Supporting Information

Divergently Access N-center 5,6,7-Perifused Cycle

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1. General experimental

All reactions were carried out under an argon atmosphere with magnetic stirring unless otherwise noted, tetrahydrofuran (THF) was dried by sodium sand solvent purification system before used. All other reagents were purchased from suppliers and used as received unless noted otherwise. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, high-resolution mass spectroscopy (HRMS).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using Bruker 400 MHz or Bruker 500 MHz. Chemical shift (δ) was reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm), $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm). Coupling constants (*J*) were reported in Hz. Multiplicities were reported using the following abbreviations: s (singlet); d (doublet); t (triplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); td (triplet of doublets); dt (doublet of triplets); m (multiplet); Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded using Bruker 400 MHz spectrometers at 101 MHz or Bruker 500 MHz spectrometers at 126 MHz. Chemical shift was reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm) or DMSO-d_6 (39.50 ppm). Fluorine-19 (^{19}F NMR) nuclear magnetic resonance spectra were recorded using Bruker 400 MHz at 377 MHz or Bruker 600 MHz at 564 MHz, respectively.

Infrared (IR) spectra were measured on Thermofisher Nicolet iN10 FM-IR spectrometer using KBr plates.

High resolution mass spectral analysis (HRMS) were recorded on a FT-ICR (Fourier Transform-Ion Cyclotron Resonance) mass spectrometer by using electrospray ionization (ESI) techniques.

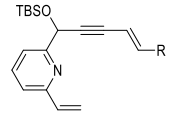
Single crystal X-ray diffraction measurements were performed on an Agilent SuperNova-CCD X-Ray diffractometer.

Column chromatographic was performed on 200−300 mesh silica gel or active aluminum oxide, reactions were monitored by thin layer chromatography (TLC) using silica gel GF 254 plates. Visualisation was by ultraviolet fluorescene (λ = 254 nm) and staining with phosphomolybdic acid.

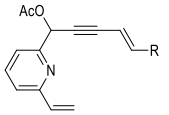
2. The preparation of substrates 1 and 3

1a − **1a'**[1–3], **3a** − **3j**[4] were synthesized according to literatures.

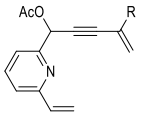
substrates 1



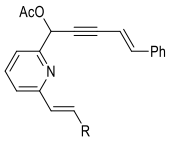
1a, R = 4-OMe-Ph
1b, R = Ph
1d, R = 4-Me-Ph
1f, R = 4-F-Ph
1g, R = 3-thienyl
1h, R = 2-pyridyl
1j, R = cyclohexyl
1k, R = *n*-hexyl



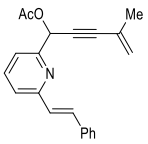
1c, R = Ph
1e, R = 4-Br-Ph
1i, R = styrenyl



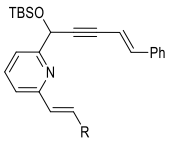
1l, R = 4-OMe-Ph
1m, R = 4-Cl-Ph
1n, R = Me



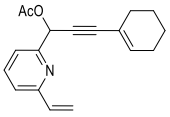
1p, R = Ph
1q, R = 4-OMe-Ph
1r, R = 4-Me-Ph
1s, R = 4-Br-Ph
1u, R = styrenyl
1v, R = cyclohexyl
1w, R = Me



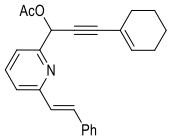
1o



1t, R = 2-pyridyl



1x



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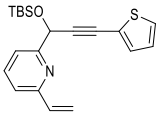

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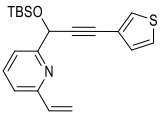
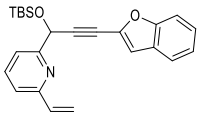
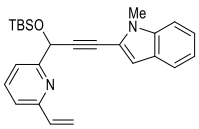


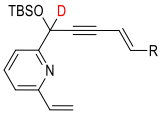
1aa



1ab



1ac



1a', R = 4-OMe-Ph

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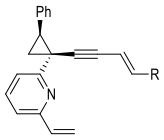
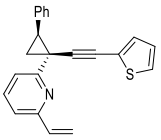
substrates 3



3a, R = Ph
3b, R = 3-thienyl
3c, R = styrenyl
3d, R = *n*-hexyl
3e, R = cyclohexyl



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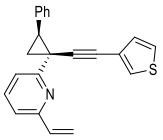

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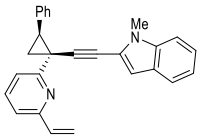
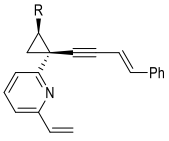
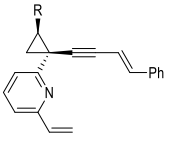


3h

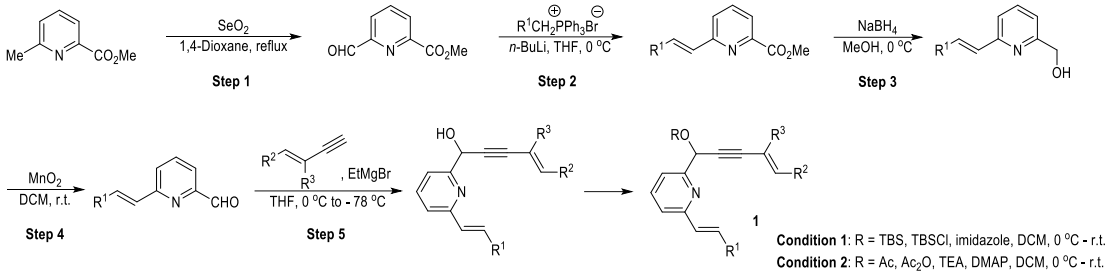


3i, R = 4-Me-Ph



3j, R = 4-F-Ph

2.1 General procedure for the synthesis of substrates 1



Step 1: The methyl 6-methylpicolinate (100.0 mmol, 1.0 equiv.) was dissolved in 1,4-Dioxane (80.0 mL) for a 200.0 mL round bottom flask, followed SeO_2 (200.0 mmol, 2.0 equiv.) was added, the reaction mixture was refluxed until the material was completely consumed. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford the methyl 6-formylpicolinate as a colorless solid in 71% yield.

Step 2: The wittig regent (11.0 mmol, 1.1 equiv.) was dissolved in dried THF (20.0 mL) for a 50.0 mL round bottom flask, followed *n*-BuLi (2.5 M in Hexane, 11.0 mmol, 1.1 equiv.) was added dropwise at 0 °C for 0.5 h, then the methyl 6-formylpicolinate obtained from **step 1** (10.0 mmol, 1.0 equiv.) was added to the mixture at 0 °C and stirred until methyl 6-formylpicolinate was completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined the organic solution and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under *vacuo*, the residue was purified by column chromatography on silica gel to afford the methyl 6-vinylpicolinate.

Step 3: The methyl 6-vinylpicolinate (1.0 equiv.) obtained from **step 2** was dissolved in MeOH (15.0 mL) for a 50.0 mL round bottom flask, followed $NaBH_4$ (1.1 equiv.) was added slowly at 0 °C and stirred until the methyl 6-vinylpicolinate was completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined the organic solution and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under *vacuo*, the residue was purified by column chromatography on silica gel to afford the alcohol.

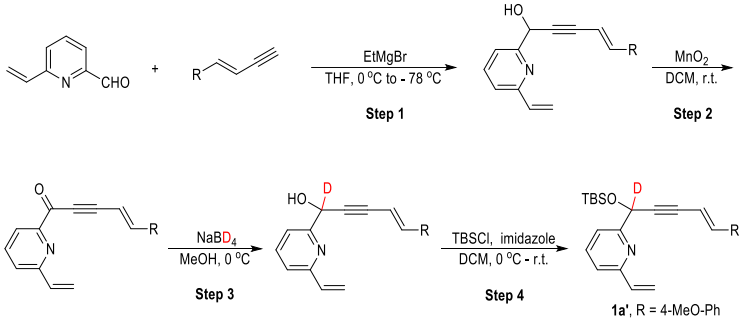
Step 4: The alcohol (1.0 equiv.) obtained from **step 3** was dissolved in DCM (15.0 mL) for a 50.0 mL round bottom flask, followed MnO_2 (5.0 equiv.) was added at room temperature and stirred until the alcohol was completely consumed. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford the aldehyde.

Step 5: The alkyne (5.0 mmol, 1.2 equiv.) was dissolved in dried THF (10.0 mL) for a 50.0 mL round bottom flask, followed EtMgBr (2.0 M in THF, 5.0 mmol, 1.2 equiv.) was added dropwise at 0 °C, the reaction mixture was stirred at 0 °C for 0.5 h and then cooled to – 78 ℃, a solution of aldehyde (4.2 mmol, 1.0 equiv.) obtained from **step 4** in THF (3.0 mL) was added dropwise, the reaction mixture was stirred at – 78 ℃ until the aldehyde was completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined organic solution and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford the alcohol.

Condition 1: The alcohol (1.0 equiv.) obtained from **step 5** was dissolved in DCM (15.0 mL) for a 50.0 mL round bottom flask, followed imidazole (2.2 equiv.) and TBSCl (2.2 equiv.) were added at 0 °C, and the resulting mixture was warmed to room temperature and stirred until the alcohol was completely consumed. After completion, the organic solution was concentrated under *vacuo*, the residue was purified by column chromatography on silica gel to afford the substrates **1**.

Condition 2: The TEA (2.0 equiv.), DMAP (10.0 mol%), and alcohol (1.0 equiv.) obtained from **step 5** were dissolved in DCM (15.0 mL) for a 50.0 mL round bottom flask, followed acetic anhydride (2.0 equiv.) was added dropwise at 0 °C, and the resulting mixture was warmed to room temperature and stirred until alcohol completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined organic solution and dried over anhydrous Na_2SO_4, then the organic solution concentrated was under *vacuo*, residue was purified by column chromatography on silica gel to afford the substrates **1**.

2.2 The synthesis of deuterated substrate 1a'



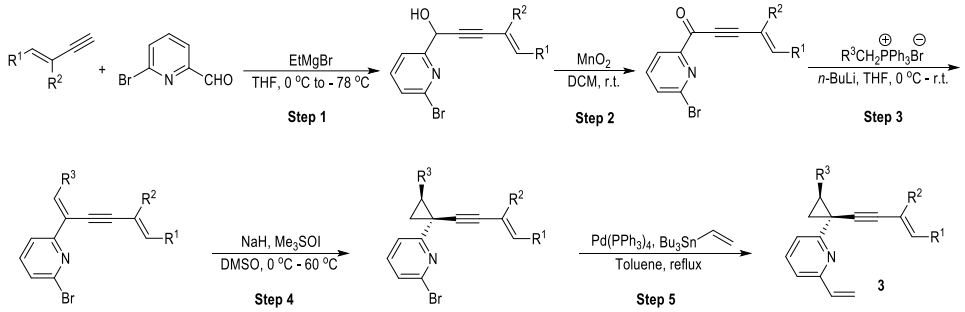
Step 1: The alkyne (5.0 mmol, 1.2 equiv.) was dissolved in dried THF (10.0 mL) for a 50.0 mL round bottom flask, followed EtMgBr (2.0 M in THF, 5.0 mmol, 1.2 equiv.) was added dropwise at 0 °C, the reaction mixture was stirred at 0 °C for 0.5 h and then cooled to – 78 °C, a solution of aldehyde (4.2 mmol, 1.0 equiv.) in THF (3.0 mL) was added dropwise, the reaction mixture was stirred at –78 °C until the aldehyde was completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined organic solution and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford the alcohol.

Step 2: The alcohol (2.8 mmol, 1.0 equiv.) obtained from **step 1** was dissolved in DCM (10.0 mL) for a 50.0 mL round bottom flask, followed MnO_2 (14.0 mmol, 5.0 equiv.) was added at room temperature, stirred at room temperature until the alcohol was completely consumed. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford ketone.

Step 3: The ketone (2.7 mmol, 1.0 equiv.) obtained from **step 2** was dissolved in MeOH (10.0 mL) for a 50.0 mL round bottom flask, followed $NaBD_4$ (3.0 mmol, 1.1 equiv.) was added slowly at 0 °C, the reaction mixture was stirred at 0 °C until the ketone was completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined organic solution and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under vacuo, residue was purified by column chromatography on silica gel to afford the alcohol.

Step 4: The alcohol (2.5 mmol, 1.0 equiv.) obtained from **step 3** was dissolved in DCM (10.0 mL) for a 50.0 mL round bottom flask, followed imidazole (5.5 mmol, 2.2 equiv.) and TBSCl (5.5 mmol, 2.2 equiv.) were added at 0 °C, and the resulting mixture was warmed to room temperature and stirred until the alcohol was completely consumed. After completion, the organic solution was concentrated under *vacuo*, the residue was purified by column chromatography on silica gel to afford the **1a'**.

2.3 General procedure for the synthesis of substrates 3



Step 1: The alkyne (12.0 mmol, 1.2 equiv.) was dissolved in dried THF (20.0 mL) for a 100.0 mL round bottom flask, followed EtMgBr (2.0 M in THF, 12.0 mmol, 1.2 equiv.) was added dropwise at 0 °C, the reaction mixture was stirred at 0 °C for 1.0 h and then cooled to – 78 °C, a solution of aldehyde (10.0 mmol, 1.0 equiv.) in THF (5.0 mL) was added dropwise, the reaction mixture was stirred at – 78 °C until the aldehyde was completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined organic solution and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford the alcohol.

Step 2: The alcohol (1.0 equiv.) obtained from **step 1** was dissolved in DCM (20.0 mL) for a 50.0 mL round bottom flask, followed MnO_2 (5.0 equiv.) was added at room temperature, stirred at room temperature until the alcohol was completely consumed. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford ketone.

Step 3: The wittig regent (1.1 equiv.) was dissolved in dried THF (20.0 mL) for a 50.0 mL round bottom flask, followed *n*-BuLi (2.5 M in Hexane, 1.1 equiv.) was added dropwise at 0 °C, the reaction was stirred at 0 °C for 0.5 h, then the ketone (1.0 equiv.) obtained from **step 2** was added to the mixture at 0 °C, and the resulting mixture was warmed to room temperature and stirred until the ketone was completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined organic solution and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford diene.

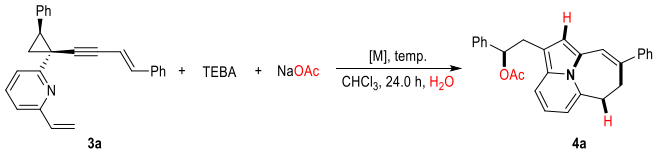
Step 4: The trimethylsulfoxonium iodide (1.5 equiv.) was dissolved in DMSO (15.0 mL) for a 50.0 mL round bottom flask, followed NaH (1.5 equiv.) was added slowly at 0 °C, the reaction mixture was stirred at 0 °C for 0.5 h, a solution of diene (1.0 equiv.) obtained from **step 3** in DMSO (5.0 mL) was added dropwise, then the mixture was heat to 60 °C and stirred until the diene was completely consumed. After completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution, the aqueous phase was extracted by DCM (3 × 20 mL), combined organic solution

and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford the bromocyclopropane.

Step 5: The $Pd(PPh_3)_4$ (1.0 mol%) and bromocyclopropane (1.0 equiv.) obtained from **step 4** were dissolved in toluene (15.0 mL) for a 50.0 mL round bottom flask, followed tributyl(vinyl)tin (1.1 equiv.) was added at room temperature, the reaction mixture was refluxed until the material were completely consumed, then reaction mixture cooled to room temperature, KF (2.0 equiv.) was added and stirred for 2.0 h. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo,* residue was purified by column chromatography on silica gel to afford the **3a** − **3j**.

3. Optimization conditions for the synthesis of 4a

Table S1. Optimization conditions for the synthesis of 4a[a,b]



entry	[M]	NaOAc/(equiv.)	Solvents	Temp. (°C)	yield (%)
1	CuTc	2	$CHCl_3$	90	11
2	$Cu(OAc)_2$	2	$CHCl_3$	90	15
3	$CuSO_4$	2	$CHCl_3$	90	27
4	$Cu(OTf)_2$	2	$CHCl_3$	90	38
5	AgOAc	2	$CHCl_3$	90	41
6	CF_3CO_2Ag	2	$CHCl_3$	90	44
7	Ag_3PO_4	2	$CHCl_3$	90	65
8	$AgSbF_6$	2	$CHCl_3$	90	36
9	AgCl	2	$CHCl_3$	90	46
10	Ag_3PO_4	2	THF	90	22
11	Ag_3PO_4	2	toluene	90	19
12	Ag_3PO_4	2	DMF	90	41
13	Ag_3PO_4	3	$CHCl_3$	90	74
14	**Ag_3PO_4**	**3**	**$CHCl_3$**	**100**	**80**
15	Ag_3PO_4	3	$CHCl_3$	110	77

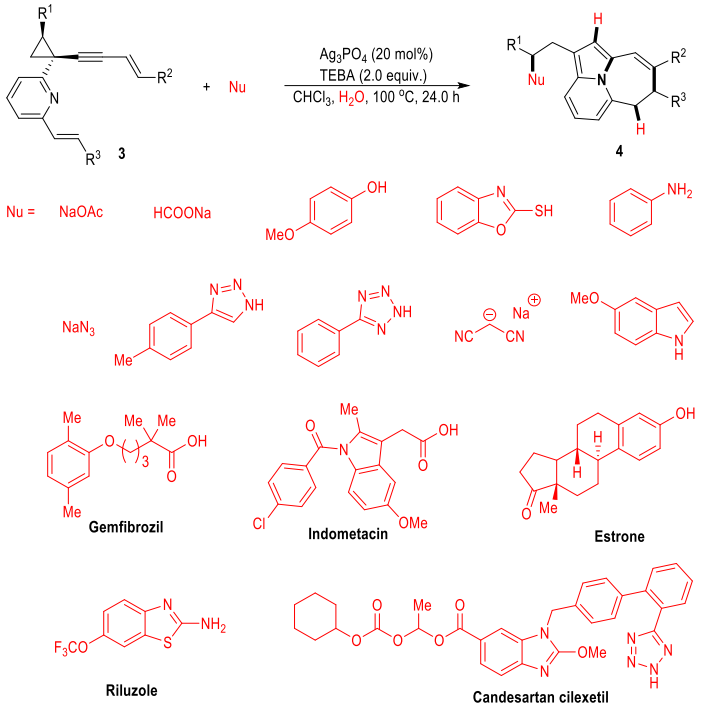
[a]All reactions were performed with **3a** (0.1 mmol, 1.0 equiv.), catalyst (20.0 mol%), TEBA (0.2 mmol, 2.0 equiv.) and NaOAc in the solvent (2.0 mL) were stirred for 24.0 h. [b]Isolated yield. TEBA: benzyltriethylammonium chloride.

4. General procedure for the synthesis of products

4.1 Procedure A: The synthesis of products 2a − 2ac

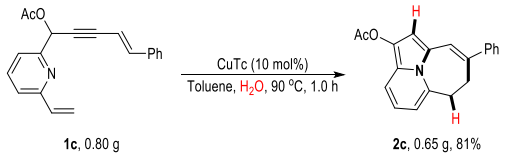
The freshly prepared **1** (0.05 mmol, 1.0 equiv.), CuTc (10.0 mol%), and toluene (1.0 mL) were added to a 5.0 mL round bottom flask at room temperature, the reaction mixture was stirred at 90 °C for 0.5 h and then cooled to room temperature. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on alkaline alumina to afford the **2a** − **2ac**.

4.2 Procedure B: The synthesis of products 4a − 4x



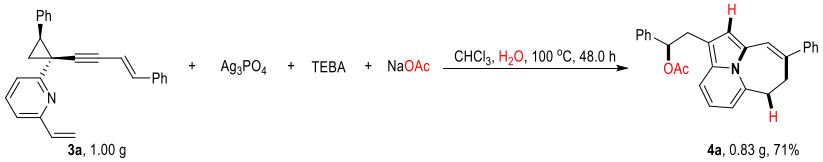
Ag_3PO_4 (20.0 mol%), TEBA (0.2 mmol, 2.0 equiv.) and nucleophilic reagent (0.3 mmol, 3.0 equiv.) were added to a solution of freshly prepared **3** (0.1 mmol, 1.0 equiv.) in $CHCl_3$ (2.0 mL) for a Schlenk tube at room temperature, the reaction mixture was stirred at 100 °C for 24.0 h and then cooled to room temperature. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford the **4a** − **4x**.

5. The gram-scale synthesis of 2c and 4a



1c, 0.80 g **2c**, 0.65 g, 81%

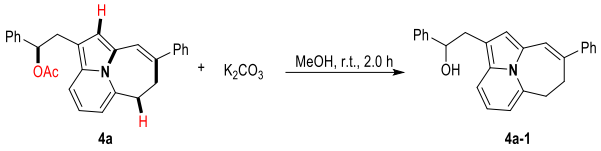
The freshly prepared **1c** (2.64 mmol, 0.80 g, 1.0 equiv.), CuTc (10.0 mol%), and toluene (20.0 mL) were added to a 50.0 mL round bottom flask at room temperature, the reaction mixture was stirred at 90 °C for 1.0 h and then cooled to room temperature. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on alkaline alumina to afford the **2c** as yellow thick liquid (0.65 g, 81%).



3a, 1.00 g **4a**, 0.83 g, 71%

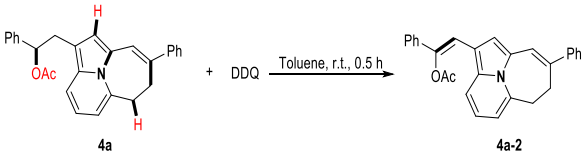
Ag_3PO_4 (20.0 mol%), TEBA (5.76 mmol, 2.0 equiv.) and Nucleophilic reagent (8.64 mmol, 3.0 equiv.) were added to a solution of freshly prepared **3a** (2.88 mmol, 1.00 g, 1.0 equiv.) in $CHCl_3$ (20.0 mL) for a 50.0 mL round bottom flask at room temperature, the reaction mixture was stirred at 100 °C for 48.0 h and then cooled to room temperature. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on silica gel to afford **4a** as yellow thick liquid (0.83 g, 71%).

6. Procedure for the synthetic transformations of 4a



4a **4a-1**

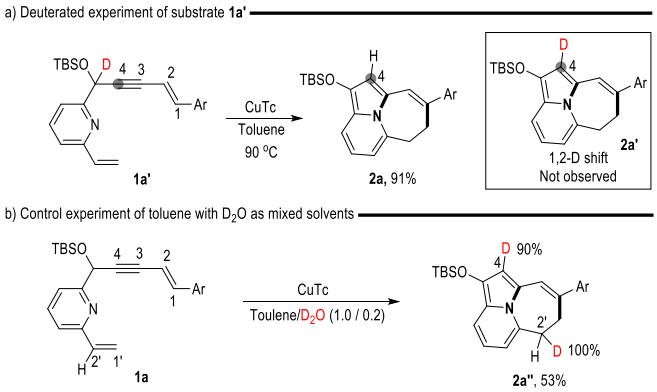
The **4a** (0.1 mmol, 1.0 equiv.), K_2CO_3 (0.4 mmol, 4.0 equiv.) and MeOH (1.0 mL) were added to a 5.0 mL round bottom flask at room temperature, then the reaction mixture was stirred at room temperature for 2.0 h. After completion, the organic solution was concentrated under *vacuo* and purified by column chromatography on silica gel afford **4a-1** in 96% yield as yellow amorphous solid.



4a **4a-2**

The **4a** (0.1 mmol, 1.0 equiv.), DDQ (0.15 mmol, 1.5 equiv.) and toluene (2.0 mL) were added to a 5.0 mL round bottom flask at room temperature, then the reaction mixture was stirred at room temperature for 0.5 h. After completion, the organic solution was concentrated under *vacuo*, the residue was purified by column chromatography on silica gel to afford **4a-2** in 86% yield as yellow amorphous solid.

7. Mechanistic studies



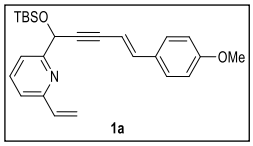
Deuterated experiment: The freshly prepared **1a'** (0.05 mmol, 1.0 equiv.), CuTc (10.0 mol%), and toluene (1.0 mL) were added to a 5.0 mL round bottom flask at room temperature, the reaction mixture was stirred at 90 °C for 0.5 h and then cooled to room temperature. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on alkaline alumina to afford the **2a** in 91% yield as yellow amorphous solid.

Control experiment: The freshly prepared **1a** (0.05 mmol, 1.0 equiv.), CuTc (10.0 mol%), dried toluene (1.0 mL) and D_2O (0.2 mL) were added to a 5.0 mL round bottom flask at room temperature, the mixture was stirred at 90 °C for 0.5 h and then cooled to room temperature. After completion, the reaction mixture was filtered, and the organic solution was concentrated under *vacuo*, residue was purified by column chromatography on alkaline alumina to afford the **2a''** in 53% yield as yellow amorphous solid.

8. Characterization data for key compounds

(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)-5-(4-methoxyphenyl) pent-4-en-2-yn-1-yl)-6-vinylpyridine

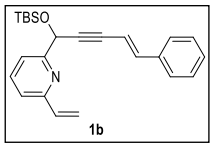
Compound **1a** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 (t, 1H, *J* = 7.5 Hz), 7.55 (d, 1H, *J* = 7.5 Hz), 7.29 – 7.26 (m, 3H), 6.89 – 6.82 (m, 4H), 6.21 (d, 1H, *J* = 16.0 Hz), 6.04 (d, 1H, *J* = 16.0 Hz), 5.72 (s, 1H), 5.48 (d, 1H, *J* = 11.0 Hz), 3.78 (s, 3H), 0.97 (s, 9H), 0.25 (s, 3H), 0.18 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.6, 160.0, 154.8, 140.9, 137.3, 136.9, 129.0, 127.5, 119.8, 119.0, 118.3, 114.0, 105.4, 91.0, 85.1, 67.3, 55.2, 25.8, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3028, 2924, 2850, 2210, 1631, 1449, 1395, 1083, 957, 854; **HRMS** m/z (ESI) calculated for $C_{25}H_{32}NO_2Si$ $[M + H]^+$: 406.2197, found: 406.2199.



1a

(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)-5-(p-tolyl) pent-4-en-2-yn-1-yl)-6-vinylpyridine

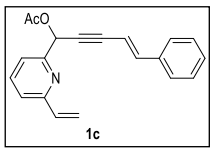
Compound **1b** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (t, 1H, *J* = 7.5 Hz), 7.57 (d, 1H, *J* = 7.5 Hz), 7.38 – 7.27 (m, 6H), 6.94 (d, 1H, *J* = 17.0 Hz), 6.86 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.5 Hz), 6.25 – 6.18 (m, 2H), 5.74 (s, 1H), 5.50 (d, 1H, *J* = 10.5 Hz), 0.98 (s, 9H), 0.26 (s, 3H), 0.19 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.5, 154.9, 141.4, 137.4, 136.9, 136.2, 128.6, 128.5, 126.2, 119.9, 119.0, 118.3, 107.9, 91.8, 84.8, 67.3, 25.8, 18.4, -4.5, -4.9; **IR (cm^{-1})**: *v* 3029, 2926, 2824, 2206, 1601, 1491, 1361, 1082, 748; **HRMS** m/z (ESI) calculated for $C_{24}H_{30}NOSi$ $[M + H]^+$: 376.2091, found: 376.2089.



1b

(*E*)-5-phenyl-1-(6-vinylpyridin-2-yl)pent-4-en-2-yn-1-yl acetate

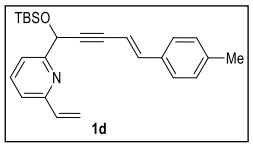
Compound **1c** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.67 (t, 1H , *J* = 7.5 Hz), 7.47 (d, 1H, *J* = 7.5 Hz), 7.34 – 7.24 (m, 6H), 6.99 (d, 1H, *J* = 17.5 Hz), 6.82 (dd, 1H, J_1 = 17.5 Hz, J_2 = 11.0 Hz), 6.66 (s, 1H), 6.23 (d, 1H, *J* = 17.5 Hz), 6.17 (d, 1H, *J* = 17.5 Hz), 5.48 (d, 1H, *J* = 11.0 Hz), 2.14 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.3, 155.5, 155.4, 142.6, 137.3, 136.4, 135.6, 128.7, 128.5, 126.2, 120.6, 120.2, 118.8, 106.8, 86.9, 86.4, 67.3, 20.8; **IR (cm^{-1})**: *v* 3028, 2928, 2815, 2214, 1746, 1620, 1021, 928, 749; **HRMS** m/z (ESI) calculated for $C_{20}H_{18}NO_2$ $[M + H]^+$: 304.1332, found: 304.1326.



1c

(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)-5-(p-tolyl)pent-4-en-2-yn-1-yl)-6-vinylpyridine

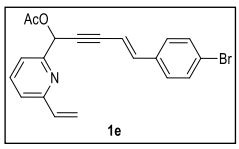
Compound **1d** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (t , 1H, *J* = 7.5 Hz), 7.52 (d, 1H, *J* = 7.5 Hz), 7.26 – 7.22 (m, 3H), 7.09 – 7.07 (m, 2H), 6.88 – 6.79 (m, 2H), 6.18 (d, 1H, *J* = 17.0 Hz), 6.10 (d, 1H, *J* = 17.0 Hz), 5.69 (s, 1H), 5.45 (d, 1H, *J* = 11.0 Hz), 2.30 (s, 3H), 0.93 (s, 9H), 0.21 (s, 3H), 0.14 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.5, 154.8, 141.4, 138.6, 137.4, 136.9, 133.4, 129.3, 126.1, 119.8, 119.0, 118.3, 106.7, 91.4, 85.0, 67.3, 25.8, 21.3, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3026, 2954, 2856, 2210, 1628, 1454, 1389, 1082, 918, 837; **HRMS** m/z (ESI) calculated for $C_{25}H_{32}NOSi$ $[M + H]^+$: 390.2248, found: 390.2247.



1d

(*E*)-5-(4-bromophenyl)-1-(6-vinylpyridin-2-yl)pent-4-en-2-yn-1-yl acetate

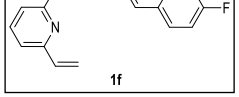
Compound **1e** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (t, 1H, *J* = 7.6 Hz), 7.46 (d, 1H, *J* = 7.6 Hz), 7.43 (d, 1H, *J* = 1.2 Hz), 7.41(d, 1H, *J* = 1.2 Hz), 7.31 (d, 1H, *J* = 7.6 Hz), 7.21 (d, 1H, *J* = 1.2 Hz), 7.18 (d, 1H, *J* = 1.2 Hz), 6.91 (d, 1H, *J* = 16.0 Hz), 6.83 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.63 (d, 1H, *J* = 1.6 Hz), 6.23 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.6 Hz), 6.18 – 6.13 (m, 1H), 5.50 (d, 1H, *J* = 10.8 Hz), 2.16 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.4, 155.5, 141.3, 137.4, 134.6, 131.7, 127.7, 122.7, 120.7, 120.2, 118.9, 107.7, 87.6, 86.1, 67.3, 20.9; **IR (cm^{-1})**: *v* 3036, 2927, 2833, 2100, 1745, 1627, 1071, 959, 804; **HRMS** m/z (ESI) calculated for $C_{20}H_{16}BrNNaO_2$ $[M + Na]^+$: 404.0257, found: 404.0251.



1e

(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)-5-(4-fluorophenyl)pent-4-en-2-yn-1-yl)-6-vinylpyridine

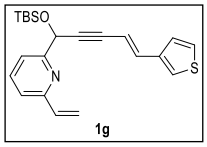
Compound **1f** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.60 (t, 1 H, *J* = 7.5 Hz), 7.47 (d, 1H, *J* = 7.5 Hz), 7.23 – 7.18 (m, 3H), 6.91 – 6.88 (m, 2H), 6.80 – 6.73 (m, 2H), 6.13 (d, 1H, *J* = 17.5 Hz), 6.00 (d, 1H, *J* = 17.5 Hz), 5.65 (s, 1H), 5.39 (d, 1H, *J* = 11.0 Hz), 0.89 (s, 9H), 0.17 (s, 3H), 0.10 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.8, 161.8, 160.4, 154.8, 140.1, 137.3, 136.9, 132.3 (d, *J* = 3.4 Hz), 127.8 (d, *J* = 8.1 Hz), 119.9, 118.6 (d, *J* = 78.5 Hz), 115.6 (d, *J* = 21.8 Hz), 107.6 (d, *J* = 2.4 Hz), 91.8, 84.5, 67.3, 25.8, 18.3, -4.5, -4.9; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -112.47 (t, *J* = 7.3 Hz, 1F); **IR (cm^{-1}):** *v* 3022, 2929, 2857, 2205, 1610, 1455, 1361, 1096, 934, 837; **HRMS** m/z (ESI) calculated for $C_{24}H_{29}FNOSi$ $[M + H]^+$: 394.1997, found: 394.2000.



1f

(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)-5-(thiophen-3-yl)pent-4-en-2-yn-1-yl)-6-vinylpyridine

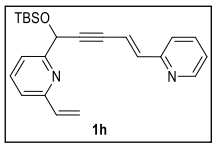
Compound **1g** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 (t, 1H, *J* = 7.5 Hz), 7.53 (d, 1H, *J* = 7.5 Hz), 7.28 – 7.24 (m, 2H), 7.19 (s, 1H), 7.18 (d, 1H, *J* = 4.0 Hz), 6.90 (d, 1H, *J* = 17.5 Hz), 6.83 (dd, 1H, J_1 = 17.5 Hz, J_2 = 11.0 Hz), 6.19 (d, 1H, *J* = 17.5 Hz), 6.00 (d, 1H, *J* = 17.5 Hz), 5.69 (s, 1H), 5.47 (d, 1H, *J* = 11.0 Hz), 0.95 (s, 9H), 0.22 (s, 3H), 0.16 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.5, 154.8, 139.1, 137.3, 136.9, 135.4, 126.4, 124.3, 123.5, 119.8, 119.0, 118.3, 107.6, 91.7, 84.7, 67.3, 25.8, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3033, 2955, 2856, 2206, 1664, 1454, 1361, 1085, 949, 749; **HRMS** m/z (ESI) calculated for $C_{22}H_{28}NOSSi$ $[M + H]^+$: 382.1655, found: 382.1658.



1g

(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)-5-(pyridin-2-yl)pent-4-en-2-yn-1-yl)-6-vinylpyridine

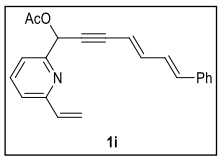
Compound **1h** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.52 (s, 1H), 7.66 (t, 1H, *J* = 7.5 Hz), 7.58 (t, 1H, *J* = 7.5 Hz), 7.52 (d, 1H, *J* = 7.5 Hz), 7.24 (s, 1H), 7.18 (d, 1H, *J* = 7.5 Hz), 7.12 – 7.10 (m, 1H), 6.92 (d, 1H, *J* = 17.5 Hz), 6.81 (dd, 1H, J_1 = 17.5 Hz, J_2 = 10.5 Hz), 6.73 (d, 1H, *J* = 17.5 Hz), 6.18 (d, 1H, *J* = 17.5 Hz), 5.70 (s, 1H), 5.45 (d, 1H, *J* = 10.5 Hz), 0.94 (s, 9H), 0.21 (s, 3H), 0.15 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.3, 154.9, 154.1, 149.7, 140.3, 137.3, 136.9, 136.5, 122.9, 122.0, 119.9, 119.0, 118.3, 112.4, 93.9, 84.5, 67.4, 25.8, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3022, 2928, 2856, 2110, 1584, 1455, 1092, 991, 779; **HRMS** m/z (ESI) calculated for $C_{23}H_{29}N_2OSi$ $[M + H]^+$: 377.2044, found: 377.2047.



1h

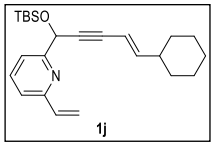
(4*E*,6*E*)-7-phenyl-1-(6-vinylpyridin-2-yl)hepta-4,6-dien-2-yn-1-yl acetate

Compound **1i** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, 1H, *J* = 7.6 Hz), 7.50 (d, 1H, *J* = 7.6 Hz), 7.43 (d, 1H, *J* = 1.2 Hz), 7.41 (s, 1H), 7.36 – 7.32 (m, 3H), 7.28 – 7.25 (m, 1H), 6.91 – 6.86 (m, 1H), 6.84 (d, 1H, *J* = 3.2 Hz), 6.81 (d, 1H, *J* = 4.4 Hz), 6.69 (d, 1H, *J* = 2.0 Hz), 6.66 – 6.62 (m, 1H), 6.27 (dd, 1H, J_1 = 17.2 Hz, J_2 = 1.2 Hz), 5.82 – 5.74 (m, 1H), 5.54 (dd, 1H, J_1 = 10.8 Hz, J_2 = 1.2 Hz), 2.19 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 155.7, 155.6, 143.3, 137.4, 136.6, 136.5, 135.4, 128.7, 128.2, 127.7, 126.7, 120.7, 120.3, 118.9, 110.1, 88.0, 86.8, 67.5. 21.0; **IR (cm^{-1})**: *v* 3025, 2941, 2855, 2210, 1717, 1615, 1020, 984, 749; **HRMS** m/z (ESI) calculated for $C_{22}H_{19}NNaO_2$ $[M + Na]^+$: 352.1308, found: 352.1305.



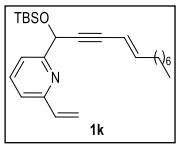
(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)-5-cyclohexylpent-4-en-2-yn-1-yl)-6-vinylpyridine

Compound **1j** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (t, 1H, *J* = 8.0 Hz), 7.51 (d, 1H, *J* = 8.0 Hz), 7.25 (d, 1H, *J* = 8.0 Hz), 6.82 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.18 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.2 Hz), 6.07 (dd, 1H, J_1 = 16.0 Hz, J_2 = 6.8 Hz), 5.63 (d, 1H, *J* = 1.2 Hz), 5.47 – 5.41 (m, 2H), 2.03 – 1.96 (m, 1H), 1.73 – 1.61 (m, 5H), 1.29 – 1.00 (m, 5H), 0.93 (s, 9H), 0.20 (s, 3H), 0.13 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.7, 154.7, 150.4, 137.3, 137.0, 119.7, 119.0, 118.2, 106.9, 88.1, 84.7, 77.3, 77.0, 76.7, 67.3, 41.1, 32.1, 26.0, 25.8, 25.8, 18.3, -4.5, -5.0; **IR (cm^{-1}):** *v* 3058, 2928, 2855, 2213, 1626, 1453, 1361, 1082, 957, 749; **HRMS** m/z (ESI) calculated for $C_{24}H_{36}NOSi$ $[M + H]^+$: 382.2561, found: 382.2554.



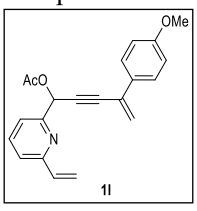
(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)dodec-4-en-2-yn-1-yl)-6-vinylpyridine

Compound **1k** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (t, 1H, *J* = 7.5 Hz), 7.51 (d, 1H, *J* = 7.5 Hz), 7.25 (d, 1H, *J* = 7.5 Hz), 6.81 (dd, 1H, J_1 = 17.5 Hz, J_2 = 11.0 Hz), 6.18 (d, 1H, *J* = 17.5 Hz), 6.15 – 6.09 (m, 1H), 5.64 (s, 1H), 5.49 (m, 2H), 2.07 (dd, 2H, J_1 = 14.0 Hz, J_2 = 7.0 Hz), 1.37 – 1.33 (m, 2H), 1.30 – 1.25 (m, 8H), 0.94 (s, 9H), 0.87 (t, 3H, *J* = 6.5 Hz), 0.21 (s, 3H), 0.14 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.7, 154.8, 145.1, 137.2, 137.0, 119.7, 118.9, 118.1, 109.1, 87.9, 84.5, 67.3, 33.0, 31.7, 29.0, 29.0, 28.6, 22.6, 18.3, 14.0, -4.5, -4.9; **IR (cm^{-1})**: *v* 3015, 2926, 2851, 2207, 1621, 1455, 1252, 1082, 956, 749; **HRMS** m/z (ESI) calculated for $C_{25}H_{40}NOSi$ $[M + H]^+$: 398.2874, found: 398.2873.



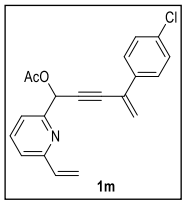
4-(4-methoxyphenyl)-1-(6-vinylpyridin-2-yl)pent-4-en-2-yn-1-yl acetate

Compound **1l** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, DMSO-*d_6*)** δ 7.88 (t, 1H, *J* = 7.6 Hz), 7.64 – 7.60 (m, 2H), 7.53 (d, 2H, *J* = 7.6 Hz), 6.94 – 6.89 (m, 2H), 6.86 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.63 (s, 1H), 6.29 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.2 Hz), 6.05 (s, 1H), 5.60 (s, 1H), 5.54 (dd, 1H, J_1 = 10.8 Hz, J_2 = 1.2 Hz), 3.76 (s, 3H), 2.16 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d_6*)** δ 169.3, 159.7, 155.2, 154.9, 138.3, 136.4, 128.4, 128.0, 127.1, 121.4, 120.4, 120.4, 119.2, 113.9, 86.9, 86.0, 66.7, 55.2, 20.6; **IR (cm^{-1})**: *v* 3017, 2933, 2856, 2210, 1745, 1607, 1027, 993; **HRMS** m/z (ESI) calculated for $C_{21}H_{19}NNaO_3$ $[M + Na]^+$: 356.1257, found: 356.1267.



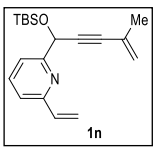
4-(4-chlorophenyl)-1-(6-vinylpyridin-2-yl)pent-4-en-2-yn-1-yl acetate

Compound **1m** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.87 (t, 1H, *J* = 7.6 Hz), 7.71 – 7.67 (m, 2H), 7.52 (d, 2H, *J* = 7.6 Hz), 7.43 – 7.40 (m, 2H), 6.85 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.64 (s, 1H), 6.28 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.2 Hz), 6.21 (s, 1H), 5.77 (s, 1H), 5.53 (dd, 1H, J_1 = 10.8 Hz, J_2 = 1.2 Hz), 2.16 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 169.8, 155.5, 155.4, 138.8, 136.9, 135.3, 133.9, 129.1, 128.0, 127.9, 124.0, 122.0, 121.0, 119.7, 88.0, 85.7, 67.1, 21.1; **IR (cm^{-1})**: *v* 3019, 2928, 2208, 1747, 1631, 1013, 994; **HRMS** m/z (ESI) calculated for $C_{20}H_{16}ClNNaO_2$ $[M + Na]^+$: 360.0762, found: 360.0767.



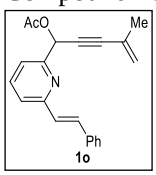
2-(1-((tert-butyldimethylsilyl)oxy)-4-methylpent-4-en-2-yn-1-yl)-6-vinylpyridine

Compound **1n** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.59 (t, 1H, *J* = 7.5 Hz), 7.45 (d, 1H, *J* = 7.5 Hz), 7.17 (d, 1H, *J* = 7.5 Hz), 6.75 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.0 Hz), 6.13 (d, 1H, *J* = 17.0 Hz), 5.59 (s, 1H), 5.39 (d, 1H, *J* = 11.0 Hz), 5.21 (s, 1H), 5.13 (s, 1H), 1.80 (s, 3H), 0.88 (s, 9H), 0.16 (s, 3H), 0.09 (s, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 160.4, 154.7, 137.2, 136.9, 126.4, 121.9, 119.8, 118.9, 118.2, 88.6, 86.7, 67.1, 25.8, 23.2, 18.3, -4.6, -4.9; **IR (cm^{-1})**: *v* 3097, 2956, 2857, 2225, 1615, 1454, 1361, 1088, 990, 778; **HRMS** m/z (ESI) calculated for $C_{19}H_{28}NOSi$ $[M + H]^+$: 314.1935, found: 314.1926.



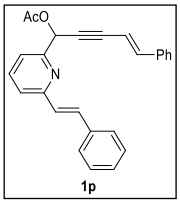
(*E*)-4-methyl-1-(6-styrylpyridin-2-yl)pent-4-en-2-yn-1-yl acetate

Compound **1o** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.49 (t, 1H, *J* = 7.6 Hz), 7.38 (d, 1H, *J* = 7.6 Hz), 7.30 – 7.21 (m, 5H), 7.13 (d, 1H, *J* = 7.6 Hz), 6.84 (d, 1H, *J* = 12.4 Hz), 6.69 (d, 1H, *J* = 12.4 Hz), 6.54 (s, 1H), 5.37 (s, 1H), 5.28 (s, 1H), 2.14 (s, 3H), 1.89 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.5, 156.1, 155.7, 136.6, 136.5, 133.7, 130.1, 128.9, 128.2, 127.6, 125.9, 123.6, 123.3, 119.7, 88.4, 83.9, 67.2, 23.1, 21.0; **IR (cm^{-1})**: *v* 3022, 2922, 2855, 2200, 1748, 1613, 1019, 971, 751; **HRMS** m/z (ESI) calculated for $C_{21}H_{20}NO_2$ $[M + H]^+$: 318.1489, found: 318.1482.



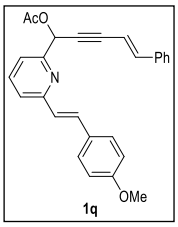
(*E*)-5-phenyl-1-(6-((*E*)-styryl)pyridin-2-yl)pent-4-en-2-yn-1-yl acetate

Compound **1p** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.51 (t, 1H, *J* = 8.0 Hz), 7.42 (d, 1H, *J* = 8.0 Hz), 7.38 – 7.23 (m, 10H), 7.15 (d, 1H, *J* = 8.0 Hz), 7.02 (d, 1H, *J* = 16.0 Hz), 6.86 (d, 1H, *J* = 12.4 Hz), 6.71 (d, 1H, *J* = 12.4 Hz), 6.60 (d, 1H, *J* = 2.0 Hz), 6.19 (dd, 1H, J_1 = 16.0 Hz, J_2 = 2.0 Hz), 2.16 (m, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.5, 156.2, 155.7, 142.8, 136.6, 136.5, 135.9, 133.8, 130.1, 128.9, 128.9, 128.7, 128.2, 127.6, 126.3, 123.7, 119.7, 107.0, 87.0, 86.6, 67.4, 21.0; **IR (cm^{-1})**: *v* 3025, 2929, 2841, 2214, 1744, 1637, 1026, 957, 749; **HRMS** m/z (ESI) calculated for $C_{26}H_{22}NO_2$ $[M + H]^+$: 380.1645, found: 380.1637.



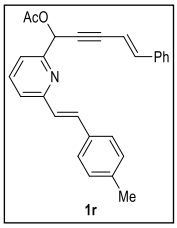
(*E*)-1-(6-((*E*)-4-methoxystyryl)pyridin-2-yl)-5-phenylpent-4-en-2-yn-1-yl acetate

Compound **1q** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (t, 1H, *J* = 8.0 Hz), 7.42 (d, 1H, *J* = 8.0 Hz), 7.38 – 7.28 (m, 7H), 7.21 (d, 1H, *J* = 8.0 Hz), 7.02 (d, 1H, *J* = 16.4 Hz), 6.80 – 6.76 (m, 3H), 6.62 – 6.51 (m, 2H), 6.20 (dd, 1H, J_1 = 17.6 Hz, J_2 = 2.0 Hz), 3.78 (s, 3H), 2.17 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 159.1, 156.6, 155.6, 142.8, 136.7, 135.8, 133.4, 130.5, 128.9, 128.7, 128.4, 126.3, 123.7, 119.5, 113.6, 107.0, 87.0, 86.5, 67.5, 55.1, 21.1; **IR (cm^{-1})**: *v* 3027, 2933, 2856, 2210, 1744, 1605, 1030, 958, 833; **HRMS** m/z (ESI) calculated for $C_{25}H_{22}NO_3$ $[M + H]^+$: 384.1594, found: 384.1593.



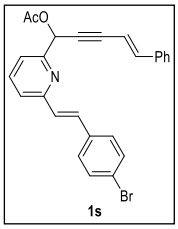
(*E*)-1-(6-((*E*)-4-methylstyryl)pyridin-2-yl)-5-phenylpent-4-en-2-yn-1-yl acetate

Compound **1r** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (t, 1H, *J* = 8.0 Hz), 7.76 (d, 1H, *J* = 8.0 Hz), 7.66 – 7.52 (m, 5H), 7.49 – 7.45 (m, 3H), 7.35 – 7.30 (m, 3H), 7.08 (d, 1H, *J* = 12.4 Hz), 6.92 (d, 1H, *J* = 12.4 Hz), 6.87 (d, 1H, *J* = 1.6 Hz), 6.46 (dd, 1H, J_1 = 16.0 Hz, J_2 = 1.6 Hz), 2.58 (s, 3H), 2.43 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 156.5, 155.7, 142.8, 137.6, 136.6, 135.9, 133.8, 133.6, 129.4, 129.0, 128.9, 128.9, 128.7, 126.4, 123.7, 119.6, 107.1, 87.0, 86.6, 67.5, 21.2, 21.1; **IR (cm^{-1})**: *v* 3024, 2922, 2851, 2218, 1745, 1616, 1013, 980, 749; **HRMS** m/z (ESI) calculated for $C_{27}H_{24}NO_2$ $[M + H]^+$: 394.1802, found: 394.1801.



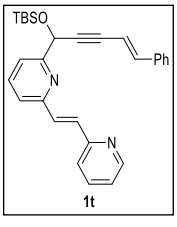
(*E*)-1-(6-((*E*)-4-bromostyryl)pyridin-2-yl)-5-phenylpent-4-en-2-yn-1-yl acetate

Compound **1s** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (t, 1H, *J* = 8.0 Hz), 7.43 (d, 1H, *J* = 8.0 Hz), 7.39 – 7.29 (m, 7H), 7.23 (s, 1H), 7.21 (s, 1H), 7.14 (d, 1H, *J* = 8.0 Hz), 7.02 (d, 1H, *J* = 16.0 Hz), 6.75 (d, 1H, *J* = 12.8 Hz), 6.71 (d, 1H, *J* = 12.8 Hz), 6.59 (d, 1H, *J* = 2.0 Hz), 6.19 (dd, 1H, J_1 = 16.0 Hz, J_2 = 2.0 Hz), 2.16 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 155.9, 155.8, 142.9, 136.9, 135.9, 135.4, 132.5, 131.4, 130.8, 130.6, 128.9, 128.7, 126.4, 123.7, 121.7, 119.9, 107.0, 86.9, 86.6, 67.4, 21.0; **IR (cm^{-1})**: *v* 3017, 2924, 2856, 2215, 1744, 1623, 1010, 956, 748; **HRMS** m/z (ESI) calculated for $C_{26}H_{21}BrNO_2$ $[M + H]^+$: 458.0750, found: 458.0755.



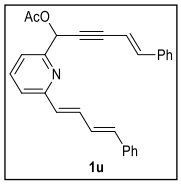
2-((*E*)-1-((tert-butyldimethylsilyl)oxy)-5-phenylpent-4-en-2-yn-1-yl)-6-((*E*)-2-(pyridin-2-yl)vinyl)pyridine

Compound **1t** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.52 (d, 1H, *J* = 3.0 Hz), 7.66 (m, 3H), 7.55 (dd, 1H, J_1 = 15.0 Hz, J_2 = 7.5 Hz), 7.48 (d, 1H, *J* = 7.5 Hz), 7.34 (d, 1H, *J* = 7.5 Hz), 7.27 – 7.24 (m, 3H), 7.20 – 7.12 (m, 3H), 7.04 (t, 1H, *J* = 6.0 Hz), 6.84 (d, 1H, *J* = 16.0 Hz), 6.09 (d, 1H, *J* = 16.0 Hz), 5.67 (s, 1H), 0.88 (s, 9H), 0.17 (s, 3H), 0.10 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.7, 155.0, 153.9, 149.6, 141.4, 137.4, 136.5, 136.0, 132.0, 131.7, 128.6, 128.5, 126.1, 122.8, 122.4, 121.9, 119.2, 107.7, 91.8, 84.8, 67.4, 25.8, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3016, 2928, 2856, 2217, 1630, 1450, 1328, 1077, 954, 746; **HRMS** m/z (ESI) calculated for $C_{29}H_{33}N_2OSi$ $[M + H]^+$: 453.2357, found: 453.2352.



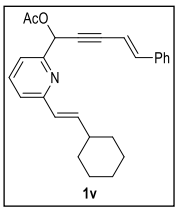
(*E*)-5-phenyl-1-(6-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)pyridin-2-yl)pent-4-en-2-yn-1-yl acetate

Compound **1u** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (t, 1H, *J* = 7.6 Hz), 7.35 – 7.26 (m, 4H), 7.22 – 7.07 (m, 9H), 6.89 – 6.79 (m, 2H), 6.63 (d, 1H, *J* = 15.6 Hz), 6.58 (d, 1H, *J* = 16.4 Hz), 6.50 (s, 1H), 6.04 (dd, 1H, J_1 = 16.4 Hz, J_2 = 2.0 Hz), 2.02 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 155.8, 155.5, 142.8, 137.3, 136.9, 135.8, 135.5, 133.9, 131.5, 128.8, 128.7, 128.6, 128.3, 127.9, 126.6, 126.3, 121.4, 119.7, 107.0, 87.0, 86.5, 67.6, 21.0; **IR (cm^{-1})**: *v* 3020, 2924, 2849, 2214, 1743, 1618, 1025, 957, 749; **HRMS** m/z (ESI) calculated for $C_{28}H_{24}NO_2$ $[M + H]^+$: 406.1802, found: 406.1795.



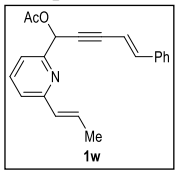
(*E*)-1-(6-((*E*)-2-cyclohexylvinyl)pyridin-2-yl)-5-phenylpent-4-en-2-yn-1-yl acetate

Compound **1v** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (t, 1H, *J* = 8.0 Hz), 7.31 (d, 1H, *J* = 8.0 Hz), 7.25 – 7.13 (m, 5H), 7.03 (d, 1H, *J* = 8.0 Hz), 6.90 (d, 1H, *J* = 16.4 Hz), 6.55 (s, 1H), 6.22 (d, 1H, *J* = 12.0 Hz), 6.08 (dd, 1H, J_1 = 16.4 Hz, J_2 = 2.0 Hz), 5.63 (dd, 1H, J_1 = 12.0 Hz, J_2 = 9.6 Hz), 3.22 – 3.14 (m, 1H), 2.05 (s, 3H), 1.75 – 1.72 (m, 2H), 1.64 – 1.55 (m, 3H), 1.31 – 1.22 (m, 2H), 1.16 – 0.99 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.4, 156.6, 155.2, 144.2, 142.6, 136.9, 135.7, 128.7, 128.6, 126.2, 125.6, 123.4, 118.6, 107.0, 87.2, 86.1, 67.4, 37.0, 32.6, 26.0, 25.6, 20.9; **IR (cm^{-1})**: *v* 3009, 2923, 2848, 2215, 1745, 1640, 1026, 957, 748; **HRMS** m/z (ESI) calculated for $C_{26}H_{28}NO_2$ $[M + H]^+$: 386.2115, found: 386.2109.



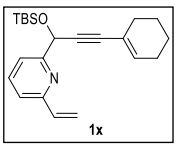
(*E*)-5-phenyl-1-(6-((*E*)-prop-1-en-1-yl)pyridin-2-yl)pent-4-en-2-yn-1-yl acetate

Compound **1w** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (t, 1H, *J* = 7.6 Hz), 7.41 (d, 1H, *J* = 7.6 Hz), 7.38 – 7.28 (m, 5H), 7.22 (d, 1H, *J* = 7.6 Hz), 7.01 (d, 1H, *J* = 16.0 Hz), 6.83 – 6.74 (m, 1H), 6.55 (d, 1H, *J* = 2.0 Hz), 6.53 (dd, 1H, J_1 = 16.0 Hz, J_2 = 2.0 Hz), 6.19 (dd, 1H, J_1 = 16.0 Hz, J_2 = 2.0 Hz), 2.17 (s, 3H), 1.93 (dd, 1H, J_1 = 6.8 Hz, J_2 = 2.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 156.0, 155.5, 142.7, 137.3, 135.9, 131.6, 130.9, 128.8, 128.7, 126.3, 120.4, 119.4, 107.0, 87.1, 86.4, 67.6, 21.0, 18.3; **IR (cm^{-1})**: *v* 3027, 2931, 2853, 2215, 1743, 1644, 1025, 957, 749; **HRMS** m/z (ESI) calculated for $C_{21}H_{20}NO_2$ $[M + H]^+$: 318.1489, found: 318.1481.



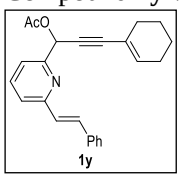
2-(1-((tert-butyldimethylsilyl)oxy)-3-(cyclohex-1-en-1-yl)prop-2-yn-1-yl)-6-vinylpyridine

Compound **1x** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 (t, 1H, *J* = 7.5 Hz), 7.41 (d, 1H, *J* = 7.5 Hz), 7.13 (d, 1H, *J* = 7.5 Hz), 6.71 (dd, 1H, J_1 = 17.5 Hz, J_2 = 11.0 Hz), 6.08 (d, 1H, *J* = 17.5 Hz), 5.97 (s, 1H), 5.54 (s, 1H), 5.35 (d, 1H, *J* = 11.0 Hz), 1.99 – 1.94 (m, 4H), 1.49 – 1.43 (m, 4H), 0.84 (s, 9H), 0.11 (s, 3H), 0.04 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.8, 154.7, 137.2, 136.9, 134.8, 120.3, 119.7, 119.0, 118.1, 87.4, 86.9, 67.3, 28.9, 25.8, 25.5, 22.2, 21.4, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3016, 2928, 2851, 2217, 1630, 1454, 1332, 1082, 991; **HRMS** m/z (ESI) calculated for $C_{22}H_{32}NOSi$ $[M + H]^+$: 354.2248, found: 354.2242.



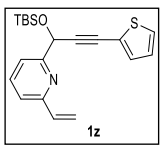
(*E*)-3-(cyclohex-1-en-1-yl)-1-(6-styrylpyridin-2-yl)prop-2-yn-1-yl acetate

Compound **1y** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (t, 1H, *J* = 8.0 Hz), 7.39 (d, 1H, *J* = 8.0 Hz), 7.31 – 7.22 (m, 5H), 7.12 (d, 1H, *J* = 8.0 Hz), 6.83 (d, 1H, *J* = 12.4 Hz), 6.68 (d, 1H, *J* = 12.4 Hz), 6.54 (s, 1H), 6.20 – 6.17 (m, 1H), 2.15 – 2.06 (m, 7H), 1.64 – 1.53 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.5, 156.1, 156.0, 136.6, 136.5, 136.5, 133.6, 130.2, 128.9, 128.2, 127.6, 123.5, 119.8, 119.7, 89.2, 82.3, 67.4, 28.8, 25.6, 22.1, 21.3, 21.1; **IR (cm^{-1})**: *v* 3021, 2928, 2851, 2216, 1768, 1635, 1022, 912, 699; **HRMS** m/z (ESI) calculated for $C_{24}H_{24}NO_2$ $[M + H]^+$: 358.1802, found: 358.1793.



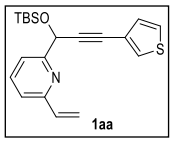
2-(1-((tert-butyldimethylsilyl)oxy)-3-(thiophen-2-yl)prop-2-yn-1-yl)-6-vinylpyridine

Compound **1z** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (t, 1H, *J* = 7.5 Hz), 7.59 (d, 1H, *J* = 7.5 Hz), 7.30 (d, 1H, *J* = 7.5 Hz), 7.24 (dd, 1H, J_1 = 5.0 Hz, J_2 = 1.0 Hz), 7.21 – 7.20 (m, 1H), 6.96 (dd, 1H, J_1 = 5.0 Hz, J_2 = 3.5 Hz), 6.86 (dd, 1H, J_1 = 17.5 Hz, J_2 = 11.0 Hz), 6.24 (d, 1H, *J* = 17.5 Hz), 5.80 (s, 1H), 5.51 (d, 1H, *J* = 11.0 Hz), 1.00 (s, 9H), 0.28 (s, 3H), 0.21 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)**, δ 160.1, 154.3, 137.3, 136.8, 132.0, 127.0, 126.8, 122.8, 120.0, 119.0, 118.4, 93.4, 78.9, 67.3, 25.8, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3016, 2929, 2856, 2221, 1613, 1454, 1360, 1084, 991; **HRMS** m/z (ESI) calculated for $C_{20}H_{26}NOSSi$ $[M + H]^+$: 356.1499, found: 356.1498.



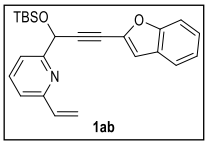
2-(1-((tert-butyldimethylsilyl)oxy)-3-(thiophen-3-yl)prop-2-yn-1-yl)-6-vinylpyridine

Compound **1aa** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.73 (t, 1H, *J* = 8.0 Hz), 7.63 (d, 1H, *J* = 8.0 Hz), 7.47(s, 1H), 7.31 (d, 1H, *J* = 8.0 Hz), 7.26 – 7.25 (m, 1H), 7.14 (d, 1H, *J* = 4.5 Hz), 6.89 (dd, 1H, J_1 = 17.5 Hz, J_2 = 11.0 Hz), 6.27 (d, 1H, *J* = 17.5 Hz), 5.83 (s, 1H), 5.53 (d, 1H, *J* = 4.5 Hz), 1.04 (s, 9H), 0.32 (s, 3H), 0.25 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.3, 154.8, 137.2, 136.8, 129.7, 128.7, 125.0, 121.8, 119.9, 118.9, 118.3, 89.2, 80.7, 67.2, 25. 8, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3108, 2928, 2856, 2226, 1620, 1360, 1083, 930; **HRMS** m/z (ESI) calculated for $C_{20}H_{26}NOSSi$ $[M + H]^+$: 356.1499, found: 356.1497.



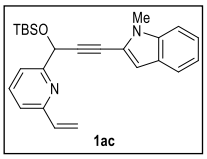
2-(3-(benzofuran-2-yl)-1-((tert-butyldimethylsilyl)oxy)prop-2-yn-1-yl)-6-vinylpyridine

Compound **1ab** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (t, 1H, *J* = 7.6 Hz), 7.61 (d, 1H, *J* = 7.6 Hz), 7.54 (d, 1H, *J* = 7.6 Hz), 7.49 (d, 1H, *J* = 7.6 Hz), 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 6.94 (s, 1H), 6.86 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.26 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.2 Hz), 5.85 (s, 1H), 5.51 (dd, 1H, J_1 = 10.8 Hz, J_2 = 1.2 Hz), 1.01 (s, 9H), 0.30 (s, 3H), 0.22 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.5, 154.9, 154.7, 138.3, 137.4, 136.7, 127.4, 125.5, 123.1, 121.1, 120.2, 119.0, 118.5, 111.8, 111.1, 95.5, 75.9, 67.2, 25.8, 18.3, -4.6, -5.0; **IR (cm^{-1})**: *v* 3060, 2929, 2856, 2213, 1670, 1451, 1347, 1109, 991, 749; **HRMS** m/z (ESI) calculated for $C_{24}H_{28}NO_2Si$ $[M + H]^+$: 390.1884, found: 390.1882.



2-(3-((tert-butyldimethylsilyl)oxy)-3-(6-vinylpyridin-2-yl)prop-1-yn-1-yl)-1-methyl-1H-indole

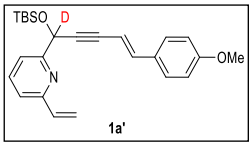
Compound **1ac** was obtained as a yellow liquid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.73 (t, 1H, *J* = 8.0 Hz), 7.61 (d, 1H, *J* = 8.0 Hz), 7.57 (d, 1H, *J* = 8.0 Hz), 7.30 (d, 1H, *J* = 8.0 Hz), 7.25 – 7.24 (m, 2H), 7.12 – 7.09 (m, 1H), 6.85 (dd, 1H, J_1 = 17.5 Hz, J_2 = 11.0 Hz), 6.75 (s, 1H), 6.25 (d, 1H, *J* = 17.5 Hz), 5.87 (s, 1H), 5.50 (d, 1H, *J* = 11.0 Hz), 3.76 (s, 3H), 1.00 (s, 9H), 0.29 (s, 3H), 0.22 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.1, 154.9, 137.4, 137.1, 136.8, 127.1, 122.9, 121.7, 120.9, 120.1, 120.0, 118.9, 118.4, 109.3, 107.3, 95.7, 77.4, 67.4, 30.5, 25.8, 18.4, -4.5, -4.9; **IR (cm^{-1})**: *v* 3054, 2928, 2855, 2224, 1651, 1455, 1342, 1100, 991, 748; **HRMS** m/z (ESI) calculated for $C_{25}H_{31}N_2OSi$ $[M + H]^+$: 403.2200, found: 403.2209.



1ac

(*E*)-2-(1-((tert-butyldimethylsilyl)oxy)-5-(4-methoxyphenyl)pent-4-en-2-yn-1-yl-1-d)-6-vinylpyridine

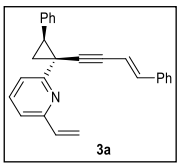
Compound **1a'** was obtained as a yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (t, 1H, *J* = 7.6 Hz), 7.38 (d, 1H, *J* = 7.6 Hz), 7.12 – 7.08 (m, 3H), 6.72 – 6.63 (m, 4H), 6.03 (d, 1H, *J* = 16.0 Hz), 5.86 (d, 1H, *J* = 16.0 Hz), 5.30 (dd, 1H, J_1 = 10.8 Hz, J_2 = 0.8 Hz), 3.60 (s, 3H), 0.79 (s, 9H), 0.07 (s, 3H), 0.00 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.5, 159.9, 154.8, 140.9, 137.3, 136.9, 129.0, 127.5, 119.8, 119.0, 118.2, 114.0, 105.4, 90.9, 85.1, 55.2, 25.8, 18.3, -4.5, -4.9; **IR (cm^{-1})**: *v* 3033, 2929, 2856, 2208, 1605, 1454, 1250, 1082, 780; **HRMS** m/z (ESI) calculated for $C_{25}H_{31}DNO_2Si$ $[M + H]^+$: 407.2260, found: 407.2251.



1a'

(*E*)-2-(2-phenyl-1-(4-phenylbut-3-en-1-yn-1-yl)cyclopropyl)-6-vinylpyridine

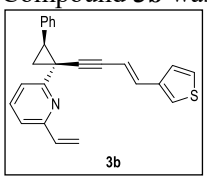
Compound **3a** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, 1H, *J* = 7.6 Hz), 7.58 (d, 1H, *J* = 7.6 Hz), 7.34 – 7.28 (m, 10H), 7.11 (d, 1H, *J* = 7.6 Hz), 6.78 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.64 (d, 1H, *J* = 16.4 Hz), 6.26 (d, 1H, *J* = 17.6 Hz), 6.06 (d, 1H, *J* = 16.4 Hz), 5.44 (d, 1H, *J* = 10.8 Hz), 3.18 (t, 1H, *J* = 7.6 Hz), 2.46 (dd, 1H, J_1 = 8.8 Hz, J_2 = 4.0 Hz), 1.93 (dd, 1H, J_1 = 7.6 Hz, J_2 = 4.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.8, 154.7, 140.5, 137.8, 137.0, 136.5, 136.4, 128.6, 128.6, 128.3, 127.8, 126.4, 126.0, 120.3, 118.7, 117.8, 108.3, 92.0, 83.0, 38.0, 28.2, 25.6; **IR (cm^{-1})**: *v* 3051, 2925, 2850, 2206, 1570, 1237, 952, 696; **HRMS** m/z (ESI) calculated for $C_{26}H_{22}N$ $[M + H]^+$: 348.1747, found: 348.1754.



3a

(*E*)-2-(2-phenyl-1-(4-(thiophen-3-yl)but-3-en-1-yn-1-yl)cyclopropyl)-6-vinylpyridine

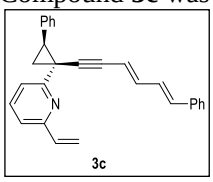
Compound **3b** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, 1H, *J* = 7.6 Hz), 7.57 (t, 1H, *J* = 7.6 Hz), 7.33 – 7.32 (m, 4H), 7.26 – 7.22 (m, 2H), 7.13 – 7.09 (m, 3H), 6.78 (dd, 1H, J_1= 17.2 Hz, J_2 = 10.8 Hz), 6.65 (d, 1H, *J* = 16.0 Hz), 6.25 (d, 1H, *J* = 17.2 Hz), 5.90 (d, 1H, *J* = 16.0 Hz), 5.43 (d, 1H, *J* = 10.8 Hz), 3.19 – 3.15 (m, 1H), 2.45 (ddd, 1H, J_1 = 8.8 Hz, J_2 = 4.0 Hz, J_3 = 1.6 Hz), 1.92 (ddd, 1H, J_1 = 7.6 Hz, J_2 = 4.0 Hz, J_3 = 1.6 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.9, 154.6, 139.3, 137.8, 137.0, 134.6, 128.6, 127.7, 126.4, 126.3, 124.3, 122.9, 120.3, 118.7, 117.8, 108.1, 91.8, 82.9, 77.3, 77.0, 76.7, 37.9, 28.1, 25.6; **IR (cm^{-1})**: *v* 3029, 2931, 2855, 2209, 1570, 1274, 991, 697; **HRMS** m/z (ESI) calculated for $C_{24}H_{20}NS$ $[M + H]^+$: 354.1311, found: 354.1318.



3b

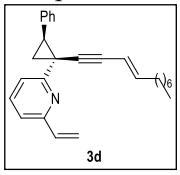
2-(2-phenyl-1-((3*E*,5*E*)-6-phenylhexa-3,5-dien-1-yn-1-yl)cyclopropyl)-6-vinylpyridine

Compound **3c** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, 1H, *J* = 7.6 Hz), 7.60 (t, 1H, *J* = 7.6 Hz), 7.41 – 7.23 (m, 10H), 7.13 (d, 1H, *J* = 7.6 Hz), 6.85 – 6.73 (m, 2H), 6.57 – 6.47 (m, 2H), 6.29 (d, 1H, *J* = 17.2 Hz), 5.66 (d, 1H, *J* = 15.2 Hz), 5.47 (d, 1H, *J* = 10.8 Hz), 3.21 (t, 1H, *J* = 7.6 Hz), 2.49 (ddd, 1H, J_1 = 5.2 Hz, J_2 = 4.0 Hz, J_3 = 1.2 Hz), 1.96 (ddd, 1H, J_1 = 5.2 Hz, J_2 = 4.0 Hz, J_3 = 1.2 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.8, 154.6, 141.1, 137.8, 136.9, 136.8, 136.5, 133.7, 128.6, 128.5, 128.1, 127.9, 127.7, 126.5, 126.4, 120.3, 118.8, 117.8, 111.7, 93.2, 83.4, 38.1, 28.2, 25.7; **IR (cm^{-1})**: *ν* 3025, 2925, 2855, 2207, 1631, 1271, 983, 692; **HRMS** m/z (ESI) calculated for $C_{28}H_{24}N$ $[M + H]^+$: 374.1903, found: 374.1900.



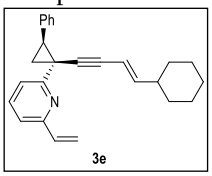
(*E*)-2-(2-phenyl-1-(undec-3-en-1-yn-1-yl)cyclopropyl)-6-vinylpyridine

Compound **3d** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, 1H, *J* = 7.6 Hz), 7.57 (t, 1H, *J* = 7.6 Hz), 7.34 – 7.30 (m, 4H), 7.24 – 7.21 (m, 1H), 7.10 (d, 1H, *J* = 7.6 Hz), 6.78 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.25 (d, 1H, *J* = 17.6 Hz), 5.91 – 5.84 (m, 1H), 5.45 – 5.36 (m, 2H), 3.13 (t, 1H, *J* = 7.6 Hz), 2.41 (dd, 1H, J_1 = 8.8 Hz, J_2 = 4.0 Hz), 2.03 (dd, 2H, J_1 = 14.0 Hz, J_2 = 6.8 Hz), 1.87 (dd, 1H, J_1 = 7.6 Hz, J_2 = 4.0 Hz), 1.35 – 1.27 (m, 10H), 0.89 (t, 3H, *J* = 6.8 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.1, 154.6, 144.1, 138.0, 137.0, 136.4, 128.6, 127.6, 126.3, 120.3, 118.6, 117.7, 109.3, 87.5, 82.6, 37.7, 32.9, 31.8, 29.1, 29.0, 28.8, 27.9, 25.5, 22.6, 14.1; **IR (cm^{-1})**: *ν* 3034, 2925, 2854, 2205, 1570, 1233, 954, 696; **HRMS** m/z (ESI) calculated for $C_{27}H_{32}N$ $[M + H]^+$: 370.2529, found: 370.2538.



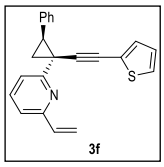
(*E*)-2-(1-(4-cyclohexylbut-3-en-1-yn-1-yl)-2-phenylcyclopropyl)-6-vinylpyridine

Compound **3e** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, 1H, *J* = 7.6 Hz), 7.56 (d, 1H, *J* = 7.6 Hz), 7.33 – 7.29 (m, 4H), 7.25 – 7.21 (m, 1H), 7.09 (d, 1H, *J* = 7.6 Hz), 6.77 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.8 Hz), 6.25 (dd, 1H, J_1 = 17.2 Hz, J_2 = 1.2 Hz), 5.83 (dd, 1H, J_1 = 16.0 Hz, J_2 = 7.6 Hz), 5.43 (dd, 1H, J_1 = 10.8 Hz, J_2 = 1.2 Hz), 5.33 (dd, 1H, J_1 = 16.0 Hz, J_2 = 1.2 Hz), 3.12 (t, 1H, *J* = 7.6 Hz), 2.41 (dd, 1H, J_1 = 8.8 Hz, J_2 = 4.0 Hz), 1.97 – 1.93 (m, 1H), 1.86 (dd, 1H, J_1 = 7.6 Hz, J_2 = 4.0 Hz), 1.73 – 1.62 (m, 5H), 1.29 – 0.98 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.1, 154.5, 149.4, 137.9, 137.0, 136.4, 128.5, 127.6, 126.3, 120.3, 118.6, 117.7, 107.1, 87.8, 82.8, 41.1, 37.7, 32.3, 28.0, 26.0, 25.8, 25.5; **IR (cm^{-1})**: *ν* 3028, 2924, 2850, 2208, 1605, 1273, 957, 696; **HRMS** m/z (ESI) calculated for $C_{26}H_{28}N$ $[M + H]^+$: 354.2216, found: 354.2226.



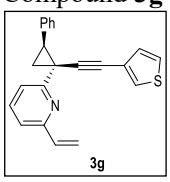
2-(2-phenyl-1-(thiophen-2-ylethynyl)cyclopropyl)-6-vinylpyridine

Compound **3f** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, 1H, J = 7.6 Hz), 7.62 (t, 1H, J = 7.6 Hz), 7.37 – 7.36 (m, 4H), 7.30 – 7.26 (m, 1H), 7.17 – 7.14 (m, 2H), 6.99 (dd, 1H, J_1 = 4.0 Hz, J_2 = 1.6 Hz), 6.91 (dd, 1H, J_1 = 5.2 Hz, J_2 = 4.0 Hz), 6.82 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.30 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.6 Hz), 5.48 (dd, 1H, J_1 = 10.8 Hz, J_2 = 1.6 Hz), 3.25 (dd, 1H, J_1 = 8.8 Hz, J_2 = 7.6 Hz), 2.53 (dd, 1H, J_1 = 8.8 Hz, J_2 = 4.4 Hz), 2.02 (dd, 1H, J_1 = 7.6 Hz, J_2 = 4.4 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 154.7, 137.6, 136.9, 136.5, 131.4, 128.5, 127.8, 126.7, 126.5, 126.3, 123.6, 120.3, 118.8, 117.9, 93.6, 38.1, 28.0, 25.6; **IR (cm^{-1})**: *v* 3055, 2922, 2851, 2210, 1603, 1223, 991, 699; **HRMS** m/z (ESI) calculated for $C_{22}H_{18}NS$ $[M + H]^+$: 328.1154, found: 328.1153.



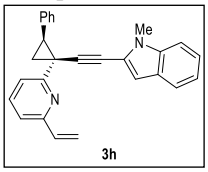
2-(2-phenyl-1-(thiophen-3-ylethynyl)cyclopropyl)-6-vinylpyridine

Compound **3g** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, 1H, J = 8.0 Hz), 7.58 (t, 1H, J = 8.0 Hz), 7.37 – 7.31 (m, 4H), 7.27 – 7.23 (m, 1H), 7.18 – 7.15 (m, 2H), 7.11 (d, 1H, J = 8.0 Hz), 6.86 (dd, 1H, J_1 = 4.8 Hz, J_2 = 1.6 Hz), 6.79 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 6.27 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.6 Hz), 5.45 (dd, 1H, J_1 = 10.8 Hz, J_2 = 1.6 Hz), 3.20 (dd, 1H, J_1 = 8.8 Hz, J_2 = 7.6 Hz), 2.47 (dd, 1H, J_1 = 8.8 Hz, J_2 = 4.0 Hz), 1.97 (dd, 1H, J_1 = 7.6 Hz, J_2 = 4.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.8, 154.6, 137.9, 137.0, 136.5, 129.9, 128.6, 127.9, 127.7, 126.4, 124.9, 122.5, 120.3, 118.8, 117.8, 89.0, 78.6, 37.8, 27.8, 25.3; **IR (cm^{-1})**: *v* 3058, 2923, 2851, 2229, 1602, 1272, 932, 697; **HRMS** m/z (ESI) calculated for $C_{22}H_{18}NS$ $[M + H]^+$: 328.1154, found: 328.1150.



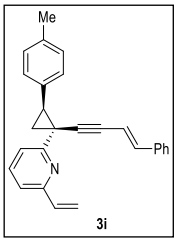
1-methyl-2-((2-phenyl-1-(6-vinylpyridin-2-yl)cyclopropyl)ethynyl)-1H-indole

Compound **3h** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, 1H, J = 7.6 Hz), 7.63 (t, 1H, J = 7.6 Hz), 7.54 (d, 1H, J = 7.6 Hz), 7.39 – 7.32 (m, 4H), 7.29 – 7.24 (m, 1H), 7.22 – 7.15 (m, 3H), 7.09 (t, 1H, J = 7.6 Hz), 6.82 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.8 Hz), 6.65 (s, 1H), 6.31 (d, 1H, J = 17.2 Hz), 5.48 (d, 1H, J = 10.8 Hz), 3.33 (t, 1H, J = 8.0 Hz), 3.27 (s, 3H), 2.53 (dd, 1H, J_1 = 8.0 Hz, J_2 = 4.4 Hz), 2.09 (dd, 1H, J_1 = 7.6 Hz, J_2 = 4.4 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 154.7, 137.6, 136.9, 136.8, 136.6, 128.8, 128.0, 127.0, 126.7, 122.6, 122.2, 120.6, 120.3, 119.8, 118.9, 118.0, 109.2, 106.8, 95.6, 74.9, 37.9, 29.9, 27.9, 25.2; **IR (cm^{-1})**: *v* 3057, 2925, 2851, 2215, 1629, 1265, 991, 693; **HRMS** m/z (ESI) calculated for $C_{27}H_{23}N_2$ $[M + H]^+$: 375.1856, found: 375.1855.



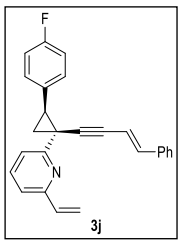
(*E*)-2-(1-(4-phenylbut-3-en-1-yn-1-yl)-2-(p-tolyl)cyclopropyl)-6-vinylpyridine

Compound **3i** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, 1H, J = 8.0 Hz), 7.60 (t, 1H, J = 8.0 Hz), 7.34 – 7.29 (m, 4H), 7.27 – 7.23 (m, 3H), 7.17 – 7.11 (m, 3H), 6.80 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.8 Hz), 6.68 (d, 1H, J = 16.0 Hz), 6.27 (dd, 1H, J_1 = 17.2 Hz, J_2 = 1.2 Hz), 6.10 (d, 1H, J = 16.0 Hz), 5.45 (dd, 1H, J_1 = 10.8 Hz, J_2 = 1.2 Hz), 3.15 (t, 1H, J = 8.0 Hz), 2.46 (dd, 1H, J_1 = 8.8 Hz, J_2 = 4.4 Hz), 2.37 (s, 3H), 1.92 (dd, 1H, J_1 = 8.0 Hz, J_2 = 4.4 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.9, 154.6, 140.4, 137.0, 136.5, 136.4, 135.9, 134.7, 128.6, 128.5, 128.4, 128.3, 126.0, 120.3, 118.7, 117.8, 108.4, 92.2, 83.0, 37.9, 28.1, 25.7, 21.1; **IR (cm^{-1})**: *v* 3025, 2922, 2851, 2200, 1570, 1275, 747; **HRMS** m/z (ESI) calculated for $C_{27}H_{24}N$ $[M + H]^+$: 362.1903, found: 362.1911.



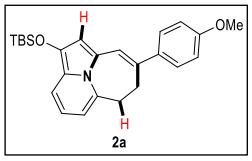
(*E*)-2-(2-(4-fluorophenyl)-1-(4-phenylbut-3-en-1-yn-1-yl)cyclopropyl)-6-vinylpyridine

Compound **3j** was obtained as a colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.4 Hz), 7.6 (td, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.35 – 7.26 (m, 7H), 7.14 (d, 1H, *J* = 8.0 Hz), 7.08 – 7.03 (m, 2H), 6.81(ddd, 1H, J_1 = 17.2 Hz, J_2 = 10.8 Hz, J_3 = 2.0 Hz), 6.70 (dd, 1H, J_1 = 16.0 Hz, J_2 = 2.4 Hz), 6.28 (dt, 1H, J_1 = 17.2 Hz, J_2 = 2.0 Hz), 6.10 (dd, 1H, J_1 = 16.0 Hz, J_2 = 2.0 Hz), 5.47 (dt, 1H, J_1 = 10.8 Hz, J_2 = 2.0 Hz), 3.22 – 3.18 (m, 1H), 2.49 – 2.45 (m, 1H), 1.96 – 1.89 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 160.5, 158.6, 154.6, 140.7, 136.7 (d, *J* = 38.7 Hz), 136.3, 133.6 (d, *J* = 3.3 Hz), 130. 0 (d, *J* = 8.0 Hz), 128.6, 128.4, 126.0, 120.3, 118.8, 117.9, 114.6 (d, *J* = 21.2 Hz), 108.1, 91.7, 83.1, 37.0, 27.9, 25.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -116.44 (s, 1F); **IR (cm^{-1}):** *ν* 3056, 2926, 2849, 2208, 1604, 1228, 952, 747; **HRMS** m/z (ESI) calculated for $C_{26}H_{21}FN$ $[M + H]^+$: 366.1653, found: 366.1655.



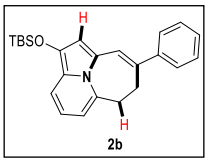
2-((tert-butyldimethylsilyl)oxy)-8-(4-methoxyphenyl)-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure A, compound **2a** was obtained as a yellow amorphous solid in 96% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.37 (m, 2H), 7.30 (d, 1H, *J* = 8.8 Hz), 6.94 – 6.90 (m, 2H), 6.77 (s, 1H), 6.54 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.8 Hz), 6.45 (s, 1H), 6.24 (d, 1H, *J* = 6.8 Hz), 3.85 (s, 3H), 3.18 (t, 2H, *J* = 4.8 Hz), 3.07 (t, 2H, *J* = 4.8 Hz), 1.10 (s, 9H), 0.27 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1, 138.3, 136.3, 133.5, 126.4, 126.1, 120.8, 117.8, 114.8, 114.8, 113.7, 110.3, 108.2, 55.3, 34.5, 32.3, 25.8, 18.2, -4.6; **IR (cm^{-1})**: *ν* 3023, 2929, 2856, 1618, 1433, 1395, 1252, 1037, 807; **HRMS** m/z (ESI) calculated for $C_{25}H_{32}NO_2Si$ $[M + H]^+$: 406.2197, found: 406.2199.



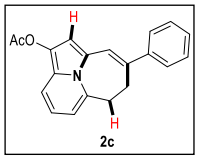
2-((tert-butyldimethylsilyl)oxy)-8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure A, compound **2b** was obtained as a yellow thick liquid in 92% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.44 (m, 2H), 7.38 – 7.34 (m, 2H), 7.28 (d, 1H, *J* = 8.8 Hz), 7.22 (t, 1H, *J* = 7.2 Hz), 6.82 (s, 1H), 6.54 (dd, 1H, J_1 = 8.8 Hz, J_2 = 7.2 Hz), 6.44 (s, 1H), 6.25 (d, 1H, *J* = 7.2 Hz), 3.19 (t, 2H, *J* = 4.0 Hz), 3.11 (t, 2H, *J* = 4.0 Hz), 1.07 (s, 9H), 0.25 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.5, 138.5, 133.7, 133.6, 128.3, 126.5, 125.9, 125.3, 120.7, 119.3, 115.2, 114.8, 110.5, 108.6, 34.5, 32.2, 25.8, 18.2, -4.6; **IR (cm^{-1})**: *ν* 3021, 2928, 2851, 1617, 1447, 1361, 1254, 1046, 741; **HRMS** m/z (ESI) calculated for $C_{24}H_{30}NOSi$ $[M + H]^+$: 376.2091, found: 376.2096.



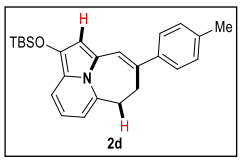
8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2c** was obtained as a yellow thick liquid in 90% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 – 7.48 (m, 2H), 7.43 – 7.40 (m, 2H), 7.31 – 7.29 (m, 2H), 6.94 (s, 1H), 6.91 (s, 1H), 6.72 (t, 1H, *J* = 7.5 Hz), 6.35 (d, 1H, *J* = 7.5 Hz), 3.20 (t, 2H, *J* = 5.0 Hz), 3.10 (t, 2H, *J* = 5.0 Hz), 2.41 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.6, 143.0, 138.7, 134.9, 128.1, 127.8, 126.1, 126.0, 125.2, 121.6, 119.0, 117.4, 113.7, 110.7, 110.3, 34.2, 31.9, 20.6; **IR (cm^{-1})**: *ν* 3051, 2988, 2856, 1764, 1620, 1201, 1011, 761; **HRMS** m/z (ESI) calculated for $C_{20}H_{18}NO_2$ $[M + H]^+$: 304.1332, found: 304.1336.



2-((tert-butyldimethylsilyl)oxy)-8-(p-tolyl)-6,7-dihydroazepino[2,1,7-cd]indolizine

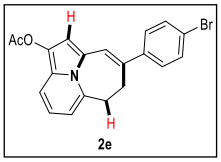
According to the procedure A, compound **2d** was obtained as a yellow thick liquid in 93% yield;



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 2H), 7.16 (d, 1H, *J* = 8.0 Hz), 7.07 – 7.05 (m, 2H), 6.68 (s, 1H), 6.42 (t, 1H, *J* = 6.8 Hz), 6.31 (s, 1H), 6.13 (d, 1H, *J* = 6.8 Hz), 3.07 (t, 2H, *J* = 4.0 Hz), 2.98 (s, 2H, *J* = 4.0 Hz), 2.26 (s, 3H), 0.95 (s, 9H), 0.13 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.7, 138.4, 135.6, 133.8, 133.6, 129.0, 126.3, 125.2, 120.8, 118.5, 115.0, 114.8, 110.4, 108.4, 34.5, 32.2, 25.8, 21.0, 18.2, -4.6; **IR (cm^{-1})**: *v* 3021, 2927, 2850, 1619, 1429, 1394, 1252, 1047, 716; **HRMS** m/z (ESI) calculated for $C_{25}H_{32}NOSi$ $[M + H]^+$: 390.2248, found: 390.2241.

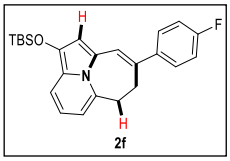
8-(4-bromophenyl)-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2e** was obtained as a yellow thick liquid in 91% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.43 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 (d, 1H, *J* = 8.8 Hz), 6.85 (s, 1H), 6.80 (s, 1H), 6.70 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.34 (d, 1H, *J* = 6.4 Hz), 3.18 (t, 2H, *J* = 4.4 Hz), 3.02 (t, 2H, *J* = 4.4 Hz), 2.37 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.1, 142.0, 138.8, 133.5, 131.3, 127.9, 126.9, 126.5, 121.5, 119.9, 119.5, 117.9, 113.9, 111.0, 110.7, 34.3, 31.8, 20.8; **IR (cm^{-1})**: *v* 3049, 2952, 2855, 1767, 1619, 1201, 1027, 712; **HRMS** m/z (ESI) calculated for $C_{20}H_{16}BrNNaO_2$ $[M + Na]^+$: 404.0257, found: 404.0251.



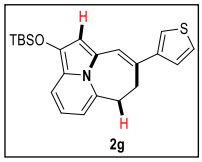
2-((tert-butyldimethylsilyl)oxy)-8-(4-fluorophenyl)-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure A, compound **2f** was obtained as a yellow thick liquid in 90% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 – 7.37 (m, 2H), 7.31 (d, 1H, *J* = 8.5 Hz), 7.05 (t, 2H, *J* = 8.5 Hz), 6.76 (s, 1H), 6.56 (t, 1H, *J* = 7.5 Hz), 6.45 (s, 1H), 6.25 (d, 1H, *J* = 6.0 Hz), 3.17 (t, 2H, *J* = 5.0 Hz), 3.06 (t, 2H, *J* = 5.0 Hz), 1.09 (s, 9H), 0.26 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.3, 160.4, 139.7 (d, *J* = 3.3 Hz), 138.3, 133.7, 132.6, 126.7 (d, *J* = 7.7 Hz), 126.5, 120.4, 119.1, 115.2 (d, *J* = 10.1 Hz), 114.9 (d, *J* = 12.5 Hz), 110.6, 108.6, 34.5, 32.3, 25.8, 18.2, -4.6; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -117.11 (s, 1F); **IR (cm^{-1})**: *v* 3043, 2952, 2857, 1617, 1435, 1391, 1252, 1049, 716; **HRMS** m/z (ESI) calculated for $C_{24}H_{29}FNOSi$ $[M + H]^+$: 394.1997, found: 394.1997.



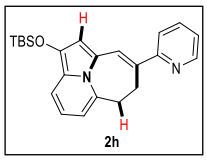
2-((tert-butyldimethylsilyl)oxy)-8-(thiophen-3-yl)-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure A, compound **2g** was obtained as a yellow amorphous solid in 92% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 – 7.26 (m, 3H), 7.09 (s, 1H), 6.91 (s, 1H), 6.54 (t, 1H, *J* = 8.5 Hz), 6.43 (d, 1H, *J* = 6.0 Hz), 6.24 (d, 1H, *J* = 6.0 Hz), 3.17 (t, 2H, *J* = 5.0 Hz), 3.07 (s, 2H, *J* = 5.0 Hz), 1.07 (s, 9H), 0.25 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.7, 138.2, 133.7, 129.1, 126.6, 125.7, 125.0, 120.3, 117.9, 117.7, 115.2, 114.8, 110.5, 108.4, 34.3, 31.9, 25.8, 18.2, -4.6; **IR (cm^{-1})**: *v* 3092, 2950, 2857, 1612, 1435, 1361, 1252, 1047, 715; **HRMS** m/z (ESI) calculated for $C_{22}H_{28}NOSSi$ $[M + H]^+$: 382.1655, found: 382.1655.



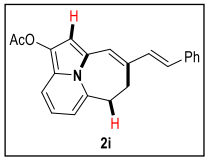
2-((tert-butyldimethylsilyl)oxy)-8-(pyridin-2-yl)-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure A, compound **2h** was obtained as a yellow thick liquid in 91% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.54 (s, 1H), 7.58 (t, 1H, *J* = 7.5 Hz), 7.44 (d, 1H, 7.5 Hz), 7.39 (s, 1H), 7.24 (d, 1H, *J* = 6.0 Hz), 7.02 – 6.99 (m, 1H), 6.56 (t, 1H, *J* = 7.5 Hz), 6.49 (s, 1H), 6.26 (d, 1H, *J* = 6.0 Hz), 3.21 – 3.17 (m, 4H), 1.01 (s, 9H), 0.20 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.7, 148.8, 139.0, 136.2, 134.0, 131.8, 127.6, 121.5, 120.3, 120.1, 118.9, 116.2, 114.8, 110.9, 109.6, 34.5, 29.7, 25.8, 18.2, -4.6; **IR (cm^{-1})**: *v* 3054, 2928, 2855, 1617, 1435, 1260, 1049, 719; **HRMS** m/z (ESI) calculated for $C_{23}H_{29}N_2OSi$ $[M + H]^+$: 377.2044, found: 377.2034.



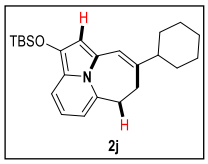
(*E*)-8-styryl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2i** was obtained as a yellow amorphous solid in 91% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.45 (m, 2H), 7.36 – 7.32 (m, 2H), 7.24 – 7.20 (m, 2H), 6.95 (d, 1H, *J* = 16.0 Hz), 6.84 (s, 1H), 6.71 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.63 (s, 1H), 6.48 (d, 1H, *J* = 16.0 Hz), 6.36 (d, 1H, *J* = 6.4 Hz), 3.15 (t, 2H, *J* = 4.4 Hz), 2.92 (t, 2H, *J* = 4.4 Hz), 2.37 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.1, 139.0, 137.9, 133.9, 132.4, 128.6, 128.2, 126.9, 126.7, 126.0, 125.0, 123.0, 121.7, 118.1, 113.9, 111.3, 110.5, 33.7, 27.4, 20.8; **IR (cm^{-1})**: *v* 3052, 2928, 2855, 1749, 1588, 1200, 1049, 719; **HRMS** m/z (ESI) calculated for $C_{22}H_{20}NO_2$ $[M + H]^+$: 330.1489, found: 330.1493.



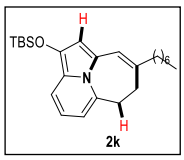
2-((tert-butyldimethylsilyl)oxy)-8-cyclohexyl-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure A, compound **2j** was obtained as a yellow thick liquid in 90% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 (d, 1H, *J* = 8.8 Hz), 6.42 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.8 Hz), 6.29 (s, 1H), 6.24 (s, 1H), 6.11 (d, 1H, *J* = 6.8 Hz), 3.01 (t, 2H, *J* = 4.8 Hz), 2.61 (t, 2H, *J* = 4.8 Hz), 2.05 – 2.00 (m, 1H), 1.83 – 7.73 (m, 5H), 1.40 – 1.17 (m, 5H), 1.08 (s, 9H), 0.25 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.0, 137.9, 132.9, 125.1, 120.9, 114.9, 114.7, 113.8, 109.8, 106.8, 77.3, 77.0, 76.7, 48.0, 34.7, 31.9, 31.7, 26.6, 26.3, 25.8, 18.2, -4.6; **IR (cm^{-1})**: *v* 3048, 2926, 2854, 1659, 1458, 1384, 1256, 1059, 759; **HRMS** m/z (ESI) calculated for $C_{24}H_{35}NOSi$ [M]: 381.2488, found: 381.2480.



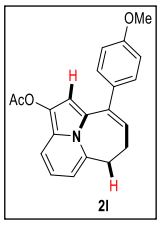
2-((tert-butyldimethylsilyl)oxy)-8-heptyl-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure A, compound **2k** was obtained as a yellow thick liquid in 89% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.22 (d, 1H, *J* = 8.5 Hz), 6.42 (t, 1H, *J* = 8.5 Hz), 6.26 (s, 1H), 6.23 (s, 1H), 6.12 (d, 1H, *J* = 6.0 Hz), 3.03 (t, 2H, *J* = 4.0 Hz), 2.61 (t, 2H, *J* = 4.0 Hz), 2.19 (t, 2H, *J* = 7.0 Hz), 1.52 – 1.49 (m, 2H), 1.35 – 1.32 (m, 8H), 1.06 (s, 9H), 0.94 – 0.91 (m, 3H), 0.23 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.0, 137.1, 132.9, 125.1, 120.8, 116.8, 114.8, 113.8, 110.0, 106.7, 40.5, 34.4, 33.2, 31.9, 29.3, 29.2, 28.2, 25.8, 22.7, 18.2, 14.1, -4.6; **IR (cm^{-1})**: *v* 3022, 2927, 2855, 1621, 1434, 1361, 1250, 1047, 715; **HRMS** m/z (ESI) calculated for $C_{25}H_{40}NOSi$ $[M + H]^+$: 398.2874, found: 398.2875.



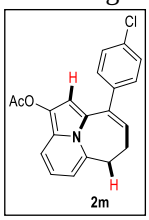
9-(4-methoxyphenyl)-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2l** was obtained as a yellow thick liquid in 95% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.35 (m, 2H), 7.20 (d, 1H, *J* = 9.2 Hz), 6.93 – 6.89 (m, 2H), 6.68 (dd, 1H, J_1 = 9.2 Hz, J_2 = 6.8 Hz), 6.44 (d, 1H, *J* = 1.6 Hz), 6.31 (t, 1H, *J* = 6.8 Hz), 5.79 (t, 1H, *J* = 6.8 Hz), 3.85 (s, 3H), 3.20 (t, 2H, *J* = 4.4 Hz), 2.76 – 2.72 (m, 2H), 2.30 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.2, 158.7, 139.4, 135.9, 135.4, 130.1, 127.0, 126.6, 126.1, 123.9, 117.4, 113.8, 113.2, 111.0, 110.9, 55.2, 35.9, 28.8, 20.7; **IR (cm^{-1})**: *ν* 3052, 2928, 2856, 1770, 1631, 1208, 1083, 719; **HRMS** m/z (ESI) calculated for $C_{21}H_{20}NO_3$ $[M + H]^+$: 334.1438, found: 334.1432.



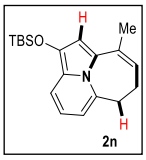
9-(4-chlorophenyl)-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2m** was obtained as a yellow thick liquid in 92% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.31 (m, 4H), 7.19 (dd, 1H, J_1 = 8.8 Hz, J_2 = 1.2 Hz), 6.70 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.36 (s, 1H), 6.33 (d, 1H, *J* = 6.4 Hz), 5.78 (t, 1H, *J* = 6.4 Hz), 3.19 (t, 2H, *J* = 4.8 Hz), 2.76 – 2.72 (m, 2H), 2.30 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.3, 141.9, 139.4, 134.9, 132.9, 130.5, 128.1, 127.1, 126.8, 123.2, 117.7, 113.9, 111.3, 110.8, 35.8, 28.9, 20.7; **IR (cm^{-1})**: *ν* 3048, 2928, 2854, 1766, 1618, 1218, 1014, 763; **HRMS** m/z (ESI) calculated for $C_{20}H_{16}ClNNaO_2$ $[M + Na]^+$: 360.0762, found: 360.0765.



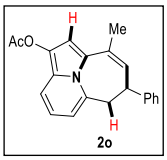
2-((tert-butyldimethylsilyl)oxy)-9-methyl-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure A, compound **2n** was obtained as a yellow thick liquid in 88% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.14 (d, 1H, *J* = 8.5 Hz), 6.38 – 6.35 (m, 2H), 6.01 (d, 1H, *J* = 6.0 Hz), 5.54 (t, 1H, *J* = 6.0 Hz), 2.93 (t, 2H, *J* = 4.5 Hz), 2.49 (t, 2H, *J* = 4.5 Hz), 2.06 (s, 3H), 0.96 (s, 9H), 0.13 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.9, 132.8, 127.7, 125.9, 123.3, 122.6, 114.7, 114.6, 110.2, 105.8, 35.4, 29.0, 25.8, 23.5, 18.2, -4.6; **IR (cm^{-1})**: *ν* 3010, 2928, 2856, 1628, 1431, 1387, 1251, 1058, 716; **HRMS** m/z (ESI) calculated for $C_{19}H_{28}NOSi$ $[M + H]^+$: 314.1935, found: 314.1934.



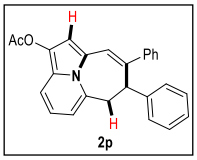
9-methyl-7-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2o** was obtained as a yellow thick liquid in 92% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.29 (m, 2H), 7.24 – 7.21 (m, 2H), 7.15 – 7.13 (m, 2H), 7.00 (s, 1H), 6.63 (dd, 1H, J_1 = 8.4 Hz, J_2 = 6.8 Hz), 6.19 (d, 1H, *J* = 6.0 Hz), 5.80 (d, 2H, *J* = 4.0 Hz), 3.91 (s, 1H), 3.31 – 3.20 (m, 2H), 2.38 (s, 3H), 2.27 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.4, 145.6, 137.4, 128.6, 127.7, 127.4, 127.2, 127.0, 126.4, 126.2, 123.2, 117.5, 113.8, 112.1, 108.0, 45.6, 43.2, 23.7, 20.9; **IR (cm^{-1})**: *ν* 3022, 2924, 2855, 1766, 1631, 1210, 1013, 701; **HRMS** m/z (ESI) calculated for $C_{21}H_{20}NO_2$ $[M + H]^+$: 318.1489, found: 318.1483.



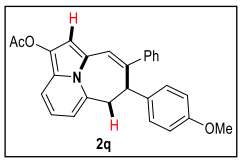
7,8-diphenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2p** was obtained as a yellow thick liquid in 86% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.38 (m, 2H), 7.30 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 7.14 – 7.06 (m, 3H), 7.02 – 7.01 (m, 3H), 6.55 (t, 1H, J = 7.6 Hz), 6.12 (d, 1H, J = 7.6 Hz), 4.83 (d, 1H, J = 4.8 Hz), 3.48 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 3.22 (d, 1H, J = 6.4 Hz), 2.36 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 143.3, 143.2, 136.0, 135.0, 128.6, 128.4, 128.0, 127.2, 126.4, 126.3, 126.2, 125.6, 121.1, 120.5, 117.9, 113.7, 113.2, 110.9, 49.3, 41.3, 21.0; **IR (cm^{-1})**: *v* 3058, 2924, 2855, 1765, 1621, 1201, 1028, 699; **HRMS** m/z (ESI) calculated for $C_{26}H_{21}NNaO_2$ $[M + Na]^+$: 402.1465, found: 402.1469.



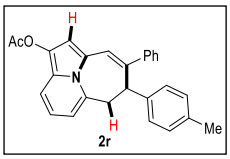
7-(4-methoxyphenyl)-8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2q** was obtained as a yellow thick liquid in 88% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.42 (m, 2H), 7.32 – 7.28 (m, 2H), 7.22 – 7.19 (m, 3H), 7.05 (d, 1H, J = 2.4 Hz), 6.97 – 6.95 (m, 2H), 6.68 – 6.65 (m, 2H), 6.58 (dd, 1H, J_1 = 8.4 Hz, J_2 = 6.8 Hz), 6.15 (d, 1H, J = 6.8 Hz), 4.79 (d, 1H, J = 6.4 Hz), 3.67 (s, 3H), 3.45 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 3.21 (d, 1H, J = 14.4 Hz), 2.38 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 157.9, 143.1, 136.1, 135.4, 135.3, 128.3, 128.1, 127.9, 126.2, 126.1, 125.5, 121.0, 120.2, 117.9, 113.8, 113.6, 113.2, 110.8, 54.9, 48.4, 41.3, 20.9; **IR (cm^{-1})**: *v* 3051, 2928, 2855, 1749, 1609, 1249, 1034, 739; **HRMS** m/z (ESI) calculated for $C_{27}H_{24}NO_3$ $[M + H]^+$: 410.1751, found: 410.1744.



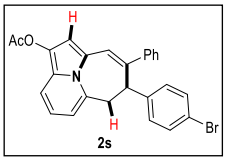
8-phenyl-7-(p-tolyl)-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2r** was obtained as a yellow thick liquid in 86% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.42 (m, 2H), 7.31 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 7.05 (s, 1H), 6.94 – 6.93 (m, 4H), 6.57 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.15 (d, 1H, J = 6.4 Hz), 4.81 (d, 1H, J = 5.2 Hz), 3.48 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 3.23 (d, 1H, J = 14.4 Hz), 2.38 (s, 3H), 2.22 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 143.2, 140.2, 136.2, 135.7, 135.3, 129.3, 128.3, 127.9, 127.0, 126.2, 126.1, 125.6, 121.1, 120.3, 117.9, 113.6, 113.2, 110.8, 48.9, 41.2, 20.9; **IR (cm^{-1})**: *v* 3025, 2922, 2851, 1766, 1621, 1221, 1017, 720; **HRMS** m/z (ESI) calculated for $C_{27}H_{24}NO_2$ $[M + H]^+$: 394.1802, found: 394.1801.



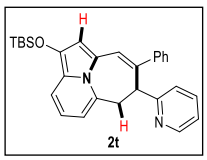
7-(4-bromophenyl)-8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2s** was obtained as a yellow thick liquid in 81% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 – 7.24 (m, 2H), 7.21 – 7.16 (m, 2H), 7.14 – 7.08 (m, 5H), 6.93 (t, 1H, J = 4.0 Hz), 6.81 – 6.78 (m, 2H), 6.47 (t, 1H, J = 7.6 Hz), 6.03 (d, 1H, J = 6.4 Hz), 4.68 (d, 1H, J = 4.8 Hz), 3.34 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 3.10 (d, 1H, J = 14.4 Hz), 2.26 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 142.9, 142.2, 135.6, 134.4, 131.7, 129.0, 128.4, 128.1, 126.4, 126.4, 125.5, 120.9, 120.7, 120.3, 118.0, 114.0, 113.4, 111.1, 48.7, 41.0, 20.9; **IR (cm^{-1})**: *v* 3027, 2922, 2855, 1765, 1621, 1210, 1010, 697; **HRMS** m/z (ESI) calculated for $C_{26}H_{21}BrNO_2$ $[M + H]^+$: 458.0750, found: 458.0759.



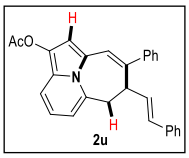
8-phenyl-7-(pyridin-2-yl)-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2t** was obtained as a yellow thick liquid in 85% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.57 (d, 1H, *J* = 4.0 Hz), 7.43 – 7.42 (m, 2H), 7.31 – 7.16 (m, 6H), 6.97 (t, 1H, *J* = 6.5 Hz), 6.63 (d, 1H, *J* = 8.5 Hz), 6.59 (s, 1H), 6.42 (dd, 1H, J_1 = 8.5 Hz, J_2 = 6.5 Hz), 6.11 (d, 1H, *J* = 6.0 Hz), 5.11 (d, 1H, *J* = 6.0 Hz), 3.84 (dd, 1H, J_1 = 14.5 Hz, J_2 = 6.5 Hz), 3.13 (d, 1H, *J* = 14.5 Hz), 1.05 (s, 9H), 0.27 (s, 3H), 0.24 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.4, 149.2, 142.7, 136.7, 135.3, 133.5, 132.2, 128.4, 126.9, 125.9, 125.3, 121.4, 121.1, 120.7, 119.9, 115.9, 114.5, 112.9, 109.2, 77.3, 77.0, 76.7, 51.5, 39.7, 25.7, 18.2, -4.5, -4.7; **IR (cm^{-1})**: *ν* 3055, 2953, 2855, 1617, 1425, 1360, 1252, 1051, 694; **HRMS** m/z (ESI) calculated for $C_{29}H_{33}N_2OSi$ $[M + H]^+$: 453.2357, found: 453.2351.



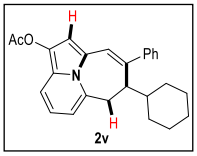
(*E*)-8-phenyl-7-styryl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2u** was obtained as a yellow amorphous solid in 91% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.53 (m, 2H), 7.36 – 7.32 (m, 2H), 7.26 – 7.20 (m, 2H), 7.18 – 7.09 (m, 5H), 7.04 (s, 1H), 6.97 (s, 1H), 6.69 (dd, 1H, J_1 = 8.0 Hz, J_2 = 6.8 Hz), 6.41 (d, 1H, *J* = 6.8 Hz), 6.34 (d, 1H, *J* = 15.6 Hz), 6.05 (dd, 1H, J_1 = 15.6 Hz, J_2 = 6.8 Hz), 4.37 (t, 1H, *J* = 6.4 Hz), 3.42 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 3.04 (d, 1H, *J* = 14.4 Hz), 2.34 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 143.0, 137.0, 136.2, 135.2, 131.0, 130.2, 128.4, 128.2, 128.0, 127.1, 126.3, 126.2, 125.6, 121.1, 119.3, 117.8, 114.0, 112.9, 110.8, 46.3, 39.9, 20.9; **IR (cm^{-1})**: *ν* 3049, 2924, 2851, 1746, 1637, 1223, 1019, 692; **HRMS** m/z (ESI) calculated for $C_{28}H_{24}NO_2$ $[M + H]^+$: 406.1802, found: 406.1795.



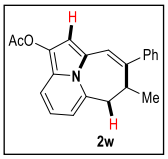
7-cyclohexyl-8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2v** was obtained as a yellow thick liquid in 82% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.35 (m, 2H), 7.24 – 7.20 (m, 2H), 7.17 – 7.15 (m, 1H), 7.11 – 7.08 (m, 1H), 6.80 – 6.78 (m, 1H), 6.73 (d, 1H, *J* = 2.0 Hz), 6.62 – 6.58 (m, 1H), 6.32 (dd, 1H, J_1 = 6.8 Hz, J_2 = 1.2 Hz), 3.36 – 3.24 (m, 2H), 2.71 (d, 1H, *J* = 14.4 Hz), 2.23 (s, 3H), 1.95 – 1.93 (m, 1H), 1.49 – 1.32 (m, 4H), 0.91 – 0.66 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.1, 145.2, 139.5, 136.3, 128.3, 127.7, 126.0, 125.7, 125.6, 121.3, 118.4, 117.3, 113.7, 113.1, 109.9, 48.6, 42.2, 36.5, 31.8, 30.6, 26.3, 26.1, 25.9, 20.9; **IR (cm^{-1})**: *ν* 3051, 2925, 2851, 1764, 1618, 1213, 1026, 761; **HRMS** m/z (ESI) calculated for $C_{26}H_{28}NO_2$ $[M + H]^+$: 386.2115, found: 386.2108.



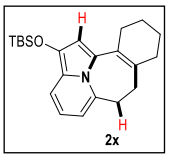
7-methyl-8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl acetate

According to the procedure A, compound **2w** was obtained as a yellow thick liquid in 86% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.54 (m, 2H), 7.42 – 7.26 (m, 4H), 6.95 (s, 1H), 6.90 (s, 1H), 6.77 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.8 Hz), 6.49 (d, 1H, *J* = 6.8 Hz), 3.74 – 3.68 (m, 1H), 3.20 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 2.95 (d, 1H, *J* = 6.4 Hz), 2.40 (s, 3H), 1.07 (d, 3H, *J* = 7.6 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.2, 142.9, 139.9, 136.5, 128.4, 127.9, 126.3, 126.0, 125.4, 121.3, 117.6, 117.5, 113.9, 113.0, 110.4, 40.0, 36.6, 20.9, 19.8; **IR (cm^{-1})**: *ν* 3033, 2958, 2854, 1750, 1617, 1225, 1049, 702; **HRMS** m/z (ESI) calculated for $C_{21}H_{20}NO_2$ $[M + H]^+$: 318.1489, found: 318.1481.



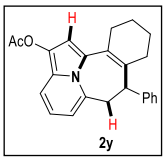
4,5,6,7,8,9-hexahydrobenzo[3,4]azepino[2,1,7-cd]indolizin-11-yl acetate

According to the procedure A, compound **2x** was obtained as a yellow thick liquid in 90% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20 (d, 1H, *J* = 8.8 Hz), 6.46 (s, 1H), 6.39 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.8 Hz), 6.08 (d, 1H, *J* = 6.8 Hz), 3.04 (t, 2H, *J* = 4.0 Hz), 2.52 – 2.46 (m, 4H), 2.22 (t, 2H, *J* = 4.0 Hz), 1.75 – 1.60 (m, 4H), 1.05 (s, 9H), 0.21 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.4, 132.9, 132.7, 124.7, 124.0, 123.0, 114.6, 113.4, 109.2, 104.2, 77.3, 77.0, 76.7, 35.3, 35.0, 33.6, 29.4, 25.8, 23.0, 22.9, 18.2, -4.5; **IR (cm^{-1})**: *ν* 3013, 2928, 2856, 1629, 1420, 1387, 1250, 756; **HRMS** m/z (ESI) calculated for $C_{22}H_{32}NOSi$ $[M + H]^+$: 354.2248, found: 354.2248.



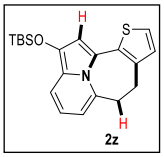
5-phenyl-4,5,6,7,8,9-hexahydrobenzo[3,4]azepino[2,1,7-cd]indolizin-11-yl acetate

According to the procedure A, compound **2y** was obtained as a yellow thick liquid in 92% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.14 – 7.06 (m, 5H), 6.94 – 6.93 (m, 2H), 6.44 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.8 Hz), 5.99 (d, 1H, *J* = 6.8 Hz), 4.05 (d, 1H, *J* = 4.8 Hz), 3.36 – 3.25 (m, 2H), 2.78 – 2.76 (m, 2H), 2.37 – 2.22 (m, 5H), 2.00 – 1.97 (m, 1H), 1.83 – 1.80 (m, 1H), 1.72 – 1.62 (m, 1H), 1.54 – 1.44 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.2, 142.5, 136.0, 133.7, 128.1, 127.6, 127.1, 126.1, 124.8, 124.2, 116.4, 113.3, 111.8, 106.2, 51.7, 40.8, 33.1, 29.6, 22.9, 22.8, 20.8; **IR (cm^{-1})**: *ν* 3058, 2930, 2858, 1747, 1610, 1224, 1038, 702; **HRMS** m/z (ESI) calculated for $C_{24}H_{24}NO_2$ $[M + H]^+$: 358.1802, found: 358.1793.



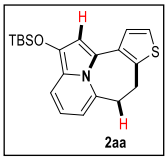
5-phenyl-4,5,6,7,8,9-hexahydrobenzo[3,4]azepino[2,1,7-cd]indolizin-11-yl acetate

According to the procedure A, compound **2z** was obtained as a yellow amorphous solid in 89% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (d, 1H, *J* = 8.8 Hz), 6.91 (d, 1H, *J* = 4.8 Hz), 6.74 (d, 1H, *J* = 4.8 Hz), 6.63 (s, 1H), 6.45 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.21 (d, 1H, *J* = 6.4 Hz), 3.19 – 3.12 (m, 4H), 1.09 (s, 9H), 0.27 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.6, 135.8, 133.6, 132.2, 129.8, 125.3, 119.7, 117.0, 115.4, 114.0, 111.7, 104.6, 35.0, 29.6, 25.8, 18.2, -4.6; **IR (cm^{-1})**: *ν* 3049, 2952, 2856, 1630, 1458, 1390, 1247, 1053, 722; **HRMS** m/z (ESI) calculated for $C_{20}H_{25}NOSSi$ [M]: 355.1426, found: 355.1416.



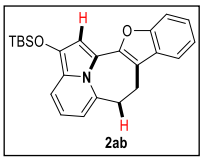
5-((tert-butyldimethylsilyl)oxy)-9,10-dihydrothieno[3',2':3,4]azepino[2,1,7-cd]indolizine

According to the procedure A, compound **2aa** was obtained as a yellow amorphous solid in 93% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.26 – 7.23 (m, 2H), 7.00 (d, 1H, *J* = 5.5 Hz), 6.61 (s, 1H), 6.41 (t, 1H, *J* = 7.5 Hz), 6.18 (d, 1H, *J* = 7.5 Hz), 3.23 – 3.18 (m, 4H), 1.04 (s, 9H), 0.21 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.2, 133.3, 132.9, 130.7, 127.3, 125.0, 121.9, 119.1, 115.4, 113.5, 111.5, 104.6, 35.7, 28.9, 25.8, 18.2, -4.5; **IR (cm^{-1})**: *ν* 3055, 2952, 2856, 1632, 1426, 1360, 1247, 1086, 730; **HRMS** m/z (ESI) calculated for $C_{20}H_{25}NOSSi$ [M]: 355.1426, found: 355.1416.



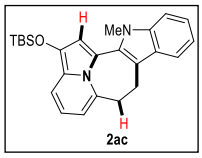
12-((tert-butyldimethylsilyl)oxy)-4,5-dihydrobenzofuro[2',3':3,4]azepino[2,1,7-cd]indolizine

According to the procedure A, compound **2ab** was obtained as a yellow amorphous solid in 92% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 7.48 (m, 1H), 7.43 – 7.38 (m, 2H), 7.26 – 7.21 (m, 2H), 7.03 (t, 1H, *J* = 2.0 Hz), 6.61 – 6.57 (m, 1H), 6.36 (d, 1H, *J* = 6.4 Hz), 3.28 – 3.25 (m, 2H), 3.20 – 3.16 (m, 2H), 1.13 (t, 9H, *J* = 1.6 Hz), 0.33 (t, 6H, *J* = 1.6 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.7, 146.9, 137.7, 134.1, 130.1, 126.9, 122.8, 122.5, 117.6, 115.6, 115.3, 114.1, 113.0, 112.0, 110.5, 103.9, 34.3, 25.8, 22.8, 18.2, -4.5; **IR (cm^{-1})**: *v* 3056, 2953, 2855, 1621, 1457, 1300, 1249, 1052, 741; **HRMS** m/z (ESI) calculated for $C_{24}H_{27}NO_2Si$ [M]: 389.1811, found: 389.1802.



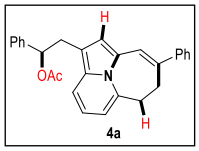
12-((tert-butyldimethylsilyl)oxy)-aza-methyl-4,5-dihydrobenzofuro[2',3':3,4]azepino[2,1,7-cd]indolizine

According to the procedure A, compound **2ac** was obtained as a yellow amorphous solid in 91% yield; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 (d, 1H, *J* = 7.0 Hz), 7.21 – 7.17 (m, 2H), 7.09 – 7.06 (m, 1H), 7.03 – 7.00 (m, 1H), 6.61 (d, 1H, *J* = 2.5 Hz), 6.41 – 6.37 (m, 1H), 6.13 (d, 1H, *J* = 7.0 Hz), 3.82 (s, 3H), 3.1 – 3.10 (m, 4H), 0.97 (t, 9H, *J* = 3.0 Hz), 0.16 (t, 6H, *J* = 3.0 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.8, 138.5, 133.4, 131.4, 127.2, 125.7, 121.1, 119.4, 117.1, 115.2, 114.8, 114.7, 114.6, 111.9, 109.1, 105.8, 37.8, 33.0, 25.8, 23.7, 18.3, -4.5; **IR (cm^{-1})**: *v* 3053, 2952, 2855, 1632, 1469, 1361, 1248, 1059, 737; **HRMS** m/z (ESI) calculated for $C_{25}H_{31}N_2OSi$ [M + H]$^+$: 403.2200, found: 403.2209.



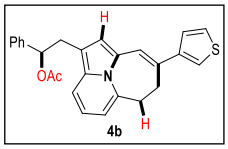
1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl acetate

According to the procedure B, compound **4a** was obtained as a yellow thick liquid in 80% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.04 (m, 11H), 6.70 (s, 1H), 6.50 (t, 1H, *J* = 7.6 Hz), 6.44 (s, 1H), 6.14 (d, 1H, *J* = 7.6 Hz), 5.87 – 5.82 (m, 1H), 3.24 (dd, 1H, J_1 = 14.4 Hz, J_2 = 7.6 Hz), 3.11 – 3.05 (m, 1H), 3.01 (t, 2H, *J* = 3.2 Hz), 2.90 (t, 2H, *J* = 3.2 Hz), 1.9 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.1, 143.4, 140.3, 139.3, 134.9, 133.6, 128.2, 127.8, 126.5, 125.9, 125.2, 124.3, 119.8, 119.2, 117.4, 115.1, 110.4, 109.6, 76.5, 34.3, 33.0, 32.0, 21.2; **IR (cm^{-1})**: *v* 3027, 2959, 2851, 1740, 1630, 1236, 1022, 758; **HRMS** m/z (ESI) calculated for $C_{28}H_{26}NO_2$ [M + H]$^+$: 408.1958, found: 408.1960.



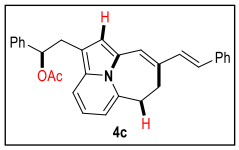
1-phenyl-2-(8-(thiophen-3-yl)-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl acetate

According to the procedure B, compound **4b** was obtained as a yellow thick liquid in 89% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.25 (m, 7H), 7.20 (d, 1H, *J* = 9.2 Hz), 7.05 (s, 1H), 6.89 (s, 1H), 6.62 (t, 1H, *J* = 6.4 Hz), 6.54 (s, 1H), 6.28 (d, 1H, *J* = 6.4 Hz), 5.94 (t, 1H, *J* = 6.4 Hz), 3.35 (dd, 1H, J_1 = 14.8 Hz, J_2 = 7.6 Hz), 3.21 – 3.15 (m, 3H), 3.02 (t, 2H, *J* = 3.2 Hz), 2.03 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.2, 144.7, 140.4, 139.2, 135.0, 129.0, 128.3, 127.8, 126.6, 125.7, 125.0, 124.0, 119.6, 117.9, 117.5, 115.2, 110.5, 109.7, 76.6, 34.2, 33.0, 31.8, 21.3; **IR (cm^{-1})**: *v* 3033, 2921, 2855, 1736, 1618, 1238, 1024, 699; **HRMS** m/z (ESI) calculated for $C_{26}H_{24}NO_2S$ [M + H]$^+$: 414.1522, found: 414.1525.



(*E*)-1-phenyl-2-(8-styryl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl acetate

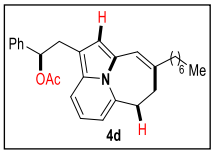
According to the procedure B, compound **4c** was obtained as a yellow amorphous solid in 75% yield;



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.35 – 7.30 (m, 7H), 7.25 – 7.18 (m, 2H), 6.95 (d, 1H, J = 16.0 Hz), 6.69 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.23 (s, 1H), 6.56 (s, 1H), 6.45 (d, 1H, J = 16.0 Hz), 6.36 (d, 1H, J = 6.4 Hz), 5.96 (t, 1H, J = 6.4 Hz), 3.37 (dd, 1H, J_1 = 14.8 Hz, J_2 = 7.6 Hz), 3.23 – 3.14 (m, 3H), 2.93 (t, 2H, J = 3.2 Hz), 2.07 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.3, 140.3, 139.5, 138.1, 135.6, 132.7, 132.6, 128.6, 128.3, 127.9, 126.6, 126.5, 125.9, 124.5, 124.3, 123.2, 120.1, 118.1, 115.2, 110.9, 110.2, 76.5, 33.8, 33.0, 27.5, 21.3; **IR (cm^{-1})**: *v* 3028, 2922, 2855, 1736, 1604, 1207, 1026, 699; **HRMS** m/z (ESI) calculated for $C_{30}H_{28}NO_2$ $[M + H]^+$: 434.2115, found: 434.2106.

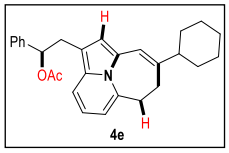
2-(8-heptyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)-1-phenylethyl acetate

According to the procedure B, compound **4d** was obtained as a yellow thick liquid in 75% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.26 (m, 5H), 7.18 (d, 1H, J = 8.8 Hz), 6.56 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.42 (s, 1H), 6.27 (s, 1H), 6.21 (d, 1H, J = 6.4 Hz), 5.95 (t, 1H, J = 6.4 Hz), 3.36 (dd, 1H, J_1 = 14.8 Hz, J = 7.6 Hz), 3.19 (dd, 1H, J_1 = 14.8 Hz, J_2 = 6.4 Hz), 3.06 (t, 2H, J = 4.4 Hz), 2.61 (t, 2H, J = 4.4 Hz), 2.18 (t, 2H, J = 7.2 Hz), 2.05 (s, 3H), 1.51 – 1.44 (m, 2H), 1.34 – 1.30 (m, 8H), 0.92 (t, 3H, J = 6.4 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.2, 140.6, 139.0, 137.0, 133.9, 128.2, 127.8, 126.6, 124.5, 117.4, 116.8, 116.3, 115.1, 110.0, 108.7, 76.8, 40.5, 34.3, 33.1, 31.8, 29.3, 29.2, 28.1, 22.6, 21.3, 14.1; **IR (cm^{-1})**: *v* 3025, 2925, 2853, 1739, 1618, 1236, 1022, 699; **HRMS** m/z (ESI) calculated for $C_{29}H_{36}NO_2$ $[M + H]^+$: 430.2741, found: 430.2734.



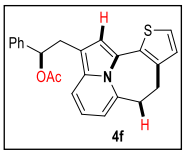
2-(8-cyclohexyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)-1-phenylethyl acetate

According to the procedure B, compound **4e** was obtained as a yellow thick liquid in 83% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.29 (m, 5H), 7.19 (d, 1H, J = 8.8 Hz), 6.52 – 6.48 (m, 1H), 6.47 (s, 1H), 6.23 (s, 1H), 6.14 (d, 1H, J = 6.4 Hz), 5.94 – 5.90 (m, 1H), 3.38 (dd, 1H, J_1 = 14.4 Hz, J_2 = 7.6 Hz), 3.32 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.0 Hz), 2.99 (t, 2H, J = 4.4 Hz), 2.56 (t, 2H, J = 4.4 Hz), 2.04 – 1.94 (m, 4H), 1.79 – 1.63 (m, 5H), 1.34 – 1.14 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.1, 141.8, 140.6, 139.0, 133.9, 128.2, 127.7, 126.6, 124.7, 117.5, 116.3, 115.0, 114.8, 109.8, 108.7, 76.7, 47.9, 34.6, 33.1, 31.8, 31.6, 26.6, 26.3, 21.3; **IR (cm^{-1})**: *v* 3035, 2923, 2848, 1740, 1633, 1236, 1023, 699; **HRMS** m/z (ESI) calculated for $C_{28}H_{32}NO_2$ $[M + H]^+$: 414.2428, found: 414.2422.



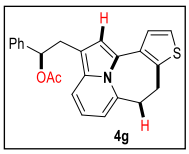
2-(6,7-dihydrothieno[3',2':3,4]azepino[2,1,7-cd]indolizin-2-yl)-1-phenylethyl acetate

According to the procedure B, compound **4f** was obtained as a yellow thick liquid in 69% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.27 (m, 5H), 7.22 (d, 1H, J = 8.8 Hz), 6.92 (d, 1H, J = 5.2 Hz), 6.81 (s, 1H), 6.74 (d, 1H, J = 5.2 Hz), 6.57 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.29 (d, 1H, J = 6.4 Hz), 5.96 (dd, 1H, J_1 = 7.6 Hz, J_2 = 6.4 Hz), 3.37 (dd, 1H, J_1 = 14.4 Hz, J_2 = 7.6 Hz), 3.24 – 3.19 (m, 3H), 3.13 (t, 2H, J = 4.0 Hz), 2.07 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.1, 140.3, 138.6, 135.6, 133.8, 132.0, 129.7, 128.2, 127.8, 126.5, 120.7, 120.0, 116.3, 115.6, 115.2, 111.6, 109.7, 76.6, 34.9, 33.1, 29.4, 21.2; **IR (cm^{-1})**: ν 3025, 2913, 2854, 1736, 1615, 1237, 1023, 700; **HRMS** m/z (ESI) calculated for $C_{24}H_{22}NO_2S$ $[M + H]^+$: 388.1366, found: 388.1367.



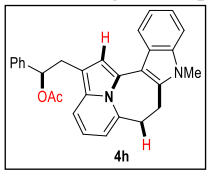
2-(6,7-dihydrothieno[3',2':3,4]azepino[2,1,7-cd]indolizin-2-yl)-1-phenylethyl acetate

According to the procedure B, compound **4g** was obtained as a yellow thick liquid in 78% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.27 (m, 5H), 7.23 – 7.20 (m, 2H), 6.99 (d, 1H, J = 5.6 Hz), 6.78 (s, 1H), 6.54 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.26 (d, 1H, J = 6.4 Hz), 5.98 – 5.94 (m, 1H), 3.41 – 3.35 (m, 1H), 3.24 – 3.19 (m, 5H), 2.03 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.2, 140.4, 138.3, 133.7, 132.8, 130.6, 128.3, 127.8, 127.3, 126.6, 122.8, 121.9, 116.0, 115.8, 115.0, 111.5, 109.1, 77.3, 77.0, 76.7, 35.6, 33.2, 28.8, 21.3; **IR (cm^{-1})**: ν 3033, 2955, 2850, 1736, 1631, 1238, 1032, 700; **HRMS** m/z (ESI) calculated for $C_{24}H_{22}NO_2S$ $[M + H]^+$: 388.1366, found: 388.1367.



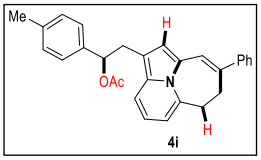
2-(aza-methyl-6,7-dihydrobenzo[4',5']indole[2',3':3,4]azepino[2,1,7-cd]indolizin-2-yl)-1-phenylethyl acetate

According to the procedure B, compound **4h** was obtained as a yellow thick liquid in 71% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, 1H, J = 7.6 Hz), 7.39 – 7.30 (m, 7H), 7.22 (t, 1H, J = 7.6 Hz), 7.15 (t, 1H, J = 7.6 Hz), 6.72 – 6.67 (m, 2H), 6.38 (d, 1H, J = 6.8 Hz), 6.03 (td, 1H, J_1 = 6.8 Hz, J_2 = 1.6 Hz), 3.80 (s, 3H), 3.49 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.8 Hz), 3.34 – 3.22 (m, 5H), 2.10 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.3, 140.4, 139.9, 138.4, 134.3, 131.3, 128.3, 127.9, 127.1, 126.8, 121.1, 119.3, 118.4, 117.1, 117.1, 116.3, 115.6, 114.4, 111.9, 109.1, 76.6, 37.6, 33.1, 33.0, 23.6, 21.4; **IR (cm^{-1})**: ν 3055, 2924, 2853, 1734, 1636, 1238, 1023, 700; **HRMS** m/z (ESI) calculated for $C_{29}H_{27}N_2O_2$ $[M + H]^+$: 435.2067, found: 435.2065.



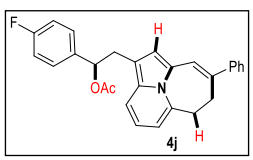
2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)-1-(p-tolyl)ethyl acetate

According to the procedure B, compound **4i** was obtained as a yellow thick liquid in 85% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.33 (m, 2H), 7.28 – 7.24 (m, 2H), 7.20 – 7.11 (m, 4H), 7.06 – 7.05 (m, 2H), 6.75 (d, 1H, J = 2.0 Hz), 6.60 – 6.56 (m, 1H), 6.50 (d, 1H, J = 2.0 Hz), 6.22 (d, 1H, J = 6.8 Hz), 5.86 (td, 1H, J_1 = 6.8 Hz, J_2 = 2.0 Hz), 3.29 (ddd, 1H, J_1 = 14.4 Hz, J_2 = 7.6 Hz, J_3 = 2.0 Hz), 3.15 – 3.09 (m, 3H), 2.99 (t, 2H, J = 3.2 Hz), 2.26 (s, 3H), 1.95 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.2, 143.5, 139.4, 137.5, 137.4, 134.9, 133.6, 129.0, 128.3, 126.6, 125.9, 125.3, 124.3, 119.8, 119.3, 117.4, 115.2, 110.5, 109.9, 77.3, 77.0, 76.7, 76.5, 34.4, 32.9, 32.1, 21.3, 21.1., 110.5, 109.9, 76.5, 34.4, 32.9, 32.1, 21.3, 21.1; **IR (cm^{-1})** v 3033, 2922, 2850, 1737, 1620, 1237, 1020, 697; **HRMS** m/z (ESI) calculated for $C_{29}H_{28}NO_2$ $[M + H]^+$: 422.2115, found: 422.2111.



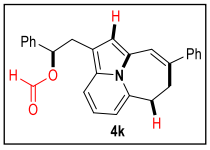
1-(4-fluorophenyl)-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl acetate

According to the procedure B, compound **4j** was obtained as a yellow thick liquid in 77% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.43 (m, 2H), 7.39 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 2H), 7.04 – 7.00 (m, 2H), 6.85 (d, 1H, J = 1.2 Hz), 6.70 – 6.65 (m, 1H), 6.56 (d, 1H, J = 1.2 Hz), 6.34 (d, 1H, J = 6.8 Hz), 5.95 (td, 1H, J_1 = 6.8 Hz, J_2 = 2.0 Hz), 3.37 (ddd, 1H, J_1 = 14.4 Hz, J_2 = 7.2 Hz, J_3 = 1.6 Hz), 3.22 – 3.17 (m, 3H), 3.11 (t, 2H, J = 3.6 Hz), 2.07 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.2, 163.5, 161.1, 143.4, 139.5, 136.2 (d, J = 3.1 Hz), 134.4 (d, J = 112.0 Hz), 128.4 (d, J = 8.2 Hz), 128.3, 126.0, 125.3, 124.4, 119.5 (d, J = 61.5 Hz), 117.6, 115.3, 115.1 (d, J = 2.7 Hz), 110.5, 109.3, 76.0, 34.5, 33.0, 32.1, 21.3; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -114.25 (t, J = 4.1 Hz, 1F); **IR (cm^{-1})**: v 3023, 2924, 2851, 1739, 1620, 1227, 1028, 698; **HRMS** m/z (ESI) calculated for $C_{28}H_{25}FNO_2$ $[M + H]^+$: 426.1864, found: 426.1857.



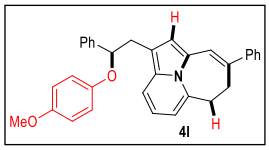
1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl formate

According to the procedure B, compound **4k** was obtained as a yellow thick liquid in 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (s, 1H), 7.45 – 7.31 (m, 9H), 7.25 – 7.22 (m, 2H), 6.85 (s, 1H), 6.70 – 6.66 (m, 1H), 6.61 (s, 1H), 6.34 (d, 1H, J = 6.8 Hz), 6.08 (t, 1H, J = 6.8 Hz), 3.43 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.8 Hz), 3.29 – 3.20 (m, 3H), 3.10 (t, 2H, J = 4.4 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.4, 143.4, 139.7, 139.5, 134.9, 133.9, 128.4, 128.3, 128.1, 126.7, 126.0, 125.3, 124.5, 119.8, 119.2, 117.7, 115.0, 110.5, 109.2, 76.5, 34.5, 33.0, 32.2; **IR (cm^{-1})**: v 3025, 2923, 2854, 1723, 1622, 1260, 698; **HRMS** m/z (ESI) calculated for $C_{27}H_{23}NNaO_2$ $[M + Na]^+$: 416.1621, found: 416.1630.



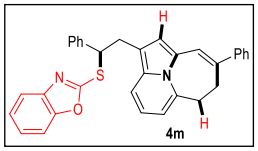
2-(2-(4-methoxyphenoxy)-2-phenylethyl)-8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure B, compound **4l** was obtained as a yellow thick liquid in 52% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.20 (m, 11H), 6.86 (s, 1H), 6.77 – 6.63 (m, 6H), 6.32 (d, 1H, J = 6.4 Hz), 5.21 (dd, 1H, J_1 = 7.6 Hz, J_2 = 5.2 Hz), 3.69 (s, 3H), 3.44 (dd, 1H, J_1 = 14.4 Hz, J_2 = 7.6 Hz), 3.25 – 3.20 (m, 3H), 3.11 (t, 2H, J = 4.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.6, 152.3, 143.5, 142.0, 139.4, 135.0, 133.5, 128.4, 128.3, 127.5, 126.2, 125.9, 125.3, 124.3, 120.1, 119.4, 117.3, 117.0, 115.4, 114.4, 110.9, 110.4, 81.9, 55.6, 35.3, 34.5, 32.2; **IR (cm^{-1})**: *v* 3022, 2922, 2851, 1619, 1227, 1033, 699; **HRMS** m/z (ESI) calculated for $C_{33}H_{30}NO_2$ $[M + H]^+$: 472.2271, found: 472.2279.



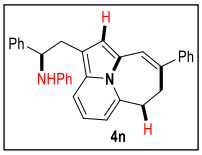
2-((1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl)thio)benzo[d]oxazole

According to the procedure B, compound **4m** was obtained as a yellow amorphous solid in 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, 1H, J = 8.0 Hz), 7.41 – 7.14 (m, 14H), 6.70 (s, 1H), 6.66 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.46 (s, 1H), 6.27 (d, 1H, J = 6.4 Hz), 5.19 – 5.15 (m, 1H), 3.69 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 3.49 (dd, 1H, J_1 = 14.4 Hz, J_2 = 8.8 Hz), 3.09 (t, 2H, J = 4.0 Hz), 2.98 (t, 2H, J = 4.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.1, 151.6, 143.4, 141.9, 140.0, 139.4, 134.9, 133.6, 128.6, 128.3, 128.0, 127.9, 125.9, 125.3, 124.3, 124.1, 123.8, 119.9, 119.2, 118.5, 117.7, 115.3, 110.7, 110.5, 109.8, 52.8, 34.4, 33.6, 32.1; **IR (cm^{-1})**: *v* 3058, 2922, 2851, 1619, 1452, 1221, 1095, 697; **HRMS** m/z (ESI) calculated for $C_{33}H_{27}N_2OS$ $[M + H]^+$: 499.1839, found: 499.1836.



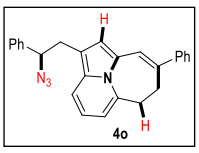
N-(1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl)aniline

According to the procedure B, compound **4n** was obtained as a yellow amorphous solid in 72% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.30 (m, 7H), 7.24 – 7.19 (m, 3H), 7.15 (d, 1H, J = 8.8 Hz), 7.05 – 7.01 (m, 2H), 6.84 (s, 1H), 6.68 – 6.60 (m, 3H), 6.45 (d, 2H, J = 8.0 Hz), 6.34 (d, 1H, J = 6.4 Hz), 4.63 (dd, 1H, J_1 = 8.0 Hz, J_2 = 5.2 Hz), 4.24 (s, 1H), 3.31 – 3.11 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.4, 144.0, 143.4, 139.6, 135.0, 134.1, 128.9, 128.5, 128.3, 126.9, 126.4, 126.1, 125.4, 124.7, 119.5, 119.2, 117.7, 117.3, 115.0, 113.7, 110.6, 110.1, 58.7, 35.3, 34.5, 32.2; **IR (cm^{-1})**: *v* 3405, 3024, 2920, 2856, 1600, 1258, 1029, 697; **HRMS** m/z (ESI) calculated for $C_{32}H_{29}N_2$ $[M + H]^+$: 441.2325, found: 441.2328.



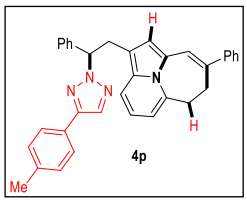
2-(2-azido-2-phenylethyl)-8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure B, compound **4o** was obtained as a yellow thick liquid in 71% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.33 (m, 9H), 7.26 – 7.22 (m, 2H), 6.89 (s, 1H), 6.72 – 6.68 (m, 2H), 6.35 (d, 1H, J = 6.8 Hz), 4.73 (dd, 1H, J_1 = 8.0 Hz, J_2 = 6.8 Hz), 3.30 – 3.17 (m, 4H), 3.11 (t, 2H, J = 3.2 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.4, 139.7, 139.6, 134.8, 134.0, 128.7, 128.3, 128.2, 126.9, 126.0, 125.3, 124.6, 119.6, 119.2, 117.7, 115.0, 110.6, 110.1, 67.4, 34.5, 33.2, 32.2; **IR (cm^{-1})**: *v* 3028, 2922, 2855, 2096, 1620, 1258, 698; **HRMS** m/z (ESI) calculated for $C_{26}H_{23}N_4$ $[M + H]^+$: 391.1917, found: 391.1918.



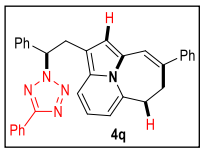
8-phenyl-2-(2-phenyl-2-(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)ethyl)-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure B, compound **4p** was obtained as a yellow amorphous solid in 56% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 (s, 1H), 7.71 – 7.68 (m, 2H), 7.50 – 7.47 (m, 2H), 7.40 – 7.26 (m, 8H), 7.23 – 7.18 (m, 3H), 6.76 (s, 1H), 6.65 (t, 1H, J = 7.6 Hz), 6.49 (s, 1H), 6.30 (d, 1H, J = 6.4 Hz), 5.94 (dd, 1H, J_1 = 9.2 Hz, J_2 = 5.2 Hz), 4.11 (dd, 1H, J_1 = 14.8 Hz, J_2 = 9.2 Hz), 3.67 (dd, 1H, J_1 = 14.8 Hz, J_2 = 5.2 Hz), 3.16 (t, 2H, J = 4.0 Hz), 3.06 (t, 2H, J = 4.0 Hz), 2.38 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.5, 143.5, 139.8, 139.5, 138.1, 134.7, 133.8, 130.7, 129.4, 128.6, 128.3, 128.1, 127.8, 127.0, 126.0, 125.9, 125.3, 124.6, 119.3, 119.3, 117.6, 115.1, 110.5, 110.2, 70.6, 34.5, 32.2, 21.3; **IR (cm^{-1})**: v 3033, 2924, 2853, 1624, 1449, 1224, 695; **HRMS** m/z (ESI) calculated for $C_{35}H_{30}N_4$ [M]: 506.2470, found: 506.2470.



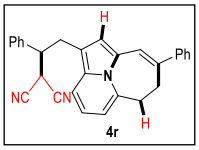
8-phenyl-2-(2-phenyl-2-(5-phenyl-2H-tetrazol-2-yl)ethyl)-6,7-dihydroazepino[2,1,7-cd]indolizine

According to the procedure B, compound **4q** was obtained as a yellow amorphous solid in 66% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.19 – 8.16 (m, 2H), 7.58 – 7.56 (m, 2H), 7.51 – 7.20 (m, 12H), 6.78 (s, 1H), 6.67 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.8 Hz), 6.54 (s, 1H), 6.31 (d, 1H, J = 6.8 Hz), 6.22 (dd, 1H, J_1 = 8.8 Hz, J_2 = 5.2 Hz), 4.16 (dd, 1H, J_1 = 14.8 Hz, J_2 = 9.6 Hz), 3.77 (dd, 1H, J_1 = 14.8 Hz, J_2 = 5.2 Hz), 3.17 (t, 2H, J = 4.4 Hz), 3.06 (t, 2H, J = 4.4 Hz); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.9, 143.5, 139.6, 138.0, 134.7, 134.2, 130.2, 128.9, 128.8, 128.8, 128.4, 127.7, 127.3, 126.9, 126.1, 125.4, 124.8, 119.2, 119.1, 118.0, 114.8, 110.7, 109.0, 69.7, 34.5, 32.2, 32.2; **IR (cm^{-1})**: v 3032, 2924, 2853, 1628, 1232, 695; **HRMS** m/z (ESI) calculated for $C_{33}H_{28}N_5$ [M + H]$^+$: 494.2339, found: 494.2333.



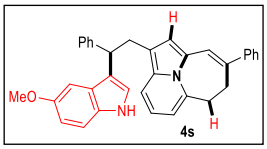
2-(1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl)malononitrile

According to the procedure B, compound **4r** was obtained as a yellow amorphous solid in 60% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.50 – 7.42 (m, 7H), 7.41 – 7.36 (m, 2H), 7.30 (d, 1H, J = 8.4 Hz), 7.27 – 7.23 (m, 1H), 6.87 (s, 1H), 6.77 (dd, 1H, J_1 = 8.4 Hz, J_2 = 6.4 Hz), 6.73 (s, 1H), 6.42 (d, 1H, J = 6.4 Hz), 4.02 – 4.01 (m, 1H), 3.53 – 3.44 (m, 2H), 3.41 – 3.35 (m, 1H), 3.25 (t, 2H, J = 4.4 Hz), 3.13 (t, 2H, J = 4.4 Hz); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.2, 139.9, 136.8, 135.2, 134.7, 129.1, 129.0, 128.4, 128.0, 126.4, 125.4, 125.3, 118.8, 118.8, 118.6, 114.7, 112.4, 111.7, 111.1, 108.8, 48.1, 34.5, 32.3, 28.8, 28.3; **IR (cm^{-1})**: v 3033, 2924, 2855, 2241, 1619, 1210, 700; **HRMS** m/z (ESI) calculated for $C_{29}H_{24}N_3$ [M + H]$^+$: 414.1965, found: 414.1961.



2-(2-(5-methoxy-1H-indol-3-yl)-2-phenylethyl)-8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizine

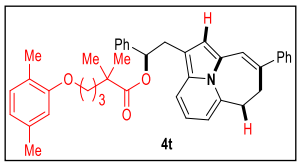
According to the procedure B, compound **4s** was obtained as a yellow amorphous solid in 51% yield;



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (s, 1H), 7.42 – 7.32 (m, 6H), 7.28 – 7.16 (m, 6H), 7.05 (d, 1H, J = 1.6 Hz), 6.83 – 6.79 (m, 3H), 6.61 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.51 (s, 1H), 6.29 (d, 1H, J = 6.4 Hz), 4.53 (t, 1H, J = 7.6 Hz), 3.73 (s, 3H), 3.64 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 3.44 (dd, 1H, J_1 = 14.4 Hz, J_2 = 8.0 Hz), 3.18 (t, 2H, J = 4.0 Hz), 3.07 (t, 2H, J = 4.0 Hz); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 153.6, 145.1, 143.5, 139.4, 134.5, 133.3, 131.6, 128.3, 128.2, 128.1, 127.5, 126.0, 125.9, 125.3, 124.1, 122.2, 119.8, 119.6, 119.4, 117.0, 115.2, 113.7, 111.9, 111.6, 110.3, 101.5, 5.7, 44.2, 34.5, 32.5, 32.1; **IR (cm^{-1})**: *v* 3440, 3033, 2925, 2853, 1621, 1213, 1031, 699; **HRMS** m/z (ESI) calculated for $C_{35}H_{31}N_2O$ $[M + H]^+$: 495.2431, found: 495.2438.

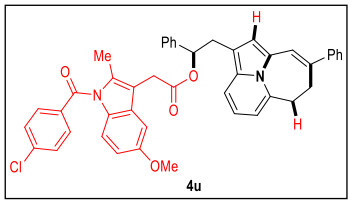
1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate

According to the procedure B, compound **4t** was obtained as a yellow thick liquid in 77% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39 – 7.16 (m, 11H), 6.97 (d, 1H, J = 7.2 Hz), 6.81 (s, 1H), 6.65 – 6.61 (m, 3H), 6.51 (s, 1H), 6.28 (d, 1H, J = 7.2 Hz), 5.97 – 5.93 (m, 1H), 3.73 – 3.63 (m, 2H), 3.35 (dd, 1H, J_1 = 14.4 Hz, J_2 = 8.0 Hz), 3.19 – 3.13 (m, 3H), 3.03 (t, 2H, J = 4.0 Hz), 2.27 (s, 3H), 2.13 (s, 3H), 1.67 – 1.57 (m, 2H), 1.52 – 1.38 (m, 2H), 1.15 (s, 3H), 1.13 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.9, 156.9, 143.4, 140.8, 139.4, 136.3, 134.9, 133.7, 130.2, 128.3, 127.7, 126.4, 125.9, 125.3, 124.3, 123.5, 120.5, 119.8, 119.1, 117.5, 115.2, 111.8, 110.5, 109.8, 76.4, 67.8, 42.0, 37.2, 34.4, 33.2, 32.1, 25.1, 25.0, 24.9, 21.4, 15.8; **IR (cm^{-1})**: *v* 3034, 2926, 2855, 1736, 1637, 1255, 1033, 699; **HRMS** m/z (ESI) calculated for $C_{41}H_{44}NO_3$ $[M + H]^+$: 598.3316, found: 598.3306.



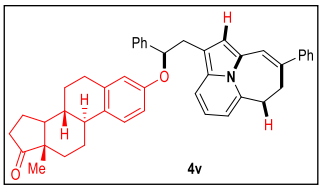
1-phenyl-2-(8-phenyl-2a1,7-dihydro-6H-benzo[cd]azulen-2-yl)ethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate

According to the procedure B, compound **4u** was obtained as a yellow amorphous solid in 82% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.59 (m, 2H), 7.46 – 7.39 (m, 6H), 7.35 – 7.34 (m, 4H), 7.29 – 7.26 (m, 2H), 7.20 (d, 1H, J = 8.0 Hz), 7.00 – 6.95 (m, 2H), 6.75 – 6.66 (m, 3H), 6.49 (d, 1H, J = 2.8 Hz), 6.35 (d, 1H, J = 6.8 Hz), 6.10 – 6.06 (m, 1H), 3.78 (s, 3H), 3.71 (s, 2H), 3.43 – 3.36 (m, 1H), 3.28 – 3.23 (m, 1H), 3.20 (t, 2H, J = 4.0 Hz), 3.08 (t, 2H, J = 4.0 Hz), 2.29 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.9, 168.1, 155.9, 143.3, 140.2, 139.3, 139.0, 135.5, 134.8, 133.8, 133.7, 131.0, 130.7, 130.5, 128.9, 128.2, 128.2, 127.9, 126.4, 125.9, 125.3, 124.3, 119.7, 119.0, 117.5, 114.9, 114.9, 112.5, 111.8, 110.4, 109.4, 101.0, 77.1 , 55.5, 34.3, 33.0, 32.0, 30.5, 13.3; **IR (cm^{-1})**: *v* 3059, 2929, 2839, 1734, 1683, 1223, 1014, 698; **HRMS** m/z (ESI) calculated for $C_{46}H_{39}ClNO_4$ $[M + H]^+$: 704.2562, found: 704.2561.



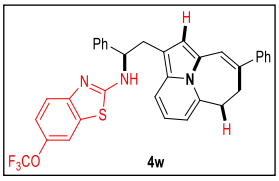
(8*R*,9*S*,13*S*)-13-methyl-3-(1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethoxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one

According to the procedure B, compound **4v** was obtained as a yellow amorphous solid in 46% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.30 (m, 8H), 7.28 – 7.20 (m, 3H), 7.06 (dd, 1H, J_1 = 8.4 Hz, J_2 = 4.0 Hz), 6.86 (s, 1H), 6.72 (s, 1H), 6.68 – 6.57 (m, 3H), 6.32 (d, 1H, J = 6.4 Hz), 5.30 – 5.25 (m, 1H), 3.43 (dd, 1H, J_1 = 14.8 Hz, J_2 = 7.6 Hz), 3.24 – 3.19 (m, 3H), 3.10 (t, 2H, J = 4.0 Hz), 2.81 – 2.75 (m, 2H), 2.48 (dd, 1H, J_1 = 19.2 Hz, J_2 = 8.4 Hz), 2.33 – 2.27 (m, 1H), 2.19 – 1.90 (m, 5H), 1.59 – 1.27 (m, 6H), 0.86 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.1, 156.1, 143.5, 142.1, 142.0, 139.4, 137.5, 137.4, 135.0, 135.0, 133.5, 131.8, 131.8, 128.5, 128.3, 127.4, 126.1, 126.0, 125.9, 125.3, 124.3, 120.1, 119.4, 117.3, 116.0, 115.7, 115.4, 115.4, 113.3, 113.0, 110.9, 110.4, 80.9, 80.8, 50.3, 47.9, 43.9, 43.9, 38.2, 38.2, 35.8, 35.4, 35.4, 34.5, 32.2, 31.5, 29.6, 29.5, 26.5, 26.4, 25.8, 25.7, 21.5, 13.8; **IR (cm^{-1})**: *v* 3057, 2921, 2855, 1728, 1618, 1221, 1047, 698; **HRMS** m/z (ESI) calculated for $C_{44}H_{44}NO_2$ $[M + H]^+$: 618.3367, found: 618.3371.



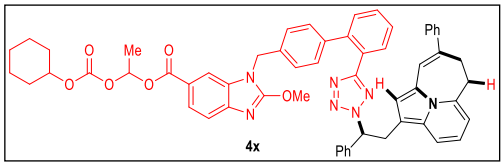
N-(1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl)-6-(trifluoromethoxy)benzo[d]thiazol-2-amine

According to the procedure B, compound **4w** was obtained as a yellow amorphous solid in 42% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.32 (m, 11H), 7.26 – 7.21 (m, 1H), 7.11 – 7.08 (m, 2H), 6.81 (s, 1H), 6.66 (t, 1H, J = 7.6 Hz), 6.58 (s, 1H), 6.35 (d, 1H, J = 7.6 Hz), 6.22 (s, 1H), 4.95 (t, 1H, J = 6.4 Hz), 3.41 (dd, 1H, J_1 = 14.4 Hz, J_2 = 5.2 Hz), 3.30 (dd, 1H, J_1 = 14.4 Hz, J_2 = 6.4 Hz), 3.20 (t, 2H, J = 4.0 Hz), 3.10 (t, 2H, J = 4.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.8, 150.0, 143.5 (d, J = 1.9 Hz), 143.4, 141.0, 139.7, 134.8 (d, J = 64.3 Hz), 131.0, 128.8, 128.3, 127.9, 126.7, 126.1, 125.4, 124.9, 121.8, 119.7, 119.6, 119.3, 119.1, 118.9, 118.1, 114.8, 114.0, 110.8, 108.4, 77.3, 77.0, 76.7, 60.5, 34.5, 34.3, 32.2; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -58.26 (s, 3F); IR (cm^{-1}): *v* 3423, 3033, 2944, 2855, 1610, 1460, 1255, 698; **HRMS** m/z (ESI) calculated for $C_{34}H_{27}F_3N_3OS$ $[M + H]^+$: 582.1821, found: 582.1816.



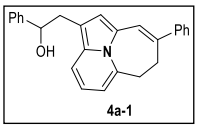
1-(((cyclohexyloxy)carbonyl)oxy)ethyl 2-ethoxy-1-((2'-(1-(1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethyl)-1H-tetrazol-5-yl)-[1,1'-biphenyl]-4-yl)methyl)-1H-benzo[d]imidazole-7-carboxylate

According to the procedure B, compound **4x** was obtained as a yellow amorphous solid in 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (ddd, 1H, J_1 = 5.2 Hz, J_2 = 4.0 Hz, J_3 = 1.2 Hz), 7.60 (d, 1H, J = 7.6 Hz), 7.46 (dd, 1H, J_1 = 7.6 Hz, J_2 = 2.8 Hz), 7.39 – 7.10 (m, 13H), 7.03 – 6.95 (m, 4H), 6.82 – 6.77 (m, 3H), 6.64 (d, 1H, J = 5.2 Hz), 6.57 – 6.52 (m, 1H), 6.23 – 6.19 (m, 2H), 5.90 (dd, 1H, J_1 = 9.6 Hz, J_2 = 6.0 Hz), 5.91 – 5.47 (m, 2H), 4.57 – 4.47 (m, 3H), 3.66 (ddd, 1H, J_1 = 11.6 Hz, J_2 = 9.6 Hz, J_3 = 2.0 Hz), 3.44 – 3.36 (m, 1H), 3.08 (t, 2H, J = 4.0 Hz), 2.98 (t, 2H, J = 4.0 Hz), 1.85 – 1.77 (m, 2H), 1.65 – 1.58 (m, 2H), 1.43 – 1.09 (m, 11H), 0.81 – 0.75 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.8, 164.0, 163.9, 158.5, 152.5, 143.4, 141.4, 140.0, 140.0, 139.5, 137.8, 137.7, 135.8, 134.5, 134.1, 131.8, 130.7, 130.2, 129.8, 129.5, 129.5, 128.6, 128.5, 128.3, 127.4, 127.1, 127.1, 126.4, 126.2, 126.2, 126.0, 125.3, 124.6, 124.0, 122.4, 120.8, 119.1, 119.0, 117.8, 117.8, 114.7, 114.6, 110.6, 108.9, 91.7, 77.5, 69.3, 66.9, 47.0, 34.4, 32.1, 32.1, 32.0, 31.3, 29.7, 25.1, 23.5, 23.5, 19.5, 19.4, 14.5; **IR (cm^{-1})**: *ν* 3032, 2927, 2855, 1752, 1618, 1451, 1278, 1036, 699; **HRMS** m/z (ESI) calculated for $C_{59}H_{56}N_7O_6$ $[M + H]^+$: 958.4287, found: 958.4282.



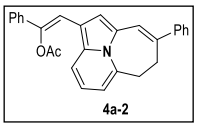
1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)ethan-1-ol

Compound **4a-1** was obtained as a yellow amorphous solid in 96% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.42 (m, 4H), 7.37 – 7.32 (m, 4H), 7.30 – 7.19 (m, 3H), 6.87 (s, 1H), 6.73 (s, 1H), 6.67 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.4 Hz), 6.34 (d, 1H, J = 6.4 Hz), 4.92 (dd, 1H, J_1 = 8.8 Hz, J_2 = 4.4 Hz), 3.22 – 3.17 (m, 3H), 3.13 – 3.08 (m, 3H), 2.11 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.0, 143.4, 139.6, 135.1, 134.2, 128.4, 128.3, 127.4, 126.1, 125.8, 125.4, 124.7, 119.7, 119.1, 117.7, 115.3, 110.7, 110.2, 74.7, 36.3, 34.5, 32.2; **IR (cm^{-1})**: *ν* 3423, 3033, 2928, 2853, 1619, 1295, 1024, 698; **HRMS** m/z (ESI) calculated for $C_{26}H_{24}NO$ $[M + H]^+$: 366.1852, found: 366.1853.



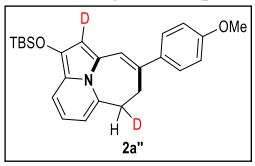
(*Z*)-1-phenyl-2-(8-phenyl-6,7-dihydroazepino[2,1,7-cd]indolizin-2-yl)vinyl acetate

Compound **4a-2** was obtained as a yellow thick liquid in 86% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.53 (m, 3H), 7.49 – 7.46 (m, 2H), 7.41 – 7.38 (m, 4H), 7.31 – 7.25 (m, 2H), 7.14 (s, 1H), 7.03 (s, 1H), 6.92 (s, 1H), 6.85 (dd, 1H, J_1 = 8.8 Hz, J_2 = 6.8 Hz), 6.45 (d, 1H, J = 6.8 Hz), 3.25 (t, 2H, J = 4.0 Hz), 3.13 (t, 2H, J = 4.0 Hz), 2.45 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 143.3, 142.8, 139.9, 136.3, 135.8, 135.6, 128.6, 128.4, 127.4, 126.4, 126.4, 125.5, 123.8, 119.6, 119.1, 117.3, 115.1, 111.7, 108.8, 107.8, 34.4, 32.1, 21.3; **IR (cm^{-1})**: *ν* 3052, 2924, 2853, 1757, 1641, 1204, 696; **HRMS** m/z (ESI) calculated for $C_{28}H_{24}NO_2$ $[M + H]^+$: 406.1802, found: 406.1811.



2-((tert-butyldimethylsilyl)oxy)-8-(4-methoxyphenyl)-6,7-dihydroazepino[2,1,7-cd]indolizine-1,6-d_2

According to the procedure A, compound **2a''** was obtained as a yellow thick liquid in 53% yield;



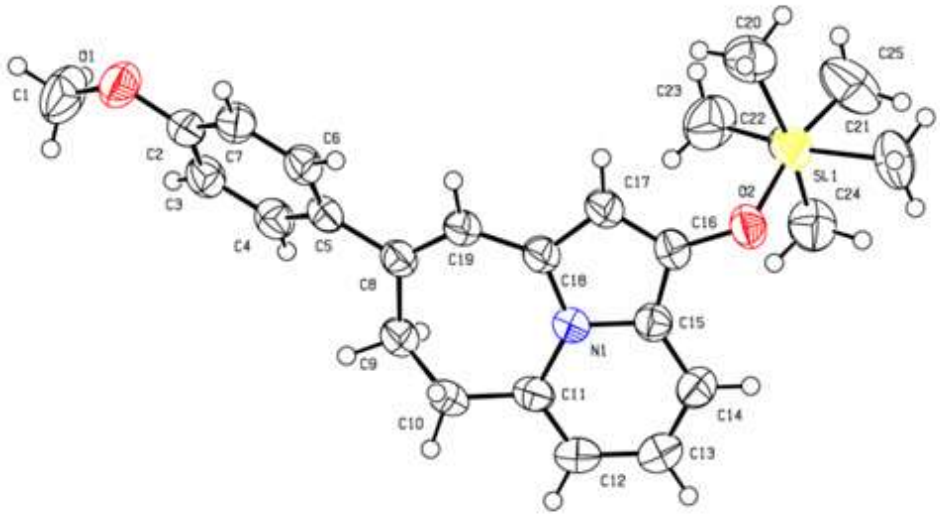
2a''

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.30 (d, 1H, *J* = 8.8 Hz), 6.94 – 6.91 (m, 2H), 6.76 (s, 1H), 6.54 (t, 1H, *J* = 7.6 Hz), 6.44 (s, 0.1H), 6.24 (d, 1H, *J* = 6.4 Hz), 3.85 (s, 3H), 3.16 – 3.07 (m, 3H), 1.09 (s, 9H), 0.27 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.0, 138.3, 136.3, 133.5, 133.4, 126.4, 126.1, 120.7, 117.8, 114.8, 114.8, 113.7, 110.3, 108.2, 55.3, 34.4, 34.3, 34.1, 33.9, 32.2, 25.8, 18.2, -4.6; **IR (cm^{-1})**: *v* 3031, 2953, 2856, 1617, 1430, 1250, 1036, 714; **HRMS** m/z (ESI) calculated for $C_{25}H_{30}D_2NO_2Si$ $[M + H]^+$: 408.2322, found: 408.2329.

9. The X-ray structure of 2a, 2z, 3a, 4m

The single crystal was obtained by slow evaporation of a saturated solution in dichloromethane and petroleum ether in a lossely capped vial. Structure information was deposited at the Cambridge Crystallographic Data Center (CCDC).

Figure S1. The X-ray crystallographic structure of **2a** (CCDC 2141700)

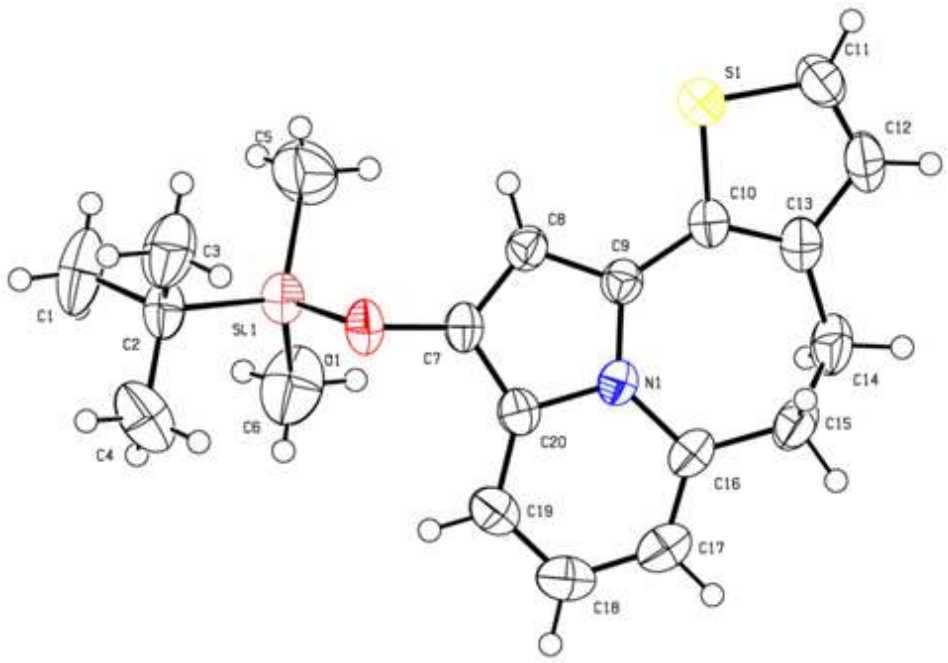


The X- ray of **2a**

The crystal **2a** was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. The ORTEP image of compound and crystallographic refinement parameters are given below.

Crystal Data for $C_{25}H_{31}NO_2Si$ (M =405.60 g/mol): triclinic, space group P-1 (no. 2), a = 8.0760(6) Å, b = 11.8269(8) Å, c = 13.0889(12) Å, α = 95.809(7) °, β = 104.901(7) °, γ = 106.302(6) °, V = 1139.12(16) $Å^3$, Z = 2, T = 293(2) K, μ(Mo Kα) = 0.123 mm^{-1}, Dcalc = 1.183 g/cm^3, 8850 reflections measured (6.886° ≤ 2Θ ≤ 58.028°), 5153 unique (R_{int} = 0.0227, R_{sigma} = 0.0474) which were used in all calculations. The final R_1 was 0.0543 (I > 2σ(I)) and wR_2 was 0.1404

Figure S2. The X-ray crystallographic structure of **2z** (CCDC 2141701)

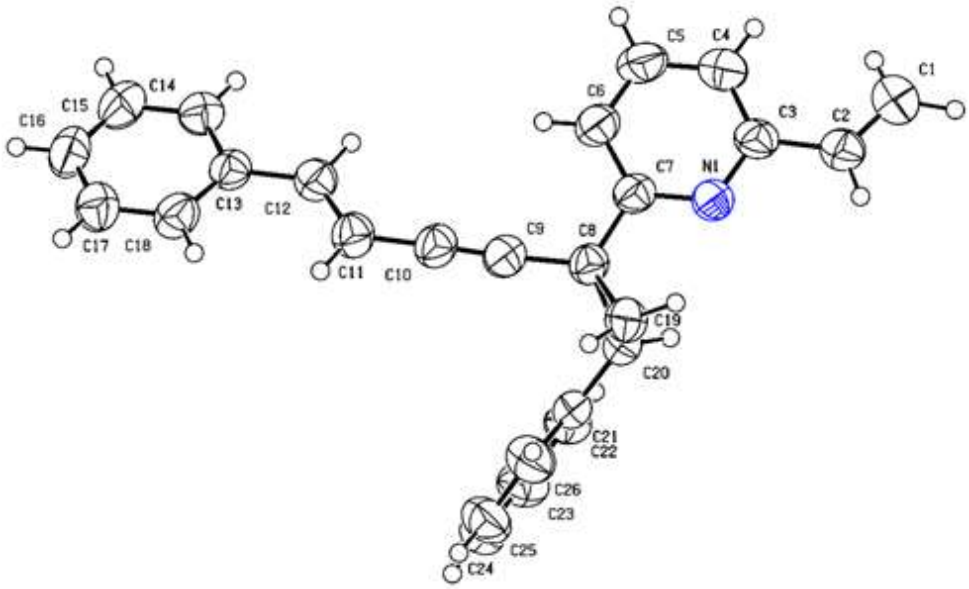


The X-ray of **2z**

The crystal **2z** was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. The ORTEP image of compound and crystallographic refinement parameters are given below.

Crystal Data for $C_{20}H_{25}NOSSi$ (M =355.56 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.7405(4) Å, b = 20.3269(14) Å, c = 12.9017(7) Å, β = 106.427(6) °, V = 1947.1(2) Å^3, Z = 4, T = 293(2) K, μ(Mo Kα) = 0.234 mm^{-1}, *Dcalc* = 1.213 g/cm^3, 8117 reflections measured (6.796° ≤ 2Θ ≤ 58.13°), 4467 unique (R_{int} = 0.0273, R_{sigma} = 0.0522) which were used in all calculations. The final R_1 was 0.0527 (I > 2σ(I)) and wR_2 was 0.1338

Figure S3. The X-ray crystallographic structure of **3a** (CCDC 2239536)

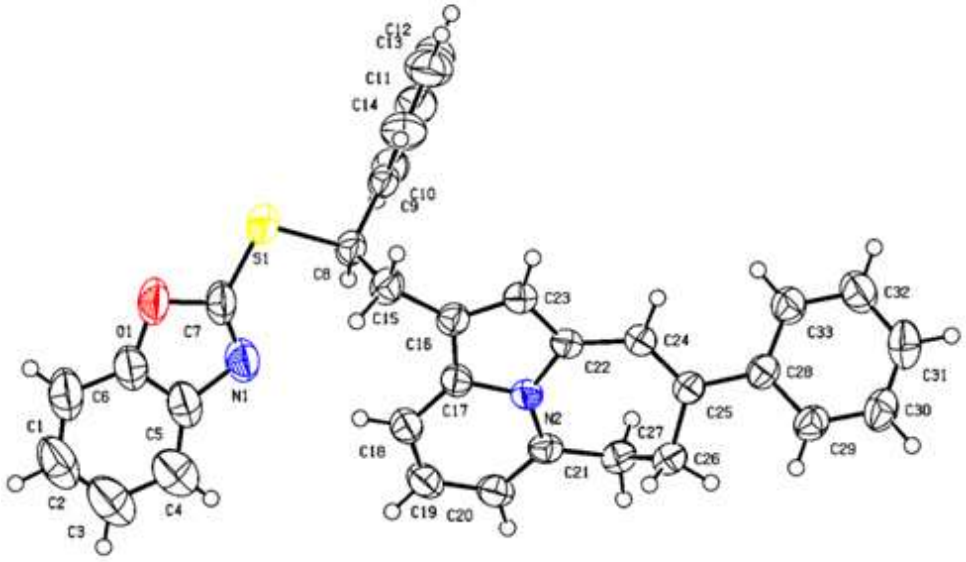


The X-ray of **3a**

The crystal **3a** was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. The ORTEP image of compound and crystallographic refinement parameters are given below.

Crystal Data for $C_{26}H_{21}N$ (M =347.44 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 5.5140(3) Å, b = 9.4541(5) Å, c = 37.289(2) Å, β = 92.380(5) °, V = 1942.20(18) Å^3, Z = 4, T = 293(2) K, μ(Mo Kα) = 0.068 mm^{-1}, *Dcalc* = 1.188 g/cm^3, 8202 reflections measured (6.962° ≤ 2Θ ≤ 58.254°), 4368 unique (R_{int} = 0.0184, R_{sigma} = 0.0368) which were used in all calculations. The final R_1 was 0.0569 (I > 2σ(I)) and wR_2 was 0.1475 (all data).

Figure S4. The X-ray crystallographic structure of **4m** (CCDC 2141703)



The X-ray of **4m**

The crystal **4m** was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. The ORTEP image of compound and crystallographic refinement parameters are given below.

Crystal Data for $C_{33}H_{26}N_2OS$ (M =498.62 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 8.8644(3) Å, b = 9.5173(3) Å, c = 30.8497(9) Å, β = 90.765(3) °, V = 2602.41(14) Å^3, Z = 4, T = 293(2) K, μ(Mo Kα) = 0.154 mm^{-1}, *Dcalc* = 1.273 g/cm^3, 22594 reflections measured (6.79° ≤ 2Θ ≤ 58.204°), 6201 unique (R_{int} = 0.0342, R_{sigma} = 0.0372) which were used in all calculations. The final R_1 was 0.0567 (I > 2σ(I)) and wR_2 was 0.1483 (all data).

10. References

1. Cao, B., Wang, Y., Ding, K., Neamati, N. & Long, Y.-Q. Synthesis of the pyridinyl analogues of dibenzylideneacetone (pyr-dba) via an improved Claisen–Schmidt condensation, displaying diverse biological activities as curcumin analogues. *Org. Biomol. Chem*. **10**, 1239–1245 (2012**)**.

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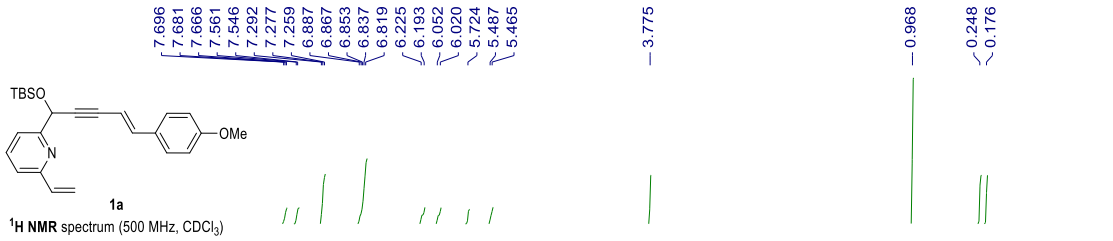
3. Smith, C. R., Bunnelle, E. M., Rhodes, A. J. & Sarpong, R. Pt-Catalyzed Cyclization/1,2-Migration for the Synthesis of Indolizines, Pyrrolones, and Indolizinones. *Org. Lett*. **9**, 1169–1171 (2007**)**.

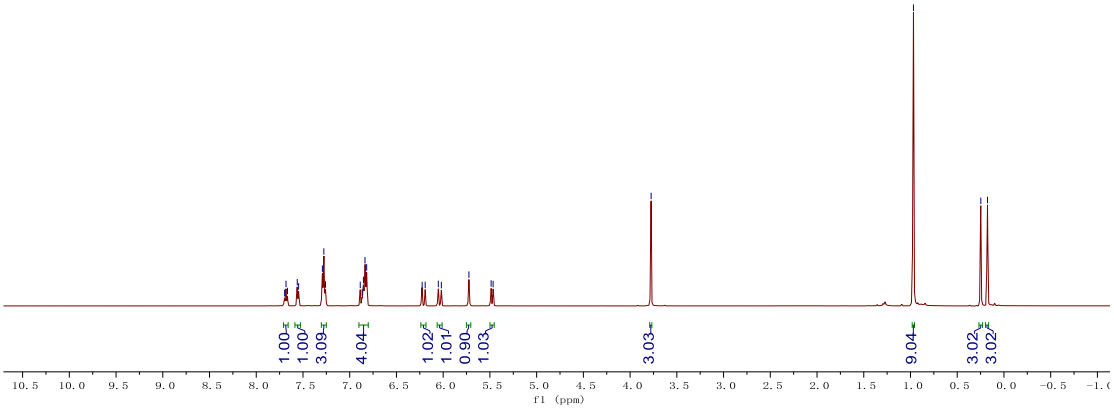
4. Liu, R.-R., Ye, S.-C., Lu, C.-J., Xiang, B., Gao, J. & Jia, Y.-X. Au-catalyzed ring-opening reactions of 2-(1-alkynyl-cyclopropyl)pyridines with nucleophiles. *Org. Biomol. Chem*. **13**, 4855–4858 (2015**)**.

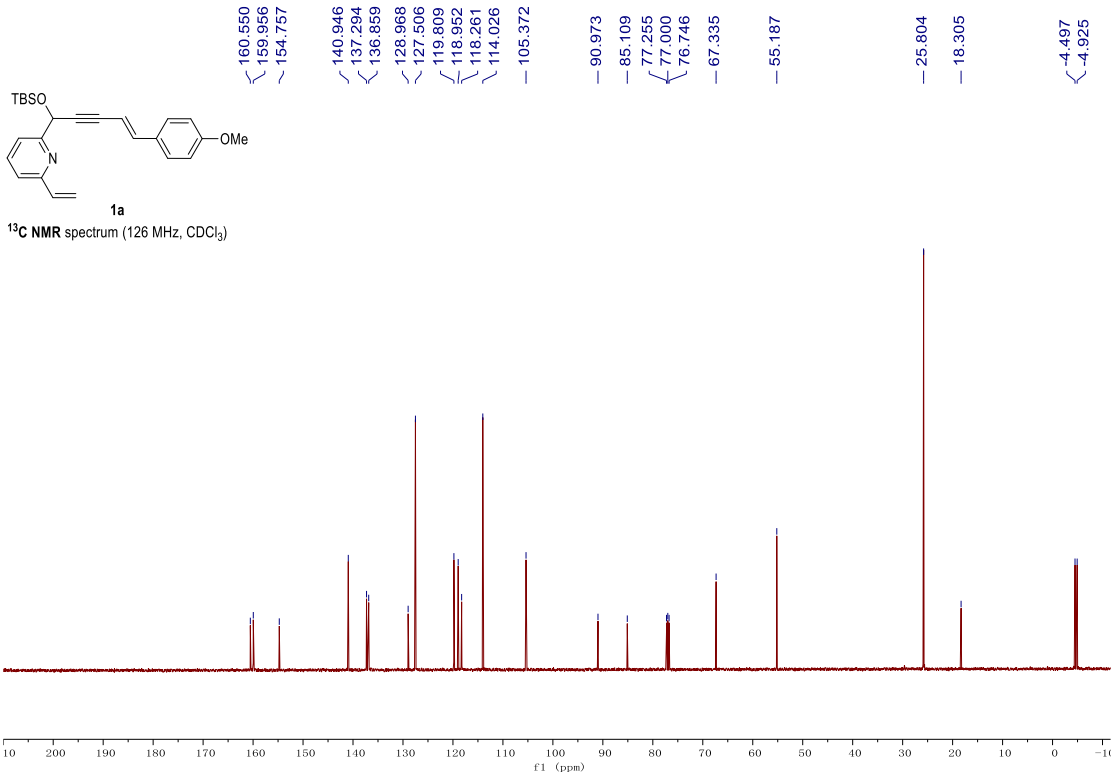
11. Copies of NMR spectra



1a

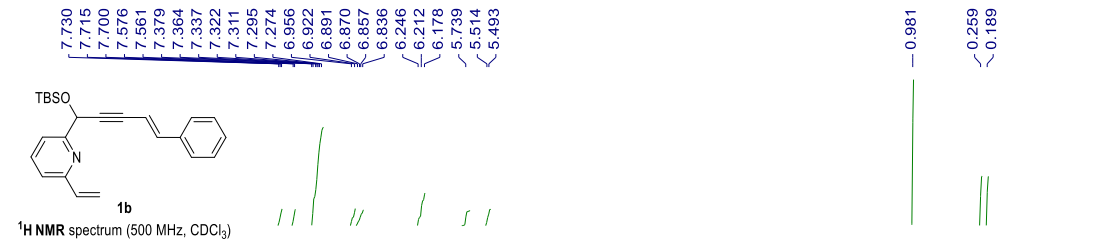
^{1}**H NMR** spectrum (500 MHz, $CDCl_3$)





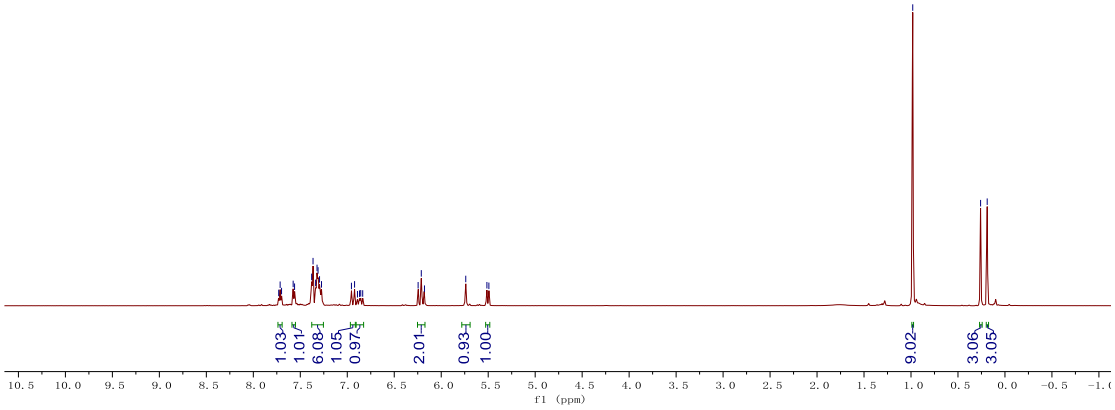
1a

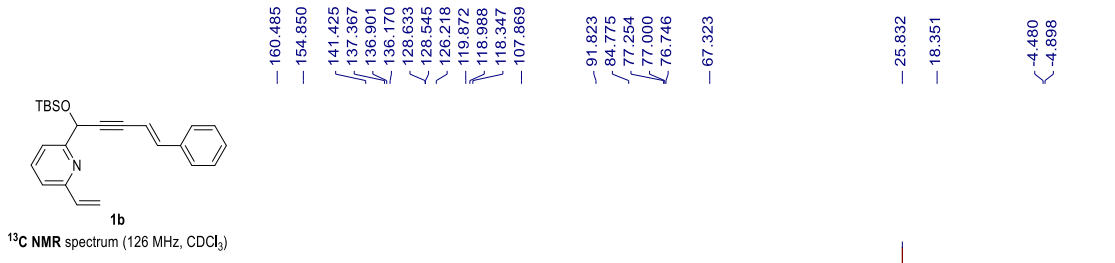
^{13}**C NMR** spectrum (126 MHz, $CDCl_3$)



1b

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





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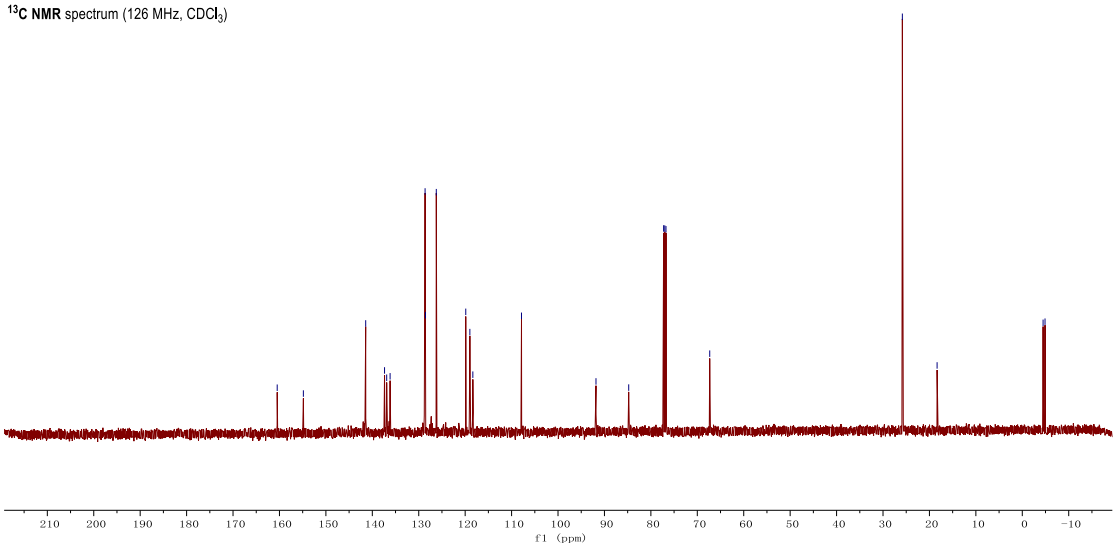
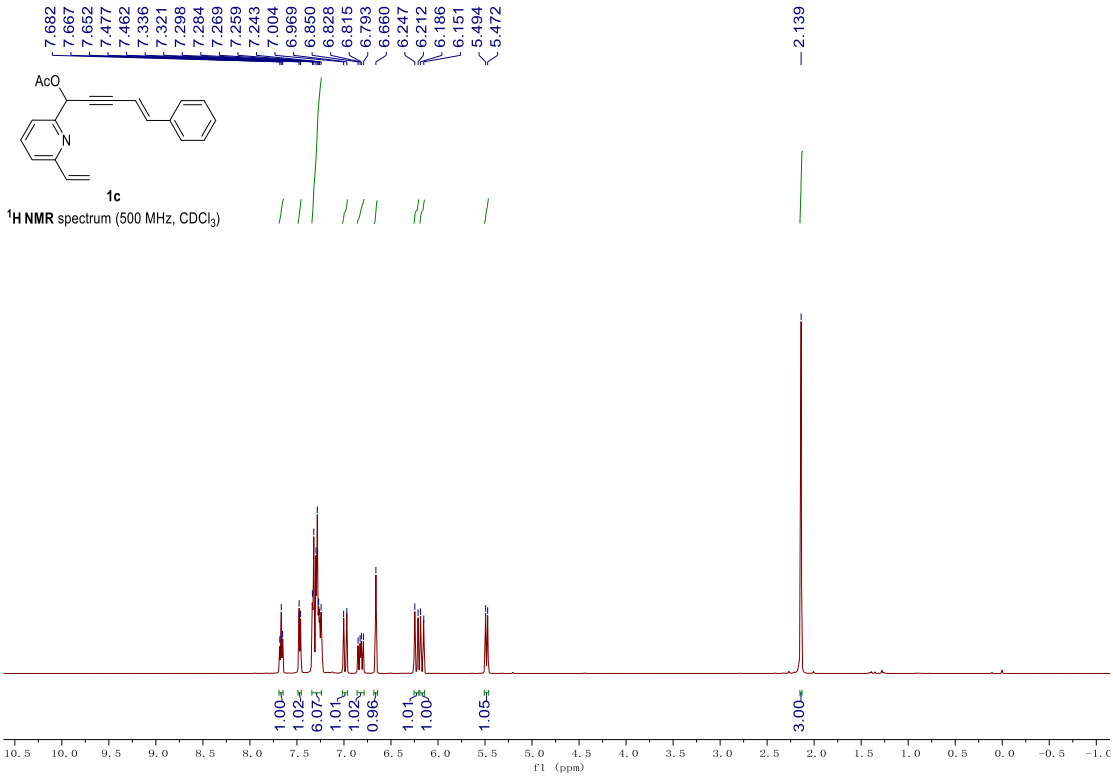
^{13}**C NMR** spectrum (126 MHz, $CDCl_3$)





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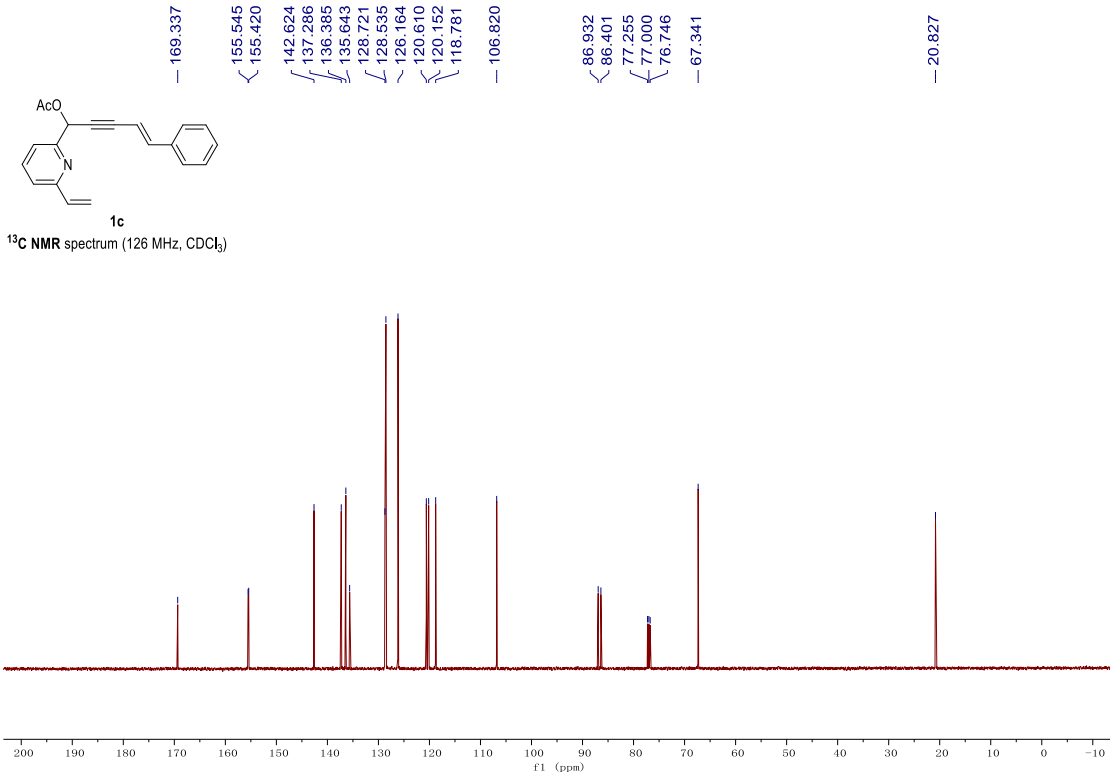
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

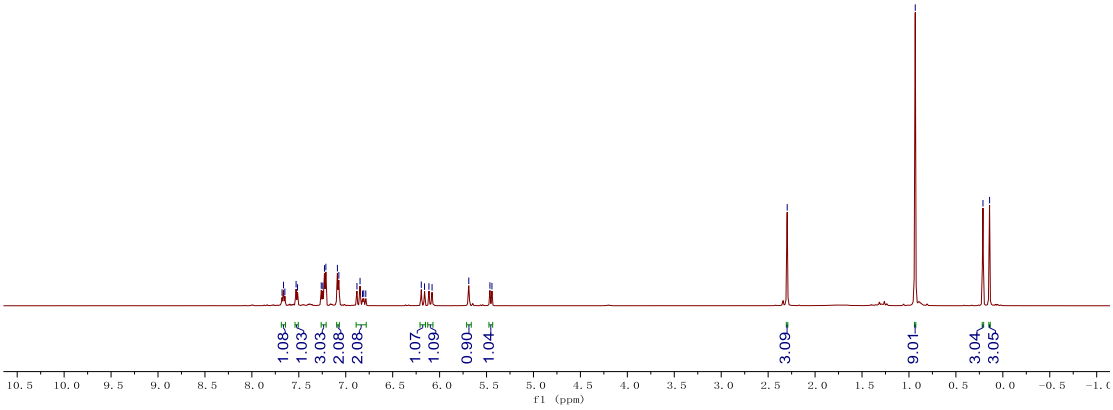


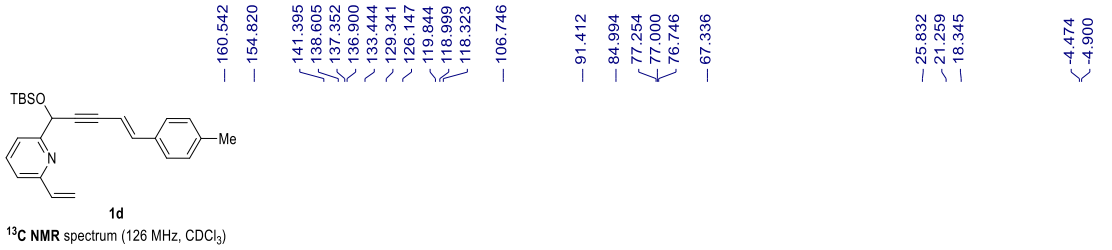
1c

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

1d

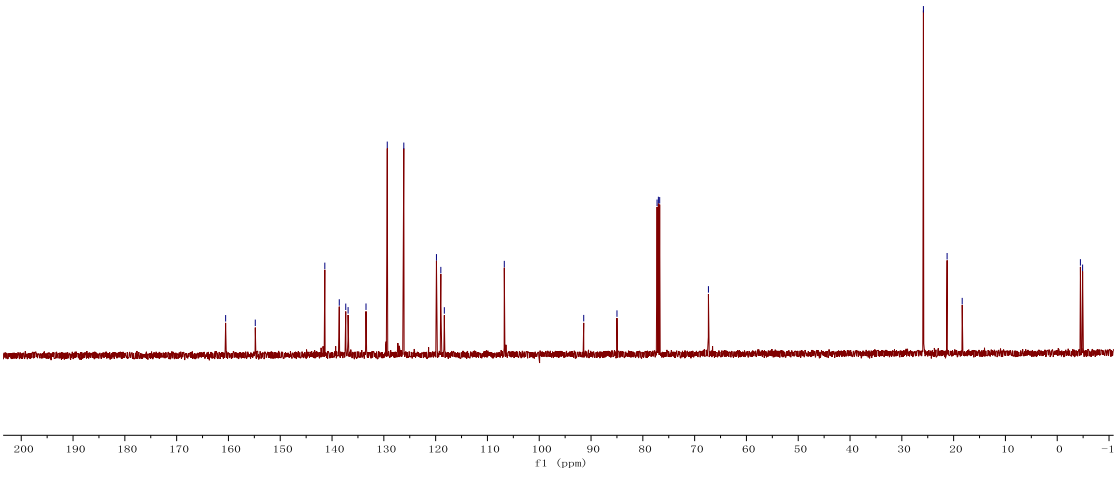
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

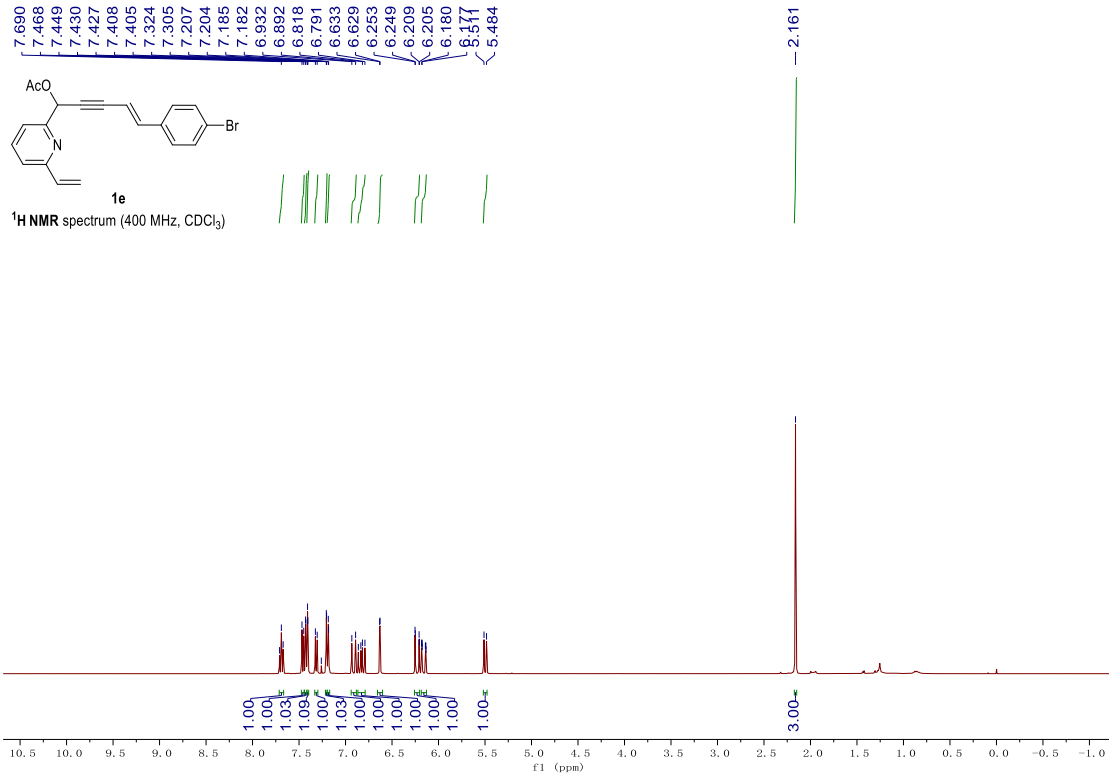




1d

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





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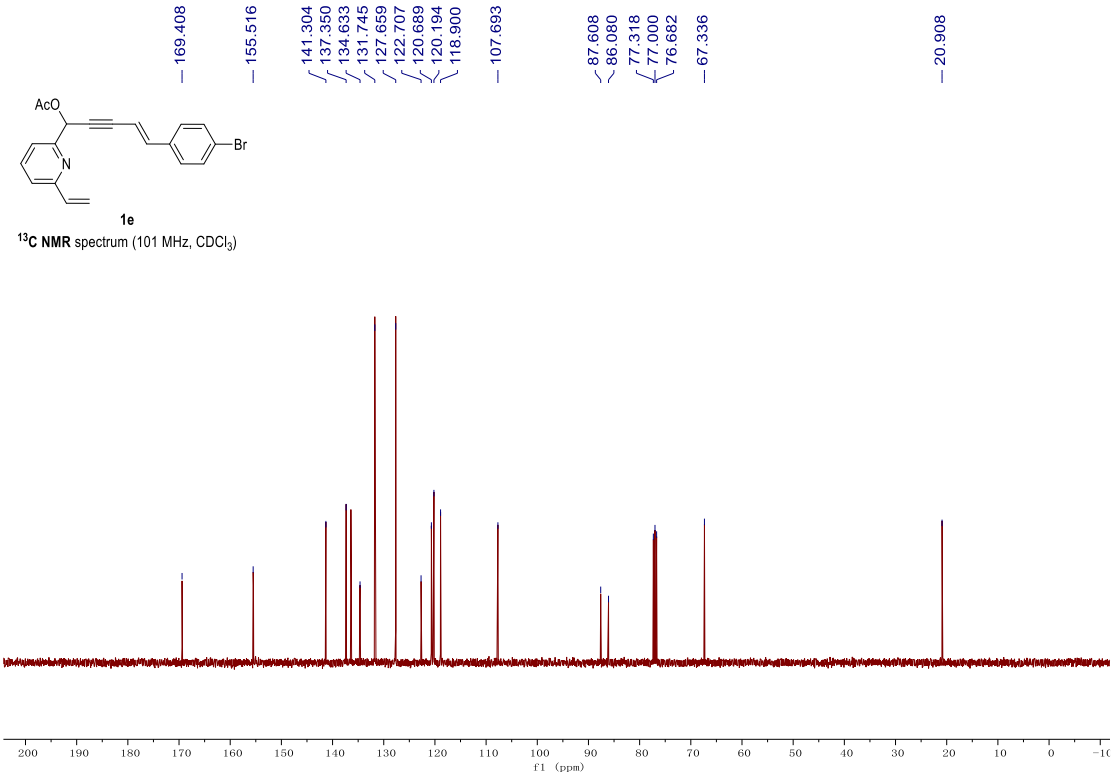
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



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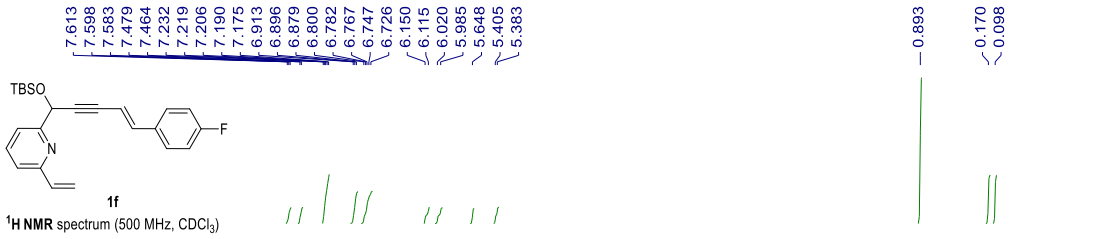
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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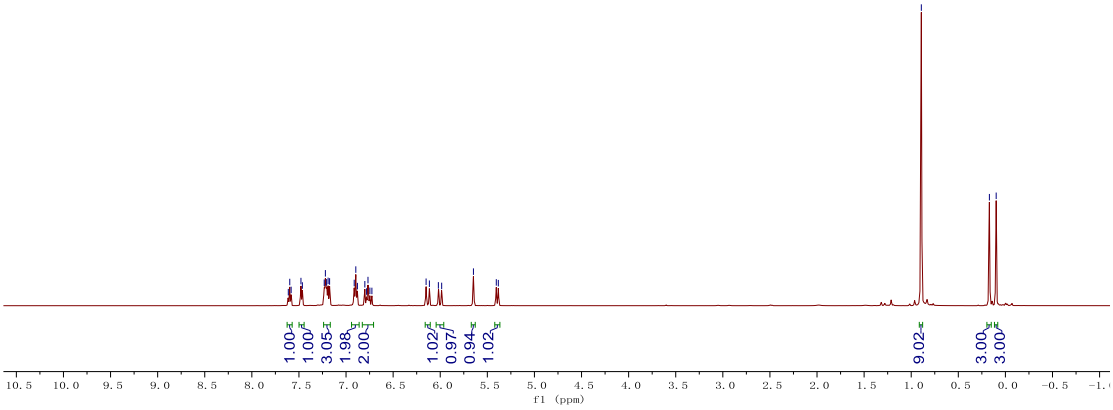
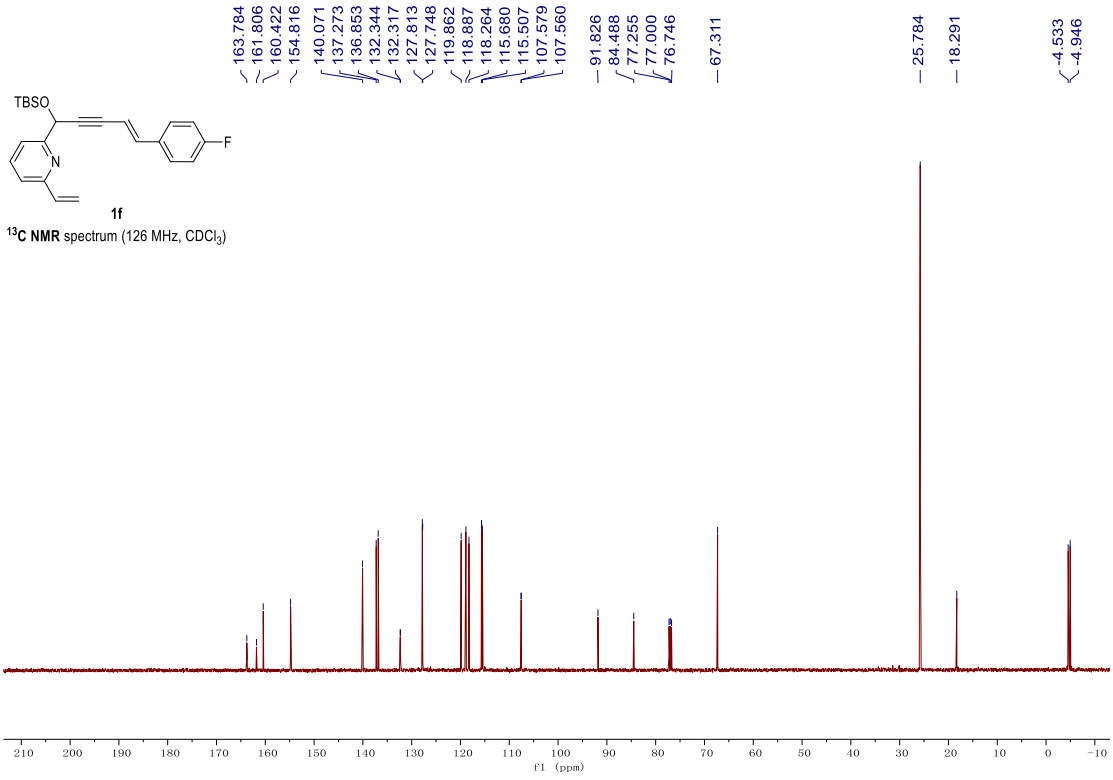
^{1}H NMR spectrum (500 MHz, $CDCl_3$)





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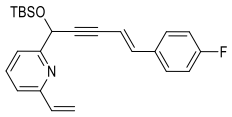
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



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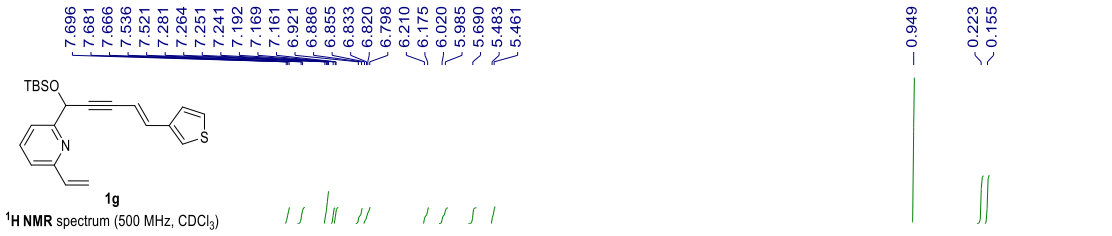
^{19}F NMR spectrum (564 MHz, $CDCl_3$)



1g

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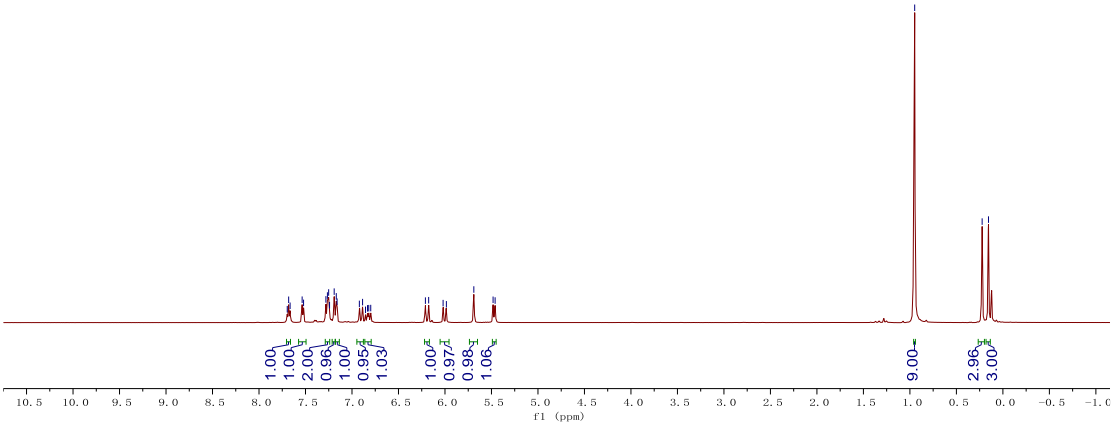

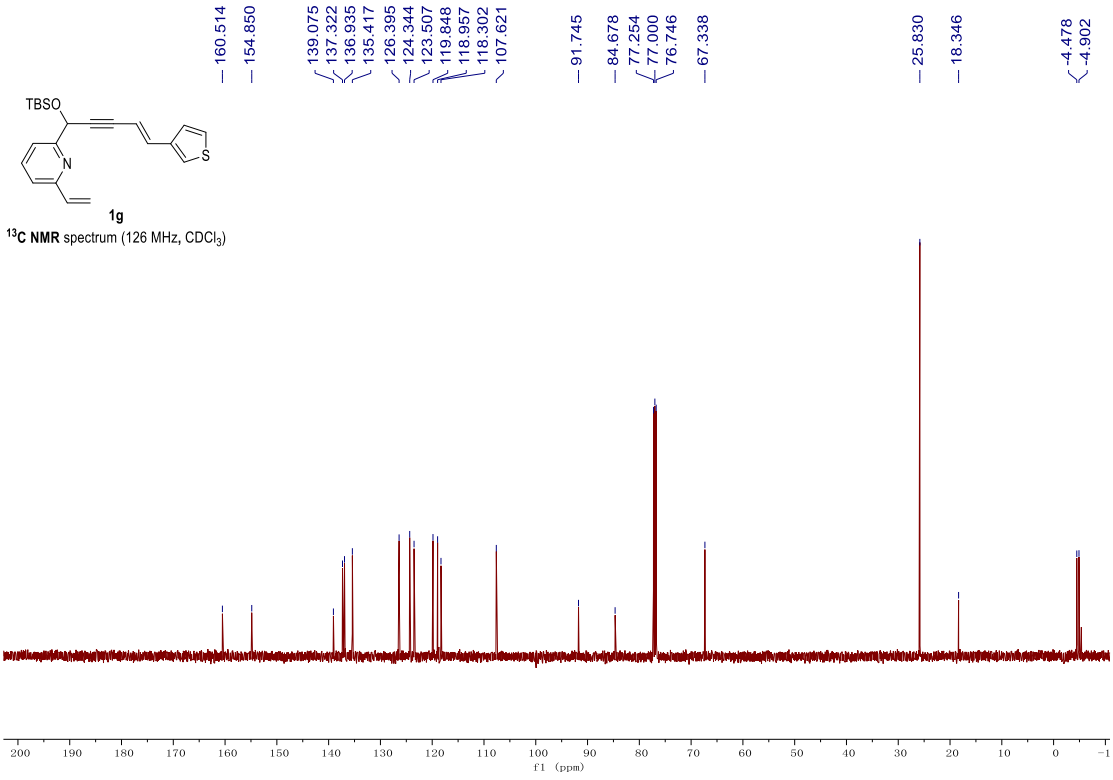

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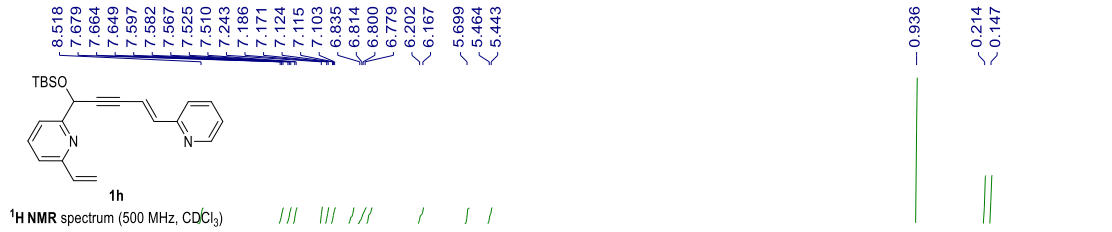

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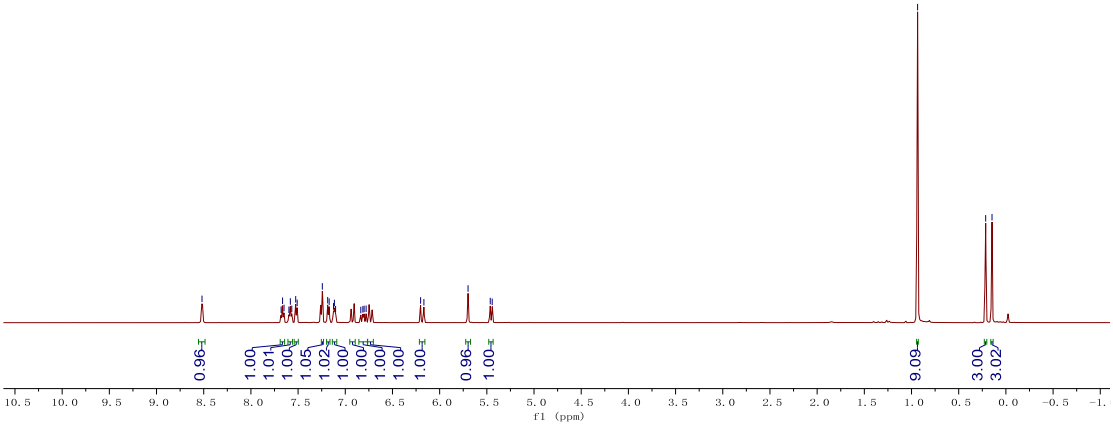

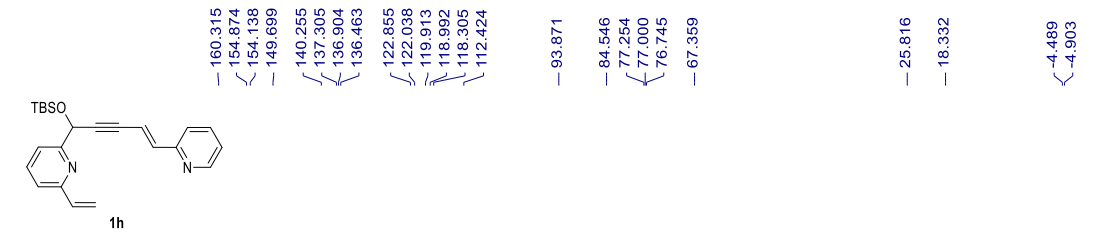

1h

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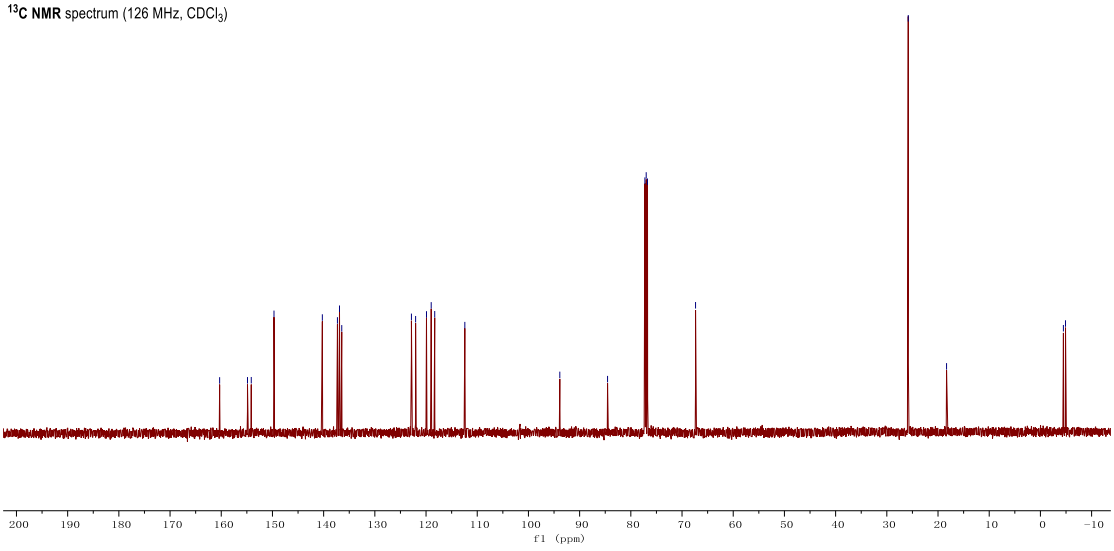

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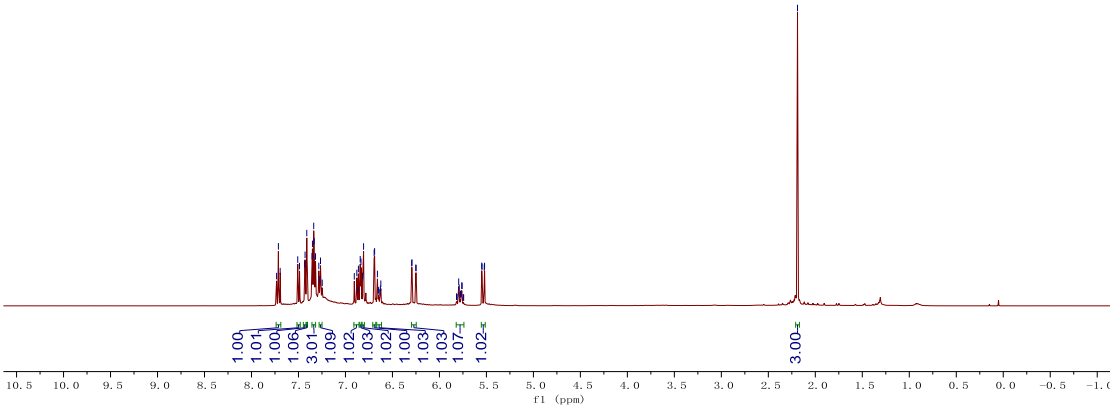

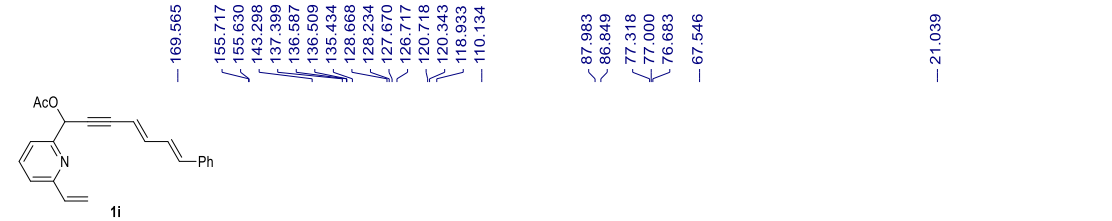

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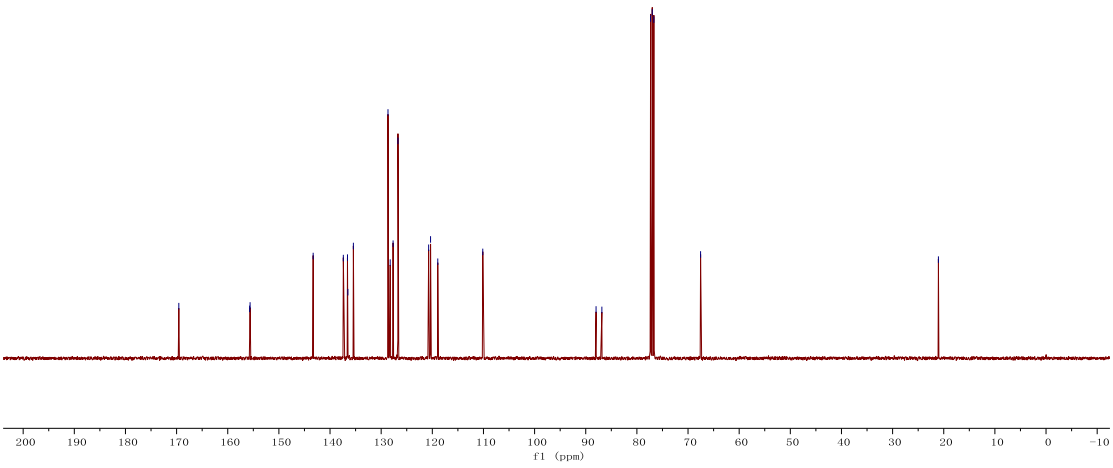
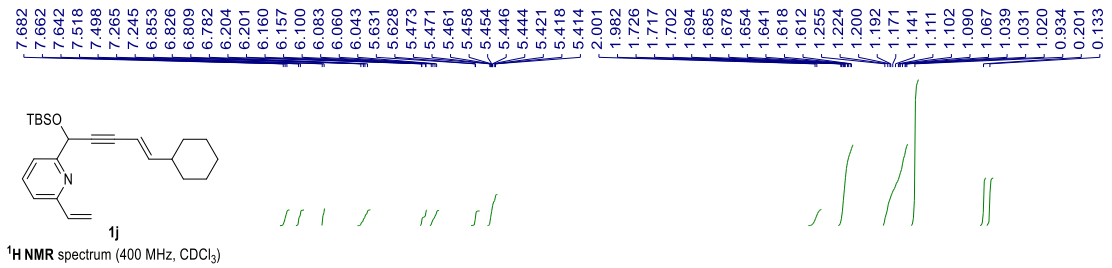
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





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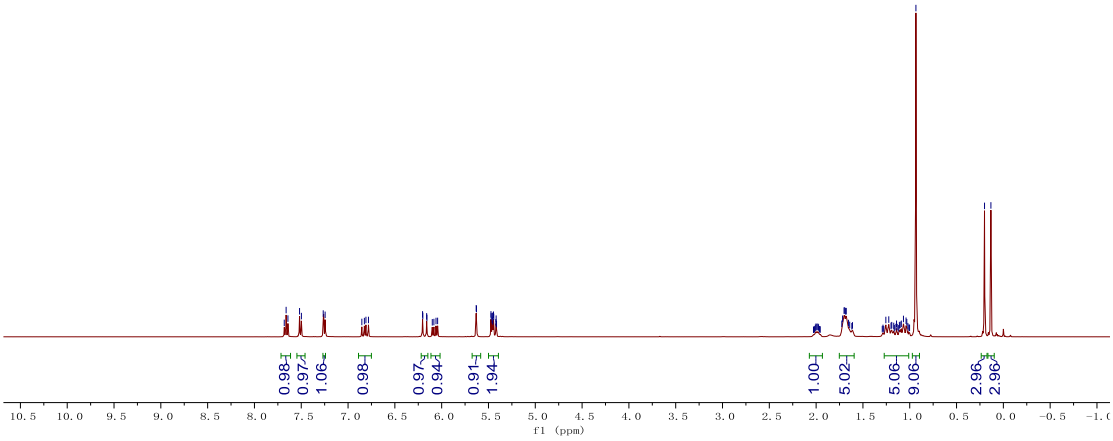
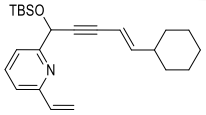
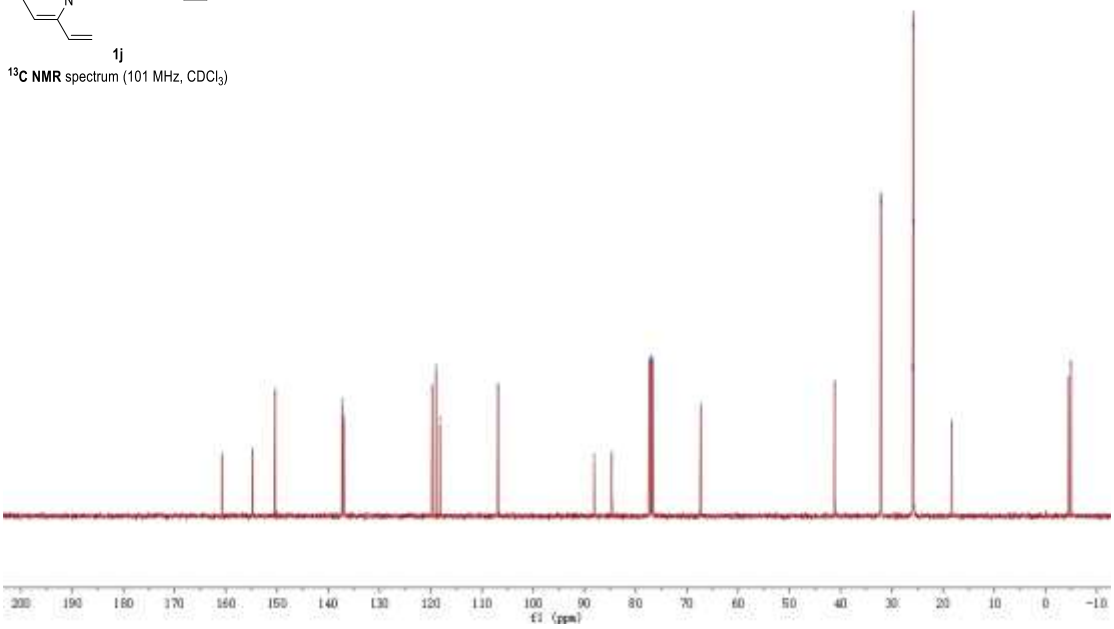
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



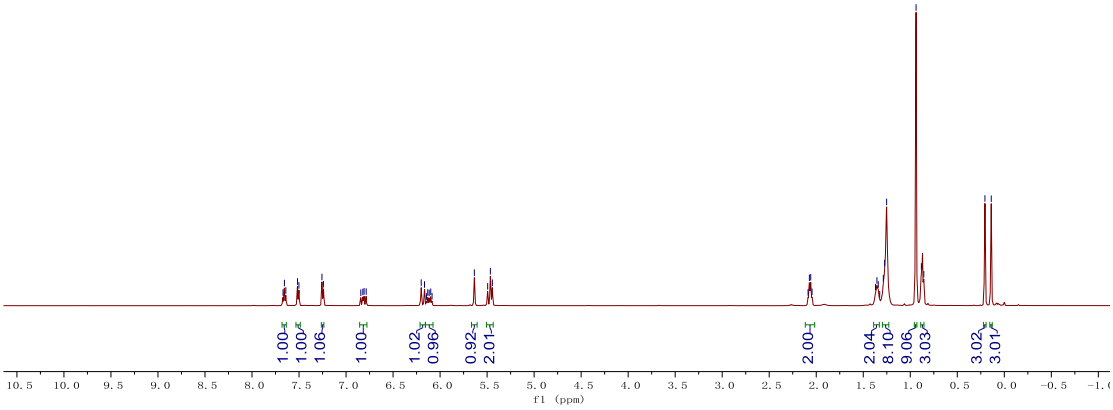


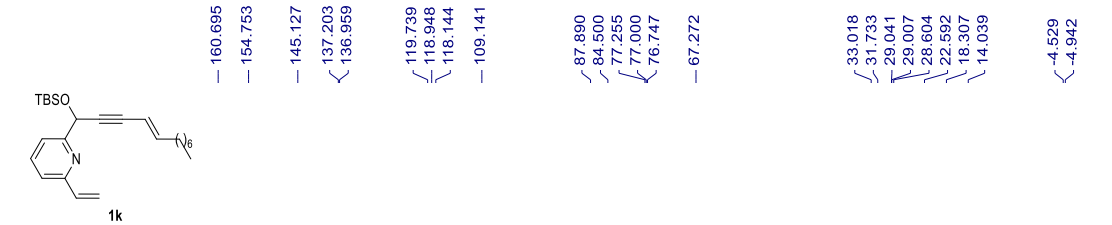
1j

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

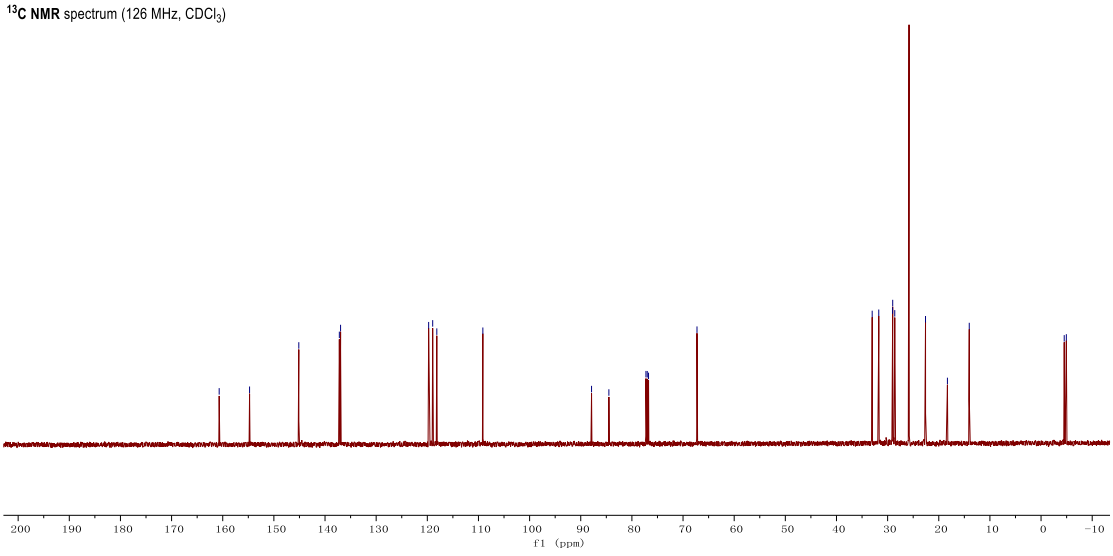


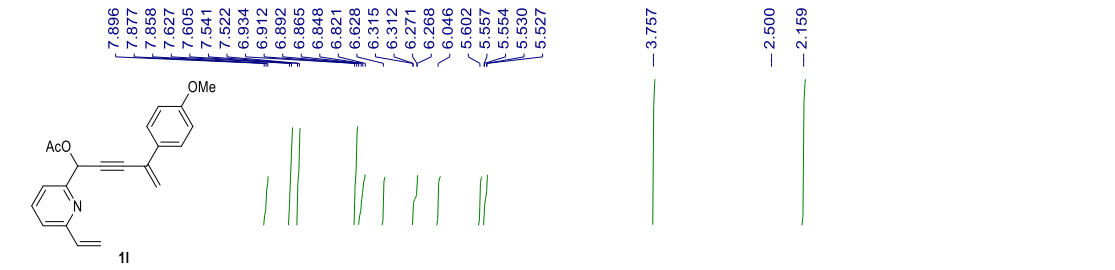
^{1}H NMR spectrum (500 MHz, $CDCl_3$)





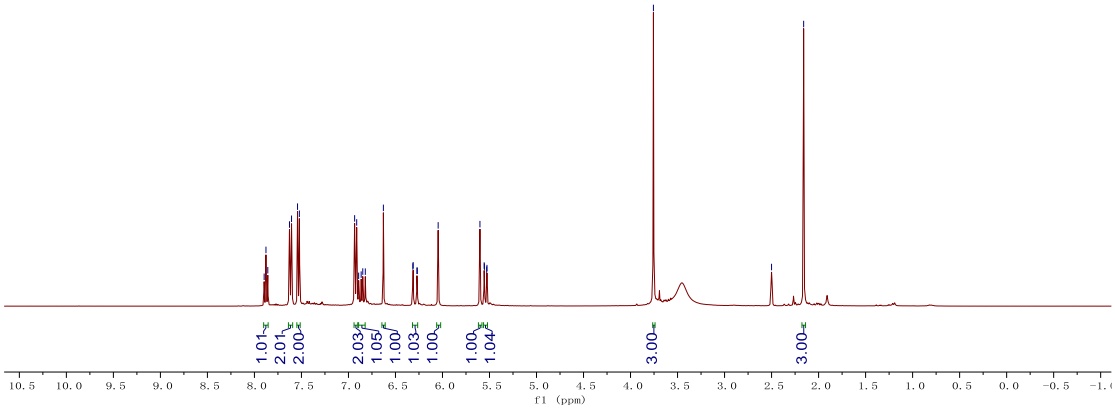
^{13}C NMR spectrum (126 MHz, $CDCl_3$)

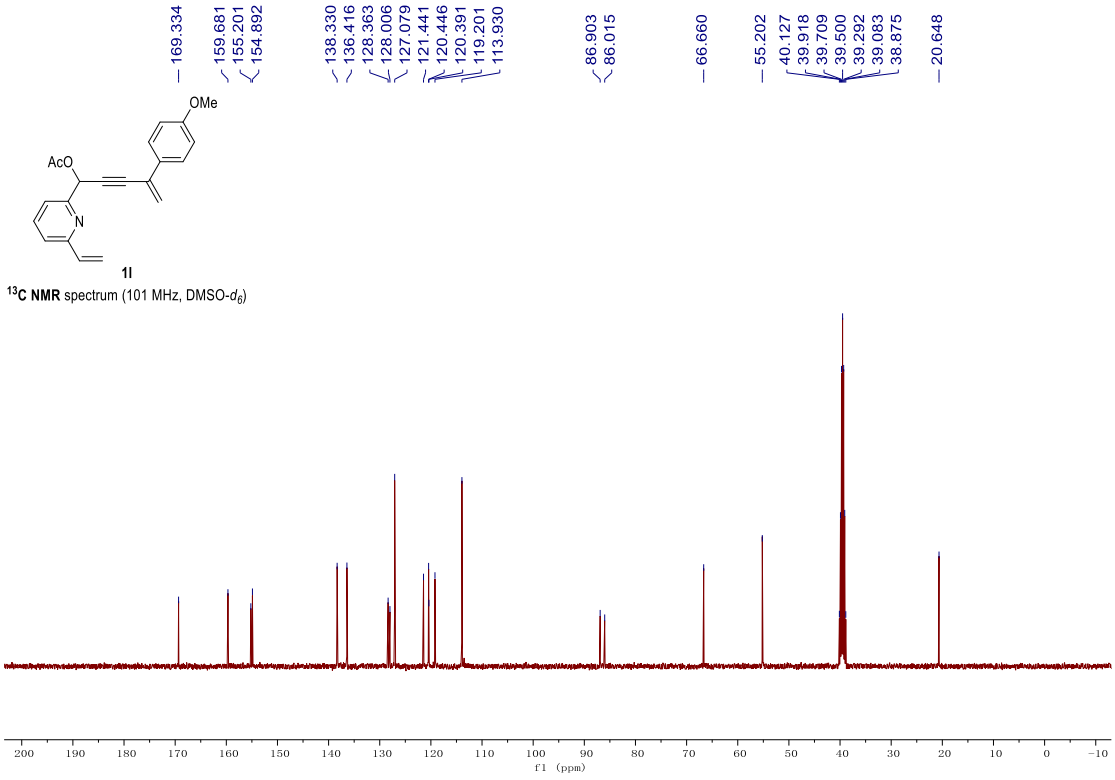




1l

^{1}H NMR spectrum (400 MHz, DMSO-d_6)





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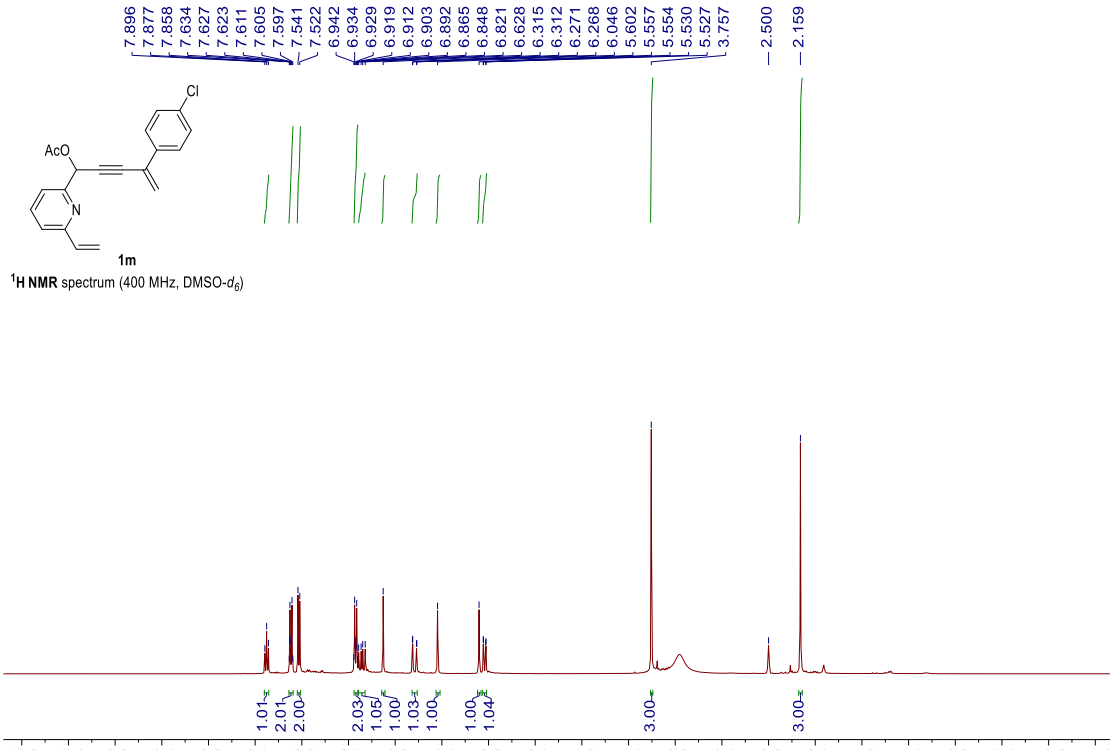

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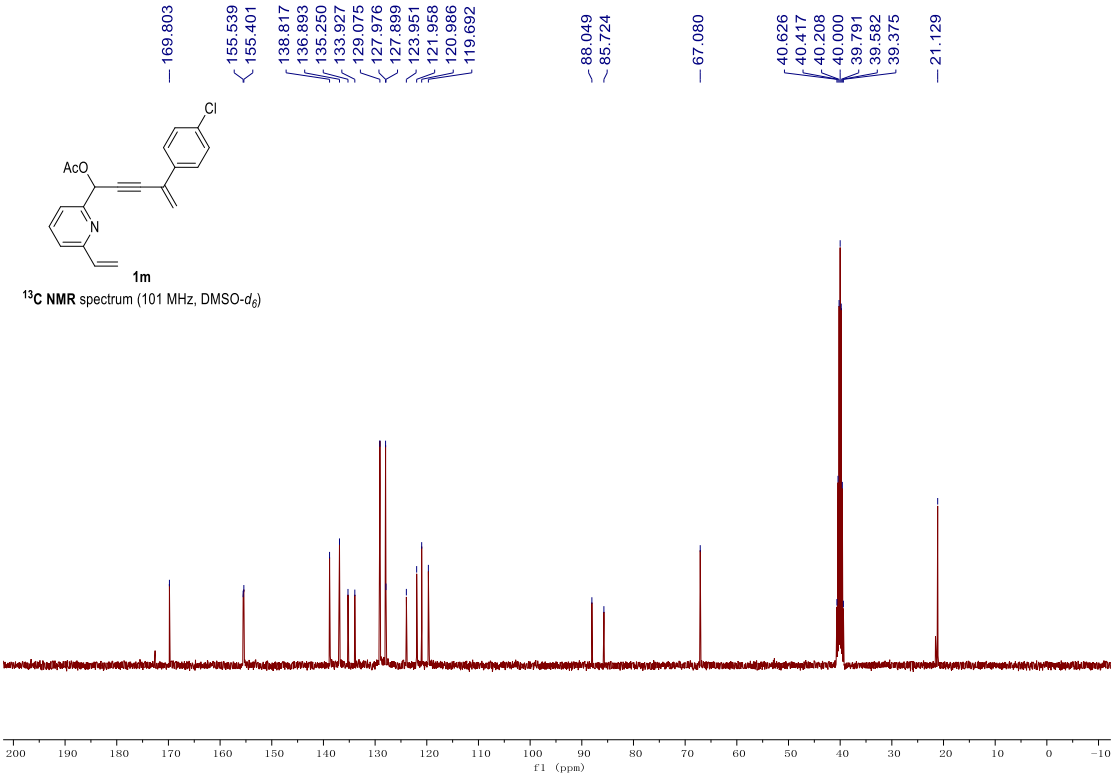
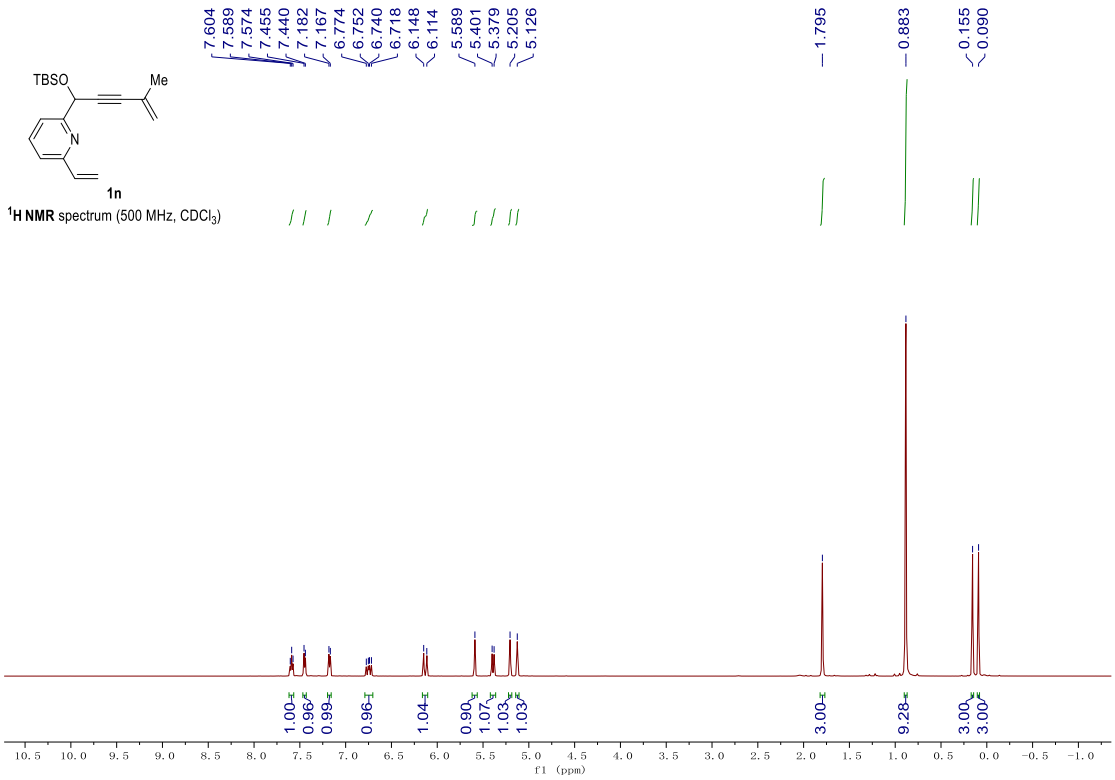
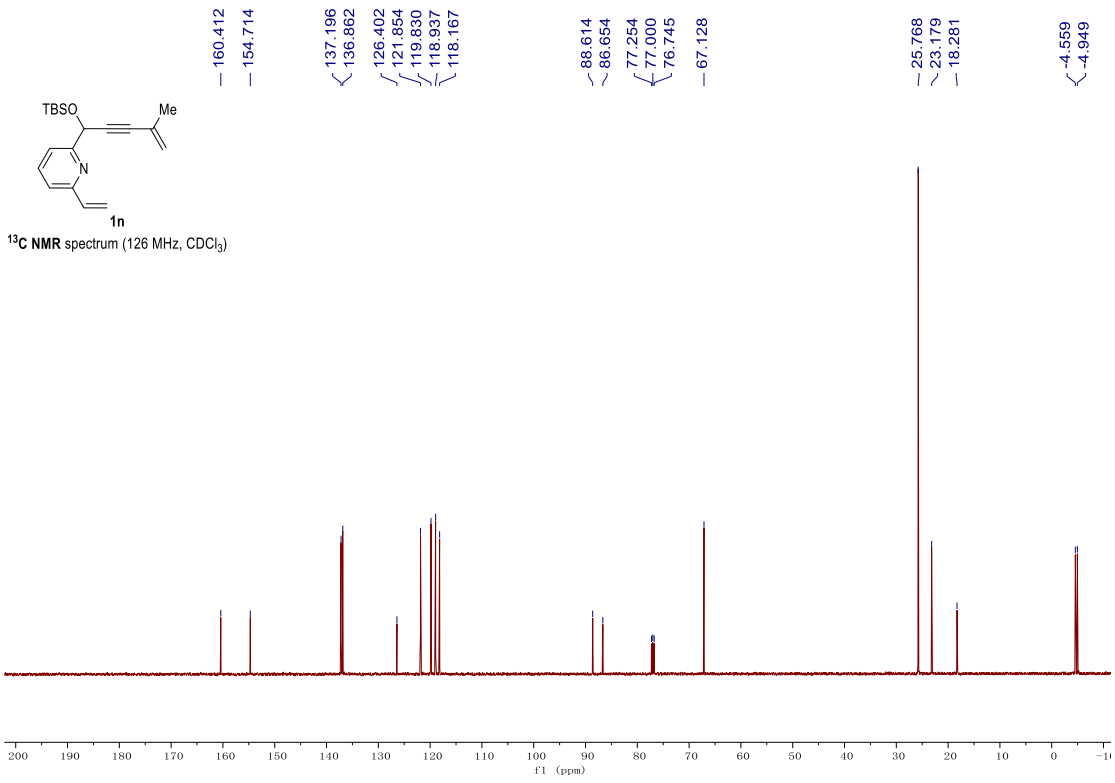


^{13}C NMR spectrum (101 MHz, DMSO-d_6)

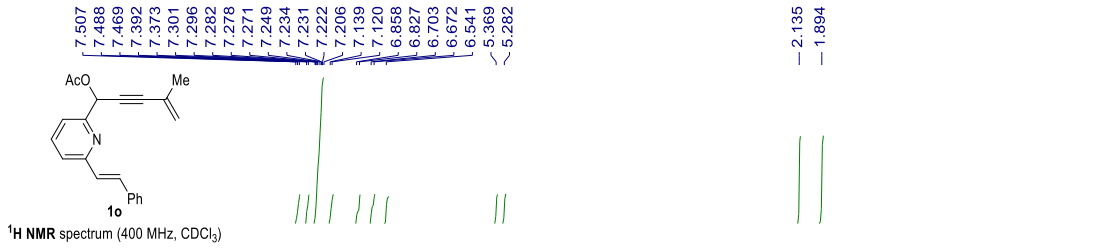


1n

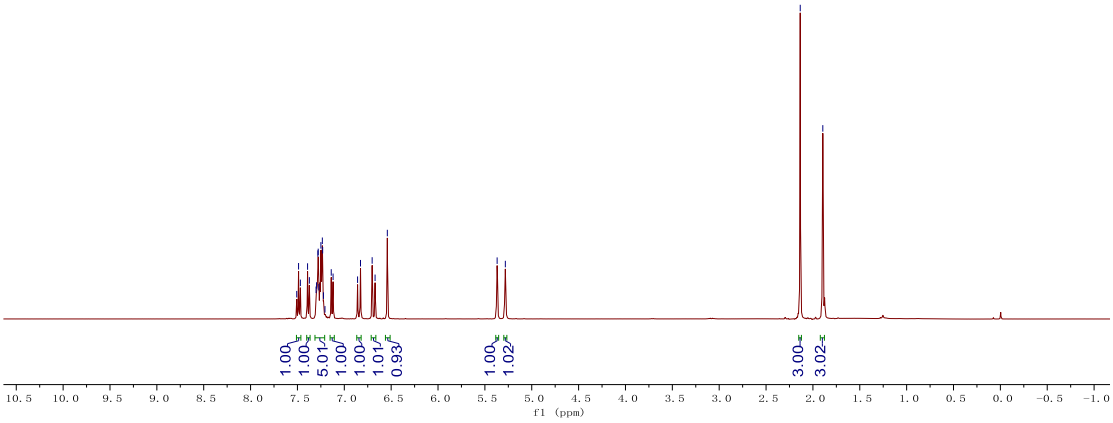
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

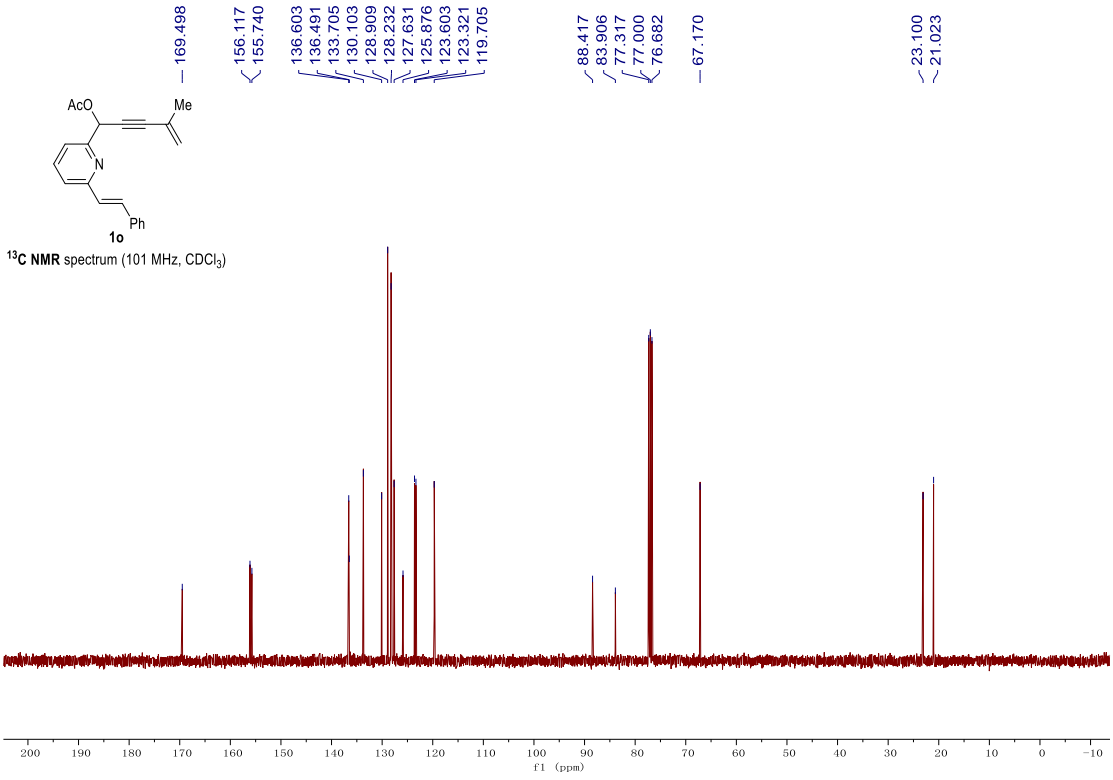


^{13}C NMR spectrum (126 MHz, $CDCl_3$)

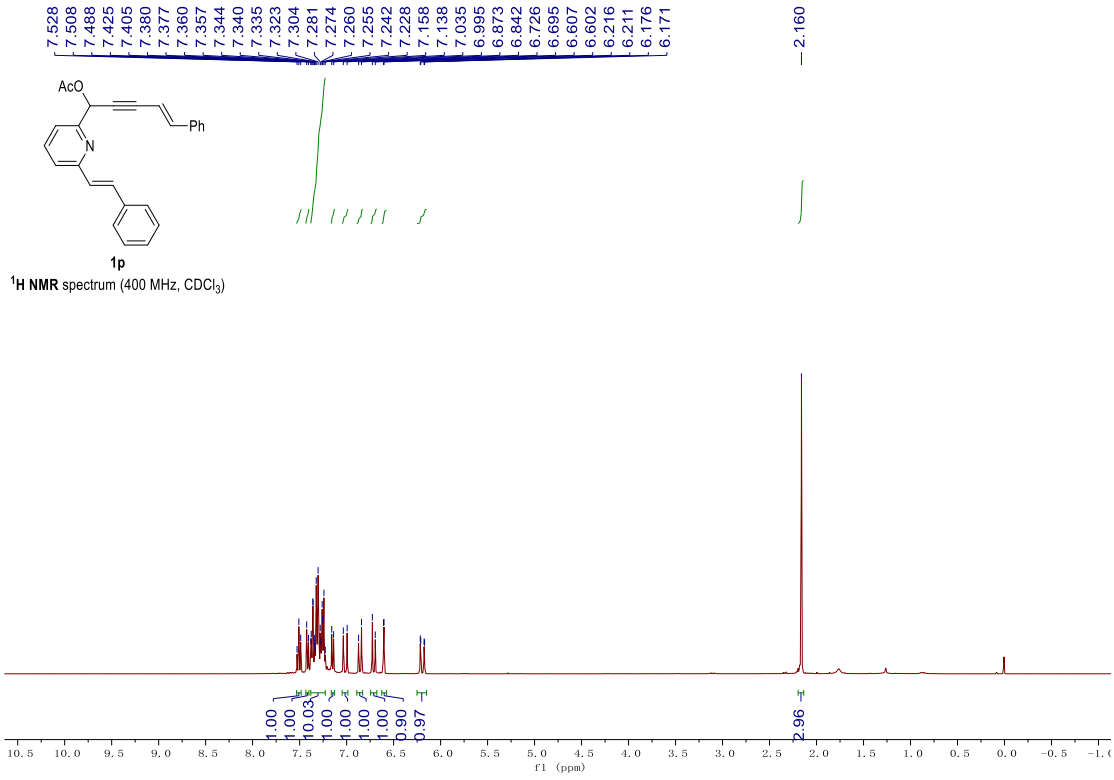


^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



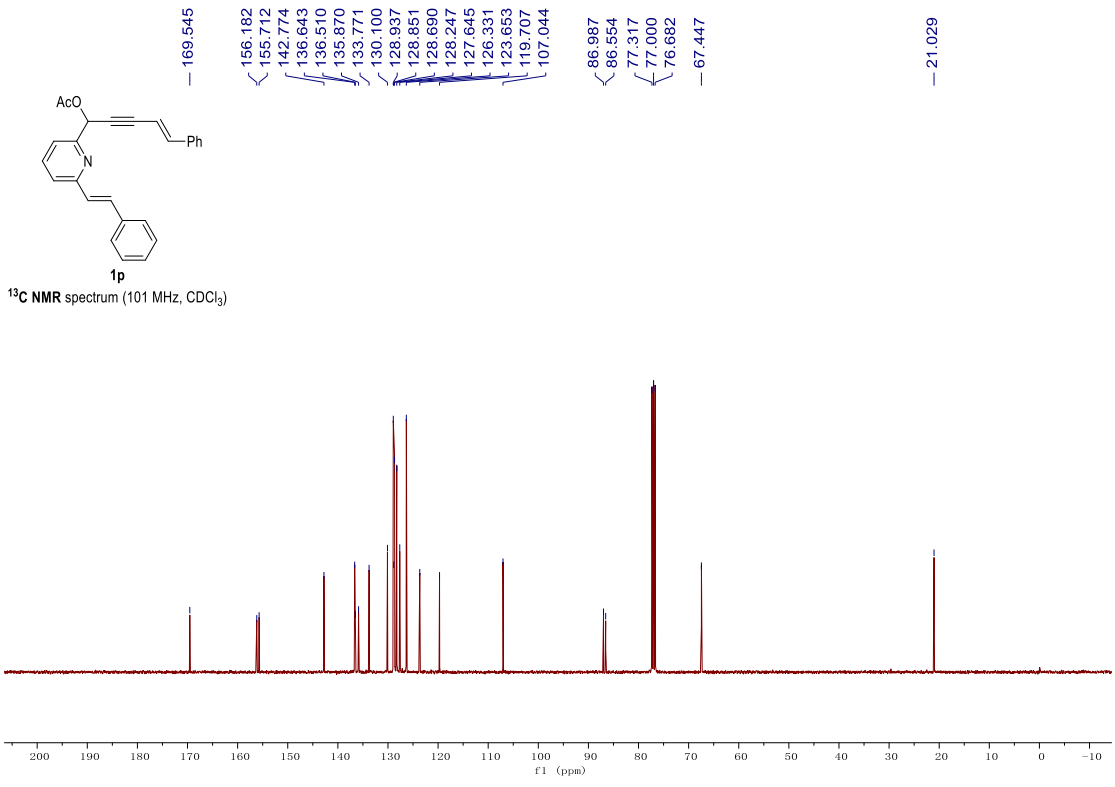


^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



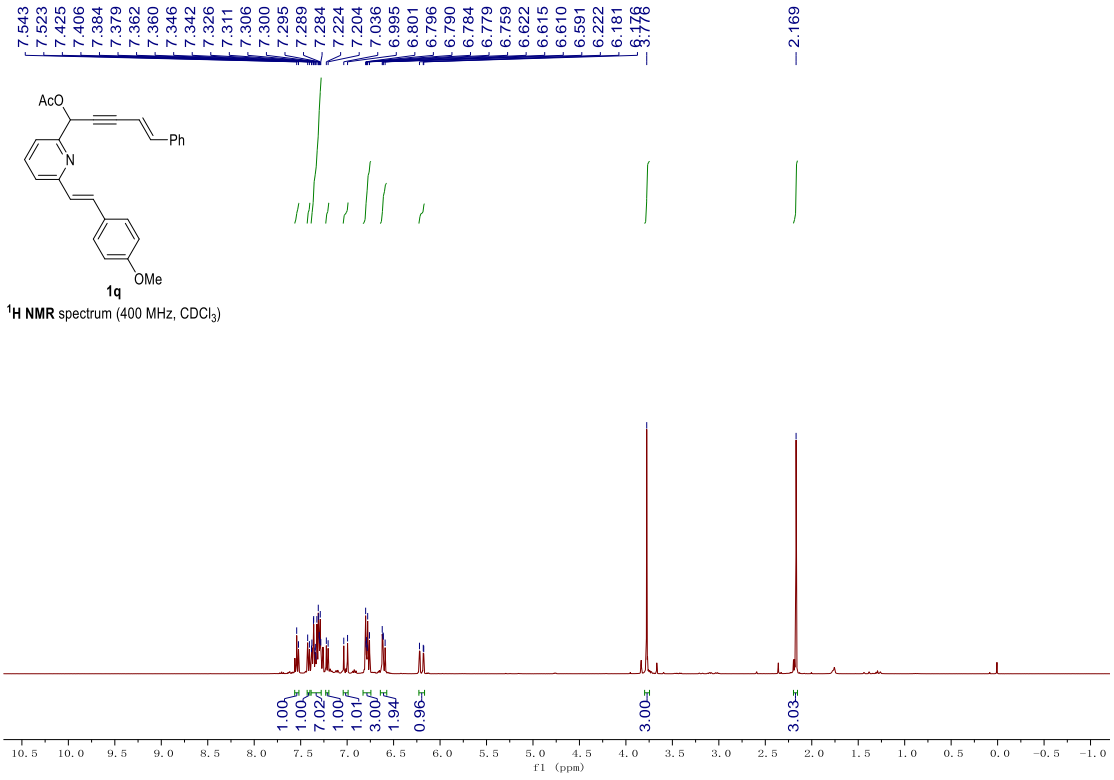
1p

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



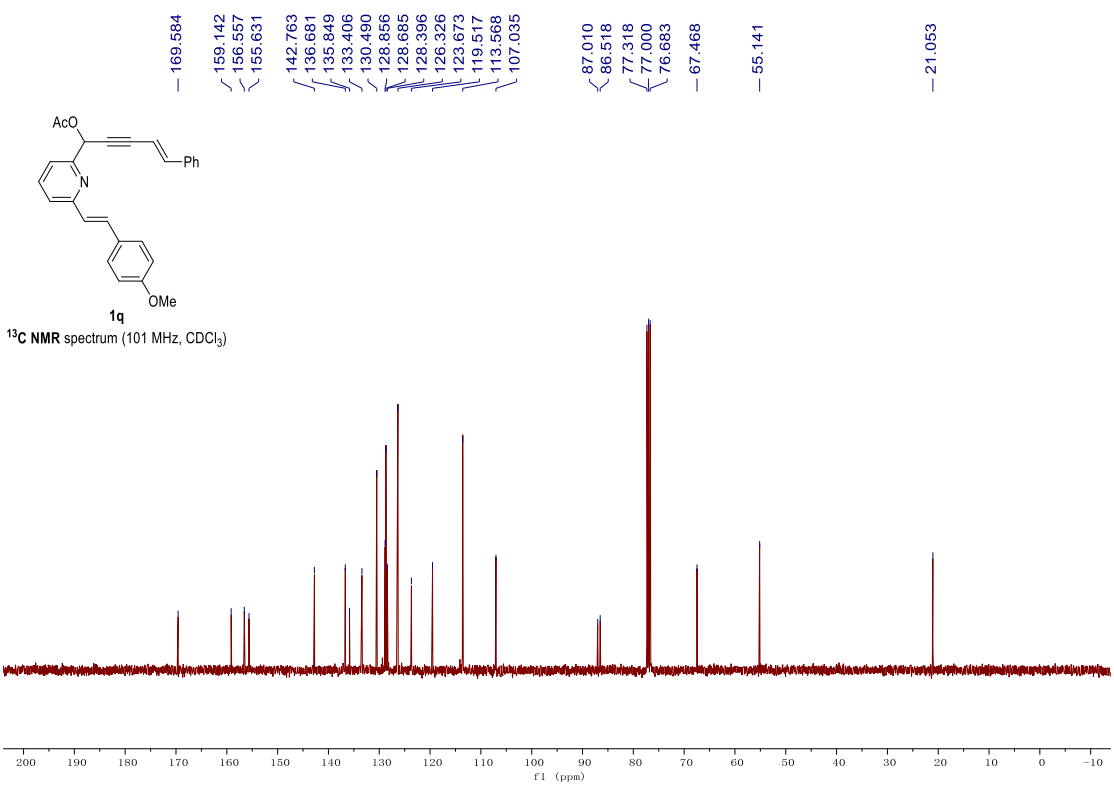
1p

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



1q

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



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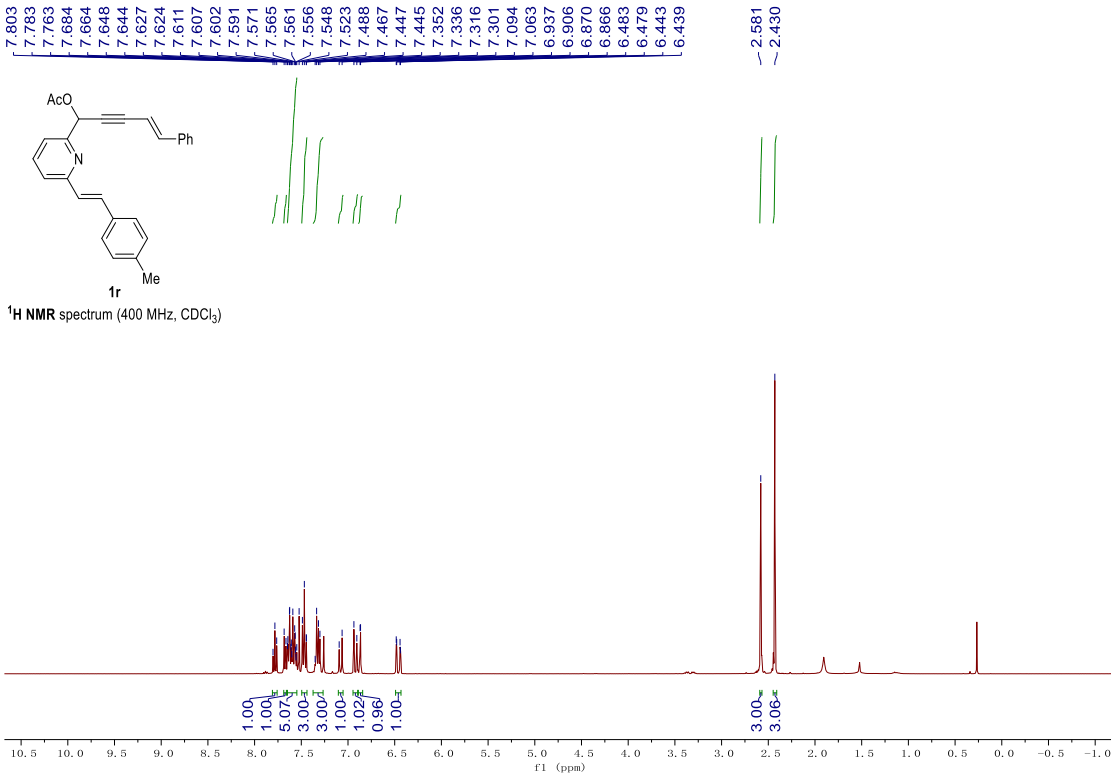
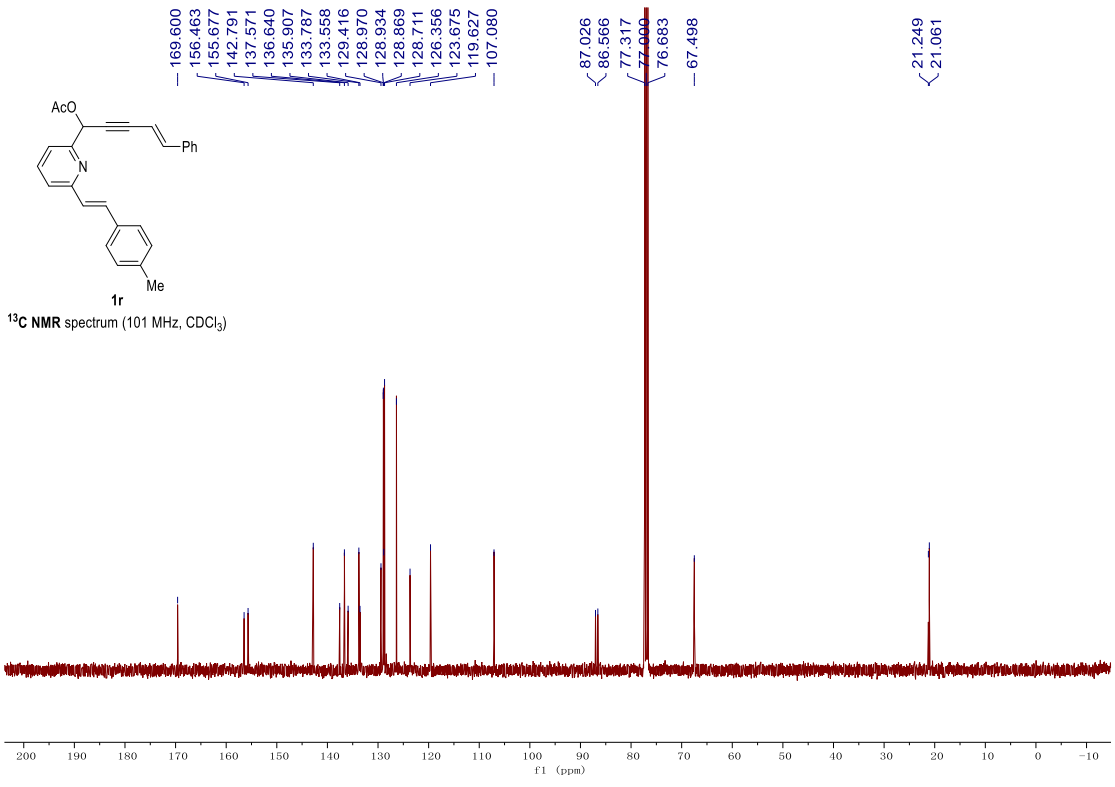
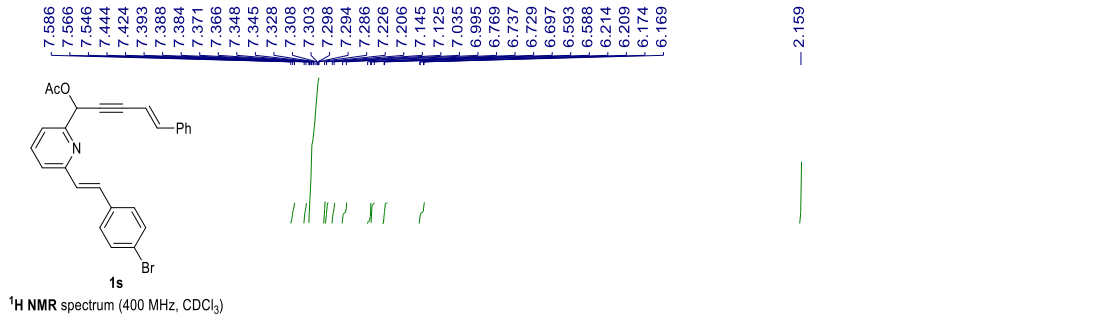
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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

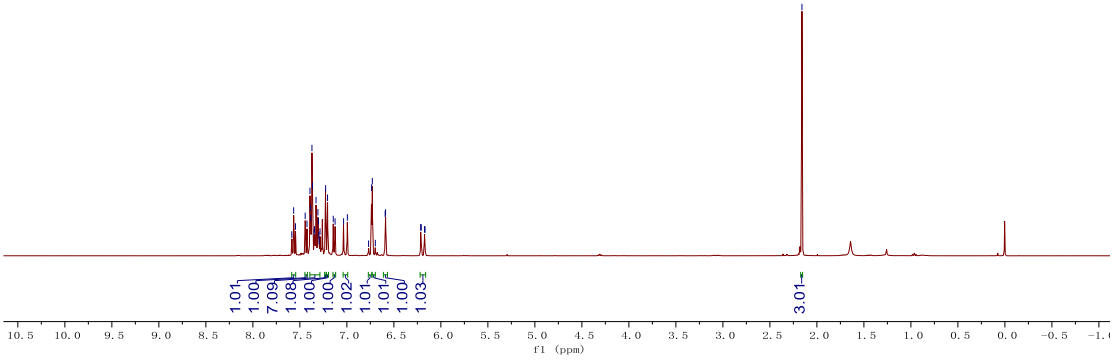


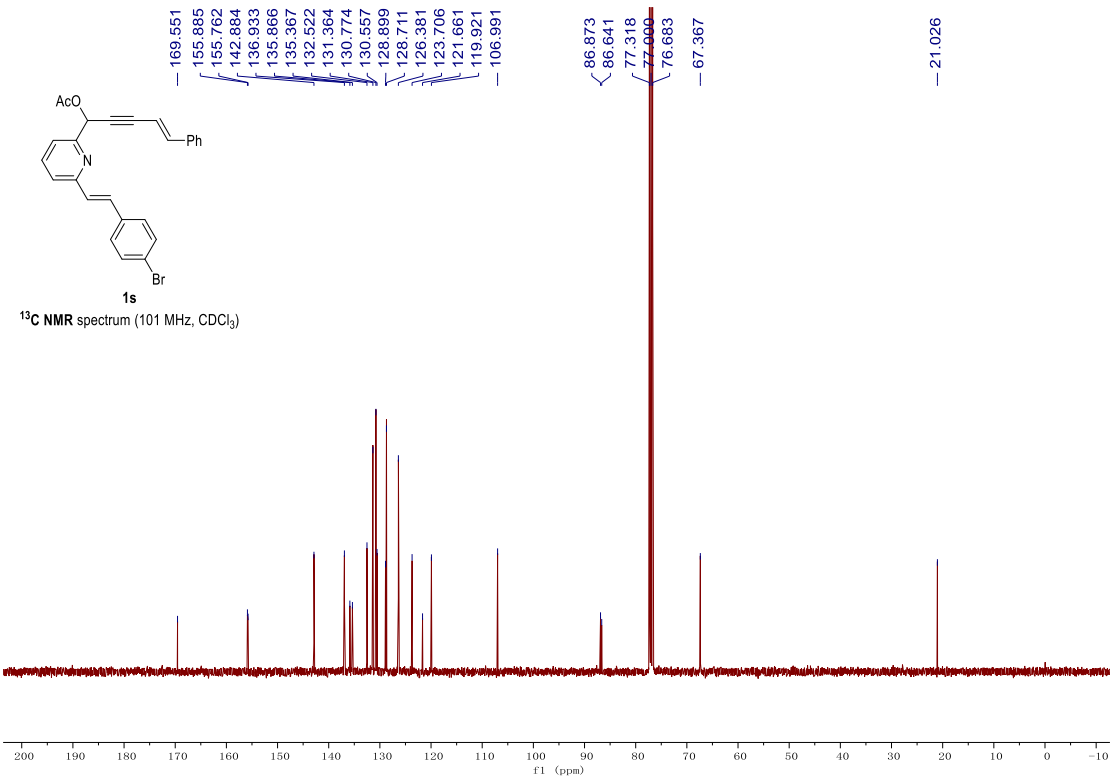
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



1s

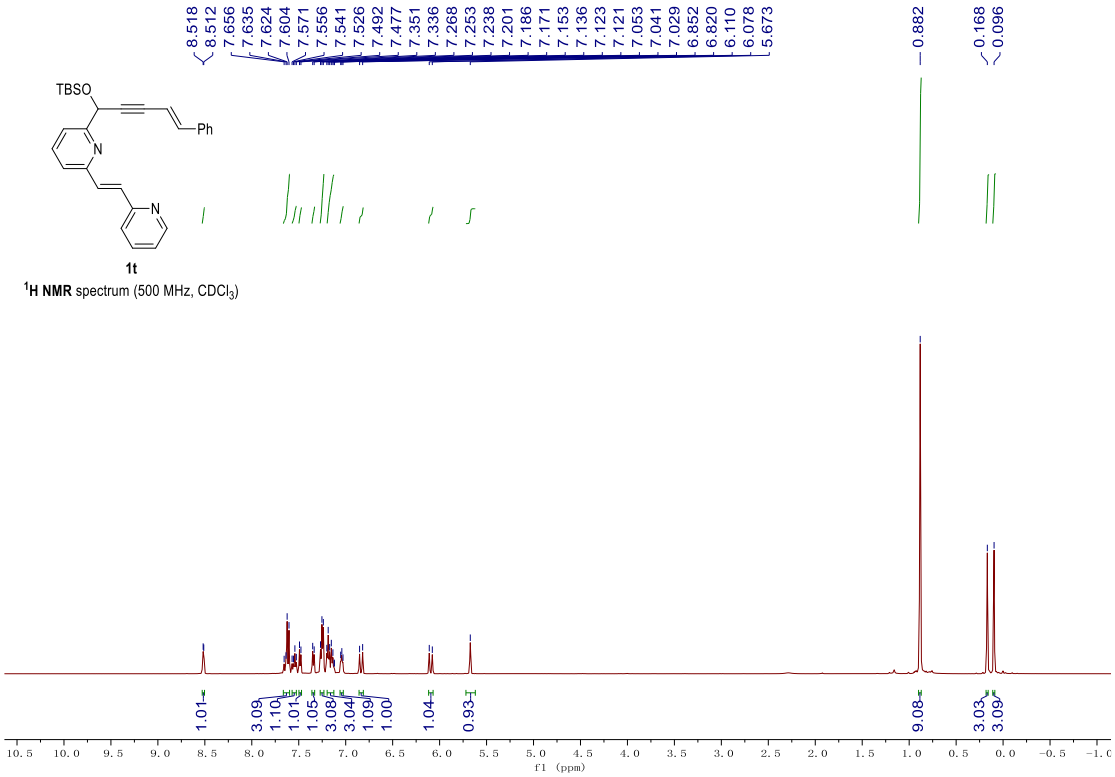
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





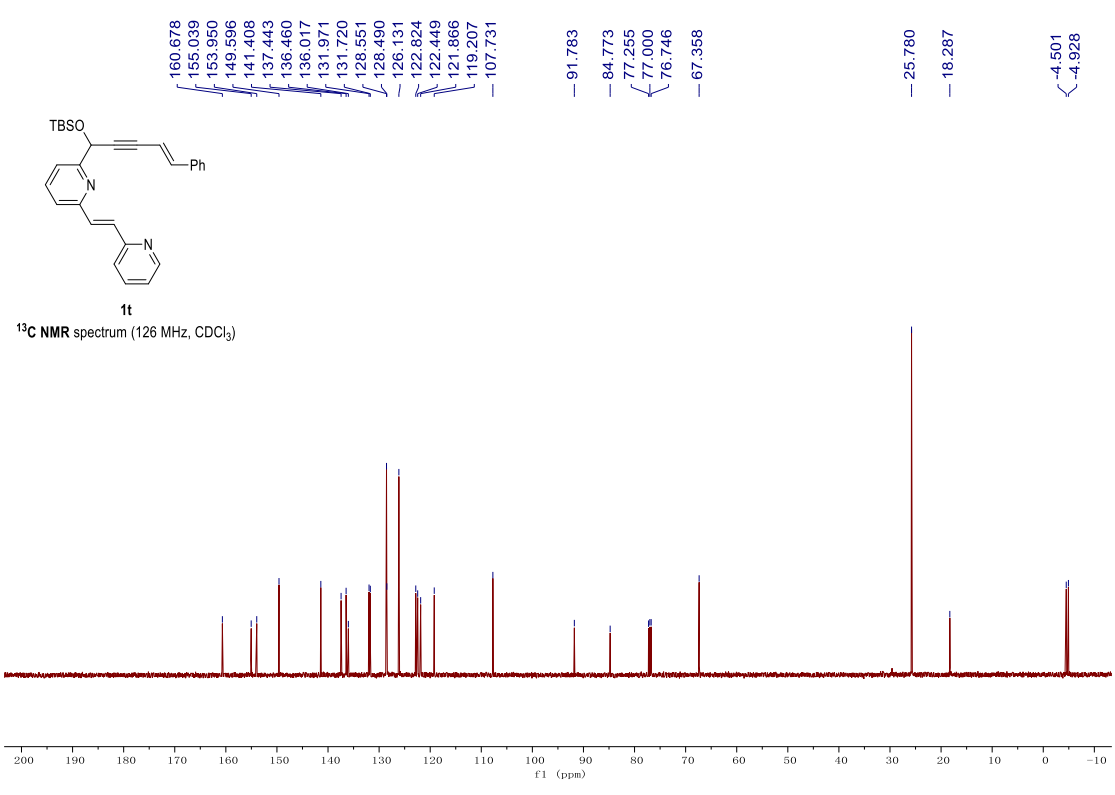
1s

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



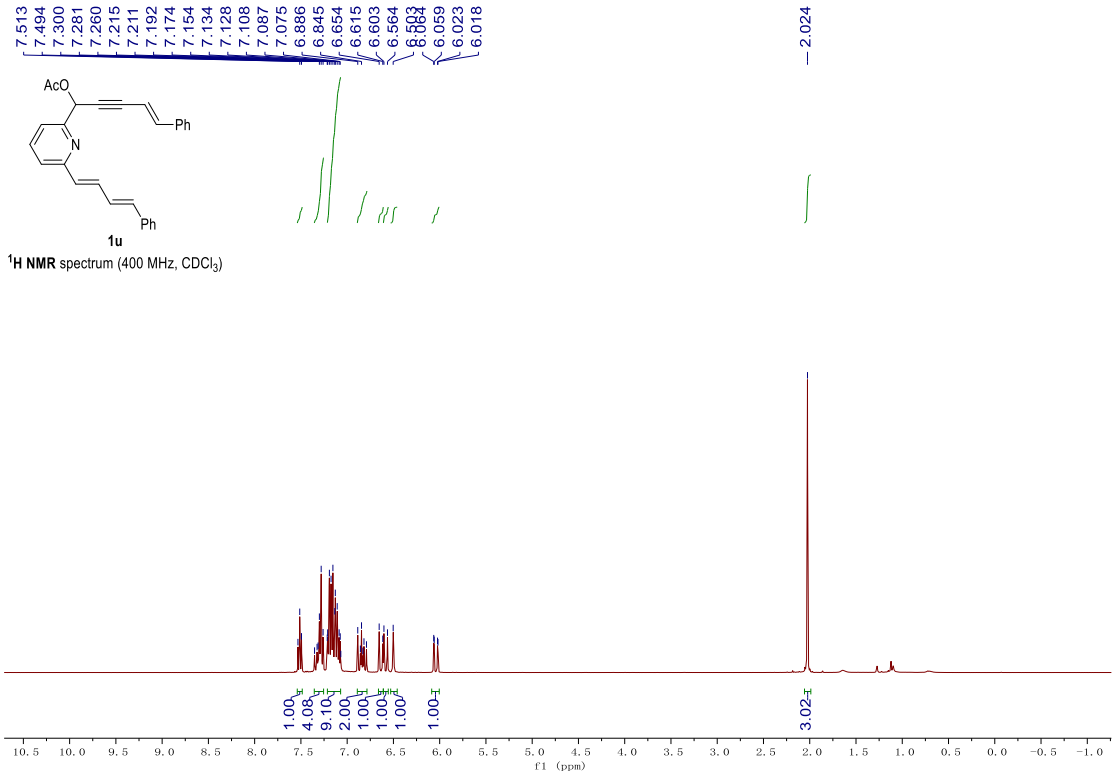
1t

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



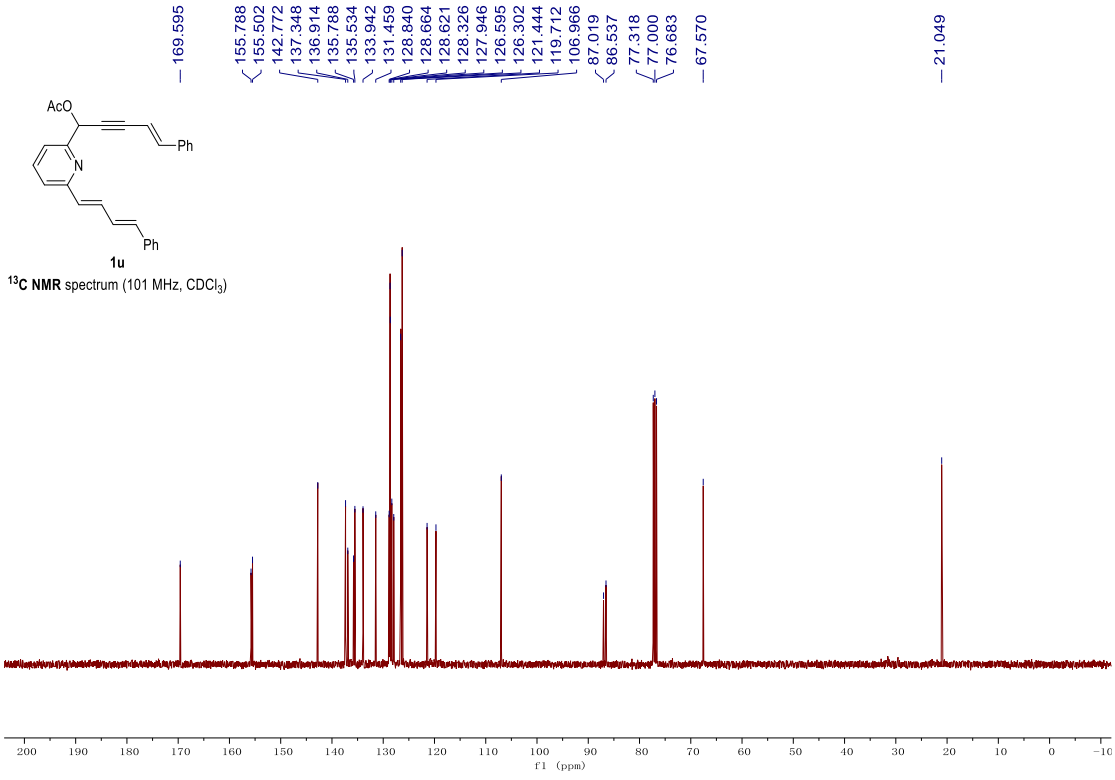
1t

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



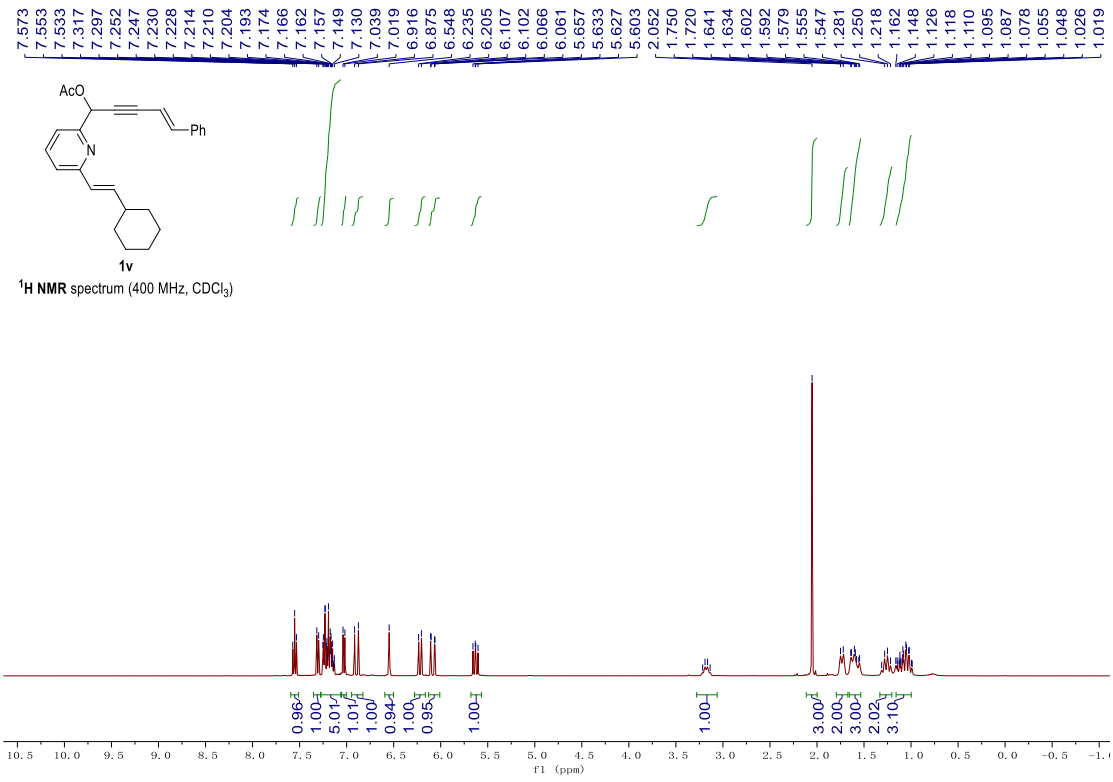
1u

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



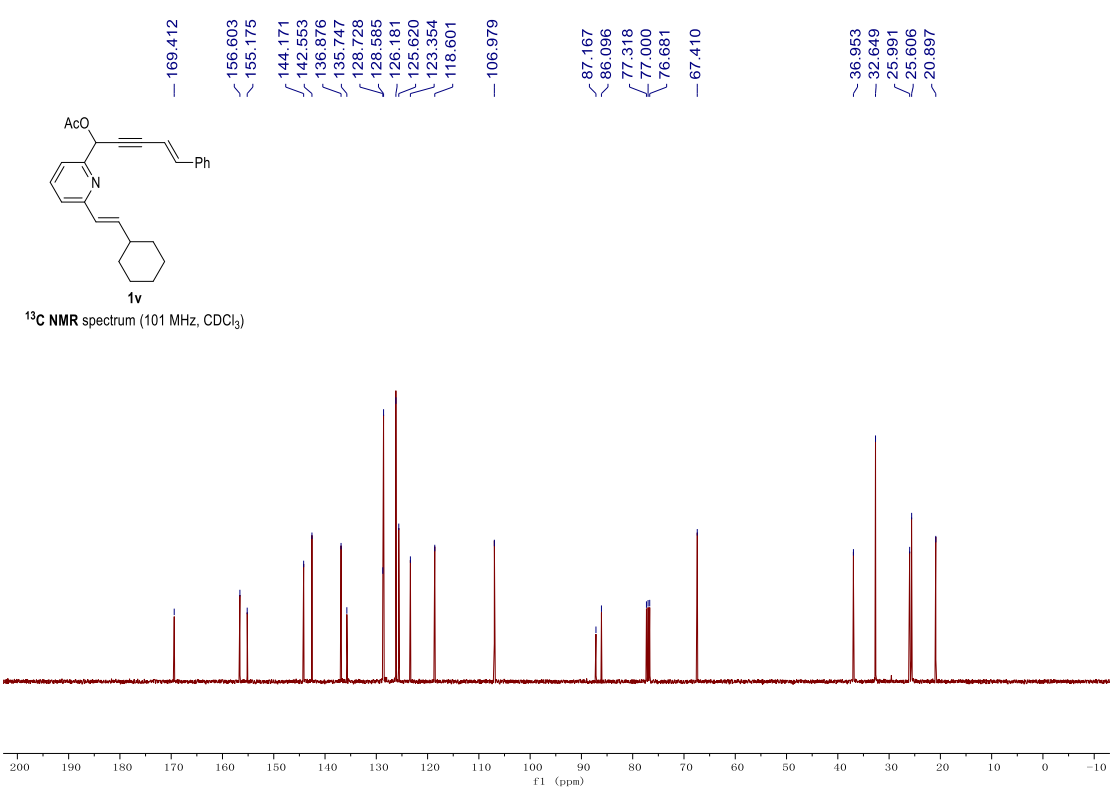
1u

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



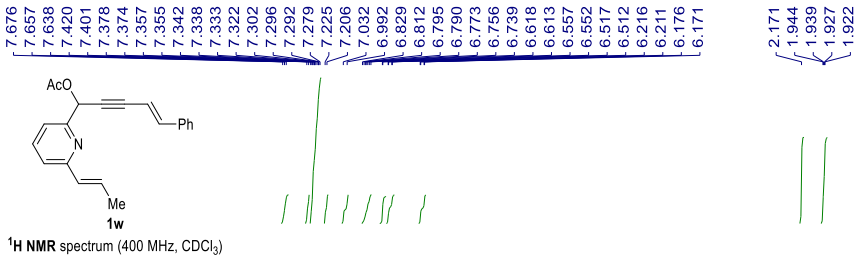
1v

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



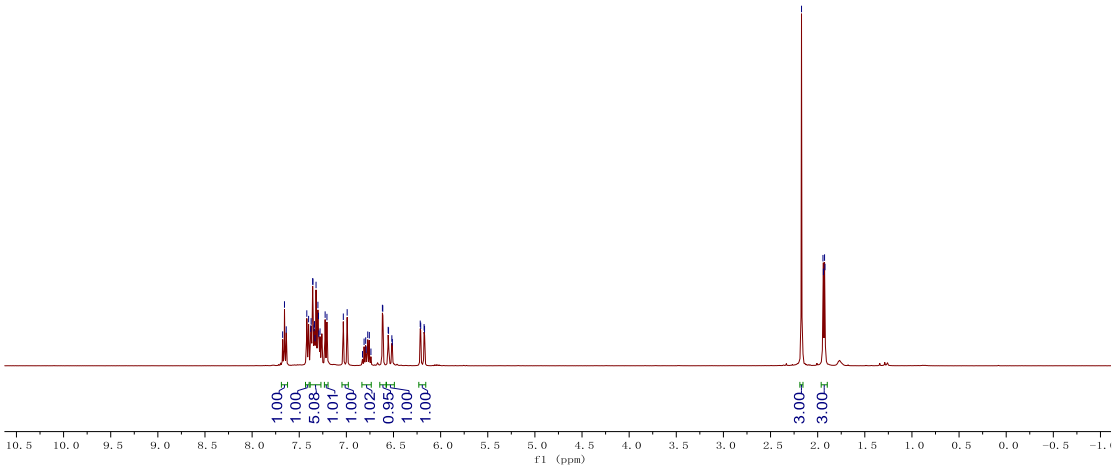
1v

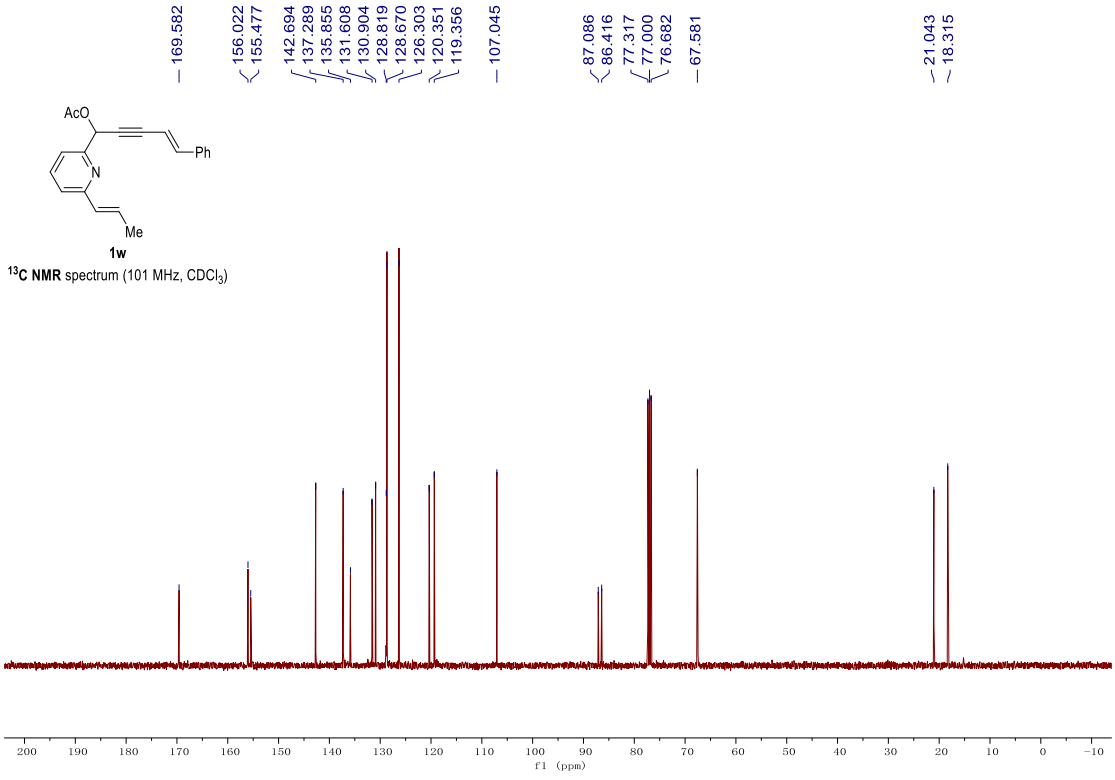
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



1w

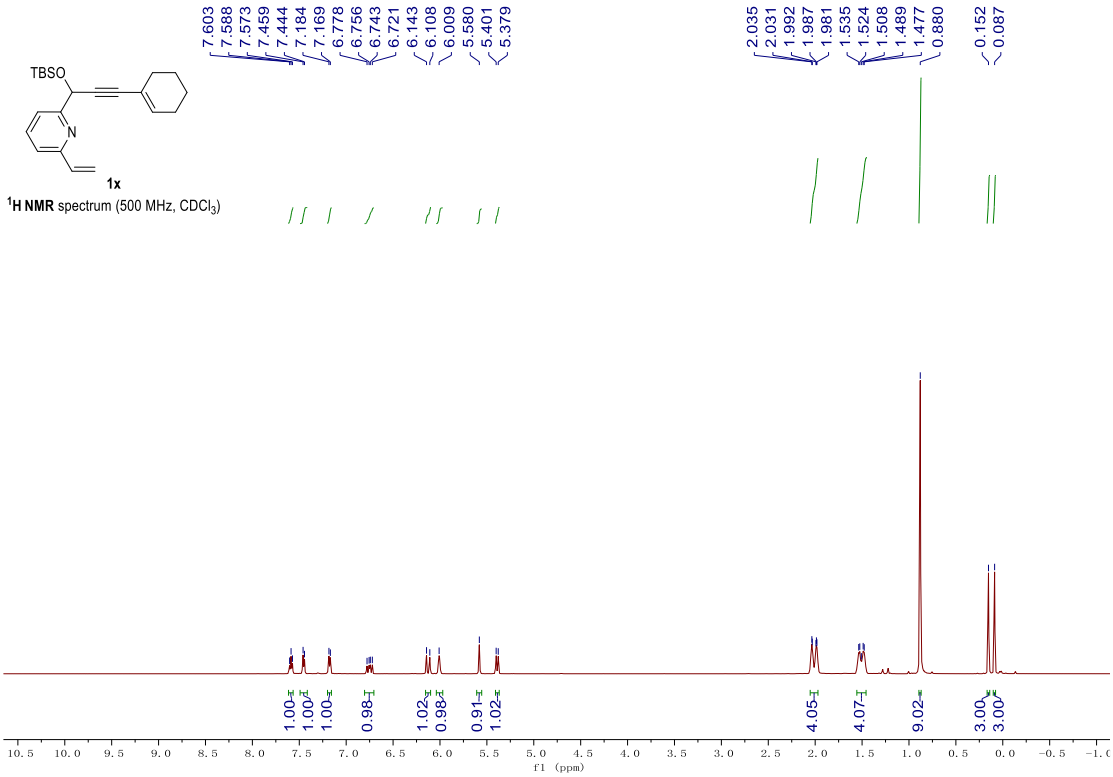
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



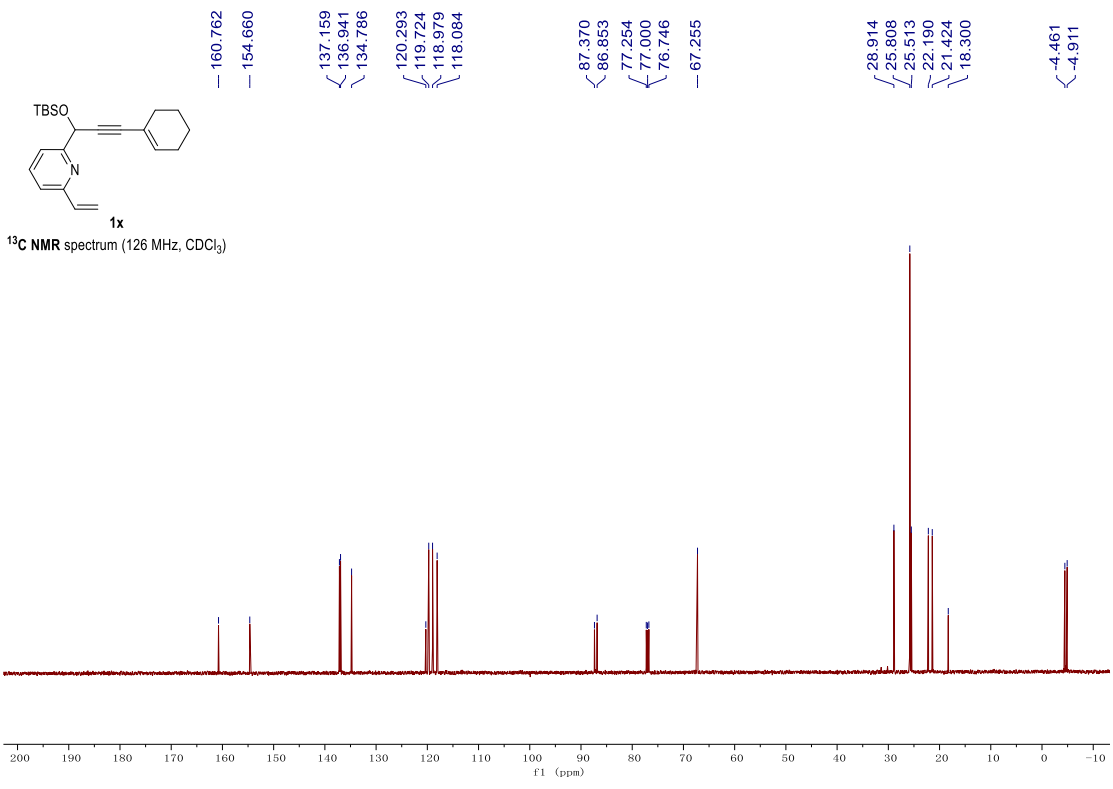


1w

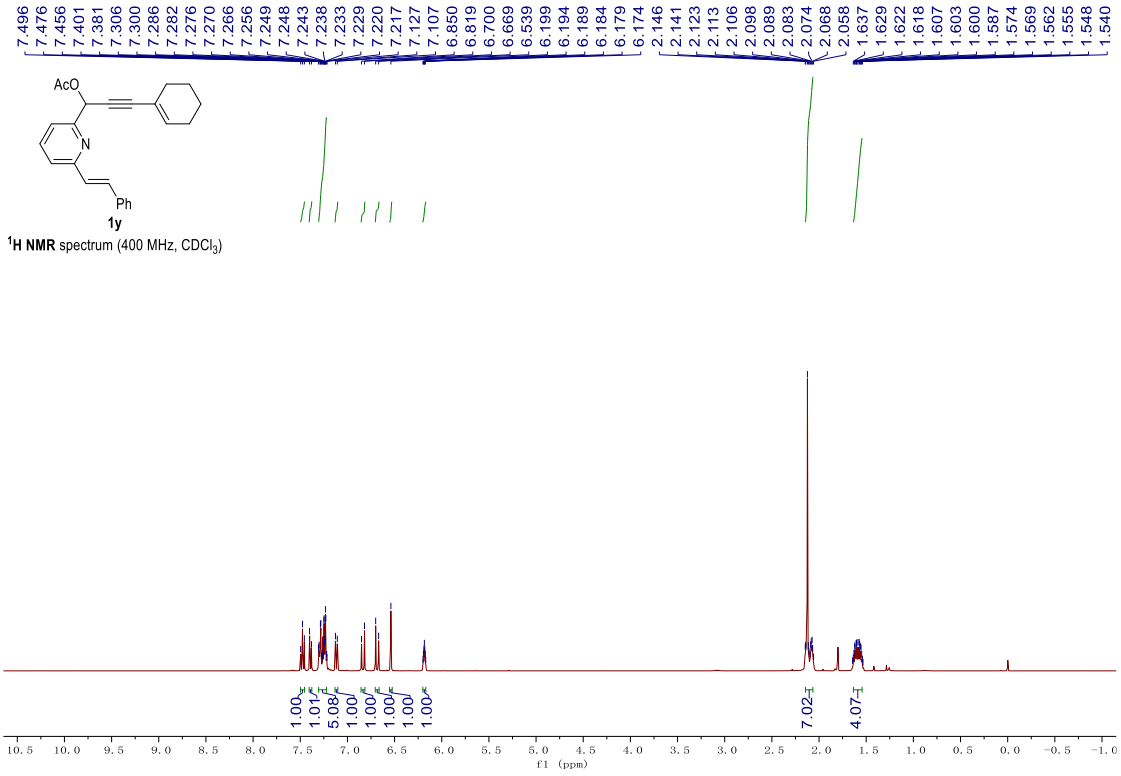
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



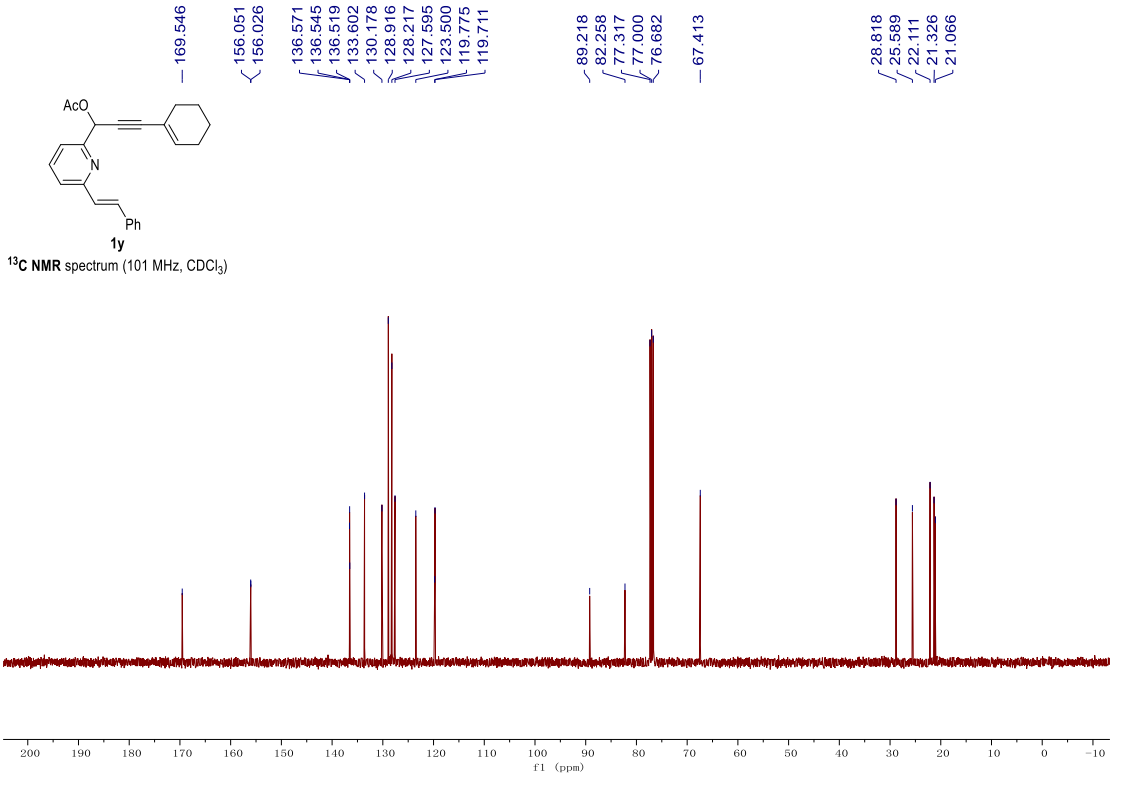
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



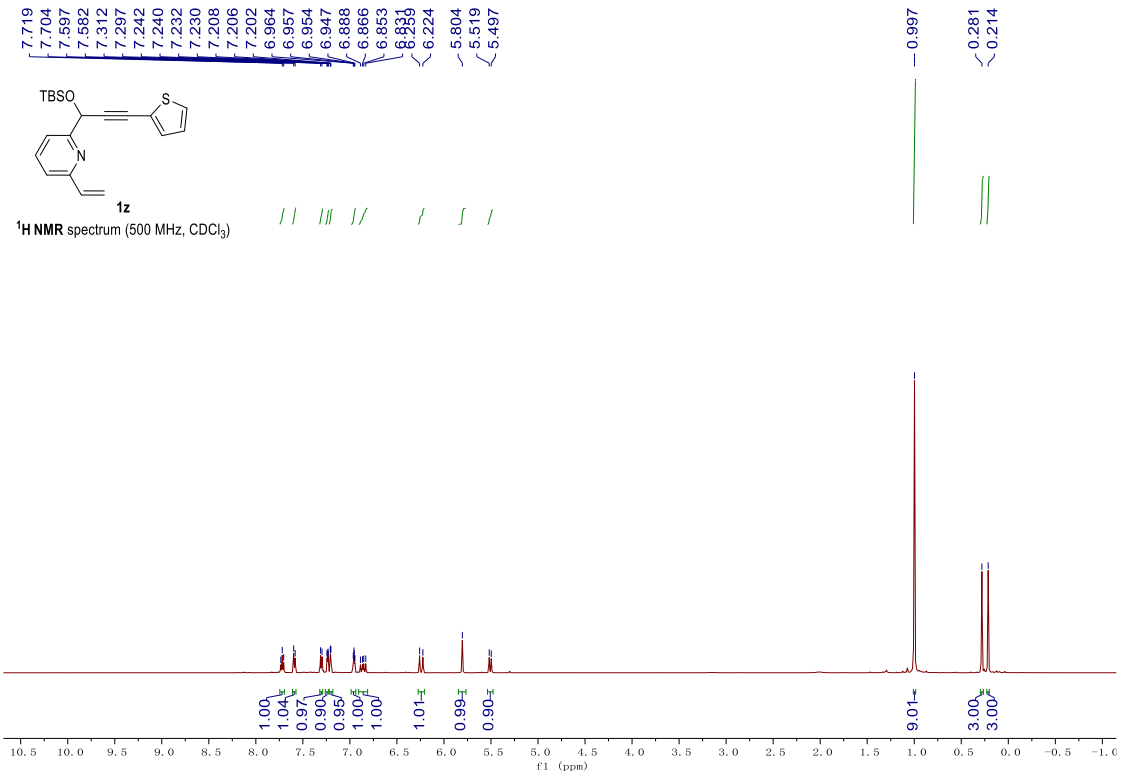
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



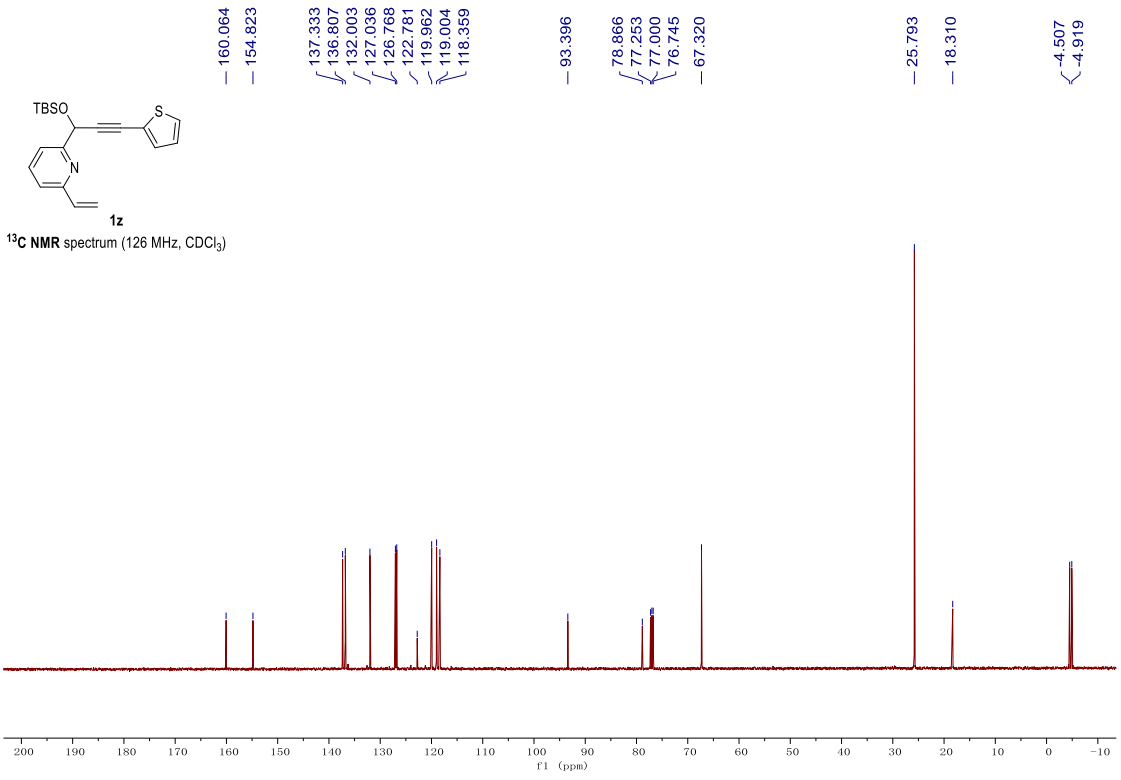
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



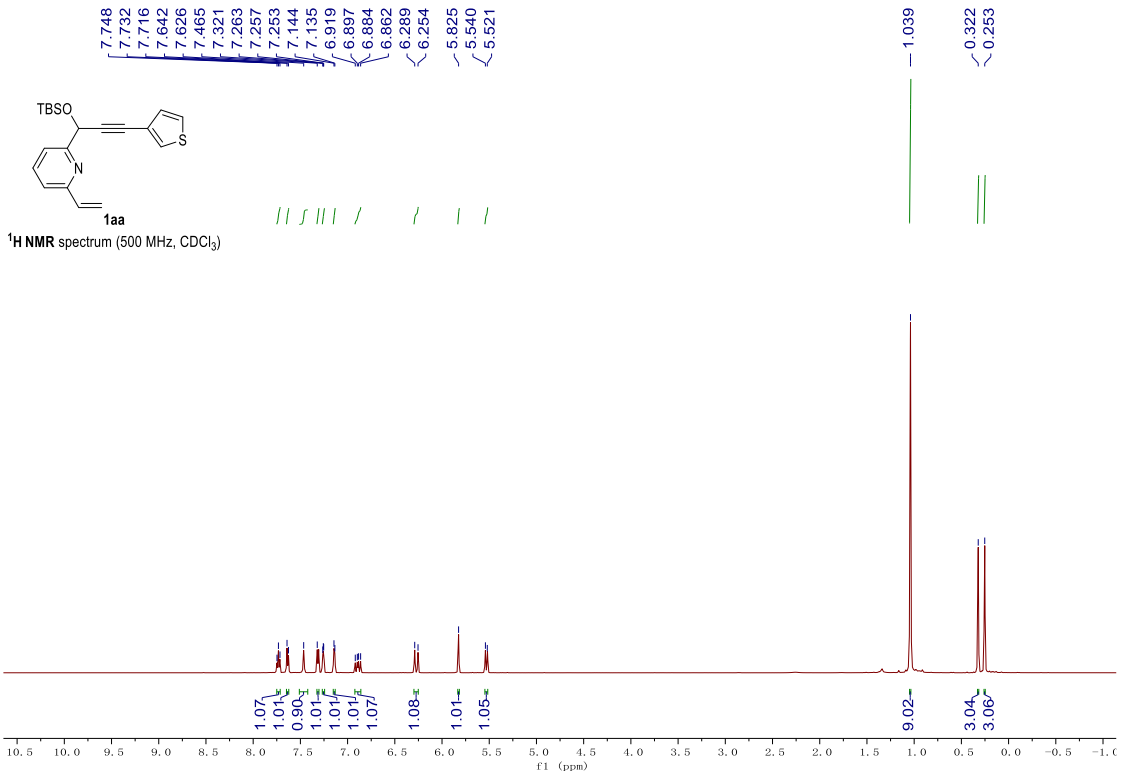
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



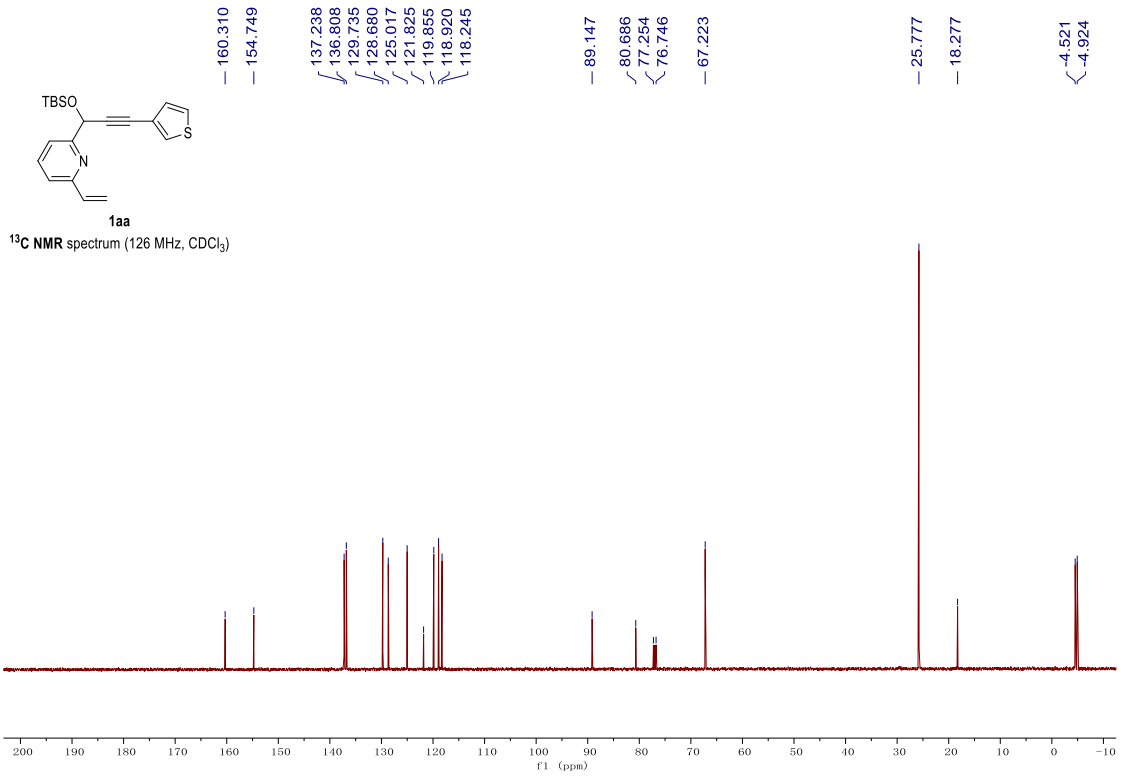
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



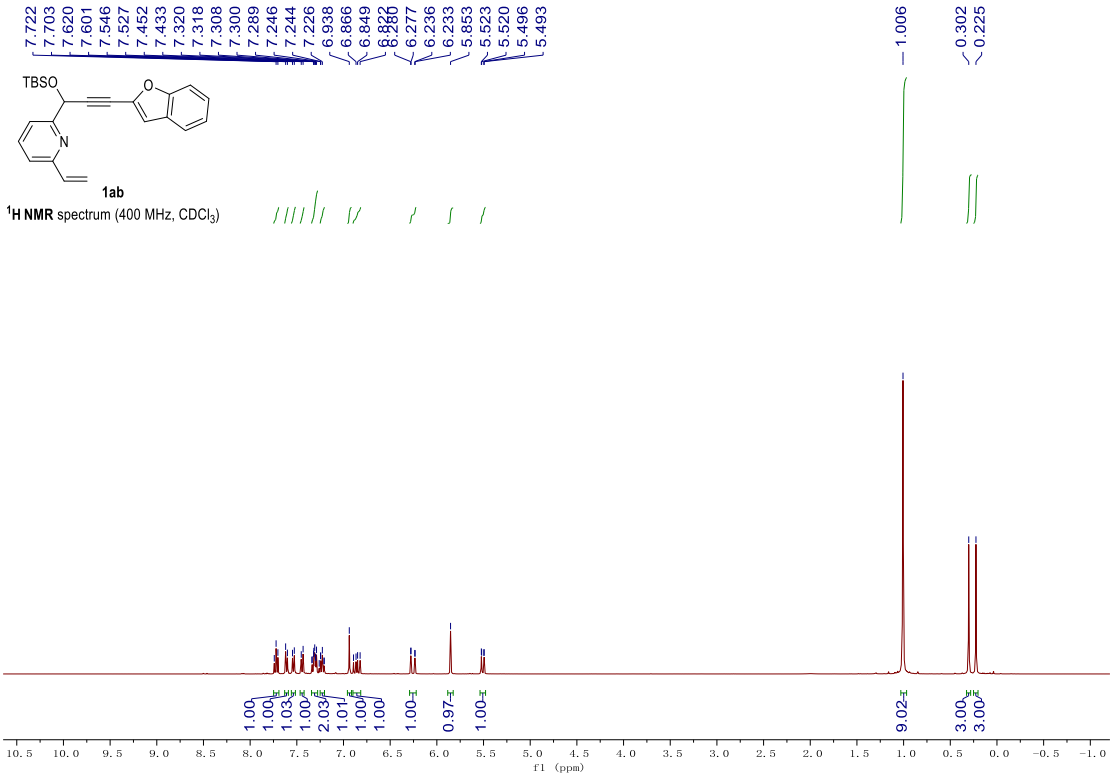
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



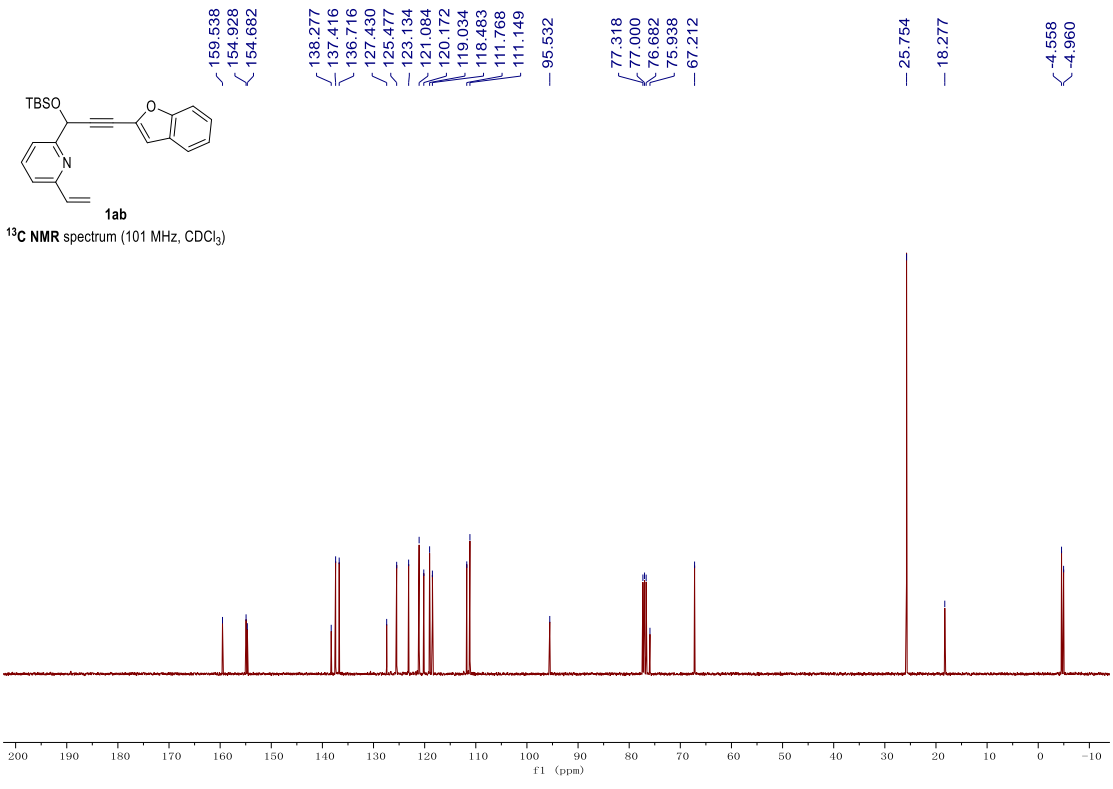
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



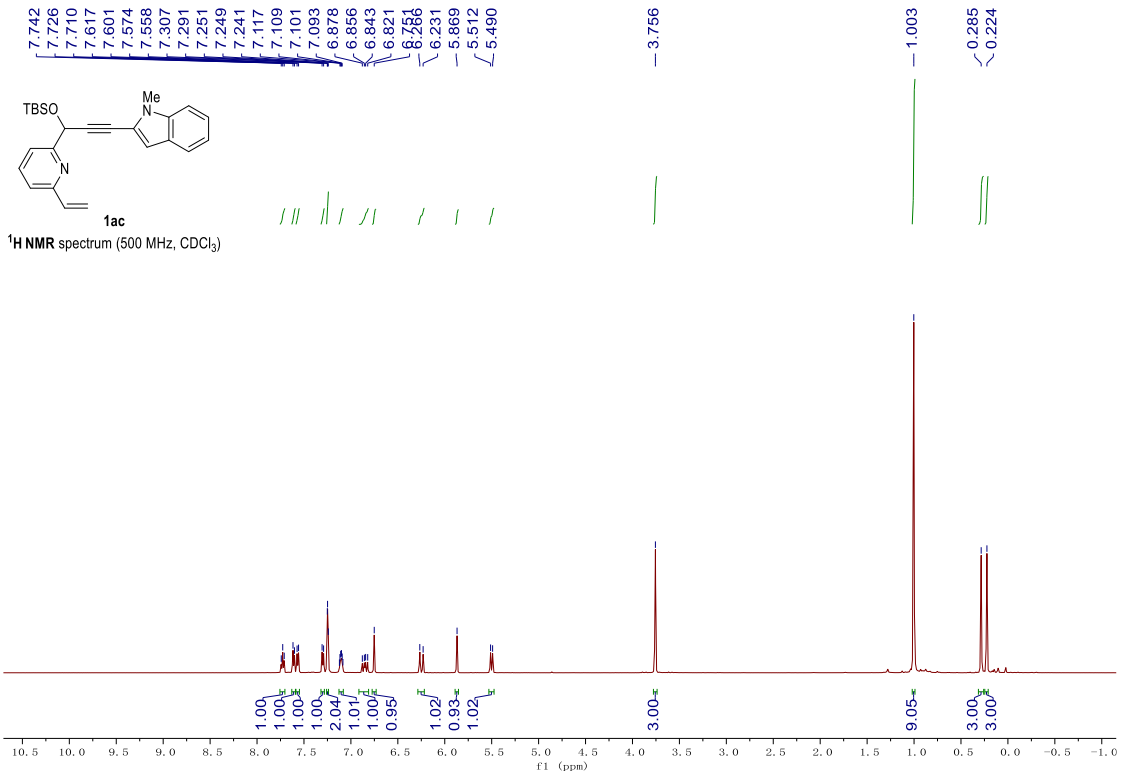
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



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

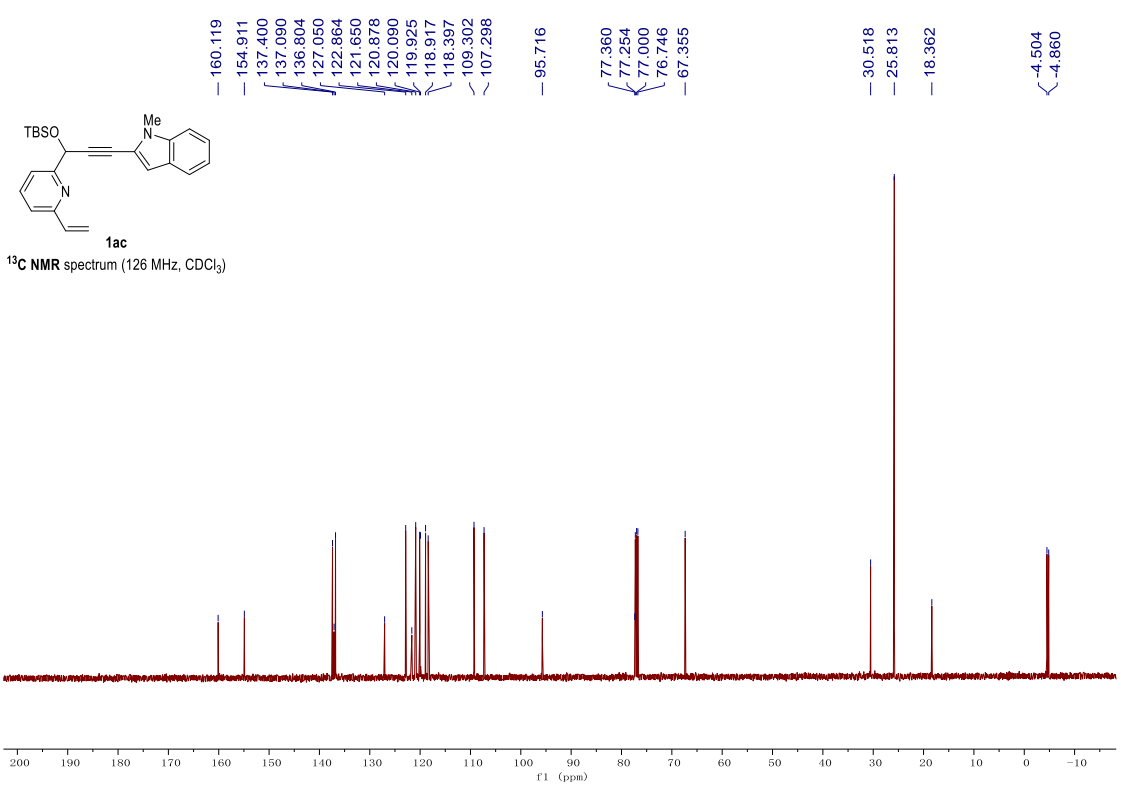


^{13}C NMR spectrum (101 MHz, $CDCl_3$)



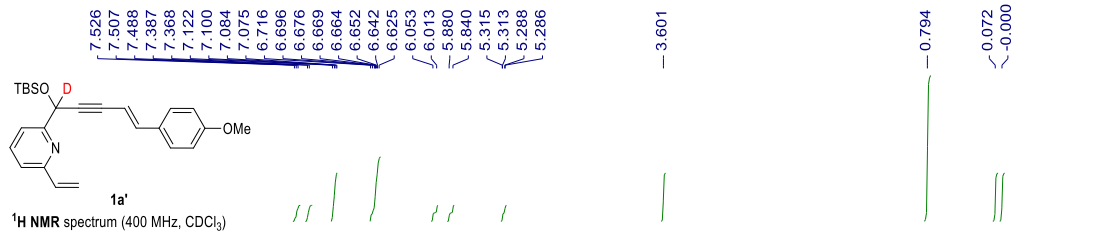
1ac

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



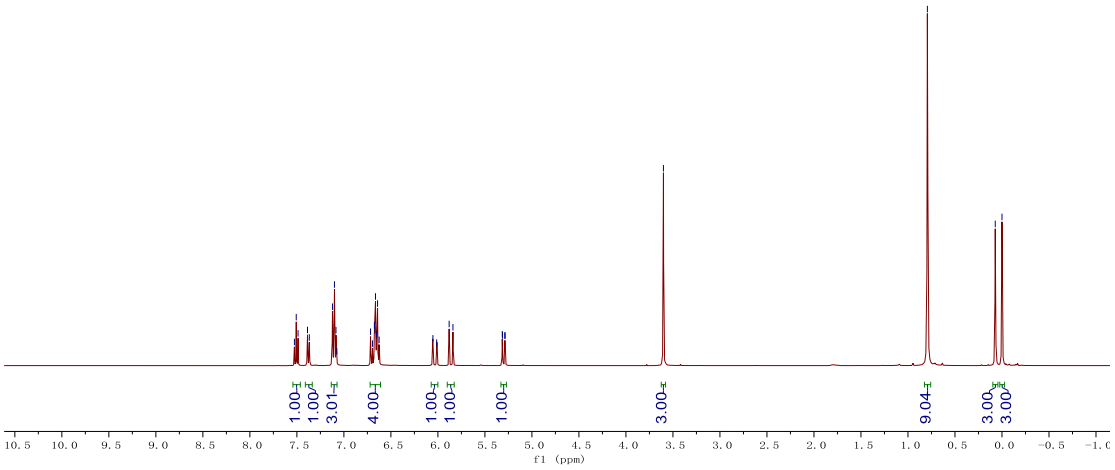
1ac

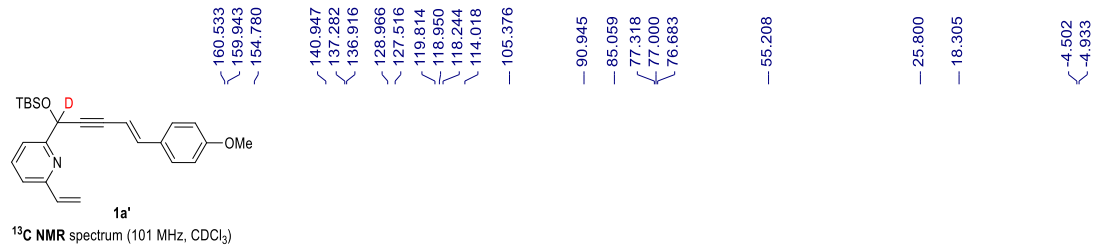
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



1a'

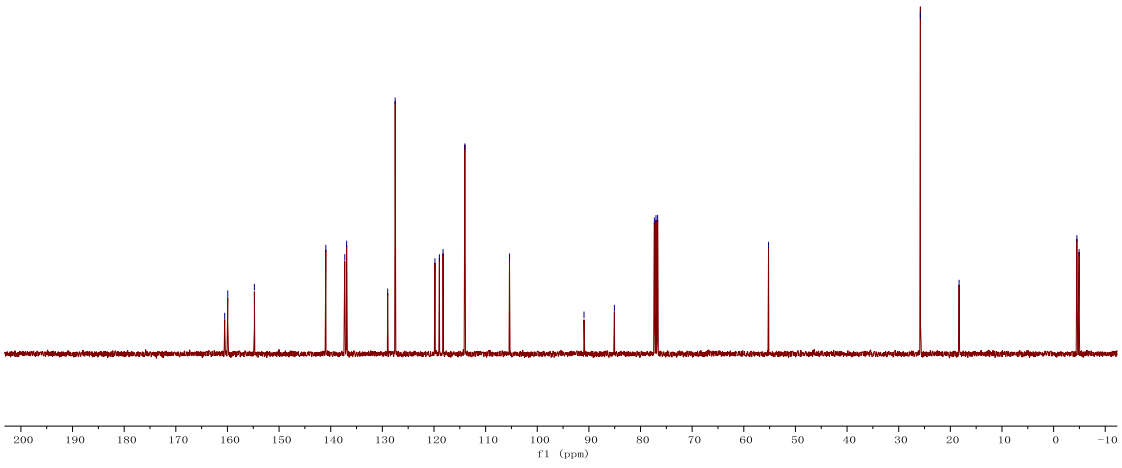
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

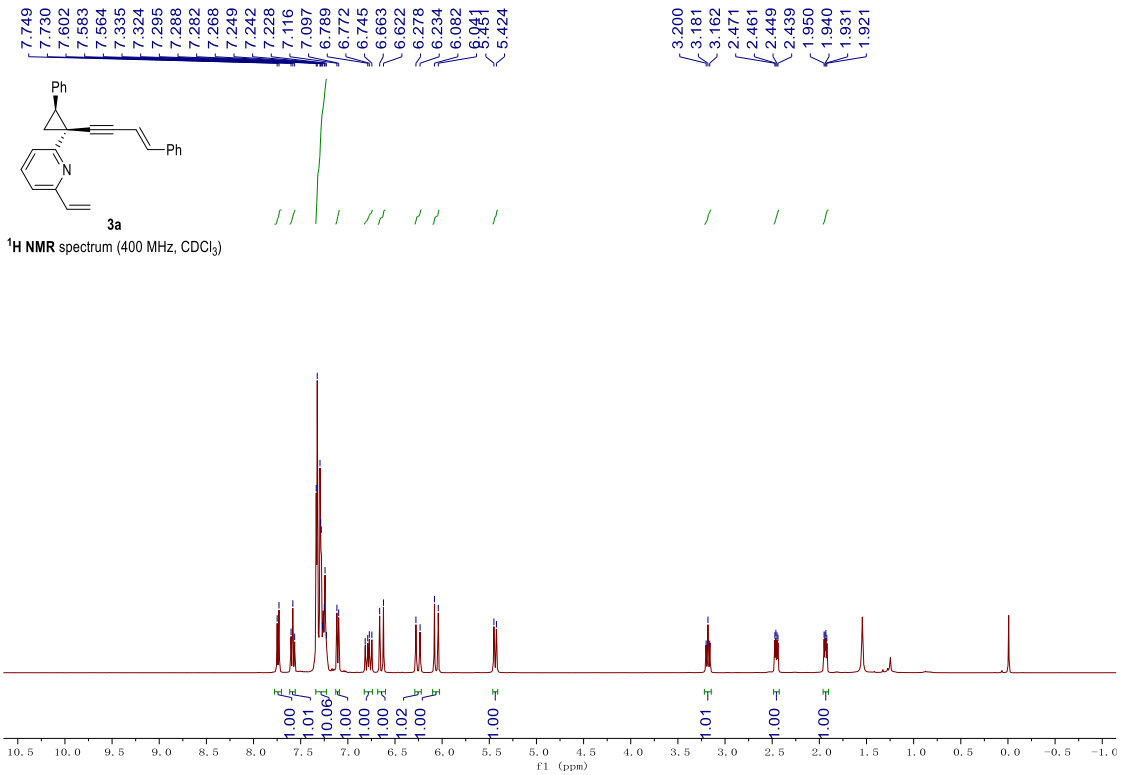




1a'

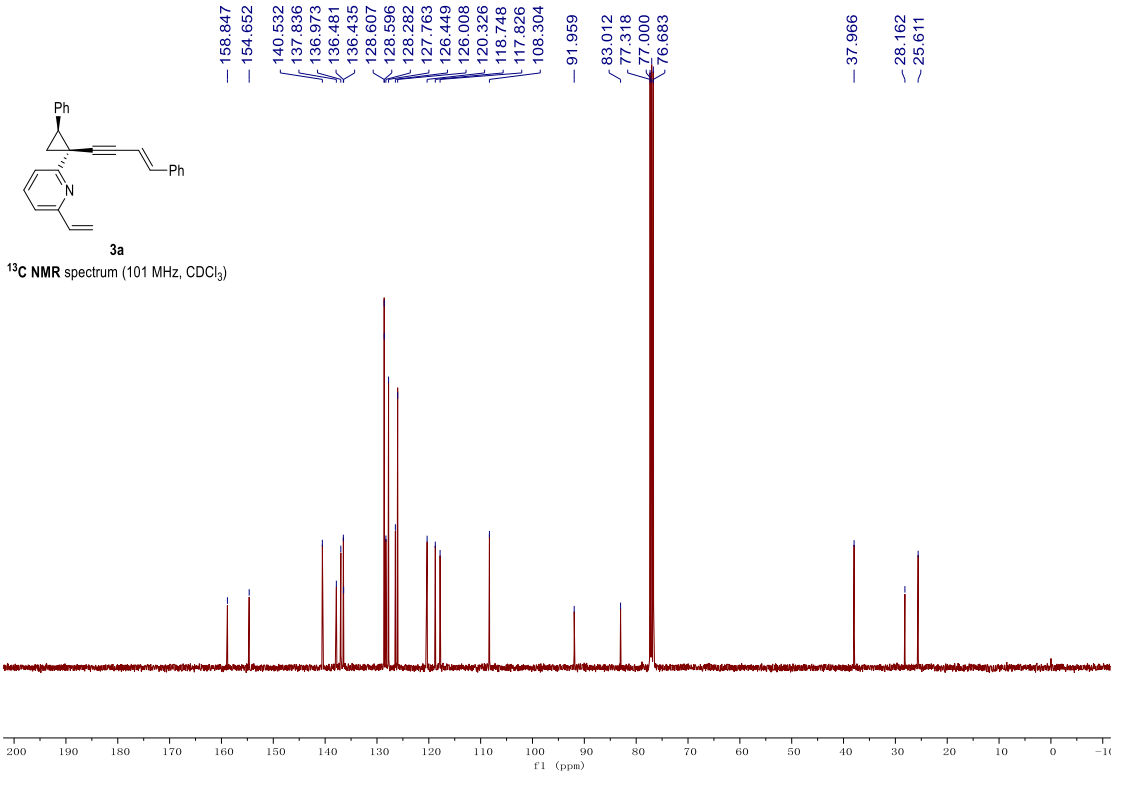
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





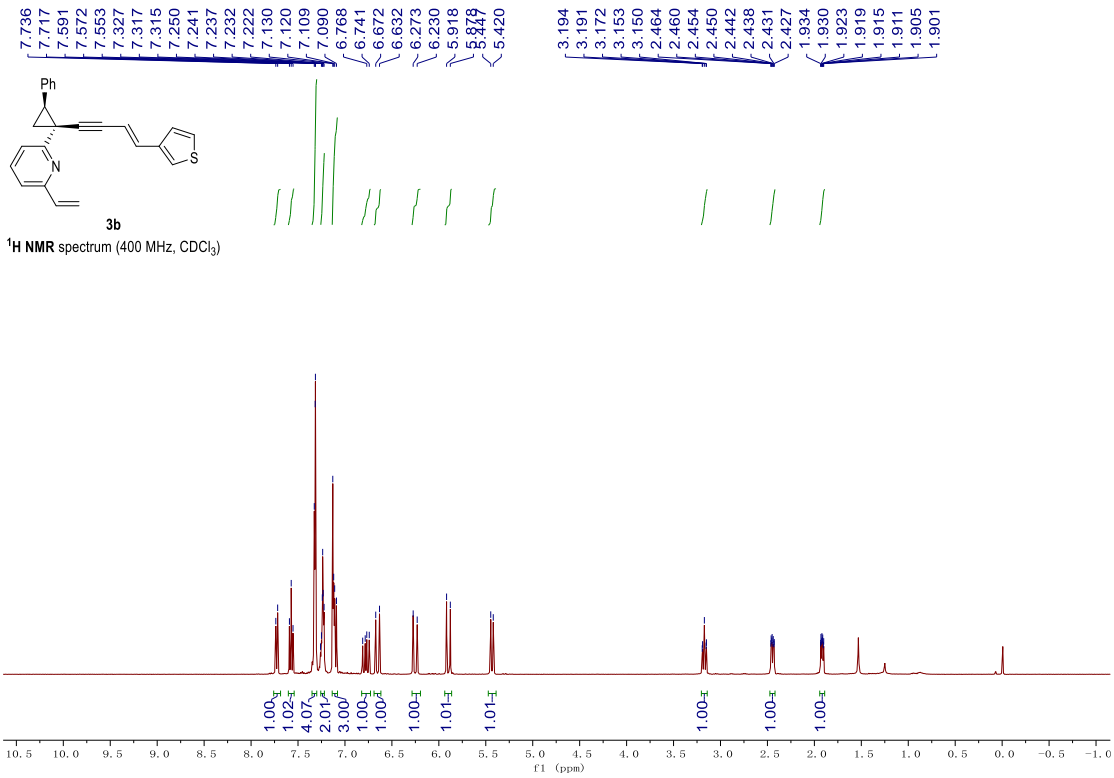
3a

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



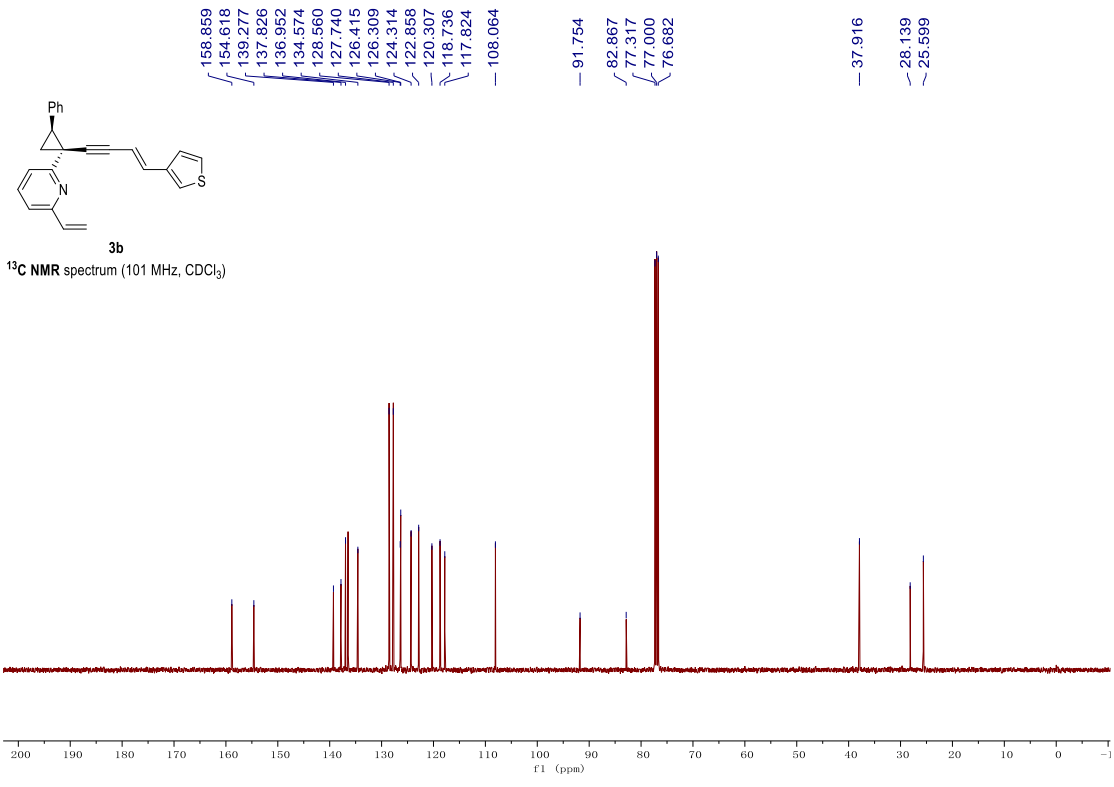
3a

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



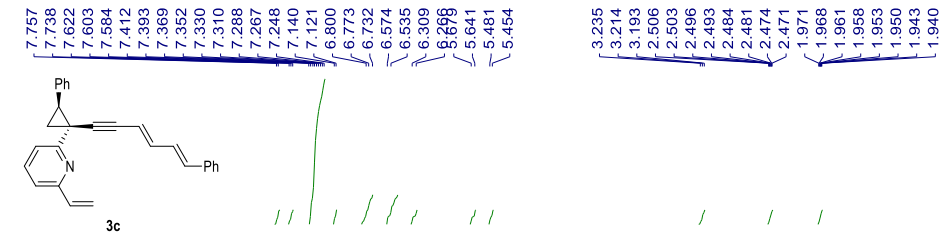
3b

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



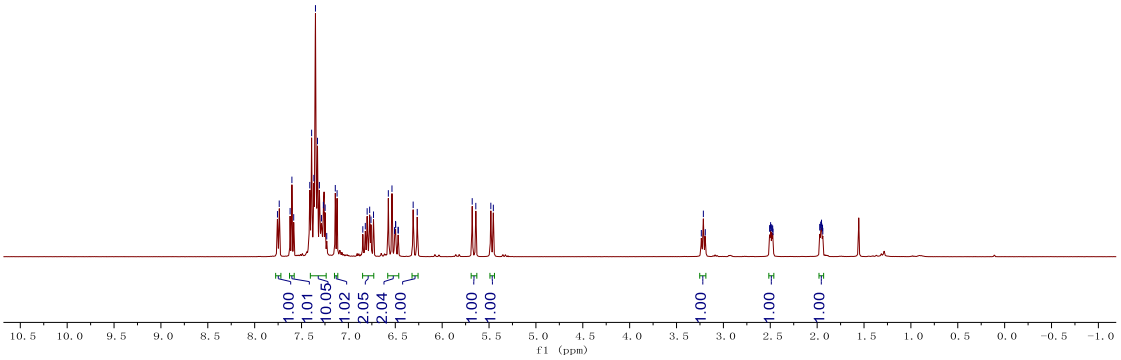
3b

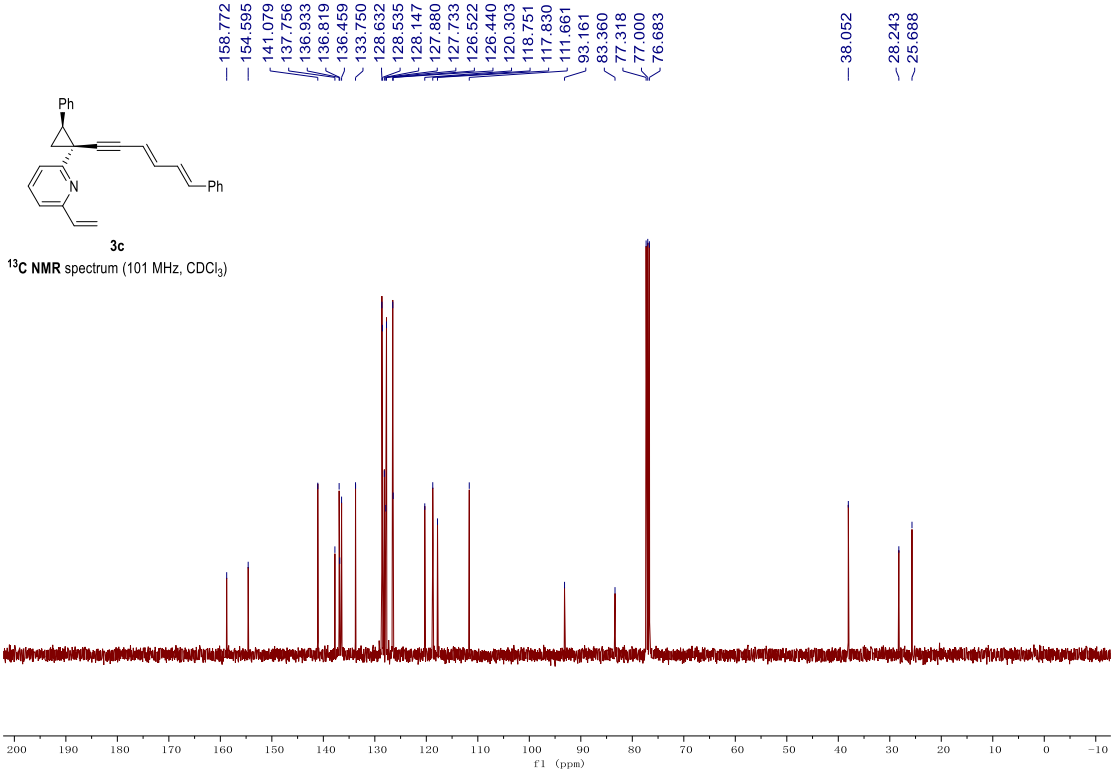
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



3c

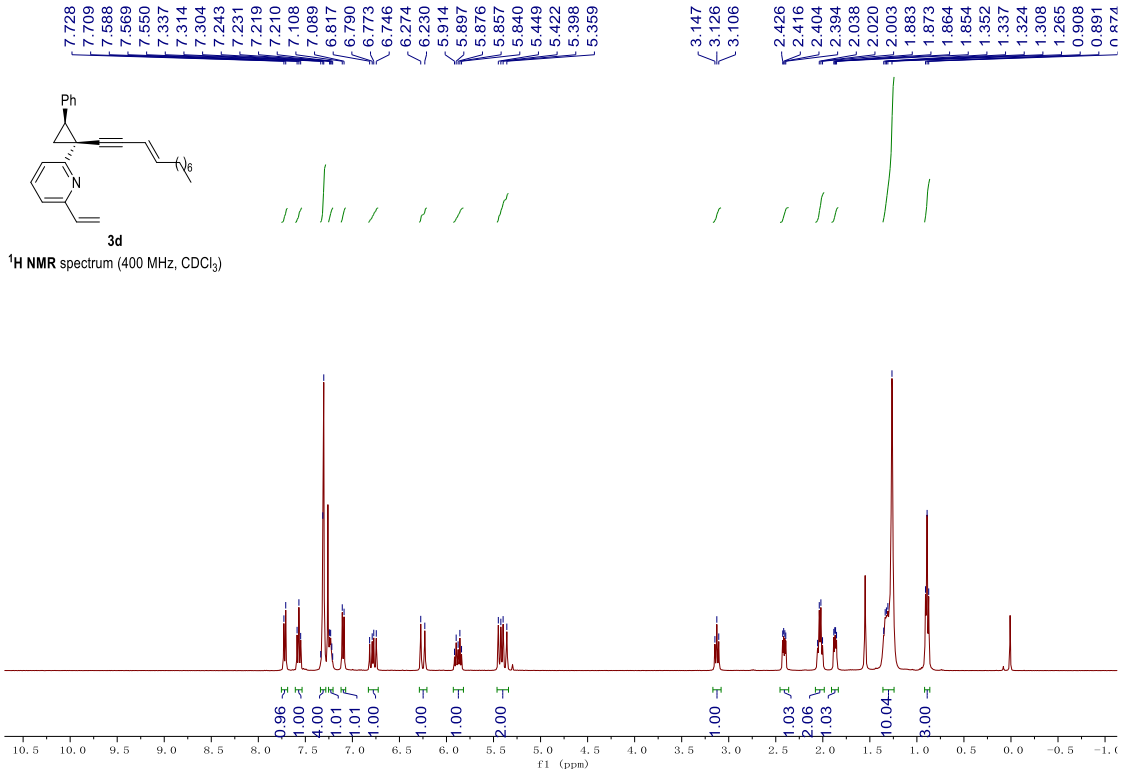
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





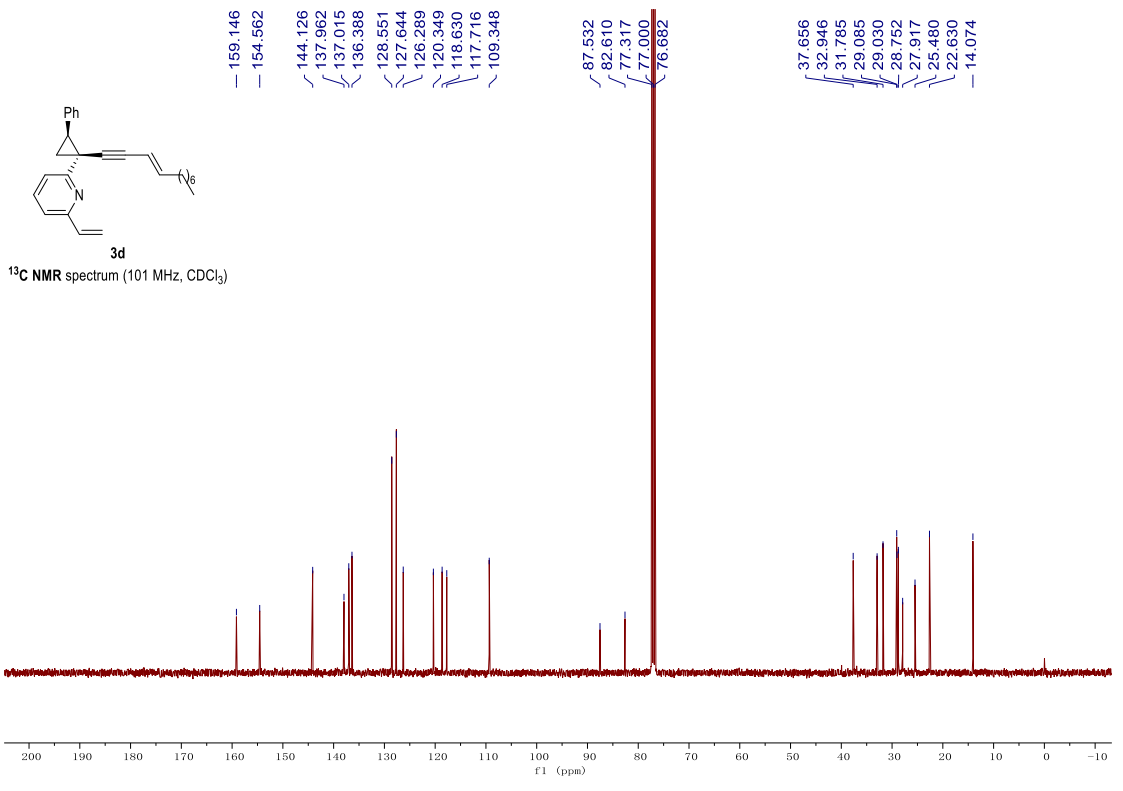
3c

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



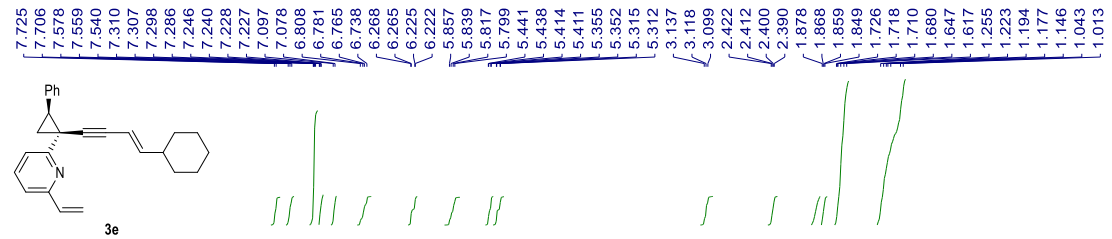
3d

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



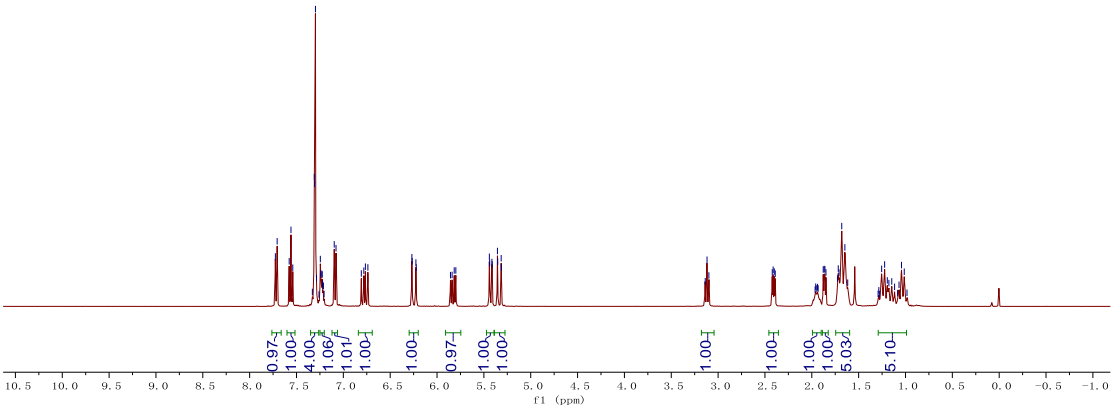
3d

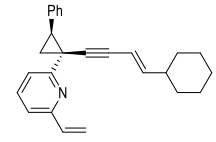
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



3e

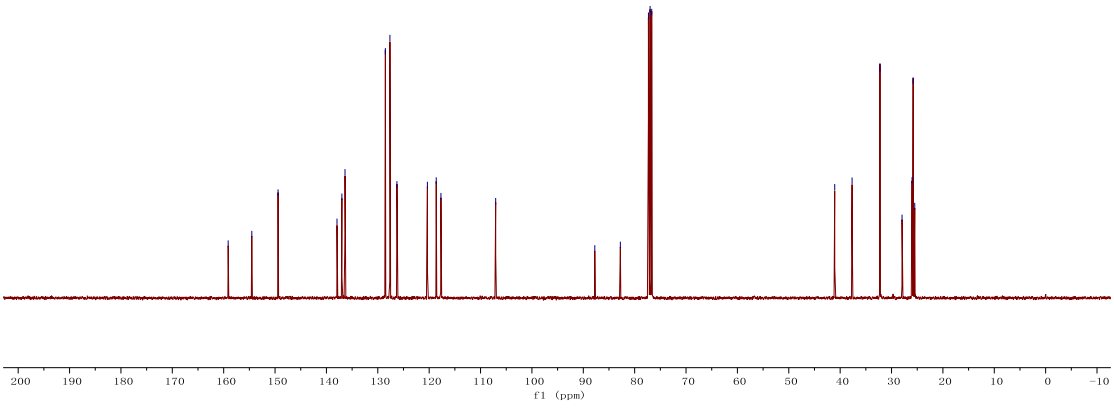
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

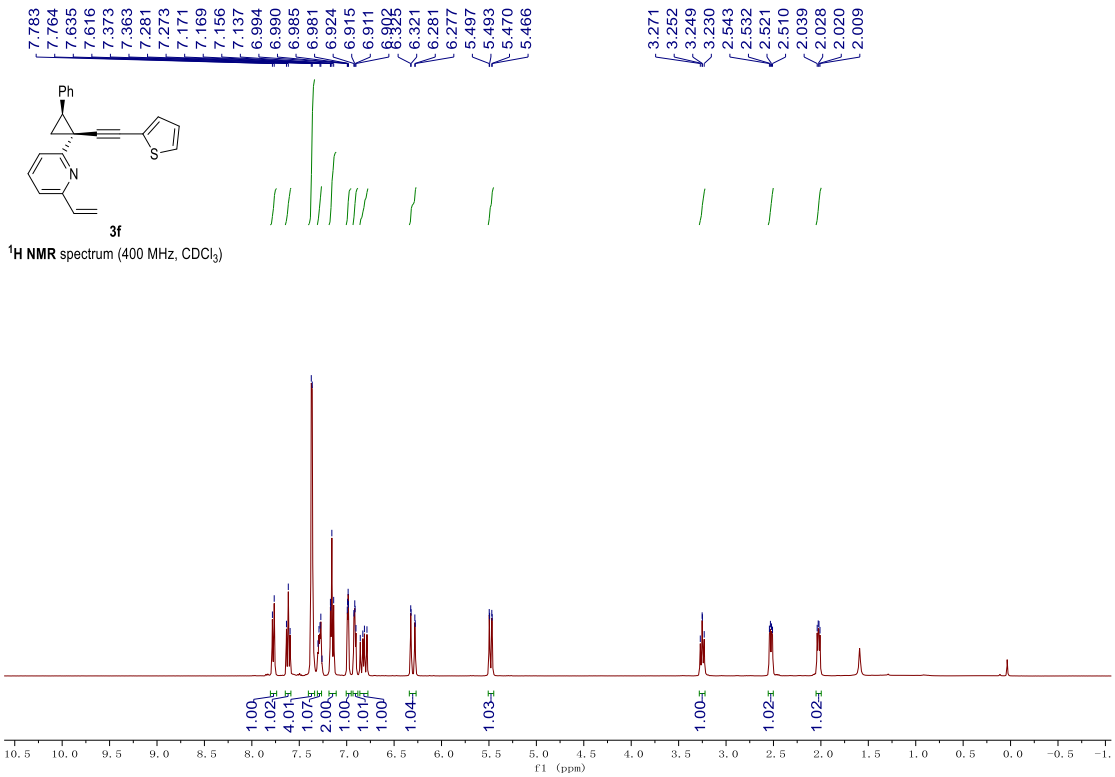




3e

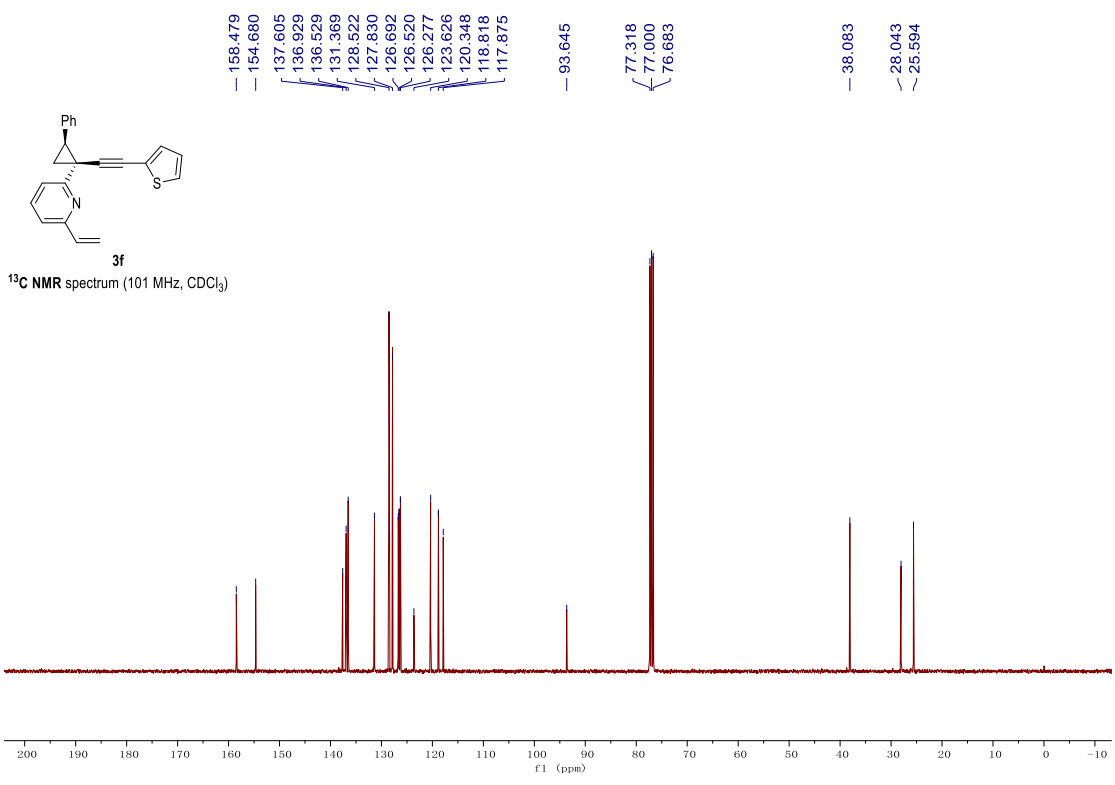
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





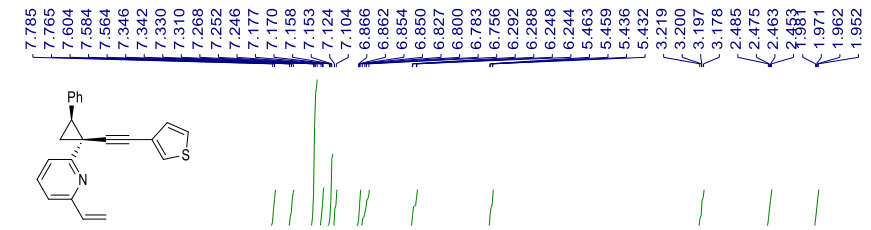
3f

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



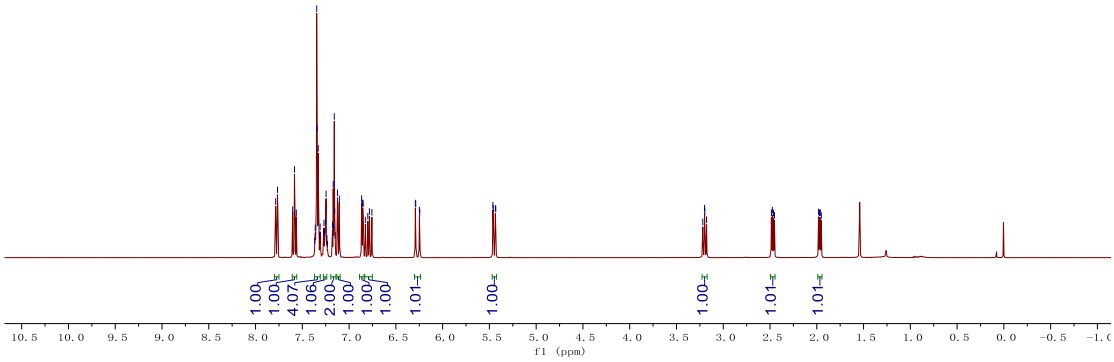
3f

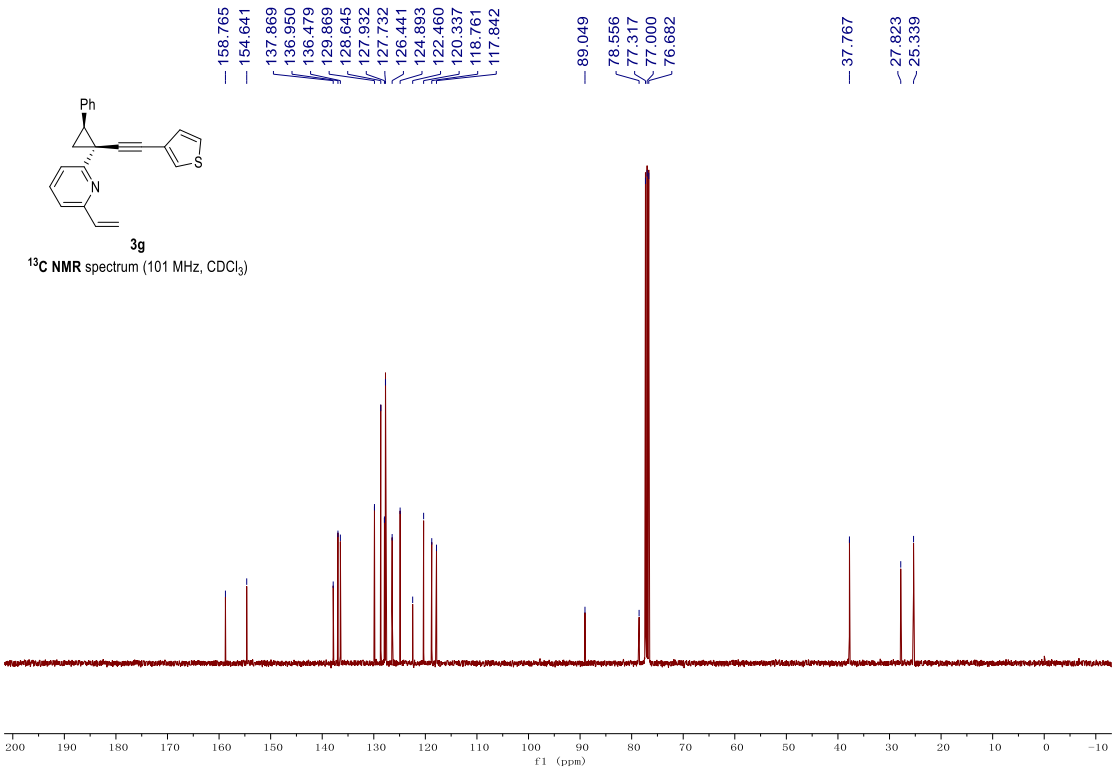
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



3g

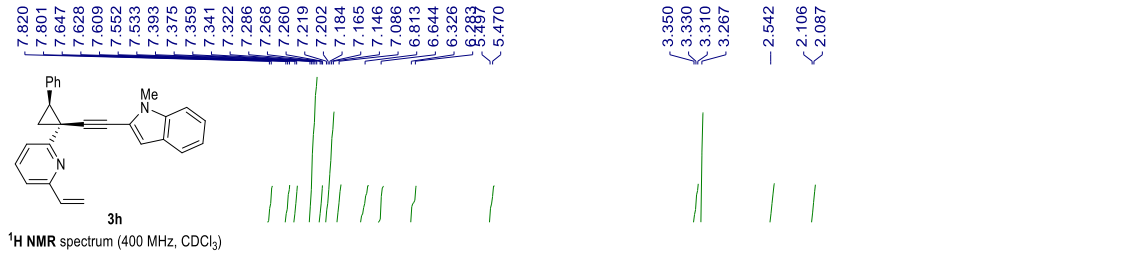
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





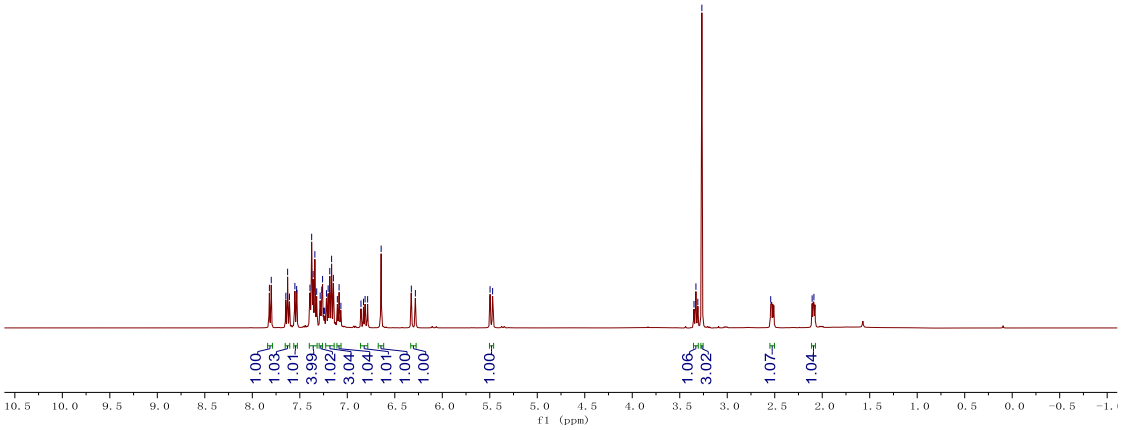
3g

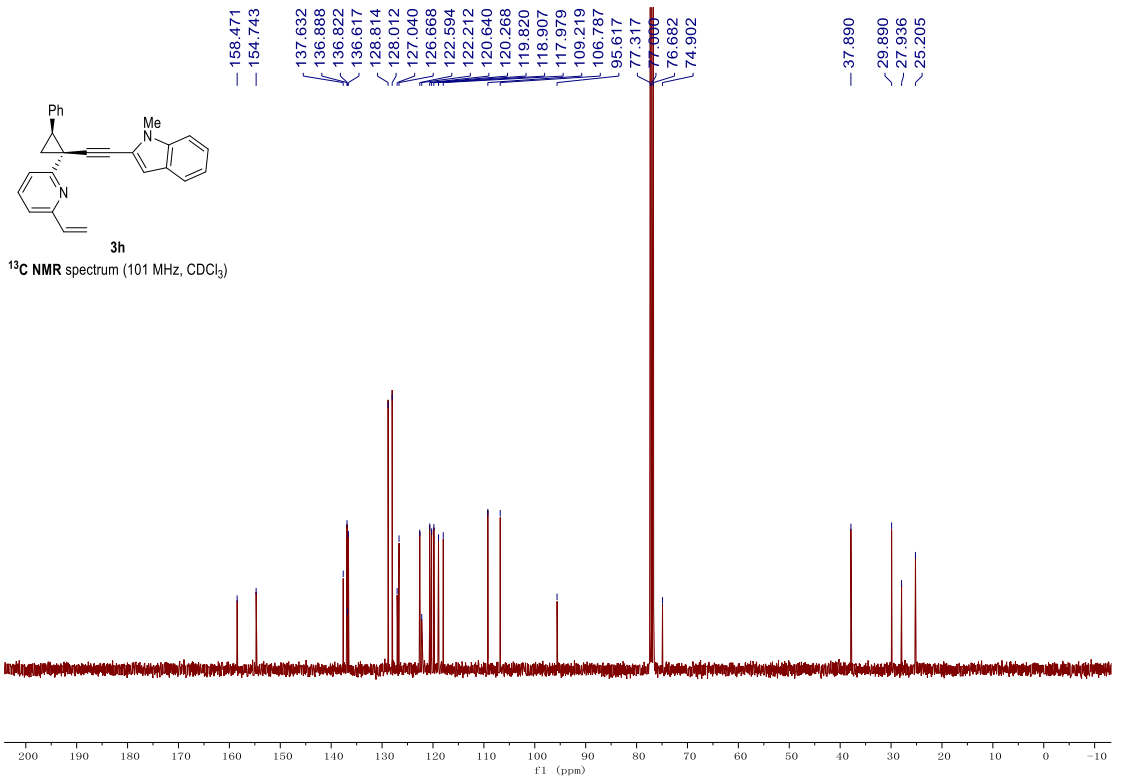
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



3h

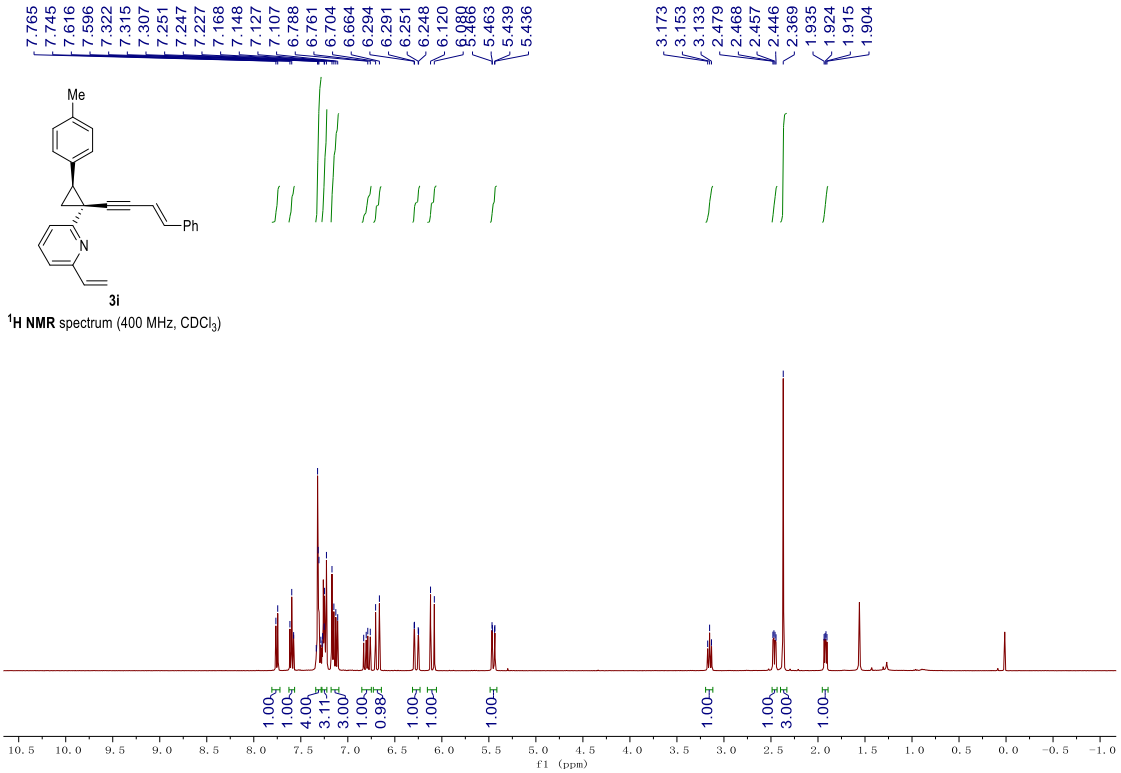
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





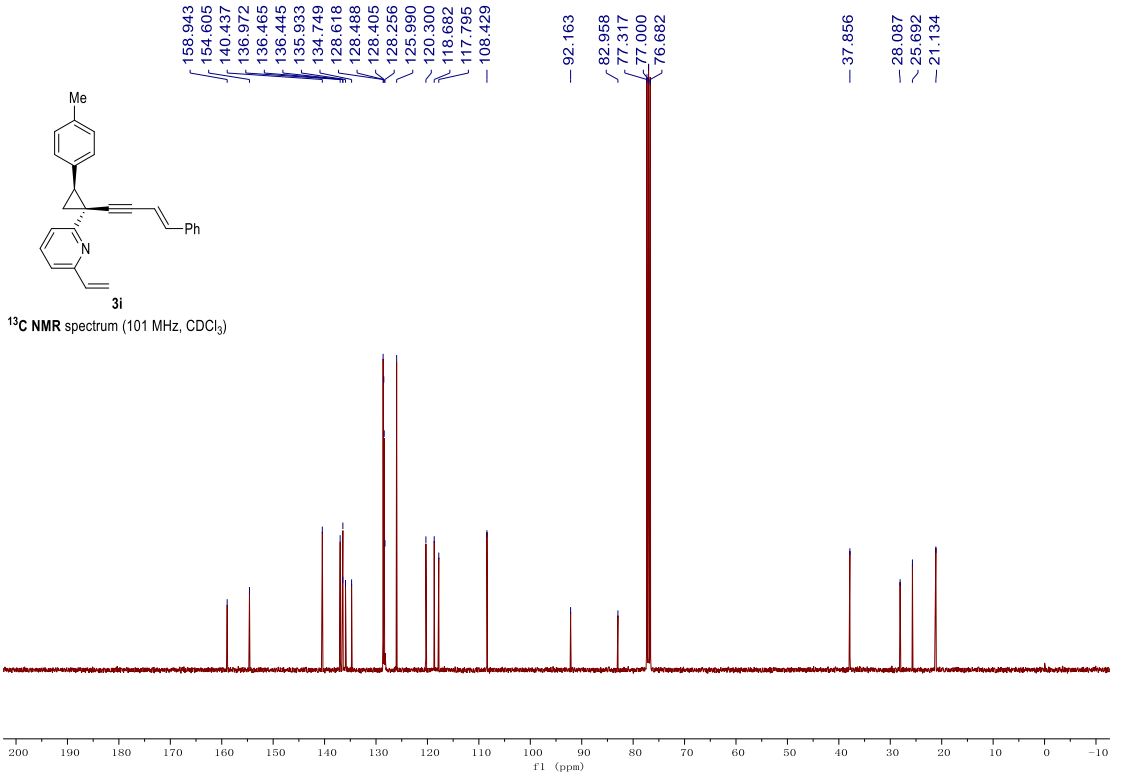
3h

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



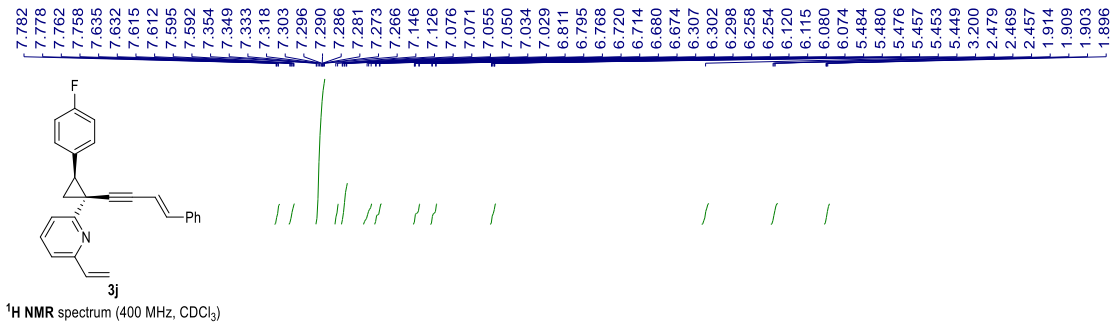
3i

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



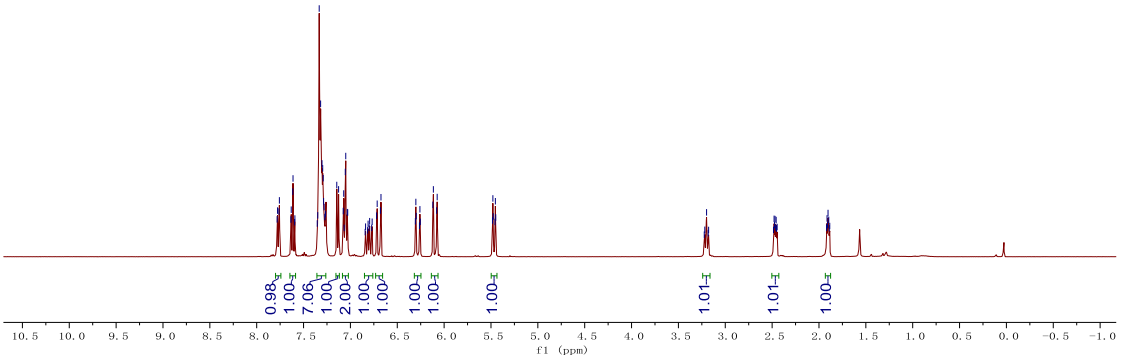
3i

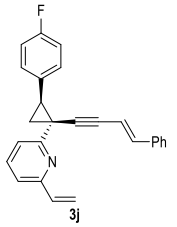
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



3j

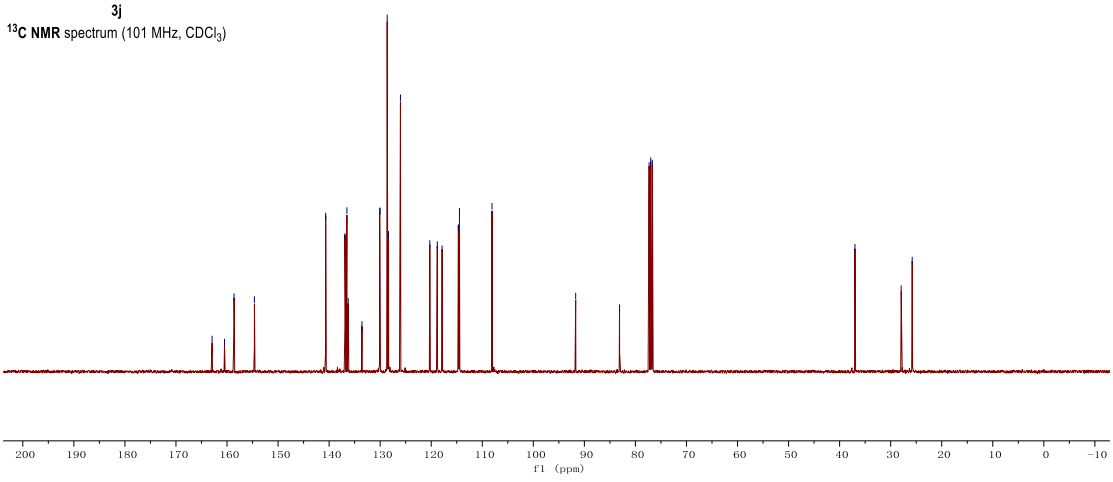
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

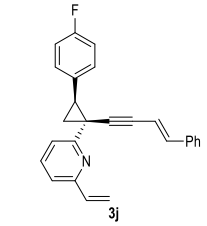




3j

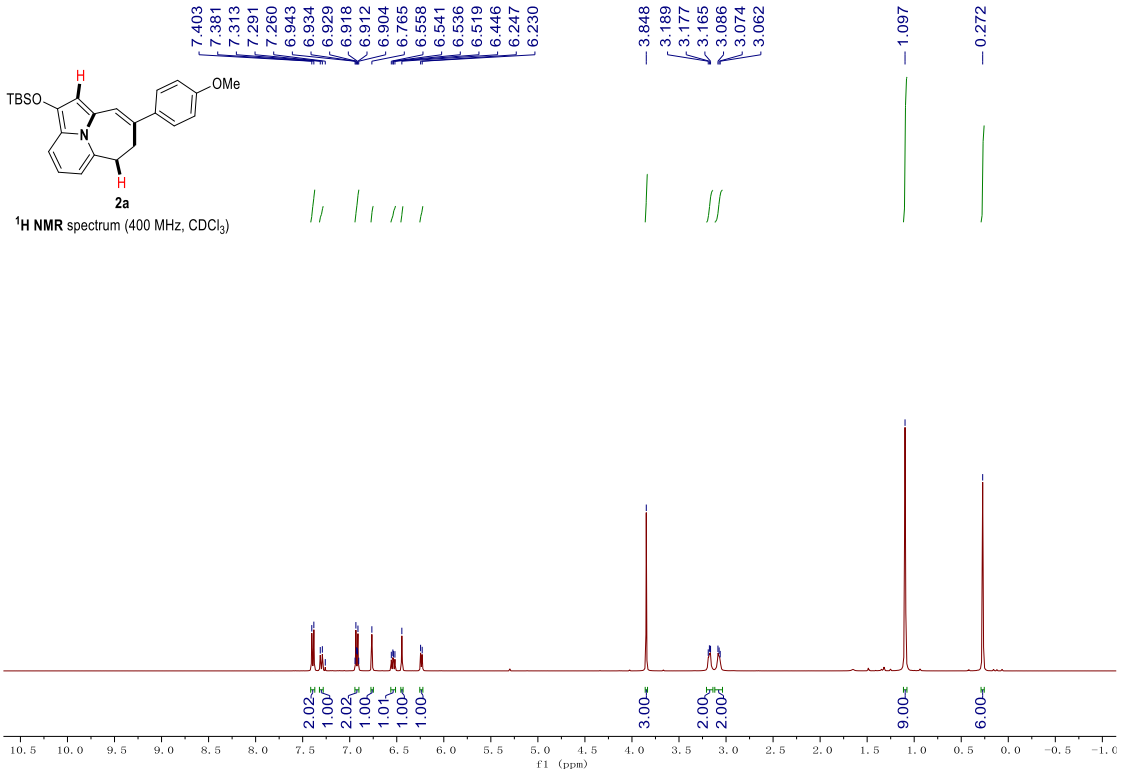
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



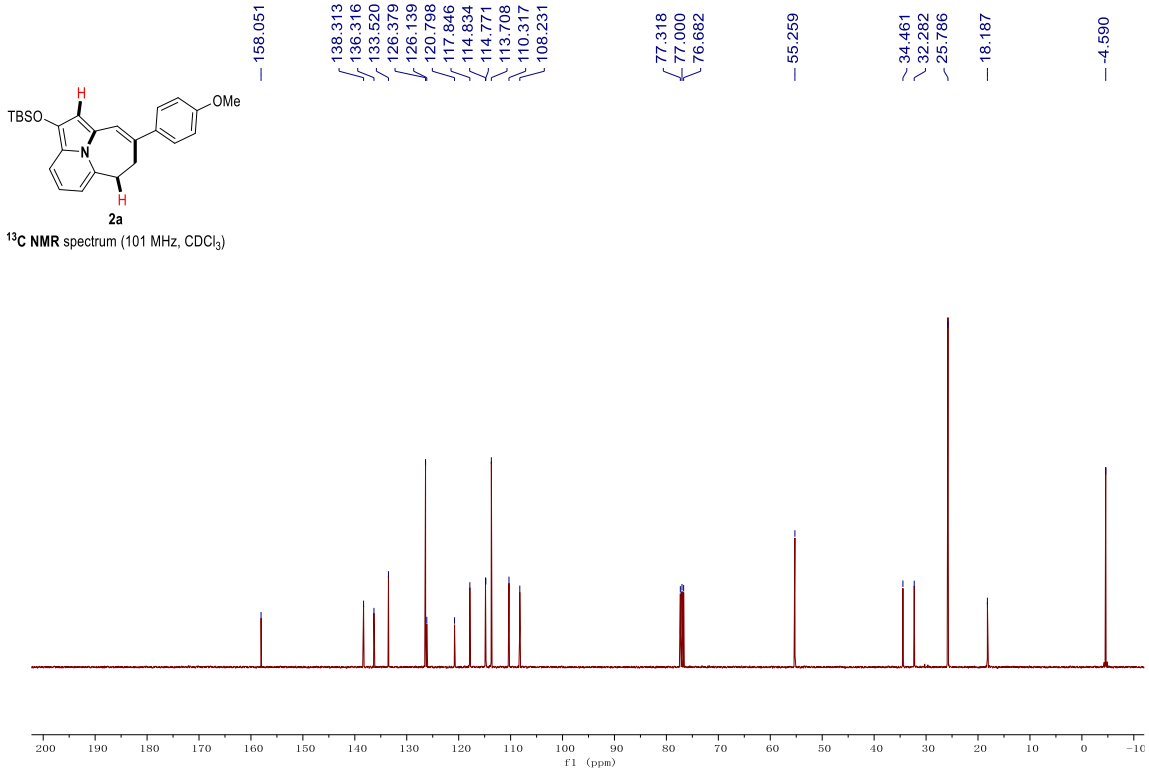


3j

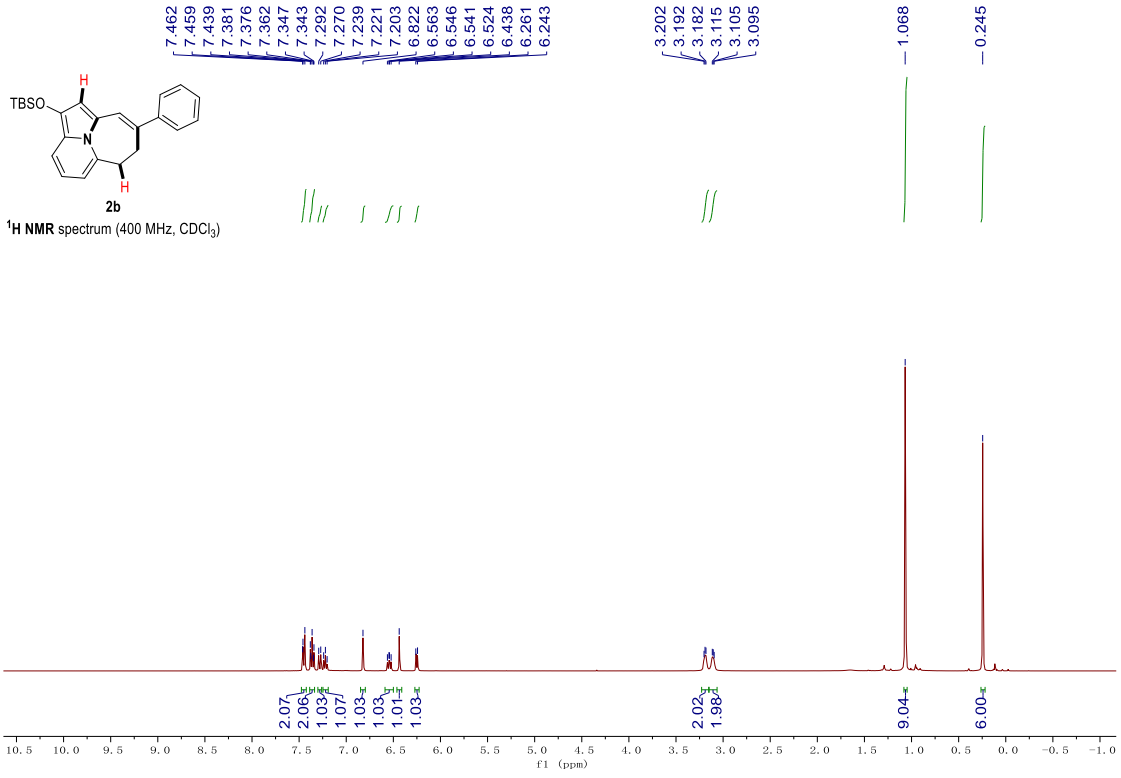
^{19}**F NMR** spectrum (377 MHz, $CDCl_3$)



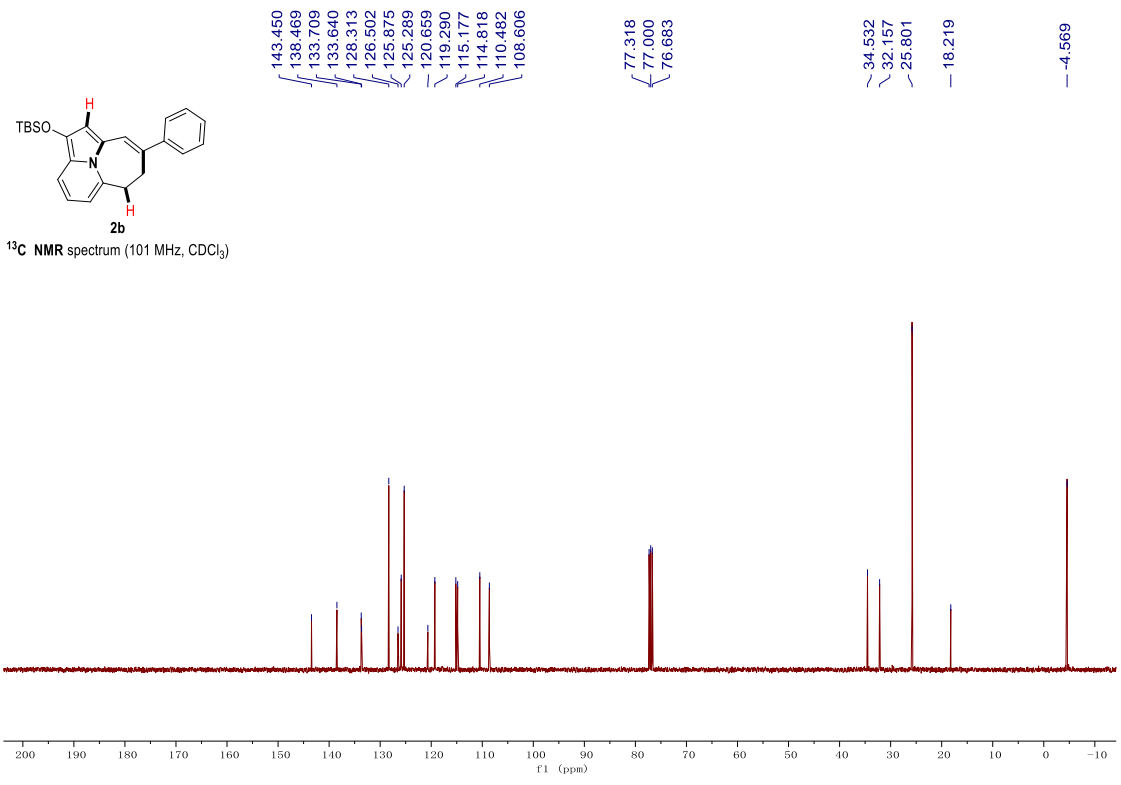
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



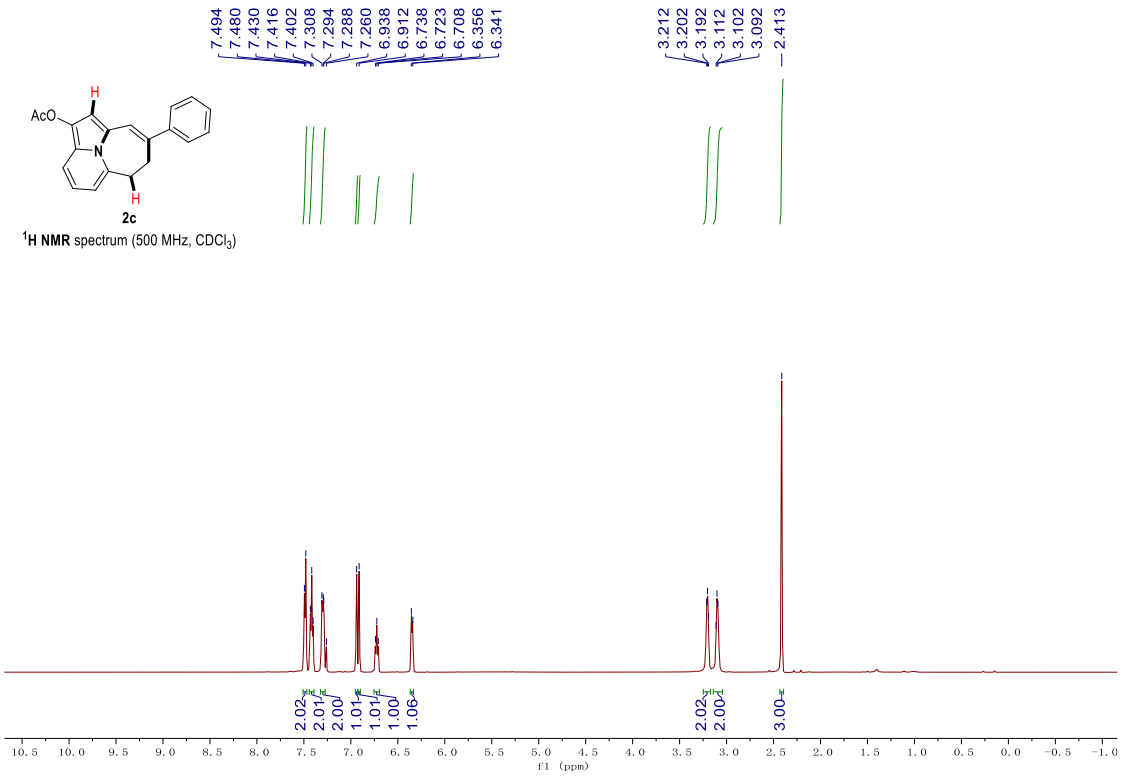
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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

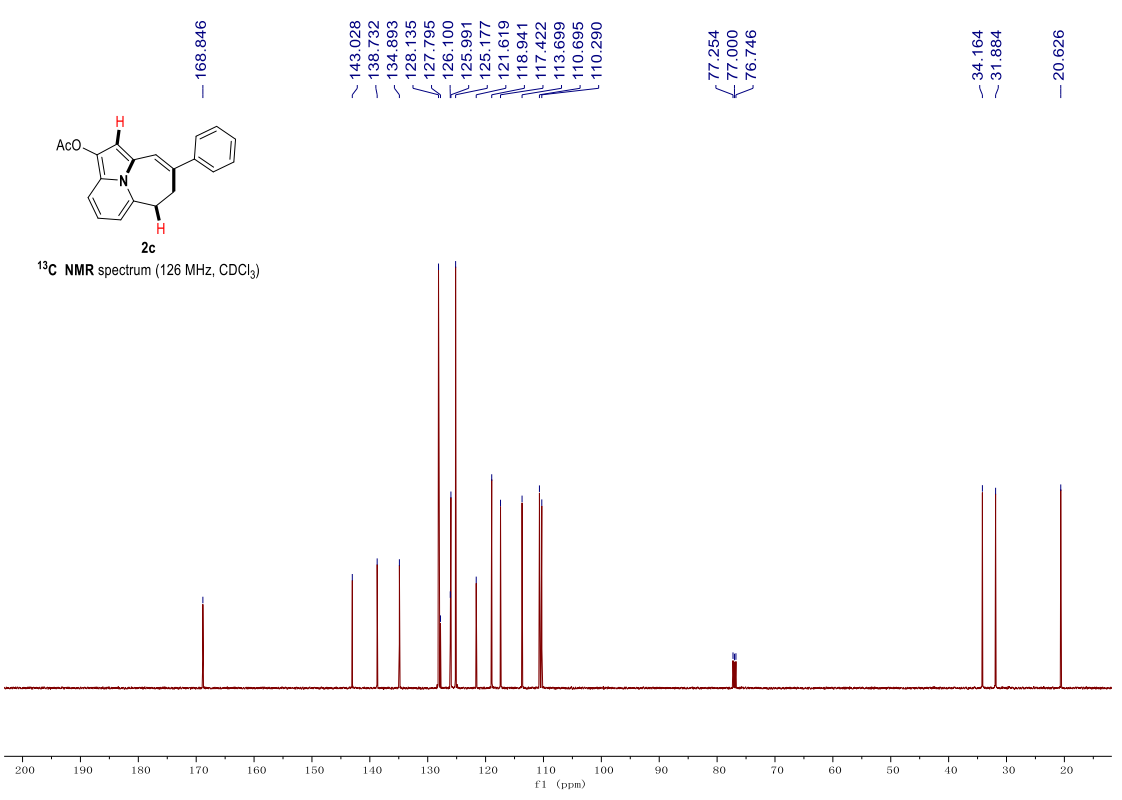


^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



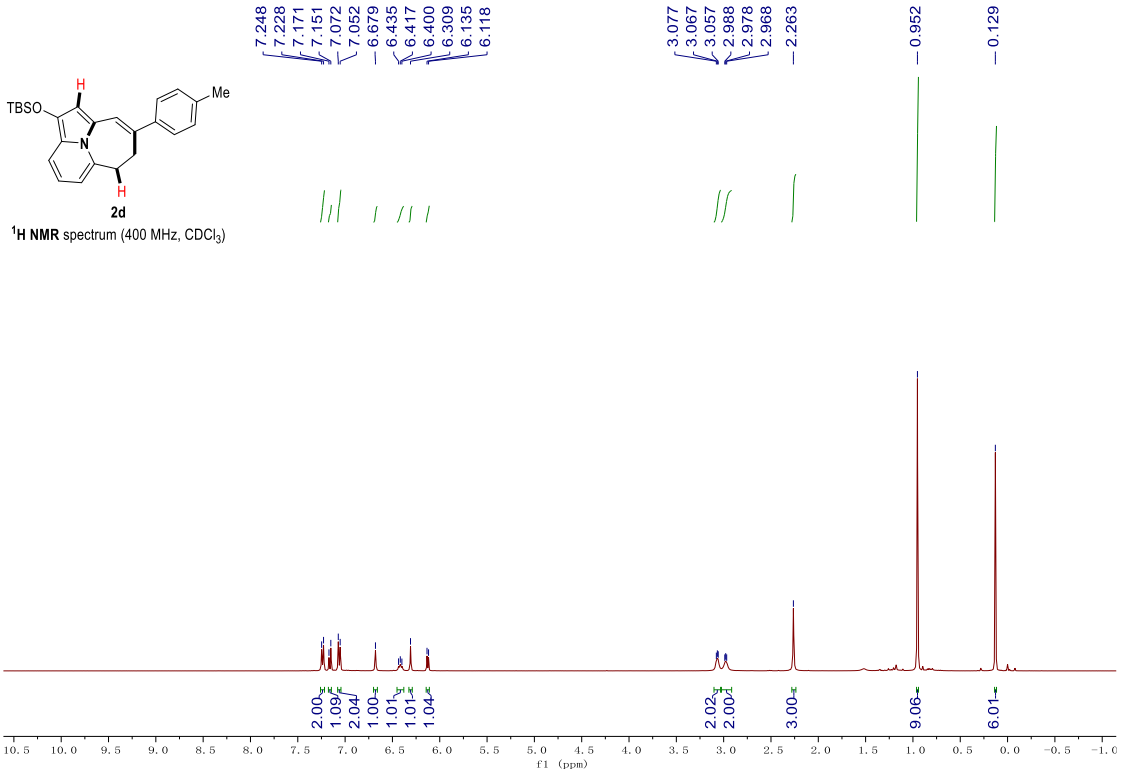
2c

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



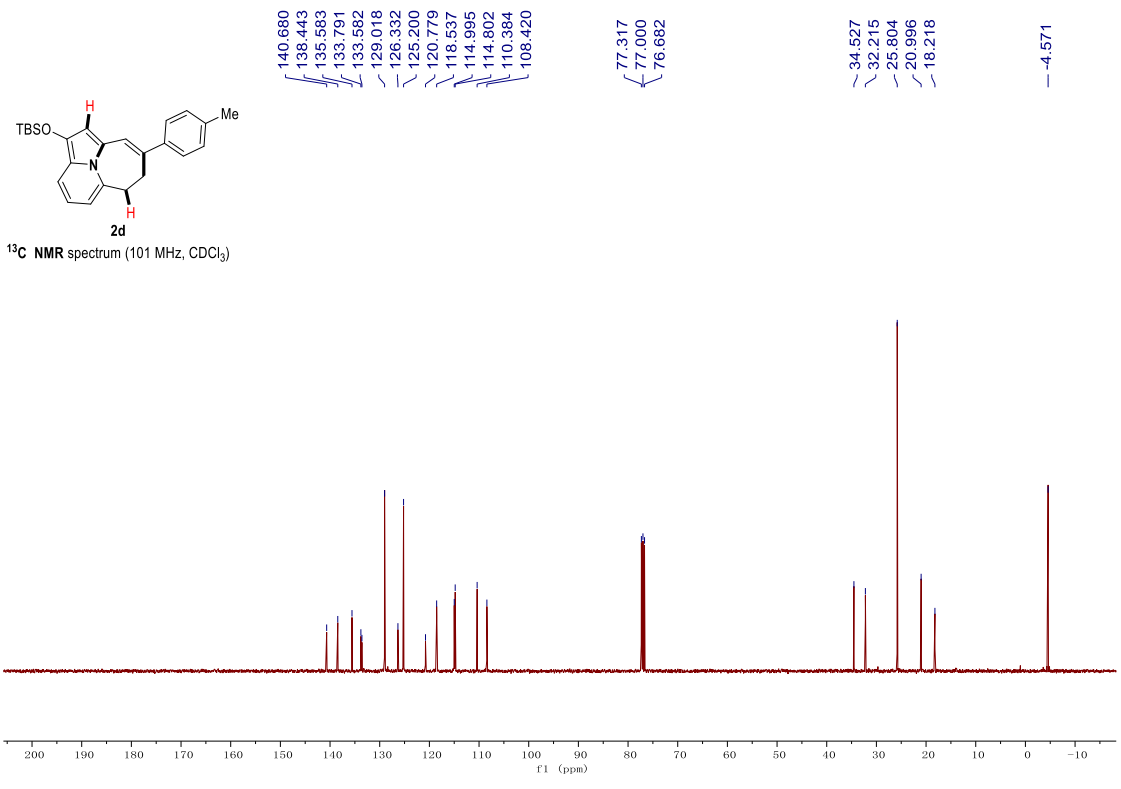
2c

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



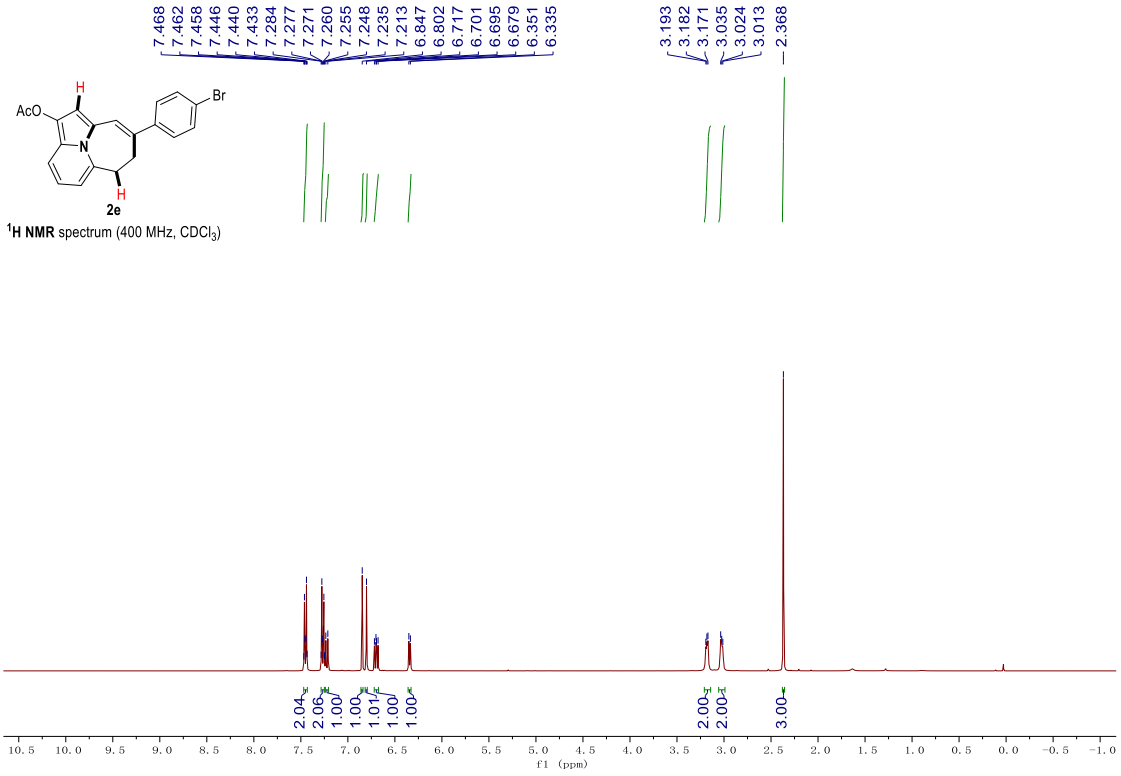
2d

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

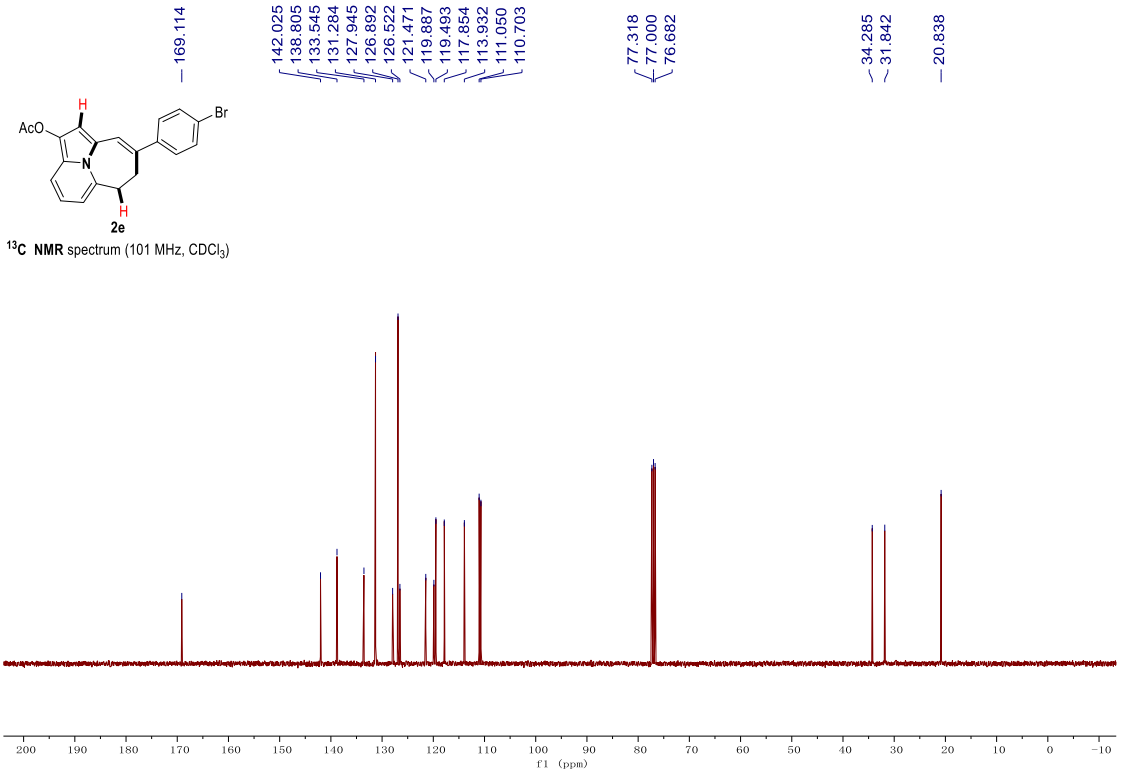


2d

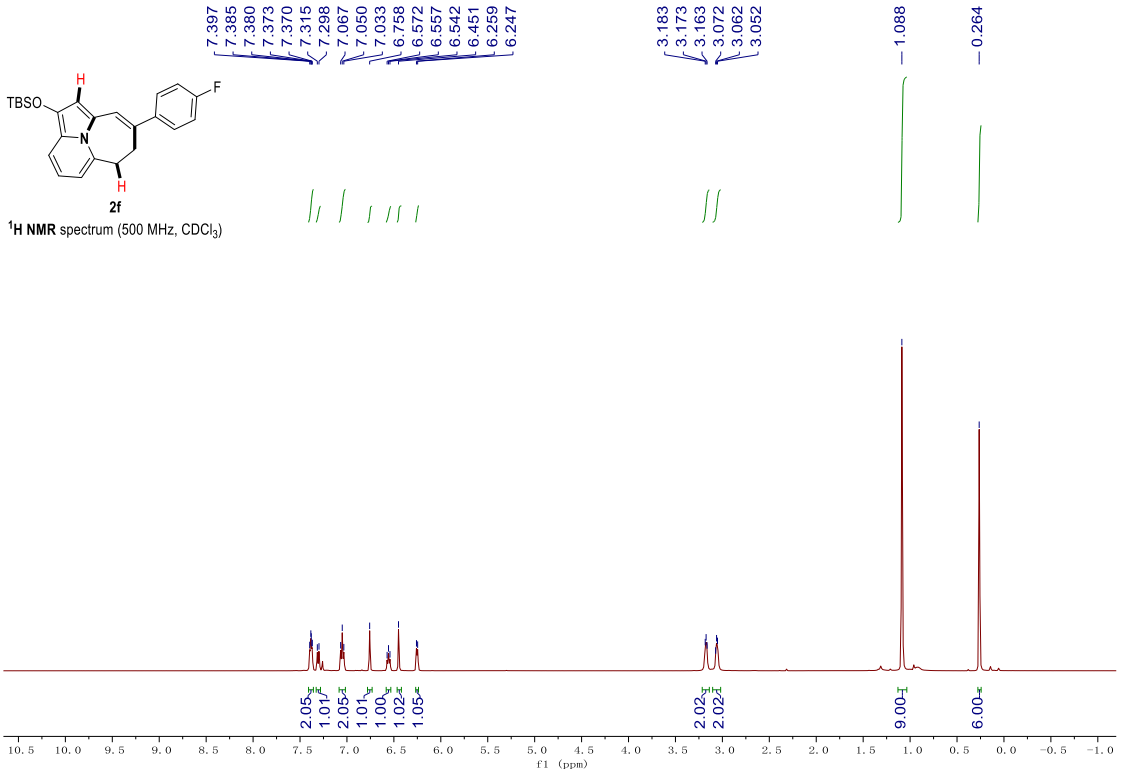
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



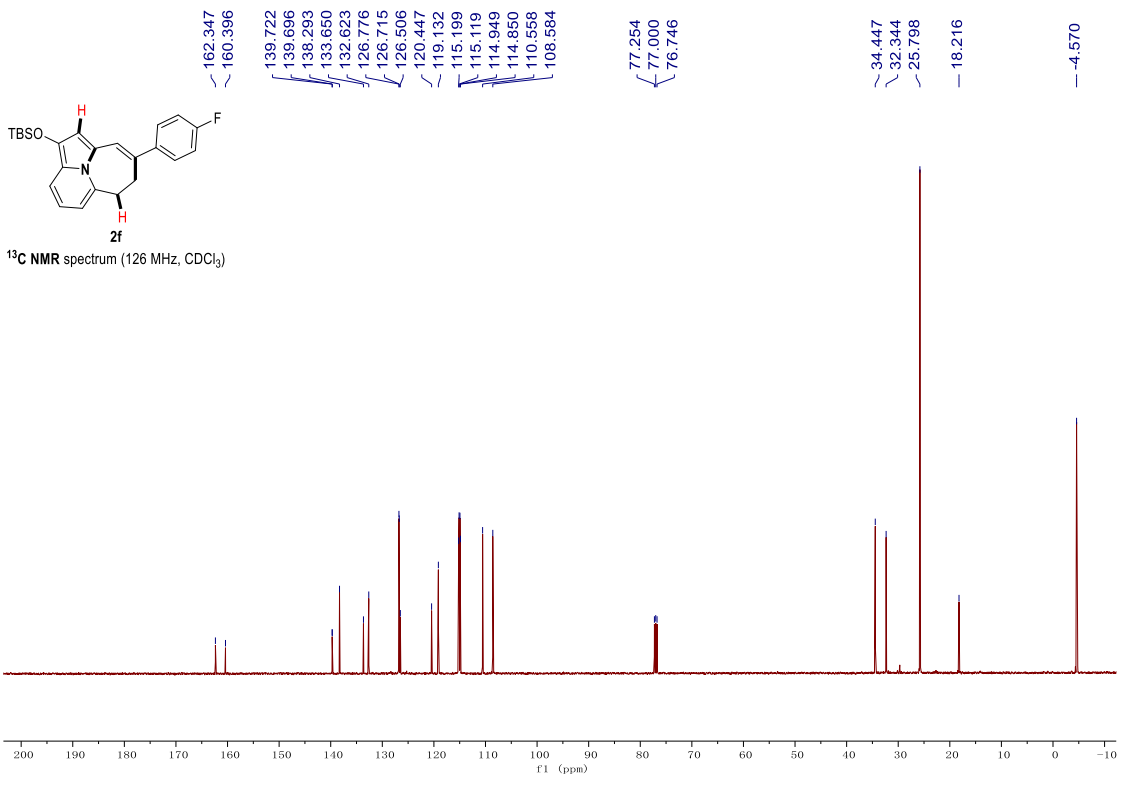
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



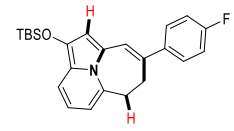
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



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

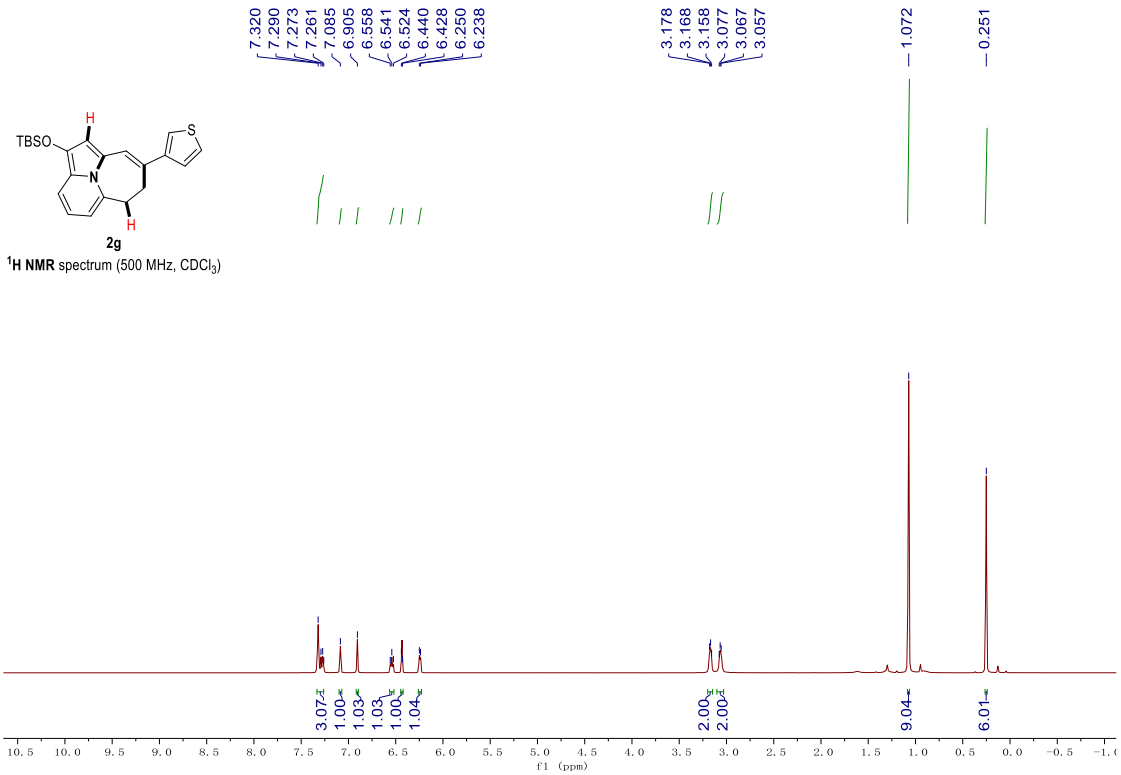


^{13}**C NMR** spectrum (126 MHz, $CDCl_3$)



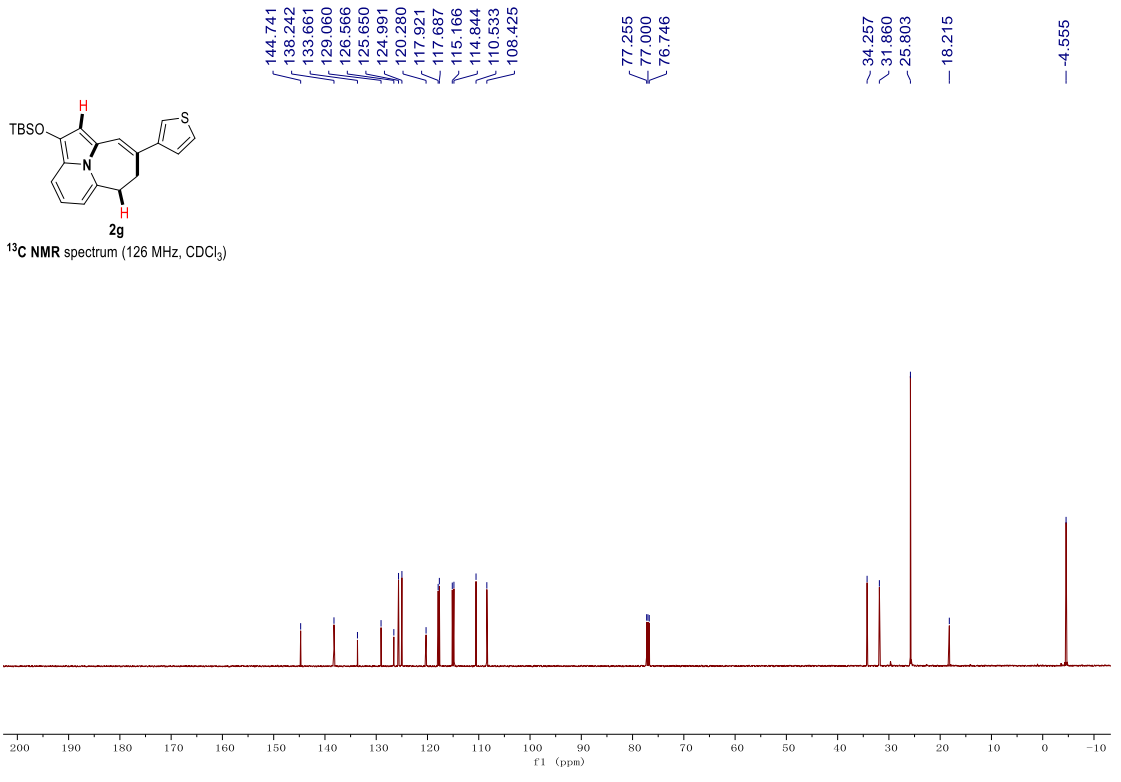
2f

^{19}F NMR spectrum (564 MHz, $CDCl_3$)



2g

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

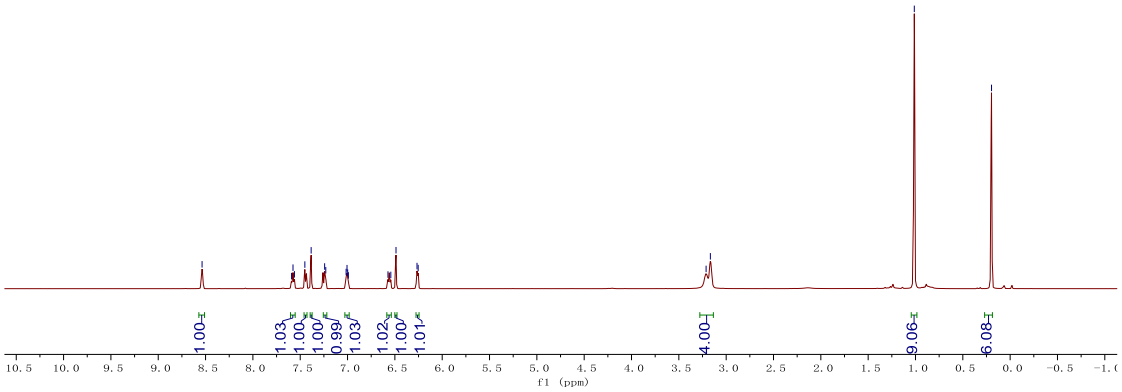


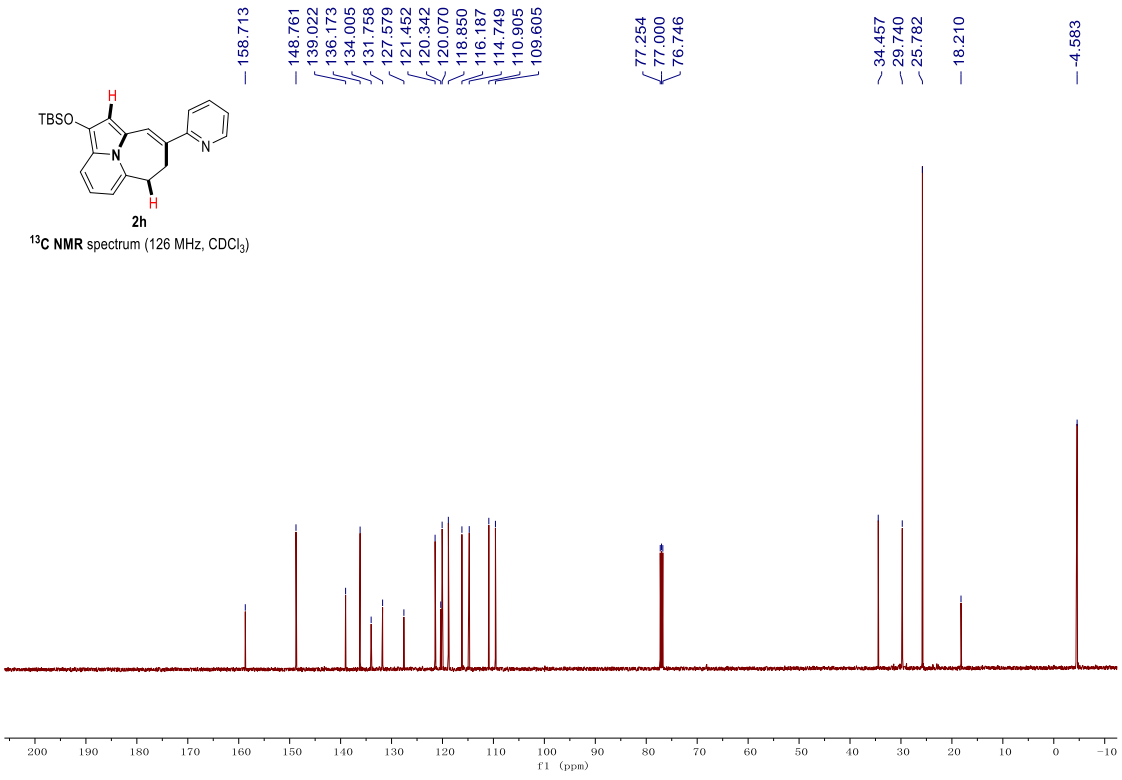
2g

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

2h

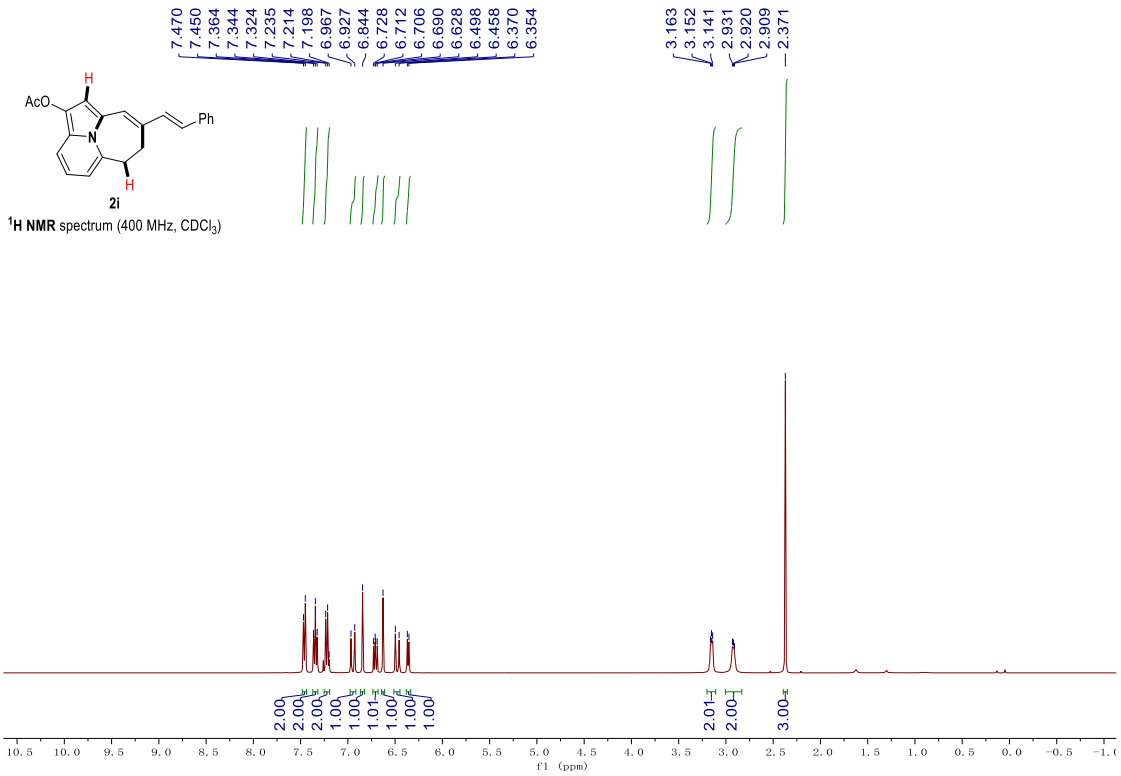
^{1}H NMR spectrum (500 MHz, $CDCl_3$)





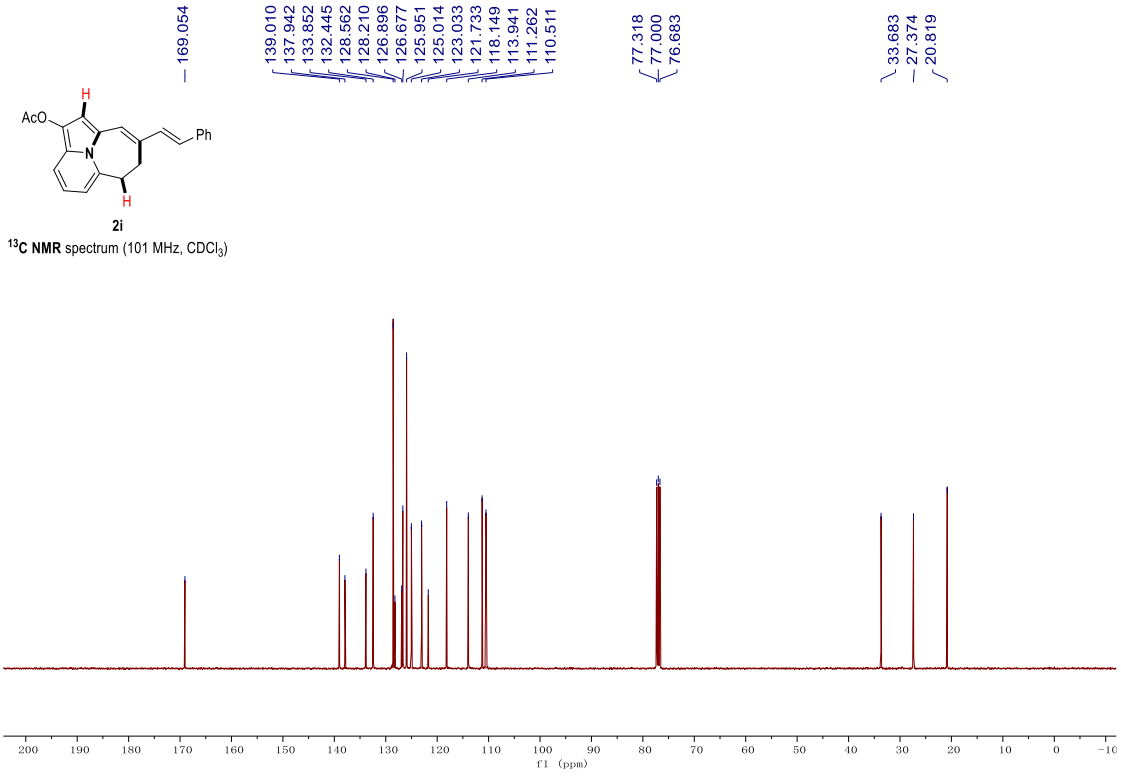
2h

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



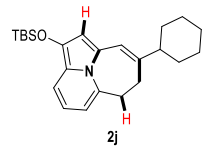
2i

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



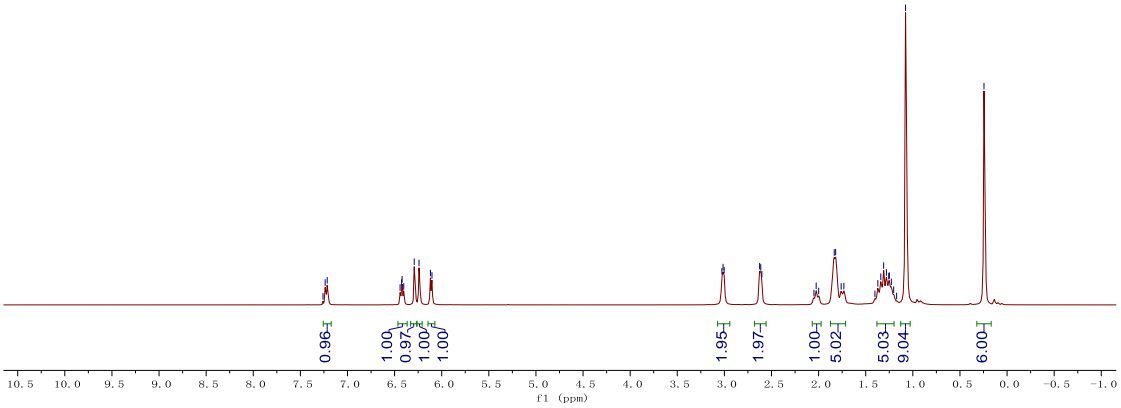
2i

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



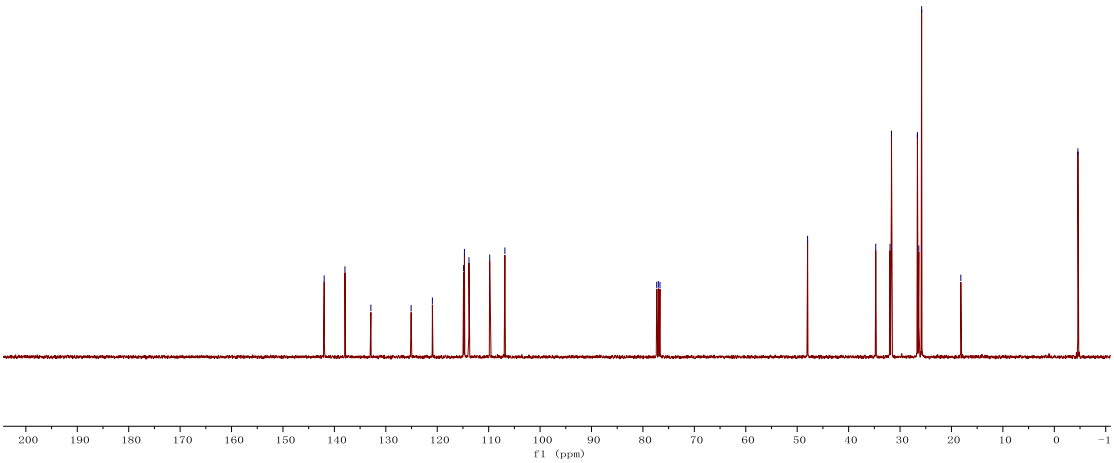
2j

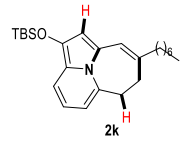
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



2j

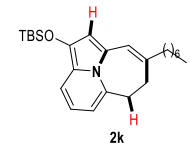
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





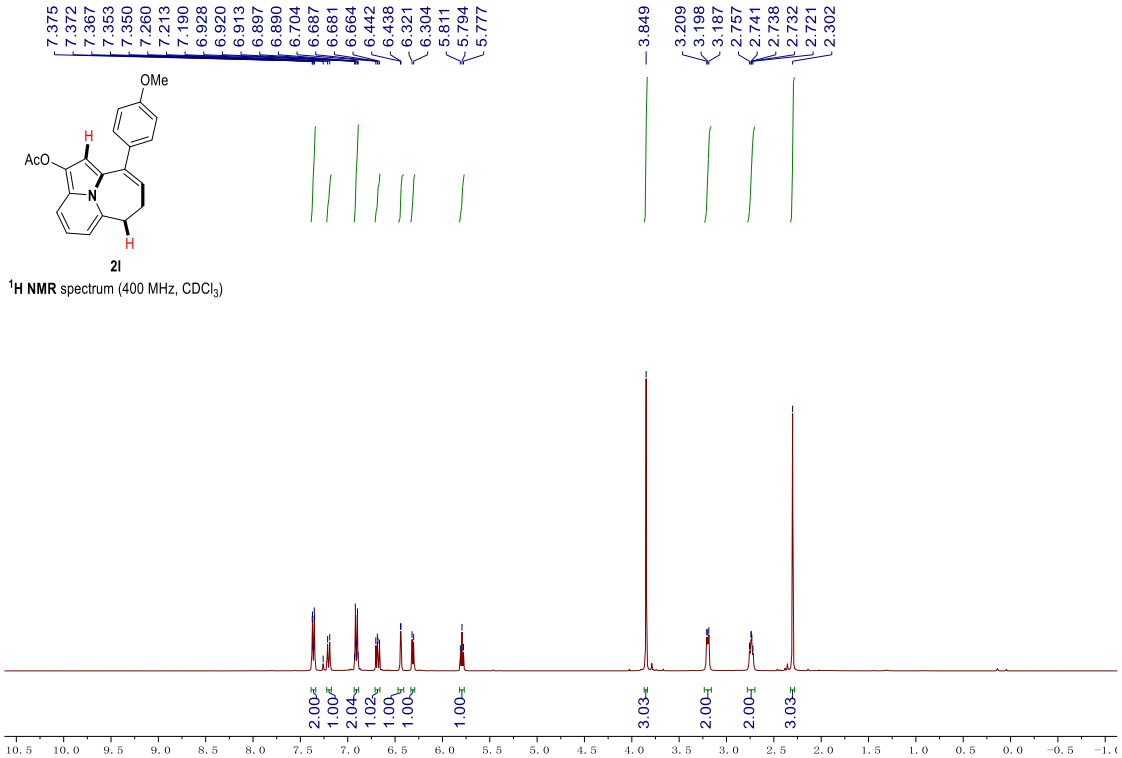
2k

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



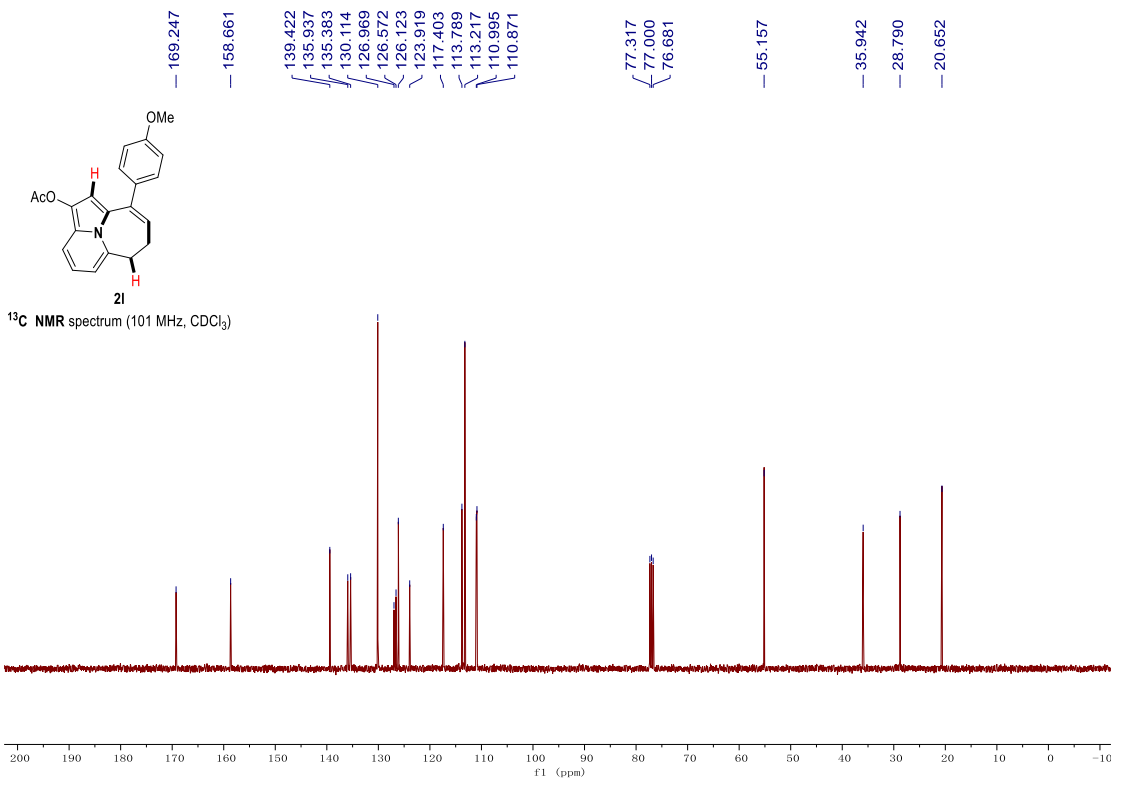
2k

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



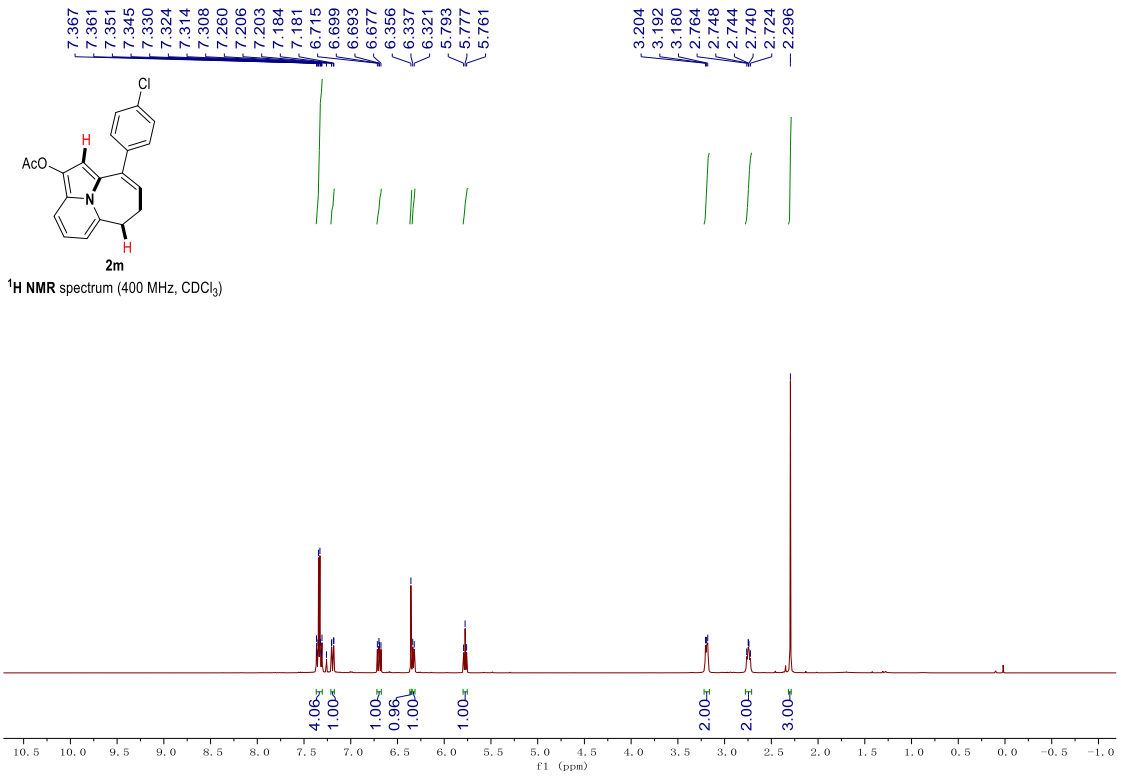
2l

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



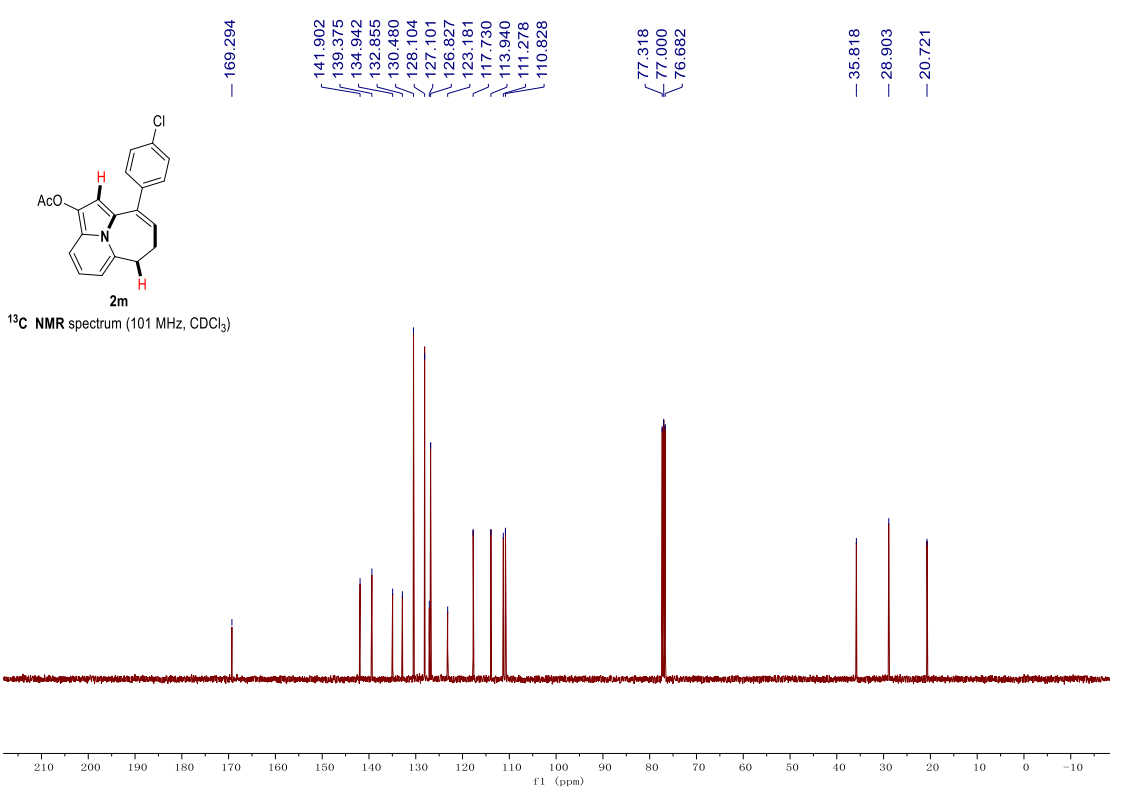
2l

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



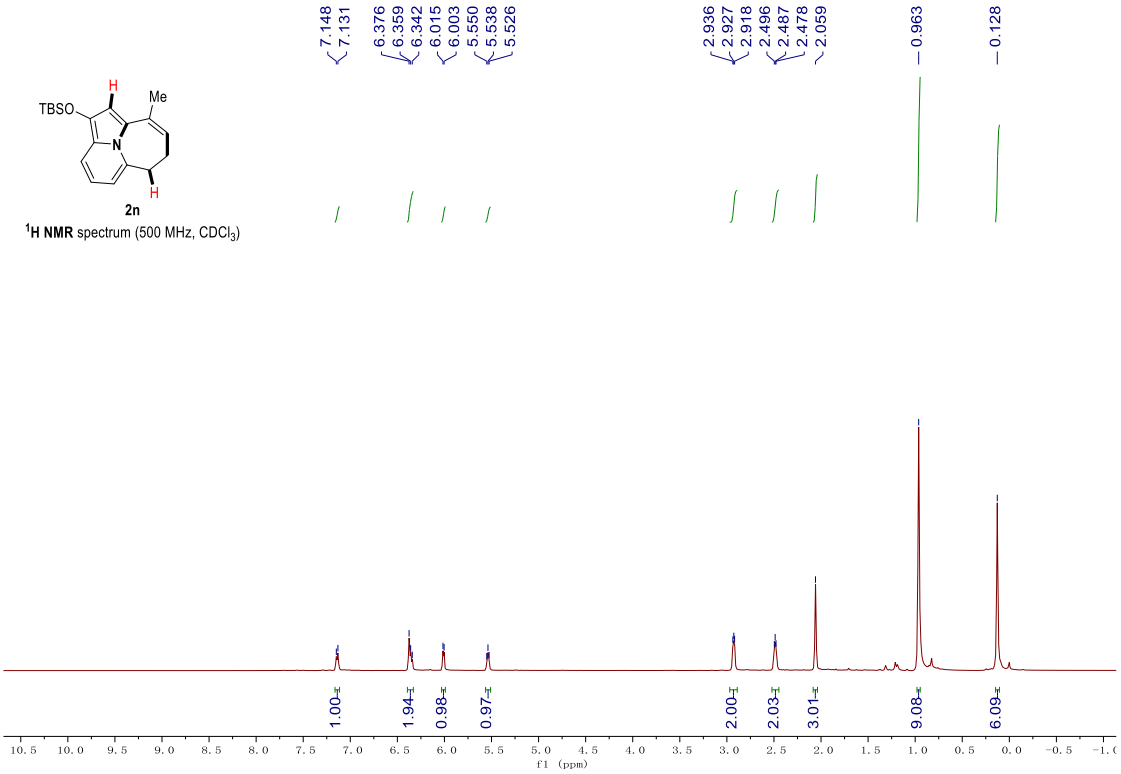
2m

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

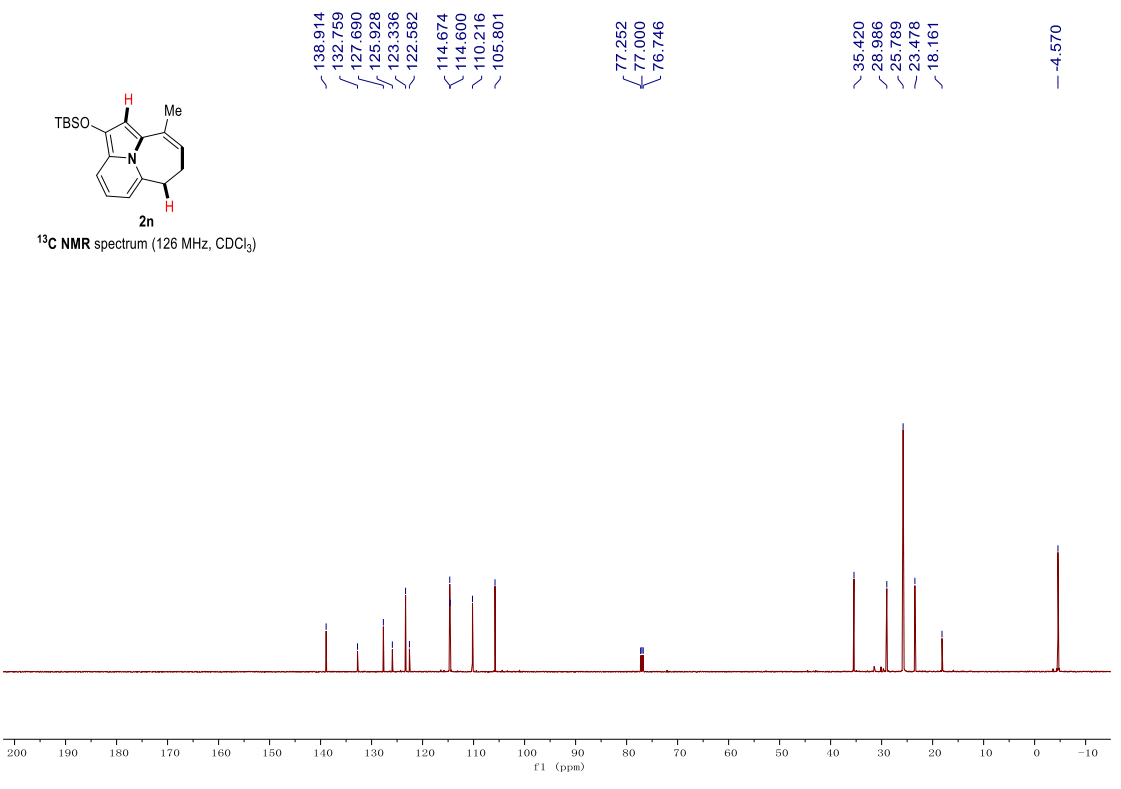


2m

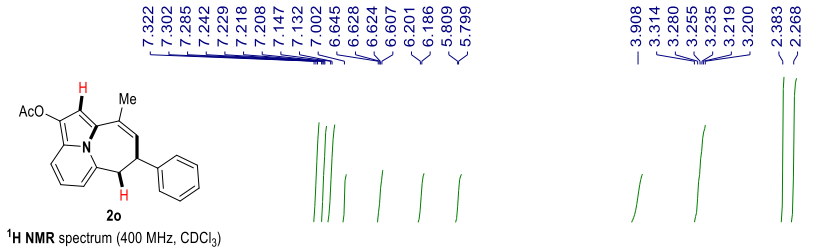
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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

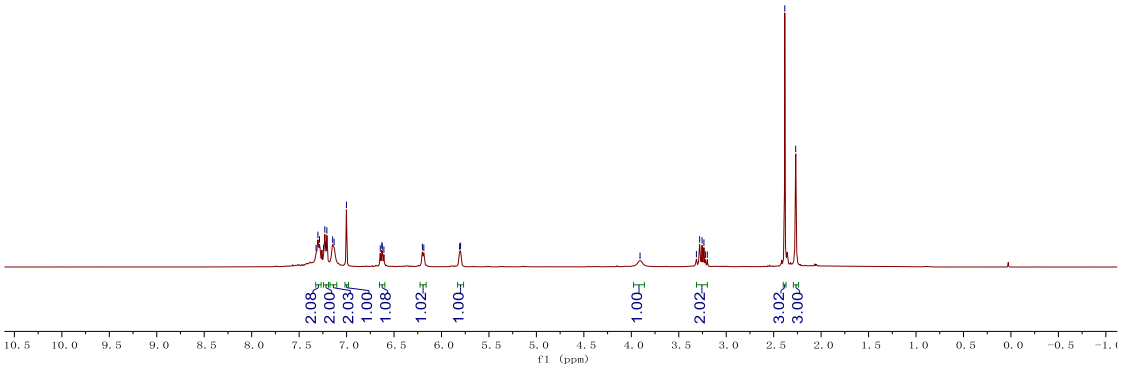


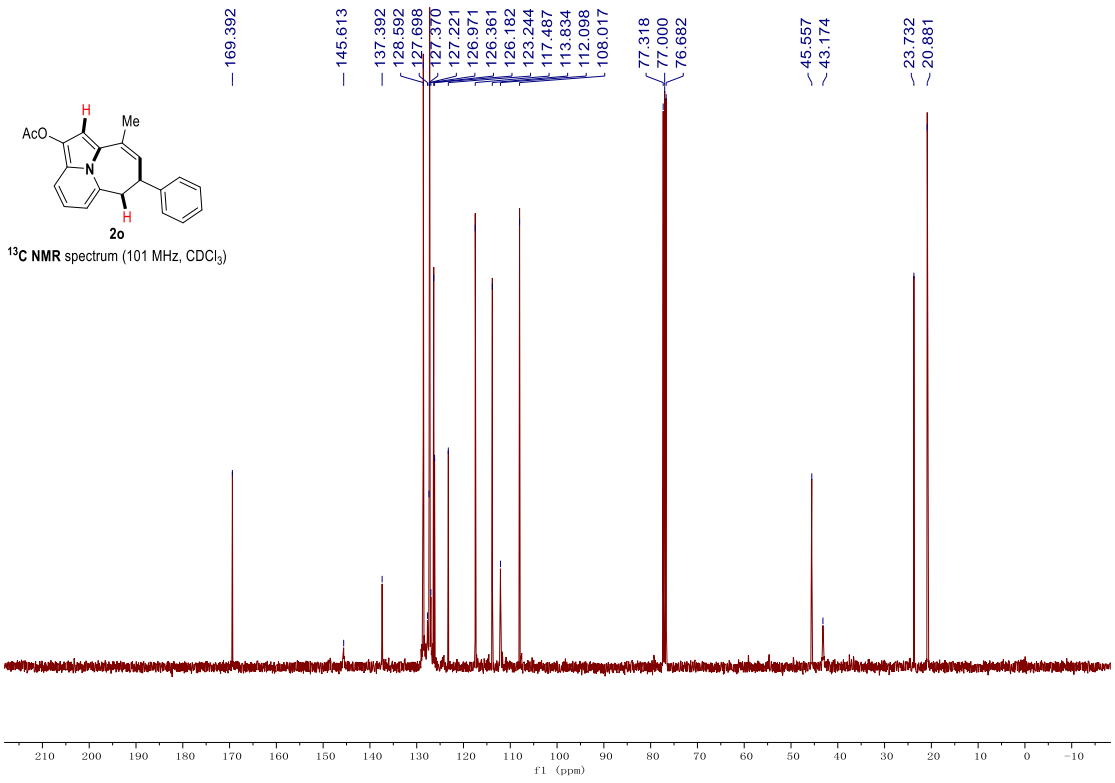
^{13}**C NMR** spectrum (126 MHz, $CDCl_3$)



2o

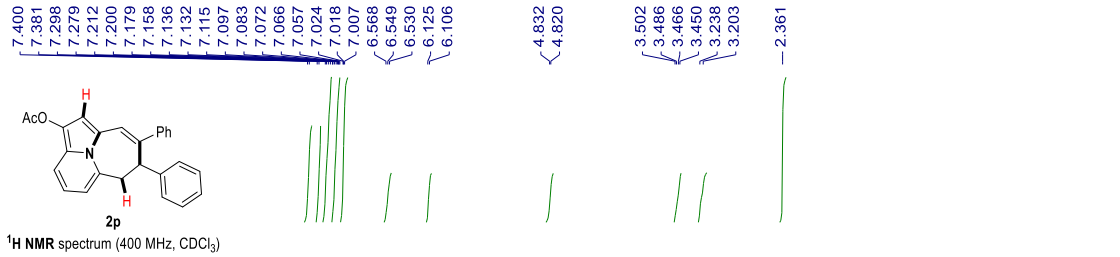
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)





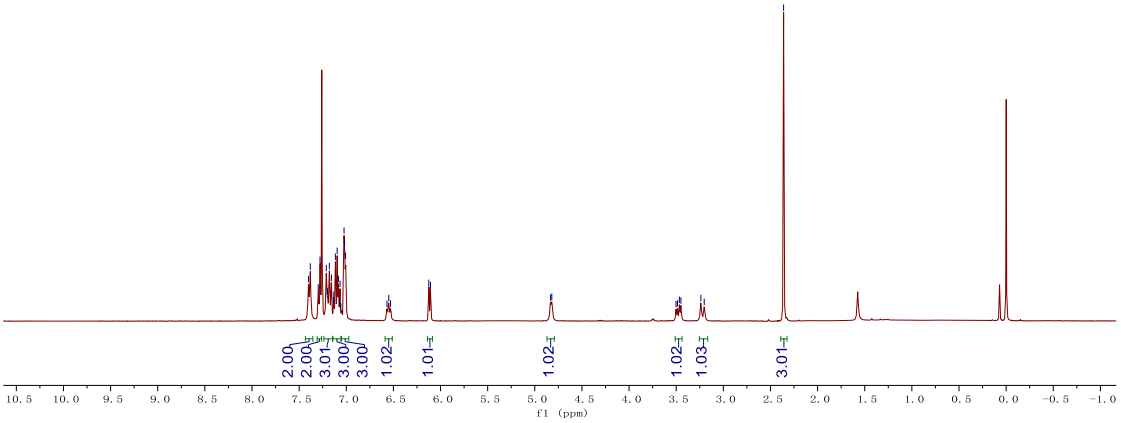
2o

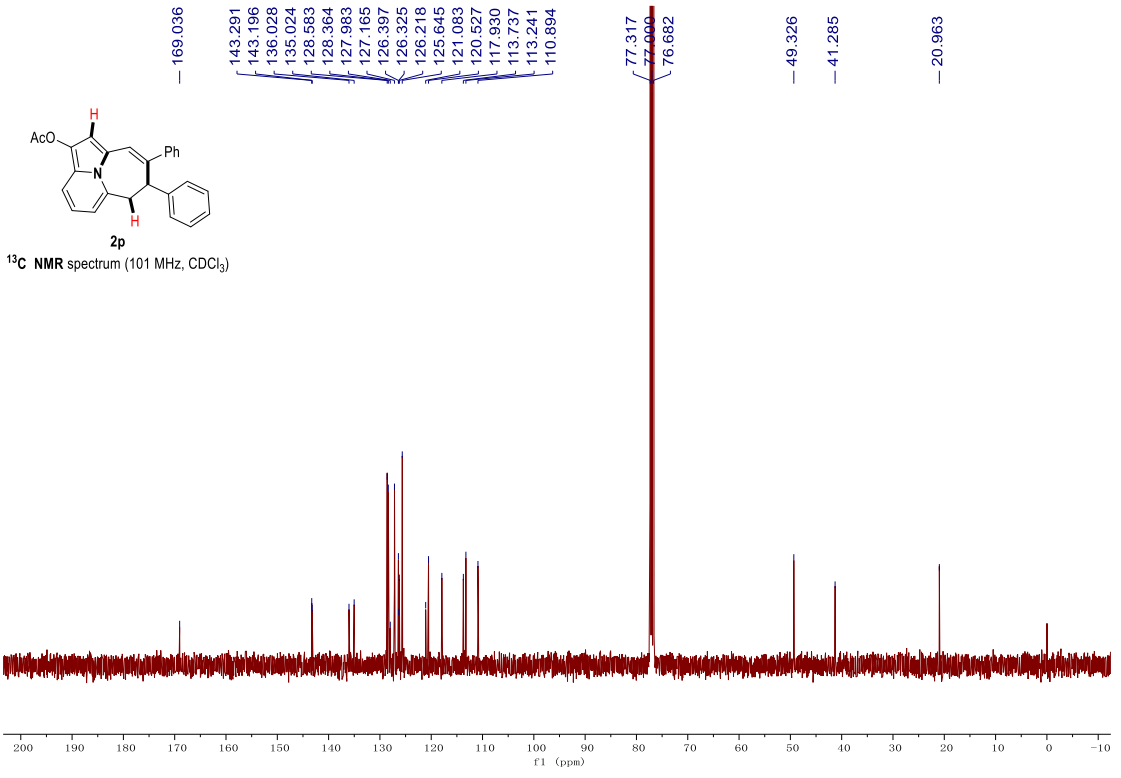
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



2p

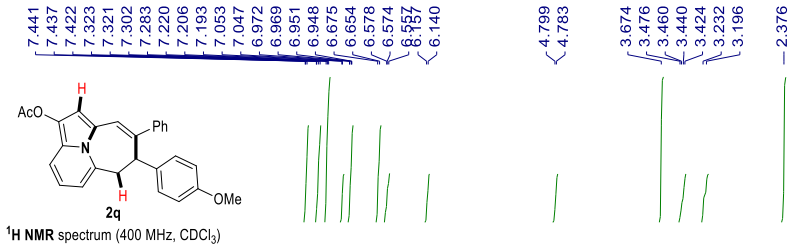
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



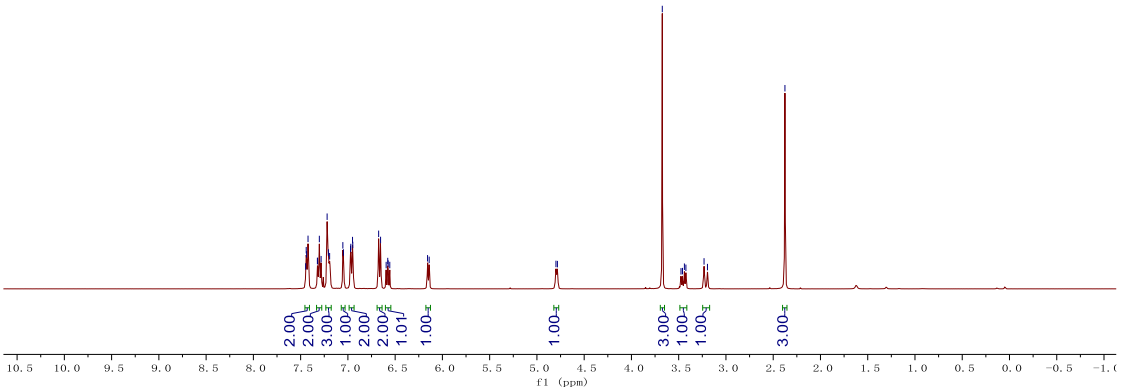


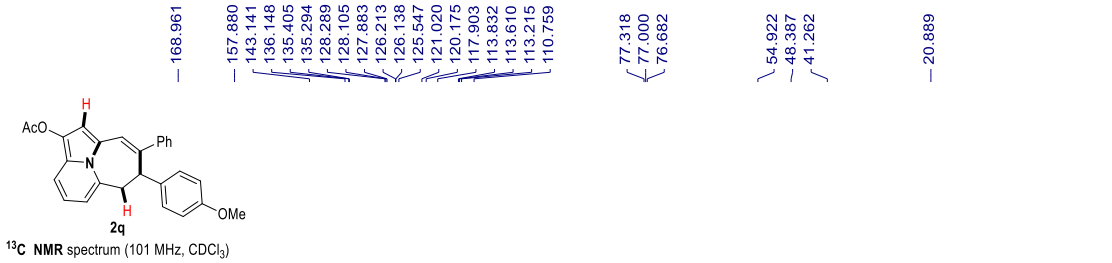
2p

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

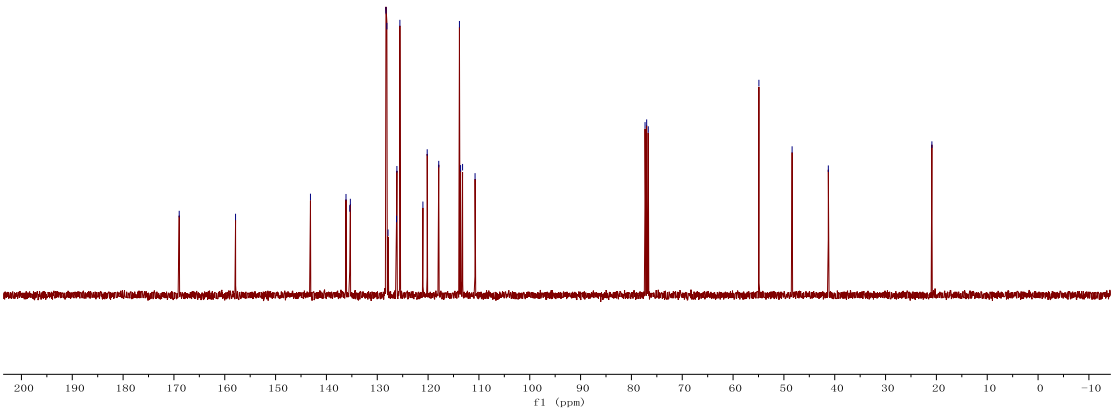


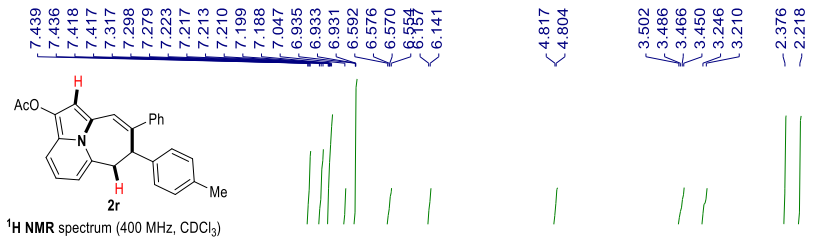
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



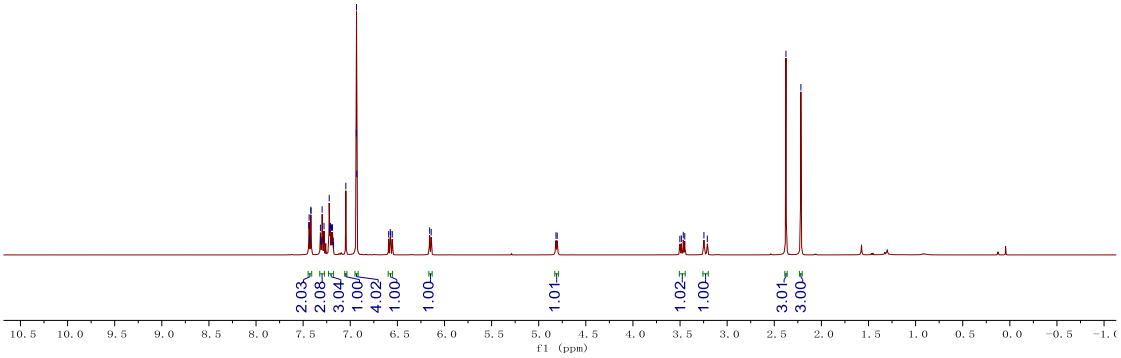


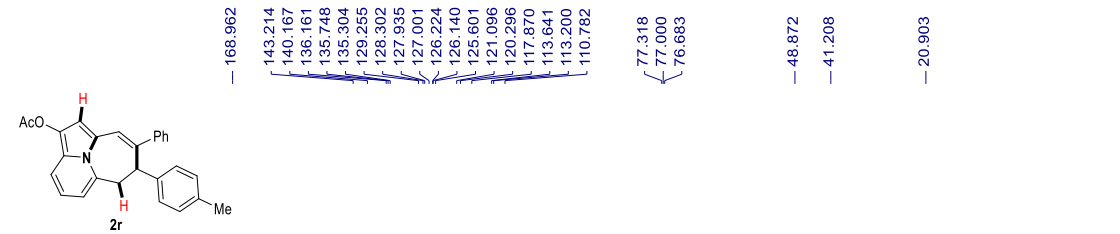
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



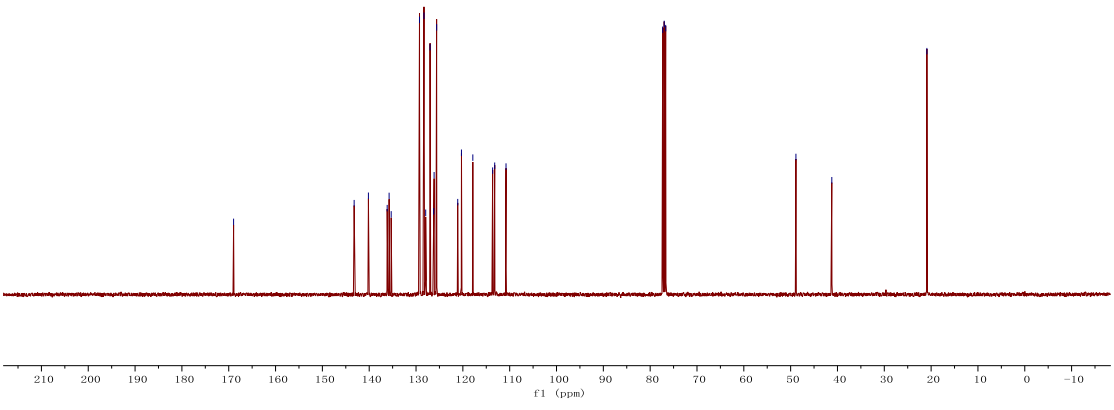


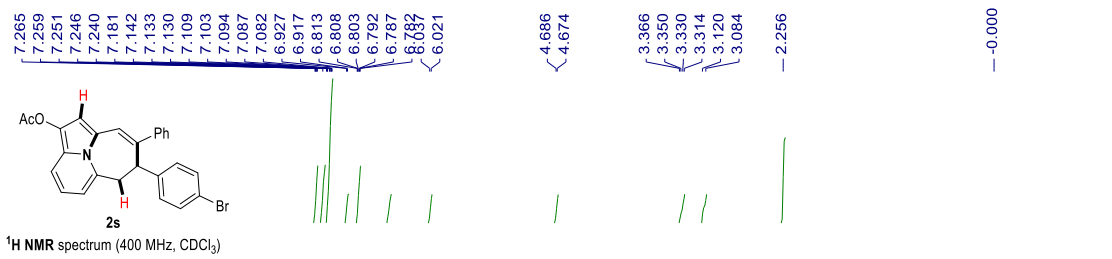
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



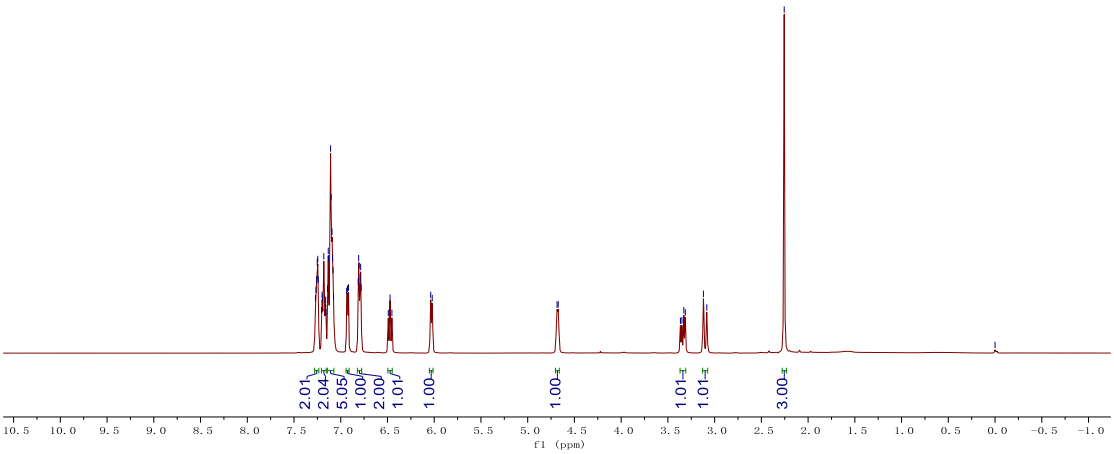


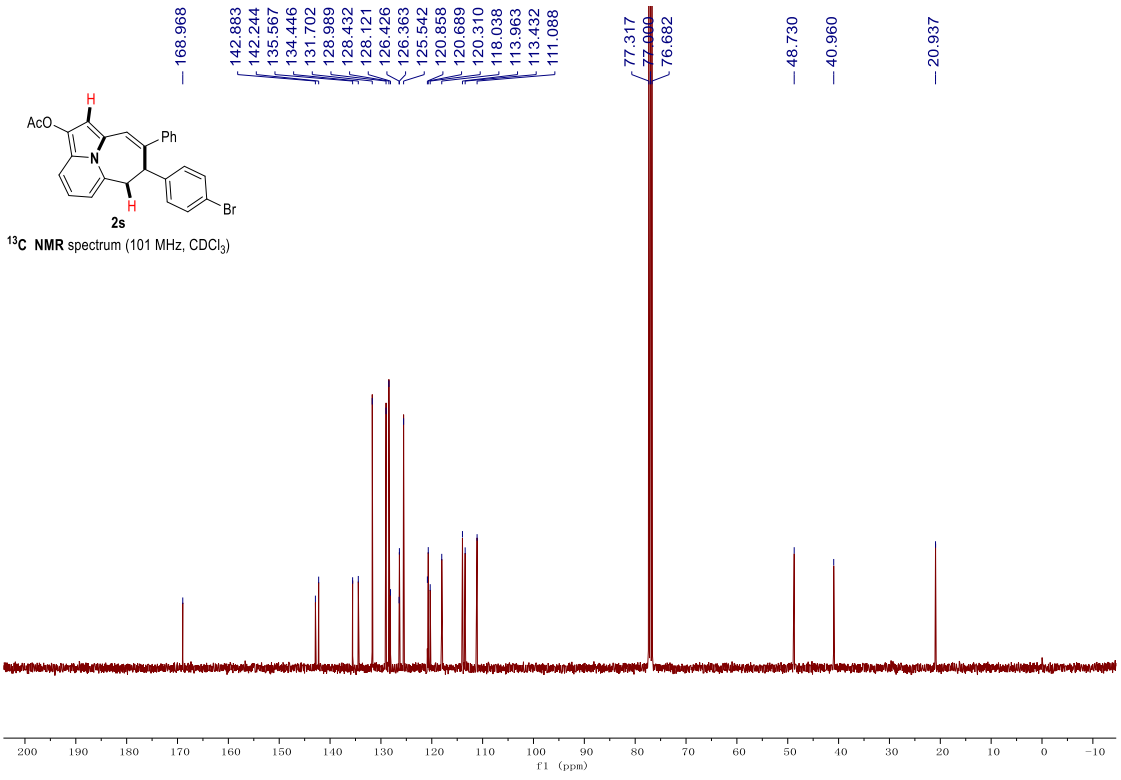
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



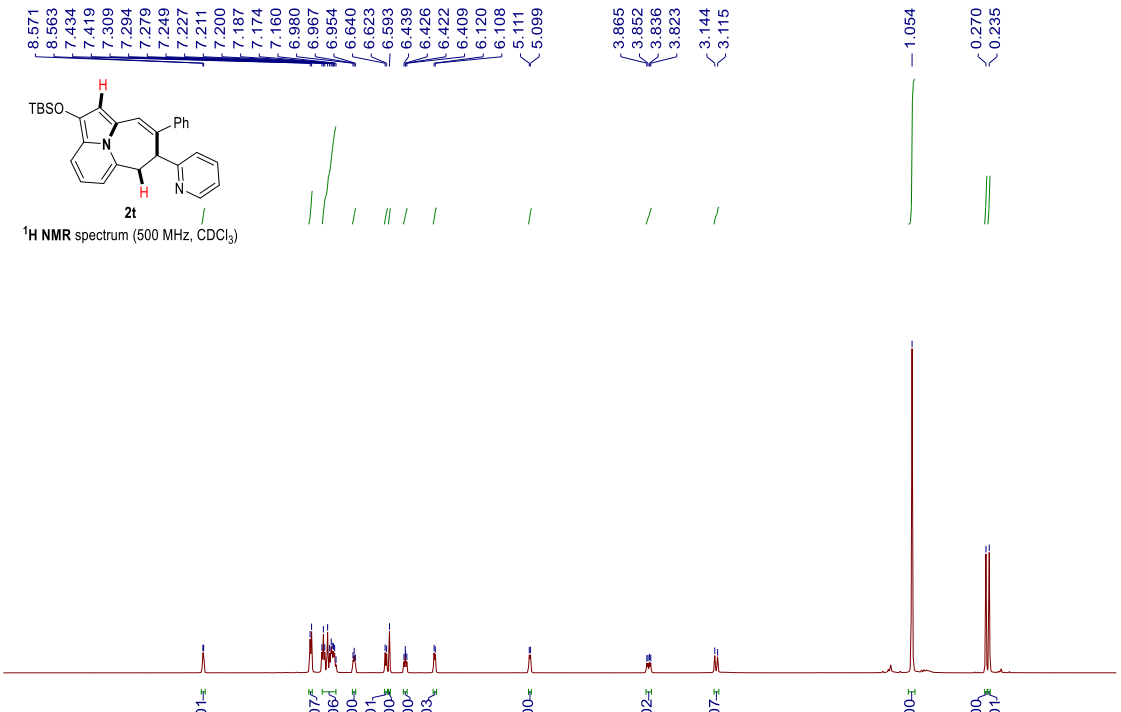


^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

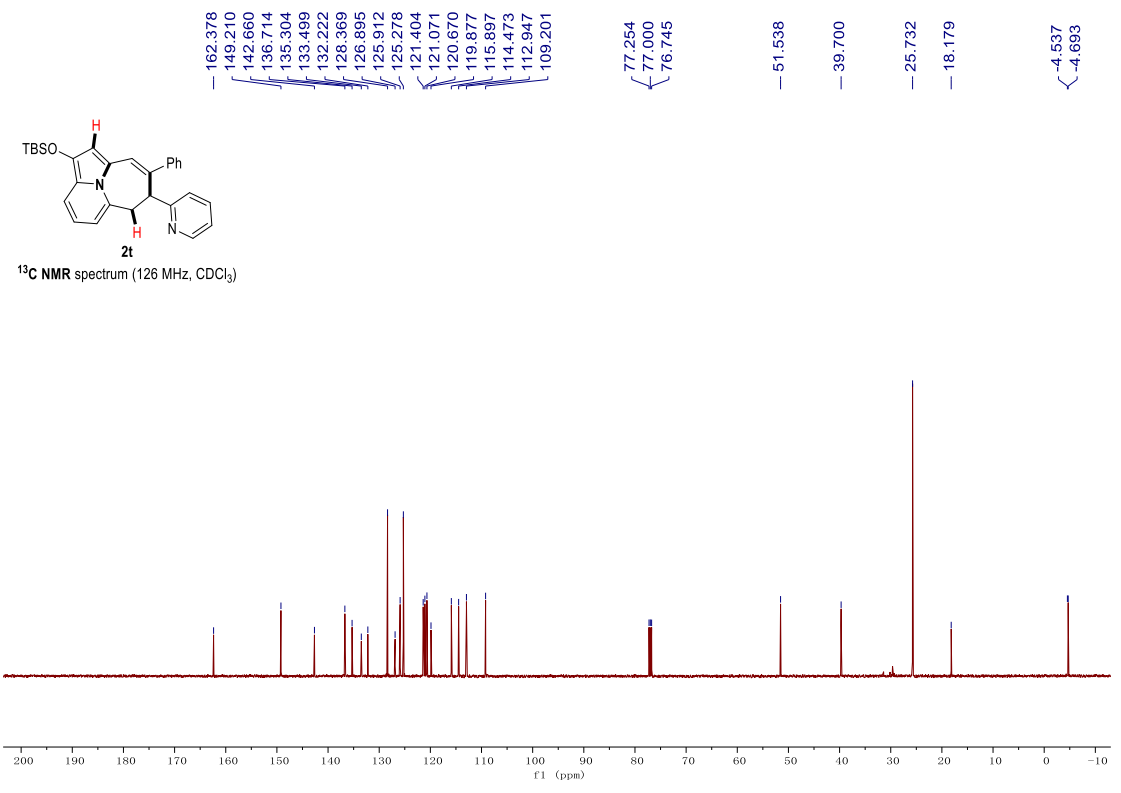




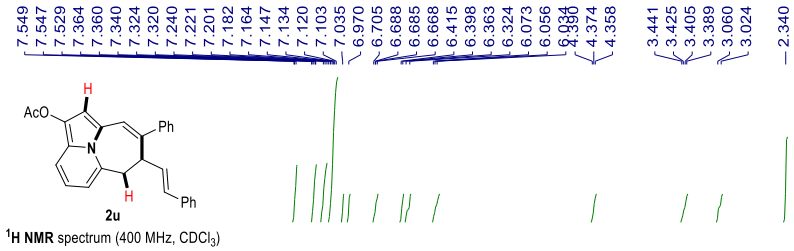
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



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

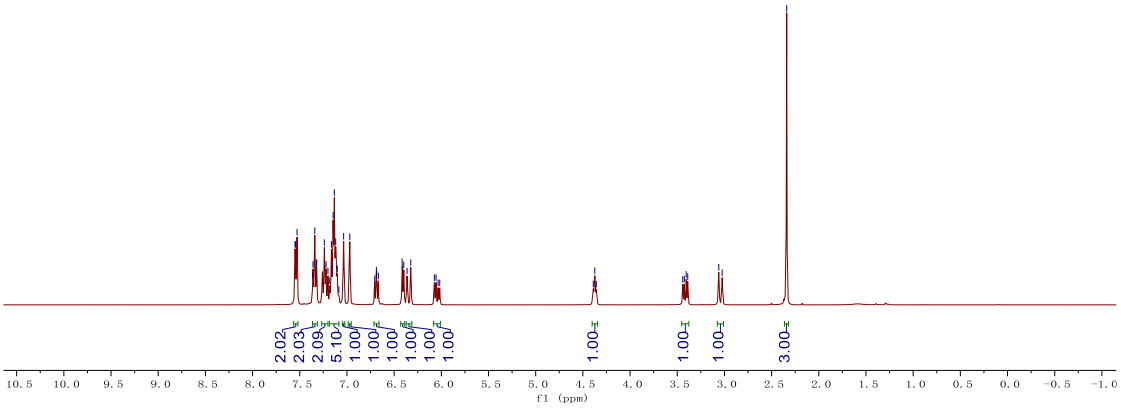


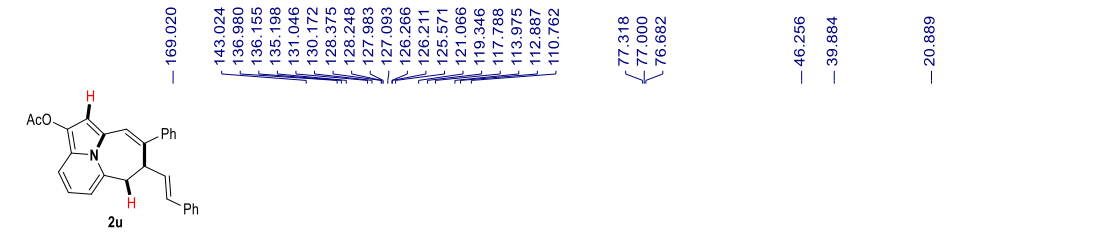
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



2u

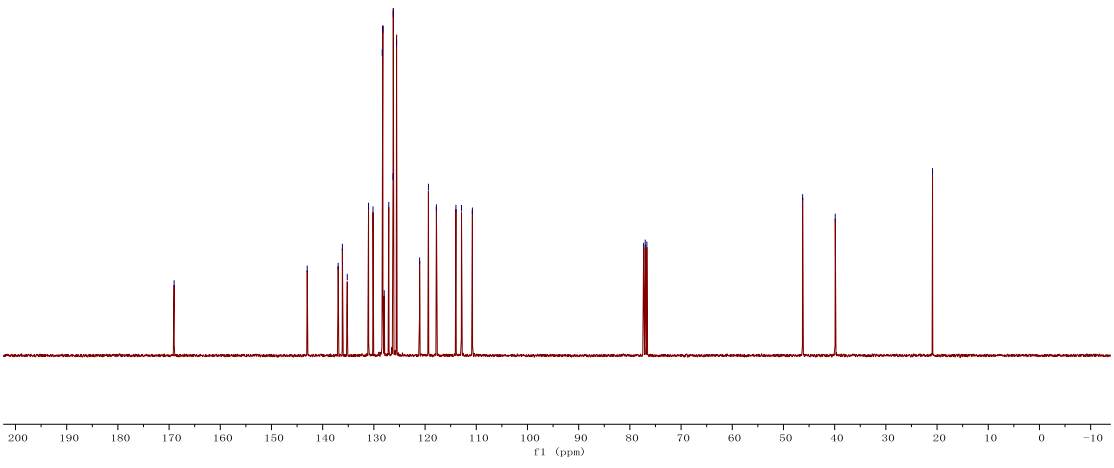
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

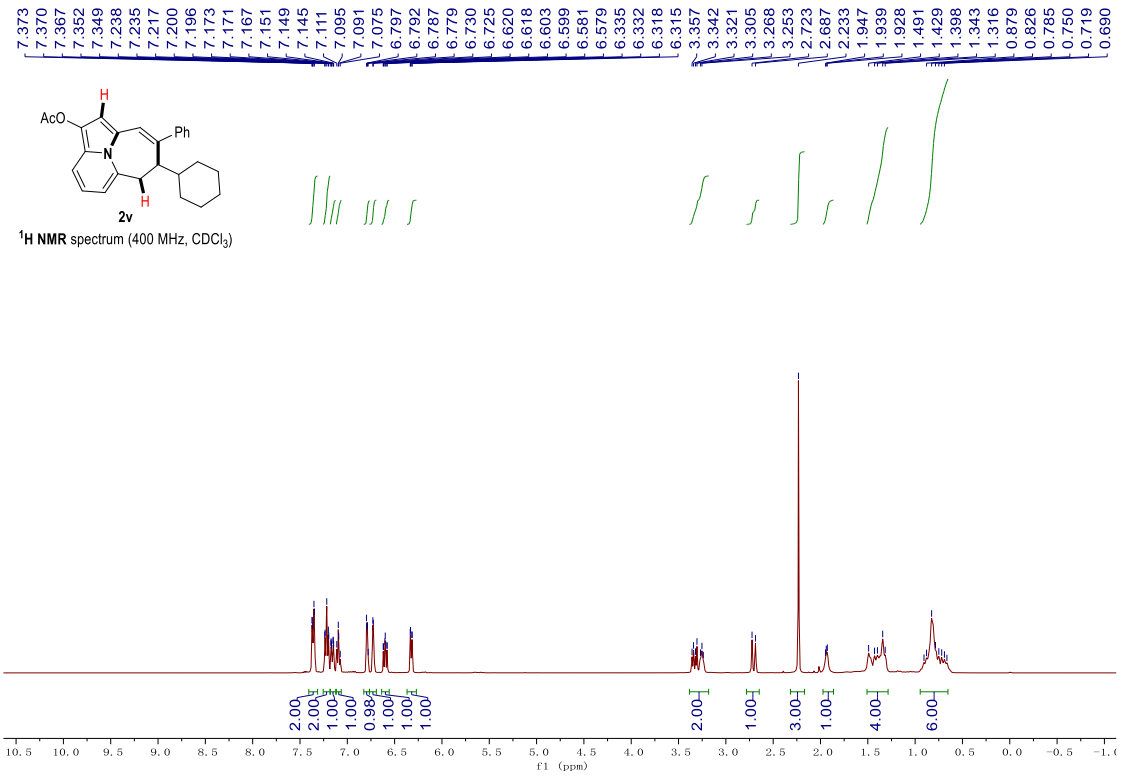




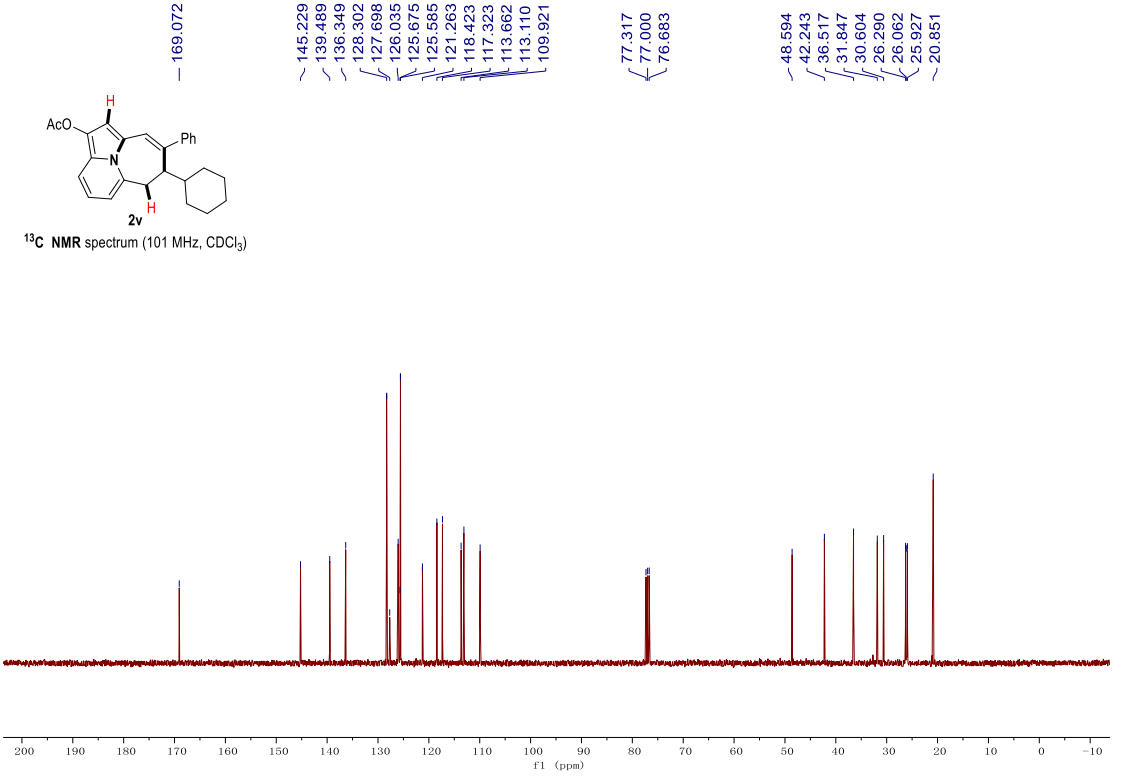
2u

^{13}**C NMR** spectrum (101MHz, $CDCl_3$)

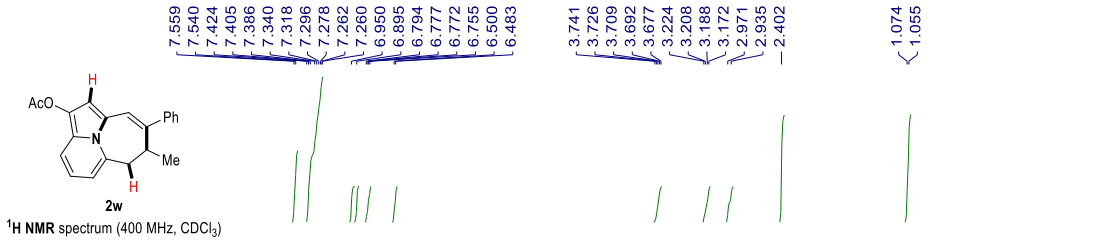




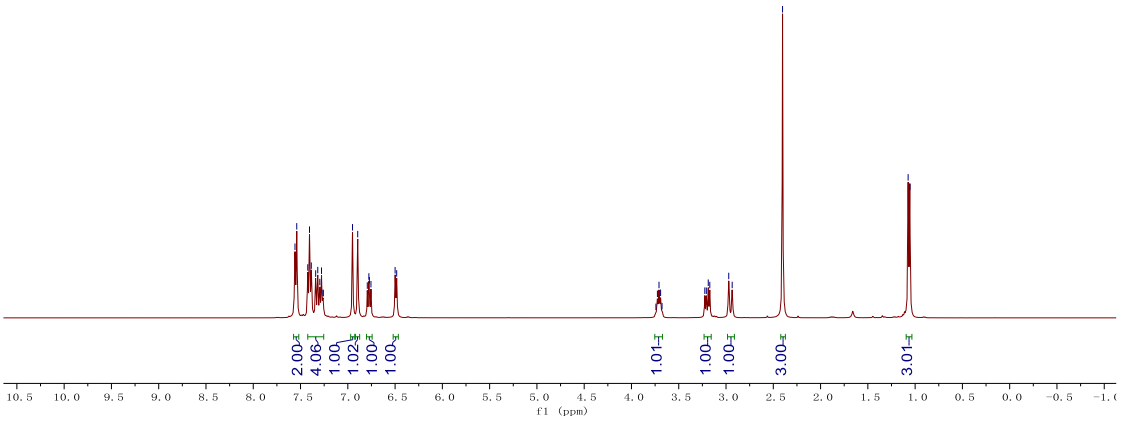
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

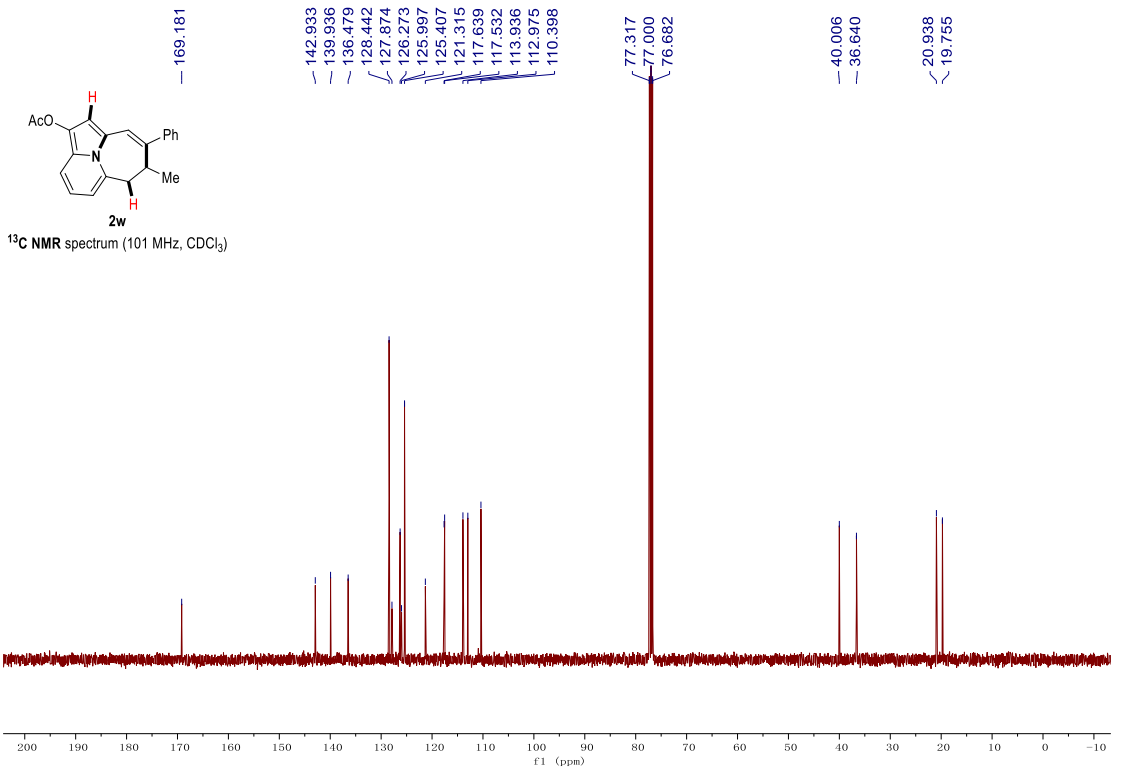


^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

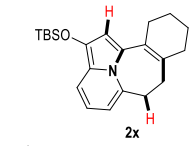


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



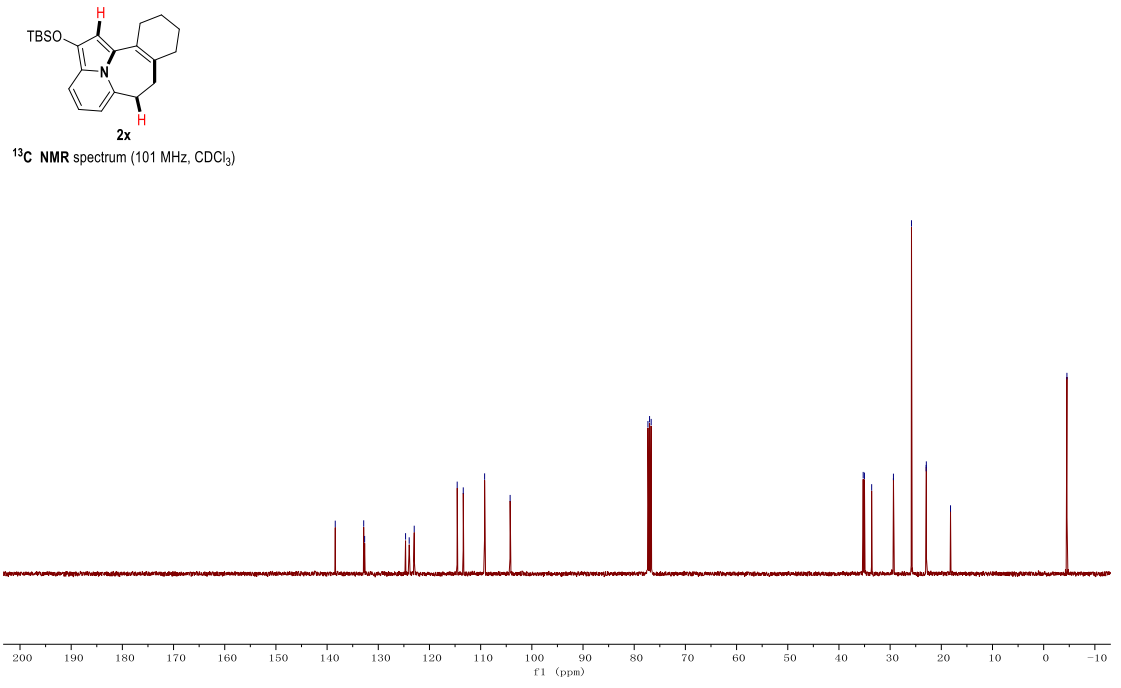


^{13}C NMR spectrum (101 MHz, $CDCl_3$)



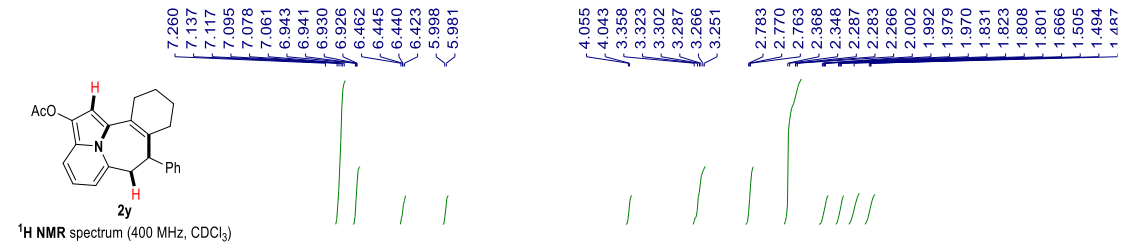
2x

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



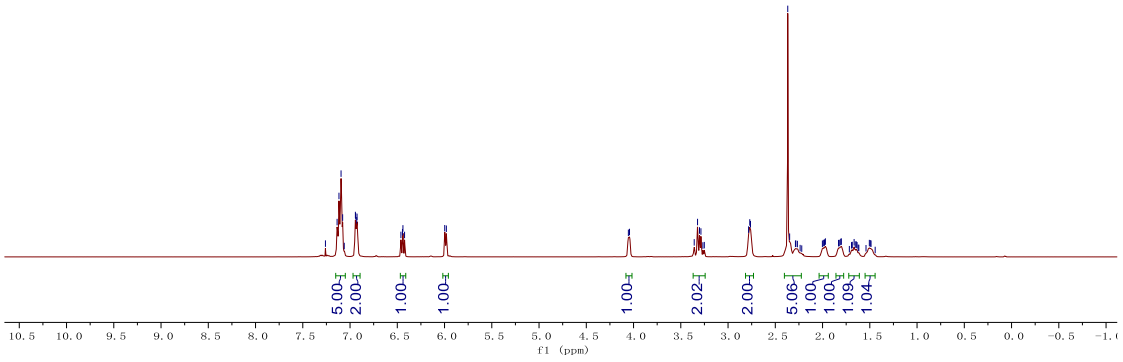
2x

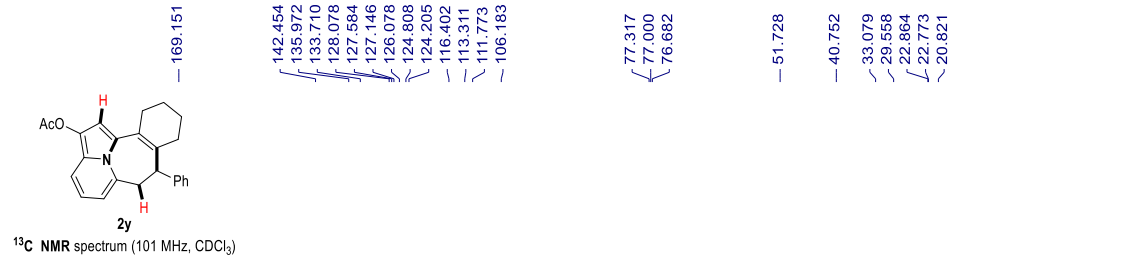
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



2y

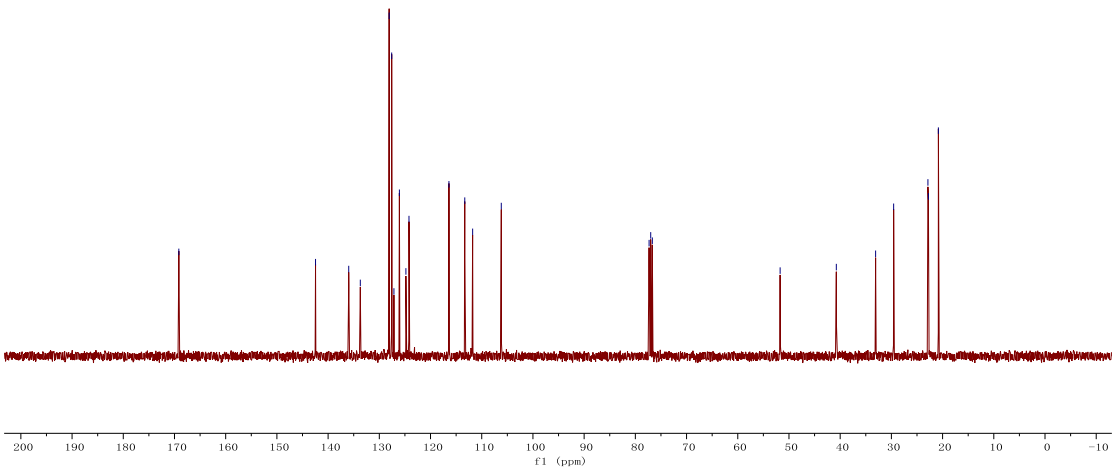
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

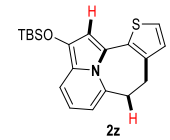




2y

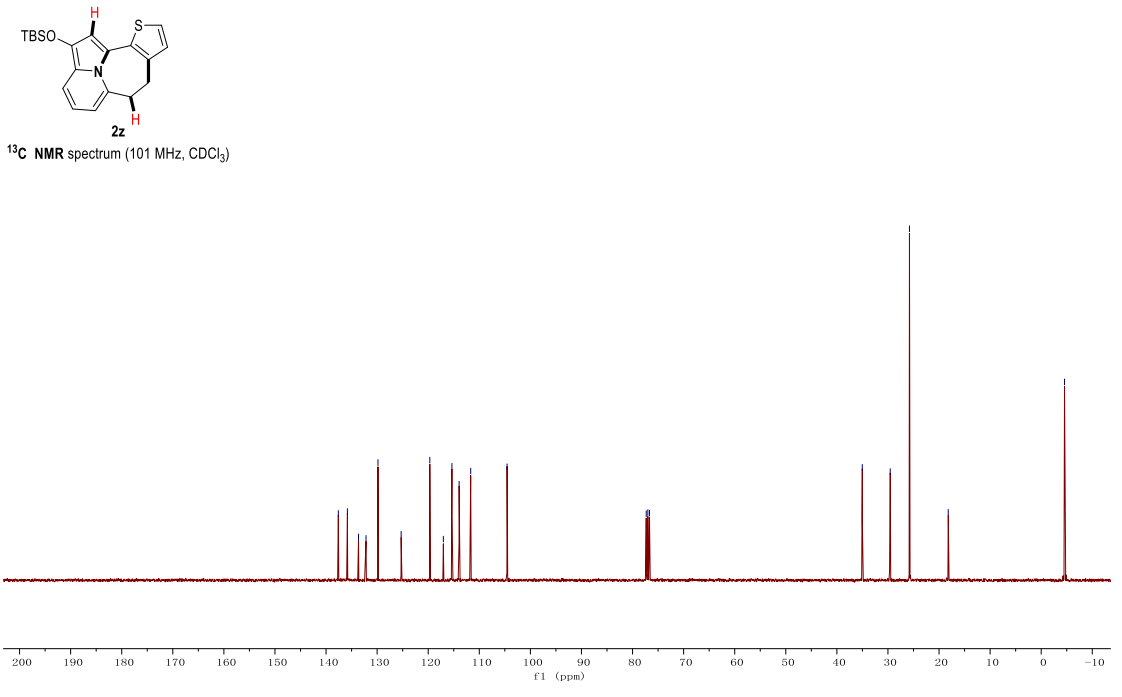
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





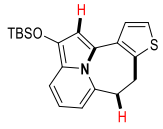
2z

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



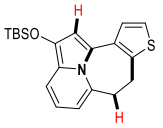
2z

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



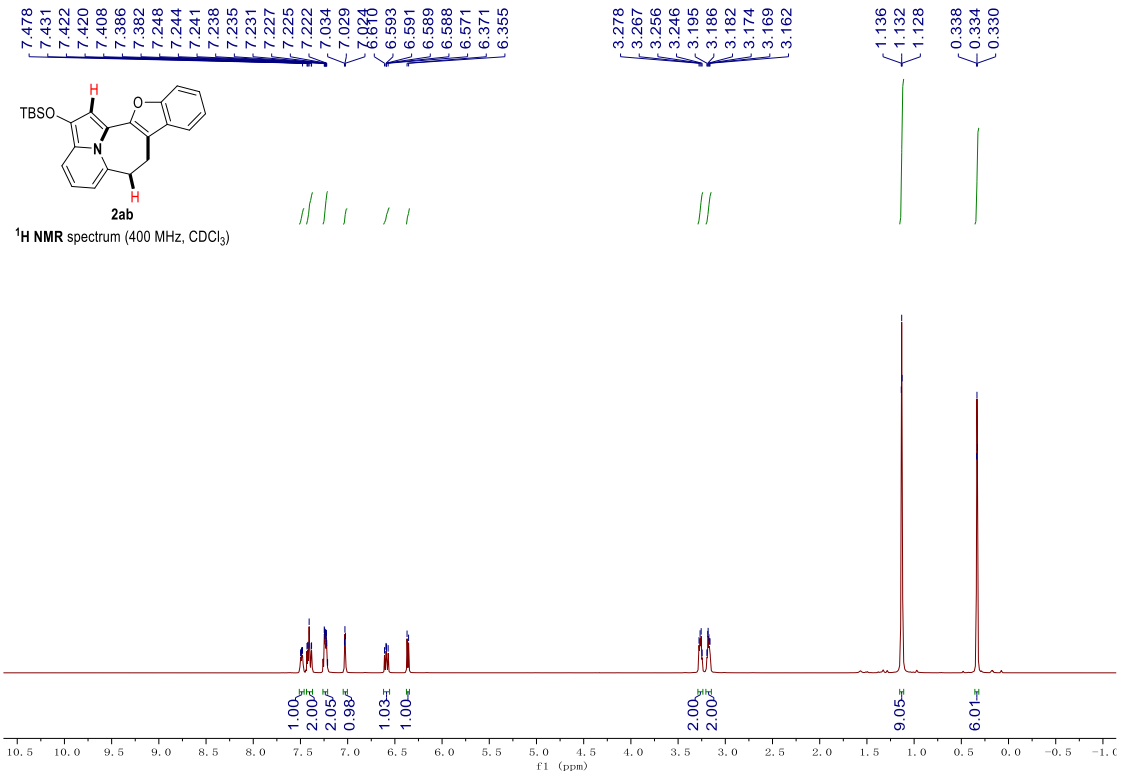
2aa

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

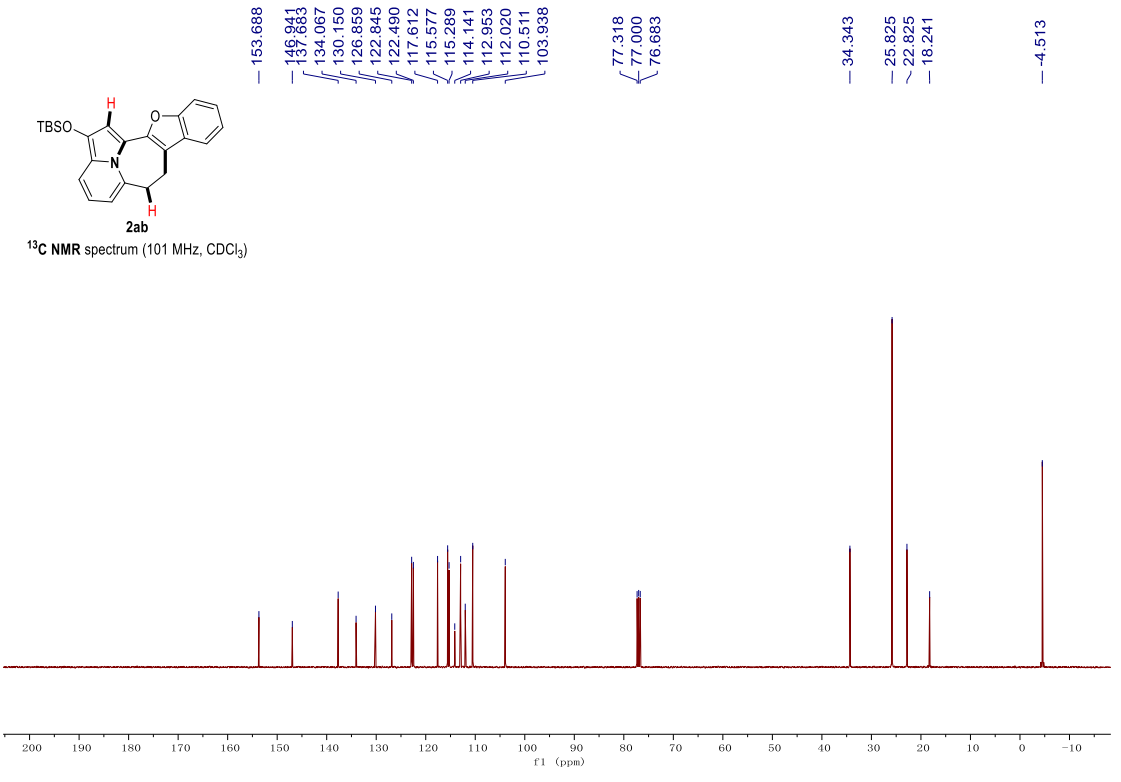


2aa

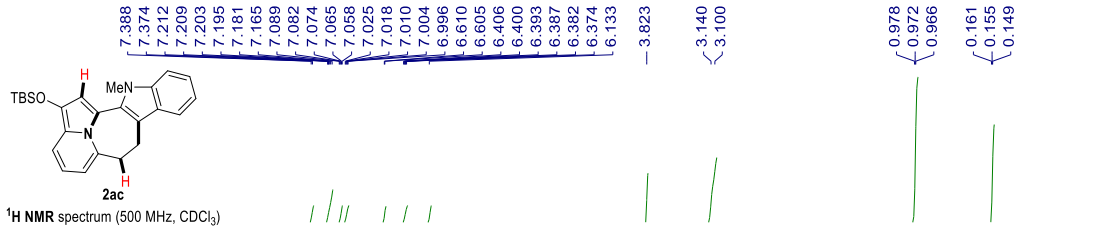
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



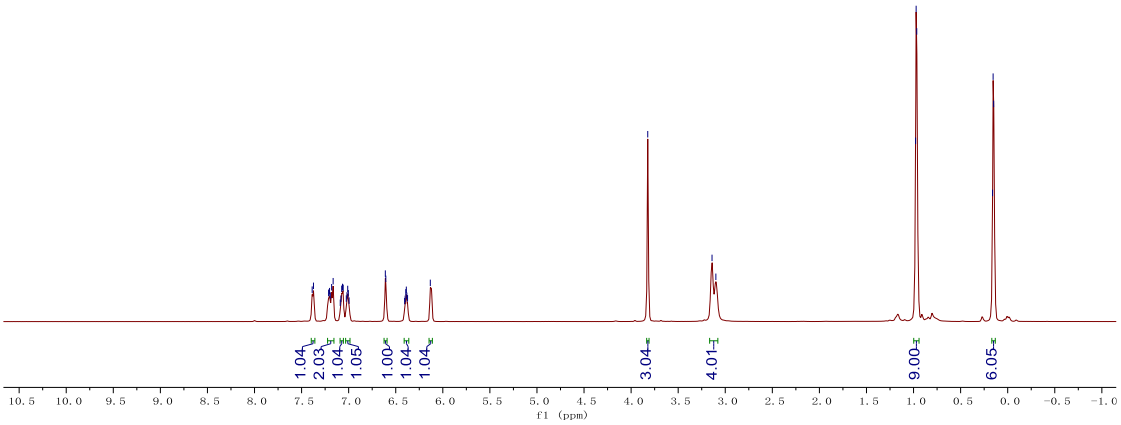
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

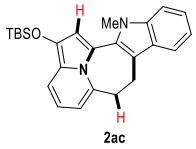


^{13}C NMR spectrum (101 MHz, $CDCl_3$)

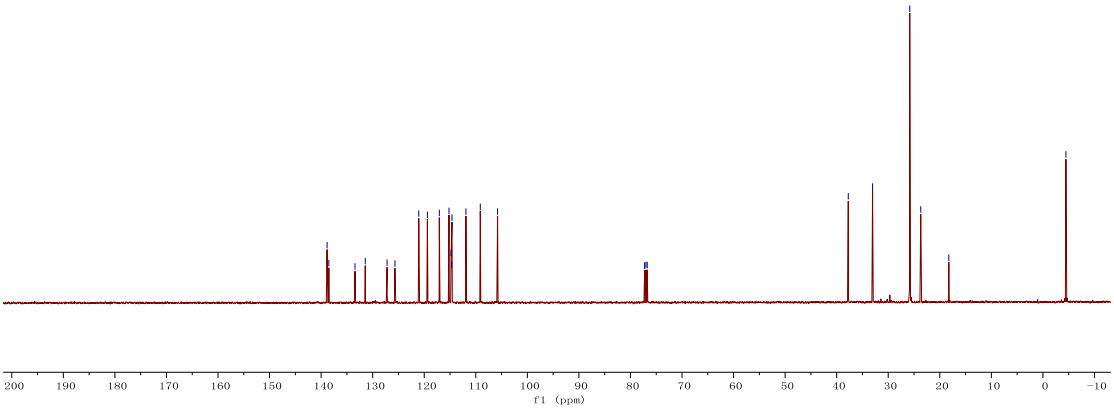


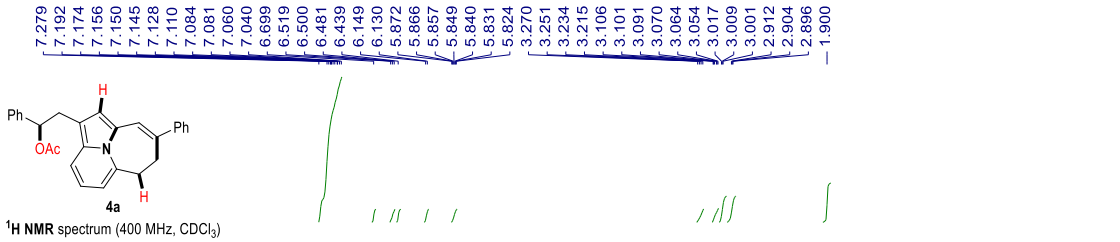
^{1}**H NMR** spectrum (500 MHz, $CDCl_3$)





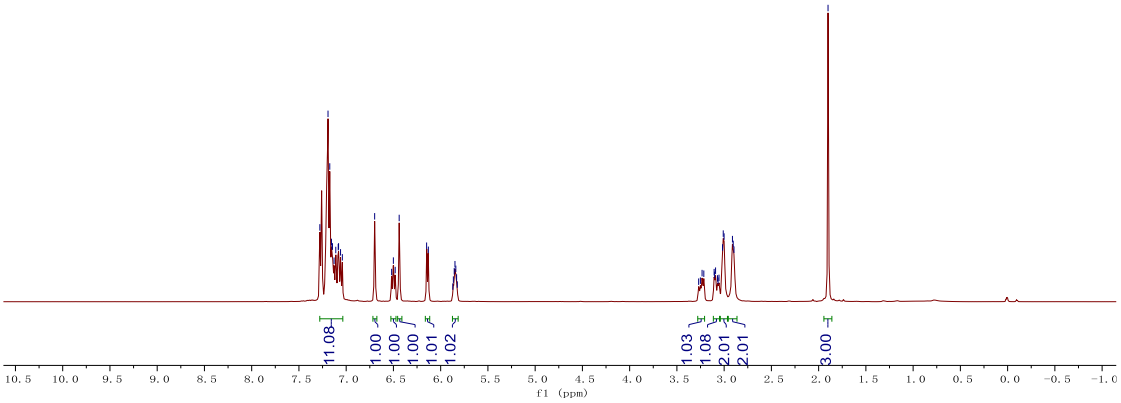
^{13}**C NMR** spectrum (126 MHz, $CDCl_3$)

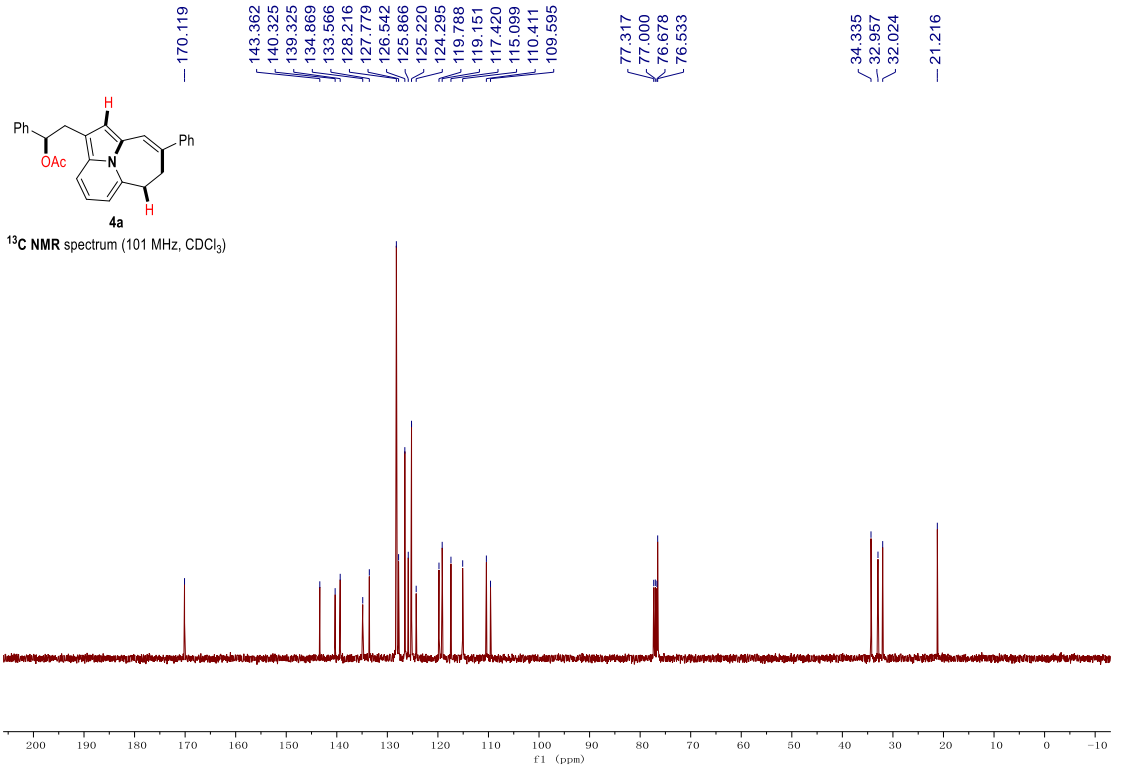




4a

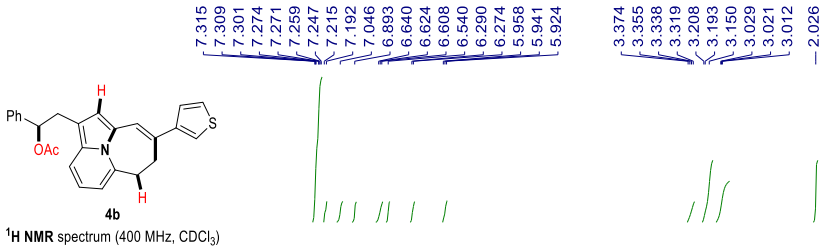
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





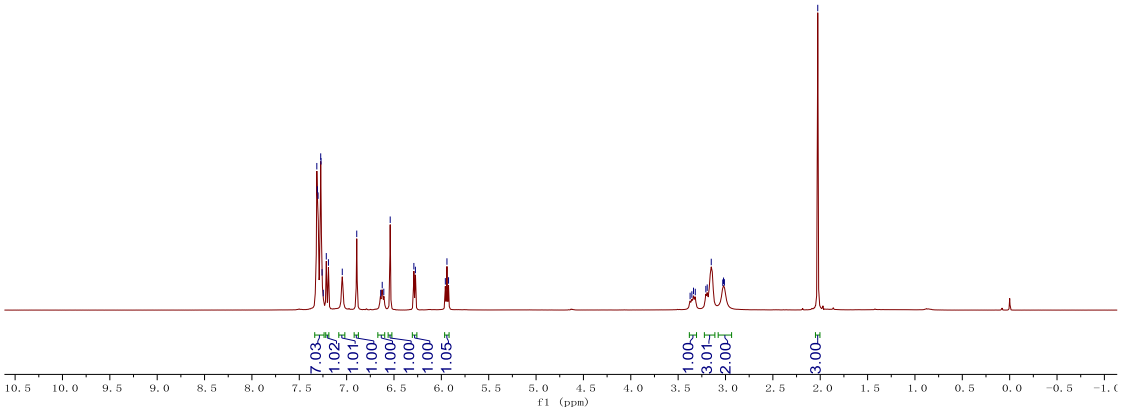
4a

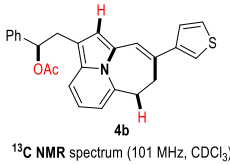
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



4b

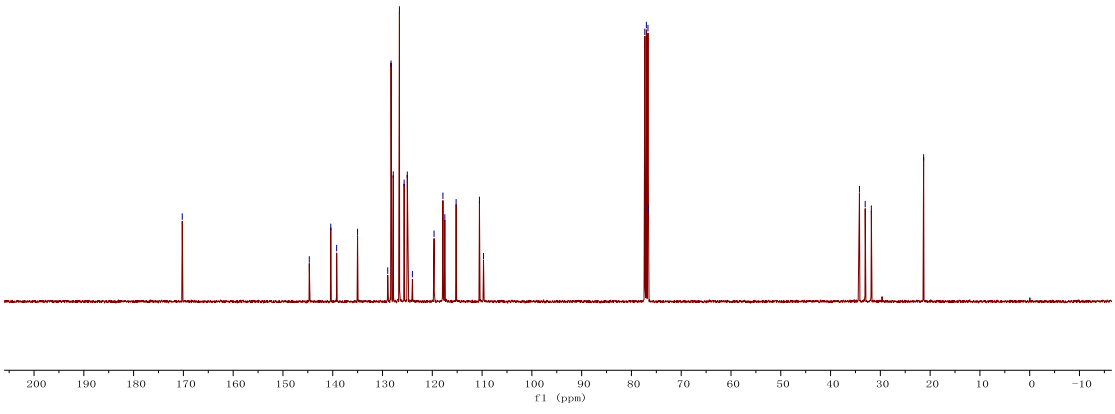
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

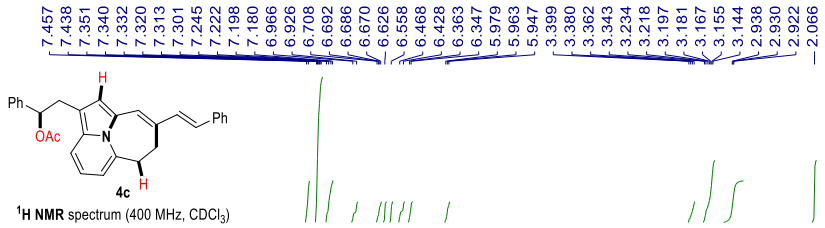




4b

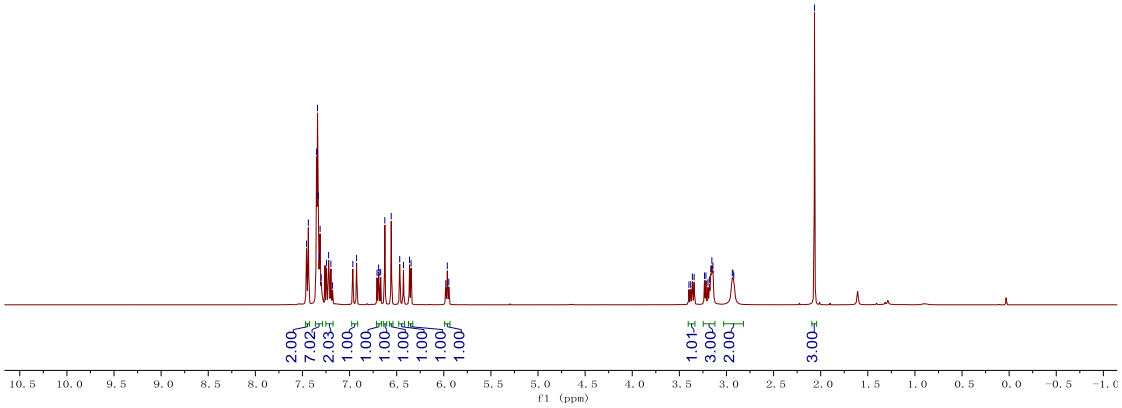
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

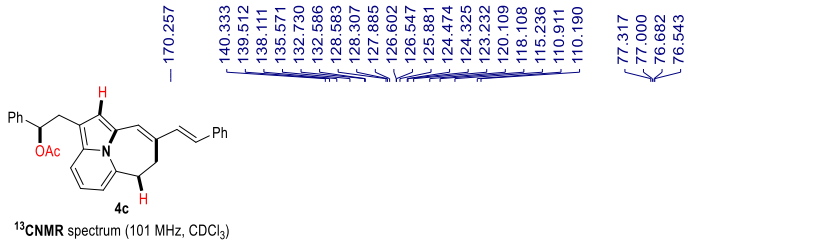




4c

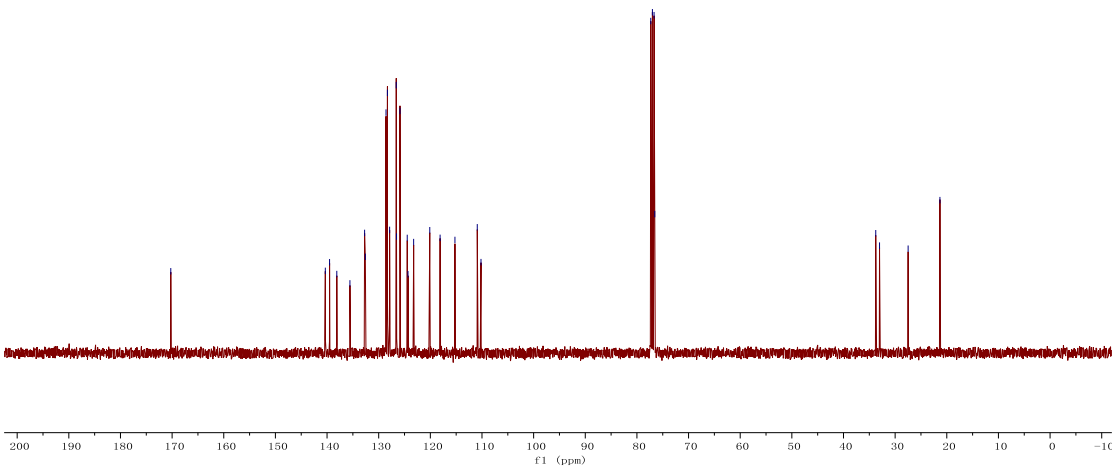
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

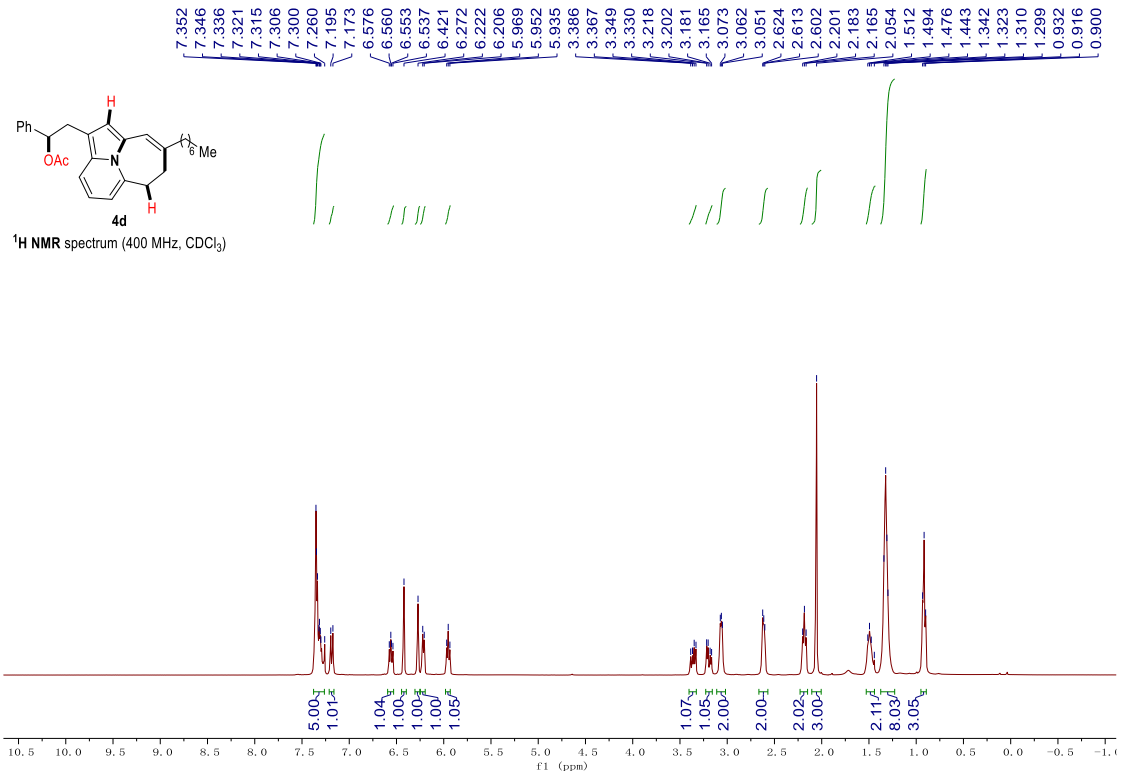




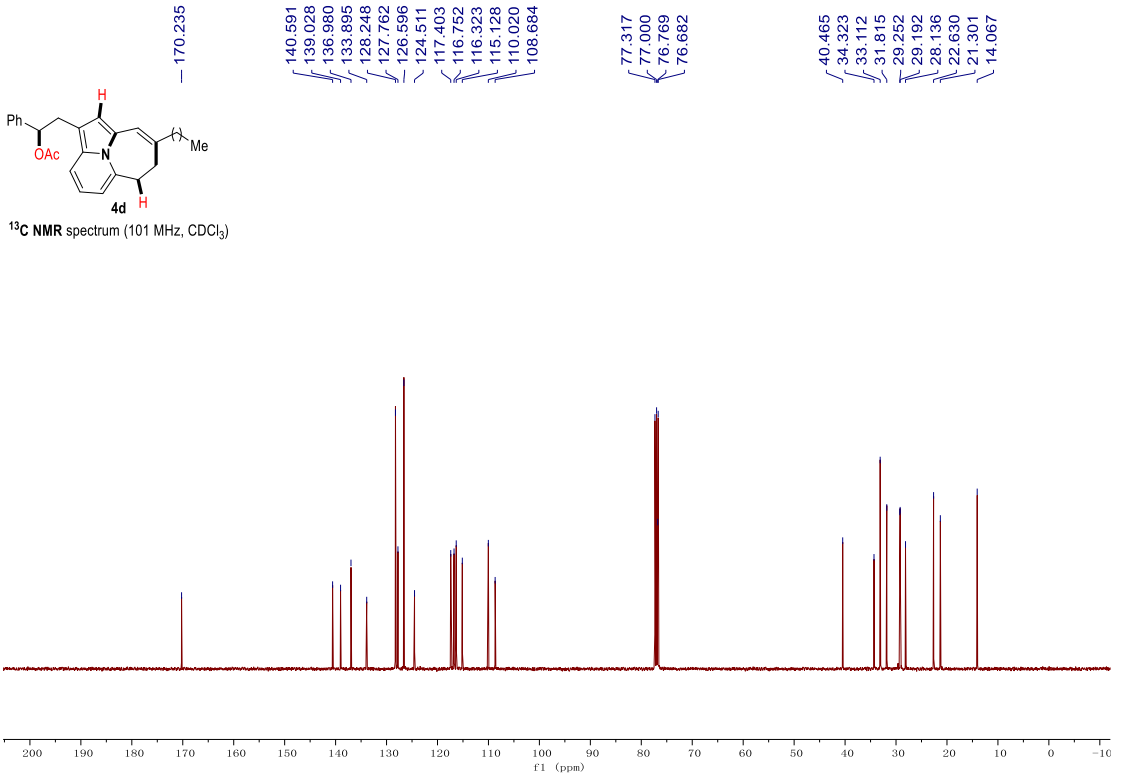
4c

^{13}CNMR spectrum (101 MHz, $CDCl_3$)

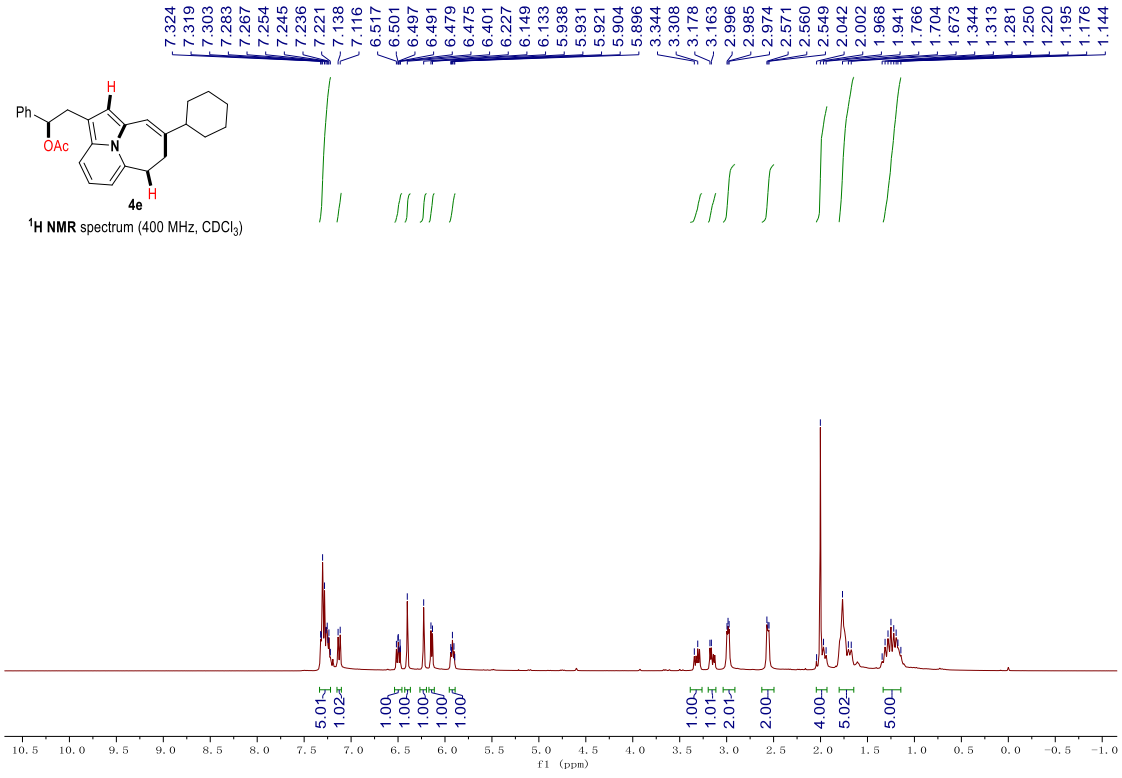




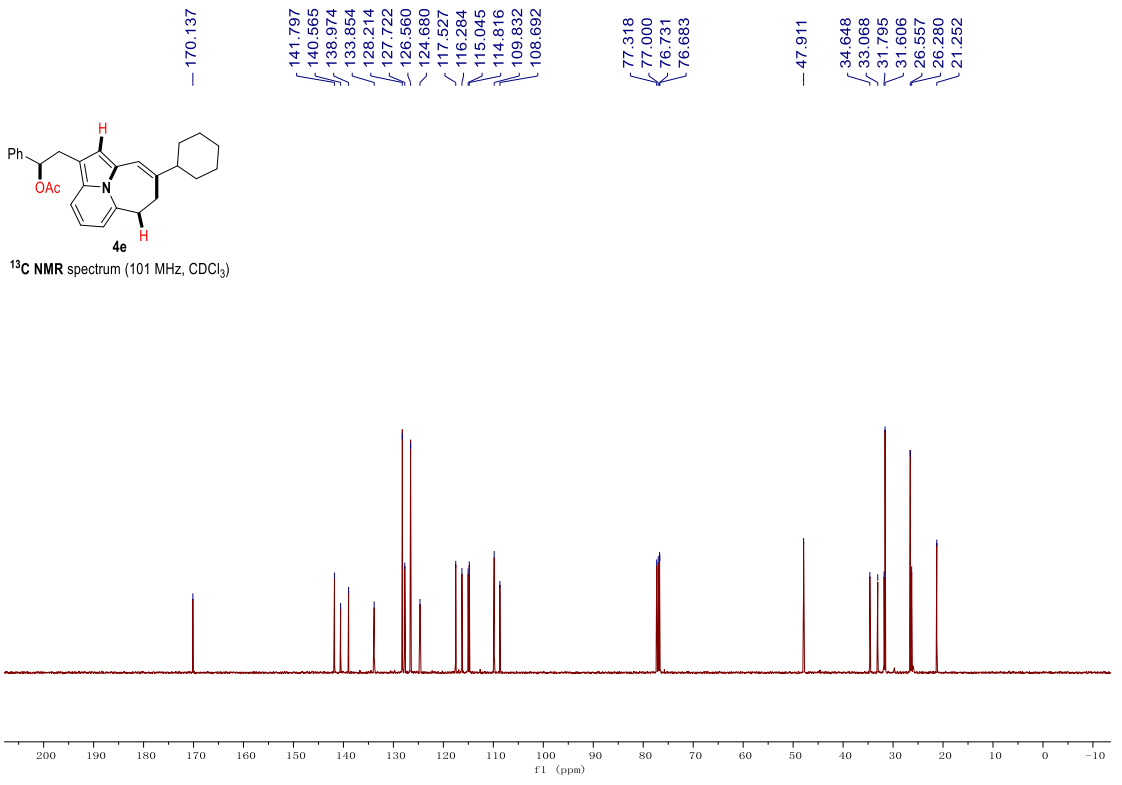
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



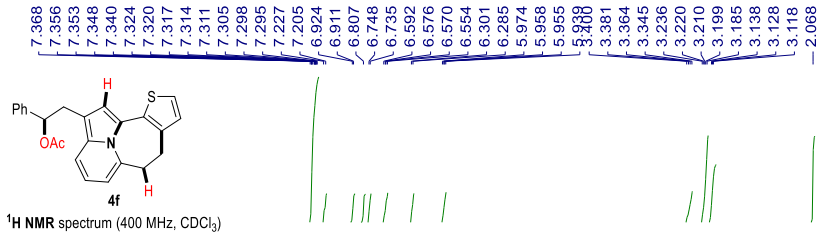
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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

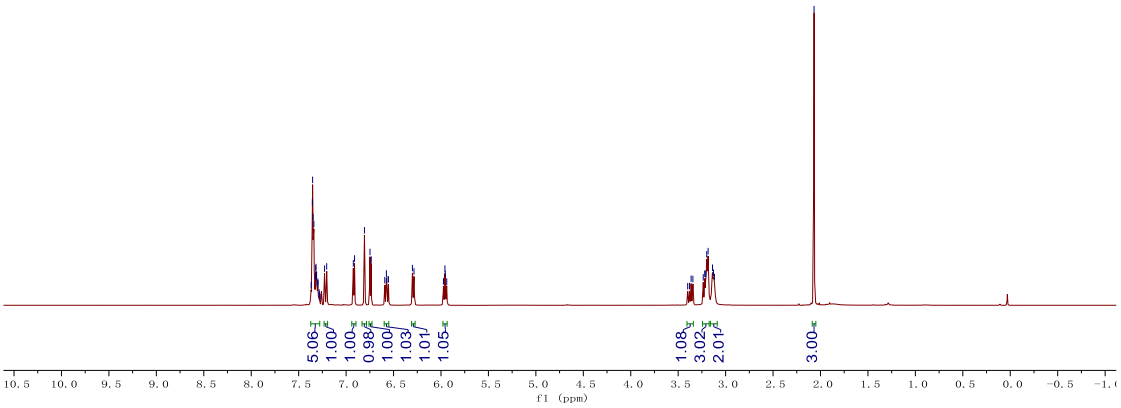


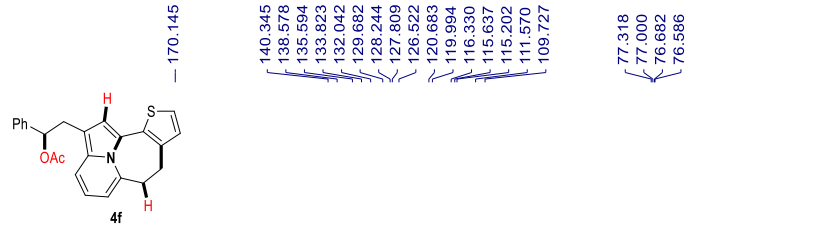
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



4f

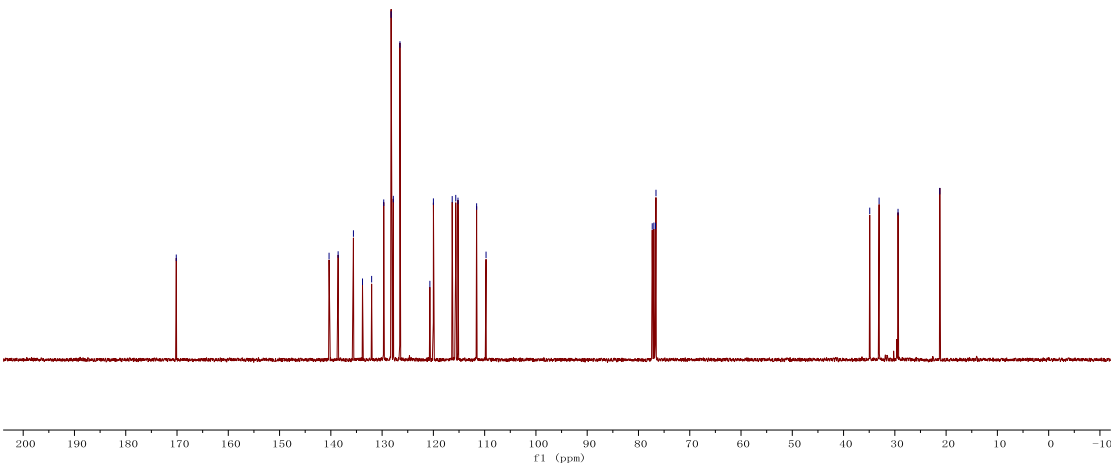
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

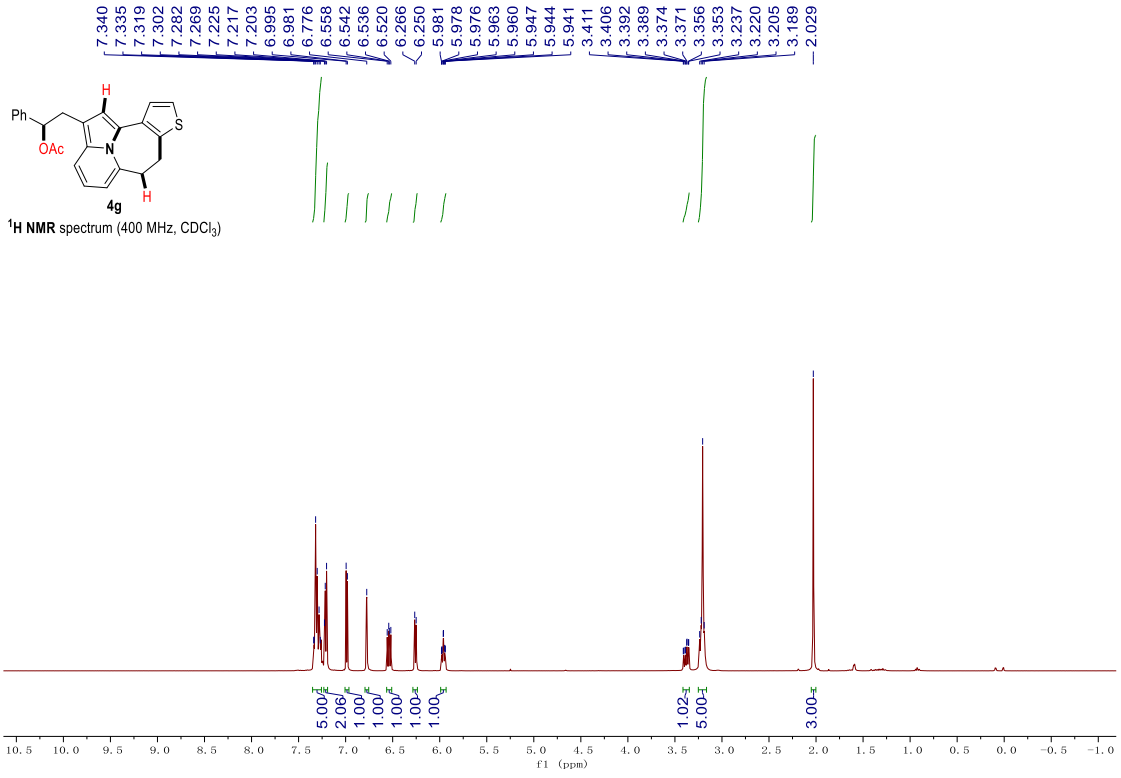




4f

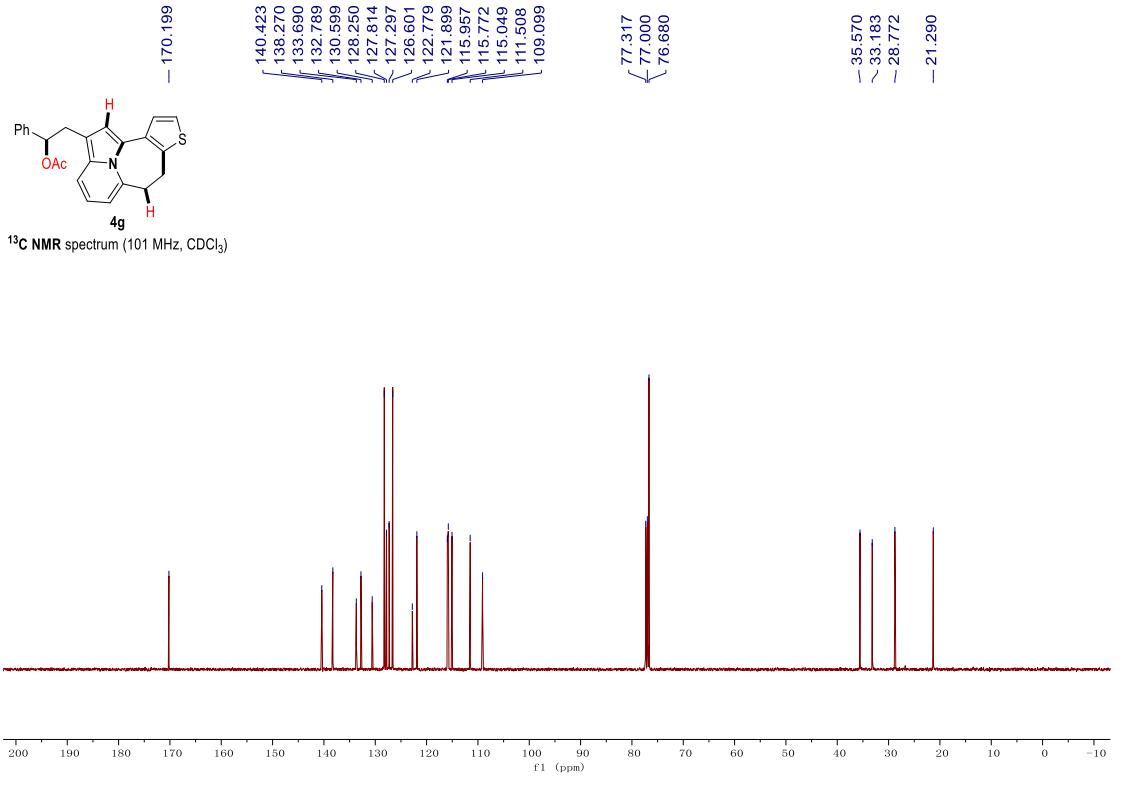
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





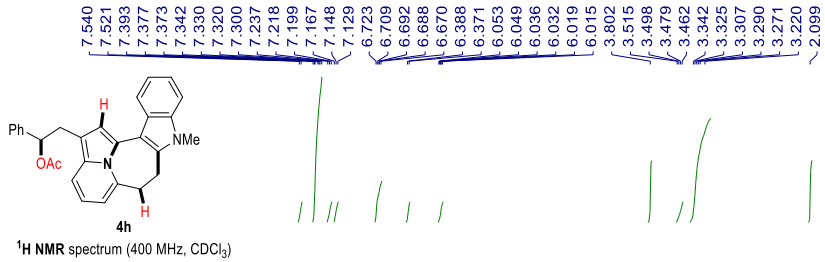
4g

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



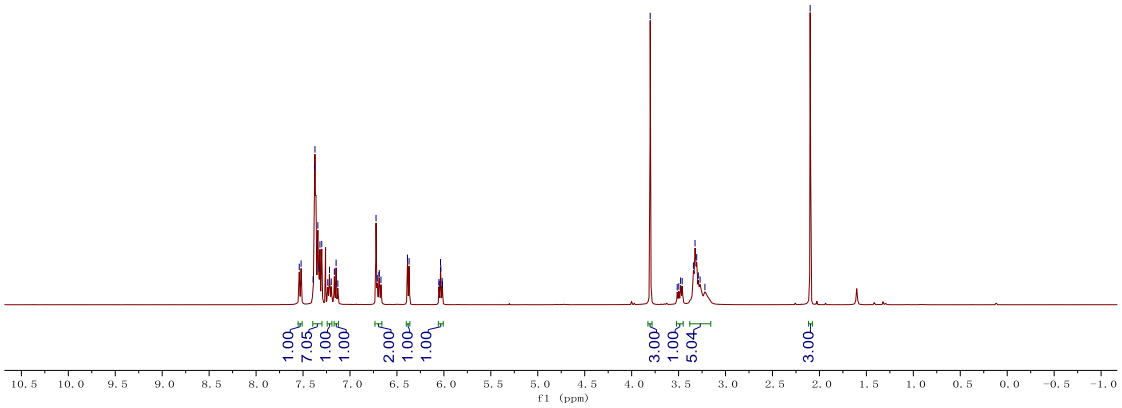
4g

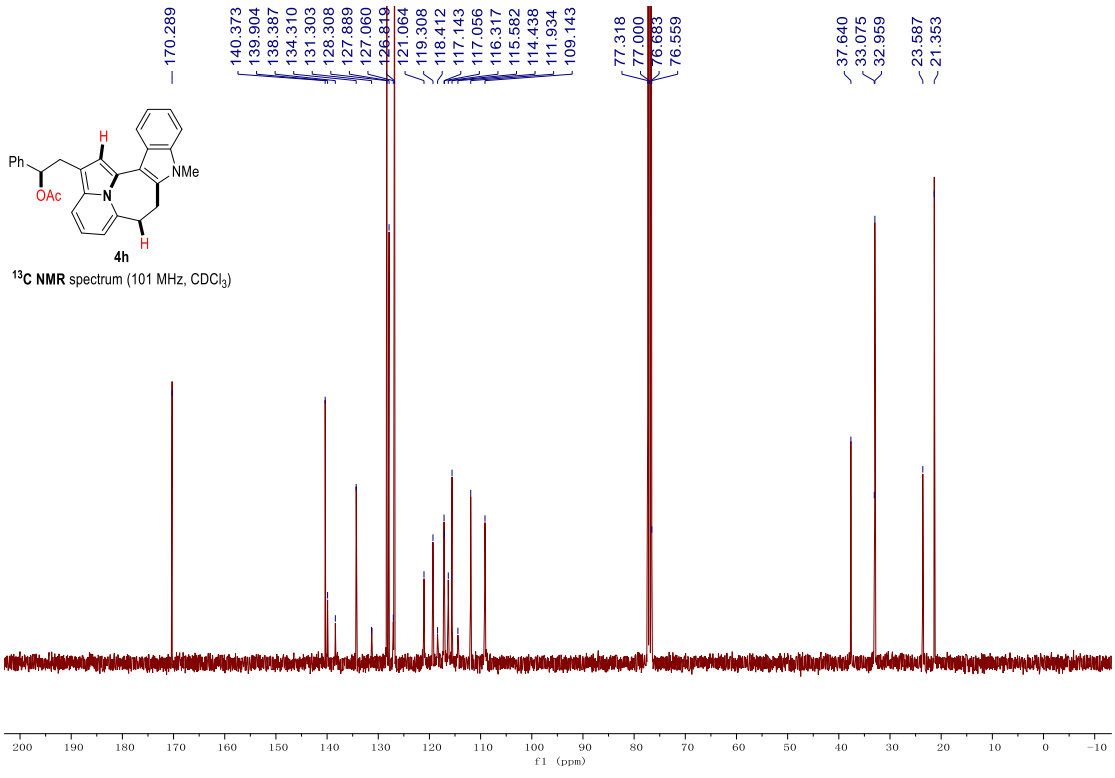
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



4h

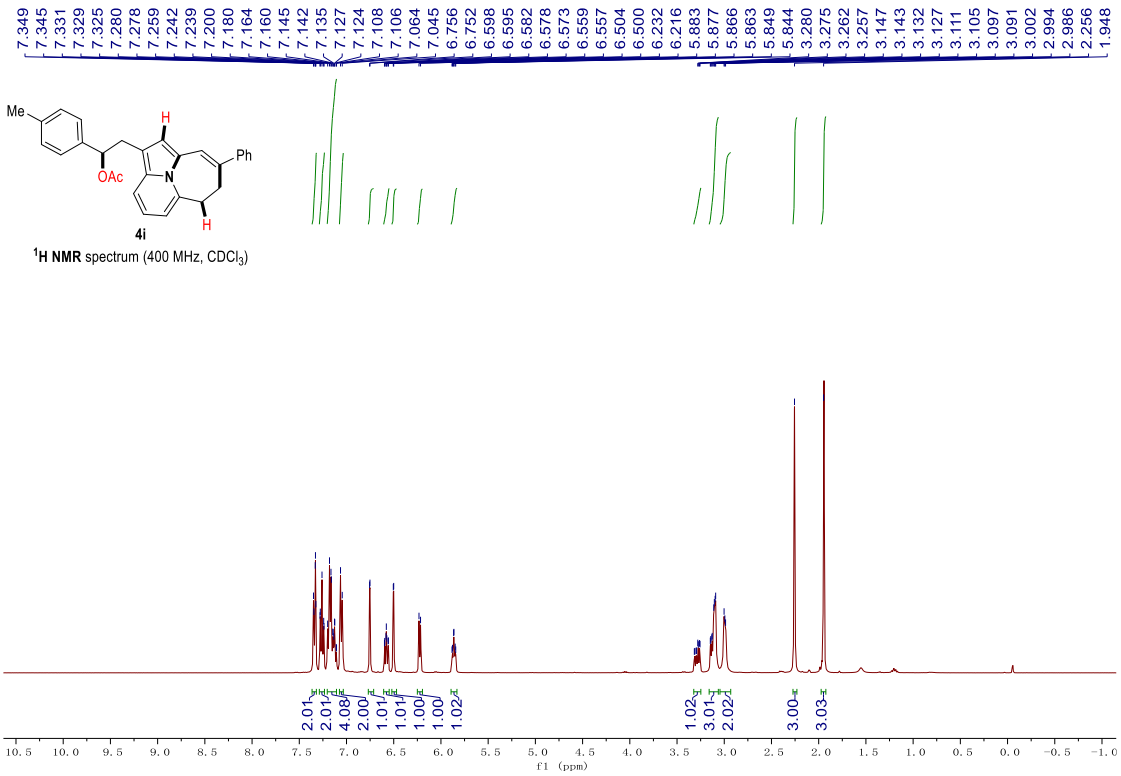
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





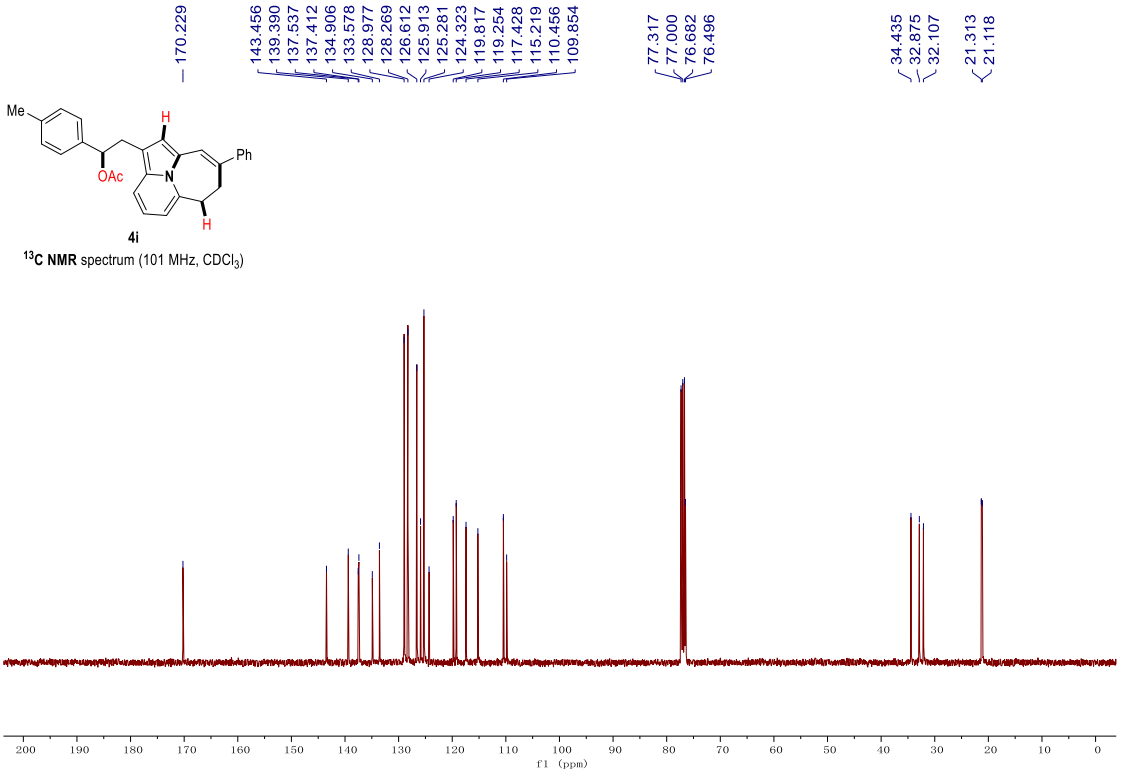
4h

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



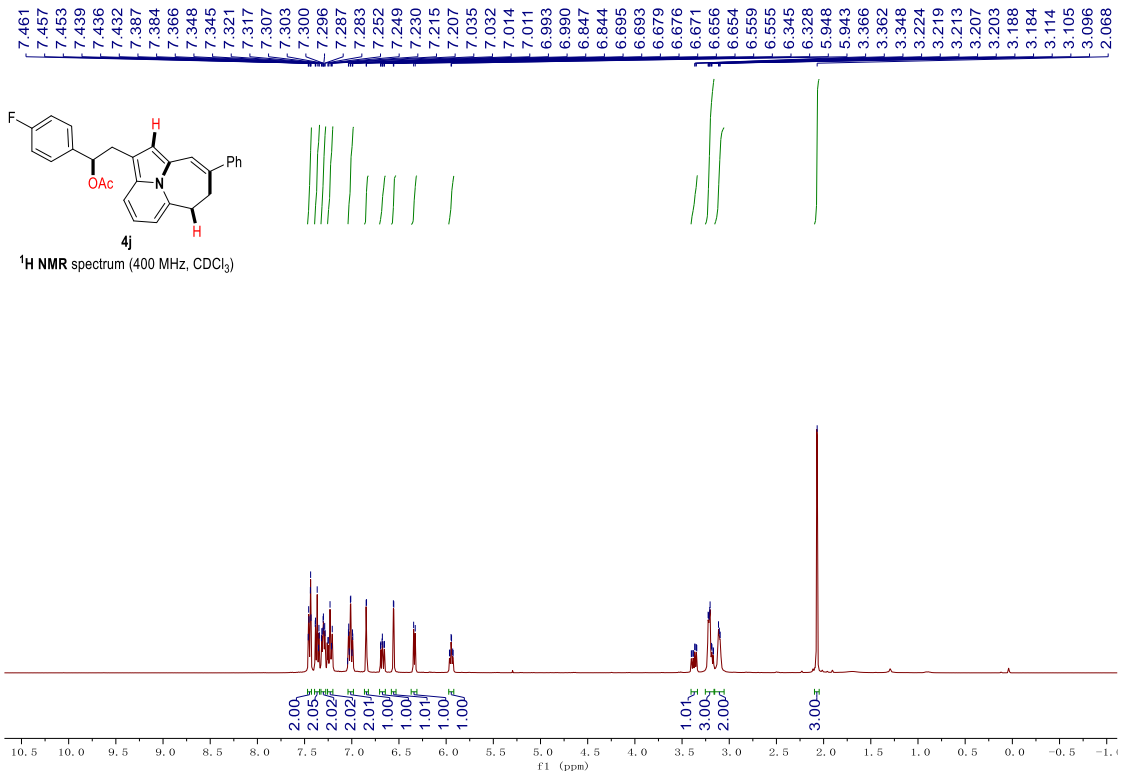
4i

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

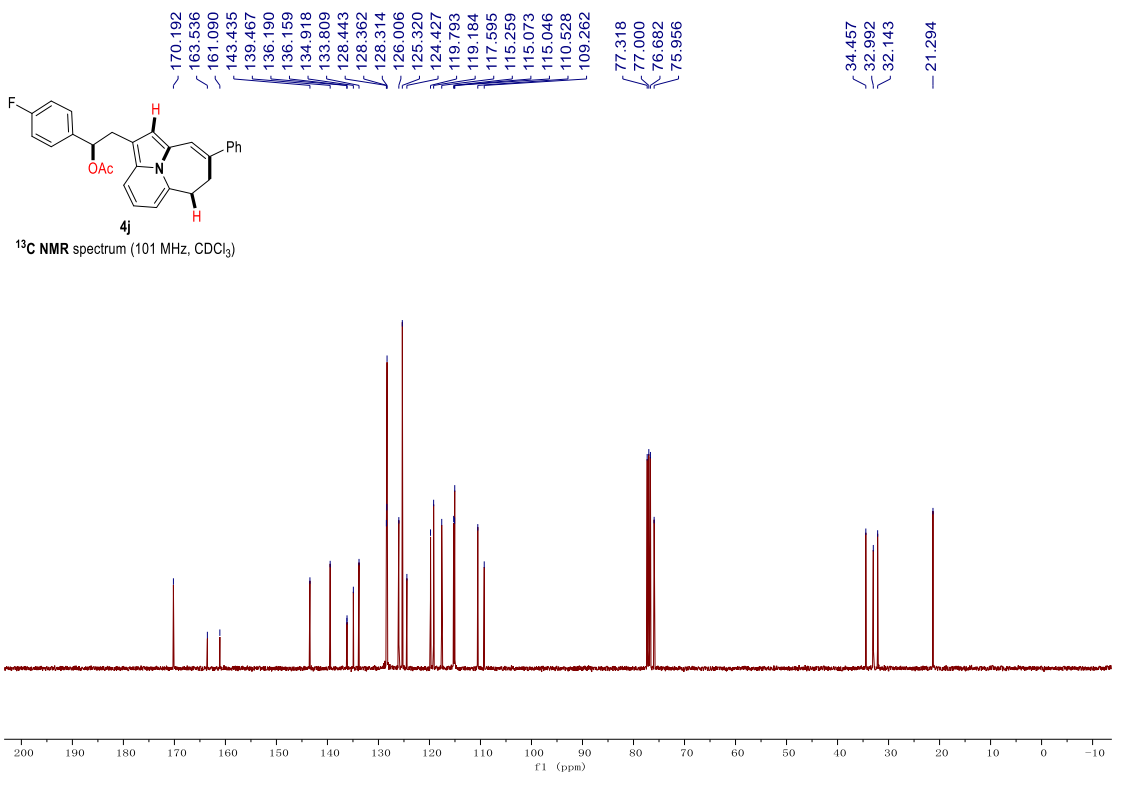


4i

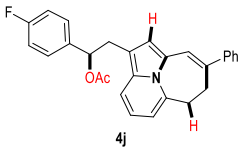
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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

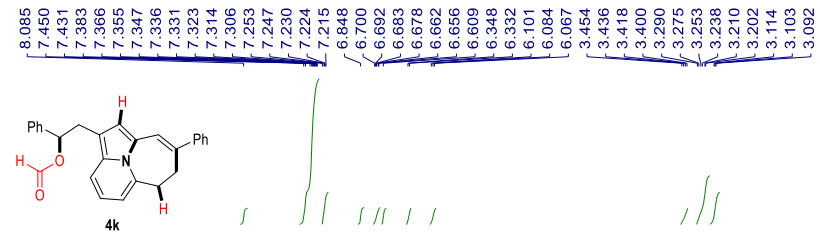


^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



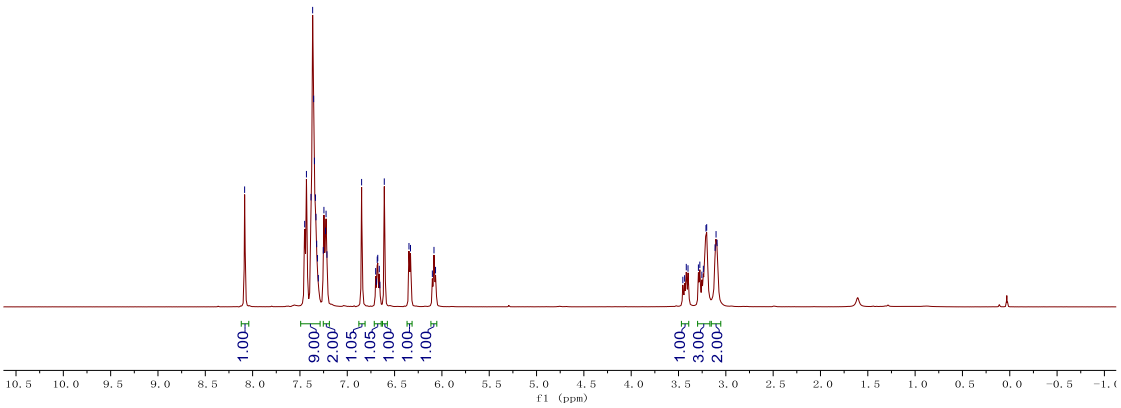
4j

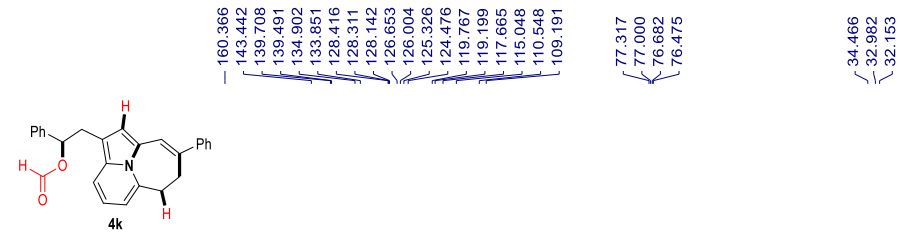
^{19}F NMR spectrum (377 MHz, $CDCl_3$)



4k

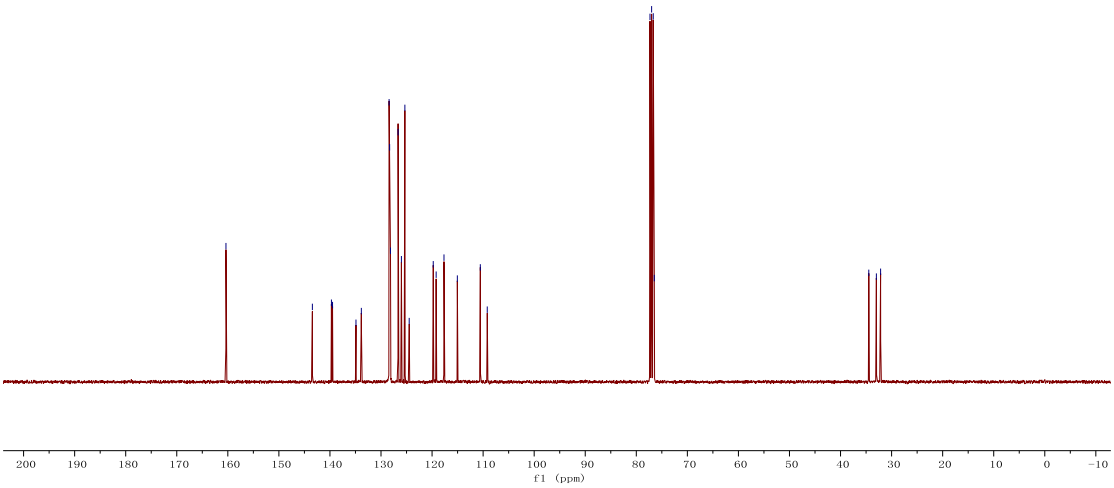
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

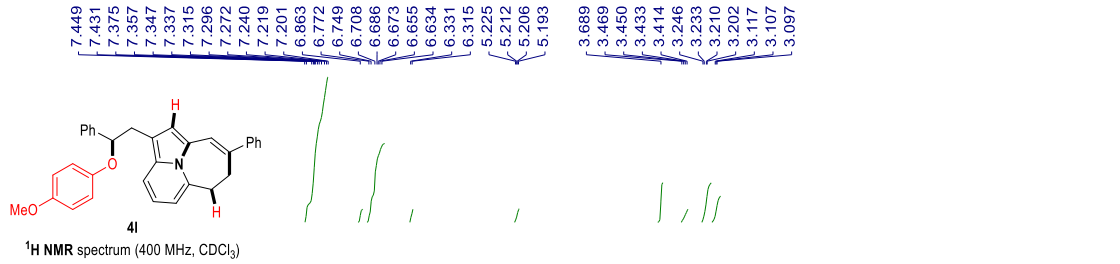




4k

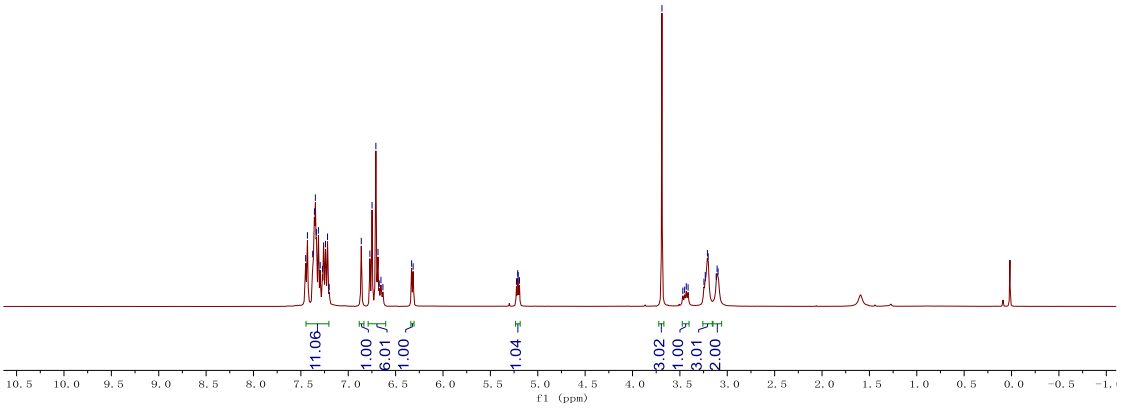
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

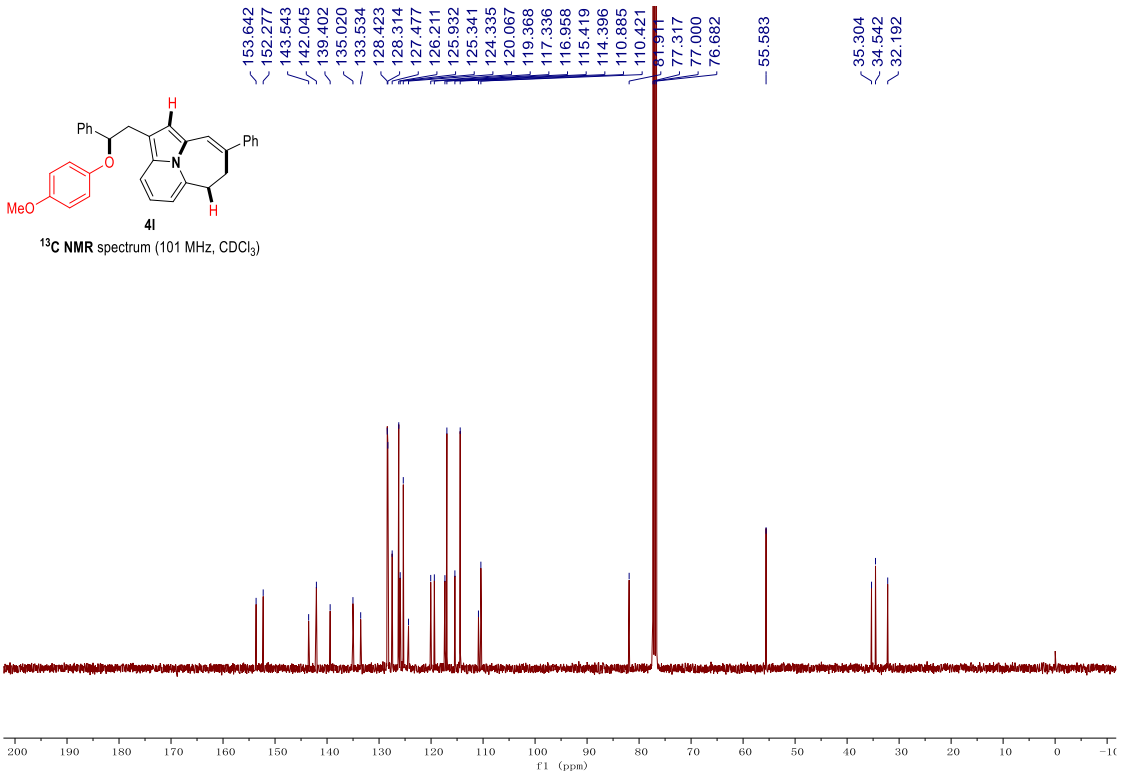




4l

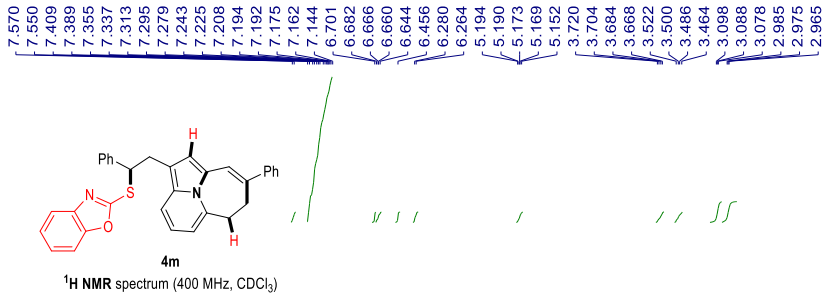
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)





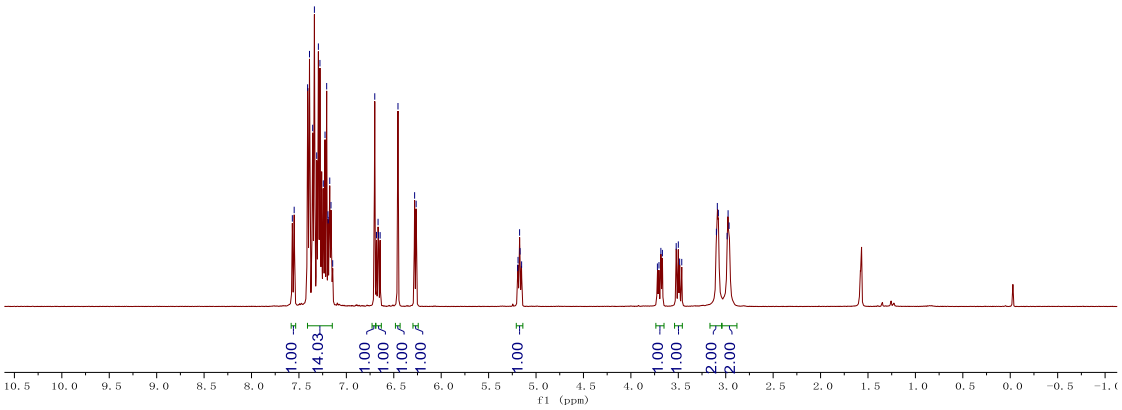
4l

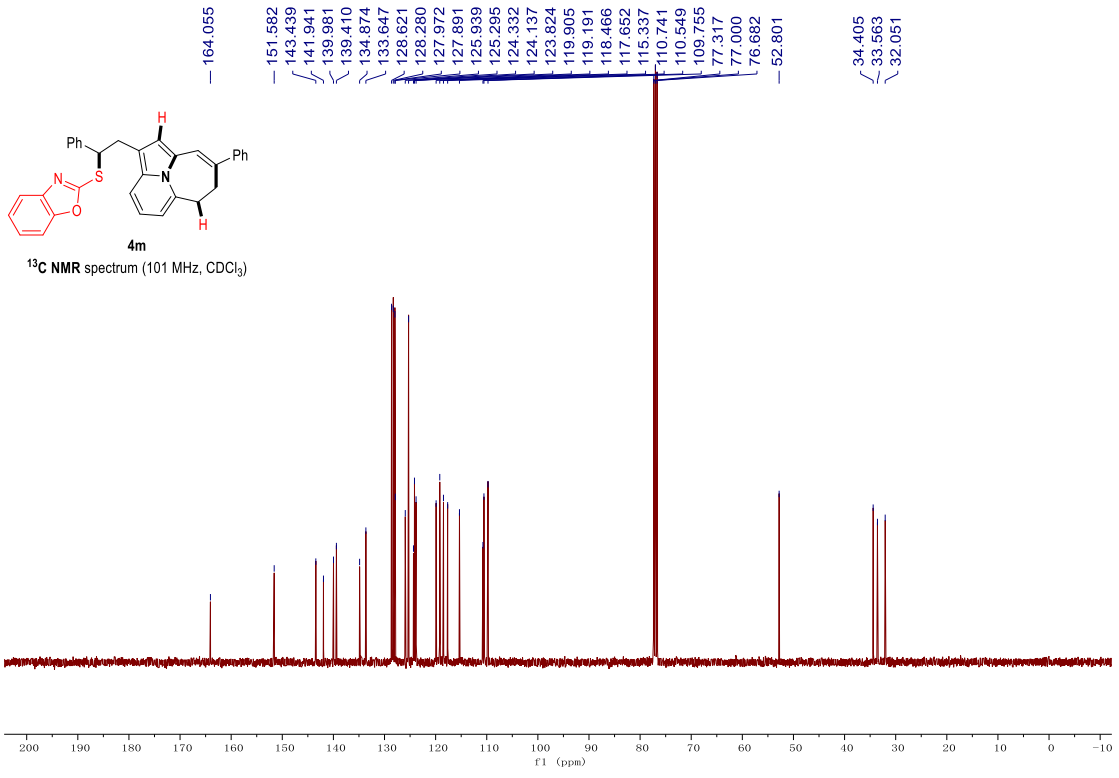
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



4m

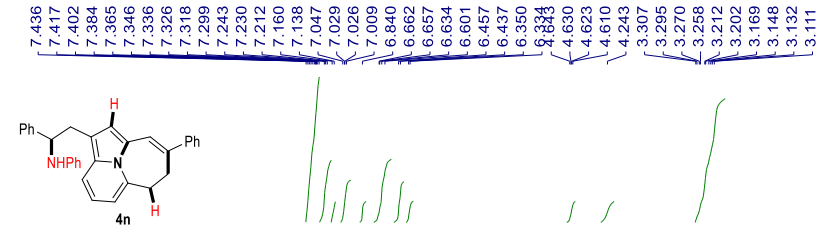
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



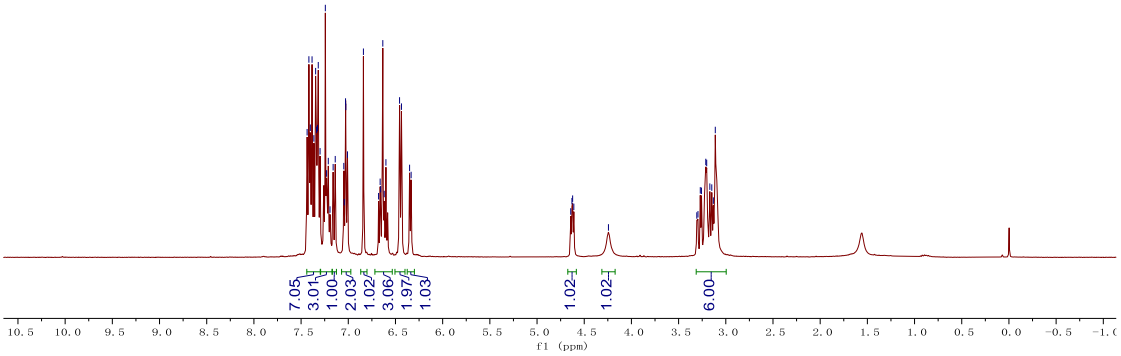


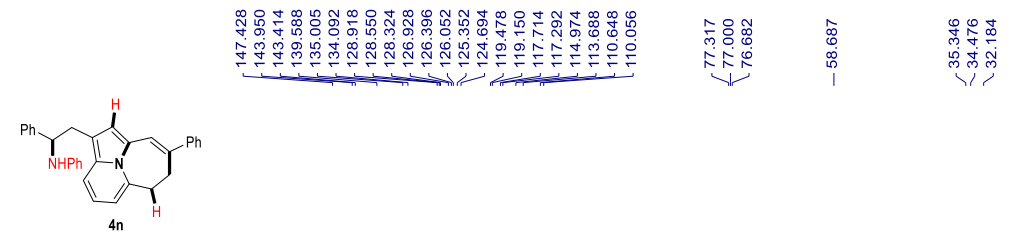
4m

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

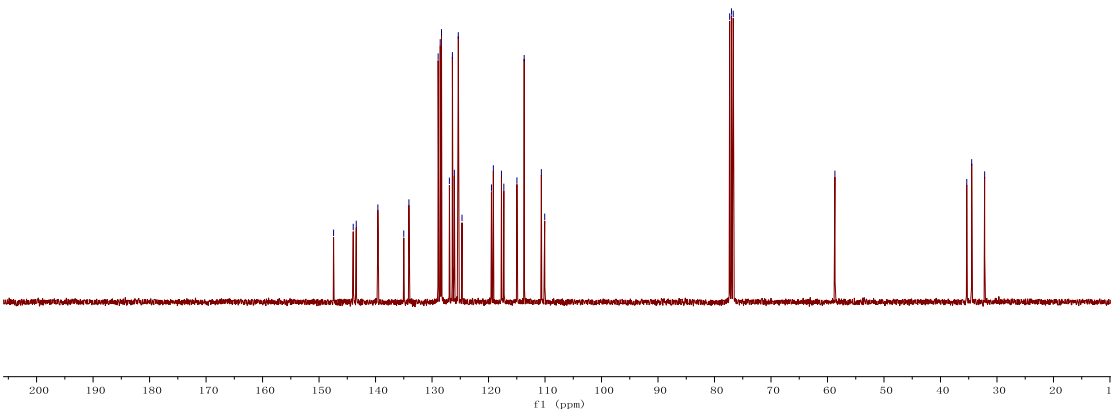


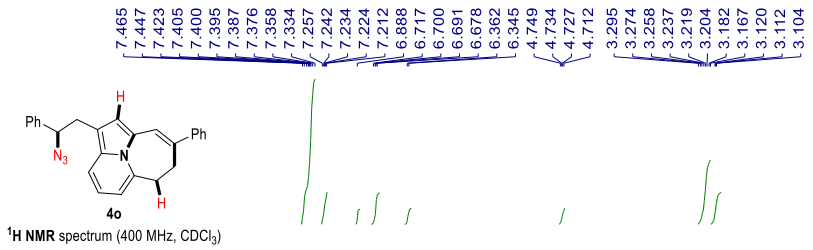
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





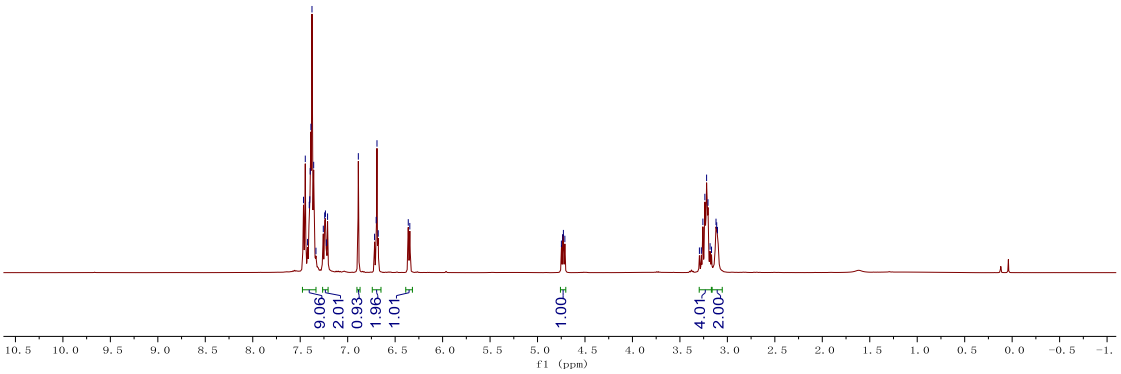
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

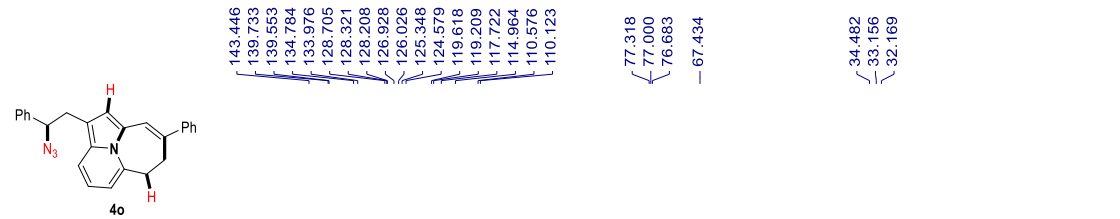




4o

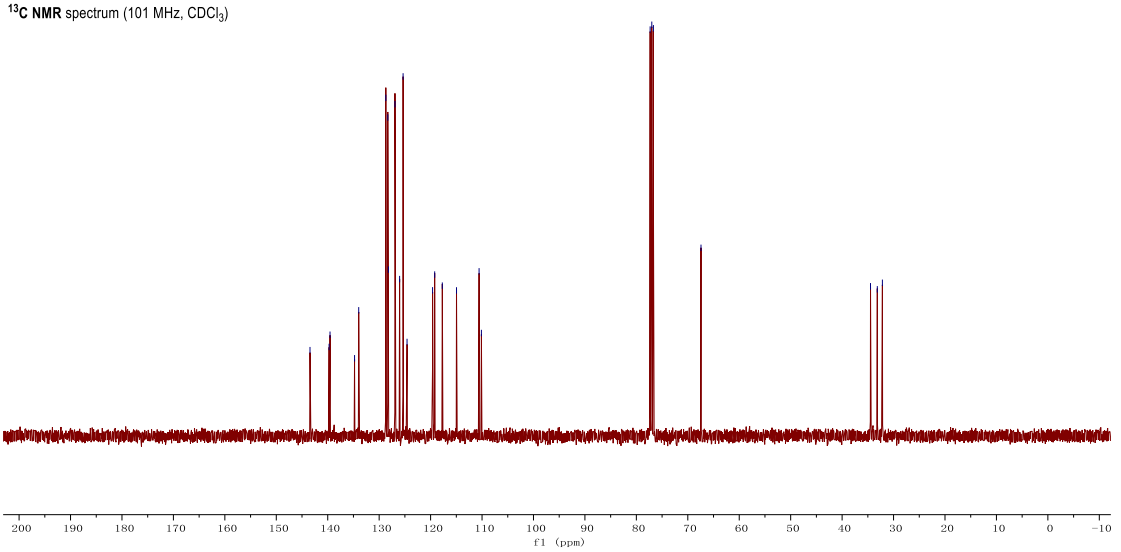
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

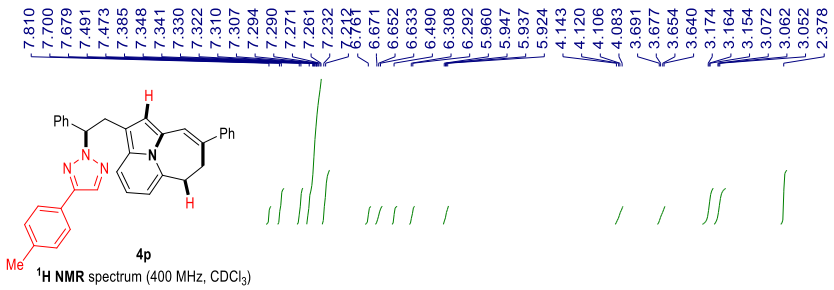




4o

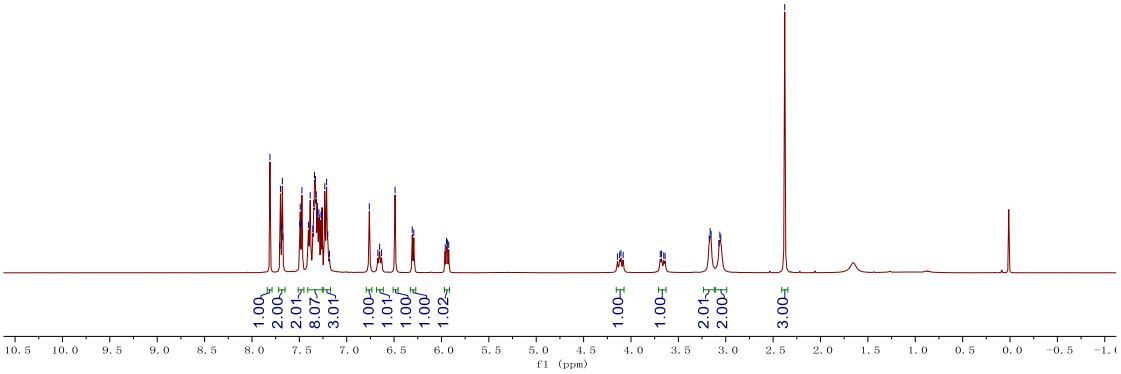
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

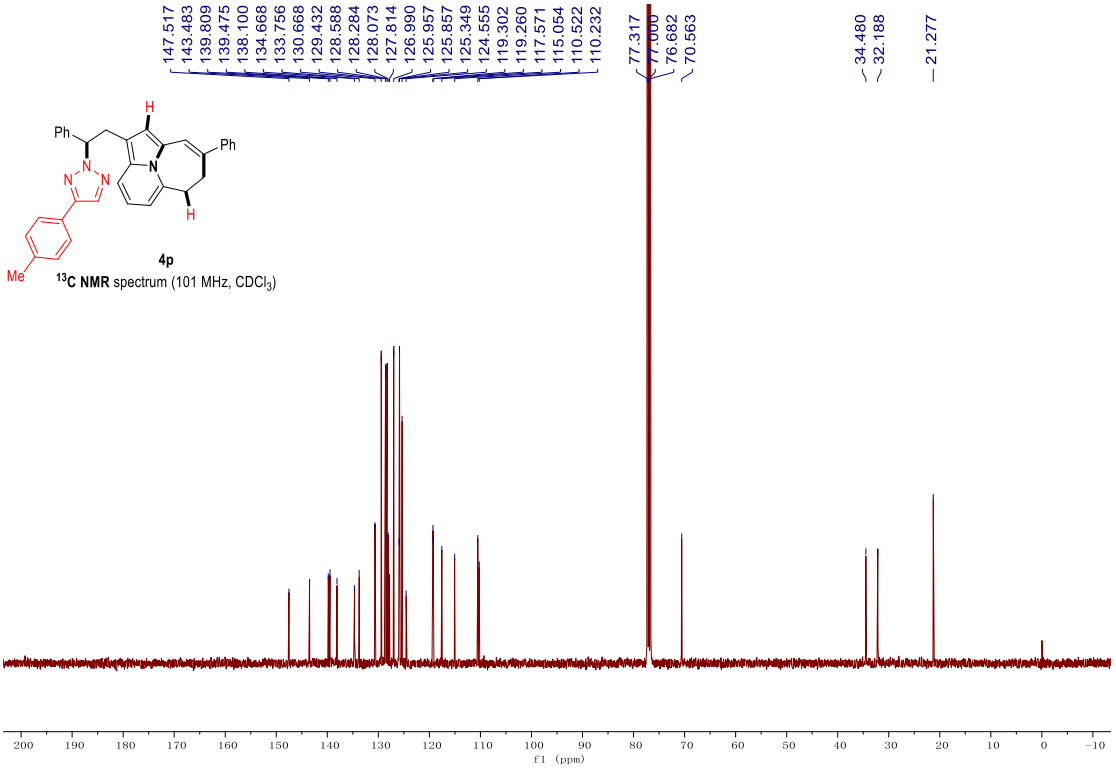




4p

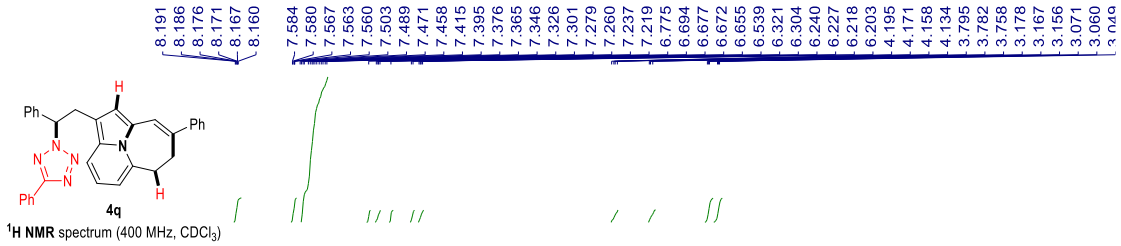
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



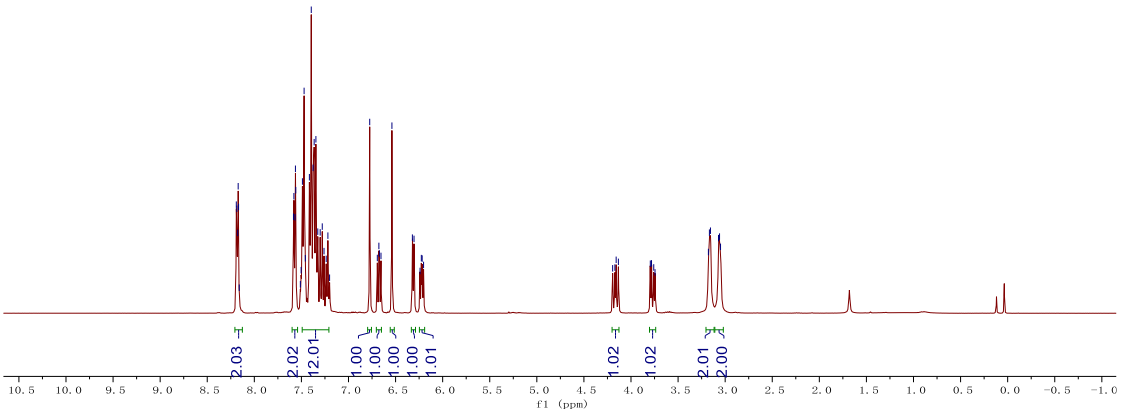


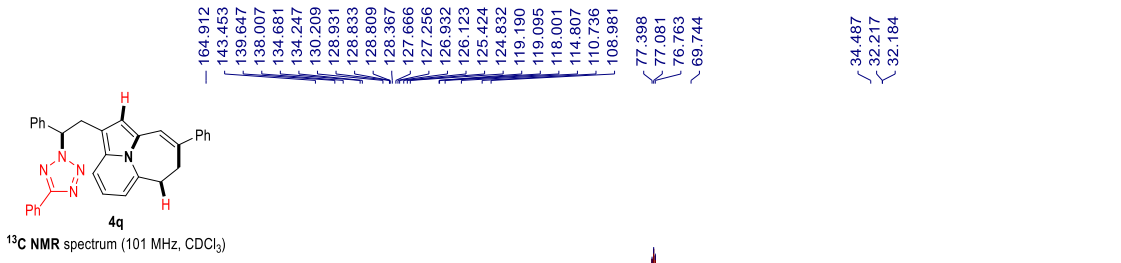
4p

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

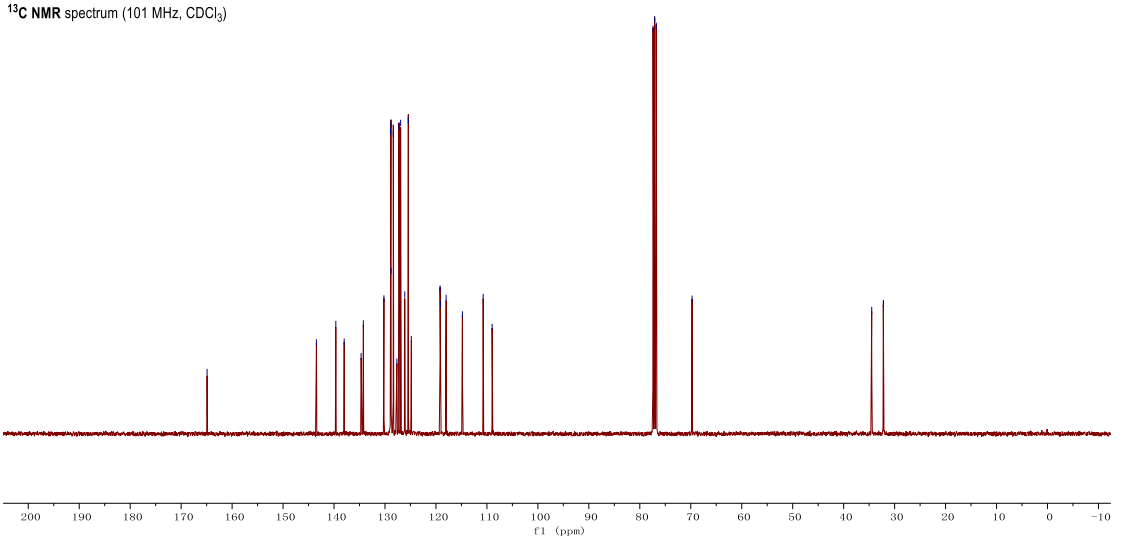


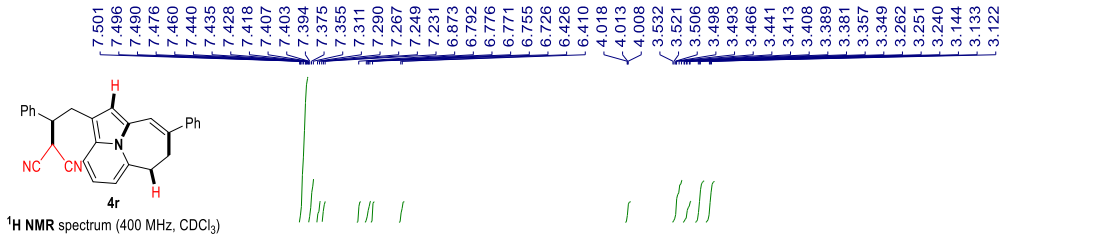
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)





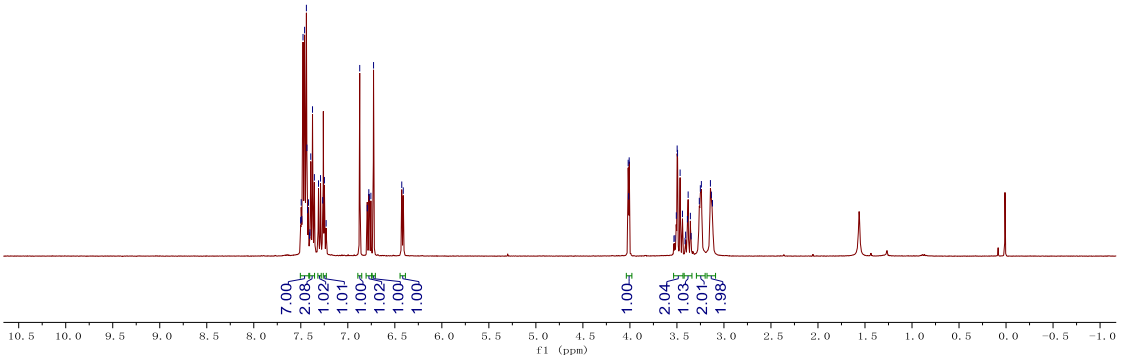
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

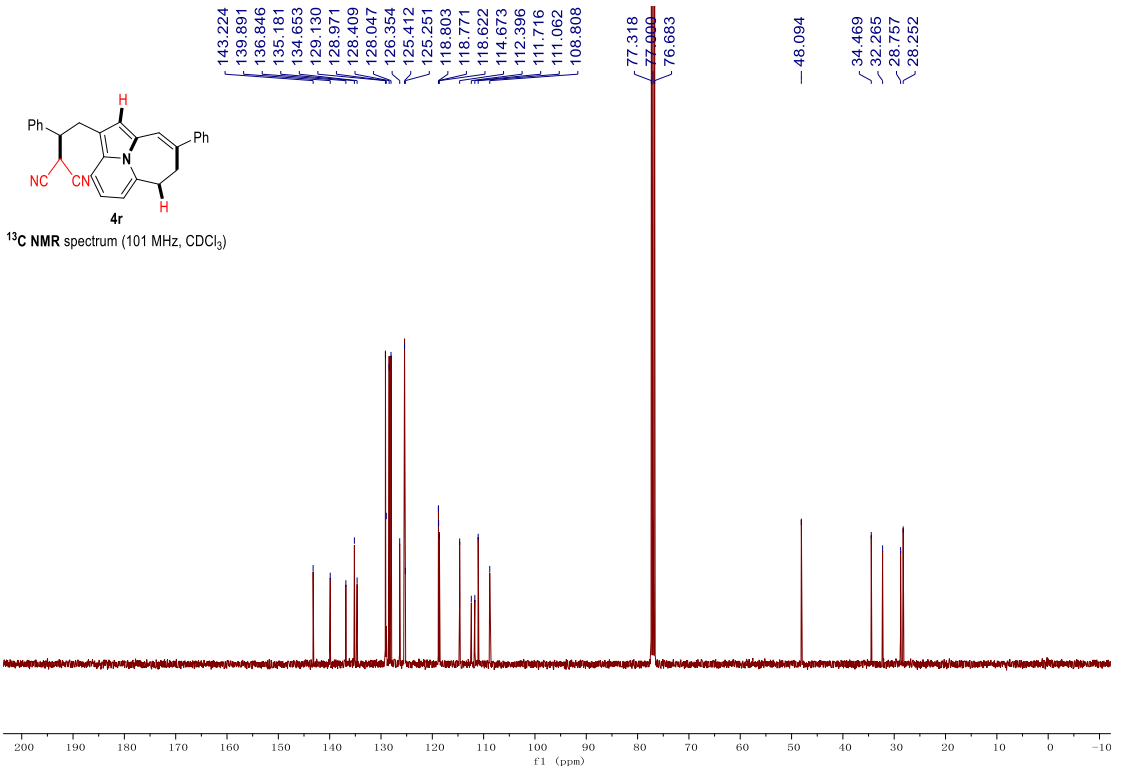




4r

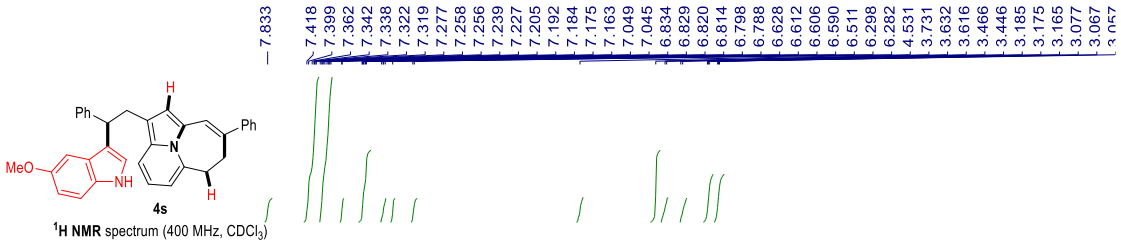
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





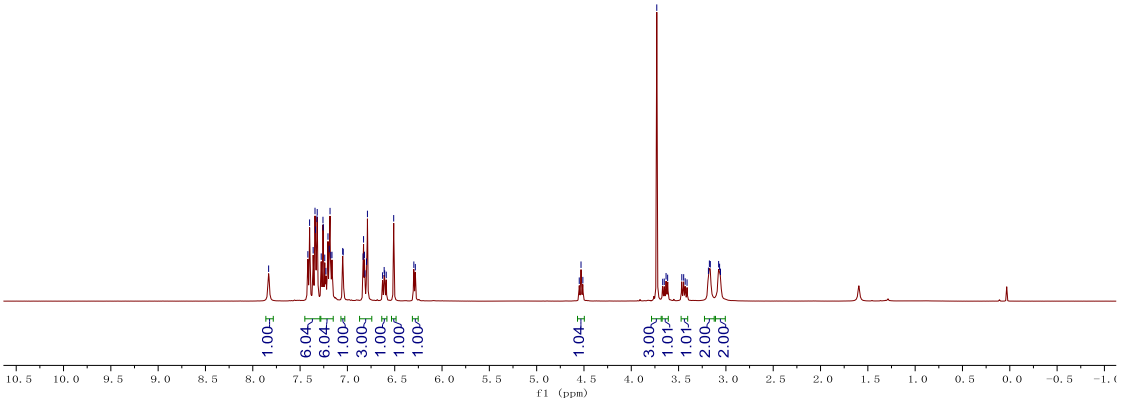
4r

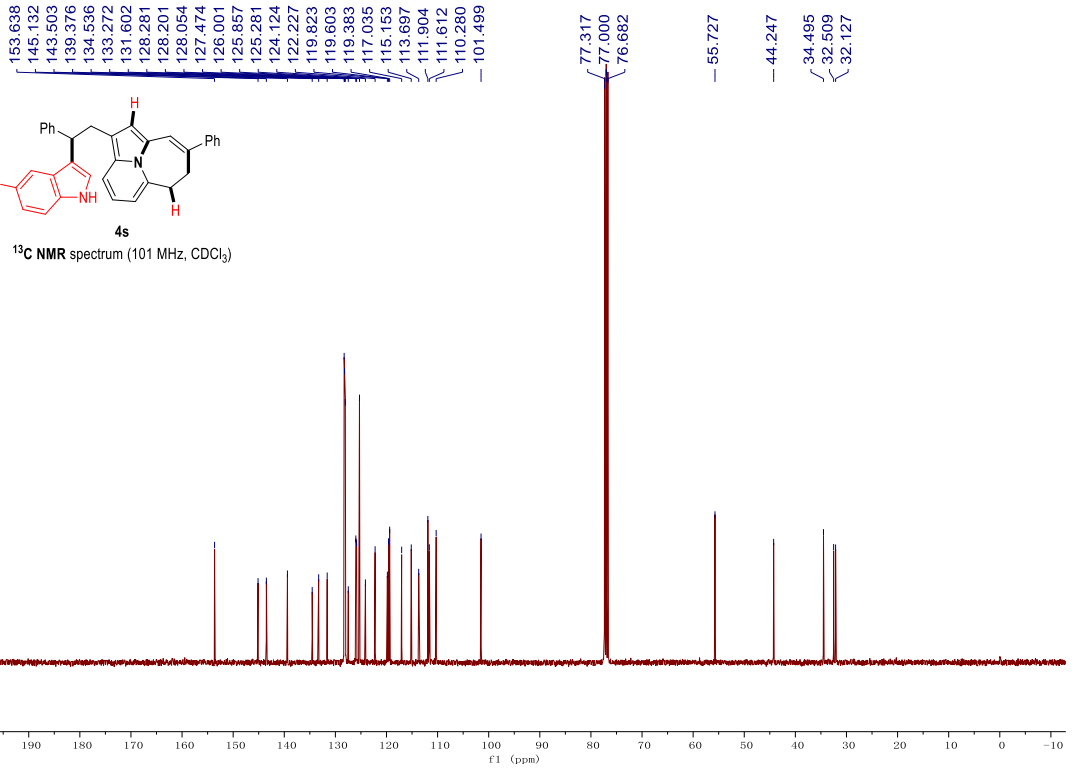
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



4s

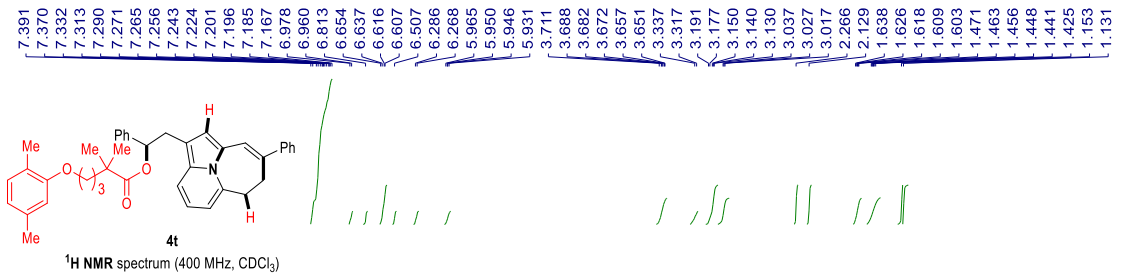
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





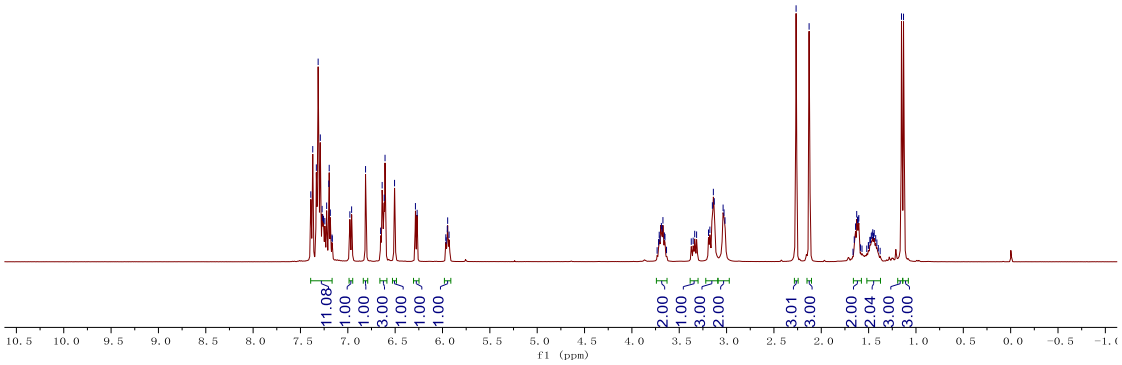
4s

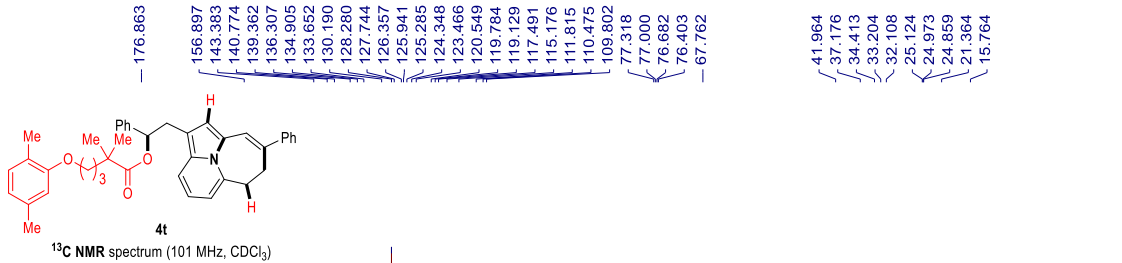
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



4t

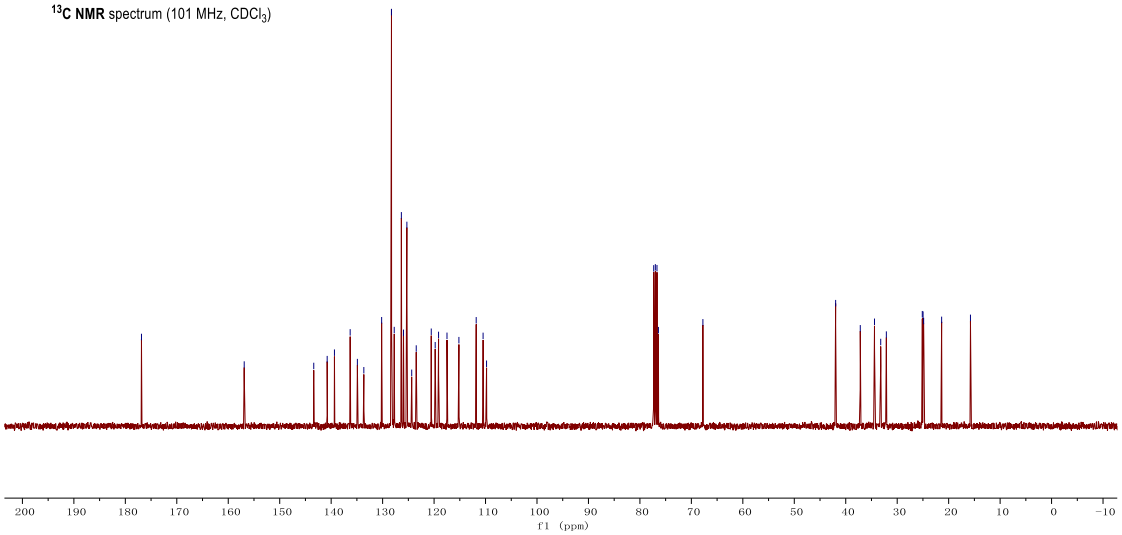
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

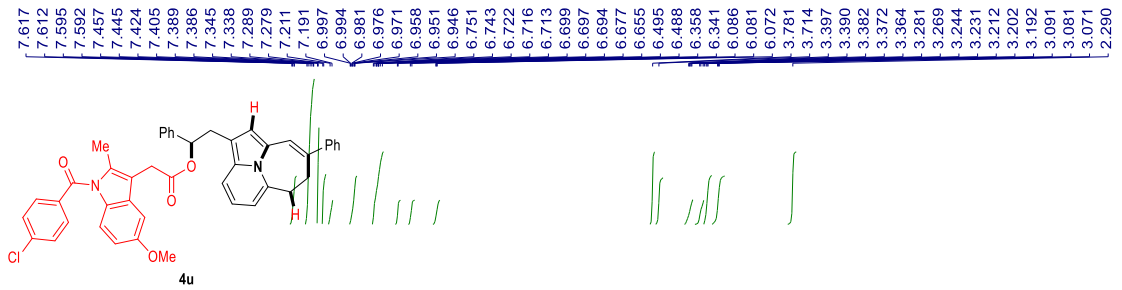




4t

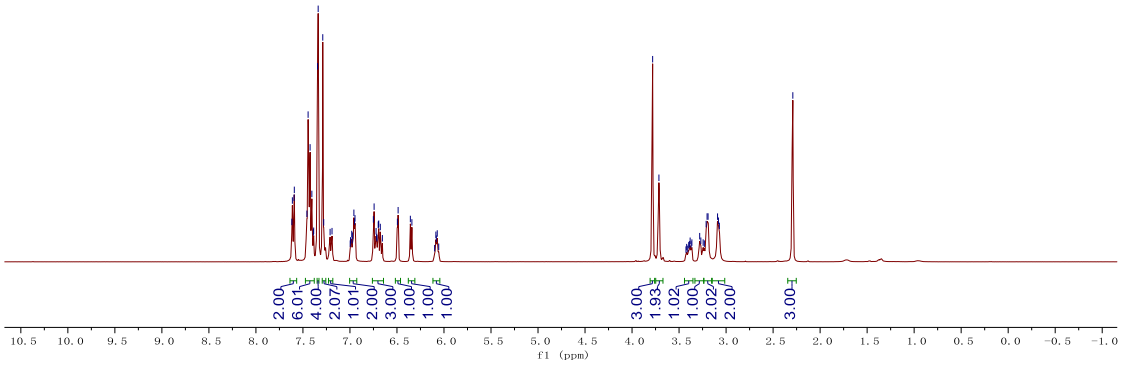
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

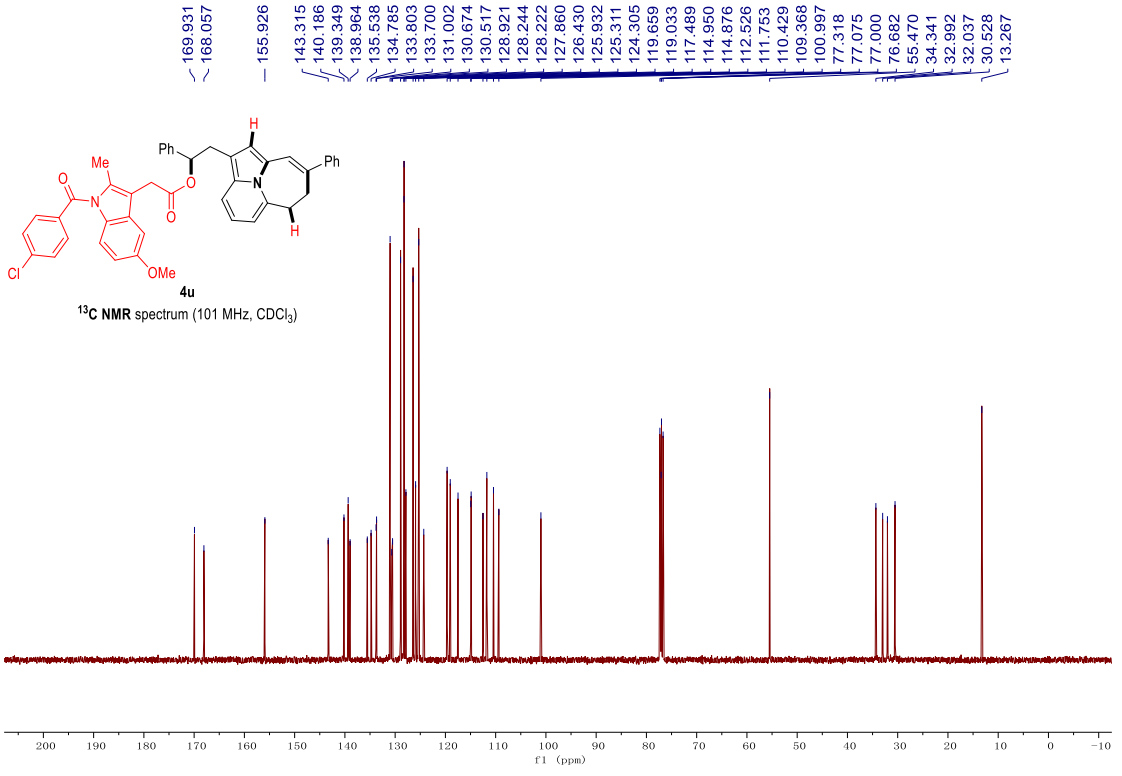




4u

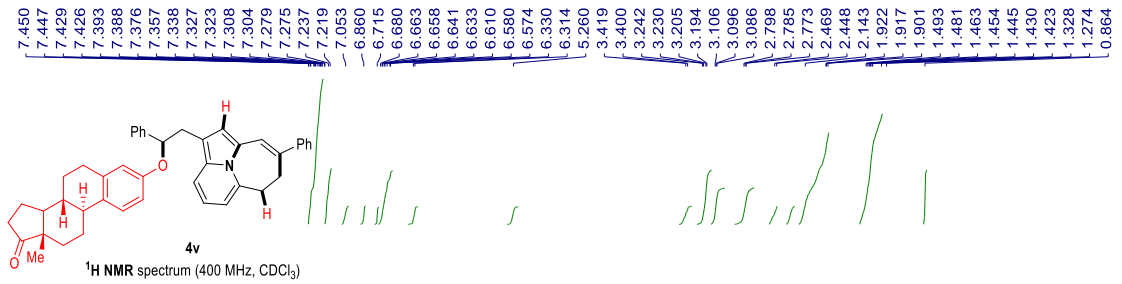
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





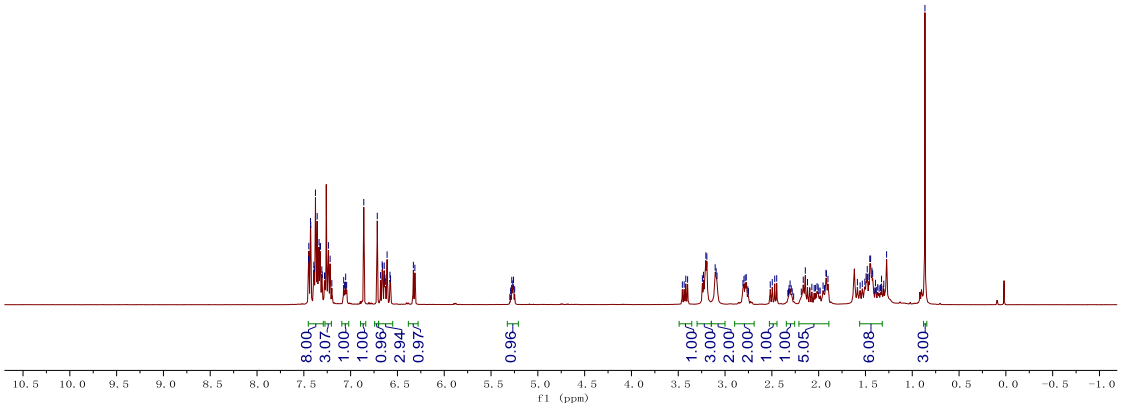
4u

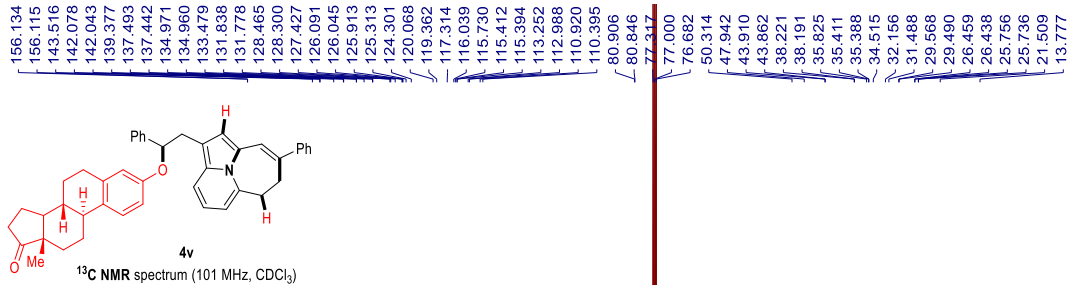
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



4v

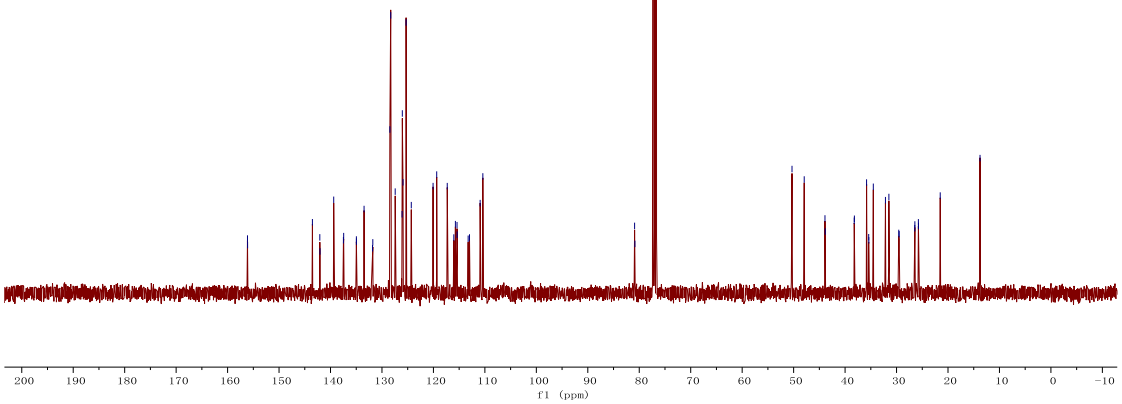
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

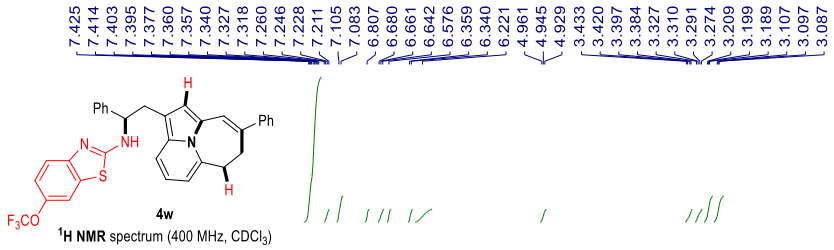




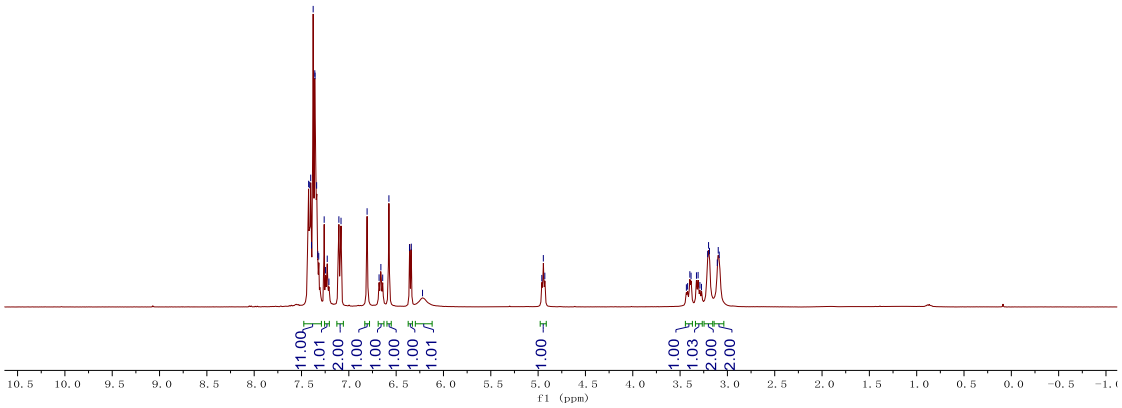
4v

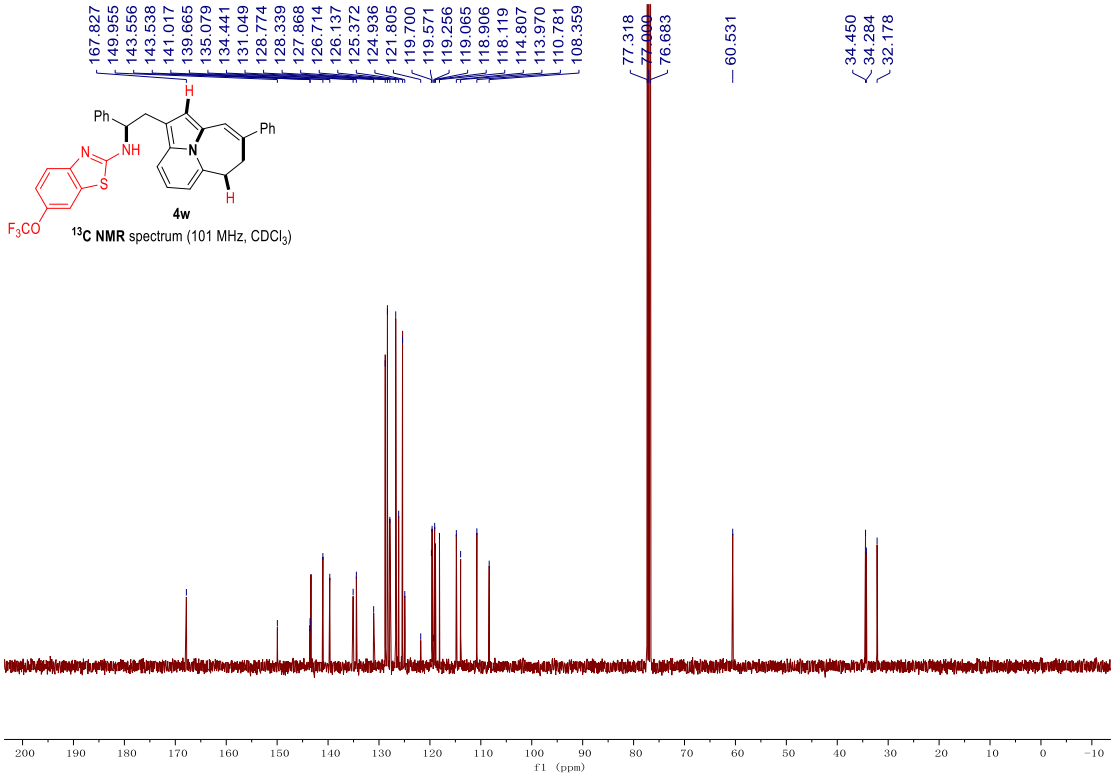
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



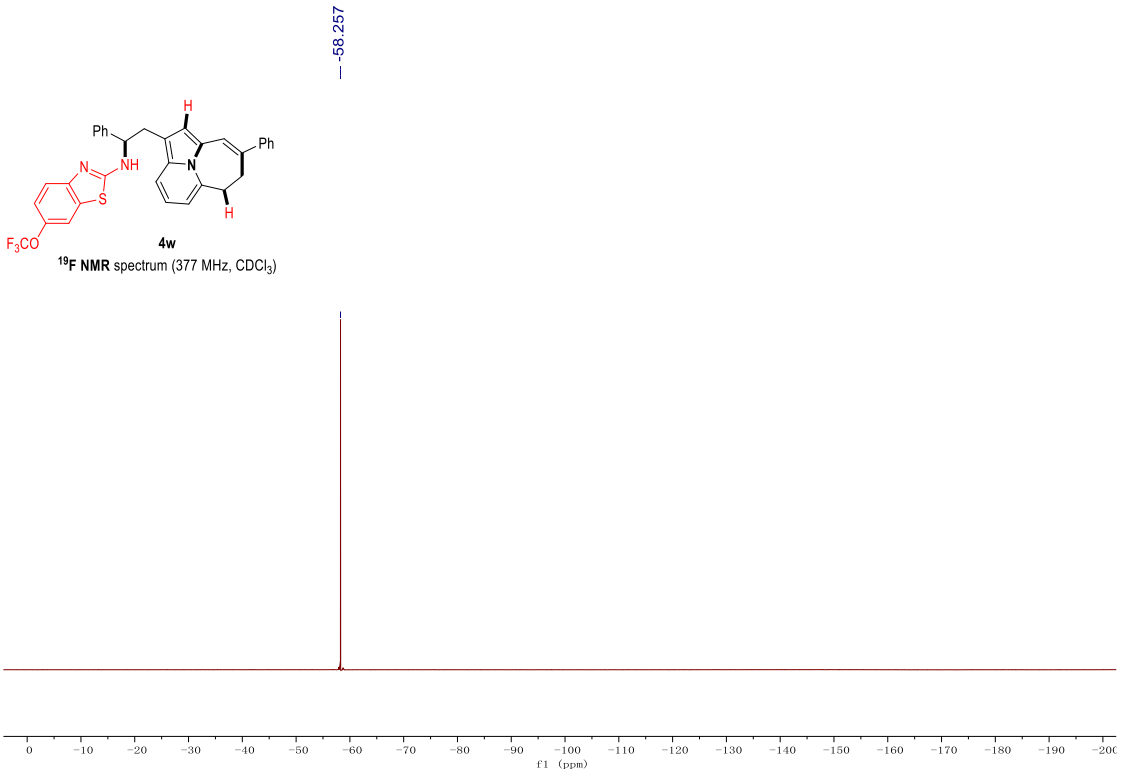


^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



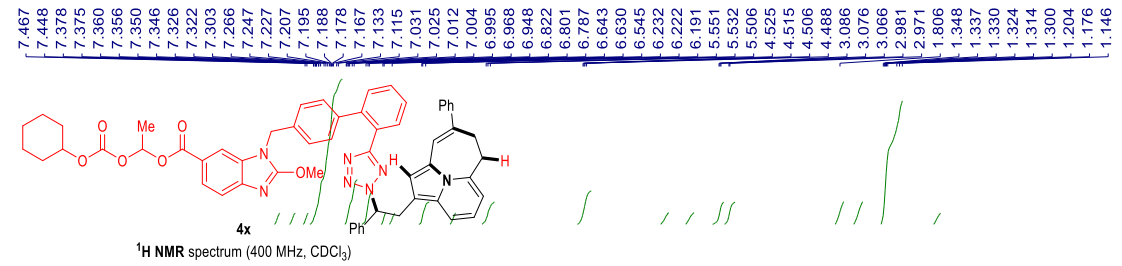


^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

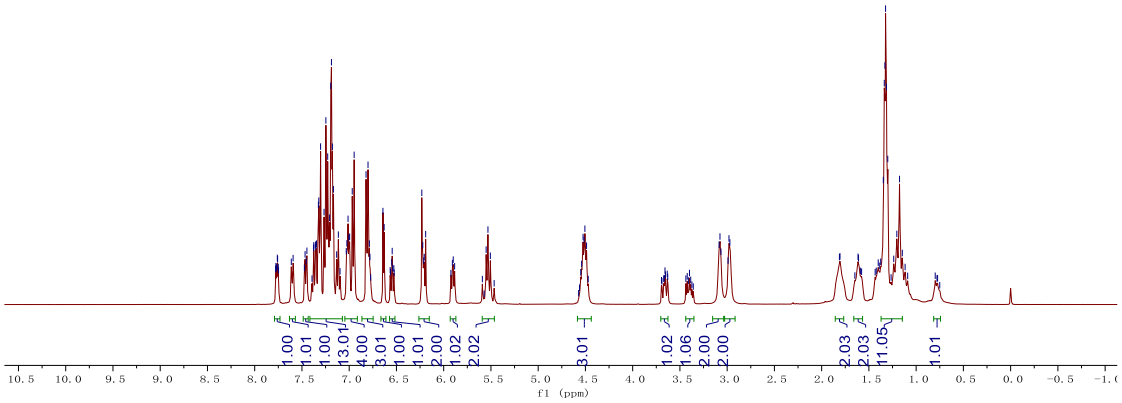


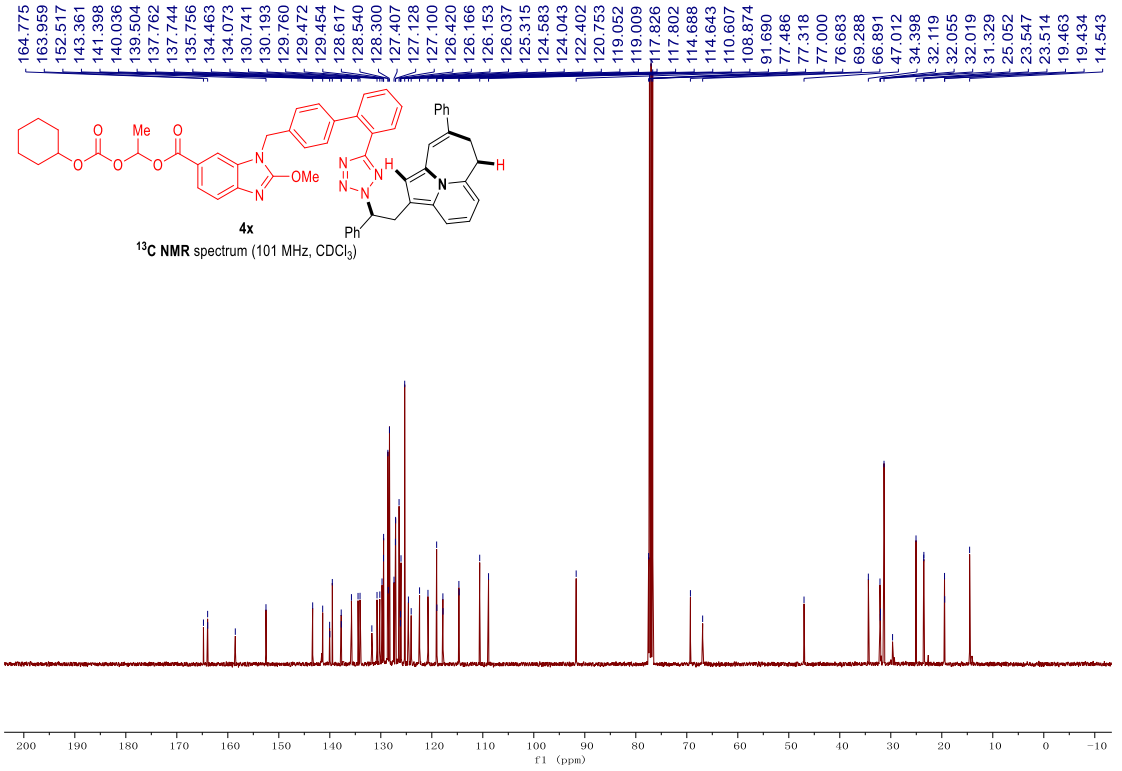
4w

^{19}F NMR spectrum (377 MHz, $CDCl_3$)

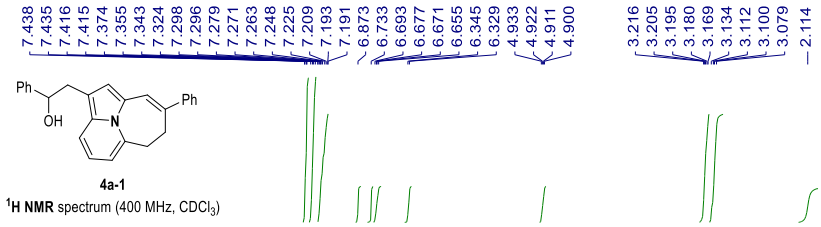


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



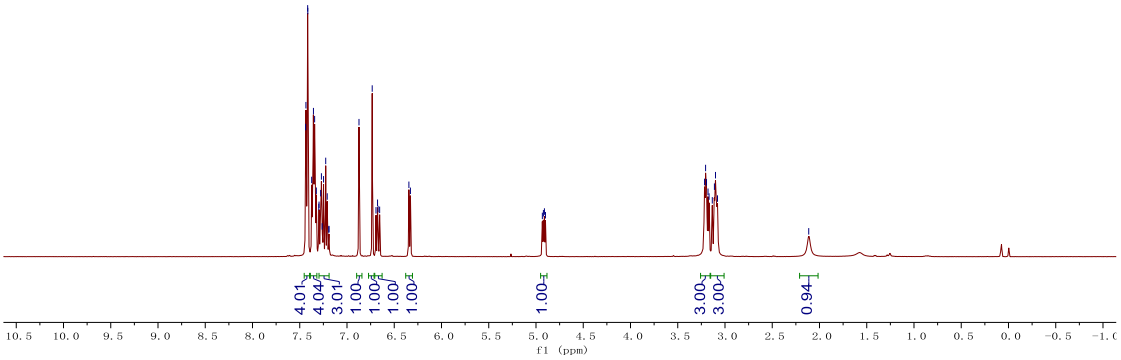


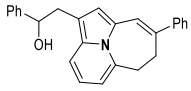
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



4a-1

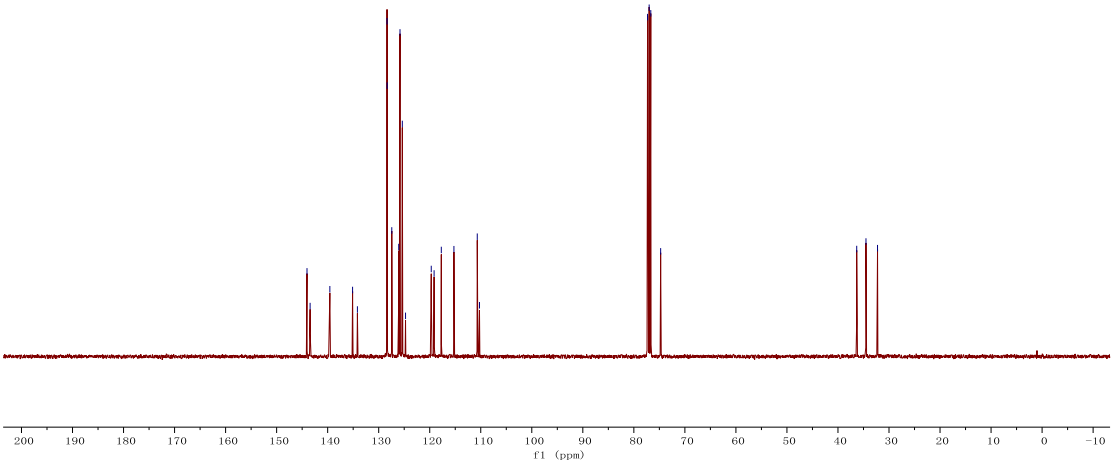
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

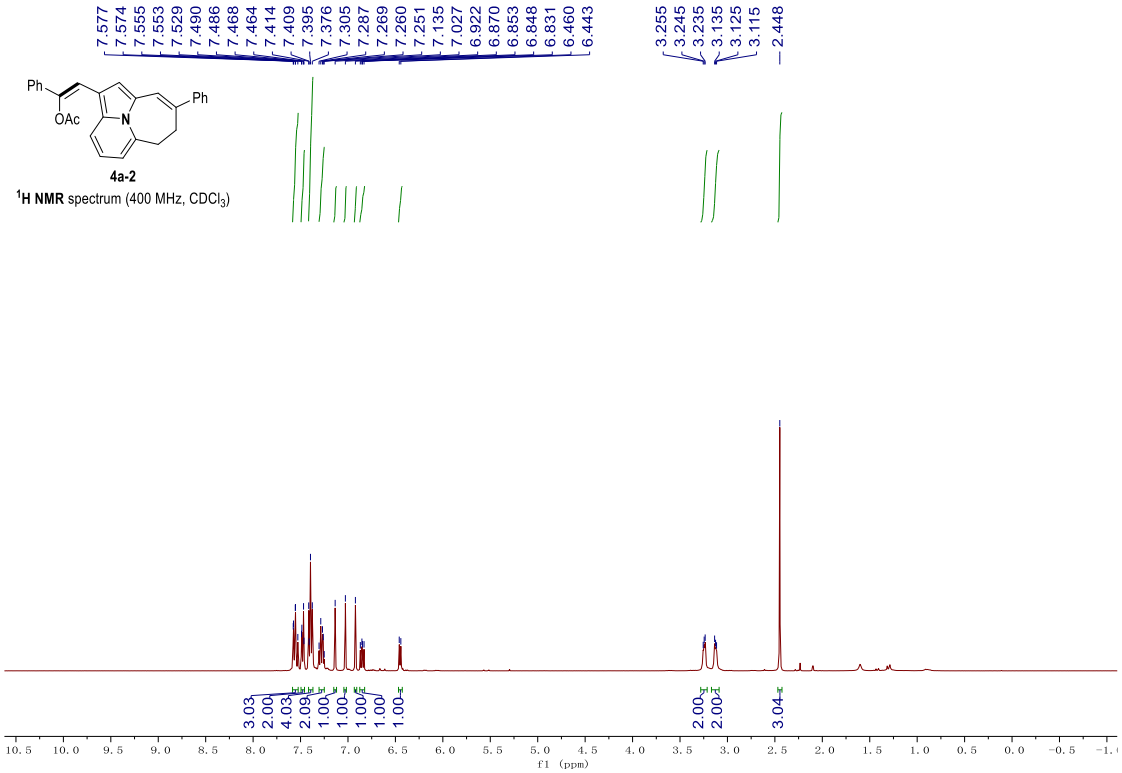




4a-1

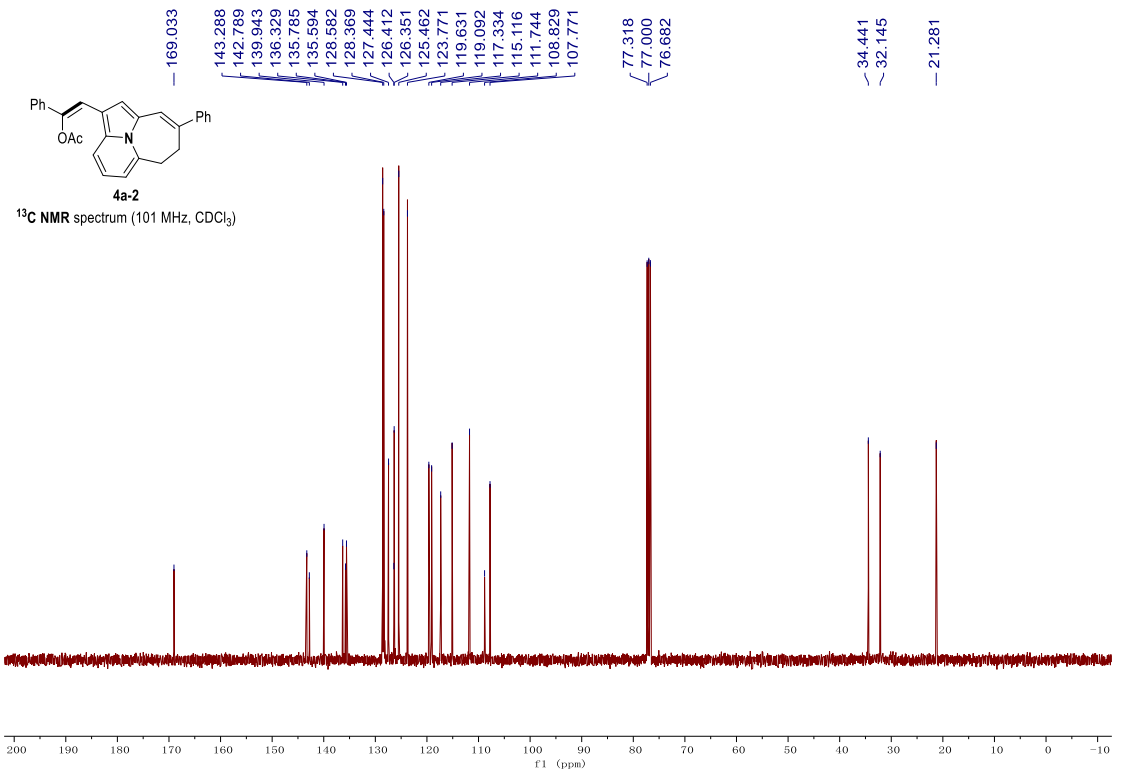
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





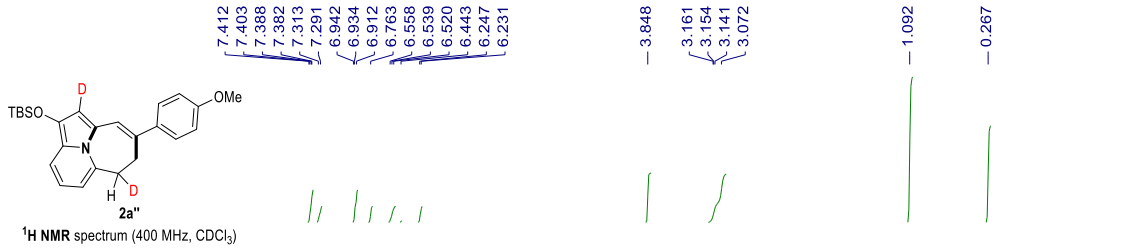
4a-2

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

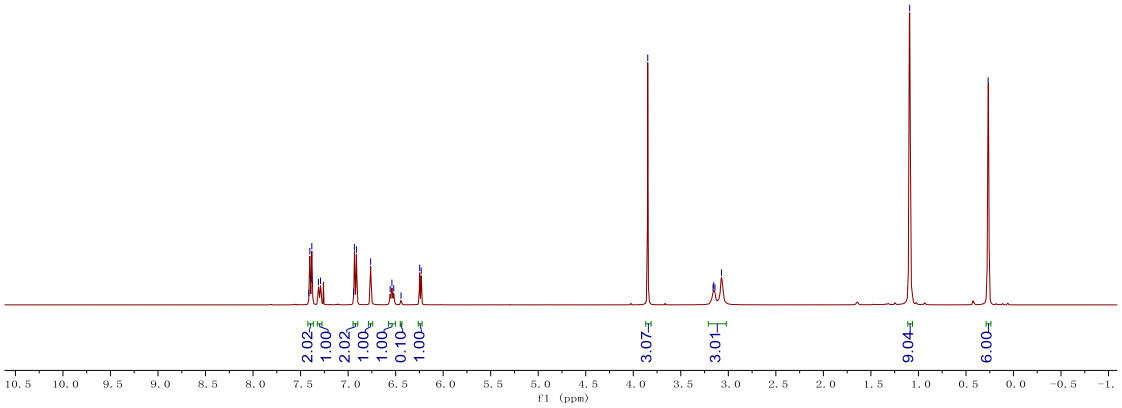


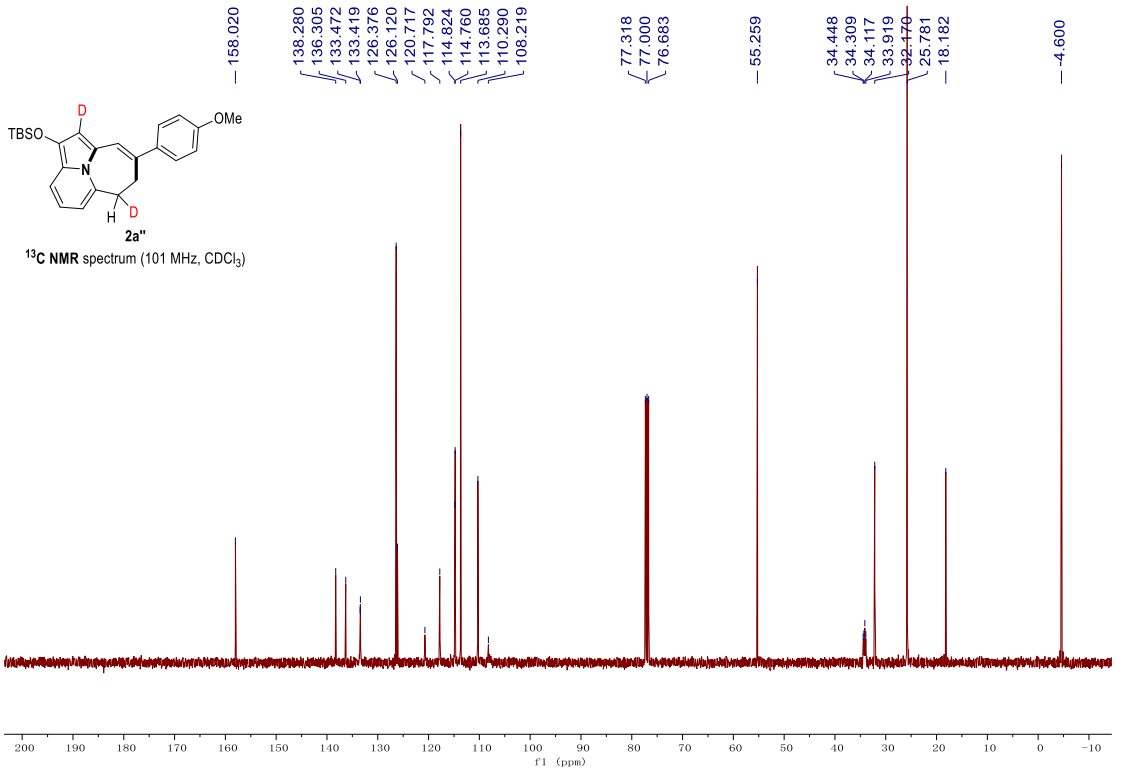
4a-2

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



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





^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)