Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Gold-Catalyzed Intermolecular Tandem Cyclization/[4+3] Cycloaddition of 2-(1-Alkynyl)-cyclopropyl Pyridines with Nitrones: An Efficient Strategy for Synthesis of [1,2]Oxazepino[5,4-a] indolizines

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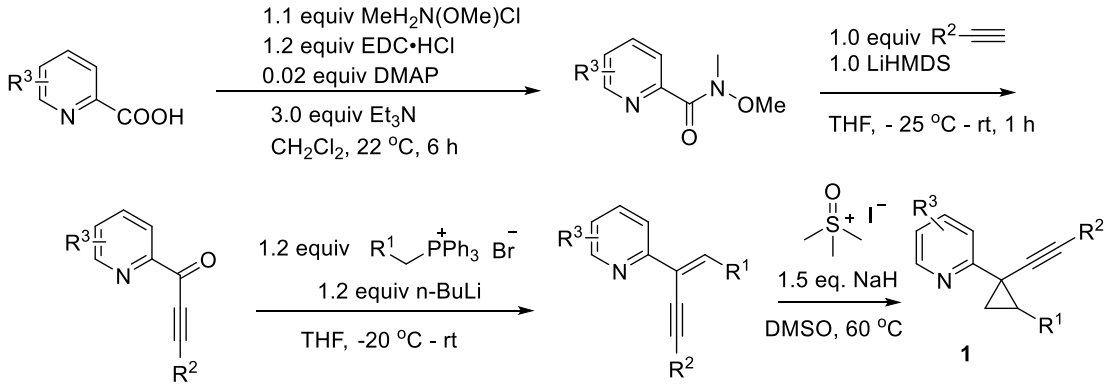
General information.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 or 500 MHz spectrometer in chloroform-d_3. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. All solvents were freshly distilled from CaH_2 before use. Melting points were measured on a YUHUA X-4 apparatus and uncorrected. Catalysts purchased from Bidepharm Co. Ltd, J&K or Energy Chemical Company were used directly. 4 Å molecular sieves purchased from Sinopharm Chemical Reagent Co., Ltd were powdered and dried at 300 °C in a muffle furnace for 8-10 hours before use.

1. Substrate synthesis

2-(1-alkynyl)-cyclopropyl pyridines **1** were synthesized according to the reported method. And the spectral data of 2-(1-alkynyl)-cyclopropyl pyridines **1a**-**1f**, **1h**, **1i**, **1l**, **1p** and **1q** are consisted with the literature (R.-R. Liu, S.-C. Ye, C.-J. Lu, B. Xiang, J. Gao, Y.-X. Jia, *Org. Biomol. Chem.* 2015, **13**, 4855-4858).



1) Weinreb's amides were prepared according to the following procedure from Picolinic acid:

Picolinic acid (1.0 eq.), DMAP (0.02 eq.), EDC (1.2 eq.), and *N*,*O*-dimethyl hydroxylamine hydrochloride (1.1 eq.) were weighed into a flame-dried round bottom flask and sealed with a septa. Dry CH_2Cl_2 was added through a syringe, and the solution was cooled to 0 ˚C (ice bath). Triethylamine (3.0 eq.) was added through a syringe and stirring was allowed to continue at 0 ˚C for 15 min. The ice bath was removed and the mixture was stirred for an additional 6 hours at rt. The reaction was then quenched through the addition of water. After the separation of the organic layer, the aqueous layer was neutralized with a saturated aqueous solution of $NaHCO_3$. When a pH of 7-8 was reached, the aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). All organic layers were combined and washed with a saturated aqueous solution of $NaHCO_3$ (2 x 30 mL), and a saturated aqueous solution of NaCl (2 x 30 mL), dried with $MgSO_4$, filtered and concentrated under reduced pressure to yield the amide as a yellow oil.

2) pyridyl-substituted alkynyl ketones**:**

A flame-dried round bottom flask was charged with a stir bar and sealed with septa. THF (40 mL) and phenylacetylene (1.0 eq.) were added through a syringe. The solution was cooled to -25 °C upon which LiHMDS (1.0 eq.) was added dropwise by syringe. The mixture was allowed to stir at -25 °C for 20 min, and a solution of Weinreb's amide (1.0 eq.) was added through a syringe. The mixture was allowed to

stir at rt for 1 h. The reaction was quenched through addition of a aqueous solution of citric acid (1%). The mixture was diluted with EtOAc (20 mL) and washed with a saturated solution of NaCl (2 x 25 mL). The aqueous layer was washed with EtOAc (2 x30 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting oil was purified by silica gel chromatography. The resulting red oil was loaded onto silica with PE:EA (10:1), to afford the pyridyl-substituted alkynyl ketones.

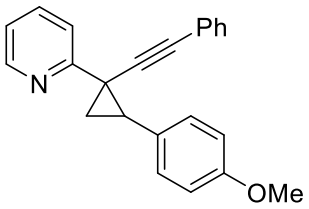
3) 2-(1-alkynyl)-2-alken-1-pyridine:

To a solution of the benzyl bromide ylide (1.2 eq.) in dry THF (50 mL) at -20 °C. n-butyllithium (1.2 eq.) was added dropwise via syringe. The white solution gradually turned red, After 15 min, pyridyl-substituted alkynyl ketones 1 (1.0 eq.) was added to the solution, and then the solution turned brown. The mixture was allowed to stir at rt , after the reaction was over, the mixture was poured into water and extracted with EtOAc (3 x 20 mL). The combined organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v), to afford the 2-(1-alkynyl)-2-alken-1-pyridine.

4) 2-(1-alkynyl)-cyclopropyl pyridines **1**:

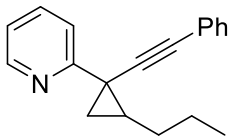
To a solution of the trimethylsulfoxonium iodide (1.0 eq.) in dry DMSO (50 mL) at rt. And then NaH (1.5 eq.) was added portion-wise. After 10 min, 2-(1-alkynyl)-2-alken-1-pyridine (1.0 eq.) was added to the solution. The mixture was allowed to stir at 60 °C. After the reaction was complete, the mixture was poured into water and extracted with EtOAc (3 x 20 mL). The combined organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v), to afford 2-(1-alkynyl)-cyclopropyl pyridines **1**. The spectral data of new 2-(1-alkynyl)-cyclopropyl pyridines **1e**, **1h**, **1k**, **1l**, **1n**, **1o** and **1p** are showed below.

2-(1-alkynyl)-cyclopropyl pyridines **1e**



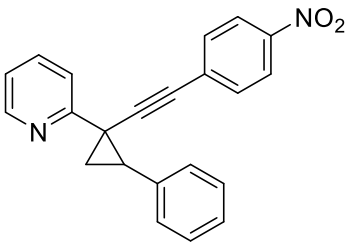
The reaction mixture was stirred for 5 hours at 60 °C until the reaction was complete (monitored by TLC, ethyl acetate:petroleum ether = 1:5). Purified by chromatography on silica gel eluting with PE/EA = 10/1; yield = 73%, white solid; m.p. 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51-8.49 (m, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.26-7.19 (m, 7H), 7.09-7.08 (m, 1H), 6.89-6.86 (m, 2H), 3.80 (s, 3H), 3.10 (t, *J* = 8.0 Hz 1H), 2.37 (dd, *J* = 8.8 Hz, 4.0 Hz 1H), 1.93 (dd, *J* = 7.6 Hz, 4.4 Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 158.4, 149.0, 136.0, 131.5, 129.9, 129.6, 128.1, 127.7, 123.5, 121.5, 120.8, 113.3, 89.6, 83.7, 55.3, 37.2, 27.6, 25.7; HRMS-TOF-ES$^+$:Calculated for$C_{23}H_{19}ONH^+$ ($[M^+H]^+$): 326.1545, Found: 326.1549.

2-(1-alkynyl)-cyclopropyl pyridines **1h**



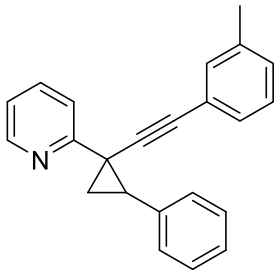
The reaction mixture was stirred for 5 hours at 60 °C until the reaction was complete (monitored by TLC, ethyl acetate:petroleum ether = 1:5). Purified by chromatography on silica gel eluting with PE/EA = 10/1; yield = 57%, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.62-7.59 (m, 1H), 7.52-7.45 (m, 2H), 7.34-7.26 (m, 3H), 7.07-7.02 (m, 1H), 1.97-1.75 (m, 1H), 1.72-1.70 (m, 1H), 1.67-1.64 (m, 1H), 1.62-1.59 (m, 1H), 1.58-1.51 (m, 2H), 1.23 (dd, *J* = 6.8 Hz, 3.8 Hz 1H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 160.7, 148.9, 135.9, 131.7, 128.3, 127.7, 123.8, 121.3, 120. 5, 90.4, 82.0, 33.1, 32.7, 27.7, 23.8, 22.3, 14.0; HRMS-TOF-ES$^+$: Calculated for $C_{19}H_{19}NH^+$ ($[M+H]^+$): 262.1596, Found: 262.1589.

2-(1-alkynyl)-cyclopropyl pyridines **1k**



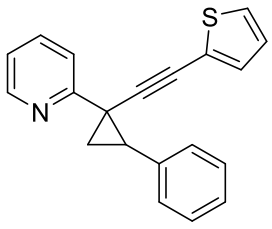
The reaction mixture was stirred for 5 hours at 60 °C until the reaction was complete (monitored by TLC, ethyl acetate:petroleum ether = 1:5). Purified by chromatography on silica gel eluting with PE/EA = 10/1; yield = 36%; brown solid, m.p. 97-99℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.0 Hz 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz 1H), 7.71-7.63 (m, 1H), 7.36-7.33 (m, 4H), 7.30-7.28 (m, 1H), 7.24-7.20 (m, 2H), 7.16-7.12 (m, 1H), 3.27 (t, *J* = 8.0 Hz 1H), 2.46 (dd, *J* = 8.8, 4.8 Hz, 1H), 2.08 (dd, *J* = 8.8, 4.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 158.4, 149.3, 146.6, 137.3, 136.2, 132.0, 130.4, 128.6, 127.9, 126.8, 123.4, 121.3, 121.2, 95.9, 82.1, 38.1, 27.8. 25.5; HRMS-TOF-ES$^+$: Calculated for $C_{22}H_{16}N_2O_2H^+$ ($[M+H]^+$): 341.1290, Found: 341.1292.

2-(1-alkynyl)-cyclopropyl pyridines **1l**



The reaction mixture was stirred for 5 hours at 60 °C until the reaction was complete (monitored by TLC, ethyl acetate:petroleum ether = 1:5). Purified by chromatography on silica gel eluting with PE/EA = 10/1; yield = 50%. yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59-8.57 (m, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.71-7.63 (m, 1H), 7.46-7.35 (m, 4H), 7.34-7.27 (m, 1H), 7.21-7.02 (m, 5H), 3.26 (t, *J* = 8.0 Hz, 1H), 2.48 (dd, *J* = 8.8, 4.4 Hz, 1H), 2.32 (s, 3H), 2.11-2.03 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 159.4, 149.0, 137.7, 137.66, 136.0, 132.1, 128.6, 128.5, 128.4, 128.0, 127.7, 126.4, 123.2, 121.5, 120.8, 88.9, 83.9, 37.6, 27.7, 25.4, 21.1; HRMS-TOF-ES$^+$: Calculated for $C_{23}H_{19}NH$ ($[M+H]^+$): 310.1596, Found: 310.1602.

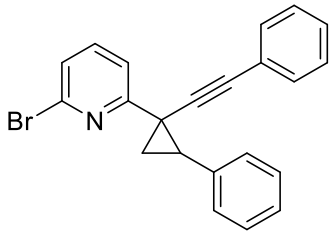
2-(1-alkynyl)-cyclopropyl pyridines **1n**



The reaction mixture was stirred for 4 hours at 60 °C until the reaction was complete (monitored by TLC, ethyl acetate:petroleum ether = 1:5). Purified by chromatography on silica gel eluting with PE/EA = 10/1; yield = 82%; yellowish solid, m.p. 62-64℃;

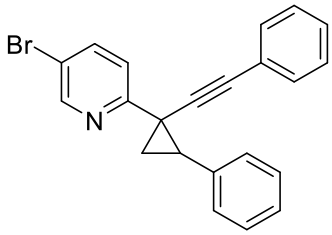
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52-8.48 (m, 1H), 7.89-7.84 (m, 1H), 7.64-7.56 (m, 1H), 7.35-7.05 (m, 5H), 7.13-7.05 (m, 2H), 6.95 (d, *J* = 4.0 Hz 1H), 6.89-6.84 (m, 1H), 3.21-3.14 (m, 1H), 2.43-2.38 (m, 1H) 2.04-1.97 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 159.0, 149.1, 137.4, 136.1, 131.4, 128.5, 127.8, 126.7, 126.6, 126.3, 123.5, 121.5, 120.9, 93.4, 76.8, 38.0, 28.0, 25.6; HRMS-TOF-ES$^+$: Calculated for $C_{20}H_{15}NSH$ ($[M+H]^+$): 302.1002, Found: 302.1003.

2-(1-alkynyl)-cyclopropyl pyridines **1o**



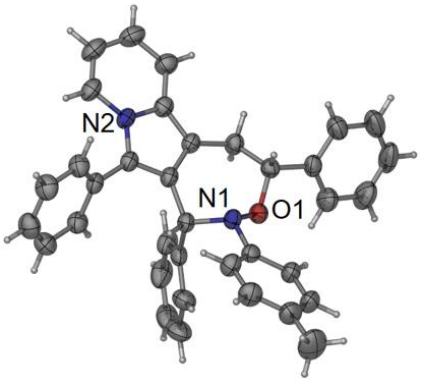
The reaction mixture was stirred for 6 hours at 60 °C until the reaction was complete (monitored by TLC, ethyl acetate:petroleum ether = 1:5). Purified by chromatography on silica gel eluting with PE/EA = 10/1; yield = 63%; yellowish solid, m.p. 61-63℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, 8.0, 0.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36-7.30 (m, 4H), 7.28-7.18 (m, 5H), 7.17-7.13 (m, 2H), 3.17 (t, *J* = 8.4 Hz, 1H), 2.41 (dd, *J* = 8.8, 4.4 Hz, 1H), 2.02 (dd, *J* = 7.6, 4.4 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 161.4, 141.6, 138.3, 137.3, 131.4, 128.6, 128.1, 127.84, 127.8, 126.7, 125.1, 123.2, 120.3, 88.4, 84.0, 38.4, 27.6, 25.9; HRMS-TOF-ES$^+$: Calculated for $C_{22}H_{16}NBrNa$ ($[M+Na]^+$): 396.0360, Found: 396.0364.

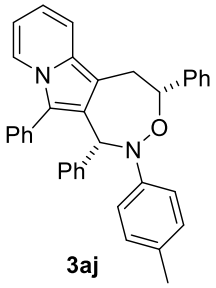
2-(1-alkynyl)-cyclopropyl pyridines **1p**



The reaction mixture was stirred for 5 hours at 60 °C until the reaction was complete (monitored by TLC, ethyl acetate:petroleum ether = 1:5). Purified by chromatography on silica gel eluting with PE/EA = 10/1; yield = 49%; yellowish solid, m.p. 77-79℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 2.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.76-7.70 (m, 1H), 7.35-7.30 (m, 4H), 7.25-7.20 (m, 4H), 7.18-7.12 (m, 2H), 3.14 (t, *J* = 8.4 Hz, 1H), 2.37 (dd, *J* = 9.2 Hz 4.4 Hz, 1H), 2.01 (dd, *J* = 7.6, 4.4 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 158.3, 150.0, 138.5, 137.4, 131.4, 128.6, 128.1, 127.8, 126.7, 123.2, 123.0, 117.6, 88.7, 83.9, 38.1, 27.5, 25.6; HRMS-TOF-ES$^+$: Calculated

for $C_{22}H_{16}NBrNa$ ([M+Na]$^+$): 396.0364, Found: 396.0365.





3aj

X-ray crystal structure of compound **3aj** (CCDC 2312481).

Structure factor report

Datablock: exp_2891

Bond precision: C-C = 0.0021 A Wavelength=1.54184

Cell: a=9.0251(3) b=11.7442(4) c=15.5807(4)
alpha=68.062(3) beta=73.701(3) gamma=68.609(3)

Temperature: 297 K

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Hall group	-P 1	-P 1
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Dx,g cm-3	1.196	1.196
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F000'	537.44	
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Nref	5025	5005
Tmin,Tmax	0.851,0.885	0.911,1.000
Tmin'	0.851	

Correction method= # Reported T Limits: Tmin=0.911 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 67.074

R(reflections)= 0.0353(4358) wR2(reflections)= 0.0994(5005)

S = 1.070 Npar= 354

The following ALERTS were generated. Each ALERT has the format
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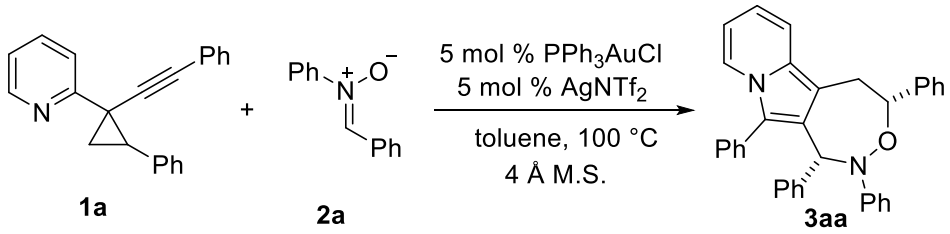
Click on the hyperlinks for more details of the test.

2. Typical procedure for Gold-catalyzed cyclization reaction.



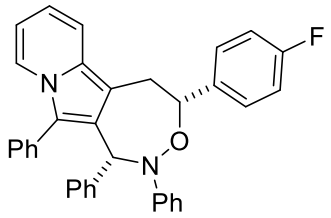
Under N_2, a flame-dried via (10 mL) was charged with 5 mol % PPh_3AuCl, 5 mol % $AgNTf_2$, dry DCM (1.5 mL), and the mixture was stirred at rt for 2 h. The resulting AgCl was filtered off, and the filtrate was collected, evaporated, and transferred into another flame-dried schlenk tube (25 mL). And then, 2-(1-alkynyl)-cyclopropyl pyridines **1a** (0.2 mmol), nitrone **2a** (0.4 mmol), 100 mg of activated 4Å molecular sieves powder (M. S.), dry toluene (2.0 mL) was successively added to the schlenk tube (25 mL). The reaction mixture was stirred at 100 °C for 16 hours until the reaction was complete (monitored by TLC, hexanes:AcOEt = 20:1). The reaction mixture was passed over a plug of silica gel with 15 mL of CH_2Cl_2. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, eluting with (hexanes:AcOEt = 100:1 to 30:1) to afford 89 mg (90%) of **3aa** (dr = 10:1), yellow solid. m.p. 207-209 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.5 Hz, 1H), 7.46-7.31 (m, 11H), 7.25-7.19 (m, 3H), 7.17-7.11 (m, 4H), 6.86-6.83 (m, 3H), 6.72-6.68 (m, 1H), 6.43 (t, *J* = 6.5 Hz, 1H), 6.07 (s, 1H), 5.29-5.26 (m, 1H), 3.60-3.54 (m, 1H), 3.50-3.46 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.6, 141.6, 139.2, 130.9, 130.2, 129.3, 129.0, 128.7, 128.4, 128.0, 127.7, 127.6, 126.9, 126.6, 126.4, 122.3, 122.2, 120.7, 117.1, 116.7, 115.9, 110.1, 109.3, 85.5, 67.0, 34.7; HRMS m/z (ESI^+): Calculated for $C_{35}H_{29}N_2O^+$ ($[M+H]^+$): 493.2274, Found: 493.2274.

Gram synthesis of indolizine 3aa.

Under N_2, a flame-dried via (20 mL) was charged with 5 mol % PPh_3AuCl, 5 mol % $AgNTf_2$, dry DCM (5 mL), and the mixture was stirred at rt for 2 h. The resulting AgCl was filtered off, and the filtrate was collected, evaporated, and transferred into another flame-dried schlenk tube (100 mL). And then, 2-(1-alkynyl)-cyclopropyl pyridines **1a** (3 mmol), nitrone **2a** (6 mmol), 800 mg of activated 4Å molecular sieves powder (M. S.), dry toluene (30 mL) was successively added to the schlenk tube. The reaction mixture was stirred at 100 °C for overnight until the reaction was complete (monitored by TLC, hexanes:AcOEt = 20:1). The reaction mixture was passed over a plug of silica gel with 100 mL of CH_2Cl_2. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, eluting

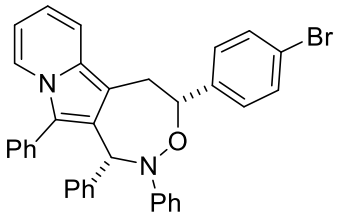
with (hexanes:AcOEt = 100:1 to 30:1) to afford 1.18 g (80%).

Synthesis of 3ba



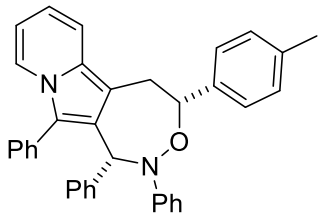
The reaction mixture was stirred for 19 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 89 mg (87%) of **3ba** (dr = 9:1), light yellow solid, m.p. 184-186 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.0 Hz, 1H), 7.47-7.39 (m, 7H), 7.25-7.23 (m, 3H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.15-7.12 (m, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 6.88-6.85 (m, 3H), 6.74-6.71 (m, 1H), 6.45 (t, *J* = 7.0 Hz, 1H), 6.10 (s, 1H), 5.31-5.28 (m, 1H), 3.61-3.54 (m, 1H), 3.52-3.48 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$): δ 162.3 (d, *J* = 244.3 Hz), 149.6, 139.1, 137.4, 130.9, 130.2, 130.1, 129.3, 129.0, 128.7, 128.1 (d, *J* = 8.0 Hz), 128.0, 127.6, 126.9, 126.6, 122.3, 120.8, 117.0, 116.7, 115.9, 115.3, 115.1, 110.2, 109.0, 84.8, 67.2, 34.7; HRMS m/z (ESI$^+$): Calculated for $C_{35}H_{28}FN_2O^+$ ([M+H]$^+$): 511.2180, Found: 511.2180.

Synthesis of 3ca



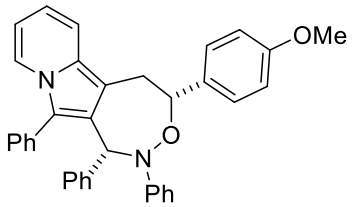
The reaction mixture was stirred for 25 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 101 mg (87%) of **3ca** (dr = 7:1); yellow solid, m.p. 171-173 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.53-7.36 (m, 7H), 7.31-7.27 (m, 3H), 7.25-7.20 (m, 3H), 7.19-7.15 (m, 2H), 7.11-7.08 (m, 2H), 6.89-6.83 (m, 3H), 6.72 (dd, *J* = 6.5, 8.5 Hz, 1H), 6.46-6.43 (m, 1H), 6.07 (s, 1H), 5.25 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.56-3.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 140.6, 139.0, 131.5, 130.9, 130.2, 129.3, 129.0, 128.7, 128.1, 128.0, 127.6, 127.0, 126.6, 122.4, 122.3, 121.6, 120.9, 117.0, 116.8, 116.0, 110.2, 108.9, 84.9, 67.4, 34.7; HRMS m/z (ESI$^+$): Calculated for $C_{35}H_{28}BrN_2O^+$ ([M+H]$^+$): 571.1380, Found: 571.1373.

Synthesis of **3da**



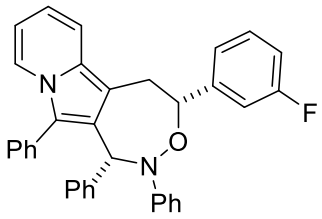
The reaction mixture was stirred for 13 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 95 mg (92%) of **3da** (dr = 12:1); yellow solid, m.p. 185-187 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.49-7.34 (m, 7H), 7.28-7.16 (m, 10H), 6.89 (d, *J* = 8.5 Hz, 3H), 6.75-6.71 (m, 1H), 6.46 (t, *J* = 6.5 Hz, 1H), 6.12 (s, 1H), 5.29 (dd, *J* = 2.0, 10.5 Hz, 1H), 3.65-3.59 (m, 1H), 3.53-3.48 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 139.2, 138.6, 137.3, 130.8, 130.1, 129.3, 129.0, 128.9, 128.6, 127.9, 127.6, 126.9, 126.5, 126.4, 122.3, 122.2, 120.6, 117.1, 116.7, 115.8, 110.1, 109.3, 85.3, 66.8, 34.6, 21.2; HRMS m/z (ESI$^+$): Calculated for $C_{36}H_{31}N_2O^+$ ([M+H]$^+$): 507.2431, Found: 507.2429.

Synthesis of **3ea**



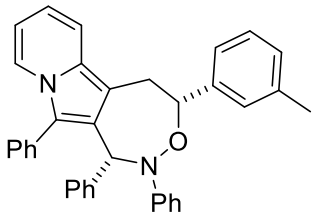
The reaction mixture was stirred for 4 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 76 mg (77%) of **3ea** (dr = 7:1); yellow solid, m.p. 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* =7.2 Hz, 1H), 7.42-7.30 (m, 7H), 7.18 (m, 2H), 7.14-7.10 (m, 5H), 7.20-7.11 (m, 2H), 6.80-9-6.76 (m, 3H), 6.68-6.62 (m, 1H), 6.42-6.35 (m, 1H), 5.83 (s, 1H), 5.18 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.57-3.4 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 149.5, 139.2, 133.8, 130.9, 130.7, 130.1, 129.3,129.0, 128.7, 128.4, 128.0, 127.8, 127.6, 127.4, 126.9, 126.5, 122.3, 120.9, 120.5, 117.1, 116.7, 115.8, 113.7, 113.4, 110.1, 109.3, 85.0, 66.7, 55.3, 34.4; HRMS m/z (ESI$^+$):Calculated for $C_{36}H_{31}N_2O_2^+$([M$^+$H]$^+$): 523.2386, Found: 523.2381.

Synthesis of 3fa



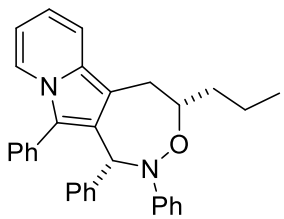
The reaction mixture was stirred for 15 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 82 mg (80%) of **3fa** (dr = 7:1); yellow solid, m.p. 205-207 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.0 Hz, 1H), 7.46-7.32 (m, 6H), 77.26-7.09 (m, 10H), 7.03 (td, *J* = 2.0, 8.5Hz, 1H), 6.90-6.84 (m, 3H), 6.75-6.71 (m, 1H), 6.45 (t, *J* = 6.5 Hz, 1H), 6.06 (s, 1H), 5.29 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.58-3.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7 (*J* = 237.5 Hz), 149.5, 144.0 (*J* = 7.5 Hz), 138.9, 130.8, 130.2, 129.9 (*J* = 7.5 Hz), 129.0, 128.7, 128.0, 127.6, 127.0, 126.5, 122.34, 122.26, 122.0 (*J* = 7.5 Hz), 121.0, 117.0, 116.8, 116.1, 114.6, 114.4, 113.4, 113.2, 110.2, 108.8, 84.8, 67.3, 34.8; HRMS m/z (ESI$^+$): Calculated for $C_{35}H_{28}FN_2O^+$ ([M+H]$^+$): 511.2180, Found: 511.2180.

Synthesis of 3ga



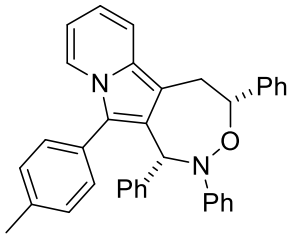
The reaction mixture was stirred for 13 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 94 mg (93%) of **3ga** (dr = 8:1); yellow solid, m.p. 199-201 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.49-7.40 (m, 5H), 7.33-7.25 (m, 7H), 7.21-7.17 (m, 5H),6.90-6.86 (m, 3H), 6.75-6.71 (m, 1H), 6.46 (t, *J* = 6.5 Hz, 1H), 6.12 (s, 2H), 5.30-5.27 (m, 1H), 3.65-3.59 (m, 1H), 3.52-3.48 (m, 1H), 2.42 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 141.5, 139.2, 137.9, 130.9, 130.2, 130.1, 129.3, 129.0, 128.7, 128.4, 128.3, 128.0, 127.6, 127.1, 126.9, 126.6, 123.5, 122.3, 122.2, 120.6, 117.1, 116.6, 115.9, 110.1, 109.4, 85.7, 66.8, 34.8, 21.5; HRMS m/z (ESI$^+$): Calculated for $C_{36}H_{31}N_2O^+$ ([M+H]$^+$): 507.2431, Found: 507.2436.

Synthesis of 3ha



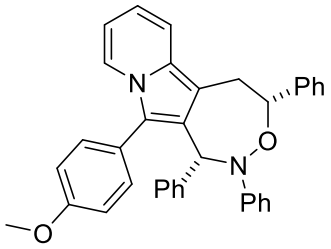
The reaction mixture was stirred for 48 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 61 mg (67%) of **3ha** (dr = 6:1); yellow solid, m.p. 141-143 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 1H), 7.48-7.35 (m, 5H), 7.23-7.15 (m, 6H), 6.97 (dd, *J* = 7.5, 18.0Hz, 4H), 6.90 (t, *J* = 7.0 Hz, 1H), 6.73-6.69 (m, 1H), 6.42 (t, *J* = 6.5 Hz, 1H), 5.96 (s, 1H), 4.33-4.30 (m, 1H), 3.37-3.32 (m, 1H), 3.21-3.15 (m, 1H), 1.86-1.79 (m, 1H), 1.64-1.57 (m, 2H), 1.53-1.46 (m, 1H), 0.96 (t, *J* = 7.0 Hz, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 139.0, 131.0, 130.1, 130.0, 129. 5, 128.9, 128.8, 128.5, 127.8, 127.4, 126.8, 122.2, 121.9, 120.9, 117.1, 116.5, 116.3, 110.0, 109.5, 84.1, 68.4, 37.2, 32.5, 19.6, 14.1; HRMS m/z (ESI$^+$): Calculated for $C_{32}H_{31}N_2O^+$ ([M+H]$^+$): 459.2431, Found: 459.2436.

Synthesis of 3ia



The reaction mixture was stirred for 11 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 94 mg (93%) of **3ia** (dr = 20:1); yellow solid, m.p. 201-203 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.46-7.34 (m, 7H), 7.28-7.23 (m, 6H), 7.20-7.15 (m, 4H), 6.91-6.86 (m, 3H), 6.73-6.69 (m, 1H), 6.44 (t, *J* = 6.5 Hz, 1H), 6.10 (s, 1H), 5.31 (dd, *J* = 2.0, 11.0 Hz, 1H), 3.64-3.58 (m, 1H), 3.52-3.48 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 141.6, 139.2, 137.8, 130.0, 129.7, 129.3, 128.6, 128.3, 127.8, 127.6, 127.6, 126.8, 126.4, 122.4, 122.3, 120.6, 117.1, 116.5, 115.9, 110.0, 109.2, 85.6, 66.91, 34.8, 21.3; HRMS m/z (ESI$^+$): Calculated for $C_{36}H_{31}N_2O^+$ ([M+H]$^+$): 507.2431, Found: 507.2431.

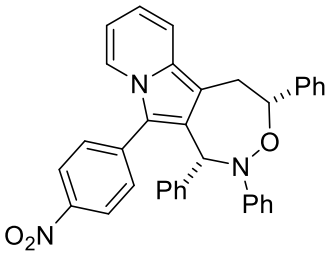
Synthesis of 3ja



The reaction mixture was stirred for 13 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 87 mg (84%) of **3ja** (dr = 20:1); yellow solid, m.p.

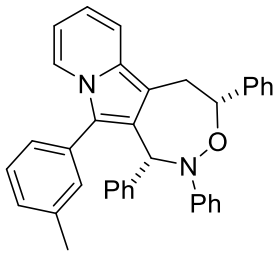
214-216 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.0 Hz, 1H), 7.46-7.34 (m, 7H), 7.26-7.23 (m, 3H), 7.21-7.14 (m, 5H), 7.01 (s, 2H), 6.91-6.87 (m, 3H), 6.72-6.68 (m, 1H), 6.46-6.42 (m, 1H), 6.08 (s, 1H), 5.32 (dd, *J* = 2.0, 11.0 Hz, 1H), 3.90 (s, 3H), 3.64-3.58 (m, 1H), 3.53-3.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 149.7, 141.6, 139.3, 131.5, 129.9, 129.3, 128.6, 128.3, 127.6, 127.6, 126.9, 126.4, 126.4, 123.0, 122.3, 122.0, 120.7, 117.0, 116.4, 116.0, 114.4, 110.0, 109.0, 85.7, 67.1, 55.2, 34.8; HRMS m/z (ESI^+): Calculated for $C_{36}H_{31}N_2O_2^+$ ($[M+H]^+$): 523.2380, Found: 523.2385.

Synthesis of 3ka



The reaction mixture was stirred for 37 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel eluting with PE/EA = 30:1 (v/v), affording 57 mg (56%) of **3ka** (dr > 99:1); red solid, m.p. 240-242℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8 Hz 1H), 8.04 (d, *J* = 8 Hz 1H), 7.43-7.32 (m, 8H), 7.22-7.13 (m, 5H), 7.04 (m, 2H), 6.89-6.77 (m, 4H), 6.55-6.52 (m, 1H), 5.99 (s, 1H), 5.30-5.26 (m, 1H), 3.56 (t, *J* = 4Hz 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 149.5, 146.5, 141.2, 138.3, 137.7, 131.8, 130.0, 129.4, 128.7, 128.4, 127.8, 127.4, 126.4, 121.9, 121.3, 119.7, 118.2, 117.5, 116.3, 111.4, 110.6, 85.6, 68.1, 34.6; HRMS-TOF-ES^+: Calculated for $C_{35}H_{27}N_3O_3K^+$ ($[M+K]^+$) : 576.1688, Found: 576.1689.

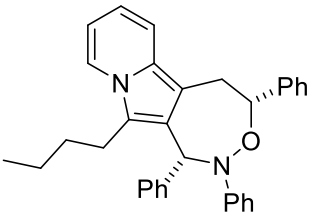
Synthesis of 3la



The reaction mixture was stirred for 15 hours at 100 °C until the reaction was complete (10 mol % catalyst used). Purified by chromatography on silica gel eluting with PE/EA = 30:1 (v/v), affording 80 mg (79%) of **3la** (dr = 17:1); red solid, m.p. 138-140℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35-8.32 (m, 1H), 8.20-8.18 (m, 1H), 7.56-7.49 (m, 2H), 7.43-7.32 (m, 7H), 7.21 (m, 5H), 7.12-7.09 (m, 5H), 6.85 (dd, *J* = 12 Hz , 8Hz 4H), 6.68 (dd, *J* = 8Hz, 8Hz 1H), 6.43-6.40 (m, 1H), 6.04 (s, 1H),

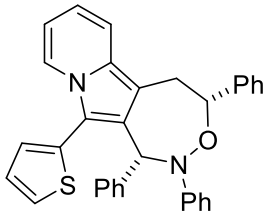
5.30-5.27 (m, 1H), 3.61-3.55 (m, 1H), 3.49 (dd, *J* = 16 Hz, 4Hz 1H), 2.32 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 149.7, 141.6, 139.2, 138.5, 129.4, 128.8, 128.7, 128.6, 128.4, 127.6, 127.5, 126.9, 126.6, 126.4, 125.5, 122.4, 120.8, 117.1, 116.6, 116.1, 110.1, 109.2, 85.7, 67.4, 34.8, 21.4; HRMS-TOF-ES$^+$: Calculated for $C_{36}H_{30}N_2OK^+$ ([M+K]$^+$): 545.1995, Found: 545.2003.

Synthesis of 3ma



The reaction mixture was stirred for 15 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 82 mg (80%) of **3ma** (dr = 10:1); yellow solid, m.p. 144-146 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.43-7.35 (m, 4H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.23-7.13 (m, 8H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.68-6.64 (m, 1H), 6.54 (t, *J* = 6.5 Hz, 1H), 6.27 (s, 1H), 5.41 (dd, *J* = 3.5, 9.0 Hz, 1H), 3.72-3.68 (m, 1H), 3.57-3.51 (m, 1H), 2.86-2.75 (m, 2H), 1.57-1.53 (m, 1H), 1.35-1.27 (m, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 141.7, 138.6, 129.6, 128.7, 128.3, 127.6, 127.4, 127.0, 126.5, 125.4, 121.4, 121.2, 120.8, 117.1, 116.7, 114.8, 109.8, 107.8, 86.0, 68.9, 33.9, 29.3, 24.0, 22.6, 13.8; HRMS m/z (ESI$^+$): Calculated for $C_{33}H_{33}N_2O^+$ ([M+H]$^+$): 473.2578, Found: 473.2590.

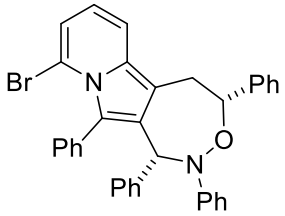
Synthesis of 3na



The reaction mixture was stirred for 42 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel eluting with PE/EA = 30:1 (v/v), affording 59 mg (61%) of **3na** (dr = 25:1); yellow solid, m.p. 238-240℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.0 Hz 1H), 7.46 (d, *J* = 4.0 Hz 1H), 7.37-7.32 (m, 7H), 7.19-7.16 (m, 6H), 7.12-7.11 (m, 1H), 7.06 (m, 2H), 6.94-6.92 (m, 2H), 6.85 (t, *J* = 8.0 Hz 1H), 6.74-6.71 (m, 1H), 6.50-6.47 (m, 1H), 6.20

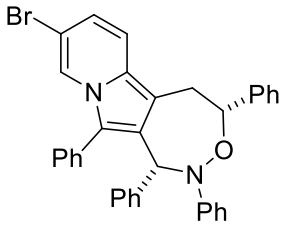
(s, 1H), 5.29 (q, *J* = 4.0 Hz 1H), 3.56-3.46 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 149.7, 141.5, 138.9, 131.2, 131.0, 129.3, 129.1, 128.7, 128.4, 127.7, 127.5, 127.3, 126.9, 126.4, 122.9, 120.8, 117.2, 116.9, 116.0, 114.5, 110.5, 109.3, 85.6, 67.3, 34.5; HRMS-TOF-ES$^+$: Calculated for $C_{33}H_{26}N_2OSK^+$ ([M+K]$^+$): 537.1403, Found: 537.1406.

Synthesis of 3oa (unsuccessful)



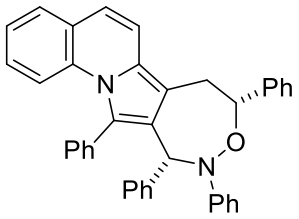
The reaction mixture was stirred for 12 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Unfortunately, a complex mixture was obtained.

Synthesis of 3pa



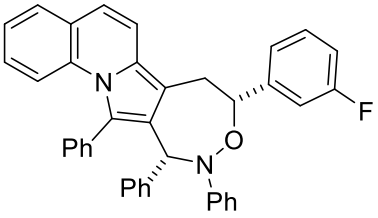
The reaction mixture was stirred for 31 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel eluting with PE/EA = 30:1 (v/v), affording 72 mg (63%) of **3pa** (dr = 50:1); brown solid, m.p. 203-205℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.43-7.31 (m, 9H), 7.25 (m, 2H), 7.18 (m, 3H), 7.16-7.12 (m, 2H), 7.05 (t, *J* = 4.0 Hz 2H), 6.84 (t, *J* = 4.0 Hz 3H), 6.75-6.72 (m, 1 H), 6.01 (s, 1H), 5.27 (q, *J* = 4.0 Hz 1H), 3.55 (dd, *J* = 16.0 Hz, 12.0 Hz 1H), 3.46 (dd, *J* = 16.0 Hz, 4.0 Hz 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 149.5, 141.3, 138.8, 130.2, 129.3, 129.2, 128.7, 128.5, 128.4, 127.7, 127.6, 127.2, 127.0, 126.4, 122.9, 122.1, 120.9, 119.9, 117.9, 116.0, 110.7, 105.5, 85.4, 67.2, 34.7; HRMS-TOF-ES$^+$: Calculated for $C_{35}H_{27}N_2OBrK^+$ ([M+K]$^+$): 609.0941, Found: 609.0944.

Synthesis of 3qa



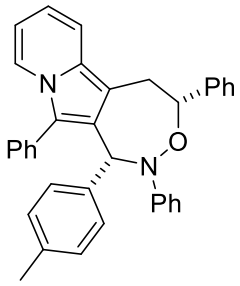
The reaction mixture was stirred for 12 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 103 mg (95%) of **3qa** (dr = 20:1); yellow solid, m.p. 231-233 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.65 (m, 3H), 7.55-7.37 (m, 8H), 7.27-7.04 (m, 12H), 6.89-6.82 (m, 3H), 5.93 (s, 1H), 5.35 (dd, *J* = 2.5, 10.5 Hz, 1H), 3.64-3.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 141.5, 139.2, 134.4, 134.3, 131.0, 130.5, 129.2, 129.1, 128.9, 128.8, 128.7, 128.5, 128.43, 128.38, 127.7, 127.52, 127.48, 126.8, 126.6, 126.5, 126.4, 125.3, 123.1, 120.6, 118.7, 117.0, 116.8, 115.6, 112.6, 85.5, 66.8, 34.8; HRMS m/z (ESI$^+$): Calculated for $C_{39}H_{31}N_2O^+$ ([M+H]$^+$): 543.2431, Found: 543.2442.

Synthesis of **3ra**



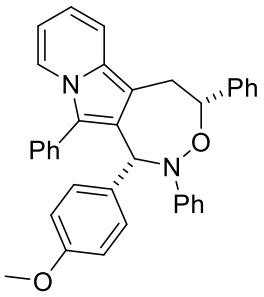
The reaction mixture was stirred for 12 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 95 mg (87%) of **3ra** (dr = 11:1); yellow solid, m.p. 221-223 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (t, *J* = 8.0 Hz, 3H), 7.53-7.50 (m, 1H), 7.39-7.34 (m, 3H), 7.26-7.16 (m, 9H), 7.09-7.04 (m, 6H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.88 (s, 1H), 5.34 (t, *J* = 6.5 Hz, 1H), 3.55-3.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8 (d, *J* = 245.0 Hz), 149.5, 143.9 (d, *J* = 7.5 Hz), 139.0, 134.3 (d, *J* = 7.5 Hz), 131.0, 130.5, 129.9 (d, *J* = 7.5 Hz), 129.2, 129.1, 128.9, 128.8, 128.7, 128.52, 128.45, 127.6, 127.4, 126.9, 126.7, 126.6, 125.2, 123.1, 122.0 (d, *J* = 2.5 Hz), 120.8, 118.8, 116.8 (d, *J* = 48.8 Hz), 115.8, 114.5 (d, *J* = 21.3 Hz), 113.3 (d, *J* = 16.2 Hz), 112.2, 84.9, 67.2, 34.8; HRMS m/z (ESI$^+$): Calculated for $C_{39}H_{30}FN_2O^+$ ([M+H]$^+$): 561.2337, Found: 561.2351.

Synthesis of 3ab



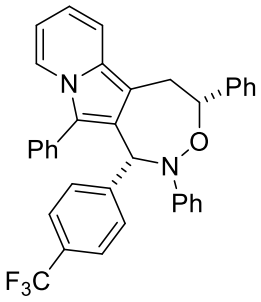
The reaction mixture was stirred for 36 hours at 100 °C until the reaction was complete (10 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 96 mg (95%) of **3ab** (dr = 20:1); yellow solid, m.p. 195-197 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.0 Hz, 1H), 7.49-7.35 (m, 11H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.07 (s, 4H), 6.92-6.87 (m, 3H), 6.75-6.71 (m, 1H), 6.46 (t, *J* = 6.5 Hz, 1H), 6.10 (s, 1H), 5.33 (dd, *J* = 2.0, 11.0 Hz, 1H), 3.68-3.61 (m, 1H), 3.55-3.50 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 141.6, 136.3, 136.2, 131.0, 130.2, 130.1, 129.2, 128.9, 128.6, 128.4, 127.9, 127.6, 126.9, 126.4, 122.3, 122.2, 120.6, 117.1, 116.6, 115.9, 110.1, 109.3, 85.7, 77.3, 77.0, 76.8, 66.8, 34.8, 21.1; HRMS m/z (ESI$^+$): Calculated for $C_{36}H_{31}N_2O^+$ ([M+H]$^+$): 507.2431, Found: 507.2444.

Synthesis of 3ac



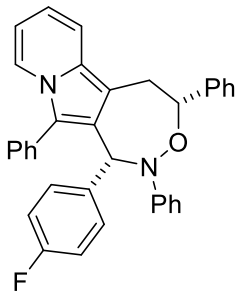
The reaction mixture was stirred for 19 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 94 mg (89%) of **3ac** (dr = 12:1); yellow solid, m.p. 193-195 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.49-7.35 (m, 11H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.92-6.87 (m, 3H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.74-6.70 (m, 1H), 6.45 (t, *J* = 6.5 Hz, 1H), 6.07 (s, 1H), 5.34 (d, *J* = 9.0 Hz, 1H), 3.82 (s, 3H), 3.67-3.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 149.8, 141.7, 131.5, 131.0, 130.4, 130.2, 128.9, 128.6, 128.3, 127.9, 127.6, 127.0, 126.4, 122.3, 122.1, 120.7, 117.1, 116.6, 116.1, 113.0, 110.1, 109.2, 85.7, 66.9, 55.0, 34.8; HRMS m/z (ESI$^+$): Calculated for $C_{36}H_{31}N_2O_2^+$ ([M+H]$^+$): 523.2380, Found: 523.2395.

Synthesis of 3ad



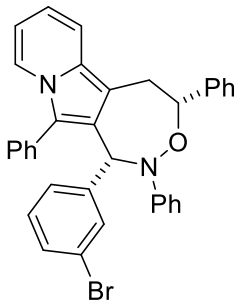
The reaction mixture was stirred for 13 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 100 mg (88%) of **3ad** (dr = 10:1); yellow solid, m.p. 208-210 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 1H), 7.48-7.35 (m, 12H), 7.25-7.16 (m, 5H), 6.91-6.86 (m, 3H), 6.75-6.71 (m, 1H), 6.46 (t, *J* = 6.5 Hz, 1H), 6.11 (s, 1H), 5.32 (t, *J* = 6.5 Hz, 1H), 3.55 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 143.3, 141.3, 130.8, 130.3, 130.1, 129.6, 129.2, 129.20, 129.1, 129.0, 128.8, 128.7, 128.5, 128.2, 127.8, 126.4, 125.8, 125.4, 124.6 (q, *J* = 3.8 Hz), 123.2, 122.4, 121.2, 117.1, 116.9, 116.0, 110.4, 109.0, 85.7, 66.9, 34.4; HRMS m/z (ESI$^+$): Calculated for $C_{36}H_{28}F_3N_2O^+$ ([M+H]$^+$): 561.2148, Found: 561.2159.

Synthesis of 3ae



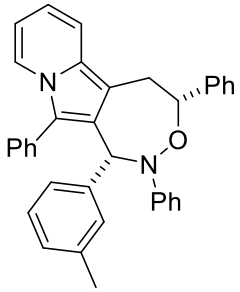
The reaction mixture was stirred for 13 hours at 100 °C until the reaction was complete (10 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 82 mg (80%) of **3ae** (dr = 20:1); yellow solid, m.p. 216-218 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 1H), 7.49-7.32 (m, 10H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.07-7.03 (m, 2H), 6.90-6.83 (m, 5H), 6.73-6.69 (m, 1H), 6.44 (t, *J* = 6.5 Hz, 1H), 6.01 (s, 1H), 5.31-5.27 (m, 1H), 3.55-3.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9 (d, *J* = 263.8 Hz), 149.5, 141.5, 135.0 (d, *J* = 2.5 Hz), 130.93, 130.87, 130.2, 130.1, 129.0, 128.7, 128.4, 128.1, 127.7, 126.5, 126.4, 122.3, 122.2, 121.0, 117.1, 116.8, 116.2, 114.4 (d, *J* = 21.3 Hz), 110.3, 109.0, 85.6, 66.9, 34.6; HRMS m/z (ESI$^+$): Calculated for $C_{35}H_{28}FN_2O^+$ ([M+H]$^+$): 511.2180, Found: 511.2182.

Synthesis of 3af



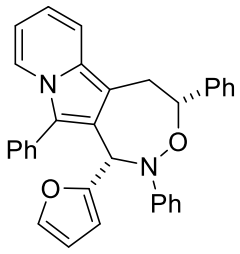
The reaction mixture was stirred for 22 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 85 mg (74%) of **3af** (dr = 10:1); yellow solid, m.p. 178-180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.0 Hz, 1H), 7.49-7.31 (m, 13H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.90-6.85 (m, 3H), 6.75-6.71 (m, 1H), 6.46 (t, *J* = 6.5 Hz, 1H), 6.03 (s, 1H), 5.31 (dd, *J* = 3.5, 9.0 Hz, 1H), 3.61-3.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 141.5, 141.4, 132.4, 130.8, 130.2, 130.0, 129.1, 129.0, 128.7, 128.4, 128.2, 127.8, 127.8, 126.4, 125.8, 122.3, 121.8, 121.1, 117.2, 116.8, 116.1, 110.3, 109.0, 85.5, 66.9, 34.5; HRMS m/z (ESI$^+$): Calculated for $C_{35}H_{28}BrN_2O^+$ ([M+H]$^+$): 571.1380, Found: 571.1373.

Synthesis of 3ag



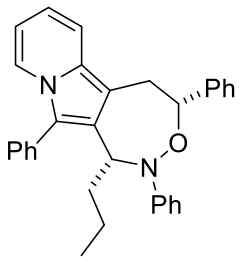
The reaction mixture was stirred for 19 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 87 mg (86%) of **3ag** (dr = 10:1); yellow solid; m.p. 197-199 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.0 Hz, 1H), 7.50-7.36 (m, 11H), 7.21-7.14 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.02-6.97 (m, 2H), 6.91-6.87 (m, 3H), 6.75-6.71 (m, 1H), 6.47 (t, *J* = 6.5 Hz, 1H), 6.10 (s, 1H), 5.34-5.31 (m, 1H), 3.68-3.61 (m, 1H), 3.55-3.51 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 141.6, 139.1, 136.9, 131.0, 130.2, 130.1, 128.9, 128.6, 128.3, 127.9, 127.7, 127.5, 126.8, 126.4, 122.3, 120.6, 117.1, 116.6, 115.9, 110.1, 109.4, 85.4, 66.8, 34.7, 21.5; HRMS m/z (ESI$^+$): Calculated for $C_{36}H_{31}N_2O^+$ ([M+H]$^+$): 507.2431, Found: 507.2443.

Synthesis of 3ah



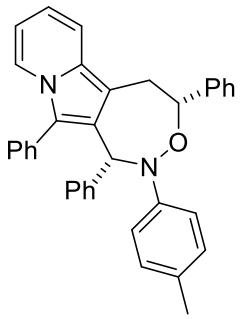
The reaction mixture was stirred for 11 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 86 mg (86%) of **3ah** (dr = 12:1); yellow solid, m.p. 180-182 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.56-7.35 (m, 12H), 7.21 (t, *J* = 8.0 Hz, 2H), 6.97-6.94 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.73-6.69 (m, 1H), 6.45 (t, *J* = 6.5 Hz, 1H), 6.32 (s, 1H), 6.05 (s, 2H), 5.32 (d, *J* = 10.0 Hz, 1H), 3.68 (dd, *J* = 11.0, 15.5 Hz, 1H), 3.48 (dd, *J* = 2.0, 15.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 150.0, 141.8, 141.6, 130.7, 130.1, 129.1, 128.5, 128.4, 128.1, 127.7, 127.2, 126.4, 125.0, 122.4, 122.1, 121.3, 117.2, 116.7, 116.2, 110.2, 109.9, 109.5, 109.3, 86.4, 62.0, 34.5; HRMS m/z (ESI^+): Calculated for $C_{33}H_{27}N_2O_2^+$ ($[M+H]^+$): 483.2067, Found: 483.2078.

Synthesis of 3ai (unsuccessful)



The reaction mixture was stirred for 12 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Unfortunately, no desired product was detected.

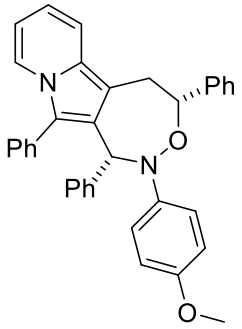
Synthesis of 3aj



The reaction mixture was stirred for 7 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 91 mg (90%) of **3aj** (dr = 10:1); yellow solid, m.p. 183-185 °C;

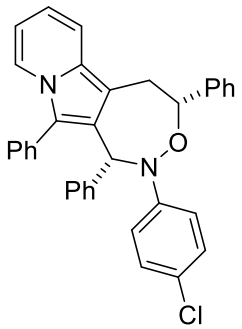
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.0 Hz, 1H), 7.46-7.33 (m, 11H), 7.26-7.24 (m, 3H), 7.16-7.14 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.73-6.69 (m, 1H), 6.44 (t, *J* = 6.5 Hz, 1H), 6.02 (s, 1H), 5.32 (dd, *J* = 2.0, 10.5 Hz, 1H), 3.64-3.58 (m, 1H), 3.55-3.50 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 141.7, 139.2, 131.0, 130.2, 129.5, 129.2, 128.9, 128.3, 127.9, 127.6, 127.5, 126.8, 126.4, 122.3, 122.2, 117.1, 116.6, 116.4, 110.1, 109.3, 85.3, 67.5, 34.7, 20.5; HRMS m/z (ESI^+): Calculated for $C_{36}H_{31}N_2O^+$ ($[M+H]^+$): 507.2431, Found: 507.2443.

Synthesis of 3ak



The reaction mixture was stirred for 18 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 89 mg (85%) of **3ak** (dr = 8:1); yellow solid, m.p. 98-100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.46-7.32 (m, 11H), 7.24-7.21 (m, 3H), 7.07 (d, *J* = 6.5 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.75-6.71 (m, 3H), 6.44 (t, *J* = 6.5 Hz, 1H), 5.85 (s, 1H), 5.38-5.34 (m, 1H), 3.75 (s, 3H), 3.66-3.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 143.8, 141.9, 138.8, 131.0, 130.2, 129.8, 128.8, 128.3, 127.9, 127.5, 127.4, 127.0, 126.8, 126.3, 122.3, 122.0, 118.5, 117.1, 116.6, 113.8, 110.1, 109.2, 85.7, 77.3, 77.0, 76.8, 69.3, 55.4, 34.9; HRMS m/z (ESI^+): Calculated for $C_{36}H_{31}N_2O_2^+$ ($[M+H]^+$): 523.2380, Found: 523.2390.

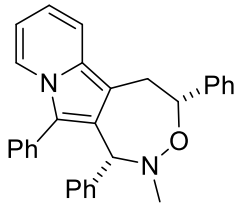
Synthesis of 3al



The reaction mixture was stirred for 43 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel, eluting with PE/EA = 30:1 (v/v), affording 85 mg (81%) of **3al** (dr = 7:1); yellow solid, m.p. 192-194 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.0 Hz, 1H), 7.49-7.35 (m,

10H), 7.28-7.24 (m, 4H), 7.15-7.10 (m, 4H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.74-6.70 (m, 1H), 6.45 (t, *J* = 6.5 Hz, 1H), 6.01 (s, 1H), 5.29-5.26 (m, 1H), 3.63-3.57 (m, 1H), 3.53-3.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 141.3, 138.8, 130. 8, 130.2, 129.3, 129.0, 128.6, 128.4, 128.1, 127.8, 127.7, 127.1, 126.4, 126.3, 125.7, 122.37, 122.3, 117.3, 117.1, 116.8, 110.3, 109.1, 85.7, 67.3, 34.6; HRMS m/z (ESI^+): Calculated for $C_{35}H_{28}N_2ClO^+$ ($[M+H]^+$): 527.1885, Found: 527.1892.

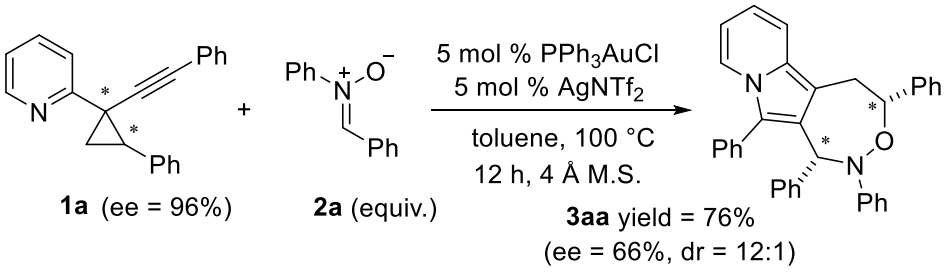
Synthesis of 3am



The reaction mixture was stirred for 14 hours at 100 °C until the reaction was complete (5 mol % catalyst used). Purified by chromatography on silica gel eluting with PE/EA = 30:1 (v/v), affording 68 mg (79%) of **3am** (dr > 99:1); brown solid, m.p. 140-142℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 4.0Hz 1H), 7.32 (s, 4H), 7.19 (m, 4H), 7.10-7.05 (m, 7H), 6.98-6.96 (m, 3H), 6.48 (t, *J* = 4.0Hz 1H), 6.27-6.23 (m, 1H), 5.43 (d, *J* = 4.0Hz 1H), 5.05 (s, 1H), 2.59 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 141.8, 131.7, 130.9, 129.2, 128.8, 128.6, 128.5, 128.1, 127.8, 127.7, 127.6, 127.0, 126.9, 121.8, 121.5, 116.6, 115.7, 109.4, 82.5, 44.3, 30.2; HRMS-TOF-ES^+: Calcd for $C_{30}H_{26}N_2OH$ ($[M+H]^+$): 430.2050, Found: 431.2100.

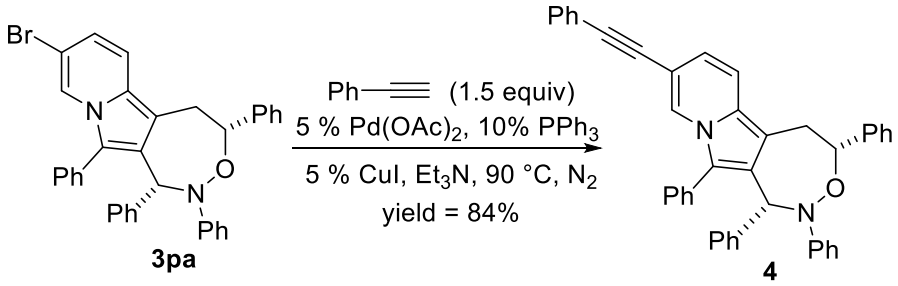
The reaction of enantioenriched 2-(1-alkynyl)-cyclopropyl pyridines 1a and nitrone 2a.

Optical resolution of racemic 2-(1-alkynyl)-cyclopropyl pyridines **1a** with (2R,3R)-2,3-dibenzoyloxybutanedioic acid (DBTA) to afford chiral 2-(1-alkynyl)-cyclopropyl pyridines **1a**, ee = 96%.



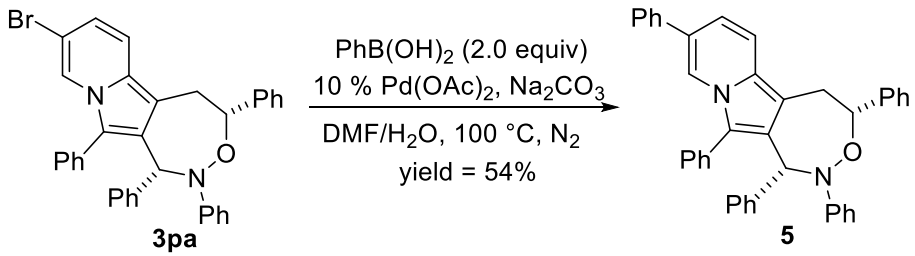
3aa, determined by HPLC, IA, Hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{major} = 10.26 min, t'_{minor} = 12.5 min).

Synthesis of 4



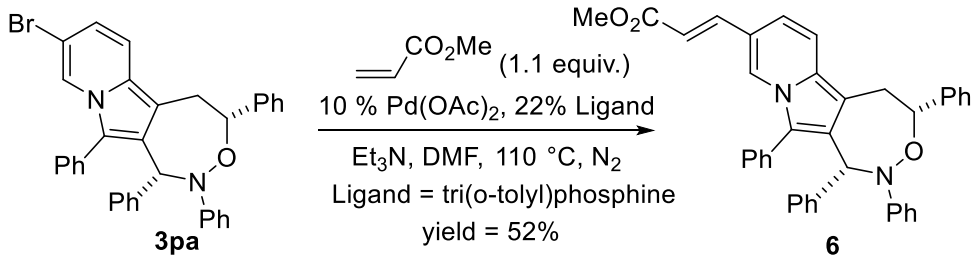
In a 25 mL tube, 5 mol% $Pd(OAc)_2$, 10 mol% PPh_3, the cycloadduct **3pa** (0.2 mmol) and 5 mol% CuI were added, and the tube was evacuated and refilled with N_2 for 3 times. After that, degassed triethylamine (2 mL) and phenylacetylene (1.5 equiv.) were added via syringe, and the mixture was stirred at 90 °C for 17 hours until the reaction was complete (monitored by TLC, PE:EA = 20:1). Purified by chromatography on silica gel eluting with PE/EA = 100/1; yield = 84% (99 mg); yellow solid, m.p. 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.55-7.31 (m, 16H), 7.24-7.07 (m, 7H), 6.89-6.78 (m, 4H), 6.07 (s, 1H), 5.30 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.62-3.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 141.3, 138.8, 131.4, 130.2, 129.3, 129.1, 128.8, 128.7, 128.4, 128.3, 128.1, 127.8, 127.7, 127.65, 127.0, 126.4, 125.9, 123.1, 122.9, 120.9, 119.2, 116.8, 116.0, 110.5, 106.5, 89.2, 87.3, 85.4, 67.2, 34.7; HRMS-TOF-ES$^+$: $[M+H]^+$ Calcd for $C_{43}H_{33}N_2O$: 593.2590, Found: 593.2593.

Synthesis of 5



In a 25 mL tube, 10 mol% $Pd(OAc)_2$, the cycloadduct **3pa** (0.2 mmol), phenylboric acid (2.0 equiv.) and Na_2CO_3 (2.0 equiv.) were added, and the tube was evacuated and refilled with N_2 for 3 times. After that, degassed 3 mL of DMF/H_2O (2/1) was added via syringe, and the mixture was stirred at 100 °C for 10 hours until the reaction was complete (monitored by TLC, PE:EA = 20:1). The reaction mixture was quenched with water (5 mL) and extracted with EA (3×5 mL), the organic phase was combined and washed with saturated NaCl(aq), and then dried over anhydrous $MgSO_4$, concentrated via evaporator and purified by chromatography on silica gel eluting with PE/EA = 80/1; yield = 54% (61 mg); yellow solid, m.p. 220-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.52-7.28 (m, 16H), 7.25-7.20 (m, 3H), 7.17-7.09 (m, 4H), 7.03-6.96 (m, 1H), 6.88-6.80 (m, 3H), 6.06 (s, 1H), 5.29 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.64-3.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 141.5, 139.1, 138.6, 130.7, 130.1, 129.4, 129.3, 129.1, 128.8, 128.7, 128.4, 128.1, 127.7, 127.6, 127.2, 127.1, 126.9, 126.6, 126.4, 124.5, 122.8, 120.7, 119.8, 117.6, 117.2, 115.9, 109.5, 85.5, 67.0, 34.8; HRMS-TOF-ES$^+$: $[M+H]^+$ Calcd for $C_{41}H_{33}N_2O$: 569.2590, Found: 569.2593.

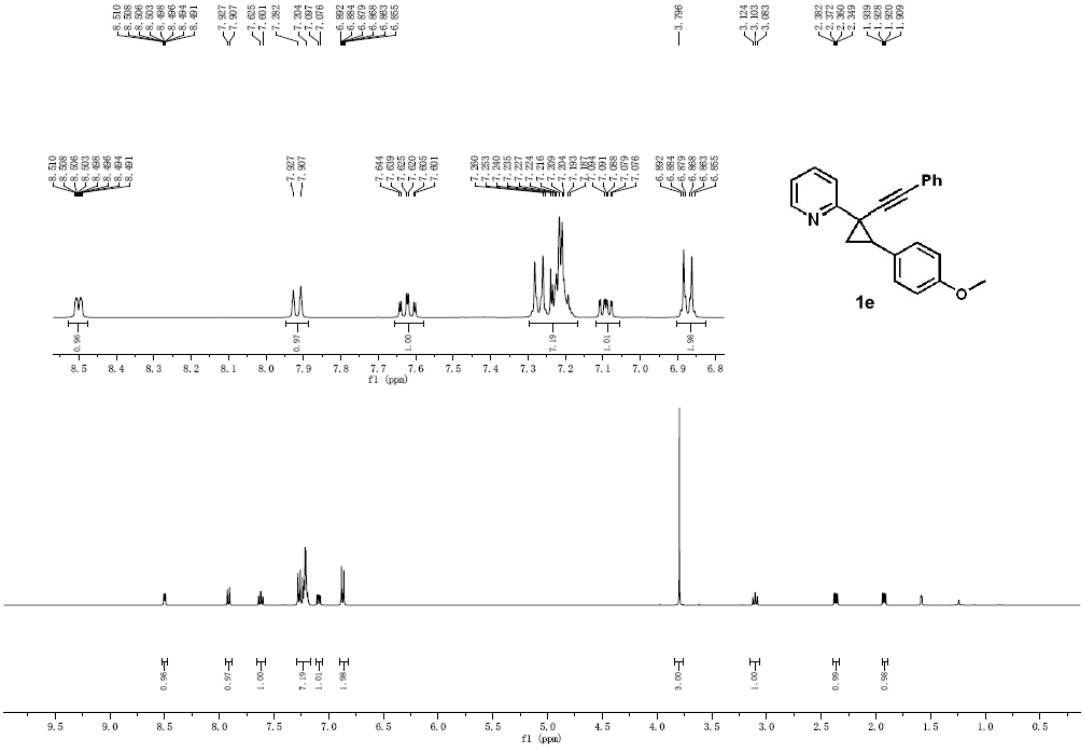
Synthesis of 6

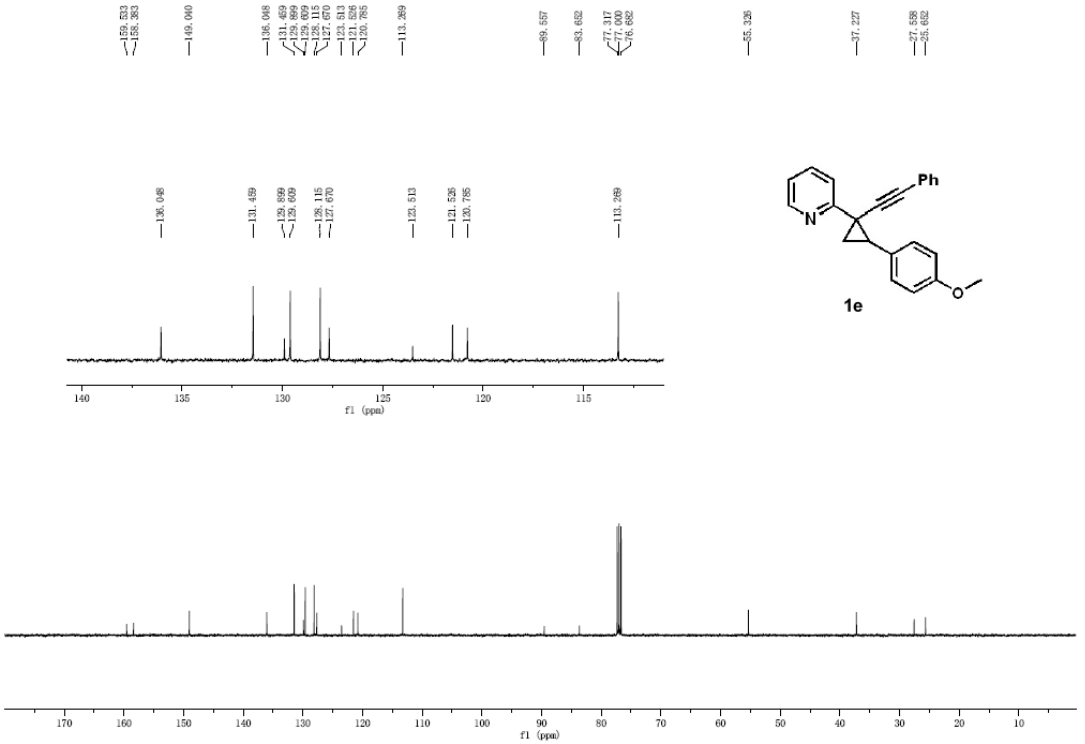


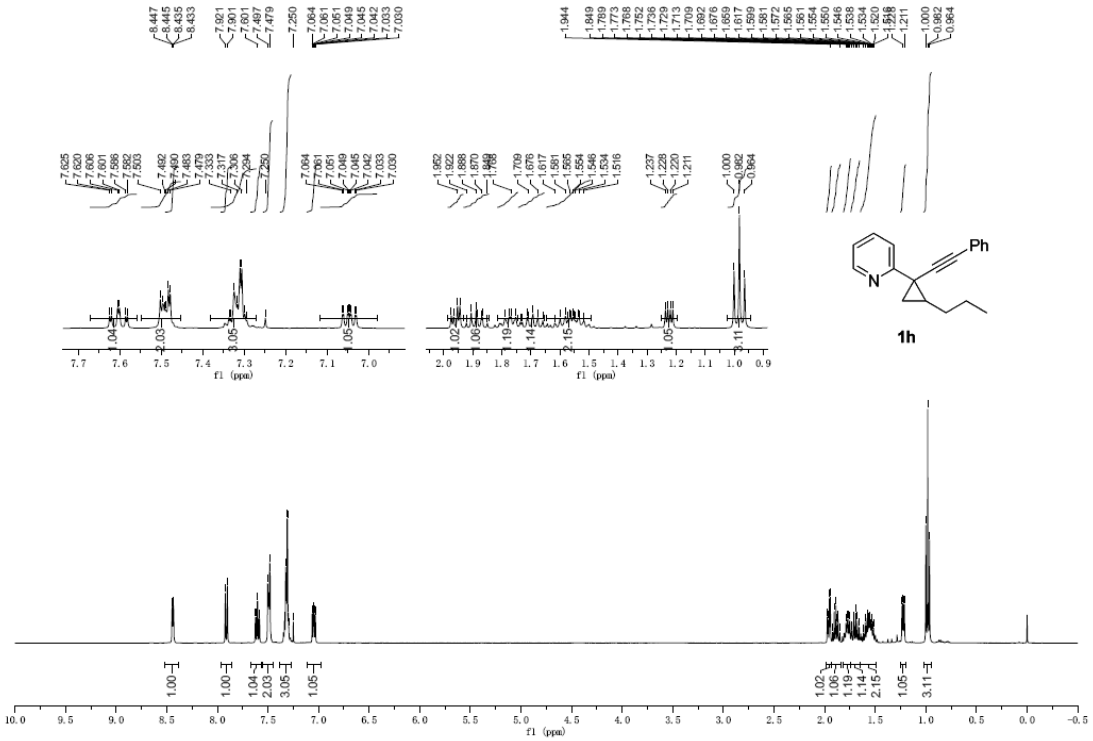
In a 25 mL tube, 10 mol% $Pd(OAc)_2$, 22% tri(o-tolyl)phosphine and the cycloadduct **3pa** (0.2 mmol) were added, and the tube was evacuated and refilled with N_2 for 3 times. After that, methyl acrylate (1.1 equiv.), degassed Et_3N (5.0 equiv.) and

degassed 2 mL of dry DMF was added via syringe, and the mixture was stirred at 110 °C for 13 hours until the reaction was complete (monitored by TLC, PE:EA = 20:1). The reaction mixture was quenched with water (5 mL) and extracted with EA (3×5 mL), the organic phase was combined and washed with saturated NaCl(aq), and then dried over anhydrous $MgSO_4$, concentrated via evaporator and purified by chromatography on silica gel eluting with PE/EA = 80/1; yield = 52% (60 mg); red solid, m.p. 220-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.50-7.44 (m, 4H), 7.40-7.30 (m, 7H), 7.23-7.11 (m, 6H), 7.07-7.05 (m, 2H), 6.91 (d, *J* = 9.2 Hz, 1H), 6.87-6.80 (m, 3H), 6.29 (d, *J* = 16.0 Hz 1H), 6.02 (s, 1H), 5.25 (dd, *J* = 10.0, 2.8 Hz, 1H), 3.78 (s, 3H), 3.56-3.44 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 167.5, 149.4, 142.3, 141.2, 138.7, 129.9, 129.5, 129.2, 129.18, 128.7, 128.6, 128.4, 128.2, 127.8, 127.7, 127.1, 126.4, 126.2, 123.9, 120.9, 118.7, 117.6, 116.0, 115.5, 113.6, 111.6, 85.3, 67.1, 51.6, 34.7; HRMS-TOF-ES$^+$: $[M+H]^+$ Calcd for $C_{39}H_{33}N_2O_3$: 577.2485, Found: 577.2491.

^{1}H and ^{13}C NMR spectra of new 2-(1-alkynyl)-cyclopropyl pyridines.



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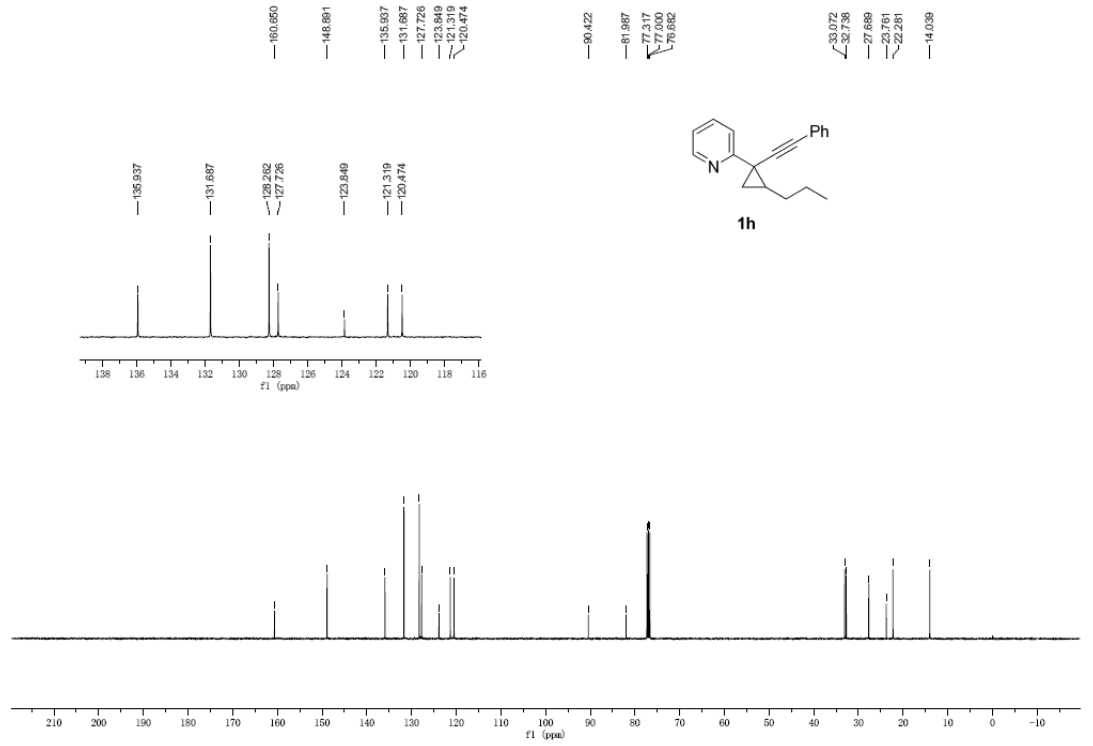
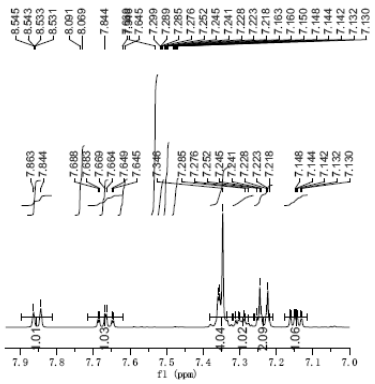
1h
f1 (ppm)


Ph
N
1h
f1 (ppm)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7.252
7.245
7.241
7.228
7.223
7.218
7.163
7.160
7.150
7.148
7.144
7.142
7.132
7.130
3.269
3.268
3.248
2.475
2.463
2.453
2.441
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2.074
2.063
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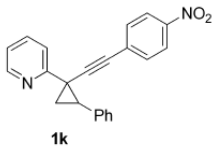
4.04
1.02
2.09
1.06
f1 (ppm)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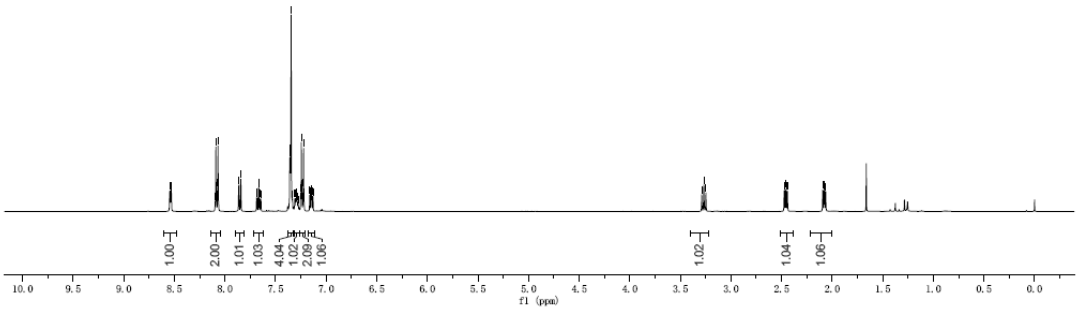
N
Ph

1k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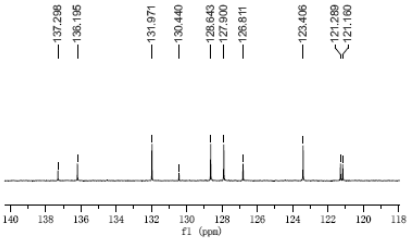
1.02
2.09
1.06
1.02
1.04
1.06
f1 (ppm)


158.401
149.262
146.559
137.298
136.195
128.643
127.900
126.811
123.406
121.289
121.160
96.929
82.051
77.317
77.000
76.682
38.103
27.809
25.445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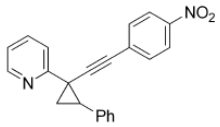
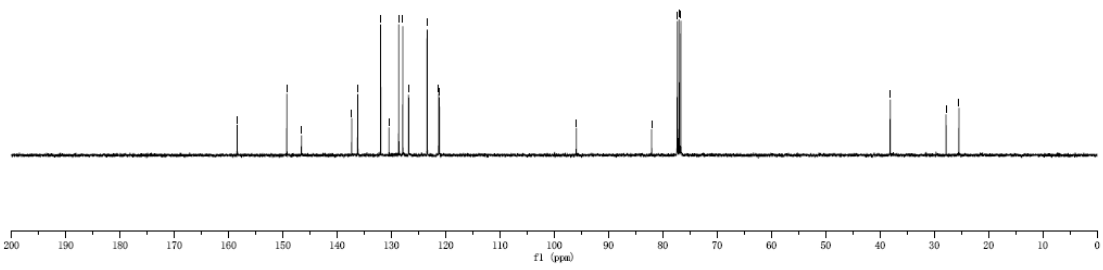
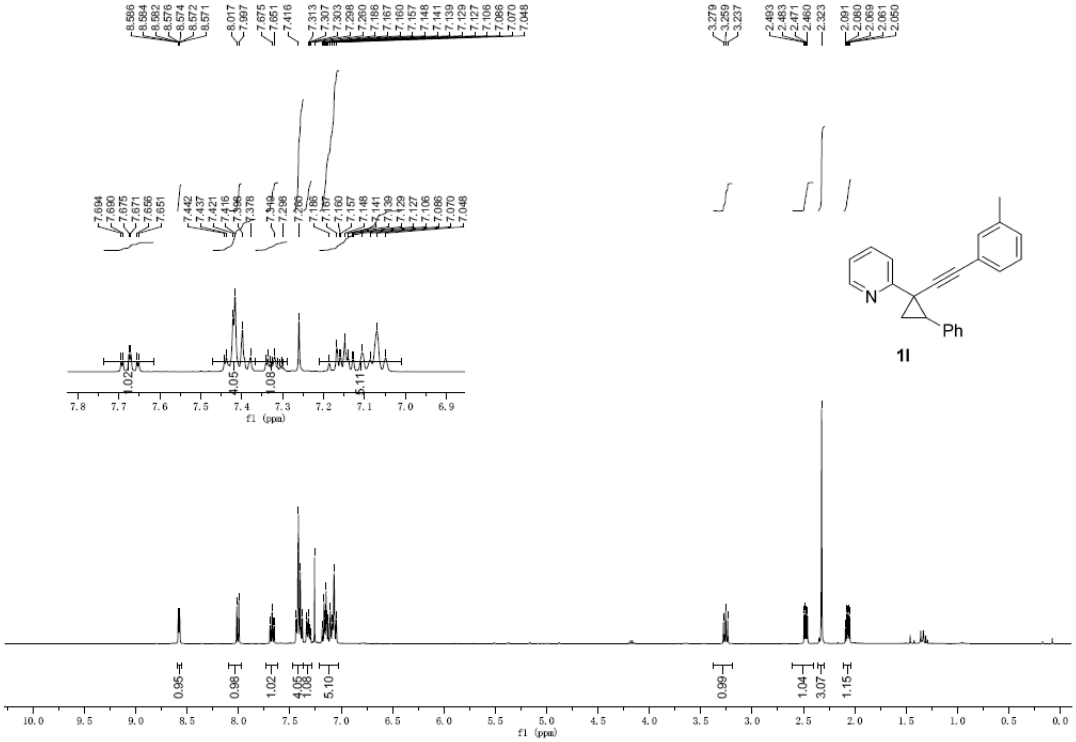
126.811
123.406
121.289
121.160
f1 (ppm)


NO2
N
Ph

1k


f1 (ppm)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7.651
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7.307
7.303
7.298
7.280
7.186
7.167
7.160
7.157
7.148
7.141
7.139
7.129
7.127
7.106
7.086
7.070
7.048
3.279
3.259
3.237
2.493
2.483
2.471
2.460
2.323
2.091
2.080
2.069
2.061
2.050
0.95
0.98
1.02
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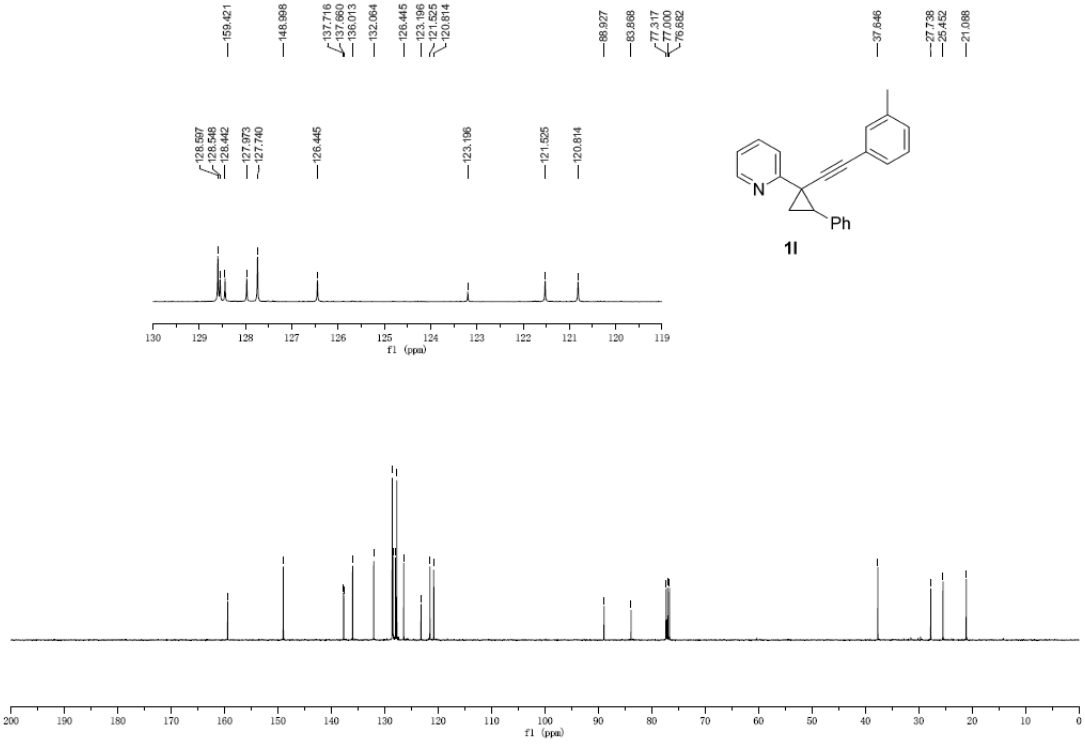
1.08
5.10
0.99
1.04
3.07
1.15
f1 (ppm)
N
Ph
1l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136.013
132.064
126.445
123.196
121.525
120.814
89.927
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77.000
76.682
37.846
27.738
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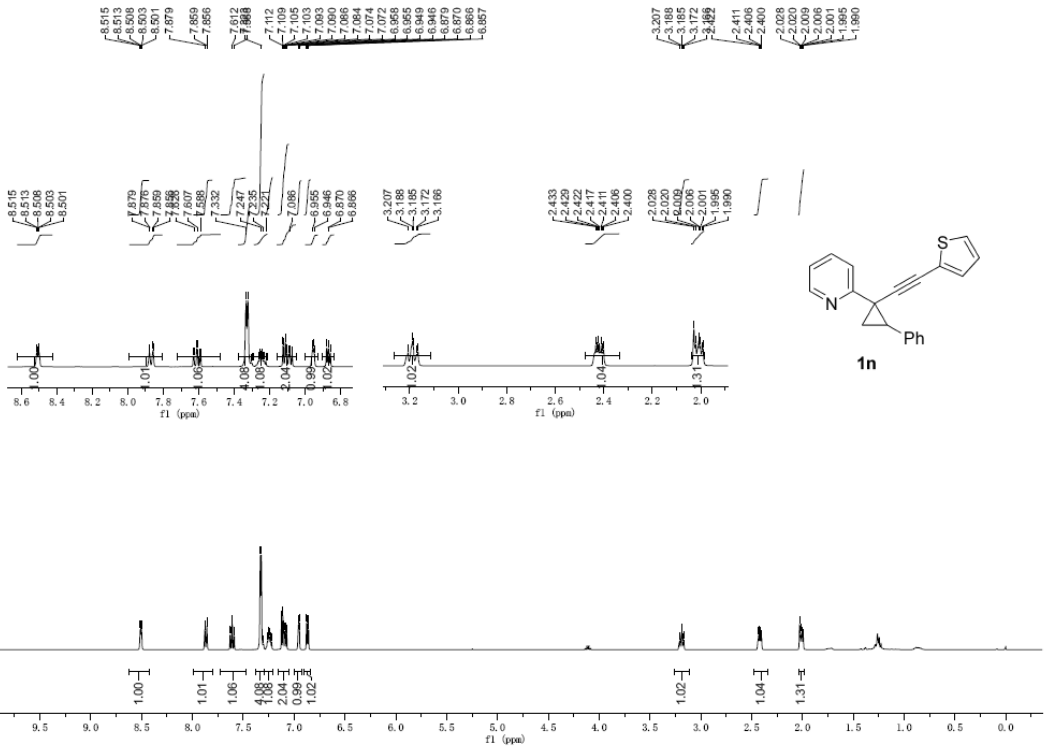
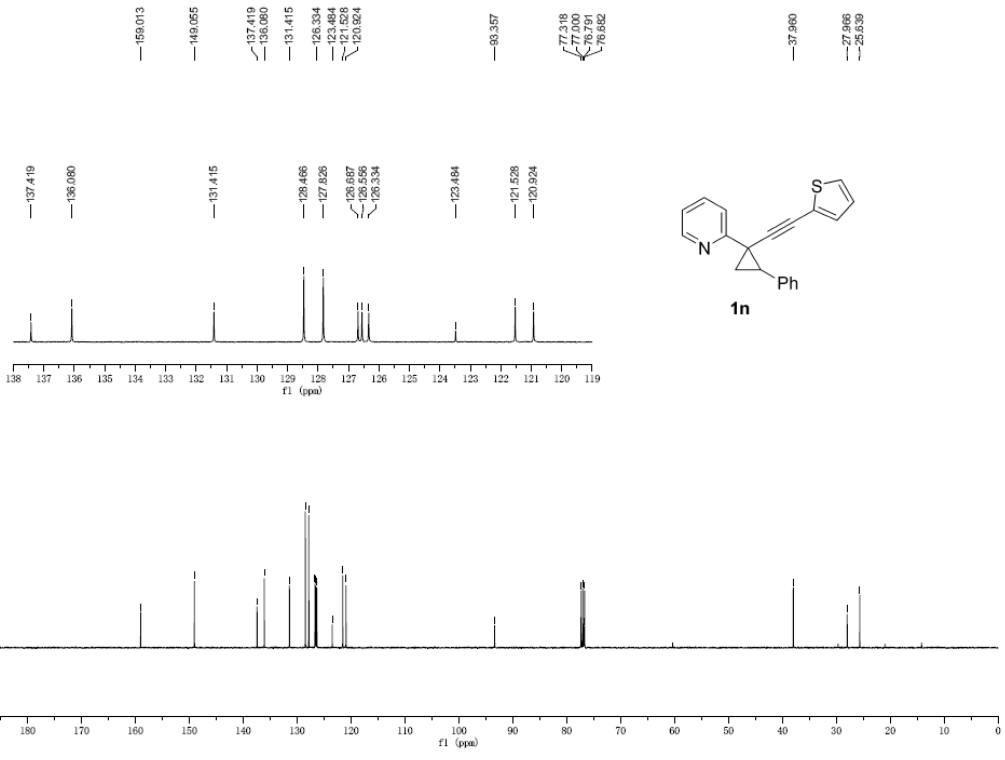
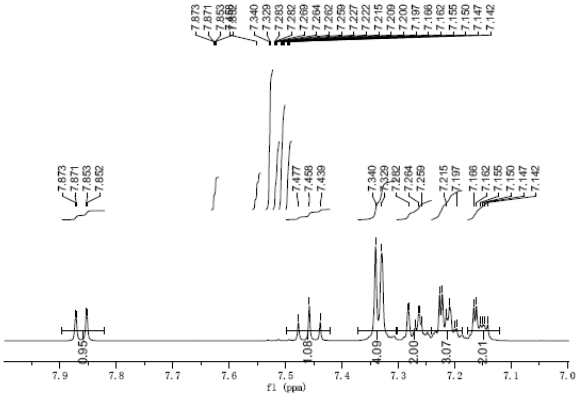
21.088
128.597
128.545
128.442
127.973
127.740
f1 (ppm)
N
Ph
1l

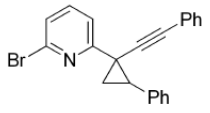

1n

f1 (ppm)

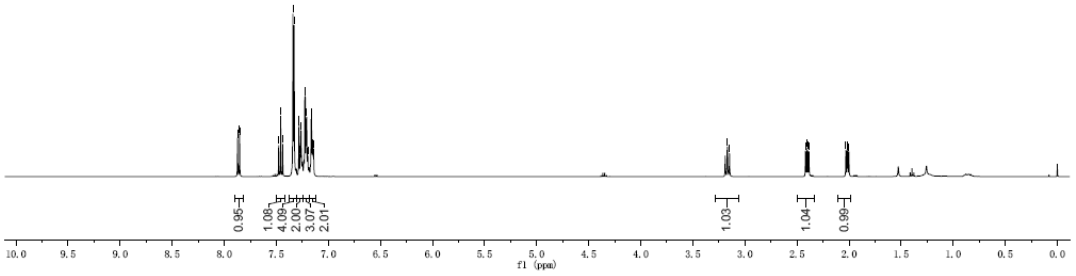

1n
f1 (ppm)

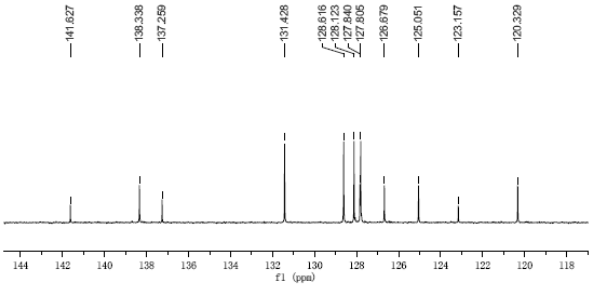
f1 (ppm)

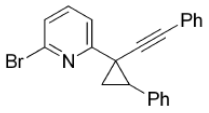




1o







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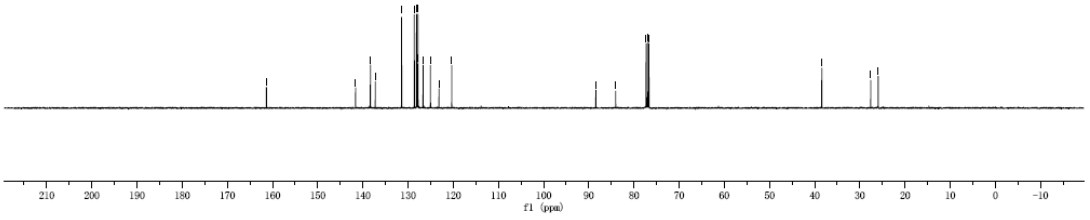

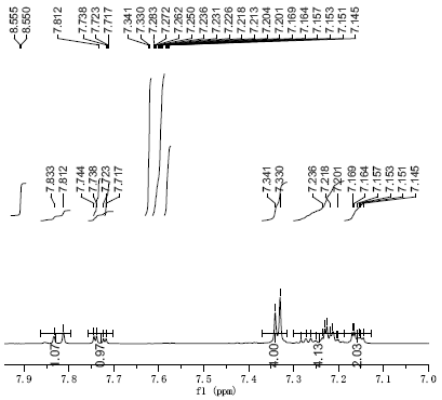
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7.231
7.226
7.218
7.213
7.204
7.201
7.169
7.164
7.157
7.153
7.151
7.145
3.157
3.135
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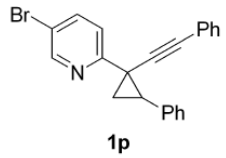
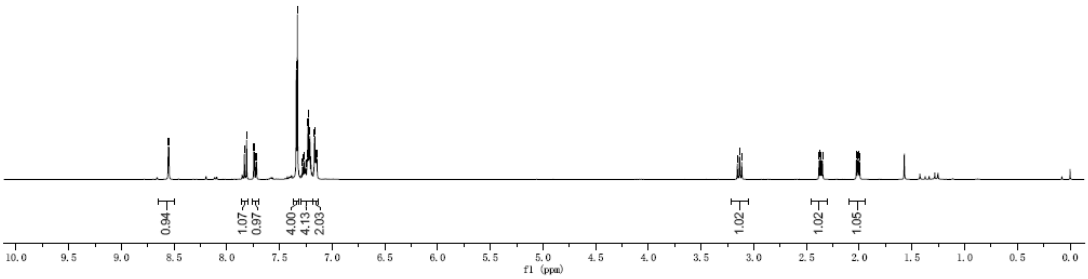
f1 (ppm)


Br
N
Ph
Ph

1p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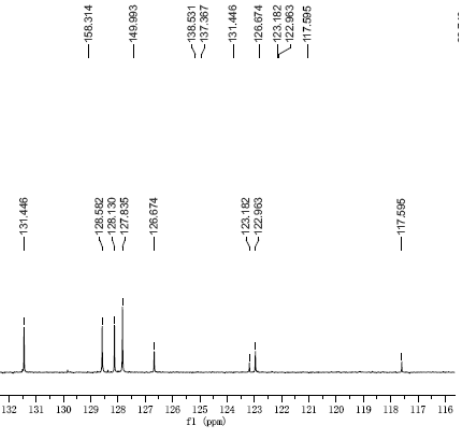
1.02
1.05
f1 (ppm)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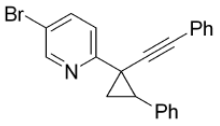
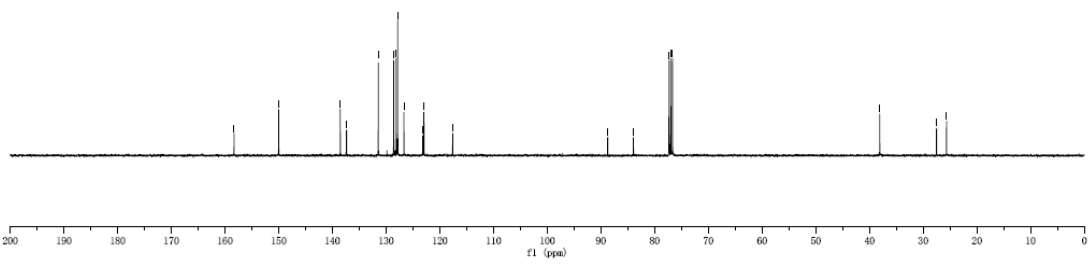
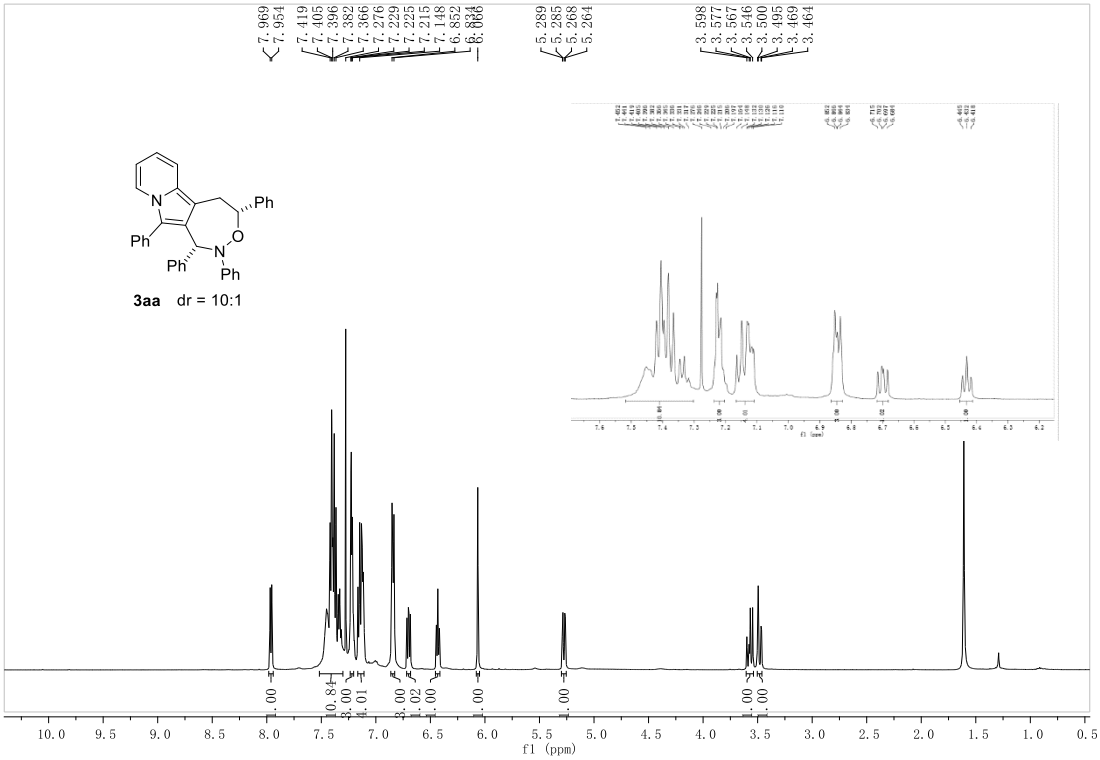
38.079
27.507
25.649
f1 (ppm)

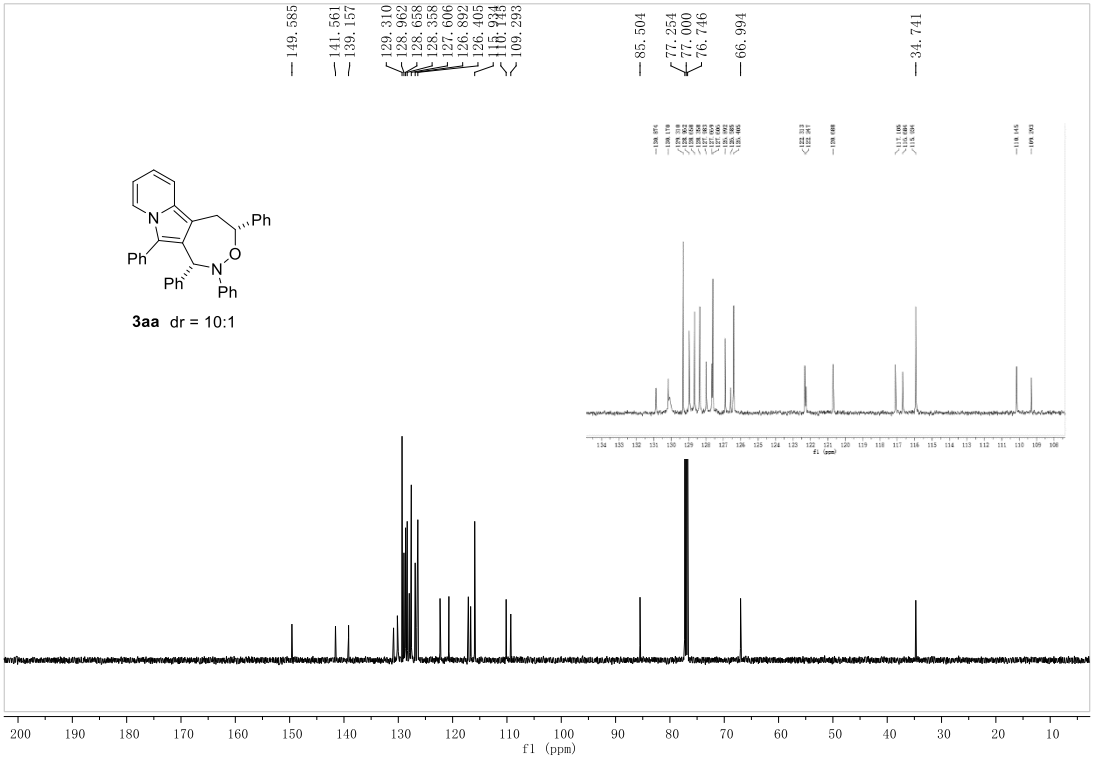

Br
N
Ph
Ph

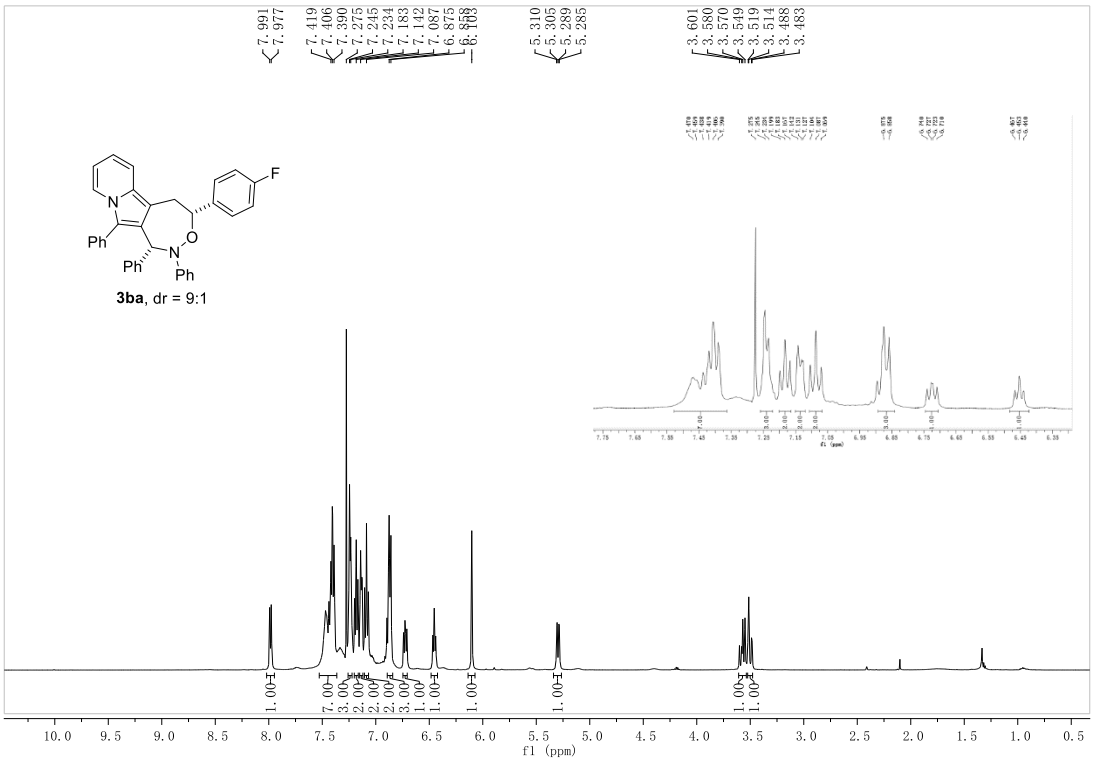
1p


f1 (ppm)

^{1}H and ^{13}C NMR spectra of products



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5.310
5.305
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5.285
3.601
3.580
3.570
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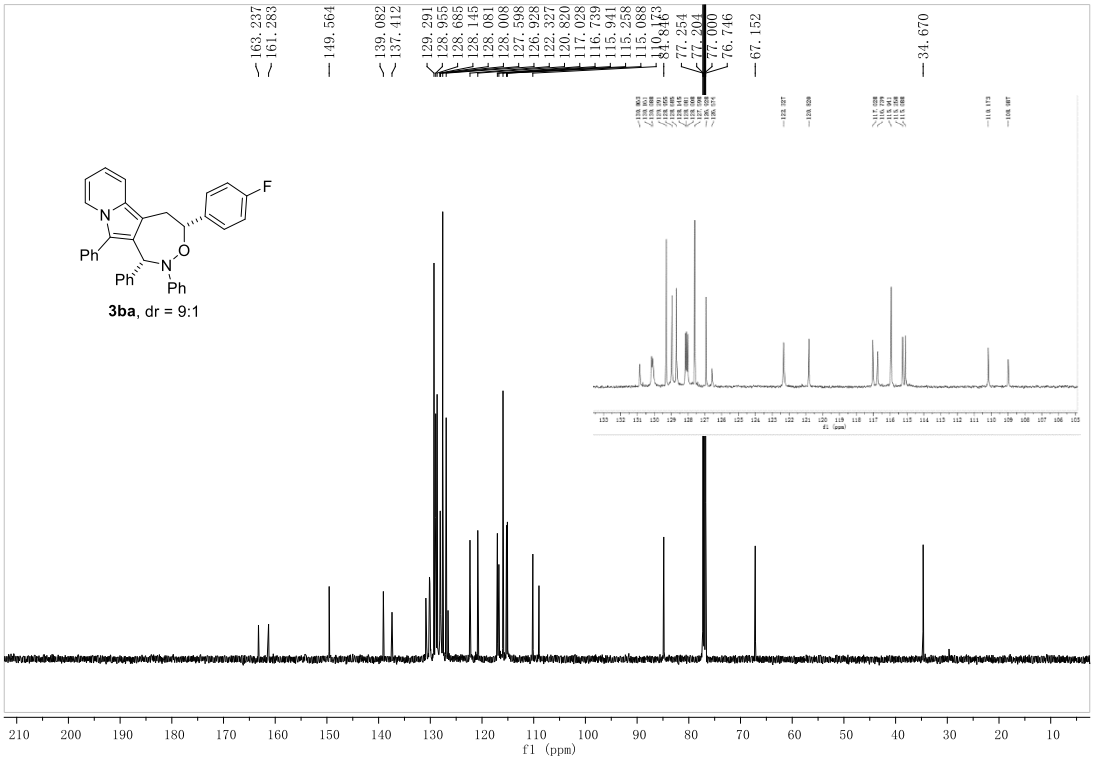
O
N
Ph
Ph
3ba, dr = 9:1
f1 (ppm)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137.412
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128.685
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128.008
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122.327
120.820
117.028
116.739
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115.258
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110.173
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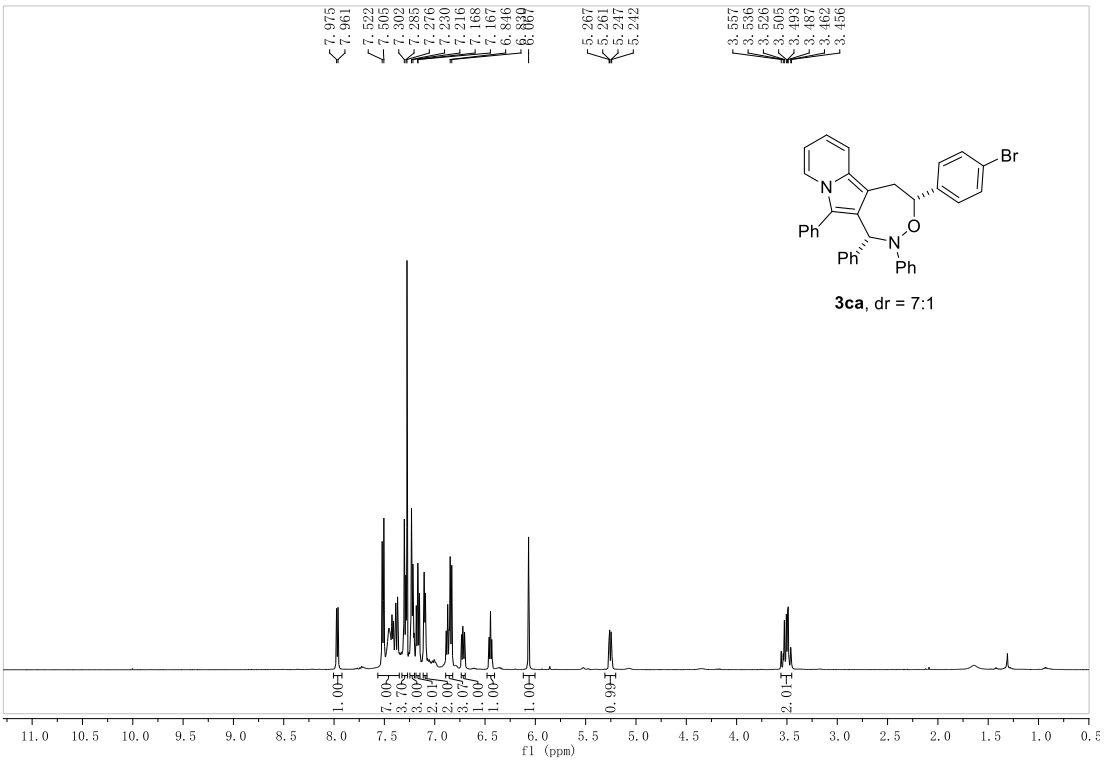
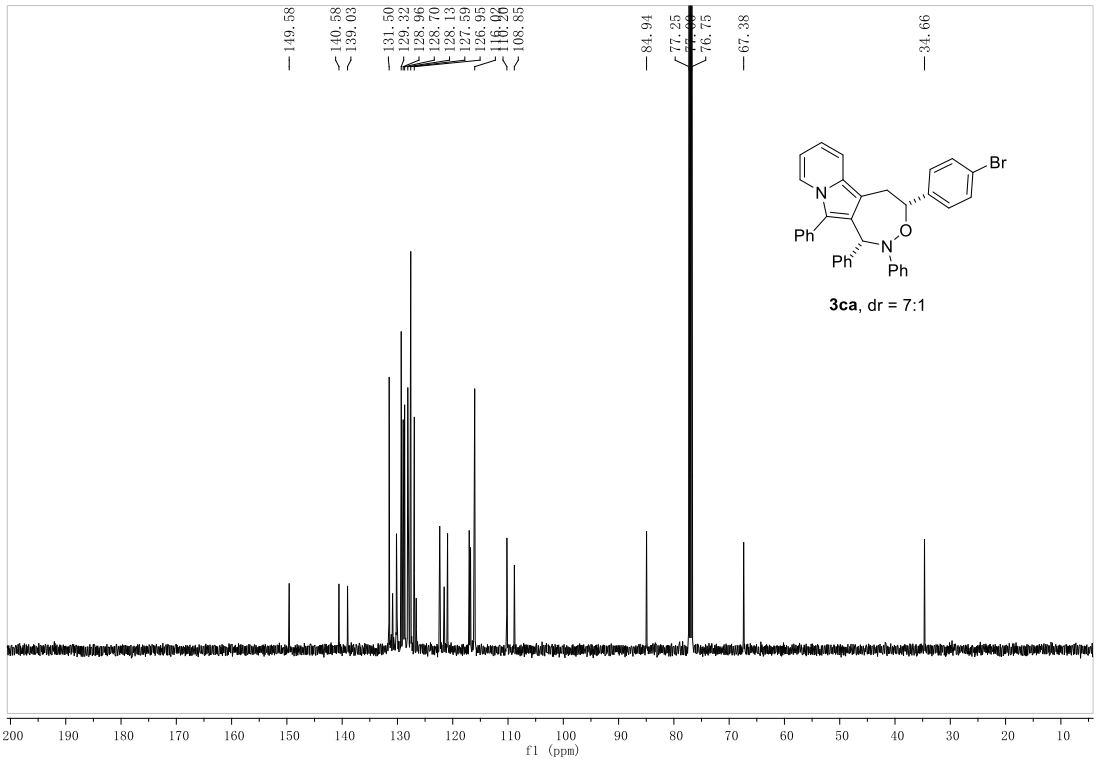
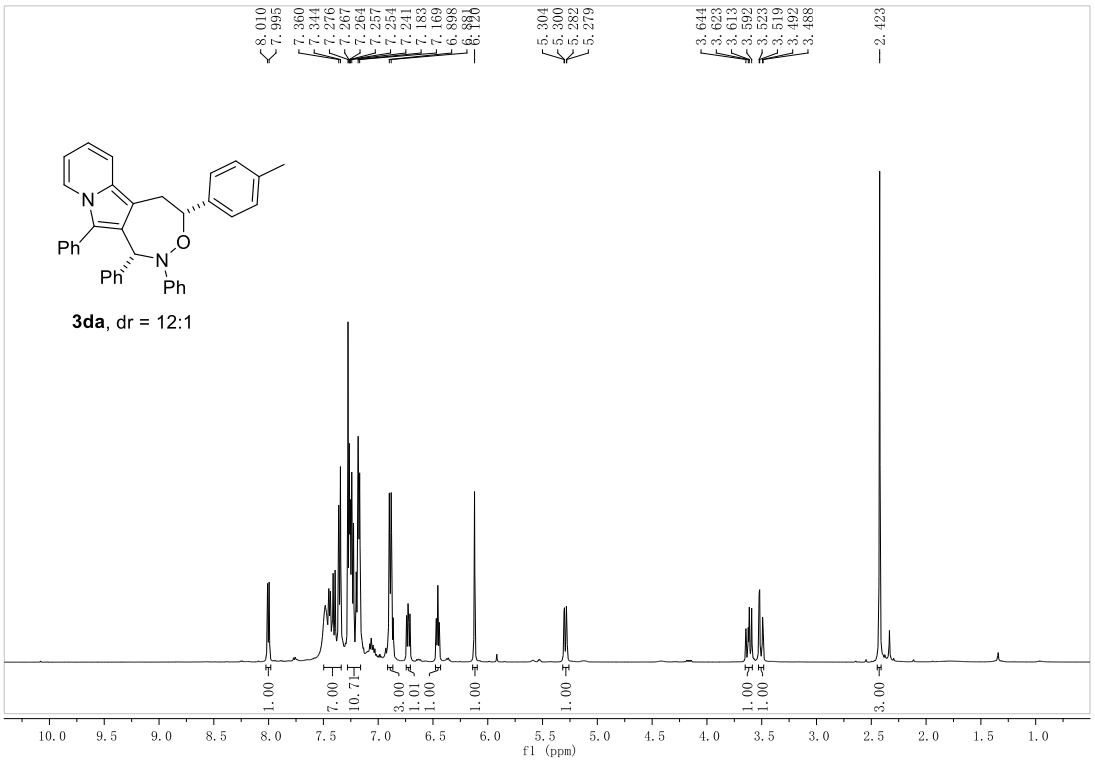
O
N
Ph
Ph
3ba, dr = 9:1
f1 (ppm)



3ca, dr = 7:1



3ca, dr = 7:1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7.254
7.241
7.183
7.169
6.898
6.891
6.880
5.304
5.300
5.282
5.279
3.644
3.623
3.613
3.592
3.523
3.519
3.492
3.488
2.423
Ph
Ph
Ph
N
O
N
3da, dr = 12:1
1.00
7.00
10.71
3.00
1.01
1.00
1.00
1.00
1.00
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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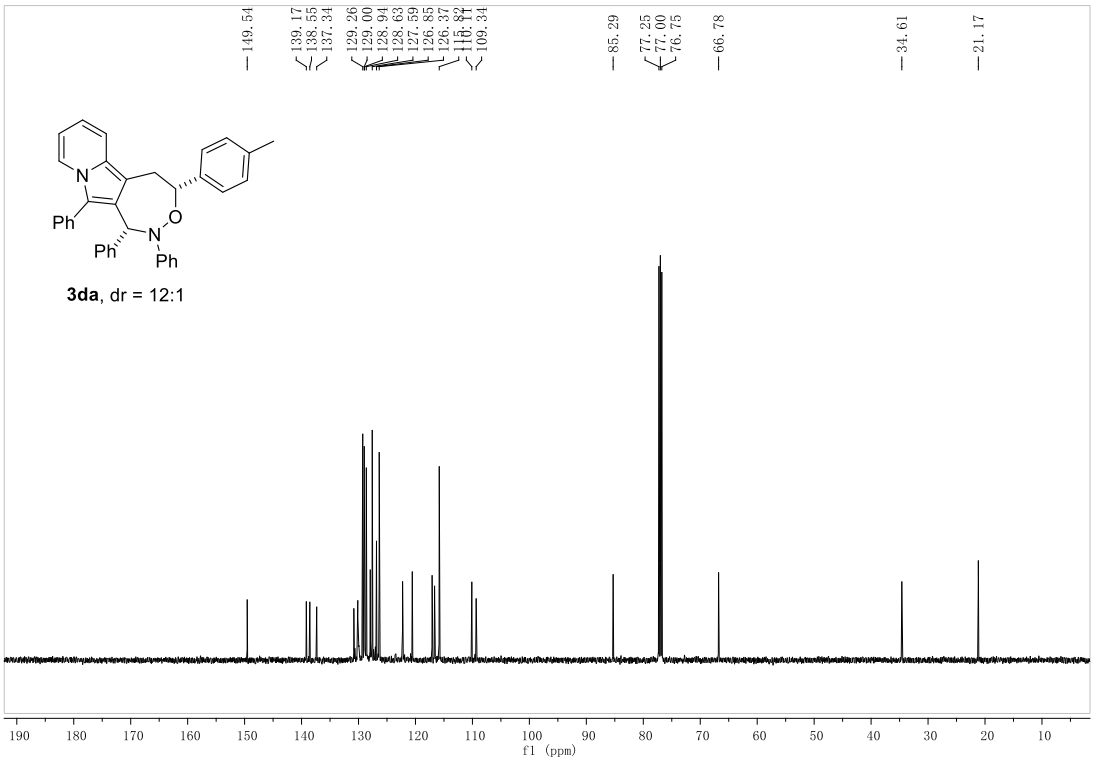
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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128.63
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126.85
126.37
116.82
116.11
109.34
85.29
77.25
77.00
76.75
66.78
34.61
21.17
Ph
Ph
Ph
N
O
N
3da, dr = 12:1
190
180
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140
130
120
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100
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80
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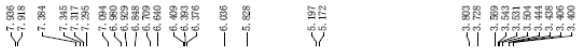
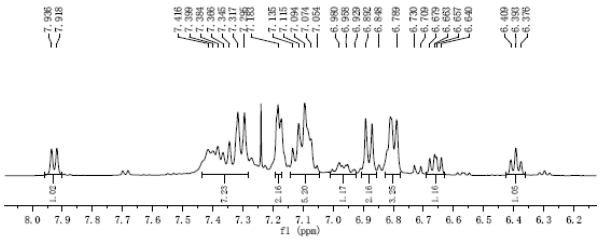
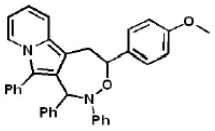
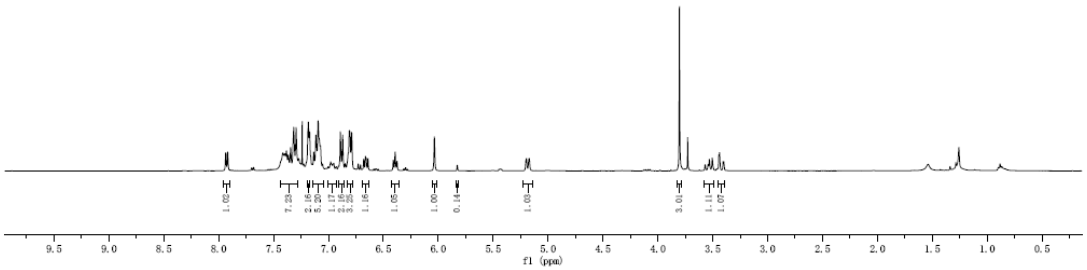
60
50
40
30
20
10
f1 (ppm)

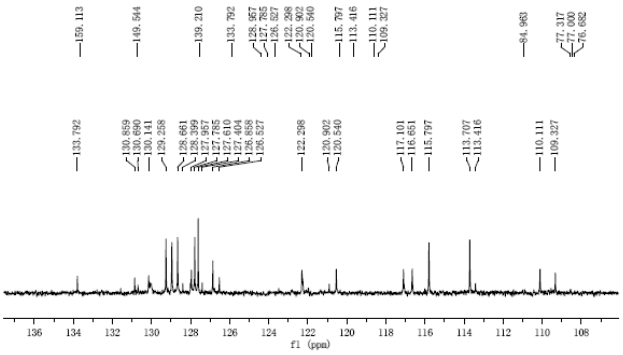


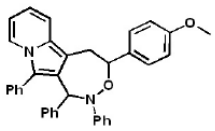




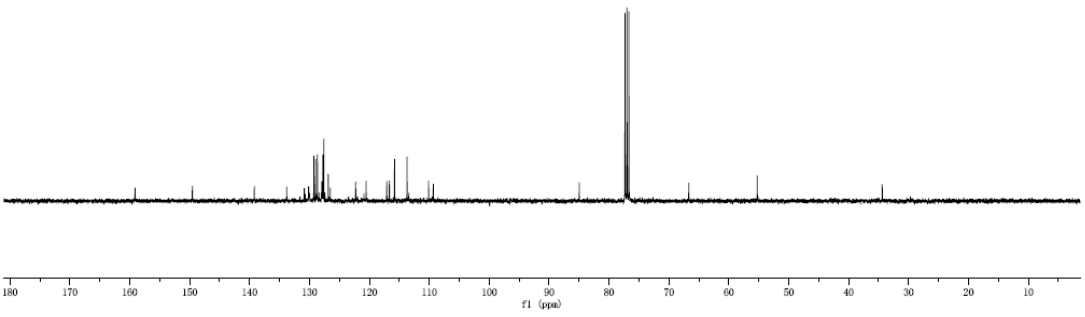
3ea d.r. = 7:1

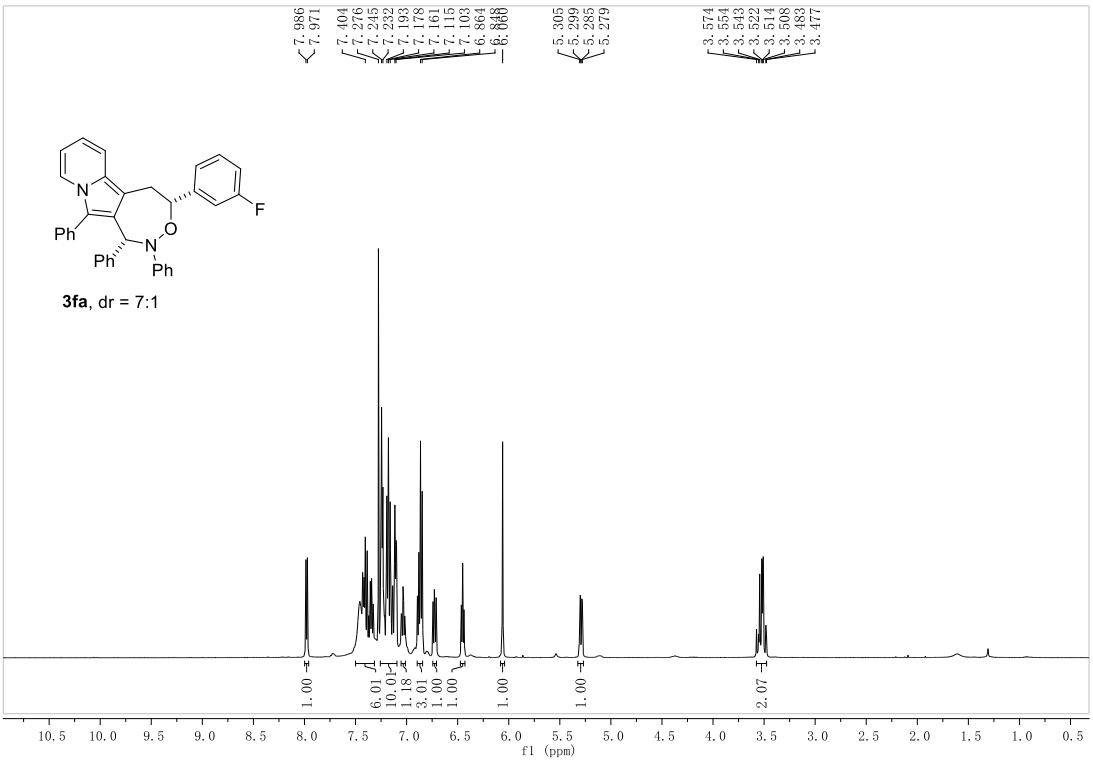




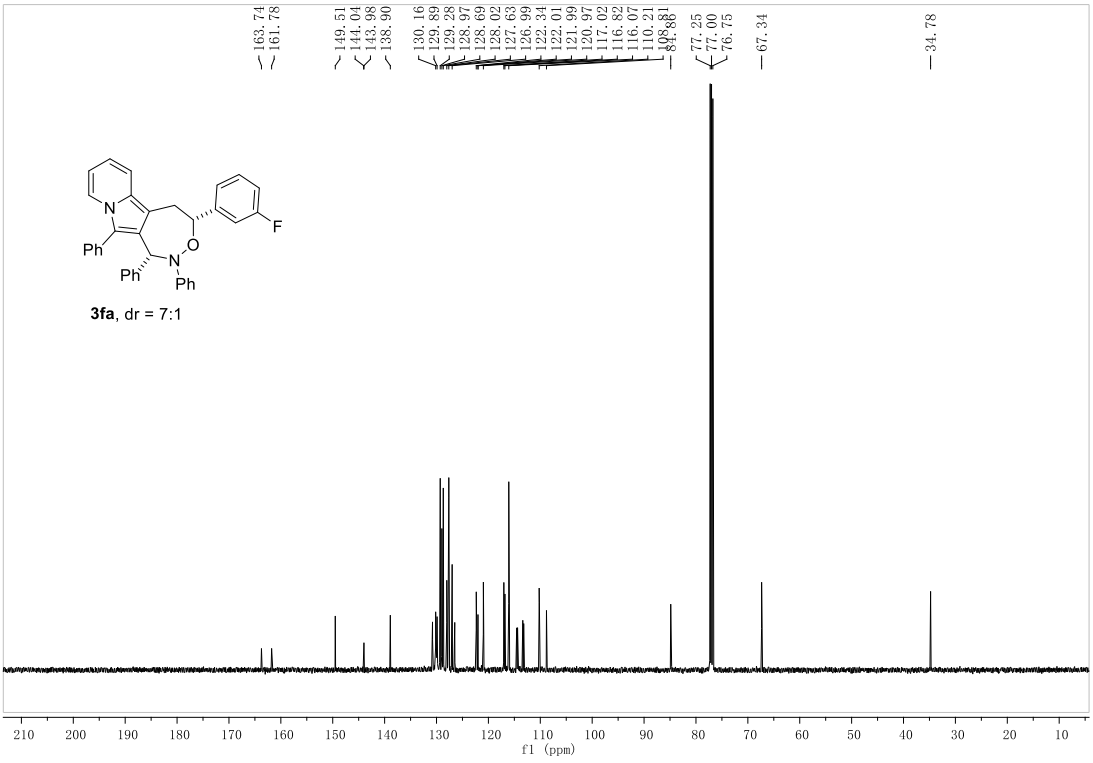


3ea d.r. = 7:1

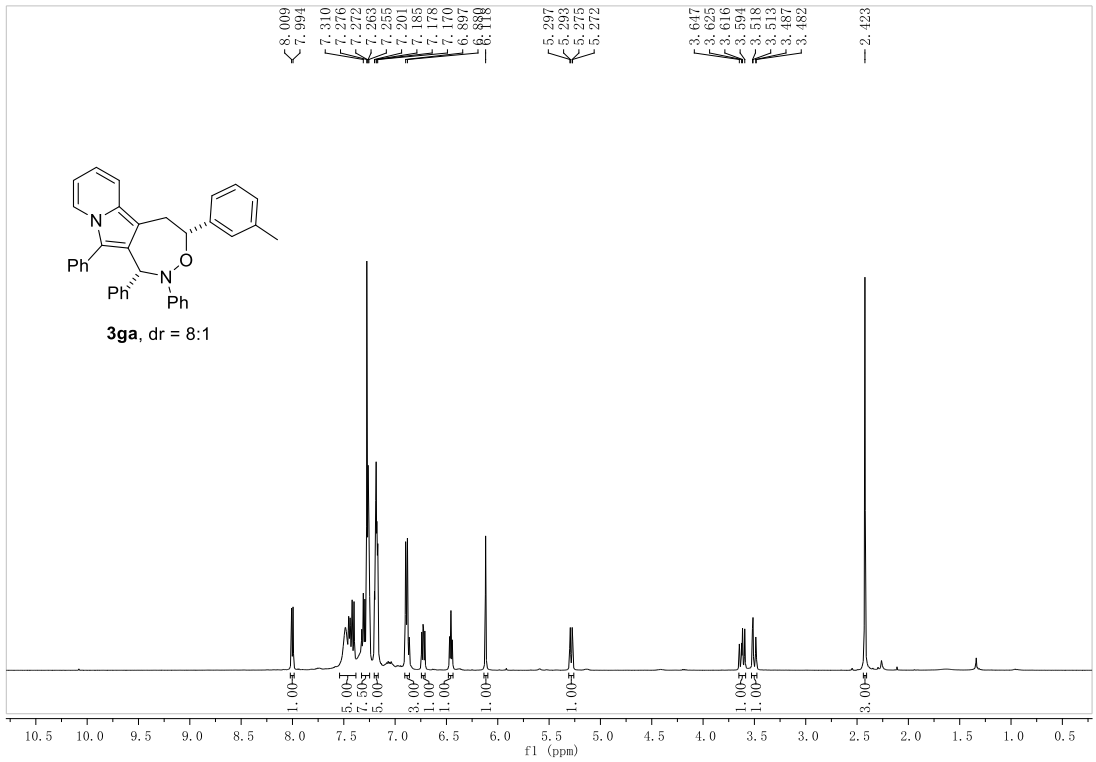




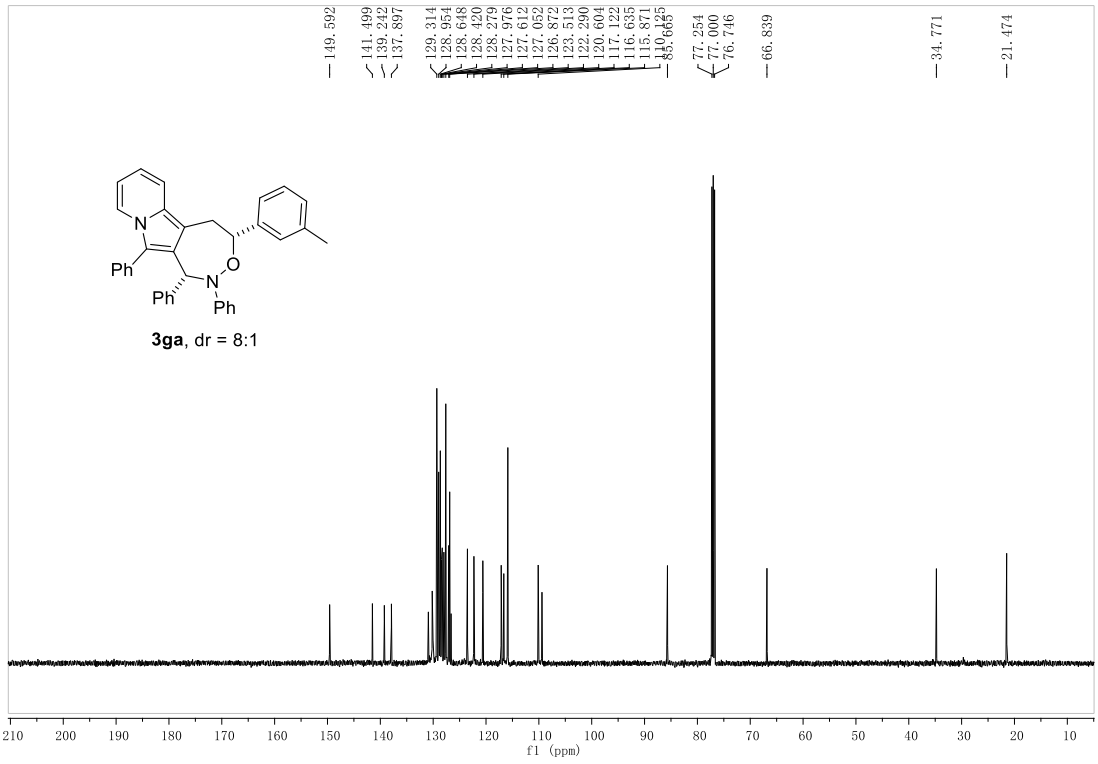
3fa, dr = 7:1



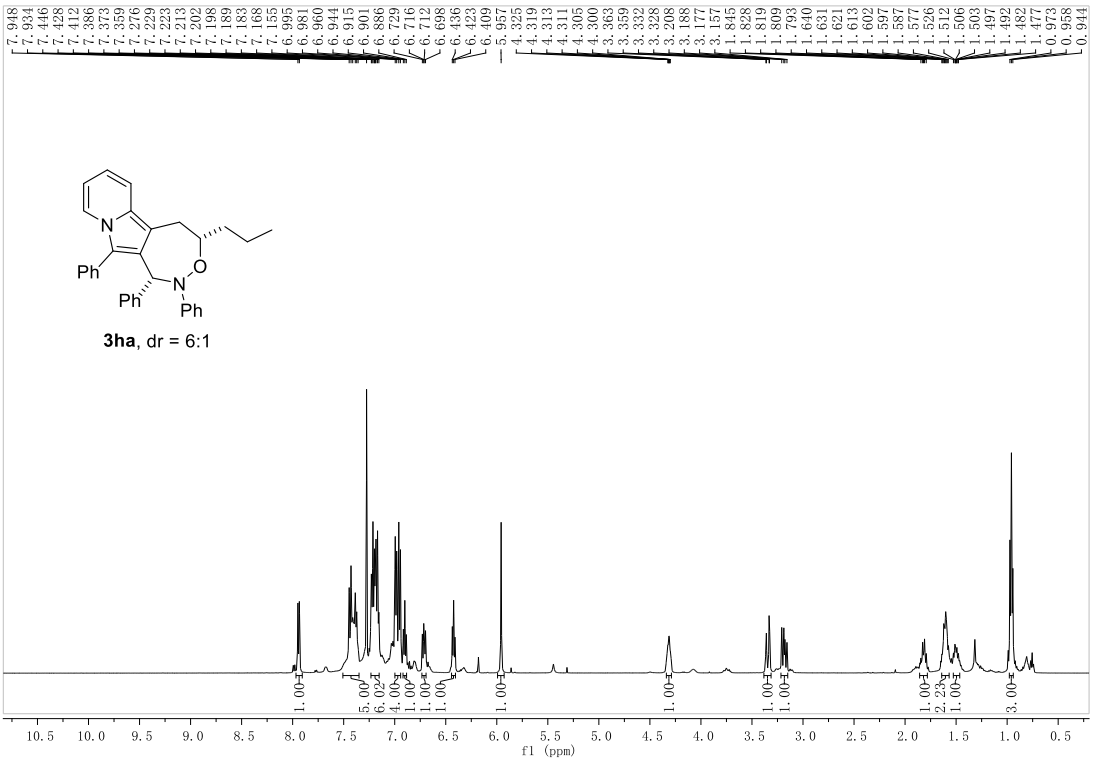
3fa, dr = 7:1



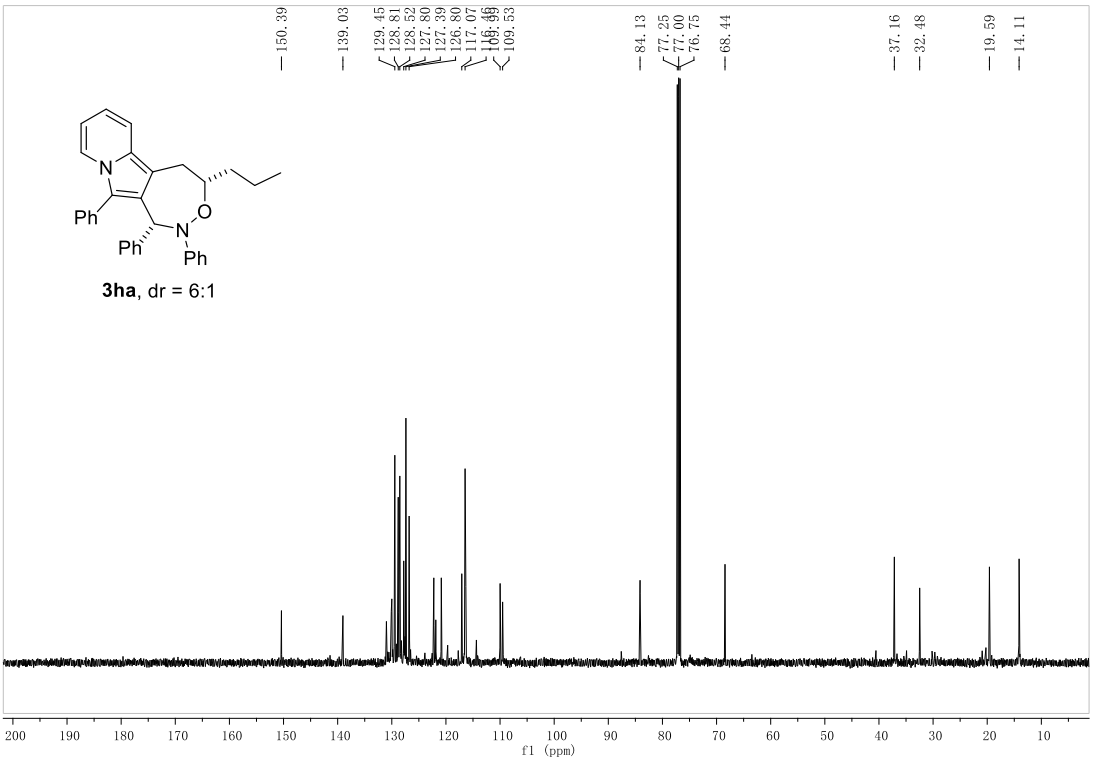
3ga, dr = 8:1



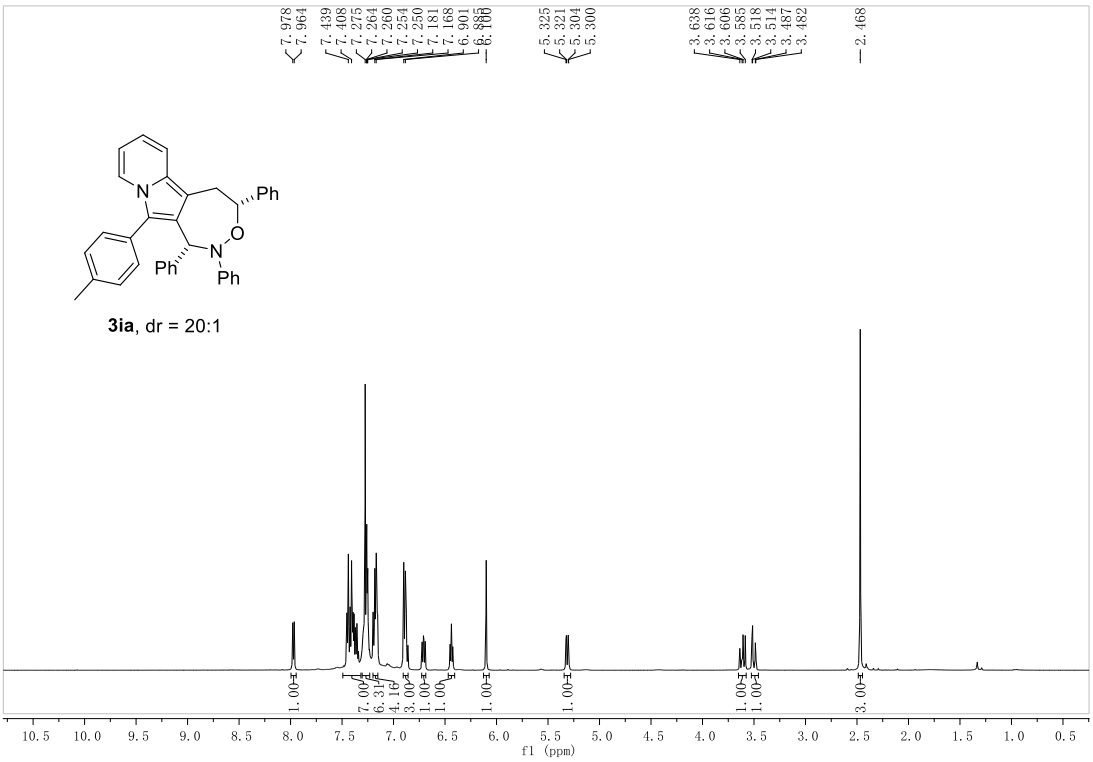
3ga, dr = 8:1



3ha, dr = 6:1



3ha, dr = 6:1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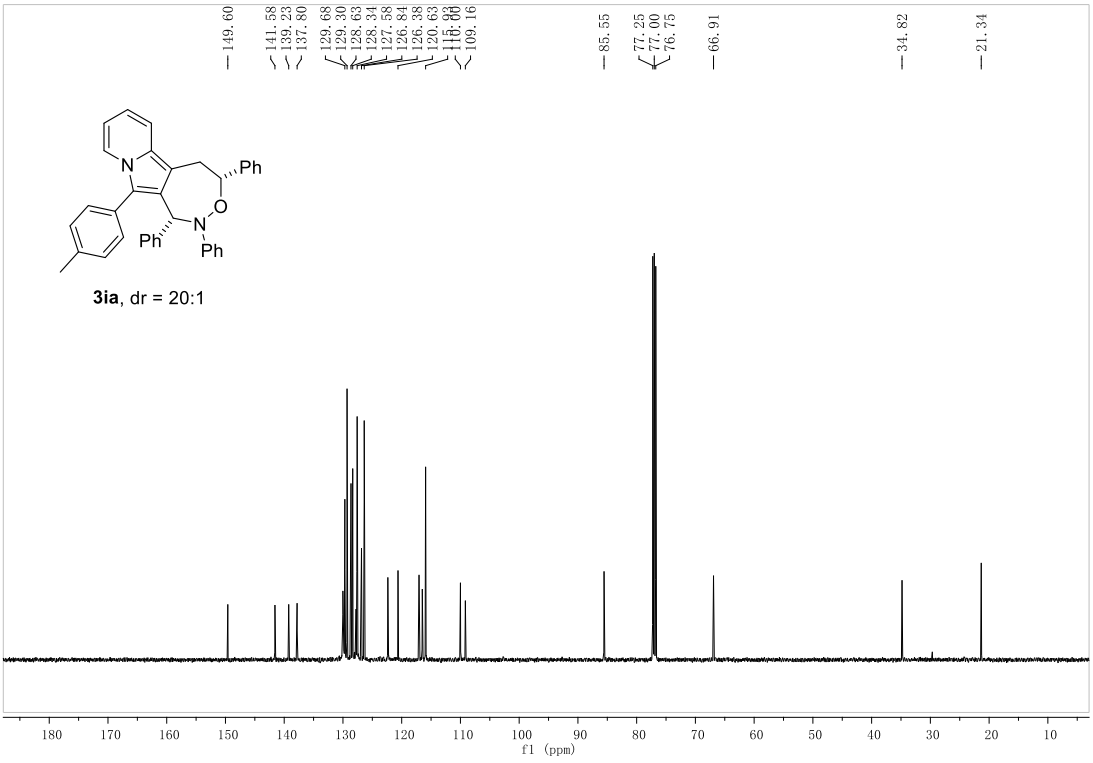
7.254
7.250
7.181
7.168
6.901
6.885
6.100
5.325
5.321
5.304
5.300
3.638
3.616
3.606
3.585
3.518
3.514
3.487
3.482
2.468
Ph
Ph
Ph
N
O
N
3ia, dr = 20:1
f1 (ppm)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126.38
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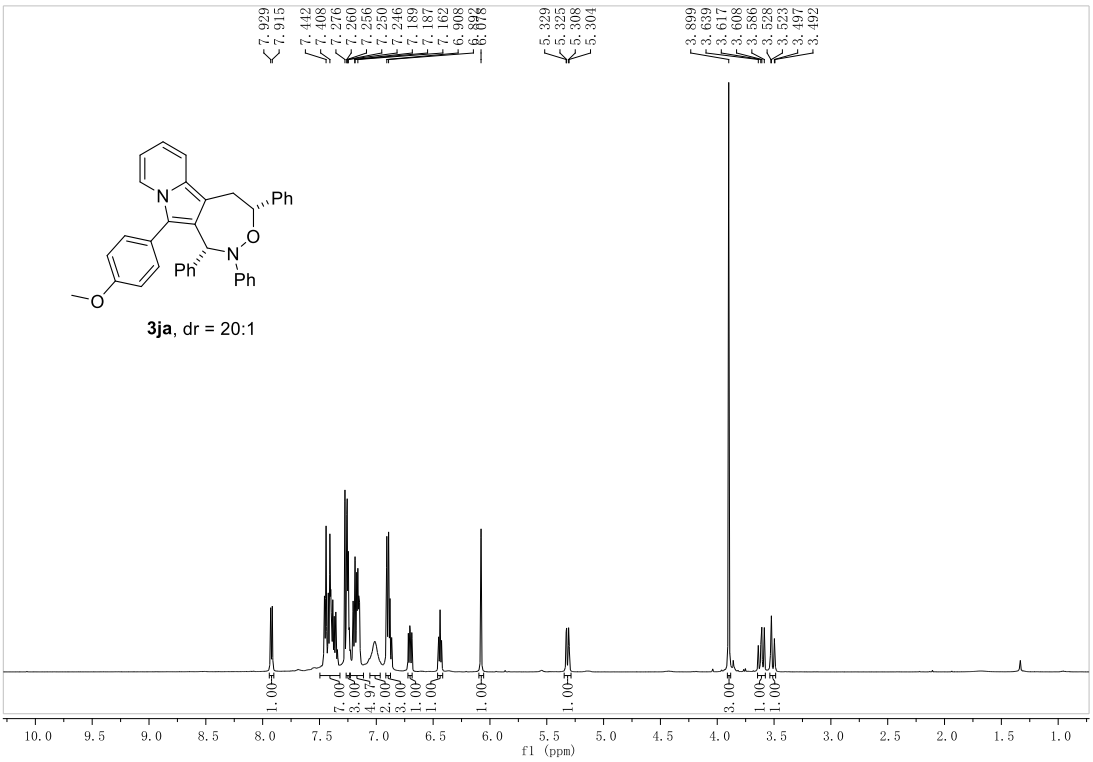
109.16
85.55
77.25
77.00
76.75
66.91
34.82
21.34
Ph
Ph
Ph
N
O
N
3ia, dr = 20:1
f1 (ppm)



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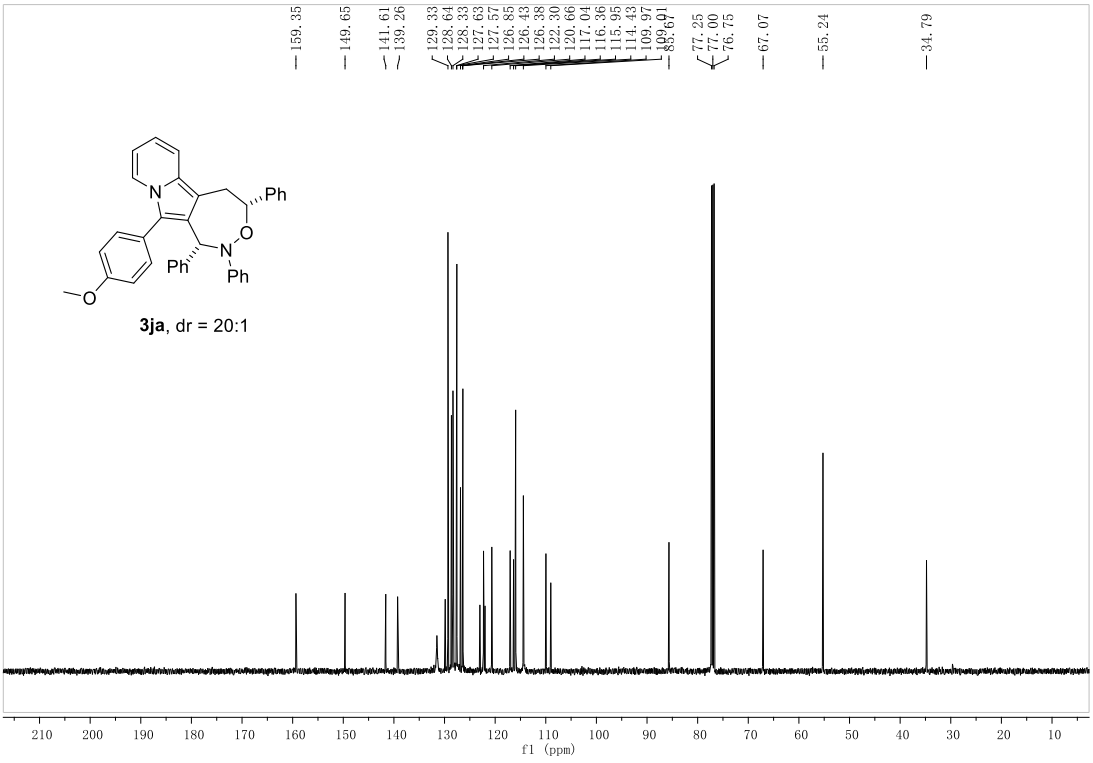
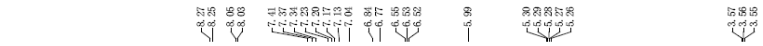
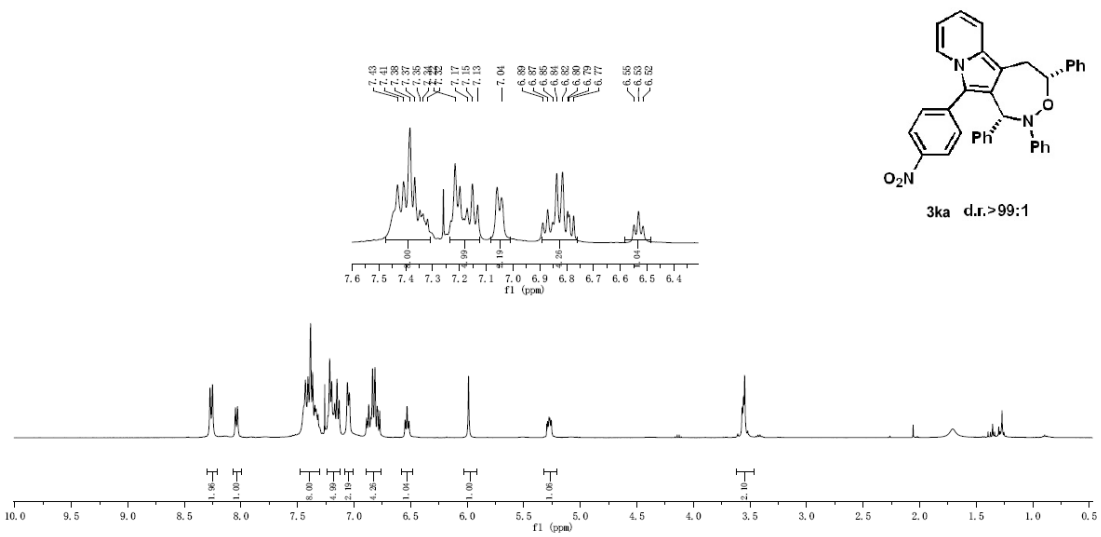
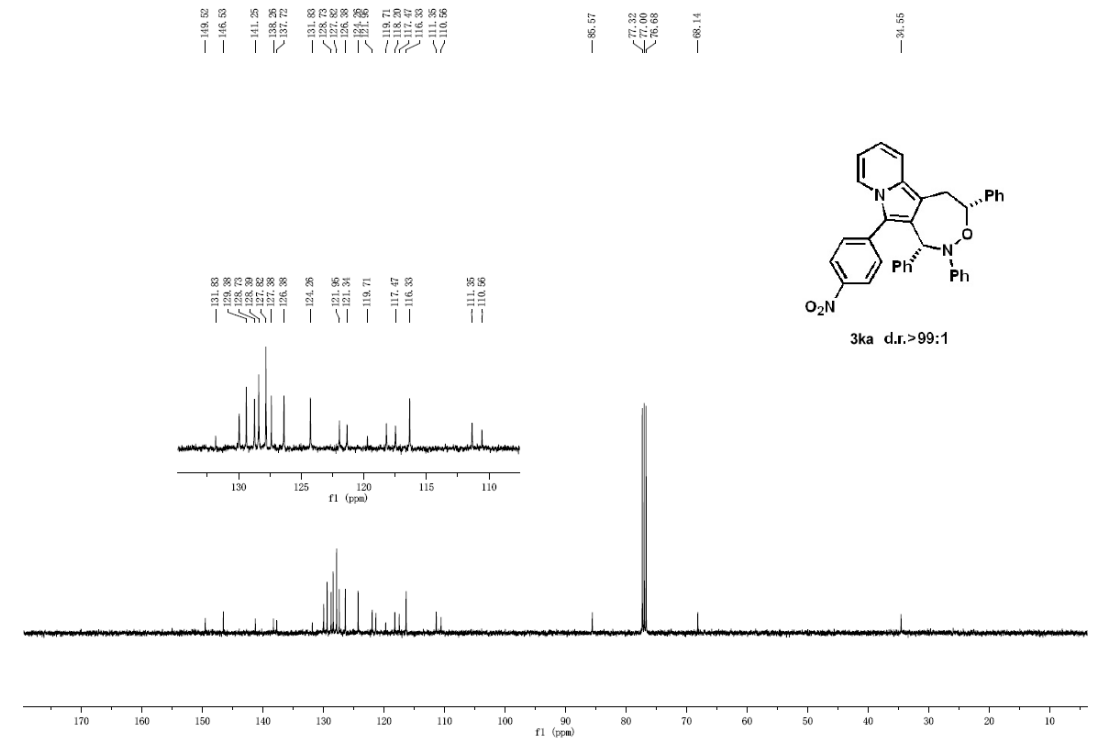


3ja, dr = 20:1

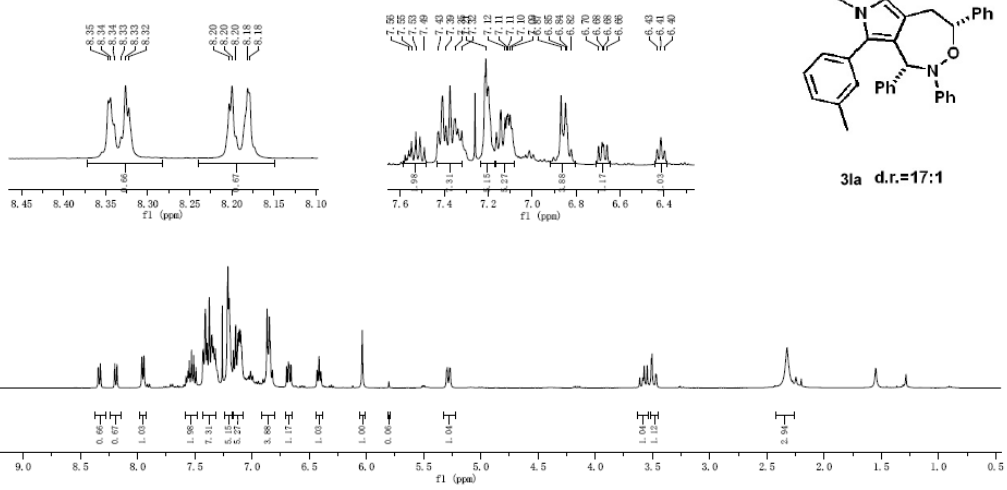




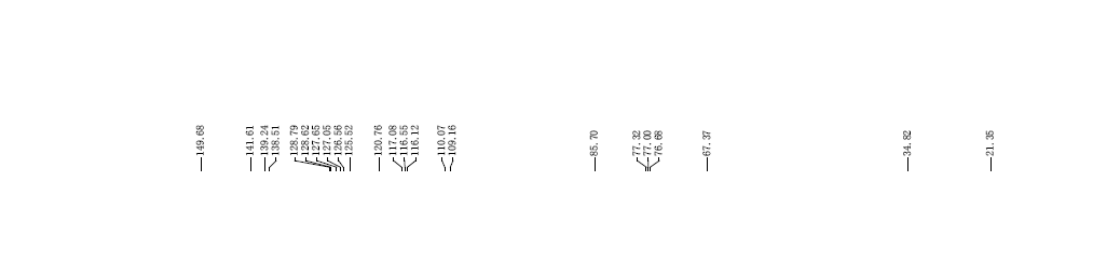
3ka d.r.>99:1

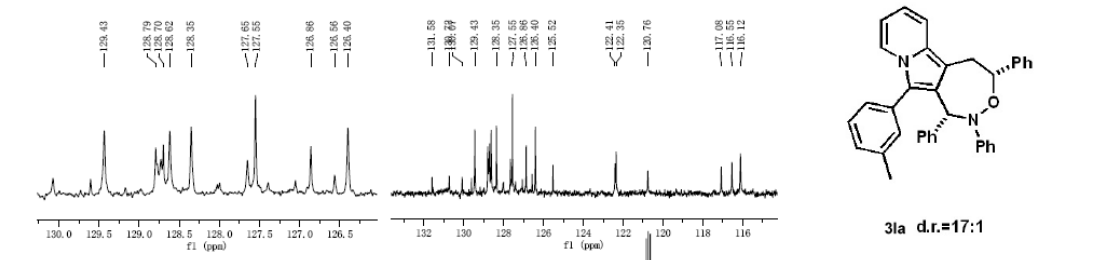


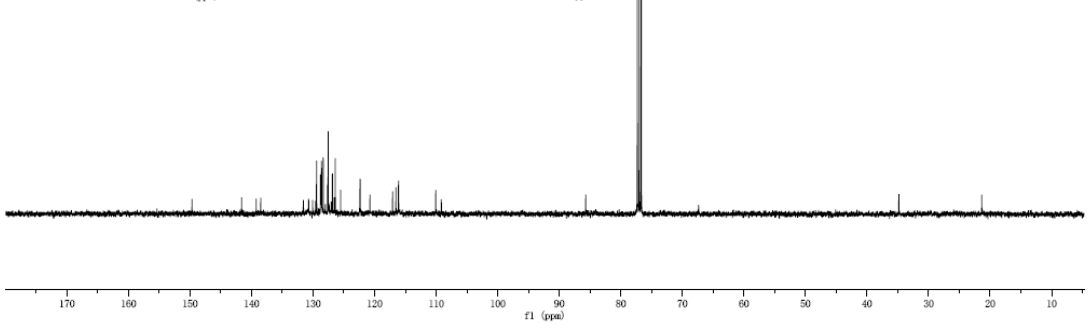
3ka d.r.>99:1



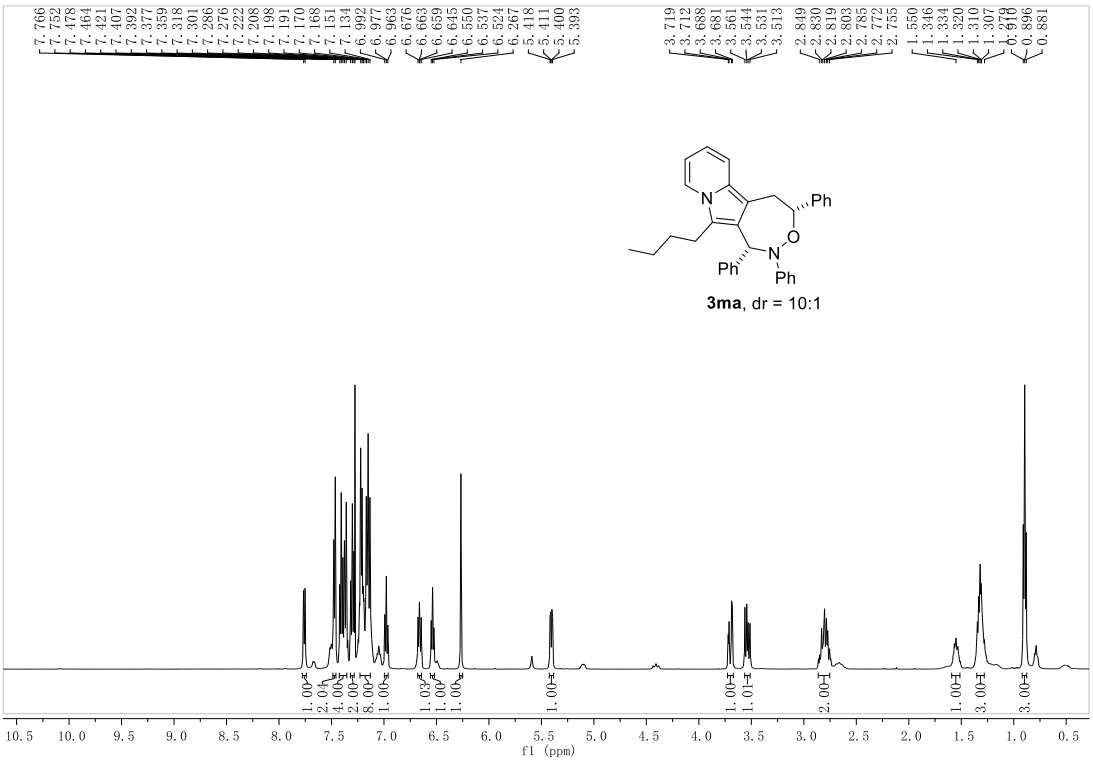
3la d.r.=17:1







3la d.r.=17:1



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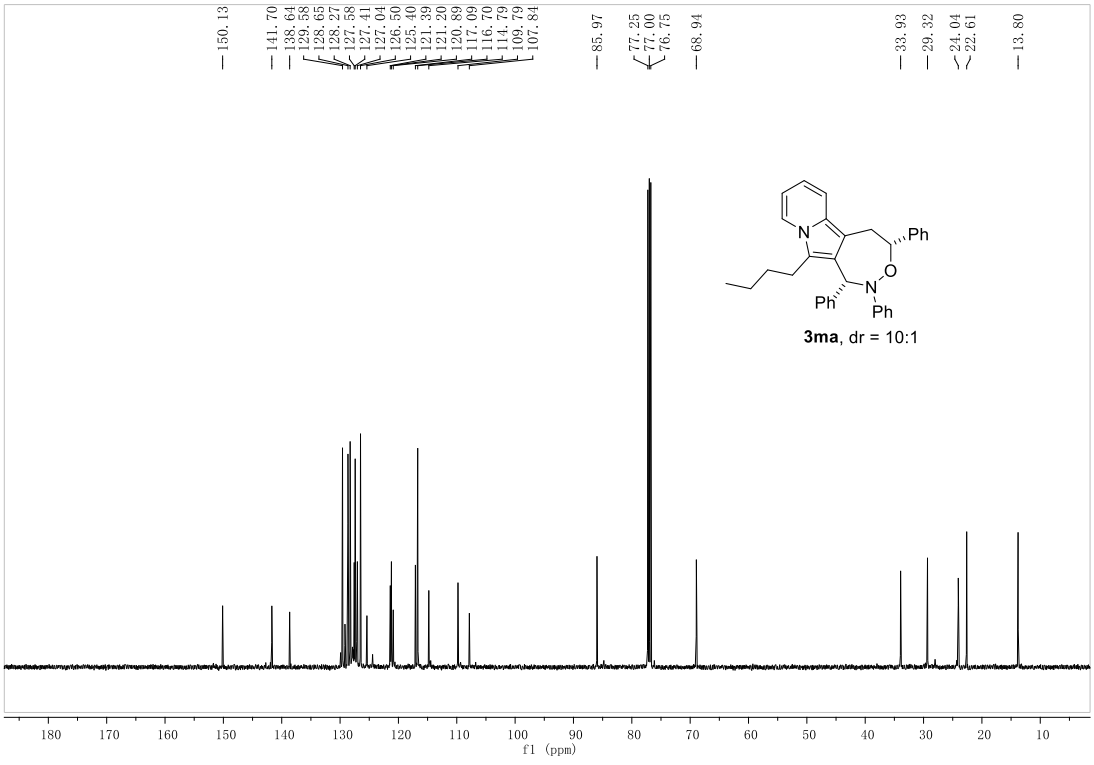
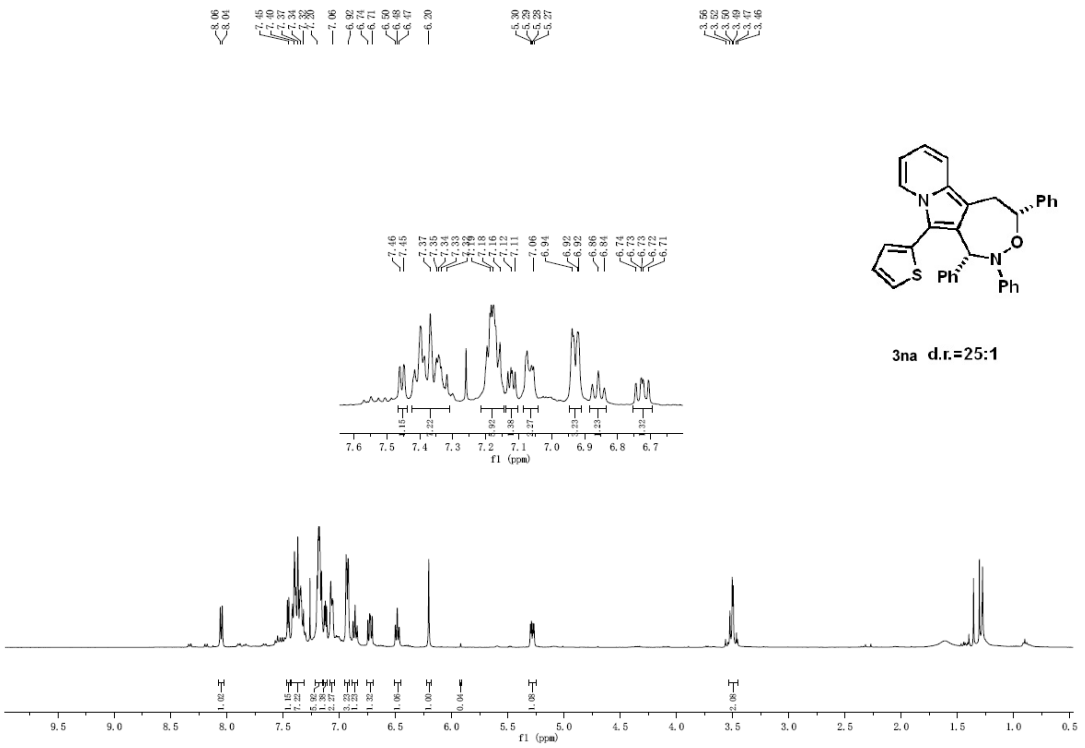


3ma, dr = 10:1



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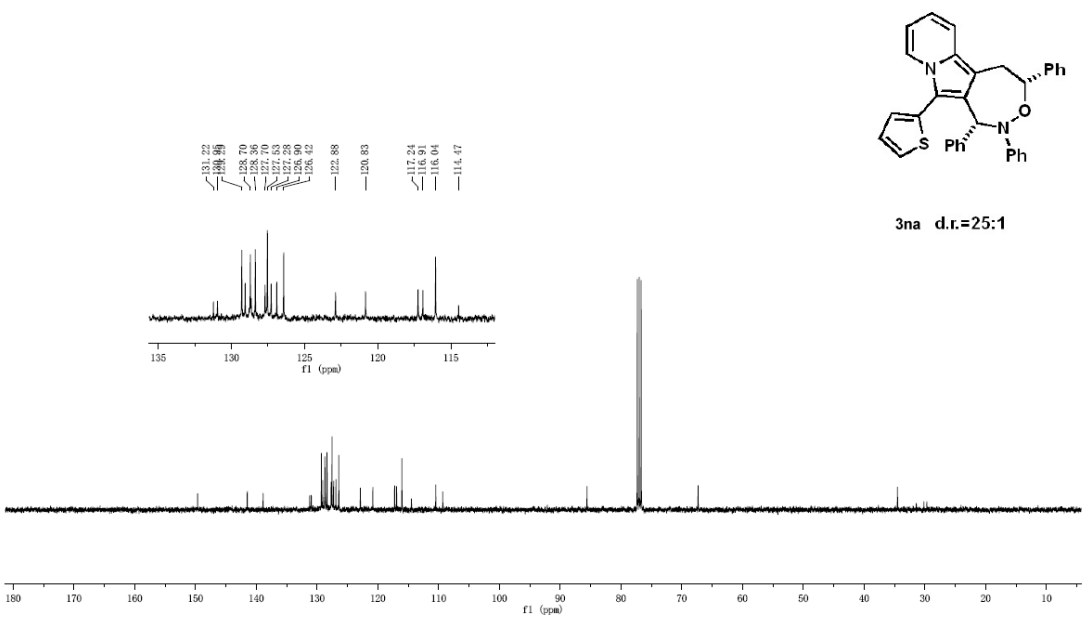

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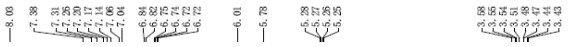

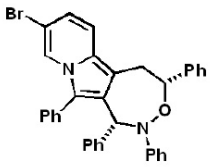

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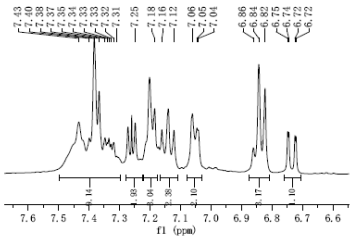

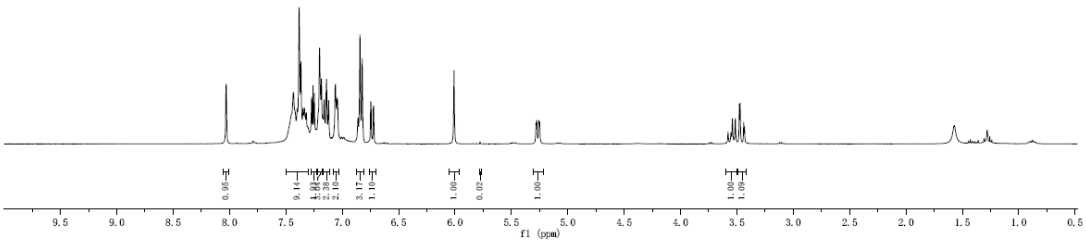

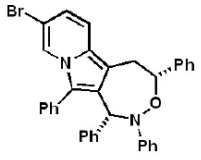

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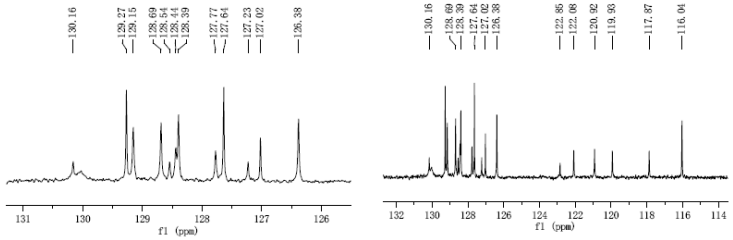
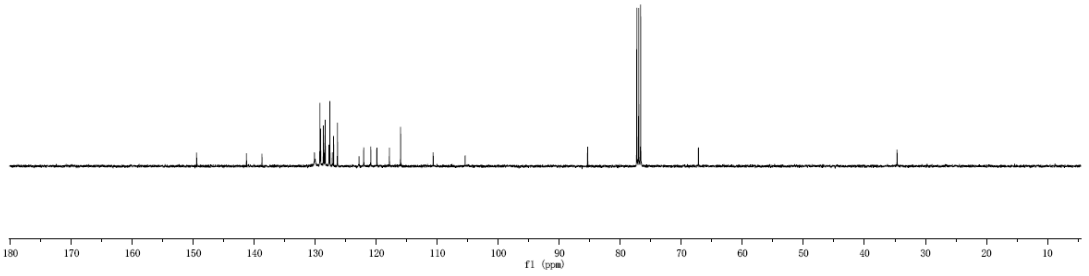
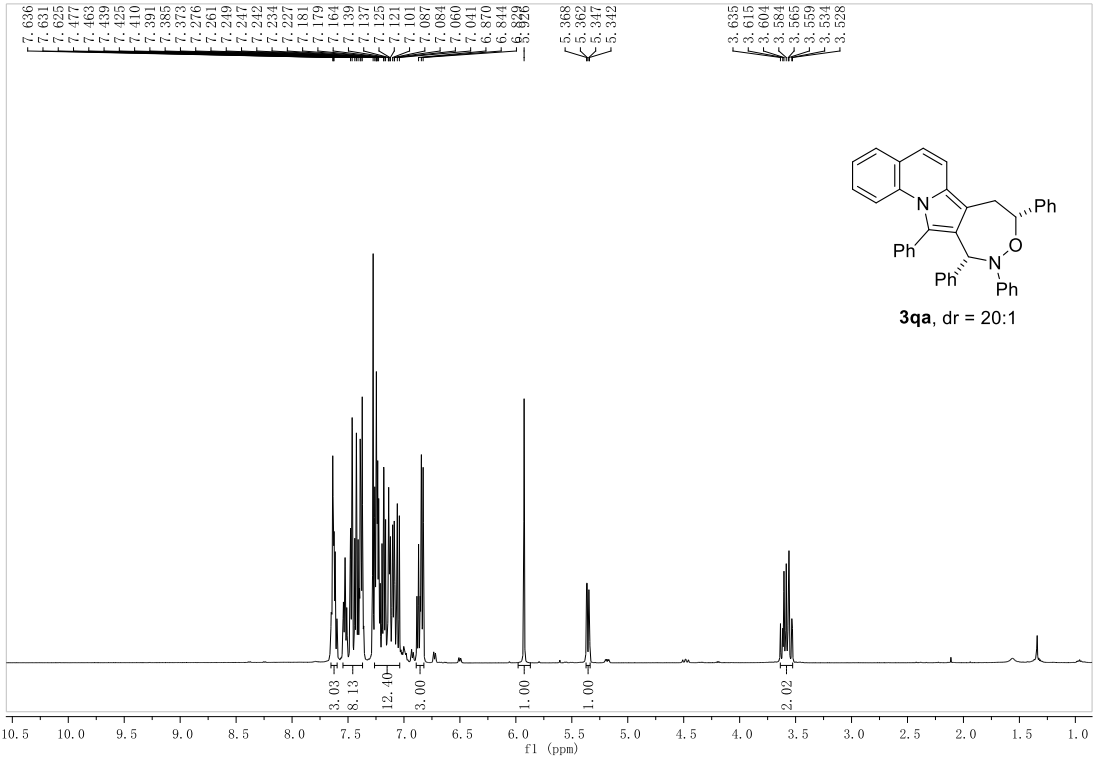
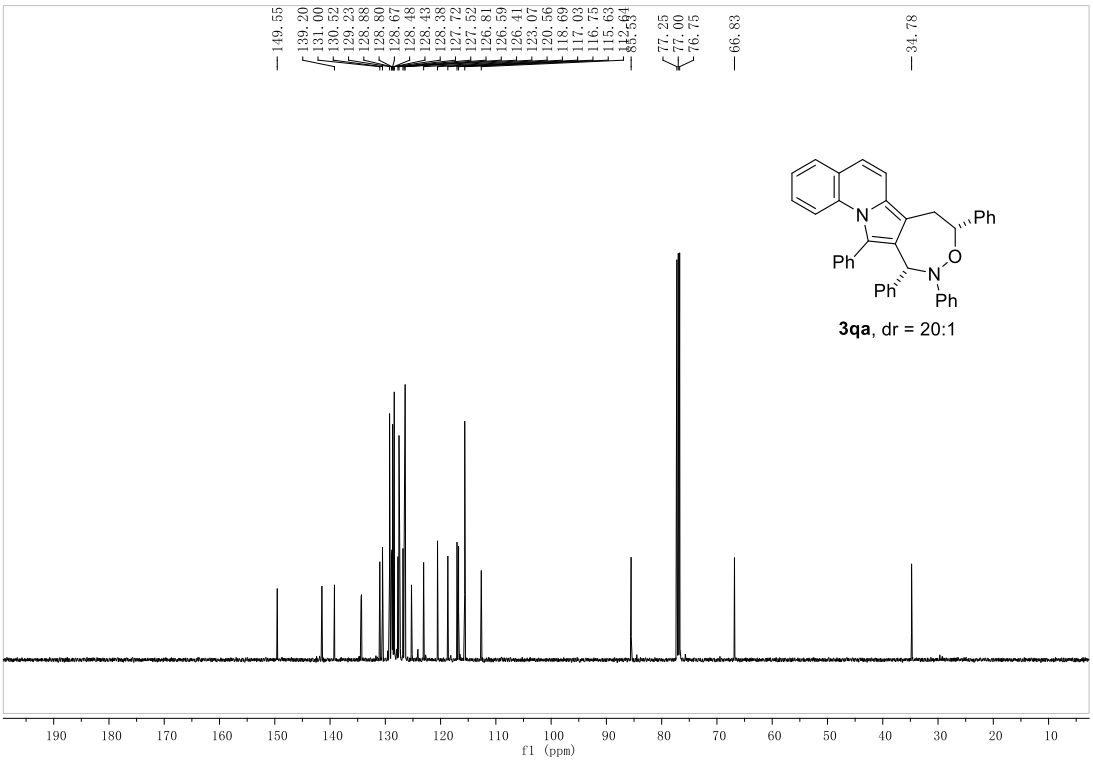






3qa, dr = 20:1



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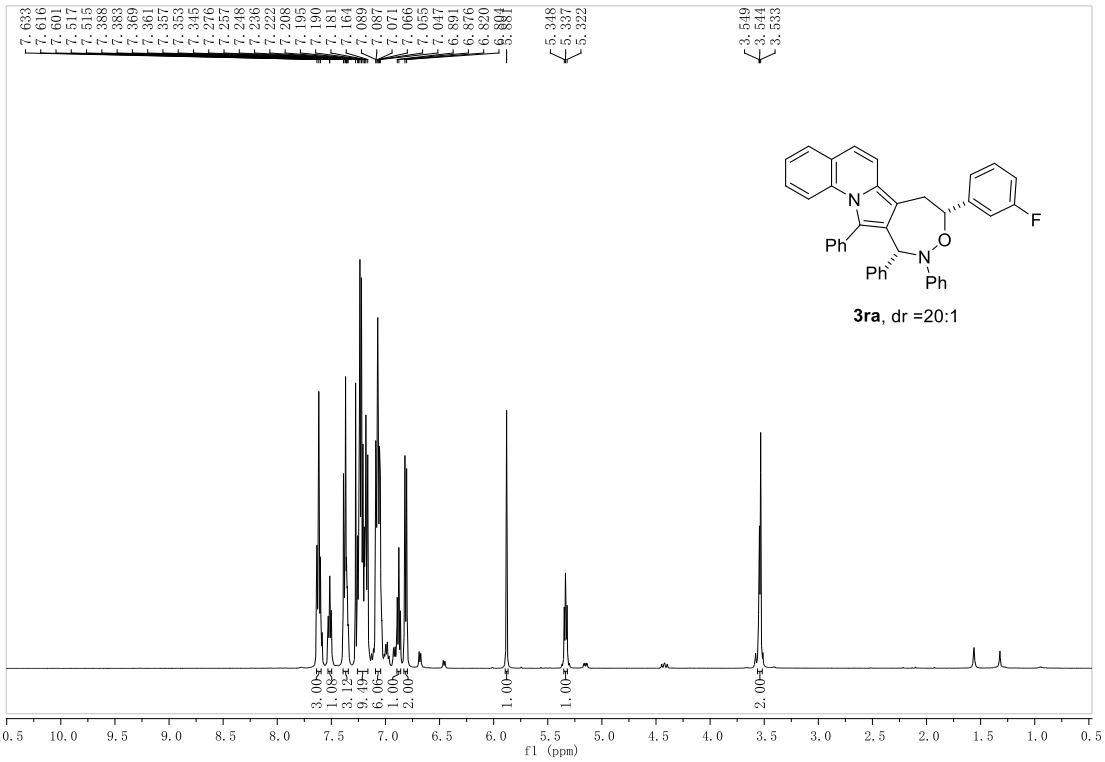

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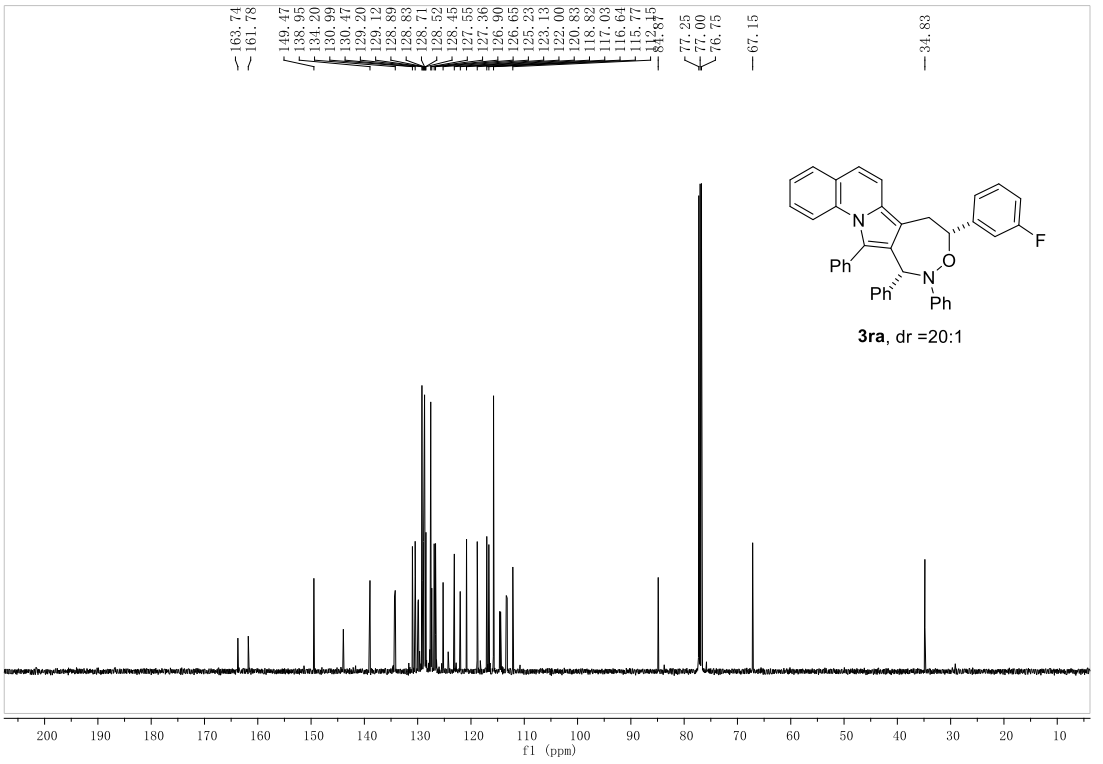

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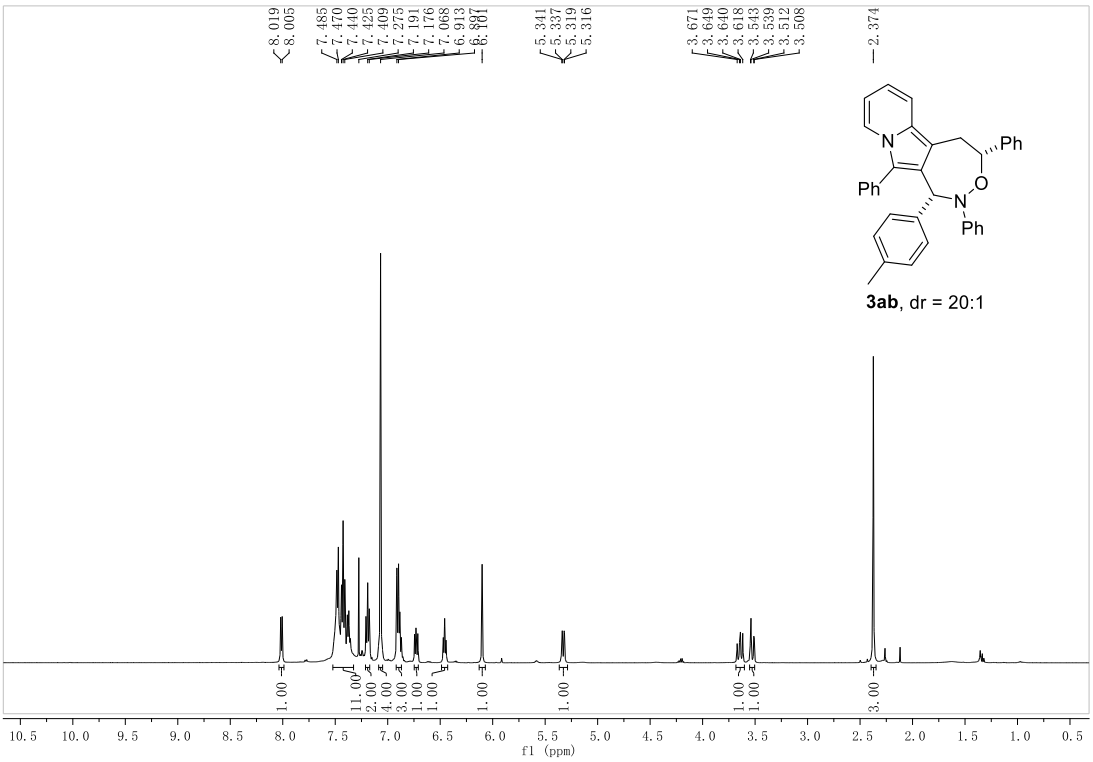
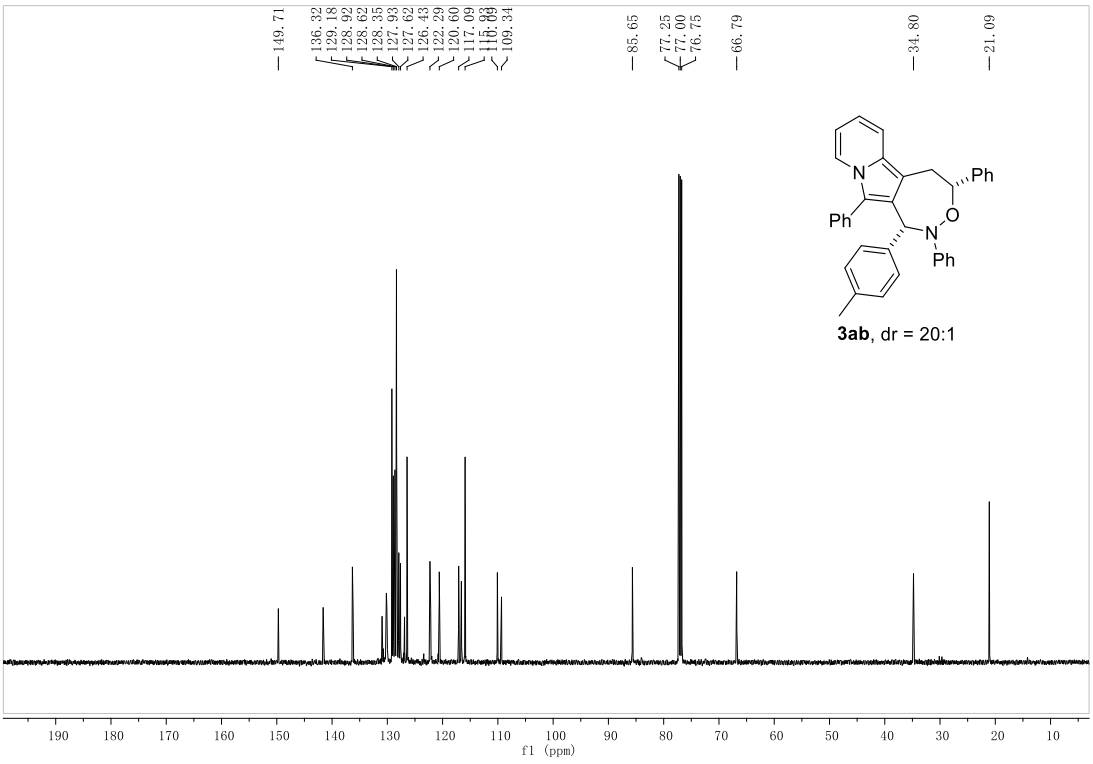


3ab, dr = 20:1



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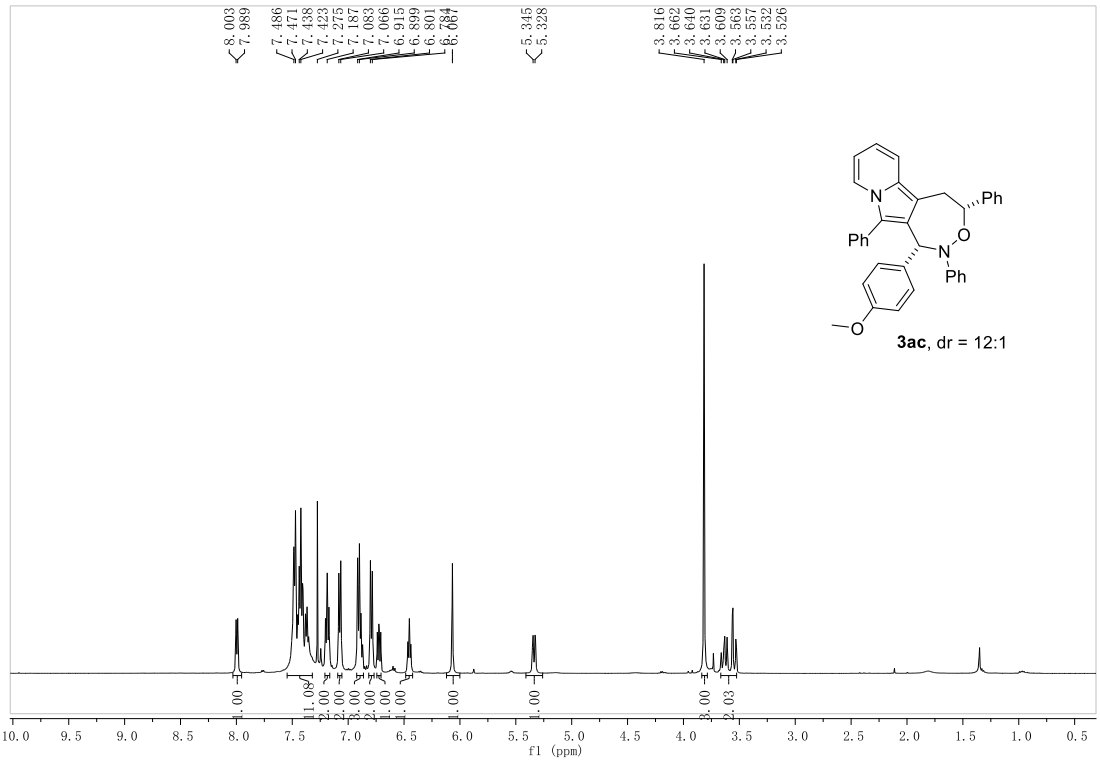
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3.532
3.526
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1.00
1.00
1.00
1.00
3.00
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9.0
8.5
8.0
7.5
7.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
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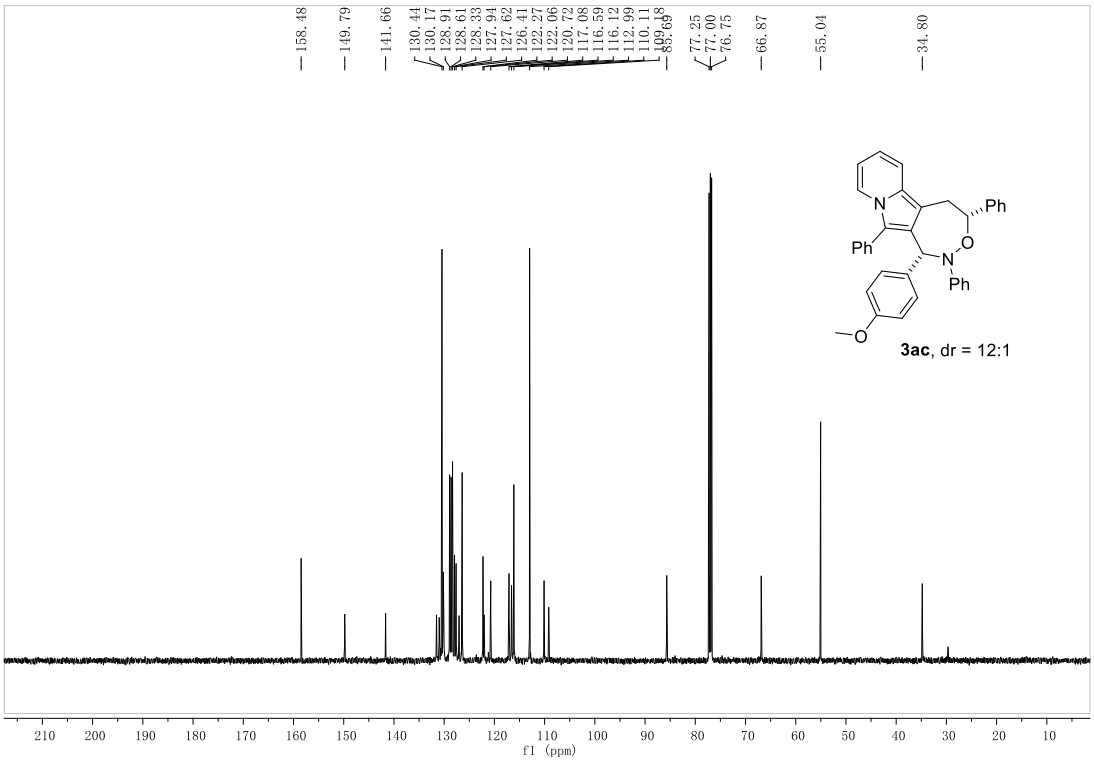
1.0
0.5
f1 (ppm)
Ph
Ph
N
O
N
Ph
O
3ac, dr = 12:1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127.62
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116.12
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110.11
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85.69
77.25
77.00
76.75
66.87
55.04
34.80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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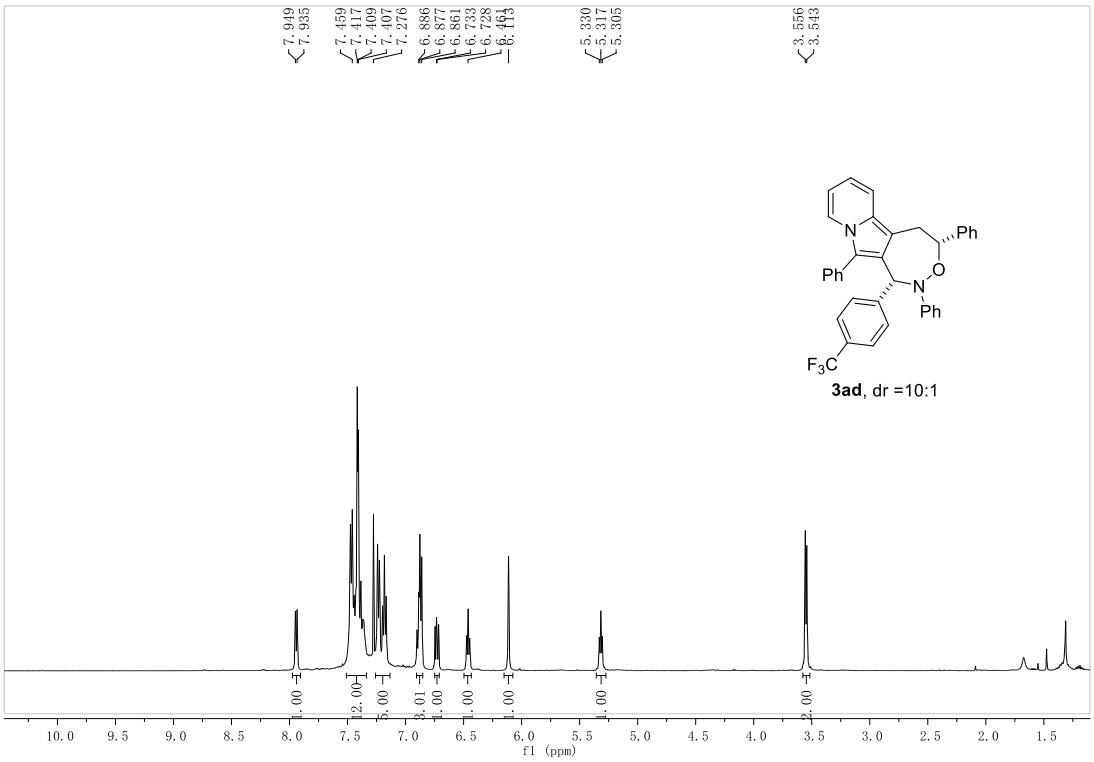
60
50
40
30
20
10
f1 (ppm)
Ph
Ph
N
O
N
Ph
O
3ac, dr = 12:1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5.305
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1.00
1.00
1.00
2.00
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9.0
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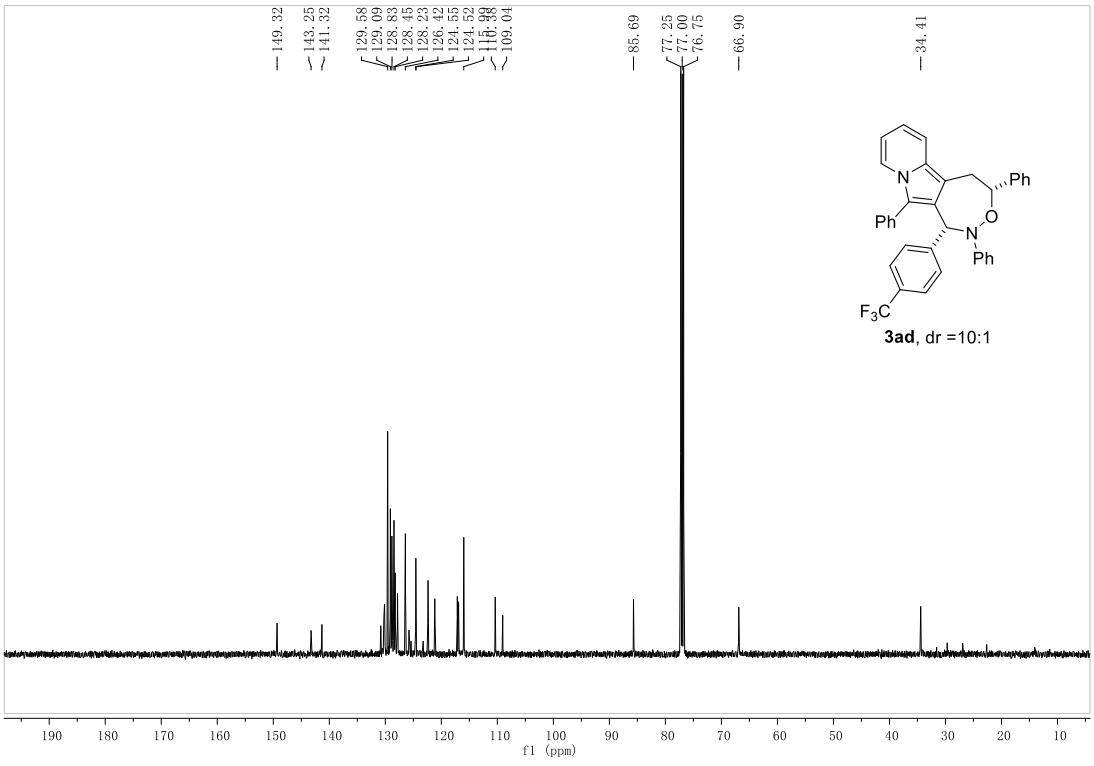
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)
N
Ph
Ph
O
N
Ph
F3C
3ad, dr =10:1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85.69
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77.00
76.75
66.90
34.41
190
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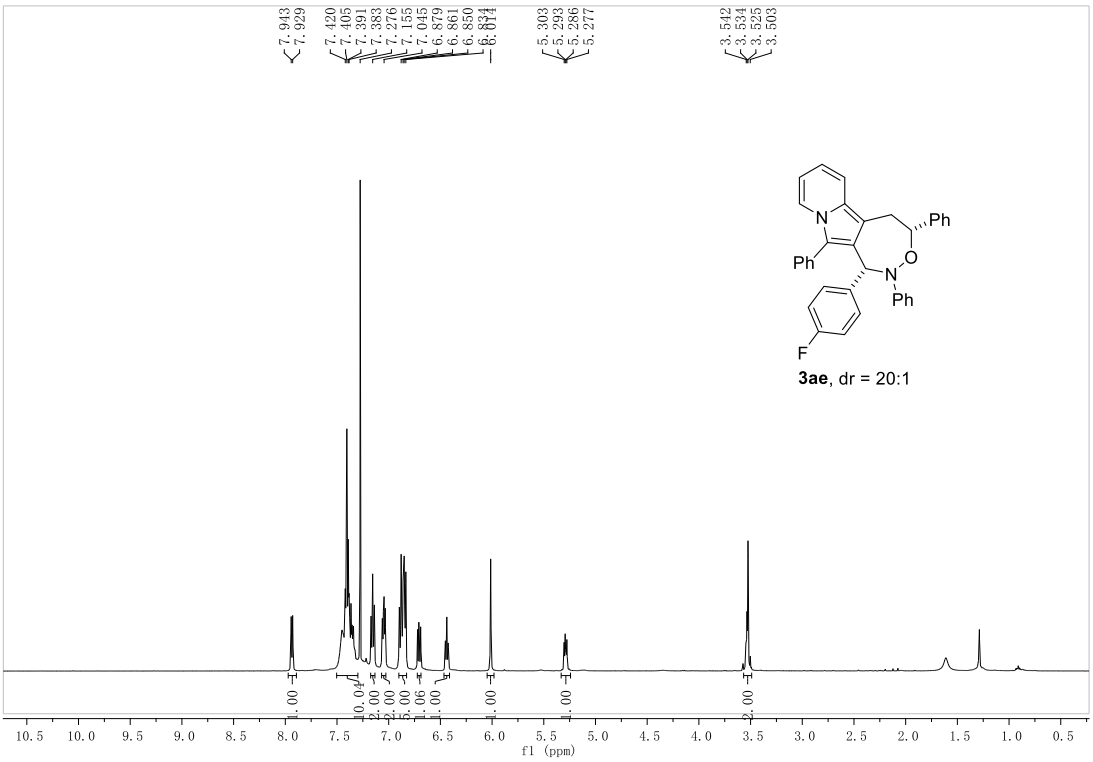
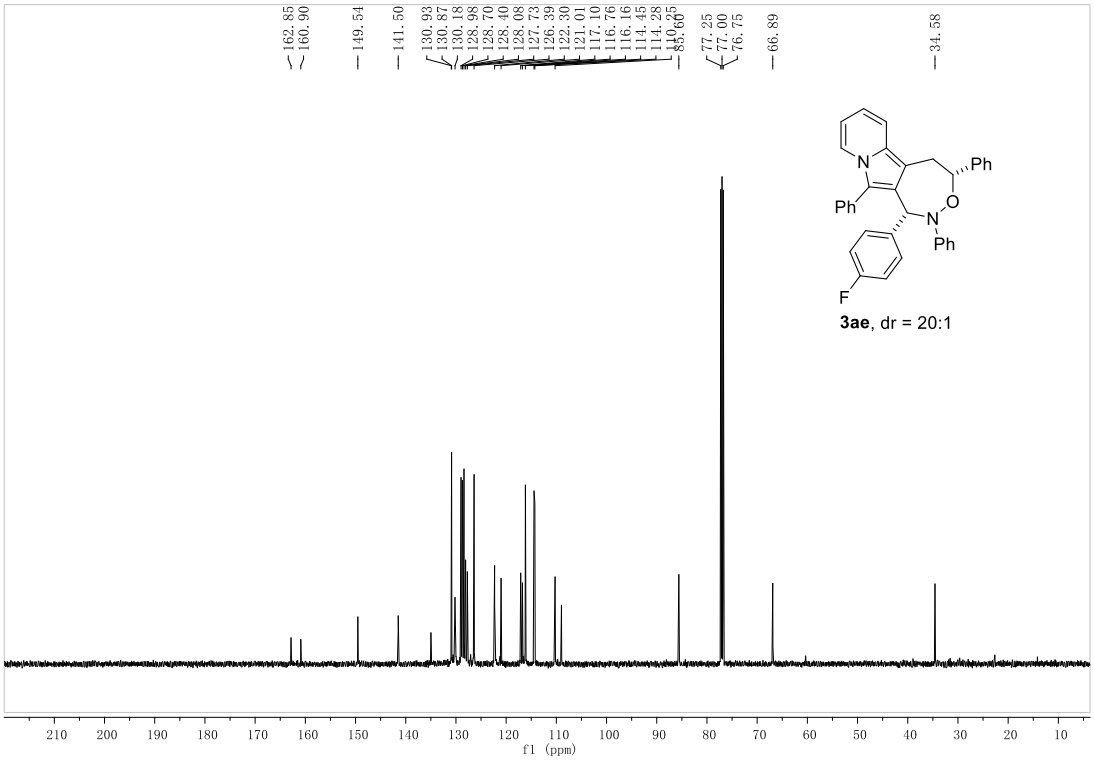
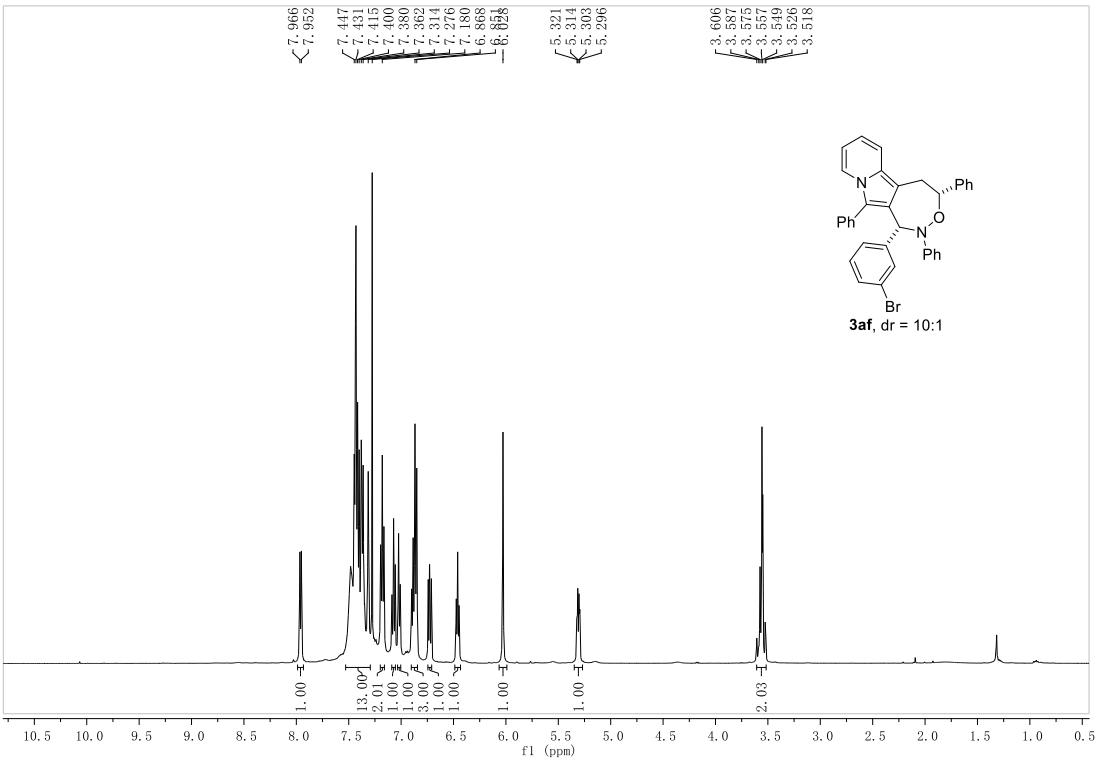
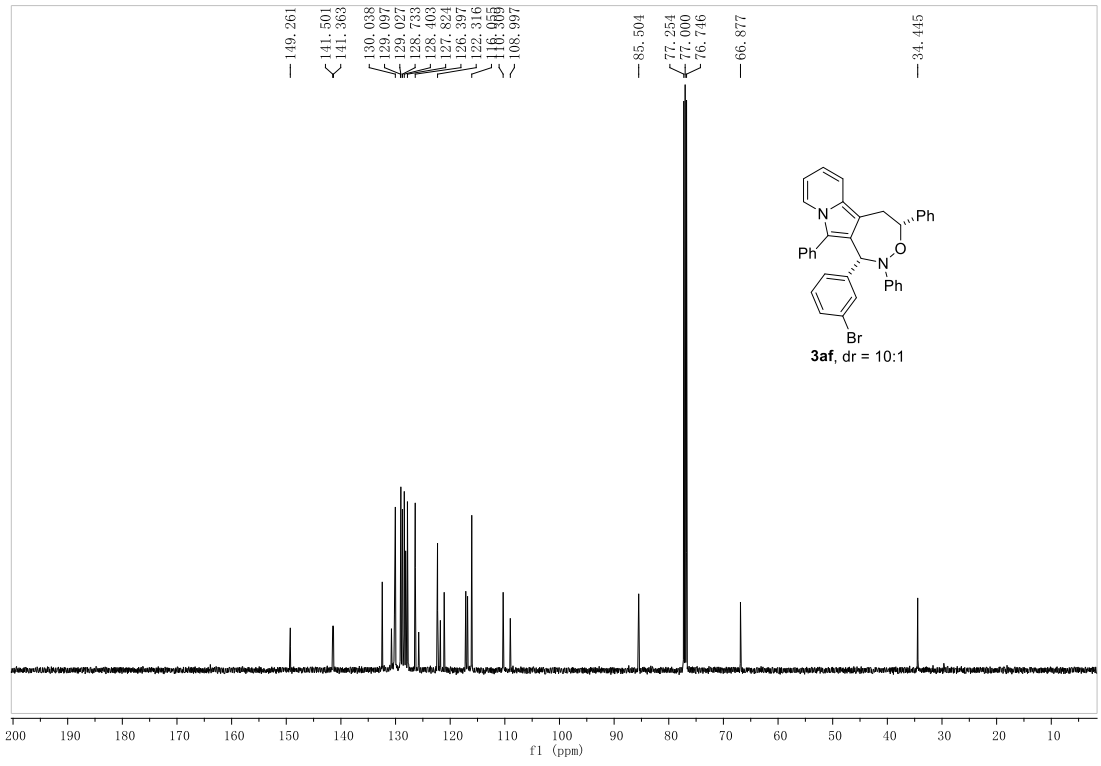
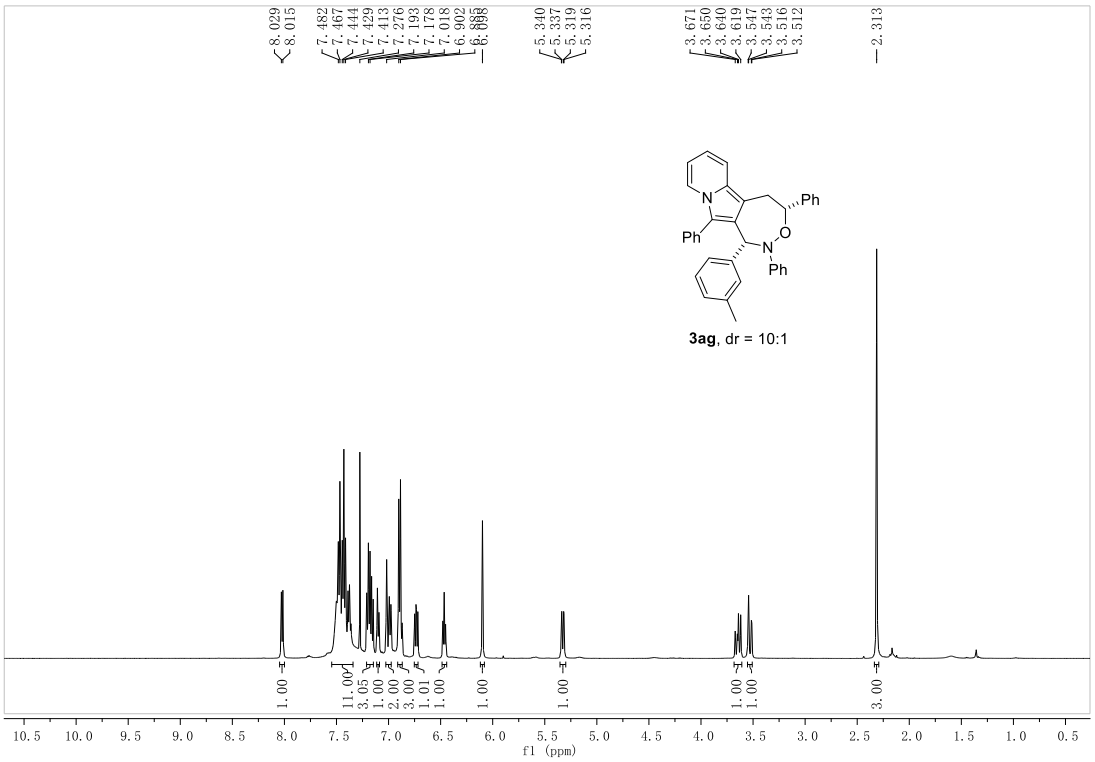
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
N
Ph
Ph
O
N
Ph
F3C
3ad, dr =10:1


7.943
7.929
7.420
7.405
7.391
7.383
7.276
7.155
7.045
6.879
6.861
6.850
6.834
6.814
5.303
5.293
5.286
5.277
3.542
3.534
3.525
3.503
Ph
Ph
N
O
N
Ph
F
3ae, dr = 20:1
f1 (ppm)

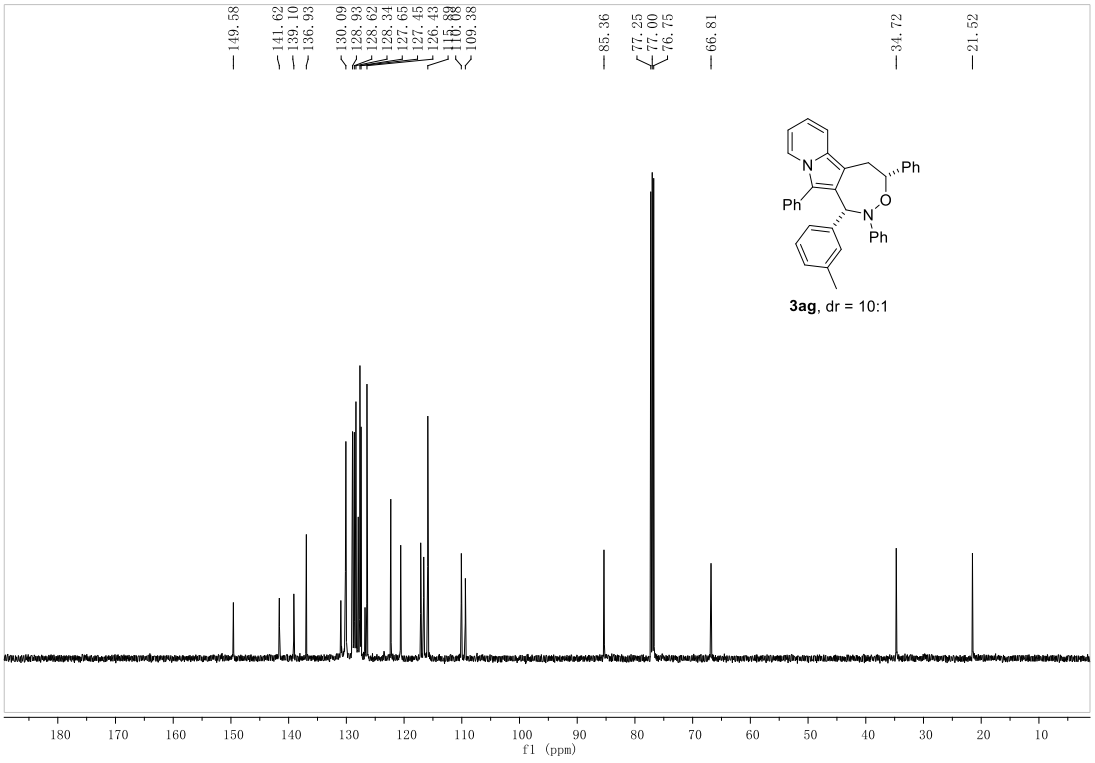

162.85
160.90
149.54
141.50
130.93
130.87
130.18
128.98
128.70
128.40
128.08
127.73
126.39
122.30
121.01
117.10
116.76
116.16
114.45
114.28
110.25
85.60
77.25
77.00
76.75
66.89
34.58
Ph
Ph
N
O
N
Ph
F
3ae, dr = 20:1
f1 (ppm)


7.966
7.952
7.447
7.431
7.415
7.400
7.380
7.362
7.314
7.276
7.180
6.868
5.321
5.314
5.303
5.296
3.606
3.587
3.575
3.557
3.549
3.526
3.518
Ph
Ph
N
O
N
Ph
Br
3af, dr = 10:1
1.00
13.00
2.01
1.00
1.00
3.00
1.00
1.00
1.00
1.00
2.03
f1 (ppm)

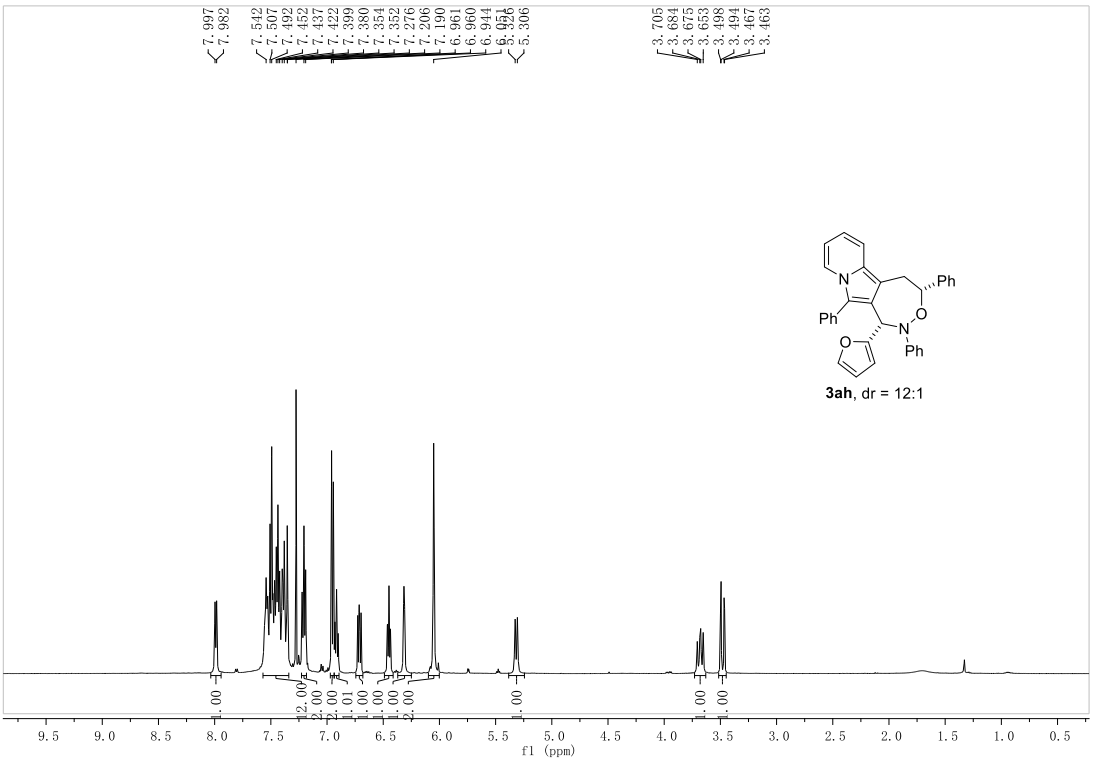

149.261
141.501
141.363
130.038
129.097
129.027
128.733
128.403
127.824
126.397
122.316
108.997
85.504
77.254
77.000
76.746
66.877
34.445
Ph
Ph
N
O
N
Ph
Br
3af, dr = 10:1
f1 (ppm)

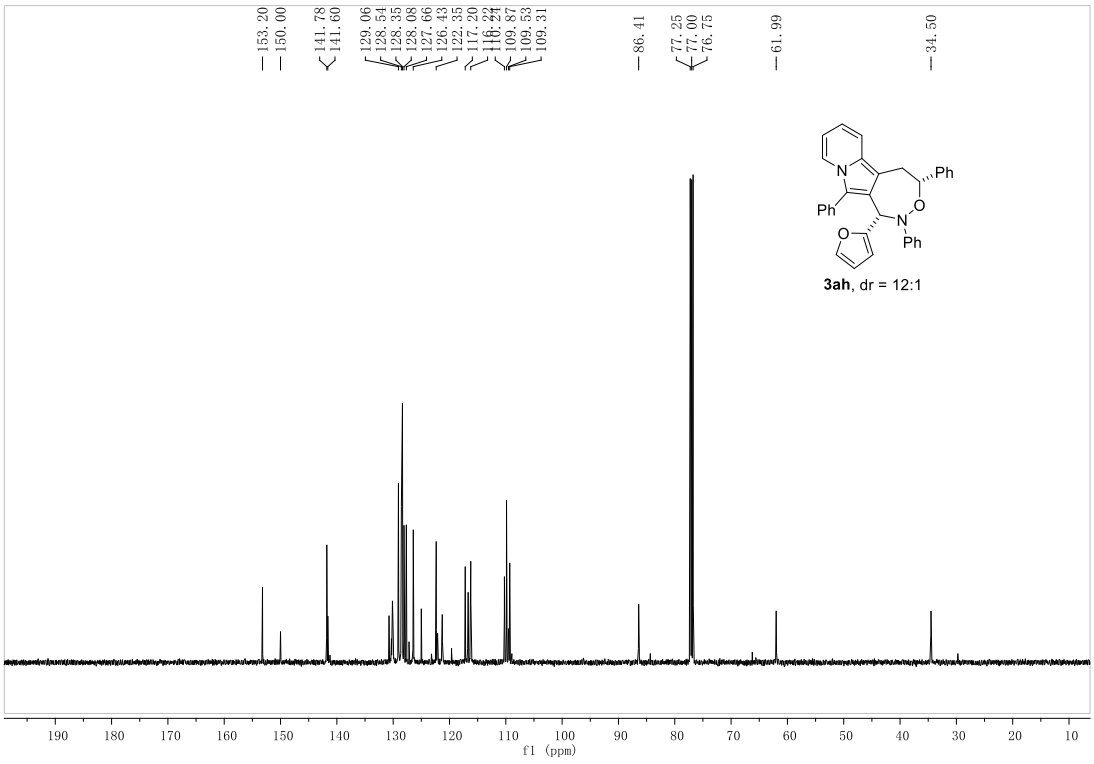


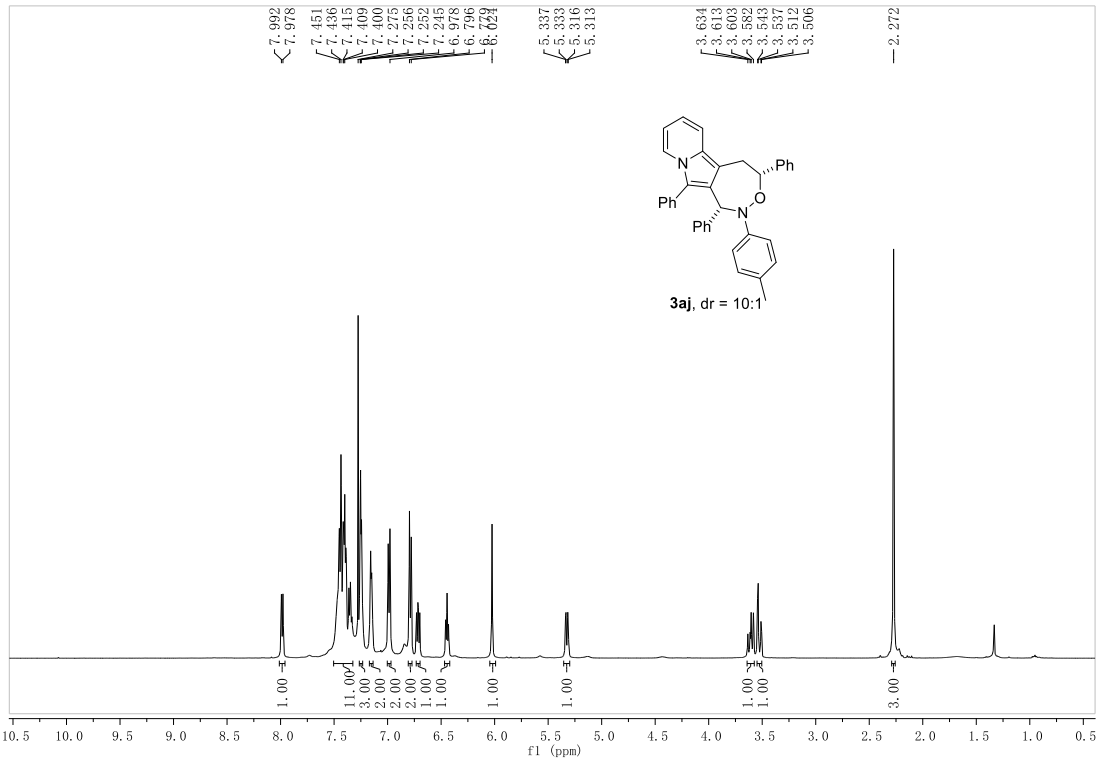
3ag, dr = 10:1

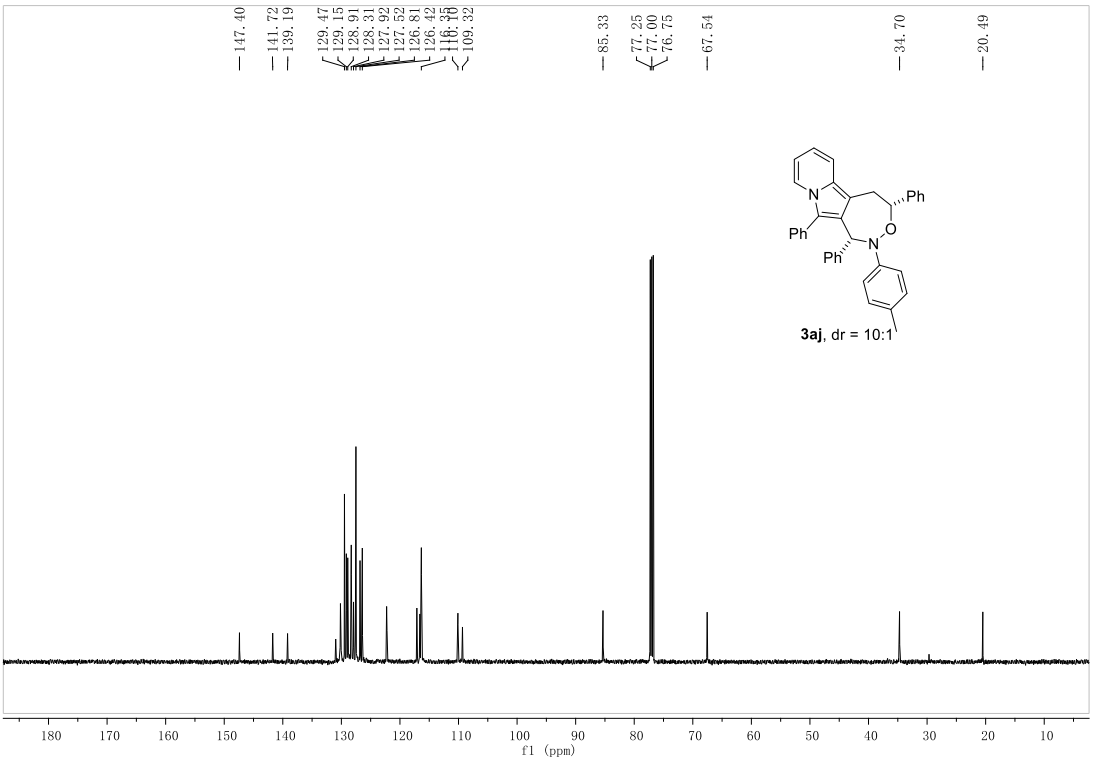


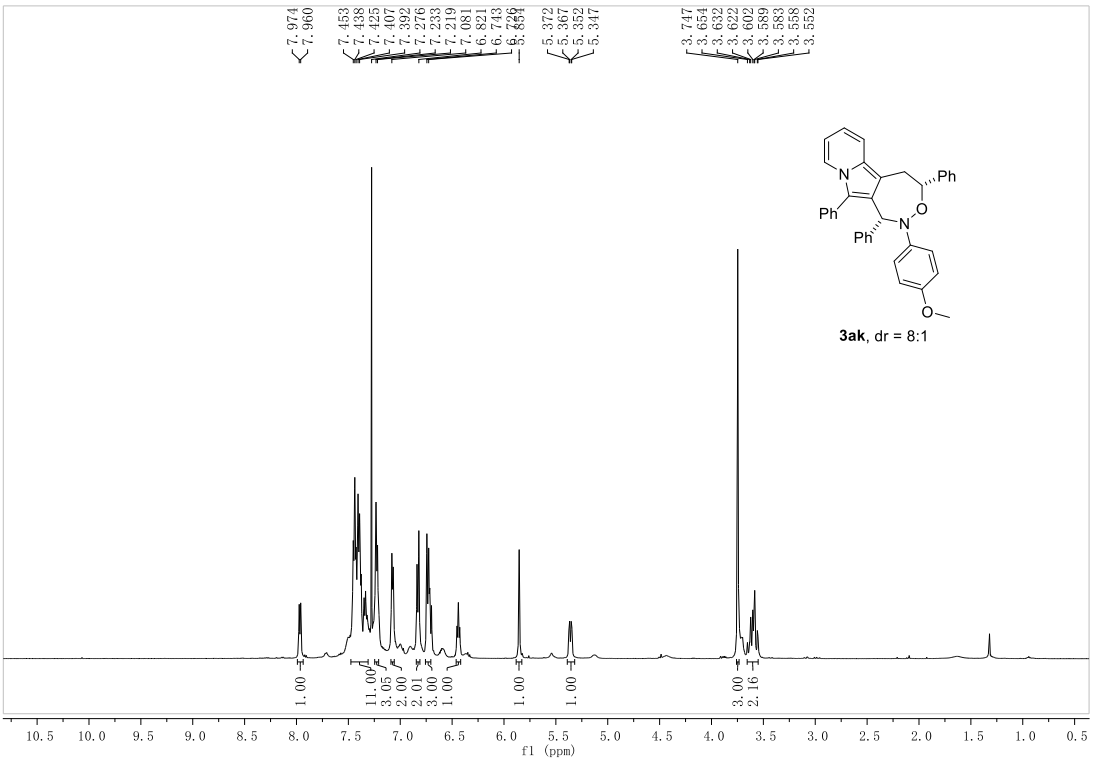
3ag, dr = 10:1

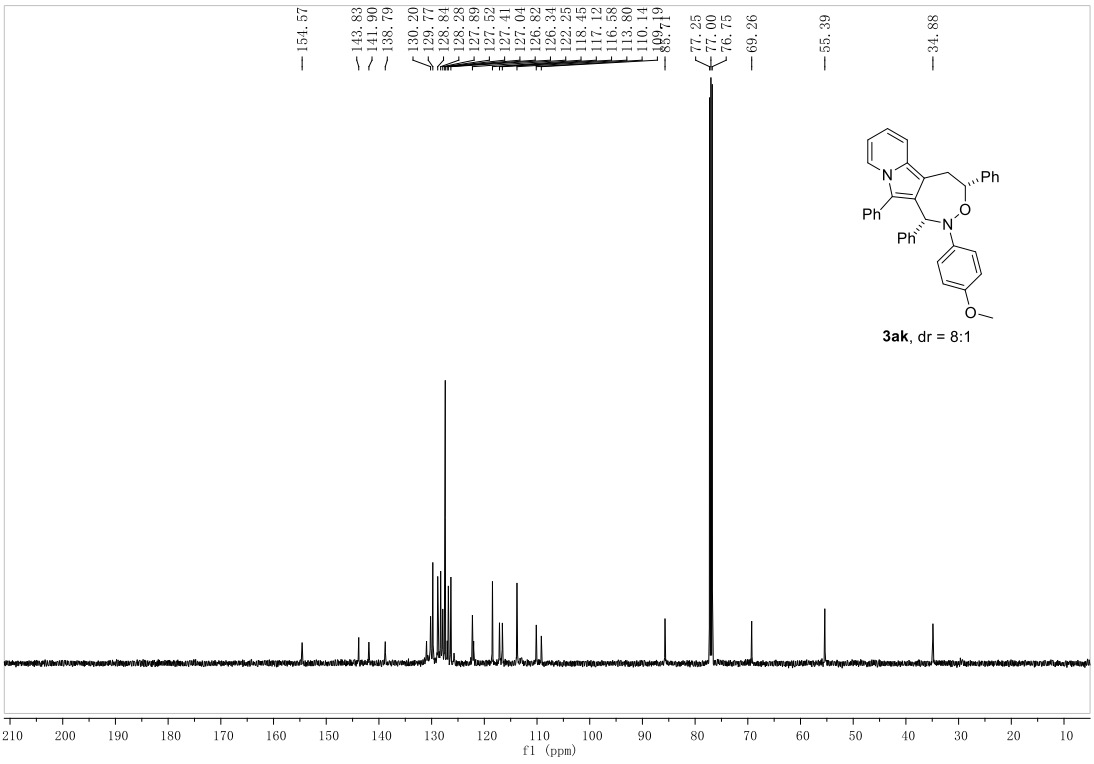

7.997
7.982
7.542
7.507
7.492
7.452
7.437
7.422
7.399
7.380
7.354
7.352
7.276
7.206
7.190
6.961
6.960
6.944
6.941
5.326
5.306
3.705
3.684
3.675
3.653
3.498
3.494
3.467
3.463
Ph
Ph
O
N
O
N
Ph
3ah, dr = 12:1
1.00
12.00
2.00
2.00
1.01
1.00
1.00
2.00
1.00
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

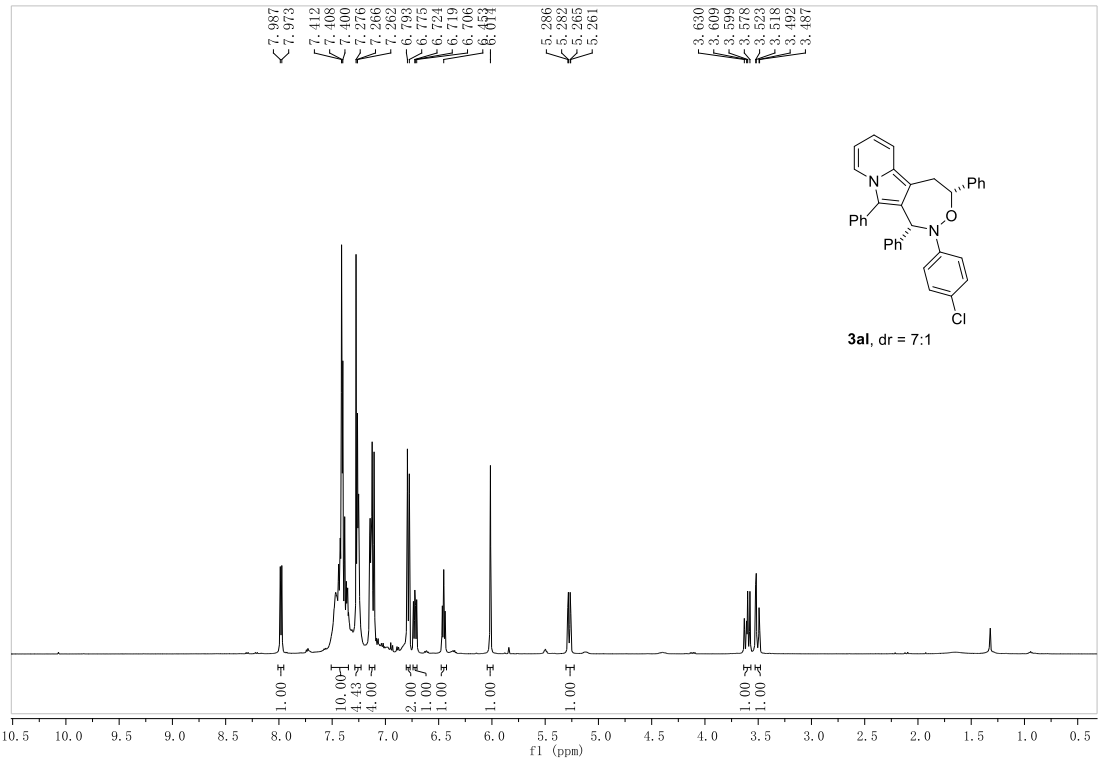

153.20
150.00
141.78
141.60
129.06
128.54
128.35
128.08
127.66
126.43
122.35
117.20
116.22
116.21
109.87
109.53
109.31
86.41
77.25
77.00
76.75
61.99
34.50
Ph
Ph
O
N
O
N
Ph
3ah, dr = 12:1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.992
7.978
7.451
7.436
7.415
7.409
7.400
7.275
7.256
7.252
7.245
6.978
6.796
6.779
6.024
5.337
5.333
5.316
5.313
3.634
3.613
3.603
3.582
3.543
3.537
3.512
3.506
2.272
Ph
Ph
Ph
N
O
N
3aj, dr = 10:1
1.00
11.00
3.00
2.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

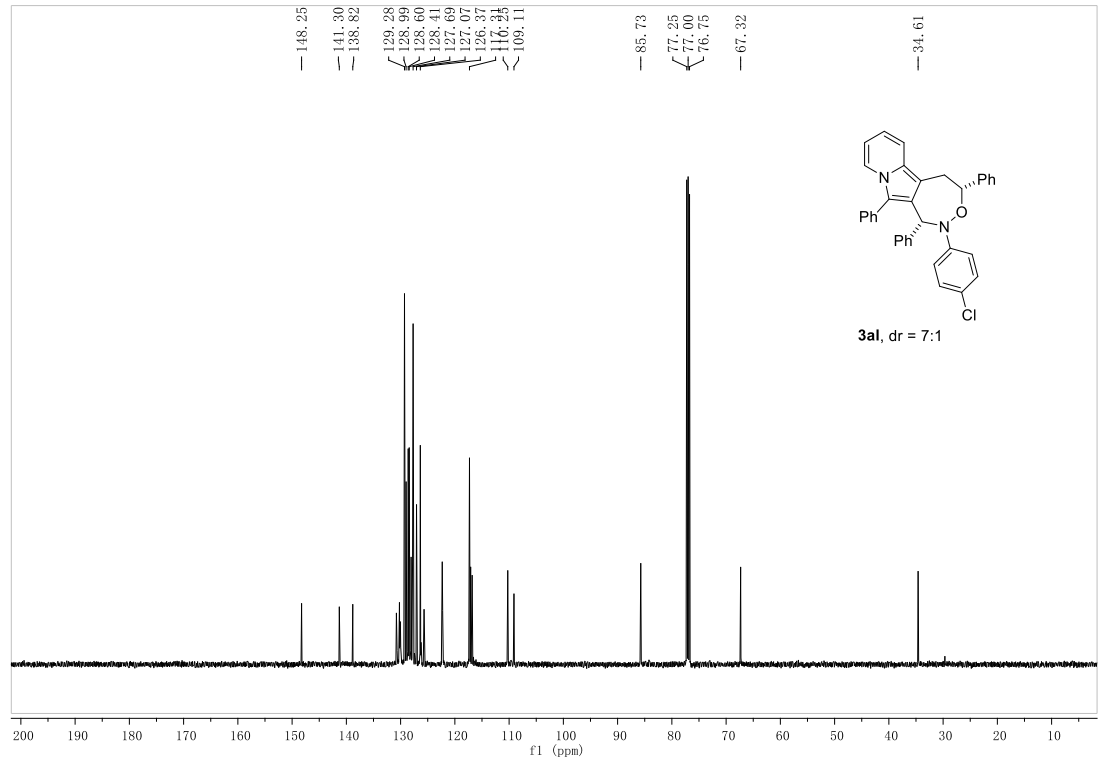

147.40
141.72
139.19
129.47
129.15
128.91
128.31
127.92
127.52
126.81
126.42
116.35
116.10
109.32
85.33
77.25
77.00
76.75
67.54
34.70
20.49
Ph
Ph
Ph
N
O
N
3aj, dr = 10:1
f1 (ppm)


7.974
7.960
7.453
7.438
7.425
7.407
7.392
7.276
7.233
7.219
7.081
6.821
6.743
5.372
5.367
5.352
5.347
3.747
3.654
3.632
3.622
3.602
3.589
3.583
3.558
3.552
1.00
11.00
3.05
2.00
2.01
3.00
1.00
1.00
1.00
3.00
2.16
Ph
Ph
Ph
N
O
N
O
3ak, dr = 8:1
f1 (ppm)

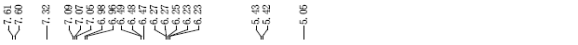

154.57
143.83
141.90
138.79
130.20
129.77
128.84
128.28
127.89
127.52
127.41
127.04
126.82
126.34
122.25
118.45
117.12
116.58
113.80
110.14
109.19
85.71
77.25
77.00
76.75
69.26
55.39
34.88
Ph
Ph
Ph
N
O
N
O
3ak, dr = 8:1
f1 (ppm)

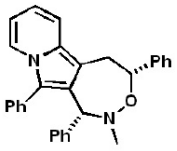


3al, dr = 7:1

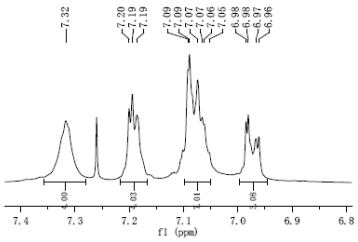


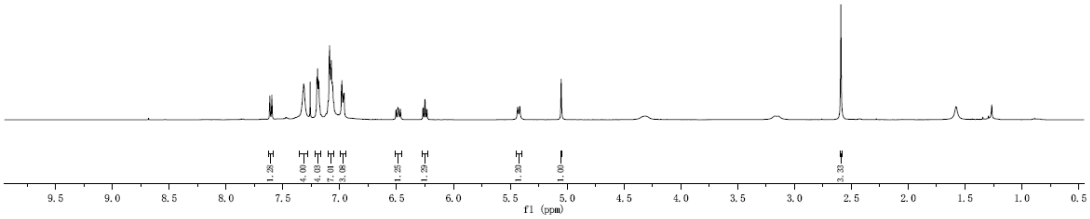
3al, dr = 7:1

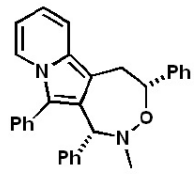




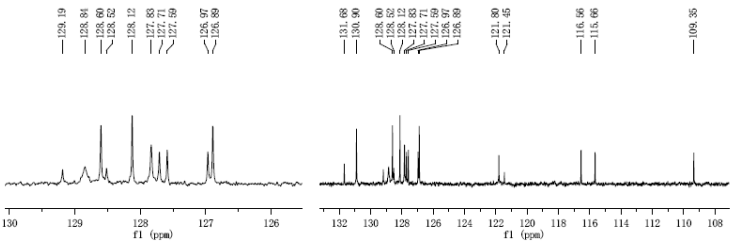
3am d.r.>99:1

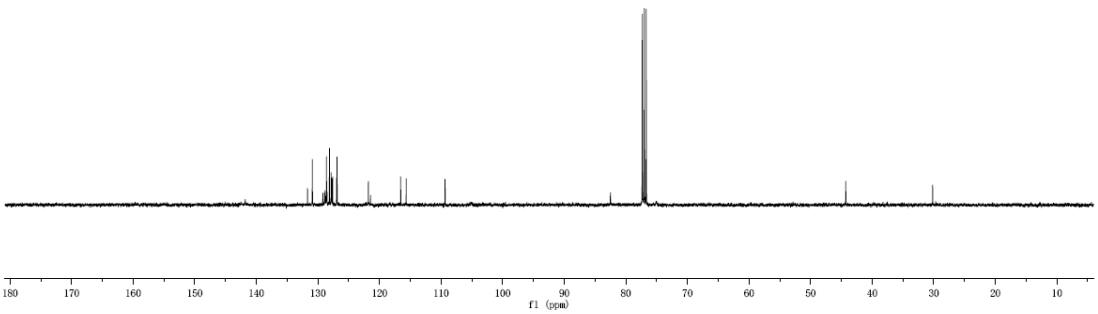


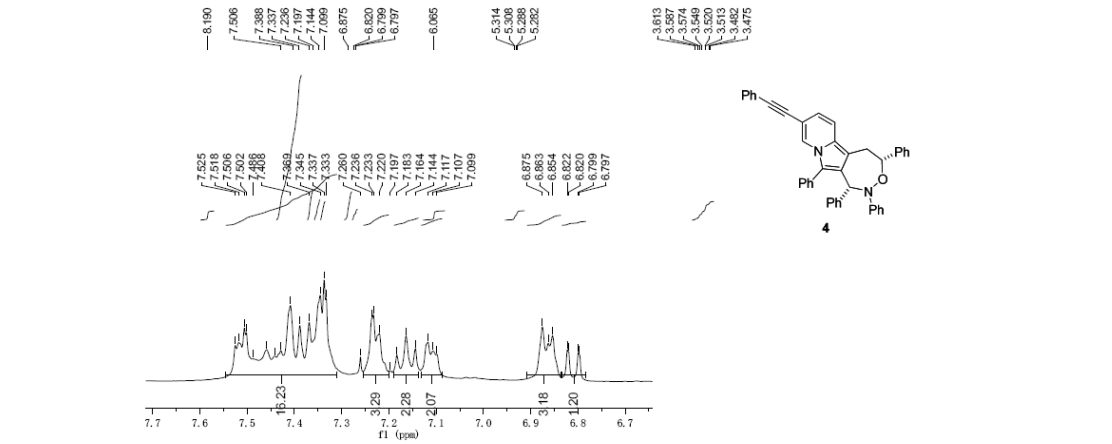


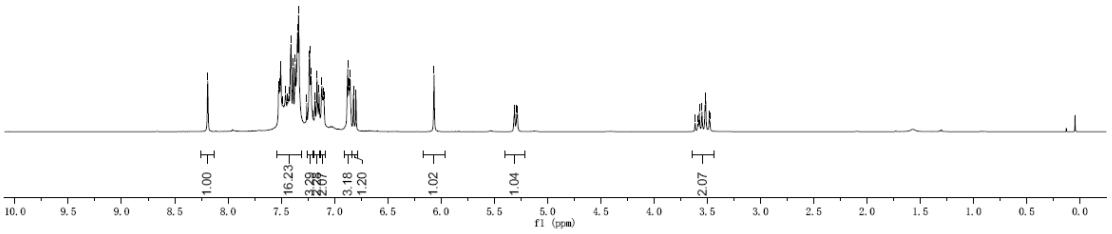


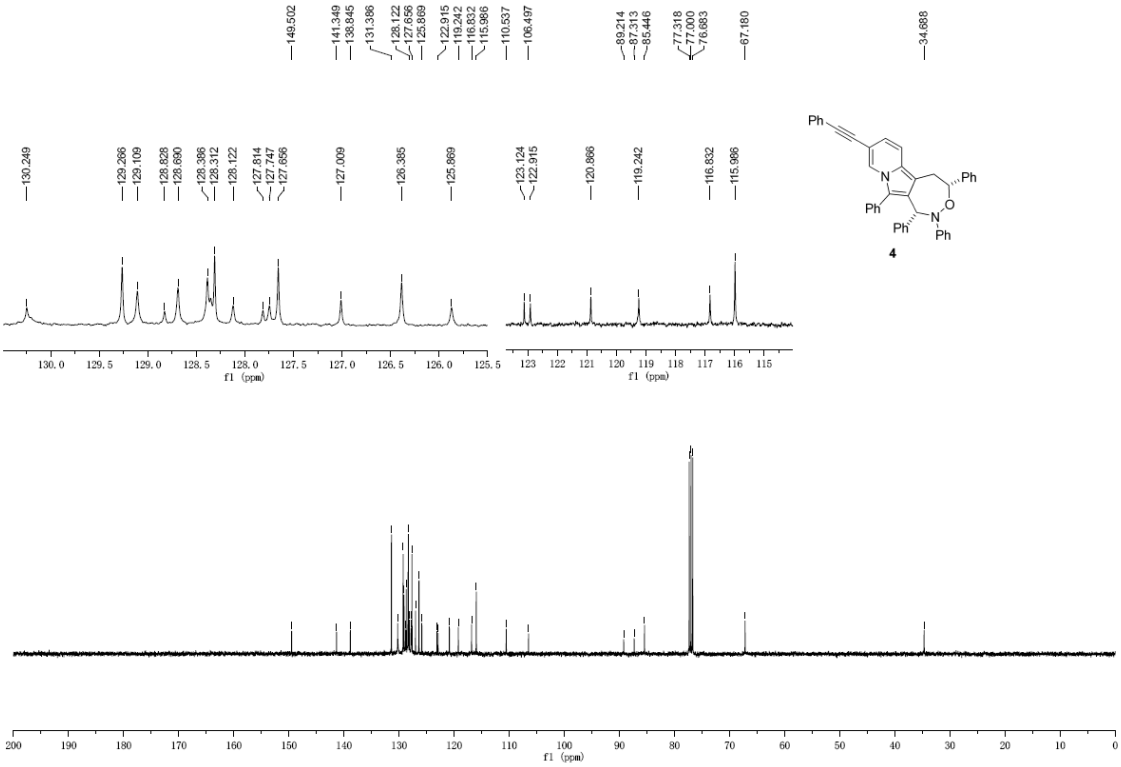
3am d.r.>99:1



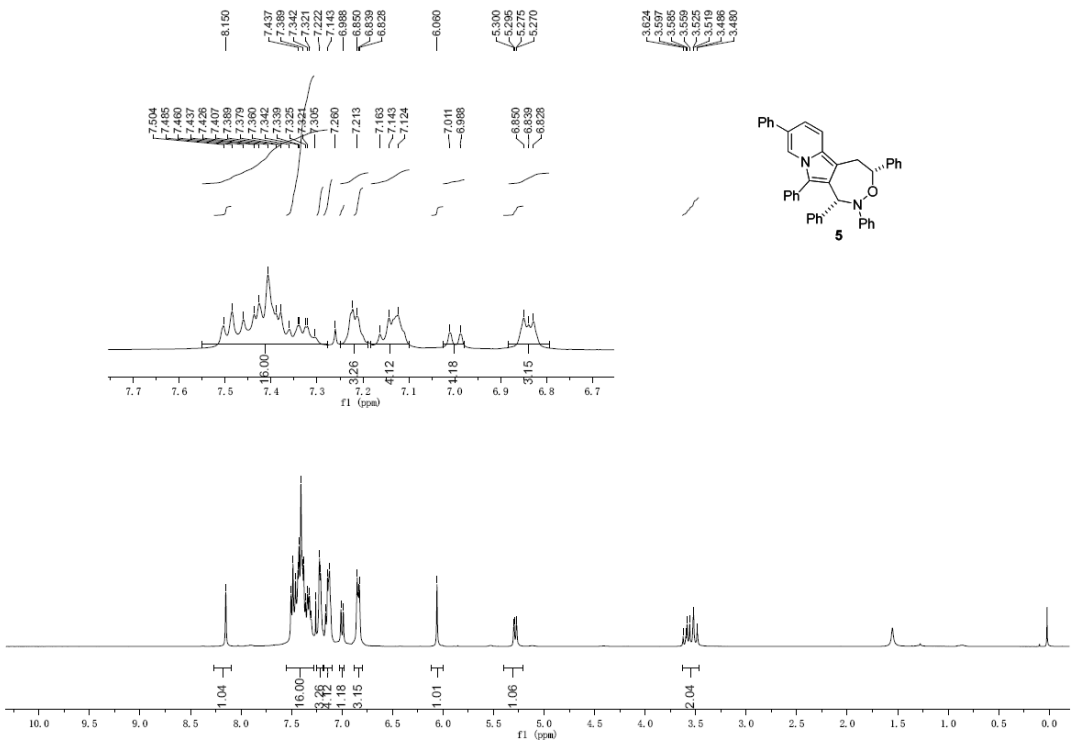


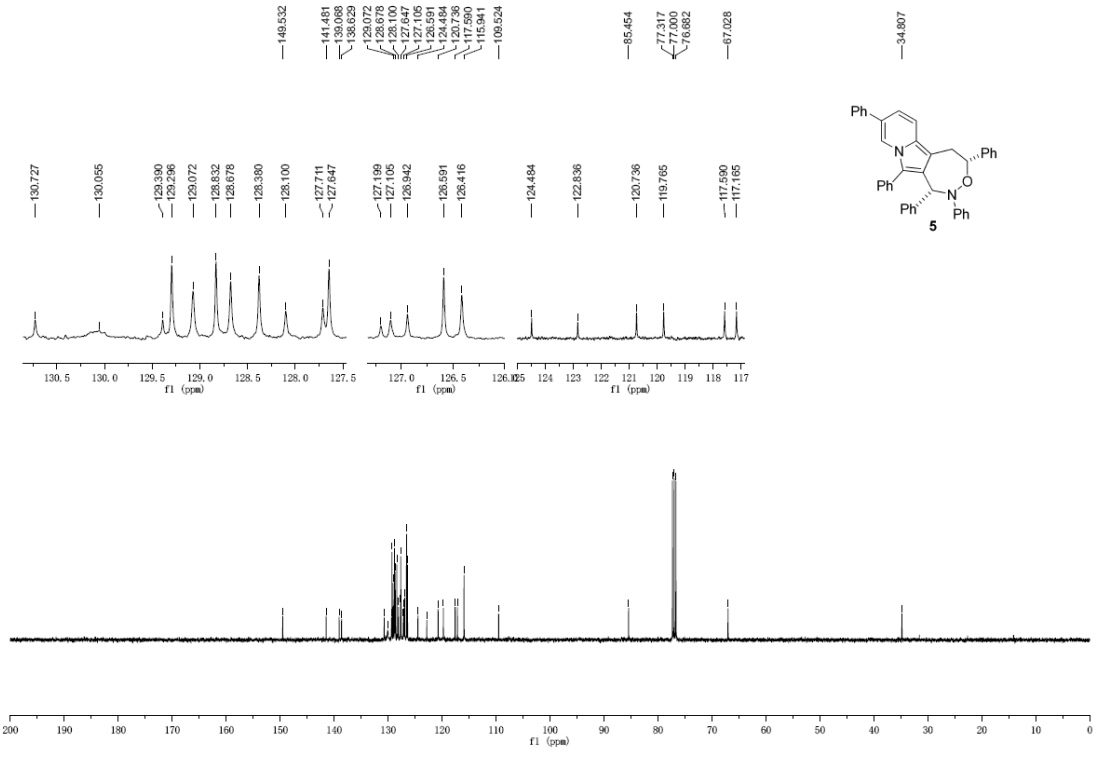

8.190
7.506
7.388
7.337
7.236
7.197
7.144
7.099
6.875
6.820
6.799
6.797
6.065
5.314
5.306
5.298
5.282
3.613
3.587
3.574
3.549
3.520
3.513
3.482
3.475
7.525
7.518
7.516
7.502
7.486
7.408
7.369
7.345
7.337
7.333
7.260
7.236
7.223
7.220
7.197
7.183
7.164
7.144
7.117
7.107
7.099
6.875
6.863
6.854
6.822
6.820
6.799
6.797
Ph
Ph
Ph
Ph
N
O
N
Ph
4
16.23
3.29
2.28
2.07
3.18
1.20
f1 (ppm)

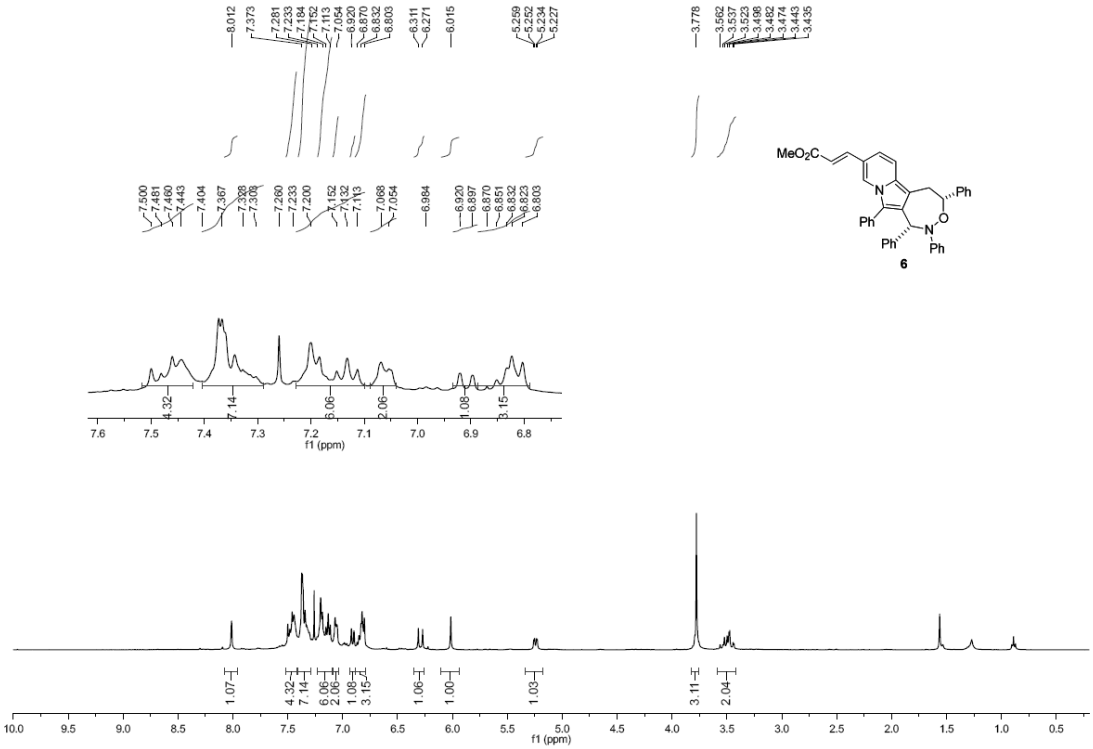

1.00
16.23
3.18
1.20
1.02
1.04
2.07
f1 (ppm)

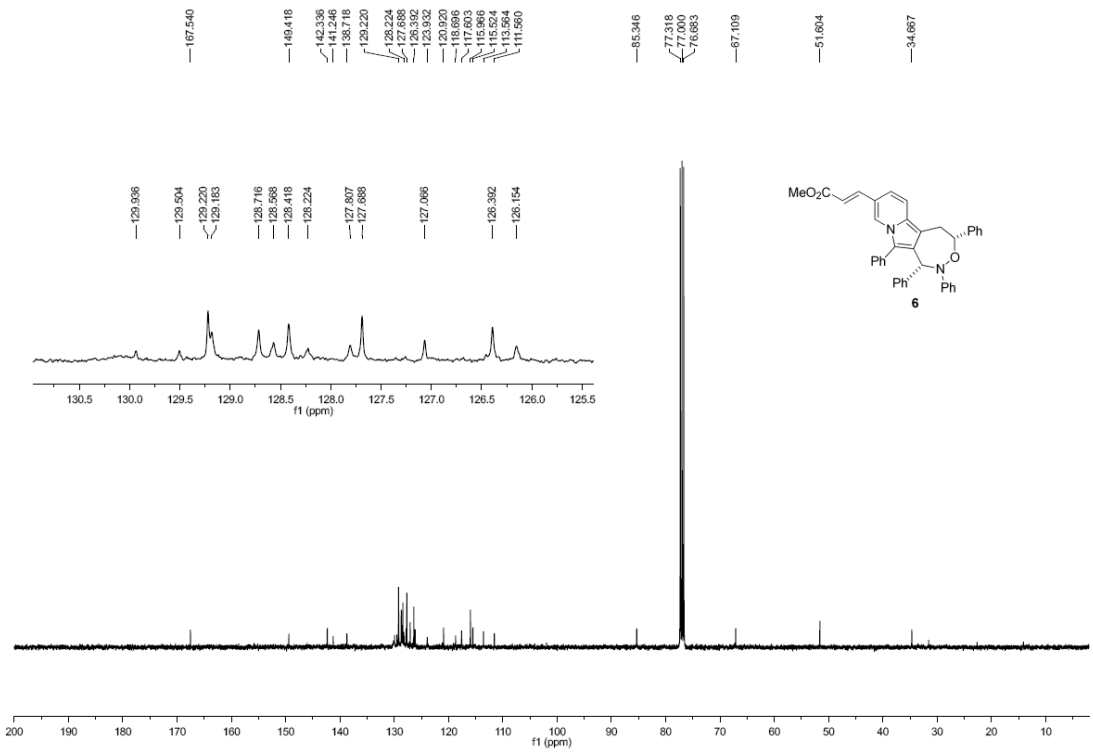

149.502
141.349
138.845
131.386
128.122
127.656
125.869
122.915
119.242
116.832
115.986
110.537
106.497
89.214
87.313
85.446
77.318
77.000
76.683
67.180
34.688
130.249
129.286
129.109
128.828
128.690
128.386
128.312
128.122
127.814
127.747
127.656
127.009
126.385
125.869
123.124
122.915
120.866
119.242
116.832
115.986
Ph
Ph
Ph
Ph
N
O
N
Ph
4
f1 (ppm)
f1 (ppm)

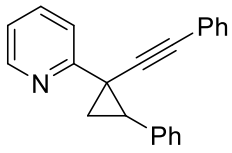
f1 (ppm)


8.150
7.437
7.389
7.342
7.321
7.222
7.143
6.988
6.850
6.839
6.828
6.060
5.300
5.295
5.275
5.270
3.624
3.597
3.585
3.539
3.525
3.519
3.496
3.480
7.504
7.485
7.460
7.437
7.426
7.407
7.389
7.379
7.360
7.342
7.339
7.321
7.305
7.260
7.213
7.163
7.143
7.124
7.011
6.988
6.860
6.839
6.828
Ph
Ph
Ph
Ph
O
N
N
Ph
5
16.00
3.26
4.12
1.18
3.15
f1 (ppm)
1.04
16.00
3.26
4.12
1.18
3.15
1.01
1.06
2.04
f1 (ppm)

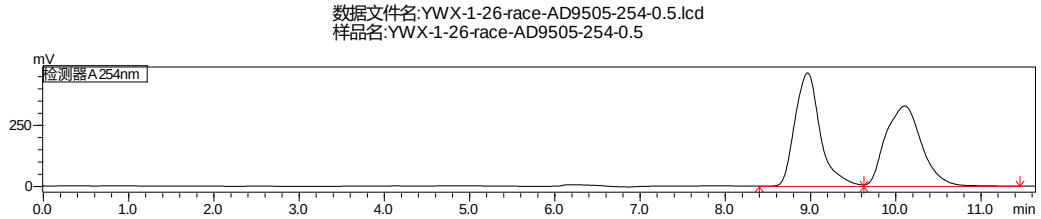

149.532
141.481
139.098
138.629
129.072
128.678
128.100
127.647
127.105
126.591
124.484
120.736
117.590
115.941
109.524
85.454
77.317
77.000
76.682
67.028
34.807
130.727
130.055
129.390
129.296
129.072
128.832
128.678
128.380
128.100
127.711
127.647
127.199
127.105
126.942
126.591
126.416
124.484
122.836
120.736
119.765
117.590
117.165
Ph
Ph
Ph
Ph
O
N
N
Ph
5
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)


8.012
7.373
7.281
7.233
7.184
7.152
7.113
7.054
6.920
6.870
6.832
6.803
6.311
6.271
6.015
5.259
5.252
5.234
5.227
3.778
3.562
3.537
3.523
3.496
3.482
3.474
3.443
3.435
MeO2C
Ph
Ph
Ph
N
O
N
Ph
6
4.32
7.14
6.06
2.06
1.08
3.15
f1 (ppm)
1.07
4.32
7.14
6.06
2.06
1.08
3.15
1.06
1.00
1.03
3.11
2.04
f1 (ppm)

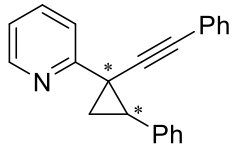

167.540
149.418
142.336
141.246
138.718
129.220
128.224
127.688
126.392
123.932
120.920
118.696
117.603
115.966
115.524
113.564
111.560
85.346
77.318
77.000
76.683
67.109
51.604
34.667
129.936
129.504
129.220
129.183
128.716
128.568
128.418
128.224
127.807
127.688
127.066
126.392
126.154
MeO2C
Ph
Ph
Ph
N
O
N
Ph
6
f1 (ppm)
f1 (ppm)



racemic **1a**

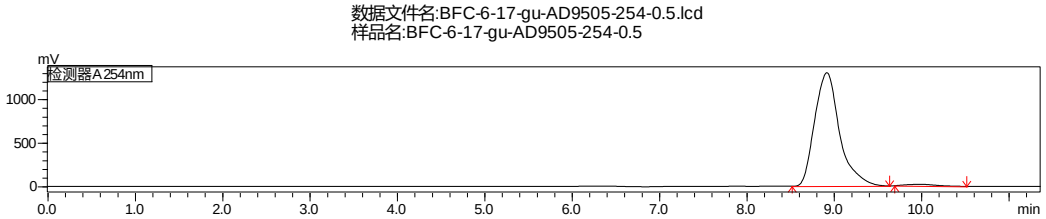


Peak#	Ret. Time	Height	Area%
1	8.971	462555	49.775
2	10.110	327419	50.225

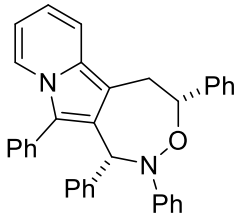


enantioenriched **1a**

ee = 95%



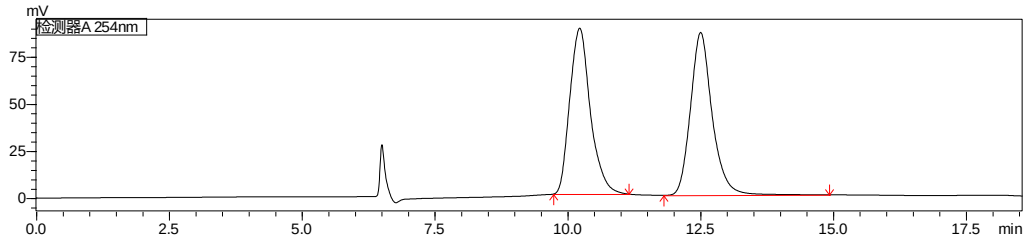
Peak#	Ret. Time	Height	Area%
1	8.920	1299447	98.389
2	9.986	18830	1.611



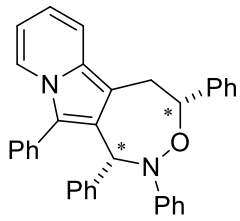
racemic **3aa**

Racemic **3aa**

数据文件名:HZC-1-4-race-IA9802-254-0.5.lcd
样品名:HZC-1-4-race-IA9802-254-0.5



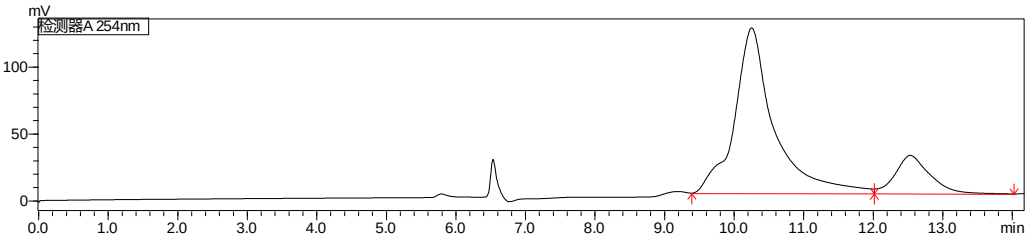
Peak#	Ret. Time	Height	Area%
1	10.230	88013	49.204
2	12.506	86392	50.796



enantioenriched **3aa**

ee = 66%

数据文件名:BFC-6-32-IA9802-254-0.5.lcd
样品名:BFC-6-32-IA9802-254-0.5



Peak#	Ret. Time	Height	Area%
1	10.259	123512	83.204
2	12.539	28545	16.796