Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

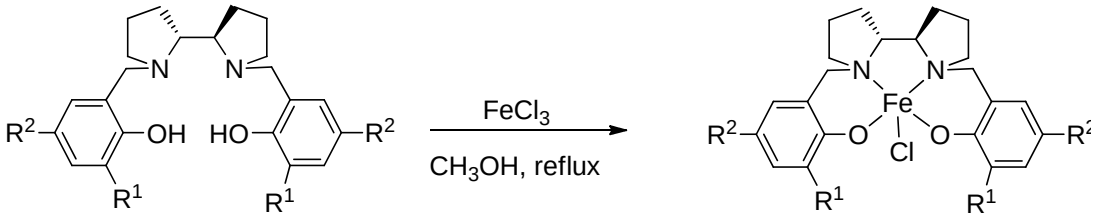
1. General Information

All non-aqueous reactions were performed in oven-dried glassware and standard Schlenk tubes under an atmosphere of argon. Solvents were refluxed over magnesium (methanol, ethanol), **a**cetonitrile (CH_3CN), dichloromethane (DCM) and 1,2-dichloroethane (DCE) were distilled from CaH_2 under inert atmosphere. Tetrahydrofuran (THF) and toluene were distilled from sodium under inert atmosphere. Chloroform ($CHCl_3$) were distilled from phosphorus pentoxide under inert atmosphere. All other solvents and reagents were used as received unless otherwise noted. Thin layer chromatography was performed using silica gel HSGF254 precoated plates (0.2~0.3 mm) and visualized by short-wave UV (254 nm) irradiation, potassium permanganate, or iodine stain. Column chromatography was performed with silica gel (200-300 mesh, Yantai Xunjiang Economic and Trade Co., Ltd). The ^{1}H NMR spectra were obtained in $CDCl_3$ using a Varian Avance III spectrometer at 400 MHz, ^{13}C and ^{19}F NMR spectra were obtained in $CDCl_3$ using a Bruker Avance III spectrometer at 500 and 376 MHz, respectively. Chemical shifts (δ) for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.26 ppm). Data**s** are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, and integration. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (δ 77.16 ppm) as the internal standard. Infrared spectra were prepared as KBr pellets or neat and were recorded on a Nicolet iN10 MX spectrometer. HRMS data were obtained on a Thermo Fisher Scientific LTQ FT Ultrasystem. Optical rotations were measured with a Perkin-Elmer 241 polarimeter at concentrations of 1.0 g/100 mL. X-ray structures were obtained with a Microfocus sealed Cu tube from Incote. HPLC analysis were conducted on an Agilent 1100 Series chromatograph. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry.

2. General procedure for the synthesis of Fe-BPsalan complexes and starting materials

General procedure for the synthesis of Fe-BPsalan complexes

Fe-BPsalan complexes (**1a-k**) with (*R*,*R'*)-bipyrrolidine backbone BPsalan ligands were prepared by the corresponding literature procedures reported by our group.[1] Iron(III) complexes were prepared by the corresponding literature procedures.



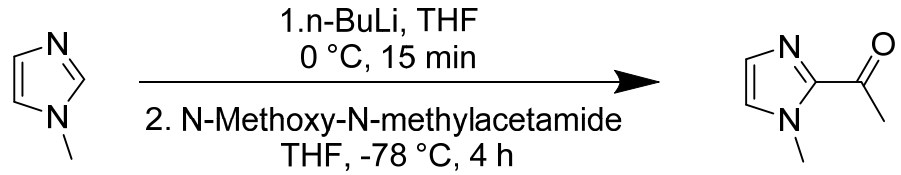
1a R^1=tBu, R^2=Br **1g** R^1=iPr, R^2

1b R^1=tBu, R^2=CF_3 **1h** R^1=Br, R^2=

1c R^1=tBu, R^2=tBu **1i** R^1=Ph, R^2

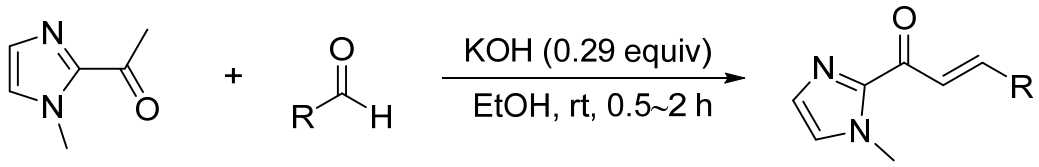
3. Synthesis of Substrates

3.1 Synthesis of 1-(1-methyl-1H-imidazol-2-yl)ethanone

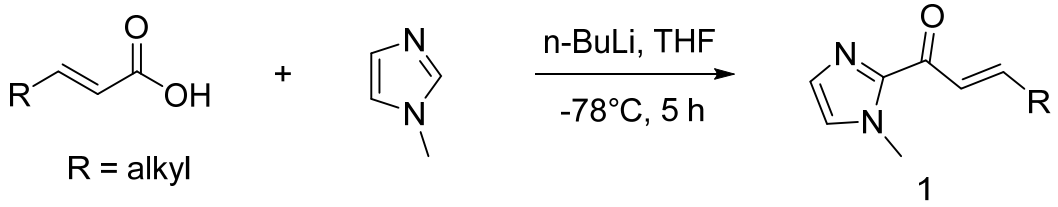


Compound S_1 was synthesized *via* a modification of the procedure as literature.[2] An oven-dried 100 mL round-bottomed flask under an argon atmosphere was charged with 1-methylimidazole (7.01 g, 6.8 mL, 85.34 mmol, 1.1 equiv) and dry THF (120 mL). The solution was cooled to -78 °C in adry ice/ethanol bath for 15 min, then *n*-BuLi (2.5 M in *n*-hexane, 49.65 mL, 124.13 mmol, 1.6 equiv) was added dropwise over 10 min. The mixture was stirred at -78 °C for 2 h, then cannulated into a solution of N-Methoxy-N-methylacetamide (8 g, 8.25 mL, 77.58 mmol, 1 equiv) in dry THF (80 mL) at -78 °C. The reaction mixture was then stirred at -78 °C for 2 h . Return to room temperature and add 120 ml water to quench n-BuLi . The aqueous phase was extracted with EtOAc (3 x 60 mL) and the combined organic layer were dried over anhydrous $MgSO_4$, gravity filtered and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with EtOAc/pentane (1:2) to provide the title compound (molecular formula: $C_6H_8N_2O$, M_W = 124.14 g/mol, 5.95 g) as a colorless oil in 62% yield. R_f: 0.31 (EtOAc/pentane = 9:1). IR (neat) 3108, 2959, 1674, 1402, 915, 776 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 0.9 Hz, 1H), 7.02 (br, s, 1H), 3.99 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2 (s), 142.9 (s), 128.7 (d), 126.7 (d), 35.9 (q), 26.8 (q). Spectroscopic data were consistent with the literature data for this compound.

3.2 Synthesis of α,β-unsaturated acyl imidazoles



α,β-unsaturated 1-acylimidazoles 2a-r were prepared according to a reported procedure. Accordingly, 1-Methyl-2-acetylimidazole (20.0 mmol, 1.0 eq) and EtOH (10 mL) were added to a 25 mL round-bottom flask followed by the aromatic aldehyde (20 mmol, 1 eq) and KOH (5.8 mmol, 0.29 eq). The solution was stirred until a lot of precipitate came out. Vacuum filtrated and flushed with PE. The filter residue was dissolved in dichloromethane and then extracted with distilled water (3 x 30 mL) for three times. The organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated. The product was recrystallized by DCM and PE.



The α,β-unsaturated substrates 1a-b were synthesized via a modification of the procedure originally reported by Evans and co-workers.[3] An oven-dried, 250 mL round-bottomed flask under an argon atmosphere was charged with 1-methylimidazole (24 mmol, 2.4 equiv) and dry THF (50 mL). The solution was cooled to −78 °C in a dry ice/ethanol bath for 15 min, then n-BuLi (2.5 M in n-hexane, 24 mmol, 2.4 equiv) was added drop-wise over 10 min. The mixture was warmed to rt and stirred for 30 min, then cooled back to −78 °C. The desired acid (10 mmol, 1 equiv) in dry THF (10 mL) was added drop-wise over a 10 min period. The resulting solution was stirred at −78 °C for 15 min, then warmed at rt and stirred for 2 h. The reaction was eventually quenched with a saturated aqueous $NaHCO_3$ solution (50 mL) and the aqueous phase was extracted with EtOAc (3 x 40 mL). The combined organic

layers were washed with brine (2 x 40 mL), dried over $MgSO_4$, gravity filtered, and concentrated under reduced pressure. The reaction residue was purified by silica gel flash chromatography, eluting with EtOAc/pentane (1:3) as the eluent.

3.3 Synthesis of *N,N'*-cyclic azomethine imines

N,N'-cyclic azomethine imines (**3a-3l**) were prepared according to a general procedure.[4] Accordingly, methacrylate (10.46 mL) was added to the solution of hydrazine hydrate (7.06 mL) in 35 mL ethanol which was cooled in an ice bath. After addition, the mixture was heated to reflux for 8 h. Then the solvent and the volatile components were removed under reduced pressure. The thick colorless oil, crude pyrazolidin-3-one, was obtained in about 95% yield. By subjecting pyrazolidin-3-one (1 equiv) to various aromatic aldehydes (1.1 equiv) in methanol (20 mmol in 15 mL of methanol) at room temperature, the crude products of the desired 3-oxo-1,2-pyrazolidinium ylides were formed. After removing the solvent methanol, the crude product was recrystallized in ethanol. Washed by ethyl acetate and dried under a vacuum, the pure product was obtained.

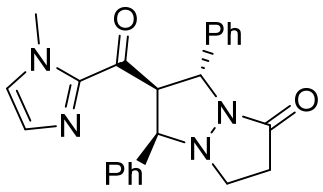
4. Asymmetric [3+2] Cycloaddition Reactions

4.1 Synthesis of racemic products as HPLC references

General Procedure: A dried 25 mL Schlenk tube was charged with *a,β*-unsaturated *a,β*-unsaturated 1-acylimidazoles **2** (0.20 mmol), *N,N'*-cyclic azomethine imines **3** (0.24 mmol) and $Cu(OTf)_2$ (3.62 mg, 5.0 mol%). The tube was purged with argon and anhydrous DCE (2 mL) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon. The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1 to 1:2, basified with 1.0% Et_3N) to afford racemic products as HPLC reference for determination of enantiomeric excess.

4.2 Substrate Scope

General Procedure: A dried 25 mL Schlenk tube was charged with chiral catalyst **Fe-BPsalan** (5.0 mol%) and added silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles (0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally *N,N'*-cyclic azomethine imines **3** (0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon. The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1 to 1:2, basified with 1.0% Et_3N) to afford chiral products.



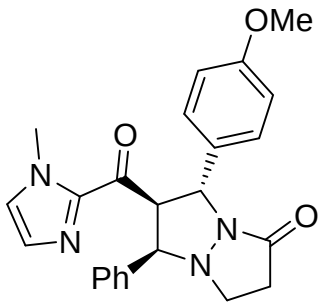
4a

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and added silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2a (42.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4a as white foamed solid (73.1 mg, yield: 95%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 95% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 20.38 min, tr(major) = 12.53 min). $[\alpha]_D$ = -53.6780 (c 1.0,

$CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.7 Hz, 2H), 7.12 (t, J = 7.5 Hz, 2H), 7.07 – 7.01 (m, 1H), 7.00 – 6.92 (m, 3H), 6.86 (dd, J = 7.1, 2.4 Hz, 2H), 6.72 (s, 1H), 6.54 (s, 1H), 5.56 (d, J = 6.1 Hz, 1H), 4.83 (dd, J = 7.8, 6.1 Hz, 1H), 4.60 (d, J = 8.0 Hz, 1H), 3.34 (s, 3H), 3.06 – 2.85 (m, 2H), 2.37 (ddd, J = 16.6, 9.3, 4.9 Hz, 1H), 2.15 (s, 1H); ^{13}C NMR (125 MHz, Chloroform-d) δ 187.37, 167.85, 142.67, 139.82, 134.09, 129.12, 129.05, 128.85, 128.36, 128.32, 127.74, 126.82, 126.37, 70.13, 65.74, 55.91, 45.57, 35.46, 34.65;

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{22}N_4O_2Na$ $[M+Na]^+$: 409.1634, found: 409.1635.



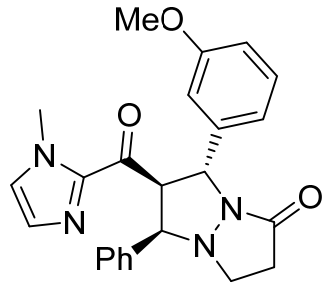
4b

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and added silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2b (48.46 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4b as white foamed solid (58.4 mg, yield: 71%, dr>99:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by

HPLC analysis, *ee* = 95% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 17.19 min, tr(major) = 9.73 min). $[\alpha]_D$ = -36.2792 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.14 (d, *J* = 7.0 Hz, 3H), 7.05 (d, *J* = 7.7 Hz, 2H), 6.91 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.73 (s, 1H), 5.74 – 5.61 (m, 1H), 5.02 (dd, *J* = 7.9, 6.1 Hz, 1H), 4.81 – 4.68 (m, 1H), 3.75 (s, 3H), 3.52 (s, 3H), 3.19 – 3.02 (m, 2H), 2.56 (dt, *J* = 16.5, 7.0 Hz, 1H), 2.38 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.58 , 167.32 , 159.16 ,142.75, 134.16 , 131.74 , 129.10 , 128.96 , 128.31 , 128.26 , 127.73 , 126.80 , 114.25 , 70.24 , 65.67 , 55.60 , 55.33 , 45.95 , 35.45 , 34.91 .

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_4O_3Na$ $[M+Na]^+$: 439.1752, found: 439.1741.



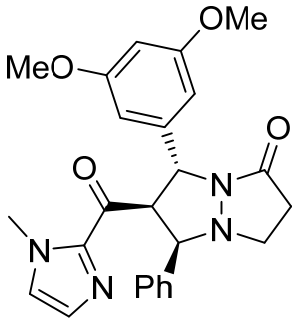
4c

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and added silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2c (48.46 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4c as white foamed solid (78.6 mg, yield: 95%, dr>70:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by

HPLC analysis, *ee* = 97% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 27.92 min, tr(major) = 14.11 min). $[\alpha]_D$ = -53.7798 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 15.4, 7.6 Hz, 1H), 7.37 (d, *J* = 5.9 Hz, 3H), 7.24 (s, 3H), 7.20 (s, 1H), 7.13 (s, 1H), 6.95 (s, 2H), 5.95 (d, *J* = 5.9 Hz, 1H), 5.33 – 5.14 (m, 1H), 5.01 (d, *J* = 7.6 Hz, 1H), 3.98 (s, 3H), 3.75 (s, 3H), 3.40 (t, *J* = 9.8 Hz, 1H), 3.30 (s, 1H), 2.77 (ddd, *J* = 15.1, 8.9, 4.7 Hz, 1H), 2.53 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.31 , 167.92 , 159.93 , 142.65 , 141.53 , 134.07 , 129.92 , 129.11 , 129.06 , 128.35 , 128.29 , 126.80 , 118.55 , 113.06 , 112.12 , 70.04 , 65.73 , 55.78 , 55.24 , 45.45 , 35.43 , 34.58 .

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_4O_3Na$ $[M+Na]^+$: 439.1745, found: 439.1741.



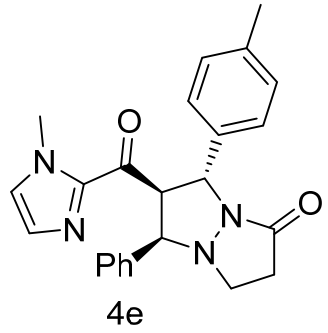
4d

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and added silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2d (54.46 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4d as white foamed solid (83.3 mg, yield: 93%, dr>90:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by

HPLC analysis, *ee* = 96% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 12.89 min, tr(major) = 9.54 min). $[\alpha]_D$ = -72.1552(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.11 (m, 3H), 7.05 – 6.98 (m, 2H), 6.90 (s, 1H), 6.73 (s, 1H), 6.59 (d, *J* = 2.3 Hz, 2H), 6.31 (d, *J* = 1.2 Hz, 1H), 5.67 (d, *J* = 5.8 Hz, 1H), 4.98 (dd, *J* = 7.8, 6.1 Hz, 1H), 4.77 (d, *J* = 7.7 Hz, 1H), 3.73 (s, 6H), 3.51 (s, 3H), 3.18 (q, *J* = 10.1 Hz, 1H), 3.05 (s, 1H), 2.53 (ddd, *J* = 15.1, 9.5, 5.1 Hz, 1H), 2.28 (s, 1H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.24 , 167.97 , 161.10 , 142.62 , 142.42 , 134.03 , 129.10 , 129.04 , 128.33 , 128.28 , 126.78 , 104.33 , 99.49 , 69.93 , 65.71 , 55.80 , 55.32 , 45.30 , 35.40 , 34.51 .

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{26}N_4O_4Na$ $[M+Na]^+$: 469.1841, found: 469.1846.



4e

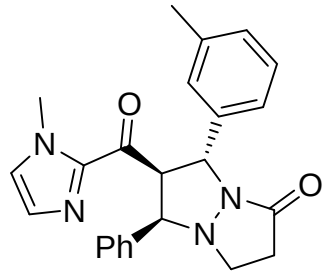
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and added silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2e (45.26 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4e as white foamed solid (71.8 mg, yield: 90%, dr>99:1), the dr value was

determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 95% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 13.51 min, tr(major) = 9.51 min). $[\alpha]_D$ = -43.8725(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.10 (m, 5H), 7.06 (d, *J* = 6.7 Hz, 2H), 6.91 (s, 1H), 6.73 (s, 1H), 5.69 (d, *J* = 5.8 Hz, 1H), 5.08 – 4.98 (m, 1H), 4.76 (d, *J* = 7.9 Hz, 1H), 3.53 (d, *J* = 1.9 Hz, 3H), 3.23 – 2.98 (m, 2H), 2.63 – 2.52 (m, 1H), 2.45 (s, 1H), 2.29 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.53 , 167.31 , 142.73 , 137.39 , 136.66 , 134.13 , 129.50 , 129.08 , 128.97 , 128.29 , 128.25 , 126.78 , 126.37 , 70.17 , 65.66 , 55.81 , 45.97 , 35.44 , 34.89 , 21.15 .

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_4O_2Na$ $[M+Na]^+$: 423.1803, found: 423.1792.



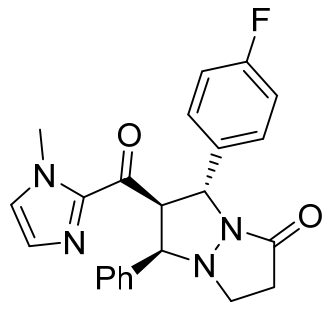
4f

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and add silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2f (45.26 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral

product 4f as white foamed solid (71.7 mg, yield: 90%, dr>50:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 95% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 10.95 min, tr(major) = 8.29 min). $[\alpha]_D$ = -59.1702(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.11 (m, 6H), 7.08 – 7.01 (m, 3H), 6.91 (s, 1H), 6.73 (s, 1H), 5.72 (d, *J* = 6.1 Hz, 1H), 5.04 – 4.99 (m, 1H), 4.79 (d, *J* = 7.6 Hz, 1H), 3.52 (s, 3H), 3.19 (q, *J* = 9.8 Hz, 1H), 3.09 (s, 1H), 2.56 (ddd, *J* = 15.0, 9.1, 4.8 Hz, 1H), 2.47 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.39 , 167.74 , 142.68 , 139.75 , 138.45 , 134.13 , 129.08 , 129.05 , 128.71 , 128.53 , 128.33 , 128.27 , 126.98 , 126.77 , 123.44 , 70.11 , 65.77 , 55.84 , 45.50 , 35.42 , 34.65 , 21.52 .

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_4O_2Na$ $[M+Na]^+$: 423.1785, found: 423.1792.



4g

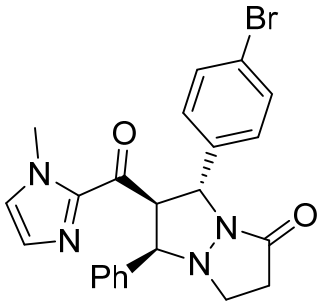
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and add silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2g (46.05mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by

TLC) under argon. The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4g as white foamed solid (45.6 mg, yield: 57%, dr>90:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 95% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 12.08 min, tr(major) = 8.63 min). $[\alpha]_D$ = -52.7004(c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ7.43 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.16 (q, *J* = 4.0 Hz, 3H), 7.10-6.97 (m, 4H), 6.94 (s, 1H), 6.76 (s, 1H), 5.76 (d, *J* = 4.0 Hz, 1H), 4.98 (t, *J* = 8.0 Hz, 1H), 4.81 (d, *J* = 4.0 Hz, 1H), 3.54 (s, 3H), 3.26 3.02 (m, 2H), 2.62-2.49 (m, 1H), 2.31 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-d) δ 187.25, 168.33, 161.38, 142.69, 135.73, 134.07, 129.25, 129.12, 128.47, 128.43, 128.25, 128.18, 126.91, 115.85, 115.68, 70.24, 65.87, 55.37, 45.38, 35.51, 34.57.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2NaF$ $[M+Na]^+$: 427.1546, found: 427.1541.



4h

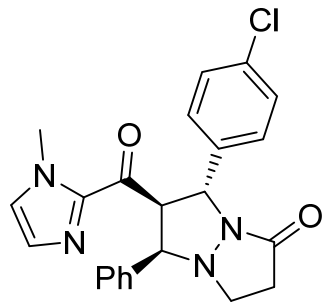
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *a,β*-unsaturated 1-acylimidazoles 2h (58.23 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under

argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4h as white foamed solid (90.4mg, yield: 97%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 98% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 30.12 min, tr(major) = 14.86 min). $[\alpha]_D$ = -46.3460(c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.39 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.16 (dd, *J* = 5.4, 1.9 Hz, 3H), 7.02 (dd, *J* = 6.8, 2.8 Hz, 2H), 6.94 (s, 1H), 6.75 (s, 1H), 5.73 (d, *J* = 6.3 Hz, 1H), 5.01 – 4.92 (m, 1H), 4.81 (d, *J* = 7.8 Hz, 1H), 3.53 (s, 3H), 3.19 (dd, *J* = 14.4, 5.8 Hz, 1H), 3.08 (q, *J* = 8.7 Hz, 1H), 2.54 (ddd, *J* = 16.9, 9.4, 4.9 Hz, 1H), 2.29 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.03 , 168.39 , 142.57 , 139.06 , 133.96 , 131.94 , 129.26 , 129.10 , 128.45 , 128.44 , 128.22 , 126.93 , 121.66 , 70.16 , 65.71 , 55.40 , 45.32 , 35.48 , 34.43 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2NaBr$ $[M+Na]^+$: 487.0751, found: 487.0740.



4i

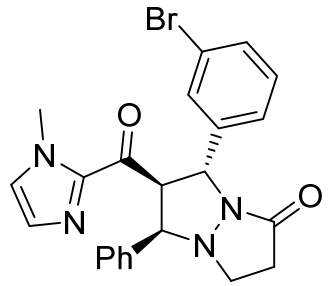
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and add silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2i (49.34mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes,

finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4i as white foamed solid (81.4 mg, yield: 97%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 98% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 30.12 min, tr(major) = 14.86 min). $[\alpha]_D$ = -50.5944(c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.14 (dd, *J* = 9.7, 3.3 Hz, 2H), 7.02 (dd, *J* = 5.7, 2.0 Hz, 3H), 6.88 (dd, *J* = 6.8, 2.8 Hz, 2H), 6.80 (s, 1H), 6.61 (s, 1H), 5.60 (d, *J* = 6.2 Hz, 1H), 4.82 (t, *J* = 7.1 Hz, 1H), 4.67 (d, *J* = 8.0 Hz, 1H), 3.39 (s, 3H), 3.06 (q, *J* = 9.8 Hz, 1H), 2.95 (s, 1H), 2.40 (ddd, *J* = 16.8, 9.3, 4.9 Hz, 1H), 2.14 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.07 , 168.37 , 142.58 , 138.53 , 133.97 , 133.49 , 129.25 , 129.09 , 128.99 , 128.44 , 128.43 , 127.87 , 126.92 , 70.17 , 65.75 , 55.34 , 45.32 , 35.46 , 34.44 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2NaCl$ $[M+Na]^+$: 443.1249, found: 443.1245.



4j

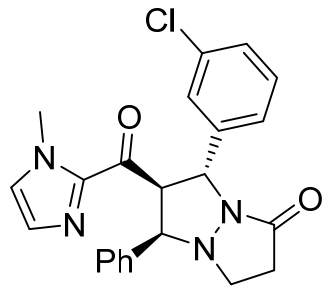
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *a,β*-unsaturated 1-acylimidazoles 2j (58.23

mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4j as white foamed solid (91.4mg, yield: 98%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 94% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 26.25 min, tr(major) = 13.03 min). $[\alpha]_D$ = -58.5334(c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 1.9 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.21 – 7.12 (m, 4H), 7.01 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.97 – 6.85 (m, 1H), 6.82 – 6.67 (m, 1H), 5.76 (d, *J* = 6.4 Hz, 1H), 4.95 (dd, *J* = 7.8, 6.4 Hz, 1H), 4.84 (s, 1H), 3.53 (s, 3H), 3.24 (q, *J* = 9.9 Hz, 1H), 3.15 – 2.98 (m, 1H), 2.53 (ddd, *J* = 16.5, 9.6, 4.8 Hz, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 186.85 , 168.88 , 142.50 , 133.94 , 130.89 , 130.43 , 129.33 , 129.25 , 129.17 , 128.48 , 128.45 , 126.92 , 125.14 , 122.95 , 70.11 , 65.83 , 55.23 , 44.86 , 35.46 , 34.18 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2NaBr$ $[M+Na]^+$: 487.0748, found: 487.0740.



4k

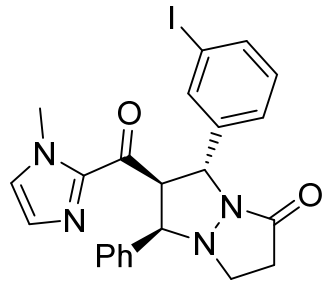
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) andsilver salt (5.0 mol% $AgSbF_6$) to the glove

box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2k (49.34 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4k as white foamed solid (80.1mg, yield: 95%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 95% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 22.05 min, tr(major) = 12.35 min). $[\alpha]_D$ = -62.4594(c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.34 – 7.21 (m, 5H), 7.12 – 7.05 (m, 2H), 7.01 (s, 1H), 6.83 (s, 1H), 5.84 (d, *J* = 6.3 Hz, 1H), 5.03 (t, *J* = 7.1 Hz, 1H), 4.91 (d, *J* = 7.9 Hz, 1H), 3.61 (s, 3H), 3.32 (q, *J* = 10.0 Hz, 1H), 3.14 (t, *J* = 12.1 Hz, 1H), 2.61 (ddd, *J* = 15.2, 9.5, 4.7 Hz, 1H), 2.30 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 186.90 , 168.81 , 142.53 , 142.21 , 134.70 , 133.96 , 130.16 , 129.25 , 129.17 , 128.48 , 128.44 , 127.95 , 126.92 , 126.47 , 124.65 , 70.13 , 65.82 , 55.30 , 44.94 , 35.46 , 34.22 .

HRMS (ESI, *m/z*) calcd for $C_{23}H_{21}N_4O_2NaCl$ $[M+Na]^+$: 443.1250, found: 443.1245.



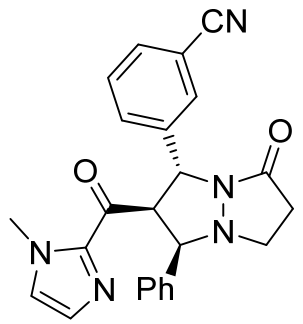
4l

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) inthe glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2l (67.63 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4l as white foamed solid (94mg, yield: 92%, dr>90:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 96% (Chiralpak column IA, λ = 254 nm,CH_3OH /*i*-PrOH =50:50, flow rate: 0.7 mL/min, 25 ℃, tr(minor) = 25.91 min, tr(major) = 8.11min). $[\alpha]_D$ = -57.1557(c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (t, *J* = 1.8 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.12 (m, 3H), 7.08 – 6.98 (m, 3H), 6.94 (s, 1H), 6.75 (s, 1H), 5.82 – 5.64 (m, 1H), 5.00 – 4.91 (m, 1H), 4.84 (d, *J* = 7.8 Hz, 1H), 3.53 (s, 3H), 3.25 (q, *J* = 9.9 Hz, 1H), 3.05 (s, 1H), 2.53 (ddd, *J* = 16.7, 9.6, 4.8 Hz, 1H), 2.22 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 186.84 , 168.88 , 142.51 , 136.86 , 135.16 , 133.96 , 130.55 , 129.25 , 129.18 , 128.48 , 128.44 , 126.91 , 125.80 , 94.90 , 70.10 , 65.84 , 55.11 , 44.85 , 35.48 , 34.17 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2NaI$ $[M+Na]^+$: 535.0620, found: 535.0601.



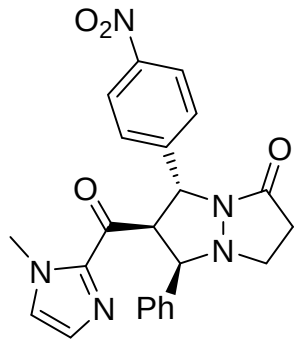
4m

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and add silver salt (5.0 mol% $AgSbF_6$)to the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2m(51.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4m as white foamed solid (57.7 mg, yield: 70%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 97% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25℃, tr(minor) = 21.96 min, tr(major) = 12.95min). $[\alpha]_D$ = -71.6221(c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 6.5, 3.7 Hz, 3H), 7.05 – 6.98 (m, 2H), 6.96 (s, 1H), 6.79 (s, 1H), 5.85 (d, *J* = 6.0 Hz, 1H), 4.90 (d, *J* = 5.9 Hz, 2H), 3.56 (s, 3H), 3.30 (q, *J* = 10.0 Hz, 1H), 3.08 (td, *J* = 10.7, 4.8 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.18 (s, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.60 , 169.62 , 142.43 , 141.97 , 133.83 , 131.45 , 131.00 , 130.09 , 129.75 , 129.41 , 129.26 , 128.61 , 127.08 , 118.77 , 112.97 , 70.22 , 65.87 , 60.46 , 55.16 , 44.65 , 35.53 , 33.91 , 21.14 , 14.27 .

HRMS (ESI, *m/z*) calcd for $C_{24}H_{21}N_5O_2Na$ $[M+Na]^+$: 434.1583, found: 434.1587.



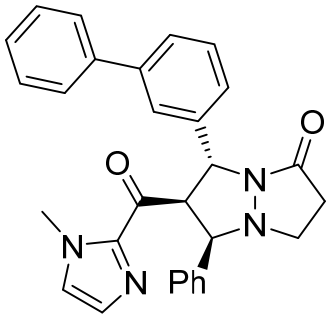
4n

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and add silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2n (51.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4n as yellow foamed solid (34.5 mg, yield: 40%, dr>20:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 90% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 56.48 min, tr(major) = 20.59min). $[\alpha]_D$ = -49.7906(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.12 (m, 2H), 7.68 – 7.61 (m, 2H), 7.24 – 7.17 (m, 3H), 7.08 – 6.93 (m, 3H), 6.79 (s, 1H), 5.94 (d, *J* = 6.3 Hz, 1H), 5.05 – 4.85 (m, 2H), 3.57 (s, 3H), 3.37 – 3.25 (m, 1H), 3.10 (s, 1H), 2.55 (ddd, *J* = 15.5, 9.8, 4.9 Hz, 1H), 2.20 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 186.44 , 169.66 , 147.45 , 142.35 , 133.72 , 129.39 , 129.21 , 128.60 , 127.35 , 127.03 , 124.18 , 70.16 , 65.70 , 60.43 , 55.31 , 44.67 , 35.49 , 33.86 , 14.22 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_5O_4Na$ $[M+Na]^+$: 454.1492, found: 454.1486.



4o

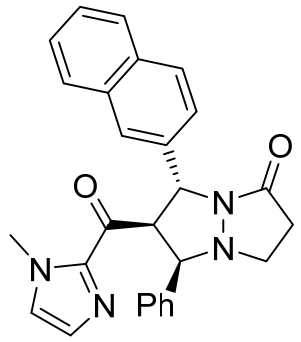
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) to the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2o(56.67 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon. The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4o as white foamed solid (85 mg, yield: 92%, dr>80:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 97% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25℃, tr(minor) = 27.40 min, tr(major) = 18.49min). $[\alpha]_D$ = -53.8854(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.58 (d, *J* = 6.9 Hz, 2H), 7.50 – 7.38 (m, 5H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 6.4 Hz, 3H), 7.07 (d, *J* = 7.6 Hz,

2H), 6.93 (s, 1H), 6.73 (s, 1H), 5.88 (d, *J* = 6.3 Hz, 1H), 5.12 – 5.04 (m, 1H), 4.86 (d, *J* = 7.7 Hz, 1H), 3.53 (s, 3H), 3.24 (q, *J* = 9.8 Hz, 1H), 3.11 (s, 1H), 2.64 – 2.54 (m, 1H), 2.34 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.22 , 168.19 , 142.62 , 141.82 , 141.09 , 140.52 , 134.10 , 129.28 , 129.12 , 128.68 , 128.38 , 128.32 , 127.32 , 127.29 , 126.81 , 126.64 , 125.23 , 70.08 , 65.90 , 55.90 , 45.29 , 35.41 , 34.51 .

HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{27}N_4O_2$ $[M+H]^+$: 463.2122, found: 463.2129.



4p

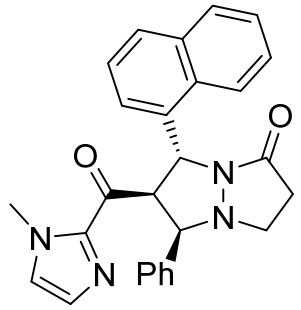
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and add silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2p (52.46 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4p as white foamed solid (83.7 mg, yield: 96%, dr>50:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 97% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 45.40 min, tr(major) = 18.30min).

$[\alpha]_D$ = -62.8942(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.86 – 7.76 (m, 3H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.19 (d, *J* = 7.0 Hz, 3H), 7.13 – 7.06 (m, 2H), 6.92 (s, 1H), 6.72 (s, 1H), 5.97 (d, *J* = 6.2 Hz, 1H), 5.17 – 5.09 (m, 1H), 4.89 (d, *J* = 7.9 Hz, 1H), 3.54 (s, 3H), 3.28 (q, *J* = 10.0 Hz, 1H), 3.14 (s, 1H), 2.62 (ddd, *J* = 16.6, 9.4, 4.8 Hz, 1H), 2.36 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.23 , 168.20 , 142.62 , 137.23 , 134.15 , 133.33 , 133.00 , 129.13 , 128.93 , 128.38 , 128.33 , 128.03 , 127.64 , 126.82 , 126.16 , 125.93 , 125.48 , 124.15 , 70.23 , 65.70 , 56.11 , 45.39 , 35.41 , 34.57 .

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{25}N_4O_2$ $[M+H]^+$: 437.1978, found: 437.1972.



4q

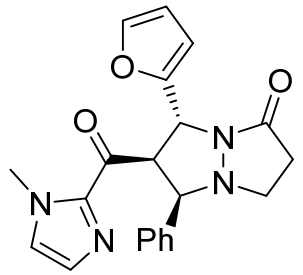
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2q (52.46mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4q as pale yellow foamed solid (78.9 mg, yield: 91%, dr>70:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 95% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH

=90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 45.37 min, tr(major) = 18.40min). $[\alpha]_D$ = -53.1880(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.87 – 7.76 (m, 3H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.37 (m, 2H), 7.19 (d, *J* = 6.7 Hz, 3H), 7.09 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.92 (s, 1H), 6.72 (s, 1H), 5.97 (d, *J* = 6.2 Hz, 1H), 5.20 – 5.07 (m, 1H), 4.89 (d, *J* = 7.9 Hz, 1H), 3.54 (s, 3H), 3.28 (q, *J* = 9.7, 9.2 Hz, 1H), 3.14 (s, 1H), 2.62 (ddd, *J* = 16.6, 9.4, 4.8 Hz, 1H), 2.36 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.31 , 168.23 , 142.70 , 137.25 , 134.22 , 133.39 , 133.06 , 129.18 , 128.98 , 128.43 , 128.37 , 128.09 , 127.68 , 126.83 , 126.21 , 125.97 , 125.55 , 124.19 , 70.28 , 65.75 , 56.17 , 45.48 , 35.48 , 34.64 .

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{25}N_4O_2$ $[M+H]^+$: 437.1964, found: 437.1972.



4r

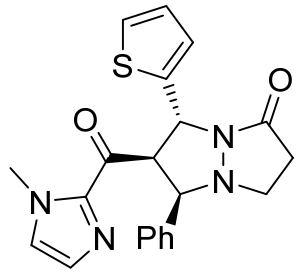
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2r (40.44 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4r as pale yellow foamed solid (18.4 mg, yield: 25%, dr>30:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by

HPLC analysis, *ee* = 88% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 36.18 min, tr(major) = 17.69min). $[\alpha]_D$ = - 15.36 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.39 (m, 1H), 7.18 – 7.07 (m, 5H), 6.90 (s, 1H), 6.73 (s, 1H), 6.45 (d, *J* = 3.2 Hz, 1H), 6.39 – 6.26 (m, 1H), 5.76 – 5.45 (m, 1H), 5.32 (dd, *J* = 7.8, 4.6 Hz, 1H), 4.66 (s, 1H), 3.60 (s, 3H), 3.28 (s, 1H), 3.02 (d, *J* = 11.0 Hz, 1H), 2.60 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.79 , 166.60 , 150.13 , 142.97 , 142.89 , 133.97 , 129.24 , 128.60 , 128.33 , 128.24 , 126.97 , 110.63 , 109.00 , 70.96 , 61.17 , 50.40 , 48.13 , 35.68 , 35.42 .

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{20}N_4O_3Na$ $[M+Na]^+$: 399.1432, found: 399.1428.



4s

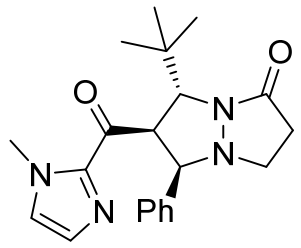
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2s(43.65 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4s as pale yellow foamed solid (25.9 mg, yield: 33%, dr>20:1), the dr value was

determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, ee = 94% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 36.18 min, tr(major) = 17.69min). $[\alpha]_D$ = - -16.93 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.22 (m, 1H), 7.20 – 7.07 (m, 6H), 7.05 – 6.86 (m, 2H), 6.75 (s, 1H), 5.96 (s, 1H), 5.16 (dd, *J* = 7.7, 5.3 Hz, 1H), 4.74 (s, 1H), 3.60 (s, 3H), 3.26 – 3.03 (m, 2H), 2.64 – 2.38 (m, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.41 , 167.51 , 143.02 , 142.77 , 133.86 , 129.29 , 128.88 , 128.41 , 128.39 , 127.07 , 126.95 , 125.67 , 125.30 , 70.46 , 65.58 , 52.44 , 46.80 , 35.64 , 35.08 .

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{20}N_4O_3Na$ $[M+Na]^+$: 415.1199, found: 415.1199.



4t

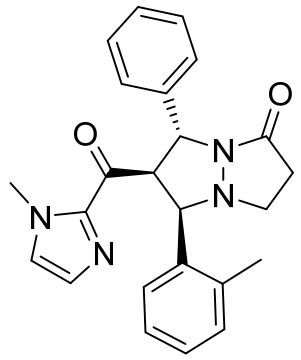
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and add silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2t (38.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (41.81 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 4t as white solid (41.8 mg, yield: 57%, dr>20:1), the dr value was determined

by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, ee = 95 % (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH/DEA = 90:10:0.1 , flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 10.06 min, tr(major) = 9.07 min). $[\alpha]_D$ = -72.9546(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.10 (m, 3H), 7.00 (s, 1H), 6.90 – 6.83 (m, 2H), 6.75 (s, 1H), 4.79 (d, *J* = 5.1 Hz, 2H), 4.70 (d, *J* = 3.1 Hz, 1H), 3.42 (s, 3H), 3.38 – 3.29 (m, 1H), 2.88 – 2.77 (m, 1H), 2.16 (ddd, *J* = 17.3, 10.4, 3.6 Hz, 1H), 1.66 – 1.54 (m, 1H), 1.01 (s, 9H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.82 , 174.12 , 142.83 , 134.88 , 130.04 , 128.99 , 128.46 , 128.27 , 126.46 , 70.55 , 61.72 , 57.25 , 41.59 , 35.27 , 32.51 , 26.69 .

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{26}N_4O_2Na$ $[M+ Na]^+$: 389.1952, found: 389.1948.



5a

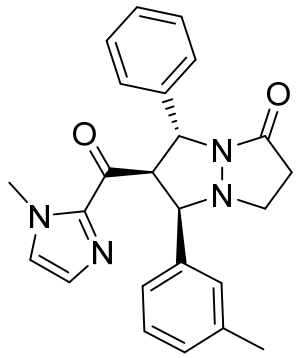
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and added silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added and stirred at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles **2a** (42.45 mg, 0.20 mmol) was added and the mixture was further stirred at room temperature for 30 minutes, finally *N,N*'-cyclic azomethine imines **3a'** (45.18 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was

purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product **5a** as white foamed solid (75.7mg, yield: 95%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 92% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 20.80 min, tr(major) = 14.07min). $[\alpha]_D$ = 22.92 (c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.1 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.22 – 7.15 (m, 1H), 7.07 – 7.01 (m, 1H), 6.97 (td, *J* = 7.5, 1.5 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 6.68 (s, 1H), 5.60 (s, 1H), 5.06 (dd, *J* = 7.8, 4.7 Hz, 1H), 4.87 (s, 1H), 3.53 (s, 3H), 3.08 (d, *J* = 74.1 Hz, 2H), 2.60 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 188.19 , 166.10 , 142.94 , 139.38 , 137.77 , 131.92 , 130.47 , 128.95 , 128.84 , 127.87 , 127.00 , 126.83 , 126.46 , 125.76 , 66.13 , 64.14 , 56.34 , 47.58 , 35.63 , 35.29 , 19.79 .

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_4O_2Na$ $[M+ Na]^+$: 423.1792, found: 423.1791.



5b

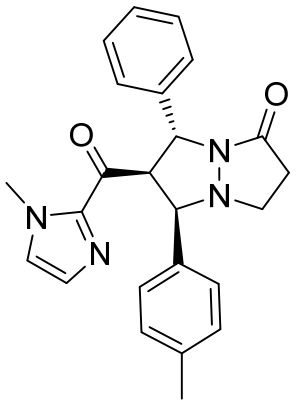
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and add silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2a(42.4 5mg, 0.20 mmol) was add continue stirring at room temperature for 30

minutes, finally N,N'-cyclic azomethine imines 3b (45.18 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon. The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 5b as white foamed solid (73 mg, yield: 91%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 91% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 26.90 min, tr(major) = 12.70min). $[\alpha]_D$ = -39.20 (c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 13.8 Hz, 2H), 6.87 (d, *J* = 5.3 Hz, 2H), 6.74 (s, 1H), 5.82 – 5.64 (m, 1H), 5.02 (dd, *J* = 7.8, 5.9 Hz, 1H), 4.72 (s, 1H), 3.55 (s, 3H), 3.15 (d, *J* = 8.5 Hz, 2H), 2.58 (dt, *J* = 16.5, 6.8 Hz, 1H), 2.39 (d, *J* = 21.9 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.64 , 167.59 , 142.82 , 139.76 , 138.05 , 133.95 , 129.81 , 129.05 , 129.00 , 128.88 , 128.23 , 127.78 , 126.75 , 126.44 , 125.87 , 70.21 , 65.70 , 56.03 , 45.87,35.47 , 34.91 , 21.30 .

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_4O_2Na$ $[M+ Na]^+$: 423.1795, found: 423.1791.



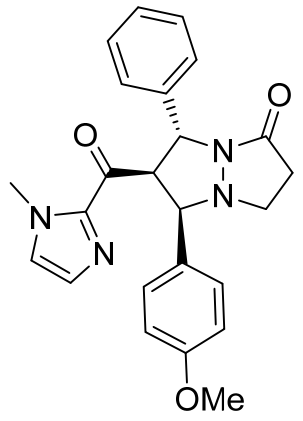
5c

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove

box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2a (42.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3c(45.18 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 5c as white foamed solid (74.5mg, yield: 93%, dr>30:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 92% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 23.25 min, tr(major) = 13.55min). $[\alpha]_D$ = -76.52 (c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.4 Hz, 2H), 7.32 (dd, *J* = 15.4, 7.6 Hz, 2H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 3H), 6.78 (s, 1H), 5.82 (d, *J* = 6.3 Hz, 1H), 5.06 – 4.97 (m, 1H), 4.85 (d, *J* = 7.6 Hz, 1H), 3.58 (s, 3H), 3.24 (q, *J* = 9.8 Hz, 1H), 3.14 – 3.01 (m, 1H), 2.56 (ddd, *J* = 14.7, 9.5, 4.9 Hz, 1H), 2.24 (s, 4H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.31 , 168.52 , 142.66 , 140.13 , 138.09 , 130.89 , 129.12 , 129.08 , 128.80 , 127.65 , 126.74 , 126.31 , 69.84 , 65.83 , 55.84 , 44.90 , 35.47 , 34.35 , 21.06 .

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_4O_2Na$ $[M+ Na]^+$: 423.1795, found: 423.1792.

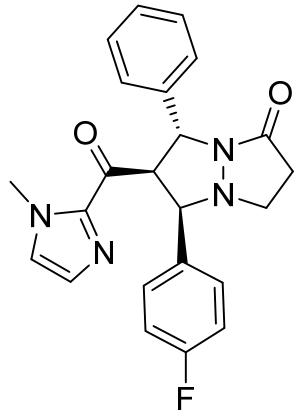


5d

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2a (42.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3d (49.01 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 5d as white foamed solid (46 mg, yield: 55%, dr>80:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, ee = 91% (Chiralpak column IG, λ = 254 nm,CH_3OH/i-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 31.64 min, tr(major) = 13.74min). $[\alpha]_D$ = -75.57 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.94 (m, 2H), 7.45 – 7.41 (m, 2H), 7.35 (dd, *J* = 8.0, 6.5 Hz, 4H), 7.32 – 7.25 (m, 1H), 6.90 (s, 1H), 6.79 (s, 1H), 5.66 (d, *J* = 5.3 Hz, 1H), 5.13 – 5.05 (m, 1H), 4.83 (s, 1H), 3.65 (s, 3H), 3.15 (t, *J* = 8.8 Hz, 2H), 2.72 – 2.51 (m, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 186.78 , 166.27 , 147.65 , 142.29 , 142.11 , 138.79 , 129.90 , 129.50 , 129.04 , 128.16 , 127.54 , 126.55 , 123.26 , 69.53 , 65.43 , 56.28 , 47.18 , 35.89 , 35.37 .



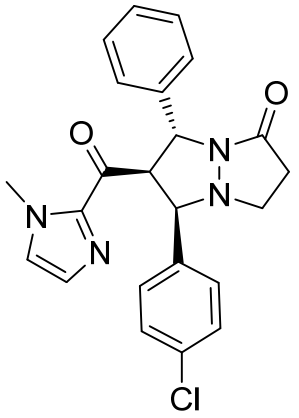
5e

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2a (42.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3e (46.13 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1, basified with 1.0% Et_3N) to afford chiral product 5e as white foamed solid (72.4mg, yield: 90%, dr>99:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 95% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.7 mL/min, 25 ℃, tr(minor) = 18.49 min, tr(major) = 11.79min). $[\alpha]_D$ = -36.94 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.06 (dd, *J* = 8.4, 5.4 Hz, 2H), 6.92 (s, 1H), 6.86 (t, *J* = 8.5 Hz, 2H), 6.78 (s, 1H), 5.72 (d, *J* = 6.0 Hz, 1H), 5.06 – 4.97 (m, 1H), 4.79 (s, 1H),

3.61 (s, 3H), 3.25 – 3.00 (m, 2H), 2.59 (ddd, *J* = 17.0, 9.2, 4.8 Hz, 1H), 2.39 (s, 1H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.26 , 167.57 , 163.46 , 161.49 , 142.56 , 139.59 , 130.84 , 130.79 , 130.02 , 130.00 , 129.27 , 128.91 , 127.86 , 127.05 , 126.42 , 115.42 , 115.25 , 69.48 , 65.63 , 55.92 , 45.82 , 35.66 , 34.78 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2FNa$ $[M+ Na]^+$: 427.1550, found: 427.1541.



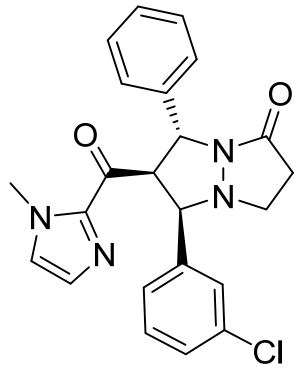
5f

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2a (42.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3f (50.07 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:2, basified with 1.0% Et_3N) to afford chiral product 5f as white foamed solid (77.5mg, yield: 92%, dr>30:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 93% (Chiralpak column IG, λ = 254 nm,CH_3OH/*i*-PrOH =60:40, flow rate: 0.7 mL/min, 25 ℃, tr(minor) = 23.49 min, tr(major) = 10.89min). $[\alpha]_D$ = -74.62 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 6.3 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.93 (s, 1H), 6.79 (s, 1H), 5.71 (d, *J* = 5.8 Hz, 1H), 5.05 – 4.96 (m, 1H), 4.78 (d, *J* = 8.0 Hz, 1H), 3.62 (s, 3H), 3.24 – 3.03 (m, 2H), 2.59 (ddd, *J* = 16.7, 9.3, 4.7 Hz, 1H), 2.40 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.11 , 167.54 , 142.51 , 139.55 , 134.28 , 132.80 , 130.43 , 129.32 , 128.93 , 128.55 , 127.90 , 127.11 , 126.43 , 69.51 , 65.65 , 55.94 , 45.82 , 35.69 , 34.78 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2ClNa$ $[M+ Na]^+$: 443.1251, found: 443.1245.



5g

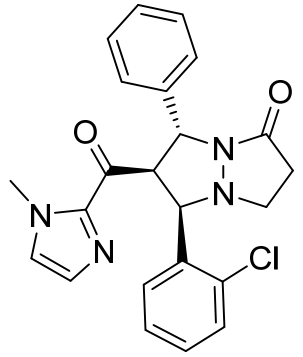
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. α,β-unsaturated 1-acylimidazoles 2a (42.45mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3g (50.07 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1, basified with 1.0% Et_3N) to afford chiral product 5g as white foamed solid (75.8mg, yield: 90%, dr>99:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by

HPLC analysis, *ee* = 96% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH =60:40, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 41.91 min, tr(major) = 15.71min). $[\alpha]_D$ = -28.21 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.09 (dd, *J* = 6.2, 3.5 Hz, 3H), 7.00 (dq, *J* = 4.7, 2.3, 1.8 Hz, 1H), 6.90 (s, 1H), 6.77 (s, 1H), 5.64 (d, *J* = 5.4 Hz, 1H), 5.02 (dd, *J* = 7.9, 5.4 Hz, 1H), 4.64 (d, *J* = 7.3 Hz, 1H), 3.63 (s, 3H), 3.25 – 3.03 (m, 2H), 2.68 – 2.45 (m, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.26 , 166.47 , 142.61 , 139.10 , 136.34 , 134.25 , 129.60 , 129.28 , 128.99 , 128.94 , 128.45 , 127.96 , 127.16 , 126.84 , 126.50 , 69.72 , 65.42 , 56.07 , 47.03 , 35.64 , 35.34 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2ClNa$ $[M+ Na]^+$: 443.1250, found: 443.1245.



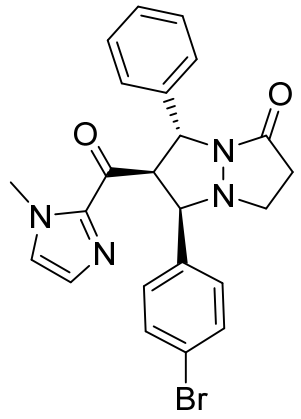
5h

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2a (42.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3h (50.07 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1, basified with 1.0% Et_3N) to afford chiral product 5h

as white foamed solid (82.5 mg, yield: 98%, dr>50:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, ee = 96% (Chiralpak column IA, λ = 254 nm,CH_3OH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 17.53 min, tr(major) = 13.69 min). $[\alpha]_D$ = 24.37 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.18 – 7.02 (m, 3H), 6.88 (s, 1H), 6.73 (s, 1H), 5.61 (s, 1H), 5.24 (s, 1H), 5.14 – 5.04 (m, 1H), 3.61 (s, 3H), 3.24 (s, 1H), 3.09 (s, 1H), 2.57 (s, 2H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.79 , 166.63 , 142.59 , 139.15 , 135.31 , 131.69 , 129.81 , 129.35 , 129.30 , 128.93 , 128.62 , 127.94 , 127.16 , 126.52 , 66.12 , 63.92 , 56.53 , 47.44 , 35.50 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_4O_2ClNa$ $[M+ Na]^+$: 443.1252, found: 443.1245.



5i

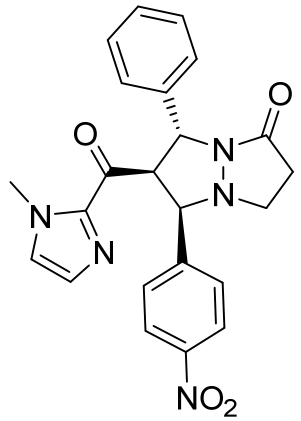
Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2a (42.45mg, 0.20 mmol) was added continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3i (60.74 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored

by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1, basified with 1.0% Et_3N) to afford chiral product 5i as white foamed solid (83.1mg, yield: 90%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 97% (Chiralpak column IA, λ = 254 nm, MeOH/*i*-PrOH =90:10, flow rate: 0.7 mL/min, 25 ℃, tr(minor) = 24.28 min, tr(major) = 11.13min). $[\alpha]_D$ = -84.83 (c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 13.8, 7.9 Hz, 4H), 7.23 (d, *J* = 7.1 Hz, 1H), 6.99 – 6.90 (m, 3H), 6.80 (s, 1H), 5.71 (d, *J* = 5.9 Hz, 1H), 5.01 (dd, *J* = 7.8, 6.1 Hz, 1H), 4.84 – 4.69 (m, 1H), 3.61 (s, 3H), 3.17 (t, *J* = 9.7 Hz, 1H), 3.07 (s, 1H), 2.59 (ddd, *J* = 16.7, 9.3, 4.7 Hz, 1H), 2.41 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.05 , 167.51 , 142.48 , 139.52 , 133.30 , 131.48 , 130.70 , 129.31 , 128.90 , 127.87 , 127.11 , 126.40 , 122.47 , 69.53 , 65.59 , 55.91 , 45.80 , 35.67 , 34.76 .

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{22}N_4O_2Br$ $[M+H]^+$: 465.0920, found: 465.0921.

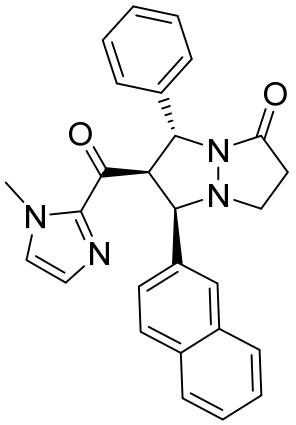


5j

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *a,β*-unsaturated 1-acylimidazoles 2a (42.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3j (52.61 mg, 0.24 mmol) was added. The reaction

mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1, basified with 1.0% Et_3N) to afford chiral product 5j as yellow foamed solid (57.4 mg, yield: 67%, dr>30:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 95% (Chiralpak column IG, λ = 254 nm,CH_3OH /*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 28.05 min, tr(major) = 12.61min). $[\alpha]_D$ = -87.17 (c 1.0, $CHCl_3$).

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_5O_4Na$ $[M+ Na]^+$: 454.1489, found: 454.1486.



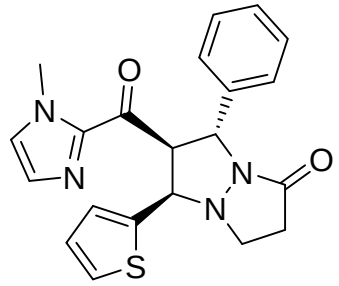
5k

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2a (42.45mg, 0.20 mmol) was added continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3k (53.82 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1, basified with 1.0%

Et_3N) to afford chiral product 5k as pale yellow foamed solid (62.7 mg, yield: 72%, dr>99:1), the dr value was determined by crude ^1H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 93% (Chiralpak column IA, λ = 254 nm CH_3OH/*i*-PrOH =90:10, flow rate: 0.7 mL/min, 25 ℃, tr(minor) = 31.05 min, tr(major) = 12.65min). $[\alpha]_D$ = -96.59 (c 1.0, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.65 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.55 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.41 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.85 (s, 1H), 6.57 (s, 1H), 5.82 (s, 1H), 5.09 (dd, *J* = 7.8, 5.9 Hz, 1H), 4.93 (s, 1H), 3.38 (s, 3H), 3.17 (t, *J* = 10.1 Hz, 2H), 2.56 (dt, *J* = 14.5, 6.9 Hz, 1H), 2.37 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.46, 167.59, 142.68, 139.77, 132.90, 131.67, 129.13, 128.93, 128.43, 128.00, 127.86, 127.53, 126.84, 126.49, 126.44, 70.36, 65.85, 56.12, 46.08, 35.39, 34.91.



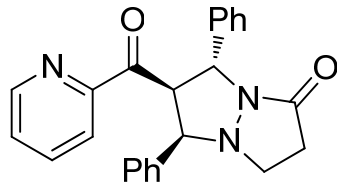
5l

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles 2a (42.45 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3l (43.25 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1, basified with 1.0% Et_3N) to afford chiral product 5l

as white crystal (22.4 mg, yield: 29%, dr>99:1), the dr value was determined by crude ^{1}H NMR analysis. Enantiomeric excess was determined by HPLC analysis, *ee* = 84% (Chiralpak column IG, λ = 254 nm, MeOH/*i*-PrOH =90:10, flow rate: 0.5 mL/min, 25 ℃, tr(minor) = 28.05 min, tr(major) = 12.61min). $[\alpha]_D$ = -89.16 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 5.1 Hz, 1H), 7.08 (s, 1H), 6.99 – 6.84 (m, 2H), 6.78 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 7.5 Hz, 1H), 5.37 (d, *J* = 7.1 Hz, 1H), 4.98 (t, *J* = 7.3 Hz, 1H), 3.71 (s, 3H), 3.43 (q, *J* = 10.0 Hz, 1H), 3.13 (q, *J* = 10.2 Hz, 1H), 2.64 (ddd, *J* = 16.7, 10.3, 6.4 Hz, 1H), 2.28 (s, 1H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 186.15 , 169.59 , 142.58 , 140.25 , 135.37 , 129.39 , 128.92 , 128.58 , 127.77 , 127.41 , 126.94 , 126.74 , 126.40 , 66.31 , 64.97 , 55.20 , 43.63 , 35.73 , 33.85 .

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{20}N_4O_2NaS$ $[M+ Na]^+$: 415.1200, found: 415.1199.



6

Following General Procedure, A dried 25 mL Schlenk tube was charged with chiral catalyst Fe-BPsalan (5.0 mol%) and silver salt (5.0 mol% $AgSbF_6$) in the glove box. Then the tube was purged with argon and anhydrous DCE (2 mL) was added. Stir at room temperature for 30 minutes. *α,β*-unsaturated 1-acylimidazoles (41.85 mg, 0.20 mmol) was add continue stirring at room temperature for 30 minutes, finally N,N'-cyclic azomethine imines 3a (43.25 mg, 0.24 mmol) was added. The reaction mixture was stirred at room temperature for indicated time (monitored by TLC) under argon.The mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 1:1, basified with 1.0% Et_3N) to afford chiral product 6 as a white foamed solid (57.2 mg, yield: 75%). m.p. 181-183 ^oC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 4.8 Hz, 1H), 7.63–7.43 (m, 4H), 7.33 (t, J = 7.6 Hz, 2H), 7.28 (s, 1H), 7.23 (d, J = 8.1 Hz, 1H), 7.13–7.04 (m, 3H), 7.02–6.93 (m, 2H), 5.94 (d, J = 6.4 Hz, 1H), 5.16 (t, J = 7.2 Hz, 1H), 4.96 (s, 1H), 3.35–3.19 (m, 1H), 3.08–2.95 (m, 1H), 2.61–2.42 (m, 1H), 2.30–2.11 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.06, 168.97, 152.70, 148.56, 140.54, 136.68, 134.19, 129.34, 128.89, 128.59, 128.38, 127.67, 127.13, 126.30, 122.28, 69.74, 65.28, 56.39, 44.73, 34.21.

HRMS (ESI, m/z) calcd for $C_{24}H_{21}N_3O_2Na$ $[M+Na]^+$: 406.1526, found: 406.1522.

HPLC: Chiralpak column AD-H, λ = 254 nm, heptane/isopropanol 70:30; flow rate=0.7 ml/min; detection. t_r (major) = 13.09 min; t_r (minor) = 21.14 min (ee = 76%).

$[\alpha]_D^{27}$ = -114.1 (c = 0.1425, $CHCl_3$)

5. ^{1}H NMR and ^{13}C NMR Spectra

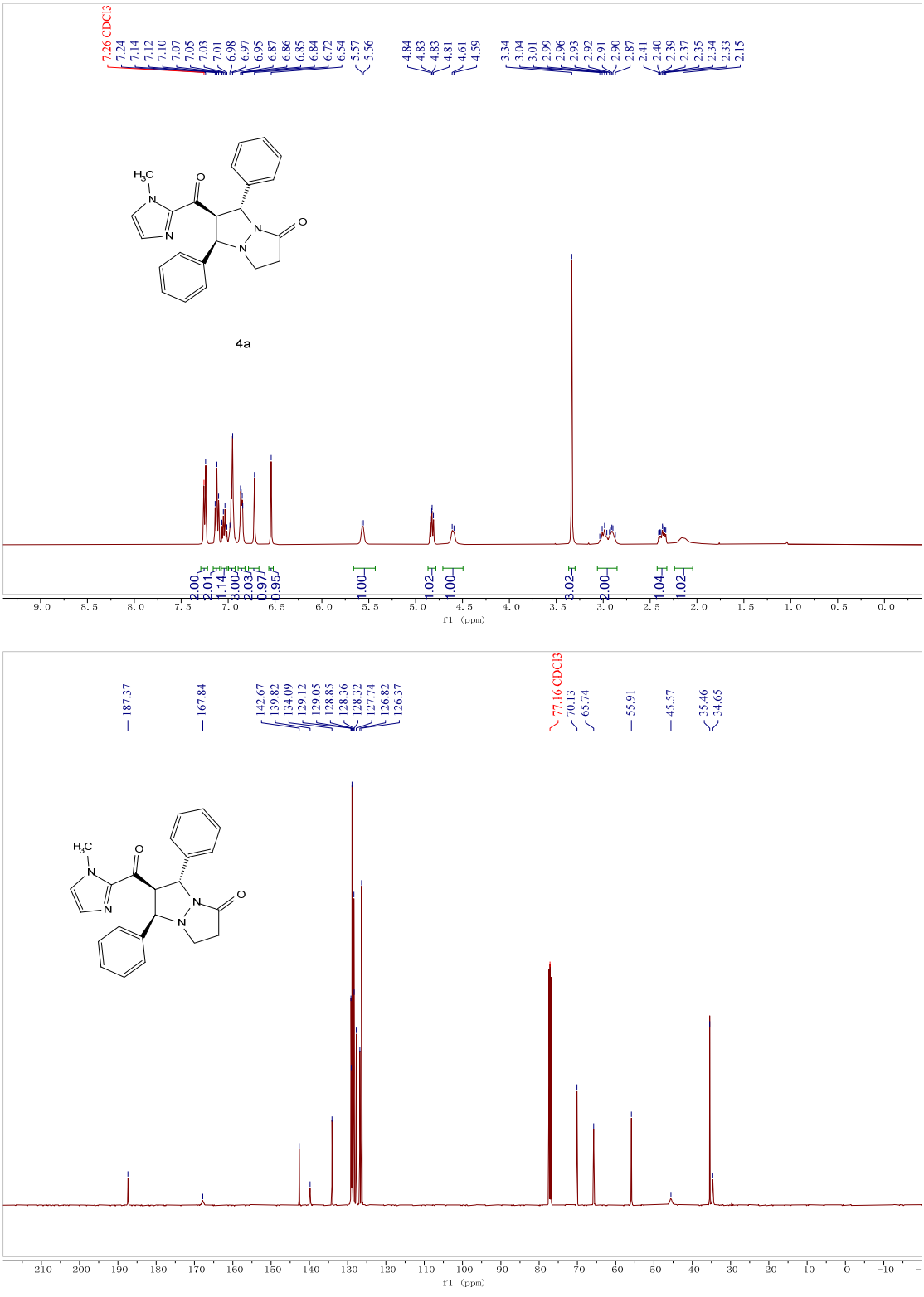


Figure S1. ^{1}H and ^{13}C NMR spectrum of **4a**.

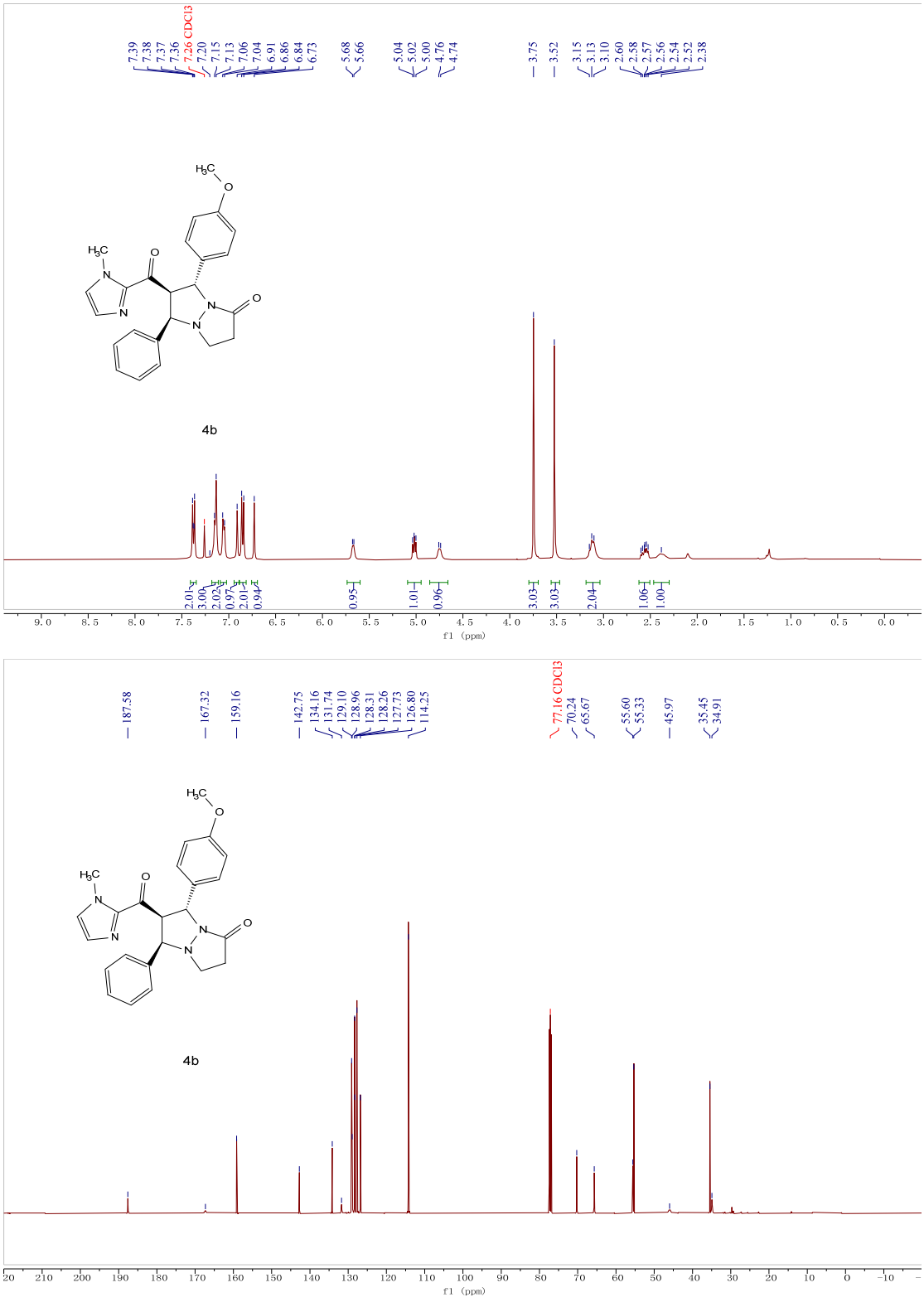


Figure S2. ^{1}H and ^{13}C NMR spectrum of **4b**.

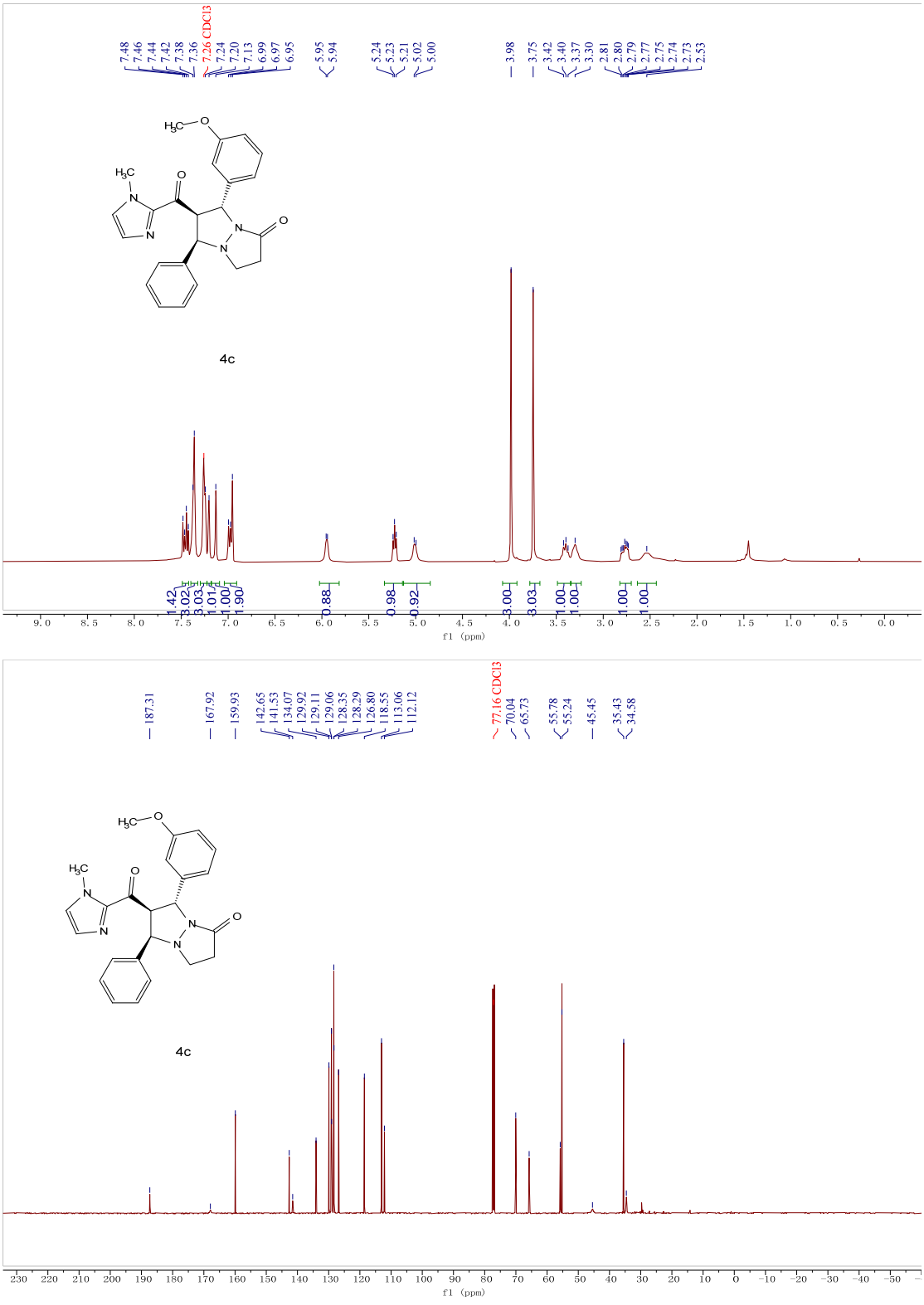


Figure S3. ^{1}H and ^{13}C NMR spectrum of **4c**.

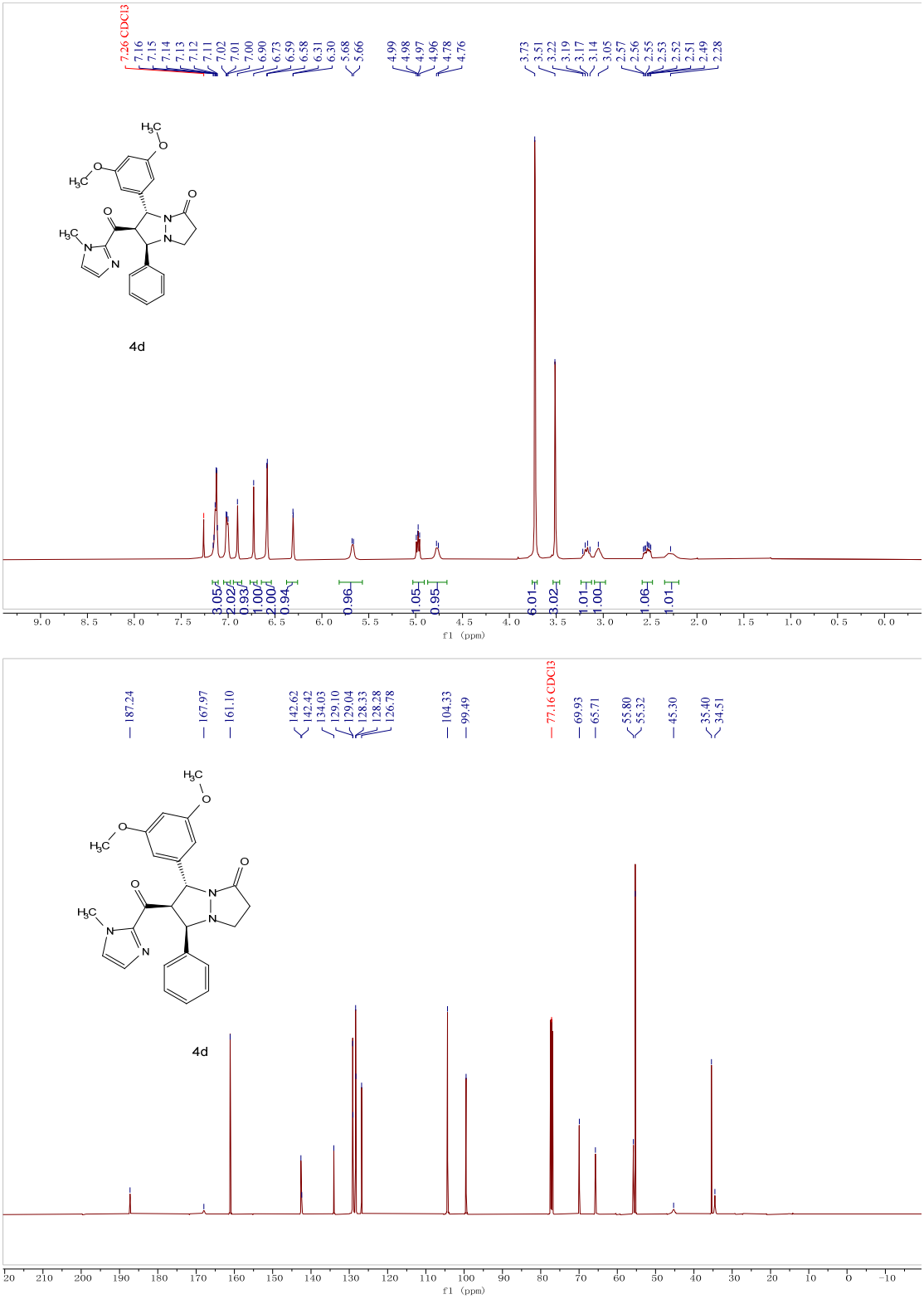


Figure S4. ^{1}H and ^{13}C NMR spectrum of **4d**.

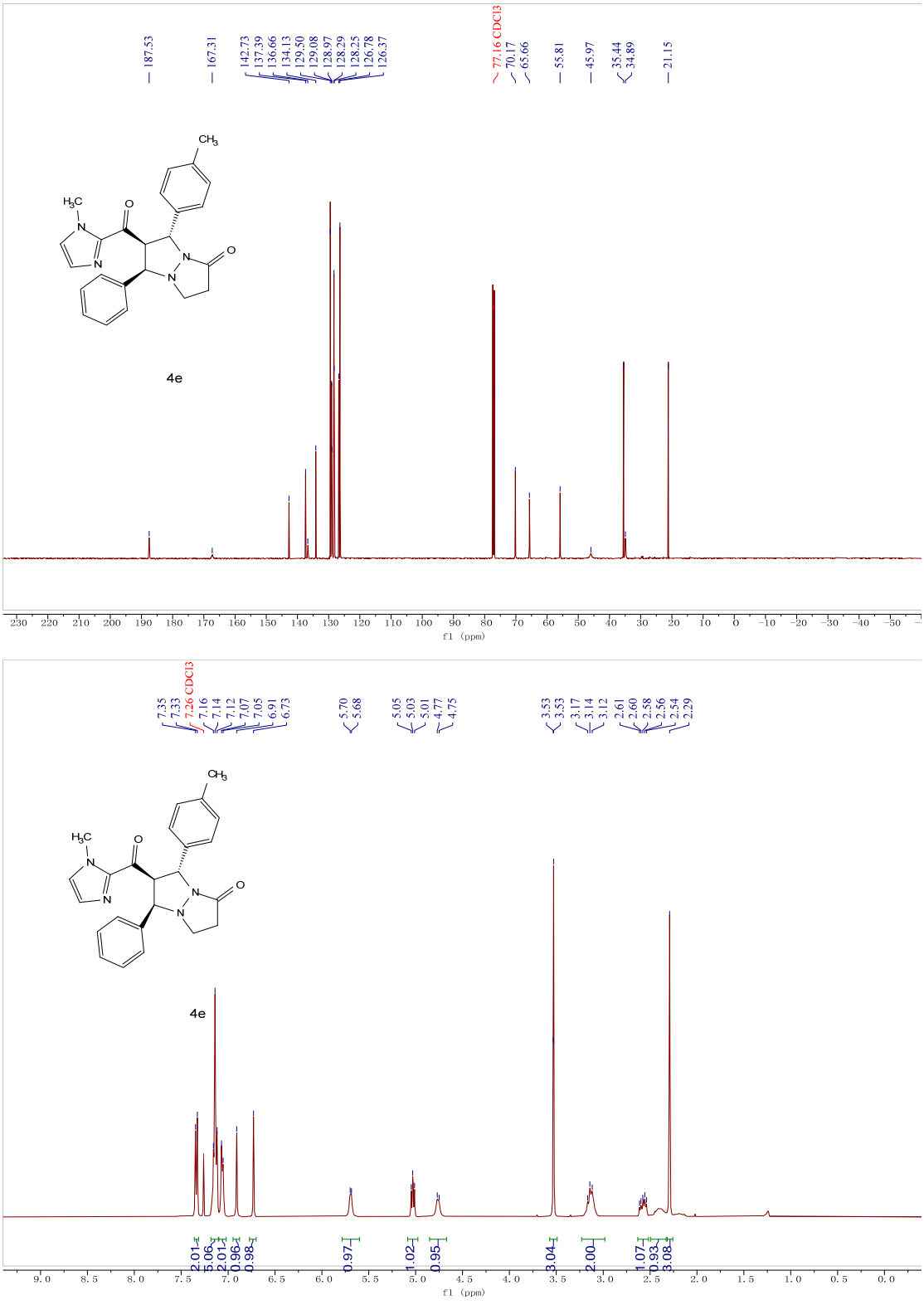


Figure S5. ^{1}H and ^{13}C NMR spectrum of **4e**.

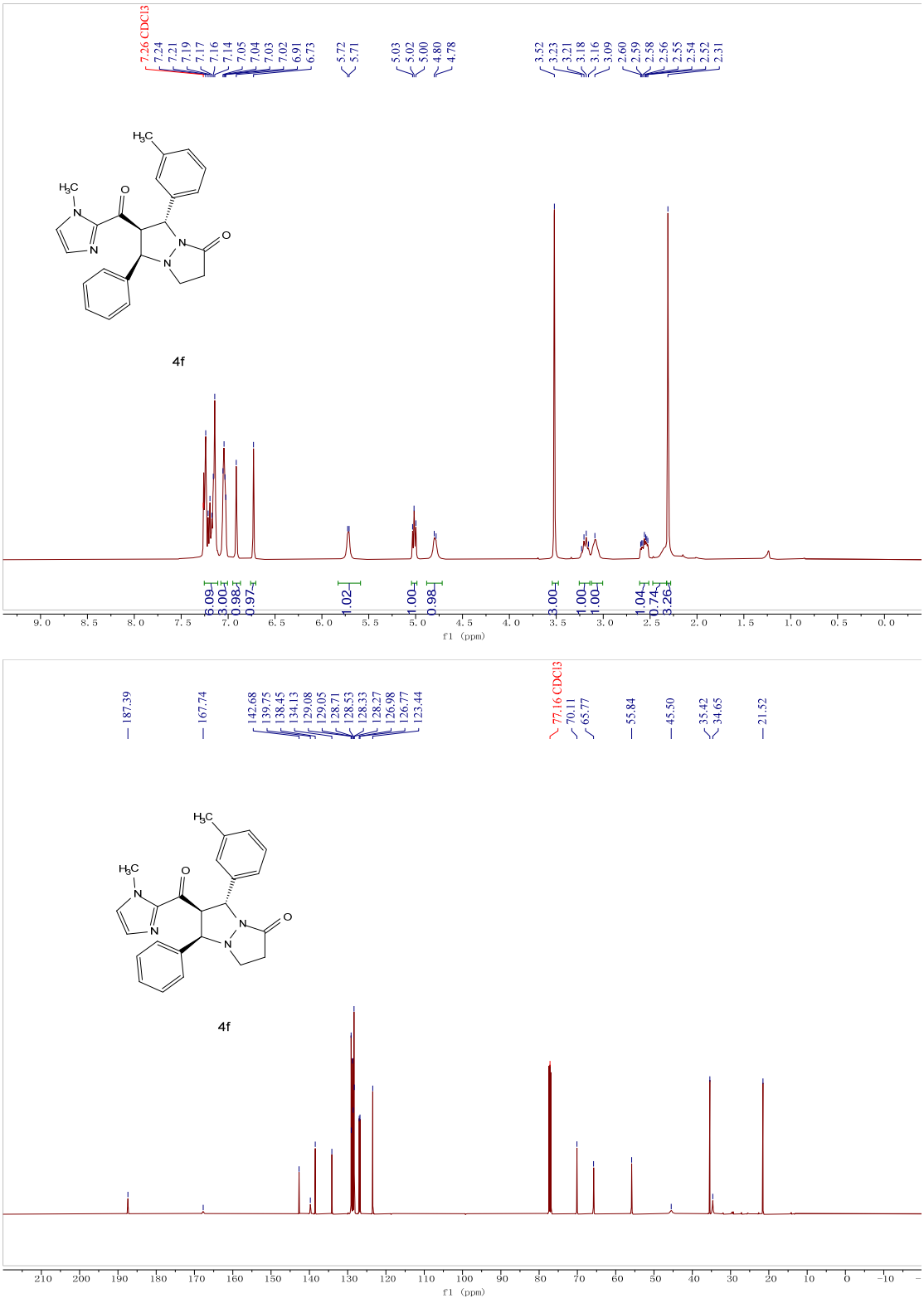


Figure S6. ^{1}H and ^{13}C NMR spectrum of **4f**.

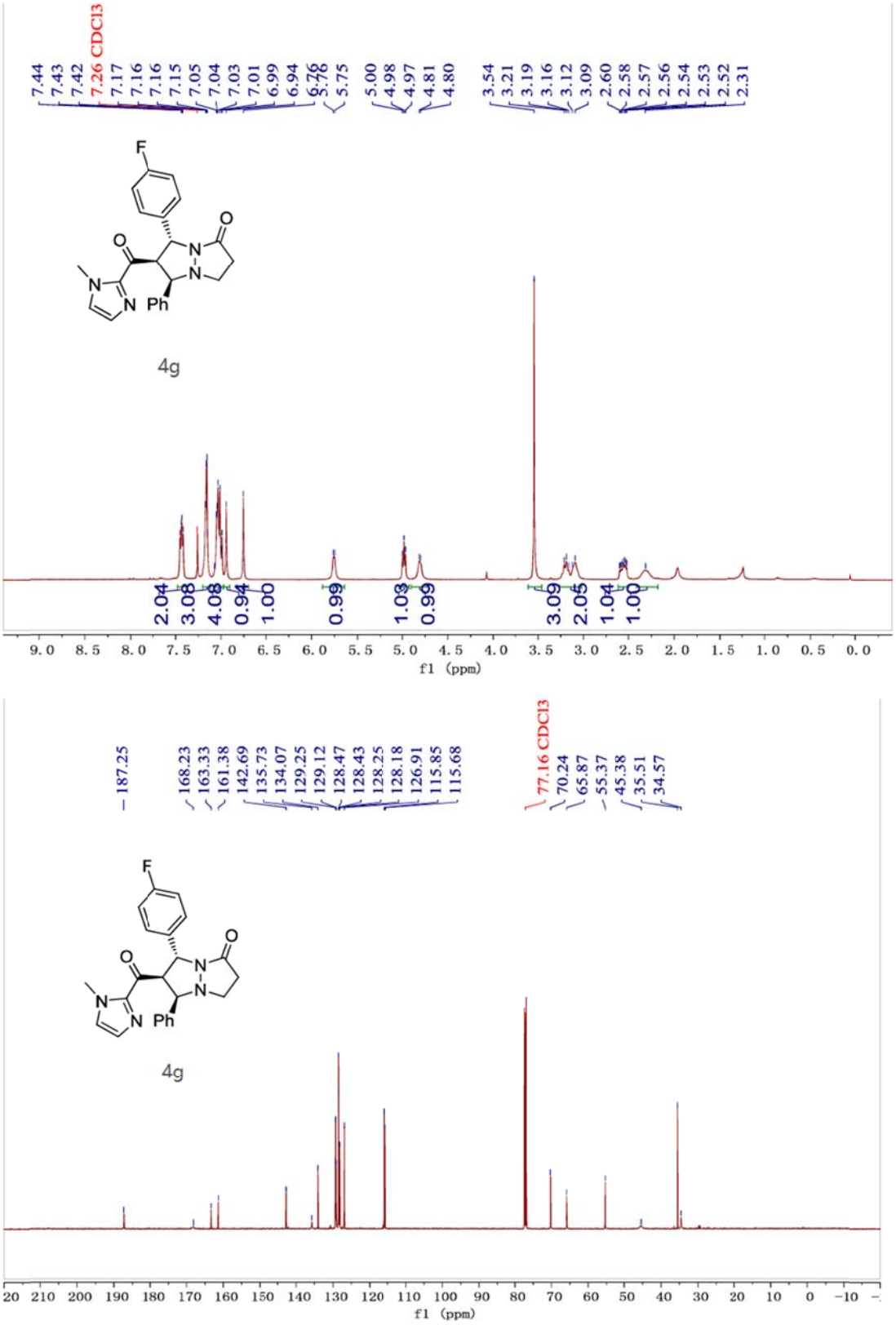


Figure S7. ^{1}H and ^{13}C NMR spectrum of **4g**.

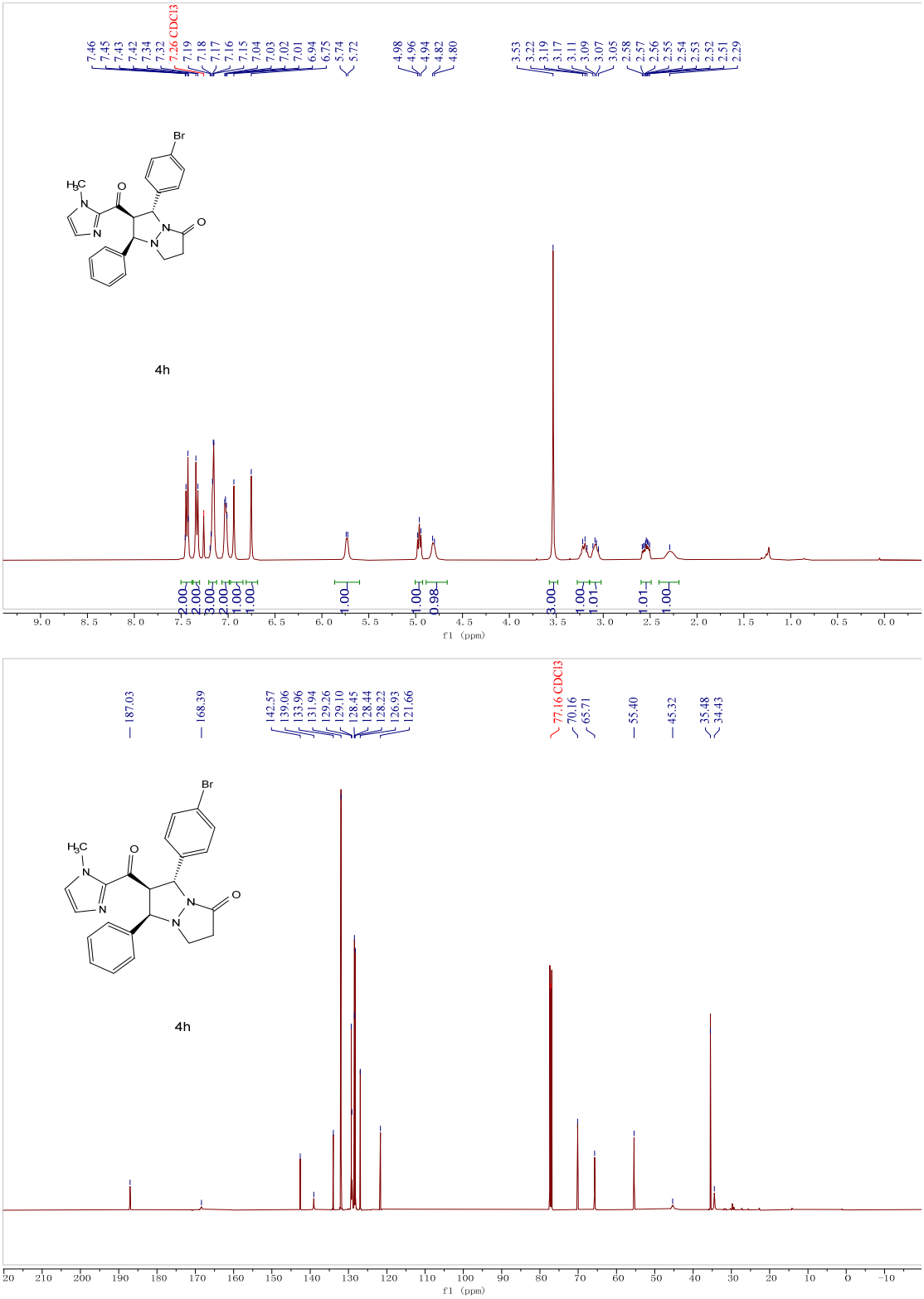


Figure S8. ^{1}H and ^{13}C NMR spectrum of **4h**.

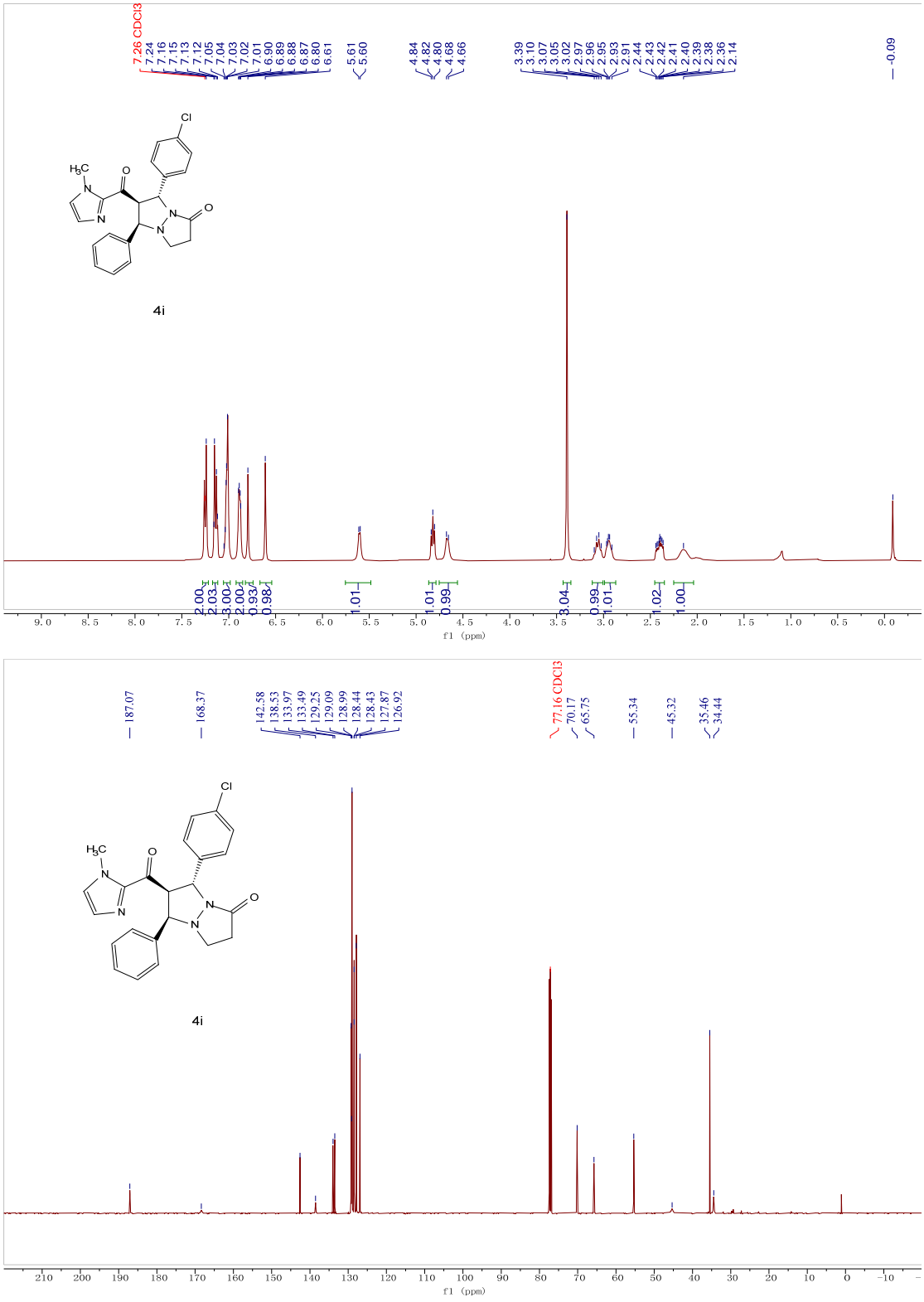


Figure S9. ^{1}H and ^{13}C NMR spectrum of **4i**.

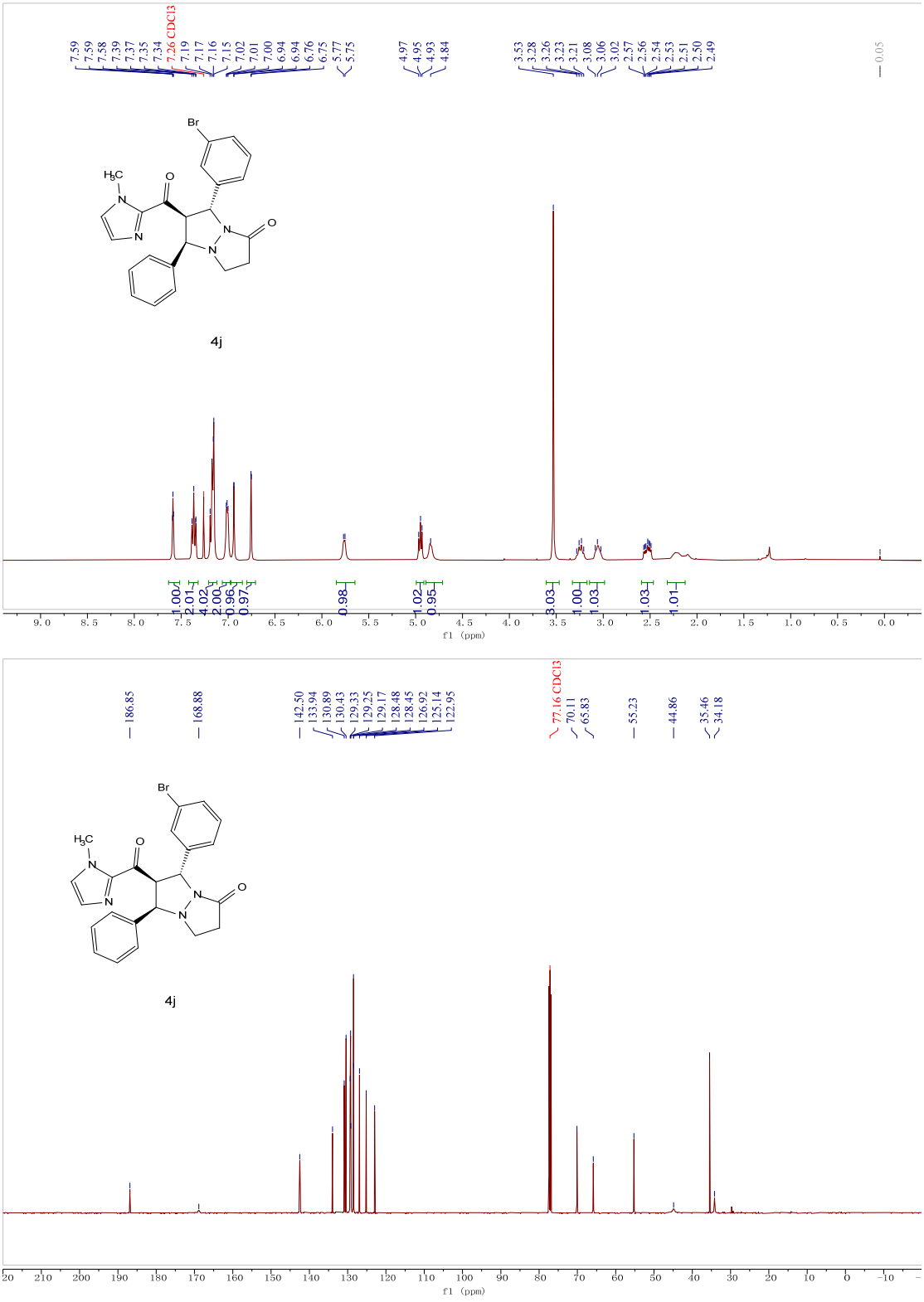


Figure S10. ^{1}H and ^{13}C NMR spectrum of **4j**.

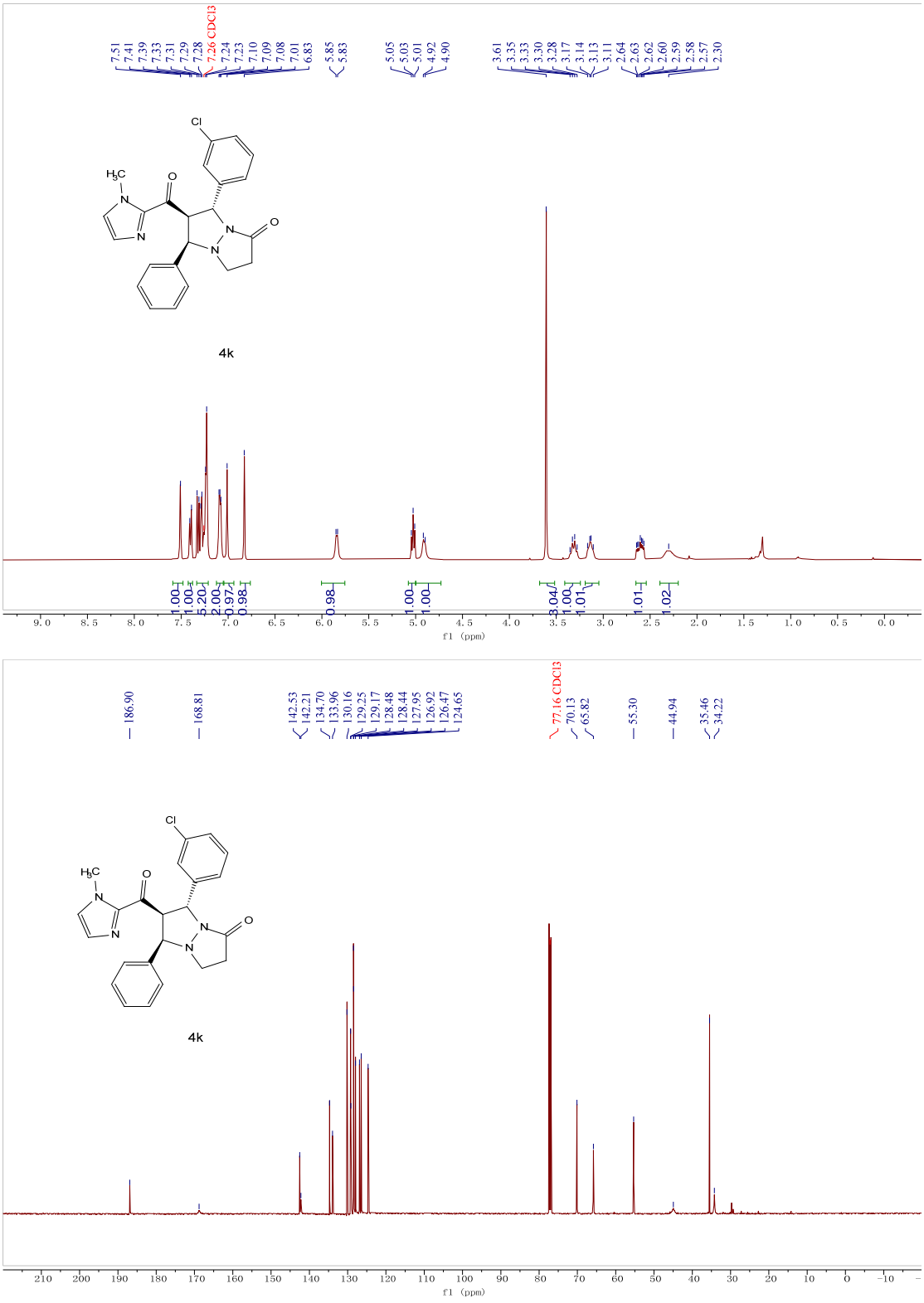


Figure S11. ^{1}H and ^{13}C NMR spectrum of **4k**.

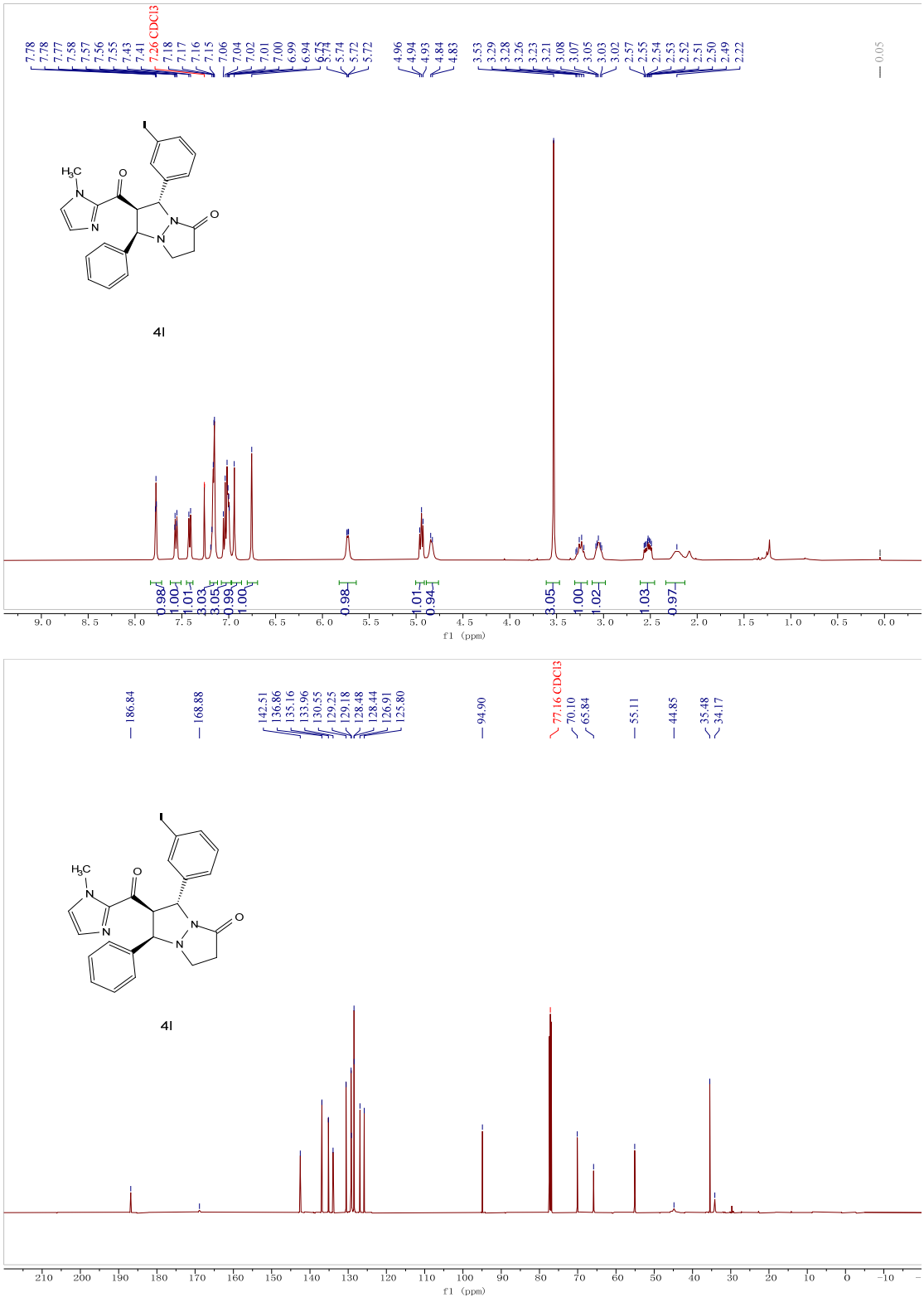


Figure S12. ^{1}H and ^{13}C NMR spectrum of **4l**.

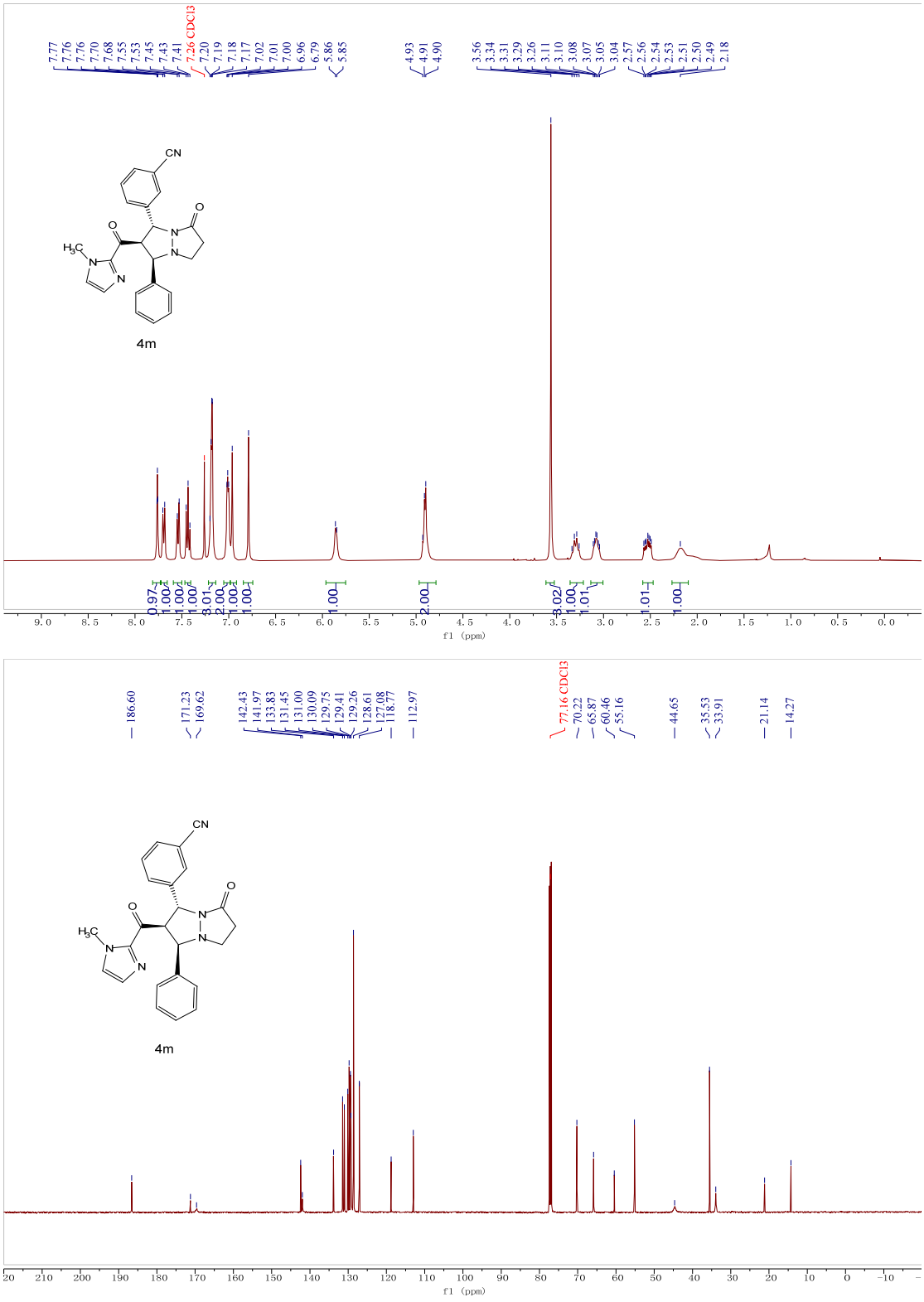


Figure S13. ^{1}H and ^{13}C NMR spectrum of **4m**.

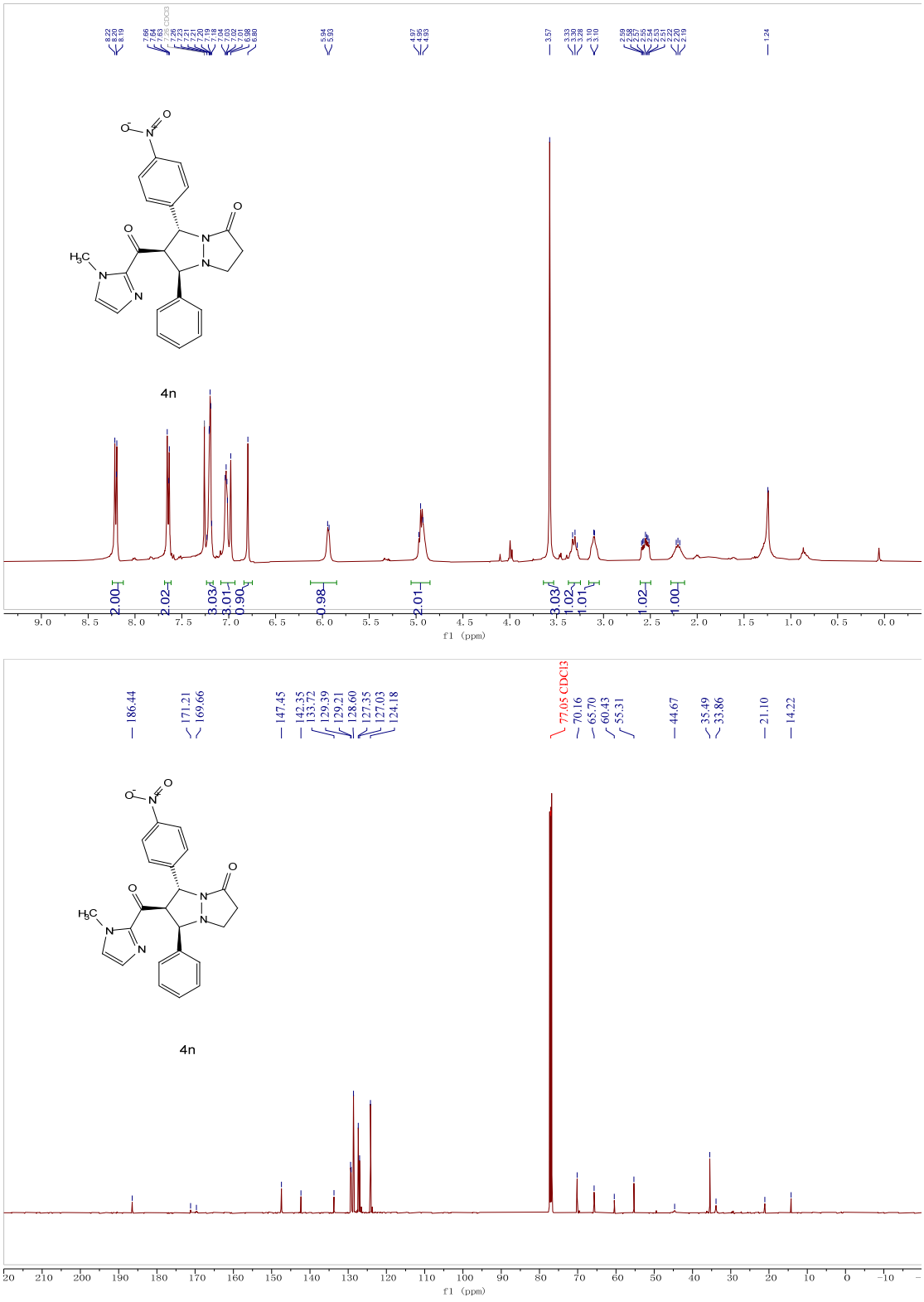


Figure S14. ^{1}H and ^{13}C NMR spectrum of **4n**.

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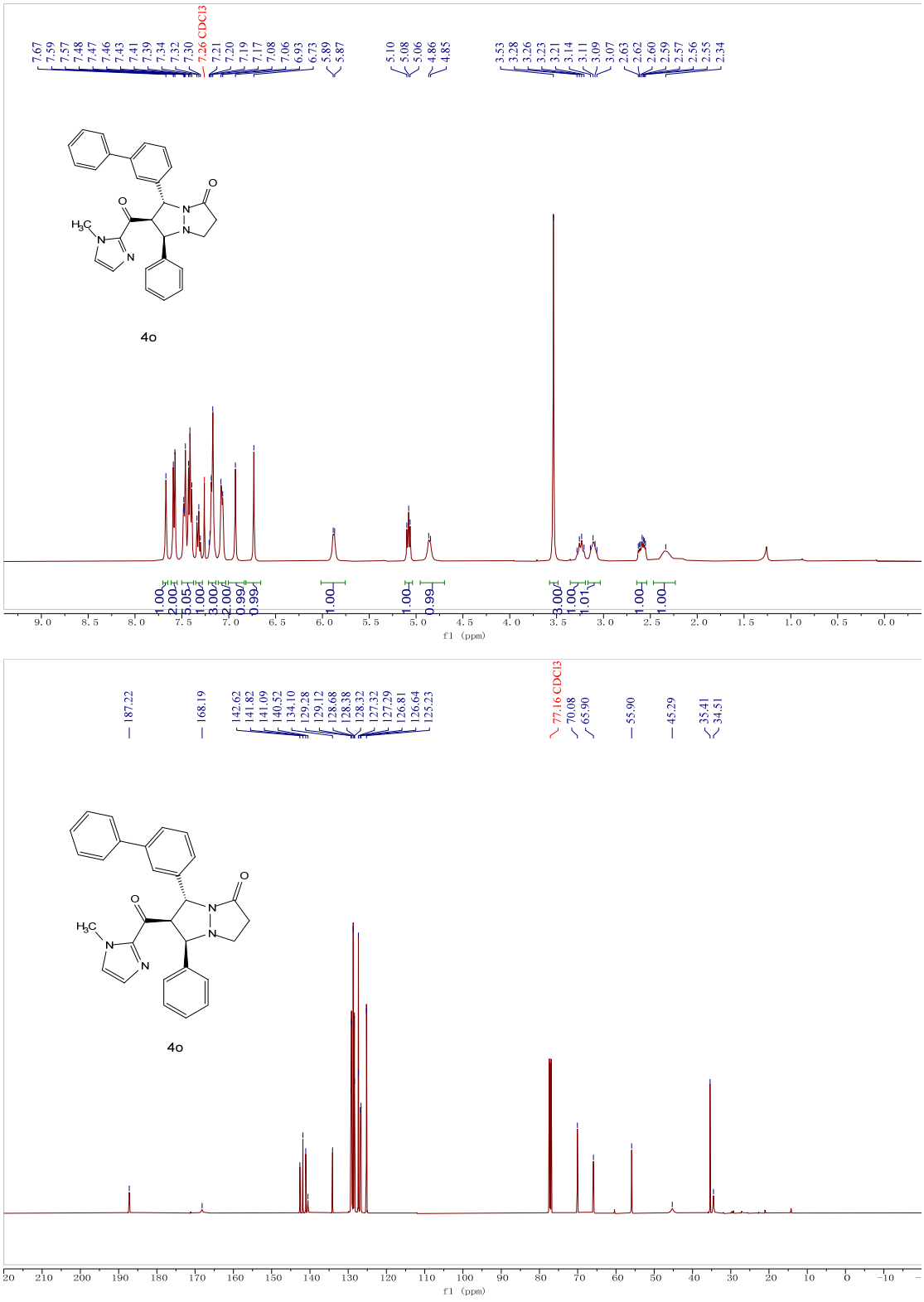

Figure S15. ^{1}H and ^{13}C NMR spectrum of **4o**.

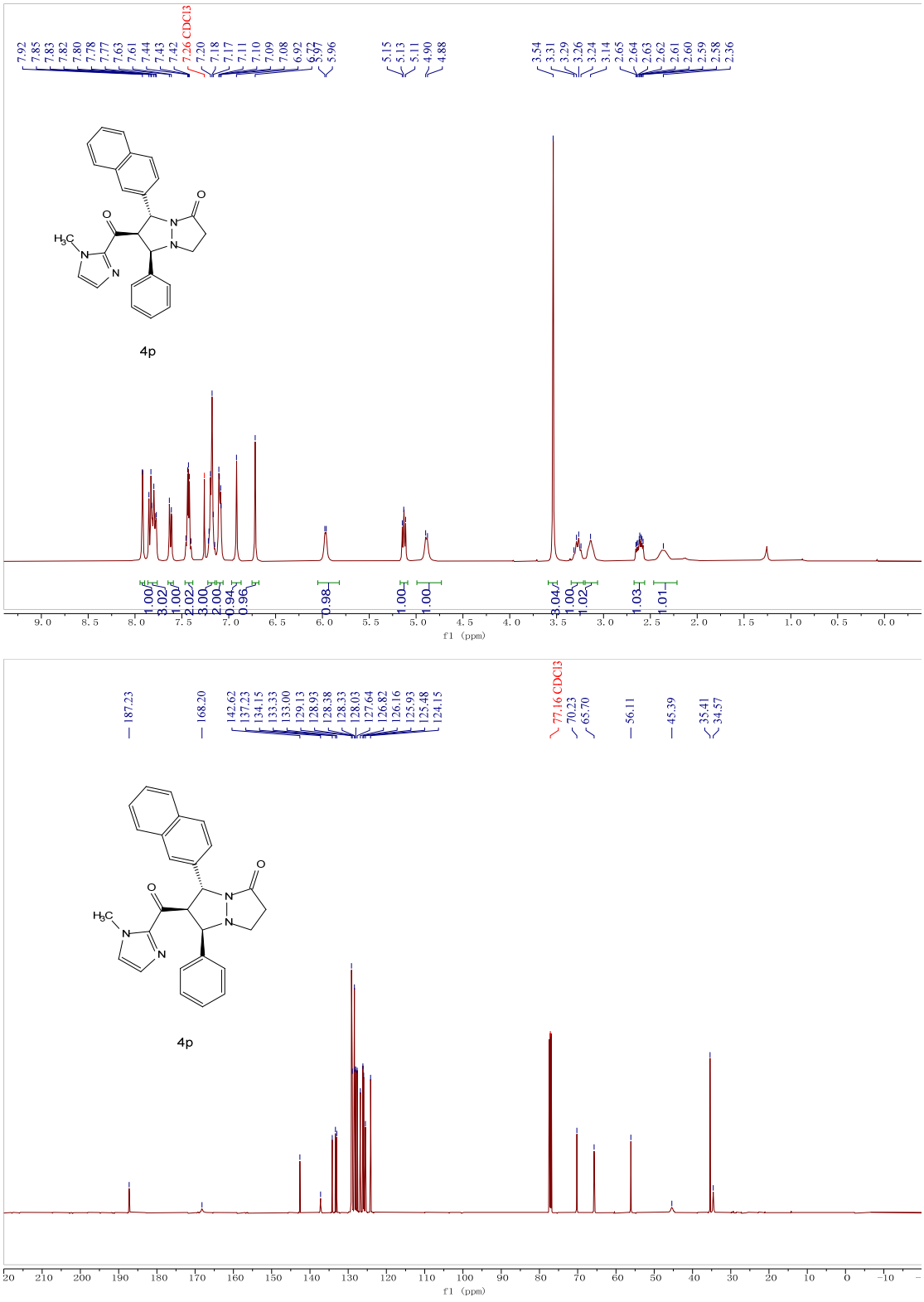

Figure S16. ^{1}H and ^{13}C NMR spectrum of **4p**.

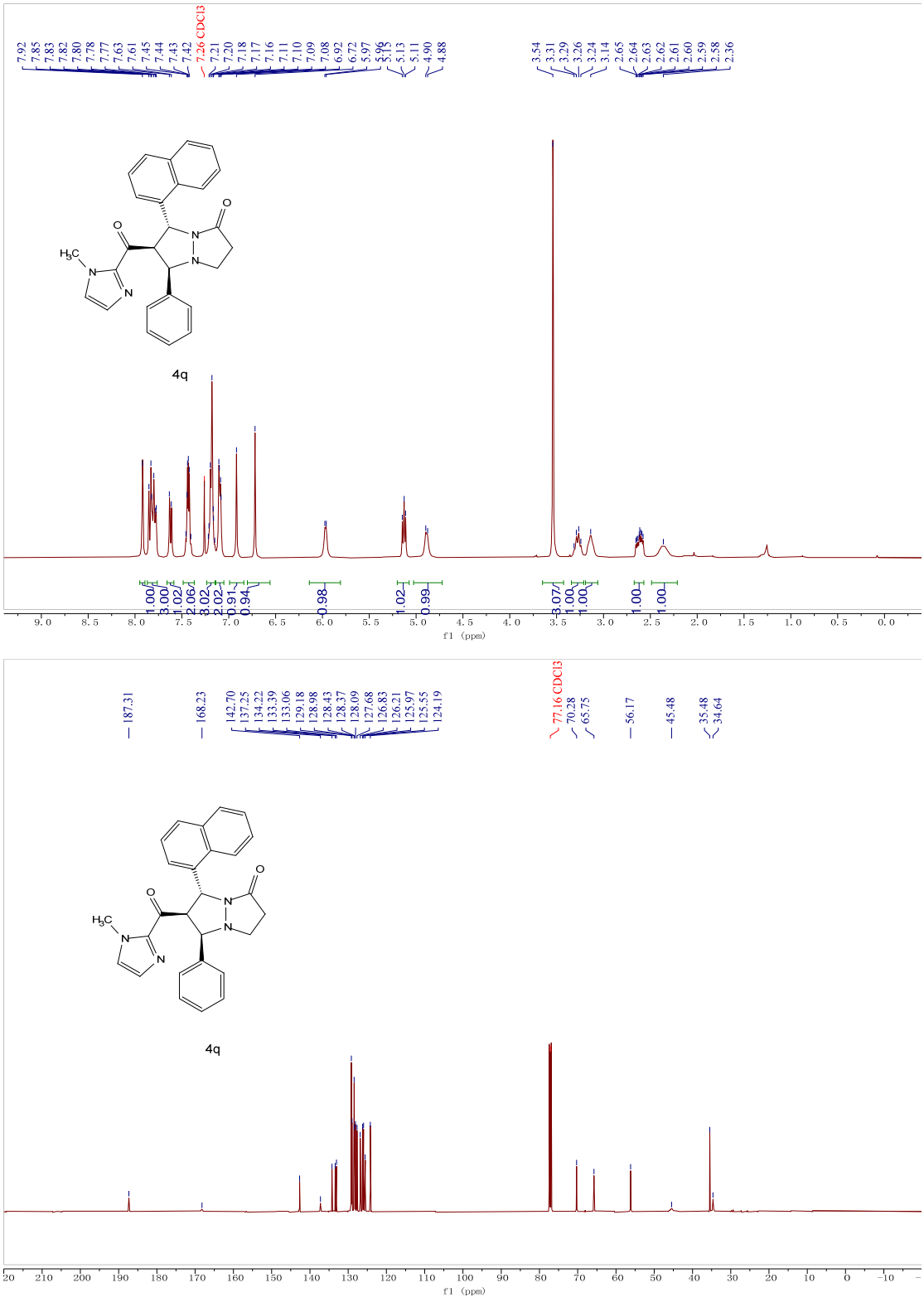

Figure S17. ^{1}H and ^{13}C NMR spectrum of **4q**.

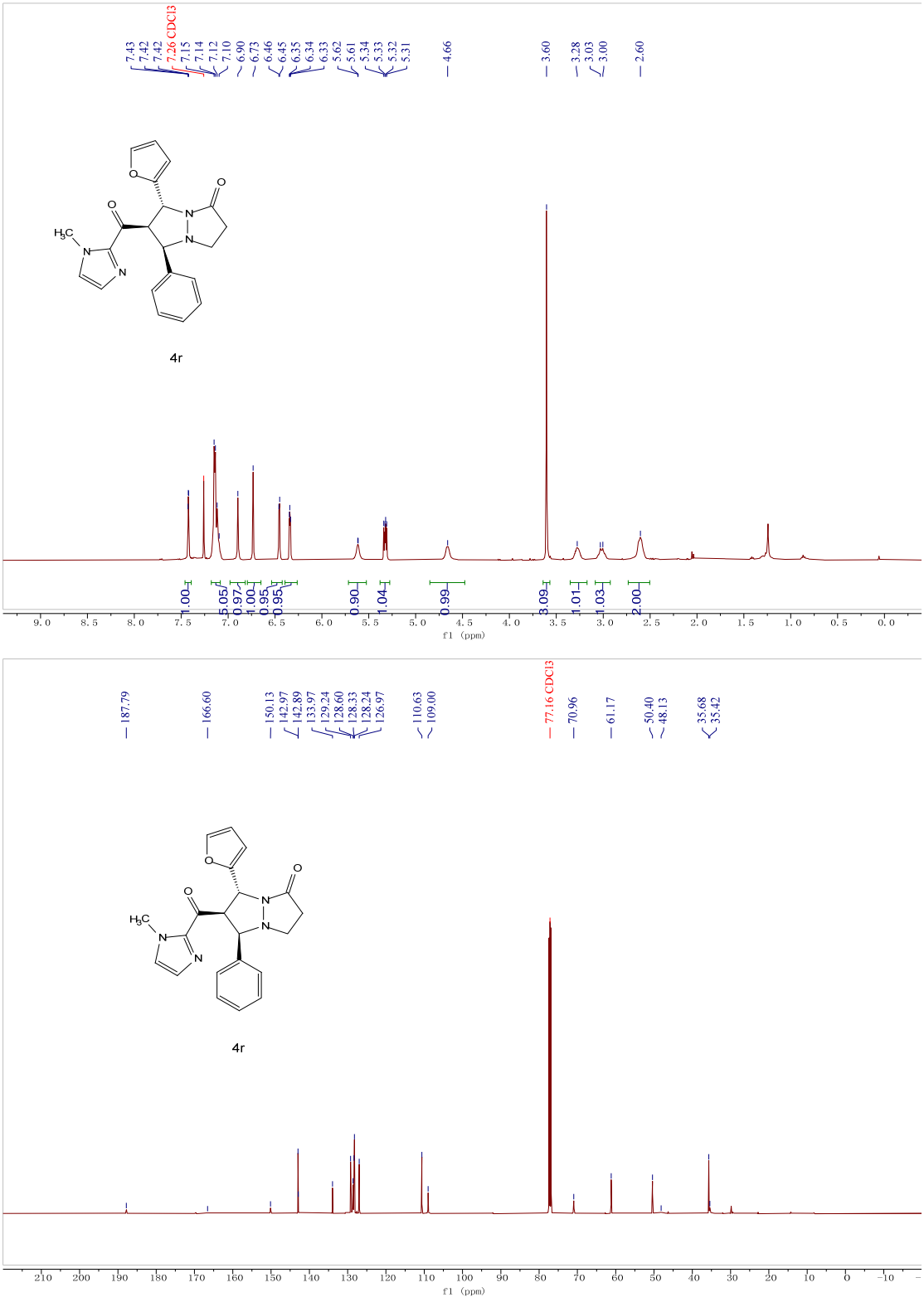

Figure S18. ^{1}H and ^{13}C NMR spectrum of **4r**.

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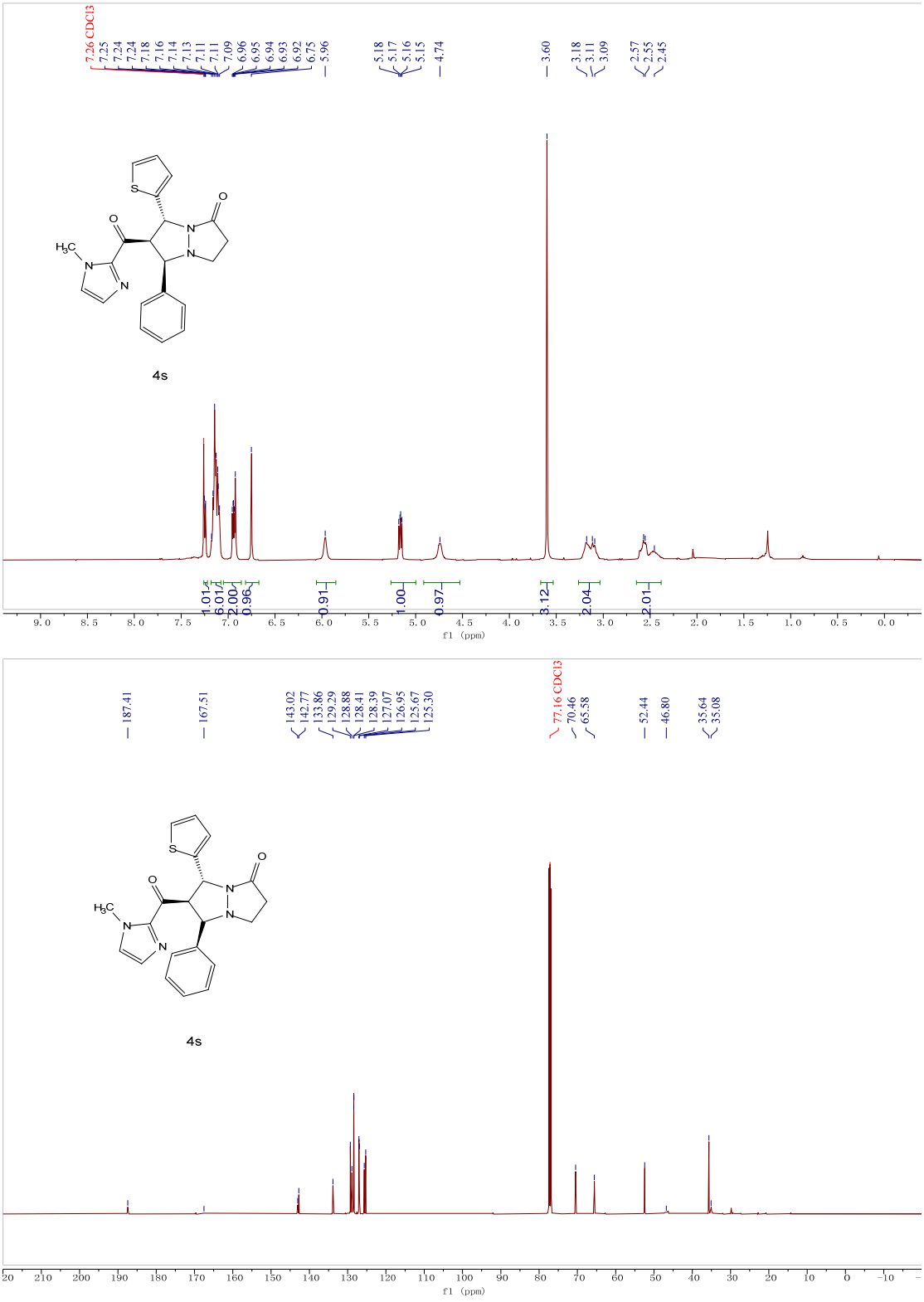

Figure S19. ^{1}H and ^{13}C NMR spectrum of **4s**.

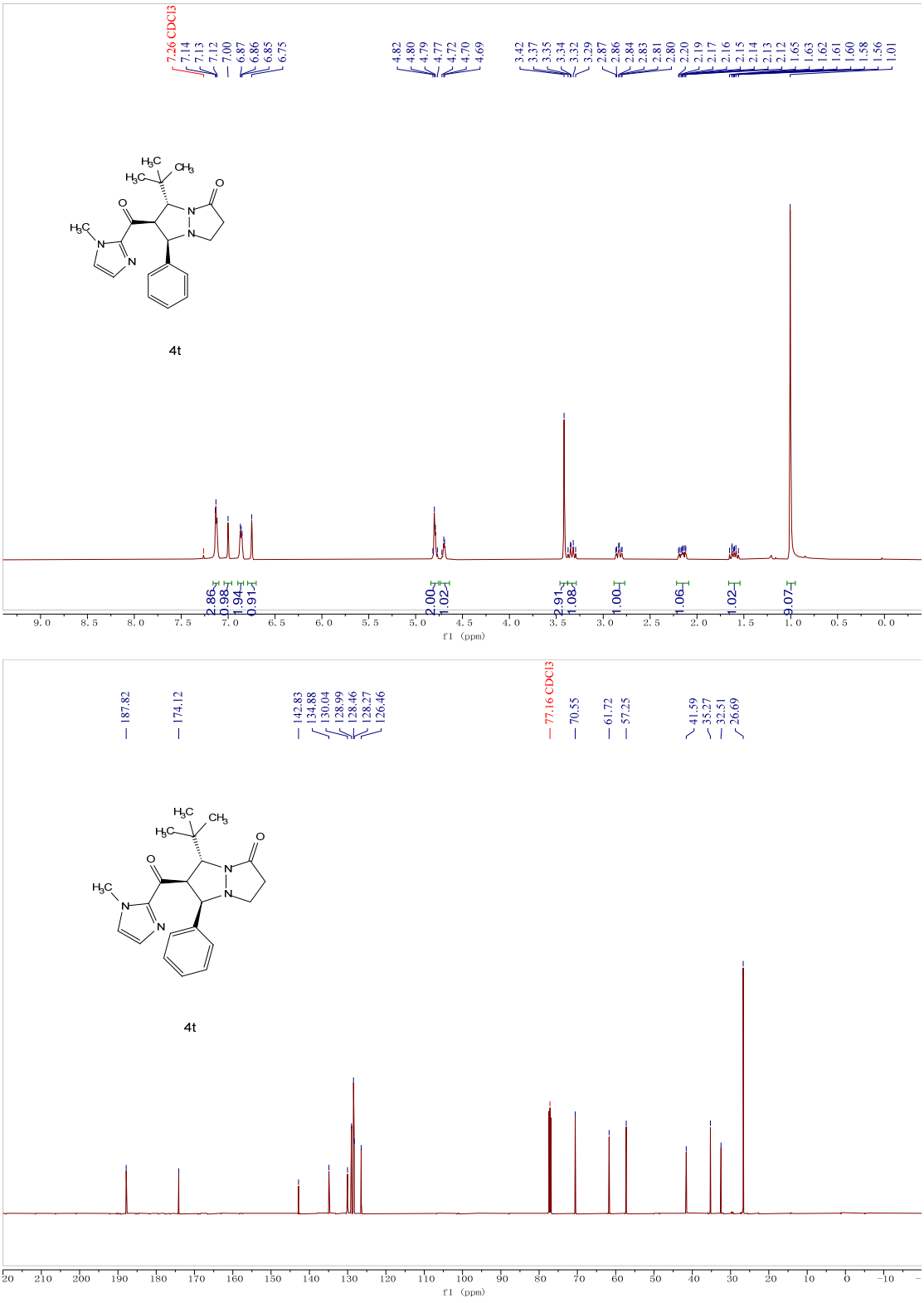

Figure S20. ^{1}H and ^{13}C NMR spectrum of **4t**.

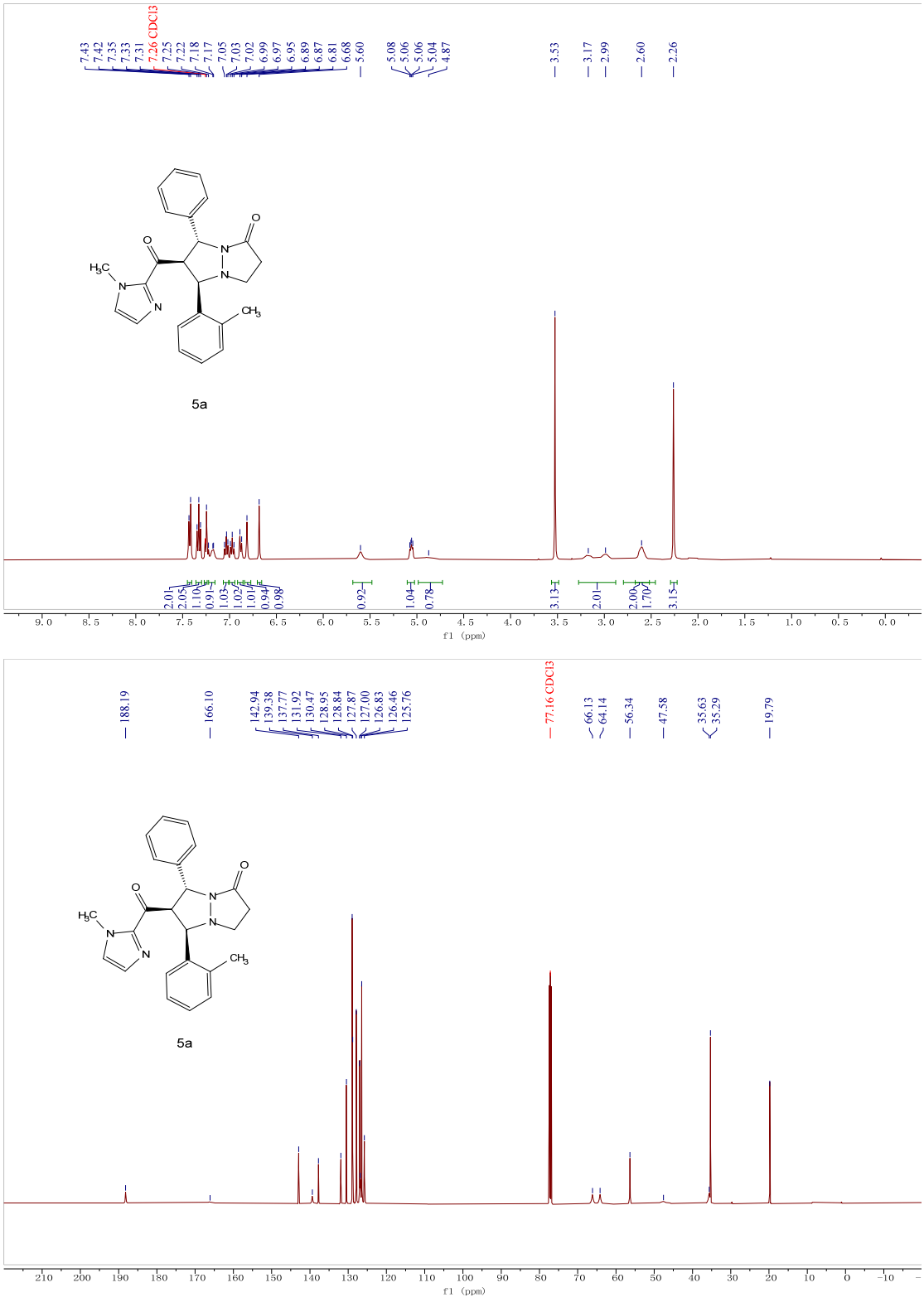

Figure S21. ^{1}H and ^{13}C NMR spectrum of **5a**.

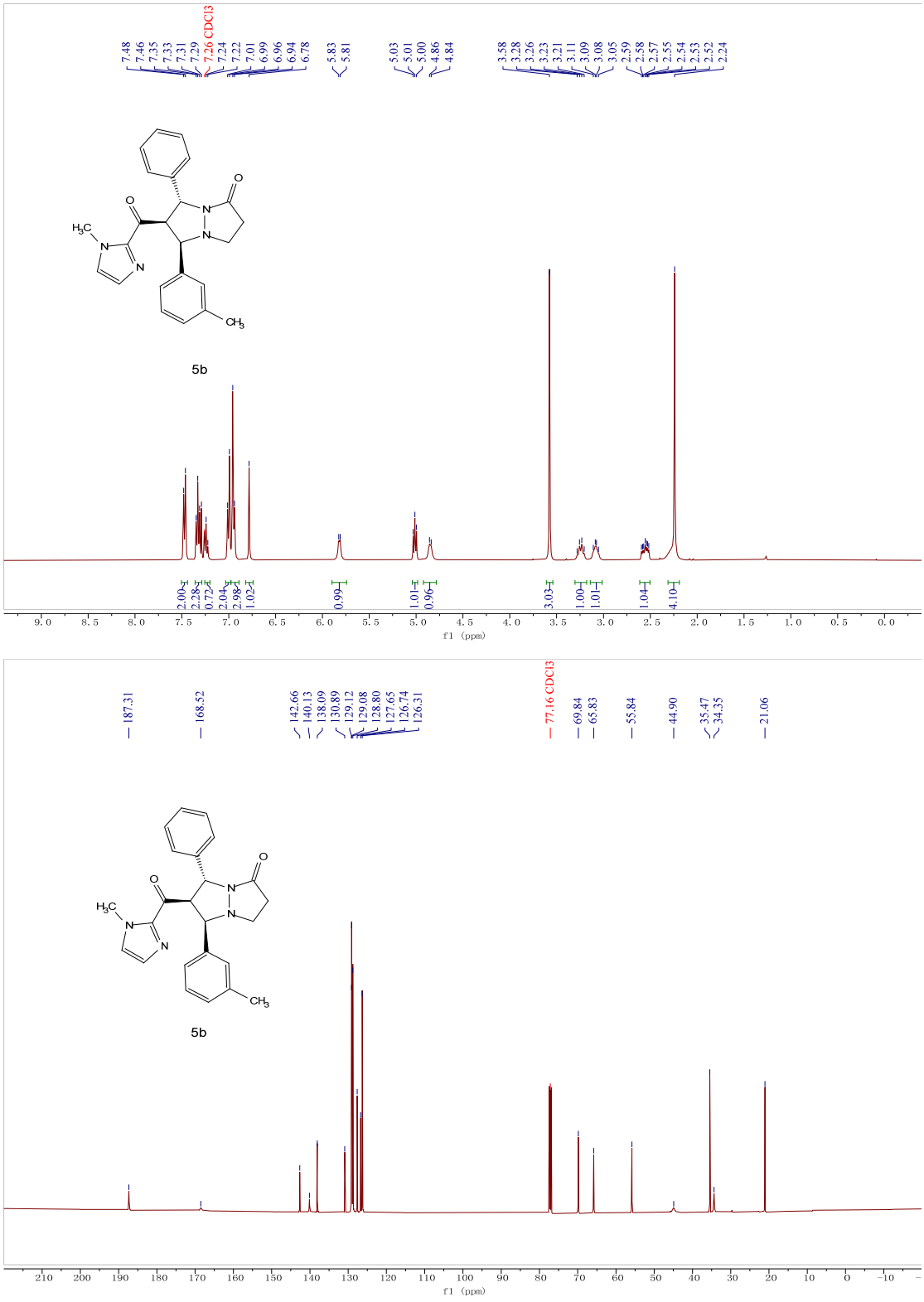

Figure S22. ^{1}H and ^{13}C NMR spectrum of **5b**.

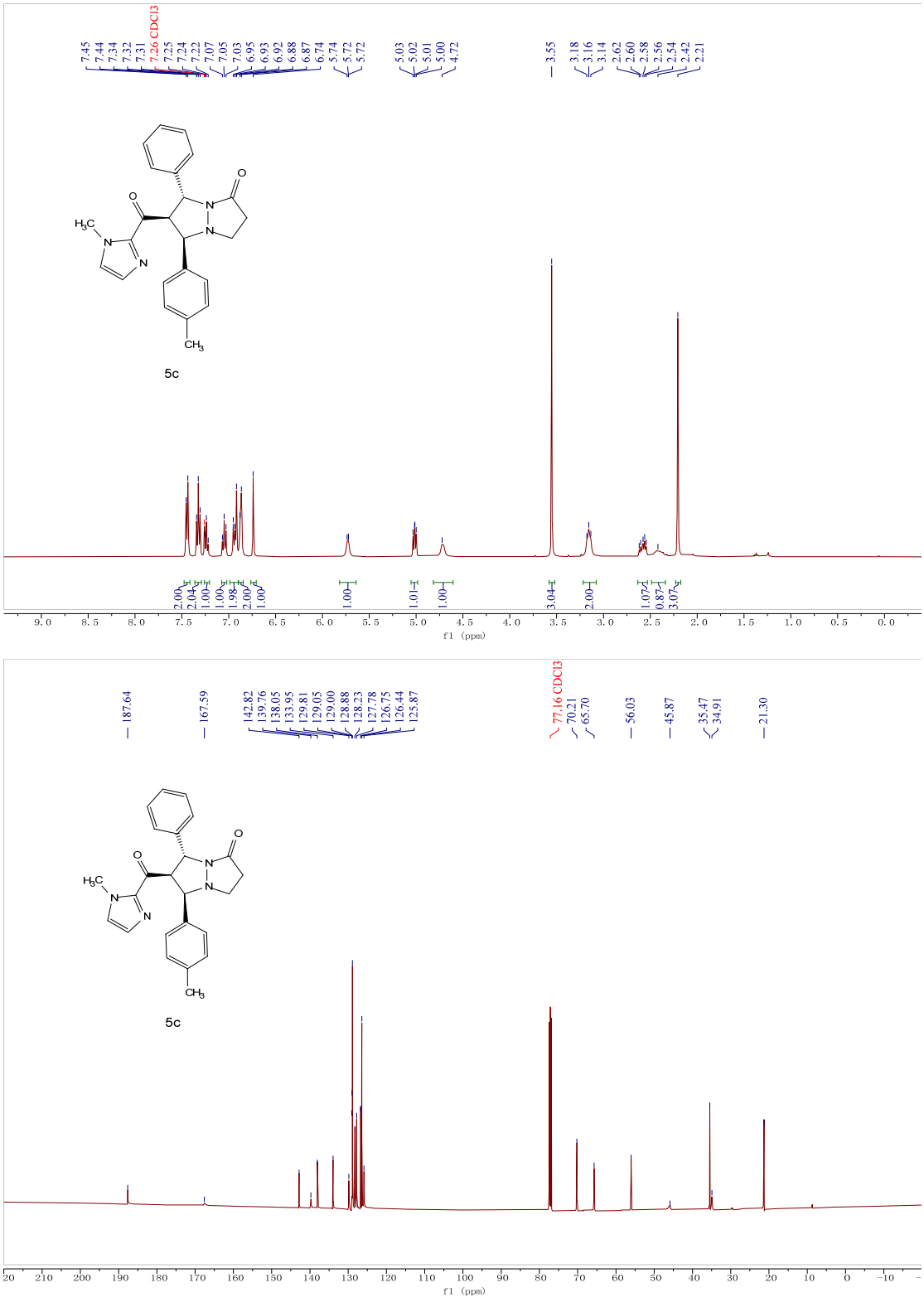

Figure S23. ^{1}H and ^{13}C NMR spectrum of **5c**.

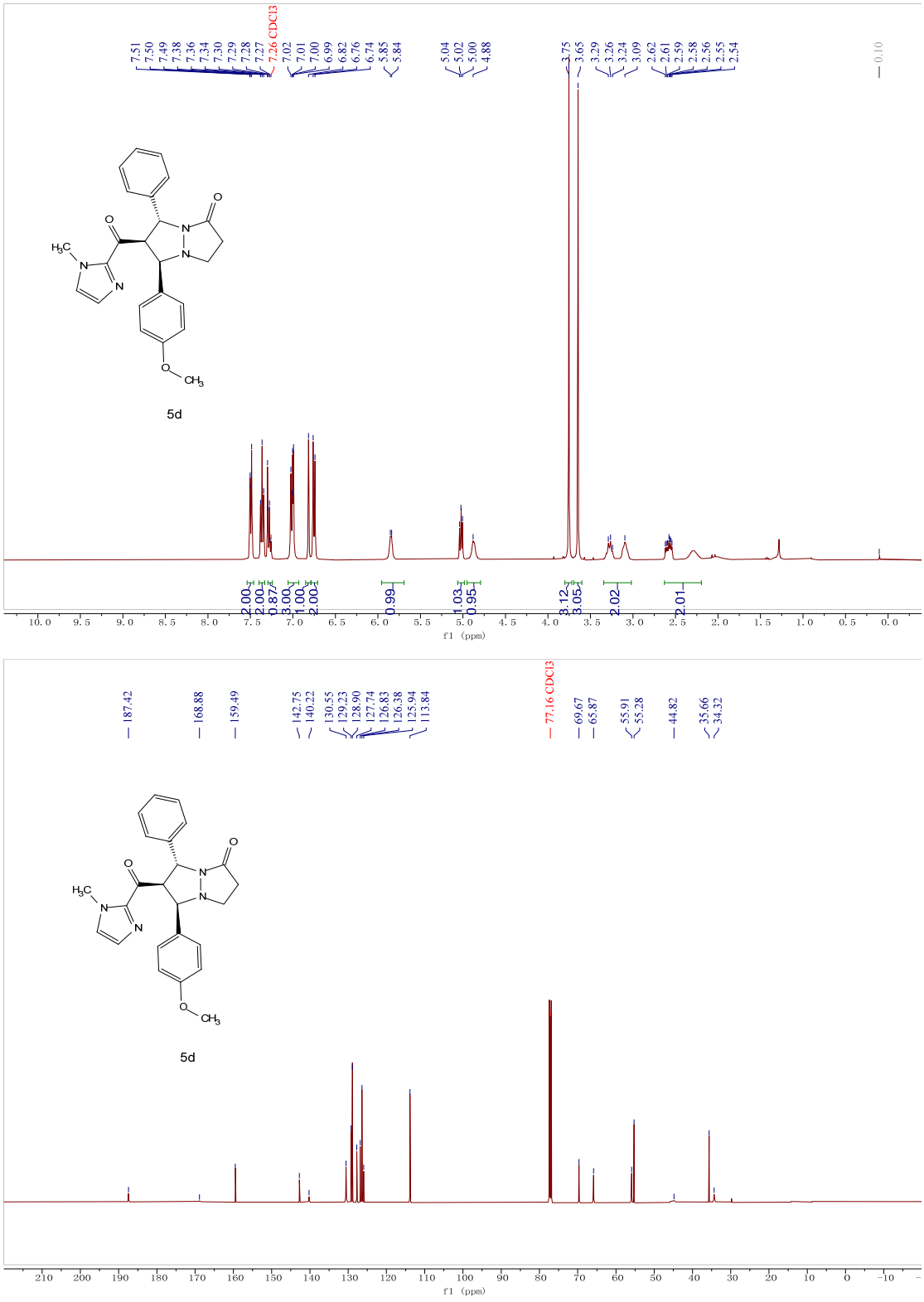

Figure S24. ^{1}H and ^{13}C NMR spectrum of 5**d**.

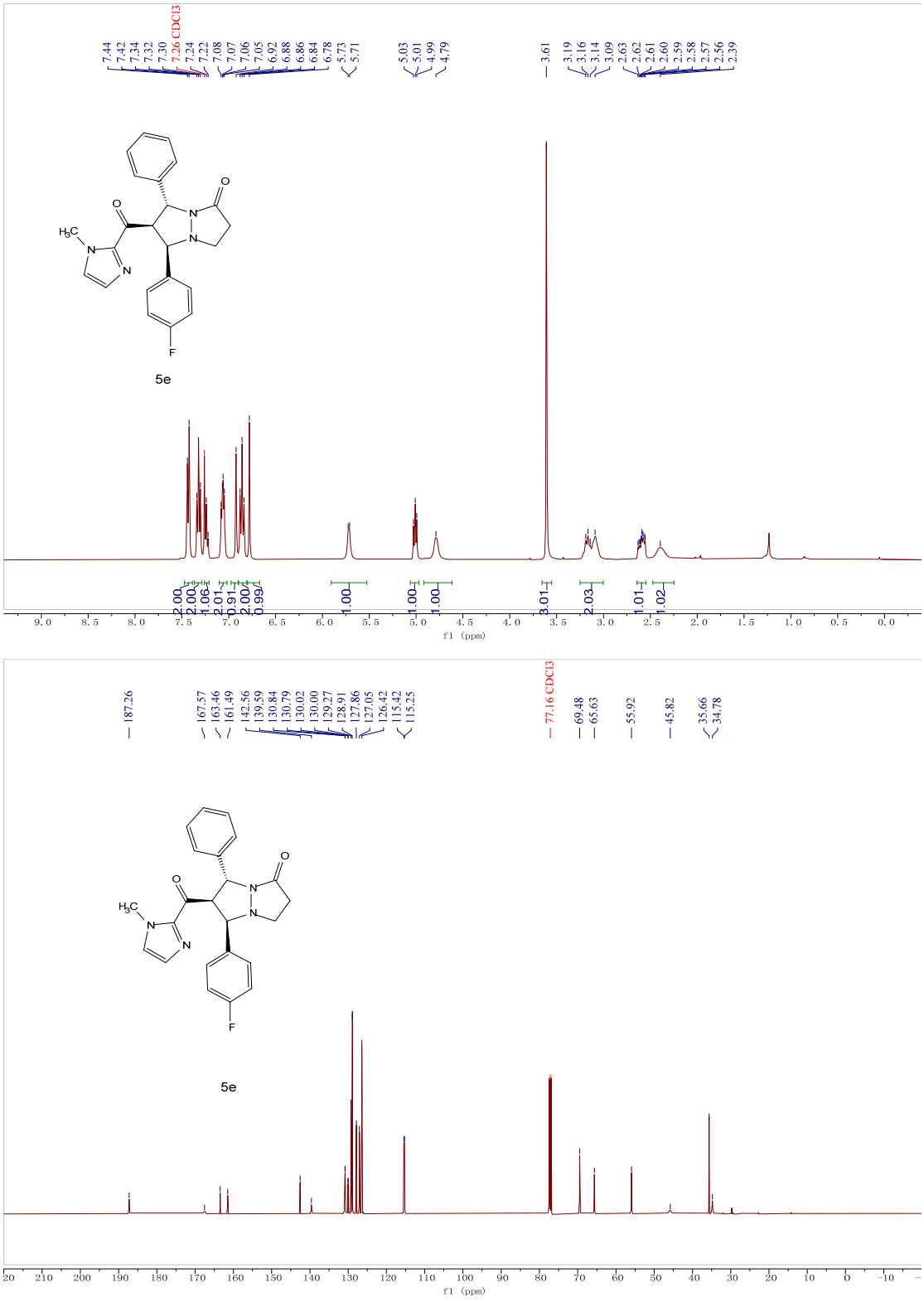

Figure S25. ^{1}H and ^{13}C NMR spectrum of **5e**.

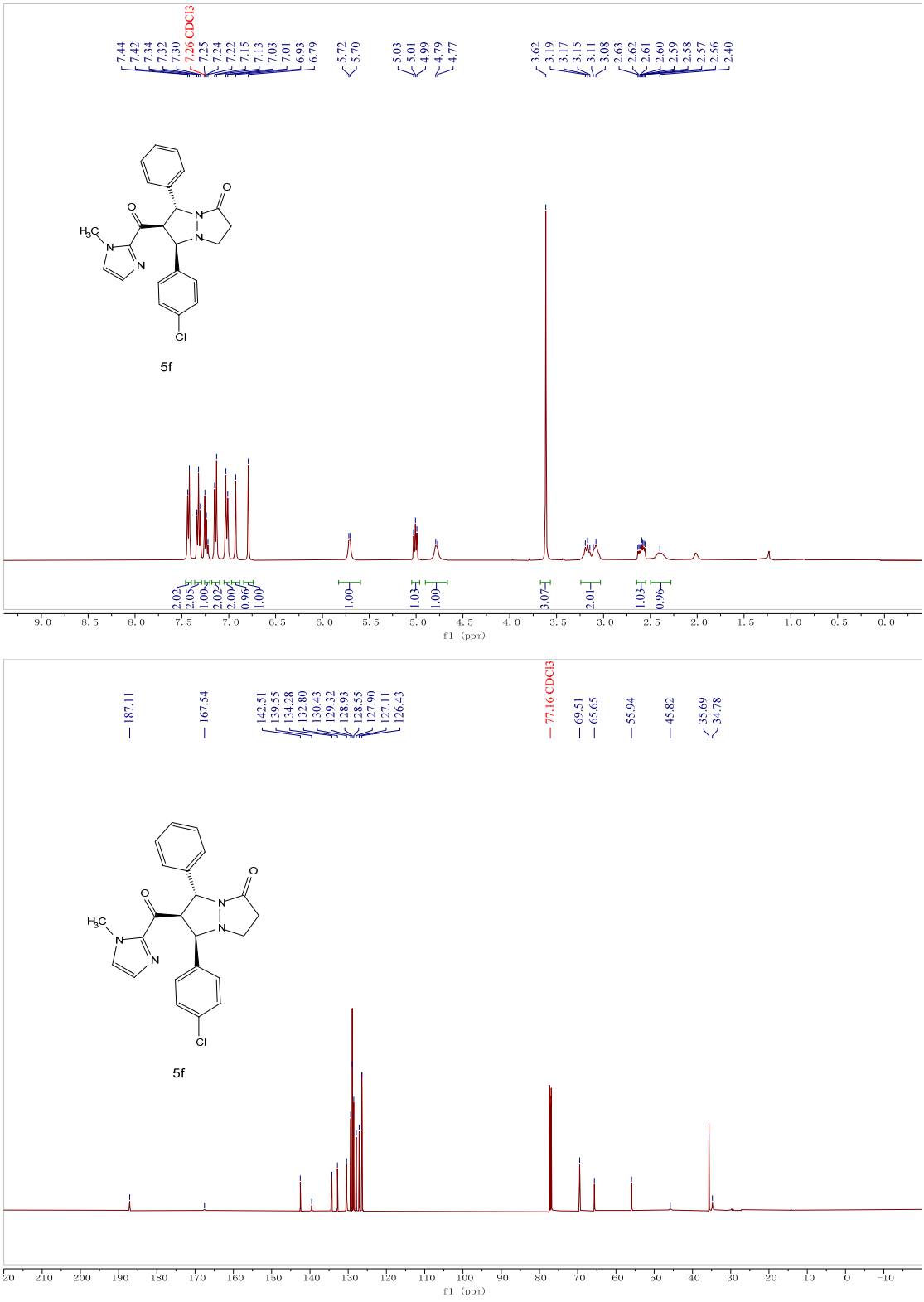

Figure S26. ^{1}H and ^{13}C NMR spectrum of of **5f**.

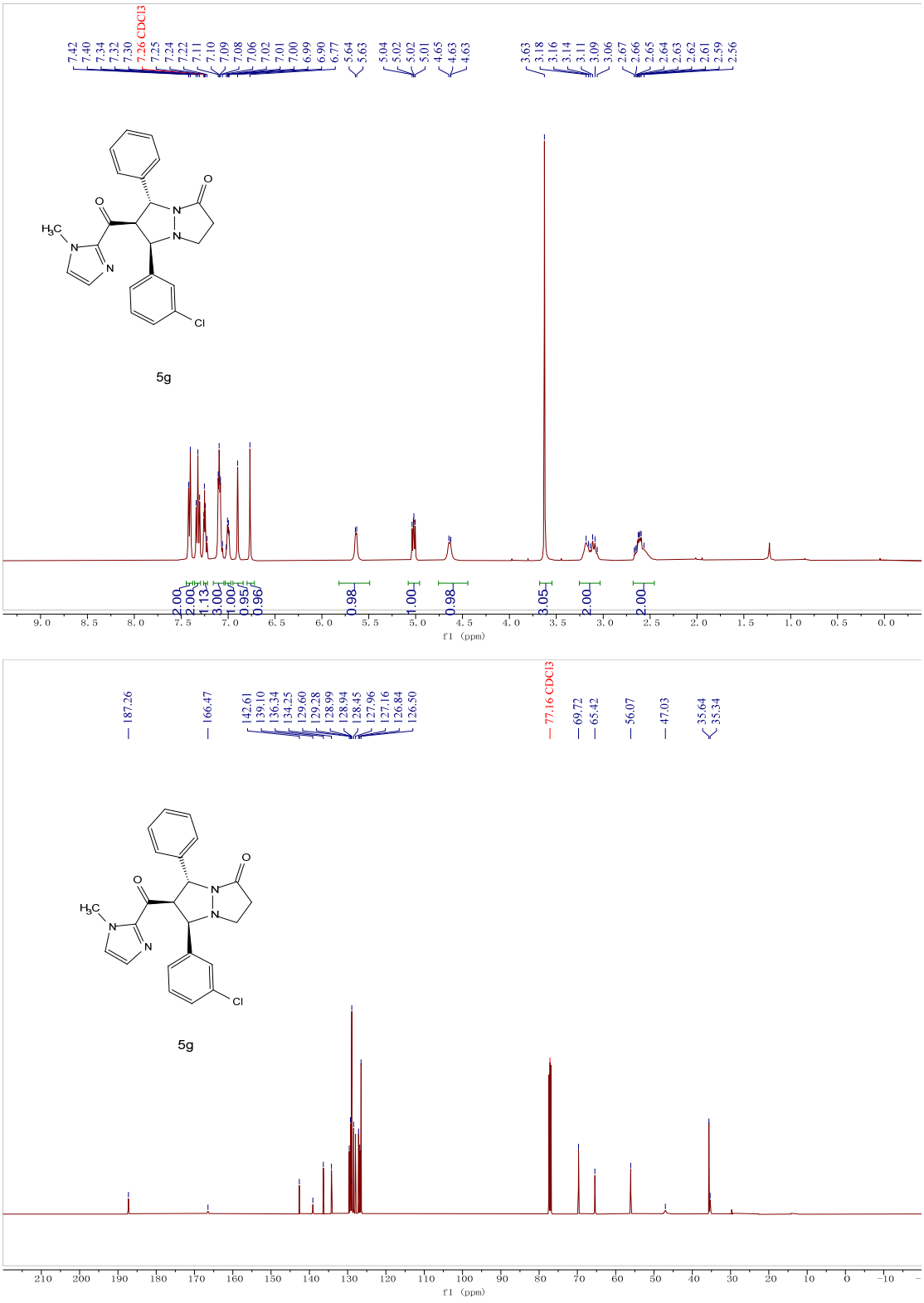

Figure S27. ^{1}H and ^{13}C NMR spectrum of of **5g**.

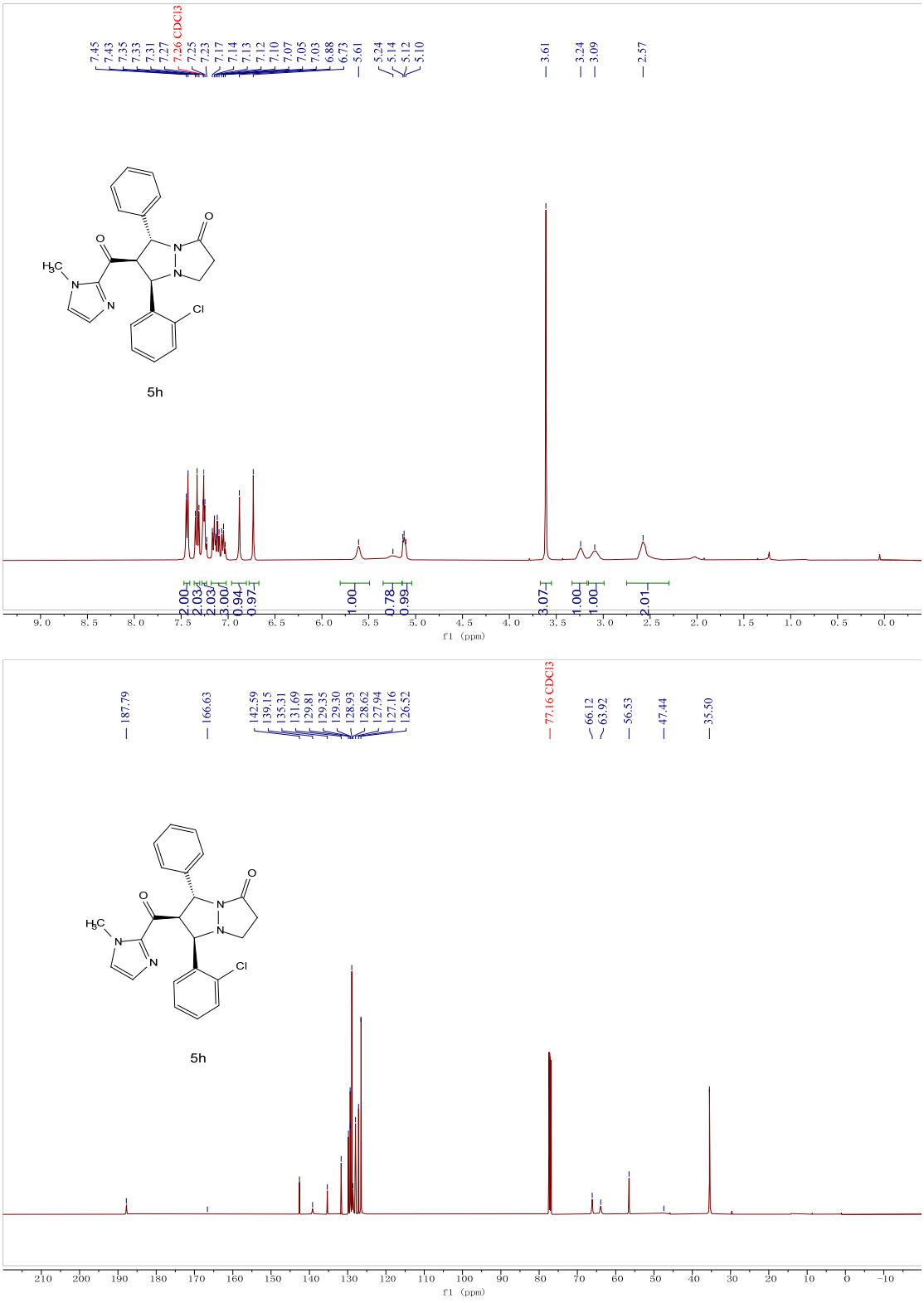

Figure S28. ^{1}H and ^{13}C NMR spectrum of of **5h**.

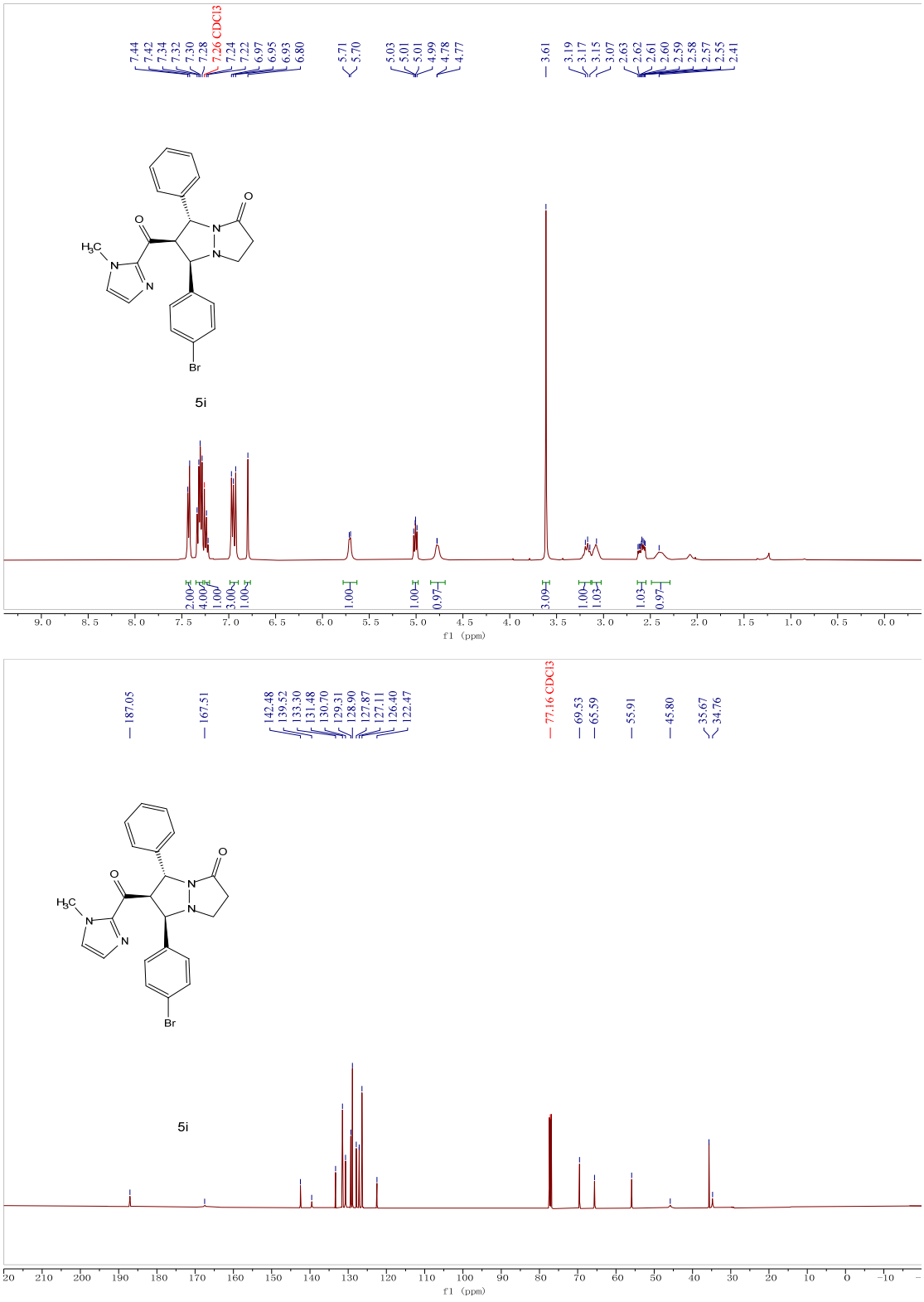

Figure S29. ^{1}H and ^{13}C NMR spectrum of **5i**.

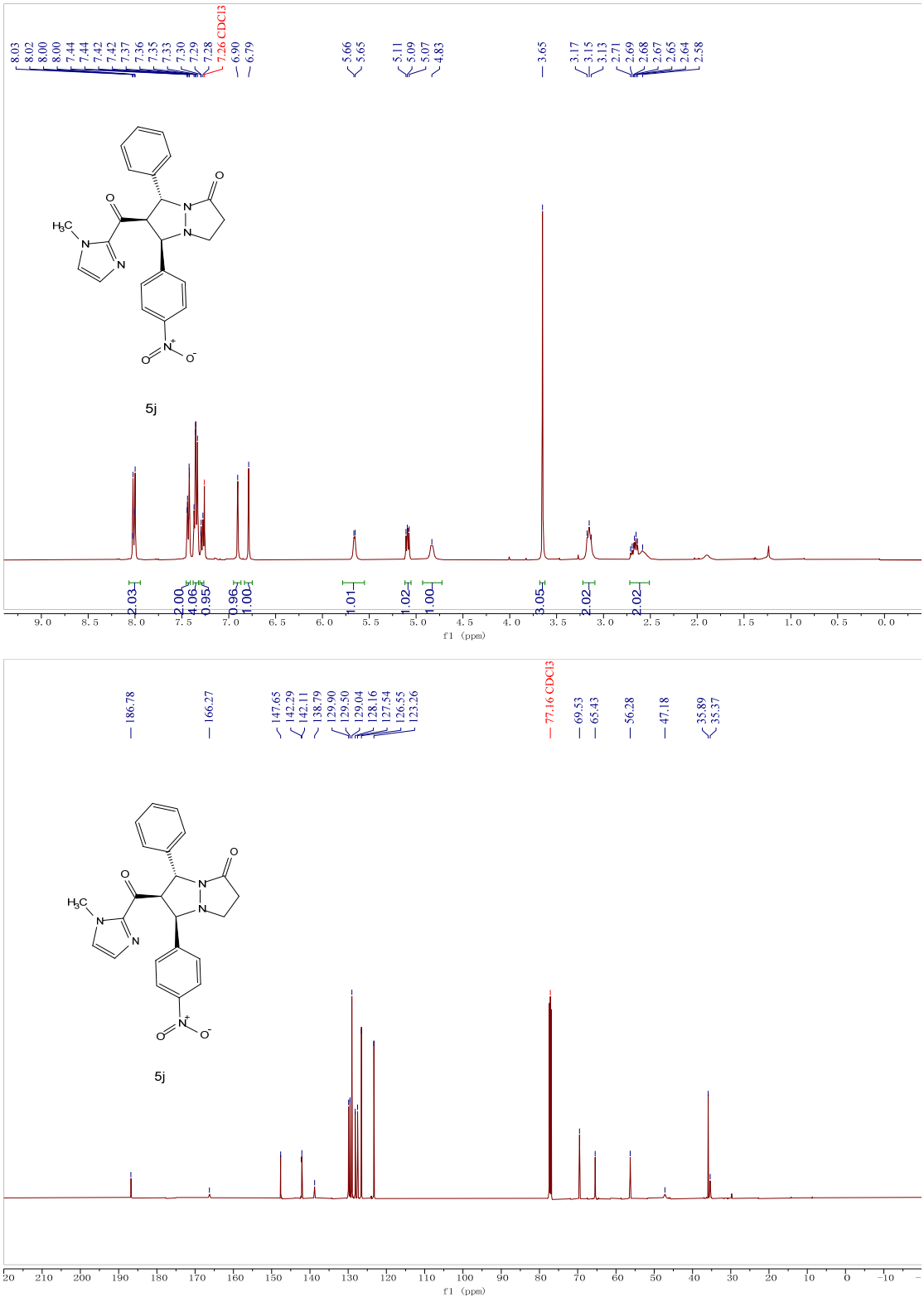

Figure S30. ^{1}H and ^{13}C NMR spectrum of **5j**.

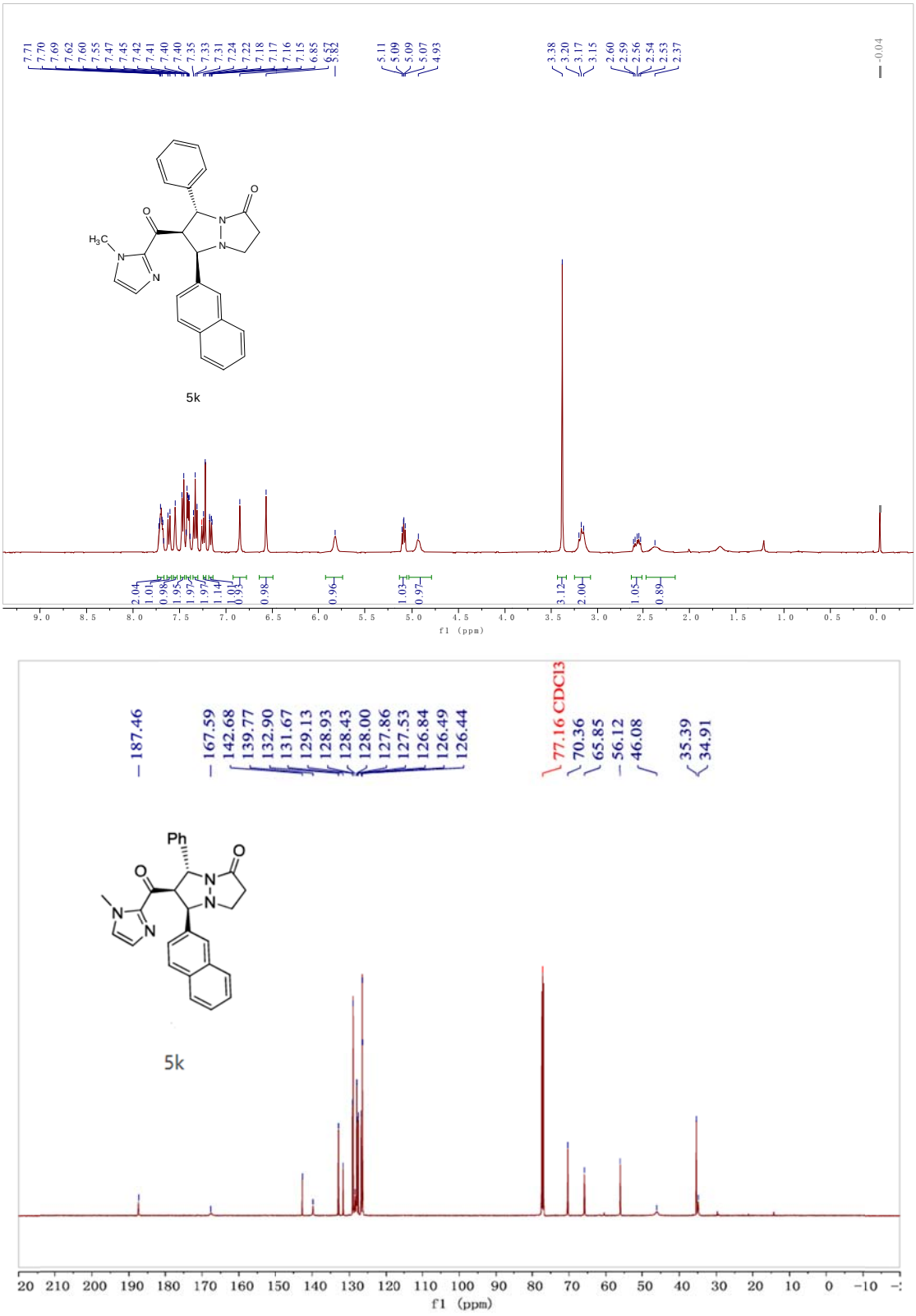

Figure S31. ^{1}H and ^{13}C NMR spectrum of **5k**.

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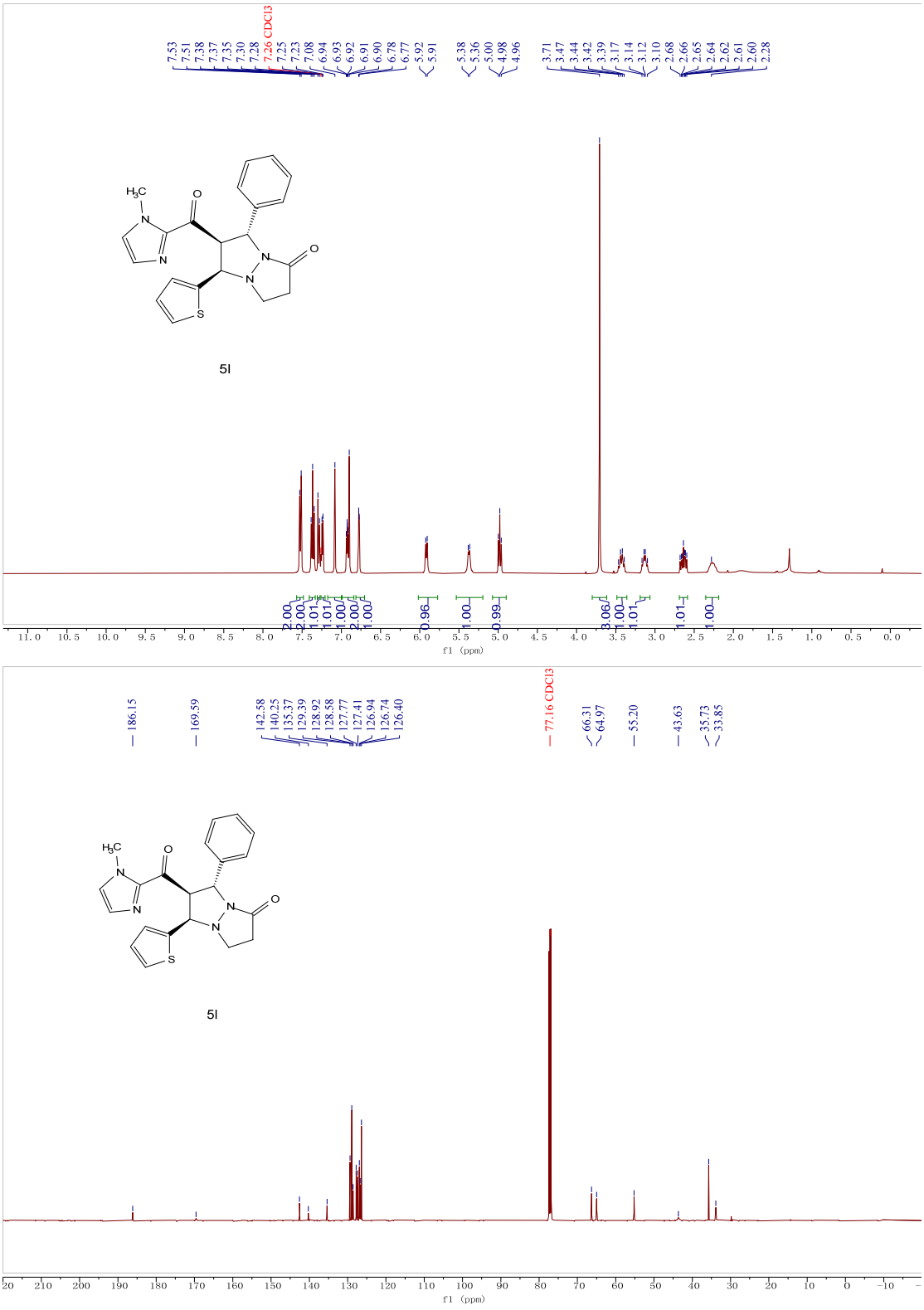


Figure S32. ^{1}H and ^{13}C NMR spectrum of **5l**.

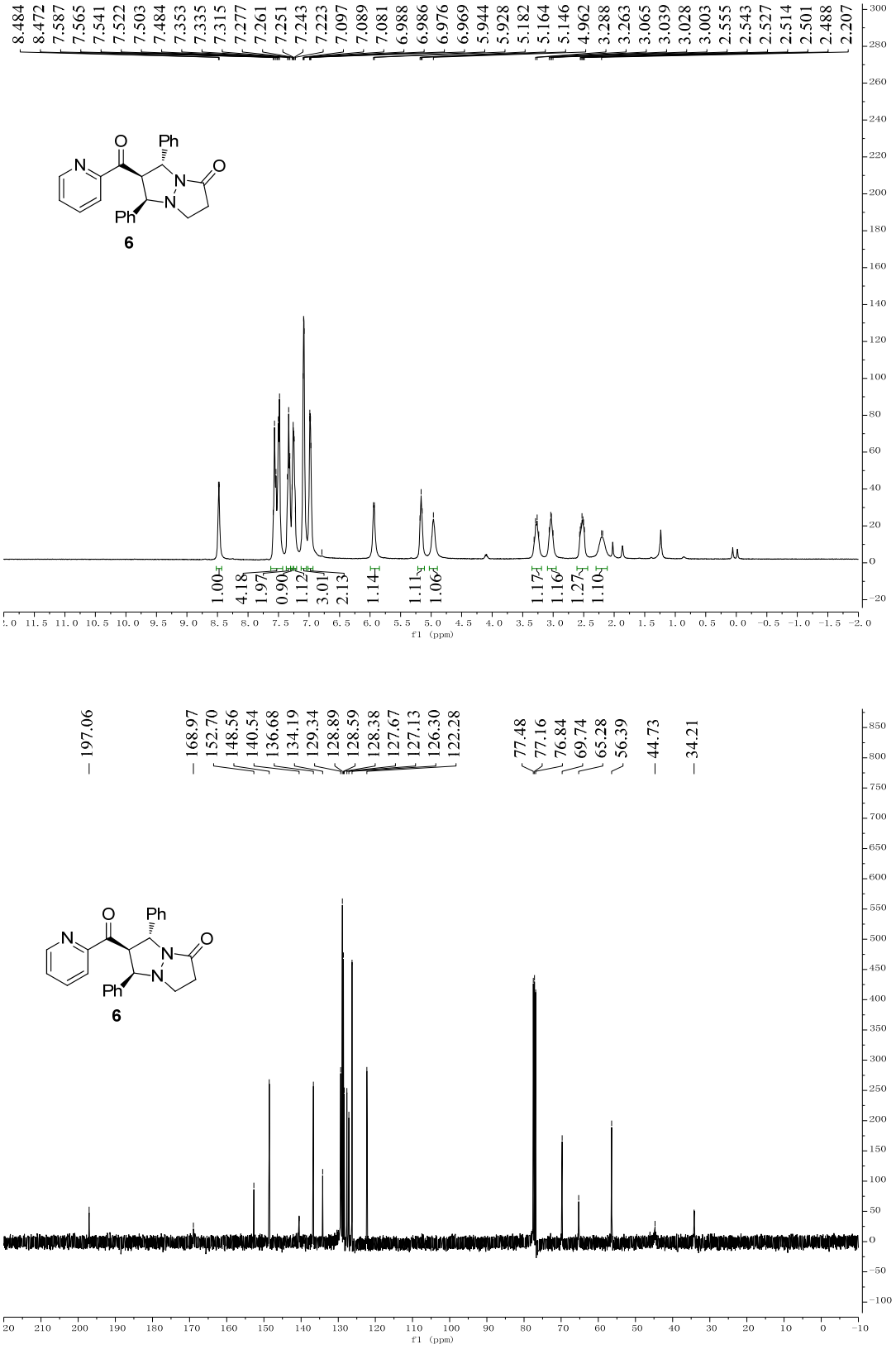
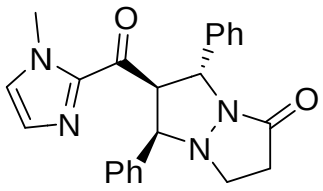


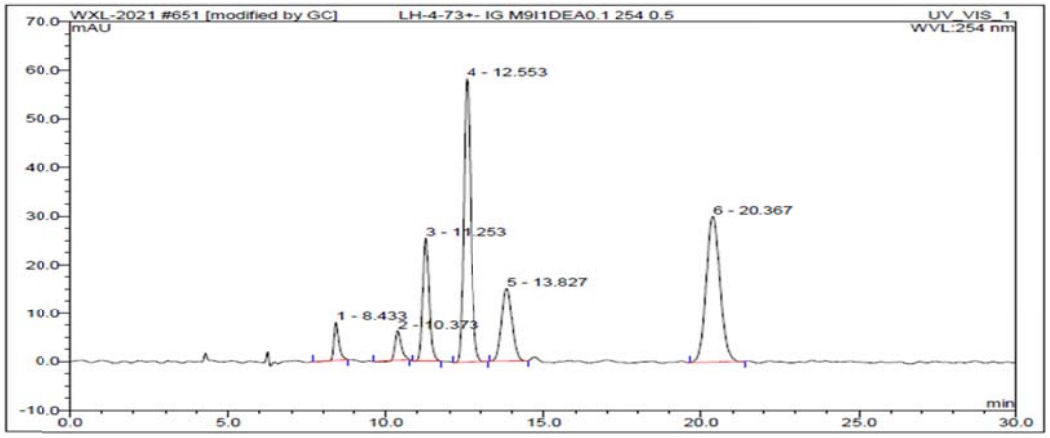
Figure S33. ^{1}H and ^{13}C NMR spectrum of **6**.

6. HPLC Traces on Chiral Stationary Phase



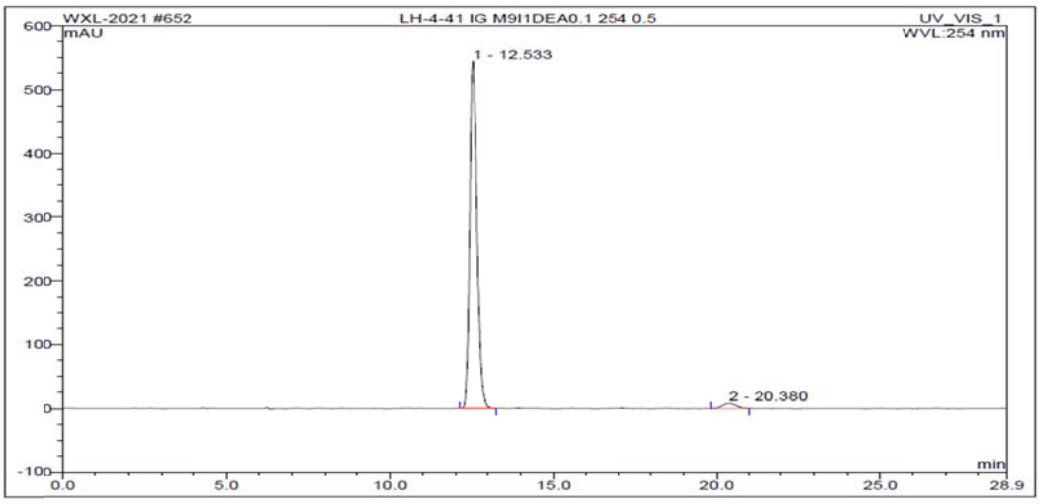
4a

Racemic 4a:



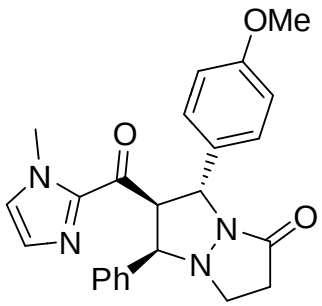
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.43	n.a.	7.786	1.358	3.02	n.a.	BMB*
2	10.37	n.a.	6.076	1.310	2.92	n.a.	BMB*
3	11.25	n.a.	25.381	5.983	13.33	n.a.	BMB*
4	12.55	n.a.	58.484	15.278	34.02	n.a.	BMB*
5	13.83	n.a.	14.986	5.775	12.86	n.a.	BMB*
6	20.37	n.a.	30.098	15.197	33.85	n.a.	BMB*
Total:			142.810	44.902	100.00	0.000	

Chiral 4a:



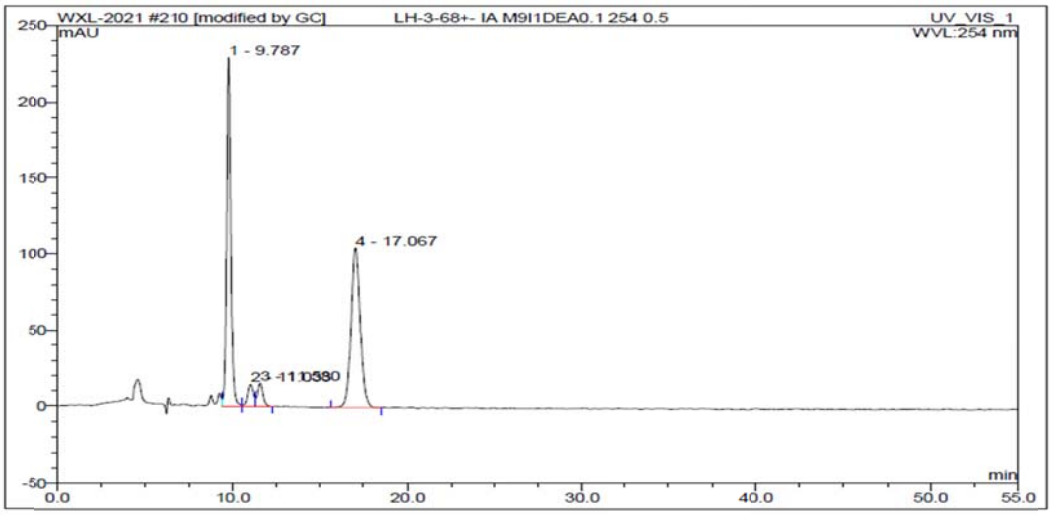
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.53	n.a.	544.368	144.325	97.35	n.a.	BMB
2	20.38	n.a.	8.009	3.922	2.65	n.a.	BMB
Total:			552.377	148.247	100.00	0.000	

Figure S33. HPLC traces of racemic **4a** (reference) and chiral **4a**. Area integration = 97.35: 2.65 (95% *ee*).



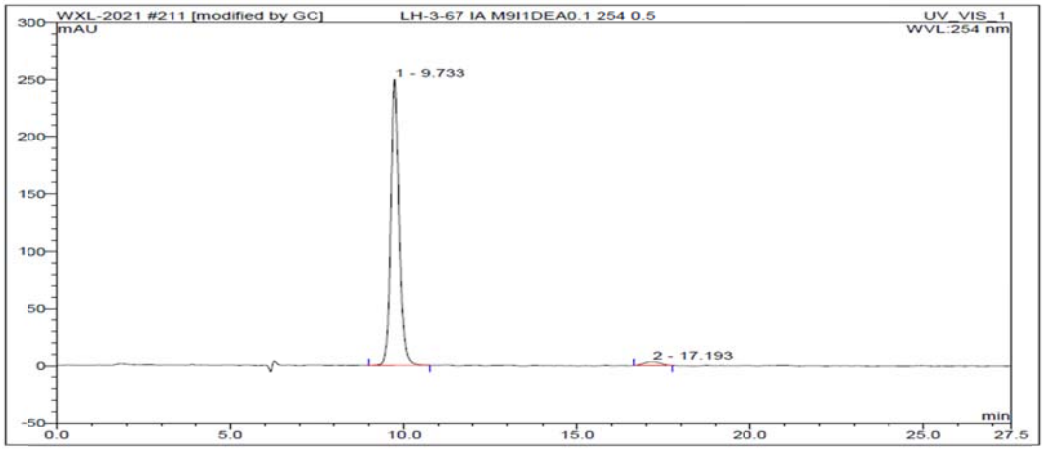
4b

Racemic 4b:



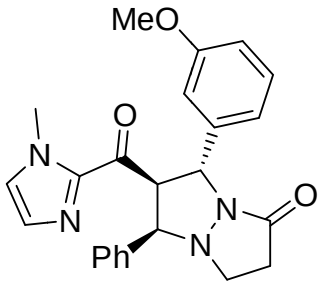
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.79	n.a.	229.487	63.787	46.02	n.a.	M *
2	11.03	n.a.	14.599	5.479	3.95	n.a.	M *
3	11.58	n.a.	15.320	5.534	3.99	n.a.	MB*
4	17.07	n.a.	104.791	63.805	46.03	n.a.	BMB*
Total:			364.197	138.605	100.00	0.000	

Chiral 4b:



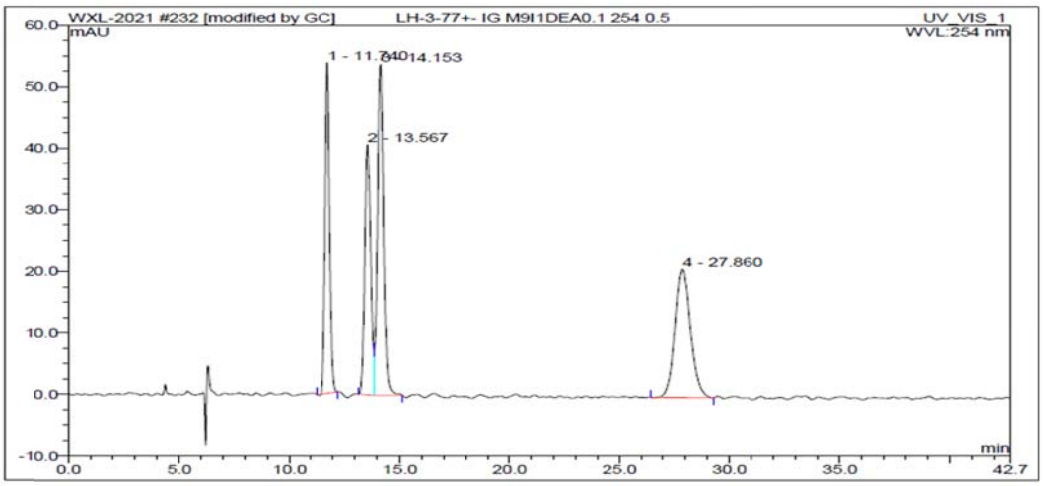
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.73	n.a.	250.039	68.987	97.47	n.a.	BMB*
2	17.19	n.a.	3.147	1.791	2.53	n.a.	BMB*
Total:			253.186	70.778	100.00	0.000	

Figure S34. HPLC traces of racemic **4b** (reference) and chiral **4b**. Area integration = 97.47:2.53 (95% *ee*).



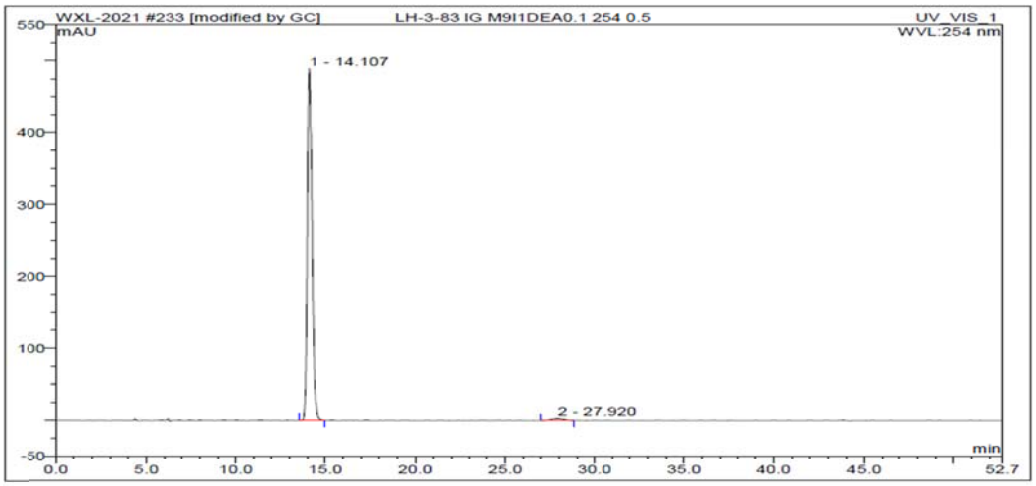
4c

Racemic **4c**:



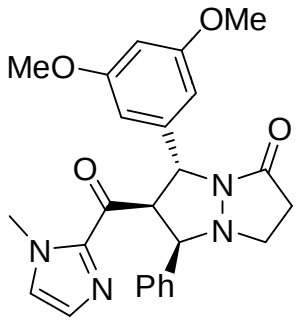
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.74	n.a.	53.780	13.005	21.77	n.a.	BMB*
2	13.57	n.a.	40.722	12.736	21.32	n.a.	BM *
3	14.15	n.a.	53.823	17.214	28.82	n.a.	MB*
4	27.86	n.a.	20.919	16.778	28.09	n.a.	BMB*
Total:			169.244	59.732	100.00	0.000	

Chiral **3c**:



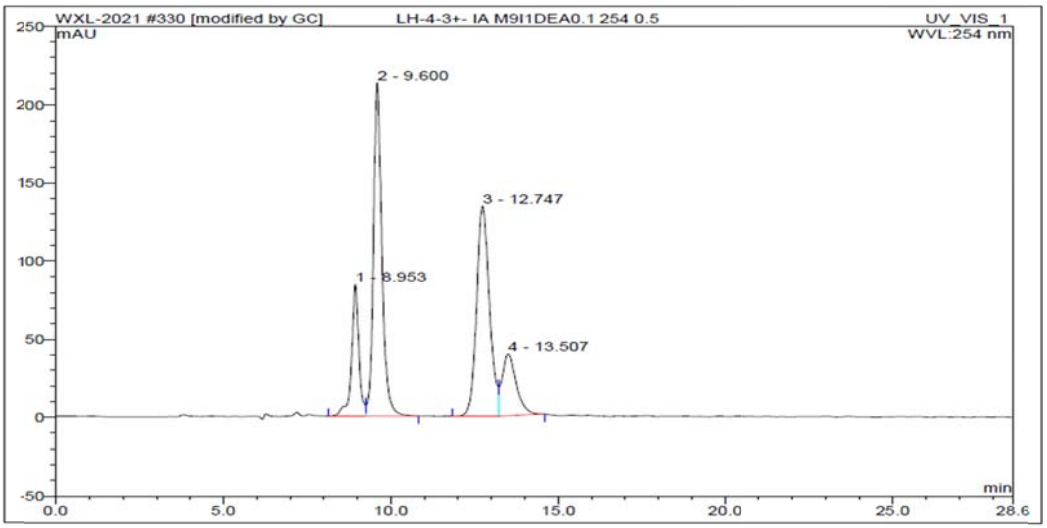
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.11	n.a.	488.548	152.477	98.51	n.a.	BMB*
2	27.92	n.a.	2.871	2.302	1.49	n.a.	BMB*
Total:			491.419	154.779	100.00	0.000	

Figure S35. HPLC traces of racemic **4c** (reference) and chiral **4c**. Area integration = 98.51:1.49 (97% *ee*).



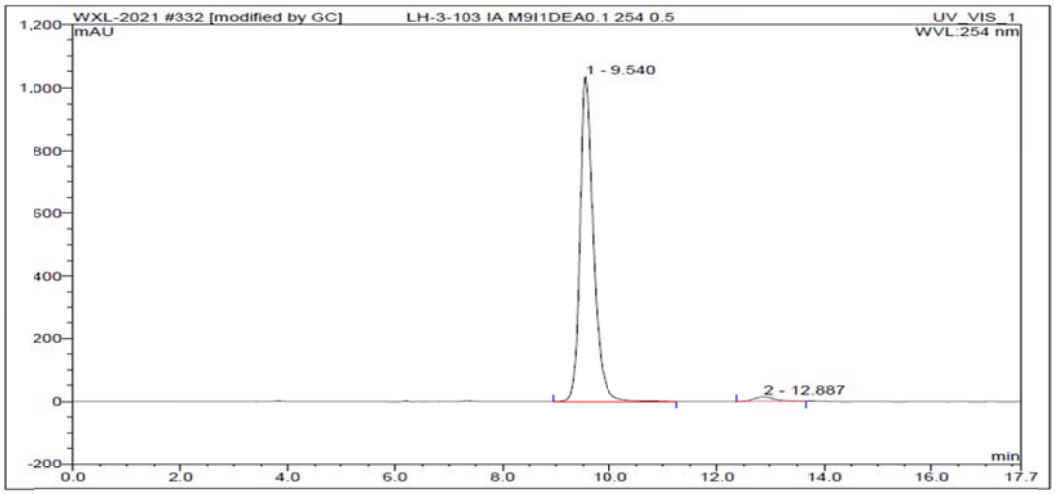
4d

Racemic **4d**:



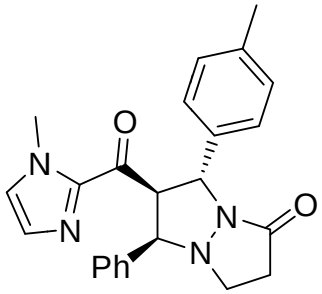
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.95	n.a.	84.733	21.419	13.16	n.a.	BM *
2	9.60	n.a.	213.244	61.683	37.90	n.a.	MB*
3	12.75	n.a.	134.562	60.511	37.18	n.a.	BM *
4	13.51	n.a.	39.799	19.144	11.76	n.a.	MB*
Total:			472.338	162.757	100.00	0.000	

Chiral **4d**:



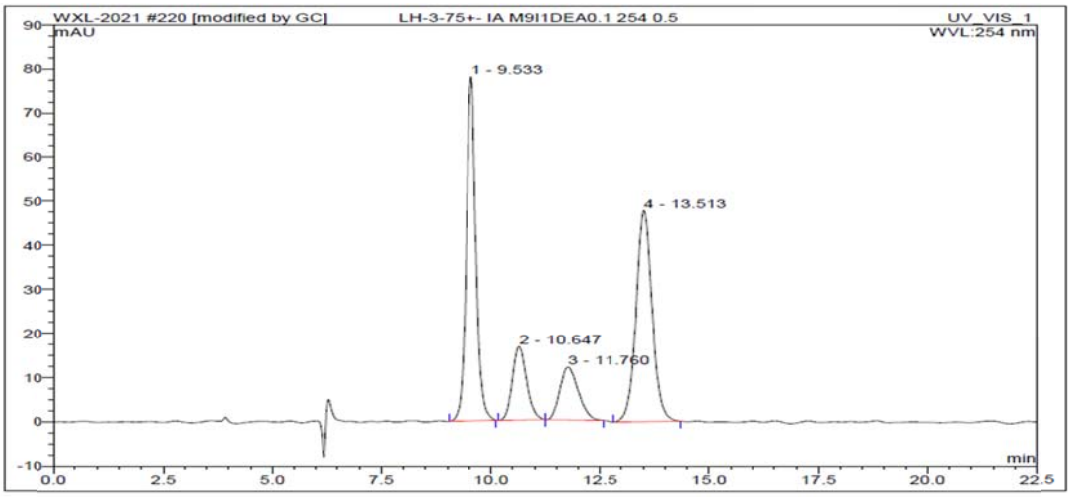
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.54	n.a.	1035.124	298.451	98.00	n.a.	BMB
2	12.89	n.a.	13.975	6.098	2.00	n.a.	BMB*
Total:			1049.098	304.550	100.00	0.000	

Figure S36. HPLC traces of racemic **4d** (reference) and chiral **4d**. Area integration = 98.00:2.00 (96% *ee*).



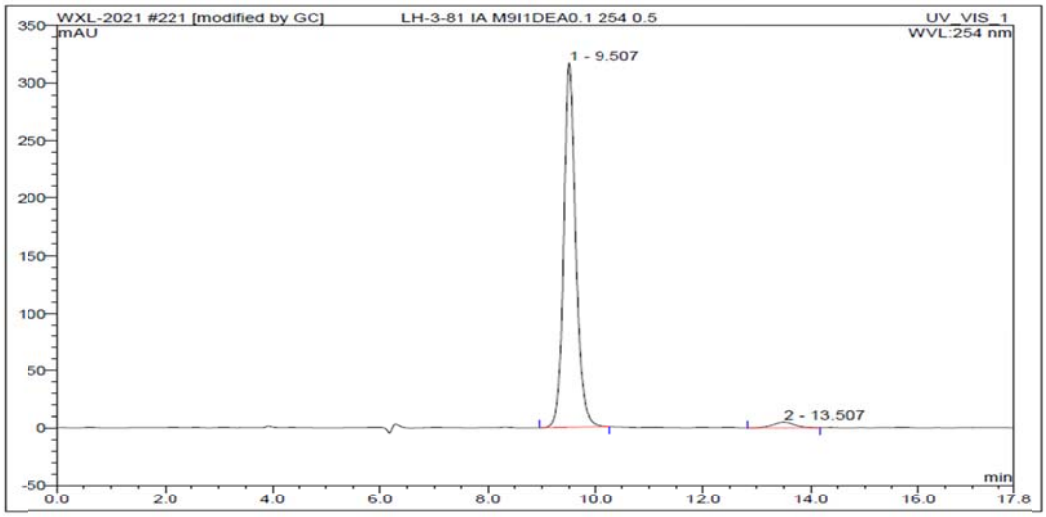
4e

Racemic **4e**:



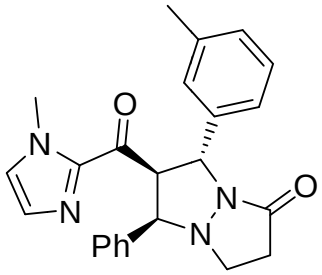
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.53	n.a.	78.110	20.124	38.16	n.a.	BMB*
2	10.65	n.a.	16.673	6.286	11.92	n.a.	BMb*
3	11.76	n.a.	11.965	5.853	11.10	n.a.	bMB*
4	13.51	n.a.	47.870	20.472	38.82	n.a.	BMB*
Total:			154.618	52.735	100.00	0.000	

Chiral **4e**:



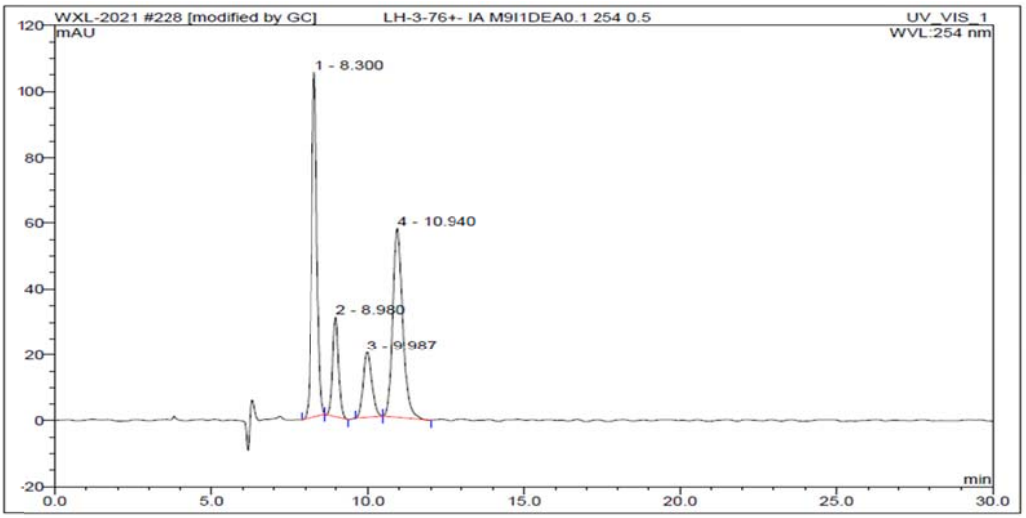
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.51	n.a.	316.837	82.018	97.27	n.a.	BMB*
2	13.51	n.a.	4.973	2.305	2.73	n.a.	BMB*
Total:			321.810	84.323	100.00	0.000	

Figure S37. HPLC traces of racemic **4e** (reference) and chiral **4e**. Area integration = 97.27:2.73 (95% *ee*).



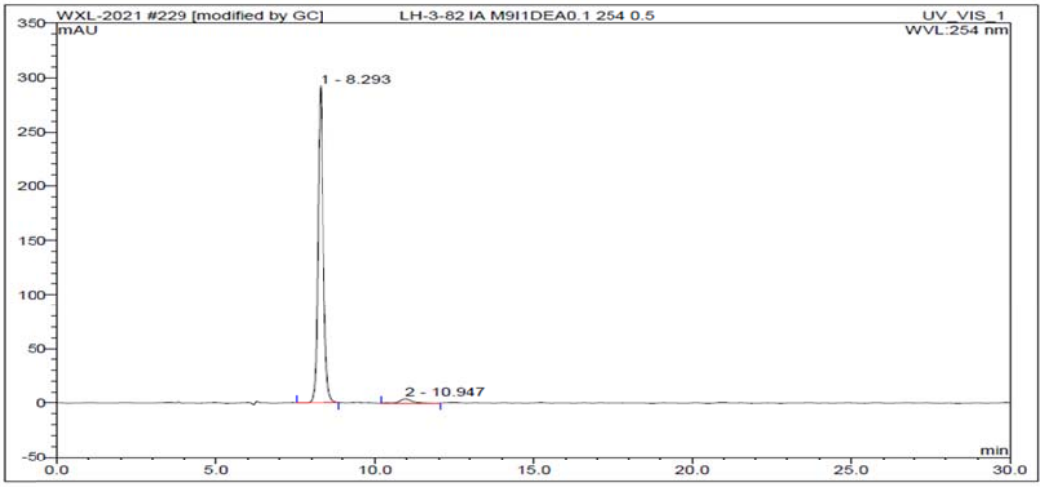
4f

Racemic **4f**:



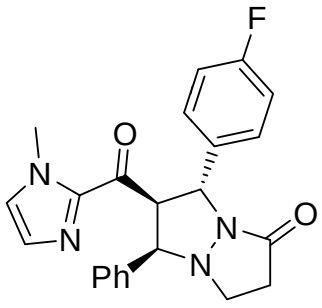
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.30	n.a.	104.685	21.063	38.37	n.a.	BMb*
2	8.98	n.a.	30.350	6.559	11.95	n.a.	bMB*
3	9.99	n.a.	19.765	6.270	11.42	n.a.	BMb*
4	10.94	n.a.	57.398	20.999	38.26	n.a.	bMB*
Total:			212.199	54.890	100.00	0.000	

Chiral **4f**:



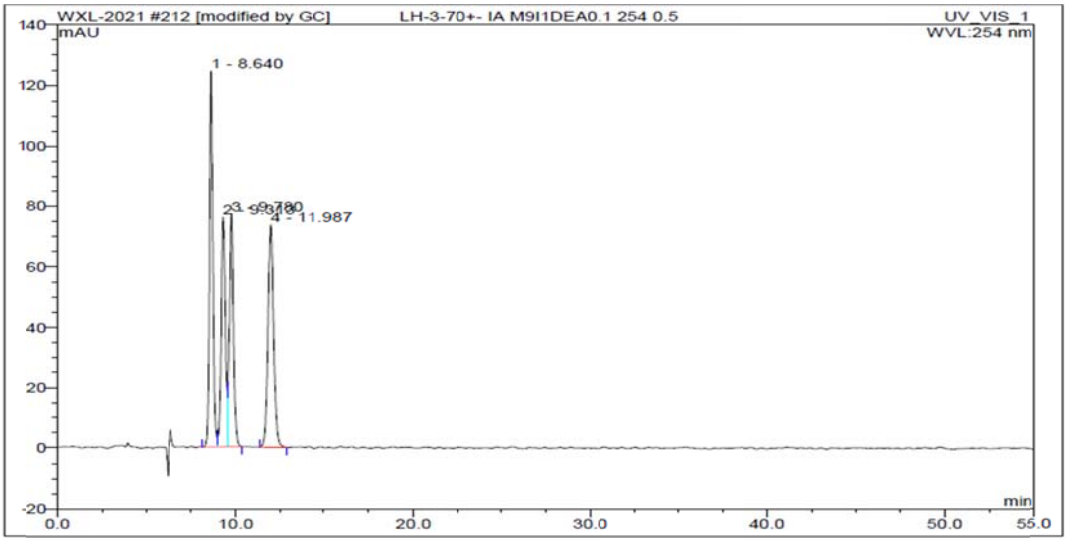
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.29	n.a.	292.167	59.627	97.51	n.a.	BMB*
2	10.95	n.a.	3.855	1.524	2.49	n.a.	BMB*
Total:			296.022	61.152	100.00	0.000	

Figure S38. HPLC traces of racemic **4f** (reference) and chiral **4f**. Area integration = 97.51:2.49 (95% *ee*).



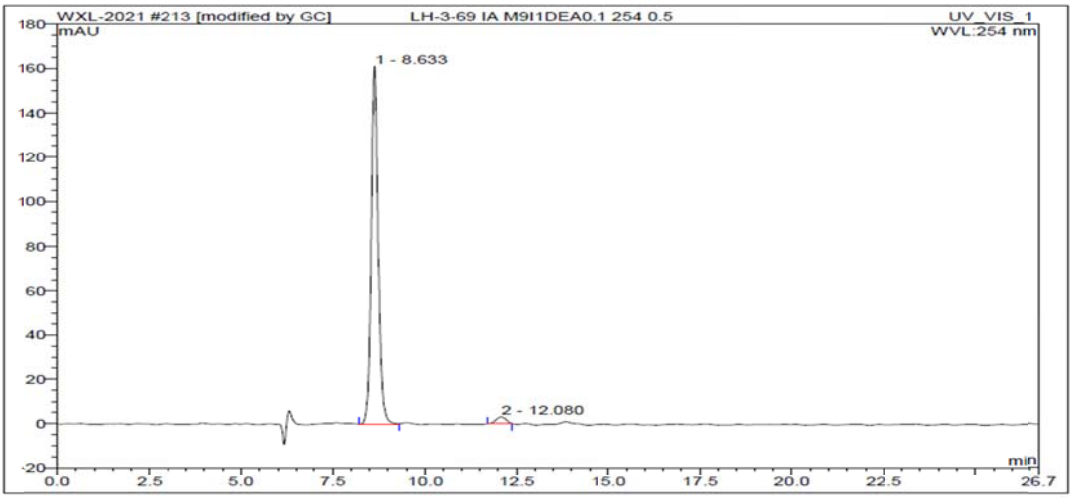
4g

Racemic **4g**:



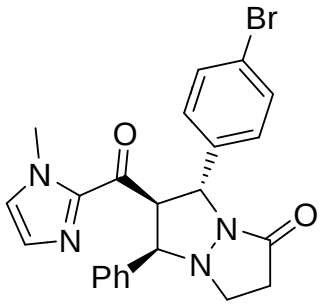
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.64	n.a.	124.265	26.989	28.34	n.a.	BM *
2	9.31	n.a.	75.938	20.318	21.34	n.a.	M *
3	9.78	n.a.	77.050	20.760	21.80	n.a.	MB*
4	11.99	n.a.	73.626	27.153	28.52	n.a.	BMB
Total:			350.880	95.220	100.00	0.000	

Chiral **4g**:



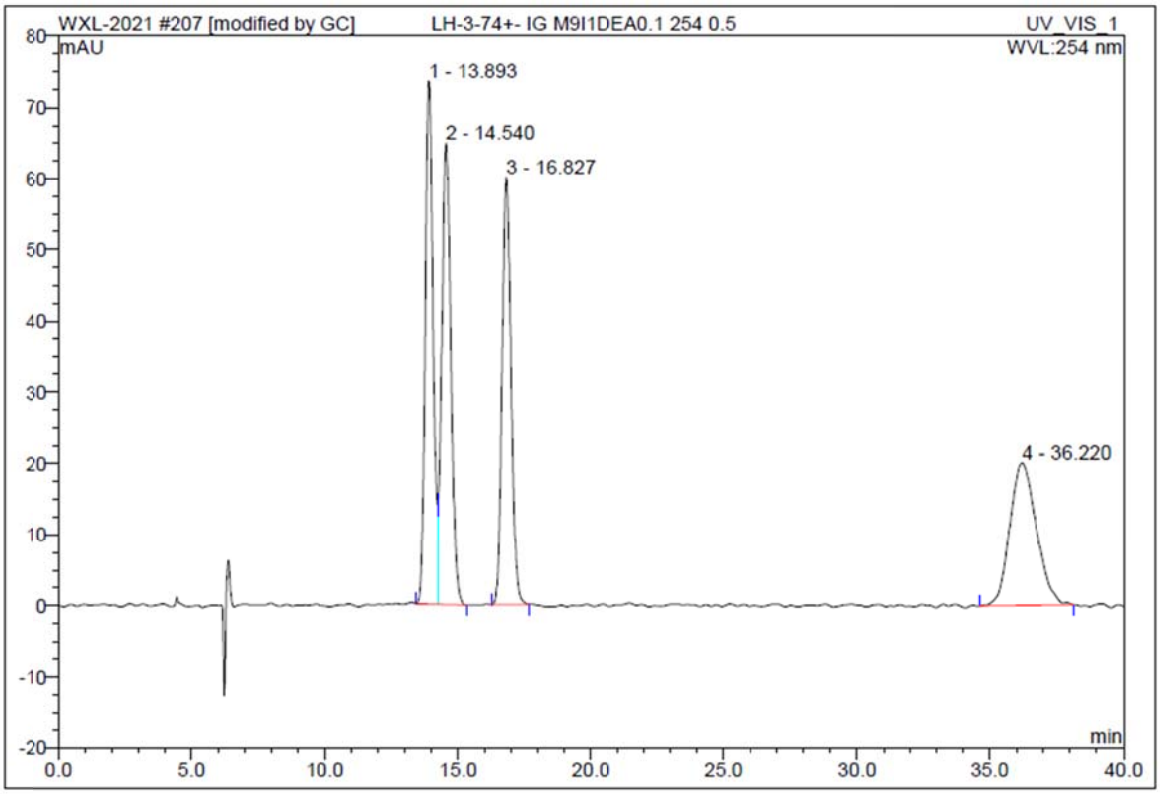
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.63	n.a.	161.096	34.754	97.28	n.a.	BM *
2	12.08	n.a.	3.079	0.970	2.72	n.a.	BMB*
Total:			164.175	35.724	100.00	0.000	

Figure S39. HPLC traces of racemic **4g** (reference) and chiral **4g**. Area integration = 97.28:2.72 (95% *ee*).

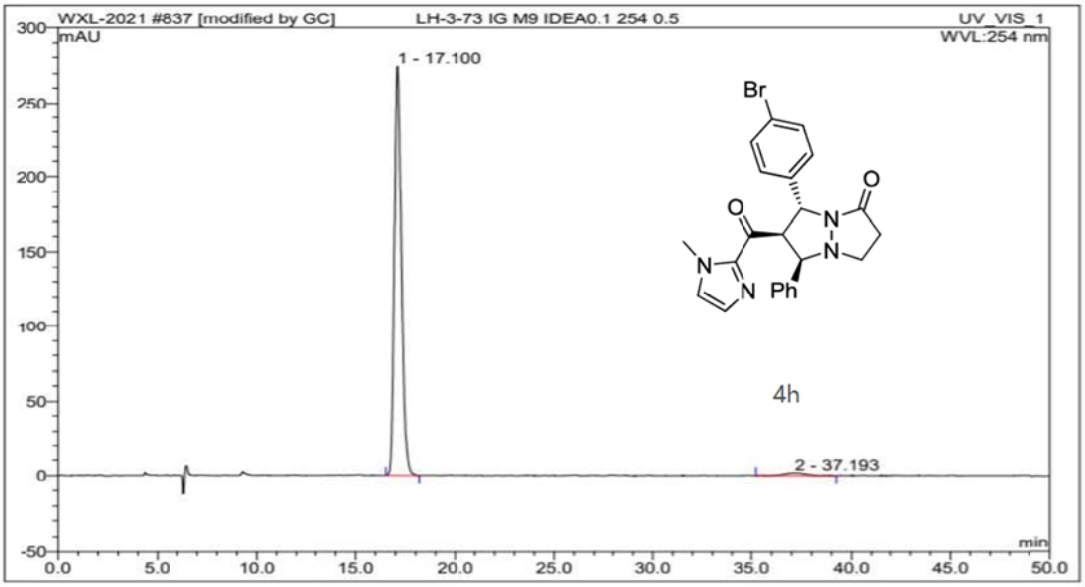


4h

Racemic **4h**:

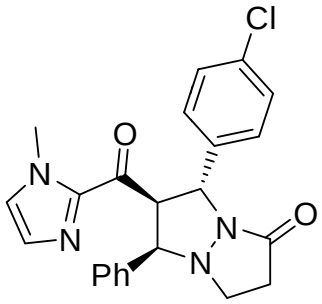


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.89	n.a.	73.430	25.035	25.53	n.a.	BM *
2	14.54	n.a.	64.885	25.912	26.42	n.a.	MB*
3	16.83	n.a.	60.067	23.587	24.05	n.a.	BMB*
4	36.22	n.a.	20.086	23.541	24.00	n.a.	BMB*
Total:			218.468	98.075	100.00	0.000	



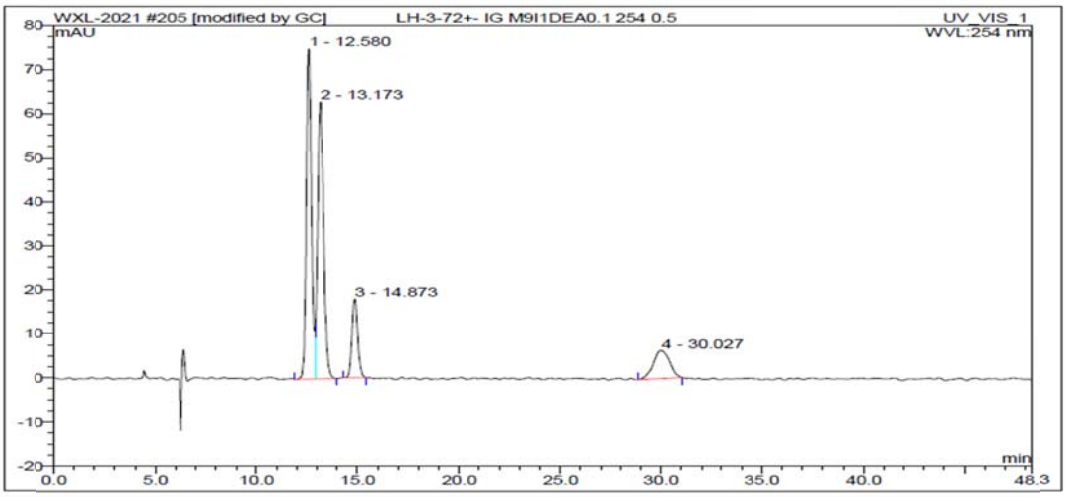
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.10	n.a.	274.136	111.703	97.93	n.a.	BMB
2	37.19	n.a.	1.756	2.356	2.07	n.a.	BMB*
Total:			275.892	114.059	100.00	0.000	

Figure S40. HPLC traces of racemic **4h** (reference) and chiral **4h**. Area integration = 99.5:0.5 (99% *ee*).



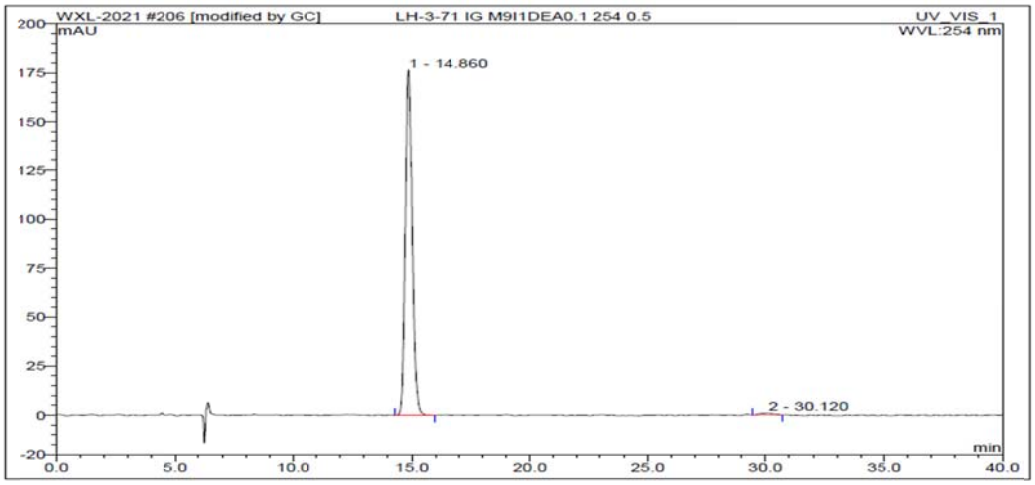
4i

Racemic **4i**:



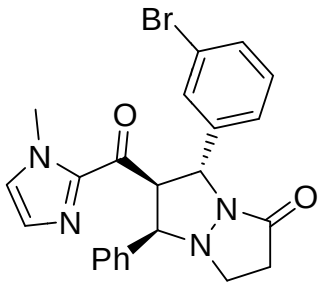
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.58	n.a.	75.041	22.022	38.95	n.a.	BM *
2	13.17	n.a.	63.019	22.501	39.80	n.a.	MB*
3	14.87	n.a.	18.002	6.005	10.62	n.a.	BMB*
4	30.03	n.a.	6.404	6.012	10.63	n.a.	BMB
Total:			162.465	56.540	100.00	0.000	

Chiral **4i**:



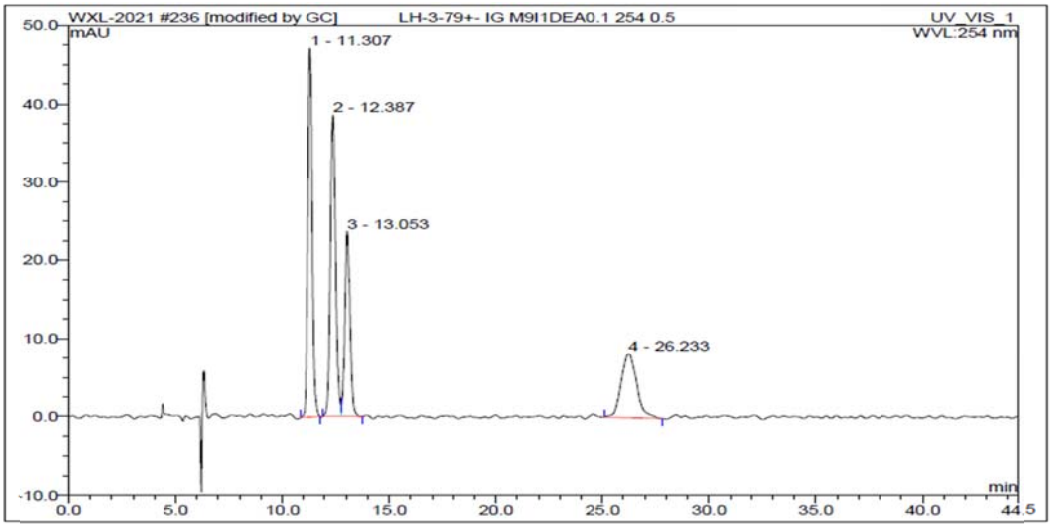
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.86	n.a.	176.507	59.685	98.96	n.a.	BMB*
2	30.12	n.a.	0.921	0.625	1.04	n.a.	BMB*
Total:			177.428	60.311	100.00	0.000	

Figure S41. HPLC traces of racemic **4i** (reference) and chiral **4i**. Area integration = 98.96:1.04 (98% *ee*).



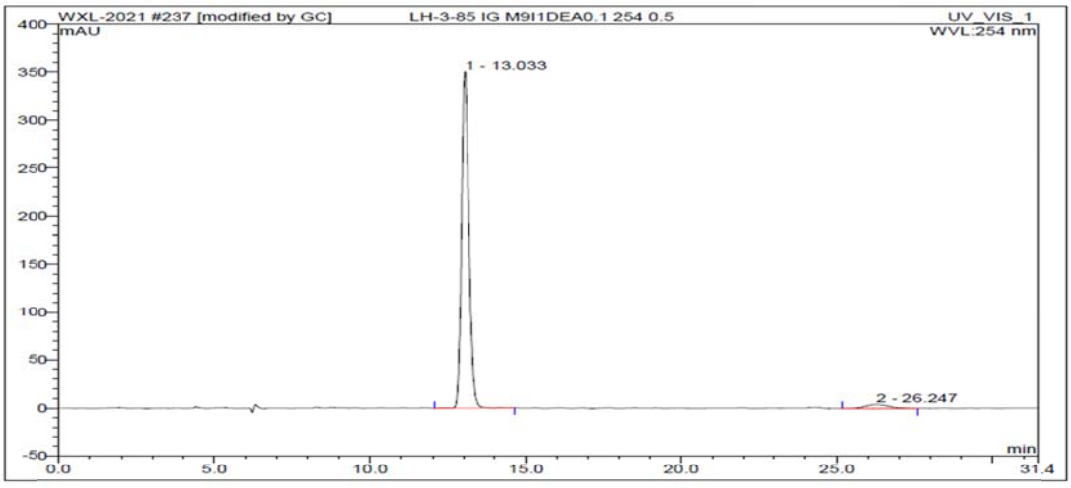
4j

Racemic **4j**:



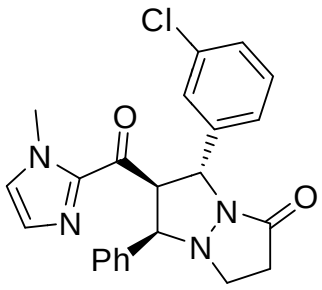
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.31	n.a.	47.190	11.249	31.35	n.a.	BMB*
2	12.39	n.a.	38.621	11.076	30.86	n.a.	BM *
3	13.05	n.a.	23.653	6.646	18.52	n.a.	MB*
4	26.23	n.a.	8.223	6.915	19.27	n.a.	BMB*
Total:			117.687	35.887	100.00	0.000	

Chiral **4j**:



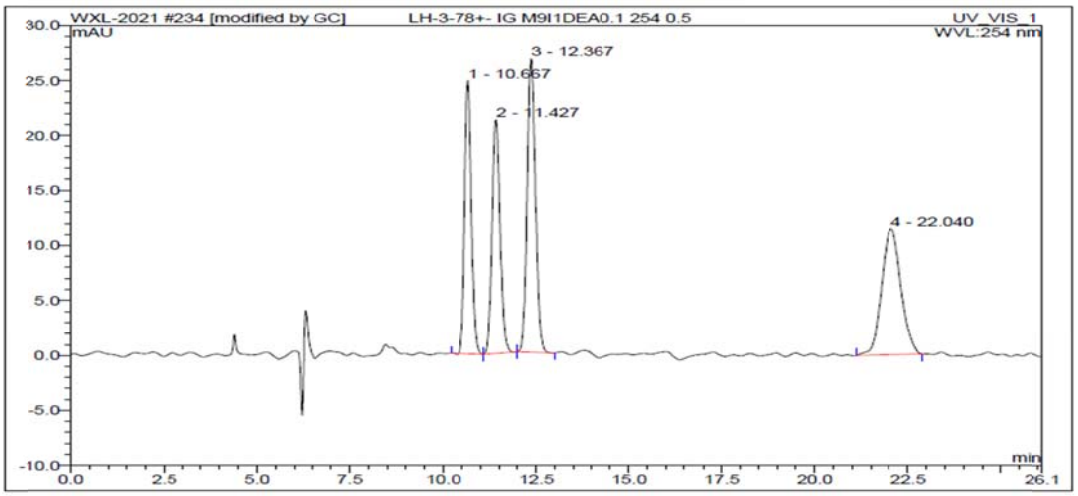
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.03	n.a.	350.226	98.768	96.78	n.a.	BMB*
2	26.25	n.a.	3.961	3.284	3.22	n.a.	BMB*
Total:			354.187	102.052	100.00	0.000	

Figure S42. HPLC traces of racemic **4j** (reference) and chiral **4j**. Area integration = 96.78:3.22 (94% *ee*).



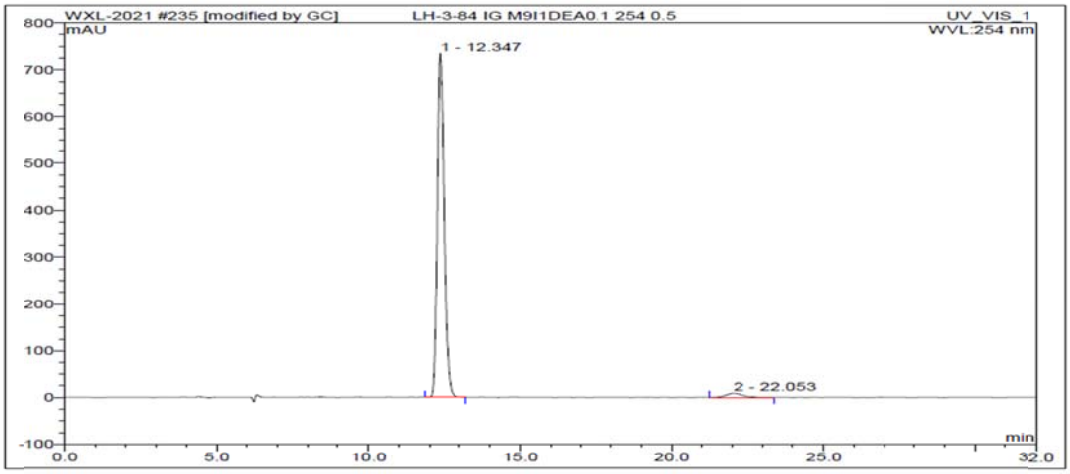
4k

Racemic **4k**:



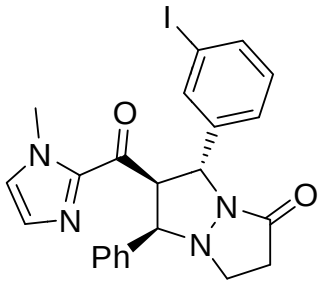
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.67	n.a.	24.854	5.265	21.54	n.a.	BMb*
2	11.43	n.a.	21.274	5.300	21.69	n.a.	bMb*
3	12.37	n.a.	26.695	6.901	28.24	n.a.	bMB*
4	22.04	n.a.	11.427	6.970	28.52	n.a.	BMB*
Total:			84.250	24.436	100.00	0.000	

Chiral **4k**



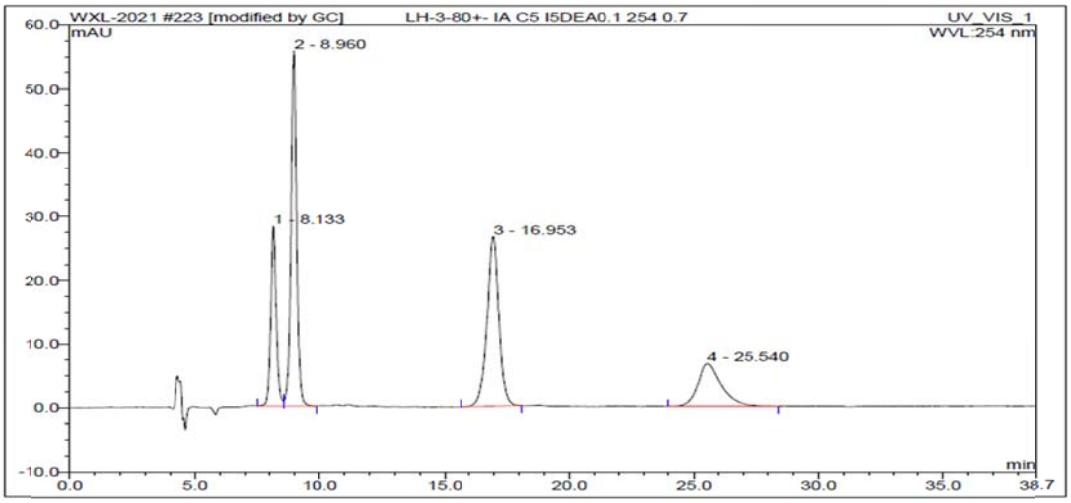
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.35	n.a.	734.518	193.517	97.32	n.a.	BMB*
2	22.05	n.a.	8.781	5.330	2.68	n.a.	BMB*
Total:			743.299	198.847	100.00	0.000	

Figure S43. HPLC traces of racemic **4k** (reference) and chiral **4k** Area integration = 97.32:2.68 (95% *ee*).



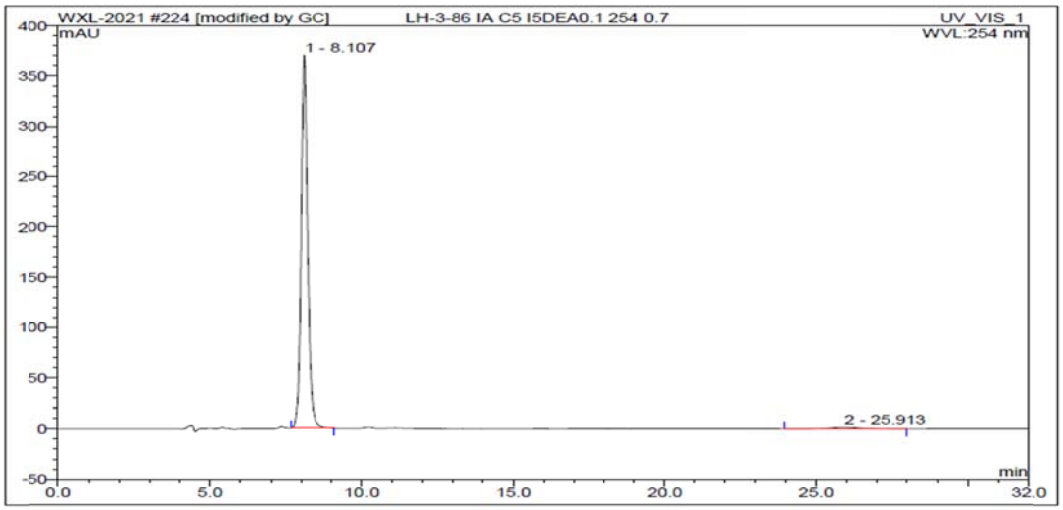
4l

Racemic **4l**:



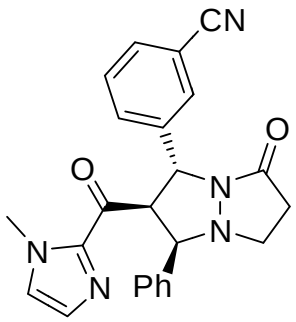
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.13	n.a.	28.193	7.237	16.41	n.a.	BM *
2	8.96	n.a.	55.708	14.801	33.55	n.a.	MB*
3	16.95	n.a.	26.599	14.792	33.53	n.a.	BMB*
4	25.54	n.a.	6.751	7.283	16.51	n.a.	BMB*
Total:			117.250	44.112	100.00	0.000	

Chiral **4l**:



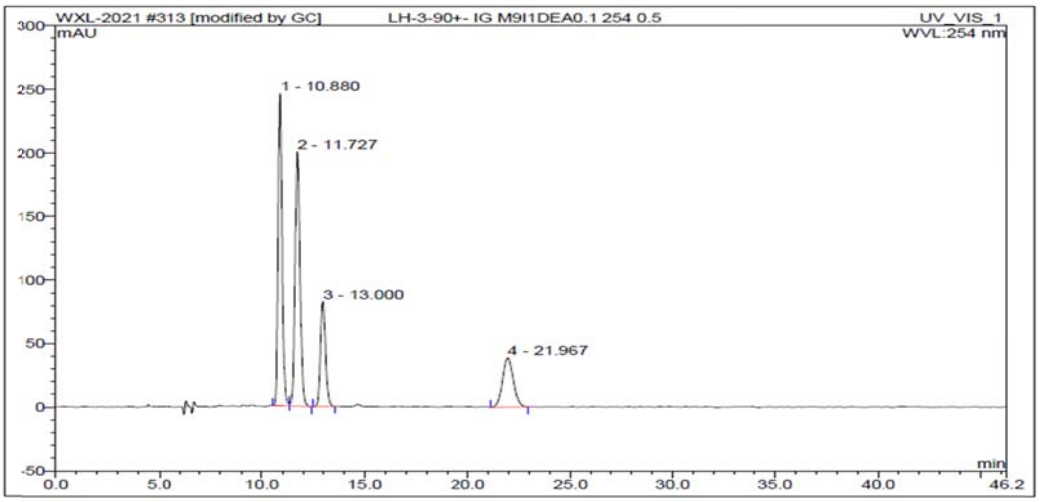
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.11	n.a.	369.783	92.373	98.11	n.a.	BMB*
2	25.91	n.a.	1.547	1.780	1.89	n.a.	BMB*
Total:			371.330	94.153	100.00	0.000	

Figure S44. HPLC traces of racemic **4l** (reference) and chiral **4l**. Area integration = 98.11:1.89(96% *ee*).



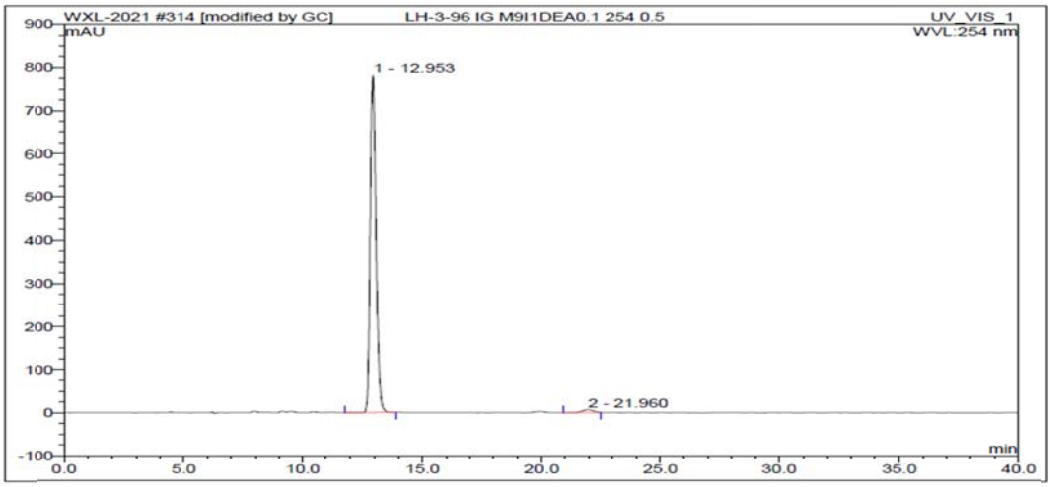
4m

Racemic **4m**:



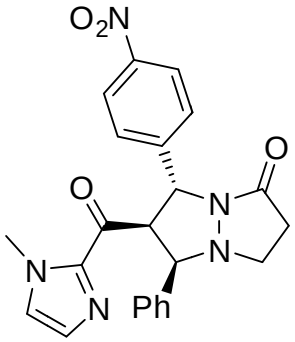
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.88	n.a.	245.873	55.769	35.14	n.a.	BM *
2	11.73	n.a.	200.368	56.045	35.32	n.a.	MB*
3	13.00	n.a.	82.903	23.452	14.78	n.a.	BMB*
4	21.97	n.a.	38.655	23.432	14.77	n.a.	BMB*
Total:			567.800	158.697	100.00	0.000	

Racemic **4m**:



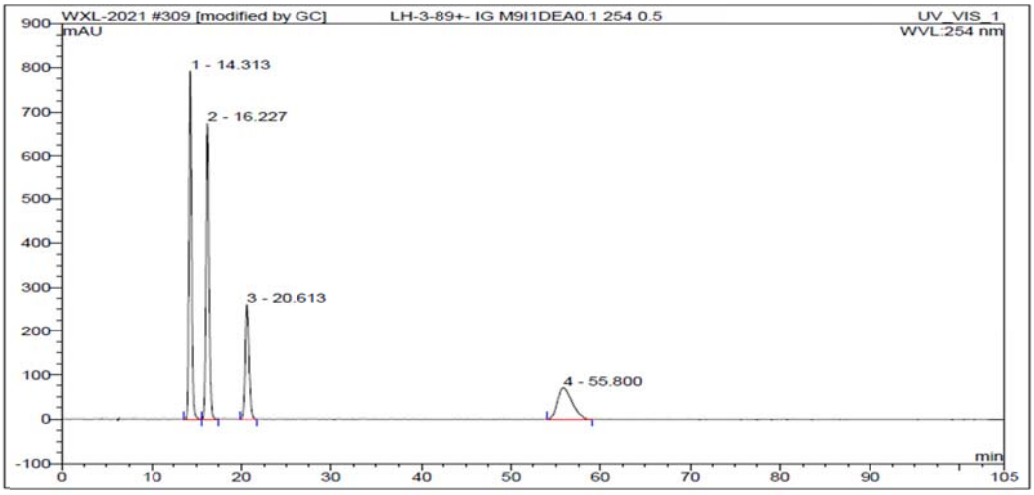
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.95	n.a.	781.123	221.855	98.41	n.a.	BMB*
2	21.96	n.a.	6.587	3.588	1.59	n.a.	BMB*
Total:			787.710	225.443	100.00	0.000	

Figure S45. HPLC traces of racemic **4m** (reference) and chiral **4m**. Area integration = 98.41:1.59 (97% *ee*).



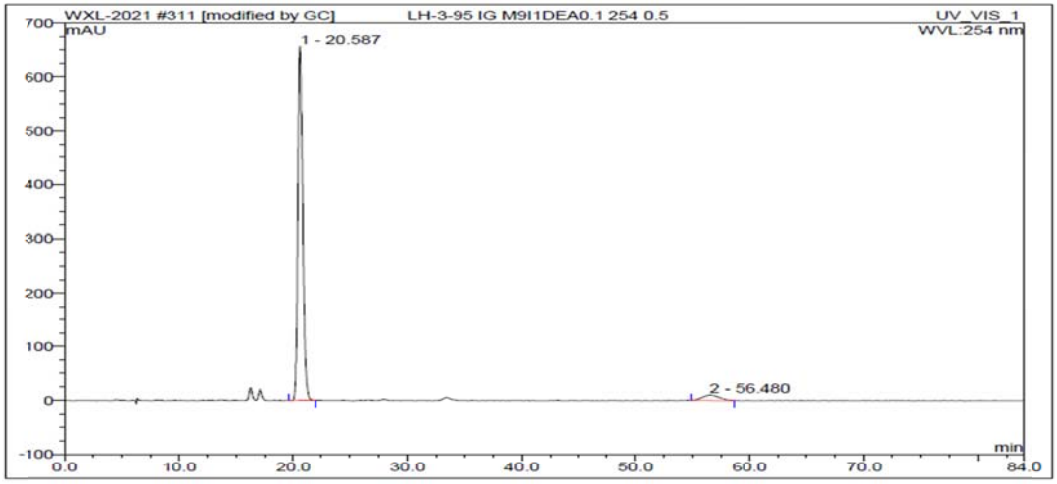
4n

Racemic **4n**:



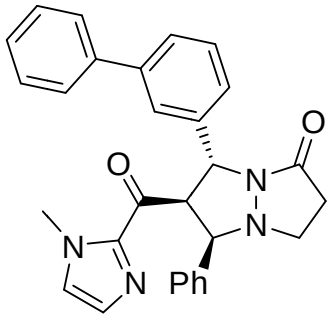
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.31	n.a.	791.568	271.707	33.94	n.a.	BM *
2	16.23	n.a.	674.676	270.267	33.76	n.a.	M *
3	20.61	n.a.	261.010	129.582	16.19	n.a.	BMB
4	55.80	n.a.	69.910	129.010	16.11	n.a.	BMB*
Total:			1797.165	800.567	100.00	0.000	

Chiral **4n**:



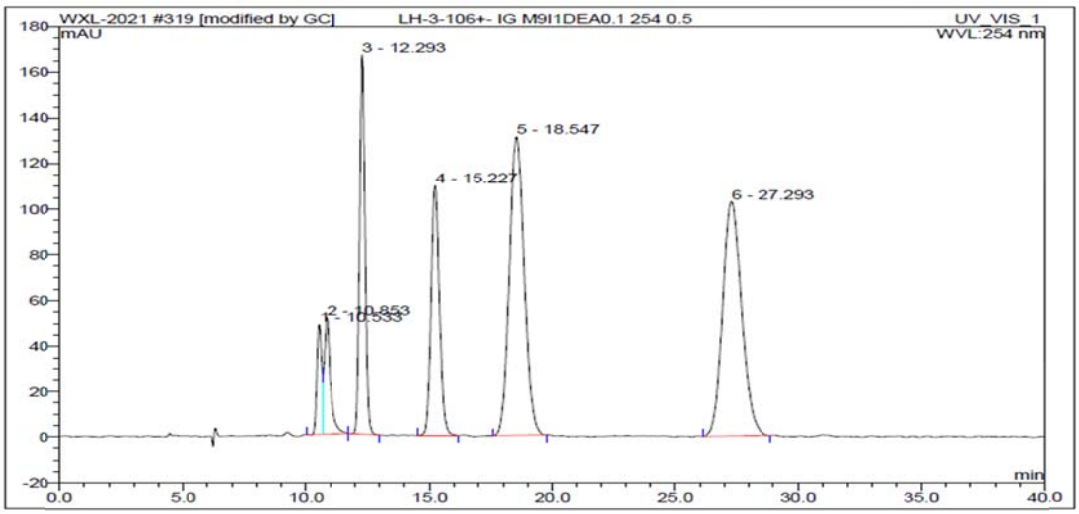
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.59	n.a.	656.298	328.402	94.95	n.a.	BMB*
2	56.48	n.a.	10.032	17.472	5.05	n.a.	BMB*
Total:			666.329	345.874	100.00	0.000	

Figure S46. HPLC traces of racemic **4n** (reference) and chiral **4n**. Area integration = 94.95:5.05 (90% *ee*).



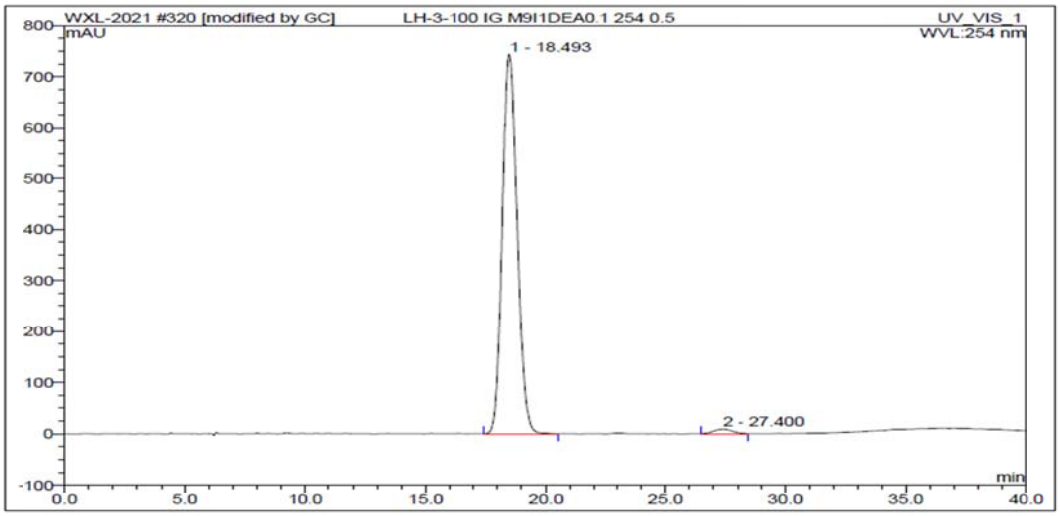
4o

Racemic **4o**:



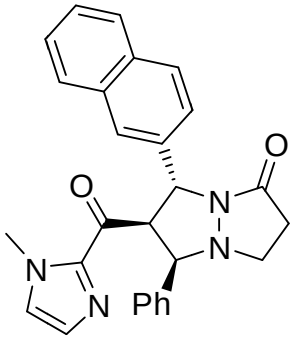
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.53	n.a.	48.470	11.140	3.74	n.a.	BM *
2	10.85	n.a.	51.486	15.011	5.04	n.a.	Mb*
3	12.29	n.a.	166.422	43.324	14.53	n.a.	bMB*
4	15.23	n.a.	109.690	43.291	14.52	n.a.	BMB*
5	18.55	n.a.	131.307	92.420	31.00	n.a.	BMB*
6	27.29	n.a.	102.925	92.901	31.17	n.a.	BMB*
Total:			610.301	298.087	100.00	0.000	

Chiral **4o**:



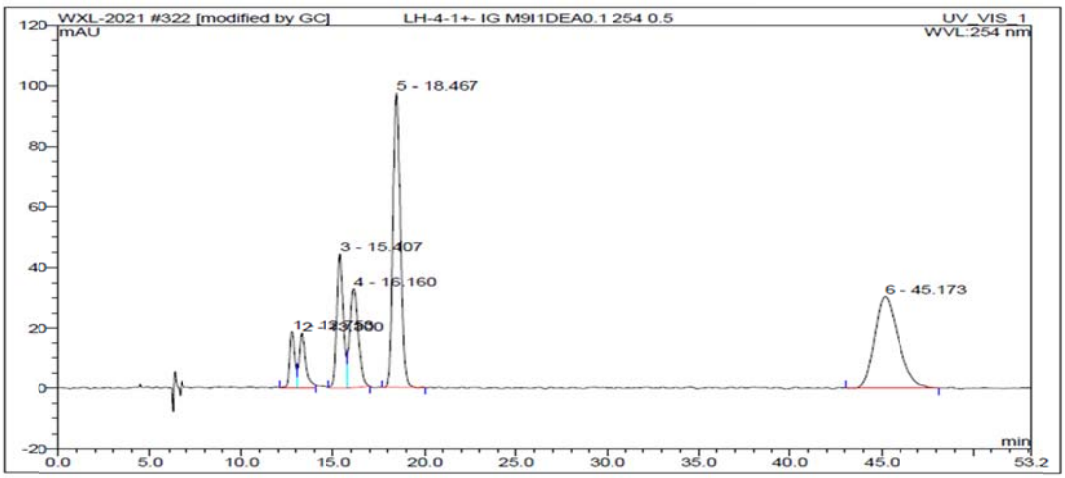
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.49	n.a.	743.970	533.605	98.59	n.a.	BMB*
2	27.40	n.a.	8.600	7.619	1.41	n.a.	BMB*
Total:			752.569	541.224	100.00	0.000	

Figure S47. HPLC traces of racemic **4o** (reference) and chiral **4o**. Area integration = 98.59:1.41 (97% *ee*).



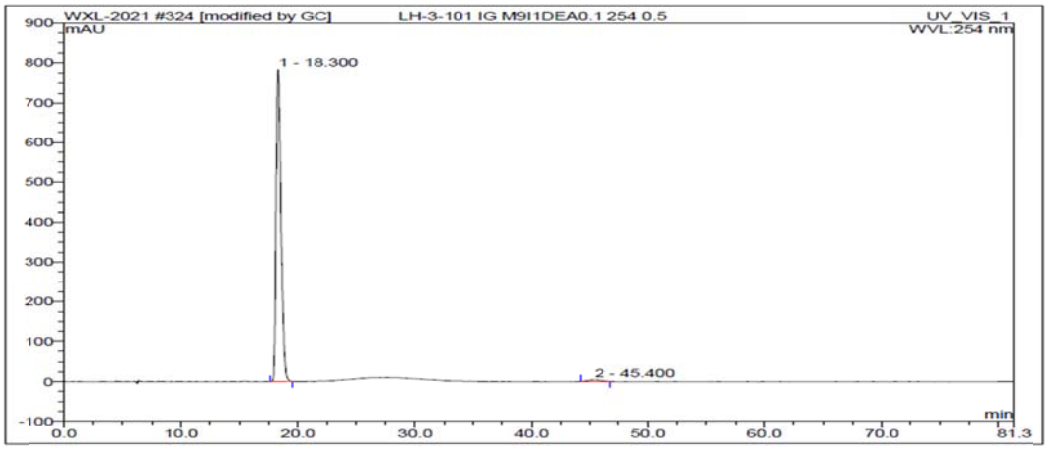
4p

Racemic **4p**:



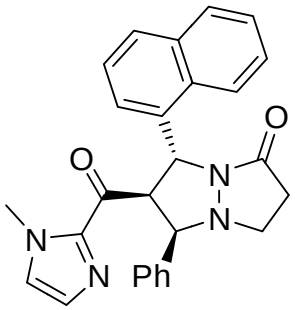
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.75	n.a.	18.739	5.903	4.18	n.a.	BM *
2	13.30	n.a.	18.316	7.535	5.33	n.a.	M *
3	15.41	n.a.	44.396	18.125	12.82	n.a.	M *
4	16.16	n.a.	32.894	17.984	12.72	n.a.	MB*
5	18.47	n.a.	97.587	46.086	32.60	n.a.	BMB*
6	45.17	n.a.	30.460	45.715	32.34	n.a.	BMB*
Total:			242.393	141.348	100.00	0.000	

Chiral **4p**:



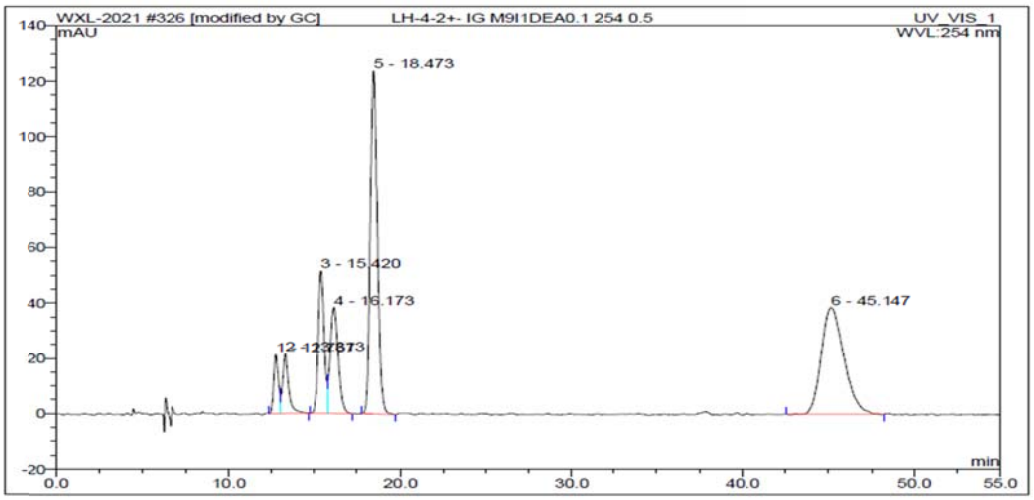
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.30	n.a.	783.768	378.567	98.50	n.a.	BMB
2	45.40	n.a.	4.291	5.756	1.50	n.a.	BMB*
Total:			788.059	384.324	100.00	0.000	

Figure S48. HPLC traces of racemic **4p** (reference) and chiral **4p**. Area integration = 98.50:1.50 (97% *ee*).



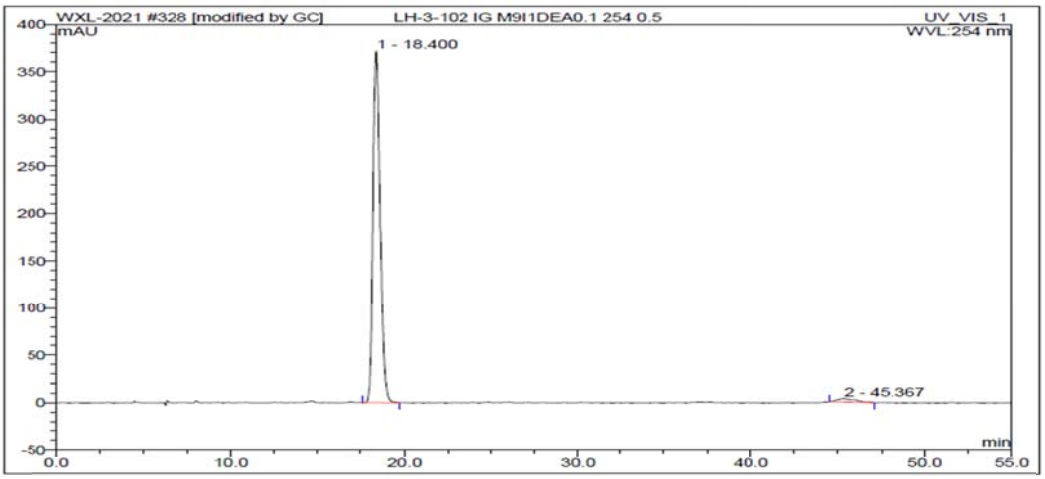
4q

Racemic **4q**:



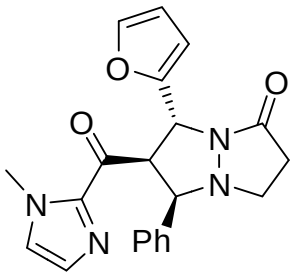
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.77	n.a.	21.344	6.775	3.88	n.a.	BM *
2	13.31	n.a.	21.500	8.607	4.93	n.a.	MB
3	15.42	n.a.	51.433	20.729	11.88	n.a.	BM
4	16.17	n.a.	38.384	20.924	11.99	n.a.	MB
5	18.47	n.a.	123.827	58.597	33.59	n.a.	BMB*
6	45.15	n.a.	38.679	58.819	33.72	n.a.	BMB*
Total:			295.167	174.450	100.00	0.000	

Chiral **4q**:



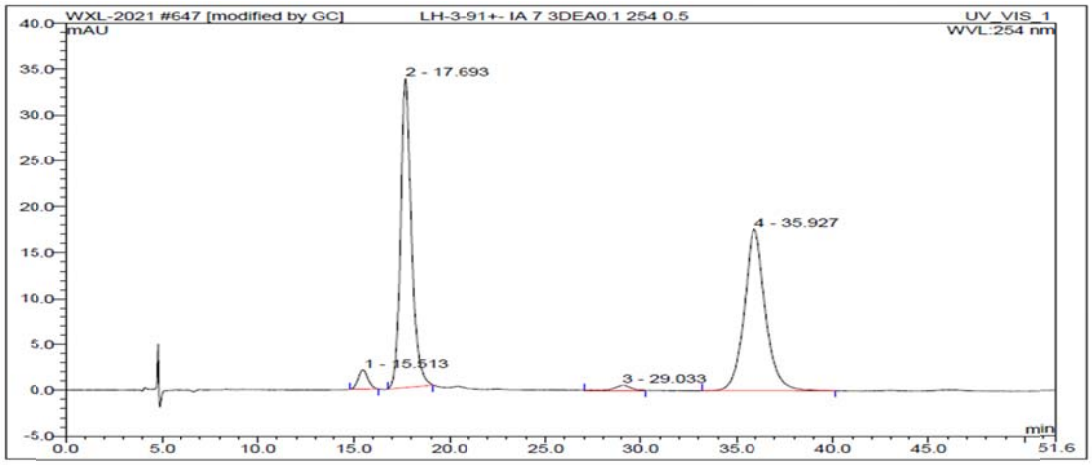
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.40	n.a.	371.881	176.032	97.53	n.a.	BMB*
2	45.37	n.a.	3.499	4.460	2.47	n.a.	BMB*
Total:			375.381	180.491	100.00	0.000	

Figure S49. HPLC traces of racemic **4q** (reference) and chiral **4q**. Area integration = 97.53:2.47 (95% *ee*).



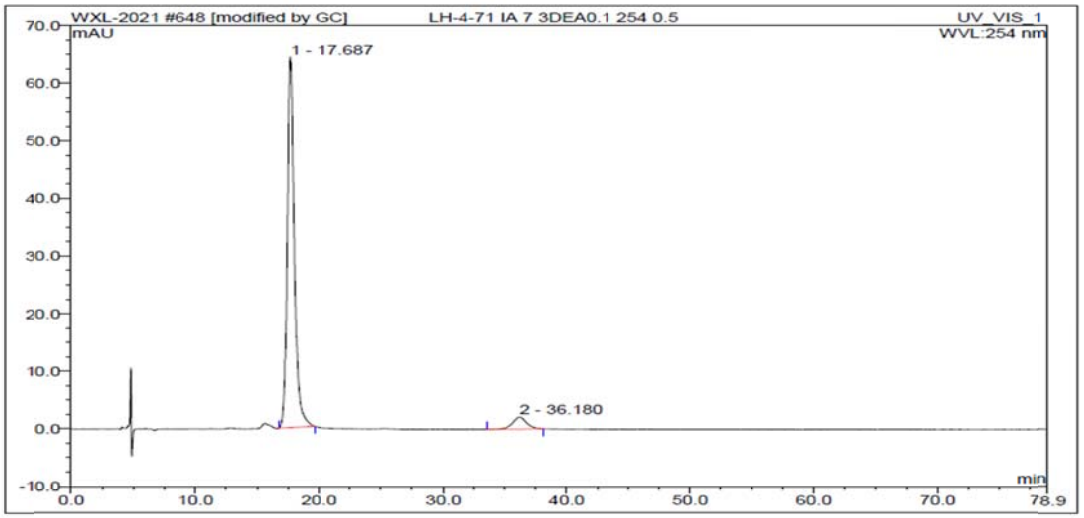
4r

Racemic **4r**:



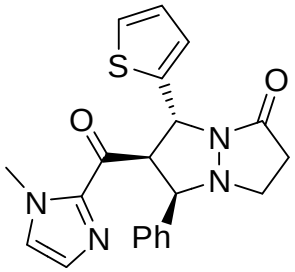
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.51	n.a.	2.077	1.208	2.60	n.a.	BMB
2	17.69	n.a.	33.703	21.868	47.14	n.a.	BMB
3	29.03	n.a.	0.537	0.493	1.06	n.a.	BMB*
4	35.93	n.a.	17.620	22.820	49.19	n.a.	BMB*
Total:			53.937	46.390	100.00	0.000	

Chiral **4r**:



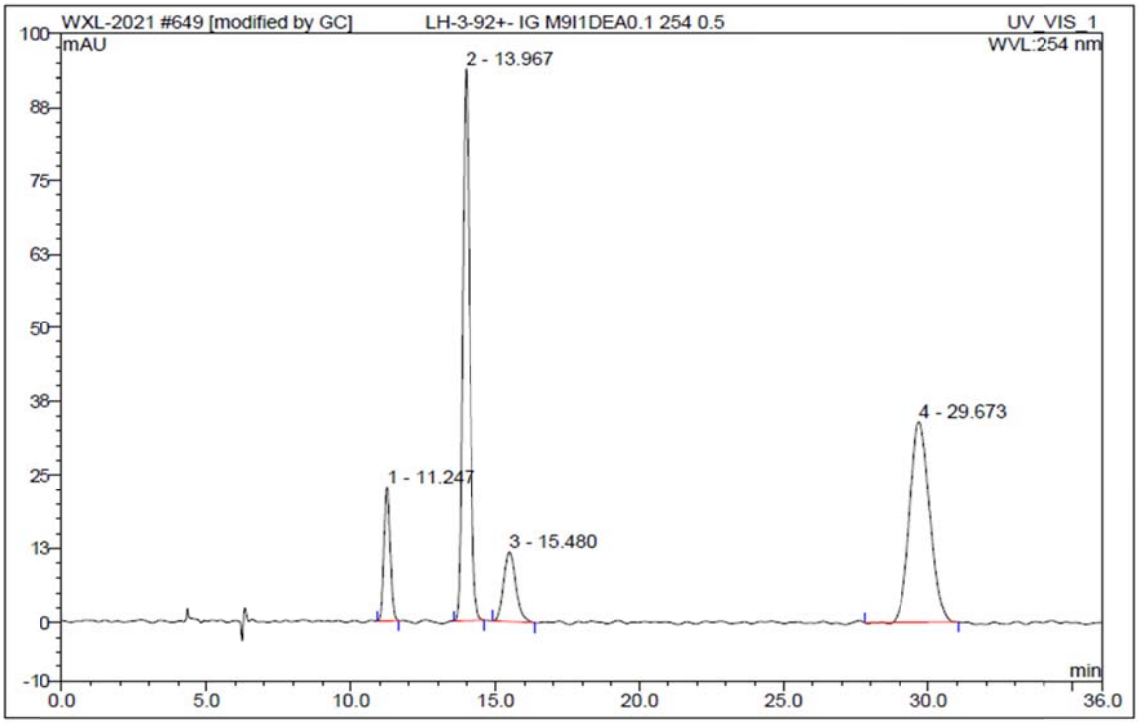
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.69	n.a.	64.360	42.409	93.98	n.a.	BMB
2	36.18	n.a.	2.081	2.717	6.02	n.a.	BMB*
Total:			66.441	45.126	100.00	0.000	

Figure S50. HPLC traces of racemic **4r** (reference) and chiral **4r**. Area integration =93.98:6.02 (88% *ee*).

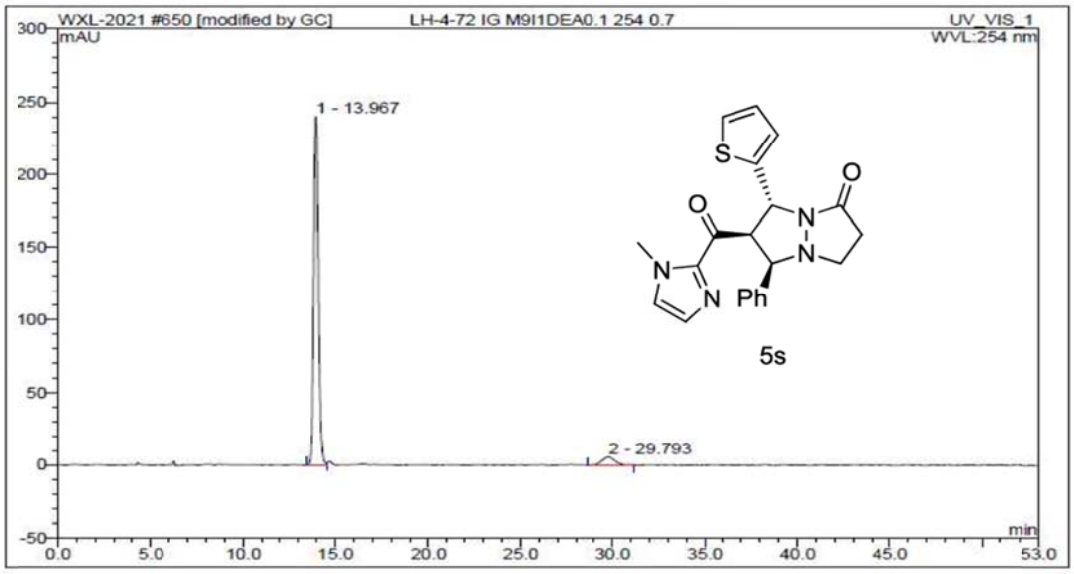


4s

Racemic **4s**:

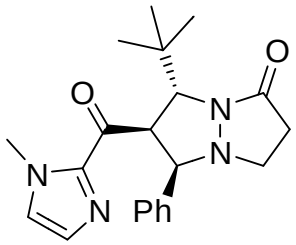


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.25	n.a.	22.692	5.599	8.51	n.a.	BMB
2	13.97	n.a.	93.689	27.140	41.26	n.a.	BMB
3	15.48	n.a.	11.678	5.755	8.75	n.a.	BMB
4	29.67	n.a.	34.000	27.284	41.48	n.a.	BMB*
Total:			162.059	65.777	100.00	0.000	



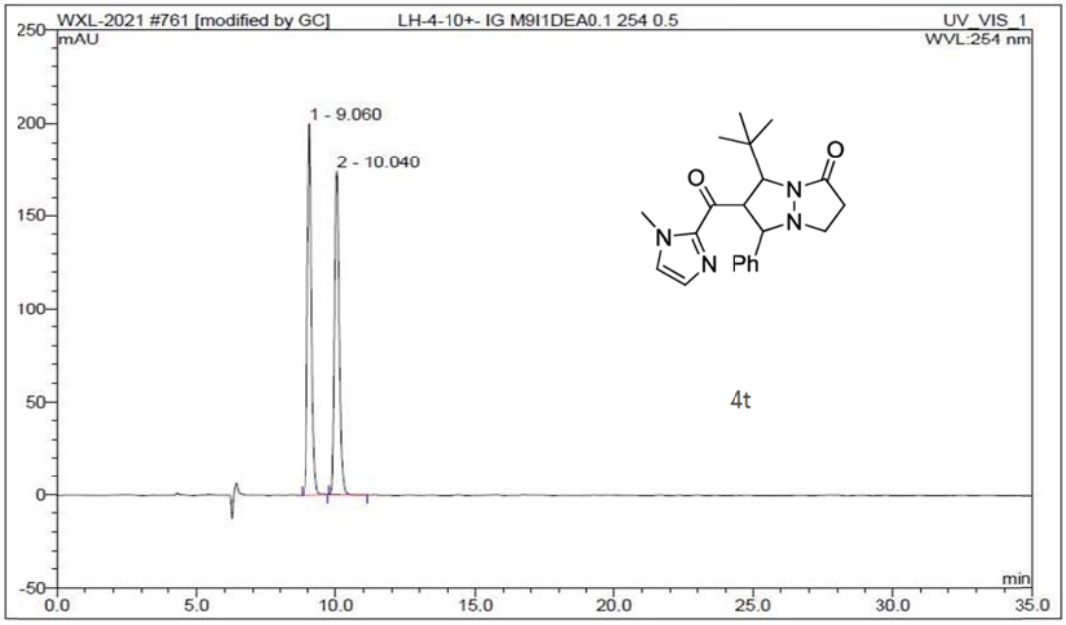
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.97	n.a.	240.627	70.885	93.61	n.a.	BM *
2	29.79	n.a.	5.890	4.839	6.39	n.a.	BMB*
Total:			246.517	75.724	100.00	0.000	

Figure S51. HPLC traces of racemic **4s** (reference) and chiral **4s**. Area integration = 99.5:0.5 (99% *ee*).



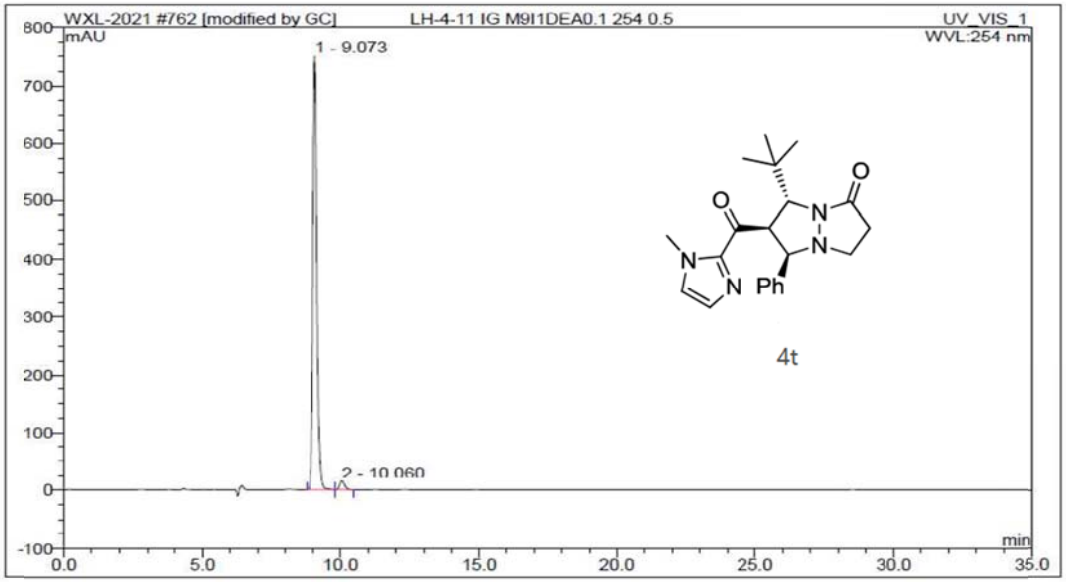
4t

Racemic 4t



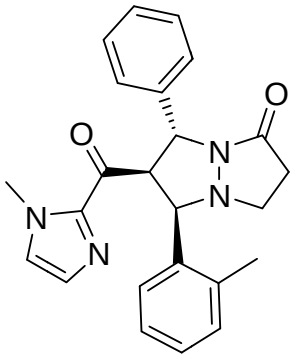
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.06	n.a.	200.405	34.176	50.04	n.a.	BMB*
2	10.04	n.a.	174.068	34.115	49.96	n.a.	BMB*
Total:			374.474	68.291	100.00	0.000	

Chiral 4t



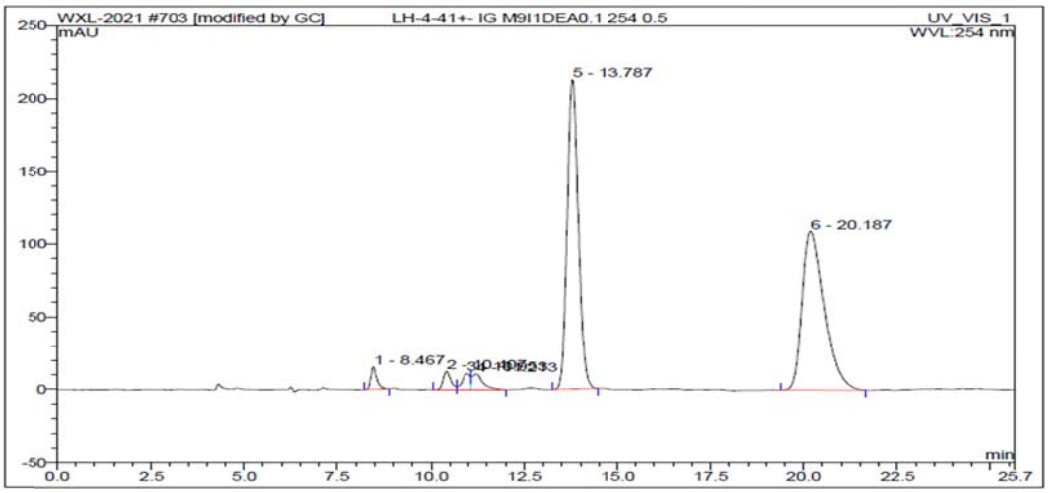
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.07	n.a.	751.390	129.903	97.69	n.a.	BM
2	10.06	n.a.	15.700	3.072	2.31	n.a.	MB
Total:			767.090	132.975	100.00	0.000	

Figure S52. HPLC traces of racemic **4t** (reference) and chiral **4t**. Area integration = 97.69:2.31 (95% *ee*).



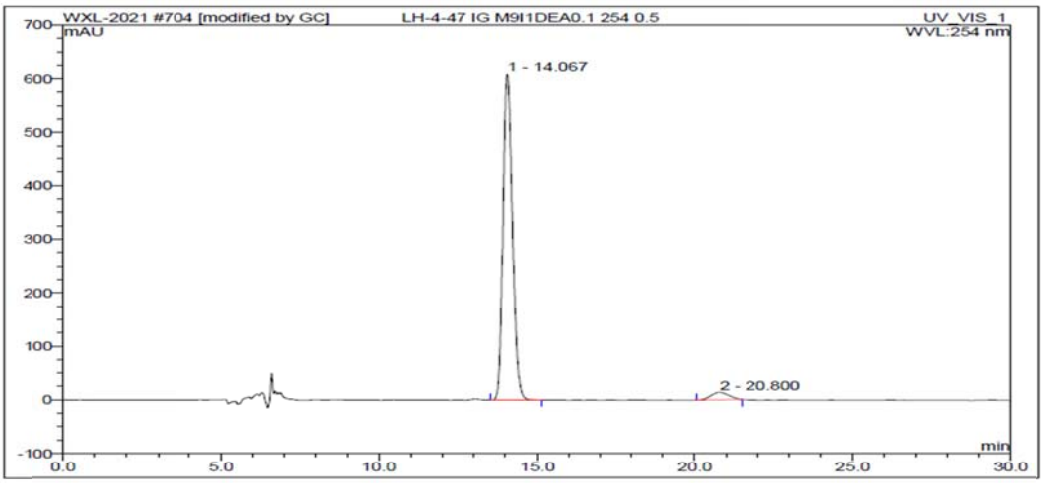
5a

Racemic **5a**:



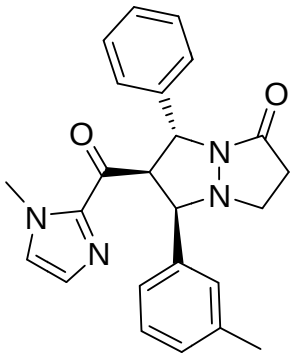
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.47	n.a.	15.586	2.793	1.74	n.a.	BMB
2	10.41	n.a.	12.726	2.975	1.85	n.a.	BM
3	10.95	n.a.	11.131	2.815	1.75	n.a.	M
4	11.21	n.a.	10.879	3.534	2.20	n.a.	MB
5	13.79	n.a.	212.698	74.056	46.05	n.a.	BMB
6	20.19	n.a.	109.248	74.633	46.41	n.a.	BMB
Total:			372.267	160.806	100.00	0.000	

Chiral **5a**:



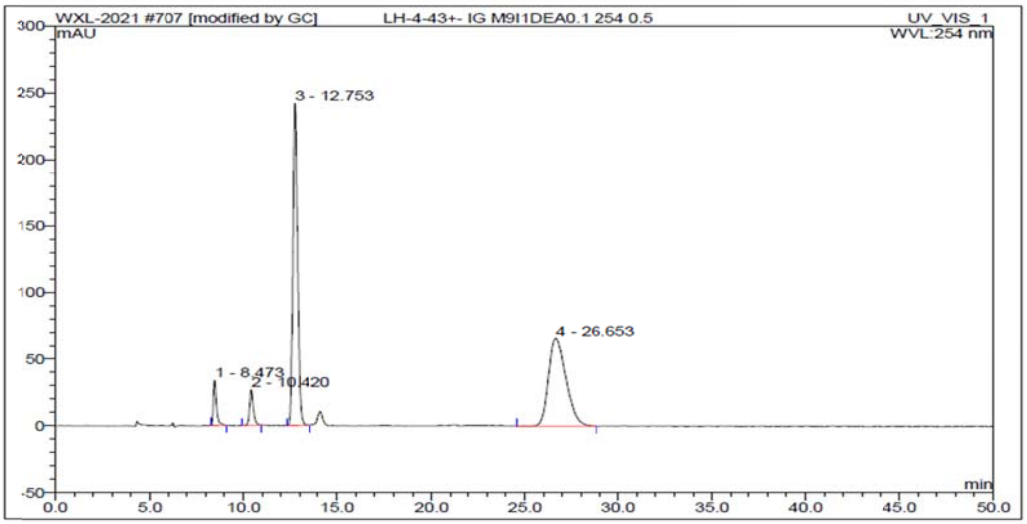
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.07	n.a.	608.942	212.358	95.88	n.a.	BMB
2	20.80	n.a.	13.882	9.130	4.12	n.a.	BMB*
Total:			622.824	221.488	100.00	0.000	

Figure S53. HPLC traces of racemic **5a** (reference) and chiral **5a**. Area integration = 95.88:4.12 (92% *ee*).



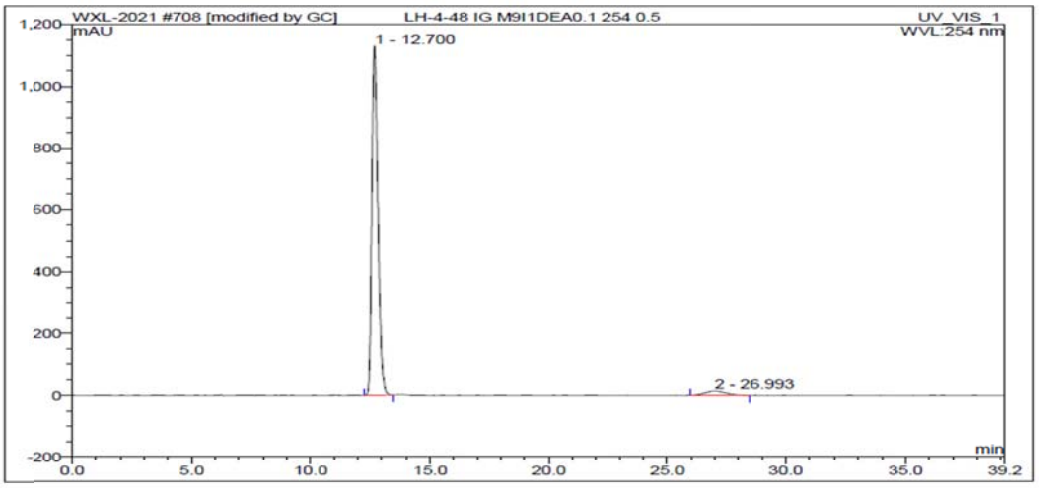
5b

Racemic **5b**:



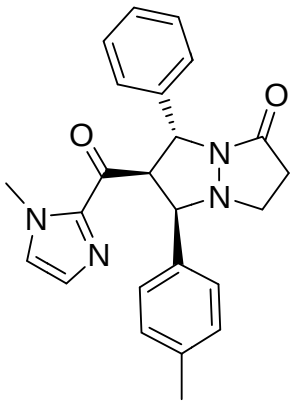
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.47	n.a.	33.821	6.268	4.07	n.a.	BMB
2	10.42	n.a.	26.555	6.101	3.96	n.a.	BMB
3	12.75	n.a.	242.418	70.411	45.74	n.a.	BMB*
4	26.65	n.a.	66.325	71.152	46.22	n.a.	BMB*
Total:			369.120	153.931	100.00	0.000	

Chiral **5b**:



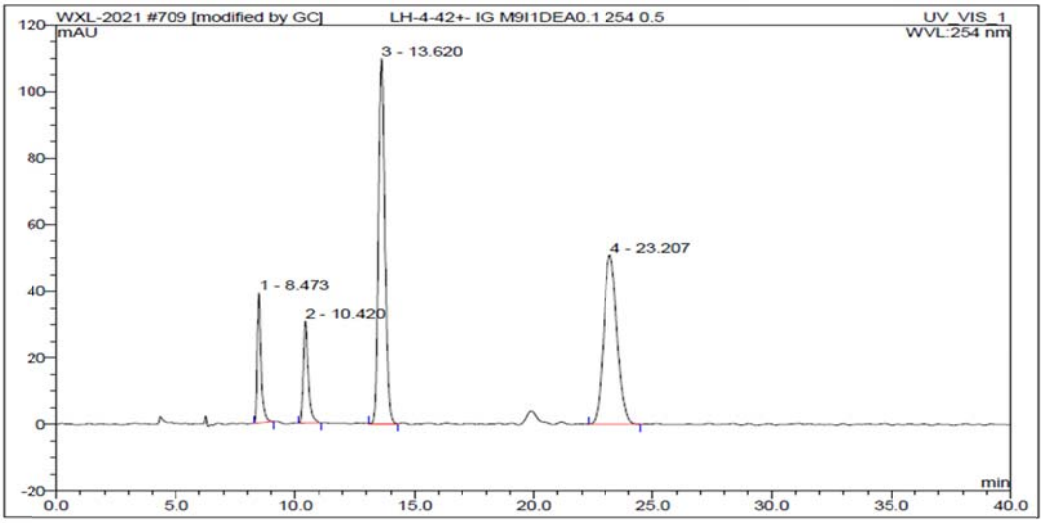
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.70	n.a.	1130.361	336.130	95.93	n.a.	BMB*
2	26.99	n.a.	13.636	14.256	4.07	n.a.	BMB*
Total:			1143.997	350.386	100.00	0.000	

Figure S54. HPLC traces of racemic **5b** (reference) and chiral **5b**. Area integration = 95.93:4.07 (92% *ee*).



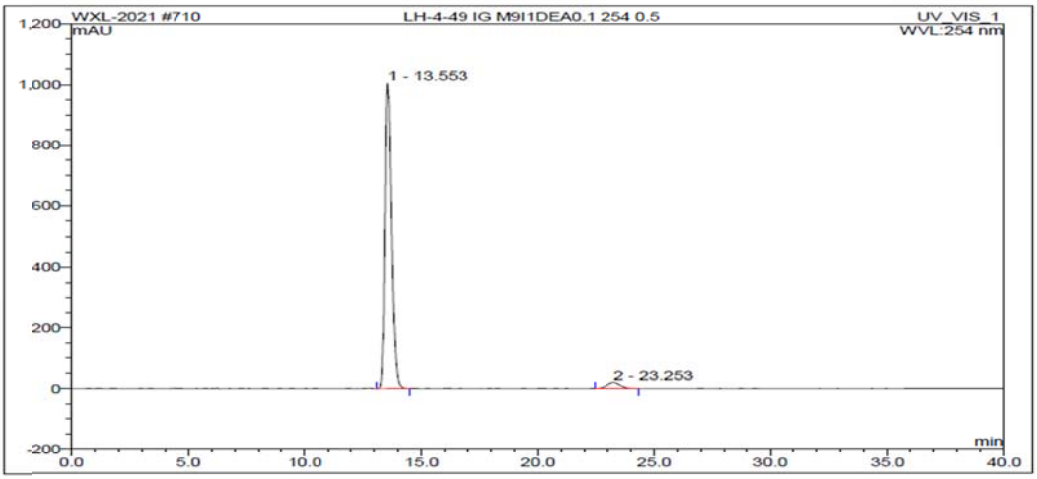
5c

Racemic **5c**:



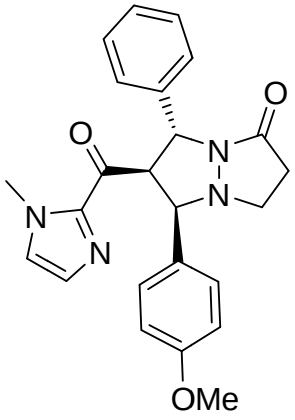
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.47	n.a.	39.181	7.212	8.72	n.a.	BMB
2	10.42	n.a.	30.784	7.263	8.78	n.a.	BMB
3	13.62	n.a.	109.793	34.042	41.16	n.a.	BMB
4	23.21	n.a.	50.955	34.186	41.34	n.a.	BMB
Total:			230.713	82.703	100.00	0.000	

Chiral **5c**:



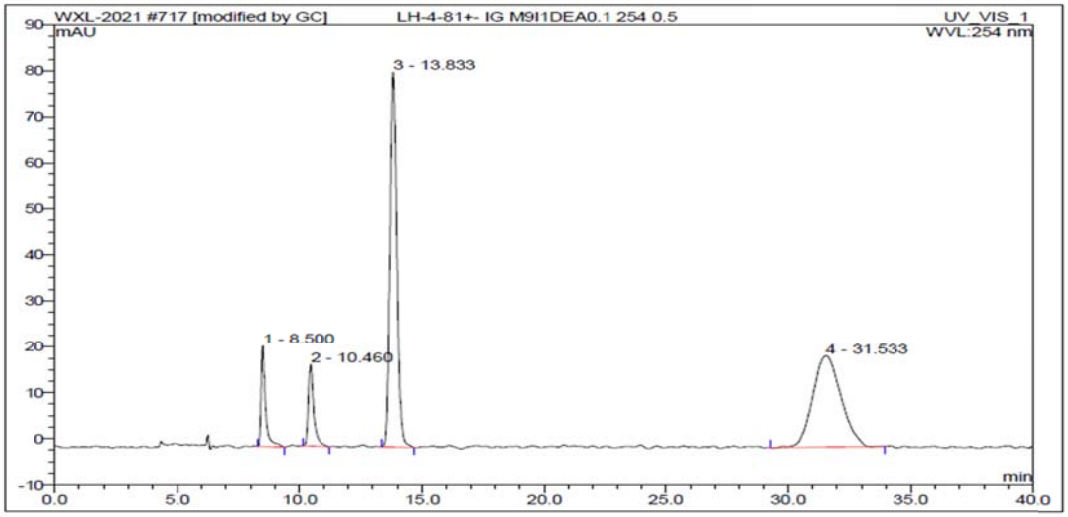
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.55	n.a.	1006.245	324.461	96.09	n.a.	BMB
2	23.25	n.a.	19.898	13.216	3.91	n.a.	BMB
Total:			1026.143	337.676	100.00	0.000	

Figure S55. HPLC traces of racemic **5c** (reference) and chiral **5c**. Area integration = 96.09:3.91 (92% *ee*).



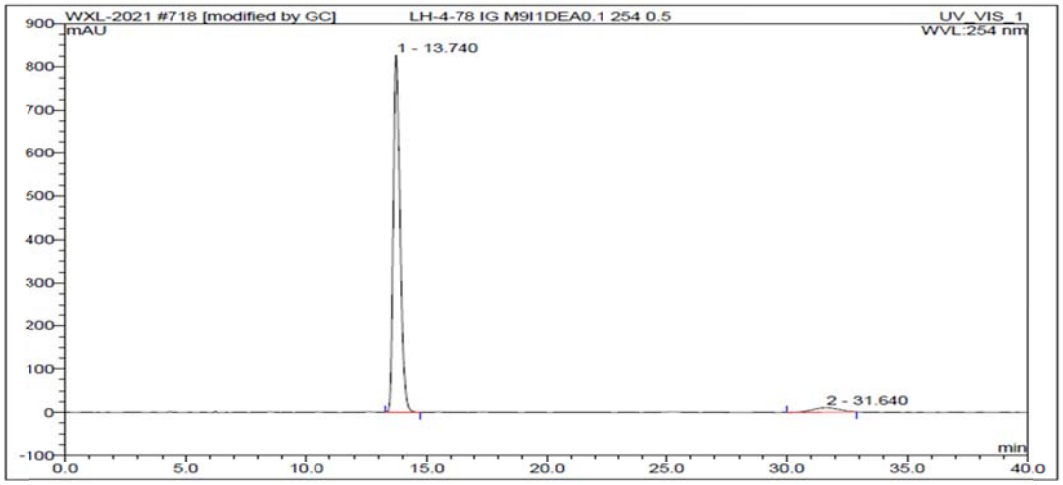
5d

Racemic **5d**:



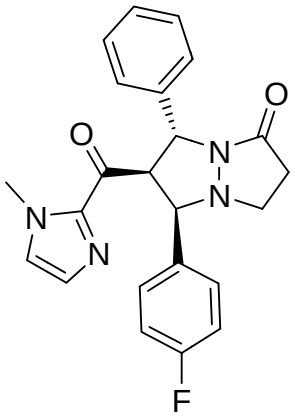
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.50	n.a.	21.921	4.557	7.36	n.a.	BMB
2	10.46	n.a.	17.739	4.527	7.31	n.a.	BMB
3	13.83	n.a.	81.594	26.410	42.66	n.a.	BMB
4	31.53	n.a.	19.864	26.412	42.66	n.a.	BMB*
Total:			141.117	61.906	100.00	0.000	

Chiral **5d**:



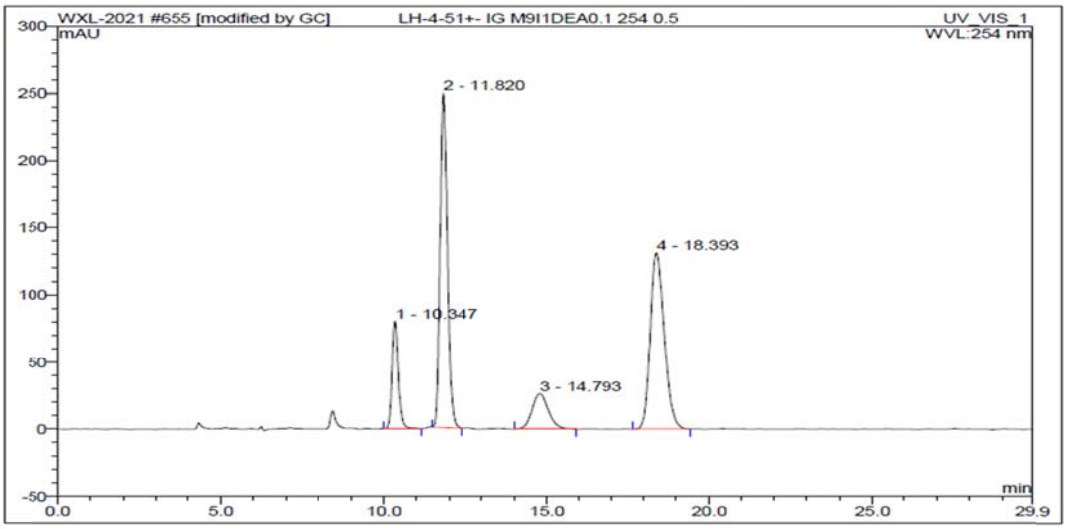
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.74	n.a.	826.644	268.082	95.47	n.a.	BMB
2	31.64	n.a.	10.365	12.722	4.53	n.a.	BMB*
Total:			837.009	280.805	100.00	0.000	

Figure S56. HPLC traces of racemic **5d** (reference) and chiral **5d**. Area integration = 95.47:4.53 (91% *ee*).



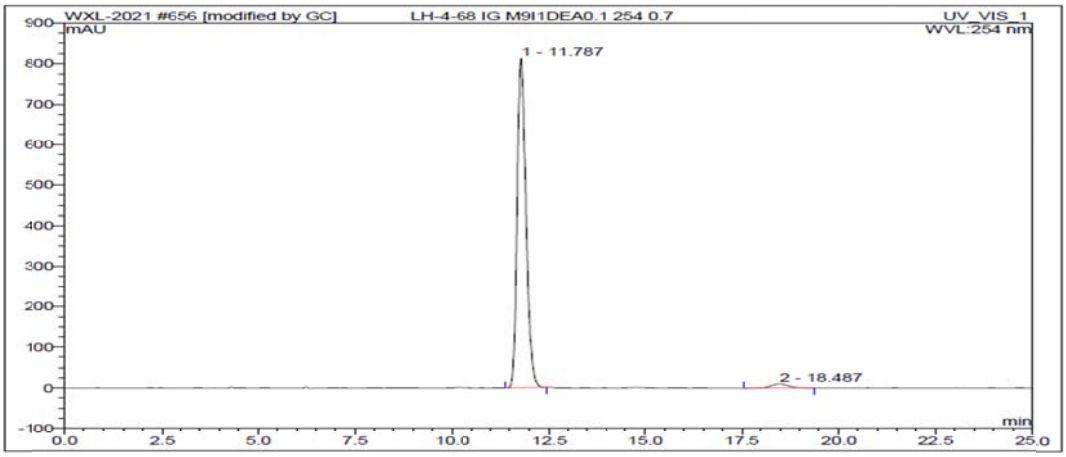
5e

Racemic **5e**:



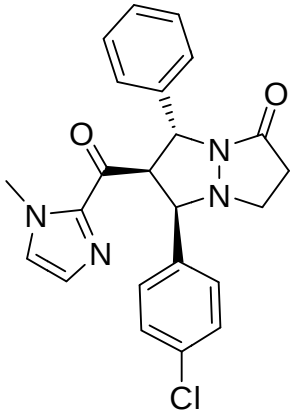
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.35	n.a.	80.831	17.787	10.89	n.a.	BMB
2	11.82	n.a.	249.318	64.643	39.59	n.a.	BMB
3	14.79	n.a.	26.684	15.429	9.45	n.a.	BMB
4	18.39	n.a.	131.186	65.422	40.07	n.a.	BMB
Total:			488.019	163.281	100.00	0.000	

Chiral **5e**:



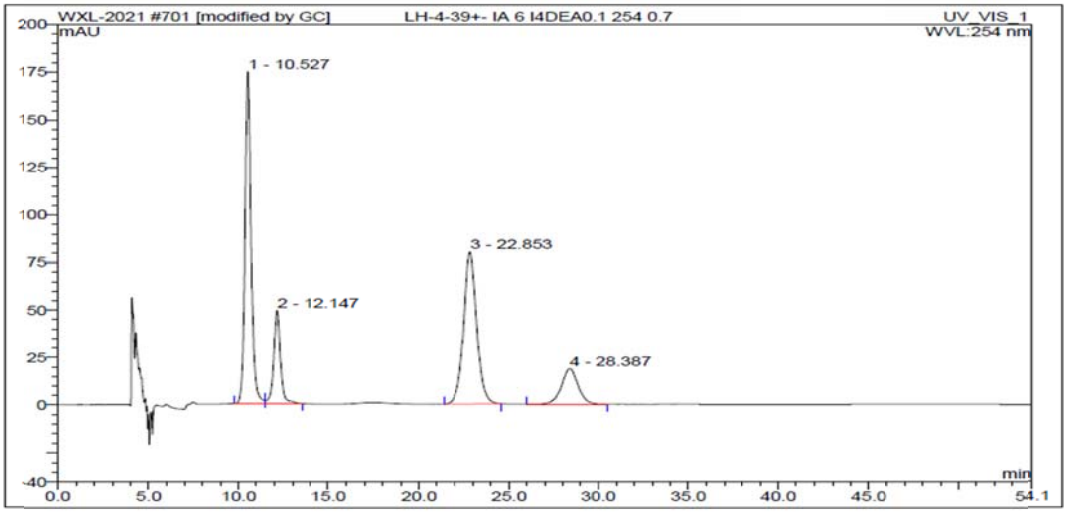
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.79	n.a.	811.693	213.785	97.54	n.a.	BMB
2	18.49	n.a.	10.167	5.401	2.46	n.a.	BMB
Total:			821.859	219.186	100.00	0.000	

Figure S57. HPLC traces of racemic **5e** (reference) and chiral **5e**. Area integration = 97.54:2.46 (95% ee).



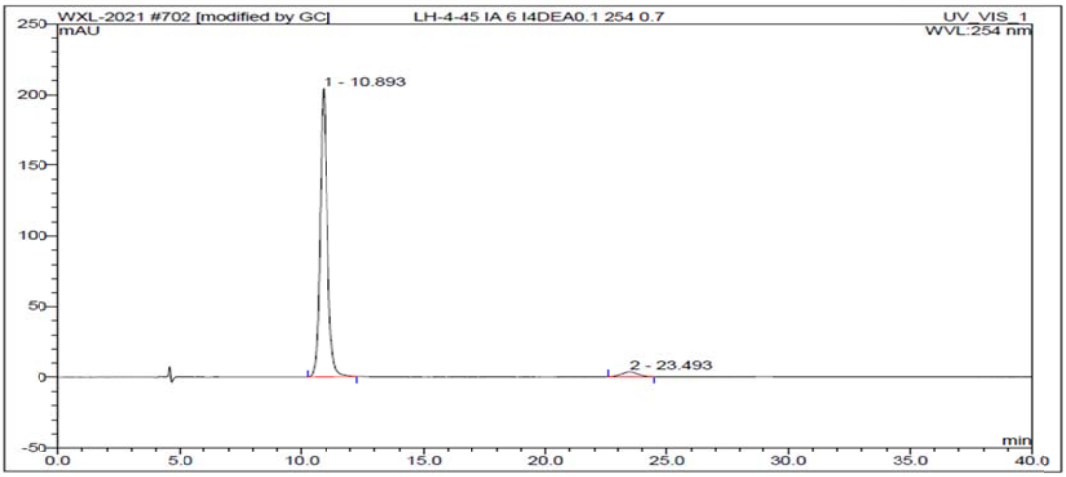
5f

Racemic **5f**:



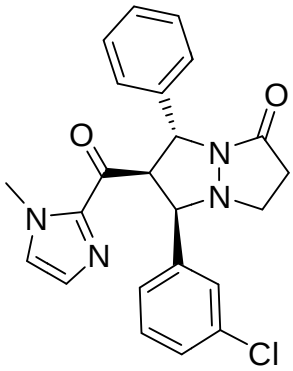
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.53	n.a.	174.567	68.573	38.53	n.a.	BM
2	12.15	n.a.	49.336	21.279	11.96	n.a.	MB
3	22.85	n.a.	80.056	68.052	38.24	n.a.	BMB
4	28.39	n.a.	18.819	20.078	11.28	n.a.	BMB*
Total:			322.778	177.982	100.00	0.000	

Chiral **5f**:



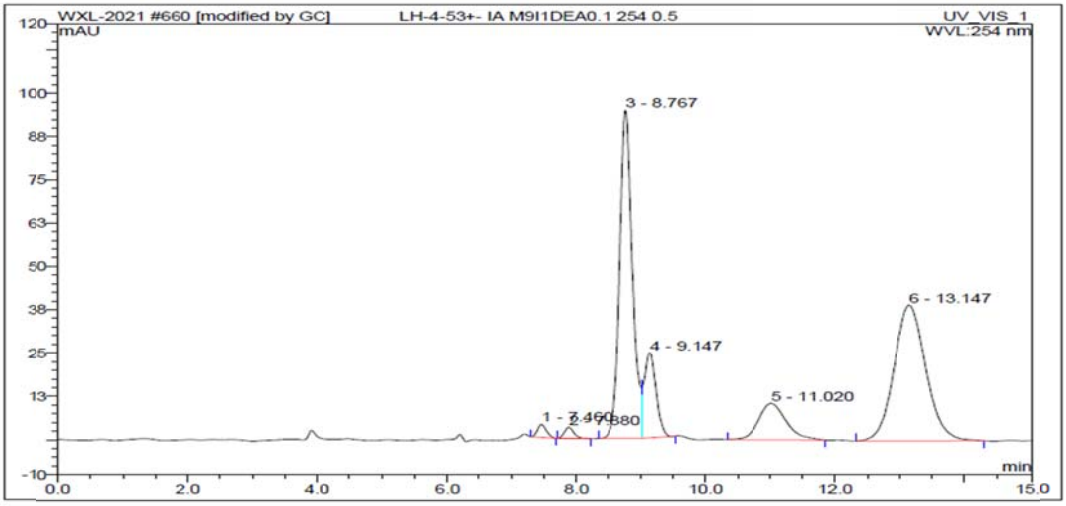
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.89	n.a.	204.041	73.309	96.53	n.a.	BMB
2	23.49	n.a.	3.426	2.637	3.47	n.a.	BMB
Total:			207.467	75.946	100.00	0.000	

Figure S58. HPLC traces of racemic **5f** (reference) and chiral **5f**. Area integration = 96.53:3.47 (93% *ee*).



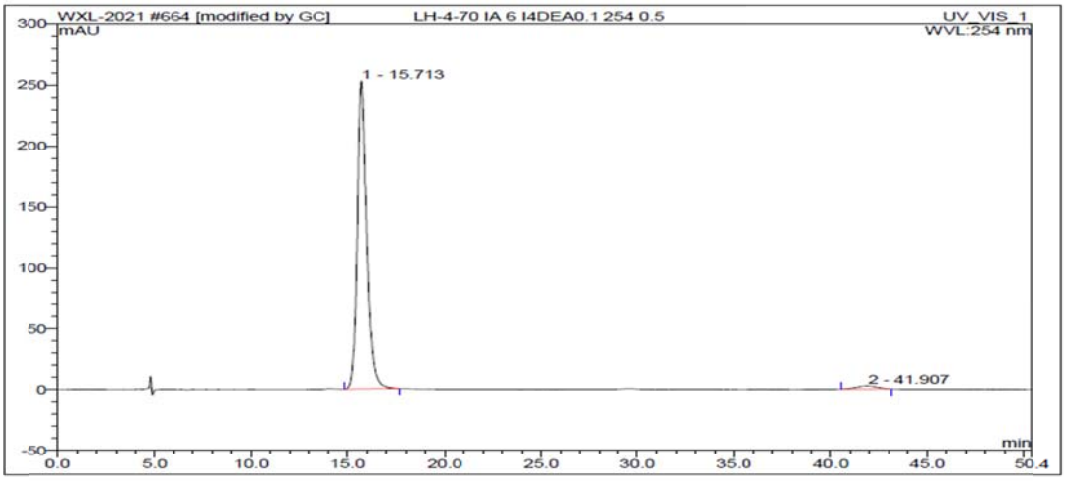
5g

Racemic **5g**:



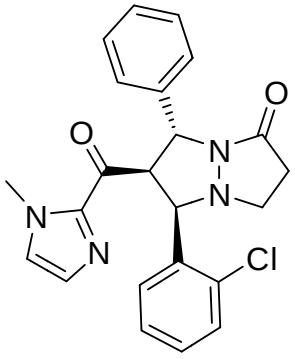
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.46	n.a.	3.686	0.589	1.06	n.a.	BMB
2	7.88	n.a.	3.194	0.551	0.99	n.a.	BMB
3	8.77	n.a.	94.785	21.799	39.13	n.a.	BM *
4	9.15	n.a.	24.451	5.158	9.26	n.a.	MB*
5	11.02	n.a.	10.455	5.164	9.27	n.a.	BMB
6	13.15	n.a.	39.165	22.448	40.29	n.a.	BMB
Total:			175.736	55.708	100.00	0.000	

Chiral **5g**:



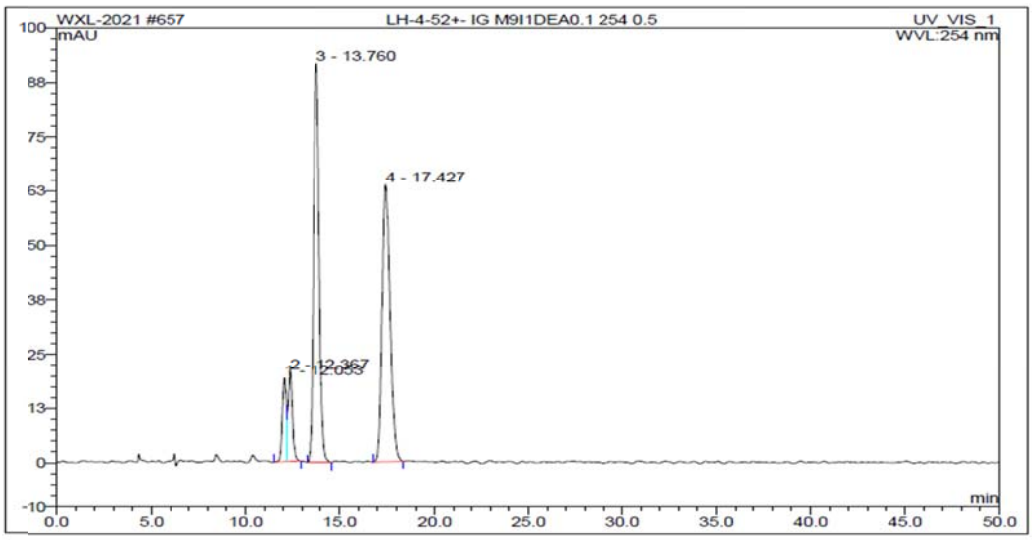
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.71	n.a.	253.271	140.908	97.78	n.a.	BMB
2	41.91	n.a.	2.559	3.202	2.22	n.a.	BMB
Total:			255.830	144.109	100.00	0.000	

Figure S59. HPLC traces of racemic **5g** (reference) and chiral **5g**. Area integration = 97.78:2.22 (96% *ee*).



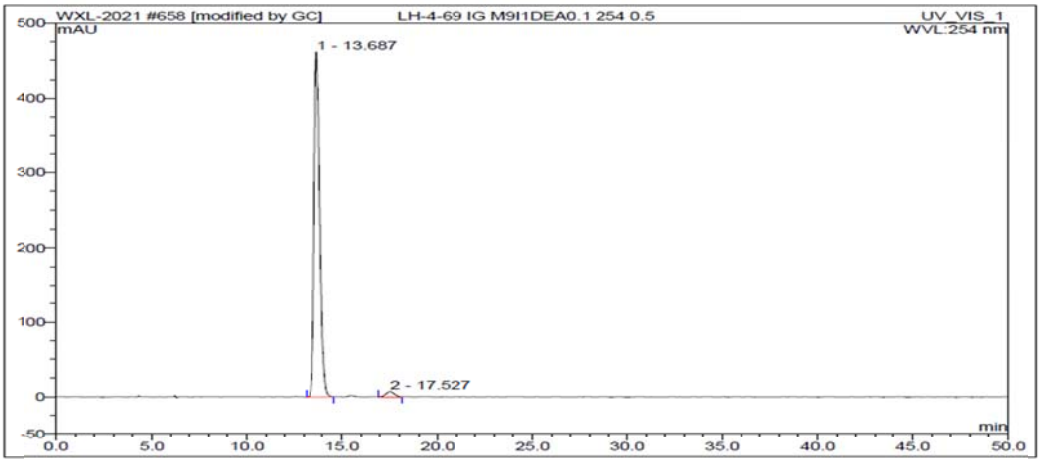
5h

Racemic **5h**:



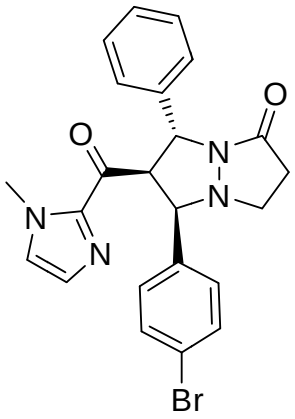
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.05	n.a.	19.234	4.835	6.58	n.a.	BM
2	12.37	n.a.	20.536	5.373	7.31	n.a.	MB
3	13.76	n.a.	91.672	31.892	43.40	n.a.	BMB
4	17.43	n.a.	63.740	31.376	42.70	n.a.	BMB
Total:			195.183	73.476	100.00	0.000	

Chiral **5h:**



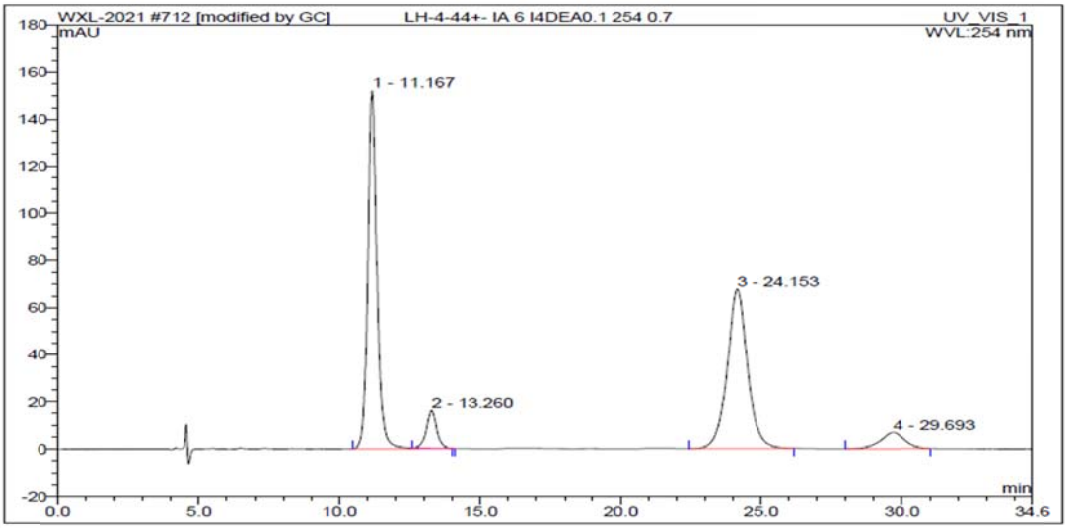
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.69	n.a.	461.567	161.946	97.86	n.a.	BMB
2	17.53	n.a.	7.044	3.546	2.14	n.a.	BMB
Total:			468.610	165.492	100.00	0.000	

Figure S60. HPLC traces of racemic **5h** (reference) and chiral **5h**. Area integration = 97.86:2.14 (96% *ee*).



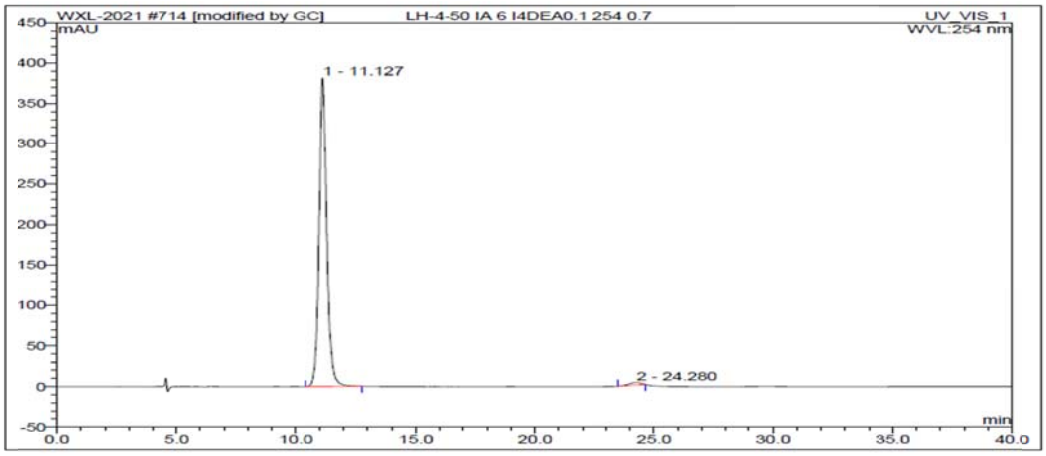
5i

Racemic **5i**:



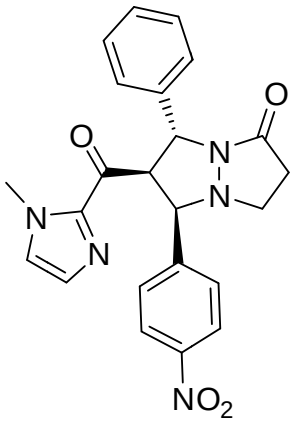
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.17	n.a.	152.209	57.187	45.02	n.a.	BMB
2	13.26	n.a.	15.882	6.562	5.17	n.a.	Rd
3	24.15	n.a.	67.823	56.857	44.76	n.a.	BMB*
4	29.69	n.a.	6.679	6.417	5.05	n.a.	BMB*
Total:			242.592	127.022	100.00	0.000	

Chiral **5i**:



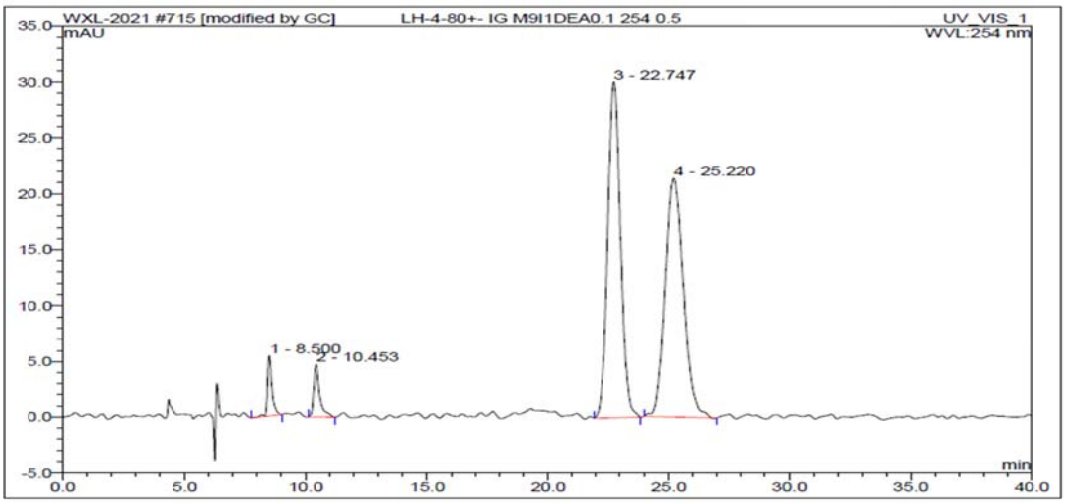
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.13	n.a.	381.714	141.193	98.67	n.a.	BMB
2	24.28	n.a.	3.281	1.900	1.33	n.a.	BMB
Total:			384.995	143.093	100.00	0.000	

Figure S61. HPLC traces of racemic **5i** (reference) and chiral **5i**. Area integration = 98.67:1.33 (97% *ee*).



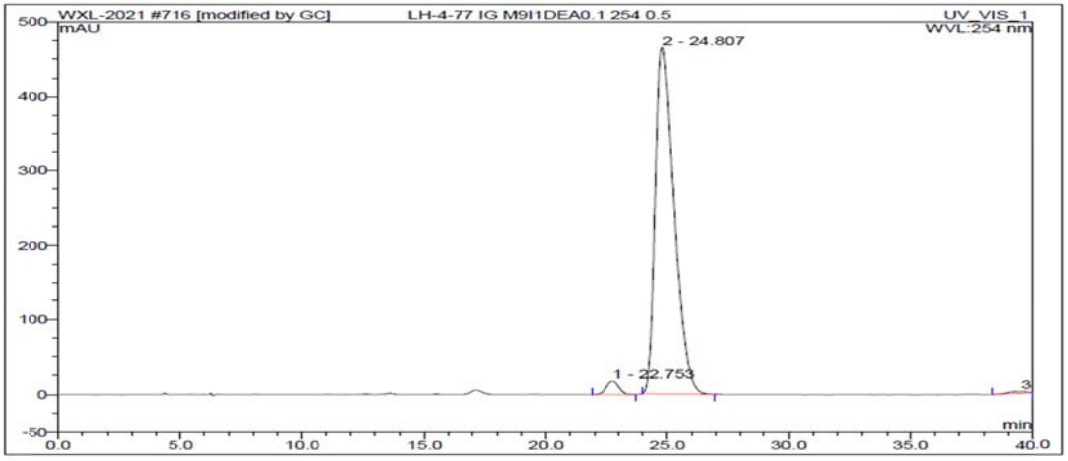
5j

Racemic **5j**:



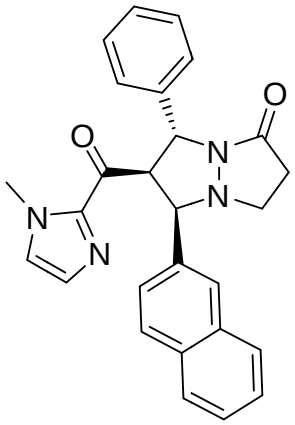
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.50	n.a.	5.464	1.152	2.89	n.a.	BMB*
2	10.45	n.a.	4.739	1.352	3.39	n.a.	BMB
3	22.75	n.a.	30.089	18.629	46.74	n.a.	BMB
4	25.22	n.a.	21.383	18.727	46.98	n.a.	BMB*
Total:			61.675	39.860	100.00	0.000	

Chiral **5j**:



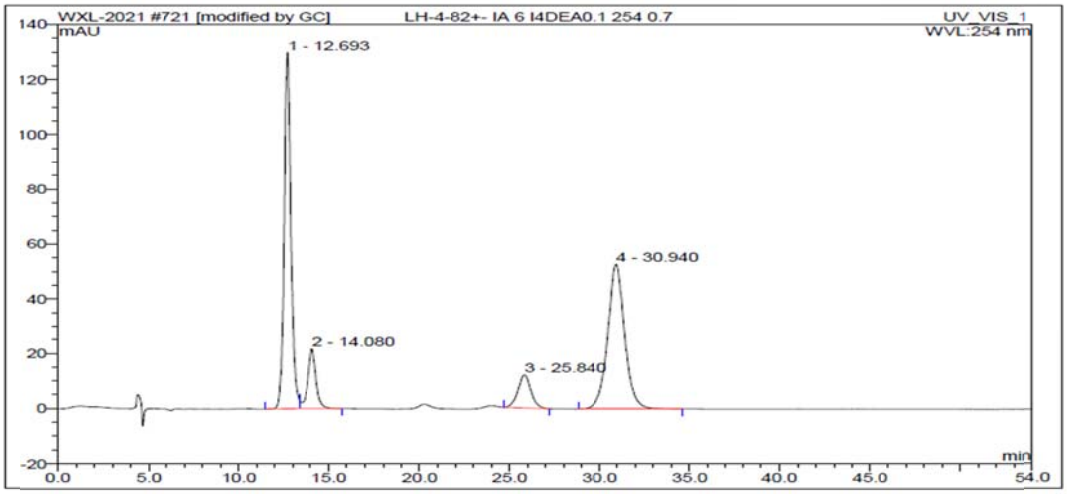
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.75	n.a.	18.014	10.803	2.55	n.a.	BMB
2	24.81	n.a.	464.918	410.544	96.93	n.a.	BMB*
3	39.53	n.a.	2.426	2.197	0.52	n.a.	BMB
Total:			485.358	423.543	100.00	0.000	

Figure S62. HPLC traces of racemic **5j** (reference) and chiral **5j**. Area integration = 96.5:3.5 (93% *ee*).



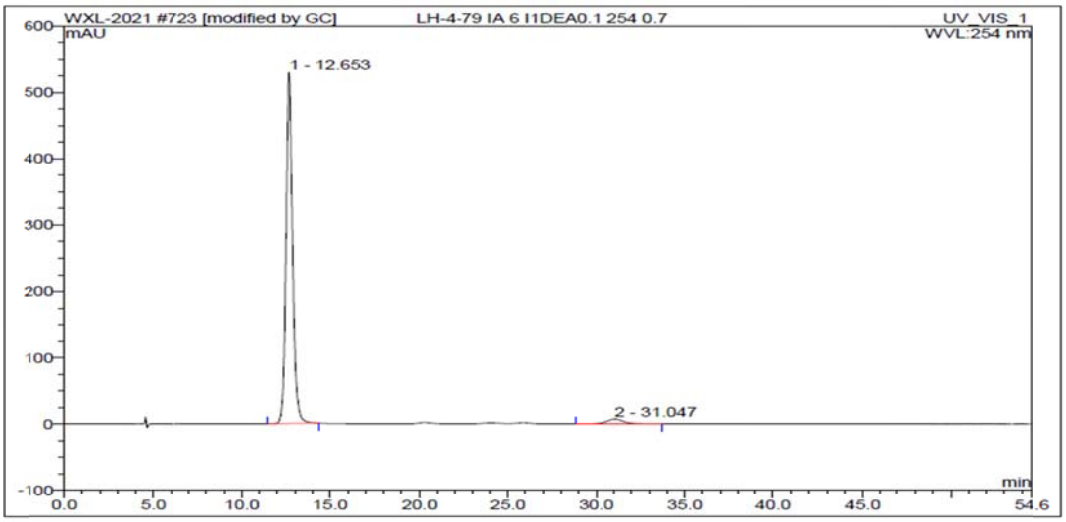
5k

Racemic **5k**:



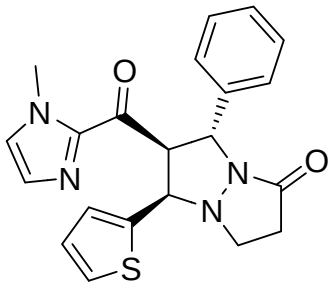
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.69	n.a.	129.969	56.049	41.56	n.a.	BM *
2	14.08	n.a.	21.703	11.556	8.57	n.a.	MB*
3	25.84	n.a.	12.006	9.908	7.35	n.a.	BMB*
4	30.94	n.a.	52.807	57.334	42.52	n.a.	BMB*
Total:			216.485	134.847	100.00	0.000	

Chiral **5k**



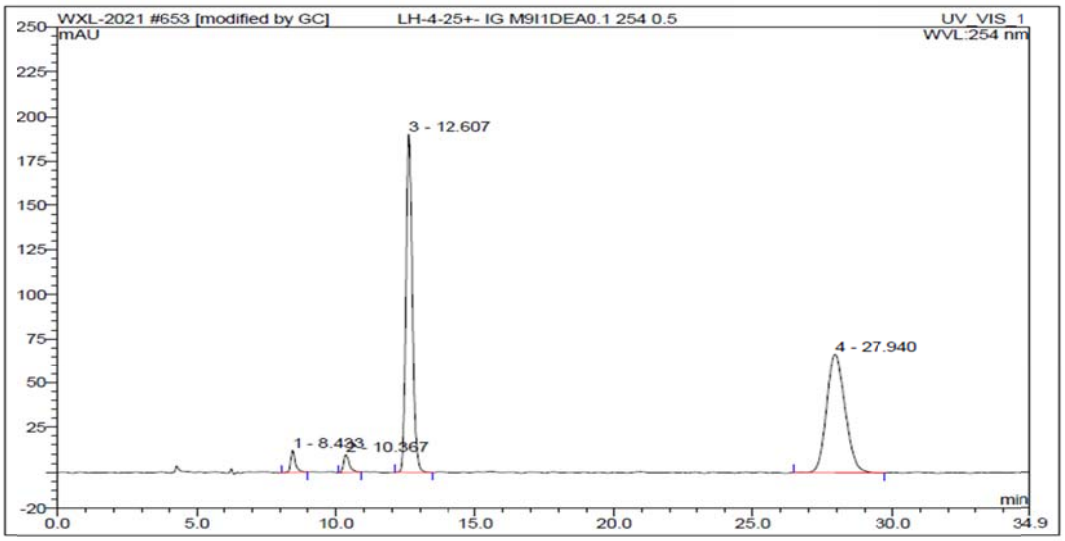
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.65	n.a.	530.019	226.527	96.52	n.a.	BMB*
2	31.05	n.a.	7.358	8.176	3.48	n.a.	BMB*
Total:			537.377	234.703	100.00	0.000	

Figure S63. HPLC traces of racemic **5k** (reference) and chiral **5k**. Area integration = 96.52:3.48 (93% *ee*).



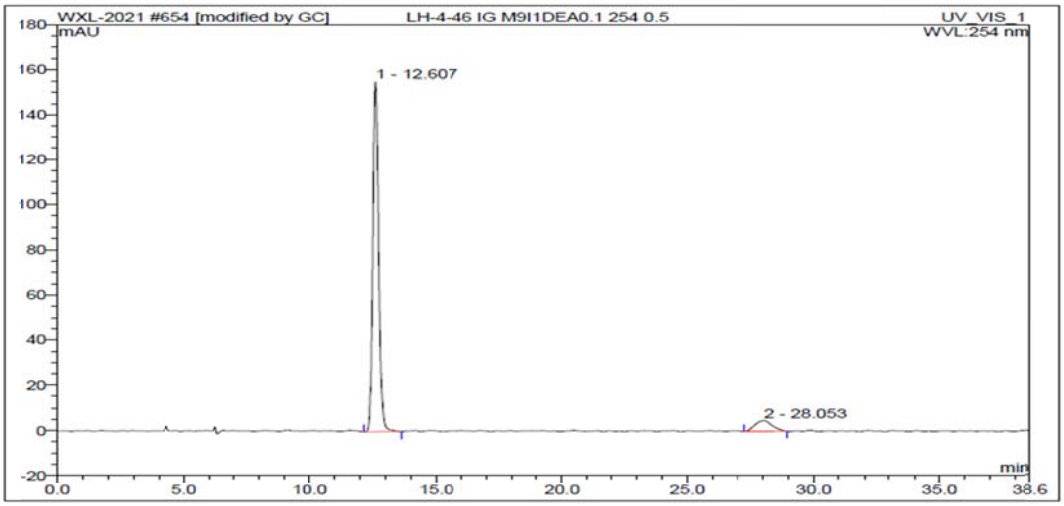
5l

Racemic **5l**:



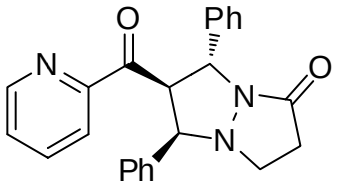
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.43	n.a.	11.999	2.373	2.27	n.a.	BMB
2	10.37	n.a.	9.619	2.308	2.21	n.a.	BMB
3	12.61	n.a.	190.235	49.810	47.65	n.a.	BMB
4	27.94	n.a.	66.430	50.041	47.87	n.a.	BMB*
Total:			278.284	104.532	100.00	0.000	

Chiral **5l**:



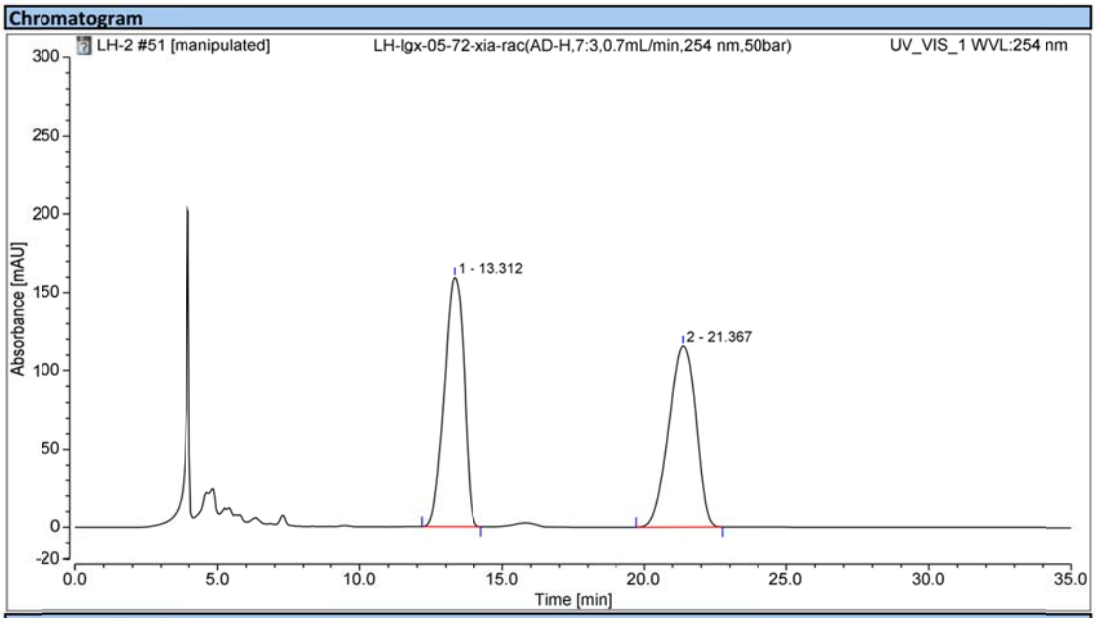
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.61	n.a.	155.383	41.030	91.75	n.a.	BMB
2	28.05	n.a.	4.736	3.691	8.25	n.a.	BMB*
Total:			160.119	44.721	100.00	0.000	

Figure S64. HPLC traces of racemic **5l** (reference) and chiral **5l**. Area integration = 91.75:8.25 (84% *ee*).



6

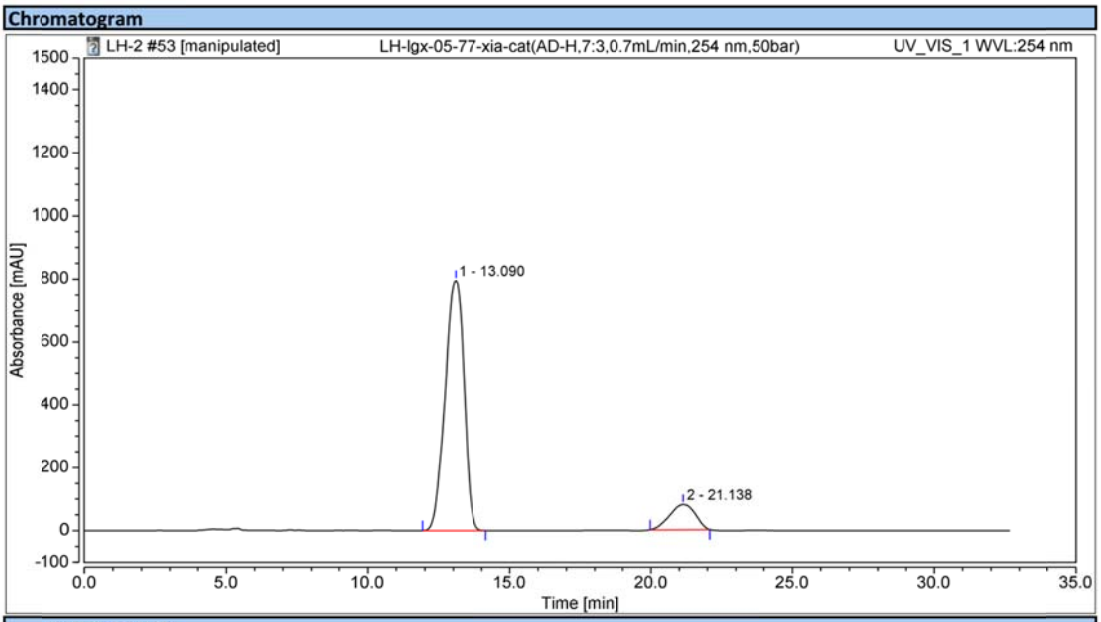
Racemic **6**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.312	127.924	159.375	49.96	57.94	n.a.
2		21.367	128.144	115.678	50.04	42.06	n.a.
Total:			**256.067**	**275.053**	**100.00**	**100.00**	

Chiral **6**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.090	616.160	795.149	88.05	90.88	n.a.
2		21.138	83.652	79.826	11.95	9.12	n.a.
Total:			**699.812**	**874.975**	**100.00**	**100.00**	

Figure S65. HPLC traces of racemic **6** (reference) and chiral **6**. Area integration = 88.05:11.95 (76% *ee*).

7. X-Ray Crystallography

Product 4i

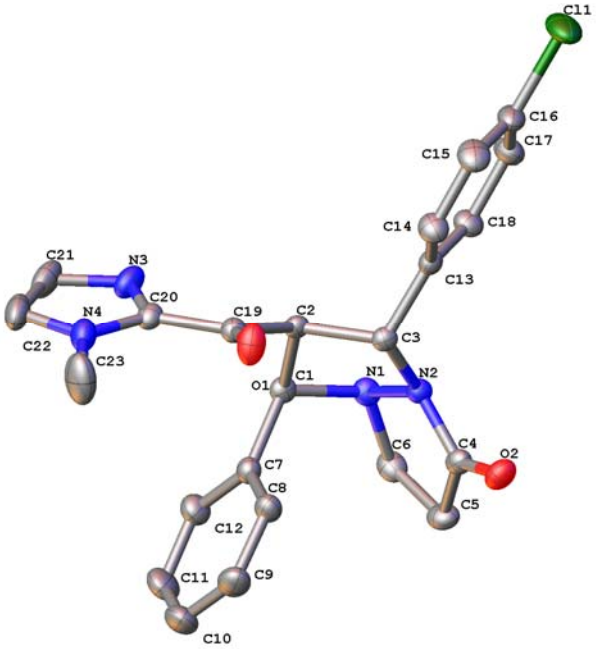


Table 1. Crystal data and structure refinement for mj21404_0m.

Identification code	mj21404_0m	
Empirical formula	C23 H21 Cl N4 O2	
Formula weight	420.89	
Temperature	212.99 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.35740(10) Å	α= 90°.
	b = 17.1204(3) Å	β= 90°.
	c = 19.4098(4) Å	γ = 90°.
Volume	2112.59(7) $Å^3$	
Z	4	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	1.196 mm^{-1}	
F(000)	880	
Crystal size	0.15 x 0.08 x 0.06 mm^3	
Theta range for data collection	2.994 to 54.816°.	
Index ranges	-7<=h<=5, -15<=k<=20, -23<=l<=17	

Reflections collected	12916
Independent reflections	3796 [R(int) = 0.0486]
Completeness to theta = 53.594°	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5250
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3796 / 0 / 272
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0854
R indices (all data)	R1 = 0.0363, wR2 = 0.0873
Absolute structure parameter	0.066(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.189 and -0.168 e.$Å^{-3}$

Table 2. Bond lengths [Å] and angles [°] for mj21404_0m.

Cl(1)-C(16)	1.742(2)
O(1)-C(19)	1.214(3)
O(2)-C(4)	1.221(3)
N(1)-N(2)	1.447(2)
N(1)-C(1)	1.495(3)
N(1)-C(6)	1.492(3)
N(2)-C(3)	1.461(2)
N(2)-C(4)	1.360(3)
N(3)-C(20)	1.328(3)
N(3)-C(21)	1.363(3)
N(4)-C(20)	1.358(3)
N(4)-C(22)	1.359(4)
N(4)-C(23)	1.463(4)
C(1)-H(1)	0.9900
C(1)-C(2)	1.550(3)
C(1)-C(7)	1.514(3)
C(2)-H(2)	0.9900
C(2)-C(3)	1.549(3)
C(2)-C(19)	1.513(3)
C(3)-H(3)	0.9900

C(3)-C(13)	1.510(3)
C(4)-C(5)	1.503(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-C(6)	1.519(4)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(7)-C(8)	1.392(3)
C(7)-C(12)	1.391(3)
C(8)-H(8)	0.9400
C(8)-C(9)	1.386(3)
C(9)-H(9)	0.9400
C(9)-C(10)	1.375(5)
C(10)-H(10)	0.9400
C(10)-C(11)	1.377(5)
C(11)-H(11)	0.9400
C(11)-C(12)	1.385(4)
C(12)-H(12)	0.9400
C(13)-C(14)	1.388(3)
C(13)-C(18)	1.381(3)
C(14)-H(14)	0.9400
C(14)-C(15)	1.390(3)
C(15)-H(15)	0.9400
C(15)-C(16)	1.370(4)
C(16)-C(17)	1.382(4)
C(17)-H(17)	0.9400
C(17)-C(18)	1.384(3)
C(18)-H(18)	0.9400
C(19)-C(20)	1.458(3)
C(21)-H(21)	0.9400
C(21)-C(22)	1.356(5)
C(22)-H(22)	0.9400
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(23)-H(23C)	0.9700

N(2)-N(1)-C(1)	103.86(14)
N(2)-N(1)-C(6)	103.53(17)

C(6)-N(1)-C(1)	117.57(17)
N(1)-N(2)-C(3)	109.90(15)
C(4)-N(2)-N(1)	114.58(16)
C(4)-N(2)-C(3)	124.83(17)
C(20)-N(3)-C(21)	104.7(2)
C(20)-N(4)-C(22)	106.7(2)
C(20)-N(4)-C(23)	128.0(2)
C(22)-N(4)-C(23)	125.1(2)
N(1)-C(1)-H(1)	108.3
N(1)-C(1)-C(2)	99.33(15)
N(1)-C(1)-C(7)	115.99(17)
C(2)-C(1)-H(1)	108.3
C(7)-C(1)-H(1)	108.3
C(7)-C(1)-C(2)	116.01(17)
C(1)-C(2)-H(2)	107.8
C(3)-C(2)-C(1)	105.88(15)
C(3)-C(2)-H(2)	107.8
C(19)-C(2)-C(1)	113.63(16)
C(19)-C(2)-H(2)	107.8
C(19)-C(2)-C(3)	113.72(16)
N(2)-C(3)-C(2)	102.55(15)
N(2)-C(3)-H(3)	108.9
N(2)-C(3)-C(13)	113.91(17)
C(2)-C(3)-H(3)	108.9
C(13)-C(3)-C(2)	113.41(16)
C(13)-C(3)-H(3)	108.9
O(2)-C(4)-N(2)	123.7(2)
O(2)-C(4)-C(5)	128.7(2)
N(2)-C(4)-C(5)	107.59(18)
C(4)-C(5)-H(5A)	110.8
C(4)-C(5)-H(5B)	110.8
C(4)-C(5)-C(6)	104.82(17)
H(5A)-C(5)-H(5B)	108.9
C(6)-C(5)-H(5A)	110.8
C(6)-C(5)-H(5B)	110.8
N(1)-C(6)-C(5)	107.36(18)
N(1)-C(6)-H(6A)	110.2
N(1)-C(6)-H(6B)	110.2

C(5)-C(6)-H(6A)	110.2
C(5)-C(6)-H(6B)	110.2
H(6A)-C(6)-H(6B)	108.5
C(8)-C(7)-C(1)	124.3(2)
C(12)-C(7)-C(1)	117.7(2)
C(12)-C(7)-C(8)	118.0(2)
C(7)-C(8)-H(8)	119.6
C(9)-C(8)-C(7)	120.8(2)
C(9)-C(8)-H(8)	119.6
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-C(8)	120.3(3)
C(10)-C(9)-H(9)	119.9
C(9)-C(10)-H(10)	120.1
C(9)-C(10)-C(11)	119.8(3)
C(11)-C(10)-H(10)	120.1
C(10)-C(11)-H(11)	120.0
C(10)-C(11)-C(12)	120.1(3)
C(12)-C(11)-H(11)	120.0
C(7)-C(12)-H(12)	119.5
C(11)-C(12)-C(7)	121.0(3)
C(11)-C(12)-H(12)	119.5
C(14)-C(13)-C(3)	119.45(19)
C(18)-C(13)-C(3)	121.52(18)
C(18)-C(13)-C(14)	119.0(2)
C(13)-C(14)-H(14)	119.9
C(13)-C(14)-C(15)	120.3(2)
C(15)-C(14)-H(14)	119.9
C(14)-C(15)-H(15)	120.2
C(16)-C(15)-C(14)	119.6(2)
C(16)-C(15)-H(15)	120.2
C(15)-C(16)-Cl(1)	119.87(19)
C(15)-C(16)-C(17)	121.1(2)
C(17)-C(16)-Cl(1)	119.0(2)
C(16)-C(17)-H(17)	120.5
C(16)-C(17)-C(18)	118.9(2)
C(18)-C(17)-H(17)	120.5
C(13)-C(18)-C(17)	121.1(2)
C(13)-C(18)-H(18)	119.5

C(17)-C(18)-H(18)	119.5
O(1)-C(19)-C(2)	122.17(19)
O(1)-C(19)-C(20)	121.95(19)
C(20)-C(19)-C(2)	115.87(18)
N(3)-C(20)-N(4)	111.6(2)
N(3)-C(20)-C(19)	123.7(2)
N(4)-C(20)-C(19)	124.7(2)
N(3)-C(21)-H(21)	124.6
C(22)-C(21)-N(3)	110.7(3)
C(22)-C(21)-H(21)	124.6
N(4)-C(22)-H(22)	126.8
C(21)-C(22)-N(4)	106.4(2)
C(21)-C(22)-H(22)	126.8
N(4)-C(23)-H(23A)	109.5
N(4)-C(23)-H(23B)	109.5
N(4)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Table 3. Torsion angles [°] for mj21404_0m.

Cl(1)-C(16)-C(17)-C(18)	179.11(19)
O(1)-C(19)-C(20)-N(3)	163.0(2)
O(1)-C(19)-C(20)-N(4)	-15.5(4)
O(2)-C(4)-C(5)-C(6)	-176.2(2)
N(1)-N(2)-C(3)-C(2)	13.98(19)
N(1)-N(2)-C(3)-C(13)	-108.97(18)
N(1)-N(2)-C(4)-O(2)	-174.01(19)
N(1)-N(2)-C(4)-C(5)	7.7(2)
N(1)-C(1)-C(2)-C(3)	-34.11(18)
N(1)-C(1)-C(2)-C(19)	-159.63(16)
N(1)-C(1)-C(7)-C(8)	79.6(3)
N(1)-C(1)-C(7)-C(12)	-99.4(2)
N(2)-N(1)-C(1)-C(2)	42.34(18)

N(2)-N(1)-C(1)-C(7)	-82.7(2)
N(2)-N(1)-C(6)-C(5)	14.2(2)
N(2)-C(3)-C(13)-C(14)	-147.9(2)
N(2)-C(3)-C(13)-C(18)	33.7(3)
N(2)-C(4)-C(5)-C(6)	1.9(2)
N(3)-C(21)-C(22)-N(4)	1.0(3)
C(1)-N(1)-N(2)-C(3)	-37.1(2)
C(1)-N(1)-N(2)-C(4)	109.33(18)
C(1)-N(1)-C(6)-C(5)	-99.6(2)
C(1)-C(2)-C(3)-N(2)	13.37(18)
C(1)-C(2)-C(3)-C(13)	136.65(17)
C(1)-C(2)-C(19)-O(1)	118.6(2)
C(1)-C(2)-C(19)-C(20)	-60.6(2)
C(1)-C(7)-C(8)-C(9)	179.9(2)
C(1)-C(7)-C(12)-C(11)	178.4(2)
C(2)-C(1)-C(7)-C(8)	-36.4(3)
C(2)-C(1)-C(7)-C(12)	144.6(2)
C(2)-C(3)-C(13)-C(14)	95.3(2)
C(2)-C(3)-C(13)-C(18)	-83.1(2)
C(2)-C(19)-C(20)-N(3)	-17.9(3)
C(2)-C(19)-C(20)-N(4)	163.6(2)
C(3)-N(2)-C(4)-O(2)	-33.3(3)
C(3)-N(2)-C(4)-C(5)	148.5(2)
C(3)-C(2)-C(19)-O(1)	-2.7(3)
C(3)-C(2)-C(19)-C(20)	178.22(18)
C(3)-C(13)-C(14)-C(15)	-178.7(2)
C(3)-C(13)-C(18)-C(17)	178.8(2)
C(4)-N(2)-C(3)-C(2)	-128.28(19)
C(4)-N(2)-C(3)-C(13)	108.8(2)
C(4)-C(5)-C(6)-N(1)	-10.3(3)
C(6)-N(1)-N(2)-C(3)	-160.48(17)
C(6)-N(1)-N(2)-C(4)	-14.0(2)
C(6)-N(1)-C(1)-C(2)	155.96(17)
C(6)-N(1)-C(1)-C(7)	30.9(3)
C(7)-C(1)-C(2)-C(3)	90.9(2)
C(7)-C(1)-C(2)-C(19)	-34.6(2)
C(7)-C(8)-C(9)-C(10)	1.1(4)
C(8)-C(7)-C(12)-C(11)	-0.7(4)

C(8)-C(9)-C(10)-C(11)	0.7(5)
C(9)-C(10)-C(11)-C(12)	-2.4(5)
C(10)-C(11)-C(12)-C(7)	2.4(4)
C(12)-C(7)-C(8)-C(9)	-1.1(3)
C(13)-C(14)-C(15)-C(16)	-0.1(4)
C(14)-C(13)-C(18)-C(17)	0.4(3)
C(14)-C(15)-C(16)-Cl(1)	-179.0(2)
C(14)-C(15)-C(16)-C(17)	0.3(4)
C(15)-C(16)-C(17)-C(18)	-0.2(4)
C(16)-C(17)-C(18)-C(13)	-0.2(4)
C(18)-C(13)-C(14)-C(15)	-0.3(4)
C(19)-C(2)-C(3)-N(2)	138.83(17)
C(19)-C(2)-C(3)-C(13)	-97.89(19)
C(20)-N(3)-C(21)-C(22)	-0.5(3)
C(20)-N(4)-C(22)-C(21)	-1.0(3)
C(21)-N(3)-C(20)-N(4)	-0.1(3)
C(21)-N(3)-C(20)-C(19)	-178.8(2)
C(22)-N(4)-C(20)-N(3)	0.7(3)
C(22)-N(4)-C(20)-C(19)	179.4(2)
C(23)-N(4)-C(20)-N(3)	175.0(3)
C(23)-N(4)-C(20)-C(19)	-6.4(4)
C(23)-N(4)-C(22)-C(21)	-175.5(3)

Table 4. Hydrogen bonds for mj21404_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

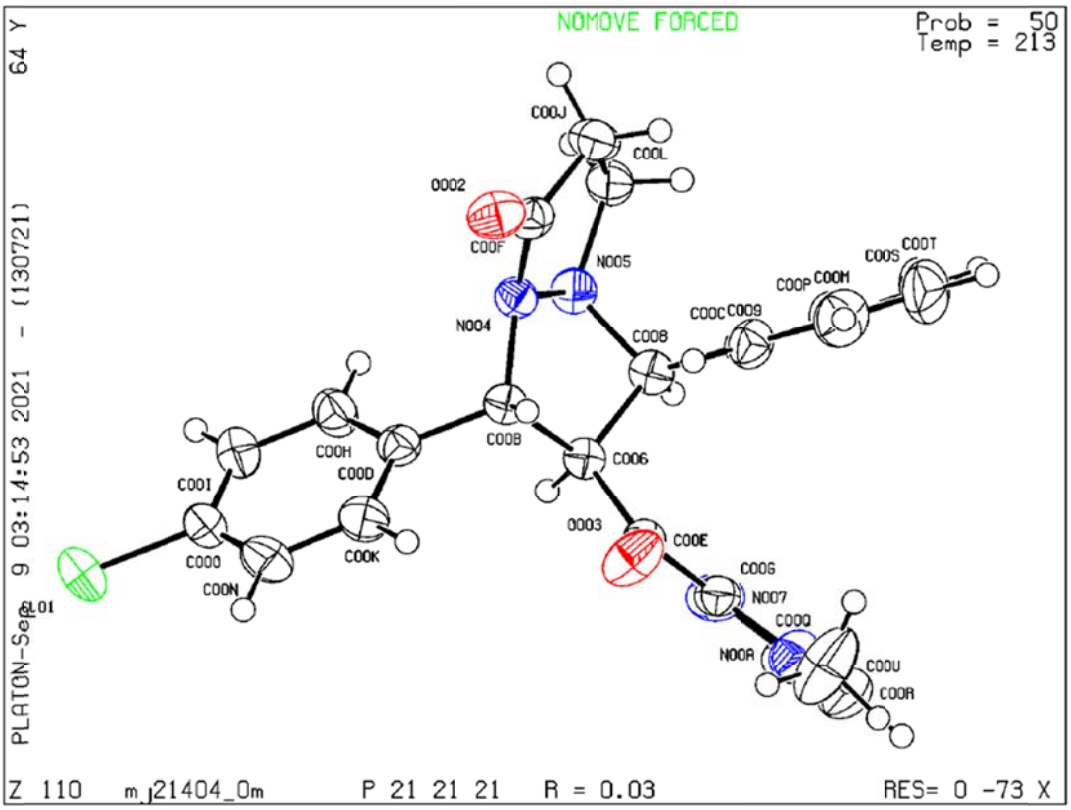


Figure S65. Perspective views showing 50% probability displacement

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