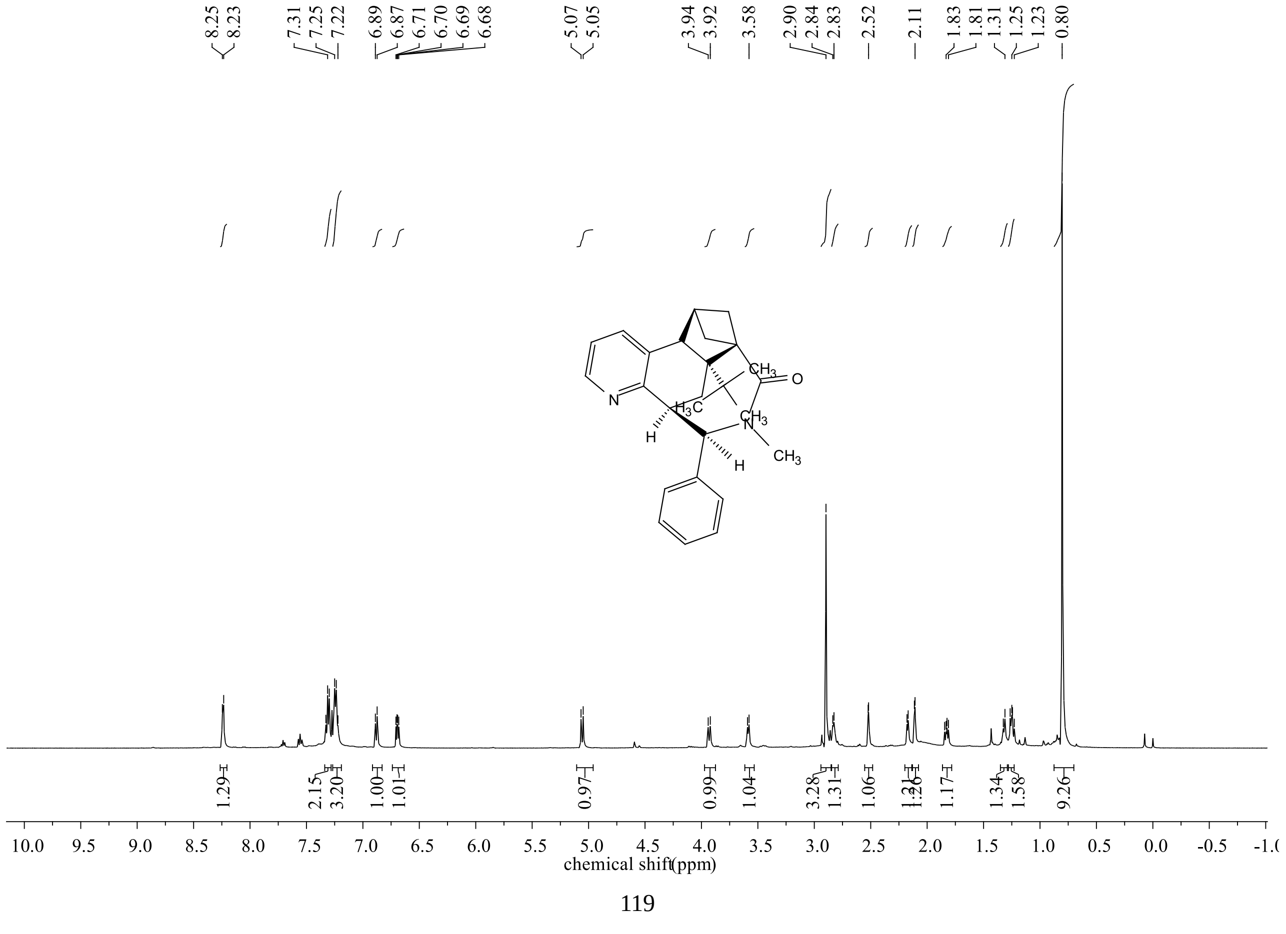
trans-**4w** ^{1}H NMR (500 MHz, CDCl$_3$)



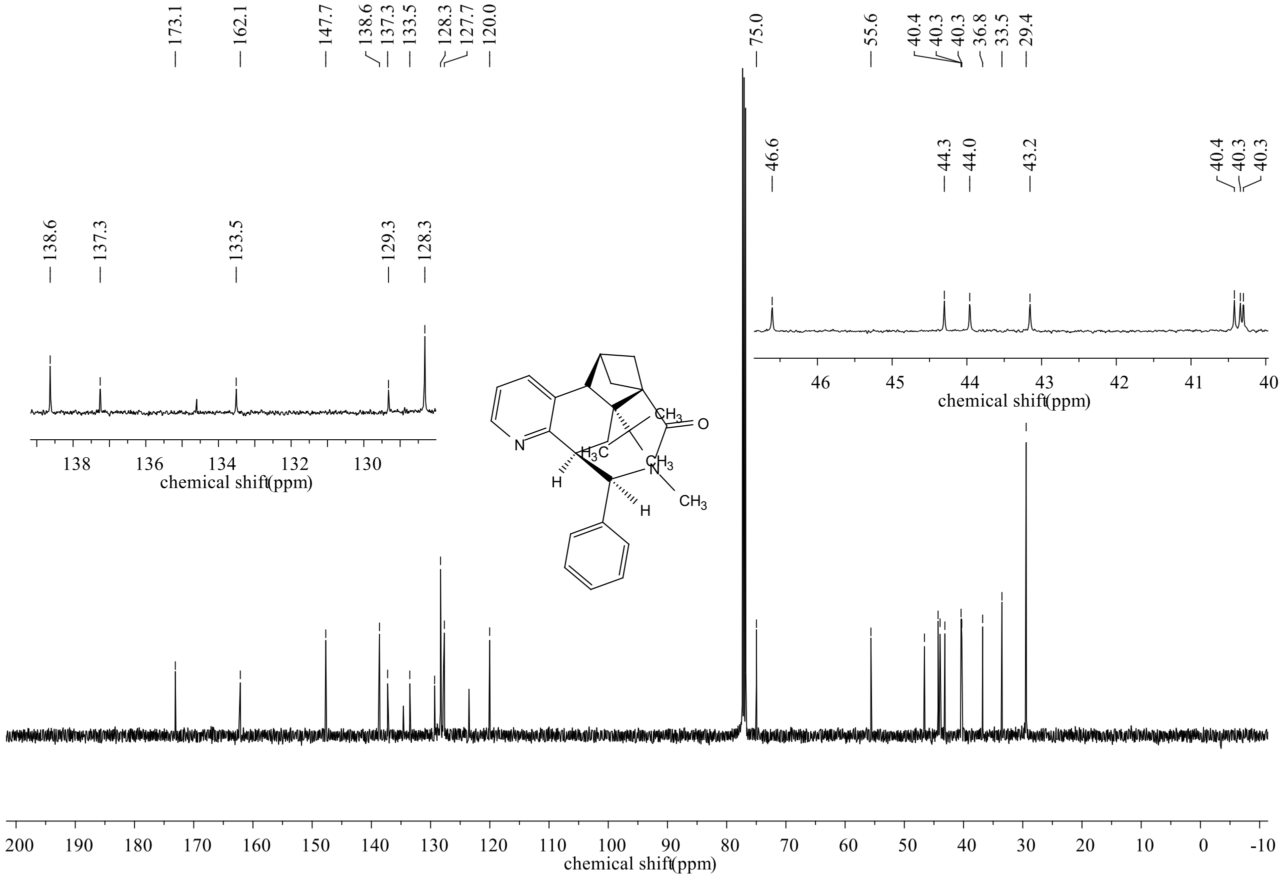
trans-**4w** ^{13}C NMR (126 MHz, CDCl$_3$)



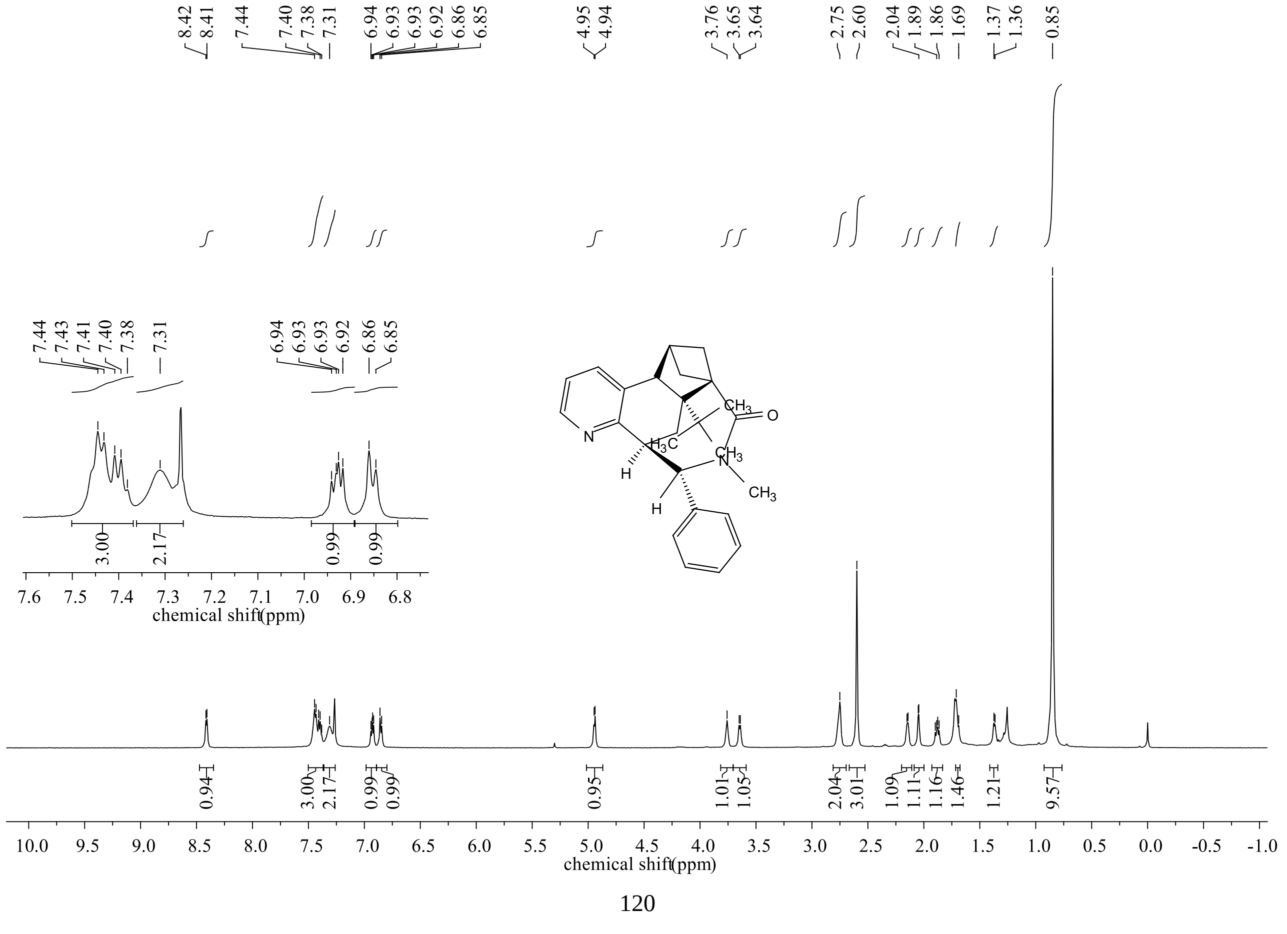
cis-**4wa** ^{1}H NMR (500 MHz, CDCl$_3$)



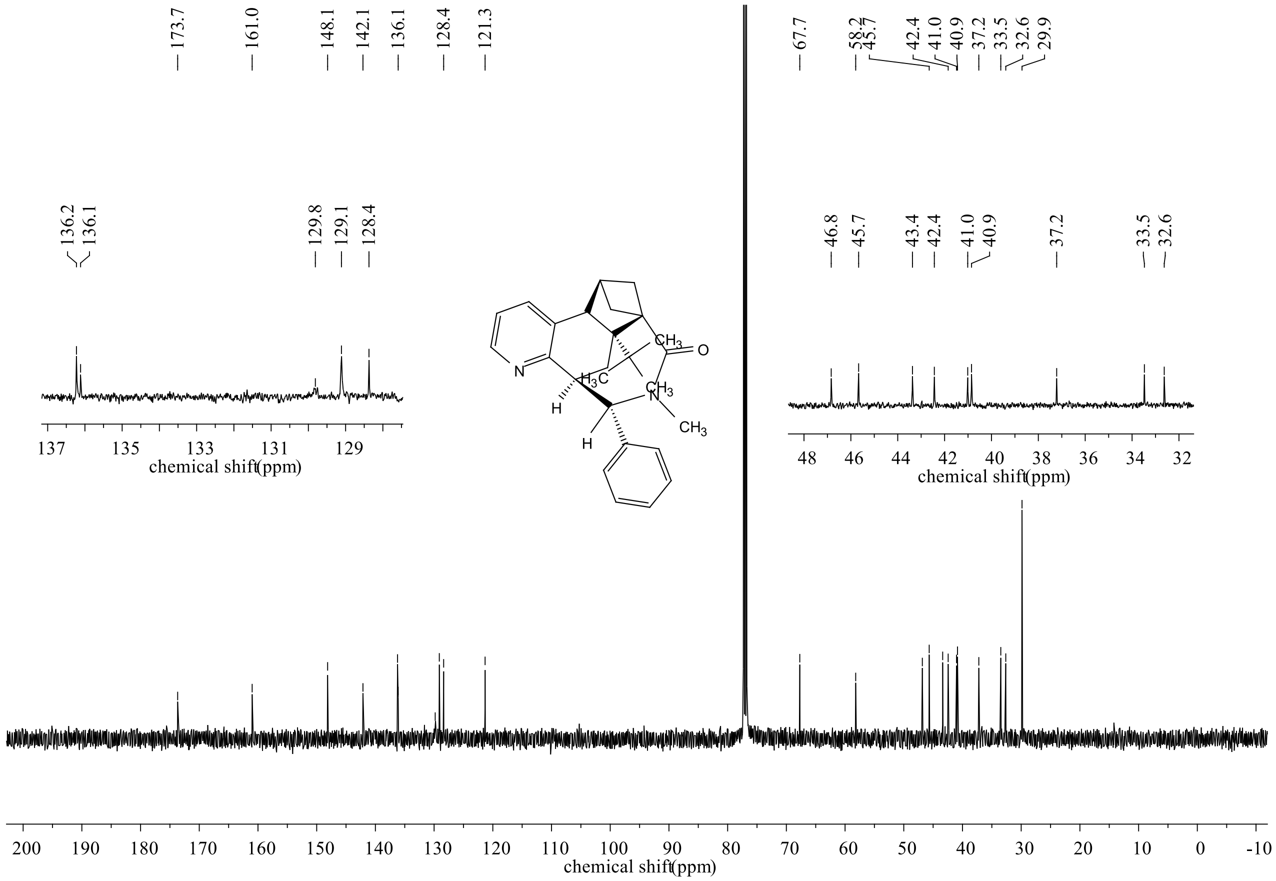
cis-**4wa** ^{13}C NMR (126 MHz, CDCl$_3$)



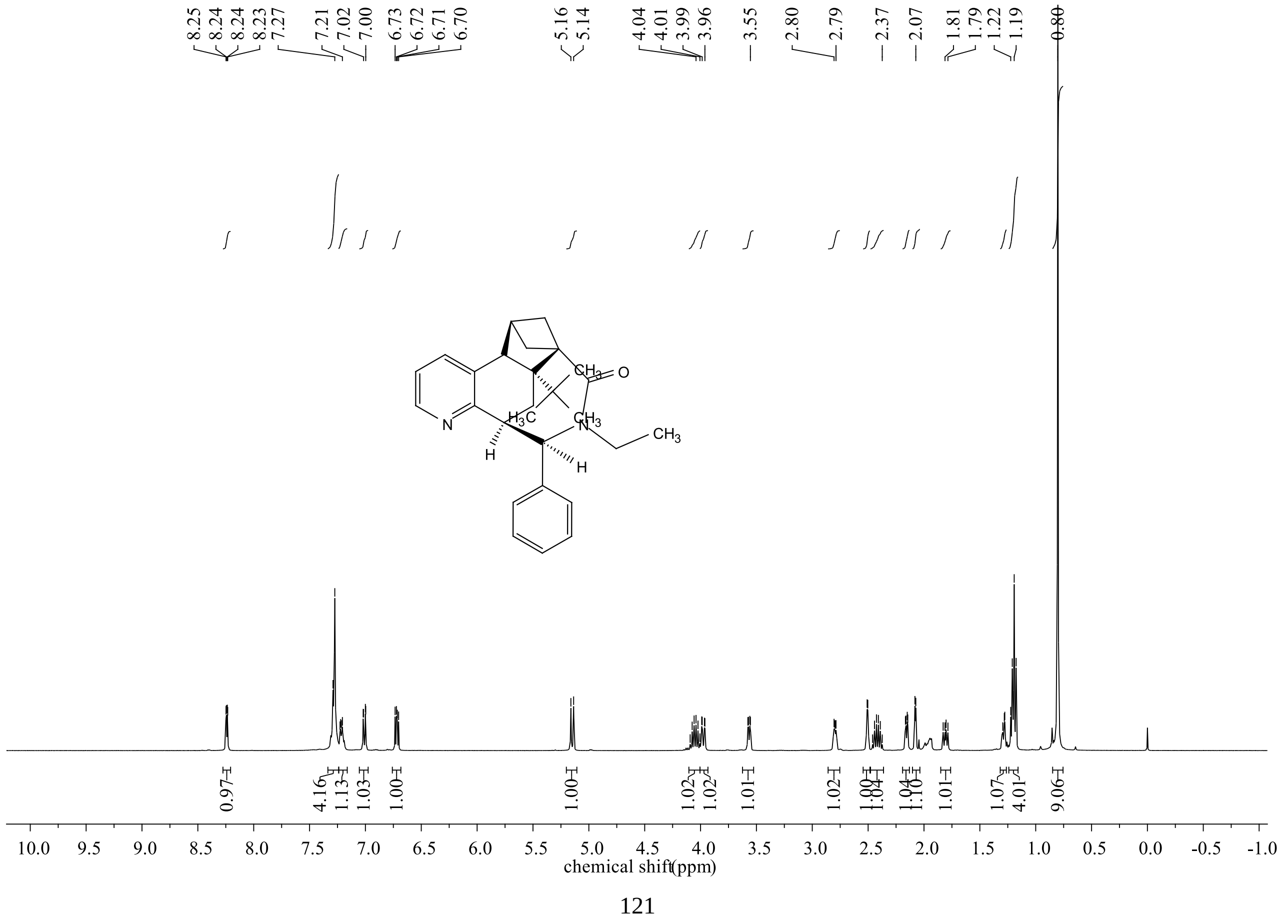
trans-**4wa** ^{1}H NMR (500 MHz, CDCl$_3$)



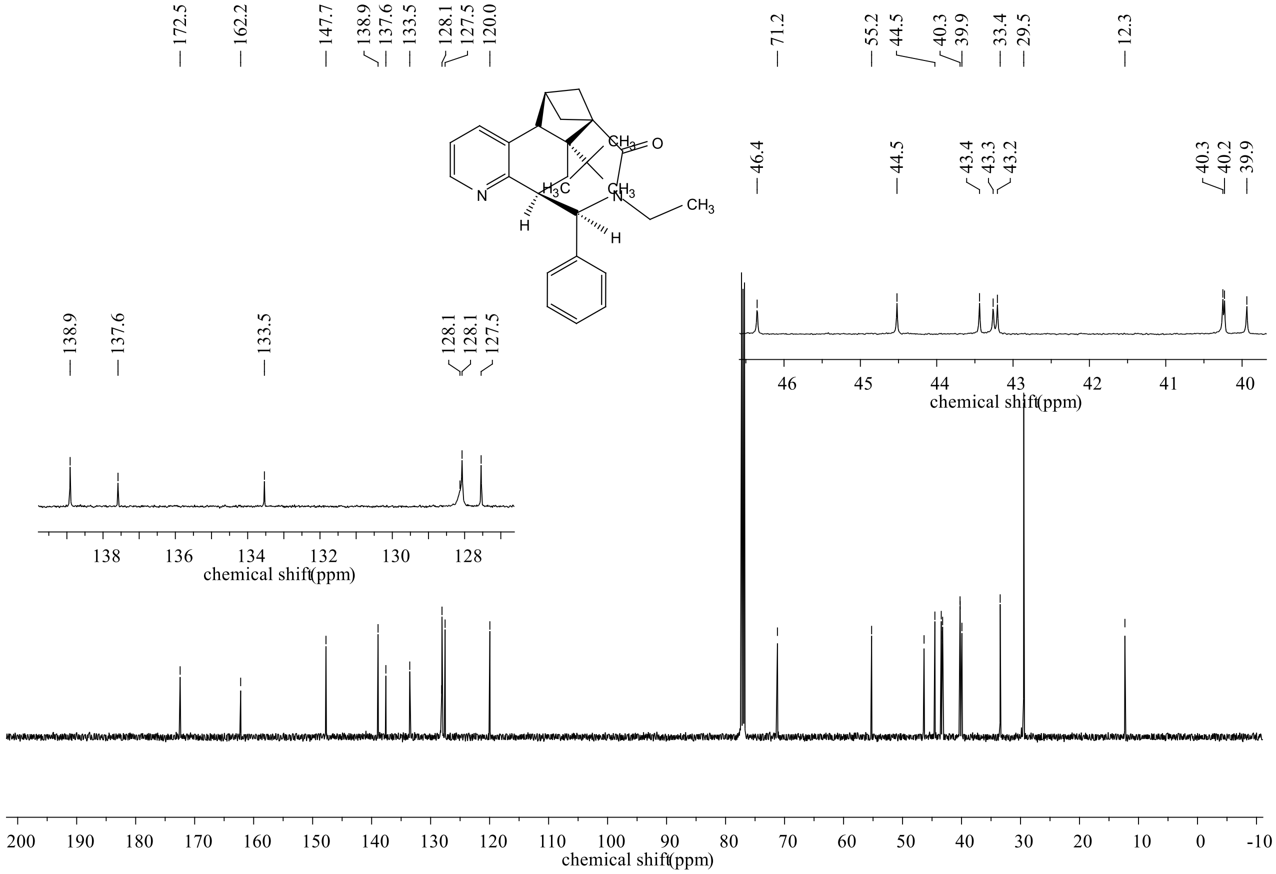
trans-**4wa** ^{13}C NMR (126 MHz, $CDCl_3$)



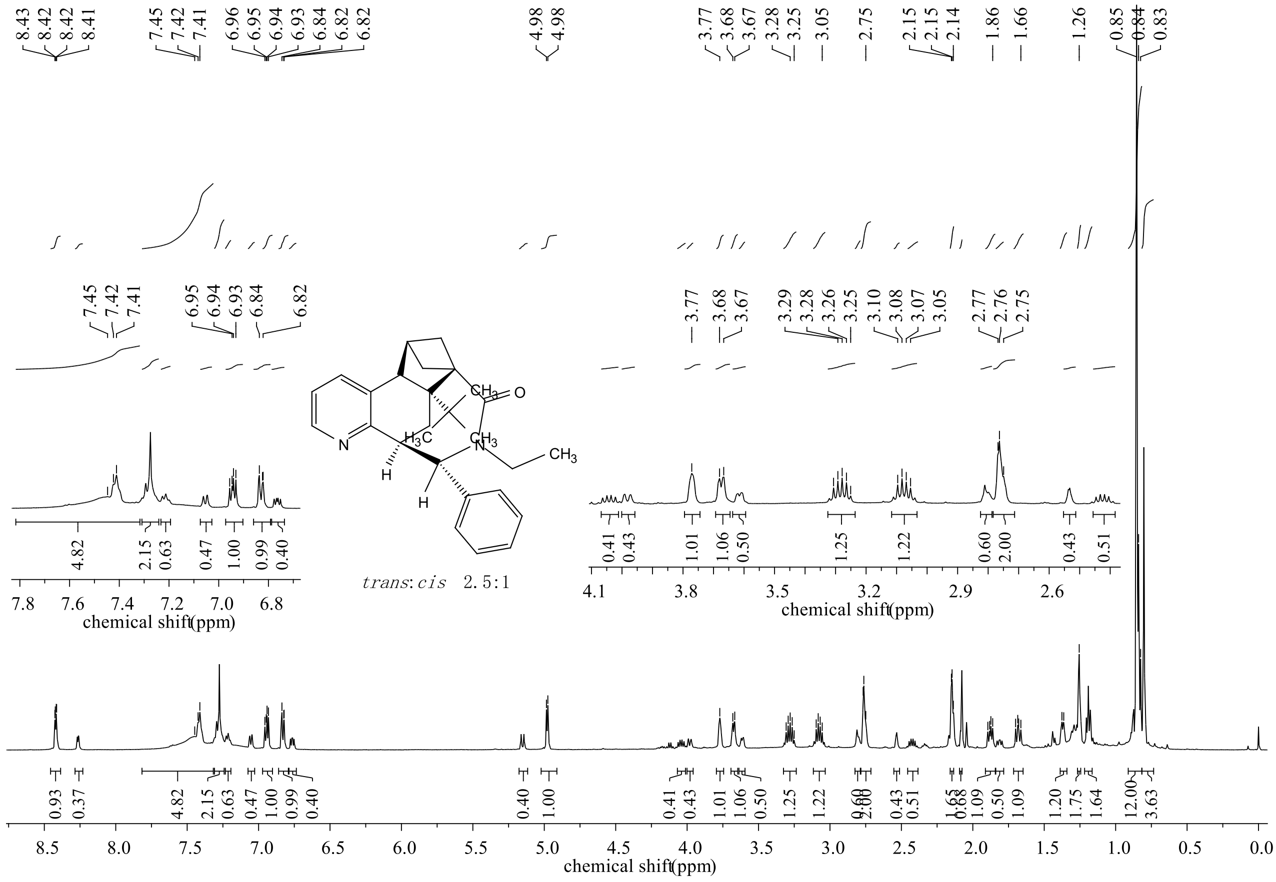
cis-**4wb** ^{1}H NMR (400 MHz, $CDCl_3$)



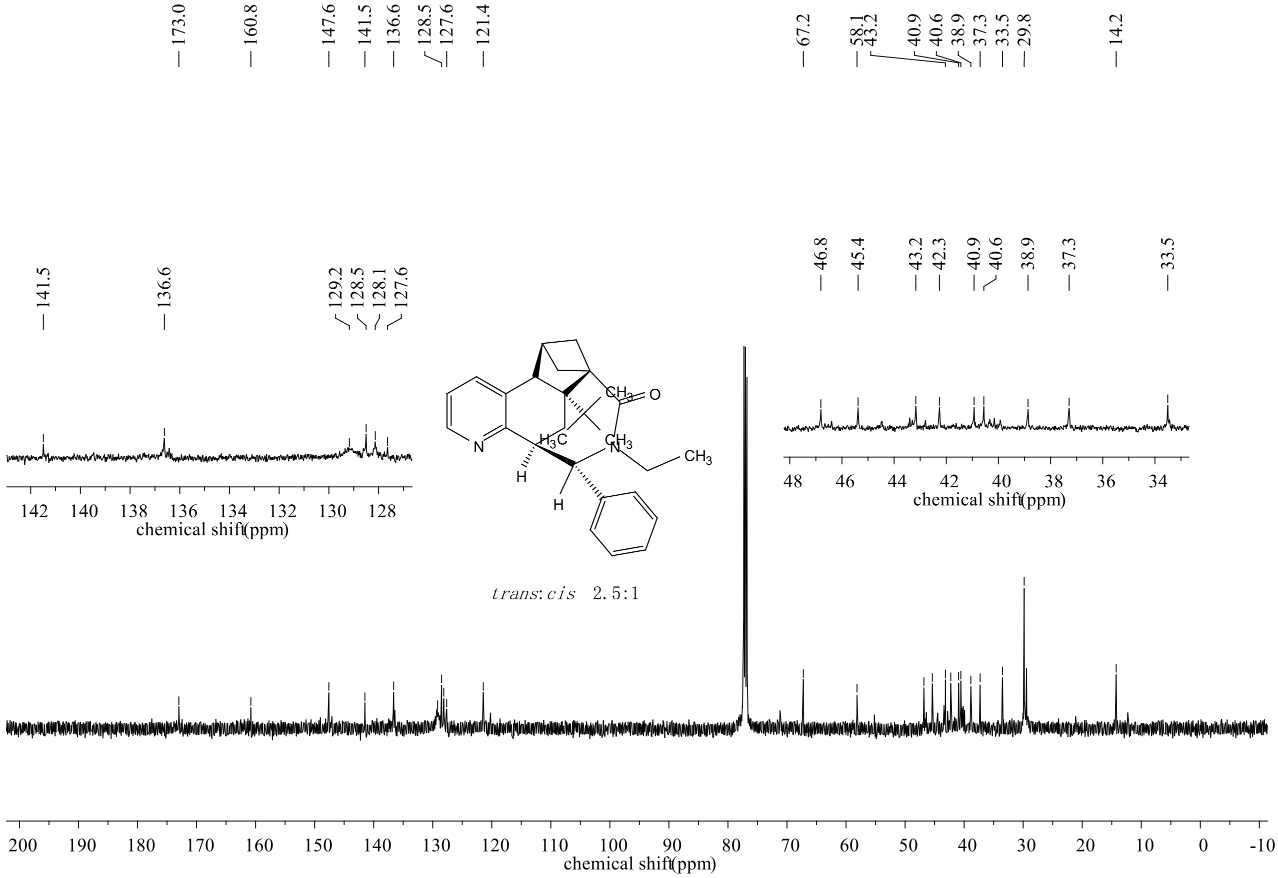
cis-**4wb** ^{13}C NMR (126 MHz, CDCl$_3$)



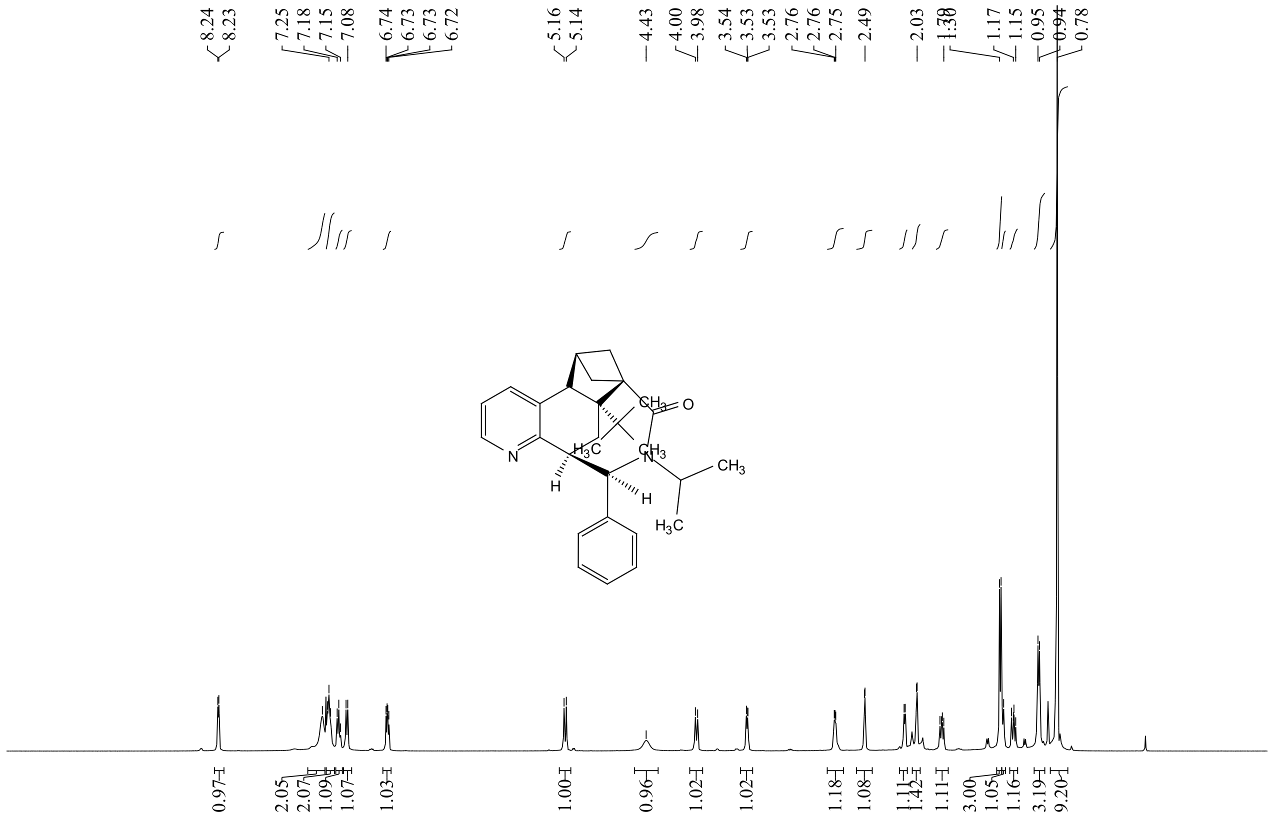
trans-**4wb** ^{1}H NMR (500 MHz, CDCl$_3$)



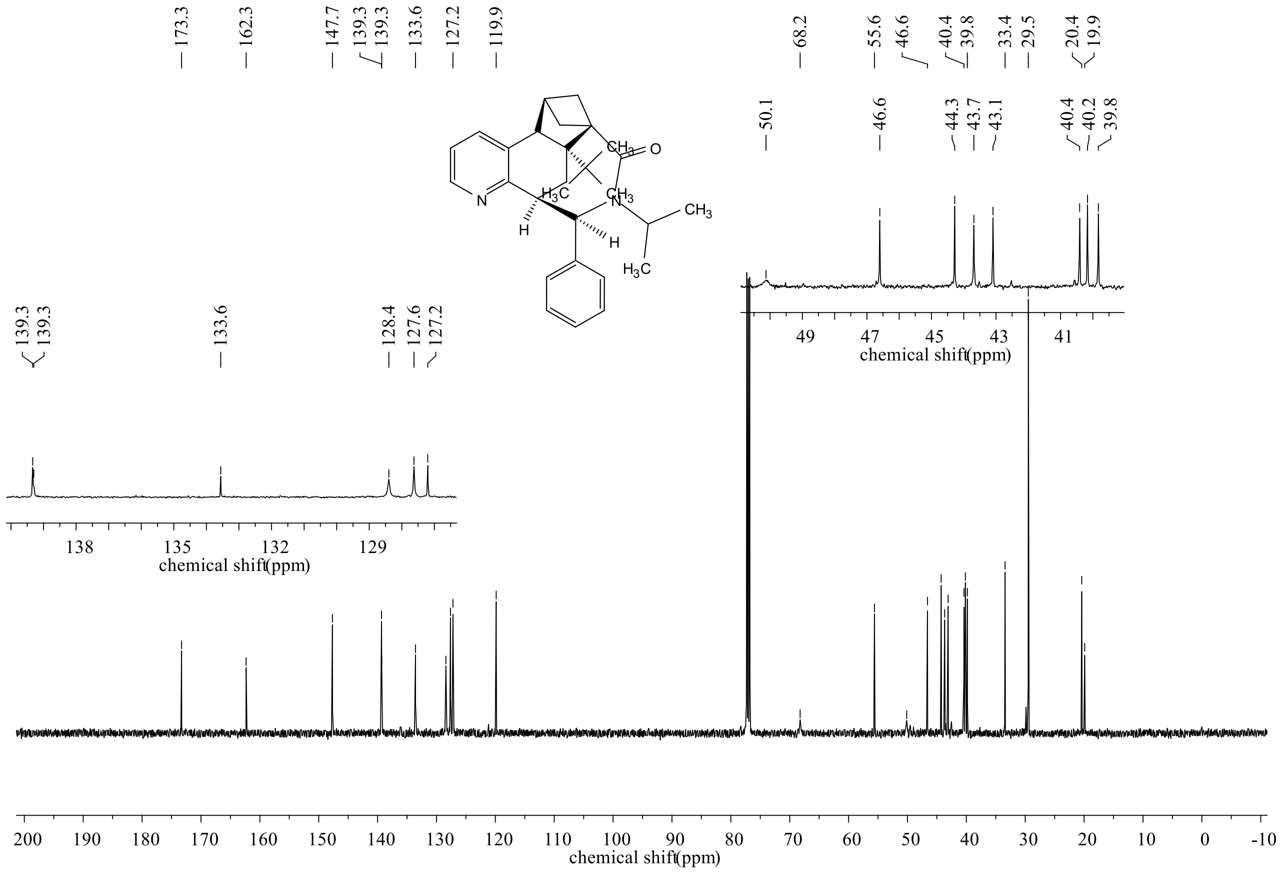
trans-**4wb** ^{13}C NMR (126 MHz, $CDCl_3$)



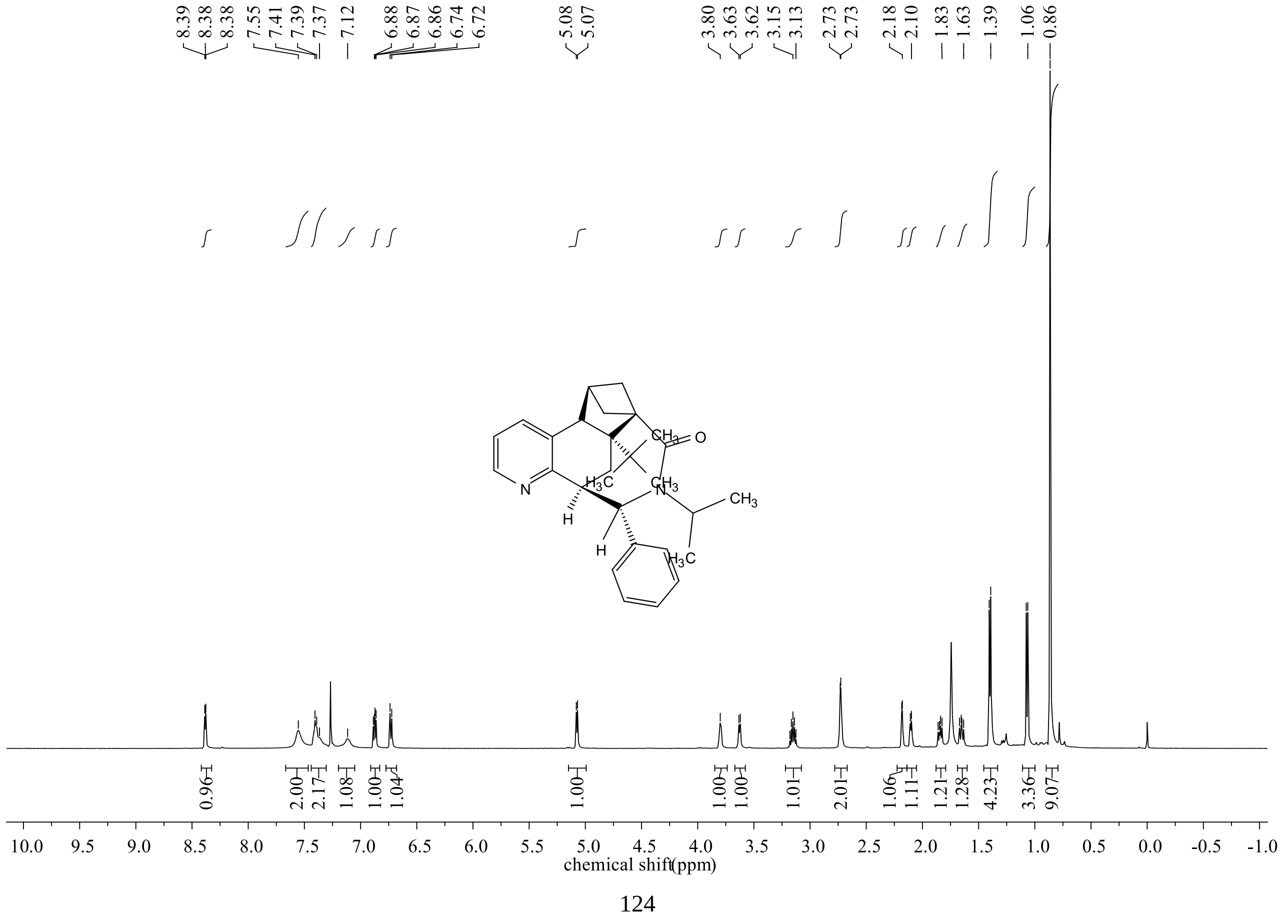
cis-**4wc** ^{1}H NMR (500 MHz, $CDCl_3$)



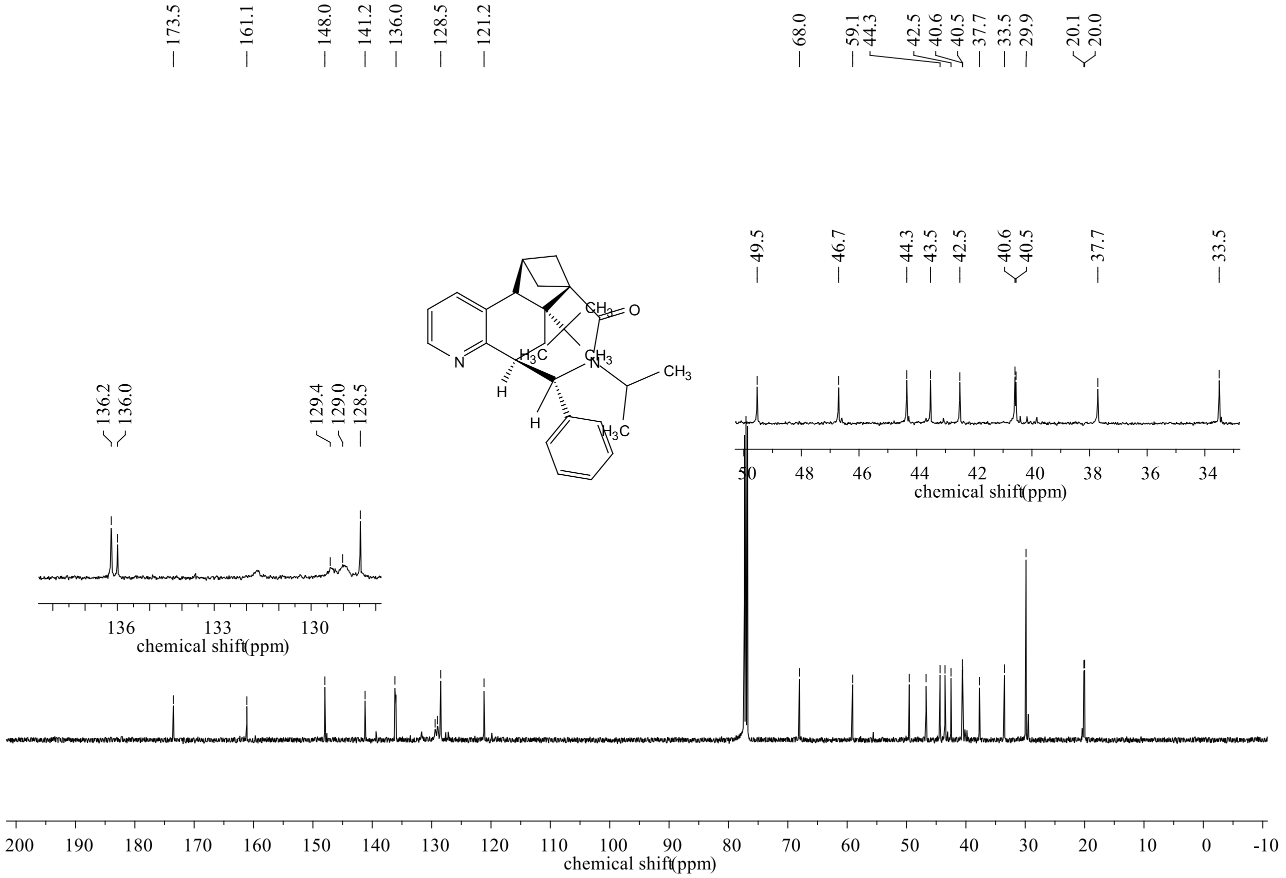
cis-**4wc** ^{13}C NMR (126 MHz, CDCl$_3$)



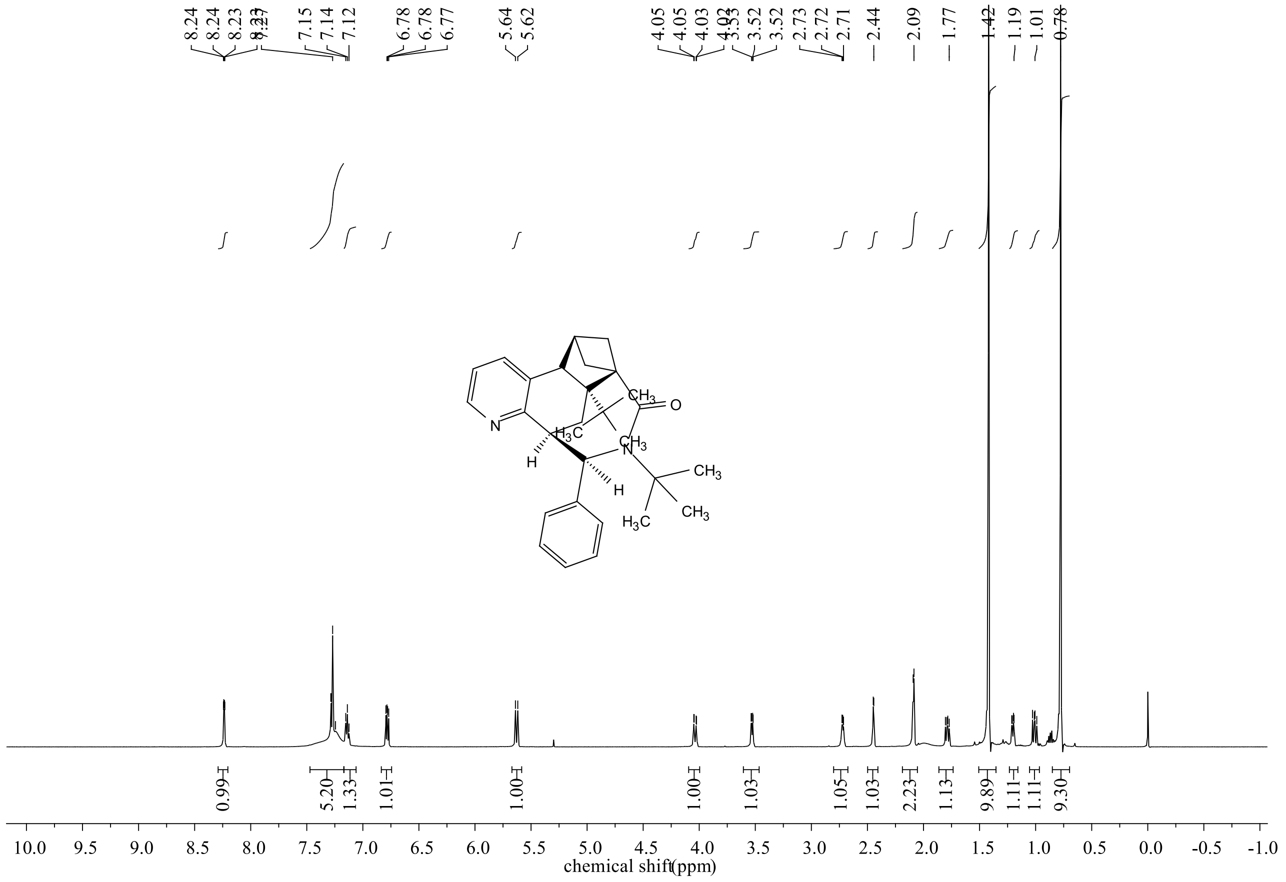
trans-**4wc** ^{1}H NMR (500 MHz, CDCl$_3$)



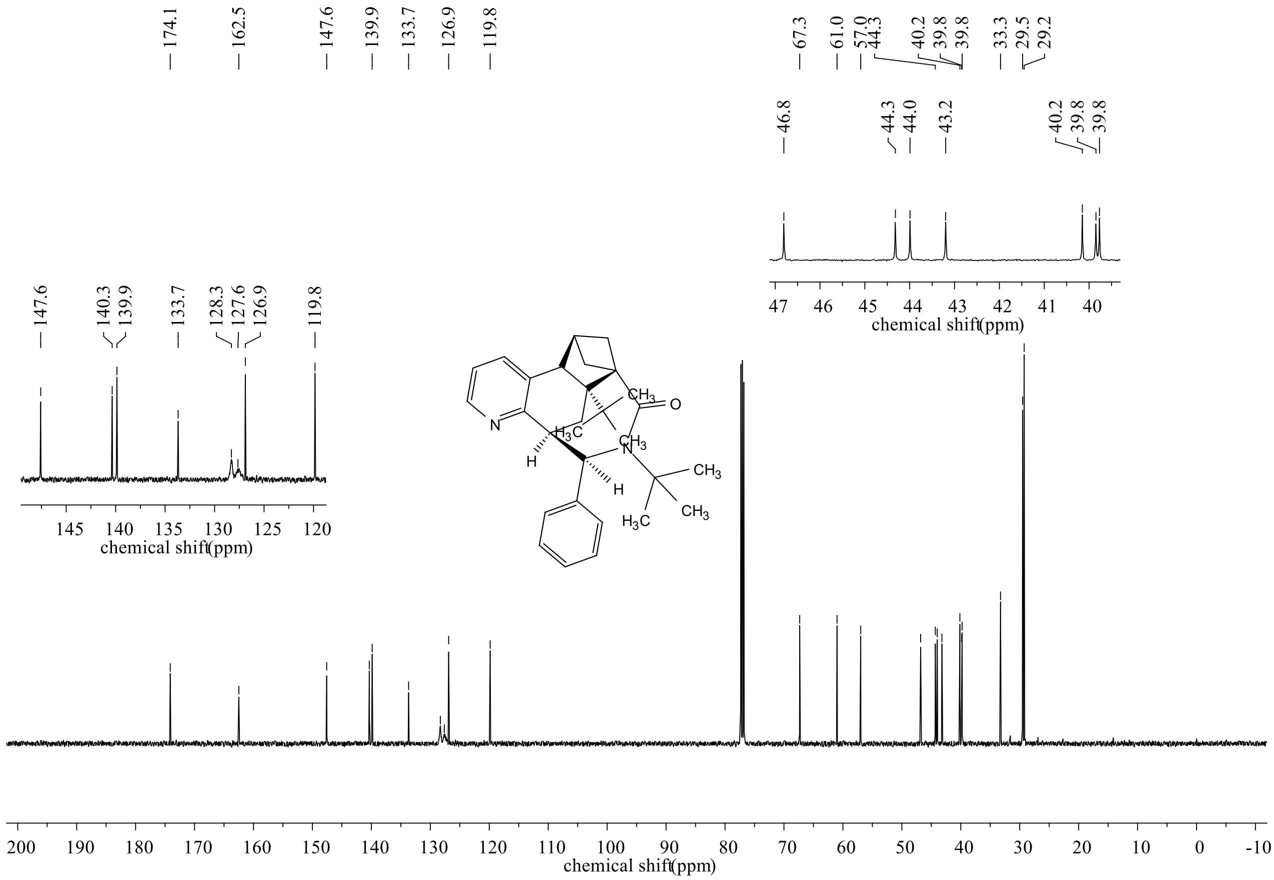
trans-**4wc** ^{13}C NMR (126 MHz, $CDCl_3$)



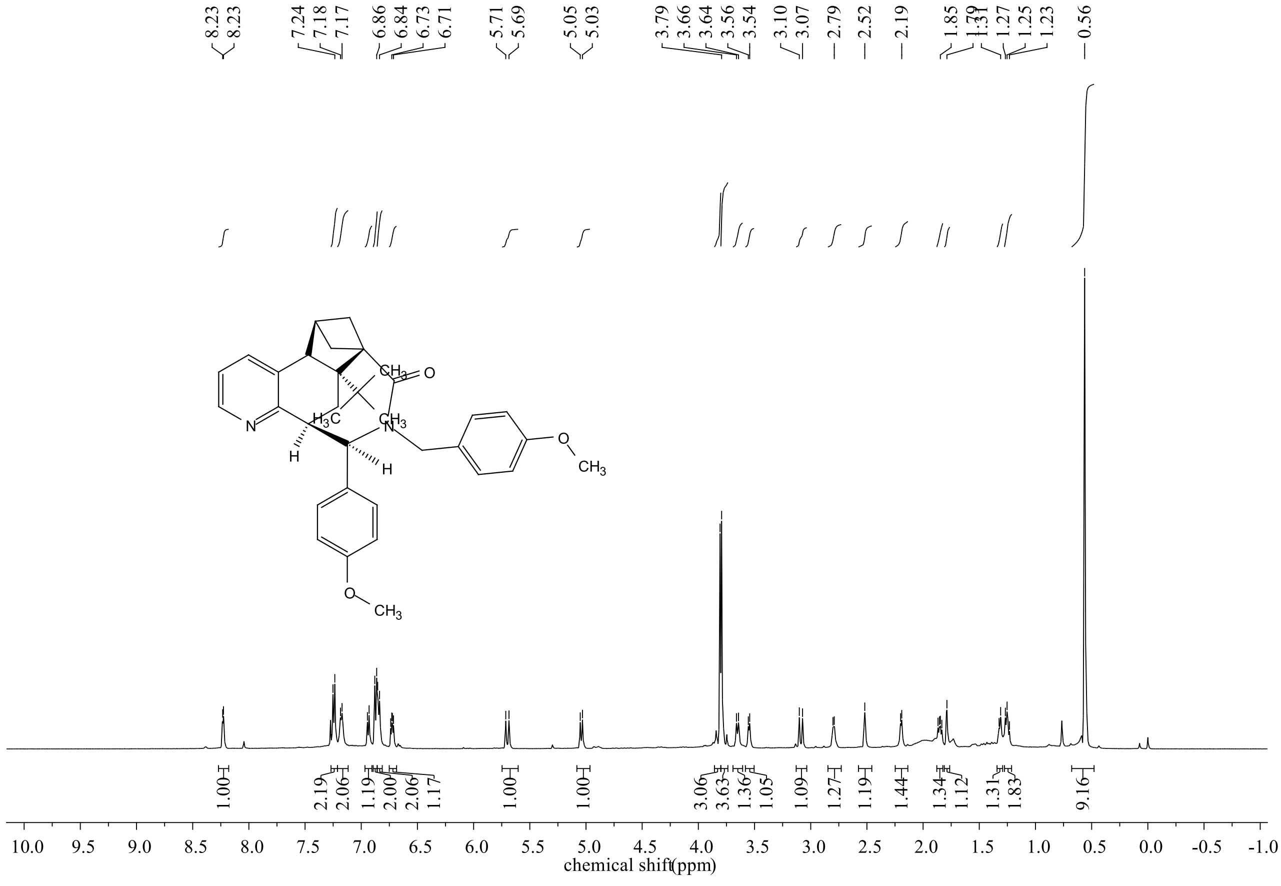
cis-**4wd** ^{1}H NMR (500 MHz, $CDCl_3$)



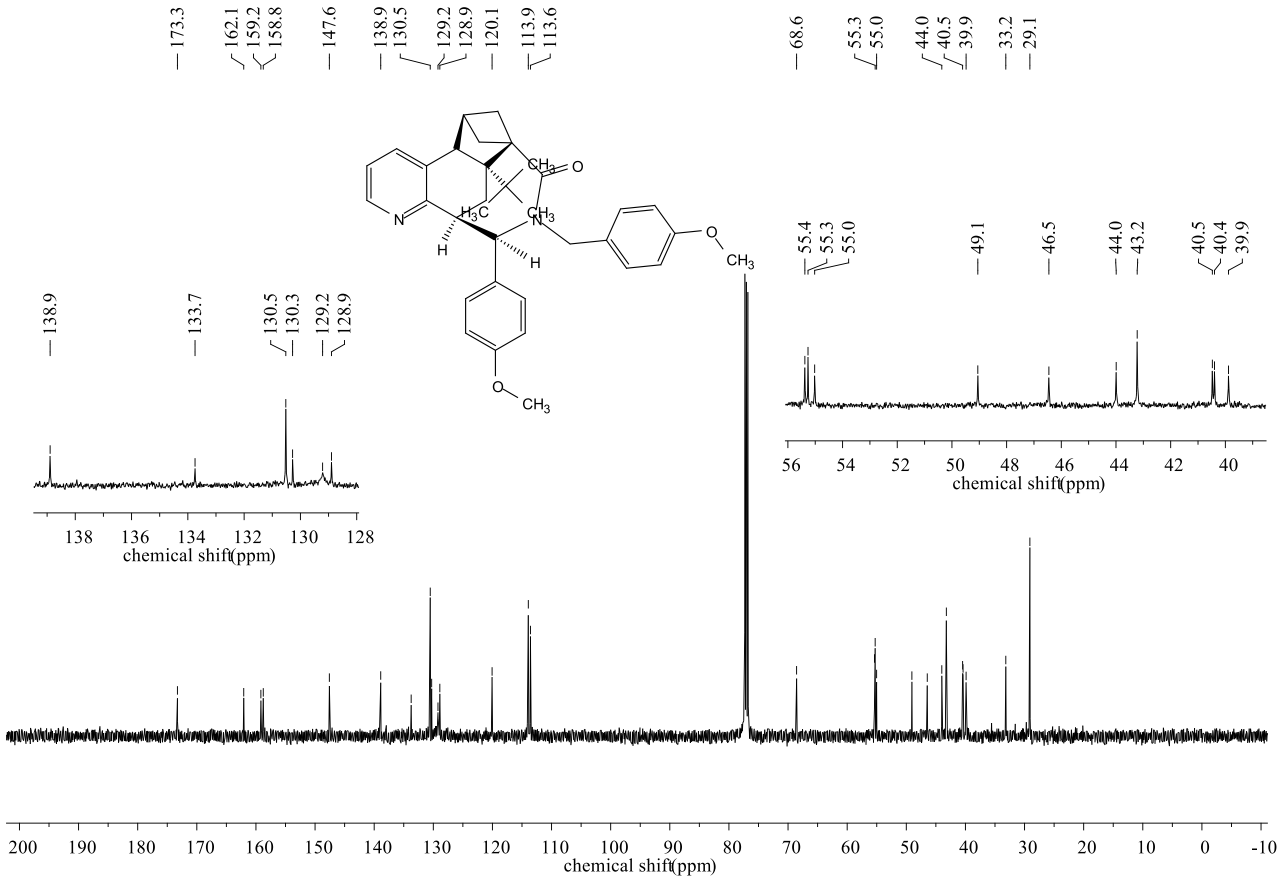
cis-**4wd** ^{13}C NMR (126 MHz, $CDCl_3$)



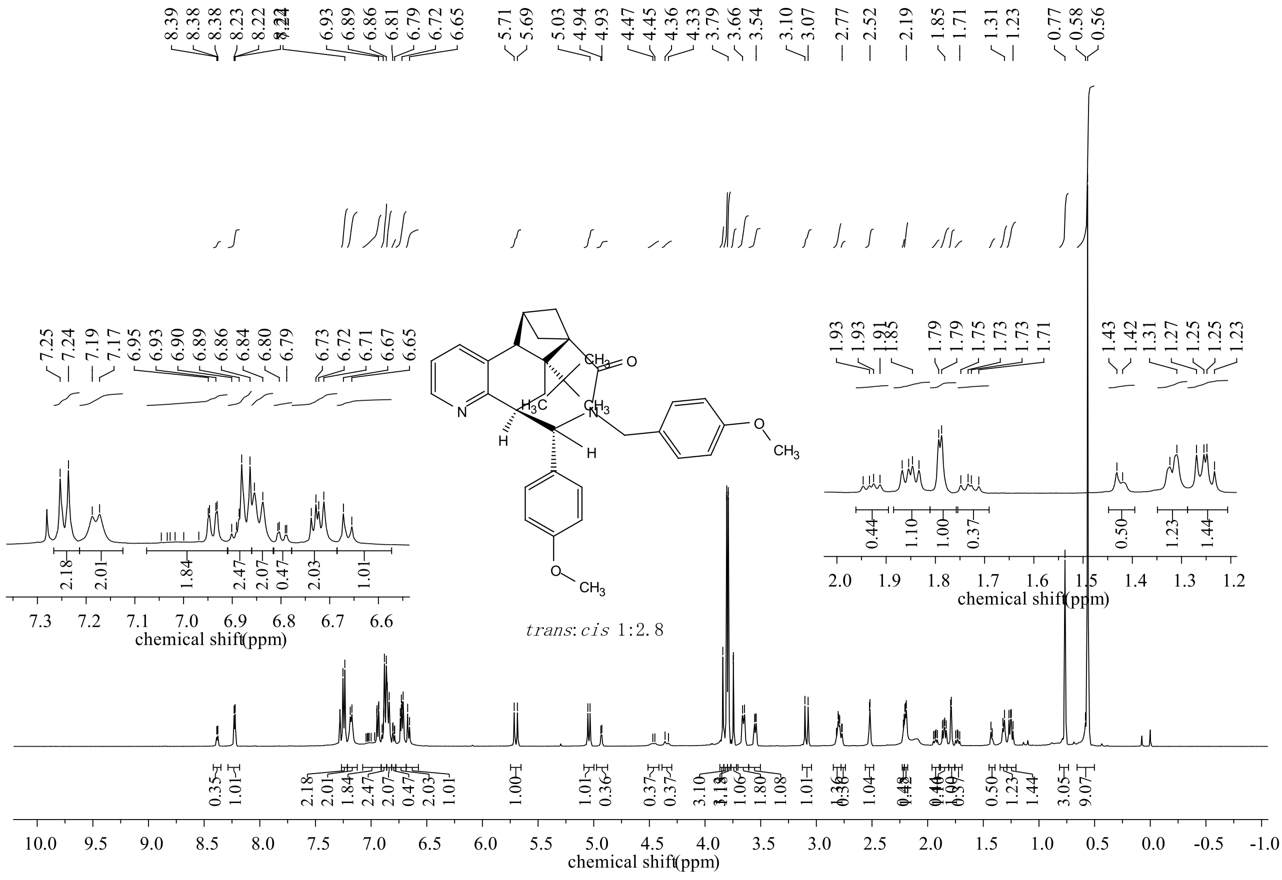
cis-**4we** ^{1}H NMR (500 MHz, $CDCl_3$)



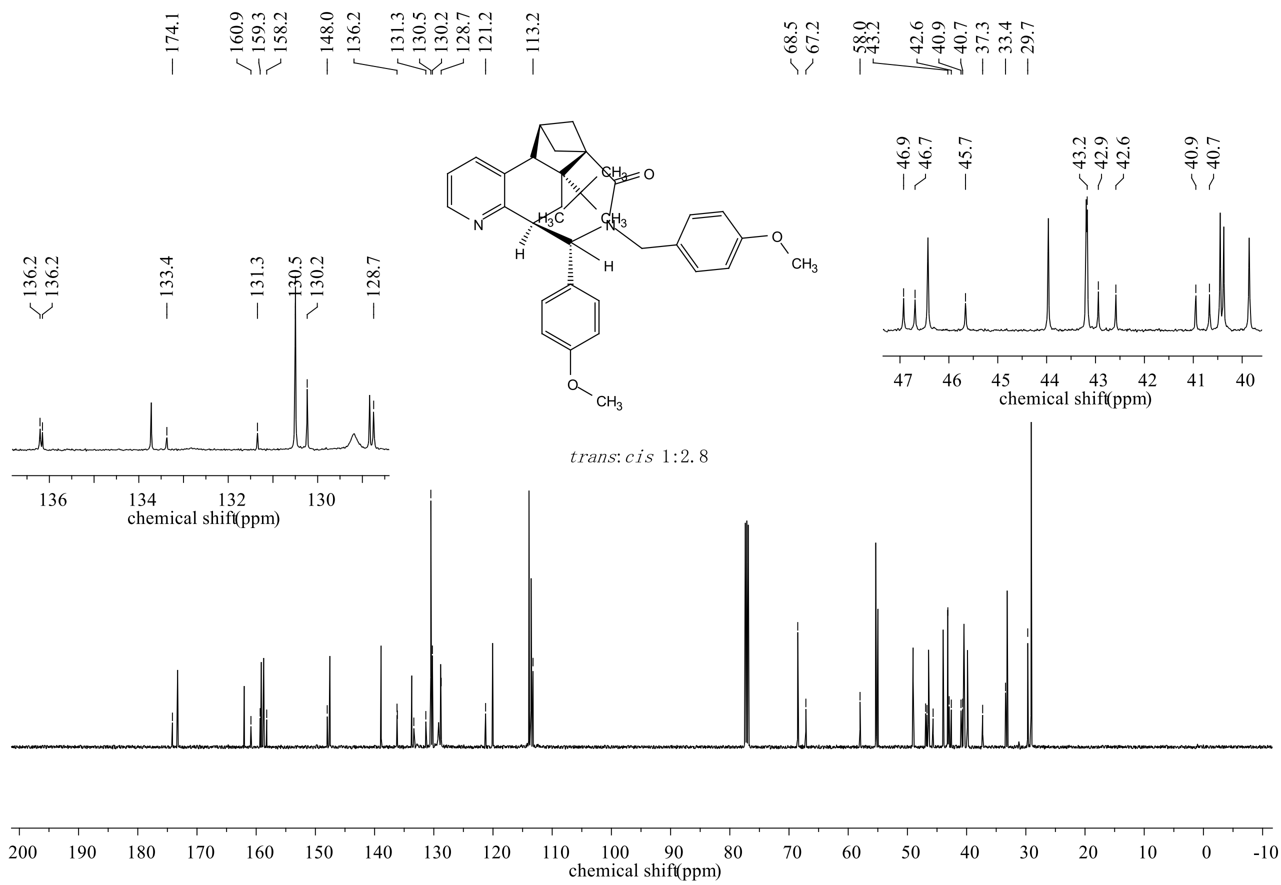
cis-**4we** ^{13}C NMR (126 MHz, CDCl$_3$)



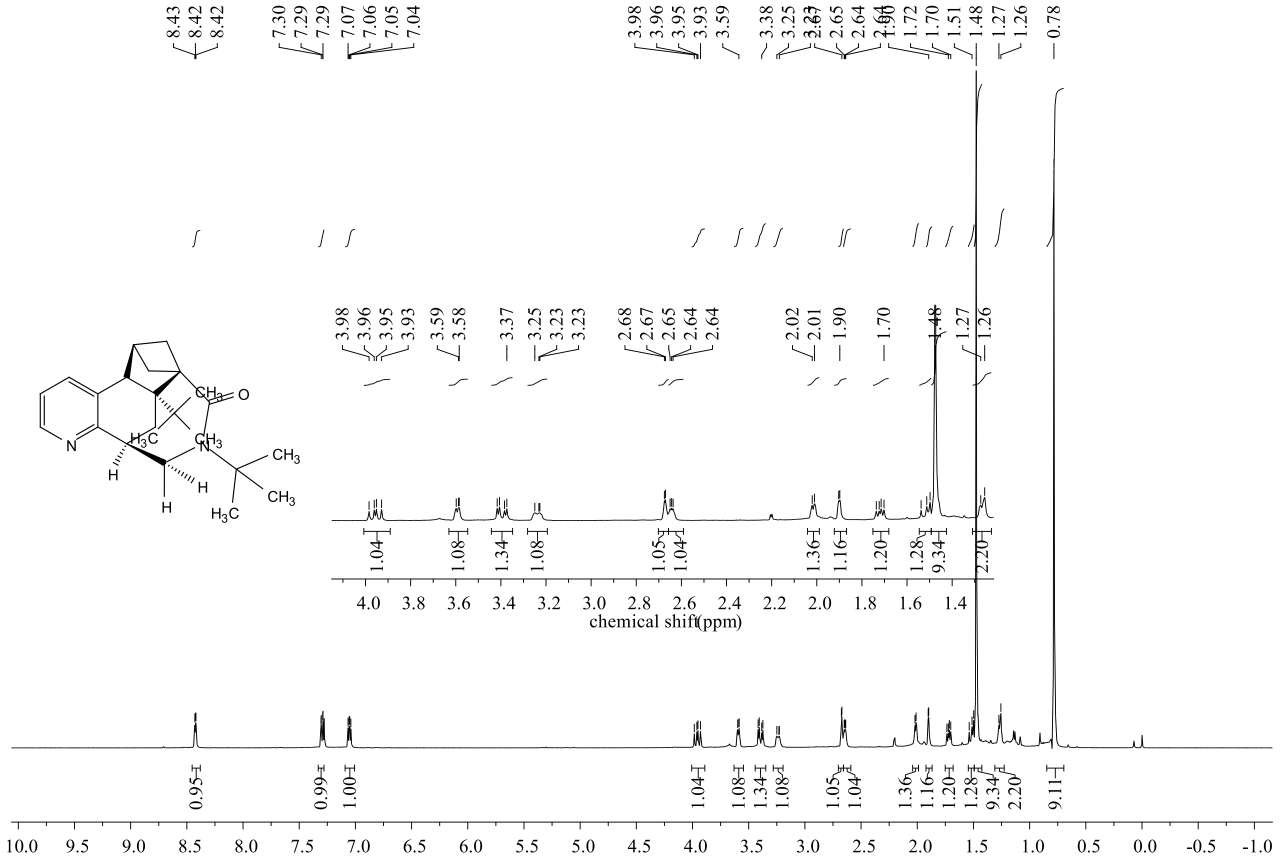
trans-**4we** ^{1}H NMR (500 MHz, CDCl$_3$)



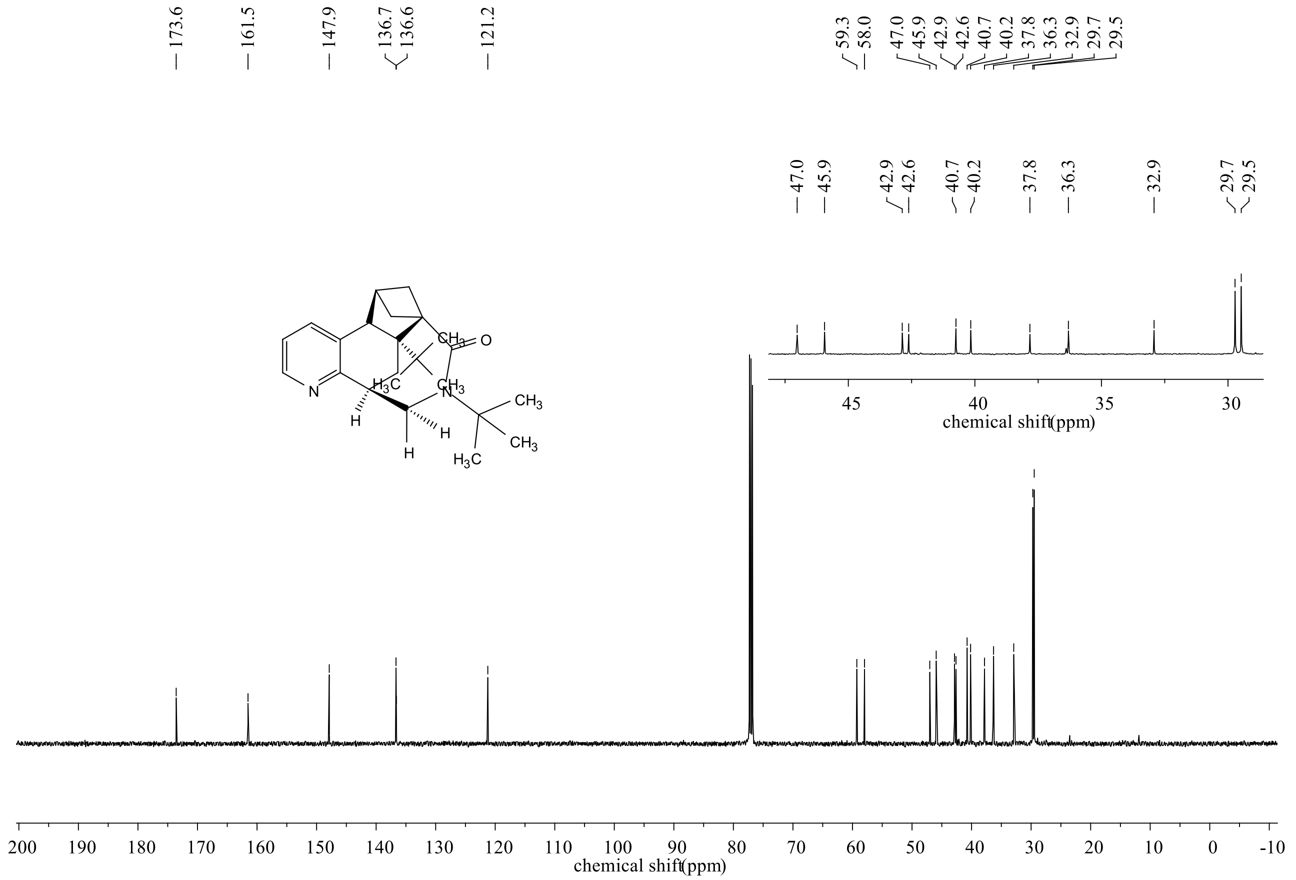
trans-**4we** ^{13}C NMR (126 MHz, $CDCl_3$)



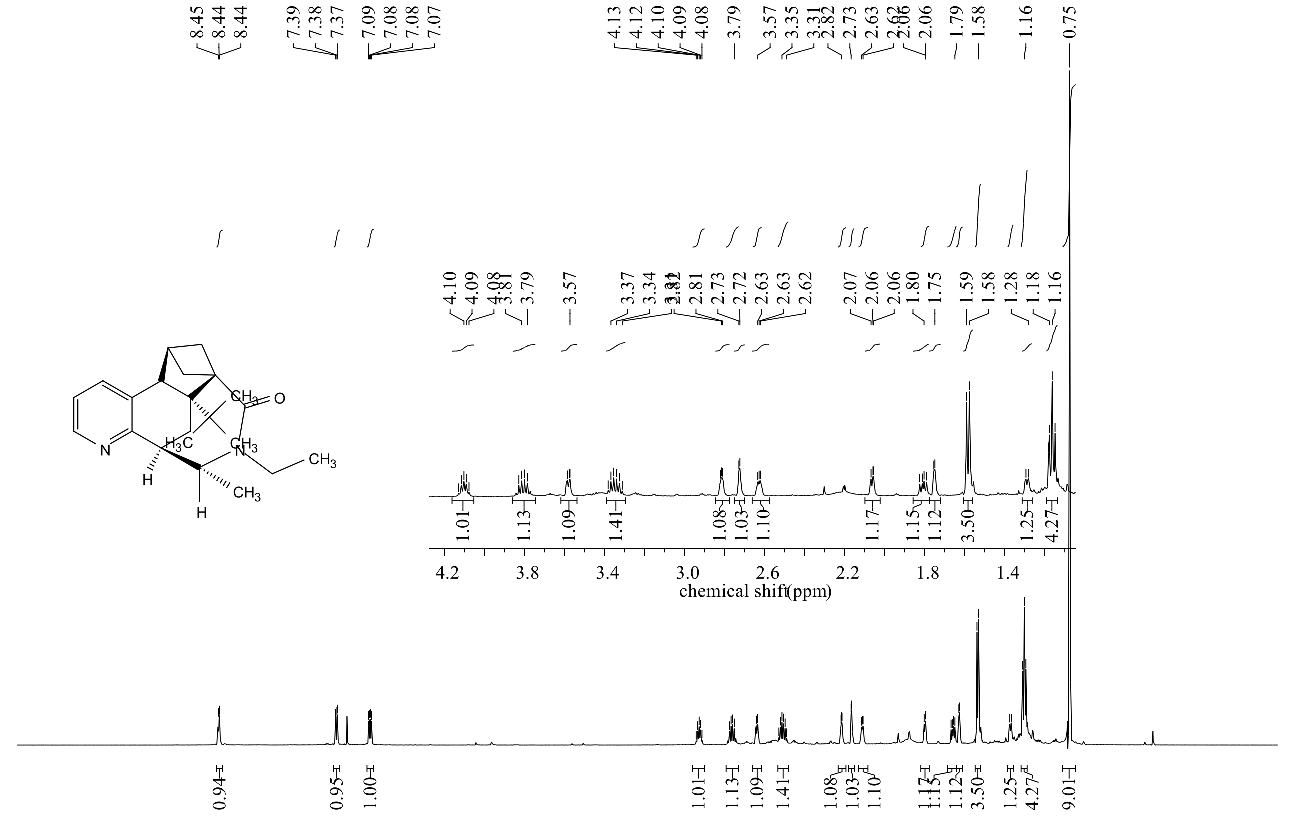
4wf ^{1}H NMR (500 MHz, $CDCl_3$)



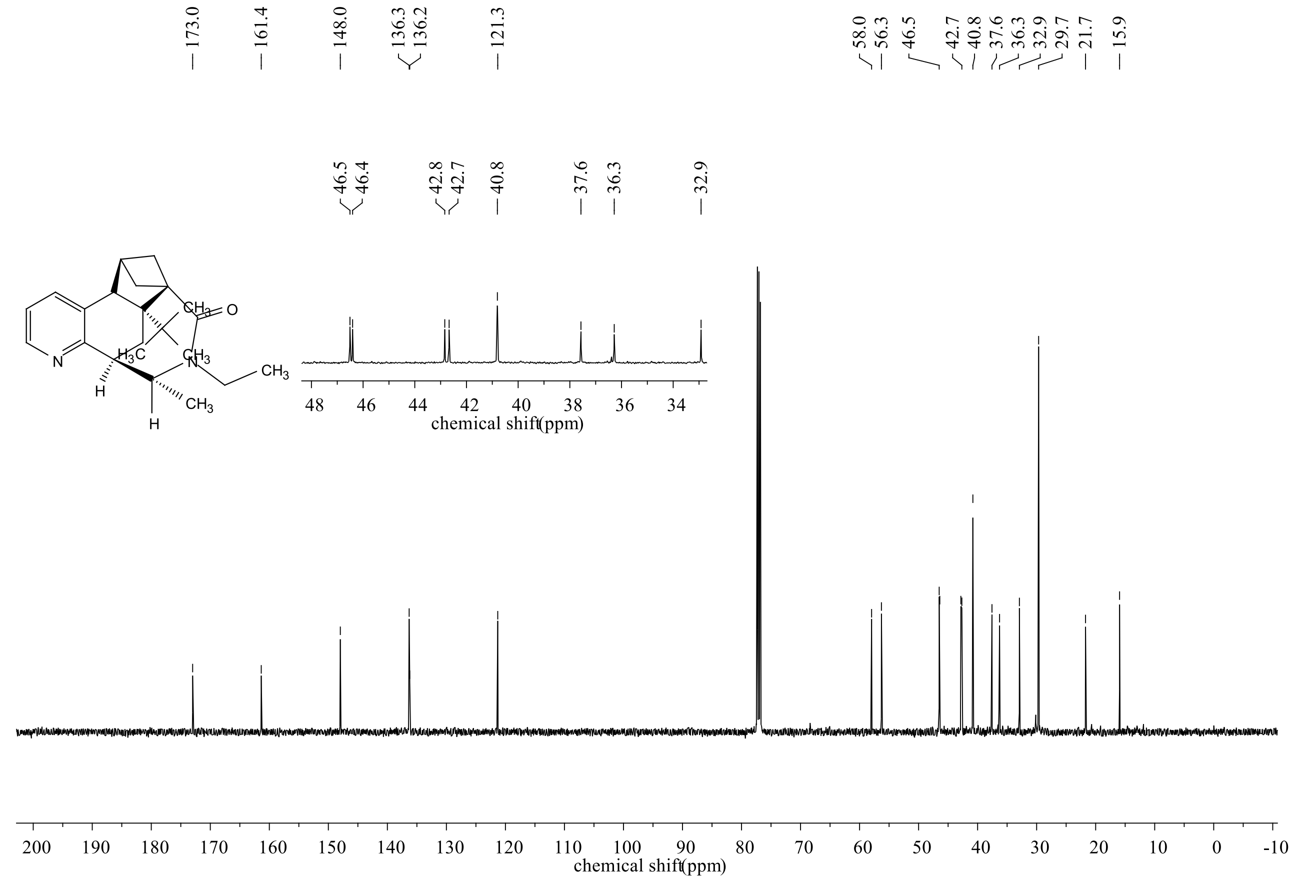
4wf ^{13}C NMR (126 MHz, CDCl$_3$)



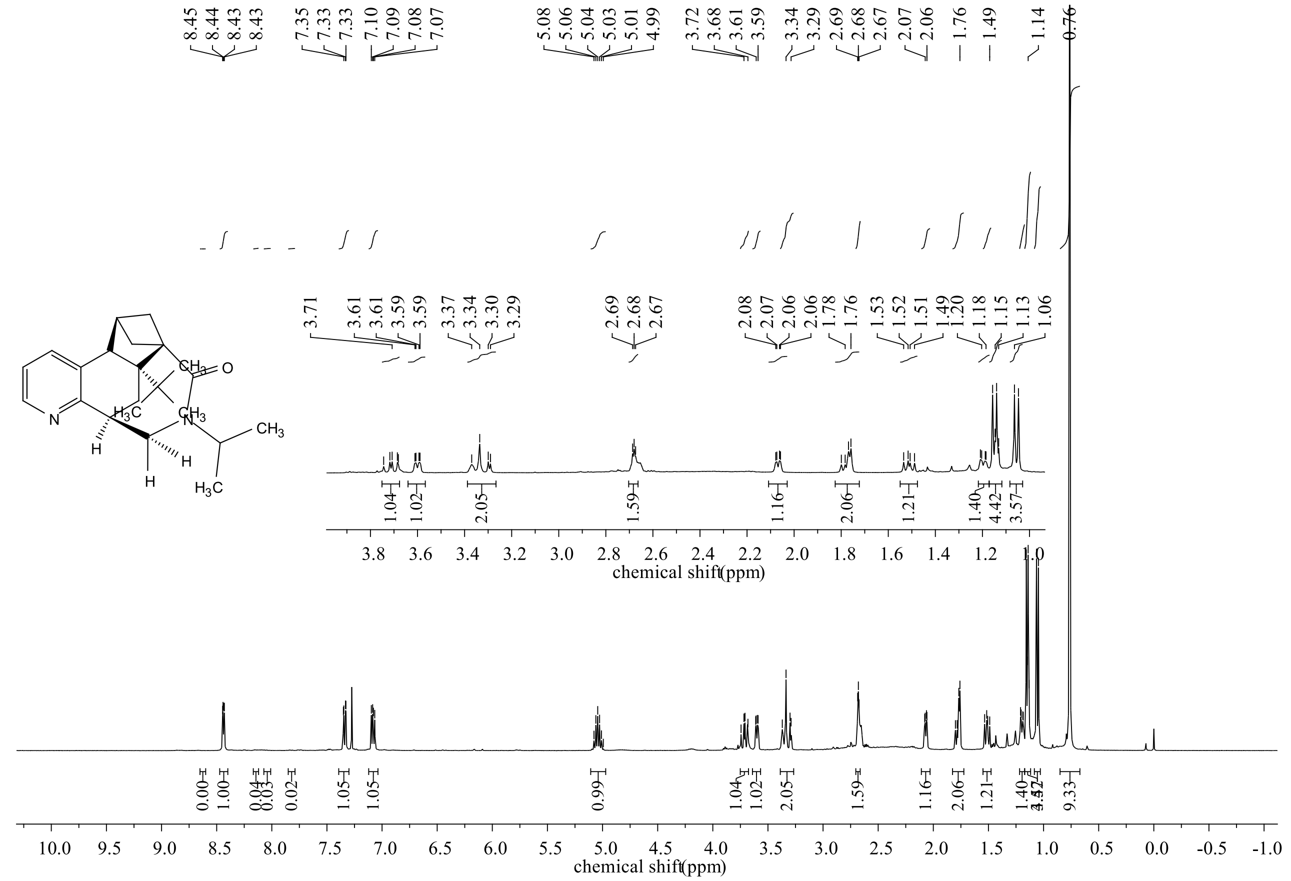
trans-**4wg** ^{1}H NMR (500 MHz, CDCl$_3$)



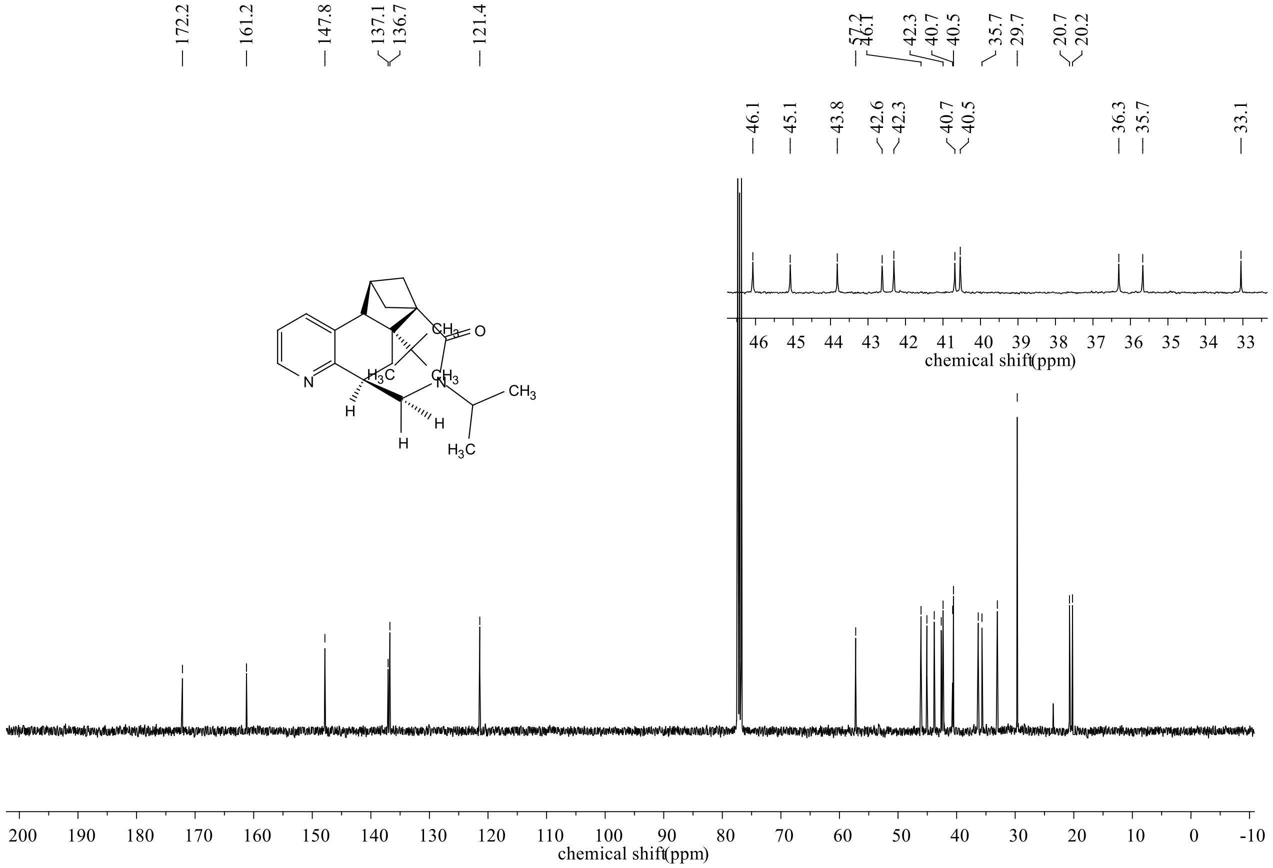
trans-**4wg** ^{13}C NMR (126 MHz, CDCl$_3$)



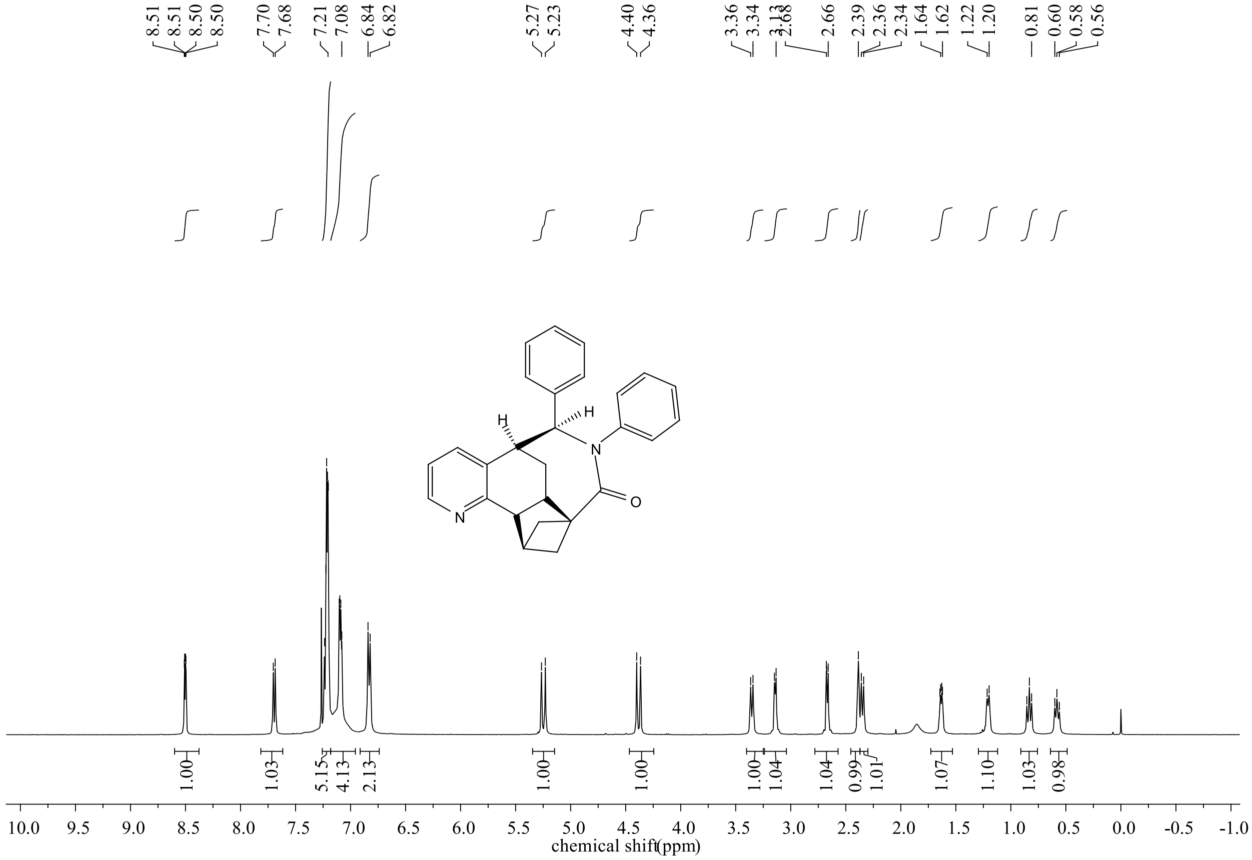
4wh ^{1}H NMR (400 MHz, CDCl$_3$)



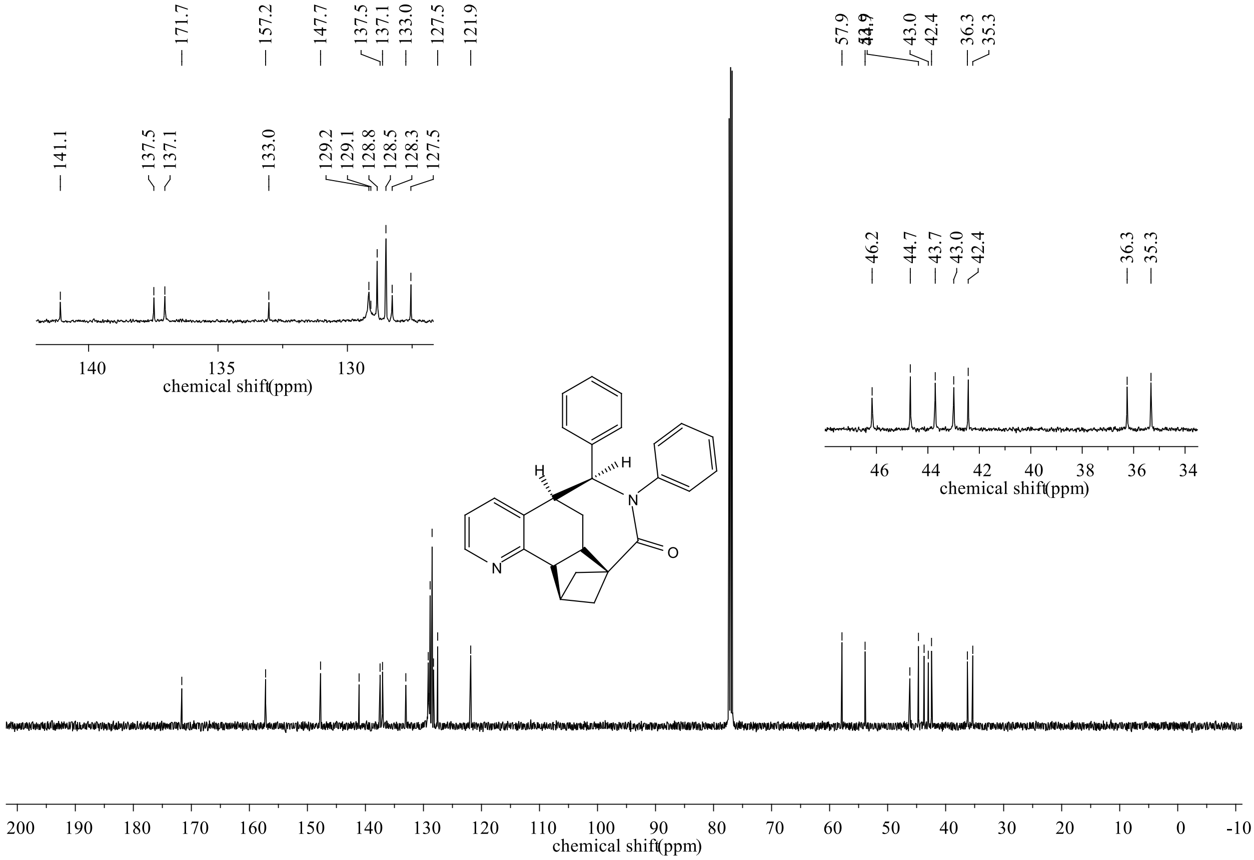
4wh ^{13}C NMR (101 MHz, $CDCl_3$)



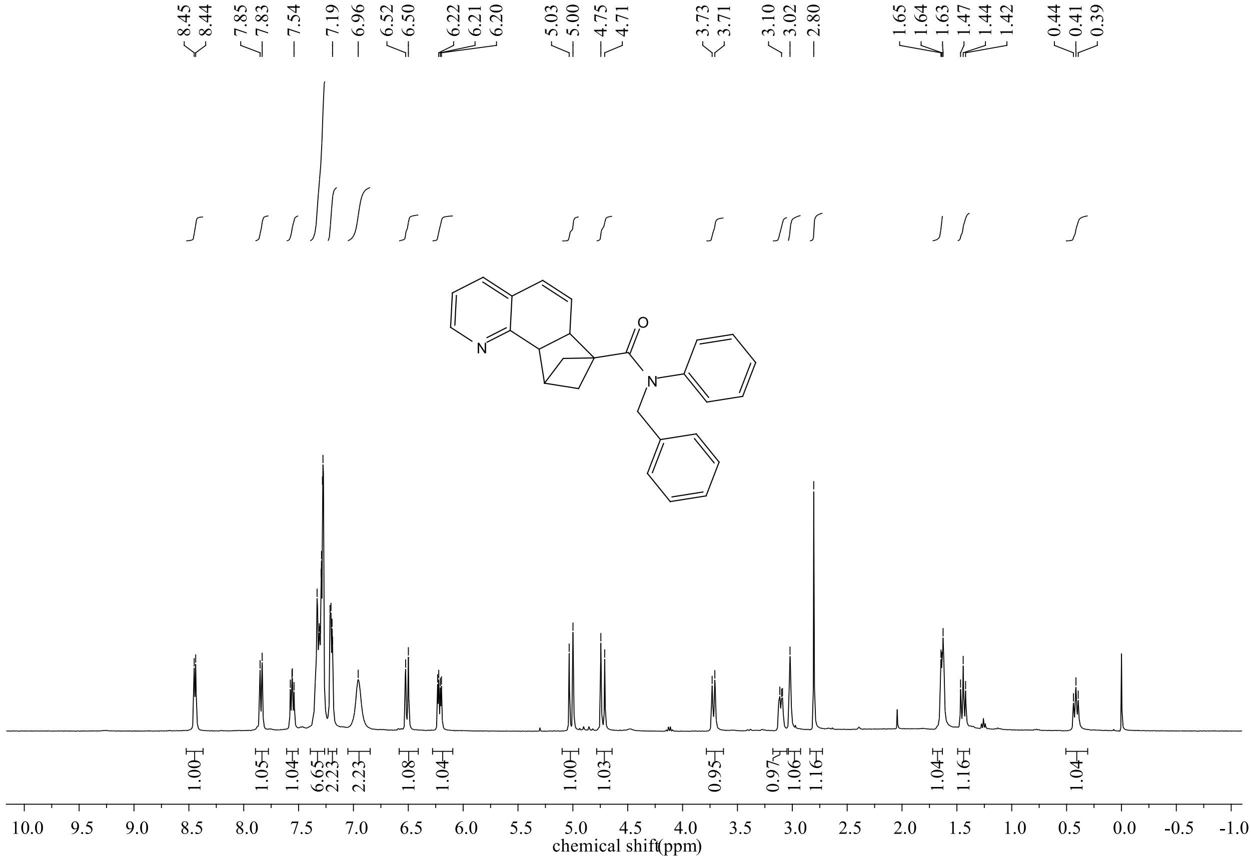
cis-**4AW** ^{1}H NMR (400 MHz, $CDCl_3$)



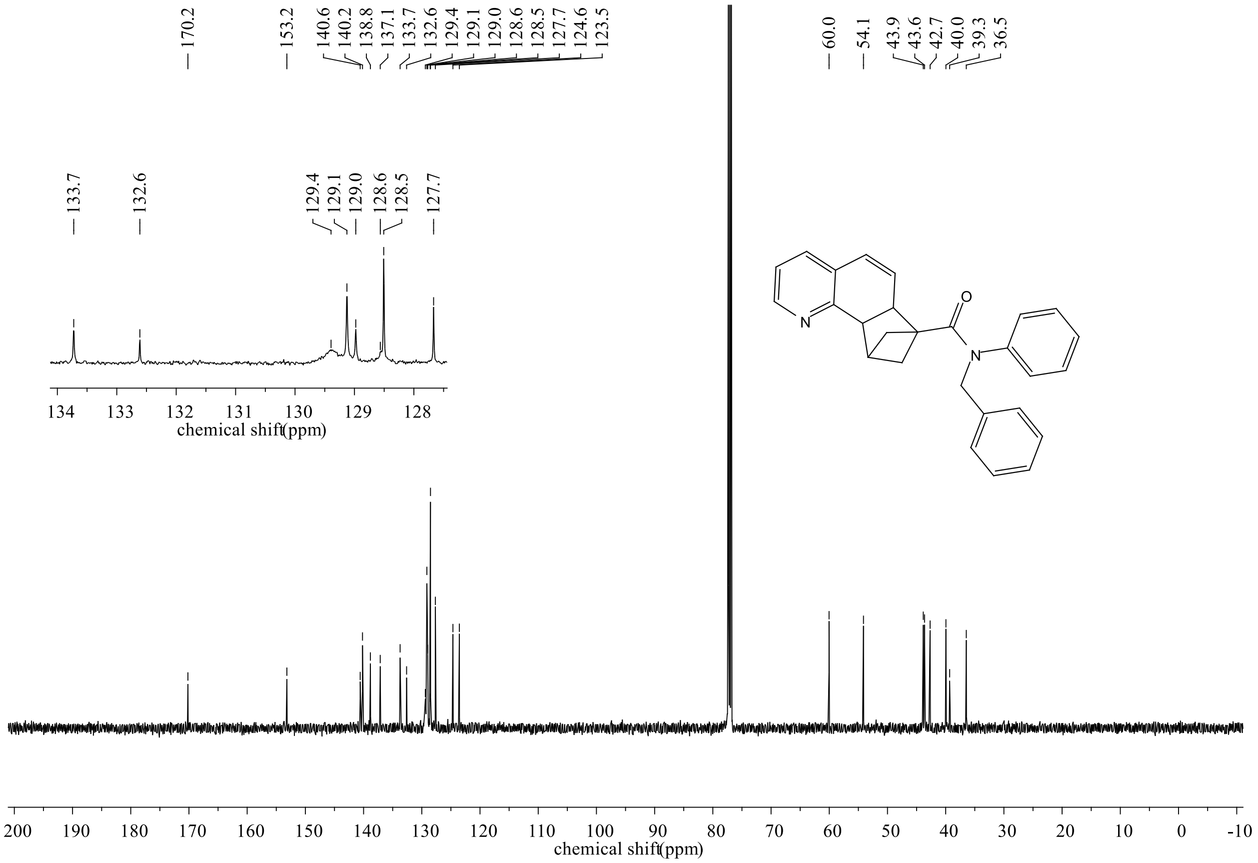
cis-**4AW** ^{13}C NMR (126 MHz, CDCl$_3$)



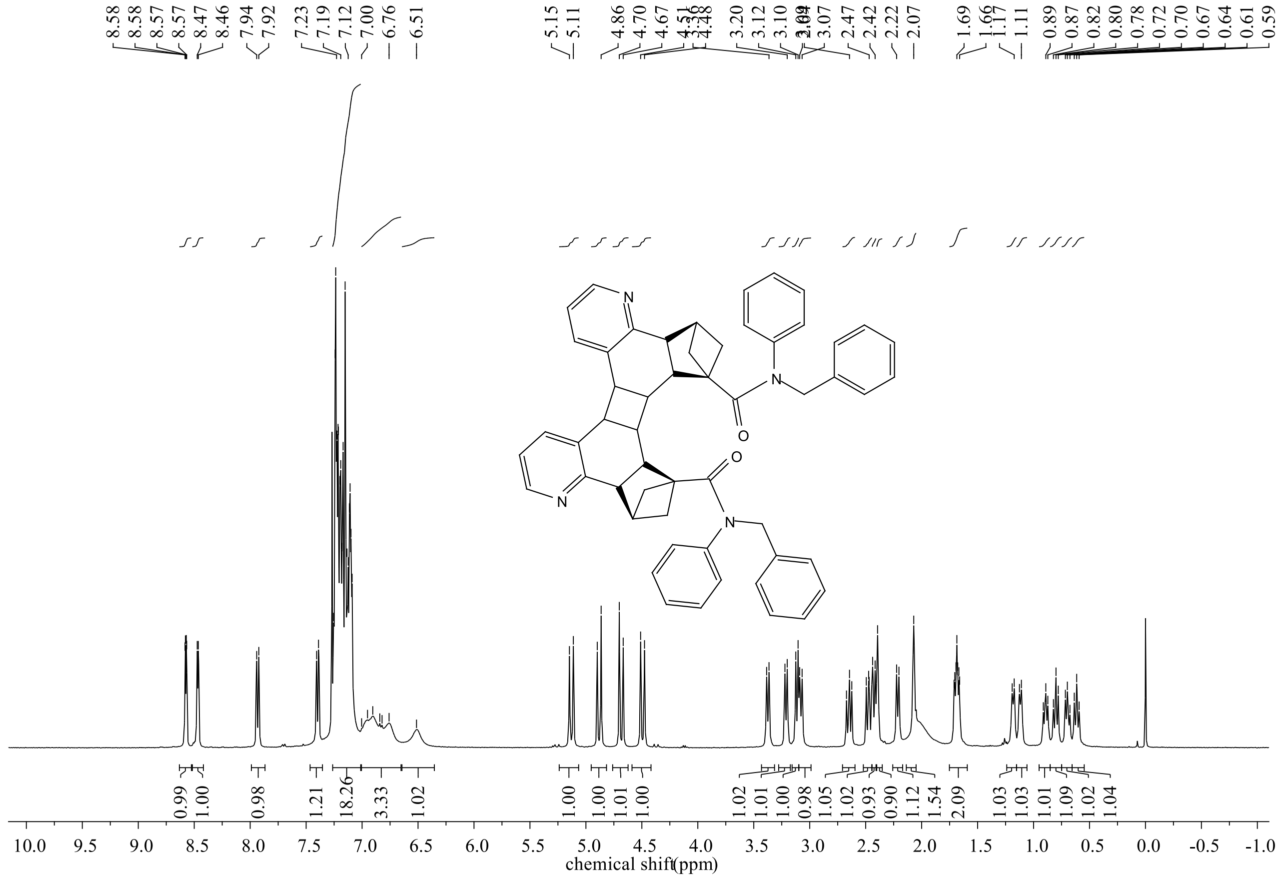
3AW ^{1}H NMR (400 MHz, CDCl$_3$)



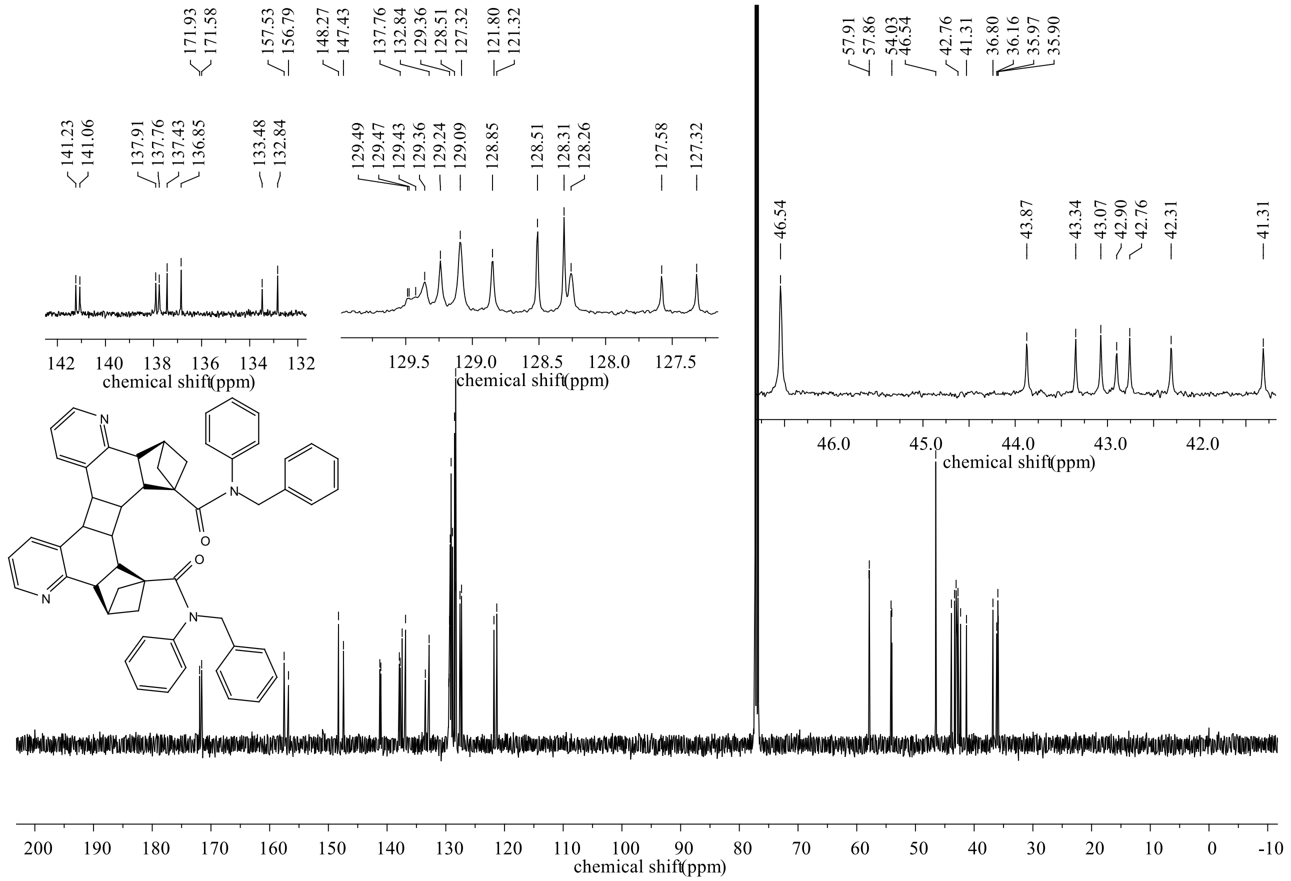
3AW ^{13}C NMR (126 MHz, $CDCl_3$)



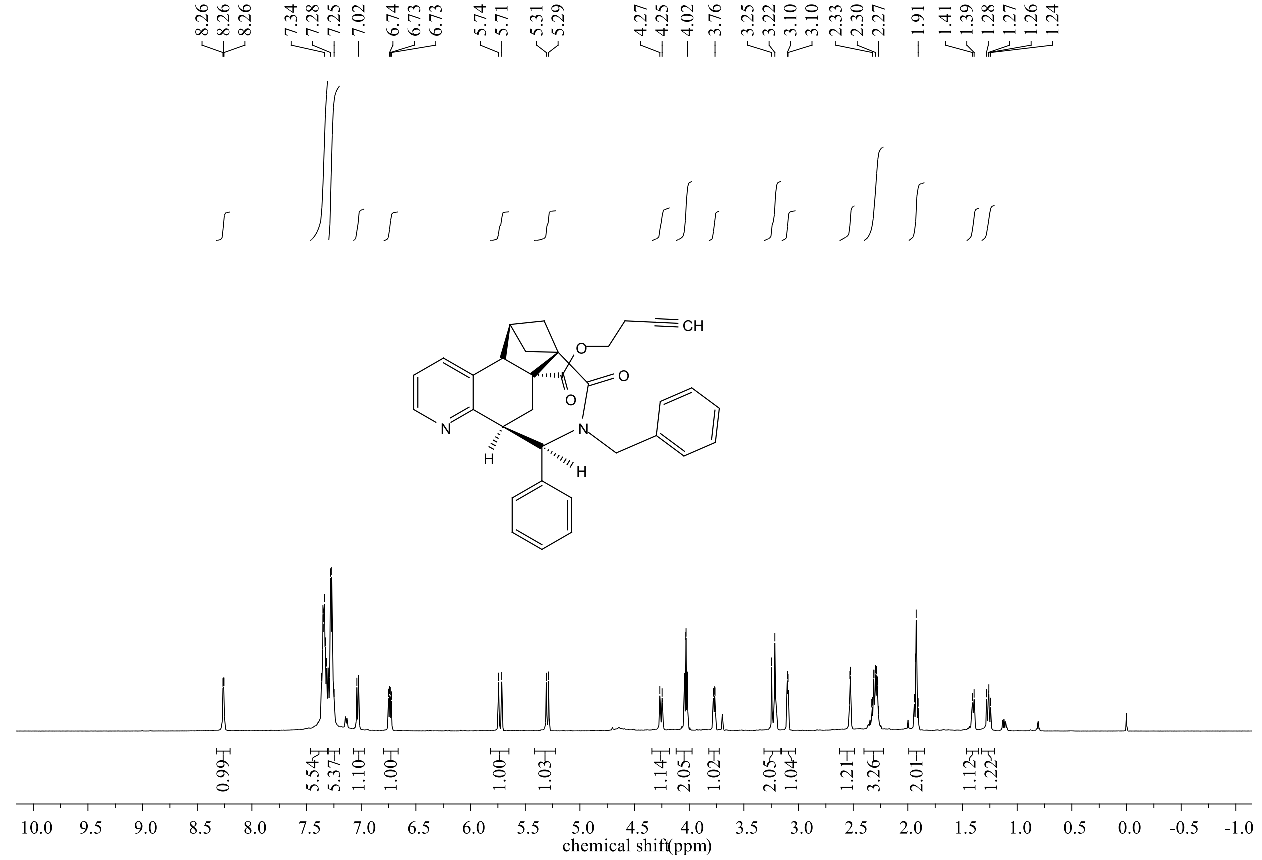
3AW-dimer ^{1}H NMR (400 MHz, $CDCl_3$)



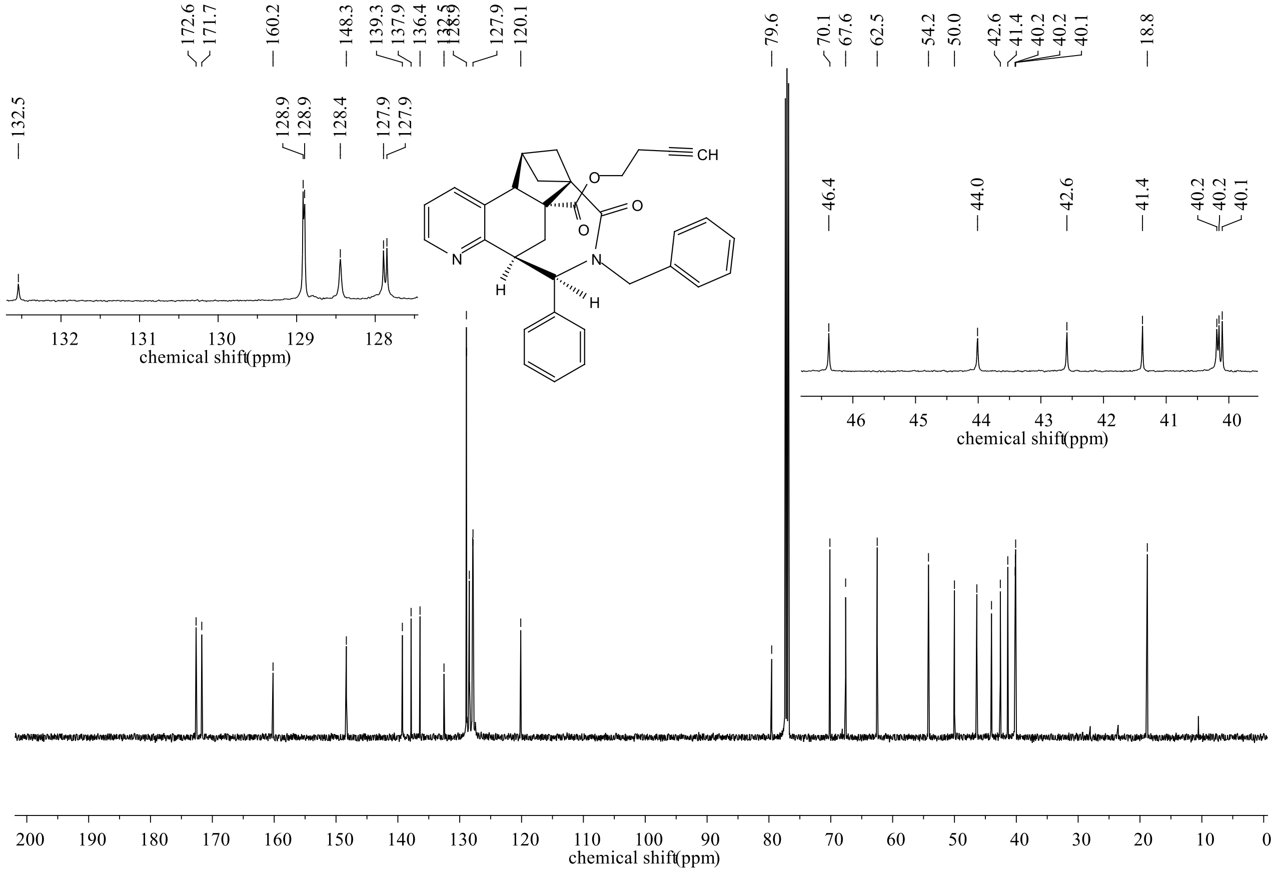
3AW-dimer ^{13}C NMR (126 MHz, CDCl$_3$)



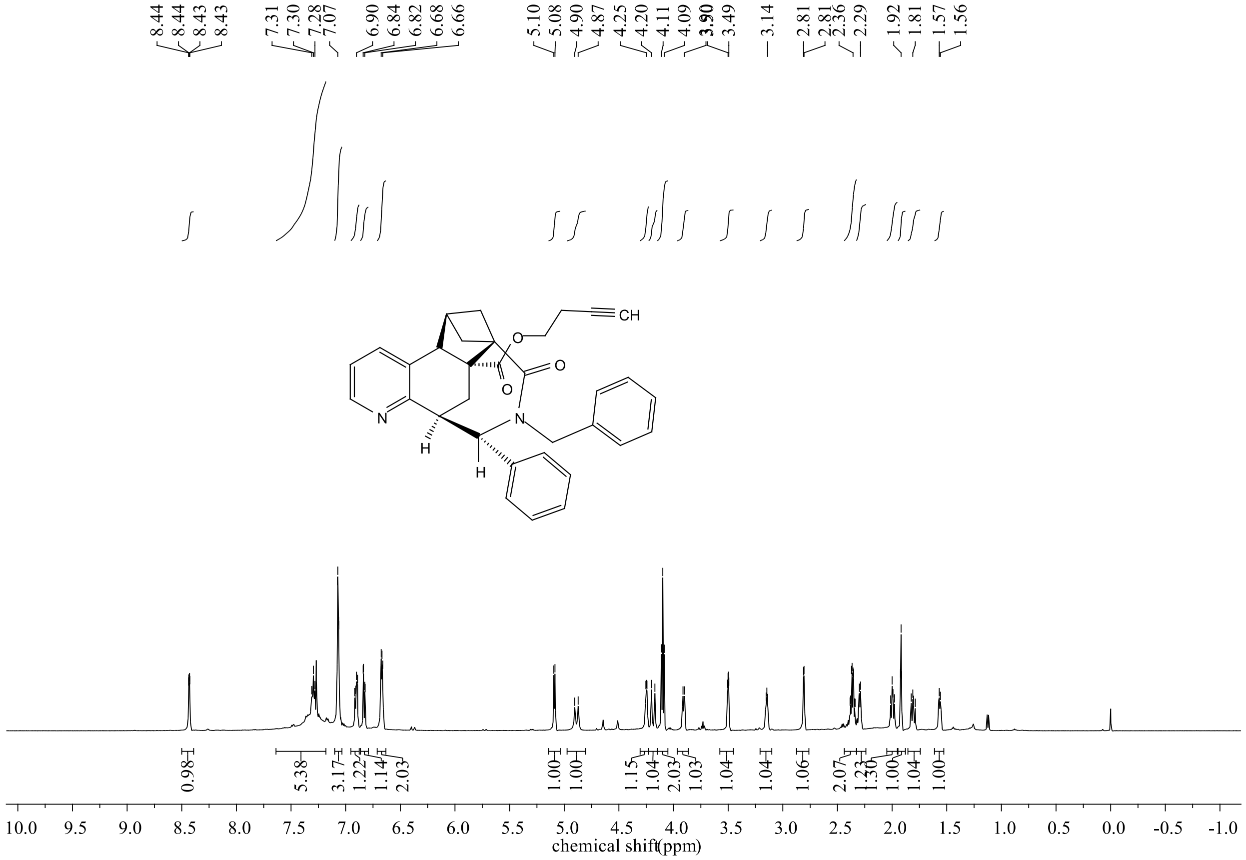
cis-**4x** ^{1}H NMR (500 MHz, CDCl$_3$)



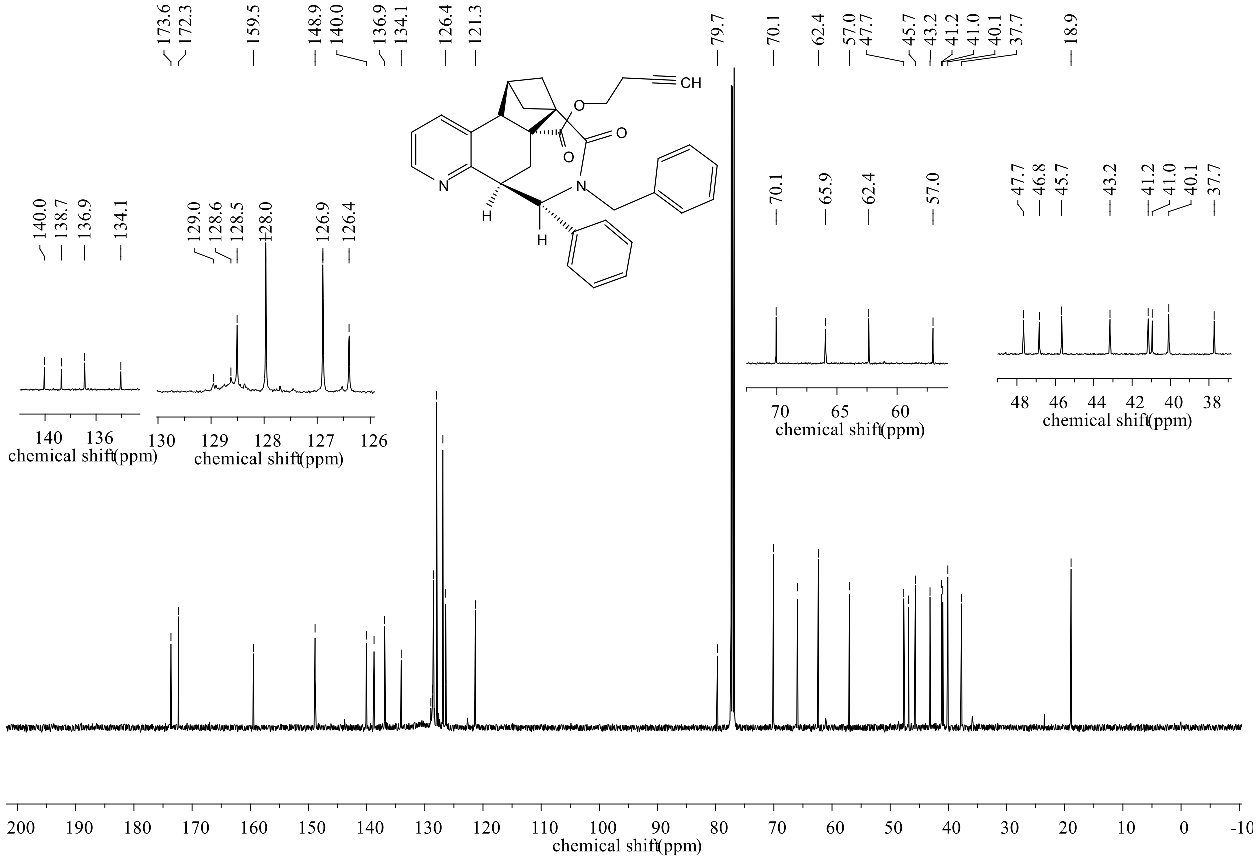
cis-**4x** ^{13}C NMR (126 MHz, CDCl$_3$)



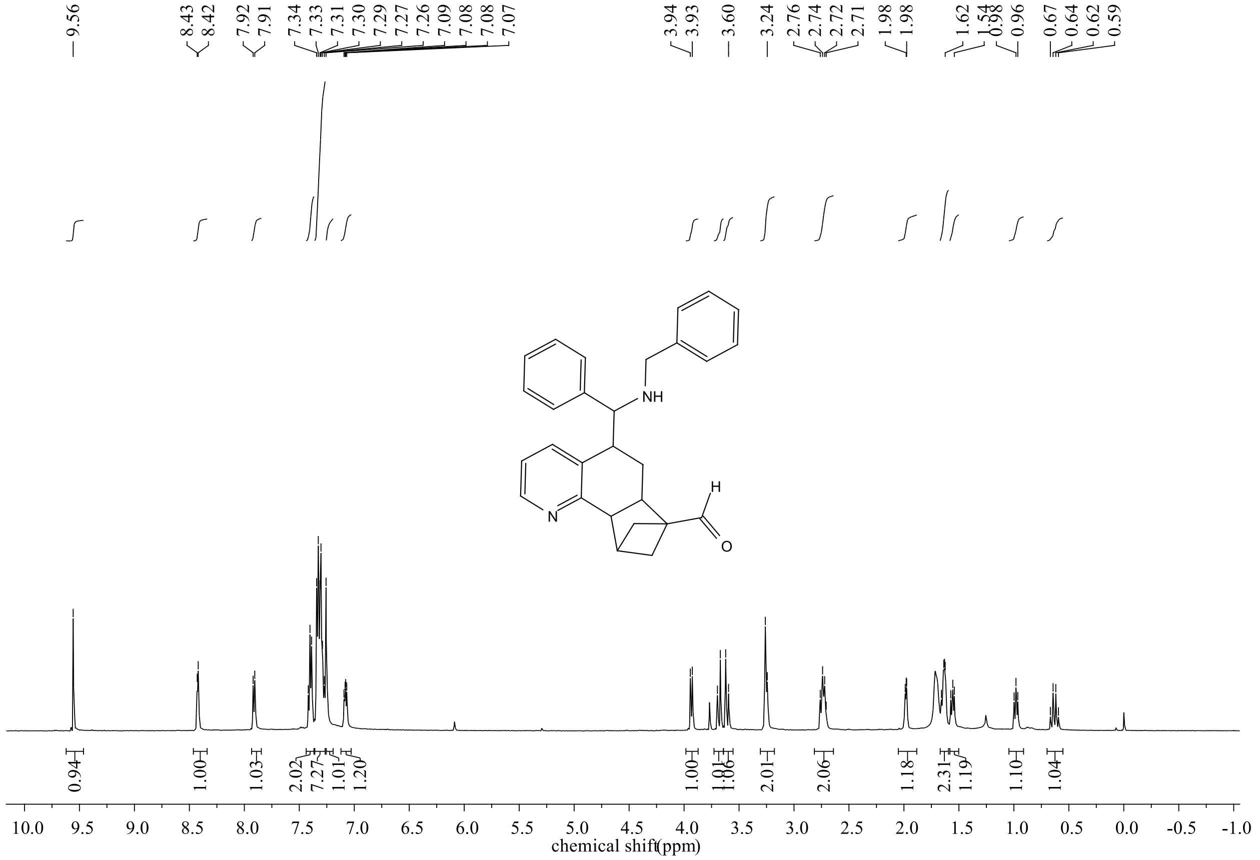
trans-**4x** ^{1}H NMR (500 MHz, CDCl$_3$)



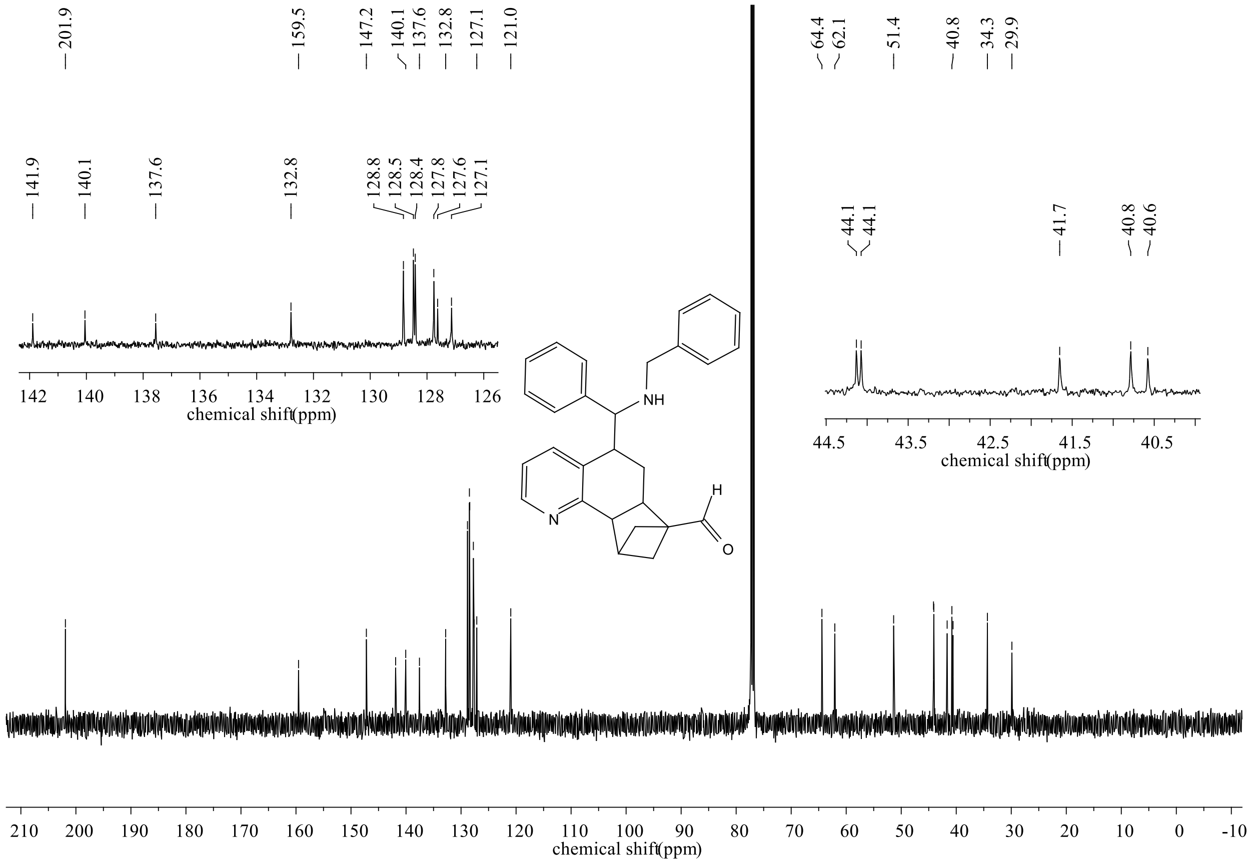
trans-**4x** ^{13}C NMR (126 MHz, CDCl$_3$)



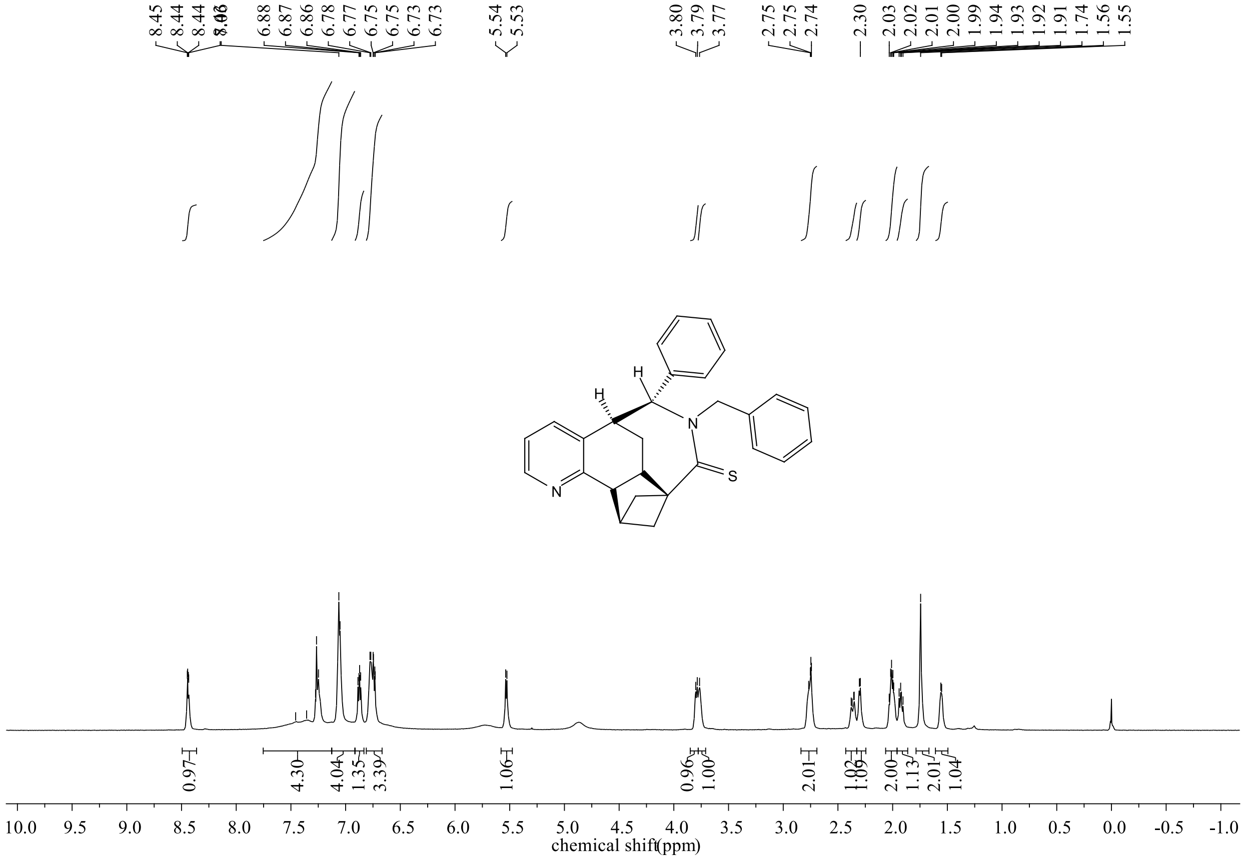
5 ^{1}H NMR (500 MHz, CDCl$_3$)



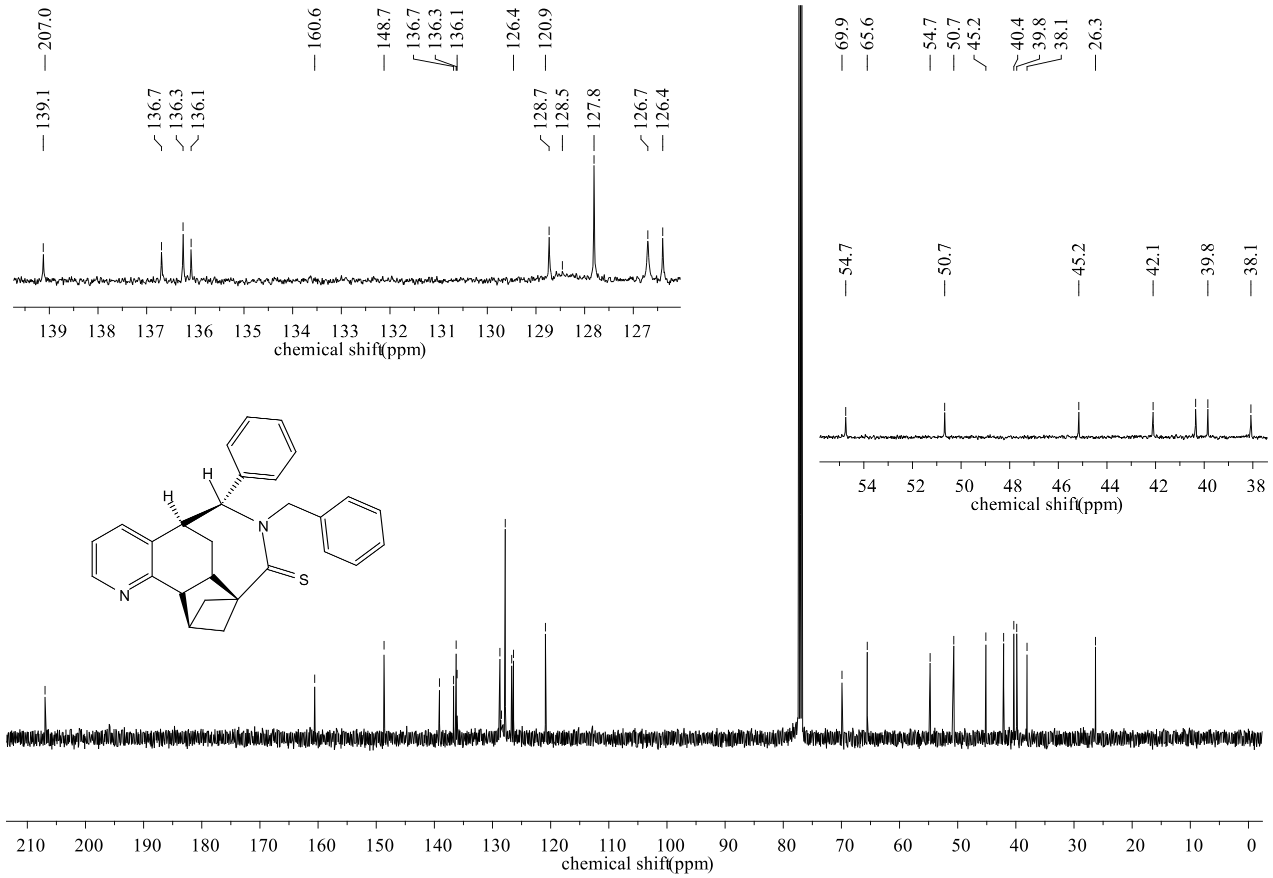
5 ^{13}C NMR (126 MHz, CDCl$_3$)



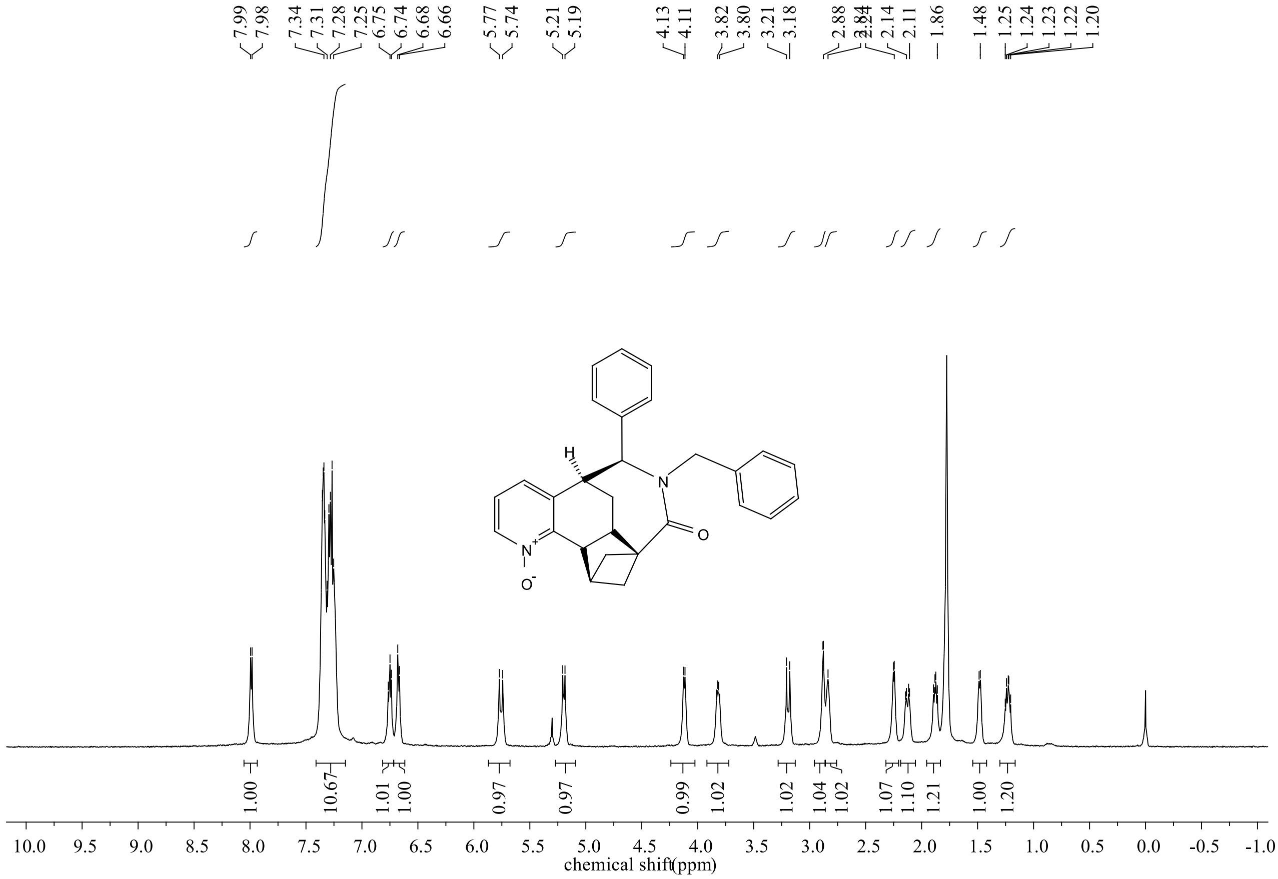
6 ^{1}H NMR (500 MHz, CDCl$_3$)



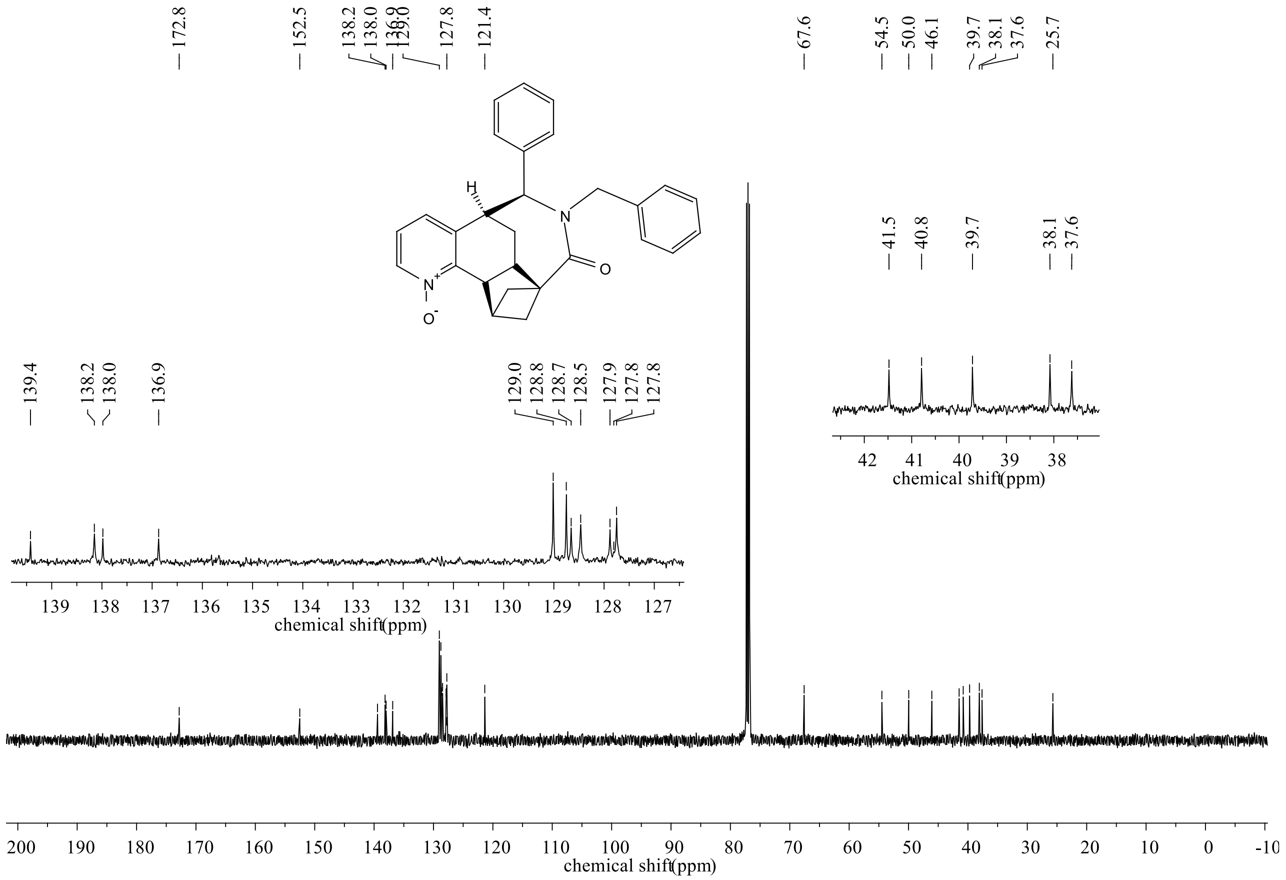
6 ^{13}C NMR (126 MHz, CDCl$_3$)



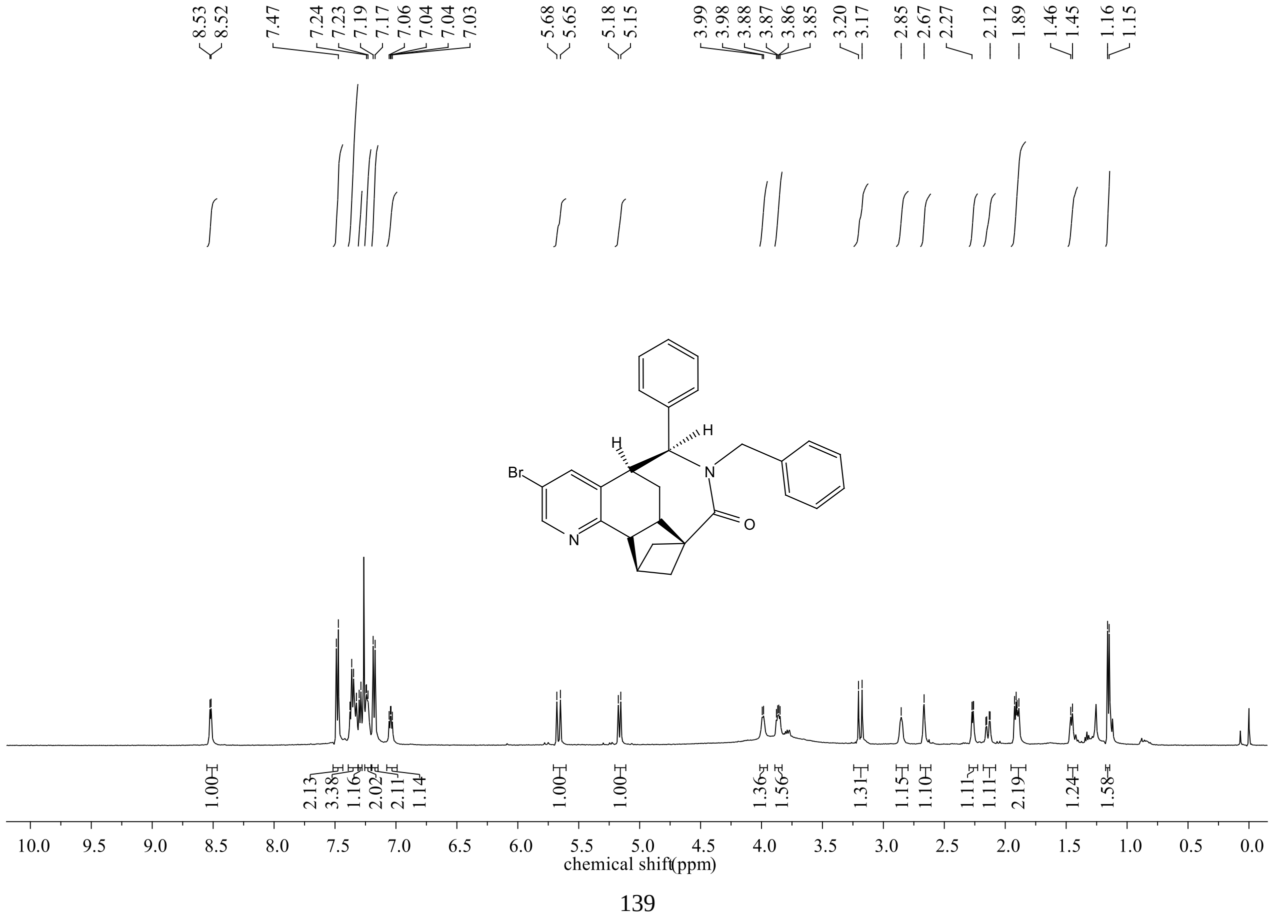
7 ^{1}H NMR (500 MHz, CDCl$_3$)



7 ^{13}C NMR (126 MHz, $CDCl_3$)



8 ^{1}H NMR (500 MHz, $CDCl_3$)



8 ^{13}C NMR (126 MHz, CDCl$_3$)