# *Supporting Information*

## Ligand-Dependent, Palladium-Catalyzed Stereodivergent Synthesis of Chiral Tetrahydroquinolines

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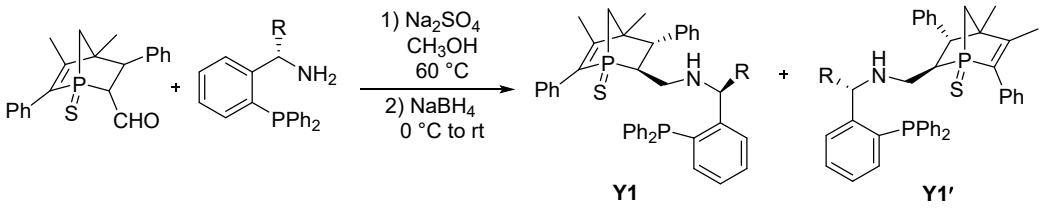
1. General experimental details.....2
2. General Procedure for Synthesis of Chiral Ligands Yue1-5.....2
3. Optimization of the Reaction Conditions.....7
   3.1 Optimization of reaction conditions with Yuephos ligands.....7
   3.2 Optimization of reaction conditions with P-N ligands.....8
   3.3 Optimization of reaction conditions with Mengphos ligands.....8
4. General Procedure for Reactions .....9
5. Copies of $^{1}$H NMR, $^{13}$C NMR, $^{31}$P NMR Spectra.....36
6. Copies of HPLC Chromatograms .....89
7. X-ray crystal structure.....136

## 1. General experimental details

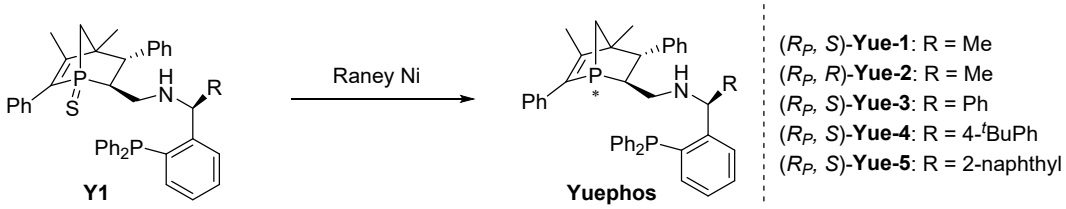
All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4°C/min, the thermometer was not corrected. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel AD-H in comparison with the authentic racemates. Chiral HPLC analysis recorded on Shanghaiyice instruments and Equipment Co. Ltd. and Shimadzu LC-20A. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification. The compounds **1**[1] and **2**[2] were prepared according to literature methods.

## 2. General Procedure for Synthesis of Chiral Ligands Yue1-5



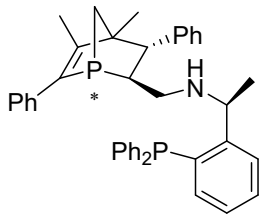

The corresponding aldehyde[3] and chiral imines[4] were prepared according to the literature methods: to a flask containing a solution of aldehyde (700 mg, 2.0 mmol) and corresponding chiral imines (3.0 mmol), then $Na_2SO_4$ (1 g) was added and the mixture was stirred at 60 ℃. The progress of the reaction was followed by $^{31}P$ NMR. Upon reaction completion, the reaction mixture was cooled to 0 ˚C and $NaBH_4$ (227 mg, 6.0 mmol, 3 equiv.) was added. The reaction mixture was stirred at 0 ˚C for 30 min and then for 2 h at room temperature. When the reaction was completed the reaction mixture was quenched with $H_2O$ and extracted with $CH_2Cl_2$, the combined

organic phases were dried over MgSO4 and the solvent was removed in vacuo. The residue was purified by silica gel chromatography (ethyl acetate /petroleum ether = 1:2) to afford the products **Y1** and **Y1'**.



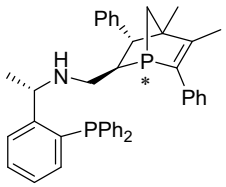

To a flame dried sealing tube, Raney nickel (20 equiv.) was added and washed 3 times with EtOH, 3 times with THF. A solution of **Y1** (1 mmol) in THF was added and the mixture was stirred at room temperature for 2 h. The progress of the reaction was followed by $^{31}$P NMR. Upon reaction completion, the resulting suspension was filtered and obtained the desired **Yue-phoses**.

**(*S*)-N-(((1*R*,2*R*,3*S*,4*S*)-4,5-dimethyl-3,6-diphenyl-1-phosphabicyclo[2.2.1]hept-5-en-2-yl)methyl)-1-(2-(diphenylphosphanyl)phenyl)ethan-1-amine (Yue-1).**



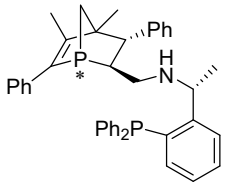

Purified by silica gel chromatography using PE/EA = 4:1, white solid (475 mg, 78% yield). $[\alpha]_D$ = +142 (*c* = 0.1, $CH_2Cl_2$, 15.9 °C). MP: 72.2 – 74.3 °C. $^{31}$P NMR ( 121 MHz，$CDCl_3$ ) $\delta$ -17.21，-17.55 ppm; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.55 – 7.51 (m, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.26 (m, 8H), 7.24 – 7.14 (m, 9H), 7.08 – 7.01 (m, 3H), 6.81 (ddd, *J* = 7.8, 4.3, 1.3 Hz, 1H), 4.53 – 4.46 (m, 1H), 2.65 – 2.42 (m, 3H), 2.37 (d, *J* = 5.4 Hz, 1H), 2.06 (s, 1H), 1.60 (dd, *J* = 11.5, 7.1 Hz, 1H), 1.43 – 1.36 (m, 4H), 1.22 (s, 3H), 0.91 (d, *J* = 6.4 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 152.2 (d, *J* = 1.1 Hz), 150.0 (d, *J* = 22.1 Hz), 141.8, 141.3 (d, *J* = 15.7 Hz), 138.9 (d, *J* = 20.7 Hz), 137.1 (d, *J* = 10.6 Hz), 136.7 (d, *J* = 10.2 Hz), 135.2 (d, *J* = 12.8 Hz), 134.3, 134.0, 133.1, 129.5, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 127.8, 126.9, 126.4, 126.4, 126.3, 126.3, 64.8 (d, *J* = 4.8 Hz), 57.5 (d, *J* = 2.3 Hz), 54.2 (d, *J* = 25.2 Hz), 52.4 (d, *J* = 17.5 Hz), 48.3 (d, *J* = 4.1 Hz), 46.9 (dd, *J* = 14.6, 2.3 Hz), 23.7, 20.7, 16.3 ppm. HRMS (ESI) calcd for $C_{41}H_{42}NP_2^+$ $[M+H]^+$: 610.2787, found 610.2794.

**(*S*)-N-(((1*R*,2*R*,3*S*,4*R*)-4,5-dimethyl-3,6-diphenyl-1-phosphabicyclo[2.2.1]hept-5-en-2-yl)methyl)-1-(2-(diphenylphosphanyl)phenyl)ethan-1-amine (Yue-1').**




Purified by silica gel chromatography using PE/EA = 4:1, white solid (500 mg, 82% yield). $[\alpha]_D$ = -138 (*c* = 0.1, $CH_2Cl_2$, 15.1 °C). MP: 75.5 – 77.2 °C. $^{31}P$ NMR ( 121 MHz，$CDCl_3$ ) $\delta$ -17.42，-18.89 ppm; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.57 (dd, *J* = 7.8, 4.3 Hz, 1H), 7.39 – 7.35 (m, 5H), 7.31 – 7.15 (m, 14H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.99 – 6.96 (m, 2H), 6.84 (dd, *J* = 7.7, 4.3 Hz, 1H), 4.61 (p, *J* = 6.7 Hz, 1H), 2.64 (ddd, *J* = 13.9, 11.4, 5.7 Hz, 1H), 2.42 – 2.32 (m, 2H), 2.29 – 2.24 (m, 1H), 1.72 (s, 1H), 1.61 – 1.53 (m, 1H), 1.42 (s, 3H), 1.41 – 1.34 (m, 1H), 1.20 (s, 3H), 1.12 (d, *J* = 6.4 Hz, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 152.3 (d, *J* = 1.0 Hz), 150.2 (d, *J* = 23.9 Hz), 141.1 (d, *J* = 15.4 Hz), 138.9 (d, *J* = 20.8 Hz), 137.1 (d, *J* = 10.4 Hz), 136.7 (d, *J* = 10.6 Hz), 135.2 (d, *J* = 13.0 Hz), 134.3, 134.2, 134.0, 133.9, 133.3, 129.5, 128.9, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 128.3, 127.7, 126.9, 126.4, 126.3, 126.0 (d, *J* = 4.9 Hz), 64.5 (d, *J* = 4.8 Hz), 57.1 (d, *J* = 2.7 Hz), 55.1 (d, *J* = 25.2 Hz), 51.8 (d, *J* = 14.2 Hz), 48.3 (d, *J* = 4.0 Hz), 48.0 (d, *J* = 14.8 Hz), 24.0, 20.7, 16.3 ppm. HRMS (ESI) calcd for $C_{41}H_{42}NP_2^+$ $[M+H]^+$: 610.2787, found 610.2791.

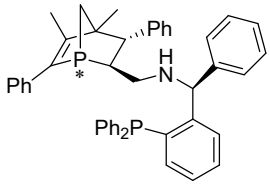
**(*R*)-N-(((1*R*,2*R*,3*S*,4*S*)-4,5-dimethyl-3,6-diphenyl-1-phosphabicyclo[2.2.1]hept-5-en-2-yl)methyl)-1-(2-(diphenylphosphanyl)phenyl)ethan-1-amine (Yue-2).**




Purified by silica gel chromatography using PE/EA = 4:1, white solid (462 mg, 76% yield). $[\alpha]_D$ = -79 (*c* = 0.1, $CH_2Cl_2$, 16.2 °C). MP: 66.1 – 67.9 °C. $^{31}P$ NMR ( 121 MHz，$CDCl_3$ ) $\delta$ -17.16，-17.51 ppm; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.53 (dd, *J* = 7.9, 4.3 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.16 (m, 17H), 7.09 – 7.01 (m, 3H), 6.81 (dd, *J* = 7.8, 4.3 Hz, 1H), 4.51 (p, *J* = 6.6 Hz, 1H), 2.65 – 2.41 (m, 3H),, 2.37 (d, *J* = 5.5 Hz, 1H), 1.82 (s, 1H), 1.60 (dd, *J* = 11.5, 7.1 Hz, 1H), 1.43 – 1.36 (m, 4H), 1.22 (s, 3H), 0.92 (d, *J* = 6.4 Hz, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 152.2 (d, *J* = 1.1 Hz), 150.0 (d, *J* = 21.9 Hz), 141.2 (d, *J* = 15.4 Hz), 138.9 (d, *J* = 20.9 Hz), 137.1 (d, *J* = 10.7 Hz), 136.7 (d, *J* = 10.3 Hz), 135.2 (d, *J* = 12.9 Hz),134.3, 134.3, 134.0,

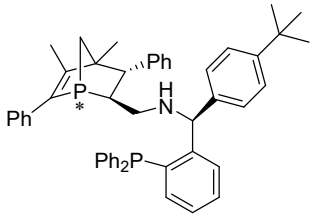
134.0, 133.1, 129.5, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.2, 127.8, 126.8, 126.4, 126.4, 126.3, 64.8 (d, $J$ = 4.8 Hz), 57.4 (d, $J$ = 2.7 Hz), 54.2 (d, $J$ = 25.3 Hz), 52.4 (d, $J$ = 17.4 Hz), 48.3 (d, $J$ = 3.9 Hz), 46.9 (dd, $J$ = 14.8, 2.4 Hz), 23.7, 20.7, 16.2 ppm. HRMS (ESI) calcd for $C_{41}H_{42}NP_2^+$ $[M+H]^+$: 610.2787, found 610.2792.

**(*S*)-N-(((1*R*,2*R*,3*S*,4*S*)-4,5-dimethyl-3,6-diphenyl-1-phosphabicyclo[2.2.1]hept-5-en-2-yl)methyl)-1-(2-(diphenylphosphanyl)phenyl)-1-phenylmethanamine (Yue-3).**



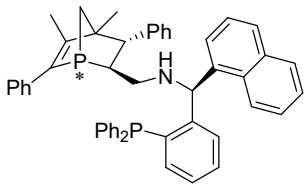

Purified by silica gel chromatography using PE/EA = 4:1, white solid (496 mg, 74% yield). $[\alpha]_D$ = +85 ($c$ = 0.1, $CH_2Cl_2$, 16.5 °C). MP: 76.6 – 78.5 °C. $^{31}$P NMR ( 121 MHz，$CDCl_3$ ) $\delta$ -16.45，-17.43 ppm; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.48 (ddd, $J$ = 7.9, 4.3, 1.3 Hz, 1H), 7.39 – 7.35 (m, 4H), 7.25 – 7.15 (m, 15H), 7.13 – 7.04 (m, 6H), 6.98 (dd, $J$ = 7.3, 2.1 Hz, 2H), 6.85 (ddd, $J$ = 7.8, 4.2, 1.3 Hz, 1H), 5.64 (d, $J$ = 7.9 Hz, 1H), 2.73 – 2.54 (m, 2H), 2.38 (d, $J$ = 5.7 Hz, 1H), 2.26 – 2.19 (m, 1H), 1.72 (s, 1H), 1.59 (ddd, $J$ = 11.6, 7.2, 1.6 Hz, 1H), 1.45 – 1.36 (m, 4H),1.19 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 152.3 (d, $J$ = 1.1 Hz), 148.3 (d, $J$ = 22.9 Hz), 141.2 (d, $J$ = 15.9 Hz), 138.9 (d, $J$ = 20.7 Hz), 137.3 (d, $J$ = 10.1 Hz), 136.7 (d, $J$ = 10.5 Hz), 135.7 (d, $J$ = 13.3 Hz), 134.1 (d, $J$ = 1.6 Hz), 133.9 (d, $J$ = 1.9 Hz), 133.8, 129.4, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.1, 126.6, 126.5, 126.4, 64.7 (d, $J$ = 4.7 Hz), 63.4 (d, $J$ = 23.2 Hz), 57.2 (d, $J$ = 2.5 Hz), 52.5 (d, $J$ = 15.6 Hz), 48.4 (d, $J$ = 3.8 Hz), 47.3 (d, $J$ = 15.0 Hz), 20.8, 16.3 ppm. HRMS (ESI) calcd for $C_{46}H_{44}NP_2^+$ $[M+H]^+$: 672.2943, found 672.2939.

**(*S*)-1-(4-(tert-butyl)phenyl)-N-(((1*R*,2*R*,3*S*,4*S*)-4,5-dimethyl-3,6-diphenyl-1-phosphabicyclo[2.2.1]hept-5-en-2-yl)methyl)-1-(2-(diphenylphosphanyl)phenyl)methanamine (Yue-4).**



Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (530 mg, 73% yield). $[\alpha]_D$ = +113 (*c* = 0.1, $CH_2Cl_2$, 17 °C). $^{31}P$ NMR ( 121 MHz，$CDCl_3$ ) $\delta$ -16.75，-17.36 ppm; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.59 – 7.54 (m, 1H), 7.40 – 7.35 (m, 4H), 7.24 – 7.17 (m, 13H), 7.09 – 6.97 (m, 9H), 6.84 (ddd, *J* = 7.8, 4.2, 1.4 Hz, 1H), 5.63 (d, *J* = 7.9 Hz, 1H), 2.75 – 2.57 (m, 2H), 2.41 (d, *J* = 5.8 Hz, 1H), 2.29 – 2.24 (m, 1H), 1.82 (s, 1H), 1.60 (ddd, *J* = 11.7, 7.1, 1.6 Hz, 1H), 1.47 – 1.43 (m, 1H), 1.41 (s, 3H), 1.22 (s, 9H), 1.20 (s, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 152.3 (d, *J* = 1.2 Hz), 149.1, 141.8, 141.2 (d, *J* = 15.6 Hz), 139.96 (d, *J* = 1.4 Hz), 138.89 (d, *J* = 21.0 Hz), 137.4 (d, *J* = 10.2 Hz), 136.6 (d, *J* = 10.4 Hz), 135.6 (d, *J* = 13.3 Hz), 134.1, 134.1, 133.8, 133.8, 133.8, 129.3, 128.9, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9 (d, *J* = 5.1 Hz), 127.7, 127.4, 126.9, 126.4, 126.3, 126.3, 124.9, 64.7 (d, *J* = 4.8 Hz), 63.1 (d, *J* = 23.6 Hz), 57.2 (d, *J* = 2.8 Hz), 52.5 (d, *J* = 15.9 Hz), 48.4 (d, *J* = 4.0 Hz), 47.2 (d, *J* = 14.9 Hz), 34.3, 31.4, 20.7, 16.3 ppm.HRMS (ESI) calcd for $C_{50}H_{52}NP_2^+$ $[M+H]^+$: 728.3570, found 728.3577.

**(*S*)-N-(((1*R*,2*R*,3*S*,4*S*)-4,5-dimethyl-3,6-diphenyl-1-phosphabicyclo[2.2.1]hept-5-en-2-yl)methyl)-1-(2-(diphenylphosphanyl)phenyl)-1-(naphthalen-1-yl)methanamine (Yue-5).**



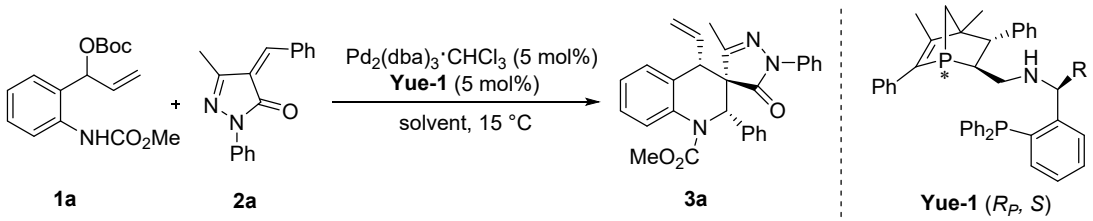

Purified by silica gel chromatography using PE/EA = 4:1, white solid (555 mg, 77% yield). $[\alpha]_D$ = +43 (*c* = 0.1, $CH_2Cl_2$, 16.8 °C). MP: 90.1 – 92 °C. $^{31}P$ NMR ( 121 MHz，$CDCl_3$ ) $\delta$ -17.13，-17.76 ppm; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.99 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.30 (m, 5H), 7.28 – 6.99 (m, 19H), 6.92 (d, *J* = 6.8 Hz, 2H), 6.37 (d, *J* = 8.2 Hz, 1H), 2.84 (ddd, *J* = 15.0, 11.5, 5.7 Hz, 1H), 2.65 (q, *J* = 9.9 Hz, 1H), 2.32 (d, *J* = 5.6 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.73 – 1.52 (m, 2H), 1.41 – 1.34 (m, 4H), 1.15 (s, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 152.4, 147.9 (d, *J* = 23.7 Hz), 141.7, 141.2 (d, *J* = 16.3 Hz), 138.9 (d, *J* = 20.8 Hz), 138.3, 136.9 (d, *J* = 9.3 Hz), 136.8 (d, *J* = 10.3 Hz), 136.1 (d, *J* = 13.1 Hz), 134.2, 134.1, 134.1, 134.0, 133.9, 133.8, 131.9, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 127.7, 127.6, 127.3, 126.5, 126.4, 125.9, 125.5, 125.4 (d, *J* = 3.1 Hz), 125.3, 124.3 (d, *J* = 5.6 Hz), 64.6 (d, *J* = 4.7 Hz), 60.9 (d, *J* = 23.4 Hz), 57.2 (d, *J* = 2.5 Hz),

53.2 (d, $J$ = 12.7 Hz), 48.32 (d, $J$ = 4.7 Hz), 47.85 (d, $J$ = 15.6 Hz), 20.7, 16.4 ppm. HRMS (ESI) calcd for $C_{50}H_{46}NP_2^+$ $[M+H]^+$: 722.3100, found 722.3109.

## 3. Optimization of the Reaction Conditions

### 3.1 Optimization of reaction conditions with Yuephos ligands.

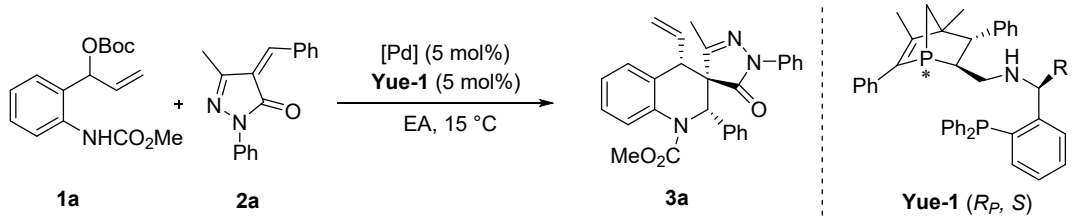
**Table S1.** Screening of the solvents. [a]




| entry | Solvent | dr[b] | yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | DCM | > 20:1 | 62 | 93 |
| 2 | EA | > 20:1 | 69 | 96 |
| 3 | THF | > 20:1 | 56 | 90 |
| 4 | Toluene | > 20:1 | 56 | 86 |
| 5 | MTBE | > 20:1 | 76 | 88 |

[a] Unless otherwise stated, reactions were performed with **1a** (60 mg, 0.2 mmol) and **2a** (26 mg, 0.1 mmol), in 1.0 mL of solvent at 15 ℃ for 72 h, MTBE = methyl tert-butyl ether. [b] The diastereomeric ratios were determined by column chromatography. [c] Isolated yield after chromatography. [d] Determined by HPLC analysis.

**Table S2.** Screening of the Pd catalysts. [a]

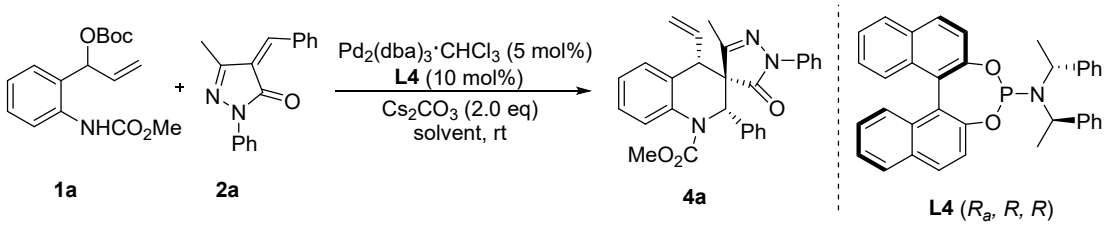



| entry | Metal | dr[b] | yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | $Pd_2(dba)_3$•$CHCl_3$ | > 20:1 | 69 | 96 |
| 2 | $[Pd(C_3H_5)Cl]_2$ | - | - | - |
| 3 | $Pd(OAc)_2$ | - | - | - |

[a] Unless otherwise stated, reactions were performed with **1a** (60 mg, 0.2 mmol) and **2a** (26 mg, 0.1 mmol), in 1.0 mL of solvent at 15 ℃ for 72 h, MTBE = methyl tert-butyl ether. [b] The diastereomeric ratios were determined by column chromatography. [c] Isolated yield after chromatography. [d] Determined by HPLC analysis.

### 3.2 Optimization of reaction conditions with P-N ligands.

**Table S3.** Screening of the solvents. [a]

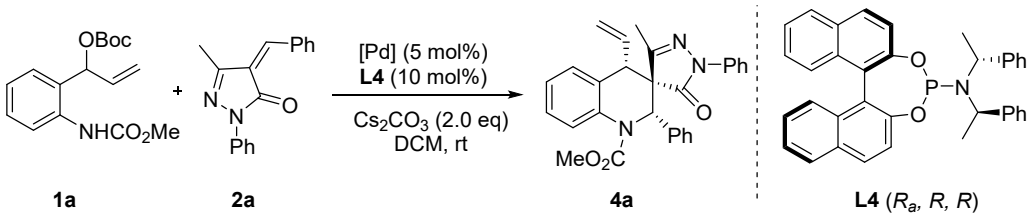



**1a** **2a** **4a** **L4** ($R_a$, *R*, *R*)

| entry | solvent | dr[b] | yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | DCM | > 20:1 | 89 | 87 |
| 2 | EA | 15:1 | 64 | 77 |
| 3 | Toluene | 10:1 | 44 | 75 |
| 4 | THF | > 20:1 | 44 | 80 |

[a] Unless otherwise stated, reactions were performed with **1a** (60 mg, 0.2 mmol) and **2a** (26 mg, 0.1 mmol), in 1.0 mL of solvent at 25 °C for 6 h. [b] The diastereomeric ratios were determined by column chromatography. [c] Isolated yield after chromatography. [d] Determined by HPLC analysis.

**Table S4.** Screening of the Pd catalysts. [a]



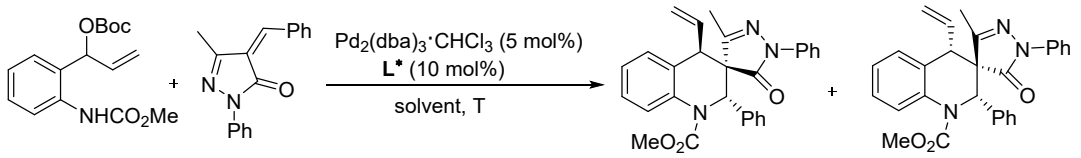

**1a** **2a** **4a** **L4** ($R_a$, *R*, *R*)

| entry | metal | dr[b] | yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | $Pd_2(dba)_3·CHCl_3$ | > 20:1 | 89 | 87 |
| 2 | $Pd_2(dba)_3$ | > 20:1 | 80 | 87 |
| 3 | $[Pd(C_3H_5)Cl]_2$ | > 20:1 | 42 | 33 |
| 4 | $Pd(OAc)_2$ | > 20:1 | 44 | 89 |
| 5 | $Pd(dba)_2$ | > 20:1 | 64 | 88 |

[a] Unless otherwise stated, reactions were performed with **1a** (60 mg, 0.2 mmol) and **2a** (26 mg, 0.1 mmol), in 1.0 mL of solvent at 25 °C for 6 h. [b] The diastereomeric ratios were determined by column chromatography. [c] Isolated yield after chromatography. [d] Determined by HPLC analysis.

### 3.3 Optimization of reaction conditions with Mengphos ligands.

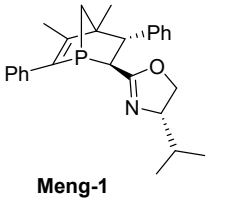
**Table S5.** Screening of the ligands, solvents and temperature. [a]



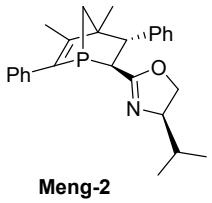

**1a** **2a** **5a** **4a**

| entry | solvent | ligand | T (℃) | yield (%)[b] | dr (**5a:4a**)[c] | ee (%)[d] |
|---|---|---|---|---|---|---|
| 1 | DCM | **Meng-1** | rt | 60 | 1:2 | 11 |
| 2 | DCE | **Meng-1** | rt | 51 | 1:1 | 7 |
| 3 | $CHCl_3$ | **Meng-1** | rt | 80 | 1:1 | 30 |
| 4 | EA | **Meng-1** | rt | trace | - | - |
| 5 | THF | **Meng-1** | rt | trace | - | - |
| 6 | $CHCl_3$ | **Meng-2** | rt | 89 | 1:1 | -28 |
| 7 | $CHCl_3$ | **Meng-3** | rt | 89 | 1:1 | 30 |
| 8 | $CHCl_3$ | **Meng-4** | rt | 60 | 1:1.25 | 26 |
| 9 | $CHCl_3$ | **L5** | rt | - | - | - |
| 10[e] | $CHCl_3$ | **L6** | rt | 82 | - | - |
| 11 | $CHCl_3$ | **Meng-1** | 0 | 56 | 1.25:1 | 32 |
| 12[f] | $CHCl_3$ | **Meng-1** | -10 | 62 | 1:1 | 52 |

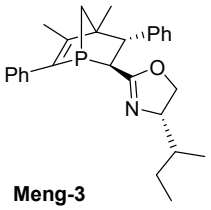
[a] Unless otherwise stated, reactions were performed with **1a** (60 mg, 0.2 mmol) and **2a** (26 mg, 0.1 mmol), in 1.0 mL of solvent at 25 ℃ for 6 h. [b] Isolated yield after chromatography. [c] The diastereomeric ratios were determined by column chromatography. [d] Determined by HPLC analysis. [e] Only **4a** was obtained. [f] Reaction was performed with **1b** (63 mg, 0.2 mmol) and **2b** (29 mg, 0.1 mmol).



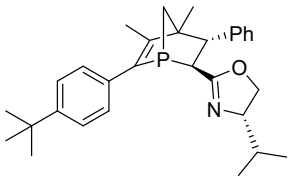

**Meng-1**



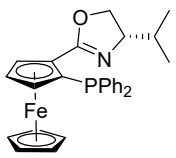

**Meng-2**



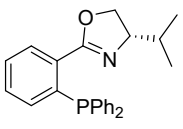

**Meng-3**




**Meng-4**

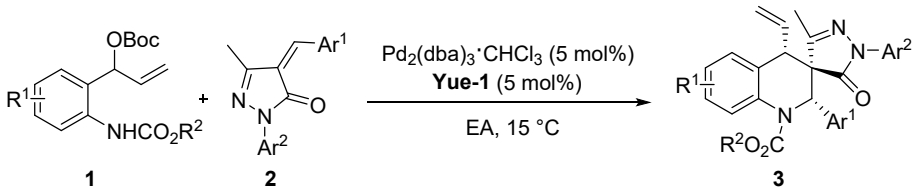



**L5**




**L6**

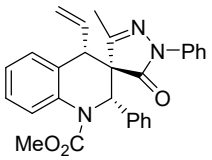
## 4. General Procedure for Reactions




**1** **2** **3**

To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.005 mmol) and ligand **Yue-1** (0.005 mmol), then 1 mL EA was added. This solution was stirred at room temperature for 0.5 h. Then, allyl carbonate **1** (0.2 mmol) and alkylidene pyrazolone **2** (0.1 mmol) were added subsequently. The reaction mixture was stirred at 15 ℃ for 72 h and monitored by TLC (ethyl acetate /petroleum ether). After complete conversion, the product **3** was obtained by chromatography on silica gel (ethyl acetate /petroleum ether).

**Methyl (2'*S*,4*R*,4'*S*)-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3a).**

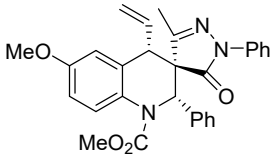



Purified by silica gel chromatography using PE/EA = 4:1, white solid (31 mg, 69% yield). $[\alpha]_D$ = +54 (*c* = 0.1, $CH_2Cl_2$, 30.1 °C). MP: 176.4 – 177.9 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.37 (m, 3H), 7.23 – 7.18 (m, 6H), 7.11 – 7.08 (m, 2H), 6.01 (s, 1H), 5.52 – 5.48 (m, 2H), 5.39 – 5.35 (m, 1H), 3.99 – 3.96 (m, 1H), 3.71 (s, 3H), 0.97 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.6, 159.3, 155.1, 138.7, 137.8, 137.4, 131.8, 130.3, 128.9, 128.6, 128.0, 127.8, 126.1, 125.7, 125.5, 125.3, 124.5, 123.3, 119.4, 67.6, 63.7, 53.4, 47.3, 16.9 ppm. HRMS (ESI) calcd for $C_{28}H_{26}N_3O_3^+$ $[M+H]^+$: 452.1969, found 452.1942. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.98 and 25.36 min.

Using (***R*$_P$, *R***)-**Yue-2** as ligand:

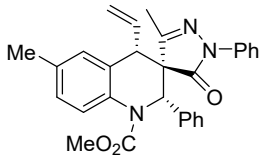
**3a':** Purified by silica gel chromatography using PE/EA = 4:1, white solid (33 mg, 73% yield). $[\alpha]_D$ = -33 (*c* = 0.1, $CH_2Cl_2$, 26.4 °C). HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.70 and 22.48 min.

**Methyl(2'*S*,4*R*,4'*S*)-6'-methoxy-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3b).**



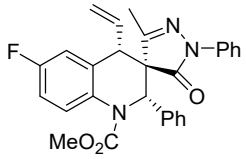
Purified by silica gel chromatography using PE/EA = 4:1, colourless oil(36 mg, 75% yield). $[\alpha]_D$ = +50 (*c* = 0.1, $CH_2Cl_2$, 30.5 °C). MP: 176.4 – 177.9 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.75 (t, *J* = 9.3 Hz, 3H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.23 – 7.18 (m, 4H), 7.10 – 7.08 (m, 2H), 6.97 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.75 (d, *J* = 2.9 Hz, 1H), 6.00 (s, 1H), 5.50 – 5.45 (m, 2H), 5.39 – 5.35 (m, 1H), 3.97 – 3.94 (m, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 1.02 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.7, 159.4, 157.1, 155.2, 138.8, 137.4, 133.3, 130.7, 130.1, 128.9, 128.6, 127.8, 126.7, 125.5, 124.5, 123.6, 119.3, 112.7, 112.2, 67.6, 63.6, 55.6, 53.4, 47.4, 16.9 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_4^+$ $[M+H]^+$: 482.2074, found 482.2073. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.03 and 23.10 min.

**Methyl(2'*S*,4*R*,4'*S*)-3,6'-dimethyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3c).**




Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (37.4 mg, 82% yield). $[\alpha]_D$ = +40 (*c* = 0.1, $CH_2Cl_2$, 27.8 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 – 7.75 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.26 – 7.15 (m, 5H), 7.11 – 7.07 (m, 2H), 2.1 Hz, 2H), 7.00 (s, 1H), 6.00 (s, 1H), 5.51 – 5.43 (m, 2H), 5.38 – 5.34 (m, 1H), 3.96 – 3.93 (m, 1H), 3.70 (s, 3H), 2.36 (s, 3H), 0.99 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.7, 159.4, 155.1, 138.8, 137.5, 135.2, 135.2, 131.6, 130.4, 128.9, 128.9, 128.6, 127.8, 126.6, 125.5, 124.5, 123.2, 119.4, 67.7, 63.7, 53.4, 47.3, 21.2, 17.0 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_3^+$ $[M+H]^+$: 466.2125, found 466.2114. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 5.67 and 15.75 min.

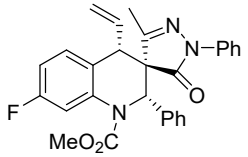
**Methyl(2'*S*,4*R*,4'*S*)-6'-fluoro-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3d).**




Purified by silica gel chromatography using PE/EA = 4:1, white solid (34 mg, 73% yield). $[\alpha]_D$ = +21 (*c* = 0.1, $CH_2Cl_2$, 28 °C). MP: 175.6 – 176.8 °C. $^1$H NMR (300

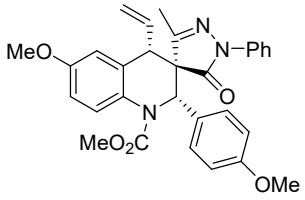
MHz, $CDCl_3$) $\delta$ 7.82 (dd, $J$ = 8.9, 5.0 Hz, 1H), 7.76 (d, $J$ = 8.1 Hz, 1H), 7.40 (t, $J$ = 7.9 Hz, 1H), 7.24 – 7.12 (m, 5H), 7.07 (dd, $J$ = 7.2, 2.5 Hz, 2H), 6.94 (dd, $J$ = 9.1, 2.9 Hz, 1H), 6.00 (s, 1H), 5.55 – 5.38 (m, 3H), 3.96 – 3.94 (m, 1H), 3.71 (s, 2H), 1.03 (s, 2H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.4, 15.8, 155.0, 138.5, 137.3, 134.0 (d, $J$ = 7.4 Hz), 133.7 (d, $J$ = 3.1 Hz), 129.6, 128.9, 128.7, 127.9, 127.2, 125.6, 124.4, 124.1, 119.3, 114.8 (d, $J$ = 22.7 Hz), 113.2 (d, $J$ = 24.2 Hz), 67.4, 63.6, 53.5, 47.1, 17.0 ppm. HRMS (ESI) calcd for $C_{28}H_{25}FN_3O_3^+$ $[M+H]^+$: 470.1874, found 470.1856. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 7.00 and 20.89 min.

**Methyl(2'*S*,4*R*,4'*S*)-7'-fluoro-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3e).**



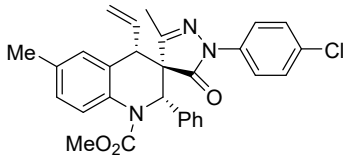

Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (24 mg, 51% yield). $[\alpha]_D$ = +32 ($c$ = 0.1, $CH_2Cl_2$, 30.5 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.77 – 7.73 (m, 2H), 7.64 (dd, $J$ = 10.1, 2.6 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.24 – 7.15 (m, 5H), 7.08 – 7.05 (m, 2H), 6.94 (td, $J$ = 8.4, 2.6 Hz, 1H), 5.97 (s, 1H), 5.53 – 5.43 (m, 2H), 5.40 – 5.36 (m, 1H), 3.94 – 3.91 (m, 1H), 3.71 (s, 3H), 1.05 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.4, 162.2 (d, $J$ = 246.0 Hz), 160.5, 158.9, 154.7, 138.9 (d, $J$ = 10.8 Hz), 138.4, 137.3, 130.1, 128.9, 128.7, 127.9, 127.3 (d, $J$ = 3.1 Hz), 127.1 (d, $J$ = 9.3 Hz), 125.6, 124.3, 123.6, 119.4, 113.2 (d, $J$ = 25.3 Hz), 112.2 (d, $J$ = 21.5 Hz), 67.3, 63.8, 53.6, 46.8, 17.2 ppm. HRMS (ESI) calcd for $C_{28}H_{25}FN_3O_3^+$ $[M+H]^+$: 470.1874, found 470.1885. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 5.71 and 15.24 min.

**Methyl(2'*S*,4*R*,4'*S*)-6'-methoxy-2'-(4-methoxyphenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3f).**



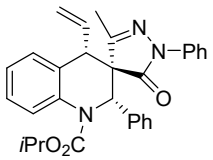
Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (27 mg, 53% yield). $[\alpha]_D$ = +26 (*c* = 0.1, $CH_2Cl_2$, 30.8 °C). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.79 – 7.76 (m, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.94 (m, 3H), 6.75 – 6.70 (m, 3H), 5.94 (s, 1H), 5.51 – 5.42 (m, 2H), 5.36 (dd, *J* = 7.1, 4.9 Hz, 1H), 3.95 – 3.92 (m, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H), 1.05 (s, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 172.7, 159.5, 158.9, 157.1, 155.2, 137.5, 133.4, 130.8, 130.7, 130.1, 128.9, 126.7, 125.6, 125.5, 123.5, 119.3, 113.9, 112.7, 112.1, 67.6, 63.2, 55.6, 55.1, 53.4, 47.3, 17.0 ppm. HRMS (ESI) calcd for $C_{30}H_{30}N_3O_5^+$ $[M+H]^+$: 512.2180, found 512.2189. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 86% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 9.25 and 17.21 min.

**Methyl(2'*S*,4*R*,4'*S*)-1-(4-chlorophenyl)-3,6'-dimethyl-5-oxo-2'-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3g).**



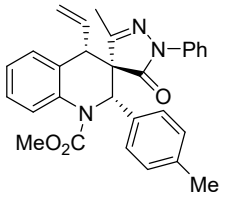

Purified by silica gel chromatography using PE/EA = 4:1, white solid (37 mg, 74% yield). $[\alpha]_D$ = +29 (*c* = 0.1, $CH_2Cl_2$, 29 °C). MP: 163.1 – 164.6 °C. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 – 7.73 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.27 – 7.23 (m, 1H), 7.21 – 7.15 (m, 3H), 7.06 (dd, *J* = 7.1, 2.6 Hz, 2H), 6.99 (d, *J* = 1.9 Hz, 1H), 5.98 (s, 1H), 5.59 – 5.41 (m, 2H), 5.37 – 5.33 (m, 1H), 3.95 – 3.92 (m, 1H), 3.70 (s, 3H), 2.37 (s, 3H), 0.98 (s, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 172.7, 159.8, 155.1, 138.7, 136.0, 135.2, 135.1, 131.4, 130.6, 130.3, 128.9, 128.6, 128.6, 127.8, 126.6, 125.5, 124.4, 123.2, 120.2, 67.8, 63.7, 53.4, 47.3, 21.2, 17.0 ppm. HRMS (ESI) calcd for $C_{29}H_{27}ClN_3O_3^+$ $[M+H]^+$: 500.1735, found 500.1697. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 83% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 7.21 and 34.99 min.

**Isopropyl(2'*S*,4*R*,4'*S*)-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3h).**



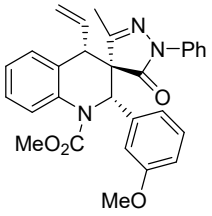
Purified by silica gel chromatography using PE/EA = 4:1, white solid (37 mg, 77% yield). $[\alpha]_D$ = +24 (*c* = 0.1, $CH_2Cl_2$, 28.8 °C). MP: 150.2 – 151.5 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.93 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.46 – 7.36 (m, 3H), 7.23 – 7.15 (m, 6H), 7.12 – 7.07 (m, 2H), 5.93 (s, 1H), 5.50 (td, *J* = 5.8, 2.5 Hz, 2H), 5.37 (dd, *J* = 7.1, 4.8 Hz, 1H), 4.91 (p, *J* = 6.2 Hz, 1H), 4.00 (dd, *J* = 5.7, 3.3 Hz, 1H), 1.23 (d, *J* = 6.2 Hz, 3H), 1.04 (s, 3H), 0.89 (d, *J* = 6.2 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.6, 159.3, 153.9, 139.3, 137.9, 137.4, 131.2, 130.5, 128.9, 128.5, 127.9, 127.6, 126.1, 125.5, 125.3, 124.9, 124.5, 123.2, 119.4,70.3, 67.2, 63.8, 47.2, 22.0, 21.5, 17.0 ppm. HRMS (ESI) calcd for $C_{30}H_{30}N_3O_3^+$ $[M+H]^+$: 480.2282, found 480.2254. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 93:7, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.99 and 11.74 min.

**Methyl(2'*S*,4*R*,4'*S*)-3-methyl-5-oxo-1-phenyl-2'-(p-tolyl)-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3i).**



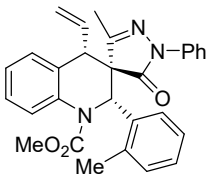

Purified by silica gel chromatography using PE/EA = 4:1, white solid (39 mg, 83% yield). $[\alpha]_D$ = +34 (*c* = 0.1, $CH_2Cl_2$, 30.1 °C). MP: 133.4 – 135.5 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.84 – 7.76 (m, 3H), 7.47 – 7.37 (m, 3H), 7.24 – 7.18 (m, 3H), 6.98 – 6.95 (m, 4H), 5.98 (s, 1H), 5.44 – 5.58 (m, 2H), 5.44 – 5.24 (m, 1H), 3.98 – 3.95 (m, 1H), 3.71 (s, 3H), 2.24 (s, 3H), 0.98 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.7, 159..5, 155.7, 137.8, 137.5, 137.4, 135.7, 131.8, 130.3, 129.3, 128.9, 128.0, 128.0, 126.1, 125.7, 125.5, 125.3, 124.3, 123.3, 119.4, 67.7, 63.5, 53.4, 47.3, 21.1, 17.0 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_3^+$ $[M+H]^+$: 466.2125, found 466.2086. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.02 and 15.99 min.

**Methyl(2'*S*,4*R*,4'*S*)-2'-(3-methoxyphenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3j).**



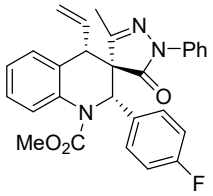

Purified by silica gel chromatography using PE/EA = 4:1, white solid (31 mg, 65% yield). $[\alpha]_D$ = +11 (*c* = 0.1, $CH_2Cl_2$, 27.5 °C). MP: 120.3 – 122.2 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83 – 7.77 (m, 3H), 7.47 – 7.36 (m, 3H), 7.22 – 7.18 (m, 3H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.70 (dd, *J* = 8.1, 2.2 Hz, 2H), 6.60 (t, *J* = 2.1 Hz, 1H), 5.98 (s, 1H), 5.52 – 5.48 (m, 2H), 5.39 – 5.35 (m, 1H), 3.98 – 3.95 (m, 1H), 3.72 (s, 3H), 3.55 (s, 3H), 0.99 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.7, 159.7, 159.4, 155.0, 140.4, 137.7, 137.4, 131.7, 130.3, 129.7, 128.9, 128.0, 126.1, 125.7, 125.5, 125.3, 123.3, 119.2, 116.6, 109.8, 67.6, 63.7, 54.9, 53.5, 47.2, 16.9 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_4^+$ $[M+H]^+$: 482.2074, found 482.2088. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 10.89 and 25.56 min.

**Methyl(2'*S*,4*R*,4'*S*)-3-methyl-5-oxo-1-phenyl-2'-(o-tolyl)-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3k).**



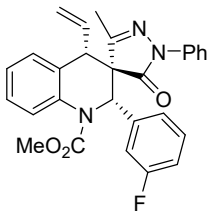

Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (32 mg, 69% yield). $[\alpha]_D$ = +18 (*c* = 0.1, $CH_2Cl_2$, 30.9 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.80 – 7.75 (m, 3H), 7.47 (dt, *J* = 8.5, 4.4 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.22 – 7.16 (m, 1H), 7.08 – 6.98 (m, 3H), 6.21 (s, 1H), 5.60 – 5.42 (m, 2H), 5.36 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.98 (d, *J* = 8.4 Hz, 1H), 3.71 (s, 3H), 2.20 (s, 3H), 1.18 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.5, 159.4, 154.8, 138.5, 137.4, 135.2, 131.9, 131.1, 130.0, 128.9, 128.0, 127.7, 126.1, 125.6, 125.4, 125.4, 125.3, 123.7, 119.0, 67.4, 60.9, 53.4, 47.5, 19.2, 17.6 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_3^+$ $[M+H]^+$: 466.2125, found 466.2132. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 80% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.19 and 11.69 min.

**Methyl(2'*S*,4*R*,4'*S*)-2'-(4-fluorophenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3l).**



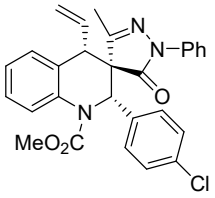

Purified by silica gel chromatography using PE/EA = 4:1, white solid (28.4 mg, 60% yield). $[\alpha]_D$ = +34 (*c* = 0.1, $CH_2Cl_2$, 27.3 °C). MP: 165.1 – 166.5 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.81 – 7.74 (m, 3H), 7.48 – 7.37 (m, 3H), 7.25 – 7.19 (m, 3H), 7.08 (dd, *J* = 8.6, 5.2 Hz, 2H), 6.89 (t, *J* = 8.6 Hz, 2H), 5.96 (s, 1H), 5.49 (td, *J* = 5.8, 2.6 Hz, 2H), 5.38 (dd, *J* = 7.1, 4.8 Hz, 1H), 3.97 (dd, *J* = 5.6, 3.3 Hz, 1H), 3.72 (s, 3H), 0.99 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.4, 163.7, 159.1, 155.0, 137.6, 137.3, 134.6 (d, *J* = 3.3 Hz), 131.6, 130.2, 128.9, 128.1, 126.2, 126.1, 125.5, 123.4, 119.3, 115.8, 115.5, 67.5, 63.3, 53.5, 47.2, 17.0 ppm. HRMS (ESI) calcd for $C_{28}H_{25}FN_3O_3^+$ $[M+H]^+$: 470.1874, found 470.1874. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.51 and 13.94 min.

**Methyl(2'*S*,4*R*,4'*S*)-2'-(3-fluorophenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3m).**



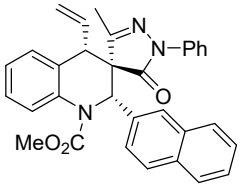

Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (25.9 mg, 55% yield). $[\alpha]_D$ = +50 (*c* = 0.1, $CH_2Cl_2$, 30.5 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.81 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.26 – 7.16 (m, 4H), 6.91 – 6.84 (m, 3H), 5.98 (s, 1H), 5.52 – 5.48 (m, 2H), 5.40 – 5.37 (m, 1H), 3.98 – 3.95 (m, 1H), 3.73 (s, 3H), 1.00 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.4, 158.9, 155.0, 137.4, 137.3, 131.5, 130.4 (d, *J* = 8.1 Hz), 130.1, 128.9, 128.2, 126.2, 125.7, 125.7, 125.5, 123.5, 120.4 (d, *J* = 3.1 Hz),119.4, 118.8, 114.8 (d, *J* = 21.4 Hz), 111.6 (d, *J* = 23.0 Hz), 67.8, 63.3, 53.6, 47.3, 16.9 ppm. HRMS (ESI) calcd for $C_{28}H_{25}FN_3O_3^+$ $[M+H]^+$: 470.1874, found 470.1874. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.96 and 13.49 min.

**Methyl(2'*S*,4*R*,4'*S*)-2'-(4-chlorophenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3n).**



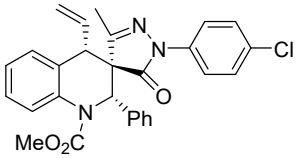

Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (26.3 mg, 54% yield). $[\alpha]_D$ = +13 (*c* = 0.1, $CH_2Cl_2$, 30.4 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.81 – 7.74 (m, 3H), 7.48 – 7.37 (m, 3H), 7.24 – 7.16 (m, 6H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.95 (s, 1H), 5.49 (td, *J* = 5.7, 2.5 Hz, 2H), 5.38 (dd, *J* = 7.1, 4.8 Hz, 1H), 3.97 (dd, *J* = 5.7, 3.3 Hz, 1H), 3.72 (s, 3H), 0.99 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.4, 158.9, 155.0, 137.5, 137.4, 137.3, 133.5, 131.5, 130.1, 128.9, 128.1, 126.2, 125.9, 125.7, 125.6, 125.5, 123.5, 119.3, 67.4, 63.3, 53.5, 47.2, 17.0 ppm. HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_3^+$ $[M+H]^+$: 486.1579, found 486.1588. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.44 and 17.03 min.

**Mmethyl(2'*S*,4*R*,4'*S*)-3-methyl-2'-(naphthalen-2-yl)-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3o).**



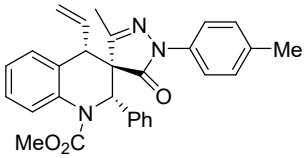

Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (36.2 mg, 72% yield). $[\alpha]_D$ = +62 (*c* = 0.1, $CH_2Cl_2$, 29.9 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.94 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.72 (m, 3H), 7.69 – 7.63 (m, 2H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.44 – 7.37 (m, 4H), 7.25 – 7.15 (m, 4H), 6.17 (s, 1H), 5.54 – 5.45 (m, 2H), 5.39 (dd, *J* = 7.1, 4.7 Hz, 1H), 4.04 (dd, *J* = 5.8, 3.3 Hz, 1H), 3.69 (s, 3H), 0.95 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.7, 159.3, 155.1, 137.9, 137.4, 133.1, 132.9, 131.8, 130.3, 128.9, 128.7, 128.1, 127.9, 127.7, 126.4, 126.2, 126.1, 125.7, 125.6, 125.4, 123.4, 123.3, 122.6, 119.5, 67.7, 63.8, 53.5, 47.3, 17.0 ppm. HRMS (ESI) calcd for $C_{32}H_{28}N_3O_3^+$ $[M+H]^+$: 502.2125, found 502.2142. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 85% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 9.20 and 18.64 min.

**Methyl(2'*S*,4*R*,4'*S*)-1-(4-chlorophenyl)-3-methyl-5-oxo-2'-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3p).**



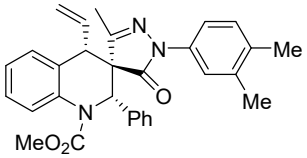

Purified by silica gel chromatography using PE/EA = 4:1, white solid (30 mg, 61% yield). $[\alpha]_D$ = +13 (*c* = 0.1, $CH_2Cl_2$, 27.7 °C). MP: 159.7 – 161.2 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.45 (ddd, *J* = 9.9, 6.4, 2.2 Hz, 1H), 7.36 – 7.34 (m, 2H), 7.23 – 7.16 (m, 5H), 7.07 (dd, *J* = 7.0, 2.6 Hz, 2H), 5.99 (s, 1H), 5.48 (td, *J* = 5.8, 4.9, 2.8 Hz, 2H), 5.40 – 5.29 (m, 1H), 4.05 – 3.92 (m, 1H), 3.71 (s, 3H), 0.97 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.6, 159.6, 155.0, 138.6, 137.7, 136.0, 131.6, 130.6, 130.2, 128.9, 128.7, 128.1, 127.9, 126.1, 125.7, 125.4, 124.4, 123.4, 120.2, 67.7, 63.7, 53.5, 47.3, 16.9 ppm. HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_3^+$ $[M+H]^+$: 486.1579, found 486.1565. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 7.64 and 30.34 min.

**Methyl(2'*S*,4*R*,4'*S*)-3-methyl-5-oxo-2'-phenyl-1-(p-tolyl)-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3q).**

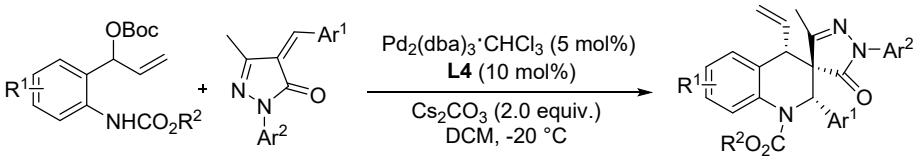



Purified by silica gel chromatography using PE/EA = 4:1, white solid (38.2 mg, 82% yield). $[\alpha]_D$ = +31 (*c* = 0.1, $CH_2Cl_2$, 28.5 °C). MP: 185.9 – 187.3 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.47 – 7.41 (m, 1H), 7.23 – 7.17 (m, 7H), 7.10 – 7.07 (m, 2H), 6.00 (s, 1H), 5.52 – 5.44 (m, 2H), 5.39 – 5.35 (m, 1H), 3.98 – 3.95 (m, 1H), 3.71 (s, 3H), 2.35 (s, 3H), 0.96 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.4, 159.1, 155.1, 138.8, 137.8, 135.3, 135.0, 131.8, 130.3, 129.4, 128.6, 128.0, 127.8, 126.1, 125.7, 125.3, 124.5, 123.2, 119.4, 67.5, 63.7, 53.4, 47.2, 21.0, 16.9 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_3^+$ $[M+H]^+$: 466.2125, found 466.2108. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 9.56 and 48.00 min.

**Methyl(2'*S*,4*R*,4'*S*)-1-(3,4-dimethylphenyl)-3-methyl-5-oxo-2'-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (3r).**



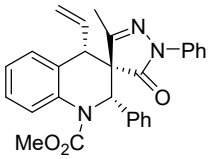

Purified by silica gel chromatography using PE/EA = 3:1, white solid (38.1 mg, 79% yield). $[\alpha]_D$ = +19 (*c* = 0.1, $CH_2Cl_2$, 29.1 °C). MP: 162.2 – 163.4 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.22 – 7.08 (m, 8H), 6.00 (s, 1H), 5.54 – 5.44 (m, 2H), 5.39 – 5.35 (m, 1H), 3.98 – 3.95 (m, 1H), 3.71 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 0.96 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.4, 159.1, 155.1, 138.8, 137.8, 137.2, 135.3, 134.1, 131.8, 130.3, 129.9, 128.6, 128.0, 127.8, 126.1, 125.7, 125.3, 124.5, 123.3, 120.5, 117.0, 67.5, 63.7, 53.4, 47.2, 20.0, 19.3, 16.9 ppm. HRMS (ESI) calcd for $C_{30}H_{30}N_3O_3^+$ $[M+H]^+$: 480.2282, found 480.2254. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 89% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 5.67 and 18.44 min.




**1** **2** **4**

To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.005 mmol) and ligand **L4** (0.01 mmol), then 1 mL DCM was added. This solution was stirred at room temperature for 0.5 h. Then, allyl carbonate **1** (0.2 mmol), alkylidene pyrazolone **2** (0.1 mmol) and $Cs_2CO_3$ (65.2 mg, 0.2 mmol, 2.0 equiv.) were added subsequently. The reaction mixture was stirred at -20 °C for 72 h and monitored by TLC. After complete conversion, the product **4** was obtained by chromatography on silica gel.

**Methyl(2'*S*,4*S*,4'*S*)-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4a).**



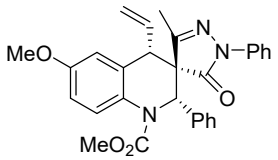

Purified by silica gel chromatography using PE/EA = 4:1, white solid (38.4 mg, 85% yield). Yield: 85%. $[\alpha]_D$ = +94 (*c* = 0.1, $CH_2Cl_2$, 28.6 °C). MP: 82.6 – 83.9 °C. $^1$H

NMR (300 MHz, $CDCl_3$) $\delta$ 7.70 (dd, $J$ = 8.1, 1.2 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.25 – 7.09 (m, 11H), 7.03 – 6.98 (m, 1H), 5.72 (s, 1H), 5.62 (dt, $J$ = 17.3, 9.6 Hz, 1H), 5.47 – 5.41 (m, 2H), 3.91 (d, $J$ = 9.6 Hz, 1H), 3.73 (s, 3H), 2.43 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.9, 157.8, 155.2, 137.7, 137.5, 136.9, 131.6, 130.4, 128.4, 128.3, 127.9, 127.7, 126.7, 126.0, 125.1, 122.0, 119.3, 65.2, 61.7, 53.4, 46.6, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{26}N_3O_3^+$ $[M+H]^+$: 452.1969, found 452.1992. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 93:7, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.62 and 17.19 min.

Using (***S*$_a$, *S*,*S***)-**L1** as ligand:

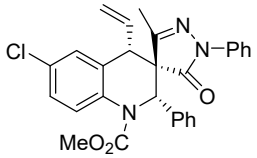
**4a':** Purified by silica gel chromatography using PE/EA = 4:1, white solid (31 mg, 69% yield). $[\alpha]_D$ = -147 (*c* = 0.1, $CH_2Cl_2$, 26.6 °C). HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 93:7, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.63 and16.88 min.

**Methyl(22'*S*,4*S*,4'*S*)-6'-methoxy-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4b).**



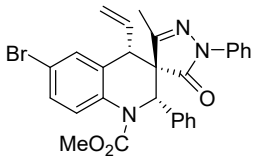

Purified by silica gel chromatography using PE/EA = 3:1, colourless oil (32.3 mg, 67% yield). $[\alpha]_D$ = +110 (*c* = 0.1,, $CH_2Cl_2$, 30.1 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.62 (d, $J$ = 8.8 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.19 – 7.11 (m, 6H), 7.06 – 7.01 (m, 1H), 6.97 (dd, $J$ = 8.8, 2.9 Hz, 1H), 6.71 – 6.70 (m, 1H), 5.74 (s, 1H), 5.62 (dt, $J$ = 17.5, 9.3 Hz, 1H), 5.46 (dq, $J$ = 13.0, 1.9 Hz, 2H), 3.90 (d, $J$ = 9.5 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.45 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.9, 157.9, 156.9, 155.4, 137.8, 136.9, 131.9, 131.5, 130.5, 128.4, 128.3, 127.9, 126.0, 125.9, 125.1, 122.2, 119.3, 112.9, 112.3, 65.1, 61.4, 55.3, 53.4, 46.6, 14.3 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_4^+$ $[M+H]^+$: 482.2074, found 482.2078. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.91 and 7.80 min.

**Methyl(2'*S*,4*S*,4'*S*)-6'-chloro-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4c).**



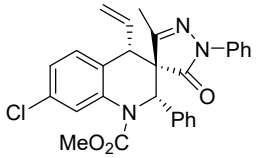

Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (34.5 mg, 71% yield). $[\alpha]_D$ = +163 (*c* = 0.1, $CH_2Cl_2$, 30.1 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.64 (d, *J* = 8.6 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.22 – 7.10 (m, 10H), 7.05 – 7.00 (m, 1H), 5.68 (s, 1H), 5.63 – 5.42 (m, 3H), 3.88 (d, *J* = 8.9 Hz, 1H), 3.73 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.8, 157.5, 154.9, 137.3, 136.7, 136.1, 132.2, 130.9, 130.6, 128.5, 128.3, 128.1, 127.8, 126.9, 126.1, 126.0, 125.3, 122.7, 119.4, 64.8, 61.7, 53.5, 46.3, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_3^+$ $[M+H]^+$: 486.1579, found 486.1552. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.66 and 7.83 min.

**Methyl(*2'S,4S,4'S*)-6'-bromo-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4d).**



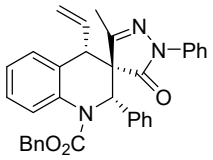

Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (22.1 mg, 42% yield). $[\alpha]_D$ = +143 (*c* = 0.1, $CH_2Cl_2$, 31.0 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.61 – 7.52 (m, 2H), 7.25 – 7.11 (m, 10H), 7.06 – 7.00 (m, 1H), 5.67 (s, 1H), 5.60 – 5.43 (m, 3H), 3.88 (d, *J* = 8.9 Hz, 1H), 3.73 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.8, 157.5, 154.8, 137.3, 136.7, 132.5, 130.9, 130.7, 129.7, 128.5, 128.3, 128.1, 126.4, 125.9, 125.3, 122.8, 119.4, 118.5, 64.8, 61.7, 53.5, 46.3, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{25}BrN_3O_3^+$ $[M+H]^+$: 530.1074, found 530.1076. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.58 and 10.41 min.

**Methyl(2'*S*,4*S*,4'*S*)-7'-chloro-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4e).**




Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (40.1 mg, 82% yield). $[\alpha]_D$ = +167 (*c* = 0.1, $CH_2Cl_2$, 30.1 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.73 (d, *J* = 2.0 Hz, 1H), 7.23 – 7.10 (m, 10H), 7.06 – 6.99 (m, 2H), 5.67 (s, 1H), 5.58 (dt, *J* = 18.1, 9.1 Hz, 1H), 5.44 (dq, *J* = 12.6, 2.1 Hz, 2H), 3.86 (d, *J* = 9.3 Hz, 1H), 3.74 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.9, 157.6, 154.8, 138.5, 137.3, 136.8, 133.2, 131.2, 128.8,128.5, 128.4, 128.1, 127.6, 126.0, 125.3, 125.2, 125.1, 122.5, 119.4, 64.9, 61.8, 53.6, 46.2, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_3^+$ $[M+H]^+$: 486.1579, found 486.1586. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 5.59 and 11.66 min.

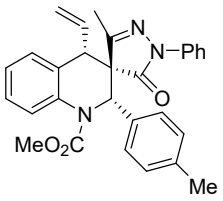
**Benzyl(2'*S*,4*S*,4'*S*)-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4f).**




Purified by silica gel chromatography using PE/EA = 3:1, colourless oil (37 mg, 70% yield). $[\alpha]_D$ = +187 (*c* = 0.1, $CH_2Cl_2$, 30.0 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.75 (d, *J* = 8.0 Hz, 1H),, 7.41 (td, *J* = 7.7, 1.7 Hz, 1H), 7.27 – 7.22 (m, 5H), 7.19 – 7.08 (m, 11H), 7.03 – 6.97 (m, 1H), 5.71 (s, 1H), 5.61 (dt, *J* = 17.2, 9.6 Hz, 1H), 5.46 – 5.40 (m, 2H), 5.17 (s, 2H), 3.92 (d, *J* = 9.6 Hz, 1H), 2.40 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.9, 157.7, 154.5, 137.8, 137.5, 136.9, 135.8, 131.7, 130.1, 128.4, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 126.7, 126.1, 125.1, 125.0, 125.0, 122.0, 119.3, 68.0, 65.0, 61.8, 46.6, 14.3 ppm. HRMS (ESI) calcd for $C_{34}H_{29}N_3NaO_3^+$ $[M+H]^+$: 550.2101, found 550.2139. HPLC: The product was analyzed by HPLC to determine

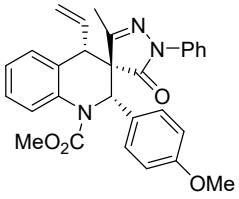
the enantiomeric excess: 93% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.47 and 23.67 min.

**Methyl(2'*S*,4*S*,4'*S*)-3-methyl-5-oxo-1-phenyl-2'-(p-tolyl)-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4g).**




Purified by silica gel chromatography using PE/EA = 4:1, white solid (41 mg, 87% yield). $[\alpha]_D$ = +122 (*c* = 0.1, $CH_2Cl_2$, 29.0 °C). MP: 78.3 – 79.6 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.68 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.12 (m, 6H), 7.05 – 6.94 (m, 5H), 5.68 (s, 1H), 5.64 – 5.55 (m, 1H), 5.46 – 5.40 (m, 2H), 3.90 (d, *J* = 9.7 Hz, 1H), 3.73 (s, 3H), 2.41 (s, 3H), 2.16 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.0, 157.9, 155.2, 137.5, 137.0, 134.7, 131.7, 130.4, 128.9, 128.4, 127.6, 126.7, 126.0, 125.1, 125.0, 121.9, 119.3, 65.2, 61.6, 53.4, 46.7, 21.0, 14.3 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_4^+$ $[M+H]^+$: 452.1969, found 452.1992. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.58 and 13.44 min.

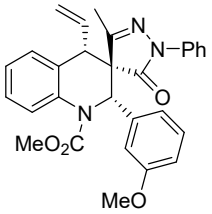
**Methyl(2'*S*,4*S*,4'*S*)-2'-(4-methoxyphenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4h).**




Purified by silica gel chromatography using PE/EA = 3:1, white solid (40 mg, 83% yield). $[\alpha]_D$ = +104 (*c* = 0.1, $CH_2Cl_2$, 28.8 °C). MP: 163.5 – 165.2 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.66 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.31 – 7.28 (m, 2H), 7.24 – 7.12 (m, 4H), 7.10 – 6.99 (m, 3H), 6.70 – 6.68 (m, 2H), 5.67 (s, 1H), 5.65 – 5.56 (m, 1H), 5.46 – 5.40 (m, 2H), 3.90 (d, *J* = 9.7 Hz, 1H), 3.73 (s, 3H), 3.64 (s, 3H), 2.41 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.0, 159.0, 157.9, 155.2,

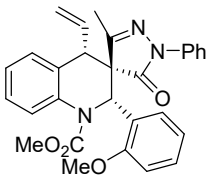
137.5, 137.0, 131.7, 130.4, 129.8, 128.4, 127.6, 127.4, 126.7, 125.1, 125.0, 121.9, 119.3, 113.7, 65.3, 61.4, 55.2, 53.4, 46.6, 14.3 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_4^+$ $[M+H]^+$: 482.2074, found 482.2089. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 9.91 and 25.75 min.

**Methyl(2'*S*,4*S*,4'*S*)-2'-(3-methoxyphenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4i).**



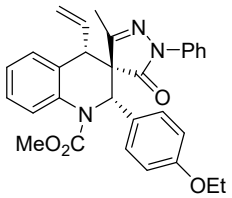

Purified by silica gel chromatography using PE/EA = 3:1, white solid (34.2 mg, 71% yield). $[\alpha]_D$ = +154 (*c* = 0.1, $CH_2Cl_2$, 23.0 °C). MP: 128.5 – 129.6 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.68 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.42 (td, *J* = 7.9, 1.4 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.21 – 6.99 (m, 6H), 6.75 – 6.72 (m, 1H), 6.69 (t, *J* = 2.1 Hz, 1H), 6.64 – 6.60 (m, 1H), 5.70 (s, 1H), 5.62 (dt, *J* = 17.3, 9.6 Hz, 1H), 5.43 (dq, *J* = 12.5, 1.8 Hz, 2H), 3.89 (d, *J* = 9.7 Hz, 1H), 3.74 (s, 3H), 3.63 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.8, 159.4, 157.8, 155.2, 139.3, 137.5, 137.0, 131.6, 130.4, 129.3, 128.4, 127.7, 126.7, 125.1, 125.0, 125.0, 122.0, 119.2, 118.3, 113.3, 111.9, 65.1, 61.6, 55.1, 53.4, 46.7, 14.3 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_4^+$ $[M+H]^+$: 482.2074, found 482.2049. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.22 and 15.44 min.

**Methyl(2'*S*,4*S*,4'*S*)-2'-(2-methoxyphenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4j).**



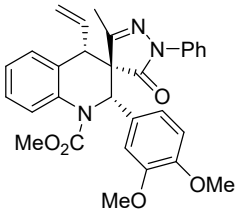
Purified by silica gel chromatography using PE/EA = 3:1, colourless oil (26.9 mg, 56% yield). $[\alpha]_D$ = +189 (*c* = 0.1, $CH_2Cl_2$, 31.0 °C). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.68 (d, *J* = 8.0 Hz, 1H), 7.43 (ddd, *J* = 8.8, 7.4, 1.6 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.21 – 7.13 (m, 4H), 7.07 – 6.98 (m, 2H), 6.81 (td, *J* = 7.6, 1.1 Hz, 1H), 6.66 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.26 (s, 1H), 5.61 (dt, *J* = 17.3, 9.6 Hz, 1H), 5.46 – 5.39 (m, 2H), 3.89 (d, *J* = 9.7 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.38 (s, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 170.0, 159.6, 155.8, 155.1, 137.9, 137.2, 131.7, 130.9, 128.7, 128.4, 128.2, 127.5, 126.8, 126.7, 125.1, 124.8, 121.9, 120.5, 119.1, 109.9, 64.6, 55.6, 54.9, 53.4, 46.8, 14.3 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_4^+$ $[M+H]^+$: 482.2074, found 482.2078. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 93:7 flow rate 1.0 mL/min, λ = 254 nm); tr = 7.89 and 10.45 min.

**Methyl(2'*S*,4*S*,4'*S*)-2'-(4-ethoxyphenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4k).**



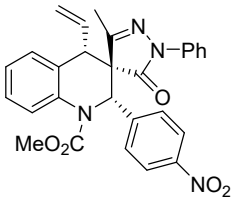

Purified by silica gel chromatography using PE/EA = 3:1, colourless oil (32.4 mg, 66% yield). $[\alpha]_D$ = +108 (*c* = 0.1, $CH_2Cl_2$, 29.9 °C). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.31 – 7.28 (m, 2H), 7.23 – 7.12 (m, 5H), 7.08 – 6.99 (m, 3H), 6.68 (d, *J* = 8.7 Hz, 2H), 5.68– 5.56 (m, 2H), 5.46 – 5.40 (m, 2H), 3.91 – 3.83 (m, 3H), 3.73 (s, 3H), 2.41 (s, 3H), 1.28 (t, *J* = 6.9 Hz, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 170.0, 158.3, 157.9, 155.2, 137.5, 137.0, 131.7, 130.4, 129.6, 128.4, 127.6, 127.4, 126.7, 125.1, 121.9, 119.3, 114.3, 65.3, 63.3, 61.4, 53.4, 46.6, 14.7, 14.3 ppm. HRMS (ESI) calcd for $C_{30}H_{30}N_3O_4^+$ $[M+H]^+$: 496.2231, found 496.2210. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10 flow rate 1.0 mL/min, λ = 254 nm); tr = 10.36 and 32.75 min.

**Methyl(2'*S*,4*S*,4'*S*)-2'-(3,4-dimethoxyphenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4l).**




Purified by silica gel chromatography using PE/EA = 2:1, colourless oil (33.2 mg, 65% yield). $[\alpha]_D$ = +112 (*c* = 0.1, $CH_2Cl_2$, 30.0 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.65 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.35 – 7.32 (m, 2H), 7.23 – 7.13 (m, 4H), 7.05 – 6.99 (m, 1H), 6.74 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.67 – 6.64 ((m, 2H), 5.69 (s, 1H), 5.65 – 5.56 (m, 1H), 5.47 – 5.40 (m, 2H), 3.89 (d, *J* = 9.7 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.69 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.0, 158.0, 155.2, 148.6, 148.4, 137.5, 137.0, 131.6, 130.6, 130.2, 128.5, 127.6, 126.7, 125.2, 125.0, 125.0, 122.0, 119.0, 118.6, 110.7, 109.5, 65.4, 61.5, 55.8, 55.7, 53.4, 46.7, 14.3 ppm. HRMS (ESI) calcd for $C_{30}H_{30}N_3O_5^+$ $[M+H]^+$: 512.2180, found 512.2147. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15 flow rate 1.0 mL/min, λ = 254 nm); tr = 10.36 and 32.75 min.

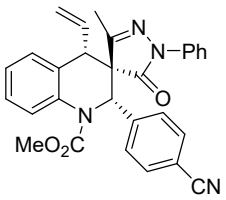
**Methyl(2'*S*,4*S*,4'*S*)-3-methyl-2'-(4-nitrophenyl)-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4m).**




Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (35 mg, 70% yield). $[\alpha]_D$ = +70 (*c* = 0.1, $CH_2Cl_2$, 29.3 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.04 (d, *J* = 8.8 Hz, 2H), 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.34 – 7.23 (m, 6H), 7.19 – 7.13 (m, 3H), 7.06 – 7.00 (m, 1H), 5.78 (s, 1H), 5.61 (dt, *J* = 18.1, 9.1 Hz, 1H), 5.48 (dq, *J* = 13.1, 2.0 Hz, 2H), 3.94 (d, *J* = 9.4 Hz, 1H), 3.76 (s, 3H), 2.46 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.4, 157.4, 155.2, 147.3, 145.3, 136.9,

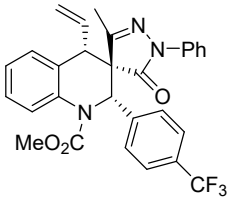
136.6, 131.0, 129.8, 128.6, 128.0, 127.2, 126.9, 125.5, 125.4, 124.9, 123.6, 122.6, 118.8, 64.8, 61.1, 53.7, 46.7, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{25}N_4O_5^+$ $[M+H]^+$: 497.1819, found 497.1822. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 84% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 80:20 flow rate 1.0 mL/min, λ = 254 nm); tr = 9.16 and 27.69 min.

**Methyl(2'*S*,4*S*,4'*S*)-2'-(4-cyanophenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4n).**




Purified by silica gel chromatography using PE/EA = 4:1, white solid (38 mg, 79% yield). $[\alpha]_D$ = +96 (*c* = 0.1, $CH_2Cl_2$, 29.9 °C). MP: 87.9 – 89.5 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.68 – 7.65 (m, 1H), 7.49 – 7.43 (m, 3H), 7.27 – 7.24 (m, 5H), 7.22 – 7.14 (m, 3H), 7.08 – 7.03 (m, 1H), 5.73 (s, 1H), 5.67 – 5.55 (m, 1H), 5.49 – 5.43 (m, 2H), 3.92 (d, *J* = 9.4 Hz, 1H), 3.76 (s, 3H), 2.44 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.5, 157.5, 155.2, 143.3, 136.9, 136.6, 132.1, 131.1, 129.9, 128.6, 127.9, 127.0, 123.9, 125.5, 124.9, 122.5, 118.9, 118.4, 111.8, 64.9, 61.2, 53.6, 46.6, 14.3 ppm. HRMS (ESI) calcd for $C_{29}H_{25}N_4O_3^+$ $[M+H]^+$: 477.1921, found 477.1907. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 86% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.71 and 27.78 min.

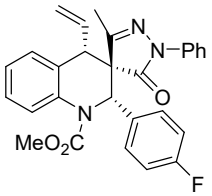
**Methyl(2'*S*,4*S*,4'*S*)-3-methyl-5-oxo-1-phenyl-2'-(4-(trifluoromethyl)phenyl)-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4o).**




Purified by silica gel chromatography using PE/EA = 4:1, white solid (30.1 mg, 58% yield). $[\alpha]_D$ = +84 (*c* = 0.1, $CH_2Cl_2$, 29.0 °C). MP: 76.5 – 78.4 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.69 – 7.66 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 3H), 7.28 – 7.23 (m, 3H), 7.21 –

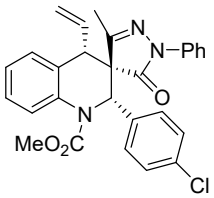
7.12 (m, 5H), 7.06 – 7.00 (m, 1H), 5.75 (s, 1H), 5.68 – 5.56 (m, 1H), 5.50 – 5.43 (m, 2H), 3.93 (d, $J$ = 9.6 Hz, 1H), 3.75 (s, 3H), 2.44 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.7, 157.6, 155.2, 148.3, 141.9, 137.1, 136.6, 131.3, 130.1,130.1(d, $J$ = 32.5 Hz), 129.8, 128.5, 127.8, 126.8, 126.6, 125.5, 125.4, 125.3, 125.0, 122.3, 119.3, 64.9, 61.2, 53.6, 46.6, 14.3 ppm. HRMS (ESI) calcd for $C_{29}H_{25}F_3N_3O_3^+$ $[M+H]^+$: 520.1843, found 520.1863. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.49 and 11.39 min.

**Methyl(2'*S*,4*S*,4'*S*)-2'-(4-fluorophenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4p).**



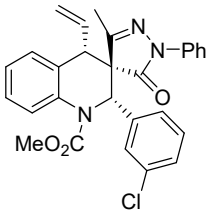

Purified by silica gel chromatography using PE/EA = 4:1, white solid (37.2 mg, 79% yield). $[\alpha]_D$ = +131 ($c$ = 0.1, $CH_2Cl_2$, 29.6 °C). MP: 105.6 – 107.4 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.66 (dd, $J$ = 8.1, 1.2 Hz, 1H), 7.44 (dddd, $J$ = 8.1, 7.3, 1.7, 0.8 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.22 – 7.11 (m, 6H), 7.06 – 7.00 (m, 1H), 6.89 – 6.83 (m, 2H), 5.69 (s, 1H), 5.64 – 5.55 (m, 1H), 5.44 (dq, $J$ = 12.7, 1.8 Hz, 2H), 3.91 (d, $J$ = 9.6 Hz, 1H), 3.74 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.8, 157.7, 155.2, 137.3, 136.8, 133.6, 133.5, 131.5, 130.3, 128.5, 128.0, 127.9, 127.7, 126.8, 125.2, 125.2, 125.0, 122.1, 119.1, 115.4, 115.1, 65.2, 61.1, 53.5, 46.6, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{25}FN_3O_3^+$ $[M+H]^+$: 470.1874, found 470.1887. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.29 and 13.30 min.

**Methyl(2'*S*,4*S*,4'*S*)-2'-(4-chlorophenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4q).**



Purified by silica gel chromatography using PE/EA = 4:1, white solid (31.7 mg, 65% yield). $[\alpha]_D$ = +114 (*c* = 0.1, $CH_2Cl_2$, 29.8 °C). MP: 177.4 – 178.6 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.44 (ddd, *J* = 8.8, 7.7, 1.4 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.22 – 7.01 (m, 9H), 5.67 (s, 1H), 5.64 – 5.55 (m, 1H), 5.45 (dq, *J* = 13.1, 1.8 Hz, 2H), 3.90 (d, *J* = 9.5 Hz, 1H), 3.74 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.7, 157.6, 155.1, 137.2, 136.8, 136.4, 133.7, 131.4, 130.2, 128.5, 127.8, 127.6, 126.8, 125.3, 125.0, 122.2, 119.2, 65.0, 61.1, 53.5, 46.7, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_3^+$ $[M+H]^+$: 486.1579, found 486.1572. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 7.97 and 14.89 min.

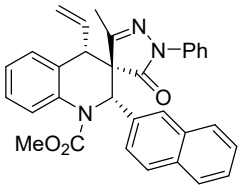
**Methyl(2'*S*,4*S*,4'*S*)-2'-(3-chlorophenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4r).**



Purified by silica gel chromatography using PE/EA = 4:1, white solid (38.4 mg, 79% yield). $[\alpha]_D$ = +112 (*c* = 0.1, $CH_2Cl_2$, 29.1 °C). MP: 75.4 – 76.9 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.68 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.33 – 7.29 (m, 2H), 7.23 – 7.01 (m, 9H), 5.67 (s, 1H), 5.64 – 5.56 (m, 1H), 5.45 (dq, *J* = 13.6, 1.9 Hz, 2H), 3.90 (d, *J* = 9.6 Hz, 1H), 3.75 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.6, 157.6, 155.2, 139.8, 137.2, 136.8, 134.1, 131.4, 130.1, 129.6, 128.5, 128.2, 127.8, 126.7, 126.2, 125.3, 125.2, 125.1, 124.4, 122.2, 119.1, 64.9, 61.1, 53.5, 46.6, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_3^+$ $[M+H]^+$: 486.1579, found 486.1595. HPLC: The product was analyzed by HPLC to determine the enantiomeric

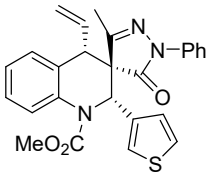
excess: 93% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.04 and 12.16 min.

**Methyl(2'*S*,4*S*,4'*S*)-3-methyl-2'-(naphthalen-2-yl)-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4s).**




Purified by silica gel chromatography using PE/EA = 3:1, white solid (33 mg, 66% yield). $[\alpha]_D$ = +95 ( *c*= 0.1, $CH_2Cl_2$, 30.0 °C). MP: 108.8 – 110.2 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.77 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.67 – 7.61 (m, 3H), 7.51 – 7.45 (m, 1H), 7.39 – 7.32 (m, 2H), 7.29 – 7.21 (m, 3H), 7.18 – 7.13 (m, 3H), 7.05 – 6.99 (m, 2H), 6.94 – 6.88 (m, 1H), 5.89 (s, 1H), 5.63 (dt, *J* = 16.9, 9.6 Hz, 1H), 5.49 – 5.42 (m, 2H), 3.96 (d, *J* = 9.6 Hz, 1H), 3.71 (s, 3H), 2.49 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.9, 157.9, 155.3, 137.6, 136.8, 135.3, 132.9, 132.8, 131.5, 130.4, 128.3, 128.2, 128.1, 127.8, 127.5, 126.7, 126.0, 126.0, 125.4, 125.2, 125.0, 124.1, 122.1, 119.2, 65.2, 61.9, 53.4, 46.9, 14.4 ppm. HRMS (ESI) calcd for $C_{32}H_{28}N_3O_3^+$ $[M+H]^+$: 502.2125, found 502.2086. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 87:13, flow rate 1.0 mL/min, λ = 254 nm); tr = 9.82 and 12.28 min.

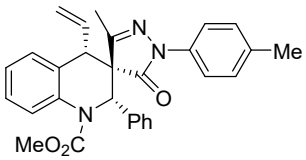
**Methyl(2'*R*,4*S*,4'*S*)-3-methyl-5-oxo-1-phenyl-2'-(thiophen-3-yl)-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4t).**




Purified by silica gel chromatography using PE/EA = 4:1, white solid (40 mg, 88% yield). $[\alpha]_D$ = +123 (*c* = 0.1, $CH_2Cl_2$, 30.1 °C). MP: 161.2 – 162.5 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.36 – 7.33 (m, 2H), 7.21 – 7.12 (m, 4H), 7.10 – 7.01 (m, 3H), 6.83 (dd, *J* = 4.9, 1.5 Hz, 1H), 5.86 (s, 1H), 5.63 (dt, *J* = 17.2, 9.6 Hz, 1H), 5.42 (dq, *J* = 13.0, 1.6 Hz, 2H), 3.87 (d, *J* = 9.7

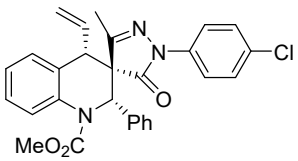
Hz, 1H), 3.75 (s, 3H), 2.39 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.0, 158.1, 155.2, 138.7, 137.1, 137.1, 131.5, 130.6, 128.5, 127.7, 126.7, 125.9, 125.5, 125.3, 125.2, 125.1, 122.0, 121.6, 119.3, 65.0, 58.1, 53.5, 46.5, 14.2 ppm. HRMS (ESI) calcd for $C_{26}H_{24}N_3O_3S^+$ $[M+H]^+$: 458.1533, found 458.1541. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 8.34 and 11.38 min.

**Methyl(2'*S*,4*S*,4'*S*)-3-methyl-5-oxo-2'-phenyl-1-(p-tolyl)-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4u).**



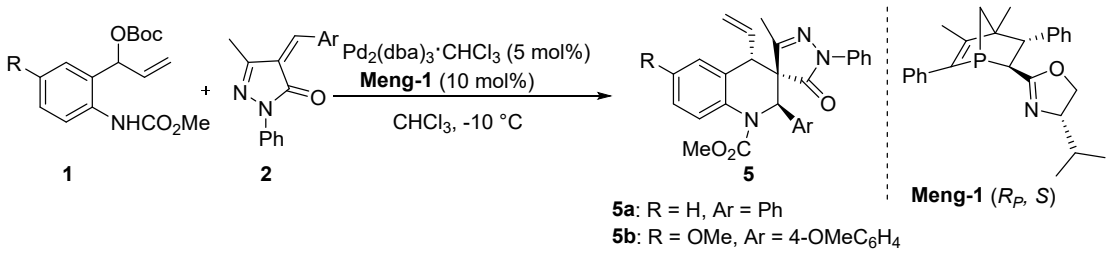

Purified by silica gel chromatography using PE/EA = 4:1, white solid (73 mg, 92% yield). $[\alpha]_D$ = +192 (*c* = 0.1, $CH_2Cl_2$, 30.0 °C). MP: 149.3 – 150.2 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.69 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.20 – 7.08 (m, 9H), 6.93 (d, *J* = 8.3 Hz, 2H), 5.71 (s, 1H), 5.61 (dt, *J* = 17.2, 9.6 Hz, 1H), 5.46 – 5.40 (m, 2H), 3.90 (d, *J* = 9.7 Hz, 1H), 3.73 (s, 3H), 2.42 (s, 3H), 2.20 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.7, 157.6, 155.2, 137.7, 137.5, 134.8, 134.5, 131.7, 130.4, 128.9, 128.2, 127.9, 127.7, 126.7, 126.0, 125.1, 125.1, 121.9, 119.3, 65.1, 61.7, 53.4, 46.6, 20.9, 14.3 ppm. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_3^+$ $[M+H]^+$: 466.2125, found 466.2126. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 7.32 and 10.32 min.

**Methyl(2'*S*,4*S*,4'*S*)-1-(4-chlorophenyl)-3-methyl-5-oxo-2'-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (4v).**




Purified by silica gel chromatography using PE/EA = 4:1, colourless oil (25 mg, 52% yield). $[\alpha]_D$ = +135 (*c* = 0.1, $CH_2Cl_2$, 30.1 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.70 (d,

*J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.08 (m, 11H), 5.71 (s, 1H), 5.60 (dt, *J* = 17.1, 9.4 Hz, 1H), 5.47 – 5.41 (m, 2H), 3.91 (d, *J* = 9.5 Hz, 1H), 3.74 (s, 3H), 2.43 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.9, 158.2, 155.1, 137.5, 137.5, 135.5, 131.5, 130.2, 130.1, 128.4, 128.3, 128.0, 127.7, 126.7, 126.0, 125.1, 125.1, 122.1, 120.1, 65.3, 61.7, 53.4, 46.5, 14.3 ppm. HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_3^+$ $[M+H]^+$: 486.1579, found 486.1583. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 7.43 and 12.55 min.




To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.005 mmol) and ligand **Meng-1** (0.01 mmol), then 1 mL $CHCl_3$ was added. This solution was stirred at room temperature for 0.5 h. Then, allyl carbonate **1** (0.2 mmol), alkylidene pyrazolone **2** (0.1 mmol) were added subsequently. The reaction mixture was stirred at -10 ℃ for 48 h and monitored by TLC (ethyl acetate /petroleum ether). After complete conversion, the product **5** was obtained by chromatography on silica gel.

**Methyl(2'S,4R,4'R)-3-methyl-5-oxo-1,2'-diphenyl-4'-vinyl-1,5-dihydro-2'H-spiro[pyrazole-4,3'-quinoline]-1'(4'H)-carboxylate (5a)**

Purified by silica gel chromatography using PE/EA = 4:1, white solid (32 mg, 62% yield). $[\alpha]_D$ = +112 (*c* = 0.1, $CH_2Cl_2$, 27.3 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.87 – 7.79 (m, 3H), 7.45 – 7.37 (m, 3H), 7.22 – 7.17 (m, 6H), 7.12 – 7.09 (m, 2H), 6.30 (ddd, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.89 (s, 1H), 5.28 (dt, *J* = 10.2, 1.2 Hz, 1H), 5.01 (dt, *J* = 17.1, 1.3 Hz, 1H), 3.71 (s, 3H), 3.60 (d, *J* = 7.0 Hz, 1H), 1.10 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.6, 160.7, 155.3, 138.5, 137.7, 137.4, 132.4, 129.7, 128.9, 128.8, 128.6, 128.2, 128.1, 126.1, 125.6, 125.3, 119.4, 119.0, 63.2, 60.2, 53.5, 46.8, 16.6 ppm. HRMS (ESI) calcd for $C_{28}H_{26}N_3O_3^+$ $[M+H]^+$: 452.1969, found 452.2003. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 32% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 16.61 and 19.22 min.

Using (***R*****$_P$**, ***R***)-**Meng-2** as ligand:

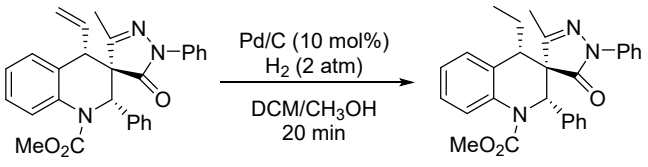
**5a':** Purified by silica gel chromatography using PE/EA = 4:1, white solid (38 mg, 80% yield). $[\alpha]_D$ = -99 (*c* = 0.1, $CH_2Cl_2$, 27.5 °C). HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 28% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm); tr = 17.41 and 19.87 min.

**Methyl(2'*S*,4*R*,4'*R*)-6'-methoxy-2'-(4-methoxyphenyl)-3-methyl-5-oxo-1-phenyl-4'-vinyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate(5b).**

Purified by silica gel chromatography using PE/EA = 4:1, yellow oil (32 mg, 62% yield). $[\alpha]_D$ = +87 (*c* = 0.1, $CH_2Cl_2$, 26.8 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.87 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.74 (dd, *J* = 5.8, 2.8 Hz, 3H), 6.20 (ddd, *J* = 17.3, 10.2, 7.4 Hz, 1H), 5.27 (d, *J* = 10.1 Hz, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 3.71 (s, 3H), 3.56 (d, *J* = 7.3 Hz, 1H), 1.20 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.7, 160.7, 159.2, 156.9, 155.5, 137.8, 132.6, 130.6, 130.5, 130.4, 128.8, 127.2, 127.1, 125.2, 119., 119.0, 114.1, 113.7, 113.3, 62.7, 59.5, 55.6, 55.2, 53.5, 46.5 ppm. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 50% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 18.79 and 24.00 min.

Using (***R*****$_P$**, ***R***)-**Meng-2** as ligand:

**5b':**Purified by silica gel chromatography using PE/EA = 4:1, yellow oil (30 mg, 58% yield). $[\alpha]_D$ = -69 (*c* = 0.1, $CH_2Cl_2$, 27 °C). HRMS (ESI) calcd for $C_{30}H_{30}N_3O_5^+$ $[M+H]^+$: 512.2180, found 512.2186. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 52% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 16.43 and 21.03 min.




**3a**
ee = 94%

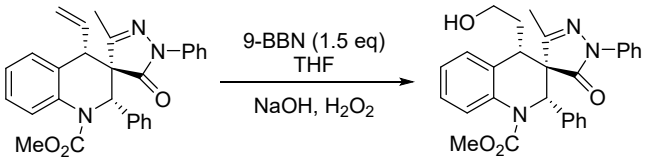
**6**
96% yield
92% ee

The compound **3a** (0.1 mmol, 45.1 mg), Pd/C (10%, 0.1 mmol, 10.6mg, 1.0 equiv) was dissolved in 3 mL of DCM and 3 mL of MeOH. Under $H_2$ at two atmosphere, the solution was stirred at room temperature for 20 min. After complete conversion, the

mixture was concentrated and the product **6** was obtained by chromatography on silica gel.

**Methyl(2'*S*,4*R*,4'*S*)-4'-ethyl-3-methyl-5-oxo-1,2'-diphenyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate (6)**

Purified by silica gel chromatography using PE/EA = 4:1, colorless oil (43 mg, 96% yield). $[\alpha]_D$ = +71 (*c* = 0.1, $CH_2Cl_2$, 17 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.89 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.35 – 7.25 (m, 3H), 7.22 – 7.17 (m, 3H), 7.09 – 7.06 (m, 2H), 6.04 (s, 1H), 3.74 (s, 3H), 3.24 (d, *J* = 10.4 Hz, 1H), 1.72 (ddd, *J* = 14.1, 10.6, 7.0 Hz, 1H), 1.55 – 1.46 (m, 1H), 1.18 (t, *J* = 7.3 Hz, 3H), 0.88 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 173.5, 160.4, 155.0, 139.0, 138.8, 137.5, 132.3, 129.0, 128.6, 127.8, 127.7, 126.0, 125.5, 124.4, 119.1, 69.0, 65.0, 53.4, 43.8, 19.5, 16.8, 13.1 ppm. HRMS (ESI) calcd for $C_{28}H_{28}N_3O_3^+$ $[M+H]^+$: 454.2125, found 454.2132. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm); tr = 6.78 and 17.59 min.




**3a**
ee = 94%

**7**
83% yield
93% ee

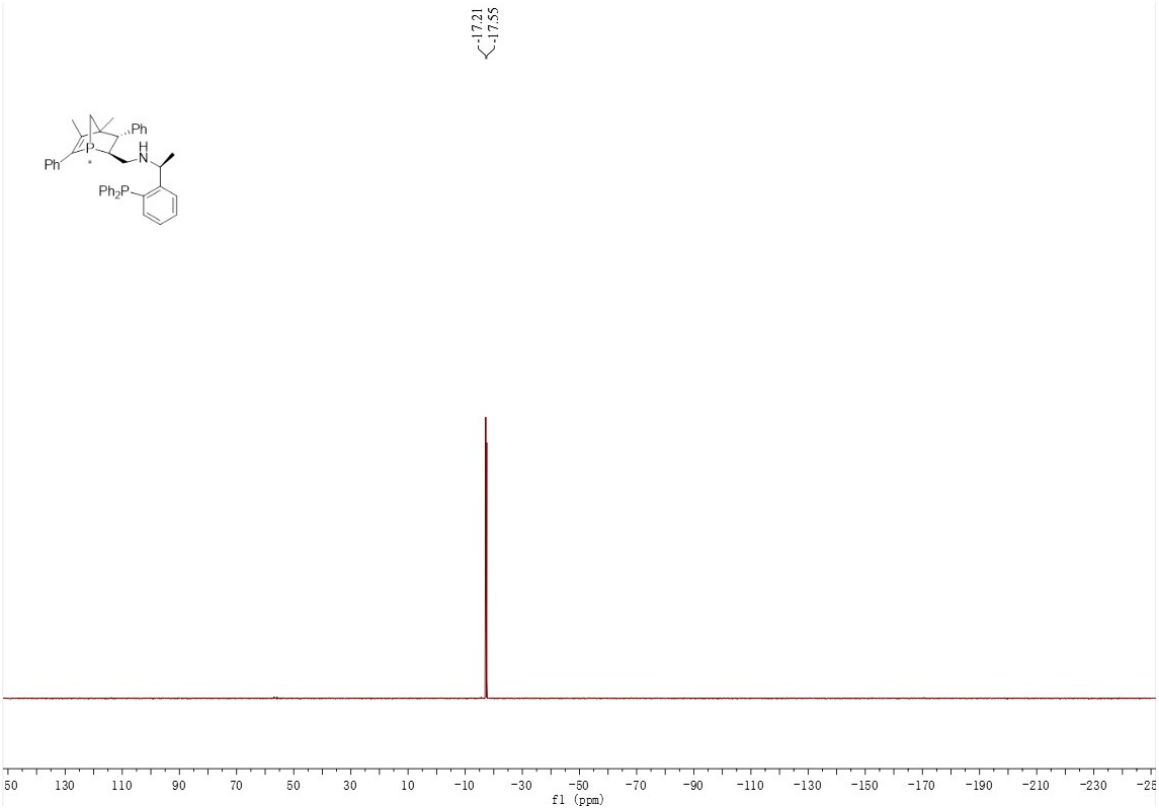
To a dry flask filled with nitrogen was added 3 ml of 9-BBN (0.5 M in THF) solution at 0 ℃, a solution of the compound **3a** (0.2 M in THF, 0.1 mmol, 45.1 mg) was added dropwise. This solution was stirred at room temperature for 24 h. Then, quenched with 2.0 mL of 2 N aqueous NaOH solution and 0.60 mL of 30% aqueous $H_2O_2$ solution. After stirring for 30 min, the reaction mixture was extracted with EtOAc, and the combined organic phases were dried over MgSO4 and the solvent was removed in vacuo. The residue was purified by silica gel chromatography to afford the product **7**.

**Methyl(2'*S*,4*R*,4'*S*)-4'-(2-hydroxyethyl)-3-methyl-5-oxo-1,2'-diphenyl-1,5-dihydro-2'*H*-spiro[pyrazole-4,3'-quinoline]-1'(4'*H*)-carboxylate(7).**

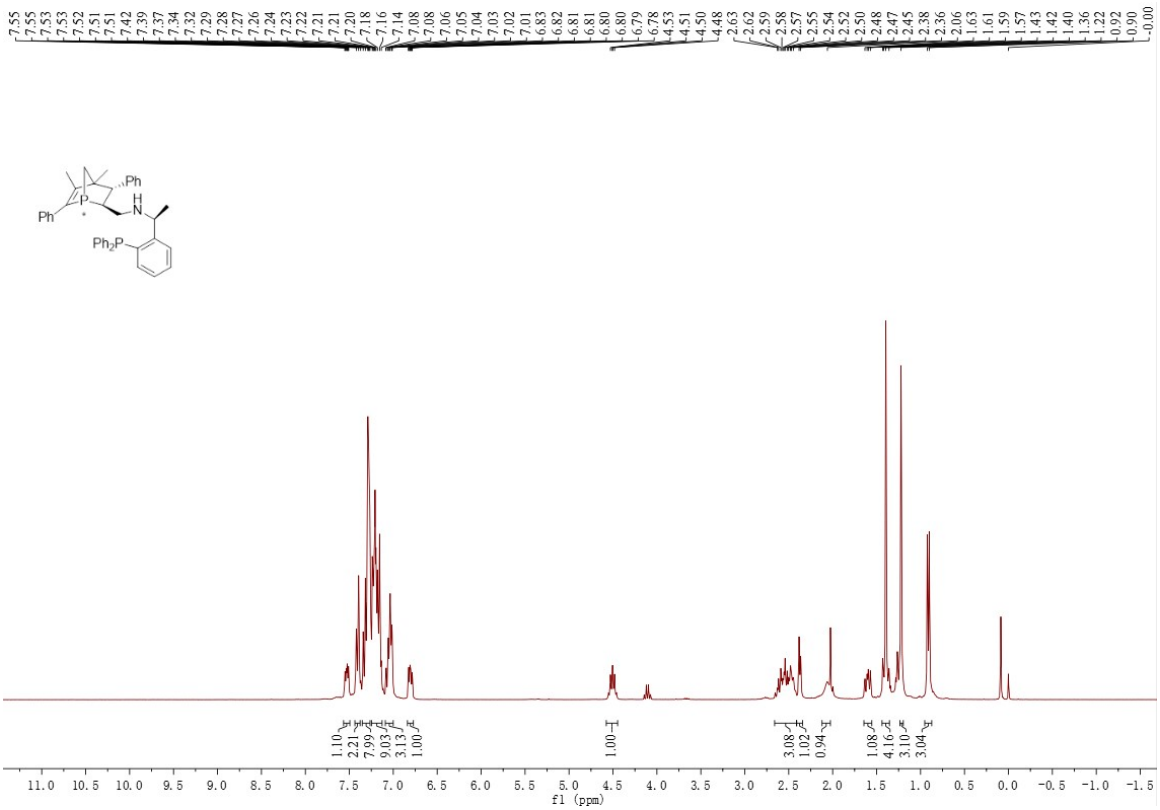
Purified by silica gel chromatography using PE/EA = 2:1, colorless oil (39 mg, 83% yield). $[\alpha]_D$ = +59 (*c* = 0.1, $CH_2Cl_2$, 16.3 °C). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.86 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.31 – 7.26 (m, 2H), 7.22 – 7.15 (m, 4H), 7.04 (dd, *J* = 6.9, 2.8 Hz, 2H), 6.01 (s, 1H), 3.86 – 3.73 (m, 2H), 3.71 (s, 3H), 3.47 (dd, *J* = 9.9, 3.0 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.60 – 1.49 (m, 1H), 0.88 (s, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 173.6, 160.5, 155.1, 138.8, 138.6, 137.2, 132.1, 129.0, 128.6, 127.9, 126.1, 125.8, 125.7, 125.2, 124.4, 119.2, 68.7, 65.1, 60.4, 53.5, 38.0, 29.5, 16.8, ppm. HRMS (ESI) calcd for $C_{28}H_{28}N_3O_4^+$ $[M+H]^+$: 470.2074, found 470.2078. HPLC: The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AD-H, *n*-hexane / *i*-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm); tr = 9.67 and 23.32 min.


1. X. Liang, T.-Y. Zhang, X.-Y. Zeng, Y. Zheng, K. Wei and Y.-R. Yang. *J. Am. Chem. Soc.* **2017**, *139*, 3364-3367.
2. Y.-C. Gong, Y. Wang, E.-Q. Li, H. Cui, Z. Duan. Adv. Synth. Catal. **2019**, *361*, 1389-1393.
3. S. Jia, M. Ma, E.-Q. Li, Z. Duan and F. Mathey. Org. Lett. **2021**, *23*, 3337-3342.
4. T. Zhou, T. Xia, Z. Liu, L. Liu, J. Zhang. Adv. Synth. Catal. **2018**, *360*, 4475-4479.

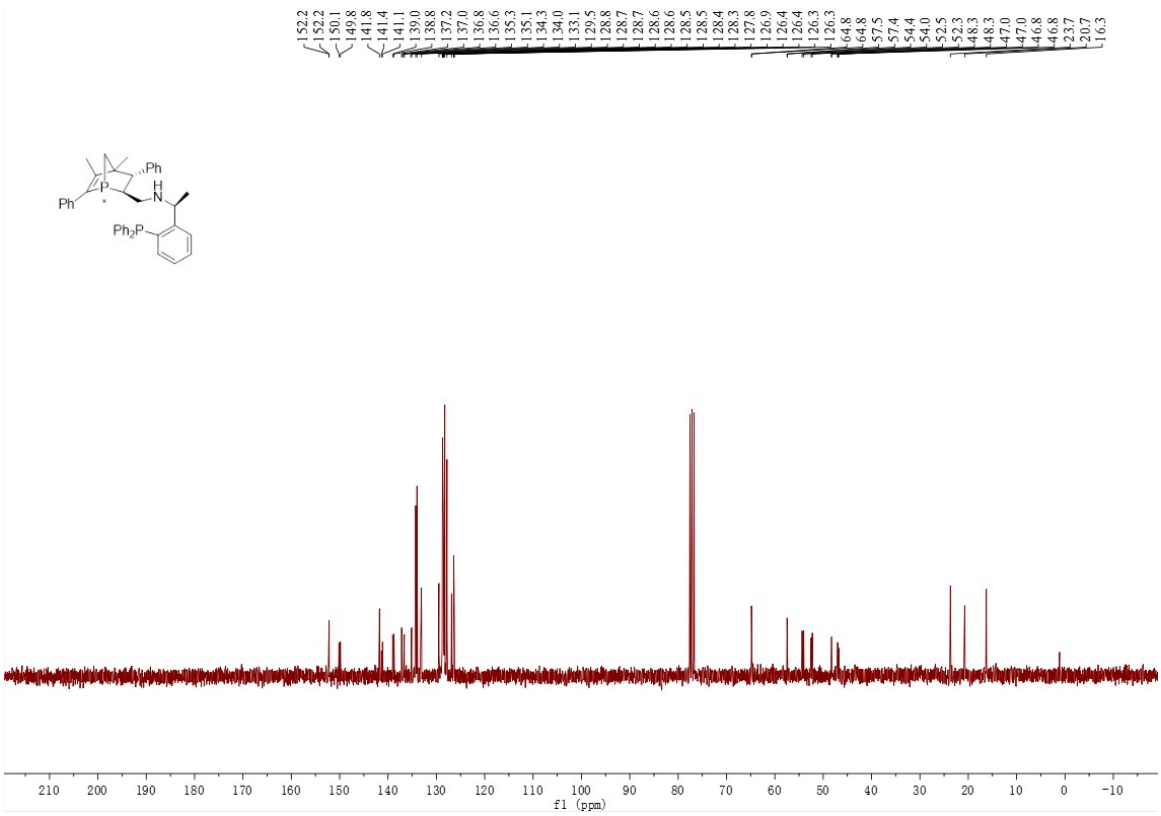
# 5. Copies of $^{1}H$ NMR, $^{13}C$ NMR, $^{31}P$ NMR Spectra



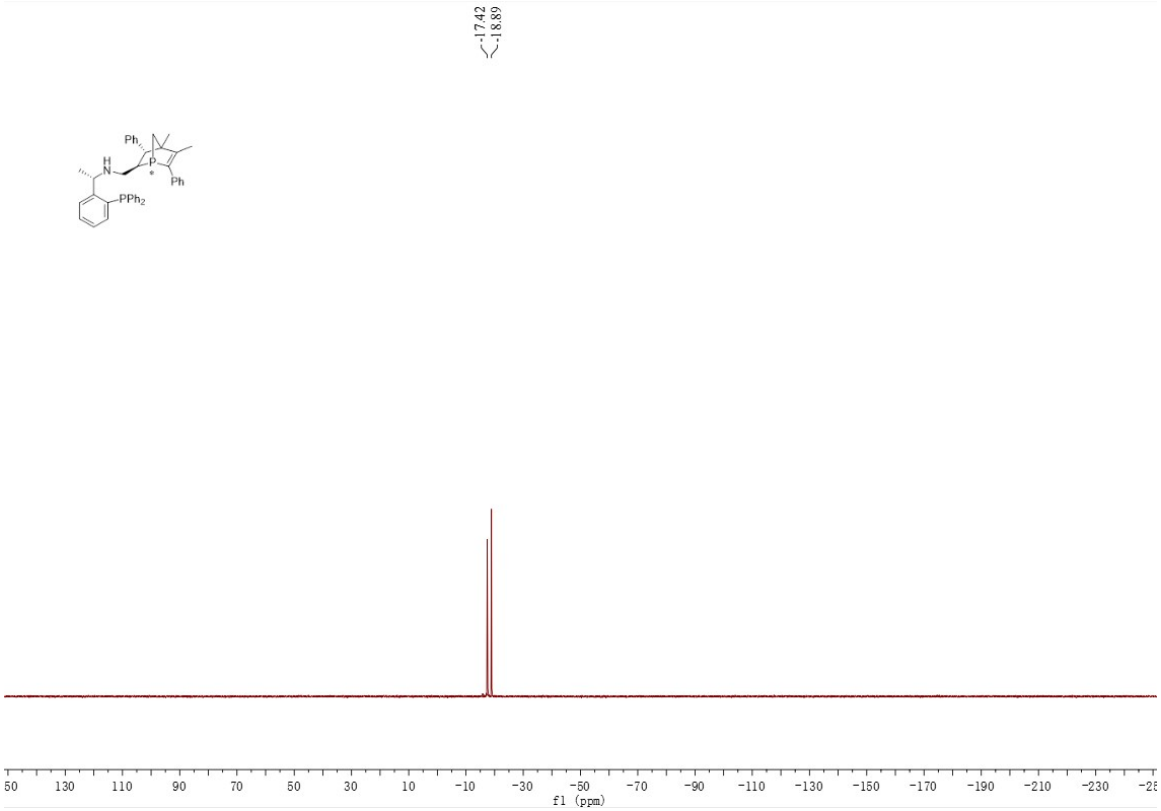

$^{31}P$ ($CDCl_3$, 121 MHz) NMR of compound **Yue-1**



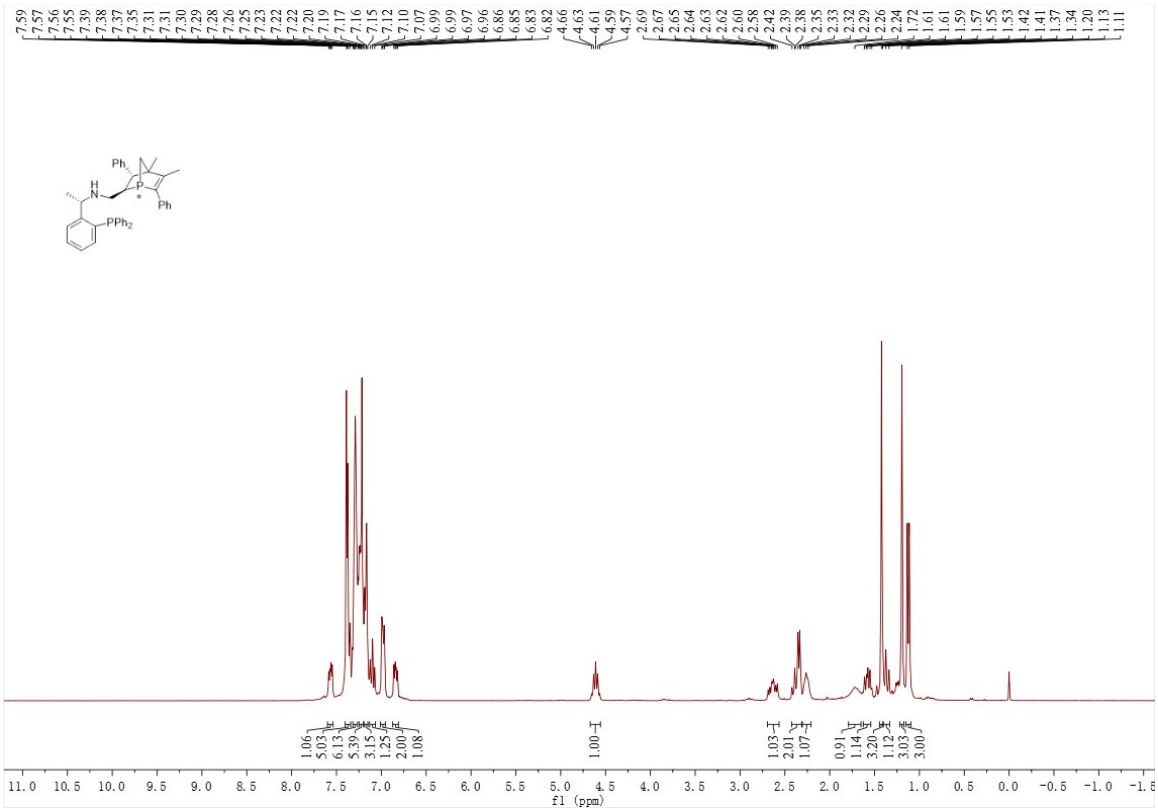

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **Yue-1**



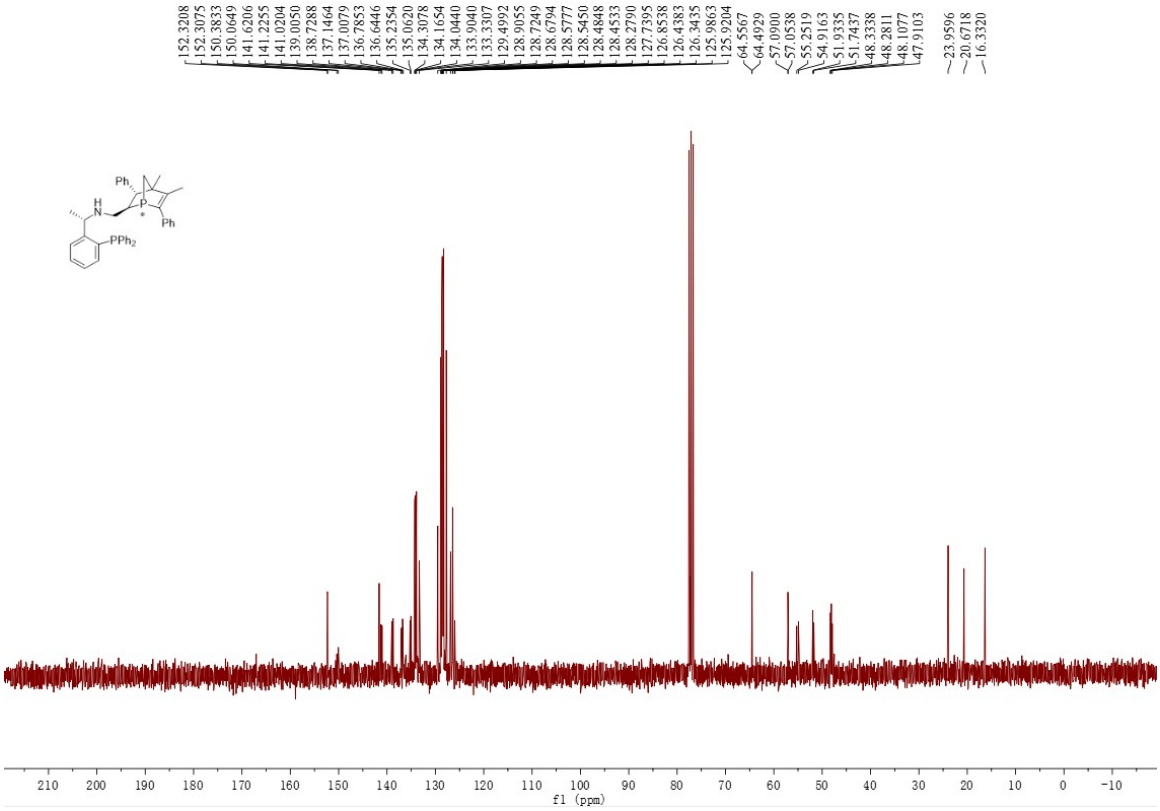

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **Yue-1**



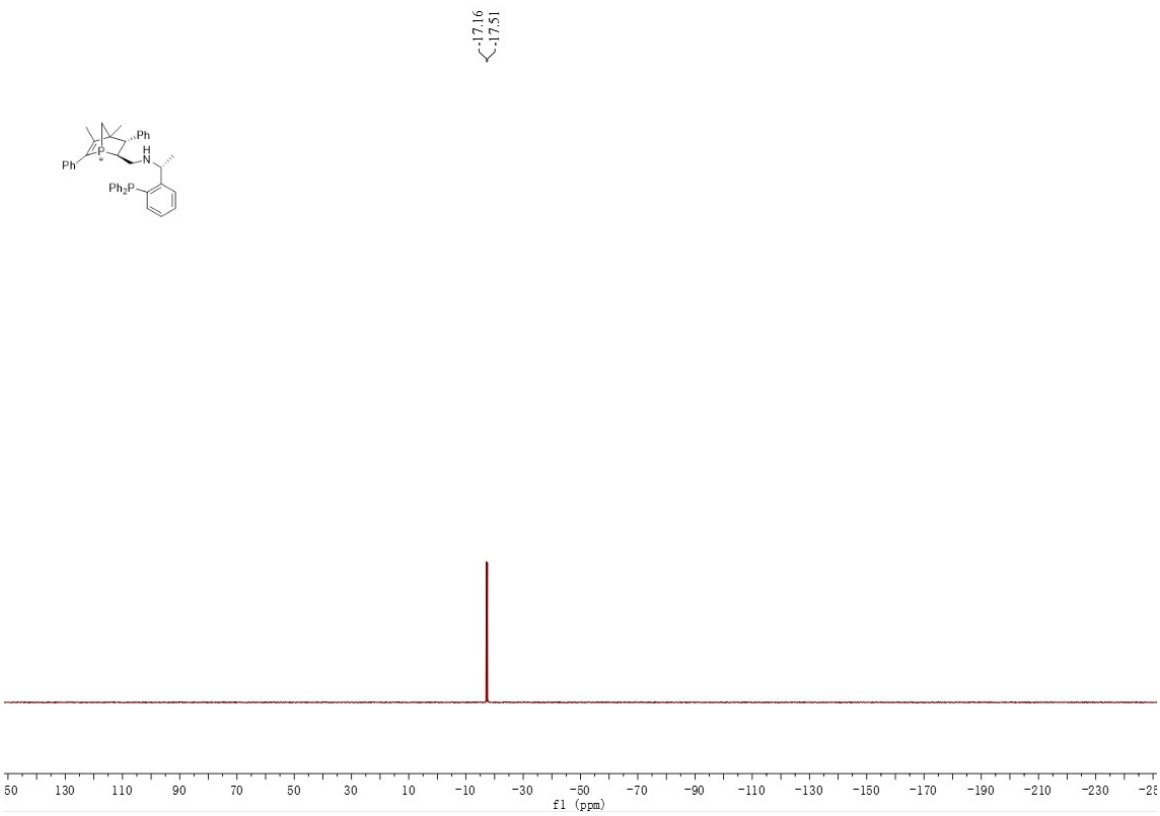

$^{31}P$ ($CDCl_3$, 121 MHz) NMR of compound **Yue-1'**



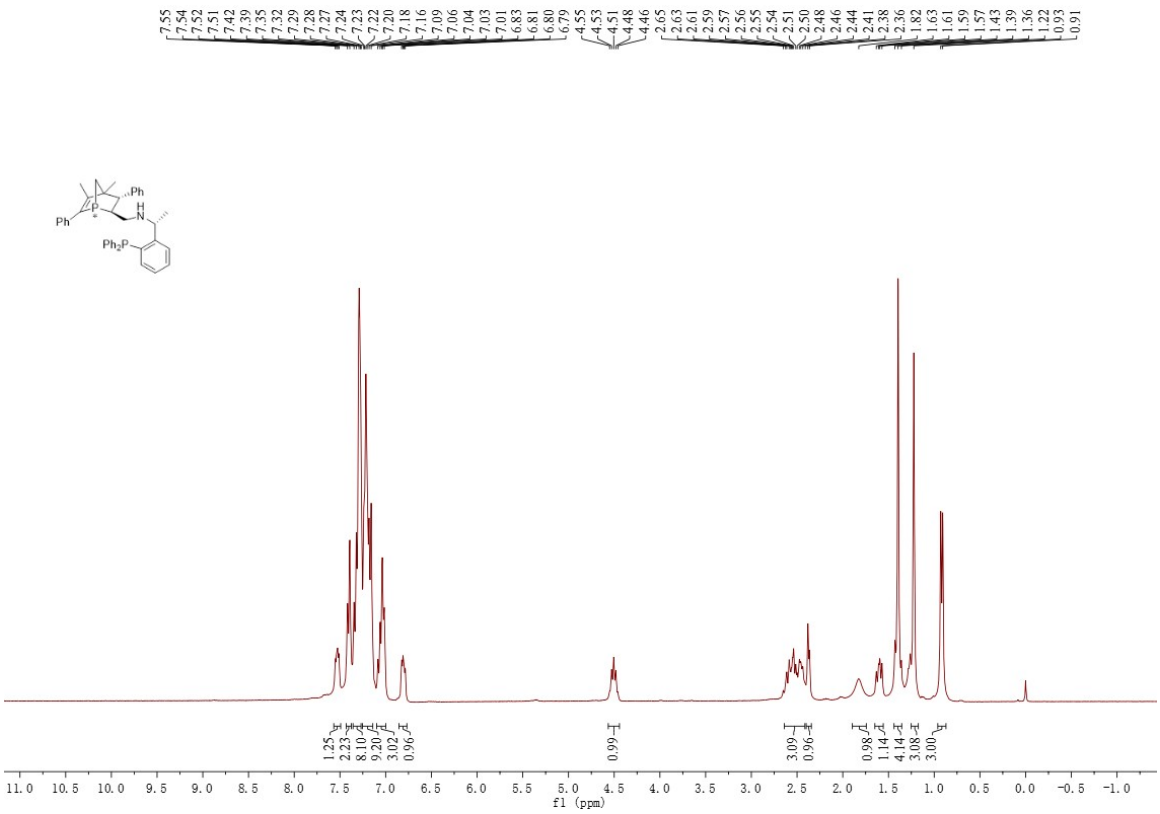
$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **Yue-1'**



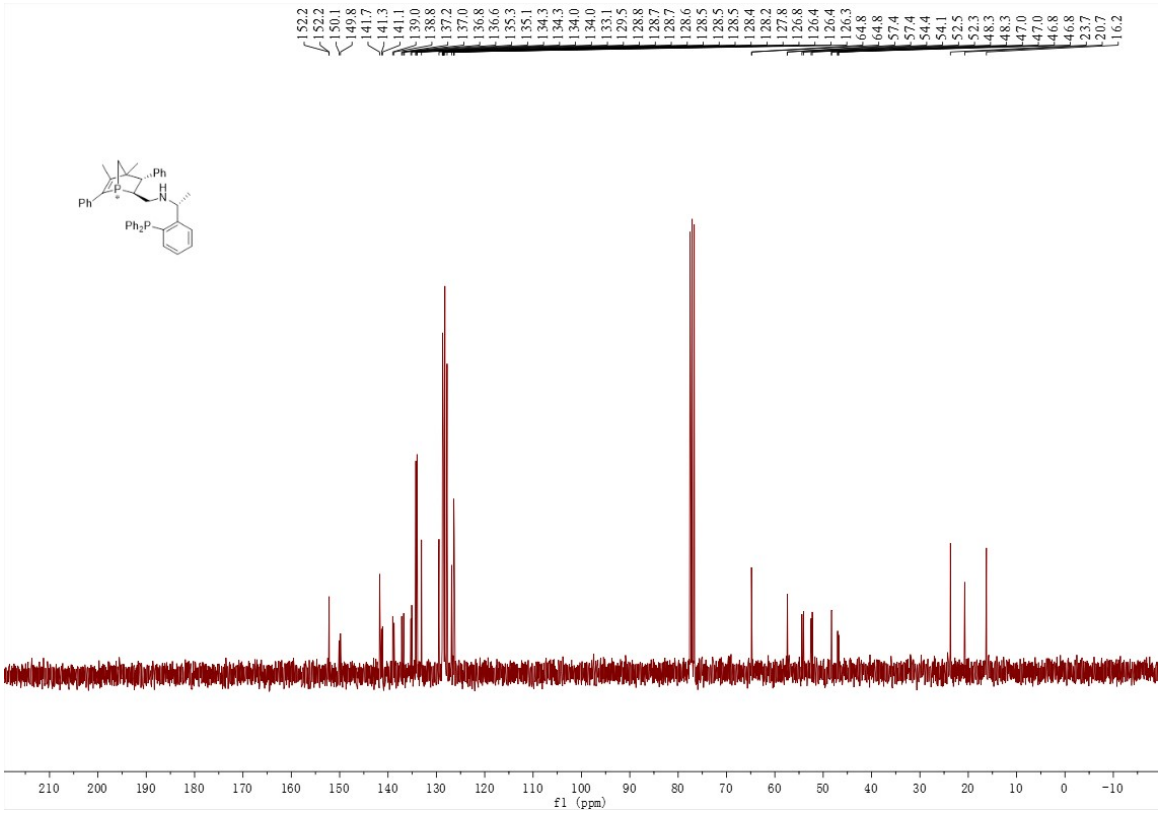
$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **Yue-1'**



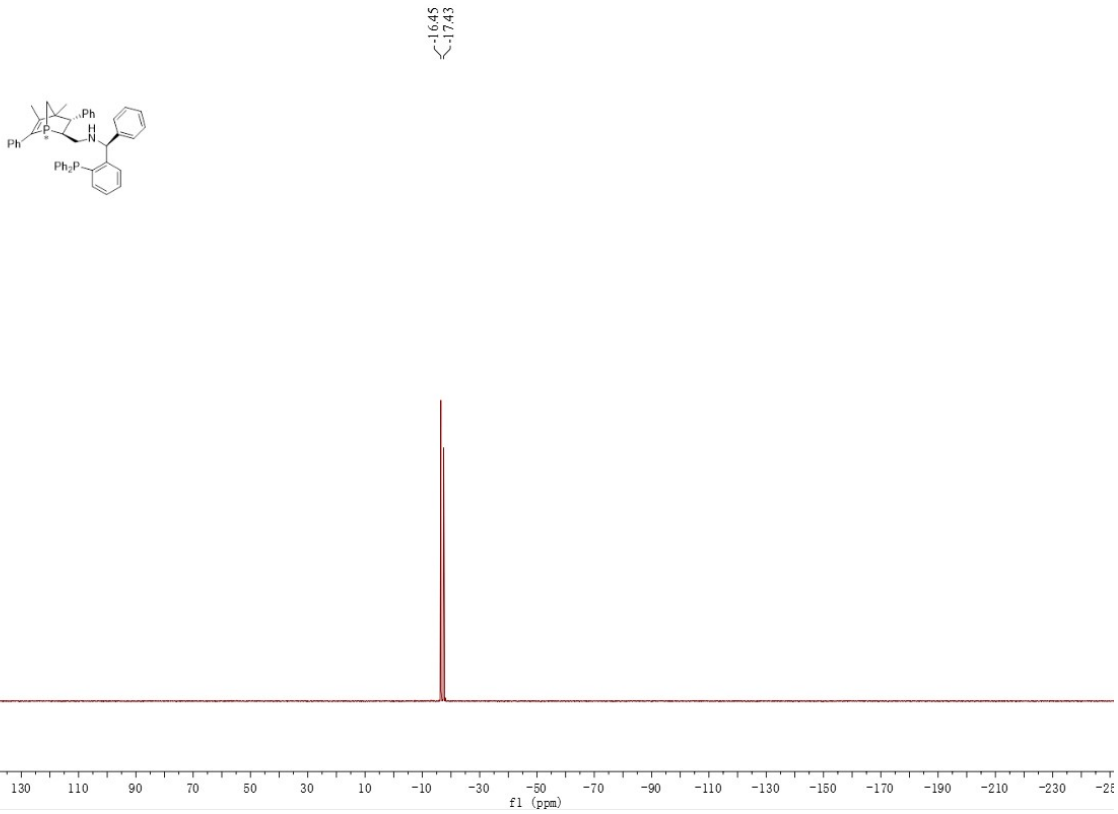

$^{31}P$ ($CDCl_3$, 121 MHz) NMR of compound **Yue-2**



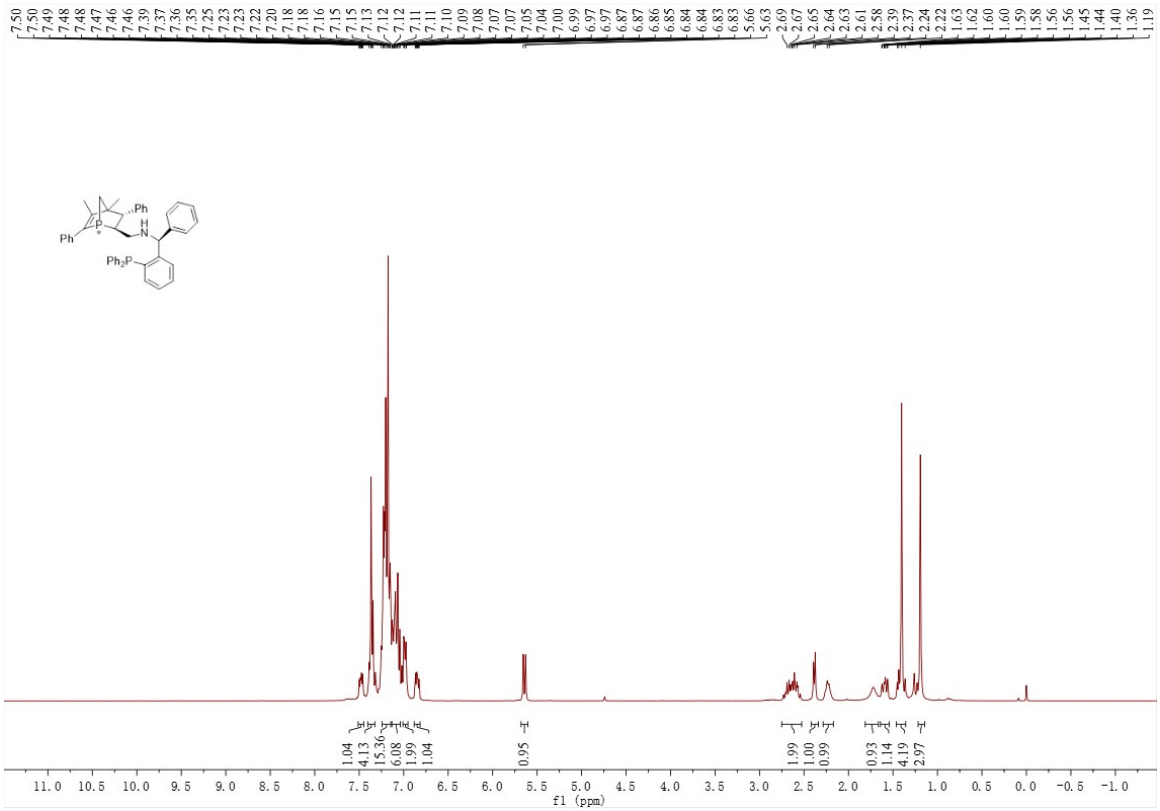

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **Yue-2**



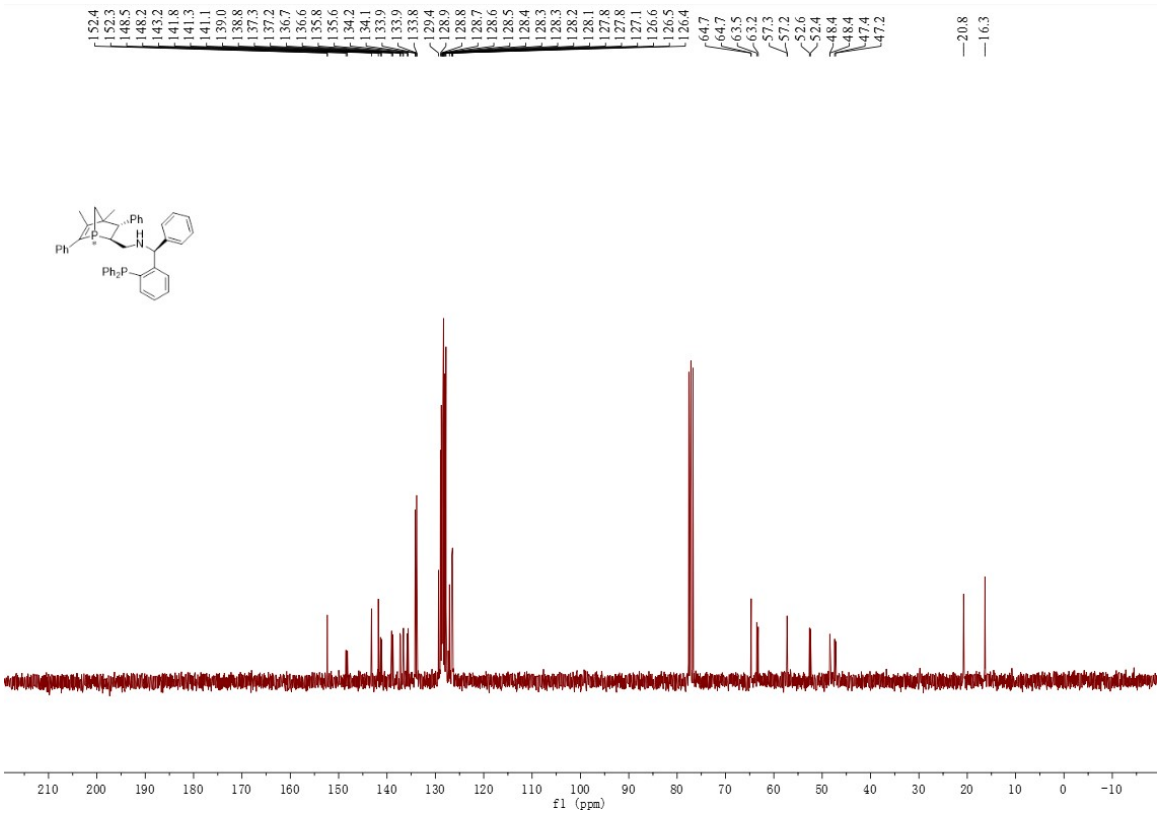

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **Yue-2**



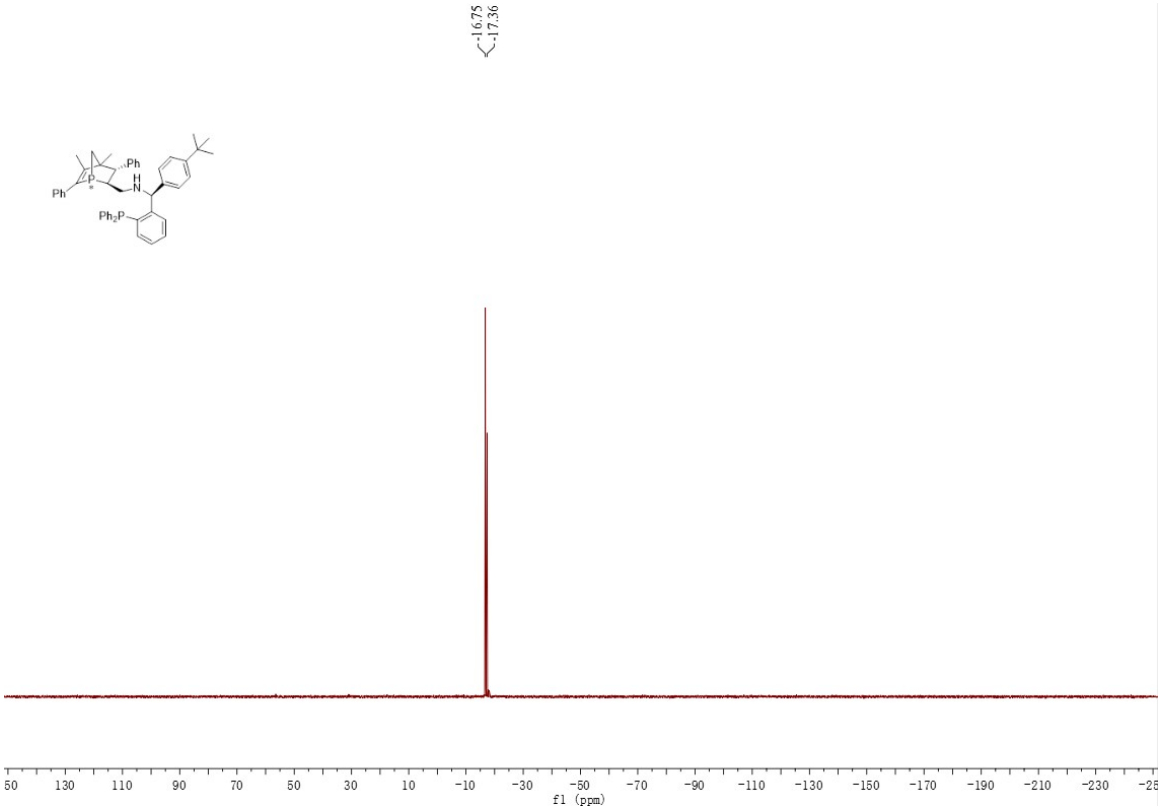

$^{31}P$ ($CDCl_3$, 121 MHz) NMR of compound **Yue-3**



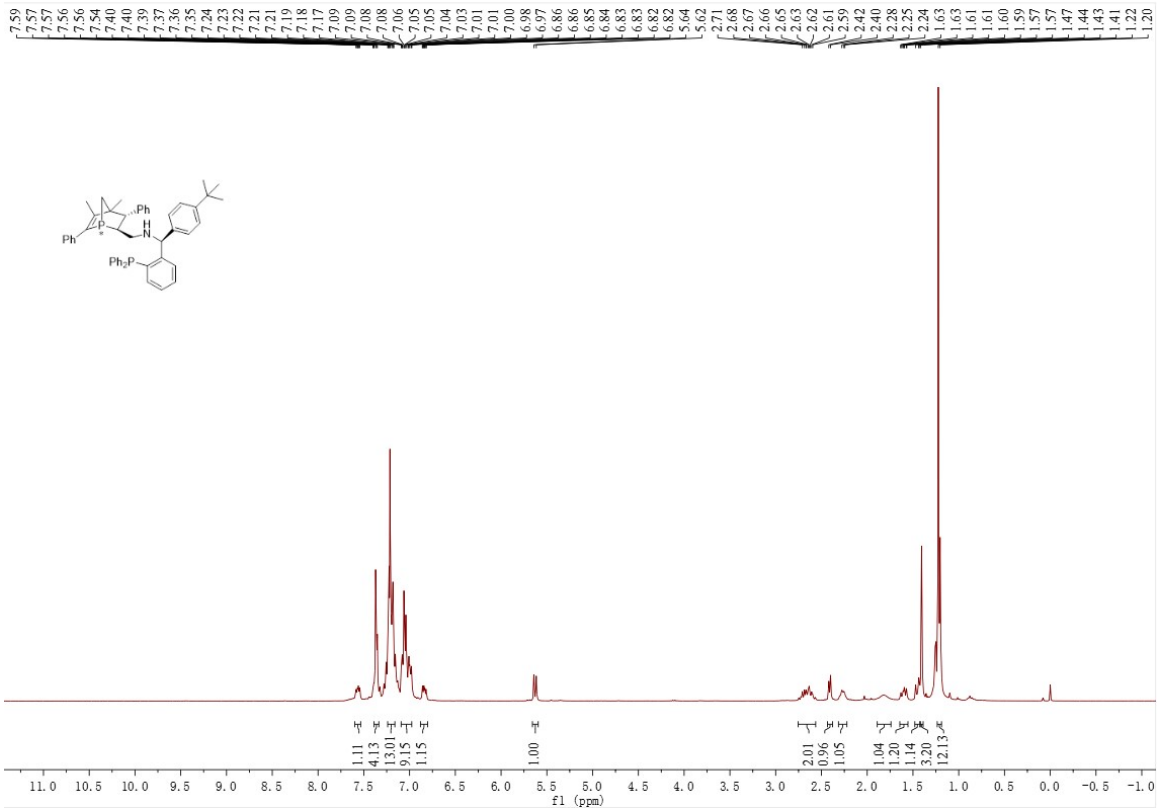
$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **Yue-3**



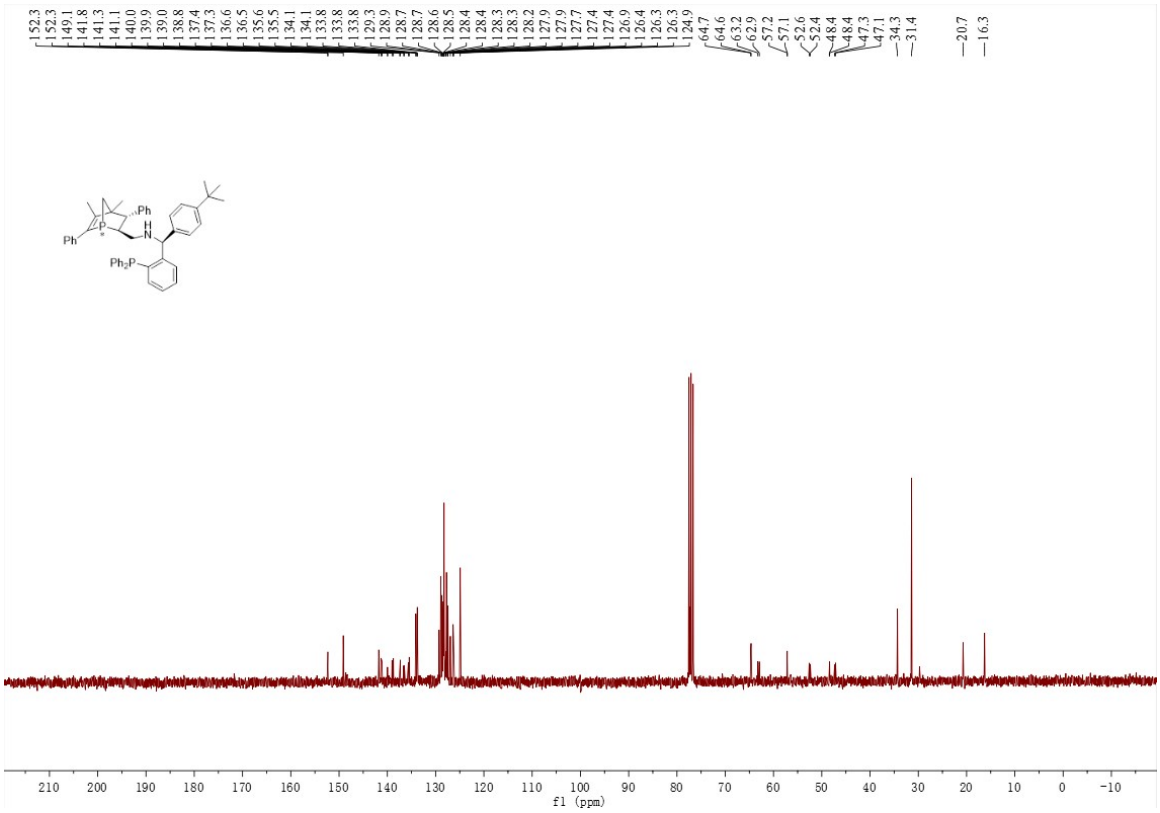
$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **Yue-3**



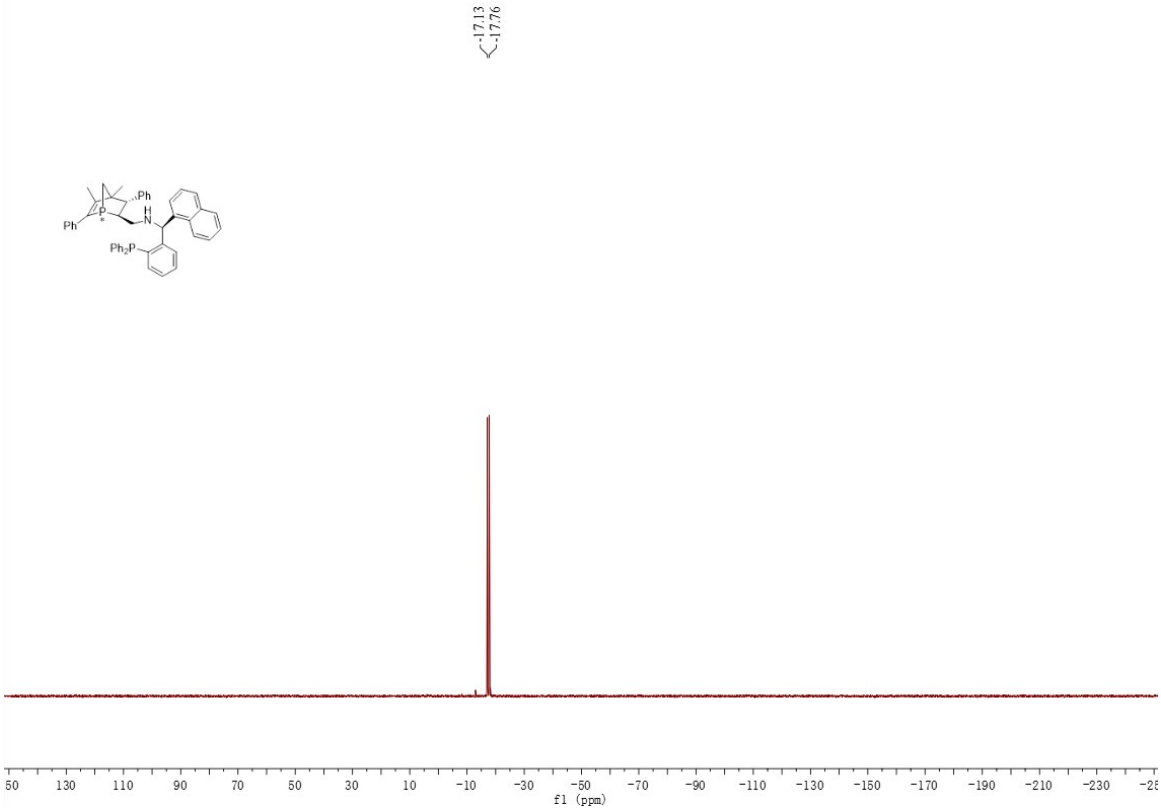

$^{31}P$ ($CDCl_3$, 121 MHz) NMR of compound **Yue-4**



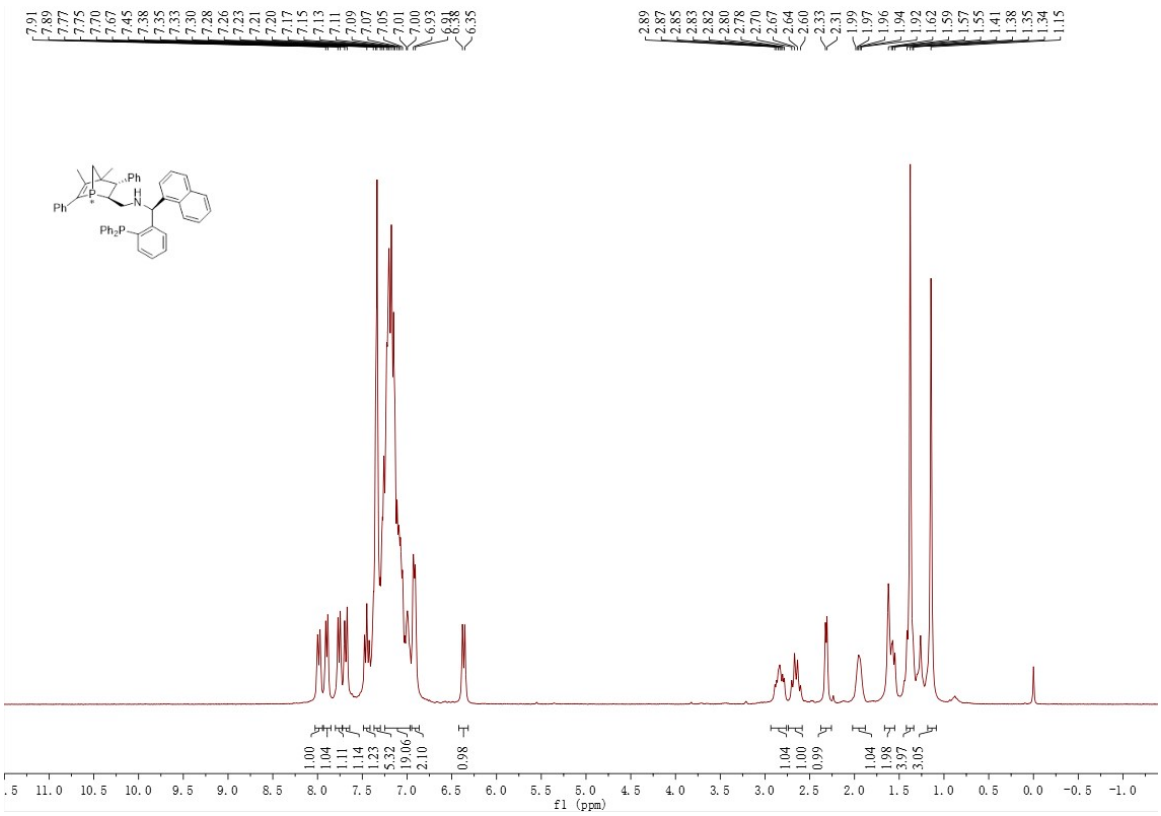

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **Yue-4**



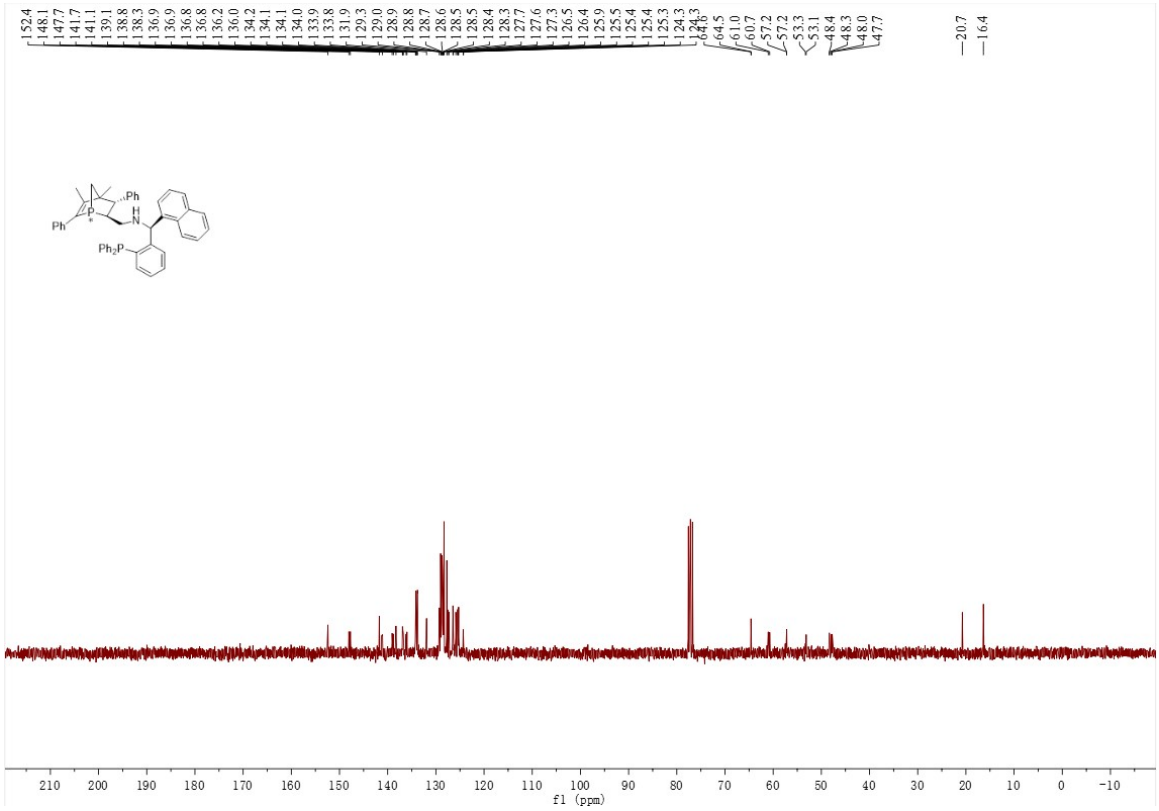

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **Yue-4**



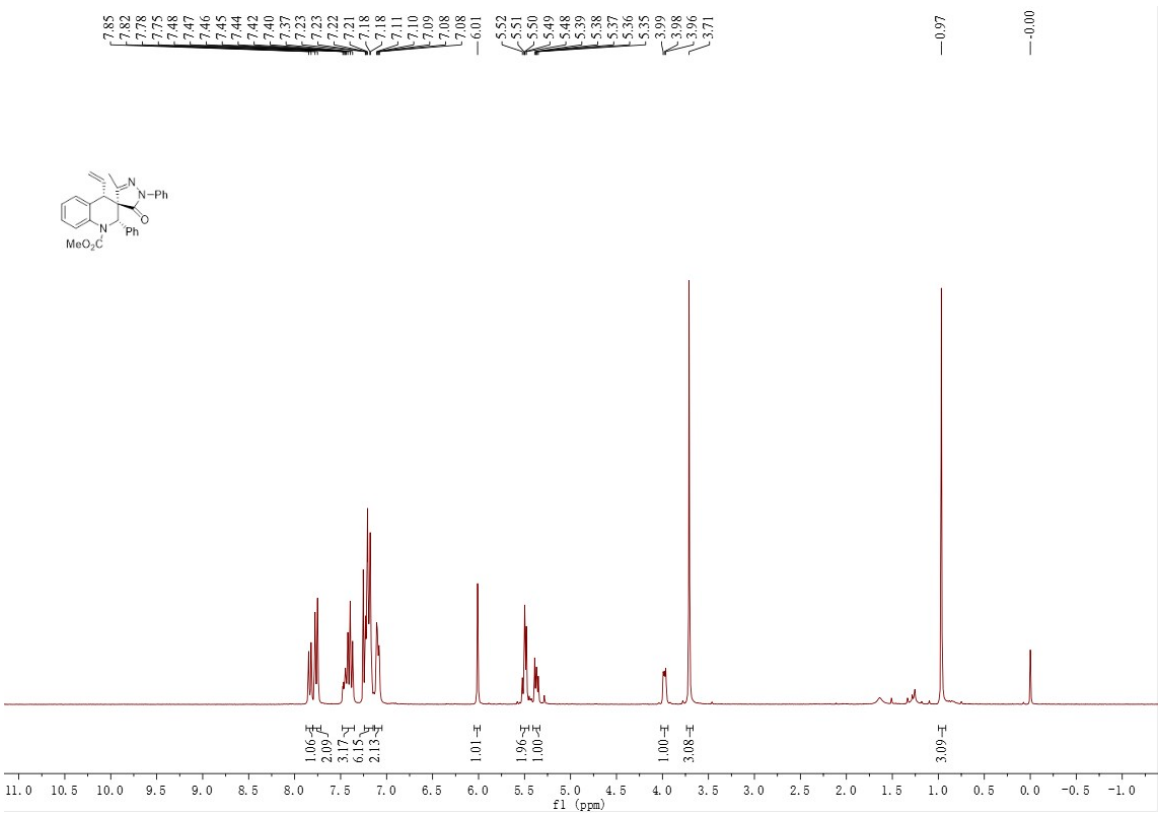

$^{31}P$ ($CDCl_3$, 121 MHz) NMR of compound **Yue-5**



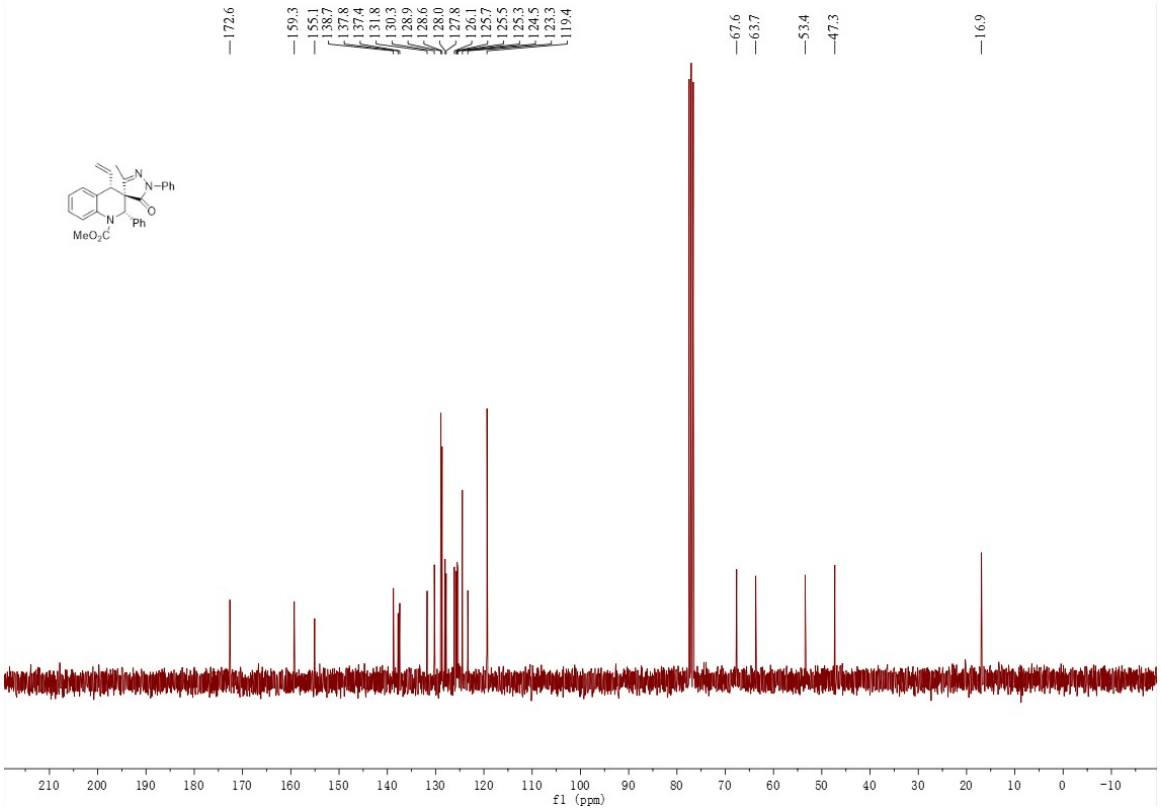
$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **Yue-5**



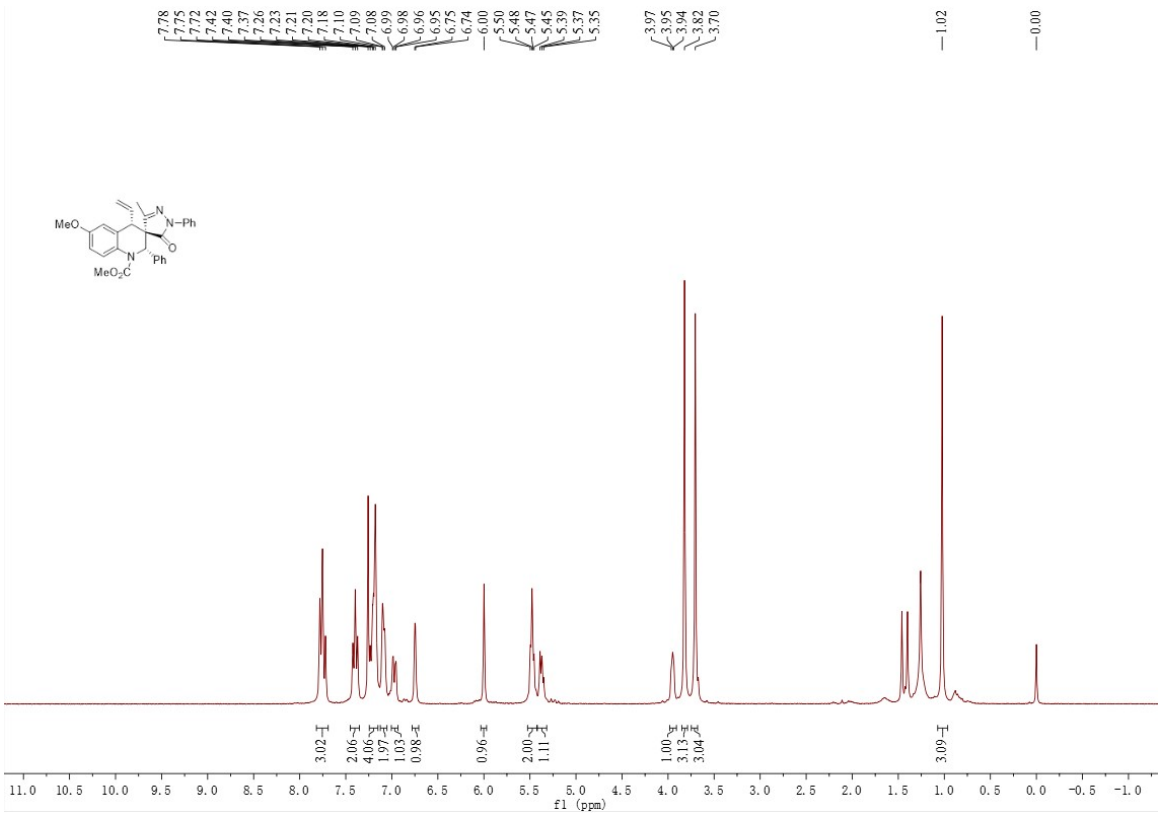
$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **Yue-5**



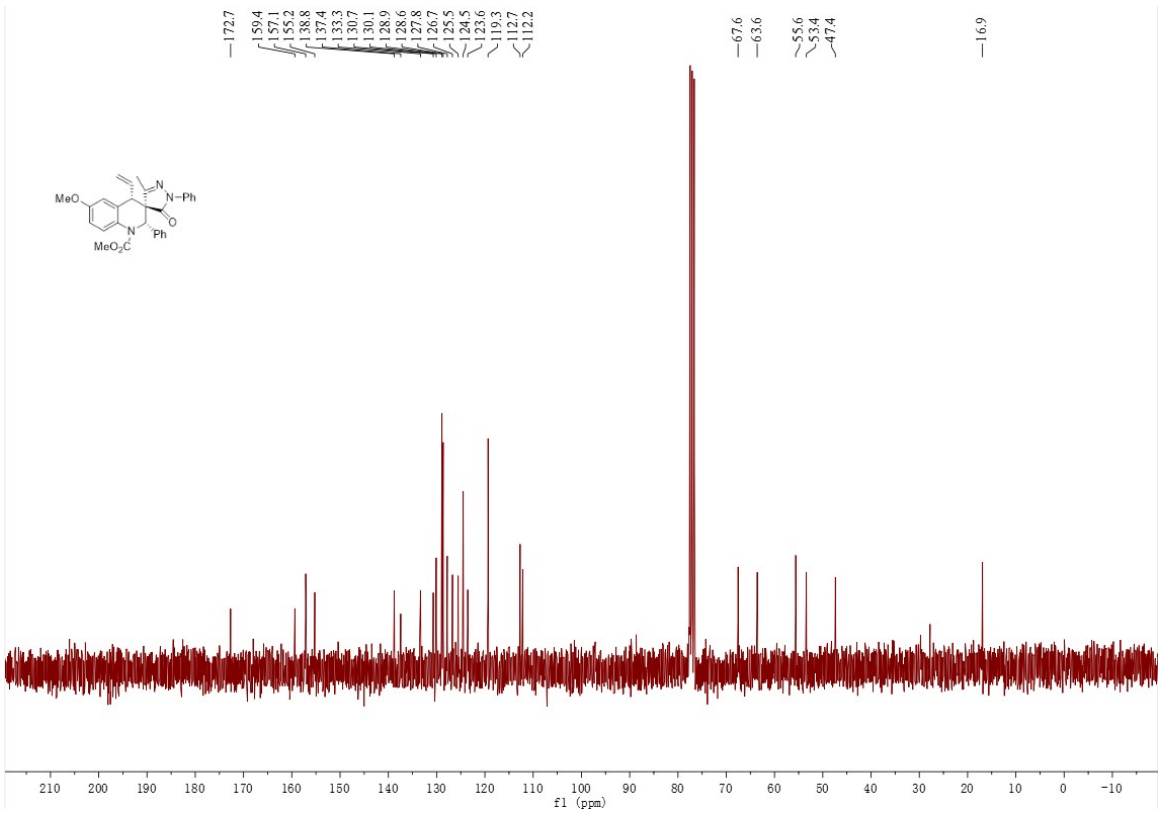

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **3a**



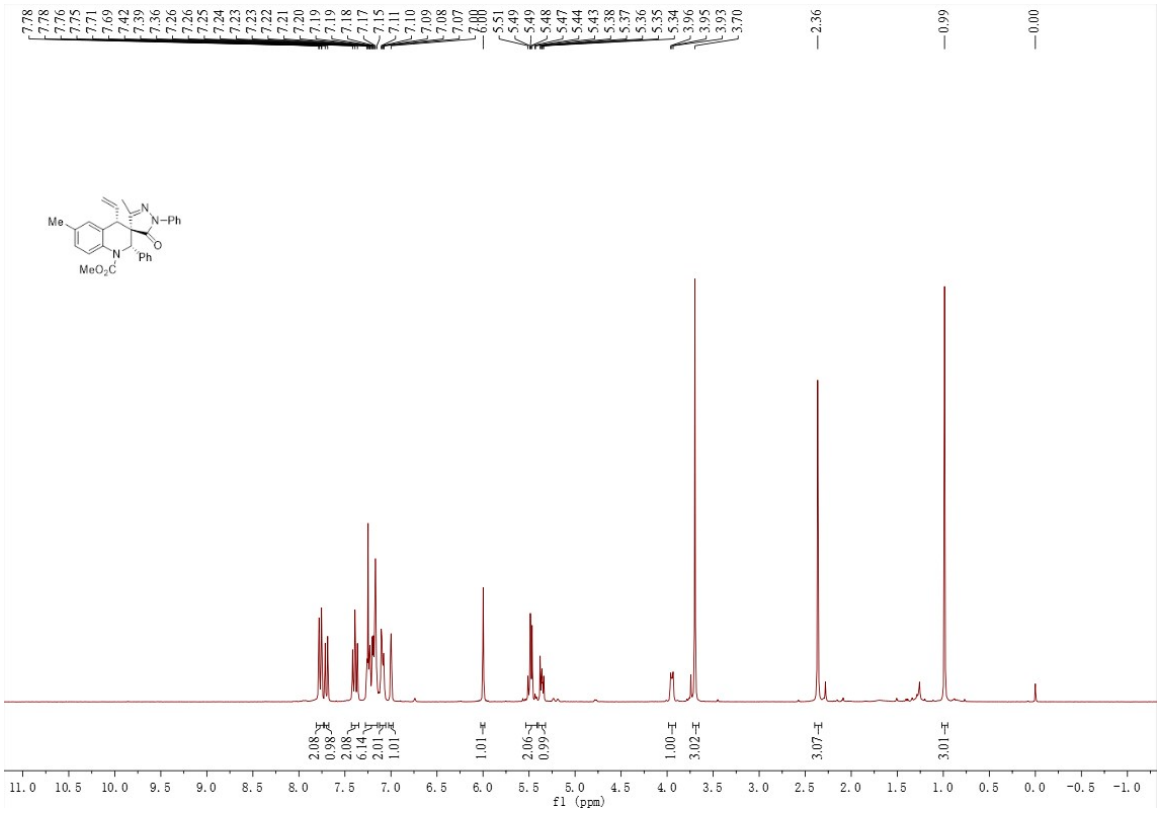

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **3a**



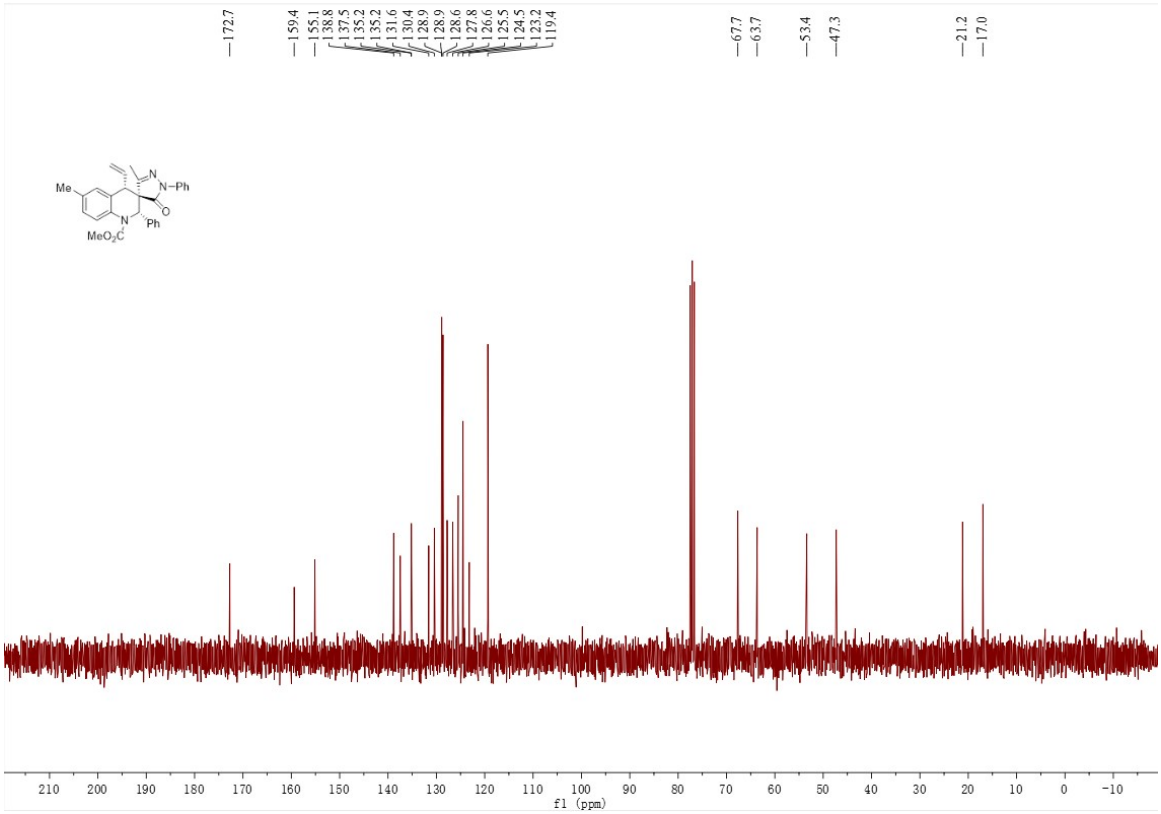

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3b**



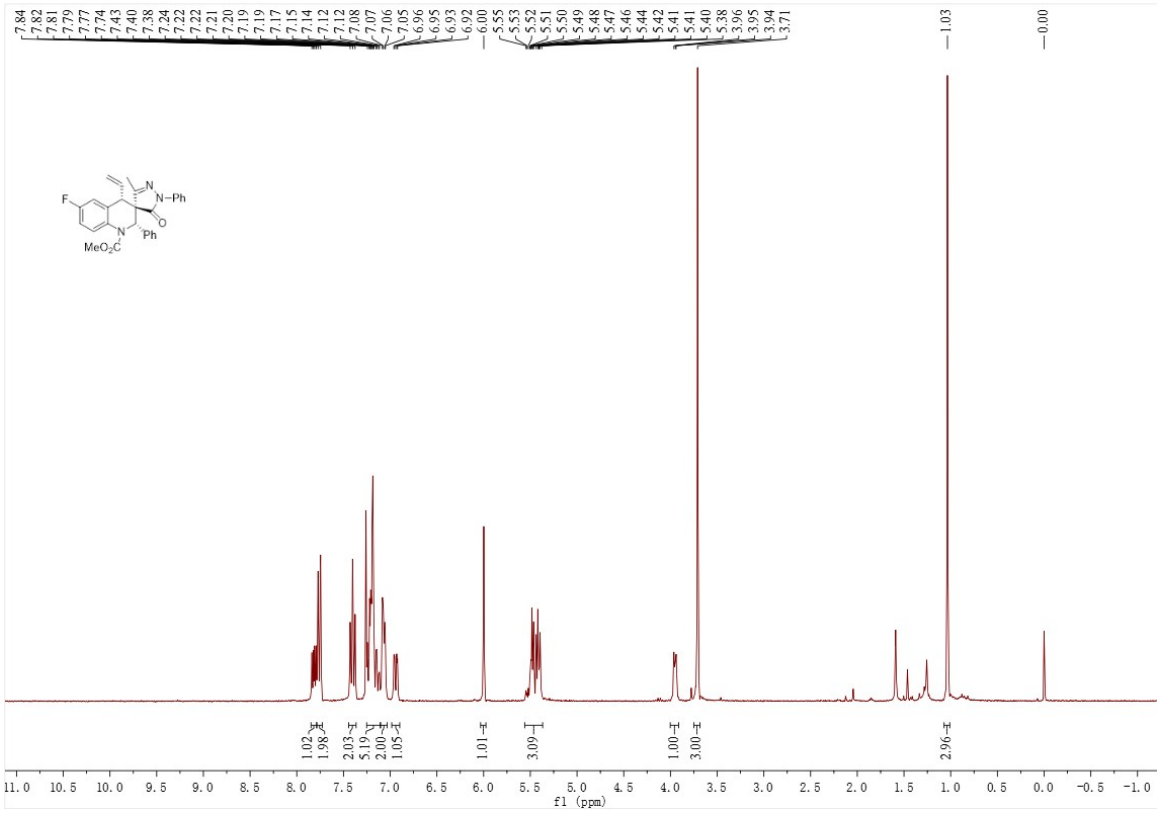

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3b**



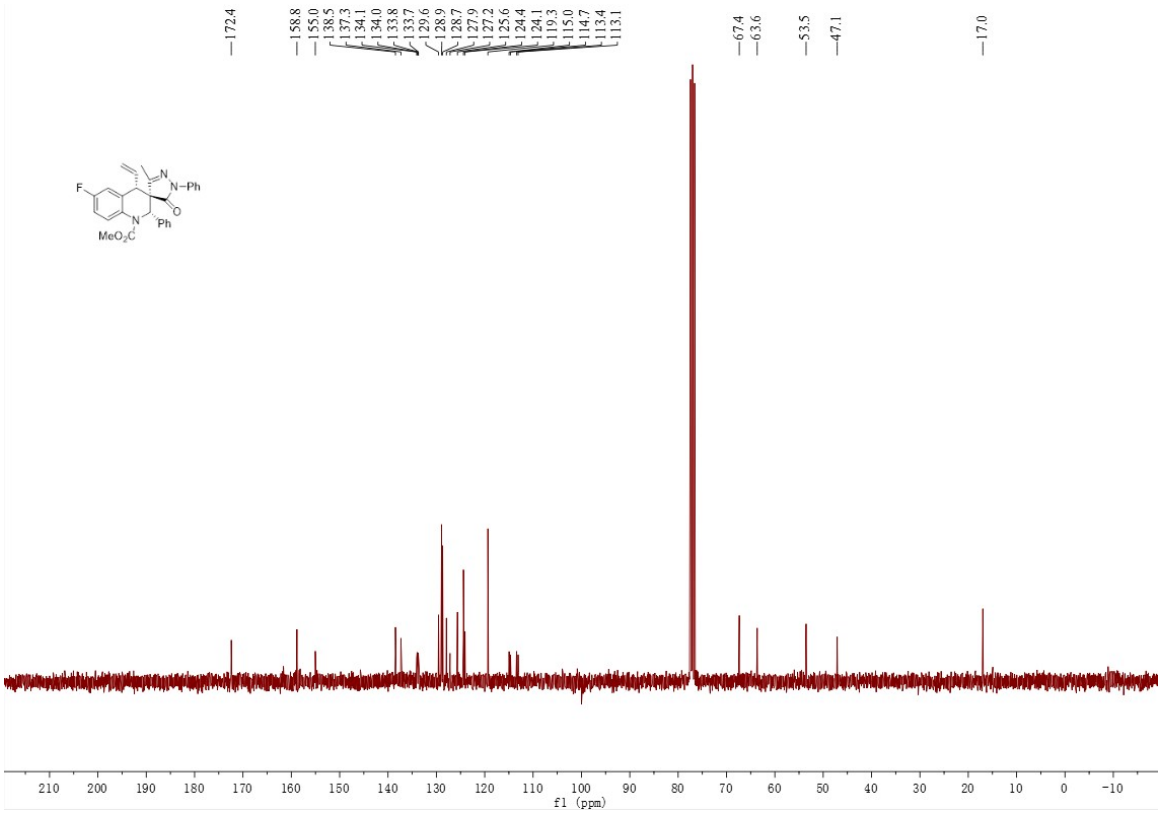

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3c**



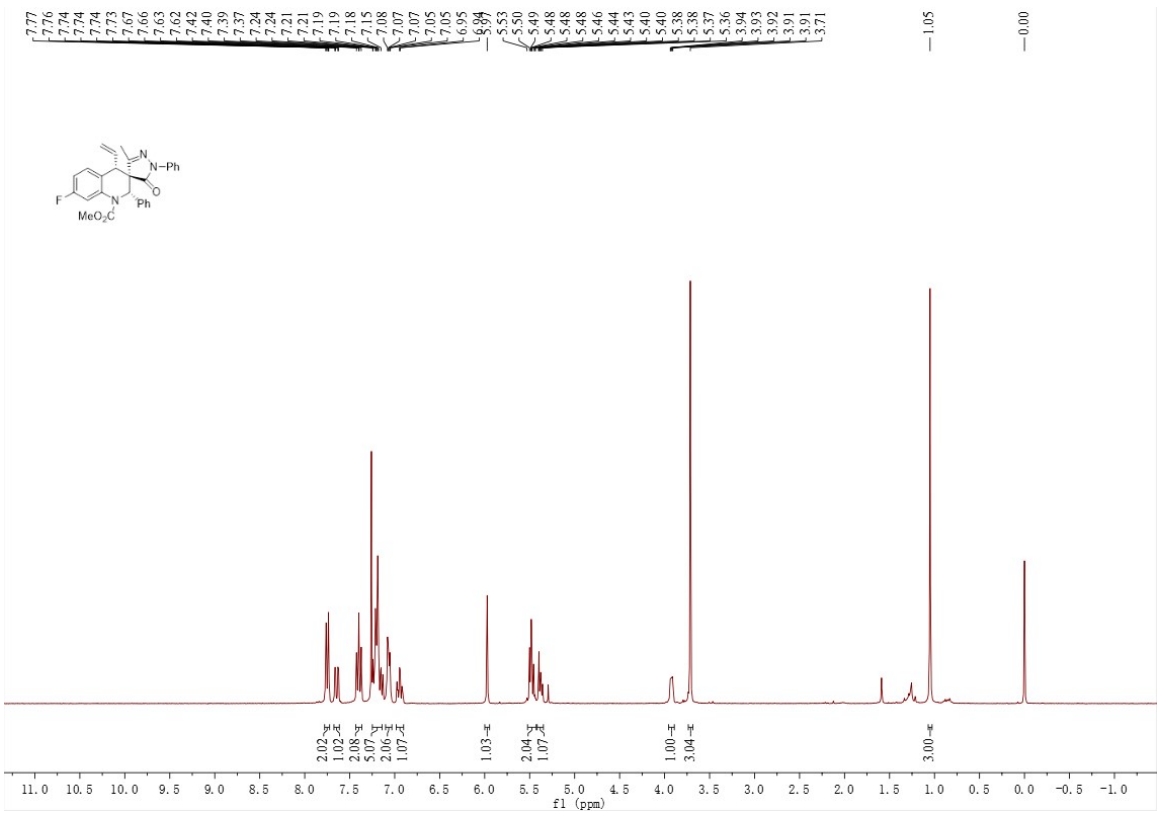

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3c**



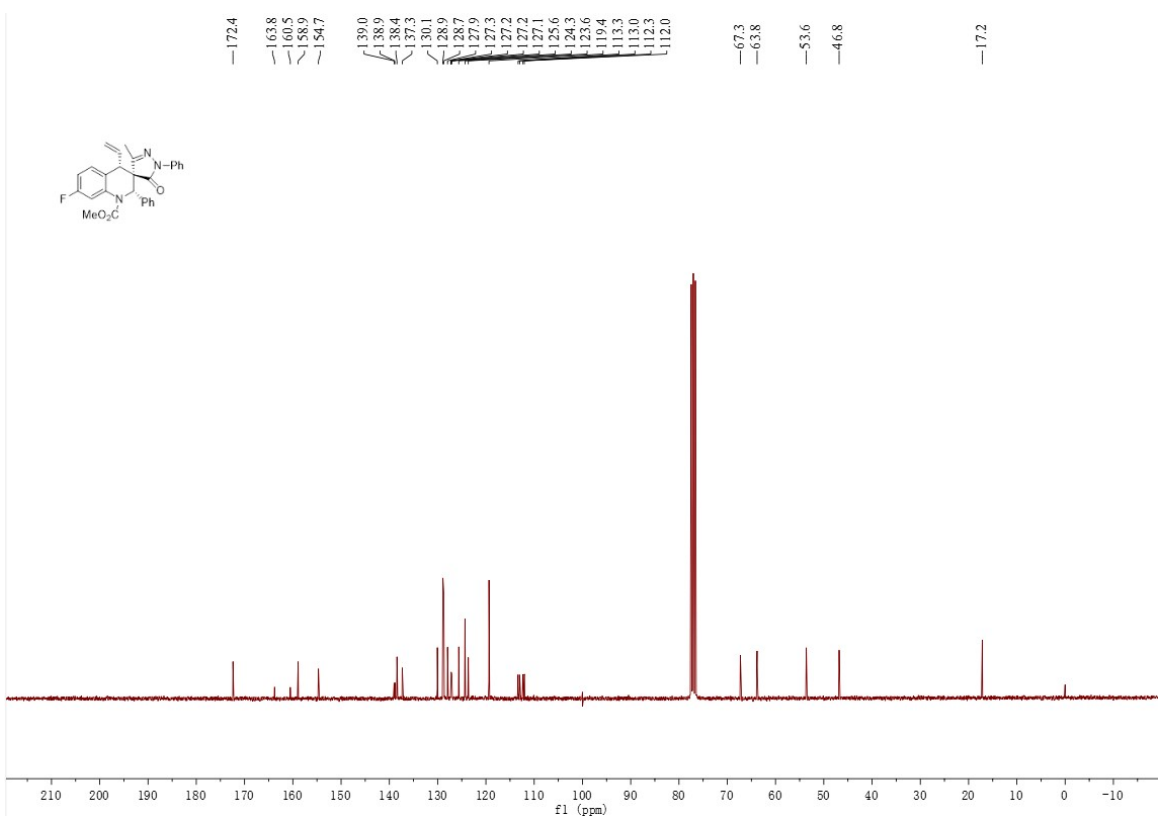
$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3d**



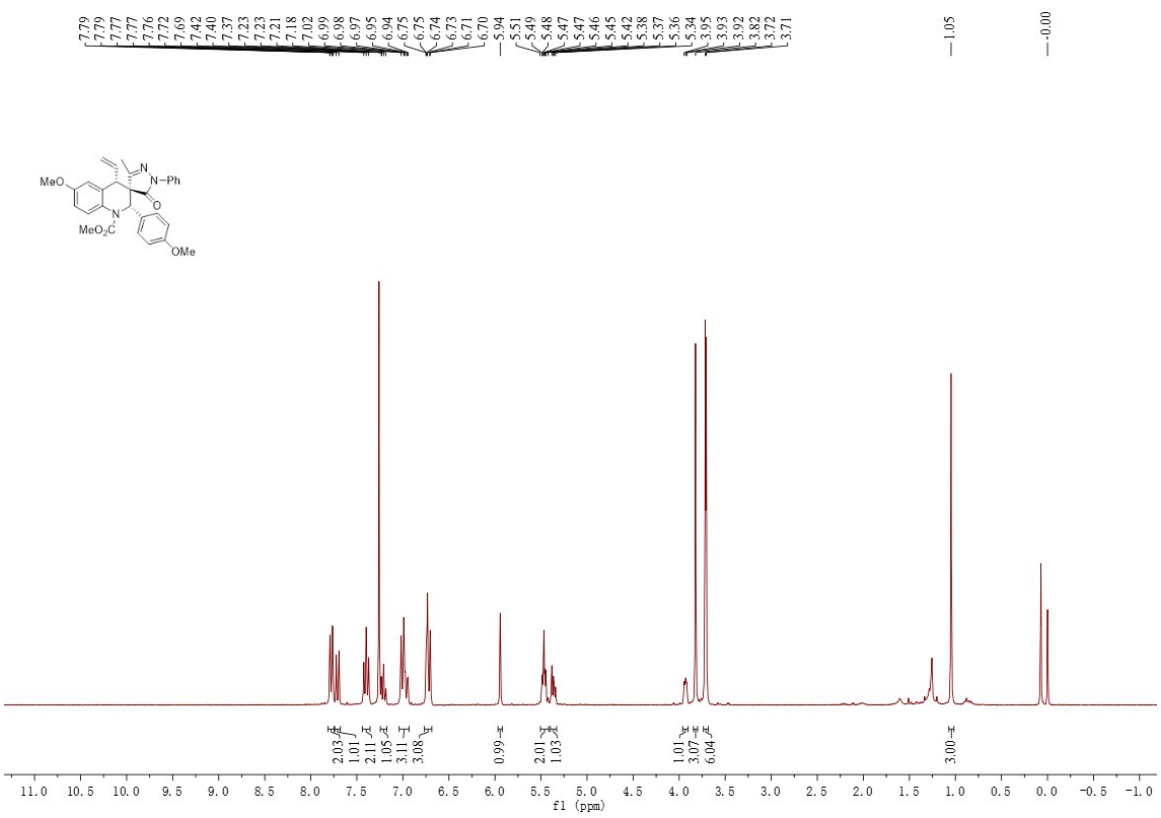
$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3d**



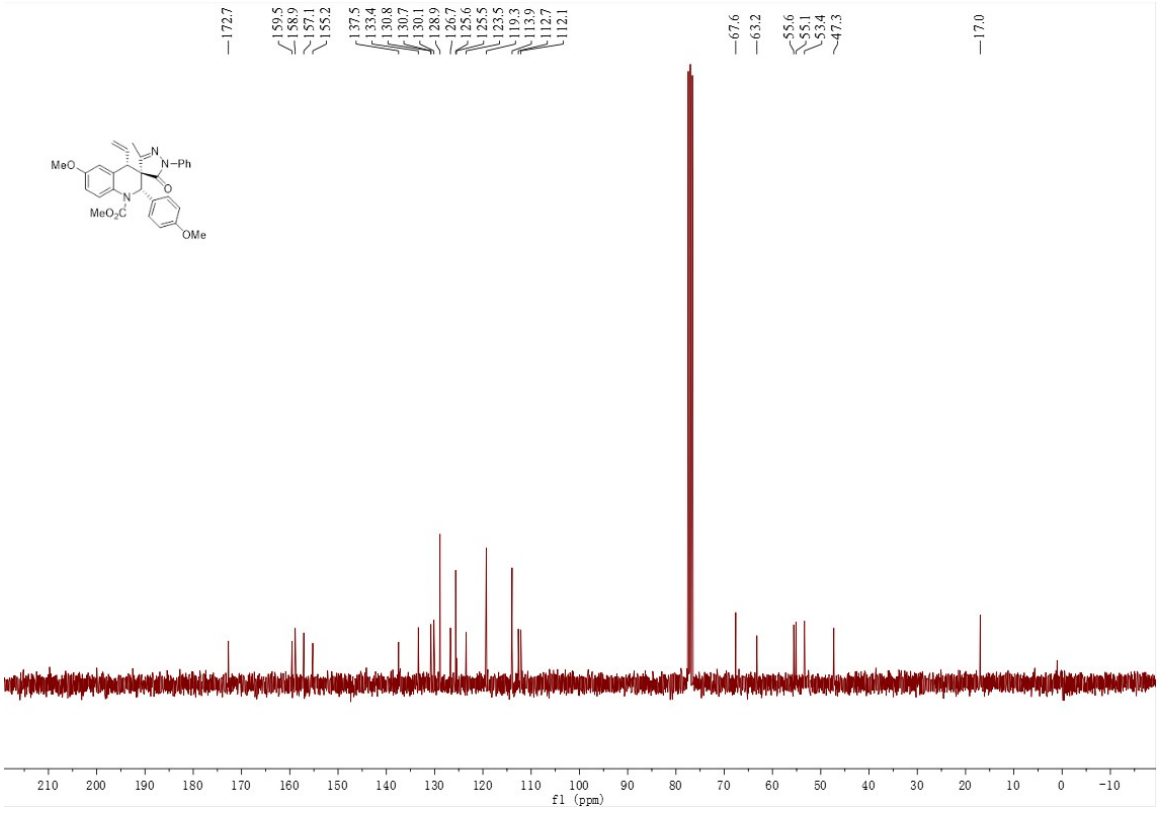

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3e**



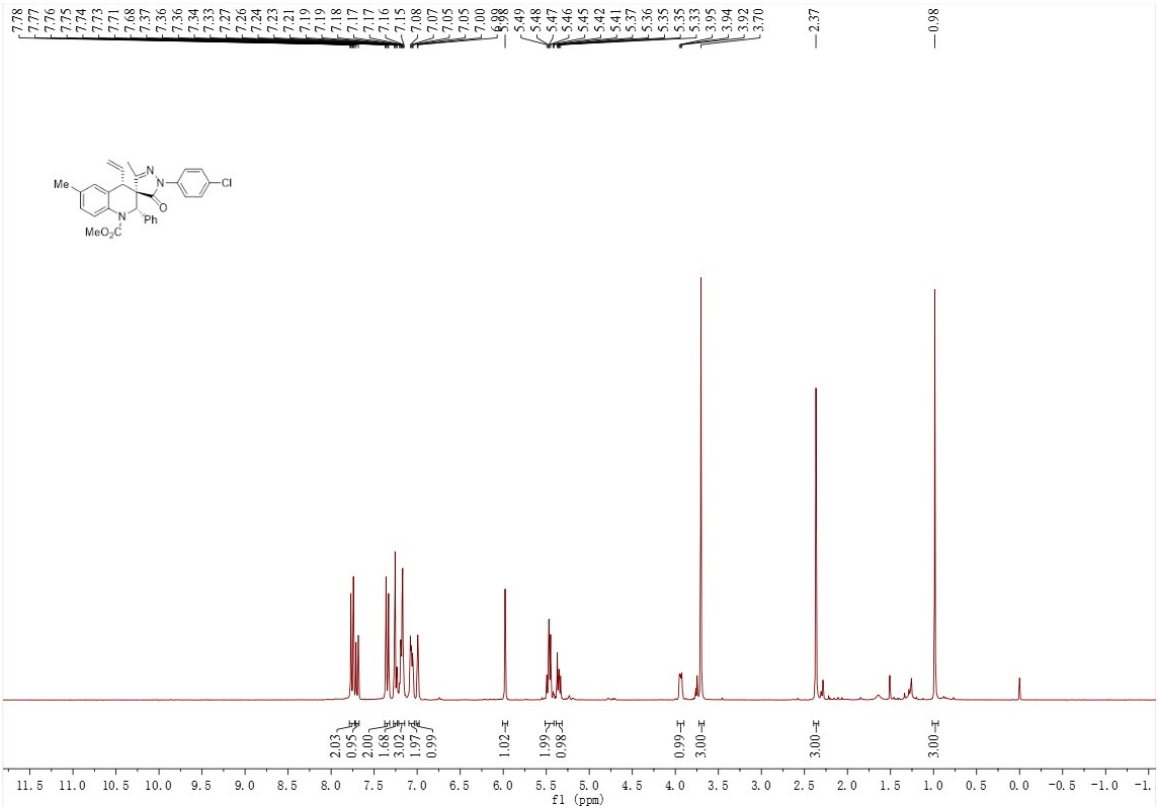

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3e**



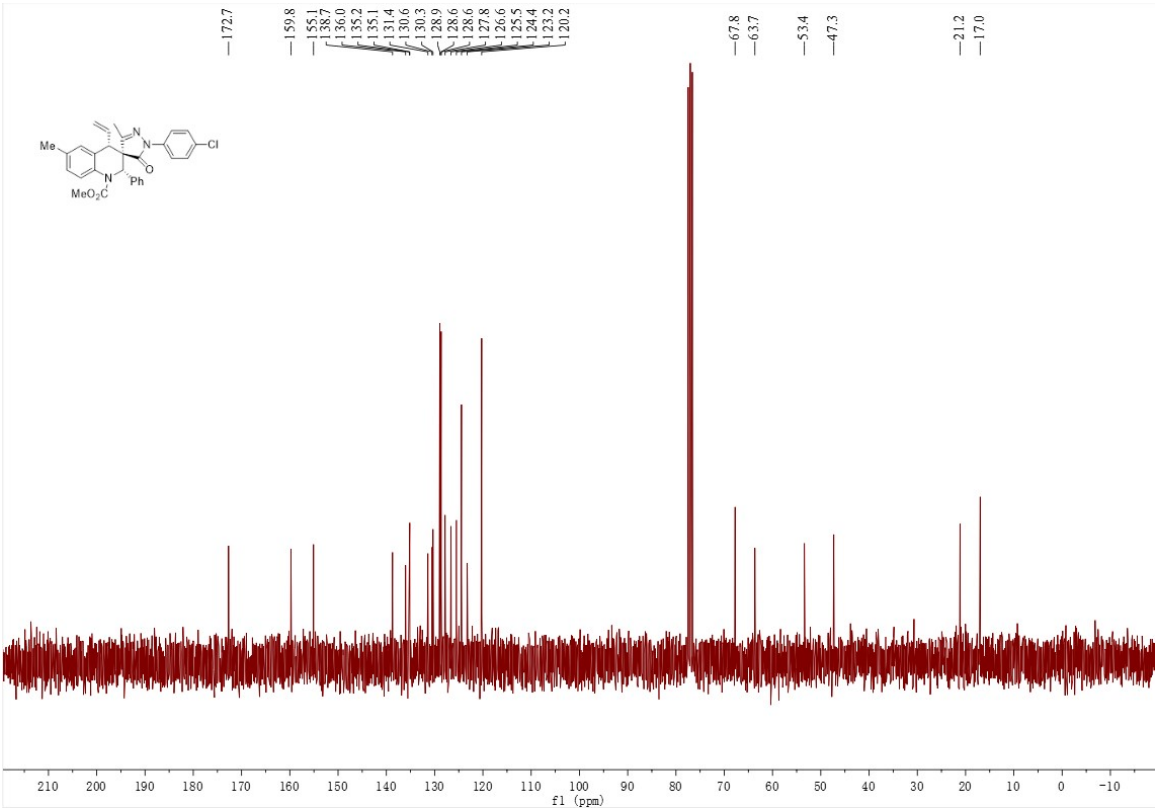

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3f**



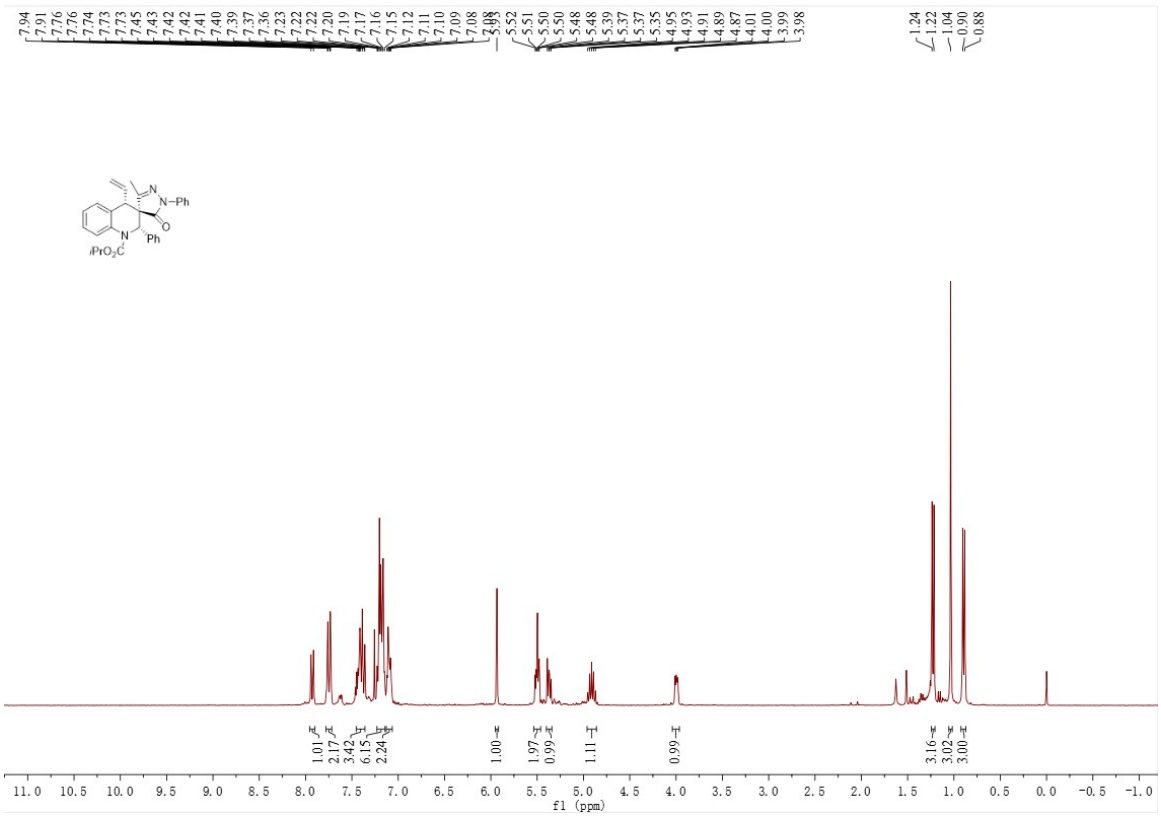

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3f**



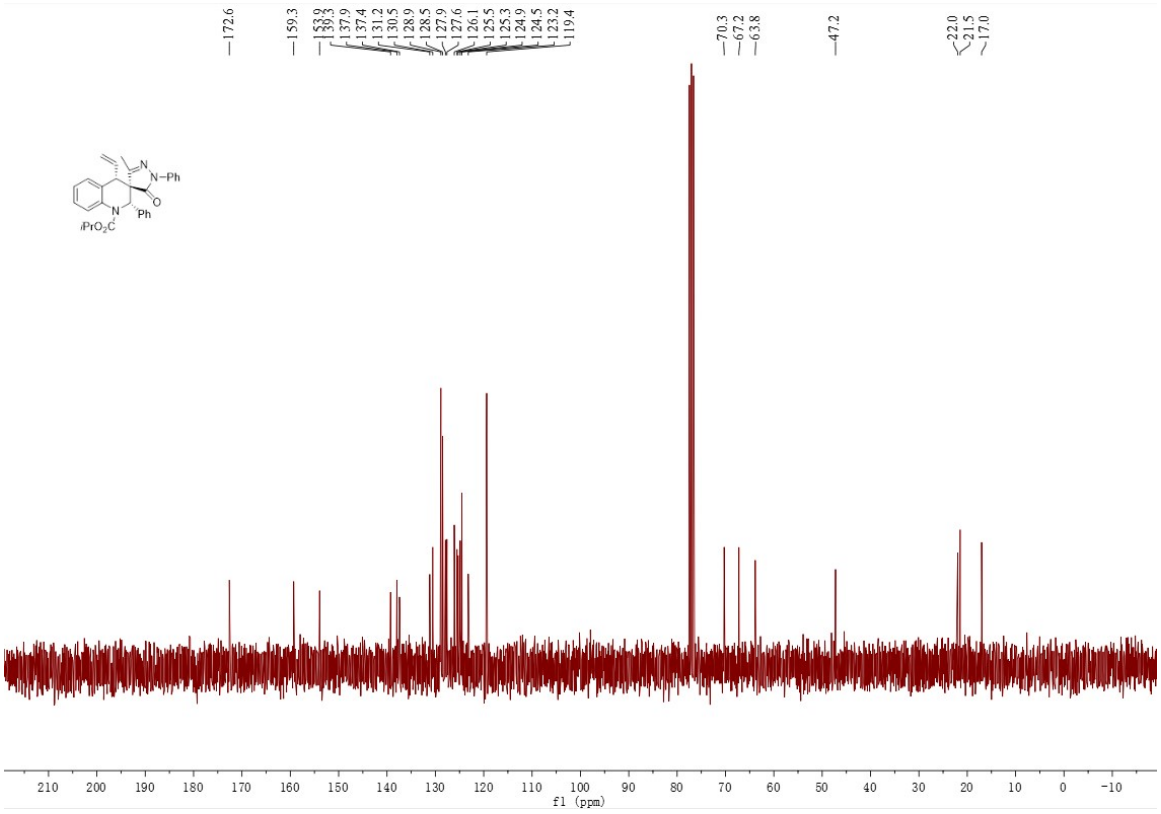

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3g**



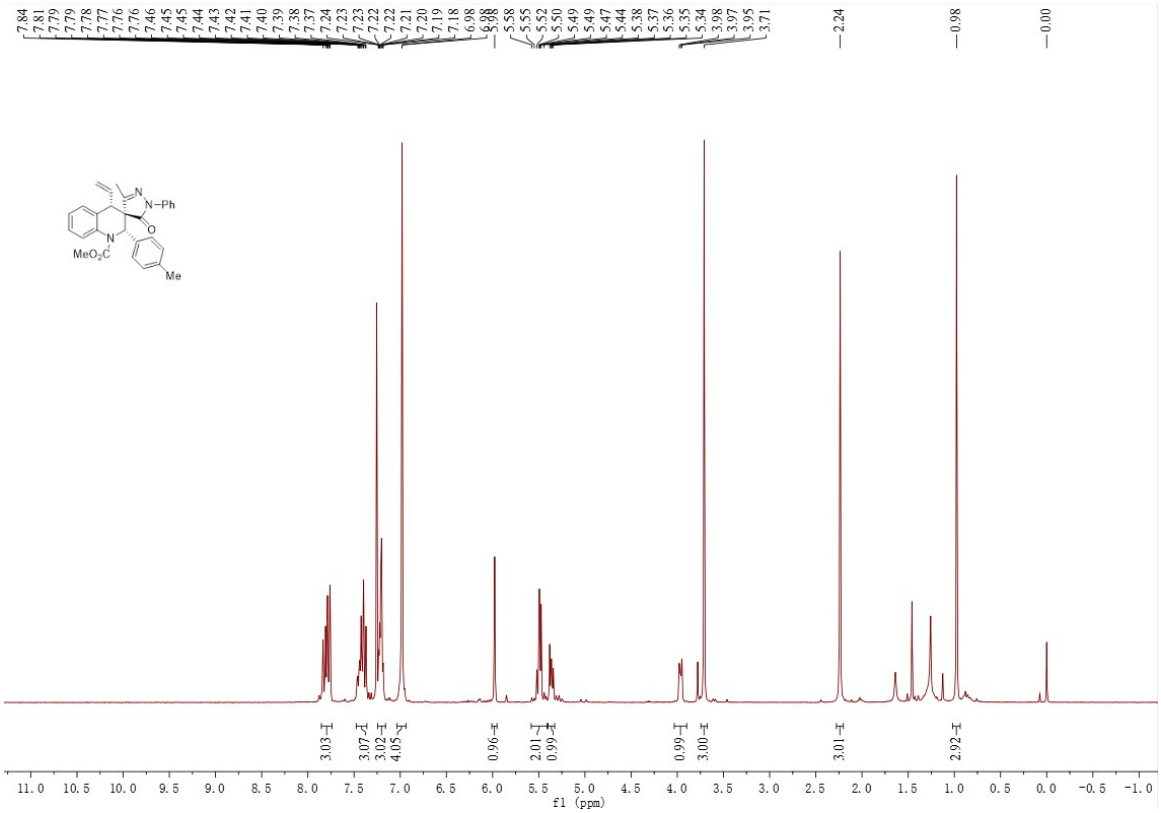

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3g**



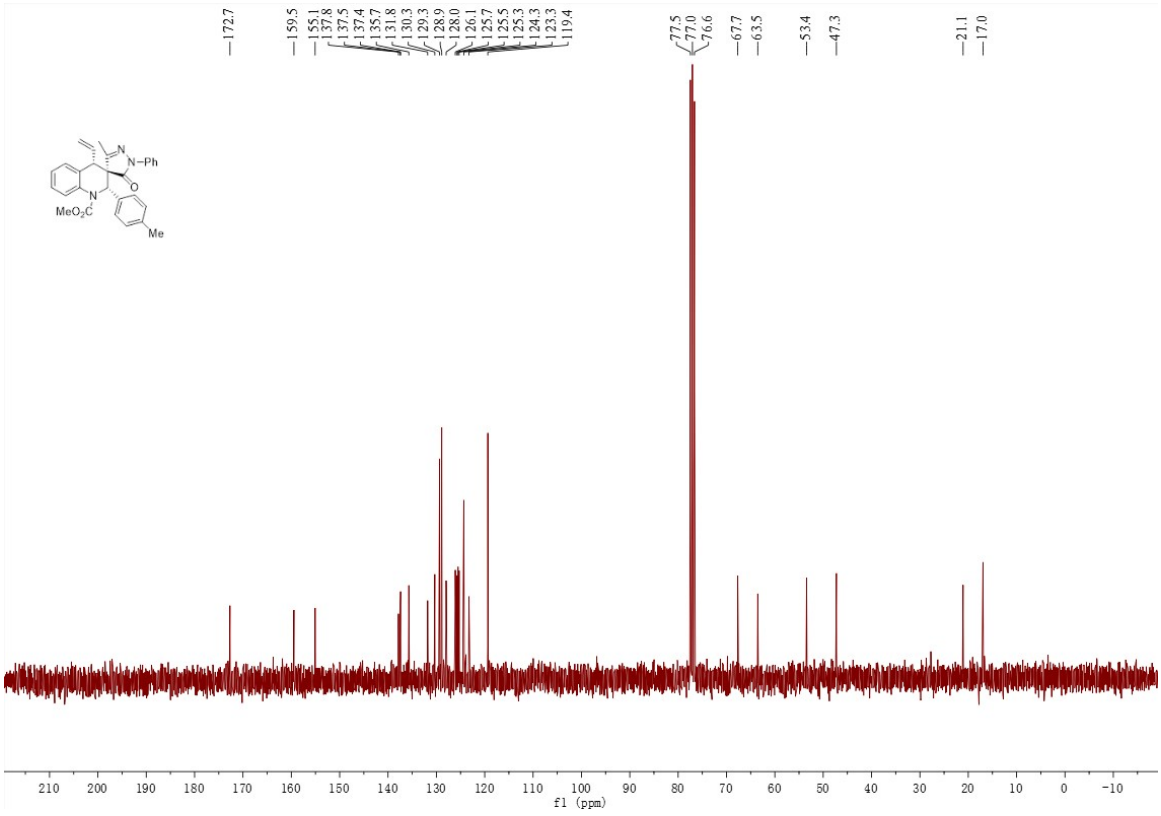

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3h**



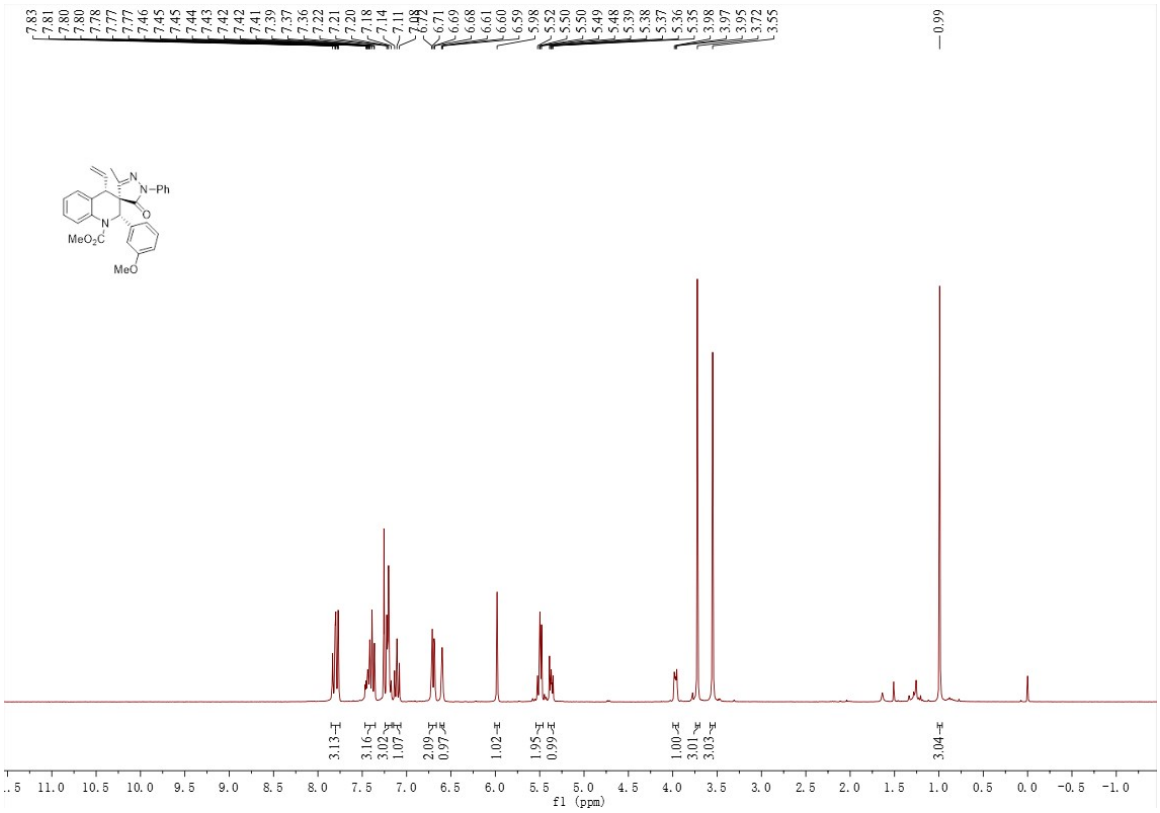

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3h**



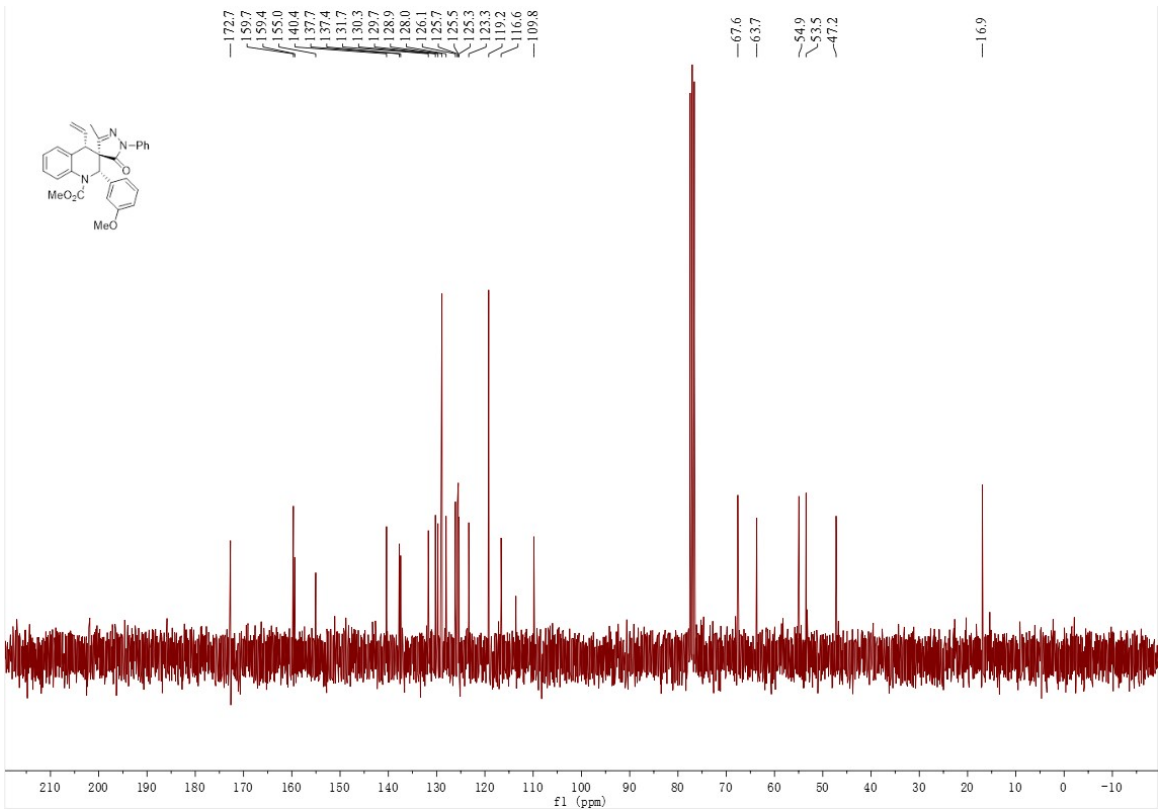
$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **3i**



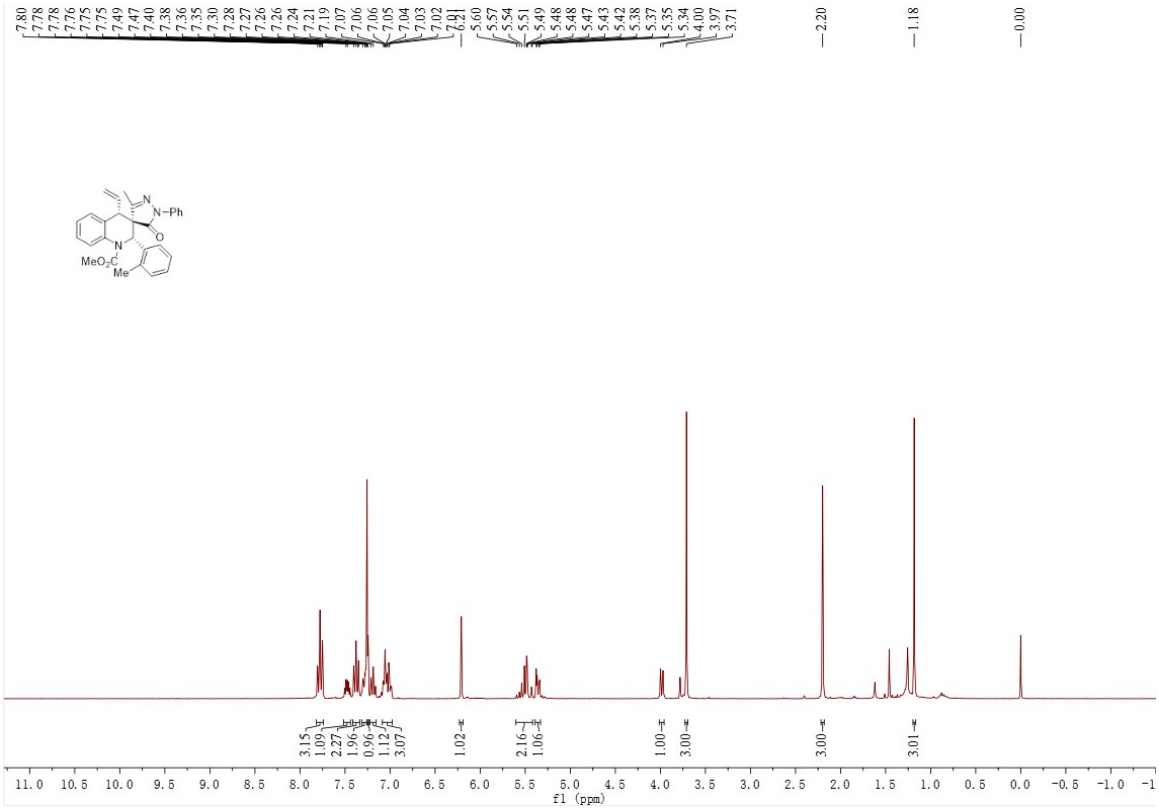
$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **3i**



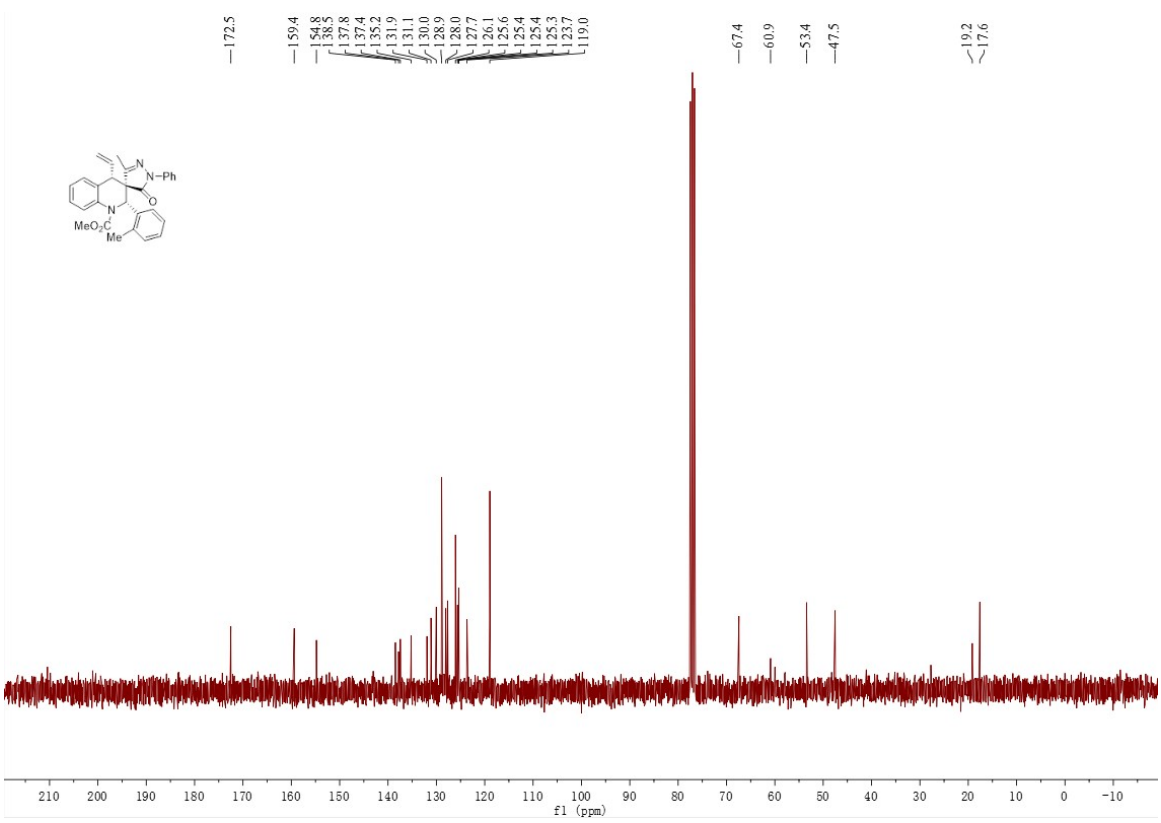

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3j**



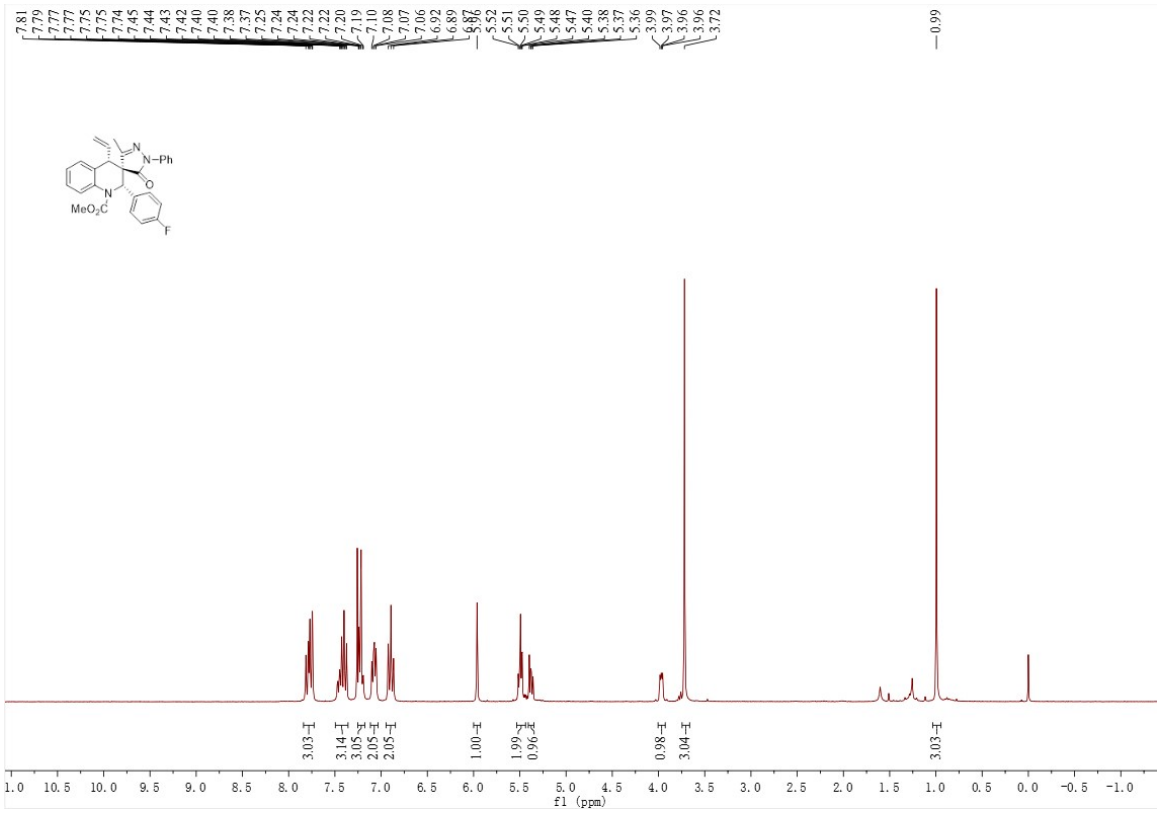

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3j**



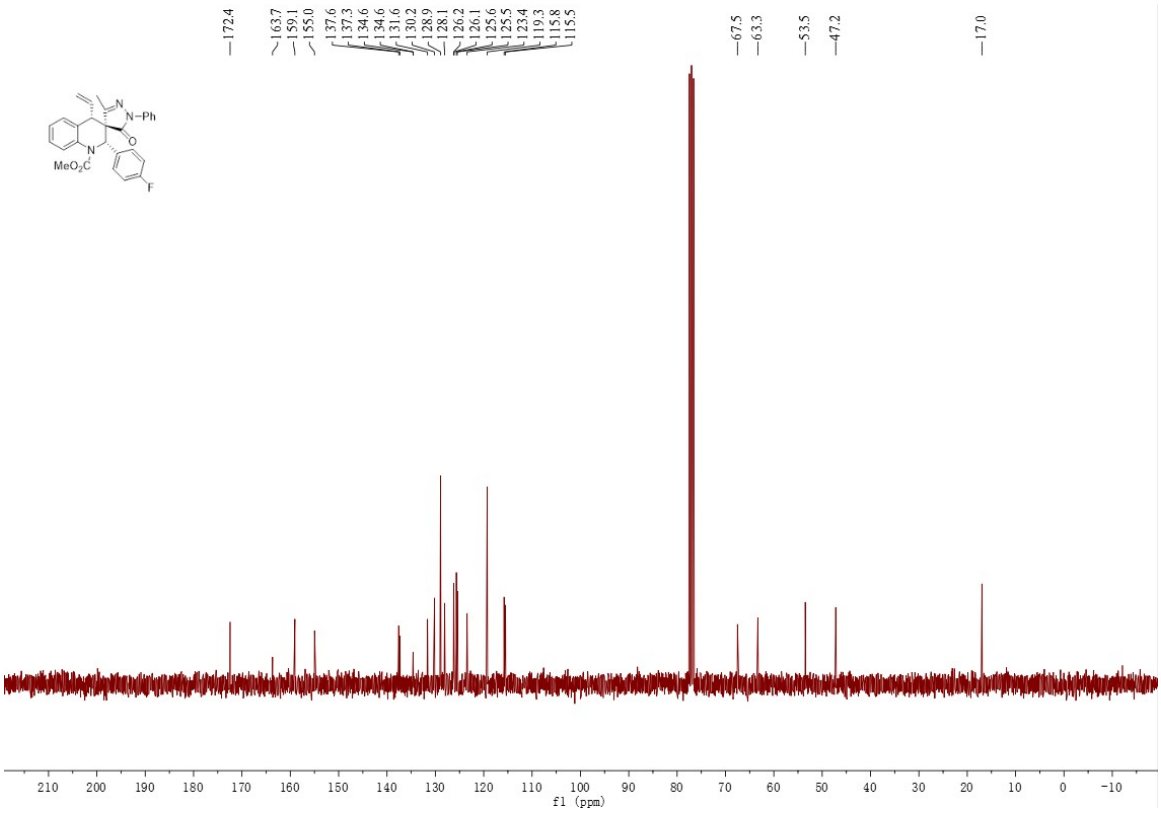

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3k**



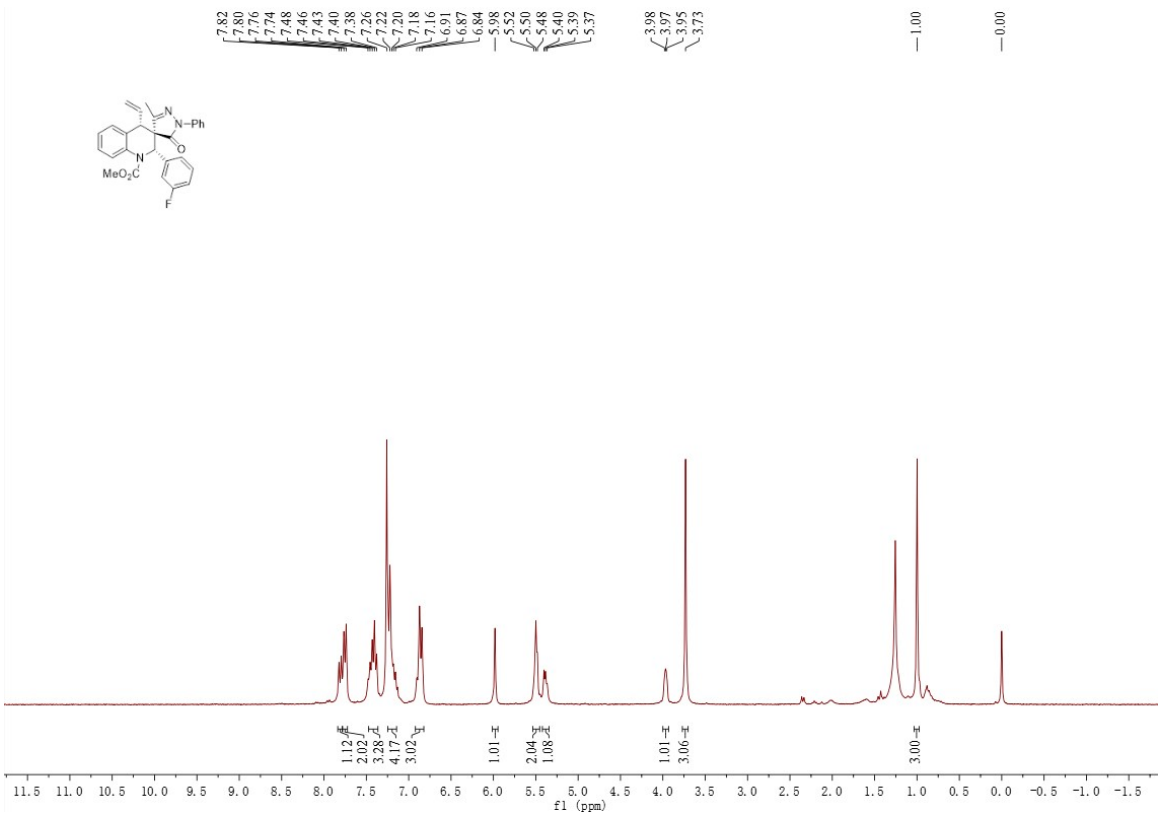

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3k**



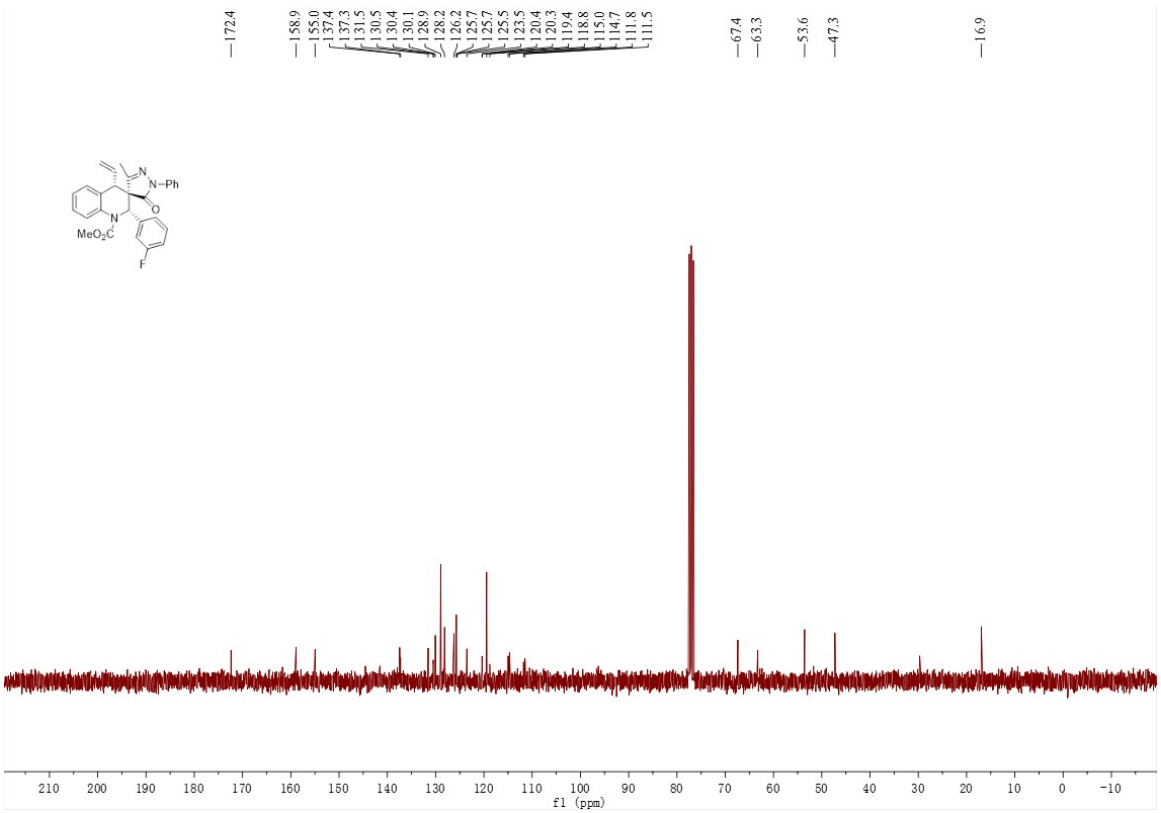

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **3l**



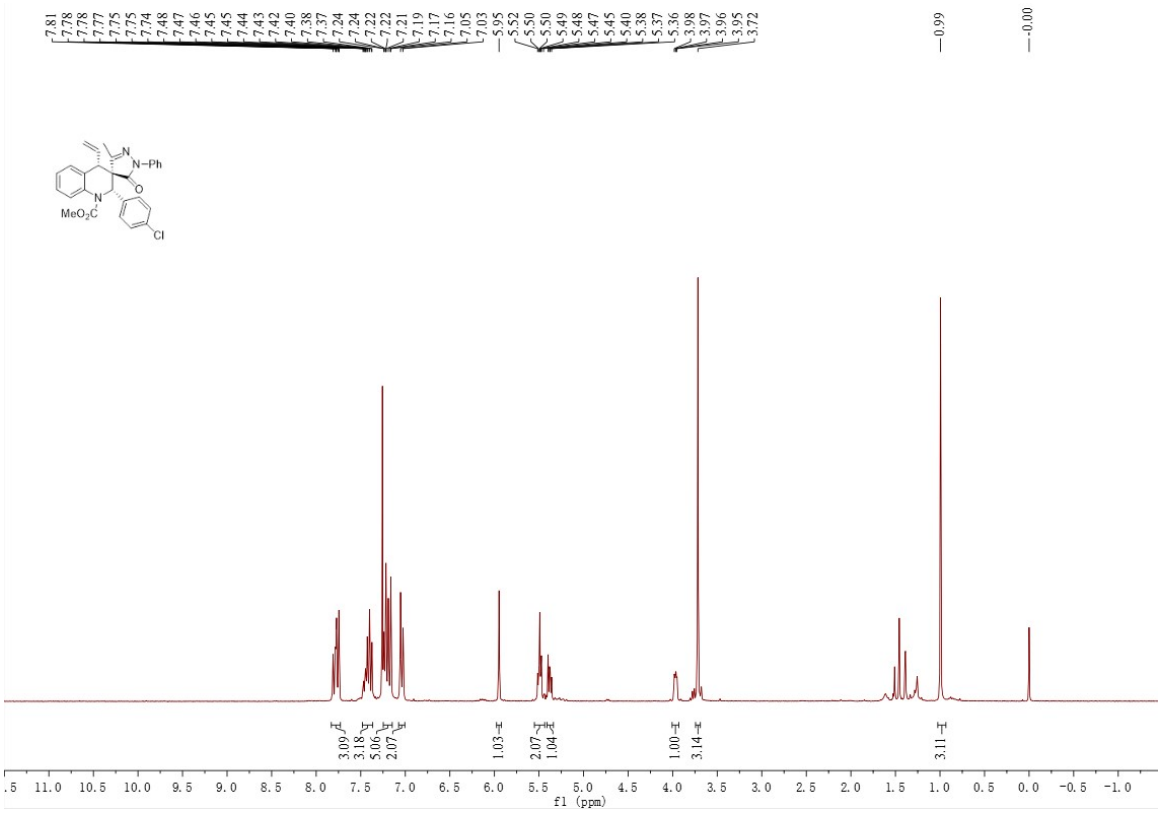

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **3l**



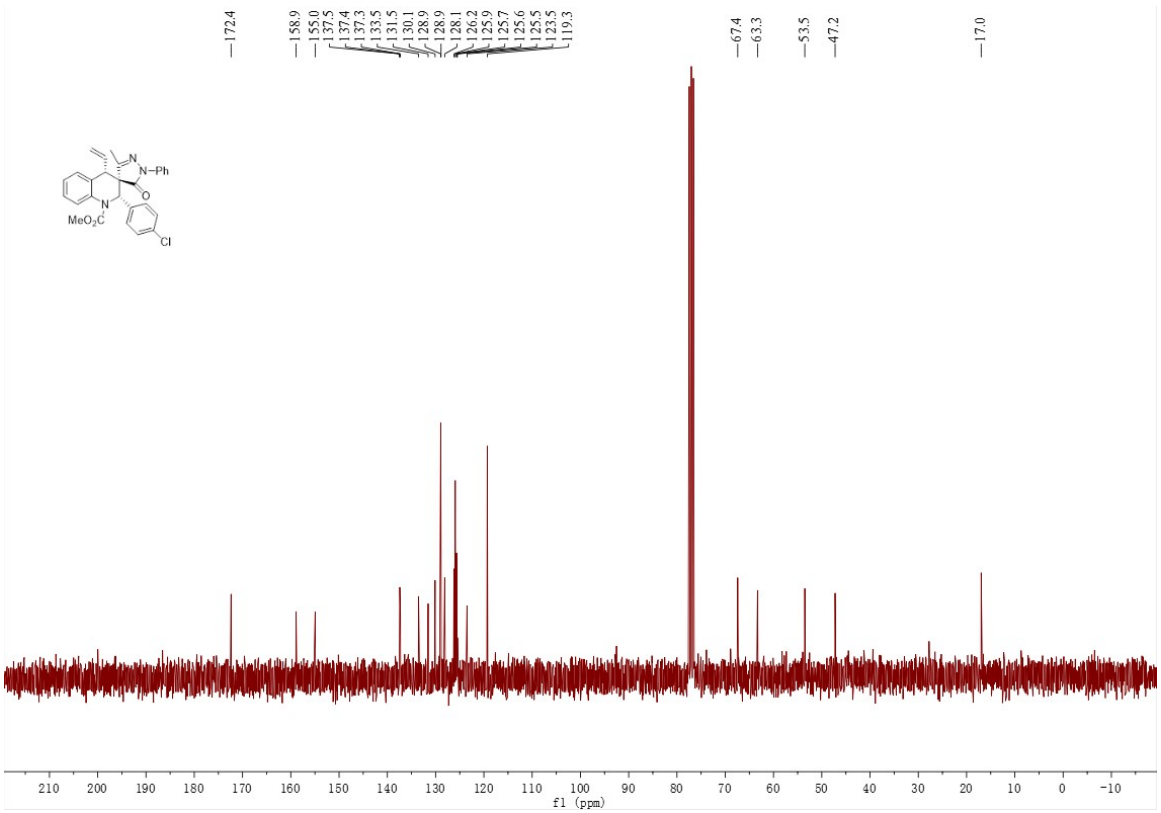

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **3m**



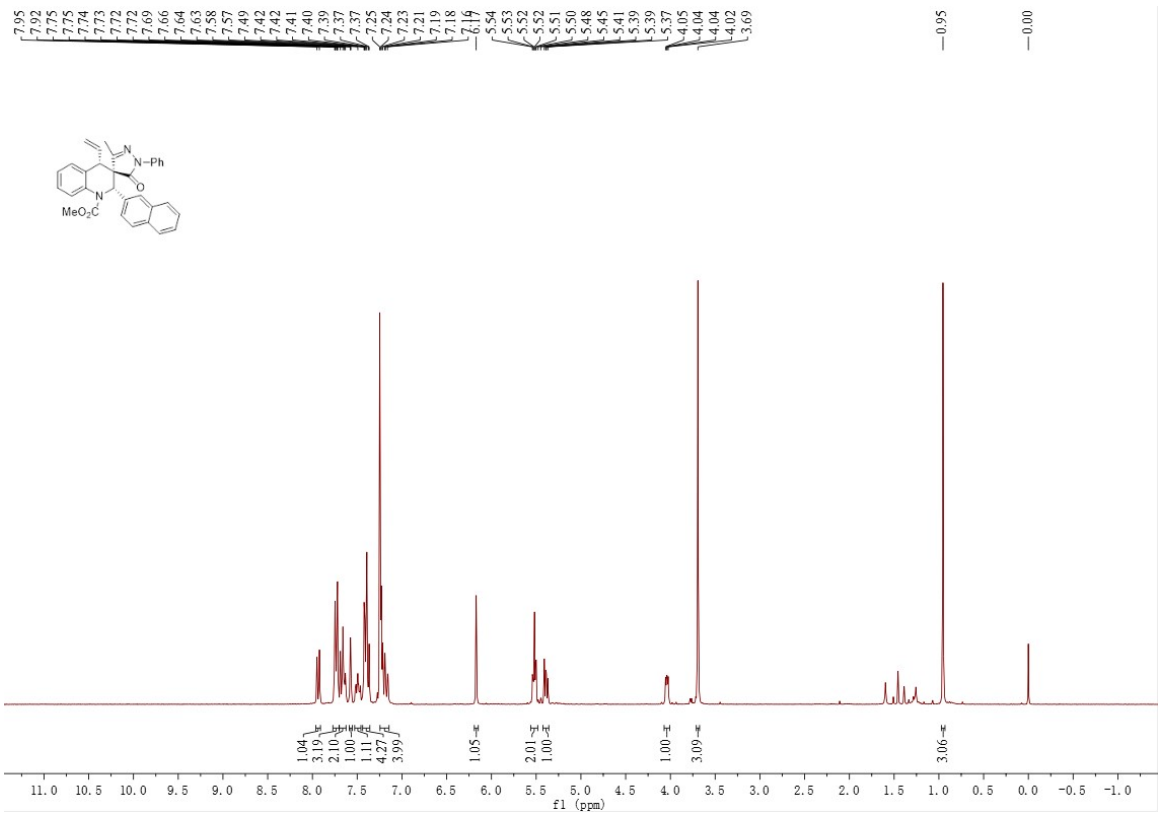

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **3m**



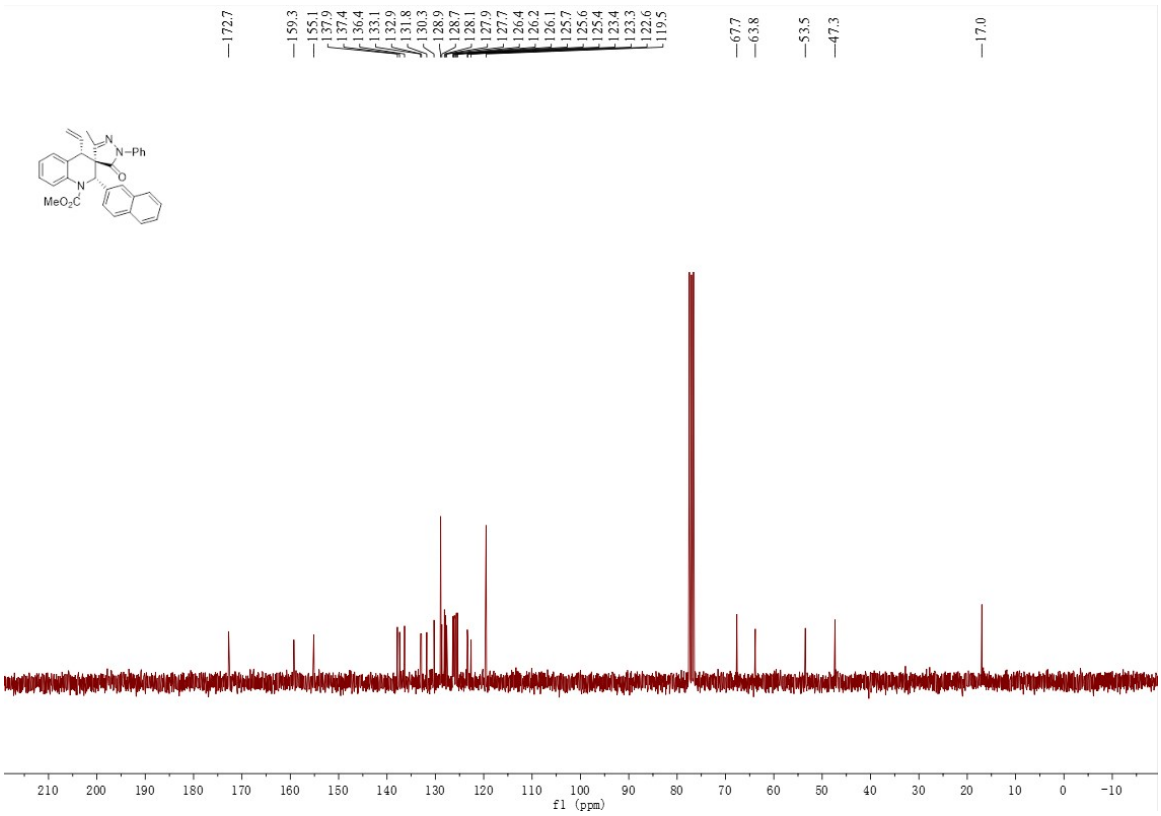

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3n**



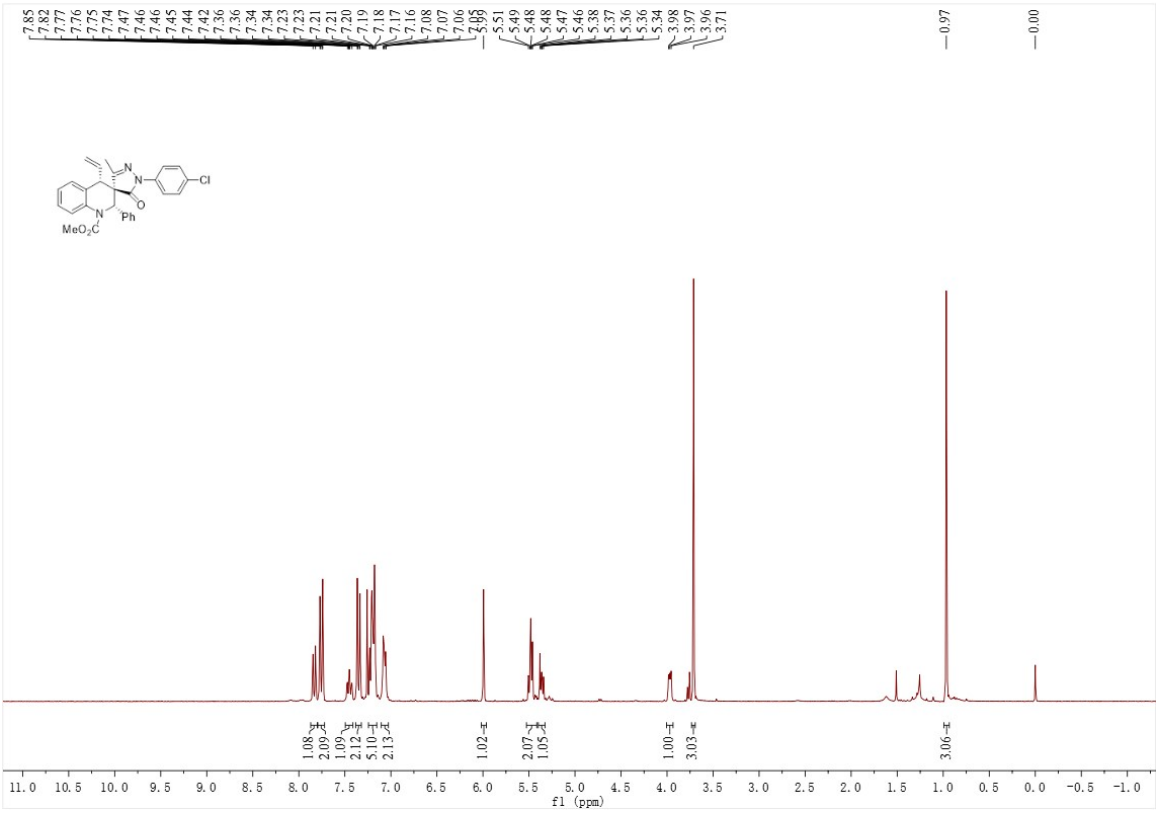

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3n**



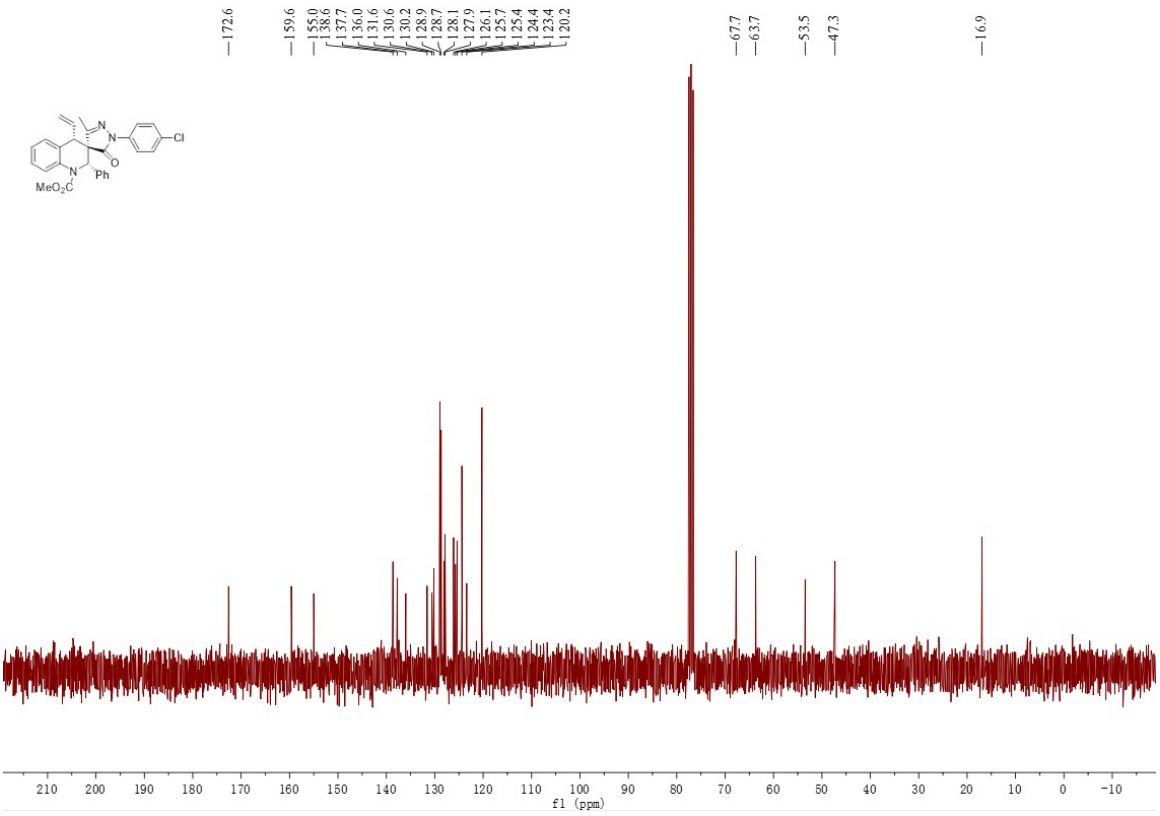

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3o**



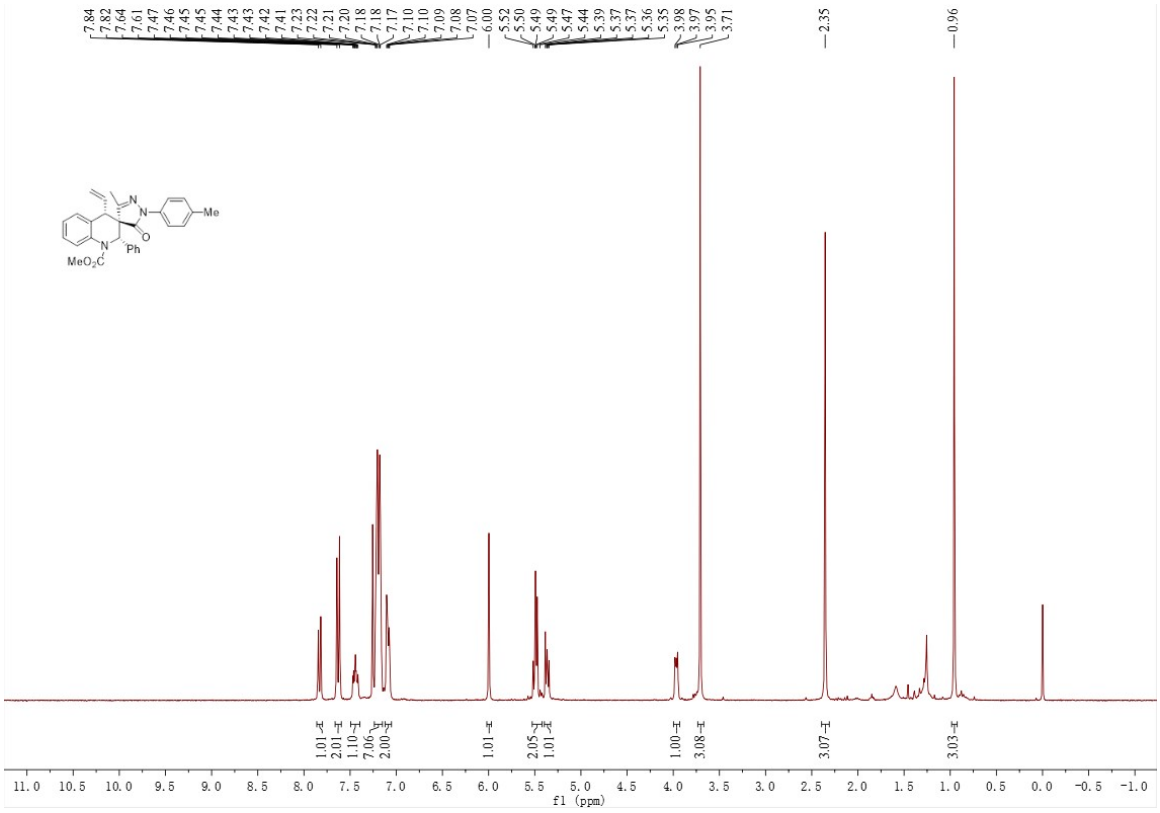

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3o**



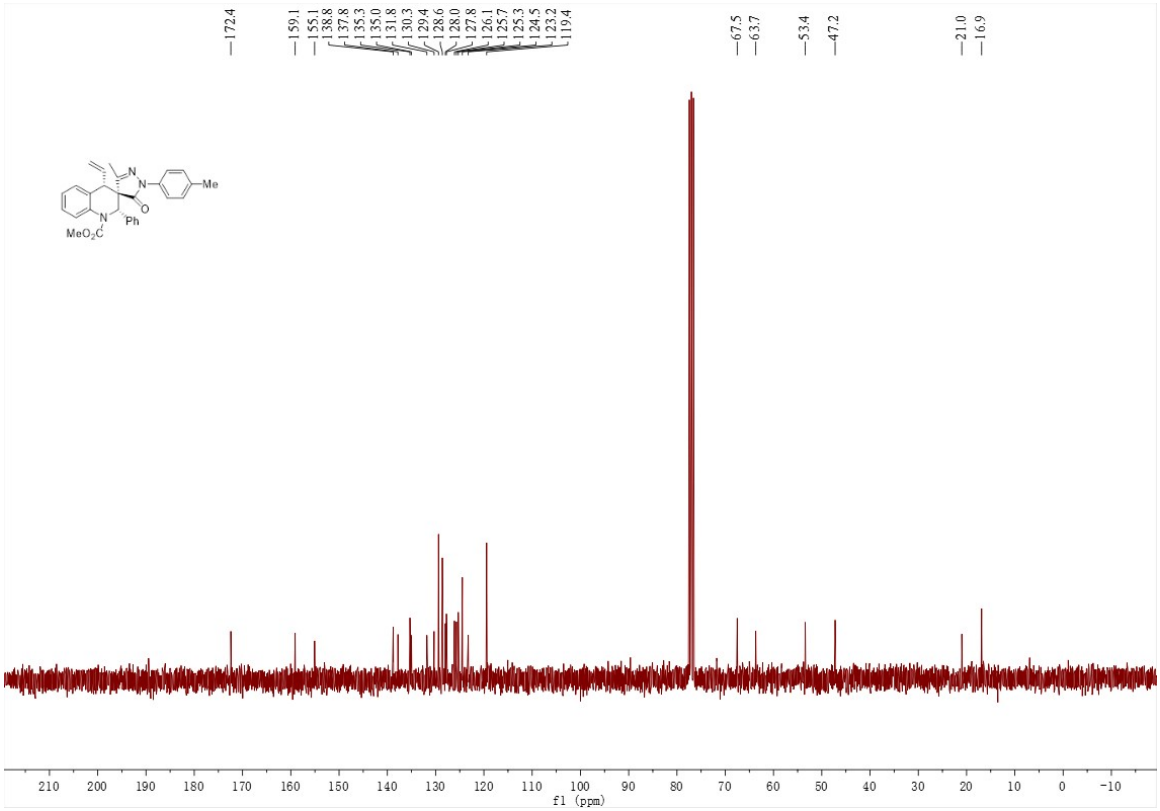

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **3p**



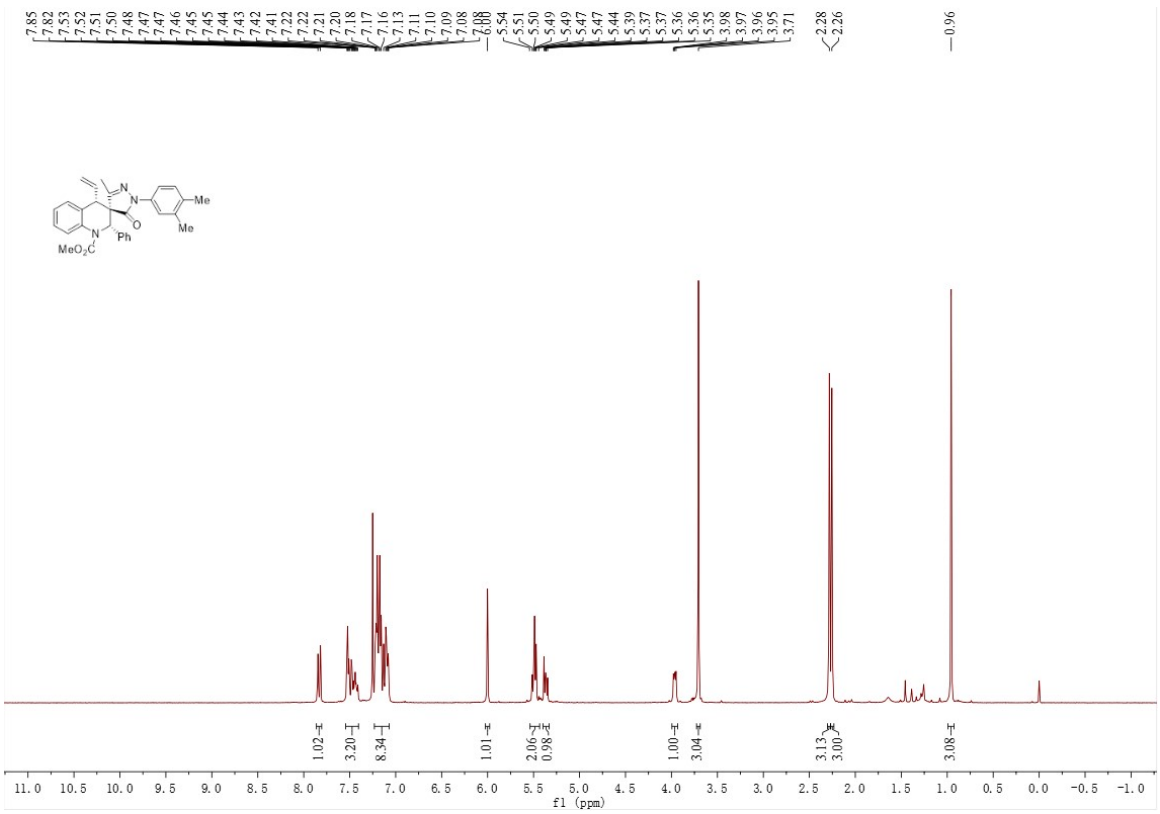

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **3p**



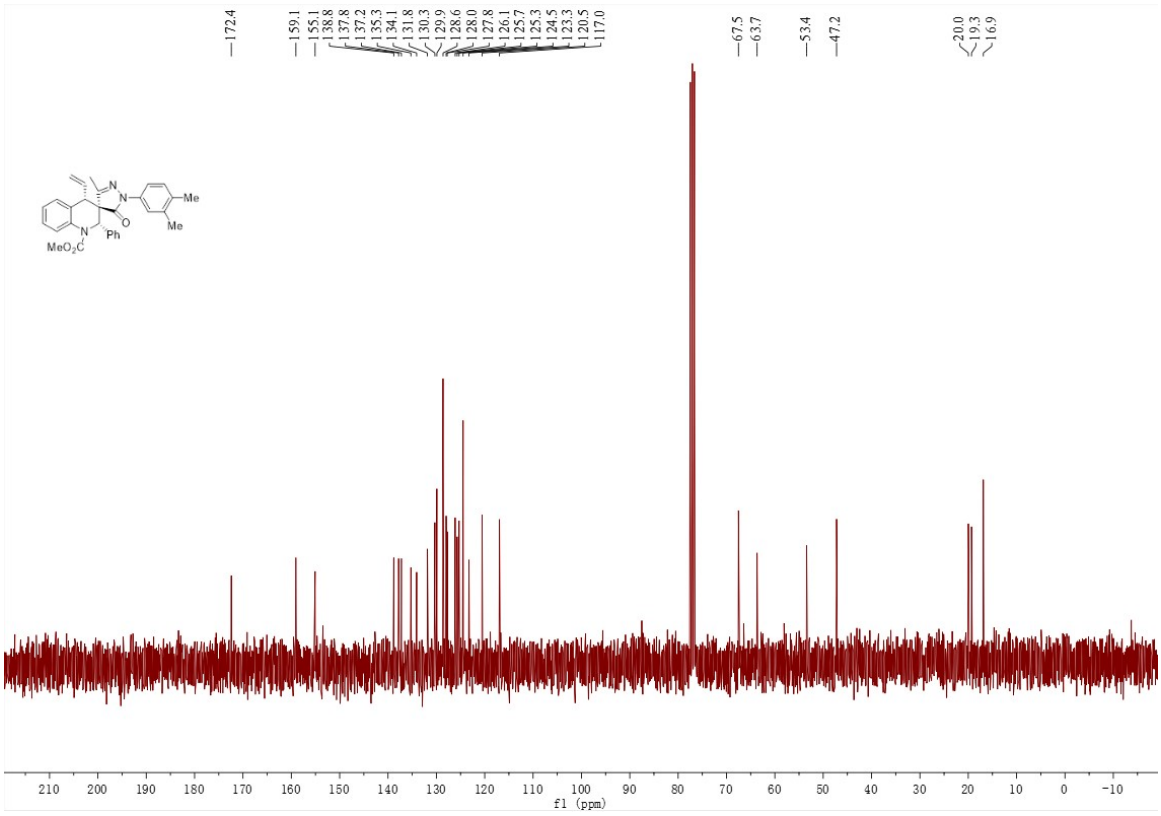

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **3q**



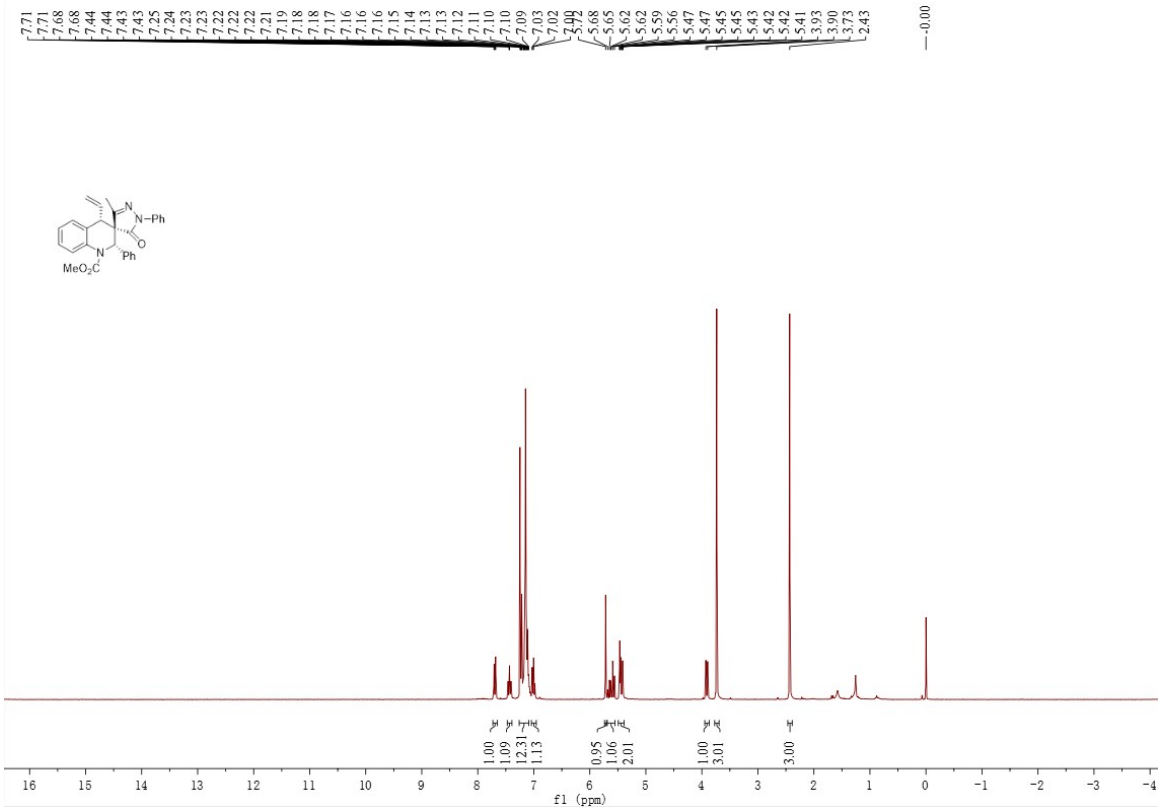

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **3q**



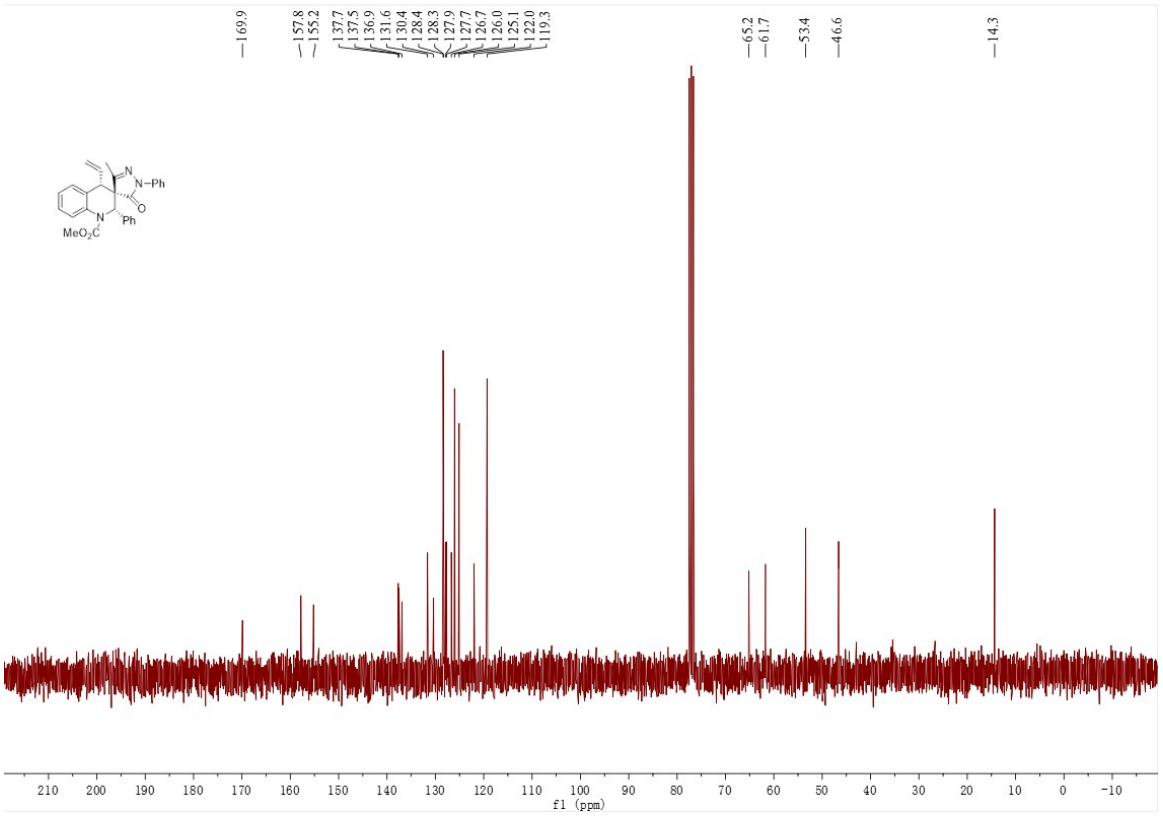

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **3r**



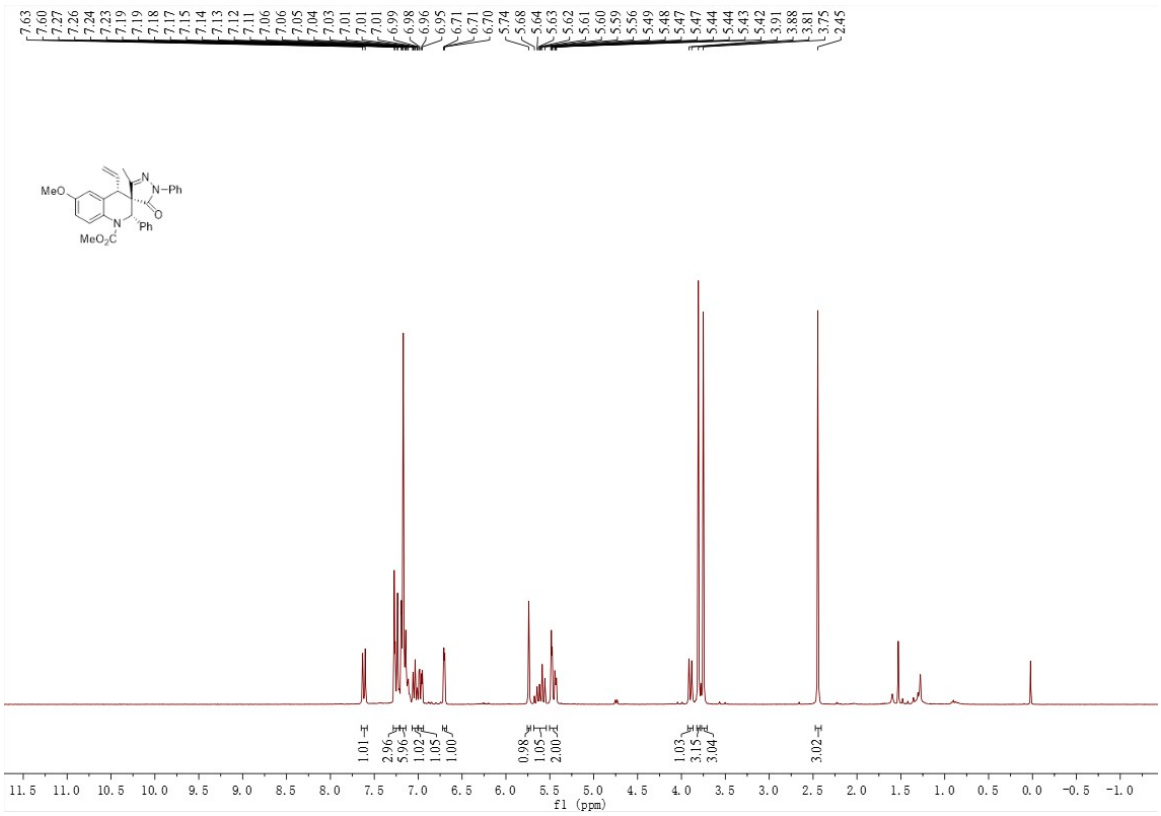

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **3r**



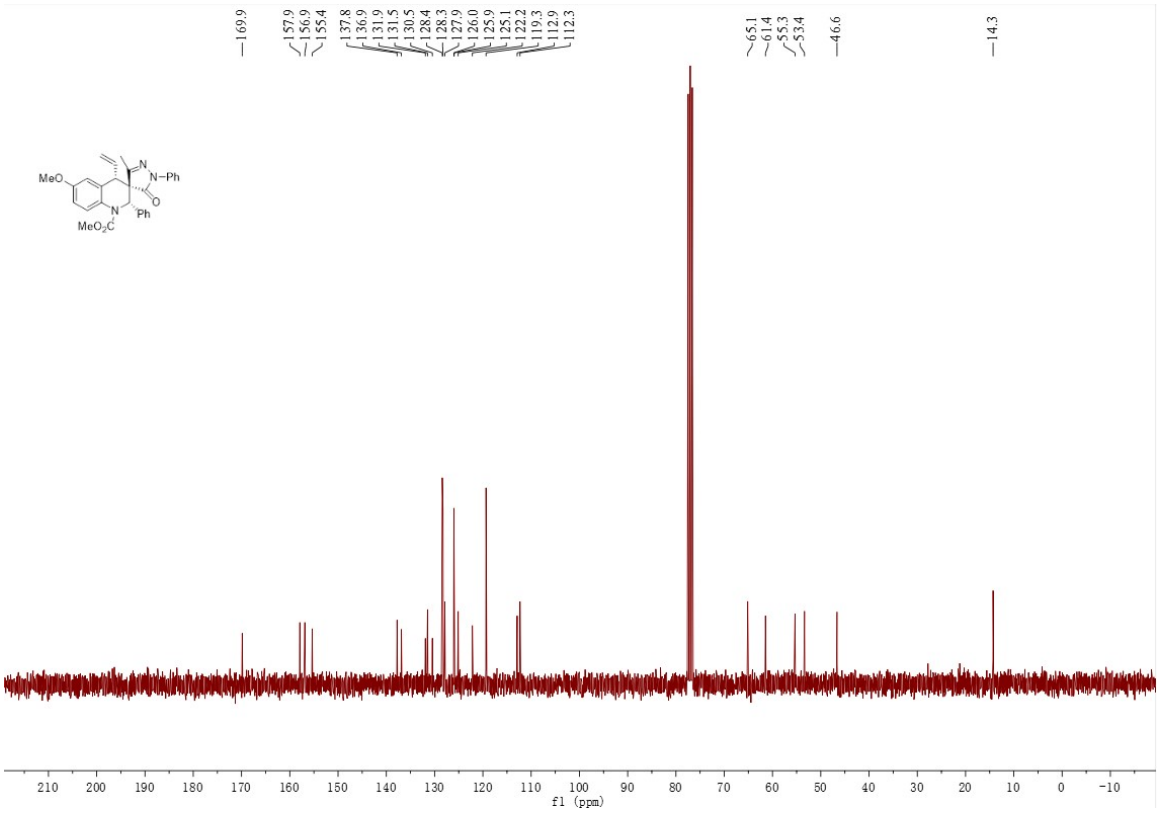

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **4a**



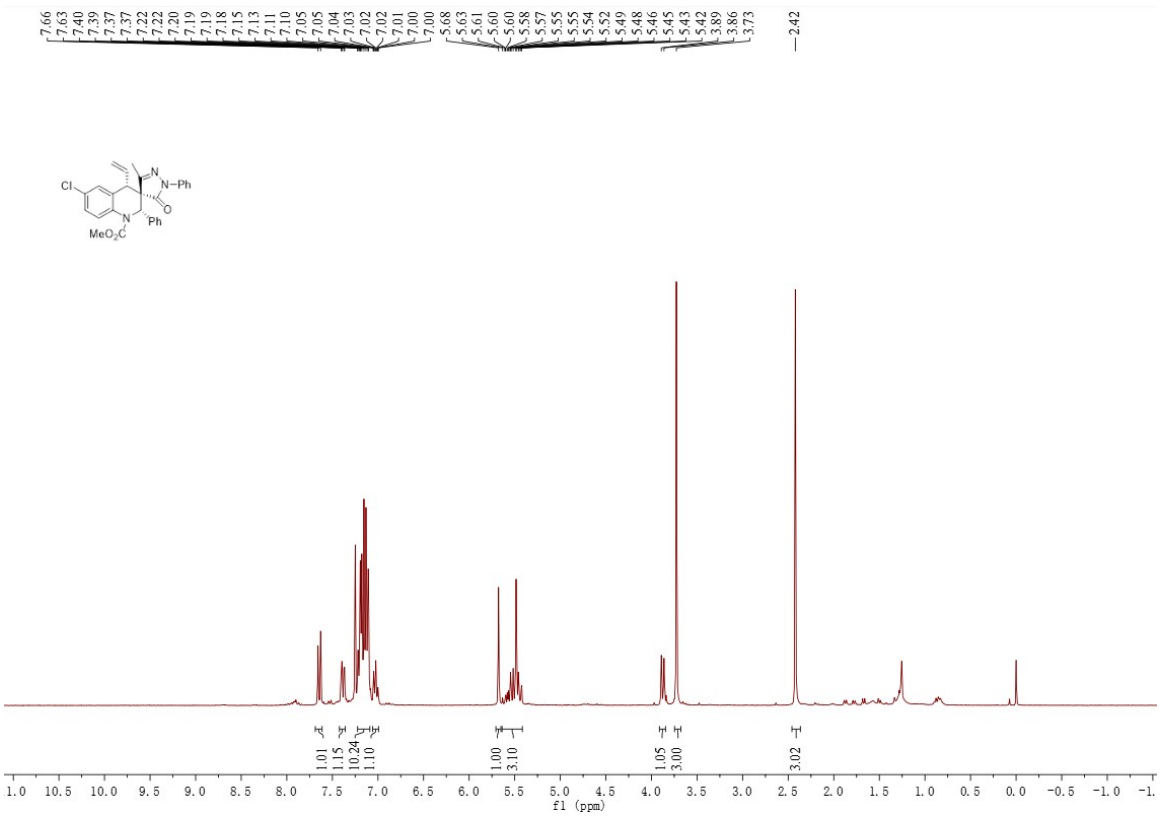

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **4a**



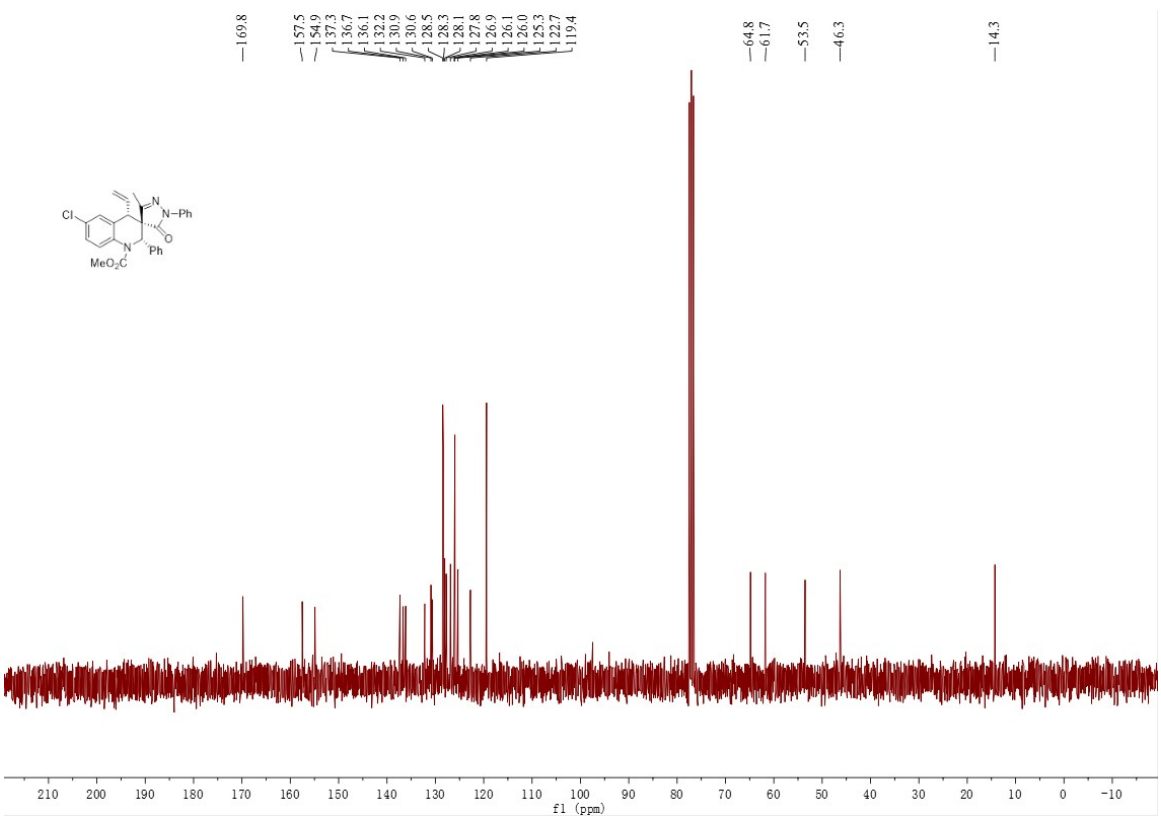

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4b**



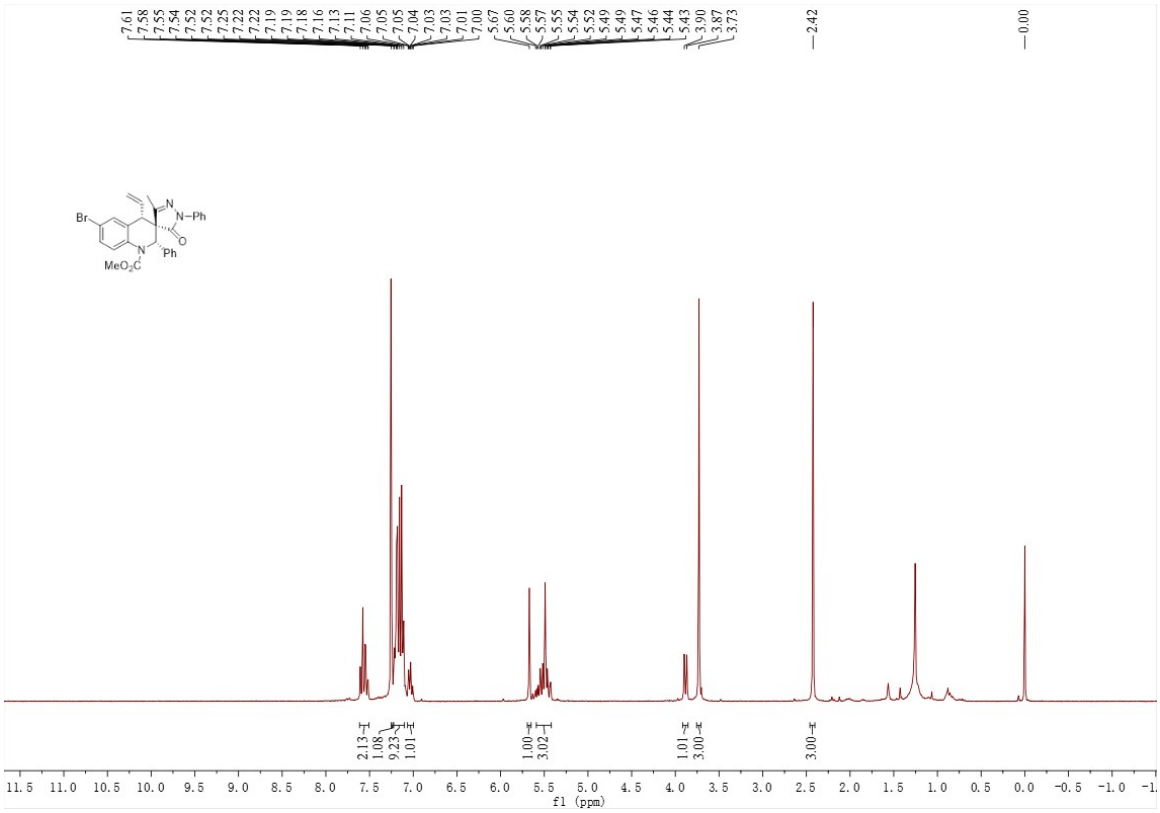

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4b**



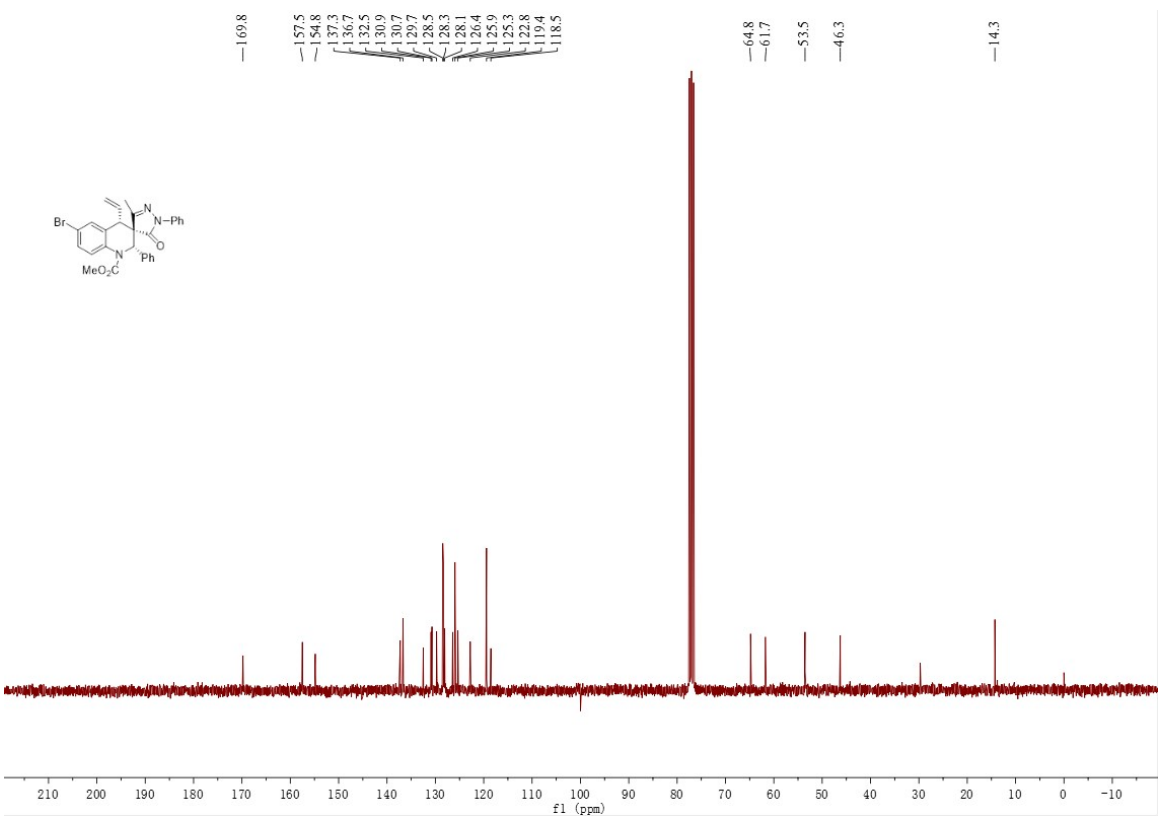

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **4c**



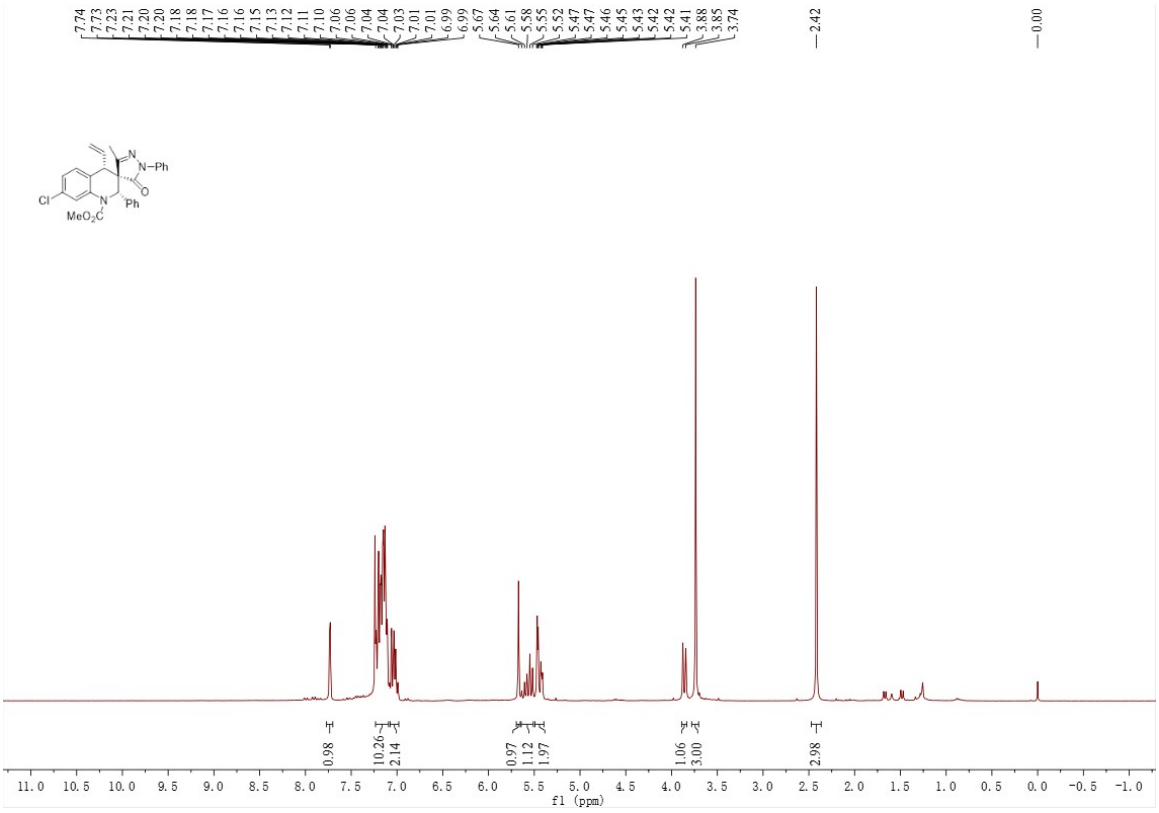

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **4c**



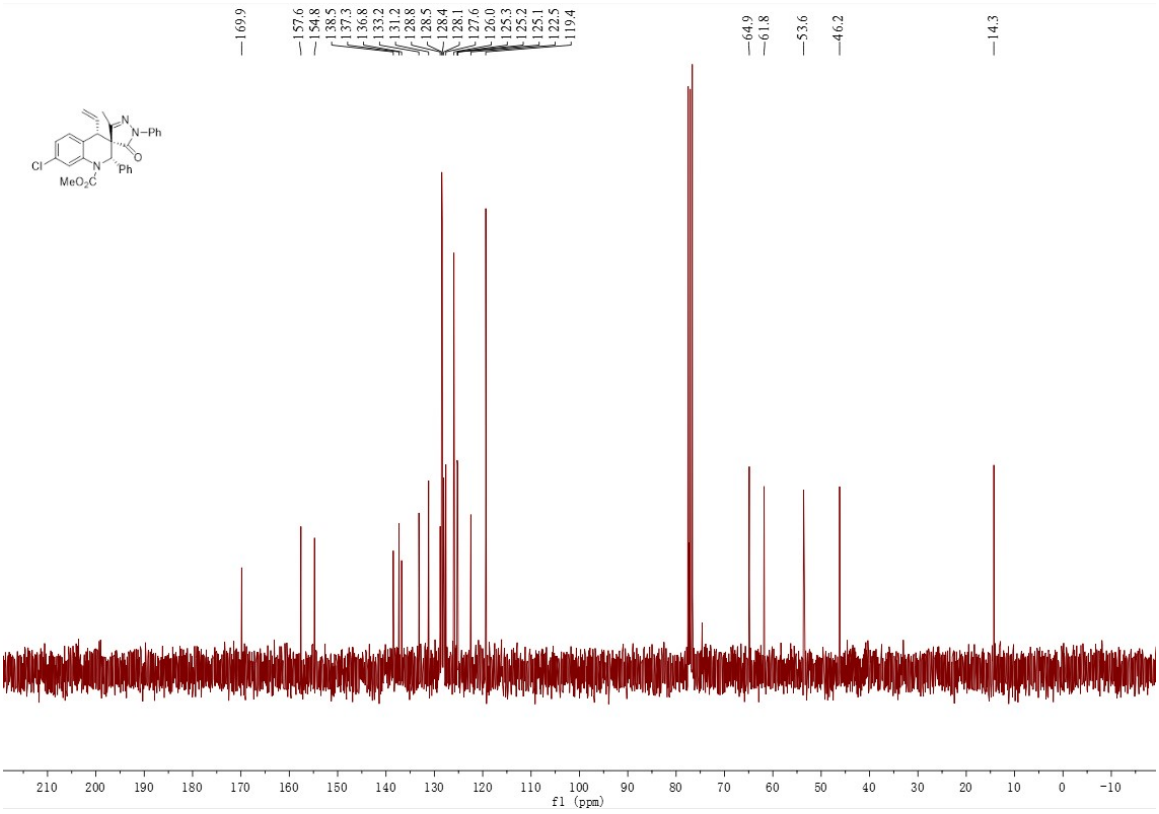

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4d**



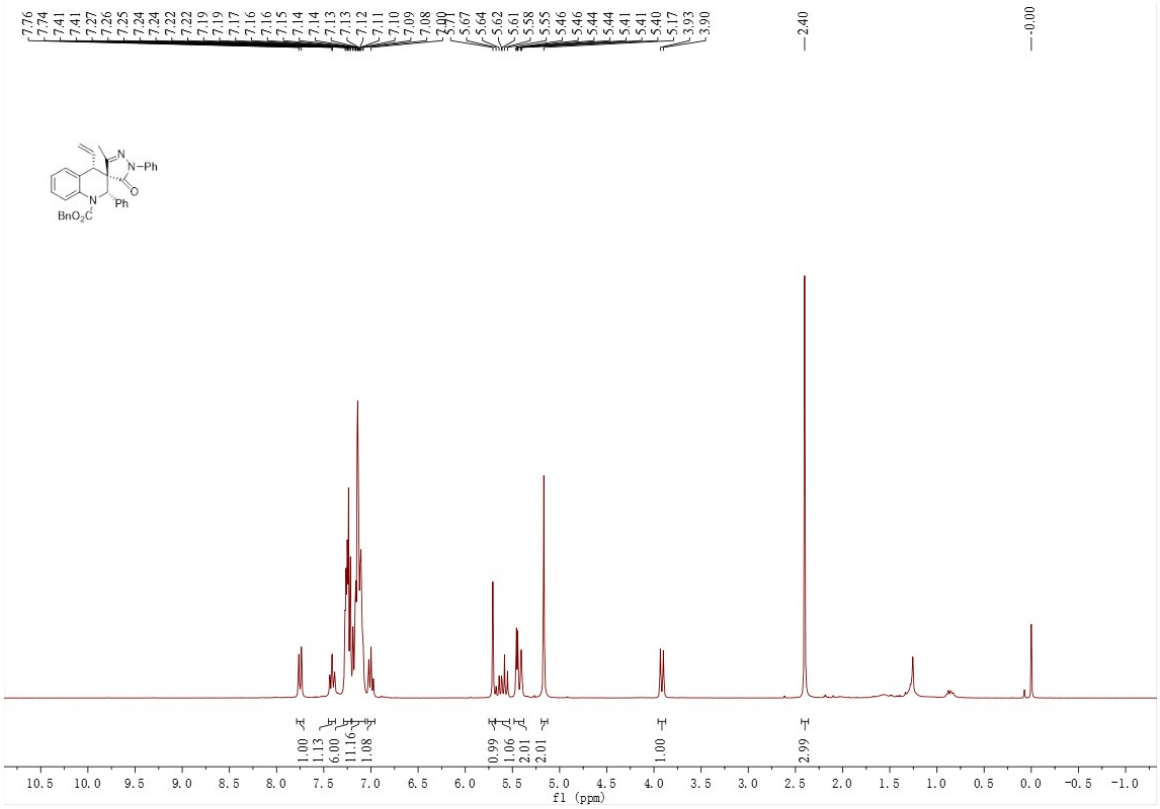

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4d**



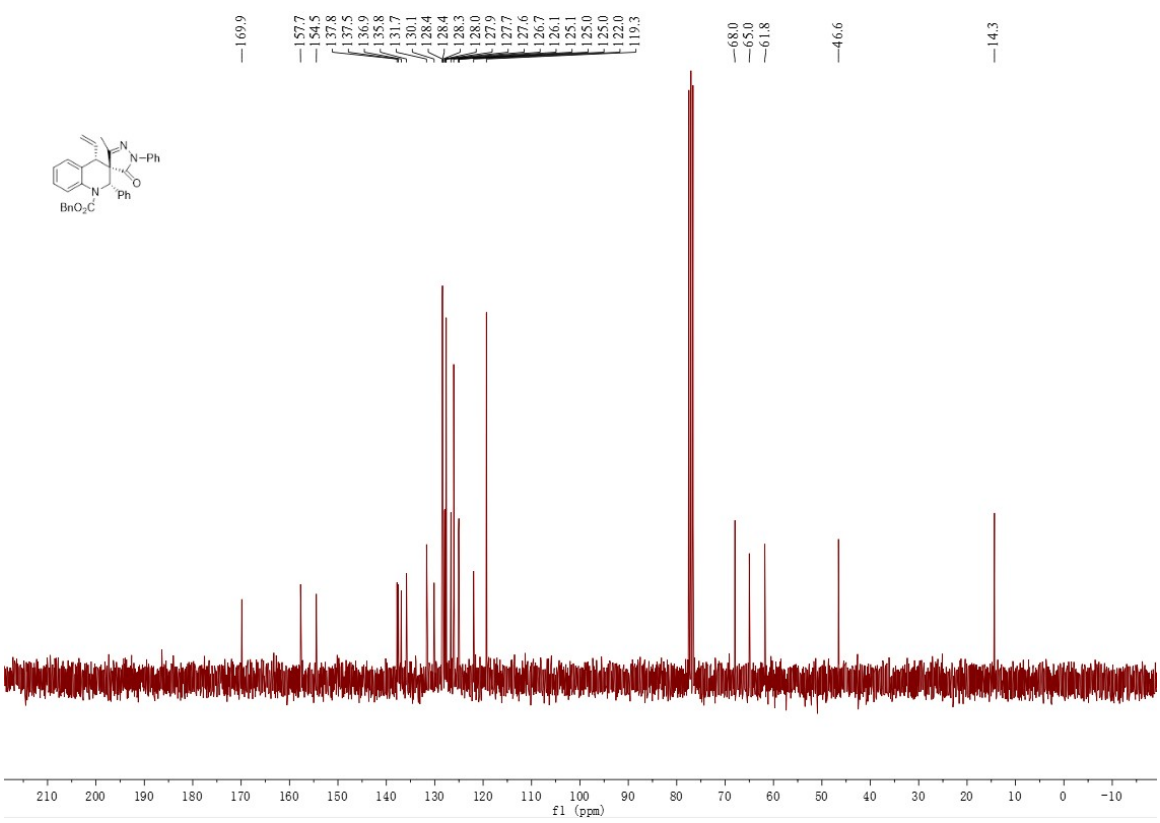

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4e**



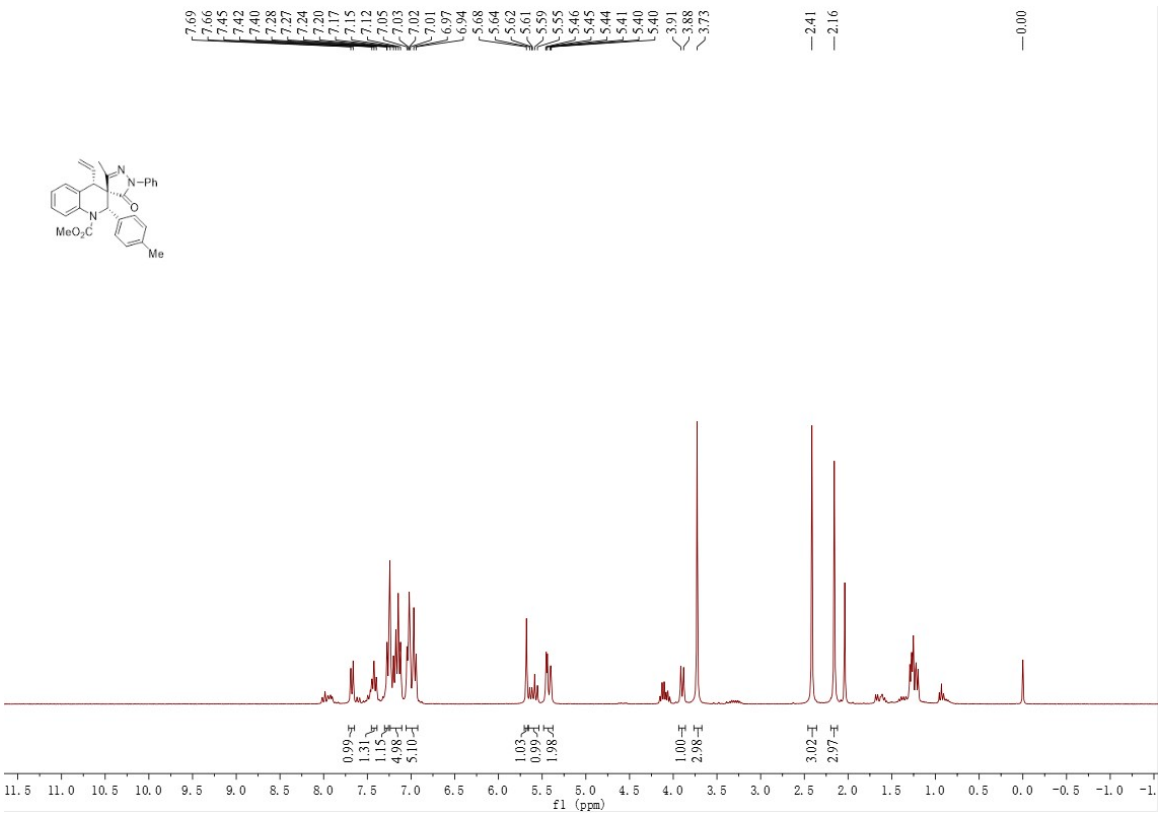

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4e**



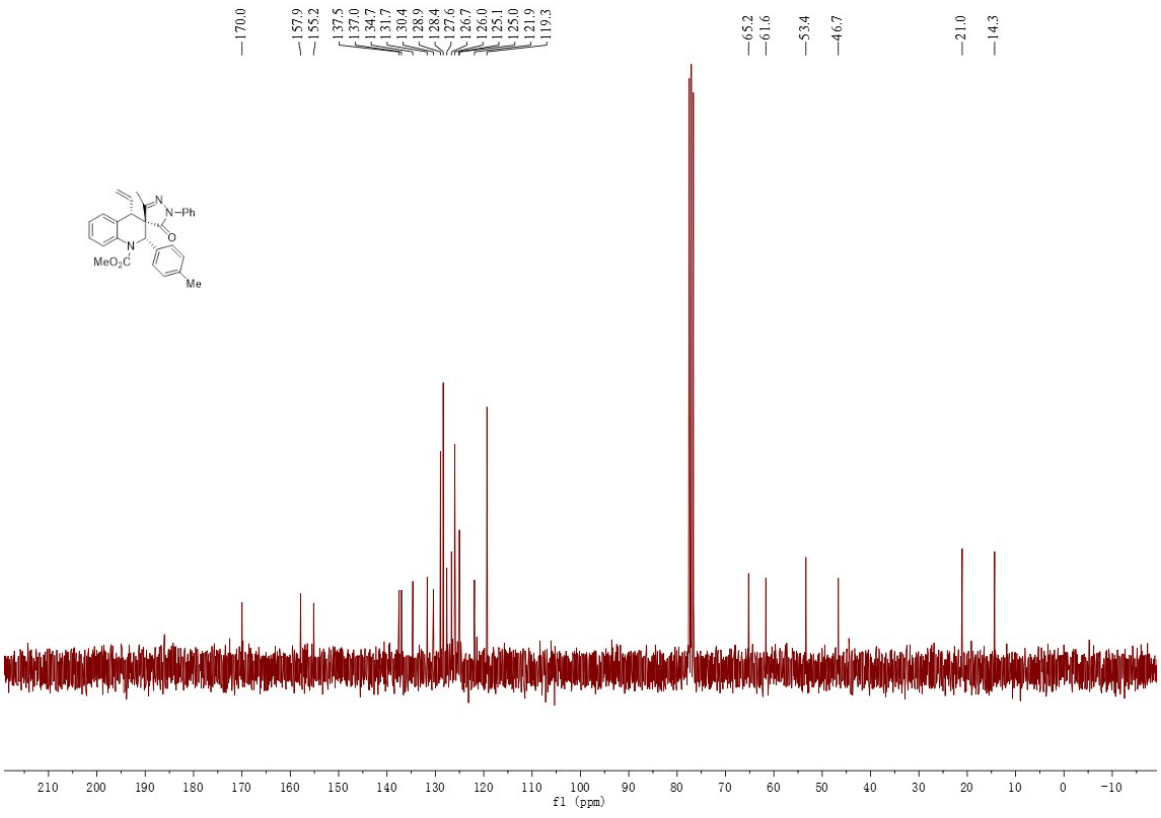

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4f**



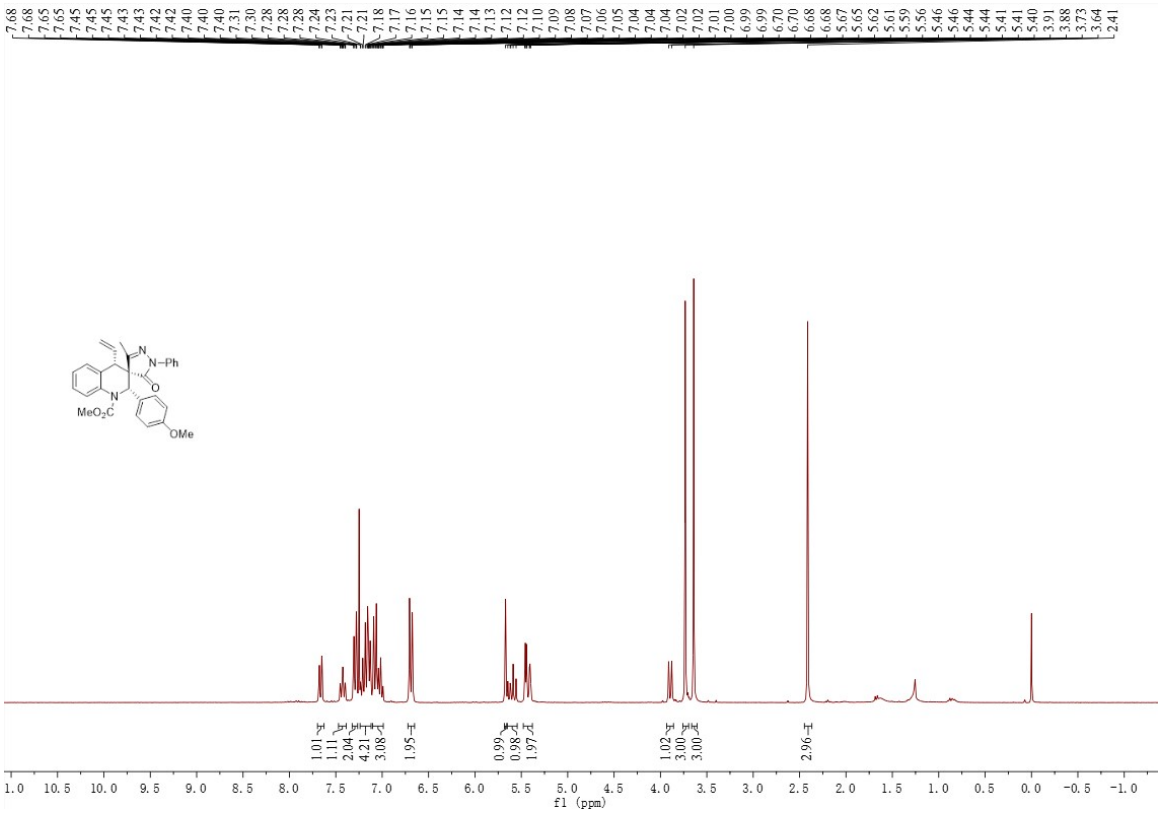

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4f**



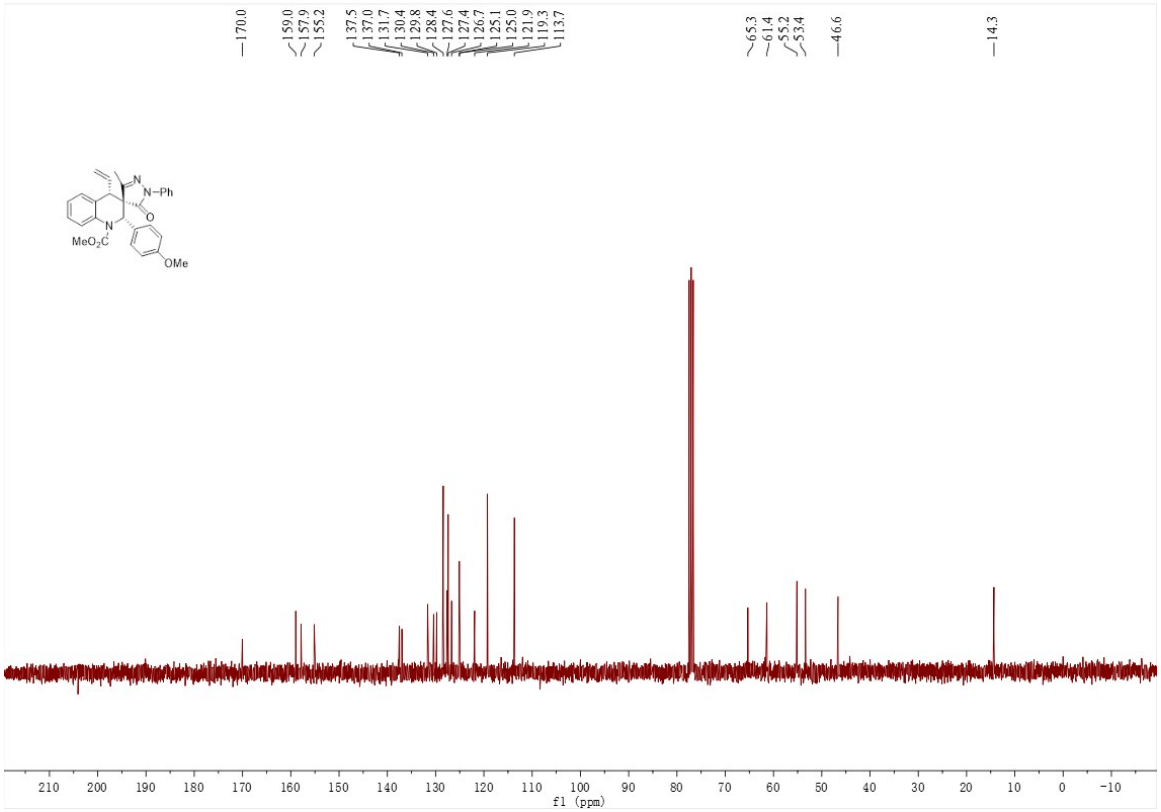

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4g**



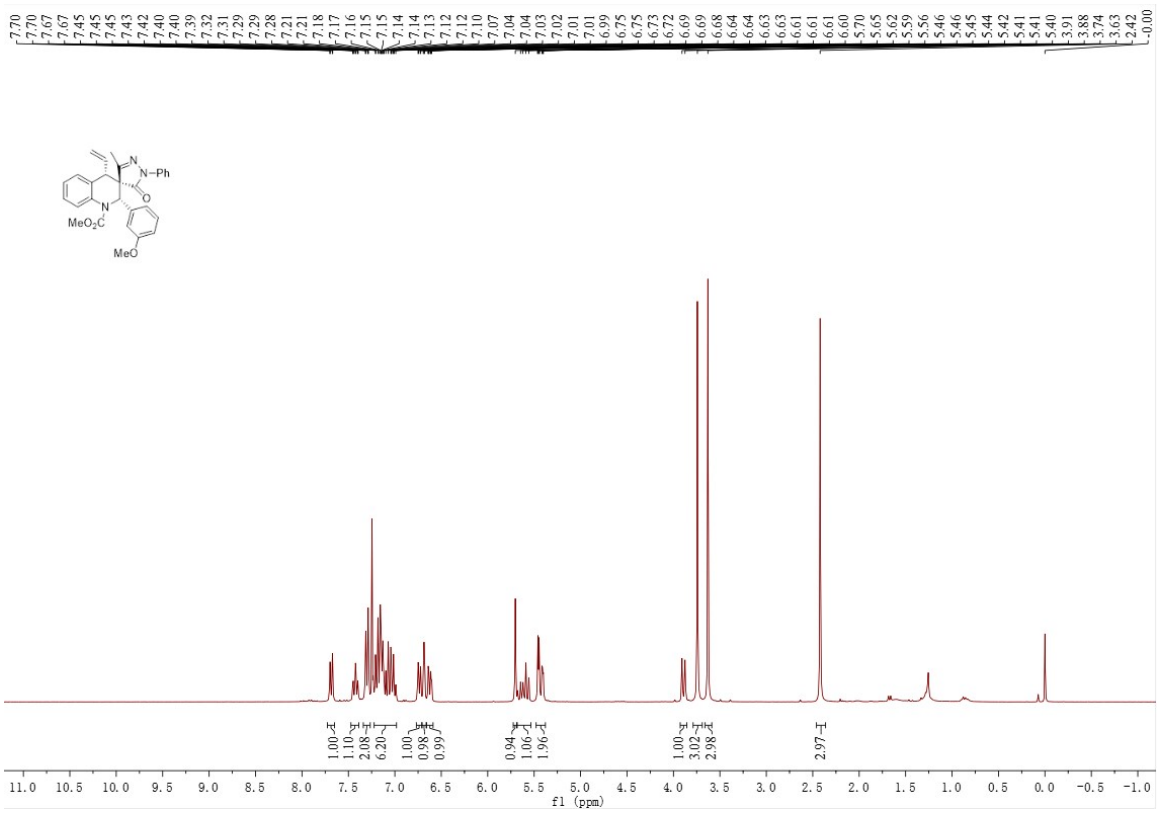

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4g**



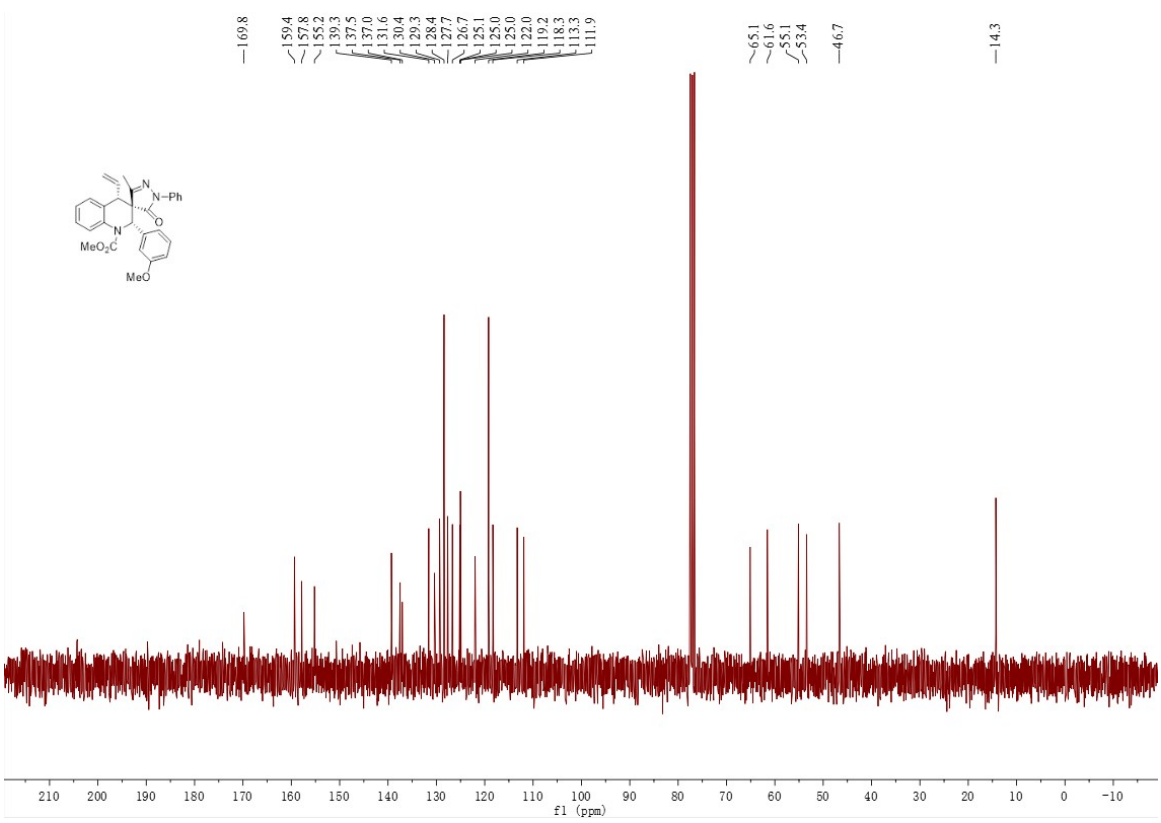

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4h**



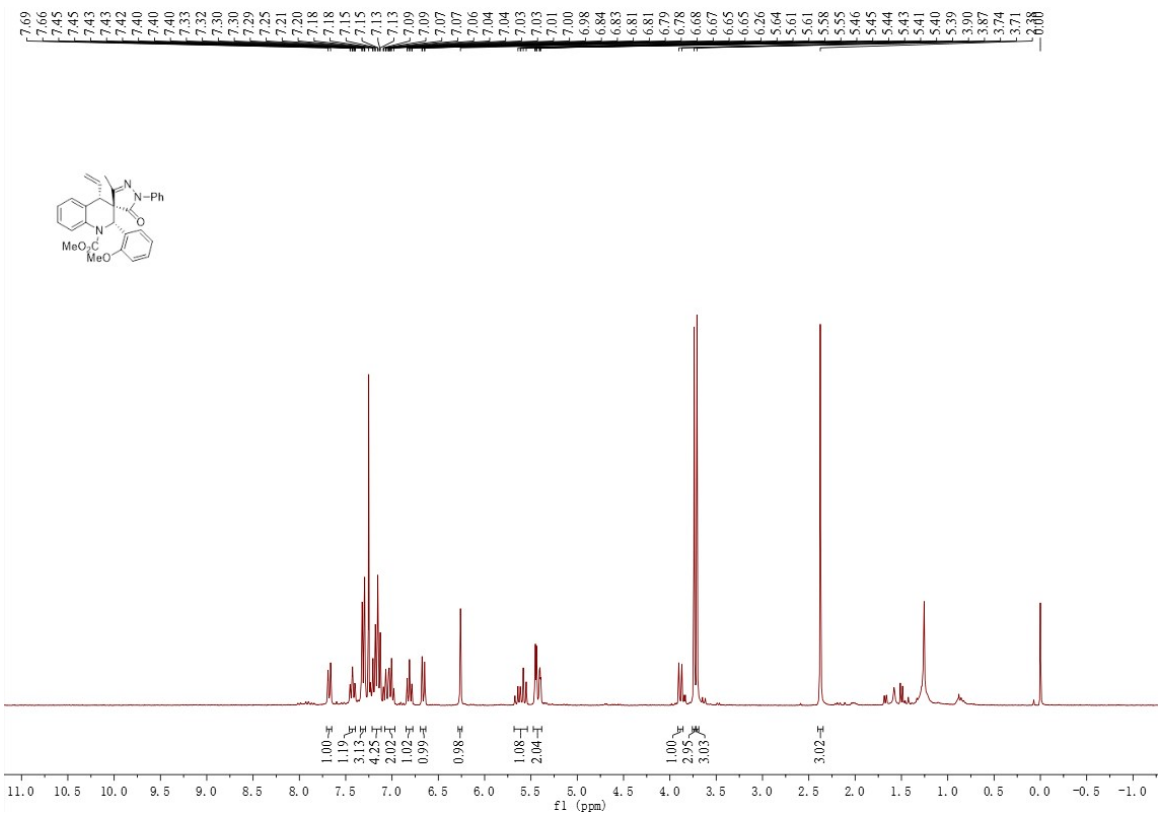

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4h**



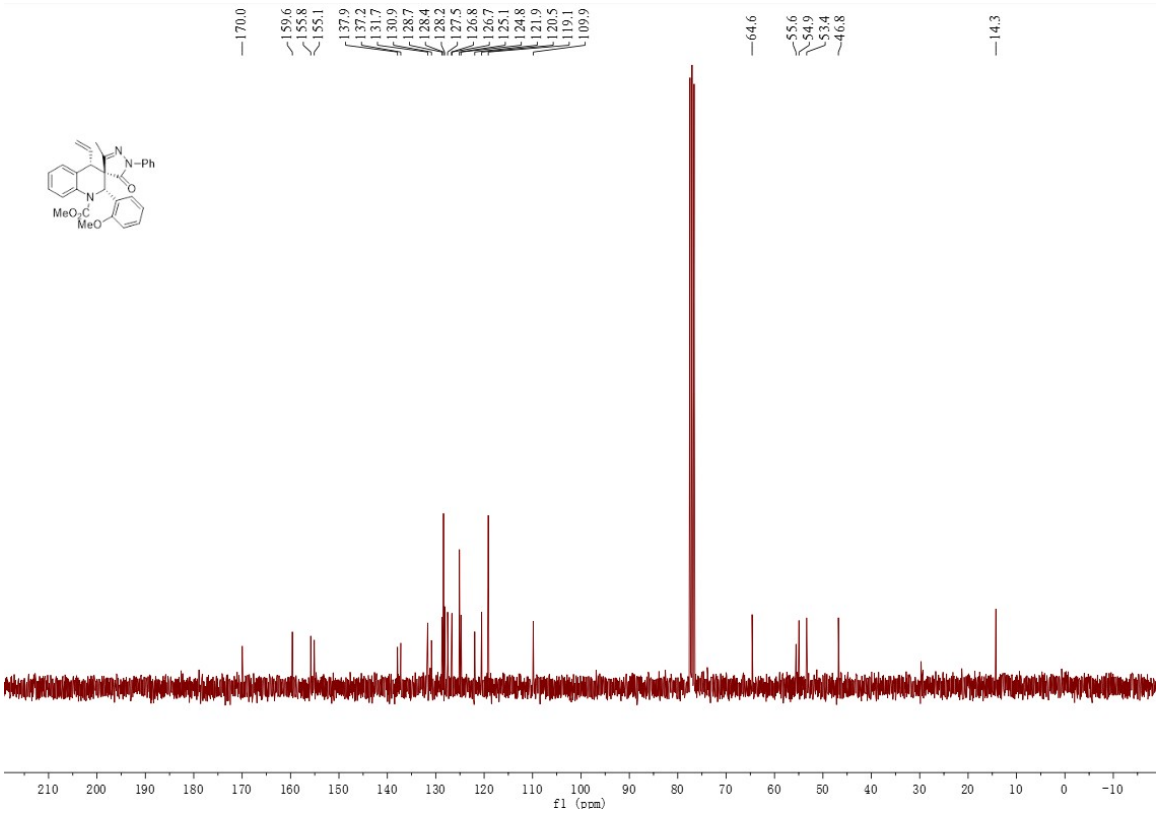

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4i**




$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4i**




$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4j**

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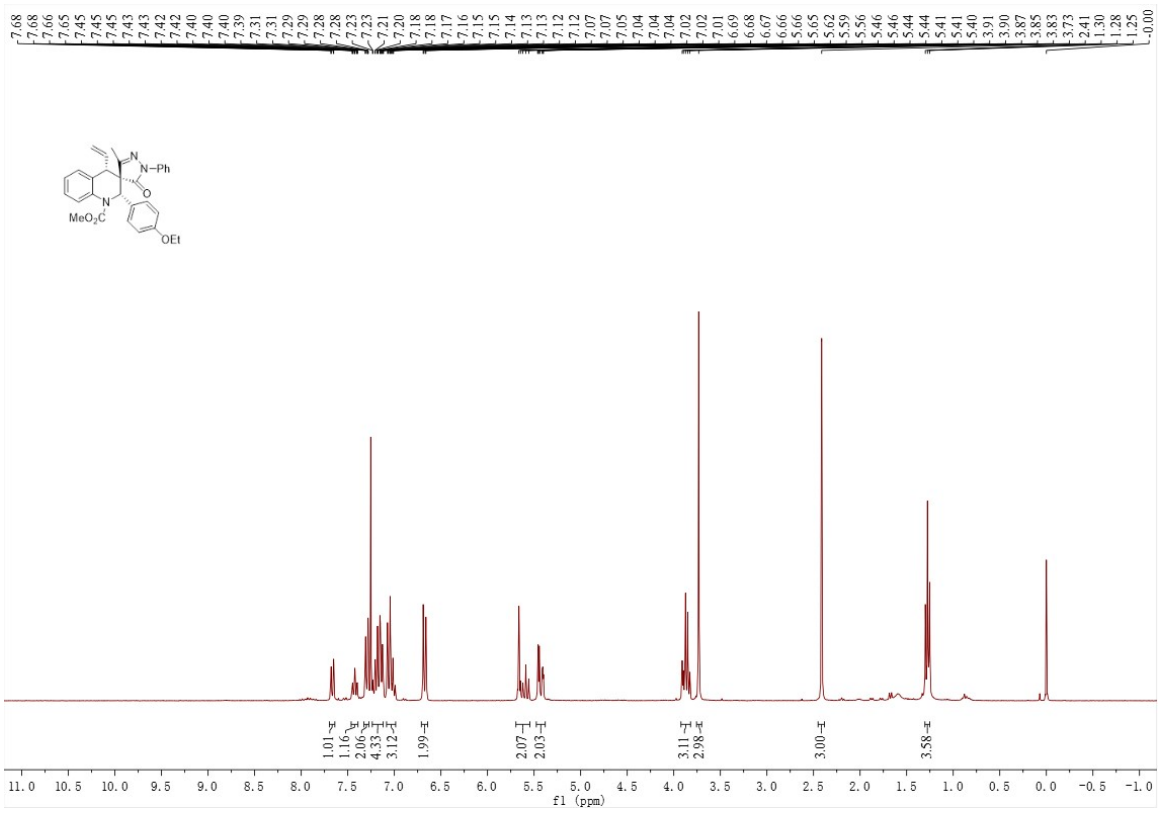
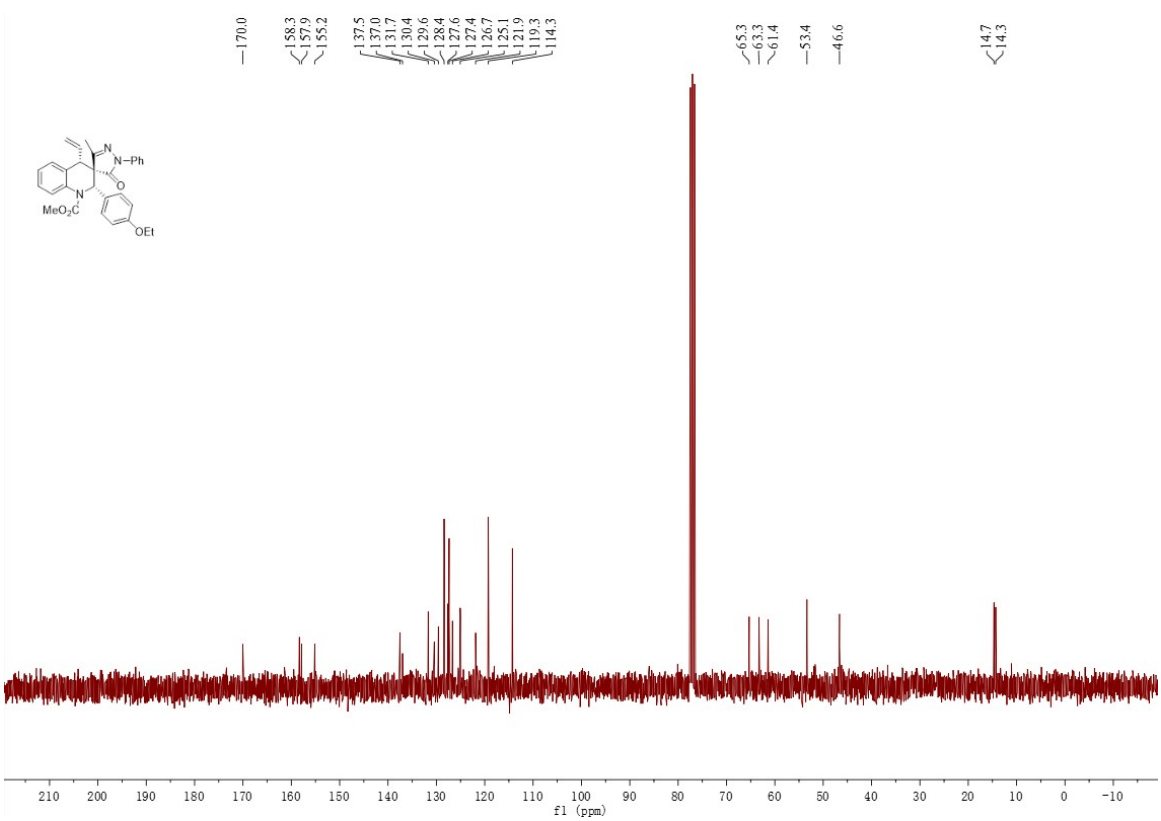
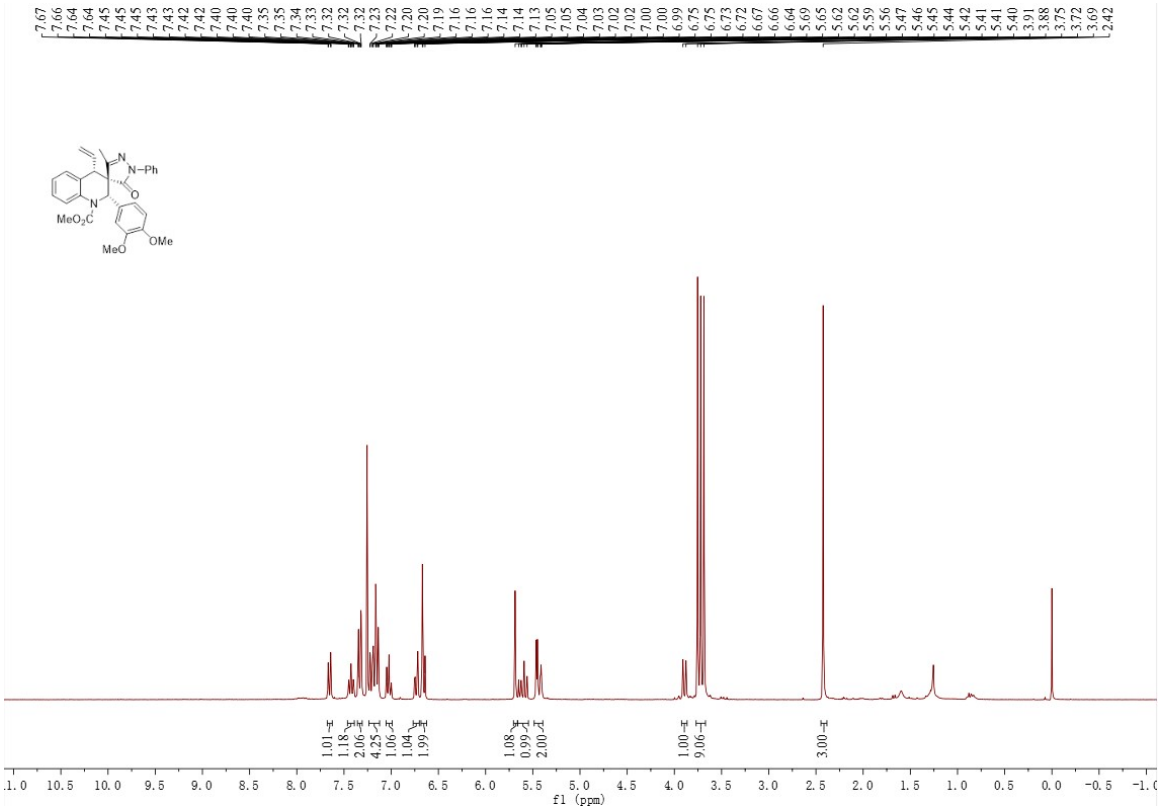


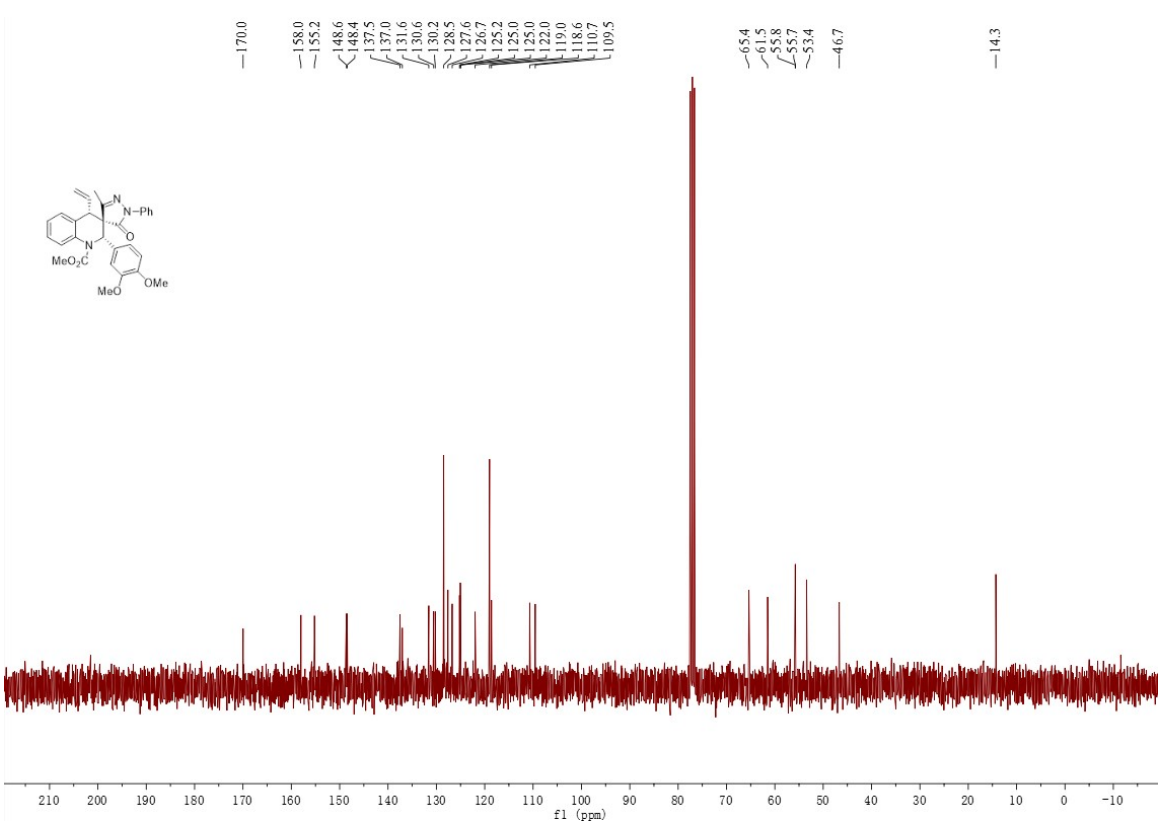

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4k**



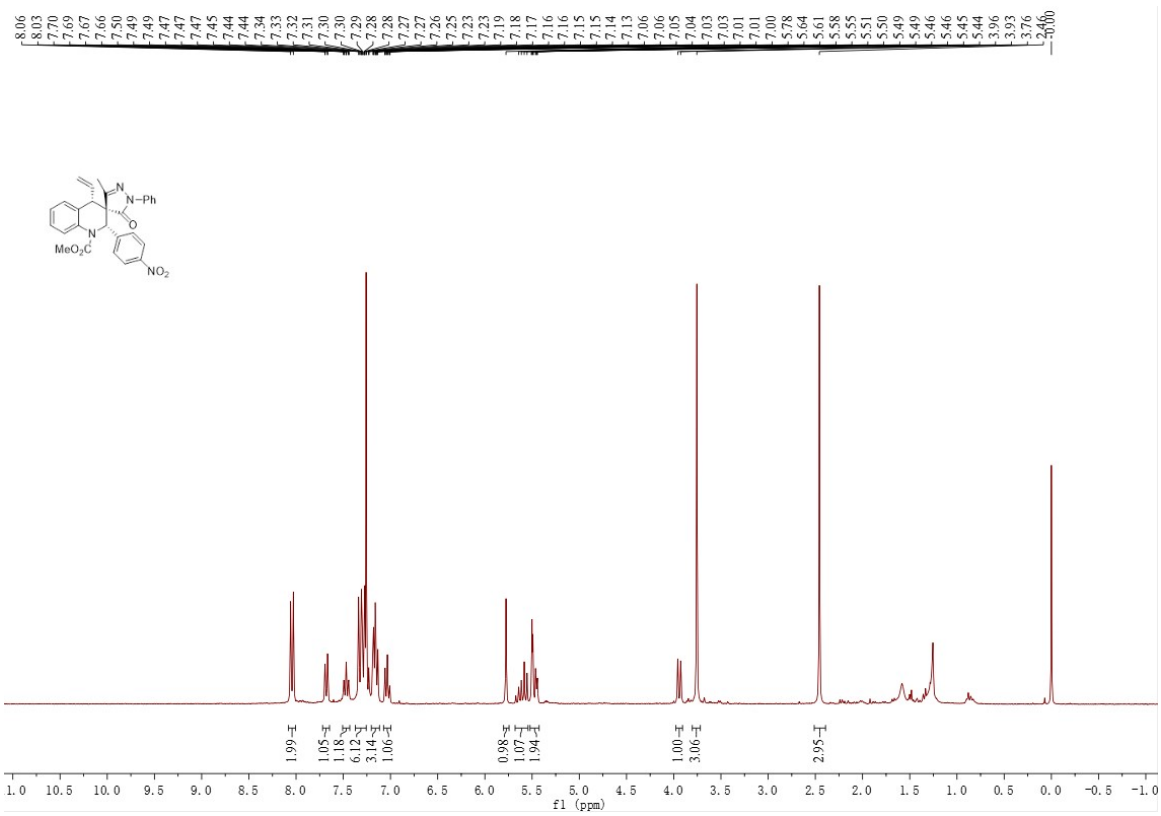

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4k**



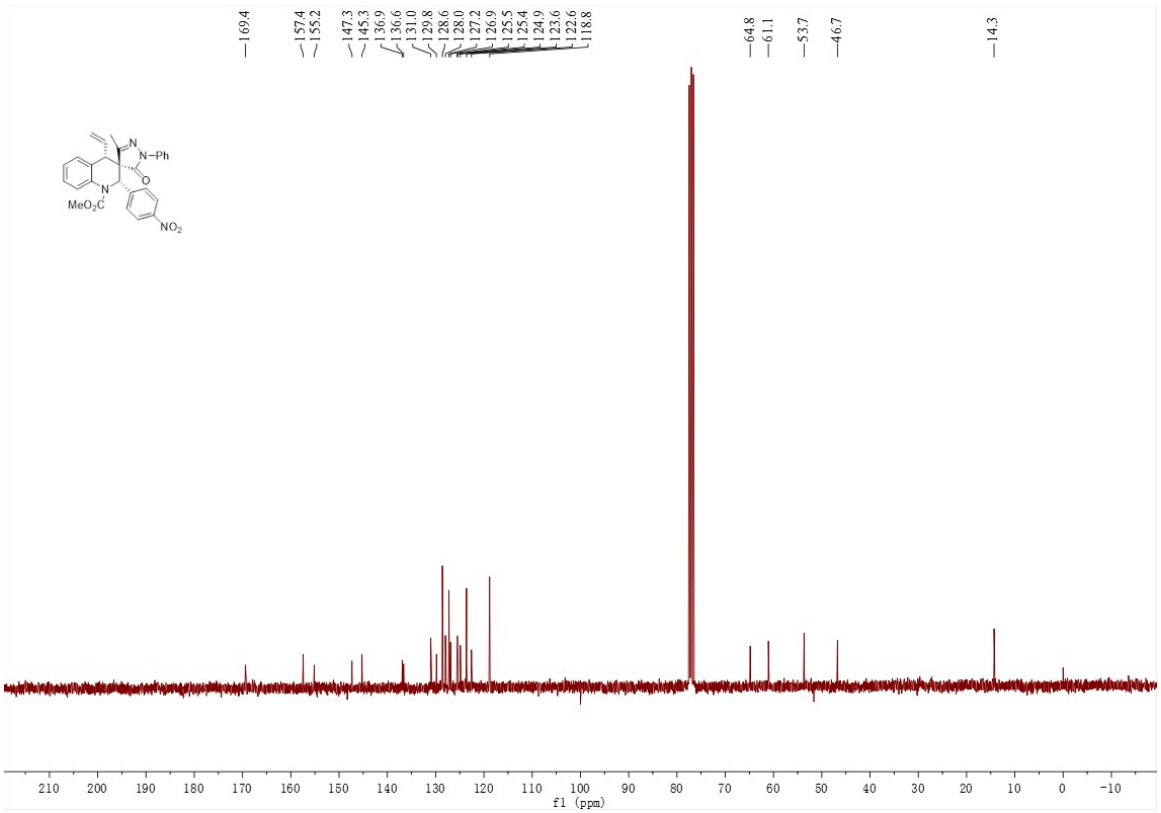

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4l**



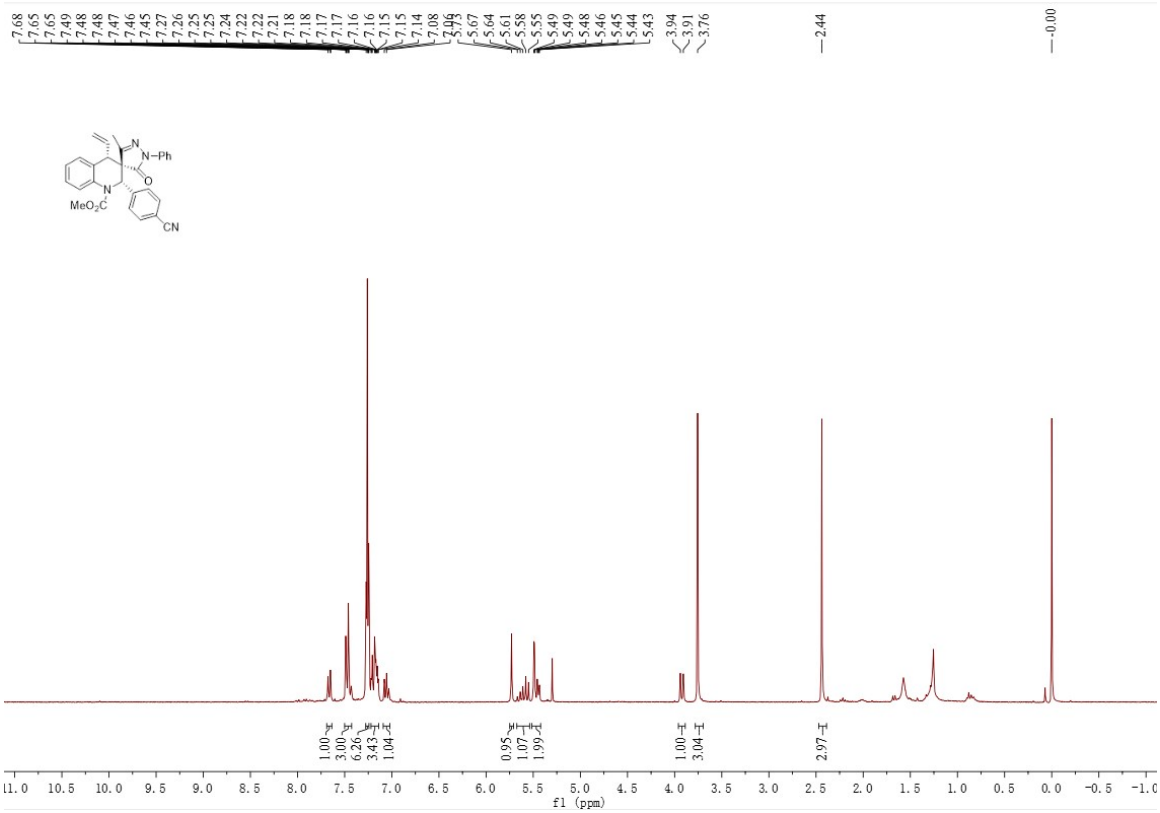

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4l**



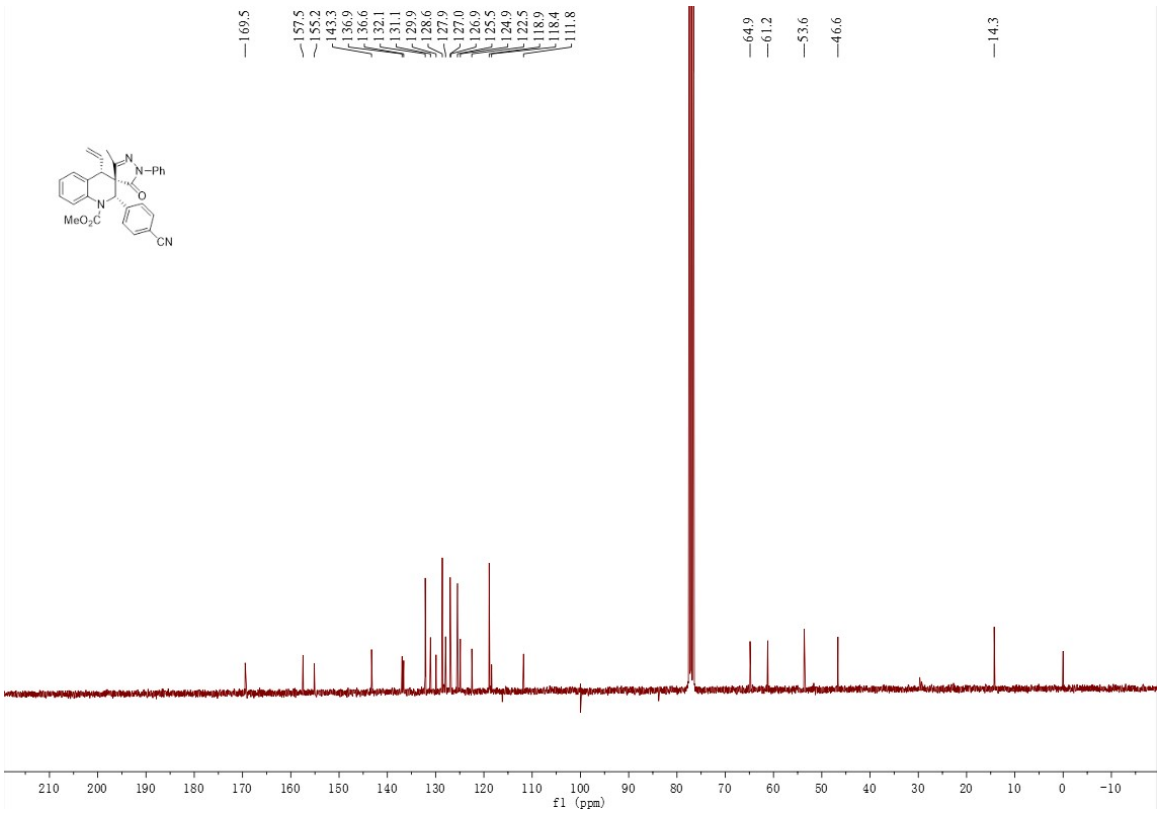

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4m**



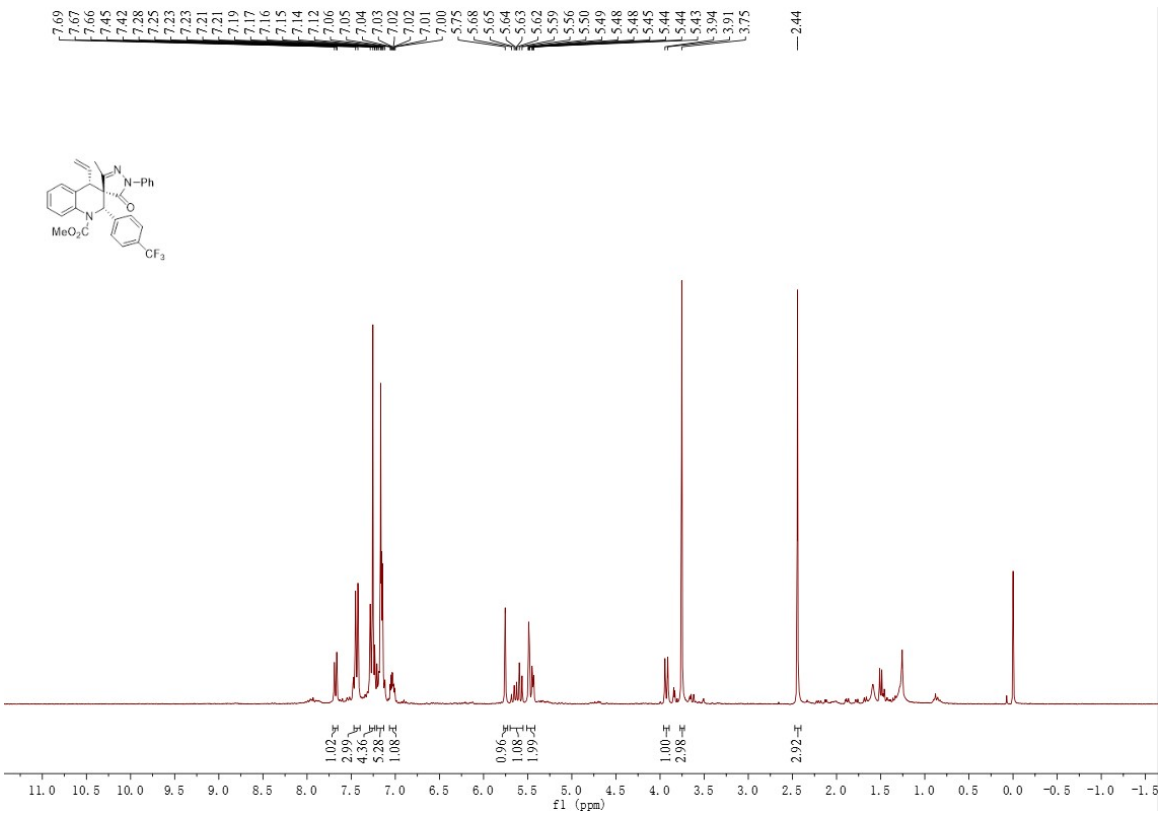

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4m**



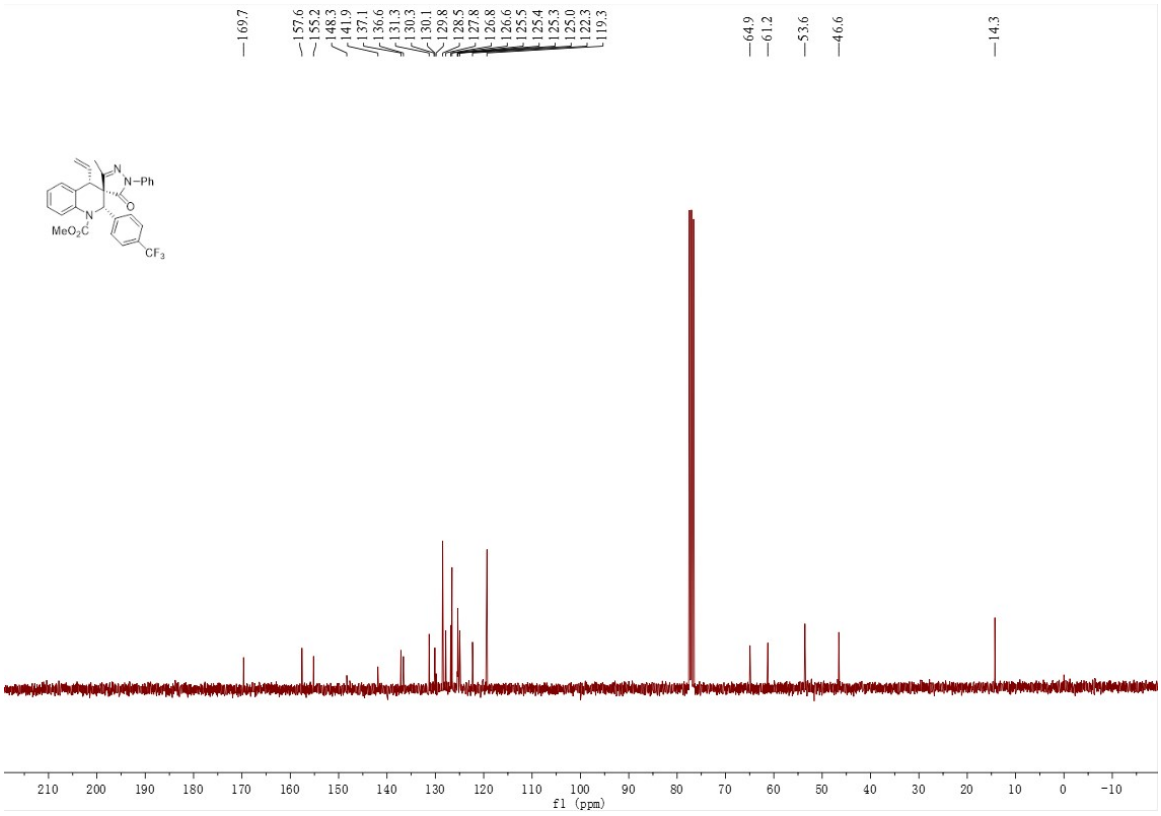

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **4n**



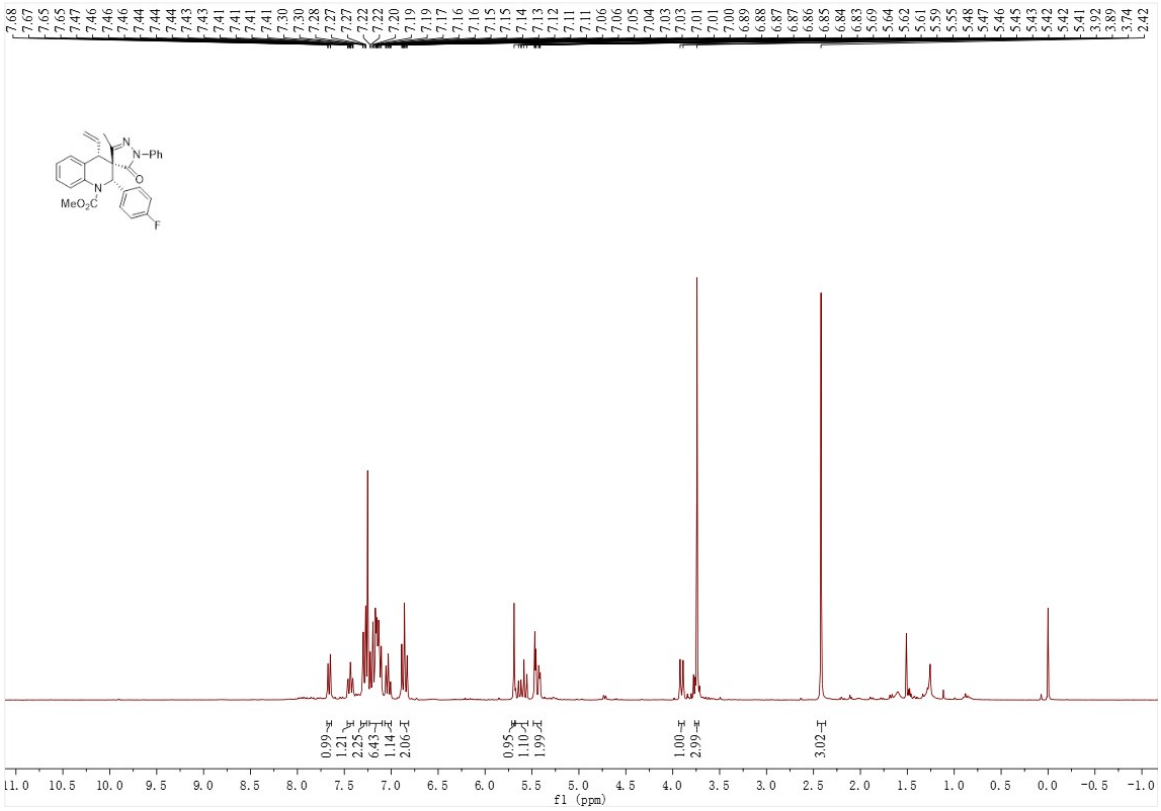

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **4n**



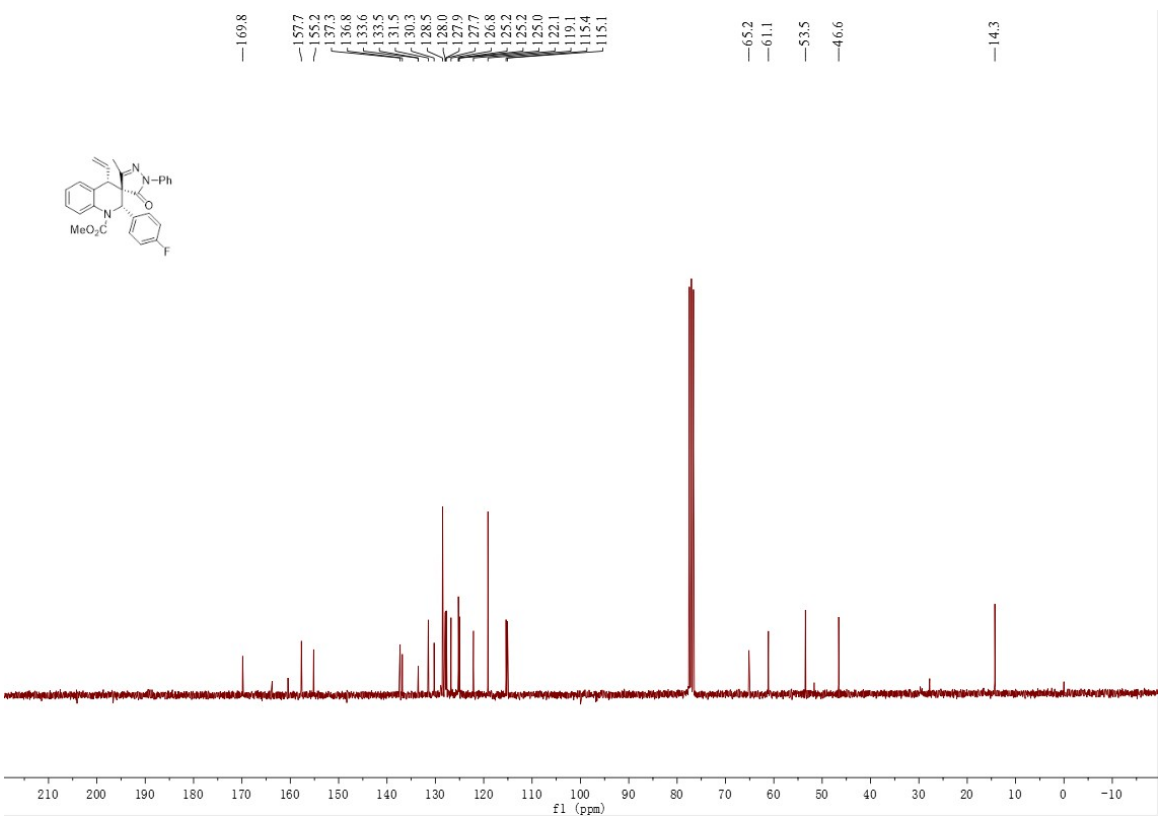

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **4o**



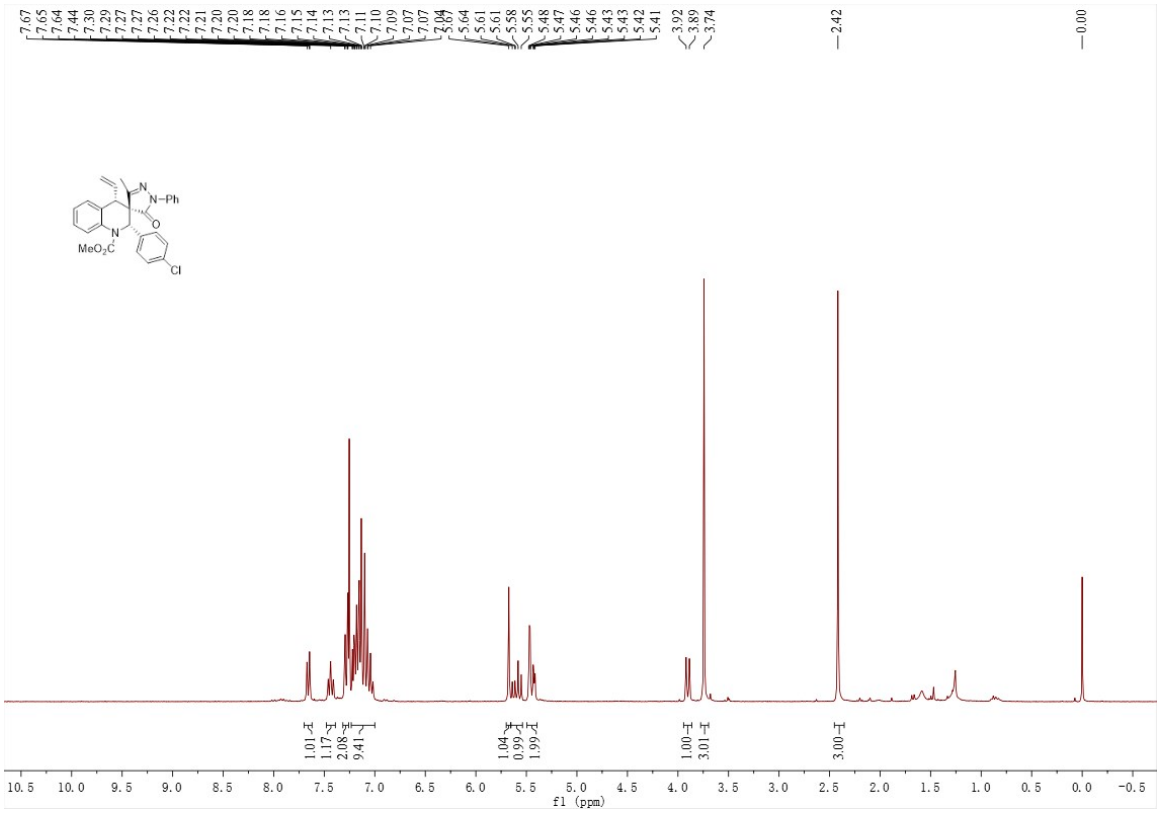

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **4o**



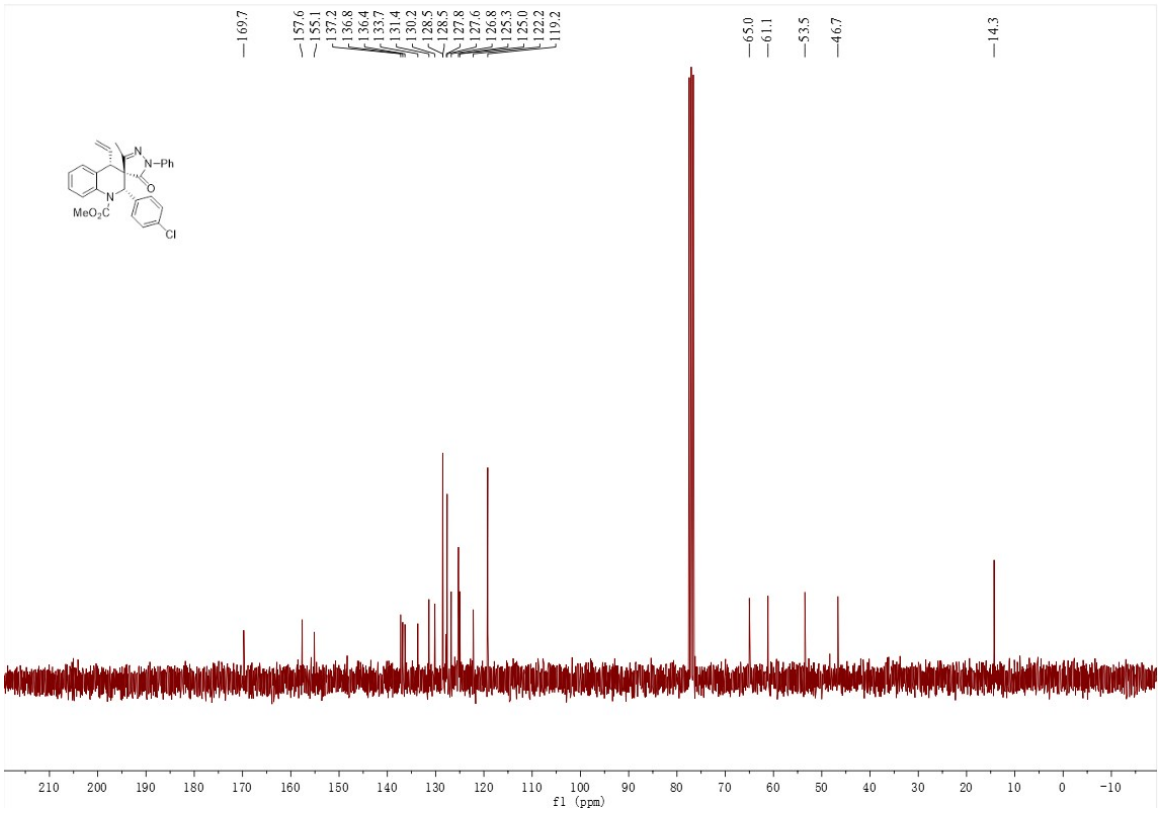

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **4p**



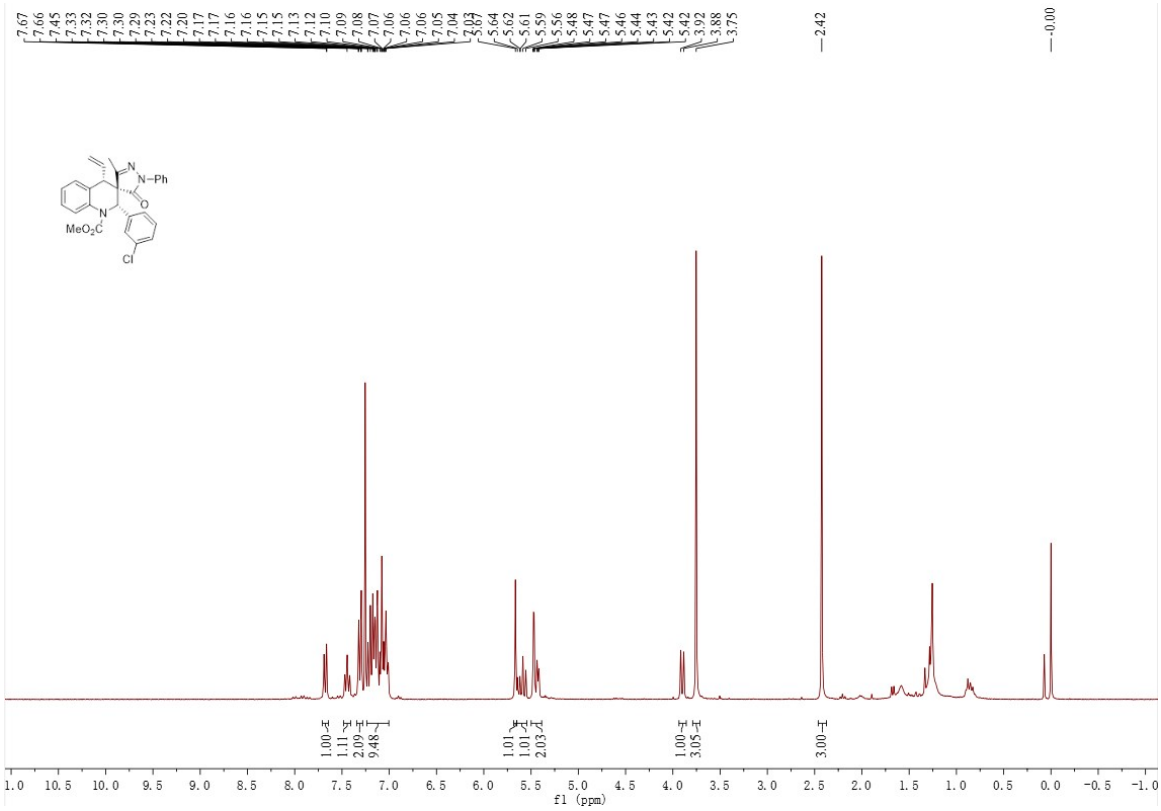

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **4p**



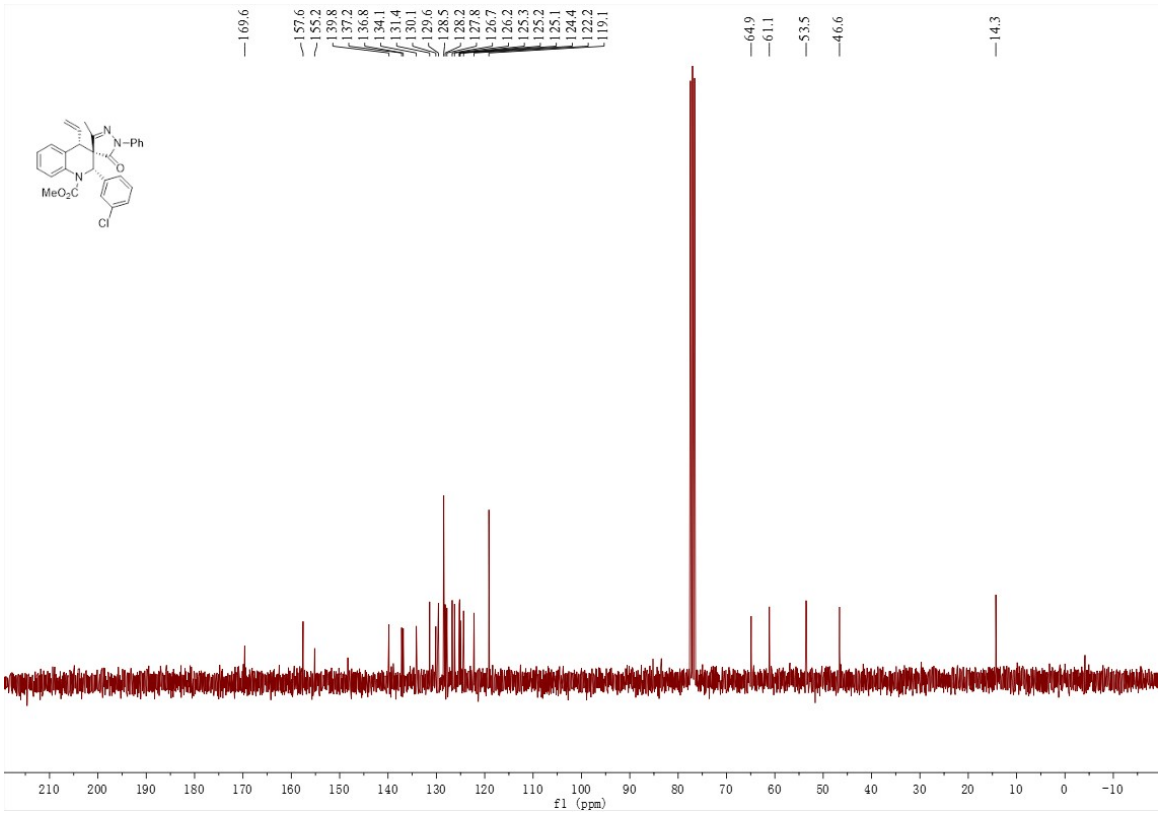

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **4q**



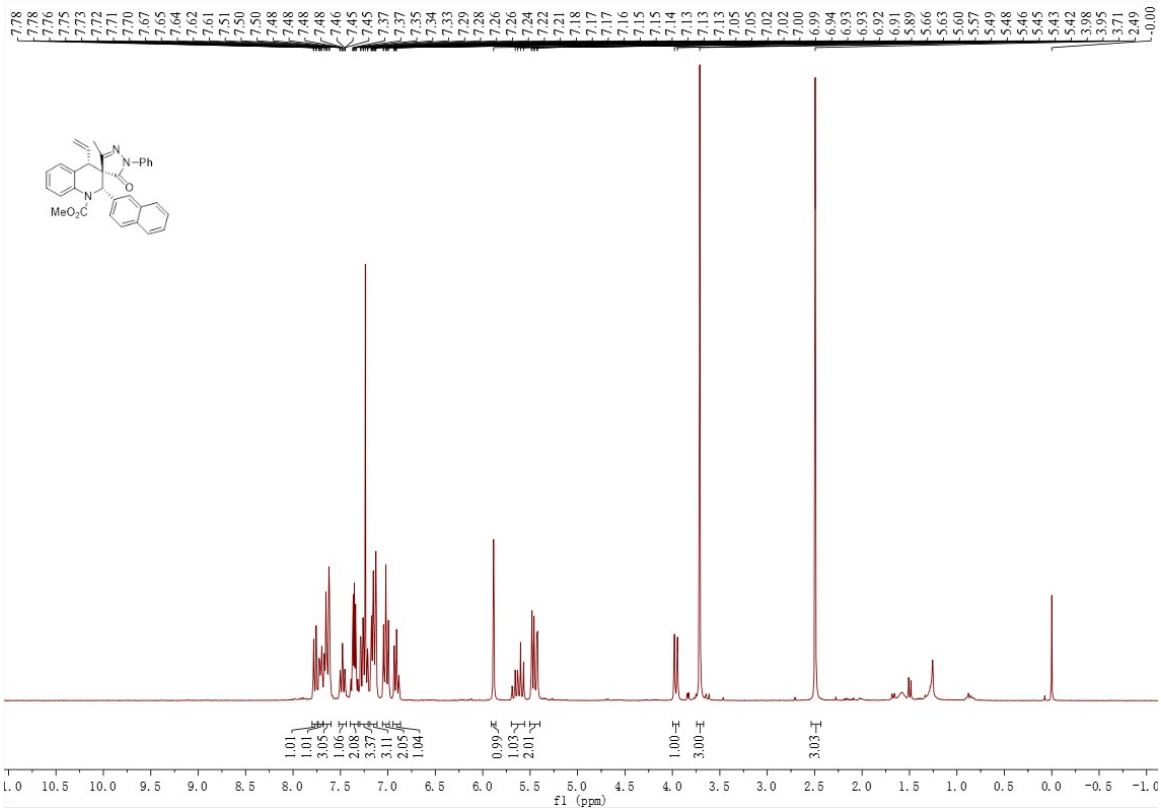

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **4q**



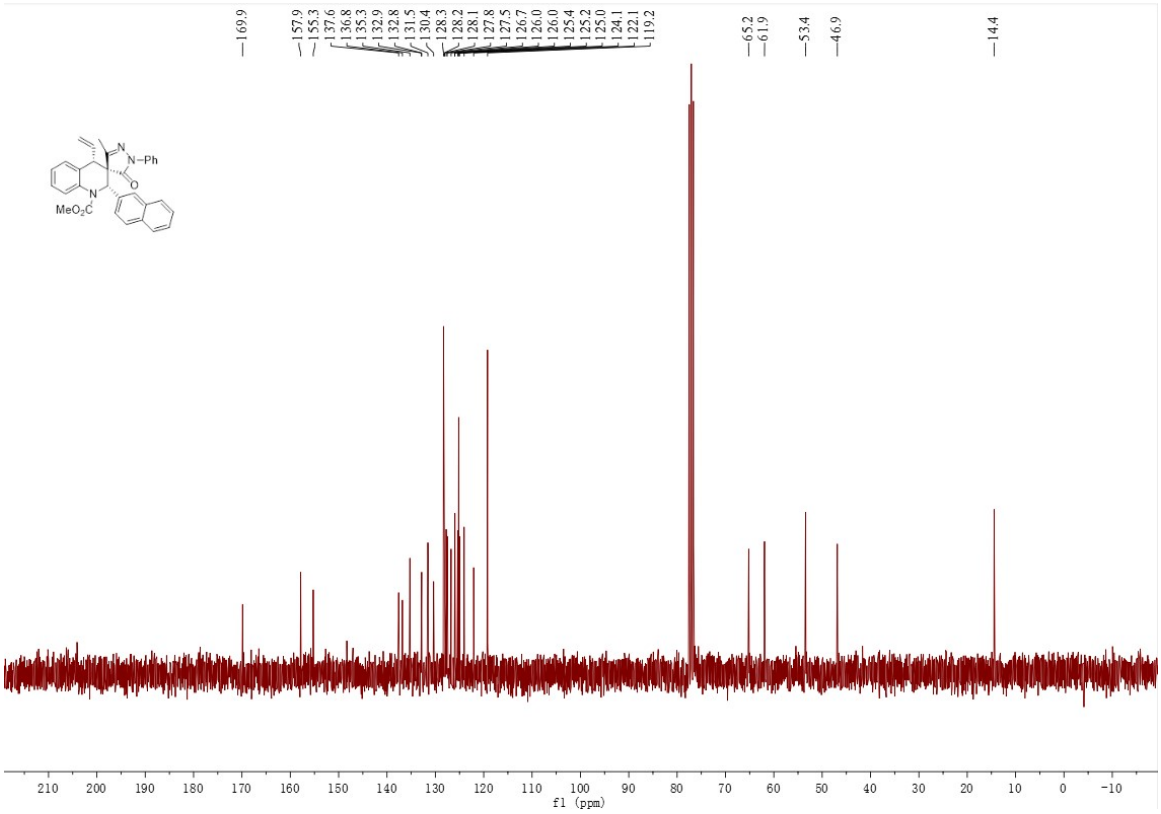

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **4r**



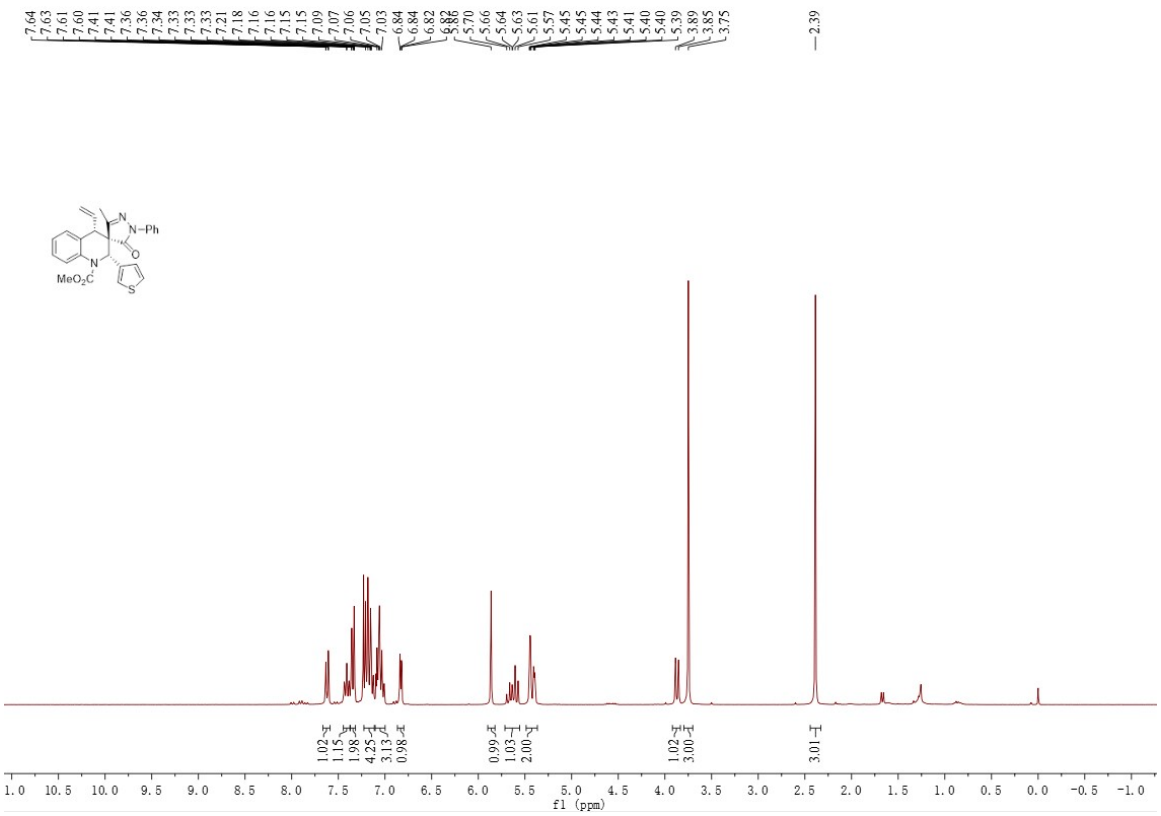

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **4r**



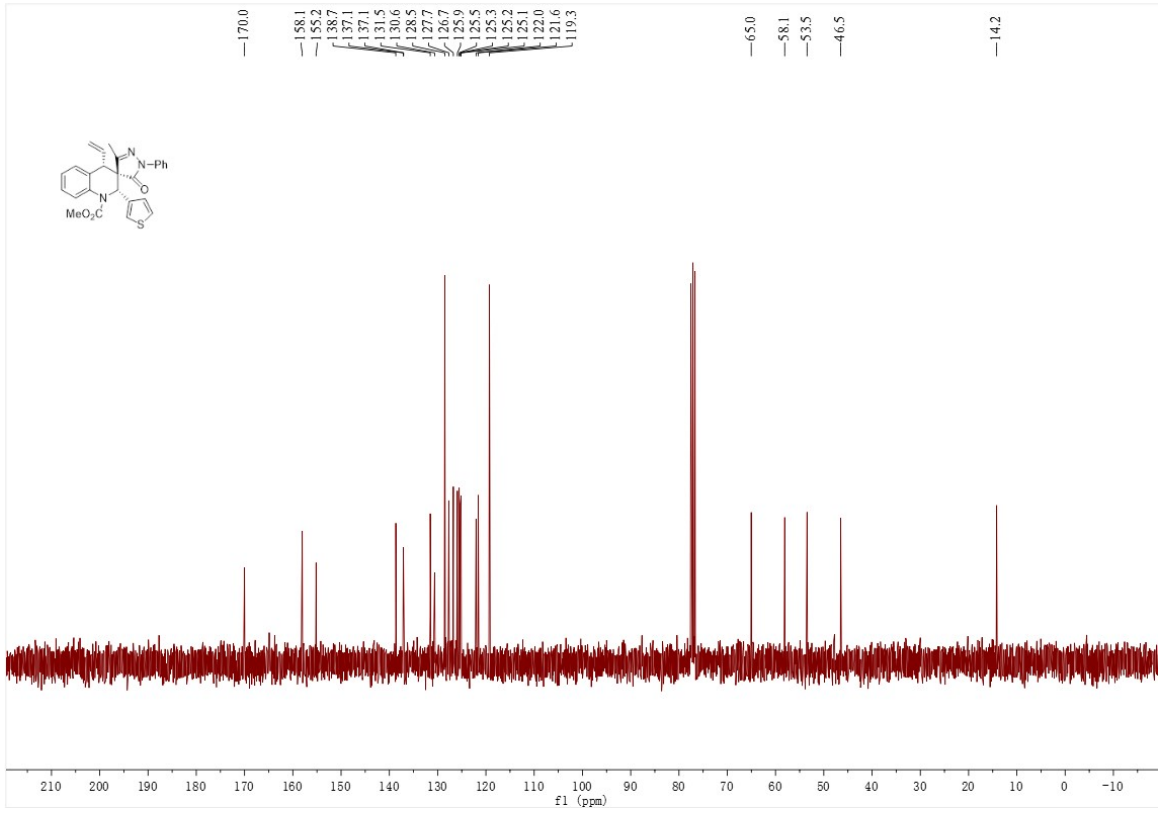

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4s**



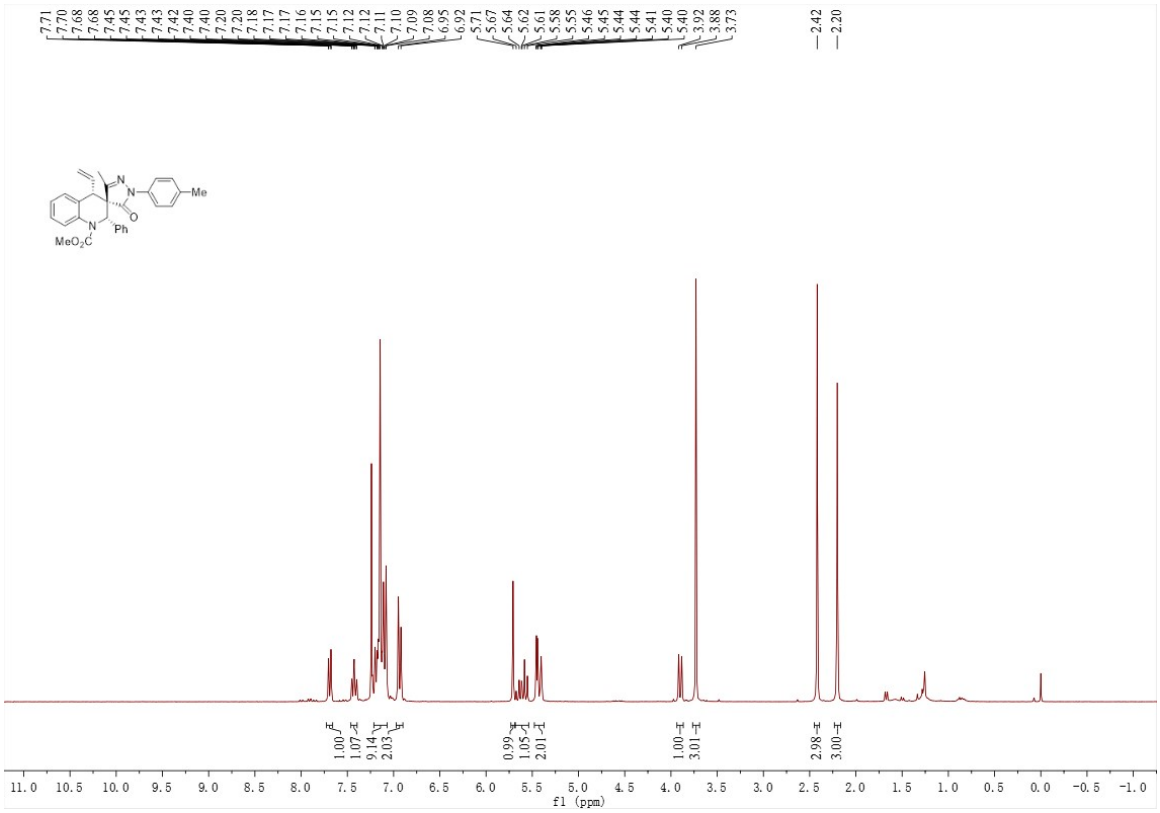

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4s**



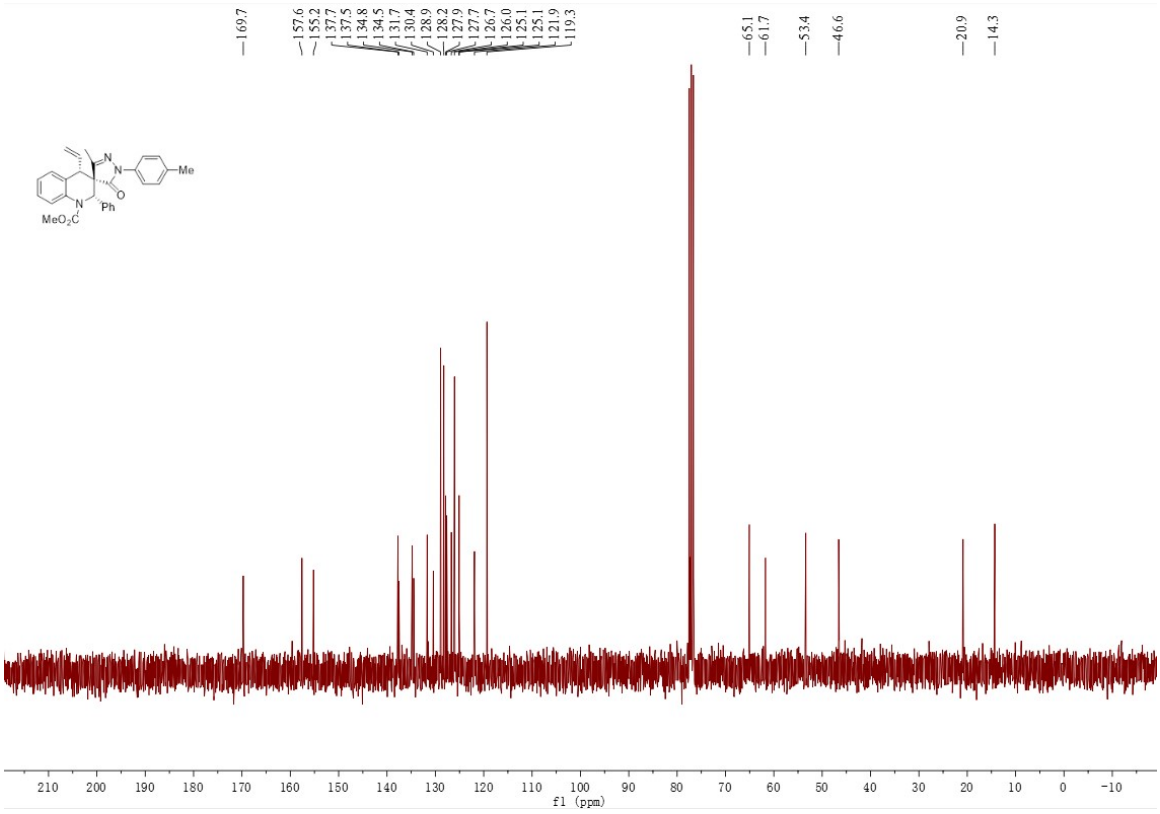

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4t**



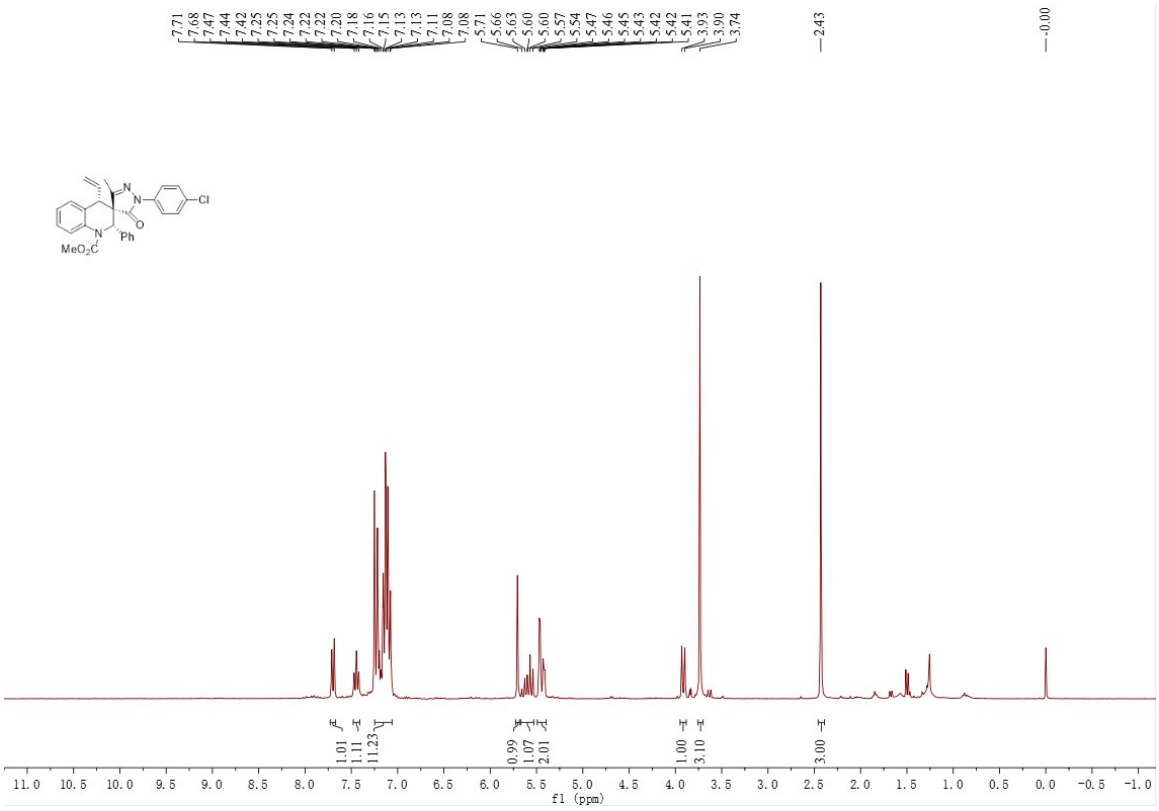

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4t**



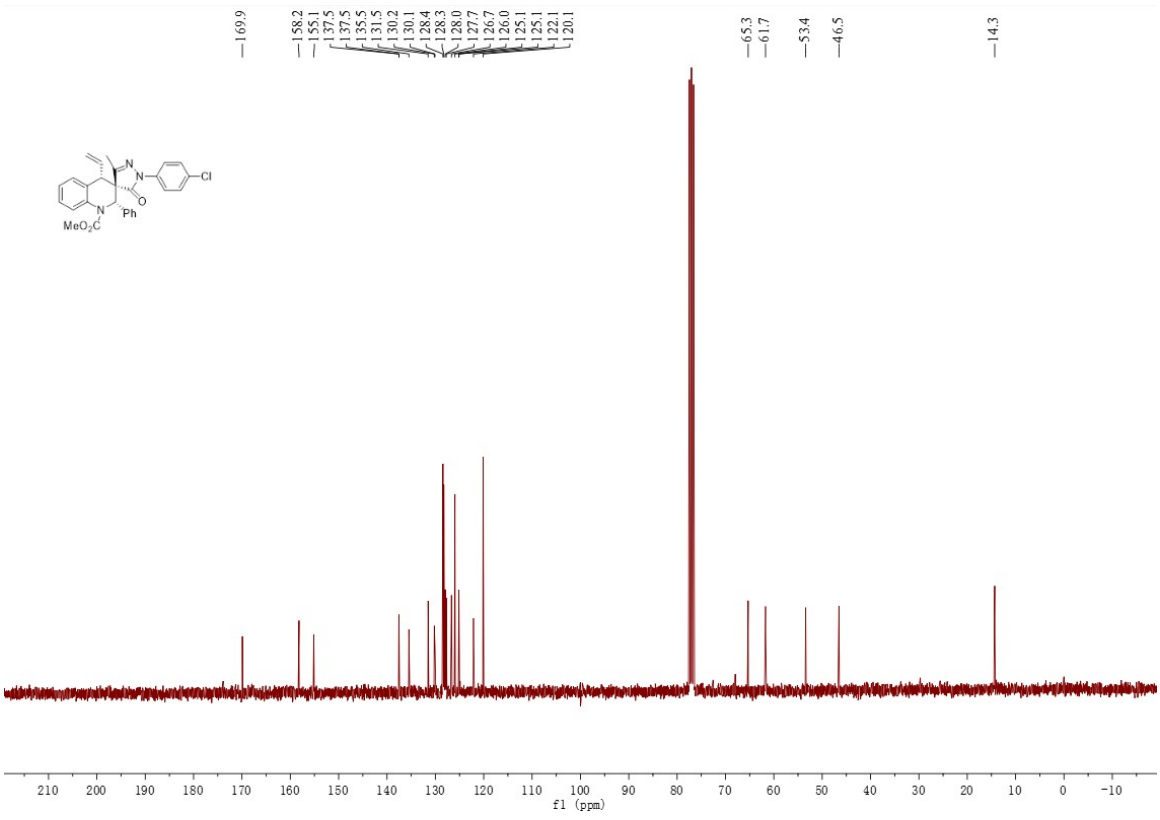

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **4u**



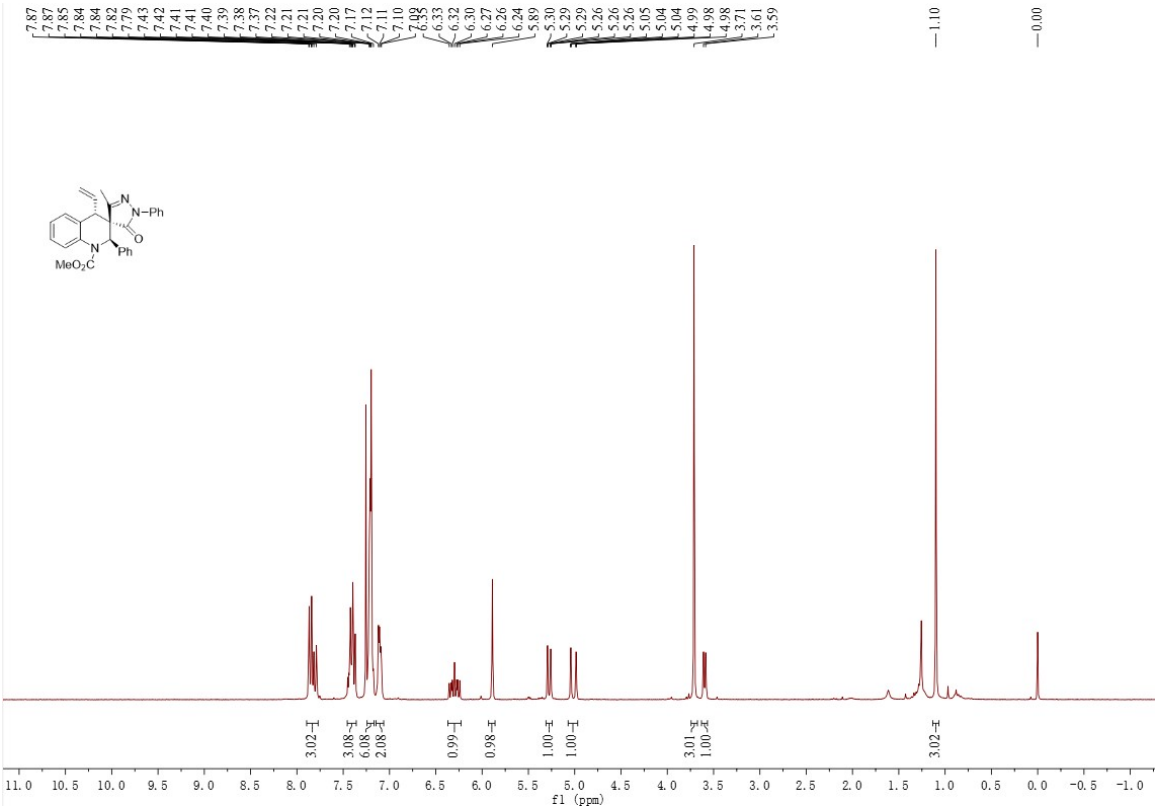

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **4u**



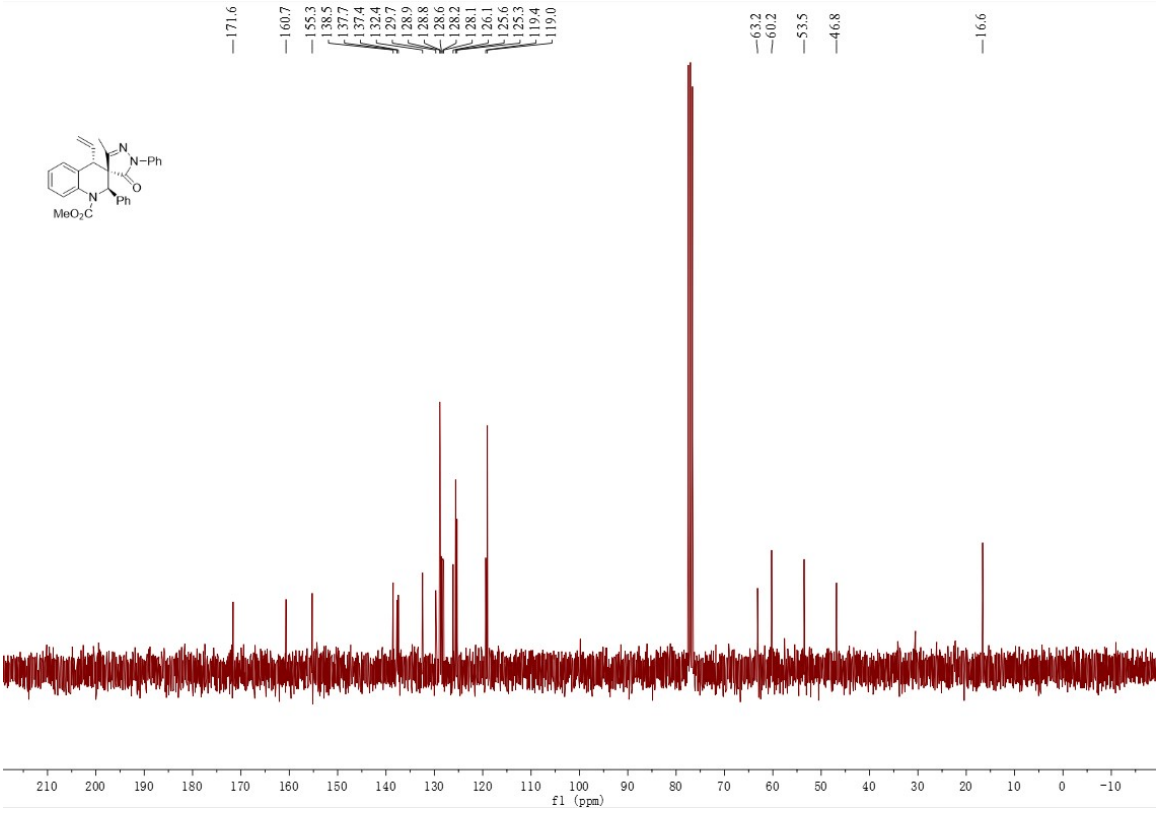

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **4v**



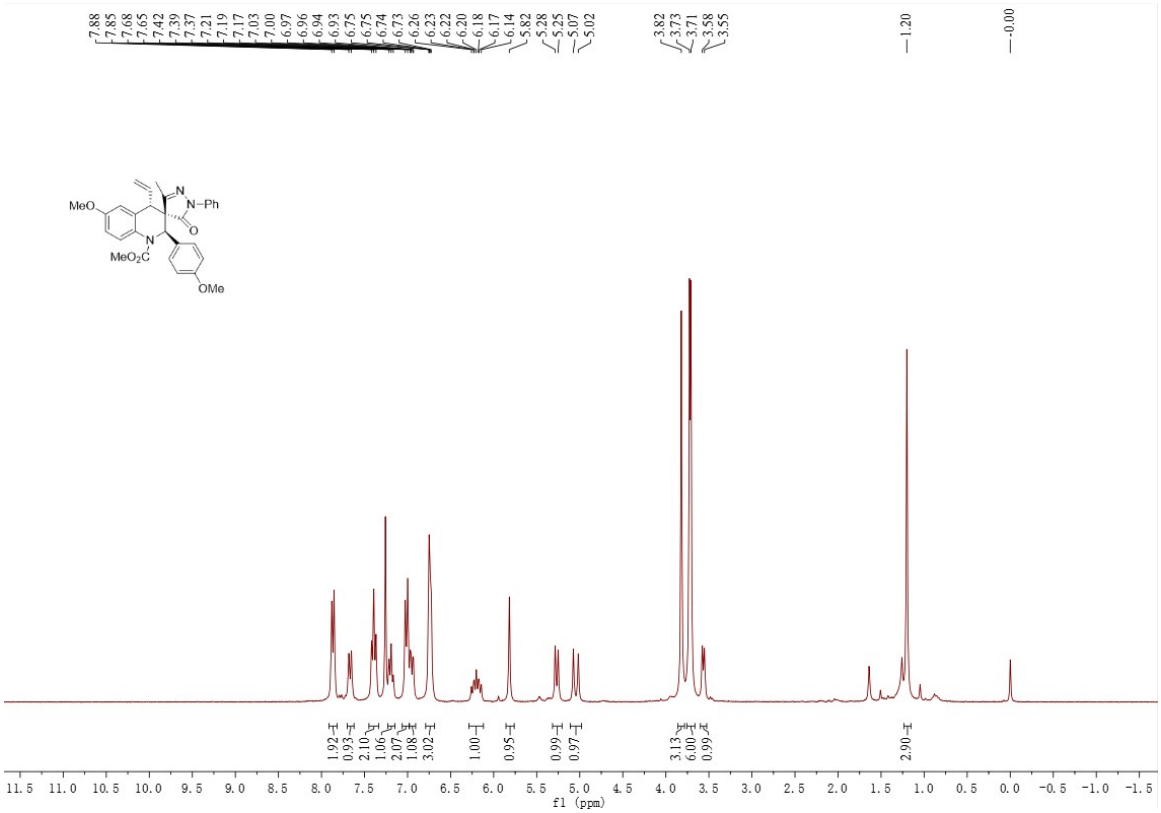

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **4v**



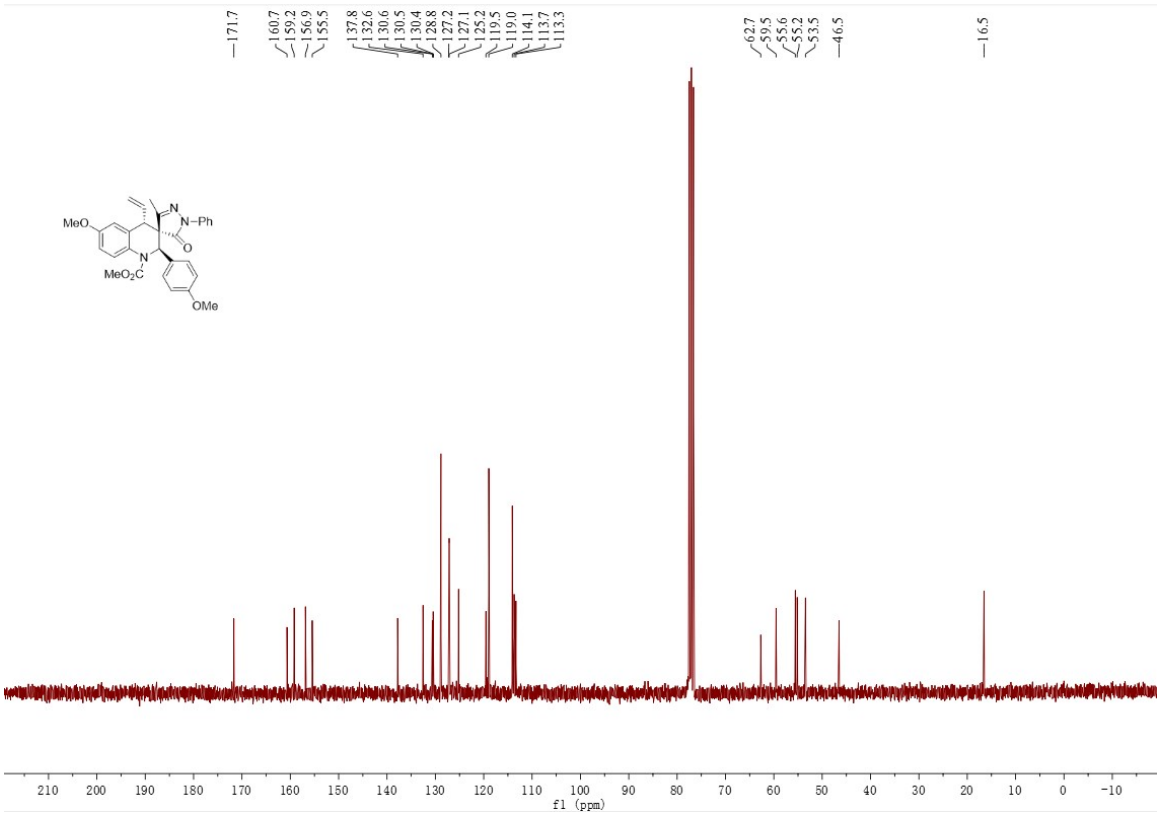
$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **5a**



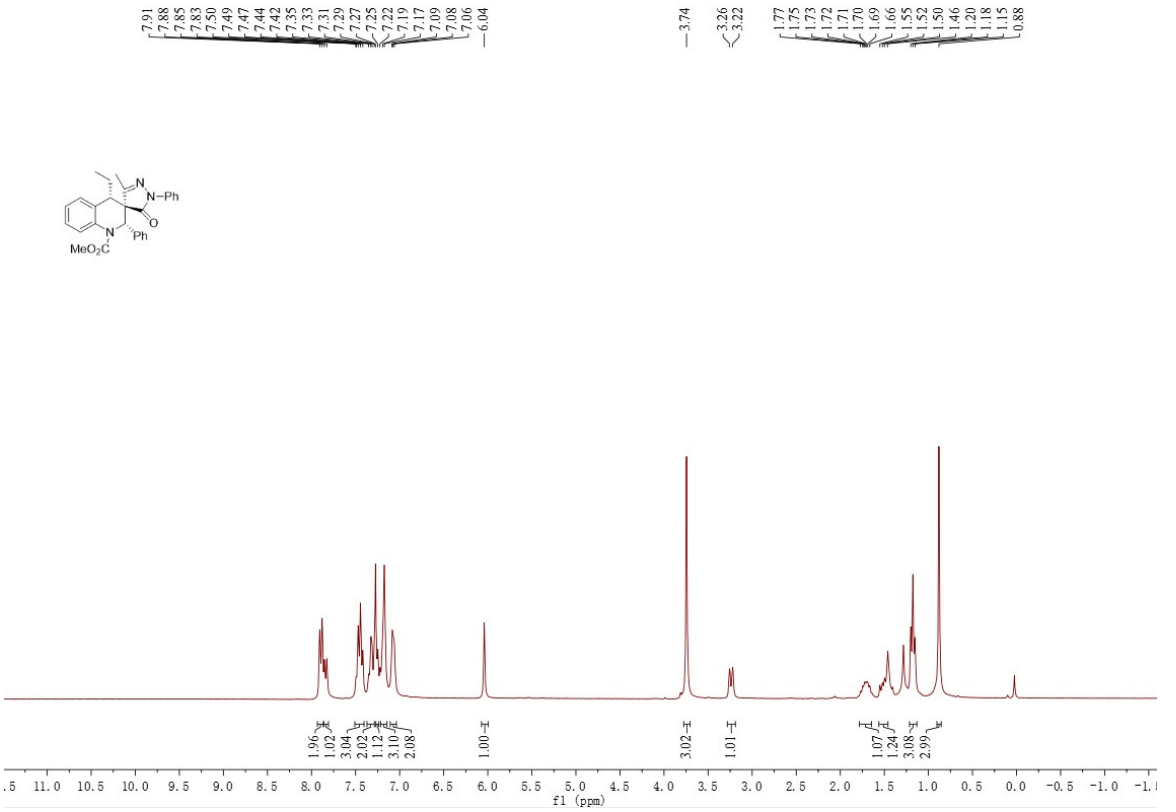
$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **5a**



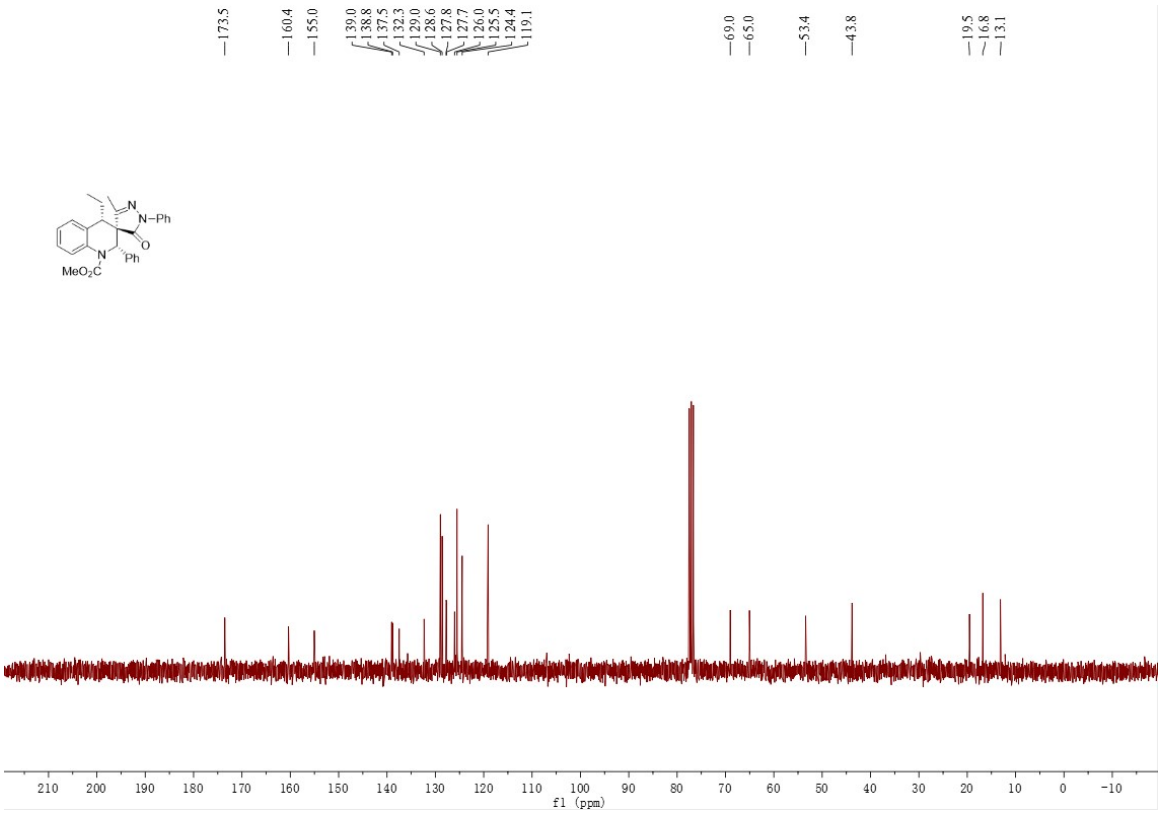

$^{1}$H ($CDCl_3$, 300 MHz) NMR of compound **5b**



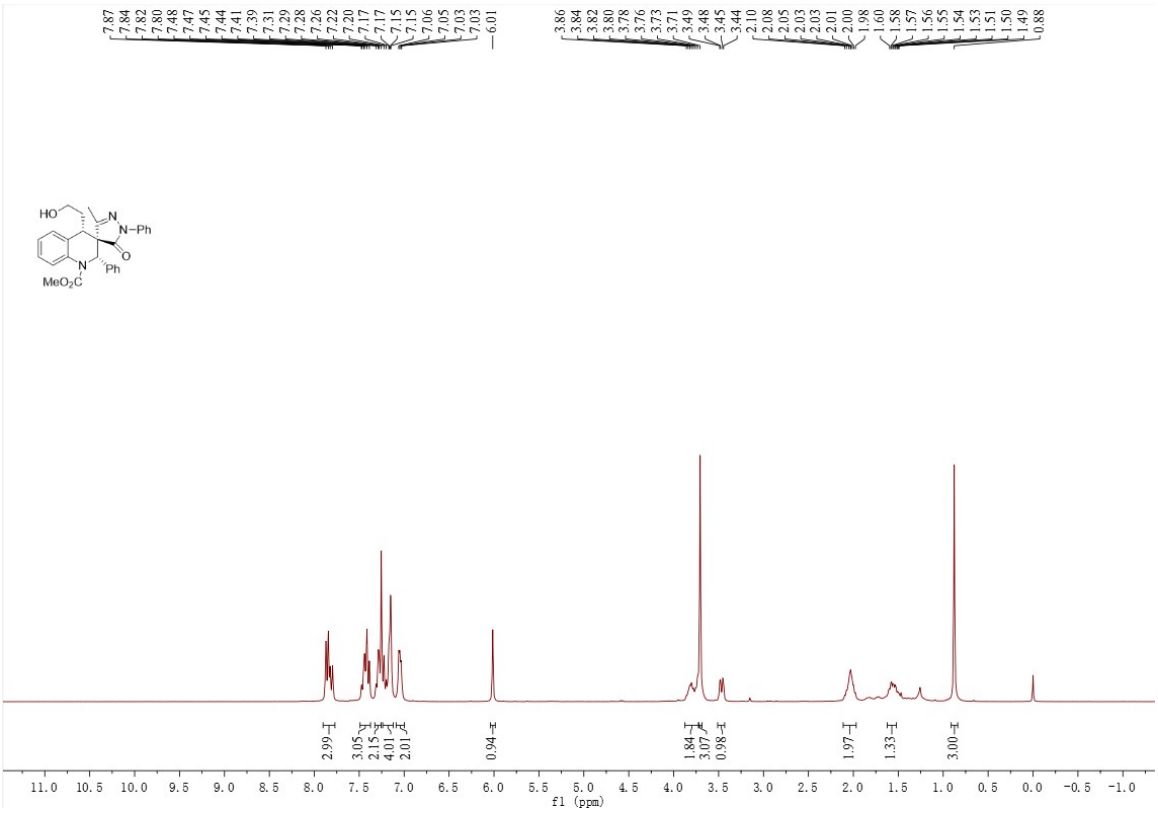

$^{13}$C ($CDCl_3$, 75 MHz) NMR of compound **5b**



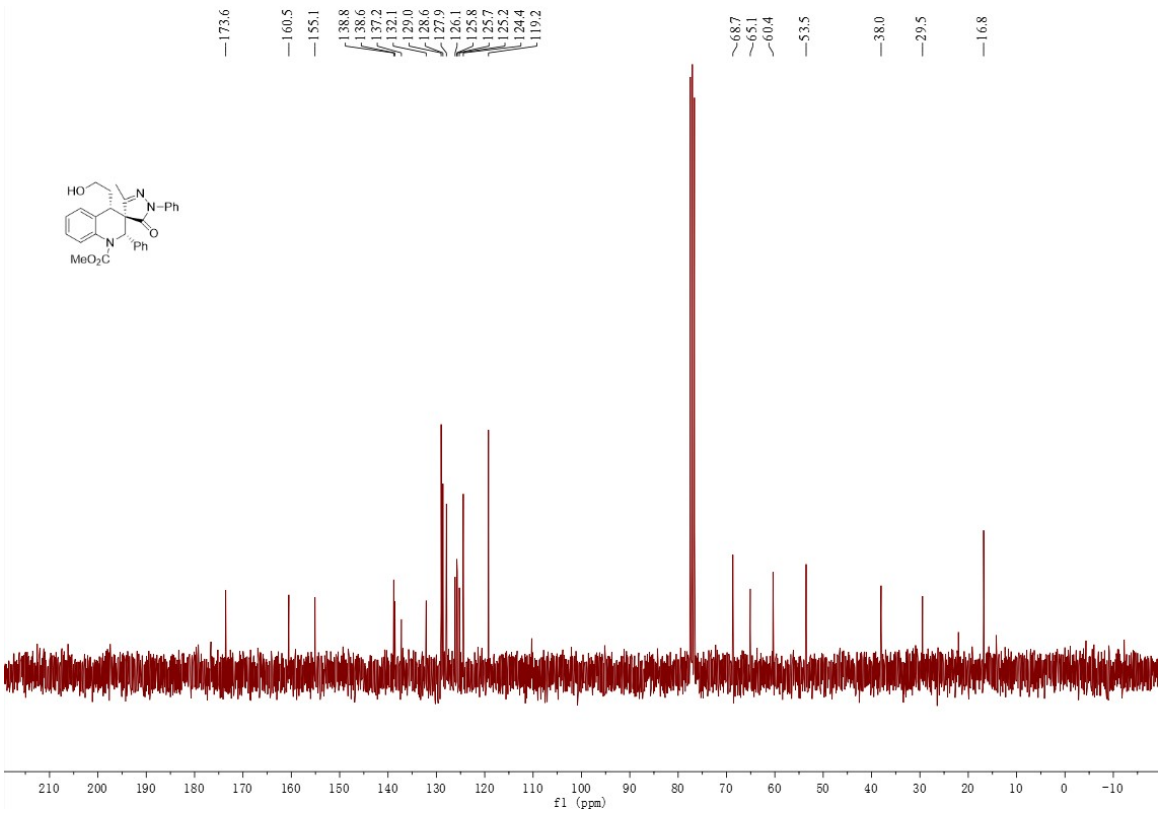

$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **6**




$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **6**

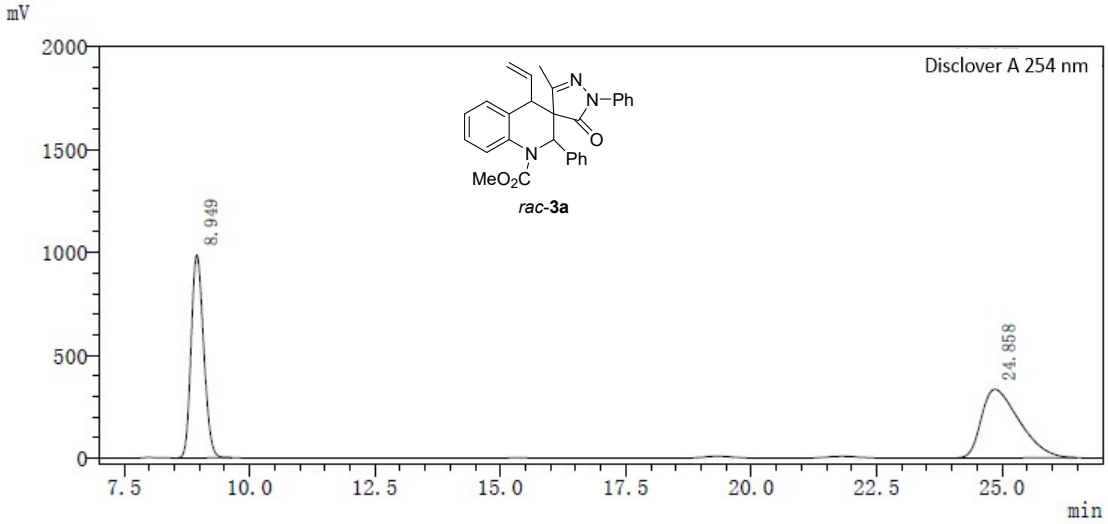



$^{1}H$ ($CDCl_3$, 300 MHz) NMR of compound **7**



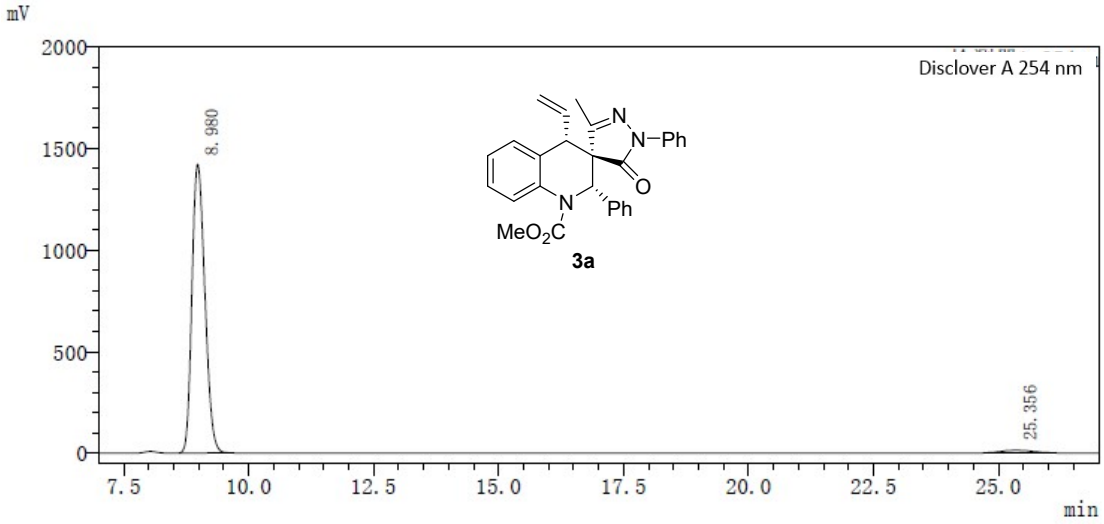

$^{13}C$ ($CDCl_3$, 75 MHz) NMR of compound **7**

# 6. Copies of HPLC Chromatograms



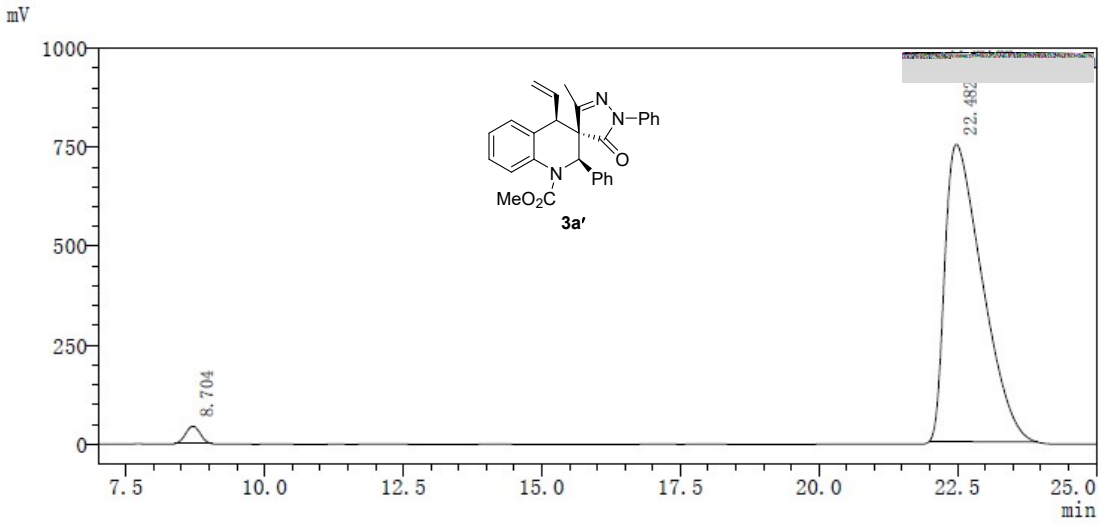

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.949 | 49.475 |
| 2 | 24.858 | 50.525 |
| total | | 100 |




Discloser A 254 nm

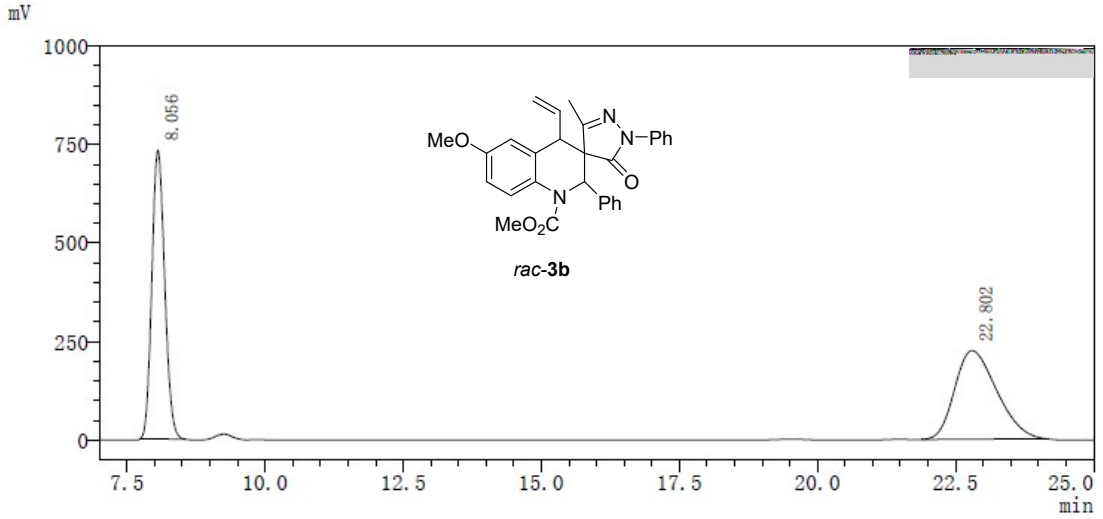
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.980 | 97.848 |
| 2 | 25.356 | 2.152 |
| total | | 100 |




**3a′**

Discloser A 254 nm

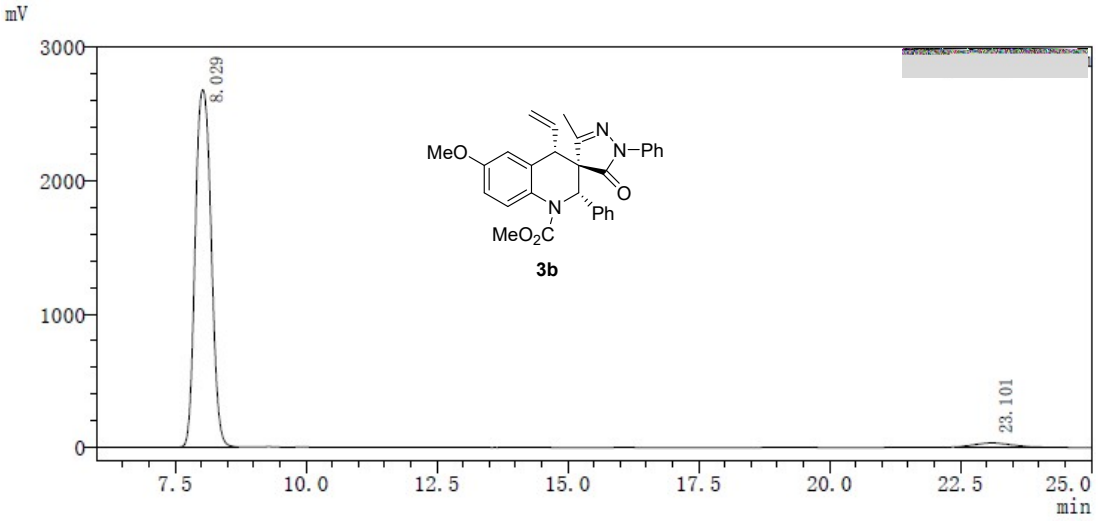
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.704 | 2.254 |
| 2 | 22.482 | 97.746 |
| total | | 100 |




*rac*-**3b**

Discloser A 254 nm

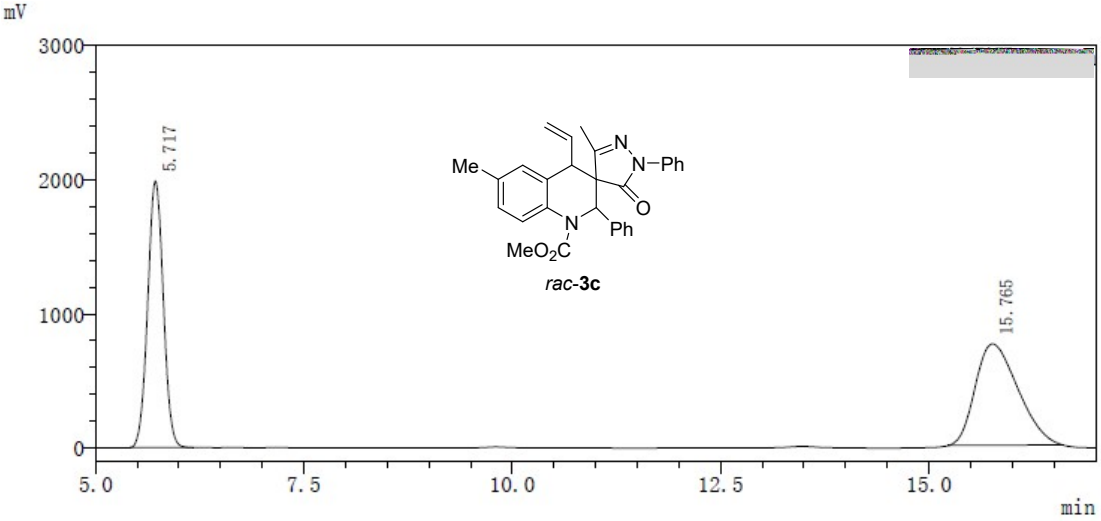
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.056 | 49.911 |
| 2 | 22.802 | 50.089 |
| total | | 100 |




**3b**

Discloser A 254 nm

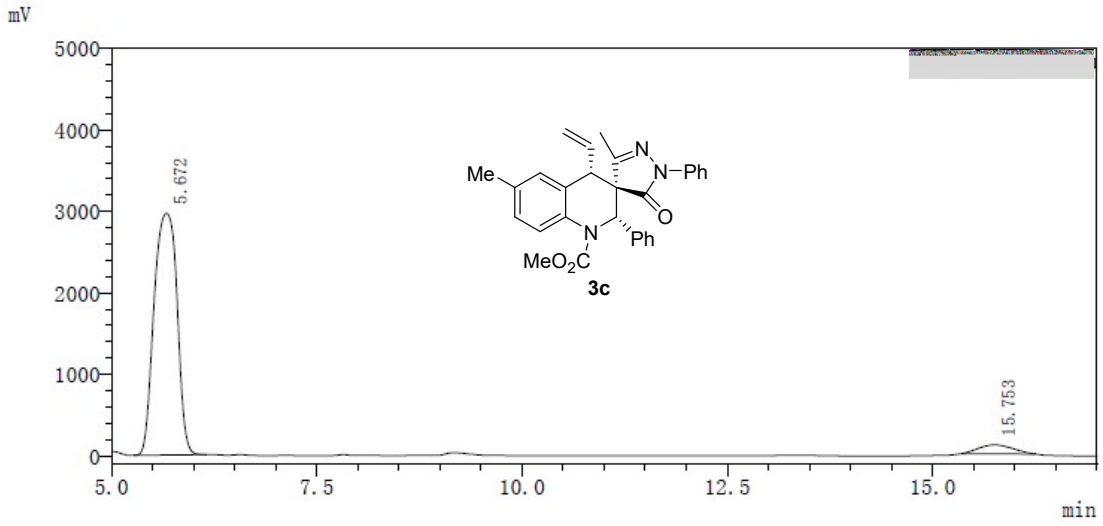
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.029 | 97.446 |
| 2 | 23.101 | 2.554 |
| total | | 100 |




*rac*-**3c**

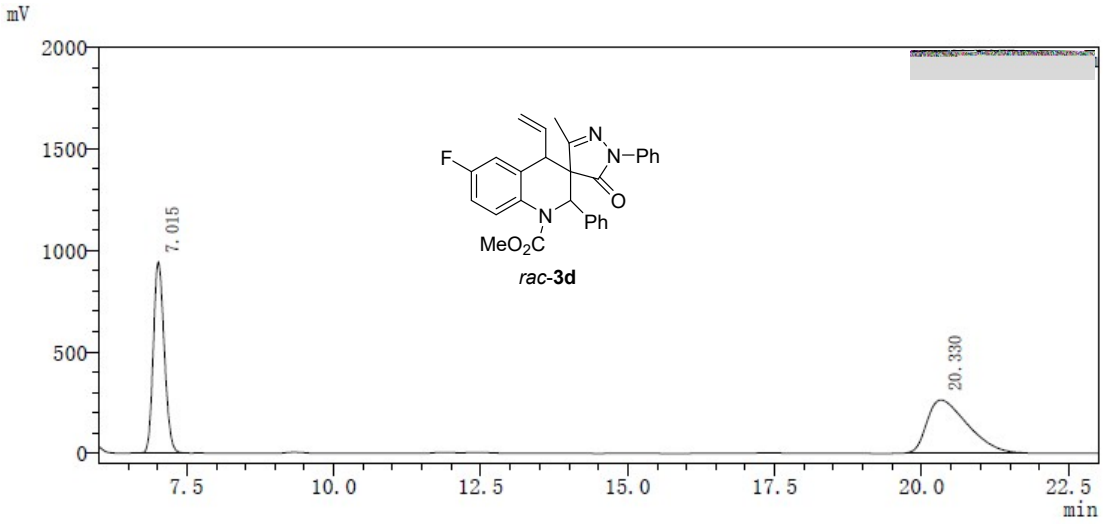
Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 5.717 | 49.063 |
| 2 | 15.765 | 50.937 |
| total | | 100 |



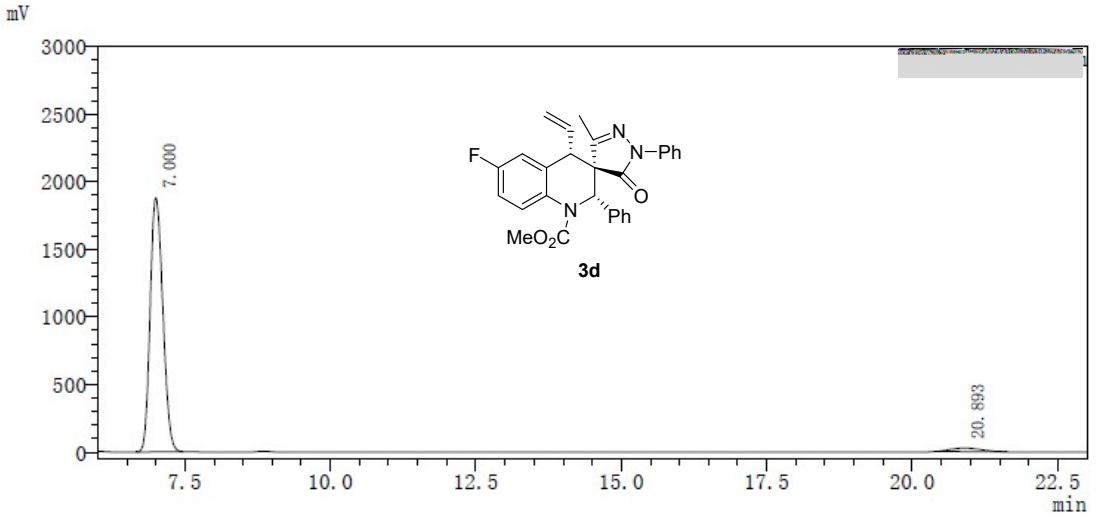

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 5.672 | 94.828 |
| 2 | 15.753 | 5.172 |
| total | | 100 |



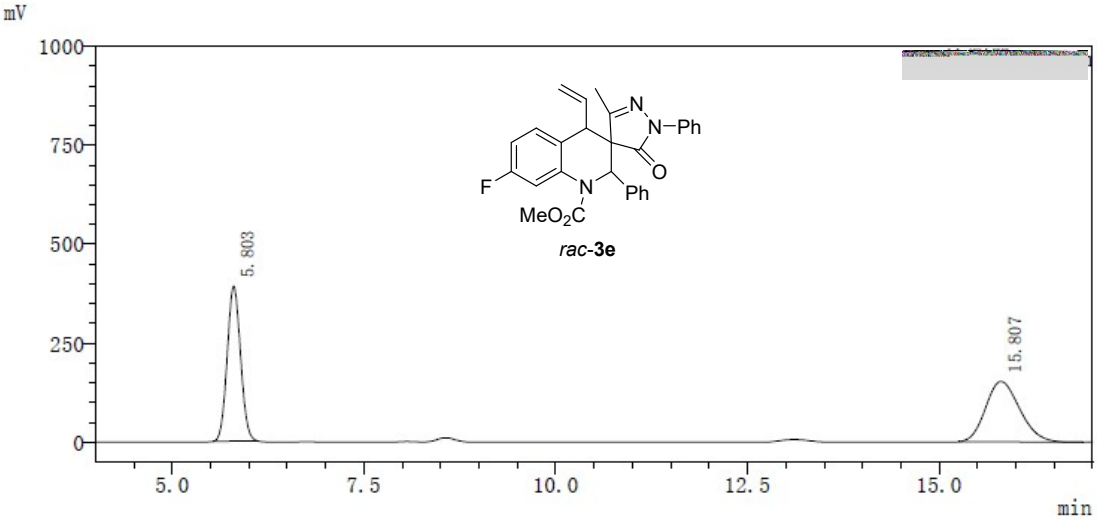

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.015 | 49.552 |
| 2 | 20.330 | 50.448 |
| total | | 100 |



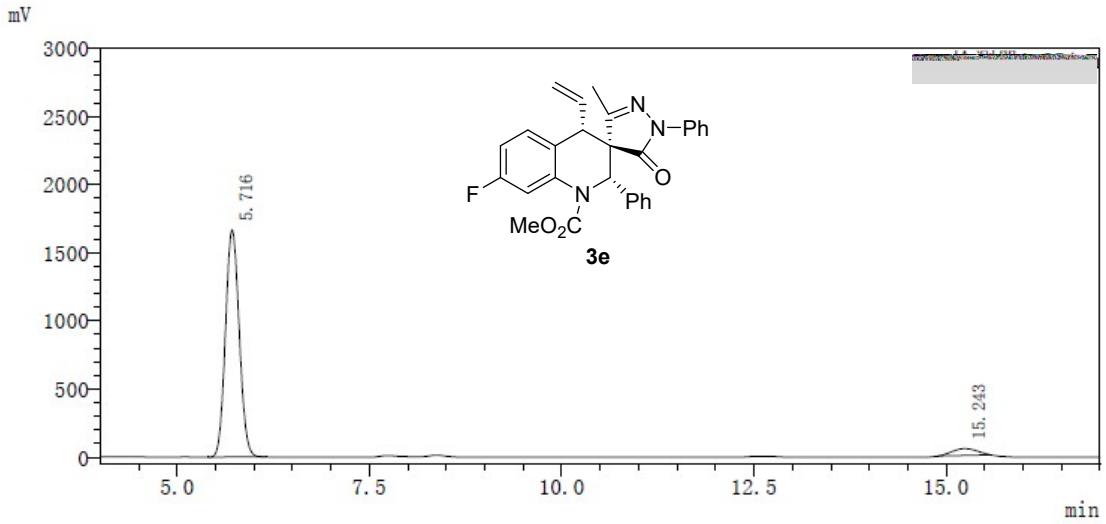

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.000 | 96.667 |
| 2 | 20.893 | 3.333 |
| total | | 100 |



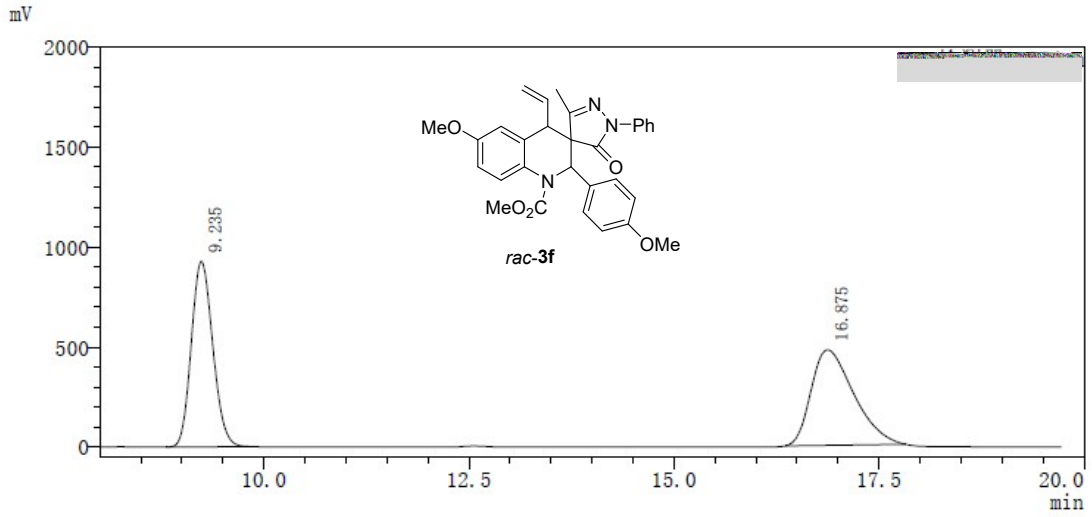

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 5.803 | 49.978 |
| 2 | 15.807 | 50.022 |
| total | | 100 |



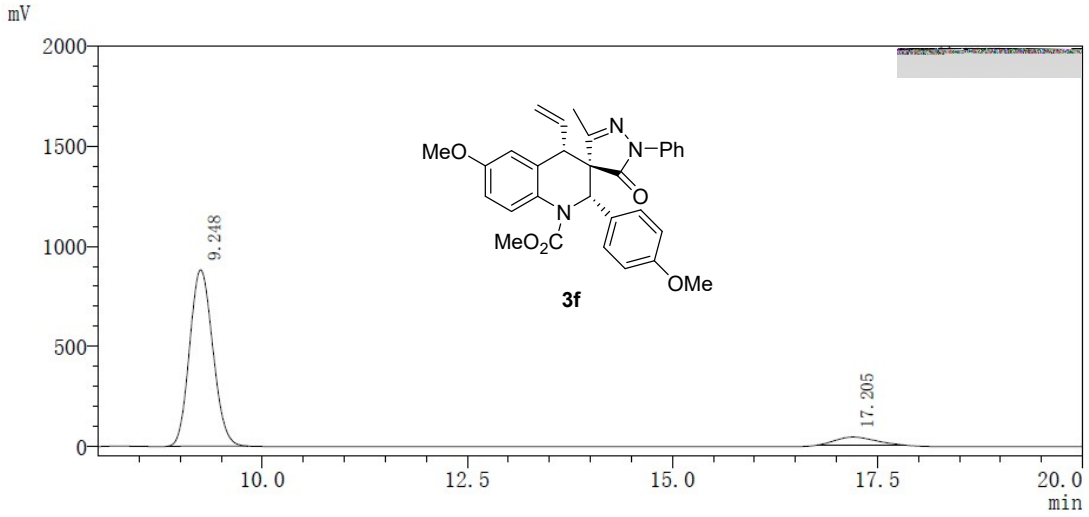

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 5.716 | 94.799 |
| 2 | 15.243 | 5.201 |
| total | | 100 |



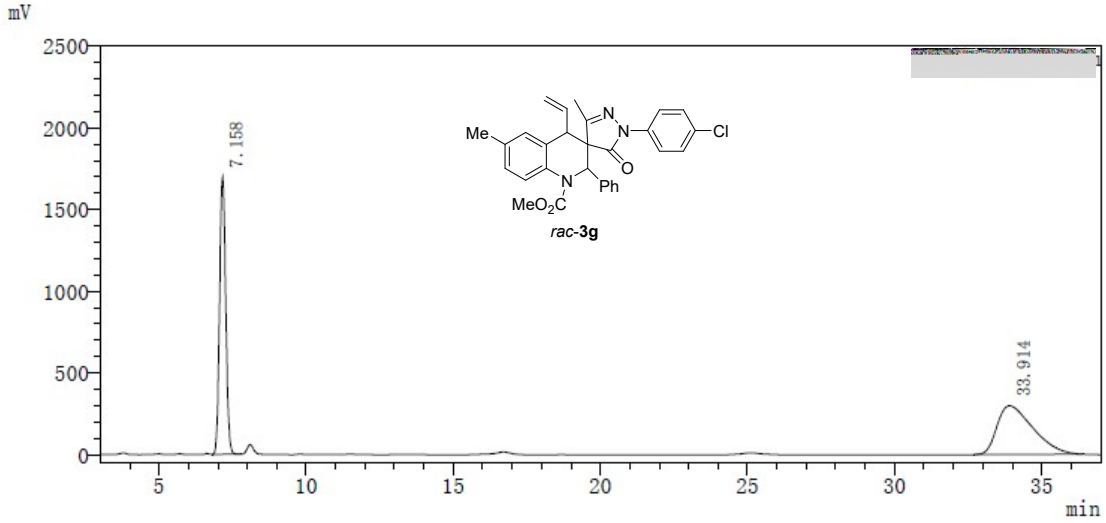

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.235 | 49.550 |
| 2 | 16.875 | 50.450 |
| total | | 100 |



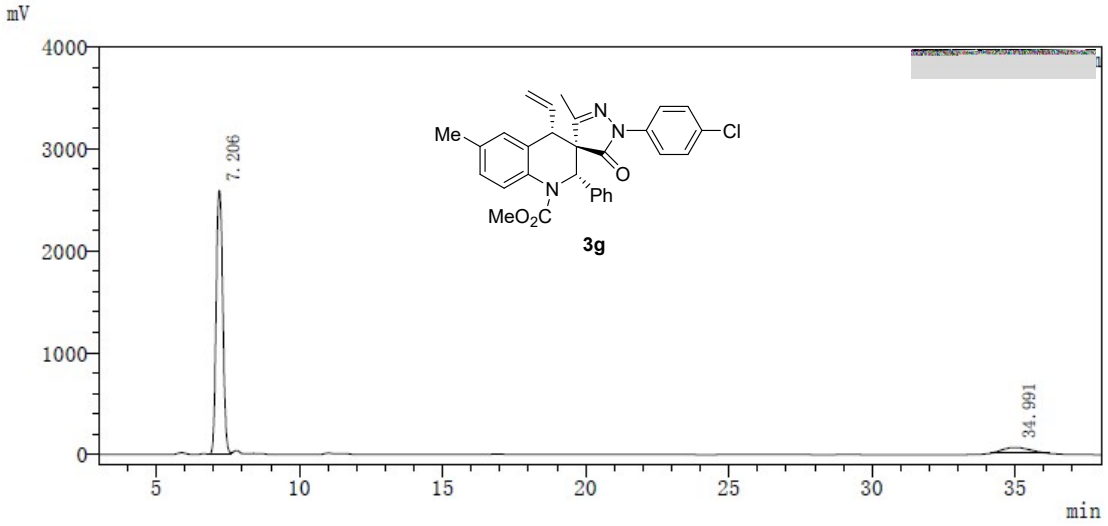

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.248 | 92.841 |
| 2 | 17.205 | 7.159 |
| total | | 100 |



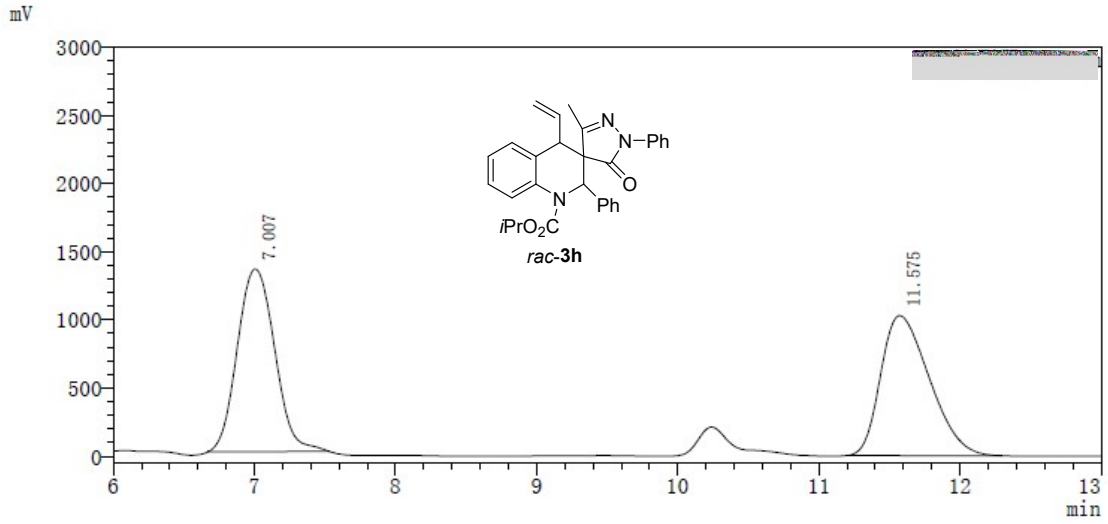

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | .7..158 | 49.360 |
| 2 | 33.914 | 50.640 |
| total | | 100 |



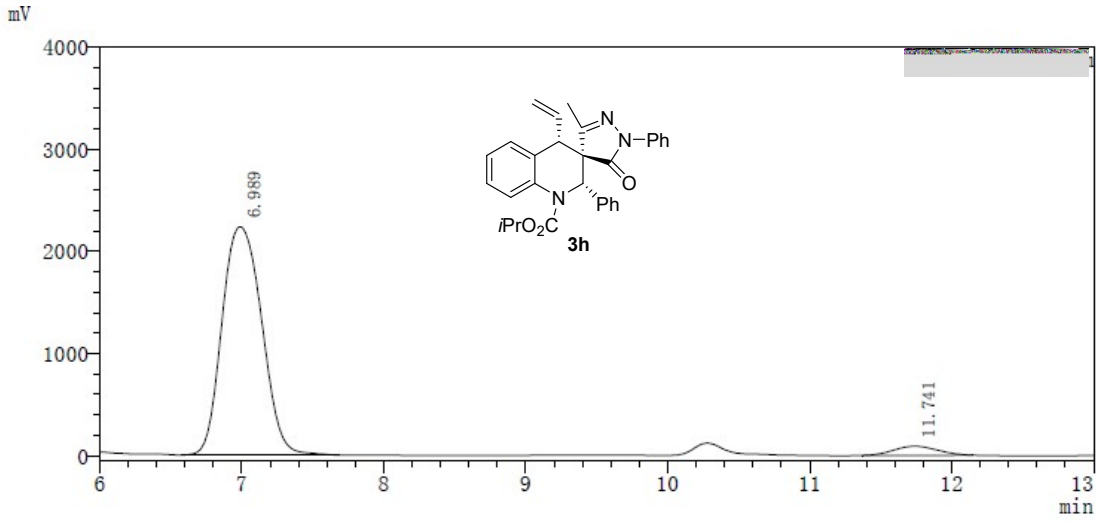

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.206 | 91.497 |
| 2 | 34.991 | 8.503 |
| total | | 100 |



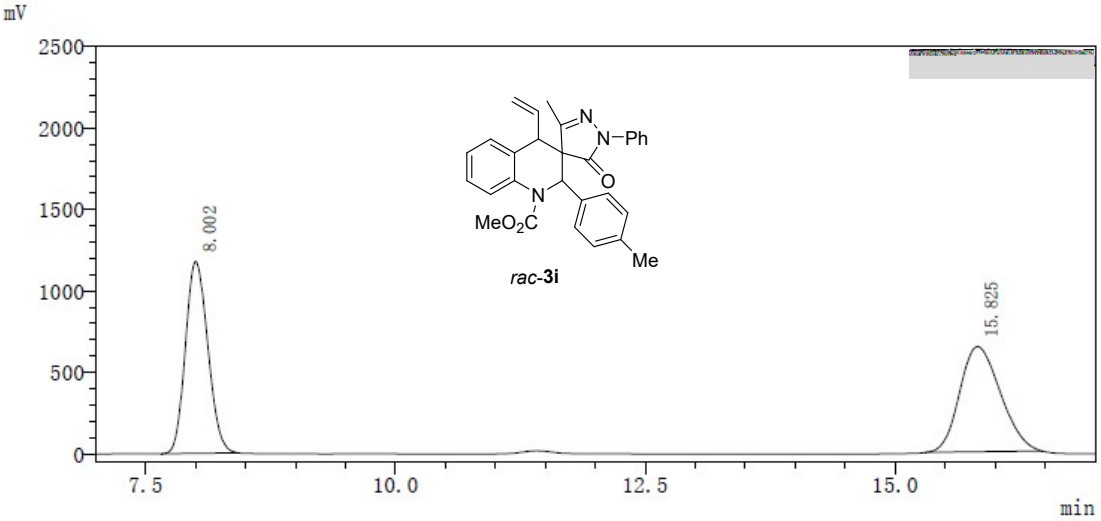

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.007 | 50.046 |
| 2 | 11.575 | 49.954 |
| total | | 100 |



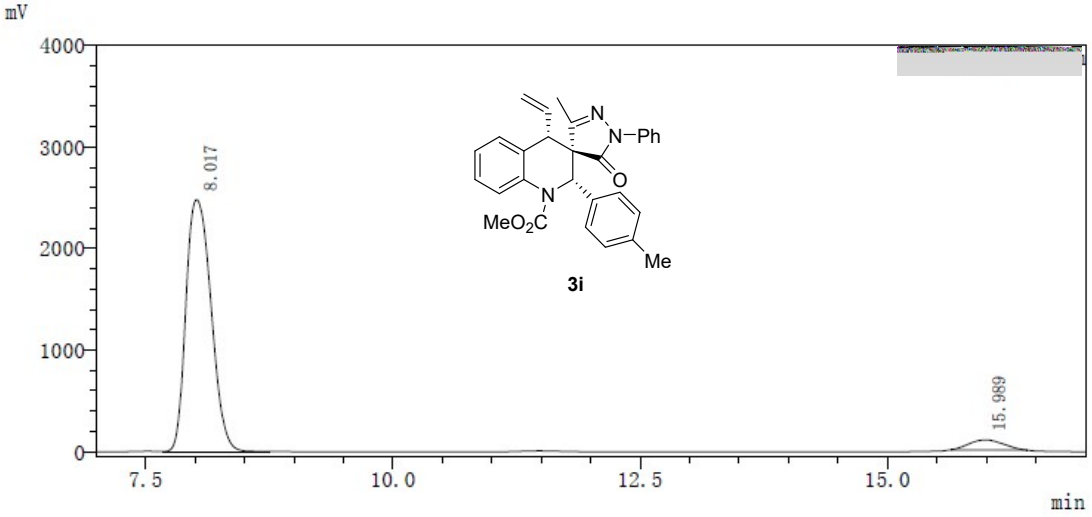

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.989 | 95.788 |
| 2 | 11.741 | 4.212 |
| total | | 100 |




Discloser A 254 nm

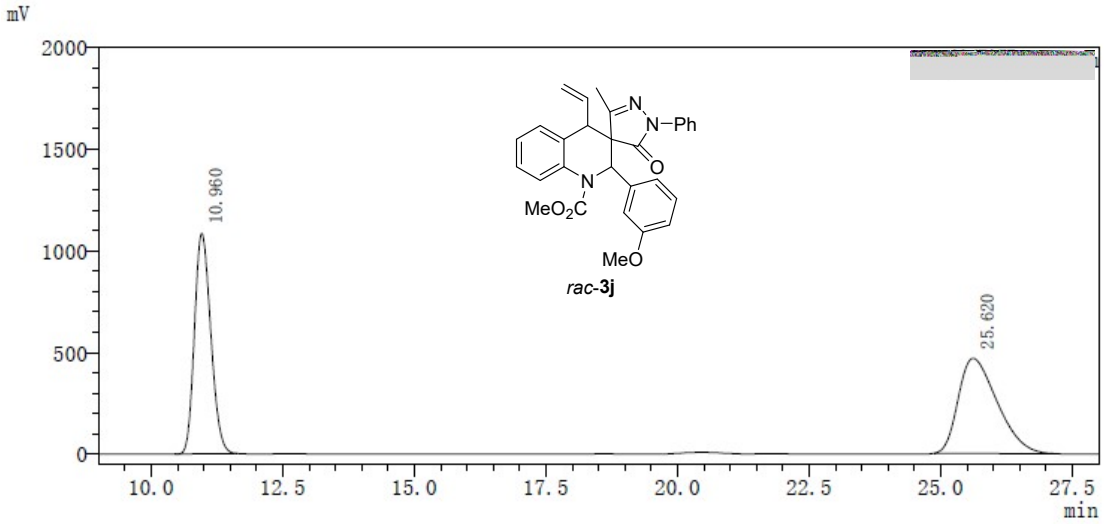
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.002 | 50.072 |
| 2 | 15.825 | 49.828 |
| total | | 100 |




**3i**

Discloser A 254 nm

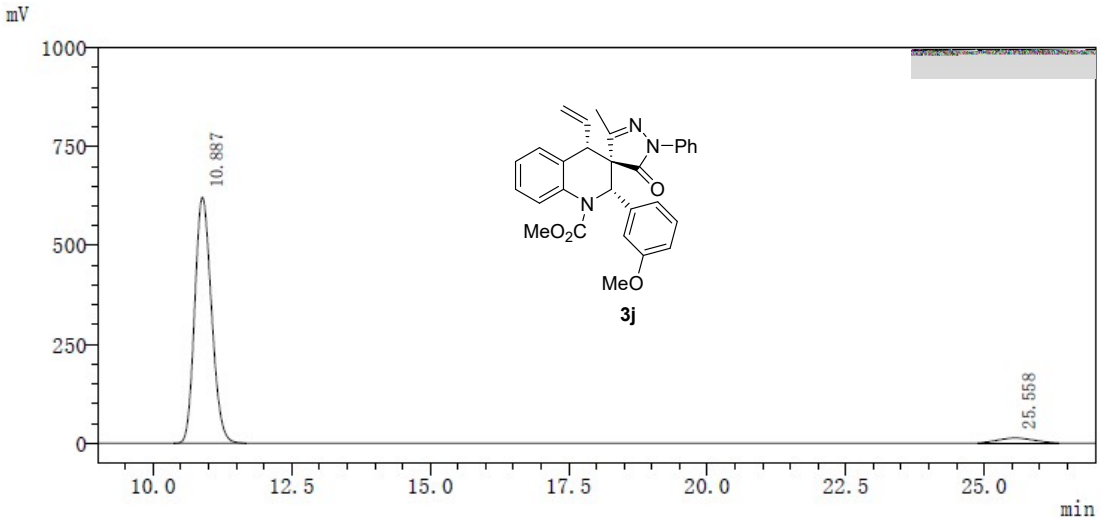
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.017 | 94.782 |
| 2 | 15.989 | 5.218 |
| total | | 100 |




*rac*-**3j**

Discloser A 254 nm

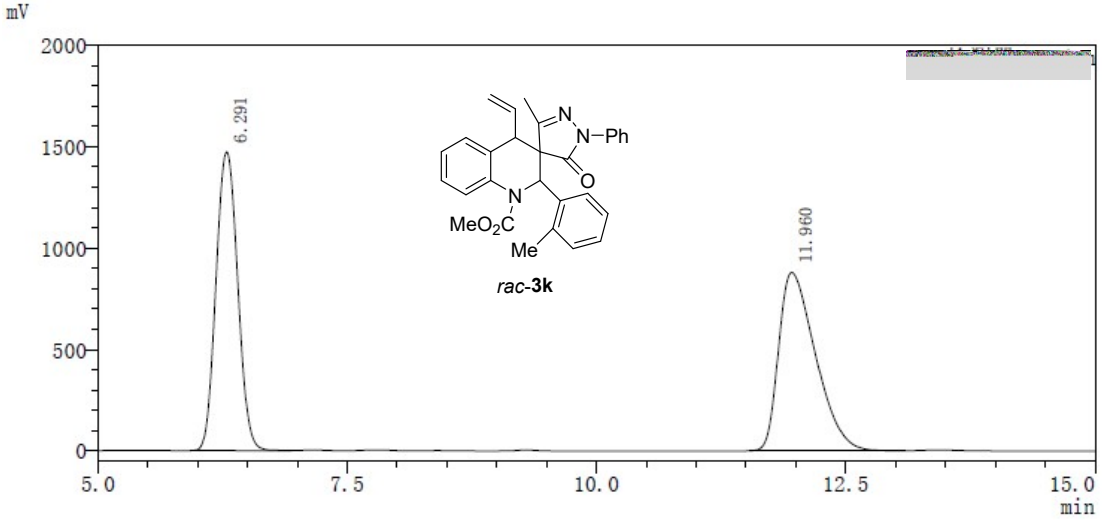
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 10.960 | 49.343 |
| 2 | 25.620 | 50.657 |
| total | | 100 |




**3j**

Discloser A 254 nm

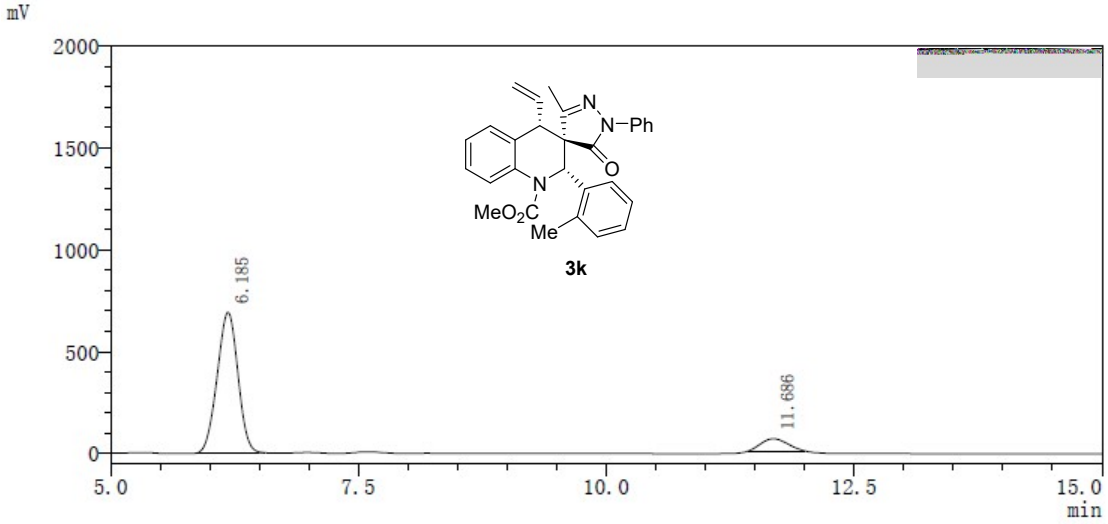
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 10.887 | 96.095 |
| 2 | 25.558 | 3.905 |
| total | | 100 |




*rac*-**3k**

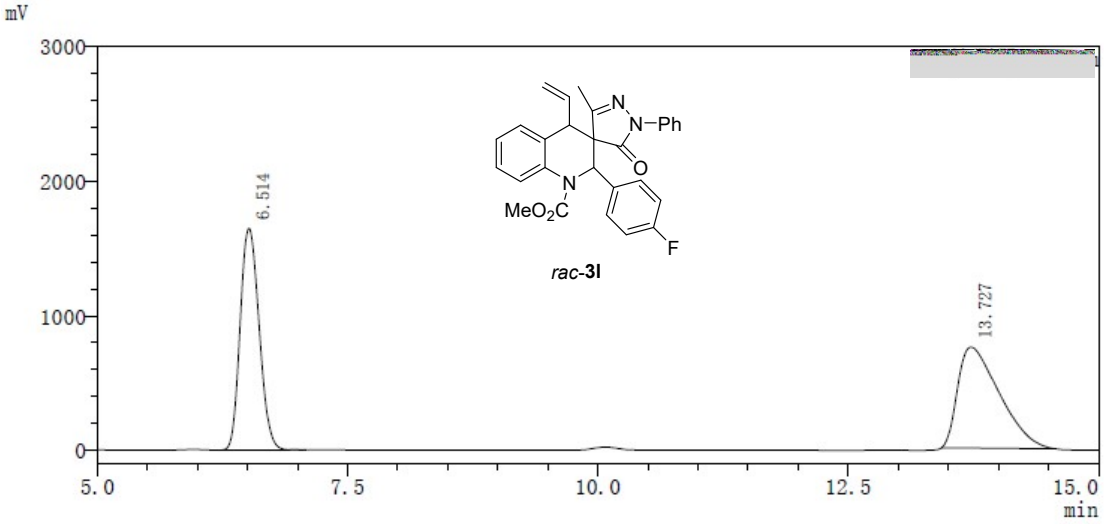
Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.291 | 49.623 |
| 2 | 11.960 | 50.377 |
| total | | 100 |



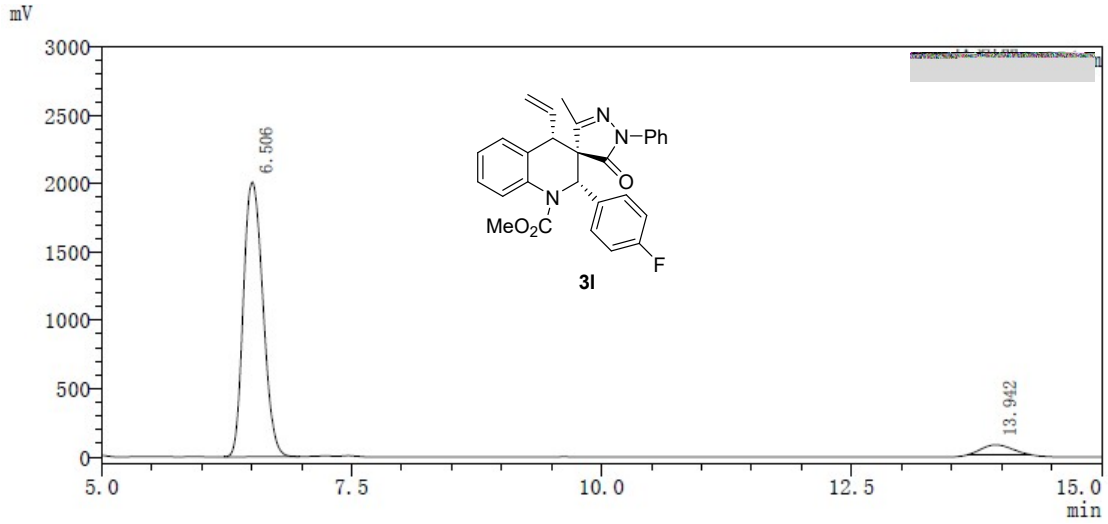

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.185 | 90.109 |
| 2 | 11.686 | 9.891 |
| total | | 100 |



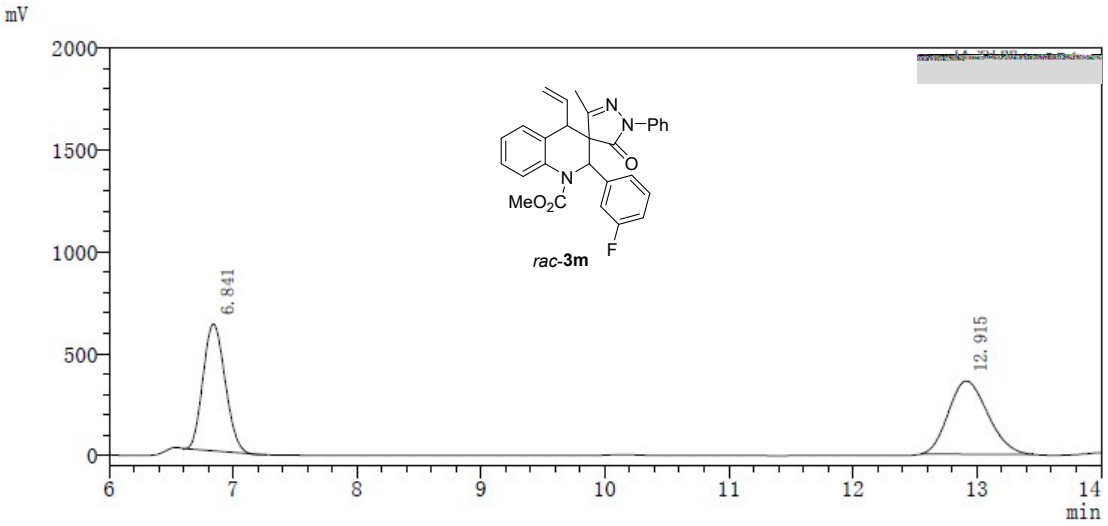

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.514 | 50.060 |
| 2 | 13.727 | 49.940 |
| total | | 100 |



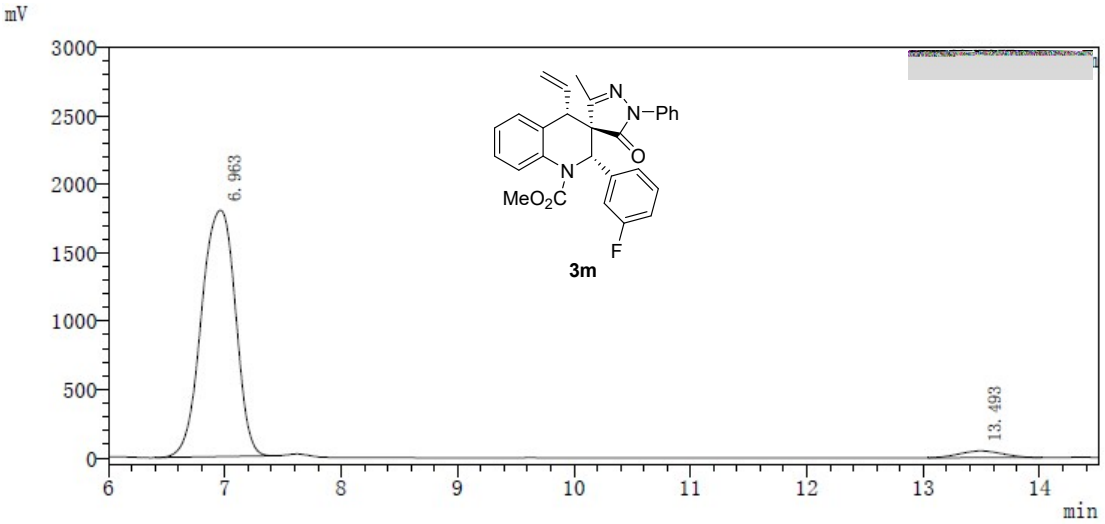

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.506 | 95.128 |
| 2 | 13.942 | 4.872 |
| total | | 100 |



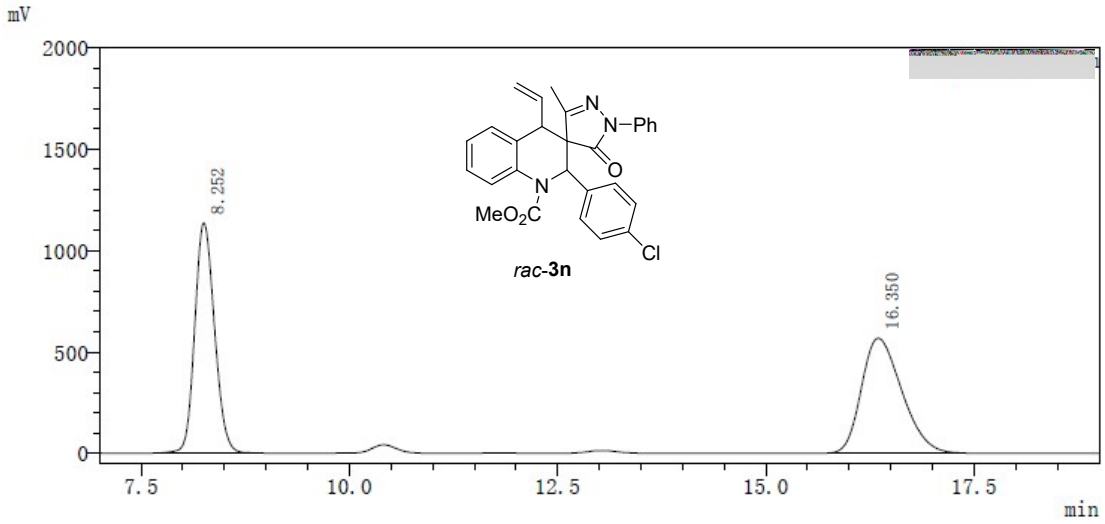

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.841 | 49.290 |
| 2 | 12.915 | 50.710 |
| total | | 100 |



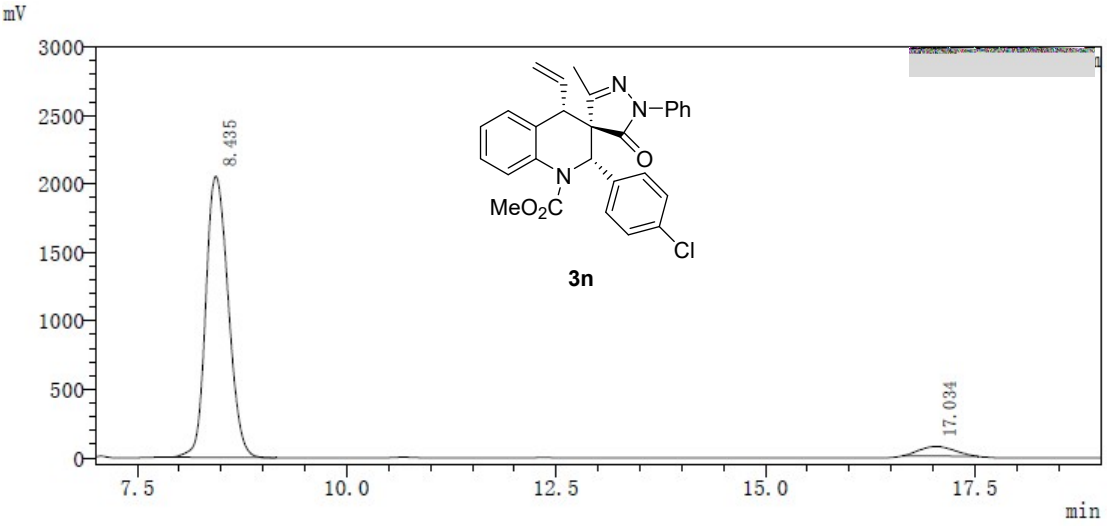

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.963 | 96.653 |
| 2 | 13.493 | 3.347 |
| total | | 100 |



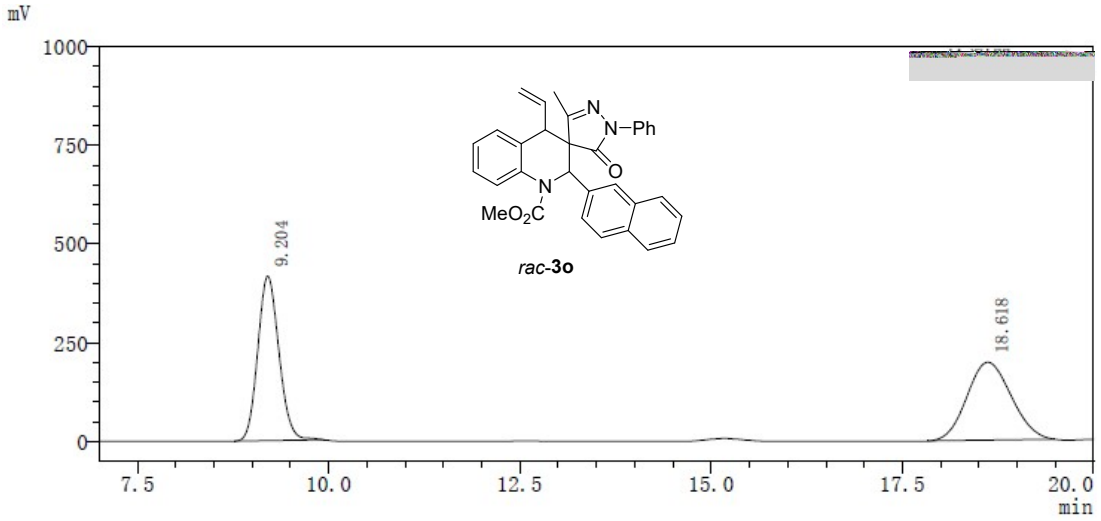

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.252 | 49.589 |
| 2 | 18.618 | 50.411 |
| total | | 100 |



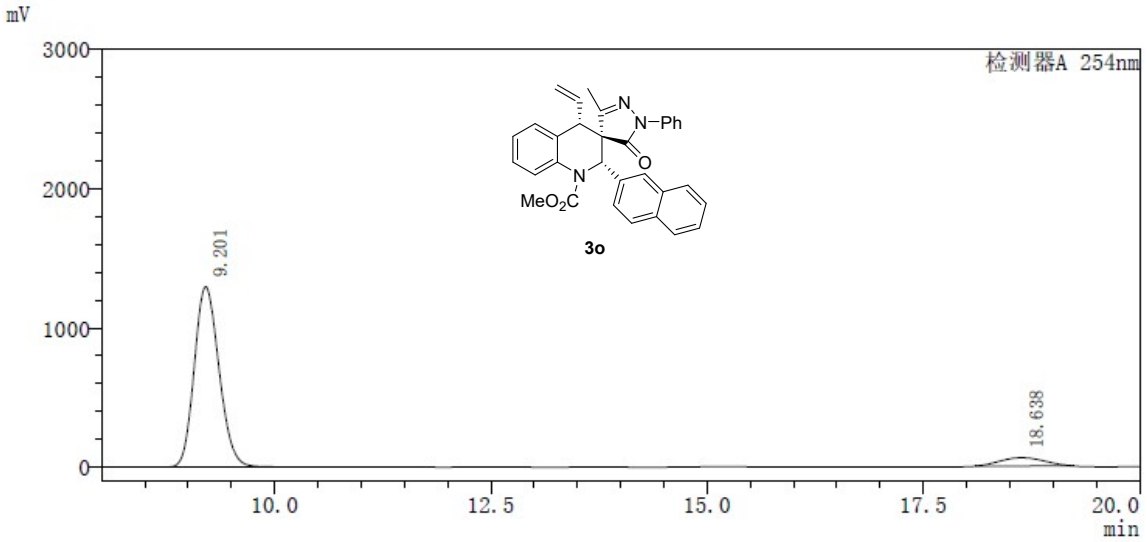

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.435 | 95.045 |
| 2 | 17.034 | 4.955 |
| total | | 100 |




Discloser A 254 nm

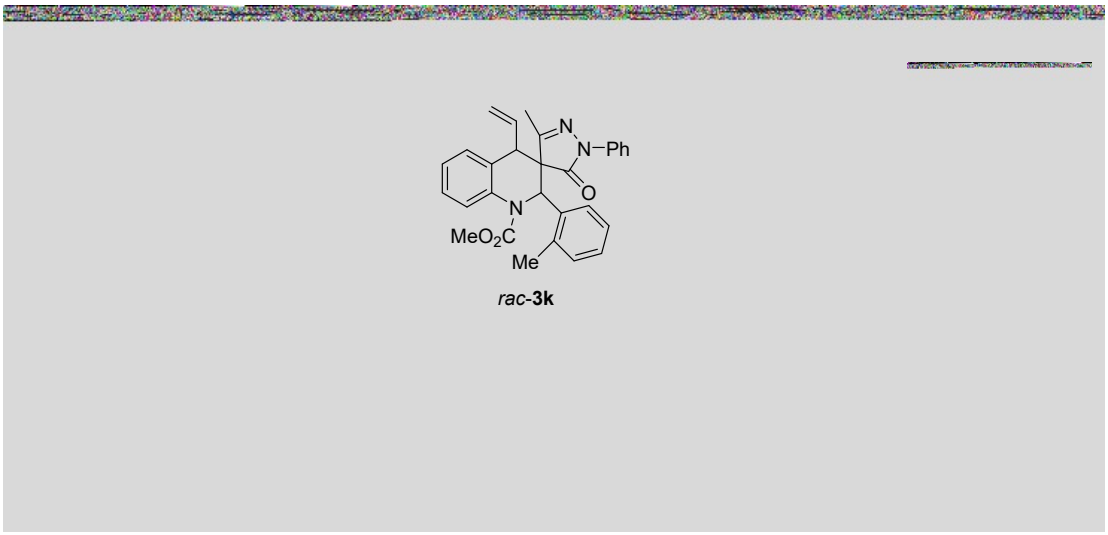
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.204 | 50.292 |
| 2 | 18.618 | 49.708 |
| total | | 100 |




**3o**

Discloser A 254 nm

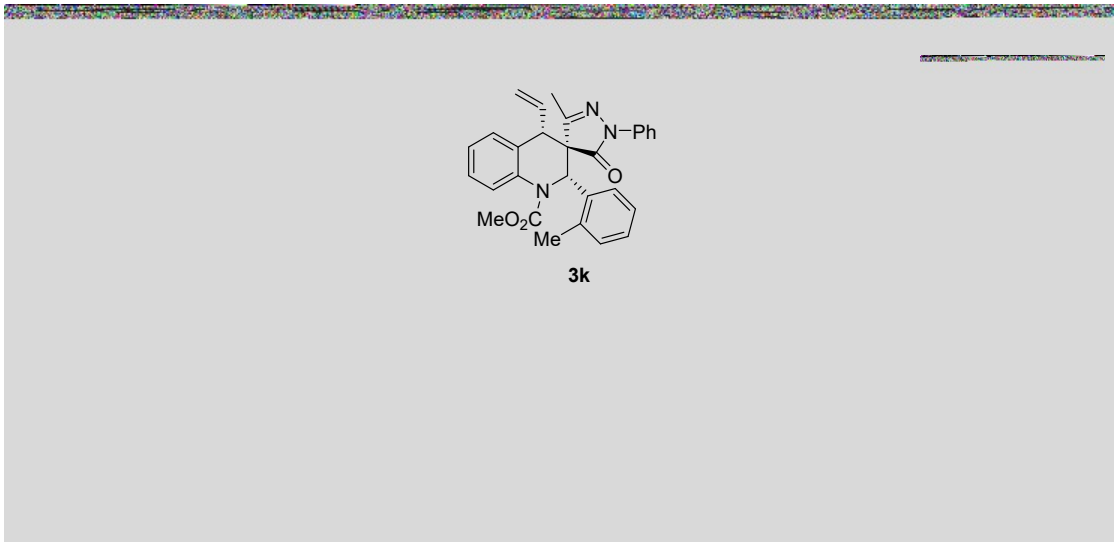
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.201 | 92.401 |
| 2 | 18.638 | 7.599 |
| total | | 100 |




*rac*-**3k**

Discloser A 254 nm

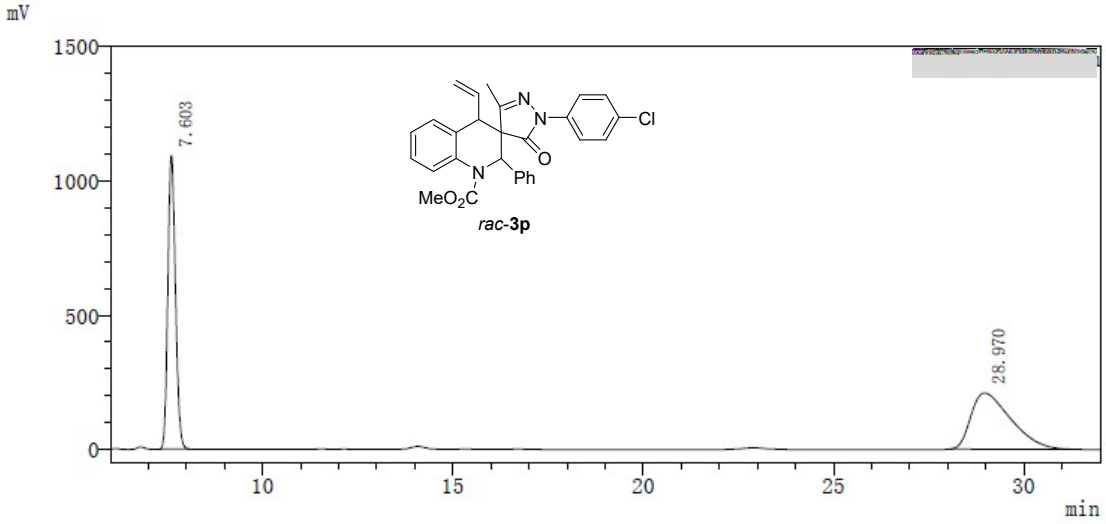
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.291 | 49.623 |
| 2 | 11.960 | 50.377 |
| total | | 100 |




**3k**

Discloser A 254 nm

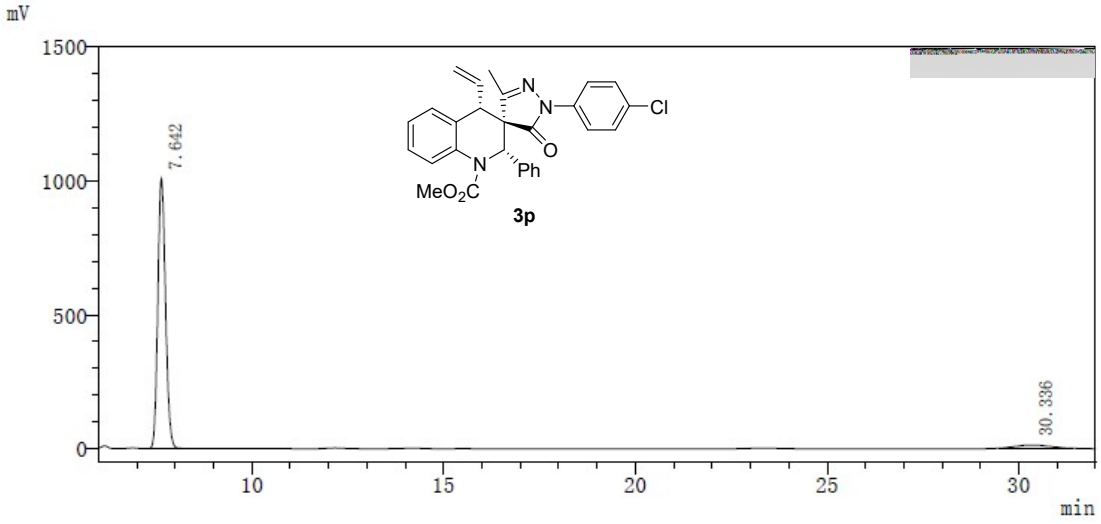
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.185 | 90.109 |
| 2 | 11.686 | 9.891 |
| total | | 100 |




*rac*-**3p**

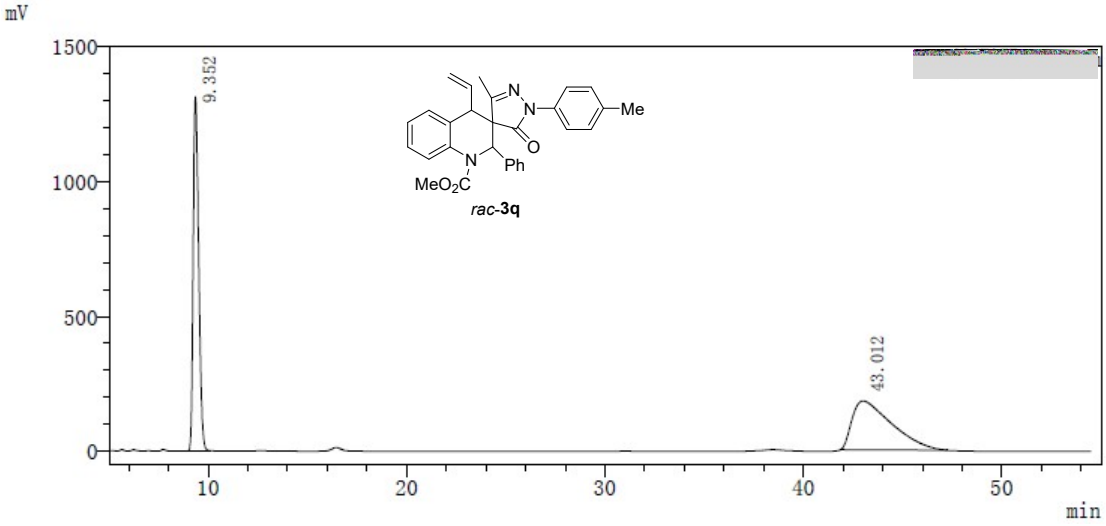
Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.603 | 49.978 |
| 2 | 28.970 | 50.022 |
| total | | 100 |



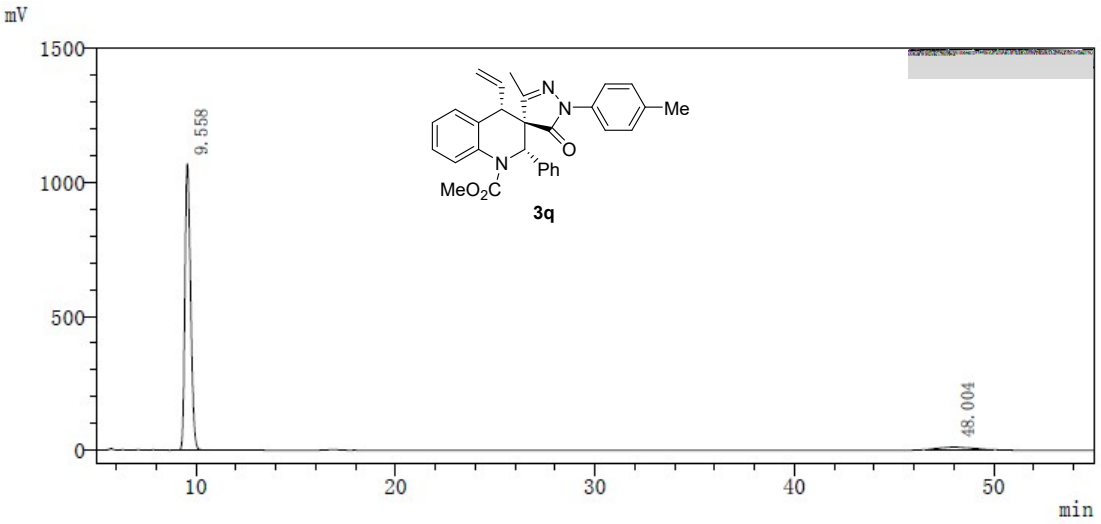

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.642 | 95.116 |
| 2 | 30.336 | 4.884 |
| total | | 100 |




Discloser A 254 nm

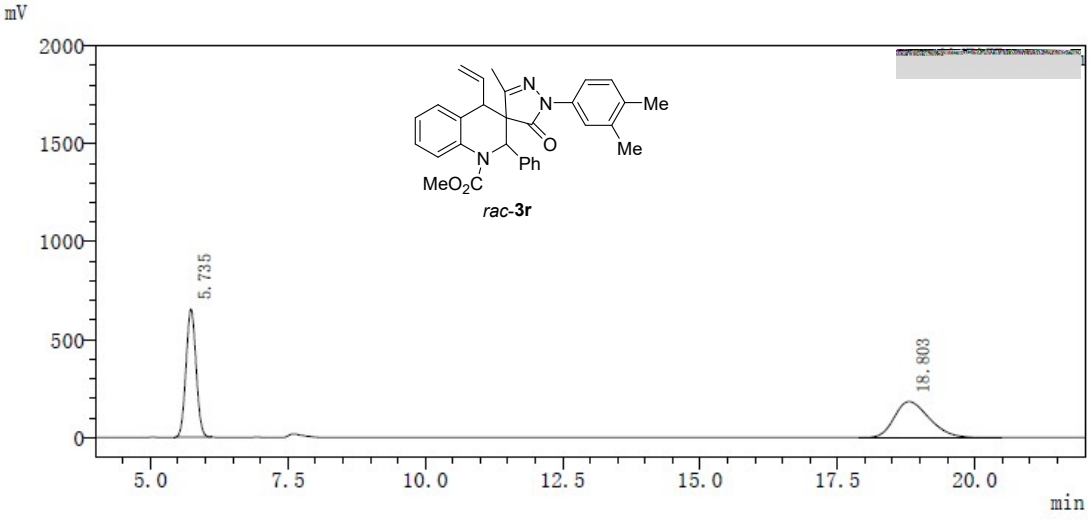
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.352 | 50.031 |
| 2 | 43.012 | 49.969 |
| total | | 100 |




**3q**

Discloser A 254 nm

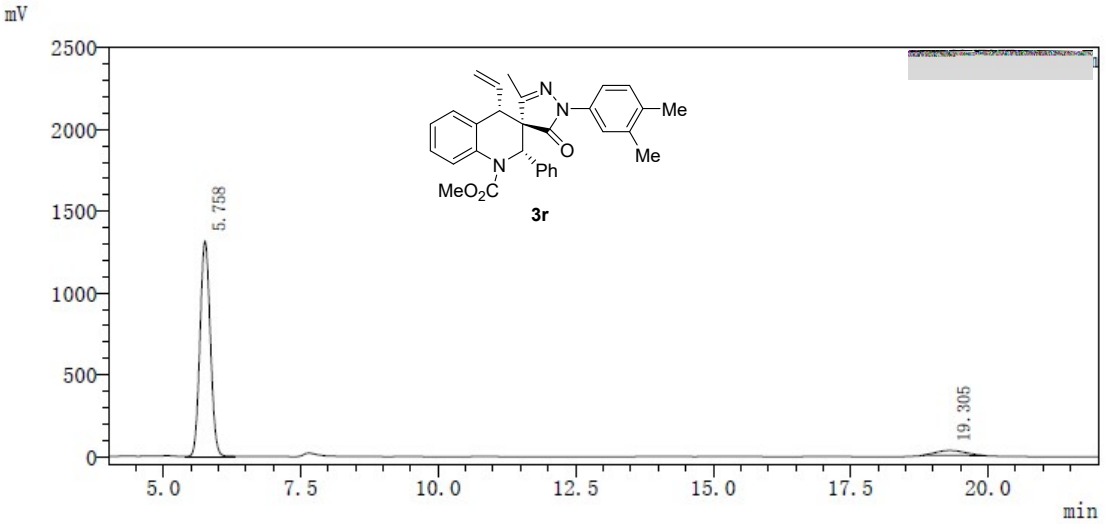
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | .9.558 | 95.180 |
| 2 | 48.004 | 4.820 |
| total | | 100 |




*rac*-**3r**

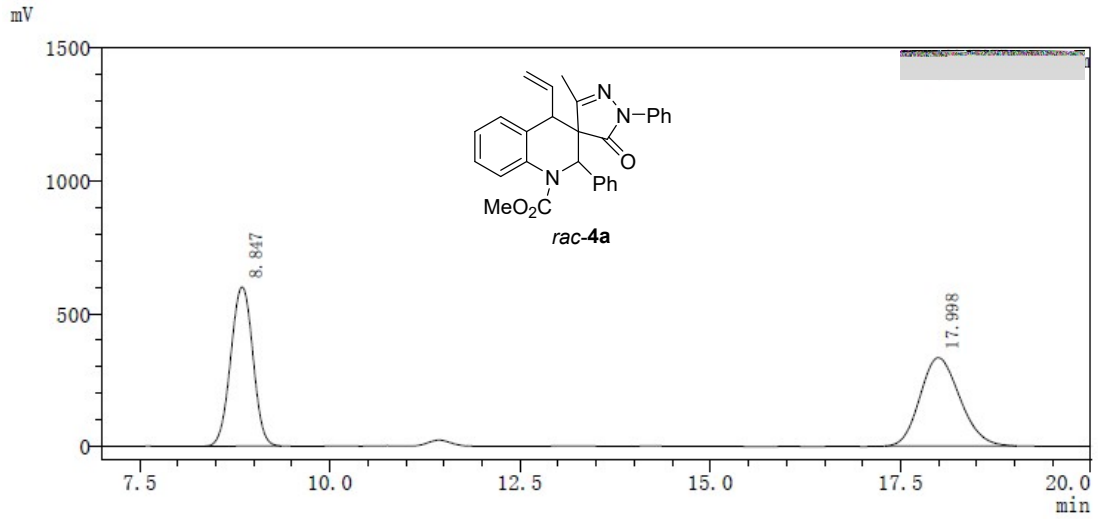
Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 5.735 | 50.571 |
| 2 | 18.803 | 49.429 |
| total | | 100 |



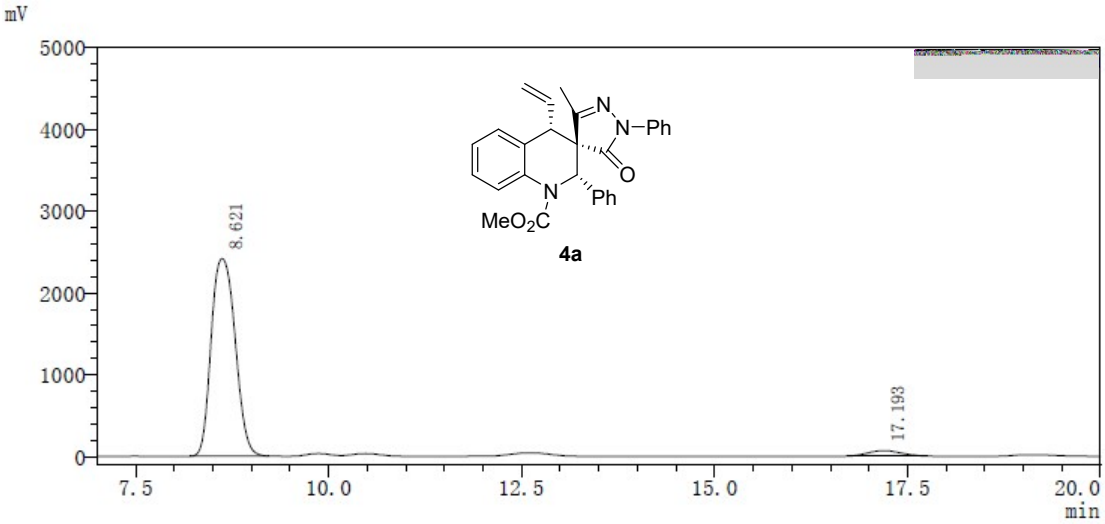

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 5.758 | 94.274 |
| 2 | 19.305 | 5.726 |
| total | | 100 |



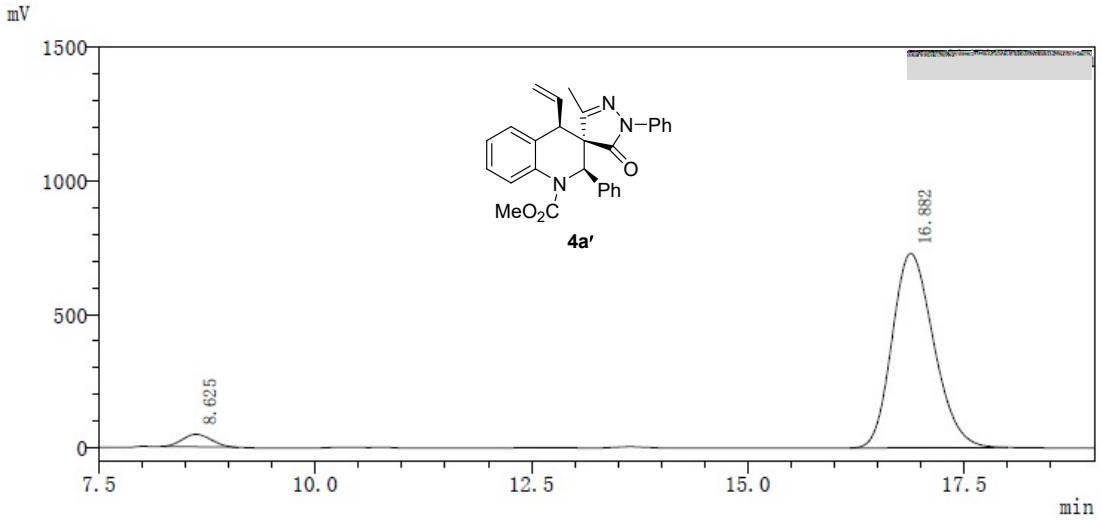

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.847 | 50.076 |
| 2 | 17.998 | 49.824 |
| total | | 100 |



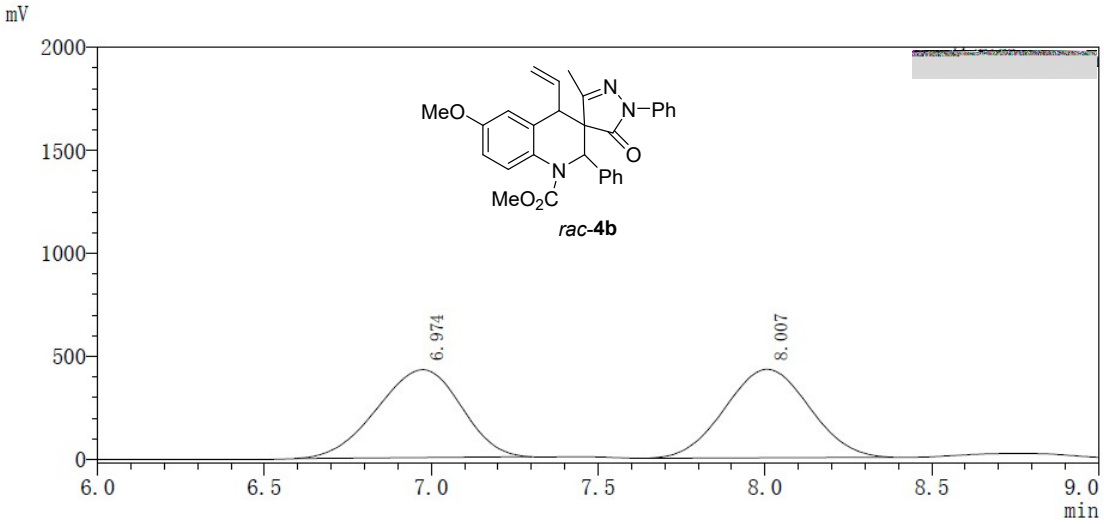

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.621 | 96.284 |
| 2 | 17.193 | 3.716 |
| total | | 100 |




Discloser A 254 nm

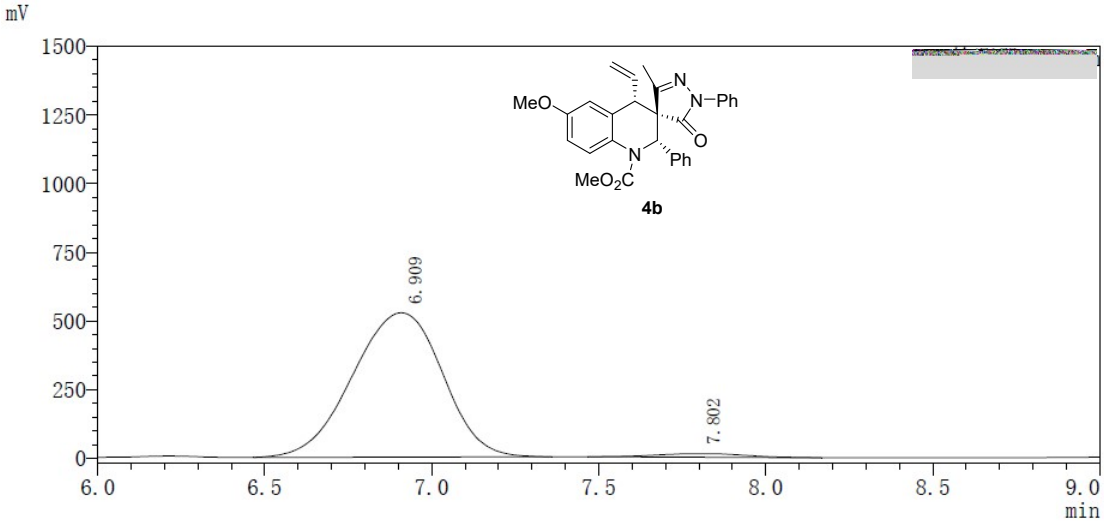
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.625 | 4.302 |
| 2 | 16.882 | 95.698 |
| total | | 100 |




*rac*-**4b**

Discloser A 254 nm

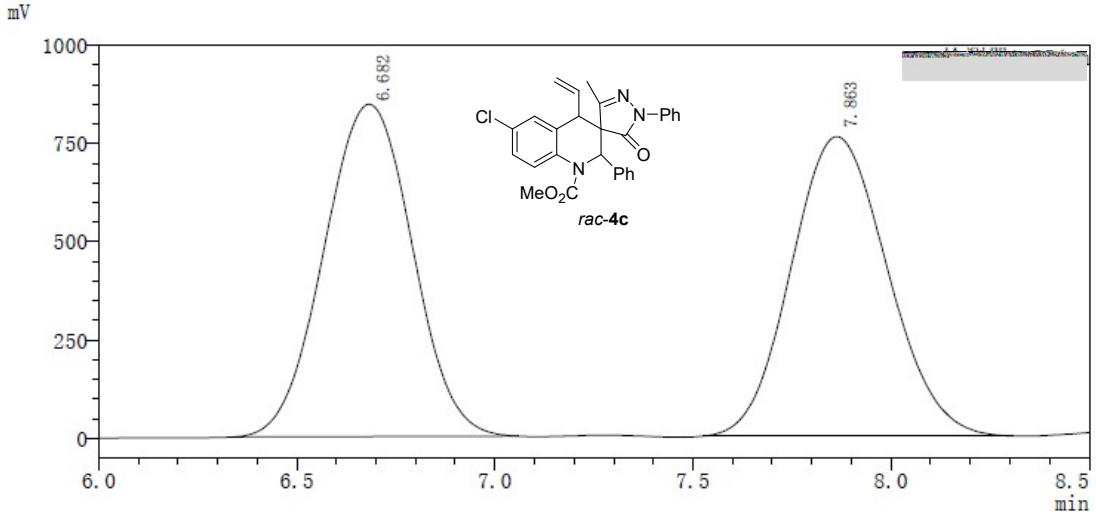
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.974 | 49.734 |
| 2 | 8.007 | 50.266 |
| total | | 100 |




**4b**

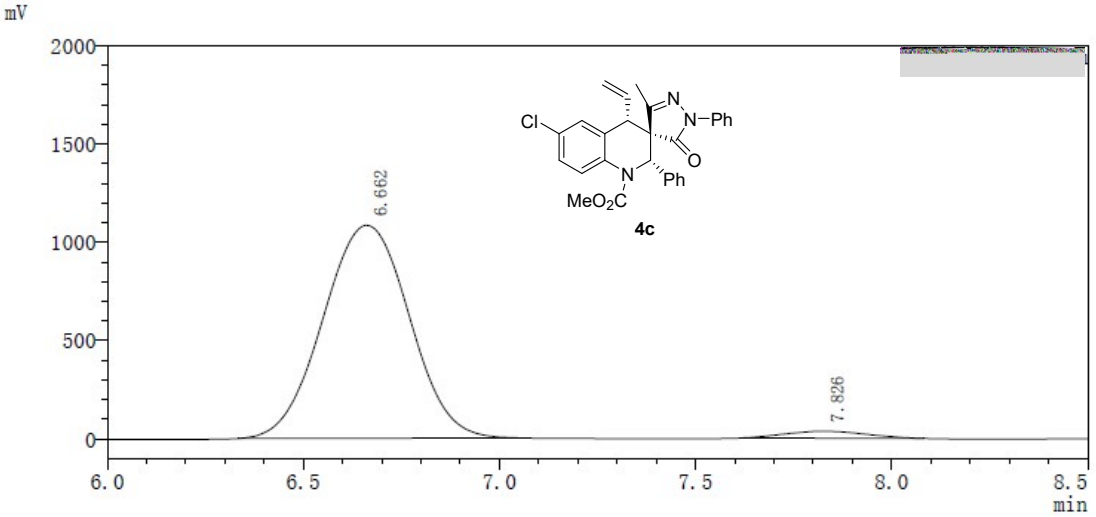
Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.909 | 97.631 |
| 2 | 7.802 | 2.369 |
| total | | 100 |



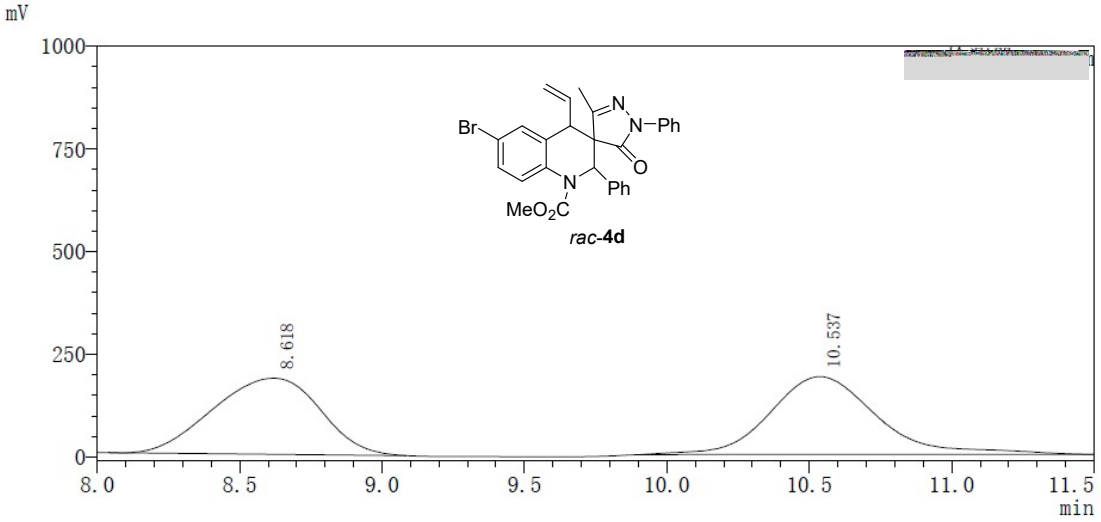

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.682 | 50.489 |
| 2 | 7.863 | 49.511 |
| total | | 100 |



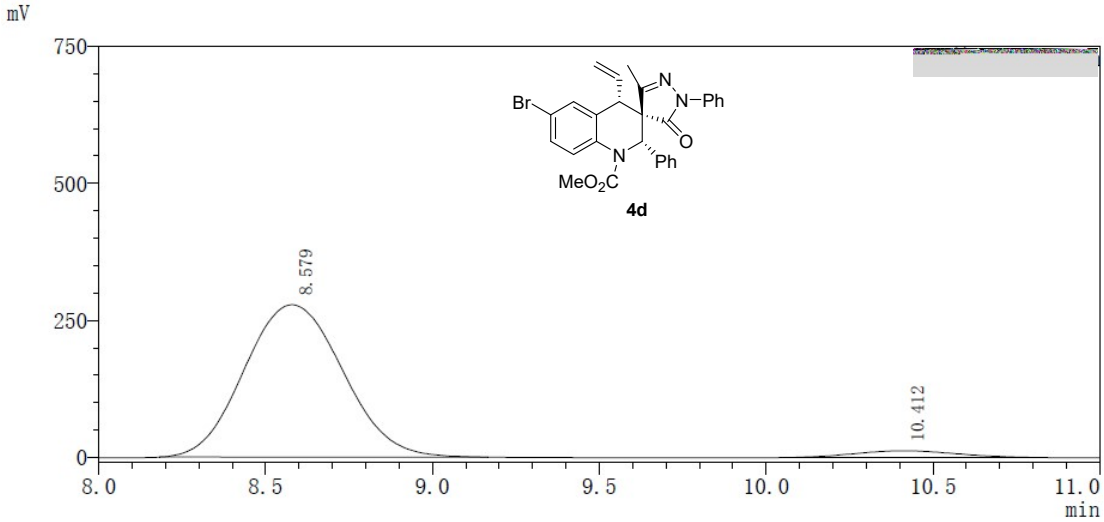

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.662 | 97.049 |
| 2 | 7.826 | 2.951 |
| total | | 100 |



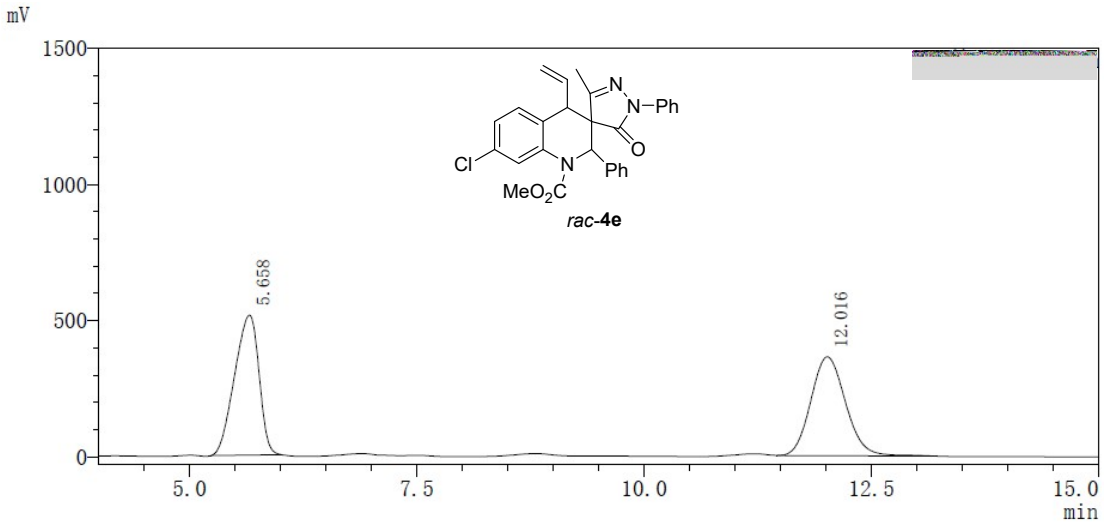

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.618 | 49.477 |
| 2 | 10.537 | 50.523 |
| total | | 100 |



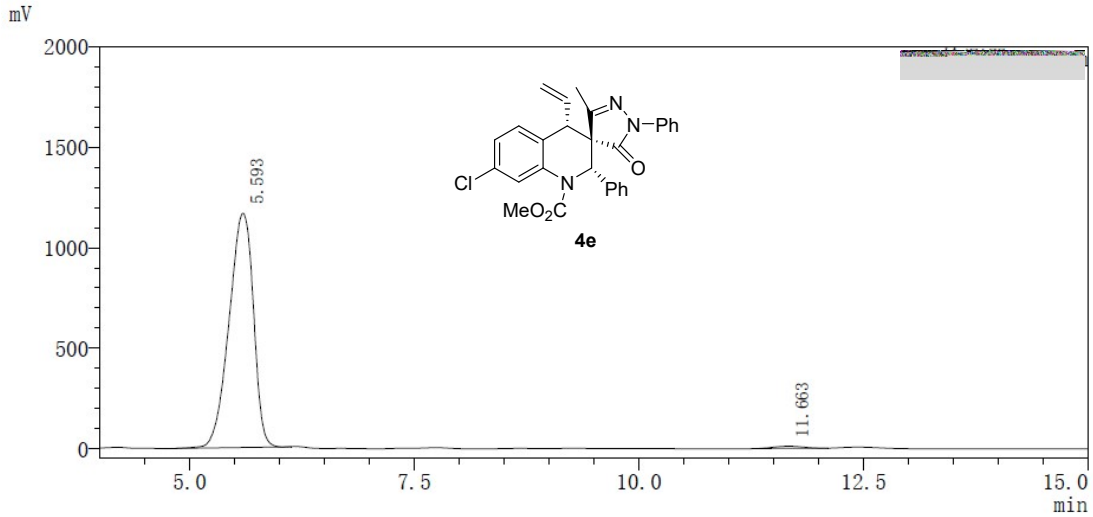

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.579 | 95.650 |
| 2 | 10.412 | 4.350 |
| total | | 100 |



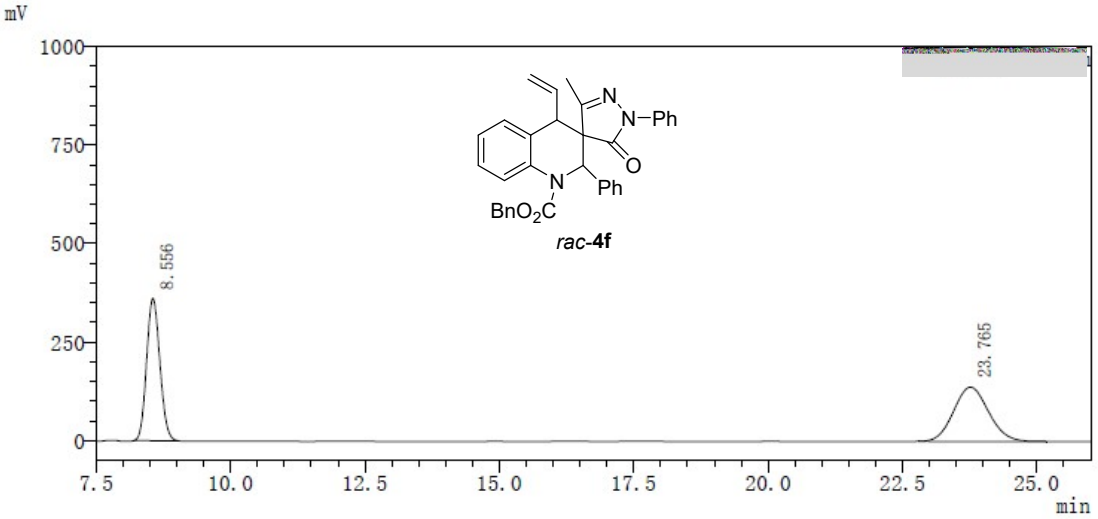

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 5.658 | 49.942 |
| 2 | 12.016 | 50.058 |
| total | | 100 |



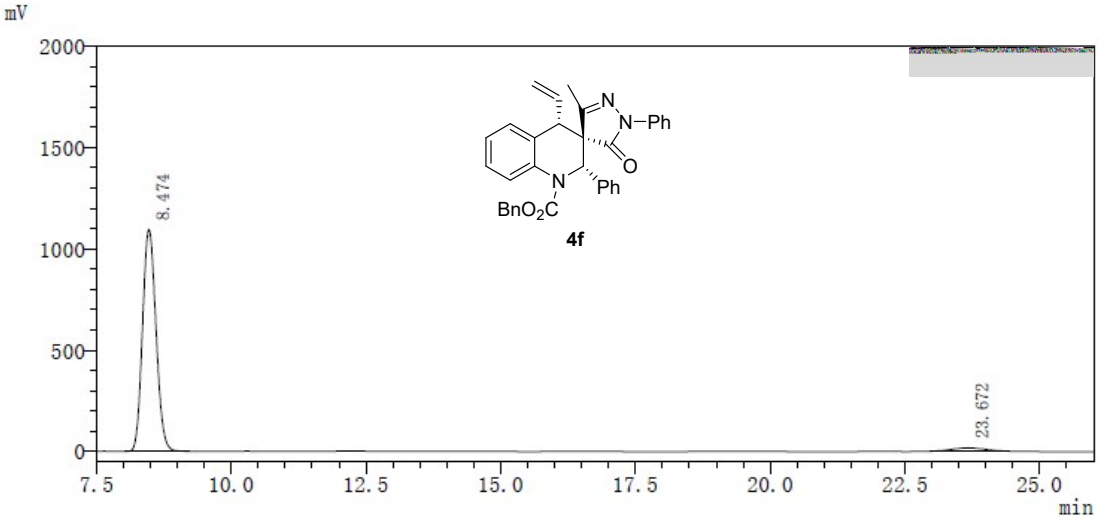

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 5.593 | 99.063 |
| 2 | 11.663 | 0.937 |
| total | | 100 |



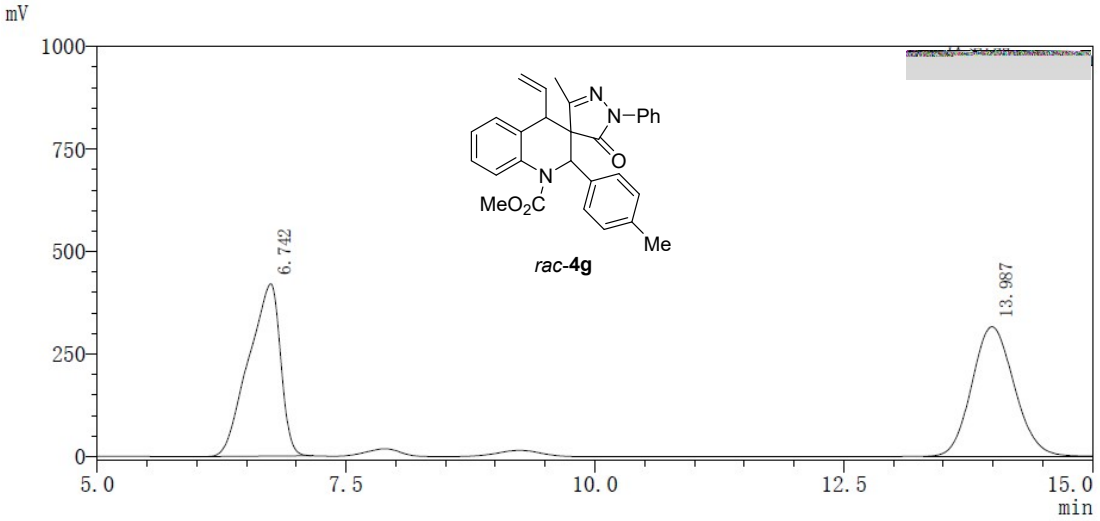

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.556 | 49.795 |
| 2 | 22.765 | 50.205 |
| total | | 100 |




Discloser A 254 nm

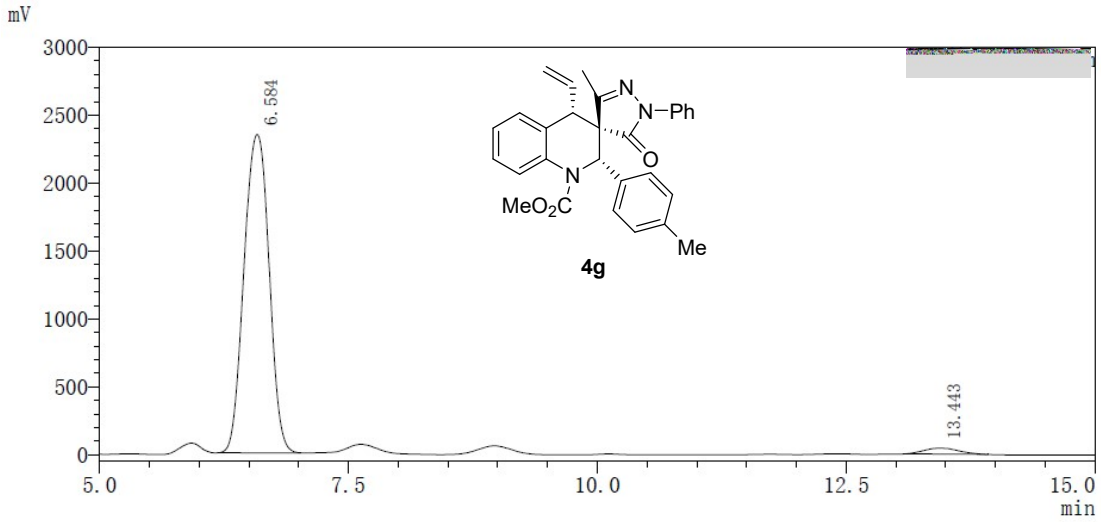
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.474 | 96.429 |
| 2 | 23.672 | 3.571 |
| total | | 100 |




*rac*-**4g**

Discloser A 254 nm

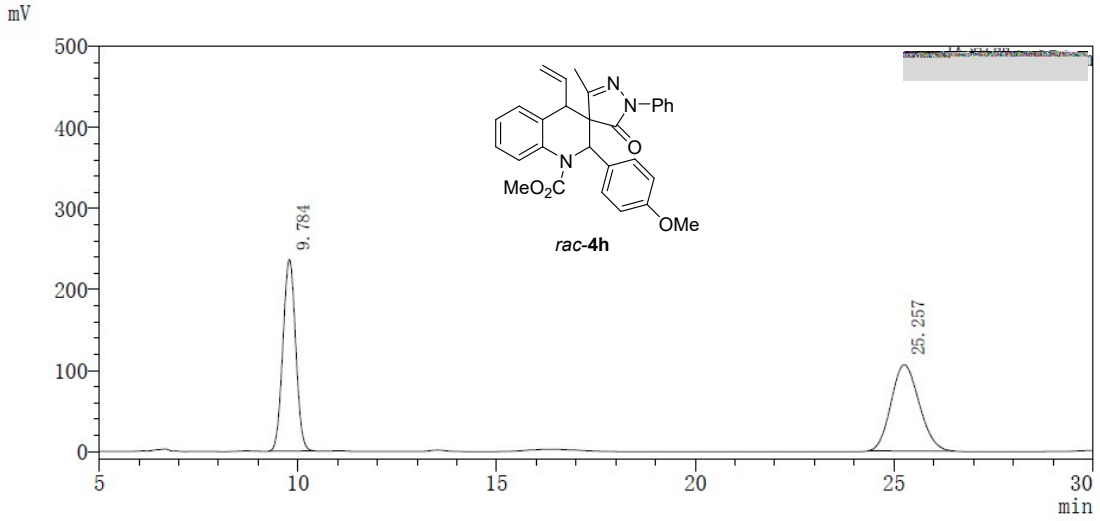
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.742 | 49.974 |
| 2 | 13.987 | 50.026 |
| total | | 100 |




**4g**

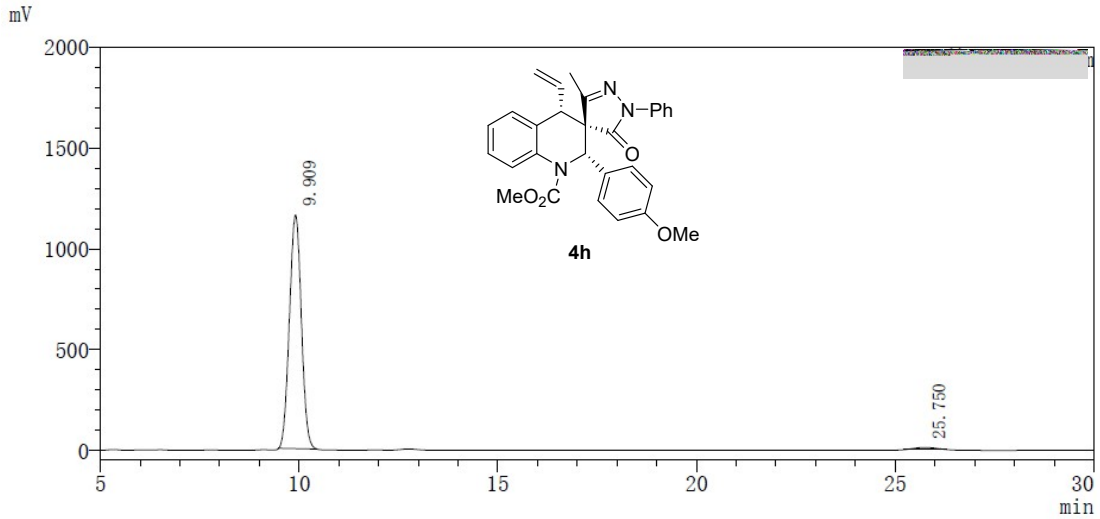
Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.584 | 97.522 |
| 2 | 13.443 | 2.478 |
| total | | 100 |



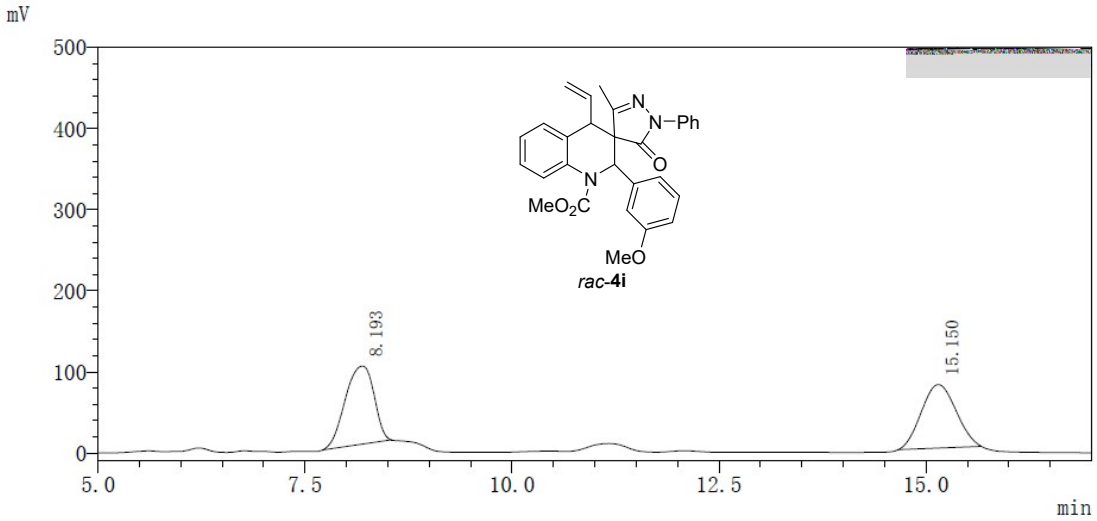

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.784 | 50.278 |
| 2 | 25.257 | 49.722 |
| total | | 100 |



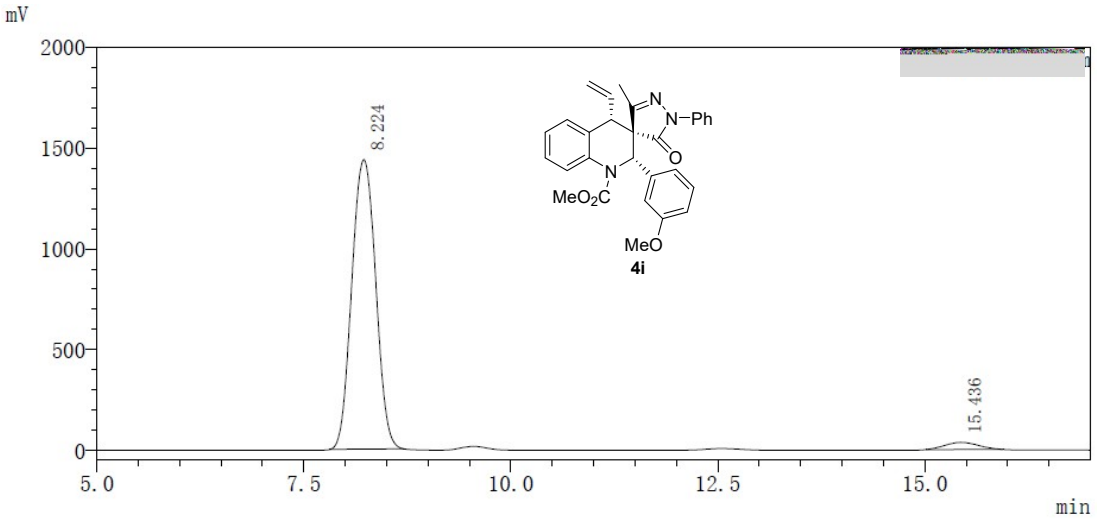

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.909 | 98.515 |
| 2 | 25.750 | 1.485 |
| total | | 100 |



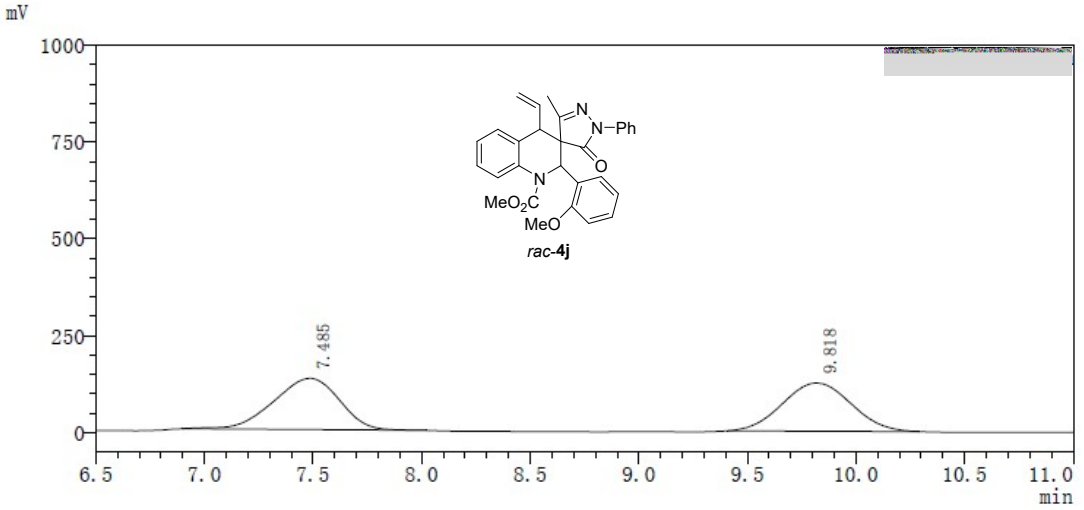

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.193 | 50.588 |
| 2 | 15.150 | 49.412 |
| total | | 100 |



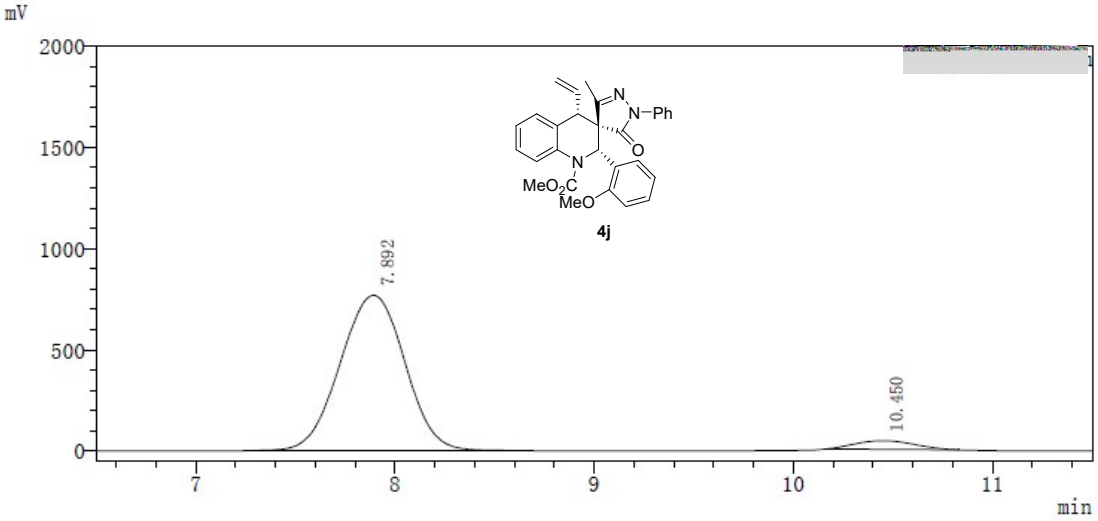

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.224 | 96.700 |
| 2 | 15.436 | 3.300 |
| total | | 100 |



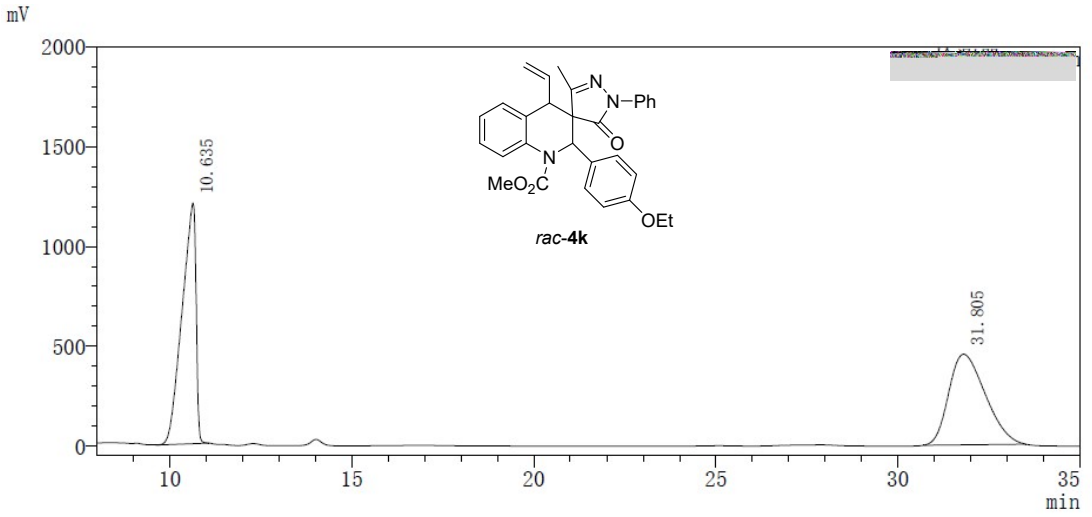

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.485 | 50.493 |
| 2 | 9.818 | 49.507 |
| total | | 100 |



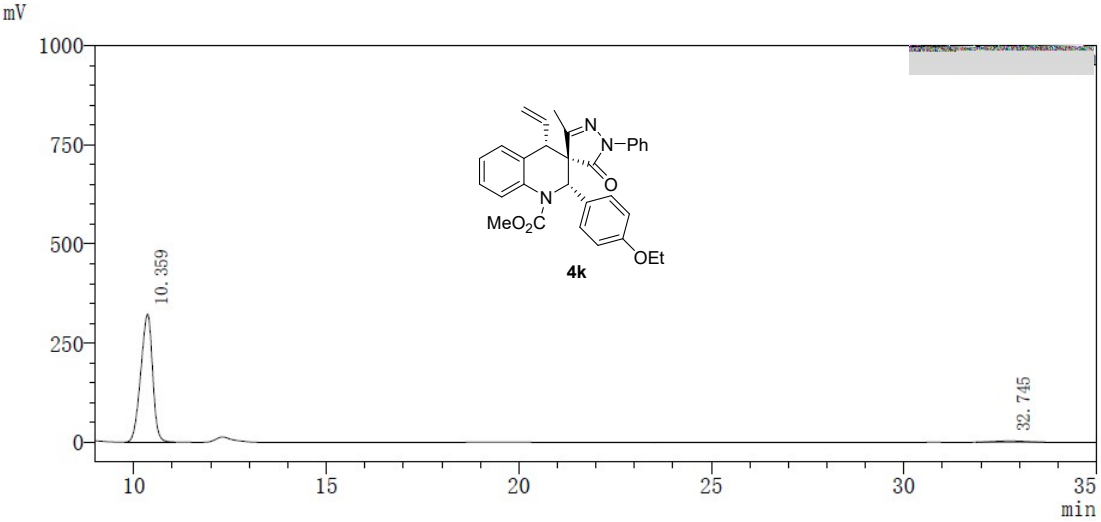

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.892 | 95.042 |
| 2 | 10.450 | 4.958 |
| total | | 100 |



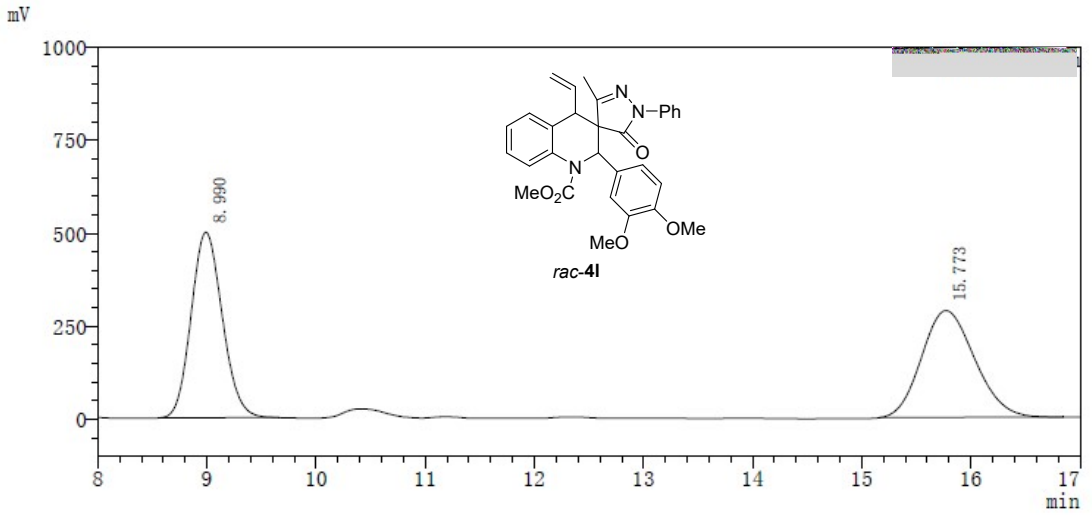

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 10.635 | 50.355 |
| 2 | 31.805 | 49.645 |
| total | | 100 |



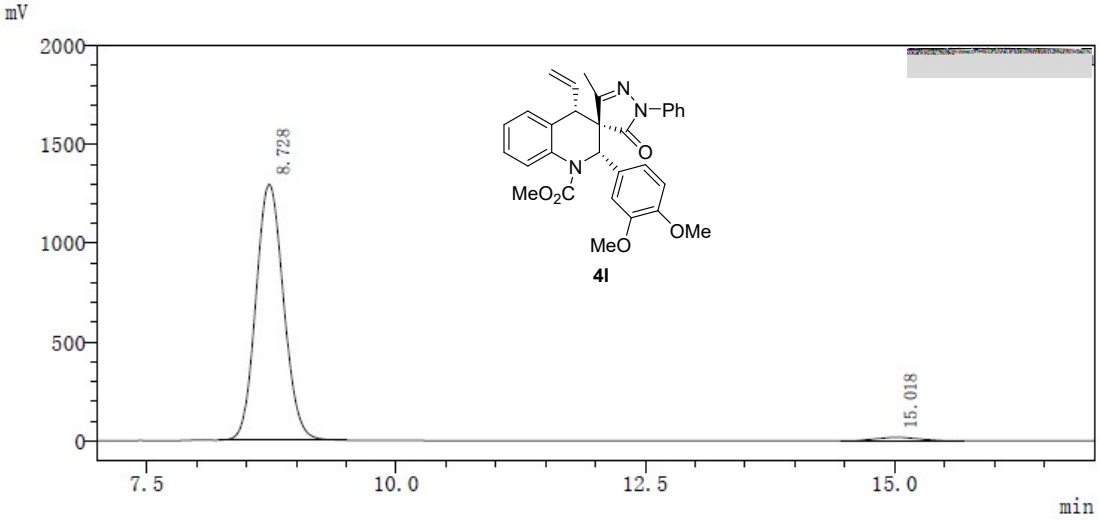

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 10.359 | 97.393 |
| 2 | 32.745 | 2.607 |
| total | | 100 |



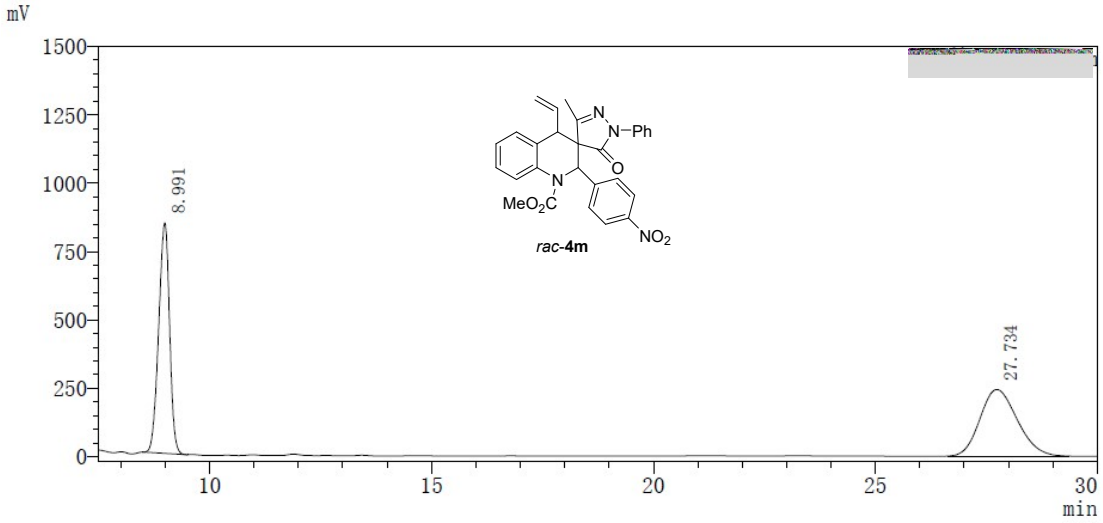

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.990 | 50.519 |
| 2 | 15.773 | 49.481 |
| total | | 100 |



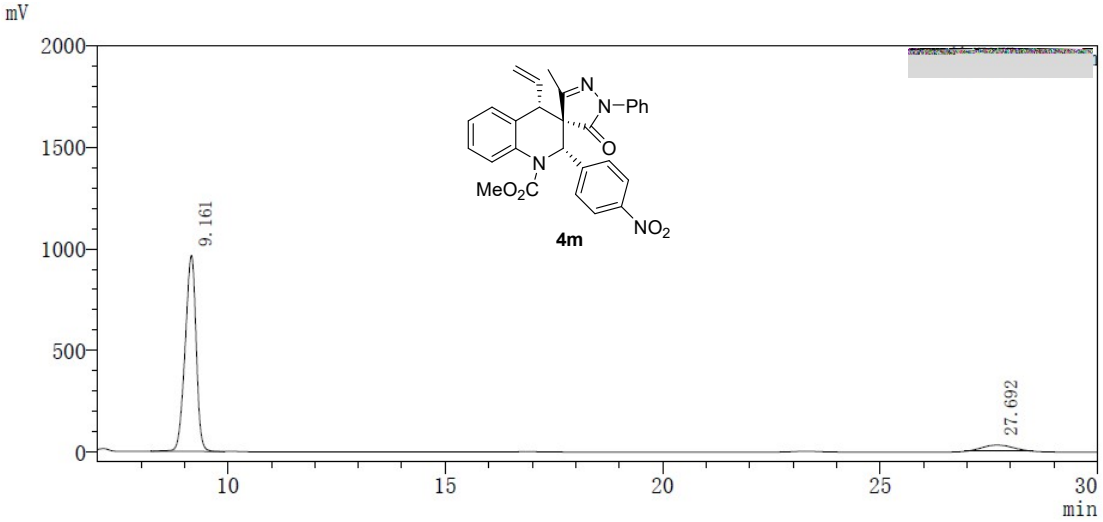

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.728 | 97.930 |
| 2 | 15.018 | 2.070 |
| total | | 100 |



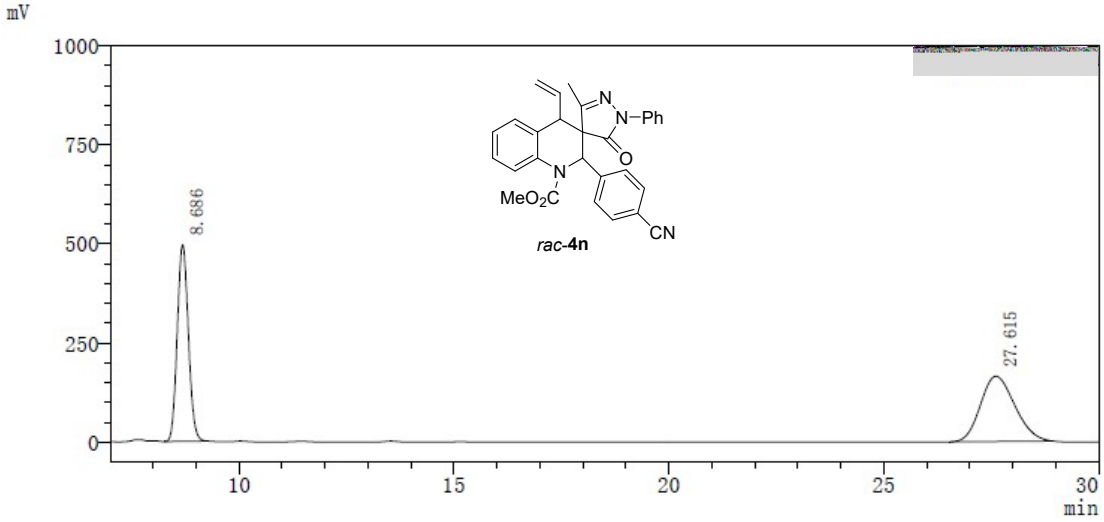

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.991 | 50.274 |
| 2 | 27.734 | 49.726 |
| total | | 100 |



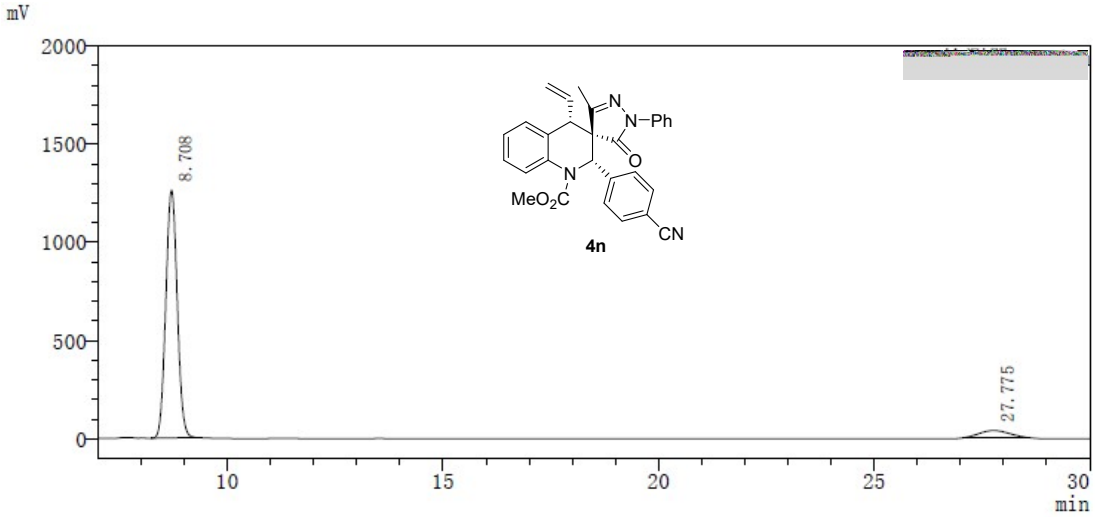

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.161 | 91.969 |
| 2 | 27.692 | 8.031 |
| total | | 100 |



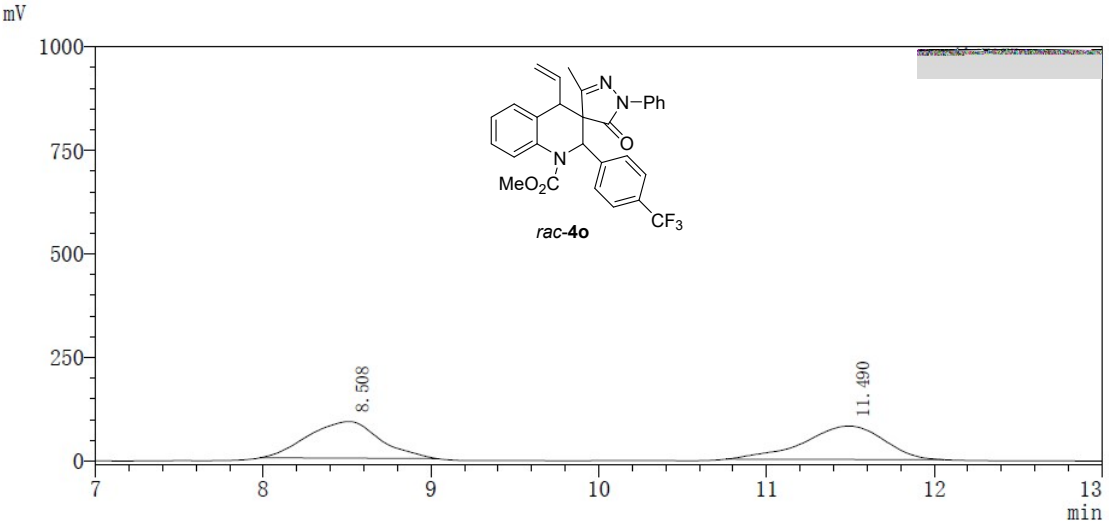

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.686 | 49.328 |
| 2 | 27.615 | 50.672 |
| total | | 100 |



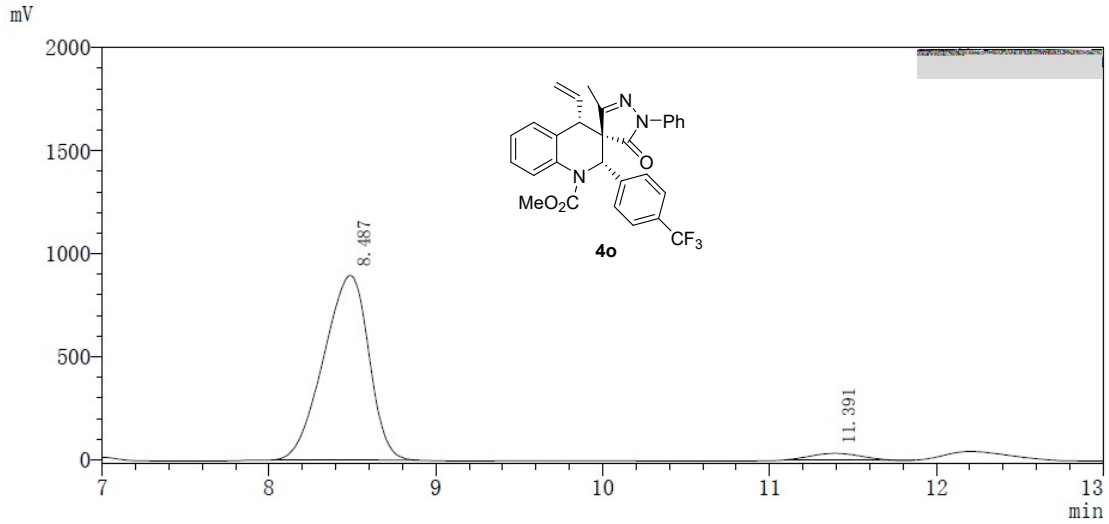

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.708 | 92.957 |
| 2 | 27.775 | 7.043 |
| total | | 100 |



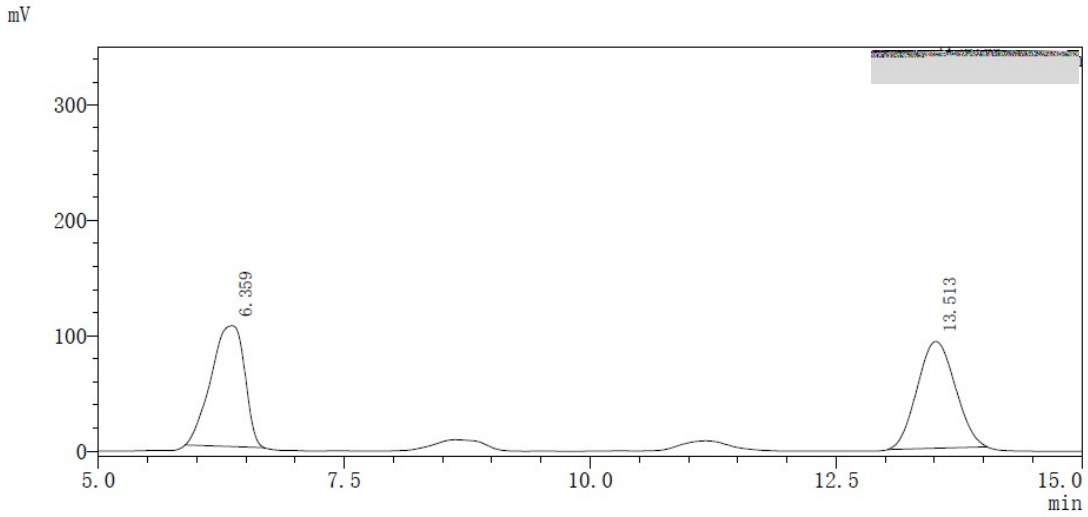

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.508 | 49.537 |
| 2 | 11.490 | 50.463 |
| total | | 100 |



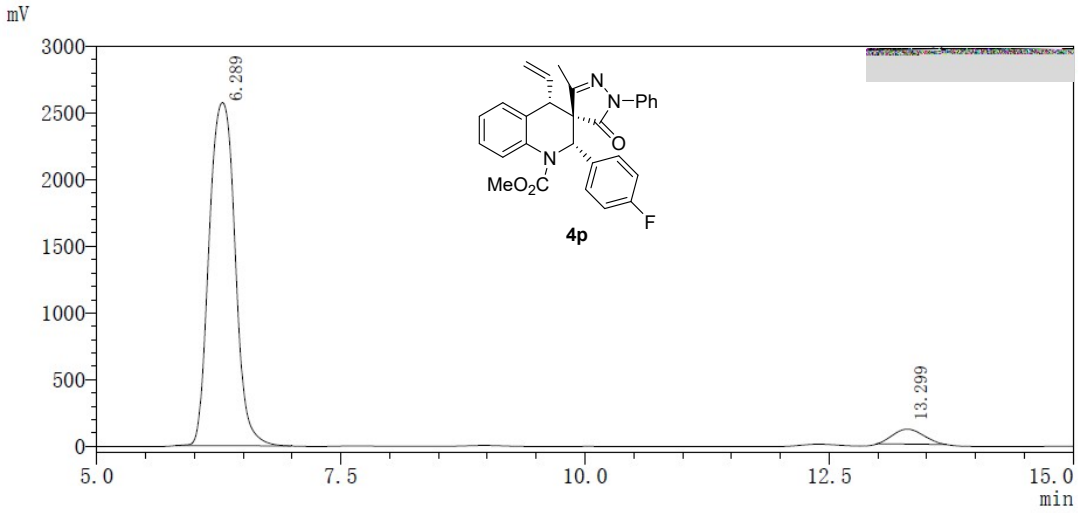

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.487 | 96.338 |
| 2 | 11.391 | 3.662 |
| total | | 100 |



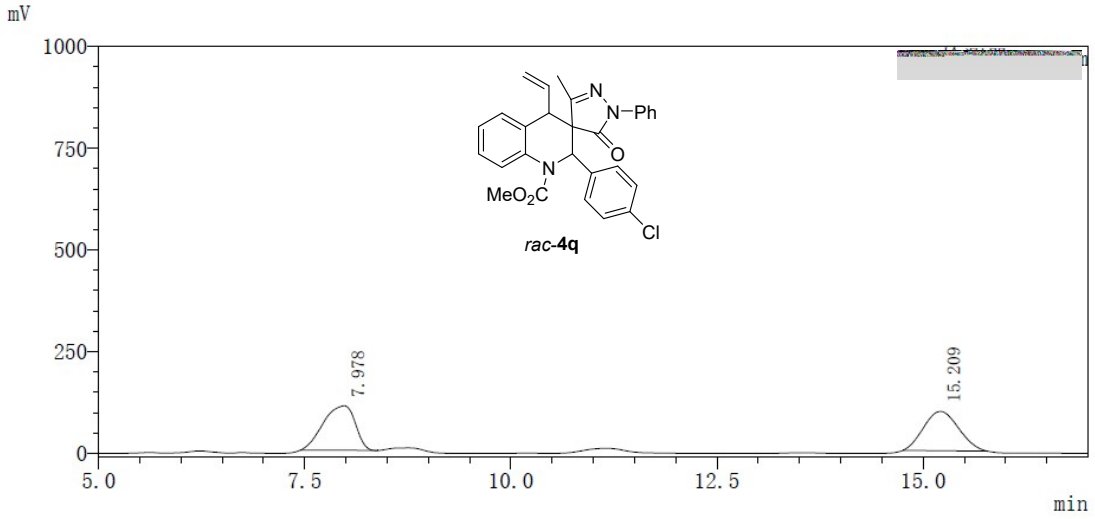

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.359 | 49.939 |
| 2 | 13.513 | 50.061 |
| total | | 100 |



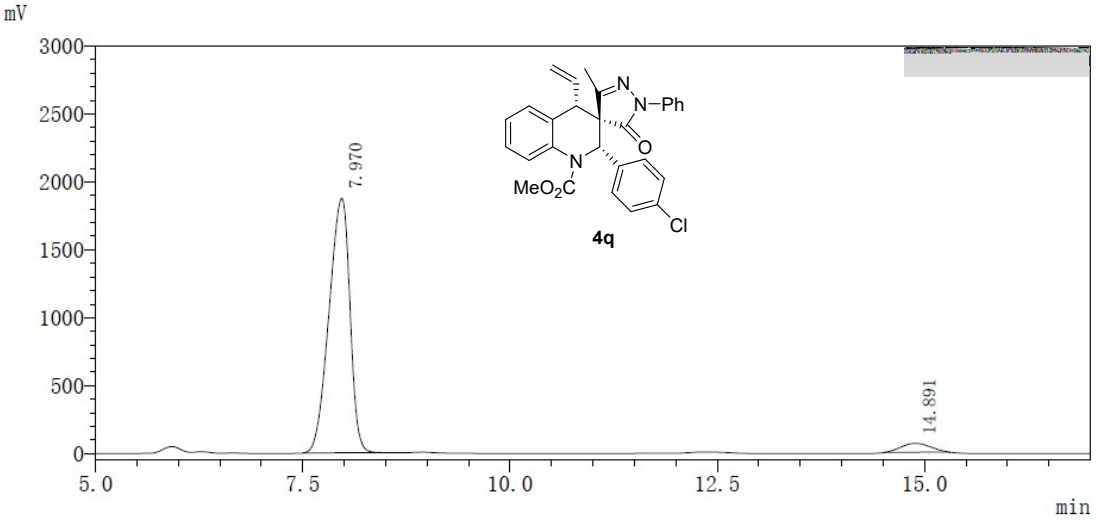

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.289 | 95.088 |
| 2 | 13.299 | 4.912 |
| total | | 100 |



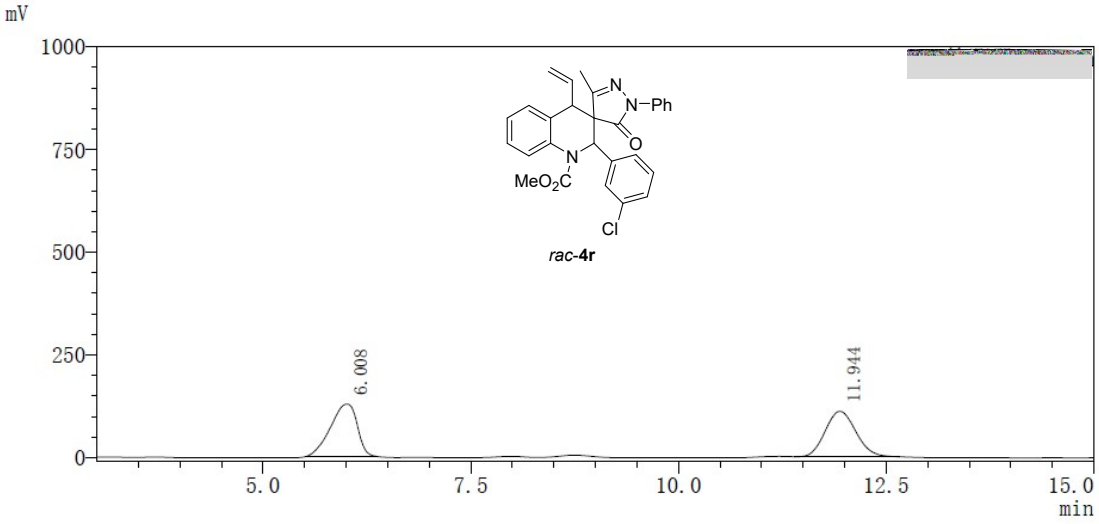

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.978 | 50.913 |
| 2 | 15.209 | 49.087 |
| total | | 100 |



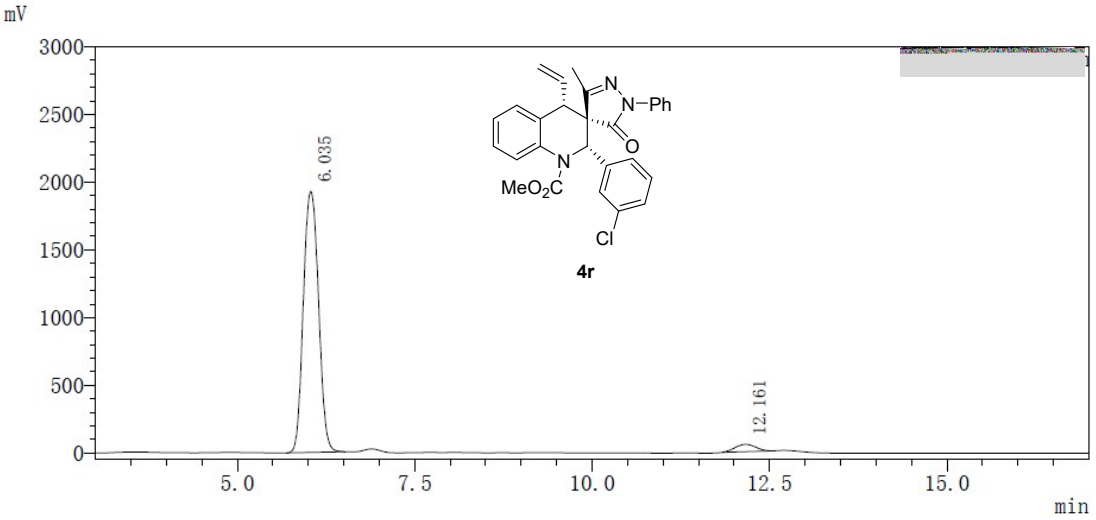

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.970 | 95.295 |
| 2 | 14.891 | 4.705 |
| total | | 100 |



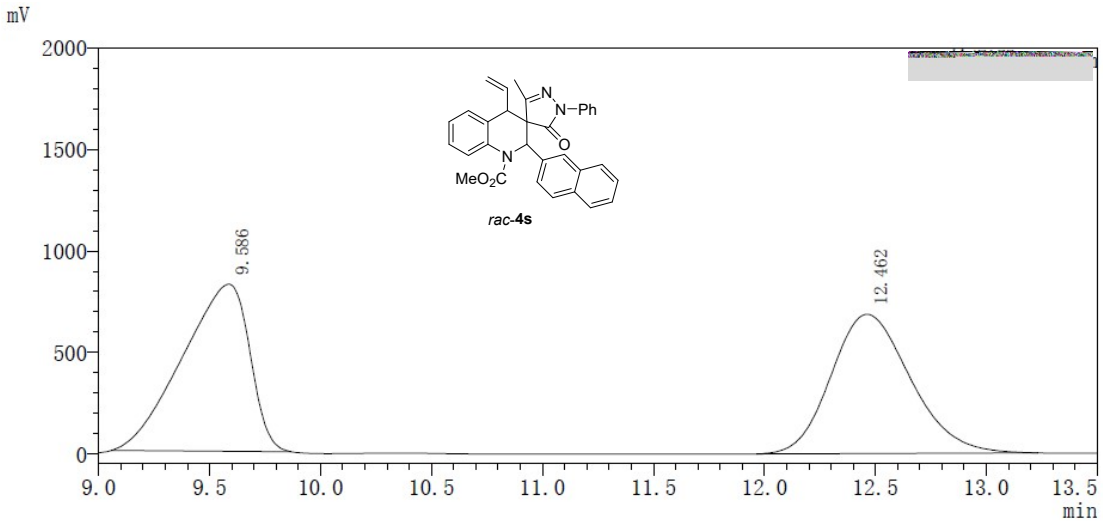

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.008 | 49.821 |
| 2 | 11.944 | 50.179 |
| total | | 100 |



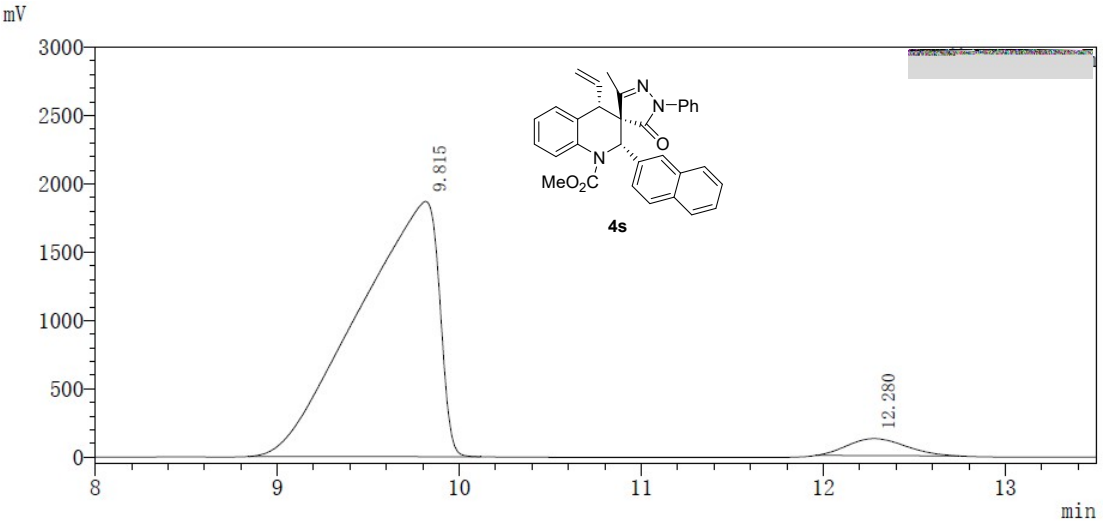

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.035 | 96.431 |
| 2 | 12.161 | 3.569 |
| total | | 100 |



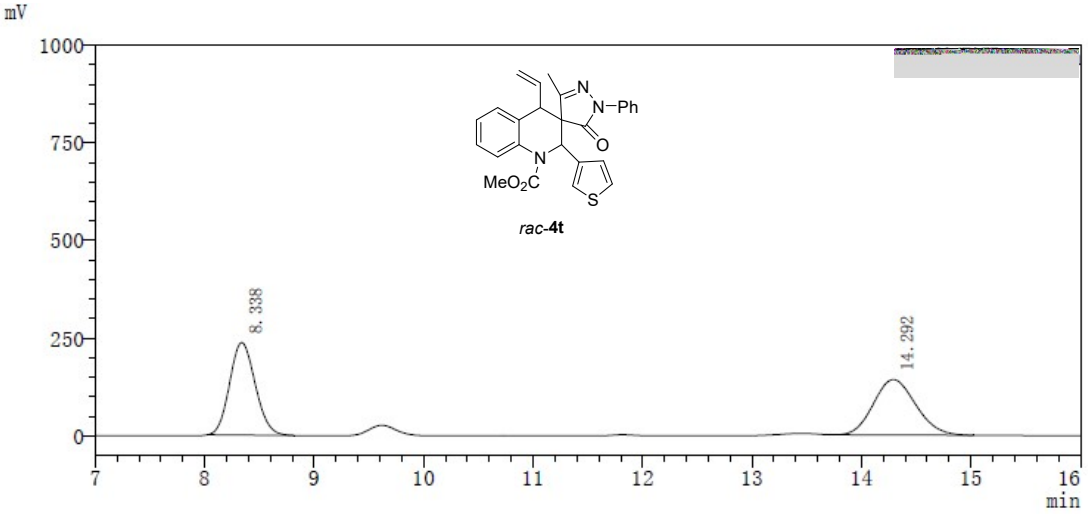

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.586 | 50.463 |
| 2 | 12.462 | 49.537 |
| total | | 100 |



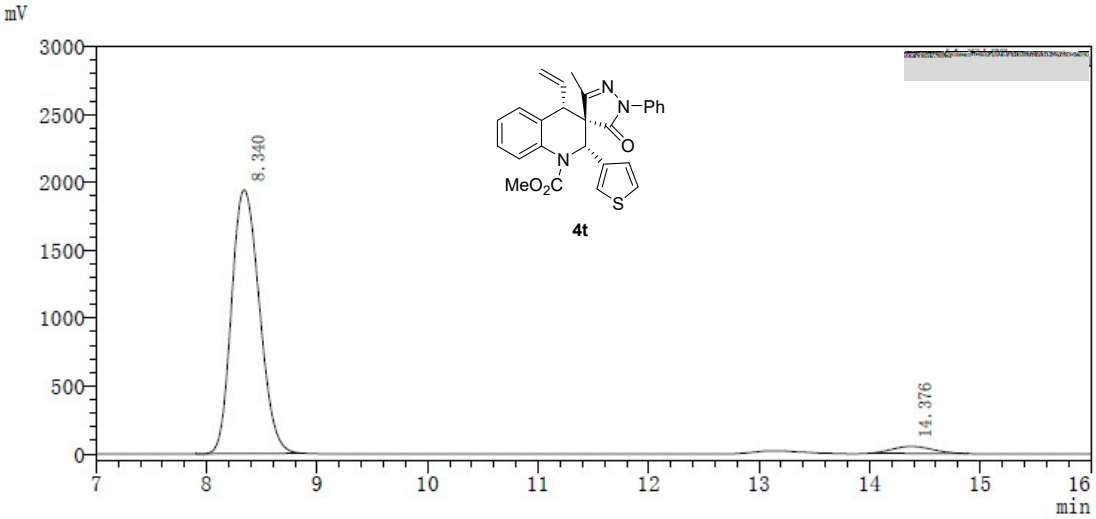

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.815 | 95.382 |
| 2 | 12.280 | 4.618 |
| total | | 100 |



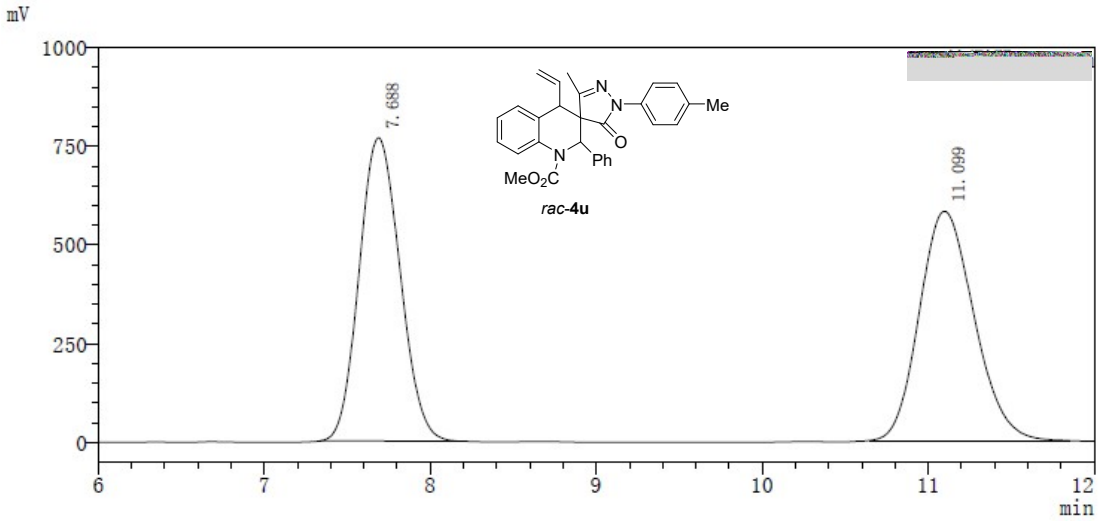

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.338 | 50.377 |
| 2 | 14.292 | 49.623 |
| total | | 100 |



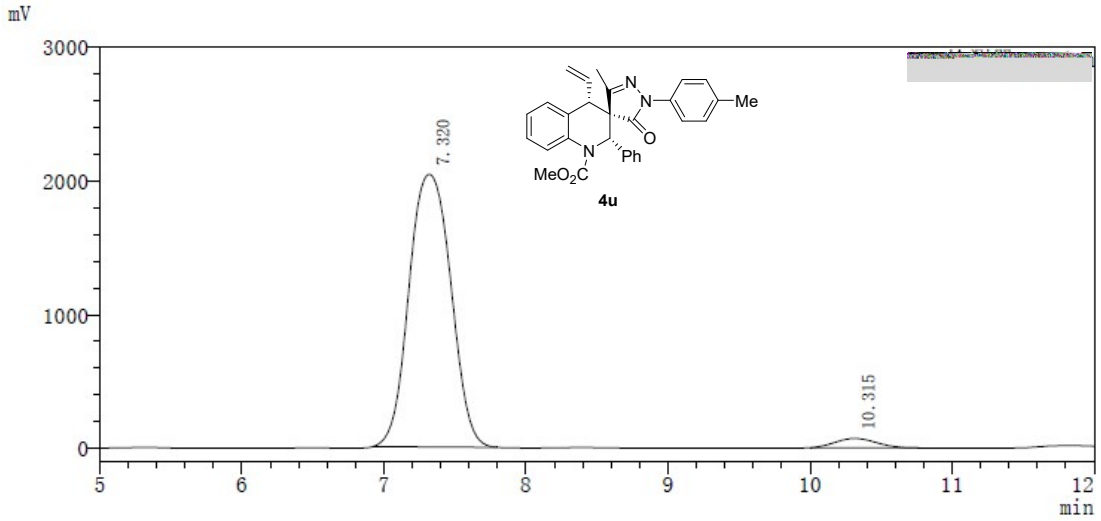

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 8.340 | 96.364 |
| 2 | 14.376 | 3.636 |
| total | | 100 |



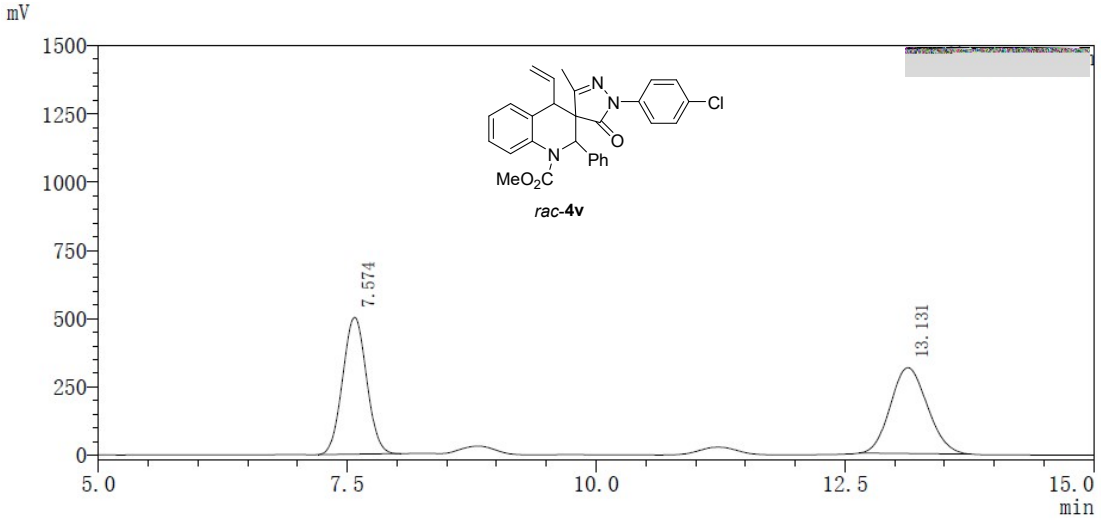

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.688 | 49.765 |
| 2 | 11.099 | 50.235 |
| total | | 100 |



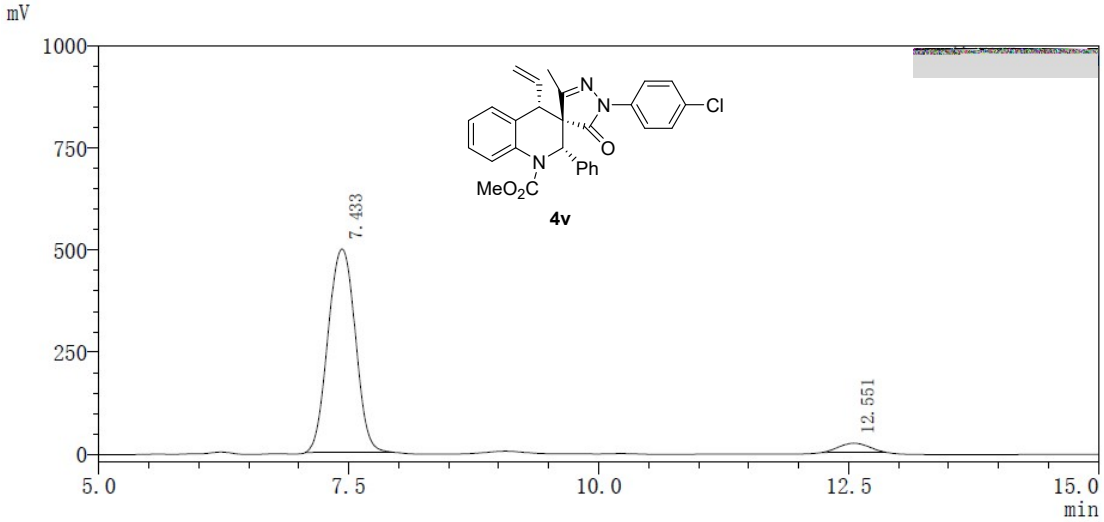

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.320 | 96.717 |
| 2 | 10.315 | 3.283 |
| total | | 100 |



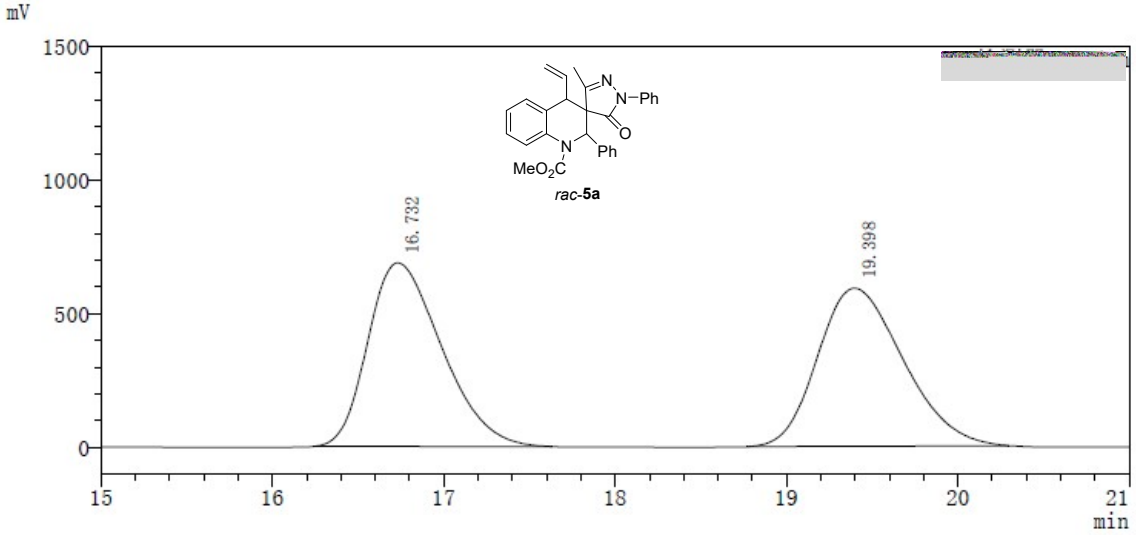

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.574 | 50.806 |
| 2 | 13.131 | 49.184 |
| total | | 100 |



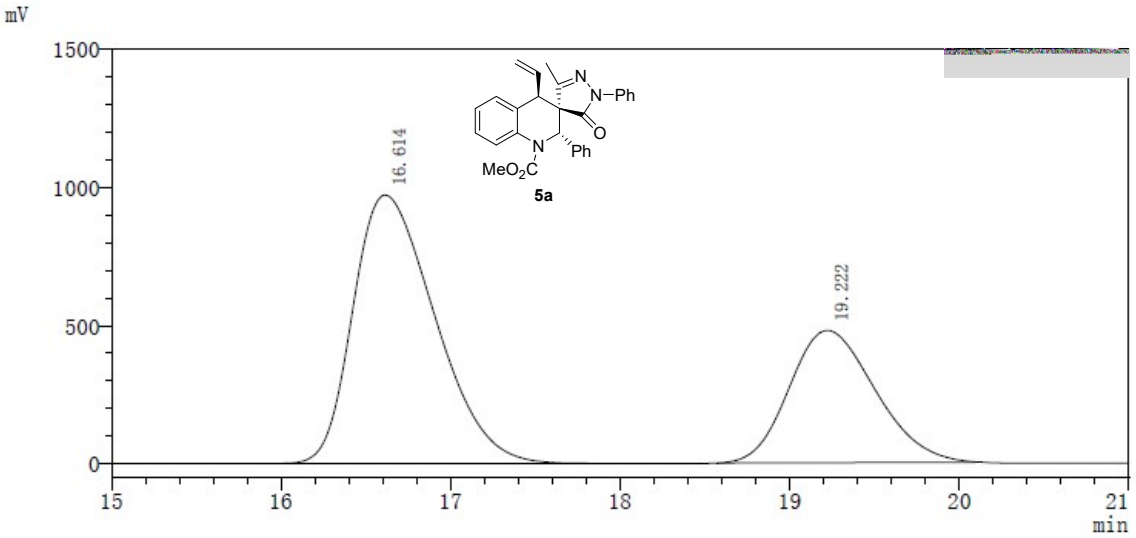

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 7.433 | 95.351 |
| 2 | 12.551 | 4.649 |
| total | | 100 |



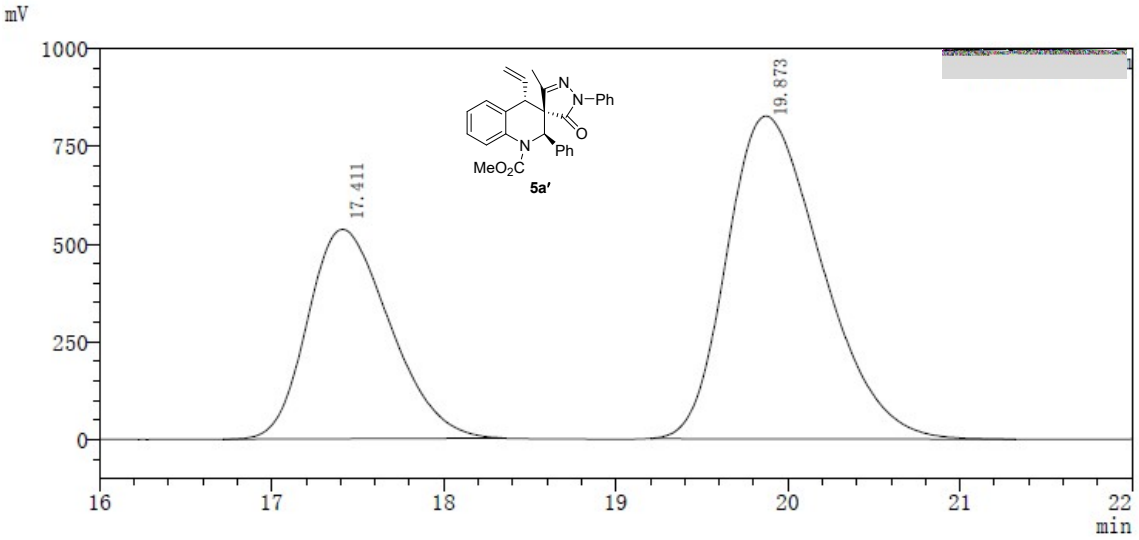

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 16.732 | 50.035 |
| 2 | 19.398 | 49.965 |
| total | | 100 |



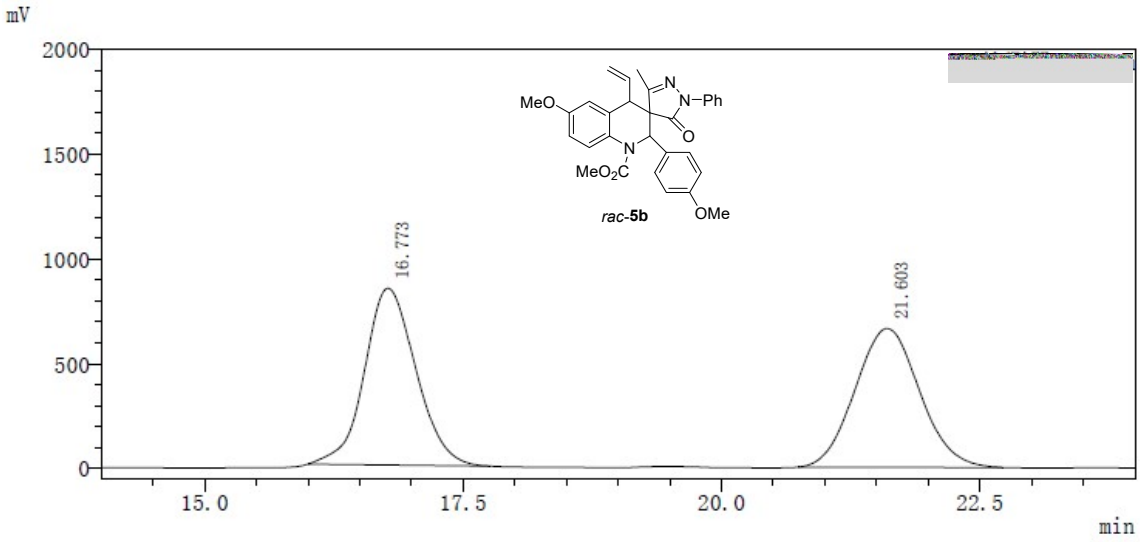

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 16.614 | 65.894 |
| 2 | 19.222 | 34.106 |
| total | | 100 |



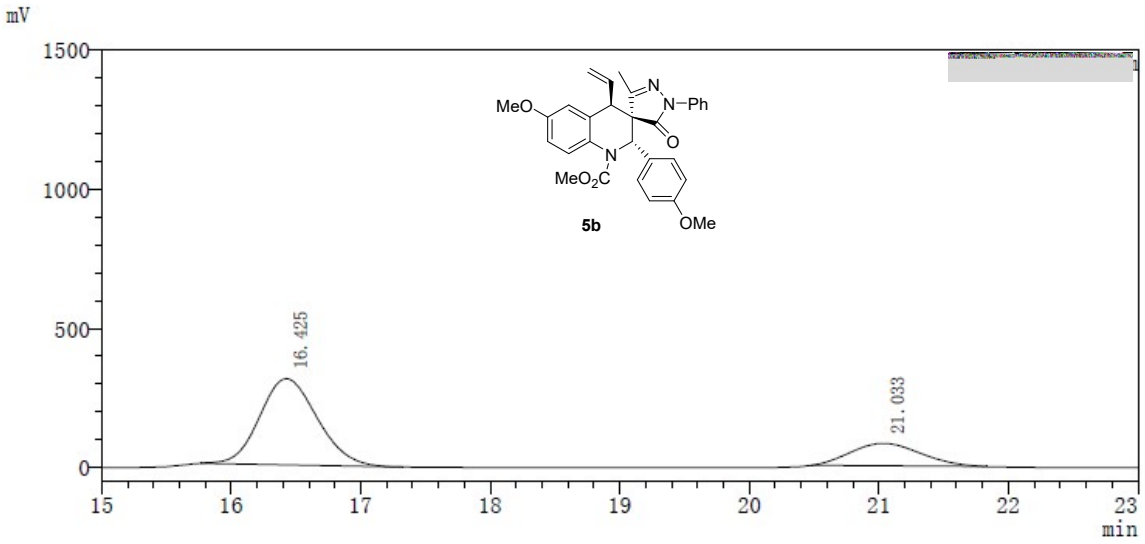

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 17.411 | 36.014 |
| 2 | 19.873 | 63.986 |
| total | | 100 |



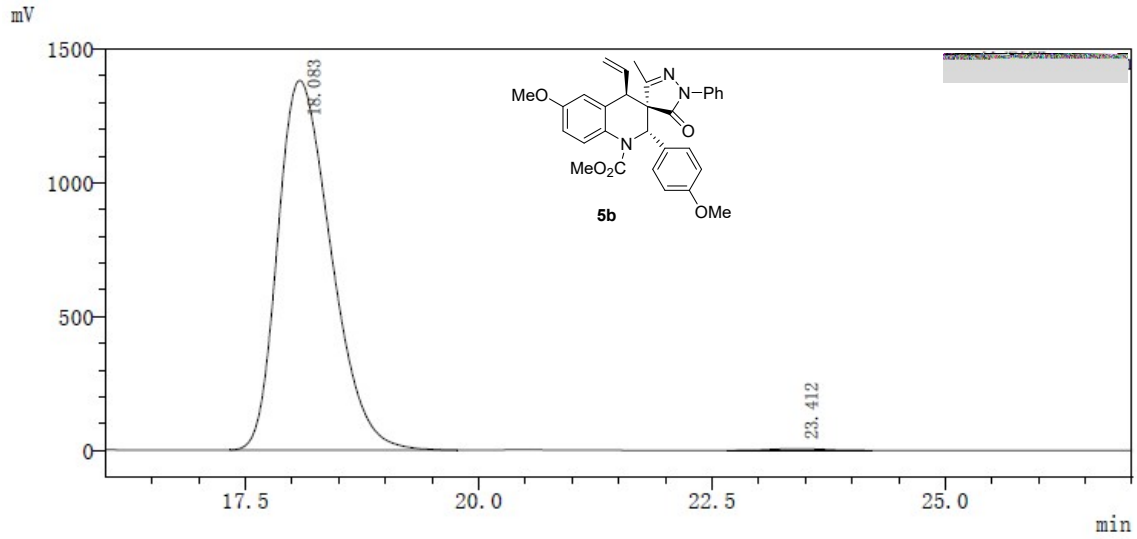

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 16.773 | 50.392 |
| 2 | 21.603 | 49.608 |
| total | | 100 |



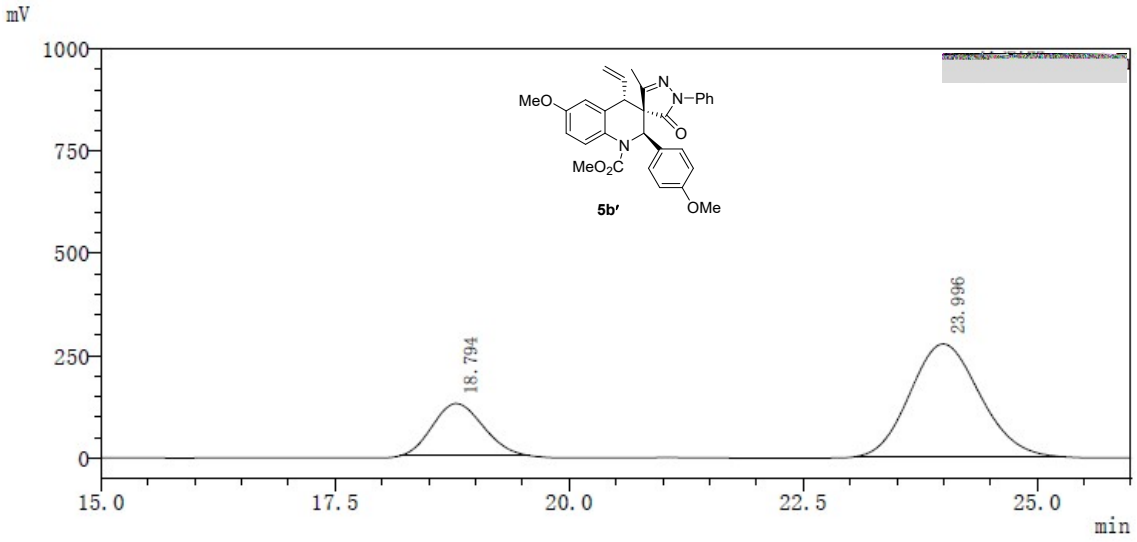

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 16.425 | 75.932 |
| 2 | 21.033 | 24.068 |
| total | | 100 |



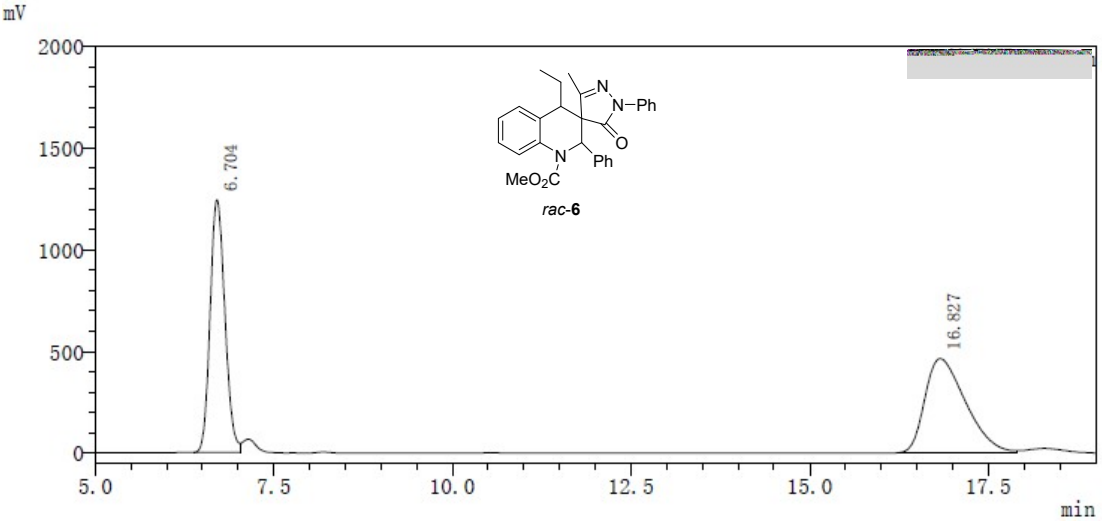

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 18.083 | 99.556 |
| 2 | 23.412 | 0.444 |
| total | | 100 |



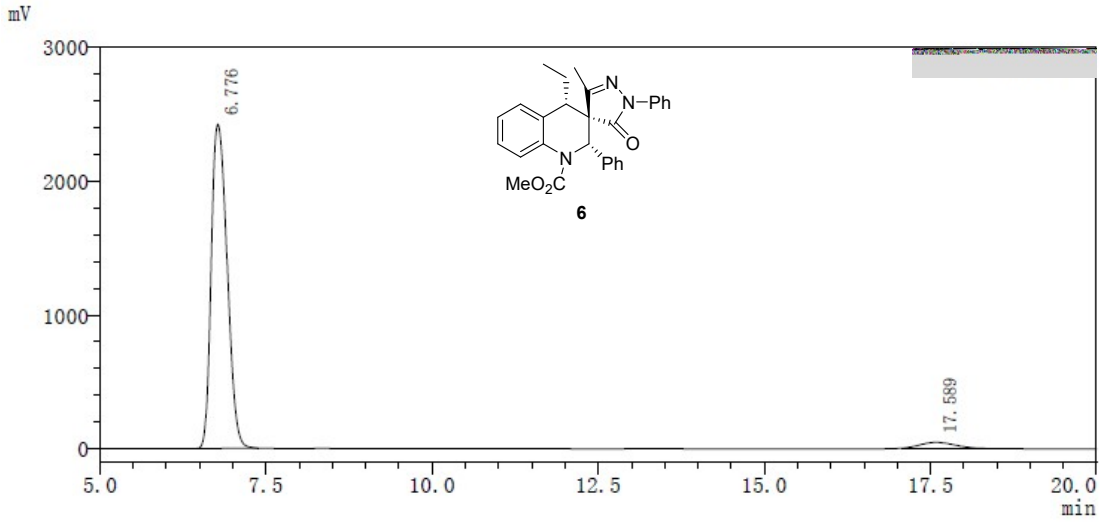

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 18.794 | 25.048 |
| 2 | 23.996 | 74.952 |
| total | | 100 |



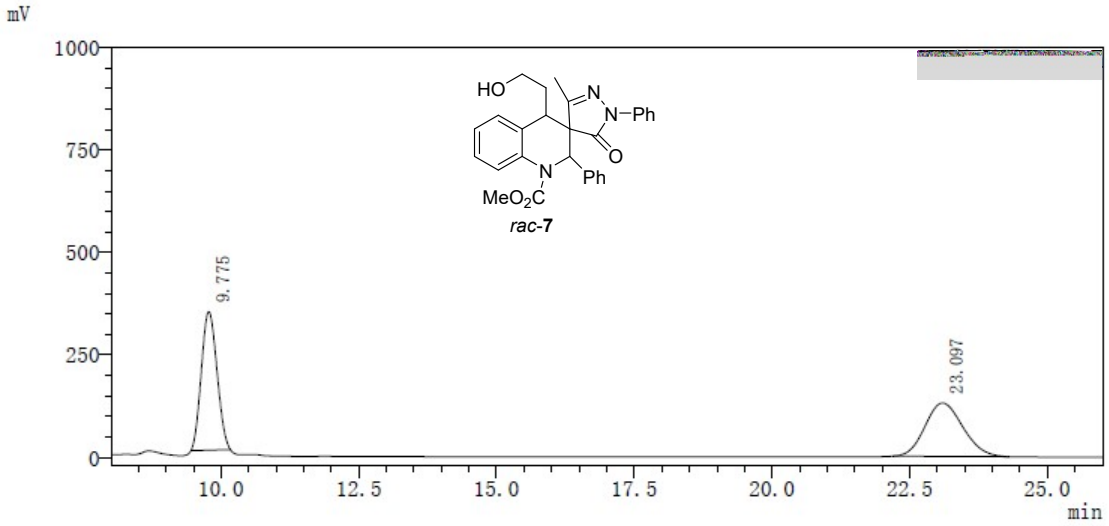

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.704 | 49.292 |
| 2 | 16.827 | 50.708 |
| total | | 100 |



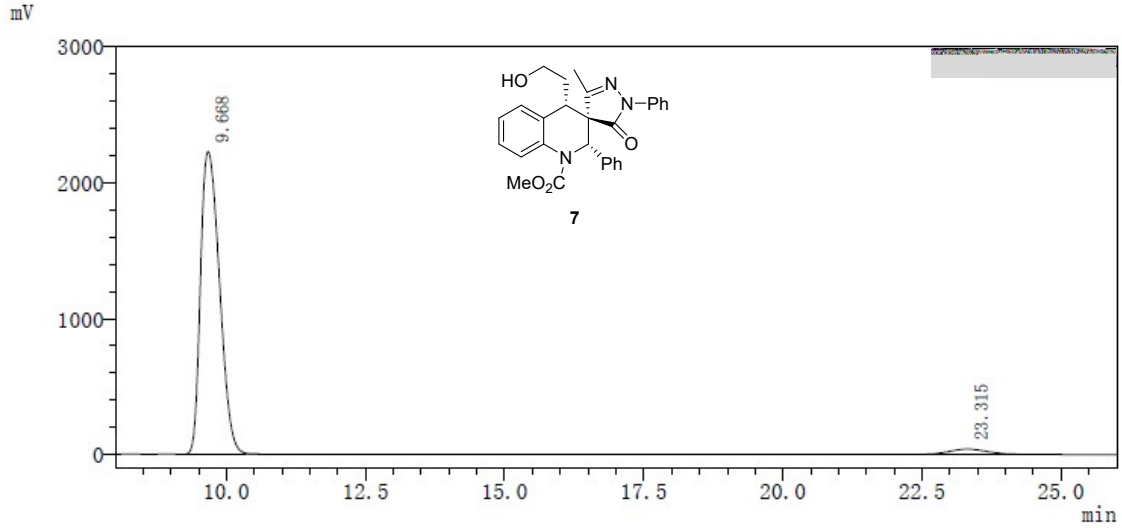

Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 6.776 | 96.191 |
| 2 | 17.589 | 3.809 |
| total | | 100 |




Discloser A 254 nm

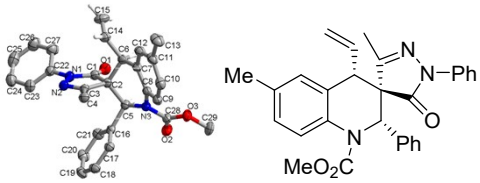
| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.775 | 51.750 |
| 2 | 23.097 | 48.250 |
| total | | 100 |




Discloser A 254 nm

| Peak | Reten time (min) | Area(%) |
|---|---|---|
| 1 | 9.668 | 96.682 |
| 2 | 23.315 | 3.318 |
| total | | 100 |

## 7. X-ray crystal structure

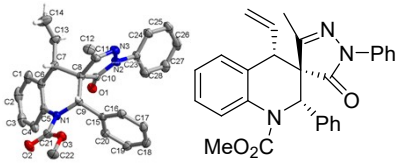



Crystal structure of **3c (CCDC: 2132601)**

Table S6 Crystal data and structure refinement for **3c**

| | |
|---|---|
| Identification code | 2132601 |
| Empirical formula | $C_{29}H_{27}N_3O_3$ |
| Formula weight | 465.53 |
| Temperature/K | 293(2) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.75496(19) |
| b/Å | 13.6686(3) |
| c/Å | 18.7757(4) |
| α/° | 90 |

| | |
|---|---|
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2503.48(8) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.235 |
| μ/mm$^{-1}$ | 0.648 |
| F(000) | 984.0 |
| Crystal size/mm$^3$ | 0.16 × 0.1 × 0.09 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 8 to 141.926 |
| Index ranges | -11 ≤ h ≤ 5, -12 ≤ k ≤ 16, -22 ≤ l ≤ 21 |
| Reflections collected | 9409 |
| Independent reflections | 4720 [$R_{int}$ = 0.0319, $R_{sigma}$ = 0.0437] |
| Data/restraints/parameters | 4720/0/320 |
| Goodness-of-fit on F$^2$ | 1.025 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0474, $wR_2$ = 0.1211 |
| Final R indexes [all data] | $R_1$ = 0.0622, $wR_2$ = 0.1354 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.13/-0.13 |

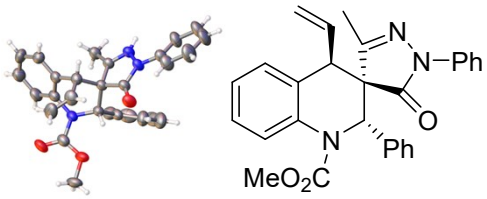



Crystal structure of **4a (CCDC: 2132611)**

Table S7 Crystal data and structure refinement for **4a**

| | |
|---|---|
| Identification code | 2132611 |
| Empirical formula | $C_{28}H_{25}N_3O_3$ |
| Formula weight | 451.51 |
| Temperature/K | 293(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 12.6477(6) |
| b/Å | 12.7165(3) |
| c/Å | 19.2801(10) |
| α/° | 90 |
| β/° | 130.968(8) |
| γ/° | 90 |
| Volume/Å$^3$ | 2341.4(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.281 |

| | |
|---|---|
| μ/mm$^{-1}$ | 0.677 |
| F(000) | 952.0 |
| Crystal size/mm$^3$ | 0.15 × 0.1 × 0.08 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.234 to 134.148 |
| Index ranges | -15 ≤ h ≤ 15, -15 ≤ k ≤ 11, -23 ≤ l ≤ 20 |
| Reflections collected | 11047 |
| Independent reflections | 4178 [$R_{int}$ = 0.0320, $R_{sigma}$ = 0.0351] |
| Data/restraints/parameters | 4178/0/310 |
| Goodness-of-fit on $F^2$ | 1.030 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0460, $wR_2$ = 0.1212 |
| Final R indexes [all data] | $R_1$ = 0.0584, $wR_2$ = 0.1326 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.25/-0.19 |

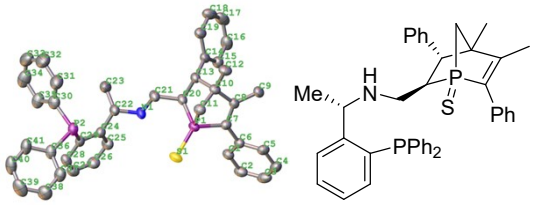



Relative configuration of **5b** and **5b' (CCDC: 2132592)**

Table S8 Crystal data and structure refinement for **5b(5b')**

| | |
|---|---|
| Identification code | 2132592 |
| Empirical formula | $C_{28}H_{24}N_3O_3$ |
| Formula weight | 450.50 |
| Temperature/K | 298.0 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| a/Å | 8.647(3) |
| b/Å | 20.509(7) |
| c/Å | 8.8540(18) |
| α/° | 90 |
| β/° | 101.501(13) |
| γ/° | 90 |
| Volume/Å$^3$ | 1538.7(8) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 0.972 |
| μ/mm$^{-1}$ | 0.064 |
| F(000) | 474.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |

| | |
|---|---|
| 2Θ range for data collection/° | 3.972 to 55.04 |
| Index ranges | $-11 \le h \le 11, -26 \le k \le 26, -10 \le l \le 11$ |
| Reflections collected | 25970 |
| Independent reflections | 7033 [$R_{int}$ = 0.0321, $R_{sigma}$ = 0.0291] |
| Data/restraints/parameters | 7033/1/310 |
| Goodness-of-fit on $F^2$ | 1.176 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0831, $wR_2$ = 0.2058 |
| Final R indexes [all data] | $R_1$ = 0.1035, $wR_2$ = 0.2212 |
| Largest diff. peak/hole / e $Å^{-3}$ | 1.17/-0.79 |




Crystal structure of **Y1' (CCDC: 2150889)**

Table S9 Crystal data and structure refinement for **Y1'**

| | |
|---|---|
| Identification code | 2150889 |
| Empirical formula | $C_{41}H_{41}NP_2S$ |
| Formula weight | 235.23 |
| Temperature/K | 200.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| a/Å | 8.80910(10) |
| b/Å | 14.29220(10) |
| c/Å | 15.6275(2) |
| α/° | 90 |
| β/° | 97.2740(10) |
| γ/° | 90 |
| Volume/$Å^3$ | 1951.69(4) |
| Z | 8 |
| $\rho_{calc}g/cm^3$ | 1.601 |
| $\mu/mm^{-1}$ | 4.231 |
| F(000) | 976.0 |
| Crystal size/$mm^3$ | 0.3 × 0.1 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 5.702 to 147.44 |
| Index ranges | $-10 \le h \le 10, -15 \le k \le 17, -18 \le l \le 19$ |
| Reflections collected | 20108 |
| Independent reflections | 6966 [$R_{int}$ = 0.0321, $R_{sigma}$ = 0.0346] |

| | |
|---|---|
| Data/restraints/parameters | 6966/1/409 |
| Goodness-of-fit on $F^2$ | 1.055 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0411$, $wR_2 = 0.1134$ |
| Final R indexes [all data] | $R_1 = 0.0436$, $wR_2 = 0.1146$ |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.37/-0.29 |
| Flack parameter | 0.036(9) |