# Supporting Information

## Regio- and Stereoselective Syntheses of Chiral *α*-Quaternary (*Z*)-Trisubstituted Allylic Amino Acids *via* Synergistic Pd/Cu Catalysis

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# 1. General information

All reactions were accomplished in Schlenk tube and round flask. Column chromatograph was performed over silica gel (200-300 mesh). $^{1}H$ NMR spectra were recorded on a Bruker AM400 spectrometer, chemical shifts (in ppm) were referred to $CDCl_3$ ($\delta$ = 7.26 ppm). $^{13}C$ NMR spectrum were obtained by using the same NMR spectrometer and were calibrated with $CDCl_3$ ($\delta$ = 77.0 ppm). The following abbreviations have been used to illuminate the diversities: $\delta$ = chemical shifts, $J$ = coupling constant, s = singlet, d= doublet, t = triplet, q = quartet, m = multiplet. HRMS were recorded on a Bruker microTOF spectrometer (ESI). Ee values were determined by Agilent high-performance liquid chromatograph (HPLC). All anhydrous solvents were dried by the standard treated method. Vinylethylene carbonates[1] and aldimine ester[2] were synthesized according to known references. All materials were obtained by commercial suppliers, unless otherwise notice, and most stating materials were purchased from Adamas, Bide and Energy Chemical. PE = petroleum ether, DCM = dichloromethane, MeOH = methanol, EA = ethyl acetate.

# 2. Procedure for the synthesis chiral *α*-quaternary (*Z*)-trisubstituted allylic amino acids

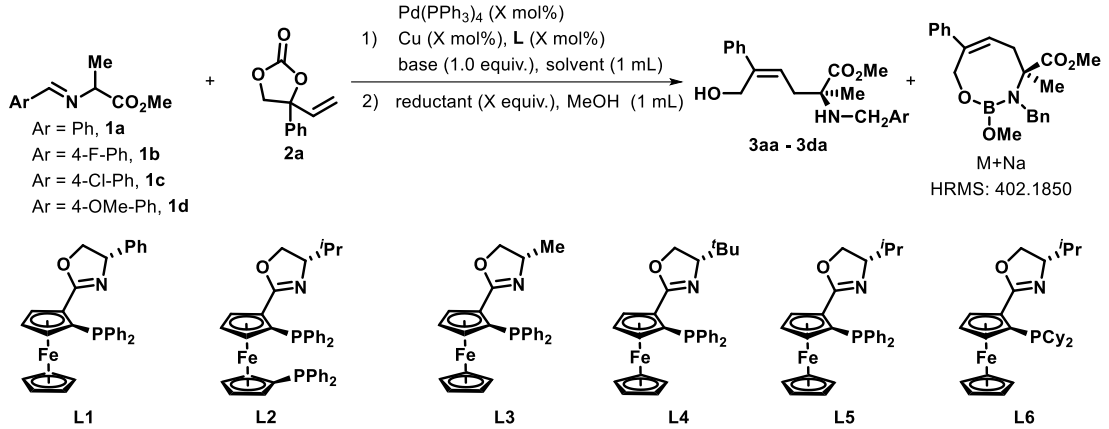
**The preparation of Cu catalyst:** $Cu(CH_3CN)_4PF_6$ (5 mol%), **L1** (6 mol%) were stirred in DCE (0.5 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 30 min.

**Method A:** To a Schlenk tube with prepared Cu catalyst were added $Cs_2CO_3$ (32.6 mg, 0.1 mmol), aldimine Schiff base (0.1 mmol, 1.0 equiv), vinylethylene carbonates (24.7 mmol, 1.3 equiv), Pd catalyst (4 mol%) and DCE (0.5 mL) under nitrogen atmosphere. The reaction mixture was stirred at 40 ºC for 4 h. To the reaction mixture was added dry MeOH (1 mL) and $NaBH_3CN$ (31.4mg, 5.0 equiv) at 0 ºC and the mixture was stirred for 2 h. Then the crude products were purified by $SiO_2$ column chromatography (PE/EA = 3:1) to give the desired products. The *ee* value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.

# 3. Results and discussion

## 3.1 Optimization of reaction conditions

**Table S1**. Screening of reaction conditions. [a]

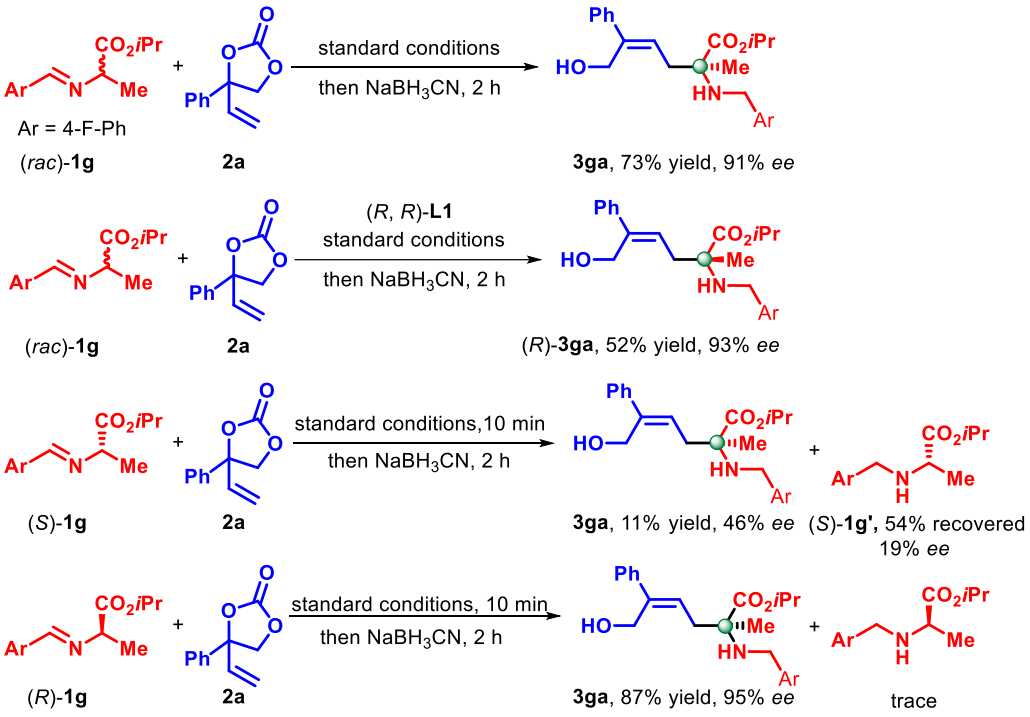



| Entry | [Cu] | L | base | solvent | yield (%)[b] | *ee* (%)[c] | *Z*/*E*[d] |
|---|---|---|---|---|---|---|---|
| 1 | $Cu(CH_3CN)_4BF_4$ | **L1** | $Cs_2CO_3$ | DCE | 66 | 92 | >20:1 |
| 2 | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | 62 | 94 | >20:1 |
| 3 | CuI | **L1** | $Cs_2CO_3$ | DCE | trace | - | - |
| 4 | CuCl | **L1** | $Cs_2CO_3$ | DCE | trace | - | - |
| 5 | $Cu(CH_3CN)_4PF_6$ | **L2** | $Cs_2CO_3$ | DCE | 31 | 35 | >20:1 |
| 6 | $Cu(CH_3CN)_4PF_6$ | **L3** | $Cs_2CO_3$ | DCE | 48 | 73 | >20:1 |
| 7 | $Cu(CH_3CN)_4PF_6$ | **L4** | $Cs_2CO_3$ | DCE | 51 | 85 | >20:1 |
| 8 | $Cu(CH_3CN)_4PF_6$ | **L5** | $Cs_2CO_3$ | DCE | 52 | 83 | >20:1 |
| 9 | $Cu(CH_3CN)_4PF_6$ | **L6** | $Cs_2CO_3$ | DCE | 50 | 29 | >20:1 |
| 10 | $Cu(CH_3CN)_4PF_6$ | **L1** | $Na_2CO_3$ | DCE | 50 | 91 | >20:1 |
| 11 | $Cu(CH_3CN)_4PF_6$ | **L1** | DIPEA | DCE | 46 | 93 | >20:1 |
| 12 | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | toluene | 27 | 82 | >20:1 |
| 13 | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCM | 55 | 88 | >20:1 |
| 14 | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | THF | 41 | 89 | >20:1 |
| 15[e] | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | 16 | 90 | >20:1 |
| 16[f] | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | ND | - | - |
| 17[g] | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | 70 | 91 | >20:1 |
| 18[h] | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | 75 | 91 | >20:1 |
| 19[i] | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | 86 | 92 | >20:1 |
| 20[j] | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | 62 | 87 | >20:1 |
| 21[k] | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | 65 | 91 | >20:1 |
| 22[l] | $Cu(CH_3CN)_4PF_6$ | **L1** | $Cs_2CO_3$ | DCE | 85 | 91 | >20:1 |

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(PPh_3)_4$ (5 mol%), Cu (10 mol%), L (12 mol%), base (1.5 equiv.), solvent (1 mL), $NaBH_4$ (5 equiv.), MeOH (1 mL), $N_2$, 9 h, r.t. [b, d] Determined by 1H NMR using $CHBr_2$ as internal standard. [c] Determined by HPLC using chiral column. [e] $LiAlH_4$ (4 equiv.). [f] $NaBH(OAc)_3$ (4 equiv.). [g] $NaBH_3CN$ (4 equiv.). [h] 40 ℃. [i] **1b** (0.1 mmol). [j] **1c** (0.1 mmol). [k] **1d** (0.1 mmol). [l] **1b** (0.1mmol), **2a** (0.13 mmol), $Pd(PPh_3)_4$ (4 mol%), $Cu(CH_3CN)_4PF_6$ (5 mol%), **L1** (6 mol%), $Cs_2CO_3$ (1 equiv.), DCE (1 mL), $NaBH_3CN$ (5 equiv.), MeOH (1.0 mL), $N_2$, 6 h, 40 ℃.

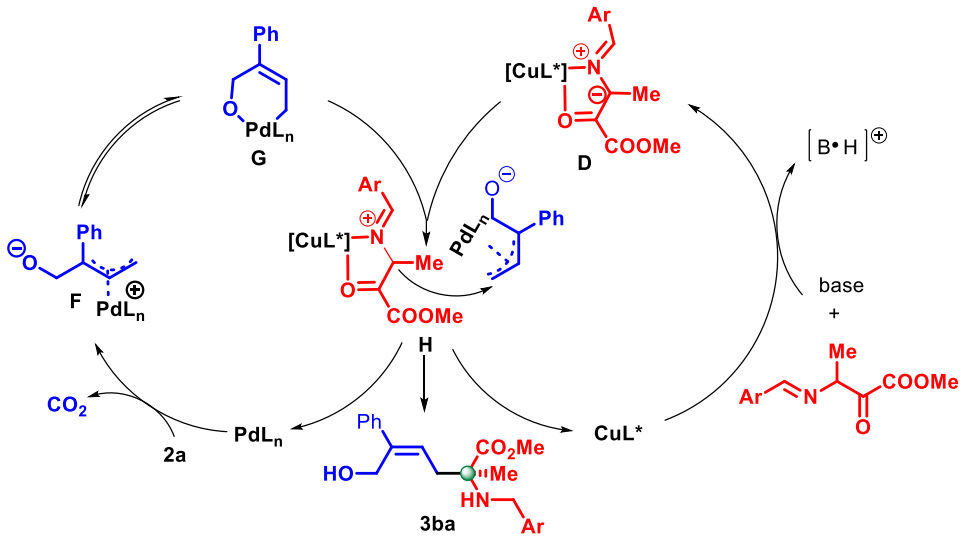
## 3.2 Stereocontrol experiments

**Scheme S1**. Stereocontrol experiments

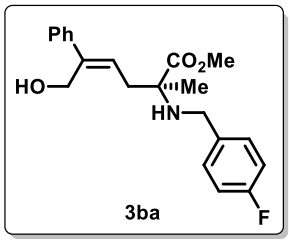



## 3.3 Reaction mechanism

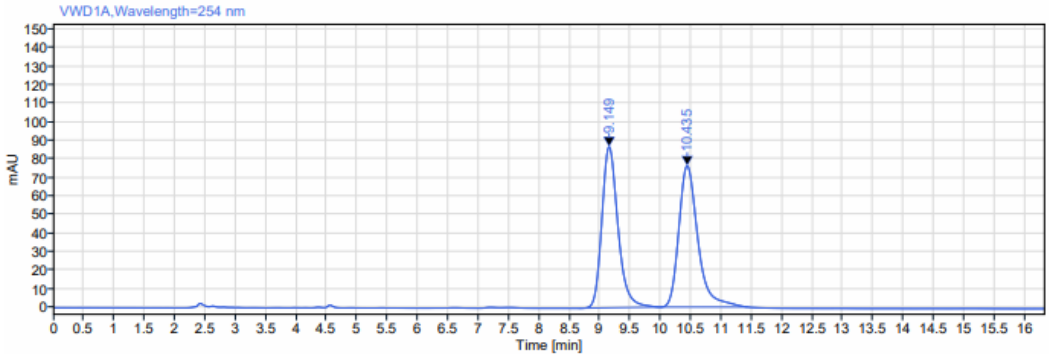
**Scheme S2**. A plausible mechanism



## 3.4. Characterization of trisubstituted allylic amino acids

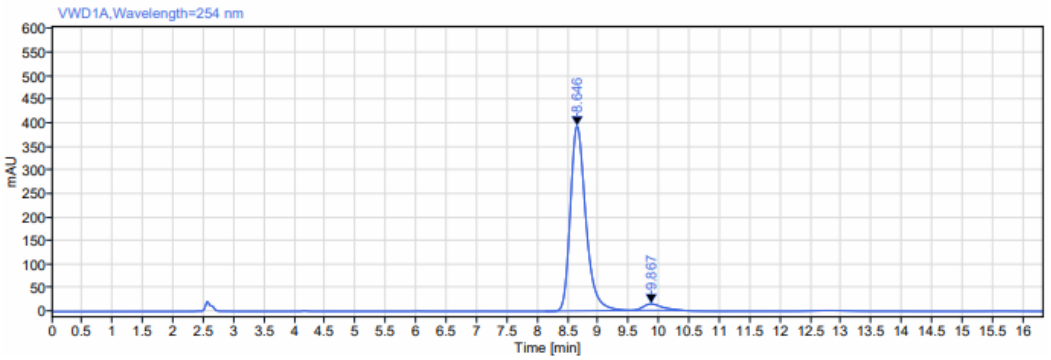



**3ba** (30.7mg, 86% yield, PE/EA=3:1, 92% *ee*, *Z/E* >20:1) was synthesized in method A afforded 86% isolated yield as a colorless oil. $[\alpha]_D^{25}$=+4 (c=0.60, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35 (d, *J* = 7.3 Hz, 2H), 7.22 (ddd, *J* = 10.0, 8.0, 4.9 Hz, 5H), 7.02 – 6.84 (m, 2H), 5.72 (dd, *J* = 9.4, 7.4 Hz, 1H), 4.34 (dd, *J* = 52.1, 12.3 Hz, 2H), 3.70 (s, 3H), 3.55 (dd, *J* = 36.3, 11.7 Hz, 2H), 2.59 (ddd, *J* = 21.2, 13.9, 8.4 Hz, 2H), 2.33 (bs, 2H), 1.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.5, 162.1 (d, *J* = 245.0 Hz), 144.6, 141.6, 134.9 (d, *J* = 3.1 Hz), 130.0 (d, *J* = 8.1 Hz), 128.4, 127.3, 126.2, 124.8, 115.4 (d, *J* = 21.4 Hz), 61.9, 59.9, 52.4, 48.2, 39.4, 21.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{24}FNO_3$ 358.1813; found: 358.1839. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 8.65 min (major), 9.87 min (minor).



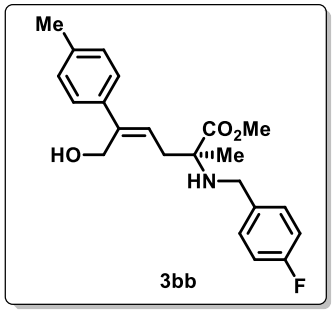

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.149 | MM m | 0.28 | 1600.59 | 86.83 | 49.06 | |
| 10.435 | MM m | 0.33 | 1661.70 | 76.13 | 50.94 | |
| | | Sum | 3262.29 | | | |

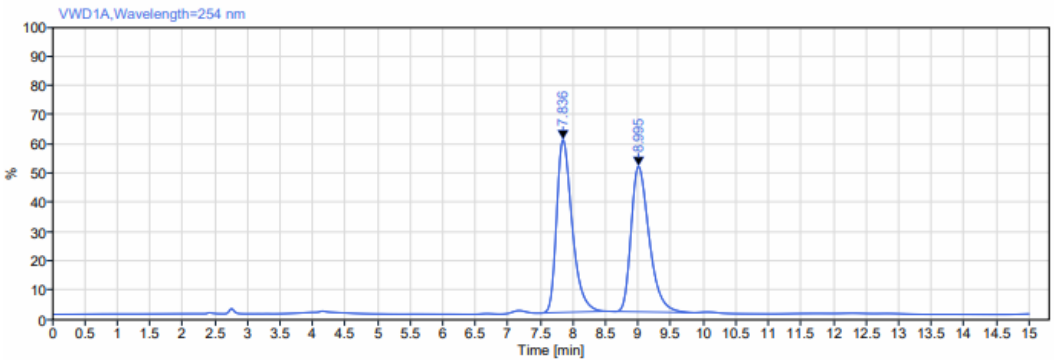



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 8.646 | MM m | 0.27 | 6927.70 | 392.06 | 95.86 | |
| 9.867 | MM m | 0.33 | 299.06 | 13.76 | 4.14 | |
| | | Sum | 7226.75 | | | |

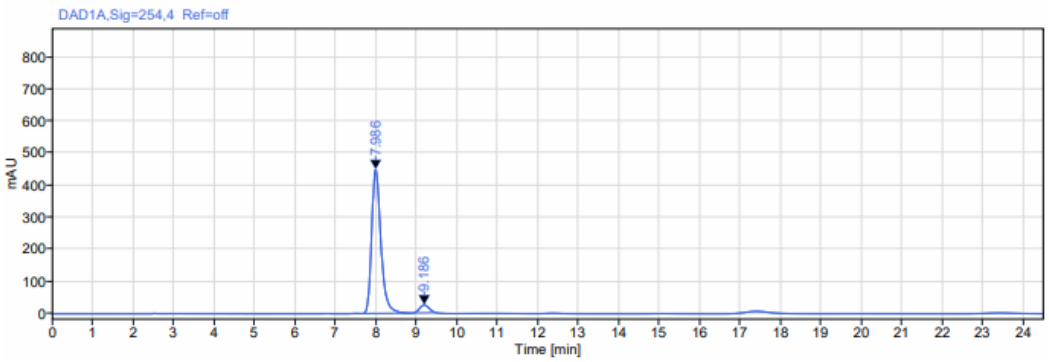



**3bb** (32.1 mg, 87% yield, PE/EA=3:1, 90% *ee*, *Z*/*E* >20:1) was synthesized in method A afforded 87% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+16 (c=0.64, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.27 – 7.17 (m, 4H), 7.05 (d, $J$ = 7.9 Hz, 2H), 6.97 – 6.86 (m, 2H), 5.68 (dd, $J$ = 9.4, 7.4 Hz, 1H), 4.32 (dd, $J$ = 57.3, 12.3 Hz, 2H), 3.70 (s, 3H), 3.55 (dd, $J$ = 41.4, 11.7 Hz, 2H), 2.81 (bs, 1H), 2.58 (ddd, $J$ = 21.1, 13.9, 8.5 Hz, 3H), 2.26 (s, 3H), 1.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, $J$ = 245.4 Hz), 144.5, 138.7, 137.1, 134.7 (d, $J$ = 2.7 Hz), 130.1 (d, $J$ = 8.0 Hz), 129.1, 126.0, 123.9, 115.4 (d, $J$ = 21.2 Hz), 61.9, 59.8, 52.4, 48.2, 39.4, 21.6, 21.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}FNO_3$ 372.1969; found: 372.1989. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 7.99 min (major), 9.19 min (minor).



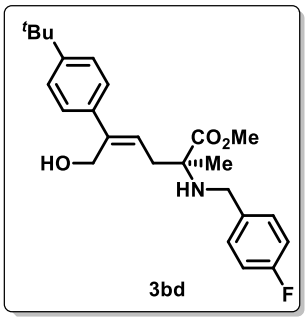

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.836 | MM m | 0.25 | 22572.19 | 1361.14 | 50.48 | |
| 8.995 | MM m | 0.30 | 22139.83 | 1146.12 | 49.52 | |
| | | Sum | 44712.02 | | | |

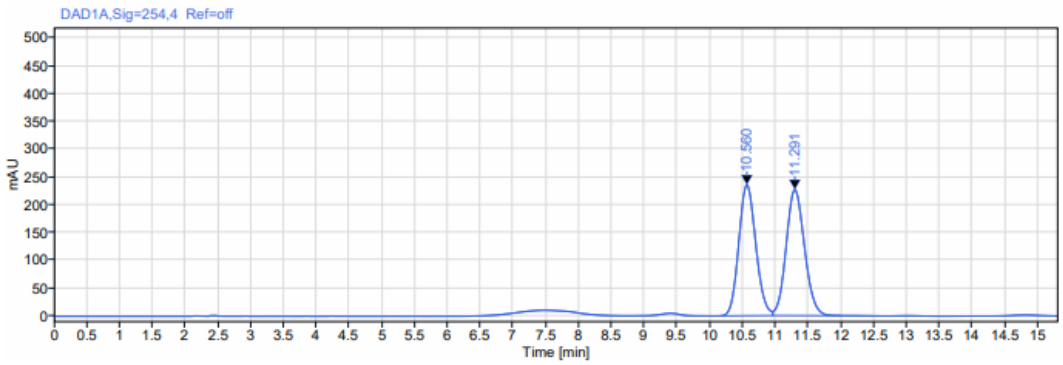



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.986 | MM m | 0.24 | 7142.27 | 448.69 | 94.78 | |
| 9.186 | MM m | 0.26 | 393.15 | 24.25 | 5.22 | |
| | | Sum | 7535.43 | | | |

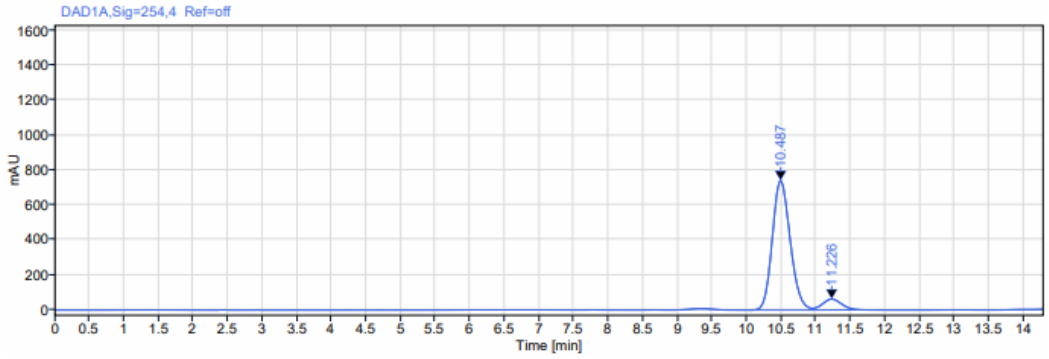



**3bc** (25.3 mg, 61% yield, PE/EA=3:1, 84% *ee*, *Z/E* >20:1) was synthesized in method A afforded 61% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+12 (c=0.51, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32 – 7.25 (m, 4H), 7.23 – 7.17 (m, 2H), 6.97 – 6.85 (m, 2H), 5.78 – 5.60 (m, 1H), 4.33 (dd, *J* = 56.9, 12.3 Hz, 2H), 3.70 (s, 3H), 3.54 (dd, *J* = 40.3, 11.6 Hz, 2H), 2.81 (bs, 1H), 2.58 (ddd, *J* = 21.0, 13.8, 8.7 Hz, 2H), 1.39 (s, 3H), 1.24 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.3 Hz), 150.3, 144.4, 138.6, 134.8 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 8.1 Hz), 125.8, 125.3, 124.0, 115.4 (d, *J* = 21.4 Hz), 61.9, 59.8, 52.4, 48.2, 39.5, 34.4, 31.3, 21.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{32}FNO_3$ 414.2439; found: 414.2465. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 95:5, 25min; $t_R$ =10.49 min (major), 11.23 min (minor).



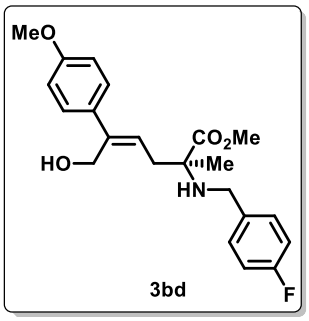

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.560 | MM m | 0.28 | 4243.93 | 235.26 | 49.05 | |
| 11.291 | MM m | 0.30 | 4408.48 | 226.54 | 50.95 | |
| | | Sum | 8652.42 | | | |

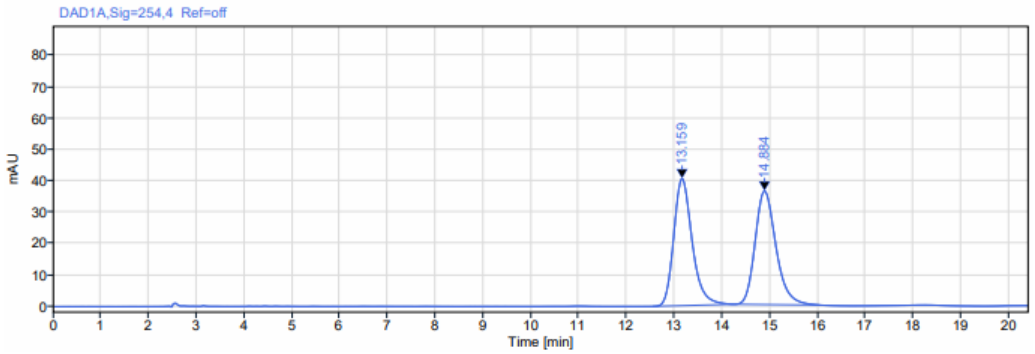



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.487 | MM m | 0.28 | 13303.32 | 740.17 | 91.76 | |
| 11.226 | MM m | 0.30 | 1194.31 | 61.84 | 8.24 | |
| | | Sum | 14497.62 | | | |

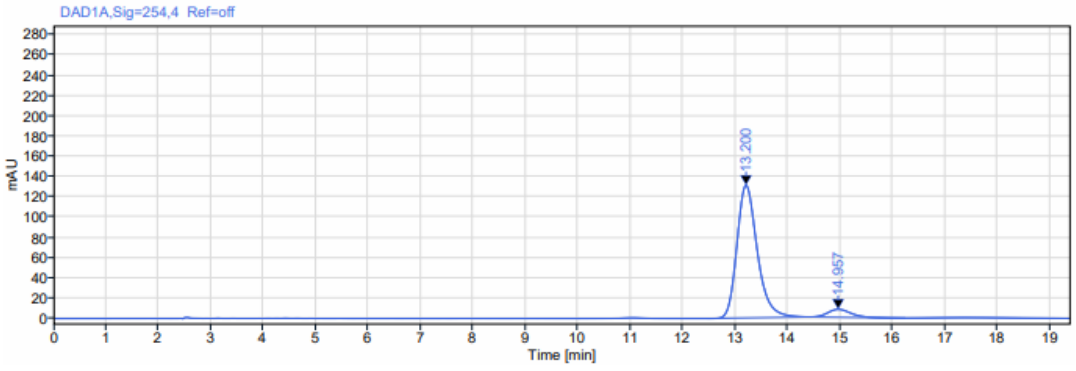



**3bd** (25.0 mg, 65% yield, PE/EA=3:1, 87% *ee*, *Z/E* >20:1) was synthesized in method A afforded 65% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =21+ (c=0.50, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33 – 7.26 (m, 2H), 7.24 – 7.18 (m, 2H), 6.96 – 6.86 (m, 2H), 6.83 – 6.71 (m, 2H), 5.63 (dd, *J* = 9.5, 7.3 Hz, 1H), 4.31 (dd, *J* = 55.3, 12.3 Hz, 2H), 3.72 (s, 3H), 3.70 (s, 3H), 3.54 (dd, *J* = 39.9, 11.6 Hz, 2H), 2.86 (bs, 1H), 2.56 (ddd, *J* = 21.2, 13.9, 8.4 Hz, 2H), 1.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.5, 162.1 (d, *J* = 245.5 Hz), 159.0, 144.0, 134.8 (d, *J* = 3.2 Hz), 134.1, 130.1 (d, *J* = 8.1 Hz), 127.3, 123.1, 115.4 (d, *J* = 21.4 Hz), 113.7, 61.9, 59.8, 55.3, 52.4, 48.2, 39.4, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}FNO_4$ 388.1919; found: 388.1943. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =13.20 min (major), 14.96 min (minor).



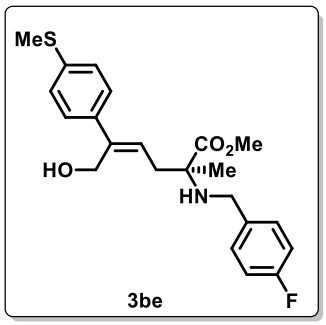

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 13.159 | MM m | 0.41 | 1084.54 | 40.50 | 49.72 | |
| 14.884 | MM m | 0.46 | 1096.72 | 36.20 | 50.28 | |
| | | Sum | 2181.26 | | | |

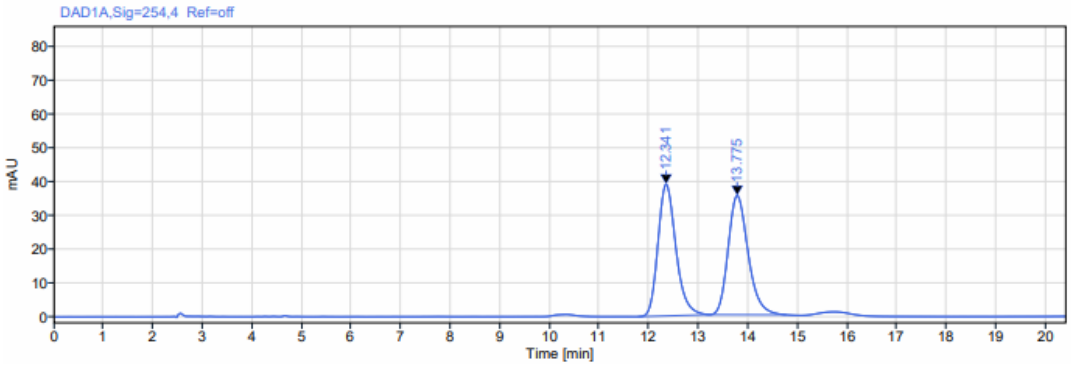



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 13.200 | MM m | 0.41 | 3534.49 | 131.03 | 93.67 | |
| 14.957 | MM m | 0.46 | 238.85 | 7.83 | 6.33 | |
| | | Sum | 3773.34 | | | |

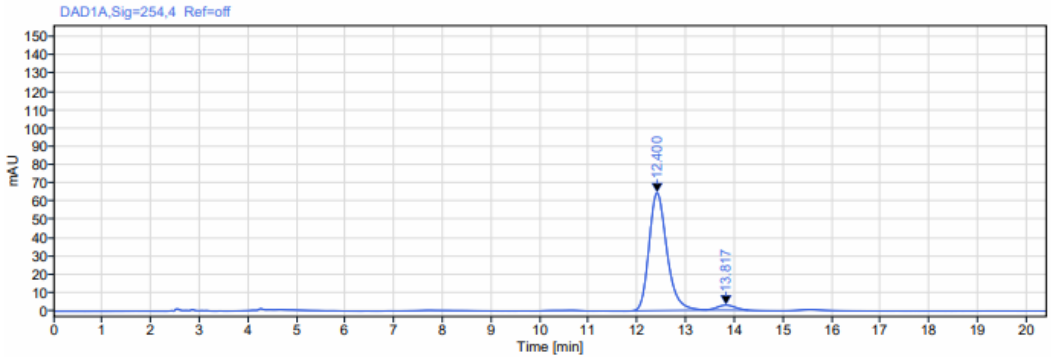



**3be** (26.9 mg, 67% yield, PE/EA=3:1, 92% *ee*, *Z/E* >20:1) was synthesized in method A afforded 67% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+17 (c=0.42, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33 – 7.25 (m, 2H), 7.24 – 7.16 (m, 2H), 7.16 – 7.08 (m, 2H), 6.98 – 6.78 (m, 2H), 5.69 (dd, *J* = 9.5, 7.3 Hz, 1H), 4.30 (dd, *J* = 57.1, 12.3 Hz, 2H), 3.71 (s, 3H), 3.54 (dd, *J* = 40.5, 11.6 Hz, 2H), 2.93 (s, 1H), 2.57 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 2.40 (s, 3H), 1.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.3 Hz), 144.1, 138.4, 137.5, 134.7 (d, *J* = 2.9 Hz), 130.1 (d, *J* = 8.1 Hz), 126.5, 126.5, 124.2, 115.4 (d, *J* = 21.3 Hz), 61.9, 59.6, 52.4, 48.2, 39.4, 21.5, 15.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}FNO_3S$ 404.1690; found:404.1715. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =12.40 min (major), 13.82 min (minor).



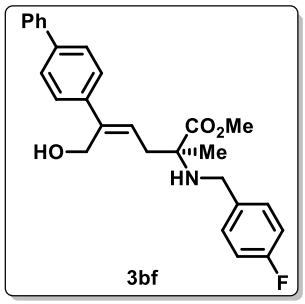

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 12.341 | MM m | 0.39 | 979.47 | 39.00 | 49.77 | |
| 13.775 | MM m | 0.43 | 988.45 | 35.30 | 50.23 | |
| | | Sum | 1967.93 | | | |

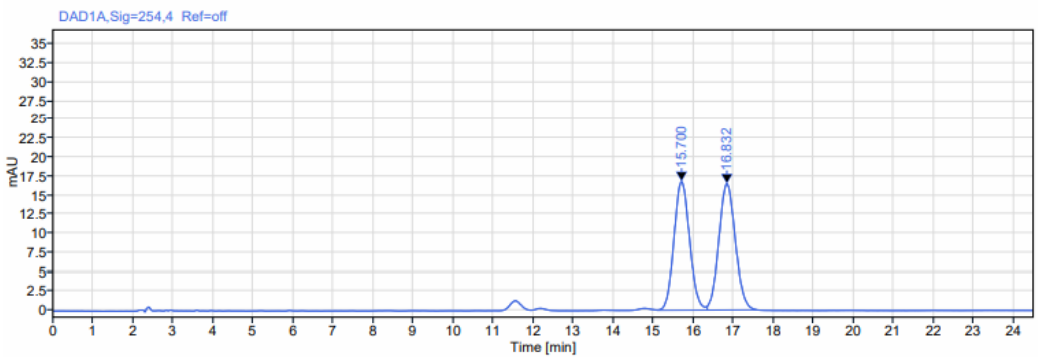



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 12.400 | MM m | 0.39 | 1646.70 | 64.47 | 95.88 | |
| 13.817 | MM m | 0.39 | 70.70 | 2.73 | 4.12 | |
| | | Sum | 1717.40 | | | |

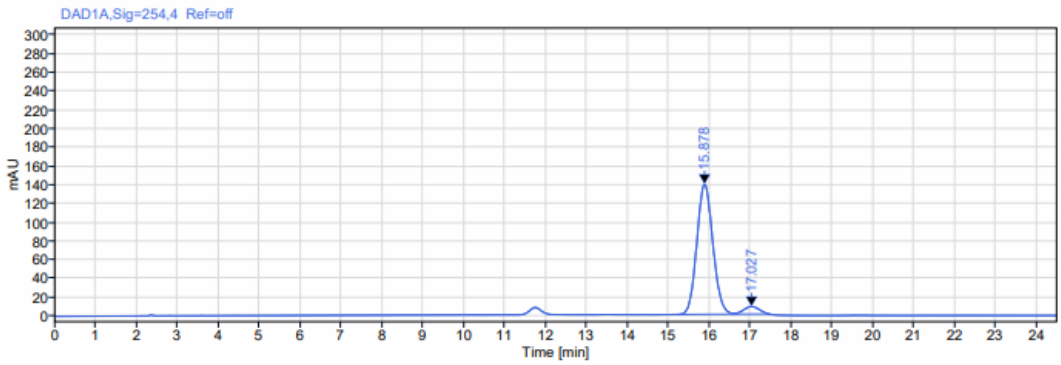



**3bf** (31.6 mg, 72% yield, PE/EA=3:1, 90% *ee*, *Z/E* >20:1) was synthesized in method A afforded 72% isolated yield as white solid. $[\alpha]_D^{25}$ =+9 (c=0.40, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.82 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.49 (m, 7H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.02 (t, *J* = 8.5 Hz, 2H), 5.87 (dd, *J* = 9.2, 7.5 Hz, 1H), 4.45 (dd, *J* = 55.9, 12.2 Hz, 2H), 3.80 (s, 3H), 3.64 (dd, *J* = 41.5, 11.5 Hz, 2H), 3.15 (bs, 1H), 2.70 (ddd, *J* = 21.1, 13.9, 8.5 Hz, 2H), 1.50 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.3 Hz), 144.3, 140.6, 140.5, 140.2, 137.5, 134.6 (d, *J* = 1.9 Hz), 132.4, 130.1 (d, *J* = 8.1 Hz), 130.0, 128.7, 128.2, 127.3, 127.1, 127.0, 126.5, 124.7, 115.5 (d, *J* = 21.4 Hz), 62.0, 59.7, 52.4, 48.3, 39.4, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{28}FNO_3$ 434.2126; found: 434.2153. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 15.88 min (major), 17.03 min (minor).



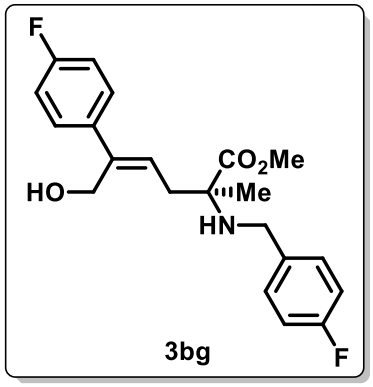

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 15.700 | MM m | 0.42 | 452.51 | 16.75 | 49.04 | |
| 16.832 | MM m | 0.45 | 470.25 | 16.42 | 50.96 | |
| | | Sum | 922.75 | | | |

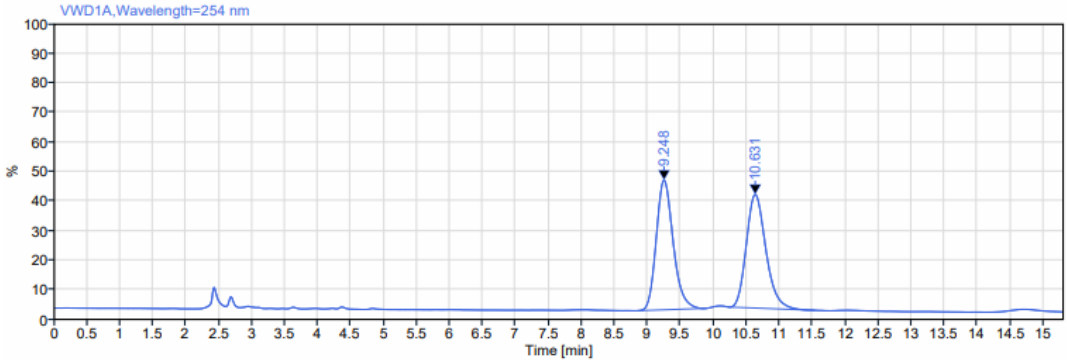



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 15.878 | MM m | 0.42 | 3787.94 | 138.80 | 94.77 | |
| 17.027 | MM m | 0.41 | 208.84 | 8.03 | 5.23 | |
| | | Sum | 3996.78 | | | |

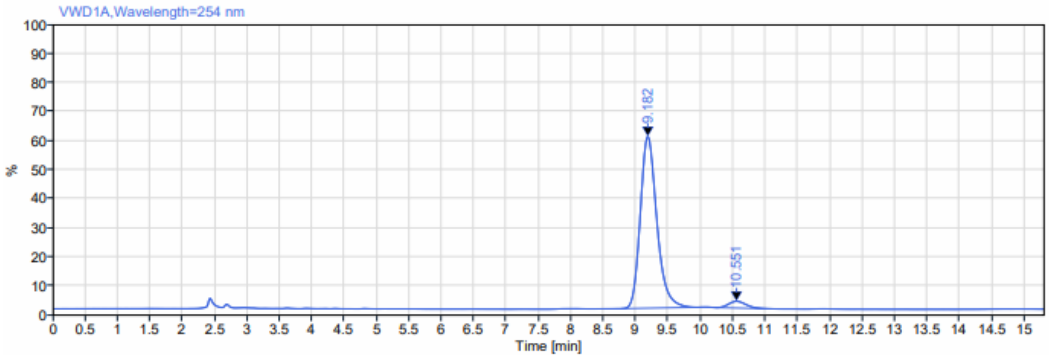



**3bg** (24.9 mg, 66% yield, PE/EA=3:1, 92% *ee*, *Z*/*E* >20:1) was synthesized in method A afforded 66% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+20 (c=0.50, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.43 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 7.07 – 6.93 (m, 4H), 5.72 (dd, *J* = 9.5, 7.3 Hz, 1H), 4.37 (dd, *J* = 62.0, 12.3 Hz, 2H), 3.79 (s, 3H), 3.63 (dd, *J* = 42.7, 11.3 Hz, 2H), 3.07 (bs, 1H), 2.65 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.48 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.3, 163.4 (d, *J* = 6.5 Hz), 161.0 (d, *J* = 5.7 Hz), 143.9, 137.7 (d, *J* = 3.0 Hz), 134.5 (d, *J* = 2.5 Hz), 130.2 (d, *J* = 8.1 Hz), 127.8 (d, *J* = 7.9 Hz), 124.5, 115.5 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.4 Hz), 62.0, 59.8, 52.5, 48.3, 39.2, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}F_2NO_3$ 376.1719; found: 376.1739. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 95:5, 25min; $t_R$ = 9.18 min (major), 10.55 min (minor).



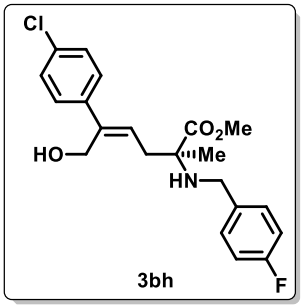

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.248 | MM m | 0.27 | 137.79 | 7.73 | 49.71 | |
| 10.631 | MM m | 0.32 | 139.41 | 6.77 | 50.29 | |
| | | Sum | 277.20 | | | |

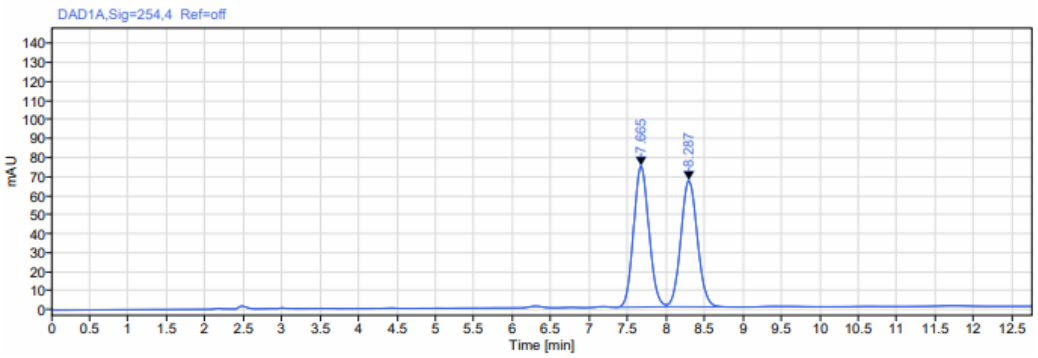



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.182 | MM m | 0.27 | 434.97 | 24.47 | 96.08 | |
| 10.551 | MM m | 0.29 | 17.73 | 0.96 | 3.92 | |
| | | Sum | 452.70 | | | |

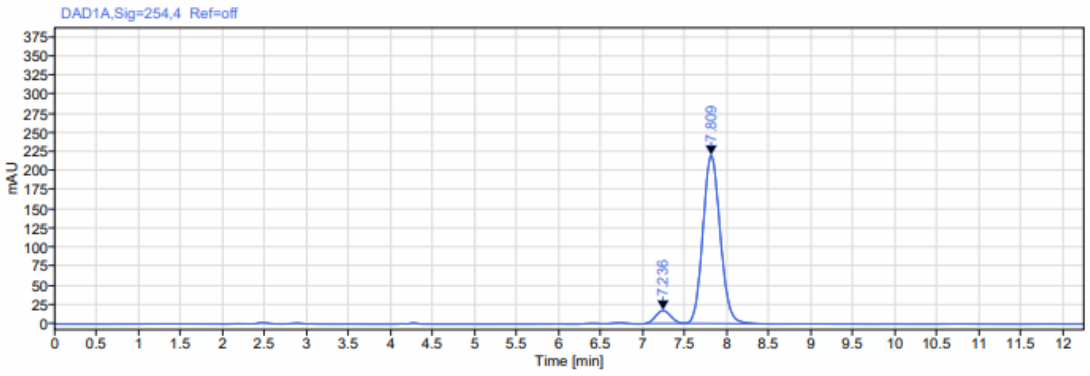



**3bh** (25.7 mg, 66% yield, PE/EA=3:1, 87% *ee*, *Z/E* >20:1) was synthesized in method A afforded 66% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+10 (c=0.51, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32 – 7.25 (m, 2H), 7.24 – 7.16 (m, 4H), 6.99 – 6.87 (m, 2H), 5.70 (dd, *J* = 9.4, 7.4 Hz, 1H), 4.28 (dd, *J* = 54.5, 12.3 Hz, 2H), 3.71 (s, 3H), 3.53 (dd, *J* = 38.1, 11.5 Hz, 2H), 2.80 (bs, 1H), 2.56 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.6 Hz), 143.6, 140.1, 134.7 (d, *J* = 3.2 Hz), 133.1, 130.1 (d, *J* = 8.1 Hz), 128.4, 127.4, 125.3, 115.45 (d, *J* = 21.3 Hz), 61.9, 59.6, 52.4, 48.2, 39.2, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}ClFNO_3$ 392.1423; found: 392.1448. HPLC conditions: OD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =7.24 min (major), 7.81 min (minor).



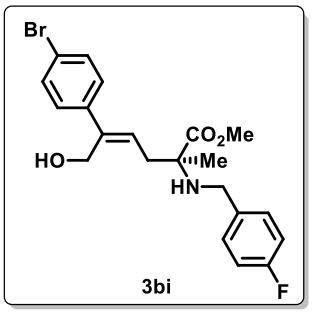

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.665 | MM m | 0.22 | 1027.87 | 74.07 | 50.86 | |
| 8.287 | MM m | 0.23 | 992.98 | 66.33 | 49.14 | |
| | | Sum | 2020.85 | | | |

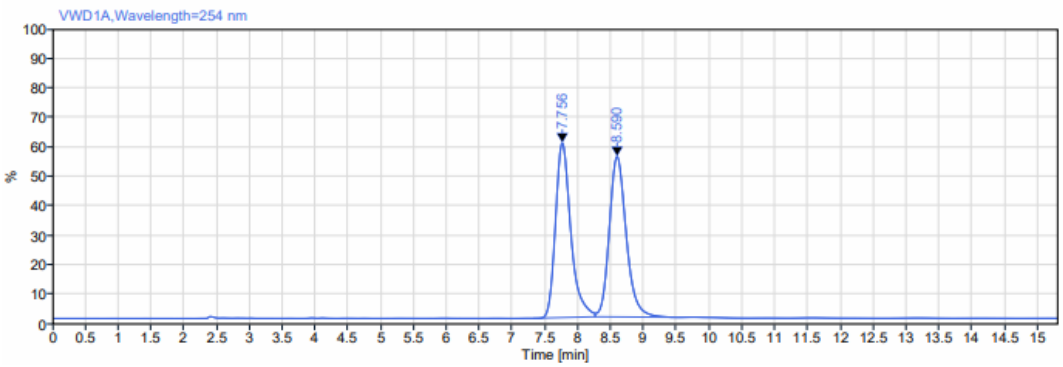



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.236 | MM m | 0.19 | 207.43 | 16.87 | 6.17 | |
| 7.809 | MM m | 0.22 | 3152.88 | 219.97 | 93.83 | |
| | | Sum | 3360.31 | | | |

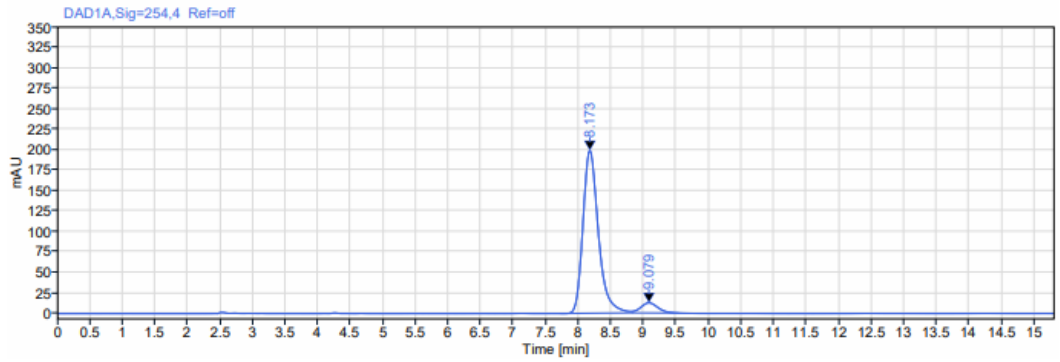



**3bi** (25.3 mg, 58% yield, PE/EA=3:1, 87% *ee*, *Z/E* >20:1) was synthesized in method A afforded 58% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+6 (c=0.51, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.45 – 7.40 (m, 2H), 7.34 – 7.23 (m, 4H), 7.06 – 6.93 (m, 2H), 5.77 (dd, *J* = 9.6, 7.3 Hz, 1H), 4.36 (dd, *J* = 62.4, 12.3 Hz, 2H), 3.79 (s, 3H), 3.63 (dd, *J* = 43.0, 11.5 Hz, 2H), 2.65 (ddd, *J* = 21.2, 13.9, 8.6 Hz, 2H), 2.12 (bs, 1H), 1.48 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.2, 162.2 (d, *J* = 245.6 Hz), 143.9, 140.6, 134.3 (d, *J* = 5.2 Hz), 131.4, 130.2 (d, *J* = 8.0 Hz), 127.8, 125.2, 121.3, 115.5 (d, *J* = 21.3 Hz), 62.0, 59.5, 52.5, 48.3, 39.2, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}BrFNO_3$ 436.0918; found: 436.0944. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =8.17 min (major), 9.08 min (minor).



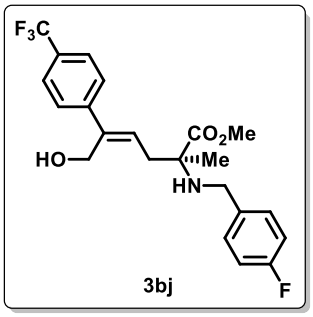

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.756 | MM m | 0.25 | 1232.14 | 76.10 | 49.54 | |
| 8.590 | MM m | 0.27 | 1255.12 | 69.89 | 50.46 | |
| | | Sum | 2487.26 | | | |

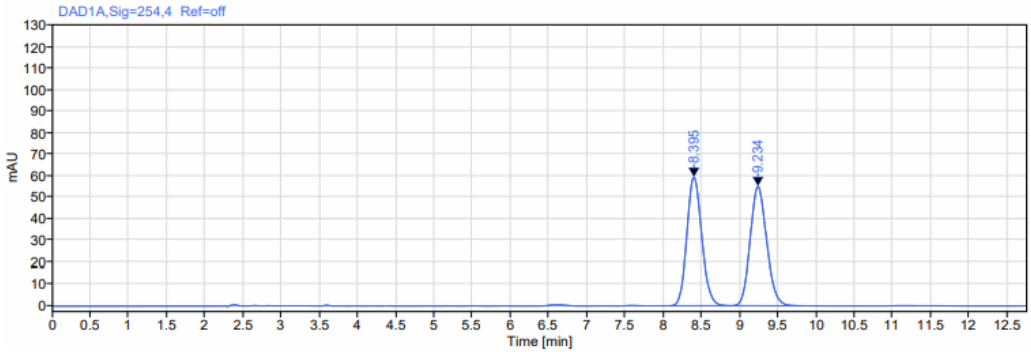



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 8.173 | MM m | 0.25 | 3271.08 | 198.84 | 93.58 | |
| 9.079 | MM m | 0.28 | 224.33 | 12.33 | 6.42 | |
| | | Sum | 3495.41 | | | |

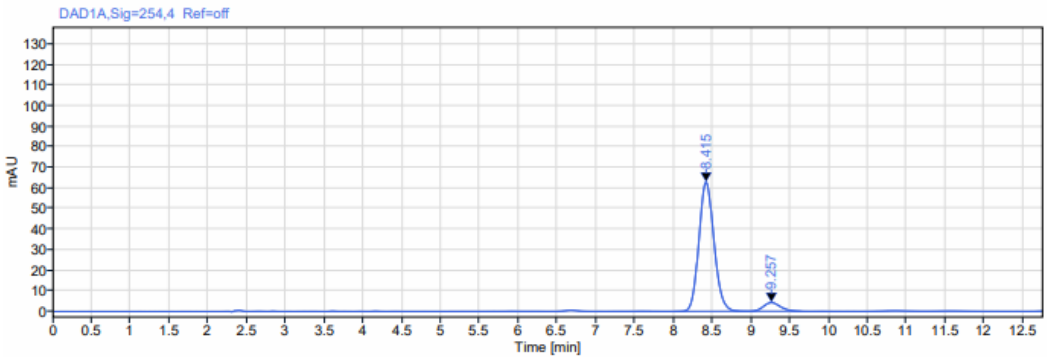



**3bj** (29.9 mg, 70% yield, PE/EA=3:1, 86% *ee*, *Z/E* >20:1) was synthesized in method A afforded 70% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+17 (c=0.30, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.58 – 7.50 (m, 4H), 7.32 – 7.26 (m, 2H), 7.05 – 6.97 (m, 2H), 5.86 (dd, *J* = 9.4, 7.4 Hz, 1H), 4.39 (dd, *J* = 58.0, 12.3 Hz, 2H), 3.79 (s, 3H), 3.62 (dd, *J* = 40.7, 11.5 Hz, 2H), 2.75 (bs, 1H), 2.68 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.48 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.2, 162.2 (d, *J* = 245.7 Hz), 145.2, 143.9, 134.4 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 8.1 Hz), 129.3 (q, *J* = 32.5 Hz), 126.8, 126.4, 125.3 (q, *J* = 7.4, 3.7 Hz), 124.2 (q, *J* = 270.3 Hz), 115.5 (d, *J* = 21.3 Hz), 62.0, 59.5, 52.5, 48.3, 39.2, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}F_4NO_3$ 426.1687; found: 426.1713. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 8.42 min (major), 9.26 min (minor).



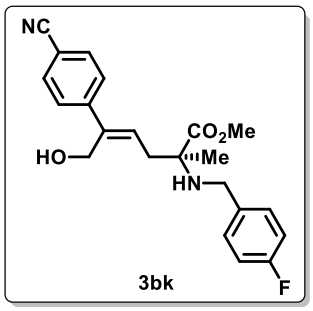

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 8.395 | MM m | 0.21 | 802.56 | 59.25 | 49.32 | |
| 9.234 | MM m | 0.23 | 824.79 | 54.95 | 50.68 | |
| | | Sum | 1627.34 | | | |

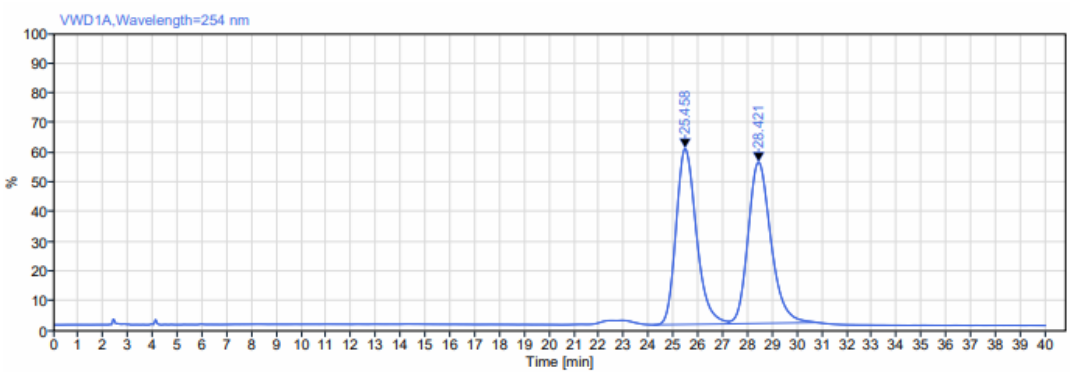



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 8.415 | MM m | 0.21 | 853.45 | 62.93 | 93.05 | |
| 9.257 | MM m | 0.23 | 63.78 | 4.23 | 6.95 | |
| | | Sum | 917.23 | | | |

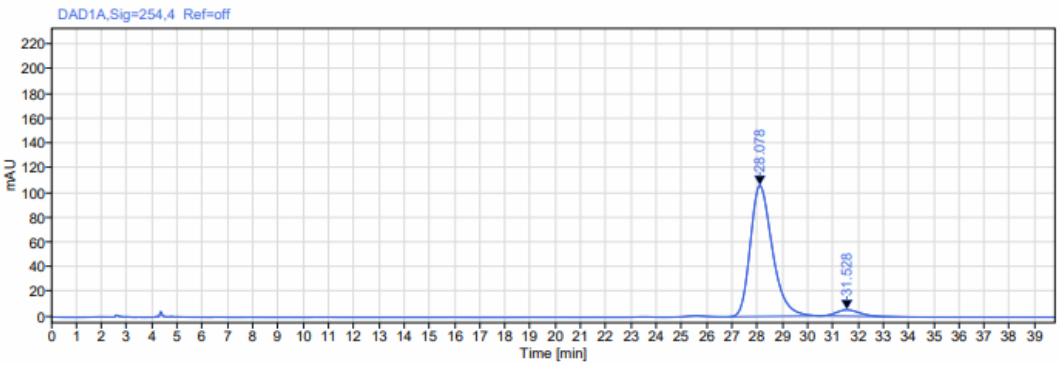



**3bk** (16.7 mg, 44% yield, PE/EA=3:1, 90% *ee*, *Z/E* >20:1) was synthesized in method A afforded 44% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+11 (c=0.29, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55 – 7.50 (m, 2H), 7.48 – 7.43 (m, 2H), 7.23 – 7.16 (m, 2H), 7.00 – 6.89 (m, 2H), 5.83 (dd, *J* = 9.1, 7.8 Hz, 1H), 4.29 (dd, *J* = 51.7, 12.3 Hz, 2H), 3.73 (s, 3H), 3.55 (dd, *J* = 37.5, 11.5 Hz, 2H), 2.87 (s, 1H), 2.60 (ddd, *J* = 21.3, 13.9, 8.5 Hz, 2H), 1.41 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.2, 162.1 (d, *J* = 245.8 Hz), 146.2, 143.5, 134.3 (d, *J* = 2.9 Hz), 132.2, 130.1 (d, *J* = 8.1 Hz), 127.8, 126.7, 118.9, 115.6, 115.4, 110.7, 61.9, 59.2, 52.6, 48.3, 39.1, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}FN_2O_3$ 383.1765; found: 383.1801. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 40 min; $t_R$ =28.08 min (major), 31.53 min (minor).



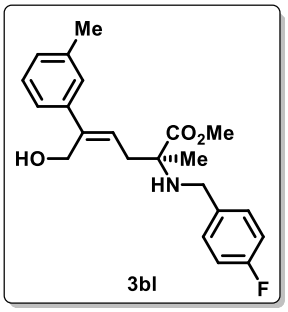

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 25.458 | MM m | 0.88 | 1470.99 | 25.78 | 49.28 | |
| 28.421 | MM m | 0.97 | 1514.00 | 23.61 | 50.72 | |
| | | Sum | 2984.99 | | | |

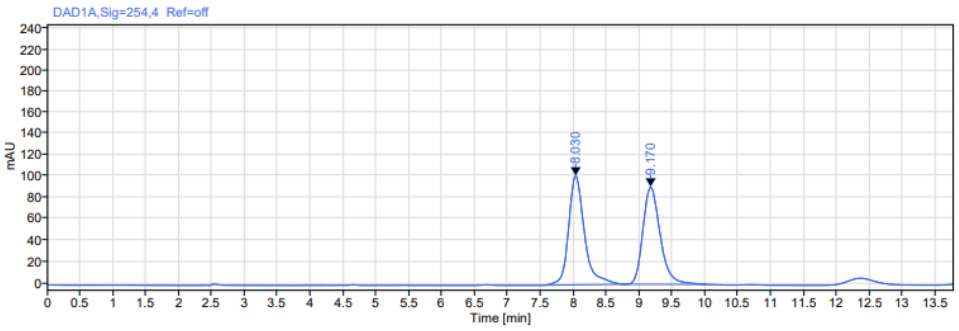



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 28.078 | MM m | 0.92 | 6423.80 | 105.77 | 95.25 | |
| 31.528 | MM m | 0.83 | 320.53 | 5.05 | 4.75 | |
| | | Sum | 6744.33 | | | |

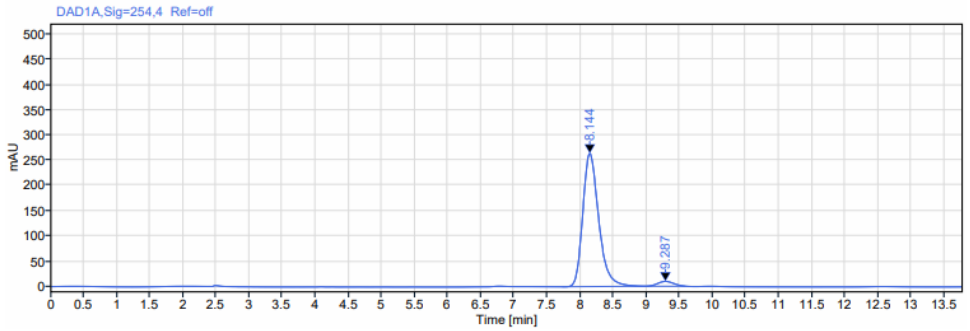



**3bl** (25.6 mg, 69% yield, PE/EA=3:1, 93% *ee*, *Z*/*E* >20:1) was synthesized in method A afforded 69% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+18 (c=0.27, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33 – 7.27 (m, 2H), 7.25 (s, 1H), 7.23 – 7.19 (m, 2H), 7.10 – 7.07 (m, 1H), 7.03 – 6.98 (m, 2H), 5.77 (dd, *J* = 9.6, 7.3 Hz, 1H), 4.40 (dd, *J* = 57.6, 12.3 Hz, 2H), 3.78 (s, 3H), 3.63 (dd, *J* = 41.1, 11.5 Hz, 2H), 3.13 (bs, 1H), 2.66 (ddd, *J* = 21.1, 13.9, 8.5 Hz, 2H), 2.35 (s, 3H), 1.45 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.5 Hz), 144.9, 141.6, 138.0, 134.7 (d, *J* = 2.5 Hz), 130.1 (d, *J* = 8.1 Hz), 128.3, 128.1, 126.9, 124.5, 123.2, 115.4 (d, *J* = 21.4 Hz), 61.9, 59.9, 52.4, 48.2, 39.4, 21.6, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}FNO_3$ 372.1969; found:372.1991. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 8.14 min (major), 9.28 min (minor).



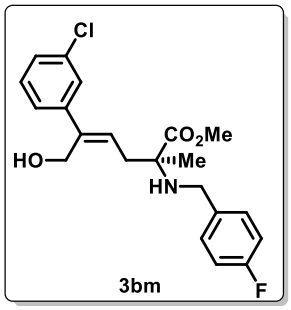

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 8.030 | MM m | 0.25 | 1699.69 | 101.13 | 50.72 | |
| 9.170 | MM m | 0.28 | 1651.39 | 90.16 | 49.28 | |
| | | Sum | 3351.08 | | | |

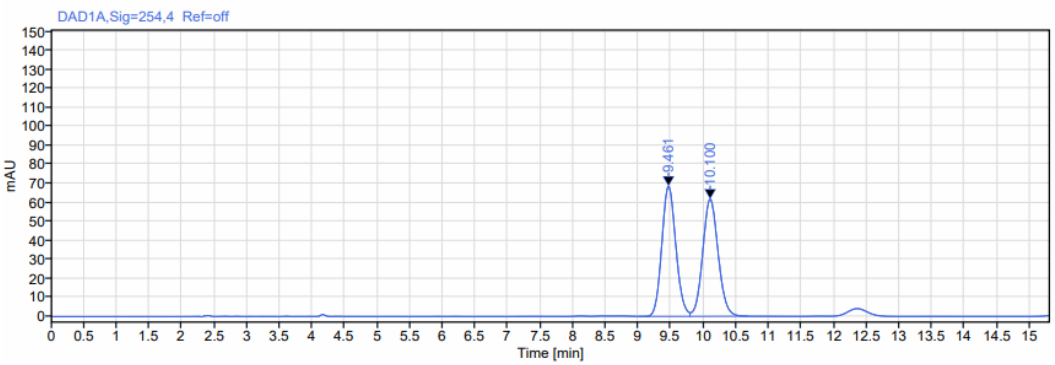



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 8.144 | MM m | 0.26 | 4381.10 | 262.63 | 96.42 | |
| 9.287 | MM m | 0.27 | 162.48 | 9.61 | 3.58 | |
| | | Sum | 4543.58 | | | |

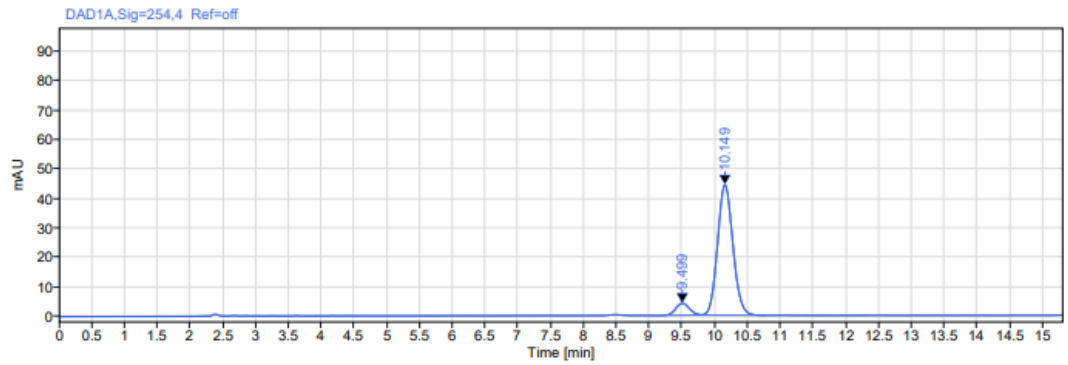



**3bm** (30.4 mg, 78% yield, PE/EA=3:1, 85% *ee*, *Z/E* >20:1) was synthesized in method A afforded 78% isolated yield as a colorless oil. $[\alpha]_D^{25}$=+15 (c=0.38, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36 – 7.31 (m, 1H), 7.25 – 7.14 (m, 6H), 6.98 – 6.88 (m, 2H), 5.73 (dd, *J* = 9.3, 7.5 Hz, 1H), 4.29 (dd, *J* = 54.7, 12.3 Hz, 2H), 3.72 (s, 3H), 3.55 (dd, *J* = 39.3, 11.5 Hz, 2H), 2.81 (bs, *J* = 76.5 Hz, 1H), 2.58 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 3H), 1.40 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.1, 162.2 (d, *J* = 245.6 Hz), 143.7, 143.5, 134.35 (d, *J* = 3.0 Hz), 134.3, 130.2 (d, *J* = 8.1 Hz), 129.6, 127.3, 126.3, 125.8, 124.4, 115.5 (d, *J* = 21.3 Hz), 62.1, 59.5, 52.5, 48.2, 39.0, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}ClFNO_3$ 382.1423; found: 382.1447. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 9.50 min (minor), 10.15 min (major).



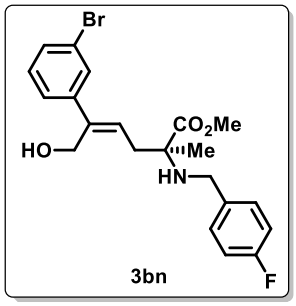

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.461 | MM m | 0.23 | 1026.98 | 68.56 | 50.25 | |
| 10.100 | MM m | 0.25 | 1016.68 | 61.73 | 49.75 | |
| | | Sum | 2043.66 | | | |

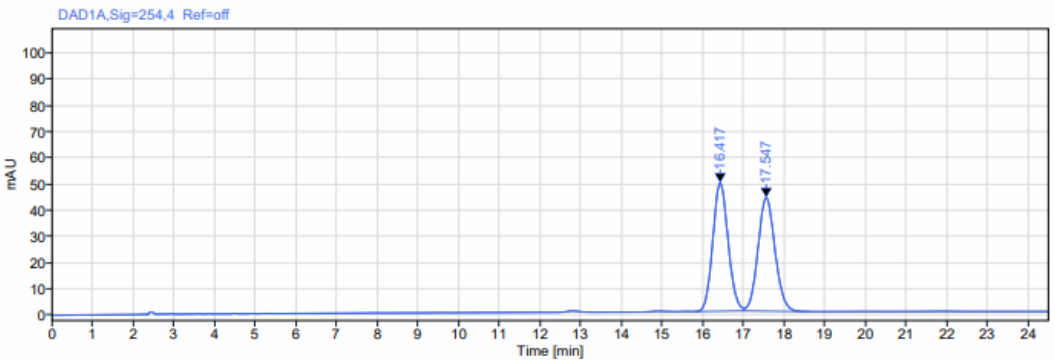



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.499 | MM m | 0.23 | 59.39 | 4.09 | 7.60 | |
| 10.149 | MM m | 0.25 | 721.69 | 44.31 | 92.40 | |
| | | Sum | 781.08 | | | |

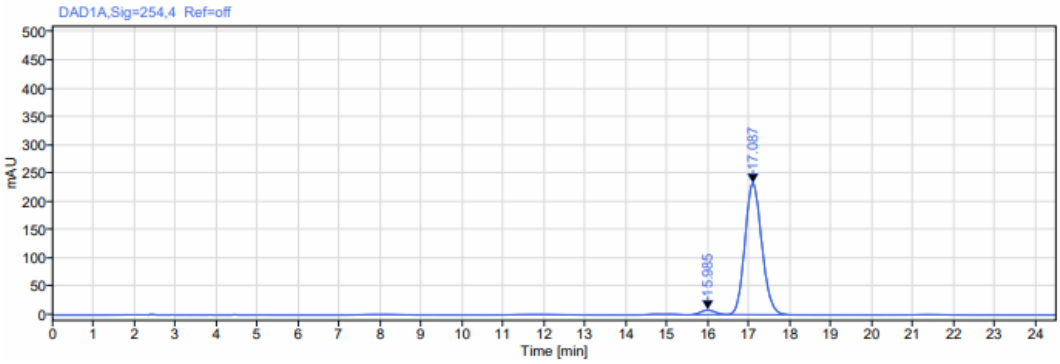



**3bn** (30.3 mg, 70% yield, PE/EA=3:1, 94% *ee*, *Z/E* >20:1) was synthesized in method A afforded 70% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+23 (c=0.28, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.59 – 7.53 (m, 1H), 7.40 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.20 – 7.15 (m, 1H), 7.06 – 6.97 (m, 2H), 5.79 (dd, *J* = 9.5, 7.4 Hz, 1H), 4.35 (dd, *J* = 55.8, 12.3 Hz, 2H), 3.79 (s, 3H), 3.62 (dd, *J* = 39.7, 11.6 Hz, 2H), 2.95 (bs, 1H), 2.65 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.47 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.3, 162.1 (d, *J* = 245.6 Hz), 143.9, 143.7, 134.5 (d, *J* = 1.9 Hz), 130.2 (d, *J* = 6.0 Hz), 130.1, 129.9, 129.2, 126.0, 124.8, 122.5, 115.5 (d, *J* = 21.3 Hz), 62.0, 59.6, 52.5, 48.3, 39.2, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}BrFNO_3$ 436.0918; found: 436.0945. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 95:5, 25min; $t_R$ =15.99 min (minor), 17.09 min (major).



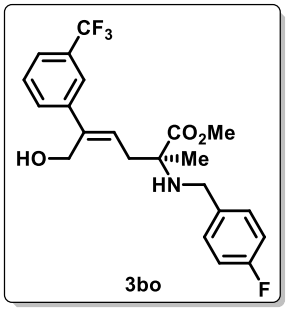

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 16.417 | MM m | 0.40 | 1279.05 | 48.94 | 50.37 | |
| 17.547 | MM m | 0.45 | 1260.11 | 43.26 | 49.63 | |
| | | Sum | 2539.16 | | | |

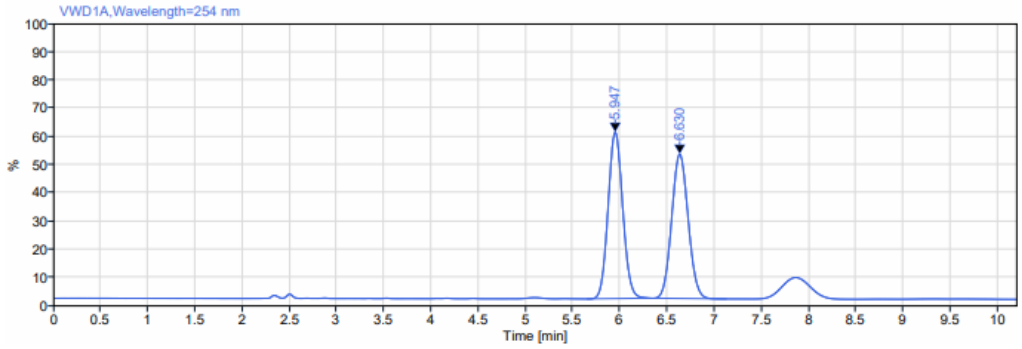



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 15.985 | MM m | 0.39 | 198.50 | 8.13 | 2.89 | |
| 17.087 | MM m | 0.45 | 6675.00 | 231.81 | 97.11 | |
| | | Sum | 6873.49 | | | |

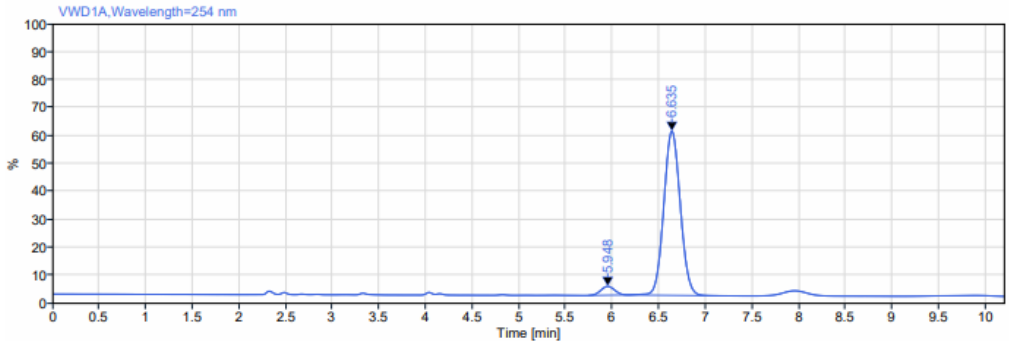



**3bo** (22.7 mg, 53% yield, PE/EA=3:1, 91% *ee*, *Z/E* >20:1) was synthesized in method A afforded 53% isolated yield as a colorless oil. $[\alpha]_D^{25}$=+10 (c=0.45, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.58 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.39 – 7.32 (m, 1H), 7.24 – 7.18 (m, 2H), 6.99 – 6.89 (m, 2H), 5.77 (dd, *J* = 9.4, 7.4 Hz, 1H), 4.32 (dd, *J* = 56.1, 12.3 Hz, 2H), 3.73 (s, 3H), 3.56 (dd, *J* = 40.1, 11.6 Hz, 2H), 2.89 (bs, 1H), 2.60 (ddd, *J* = 21.3, 13.9, 8.5 Hz, 2H), 1.41 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.3, 162.2 (d, *J* = 245.6 Hz), 143.8, 142.5, 134.5 (d, *J* = 2.6 Hz), 130.7 (q, *J* = 64.3, 32.3 Hz), 130.1 (d, *J* = 8.1 Hz), 129.5, 128.8, 126.4, 124.1 (q, *J* = 270.8 Hz), 123.9 (q, *J* = 3.6 Hz), 122.9 (q, *J* = 3.7 Hz), 115.5 (d, *J* = 21.3 Hz), 62.0, 59.6, 52.5, 48.3, 39.2, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}F_4NO_3$ 426.1687; found: 426.1712. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 5.95 min (minor), 6.64 min (major).



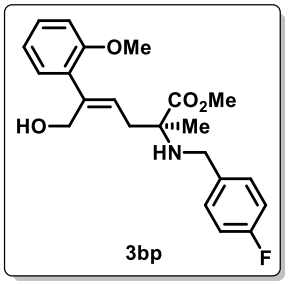

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 5.947 | MM m | 0.17 | 300.49 | 27.91 | 50.54 | |
| 6.630 | MM m | 0.19 | 294.12 | 24.21 | 49.46 | |
| | | Sum | 594.61 | | | |

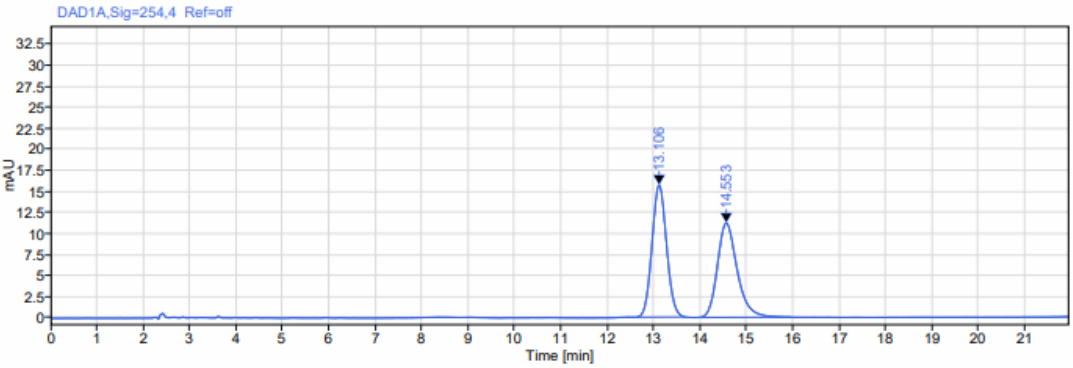



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 5.948 | MM m | 0.16 | 15.71 | 1.53 | 4.30 | |
| 6.635 | MM m | 0.19 | 349.57 | 28.40 | 95.70 | |
| | | Sum | 365.28 | | | |

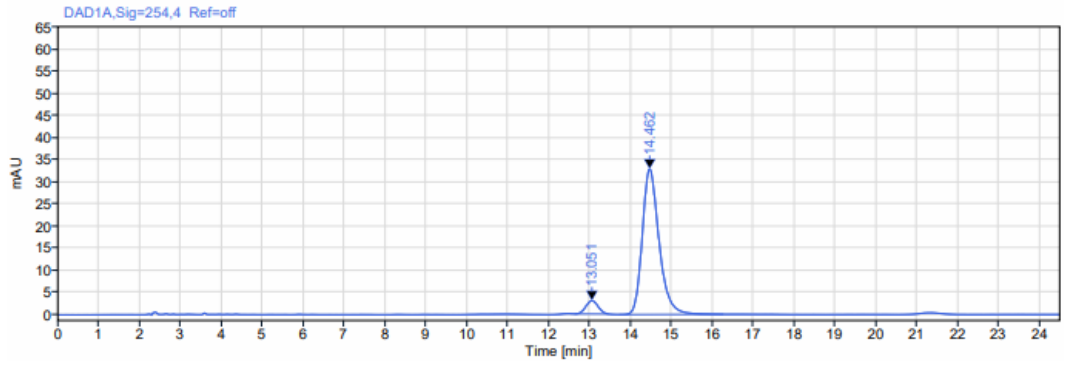



**3bp** (21.6 mg, 56% yield, PE/EA=3:1, 88% *ee*, *Z/E* >20:1) was synthesized in method A afforded 56% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+16 (c=0.43, $CHCl_3$).**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29 – 7.21 (m, 2H), 7.20 – 7.13 (m, 1H), 7.0 – 6.99 (m, 1H), 6.97 – 6.89 (m, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.50 (dd, *J* = 9.0, 7.1 Hz, 1H), 4.25 (dd, *J* = 44.8, 12.4 Hz, 2H), 3.69 (s, 3H), 3.65 (s, 3H), 3.60 (dd, 2H), 2.70 (bs, 1H), 2.63 (ddd, *J* = 21.2, 14.2, 8.1 Hz, 2H), 1.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.0 (d, *J* = 244.9 Hz), 156.2, 143.2, 135.4 (d, *J* = 3.0 Hz), 131.9, 130.1, 129.9 (d, *J* = 8.0 Hz), 128.6, 127.1, 120.8, 115.2 (d, *J* = 21.2 Hz), 110.4, 61.8, 61.0, 55.3, 52.2, 47.9, 38.3, 21.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}FNO_4$ 388.1919; found: 388.1940. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 13.05 min (minor), 14.46 min (major).



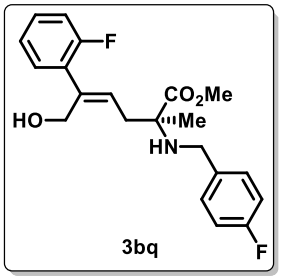

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 13.106 | MM m | 0.34 | 341.05 | 15.69 | 50.68 | |
| 14.553 | MM m | 0.45 | 331.91 | 11.21 | 49.32 | |
| | | Sum | 672.96 | | | |

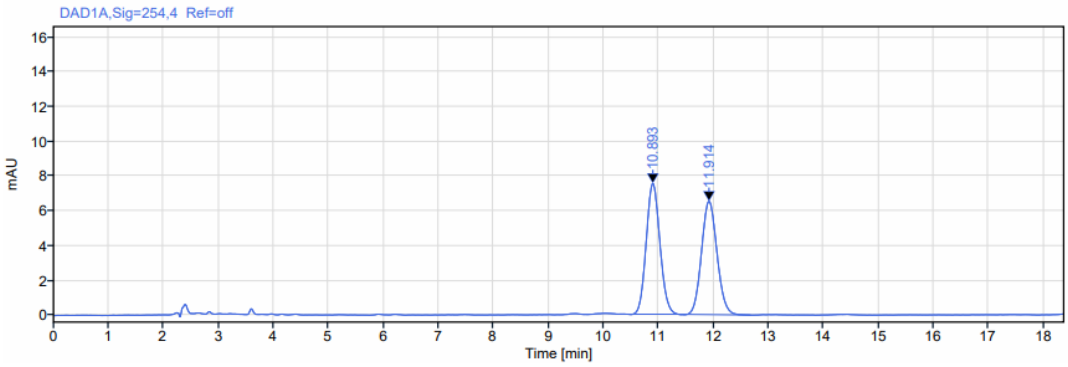



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 13.051 | MM m | 0.32 | 62.27 | 3.00 | 6.21 | |
| 14.462 | MM m | 0.43 | 940.11 | 32.94 | 93.79 | |
| | | Sum | 1002.37 | | | |

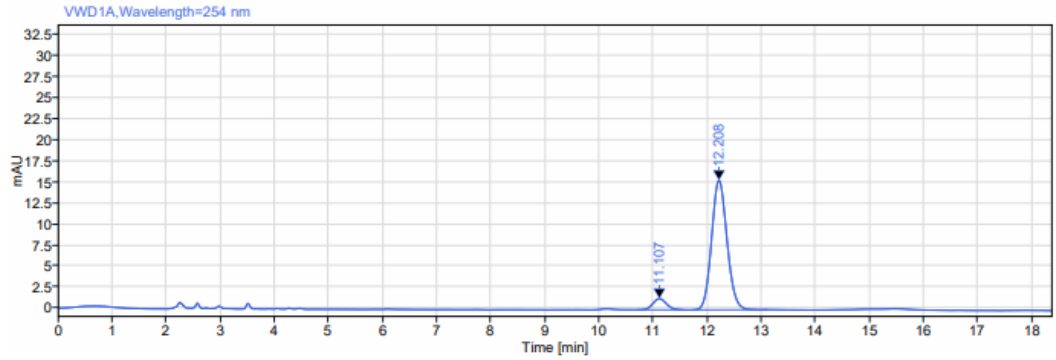



**3bq** (22.8 mg, 61% yield, PE/EA=3:1, 86% *ee*, *Z/E* >20:1) was synthesized in method A afforded 61% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+23 (c=0.46, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.27 – 7.12 (m, 5H), 7.04 – 6.99 (m, 1H), 6.98 – 6.91 (m, 3H), 5.64 (dd, *J* = 9.4, 7.2 Hz, 1H), 4.30 (dd, *J* = 62.7, 12.6 Hz, 2H), 3.71 (s, 3H), 3.57 (dd, *J* = 36.5, 11.6 Hz, 2H), 2.74 (bs, 1H), 2.62 (ddd, *J* = 21.2, 14.0, 8.3 Hz, 2H), 1.41 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.2, 163.3, 159.6 (d, *J* = 246.0 Hz), 140.1 (d, *J* = 0.8 Hz), 134.8 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 3.8 Hz), 130.0 (d, *J* = 8.1 Hz), 129.7 (d, *J* = 14.4 Hz), 128.9 (d, *J* = 8.3 Hz), 128.2 (d, *J* = 2.5 Hz), 124.1 (d, *J* = 3.4 Hz), 115.7, 115.4 (d, *J* = 21.2 Hz), 61.8, 60.5, 52.4, 48.1, 38.8, 21.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}F_2NO_3$ 376.1719; found: 376.1741. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 10.99 min (minor), 12.02 min (major).



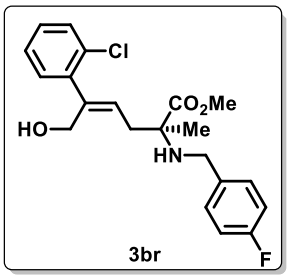

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.893 | MM m | 0.27 | 130.10 | 7.51 | 50.51 | |
| 11.914 | MM m | 0.30 | 127.46 | 6.51 | 49.49 | |
| | | Sum | 257.56 | | | |

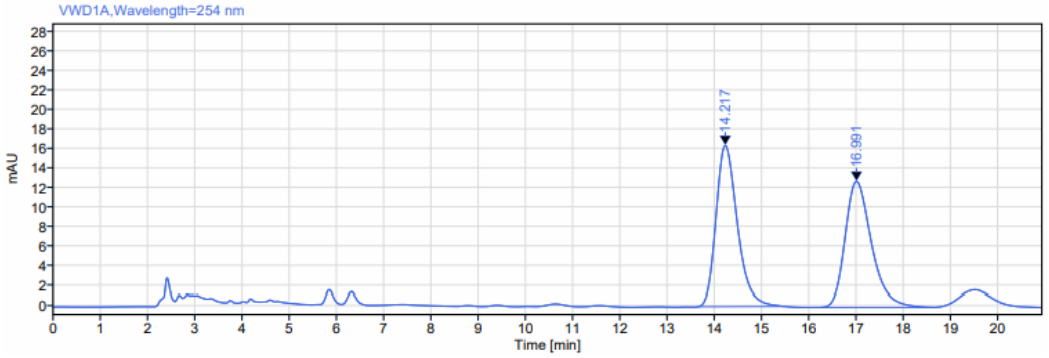



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 11.107 | MM m | 0.27 | 23.00 | 1.33 | 7.03 | |
| 12.208 | MM m | 0.31 | 304.13 | 15.40 | 92.97 | |
| | | Sum | 327.13 | | | |

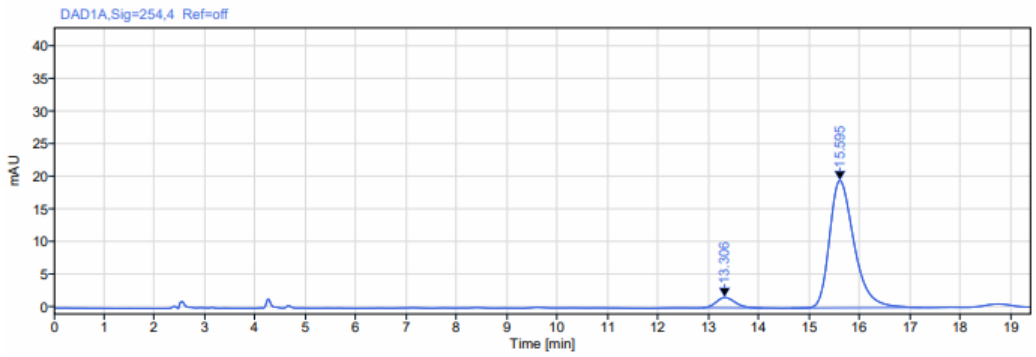



**3br** (33.5 mg, 86% yield, PE/EA=3:1, 88% *ee*, *Z/E* >20:1) was synthesized in method A afforded 86% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+16 (c=0.53, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36 – 7.30 (m, 3H), 7.21 – 7.15 (m, 2H), 7.15 – 7.09 (m, 1H), 7.06 – 6.97 (m, 2H), 5.46 (dd, *J* = 9.7, 7.1 Hz, 1H), 4.33 (dd, *J* = 82.0, 13.1 Hz, 2H), 3.78 (s, 3H), 3.74 – 3.59 (m, 2H), 2.74 (ddd, *J* = 20.6, 13.6, 9.1 Hz, 2H), 1.51 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.5 Hz), 143.6, 143.5, 134.6 (d, *J* = 3.3 Hz), 134.2, 130.1 (d, *J* = 8.1 Hz), 129.6, 127,3, 126.3, 126.0, 124.3, 115.5 (d, *J* = 21.3 Hz), 61.9, 59.6, 52.5, 48.3, 39.2, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}ClFNO_3$ 392.1423; found: 392.1447. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 13.31 min (minor), 15.60 min (major).



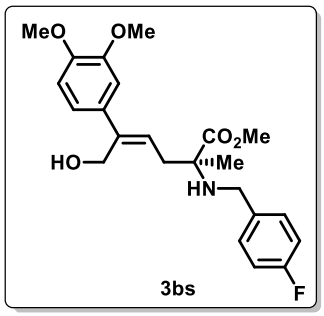

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 14.217 | MM m | 0.48 | 511.76 | 16.39 | 50.98 | |
| 16.991 | MM m | 0.58 | 492.07 | 12.80 | 49.02 | |
| | | Sum | 1003.83 | | | |

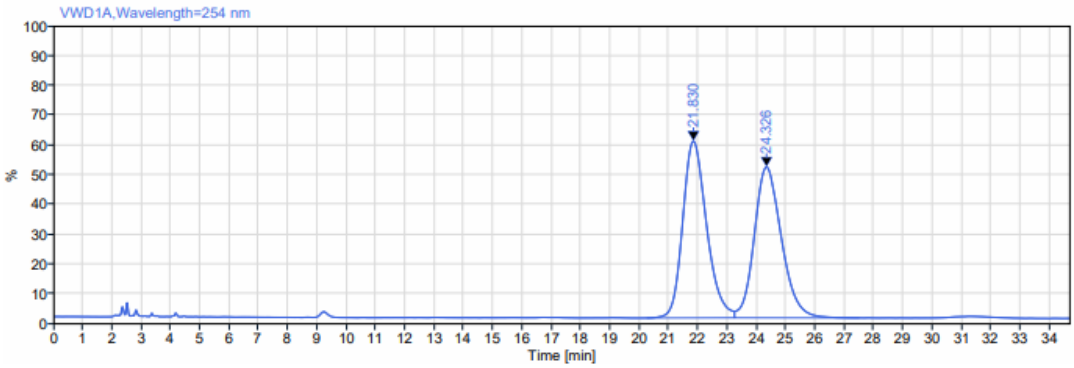



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 13.306 | MM m | 0.38 | 41.50 | 1.59 | 5.91 | |
| 15.595 | MM m | 0.52 | 660.63 | 19.45 | 94.09 | |
| | | Sum | 702.13 | | | |

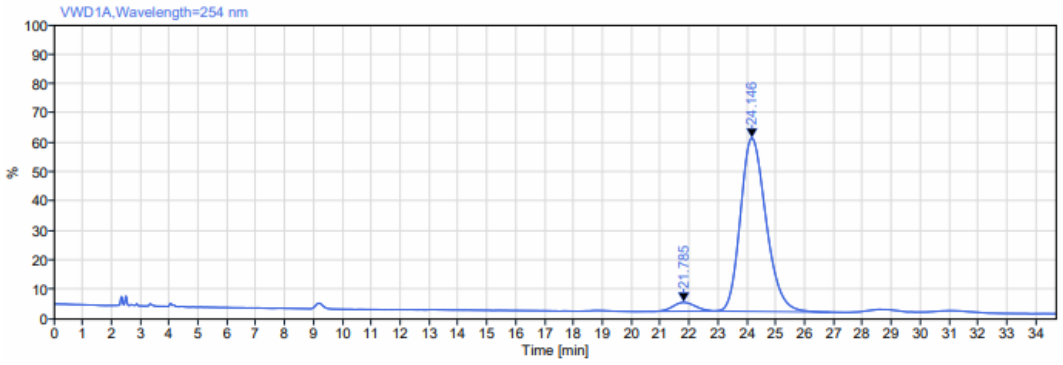



**3bs** (29.4 mg, 72% yield, PE/EA=3:1, 92% *ee*, *Z*/*E* >20:1) was synthesized in method A afforded 72% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+9 (c=0.46, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.21 (d, $J$ = 7.8 Hz, 2H), 7.07 – 6.81 (m, 4H), 6.74 (d, $J$ = 7.8 Hz, 1H), 5.64 (dd, $J$ = 11.1, 4.5 Hz, 1H), 4.31 (dd, $J$ = 56.6, 12.0 Hz, 2H), 3.80 (s, 6H), 3.71 (s, 3H), 3.55 (dd, $J$ = 39.4, 11.5 Hz, 2H), 2.61 (bs, 1H), 2.70 – 2.46 (m, 2H), 1.40 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, $J$ = 245.5 Hz), 148.7, 148.5, 144.4, 134.8 (d, $J$ = 2.7 Hz), 134.7, 130.1 (d, $J$ = 8.0 Hz), 123.4, 118.5, 115.4 (d, $J$ = 21.3 Hz), 110.9, 109.4, 62.0, 59.9, 55.9, 55.8, 52.4, 48.2, 39.4, 21.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{28}FNO_5$ 418.2024; found: 418.2048. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 30min; $t_R$ = 21.79 min (minor), 24.15 min (major).



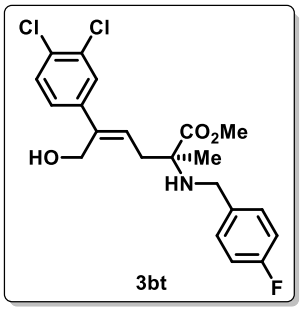

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 21.830 | MM m | 0.86 | 889.70 | 15.70 | 50.73 | |
| 24.326 | MM m | 0.92 | 864.06 | 13.39 | 49.27 | |
| | | Sum | 1753.76 | | | |

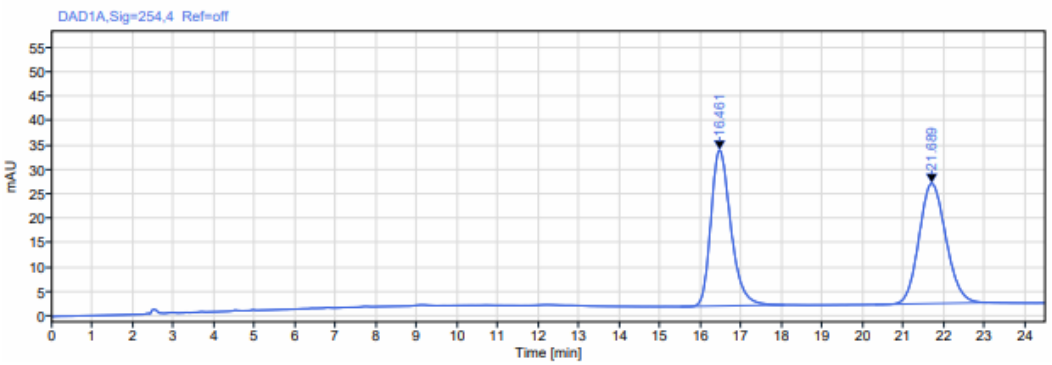



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 21.785 | MM m | 0.63 | 29.35 | 0.55 | 4.19 | |
| 24.146 | MM m | 0.93 | 671.08 | 10.88 | 95.81 | |
| | | Sum | 700.43 | | | |

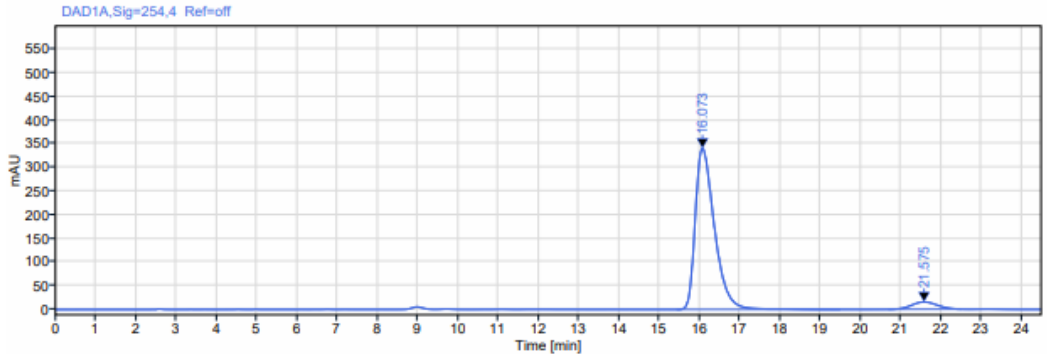



**3bt** (26.7 mg, 63% yield, PE/EA=3:1, 89% *ee*, *Z/E* >20:1) was synthesized in method A afforded 63% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+7 (c=0.53, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.44 (d, $J$ = 2.0 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.23 – 7.18 (m, 3H), 7.00 – 6.88 (m, 2H), 5.74 (dd, $J$ = 9.3, 7.5 Hz, 1H), 4.26 (dd, $J$ = 52.5, 12.3 Hz, 2H), 3.72 (s, 3H), 3.54 (dd, $J$ = 38.8, 11.5 Hz, 2H), 3.02 (bs, 1H), 2.57 (ddd, $J$ = 21.3, 13.9, 8.5 Hz, 2H), 1.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.3, 162.1 (d, $J$ = 245.6 Hz), 142.8, 141.7, 134.5 (d, $J$ = 2.7 Hz), 132.4, 131.1, 130.2 (d, $J$ = 4.9 Hz), 130.1, 128.0, 126.3, 125.5, 115.5 (d, $J$ = 21.4 Hz), 61.9, 59.3, 52.5, 48.3, 39.1, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{22}Cl_2FNO_3$ 426.1034; found: 426.1058. HPLC conditions: OJ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 16.07 min (major), 21.58 min (minor).



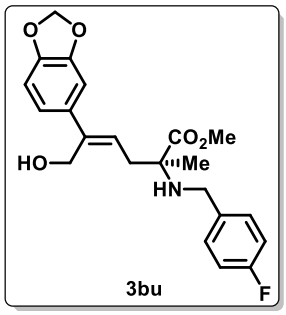

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 16.461 | MM m | 0.52 | 1087.82 | 31.84 | 49.01 | |
| 21.689 | MM m | 0.71 | 1131.73 | 24.56 | 50.99 | |
| | | Sum | 2219.55 | | | |

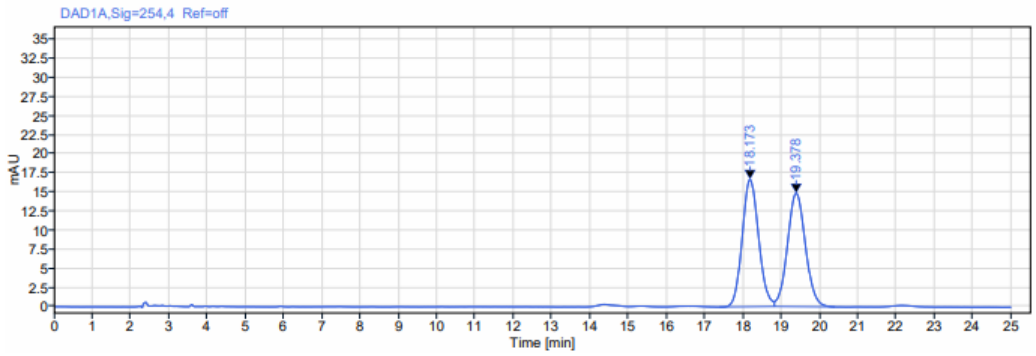



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 16.073 | MM m | 0.51 | 11279.23 | 340.42 | 94.29 | |
| 21.575 | MM m | 0.68 | 683.38 | 15.45 | 5.71 | |
| | | Sum | 11962.61 | | | |

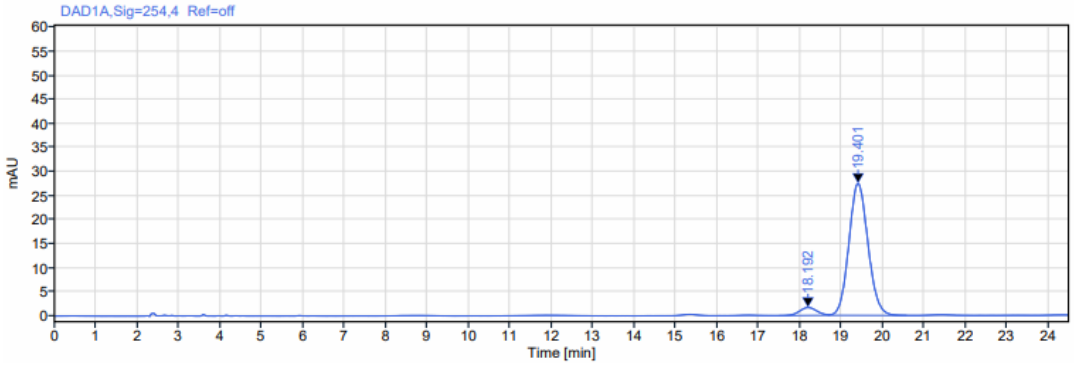



**3bu** (17.6 mg, 44% yield, PE/EA=3:1, 90% *ee*, *Z/E* >20:1) was synthesized in method A afforded 44% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+20 (c=0.30, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31 – 7.26 (m, 2H), 7.05 – 6.95 (m, 2H), 6.94 – 6.87 (m, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 2H), 5.68 (dd, *J* = 9.5, 7.3 Hz, 1H), 4.35 (dd, *J* = 56.5, 12.3 Hz, 2H), 3.78 (s, 3H), 3.62 (dd, *J* = 41.3, 11.6 Hz, 2H), 2.65 (bs, 1H), 2.62 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.46 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.4 Hz), 147.7, 146.9, 144.3, 135.9, 134.7 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 8.1 Hz), 123.6, 119.7, 115.5 (d, *J* = 21.3 Hz), 108.1, 106.8, 101.0, 62.0, 59.9, 52.4, 48.3, 39.3, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}FNO_5$ 402.1711; found: 402.1733. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 18.19 min (minor), 19.40 min (major).



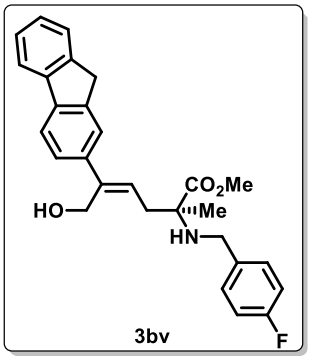

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 18.173 | MM m | 0.46 | 496.75 | 16.67 | 50.59 | |
| 19.378 | MM m | 0.51 | 485.14 | 14.85 | 49.41 | |
| | | Sum | 981.89 | | | |

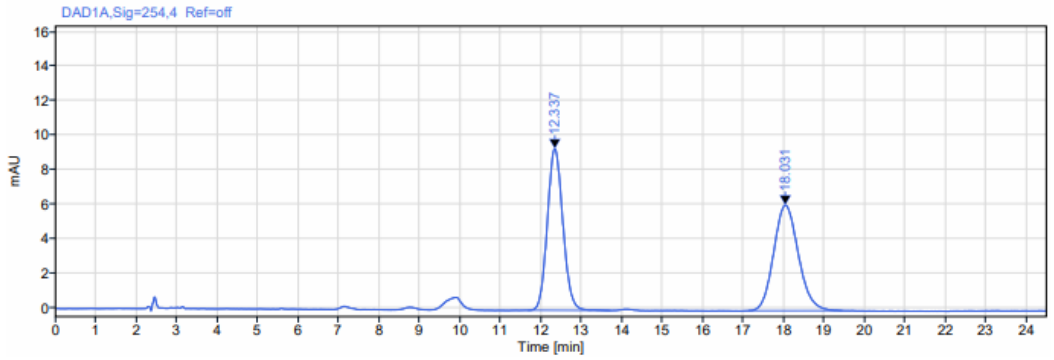



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 18.192 | MM m | 0.41 | 47.29 | 1.64 | 5.10 | |
| 19.401 | MM m | 0.50 | 880.57 | 27.46 | 94.90 | |
| | | Sum | 927.86 | | | |

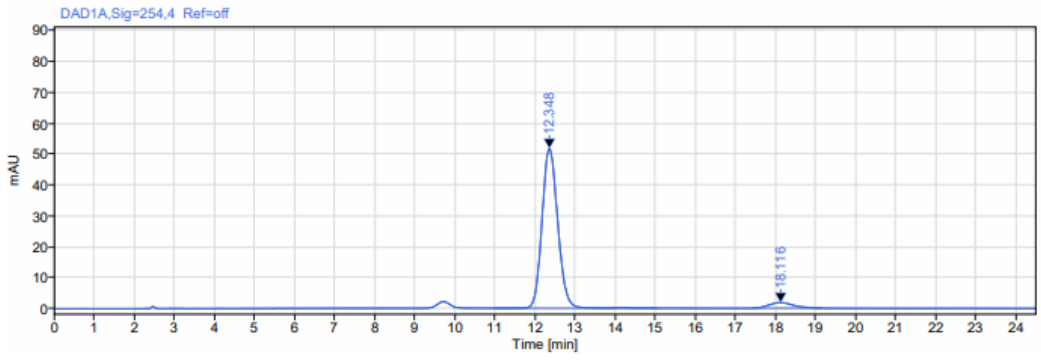



**3bv** (21.5 mg, 48% yield, PE/EA=3:1, 90% *ee*, *Z/E* >20:1) was synthesized in method A afforded 48% isolated yield as white solid. $[\alpha]_D^{25}$ =+9 (c=0.43, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.75 (dd, *J* = 18.3, 7.7 Hz, 2H), 7.63 (s, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.34–7.27 (m, 3H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.86 (dd, *J* = 9.2, 7.6 Hz, 1H), 4.47 (dd, *J* = 52.4, 12.3 Hz, 2H), 3.89 (s, 2H), 3.80 (s, 3H), 3.64 (dd, *J* = 39.7, 11.6 Hz, 2H), 3.04 (bs, 1H), 2.69 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.50 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.5, 162.1 (d, *J* = 245.4 Hz), 145.0, 143.5, 143.4, 141.3, 141.0, 140.3, 134.7 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 8.1 Hz), 126.7, 126.6, 125.0, 124.9, 124.4, 122.8, 119.8, 119.7, 115.4 (d, *J* = 21.4 Hz), 62.0, 60.0, 52.4, 48.3, 39.5, 36.9, 21.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{28}FNO_3$ 446.2126; found: 446.2154. HPLC conditions: AS-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 12.35 min (major), 18.12 min (minor).



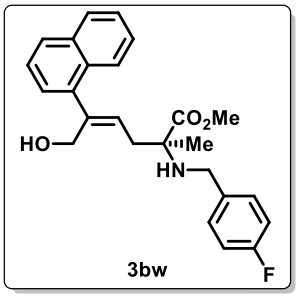

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 12.337 | MM m | 0.41 | 249.35 | 9.34 | 49.15 | |
| 18.031 | MM m | 0.64 | 258.00 | 6.10 | 50.85 | |
| | | Sum | 507.35 | | | |

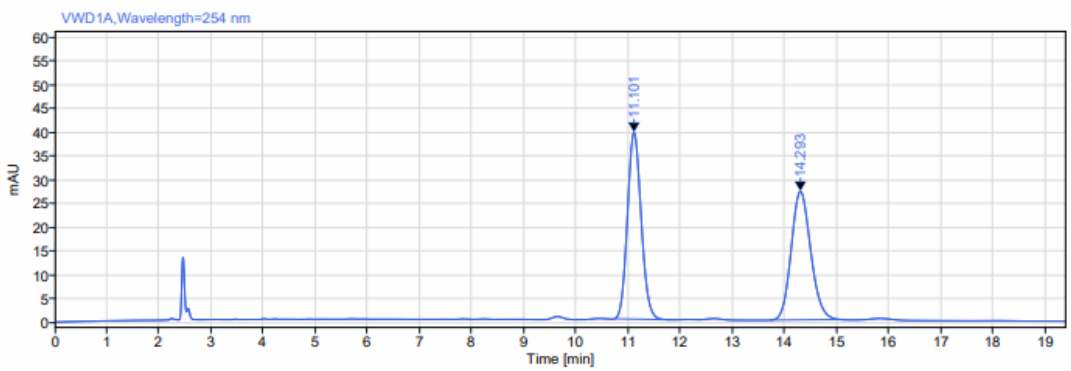



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 12.348 | MM m | 0.42 | 1411.93 | 51.73 | 94.76 | |
| 18.116 | MM m | 0.52 | 78.06 | 1.83 | 5.24 | |
| | | Sum | 1489.99 | | | |

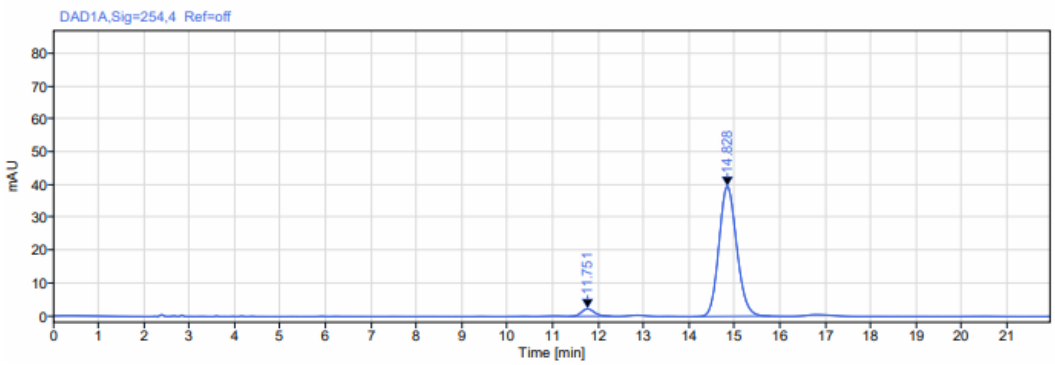



**3bw** (16.9 mg, 42% yield, PE/EA=3:1, 92% *ee*, *Z/E* >20:1) was synthesized in method A afforded 42% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =-13 (c=0.34, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.77 (dd, *J* = 12.2, 8.4 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.35 – 7.21 (m, 4H), 7.18 – 7.14 (m, 1H), 7.04 – 6.91 (m, 2H), 5.54 (dd, *J* = 10.0, 6.9 Hz, 1H), 4.32 (dd, *J* = 110.5, 12.5 Hz, 2H), 3.69 (s, 3H), 3.61 (dd, *J* = 48.6, 9.0 Hz, 2H), 3.04 (bs, 1H), 2.71 (ddd, *J* = 20.6, 13.7, 8.5 Hz, 2H), 1.47 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.2, 162.2 (d, *J* = 245.5 Hz), 145.8, 140.7, 134.8 (d, *J* = 3.0 Hz), 133.5, 131.2, 130.2 (d, *J* = 8.1 Hz), 128.3, 127.7, 127.2, 126.0, 125.9, 125.7, 125.6, 125.3, 115.5 (d, *J* = 21.3 Hz), 61.6, 61.3, 52.4, 48.2, 39.6, 21.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{26}FNO_3$ 408.1969; found: 408.1993. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 11.85 min (minor), 14.83 min (major).



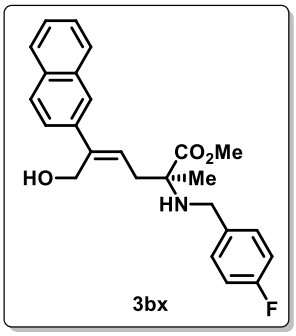

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 11.101 | MM m | 0.28 | 719.19 | 39.27 | 50.55 | |
| 14.293 | MM m | 0.40 | 703.53 | 27.03 | 49.45 | |
| | | Sum | 1422.71 | | | |

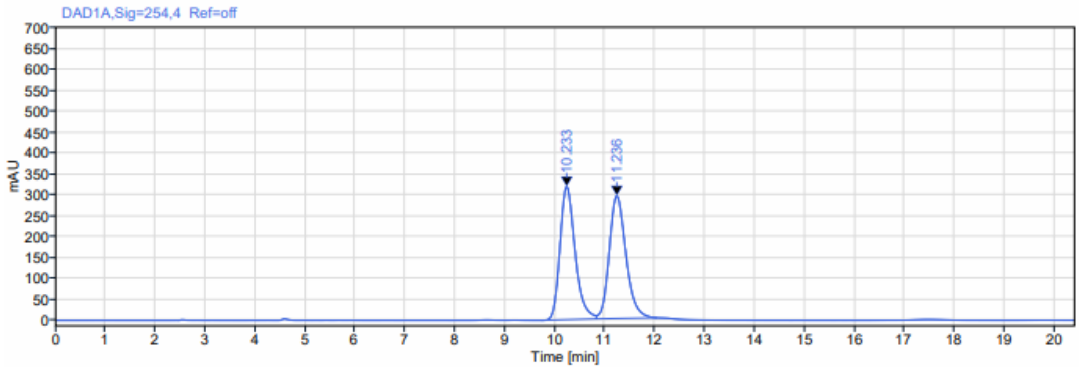



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 11.751 | MM m | 0.31 | 45.35 | 2.28 | 4.03 | |
| 14.828 | MM m | 0.42 | 1080.49 | 39.57 | 95.97 | |
| | | Sum | 1125.83 | | | |

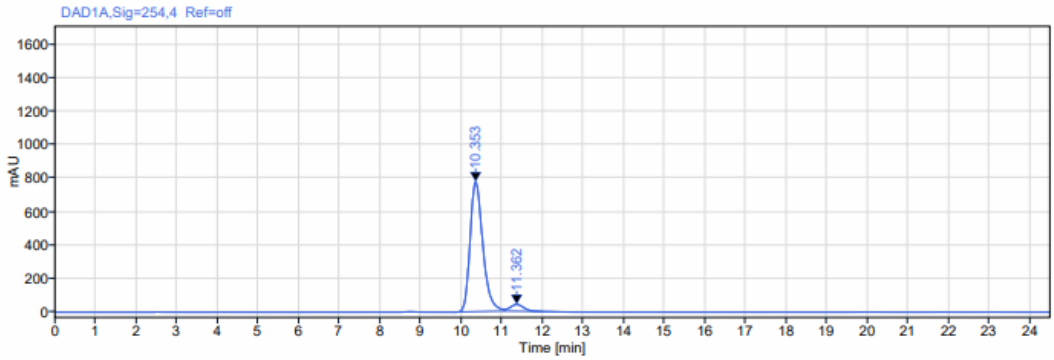



**3bx** (23.3 mg, 57% yield, PE/EA=3:1, 90% *ee*, *Z/E* >20:1) was synthesized in method A afforded 57% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+12 (c=0.30, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.90 (s, 1H), 7.85 – 7.76 (m, 3H), 7.61 – 7.55 (m, 1H), 7.49 – 7.43 (m, 2H), 7.35 – 7.28 (m, 2H), 7.07 – 6.98 (m, 2H), 5.95 (dd, *J* = 9.4, 7.4 Hz, 1H), 4.52 (dd, *J* = 49.0, 12.3 Hz, 2H), 3.80 (s, 3H), 3.65 (dd, *J* = 40.2, 11.6 Hz, 2H), 3.10 (bs, 1H), 2.73 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.50 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.5 Hz), 144.7, 138.8, 134.7 (d, *J* = 2.8 Hz), 133.3, 132.6, 130.1 (d, *J* = 8.1 Hz), 128.1,127.9, 127.5, 126.2, 125.8, 125.3, 124.7, 124.5, 115.4 (d, *J* = 21.3 Hz), 62.0, 59.8, 52.5, 48.3, 39.4, 21.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{26}FNO_3$ 408.1969; found: 408.1992. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 10.35 min (major), 11.36 min (minor).



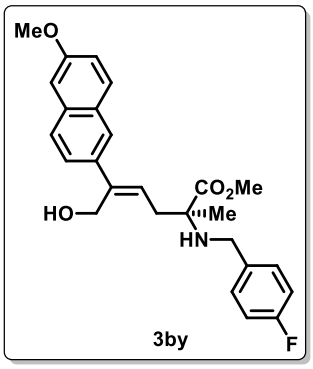

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.233 | MM m | 0.32 | 6697.77 | 318.77 | 49.57 | |
| 11.236 | MM m | 0.36 | 6813.67 | 293.85 | 50.43 | |
| | | Sum | 13511.44 | | | |

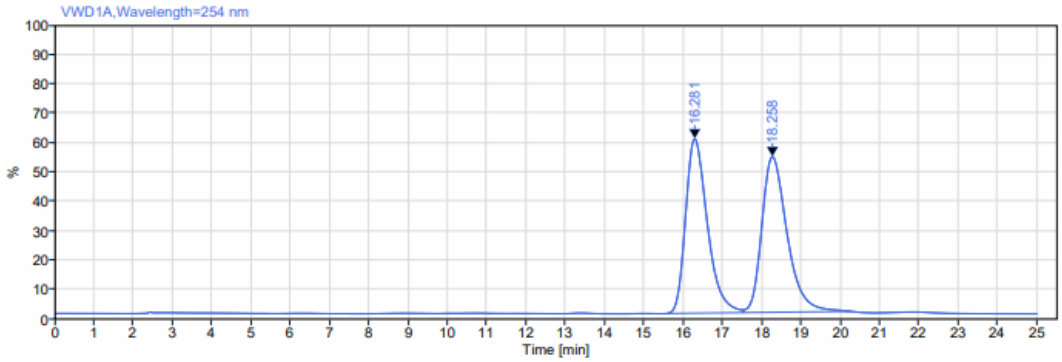



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.353 | MM m | 0.33 | 16918.17 | 776.39 | 94.83 | |
| 11.362 | MM m | 0.35 | 922.87 | 39.80 | 5.17 | |
| | | Sum | 17841.04 | | | |

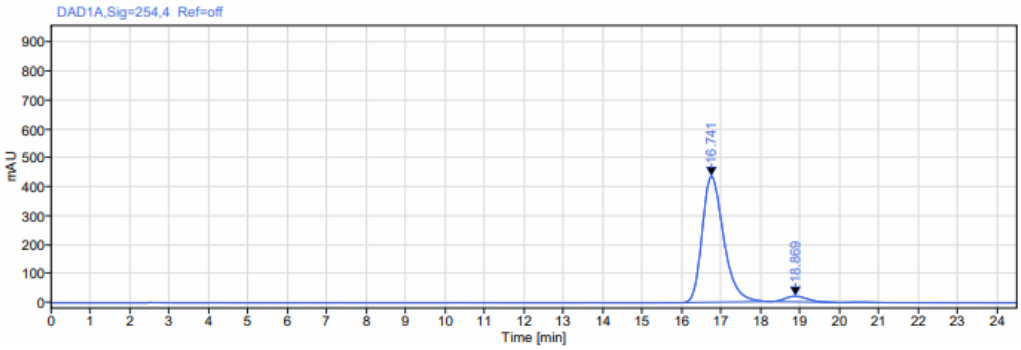



**3by** (21.4 mg, 49% yield, PE/EA=3:1, 91% *ee*, *Z/E* >20:1) was synthesized in method A afforded 49% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+11 (c=0.36, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.82 (s, 1H), 7.74 – 7.66 (m, 2H), 7.56 – 7.51 (m, 1H), 7.34 – 7.27 (m, 2H), 7.15 – 7.09 (m, 2H), 7.05 – 6.97 (m, 2H), 5.90 (dd, *J* = 9.4, 7.4 Hz, 1H), 4.50 (dd, *J* = 49.9, 12.3 Hz, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 3.71 – 3.57 (m, 2H), 3.02 (bs, 1H), 2.71 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.50 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.4 Hz), 157.6, 144.6, 136.6, 134.7 (d, *J* = 1.5 Hz), 133.8, 130.1 (d, *J* = 8.1 Hz), 129.6, 128.8, 126.8, 125.0, 124.6, 124.4, 119.0, 115.4 (d, *J* = 21.3 Hz), 105.4, 62.0, 59.8, 55.3, 52.4, 48.3, 39.5, 21.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{28}FNO_4$ 438.2075; found: 438.2100. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 16.74 min (major), 18.87 min (minor).



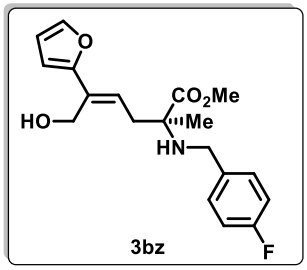

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 16.281 | MM m | 0.59 | 30055.77 | 780.20 | 49.12 | |
| 18.258 | MM m | 0.68 | 31129.42 | 696.36 | 50.88 | |
| | | Sum | 61185.18 | | | |

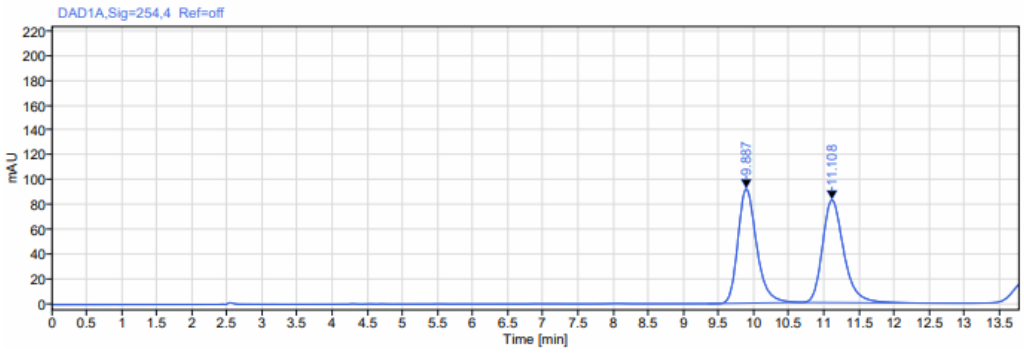



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 16.741 | MM m | 0.58 | 16497.83 | 435.30 | 95.60 | |
| 18.869 | MM m | 0.60 | 759.46 | 19.52 | 4.40 | |
| | | Sum | 17257.29 | | | |

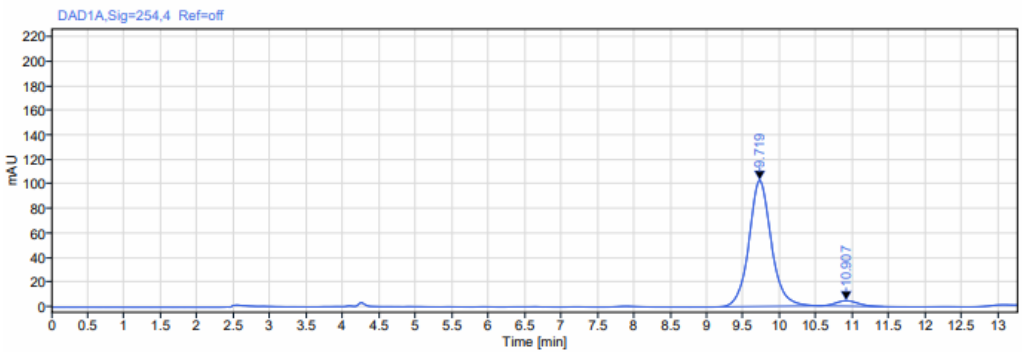



**3bz** (21 mg, 64% yield, PE/EA=3:1, 92% *ee*, *E*/*Z* >20:1) was synthesized in method A afforded 64% isolated yield as a colorless oil. $[\alpha]_D^{25}$=+22 (c=0.22, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31 – 7.26 (m, 1H), 7.24 – 7.18 (m, 2H), 6.97 – 6.87 (m, 2H), 6.33 – 6.28 (m, 2H), 6.02 (dd, J = 9.5, 7.7 Hz, 1H), 4.26 (dd, J = 39.4, 12.4 Hz, 2H), 3.72 (s, 3H), 3.55 (dd, J = 38.3, 11.6 Hz, 2H), 2.59 (ddd, J = 21.5, 14.0, 8.8 Hz, 3H), 1.40 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.5, 162.1 (d, *J* = 245.0 Hz), 144.6, 141.6, 134.9 (d, *J* = 3.1 Hz), 130.0 (d, *J* = 8.1 Hz), 128.4, 127.3, 126.2, 124.8, 115.4 (d, *J* = 21.4 Hz), 61.9, 59.9, 52.4, 48.2, 39.4, 21.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{22}FNO_4$ 348.1606; found: 348.1627. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 9.72 min (major), 10.91 min (minor).



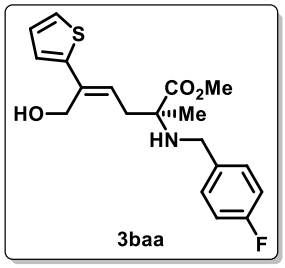

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.887 | MM m | 0.28 | 1697.82 | 91.89 | 49.47 | |
| 11.108 | MM m | 0.32 | 1734.16 | 82.48 | 50.53 | |
| | | Sum | 3431.98 | | | |

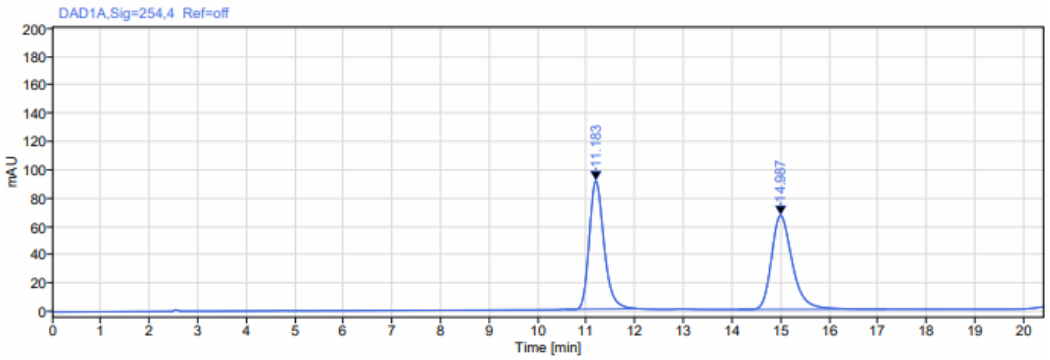



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.719 | MM m | 0.32 | 2186.93 | 102.74 | 95.94 | |
| 10.907 | MM m | 0.33 | 92.49 | 4.40 | 4.06 | |
| | | Sum | 2279.42 | | | |

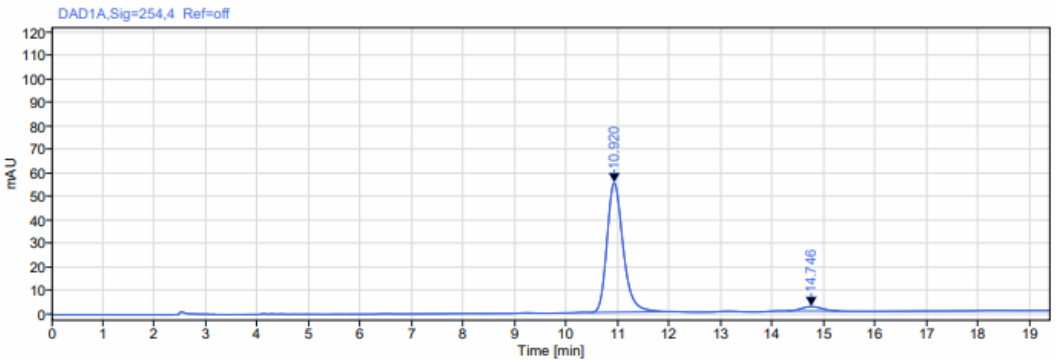



**3baa** (25.7 mg, 74% yield, PE/EA=3:1, 92% *ee*, *E/Z* >20:1) was synthesized in method A afforded 74% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+20 (c=0.40, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.23 – 7.19 (m, 2H), 7.09 – 7.06 (m, 1H), 7.06 – 7.02 (m, 1H), 6.96 – 6.89 (m, 3H), 5.87 (dd, *J* = 9.3, 7.6 Hz, 1H), 4.34 (dd, *J* = 34.4, 12.4 Hz, 2H), 3.72 (s, 3H), 3.54 (dd, *J* = 37.5, 11.6 Hz, 2H), 2.82 (bs, 1H), 2.57 (ddd, *J* = 21.5, 14.0, 8.4 Hz, 2H), 1.38 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.3, 162.1 (d, *J* = 244.0 Hz), 144.9, 138.1, 134.7 (d, *J* = 2.9 Hz), 130.1 (d, *J* = 8.1 Hz), 127.6, 124.1, 123.6, 123.0, 115.5 (d, *J* = 21.1 Hz), 62.2, 59.5, 52.4, 48.2, 38.8, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{22}FNO_3S$ 364.1377; found: 364.1397. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 10.92 min (major), 14.75 min (minor).



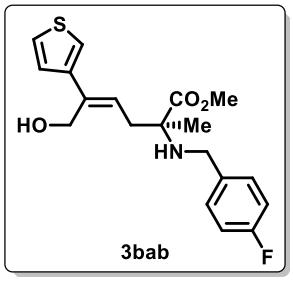

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 11.183 | MM m | 0.32 | 1910.75 | 90.46 | 49.11 | |
| 14.987 | MM m | 0.45 | 1979.75 | 66.29 | 50.89 | |
| | | Sum | 3890.51 | | | |

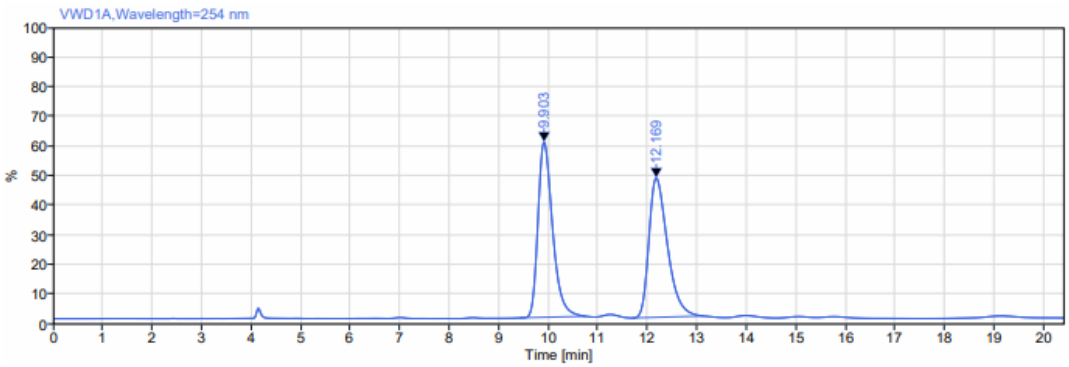



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.920 | MM m | 0.33 | 1195.11 | 54.90 | 95.92 | |
| 14.746 | MM m | 0.41 | 50.88 | 1.87 | 4.08 | |
| | | Sum | 1245.99 | | | |

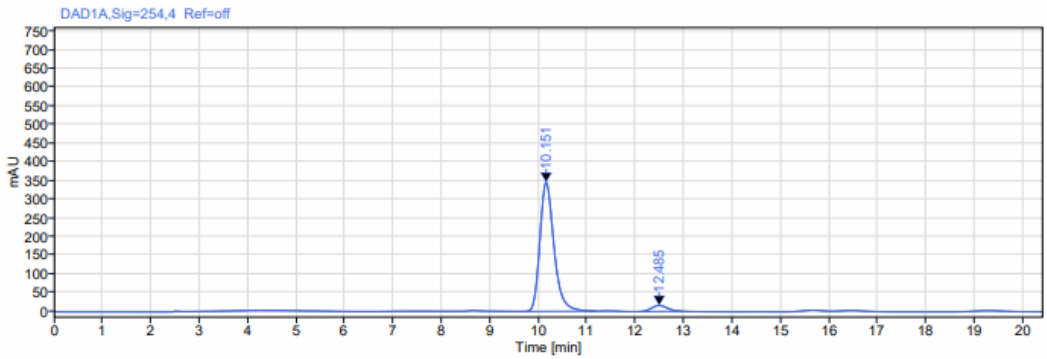



**3bab** (20.2 mg, 57% yield, PE/EA=3:1, 90% *ee*, *Z/E* >20:1) was synthesized in method A afforded 57% isolated yield as a colorless oil. $[\alpha]_D^{25}$=+17 (c=0.32, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.24 – 7.17 (m, 4H), 7.14 – 7.10 (m, 1H), 6.96 – 6.90 (m, 2H), 5.82 (dd, *J* = 9.4, 7.5 Hz, 1H), 4.31 (dd, *J* = 41.7, 12.3 Hz, 2H), 3.71 (s, 3H), 3.54 (dd, *J* = 38.2, 11.6 Hz, 2H), 2.60 (bs, 1H), 2.57 (ddd, *J* = 21.4, 14.0, 8.4 Hz, 2H), 1.38 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.1 (d, *J* = 245.5 Hz), 142.3, 139.2, 134.7 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 8.1 Hz), 125.7, 125.6, 123.0, 120.5, 115.4 (d, *J* = 21.3 Hz), 62.1, 59.5, 52.4, 48.2, 38.8, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{22}FNO_3S$ 364.1377; found: 364.1396. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 10.15 min (major), 12.48 min (minor).



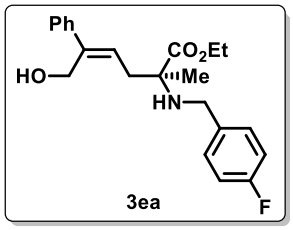

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.903 | MM m | 0.31 | 24013.65 | 1171.62 | 49.77 | |
| 12.169 | MM m | 0.40 | 24234.81 | 932.34 | 50.23 | |
| | | Sum | 48248.46 | | | |

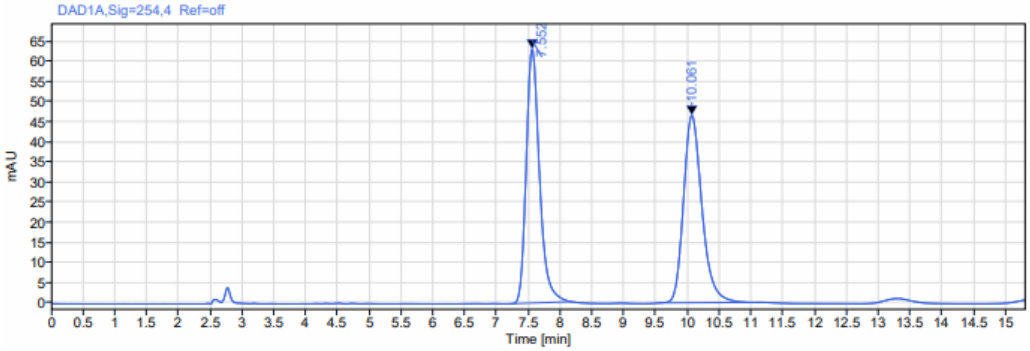



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.151 | MM m | 0.31 | 7031.46 | 345.59 | 94.96 | |
| 12.485 | MM m | 0.37 | 373.32 | 15.92 | 5.04 | |
| | | Sum | 7404.79 | | | |

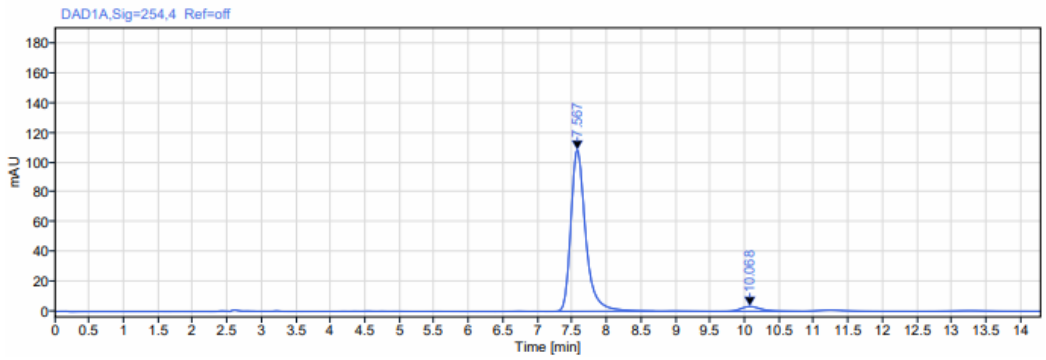



**3ea** (29.2 mg, 79% yield, PE/EA=3:1, 92% *ee*, *Z/E* >20:1) was synthesized in method A afforded 79% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+15 (c=0.36, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.39 – 7.33 (m, 2H), 7.27 – 7.18 (m, 5H), 6.98 – 6.86 (m, 2H), 5.72 (dd, *J* = 9.4, 7.5 Hz, 1H), 4.33 (dd, *J* = 52.9, 12.3 Hz, 2H), 4.22 – 4.12 (m, 2H), 3.55 (dd, *J* = 37.4, 11.5 Hz, 2H), 2.74 (bs, 1H), 2.58 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.39 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.9, 162.1 (d, *J* = 245.4 Hz), 144.7, 141.7, 134.8 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 8.1 Hz), 128.4, 127.3, 126.1, 124.8, 115.4 (d, *J* = 21.3 Hz), 61.8, 61.4, 59.8, 48.2, 39.4, 21.5, 14.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}FNO_3$ 372.1969; found: 372.1993. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =7.57 min (major), 10.07 min (minor).



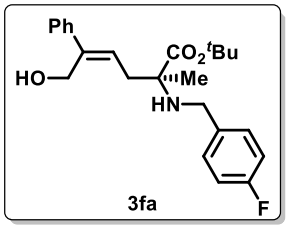

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.552 | MM m | 0.22 | 918.19 | 63.12 | 49.46 | |
| 10.061 | MM m | 0.31 | 938.21 | 46.57 | 50.54 | |
| | | Sum | 1856.40 | | | |

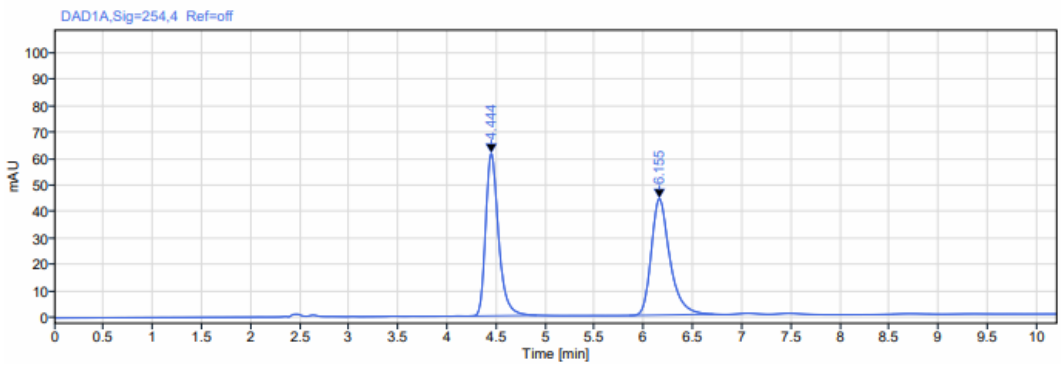



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.567 | MM m | 0.23 | 1618.44 | 108.33 | 96.13 | |
| 10.068 | MM m | 0.31 | 65.21 | 3.26 | 3.87 | |
| | | Sum | 1683.65 | | | |

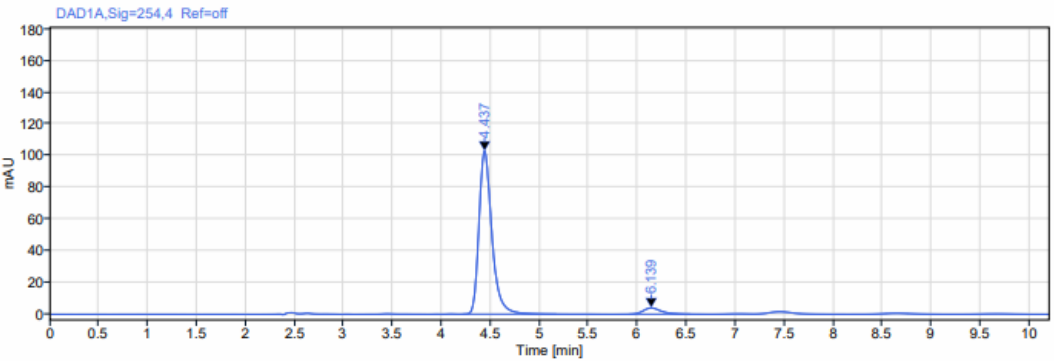



**3fa** (17.5 mg, 54% yield, PE/EA=3:1, 90% *ee*, *Z/E* >20:1) was synthesized in method A afforded 54% isolated yield as a colorless oil. $[\alpha]_D^{25}$=+13 (c=0.36, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38 – 7.32 (m, 2H), 7.27 – 7.16 (m, 6H), 6.98 – 6.89 (m, 2H), 5.73 (dd, *J* = 9.3, 7.6 Hz, 1H), 4.33 (dd, *J* = 53.9, 12.2 Hz, 2H), 3.55 (dd, *J* = 37.6, 11.4 Hz, 2H), 2.96 (bs, 1H), 2.55 (ddd, *J* = 21.1, 13.8, 8.5 Hz, 2H), 1.44 (s, 9H), 1.35 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.1, 162.1 (d, *J* = 245.3 Hz), 144.6, 141.8, 134.8, 130.1 (d, *J* = 8.0 Hz), 128.4, 127.2, 126.1, 125.0, 115.5 (d, *J* = 21.3 Hz), 81.8, 62.1, 59.8, 48.3, 39.4, 28.1, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{30}FNO_3$ 400.2282; found: 400.2309. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 10min; $t_R$ =4.44 min (major), 6.14 min (minor).



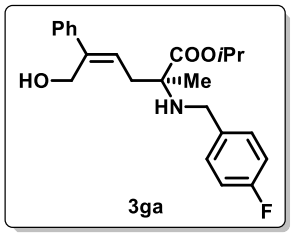

**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 4.444 | MM m | 0.14 | 558.74 | 61.28 | 49.17 | |
| 6.155 | MM m | 0.20 | 577.54 | 43.91 | 50.83 | |
| | | Sum | 1136.28 | | | |

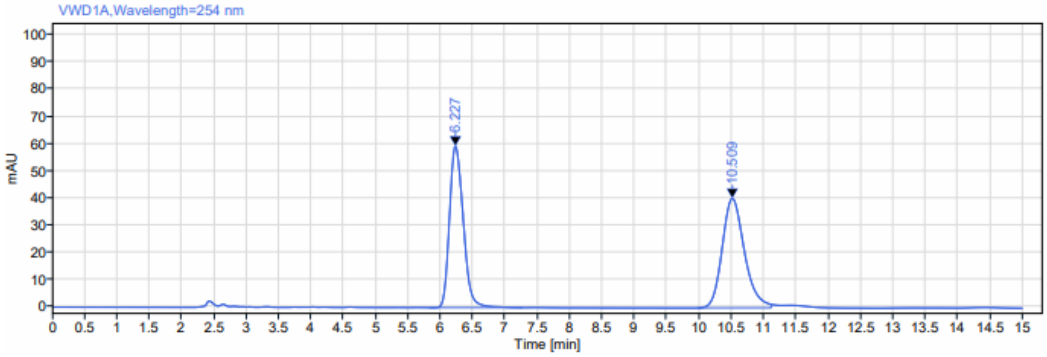



**Signal:** DAD1A,Sig=254,4 Ref=off

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 4.437 | MM m | 0.14 | 944.10 | 102.91 | 94.96 | |
| 6.139 | MM m | 0.19 | 50.14 | 3.96 | 5.04 | |
| | | Sum | 994.23 | | | |

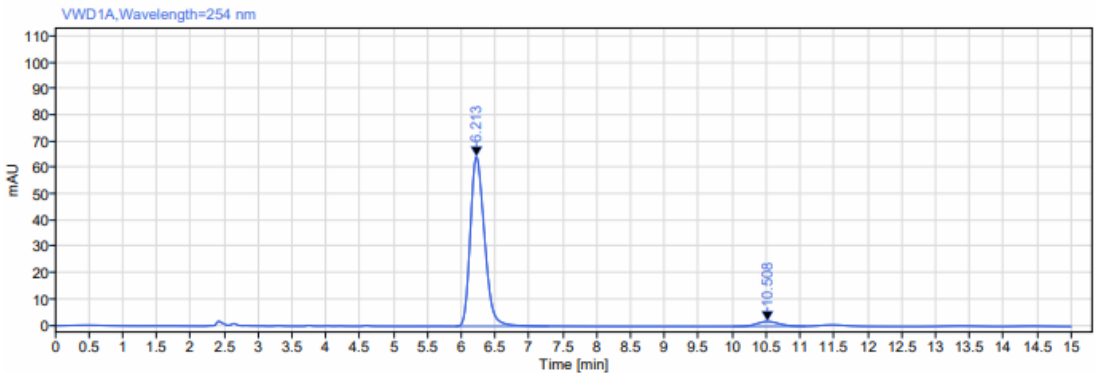



**3ga** (28.0 mg, 73% yield, PE/EA=3:1, 91% *ee*, *Z/E* >20:1) was synthesized in method A afforded 73% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+7 (c=0.56, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38 – 7.32 (m, 2H), 7.27 – 7.17 (m, 5H), 6.98 – 6.87 (m, 2H), 5.72 (dd, *J* = 9.5, 7.3 Hz, 1H), 5.09 – 4.98 (m, 1H), 4.34 (dd, *J* = 55.2, 12.3 Hz, 2H), 3.56 (dd, *J* = 39.0, 11.5 Hz, 2H), 2.99 (bs, 1H), 2.59 (ddd, *J* = 21.2, 13.9, 8.5 Hz, 2H), 1.39 (s, 3H), 1.22 (d, *J* = 6.3 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.2, 162.2 (d, *J* = 245.5 Hz), 144.6, 141.7, 134.7 (d, *J* = 1.1 Hz), 130.1 (d, *J* = 8.1 Hz), 128.4, 127.3, 126.1, 124.8, 115.5 (d, *J* = 21.4 Hz), 69.0, 61.9, 59.8, 48.2, 39.2, 21.9, 21.8, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{28}FNO_3$ 386.2126; found: 386.2153. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 15min; $t_R$ =6.21 min (major), 10.51 min (minor)



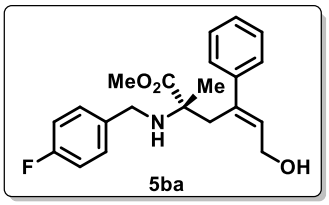

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 6.227 | MM m | 0.24 | 880.09 | 59.32 | 47.86 | |
| 10.509 | MM m | 0.37 | 958.74 | 40.22 | 52.14 | |
| | | Sum | 1838.83 | | | |



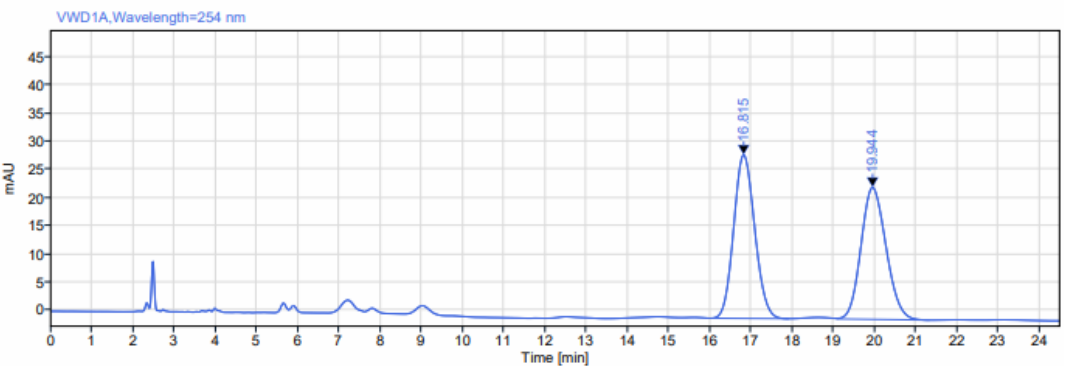

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 6.213 | MM m | 0.23 | 938.50 | 64.44 | 95.73 | |
| 10.508 | MM m | 0.35 | 41.91 | 1.84 | 4.27 | |
| | | Sum | 980.41 | | | |



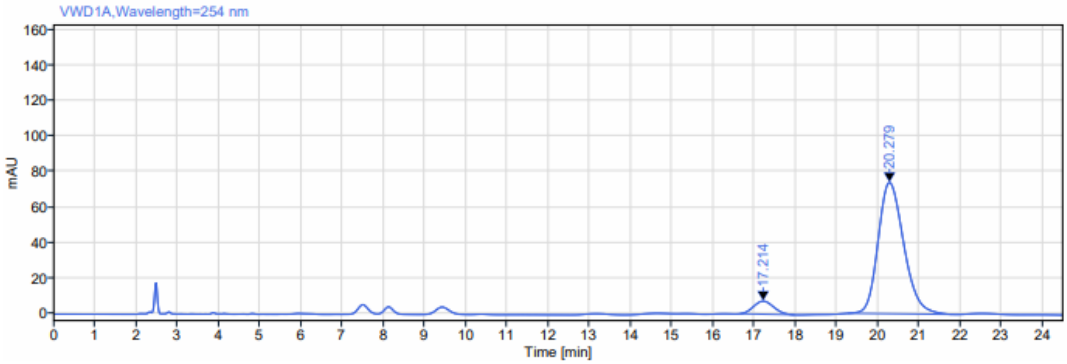
5ba

**5ba** (12.5 mg, 35% yield, PE/EA=3:1, 86% *ee*, *Z/E* >20:1) was synthesized in method A afforded 35% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+33 (c=0.20, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.24 – 7.16 (m, 7H), 6.97 – 6.92 (m, 2H), 6.03 (t, *J* = 6.9 Hz, 1H), 4.09 (ddd, *J* = 85.9, 13.2, 6.9 Hz, 2H), 3.50 (dd, *J* = 48.7, 11.2 Hz, 2H), 3.07 (s, 3H), 3.02 (s, 2H), 1.37 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.5, 162.2 (d, *J* = 244.0 Hz), 142.0, 139.1, 134.78 (d, *J* = 3.1 Hz), 132.9, 130.2 (d, *J* = 8.1 Hz), 128.2, 127.4, 126.7, 115.5 (d, *J* = 21.2 Hz), 60.5, 58.3, 51.7, 48.3, 41.7, 22.5. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{21}H_{24}FNO_3$ 358.1813; found: 358.1836. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =17.21 min (minor), 20.28 min (major).



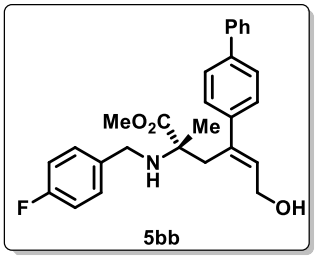

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 16.815 | MM m | 0.55 | 1028.16 | 28.97 | 50.99 | |
| 19.944 | MM m | 0.66 | 988.32 | 23.39 | 49.01 | |
| | | Sum | 2016.48 | | | |



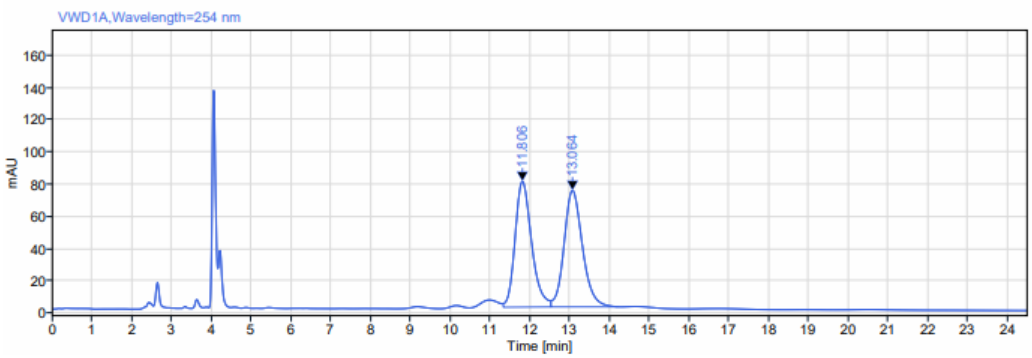

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 17.214 | MM m | 0.53 | 249.30 | 7.34 | 7.24 | |
| 20.279 | MM m | 0.67 | 3195.09 | 73.82 | 92.76 | |
| | | Sum | 3444.39 | | | |



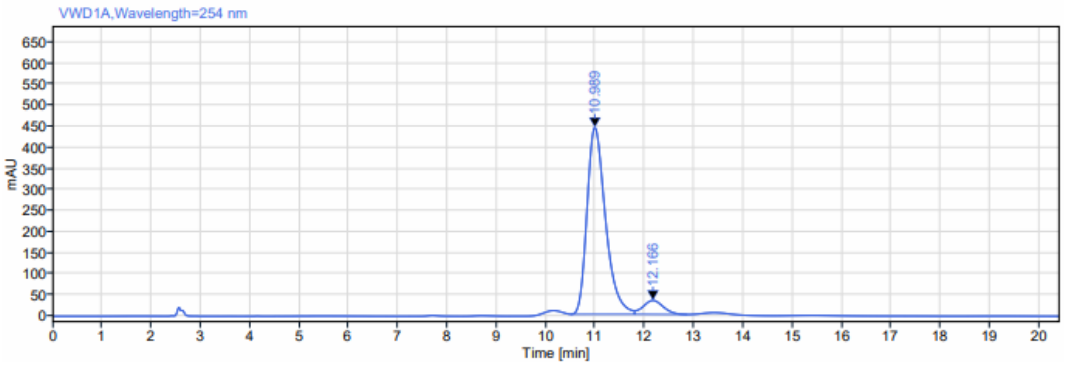
5bb

**5bb** (14.4 mg, 33% yield, PE/EA=3:1, 85% *ee*, *Z/E* >20:1) was synthesized in method A afforded 33% isolated yield as white solid. $[\alpha]_D^{25}$ =+24 (c=0.29, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.51 – 7.45 (m, 4H), 7.38 – 7.34 (m, 2H), 7.29 – 7.24 (m, 3H), 7.21 – 7.17 (m, 2H), 6.98 – 6.92 (m, 2H), 6.09 (t, *J* = 6.9 Hz, 1H), 4.11 (ddd, *J* = 83.5, 13.2, 6.9 Hz, 2H), 3.51 (dd, *J* = 50.5, 11.2 Hz, 2H), 3.10 (s, 3H), 3.05 (s, 2H), 1.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.6, 16 2.17 (d, *J* = 245.5 Hz), 140.9, 140.4, 140.2, 138.6, 134.8 (d, *J* = 3.0 Hz), 132.9, 130.2 (d, *J* = 8.1 Hz), 128.8, 127.4, 127.1, 126.9, 126.8, 115.54 (d, *J* = 21.3 Hz), 60.6, 58.3, 51.8, 48.3, 41.6, 22.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{28}FNO_3$ 434.2126; found: 434.2155. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =10.99 min (major), 12.17 min (minor).



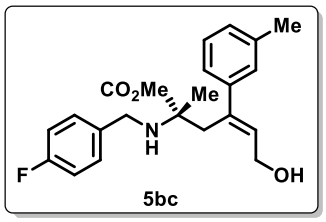

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 11.806 | MM m | 0.44 | 2249.17 | 78.08 | 49.22 | |
| 13.064 | MM m | 0.49 | 2320.82 | 72.32 | 50.78 | |
| | | Sum | 4569.99 | | | |



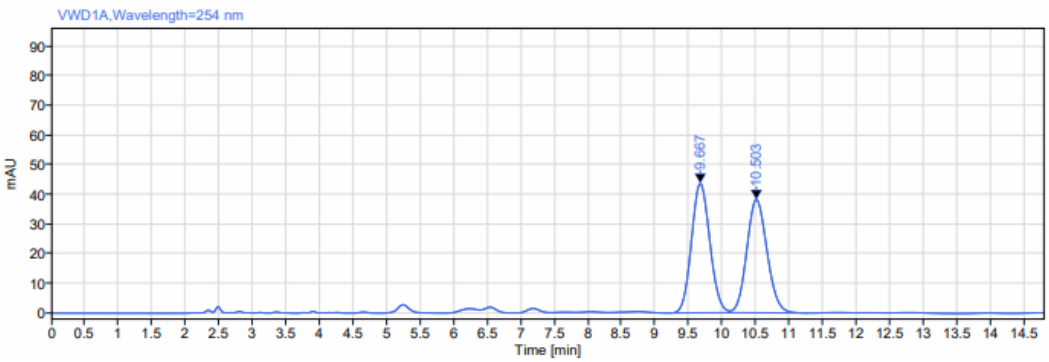

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.989 | MM m | 0.40 | 11550.88 | 443.19 | 92.53 | |
| 12.166 | MM m | 0.43 | 932.90 | 32.91 | 7.47 | |
| | | Sum | 12483.78 | | | |



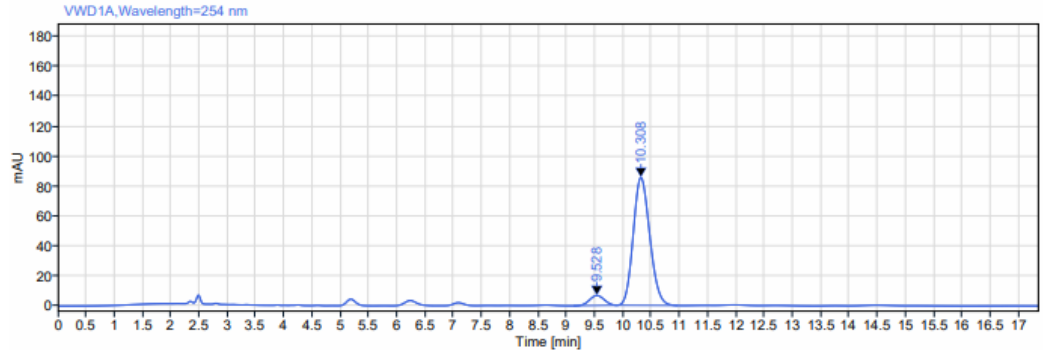
5bc

**5bc** (12.1 mg, 33% yield, PE/EA=3:1, 87% *ee*, *Z*/*E* >20:1) was synthesized in method A afforded 33% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+11 (c=0.24, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.21 – 7.17 (m, 2H), 7.12 – 7.08 (m, 1H), 6.99 – 6.92 (m, 5H), 6.03 (t, $J$ = 6.9 Hz, 1H), 4.08 (ddd, $J$ = 87.3, 13.1, 6.9 Hz, 2H), 3.50 (dd, $J$ = 48.3, 11.3 Hz, 2H), 3.10 (s, 3H), 3.00 (d, $J$ = 3.0 Hz, 2H), 2.26 (s, 3H), 1.37 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.5, 162.2 (d, $J$ = 244.1 Hz), 141.9, 139.2, 137.7, 134.7 (d, $J$ = 2.3 Hz), 132.6, 130.2 (d, $J$ = 8.1 Hz), 128.2, 128.1, 127.3, 123.8, 115.5 (d, $J$ = 21.3 Hz), 60.6, 58.2, 51.7, 48.3, 41.5, 22.5, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}FNO_3$ 372.1969; found: 372.1994. HPLC conditions: OD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =9.53 min (minor), 10.31 min (major).



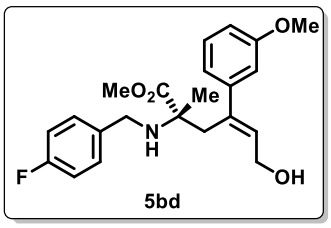

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.667 | MM m | 0.30 | 830.75 | 43.62 | 50.93 | |
| 10.503 | MM m | 0.33 | 800.45 | 38.13 | 49.07 | |
| | | Sum | 1631.20 | | | |

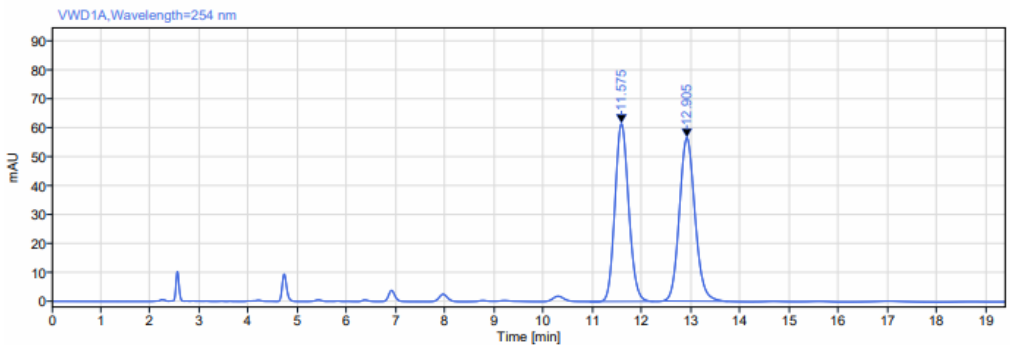



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 9.528 | MM m | 0.28 | 120.80 | 6.70 | 6.48 | |
| 10.308 | MM m | 0.32 | 1744.51 | 85.59 | 93.52 | |
| | | Sum | 1865.30 | | | |

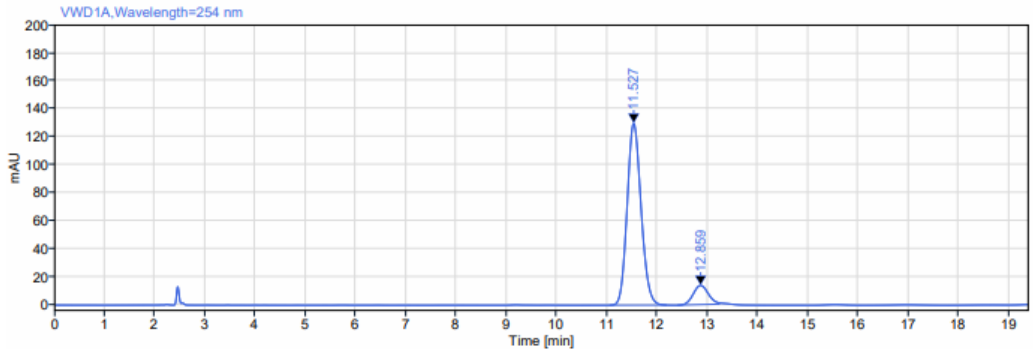



**5bd** (10.1 mg, 28% yield, PE/EA=3:1, 80% *ee*, *Z*/*E* >20:1) was synthesized in method A afforded 28% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+17 (c=0.20, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.21 – 7.17 (m, 2H), 7.15 – 7.11 (m, 1H), 6.96 – 6.92 (m, 2H), 6.78 – 6.76 (m, 1H), 6.72 – 6.71 (m, 2H), 6.08 (t, *J* = 6.9 Hz, 1H), 4.08 (ddd, *J* = 85.2, 13.1, 7.0 Hz, 2H), 3.72 (s, 3H), 3.50 (dd, *J* = 47.5, 11.2 Hz, 2H), 3.15 (s, 3H), 3.00 (s, 2H), 1.37 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.5, 162.2 (d, *J* = 244.0 Hz), 159.5, 143.4, 139.0, 134.8 (d, *J* = 1.7 Hz), 132.8, 130.2 (d, *J* = 8.0 Hz), 129.2, 119.1, 115.5 (d, *J* = 21.4 Hz), 112.8, 112.4, 60.6, 58.1, 55.3, 51.8, 48.3, 41.6, 22.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}FNO_4$ 388.1919; found: 388.1944. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =11.53 min (major), 12.86 min (minor).



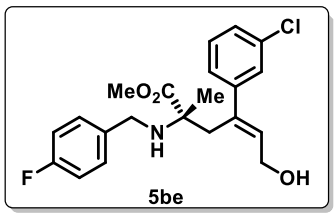

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 11.575 | MM m | 0.30 | 1195.62 | 61.44 | 48.95 | |
| 12.905 | MM m | 0.34 | 1246.74 | 56.41 | 51.05 | |
| | | Sum | 2442.36 | | | |

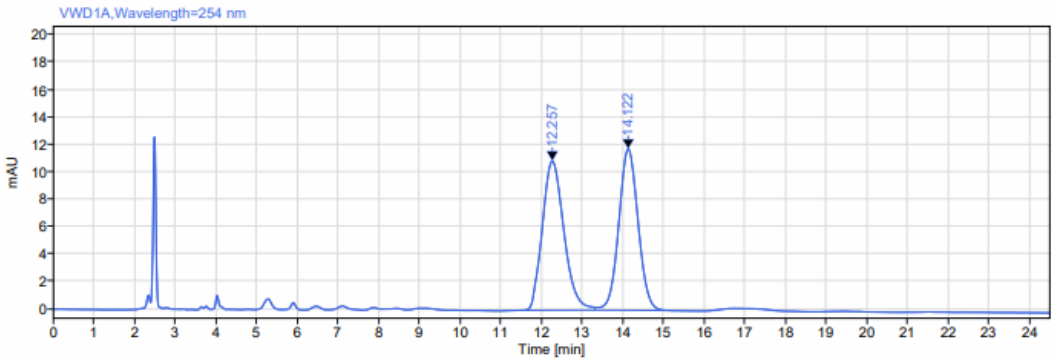



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 11.527 | MM m | 0.30 | 2498.56 | 129.98 | 89.73 | |
| 12.859 | MM m | 0.33 | 285.84 | 13.69 | 10.27 | |
| | | Sum | 2784.40 | | | |

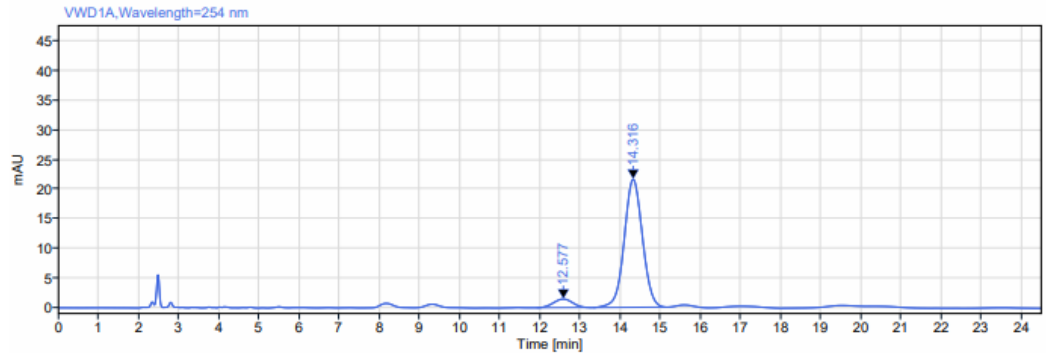



**5be** (6.2 mg, 16% yield, PE/EA=3:1, 87% *ee*, *Z/E* >20:1) was synthesized in method A afforded 16% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+21 (c=0.12, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32 – 7.18 (m, 6H), 7.16 – 7.11 (m, 1H), 7.04 – 7.00 (m, 2H), 6.12 (t, *J* = 6.7 Hz, 1H), 4.16 (ddd, *J* = 79.4, 13.3, 6.8 Hz, 2H), 3.57 (dd, *J* = 48.9, 11.2 Hz, 2H), 3.25 (s, 3H), 3.06 (q, *J* = 13.8 Hz, 2H), 1.45 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.3, 162.2 (d, *J* = 245.2 Hz), 143.8, 137.6, 134.5 (d, *J* = 3.5 Hz), 134.1, 134.0, 130.3 (d, *J* = 8.0 Hz), 129.6, 127.4, 126.6, 125.0, 115.6 (d, *J* = 21.4 Hz), 60.5, 58.2, 51.9, 48.3, 41.4, 22.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}ClFNO_3$ 392.1423; found: 392.1447. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =12.58 min (minor), 14.32 min (major).



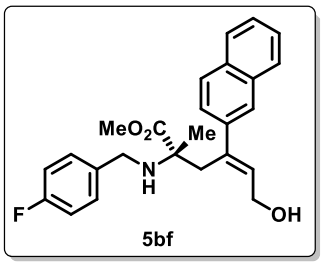

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 12.257 | MM m | 0.57 | 401.06 | 10.88 | 50.87 | |
| 14.122 | MM m | 0.51 | 387.31 | 11.76 | 49.13 | |
| | | Sum | 788.38 | | | |



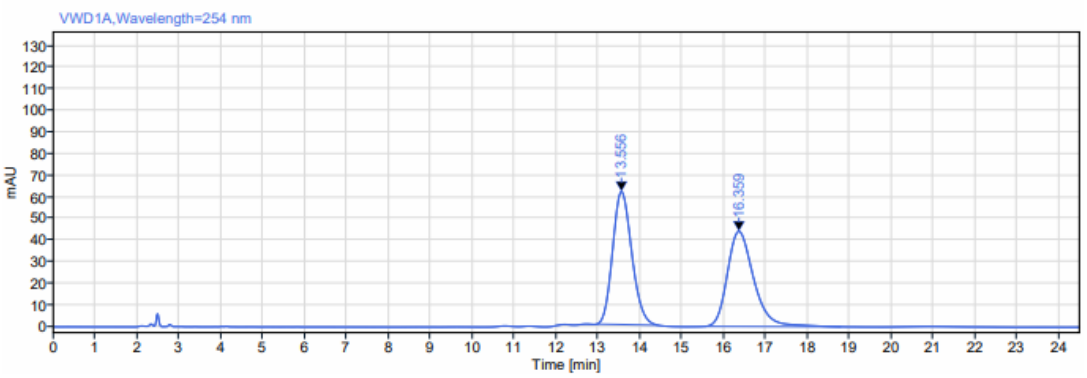

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 12.577 | MM m | 0.49 | 47.37 | 1.44 | 6.48 | |
| 14.316 | MM m | 0.49 | 684.07 | 21.69 | 93.52 | |
| | | Sum | 731.44 | | | |



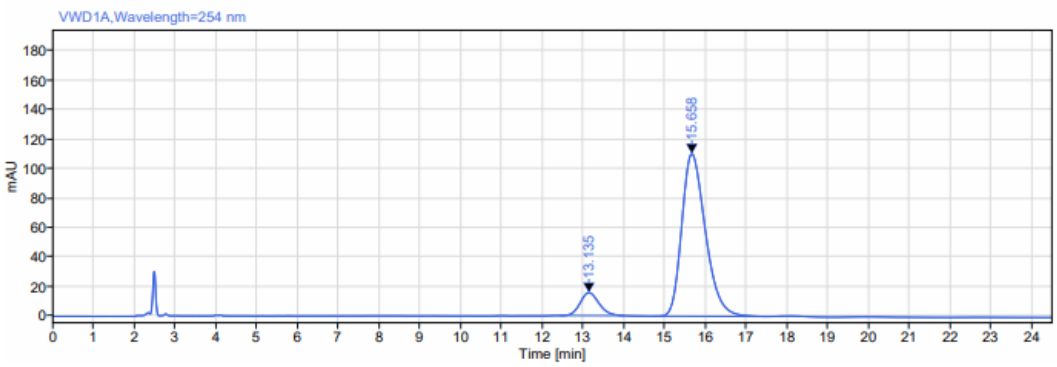
5bf

**5bf** (16.3 mg, 40% yield, PE/EA=3:1, 80% *ee*, *Z*/*E* >20:1) was synthesized in method A afforded 40% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+49 (c=0.33, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.80 – 7.76 (m, 3H), 7.71 – 7.69 (m, 1H), 7.48 – 7.38 (m, 3H), 7.27 – 7.22 (m, 2H), 7.04 – 6.94 (m, 2H), 6.26 (t, $J$ = 6.9 Hz, 1H), 4.22 (ddd, $J$ = 82.7, 13.2, 6.9 Hz, 2H), 3.57 (dd, $J$ = 54.3, 11.3 Hz, 2H), 3.21 (q, $J$ = 13.8 Hz, 2H), 2.98 (s, 3H), 1.47 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.5, 162.2 (d, $J$ = 245.4 Hz), 139.2, 138.9, 134.7 (d, $J$ = 3.2 Hz), 133.4, 133.4, 133.1, 132.7, 130.2 (d, $J$ = 8.2 Hz), 128.0, 127.9, 127.5, 126.3, 125.9, 125.7, 125.1, 115.5 (d, $J$ = 21.3 Hz), 60.7, 58.3, 51.7, 48.3, 41.5, 22.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{26}FNO_4$ 408.1919; found: 408.1998. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =13.14 min (major), 15.66 min (minor).



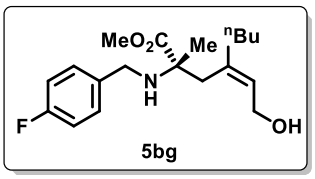

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 13.556 | MM m | 0.49 | 1952.56 | 61.54 | 50.39 | |
| 16.359 | MM m | 0.67 | 1922.52 | 44.03 | 49.61 | |
| | | Sum | 3875.08 | | | |



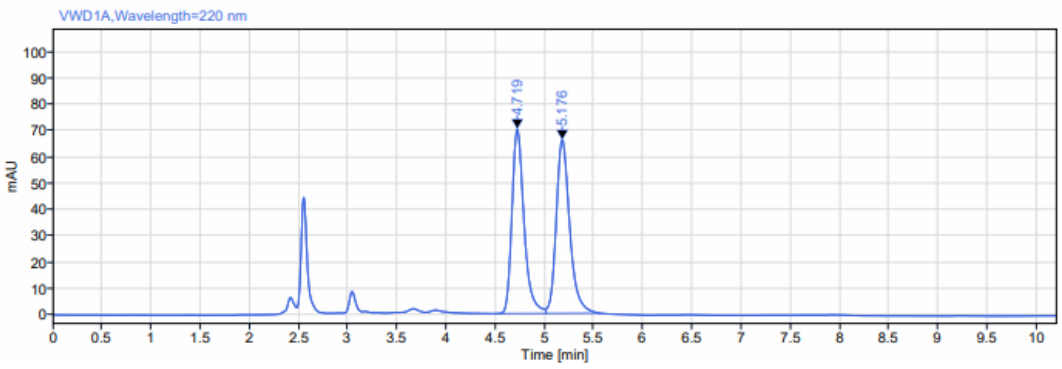

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 13.135 | MM m | 0.49 | 499.40 | 15.57 | 10.09 | |
| 15.658 | MM m | 0.62 | 4448.14 | 110.40 | 89.91 | |
| | | Sum | 4947.54 | | | |



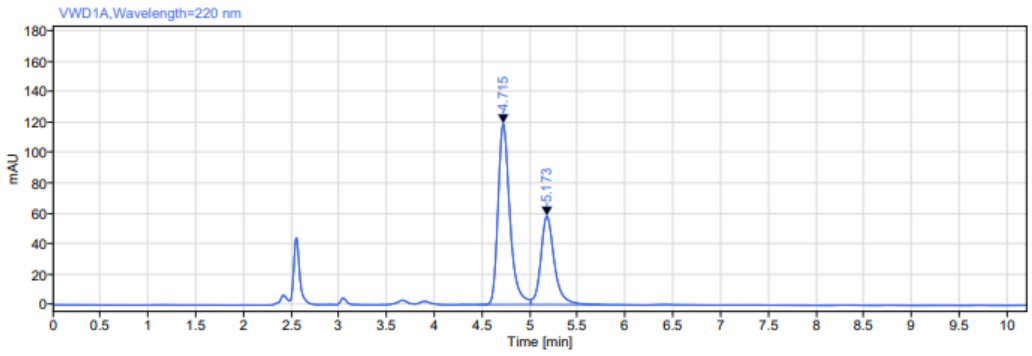
5bg

**5bg** (10.1 mg, 30% yield, PE/EA=3:1, 28% *ee*, *Z/E* >20:1) was synthesized in method A afforded 30% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+4 (c=0.20, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.28 – 7.21 (m, 2H), 7.03 – 6.99 (m, 2H), 5.73 (t, $J$ = 7.0 Hz, 1H), 3.95 (ddd, $J$ = 83.0, 12.7, 7.0 Hz, 2H), 3.78 (s, 3H), 3.63 (dd, $J$ = 24.1, 11.2 Hz, 2H), 2.59 (dd, $J$ = 75.2, 13.6 Hz, 2H), 1.92 – 1.78 (m, 2H), 1.46 (s, 3H), 1.37 – 1.24 (m, 4H), 0.86 (t, $J$ = 7.1 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.9, 162.2 (d, $J$ = 245.4 Hz), 138.8, 134.8 (d, $J$ = 2.8 Hz), 130.3 (d, $J$ = 8.1 Hz), 129.5, 115.51 (d, $J$ = 21.4 Hz), 60.5, 57.8, 52.2, 48.4, 41.7, 36.9, 30.3, 22.6, 22.3, 13.89. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{28}FNO_3$ 338.2126; found: 338.2146. HPLC conditions: OZ-H column, 220 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 10min; $t_R$ =4.72 min (major), 5.17 min (minor).



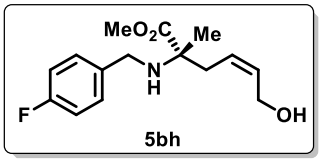

**Signal:** VWD1A,Wavelength=220 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 4.719 | MM m | 0.13 | 601.61 | 70.22 | 48.88 | |
| 5.176 | MM m | 0.15 | 629.19 | 66.04 | 51.12 | |
| | | Sum | 1230.80 | | | |

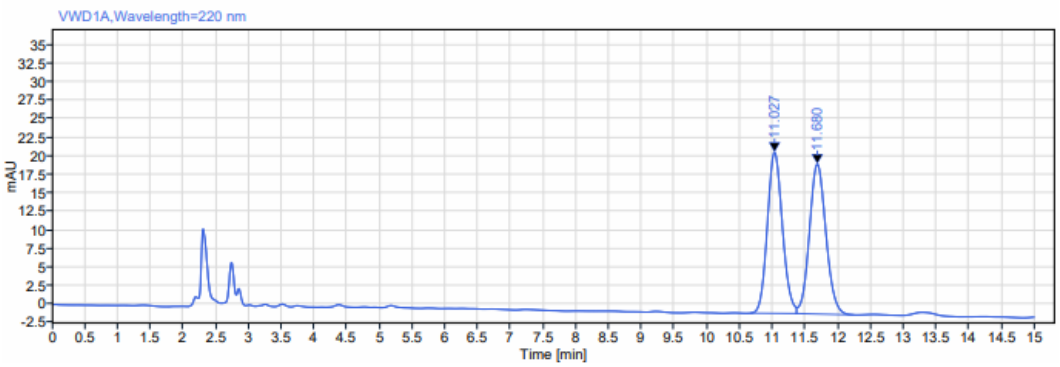



**Signal:** VWD1A,Wavelength=220 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 4.715 | MM m | 0.13 | 1027.09 | 118.99 | 64.14 | |
| 5.173 | MM m | 0.15 | 574.17 | 58.23 | 35.86 | |
| | | Sum | 1601.25 | | | |

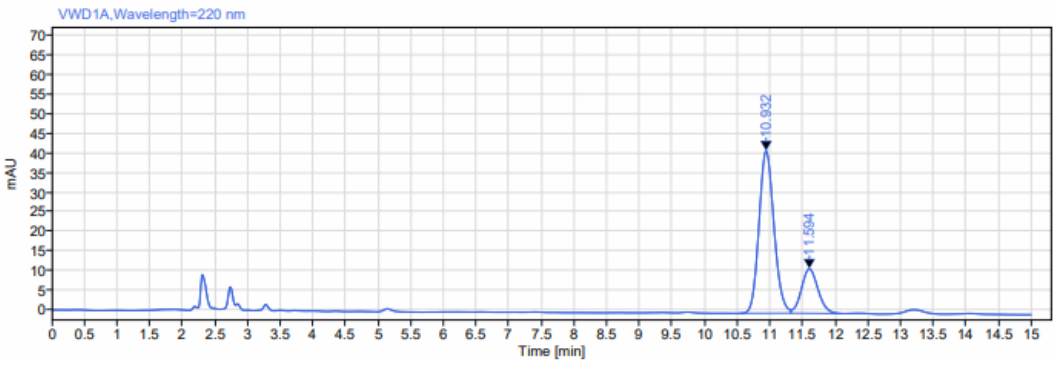



**5bh** (18.8 mg, 67% yield, PE/EA=3:1, 54% *ee*, *Z/E* >20:1) was synthesized in method A afforded 67% isolated yield as a colorless oil. $[\alpha]_D^{25}$=+5 (c=0.37, $CHCl_3$).**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.25 – 7.19 (m, 2H), 6.98 – 6.86 (m, 2H), 5.73 – 5.45 (m, 2H), 4.00 (d, *J* = 5.2 Hz, 2H), 3.66 (s, 3H), 3.53 (q, *J* = 11.9 Hz, 2H), 2.37 (qd, *J* = 14.1, 7.1 Hz, 2H), 1.86 (s, 2H), 1.27 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.4, 162.0 (d, *J* = 244.9 Hz), 135.7 (d, *J* = 3.0 Hz), 133.5, 129.9 (d, *J* = 8.0 Hz), 126.2, 115.2 (d, *J* = 21.3 Hz), 63.2, 62.3, 52.0, 47.7, 41.5, 22.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{20}FNO_3$ 282.1500; found: 282.1515. HPLC conditions: AD-H column, 220 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 95:5, 25min; $t_R$ =10.93 min (major), 11.59 min (minor).




**Signal:** VWD1A,Wavelength=220 nm

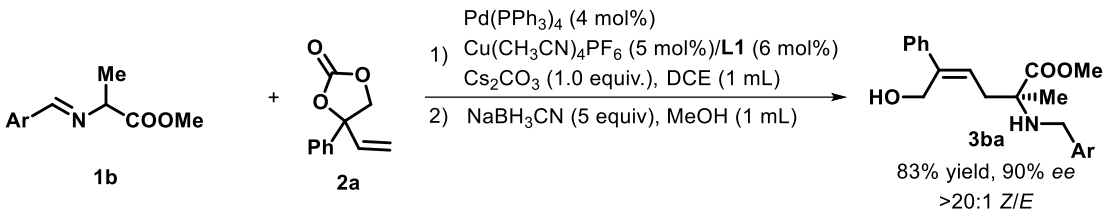
| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 11.027 | MM m | 0.25 | 346.29 | 21.72 | 49.37 | |
| 11.680 | MM m | 0.27 | 355.09 | 20.22 | 50.63 | |
| | | Sum | 701.38 | | | |




**Signal:** VWD1A,Wavelength=220 nm

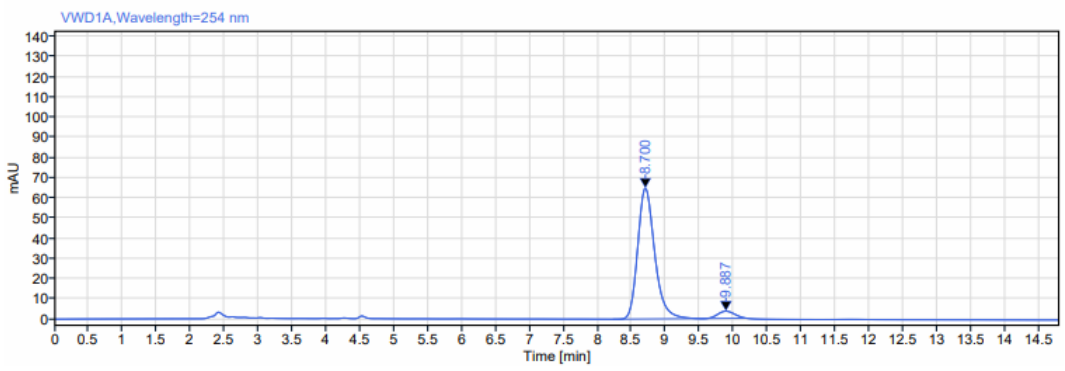
| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 10.932 | MM m | 0.25 | 660.12 | 41.49 | 76.78 | |
| 11.594 | MM m | 0.27 | 199.61 | 11.34 | 23.22 | |
| | | Sum | 859.73 | | | |

### 3.5 Gram-scale reaction for compound 3ba.




**The preparation of Cu catalyst:** $Cu(CH_3CN)_4PF_6$ (5 mol%), L (6 mol%) were stirred in DCE (20 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 30 min.

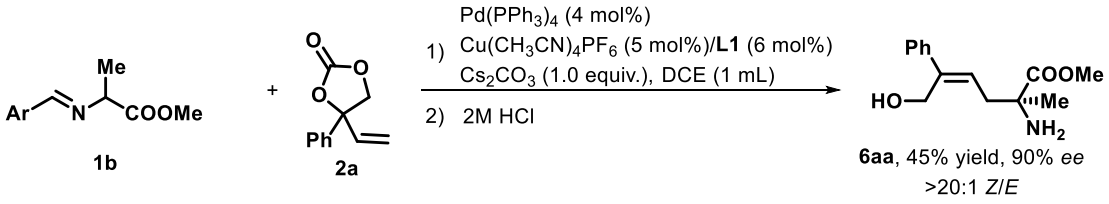
**Method:** A flame-dried Schlenk tube was cooled to r.t. and prepared with Cu catalyst. To this flask were added $Cs_2CO_3$ (1.17g, 3.6 mmol), aldimine Schiff base **1b** (3.6 mmol, 1.0 equiv) and vinylethylene carbonate **2a** (4.68 mmol, 1.3 equiv), Pd catalyst (4 mol%) and DCE (20 mL) was then added. The reaction mixture was stirred at 40 °C for 4 h. To the reaction mixture was added dry MeOH (40 mL) and $NaBH_3CN$ (1.2g, 5.0 equiv) at 0 °C and the mixture was stirred for 2 h. Extracted with EtOAc (5 mL x 3). The combined extracts were dried over $Na_2SO_4$ and concentrated in vacuo. The residue was then purified by $SiO_2$ column chromatography (PE/EA = 3:1) to give the desired products. The *ee* value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.




**Signal:** VWD1A,Wavelength=254 nm

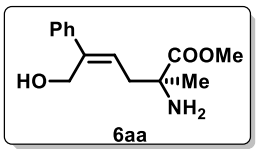
| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 8.700 | MM m | 0.27 | 1124.18 | 64.79 | 94.87 | |
| 9.887 | MM m | 0.27 | 60.82 | 3.55 | 5.13 | |
| | | Sum | 1185.00 | | | |

### 3.6 The method for the synthesis of 6aa



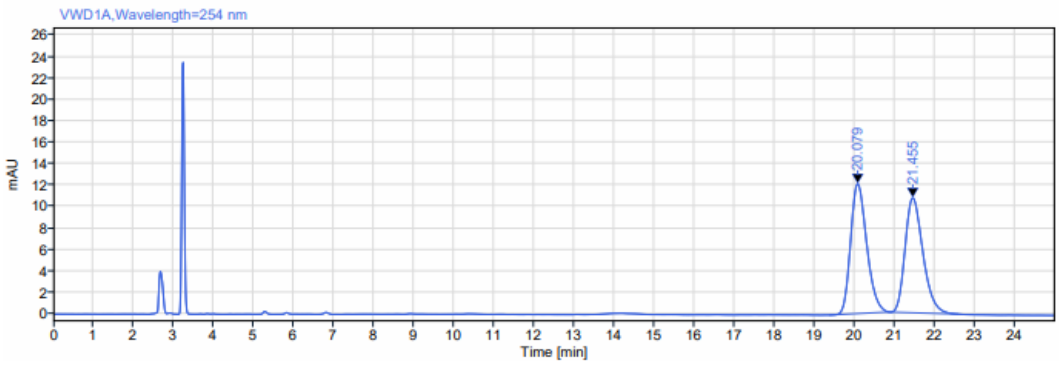
**The preparation of Cu catalyst:** $Cu(CH_3CN)_4PF_6$ (5 mol%), L (6 mol%) were stirred in THF (0.5 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 30 min.

**Method B:** A flame-dried Schlenk tube was cooled to r.t. and prepared with Cu catalyst. To this flask were added $Cs_2CO_3$ (32.6 mg, 0.1 mmol), aldimine Schiff base (0.1 mmol, 1.0 equiv) and vinylethylene carbonates (24.7 mmol, 1.3 equiv). Pd catalyst (4 mol%) and DCE (0.5 mL) was then added. The reaction mixture was stirred at 40 ºC for 4 h. To the reaction mixture was added HCl (2.0 M, 2.0 mL) at 0 ºC and the mixture was stirred for 2 h. Adjust pH to 7-8 by $NaHCO_3$, extracted with DCM (5 mL x 3). The combined extracts were dried over $Na_2SO_4$ and concentrated in vacuo. The residue was then purified by $SiO_2$ column chromatography (PE/EA = 1:2) to give the desired product. The *ee* value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.



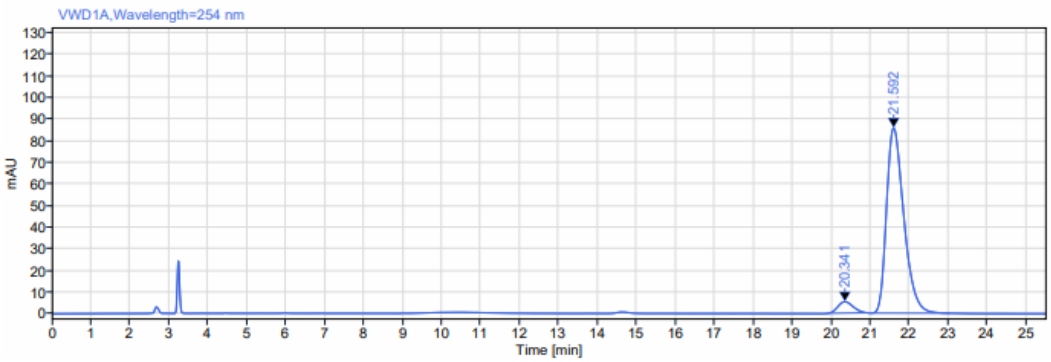
6aa

**6aa** (11.2 mg, 45% yield, PE/EA=3:1, 90% *ee*, *Z/E* >20:1) was synthesized in method B afforded 45% isolated yield as a colorless oil. $[\alpha]_D^{25}$=-29 (c=0.22, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.45 – 7.35 (m, 2H), 7.29 – 7.18 (m, 3H), 5.69 (dd, $J$ = 9.2, 7.7 Hz, 1H), 4.35 (dd, $J$ = 65.4, 12.1 Hz, 2H), 3.69 (s, 3H), 2.59 (ddd, $J$ = 30.8, 18.3, 10.2 Hz, 6H), 1.38 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 177.3, 145.3, 142.0, 128.3, 127.2, 126.1, 125.2, 59.8, 56.8, 52.7, 39.9, 26.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{19}O_3$ 250.1438; found: 250.1443. HPLC conditions: OJ-H column, 254 nm, 30 °C, flow rate: 1.2 mL/min, Hex:IPA = 95:5, 25min; $t_R$ =20.34 min (minor), 21.59 min (major).




**Signal:** VWD1A,Wavelength=254 nm

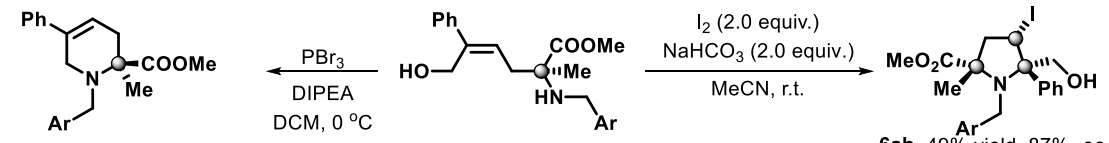
| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 20.079 | MM m | 0.43 | 338.15 | 12.10 | 50.51 | |
| 21.455 | MM m | 0.48 | 331.37 | 10.71 | 49.49 | |
| | | Sum | 669.51 | | | |




**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 20.341 | MM m | 0.42 | 142.64 | 5.27 | 5.12 | |
| 21.592 | MM m | 0.47 | 2642.65 | 85.78 | 94.88 | |
| | | Sum | 2785.30 | | | |

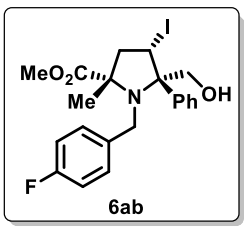
### 3.7 The method for the synthesis of 6ab and 6ac.




**6ac**, 37% yield, 87% *ee* — **3ba**, 87% ee — **6ab**, 49% yield, 87% *ee*, >20:1 *dr*

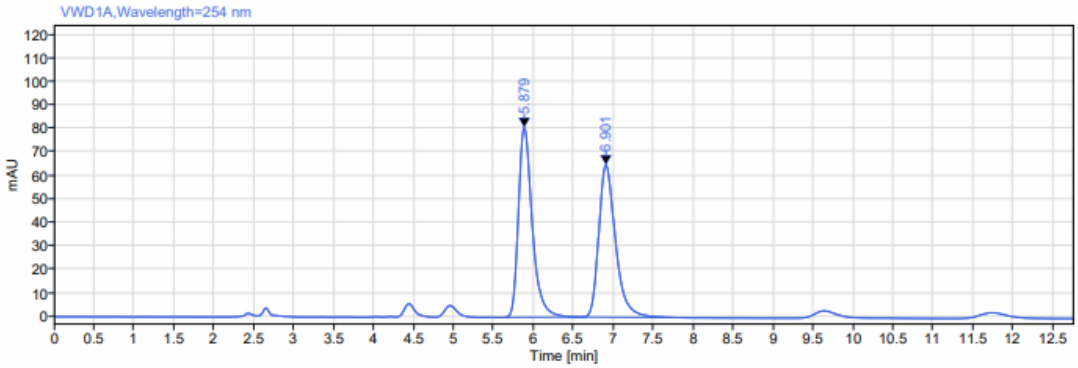
**Method C:** A flame-dried Schlenk tube was cooled to rt and filled with $N_2$. To this flask were added **3ba** (0.5 mmol, 1.0 equiv), $I_2$ (1.0 mmol, 2.0 equiv), $NaHCO_3$ (84.0 mg, 1.0 mmol) and dry MeCN at 0 °C for 30 min, then warm up to rt for 12h. The reaction mixture was quenched by $Na_2S_2O_3$(aq.) and extracted with EA, then concentrated in vacuo. The residue was then purified by $SiO_2$ column chromatography (PE/EA = 15:1) to give the desired products. The *ee* value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.

**Method D:** A flame-dried Schlenk tube was cooled to rt and filled with $N_2$. To this flask were added **3ba** (0.1 mmol, 1.0 equiv), $PBr_3$ (0.05 mmol, 0.5 equiv) and dry DCM at 0 °C for 2 hours, then add DIPEA (0.1 mmol) at 0 °C for 24 h. The reaction mixture was extracted with EA, then concentrated in vacuo. The residue was then purified by $SiO_2$ column chromatography (PE/EA = 20:1) to give the desired products. The *ee* value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.



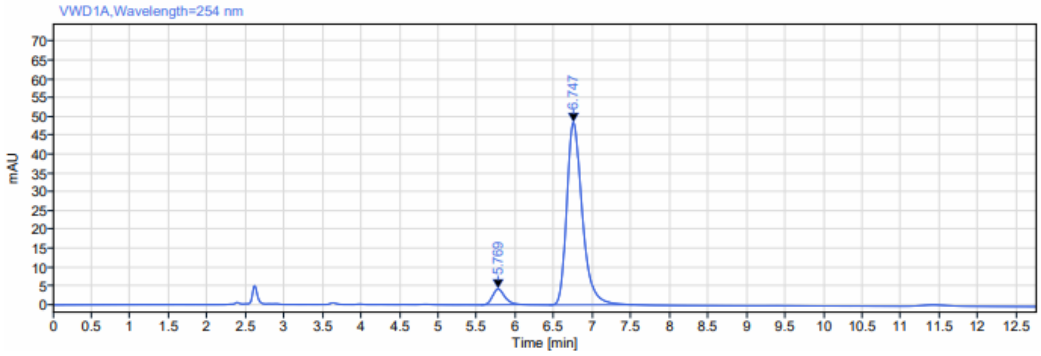

**6ab** (118.9 mg, 49% yield, PE/EA=3:1, 87% *ee*, *Z/E* >20:1) was synthesized in method C afforded 49% isolated yield as a yellow oil. $[\alpha]_D^{25}$ =+5 (c=1.20, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.46 – 7.37 (m, 2H), 7.37 – 7.32 (m, 1H), 7.29 – 7.25 (m, 2H), 6.95 – 6.80 (m, 4H), 4.56 (t, $J$ = 11.8 Hz, 1H), 4.36 (dd, $J$ = 12.9, 7.3 Hz, 1H), 4.29 (d, $J$ = 12.1 Hz, 1H), 3.80 – 3.68 (m, 3H), 3.61 (s, 3H), 3.03 (t, $J$ = 12.6 Hz, 1H), 2.33 (dd, $J$ = 12.1, 7.4 Hz, 1H), 1.57 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 177.5, 162.1 (d, $J$ = 245.9 Hz), 140.4, 133.6 (d, $J$ = 3.1 Hz),

131.2 (d, $J$ = 8.1 Hz), 128.6, 127.7, 127.0, 114.9 (d, $J$ = 21.2 Hz), 73.1, 68.4, 67.6, 52.8, 49.5, 49.2, 33.9, 22.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}FINO_3$ 484.0779; found: 484.0798. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 15min; $t_R$ =5.77 min (major), 6.75 min (minor).



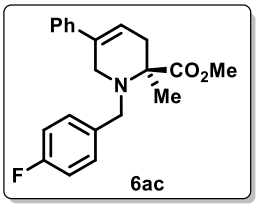

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 5.879 | MM m | 0.18 | 970.68 | 80.63 | 50.58 | |
| 6.901 | MM m | 0.22 | 948.35 | 64.72 | 49.42 | |
| | | Sum | 1919.03 | | | |



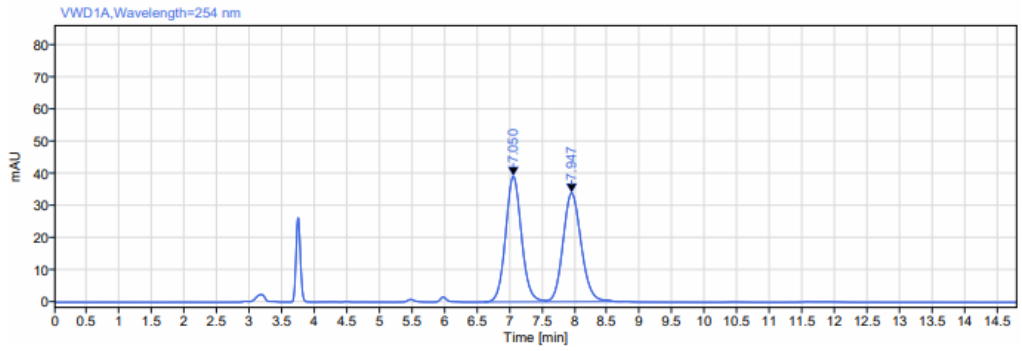

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 5.769 | MM m | 0.17 | 45.98 | 4.18 | 6.33 | |
| 6.747 | MM m | 0.21 | 680.23 | 48.46 | 93.67 | |
| | | Sum | 726.21 | | | |



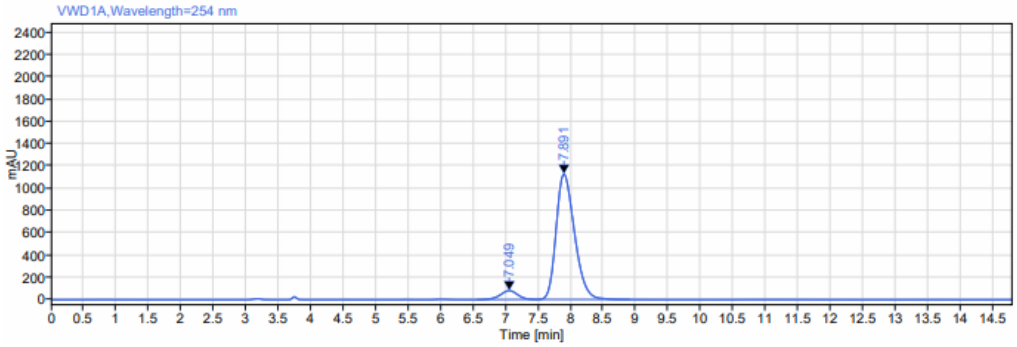

**6ac** (12.5 mg, 37% yield, PE/EA=20:1, 87% *ee*, *Z*/*E* >20:1) was synthesized in method D afforded 37% isolated yield as a colorless oil. $[\alpha]_D^{25}$ =+16 (c=0.25, $CHCl_3$). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35 – 7.25 (m, 2H), 7.23 – 7.05 (m, 5H), 7.03 – 6.80 (m, 2H), 6.01 (s, 1H), 3.78 (dd, $J$ = 151.7, 14.0 Hz, 5H), 3.52 – 3.25 (m, 2H), 2.91 – 2.23 (m, 2H), 1.43 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.0, 161.9 (d, $J$ = 244.3 Hz), 139.2, 135.7 (d, $J$ = 2.9 Hz), 134.4, 129.8 (d, $J$ = 7.9 Hz), 128.3, 127.1, 124.8, 120.2, 115.0 (d, $J$ = 21.2 Hz), 61.3, 54.7, 51.8, 49.6, 36.5, 22.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{22}FNO_2$ 340.1707;

found: 340.1726. HPLC conditions: OJ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 90:10, 15min; $t_R$ =7.05 min (minor), 7.89 min (major).




**Signal:** VWD1A,Wavelength=254 nm

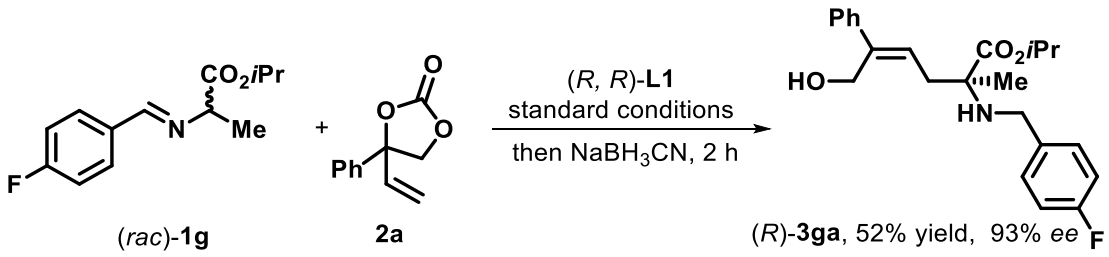
| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.050 | MM m | 0.26 | 665.59 | 39.10 | 50.27 | |
| 7.947 | MM m | 0.30 | 658.44 | 33.82 | 49.73 | |
| | | Sum | 1324.04 | | | |

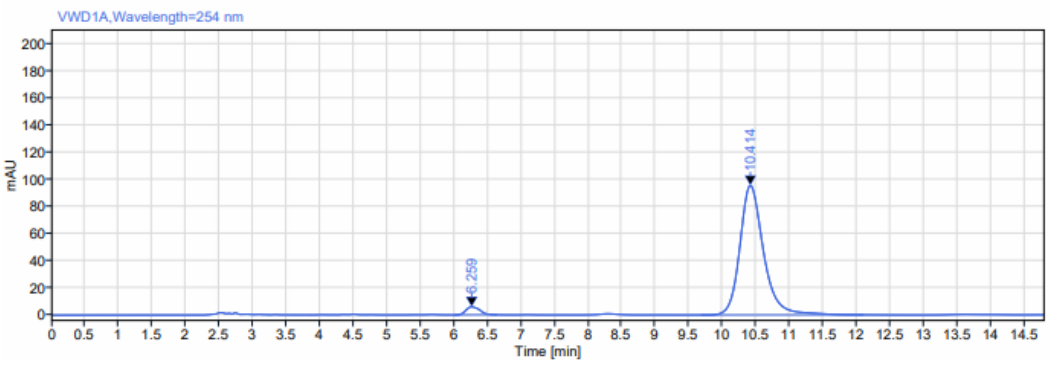



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 7.049 | MM m | 0.28 | 1483.05 | 80.17 | 6.27 | |
| 7.891 | MM m | 0.30 | 22176.03 | 1127.13 | 93.73 | |
| | | Sum | 23659.08 | | | |

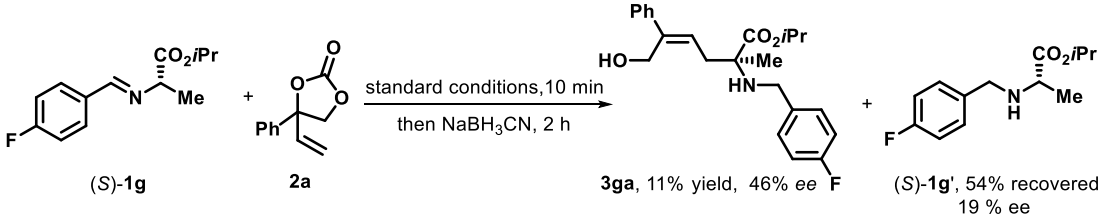
### 3.8 HPLC spectrum of compounds (*R*)-3ga, (*S*)-3ga, (*S*)-1g′, and (*R*)-1g′

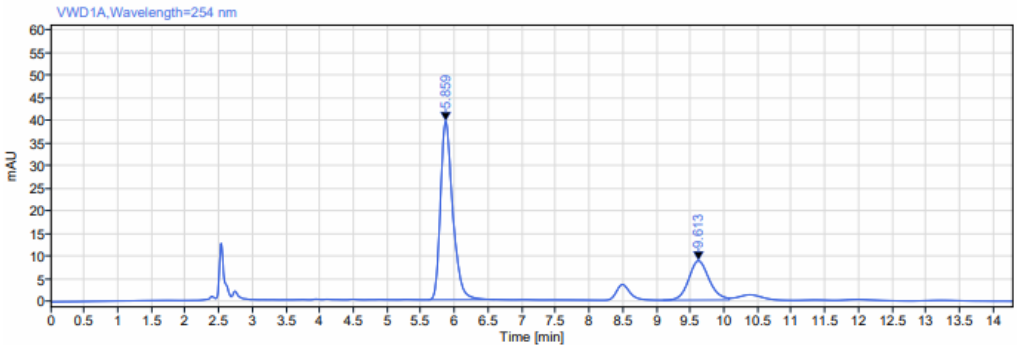





**Signal:** VWD1A,Wavelength=254 nm

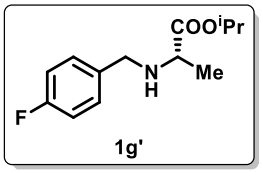
| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 6.259 | MM m | 0.20 | 84.97 | 5.95 | 3.50 | |
| 10.414 | MM m | 0.37 | 2345.28 | 95.65 | 96.50 | |
| | | Sum | 2430.25 | | | |



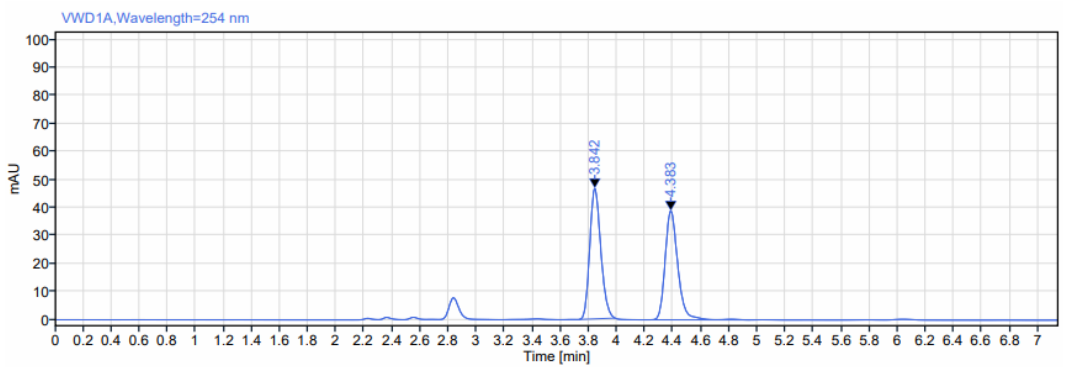




**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 5.859 | MM m | 0.19 | 498.05 | 39.38 | 73.22 | |
| 9.613 | MM m | 0.32 | 182.13 | 8.65 | 26.78 | |
| | | Sum | 680.19 | | | |

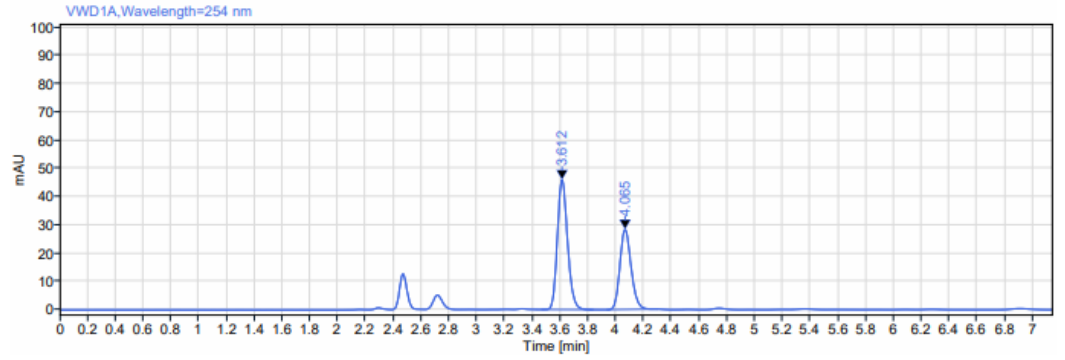



**1g'** (12.9 mg, 54% recovered, PE/EA=20:1, 19% *ee*) was colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32 – 7.13 (m, 2H), 7.08 – 6.82 (m, 2H), 5.30 – 4.69 (m, 1H), 3.62 (dd, $J$ = 57.8, 12.7 Hz, 2H), 3.24 (q, $J$ = 7.0 Hz, 1H), 1.79 (s, 1H), 1.52 – 0.89 (m, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.2, 162.0 (d, $J$ = 244.7 Hz), 135.5 (d, $J$ = 3.0 Hz), 129.8 (d, $J$ = 8.0 Hz), 115.2 (d, $J$ = 21.2 Hz), 68.2, 56.0, 51.2, 21.9, 21.8, 19.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{18}FNO_2$ 240.1394; found: 240.1411. HPLC conditions: AD-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 97:3, 15min; $t_R$ =3.61 min, 4.07 min.



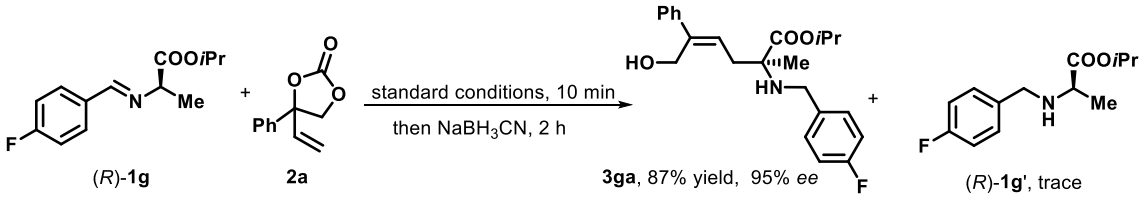

**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 3.842 | MM m | 0.08 | 254.36 | 46.57 | 50.99 | |
| 4.383 | MM m | 0.10 | 244.49 | 38.88 | 49.01 | |
| | | Sum | 498.84 | | | |

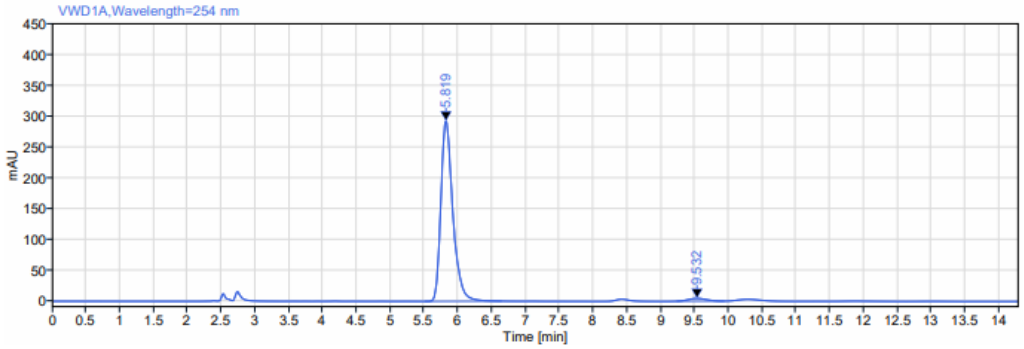



**Signal:** VWD1A,Wavelength=254 nm

| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 3.612 | MM m | 0.08 | 234.52 | 45.95 | 59.62 | |
| 4.065 | MM m | 0.09 | 158.84 | 28.32 | 40.38 | |
| | | Sum | 393.37 | | | |




(*R*)-**1g** **2a** **3ga**, 87% yield, 95% *ee* (*R*)-**1g'**, trace




**Signal:** VWD1A,Wavelength=254 nm

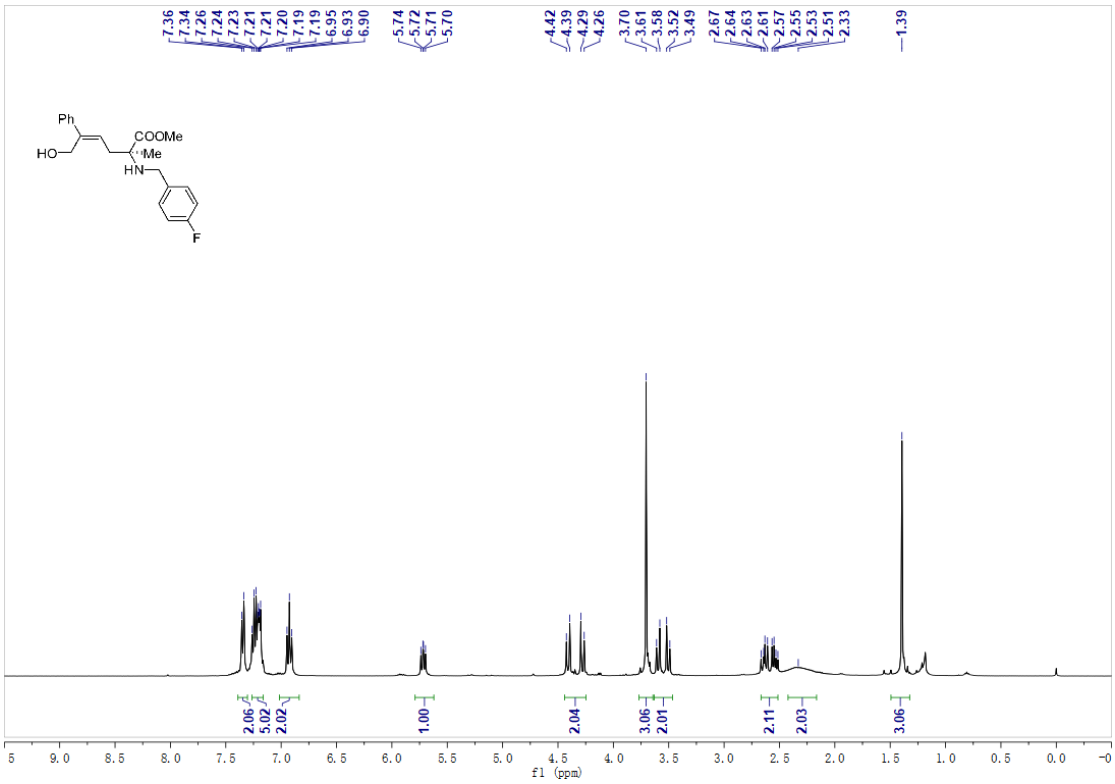
| RT [min] | Type | Width [min] | Area | Height | Area% | Name |
|---|---|---|---|---|---|---|
| 5.819 | MM m | 0.19 | 3617.94 | 293.18 | 97.66 | |
| 9.532 | MM m | 0.29 | 86.55 | 4.67 | 2.34 | |
| | | Sum | 3704.48 | | | |

## 4. References

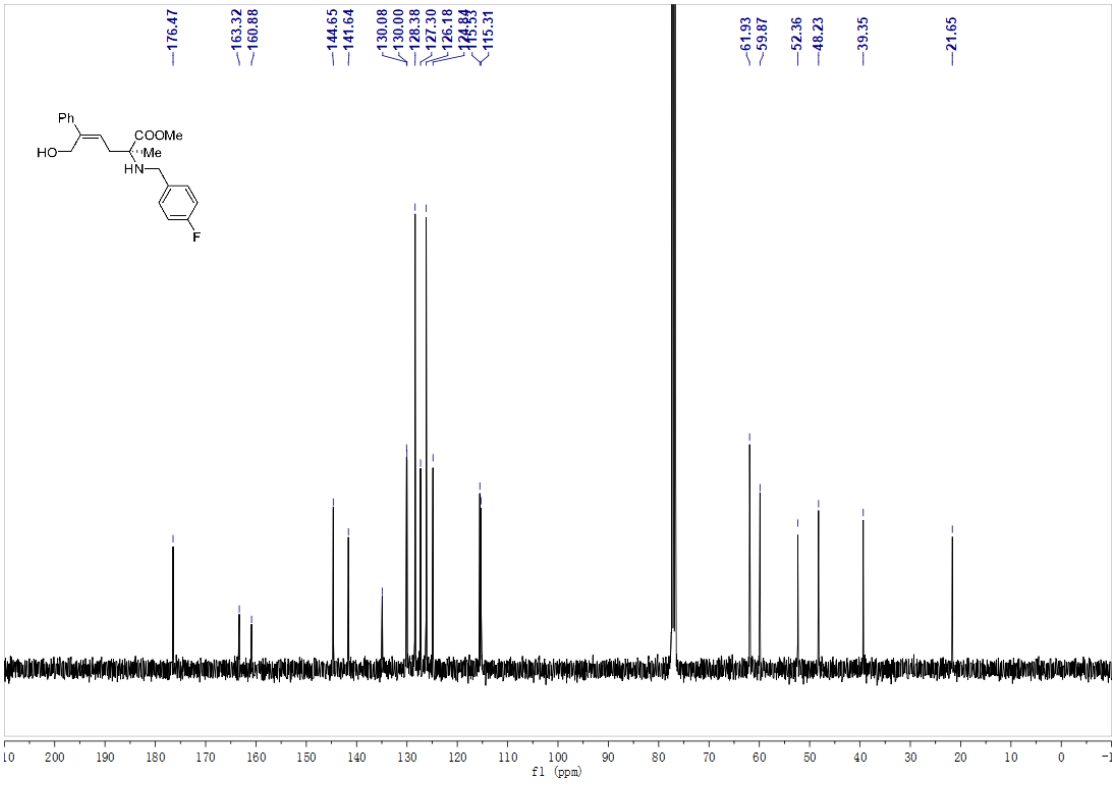
1. a) M. Ke, G. Huang, L. Ding, J. Fang, F. Chen, *ChemCatChem*, 2019, **11**, 4720-4724; b) M. Ke, Z. Liu, G. Huang, J. Wang, Y. Tao, F. Chen, *Org. Lett.* 2020, **22**, 4135-4140.
2. X. Huo, J. Zhang, J. Fu, R. He, W. Zhang, *J. Am. Chem. Soc.* 2018, **140**, 2080−2084.

## 5. Copies of $^{1}$H and $^{13}$ C spectrum of trisubstituted allylic amino acids

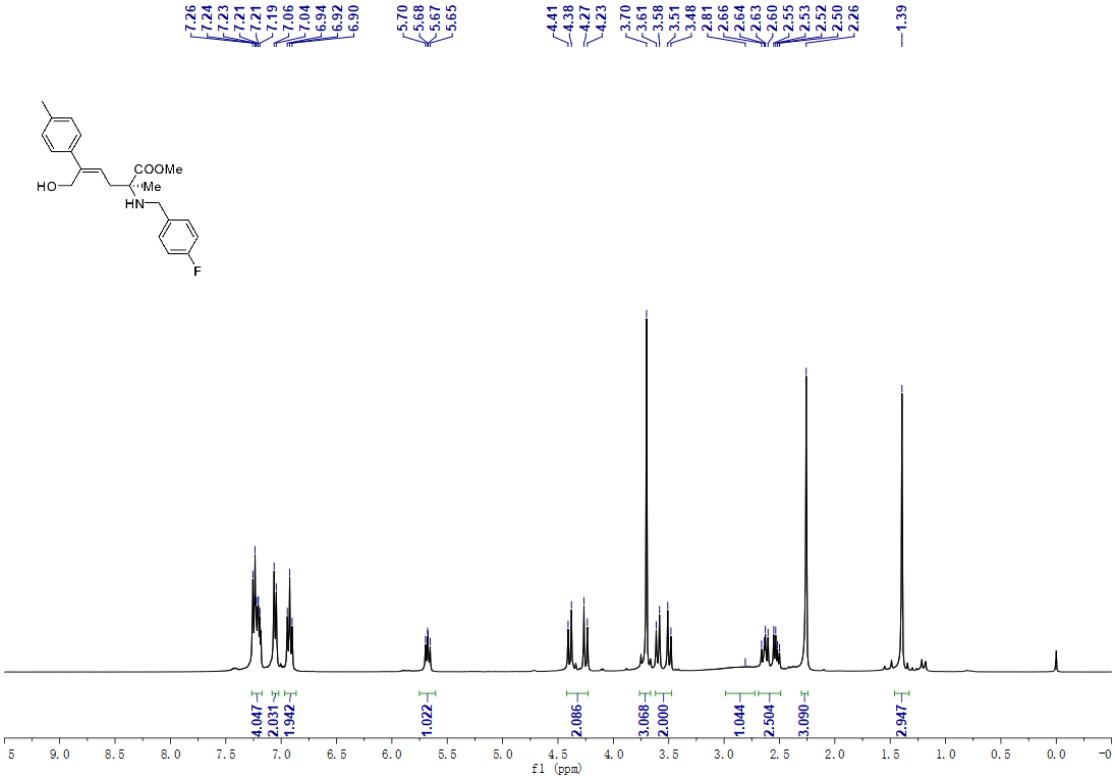
**$^{1}$H NMR** spectrum of **3ba** in $CDCl_3$



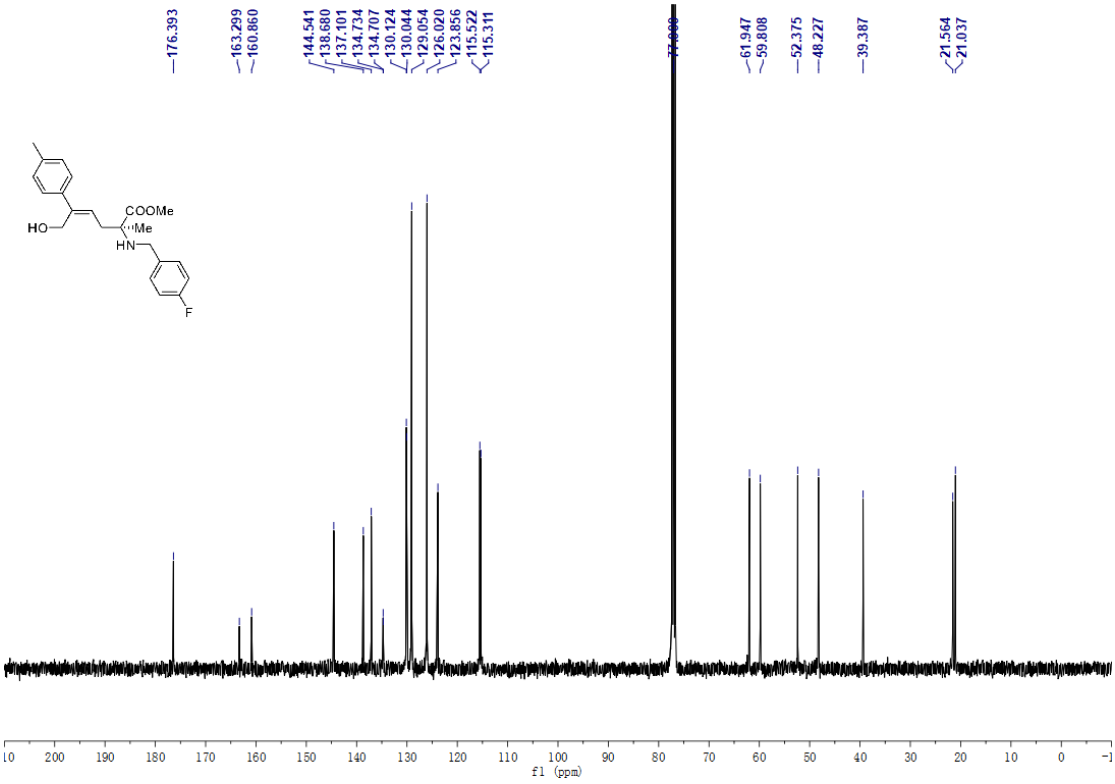

**$^{13}$C NMR** spectrum of **3ba** in $CDCl_3$



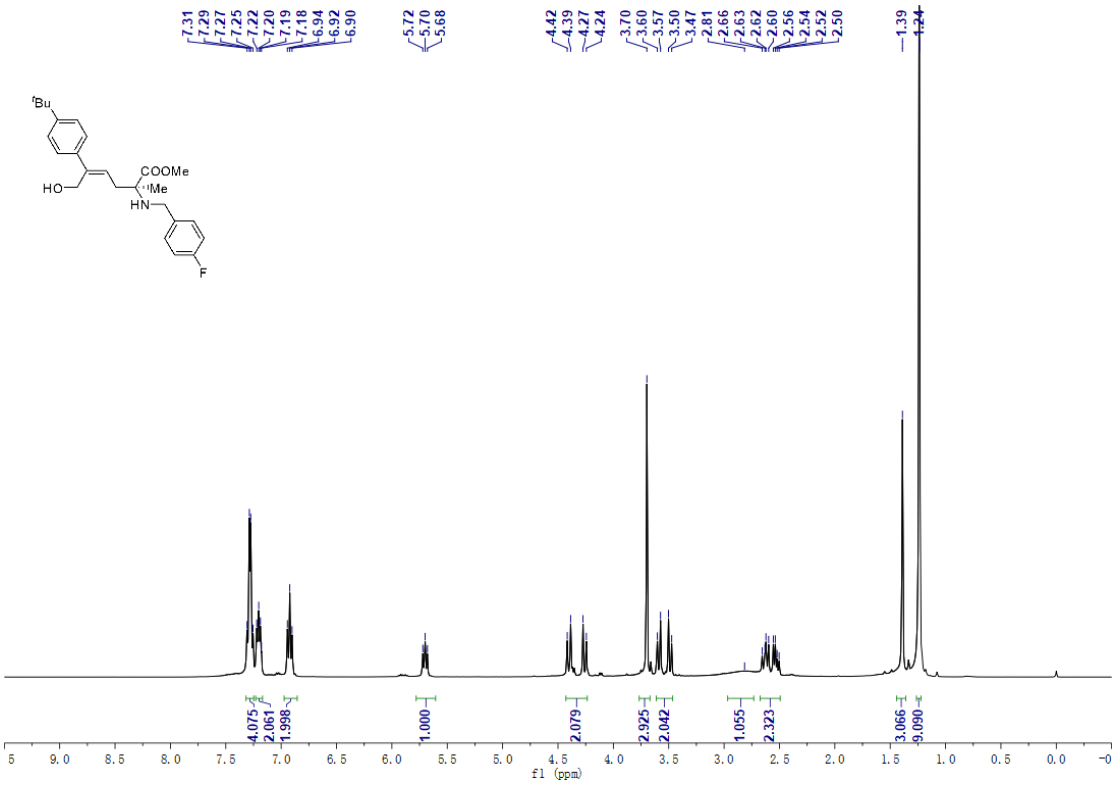
**$^{1}$H NMR** spectrum of **3bb** in $CDCl_3$



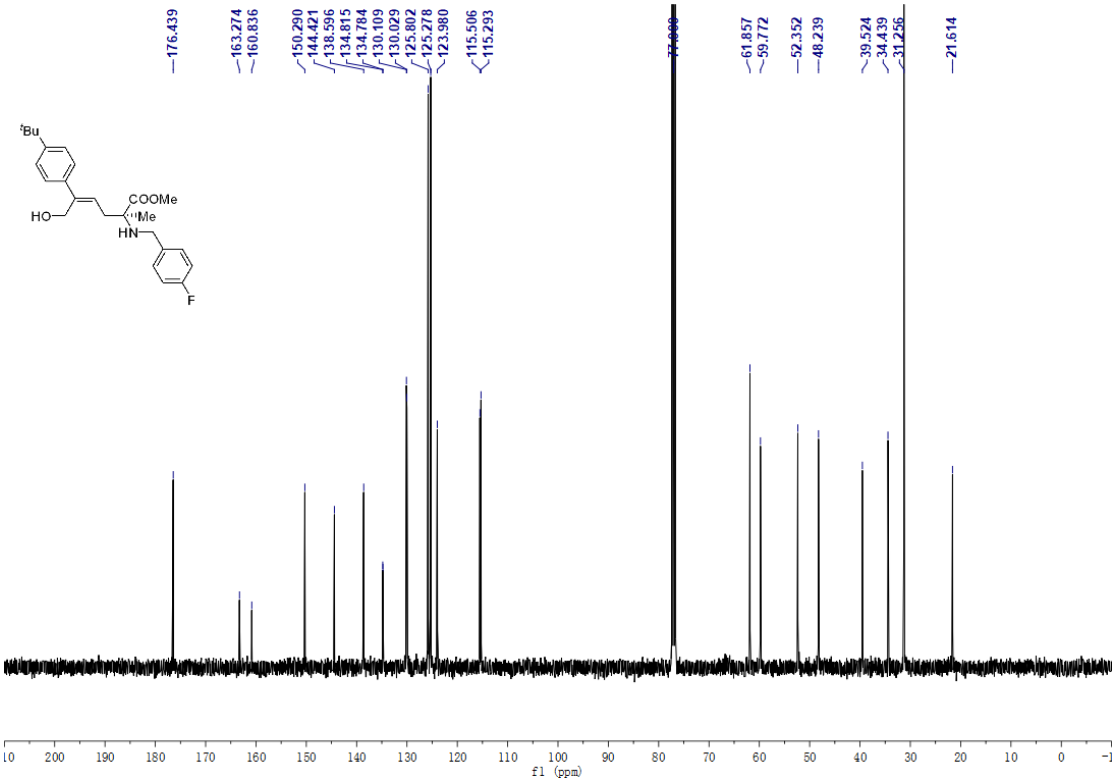

**$^{13}$C NMR** spectrum of **3bb** in $CDCl_3$



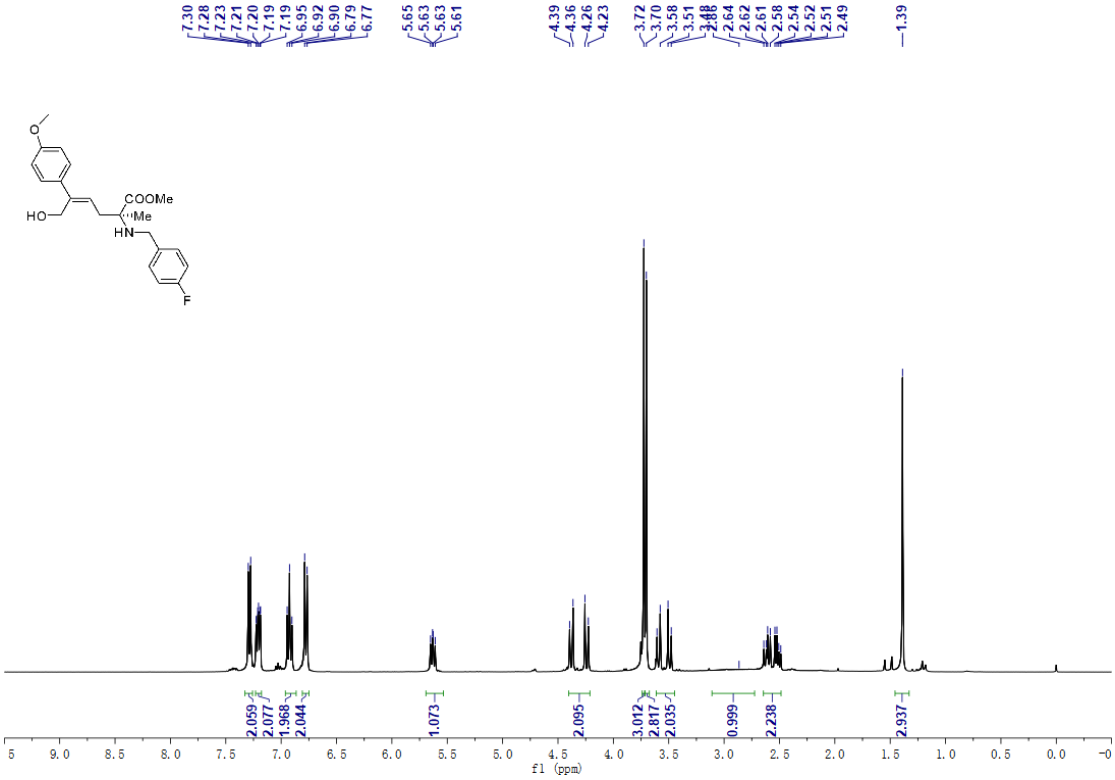
**$^{1}$H NMR** spectrum of **3bc** in $CDCl_3$



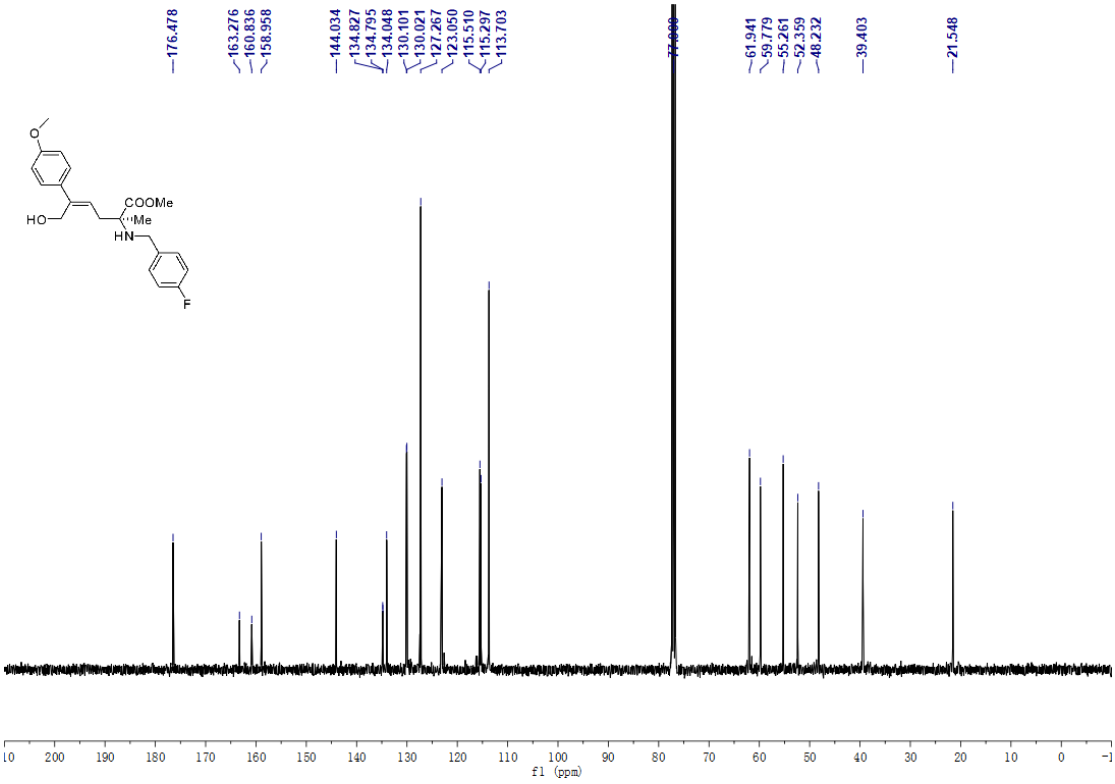

**$^{13}$C NMR** spectrum of **3bc** in $CDCl_3$



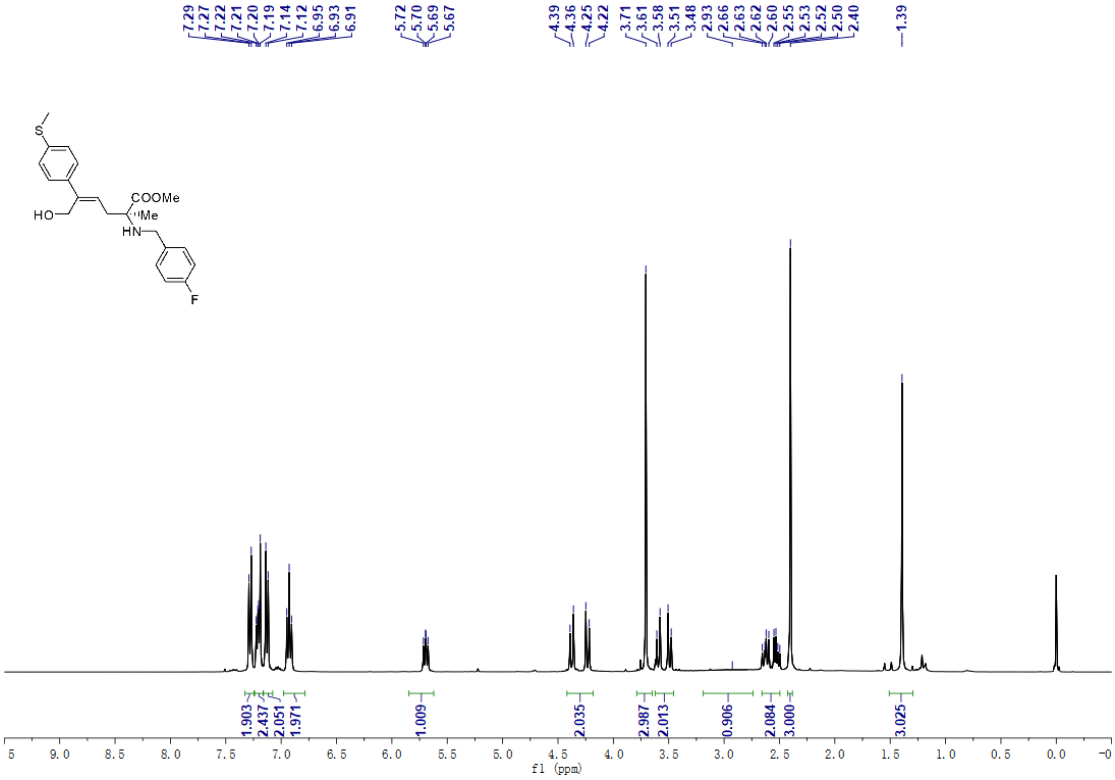
**$^{1}$H NMR** spectrum of **3bd** in $CDCl_3$



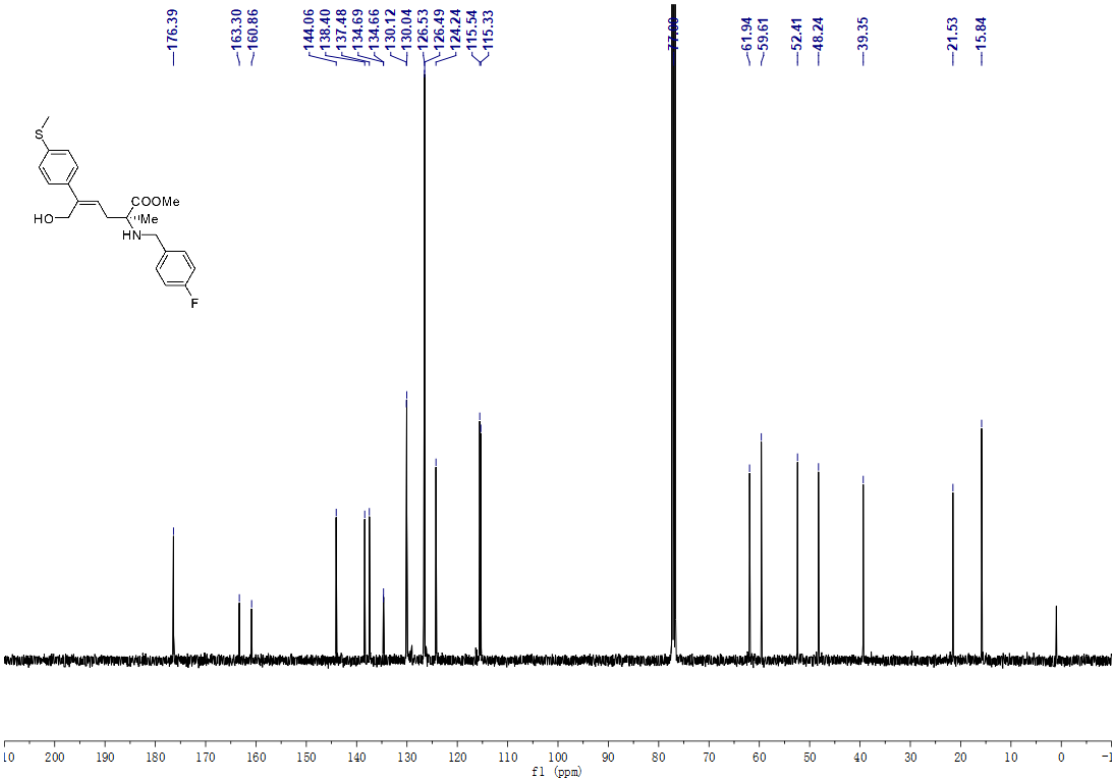

**$^{13}$C NMR** spectrum of **3bd** in $CDCl_3$



**$^{1}$H NMR** spectrum of **3be** in $CDCl_3$




**$^{13}$C NMR** spectrum of **3be** in $CDCl_3$



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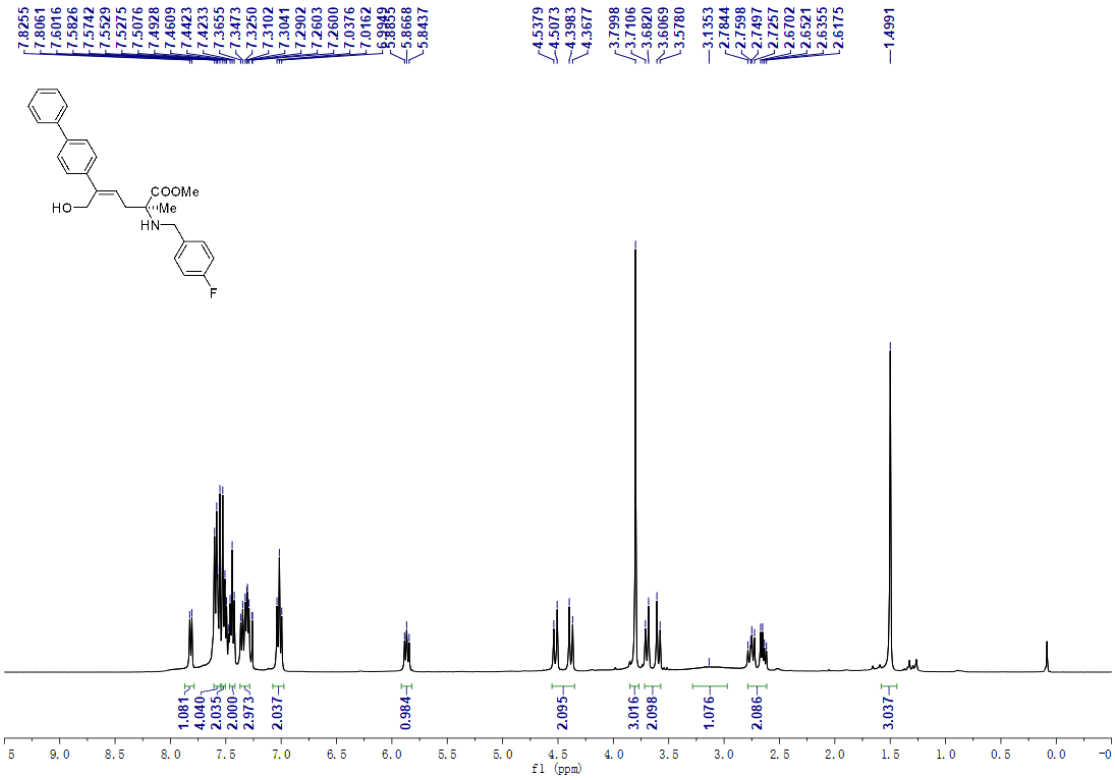
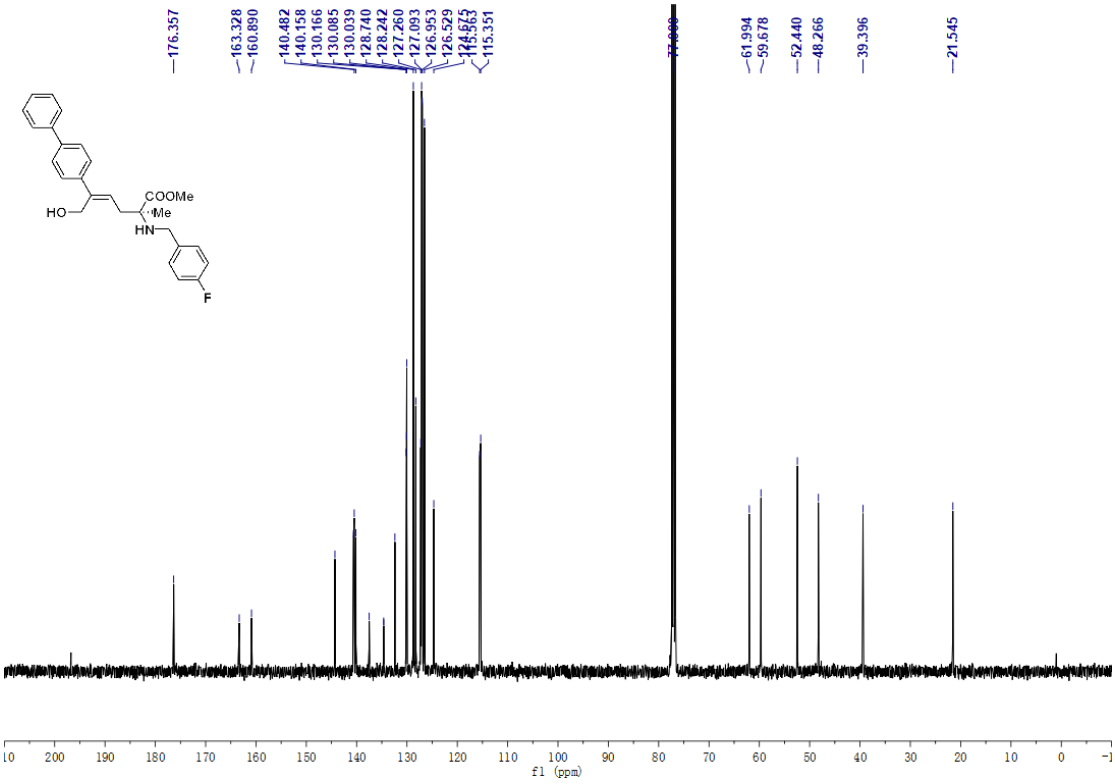
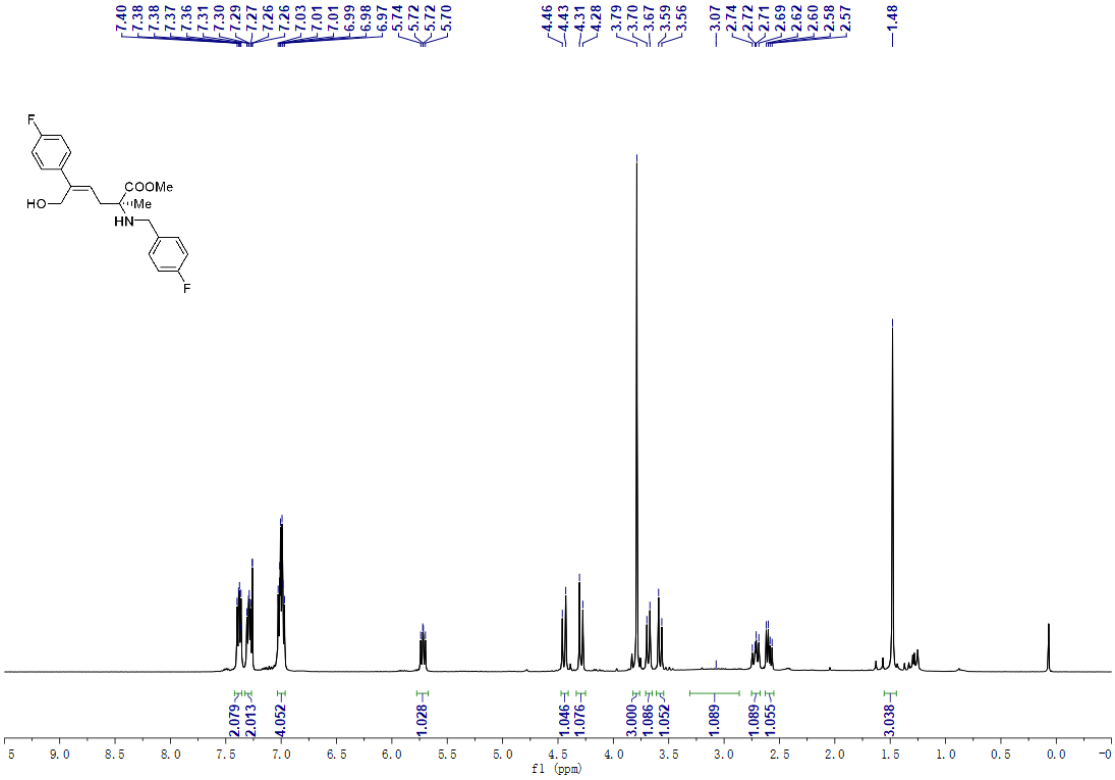


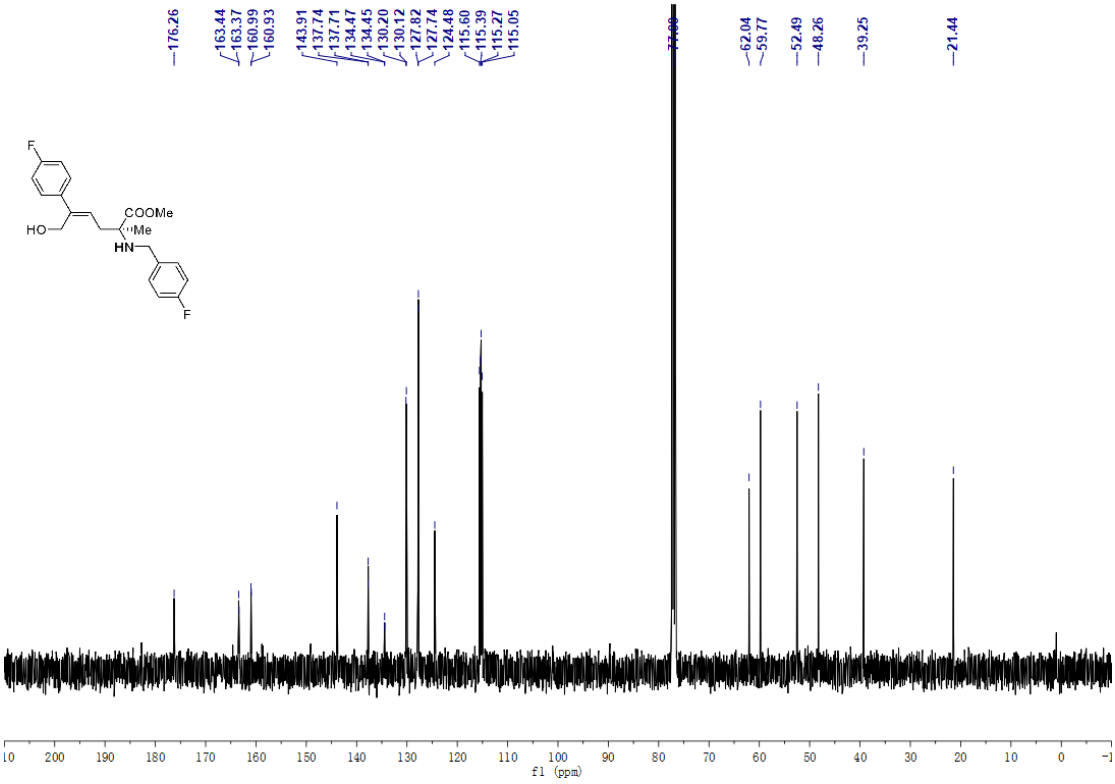

**$^{13}$C NMR** spectrum of **3bf** in $CDCl_3$



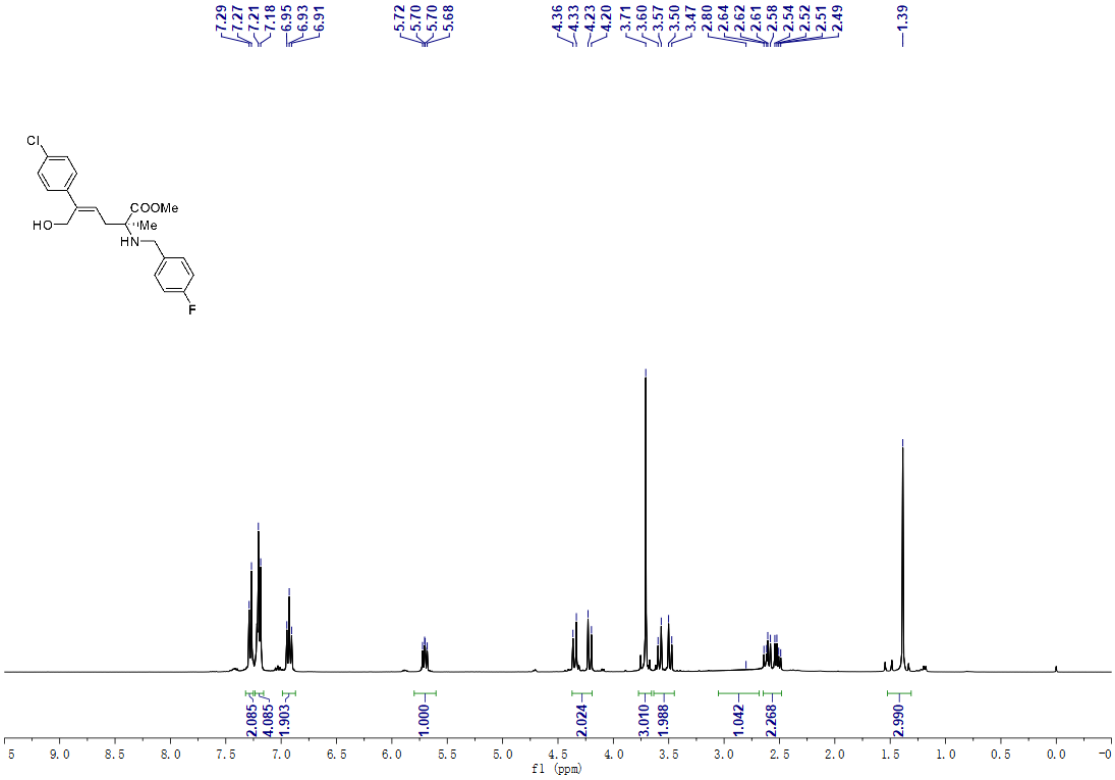
**$^{1}$H NMR** spectrum of **3bg** in $CDCl_3$



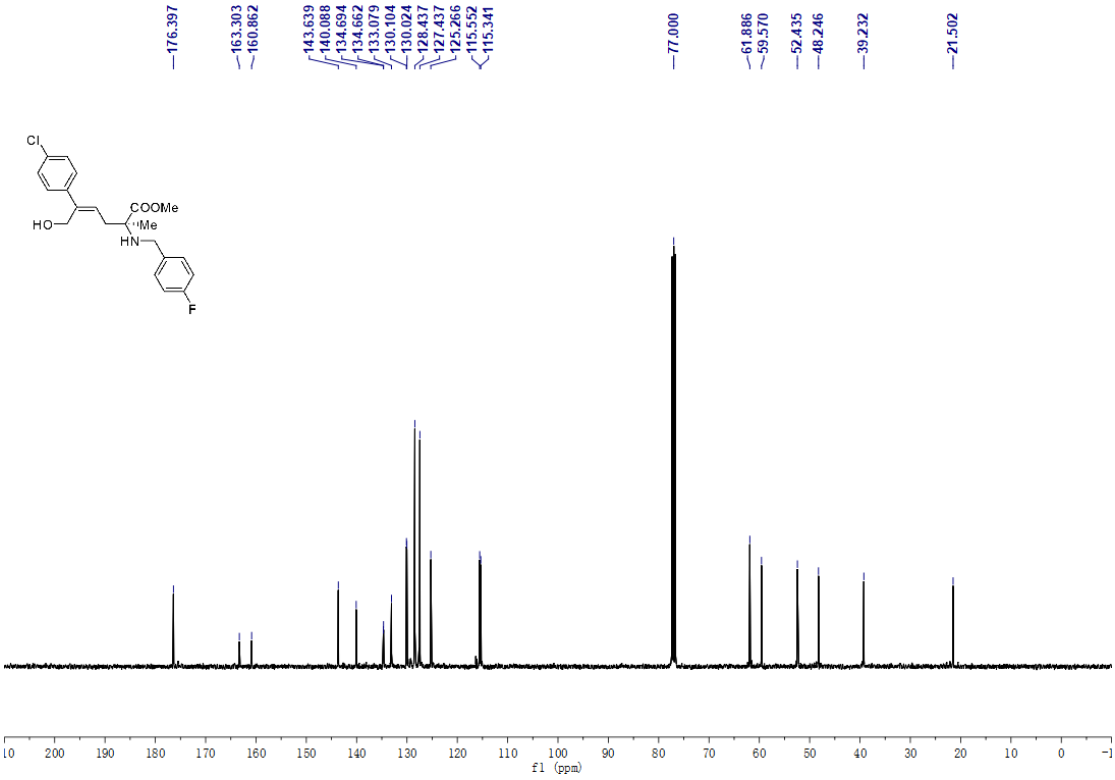

**$^{13}$C NMR** spectrum of **3bg** in $CDCl_3$



**$^{1}$H NMR** spectrum of **3bh** in $CDCl_3$




**$^{13}$C NMR** spectrum of **3bh** in $CDCl_3$



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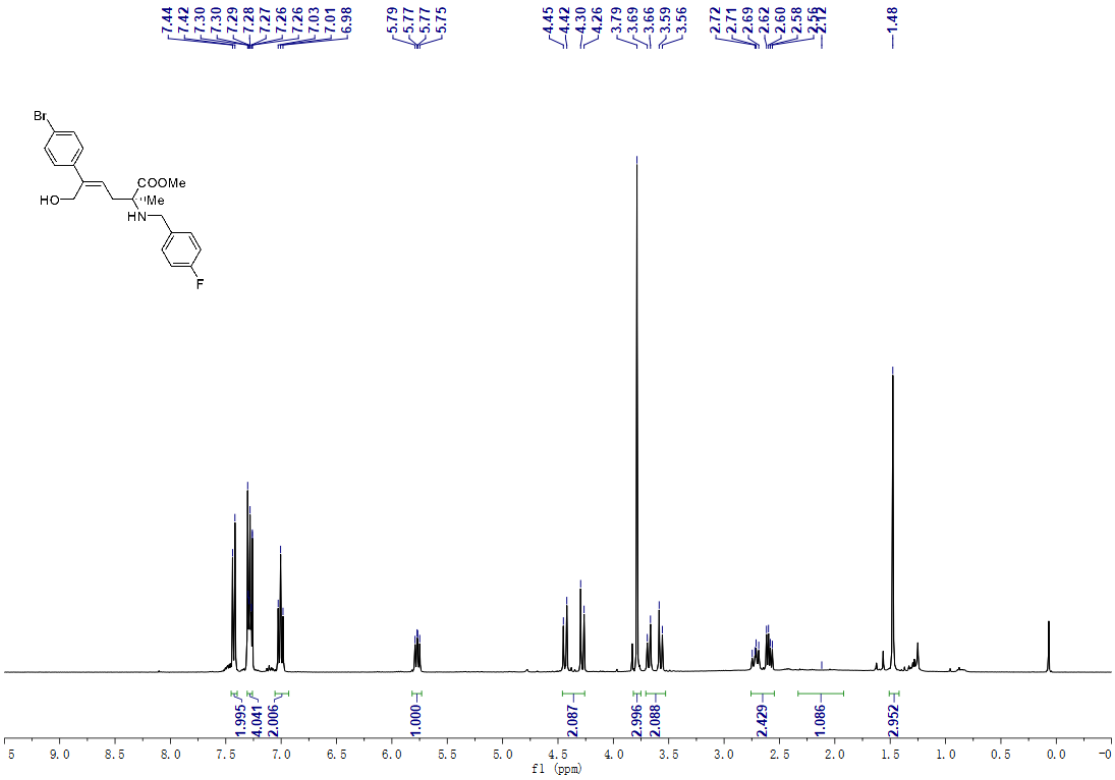
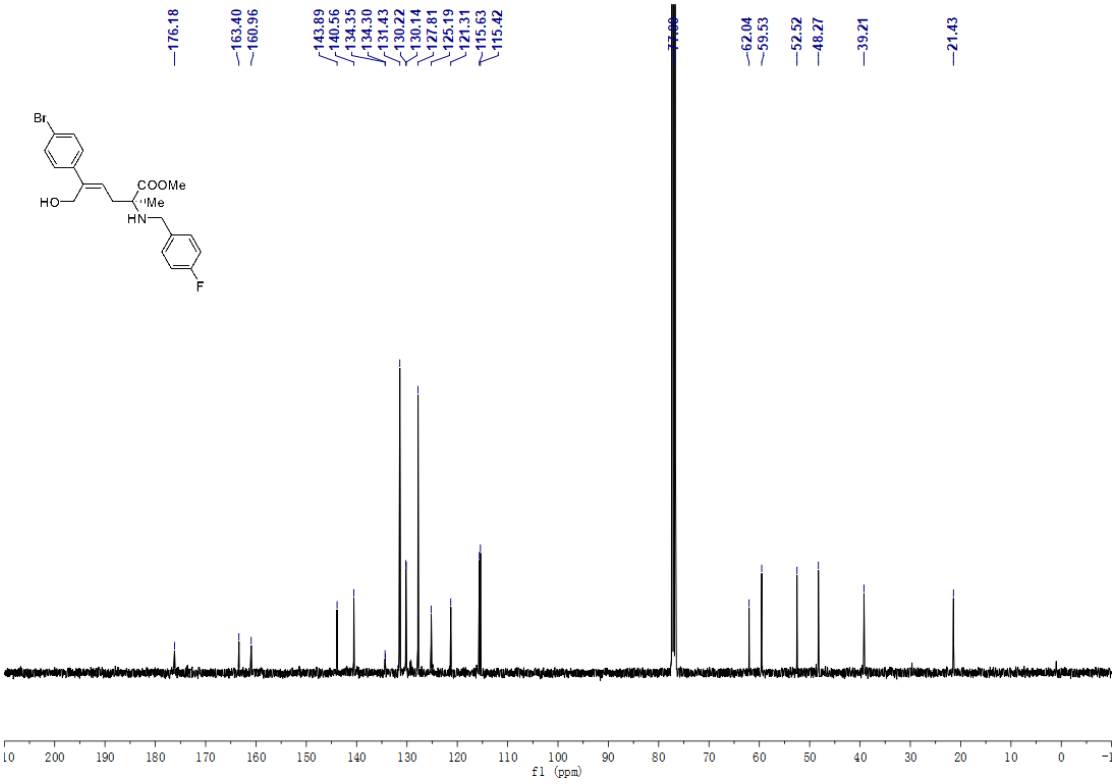
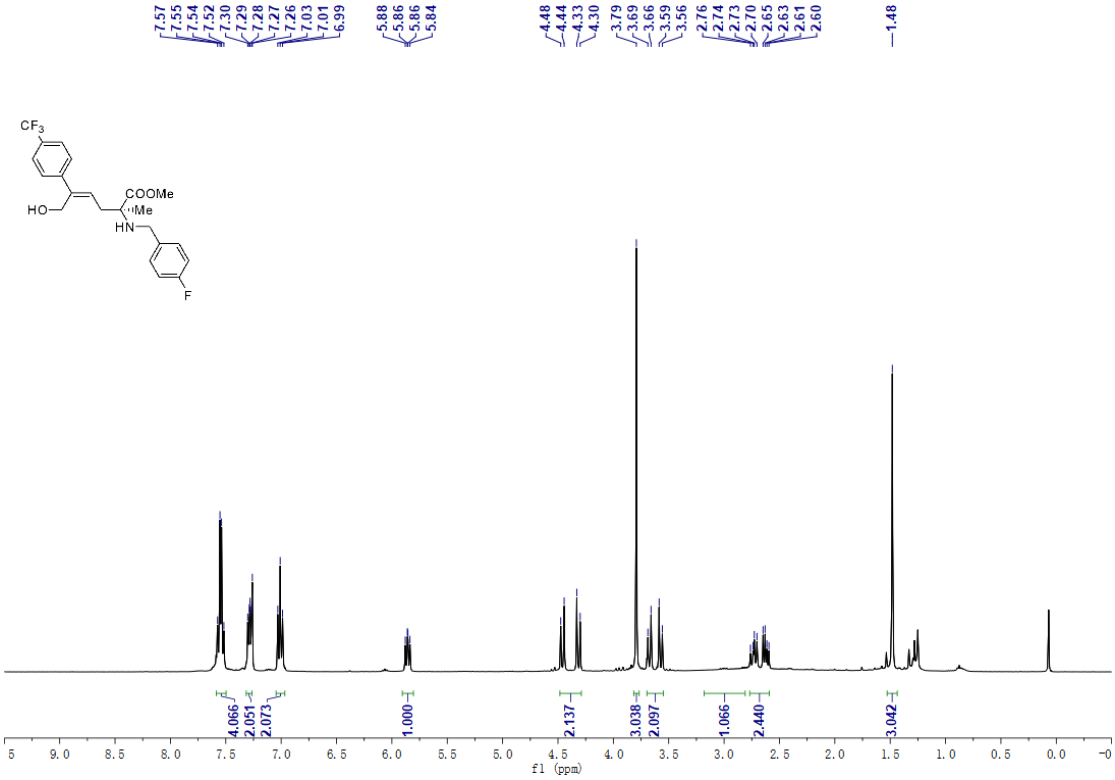


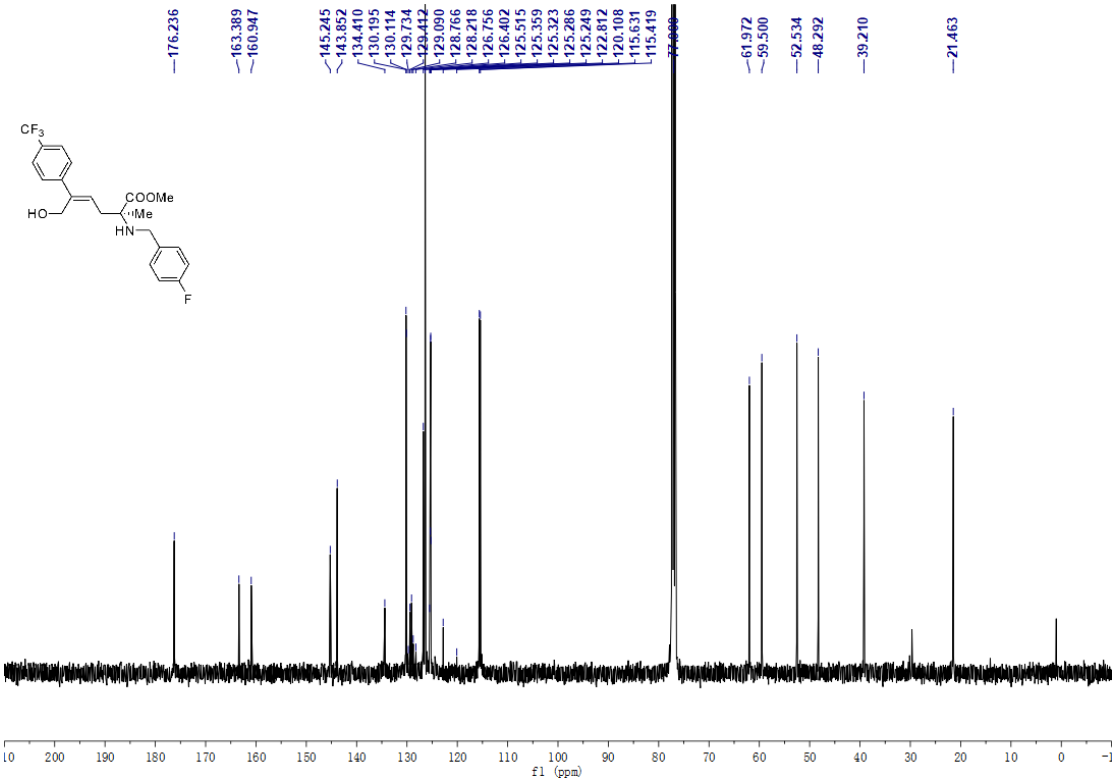

**$^{13}$C NMR** spectrum of **3bi** in $CDCl_3$



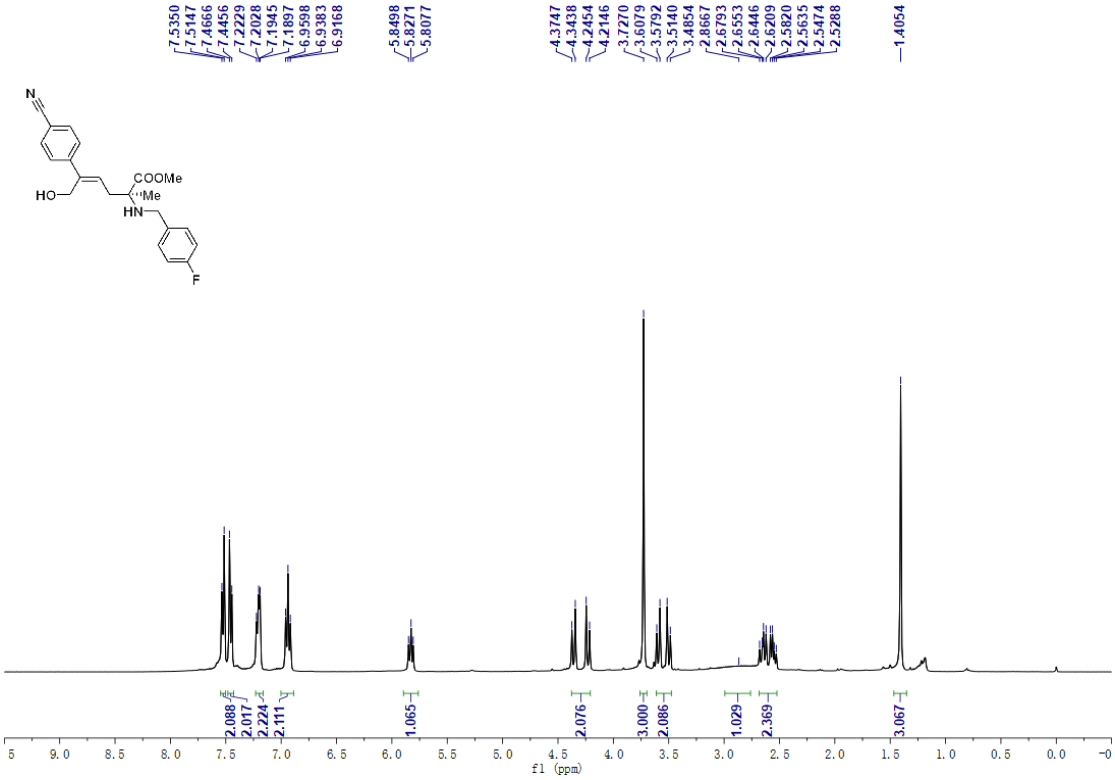
**$^{1}$H NMR** spectrum of **3bj** in $CDCl_3$



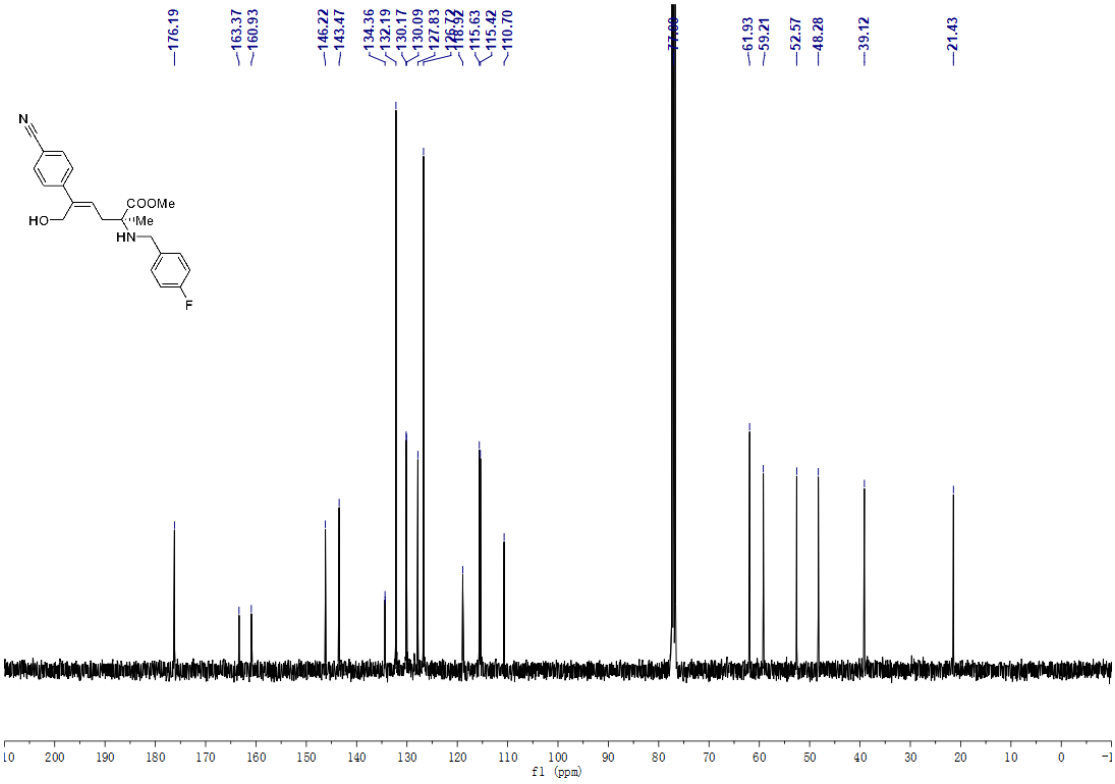

**$^{13}$C NMR** spectrum of **3bj** in $CDCl_3$



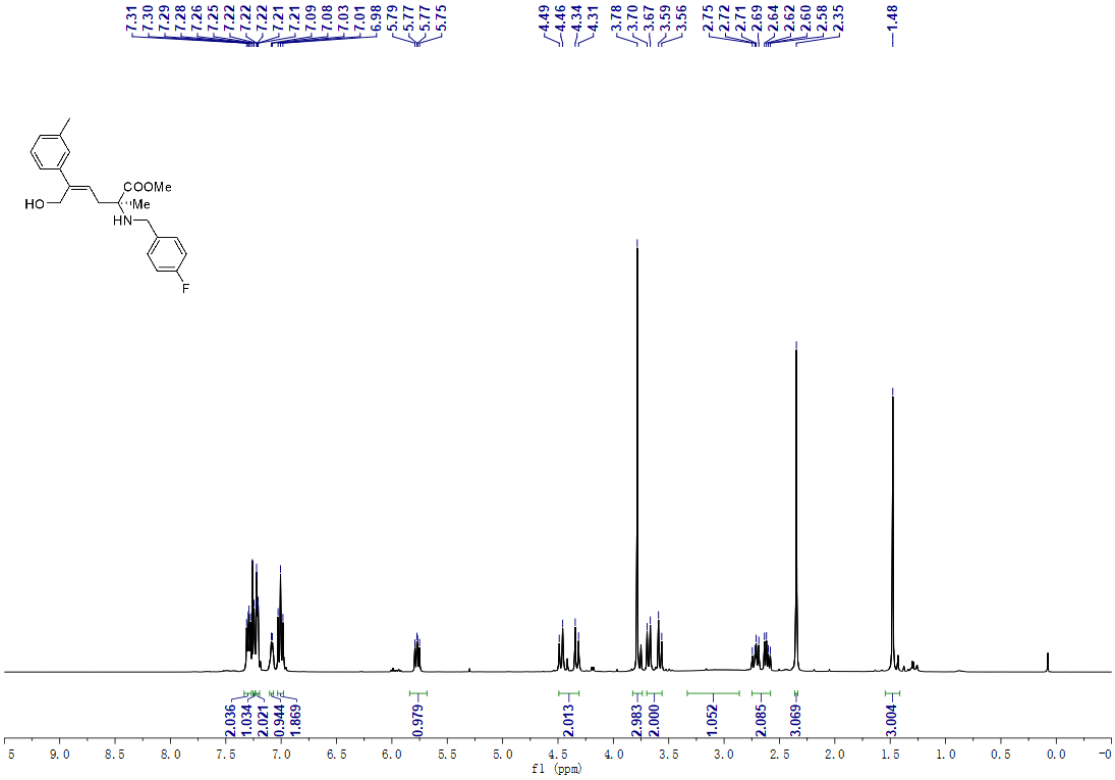
**$^{1}$H NMR** spectrum of **3bk** in $CDCl_3$



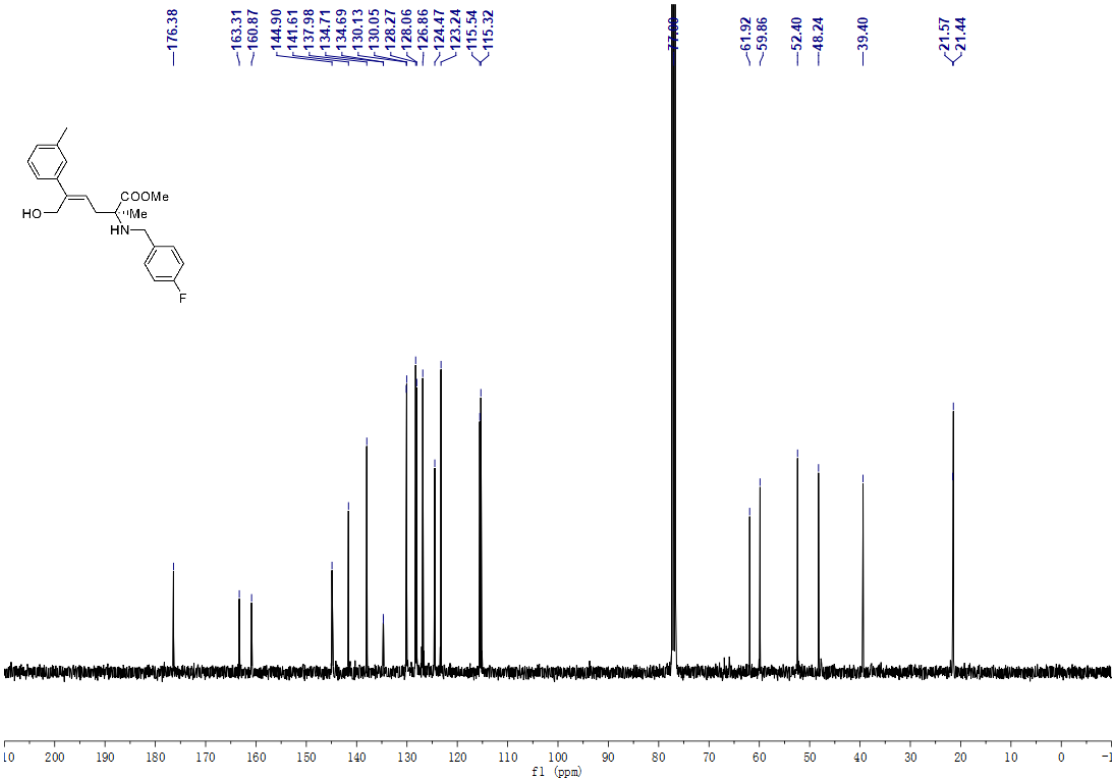

**$^{13}$C NMR** spectrum of **3bk** in $CDCl_3$



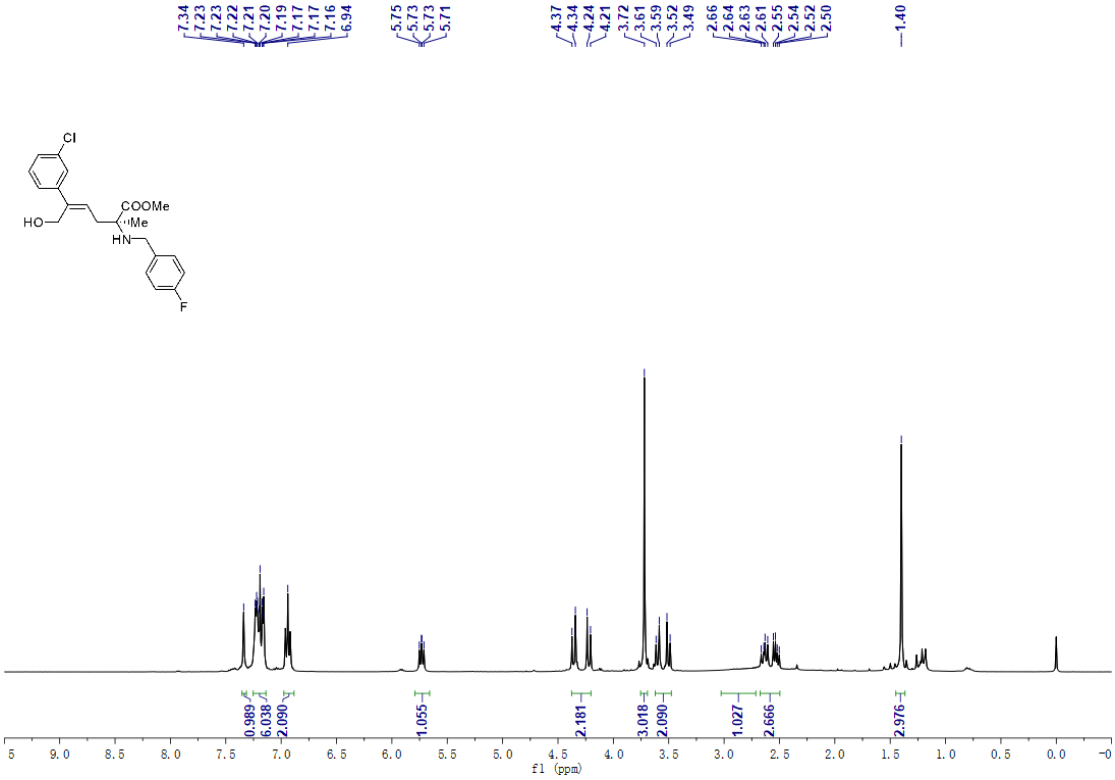
**$^{1}$H NMR** spectrum of **3bl** in $CDCl_3$



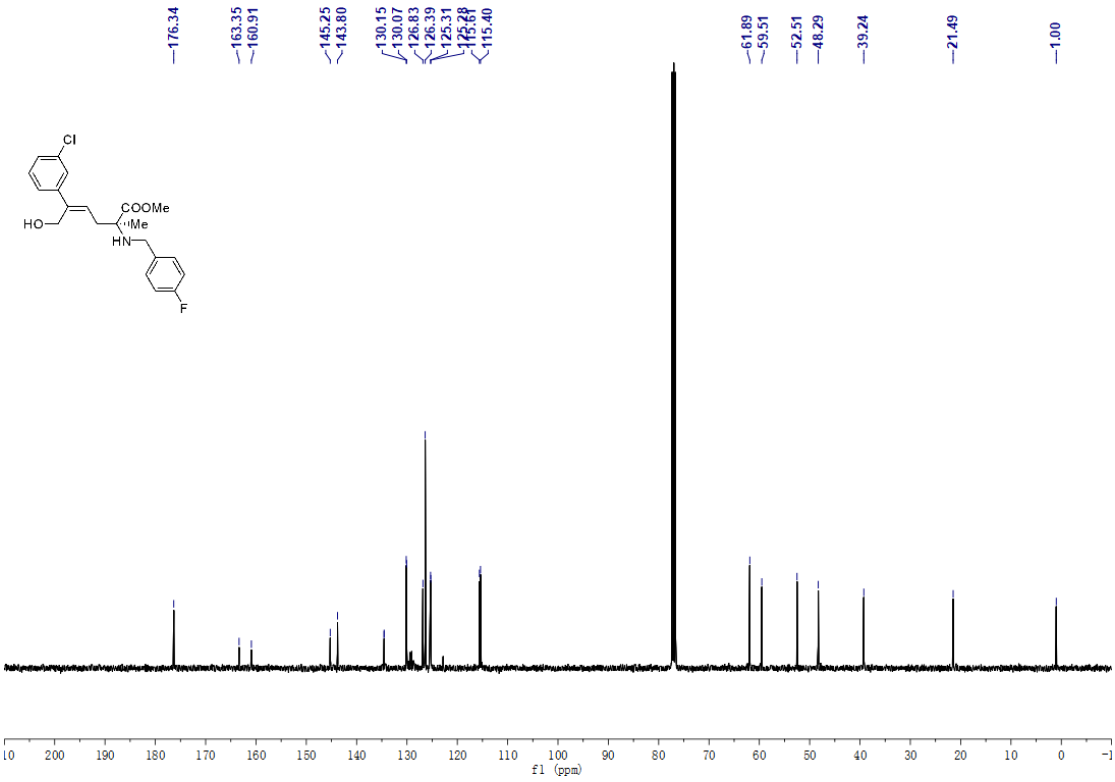

**$^{13}$C NMR** spectrum of **3bl** in $CDCl_3$



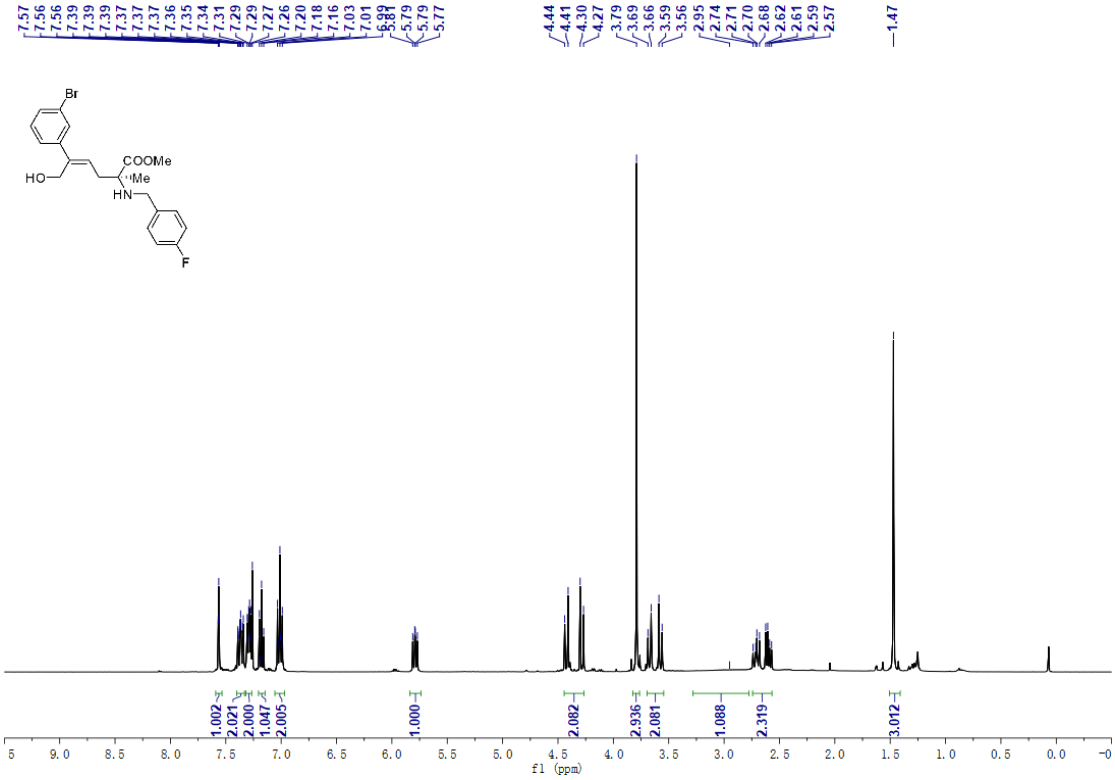
**$^{1}$H NMR** spectrum of **3bm** in $CDCl_3$



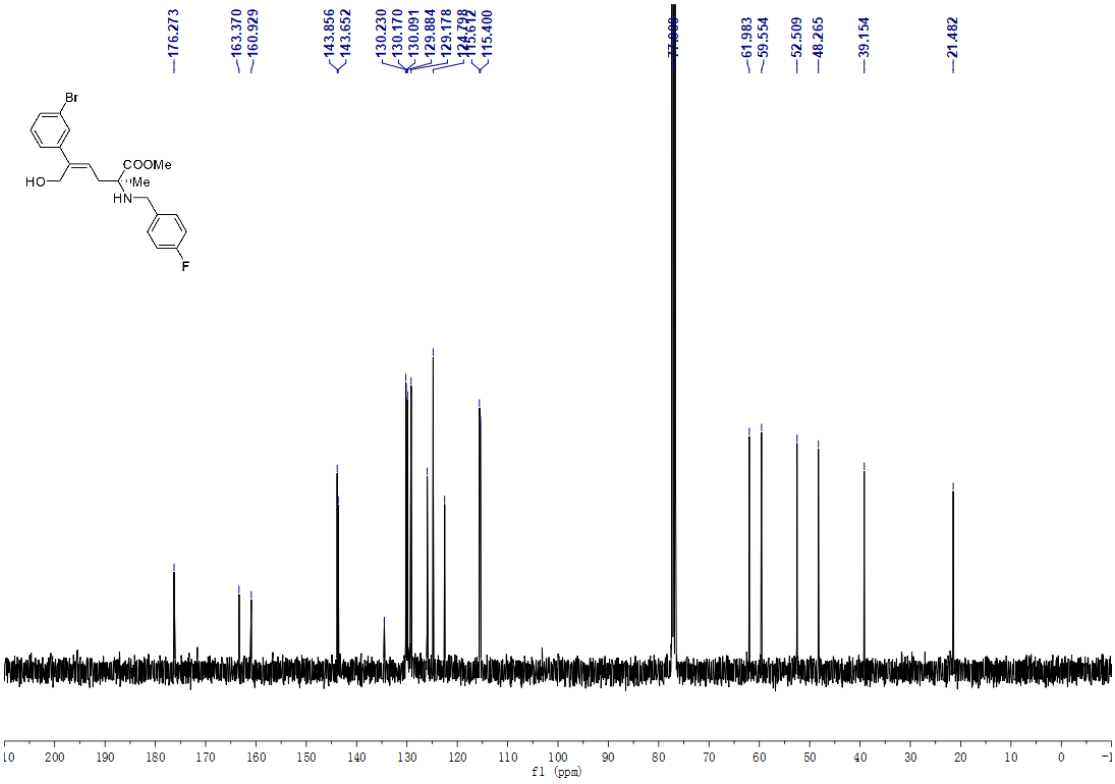

**$^{13}$C NMR** spectrum of **3bm** in $CDCl_3$



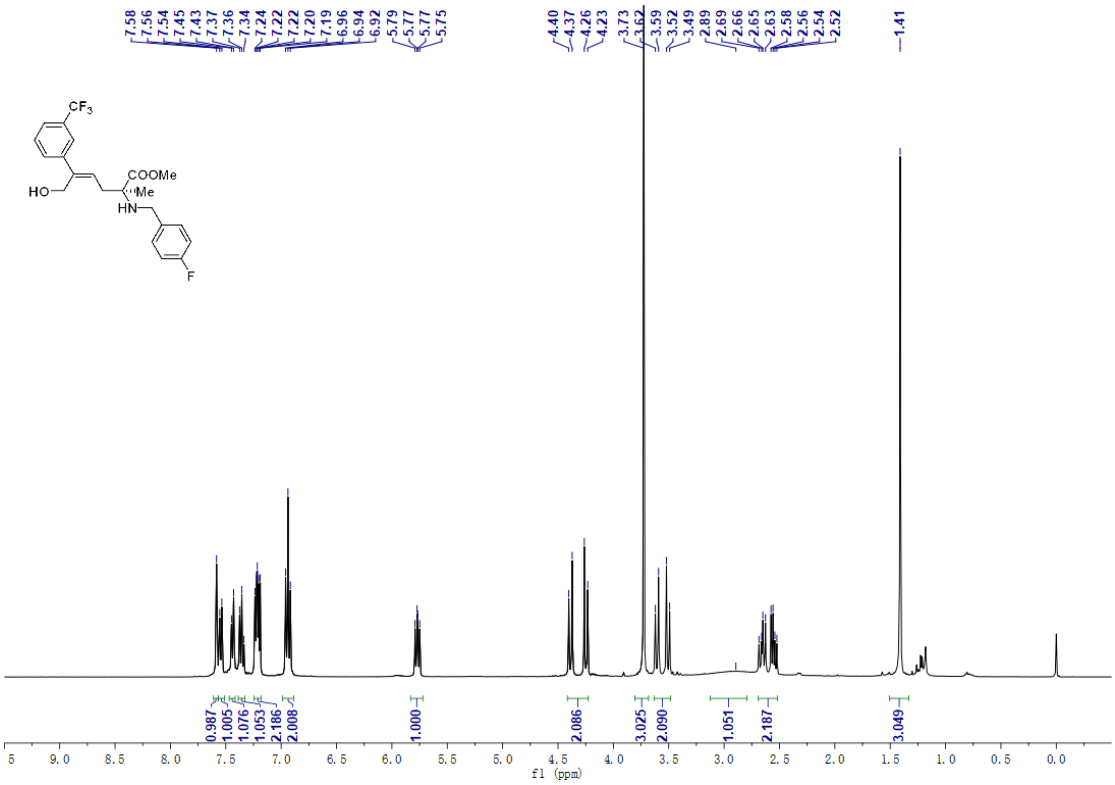
**$^{1}$H NMR** spectrum of **3bn** in $CDCl_3$



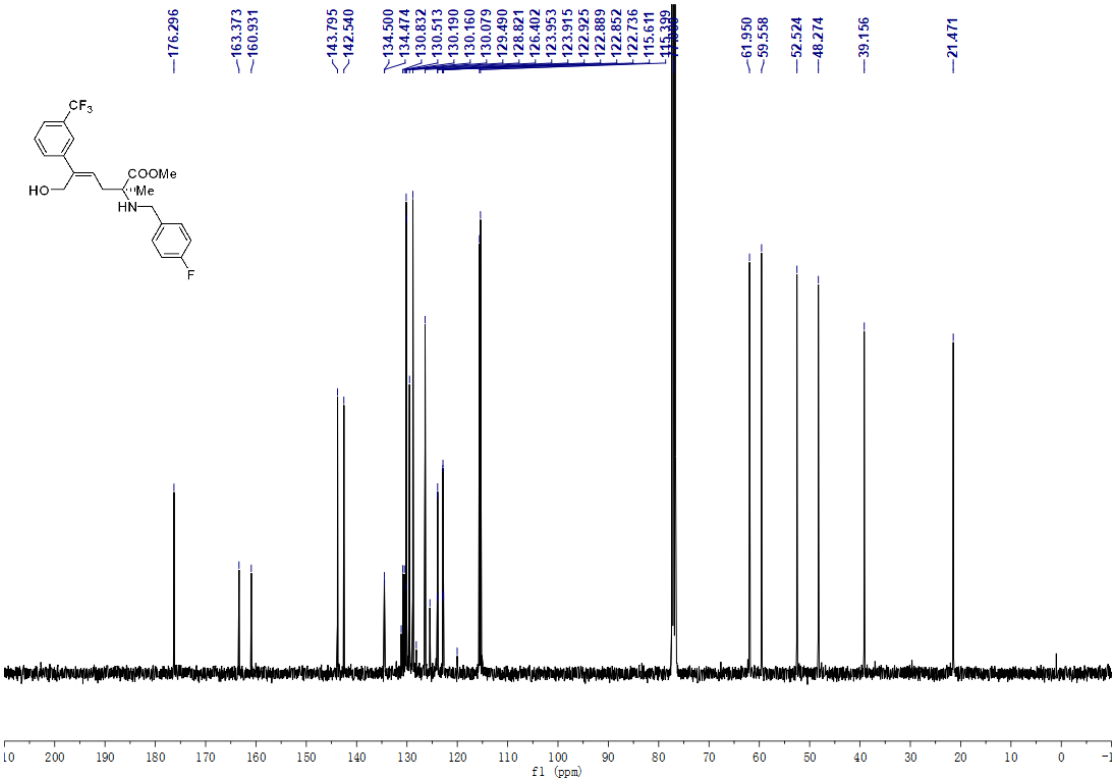

**$^{13}$C NMR** spectrum of **3bn** in $CDCl_3$



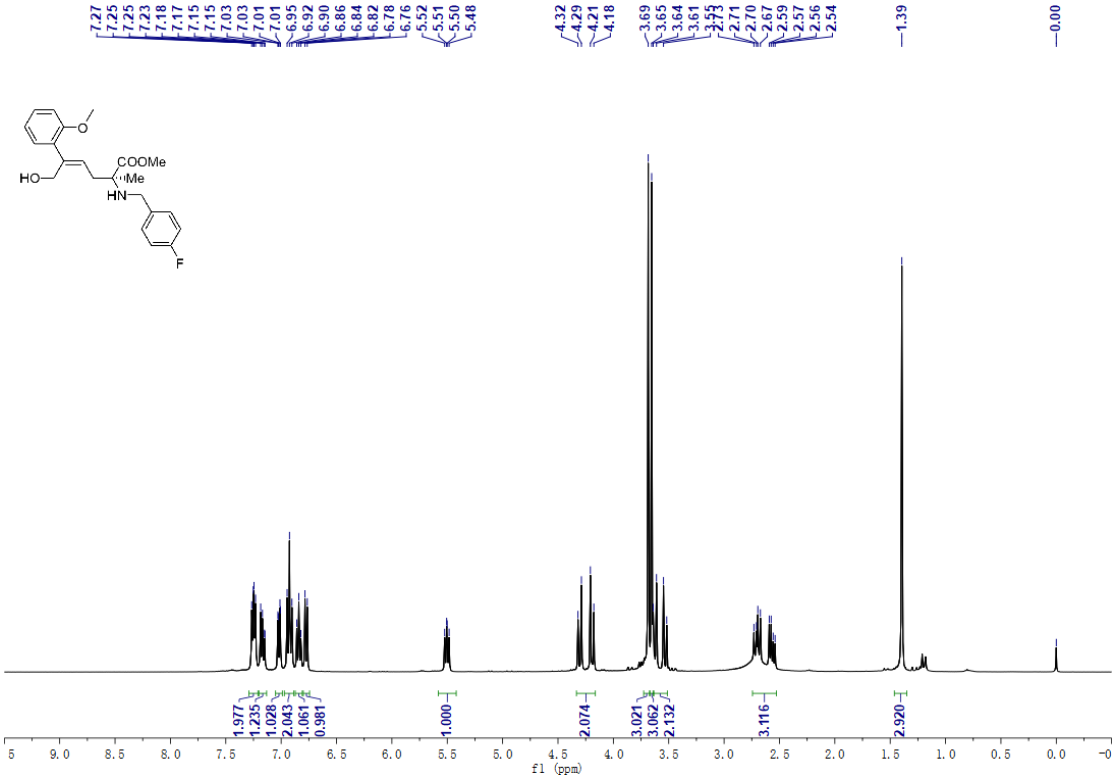
**$^{1}$H NMR** spectrum of **3bo** in $CDCl_3$



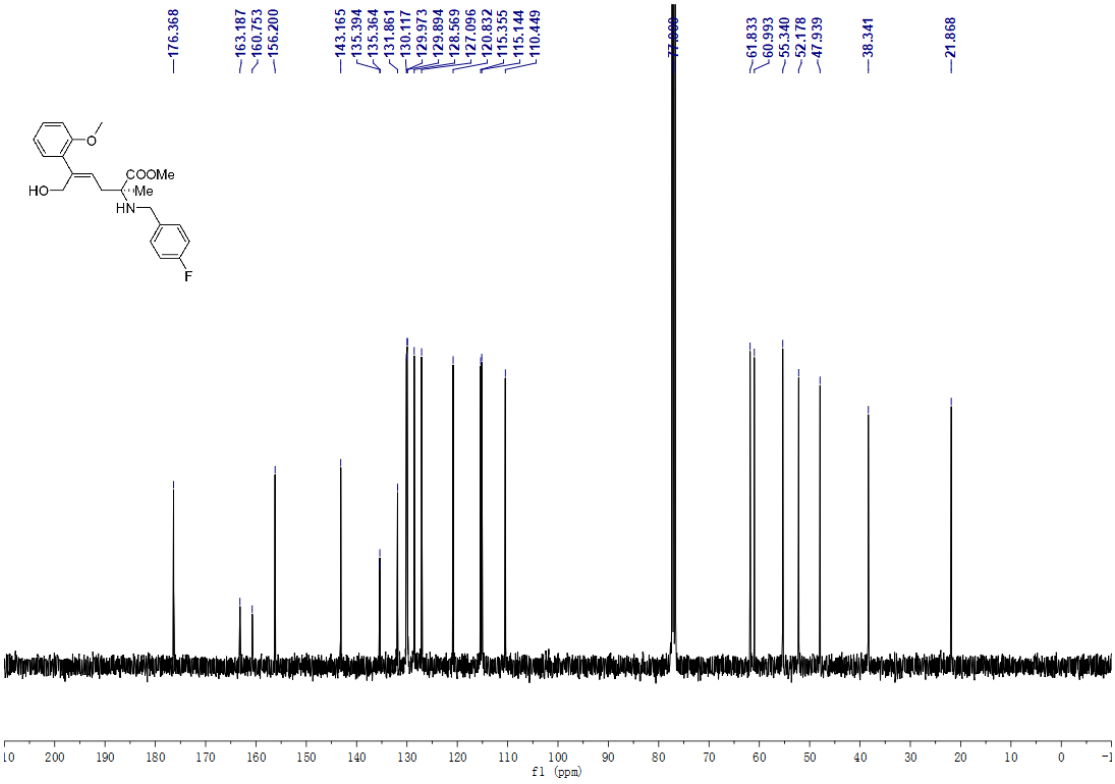

**$^{13}$C NMR** spectrum of **3bo** in $CDCl_3$



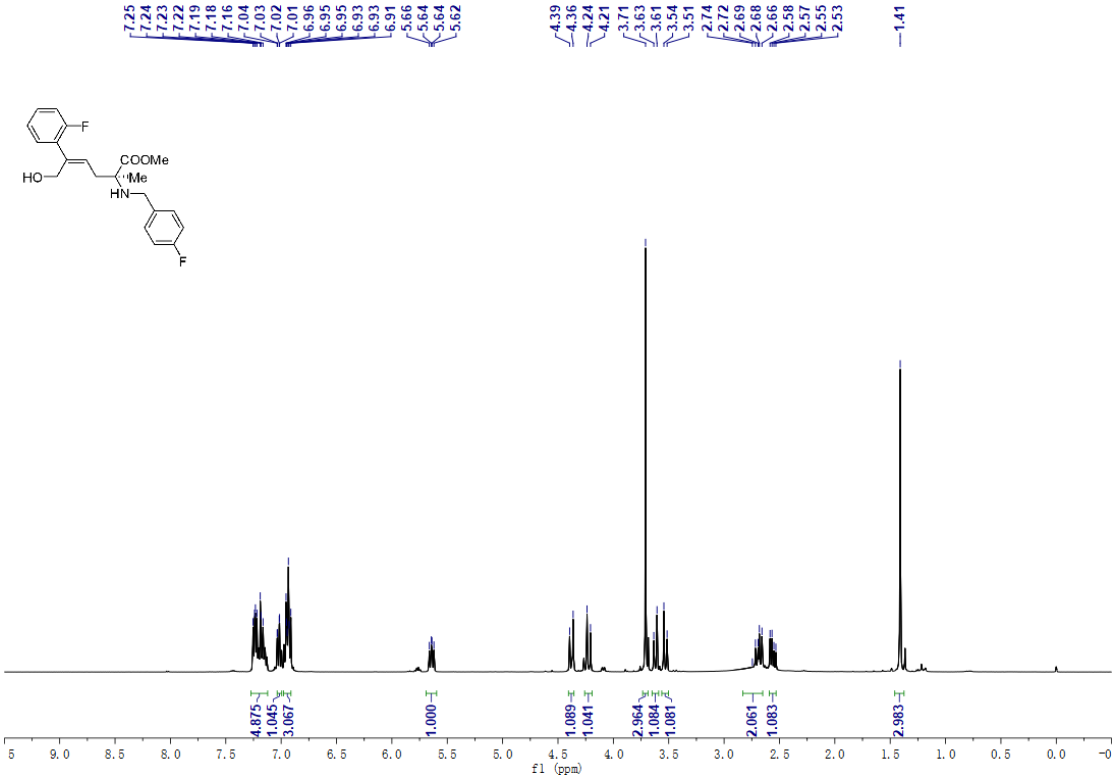
**$^{1}$H NMR** spectrum of **3bp** in $CDCl_3$



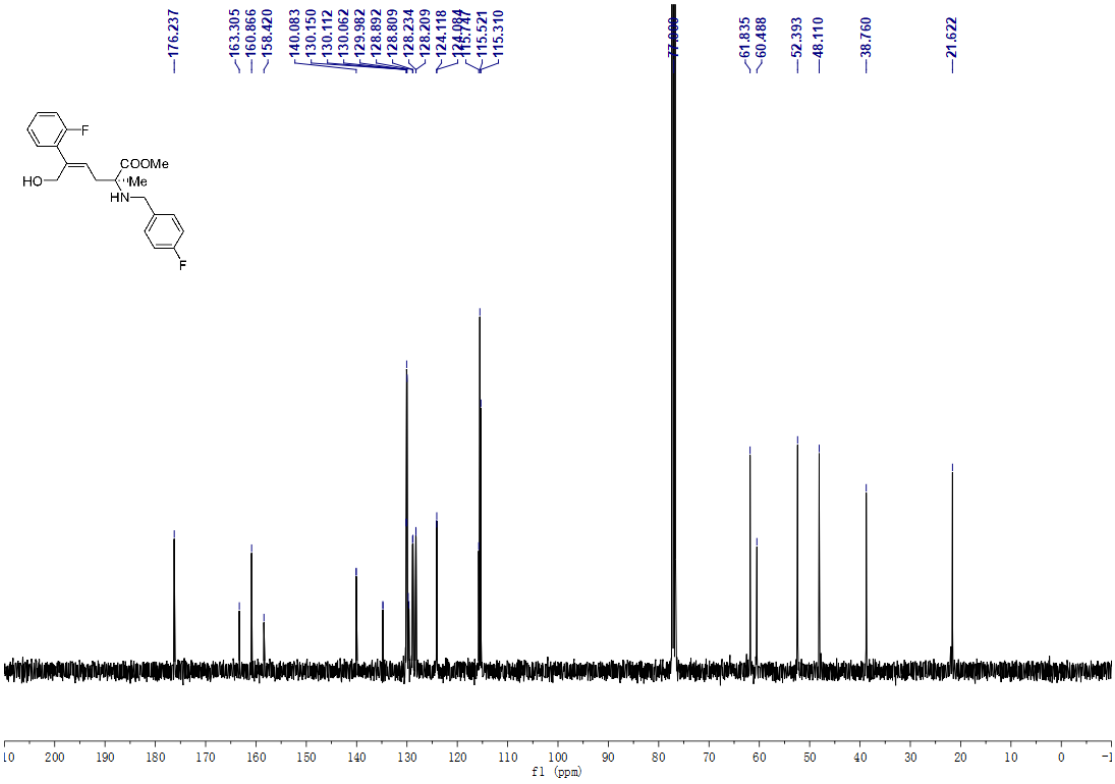

**$^{13}$C NMR** spectrum of **3bp** in $CDCl_3$



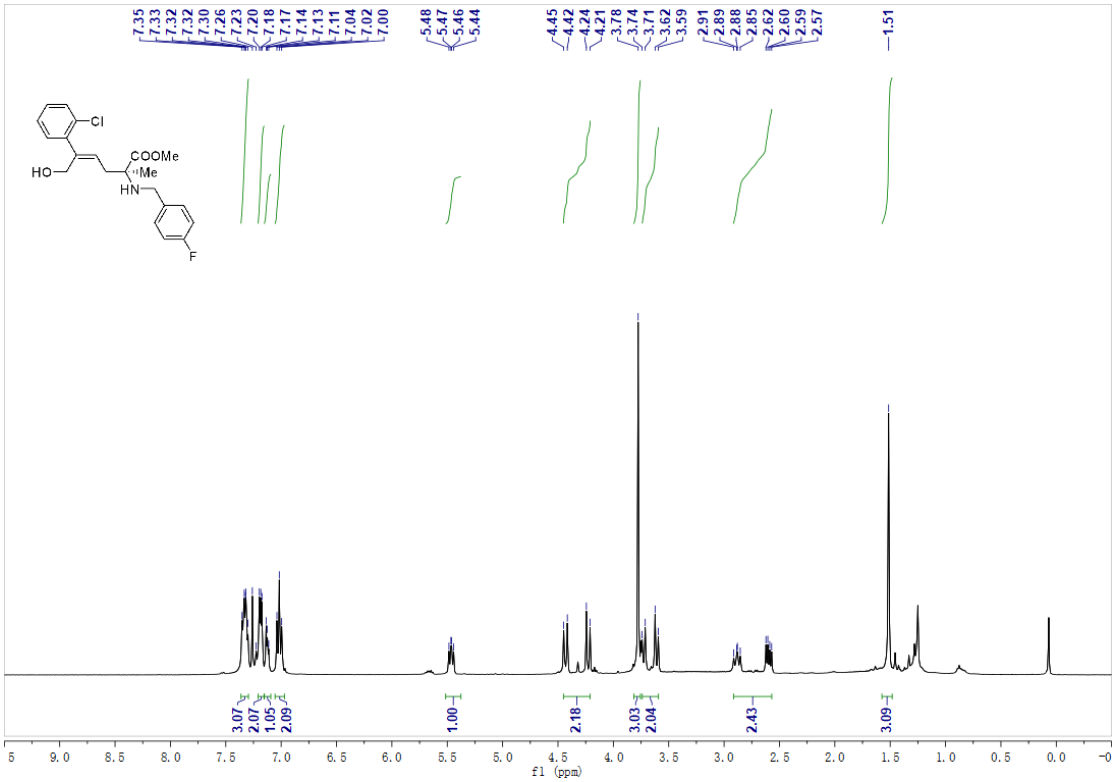
**$^{1}$H NMR** spectrum of **3bq** in $CDCl_3$



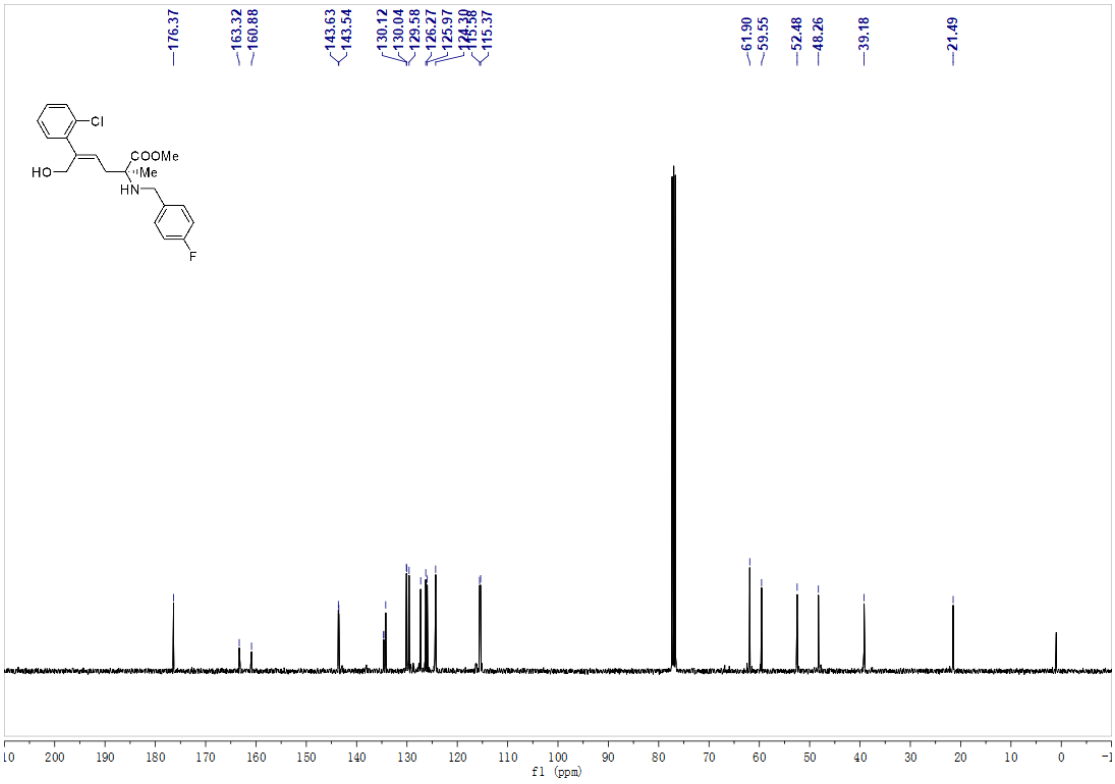

**$^{13}$C NMR** spectrum of **3bq** in $CDCl_3$



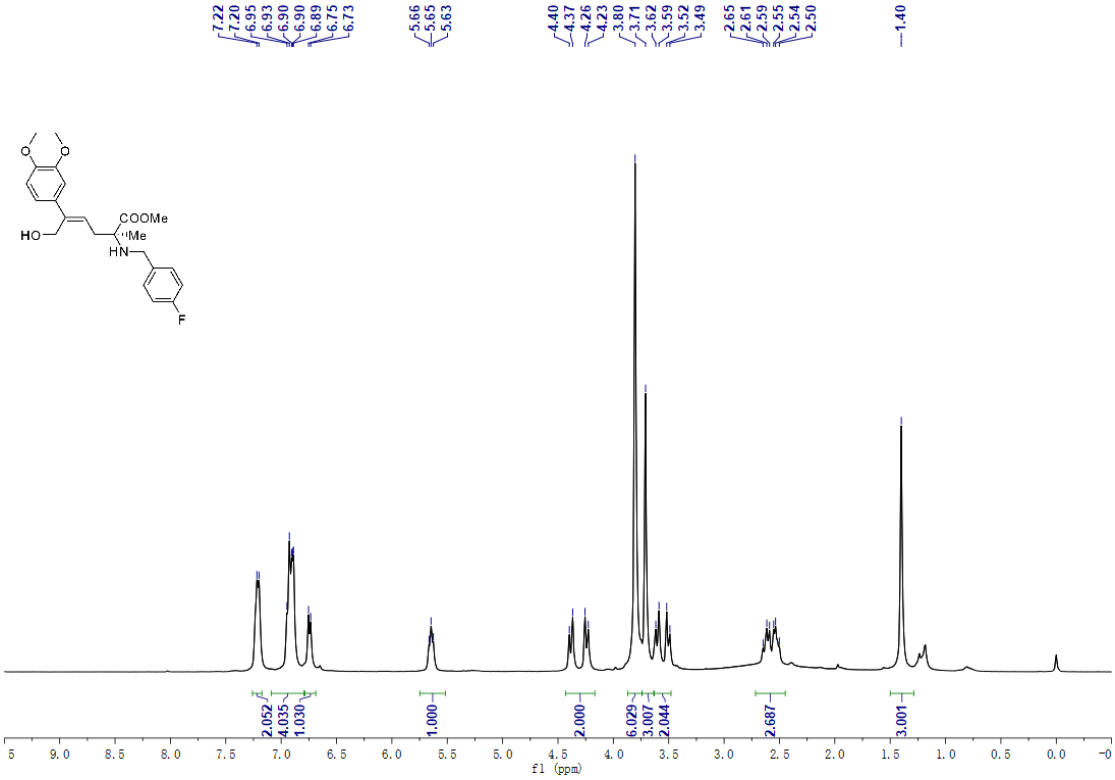
**$^{1}$H NMR** spectrum of **3br** in $CDCl_3$



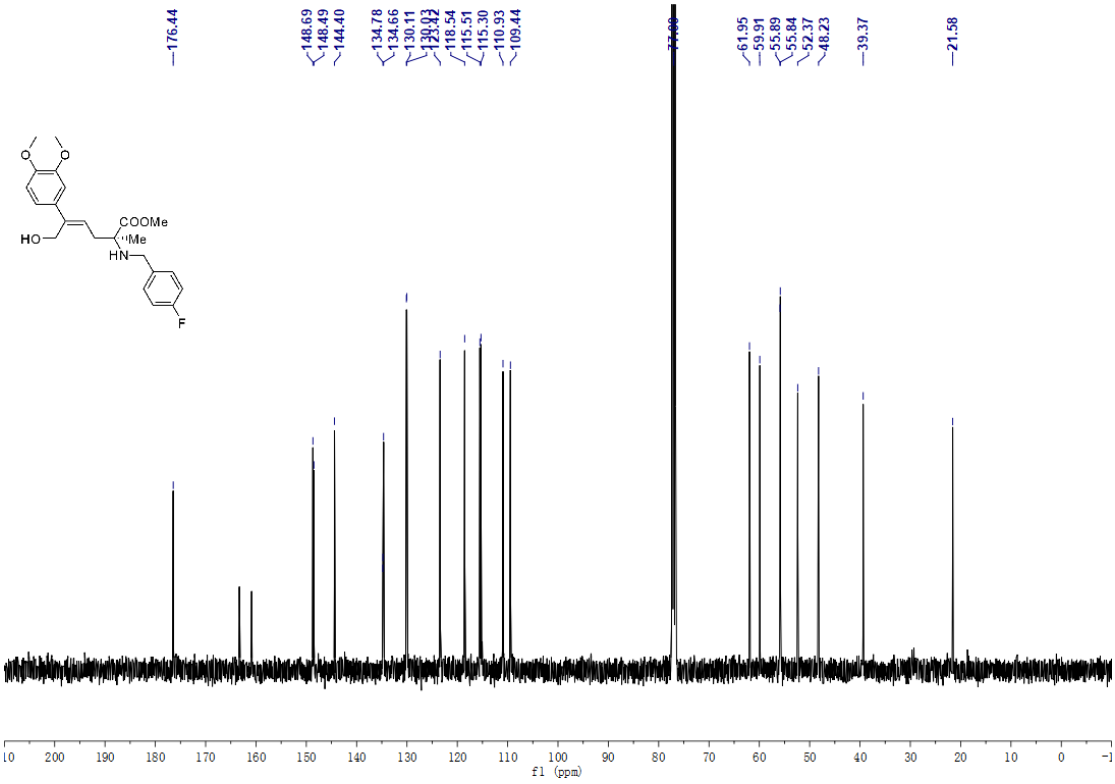

**$^{13}$C NMR** spectrum of **3br** in $CDCl_3$



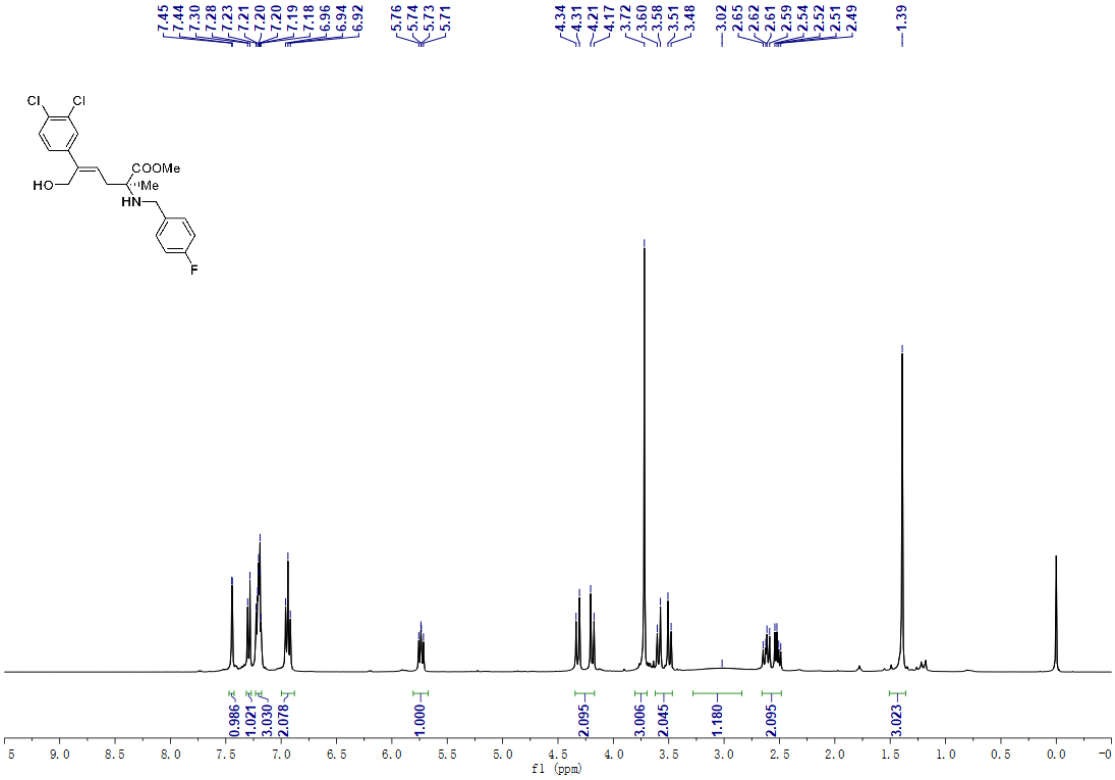
**$^{1}$H NMR** spectrum of **3bs** in $CDCl_3$



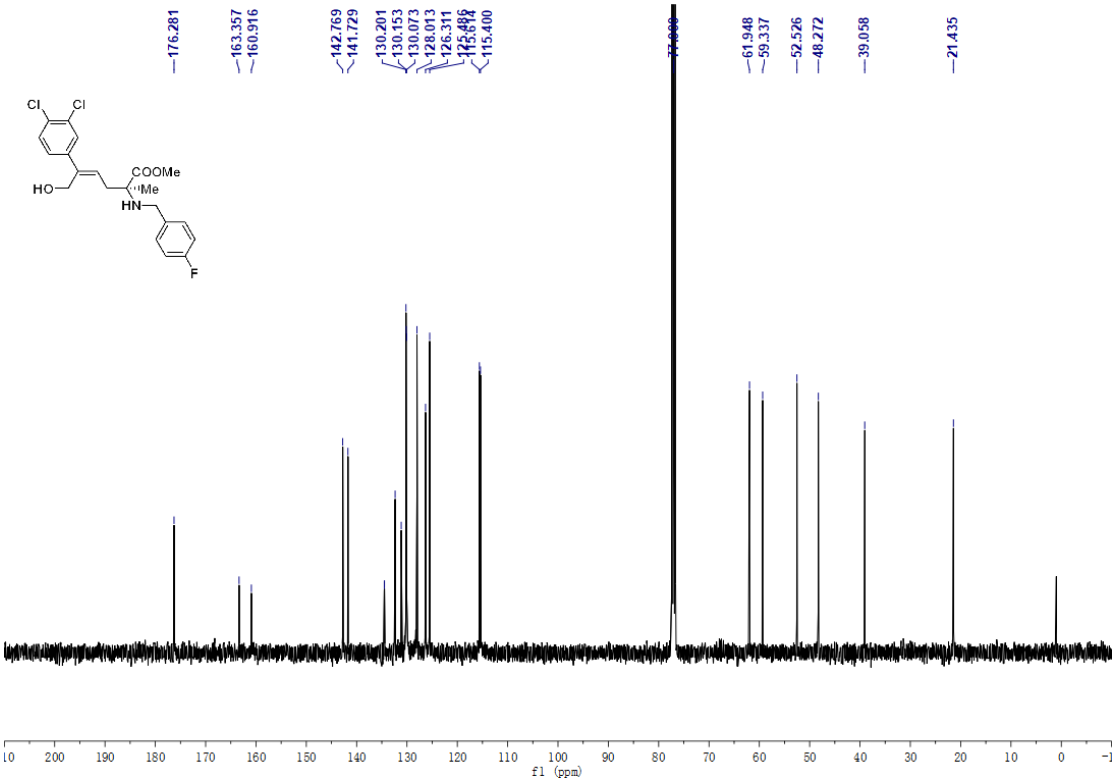

**$^{13}$C NMR** spectrum of **3bs** in $CDCl_3$



**$^{1}$H NMR** spectrum of **3bt** in $CDCl_3$




**$^{13}$C NMR** spectrum of **3bt** in $CDCl_3$



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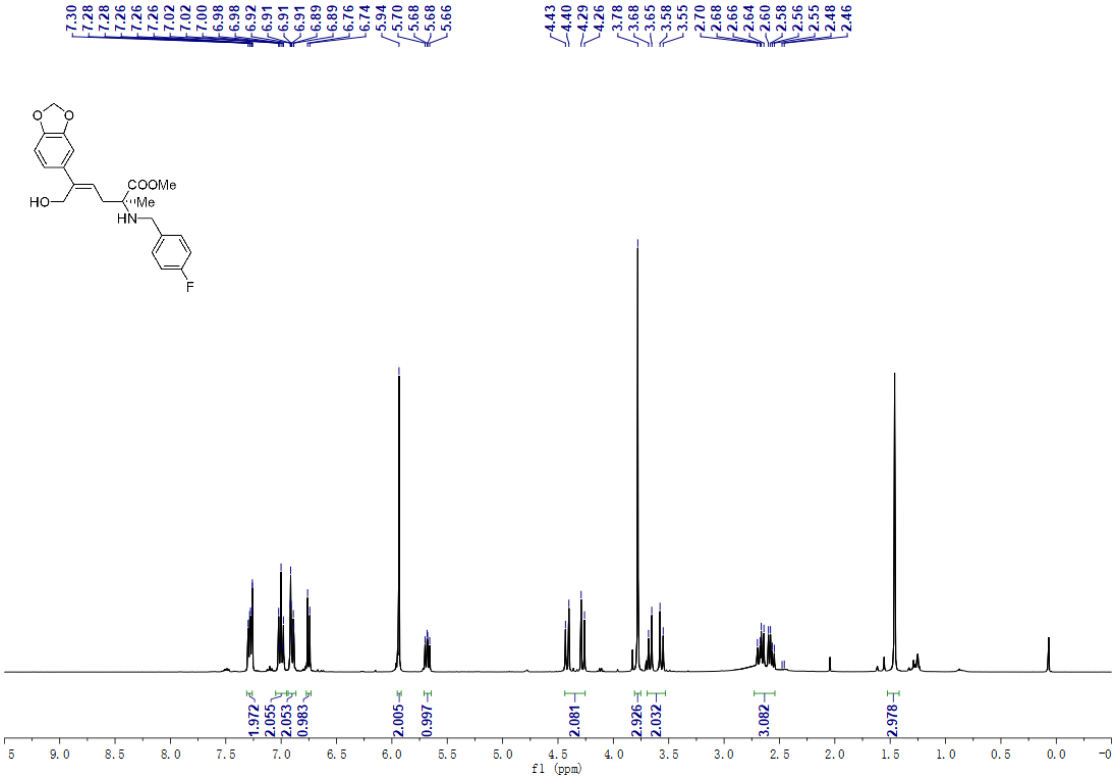
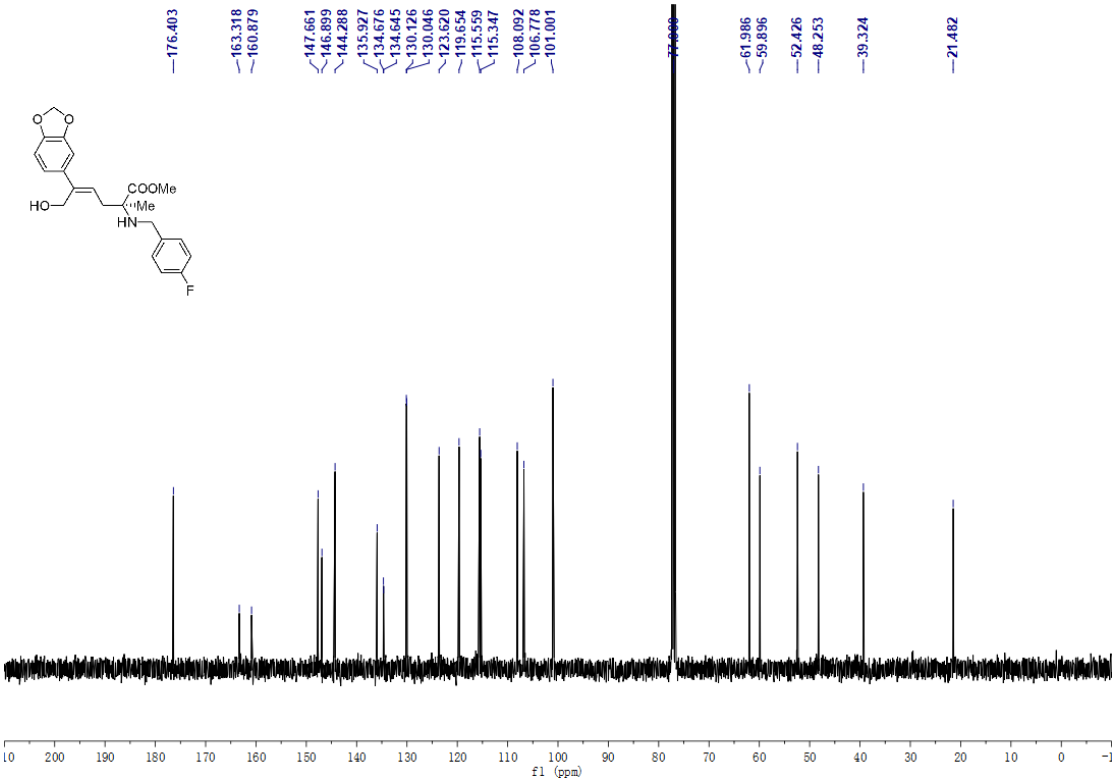
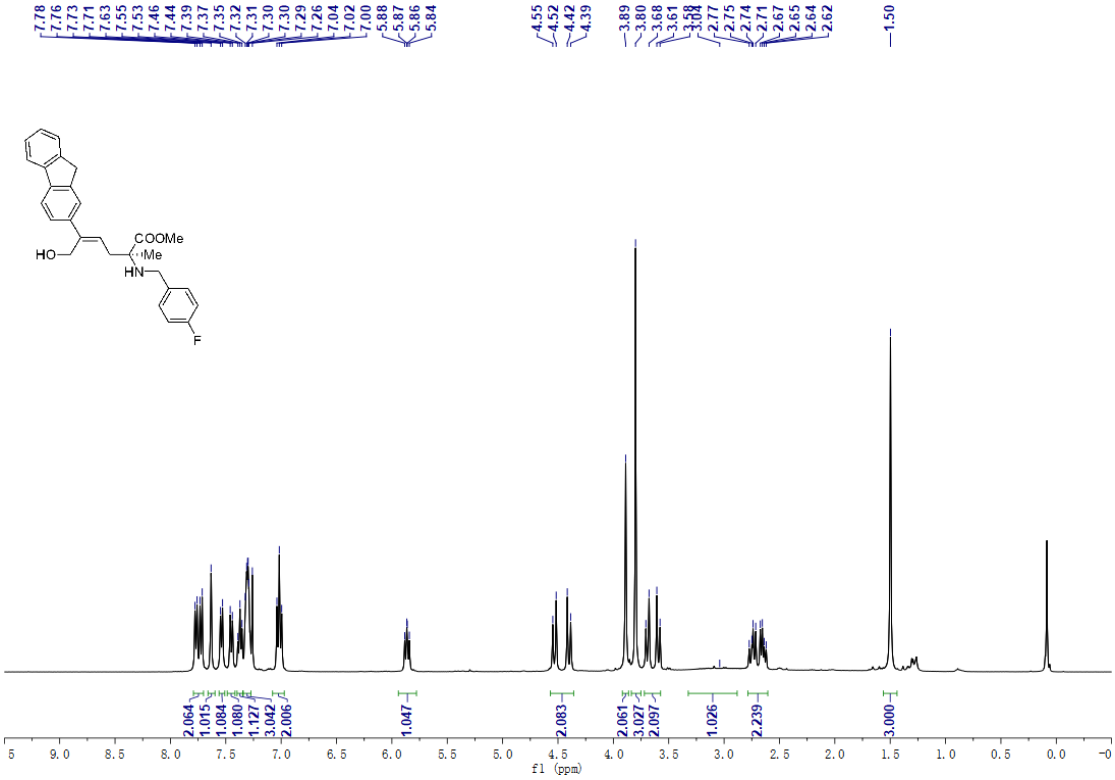


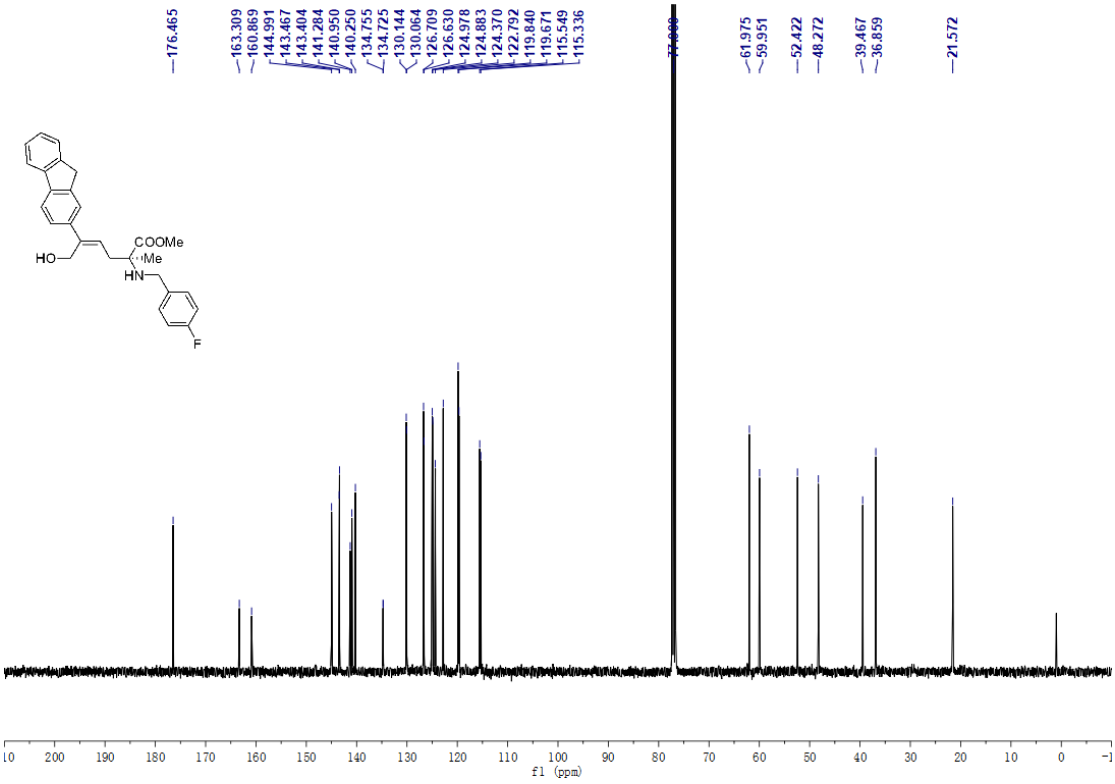

**$^{13}$C NMR** spectrum of **3bu** in $CDCl_3$



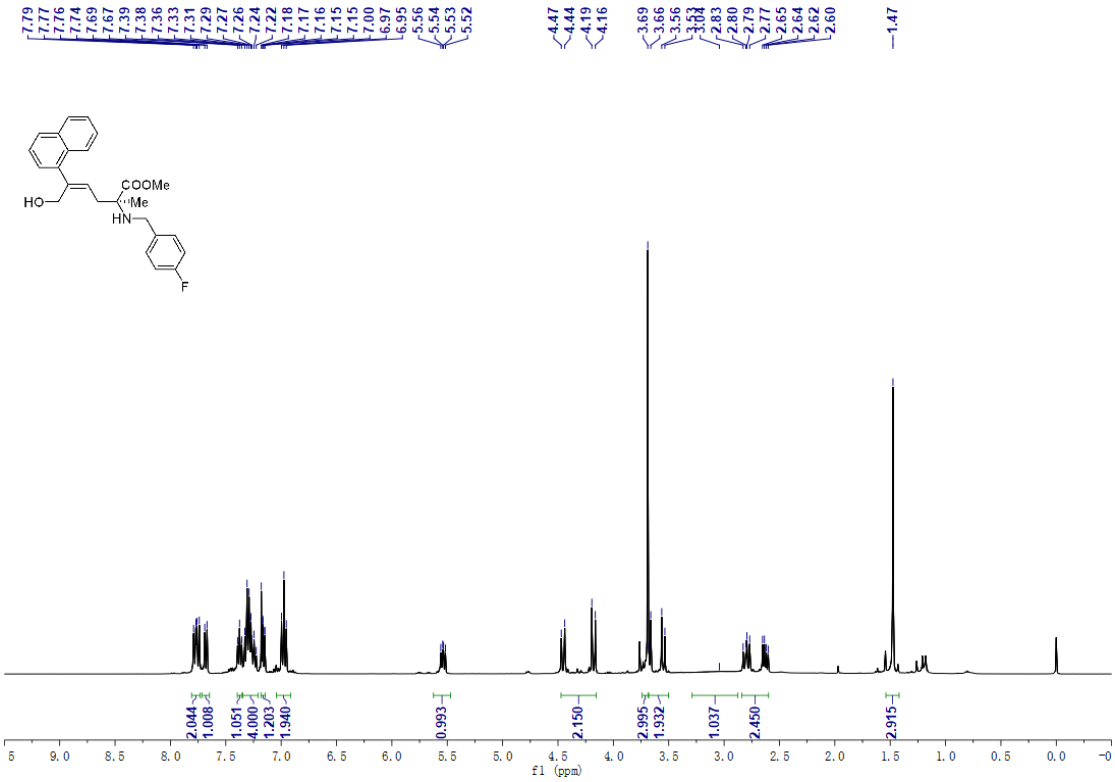
**$^{1}$H NMR** spectrum of **3bv** in $CDCl_3$



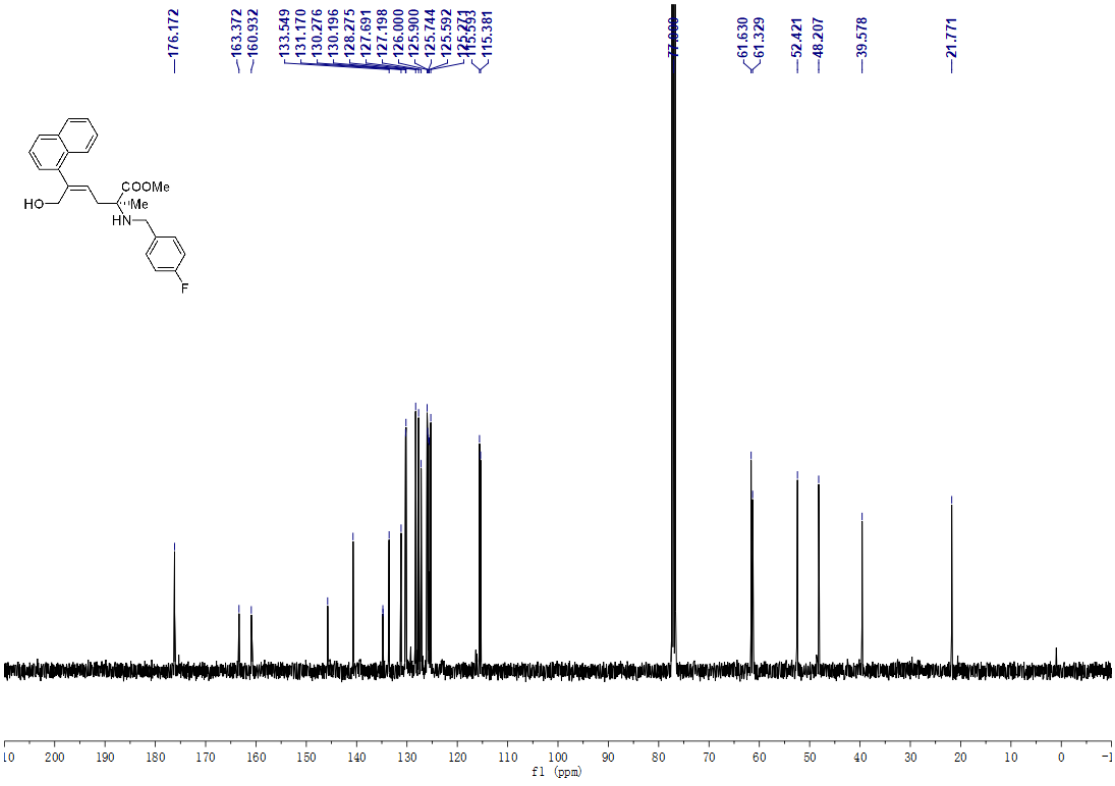

**$^{13}$C NMR** spectrum of **3bv** in $CDCl_3$



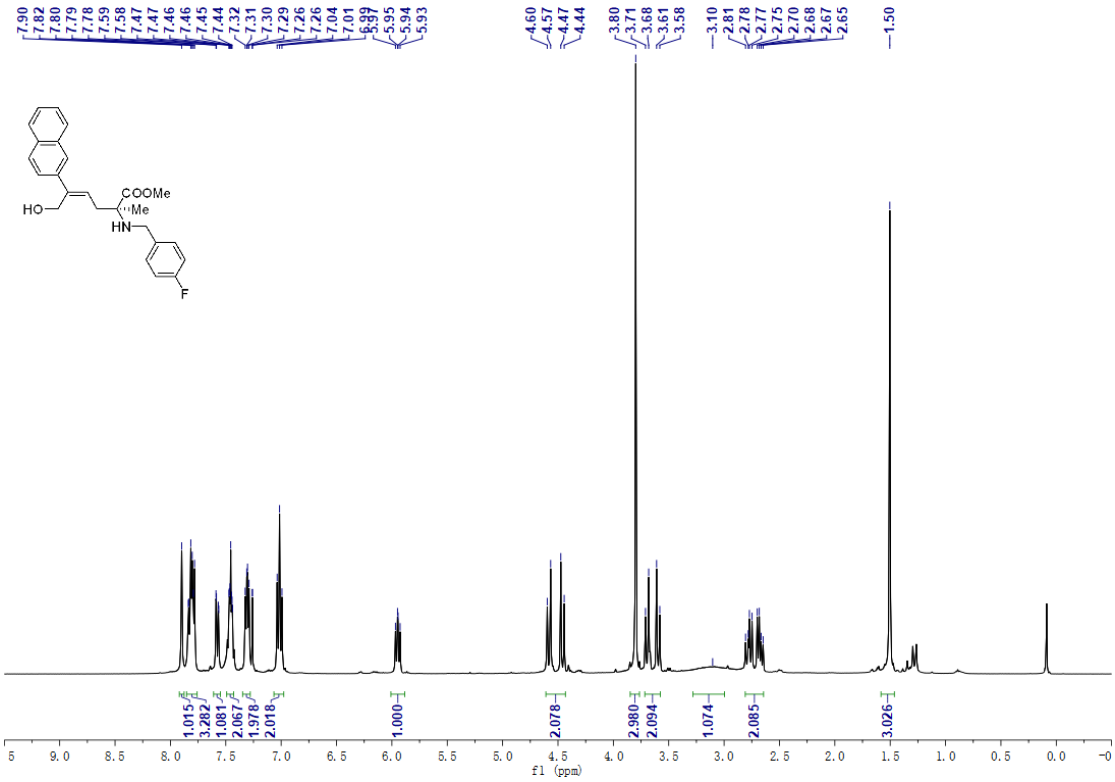
**$^{1}$H NMR** spectrum of **3bw** in $CDCl_3$



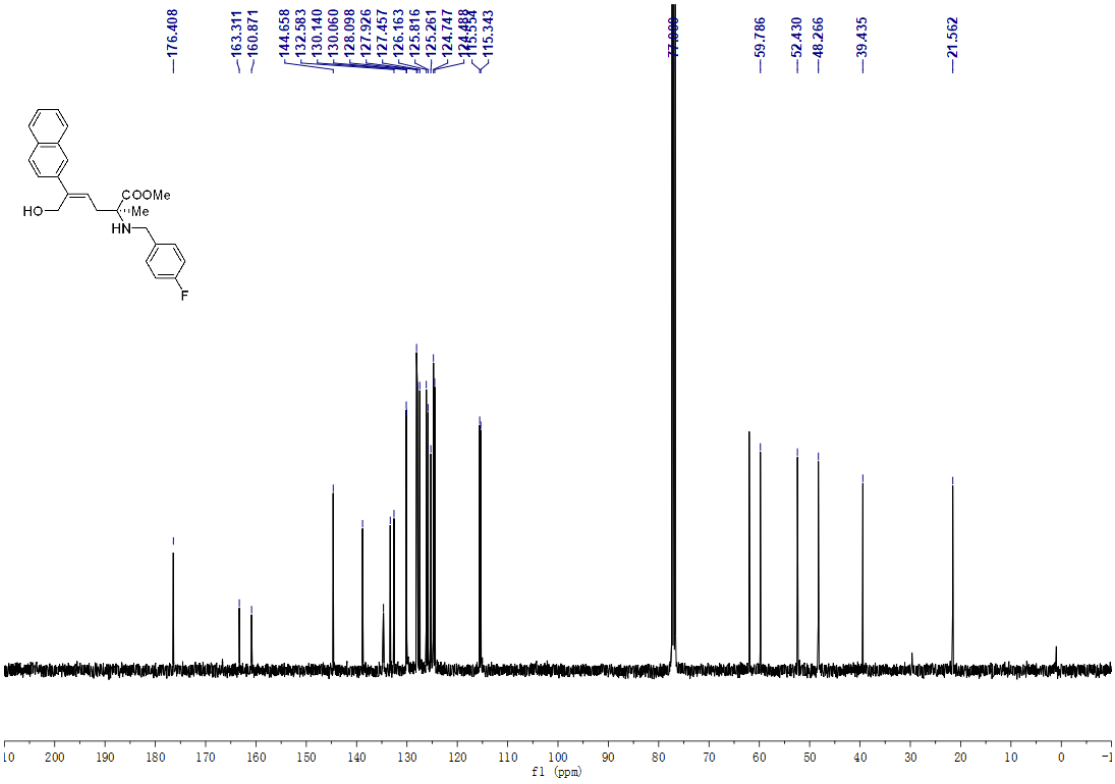

**$^{13}$C NMR** spectrum of **3bw** in $CDCl_3$



**$^{1}$H NMR** spectrum of **3bx** in $CDCl_3$




**$^{13}$C NMR** spectrum of **3bx** in $CDCl_3$



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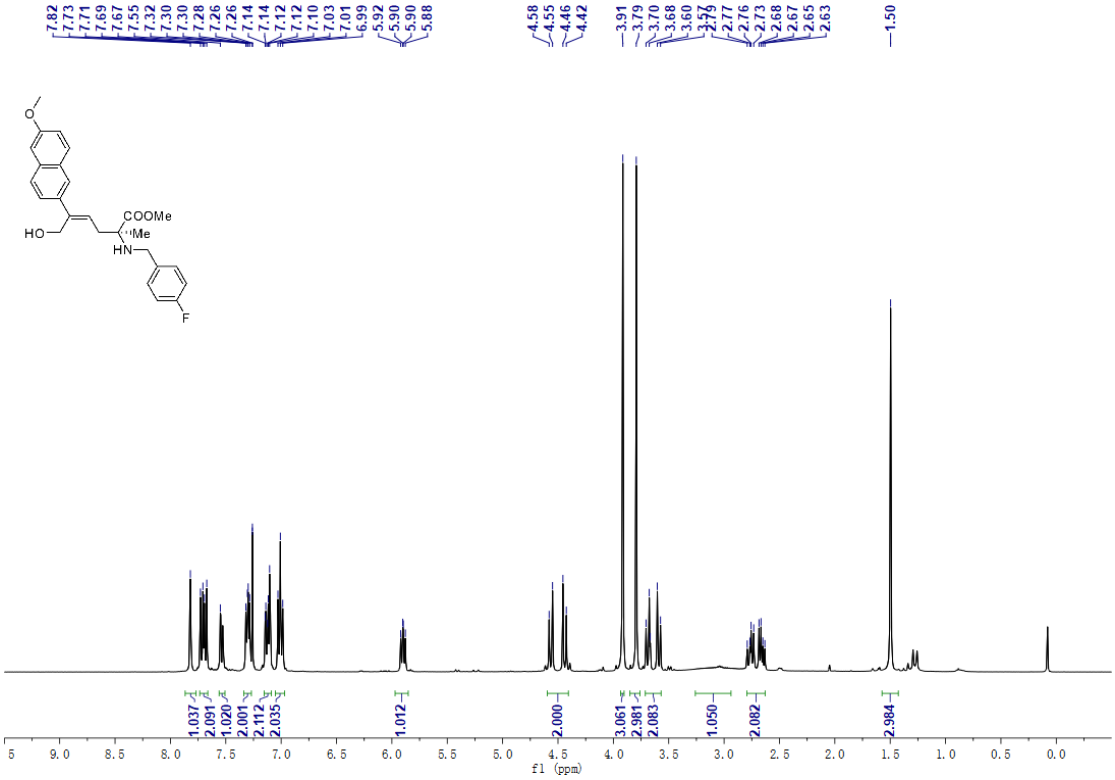
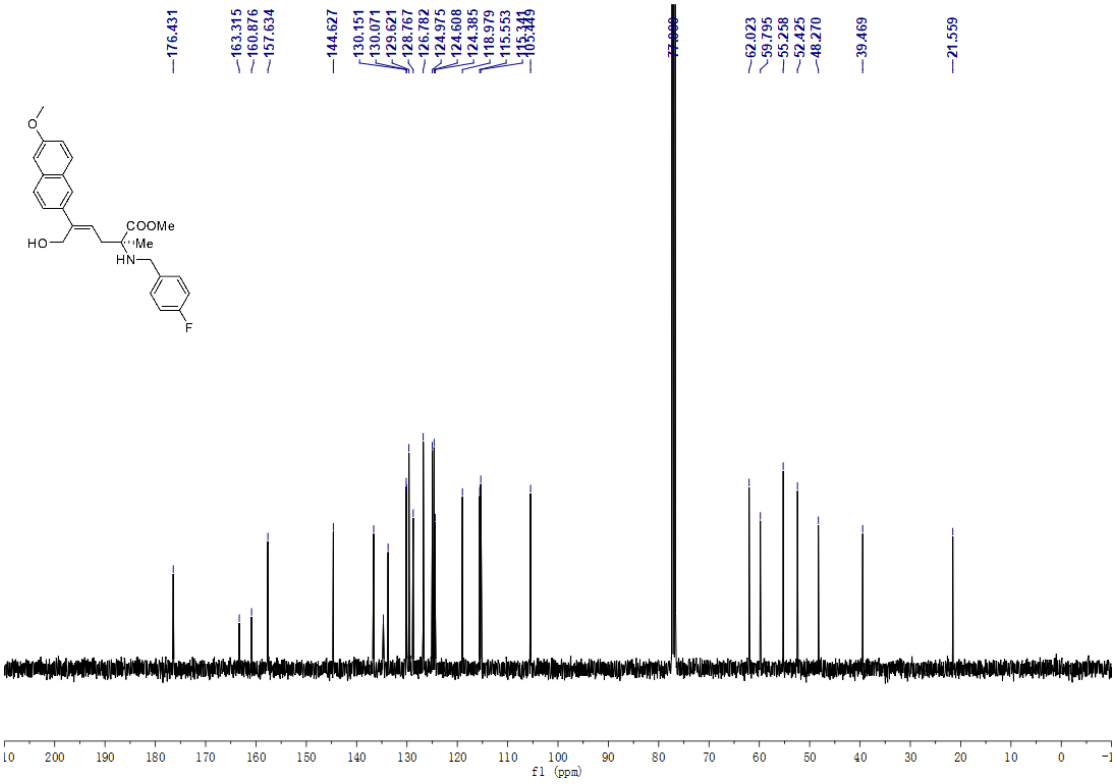



**$^{13}$C NMR** spectrum of **3by** in $CDCl_3$



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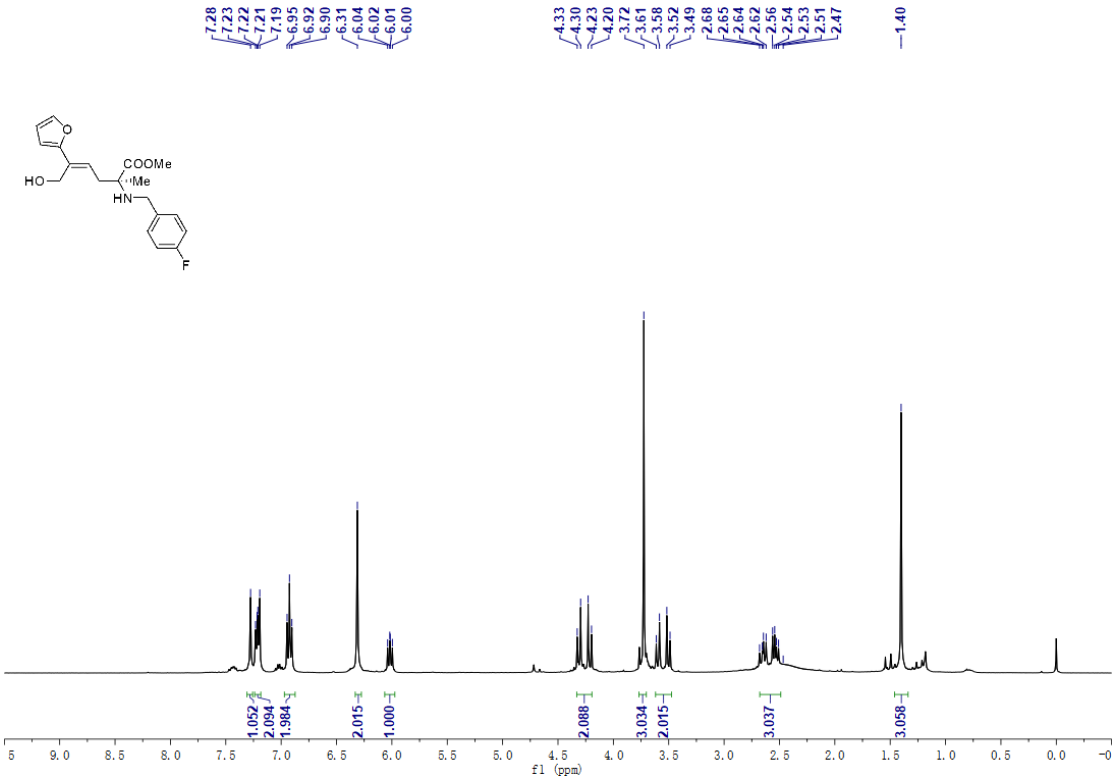
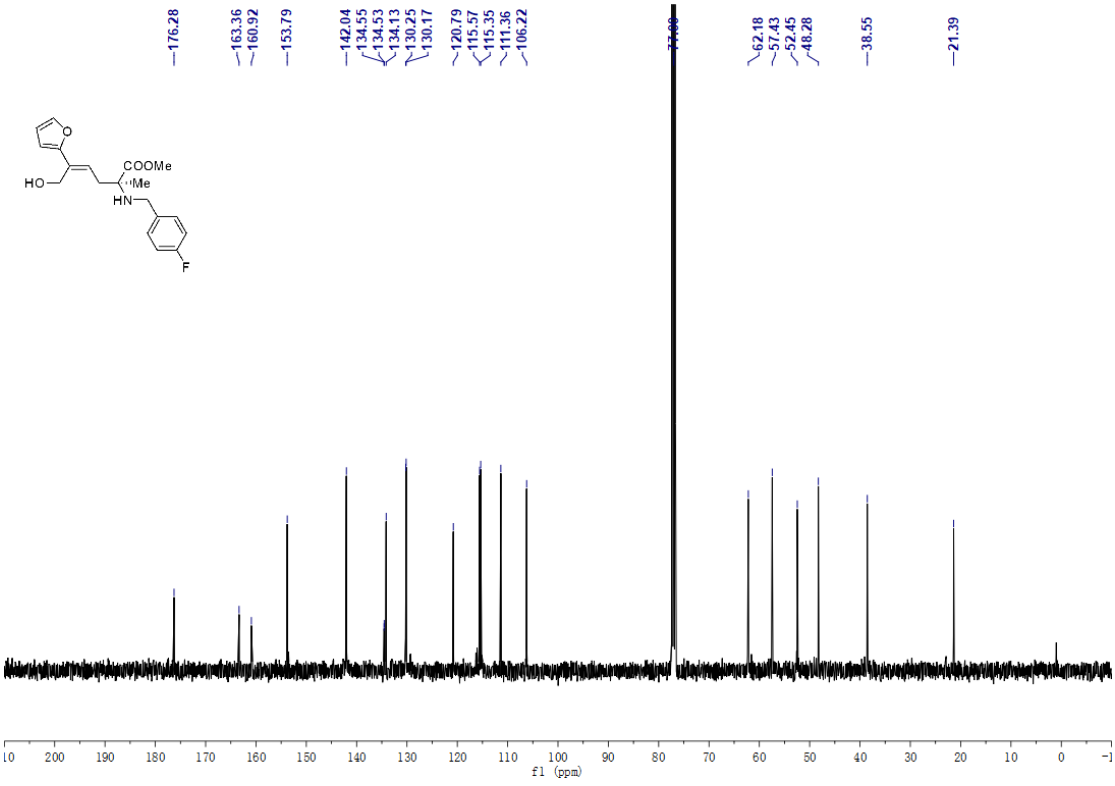
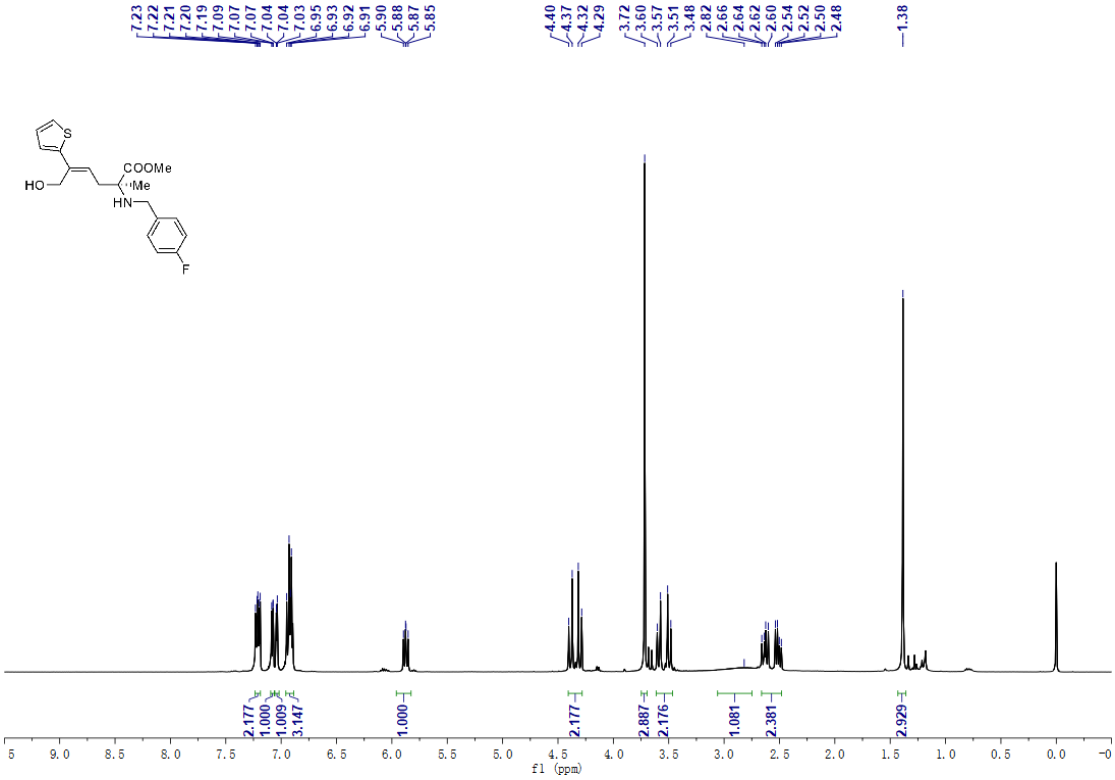


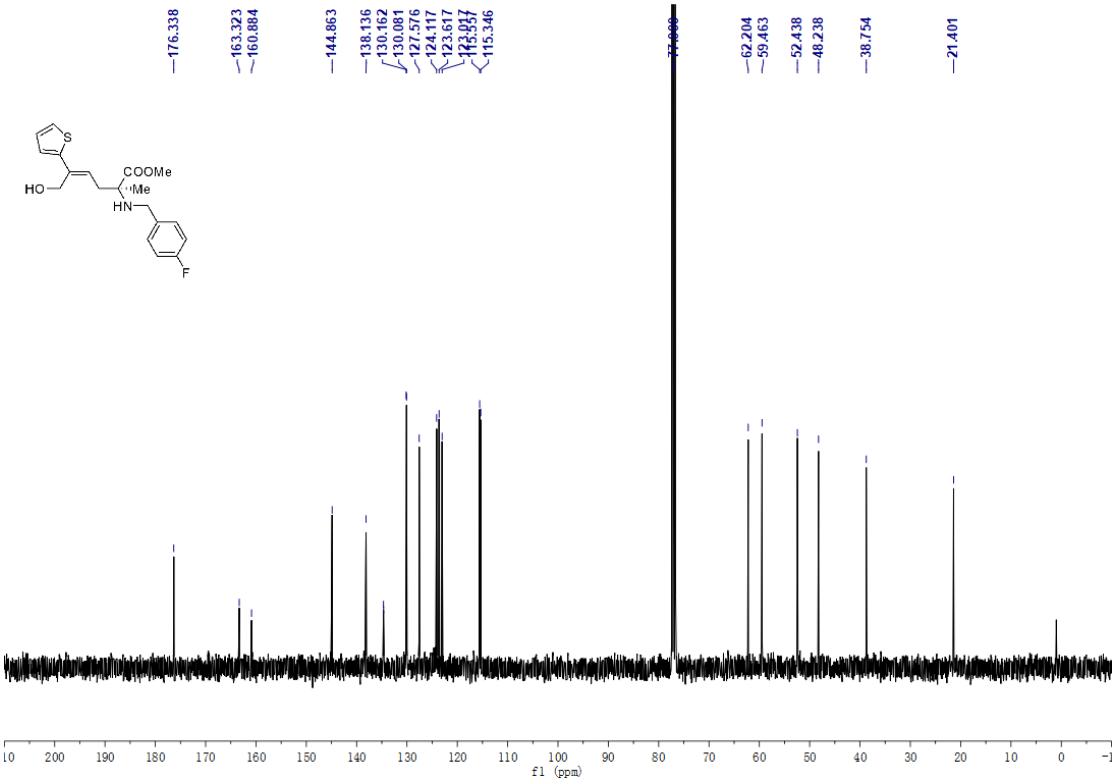

**$^{13}$C NMR** spectrum of **3bz** in $CDCl_3$



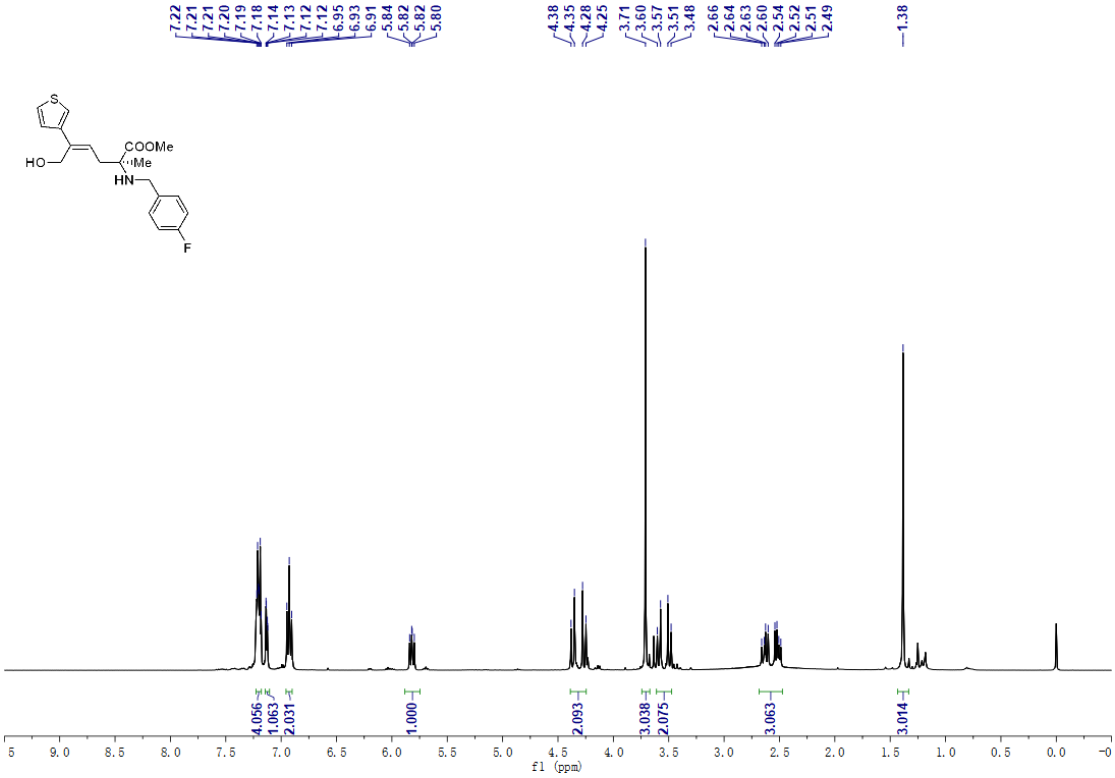
**$^{1}$H NMR** spectrum of **3baa** in $CDCl_3$



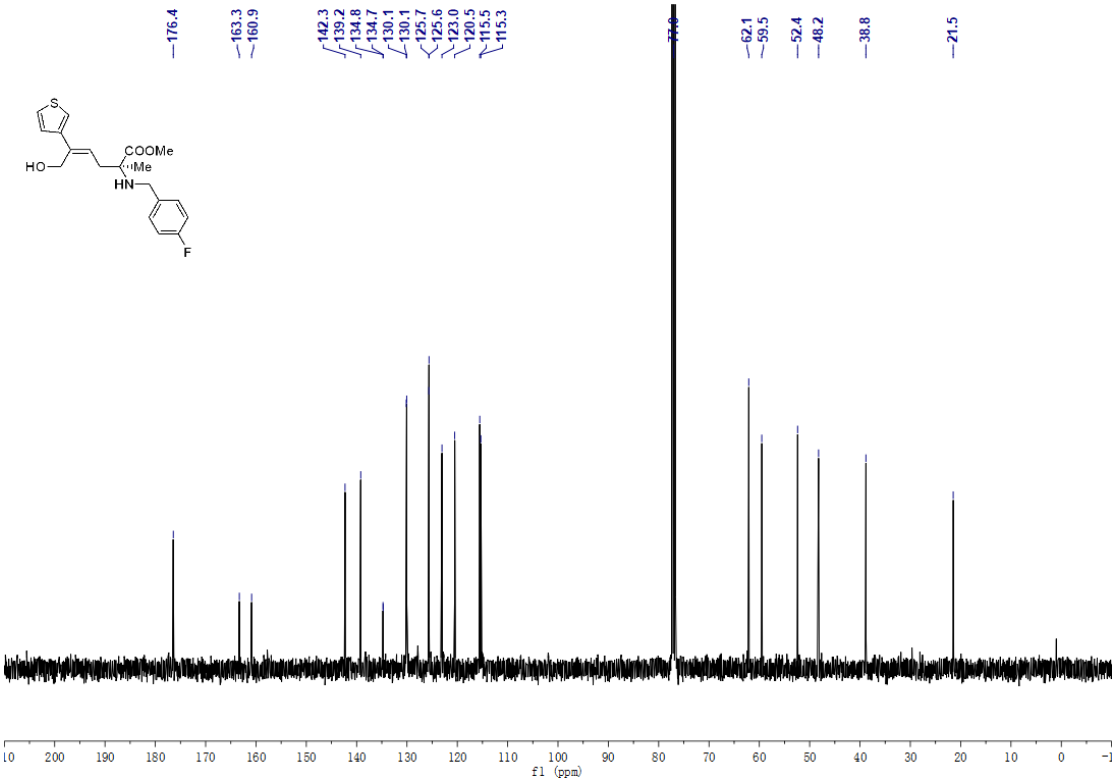

**$^{13}$C NMR** spectrum of **3baa** in $CDCl_3$



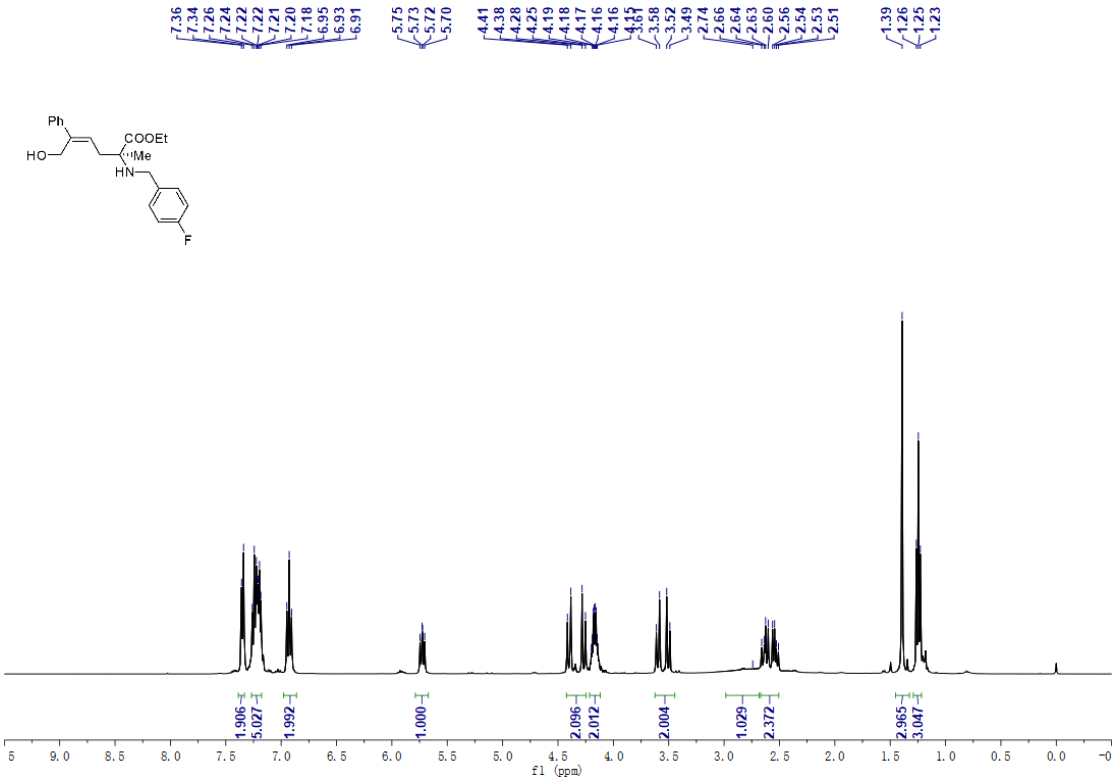
**$^{1}$H NMR** spectrum of **3bab** in $CDCl_3$



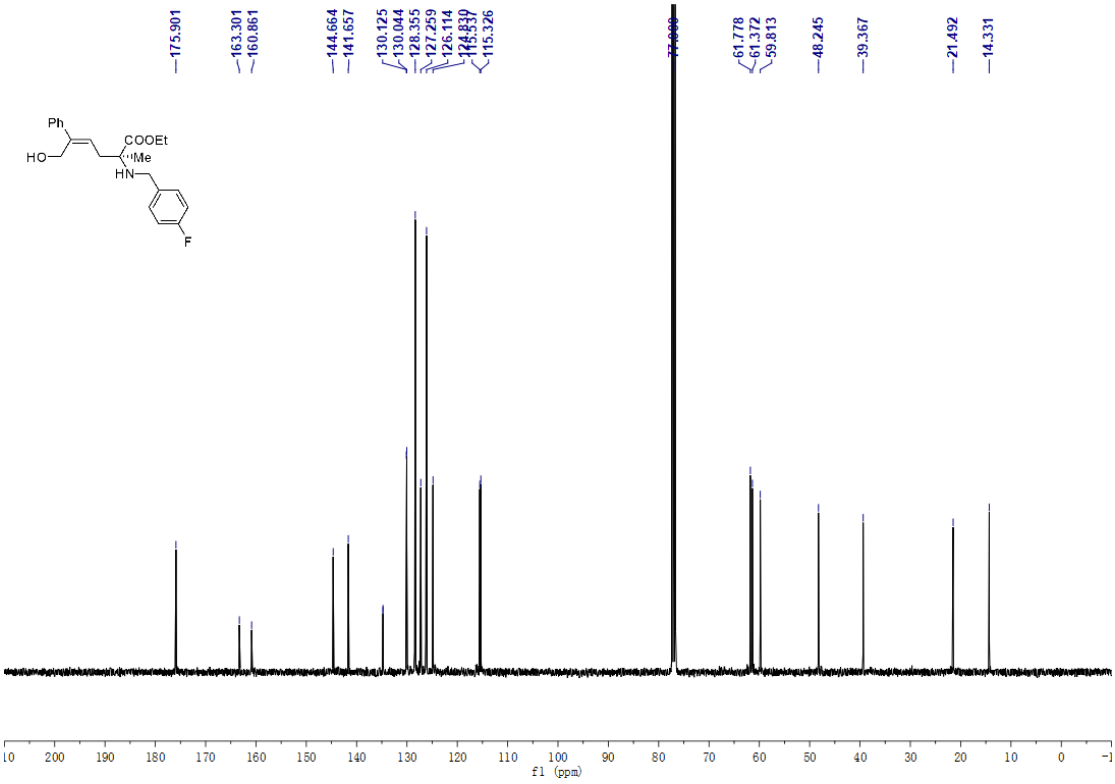

**$^{13}$C NMR** spectrum of **3bab** in $CDCl_3$



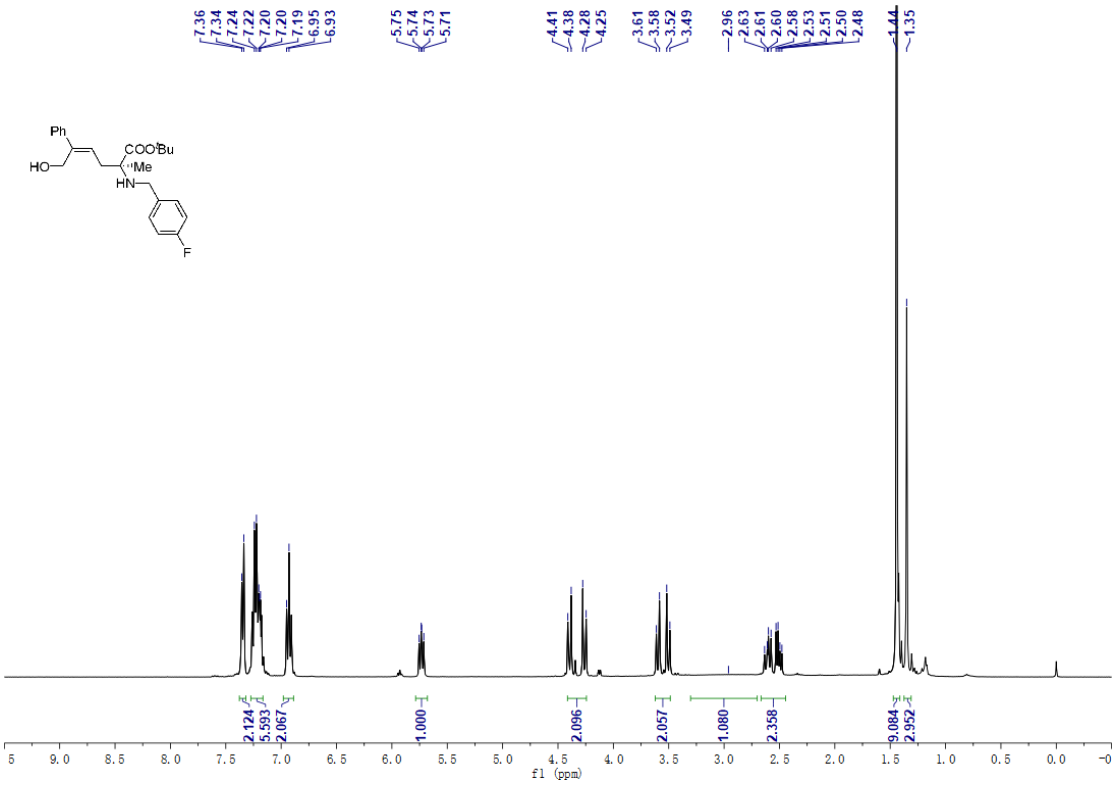
**$^{1}$H NMR** spectrum of **3ea** in $CDCl_3$



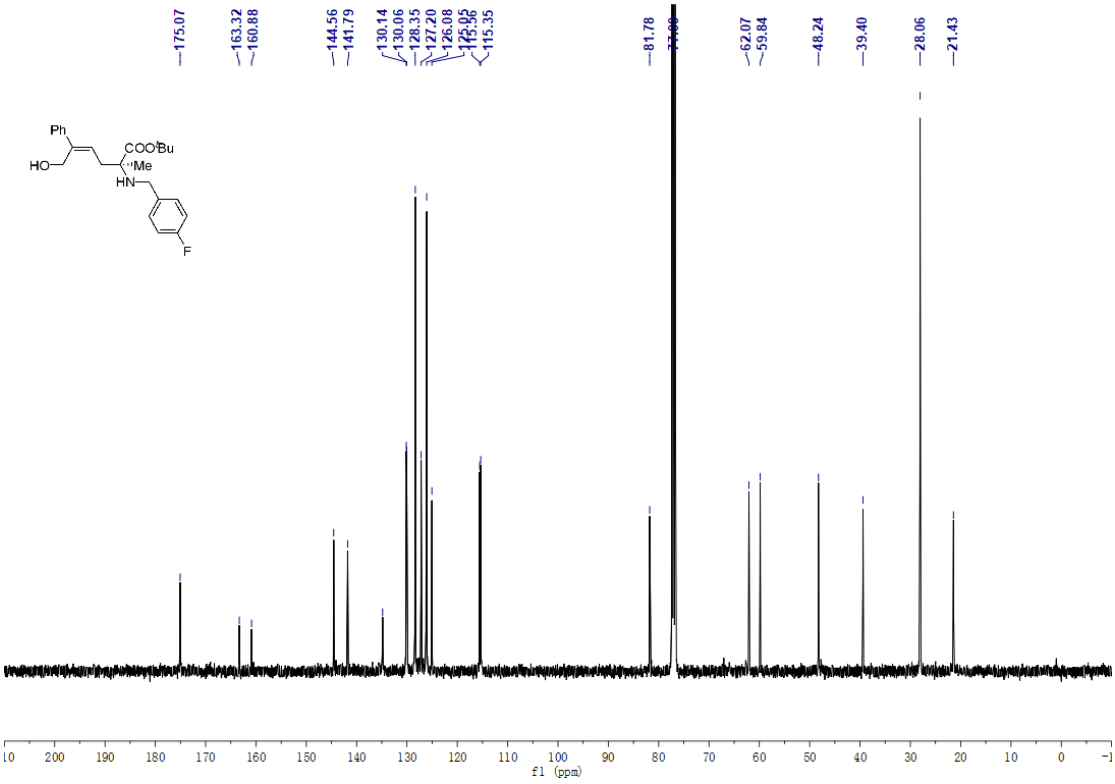

**$^{13}$C NMR** spectrum of **3ea** in $CDCl_3$



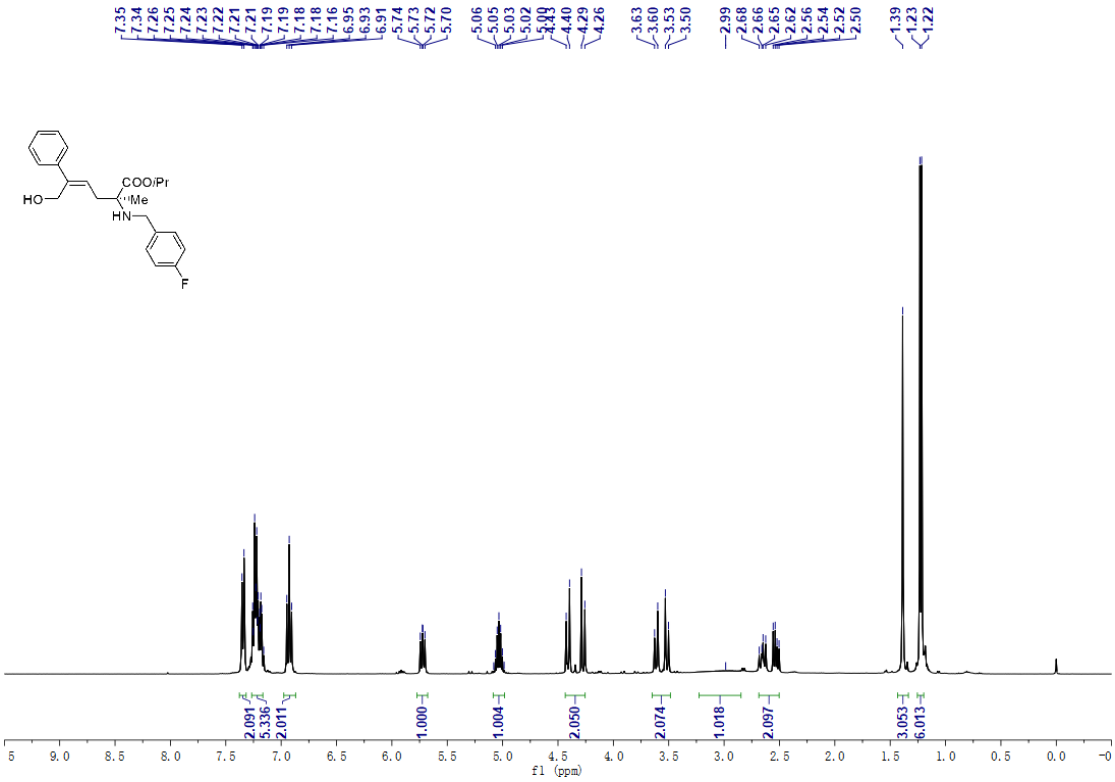
**$^{1}$H NMR** spectrum of **3fa** in $CDCl_3$



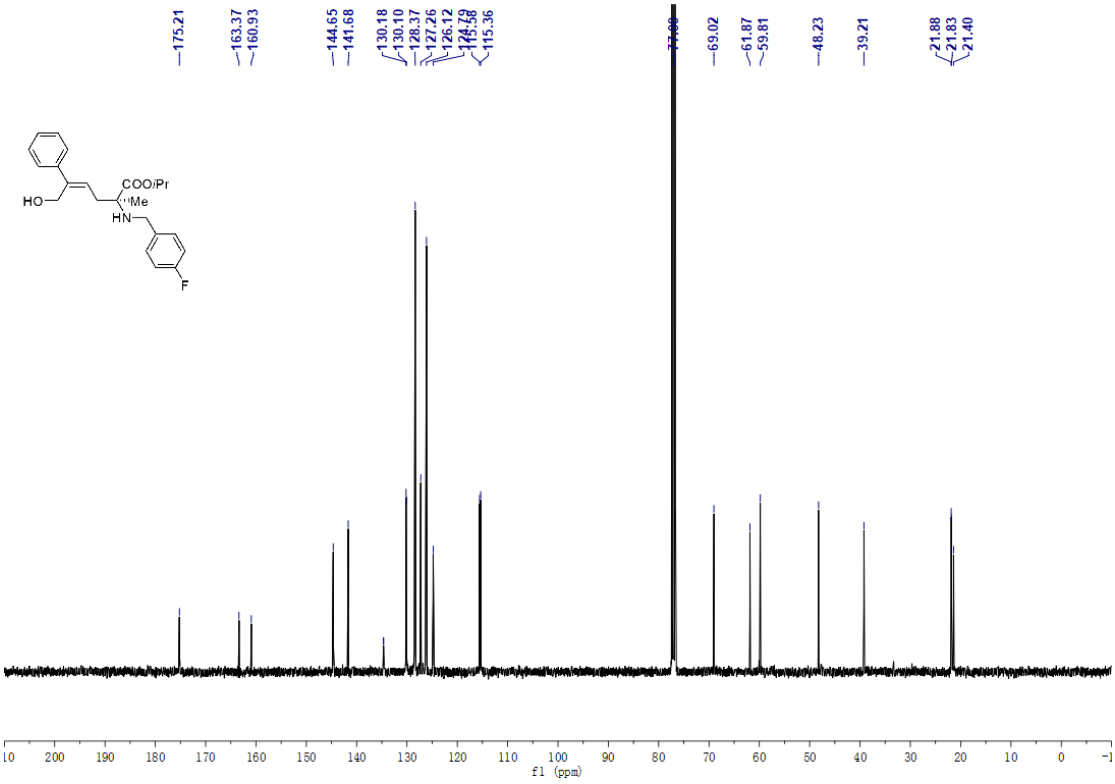

**$^{13}$C NMR** spectrum of **3fa** in $CDCl_3$



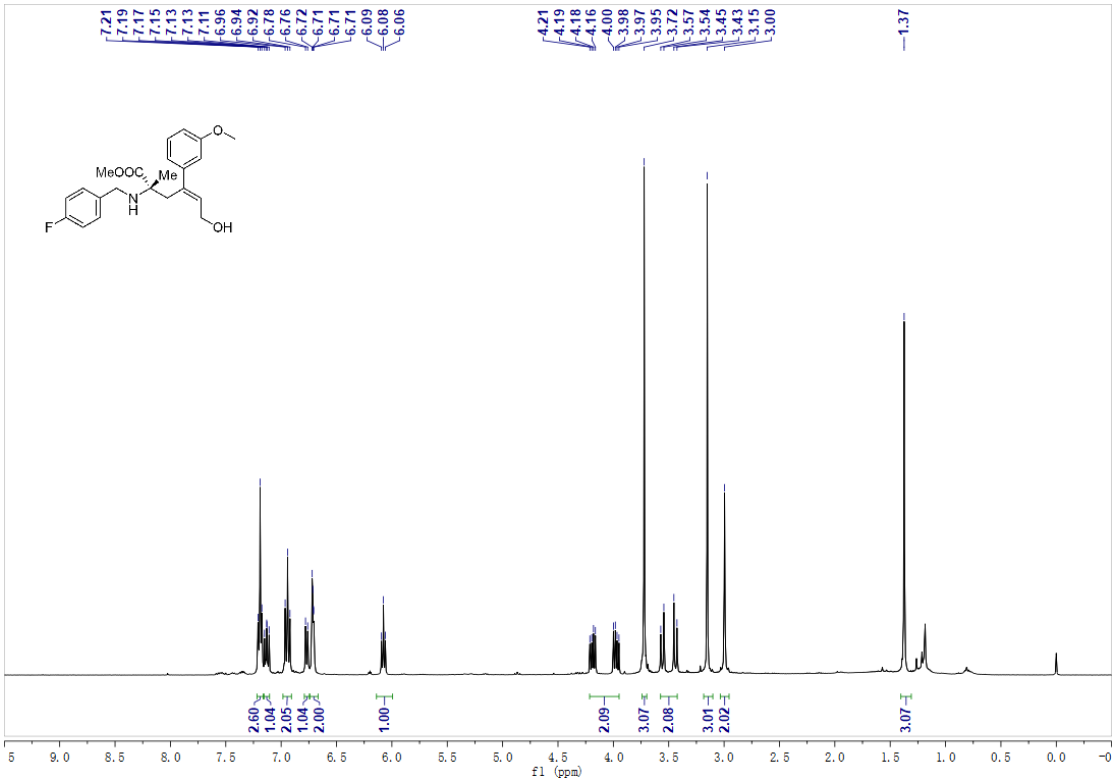
**$^{1}$H NMR** spectrum of **3ga** in $CDCl_3$



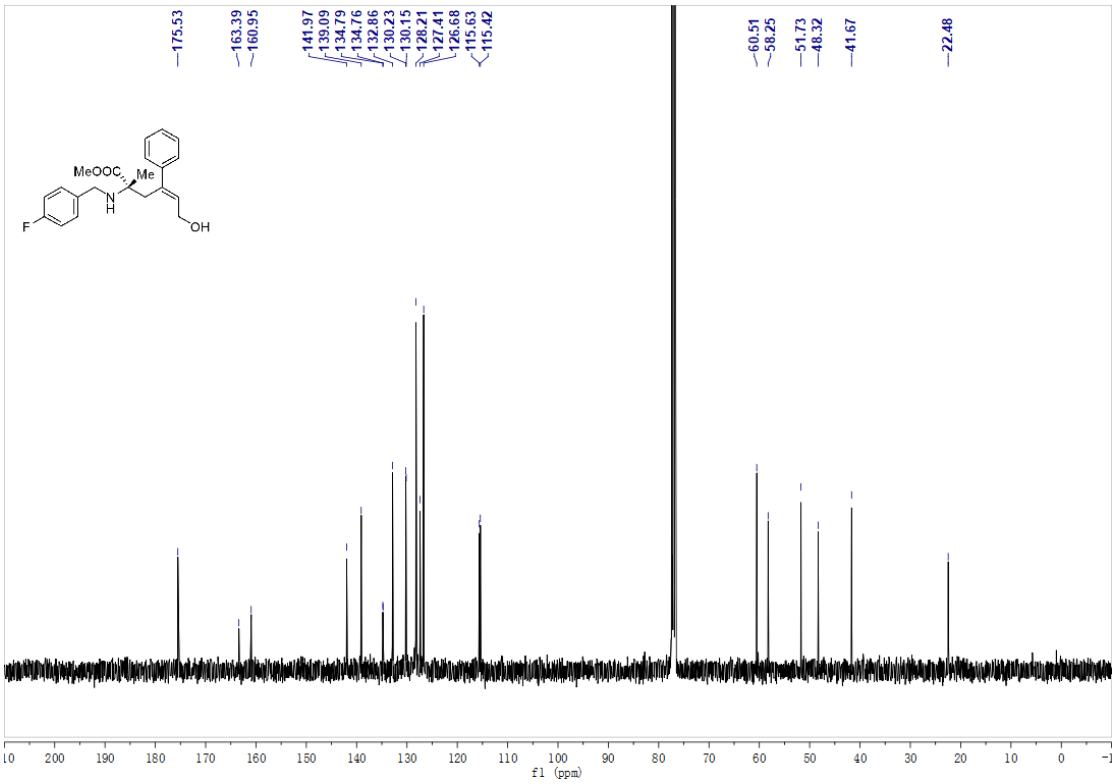

**$^{13}$C NMR** spectrum of **3ga** in $CDCl_3$



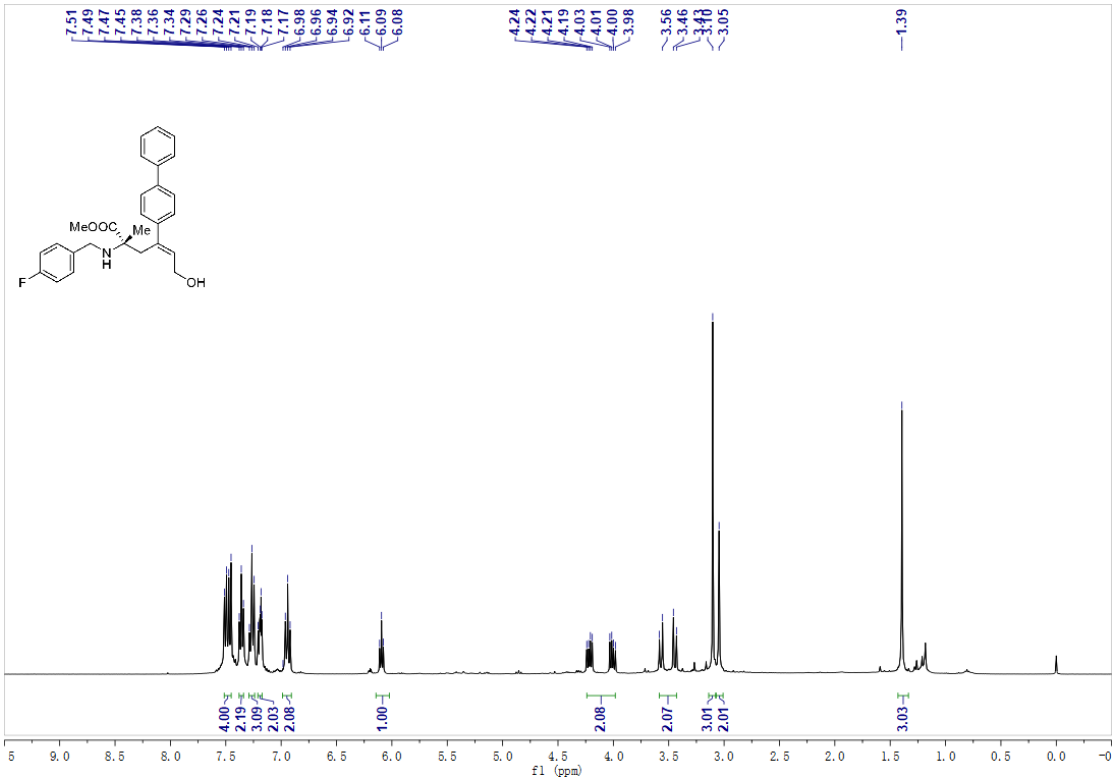
**$^{1}$H NMR** spectrum of **5ba** in $CDCl_3$



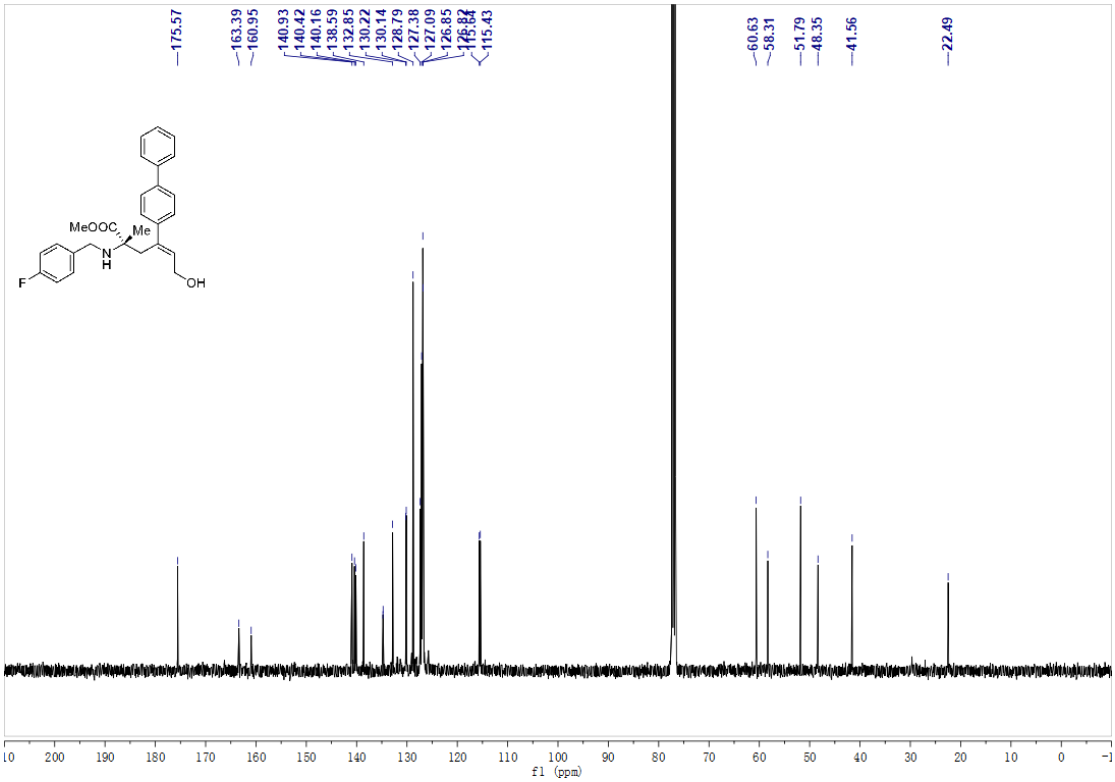

**$^{13}$C NMR** spectrum of **5ba** in $CDCl_3$



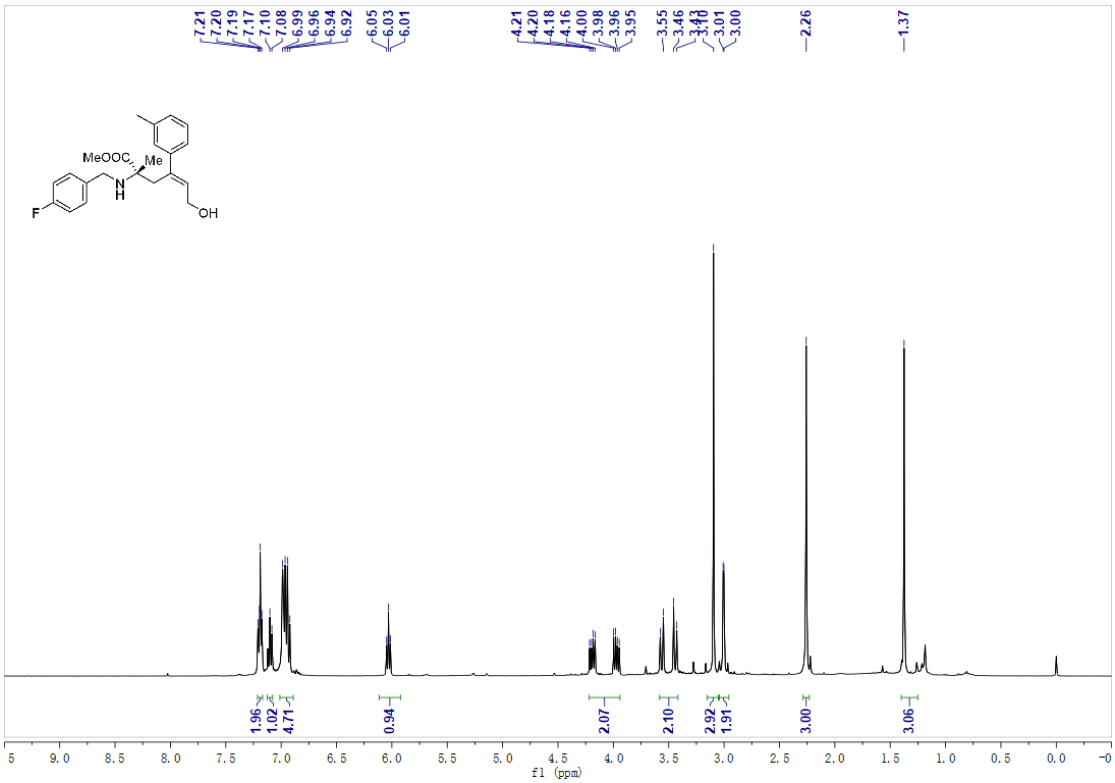
**$^{1}$H NMR** spectrum of **5bb** in $CDCl_3$



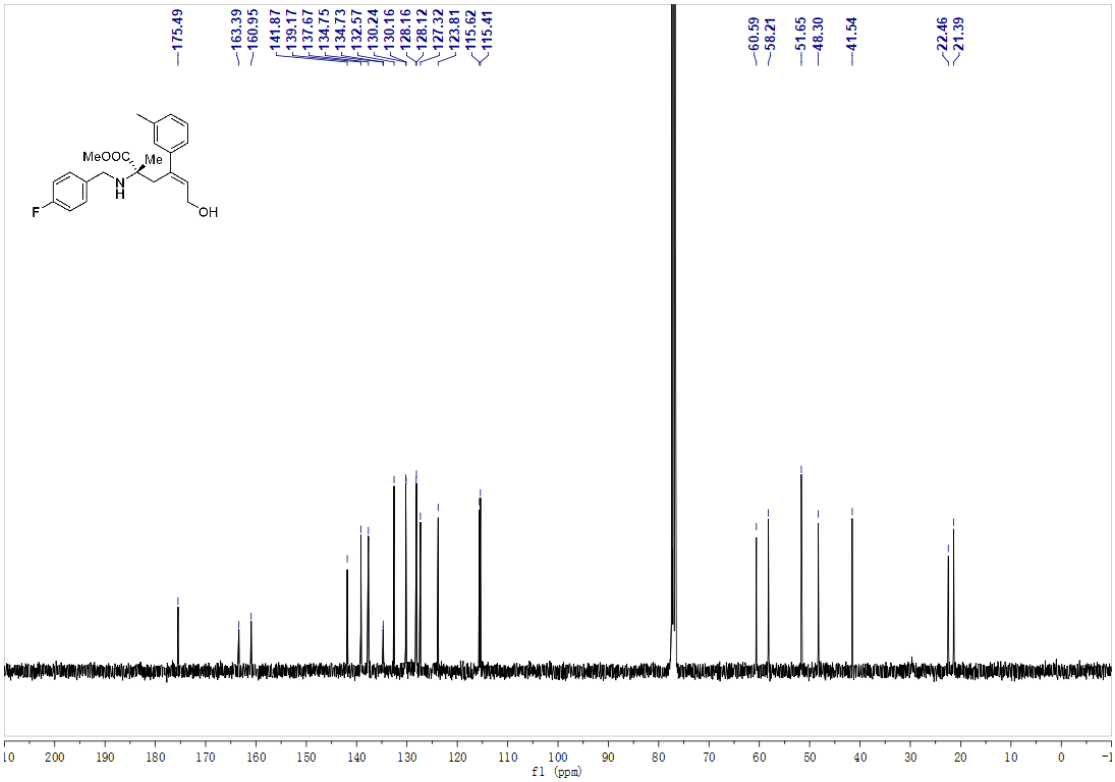

**$^{13}$C NMR** spectrum of **5bb** in $CDCl_3$



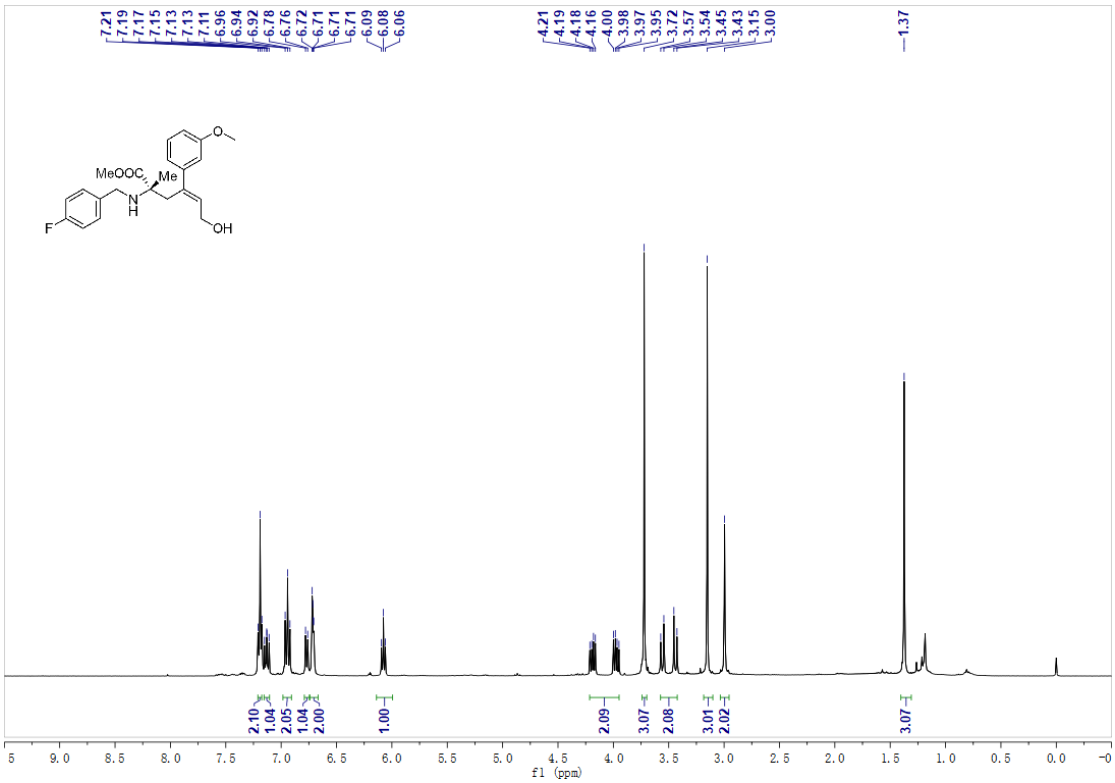
**$^{1}$H NMR** spectrum of **5bc** in $CDCl_3$



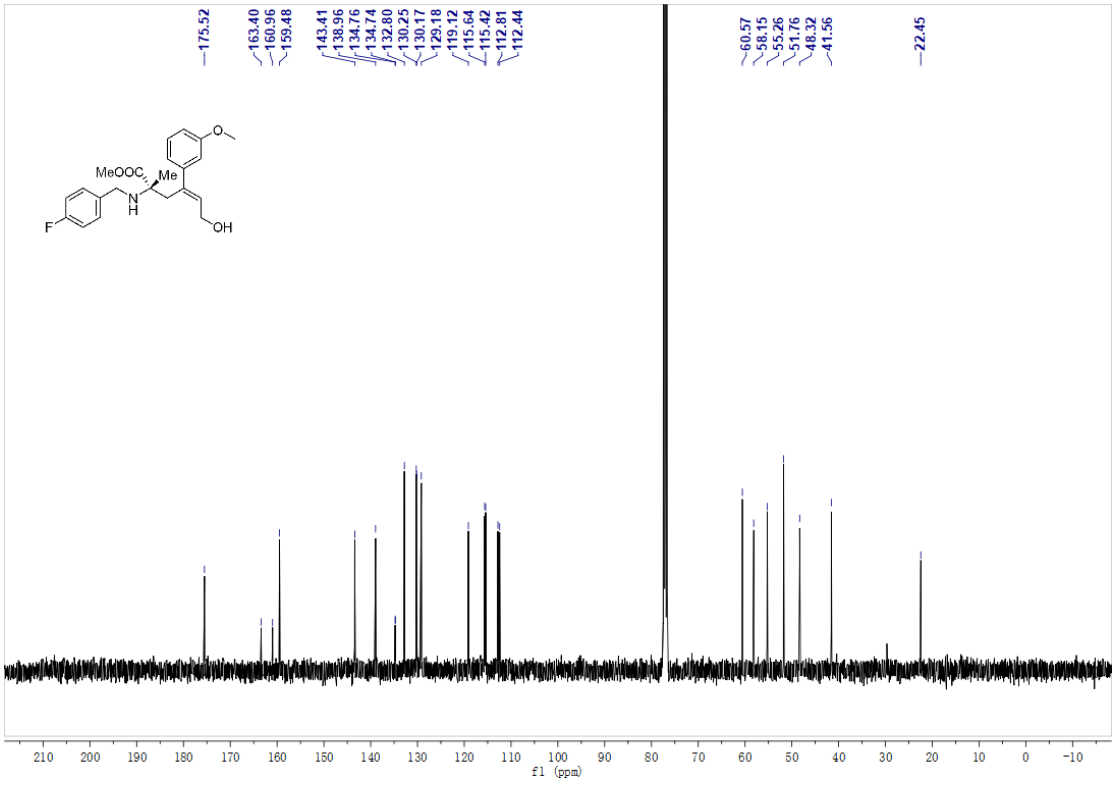

**$^{13}$C NMR** spectrum of **5bc** in $CDCl_3$



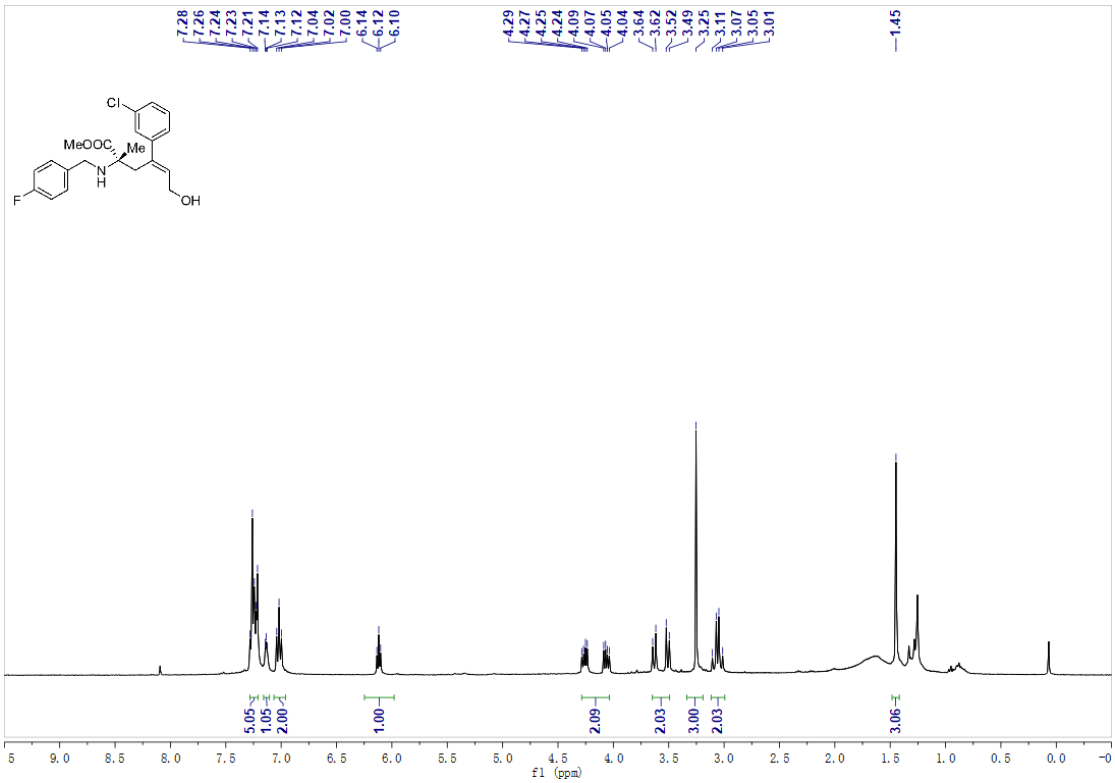
**$^{1}$H NMR** spectrum of **5bd** in $CDCl_3$



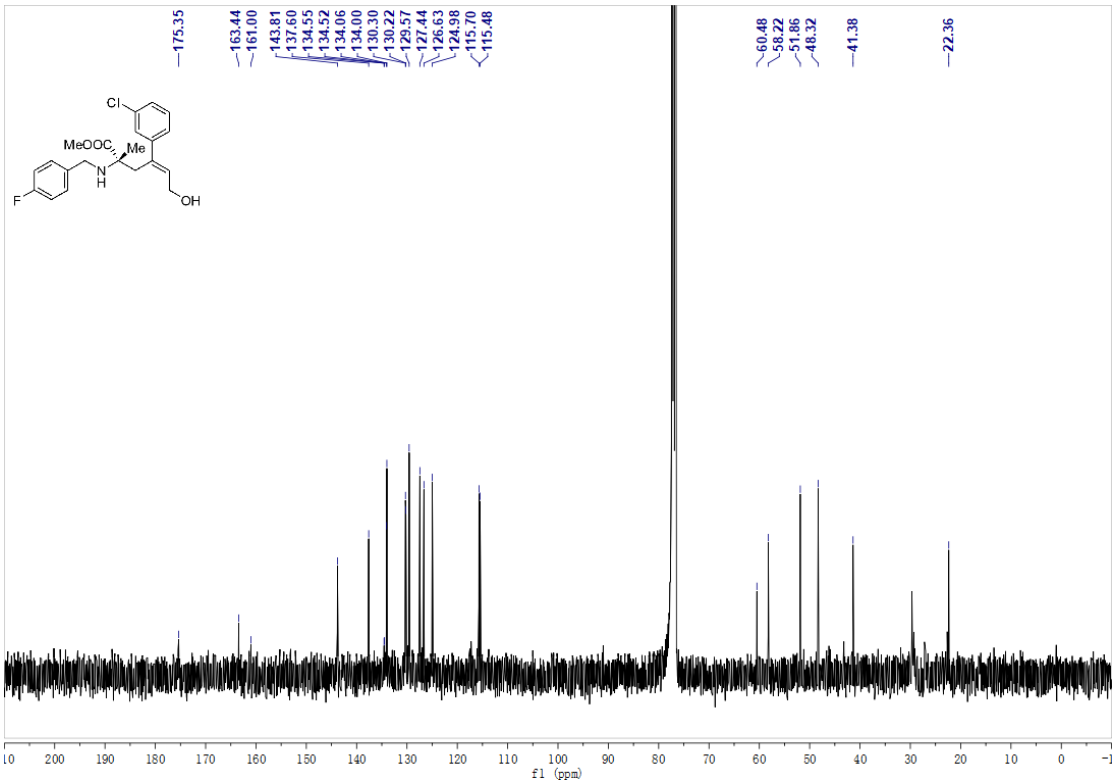

**$^{13}$C NMR** spectrum of **5bd** in $CDCl_3$



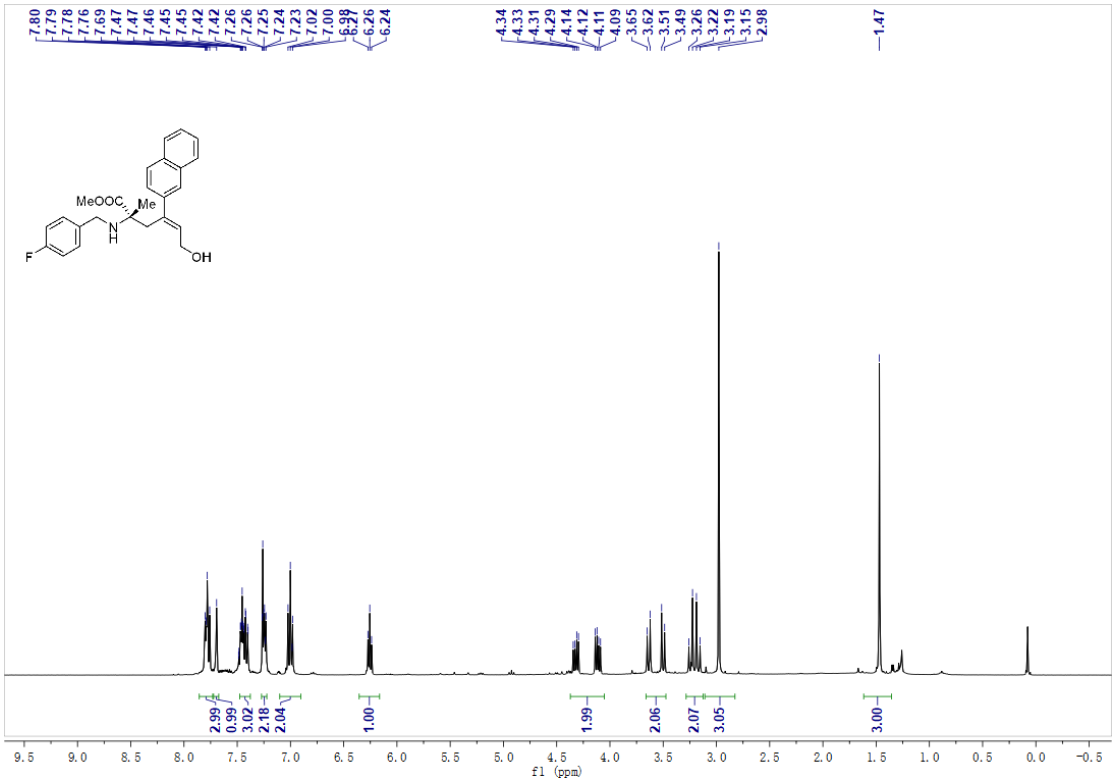
**$^{1}$H NMR** spectrum of **5be** in $CDCl_3$



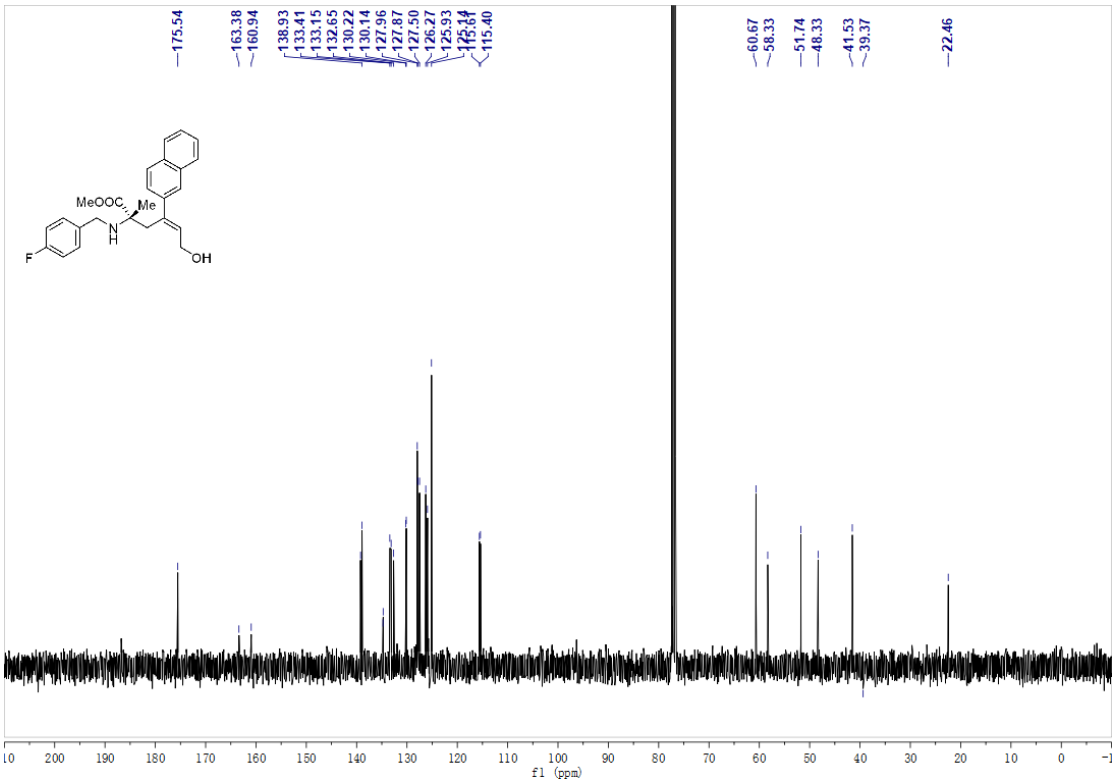

**$^{13}$C NMR** spectrum of **5be** in $CDCl_3$



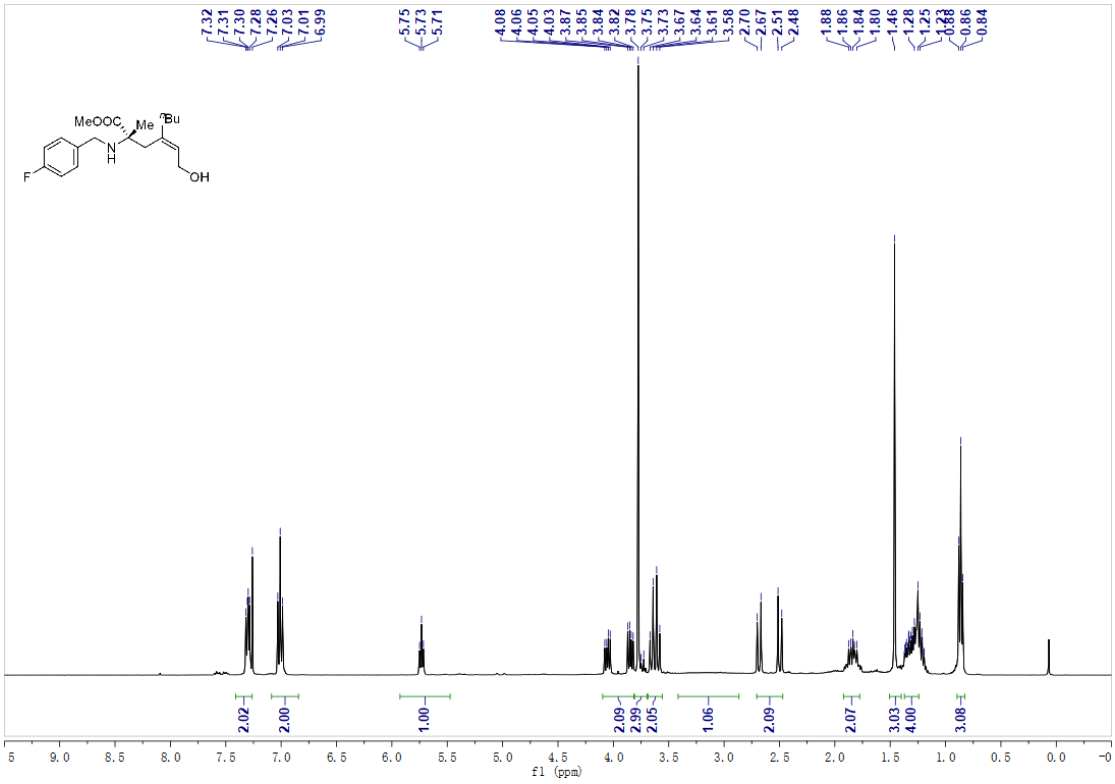
**$^{1}$H NMR** spectrum of **5bf** in $CDCl_3$



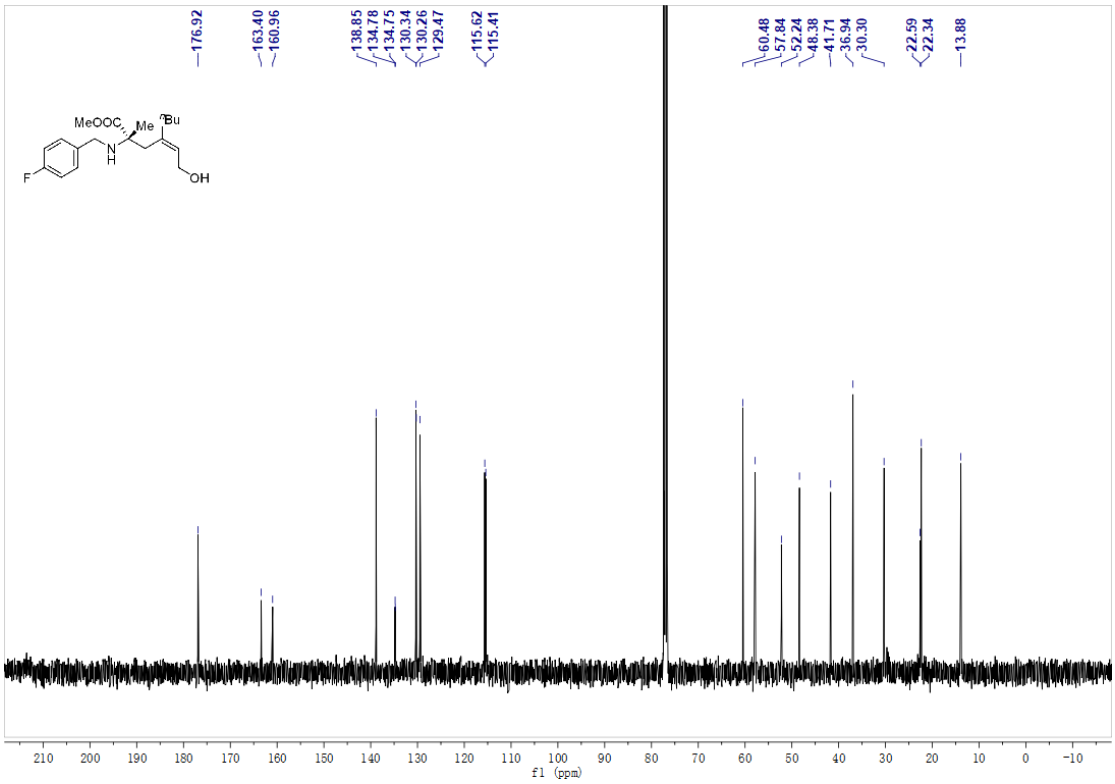

**$^{13}$C NMR** spectrum of **5bf** in $CDCl_3$



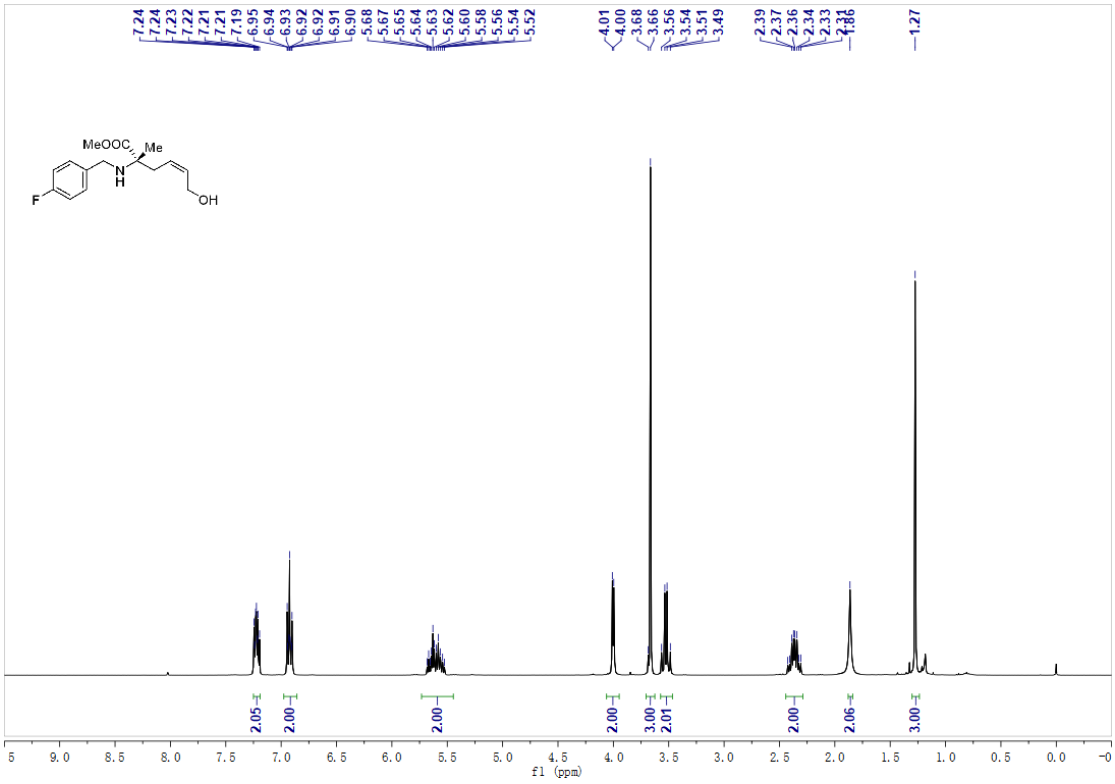
**$^{1}$H NMR** spectrum of **5bg** in $CDCl_3$



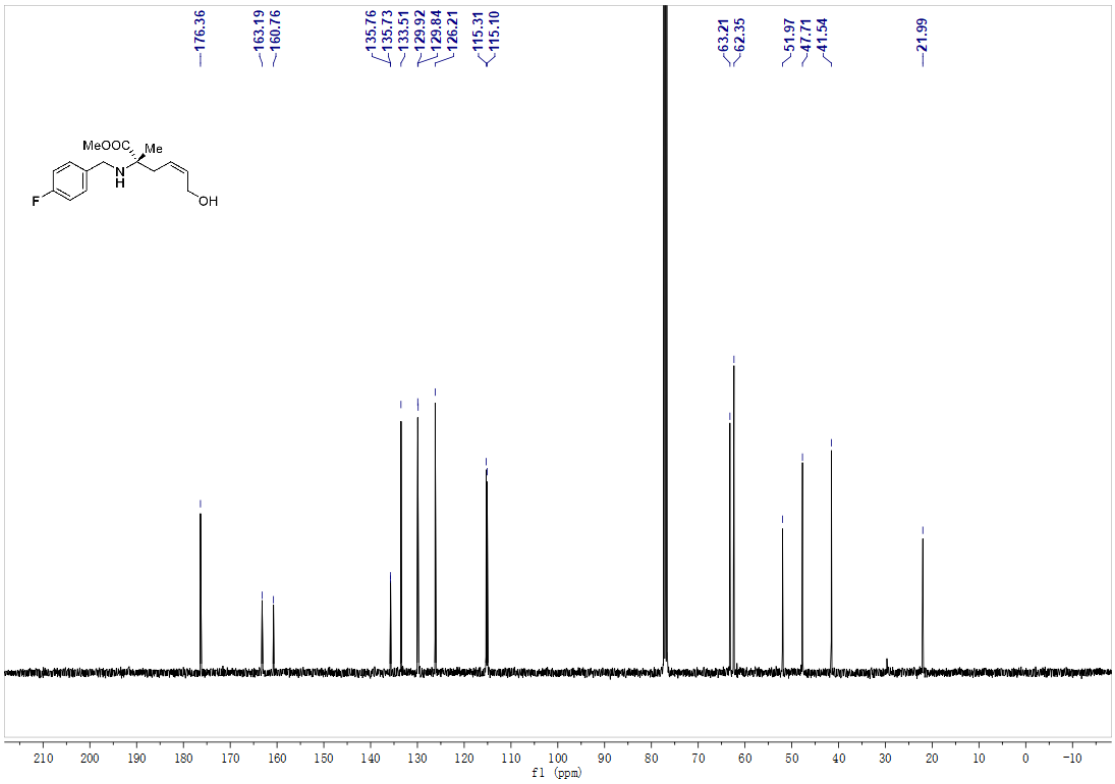

**$^{13}$C NMR** spectrum of **5bg** in $CDCl_3$



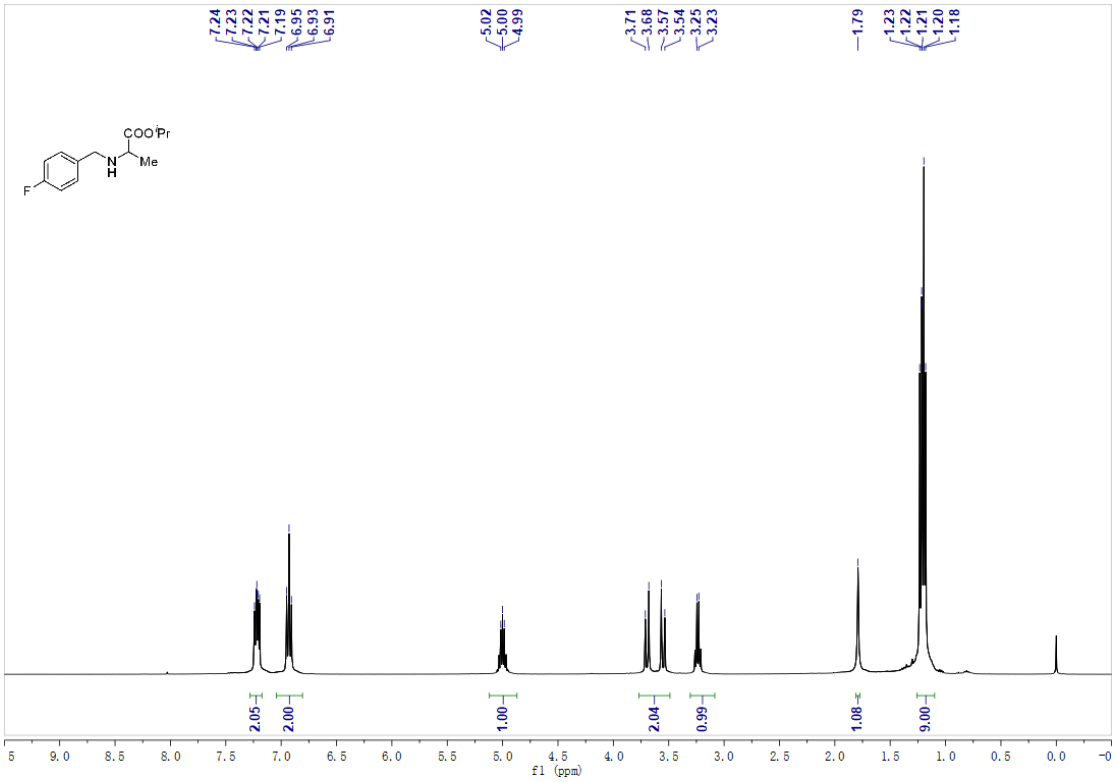
**$^{1}$H NMR** spectrum of **5bh** in $CDCl_3$



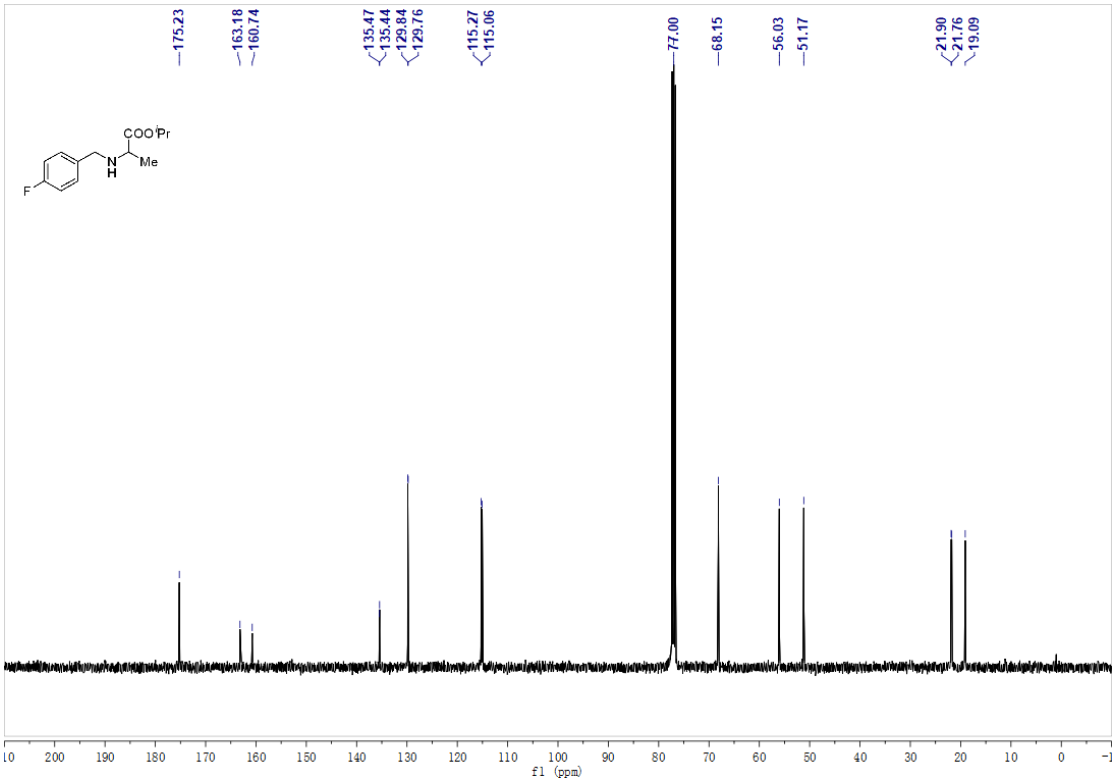

**$^{13}$C NMR** spectrum of **5bh** in $CDCl_3$



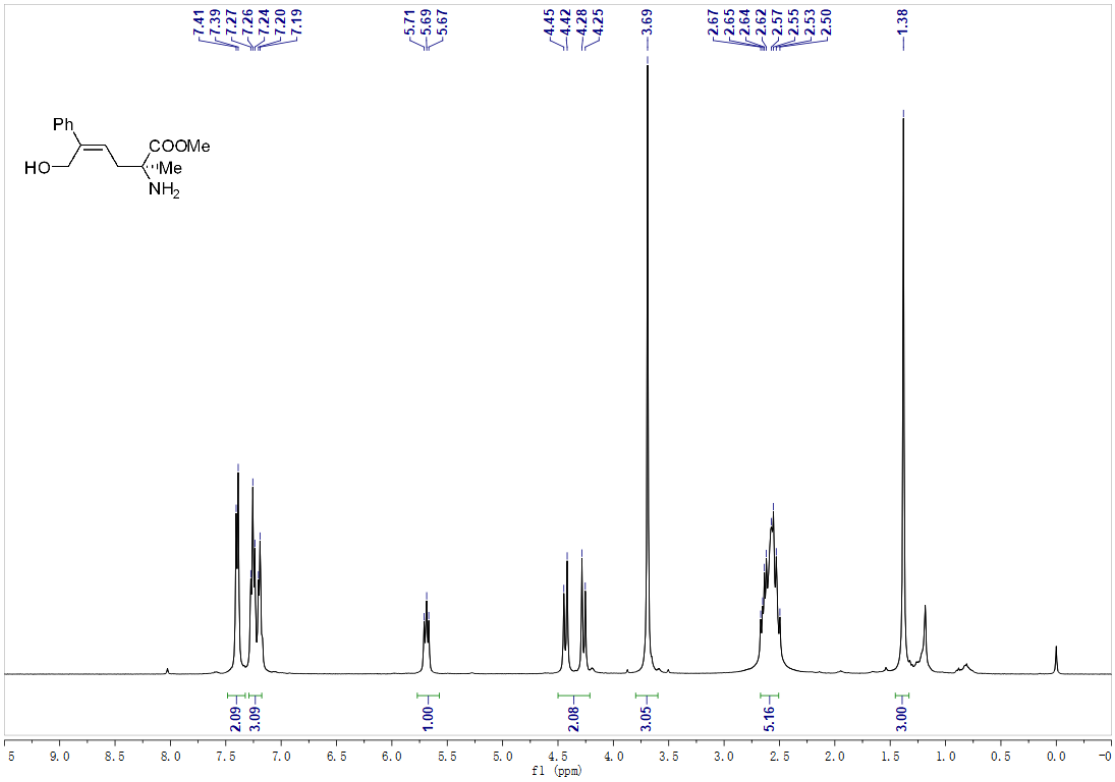
**$^{1}$H NMR** spectrum of **1g'** in $CDCl_3$



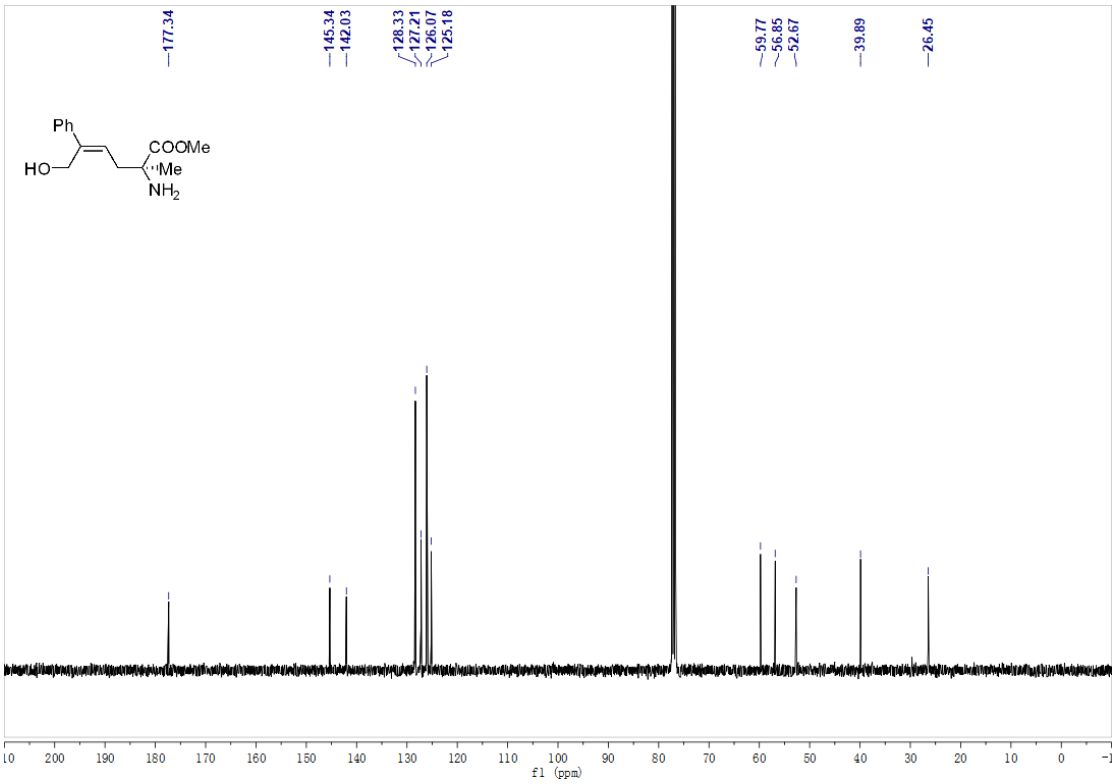

**$^{13}$C NMR** spectrum of **1g'** in $CDCl_3$



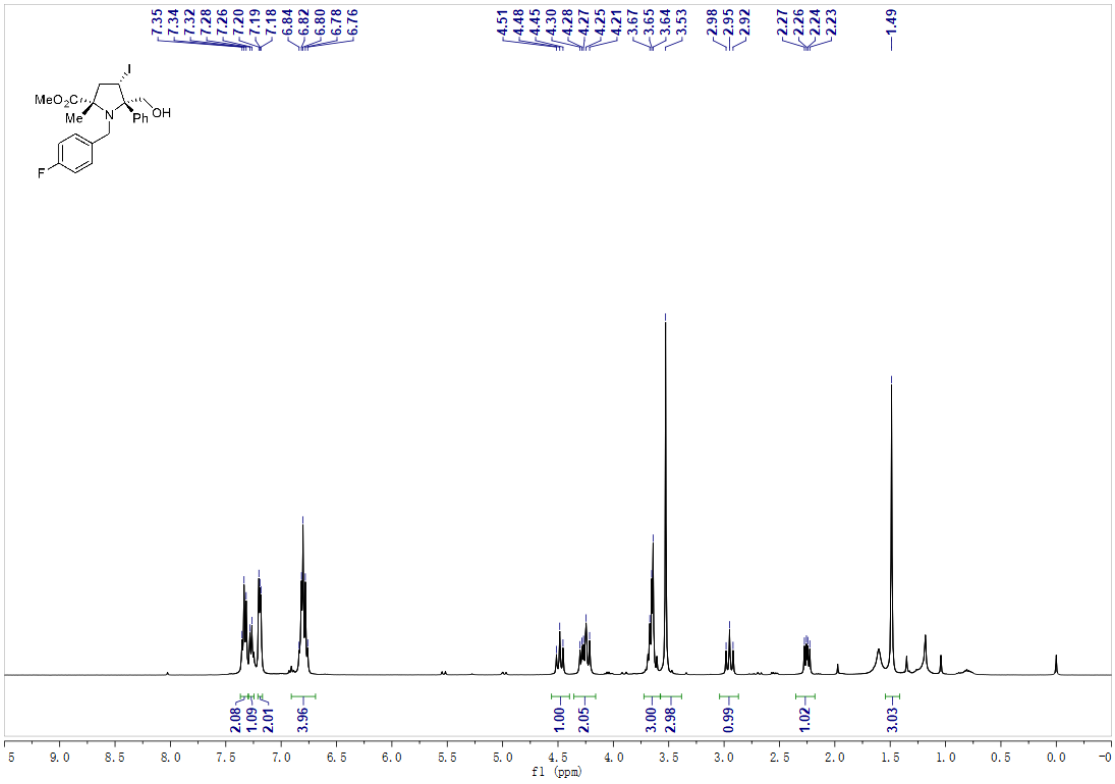
**$^{1}$H NMR** spectrum of **6aa** in $CDCl_3$



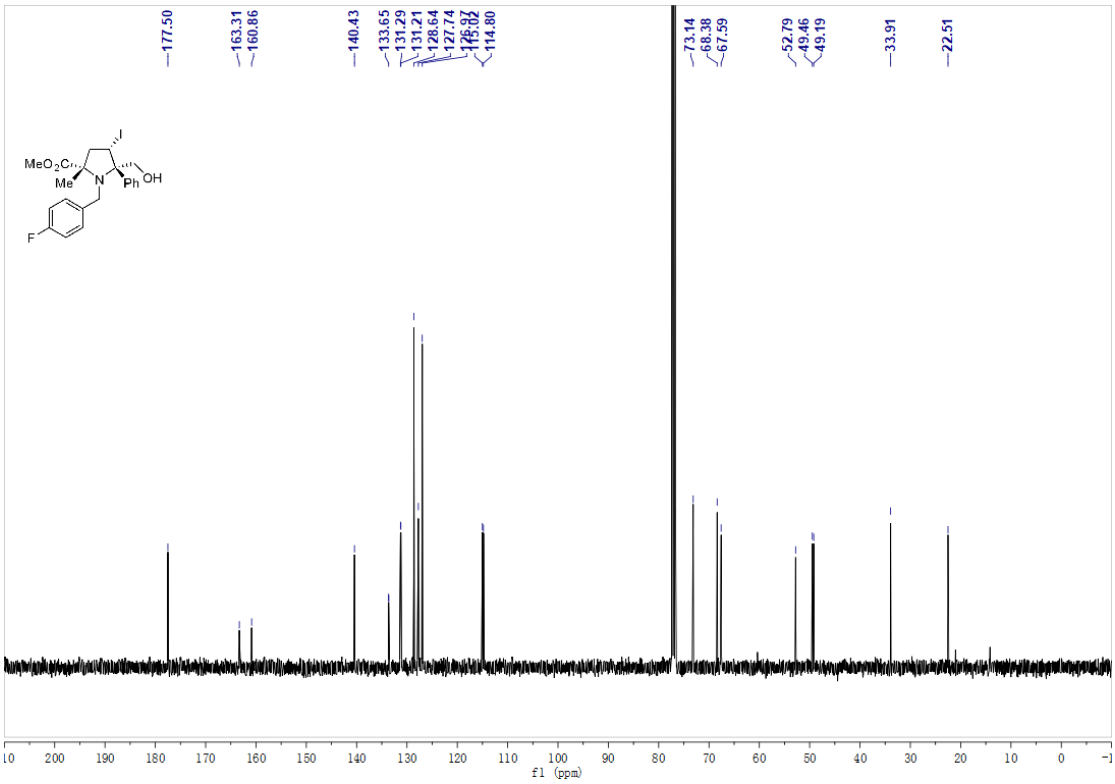

**$^{13}$C NMR** spectrum of **6aa** in $CDCl_3$



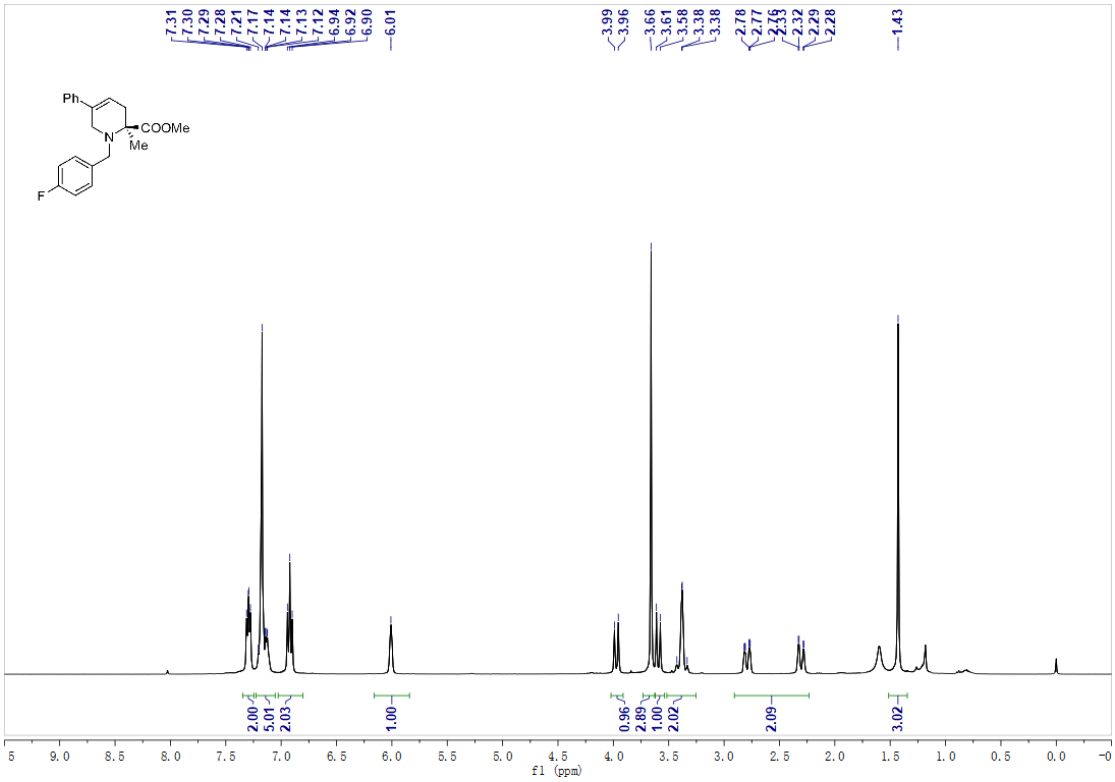
**$^{1}$H NMR** spectrum of **6ab** in $CDCl_3$




**$^{13}$C NMR** spectrum of **6ab** in $CDCl_3$



**$^{1}$H NMR** spectrum of **6ac** in $CDCl_3$




**$^{13}$C NMR** spectrum of **6ac** in $CDCl_3$