# Supporting Information

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## 1. General

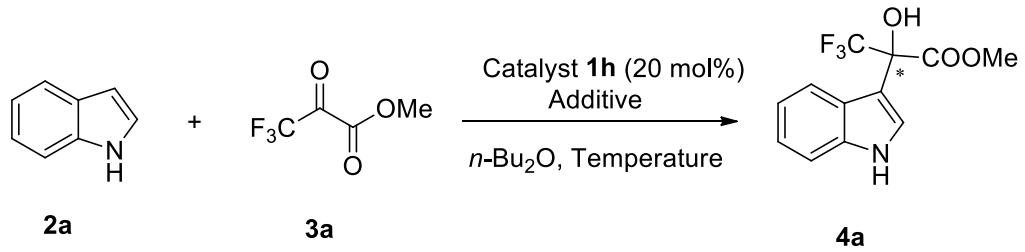
### Instrumentations

All reactions were performed under an argon atmosphere. The reactions were monitored by TLC (thin layer chromatography) method; column and preparative TLC purification were carried out using silica gel. Melting points were uncorrected and recorded on X-5 melting point apparatus. $^{1}H$ NMR and $^{13}C$ NMR spectra were measured on 400 MHz and 100 MHz spectrometers. Enantiomeric excess was decided with chiral Shimadzu LC-16 HPLC equipped with a SPD-16 UV-VIS Spectrophotometric Detector.

### Materials

All commercial reagents were purchased with the analysis purity grade. They were used without further purification unless specified. Petroleum ether (PE) and ethyl acetate (EtOAc) were distilled. *n*-butyl ether was used with the analysis purity grade, and other solvents were purchased with the ultra dry grade. General procedure of the catalytic Friedel-Crafts reaction between indole and trifluoromethylpyruvate.

## 2. Optimization of the reaction conditions[a]




**2a** **3a** **4a**

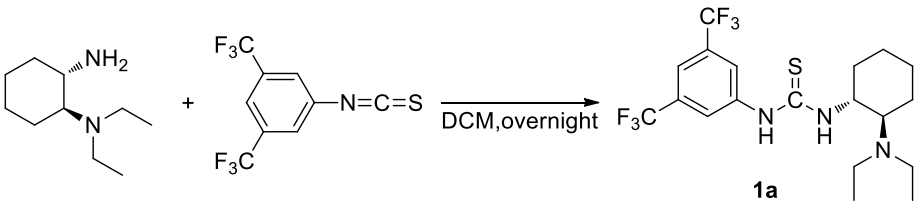
| Entry | Catalyst | Additive | Temperature | Yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|---|
| 1 | **1h** | $CF_3COOH$ | RT | 86 | 9 |
| 2 | **1h** | $CH_3COOH$ | RT | 85 | 69 |
| 3 | **1h** | $NaH_2PO_4$ | RT | 85 | 70 |
| 4 | **1h** | 4A MS | RT | 79 | 71 |
| 5 | **1h** | N-Methyl morpholine | RT | 85 | 23 |
| 6 | **1h** | $NaHCO_3$ | RT | 95 | 68 |
| 7 | **1h** | $Na_2CO_3$ | RT | 94 | 72 |
| 8 | **1h** | (*S*)-BINOL | RT | 80 | 73 |
| 9 | **1h** | (*R*)-BINOL | RT | 81 | 66 |
| 10 | **1h** | - | 0 °C | 88 | 67 |
| 11 | **1h** | - | -20 °C | 85 | 71 |

[a]Reaction conditions: 0.1 mmol **2a**, 0.12 mmol methyl trifluoropyruvate, 2.0 mL *n*-$Bu_2O$.

[b]Isolated yield.

[c]Determined by HPLC analysis on a chiral stationary phase.

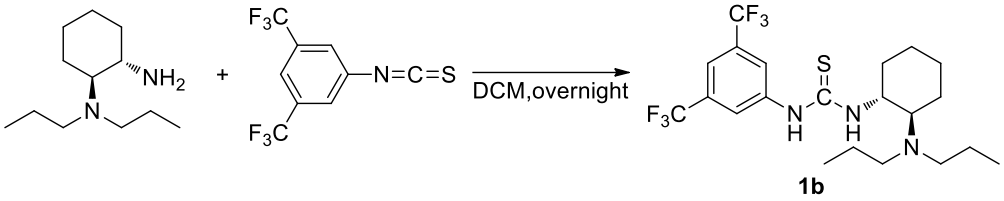
## 3. Characterization of catalysis 1




**1a**

Bifunctional organocatalyst **1a** was prepared by the literature procedure.[1]

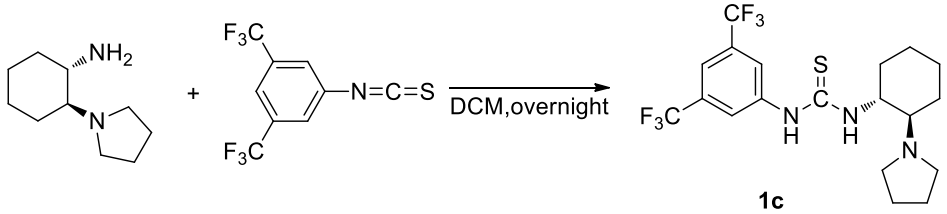
**1a**: white solid, mp 143.7-144.3°C, $[\alpha]_D^{26}$= -25.0 (c 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 7.84 (s, 2 H), 7.70 (s, 1 H), 3.77 (br, 1 H), 2.64 (s, 3 H), 2.39 (s, 3 H), 1.83-1.94 (m, 3 H), 1.19-1.36 (m, 11 H); $^{19}F$ NMR ($CDCl_3$, 564 MHz) δ -63.44 (s, 6 F).




**1b**

Bifunctional organocatalyst **1b** was prepared by the literature procedure.[2]

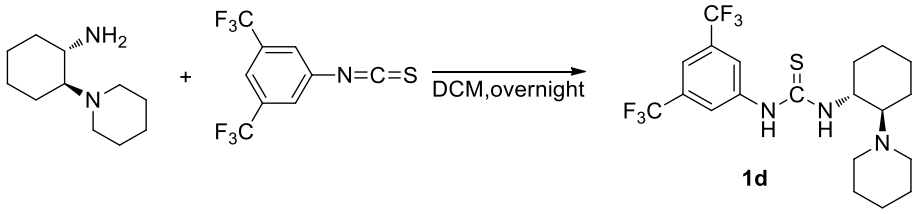
**1b**: white solid, mp 139.5-141.2°C, $[\alpha]_D^{26}$= -18.0 (c 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 7.74 (s, 2H), 7.68 (s, 1 H), 3.71 (s, 1 H), 2.85 (br, 1H), 2.26-2.47 (m, 5 H), 1.72-1.89 (m, 3 H), 1.11-1.31 (m, 8 H), 0.70-0.72 (m, 6 H); $^{19}F$ NMR ($CDCl_3$, 564 MHz) δ -63.53 (s, 6 F).




**1c**

Bifunctional organocatalyst **1c** was prepared by the literature procedure.[3]

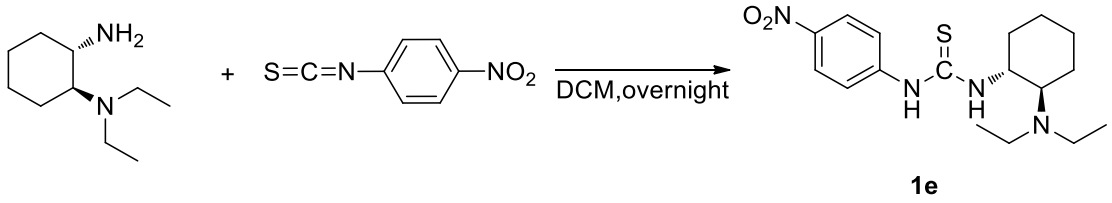
**1c**: white solid, mp 116.4-118.2°C, $[\alpha]_D^{26}$= 3.0 (c 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 9.89 (br, 1 H), 8.17 (s, 2 H), 7.54 (s, 2 H), 4.64 (s, 1 H), 3.29-3.48 (m, 4 H), 2.40 (d, *J*=12.0 Hz, 1 H), 2.00-2.14 (m, 5 H), 1.85-1.87 (m, 1 H), 1.35-1.50 (m, 4 H), 0.79-0.89 (m, 3 H); $^{19}F$ NMR ($CDCl_3$, 564 MHz) δ -63.46 (s, 6 F).




**1d**

Bifunctional organocatalyst **1d** was prepared by the literature procedure.[3]

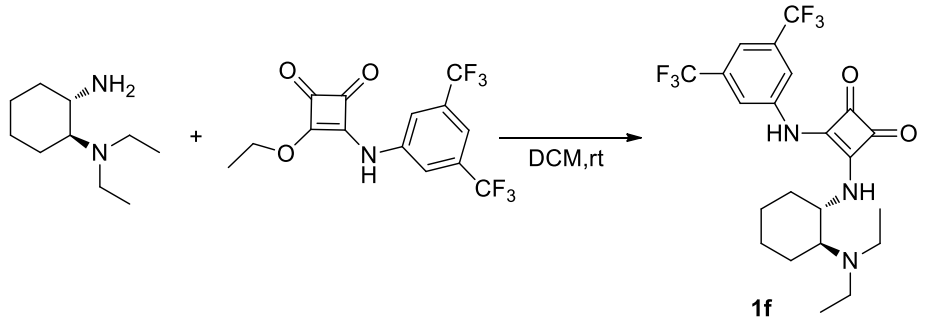
**1d**: white solid, mp 148.4-150.5°C, $[\alpha]_D^{26}$= -23.0 (c 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 7.79 (s, 2 H), 7.68 (s, 1 H), 3.74 (br, 1 H), 2.58-2.68 (m, 4 H), 2.41 (s, 2 H), 1.73-1.89 (m, 3 H), 1.18-1.29 (m, 5 H), 0.93 (s, 6 H); $^{19}F$ NMR ($CDCl_3$, 564 MHz) δ -63.44 (s, 6 F).




**1e**

Bifunctional organocatalyst **1e** was prepared by the literature procedure.[4]

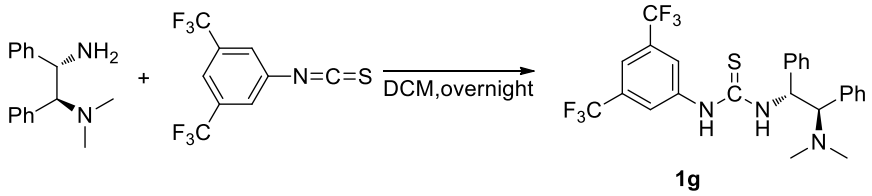
**1e**: yellow solid, mp 109.9-111.7°C, $[\alpha]_D^{26}$= -41.0 (c 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, *J*=8.0 Hz, 2 H), 7.47 (d, *J*=8.0 Hz, 2 H), 3.84 (t, *J*=12.0 Hz, 1 H), 2.53-2.75 (m, 4 H), 2.32-2.39 (m, 2 H), 1.70-1.89 (m, 3 H), 1.06-1.23 (m, 4 H), 0.93-0.96 (m, 6 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ 197.8, 145.4, 130.5, 129.7, 126.9, 100.0, 44.9, 34.1, 31.2, 26.9, 26.0, 25.3, 15.7; HRMS: (ESI+) m/z calcd for [$C_{17}H_{26}N_4O_2S_1$ + $H^+$] 351.1849, found 351.1855.




**1f**

Bifunctional organocatalyst **1f** was prepared by the literature procedure.[4]

**1f**: white solid, mp 232.5-233.1°C, $[\alpha]_D^{21}$= -16.2 (c 0.50, EtOH); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 10.15 (s, 1 H), 8.09 (s, 2 H), 7.65 (s, 1 H), 7.59 (br, 1 H), 3.92 (s, 1 H), 2.52-2.58 (m, 2 H), 2.42-2.45 (m, 1 H), 2.27-2.32 (m, 2 H), 2.02-2.09 (m, 1 H), 1.69-1.83 (m, 3 H), 1.17-1.40 (m, 5 H), 0.86-0.89 (m, 6 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ 194.2, 192.7, 143.2, 126.4, 123.7, 119.8, 65.4, 56.7, 26.7, 26.0, 16.0; $^{19}F$ NMR ($CDCl_3$, 564 MHz) δ -63.66 (s, 6 F); HRMS: (ESI+) m/z calcd for [$C_{22}H_{25}F_6N_3O_2$ + $H^+$] 478.1924, found 478.1929.




**1g**

Bifunctional organocatalyst **1g** was prepared by the literature procedure.[5]

**1g**: white solid, mp 83.0-85.6°C, $[\alpha]_D^{26}$= -157.0 (c 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.29 (br, 1 H), 7.67-7.72 (m, 3 H), 7.25-7.26 (m, 3 H), 7.15 (s, 5 H), 5.36 (br, 1 H), 3.81 (d, *J*=12.0 Hz, 1 H), 2.21 (s, 6 H); $^{19}F$ NMR ($CDCl_3$, 564 MHz) δ -63.42 (s, 6 F).

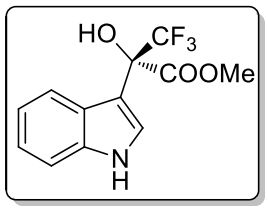
Catalyst **1h** was purchased from Daicel Chiral Technologies (China) Co., LTD.

### 4. General procedure of the catalytic Friedel-Crafts Alkylation and Characterization of compounds 4

To indoles **2** (0.1 mmol) and the catalyst **1h** (11 mg, 0.02 mmol) in dry *n*-Butyl ether (2.0 mL) was added methyl/ehyl trifluoropyruvate (0.12 mmol) at room temperature. The mixture was stirred for 6 h to 106 h at room temperature to complete checked by thin layer chromatography. The mixture was directly submitted to flash silica gel column chromatography (petrolum ether:ethyl acetate = 3:1) to furnish the product **4.**

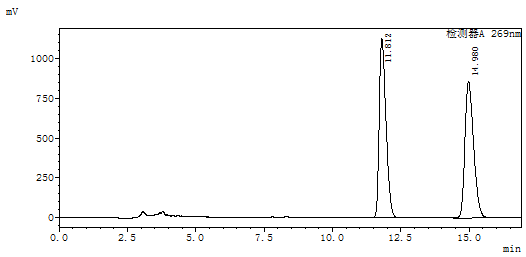
**Figure 1**. The state of substrates and catalysts during the reaction.

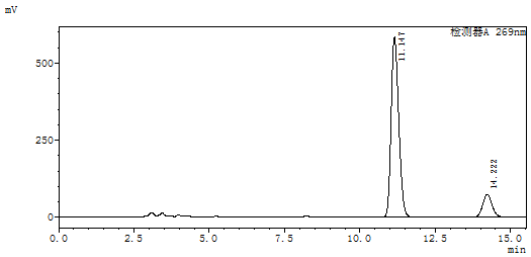
**(*R*)-methyl 3,3,3-trifluoro-2-hydroxy-2-(1H-indol-3-yl)propanoate (4a)**[6]




25.8 mg, 95% yield, white solid, mp 89-91 °C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.27 (s, 1 H), 7.84-7.87 (m, 1 H), 7.43-7.44 (m, 1 H), 7.35-7.38 (m, 1 H), 7.14-7.25 (m, 2 H), 5.19 (s, 1 H), 4.36 (s, 1 H), 3.93 (s, 3 H).

The ee was determined by HPLC analysis. CHIRALPAK AD-H; Hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 269 nm; retention time: 11.1 min (major) and 14.2 min (minor).

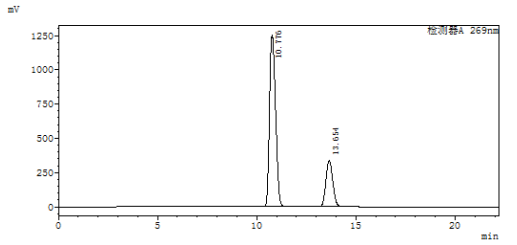


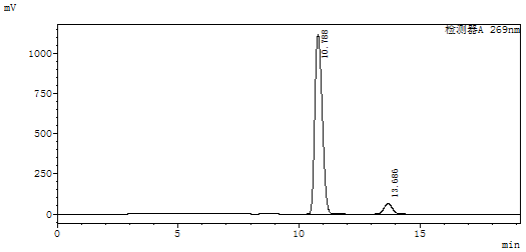

| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 11.812 | 19425436 | 1124825 | 50.659 |
| 2 | 14.980 | 18919907 | 858090 | 49.341 |

| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 11.147 | 10162037 | 582960 | 86.499 |
| 2 | 14.222 | 1586084 | 73886 | 13.501 |

**4a after crystallization**

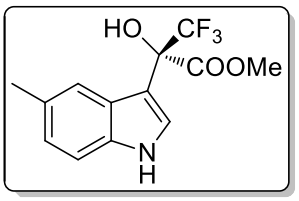



| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 10.776 | 26646036 | 1250240 | 76.614 |
| 2 | 13.654 | 8133739 | 335465 | 23.386 |



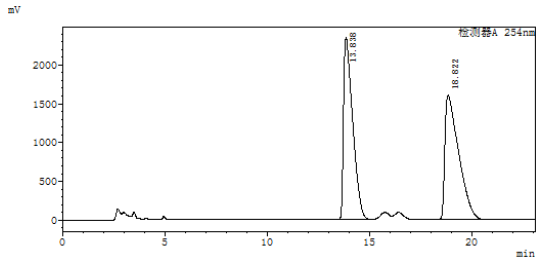

| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 10.788 | 23905919 | 1113969 | 93.867 |
| 2 | 13.686 | 1561858 | 63934 | 5.133 |

**(*R*)-methyl 3,3,3-trifluoro-2-hydroxy-2-(5-methyl-1H-indol-3-yl)propanoate (4b)**[6]

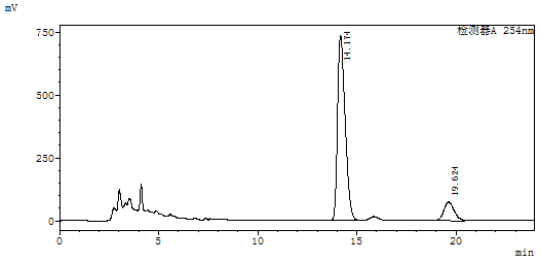



26.7 mg, 93% yield, white solid, mp 56-58 °C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.17 (s, 1 H), 7.61 (s, 1 H), 5.23 (s, 1 H), 7.31-7.33 (m, 1 H), 7.20-7.24 (m, 1 H), 7.03-7.06 (m, 14 H), 4.36 (s, 1 H), 3.92 (s, 3 H), 2.44 (s, 3 H).

The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 254 nm; retention time: 14.2 min (major) and 19.6 min (minor).

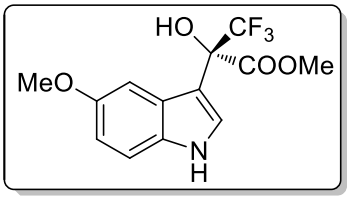



| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 13.838 | 73011737 | 2339360 | 49.602 |
| 2 | 18.822 | 74182501 | 1600567 | 50.398 |



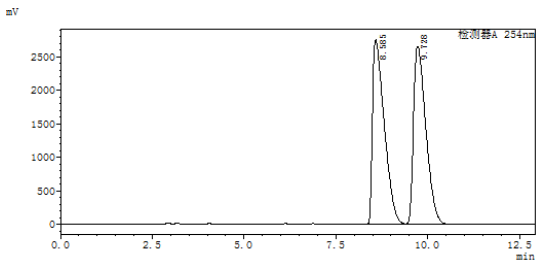

| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 14.174 | 19571755 | 732666 | 87.921 |
| 2 | 19.624 | 2688888 | 74248 | 12.079 |

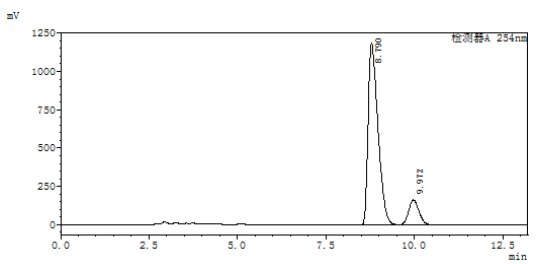
**(*R*)-methyl 3,3,3-trifluoro-2-hydroxy-2-(5-methoxy-1H-indol-3-yl)propanoate (4c)**[6]




27.8 mg, 92% yield, white solid, mp 88-90°C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.28 (s, 1 H), 7.31-7.34 (m, 2 H), 7.20 (dd, *J*=2.0 Hz, *J*=2.0 Hz 1 H), 6.88 (dd, *J*=2.8 Hz, *J*=3.2 Hz 1 H), 4.40 (s, 1 H), 3.92 (s, 3 H), 3.83 (s, 3 H).

The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 254.0 nm; retention time: 8.8 min (major) and 9.9 min (minor).

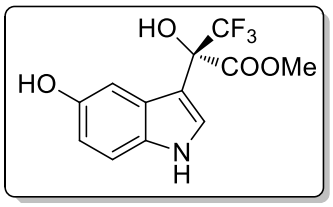


| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 8.595 | 61902670 | 2753128 | 49.929 |
| 2 | 9.728 | 62078085 | 2655107 | 50.071 |

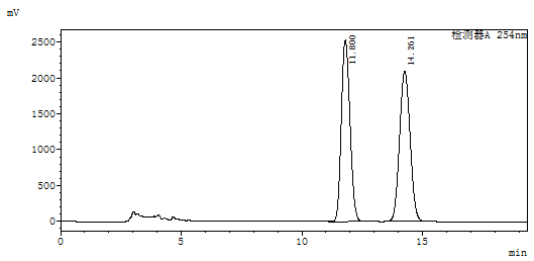
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 8.790 | 23003032 | 1184660 | 87.342 |
| 2 | 9.972 | 3333708 | 163653 | 12.658 |

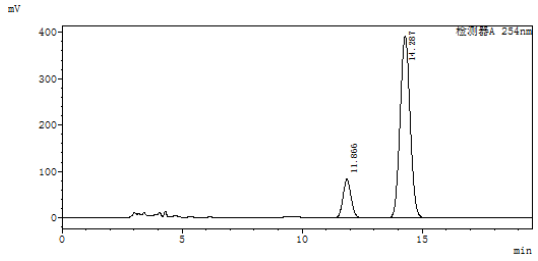
**(*R*)-methyl 3,3,3-trifluoro-2-hydroxy-2-(5-hydroxy-1H-indol-3-yl)propanoate (4d)**[6]




23.7 mg, 82% yield, colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.21 (s, 1 H), 7.43 (d, *J*=2.8 Hz, 1 H), 7.24-7.28 (m, 3 H), 6.83 (dd, *J*=2.4 Hz, *J*=2.4 Hz, 1 H), 4.68 (s, 1 H), 4.32 (s, 1 H), 3.99 (s, 3 H).

The ee was determined by HPLC analysis. CHIRALPAK AD-H; Hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 254.0 nm; retention time: 11.9 min (minor) and 14.3 min (major).

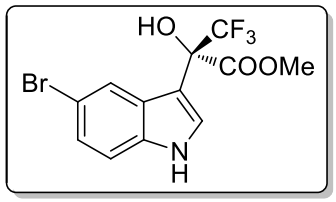



| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 11.800 | 62779934 | 2525908 | 49.742 |
| 2 | 14.261 | 63430982 | 2091341 | 50.258 |

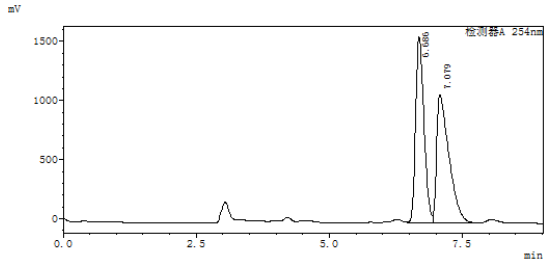
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 11.866 | 1935315 | 83005 | 14.571 |
| 2 | 14.287 | 11346605 | 390999 | 85.429 |

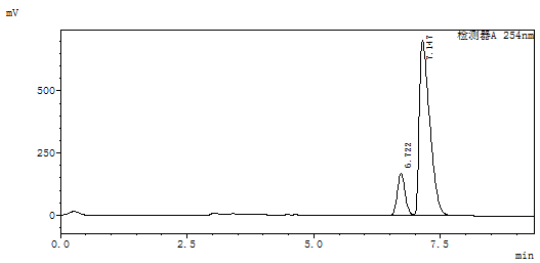
**(*R*)-methyl 2-(5-bromo-1H-indol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate (4e)**[6]




31.1 mg, 88% yield, colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.37 (s, 1 H), 8.04-8.05 (m, 1 H), 7.47 (d, *J*=2.8 Hz, 1 H), 7.30-7.33 (m, 1 H), 7.25-7.26 (m, 1 H), 4.39 (s, 1 H), 3.97 (s, 3 H);

The ee was determined by HPLC analysis. CHIRALPAK AD-H; Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 254.0 nm; retention time: 6.7 min (minor) and 7.1 min (major).

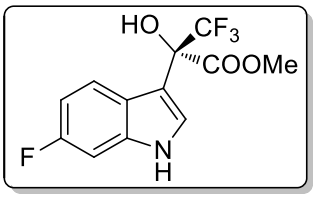



| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 6.686 | 17167868 | 1568783 | 49.430 |
| 2 | 7.079 | 17563454 | 1081703 | 50.570 |

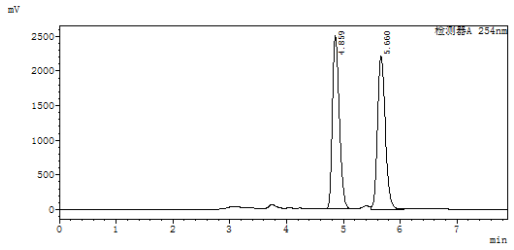
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 6.722 | 1815291 | 170235 | 15.175 |
| 2 | 7.147 | 10147098 | 704799 | 84.825 |

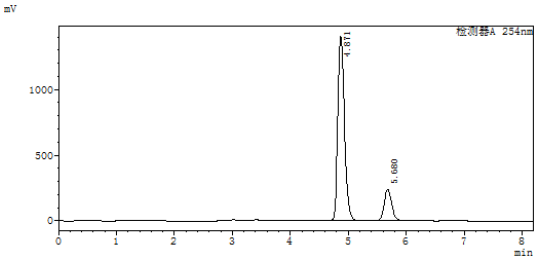
**(*R*)-methyl 3,3,3-trifluoro-2-(6-fluoro-1H-indol-3-yl)-2-hydroxypropanoate (4f)**[7]




26.3mg, 89% yield, colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.30 (s, 1 H), 7.78-7.81 (m, 1 H), 7.40-7.41 (m, 1 H), 7.02-7.05 (m, 1 H), 6.90-6.95 (m, 1 H), 4.39 (s, 1 H), 3.95 (s, 3 H).

The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 254.0 nm; retention time: 4.9 min (major) and 5.7 min (minor).

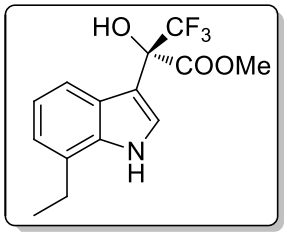



| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 4.859 | 20565142 | 2490359 | 49.225 |
| 2 | 5.660 | 21212914 | 2211045 | 50.775 |

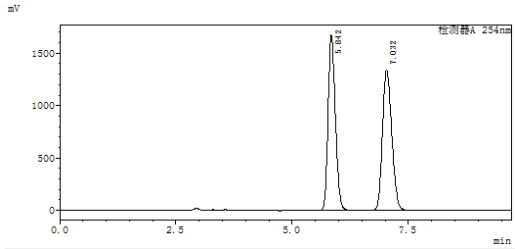
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 4.871 | 11073647 | 1397289 | 83.849 |
| 2 | 5.680 | 2132973 | 237227 | 16.157 |

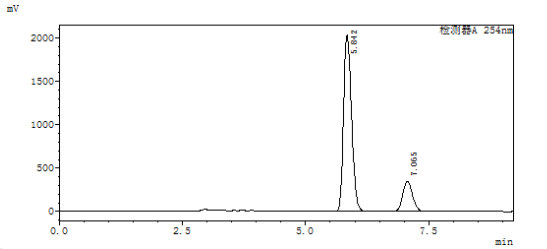
**(*R*) -methyl 2-(7-ethyl-1H-indol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate (4g)**




27.8 mg,92% yield, colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.26 (s, 1 H), 7.69 (d, *J*=8.0 Hz, 1 H), 7.40-7.41 (m, 1 H), 7.05-7.14 (m, 2 H), 4.37 (s, 1 H), 3.92 (s, 3 H), 2.82 (q, *J*=4.0 Hz, 2 H), 1.33 (t, *J*=4.0 Hz, 3 H).

The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 254.0 nm; retention time: 5.8 min (major) and 7.1 min (minor).

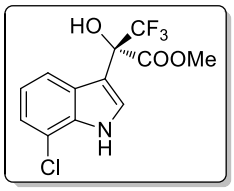



| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 5.842 | 18322573 | 1668909 | 49.789 |
| 2 | 7.032 | 18477955 | 1338576 | 50.211 |

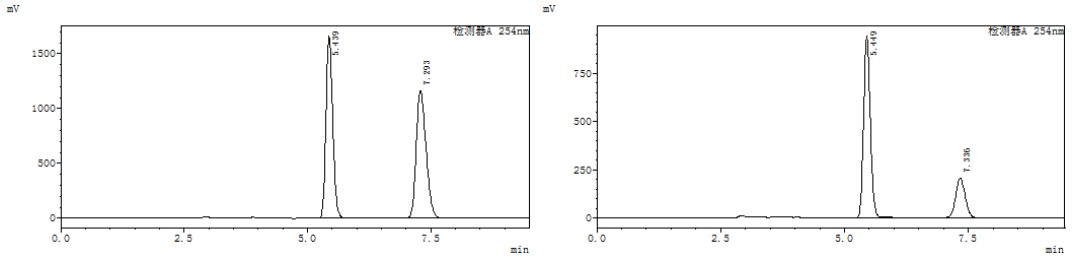
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 5.842 | 22812312 | 2029026 | 82.778 |
| 2 | 7.065 | 4746212 | 347914 | 17.222 |

**(*R*)-methyl 2-(7-chloro-1H-indol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate (4h)**




26.5 mg, 86 yield, white solid, mp 68-70 °C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.56 (s, 1 H), 7.78-7.80 (m, 1 H), 7.50 (d, *J*=2.8 Hz, 1 H), 7.22-7.25 (m, 1 H), 7.09 (t, *J*=7.6 Hz, 1 H), 4.42 (s, 1 H), 3.94 (s, 3 H).

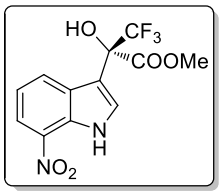
The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 254.0 nm; retention time: 5.4 min (major) and 7.3 min (minor).




| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 5.439 | 15888697 | 1654059 | 49.706 |
| 2 | 7.293 | 16076506 | 1162942 | 50.294 |

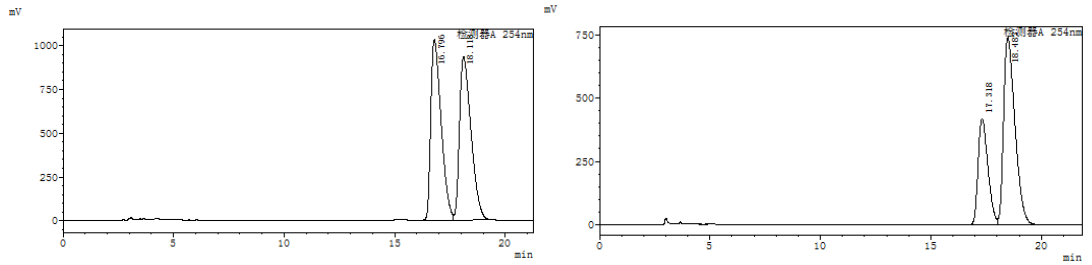
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 5.449 | 8855363 | 939982 | 76.131 |
| 2 | 7.336 | 2776434 | 206450 | 23.869 |

**(*R*)-methyl 3,3,3-trifluoro-2-hydroxy-2-(7-nitro-1H-indol-3-yl)propanoateC (4i)**




21.1 mg, 67% yield, yellow solid, mp 79-81 °C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 10.15 (s, 1 H), 8.33 (d, *J*=8.0 Hz, 1 H), 8.18 (dd, *J*=0.8 Hz, 1 H), 7.68 (d, *J*=2.8 Hz, 1 H), 7.24-7.28 (m, 1 H), 4.51 (s, 1 H), 4.00 (s, 3 H).

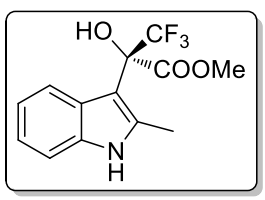
The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 254.0 nm; retention time: 17.3 min (major) and 18.5 min (minor).




| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 16.796 | 33636989 | 1030992 | 49.817 |
| 2 | 18.118 | 33884092 | 930814 | 50.183 |

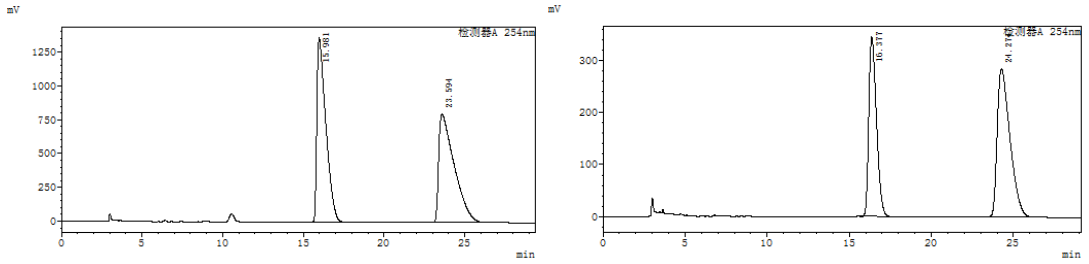
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 17.318 | 13000311 | 418712 | 32.940 |
| 2 | 18.483 | 26466112 | 737875 | 67.060 |

**(*R*)-methyl 3,3,3-trifluoro-2-hydroxy-2-(2-methyl-1H-indol-3-yl)propanoate (4j)**[8]




20.7 mg, 72% yield, white solid, mp 75-77 °C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.99 (s, 1 H), 7.73-7.79 (m, 1 H), 7.24-7.27 (m, 1 H), 7.08-7.16 (m, 1 H), 3.92 (s, 3 H), 3.89 (s, 1 H), 2.50 (s, 3 H).

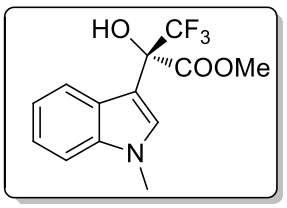
The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 254.0 nm; retention time: 16.4 min (minor) and 24.3 min (major).




| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 15.981 | 52876902 | 1363192 | 49.704 |
| 2 | 23.594 | 53507202 | 801453 | 50.296 |

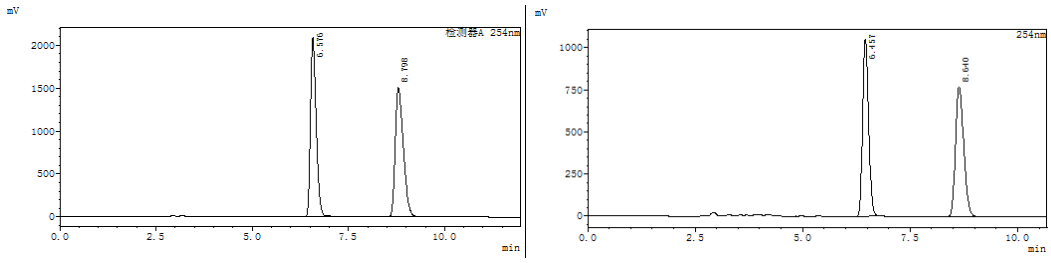
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 16.377 | 11226451 | 344861 | 42.095 |
| 2 | 24.274 | 15442714 | 285922 | 57.905 |

**(*R*)-methyl 3,3,3-trifluoro-2-hydroxy-2-(1-methyl-1H-indol-3-yl)propanoate (4k)**




40.0 mg, 81% yield, yellow oil; $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.83-7.85 (m, 1 H), 7.30-7.32 (m, 2 H), 7.25-7.27 (m, 1 H), 7.13-7.17 (m, 1 H), 3.93 (s, 1 H), 3.77 (s, 1 H).

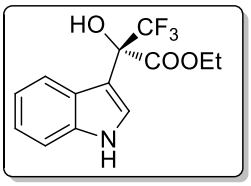
The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 254.0 nm; retention time: 6.6 min (major) and 8.8 min (minor).




| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 6.576 | 21962178 | 2084593 | 49.800 |
| 2 | 8.798 | 22138358 | 1508591 | 50.200 |

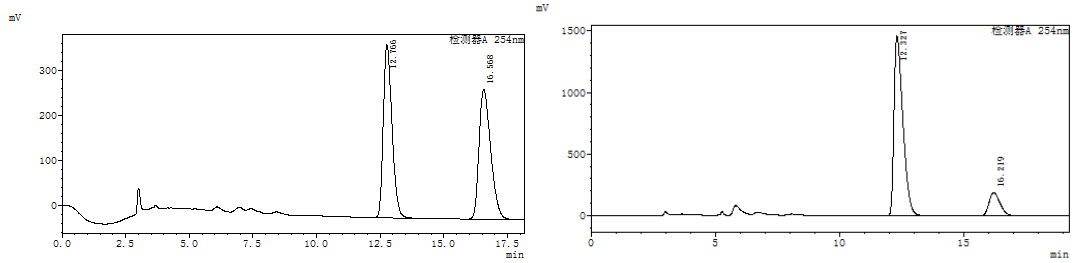
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 6.457 | 10184868 | 1459365 | 49.644 |
| 2 | 8.640 | 10331101 | 769533 | 50.356 |

**(*R*)-ethyl 3,3,3-trifluoro-2-hydroxy-2-(1H-indol-3-yl)propanoate (4l)**[6]




27.6mg, 94% yield, white solid, mp 88-90 °C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.28 (s, 1 H), 7.89 (d, *J*=8.0 Hz, 1 H), 7.43 (d, *J*=2.8 Hz, 1 H), 7.33-7.36 (m, 1 H), 7.20-7.25 (m, 1 H), 7.13-7.17 (m, 1 H), 4.41-4.49 (m, 2 H), 4.30-4.38 (m, 1 H), 1.33 (t, *J*=7.2 Hz, 3 H).

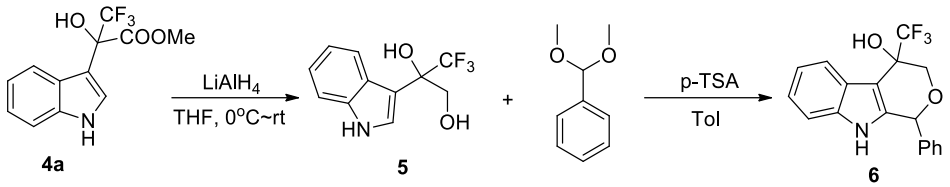
The ee was determined by HPLC analysis. CHIRALPAK OD-H; Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 254.0 nm; retention time: 12.3 min (major) and 16.2 min (minor).



| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 12.766 | 9210663 | 385687 | 49.892 |
| 2 | 16.568 | 9250626 | 290378 | 50.108 |

| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 12.327 | 36299725 | 1459365 | 86.208 |
| 2 | 16.219 | 5807182 | 188847 | 13,792 |

## 5. Preparation and characterization of 5 and 6




96% yield
73% ee

54% yield
71% ee

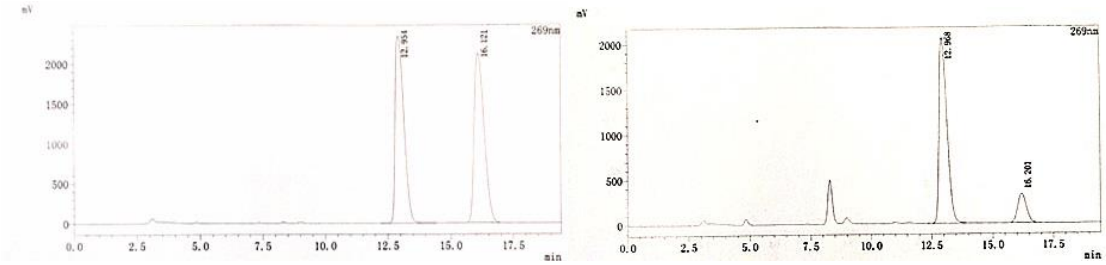
58% yield
68% ee
7.5:1 dr

To $LiAlH_4$ (0.094 g; 2.37 mmol) suspension in THF was droply added the solution of optical active compound **3a** (0.525 g, 1.9 mmol) in THF at argon atmosphere at 0 °C. The reaction was stirred to room temperature 4h, then was quenched with $Na_2SO_4 \cdot 10H_2O$ at 0°C. The mixture was filtered and condensed under vacuo. The residue prepared by silicon column chromatography (petroleum ether: ethyl acetate = 2:1) to give desired the diol **5** (0.25 g, 54% yield).

To the solution of diol **5** (0.25 g, 1.02 mmol) in toluene (6 mL) was added benzaldehyde dimethyl acetal (0.38 mL, 2.55 mmol) and $CF_3COOH$ (76 uL, 1.02 mmol). The mixture was stirred overnight and condensed under vacuo. The residue was purified by silicon column chromatography (petroleum ether: ethyl acetate = 5:1) to give the desired product **6** (0.198 g, 58% yield).

**5**: colorless oil; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.26 (s, 1 H), 7.80 (d, *J*=8.0 Hz, 1 H), 7.33-7.35 (m, 1 H), 7.20-7.24 (m, 2 H), 7.13-7.17 (m, 1 H), 4.10-4.`9 (m, 2 H), 3.72 (s, 1 H), 2.12 (t, *J*=6.8 Hz, 1 H).

The ee was determined by HPLC analysis. CHIRALPAK AD-H; Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 269 nm; retention time: 12.9 min (major) and 16.2 min (minor).

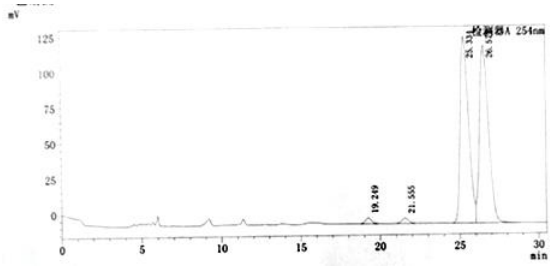


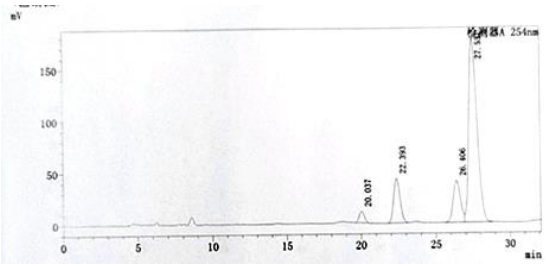

| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 12.954 | 56719271 | 2346098 | 49.034 |
| 2 | 16.121 | 58953783 | 2119341 | 50.966 |

| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 12.968 | 46694194 | 2059066 | 85.436 |
| 2 | 16.201 | 7959900 | 321691 | 14.564 |

**6**: colorless oil; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.25 (s, 1 H), 7.59-7.64 (m, 2 H), 7.36-7.46 (m, 5 H), 7.23-7.27 (m, 1 H), 7.15-7.19 (m, 1 H), 5.90 (s, 1 H), 5.05 (d, *J*=9.2 Hz, 1 H), 4.39-4.42 (m, 1 H).

The ee was determined by HPLC analysis. CHIRALPAK AS-H; Hexane/2-propanol = 95/5; flow rate 0.8 mL/min; 254 nm; retention time: 20.0 min (minor) and 22.4 min (major), 26.4 min (minor) and 27.5 min (major).

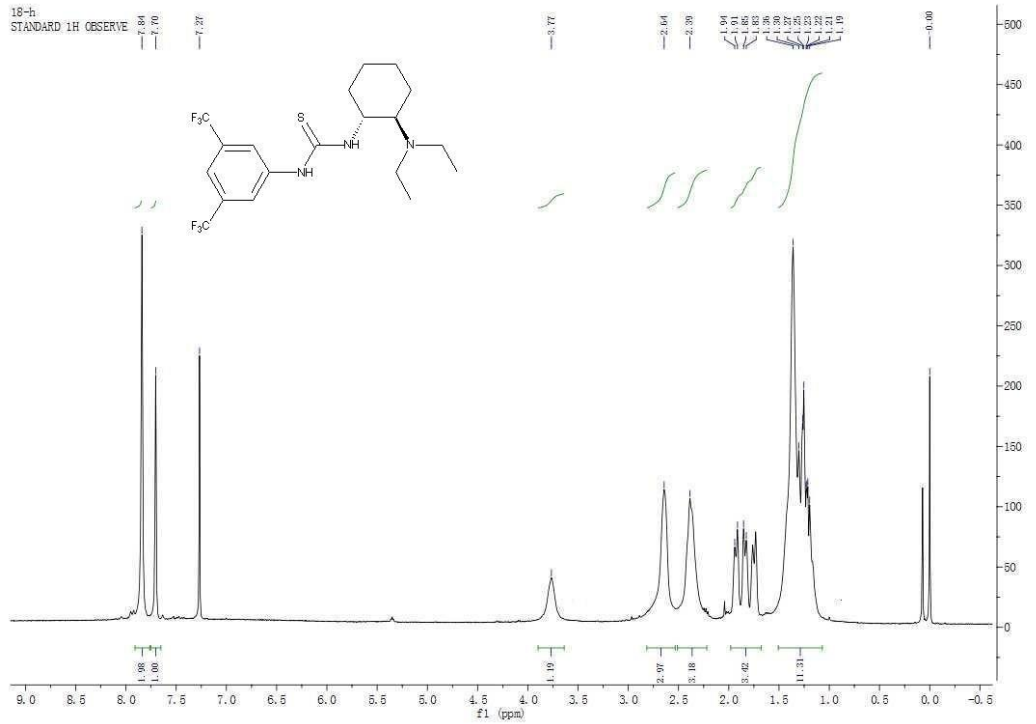


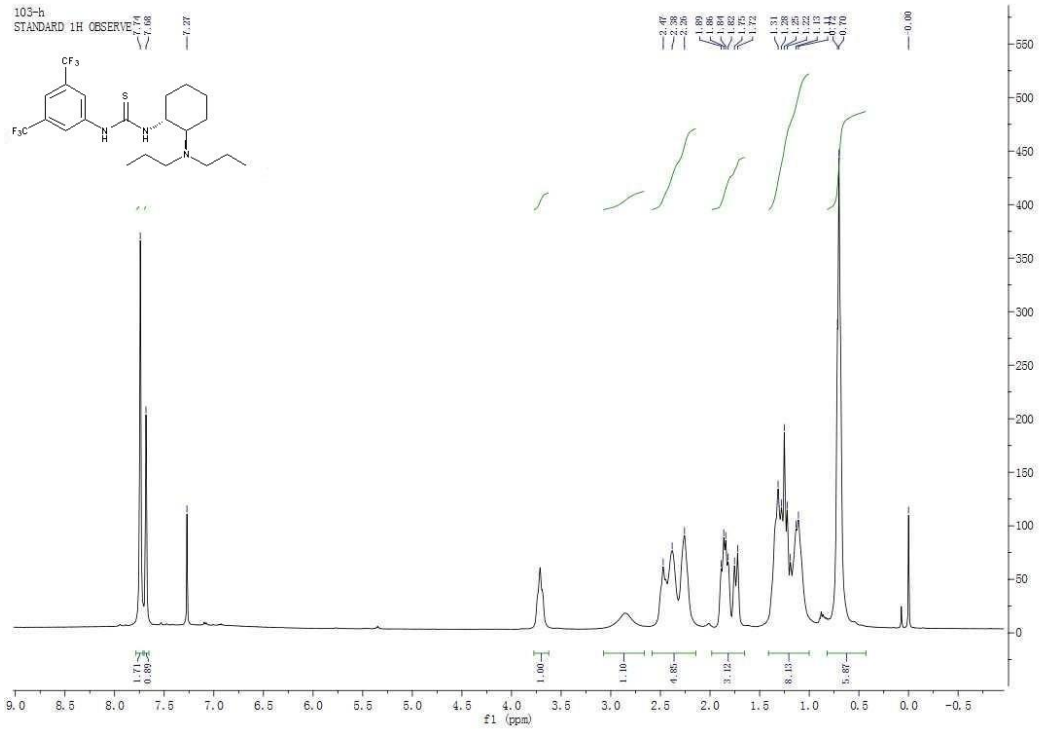



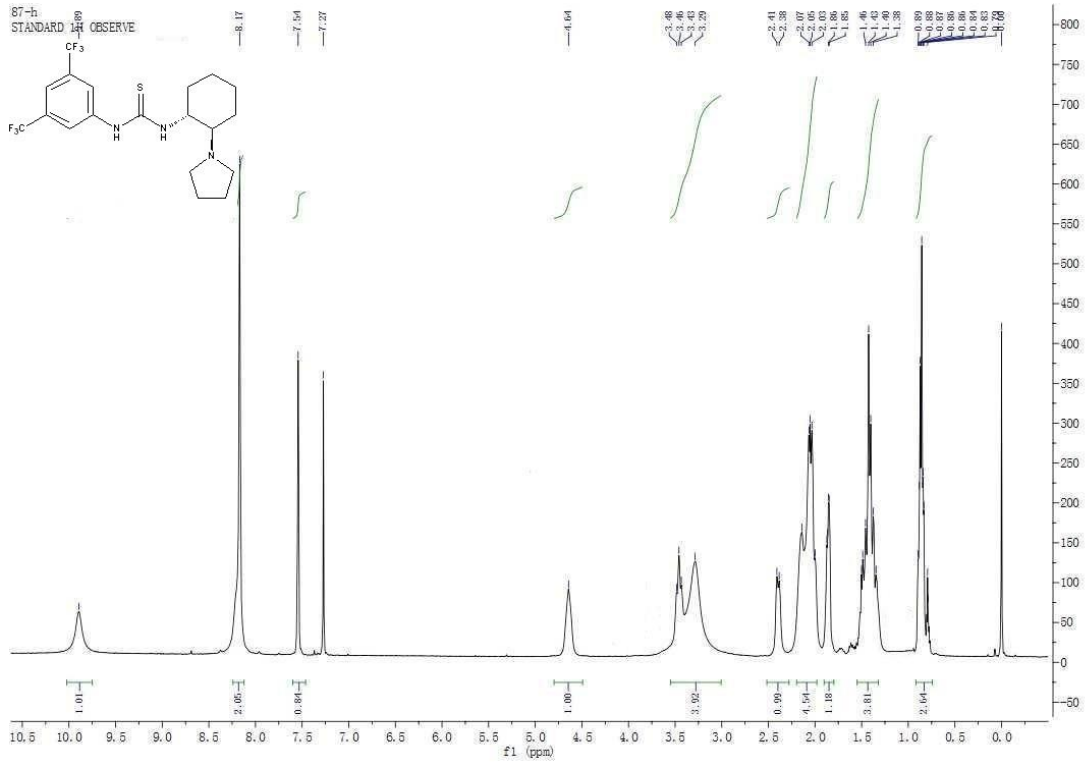

| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 19.249 | 98884 | 3995 | 0.984 |
| 2 | 21.555 | 107125 | 3794 | 1.066 |
| 3 | 25.334 | 4863504 | 132034 | 48.397 |
| 4 | 26.577 | 4979643 | 125497 | 49.553 |

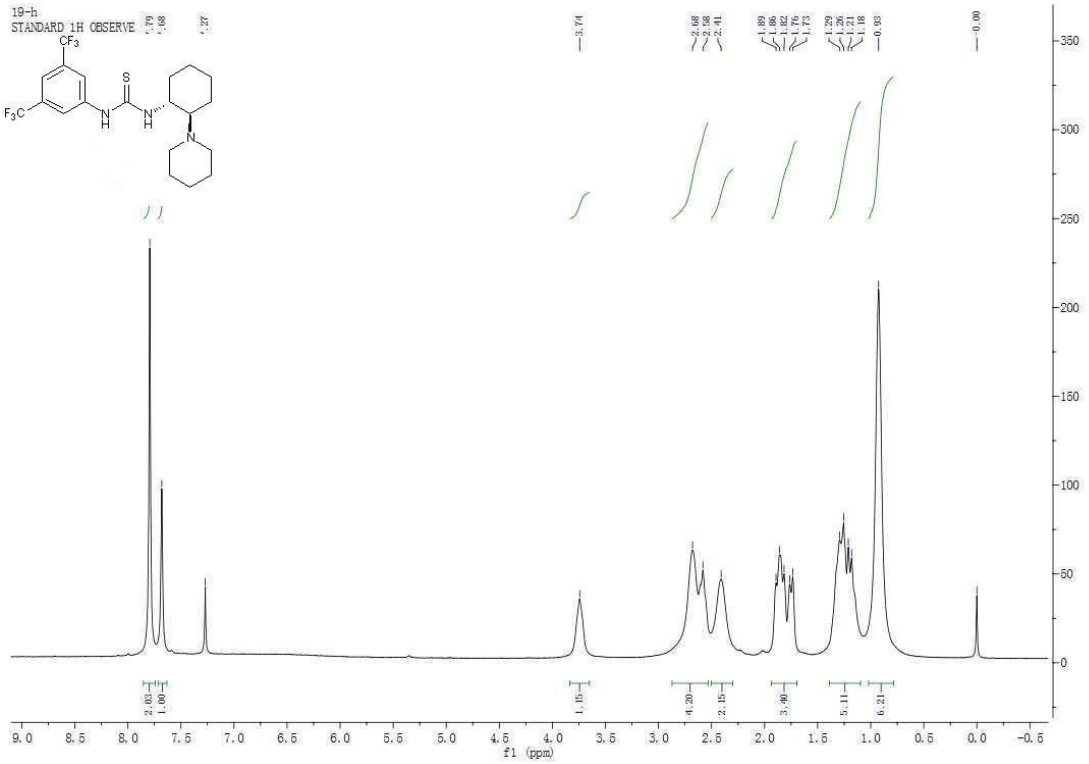
| | Retention time (min) | Area | Height | Concentration |
|---|---|---|---|---|
| 1 | 20.037 | 259473 | 10861 | 2.635 |
| 2 | 22.393 | 1281285 | 42821 | 13.012 |
| 3 | 26.406 | 1383984 | 40190 | 14.055 |
| 4 | 27.551 | 6922480 | 177963 | 70.299 |

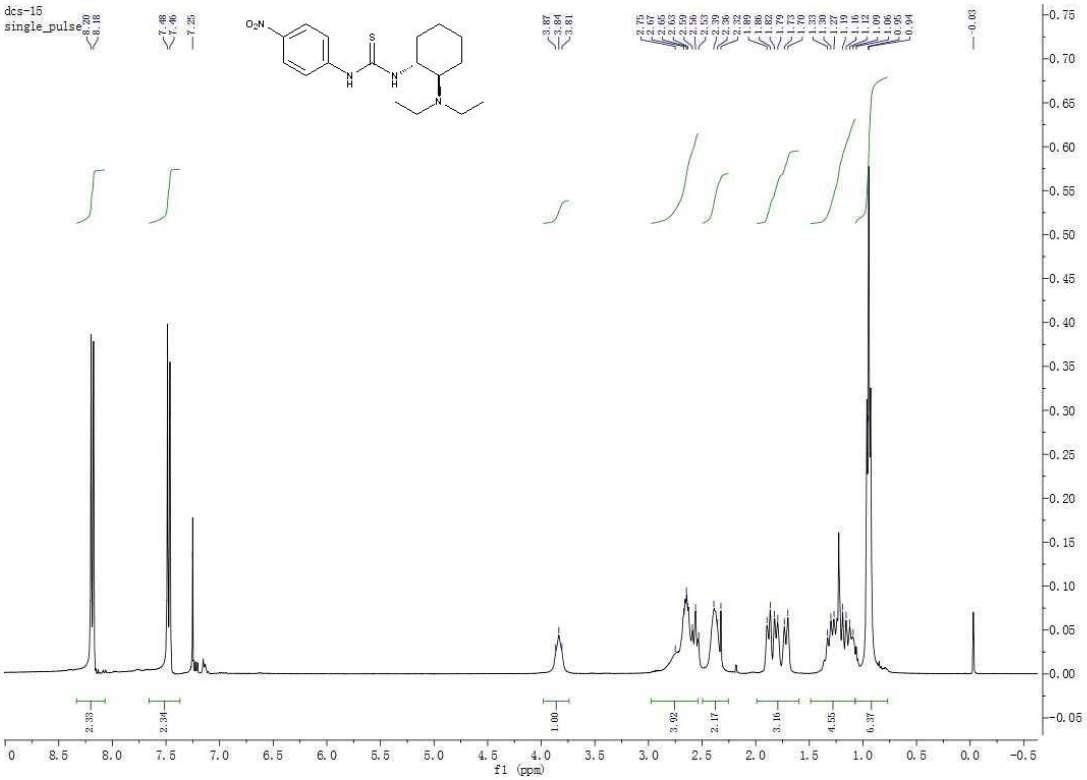
## 6. Copies of NMR spectra

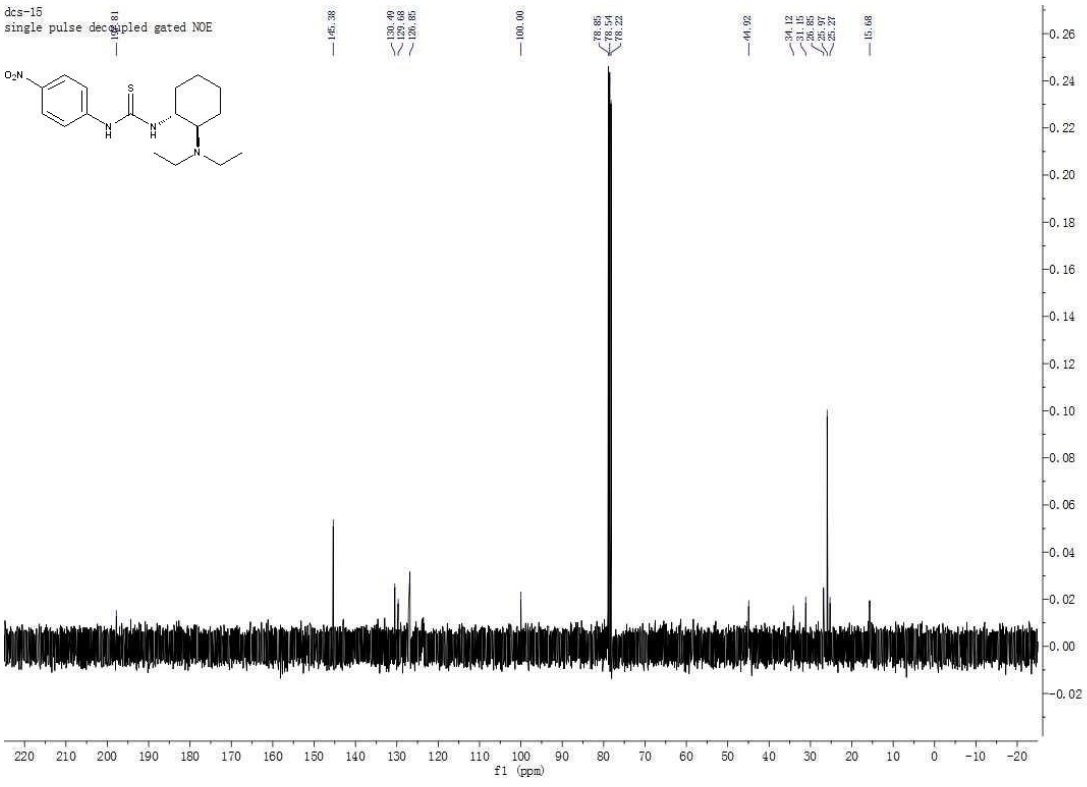


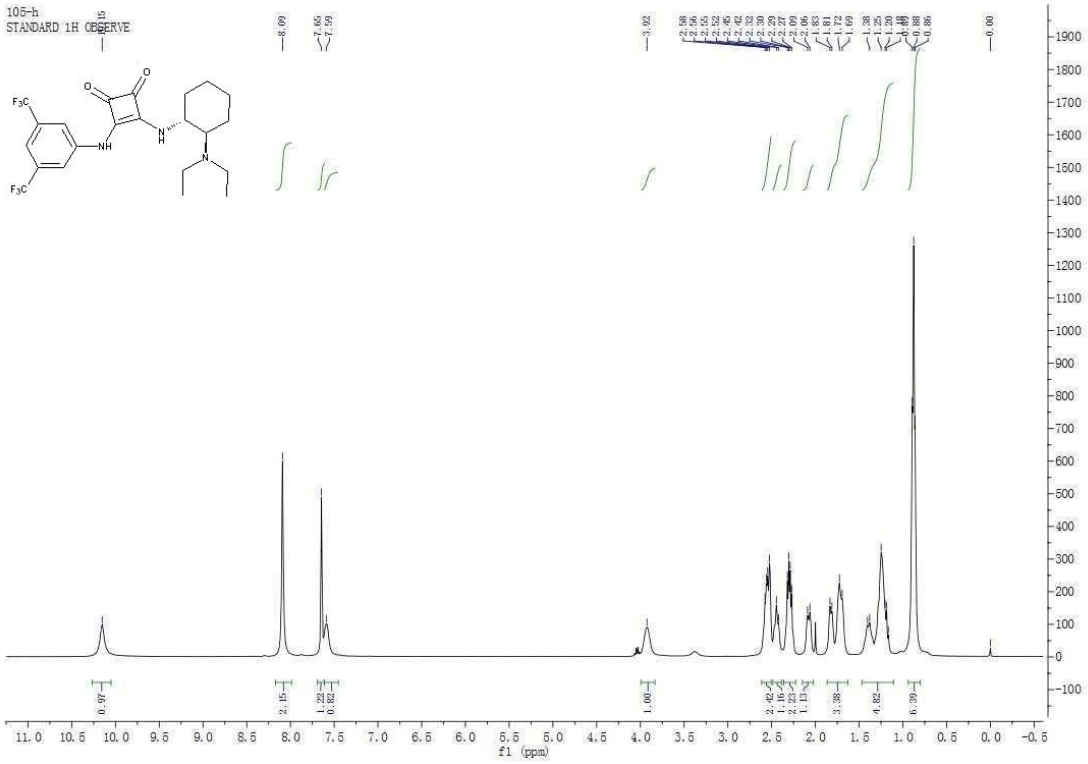



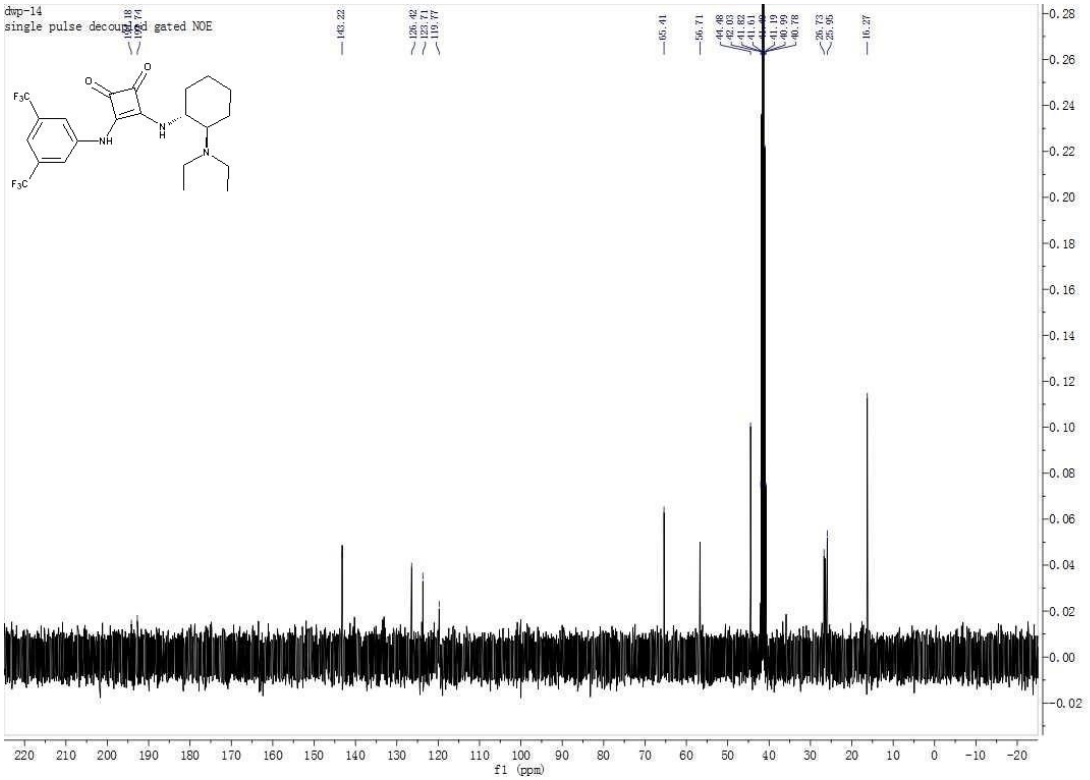

87-h
STANDARD 1H OBSERVE
f1 (ppm)

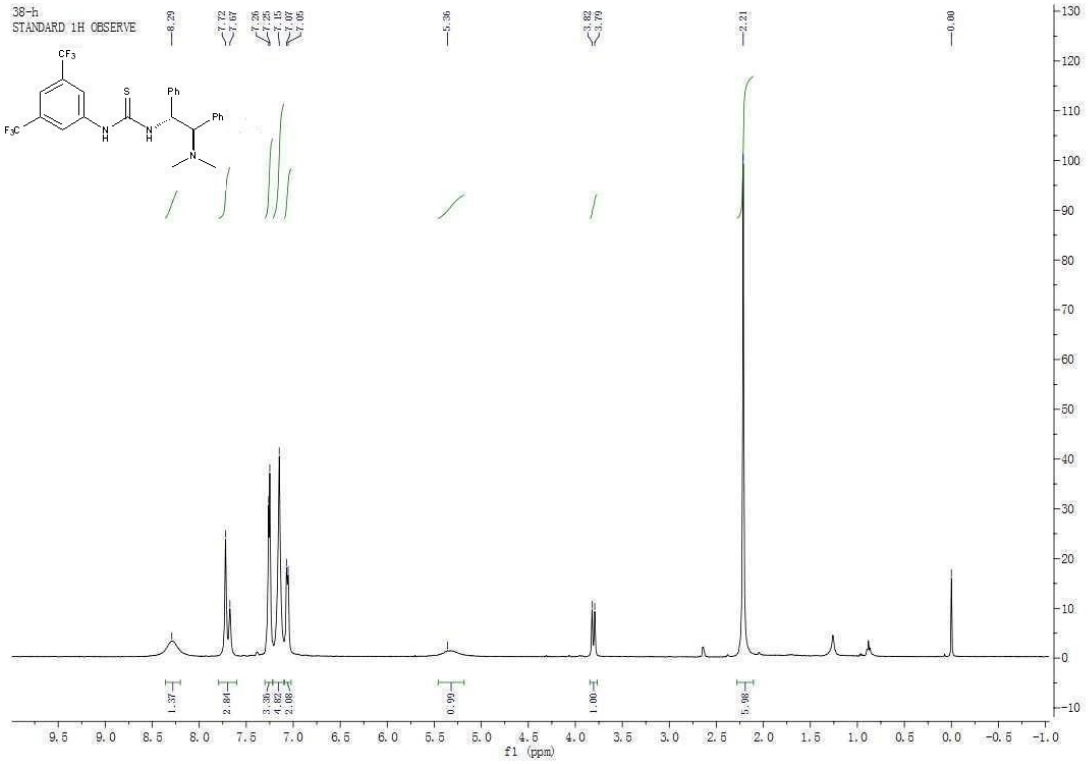

19-h
STANDARD 1H OBSERVE
f1 (ppm)

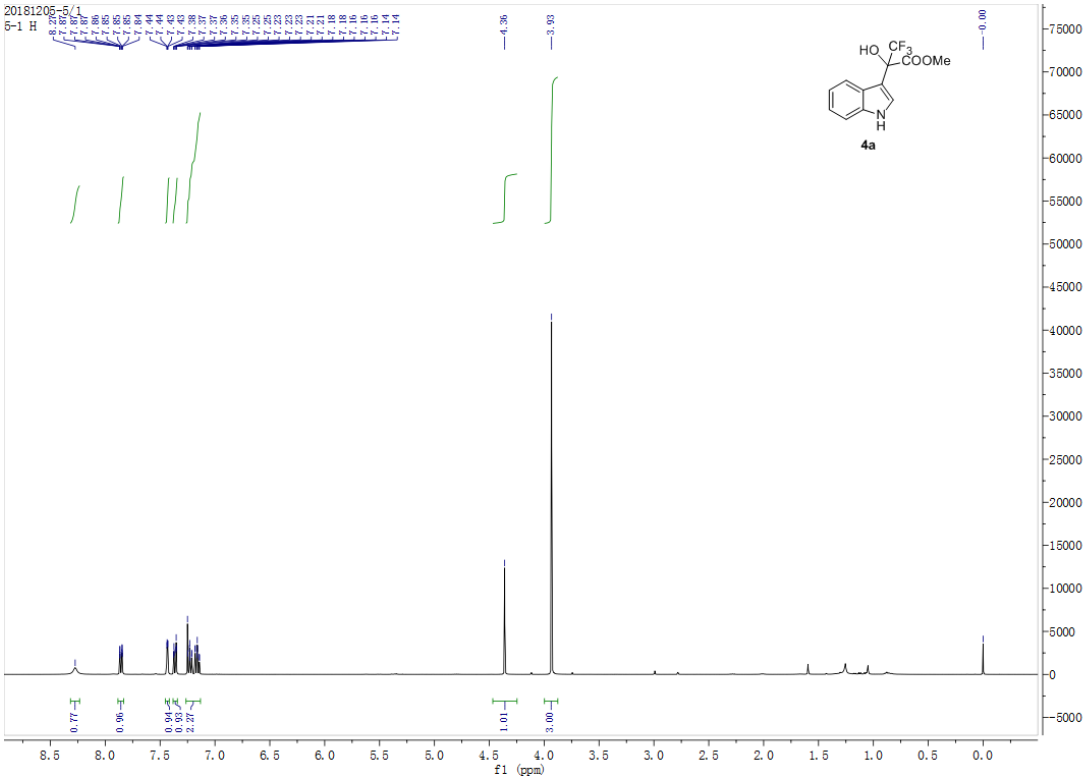

dcs-15
single_pulse
f1 (ppm)

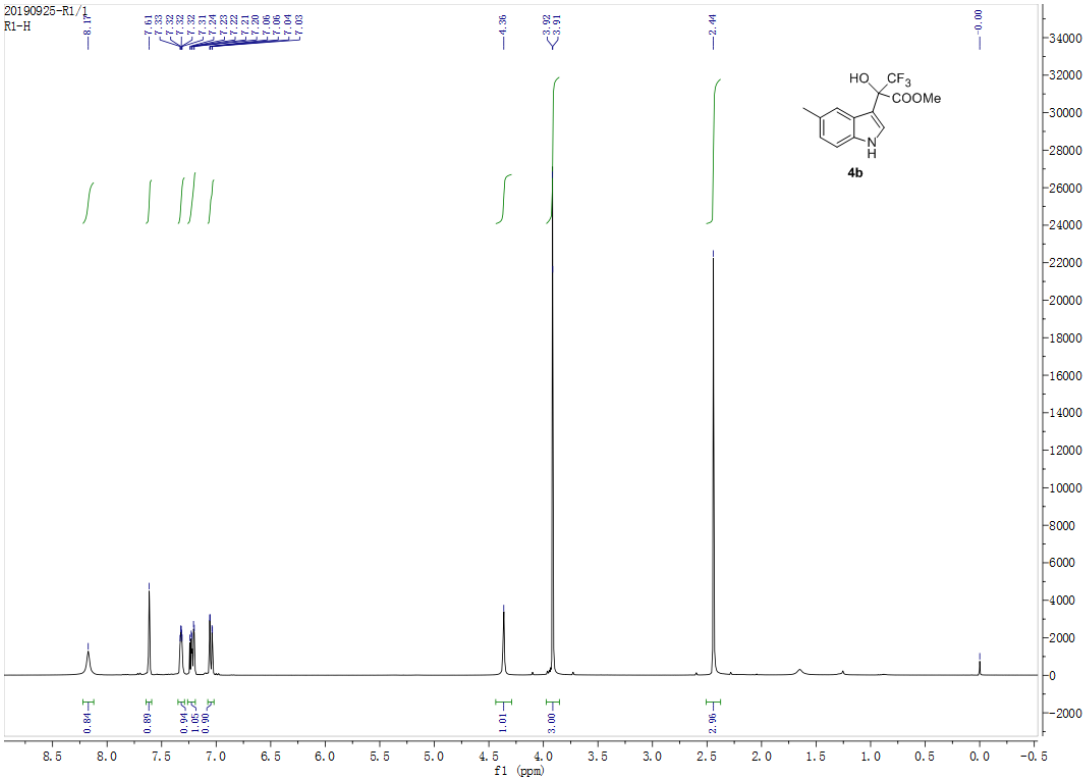

dcs-15
single pulse decoupled gated NOE
f1 (ppm)

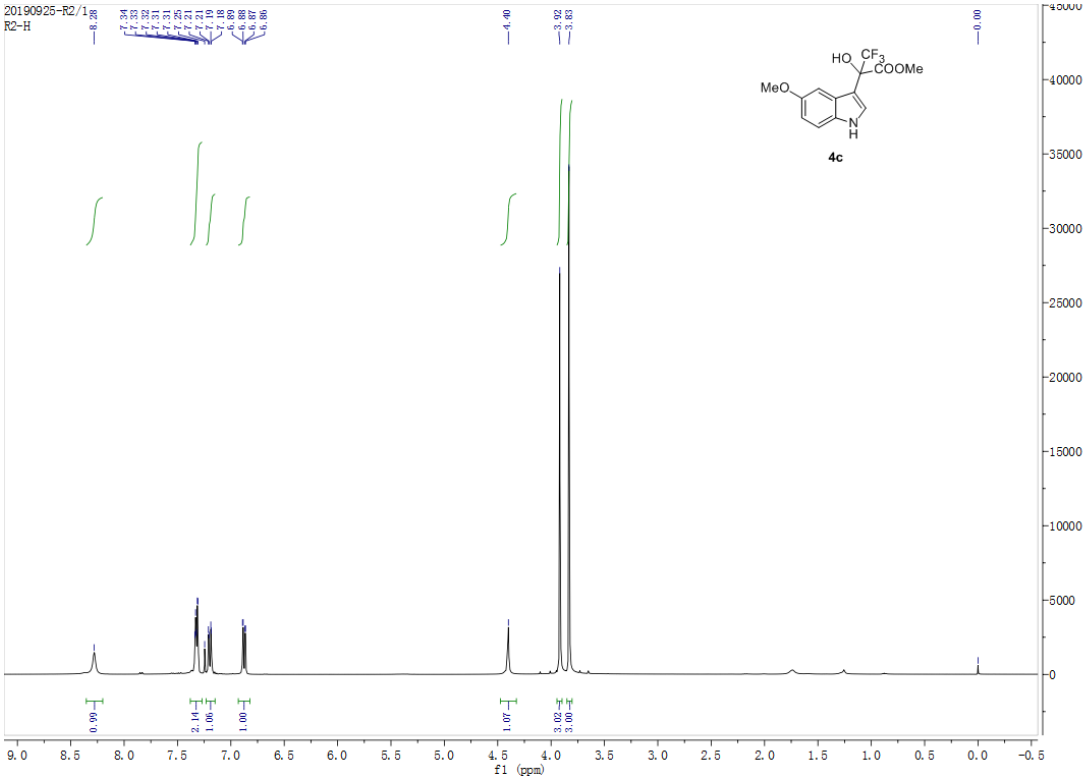

105-h
STANDARD 1H OBSERVE
f1 (ppm)

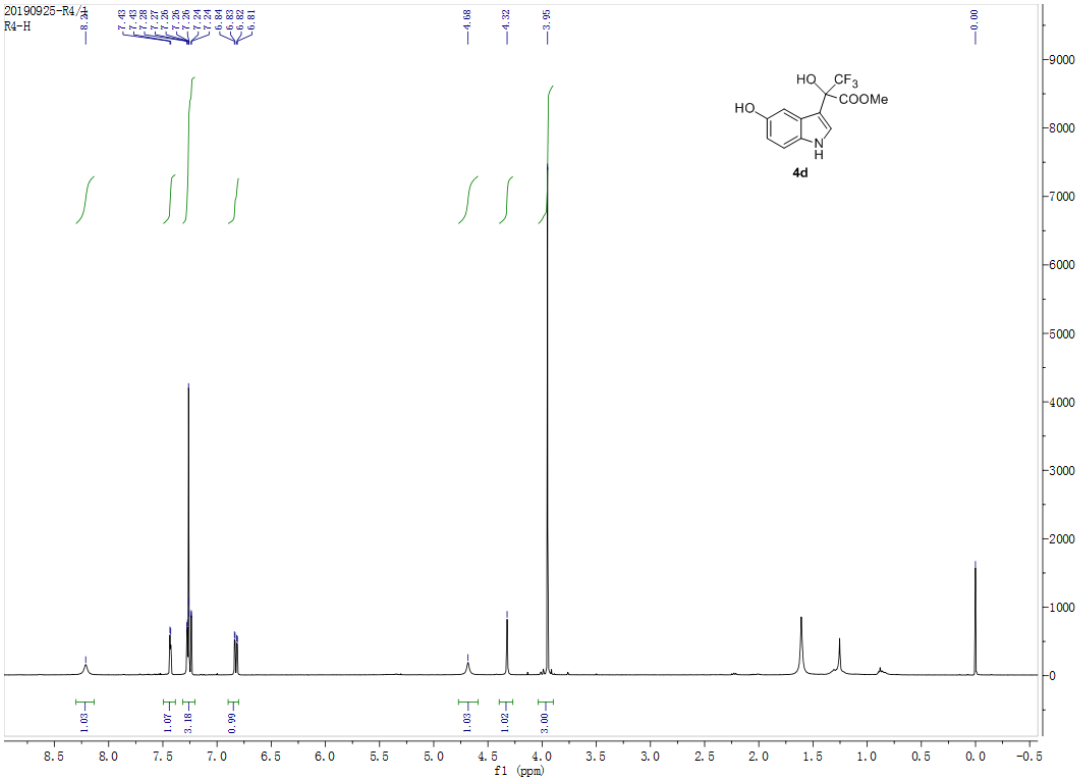

dwp-14
single pulse decoupled gated NOE
f1 (ppm)

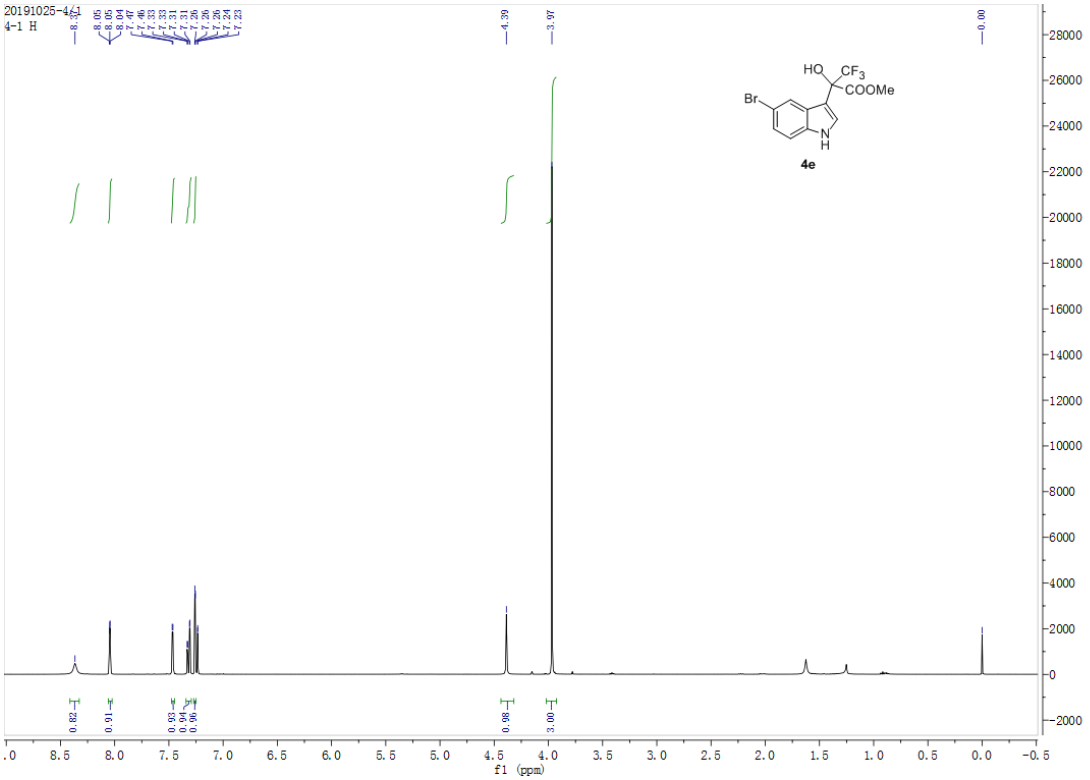

38-h
STANDARD 1H OBSERVE
8.29
7.72
7.67
7.26
7.25
7.15
7.07
7.06
5.36
3.82
3.79
2.21
0.00
CF3
F3C
S
Ph
Ph
N
H
N
H
N
1.37
2.84
3.35
4.82
2.08
0.99
1.00
5.98
f1 (ppm)

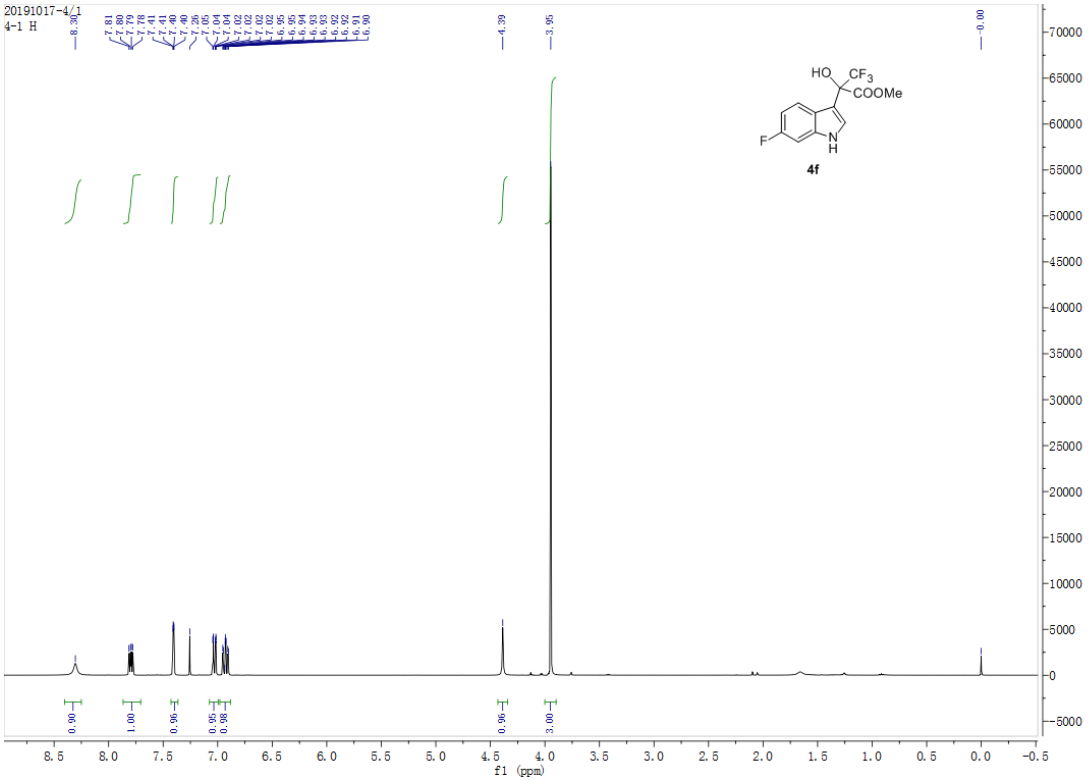

20181205-5/1
5-1 H
4.36
3.93
0.00
HO
CF3
COOMe
N
H
4a
f1 (ppm)

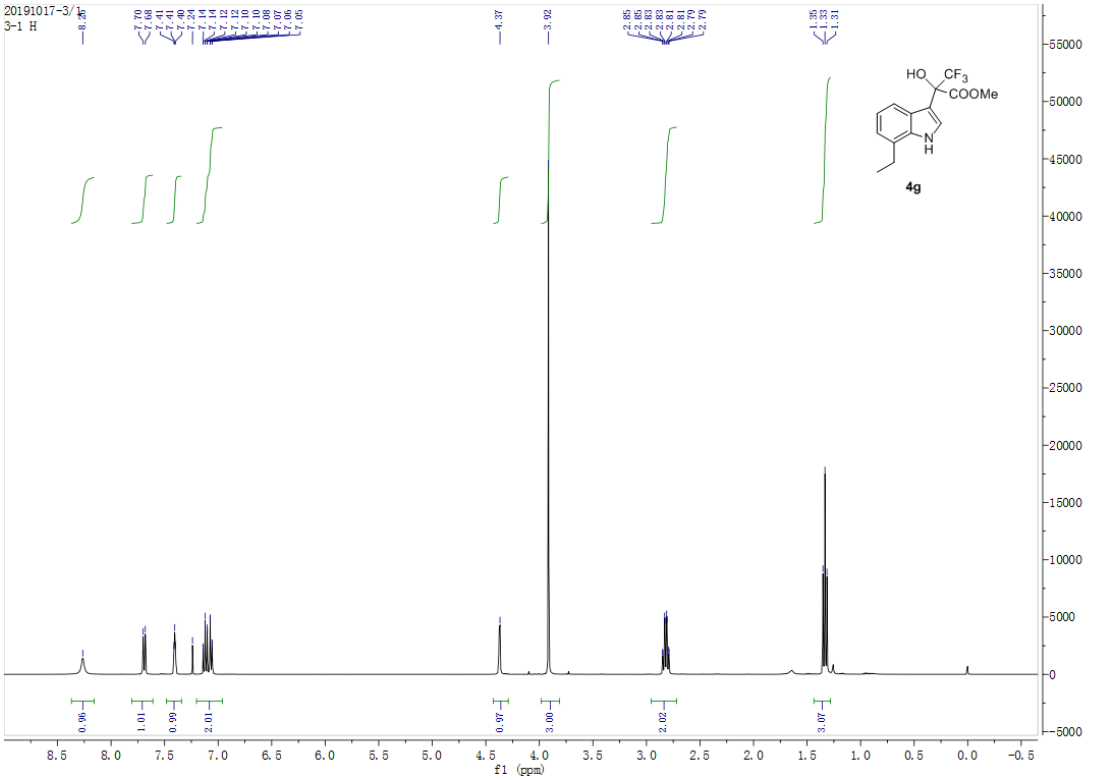

20190925-R1/1
R1-H
8.14
7.61
7.33
7.32
7.32
7.31
7.24
7.23
7.22
7.21
7.08
7.06
7.04
7.03
4.36
3.92
3.91
2.44
0.00
HO
CF3
COOMe
N
H
4b
f1 (ppm)

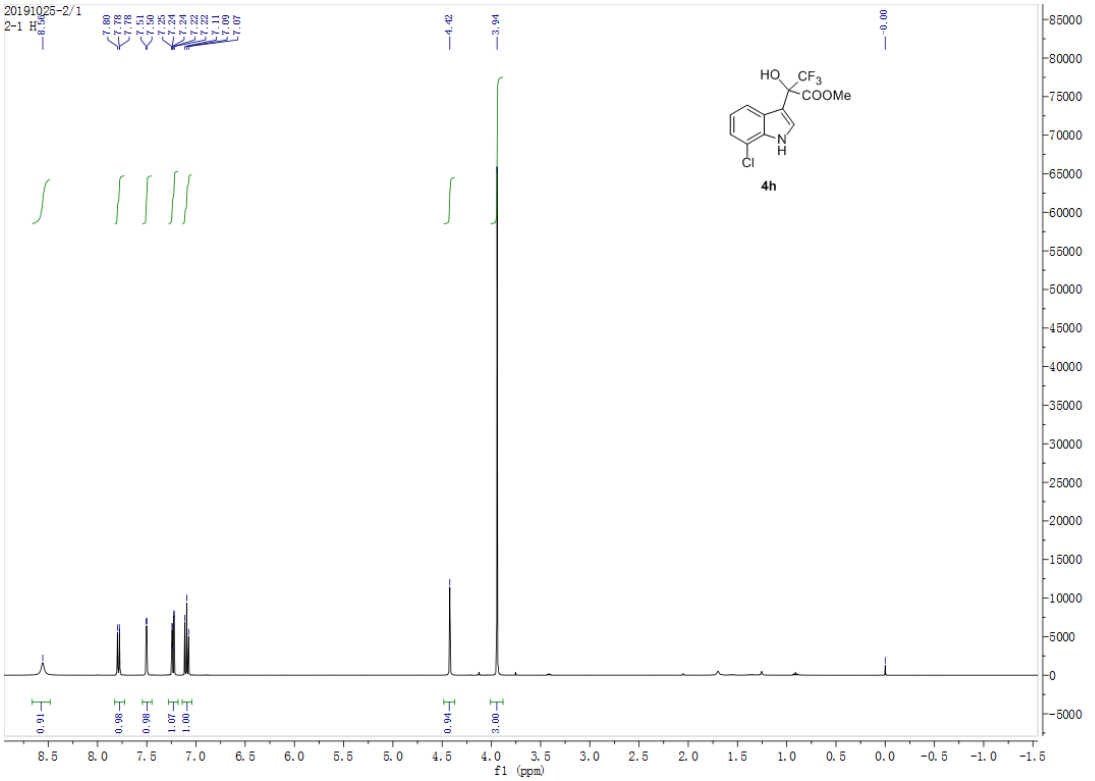

20190925-R2/1
R2-H
8.28
7.34
7.33
7.32
7.31
7.31
7.25
7.21
7.21
7.19
7.18
6.89
6.88
6.87
6.86
4.40
3.92
3.83
0.00
HO
CF3
COOMe
MeO
N
H
4c
0.99
2.14
1.06
1.00
1.07
3.02
3.00
f1 (ppm)

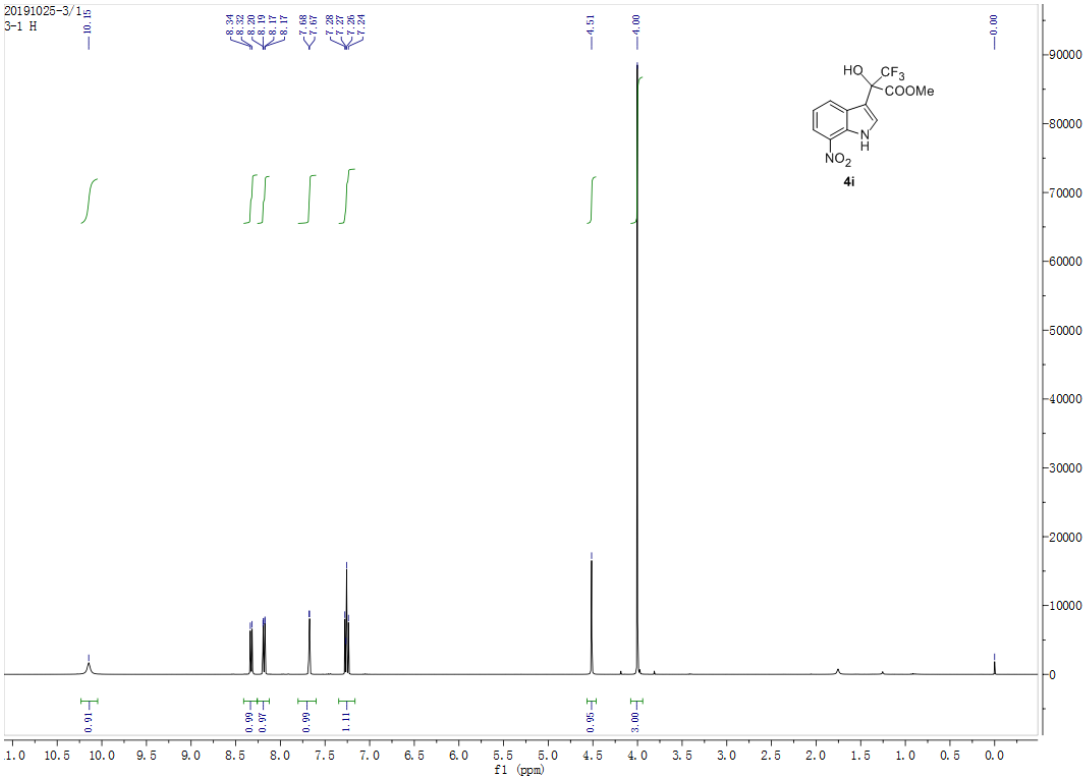

20190925-R4/1
R4-H
8.34
7.43
7.43
7.28
7.27
7.26
7.26
7.24
7.24
6.84
6.83
6.82
6.81
4.68
4.32
3.95
0.00
HO
CF3
COOMe
HO
N
H
4d
1.03
1.07
3.18
0.99
1.03
1.02
3.00
f1 (ppm)


20191025-4/1
4-1 H
8.05
8.04
7.47
7.46
7.33
7.31
7.31
7.26
7.26
7.24
7.23
4.39
3.97
0.00
HO
CF3
COOMe
Br
N
H
4e
0.82
0.91
0.93
0.94
0.96
0.98
3.00
f1 (ppm)


20191017-4/1
4-1 H
7.81
7.80
7.79
7.78
7.41
7.40
7.40
7.39
7.05
7.04
7.02
7.02
7.02
6.95
6.94
6.93
6.93
6.92
6.91
6.90
4.39
3.95
0.00
HO
CF3
COOMe
F
N
H
4f
0.90
1.00
0.96
0.95
0.98
0.96
3.00
f1 (ppm)


20191017-3/1
3-1 H
HO
CF3
COOMe
N
H
4g
f1 (ppm)


20191025-2/1
2-1 H
HO
CF3
COOMe
N
H
Cl
4h
f1 (ppm)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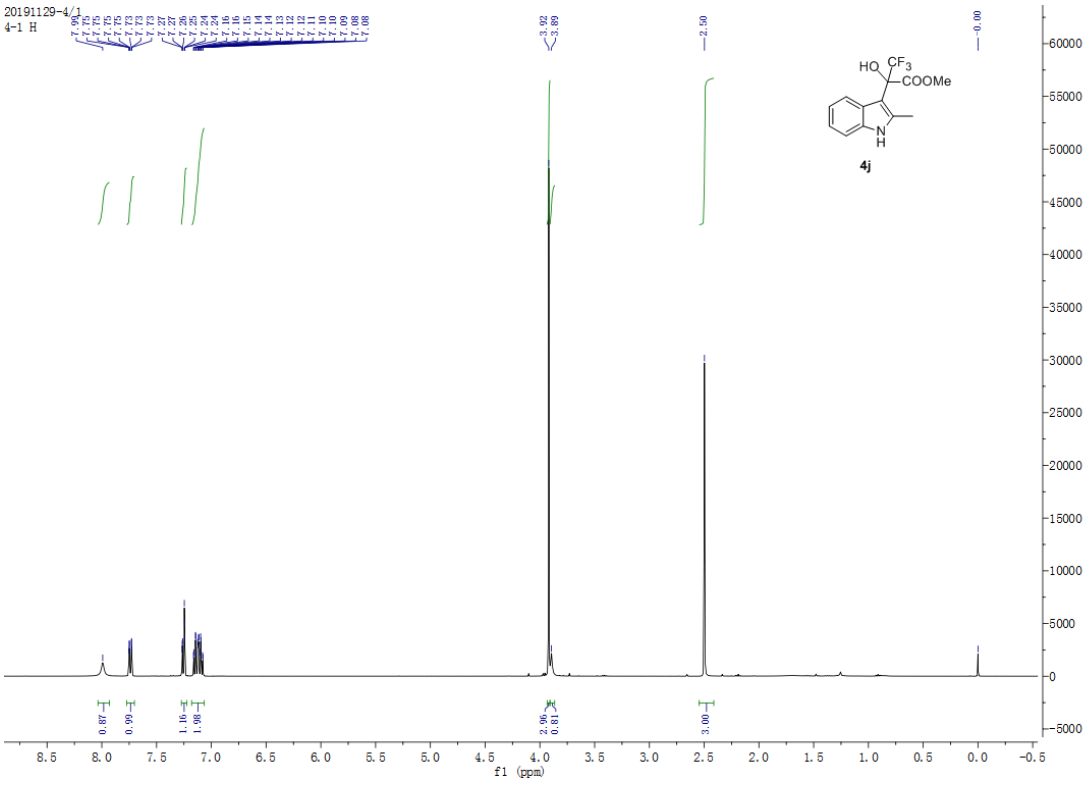
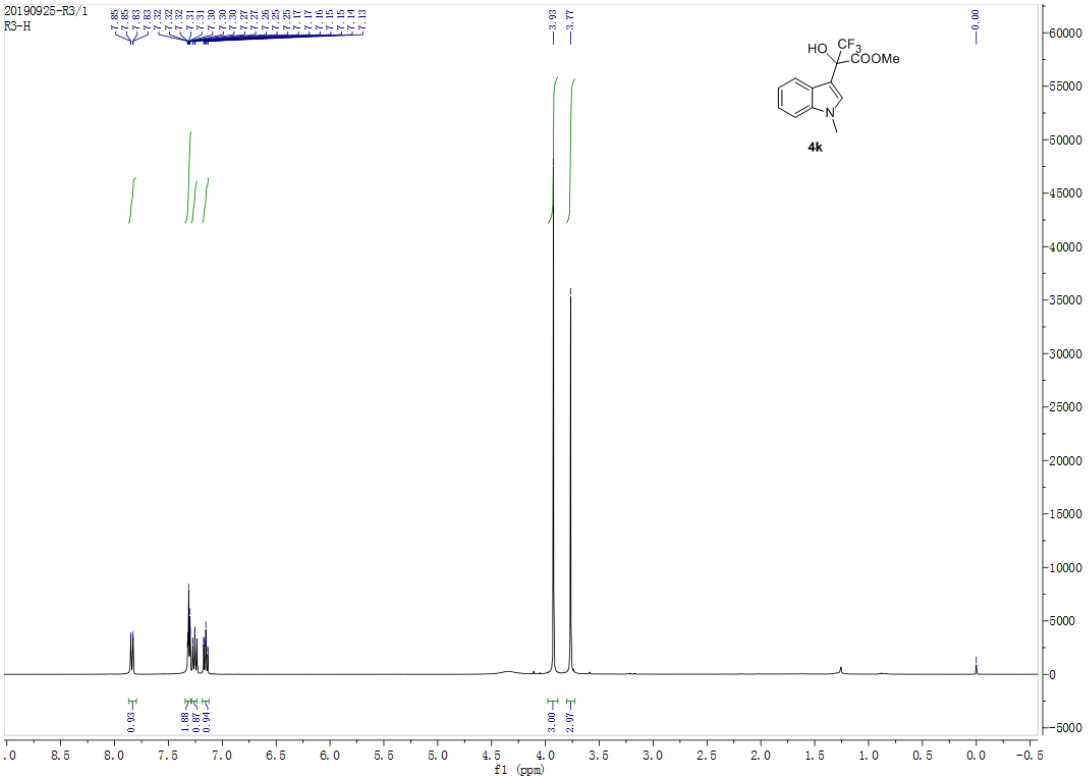
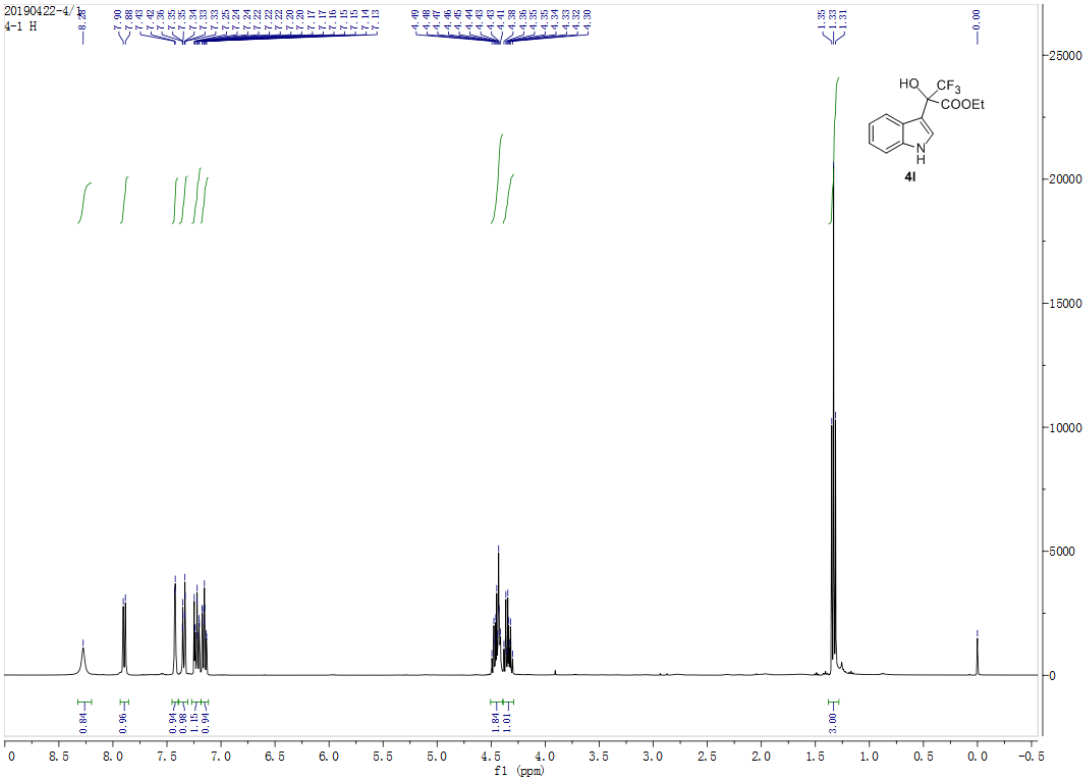
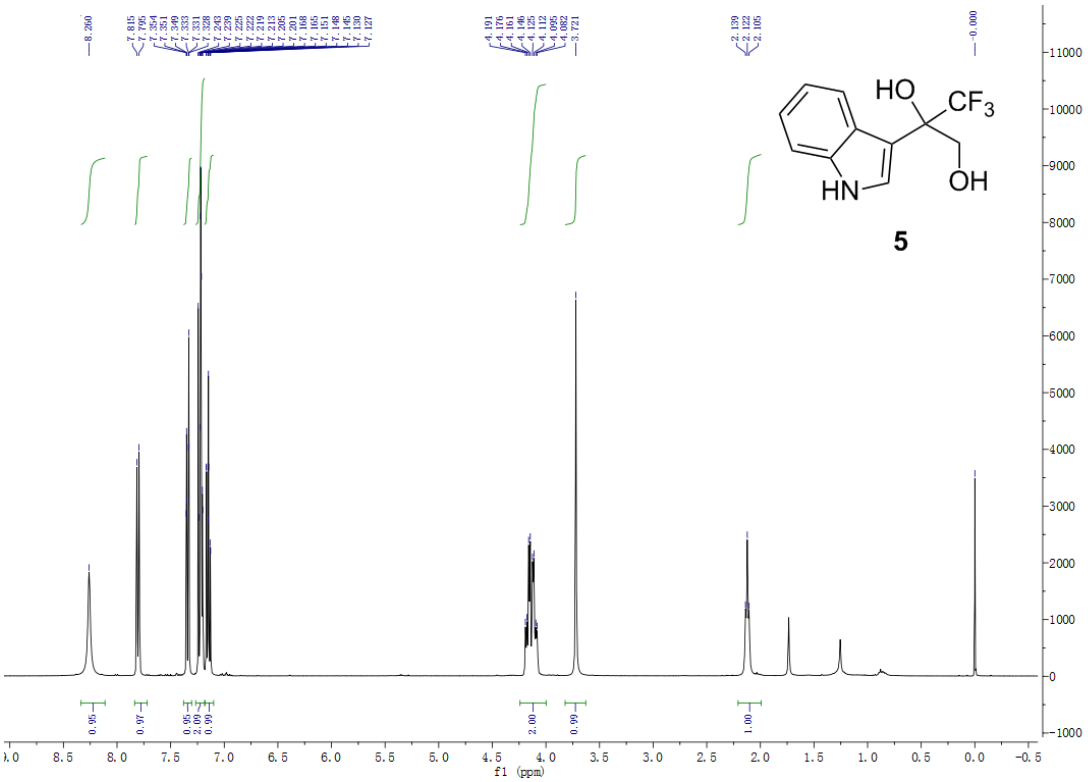
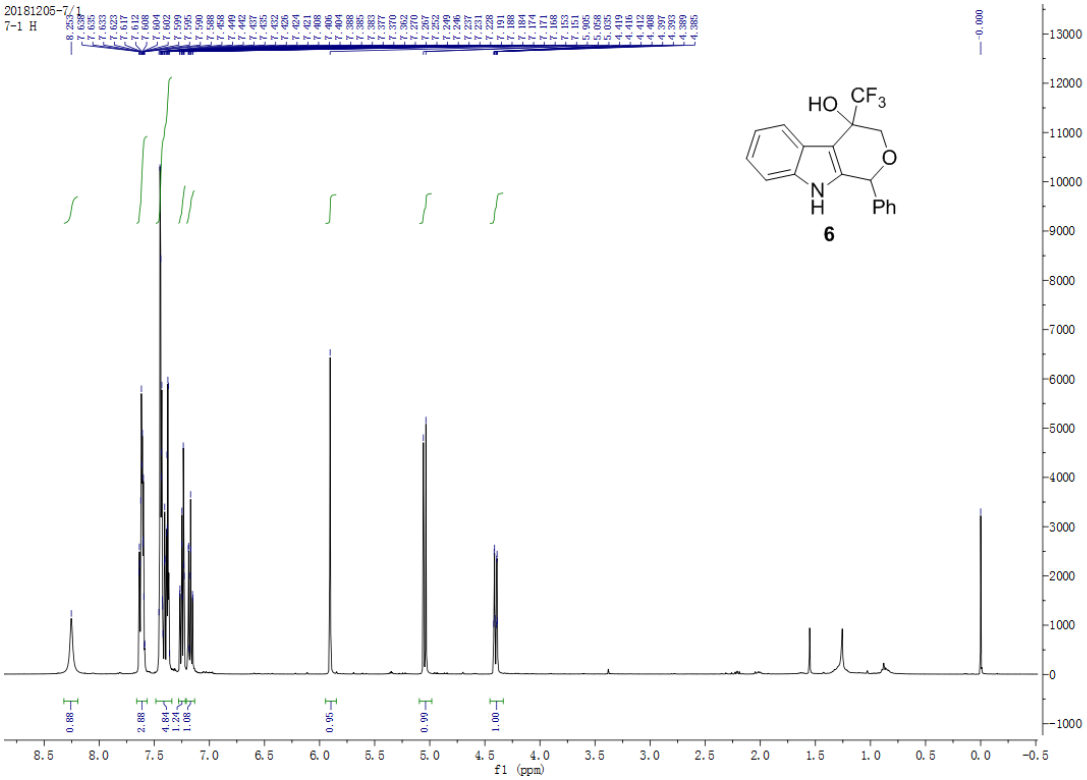
3-1 H
HO
CF3
COOMe
N
H
NO2
4i
f1 (ppm)

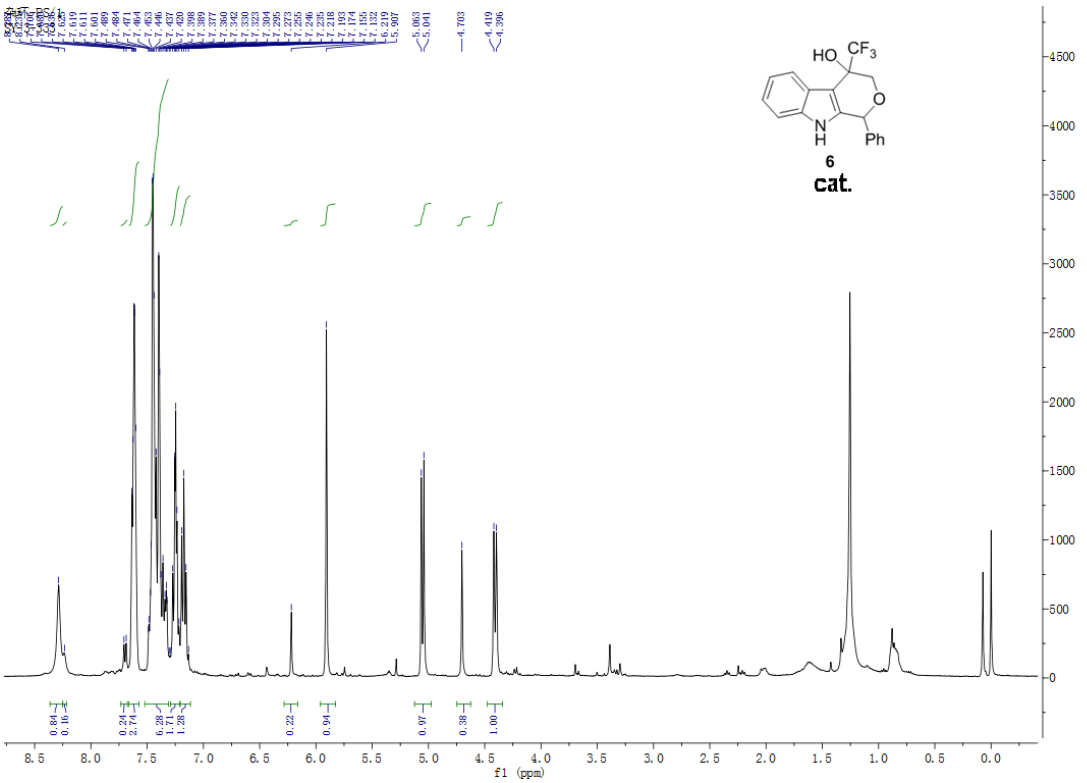

20191129-4/1
4-1 H
HO
CF3
COOMe
N
H
4j
f1 (ppm)


20190925-R3/1
R3-H
HO
CF3
COOMe
N
4k
f1 (ppm)


20190422-4/1
4-1 H
HO
CF3
COOEt
N
H
4l
f1 (ppm)


HO
CF3
HN
OH
5
f1 (ppm)


20181205-7/1
7-1 H
HO
CF3
O
N
H
Ph
6
f1 (ppm)


HO
CF3
O
N
H
Ph
6
cat.
f1 (ppm)

**Heterogeneously Organocatalytic, Enantioselective Friedel-Crafts Alkylation of Indole with Trifluoromethylpyruvate**

**7. Reference:**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