# Supporting Information

## Synthesis of Axially Chiral Biaryl-2-Carboxamides through Pd(II)-Catalyzed Atroposelective C−H Olefination

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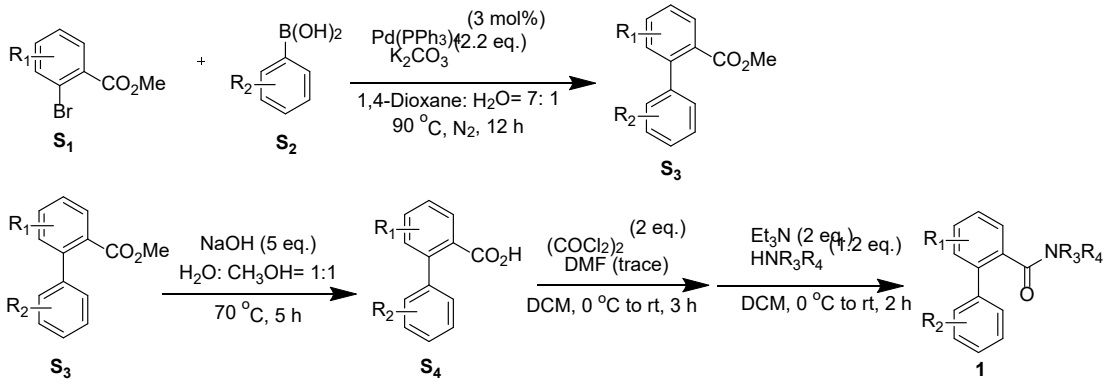
# 1. General Information

All the materials and solvents were purchased from commercial suppliers and used without additional purification. $Pd(OAc)_2$ was purchased from Laajoo (China), NMR spectra were recorded on a Bruke Avance operating for $^{1}H$ NMR at 400 MHz, $^{13}C$ NMR at 101 MHz, $^{19}F$ NMR at 376 MHz using TMS as internal standard. The peaks were internally referenced to $CDCl_3$ (7.26 ppm) or residual undeuterated solvent signal of $CDCl_3$ (77.16 ppm for $^{13}C$ NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument. The ee value was determined on Shimadzu HPLC using CHIRALPAK or Guangzhou FLM Scientific Instrument column with hexane and 2-propanol as eluent, Wavelength = 254 nm.

# 2.Experiment Details and Characterization Data

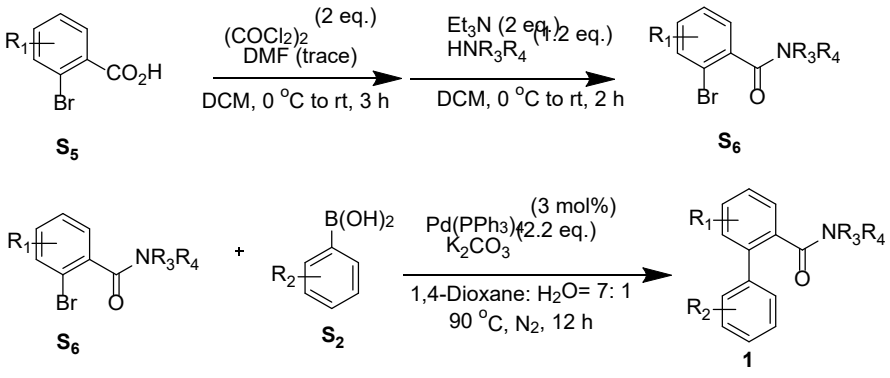
## 2.1 Preparation of Substrates




**General Preparation A:** A Schlenk tube was charged with a solution of **S1** (5 mmol) and $Pd(PPh_3)_4$ (200 mg, 0.05 equiv) in dioxane (35 mL). The reaction vessel was evacuated and back-filled with argon, and this sequence was repeated three times. A solution of $K_2CO_3$ (2.7 g, 11 mmol) in $H_2O$ (5 mL) and a solution of the corresponding **S2** (6 mmol) in dioxane (5 mL) were sequentially added. The reaction mixture was stirred at 85 °C overnight, cooled to room temperature, quenched with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 40 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and purified with a silica gel column to obtain the **S3**.

A 100 mL vial was filled with methanol (20 mL) and water (20 mL), than **S3** (5 mmol) and NaOH (4 equiv) was added. The solution was heated for 5 h at 70 °C. The reaction mixture was acidified with 6N HCl (5 mL), and the precipitation was filtrated and washed with water (3 × 20 mL) to afford **S4**.

To a solution of the **S4** (5 mmol) in DCM (30 mL) was added $(COCl_2)_2$ (2 equiv) and some drops of dry DMF at 0 °C. The reaction was allowed to stir at 0 °C to rt for 3 hours. The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride. Then DCM (30 mL) was added and the solution was cooled to 0 °C followed by drop wise addition of $NEt_3$ (2.0 equiv) and secondary amine (1.2 equiv). The reaction mixture was stirred at rt for 2 h, and then quenched with 1N HCl (15 ml). Then the mixture was extracted by DCM, and the organic layer was dried over $Na_2SO_4$. The solvent was evaporated, then purified by flash chromatography to gain the **1**.



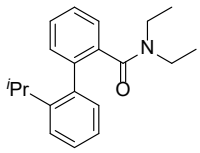

**General Preparation B:** To a solution of the **S5** in DCM (30 mL) at room temperature was added $(COCl_2)_2$ (2

equiv.) and some drops of dry DMF. The reaction was allowed to stir at 0 °C to rt for 3 hours. The solvent was then removed under reduced pressure to afford the corresponding crude acyl chloride. Then DCM (30 mL) was added and the solution was cooled to 0°C followed by drop wise addition of $NEt_3$ (2.0 equiv) and secondary amine (1.2 equiv). The reaction mixture was stirred at rt for 2 h, extracted by DCM, the organic layer was dried over $Na_2SO_4$ and the solvent was evaporated, then purified by flash chromatography to gain compound **$S_6$**.

Place **$S_6$** (5mmol), **$S_2$** (6mmol), $Pd(PPh_3)_4$ (0.05 equiv), potassium carbonate (2.1 equiv), then add a mixed solution of 35 mL dioxane and 5 mL water, vacuum and fill with nitrogen for three cycles, stirring at 95°C for 12 hours, cooling to room temperature, using Dichloromethane and water were mixed, and the dichloromethane layer was spin-dried, and then separated and purified with a silica gel column to obtain compound **1**.

Due to the weak resistance of the carbon carbon axis, multiple brs peaks and carbon peaks appear in spectra, and some of the height of the carbon peaks is too low.

## ***N,N*-diethyl-2'-isopropyl-[1,1'-biphenyl]-2-carboxamide 1a**




**1a** was prepared following General Preparation A and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give as white solid (1.15g, 78% yield)

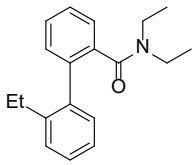
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 6.91 (m, 8H), 3.74 – 3.69 (m, 1H), 3.22 – 2.67 (m, 4H), 1.33 – 0.85 (m, 9H), 0.66 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, d6-DMSO)** δ 168.5, 146.6 (brs), 137.8, 137.0 (brs), 131.4, 123.0, 128.6, 128.0, 127.9, 127.7, 127.2, 125.1 (brs), 124.5, 42.0, 37.1, 29.3, 25.2 (brs), 22.7 (brs), 13.6, 11.6.

**(ESI)** calcd for $C_{20}H_{26}NO$ $(M+H)^+$: 296.2014, found: 296.2013

**Melting Point:** 102.7- 103.2 °C

## ***N,N*,2'-triethyl-[1,1'-biphenyl]-2-carboxamide 1b**




**1b** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid. (1.07g, 76% yield)

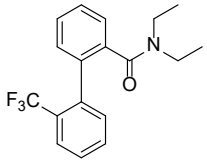
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 6.90 (m, 8H), 3.71 (q, *J* = 7.0 Hz, 1H), 3.33 – 2.62 (m, 3H), 2.54 (t, *J* = 7.8 Hz, 2H), 1.29 – 0.76 (m, 6H), 0.66 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 170.1, 143.5 (brs), 140.8 (brs), 138.8 (brs), 137.2 (brs), 132.0, 130.4, 128.3, 128.2, 128.0, 127.5, 125.9, 124.9 (brs), 42.5 (brs), 37.9, 26.2 (brs), 15.5 (brs), 13.9, 11.9.

**(ESI)** calcd for $C_{19}H_{22}NO$ $(M+H)^+$: 282.1858, found: 282.1859

**Melting Point:** 90.8- 92.1 °C

## ***N,N*-diethyl-2'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide 1c**




**1c** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 3 : 1 to give as yellow solid (1.26g, 76% yield).

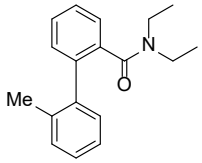
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.30 (m, 7H), 3.76 – 3.46 (m, 1H), 3.25 – 2.73 (m, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$,** ppm; list of signals, C-F coupling not resolved**)** δ 169.7, 139.3, 137.8, 136.8, 136.1, 131.0, 130.6, 130.5, 130.0, 128.3, 128.1, 128.0, 127.9, 127.0, 126.5, 126.4, 126.2, 125.8, 123.1, 42.4, 38.2, 13.9, 12.1.

**(ESI)** calcd for $C_{18}H_{19}F_3NO$ $(M+H)^+$: 322.1419, found: 322.1419

**Melting Point:** 115.1- 115.4 ºC

***N,N*-diethyl-2'-methyl-[1,1'-biphenyl]-2-carboxamide 1d**




**1d** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid. (1.09g, 82% yield)

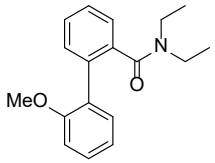
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.52 – 7.11 (m, 8H), 3.71 (q, J = 7.0 Hz, 1H), 2.85 (brs, 3H), 2.22 (s, 3H), 1.05 – 0.77 (m, 3H), 0.69 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 170.2, 139.1, 137.3, 131.1, 130.2, 128.3, 127.8, 127.5, 125.8, 125.2, 42.4, 38.0, 20.3, 13.8, 11.9.

**(ESI)** calcd for $C_{18}H_{22}NO$ $(M+H)^+$: 268.1701, found: 268.1701

**Melting Point:** 86.2- 88.1 ºC

***N,N*-diethyl-2'-methoxy-[1,1'-biphenyl]-2-carboxamide 1e**




**1e** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid (1.16g, 82% yield).

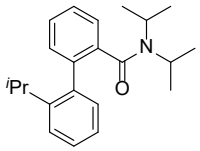
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.24 (m, 6H), 6.94 (q, *J* = 8.4, 7.9 Hz, 2H), 3.75 (s, 4H), 3.16 (s, 1H), 2.89 (s, 1H), 2.72 (s, 1H), 0.84 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 170.5, 156.4, 137.3, 135.3, 131.7, 131.1, 129.1, 128.5, 128.1, 127.4, 126.6, 120.5, 110.6, 55.4, 42.1, 38.1, 13.8, 12.0.

**(ESI)** calcd for $C_{18}H_{22}NO_2$ $(M+H)^+$: 284.1651, found: 284.1652

**Melting Point:** 96.2 - 96.8 ºC

***N,N*,2'-triisopropyl-[1,1'-biphenyl]-2-carboxamide 1f**



**1f** was prepared following General Preparation A and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid (1.41g, 87% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.7 Hz, 0.25H), 7.38 – 7.08 (m, 7H), 6.99 (d, *J* = 7.5 Hz, 0.75H), 3.63 (dp, *J* = 76.9, 6.6 Hz, 1H), 3.23 (p, *J* = 6.8 Hz, 1H), 3.04 (dp, *J* = 46.1, 6.8 Hz, 1H), 1.47 (dd, *J* = 27.4, 6.8 Hz, 3H), 1.35 (d, *J* = 6.7 Hz, 0.75H), 1.26 (d, *J* = 6.8 Hz, 2.5H), 1.22 (d, *J* = 6.9 Hz, 0.75H), 1.16 (d, *J* = 6.9 Hz, 0.75H), 1.04 (d, *J* = 6.6 Hz, 2.25H), 0.95 (dd, *J* = 15.5, 6.8 Hz, 7.5H), 0.47 (d, *J* = 6.7 Hz, 0.75H).

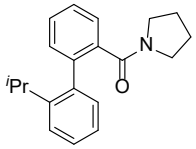
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.5, 148.3, 138.6, 138.3, 130.3, 129.5, 128.1, 128.0, 127.7, 127.2, 125.2, 125.1, 124.3, 50.2, 45.3, 30.2, 25.5, 22.2, 21.2, 20.5, 19.9.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -54.99.

**(ESI)** calcd for $C_{22}H_{30}NO$ $(M+H)^+$: 324.2327, found: 324.2326

**Melting Point:** 113.9 - 114.6 °C

**<u>*N*,*N*,2'-triisopropyl-[1,1'-biphenyl]-2-carboxamide 1g</u>**



**1g** was prepared following General Preparation A and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid (1.25g, 85% yield).

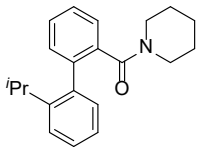
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.25 (m, 6H), 7.22 – 7.12 (m, 2H), 3.33 (td, *J* = 7.0, 3.8 Hz, 2H), 3.09 (dt, *J* = 10.3, 6.4 Hz, 1H), 2.99 (dq, *J* = 13.6, 6.9 Hz, 2H), 1.76 – 1.52 (m, 4H), 1.18 (dd, *J* = 10.2, 6.8 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.2, 146.9, 138.5, 138.4, 137.9, 130.8, 129.9, 128.4, 128.2, 127.4, 126.9, 125.8, 125.0, 48.2, 45.3, 29.8, 26.0, 25.8, 24.4, 23.5.

**(ESI)** calcd for $C_{20}H_{24}NO$ $(M+H)^+$: 294.1858, found: 294.1859

**Melting Point:** 101.1 - 102.3 °C

**<u>(2'-isopropyl-[1,1'-biphenyl]-2-yl)(piperidin-1-yl)methanone 1h</u>**



**1h** was prepared following General Preparation A and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid (1.33g, 87% yield).

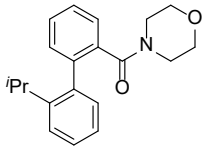
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.61 – 6.77 (m, 8H), 4.02 – 3.44 (m, 1H), 3.37 – 2.52 (m, 4H), 1.59 – 0.66 (m, 12H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.5, 148.0, 138.9, 136.7, 130.7, 129.2, 128.5, 128.2, 128.0, 127.9, 127.3,4 126.7, 126.1, 125.6, 125.4, 124.8, 48.2, 47.7, 42.4, 30.0, 29.4, 26.3, 25.5, 25.3, 24.5, 24.0, 22.9.

**(ESI)** calcd for $C_{21}H_{26}NO$ $(M+H)^+$: 308.2014, found: 308.2014

**Melting Point:** 107.8 - 108.1 °C

**(2'-isopropyl-[1,1'-biphenyl]-2-yl)(morpholino)methanone 1i**



**1i** was prepared following General Preparation A and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid (.1.22g, 79% yield).

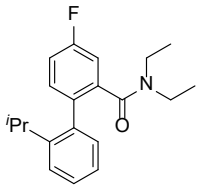
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 6.86 (m, 8H), 3.79 – 2.69 (m, 9H), 1.41 – 0.82 (m, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 170.2, 149.8, 145.9, 139.8, 138.2, 136.0, 130.8, 129.2, 128.5, 127.6, 127.0, 125.7, 125.1, 66.7, 47.4, 41.9, 30.0, 25.5, 24.0, 22.7.

**(ESI)** calcd for $C_{20}H_{24}NO_2$ $(M+H)^+$: 310.1807, found: 310.1808

**Melting Point:** 108.2 - 108.6 °C

***N,N*-diethyl-4-fluoro-2'-isopropyl-[1,1'-biphenyl]-2-carboxamide 1j**



**1j** was prepared following General Preparation A and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid (0.36g, 58% yield for 3 mmol scale).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 6.95 (m, 7H), 3.95 – 3.52 (m, 1H), 2.88 (dt, $J$ = 13.6, 6.8 Hz, 4H), 1.41 – 0.91 (m, 9H), 0.64 (t, $J$ = 7.1 Hz, 3H).

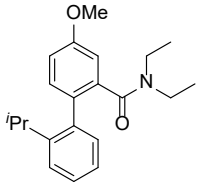
**$^{13}$C NMR (101 MHz, $CDCl_3$,** ppm; list of signals, C-F coupling not resolved**)** δ 168.6, 163.1, 160.6, 138.9, 132.2, 128.9, 128.4, 125.6, 124.9, 115.3, 115.1, 112.9, 42.6, 38.1, 29.9, 25.6, 22.6, 14.0, 11.8.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -114.61.

**(ESI)** calcd for $C_{20}H_{25}FNO$ $(M+H)^+$: 314.1920, found: 314.1921

**Melting Point:** 111.4 - 111.9 °C

***N,N*-diethyl-2'-isopropyl-4-methoxy-[1,1'-biphenyl]-2-carboxamide 1k**



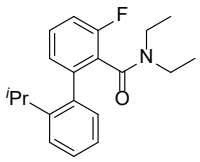
**1k** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white foam (1,17g, 72% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 6.72 (m, 7H), 3.86 (s, 4H), 3.34 – 2.50 (m, 4H), 1.29 – 0.85 (m, 9H), 0.65 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.8, 158.8, 148.6, 138.2, 136.9, 131.7, 129.2, 128.0, 125.5, 124.6, 114.2, 110.9, 55.5, 42.6, 38.0, 29.9, 25.5, 24.1, 14.0, 11.9.

**(ESI)** calcd for $C_{21}H_{28}NO_2$ $(M+H)^+$: 326.2120, found: 326.2120

**<u>*N*,*N*-diethyl-3-fluoro-2'-isopropyl-[1,1'-biphenyl]-2-carboxamide 1l</u>**




**1l** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as yellow solid (1.43g, 91% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 6.89 (m, 7H), 3.90 – 3.61 (m, 1H), 3.33 – 2.64 (m, 4H), 1.27 (dd, *J* = 10.9, 6.7 Hz, 3H), 1.18 – 1.05 (m, 3H), 1.00 (dd, *J* = 13.0, 6.9 Hz, 3H), 0.66 (td, *J* = 7.1, 3.0 Hz, 3H).

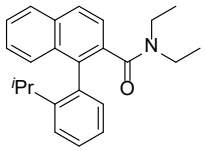
**$^{13}$C NMR (101 MHz, $CDCl_3$,** ppm; list of signals, C-F coupling not resolved**)** δ 164.9, 164.6, 160.3, 159.5, 157.9, 157.1, 148.1, 146.1, 141.5, 141.48, 140.3, 140.3, 137.4, 137.3, 136.1, 136.0, 131.3, 129.5, 129.4, 129.0, 128.9, 128.5, 128.5, 128.4, 126.46, 126.4, 126.1, 126.1, 125.7, 125.6, 125.6, 125.5, 125.3, 125.2, 125.1, 124.6, 114.7, 114.4, 42.9, 42.5, 38.2, 38.0, 30.3, 29.7, 26.3, 25.4, 23.9, 22.7, 13.9, 13.8, 11.9, 11.8.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -115.23, -115.95.

**(ESI)** calcd for $C_{20}H_{25}FNO$ $(M+H)^+$: 314.1920, found: 314.1921

**Melting Point:** 114.2 - 114.7 °C

**<u>*N*,*N*-diethyl-1-(2-isopropylphenyl)-2-naphthamide 1m</u>**




**1m** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give as yellow solid (1.37g, 78% yield).

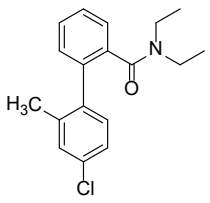
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.90 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.49 (ddd, *J* = 8.1, 6.2, 1.7 Hz, 1H), 7.45 – 7.36 (m, 5H), 7.23 – 6.99 (m, 2H), 3.82 – 3.72 (m, 1H), 3.29 (dt, *J* = 14.5, 7.3 Hz, 1H), 2.94 – 2,80 (m, 2H), 2.69 (p, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.65 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 170.0, 149.4, 135.8, 135.5, 134.3, 133.3, 133.0, 129.3, 128.5, 128.1, 127.1, 126.4, 126.4, 125.9, 124.7, 123.3, 42.9, 37.9, 30.5, 25.2, 23.1, 14.1, 11.9.

**(ESI)** calcd for $C_{24}H_{28}NO$ $(M+H)^+$: 346.2171, found: 346.2172

**Melting Point:** 137.1 - 137.4 °C

**<u>4'-chloro-*N*,*N*-diethyl-2'-methyl-[1,1'-biphenyl]-2-carboxamide 1n</u>**




**1n** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid. (1.13g, 75% yield)

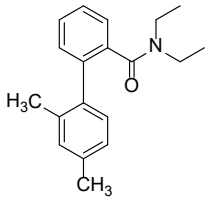
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 6.74 (m, 7H), 4.17 – 2.41 (m, 4H), 2.19 (s, 3H), 0.92 (d, *J* = 14.4 Hz, 3H), 0.77 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.9, 137.1, 133.3, 130.1, 129.9, 128.4, 127.7, 126.3, 125.2, 42.4, 38.0, 20.2, 13.8, 11.9.

**(ESI)** calcd for $C_{18}H_{21}ClNO$ $(M+H)^+$: 302.1312, found: 302.1312

**Melting Point:** 98.1 - 99.2 °C

***N*,*N*-diethyl-2',4'-dimethyl-[1,1'-biphenyl]-2-carboxamide 1o**




**1o** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid (1.07g, 78% yield).

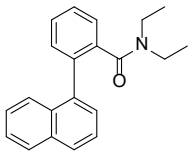
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 6.76 (m, 7H), 3.96 – 3.54 (m, 1H), 2.89 (s, 3H), 2.32 (s, 3H), 2.18 (s, 3H), 0.88 (brs, 3H), 0.73 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 170.3, 137.3, 136.1, 130.9, 130.5, 128.3, 127.3, 126.0, 42.4, 38.0, 21.2, 20.3, 13.8, 11.9.

**(ESI)** calcd for $C_{19}H_{22}NO$ $(M+H)^+$: 282.1858, found: 282.1859

**Melting Point:** 90.1 - 91.3 °C

***N*,*N*-diethyl-2-(naphthalen-1-yl)benzamide 1p**




**1p** was prepared following General Preparation B and purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give as white solid (1.31g, 86% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.04 – 7.31 (m, 11H), 3.80 – 3.47 (m, 1H), 3.36 – 2.14 (m, 3H), 1.03 – 0.13 (m, 6H).

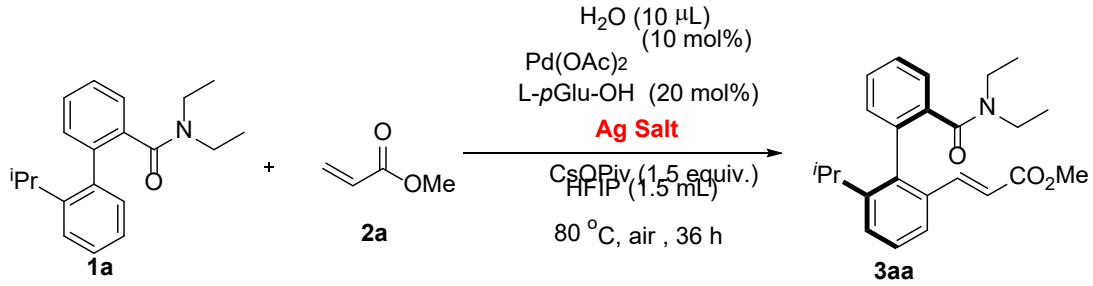
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 170.1, 138.1, 136.4, 133.8, 131.5, 128.6, 128.1, 127.9, 127.1, 126.1, 125.6, 125.4, 42.6, 37.9, 13.6, 11.8.

**(ESI)** calcd for $C_{21}H_{22}NO$ $(M+H)^+$: 304.1701, found: 304.1701

**Melting Point:** 117.5 - 118.0 °C

## 2.2 Optimization of Reaction Conditions

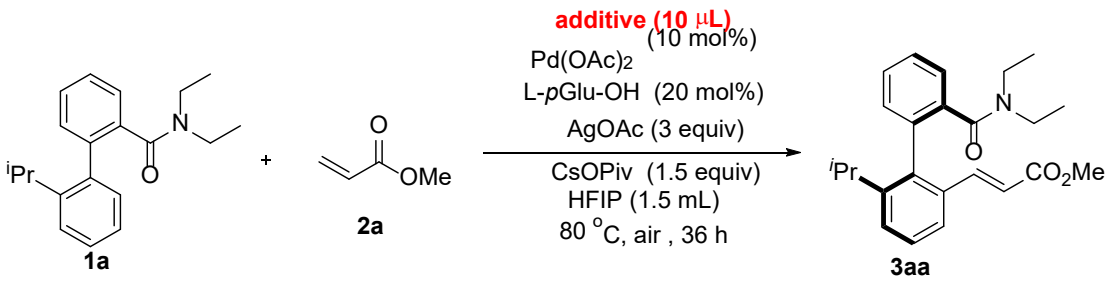
**Table S1. Optimization of Ag(I) Salt[a]**




| Ag Salt | Yield (%)[b] | ee (%)[c] |
|---|---|---|
| $Ag_2SO_4$ | 23 | 95 |
| $CH_3SO_3Ag$ | 10 | 93 |
| $CF_3CO_2Ag$ | 34 | 55 |
| $Ag_3PO_4$ | 19 | 67 |
| $Ag_2CO_3$ | 46 | 93 |
| $AgNO_3$ | 65 | 94 |

[a]Reaction Conditions: **1a** (0.1 mmol), **2a** (50 μL), $Pd(OAc)_2$ (0.01 mmol), L-*p*Glu-OH (0.02 mmol), **Ag(I)** (0.3 mmol), CsOPiv (0.15 mmol) in 1.5 mL HFIP at 80 °C under air for 36 h. [b]The yield was determined by $^1$H NMR using dibromomethane as the internal standard [c]The ee value was determined by chiral HPLC.

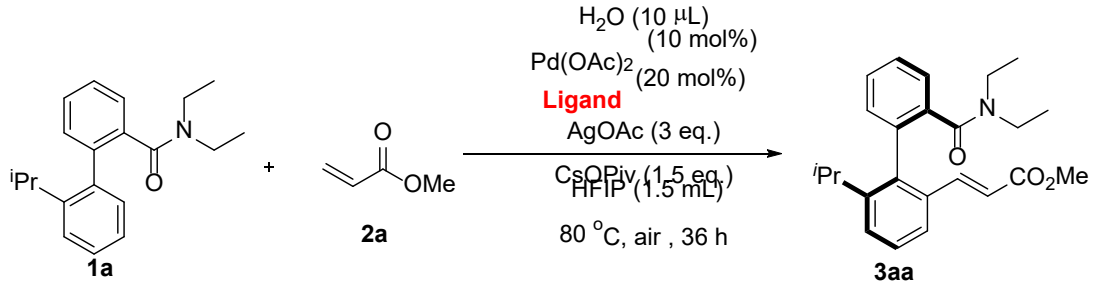
**Table S2. Optimization of solvent to combine with CsOPiv[a]**




| Additive | Yield[a]% | ee[b]% |
|---|---|---|
| DMSO | 46 | 72 |
| DMF | 54 | 88 |
| $H_2O$ | 87 | 93 |

[a]The yiled was determined by $^1$H NMR using dibromomethane as the internal standard [b]The ee value was determined by chiral HPLC. [c]Reaction Conditions: **1a** (0.1 mmol), **2a** (50 μL), $Pd(OAc)_2$ (0.01 mmol), L-*p*Glu-OH (0.02 mmol), AgOAc (0.3 mmol), CsOPiv (0.15 mmol) and **additive** (10 μL) in 1.5 mL HFIP at 80 °C under air for 36 h.

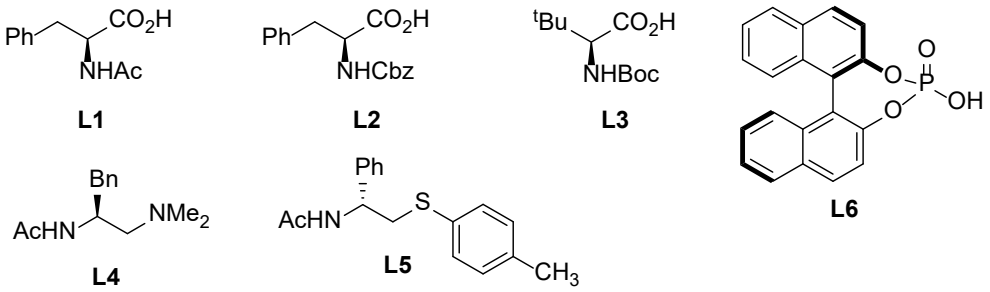
**Table S3. Optimization of Ligand[a]**



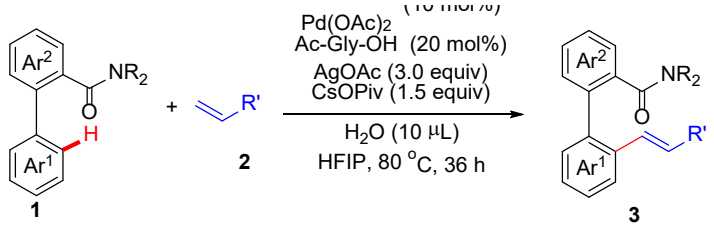

**1a** + **2a** → **3aa**

| Ligand | Yield (%)[b] | ee (%)[c] |
|---|---|---|
| **L1** | 45 | 20 |
| **L2** | 27 | 69 |
| **L3** | 65 | 56 |
| **L4** | 72 | 0 |
| **L5** | 41 | 41 |
| **L6** | N.D | - |
| L-*p*Glu-OH[d] | 89 | 69 |
| L-*p*Glu-OH[e] | 91 | 87 |

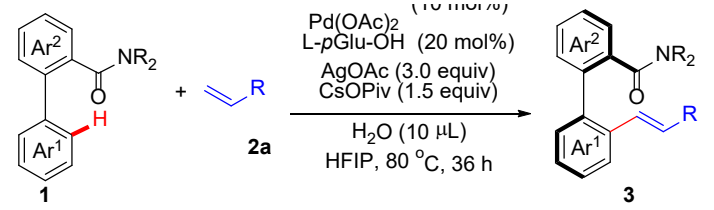
[a] Reacition Conditions: **1a** (0.1 mmol), **2a** (50 μL), $Pd(OAc)_2$ (0.01 mmol), **Ligand** (0.02 mmol), AgOAc (0.3 mmol), CsOPiv (0.15 mmol) in 1.5 mL HFIP at 80 °C under air for 36 h.[b] The yield was determined by $^1H$ NMR using dibromomethane as the internal standard [c] The ee value was determined by chiral HPLC. [d] L-*p*Glu-OH (0.005 mmol). [e] L-*p*Glu-OH (0.01 mmol).



## 2.3 General Procedure for the Intermolecular Atroposelective C-H Olefination.

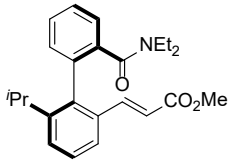



**General Procedure for the synthesis of racemic products**: To a 10 mL Schlenk tube was added substrate **1** (0.10 mmol), acrylate **2** (0.30 mmol), Ac-Gly-OH (2.3 mg, 20 mol%), $Pd(OAc)_2$ (2.2 mg, 10 mol%), AgOAc (54.1 mg, 3.0 equiv.), CsOPiv (33.1mg, 1.5 equiv.), $H_2O$ (10 μL) and HFIP (1.5 mL). The reaction mixture was stirred at 80 °C (aluminum heat transfer block) for 36 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC using Hexane/EtOAc as the eluent to afford the desired product.




**General Procedure for the synthesis of chiral products**: To a 10 mL Schlenk tube was added substrate **1** (0.10 mmol), acrylate **2** (0.30 mmol), L-*p*Glu-OH (2.6 mg, 20 mol%), $Pd(OAc)_2$ (2.2 mg, 10 mol%), AgOAc (54.1 mg, 3.0 equiv.), CsOPiv (33.1mg, 1.5 equiv.), $H_2O$(10 μL) and HFIP (1.5 mL). The reaction mixture was stirred at 80 °C (aluminum heat transfer block) for 36 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC using Hexane/EtOAc as the eluent to afford the desired product.

**methyl (*R*,*E*)-3-(2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3aa**

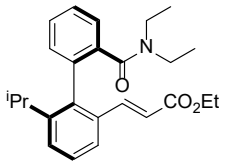



A purification by flash chromatography in petroleum ether : ethyl acetate= 4 : 1 to give **3aa** as colorless oil (34.2 mg, 93%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 5.0 min (major), 4.6 min (minor): 93% ee.

The absolute stereochemistry was assigned by analogy to compound **3ga**.

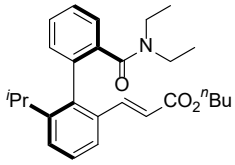
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.49 (m, 1H), 7.45 (tt, J = 7.4, 5.6 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.25 – 7.14 (m, 1H), 6.29 (d, J = 16.0 Hz, 1H), 3.67 (s, 3H), 3.47 (brs, 1H), 3.24 – 2.62 (m, 4H), 1.24 (d, J = 6.8 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H), 0.72 (t, J = 7.1 Hz, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.2, 167.5, 144.4, 139.3, 136.8, 136.5, 131.1, 128.7, 128.4, 127.6, 127.4, 126.0, 123.0, 117.6, 51.7, 43.2, 38.1, 30.6, 25.6, 22.5, 14.2, 11.9.
**(ESI)** calcd for $C_{24}H_{30}NO_3$ $(M+H)^+$: 380.2226, found: 380.2229

**ethyl (*S*,*E*)-3-(2'-(dimethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ab**



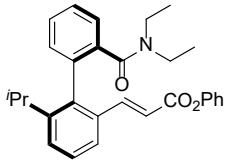

A purification by flash chromatography in petroleum ether : ethyl acetate= 4 : 1 to give **3ab** as colorless oil (36.2 mg, 92%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 0.5 mL/min, 254 nm) with tr = 10.4 min (major), 9.3 min (minor): 90% ee.
The absolute stereochemistry was assigned by analogy to compound **3ga**.
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.48 (m, 1H), 7.47 – 7.41 (m, 2H), 7.40 – 7.29 (m, 4H), 7.23 – 7.17 (m, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 4.16 – 4.08 (m, 2H), 3.48 (s, 1H), 3.20 – 3.14 (m, 1H), 3.11 – 2.75 (m, 2H), 2.74 – 2.62 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 3H), 1.21 (d, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.72 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.1, 167.0, 144.2, 139.4, 137.0, 136.6, 131.1, 128.6, 128.3, 127.5, 122.9, 118.0, 60.3, 43.2, 38.0, 30.6, 25.5, 22.5, 14.4, 14.2, 12.0.
**(ESI)** calcd for $C_{25}H_{32}NO_3$ $(M+H)^+$: 394.2328, found: 394.2327

**butyl (*S*,*E*)-3-(2'-(dimethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ac**




A purification by flash chromatography in petroleum ether : acetone= 20 : 1 to give **3ac** as colorless oil (31.1 mg, 74%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 4.9 min (major), 3.8 min (minor): 86% ee.
The absolute stereochemistry was assigned by analogy to compound **3ga**.
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, J = 7.5 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.28 (m, 4H), 7.23 – 7.17 (m, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 4.08 – 4.04 (m, 2H), 3.48 (s, 1H), 3.19 – 3.12 (m, 1H), 3.09 – 2.79 (m, 2H), 2.73 – 2.64 (m, 1H), 1.64 – 1.50 (m, 2H), 1.27 (dd, *J* = 17.5, 7.4 Hz, 5H), 1.04 (t, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.89 (td, *J* = 7.3, 1.3 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.1, 167.0, 144.1, 139.2, 136.9, 136.5, 131.0, 128.5, 128.3, 127.5, 127.2, 125.8, 122.8, 117.9, 64.2, 60.3, 43.1, 38.0, 30.7, 30.6, 27.1, 25.5, 22.4, 19.2, 14.3, 14.1, 13.8, 11.9.
**(ESI)** calcd for $C_{27}H_{36}NO_3$ $(M+H)^+$: 422.2695, found: 422.2695

**phenyl (*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ad**




A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3ad** as yellow oil (32.4 mg, 72%). The ee value was determined by HPLC analysis on a Chiralcel IBN-5 column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 7.5 min (major), 6.8 min (minor): 91% ee.

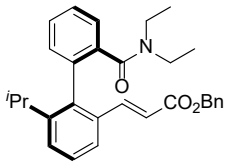
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.59 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.51 (d, *J* = 15.9 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.39 – 7.31 (m, 4H), 7.24 – 7.17 (m, 2H), 7.08 – 6.99 (m, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 3.49 (brs, 1H), 3.28 – 3.17 (m, 1H), 3.16 – 2.88 (m, 2H), 2.71 (p, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.08 (t, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.77 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.1, 165.4, 150.9, 146.2, 139.7, 136.9, 136.5, 131.1, 129.4, 128.7, 128.4, 127.7, 127.6, 126.0, 125.8, 123.1, 121.6, 116.9, 67.2, 43.2, 38.1, 30.6, 29.8, 27.2, 25.5, 22.5, 14.2, 12.0.

**(ESI)** calcd for $C_{29}H_{32}NO_3$ $(M+H)^+$: 442.2382, found: 442.2381

**benzyl (*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ae**




A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3ae** as yellow oil (42.6 mg, 93%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 8.6 min (major), 7.1 min (minor): 87% ee.

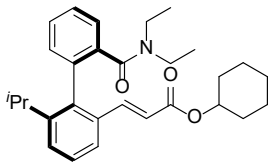
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.52 – 7.49 (m, 1H), 7.45 – 7.41 (m, 3H), 7.39 – 7.30 (m, 6H), 7.27 – 7.24 (m, 2H), 7.22 – 7.19 (m, 1H), 6.33 (dd, *J* = 16.0, 2.5 Hz, 1H), 5.12 (d, *J* = 2.5 Hz, 2H), 3.46 (brs, 1H), 3.11 (td, *J* = 8.6, 8.1, 3.8 Hz, 1H), 3.04 – 2.56 (m, 3H), 1.26 (dd, *J* = 7.0, 2.7 Hz, 3H), 1.22 (d, *J* = 2.5 Hz, 3H), 0.99 (dd, *J* = 7.0, 2.5 Hz, 3H), 0.92 (d, *J* = 7.5 Hz, 3H), 0.70 (td, *J* = 7.1, 2.5 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.0, 166.7, 144.8, 139.4, 137.0, 136.6, 136.2, 131.1, 128.7, 128.6, 128.4, 128.2, 127.9, 127.5, 127.5, 125.9, 122.8, 117.5, 66.1, 43.2, 38.0, 30.6, 27.1, 25.5, 22.5, 14.1, 11.9.

**(ESI)** calcd for $C_{30}H_{34}NO_3$ $(M+H)^+$: 456.2539, found: 456.2540

**Cyclohexyl (*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3af**




A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3af** as

yellow oil (33.1 mg, 74%). The ee value was determined by HPLC analysis on a Chiralcel NQ column (hexane/isopropanol = 70/30, flow = 0.8 mL/min, 254 nm) with tr = 5.8 min (major), 7.1 min (minor): 93% ee.

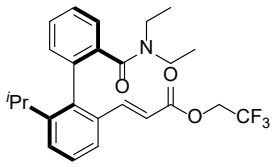
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.48 (m, 1H), 7.45 – 7.42 (m, 2H), 7.39 – 7.28 (m, 4H), 7.21 (dd, *J* = 6.8, 1.9 Hz, 1H), 6.26 (d, *J* = 15.9 Hz, 1H), 4.80 – 4.75 (m, 1H), 3.52 (brs, 1H), 3.20 – 3.15 (m, 1H), 3.06 – 2.77 (m, 2H), 2.75 – 2.69 (m, 1H), 1.75 (dt, *J* = 9.0, 5.0 Hz, 2H), 1.60 (q, *J* = 8.1, 7.6 Hz, 2H), 1.54 – 1.31 (m, 6H), 1.24 (d, *J* = 15.2 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.0, 166.9, 158.6, 145.0, 139.5, 136.5, 131.1, 129.6, 128.6, 128.4, 127.6, 126.0, 122.9, 121.3, 117.4, 114.7, 114.7, 69.2, 66.0, 62.8, 61.1, 43.2, 38.0, 30.6, 25.5, 22.5, 14.2, 12.0.

**(ESI)** calcd for $C_{29}H_{38}NO_3$ $(M+H)^+$: 448.2852, found: 448.2852

**<u>2,2,2-trifluoroethyl(*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ag</u>**




A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3ag** as yellow oil (40.2 mg, 89%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 70/30, flow = 0.8 mL/min, 254 nm) with tr = 13.9 min (major), 14.8 min (minor): 91% ee.

The absolute stereochemistry was assigned by analogy to compound **3ga**.

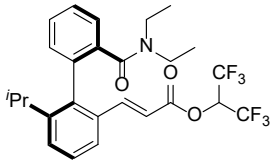
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.39 (m, 4H), 7.40 – 7.33 (m, 2H), 7.20 (dt, *J* = 6.2, 1.7 Hz, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 4.45 (q, *J* = 8.5 Hz, 2H), 3.46 (s, 1H), 3.15 (dd, *J* = 14.5, 7.2 Hz, 1H), 3.12 – 2.75 (m, 2H), 2.70 (p, *J* = 7.0 Hz, 1H), 1.26 (d, *J* = 6.7 Hz, 5H), 1.06 (t, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.73 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 168.9, 165.0, 146.7, 136.8, 136.2, 130.9, 128.5, 128.3, 127.9, 127.6, 125.9, 123.0 (d, $J_{CF}$ = 276.7 Hz), 122.9, 115.4, 60.1 (q, $J_{CF}$ = 36.4 Hz), 43.0, 37.9, 30.5, 27.1, 25.4, 22.4, 14.0, 11.9.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -73.90.

**(ESI)** calcd for $C_{25}H_{29}F_3NO_3$ $(M+H)^+$: 448.2100 found: 448.2101

**<u>1,1,1,3,3,3-hexafluoropropan-2-yl(*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ah</u>**




A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3ah** as yellow oil (34.8 mg, 67%). The ee value was determined by HPLC analysis on a Chiralcel IBN-5 column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 4.0 min (major), 4.7

min (minor): 91% ee.

The absolute stereochemistry was assigned by analogy to compound **3ga**.

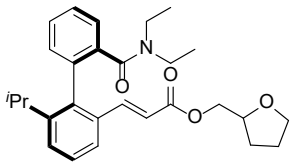
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 3H), 7.29 – 7.23 (m, 2H), 7.10 – 7.08 (m, 1H), 6.23 (dd, *J* = 15.9, 1.7 Hz, 1H), 5.67 – 5.58 (m, 1H), 3.34 (brs, 1H), 3.04 – 2.56 (m, 4H), 1.15 (d, *J* = 6.5 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.89 (dd, *J* = 6.9, 1.7 Hz, 3H), 0.61 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 168.9, 163.4, 149.1, 140.2, 136.9, 136.2, 131.0, 128.7, 128.6, 128.6, 127.8, 126.0, 123.2, 120.62 (d, $J_{CF}$ = 279.9 Hz), 113.6, 67.69 – 65.55 (m), 43.1, 38.1, 30.7, 29.8, 25.5, 22.5, 14.1, 11.9.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -73.39, -73.41, -73.43, -73.48, -73.51, -75.66.

**(ESI)** calcd for $C_{26}H_{28}F_6NO_3$ $(M+H)^+$: 516.1973 found: 516.1974

**(tetrahydrofuran-2-yl)methyl(*E*)-3-((*S*)-2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ai**




A purification by flash chromatography in petroleum ether : ethyl acetate= 3 : 1 to give **3ai** as yellow oil (41.5 mg, 92%). The ee value was determined by HPLC analysis on a Chiralcel NX column (hexane/isopropanol = 90/10, flow = 0.5 mL/min, 254 nm) with tr = 54.9 min (major), tr = 35.5 min (major), 34.2 min (minor), 30.6 min(minor): 95% ee.

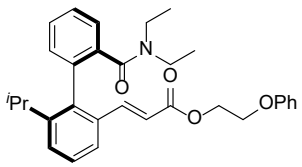
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.50 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.31 (m, 4H), 7.19 (dd, *J* = 6.6, 2.2 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 4.18 – 3.99 (m, 3H), 3.85 – 3.70 (m, 2H), 3.46 (brs, 1H), 3.18 – 3.13 (m, 1H), 2.98 – 2.85 (m, 2H), 2.70 – 2.64 (m, 1H), 1.99 – 1.81 (m, 3H), 1.56 (dq, *J* = 11.5, 7.3 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.70 (t, *J* = 7.0 Hz, 3H)..

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.1, 166.9, 144.6, 139.3, 137.0, 136.5, 131.1, 131.1, 128.6, 128.6, 128.4, 127.6, 127.4, 125.9, 125.9, 122.9, 117.6, 76.6, 68.5, 66.4, 43.2, 38.0, 30.6, 27.9, 27.2, 25.6, 25.5, 22.5, 14.2, 11.9.

**(ESI)** calcd for $C_{28}H_{36}NO_4$ $(M+H)^+$: 450.2644, found: 450.2645

**2-phenoxyethyl (*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3aj**




A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3aj** as colorless oil (38.9 mg, 79%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 10.5 min (major), 9.1 min (minor): 91% ee.

The absolute stereochemistry was assigned by analogy to compound **3ga**.

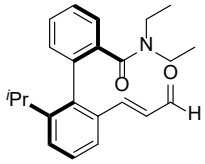
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.24 (m, 9H), 7.19 (d, *J* = 7.3 Hz, 1H),

7.02 – 6.83 (m, 4H), 6.33 (d, *J* = 15.9 Hz, 1H), 4.47 – 4.40 (m, 2H), 4.13 (t, *J* = 4.7 Hz, 2H), 3.47 (brs, 1H), 3.15 (dq, *J* = 14.5, 7.7, 7.2 Hz, 1H), 3.10 – 2.74 (m, 2H), 2.67 (dq, *J* = 16.1, 9.5, 8.1 Hz, 1H), 1.23 (d, *J* = 11.4 Hz, 3H), 1.02 – 0.97 (m, 6H), 0.71 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.1, 166.9, 158.5, 145.0, 134.0, 136.4, 131.1, 129.6, 129.6, 128.6, 128.4, 127.6, 125.9, 122.9, 121.3, 117.3, 114.7, 114.7, 114.6, 66.0, 62.8, 43.2, 38.0, 30.6, 27.2, 25.5, 22.5, 14.2, 11.9

**(ESI)** calcd for $C_{31}H_{36}NO_4$ $(M+H)^+$: 486.2644 found: 486.2644

**(*S*,*E*)-2'-isopropyl-N,N-dimethyl-6'-(3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxamide 3ak**



A purification by flash chromatography in petroleum ether : ethyl acetate= 4 : 1 to give **3ak** as yellow oil (21.2 mg, 60%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 6.2 min (major), 7.1 min (minor): 87% ee.

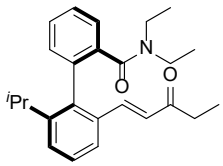
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 9.38 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.49 – 7.35 (m, 5H), 7.24 – 7.11 (m, 2H), 6.56 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.55 – 2.98 (m, 4H), 2.72 – 2.58 (m, 1H), 1.22 (s, 3H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.74 (t, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 194.2, 183.5, 169.0, 152.9, 140.5, 136.4, 131.3, 128.8, 128.7, 128.6, 128.1, 127.8, 126.1, 123.6, 43.0, 38.3, 30.6, 27.2, 25.7, 22.6, 14.3, 12.1.

**(ESI)** calcd for $C_{23}H_{28}NO_3$ $(M+H)^+$: 350.2120 found: 350.2119

**(*S*,*E*)-N,N-diethyl-2'-isopropyl-6'-(3-oxopent-1-en-1-yl)-[1,1'-biphenyl]-2-carboxamide 3al**



A purification by flash chromatography in petroleum ether : ethyl acetate= 4 : 1 to give **3al** as yellow oil (20.1 mg, 53%). The ee value was determined by HPLC analysis on a Chiralcel IBN-5 column (hexane/isopropanol = 90/10, flow = 0.5 mL/min, 254 nm) with tr = 6.3 min (major), 7.1 min (minor): 93% ee.

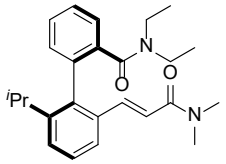
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 7.4 Hz, 1H), 7.43 (q, *J* = 6.2, 5.0 Hz, 2H), 7.41 – 7.30 (m, 3H), 7.26 – 7.14 (m, 2H), 6.54 (d, *J* = 16.2 Hz, 1H), 3.63 – 2.79 (m, 4H), 2.68 (p, *J* = 7.0 Hz, 1H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.03 (dt, *J* = 19.8, 7.1 Hz, 9H), 0.72 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 202.3, 169.0, 144.4, 139.6, 136.8, 136.5, 131.2, 128.5, 128.3, 127.6, 127.2, 126.1, 125.9, 122.9, 42.9, 38.0, 30.5, 27.1, 26.0, 22.4, 14.1, 12.0, 8.3.

**(ESI)** calcd for $C_{25}H_{32}NO_2$ $(M+H)^+$: 378.2433 found: 378.2434

**(*S*,*E*)-2'-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-6'-isopropyl-*N*,*N*-dimethyl-[1,1'-biphenyl]-2-carboxamide 3am**



A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3am** as yellow oil (25.6 mg, 65%). The ee value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 80/20, flow = 1.2 mL/min, 254 nm) with tr = 17.1 min (major), 13.1 min (minor): 78% ee.

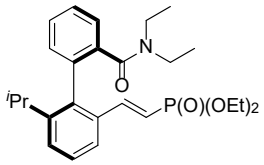
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.48 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.38 – 7.27 (m, 4H), 7.19 (dd, *J* = 7.2, 1.7 Hz, 1H), 6.68 (d, *J* = 15.4 Hz, 1H), 3.49 (s, 1H), 3.24 – 3.18 (m, 1H), 3.07 (s, 3H), 3.06 – 2.98 (m, 1H), 2.96 (s, 3H), 2.90 – 2.84 (m, 1H), 2.70 (p, *J* = 6.8 Hz, 1H), 1.25 – 1.22 (m, 3H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.72 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.3, 166.7, 141.7, 137.0, 131.2, 128.6, 128.2, 127.5, 126.6, 126.0, 122.9, 117.8, 43.3, 38.0, 37.5, 35.9, 30.6, 29.8, 25.6, 22.5, 14.2, 12.1.

**(ESI)** calcd for $C_{25}H_{33}N_2O_2$ $(M+H)^+$: 393.2542 found: 393.2542

**Diethyl(*S*,*E*)-(2-(2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)vinyl)phosphonate 3an**



A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3an** as yellow oil (43.4 mg, 94%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 80/20, flow = 1 mL/min, 254 nm) with tr = 5.2 min (major), 4.7 min (minor): 86% ee.

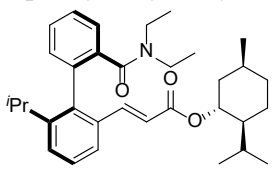
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.41 (m, 3H), 7.36 (q, *J* = 7.4 Hz, 3H), 7.22 – 7.17 (m, 1H), 7.06 (dd, *J* = 23.0, 17.5 Hz, 1H), 6.10 (t, *J* = 18.3 Hz, 1H), 3.97 (p, *J* = 7.3 Hz, 4H), 3.47 (brs, 1H), 3.20 – 2.87 (m, 3H), 2.77 – 2.65 (m, 1H), 1.21 (ddd, *J* = 11.0, 7.2, 3.5 Hz, 9H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.70 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$,** ppm; list of signals, C-P coupling not resolved**)** δ 168.9, 155.4, 140.7, 131.2, 128.4, 128.3, 127.5, 125.9, 116.8, 113.0, 61.7, 37.9, 30.5, 25.5, 22.3, 16.3, 16.3, 14.0, 11.9.

**(ESI)** calcd for $C_{26}H_{37}NO_4P$ $(M+H)^+$: 458.2460 found: 458.2460

**(*1R*,*2S*,*5S*)-2-isopropyl-5-methylcyclohexyl(*E*)-3-((*S*)-2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ao**



A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3ao** as yellow oil (44.6 mg, 88%). The ee value was determined by HPLC analysis on a Chiralcel IC

column (hexane/isopropanol = 90/10, flow = 0.3 mL/min, 254 nm) with tr = 21.2 min (major), 22.3 min (minor): 92% ee.

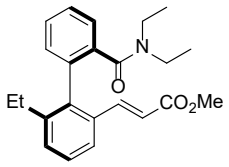
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.51 (t, *J* = 6.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.32 (m, 3H), 7.28 (t, *J* = 5.8 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.27 (dd, *J* = 16.0, 6.2 Hz, 1H), 4.67 – 4.61 (m, 1H), 3.52 (brs, 1H), 3.24 – 3.17 (m, 1H), 3.12 – 2.77 (m, 2H), 2.71 (dt, *J* = 13.6, 6.9 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.89 – 1.60 (m, 4H), 1.47 (dt, *J* = 15.8, 5.1 Hz, 1H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.07 (t, *J* = 6.8 Hz, 3H), 1.00 (t, *J* = 6.6 Hz, 3H), 0.87 (dt, *J* = 13.1, 6.6 Hz, 8H), 0.76 – 0.68 (m, 7H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.1, 166.5, 143.9, 139.4, 136.92, 136.7, 131.1, 128.5, 128.3, 127.5, 127.2, 125.8, 122.8, 118.3, 74.2, 47.2, 43.2, 41.1, 38.0, 34.4, 34.3, 31.4, 30.6, 26.5, 25.5, 23.7, 22.5, 22.1, 20.8, 20.8, 16.6, 14.1, 11.8.

**(ESI)** calcd for $C_{33}H_{46}NO_3$ $(M+H)^+$: 504.3470 found: 504.3471

**methyl (*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-ethyl-[1,1'-biphenyl]-2-yl)acrylate 3ba**




A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3ba** as yellow oil (31.7 mg, 85%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 5.8 min (major), 5.3 min (minor): 91% ee.

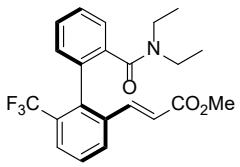
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.57 – 7.49 (m, 1H), 7.49 – 7.40 (m, 2H), 7.40 – 7.28 (m, 4H), 7.21 (d, *J* = 6.9 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 3.68 (s, 3H), 3.49 (brs, 1H), 3.17 (dd, *J* = 14.6, 7.4 Hz, 1H), 3.11 – 2.71 (m, 2H), 2.51 (dq, *J* = 15.3, 7.7 Hz, 1H), 2.35 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.10 – 1.01 (m, 6H), 0.70 (t, *J* = 6.3 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.1, 167.3, 144.1, 140.0, 136.9, 136.4, 130.9, 129.8, 128.7, 128.1, 127.6, 125.9, 122.8, 117.6, 51.6, 43.1, 37.9, 26.7, 15.0, 14.2, 11.8.

**(ESI)** calcd for $C_{23}H_{28}NO_3$ $(M+H)^+$: 366.2069 found: 366.2069

**methyl (*R*,*E*)-3-(2'-(diethylcarbamoyl)-6-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)acrylate 3ca**




A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3ca** as yellow oil (25.9 mg, 64%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 5.1 min (major), 5.8 min (minor): 89% ee.

The absolute stereochemistry was assigned by analogy to compound **3ga**.

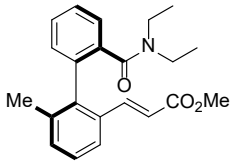
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.57 – 7.28 (m, 5H), 7.24 – 7.19 (m, 1H), 6.30 (d, J = 16.0 Hz, 1H), 3.66 (s, 3H), 3.44 – 3.09 (m, 4H), 1.18 (t, J = 7.1 Hz, 3H), 0.85 (t, J = 7.0 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$,** ppm; list of signals, C-F coupling not resolved**)** δ 168.7, 167.0, 143.0, 139.1, 135.7, 135.4, 131.4, 129.0, 128.2, 128.2, 127.9, 127.2, 126.0, 119.7, 51.8, 43.0, 38.4, 27.2, 14.2, 11.9.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -55.96.

**(ESI)** calcd for $C_{23}H_{28}NO_3$ $(M+H)^+$: 406.1630 found: 406.1632

**methyl (*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-methyl-[1,1'-biphenyl]-2-yl)acrylate 3da**




A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3da** as white foam (33.2 mg, 95%). The ee value was determined by HPLC analysis on a Chiralcel IBN-5 column (hexane/isopropanol = 90/10, flow = 0.5 mL/min, 254 nm) with tr = 13.3 min (major), 14.3 min (minor): 83% ee.

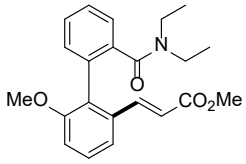
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.49 (m, 1H), 7.49 – 7.34 (m, 4H), 7.26 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.19 (dt, *J* = 7.4, 1.9 Hz, 1H), 6.30 (dd, *J* = 16.0, 1.8 Hz, 1H), 3.68 (s, 3H), 3.51 (brs, 1H), 3.31 – 3.12 (m, 1H), 3.13 – 2.73 (m, 2H), 2.11 (d, *J* = 1.8 Hz, 3H), 1.06 (t, *J* = 6.2 Hz, 3H), 0.71 (t, *J* = 6.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.2, 167.4, 144.0, 140.8, 136.9, 136.9, 131.8, 130.6, 129.0, 128.0, 127.6, 126.0, 122.9, 117.7, 51.6, 43.2, 38.0, 21.0, 14.2, 11.8.

**(ESI)** calcd for $C_{22}H_{26}NO_3$ $(M+H)^+$: 352.1913 found: 352.1913

**methyl (*R*,*E*)-3-(2'-(diethylcarbamoyl)-6-methoxy-[1,1'-biphenyl]-2-yl)acrylate 3ea**



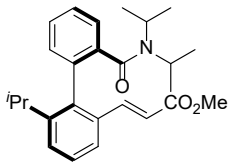

A purification by flash chromatography in petroleum ether : ethyl acetate= 4 : 1 to give **3ea** as yellow oil (11.4 mg, 31%).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.37 (m, 4H), 7.35 – 7.27 (m, 2H), 7.18 (dd, *J* = 6.9, 1.8 Hz, 1H), 7.01 – 6.87 (m, 1H), 6.30 (d, J = 16.0 Hz, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 2.98 (brs, 4H), 1.04 (t, *J* = 6.9 Hz, 3H), 0.76 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.2, 167.4, 144.0, 140.8, 136.9, 136.9, 131.8, 130.6, 129.0, 128.0, 127.6, 126.0, 122.9, 117.7, 51.6, 43.2, 38.0, 21.0, 14.2, 11.8.

**(ESI)** calcd for $C_{22}H_{26}NO_4$ $(M+H)^+$: 368.1862 found: 368.1863

**methyl (*S*,*E*)-3-(2'-(diisopropylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3fa**




A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3ea** as

white foam (33.3 mg, 82%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 4.2 min (major), 4.0 min (minor): 89% ee.

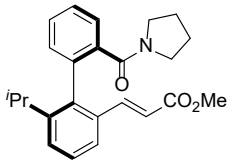
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.27 (m, 6H), 7.14 (d, *J* = 7.7 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 3.68 (s, 3H), 3.66 – 3.53 (m, 1H), 3.27 – 3.12 (m, 1H), 3.03 – 2.81 (m, 1H), 1.42 (d, *J* = 6.7 Hz, 3H), 1.31 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H), 0.71 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.0, 167.4, 150.2, 143.8, 139.4, 138.2, 134.8, 132.6, 131.5, 128.4, 127.9, 127.4, 125.8, 122.7, 117.8, 51.6, 49.8, 45.5, 30.8, 25.8, 21.7, 21.3, 20.6, 20.1.

**(ESI)** calcd for $C_{26}H_{34}NO_3$ $(M+H)^+$: 408.2539 found: 408.2540

**<u>methyl (*S*,*E*)-3-(6-isopropyl-2'-(pyrrolidine-1-carbonyl)-[1,1'-biphenyl]-2-yl)acrylate 3ga</u>**




A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3ga** as yellow solid (36.2 mg, 96%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 7.3 min (major), 9.2 min (minor): 87% ee.

The absolute stereochemistry was assigned by X-ray diffraction analysis.

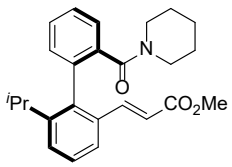
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.44 (td, *J* = 16.8, 15.3, 7.7 Hz, 5H), 7.37 – 7.30 (m, 2H), 7.18 (d, *J* = 6.5 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 3.66 (s, 3H), 3.39 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.35 – 3.21 (m, 3H), 2.74 – 2.56 (m, *J* = 7.0 Hz, 1H), 1.77 (tt, *J* = 12.0, 6.5 Hz, 3H), 1.57 (m, 1H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.05 (d, J = 6.9 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 167.9, 167.4, 148.8, 144.5, 139.8, 137.3, 137.2, 132.6, 131.1, 129.1, 128.3, 127.5, 127.4, 127.0, 123.1, 117.5, 51.6, 49.1, 45.7, 30.6, 26.2, 25.1, 24.3, 23.0.

**(ESI)** calcd for $C_{24}H_{28}NO_3$ $(M+H)^+$: 378.2069 found: 378.2068

**Melting Point:** 187.1 - 188.3 °C

**<u>methyl (*S*,*E*)-3-(6-isopropyl-2'-(piperidine-1-carbonyl)-[1,1'-biphenyl]-2-yl)acrylate 3ha</u>**



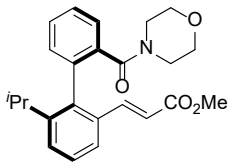

A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3ha** as yellow oil (34.5 mg, 88%). The ee value was determined by HPLC analysis on a Chiralcel NT(2) column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 19.1 min (major), 32.9 min (minor): 87% ee.

The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.51 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.36 (dd, *J* = 7.1, 1.9 Hz, 2H), 7.31 (d, *J* = 15.9 Hz, 1H), 7.22 – 7.12 (m, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 3.30 – 2.70 (m, 4H), 3.43 – 2.51 (m, 4H), 1.57 – 1.32 (m, 6H), 1.30 – 1.24 (m, 3H), 0.99 (d, *J* = 6.8 Hz, 3H).

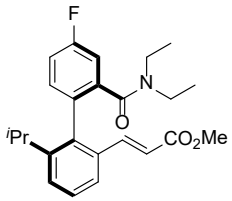
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.0, 168.5, 167.4, 139.5, 131.4, 128.9, 128.4, 127.6, 126.9, 123.12, 117.7, 64.5, 51.6, 42.7, 30.8, 27.1, 26.5, 25.6, 25.4, 24.6.
**(ESI)** calcd for $C_{25}H_{30}NO_3$ $(M+H)^+$: 392.2226 found: 392.2227

**methyl (*S*,*E*)-3-(6-isopropyl-2'-(morpholine-4-carbonyl)-[1,1'-biphenyl]-2-yl)acrylate 3ia**



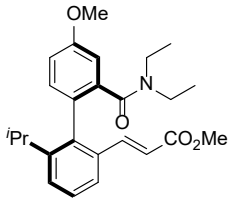

A purification by flash chromatography in petroleum ether : ethyl acetate= 1 : 1 to give **3ia** as yellow oil (17.8 mg, 45%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 24.0 min (major), 15.0 min (minor): 87% ee.
The absolute stereochemistry was assigned by analogy to compound **3ga**.
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.54 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.51 – 7.28 (m, 6H), 7.19 (dd, *J* = 6.9, 1.9 Hz, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 3.67 (s, 3H), 3.66 – 3.06 (m, 8H), 2.68 (s, 1H), 1.27 – 1.25 (m, 3H), 1.00 (d, *J* = 6.9 Hz, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 168.6, 167.4, 144.2, 131.6, 129.3, 128.6, 127.7, 127.2, 123.1, 117.8, 66.9, 51.7, 47.8, 42.1, 30.7, 27.2, 25.4, 22.6.
**(ESI)** calcd for $C_{24}H_{28}NO_4$ $(M+H)^+$: 394.2018 found: 394.2018

**methyl (*S*,*E*)-3-(2'-(diethylcarbamoyl)-4'-fluoro-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3ja**




A purification by flash chromatography in petroleum ether : ethyl acetate= 4 : 1 to give **3ja** as yellow oil (28.1 mg, 69%). The ee value was determined by HPLC analysis on a Chiralcel NQ column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 6.2 min (major), 9.5 min (minor): 89% ee.
The absolute stereochemistry was assigned by analogy to compound **3ga**.
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.50 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.43 – 7.30 (m, 3H), 7.22 – 7.10 (m, 2H), 7.08 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 3.69 (s, 3H), 3.48 (brs, 1H), 3.15 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.94 (d, *J* = 48.3 Hz, 2H), 2.67 (p, *J* = 6.8 Hz, 1H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.70 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$,** ppm; list of signals, C-F coupling not resolved**)** δ 167.6, 167.4, 160.5, 144.1, 138.2, 132.9 (d, *J* = 7.6 Hz), 132.4, 128.6, 127.5, 123.0, 117.9, 115.8 (d, *J* = 21.1 Hz), 113.3 (d, *J* = 22.5 Hz), 51.7, 43.2, 38.1, 30.6, 25.5, 22.4, 14.2, 11.9.
**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -113.64.
**(ESI)** calcd for $C_{24}H_{29}FNO_3$ $(M+H)^+$: 398.2131 found: 398.2131

**Methyl(*S*,*E*)-3-(2'-(diethylcarbamoyl)-6-isopropyl-4'-methoxy-[1,1'-biphenyl]-2-yl)acrylate 3ka**




A purification by flash chromatography in petroleum ether : ethyl acetate= 3 : 1 to give **3ka** as yellow oil (29.6 mg, 72%). The ee value was determined by HPLC analysis on a Chiralcel NQ column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 15.3 min (major), 9.4 min (minor): 87% ee.

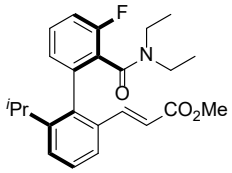
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 7.5 Hz, 1H), 7.44 – 7.28 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.98 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.89 (s, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.48 (brs, 1H), 3.18 (s, 1H), 3.13 – 2.65 (m, 3H), 1.23 (d, *J* = 2.0 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.70 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 168.9, 167.5, 158.7, 144.6, 139.1, 132.2, 128.3, 127.4, 122.9, 117.5, 114.3, 111.5, 55.5, 51.7, 38.0, 30.5, 27.2, 25.6, 22.5, 14.3, 11.9.

**(ESI)** calcd for $C_{25}H_{32}NO_4$ $(M+H)^+$: 410.2331 found: 410.2331

**Methyl(*S*,*E*)-3-(2'-(diethylcarbamoyl)-3'-fluoro-6-isopropyl-[1,1'-biphenyl]-2-yl)acrylate 3la**




A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3la** as yellow oil (27.5 mg, 69%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 0.8 mL/min, 254 nm) with tr = 4.9 min (major), 5.5 min (minor): 92% ee.

The absolute stereochemistry was assigned by analogy to compound **3ga**.

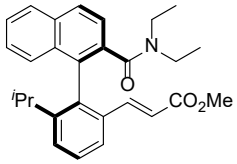
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.50 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.44 – 7.27 (m, 4H), 7.20 – 7.13 (m, 1H), 6.98 (dd, *J* = 13.8, 7.6 Hz, 1H), 6.28 (dd, *J* = 24.6, 16.0 Hz, 1H), 3.68 (d, *J* = 18.1 Hz, 3H), 3.56 (dq, *J* = 14.2, 7.3 Hz, 1H), 3.44 – 3.15 (m, 1H), 3.08 – 2.51 (m, 3H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.82 – 0.64 (m, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$,** ppm; list of signals, C-F coupling not resolved**)** δ 167.7, 167.4, 164.3, 159.9, 157.4, 150.0, 146.8, 144.8, 143.7, 138.80, 137.9, 132.1, 130.0, 130.0, 128.8, 128.7, 127.7, 126.8, 126.7, 126.5, 125.3, 125.1, 123.7, 122.8, 118.3, 117.8, 115.3, 115.1, 69.2, 64.6, 51.8, 51.6, 43.4, 42.9, 38.4, 37.9, 30.8, 30.4, 26.0, 25.6, 22.7, 22.2, 21.1, 19.2, 13.8, 13.8, 12.3, 11.7.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -113.21, -114.29.

**(ESI)** calcd for $C_{24}H_{29}FNO_3$ $(M+H)^+$: 398.2131 found: 398.2131

**methyl (*S*,*E*)-3-(2-(2-(diethylcarbamoyl)naphthalen-1-yl)-3-isopropylphenyl)acrylate 3ma**



A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3ma** as yellow oil (27.1 mg, 62%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 0.8 mL/min, 254 nm) with tr = 4.8 min (major), 5.5 min (minor): 87% ee.

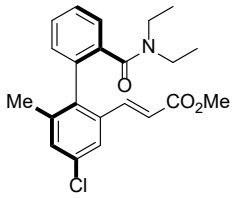
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.99 – 7.88 (m, 2H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.41 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.09 (d, *J* = 15.9 Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 3.57 (s, 4H), 3.28 – 2.66 (m, 3H), 2.42 (p, *J* = 6.8 Hz, 1H), 1.27 (d, *J* = 12.7 Hz, 3H), 1.09 (s, 3H), 0.80 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.3, 167.3, 144.3, 133.2, 128.7, 128.3, 128.2, 126.9, 126.8, 126.75, 123.2, 117.7, 60.5, 51.5, 43.2, 43.1, 30.8, 27.2, 25.2, 14.3, 14.2.

**(ESI)** calcd for $C_{28}H_{32}NO_3$ $(M+H)^+$: 430.2382 found: 430.2382

**methyl (*S*,*E*)-3-(4-chloro-2'-(diethylcarbamoyl)-6-methyl-[1,1'-biphenyl]-2-yl)acrylate 3na**



A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3na** as yellow oil (15.2 mg, 39%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 7.2 min (major), 5.6 min (minor): 99% ee.

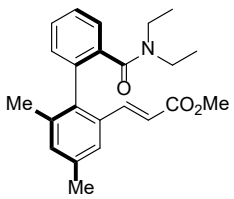
The absolute stereochemistry was assigned by analogy to compound **3ga**.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.40 (m, 3H), 7.36 (d, *J* = 6.4 Hz, 1H), 7.29 (s, 1H), 7.25 (s, 1H), 7.15 (d, *J* = 6.6 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 3.69 (brs, 3H), 3.51 (brs, 1H), 3.20 (brs, 1H), 3.03 brs(s, 1H), 2.83 (dd, *J* = 16.4, 7.0 Hz, 1H), 2.09 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.0, 167.0, 142.6, 139.3, 136.9, 136.0, 133.8, 131.4, 130.6, 129.2, 127.9, 126.1, 122.7, 119.0, 51.8, 43.3, 38.2, 20.9, 14.3, 12.0.

**(ESI)** calcd for $C_{22}H_{25}ClNO_3$ $(M+H)^+$: 386.1532 found: 386.1532

**methyl (*S*,*E*)-3-(2'-(diethylcarbamoyl)-4,6-dimethyl-[1,1'-biphenyl]-2-yl)acrylate 3oa**



A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3oa** as yellow oil (15.6 mg, 43%). The ee value was determined by HPLC analysis on a Chiralcel IBN-5

column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 8.6 min (major), 6.2 min (minor): 90% ee.

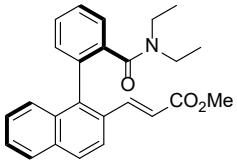
The absolute stereochemistry was assigned by analogy to compound **3ga.**

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.43 (dtd, *J* = 18.8, 7.4, 1.5 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.19 – 7.14 (m, 1H), 7.10 (s, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 3.52 – 3.18 (s, 3H), 3.35 (m, 2H), 3.12 – 2.72 (m, 2H), 2.34 (s, 3H), 2.06 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.3, 167.5, 144.1, 138.2, 137.4, 137.0, 132.8, 130.8, 129.0, 127.5, 125.9, 123.3, 117.4, 51.6, 43.2, 38.0, 27.2, 21.3, 20.9, 14.2, 11.8.

**(ESI)** calcd for $C_{23}H_{28}NO_3$ $(M+H)^+$: 366.2069 found: 366.2069

**methyl (*R*,*E*)-3-(1-(2-(diethylcarbamoyl)phenyl)naphthalen-2-yl)acrylate 3pa**




A purification by flash chromatography in petroleum ether : ethyl acetate= 5 : 1 to give **3pa** as yellow oil (28.6 mg, 74%). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm) with tr = 5.2 min (major), 4.7 min (minor): 91% ee.

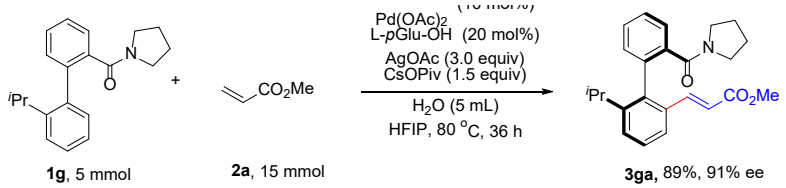
The absolute stereochemistry was assigned by analogy to compound **3ga.**

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.97 – 7.68 (m, 3H), 7.64 – 7.19 (m, 8H), 6.19 (dd, J = 211.4, 15.8 Hz, 1H), 3.64 (d, J = 57.1 Hz, 3H), 3.56 – 2.57 (m, 4H), 1.15 – 0.92 (m, 3H), 0.72 – 0.22 (m, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 169.9, 167.5, 148.3, 143.7, 138.0, 137.0, 135.4, 134.7, 134.0, 131.8, 130.6, 129.1, 128.8, 128.6, 128.2, 127.9, 127.8, 127.5, 127.1, 126.4, 126.2, 125.7, 124.7, 118.2, 51.7, 42.6, 37.9, 27.2, 14.1, 14.1, 11.5.

**(ESI)** calcd for $C_{23}H_{28}NO_3$ $(M+H)^+$: 388.1913 found: 388.1915

## 2.4 Procedure for 5 mmol Scale Reaction of 3ga

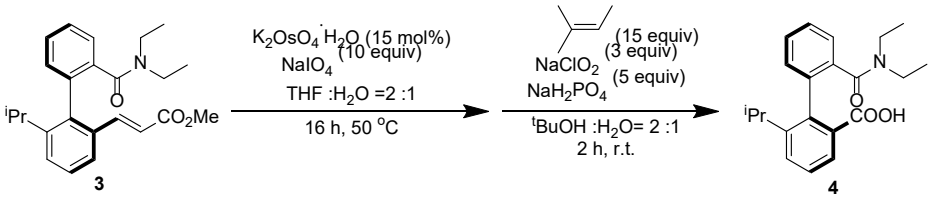



**1g**, 5 mmol **2a**, 15 mmol **3ga,** 89%, 91% ee

To a 100 mL Schlenk tube was added substrate **1g** (1.46 g, 5.0 mmol), **2a** (1.92g, 15 mmol), L-pGlu-OH (129 mg, 20 mol%), CsOPiv (1.75 g, 7.5 mmol), $Pd(OAc)_2$ (110 mg, 10 mol%), AgOAc (2.49g, 15 mmol), $H_2O$ (5 mL) and HFIP (50 mL). The reaction mixture was stirred at 80 °C (oil bath) for 36 h. After cooling to room temperature, the the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by flash chromatography in petroleum ether : ethyl acetate = 5 : 1 to give **3ga** as yellow solid (1.68g, 89% 91% ee)

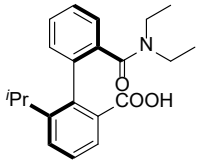
## 2.5 Transformations and Applications of the Olefination Reaction

## 2.5.1 Prepration of Chiral Carboxylic Acids




**General Preparation C**: To a solution of **3** (0.1 mmol, 1 equiv) in THF (1.8 mL) and $H_2O$ (0.9 mL), $K_2OsO_4 \cdot 2H_2O$ (15 mol %) and $NaIO_4$ (10 equiv) were added at 25 °C, the reaction mixture was stirred at 50 °C for 16 h. The reaction mixture was then quenched with sat. aqueous $Na_2S_2O_3$ (5 mL) and stirred vigorously for 30 min. The biphasic reaction mixture was extracted with EtOAc (3 × 20 mL) and then the combined organic layers were washed with brine (20 mL), dried over $Na_2SO_4$, and concentrated. To a solution of crude product and 2-methyl-2-butene (10 equiv) in *tert*-BuOH:THF (0.7:0.3 mL) were added aqueous solutions of $NaH_2PO_4$ (0.5 M, 5.0 equiv) and $NaClO_2$ (1.0 M, 3.0 equiv) sequentially at 0 °C. After stirring vigorously at room temperature for 1 hour, the resulting reaction mixture was quenched by the addition of 1.0 M aqueous solution of HCl (2.5 mL) and diluted with EtOAc (3.0 mL). The organic layer was separated, and the aqueous layer was further extracted with EtOAc (2 × 3.0 mL). The combined organic layers were then extracted with a 2.0 M aqueous solution of NaOH (3 × 5.0 mL) before reacidifying by addition of a 1.0 M aqueous solution of HCl. The aqueous layer was extracted with EtOAc (3 × 15 mL) and the combined organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo to give **4.**

**(*R*)-2'-(diethylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-carboxylic acid 4aa**




**4aa** was prepared following General Preparation **C** and purified by flash chromatography in petroleum ether : ethyl acetate: acetic acid = 50: 10: 1 to give as white solid. (84% yield, 0.57 g for 5 mmol scale).The ee value was determined by HPLC analysis on a Chiralcel NQ column (hexane/isopropanol = 80/20, flow = 1 mL/min, 254 nm) with tr = 15.9 min (major), 13.9 min (minor): 90% ee.

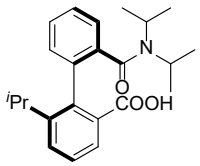
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 14.08 (brs, 1H), 7.54 – 7.33 (m, 6H), 7.25 (d, *J* = 1.7 Hz, 1H), 3.70 – 3.60 (m, 2H), 3.24 - 3.13 (m, 2H), 2.45 (hept, *J* = 6.9 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.97 (dd, *J* = 8.5, 6.8 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.0, 171.4, 146.2, 137.9, 136.8, 134.1, 133.5, 131.6, 130.6, 128.9, 127.9, 126.9, 125.7, 125.4, 43.3, 39.6, 30.2, 25.3, 22.7, 14.2, 12.3.

**(ESI)** calcd for $C_{21}H_{24}NO_3^-$ $(M-H)^-$: 338.1756 found: 338.1756

**Melting Point:** 192.1 - 192.3 °C

**(*R*)-2'-(diisopropylcarbamoyl)-6-isopropyl-[1,1'-biphenyl]-2-carboxylic acid 4fa**




**4fa** was prepared following General Preparation **C** and purified by flash chromatography in petroleum ether : ethyl acetate: acetic acid = 50: 10: 1 to give as white solid. (83% yield, 0.62 g for 5 mmol scale).The ee value was determined by HPLC analysis on a Chiralcel IBN-5 column (hexane/isopropanol = 90/10, flow = 1.2 mL/min, 254 nm) with tr = 24.2 min (major), 22.2 min (minor): 90% ee.

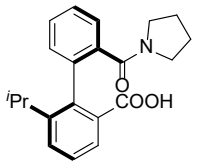
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 14.42 (brs, 1H), 7.50 – 7.37 (m, 5H), 7.34 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 4.32 (hept, *J* = 6.6 Hz, 1H), 3.49 (hept, *J* = 6.9 Hz, 1H), 2.55 (hept, *J* = 6.8 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 171.7, 171.5, 145.4, 138.0, 137.2, 135.0, 134.0, 132.6, 130.3, 128.7, 127.8, 126.5, 125.8, 125.7, 51.5, 47.8, 30.2, 25.7, 23.1, 21.7, 20.8, 20.2, 20.1.

**(ESI)** calcd for $C_{23}H_{28}NO_3^-$ $(M-H)^-$: 366.2096 found: 366.2096

**Melting Point:** 211.3 - 211.5 ºC

**(*R*)-6-isopropyl-2'-(pyrrolidine-1-carbonyl)-[1,1'-biphenyl]-2-carboxylic acid 4ga**




**4ga** was prepared following General Preparation **C** and purified by flash chromatography in petroleum ether : ethyl acetate: acetic acid = 50: 10: 1 to give as white solid. (89% yield, 0.21 g for 2 mmol scale).The ee value was determined by HPLC analysis on a Chiralcel NT(2) column (hexane/isopropanol = 80/20, flow = 1.2 mL/min, 254 nm) with tr = 8.1 min (major), 9.6 min (minor): 91% ee.

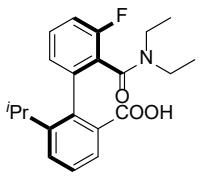
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 14.11 (brs, 1H), 7.51 – 7.34 (m, 6H), 7.24 – 7.17 (m, 1H), 3.69 (td, *J* = 10.0, 6.5 Hz, 1H), 3.58 (ddd, *J* = 12.2, 7.6, 4.0 Hz, 1H), 3.50 – 3.30 (m, 2H), 2.45 (p, *J* = 6.9 Hz, 1H), 2.09 – 1.76 (m, 4H), 1.09 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 171.4, 170.3, 146.1, 137.9, 136.6, 134.5, 133.9, 131.5, 130.8, 128.88, 128.0, 127.2, 126.4, 125.7, 49.6, 46.5, 30.3, 26.3, 24.8, 24.4, 23.5.

**(ESI)** calcd for $C_{21}H_{22}NO_3^-$ $(M-H)^-$: 336.1600 found: 336.1601

**Melting Point:** 191.6 - 192.0 ºC

**(*R*)-2'-(diethylcarbamoyl)-3'-fluoro-6-isopropyl-[1,1'-biphenyl]-2-carboxylic acid 4la**



**4la** was prepared following General Preparation **C** and purified by flash chromatography in petroleum ether : ethyl acetate: acetic acid = 50: 10: 1 to give as white solid. (80% yield, 127 mg for 1.5 mmol scale) The ee value was determined by HPLC analysis on a Chiralcel NT(2) column (hexane/isopropanol = 90/10, flow = 1.2 mL/min, 254 nm) with tr = 12.7 min (major), 20.7 min (minor): 87% ee.

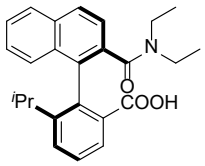
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 13.93 (brs, 1H), 7.50 – 7.35 (m, 4H), 7.18 (t, *J* = 8.9 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 3.59 (tq, *J* = 13.6, 7.4 Hz, 2H), 3.28 - 3.18 (m, 2H), 2.47 (hept, *J* = 6.7 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 4H), 1.20 (d, *J* = 6.9 Hz, 3H), 0.95 (dt, *J* = 7.2, 3.8 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$,** ppm; list of signals, C-F coupling not resolved**)** δ 171.1, 166.8, 146.0, 136.9, 132.0, 131.9, 129.3, 127.3, 126.9, 125.9, 115.8, 115.6, 43.5, 39.2, 30.2, 25.6, 22.5, 13.3, 12.3.

**(ESI)** calcd for $C_{21}H_{23}FNO_3^-$ $(M-H)^-$: 356.1662 found: 356.1661

**Melting Point:** 254.1 - 254.7 °C

**(*R*)-2-(2-(diethylcarbamoyl)naphthalen-1-yl)-3-isopropylbenzoic acid 4ma**




**4ma** was prepared following General Preparation **C** and purified by flash chromatography in petroleum ether : ethyl acetate: acetic acid = 50: 10: 1 to give as white solid. (85% yield, 240 mg) The ee value was determined by HPLC analysis on a Chiralcel NQ column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 15.9 min (major), 22.5 min (minor): 85% ee.

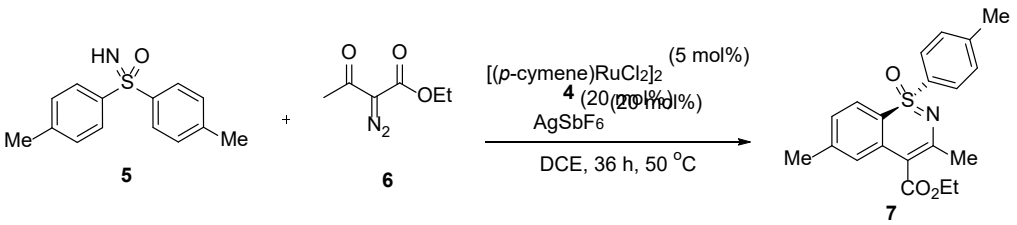
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 14.19 (brs, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.46 (m, 4H), 7.46 – 7.33 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 1H), 3.92 – 3.53 (m, 2H), 3.27 - 3.16 (m, 2H), 2.36 (h, *J* = 6.8 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.7, 171.2, 147.1, 137.7, 135.8, 134.1, 133.3, 131.5, 130.7, 129.30, 128.8, 128.2, 127.8, 127.7, 127.5, 127.1, 126.0, 121.9, 43.4, 39.6, 30.4, 25.4, 23.5, 14.1, 12.4.

**(ESI)** calcd for $C_{25}H_{26}NO_3^-$ $(M-H)^-$: 388.1913 found: 388.1914

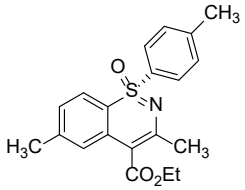
**Melting Point:** 311.1 - 311.4 °C

## 2.5.2 Ru(II)-Catalyzed Asymmetric C–H Functionalization




According to the methods previously reported by the Shi group.[2] To a 10 mL Schlenk tube was added sulfoximines **5** (0.10 mmol), diazoniums **6** (25μL, 0.15 mmol), **4** (20 mol%), $AgSbF_6$ (6.9 mg, 20 mol%), [(*p*-cymene)$RuCl_2$]$_2$ (2.0 mg, 2.5 mol%) and DCE (1.0 mL). The reaction flask was degassed three times with $N_2$. Then stirred at 50 ℃ (aluminum heat transfer block) for 36 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the desired product **7**.[1]

**ethyl (R)-3,6-dimethyl-1-(p-tolyl)-1l4-benzo[e][1,2]thiazine-4-carboxylate 1-oxide 7**




**7** was purified by flash chromatography in petroleum ether : ethyl acetate= 6:1 to give as white solid. The ee value was determined by HPLC analysis on a Chiralcel AS-H column (hexane/isopropanol = 60/40, flow = 1.0 mL/min) with tr = 7.7 min (minor), 9.7 min (major): 72% ee.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, J = 8.3 Hz, 2H), 7.48 (s, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.2 Hz, 1H), 7.04 (dd, J = 8.3, 1.6 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 2.38 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H).

## 2.6 Measurements of Rotation Barriers

### 2.6.1 Experimental Procedure

Diaryl (0.1 mmol) and a magnetic stir bar were added into a short test tube to which a rubber septum was mounted. The air in the tube was then carefully flushed with argon via a syringe needle and an argon balloon is remained to equalize the pressure during the following process. Solvent (5 mL) was added to dissolve the solid. The test tube was submerged into an oil bath preheated to the desired temperature. About 3 minutes later, 0.1 mL of solution was extracted via a long needle, transferred into a small vial and dissolved in 1.5 mL of HPLC grade isopropanol. The solution was filtered before HPLC analysis. The time of each extraction was precisely recorded.

### 2.6.2 Data processing

According to the reversible first-order reaction dynamics, the rate constant of racemization krac is the slope of the function of -ln ee to time

$$-\ln\ ee = k_{rac}t + C$$

where $C$ is a constant.

The Gibbs free energy is degenerated in an achiral environment for a pair of enantiomers. Therefore, the forward rate constant is equal to the backward one.

$$k_{\mathrm{atrp+}} = k_{\mathrm{atrp-}}$$

Since an atropisomerization of one molecule eliminates a molecule of one configuration and adds one molecule to the other configuration, the rate constant of atropisomerization $k_{\mathrm{atrp}}$ is half of $k_{\mathrm{rac}}$.

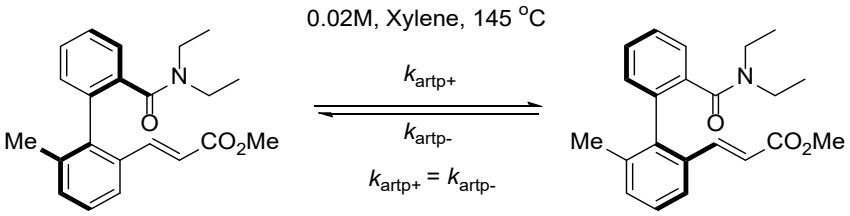
$$k_{\mathrm{atrp}} = 1/2\ k_{\mathrm{rac}}$$

The energy barrier of atropisomerization can be calculated by Erying equation

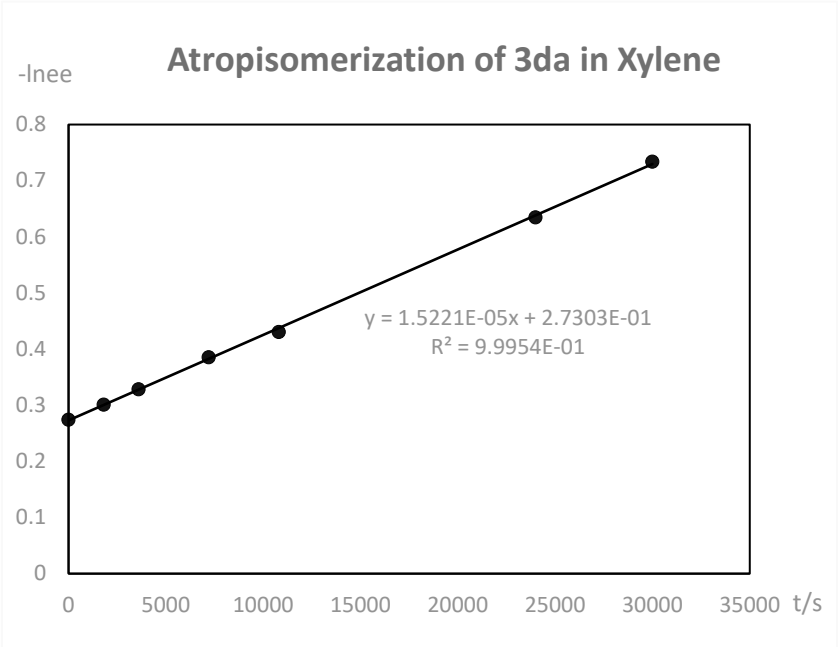
$$\Delta G^{\neq}_{\mathrm{atrp}} = -RT\ln\frac{k_{\mathrm{artp}}h}{k_B T}$$

where R is ideal gas constant, T is absolute temperature, h is Planck constant, $k_B$ is Boltzmann constant.

## Data for 3da in Xylene




| N° | Δt/s | ee/% | -ln ee |
|---|---|---|---|
| 1 | 0 | 76 | 0.2744 |
| 2 | 1800 | 74 | 0.3011 |
| 3 | 3600 | 72 | 0.3285 |
| 4 | 7200 | 68 | 0.3857 |
| 5 | 10800 | 65 | 0.4308 |
| 6 | 24000 | 53 | 0.6349 |
| 7 | 30000 | 48 | 0.7340 |



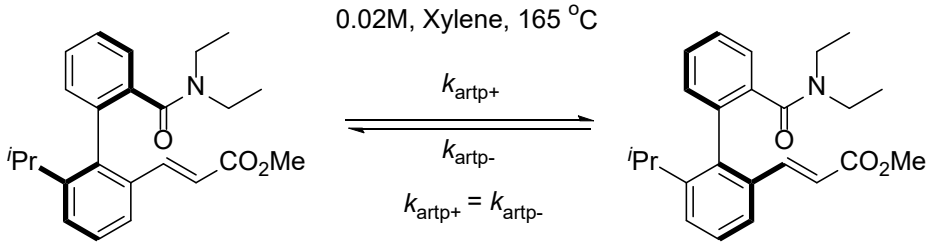

$k_{rac}$（145°C） $= 0.0000152\ s^{-1}$

$k_{artp}$（145°C） $= 0.0000076\ s^{-1}$

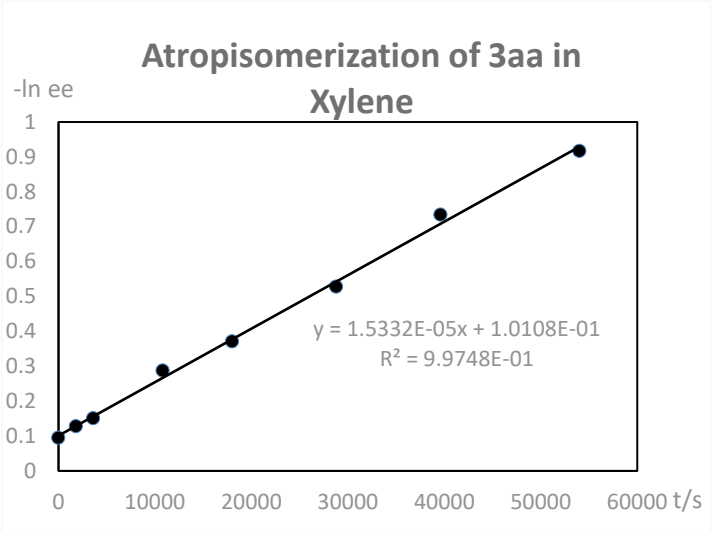
$\Delta G^{\neq}_{artp} = 144.6\ kJ/mol = 34.54\ kcal/mol$

$t_{1/2}(145^{o}C) = \frac{\ln 2}{k_{rac}} = 45601 s^{-1}$

## Data for 3aa in Xylene




| N° | Δt/s | ee/% | -ln ee |
|---|---|---|---|
| 1 | 0 | 91 | 0.0943 |
| 2 | 1800 | 88 | 0.1278 |
| 3 | 3600 | 86 | 0.1508 |
| 4 | 10800 | 75 | 0.2877 |
| 5 | 18000 | 69 | 0.3710 |
| 6 | 28800 | 59 | 0.5276 |
| 7 | 39600 | 48 | 0.7340 |
| 8 | 54000 | 40 | 0.9162 |




$k_{rac}$（165°C） $= 0.0000153\ s^{-1}$

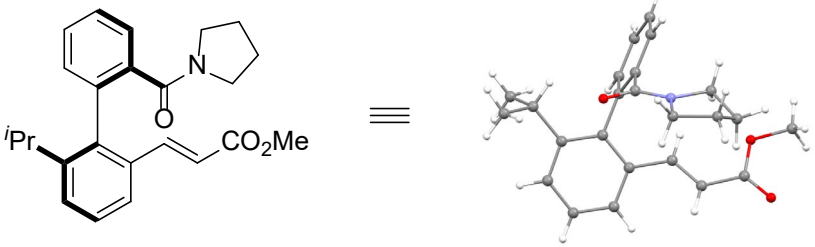
$k_{artp}$（165°C） $= 0.0000076\ s^{-1}$

$\Delta G^{\neq}_{artp} = 151.7\ kJ/mol = 36.24\ kcal/mol$

$$t_{1/2}(160^{\circ}C) = \frac{\ln 2}{k_{rac}} = 45304 s^{-1}$$

# 3.Crystal Structure

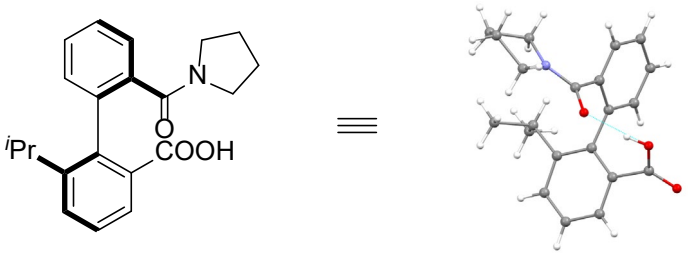
A single crystal of **3ga** suitable for X-ray crystallography was obtained by crystallization via evaporation from its hexane/ethyl acetate solution.




| **Compound** | **3ga** |
|---|---|
| Formula | $C_{24}H_{27}NO_3$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.211 |
| $\mu$/mm$^{-1}$ | 0.401 |
| Formula Weight | 377.46 |
| Colour | colourless |
| Shape | needle-shaped |
| Size/mm$^3$ | 0.11×0.05×0.04 |
| $T$/K | 170 |
| Crystal System | triclinic |
| Flack Parameter | 0.05(4) |
| Hooft Parameter | 0.03(4) |
| Space Group | $P$1 |
| $a$/Å | 7.9599(3) |
| $b$/Å | 11.3575(5) |
| $c$/Å | 11.6102(5) |
| $\alpha$/° | 86.482(2) |
| $\beta$/° | 83.174(2) |
| $\gamma$/° | 83.793(2) |
| V/Å$^3$ | 1034.81(7) |
| $Z$ | 2 |
| $Z'$ | 2 |
| Wavelength/Å | 1.34139 |
| Radiation type | GaK□ |
| $\Theta_{min}$/° | 3.339 |
| $\Theta_{max}$/° | 60.678 |
| Measured Refl's. | 66610 |
| Indep't Refl's | 8998 |
| Refl's I≥2 $\sigma$(I) | 8795 |

| | |
|---|---|
| $R_{int}$ | 0.0403 |
| Parameters | 511 |
| Restraints | 3 |
| Largest Peak | 0.156 |
| Deepest Hole | -0.162 |
| GooF | 1.079 |
| $wR_2$ (all data) | 0.085 |
| $wR_2$ | 0.0846 |
| $R_1$ (all data) | 0.0344 |
| $R_1$ | 0.0338 |

A single crystal of **4ga** suitable for X-ray crystallography was obtained by crystallization via evaporation from its hexane/ethyl acetate solution.




| **Compound** | **4ga** |
|---|---|
| Formula | $C_{21}H_{23}NO_3$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.241 |
| $\mu$/mm$^{-1}$ | 0.422 |
| Formula Weight | 337.4 |
| Colour | colourless |
| Shape | block-shaped |
| Size/mm$^3$ | 0.15×0.09×0.05 |
| $T$/K | 170 |
| Crystal System | orthorhombic |
| Flack Parameter | 0.03(5) |
| Hooft Parameter | 0.02(5) |
| Space Group | $P2_12_12_1$ |
| $a$/Å | 8.6551(4) |
| $b$/Å | 10.6157(4) |
| $c$/Å | 19.6488(8) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| V/Å$^3$ | 1805.33(13) |
| $Z$ | 4 |
| $Z'$ | 1 |

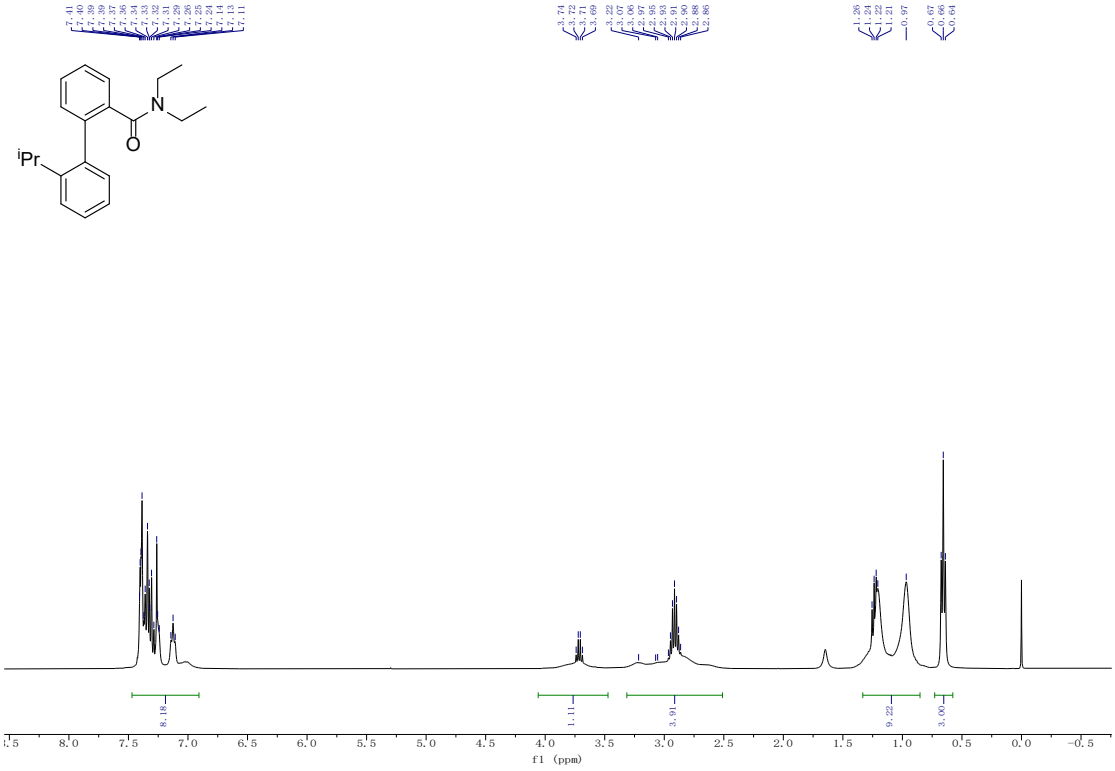
| | |
|---|---|
| Wavelength/Å | 1.34139 |
| Radiation type | GaK□ |
| $\Theta_{min}/^{\circ}$ | 3.915 |
| $\Theta_{max}/^{\circ}$ | 60.778 |
| Measured Refl's. | 31307 |
| Indep't Refl's | 4147 |
| Refl's I≥2 $\sigma$(I) | 4035 |
| $R_{int}$ | 0.0307 |
| Parameters | 229 |
| Restraints | 0 |
| Largest Peak | 0.121 |
| Deepest Hole | -0.181 |
| GooF | 1.092 |
| $wR_2$ (all data) | 0.0776 |
| $wR_2$ | 0.0767 |
| $R_1$ (all data) | 0.0311 |
| $R_1$ | 0.0302 |

# 4. References

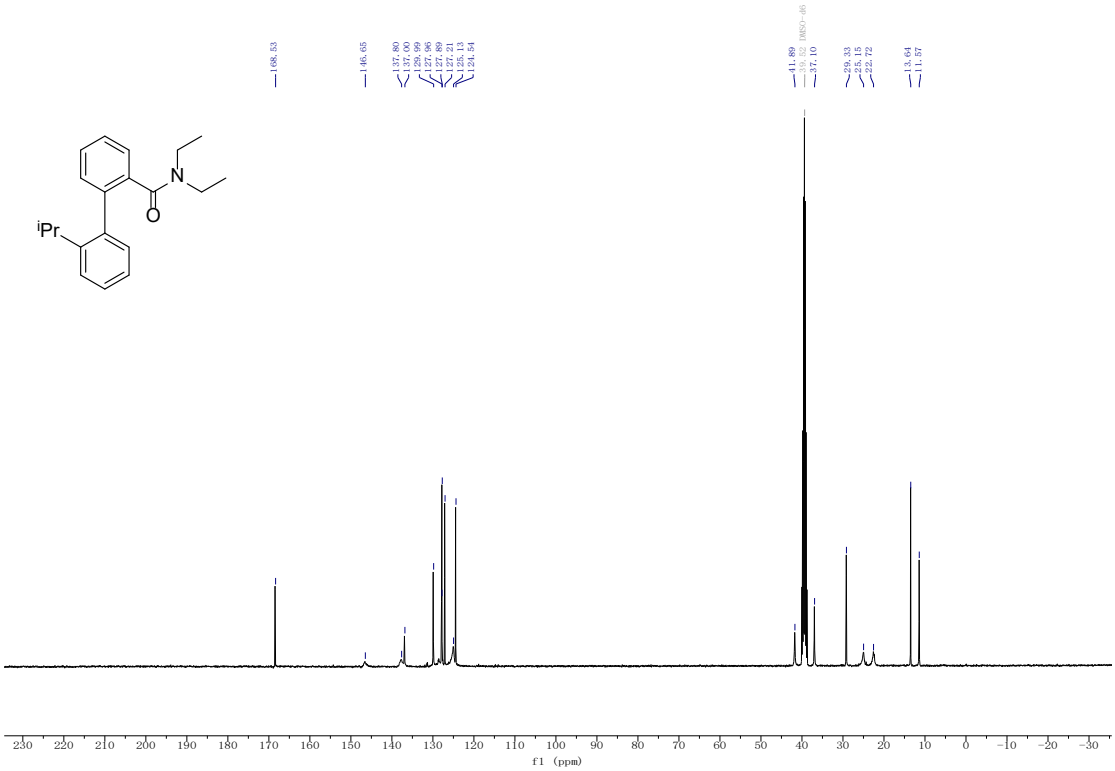
1. J.-Y. Li, P.-P. Xie, T. Zhou, P.-F. Qian, Y.-B. Zhou, H.-C. Li, X. Hong and B.-F. Shi, Ir(III)-Catalyzed Asymmetric C–H Activation/Annulation of Sulfoximines Assisted by the Hydrogen-Bonding Interaction, *ACS Catal.* 2022, **12**, 9083-9091.

# 5.NMR Spectra

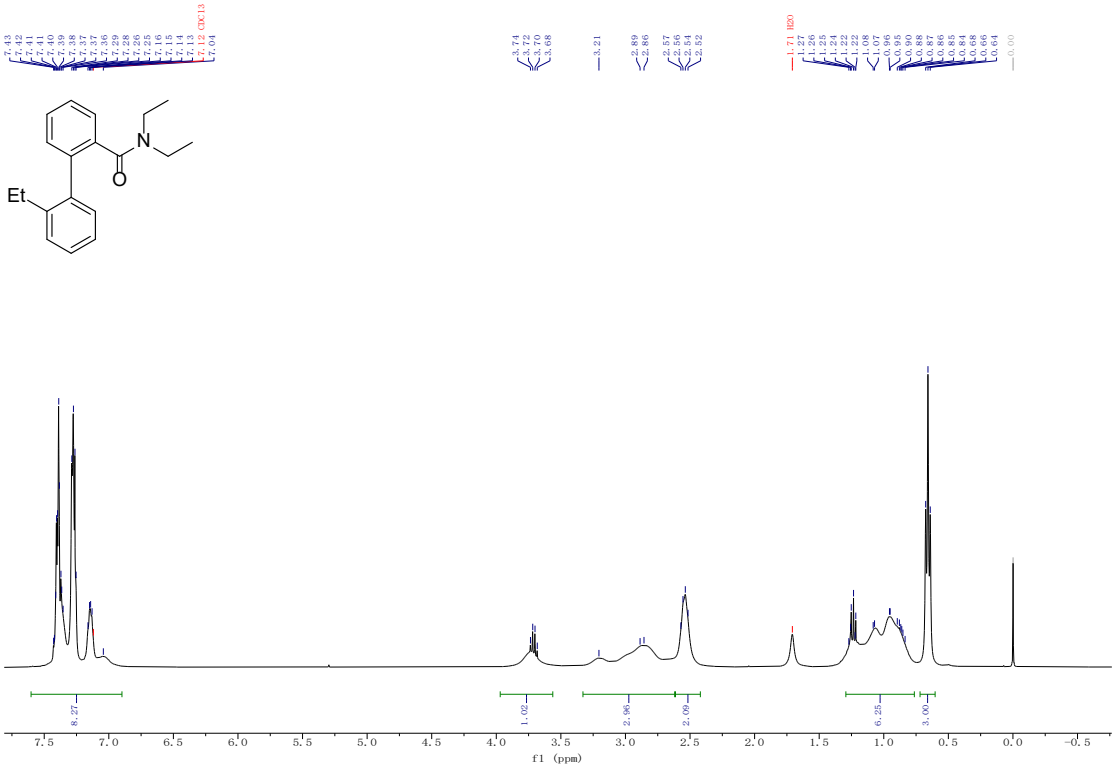
### 1a, $^{1}$H NMR (400 MHz, $CDCl_3$)



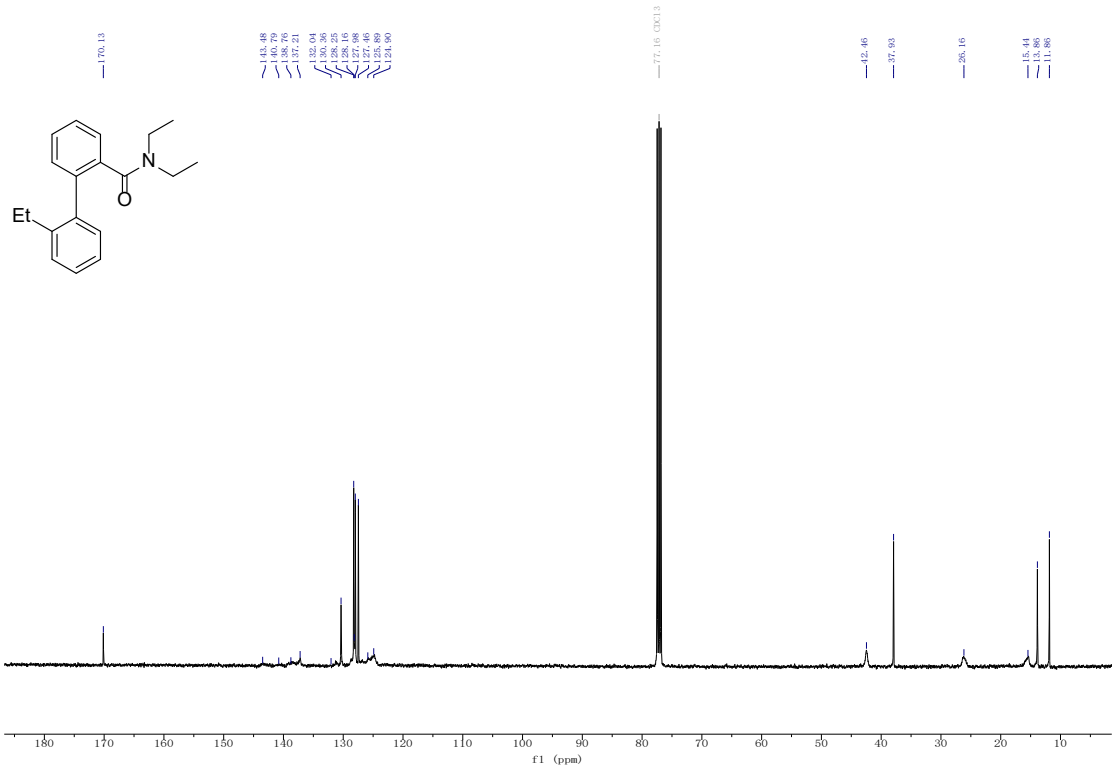

### 1a, $^{13}$C NMR (101 MHz, $d_6$-DMSO)



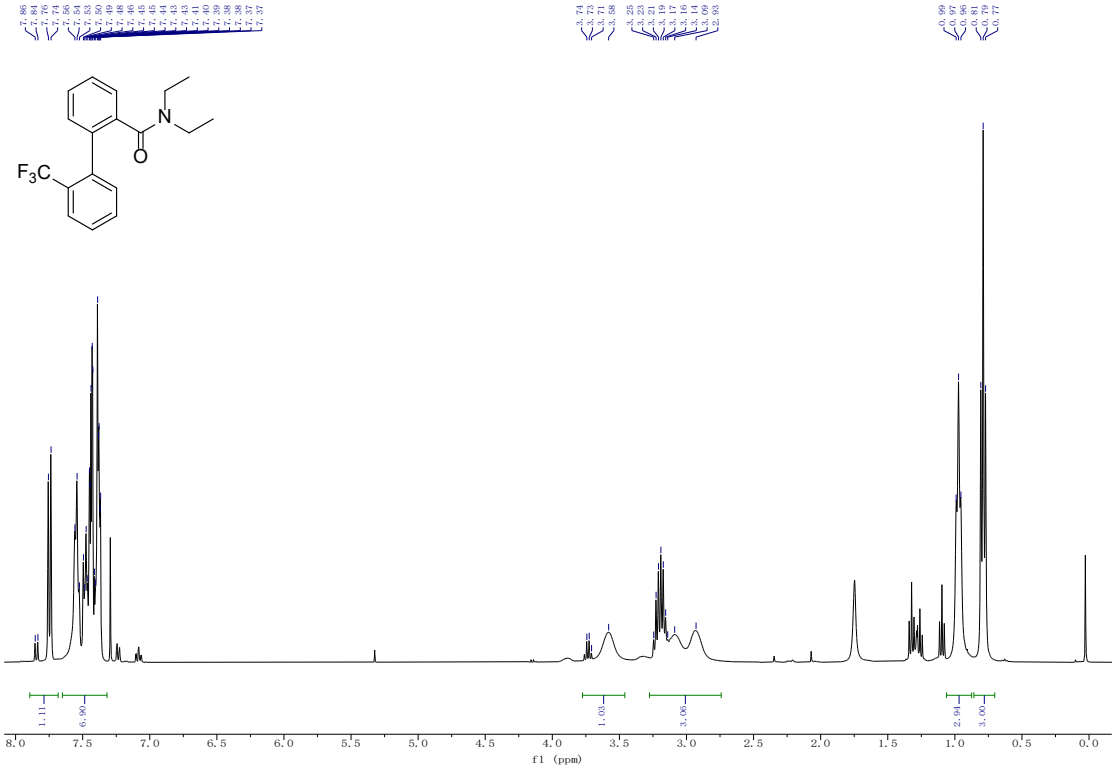
**1b, $^{1}$H NMR (400 MHz, $CDCl_3$)**



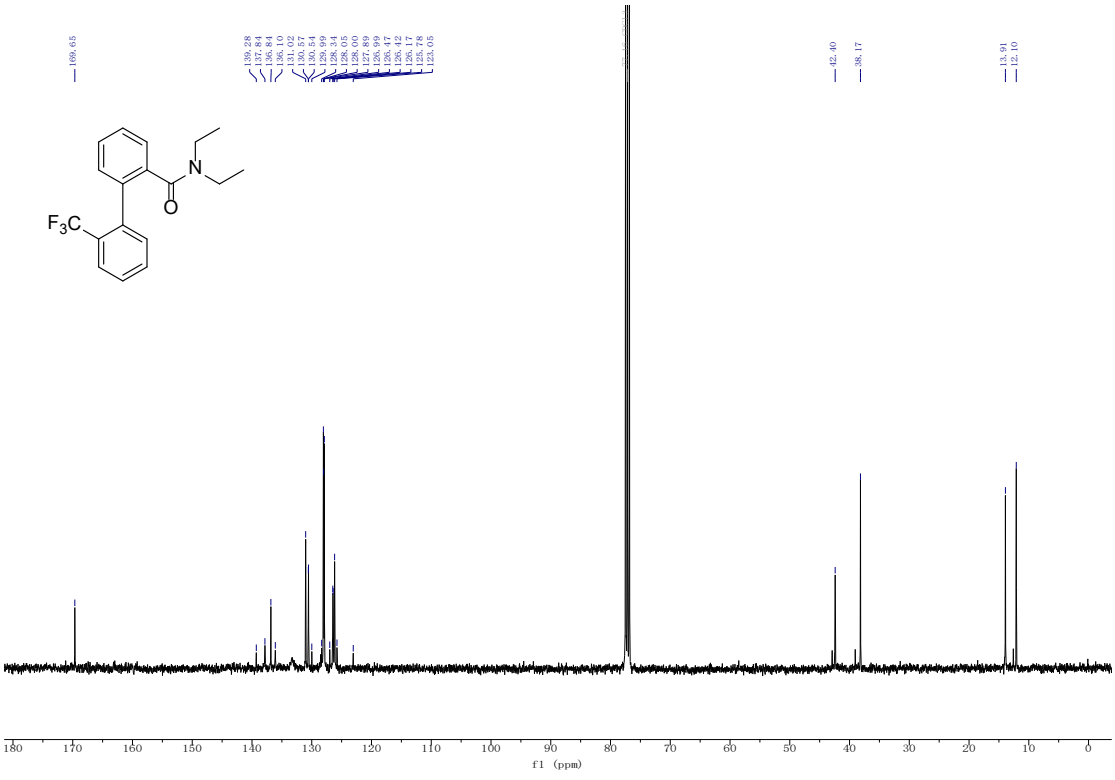

**1b, $^{13}$C NMR (101 MHz, $CDCl_3$)**



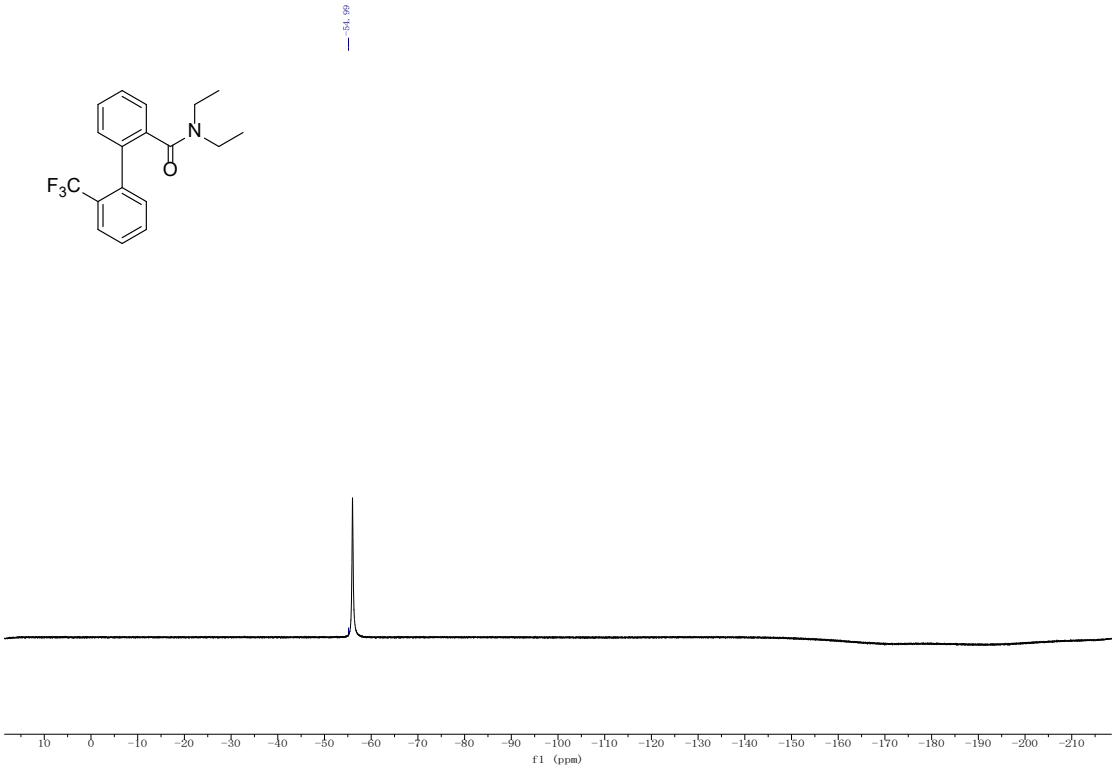
## 1c, $^{1}$H NMR (400 MHz, $CDCl_3$)



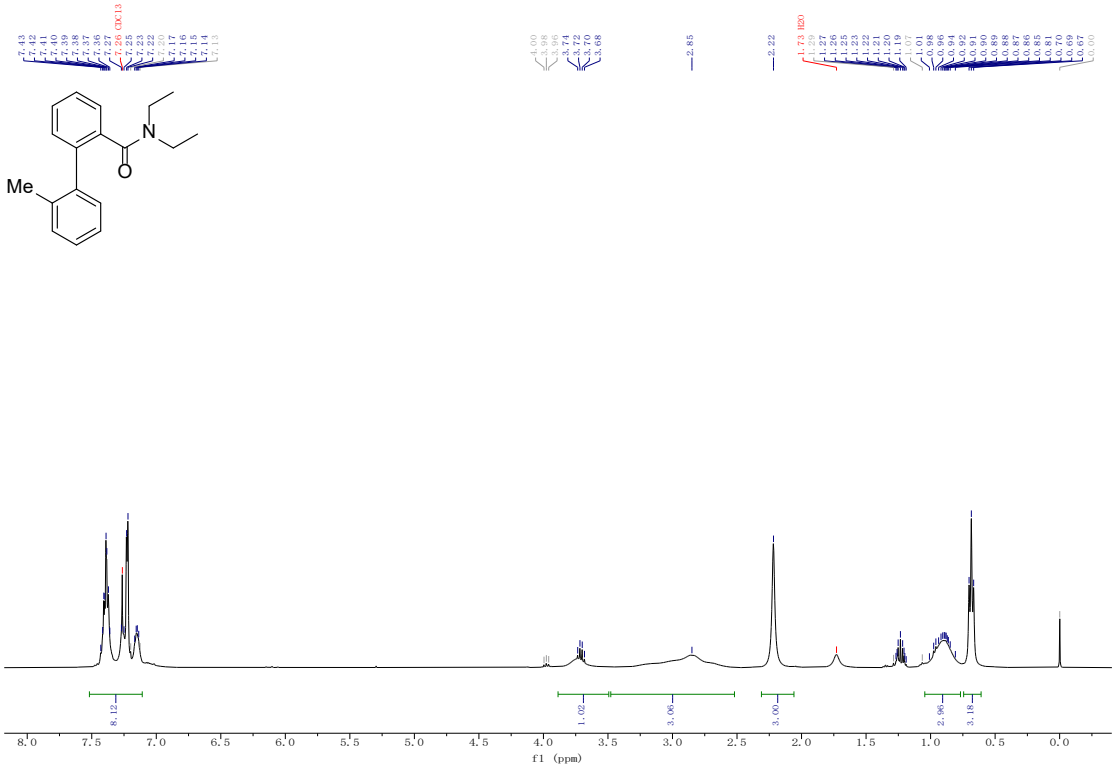

## 1c, $^{13}$C NMR (101 MHz, $CDCl_3$)



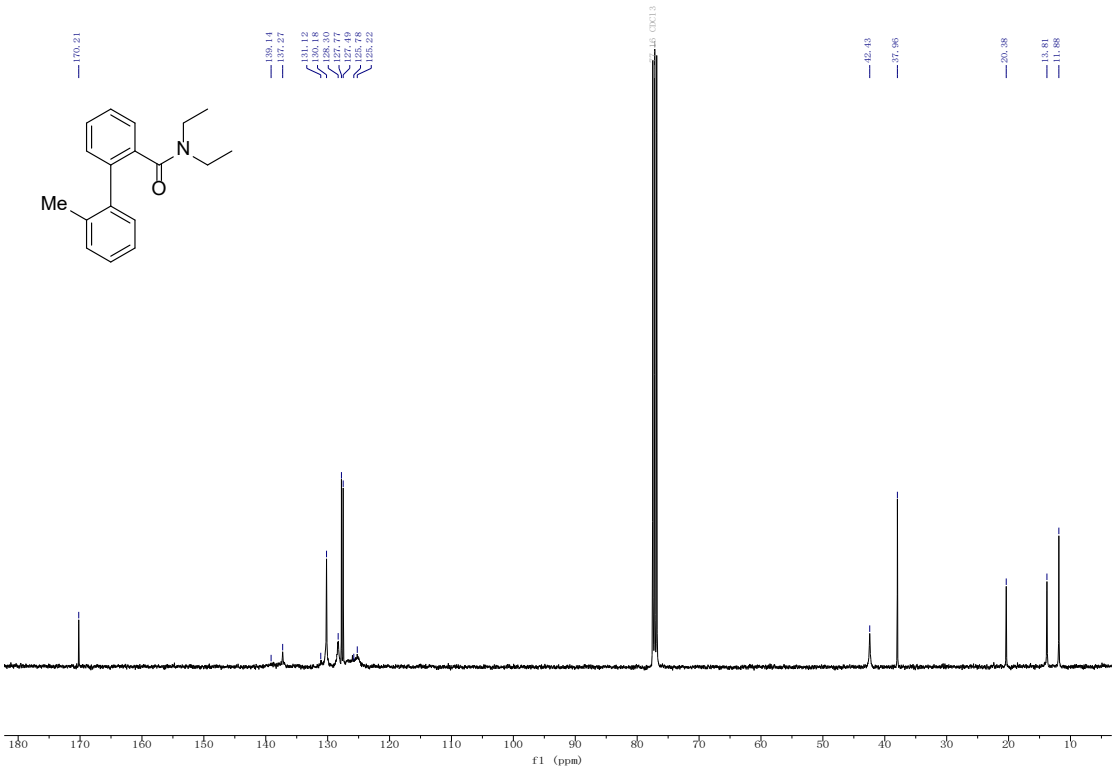
**1c, $^{19}F$ NMR (376 MHz, $CDCl_3$)**



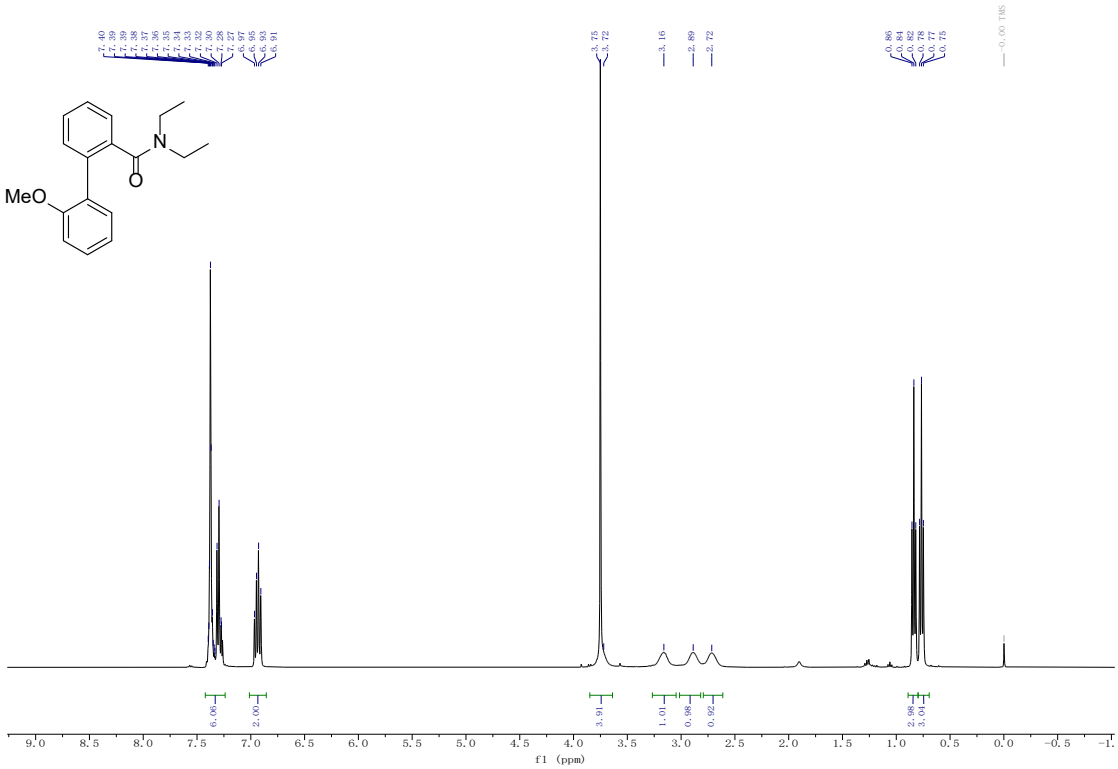
## 1d, $^{1}$H NMR (400 MHz, $CDCl_3$)



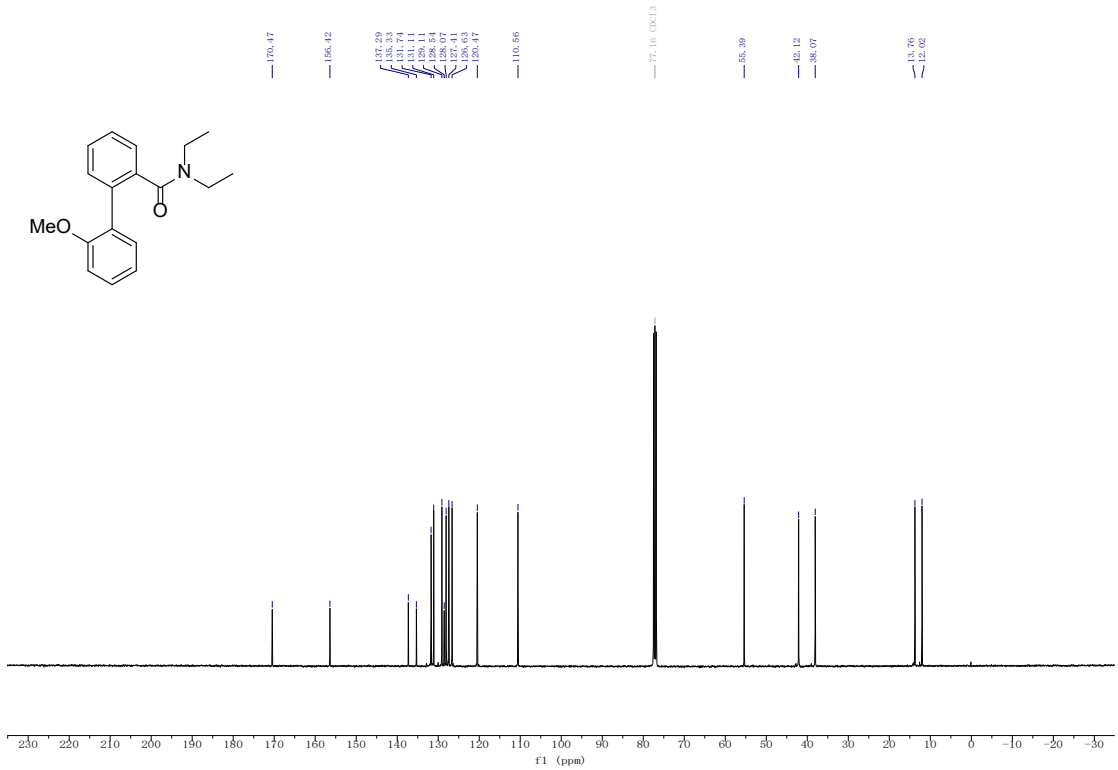

## 1d, $^{13}$C NMR (101 MHz, $CDCl_3$)



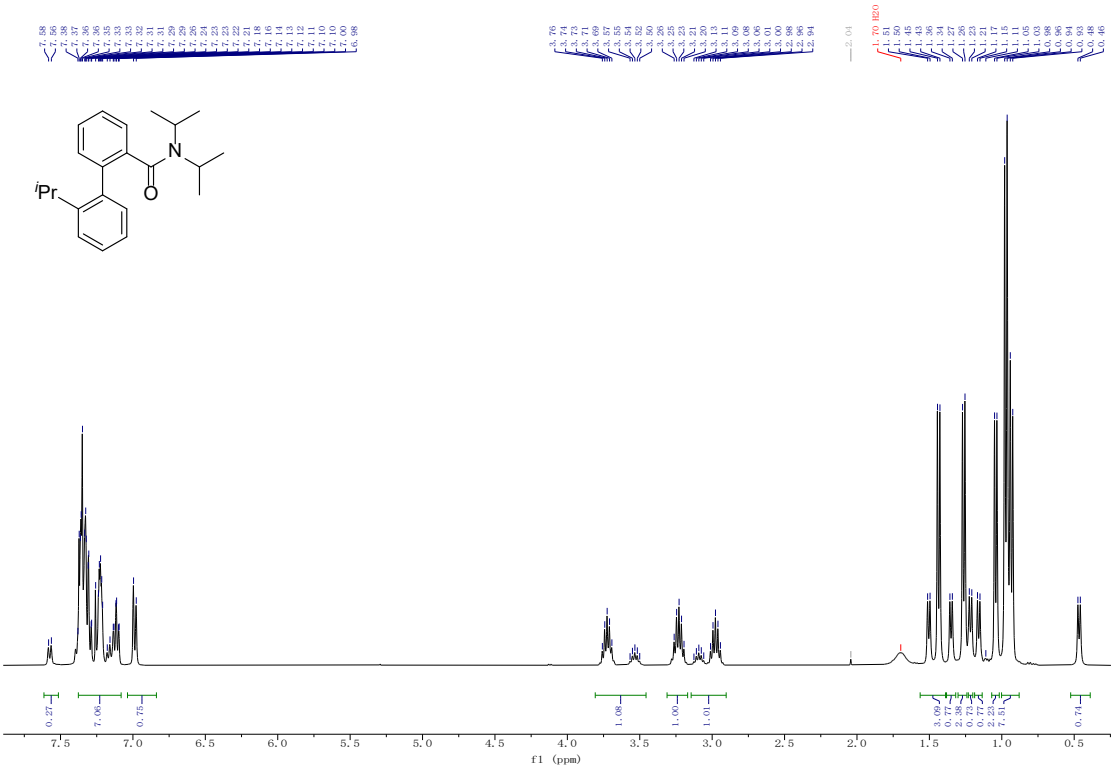
**1e, $^{1}$H NMR (400 MHz, $CDCl_3$)**



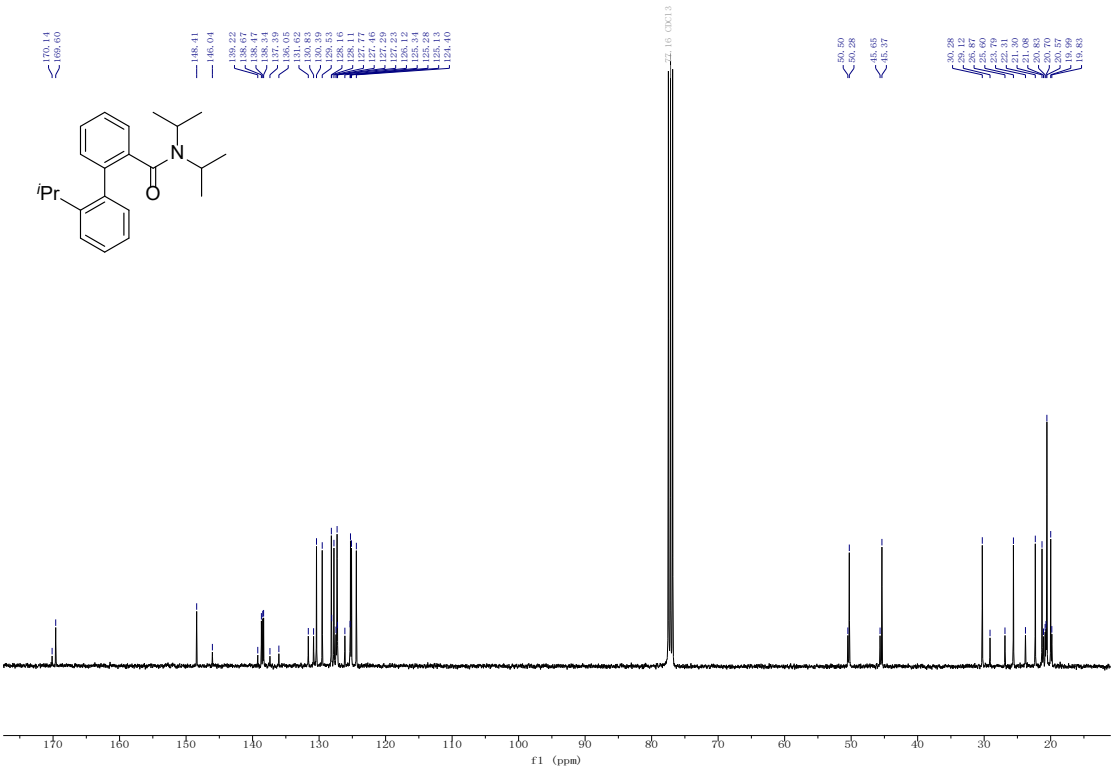

**1e, $^{13}$C NMR (101 MHz, $CDCl_3$)**



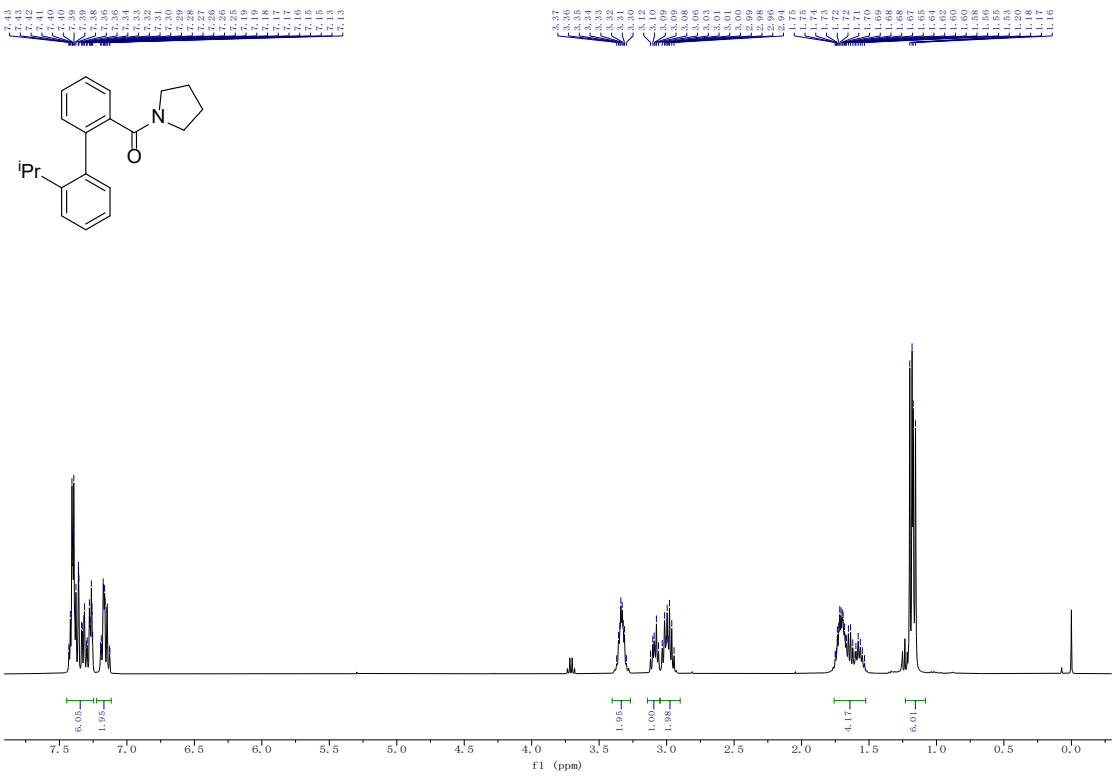
## 1f, $^{1}$H NMR (400 MHz, $CDCl_3$)



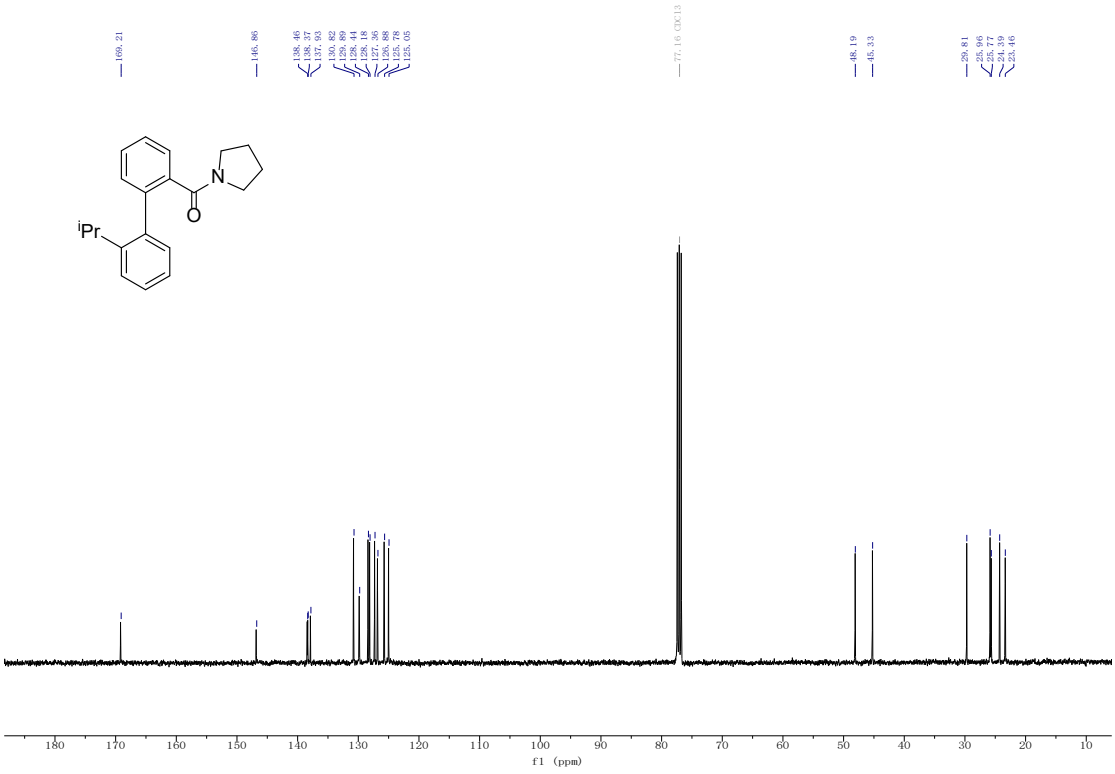

## 1f, $^{13}$C NMR (101 MHz, $CDCl_3$)



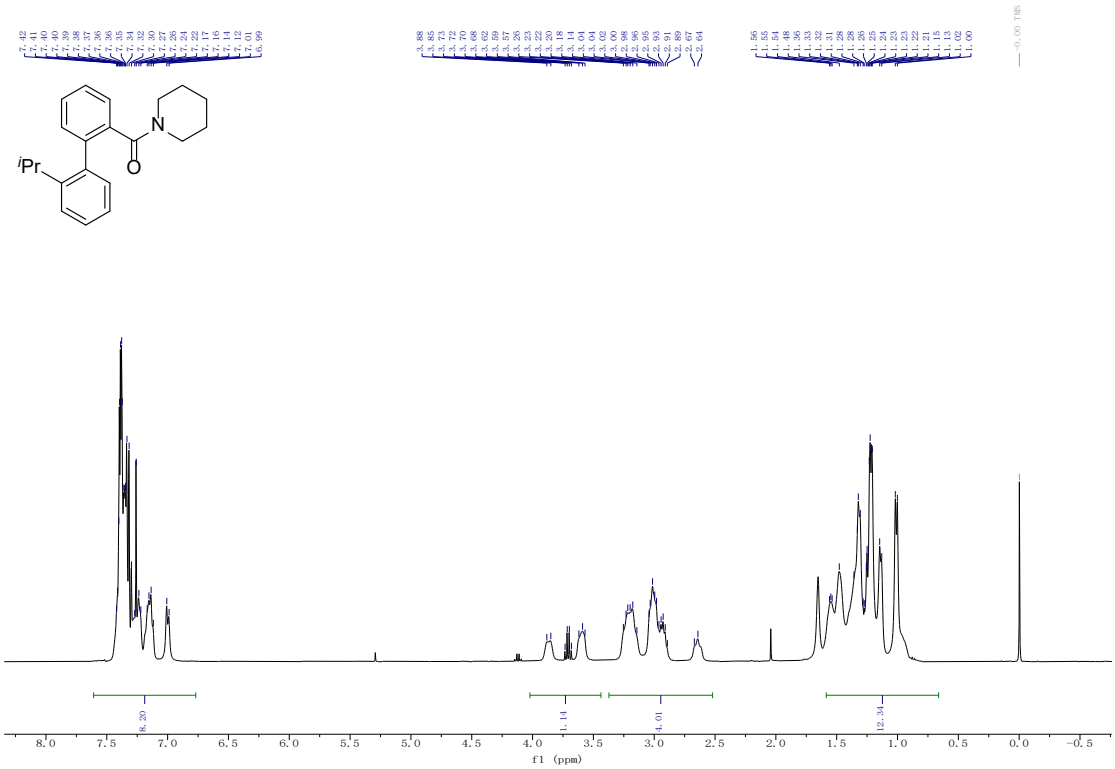
**1g, $^{1}$H NMR (400 MHz, $CDCl_3$)**



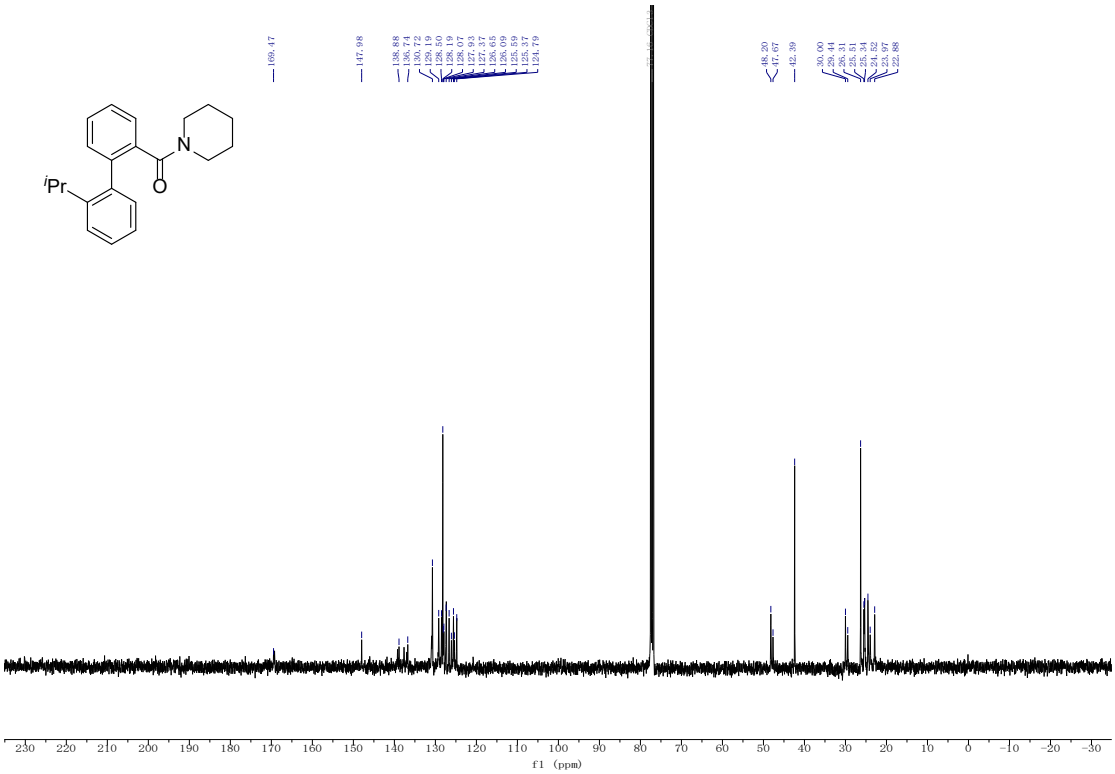

**1g, $^{13}$C NMR (101 MHz, $CDCl_3$)**



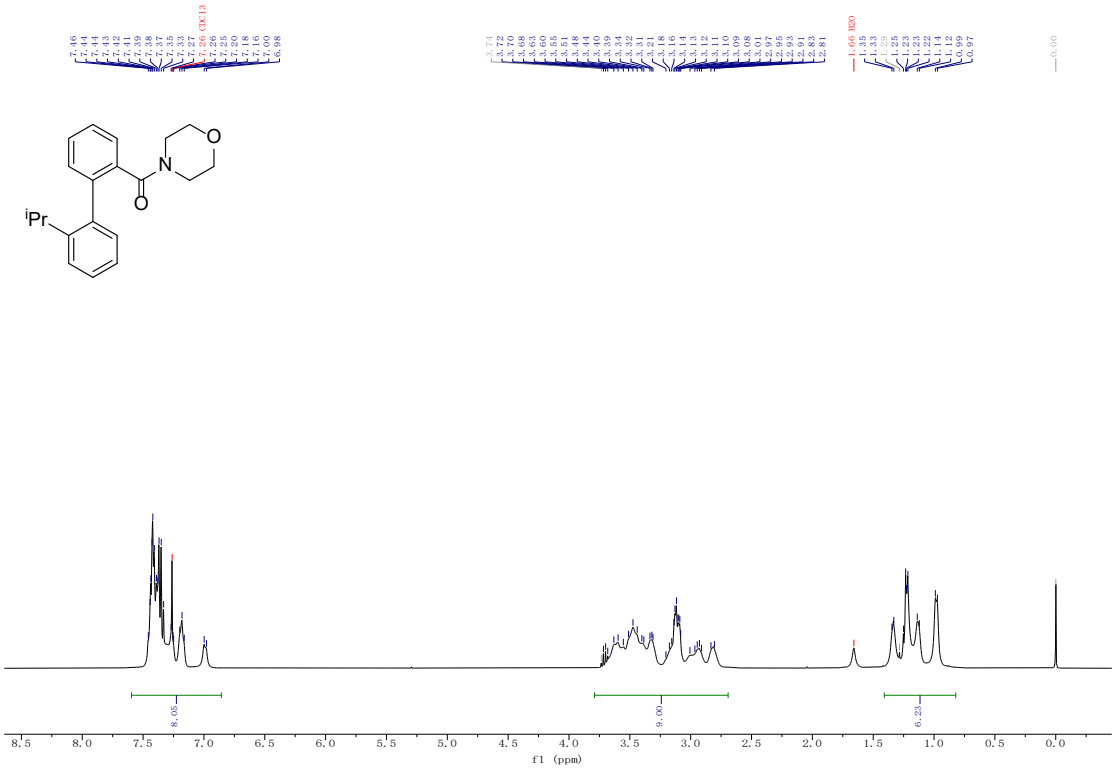
**1h, $^{1}$H NMR (400 MHz, $CDCl_3$)**



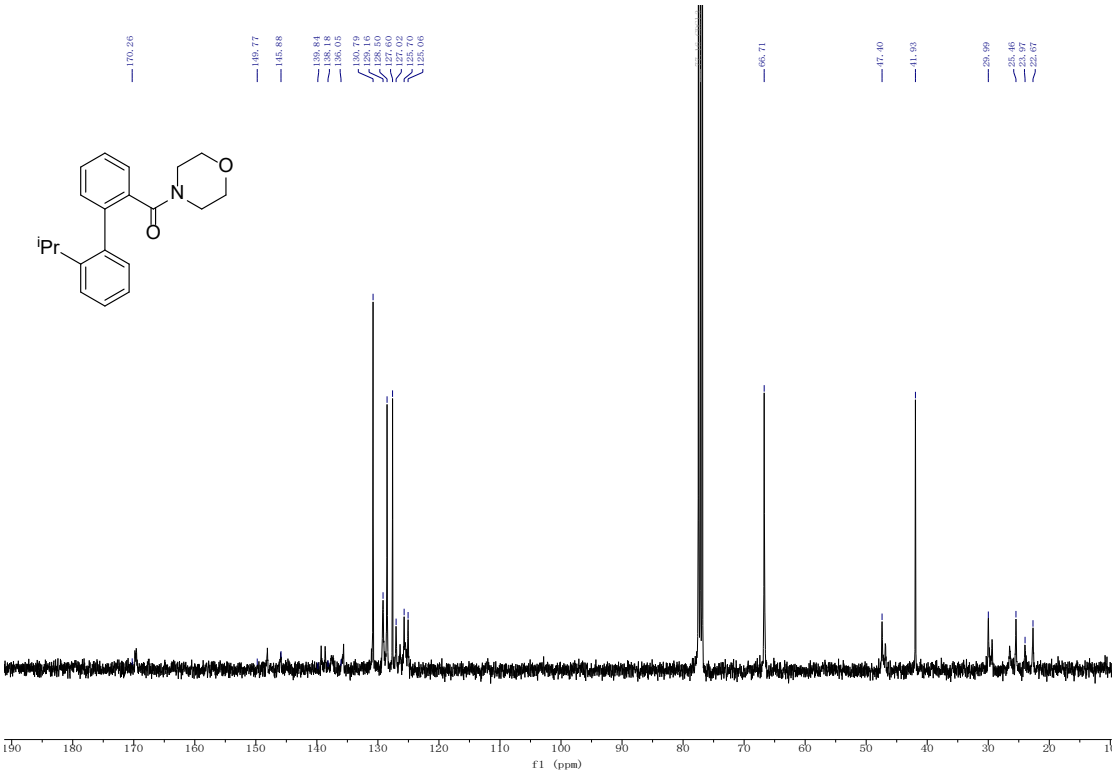

**1h, $^{13}$C NMR (101 MHz, $CDCl_3$)**



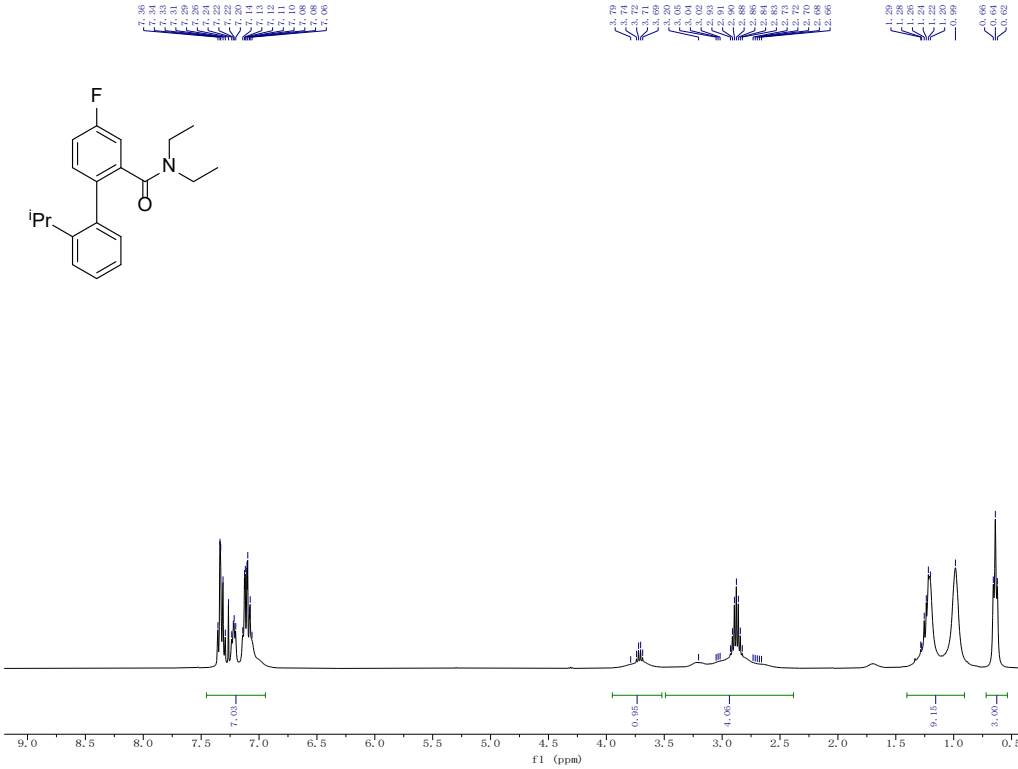
## 1i, $^{1}$H NMR (400 MHz, $CDCl_3$)



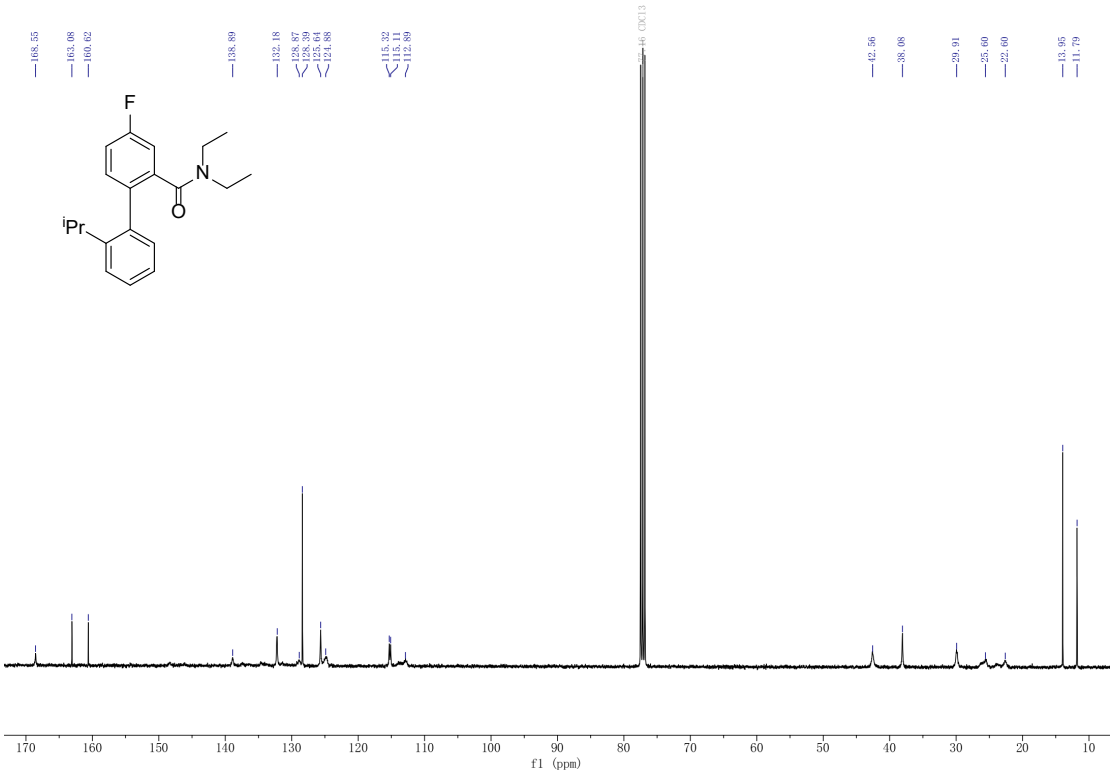

## 1i, $^{13}$C NMR (101 MHz, $CDCl_3$)



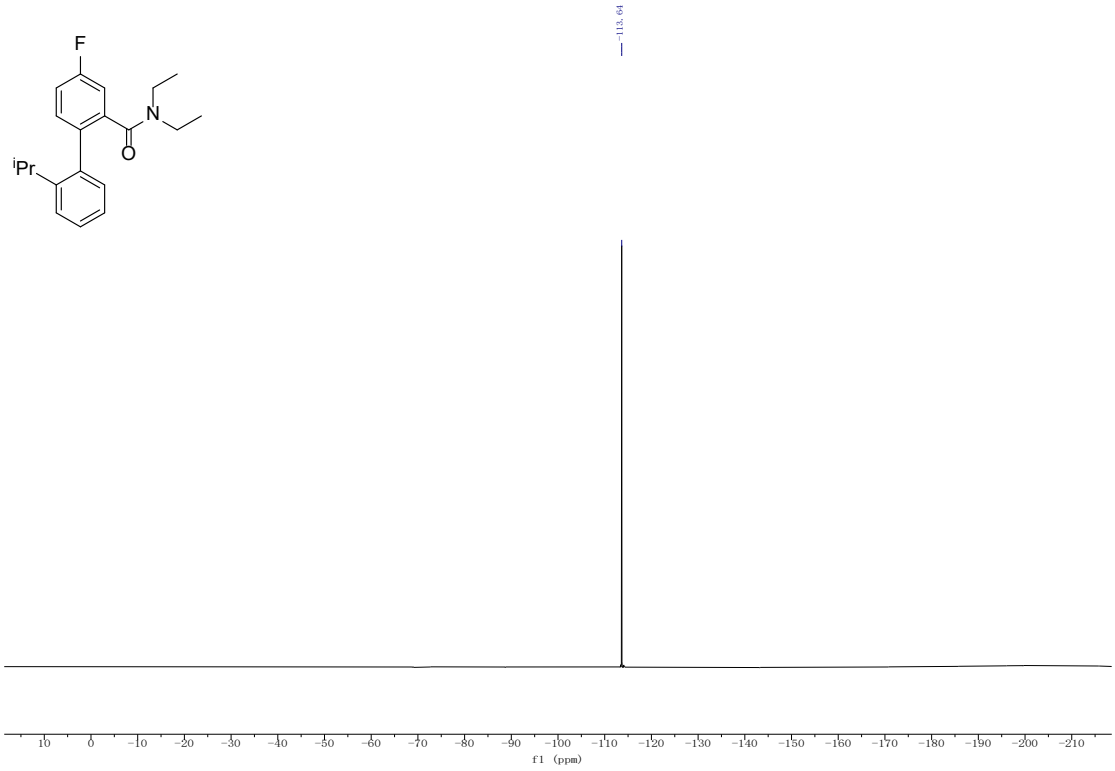
## 1j, $^{1}$H NMR (400 MHz, $CDCl_3$)



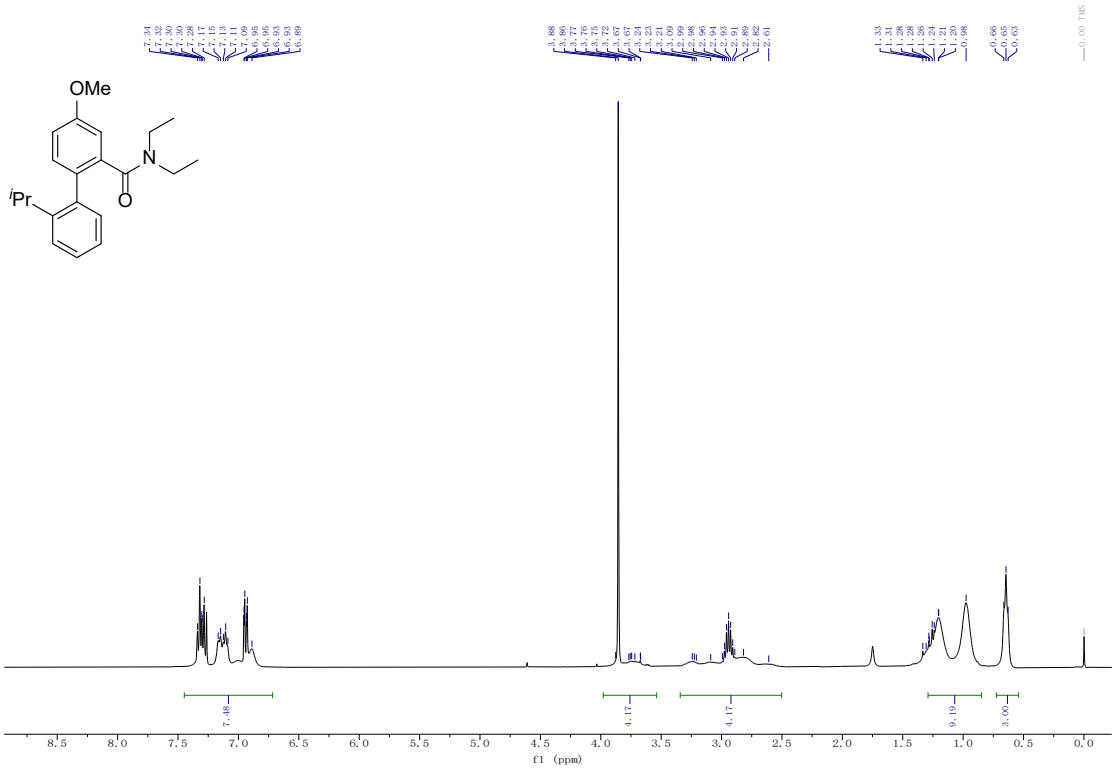

## 1j, $^{13}$C NMR (101 MHz, $CDCl_3$)



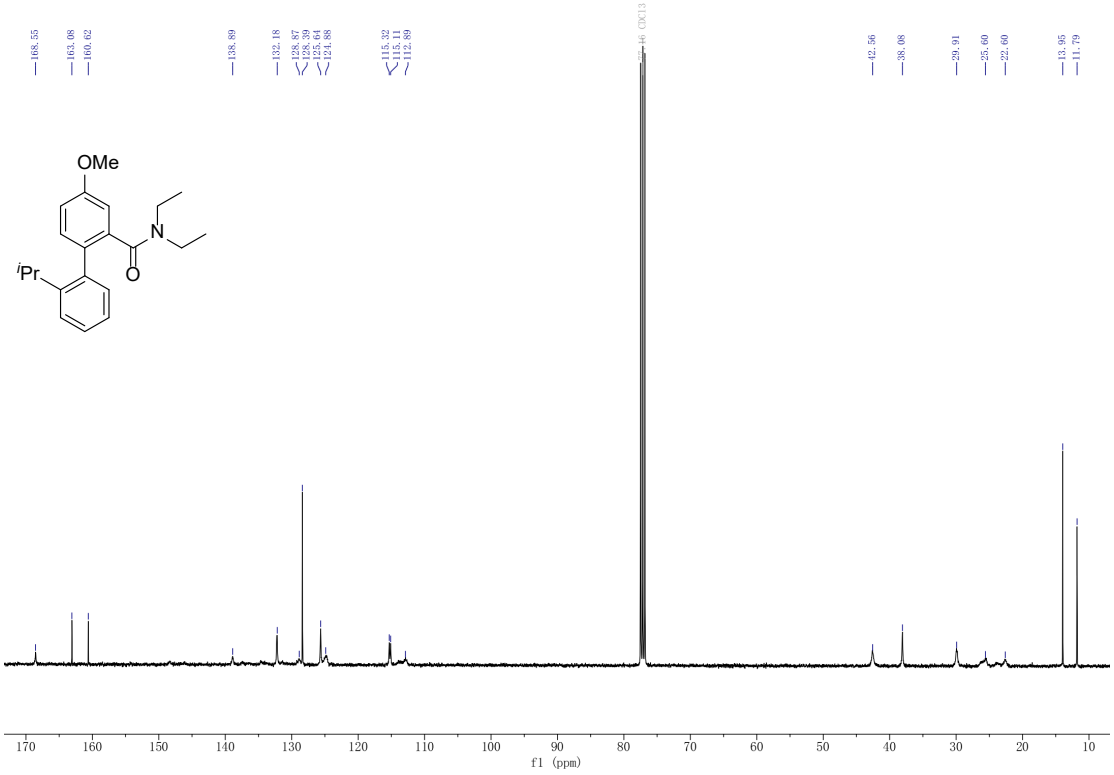
**1j, $^{19}F$ NMR (376 MHz, $CDCl_3$)**



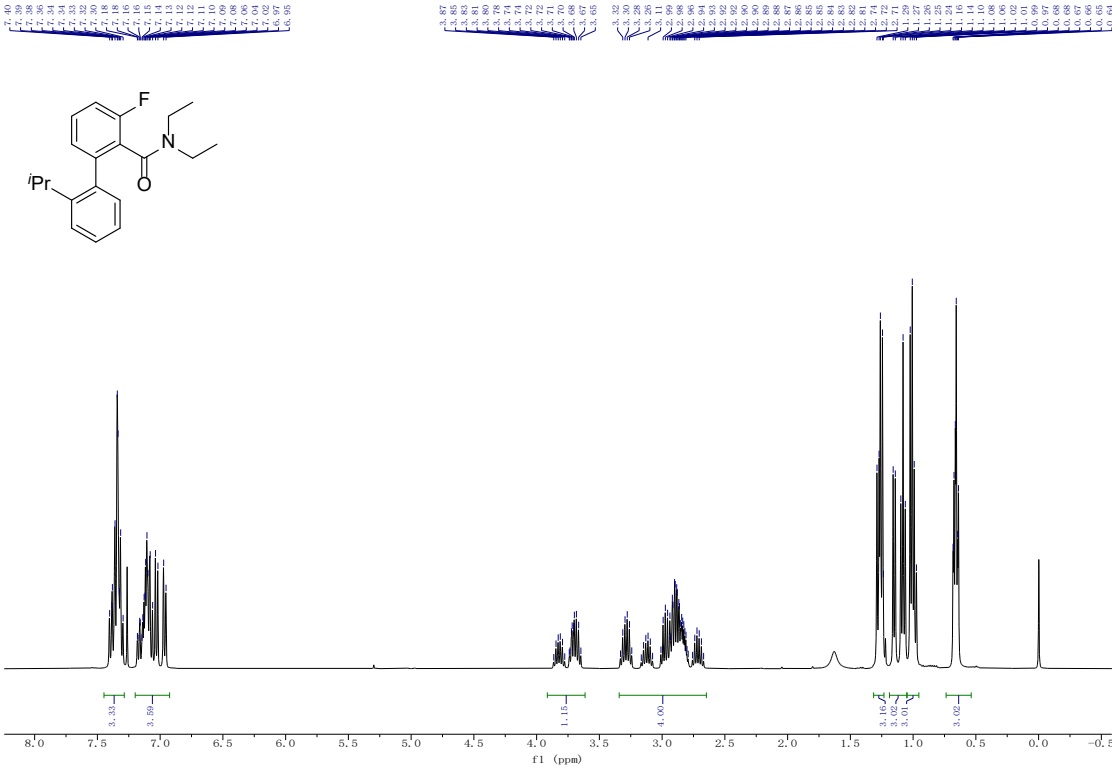
**1k, $^{1}$H NMR (400 MHz, $CDCl_3$)**



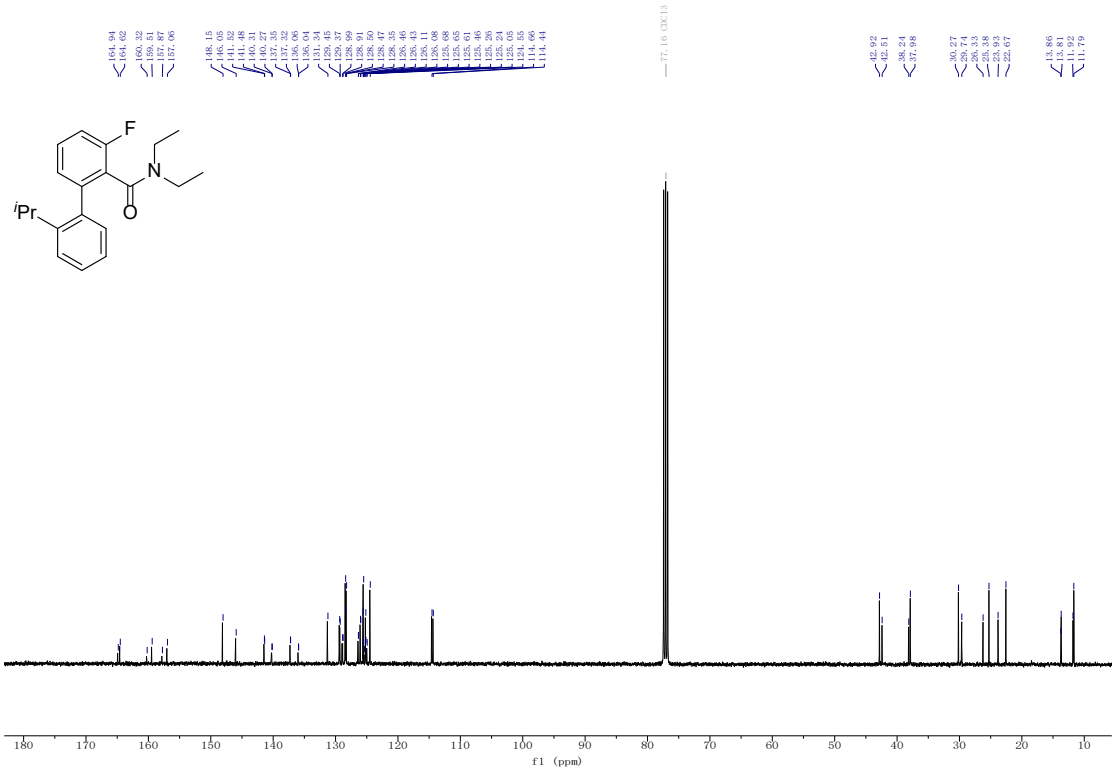

**1k, $^{13}$C NMR (101 MHz, $CDCl_3$)**



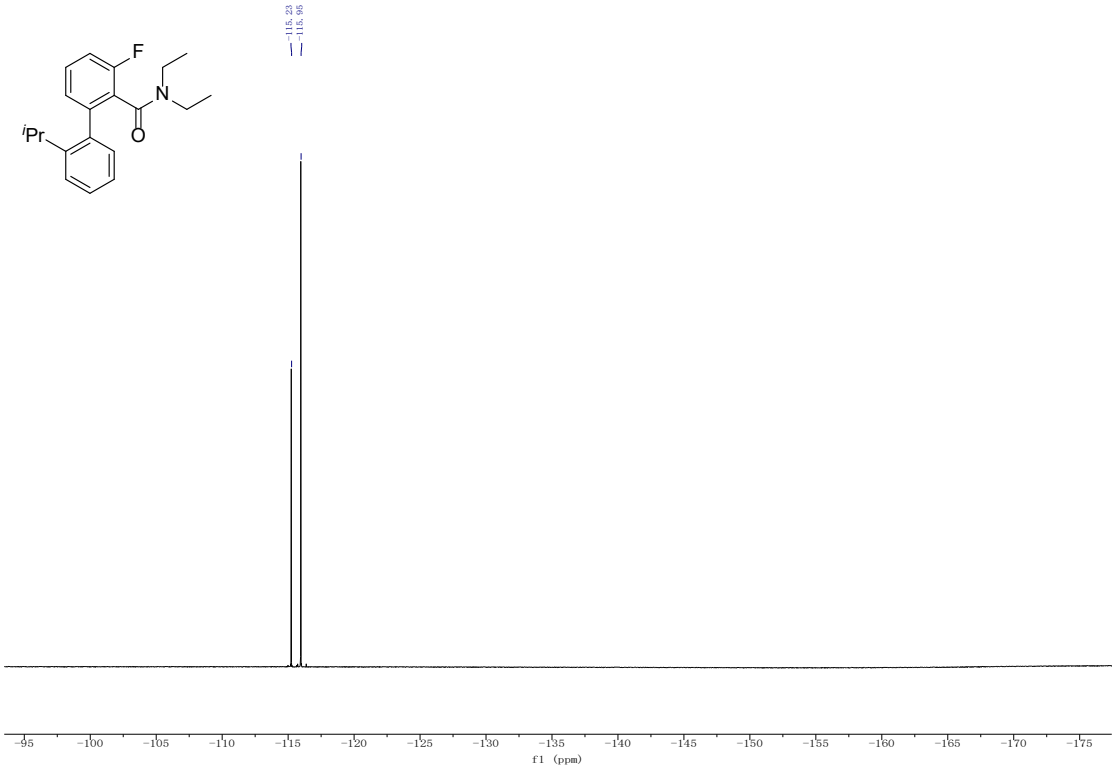
## 1l, $^{1}$H NMR (400 MHz, $CDCl_3$)



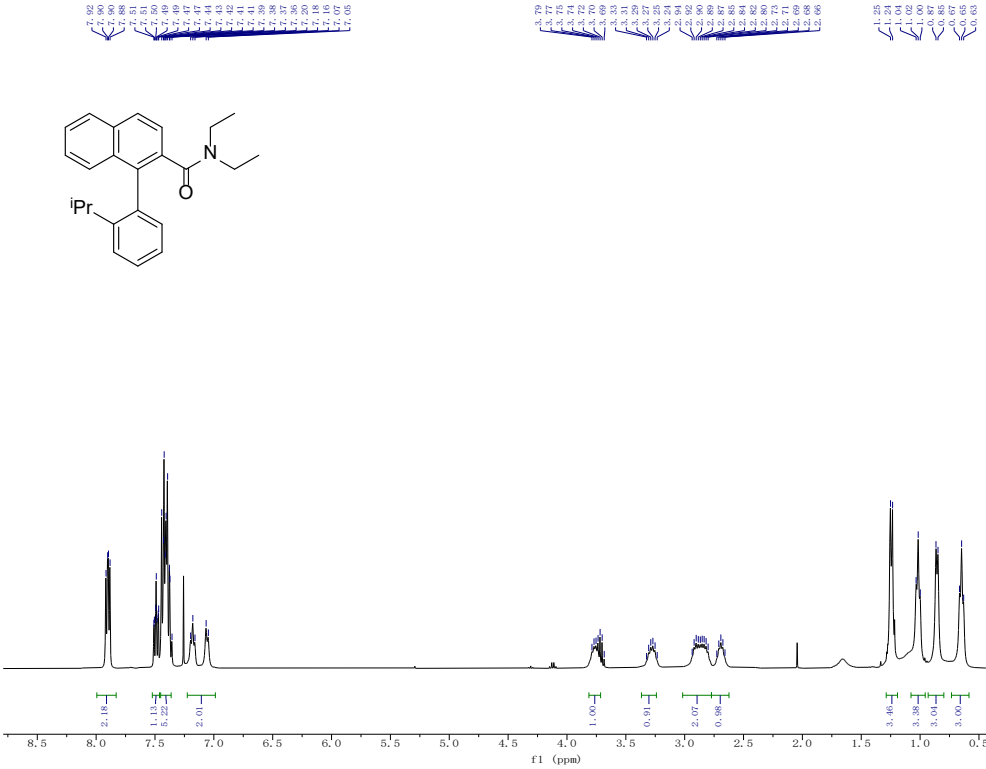

## 1l, $^{13}$C NMR (101 MHz, $CDCl_3$)



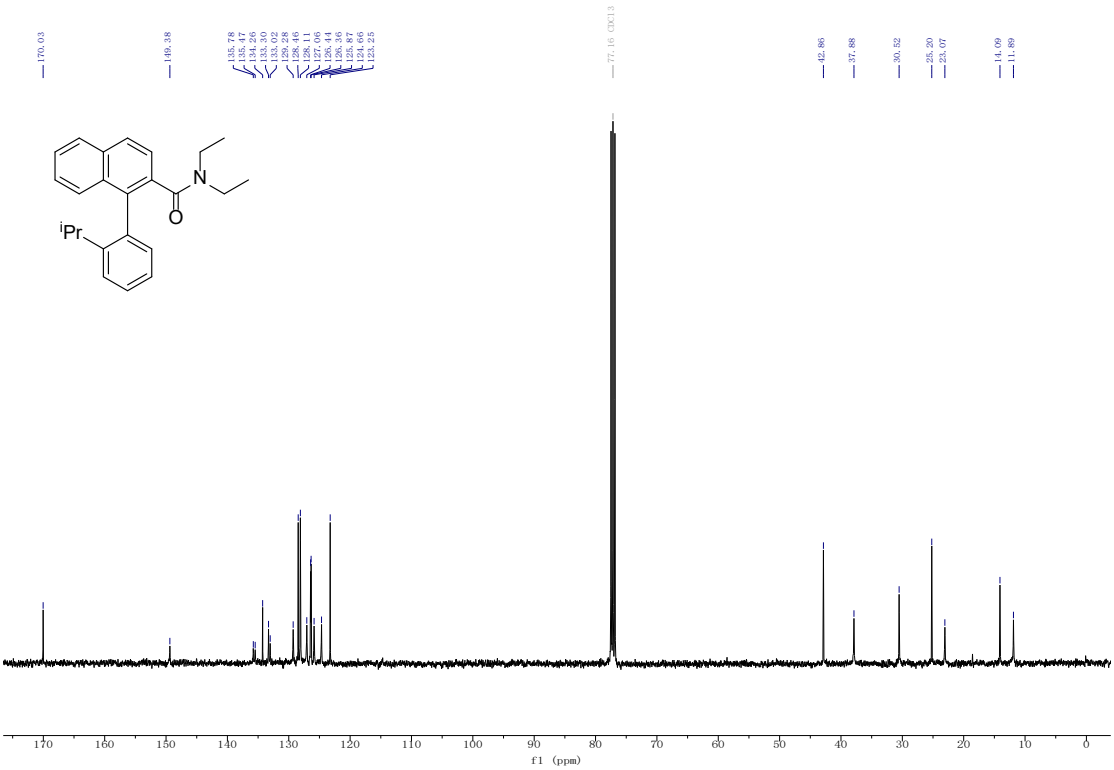
**1l, $^{19}$F NMR (376 MHz, $CDCl_3$)**



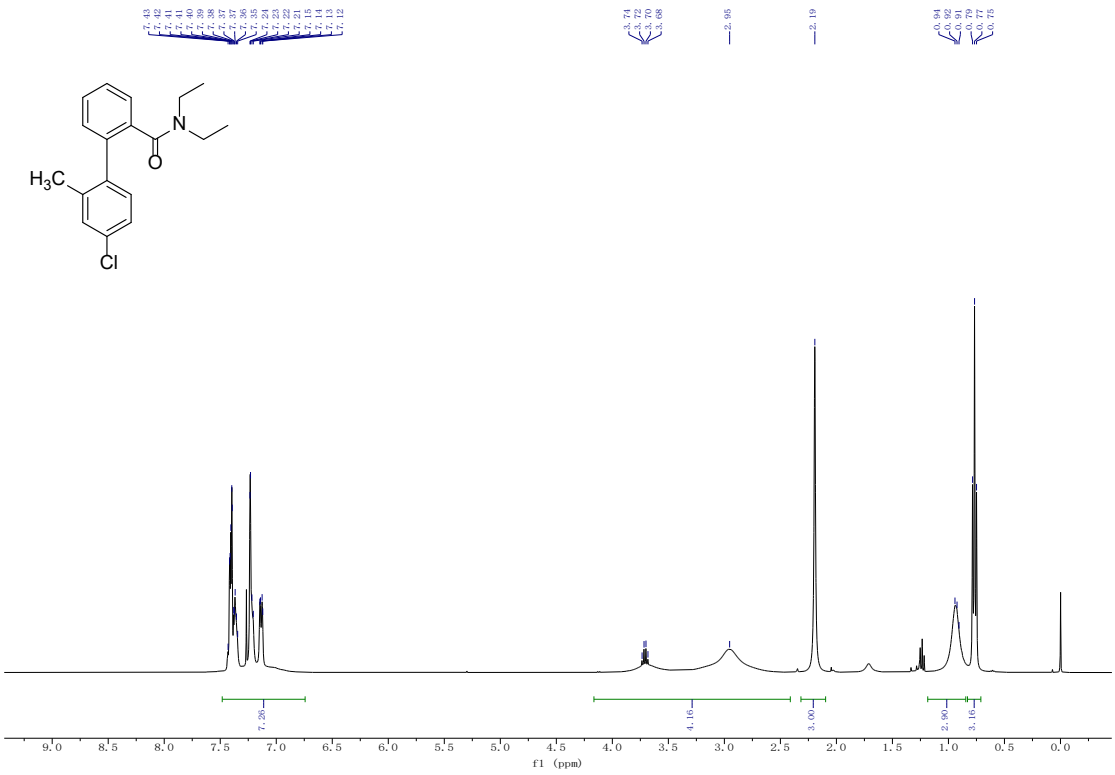
## 1m, $^{1}$H NMR (400 MHz, $CDCl_3$)



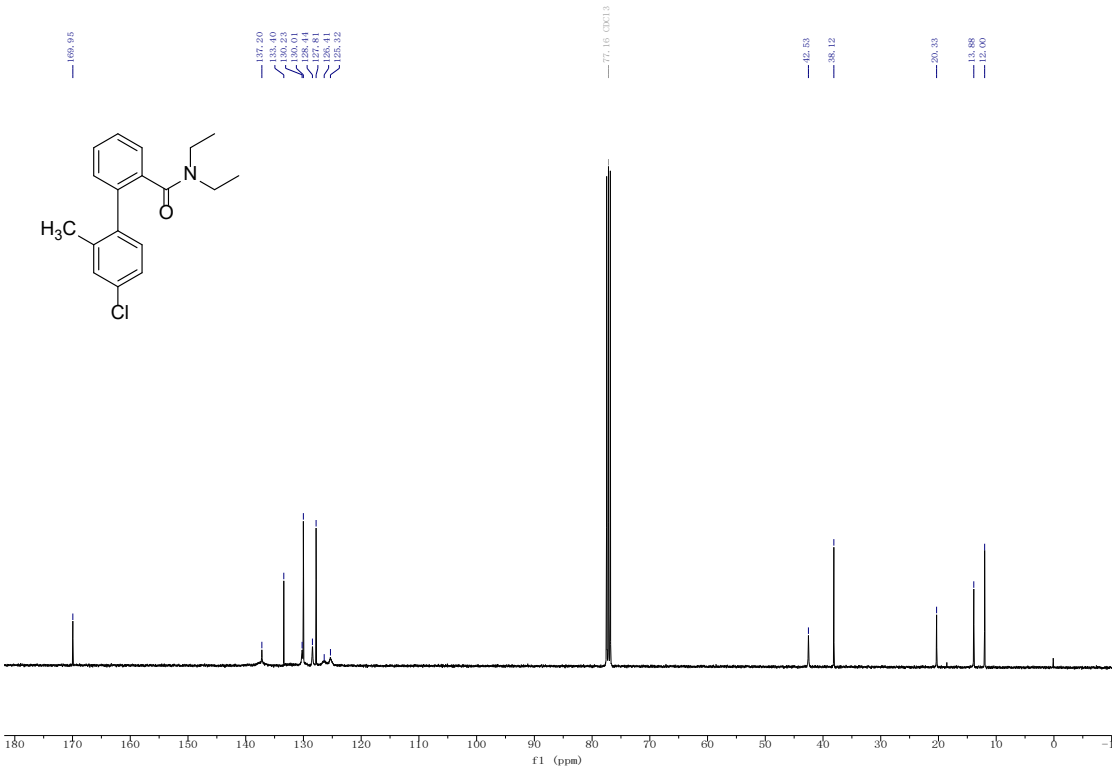

## 1m, $^{13}$C NMR (101 MHz, $CDCl_3$)



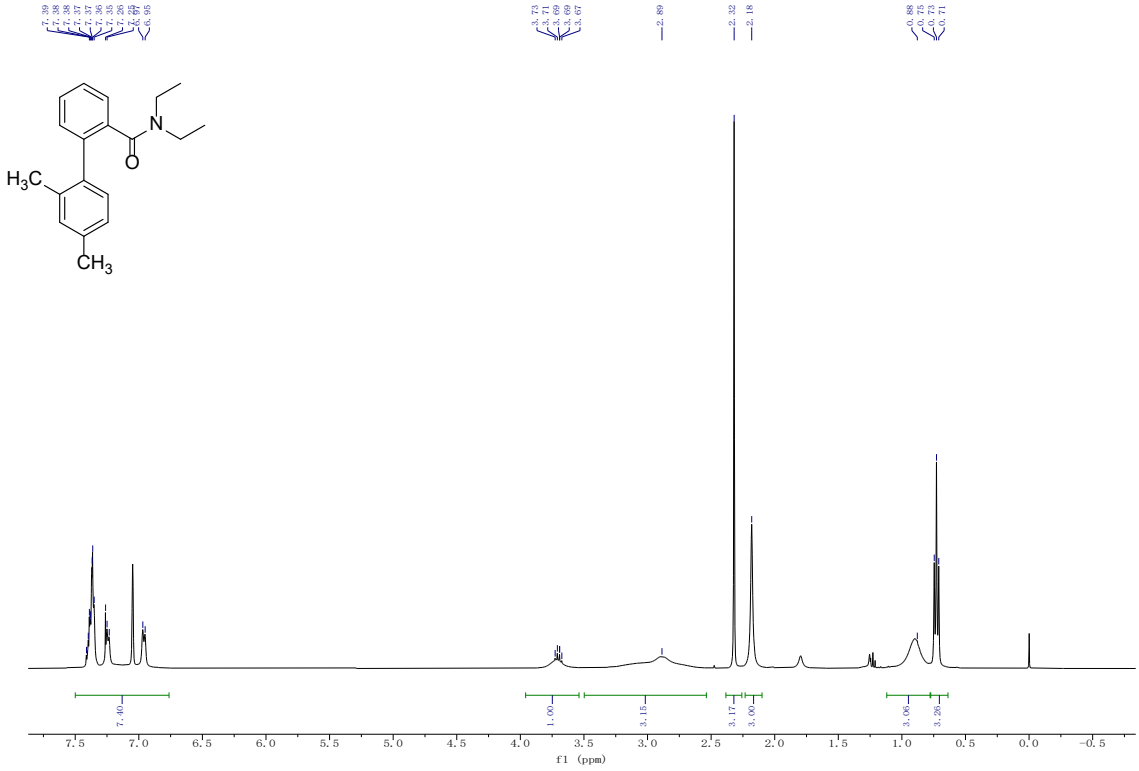
**1n, $^{1}$H NMR (400 MHz, $CDCl_3$)**



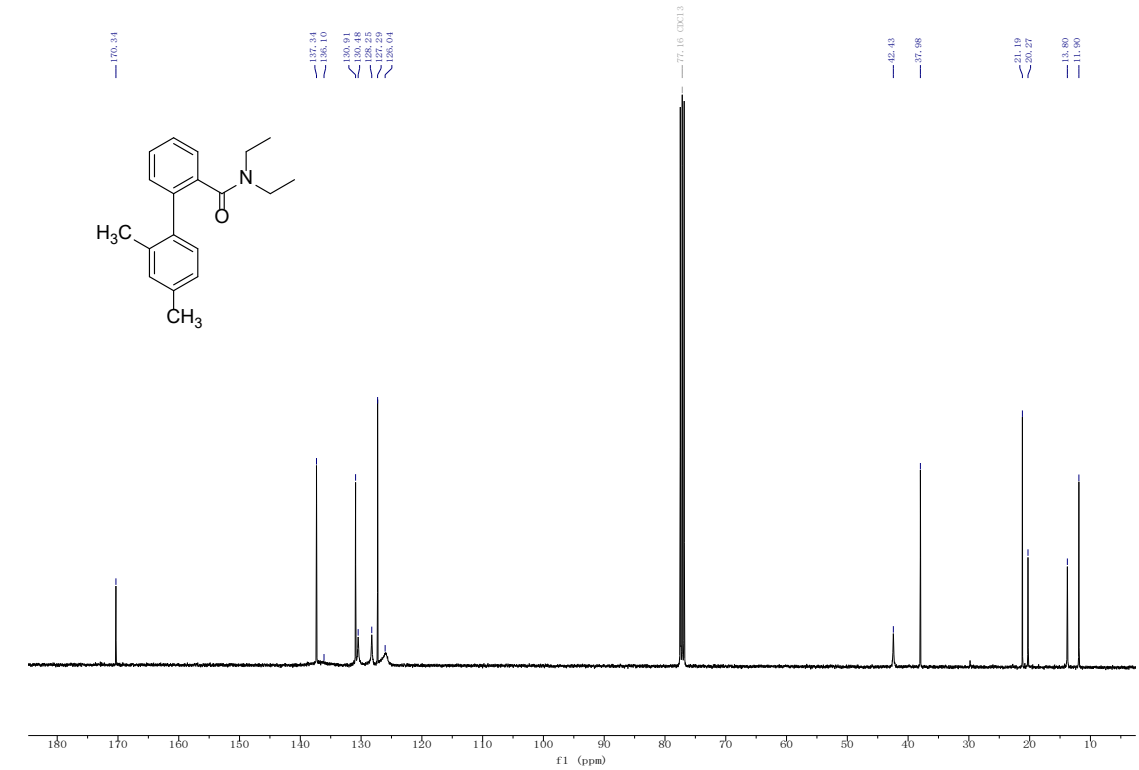

**1n, $^{13}$C NMR (101 MHz, $CDCl_3$)**



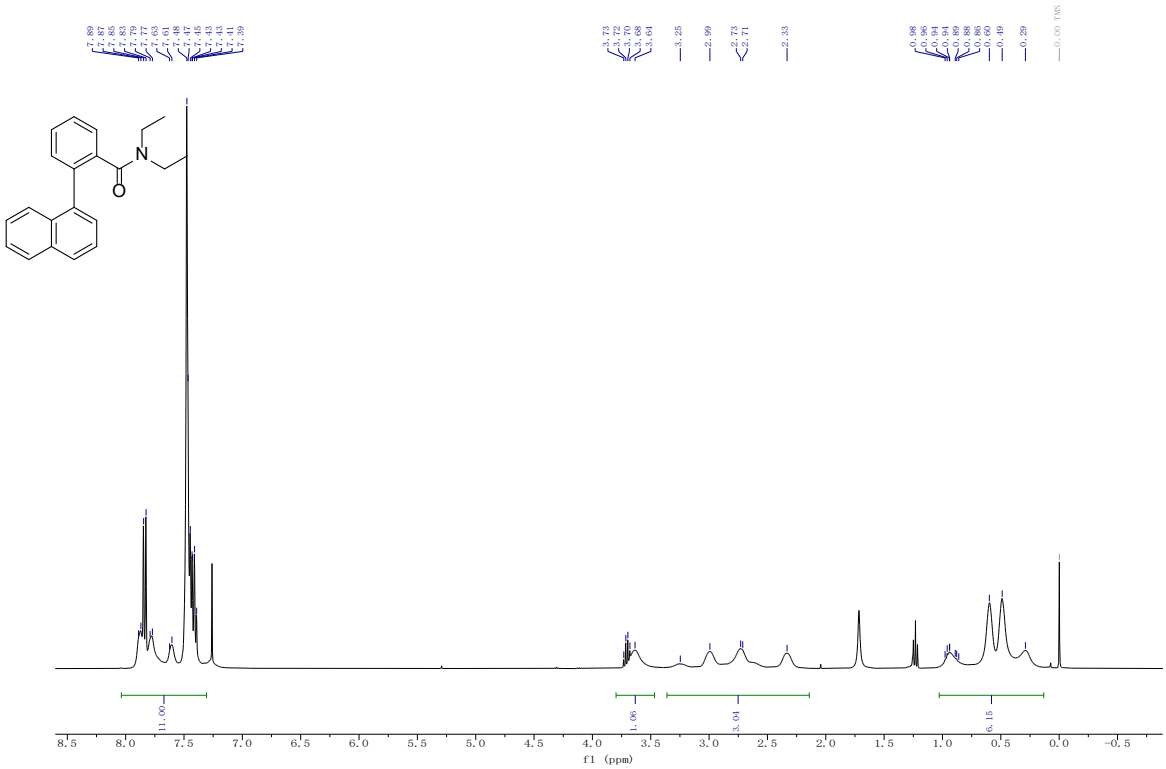
**1o, $^{1}$H NMR (400 MHz, $CDCl_3$)**



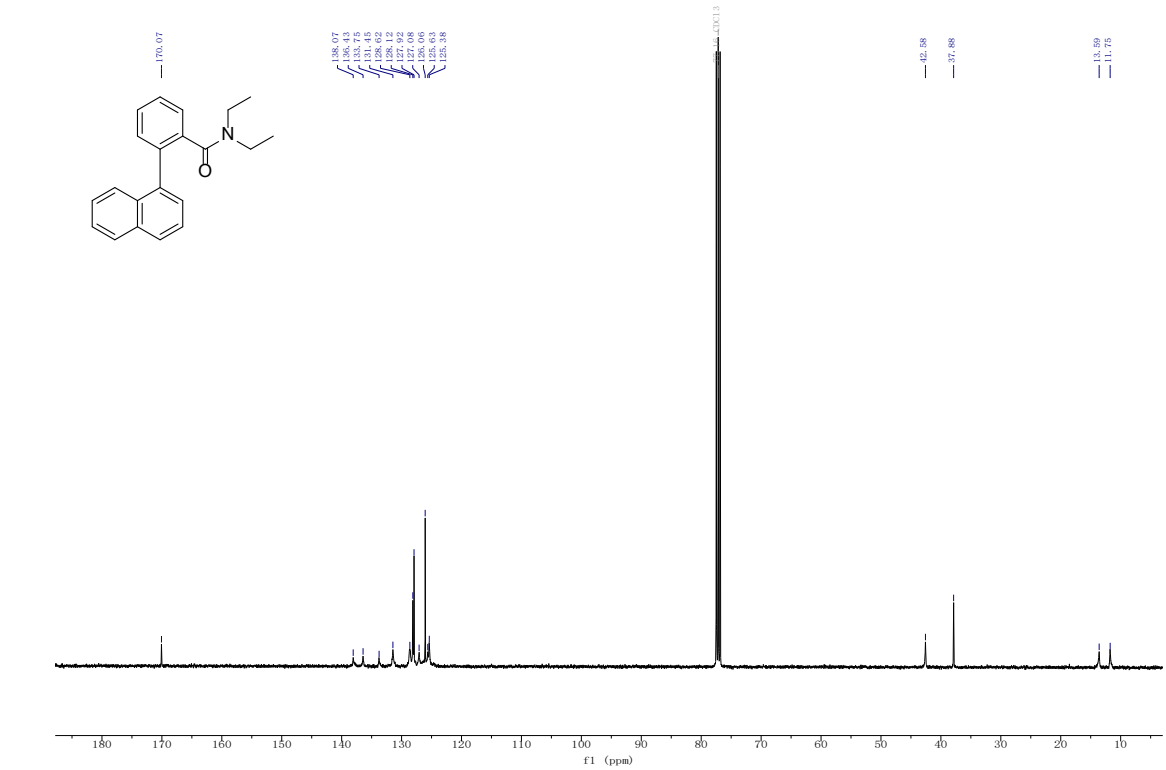

**1o, $^{13}$C NMR (101 MHz, $CDCl_3$)**



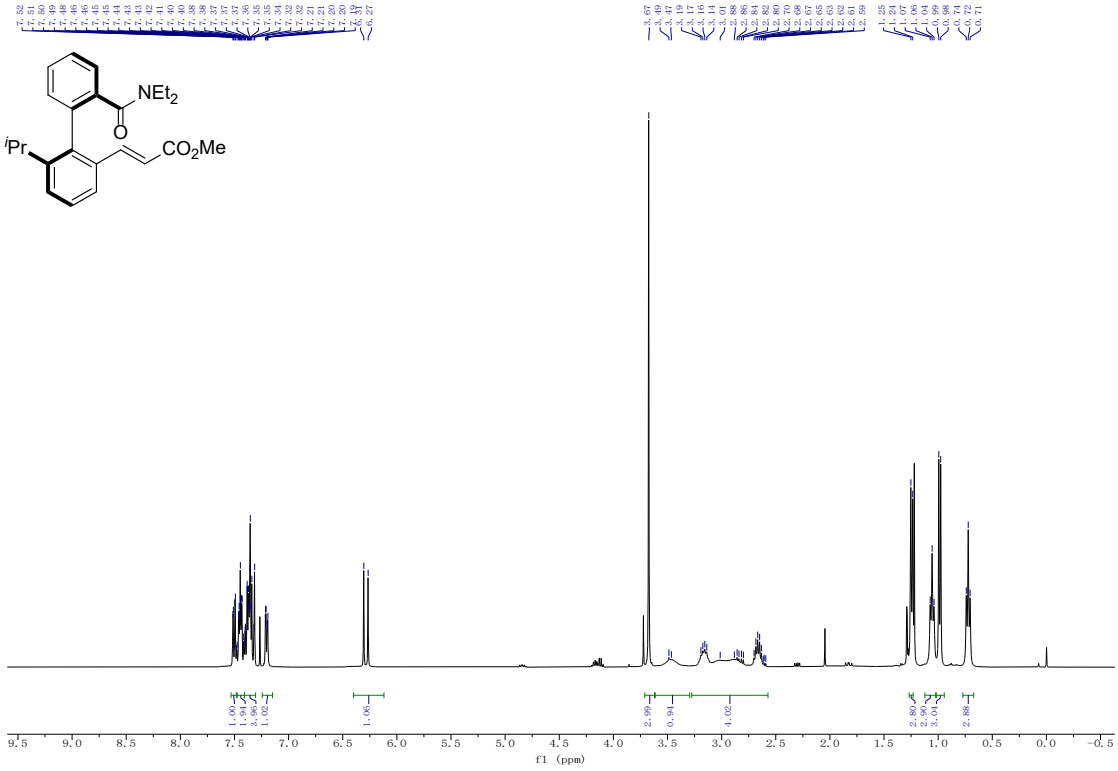
**1p, $^{1}$H NMR (400 MHz, $CDCl_3$)**



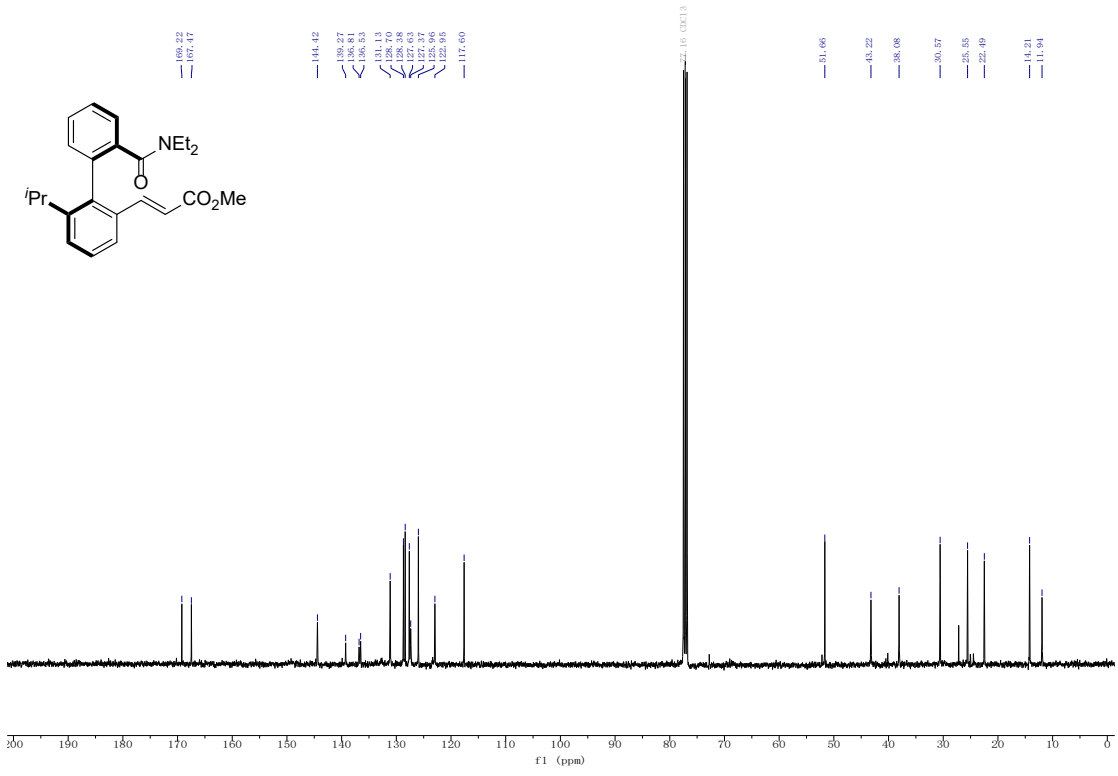

**1p, $^{13}$C NMR (101 MHz, $CDCl_3$)**



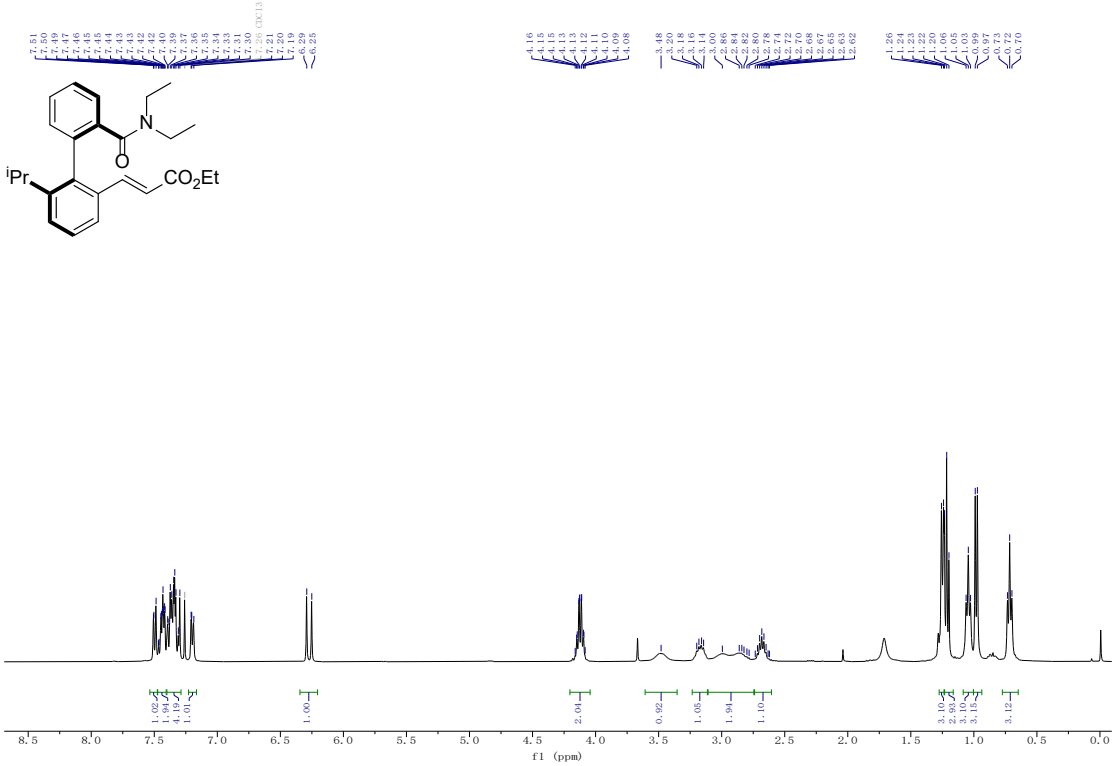
**3aa, $^{1}$H NMR (400 MHz, $CDCl_3$)**



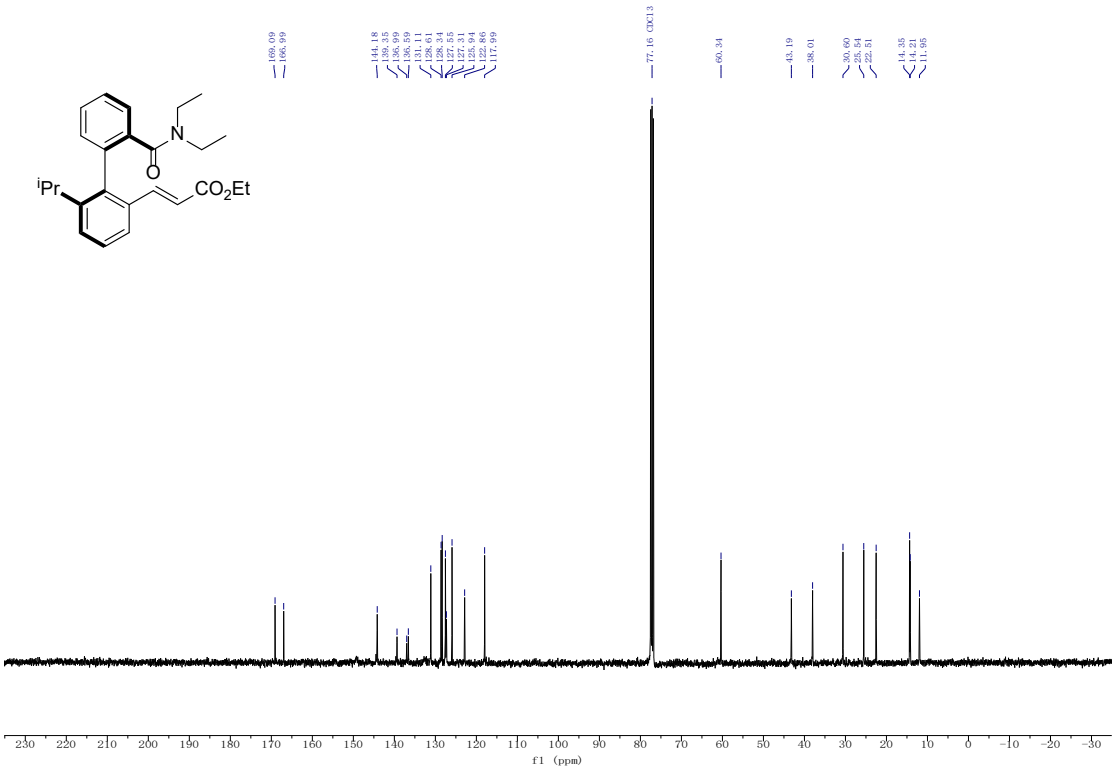

**3aa, $^{13}$C NMR (101 MHz, $CDCl_3$)**



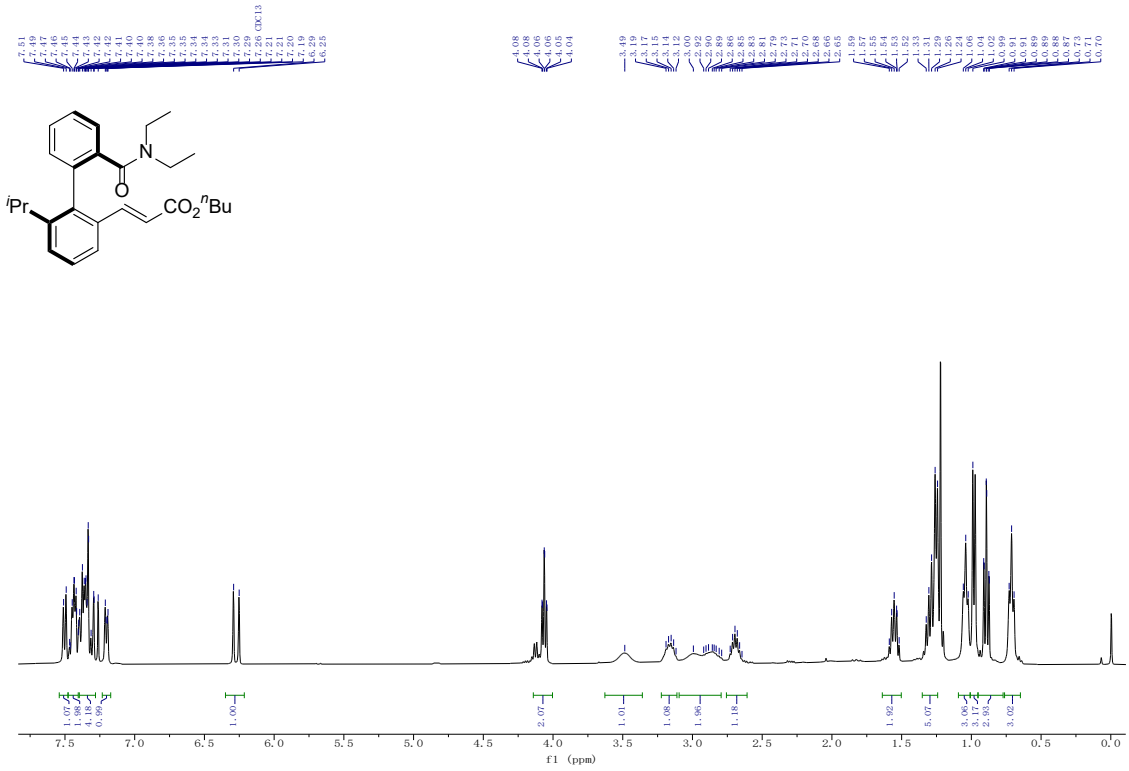
**3ab, $^{1}$H NMR (400 MHz, $CDCl_3$)**



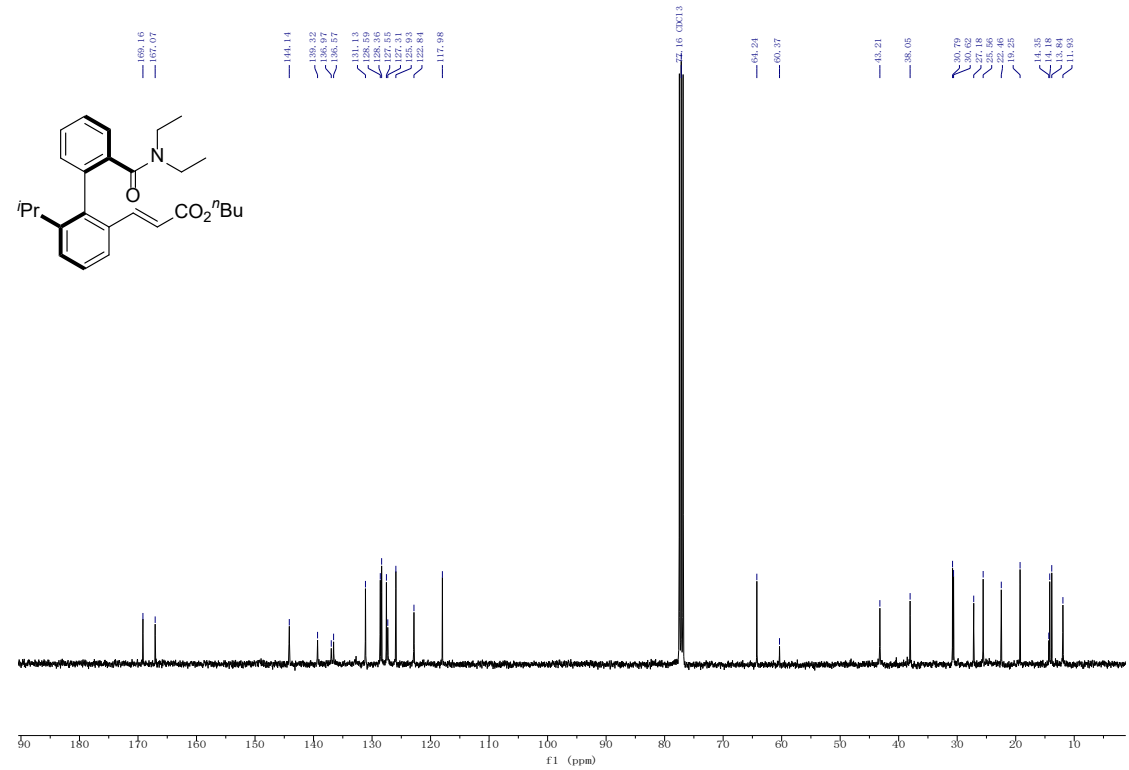

**3ab, $^{13}$C NMR (101 MHz, $CDCl_3$)**



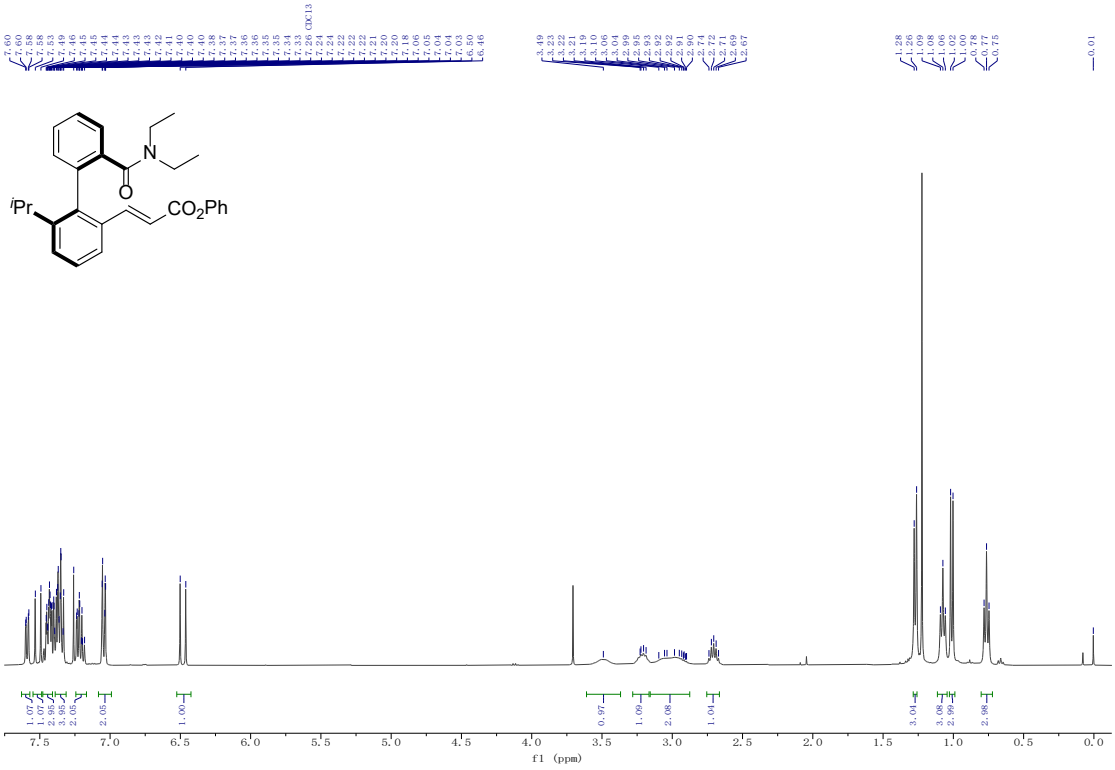
**3ac, $^{1}$H NMR (400 MHz, $CDCl_3$)**



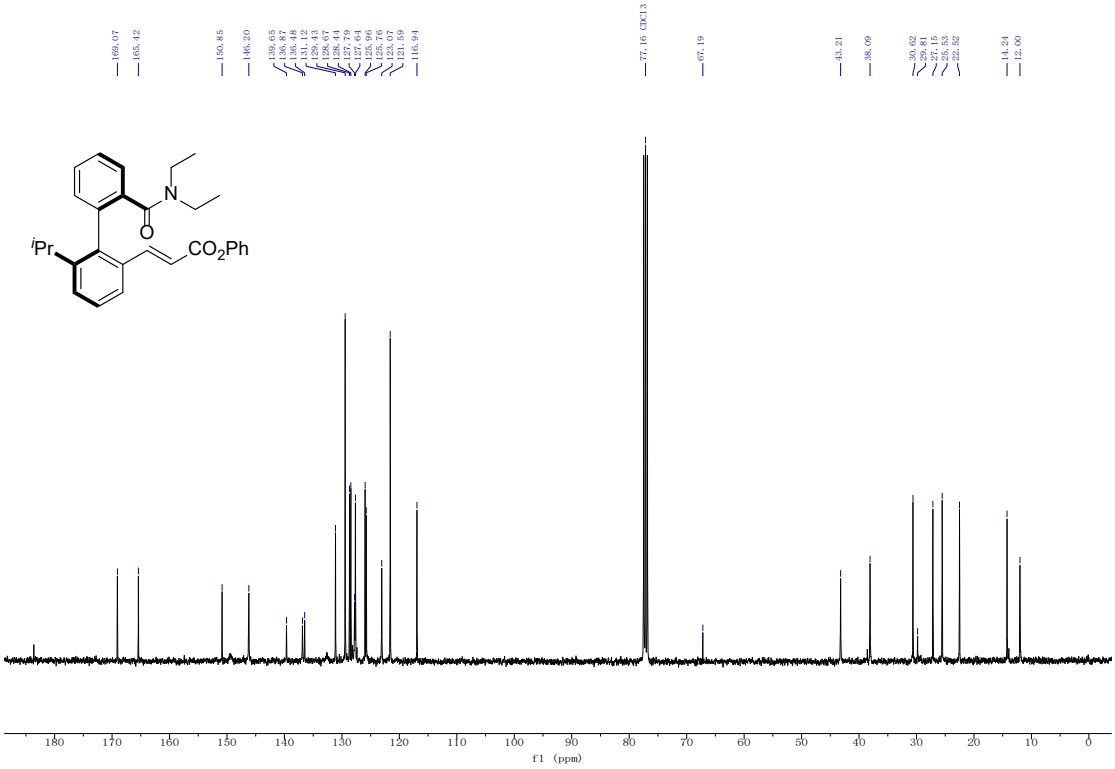

**3ac, $^{13}$C NMR (101 MHz, $CDCl_3$)**



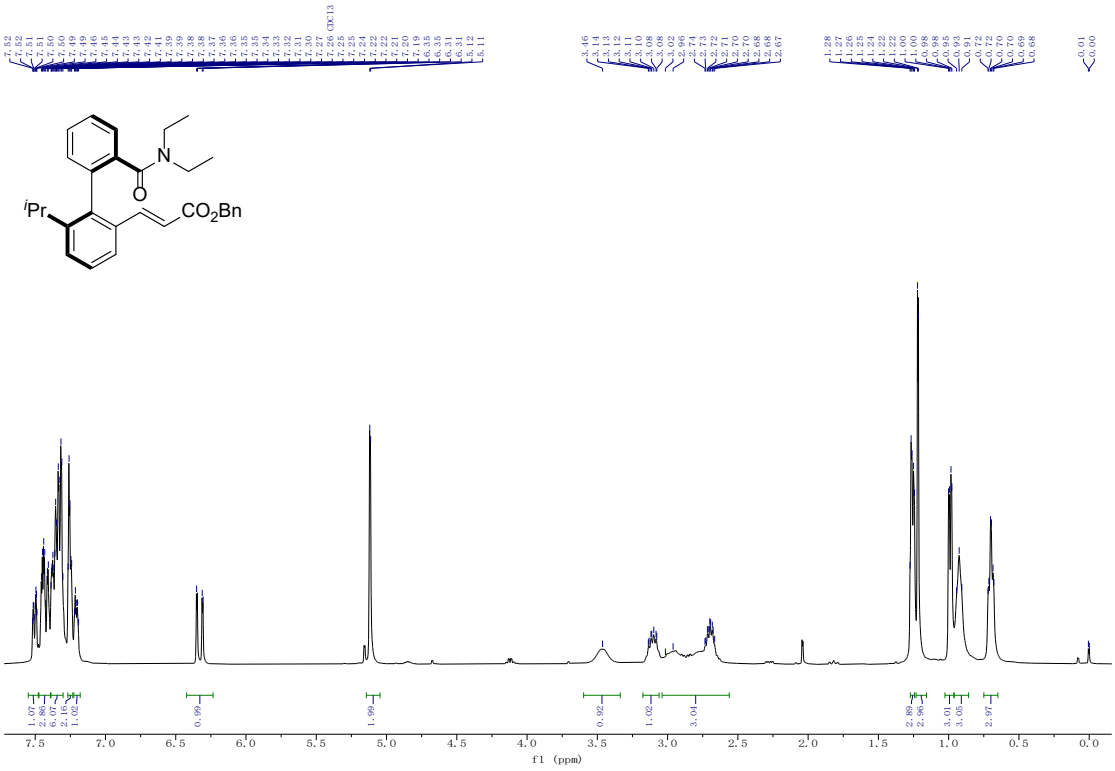
**3ad, $^{1}$H NMR (400 MHz, $CDCl_3$)**



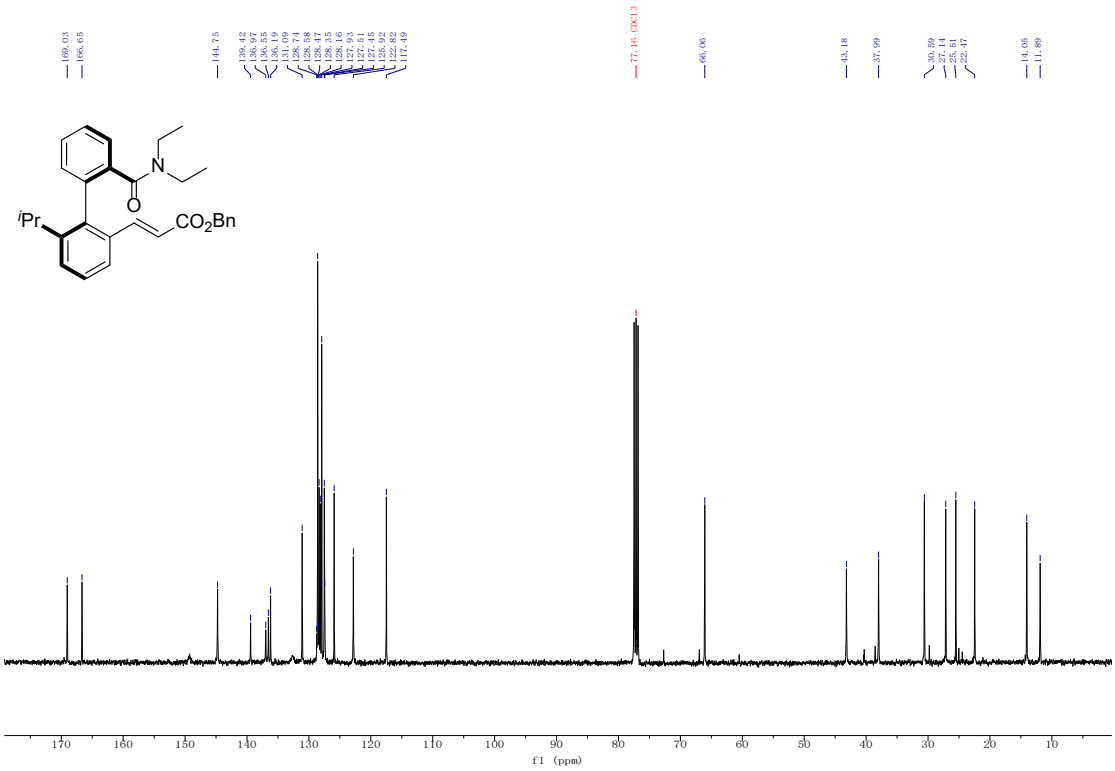

**3ad, $^{13}$C NMR (101 MHz, $CDCl_3$)**



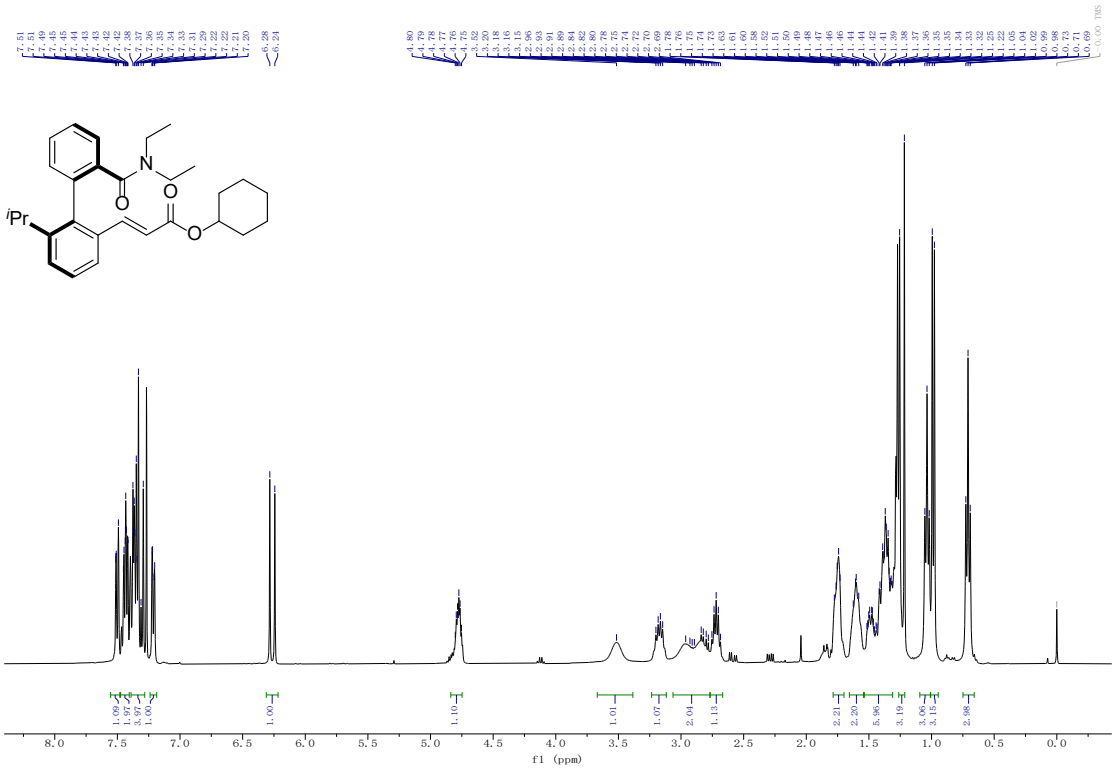
**3ae, $^{1}$H NMR (400 MHz, $CDCl_3$)**



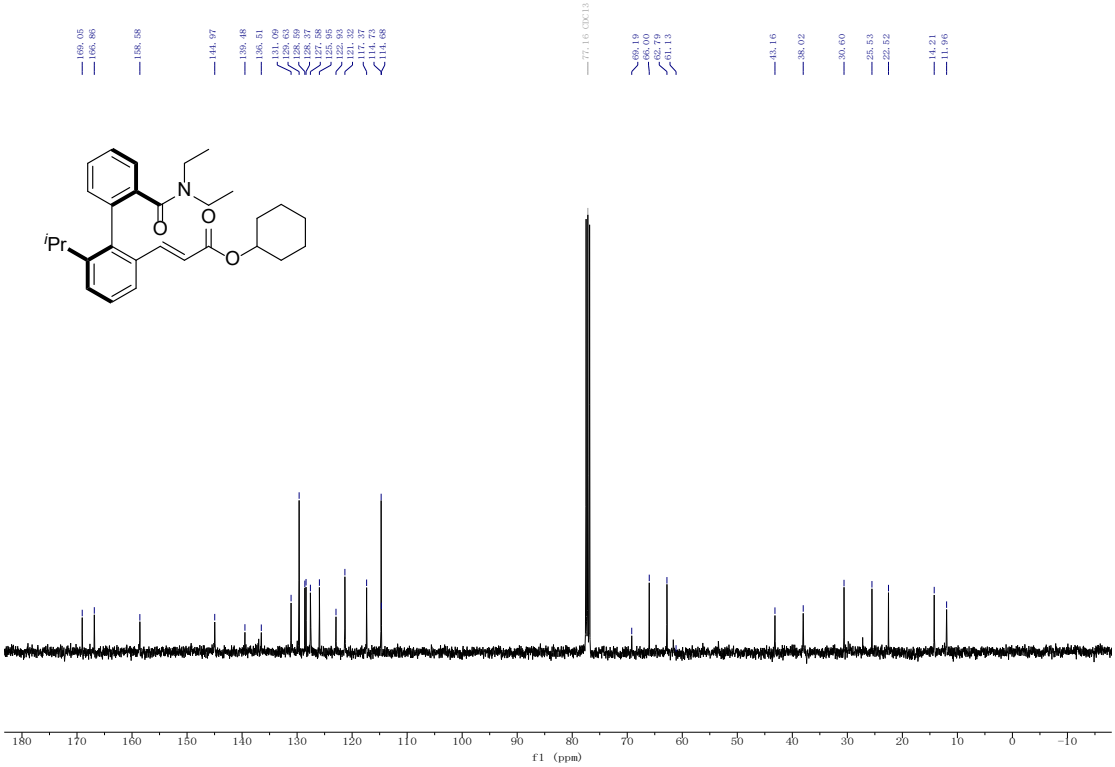

**3ae, $^{13}$C NMR (101 MHz, $CDCl_3$)**



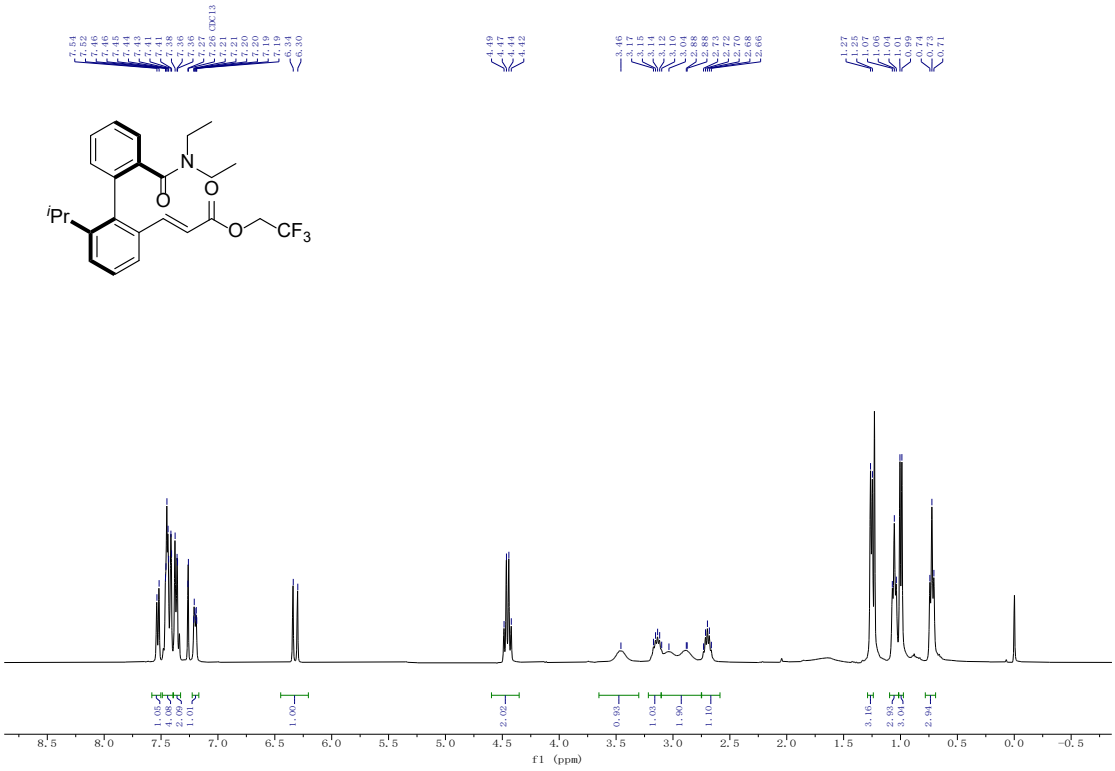
## 3af, $^{1}$H NMR (400 MHz, $CDCl_3$)



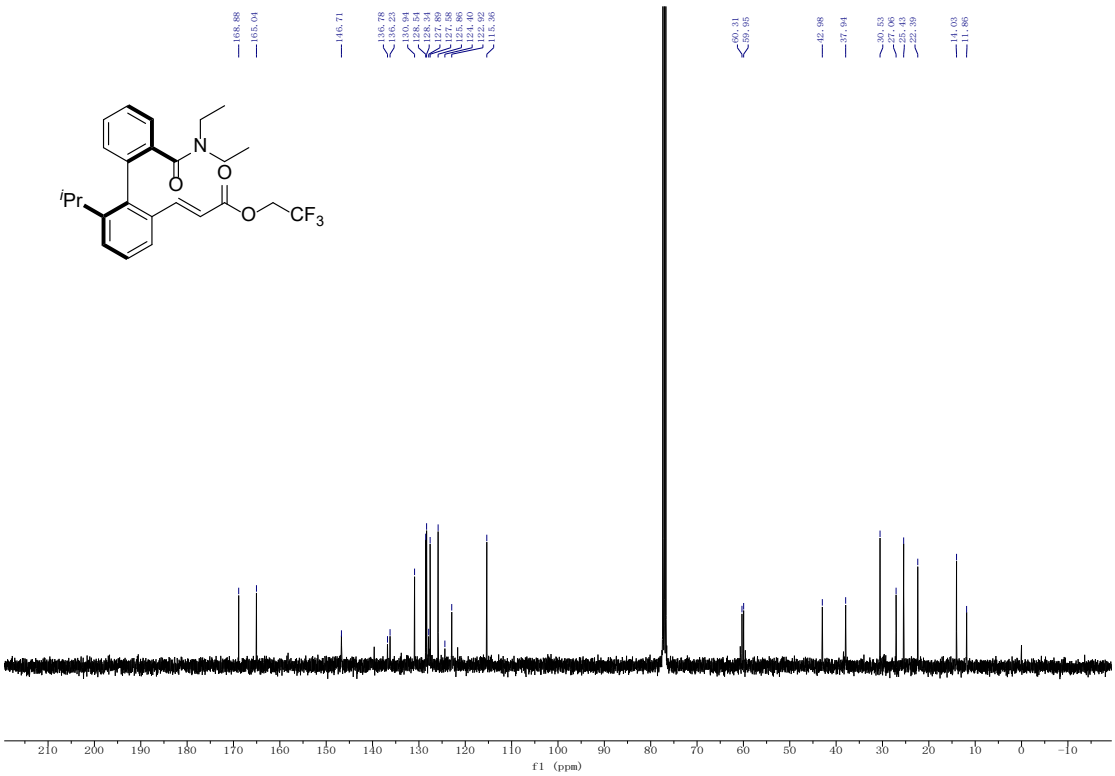

## 3af, $^{13}$C NMR (101 MHz, $CDCl_3$



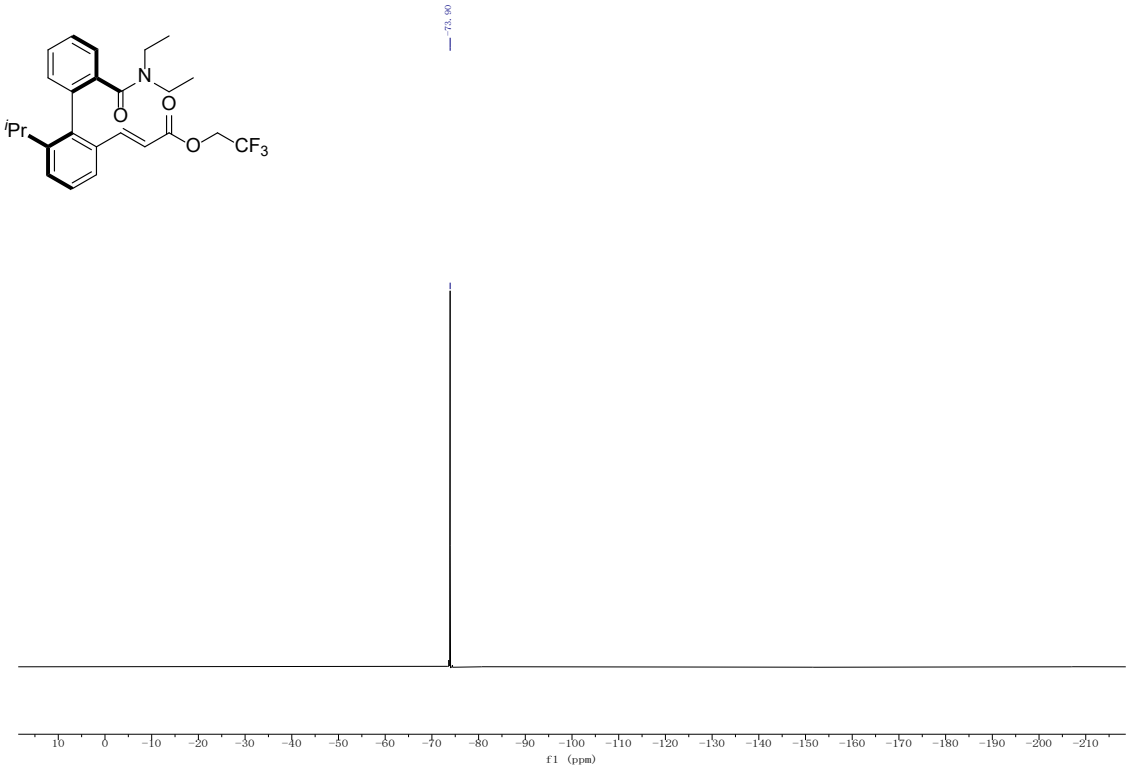
**3ag, $^{1}$H NMR (400 MHz, $CDCl_3$)**



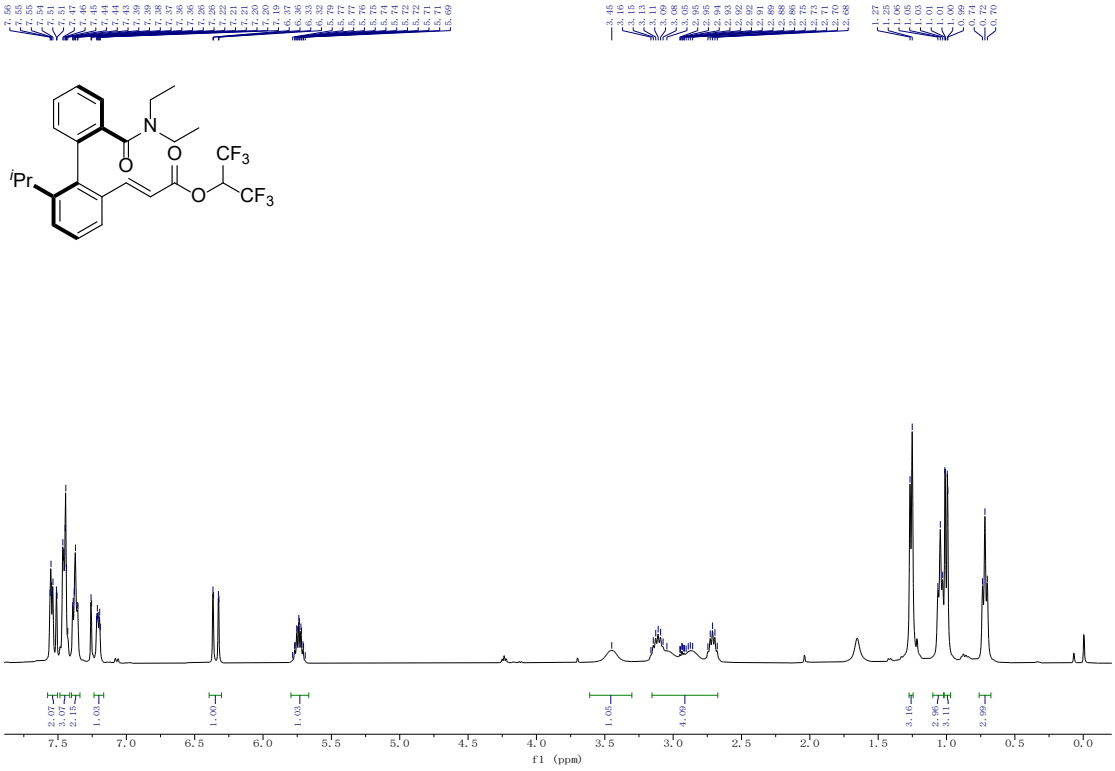
**3ag, $^{13}$C NMR (101 MHz, $CDCl_3$**



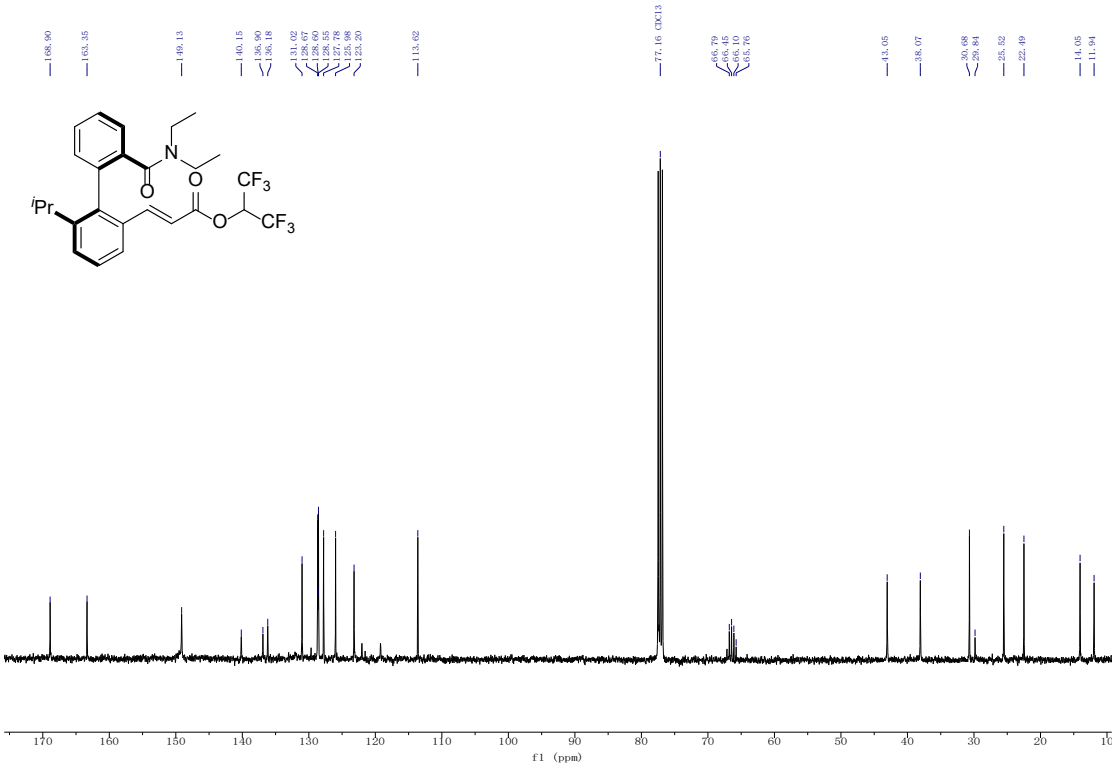
**3ag, $^{19}$F NMR (376 MHz, $CDCl_3$)**



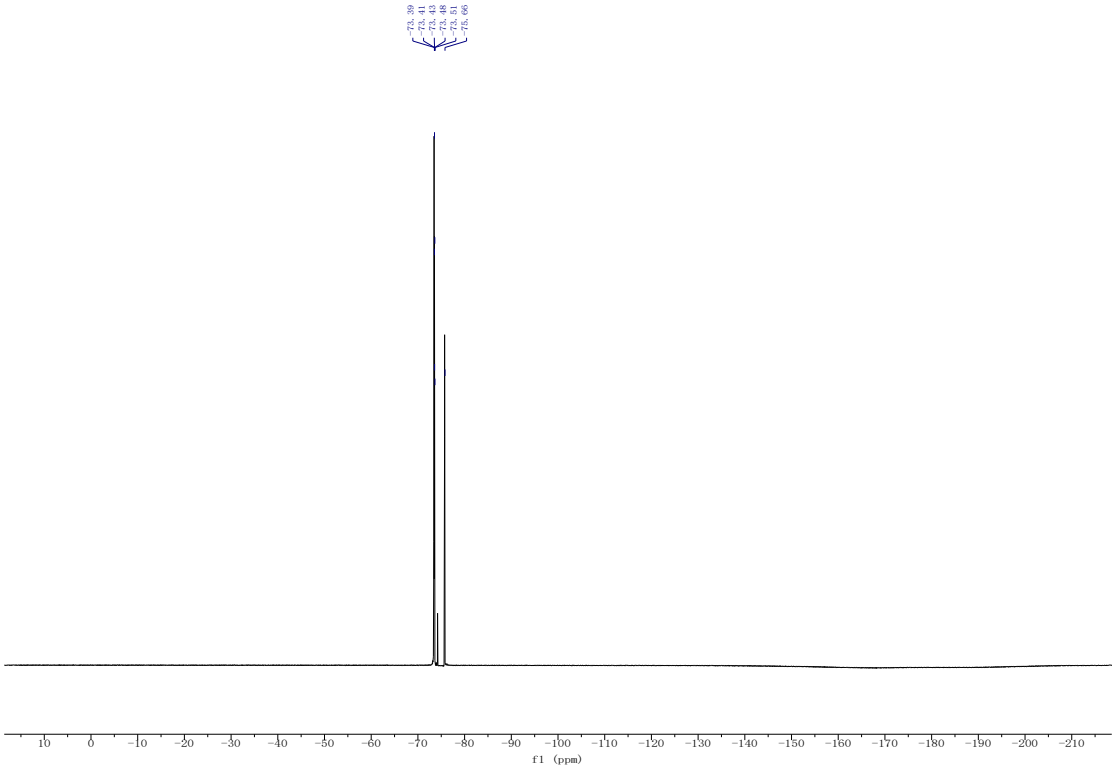
## 3ah, $^{1}$H NMR (400 MHz, $CDCl_3$)



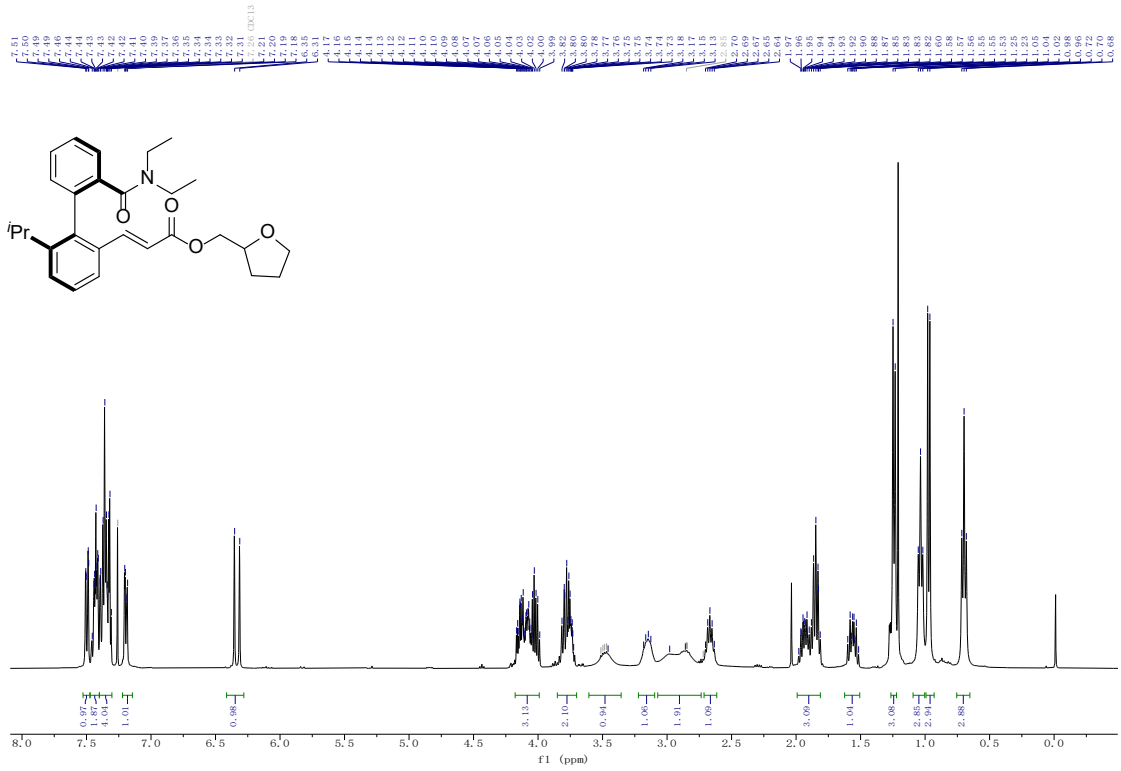
## 3ah, $^{13}$C NMR (101 MHz, $CDCl_3$)



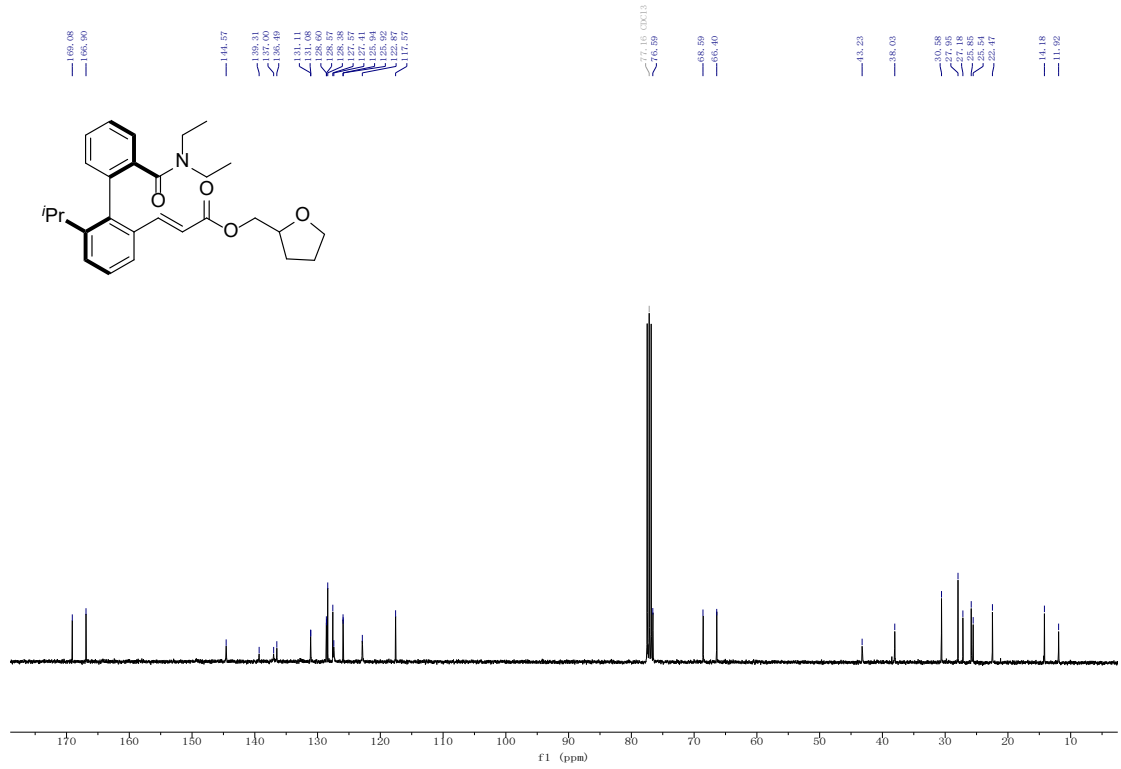
**3ah, $^{19}F$ NMR (376 MHz, $CDCl_3$)**



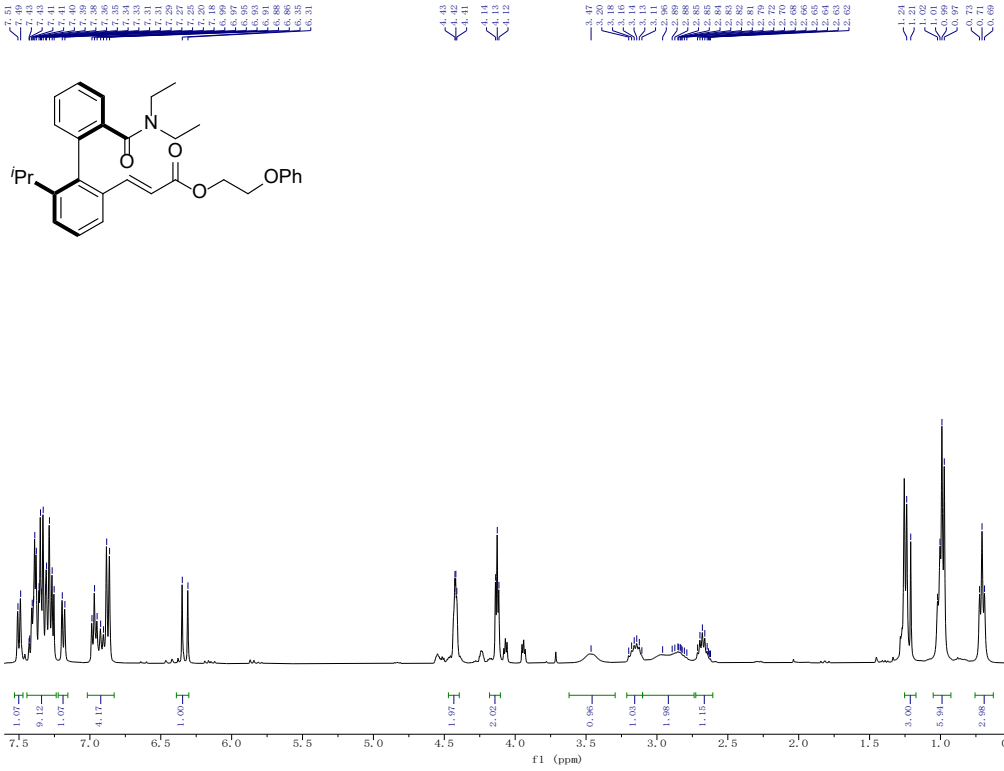
**3ai, $^{1}$H NMR (400 MHz, $CDCl_3$)**



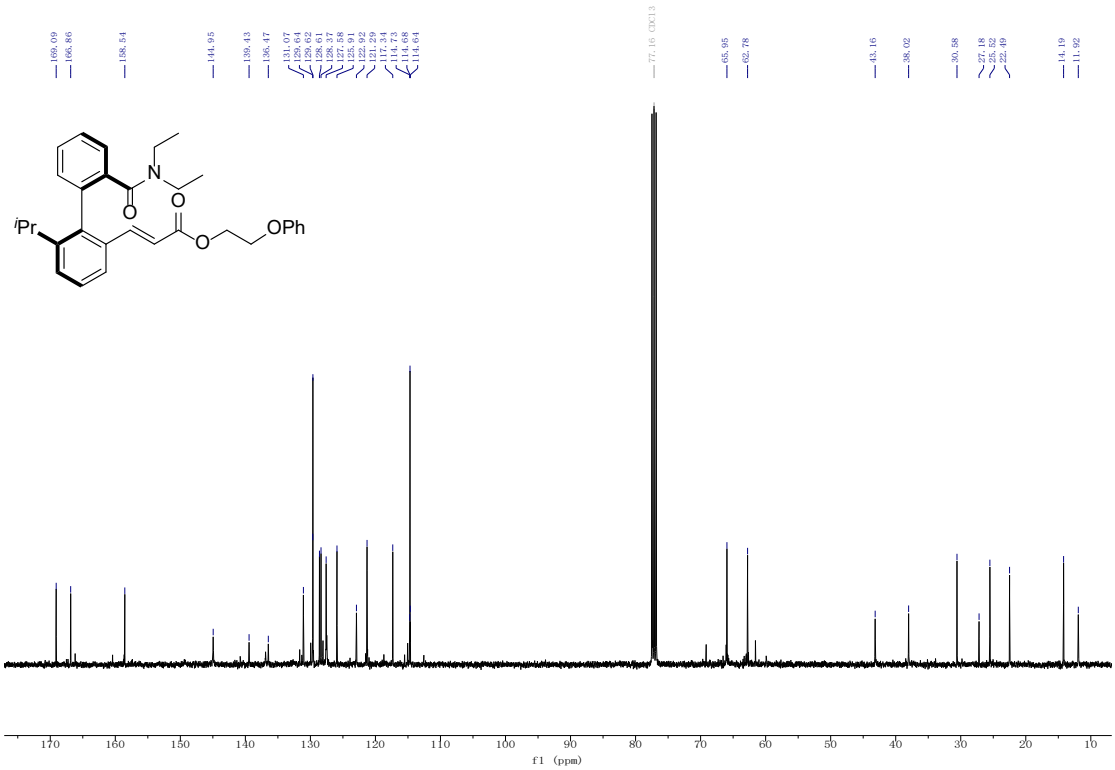
**3ai, $^{13}$C NMR (101 MHz, $CDCl_3$)**



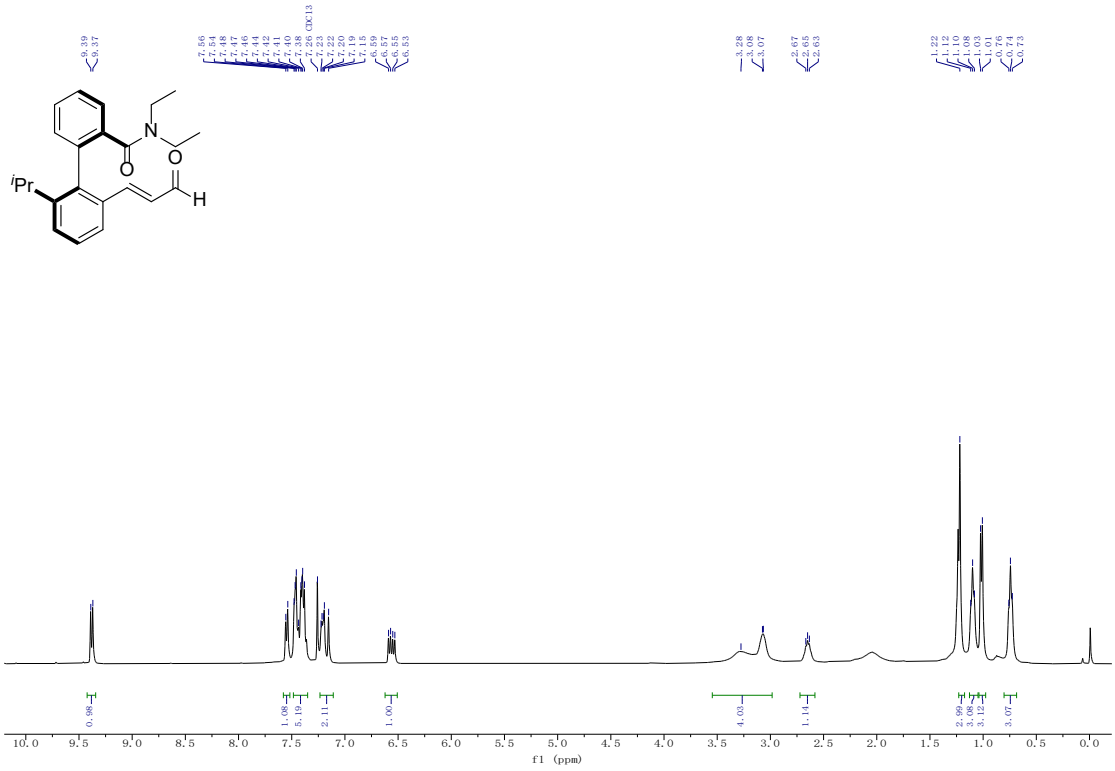
## 3aj, $^{1}$H NMR (400 MHz, $CDCl_3$)



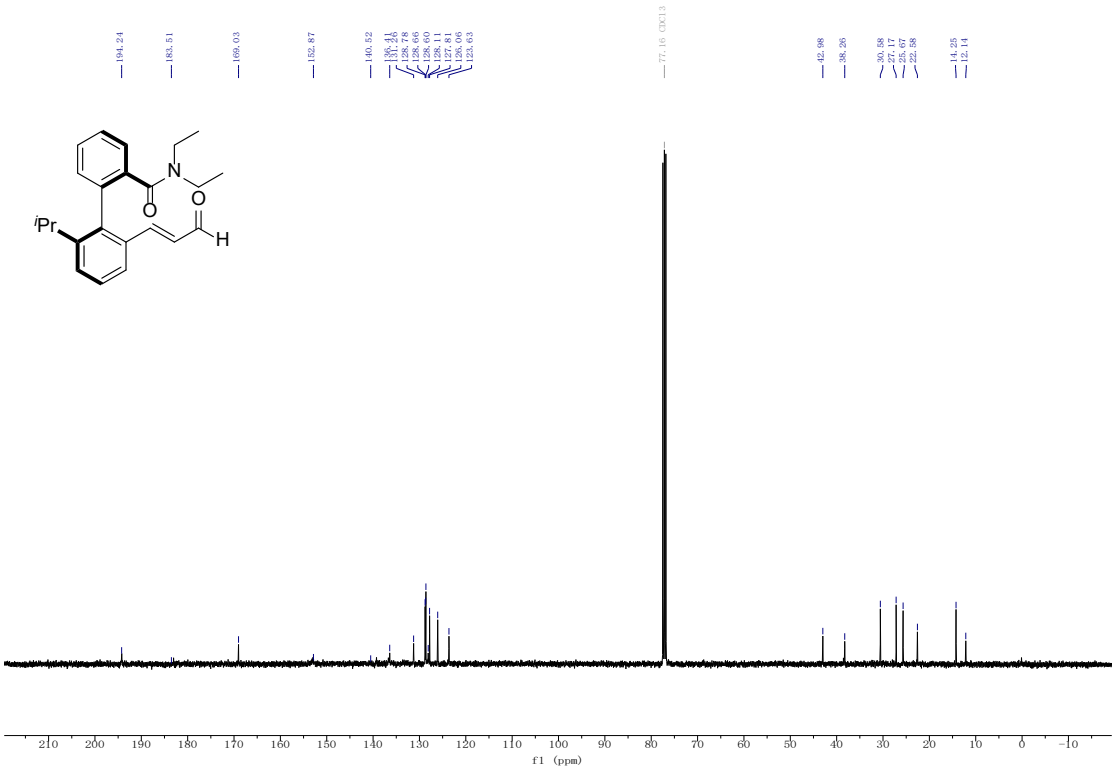

## 3aj, $^{13}$C NMR (101 MHz, $CDCl_3$)



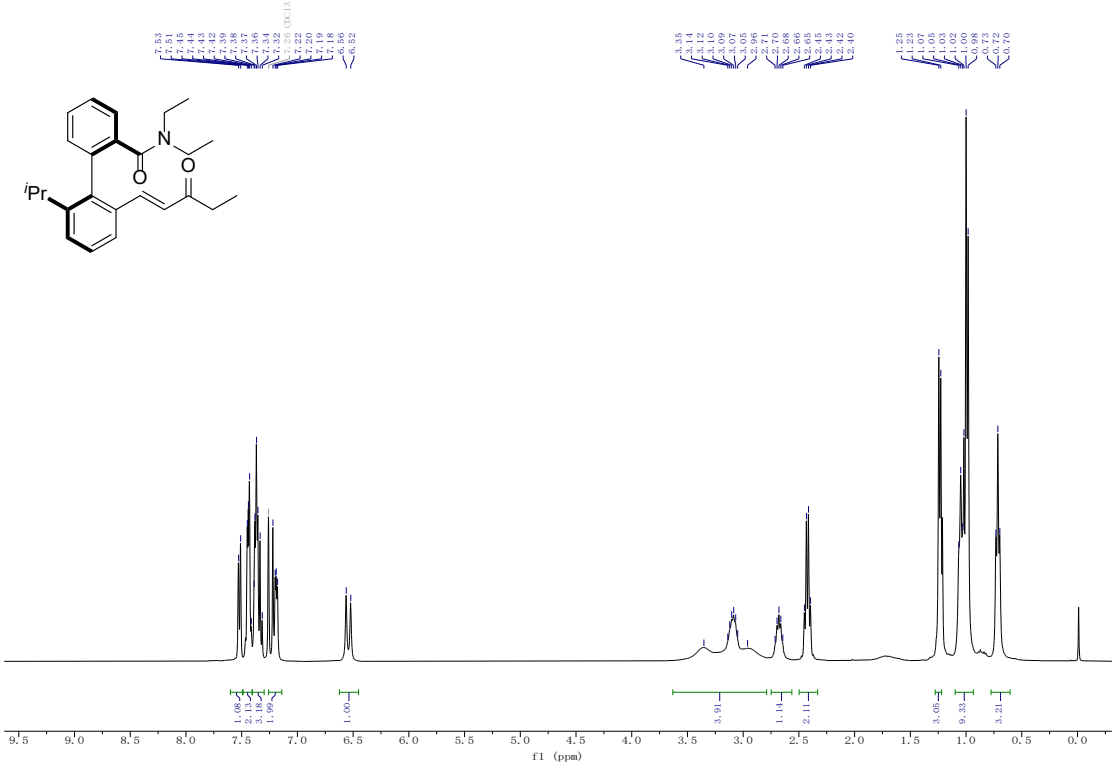
**3ak, $^{1}$H NMR (400 MHz, $CDCl_3$)**



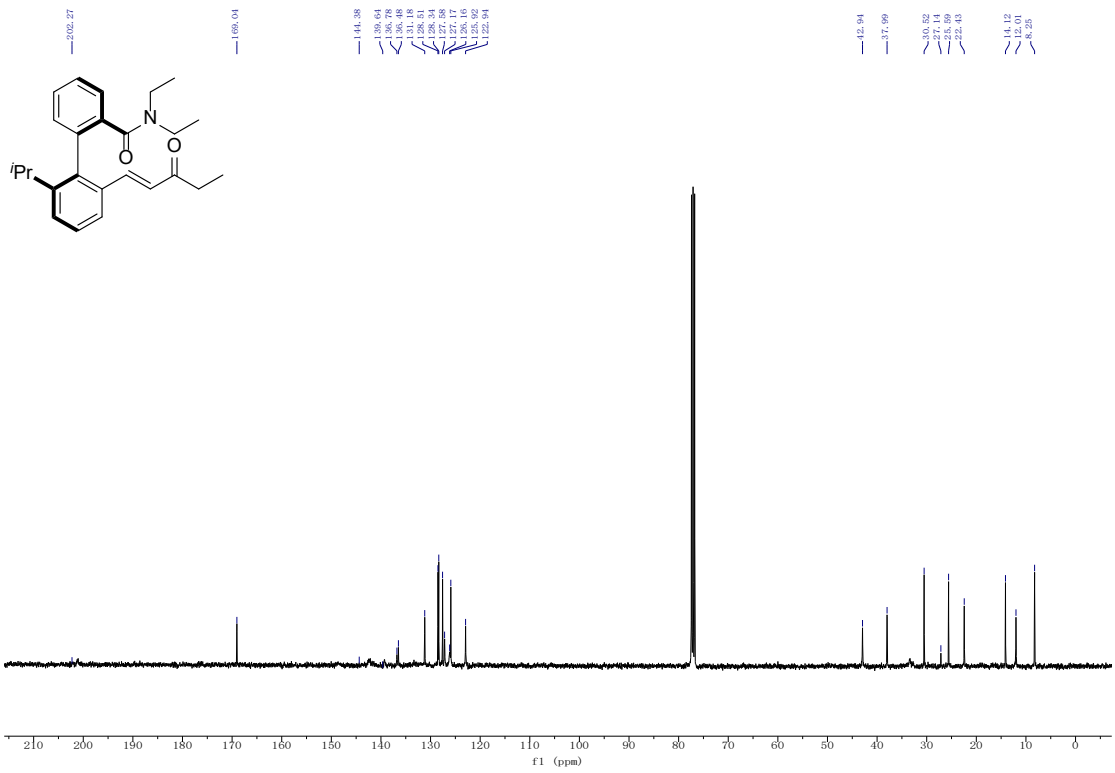

**3ak, $^{13}$C NMR (101 MHz, $CDCl_3$)**



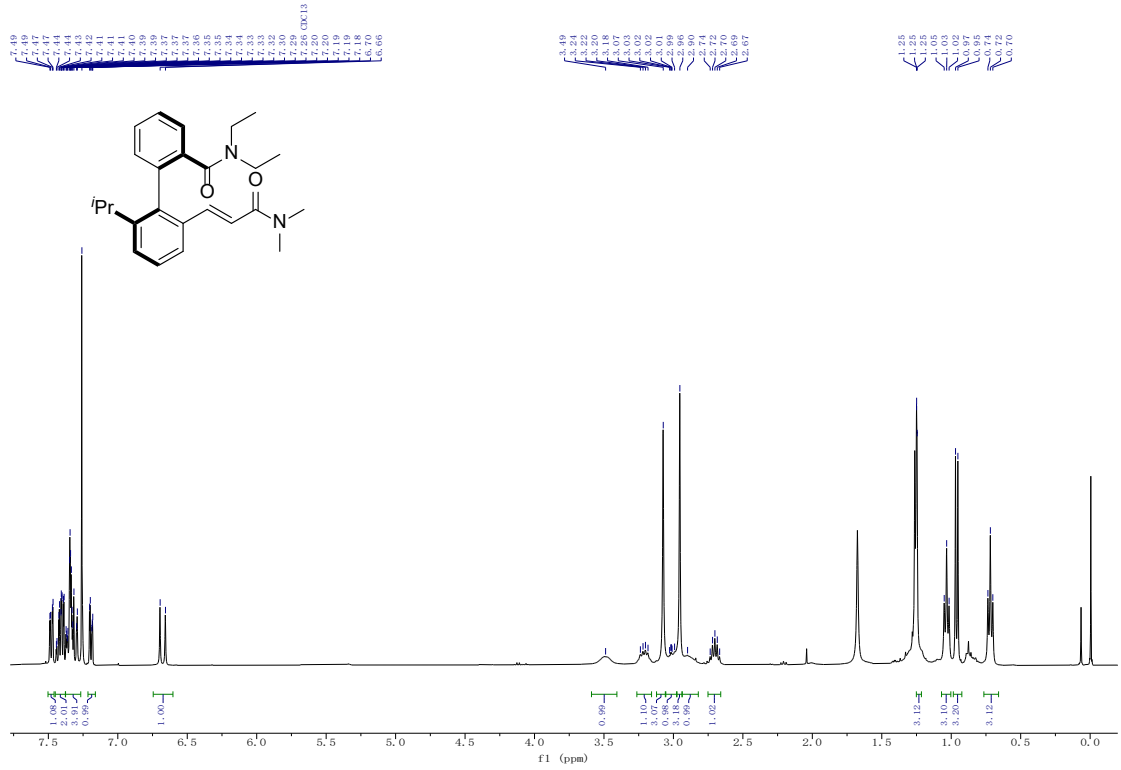
**3al, $^{1}$H NMR (400 MHz, $CDCl_3$)**



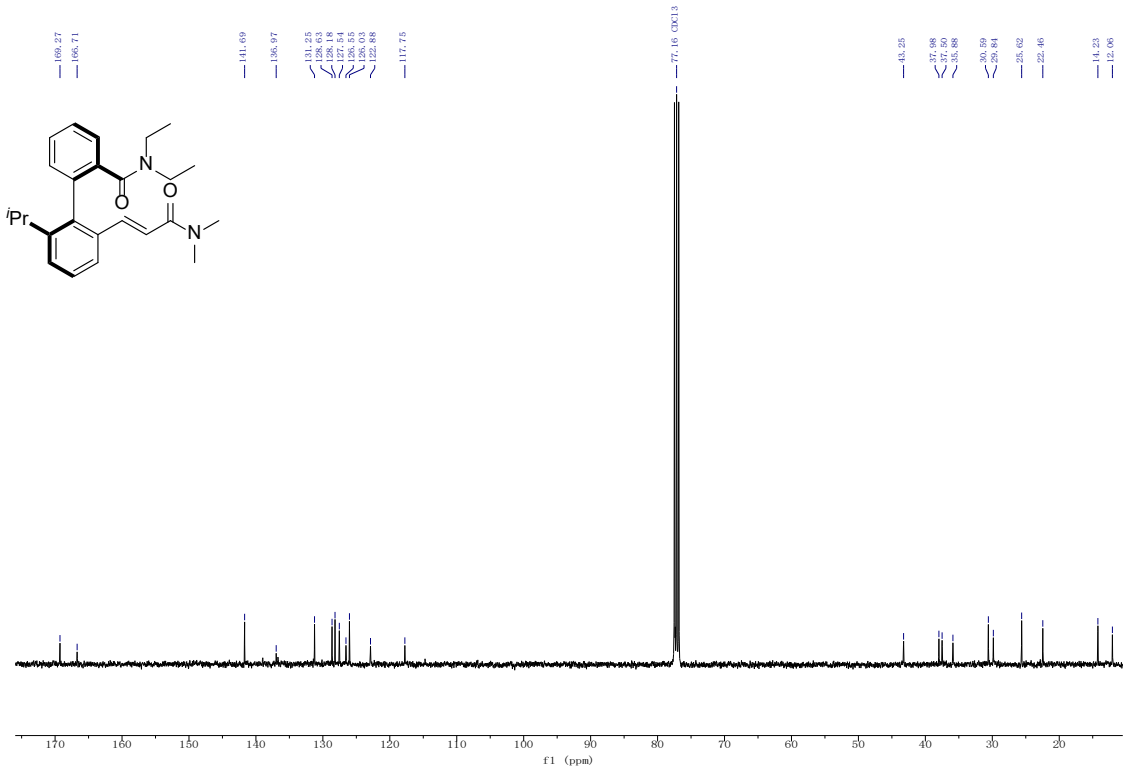
**3al, $^{13}$C NMR (101 MHz, $CDCl_3$)**



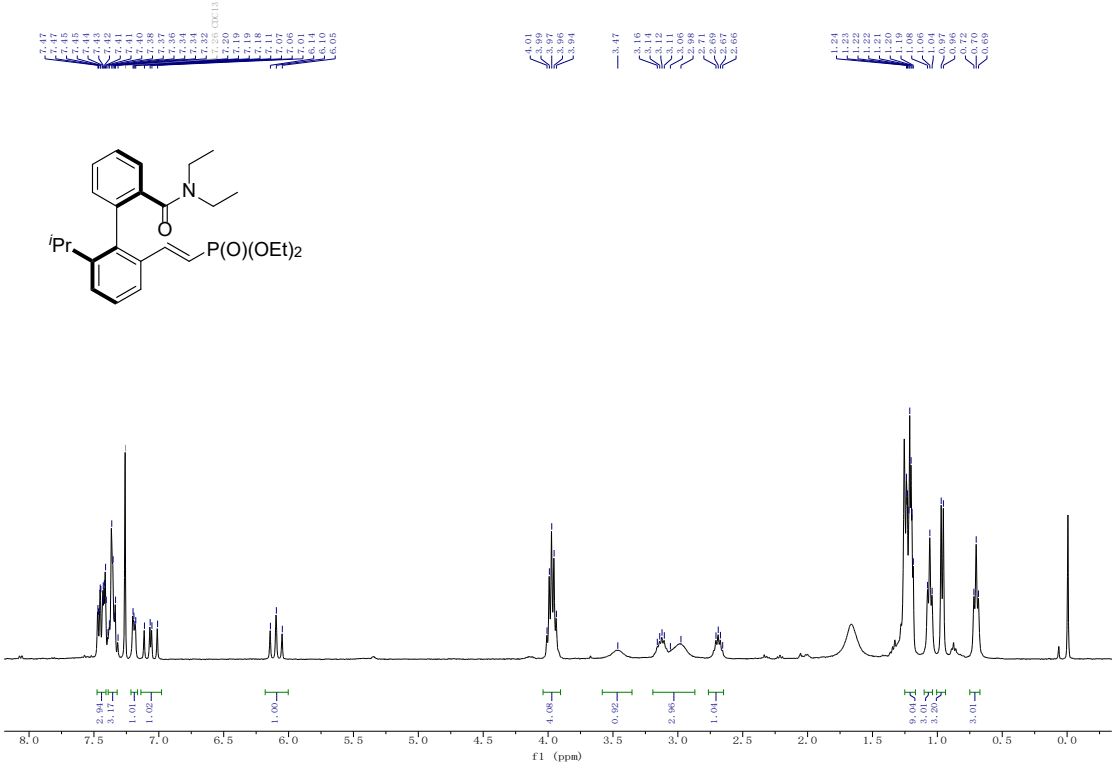
**3am, $^{1}$H NMR (400 MHz, $CDCl_3$)**



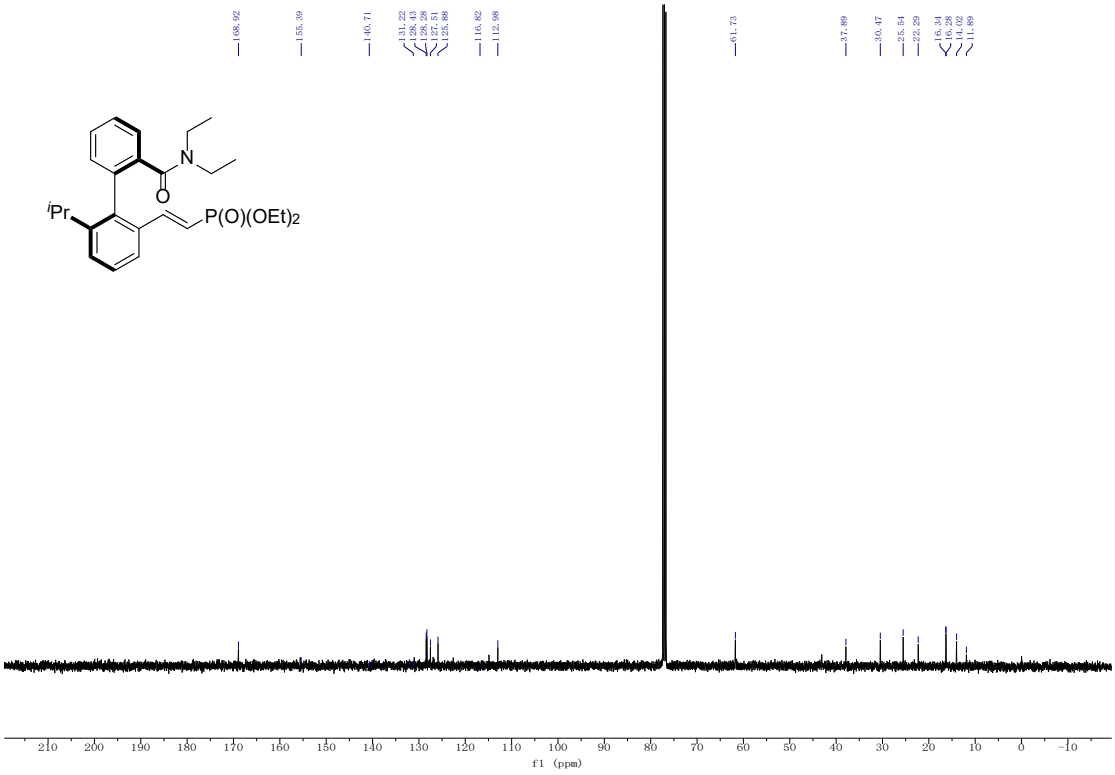
**3am, $^{13}$C NMR (101 MHz, $CDCl_3$)**



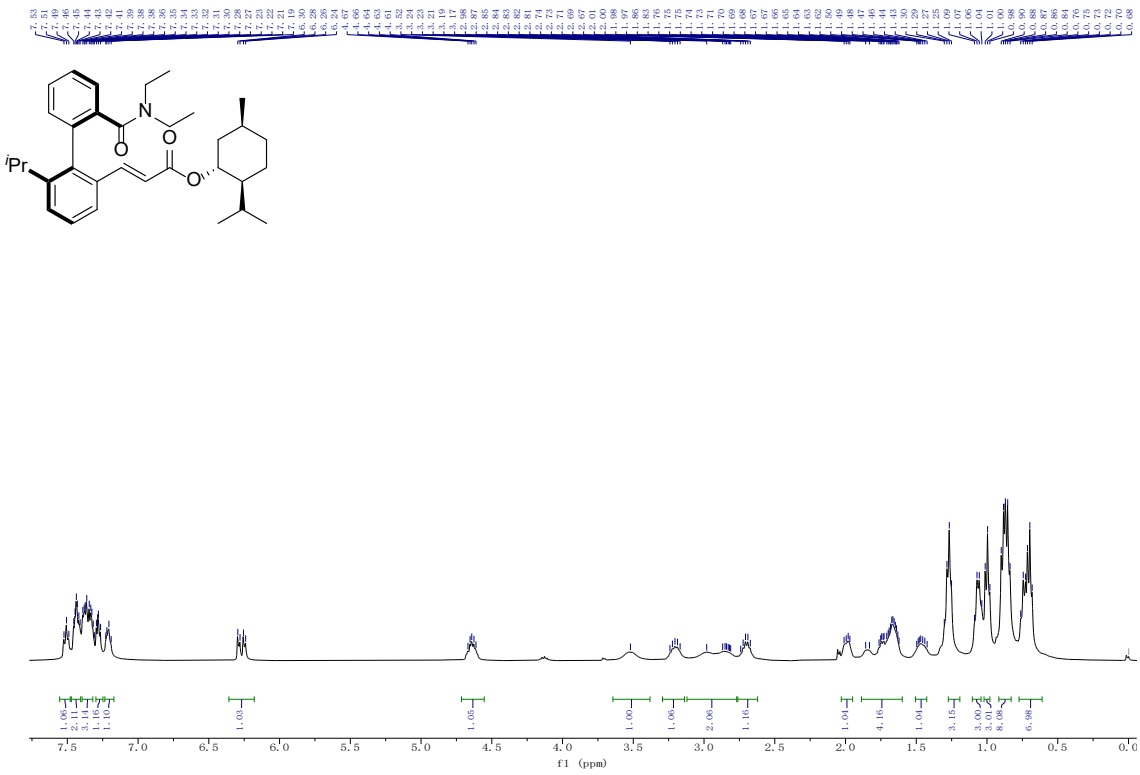
**3an, $^{1}$H NMR (400 MHz, $CDCl_3$)**



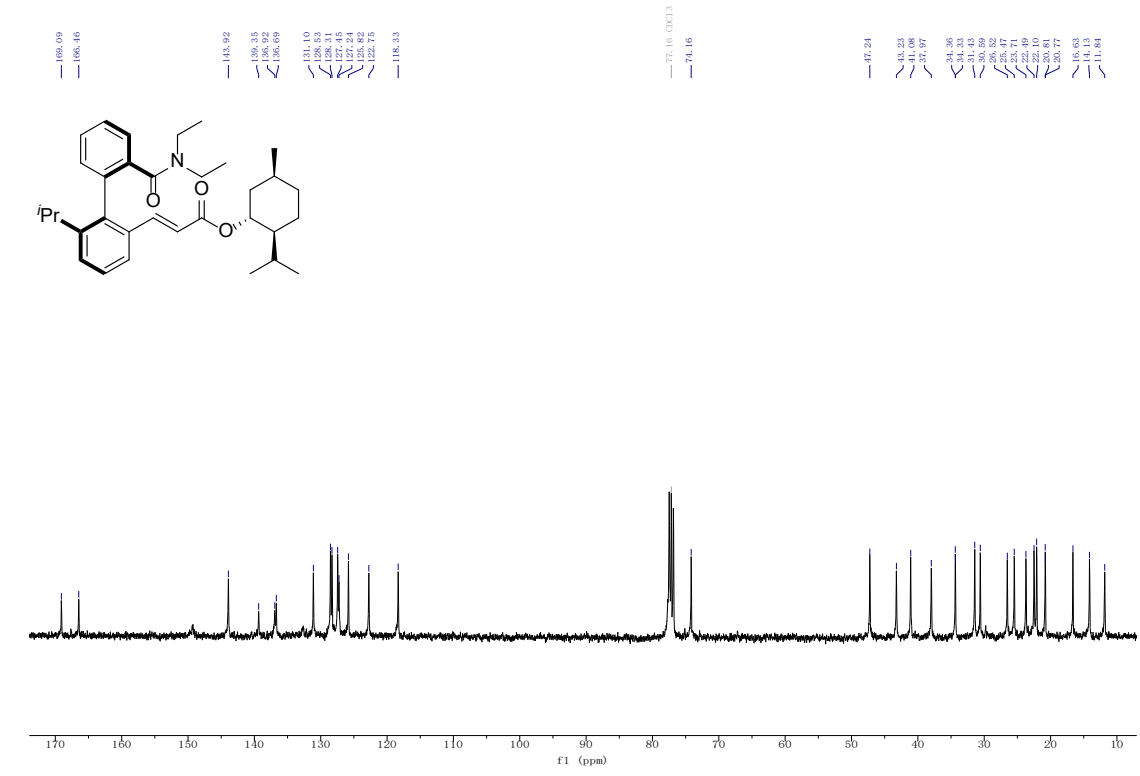

**3an, $^{13}$C NMR (101 MHz, $CDCl_3$)**



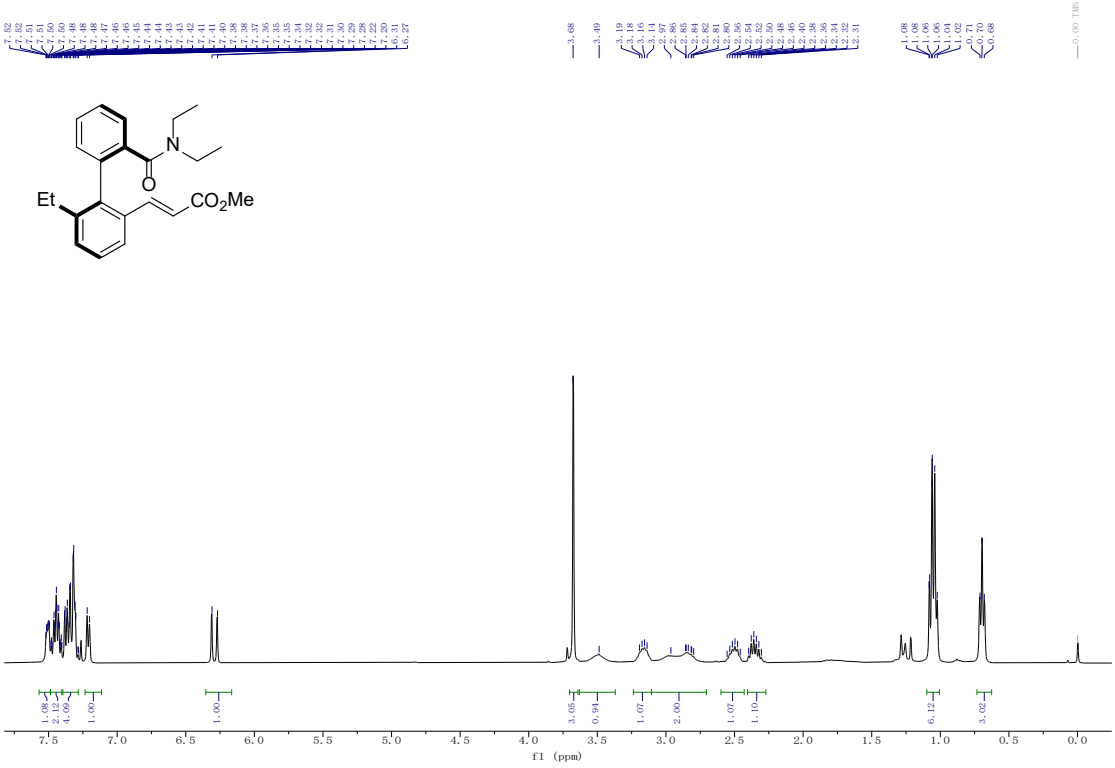
## 3ao, $^{1}$H NMR (400 MHz, $CDCl_3$)



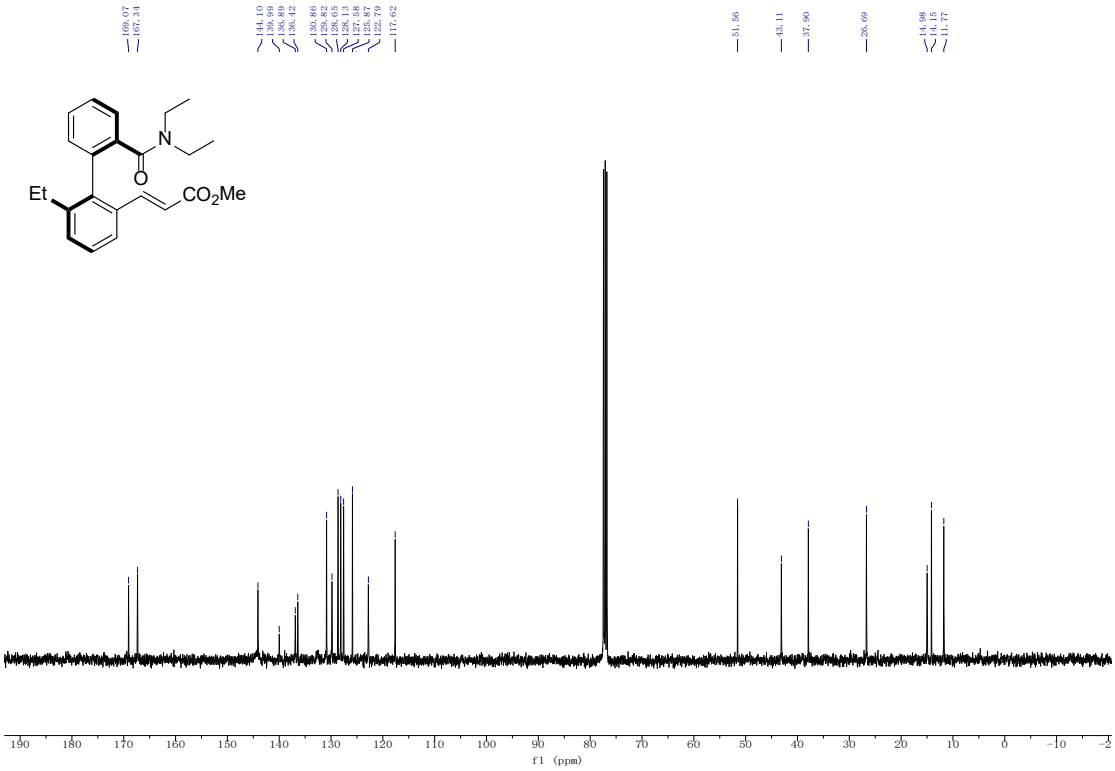
## 3ao, $^{13}$C NMR (101 MHz, $CDCl_3$)



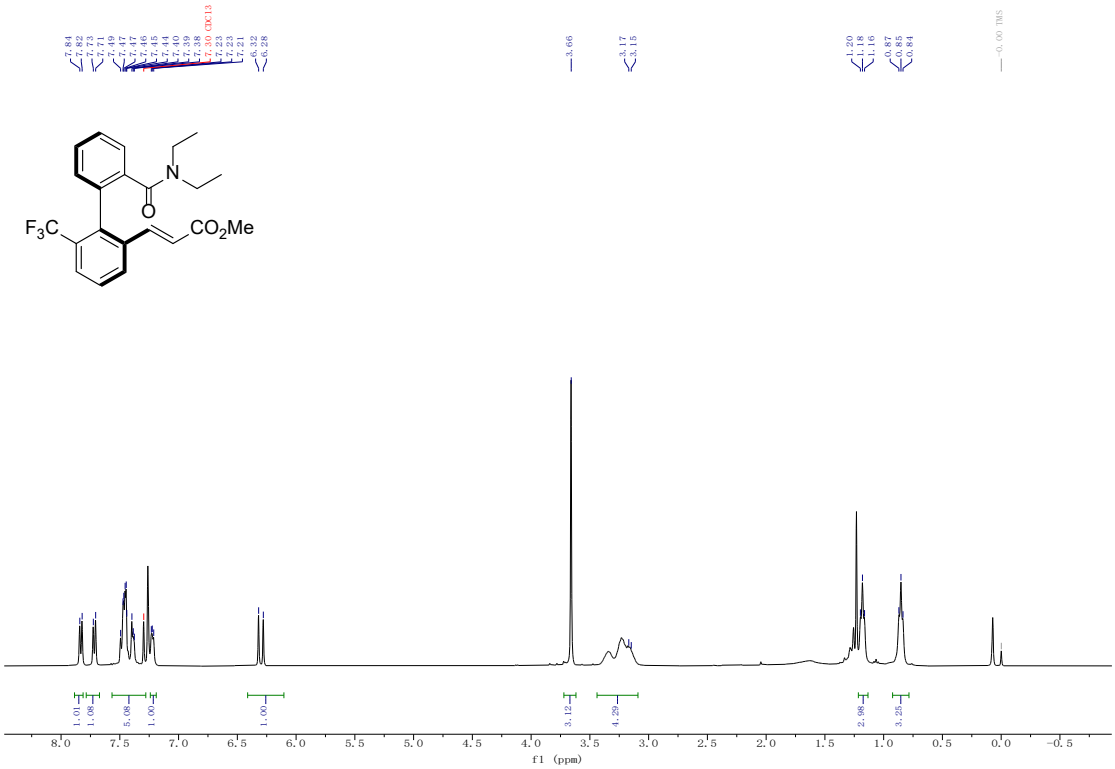
## 3ba, $^{1}$H NMR (400 MHz, $CDCl_3$)



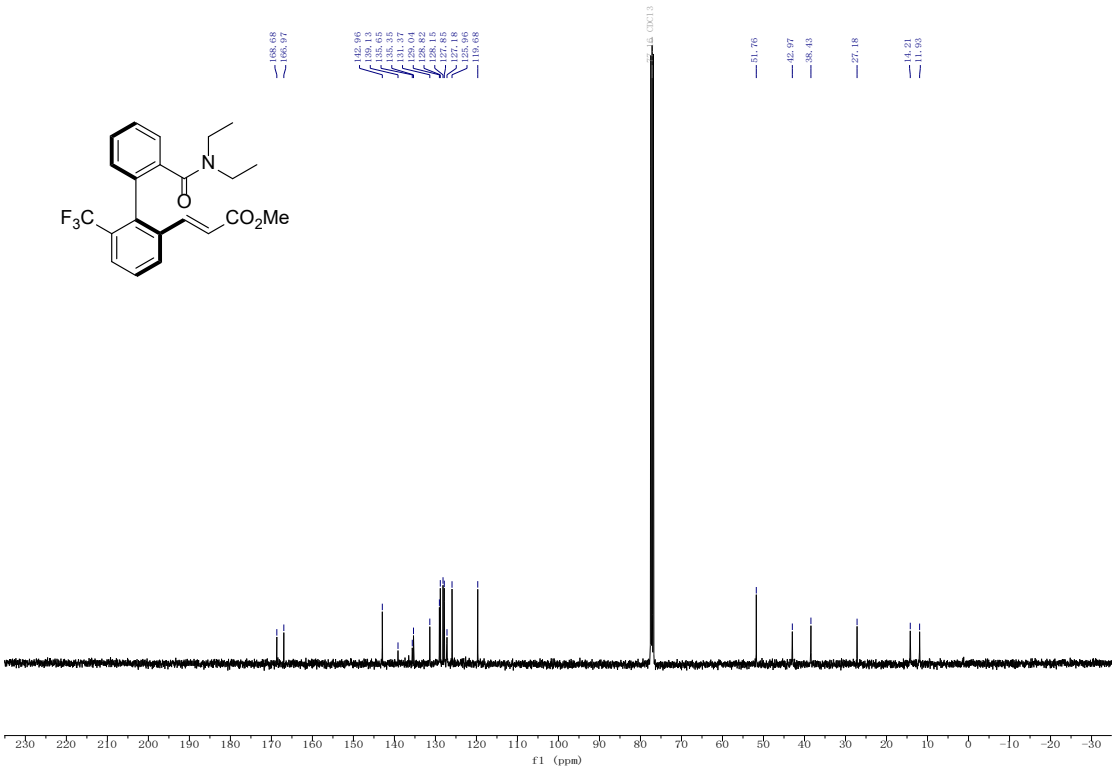

## 3ba, $^{13}$C NMR (101 MHz, $CDCl_3$)



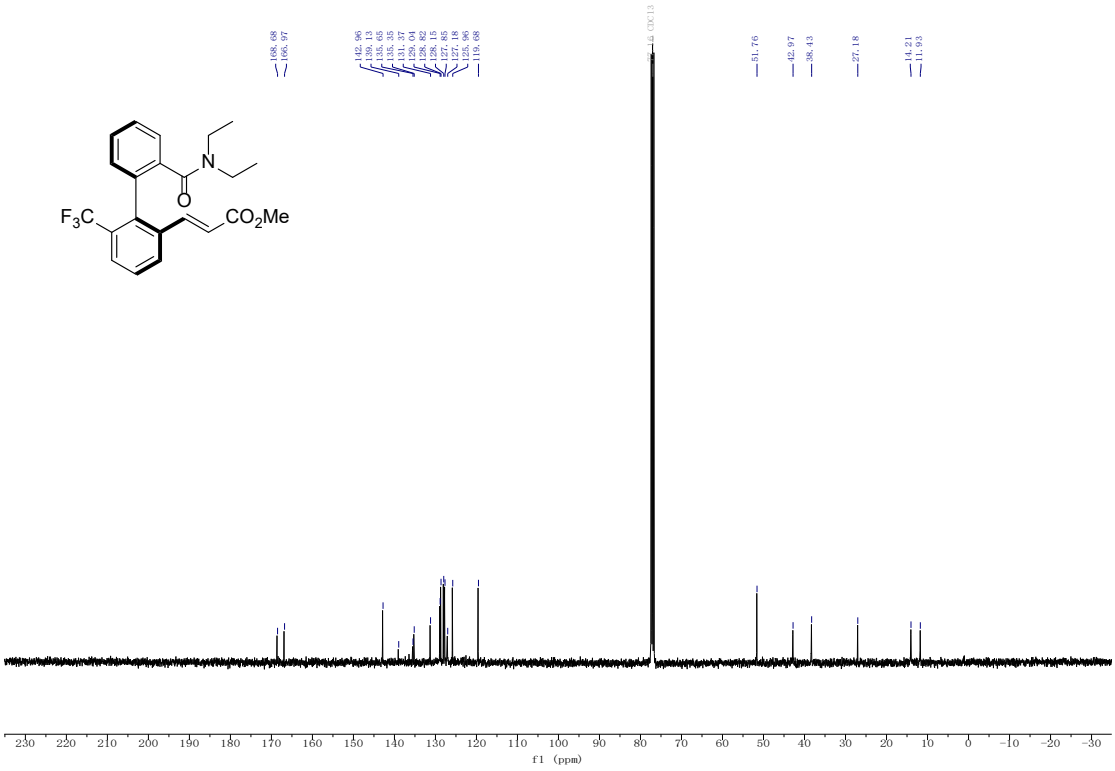
**3ca, $^{1}$H NMR (400 MHz, $CDCl_3$)**



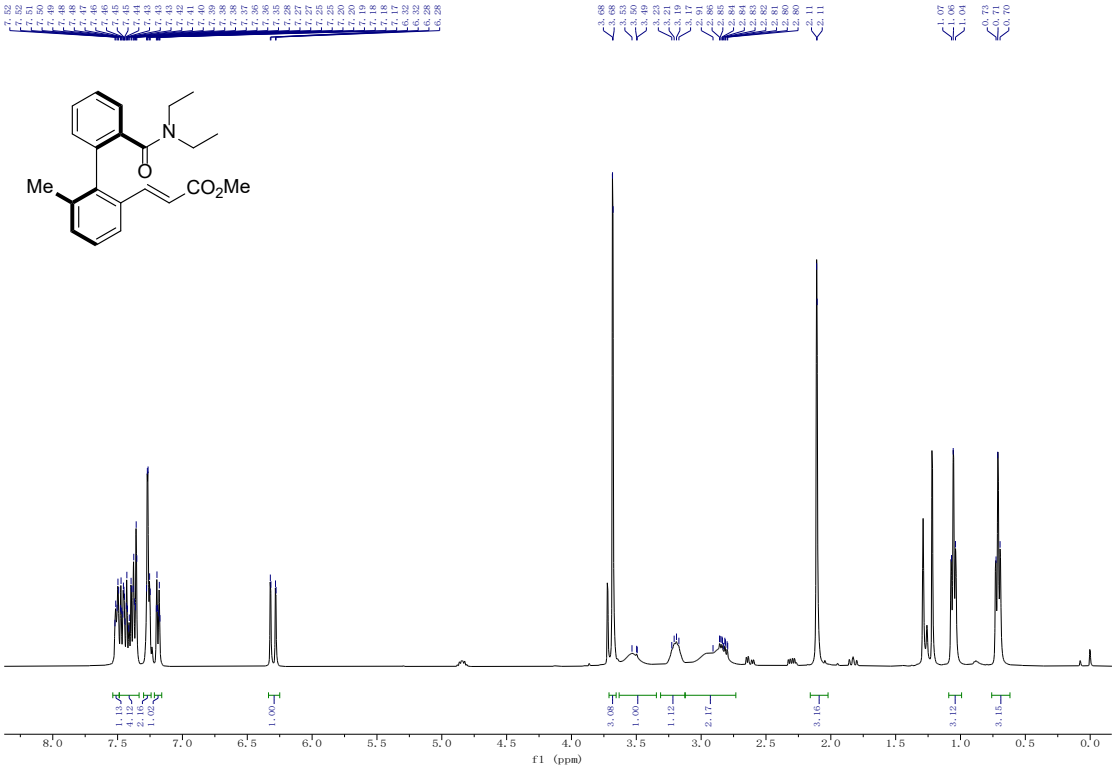

**3ca, $^{13}$C NMR (101 MHz, $CDCl_3$)**



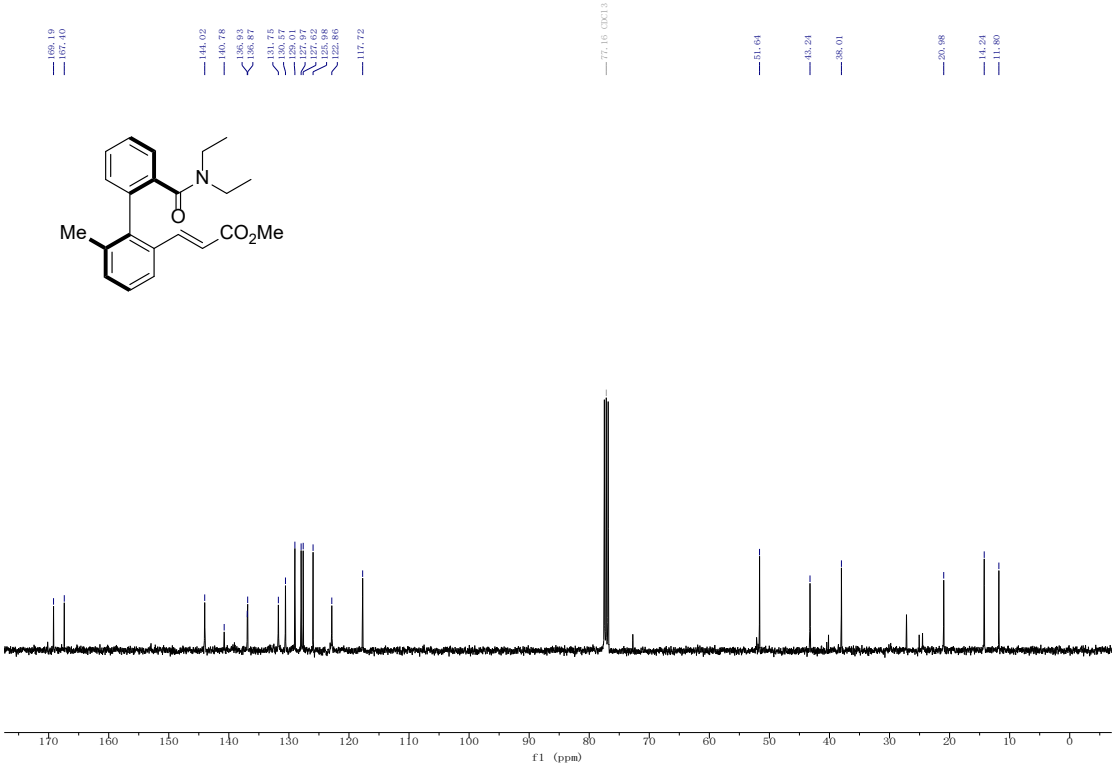
**3ca, $^{13}C$ NMR (101 MHz, $CDCl_3$)**



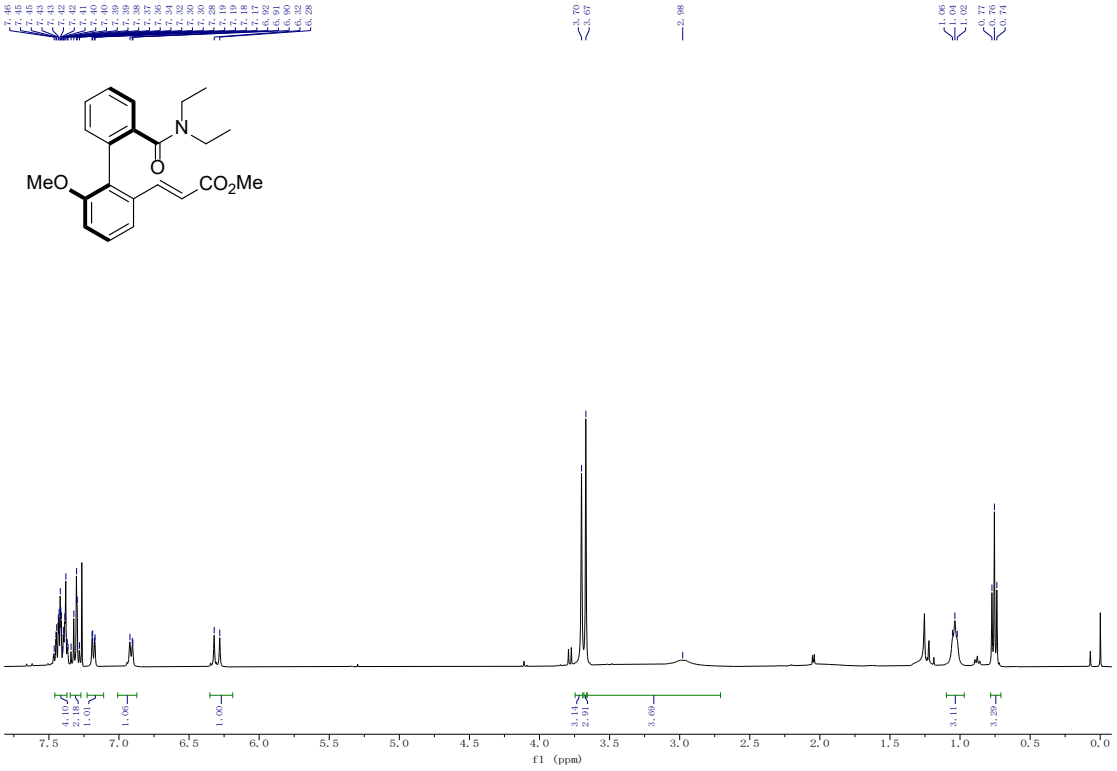
## 3da, $^{1}$H NMR (400 MHz, $CDCl_3$)



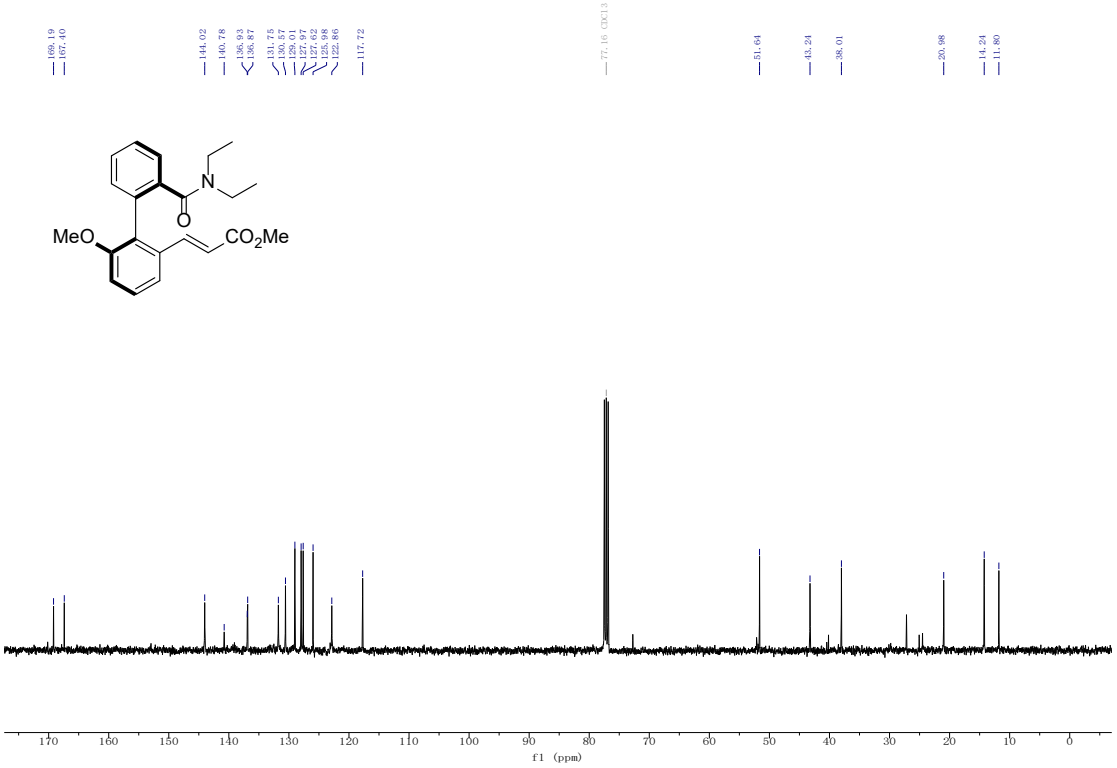

## 3da, $^{13}$C NMR (101 MHz, $CDCl_3$)



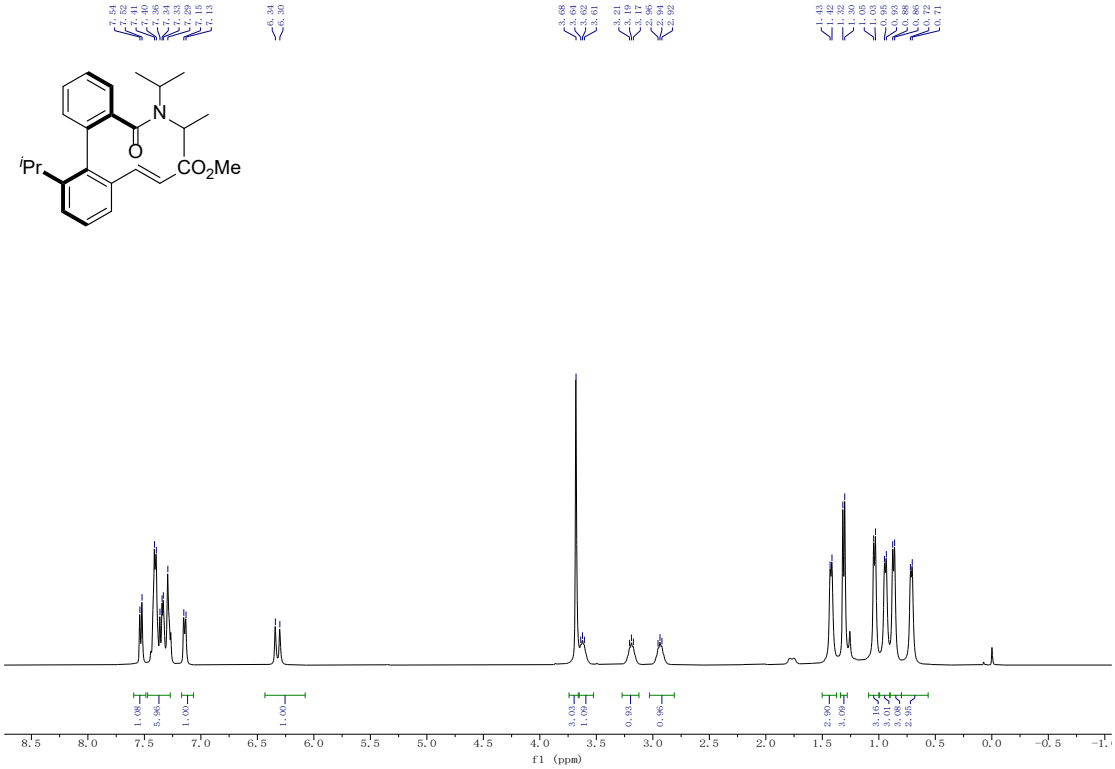
## 3ea, $^{1}$H NMR (400 MHz, $CDCl_3$)



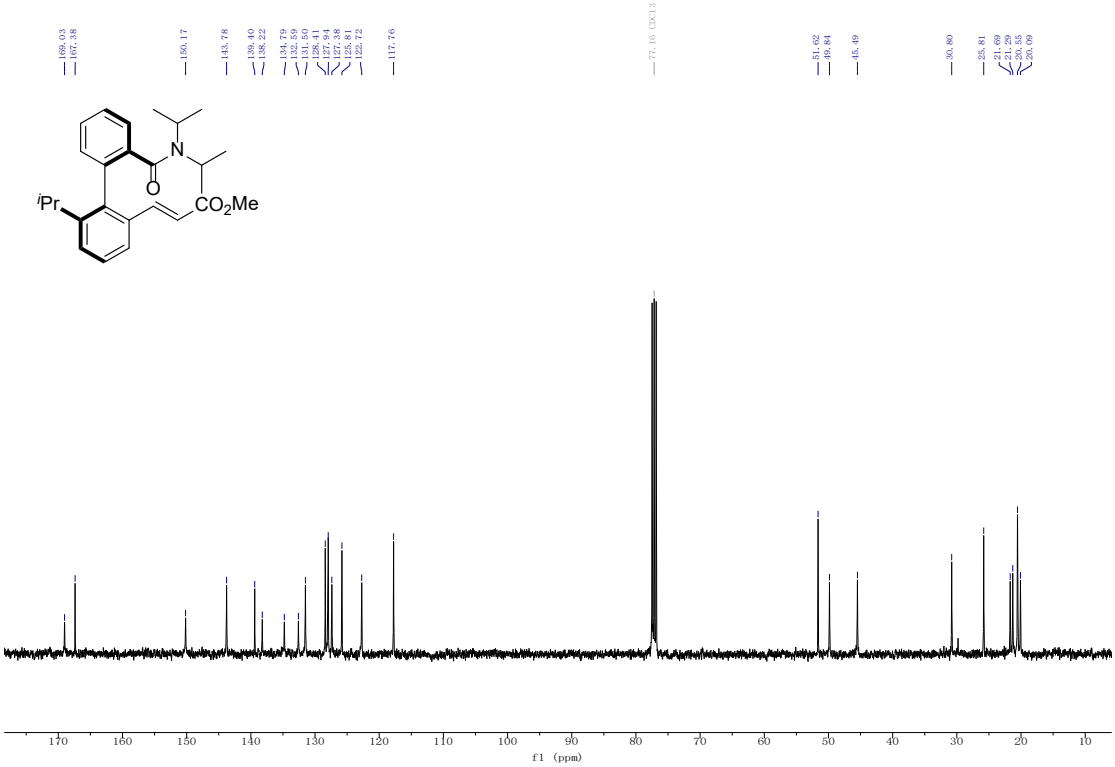

## 3ea, $^{13}$C NMR (101 MHz, $CDCl_3$)



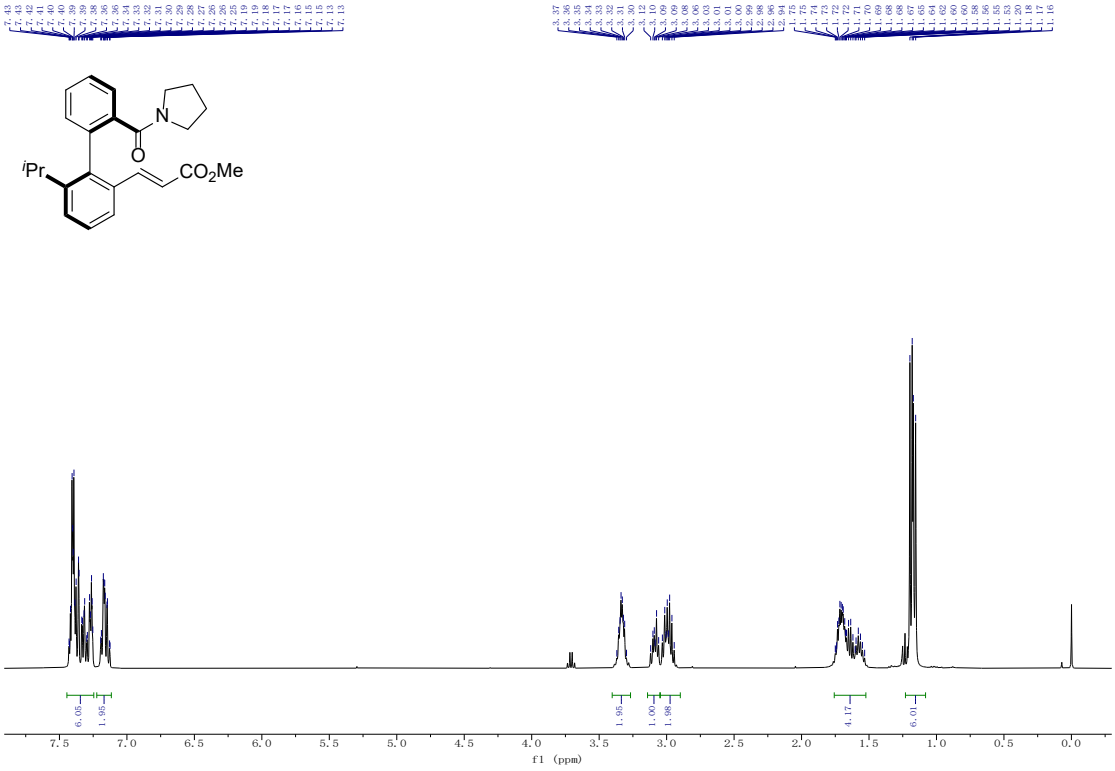
**3fa, $^{1}$H NMR (400 MHz, $CDCl_3$)**



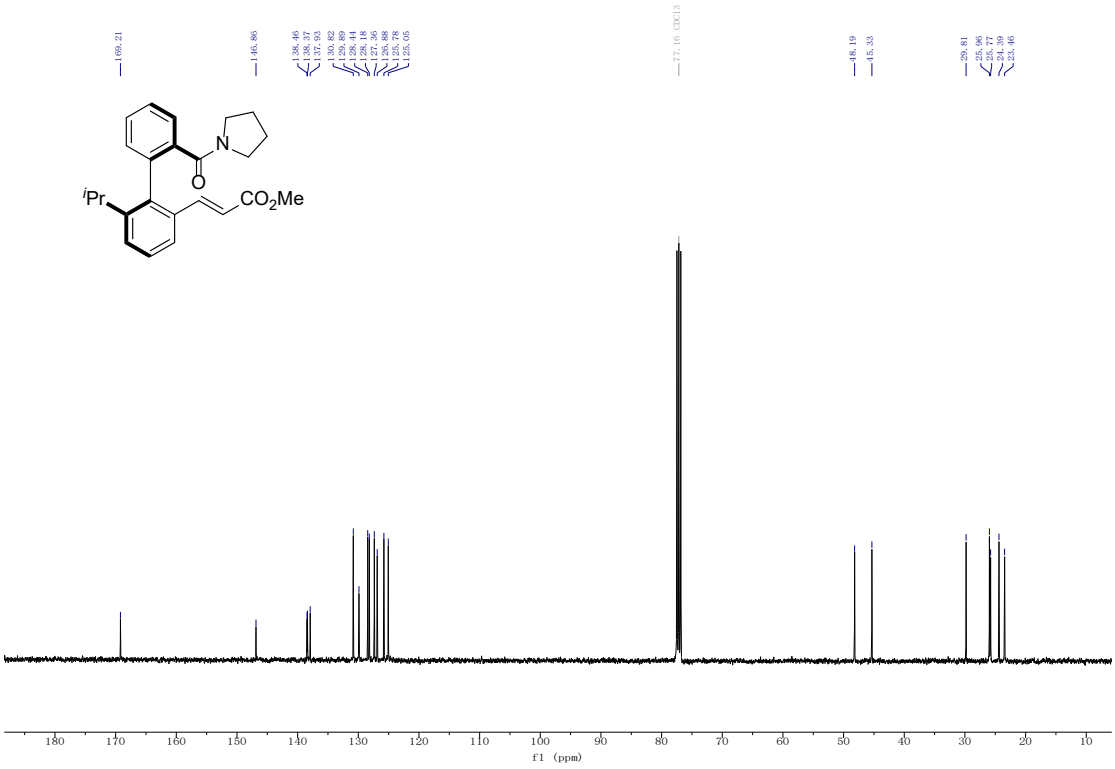

**3fa, $^{13}$C NMR (101 MHz, $CDCl_3$)**



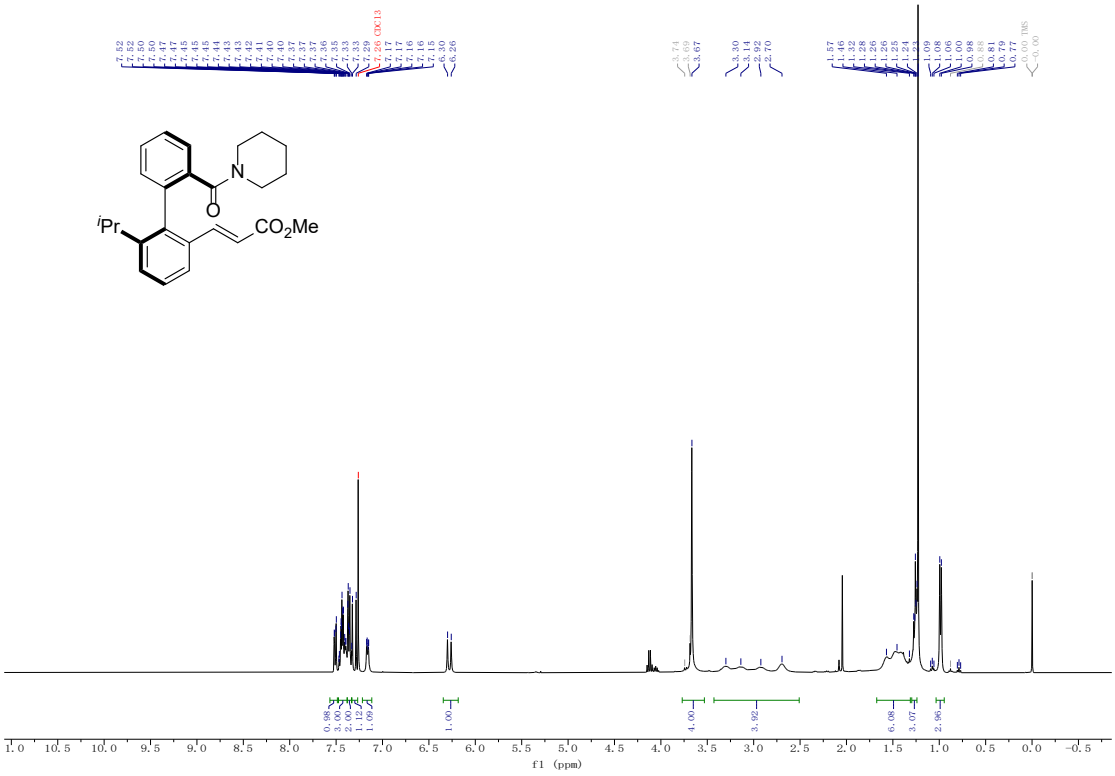
## 3ga, $^{1}$H NMR (400 MHz, $CDCl_3$)



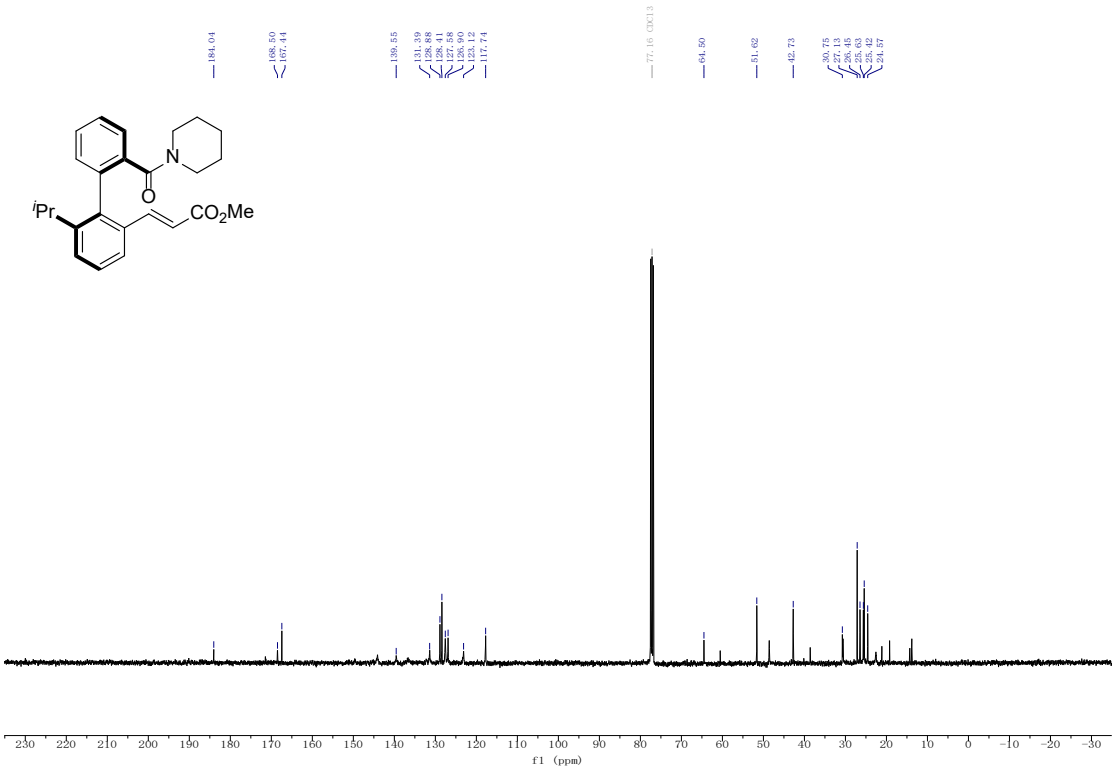

## 3ga, $^{13}$C NMR (101 MHz, $CDCl_3$)



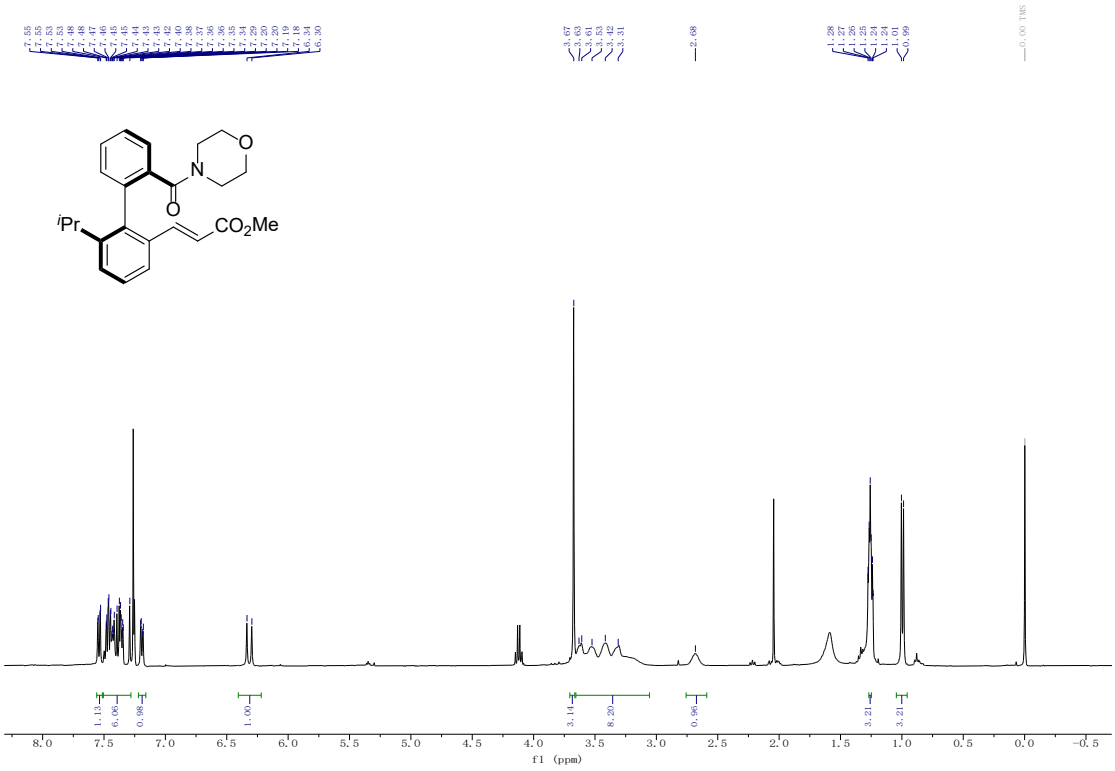
**3ha, $^{1}$H NMR (400 MHz, $CDCl_3$)**



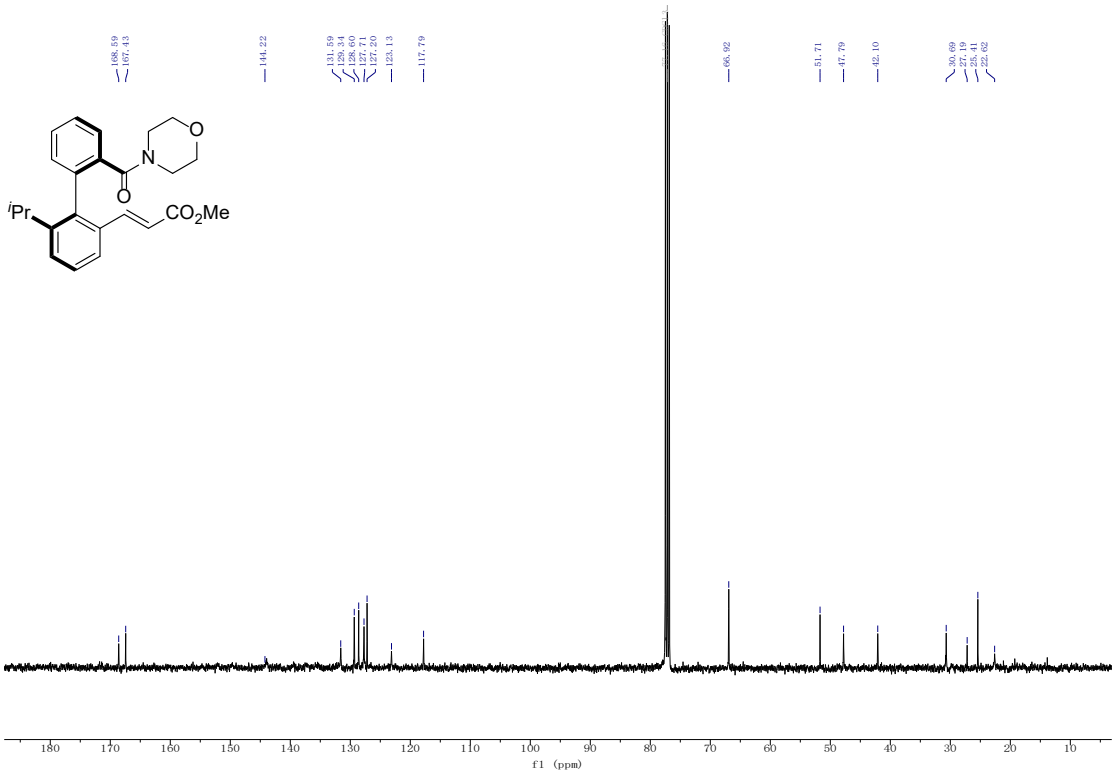
**3ha, $^{13}$C NMR (101 MHz, $CDCl_3$)**



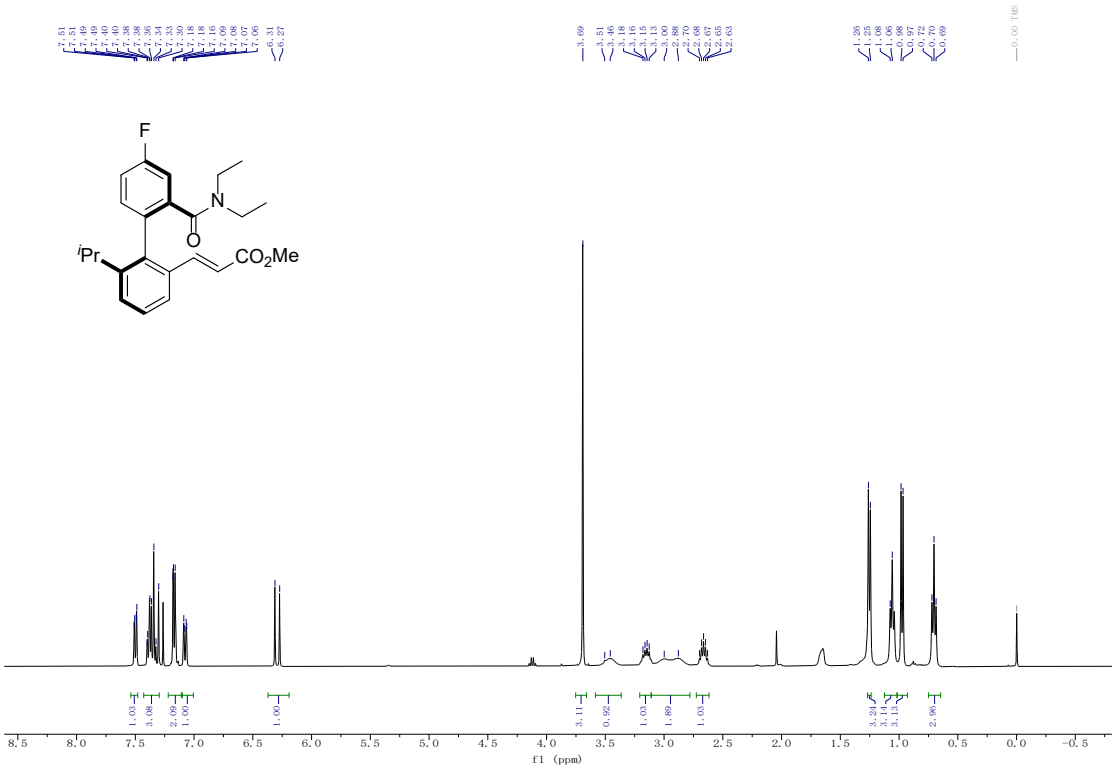
**3ia, $^{1}$H NMR (400 MHz, $CDCl_3$)**



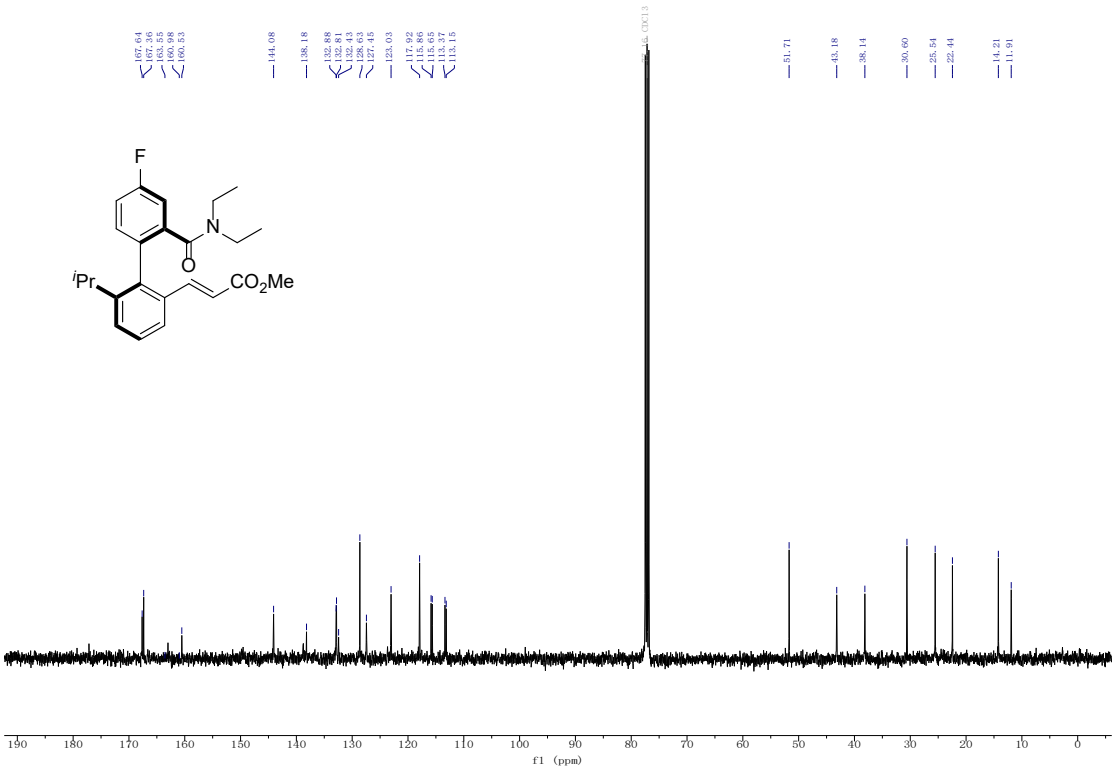

**3ia, $^{13}$C NMR (101 MHz, $CDCl_3$)**



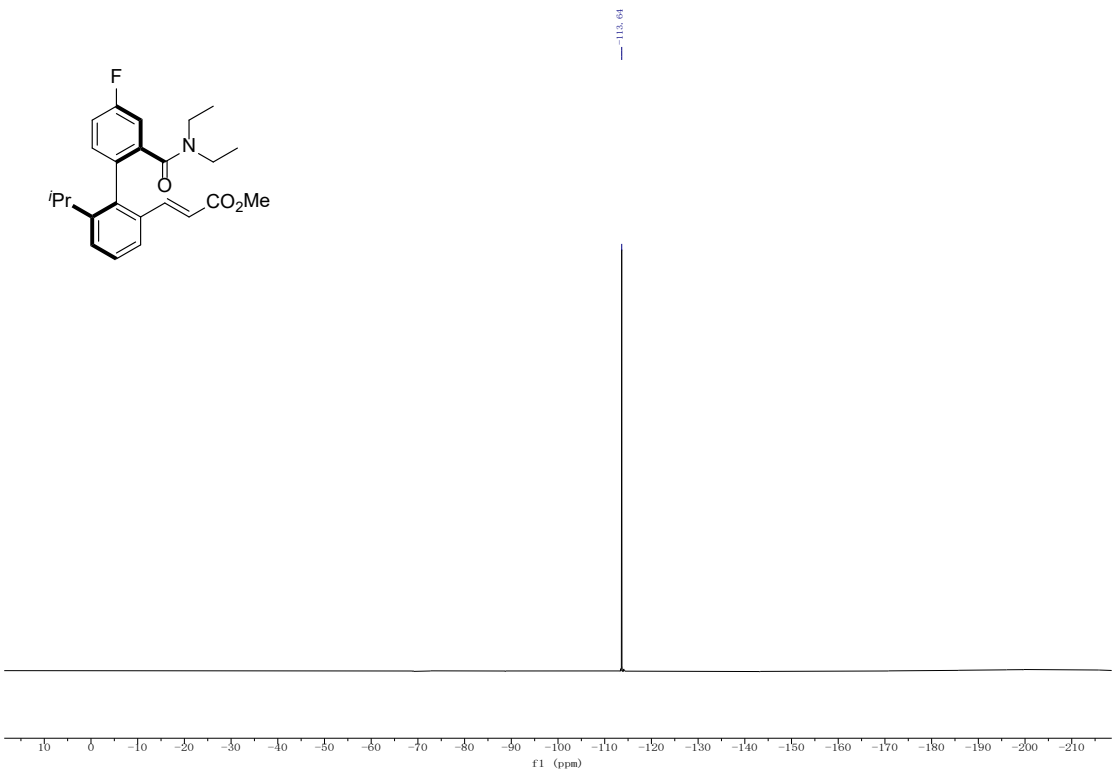
## 3ja, $^{1}$H NMR (400 MHz, $CDCl_3$)



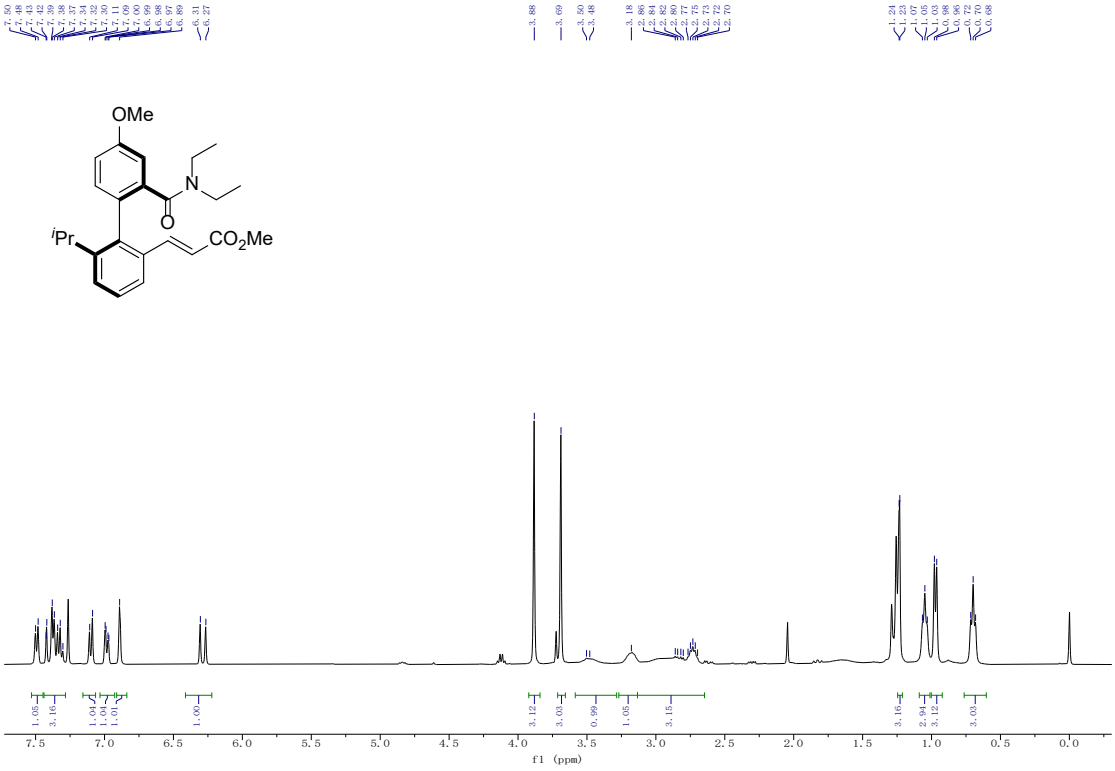

## 3ja, $^{13}$C NMR (101 MHz, $CDCl_3$)



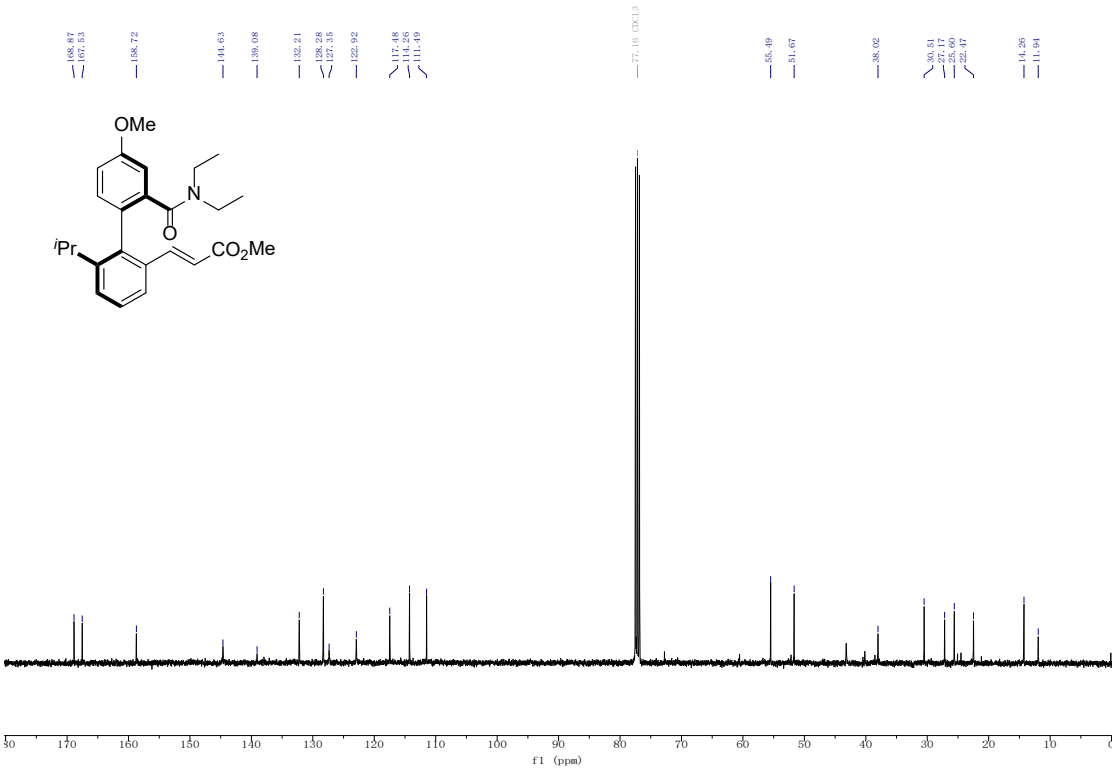
**3ja, $^{19}$F NMR (376 MHz, $CDCl_3$)**



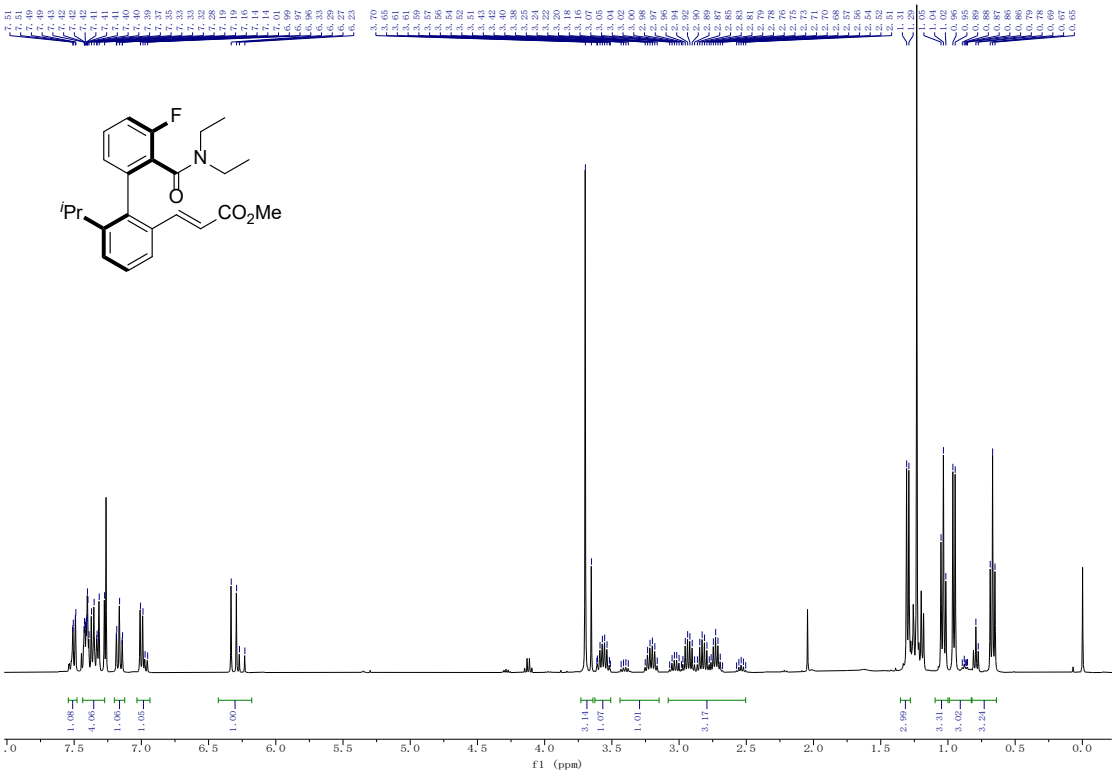
**3ka, $^{1}$H NMR (400 MHz, $CDCl_3$)**



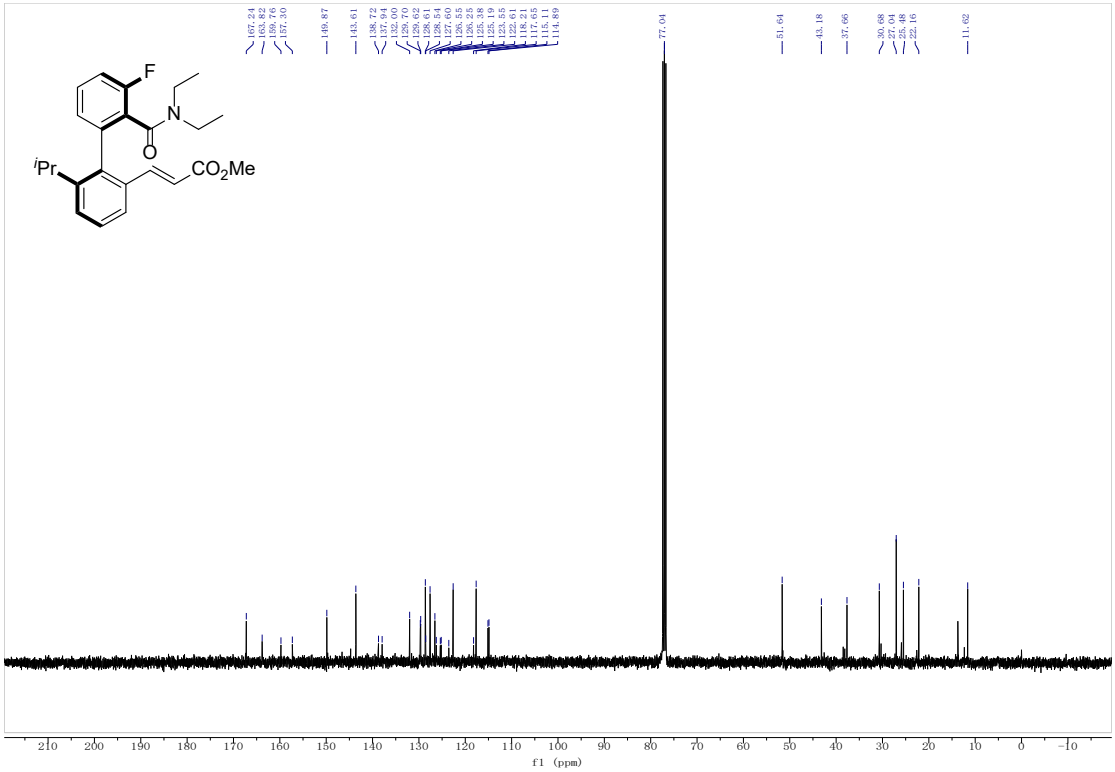

**3ka, $^{13}$C NMR (101 MHz, $CDCl_3$)**



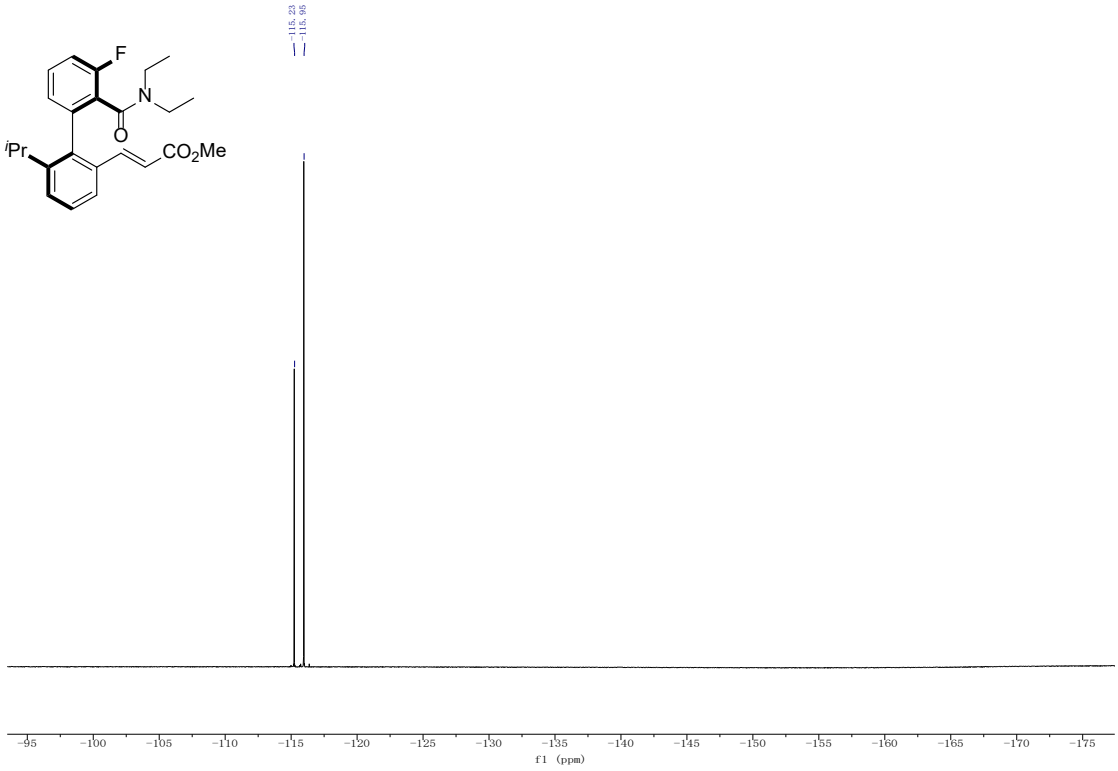
## 3la, $^{1}$H NMR (400 MHz, $CDCl_3$)



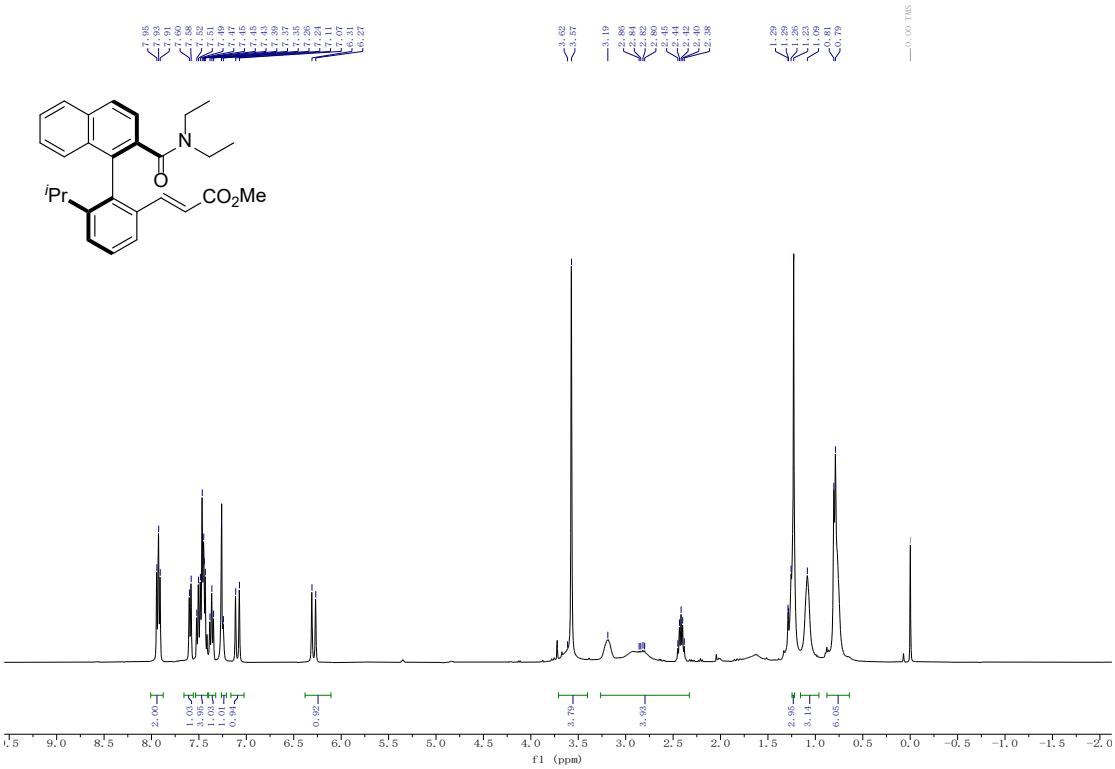

## 3la, $^{13}$C NMR (101 MHz, $CDCl_3$)



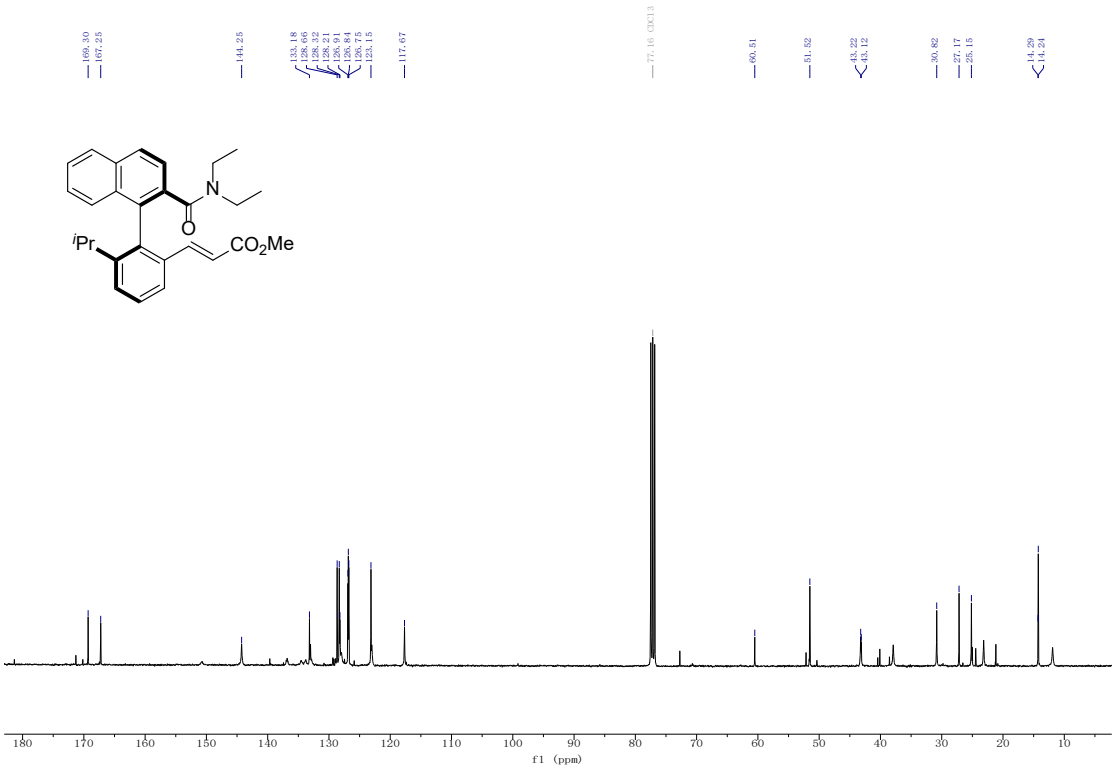
**3ja, $^{19}F$ NMR (376 MHz, $CDCl_3$)**



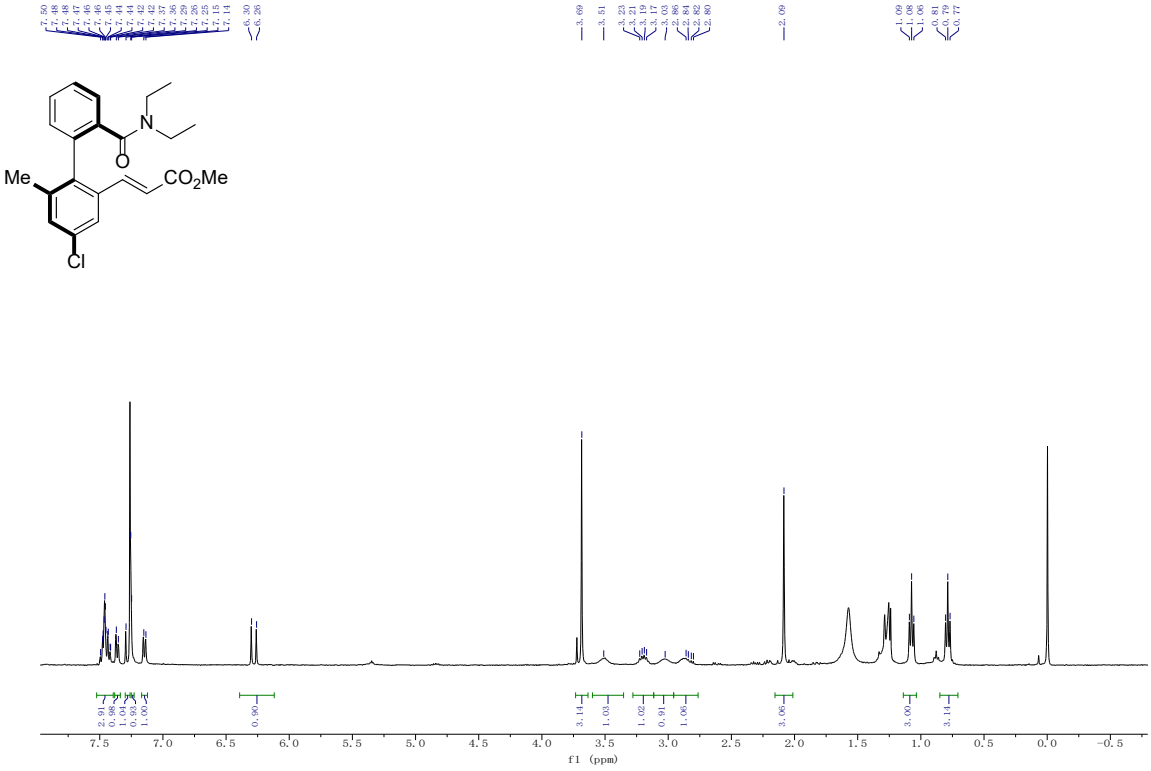
**3ma, $^{1}$H NMR (400 MHz, $CDCl_3$)**



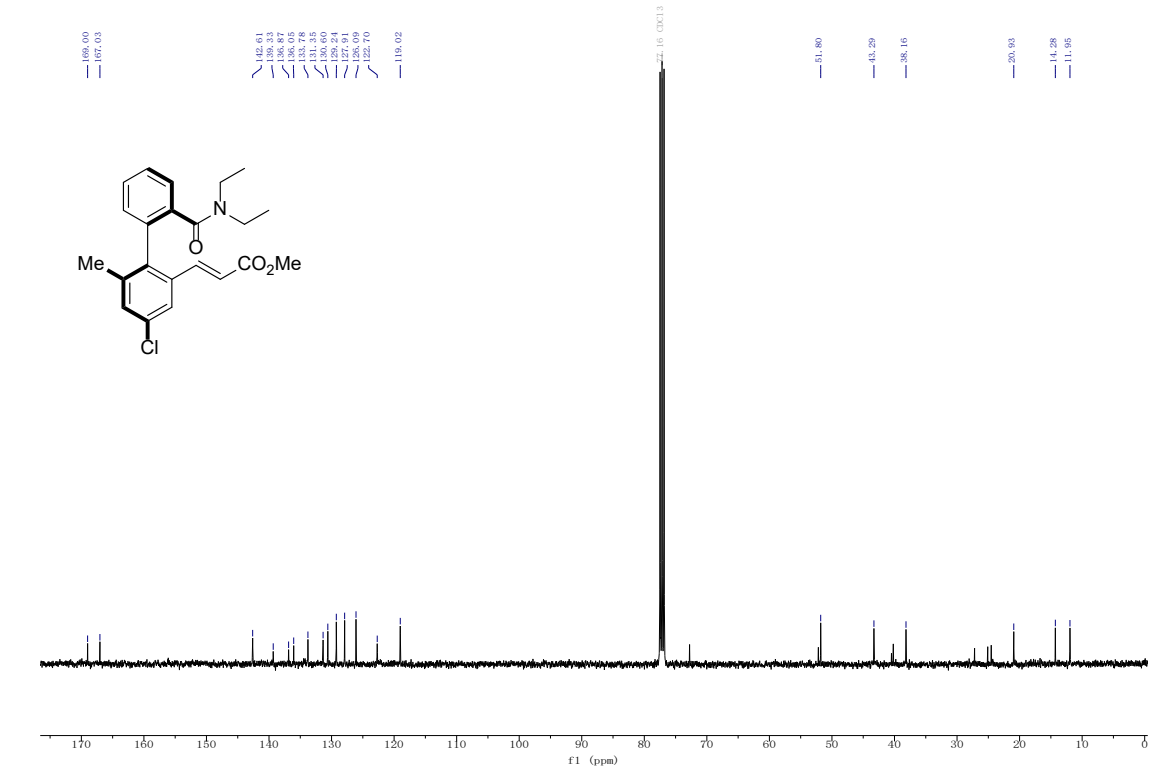

**3ma, $^{13}$C NMR (101 MHz, $CDCl_3$)**



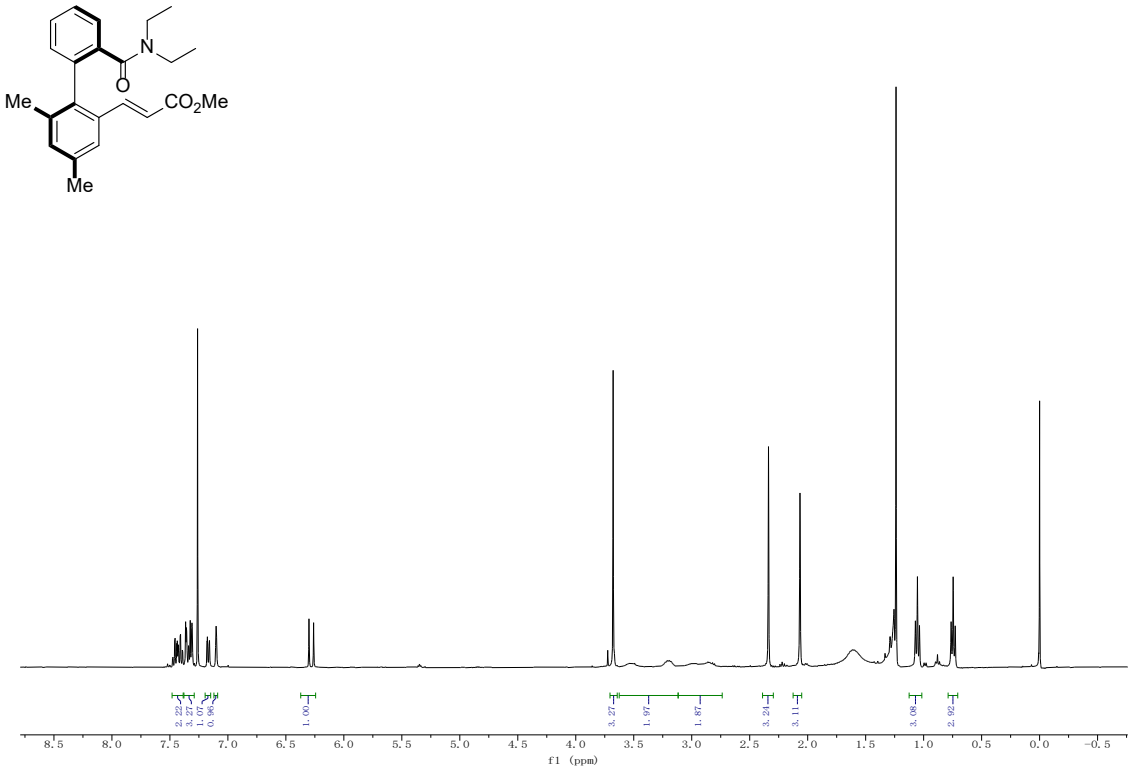
## 3na, $^{1}$H NMR (400 MHz, $CDCl_3$)



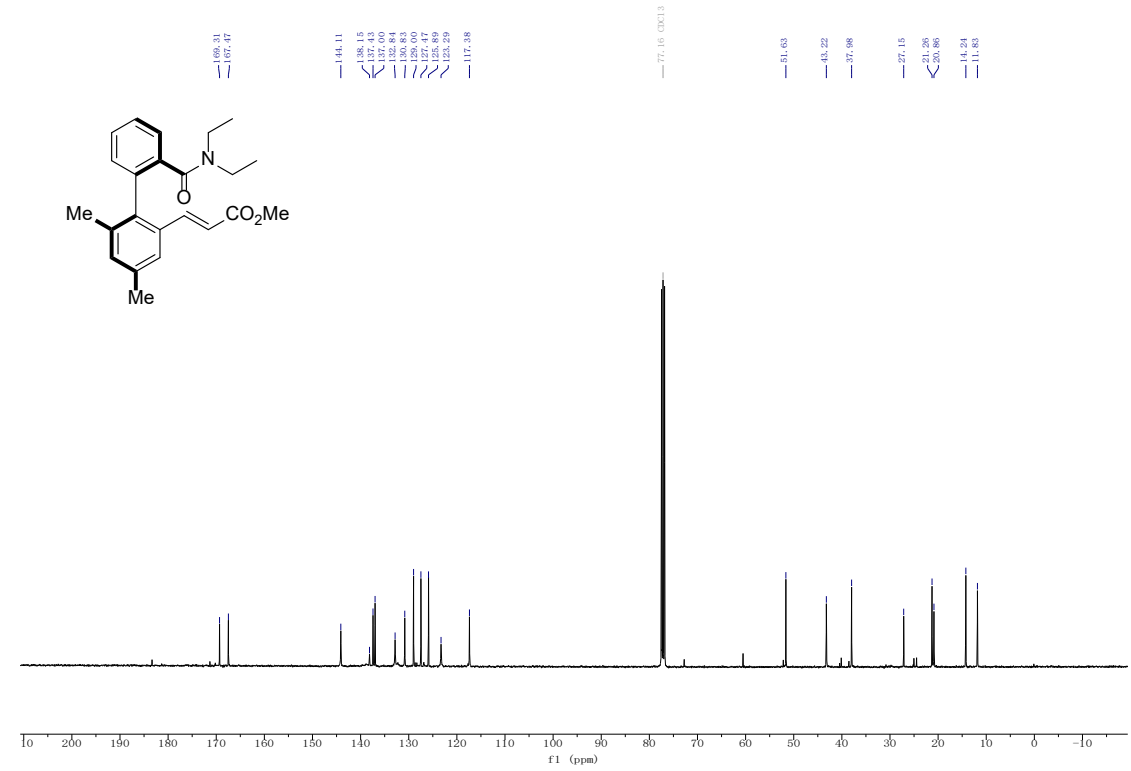

## 3na, $^{13}$C NMR (101 MHz, $CDCl_3$)



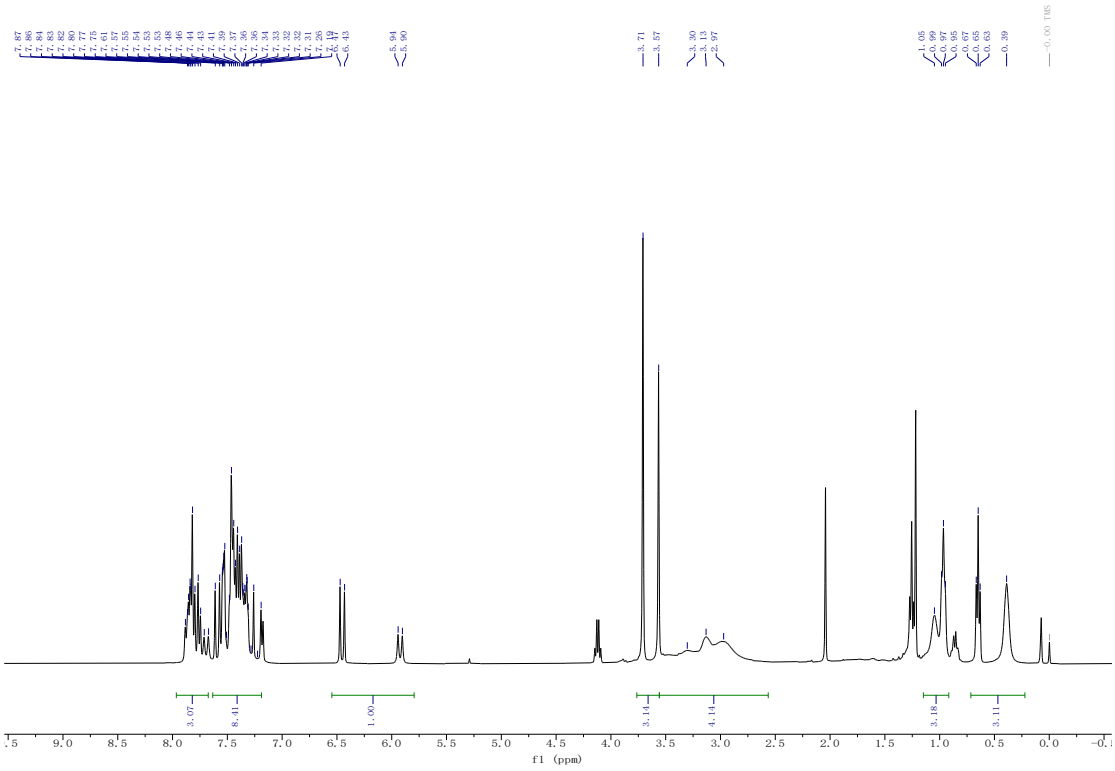
**3oa, $^{1}$H NMR (400 MHz, $CDCl_3$)**



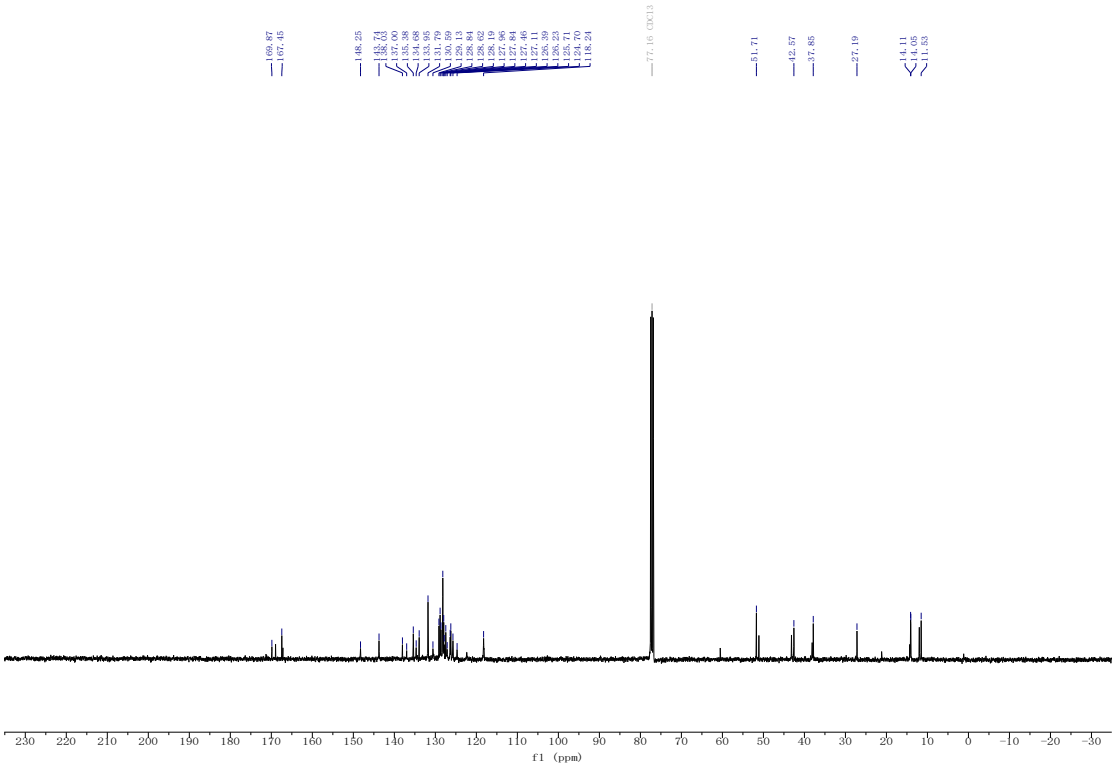

**3oa, $^{13}$C NMR (101 MHz, $CDCl_3$)**



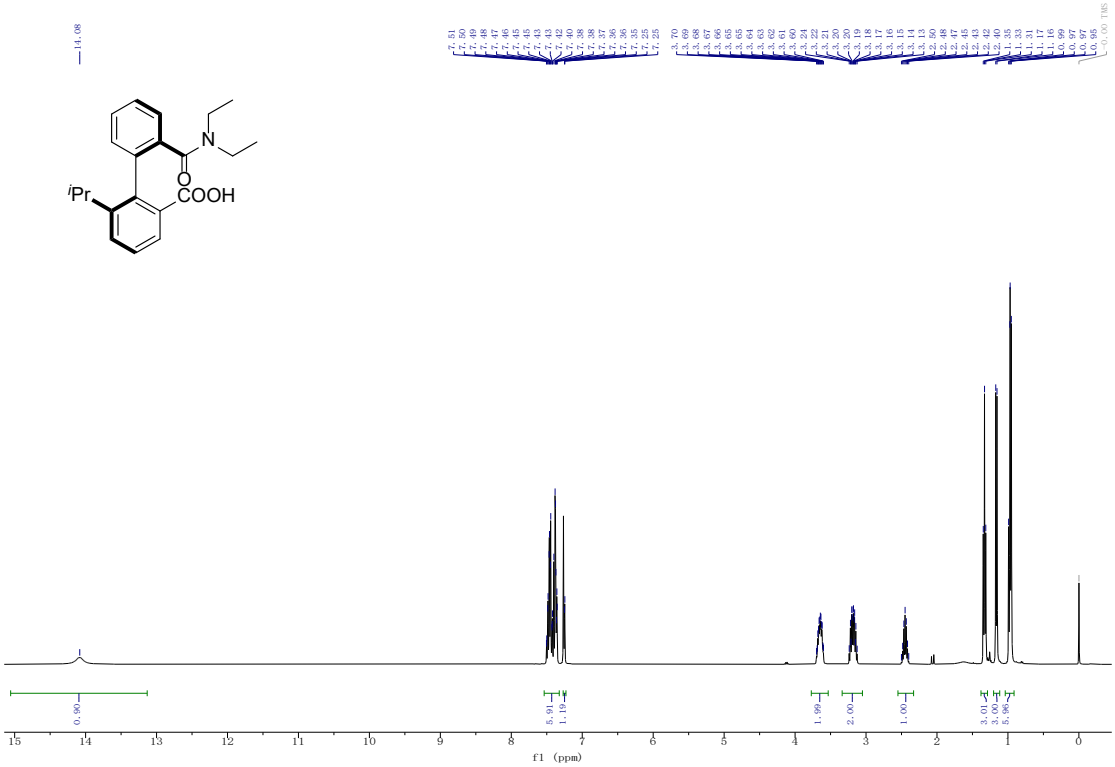
**3pa, $^{1}$H NMR (400 MHz, $CDCl_3$)**



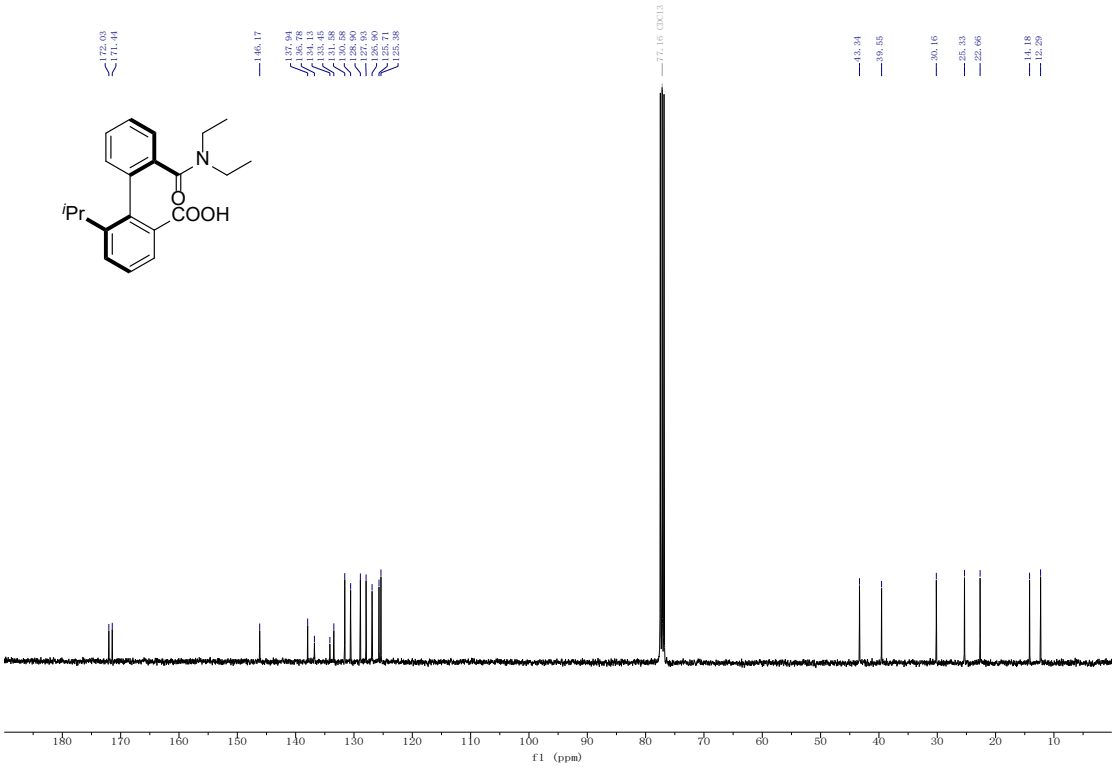
**3pa, $^{13}$C NMR (101 MHz, $CDCl_3$)**



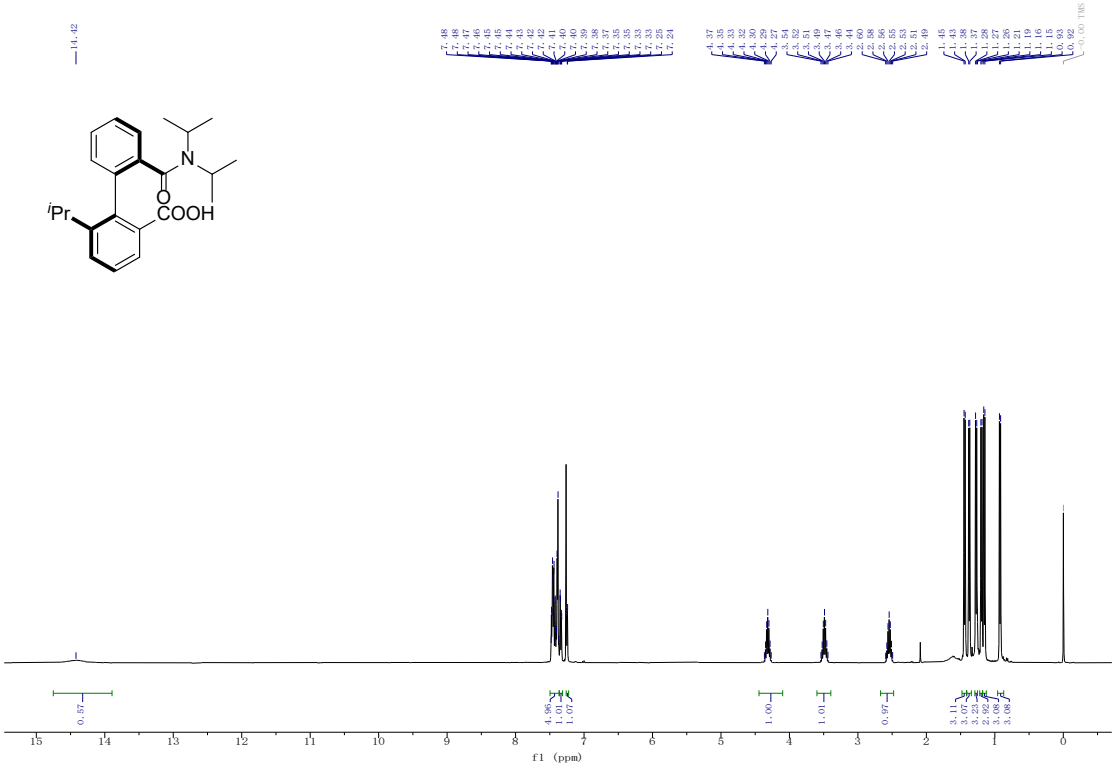
**4aa, $^{1}$H NMR (400 MHz, $CDCl_3$)**



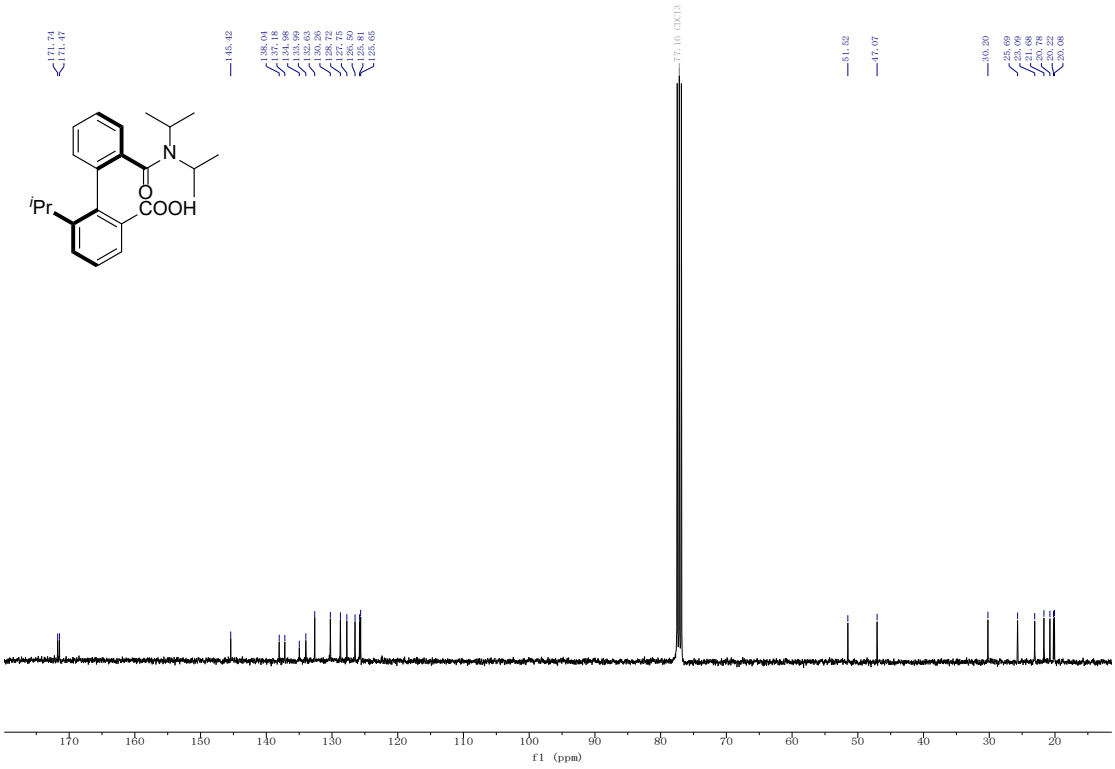

**4aa, $^{13}$C NMR (101 MHz, $CDCl_3$)**



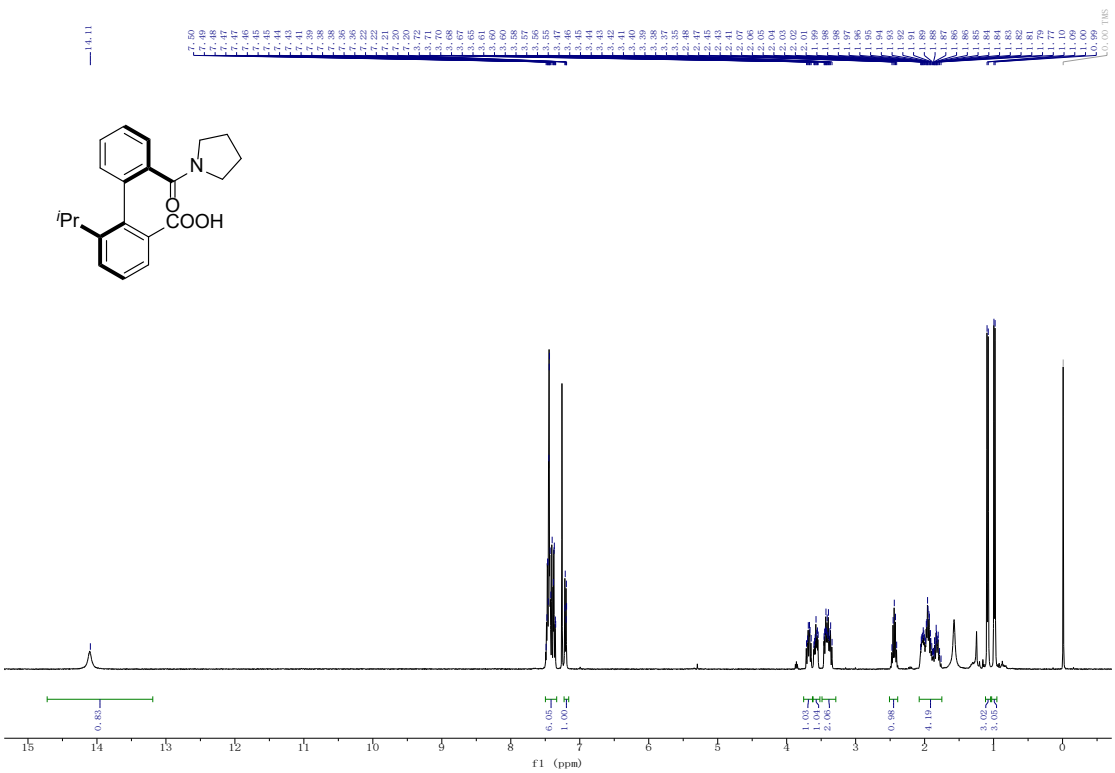
**4fa, $^{1}$H NMR (400 MHz, $CDCl_3$)**



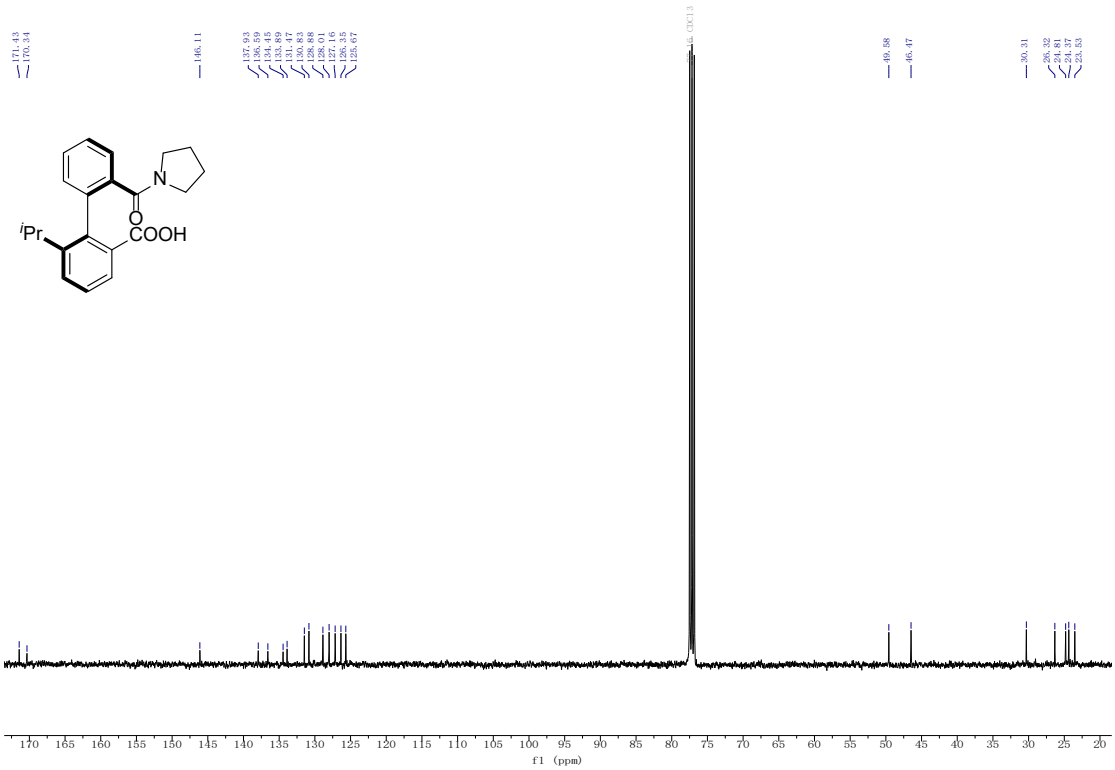

**4fa, $^{13}$C NMR (101 MHz, $CDCl_3$)**



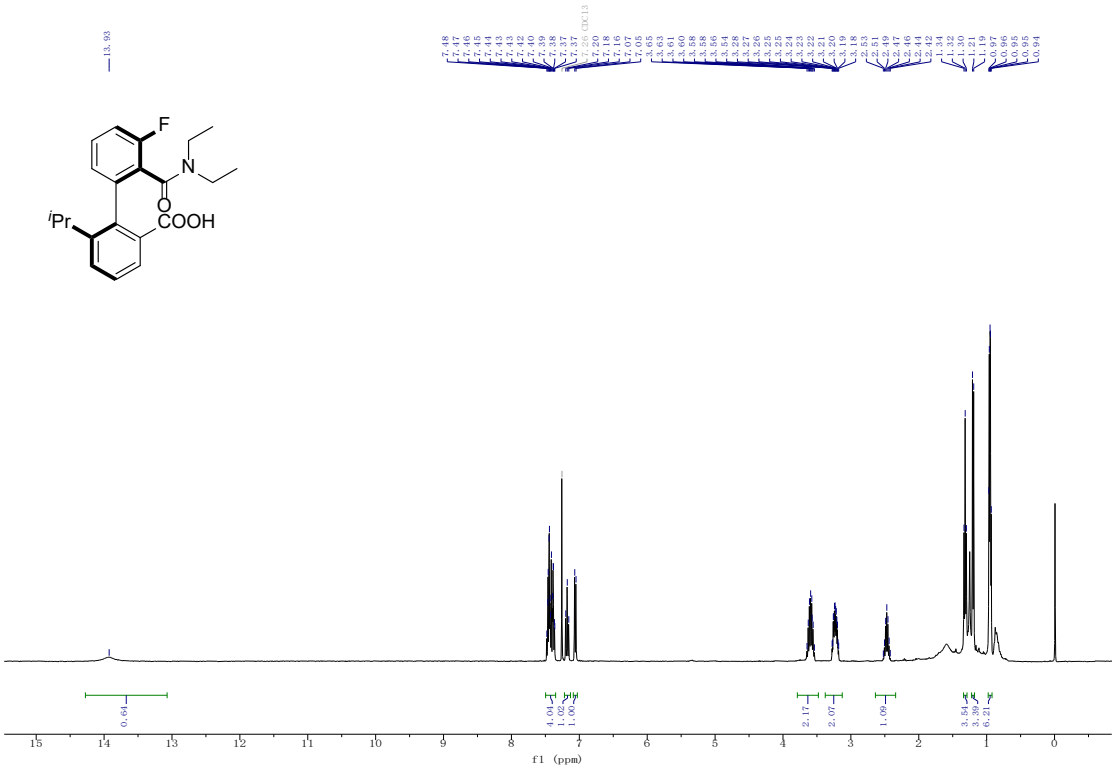
**4ga, $^{1}$H NMR (400 MHz, $CDCl_3$)**



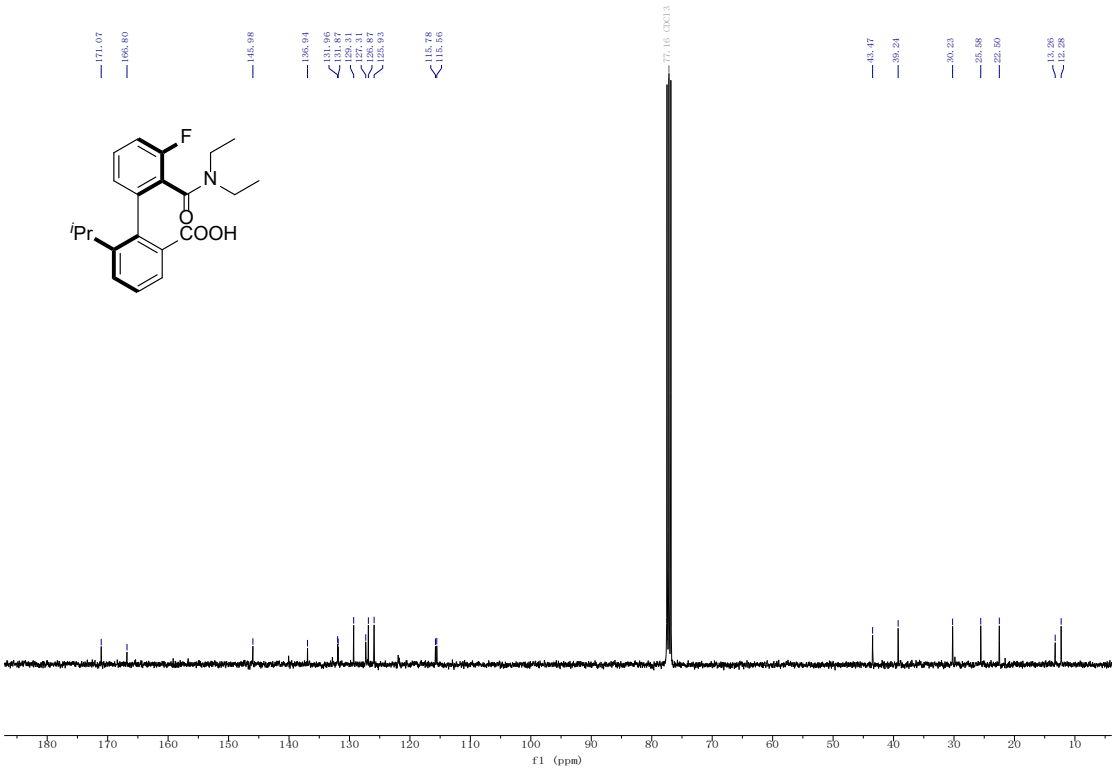

**4ga, $^{13}$C NMR (101 MHz, $CDCl_3$)**



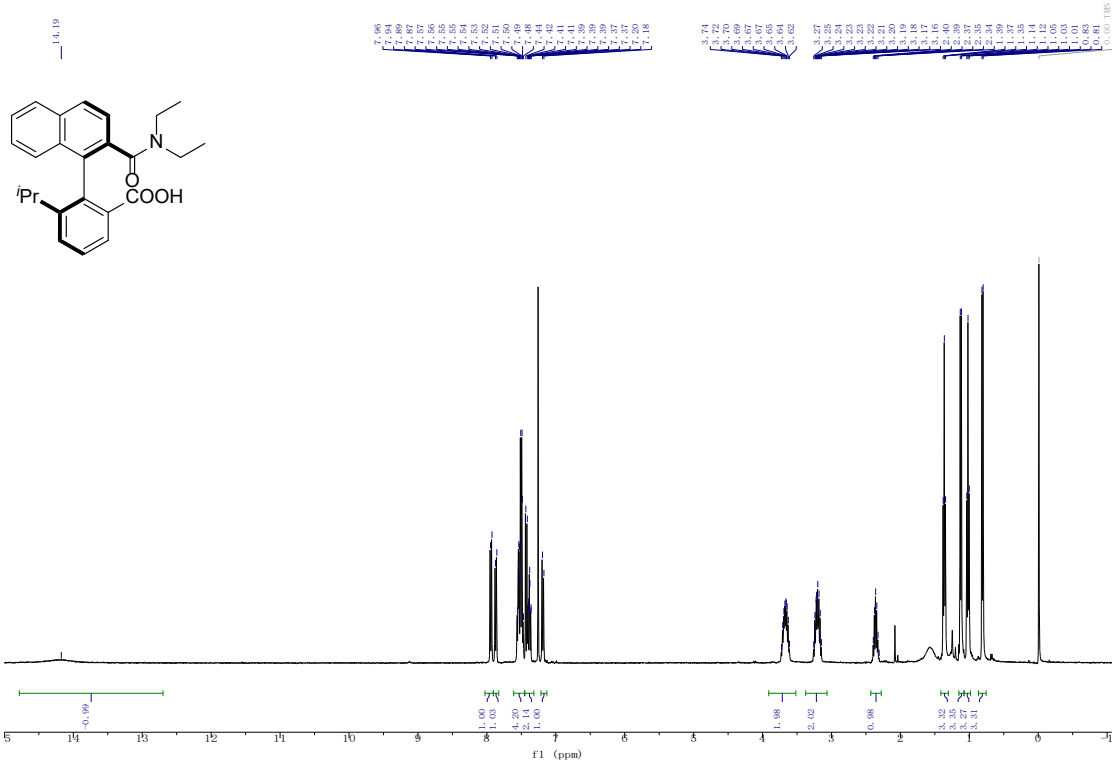
**4la, $^{1}$H NMR (400 MHz, $CDCl_3$)**



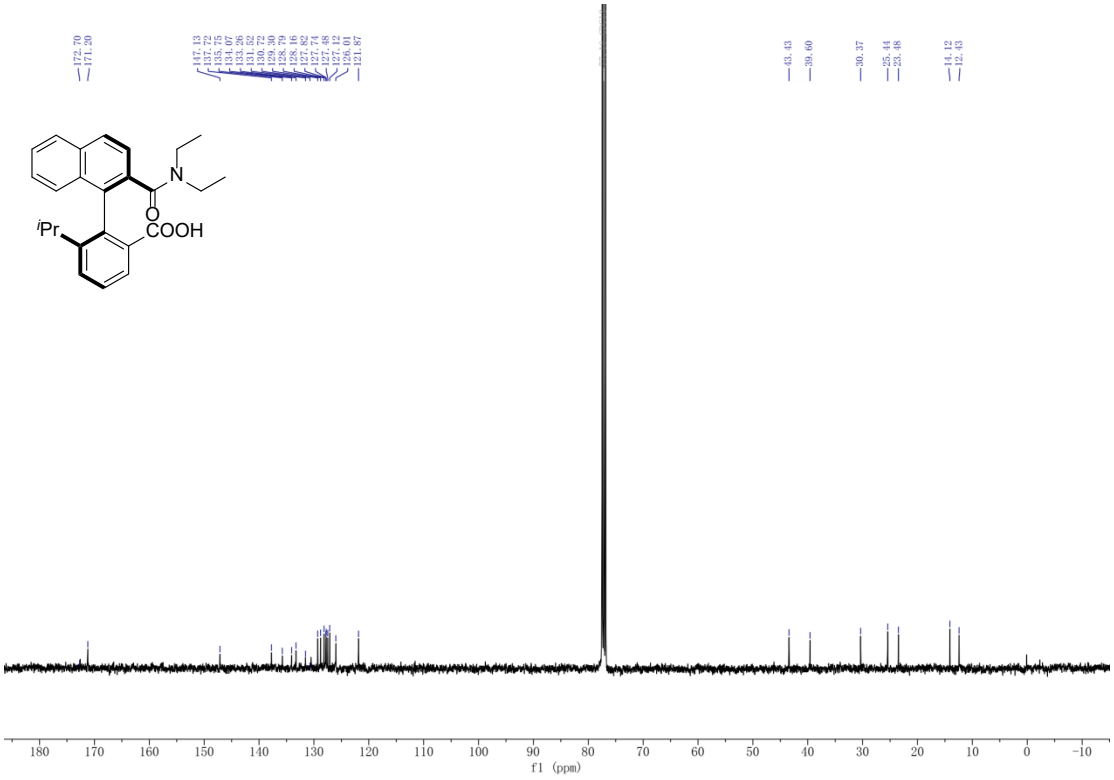

**4la, $^{13}$C NMR (101 MHz, $CDCl_3$)**



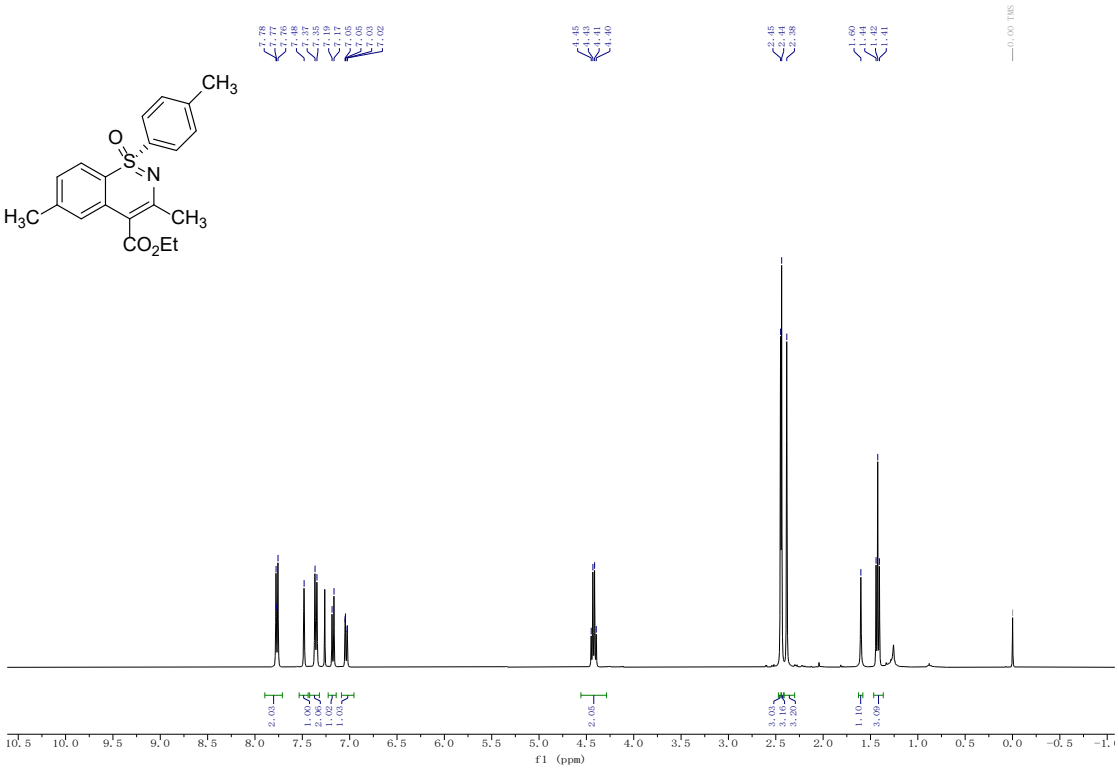
**4ma, $^{1}$H NMR (400 MHz, $CDCl_3$)**




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



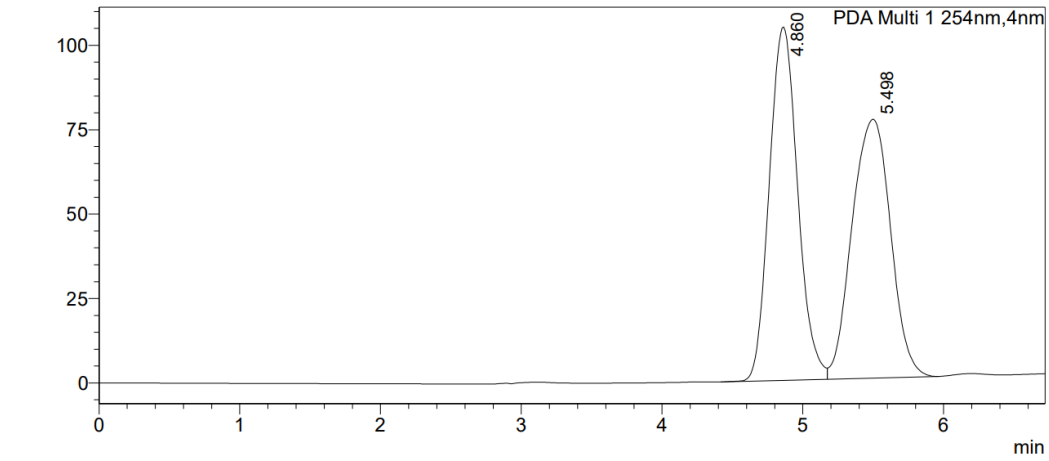
**7, $^1$H NMR (400 MHz, $CDCl_3$)**



# 6. HPLC Charts

**3aa**, Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm)

**<Chromatogram>**

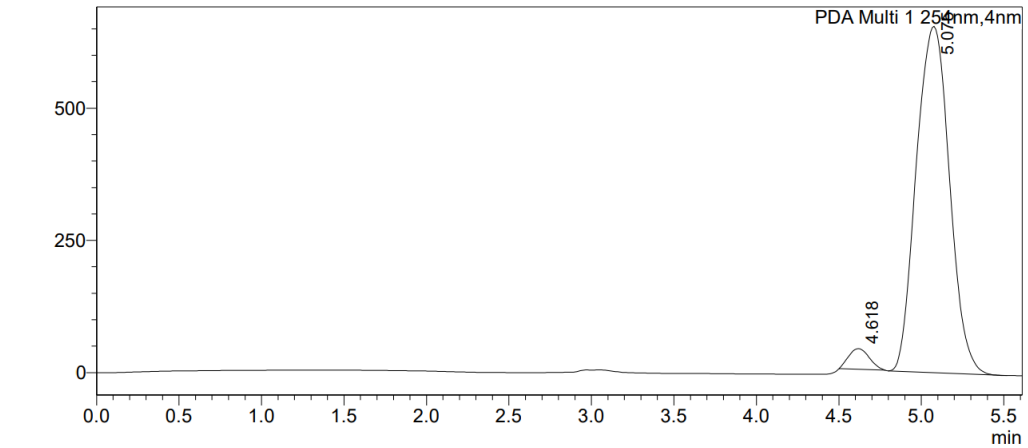



**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Area% | Height |
|---|---|---|---|
| 4.860 | 1468851 | 50.110 | 104633 |
| 5.498 | 1462401 | 49.890 | 76649 |
| | 2931251 | 100.000 | 181282 |

**<Chromatogram>**



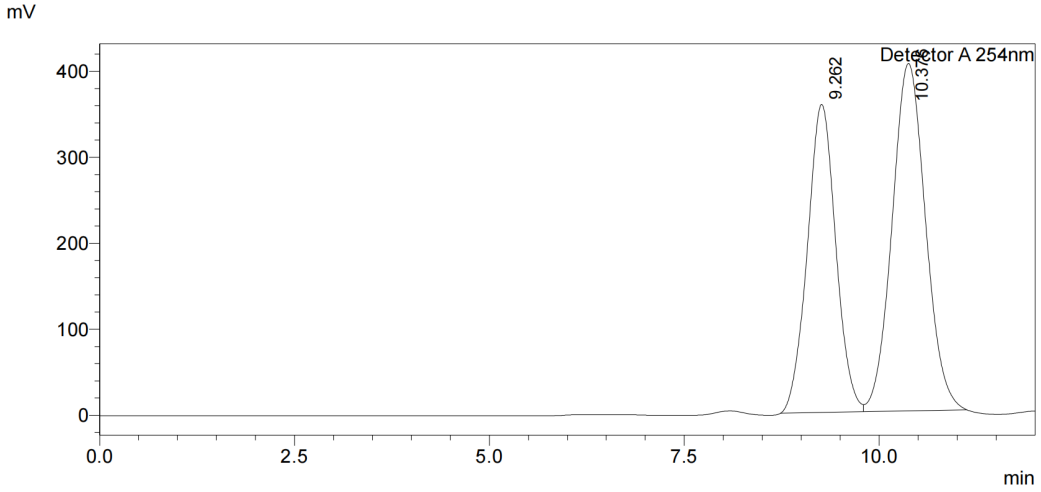

**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.618 | 339597 | 39127 | 3.568 |
| 5.075 | 9177877 | 654654 | 96.432 |
| | 9517474 | 693782 | 100.000 |

**3ab**, Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 0.5 mL/min, 254 nm)

**<Chromatogram>**

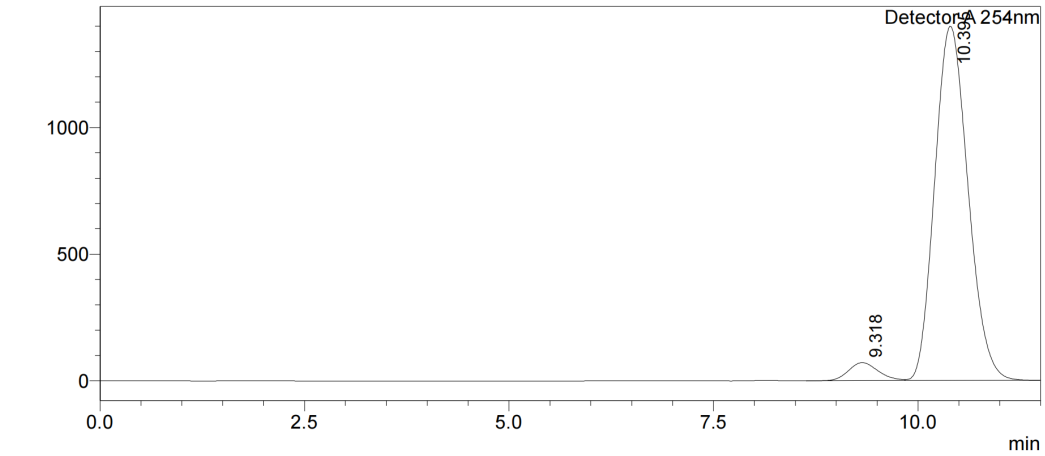



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 9.262 | 9101591 | 358257 | 43.003 |
| 10.376 | 12063560 | 404059 | 56.997 |
| | 21165152 | 762317 | 100.000 |

**<Chromatogram>**



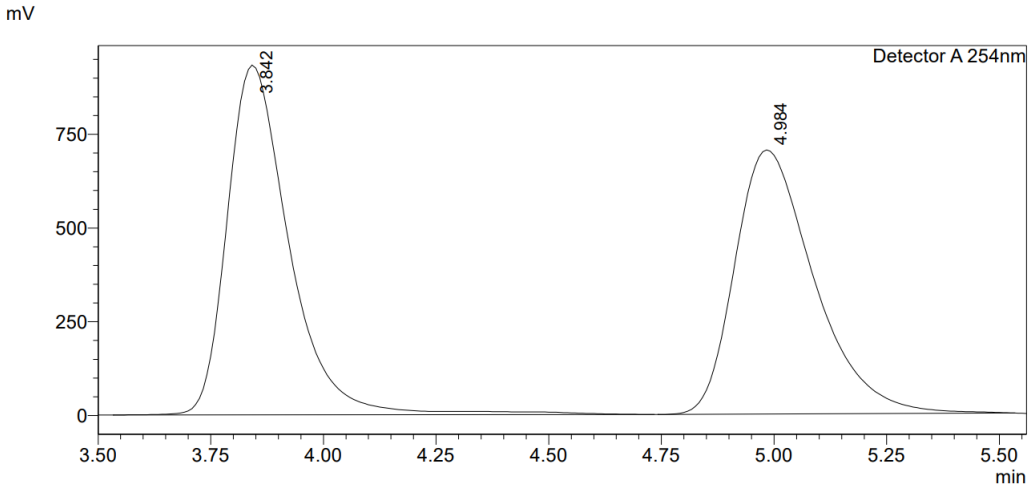

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 9.318 | 1827914 | 71691 | 4.412 |
| 10.395 | 39604359 | 1398144 | 95.588 |
| | 41432274 | 1469835 | 100.000 |

**3ac**, Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

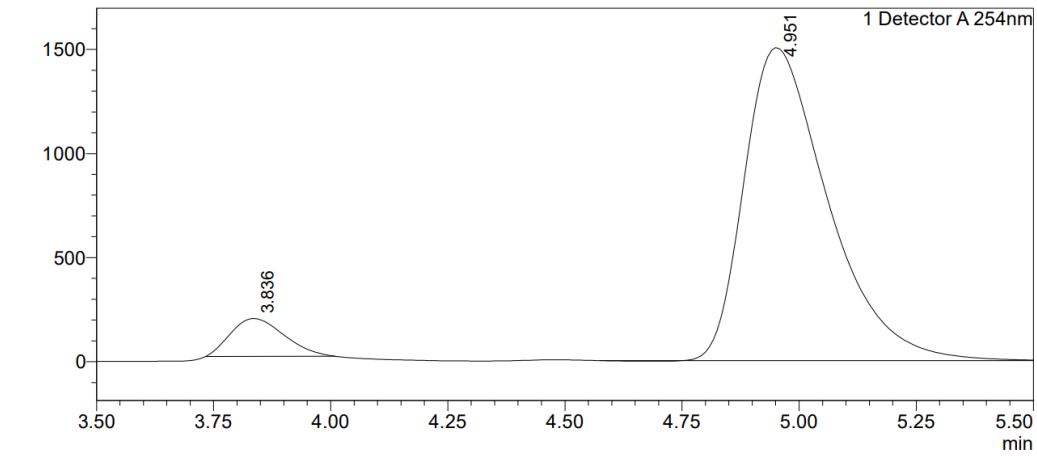



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 3.842 | 8965020 | 50.967 |
| 2 | 4.984 | 8624949 | 49.033 |
| Total | | 17589969 | 100.000 |

**<Chromatogram>**



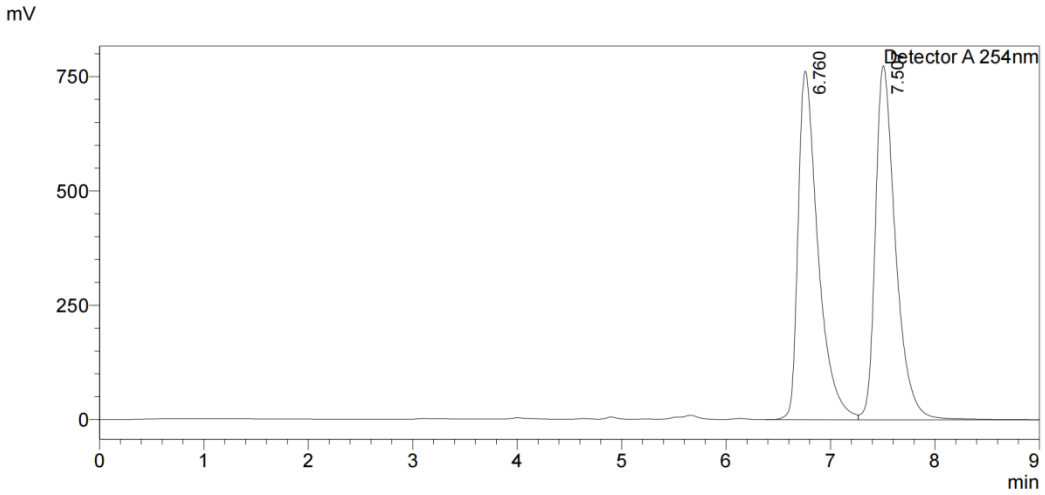

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 3.836 | 1444946 | 182017 | 7.155 |
| 2 | 4.951 | 18749502 | 1503830 | 92.845 |
| Total | | 20194447 | 1685847 | 100.000 |

**3ad**, IBN-5 column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

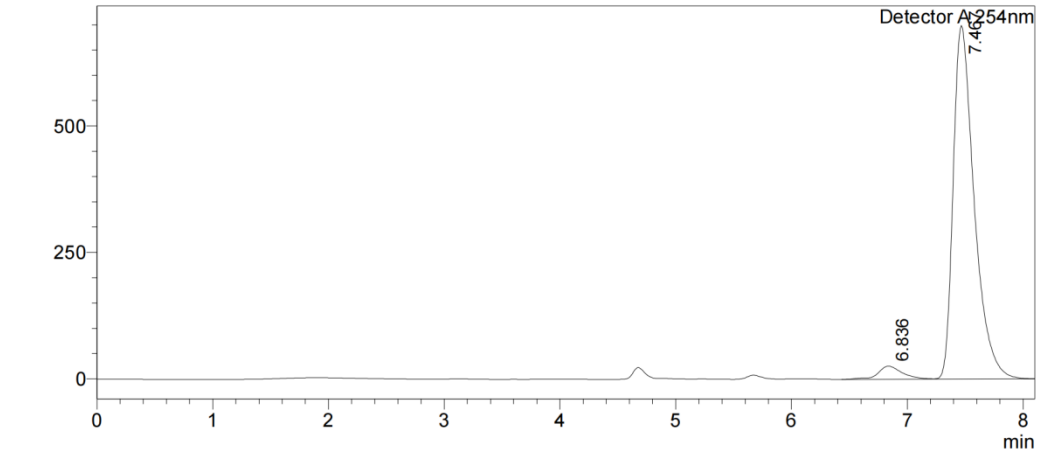



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.760 | 10125806 | 762482 | 49.379 |
| 7.507 | 10380459 | 774049 | 50.621 |
| | 20506266 | 1536531 | 100.000 |

**<Chromatogram>**



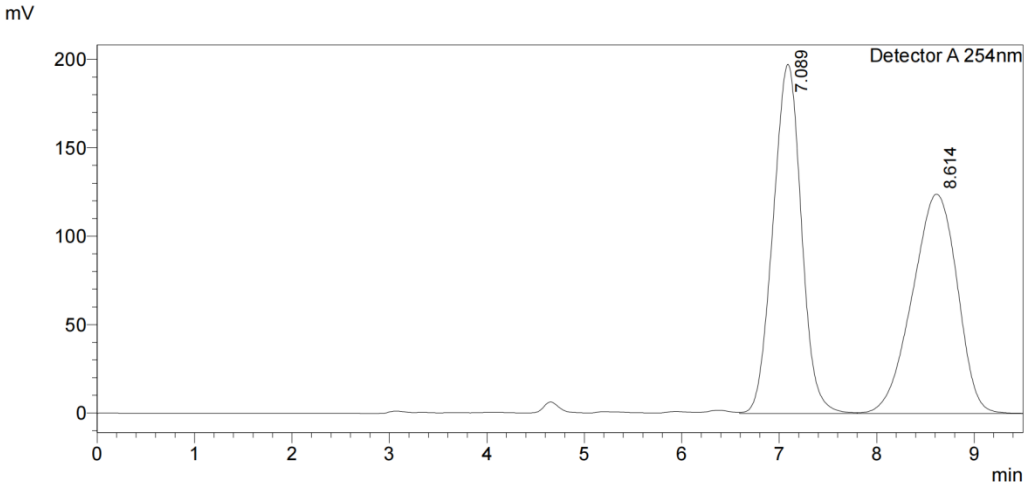

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.836 | 378601 | 25928 | 4.121 |
| 7.467 | 8807650 | 698480 | 95.879 |
| | 9186252 | 724408 | 100.000 |

**3ae**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

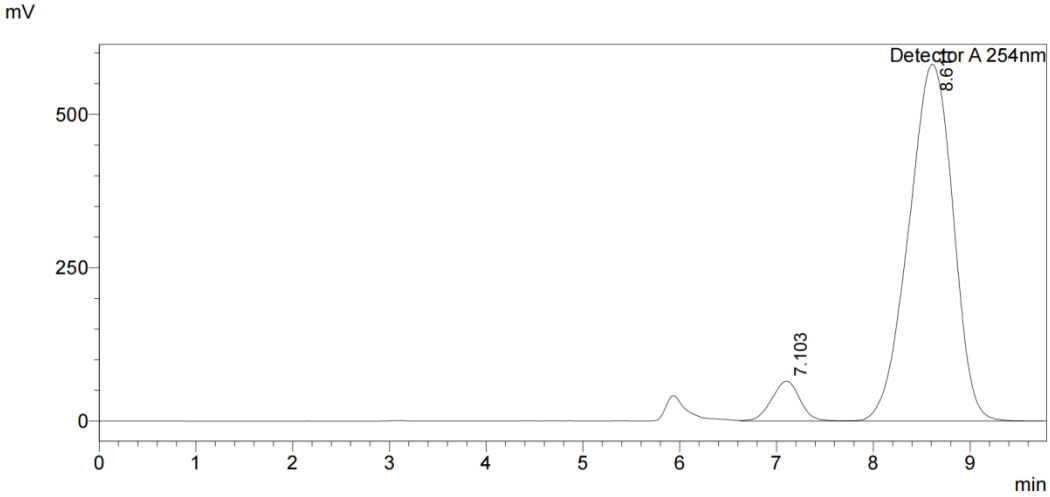



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 7.089 | 3990023 | 197304 | 50.156 |
| 8.614 | 3965222 | 123940 | 49.844 |
| | 7955245 | 321245 | 100.000 |

**<Chromatogram>**



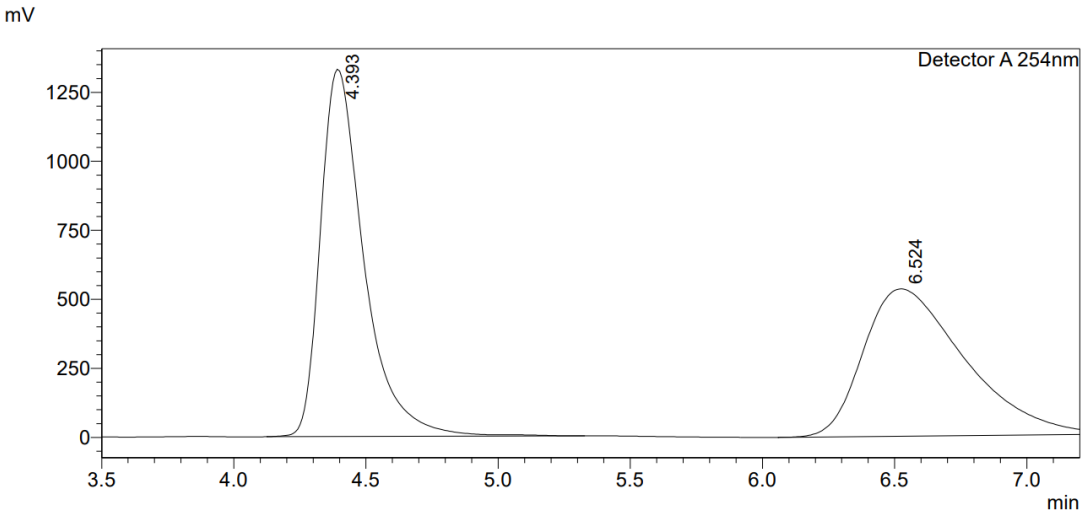

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 7.103 | 1327186 | 65107 | 6.683 |
| 8.611 | 18531497 | 581413 | 93.317 |
| | 19858682 | 646520 | 100.000 |

**3af**, NQ column (hexane/isopropanol = 70/30, flow = 0.8 mL/min, 254 nm)

**<Chromatogram>**

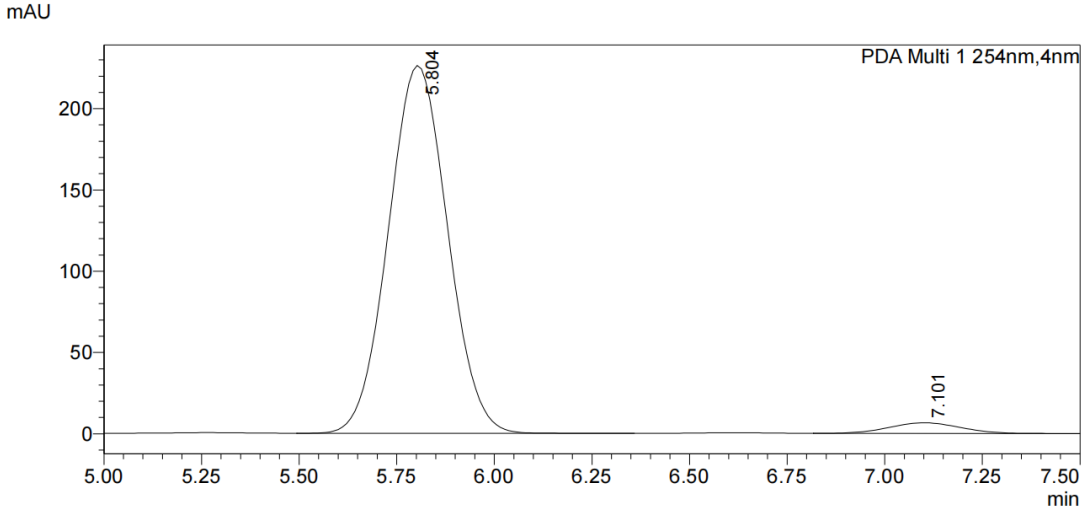



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.393 | 15259672 | 1330340 | 51.587 |
| 6.524 | 14320819 | 533688 | 48.413 |
| | 29580491 | 1864028 | 100.000 |

**<Chromatogram>**



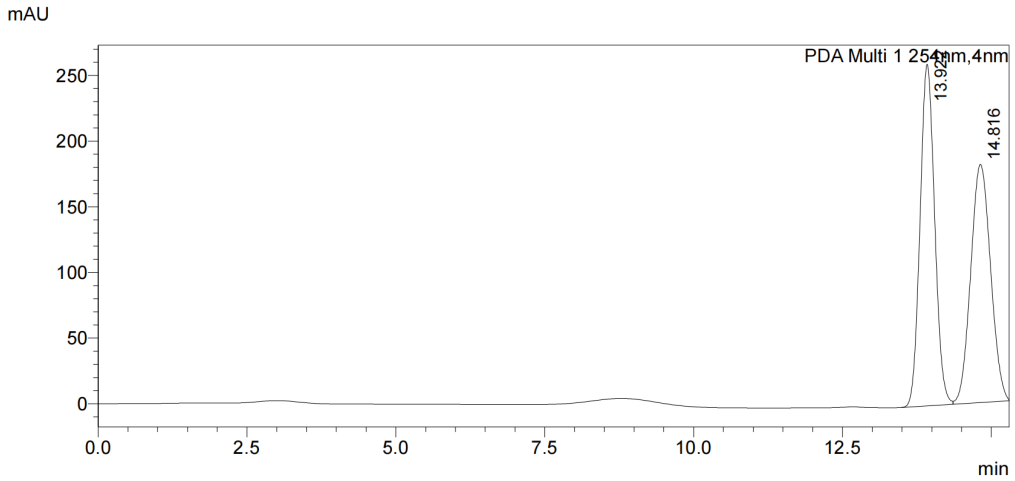

**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.804 | 2387347 | 226198 | 96.586 |
| 7.101 | 84378 | 6554 | 3.414 |
| | 2471725 | 232752 | 100.000 |

**3ag**, NX column (hexane/isopropanol = 70/30, flow = 0.8 mL/min, 254 nm)

**<Chromatogram>**

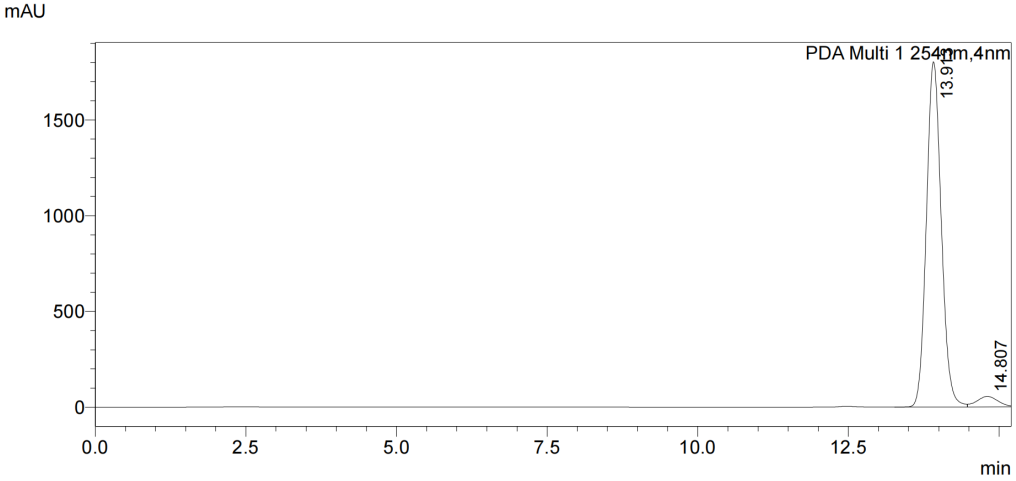



**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 13.922 | 4442191 | 259976 | 51.343 |
| 14.816 | 4209850 | 181380 | 48.657 |
| | 8652041 | 441356 | 100.000 |

**<Chromatogram>**



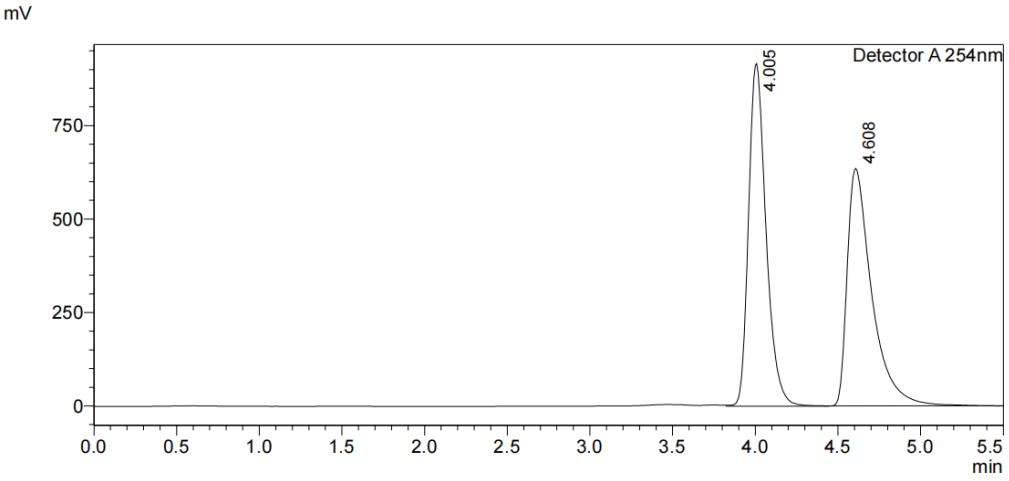

**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 13.913 | 30999752 | 1802080 | 95.731 |
| 14.807 | 1382306 | 55019 | 4.269 |
| | 32382058 | 1857098 | 100.000 |

**3ah**, IBN-5 column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

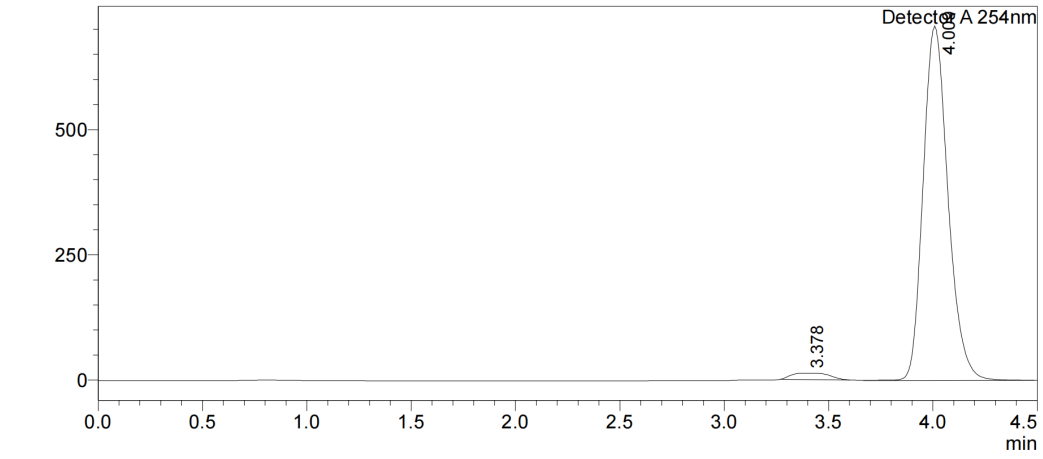



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.005 | 6760606 | 916339 | 50.778 |
| 4.608 | 6553466 | 635502 | 49.222 |
| | 13314071 | 1551841 | 100.000 |

**<Chromatogram>**



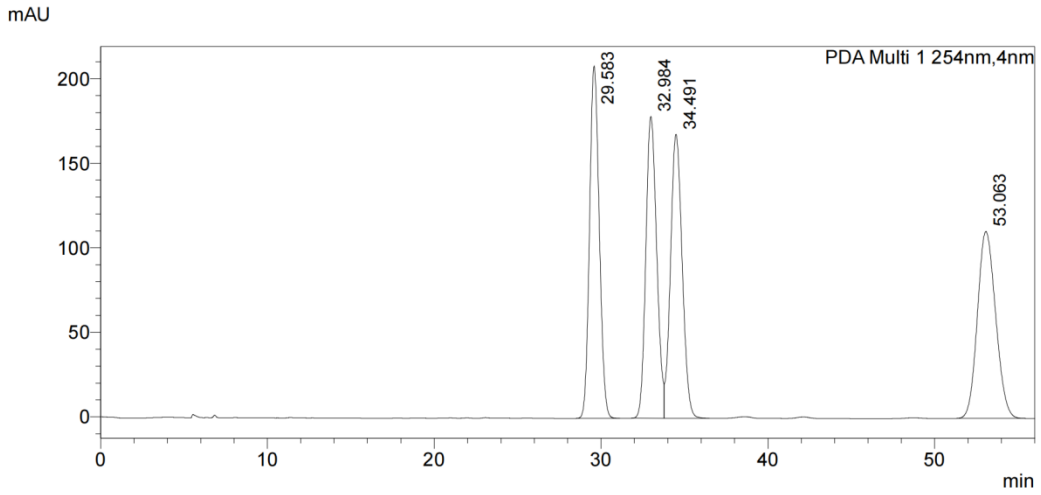

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 3.378 | 161808 | 12667 | 2.682 |
| 4.009 | 5871410 | 707208 | 97.318 |
| | 6033219 | 719875 | 100.000 |

**3ai**, NX column (hexane/isopropanol = 90/10, flow = 0.5 mL/min, 254 nm)

**<Chromatogram>**

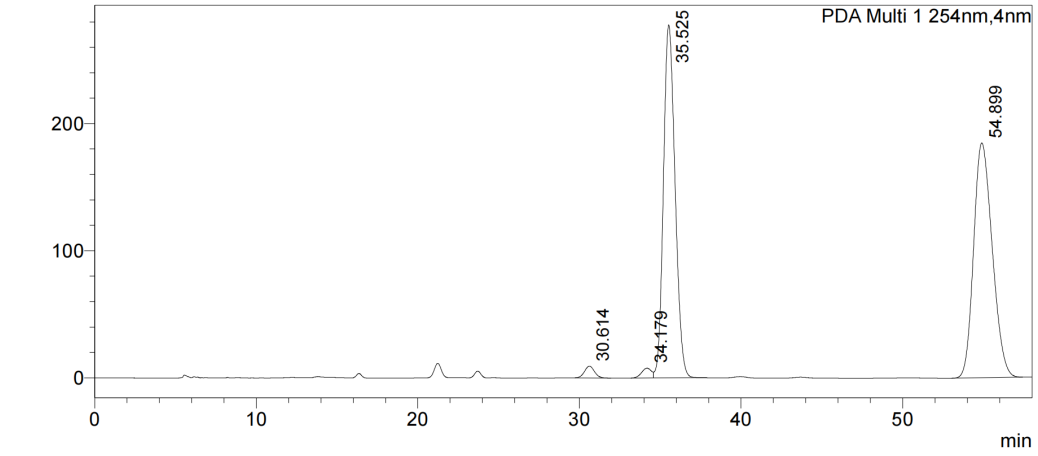



**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 29.583 | 8418509 | 208303 | 25.437 |
| 32.984 | 8093632 | 178403 | 24.456 |
| 34.491 | 8177884 | 167908 | 24.710 |
| 53.063 | 8405081 | 110496 | 25.397 |
| | 33095106 | 665111 | 100.000 |

**<Chromatogram>**



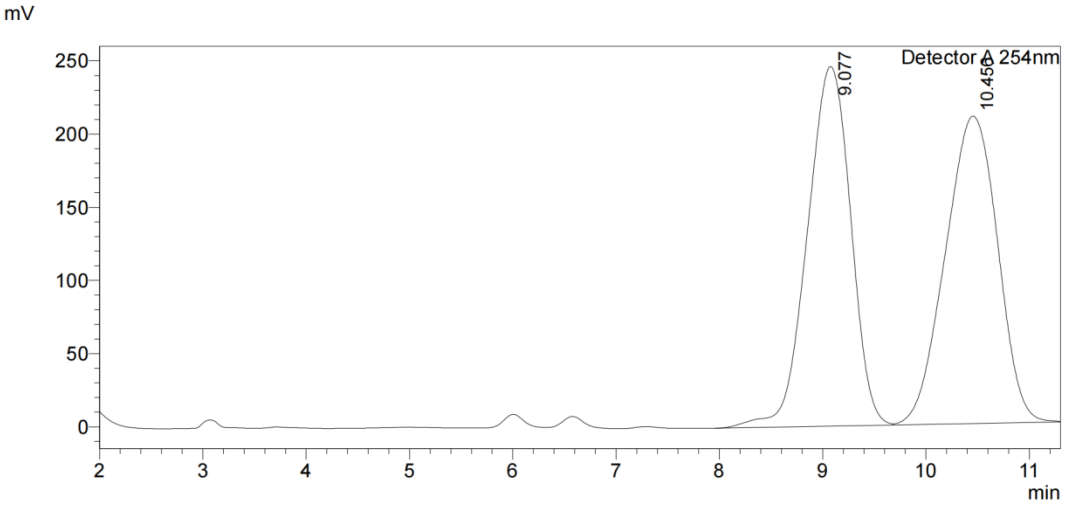

**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 30.614 | 395922 | 9244 | 1.345 |
| 34.179 | 328919 | 7715 | 1.118 |
| 35.525 | 13918333 | 277575 | 47.290 |
| 54.899 | 14788763 | 184687 | 50.247 |
| | 29431936 | 479221 | 100.000 |

**3aj**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

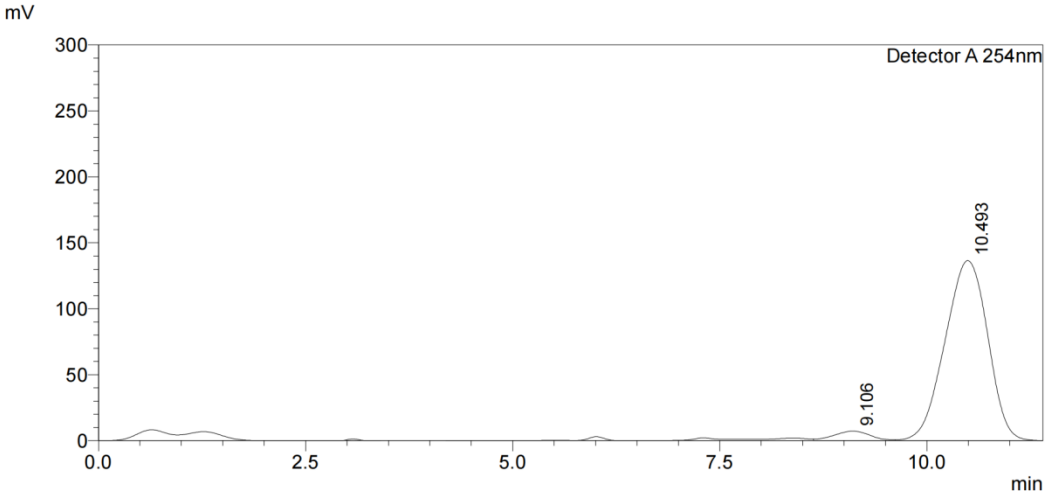



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 9.077 | 7193545 | 245781 | 49.304 |
| 10.456 | 7396703 | 210099 | 50.696 |
| | 14590247 | 455880 | 100.000 |

**<Chromatogram>**



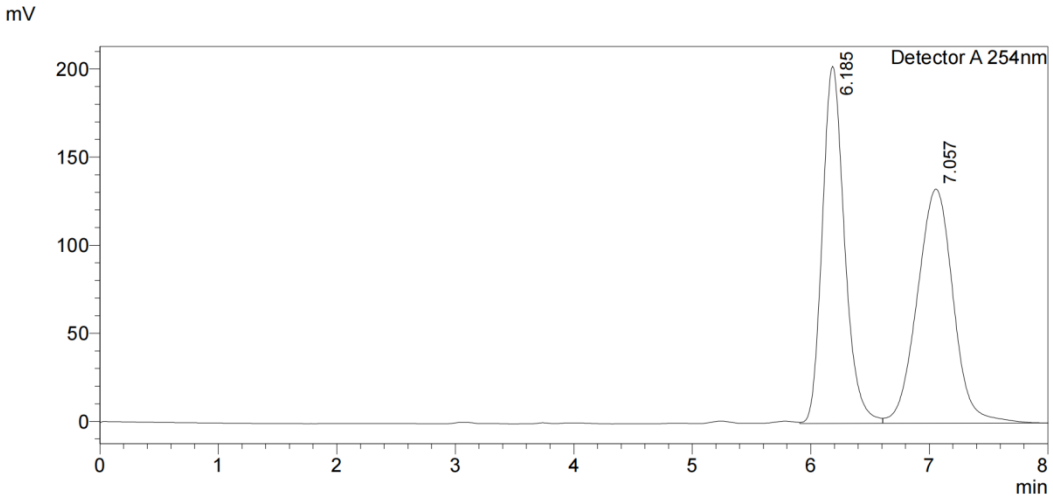

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 9.106 | 223110 | 7267 | 4.357 |
| 10.493 | 4897435 | 136527 | 95.643 |
| | 5120546 | 143794 | 100.000 |

**3ak**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

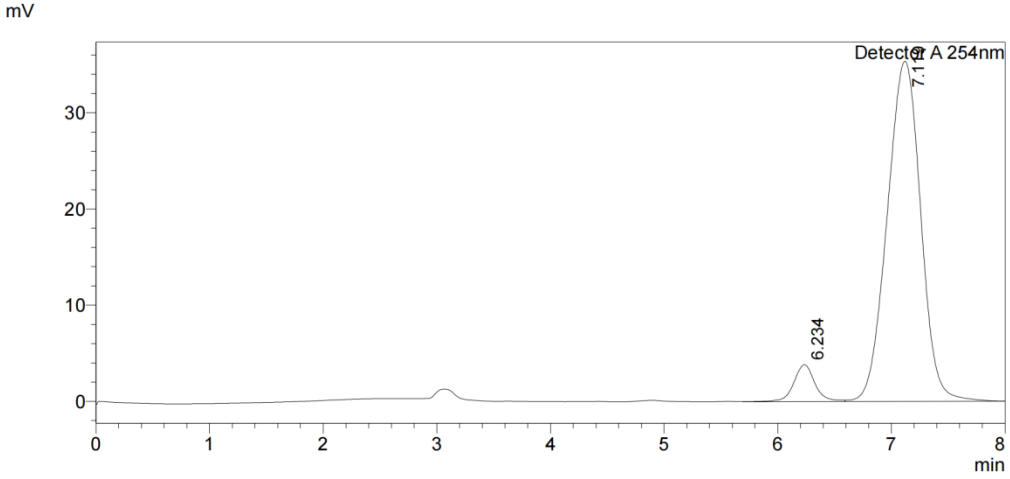



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.185 | 2645627 | 202610 | 48.563 |
| 7.057 | 2802208 | 132868 | 51.437 |
| | 5447835 | 335478 | 100.000 |

**<Chromatogram>**



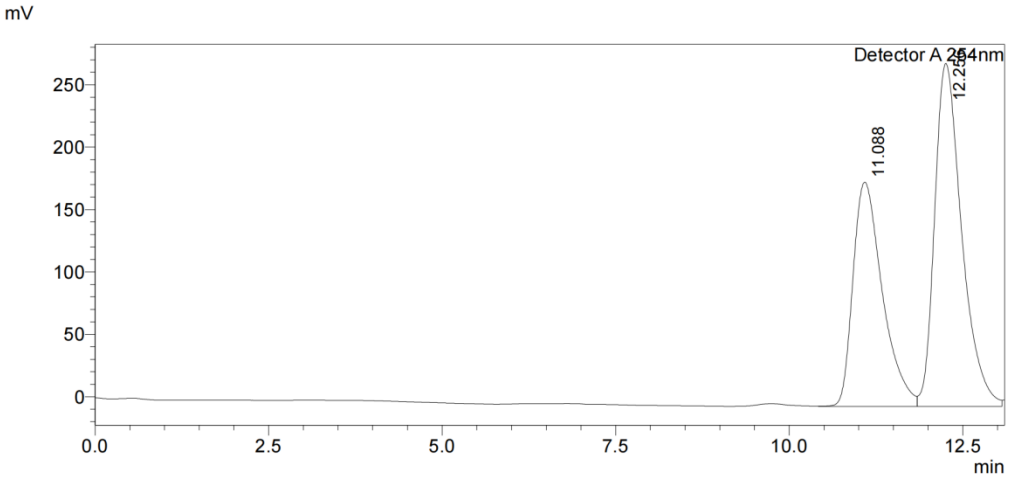

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.234 | 49989 | 3840 | 6.443 |
| 7.119 | 725811 | 35371 | 93.557 |
| | 775799 | 39211 | 100.000 |

**3al**, IBN-5 column (hexane/isopropanol = 90/10, flow = 0.5 mL/min, 254 nm)

**<Chromatogram>**

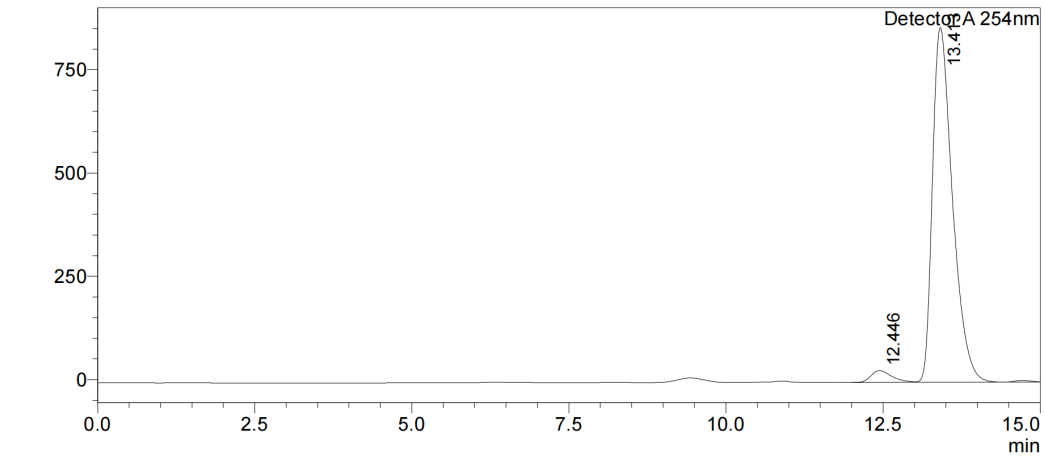



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 11.088 | 5294865 | 179652 | 41.503 |
| 12.256 | 7463045 | 274788 | 58.497 |
| | 12757910 | 454440 | 100.000 |

**<Chromatogram>**



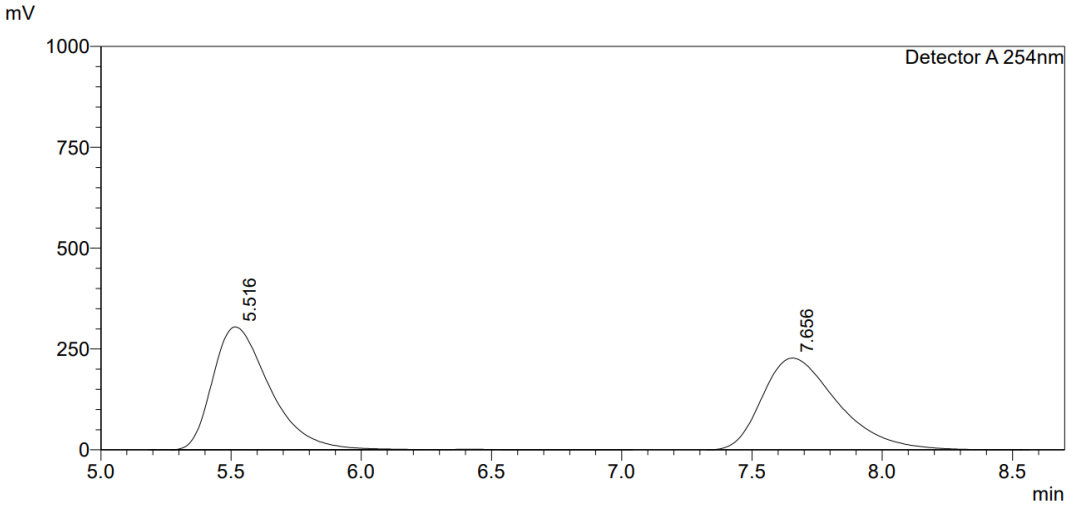

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 12.446 | 659224 | 28624 | 3.330 |
| 13.413 | 19136408 | 858424 | 96.670 |
| | 19795632 | 887049 | 100.000 |

**3am**, IA column (hexane/isopropanol = 80/20, flow = 1.2 mL/min, 254 nm)

**<Chromatogram>**

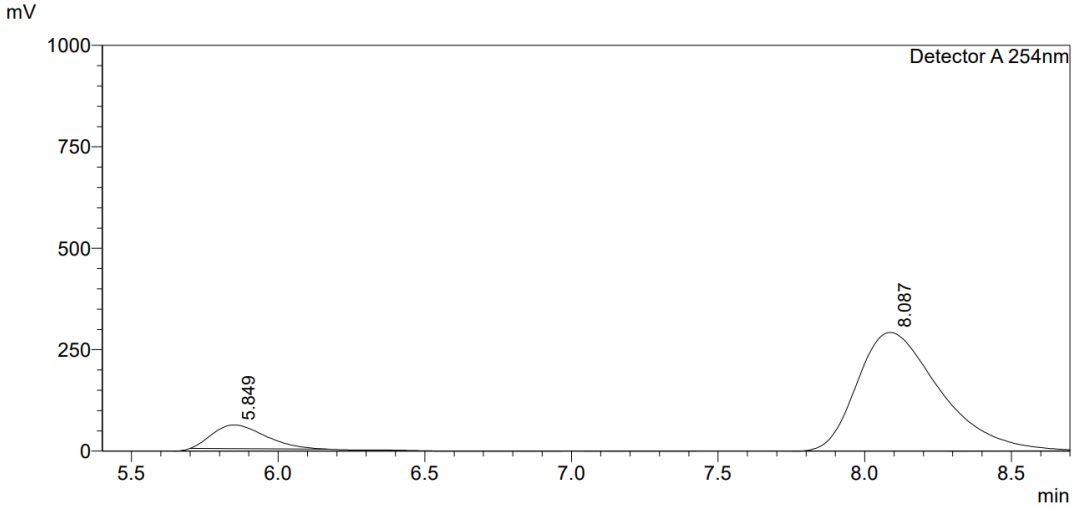



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.516 | 4633503 | 304968 | 50.074 |
| 7.656 | 4619880 | 228228 | 49.926 |
| | 9253383 | 533196 | 100.000 |

**<Chromatogram>**



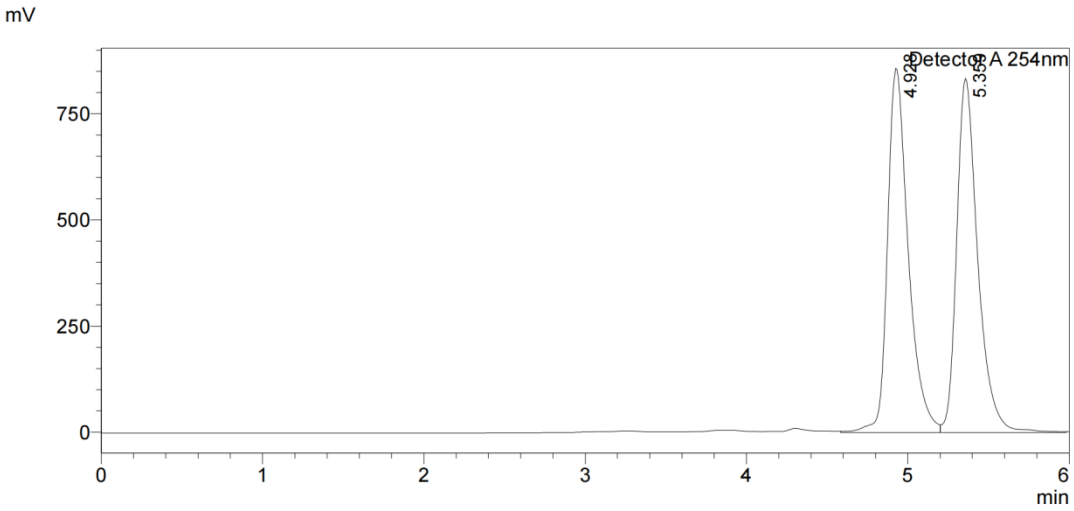

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.849 | 731594 | 58381 | 11.209 |
| 8.087 | 5795462 | 293222 | 88.791 |
| | 6527056 | 351603 | 100.000 |

**3an**, IBN-5 column (hexane/isopropanol = 80/20, flow = 0.8 mL/min, 254 nm)

**<Chromatogram>**

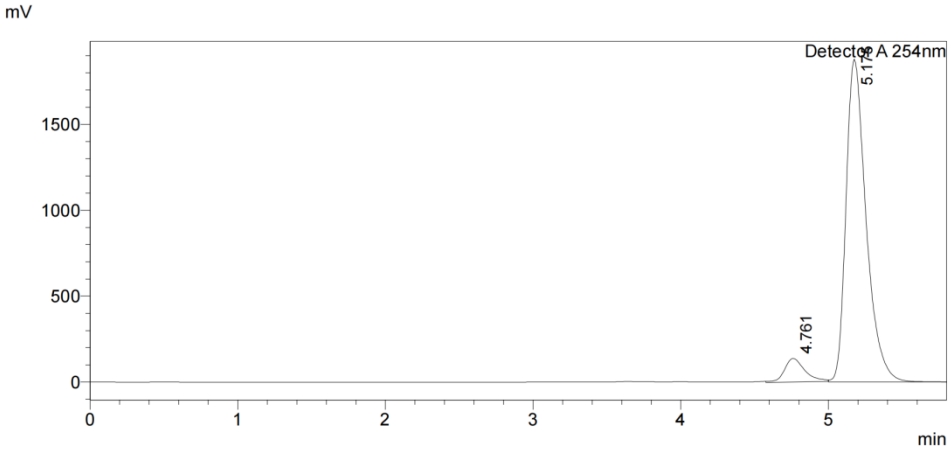



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.928 | 7656636 | 857697 | 50.159 |
| 5.359 | 7608182 | 833918 | 49.841 |
| | 15264818 | 1691615 | 100.000 |

**<Chromatogram>**



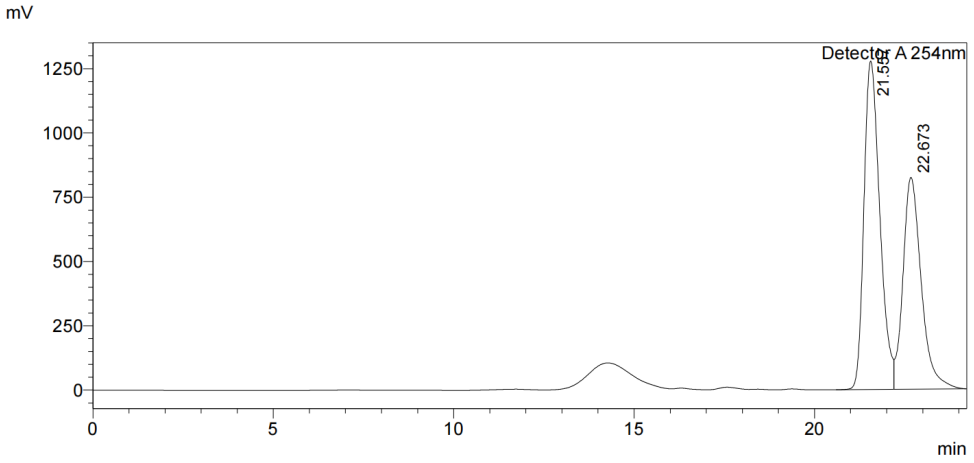

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.761 | 1335625 | 137774 | 6.985 |
| 5.175 | 17785877 | 1878240 | 93.015 |
| | 19121501 | 2016015 | 100.000 |

**3ao**, IC column (hexane/isopropanol = 90/10, flow = 0.3 mL/min, 254 nm)

**<Chromatogram>**

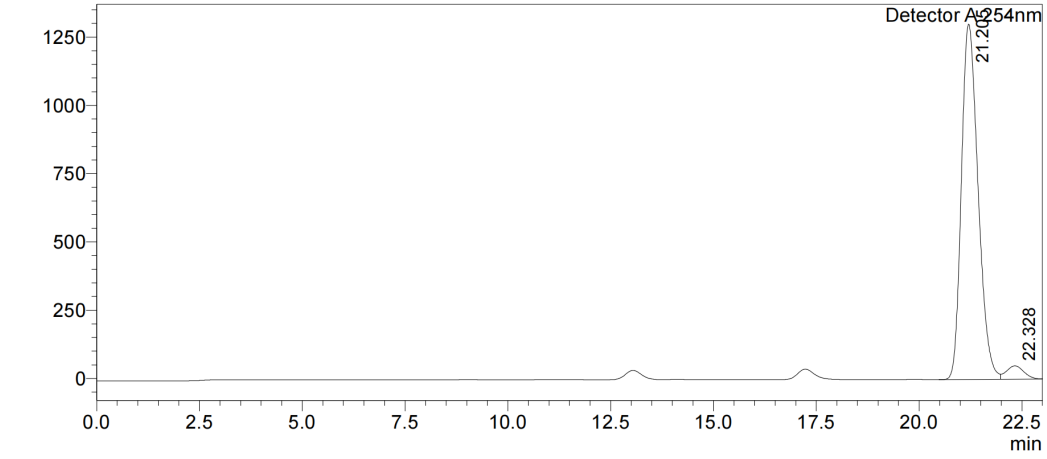



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 21.557 | 39103567 | 1277206 | 57.384 |
| 22.673 | 29039956 | 823466 | 42.616 |
| | 68143522 | 2100672 | 100.000 |

**<Chromatogram>**



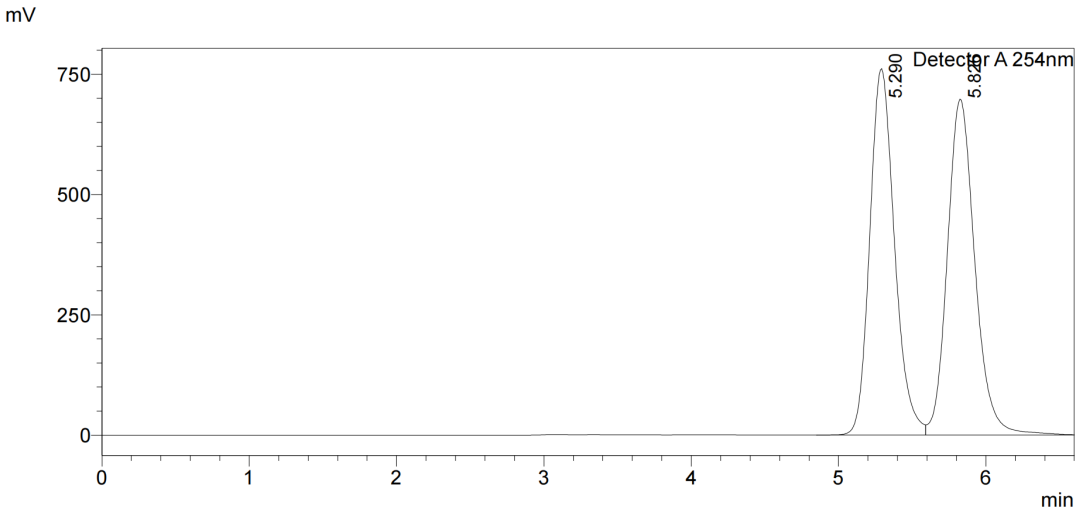

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 21.205 | 36700221 | 1300644 | 96.246 |
| 22.328 | 1431528 | 48690 | 3.754 |
| | 38131749 | 1349334 | 100.000 |

**3ba**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

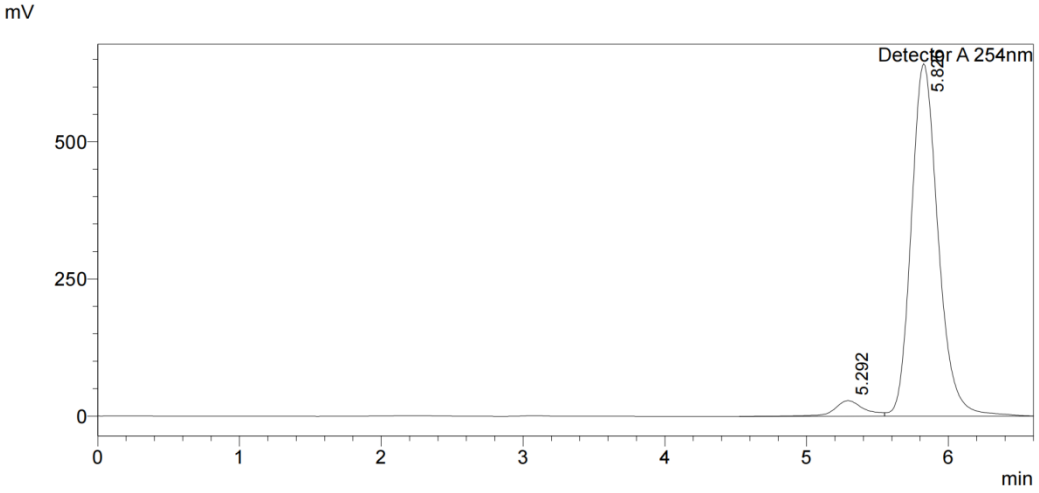



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.290 | 8892291 | 761192 | 49.493 |
| 5.826 | 9074301 | 698232 | 50.507 |
| | 17966592 | 1459424 | 100.000 |

**<Chromatogram>**



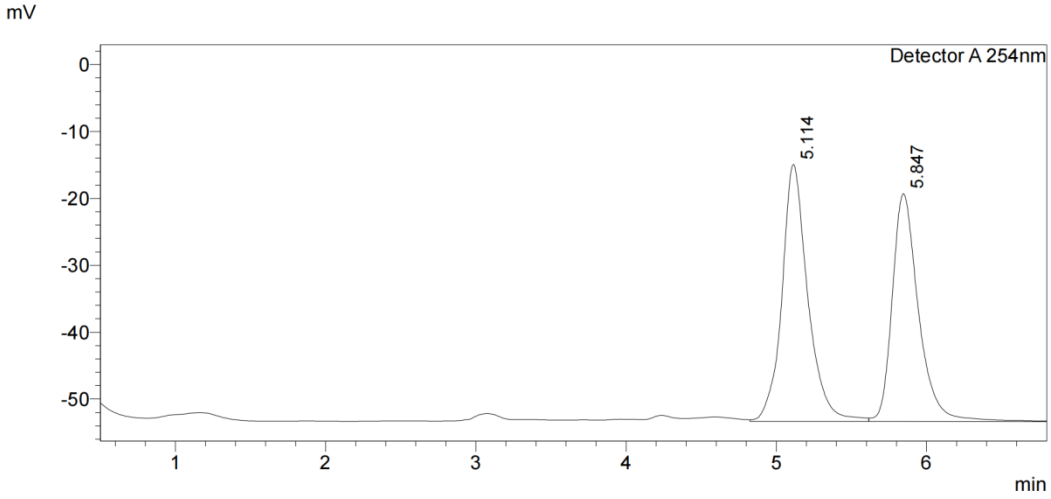

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.292 | 427883 | 28806 | 4.799 |
| 5.826 | 8488580 | 642418 | 95.201 |
| | 8916463 | 671224 | 100.000 |

**3ca**, AD column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm)

**<Chromatogram>**

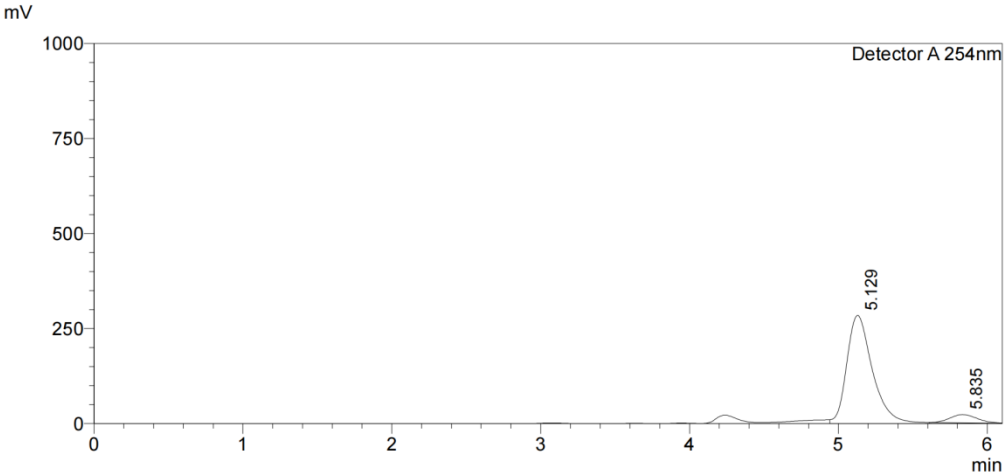



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.114 | 461865 | 38399 | 52.157 |
| 5.847 | 423657 | 34043 | 47.843 |
| | 885522 | 72441 | 100.000 |

**<Chromatogram>**



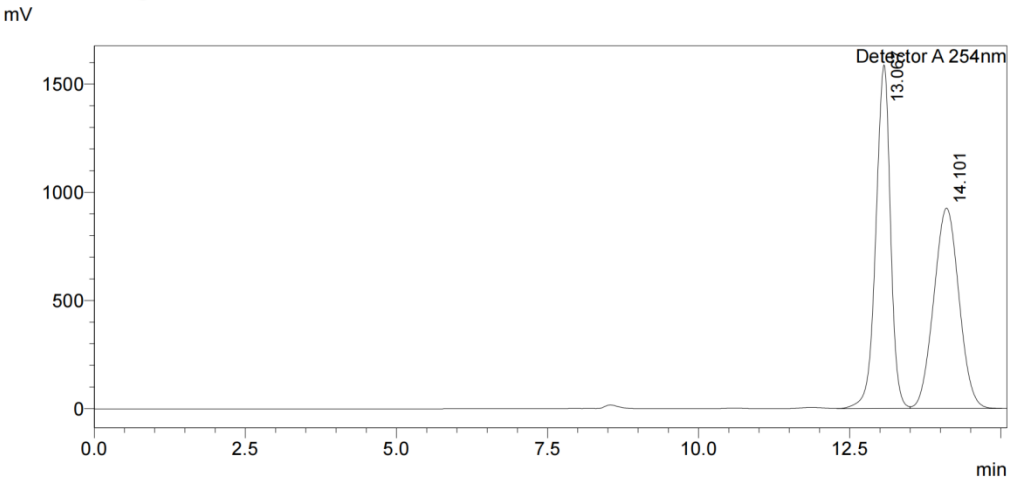

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.129 | 3409866 | 284802 | 92.588 |
| 5.835 | 272988 | 21603 | 7.412 |
| | 3682854 | 306405 | 100.000 |

**3da**, IBN-5 column (hexane/isopropanol = 90/10, flow = 0.5 mL/min, 254 nm)

**<Chromatogram>**

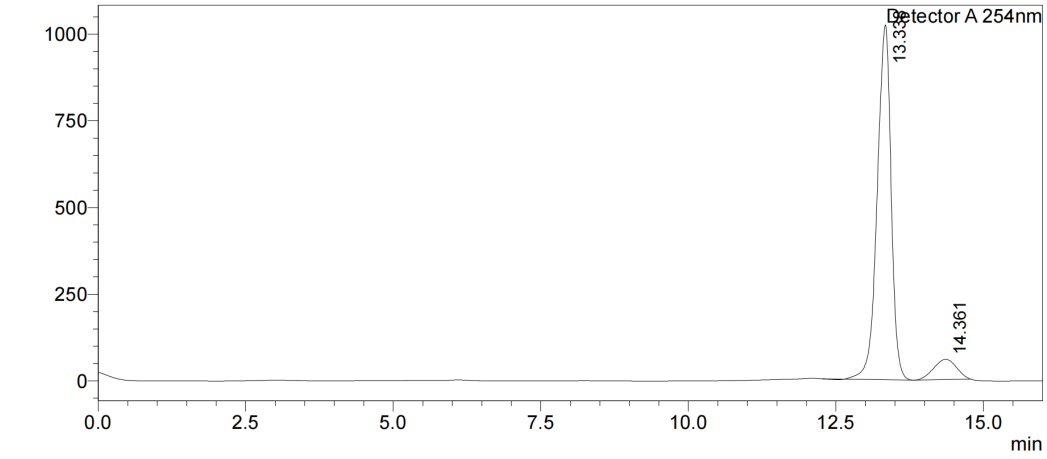



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 13.067 | 26802412 | 1588119 | 49.929 |
| 14.101 | 26878756 | 926185 | 50.071 |
| | 53681168 | 2514304 | 100.000 |

**<Chromatogram>**



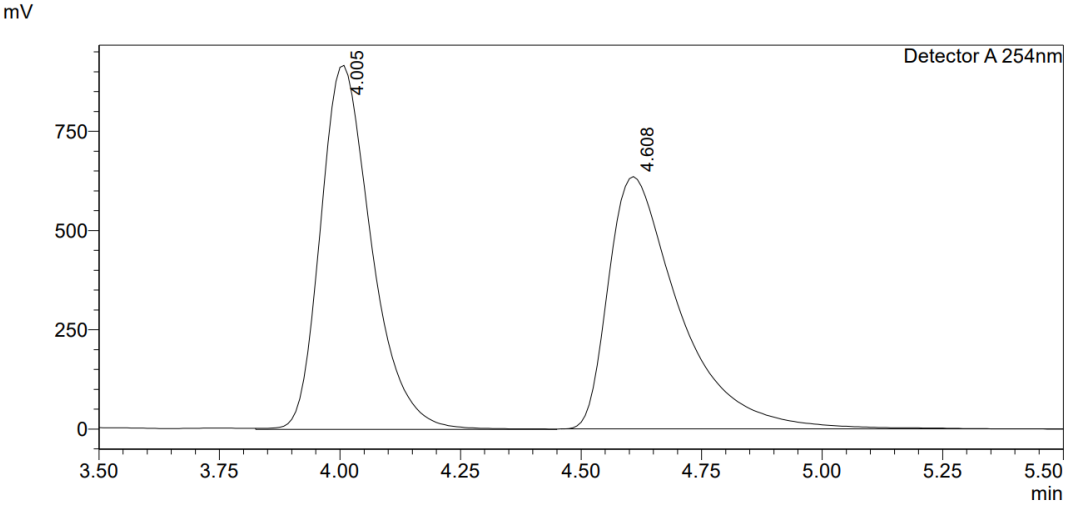

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 13.338 | 16766468 | 1022758 | 91.396 |
| 14.361 | 1578321 | 58586 | 8.604 |
| | 18344789 | 1081344 | 100.000 |

**3fa**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

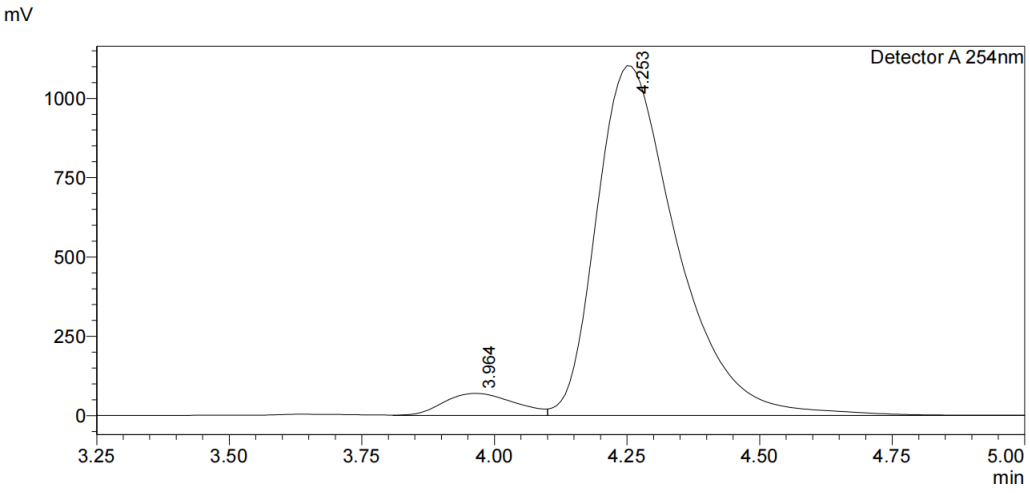



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.005 | 6760606 | 916339 | 50.778 |
| 4.608 | 6553466 | 635502 | 49.222 |
| | 13314071 | 1551841 | 100.000 |

**<Chromatogram>**



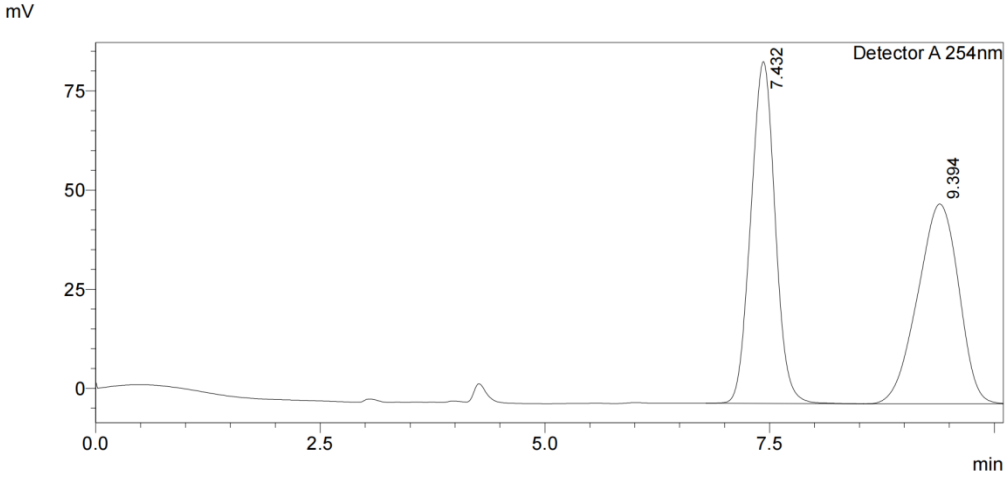

**<Peak Table>**

Detector A 254nm

| Ret. Time | Height | Area | Area% |
|---|---|---|---|
| 3.964 | 69996 | 659630 | 5.363 |
| 4.253 | 1102443 | 11639693 | 94.637 |
| | 1172438 | 12299323 | 100.000 |

**3ga**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

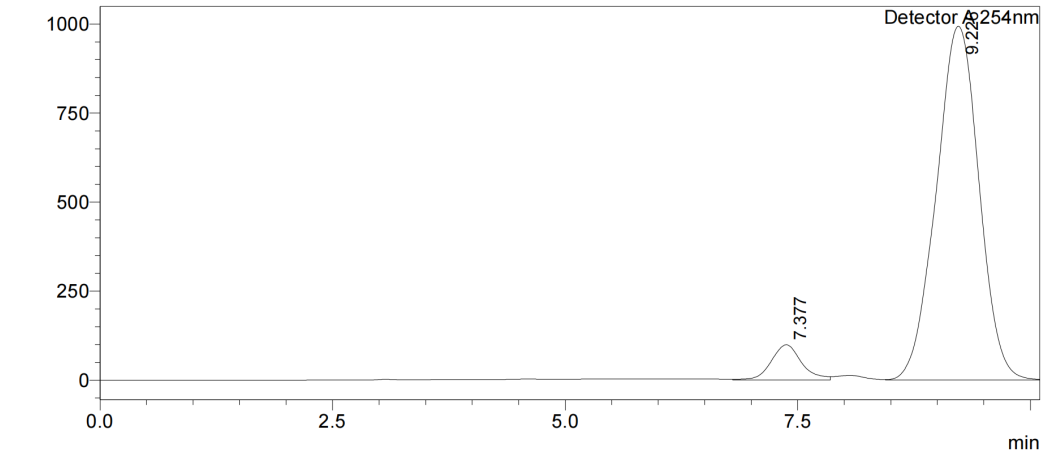



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 7.432 | 1621584 | 86186 | 50.256 |
| 9.394 | 1605076 | 50397 | 49.744 |
| | 3226661 | 136583 | 100.000 |

**<Chromatogram>**



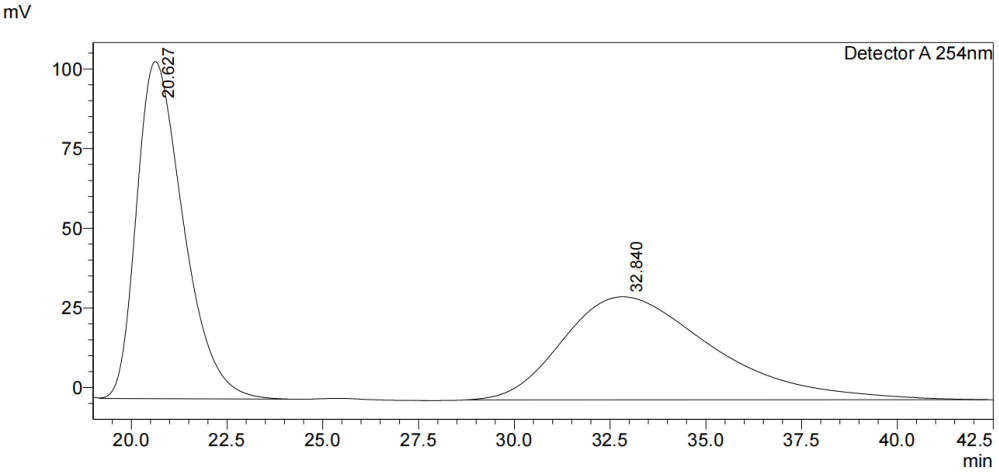

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Area% | Height |
|---|---|---|---|
| 7.377 | 2270271 | 6.658 | 99099 |
| 9.226 | 31830052 | 93.342 | 993651 |
| | 34100323 | 100.000 | 1092749 |

**3ha**, NT(2) column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

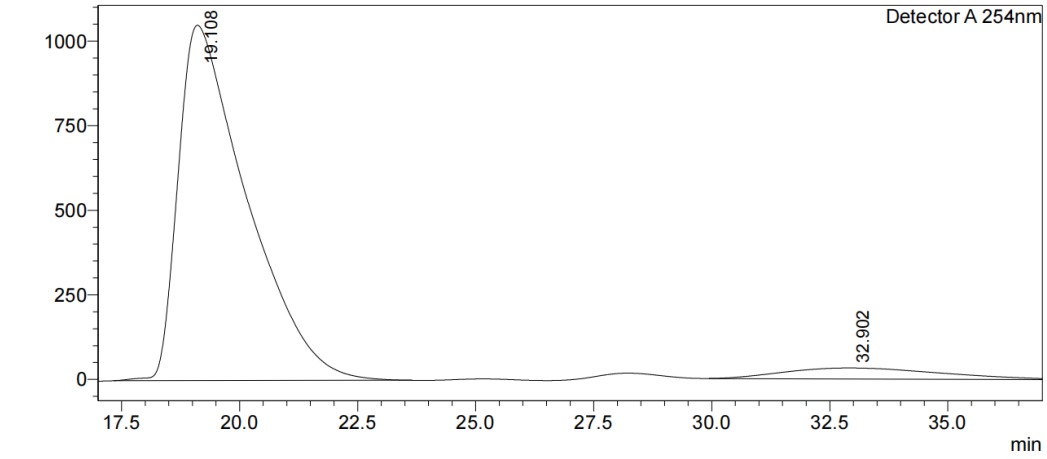



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 20.627 | 9009939 | 105770 | 50.436 |
| 32.840 | 8854051 | 32327 | 49.564 |
| | 17863990 | 138097 | 100.000 |

**<Chromatogram>**



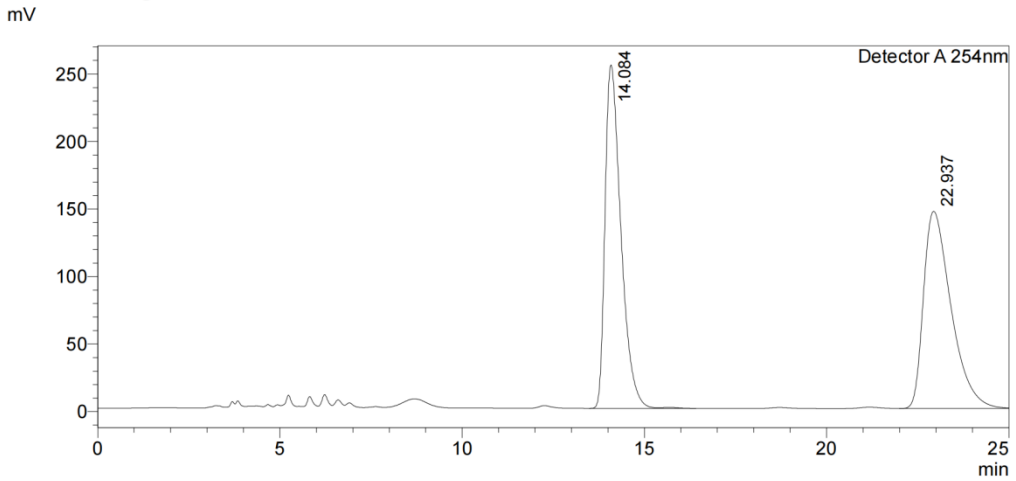

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 19.108 | 106302171 | 1050329 | 93.392 |
| 32.902 | 7521566 | 32464 | 6.608 |
| | 113823738 | 1082793 | 100.000 |

**3ia**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

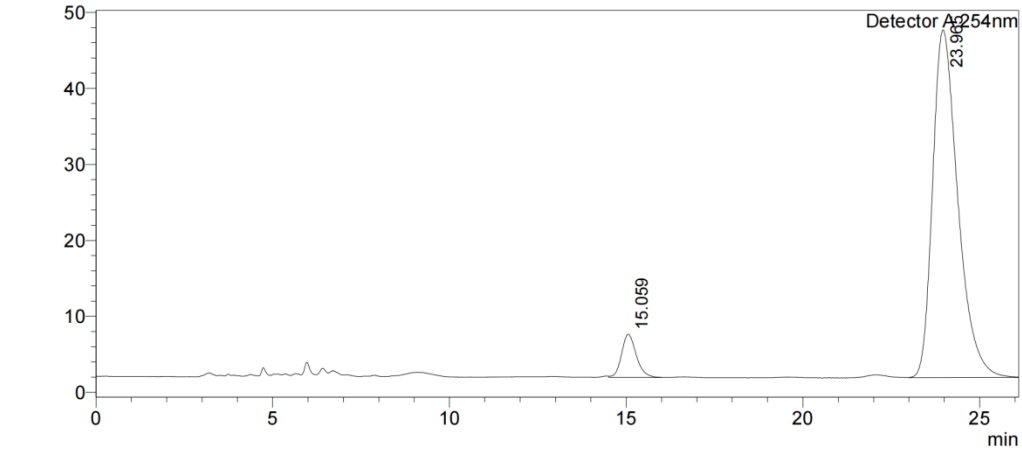



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 14.084 | 7719653 | 254252 | 50.151 |
| 22.937 | 7673020 | 146035 | 49.849 |
| | 15392673 | 400288 | 100.000 |

**<Chromatogram>**



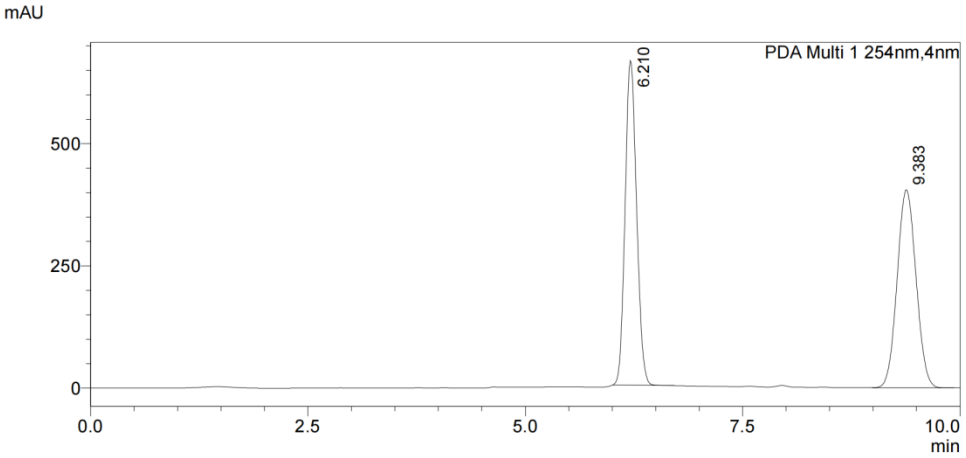

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 15.059 | 164522 | 5681 | 6.739 |
| 23.965 | 2276775 | 45785 | 93.261 |
| | 2441297 | 51466 | 100.000 |

**3ja**, NQ column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

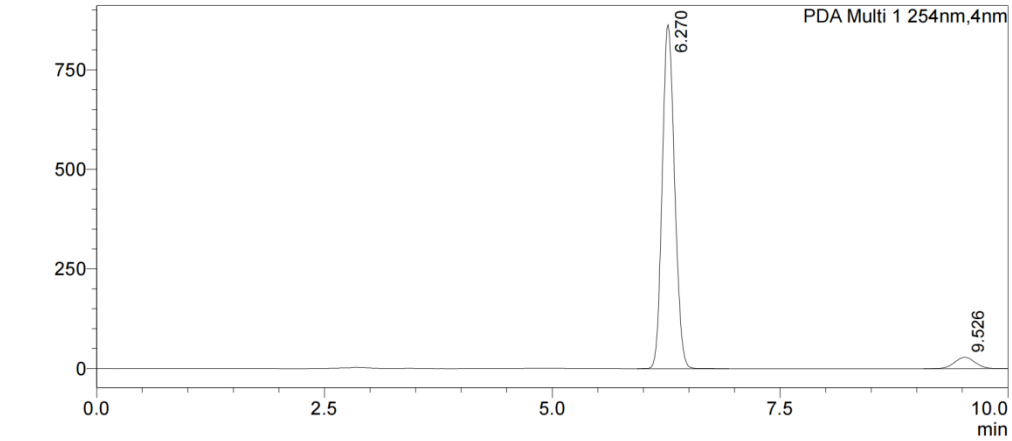



**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.210 | 6097958 | 663810 | 49.838 |
| 9.383 | 6137697 | 405225 | 50.162 |
| | 12235655 | 1069035 | 100.000 |

**<Chromatogram>**



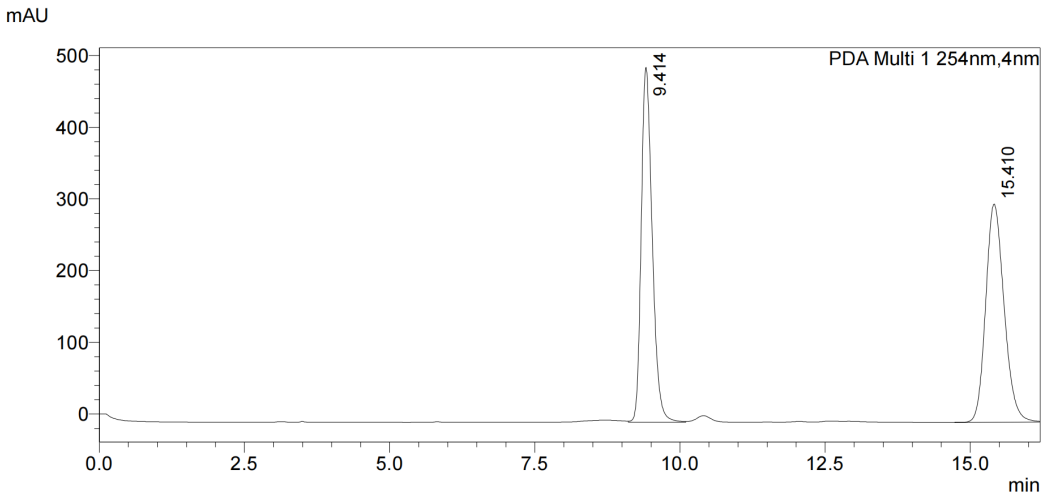

**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.270 | 8139055 | 862893 | 94.843 |
| 9.526 | 442515 | 28327 | 5.157 |
| | 8581570 | 891220 | 100.000 |

**3ka**, NQ column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

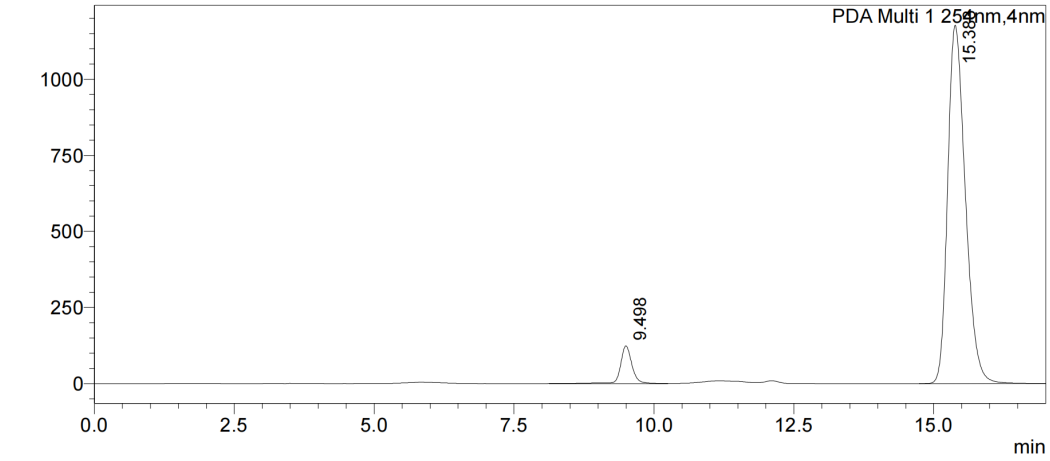



**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 9.414 | 6531035 | 494715 | 49.308 |
| 15.410 | 6714218 | 304119 | 50.692 |
| | 13245252 | 798834 | 100.000 |

**<Chromatogram>**




**<Peak Table>**

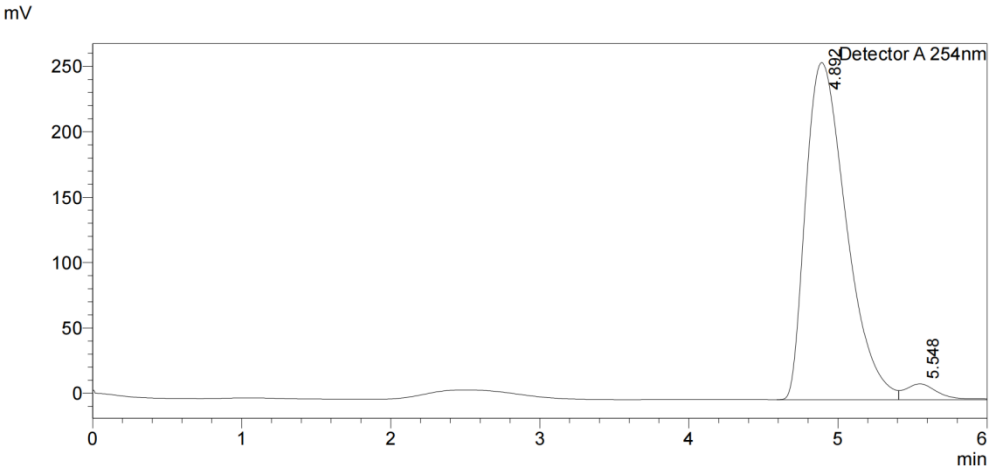
PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 9.498 | 1774974 | 123807 | 6.415 |
| 15.383 | 25893270 | 1177363 | 93.585 |
| | 27668244 | 1301170 | 100.000 |

**3la**, AD-H column (hexane/isopropanol = 90/10, flow = 0.8 mL/min, 254 nm)

`

**<Chromatogram>**

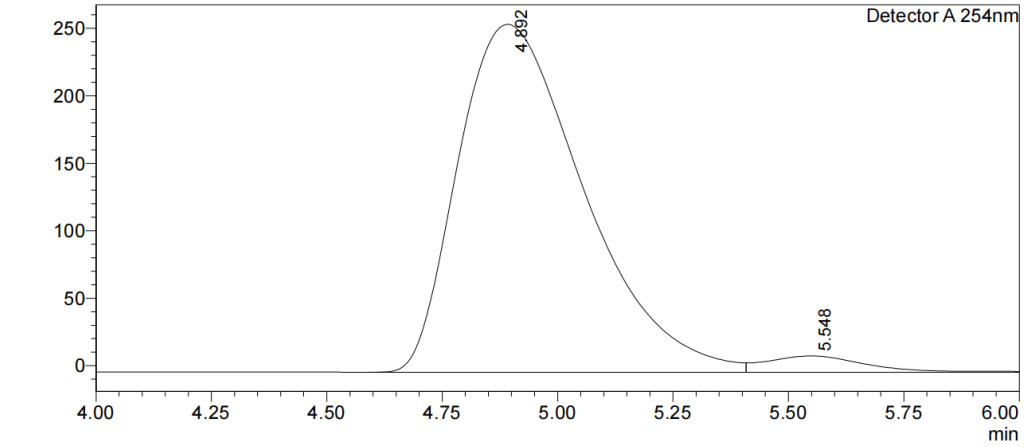



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.892 | 4881281 | 257837 | 96.299 |
| 5.548 | 187583 | 12034 | 3.701 |
| | 5068864 | 269871 | 100.000 |

**<Chromatogram>**



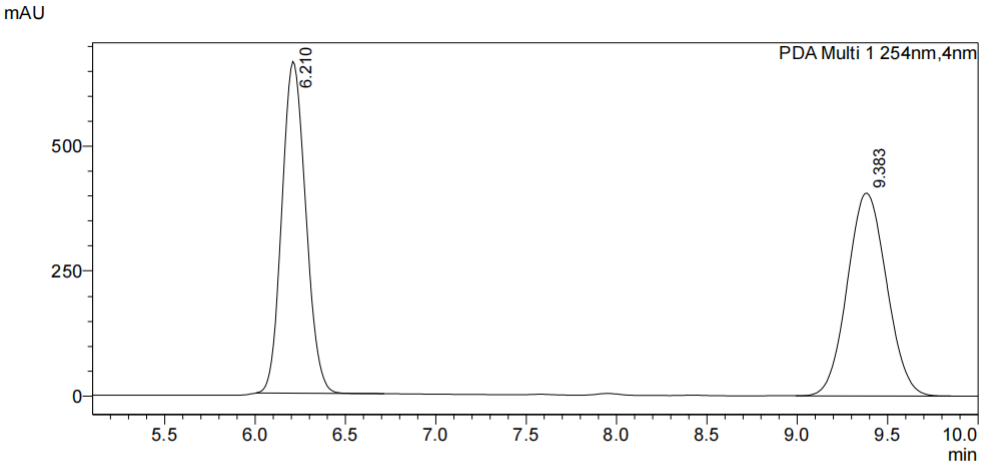

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.892 | 4881281 | 257837 | 96.299 |
| 5.548 | 187583 | 12034 | 3.701 |
| | 5068864 | 269871 | 100.000 |

**3ma**, IBN-5 column (hexane/isopropanol = 90/10, flow = 0.8 mL/min, 254 nm)

**<Chromatogram>**

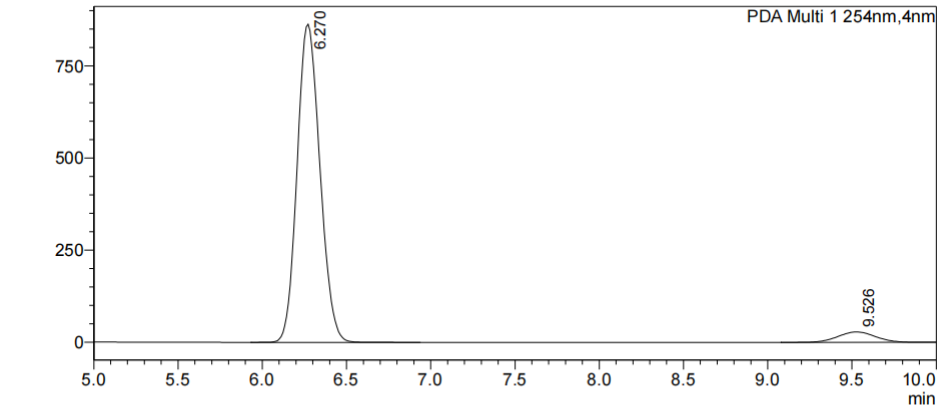



**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.210 | 6097958 | 663810 | 49.838 |
| 9.383 | 6137697 | 405225 | 50.162 |
| | 12235655 | 1069035 | 100.000 |

**<Chromatogram>**



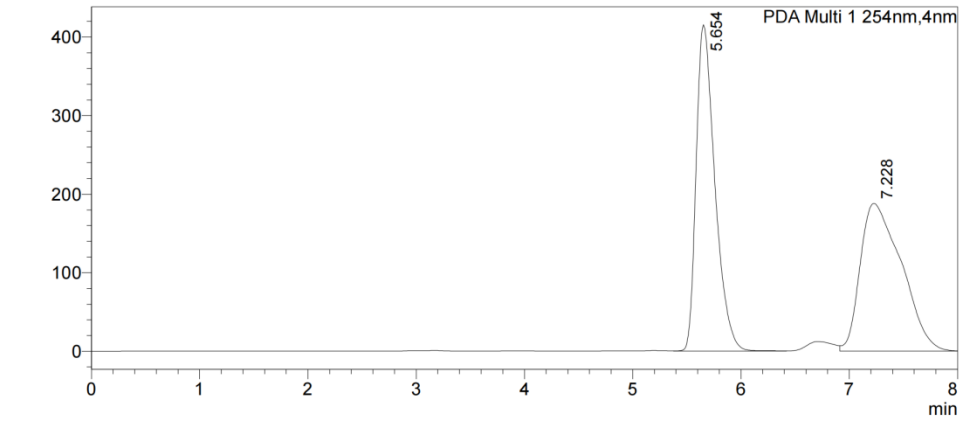

**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.270 | 8139055 | 862893 | 94.843 |
| 9.526 | 442515 | 28327 | 5.157 |
| | 8581570 | 891220 | 100.000 |

**3na**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

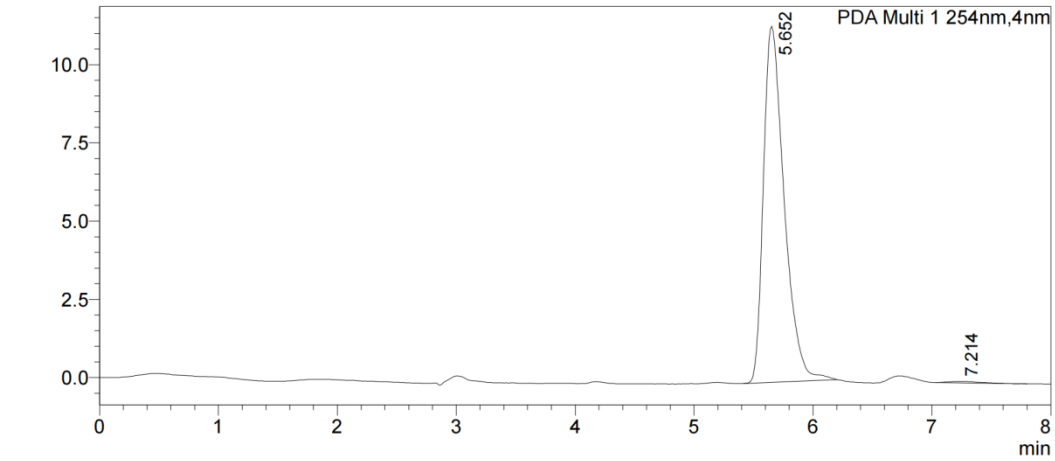



**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.654 | 5004644 | 415136 | 50.171 |
| 7.228 | 4970577 | 187865 | 49.829 |
| | 9975222 | 603001 | 100.000 |

**<Chromatogram>**



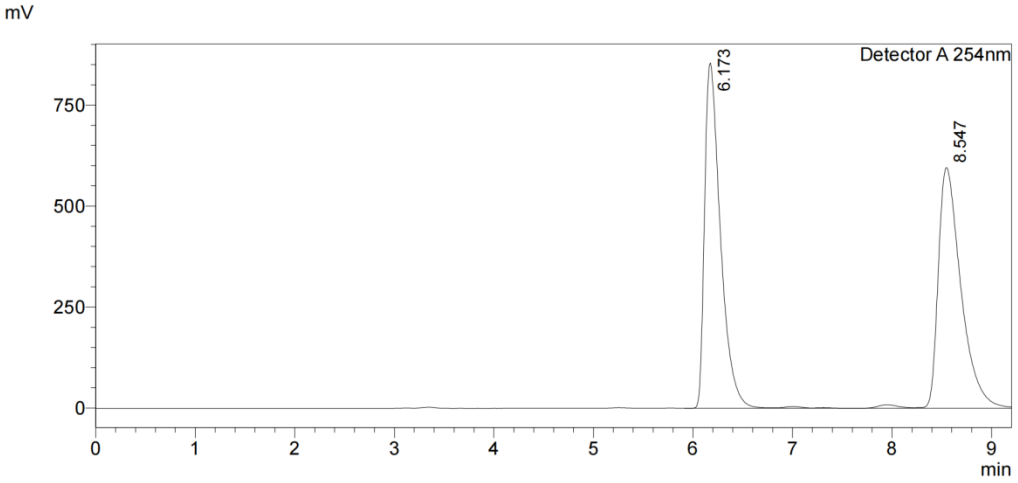

**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 5.652 | 138206 | 11375 | 99.457 |
| 7.214 | 754 | 45 | 0.543 |
| | 138960 | 11420 | 100.000 |

**3oa**, IBN-5 column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

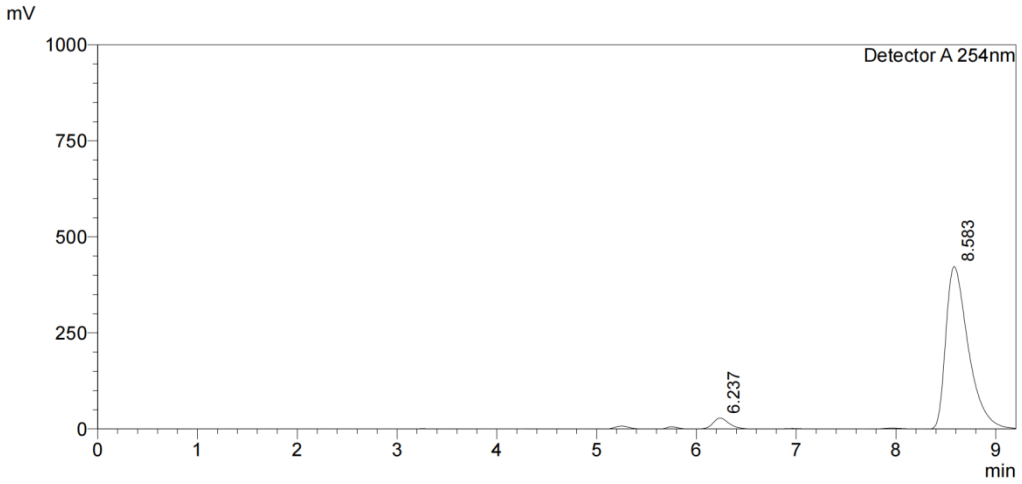



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.173 | 9660731 | 854459 | 50.630 |
| 8.547 | 9420285 | 595424 | 49.370 |
| | 19081017 | 1449883 | 100.000 |

**<Chromatogram>**



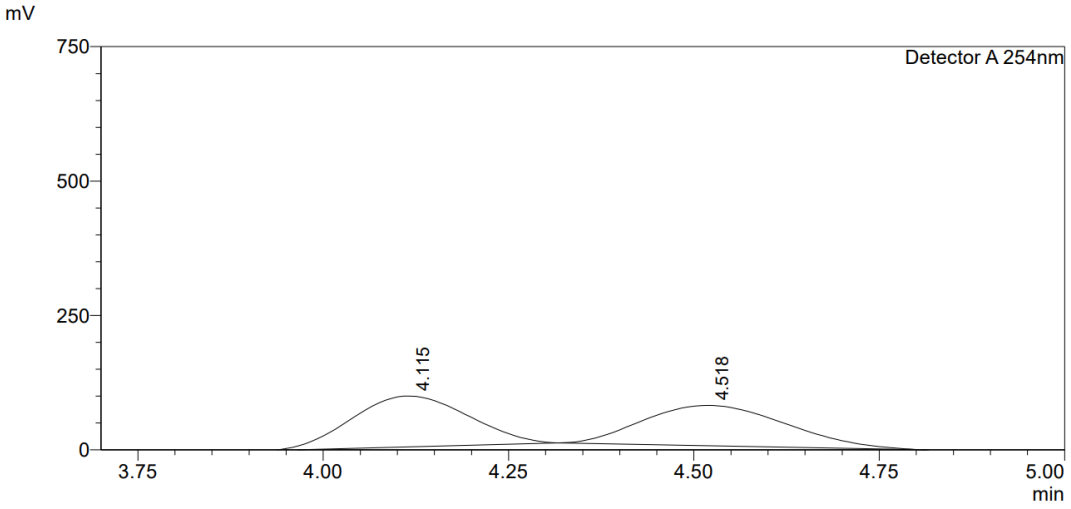

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 6.237 | 347021 | 29143 | 4.957 |
| 8.583 | 6653072 | 423155 | 95.043 |
| | 7000093 | 452297 | 100.000 |

**3pa**, AD-H column (hexane/isopropanol = 90/10, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

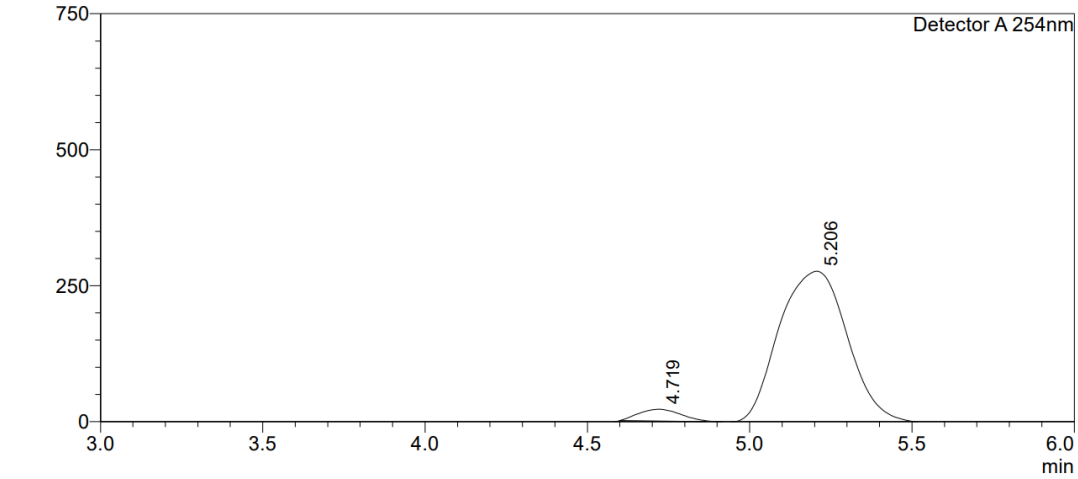



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 4.115 | 1039099 | 94726 | 50.669 |
| 4.518 | 1011646 | 75049 | 49.331 |
| | 2050746 | 169775 | 100.000 |

**<Chromatogram>**



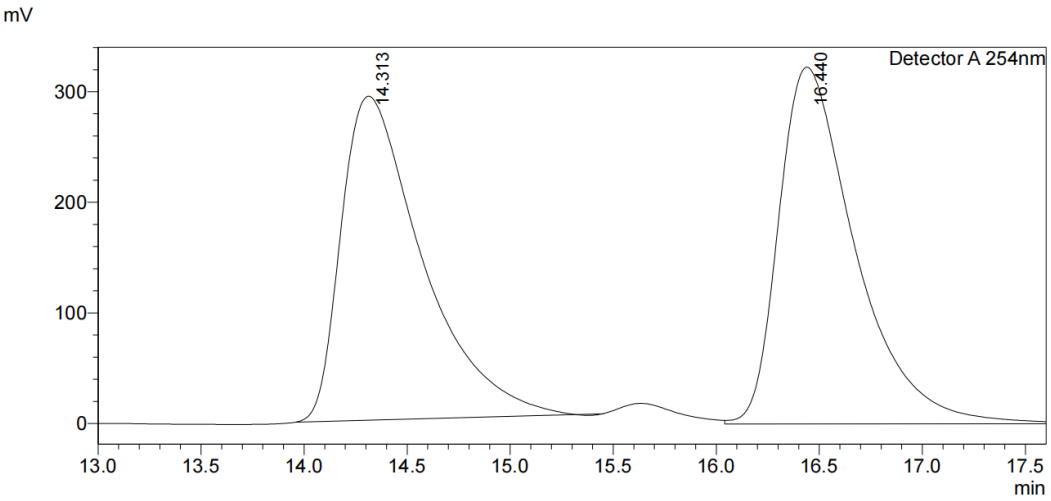

**<Peak Table>**

Detector A 254nm

| Ret. Time | Height | Area | Area% |
|---|---|---|---|
| 4.719 | 21755 | 201340 | 4.584 |
| 5.206 | 280362 | 4191092 | 95.416 |
| | 302117 | 4392433 | 100.000 |

**4aa**, Chiralcel NQ column (hexane/isopropanol = 80/20, flow = 1 mL/min, 254 nm)

**<Chromatogram>**

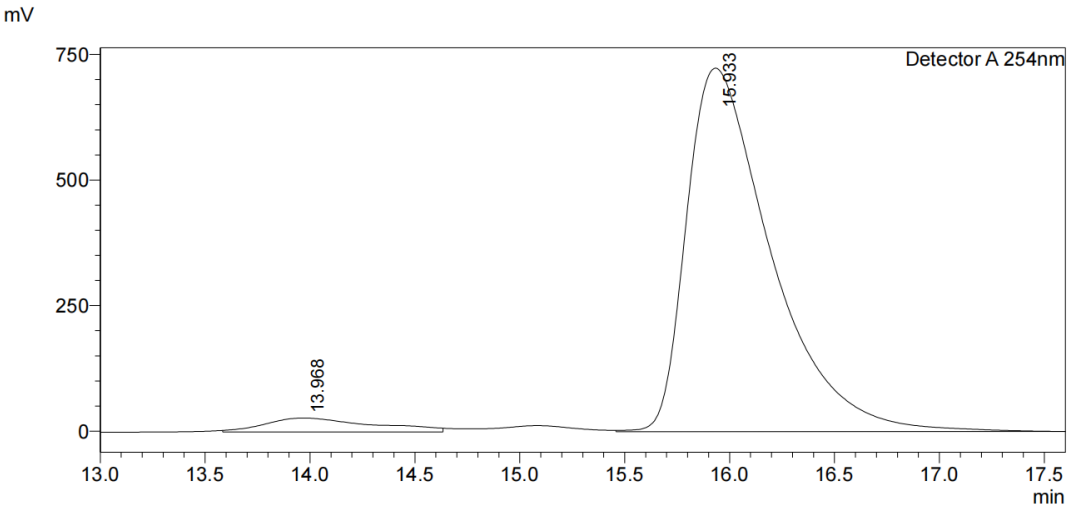



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 14.313 | 8026010 | 292848 | 48.910 |
| 16.440 | 8383721 | 322589 | 51.090 |
| | 16409731 | 615437 | 100.000 |

**<Chromatogram>**



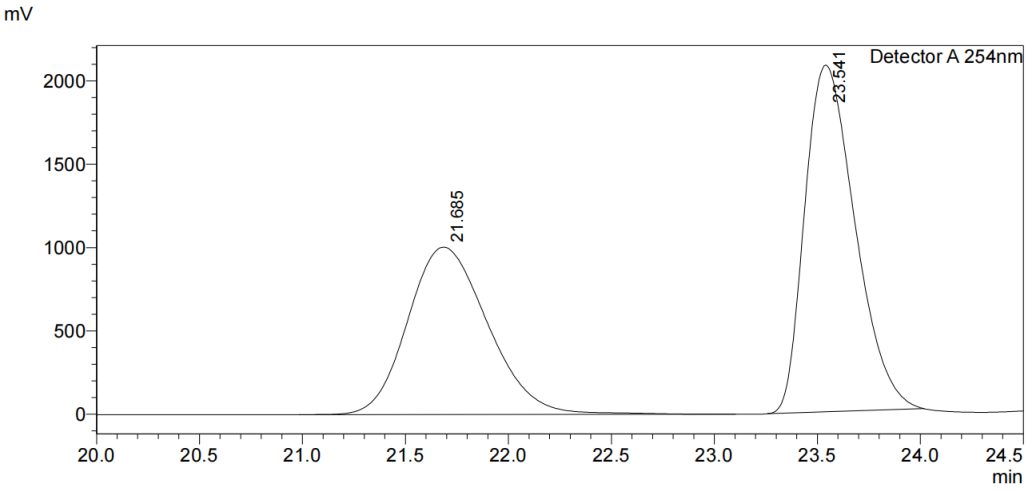

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 13.968 | 1012523 | 27853 | 4.748 |
| 15.933 | 20312576 | 724053 | 95.252 |
| | 21325099 | 751906 | 100.000 |

**4fa**, Chiralcel IBN-5 column (hexane/isopropanol = 90/10, flow = 1.2 mL/min, 254 nm)

**<Chromatogram>**

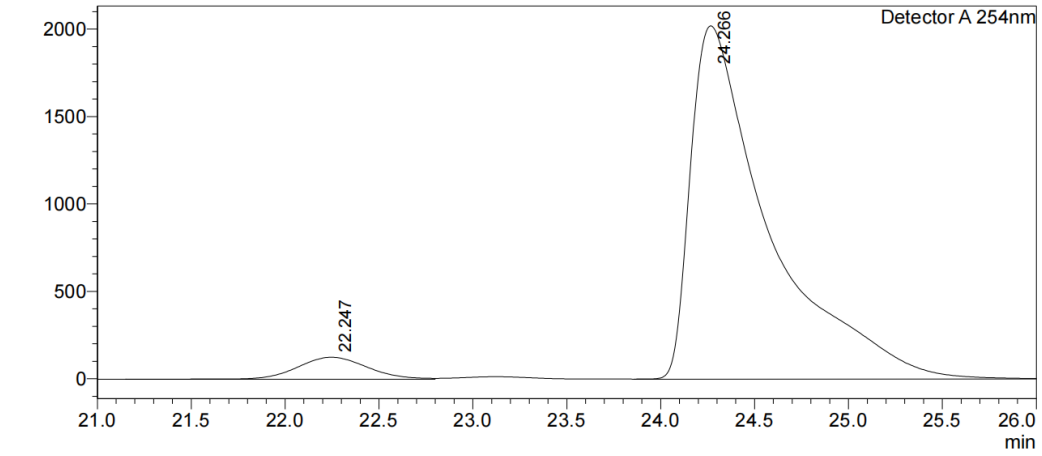



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 21.685 | 27241736 | 1004081 | 43.524 |
| 23.541 | 35348155 | 2079978 | 56.476 |
| | 62589892 | 3084060 | 100.000 |

**<Chromatogram>**



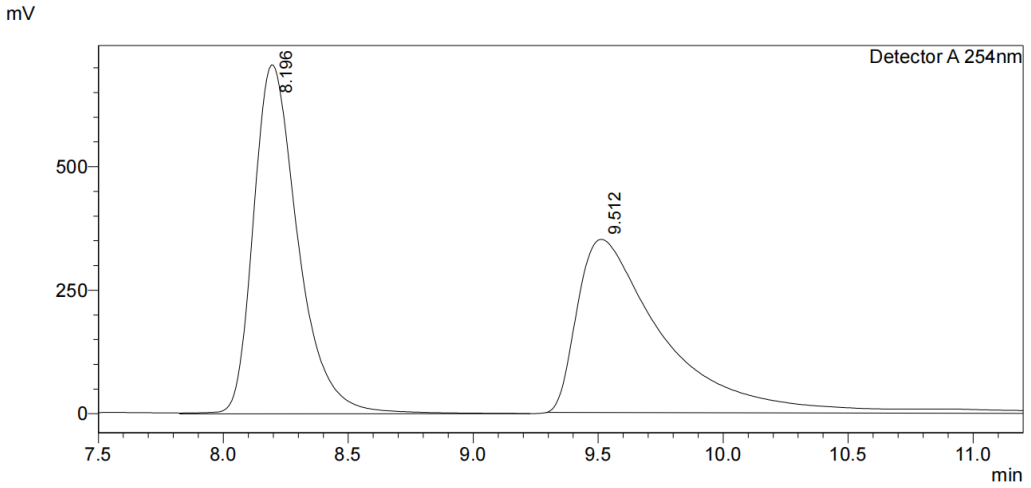

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 22.247 | 3227539 | 125266 | 5.193 |
| 24.266 | 58927146 | 2021302 | 94.807 |
| | 62154685 | 2146569 | 100.000 |

**4ga**, Chiralcel NT(2) column (hexane/isopropanol = 80/20, flow = 1.2 mL/min, 254 nm)

**<Chromatogram>**

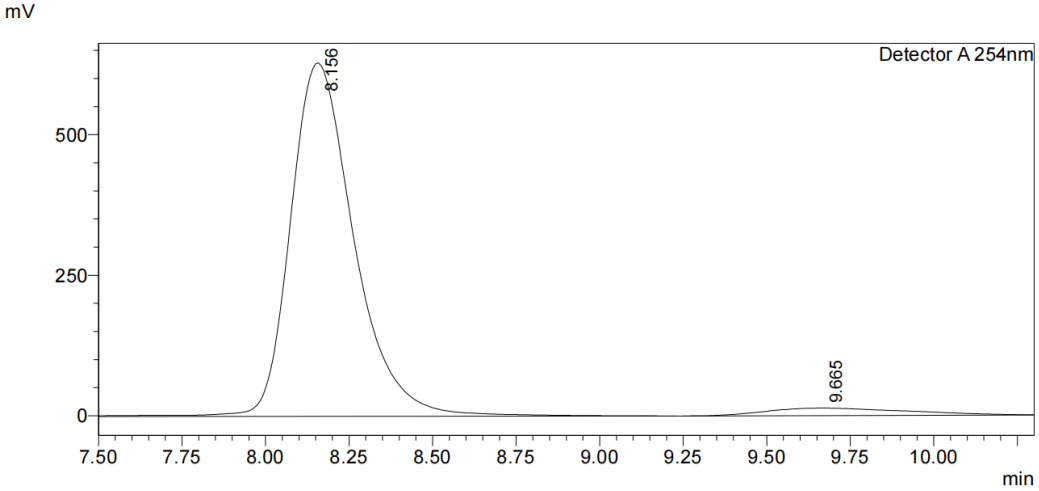



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 8.196 | 8769918 | 705576 | 50.505 |
| 9.512 | 8594391 | 350311 | 49.495 |
| | 17364309 | 1055887 | 100.000 |

**<Chromatogram>**



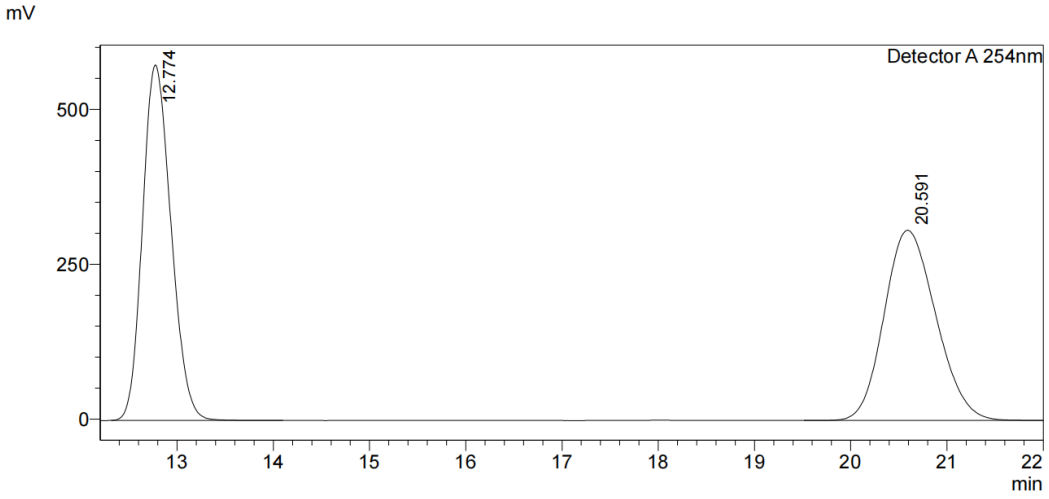

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 8.156 | 8332902 | 628439 | 95.559 |
| 9.665 | 387229 | 13265 | 4.441 |
| | 8720131 | 641704 | 100.000 |

**4la**, Chiralcel NT(2) column (hexane/isopropanol = 90/10, flow = 1.2 mL/min, 254 nm)

**<Chromatogram>**

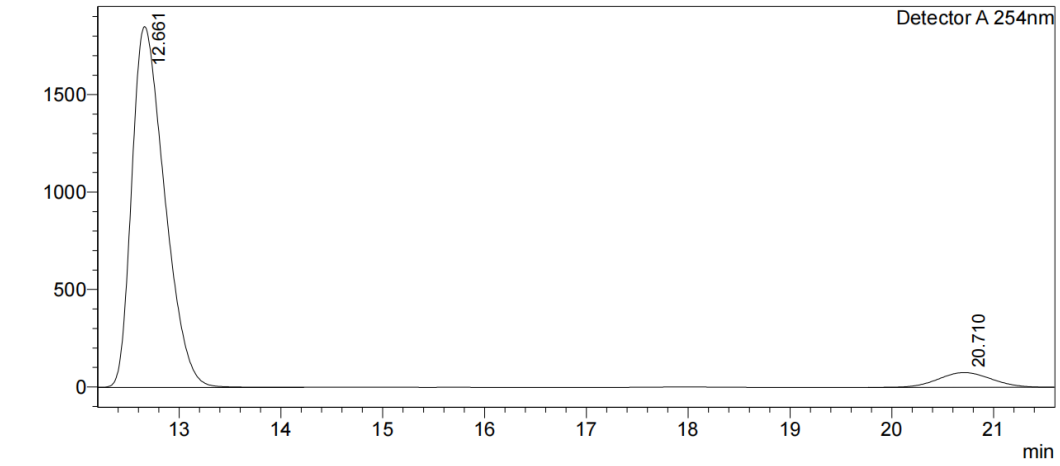



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 12.774 | 11835517 | 574069 | 50.752 |
| 20.591 | 11484562 | 307250 | 49.248 |
| | 23320078 | 881319 | 100.000 |

**<Chromatogram>**



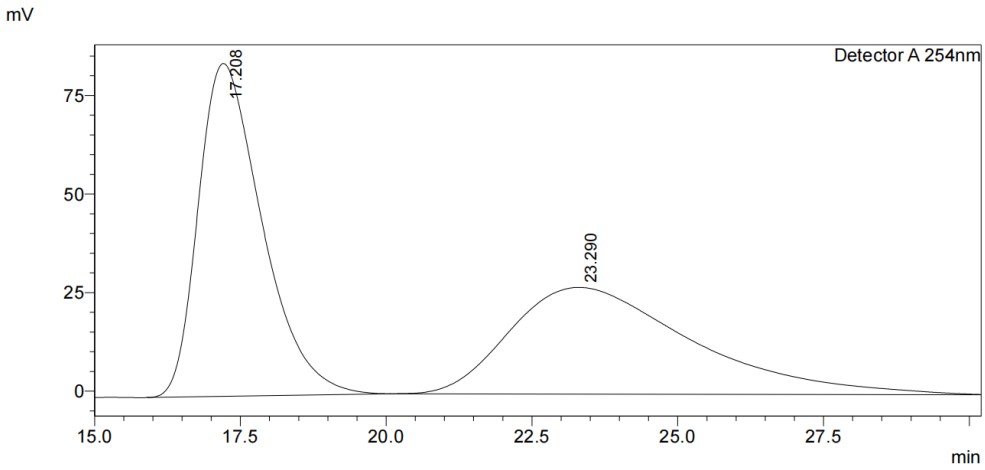

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 12.661 | 41417611 | 1851000 | 93.729 |
| 20.710 | 2771072 | 75800 | 6.271 |
| | 44188682 | 1926800 | 100.000 |

**4ma**, Chiralcel NQ column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm)

**<Chromatogram>**

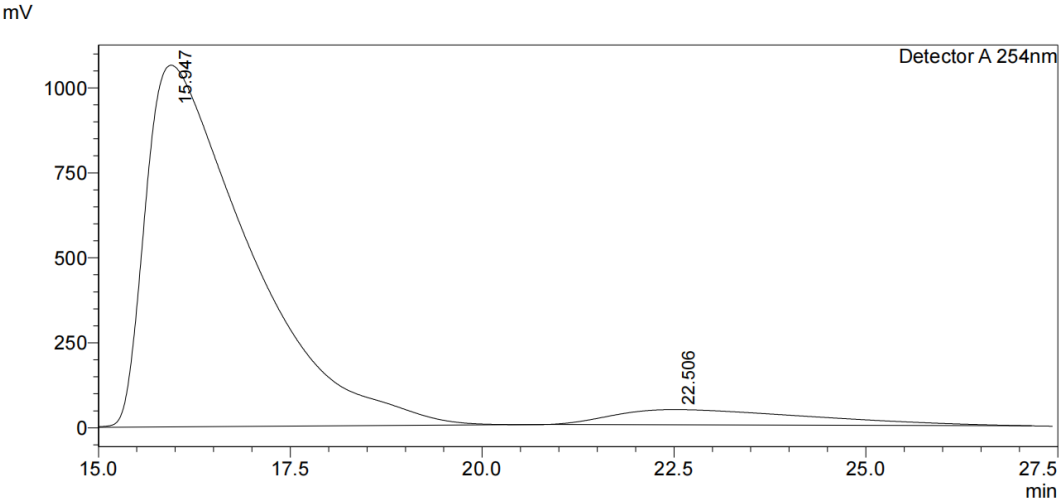



**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Area% | Height |
|---|---|---|---|
| 17.208 | 6416430 | 52.130 | 84426 |
| 23.290 | 5892201 | 47.870 | 27057 |
| | 12308630 | 100.000 | 111483 |

**<Chromatogram>**



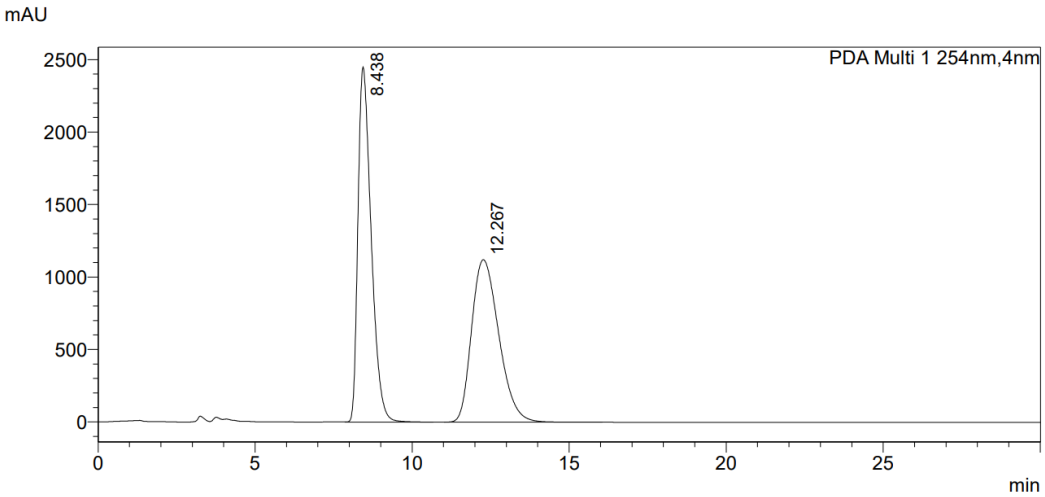

**<Peak Table>**

Detector A 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 15.947 | 99793591 | 1063688 | 92.490 |
| 22.506 | 8103153 | 44872 | 7.510 |
| | 107896743 | 1108560 | 100.000 |

**7**, Chiralcel AS-H column (hexane/isopropanol = 60/40, flow = 1.0 mL/min, 254 nm)

**<Chromatogram>**

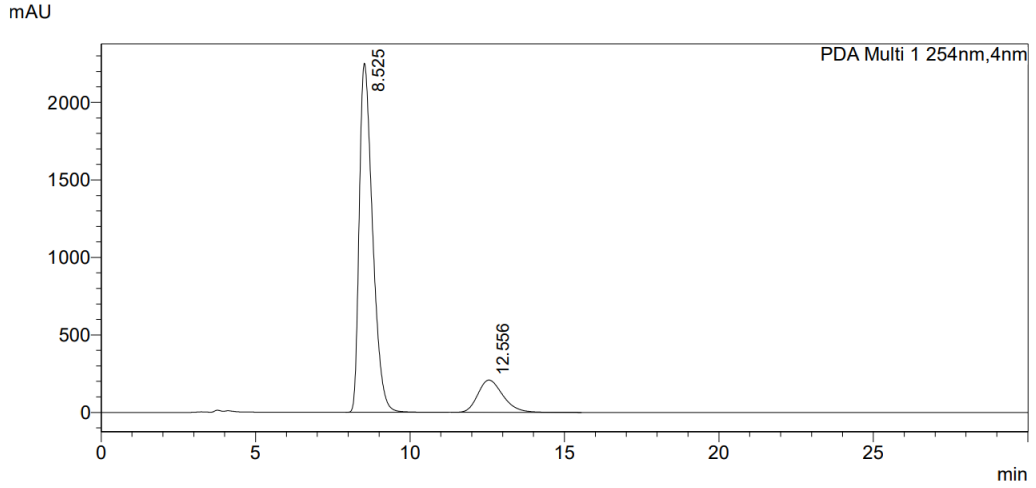



**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Area% | Height |
|---|---|---|---|
| 8.438 | 71789417 | 51.576 | 2449370 |
| 12.267 | 67402734 | 48.424 | 1120634 |
| | 139192151 | 100.000 | 3570005 |

**<Chromatogram>**




**<Peak Table>**

PDA Ch1 254nm

| Ret. Time | Area | Height | Area% |
|---|---|---|---|
| 8.525 | 67413853 | 2251328 | 85.140 |
| 12.556 | 11766239 | 208262 | 14.860 |
| | 79180092 | 2459590 | 100.000 |